A general Pd−catalyzed α− and γ−benzylation of aldehydes for the formation of quaternary centers

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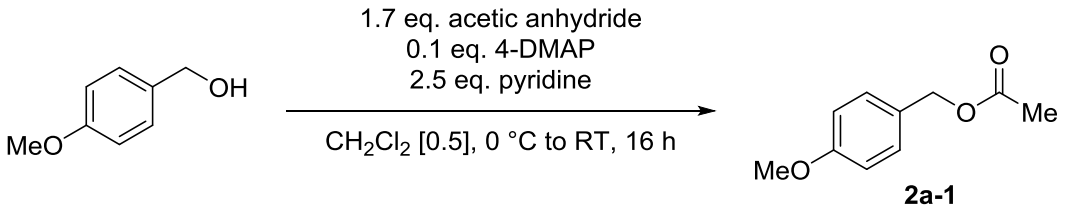
1 General Information

All reactions were carried out under an inert atmosphere of nitrogen using either two-manifold vacuum/inert gas lines or a M.Braun glove-box, unless otherwise noted. Solvents were dried over activated alumina columns or by distillation from sodium and further degassed by three successive 'freeze-pump-thaw' cycles. *N,N*-dimethylformamide was stored in the dark and weekly degassed to remove possible decomposition products (*i.e.* dimethylamine and carbon monoxide). NMR spectra were recorded on AMX-400 and AMX-500 Bruker Avance spectrometers at 298K unless otherwise noted. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Spin multiplicities are reported as a singlet (s), doublet (d), triplet (t), quartet (q) and heptet (hept) with coupling constants (*J*) given in Hz, or multiplet (m). Broad signals are indicated as 'br'. ^{1}H and ^{13}C resonances were assigned with the aid of additional information from 1D and 2D NMR experiments (H,H-COSY, DEPT135, HSQC, HMBC and NOESY). ^{1}H and ^{13}C NMR chemical shifts are given in ppm relative to $SiMe_4$, with the solvent resonance used as internal reference. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm) or CD_2Cl_2 (5.30 ppm) and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.36 ppm) unless otherwise indicated. $^{31}P\{^{1}H\}$ NMR chemical shifts are reported in ppm relative to H_3PO_4. $^{19}F\{^{1}H\}$NMR chemical shifts are reported in ppm with absolute reference to ^{1}H. Infrared spectra were obtained on a Perkin-Elmer 1650 FT-IR spectrometer using neat samples on a diamond ATR Golden Gate sampler. Optical rotations were measured on a Perkin-Elmer 241 polarimeter equipped with a Na-lamp at 20 °C unless otherwise noted. The mass spectrometric data were obtained at the mass spectrometry facility of the University of Geneva (http://www.unige.ch/sciences/sms/index.html). Chiral HPLC analyses were performed on Shimadzu CTO-20AA at 30 °C. Retention times are given in minutes. Commercial reagents were purchased from Aldrich, Acros or Strem and used without further purification unless otherwise noted. Liquid reagents were transferred by stainless steel syringes or by cannula. Thin layer chromatography (TLC) was performed on plates of silica pre-coated with 0.25 mm Kieselgel 60 F_{254}. Flash chromatography was performed using silica gel 60 (230–400 mesh ASTM) from SiliCycle. Abbreviations used: THF (tetrahydrofuran); DMF (*N,N*-dimethylformamide); TFA (Trifluoroacetate); 4-DMAP (4-dimethylaminopyridine).

2 Synthesis of the electrophiles

2.1 Synthesis of 4-methoxybenzyl acetate (2a-1)

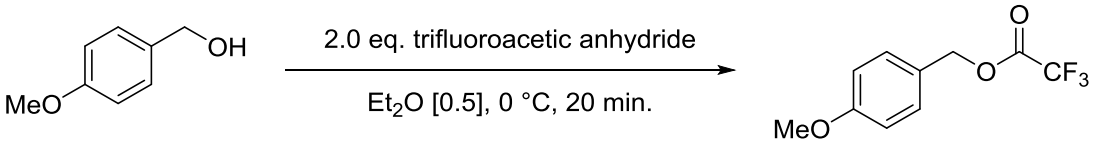


2a-1

In a 100 mL flame-dried round-bottom flask 4-methoxybenzylic alcohol (1.86 mL, 15 mmol, 1.0 eq.), 4-DMAP (183 mg, 1.5 mmol, 0.1 eq.) and pyridine (3.1 mL, 37.5 mmol, 2.5 eq.) were dissolved in dry dichloromethane (30 mL, 0.5 M) under a nitrogen atmosphere. After cooling to 0 °C, acetic anhydride (2.84 mL, 30 mmol, 2.0 eq.) was added dropwise and the reaction stirred at room temperature for 16 h (TLC eluent pentane/CH_2Cl_2 1:1). The reaction was carefully quenched with 60 mL of a saturated $NaHCO_3$ solution and the aqueous phase was extracted with dichloromethane (15 mL x 3). The combined organic layers were dried over Na_2SO_4 and the solvent evaporated. The crude mixture was purified by flash chromatography (SiO_2, eluent pentane/CH_2Cl_2 1:1) to afford the benzyl acetate as colorless oil (2.48 g, 92% yield).

All spectroscopic and spectrometric data are consistent with those reported in the literature for this compound.[1]

2.2 Synthesis of 4-methoxybenzyl trifluoroacetate (2a-2)



2a-2

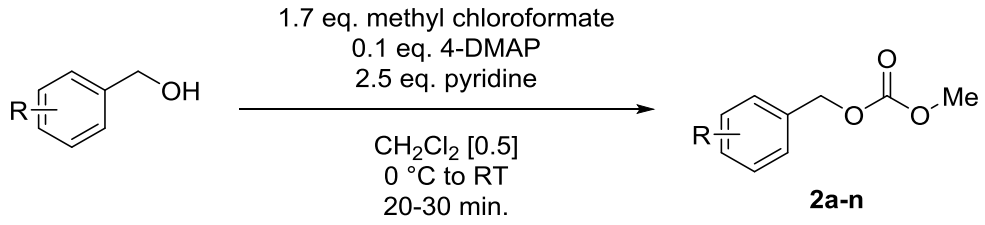
In a 50 mL flame-dried round-bottom flask 4-methoxybenzylic alcohol (2.48 mL, 20 mmol, 1.0 eq.) was dissolved in dry diethyl ether (27 mL, 0.5 M) under a nitrogen atmosphere. After cooling to 0 °C, trifluoroacetic anhydride (5.6 mL, 40 mmol, 2.0 eq.) was added dropwise and the reaction stirred at the same temperature for 20 min. (TLC eluent pentane/CH_2Cl_2 1:1). The reaction was carefully quenched with 60 mL of a saturated $NaHCO_3$ solution and

[1] *Tetrahedron Lett.* **2014**, *55*, 1784; *Org. Lett.* **2013**, *15*, 5798

the organic phase was further washed with sat. $NaHCO_3$.The organic layer was dried over Na_2SO_4 and the solvent evaporated. The crude mixture was purified by flash chromatography (SiO_2, eluent pentane/CH_2Cl_2 2:1) to afford the benzyl trifluoroacetate as colorless oil (3.52 g, 75% yield).

All spectroscopic and spectrometric data are consistent with those reported in the literature for this compound.[2]

2.3 Synthesis of benzyl methyl carbonates (2a-n)



In a 100 mL flame-dried round-bottom flask the appropriate benzyl alcohol (12 mmol, 1.0 eq.), 4-DMAP (147 mg, 1.2 mmol, 0.1 eq.) and pyridine (2.45 mL, 30 mmol, 2.5 eq.) were dissolved in dry dichloromethane (24 mL, 0.5 M) under a nitrogen atmosphere. After cooling to 0 °C, methyl chloroformate (1.58 mL, 20.4 mmol, 1.7 eq.) was added dropwise and the reaction stirred at room temperature until complete reaction was indicated by TLC (TLC eluent pentane/CH_2Cl_2 1:1, reaction time 20-30 min.). The reaction was carefully quenched with 40 mL of a saturated $NaHCO_3$ solution and the aqueous phase was extracted with dichloromethane (15 mL x 3).The combined organic layers were dried over Na_2SO_4 and the solvent evaporated. The crude mixture was purified by flash chromatography (SiO_2, eluent pentane/CH_2Cl_2).

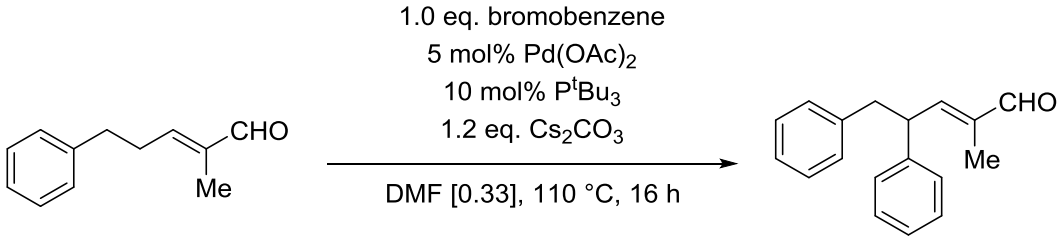
All spectroscopic and spectrometric data are consistent with those reported in the literature for these compounds.[3]

[2] *Angew. Chem. Int. Ed.* **2014**, 53, 4685.
[3] *Org. Lett.* **2010**, *12*, 1360; *Org. Lett.* 2012, 14, 338; *Org. Lett.* **2011**, *13*, 430; *J. Am. Chem. Soc.* **2007**, *129*, 14193; *New J. Chem.* **2013**, *37*, 3057; *Chem. Lett.* **2007**, *36*, 606; *J. Am. Chem. Soc.* **2012**, *134*, 111.

3 Synthesis of the nucleophiles

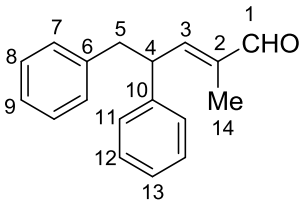
Aldehydes **1a**, **1b**, **1c**, **1d**, **1e** and **6**a are commercially available. Aldehydes **7a**, **7b**, **7c**, **7d**, **7e**, **7f**, **7g**, **7h** and **7i** were prepared following the procedure reported by List and co-workers (*Angew. Chem. Int. Ed.* **2014**, *53*, 282). Aldehydes **11a**, **11b** and **11c** were prepared following the procedure previously reported by our group (*Chem. Sci.* **2013**, *4*, 2619).

3.1 Synthesis of (*E*)-2-methyl-4,5-diphenylpent-2-enal (12d)



12d

In a 25 mL flame-dried Schlenk under a nitrogen atmosphere $Pd(OAc)_2$ (32.2 mg, 0.14 mmol, 0.05 eq.), *t*-Bu_3P (58.1 mg, 0.29 mmol, 0.10 eq.) and Cs_2CO_3 (1122 mg, 3.44 mmol, 1.2 eq.) were mixed in dry and degassed dimethylformamide (8.7 mL, 0.33 M). After 10 min. stirring at room temperature, bromobenzene (302 µL, 2.87 mmol, 1.0 eq.) and the appropriate aldehyde (500 mg, 2.87 mmol, 1.0 eq.) were added. The tube was sealed and placed at 110 °C for 16 h. The reaction was filtered through Celite® and the solvent evaporated. The crude mixture was purified by flash chromatography (SiO_2, eluent pentane/ CH_2Cl_2 2:1) to afford the desired product as yellow oil (521 mg, 72% yield).



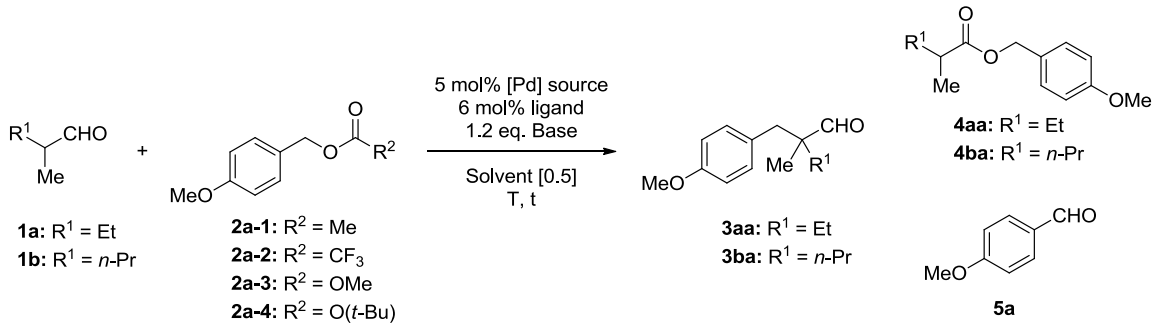
12d
Chemical Formula: $C_{18}H_{18}O$
Molecular Weight: 250.34

Yellow oil; **R_f** = 0.53 (SiO_2, pentane/ CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.54 (d, $^4J_{HH}$ = 1.4 Hz, 3H, H-14); 3.04 (dd, $^3J_{HH}$ = 8.8 Hz, $^2J_{HH}$ = 13.5 Hz, 1H, H-5); 3.20 (dd, $^3J_{HH}$ = 6.1 Hz, $^2J_{HH}$ = 13.5 Hz, 1H, H-5); 4.04-4.11 (m, 1H, H-4); 6.64 (dq, $^4J_{HH}$ = 1.4 Hz, $^3J_{HH}$ = 9.9 Hz, 1H, H-3); 7.07-7.09 (m, 2H, H-7); 7.16-7.27 (m, 6H, H-8, H-9, H-11 and H-13); 7.32-7.36

(m, 2H, H-12); 9.39 (s, 1H, H-1). **$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 9.6 (C-14); 42.9 (C-5); 47.6 (C-4); 126.8 (C-9); 127.4 (C-13); 127.8 (C-11); 128.7 (C-8); 129.2 (C-12); 129.3 (C-7); 139.1 (C-6); 139.4 (C-9); 142.4 (C-10); 156.0 (C-3); 195.4 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 3027, 1679, 1494, 1453, 1007, 755, 696. **HRMS** *(method: ESI positive)* calculated for $C_{18}H_{18}NaO$ 273.1250 $[M+Na]^+$, found 273.1248.

4 Reaction optimization

General procedure: All reactions were conducted on a 0.4-0.5 mmol scale. All conversions were determined by ^{1}HNMR analysis of the crude mixture referring to an internal standard (1,3-di-*tert*-butyl-2-methoxy-5-methylbenzene).



Inside a glove box, a 5 mL Young valve Schlenk tube was charged with the palladium source (0.02 mmol, 0.05 eq.), the ligand (0.024 mmol, 0.06 eq.) and the base (0.48 mmol, 1.2 eq.). The tube was sealed and taken outside the glove box and connected to a Schlenk line. After conditioning, dry and degassed solvent (0.5 M) was added and after 10 min. of additional stirring at room temperature the carbonate (0.40 mmol, 1.0 eq.), the aldehyde (0.80 mmol, 2.0 eq.) and the internal standard (0.5 eq.) were added. The tube was sealed and placed at the given temperature for the indicated time. After cooling to room temperature, the reaction was then filtered through Celite® and the solvent evaporated under reduced pressure. The crude mixture was analyzed by ^{1}HNMR to access conversions.

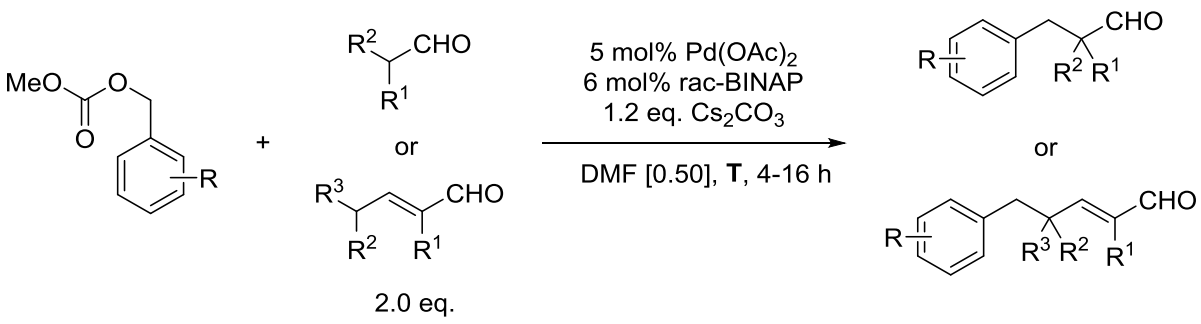
1	2	[Pd]	Ligand	Base	Solvent	T (°C)	t (h)	Conv. % (3 : 4 : 5)[a]
1a	**2a-1**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	DMF	80	16	< 5 (-:-:-)
1a	**2a-2**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	DMF	80	16	18 (3:2:1)
1a	**2a-2**	$Pd(OAc)_2$	*t*-Bu_3P[b]	Cs_2CO_3	DMF	80	16	16 (0:1:2)
1a	**2a-2**	$Pd(OAc)_2$	Ph_3P[b]	Cs_2CO_3	DMF	80	16	27 (0:5:1)
1a	**2a-2**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	THF	80	16	58 (1:9:1)
1a	**2a-2**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	Toluene	80	16	62 (1:10:1)
1a	**2a-2**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	DMA	80	16	20 (2:2:1)
1a	**2a-4**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	DMF	80	16	29 (5:1:0)
1a	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	DMF	80	16	69 (11:1:1)
1a	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	(*i*-Pr)NEt_2	DMF	80	16	< 5 (-:-:-)
1a	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	NaOAc	DMF	80	16	< 5 (-:-:-)
1a	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	Na_2CO_3	DMF	80	16	< 5 (-:-:-)
1a	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	Et_3N	DMF	80	16	< 5 (-:-:-)

1a	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	THF	80	16	< 5 (-:-:-)
1a	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	Toluene	80	16	< 5 (-:-:-)
1a	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	Dioxane	80	16	< 5 (-:-:-)
1a	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	MeCN	80	16	6 (1:1:10)
1a	**2a-3**	$Pd(dba)_2$	*rac*-BINAP	Cs_2CO_3	DMF	80	16	28 (3:4:2)
1a	**2a-3**	$Pd(TFA)_2$	*rac*-BINAP	Cs_2CO_3	MeCN	80	16	20 (0:3:1)
1b	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	DMF	80	4	62 (41:1:3)
1b	**2a-3**[c]	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	DMF	80	4	90 (5:1:3)
1b[d]	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	Cs_2CO_3	DMF	80	4	80 (48:1:-)
1b	**2a-3**	$Pd(OAc)_2$	*rac*-BINAP	-	DMF	80	4	< 5 (-:-:-)

[a] Conversions and product distribution determined by ^{1}HNMR analysis of the crude mixture; [b] 10 mol% of ligand; [c] 2.0 eq. of carbonate; [d] 2.0 eq. of aldehyde.

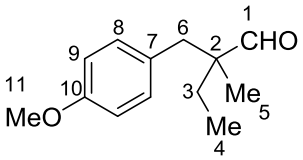
5 Pd−catalyzed α− and γ−benzylation of aldehydes

5.1 General procedure



Inside a glove box, a 5 mL Young valve Schlenk tube was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.05 eq.), *rac*-BINAP (14.9 mg, 0.024 mmol, 0.06 eq.) and Cs_2CO_3 (156.4 mg, 0.48 mmol, 1.2 eq.). The tube was sealed and taken outside the glove box and connected to a Schlenk line. After conditioning, dry and degassed dimethylformamide (0.8 mL, 0.5 M) was added and after 10 min. of additional stirring at room temperature the carbonate (0.40 mmol, 1.0 eq.), the aldehyde (0.80 mmol, 2.0 eq.) and the internal standard (0.5 eq.) were added. The tube was sealed and placed at the appropriate temperature for 4 or 16 h. After cooling to room temperature, the reaction was filtered through Celite® and the solvent evaporated under vacuum. The crude mixture was purified by flash chromatography (SiO_2, eluent pentane/CH_2Cl_2 or pentane/Et_2O).

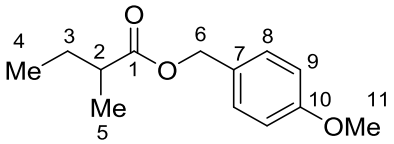
5.2 Characterization data of aldehydes



3aa
Chemical Formula: $C_{13}H_{18}O_2$
Molecular Weight: 206.29

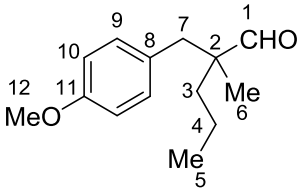
2-(4-methoxybenzyl)-2-methylbutanal (**3aa**). Pale yellow oil; SiO_2, pentane/Et_2O 5:1; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.87 (t, $^3J_{HH}$ = 7.6 Hz, 3H, H-4); 0.98 (s, 3H, H-5); 1.41-1.50 and 1.60-1.69 (2m, 1H+1H, H-3); 2.67 and 2.81 (2d, $^2J_{HH}$ = 13.8 Hz, 1H+1H, H-6); 3.78 (2, 3H, H-11); 6.80 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H-9); 7.00 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H-8); 9.55 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 8.9 (C-4); 18.0 (C-5); 28.4 (C-3); 41.1 (C-6);

50.9 (C-2); 55.5 (C-11); 113.9 (C-9); 129.2 (C-7); 131.5 (C-8); 158.6 (C-10); 207.1 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2966, 1724, 1611, 1511, 1460, 1246, 1178, 1034, 835, 818. **HRMS** *(method: ESI positive)* calculated for $C_{13}H_{22}NO_2$ 224.1645 $[M+NH_4]^+$, found 224.1639. **Chiral HPLC conditions** Column IC, λ = 219 nm, hexanes/^{i}PrOH 99:1, 1 mL/min., t_1 = 10.76 and t_2 = 11.51 min.



4aa
Chemical Formula: $C_{13}H_{18}O_3$
Molecular Weight: 222.28

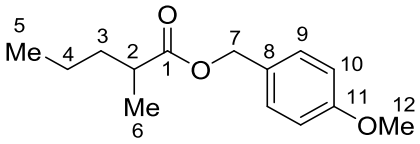
4-methoxybenzyl 2-methylbutanoate (**4aa**). Pale yellow oil; SiO_2, pentane/Et_2O 5:1; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.88 (t, $^3J_{HH}$ = 7.4 Hz, 3H, H-4); 1.14 (d, $^3J_{HH}$ = 7.0 Hz, 3H, H-5); 1.42-1.50 and 1.65-1.72 (2m, 1H+1H, H-3); 2.35-2.44 (m, 1H, H-2); 3.81 (s, 3H, H-11); 5.05 (s, 2H, H-6); 6.89 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-9); 7.29 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-8). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 11.9 (C-4); 16.9 (C-5); 27.1 (C-3); 41.4 (C-2); 55.6 (C-11); 66.1 (C-6); 114.2 (C-9); 128.8 (C-7); 130.2 (C-8); 159.8 (C-10); 177.0 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2967, 1728, 1613, 1514, 1460, 1246, 1173, 1142, 1033, 819. **LRMS** *(method: ESI positive)* calculated for $C_{13}H_{20}O_4$ 240.1 $[M+OH_2]^+$, found 239.9.



3ba
Chemical Formula: $C_{14}H_{20}O_2$
Molecular Weight: 220.31

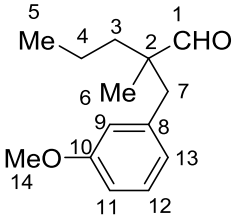
2-(4-methoxybenzyl)-2-methylpentanal (**3ba**). Colorless oil; **R_f** = 0.42 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H-5); 0.98 (s, 3H, H-6); 1.20-1.33 (m, 2H, H-4); 1.36-1.42 and 1.51-1.59 (2m, 1+1H, H-3); 2.66 (d, $^2J_{HH}$ = 13.8 Hz, 1H, H-7); 2.80 (d, $^2J_{HH}$ = 13.8 Hz, 1H, H-7); 3.78 (s, 3H, H-12); 6.80 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H-10); 6.99 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H-9); 9.55 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 15.0 (C-5); 17.9 (C-4); 18.5 (C-6); 38.2 (C-3); 41.5 (C-7); 50.8 (C-2); 55.5 (C-12); 113.9 (C-10); 129.2 (C-8); 131.5 (C-9); 158.6 (C-11); 207.1 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2959, 1724, 1612, 1511, 1461, 1246, 1178, 1034, 831. **HRMS** *(method: ESI positive)*

calculated for $C_{14}H_{24}NO_2$ 238.1802 $[M+NH_4]^+$, found 238.1807. **Chiral HPLC conditions** Column IC, λ = 219 nm, hexanes/^{i}PrOH 99:1, 1 mL/min., t_1 = 9.87 and t_2 = 11.33 min.



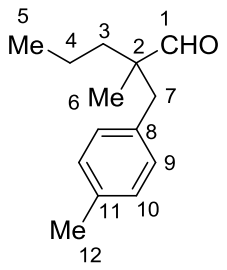
4ba
Chemical Formula: $C_{14}H_{20}O_3$
Molecular Weight: 236.31

4-methoxybenzyl 2-methylpentanoate (**4ba**). Colorless oil; **R_f** = 0.42 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.88 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H-5); 1.14 (d, $^3J_{HH}$ = 7.0 Hz, 3H, H-6); 1.24-1.34 (m, 2H, H-4); 1.37-1.43 and 1.60-1.69 (2m, 1+1H, H-3); 2.43-2.51 (m, 1H, H-2); 3.81 (s, 3H, H-12); 5.04 (s, 2H, H-7); 6.89 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H-10); 7.29 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H-9). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 14.3 (C-5); 17.3 (C-6); 20.7 (C-4); 36.3 (C-3); 39.7 (C-2); 55.6 (C-12); 66.1 (C-7); 114.2 (C-10); 128.8 (C-8); 130.2 (C-9); 159.8 (C-11); 177.2 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2959, 1729, 1613, 1514, 1245, 1170, 1143, 1033, 822. **HRMS** *(method: ESI positive)* calculated for $C_{14}H_{20}O_3Na$ 259.1305 $[M+Na]^+$, found 259.1309.



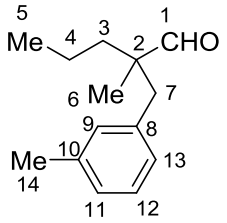
3bb
Chemical Formula: $C_{14}H_{20}O_2$
Molecular Weight: 220.31

2-methyl-2-(3-methoxylbenzyl)pentanal (**3bb**). Colorless oil; **R_f** = 0.47 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H-5); 1.00 (s, 3H, H-6); 1.23-1.33 (m, 2H, H-4); 1.37-1.45 and 1.52-1.60 (2m, 1+1H, H-3); 2.68 and 2.84 (2d, $^2J_{HH}$ = 7.2 Hz, 1+1H, H-7); 3.78 (s, 3H, H-14); 6.62-6.63 (m, 1H, H-9); 6.67 (br d, $^3J_{HH}$ = 8.3 Hz, 1H, H-13); 6.76 (ddd, $^4J_{HH}$ = 0.8 Hz, $^4J_{HH}$ = 2.5 Hz, $^3J_{HH}$ = 8.3 Hz, 1H, H-11); 7.18 (t, $^3J_{HH}$ = 8.3 Hz, 1H, H-12); 9.56 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 15.0 (C-5); 17.9 (C-4); 18.7 (C-6); 38.3 (C-3); 42.3 (C-7); 50.7 (C-2); 55.5 (C-14); 111.9 (C-11); 116.6 (C-9); 123.0 (C-13); 129.4 (C-12); 138.8 (C-8); 159.7 (C-10); 206.8 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2959, 1724, 1600, 1584, 1489, 1457, 1261, 1154, 1043, 785, 739, 697. **LRMS** *(method: ESI positive)* calculated for $C_{14}H_{21}O_2$ 221.2 $[M+H]^+$, found 221.3.



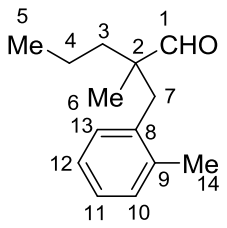
3bd
Chemical Formula: $C_{14}H_{20}O$
Molecular Weight: 204.31

2-benzyl-2-(4-methylbenzyl)pentanal (**3bd**). Colorless oil; **R_f** = 0.59 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H-5); 0.99 (s, 3H, H-6); 1.22-1.32 (m, 2H, H-4); 1.35-1.43 and 1.52-1.58 (2m, 1+1H, H-3); 2.31 (s, 3H, H-12); 2.68 and 2.82 (2d, $^2J_{HH}$ = 13.7 Hz, 1+1H, H-7); 6.96 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-9); 7.07 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-10); 9.56 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 15.0 (C-5); 17.9 (C-4); 18.6 (C-6); 21.3 (C-12); 38.2 (C-3); 42.0 (C-7); 50.8 (C-2); 129.2 (C-10); 130.5 (C-9); 134.1 (C-8); 136.4 (C-11); 207.0 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2959, 1724, 1514, 1458, 1179, 812. **LRMS** *(method: ESI positive)* calculated for $C_{14}H_{20}NaO$ 227.1 $[M+Na]^+$, found 227.2.



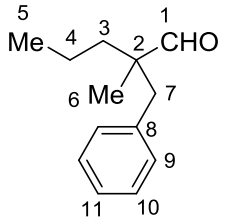
3be
Chemical Formula: $C_{14}H_{20}O$
Molecular Weight: 204.31

2-methyl-2-(3-methylbenzyl)pentanal (**3be**). Colorless oil; **R_f** = 0.58 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.91 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H-5); 0.99 (s, 3H, H-6); 1.22-1.34 (m, 2H, H-4); 1.39-1.44 and 1.52-1.60 (2m, 1+1H, H-3); 2.32 (s, 3H, H-14); 2.67 and 2.83 (2d, $^2J_{HH}$ = 13.6 Hz, 1+1H, H-7); 6.87-6.88 (m, 2H, H-9 and H-13); 7.02-7.04 (m, 1H, H-11); 7.13-7.17 (m, 1H, H-12); 9.57 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 15.0 (C-5); 17.9 (C-4); 18.6 (C-6); 21.8 (C-14); 38.3 (C-3); 42.3 (C-7); 50.7 (C-2); 127.6 (C-11); 127.6 (C-13); 128.4 (C-12); 131.3 (C-9); 137.2 (C-8); 138.0 (C-10); 207.0 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2960, 1726, 1459, 1146, 790, 138, 700. **LRMS** *(method: ESI positive)* calculated for $C_{14}H_{20}NaO$ 227.1 $[M+Na]^+$, found 227.4.



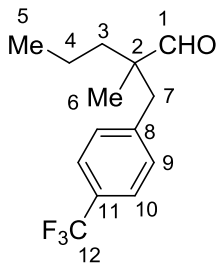
3bf
Chemical Formula: $C_{14}H_{20}O$
Molecular Weight: 204.31

2-methyl-2-(2-methylbenzyl)pentanal (**3bf**). Colorless oil; **R_f** = 0.61 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.92 (t, $^3J_{HH}$ = 7.1 Hz, 3H, H-5); 1.01 (s, 3H, H-6); 1.19-1.37 (m, 2H, H-4); 1.42-1.50 and 1.63-1.71 (2m, 1+1H, H-3); 2.29 (s, 3H, H-14); 2.77 and 2.90 (2d, $^2J_{HH}$ = 14.1 Hz, 1+1H, H-7); 6.98-7.02 (m, 1H, H-13); 7.08-7.15 (m, 3H, H-10, H-11 and H-12); 9.56 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 15.1 (C-5); 17.9 (C-4); 18.1 (C-6); 20.7 (C-14); 38.9 (C-3); 39.0 (C-7); 51.4 (C-2); 126.0, 127.0 and 131.0 (C-10, C-11 and C-12); 131.2 (C-13); 135.7 (C-8); 137.1 (C-9); 207.0 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2959, 2872, 1724, 1458, 1145, 739. **LRMS** *(method: ESI positive)* calculated for $C_{14}H_{21}O$ 205.1 $[M+H]^+$, found 205.1.



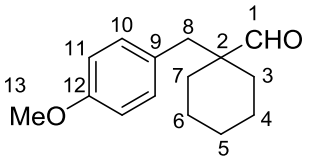
3bg
Chemical Formula: $C_{13}H_{18}O$
Molecular Weight: 190.29

2-benzyl-2-methylpentanal (**3bg**). Colorless oil; **R_f** = 0.53 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.91 (t, $^3J_{HH}$ = 7.3 Hz, 3H, H-5); 1.00 (s, 3H, H-6); 1.22-1.33 (m, 2H, H-4); 1.40-1.44 and 1.52-1.60 (2m, 1+1H, H-3); 2.71 and 2.87 (2d, $^2J_{HH}$ = 13.6 Hz, 1+1H, H-7); 7.07-7.09 (m, 2H, H-4); 7.21-7.28 (m, 3H, H-10 and H-11); 9.57 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 15.0 (C-5); 17.9 (C-4); 18.6 (C-6); 38.3 (C-3); 42.3 (C-7); 50.7 (C-2); 126.8 (C-11); 125.8 (C-10); 130.6 (C-9); 137.3 (C-8); 206.9 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2960, 2873, 1723, 1454, 1179, 735, 700. **LRMS** *(method: ESI positive)* calculated for $C_{13}H_{17}O$ 189.1 $[M-H]^+$, found 189.2.



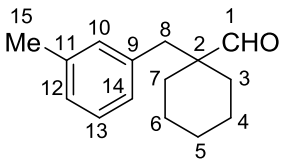
3bh
Chemical Formula: $C_{14}H_{17}F_3O$
Molecular Weight: 258.28

2-methyl-2-(4-(trifluoromethyl)benzyl)pentanal (**3bh**). Colorless oil; **R_f** = 0.53 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 500 MHz)** δ (ppm) = 0.92 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H-5); 1.00 (s, 3H, H-6); 1.26-1.34 (m, 2H, H-4); 1.39-1.44 and 1.51-1.58 (2m, 1+1H, H-3); 2.77 and 2.93 (2d, $^2J_{HH}$ = 13.6 Hz, 1+1H, H-7); 7.20 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-9); 7.52 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-10); 9.55 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz)** δ (ppm) = 15.0 (C-5); 17.8 (C-4); 18.8 (C-6); 38.4 (C-3); 41.6 (C-7); 50.7 (C-2); 124.5 (q, $^1J_{CF}$ = 271.8 Hz, C-12); 125.4 (q, $^3J_{CF}$ = 3.7 Hz, -10); 129.2 (q, $^2J_{CF}$ = 32.4 Hz, C-11); 130.9 (C-9); 141.6 (C-8); 206.1 (C-1). **^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz)** δ (ppm) = − 61.73 (s). **IR spectrum (neat)** ν (cm^{-1}) = 2963, 1727, 1619, 1323, 1163, 1119, 1066, 1018, 848. **LRMS** *(method: ESI positive)* calculated for $C_{14}H_{18}F_3O$ 259.1 $[M+H]^+$, found 259.2.



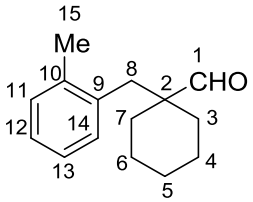
3ca
Chemical Formula: $C_{15}H_{20}O_2$
Molecular Weight: 232.32

1-(4-methoxybenzyl)cyclohexanecarbaldehyde (**3ca**). Colorless oil; **R_f** = 0.45 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.21-1.33, 1.53-1.64 and 1.88-1.92 (3m, 5+3+2H, H-3, H-4, H-5, H-6 and H-7); 2.66 (s, 2H, H-8); 3.78 (s, 3H, H-13); 6.79 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H-11); 6.97 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H-10); 9.50 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 23.1 (C-3 and C-5); 26.0 (C-4); 31.5 (C-2 and C-6); 43.0 (C-7); 51.1 (C-2); 55.6 (C-13); 113.9 (C-11); 128.5 (C-9); 131.5 (C-10); 158.6 (C-12); 208.0 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2966, 1724, 1612, 1512, 1460, 1245, 1178, 1033, 826. **LRMS** *(method: ESI positive)* calculated for $C_{15}H_{21}O_2$ 233.1 $[M+H]^+$, found 233.1.



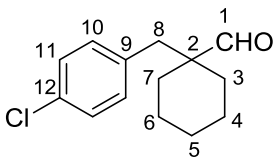
3ce
Chemical Formula: $C_{15}H_{20}O$
Molecular Weight: 216.32

1-(3-methybenzyl)cyclohexanecarbaldehyde (**3ce**). Colorless oil; **R_f** = 0.59 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.24-1.34, 1.54-1.64 and 1.89-1.93 (3m, 5+3+2H, H-3m H-4, H-5, H-6 and H-7); 2.31 (2, 3H, H-15); 2.68 (s, 2H, H-8), 6.84-8.68 (m, 2H, H-10and H.14); 7.01-7.03 (m, 1H, H-12); 7.12-7.16 (m, 1H, H-13); 9.52 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 21.4 (C-15); 22.8 (C-4 and C-6); 25.6 (C-5); 31.2 (C-3 and C-7); 43.6 (C-8); 50.6 (C-2); 127.3 (C-12 and C-14); 128.0 (C-13); 131.0 (C-10); 136.1 (C-9); 137.7 (C-11); 207.5 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2926, 1723, 1450, 1167, 787, 738, 700. **LRMS** *(method: ESI positive)* calculated for $C_{15}H_{20}NaO$ 239.1 $[M+Na]^+$, found 239.3.



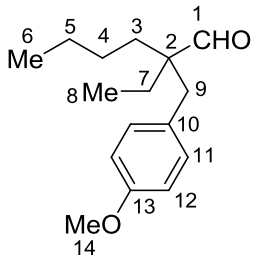
3cf
Chemical Formula: $C_{15}H_{20}O$
Molecular Weight: 216.32

1-(2-methybenzyl)cyclohexanecarbaldehyde (**3cf**). Colorless oil; **R_f** = 0.48 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.14-1.39, 1.56-1.64 and 2.01-2.05 (3m, 4+4+2H, H-3, 4, 5, 6 and H-7); 2.28 (s, 3H, H-15); 2.73 (s, 2H, H-8); 7.01-7.06 (m, 1H, H-14); 7.08-7.14 (m, 3H, H-11, 12 and H-13); 9.51 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 20.7 (C-15); 23.3, 25.9 and 31.9 (C-3, 4, 5, 6 and C-7); 40.9 (C-8); 51.7 (C-2); 125.8 (C-11); 127.0 (C-12); 131.0 (C-13); 131.6 (C-14); 134.8 (C-9); 137.1 (C-10); 207.8 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2928, 2854, 1724, 1452, 763, 754. **LRMS** *(method: ESI positive)* calculated for $C_{15}H_{21}O$ 217.2 $[M+H]^+$, found 217.3.



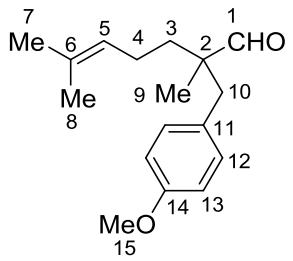
3ci
Chemical Formula: $C_{14}H_{17}ClO$
Molecular Weight: 236.74

1-(4-chlorobenzyl)cyclohexanecarbaldehyde (**3ci**). Colorless oil; **R_f** = 0.50 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.25-1.33, 1.54-1.65 and 1.87-1.91 (3m, 4+4+2H, H-3, 4, 5, 6 and H-7); 2.69 (s, 2H, H-8); 6.98 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-10); 7.22 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-11); 9.50 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 23.0, 25.9 and 31.5 (C-3, 4, 5, 6 and C-7); 43.0 (C-8); 51.0 (C-2); 128.6 (C-11); 131.8 (C-10); 132.7 (C-9); 135.1 (C-12); 207.3 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2928, 2853, 1722, 1491, 1452, 1408, 1015, 830, 811. **LRMS** *(method: ESI positive)* calculated for $C_{14}H_{18}ClO$ 237.1 $[M+H]^+$, found 237.3.



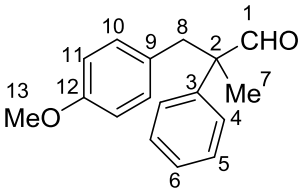
3da
Chemical Formula: $C_{16}H_{24}O_2$
Molecular Weight: 248.37

2-ethyl-2-(4-methoxybenzyl)hexanal (**3da**). Colorless oil; **R_f** = 0.45 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.84-0.93 (m, 6H, H-8 and H-8); 1.19-1.35 (m, 4H, H-4 and H-5); 1.40-1.61 (m, 4H, H-3 and H-7); 2.77 (s, 2H, H-9); 3.78 (s, 3H, H-14); 6.79 (d, $^3J_{HH}$ = 8.6 Hz, 2H, H-12); 6.99 (d, $^3J_{HH}$ = 8.6 Hz, 2H, H-11); 9.54 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 8.4 (C-8); 14.3 (C-6); 23.7 (C-4); 24.5 (C-7); 26.1 (C-5); 31.4 (C-3); 38.1 (C-9); 54.0 (C-2); 55.6 (C-14); 113.9 (C-12); 129.3 (C-10); 131.3 (C-11); 158.5 (C-13); 207.8 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2933, 1721, 1612, 1512, 1460, 1247, 1178, 1035, 826. **LRMS** *(method: ESI positive)* calculated for $C_{16}H_{25}O_2$ 249.2 $[M+H]^+$, found 249.4.



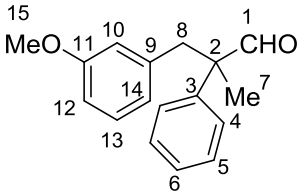
3ea
Chemical Formula: $C_{17}H_{24}O_2$
Molecular Weight: 260.38

2-(4-methoxybenzyl)-2,6-dimethylhept-5-enal (**3ea**). Colorless oil; **R_f** = 0.35 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.00 (s, 3H, H-9); 1.40-1.47 and 1.57-1.65 (2m, 1+1H, H-3); 1.58 (s, 3H, H-8); 1.67 (s, 3H, H-7); 1.84-2.03 (m, 2H, H-4); 2.67 and 2.81 (2d, $^2J_{HH}$ = 13.8 Hz, 1+1H, H-10); 3.78 (s, 3H, H-15); 5.02-5.06 (m, 1H, H-5); 6.80 (d, $^3J_{HH}$ = 8.6 Hz, 2H, H-13); 7.00 (d, $^3J_{HH}$ = 8.6 Hz, 2H, H-12); 9.55 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.0 (C-8); 18.4 (C-9); 23.3 (C-4); 26.0 (C-7); 36.1 (C-3); 41.6 (C-10); 50.7 (C-2); 55.6 (C-15); 113.9 (C-13); 124.1 (C-5); 129.1 (C-11); 131.5 (C-12); 132.6 (C-6); 158.6 (C-14); 206.8 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2920, 1721, 1511, 1245, 1178, 1036, 827. **LRMS** *(method: ESI positive)* calculated for $C_{17}H_{27}O_3$ 279.2 $[M+H_3O]^+$, found 279.5.



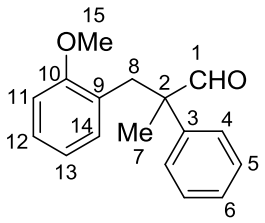
7aa
Chemical Formula: $C_{17}H_{18}O_2$
Molecular Weight: 254.33

3-(4-methoxyphenyl)-2-methyl-2-phenylpropanal (**7aa**). Colorless oil; **R_f** = 0.35 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.37 (s, 3H, H-7); 3.09-3.19 (m 2H, H-8); 3.74 (s, 3H, H-13); 6.67-6.72 (m, 4H, H-10 and H-11); 7.17-7.19 (m, 2H, H-4); 7.28-7.32 (m, 1H, H-6); 7.35-7.38 (m, 2H, H-5); 9.63 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.6 (C-7); 42.2 (C-8); 55.5 (C-13); 55.5 (C-2); 113.6 (C-11); 127.7 (C-6); 127.9 (C-4); 129.1 (C-5 and C-9); 131.2(C-10); 139.7 (C-3); 158.5 (C-12); 202.6 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2934, 1721, 1610, 1511, 1444, 1243, 1178, 1032, 820, 757, 698, 572. **HRMS** *(method: ESI positive)* calculated for $C_{17}H_{22}NO_2$ 272.1645 $[M+NH_4]^+$, found 272.1647. **Chiral HPLC conditions** Column IC, $\lambda = 208$ nm, hexanes/^{i}PrOH 99:1, 1 mL/min., t_1 = 11.30 and t_2 = 12.94 min.



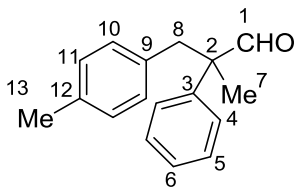
7ab
Chemical Formula: $C_{17}H_{18}O_2$
Molecular Weight: 254.33

3-(3-methoxyphenyl)-2-methyl-2-phenylpropanal (**7ab**). Colorless oil; **R_f** = 0.37 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.39 (s, 3H, H-7); 3.13-3.21 (m, 2H, H-8); 3.61 (s, 3H, H-15); 6.24-6.25 (m, 1H, H-10); 6.43 (d, $^3J_{HH}$ = 7.9 Hz, 1H, H-14); 6.70 (ddd, $^4J_{HH}$ = 0.9 Hz, $^4J_{HH}$ = 2.6 Hz, $^3J_{HH}$ = 7.9 Hz, 1H, H-12); 7.06 (t, $^3J_{HH}$ = 7.9 Hz, 1H, H-13); 7.18-7.20 (m, 2H, H-4); 7.29-7.32 (m, 1H, H-6); 7.36-7.39 (m, 2H, H-5); 9.63 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.1 (C-7); 42.7 (C-8); 54.8 (C-15); 54.9 (C-2); 112.1 (C-12); 115.6 (C-10); 122.8 (C-14); 127.3 (C-6); 127.6 (C-4); 128.6 (C-13); 128.7 (C-5); 138.2 (C-9); 139.2 (C-3); 158.9 (C-11); 201.8 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2940, 1721, 1599, 1583, 1449, 1263, 1154, 1043, 784, 761. **LRMS** *(method: ESI positive)* calculated for $C_{17}H_{19}O_2$ 255.1 $[M+H]^+$, found 255.0.



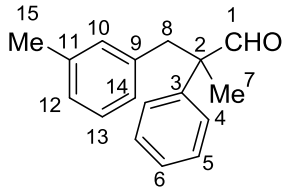
7ac
Chemical Formula: $C_{17}H_{18}O_2$
Molecular Weight: 254.33

3-(2-methoxyphenyl)-2-methyl-2-phenylpropanal (**7ac**). Colorless oil; **R_f** = 0.50 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.32 (s, 3H, H-7); 3.03 and 3.56 (2d, $^2J_{HH}$ = 13.4 Hz, 1+1H, H-8); 3.68 (s, 3H, H-15); 6.77-6.85 (m, 3H, H-11, H-13 and H-14); 7.16-7.20 (m, 1H, H-12); 7.27-7.31 (m, 3H, H-4 and H-6); 7.35-7.40 (m, 2H, H-5); 9.65 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.9 (C-7); 36.7 (C-8); 55.2 (C-15); 55.2 (C-2); 110.7 (C-14); 120.4 (C-11); 125.7 (C-9); 127.5 (C-6); 127.7 (C-4); 128.4 (C-12); 129.0 (C-5); 132.5 (C-11); 141.1 (C-3); 157.9 (C-10); 202.2 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2831, 1713, 1599, 1492, 1463, 1439, 1244, 1024, 753, 696. **HRMS** *(method: ESI positive)* calculated for $C_{17}H_{19}O_2$ 255.1380 $[M+H]^+$, found 255.1376.



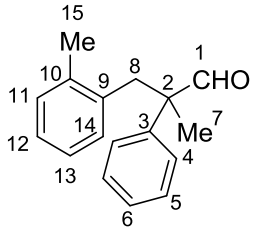
7ad
Chemical Formula: $C_{17}H_{18}O$
Molecular Weight: 238.33

2-methyl-2-phenyl-3-(p-tolyl)propanal (**7ad**). Colorless oil; **R_f** = 0.54 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.37 (s, 3H, H-7); 2.27 (s, 3H, H-13); 3.13 and 3.20 (2d, $^2J_{HH}$ = 13.7 Hz, 1+1H, H-8); 6.69 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-10); 6.95 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-11); 7.18-7.20 (m, 2H, H-4); 7.28-7.32 (m, 1H, H-6); 7.35-7.39 (m, 2H, H-5); 9.63 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.6 (C-7); 21.3 (C-13); 42.6 (C-8); 55.4 (C-2); 127.7 (C-6); 127.9 (C-4); 128.9 (C-11); 129.1 (C-5); 130.6 (C-10); 133.9 (C-9); 136.2 (C-12); 139.8 (C-3); 202.5 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2925, 2707, 1722, 1513, 1494, 1445, 805, 759, 698, 569. **LRMS** *(method: ESI positive)* calculated for $C_{17}H_{19}O$ 239.1 $[M+H]^+$, found 239.1.



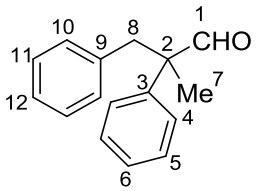
7ae
Chemical Formula: $C_{17}H_{18}O$
Molecular Weight: 238.33

2-methyl-2-phenyl-3-(m-tolyl)propanal (**7ae**). Colorless oil; **R_f** = 0.53 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.40 (s, 3H, H-7); 2.24 (s, 3H, H-15); 3.14 and 3.23 (2d, $^2J_{HH}$ = 13.6 Hz, 1+1H, H-8); 6.61-6.63 (m, 2H, H-10 and H-14); 6.98-7.00 (m, 1H, H-10); 7.05 (t, $^3J_{HH}$ = 7.6 Hz, 1H, H-13); 7.20-7.22 (m, 2H, H-4); 7.31-7.35 (m, 1H, H-6); 7.38-7.41 (m, 2H, H-5); 9.66 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.7 (C-7); 21.7 (C-15); 43.0 (C-8); 55.4 (C-2); 127.5 (C-12); 127.7 (C-6 and C-14); 127.9 (C-4); 128.0 (C-13); 129.0 (C-5); 131.6 (C-10); 137.0 (C-9); 137.7 (C-11); 139.8 (C-3); 202.4 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2936, 1722, 1445, 786, 759, 696. **LRMS** *(method: ESI positive)* calculated for $C_{18}H_{22}O_2$ 270.2 $[M+OMe]^+$, found 270.4.



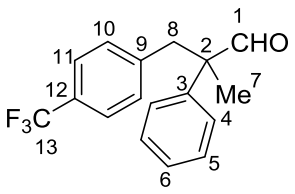
7af
Chemical Formula: $C_{17}H_{18}O$
Molecular Weight: 238.33

2-methyl-2-phenyl-3-(o-tolyl)propanal (**7af**). Colorless oil; **R_f** = 0.53 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.40 (s, 3H, H-7); 1.99 (s, 3H, H-15); 3.16 and 3.32 (2d, $^2J_{HH}$ = 14.1 Hz, 1+1H, H-8); 6.70 (br d, $^3J_{HH}$ = 7.6 Hz, 1H, H-14); 6.95-6.99 (m, 1H, H-13); 7.04-7.09 (m, 2H, H-11 and H-12); 7.14-7.16 (m, 2H, H-4); 7.28-7.37 (m, 3H, H-5 and H-6); 9.67 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.6 (C-7); 20.2 (C-15); 38.9 (C-8); 55.8 (C-2); 125.7 (C-13); 126.8 (C-12); 127.8 (C-6); 128.0 (C-4); 129.1 (C-5); 130.7 (C-11); 131.4 (C-14); 135.6 (C-9); 137.7 (C-10); 140.1 (C-3); 202.5 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2966, 1721, 1493, 1446, 1029, 762, 697. **LRMS** *(method: ESI positive)* calculated for $C_{17}H_{19}O$ 239.1 $[M+H]^+$, found 239.0. **HPLC conditions** Column ODH, λ = 210 nm, hexanes/^{i}PrOH 99:1, 1 mL/min., t_1 = 8.38 and t_2 = 10.28 min.



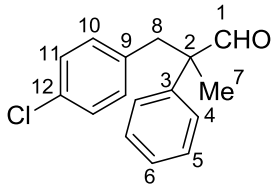
7ag
Chemical Formula: $C_{16}H_{16}O$
Molecular Weight: 224.30

2-methyl-2,3-diphenylpropanal (**7ag**). Colorless oil; **R_f** = 0.54 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.38 (s, 3H, H-7); 3.18 and 3.23 (2d, $^2J_{HH}$ = 13.6 Hz, 1+1H, H-8); 6.79-6.81 (m, 2H, H-10); 7.13-7.15 (m, 3H, H-11 and H-12); 7.17-7.19 (m, 2H, H-4); 7.29-7.32 (m, 1H, H-6); 7.35-7.39 (m, 2H, H-5); 9.64 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.6 (C-7); 43.0 (C-8); 55.4 (C-2); 126.7 (C-12); 127.8 (C-6); 127.9 (C-4); 128.2 (C-11); 129.1 (C-5); 130.7 (C-10); 137.1 (C-9); 139.6 (C-3); 202.3 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 1721, 1494, 1449, 759, 697. **LRMS** *(method: ESI positive)* calculated for $C_{16}H_{17}O$ 225.1 $[M+H]^+$, found 225.0. **Chiral HPLC conditions** Column ODH, λ = 208 nm, hexanes/^{i}PrOH 99:1, 1 mL/min., t_1 = 8.57 and t_2 = 10.82 min.



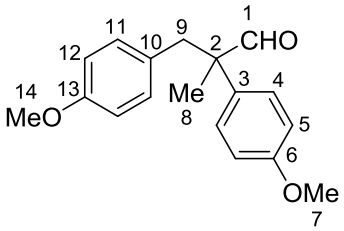
7ah
Chemical Formula: $C_{17}H_{15}F_3O$
Molecular Weight: 292.30

2-methyl-2-phenyl-3-(4-(trifluoromethyl)phenyl)propanal (**7ah**). Colorless oil; **R_f** = 0.56 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.41 (s, 3H, H-7); 3.21-3.28 (m, 2H, H-8); 6.89 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-10); 7.15-7.18 (m, 2H, H-4); 7.33-7.42 (m, 5H, H-5, H-6 and H-11); 9.61 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.3 (C-7); 42.9 (C-8); 55.3 (C-2); 124.6 (q, $^1J_{CF}$ = 271.8 Hz, C-13); 125.0 (q, $^3J_{CF}$ = 3.7 Hz, C-11); 127.9 (C-4); 128.1 (C-6); 129.1 (q, $^2J_{CF}$ = 32.5 Hz, C-12); 129.3 (C-5); 131.0 (C-10); 138.8 (C-3); 141.45 (C-9); 201.6 (C-1). **^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz)** δ (ppm) = -61.7 (s). **IR spectrum (neat)** ν (cm^{-1}) = 1723, 1619, 1322, 1162, 1115, 1066, 1018, 822, 699. **LRMS** *(method: ESI positive)* calculated for $C_{18}H_{19}F_3O_2$ 324.2 $[M+OMe]^+$, found 324.5.



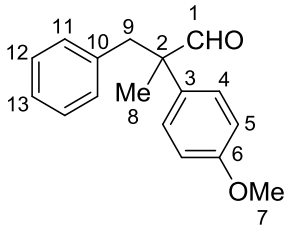
7ai
Chemical Formula: $C_{16}H_{15}ClO$
Molecular Weight: 258.75

3-(4-chlorophenyl)-2-methyl-2-phenylpropanal (**7ai**). Colorless oil; **R_f** = 0.52 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.37 (s, 3H, H-7); 3.14 (s, 2H, H-8); 6.69 (d, $^2J_{HH}$ = 8.6 Hz, 2H, H-10); 7.09 (d, $^2J_{HH}$ = 8.6 Hz, 2H, H-11); 7.13-7.15 (m, 2H, H-4); 7.29-7.32 (m, 1H, H-6); 7.35-7.39 (m, 2H, H-5); 9.59 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.4 (C-7); 42.4 (C-8); 55.3 (C-2); 127.9 (C-4); 128.0 (C-6); 128.3 (C-11); 129.2 (C-5); 132.0 (C-10); 132.6 (C-12); 135.6 (C-9); 139.1 (C-3); 201.9 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2934, 1721, 1677, 1491, 1445, 1090, 1015, 810, 760, 698. **LRMS** *(method: ESI positive)* calculated for $C_{17}H_{19}ClO_2$ 290.1 $[M+OMe]^+$, found 290.0.



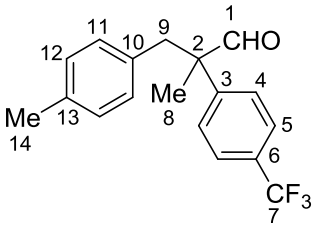
7ba
Chemical Formula: $C_{18}H_{20}O_3$
Molecular Weight: 284.36

2,3-bis(4-methoxyphenyl)-2-methylpropanal (**7ba**). Colorless oil; **R_f** = 0.31 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.33 (s, 3H, H-8); 3.06-3.15 (m, 2H, H-9); 3.74 (s, 3H, H-7); 3.82 (s, 3H, H-14); 6.67-6.73 (m, 4H, H-4 and H-5); 6.90 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H-12); 7.09 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H-11); 9.57 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.7 (C-8); 42.1 (C-9); 54.8 (C-2); 55.5 (C-7); 55.6 (C-14); 113.6 (C-4 or C-5); 114.4 (C-12); 129.1 (C-11); 129.2 (C-10); 131.7 (C-3); 131.7 (C-4 or C-5); 158.5 (C-6); 159.1 (C-13); 202.5 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2941, 1719, 1609, 1510, 1460, 1244, 1179, 1030, 826. **LRMS** *(method: ESI positive)* calculated for $C_{18}H_{21}O_3$ 285.1 $[M+H]^+$, found 285.3.



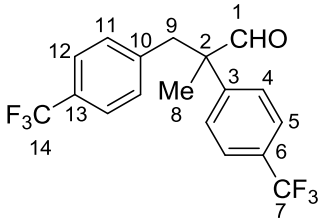
7bg
Chemical Formula: $C_{17}H_{18}O_2$
Molecular Weight: 254.33

2-(4-methoxyphenyl)-2-methyl-3-phenylpropanal (**7bg**). Colorless oil; **R_f** = 0.47 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.34 (s, 3H, H-8); 3.12-3.21 (m, 2H, H-9); 3.82 (s, 3H, H-7); 6.79-6.82 (m, 2H, H-11); 6.90 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H-5); 7.09 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H-4); 7.14-7.15 (m, 3H, H-12 and H-13); 9.57 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.6 (C-8); 43.0 (C-9); 54.7 (C-2); 55.6 (C-7); 114.5 (C-5); 126.7 (C-13); 128.2 (C-12); 129.1 (C-4); 130.7 (C-11); 131.3 (C-3); 137.3 (C-10); 159.2 (C-6); 202.2 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2935, 1719, 1607, 1511, 1454, 1249, 1183, 1030, 827, 750, 699. **LRMS** *(method: ESI positive)* calculated for $C_{17}H_{19}O_2$ 255.1 $[M+H]^+$, found 255.4.



7cd
Chemical Formula: $C_{18}H_{17}F_3O$
Molecular Weight: 306.33

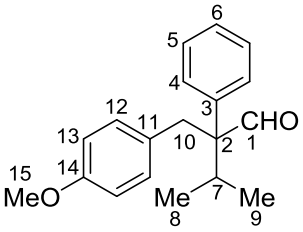
2-methyl-3-(p-tolyl)-2-(4-(trifluoromethyl)phenyl)propanal (**7cd**). Yellow oil; **R_f** = 0.64 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.41 (s, 3H, H-8); 2.27 (s, 3H, H-14); 3.12-3.22 (m, 2H, H-9); 6.68 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-11); 6.96 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-12); 7.29 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H-4); 7.62 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H-5); 9.65 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.8 (C-8); 21.3 (C-14); 42.8 (C-9); 55.6 (C-2); 124.4 (q, $^1J_{CF}$ = 272 Hz, C-7); 125.8 (q, $^3J_{CF}$ = 3.7 Hz, C-5); 128.4 (C-4); 129.1 (C-12); 130.0 (q, $^2J_{CF}$ = 32.6 Hz, C-6); 130.5 (C-11); 133.2 (C-10); 136.6 (C-13); 144.1 (C-3); 201.8 (C-1). **^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz)** δ (ppm) = -61.9 (s). **IR spectrum (neat)** ν (cm^{-1}) = 2930, 1725, 1324, 1165, 1118, 1075, 834. **LRMS** *(method: ESI positive)* calculated for $C_{19}H_{20}F_3O_2$ 338.1 $[M+OMe]^+$, found 338.0.



7ch
Chemical Formula: $C_{18}H_{14}F_6O$
Molecular Weight: 360.30

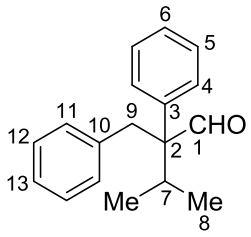
2-methyl-2,3-bis(4-(trifluoromethyl)phenyl)propanal (**7ch**). Colorless oil; **R_f** = 0.68 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.44 (s, 3H, H-8); 3.20-3.30 (m, 2H, H-9); 6.88 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-11); 7.28 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H-4); 7.40 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H-12); 7.64 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H-5); 9.60 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.5 (C-8); 42.9 (C-9); 55.4 (C-2); 124.2 (q, $^1J_{CF}$ = 272.1 Hz, C-14); 124.5 (q, $^1J_{CF}$ = 272.0 Hz, C-7); 125.2 (q, $^3J_{CF}$ = 3.7 Hz, C-12); 126.1 (q, $^3J_{CF}$ = 3.7 Hz, C-5); 128.3 (C-4); 129.4 (q, $^2J_{CF}$ = 32.4 Hz, C-13); 130.4 (q, $^2J_{CF}$ = 32.8 Hz, C-6); 131.0 (C-11); 140.7 (C-10); 143.2 (C-3); 200.9 (C-1). **^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz)** δ (ppm) = − 61.9 (s); − 61.8 (s). **IR spectrum (neat)** ν (cm^{-1}) = 2941, 1726, 1619, 1321, 1163, 1111, 1065,

835. **LRMS** *(method: ESI positive)* calculated for $C_{19}H_{20}F_6O_3$ 410.1 $[M+H_2O+OMe]^+$, found 410.5.



7da
Chemical Formula: $C_{19}H_{22}O_2$
Molecular Weight: 282.38

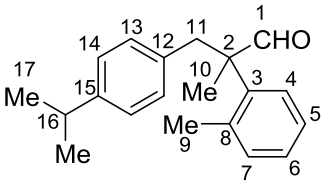
2-(4-methoxybenzyl)-3-methyl-2-phenylbutanal (**7da**). Colorless oil; **R_f** = 0.36 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 0.98-1.02 (m, 6H, H-8 and H-9); 2.45 (h, 1H, H-7); 3.09-3.20 (m, 2H, H-10); 3.72 (s, 3H, H-15); 6.62-6.68 (m, 4H, H-12 and H-13); 6.99-7.01 (m, 2H, H-4); 7.27-7.34 (m, 3H, H-5 and H-6); 9.86 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.5 and 18.8 (C-8 and C-9); 31.4 (C-7); 39.5 (C-10); 55.4 (C-15); 62.2 (C-2); 113.4 (C-13); 127.3 (C-6); 128.5 (C-5); 129.0 (C-11); 129.2 (C-4); 131.8 (C-12); 138.5 (C-3); 158.3 (C-14); 205.5 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2961, 1719, 1611, 1511, 1248, 1178, 1033, 824, 701. **HRMS** *(method: ESI positive)* calculated for $C_{19}H_{24}O_3$ 300.1720 $[M+H_2O]^+$, found 300.1717. **Chiral HPLC conditions** Column ADH, λ = 220 nm, hexanes/^{i}PrOH 99:1, 1 mL/min., t_1 = 9.65 and t_2 = 12.00 min.



7dg
Chemical Formula: $C_{18}H_{20}O$
Molecular Weight: 252.36

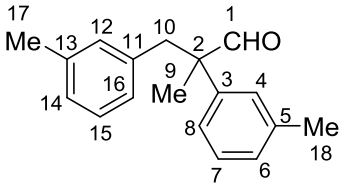
2-benzyl-3-methyl-2-phenylbutanal (**7dg**). Colorless oil; **R_f** = 0.47 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.01-1.03 (m, 6H, H-8); 2.47 (hept, $^3J_{HH}$ = 6.9 Hz, 1H, H-7); 3.15 and 3.23 (2d, $^2J_{HH}$ = 13.9 Hz, 1+1H, H-9); 6.73-6.76 (m, 2H, H-11); 6.98-7.00 (m, 2H, H-4); 7.05-7.10 (m, 3H, H-12 and H-13); 7.27-7.33 (m, 3H, H-5 and H-6); 9.88 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.6 and 18.8 (C-8); 31.6 (C-7); 40.4 (C-9); 62.2 (C-2); 126.6 (C-13); 127.3 (C-6); 128.0 (C-12); 128.6 (C-5); 129.2(C-4); 130.9 (C-11); 137.1 (C-10); 138.4 (C-3); 205.3 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2963,

1720, 1495, 1450, 1028, 761, 697. **LRMS** *(method: ESI positive)* calculated for $C_{18}H_{24}NO$ 270.2 $[M+NH_4]^+$, found 270.8. **Chiral HPLC conditions** Column ASH, $\lambda = 208$ nm, hexanes/^{i}PrOH 99:1, 1 mL/min., $t_1 = 4.82$ and $t_2 = 5.97$ min.



7ej
Chemical Formula: $C_{20}H_{24}O$
Molecular Weight: 280.41

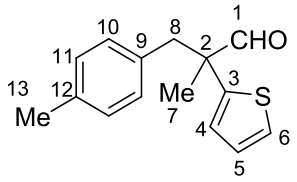
3-(4-isopropylphenyl)-2-methyl-2-(o-tolyl)propanal (**7ej**). Colorless oil; $\mathbf{R_f}$ = 0.55 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.18-1.20 (2d superimposed, $^3J_{HH}$ = 6.9 Hz, 3+3H, H-17); 1.33 (s, 3H, H-10); 2.80 (hept, $^3J_{HH}$ = 6.9 Hz, 1H, H-16); 3.18 and 3.23 (2d, $^2J_{HH}$ = 13.7 Hz, 1+1H, H-11); 6.60 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-13); 6.96 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-14); 7.13-7.15 (m, 1H, H-5 or H-6); 7.22-7.24 (m, 3H, H-4, H-5 or H-6 and H-7); 9.72 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 20.6 (C-10); 21.6 (C-9); 24.3 and 24.3 (C-17); 33.9 (C-16); 39.8 (C-11); 55.7 (C-2); 126.0 (C-14); 126.4 (C-5 or C-6); 128.0 and 128.7 (C-5 or C-6 and C-4); 130.9 (C-13); 132.4 (C-7); 134.3 (C-12); 136.8 (C-8); 138.3 (C-3); 147.1 (C-15); 204.3 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2960, 1721, 1513, 1459, 1383, 903, 824, 758, 724. **HRMS** *(method: ESI positive)* calculated for $C_{20}H_{25}O$ 281.1900 $[M+H]^+$, found 281.1907.



7fe
Chemical Formula: $C_{18}H_{20}O$
Molecular Weight: 252.36

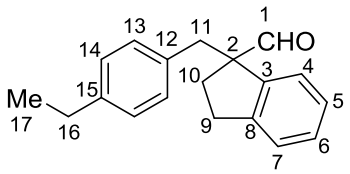
2-methyl-2,3-di-m-tolylpropanal (**7fe**). Colorless oil; $\mathbf{R_f}$ = 0.53 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.35 (s, 3H, H-9); 2.23 (s, 3H, H-17); 2.35 (s, 3H, H-18); 3.09 and 3.21 (2d, $^2J_{HH}$ = 13.6 Hz, 1+1H, H-10); 6.61 (br d, $^3J_{HH}$ = 7.7 Hz, 1H, H-14); 6.63 (br s, 1H, H-12); 6.96-7.00 (m, 3H, H-4, H-8 and H-16); 7.04 (t, $^3J_{HH}$ = 7.7 Hz, 1H, H-15); 7.12 (br d, $^3J_{HH}$ = 7.8 Hz, 1H, H-6); 7.24-7.27 (m, 1H, H-7); 9.62 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.7 (C-9); 21.7 (C-17); 21.9 (C-18); 42.8 (C-10); 55.3 (C-2); 124.9 (C-8); 127.4 (C-16); 127.8 (C-14); 128.0 (C-15); 128.5 (C-4); 128.6 (C-6); 128.9 (C-7);

131.6 (C-12); 137.1 (C-11); 137.7 (C-13); 138.7 (C-5); 139.8 (C-3); 202.4 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2924, 1722, 1605, 1455, 782, 702. **HRMS** *(method: ESI positive)* calculated for $C_{18}H_{20}NaO$ 275.1406 $[M+Na]^+$, found 275.1403.



7ge
Chemical Formula: $C_{15}H_{16}OS$
Molecular Weight: 244.35

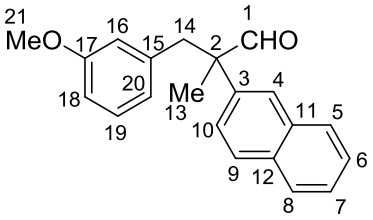
2-methyl-2-(thiophen-2-yl)-3-(p-tolyl)propanal (**7ge**). Yellow oil; **R_f** = 0.53 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.42 (s, 3H, H-7); 2.29 (s, 3H, H-13); 3.12 and 3.28 (2d, $^2J_{HH}$ = 13.7 Hz, 1+1H, H-8); 6.84 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H-10); 6.88 (dd, $^4J_{HH}$ = 1.1 Hz, $^3J_{HH}$ = 3.6 Hz, 1H, H-4); 7.01 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H-11); 7.04 (dd, $^3J_{HH}$ = 3.6 Hz, $^3J_{HH}$ = 5.1 Hz, 1H, H-5); 7.30 (dd, $^4J_{HH}$ = 1.1 Hz, $^3J_{HH}$ = 5.1 Hz, 1H, H-6); 9.61 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 20.1 (C-7); 21.4 (C-13); 43.7 (C-8); 53.8 (C-2); 125.7 (C-6); 125.8 (C-4); 127.7 (C-5); 129.1 (C-11); 130.5 (C-10); 133.3 (C-9); 136.6 (C-12); 144.7 (C-3); 200.1 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2925, 1723, 1514, 1453, 1237, 821, 798, 697. **HRMS** *(method: ESI positive)* calculated for $C_{15}H_{16}NaOS$ 267.0814 $[M+Na]^+$, found 267.0820.



7hk
Chemical Formula: $C_{19}H_{20}O$
Molecular Weight: 264.37

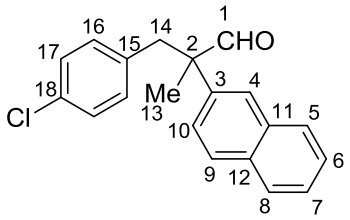
1-(4-ethylbenzyl)-2,3-dihydro-1H-indene-1-carbaldehyde (**7hk**). Yellow oil; **R_f** = 0.55 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.19 (t, $^3J_{HH}$ = 7.6 Hz, 3H, H-17); 2.10 (ddd, $^3J_{HH}$ = 5.6 Hz, $^3J_{HH}$ = 8.7 Hz, $^2J_{HH}$ = 13.3 Hz, 1H, H-10); 2.40 (ddd, $^3J_{HH}$ = 6.3 Hz, $^3J_{HH}$ = 8.9 Hz, $^2J_{HH}$ = 13.3 Hz, 1H, H-10'); 2.43-2.62 (m, 3H, H-9 and H-16); 2.82 (ddd, $^3J_{HH}$ = 5.6 Hz, $^3J_{HH}$ = 8.9 Hz, $^2J_{HH}$ = 14.7 Hz, 1H, H-9'); 3.01 and 3.32 (2d, $^2J_{HH}$ = 13.8 Hz, 1+1H, H-11); 6.87 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H-13); 7.01 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H-14); 7.19-7.27 (m, 4H, H-4, H-5, H-6 and H-7); 9.66 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 15.9 (C-17); 28.7 (C-16); 30.9 (C-10); 31.2 (C-9); 40.6 (C-11); 65.0 (C-2); 125.8, 125.4 , 127.1 and 128.5 (C-4, C-5, C-6 and C-7); 127.9 (C-14); 130.3 (C-13); 134.5 (C-12); 142.2

(C-3); 142.7 (C-15); 145.6 (C-8); 201.5 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2963, 1719, 1512, 1454, 827, 754, 722. **HRMS** *(method: ESI positive)* calculated for $C_{19}H_{21}O$ 265.1587 $[M+H]^+$, found 265.1591.



7ib
Chemical Formula: $C_{21}H_{20}O_2$
Molecular Weight: 304.39

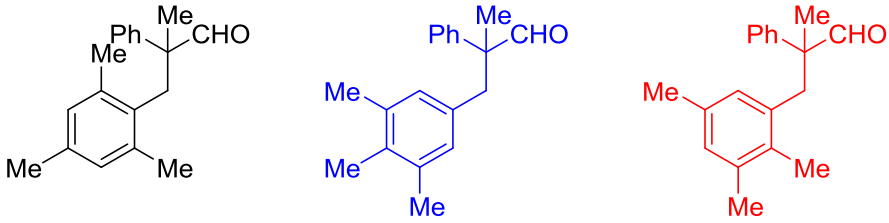
3-(3-methoxyphenyl)-2-methyl-2-(naphthalen-2-yl)propanal (**7ib**). Colorless oil; **R_f** = 0.58 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.49 (s, 3H, H-13); 3.28 (s, 2H, H-14); 3.50 (s, 3H, H-21); 6.28-6.29 (m, 1H, H-16); 6.43 (br d, $^3J_{HH}$ = 7.8 Hz, 1H, H-20); 6.66-6.68 (m, 1H, H-18); 7.01-7.05 (m, 1H, H-19); 7.35 (dd, $^4J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, H-10); 7.47-7.52 (m, 2H, H-6 and H-7); 7.61 (d, $^4J_{HH}$ = 2.0 Hz, 1H, H-4); 7.78-7.80 (m, 1H, H-5); 7.83-7.87 (m, 2H, H-8 and H-9); 9.68 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.7 (C-13); 42.9 (C-14); 55.2 (C-21); 55.6 (C-2); 112.5 (C-18); 116.1 (C-16); 123.2 (C-20); 125.7 (C-10); 126.7 (C-6 and C-7); 127.1 (C-4); 127.9 (C-8); 128.4 (C-5); 128.8 (C-9); 129.1 (C-19); 132.8 (C-12); 133.7 (C-11); 137.0 (C-3); 138.7 (C-15); 159.4 (C-17); 202.2 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2935, 1834, 1720, 1597, 1488, 1263, 1154, 1043, 817, 745, 697. **LRMS** *(method: ESI positive)* calculated for $C_{21}H_{22}O_2$ 305.1 $[M+H]^+$, found 305.6.



7ii
Chemical Formula: $C_{20}H_{17}ClO$
Molecular Weight: 308.81

3-(4-chlorophenyl)-2-methyl-2-(naphthalen-2-yl)propanal (**7ii**). Colorless oil; **R_f** = 0.60 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.48 (s, 3H, H-13); 3.20-3.31 (m, 2H, H-14); 6.70 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-16); 7.06 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-17); 7.30 (dd, $^4J_{HH}$ = 1.9 Hz, $^3J_{HH}$ = 8.7 Hz, 1H, H-10); 7.48-7.54 (m, 2H, H-6 and H-7); 7.58 (d, $^4J_{HH}$ = 1.9 Hz, 1H, H-4); 7.78-7.81 (m, 1H, H-5); 7.84-7.88 (m, 2H, H-8 and H-9); 9.64 (s, 1H, H-1).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) = 18.5 (C-13); 42.2 (C-14); 55.5 (C-2); 125.6 (C-10); 126.8 (C-6 and C-7); 127.1 (C-4); 127.9 (C-8); 128.3 (C-17); 128.4 (C-5); 128.9 (C-9); 132.0 (C-16); 132.7 (C-18); 132.8 (C-11); 133.6 (C-12); 135.6 (C-15); 136.4 (C-3); 201.9 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 3055, 2972, 2806, 2705, 1720, 1490, 1090, 1015, 816, 745. **LRMS** *(method: ESI positive)* calculated for $C_{21}H_{20}ClO$ 340.1 $[M+OMe]^+$, found 340.3.



7al-1 **7al-2** **7al-3**

Chemical Formula: $C_{19}H_{22}O$
Molecular Weight: 266.38

Mixture of inseparable isomers **7al-1, 7al-2** and **7al-3**. Colorless oil; **R_f** = 0.60 (SiO_2, pentane/CH_2Cl_2 1:1);

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) = All the protons from the phenyl group cannot be assigned due to superimposing of signals.

7al-1: 1.33 (s, 3H, α-Me); 1.92 (s, 6H, *o*-Me); 2.23 (s, 3H, *p*-Me); 3.09 and 3.56 (2d, $^{2}J_{HH}$ = 14.6 Hz, 1+1H, -CH_2); 6.77 (s, 2H, *m*-H); 9.66 (s, 1H, H-aldehyde).

7al-2: 1.36 (s, 3H, α-Me); 2.09 (2, 3H, *p*-Me); 2.14 (s, 6H, *m*-Me); 3.04 and 3.18 (2d, $^{2}J_{HH}$ = 13.6 Hz, 1+1H, -CH_2); 6.45 (s, 2H, *o*-H); 9.69 (s, 1H, H-aldehyde).

7al-3: 1.37 (s, 3H, α-Me); 1.85 (s, 3H, *o*-Me); 2.12 (s, 3H, *m*-Me); 2.17 (s, 3H, *p*-Me); 3.14 and 3.36 (2d, $^{2}J_{HH}$ = 14.1 Hz, 1+1H, -CH_2); 6.37 (s, 1H, *o*-H); 6.81 (s, 1H, *p*-H); 9.65 (s, 1H, H-aldehyde).

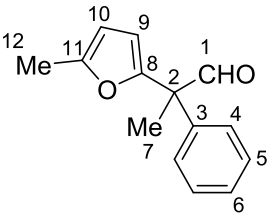
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) δ (ppm) = All the carbon not listed here cannot be assigned due to superimposing of signals in both mono- and bi-dimensional spectra.

7al-1: 18.3 (α-Me); 21.1 (*p*-Me); 21.3 (*o*-Me); 35.5 (-CH_2); 55.3 (α-C); 129.5 (*m*-C); 202.6 (C-aldehyde).

7al-2: 15.4 (*p*-Me); 18.6 or 18.8 (α-Me); 20.8 (*m*-Me); 42.5 (-CH_2); 55.3 or 55.9 (α-C); 130.0 (*o*-C); 202.8 (C-aldehyde).

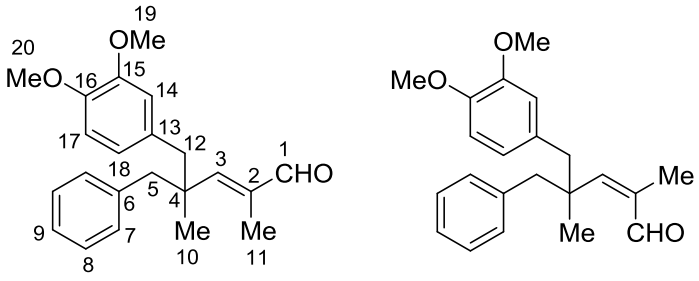
7al-3: 15.8 (*o*-Me); 18.6 or 18.8 (α-Me); 39.4 (-CH_2); 55.3 or 55.9 (α-C); 129.5 (*p*-C); 130.1 (*o*-C); 202.7 (C-aldehyde).

LRMS *(method: ESI positive)* calculated for $C_{19}H_{22}NaO$ 289.2 $[M+Na]^+$, found 289.1.



7am
Chemical Formula: $C_{14}H_{14}O_2$
Molecular Weight: 214.26

2-(5-methylfuran-2-yl)-2-phenylpropanal (**7am**). Colorless oil; **R_f** = 0.60 (SiO_2, pentane/CH_2Cl_2 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.72 (s, 3H, H-7); 2.28 (d, $^4J_{HH}$ = 1.0 Hz, 3H, H-12); 5.98-5.99 (m, 1H, H-10); 6.15 (d, $^3J_{HH}$ = 3.1 Hz, 1H, H-9); 7.11-7.13 (m, 2H, H-4); 7.27-7.32 (m, 1H, H-6); 7.34-7.38 (m, 2H, H-5); 9.85 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 14.0 (C-12); 21.1 (C-7); 57.1 (C-2); 106.7 (C-10); 109.8 (C-9); 127.7 (C-4); 127.8 (C-6); 129.2 (C-5); 140.7 (C-3); 152.1 (C-8); 153.2 (C-11); 198.2 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2986, 1724, 1493, 1446, 1216, 1023, 784, 760, 697. **HRMS** *(method: ESI positive)* calculated for $C_{14}H_{14}NaO_2$ 237.0886 $[M+Na]^+$, found 237.0886.



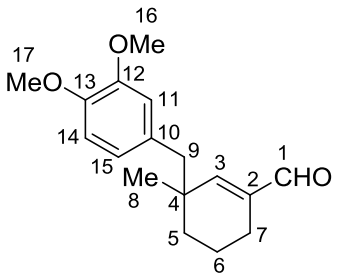
12an
Chemical Formula: $C_{22}H_{26}O_3$
Molecular Weight: 338.45

The two isomers of **12an** are not separable by chromatography

***E* isomer:** (*E*)-4-benzyl-5-(3,4-dimethoxyphenyl)-2,4-dimethylpent-2-enal. Colorless oil; **R_f** = 0.44 (SiO_2, pentane/Et_2O 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.16 (s, 3H, H-10); 1.44 (br s, 3H, H-11); 2.85-2.95 (m, 2H, H-12); 3.32 (s, 2H, H-5); 3.82 (s, 3H, H-19); 3.86 (s, 3H, H-20); 5.20 (br s, 1H, H-3); 9.54 (s, 1H, H-1); Protons H-7, 8, 9, 14, 17 and 18 cannot be assigned due to overlapping of signals. **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 17.6 (C-11); 21.6 (C-10); 42.3 (C-12); 47.6 (C-5); 52.3 (C-4); 56.2 (C-19 and C-20); 127.7 (C-3); 203.8 (C-1); Carbons C-2, 6, 7, 8, 9, 13, 14, 15, 16, 17 and 18 cannot be assigned due to overlapping of signals.

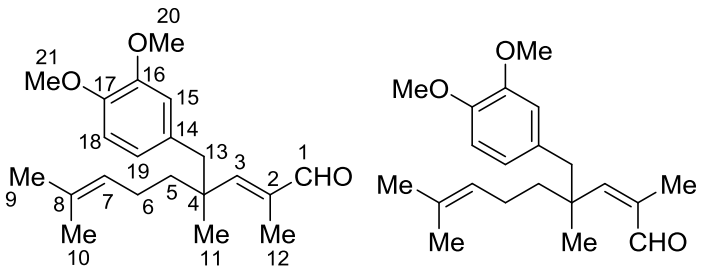
***Z* isomer:** (*Z*)-4-benzyl-5-(3,4-dimethoxyphenyl)-2,4-dimethylpent-2-enal. Colorless oil; **R_f** = 0.44 (SiO_2, pentane/Et_2O 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.20 (s, 3H, H-10); 1.65 (br s, 3H, H-11); 2.91-2.99 (m, 2H, H-12); 3.18 and 3.27 (2d, $^2J_{HH}$ = 15.4 Hz, 1+1H, H-5); 3.83 (s, 3H, H-19); 3.87 (s, 3H, H-20); 5.29 (br s, 1H, H-3); 9.65 (s, 1H, H-1); Protons H-7, 8, 9, 14, 17 and 18 cannot be assigned due to overlapping of signals. **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 21.8 (C-10); 24.6 (C-11); 39.0 (C-5); 43.1 (C-12); 52.4 (C-4); 56.1 (C-19 and C-20); 128.4 (C-3); 203.7 (C-1); Carbons C-2, 6, 7, 8, 9, 13, 14, 15, 16, 17 and 18 cannot be assigned due to overlapping of signals.

Mixture IR spectrum (neat) ν (cm^{-1}) = 2933, 1718, 1589, 1513, 1452, 1263, 1236, 1147, 1027, 852, 809, 738, 699. **LRMS** *(method: ESI positive)* calculated for $C_{22}H_{27}O_3$ 339.2 $[M+H]^+$, found 339.5.



12bn
Chemical Formula: $C_{17}H_{22}O_3$
Molecular Weight: 274.36

3-(3,4-dimethoxybenzyl)-3-methylcyclohex-1-enecarbaldehyde (**12bn**). Colorless oil; **R_f** = 0.45 (SiO_2, pentane/Et_2O 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.36-1.44, 1.55-1.60 and 1.79-1.90 (3m, 1+2+3H, H-5, H-6 and H-7); 1.73 (s, 3H, H-8); 2.73-2.86 (AB system, $^2J_{HH}$ = 13.8 Hz, 2H, H-9); 3.84 (s, 3H, H-16); 3.85 (s, 3H, H-17); 5.26 (br s, 1H, H-3); 6.62-6.65 (m, 2H, H-11 and H-15); 6.76 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H-14); 9.50 (s, 1H, H-1). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 19.3, 27.4 and 29.6 (C-5, C-6 and C-7); 24.1 (C-8); 42.2 (C-9); 52.2 (C-4); 55.7 and 55.73 (C-16 and C-17); 110.7 (C-14); 113.4 (C-11); 120.5 (C-3); 122.3 (C-15); 129.2 (C-10); 139.7 (C-2); 147.6 (C-13); 148.3 (C-12); 203.6 (C-1). **IR spectrum (neat)** ν (cm^{-1}) = 2932, 2833, 1717, 1513, 1448, 1418, 1260, 1235, 1155, 1141, 1026, 855, 809, 765, 740. **LRMS** *(method: ESI positive)* calculated for $C_{17}H_{23}O_3$ 275.2 $[M+H]^+$, found 275.5.



***E* isomer** ***Z* isomer**

12cn

Chemical Formula: $C_{21}H_{30}O_3$

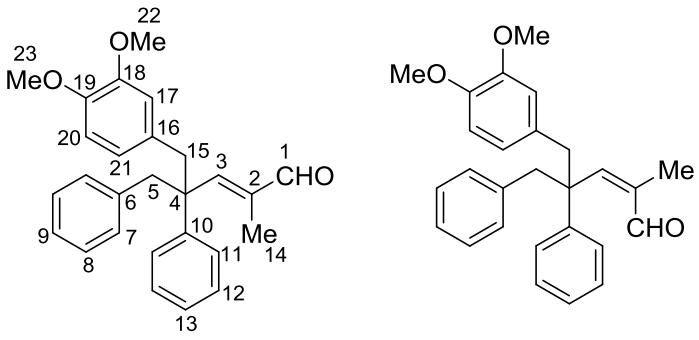
Molecular Weight: 330.47

The two isomers of **12cn** are not separable by chromatography

***E* isomer:** (*E*)-4-(3,4-dimethoxybenzyl)-2,4,8-trimethylnona-2,7-dienal. Colorless oil; **R_f** = 0.50 (SiO_2, pentane/Et_2O 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.13 (s, 3H, H-11); 1.52 (d, $^4J_{HH}$ = 1.1 Hz, 3H, H-12); 1.63 (s, 3H, H-10); 1.71 (s, 3H, H-9); 9.53 (s, 1H, H-1). Protons H-3, 5, 6, 7, 13, 15, 18 and 19 cannot be precisely assigned due to overlapping of signals. **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 17.8 (C-12); 18.1 (C-10); 21.4 (C-11); 26.0 (C-9); 27.1 and 41.1 (C-5 and C-6); 42.1 (C-13); 52.1 (C-4); 123.1 (C-19); 124.0 (C-7); 125.9 (C-3); 130.0 (C-14); 132.2 (C-8); 141.1 (C-2); 204.0 (C-1). Carbons C-15, 16, 17, 18, 20 and 21 cannot be precisely assigned due to overlapping of signals.

***Z* isomer:** (*Z*)-4-(3,4-dimethoxybenzyl)-2,4,8-trimethylnona-2,7-dienal. Colorless oil; **R_f** = 0.50 (SiO_2, pentane/Et_2O 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.11 (s, 3H, H-11); 1.60 (s, 3H, H-10); 1.69 (s, 3H, H-9); 1.79 (d, $^4J_{HH}$ = 1.4 Hz, 3H, H-12); 9.55 (s, 1H, H-1). Protons H-3, 5, 6, 7, 13, 15, 18 and 19 cannot be precisely assigned due to overlapping of signals. **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 18.0 (C-10); 21.7 (C-11); 24.2 (C-12); 26.0 (C-9); 26.6 and 33.3 (C-5 and C-6); 42.6 (C-13); 52.1 (C-4); 123.0 (C-19); 123.8 (C-7); 127.0 (C-3); 130.0 (C-14); 132.6 (C-8); 141.0 (C-2); 204.0 (C-1). Carbons C-15, 16, 17, 18, 20 and 21 cannot be precisely assigned due to overlapping of signals.

Mixture IR spectrum (neat) ν (cm^{-1}) = 2924, 1719, 1514, 1450, 1263, 1232, 1149, 1029, 809, 765. **LRMS** *(method: ESI positive)* calculated for $C_{21}H_{31}O_3$ 331.3 $[M+H]^+$, found 331.8.



***E* isomer** ***Z* isomer**

12dn

Chemical Formula: $C_{27}H_{28}O_3$
Molecular Weight: 400.52

The two isomers of **12dn** are not separable by chromatography

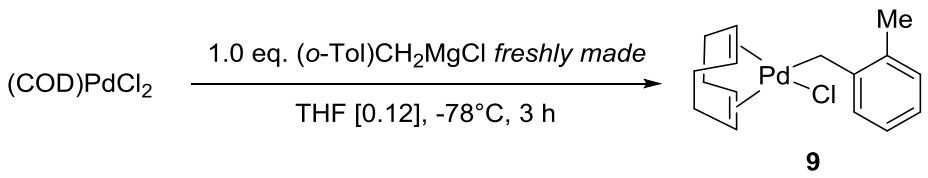
***E* isomer:** (*E*)-4-benzyl-5-(3,4-dimethoxyphenyl)-2-methyl-4-phenylpent-2-enal.Colorless oil; **R_f** = 0.38 (SiO_2, pentane/Et_2O 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.28 (s, 3H, H-14); 2.98 and 3.06 (2d, $^2J_{HH}$ = 13.6 Hz, 1+1H, H-15); 3.69 (br s, 2H, H-5); 3.75 (s, 3H, H-22); 5.80 (br s, 1H, H-3); 9.67 (s, 1H, H-1). Protons H-7, 8, 9, 11, 12, 13, 17, 20, 21 and 23 cannot be precisely assigned due to overlapping of signals. **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 22.1 (C-14); 36.3 (C-5); 42.9 (C-15); 53.1 (C-4); 56.1 (C-22); 132.3 (C-3); 203.5 (C-1). Carbons 2, 6, 7, 8, 9, 10, 11, 12, 13, 16, 17, 18, 19, 20, 21 and 23 cannot be precisely assigned due to overlapping of signals.

***Z* isomer:** *(Z)-4-benzyl-5-(3,4-dimethoxyphenyl)-2-methyl-4-phenylpent-2-enal.* Colorless oil; **R_f** = 0.38 (SiO_2, pentane/Et_2O 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.00 (s, 3H, H-14); 2.73-2.81 (m, 2H, H-15); 3.57 (br s, 2H, H-5); 3.82 (s, 3H, H-22); 5.42 (br s, 1H, H-3); 9.16 (s, 21H, H-1). Protons H-7, 8, 9, 11, 12, 13, 17, 20, 21 and 23 cannot be precisely assigned due to overlapping of signals. **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 22.0 (C-14); 43.5 (C-15); 48.4 (C-5); 53.0 (C-4); 56.3 (C-22); 130.6 (C-3); 202.1 (C-1). Carbons 2, 6, 7, 8, 9, 10, 11, 12, 13, 16, 17, 18, 19, 20, 21 and 23 cannot be precisely assigned due to overlapping of signals.

Mixture IR spectrum (neat) ν (cm^{-1}) = 2932, 1718, 1513, 1494, 1450, 1262, 1236, 1145, 1026, 755, 725, 697. **LRMS** *(method: ESI positive)* calculated for $C_{27}H_{29}O_3$ 401.2 $[M+H]^+$, found 401.5.

6 Supporting organometallic chemistry

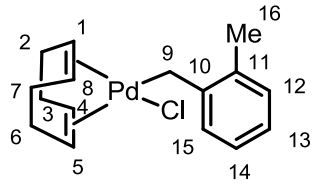
6.1 Synthesis of Chloro[(1,2,5,6-η)-1,5-cyclooctadiene][(2-methylphenyl)methyl]-palladium (9)



9

In a 10 mL flame-dried Young valve Schlenk tube connected to a Schlenk line [(COD)$PdCl_2$] (150 mg, 0.53 mmol, 1.0 eq.) was suspended in dry THF (4.4 mL, 0.12 M) under a nitrogen atmosphere. After cooling to − 78 °C, a freshly prepared solution of the Grignard reagent was slowly added over 20-30 minutes. The mixture was stirred for 3 h at − 78 °C and then gently warmed to room temperature. The solvents were evaporated and the residue was dissolved in 15 mL of CH_2Cl_2. The resulting solution was washed with water (5 mL x 2), the organic phase dried over $MgSO_4$ and the solvent evaporated. The resulting dark residue was dissolved in a small amount of acetone (ca. 10 mL, gently heated if necessary), the solution filtered through Celite® and the solvent evaporated to afford a yellow solid. The crude mixture was purified by flash chromatography (SiO_2, eluent CH_2Cl_2 then CH_2Cl_2/Acetone 8:1) to afford the final compound as a yellow solid (62 mg, 33% yield).

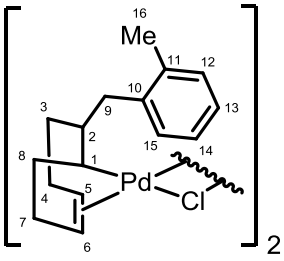
During the elution with CH_2Cl_2 it is possible to recover the following by product: di-μ-chloro[(1,4,5-η)-8-(2-methylbenzyl)-4-cycloocten-1-yl]dipalladium.



9
Chemical Formula: $C_{16}H_{21}ClPd$
Molecular Weight: 355.21

Chloro[(1,2,5,6-η)-1,5-cyclooctadiene][(2-methylphenyl)methyl]-palladium (**9**). Yellow solid; **R_f** = 0.13 (SiO_2, CH_2Cl_2); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 2.37-2.56 (m, 11H, -CH_2- of COD and H-16); 3.66 (s, 2H, H-9); 4.26 and 5.94 (2br s, 2+2H, Olefinic -CH- of COD); 6.98-7.01 (m, 1H, H-14); 7.06-7.08 (m, 1H, H-15); 7.12-7.16 (m, 1H, H-12); 7.16-7.20 (m, 1H, H-13). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 21.6 (C-16); 20.8 and 31.3 (-CH_2- of COD);

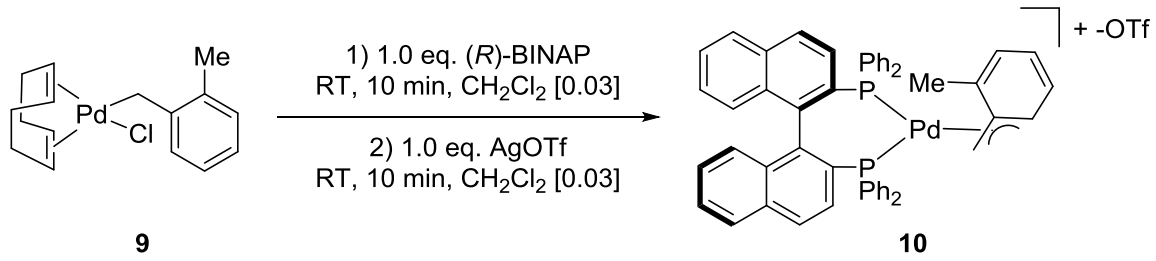
35.8 (C-9); 107.3 and 123.9 (olefinic -CH- of COD); 126.2 (C-14); 126.5 (C-12); 129.6 (C-13); 131.0 (C-15); 136.7 (C-11); 144.7 (C-10). **IR spectrum (neat)** ν (cm^{-1}) = 2946, 1580, 1479, 1435, 1043, 999, 858, 842, 818, 769, 748, 674. **LRMS** *(method: ESI positive)* calculated for $C_{32}H_{42}ClPd_2$ 673.1 $[2M\text{-}Cl]^+$, found 673.3.



Chemical Formula: $C_{32}H_{42}Cl_2Pd_2$
Molecular Weight: 710.43

Di-µ-chloro[(1,4,5-η)-8-(2-methylbenzyl)-4-cycloocten-1-yl]dipalladium. White solid; R_f = 0.57 (SiO_2, CH_2Cl_2); **^{1}H NMR ($CDCl_3$, 400 MHz)** δ (ppm) = 1.31-1.36 (m, 1H, H-8); 1.69-1.76 (m, 2H, H-3); 2.02-2.07 (m, 1H, H-2); 2.17-2.50 (m, 9H, H-4, H-7, H-8', H-9 and H-16); 2.67 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H-9'); 3.60 (br s, 1H, H-1); 5.47-5.49 (m, 1H, H-5); 5.93-5.99 (m, 1H, H-5); 7.00-7.03 (m, 1H, H-15); 7.07-7.14 (m, 3H, H-12, H-13 and H-14). **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)** δ (ppm) = 20.0 (C-16); 27.1 (C-7); 30.2 (C-4); 30.5 (C-3); 36.3 (C-8); 37.2 (C-9); 44.5 (C-2); 60.4 (C-1); 101.5 (C-5); 105.3 (C-6); 126.0, 126.4 and 130.7 (C-12, C-13 and C-14); 130.1 (C-15); 136.7 (C-11); 139.0 (C-10). The signals of carbons 1-5-6 and 10 are very broad. **IR spectrum (neat)** ν (cm^{-1}) = 2924, 2873, 1444, 1328, 1231, 1207, 1124, 1044, 986, 866, 741. **LRMS** *(method: ESI positive)* calculated for $C_{32}H_{42}ClPd_2$ 673.1 $[M\text{-}Cl]^+$, found 673.3.

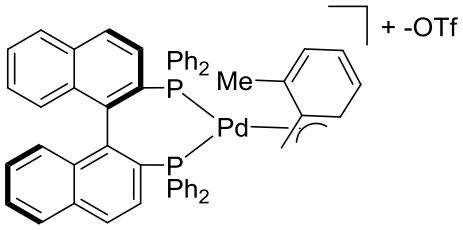
6.2 Synthesis of [(*R*)-(BINAP)Pd(2-methylbenzyl)]OTf (10)



9 **10**

Inside a glove box, the palladium complex **9** (51.6 mg, 0.15 mmol, 1.0 eq.) and (*R*)-BINAP (90.5 mg, 0.15 mmol, 1.0 eq.) were dissolved in dry and degassed CH_2Cl_2 (4.8 mL, 0.03M). After 10 minutes stirring at room temperature, AgOTf (37.3 mg, 0.15 mmol, 1.0 eq.) was added in the dark and the stirring prolonged for 10 additional minutes at room temperature.

The mixture was filtered through Celite® and the solvent evaporated to reduce the volume to ca. 1 mL. The solution was layered with Et_2O and left in the freezer at ca − 30 °C overnight. The yellow crystals thus obtained were filtered, washed with Et_2O and dried (129 mg, 90% yield).



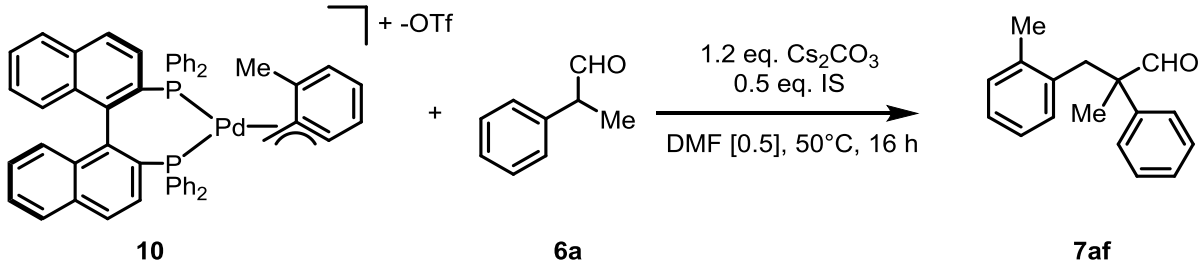
10

Chemical Formula: $C_{53}H_{42}F_3O_3P_2PdS$
Molecular Weight: 984.34

Two isomeric species have been detected in CD_2Cl_2 at room temperature while a single species was seen in DMF-d_7 at room temperature. In the NMR section of the Supporting Information, you will find the spectra recorded in DMF-d_7, followed by the ^1H and $^{31}P\{^1H\}$ spectra recorded in CD_2Cl_2 at 298 K and 243 K. Complete assignment of all carbon was not possible.

[(R)-(BINAP)Pd(2-methylbenzyl)]OTf (**10**). Yellow solid; **^{1}H NMR (DMF-d_7 , 400 MHz)** δ (ppm) = 2.38 (s, 3H); 3.09-3.13 (m, 1H); 3.76-3.79 (m, 1H); 6.53 (d, *J* = 8.7 Hz, 1H); 6.56-6.60 (m, 1H); 6.77-6.81 (m, 5H); 6.90-6.98 (m, 4H); 7.02 (t, *J* = 9.0 Hz, 1H); 7.13-7.19 (m, 5H); 7.24-7.28 (m, 1H); 7.41-7.51 (m, 4H); 7.57 (d, *J* = 7.2 Hz, 1H); 7.66-7.70 (m, 3H); 7.72-7.79 (m, 7H); 7.93-7.95 (m, 1H); 7.99-8.04 (m, 2H). **$^{31}P\{^1H\}$ NMR (DMF-d_7 , 162 MHz)** δ (ppm) = 21.4 (d, $^3J_{PP}$ = 56.4 Hz); 33.4 (d, $^3J_{PP}$ = 56.4 Hz). **$^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz)** δ (ppm) = -78.1 (s). **IR spectrum (neat)** ν (cm^{-1}) = 3054, 1502, 1477, 1435, 1262, 1143, 1029, 813, 746, 695, 634. **LRMS** *(method: ESI positive)* calculated for $C_{96}H_{74}P_4Pd_2$ 1562.3 $[2M\text{-}2OTf\text{-}Benzyl\ fragment]^+$, found 1562.7.

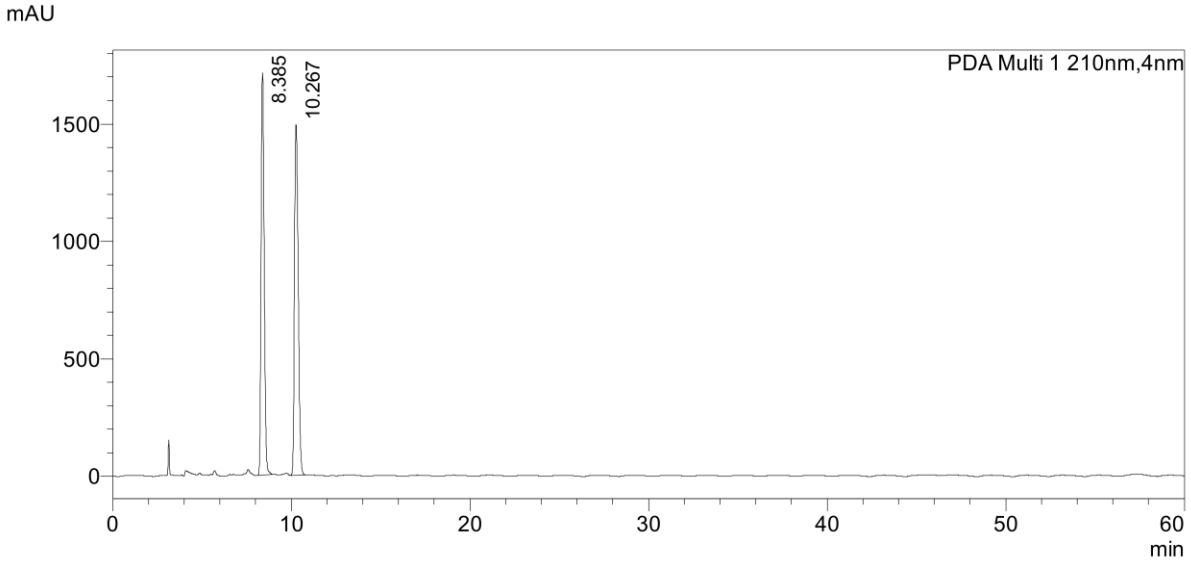
6.3 Stoichiometric cross coupling reaction using 10



10 **6a** **7af**

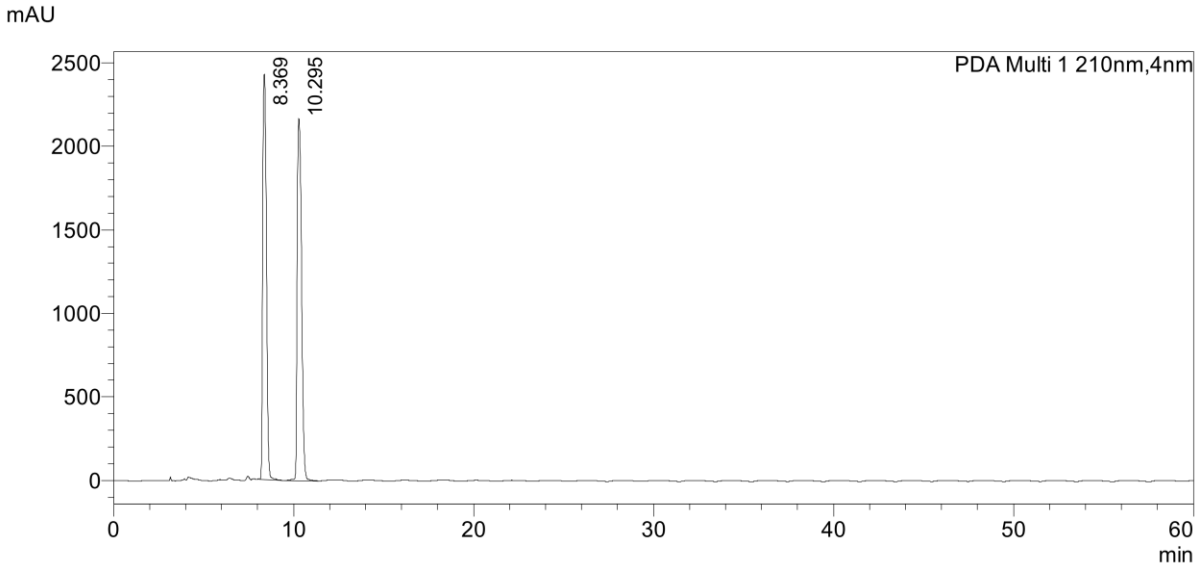
Inside a glove box, a 2 mL Young valve Schlenk tube was charged with complex **10** (49.2 mg, 0.05 mmol, 1.0 eq.) and Cs_2CO_3 (19.5 mg, 0.06 mmol, 1.2 eq.). The tube was sealed, taken outside the glove box and connected to a Schlenk line. After conditioning, dry and degassed *N,N*-dimethylformamide (0.1 mL, 0.5 M) was added and after 10 min. stirring at room temperature the aldehyde **6a** (13 μL, 0.10 mmol, 2.0 eq.) and the internal standard (5.9 mg, 0.025 mmol, 0.5 eq.) were added. The tube was sealed and placed at 50 °C for 16 h. After cooling to room temperature, the reaction was filtered through Celite® and the solvent evaporated under vacuum. The crude mixture was purified by flash chromatography (SiO_2, eluent pentane/CH_2Cl_2 3:2) to afford the final product as a colorless oil (9.5 mg, 84% yield, **<5% *ee***).

HPLC trace (racemic): Column ODH, hexane/i-PrOH (99:1), 1 mL/min., λ = 210 nm.



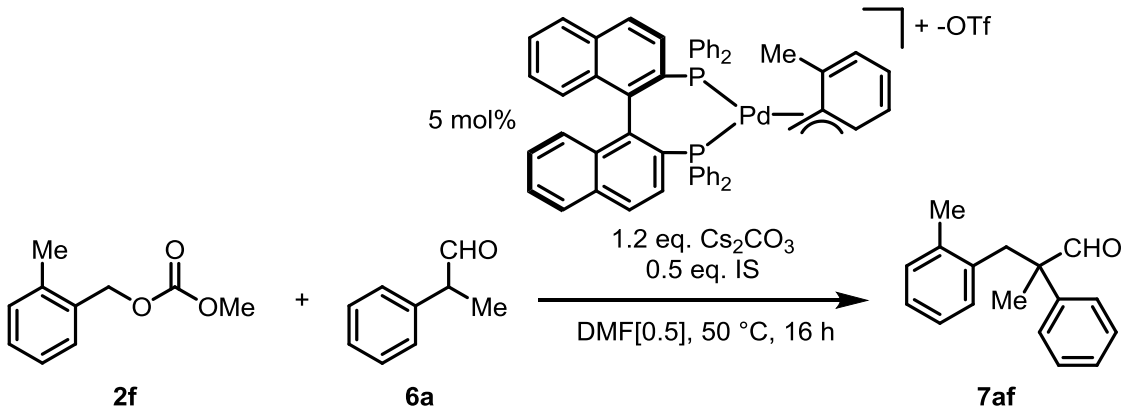
Peak#	Ret. Time	Area%
1	8.385	49.368
2	10.267	50.632
Total		100.000

HPLC trace of the stoichiometric experiment



Peak#	Ret. Time	Area%
1	8.369	48.979
2	10.295	51.021
Total		100.000

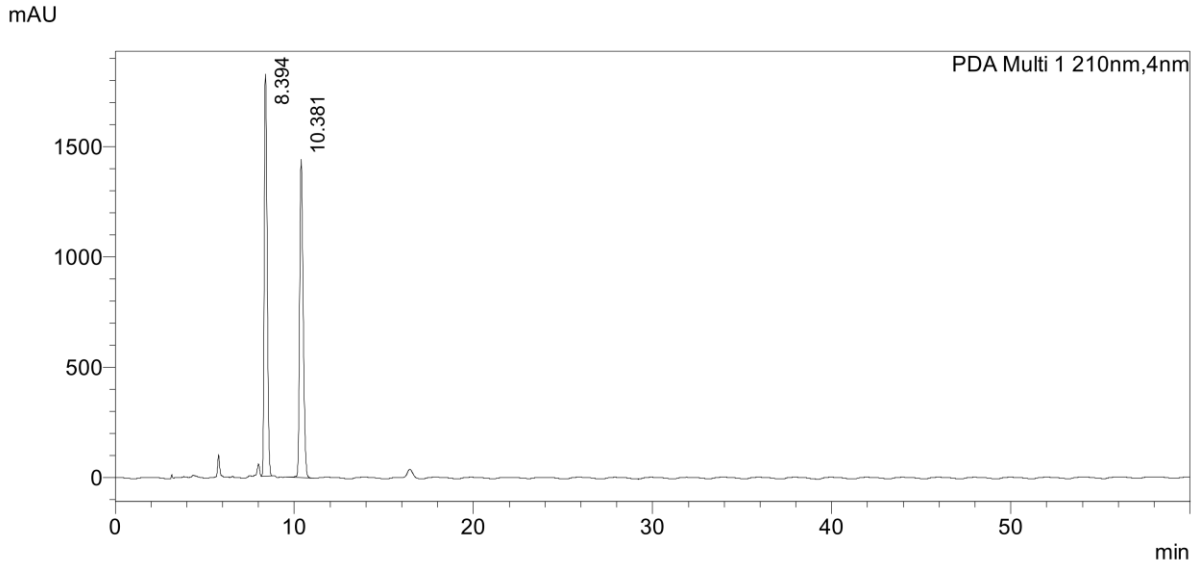
6.4 *Ex situ* cross coupling reaction



Inside a glove box, a 2 mL Young valve Schlenk tube was charged with complex **10** (12.3 mg, 0.01 mmol, 0.05 eq.) and Cs_2CO_3 (97.7 mg, 0.30 mmol, 1.2 eq.). The tube was sealed, taken outside the glove box and connected to a Schlenk line. After conditioning, dry and degassed N,N-dimethylformamide (0.5 mL, 0.5 M) was added and after 10 min. of additional stirring at room temperature the carbonate **2f** (45.1 mg, 0.25 mmol, 1.0 eq.), the aldehyde **6a** (67 μL, 0.50 mmol, 2.0 eq.) and the internal standard (29.3 mg, 0.13 mmol, 0.5 eq.) were added. The tube was sealed and placed at 50 °C for 16 h. After cooling to room temperature, the reaction was filtered through Celite® and the solvent evaporated under

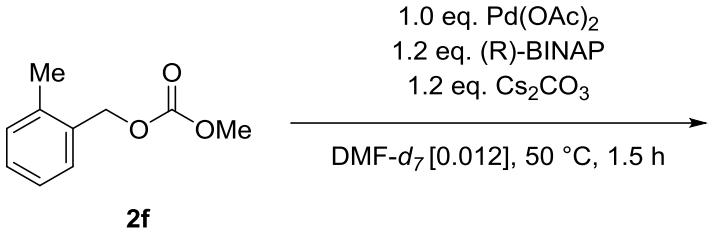
vacuum. The crude mixture was purified by flash chromatography (SiO_2, eluent pentane/CH_2Cl_2 3:2) to afford the final product as colorless oil (34 mg, 57% yield, < 5% *ee*).

HPLC trace of the reaction



Peak#	Ret. Time	Area%
1	8.394	51.271
2	10.381	48.729
Total		100.000

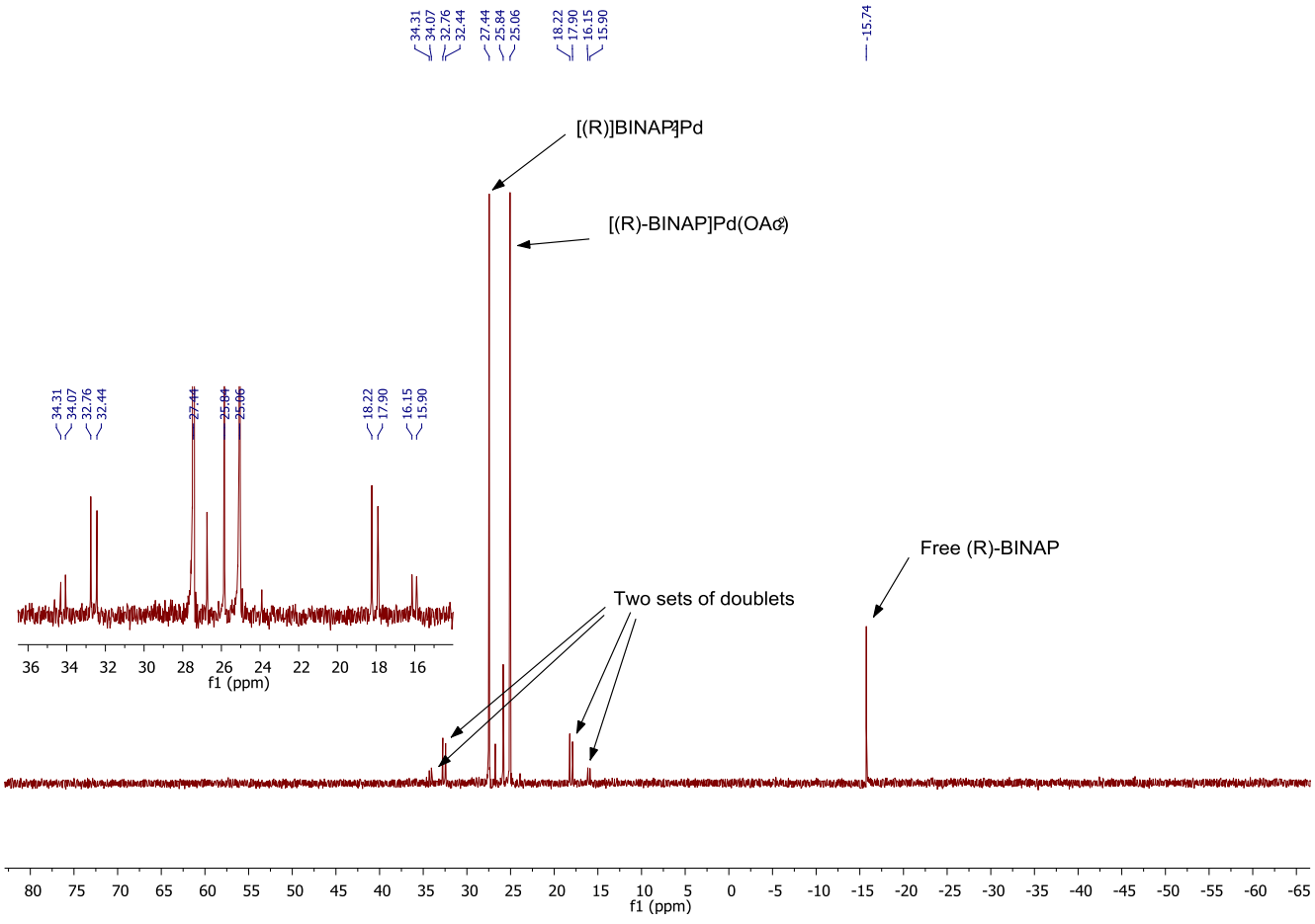
7 Monitoring experiment



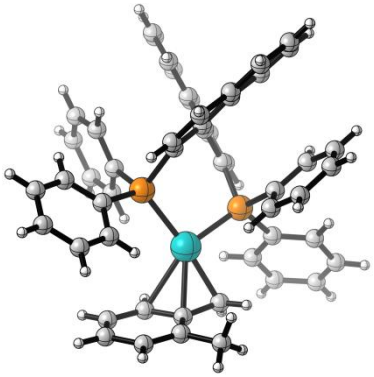
2f

Inside a glove box, a Young valve NMR tube was charged with $Pd(OAc)_2$ (1.6 mg, 0.007 mmol, 1.0 eq.), (*R*)-BINAP (5.2 mg, 0.008 mmol, 1.2 eq.) and Cs_2CO_3 (2.7 mg, 0.008 mmol 1.2 eq.). DMF-d_7 (0.6 mL, 0.012M) was added the reaction mixed for 10 minutes at room temperature. Next, 2-methylbenzyl methyl carbonate **2f** (1.3 mg, 0.007 mmol, 1.0 eq.) was added and the tube placed at 50 °C for 1.5 h. After cooling to room temperature, NMR spectra were recorded.

$^{31}P\{^{1}H\}$NMR, DMF-d_7, 162 MHz, 298 K



8 Crystal data and structure refinement for complex 10

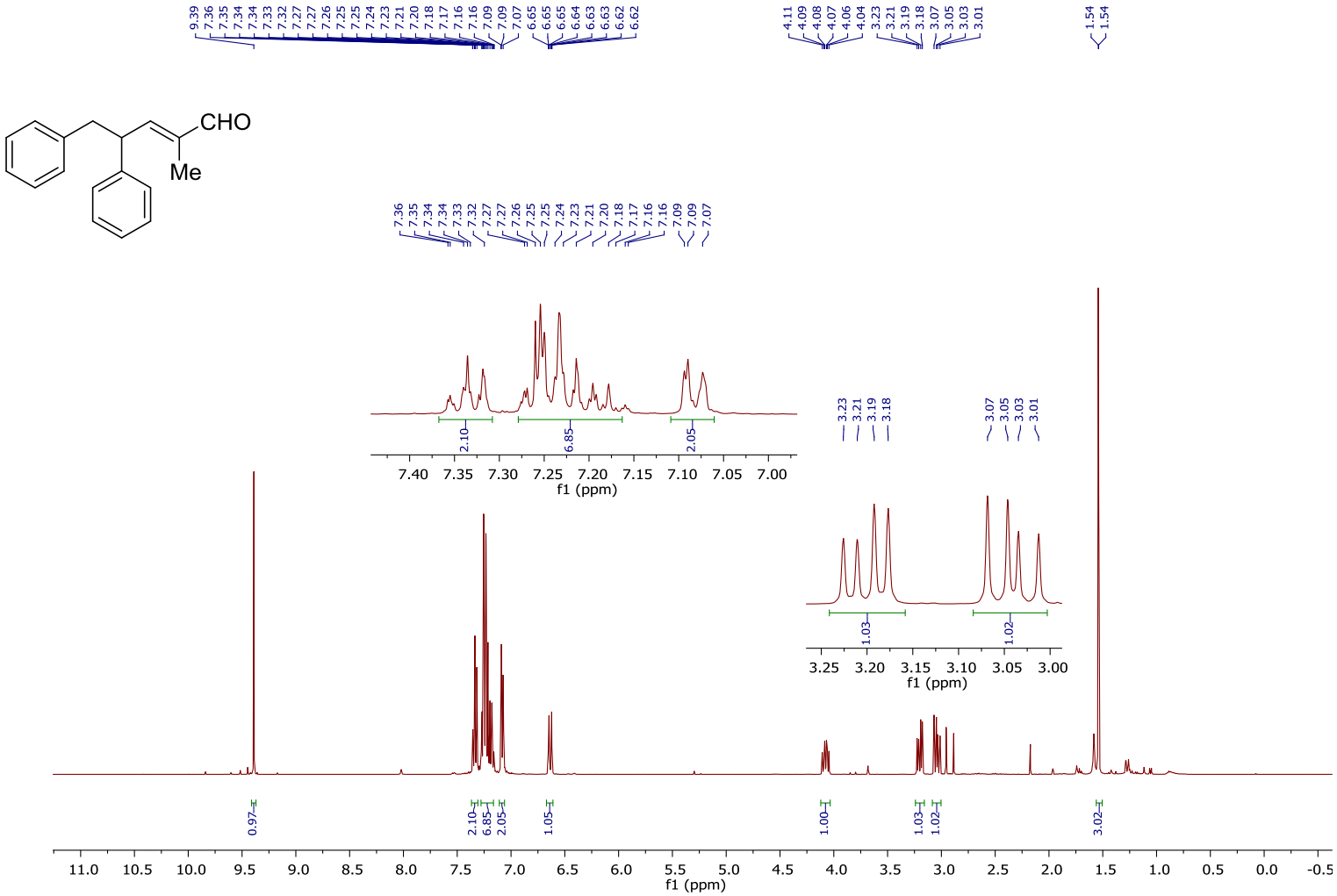


Empirical formula	$C_{54}\ H_{43}\ Cl_2\ F_3\ O_3\ P_2\ Pd\ S$	
Formula weight	1068.18	
Temperature	180(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 10.9070(3) Å	α= 90°
	b = 20.1115(5) Å	β= 99.508(3)°
	c = 11.0941(3) Å	γ = 90°
Volume	2400.12(11) $Å^3$	
Z	2	
Density (calculated)	1.478 Mg/m^3	
Absorption coefficient	5.641 mm^{-1}	
F(000)	1088	
Crystal size	0.3239 x 0.1751 x 0.0297 mm^3	
Theta range for data collection	4.04 to 73.62°.	
Index ranges	-13<=h<=13, -24<=k<=24, -13<=l<=8	
Reflections collected	17699	
Independent reflections	9439 [R(int) = 0.0252]	
Completeness to theta = 67.50°	100.0 %	
Absorption correction	Analytical	
Max. and min. transmission	0.918 and 0.606	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9439 / 1 / 571	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0605, wR2 = 0.1619	
R indices (all data)	R1 = 0.0630, wR2 = 0.1652	
Absolute structure parameter	-0.003(10)	
Largest diff. peak and hole	2.178 and -1.120 $e.Å^{-3}$	

9 NMR spectra

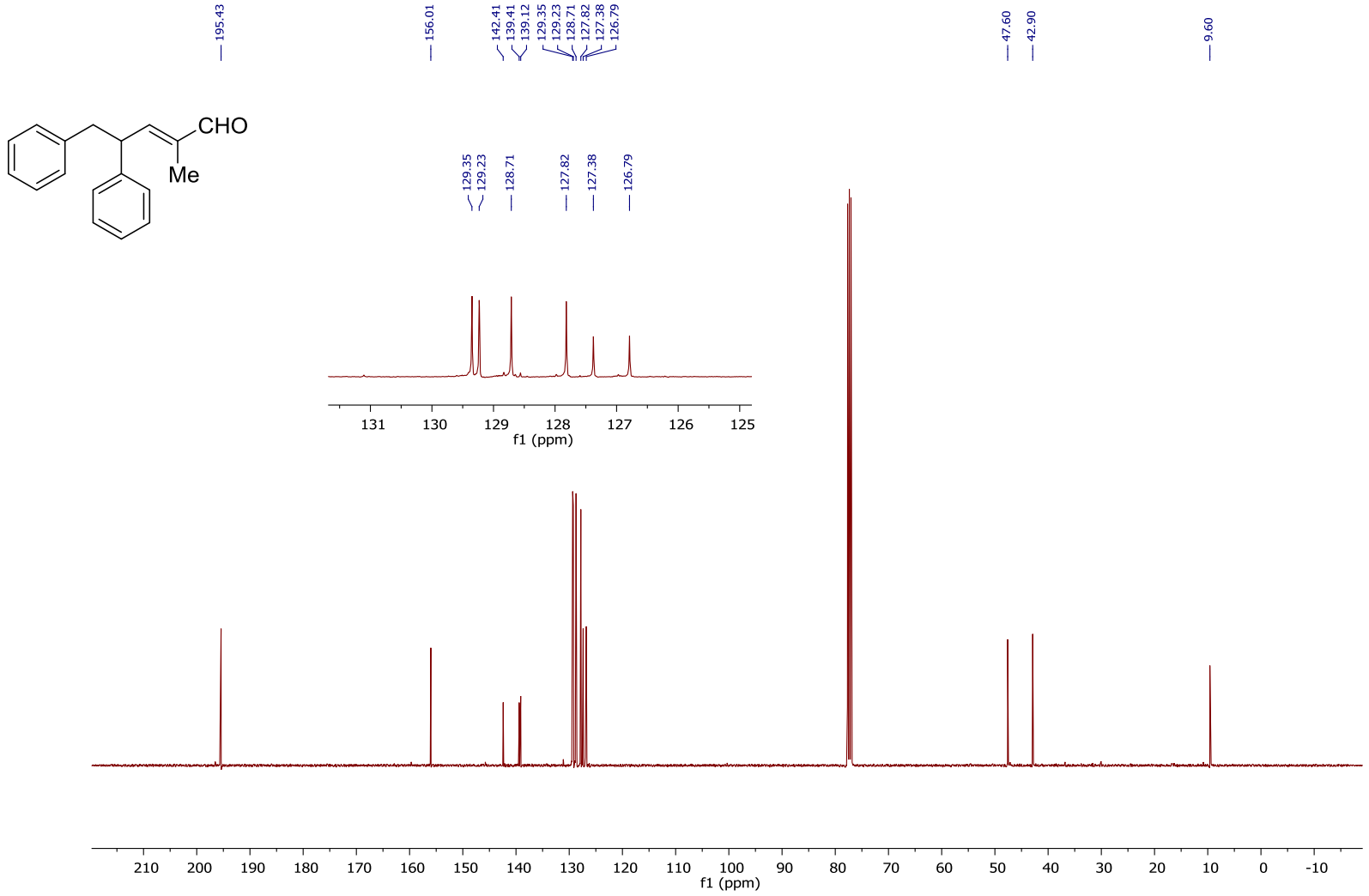
(*E*)-2-methyl-4,5-diphenylpent-2-enal (12d)

^{1}H NMR (400 MHz, $CDCl_3$):



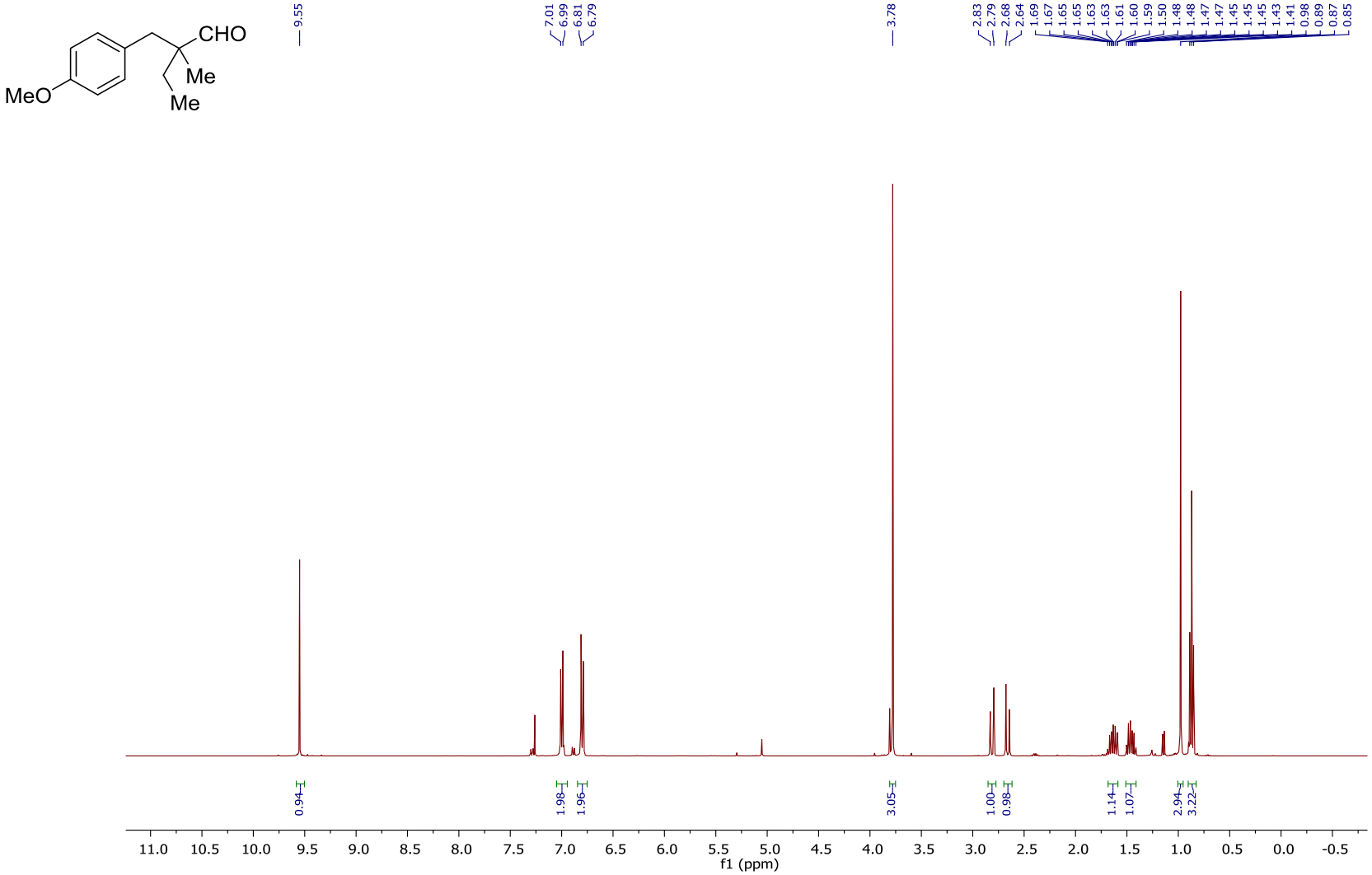
(*E*)-2-methyl-4,5-diphenylpent-2-enal (12d)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



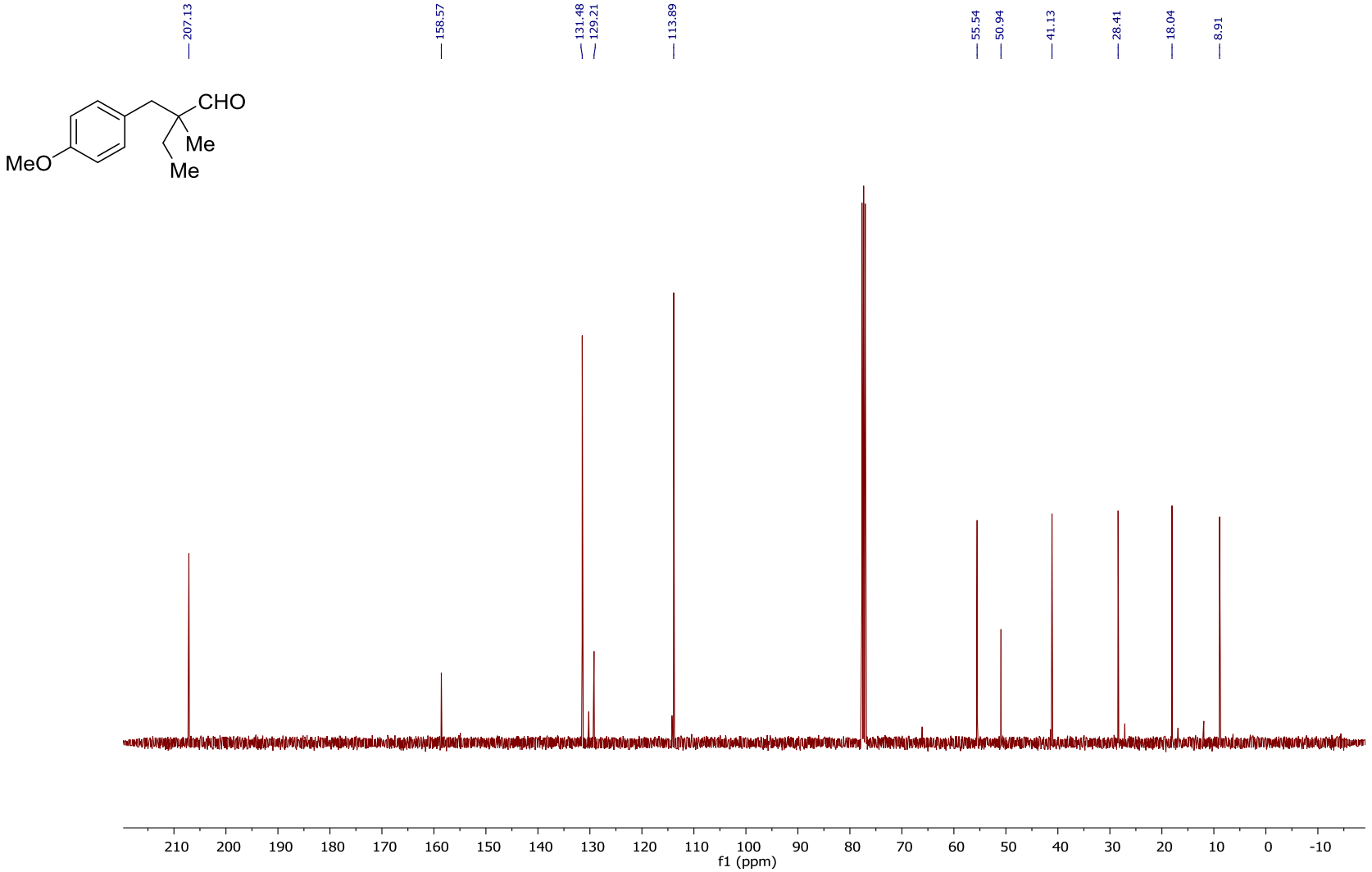
2-(4-methoxybenzyl)-2-methylbutanal (3aa)

^{1}H NMR (400 MHz, $CDCl_3$):



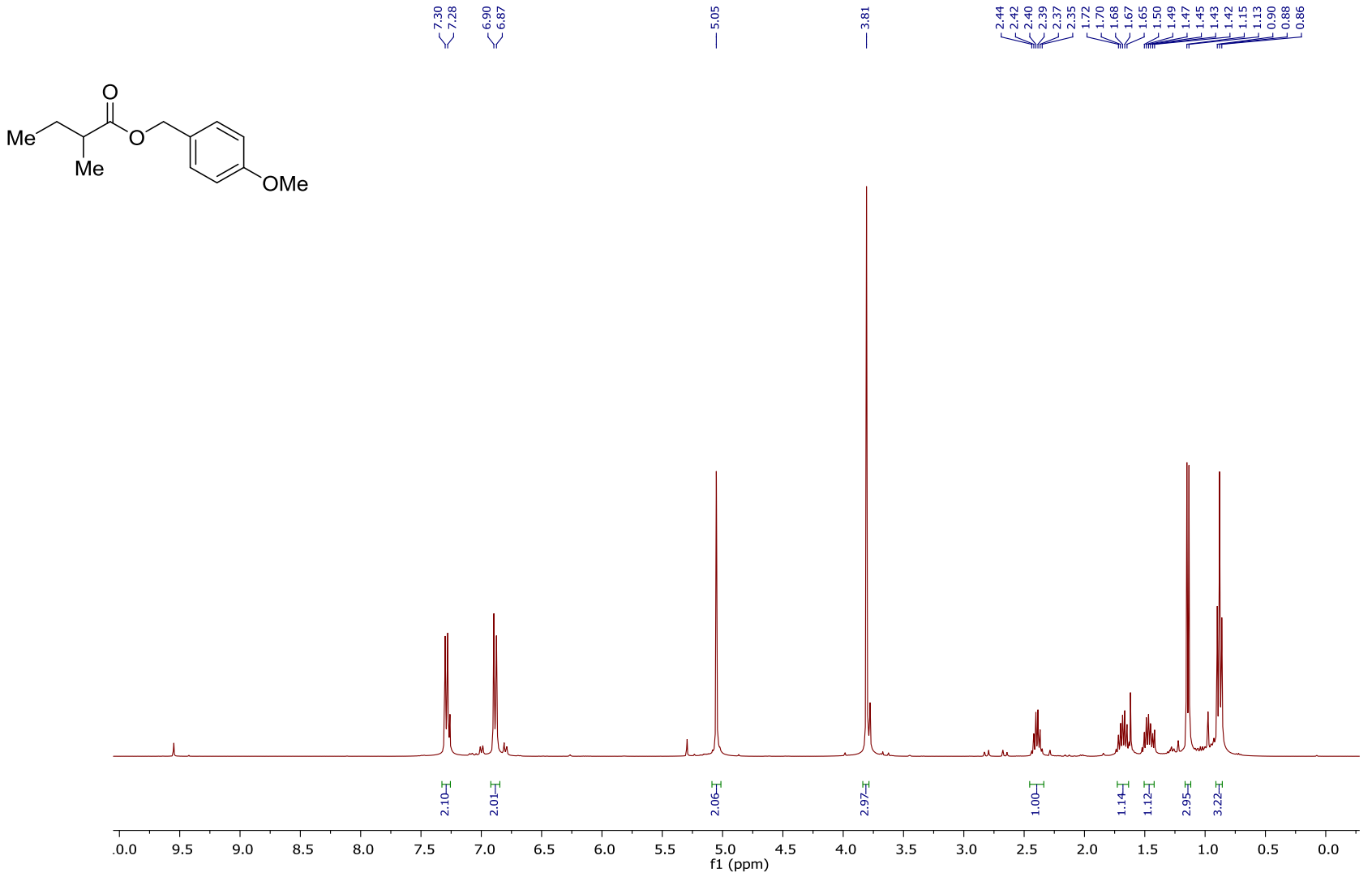
2-(4-methoxybenzyl)-2-methylbutanal (3aa)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



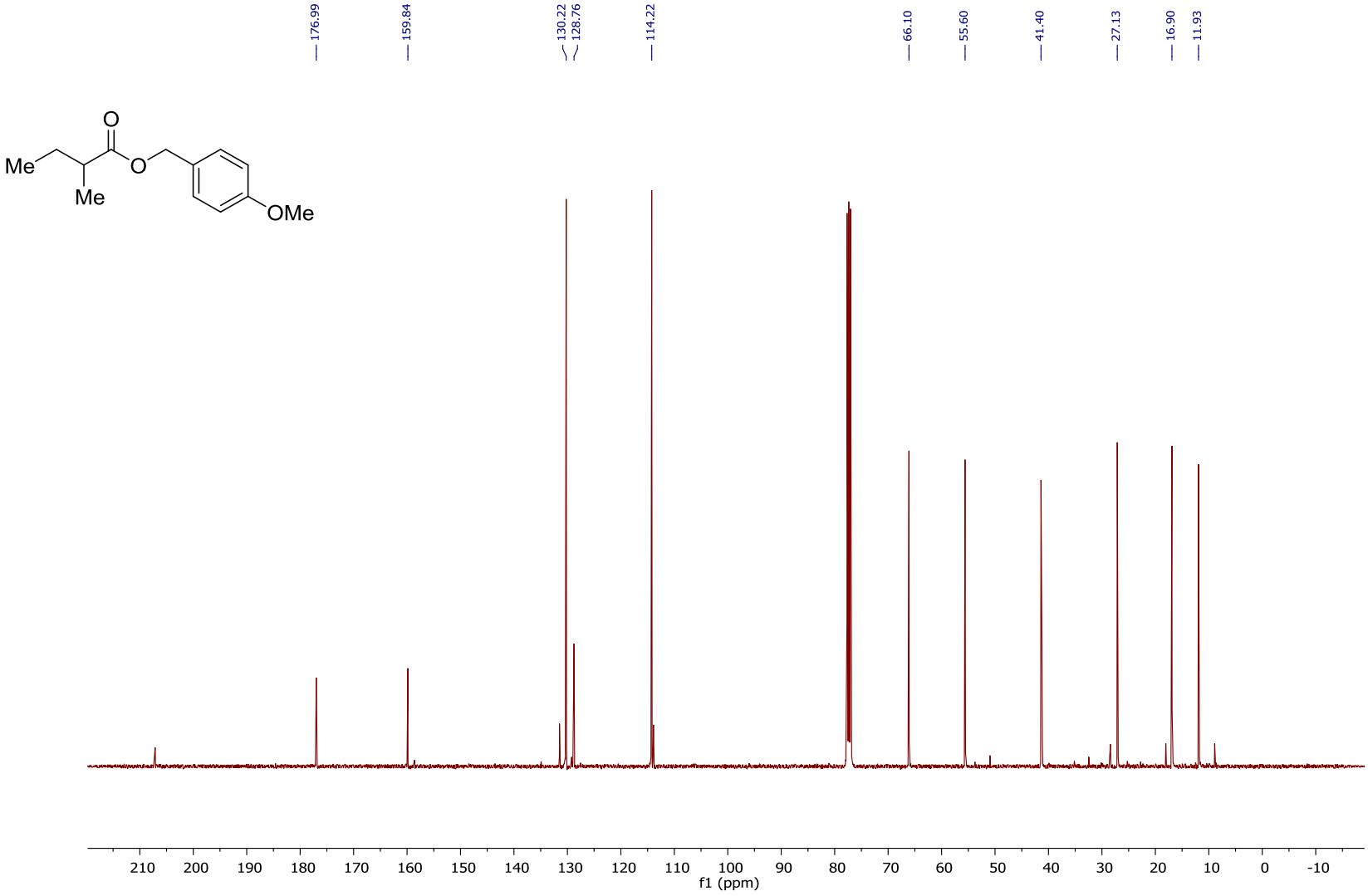
4-methoxybenzyl 2-methylbutanoate (4aa)

^{1}H NMR (400 MHz, $CDCl_3$):



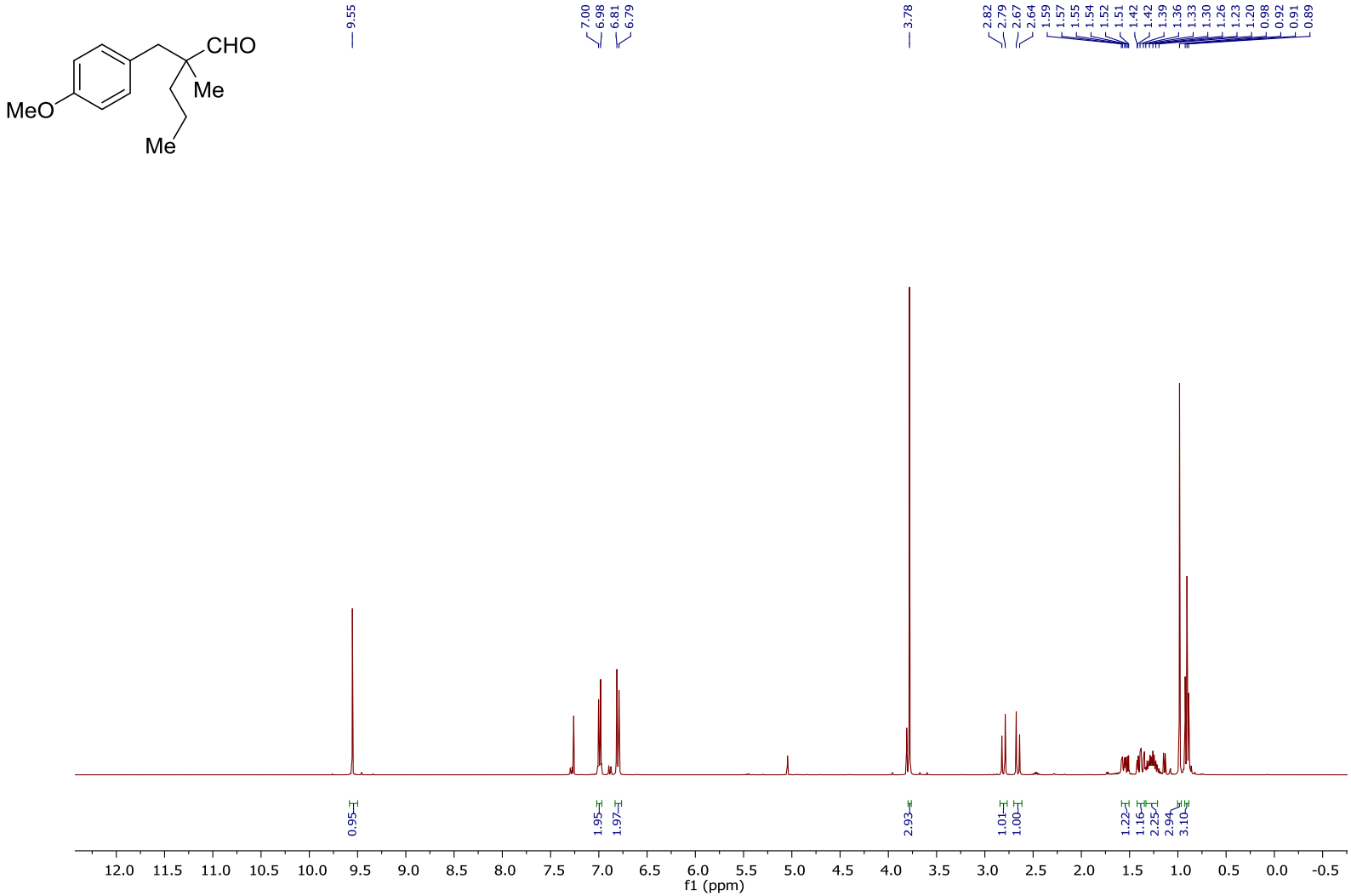
4-methoxybenzyl 2-methylbutanoate (4aa)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



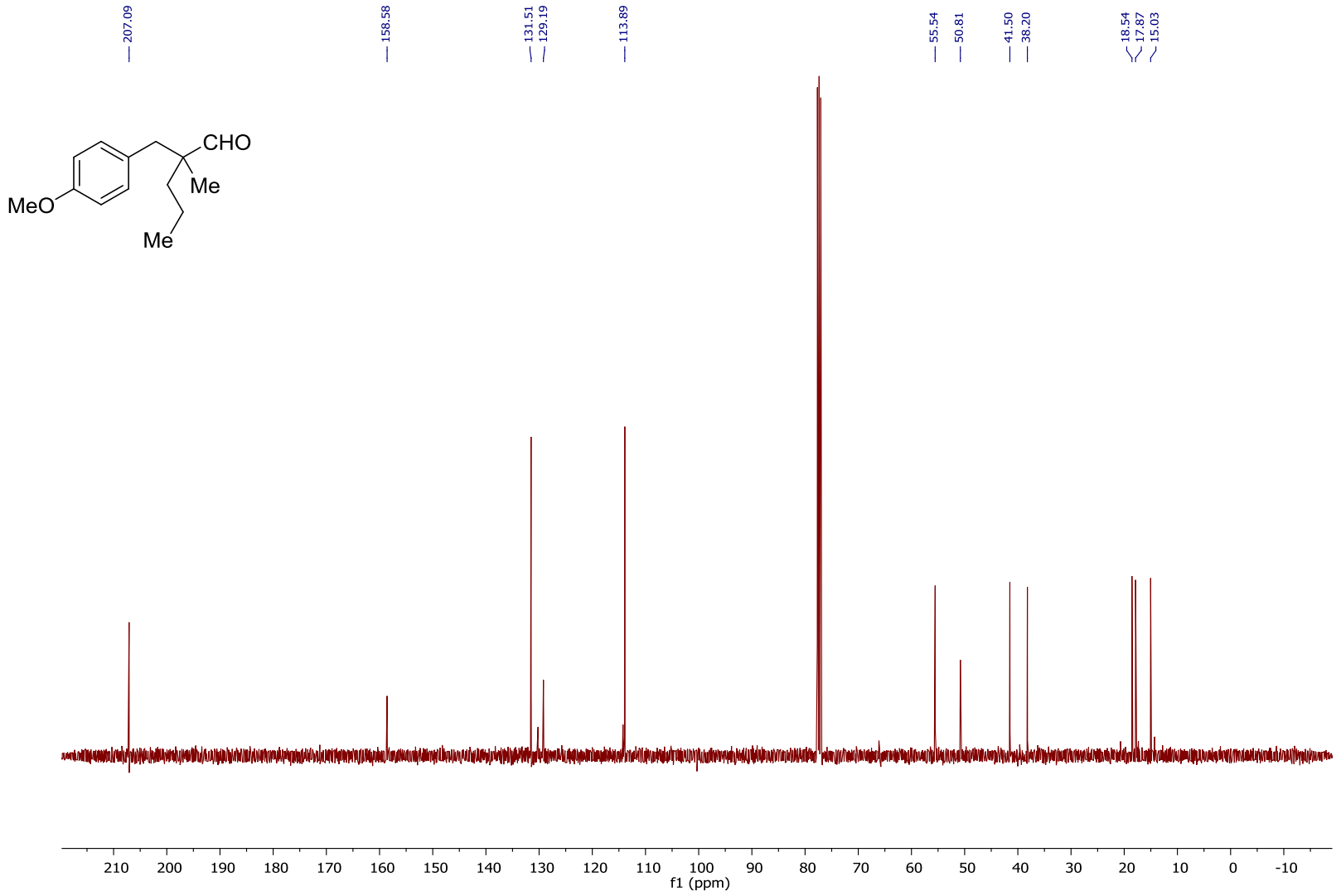
2-(4-methoxybenzyl)-2-methylpentanal (3ba)

^{1}H NMR (400 MHz, $CDCl_3$):



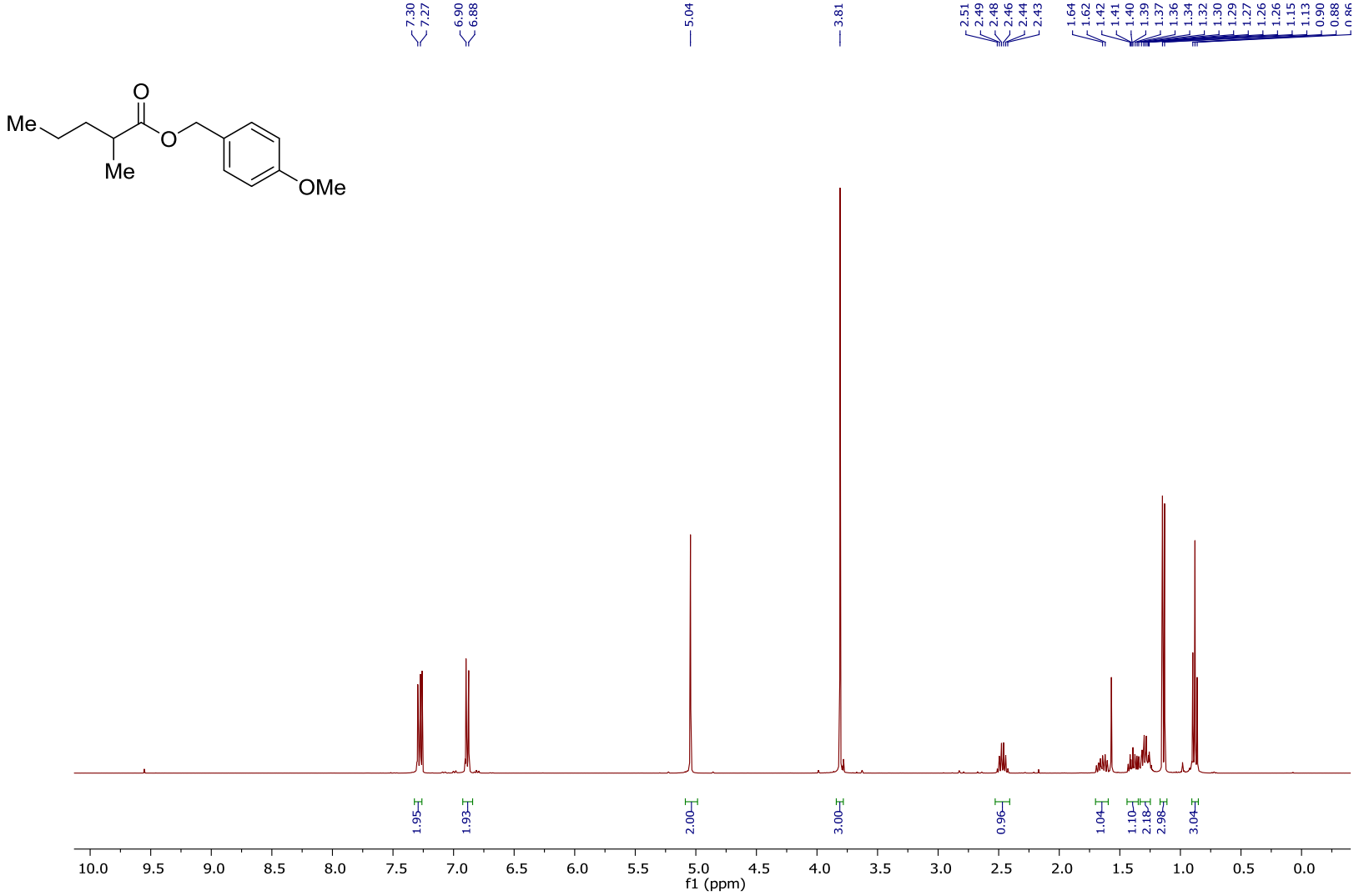
2-(4-methoxybenzyl)-2-methylpentanal (3ba)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



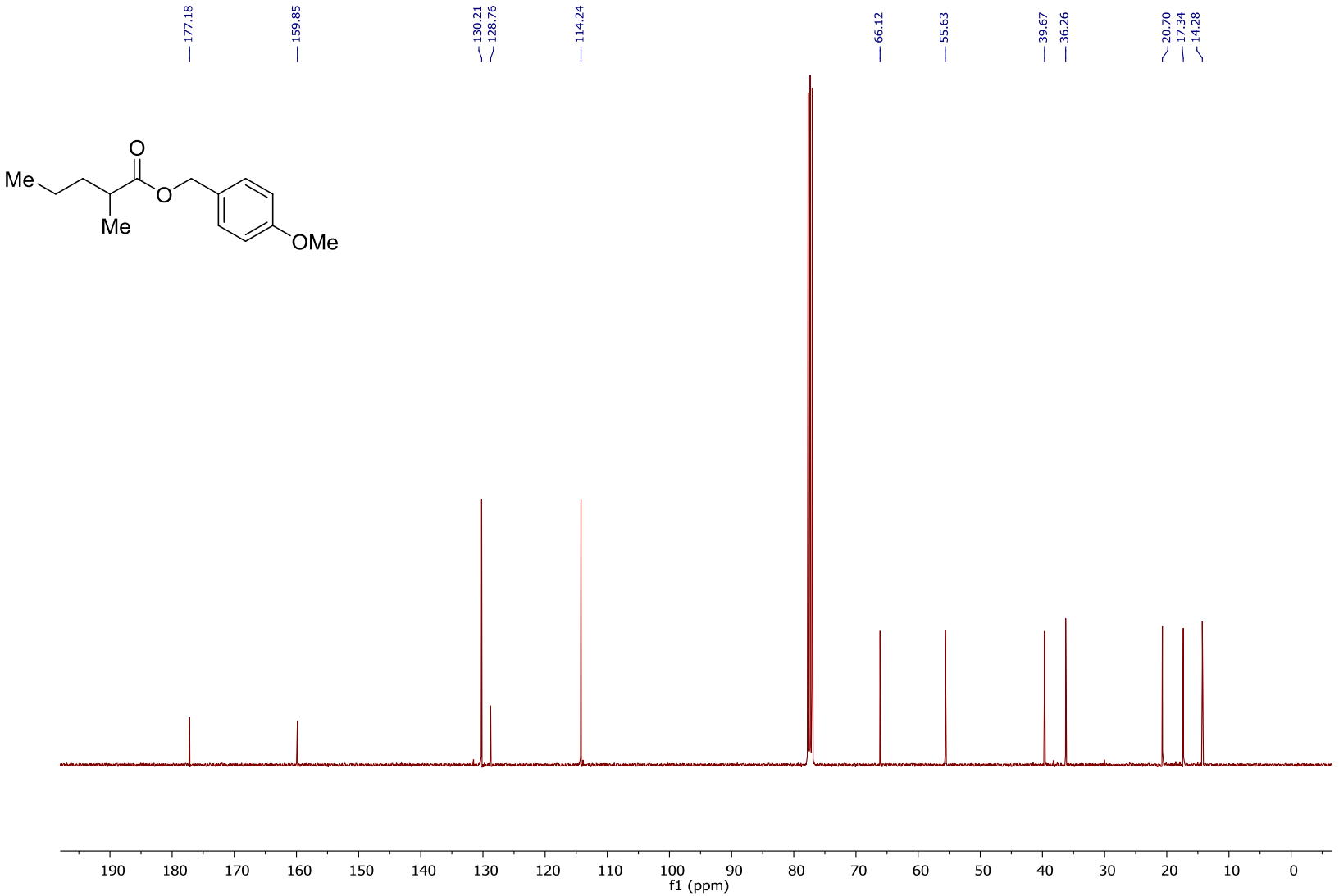
4-methoxybenzyl 2-methylpentanoate (4ba)

^{1}H NMR (400 MHz, $CDCl_3$):



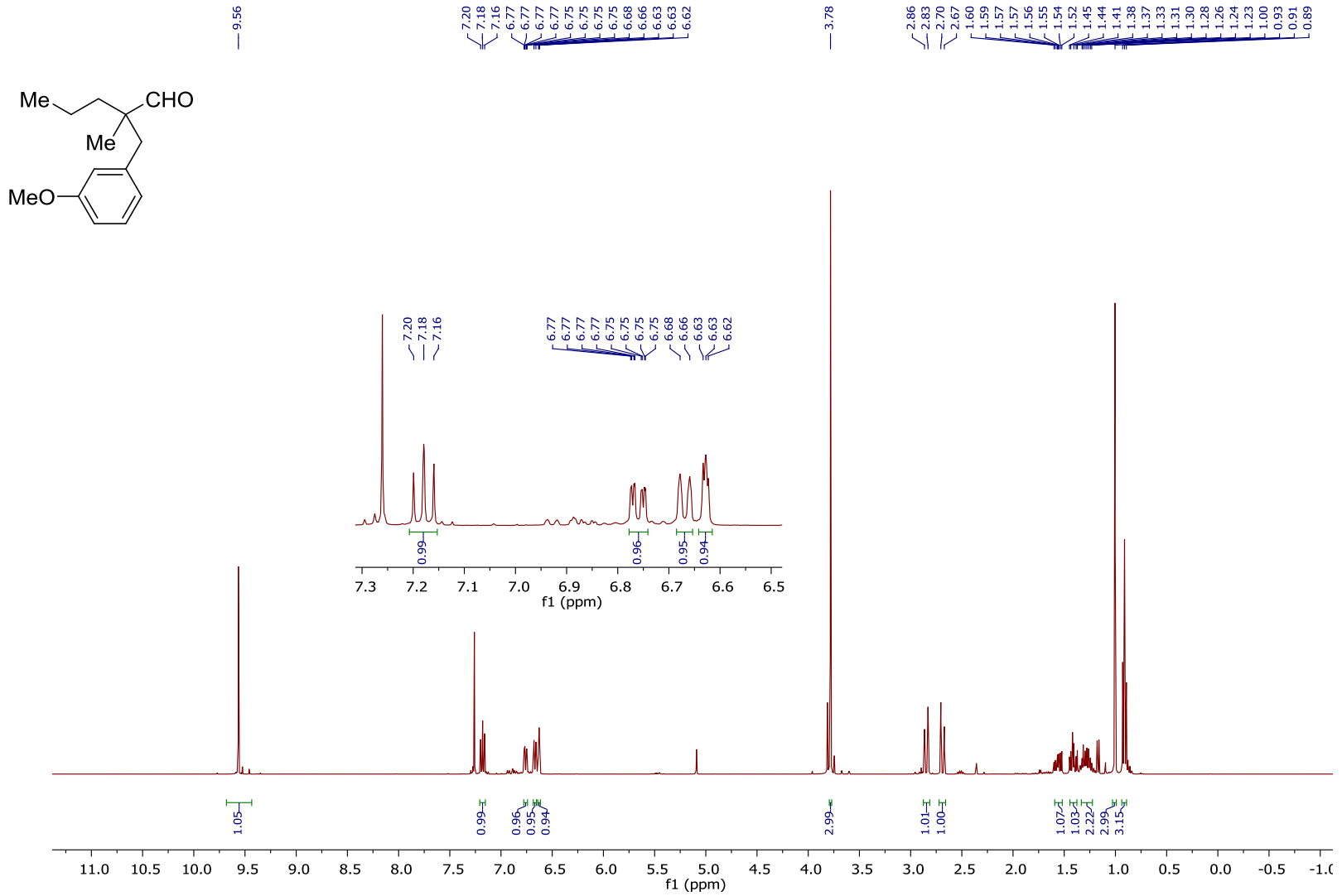
4-methoxybenzyl 2-methylpentanoate (4ba)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



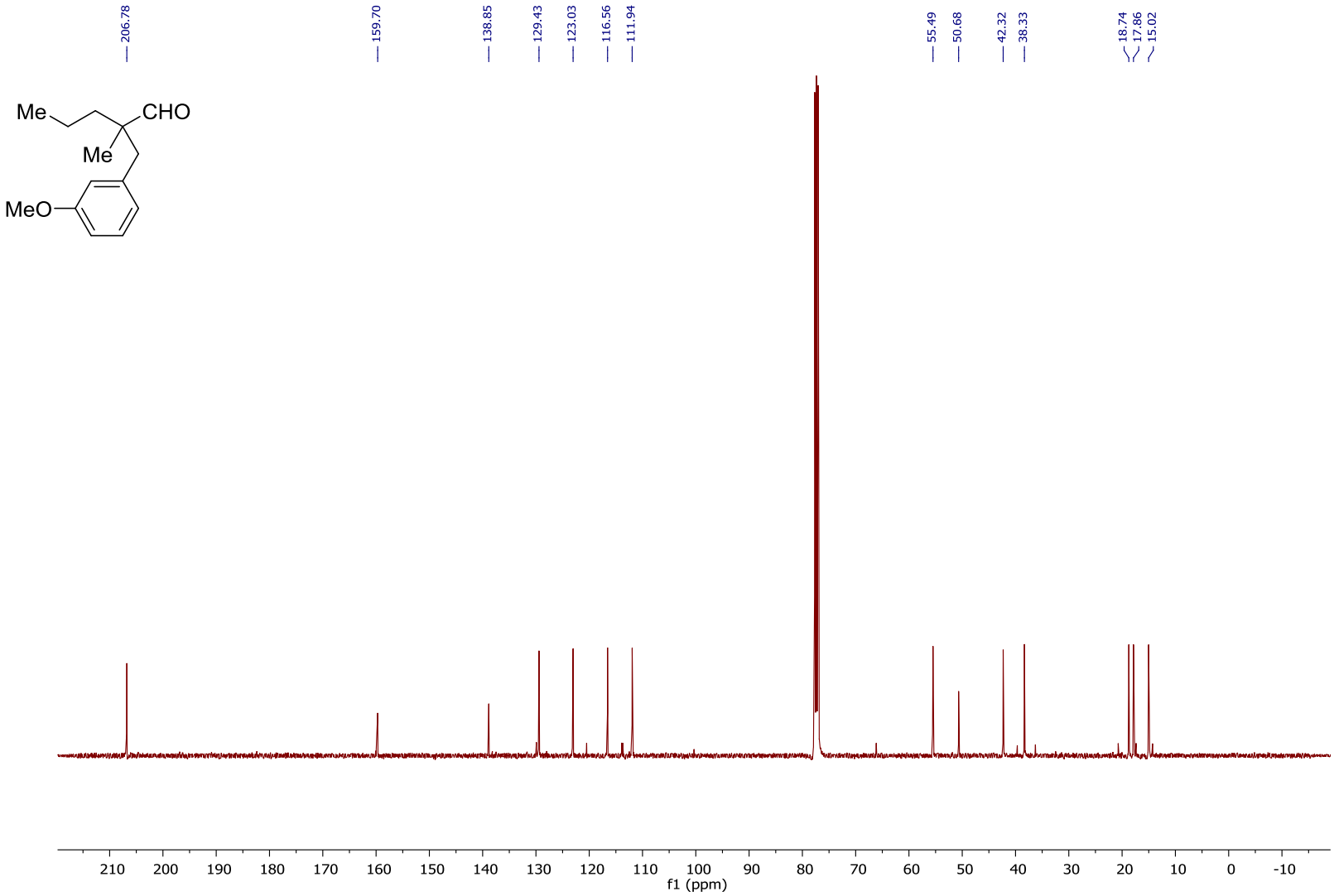
2-methyl-2-(3-methoxylbenzyl)pentane (3bb)

^{1}H NMR (400 MHz, $CDCl_3$):



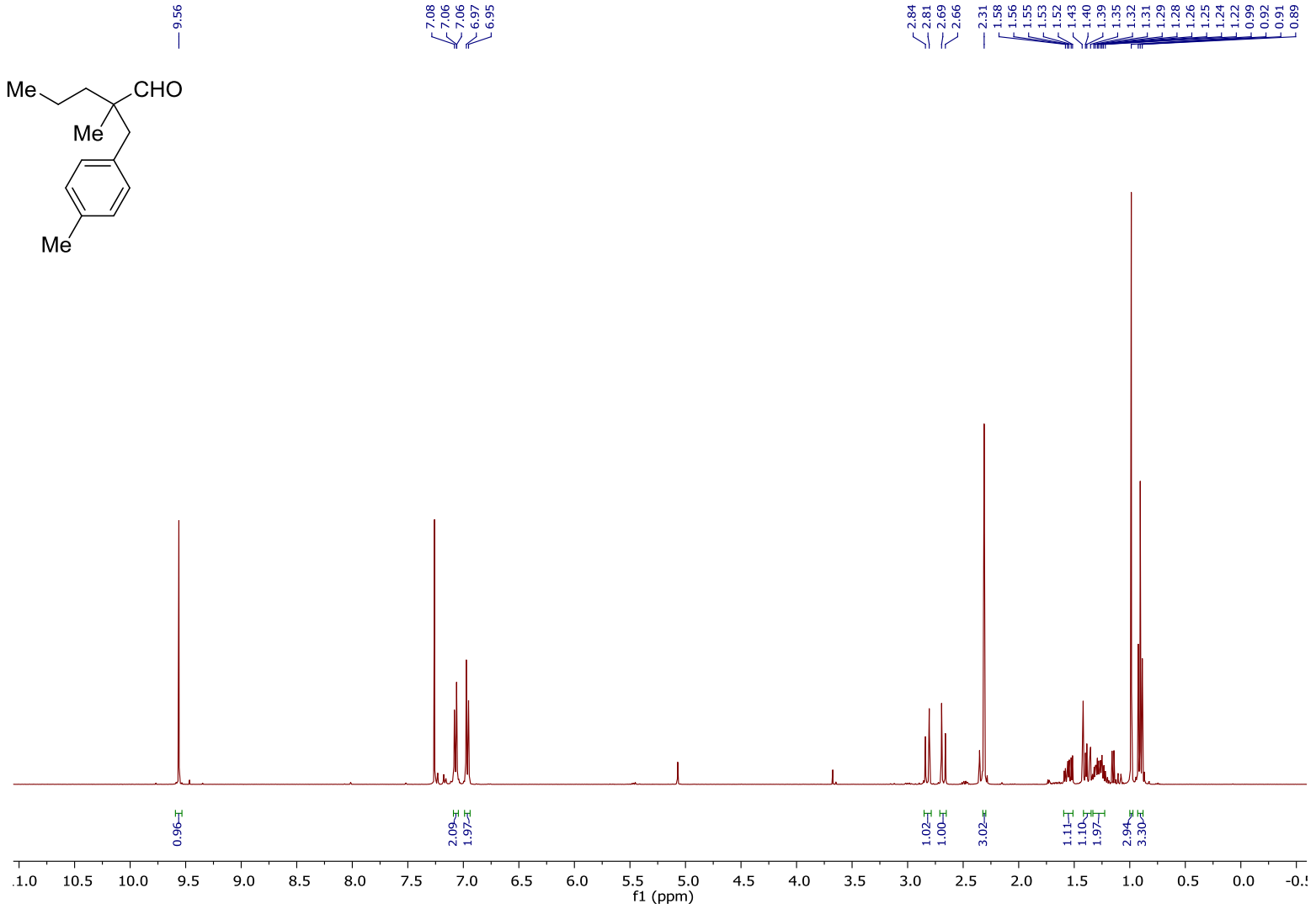
2-methyl-2-(3-methoxylbenzyl)pentane (3bb)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



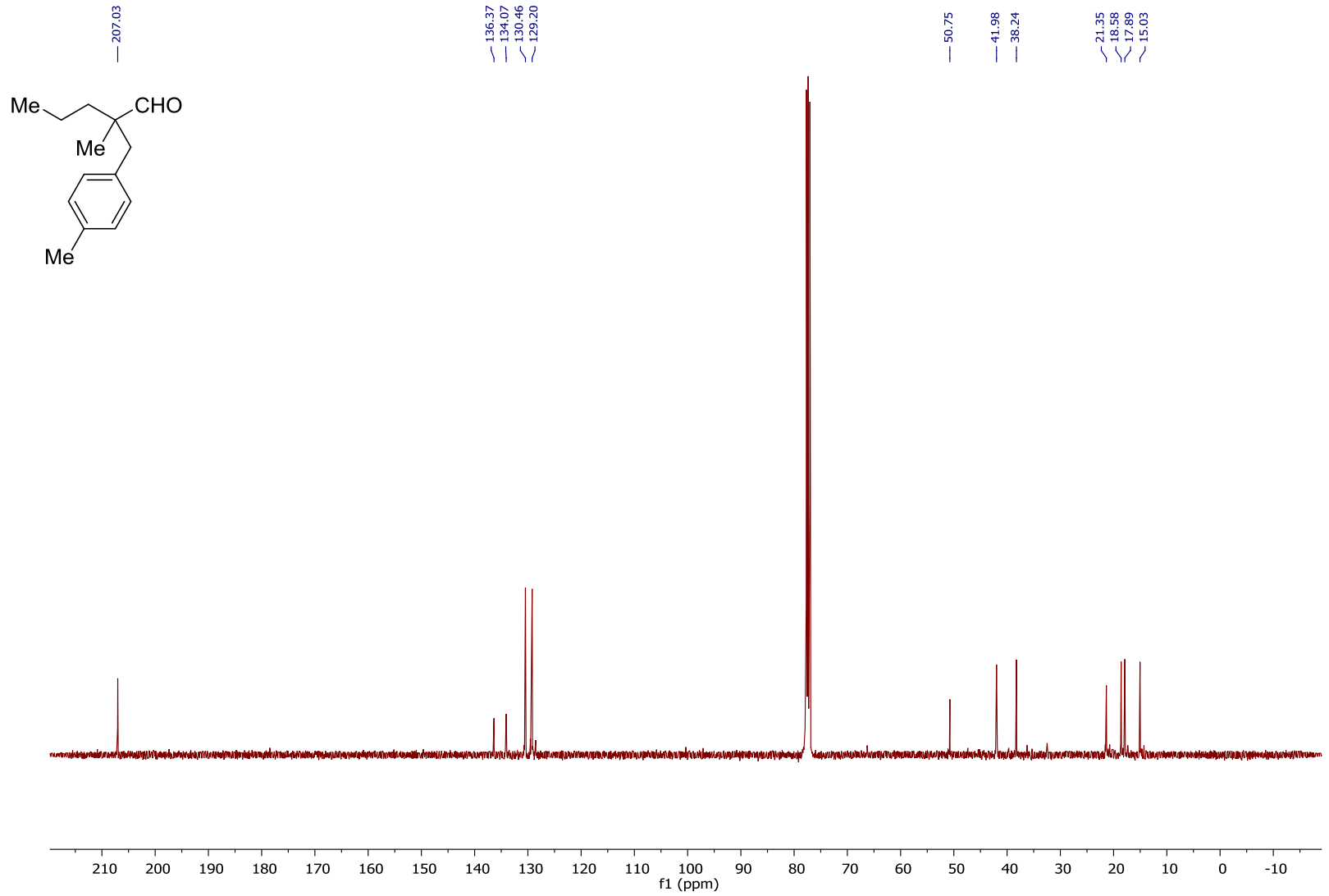
2-benzyl-2-(4-methylbenzyl)pentanel (3bd)

^{1}H NMR (400 MHz, $CDCl_3$):



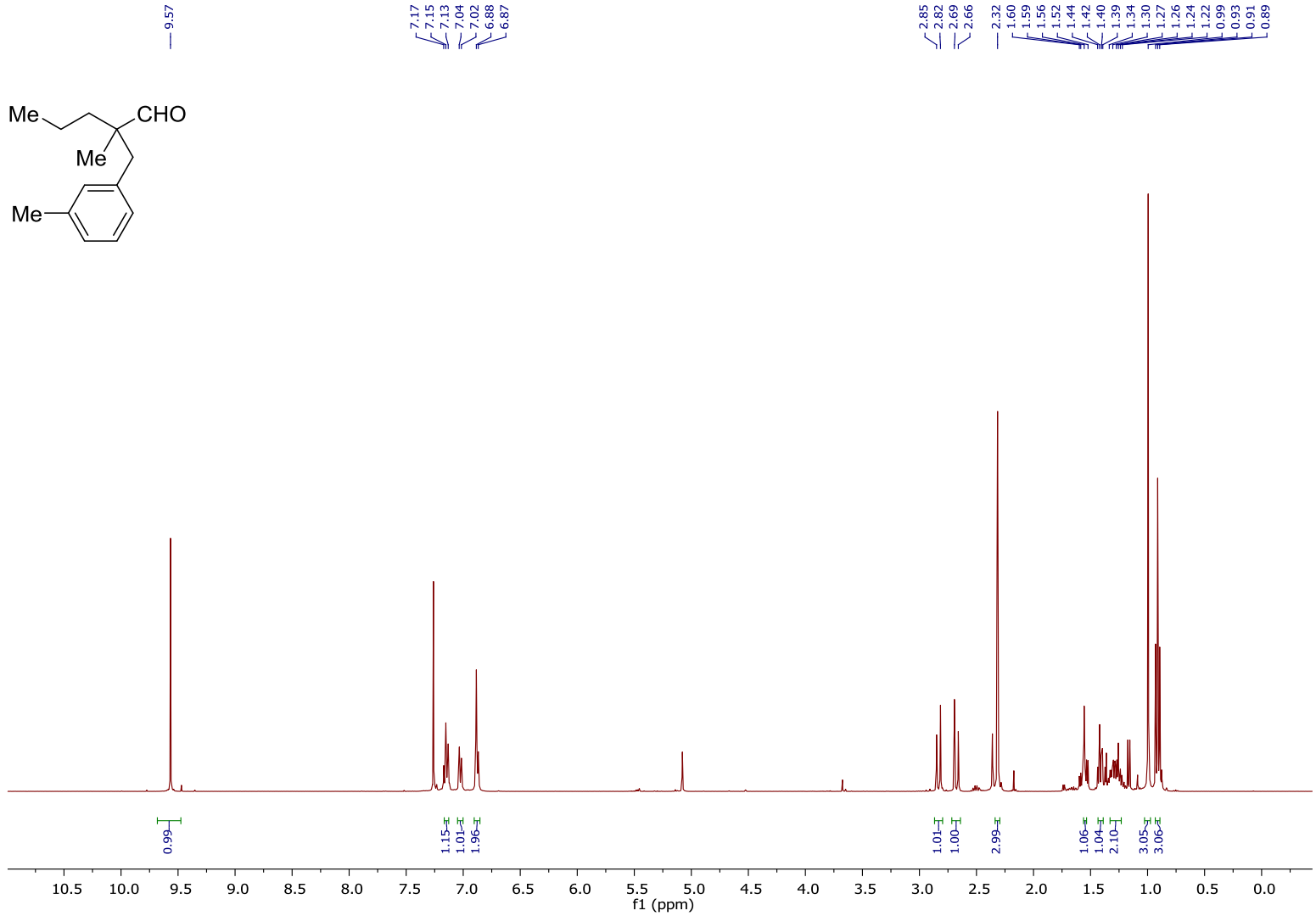
2-benzyl-2-(4-methylbenzyl)pentanel (3bd)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



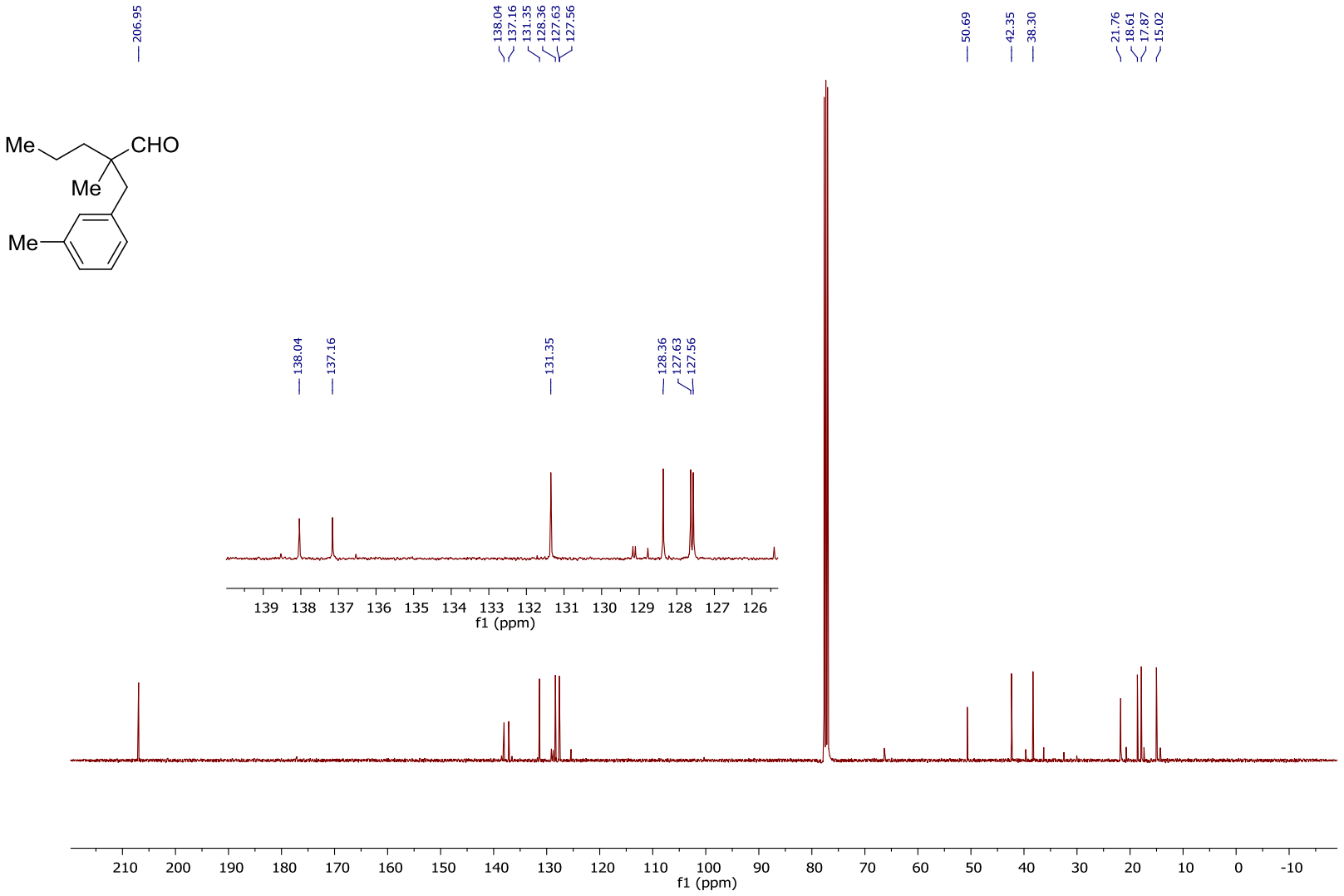
2-methyl-2-(3-methylbenzyl)pentanal (3be)

^{1}H NMR (400 MHz, $CDCl_3$):



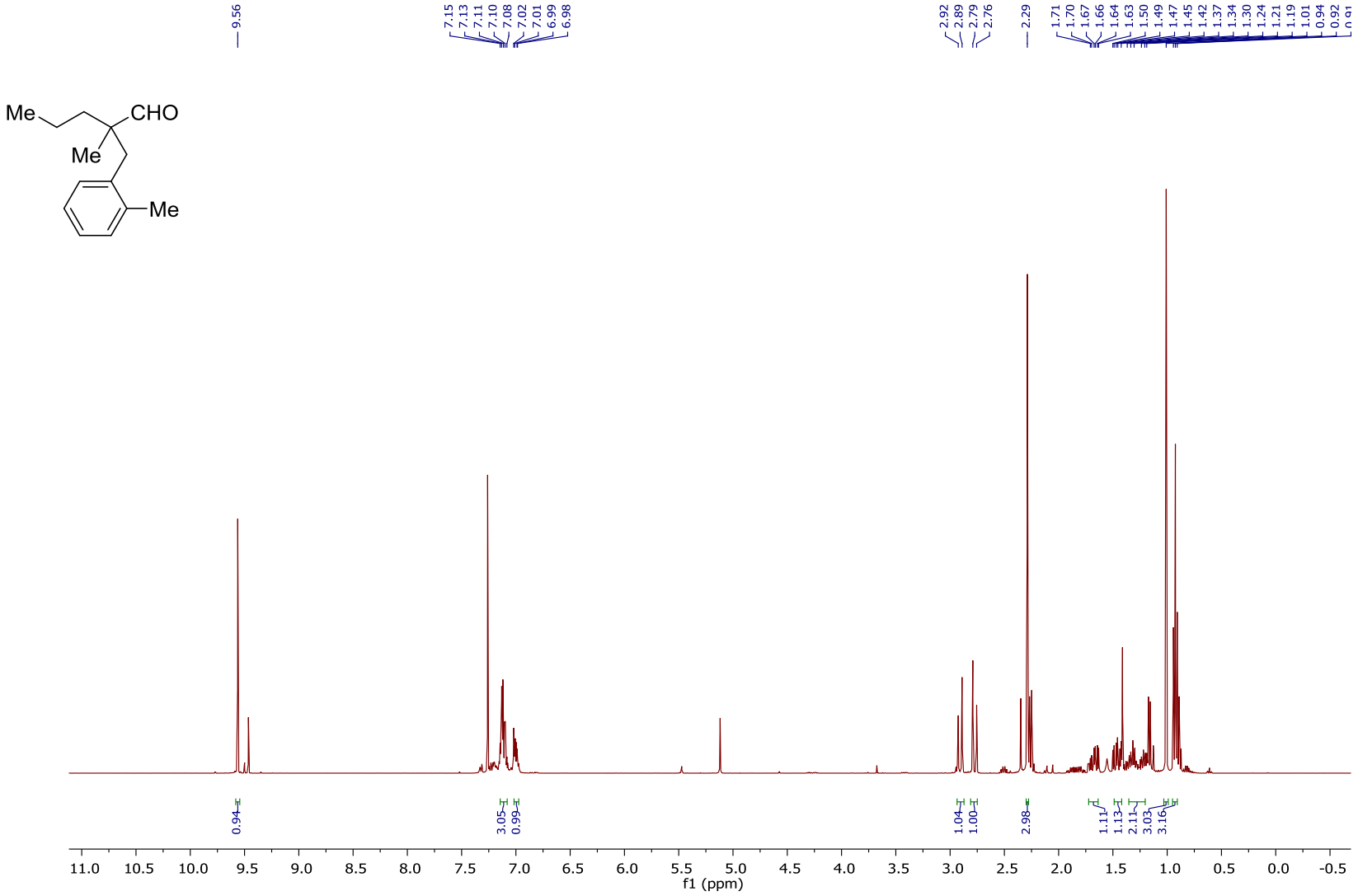
2-methyl-2-(3-methylbenzyl)pentanal (3be)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



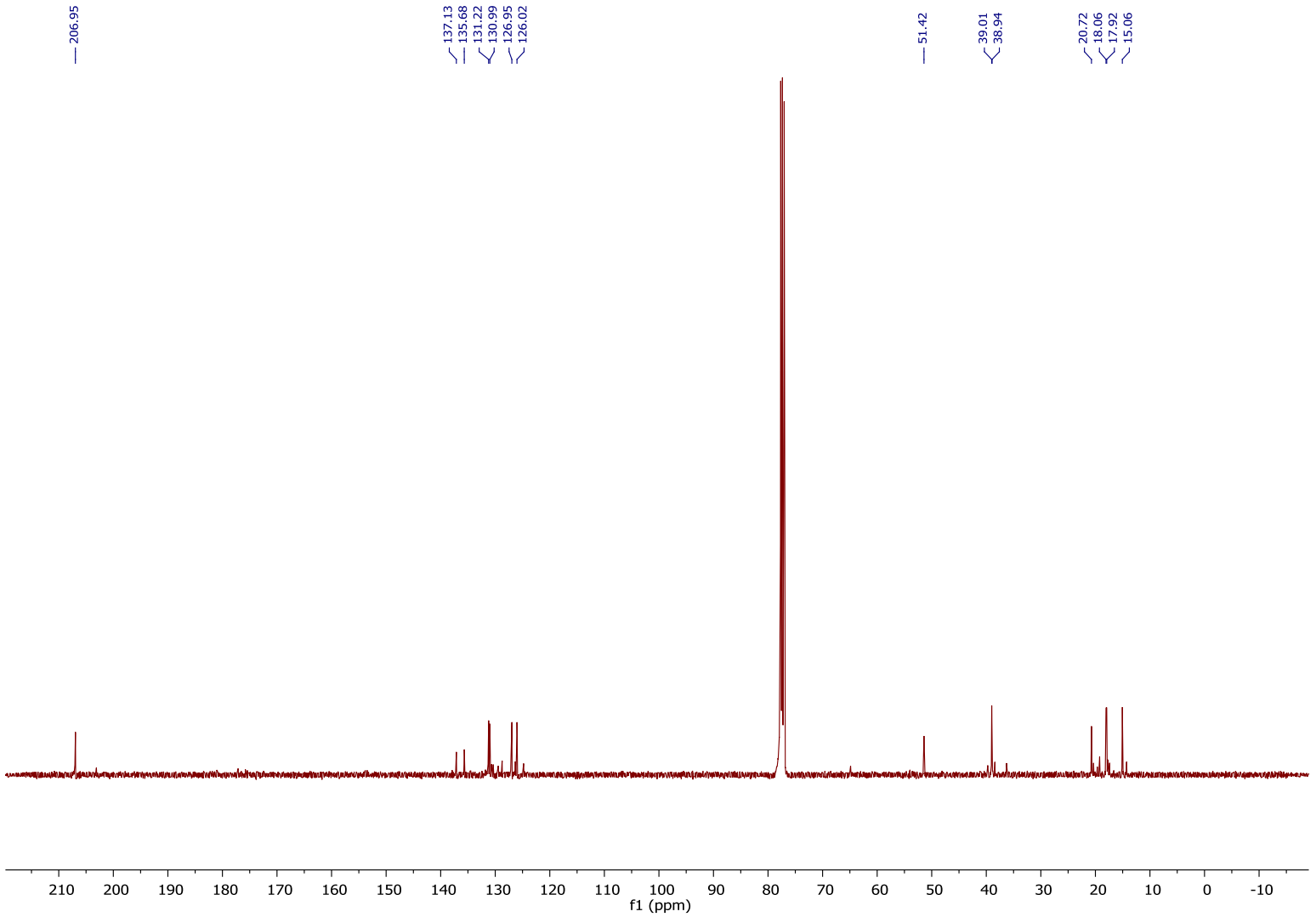
2-methyl-2-(2-methylbenzyl)pentanal (3bf)

^{1}H NMR (400 MHz, $CDCl_3$):



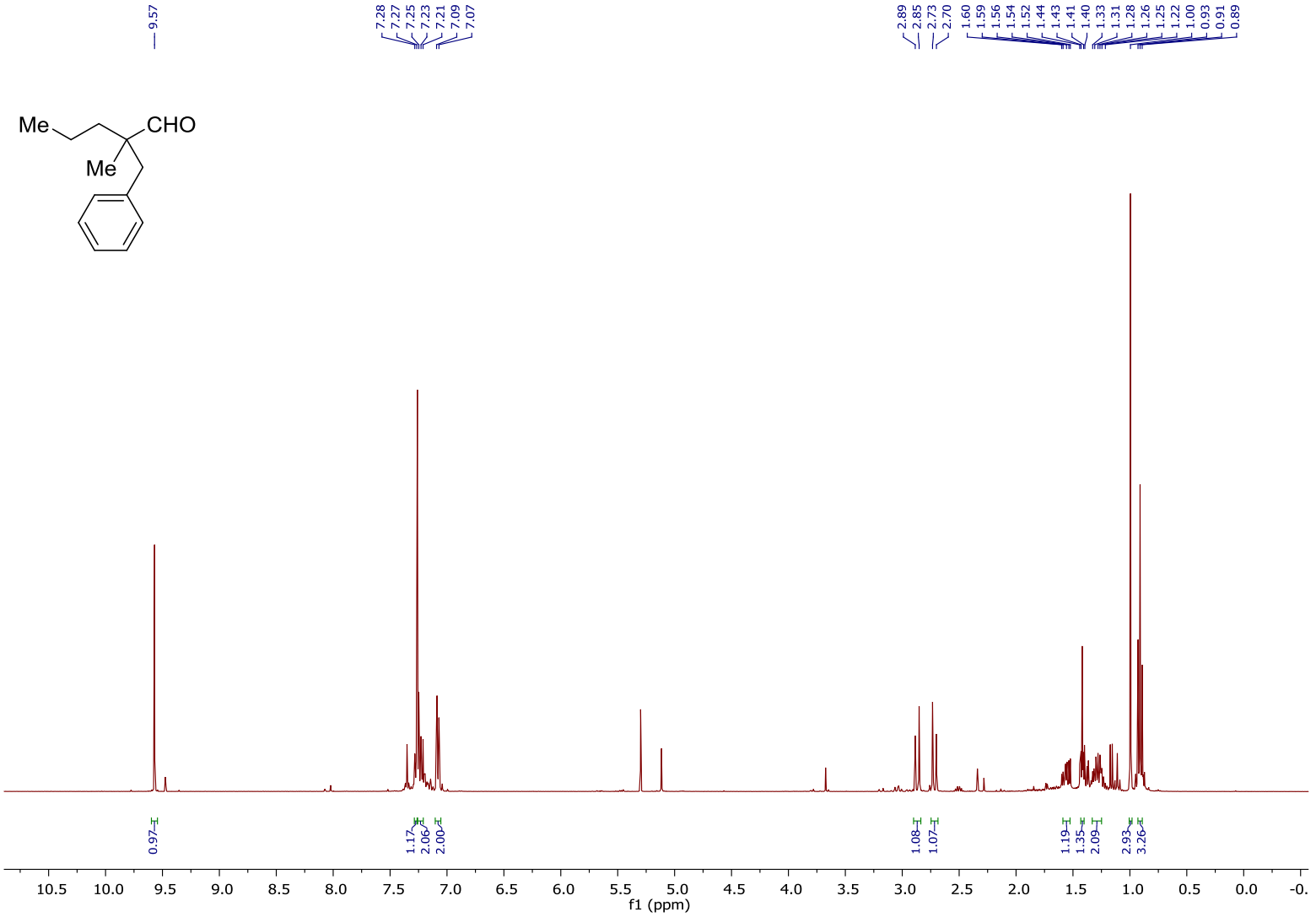
2-methyl-2-(2-methylbenzyl)pentanal (3bf)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



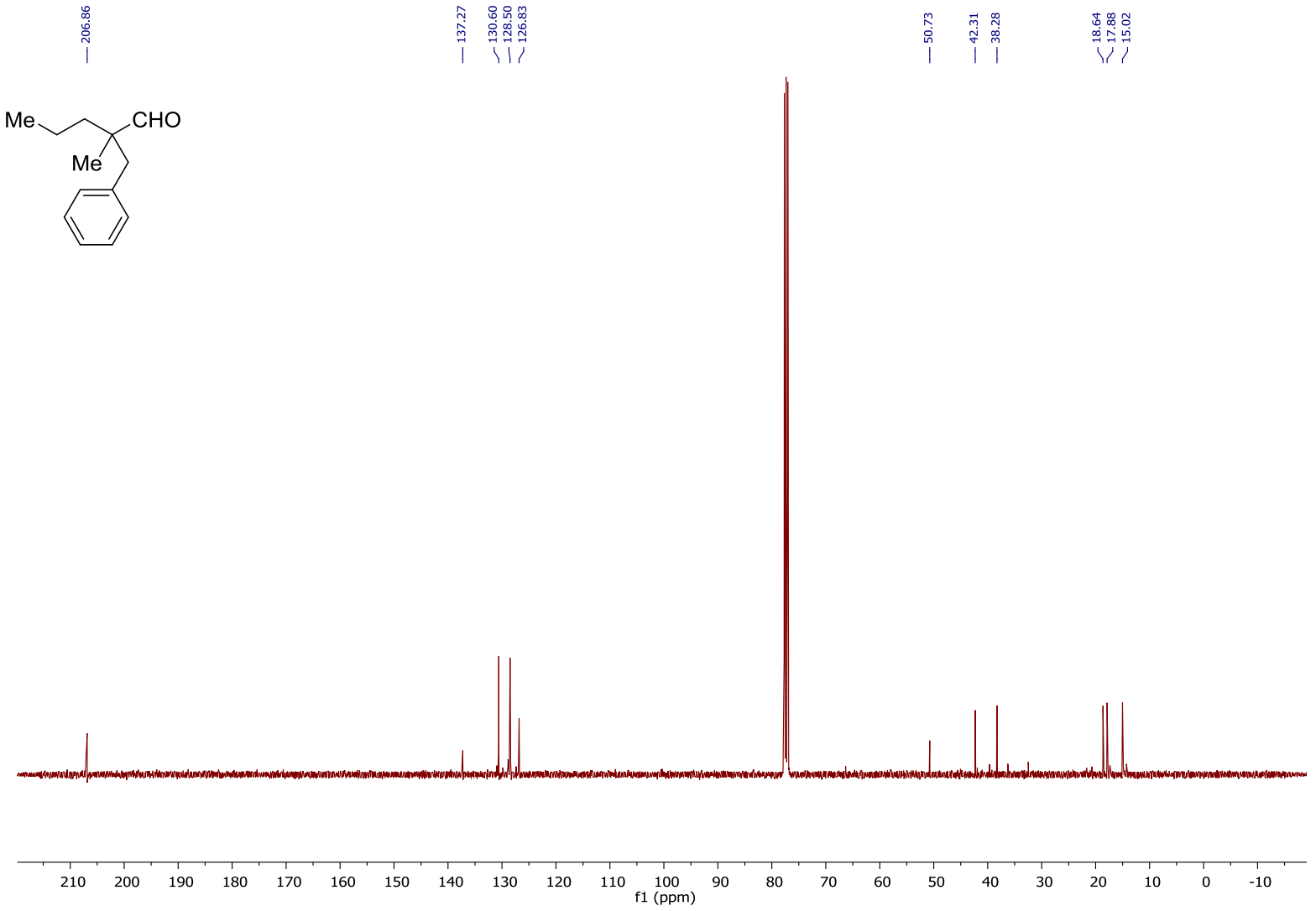
2-benzyl-2-methylpentanal (3bg)

^{1}H NMR (400 MHz, $CDCl_3$):



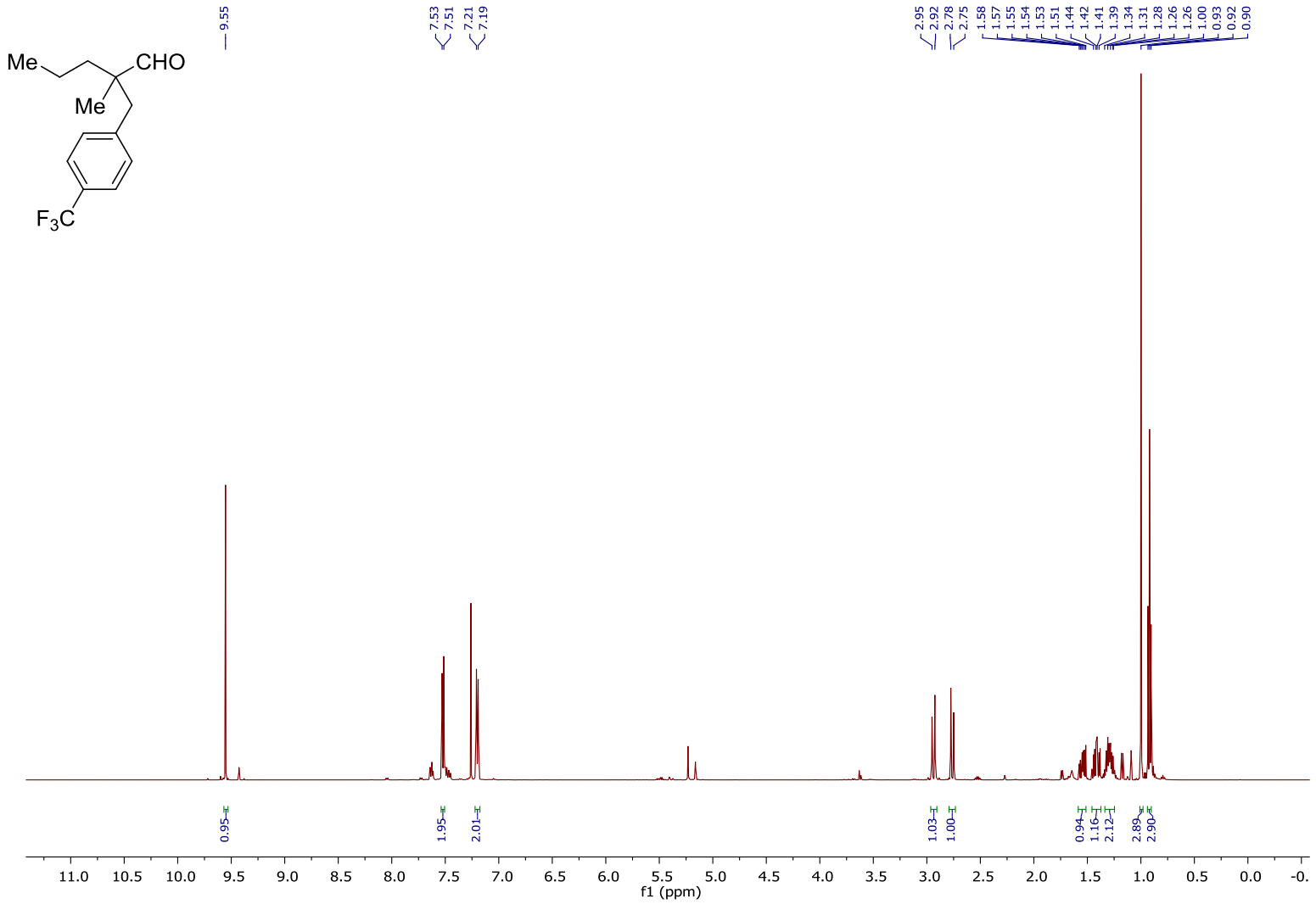
2-benzyl-2-methylpentanal (3bg)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



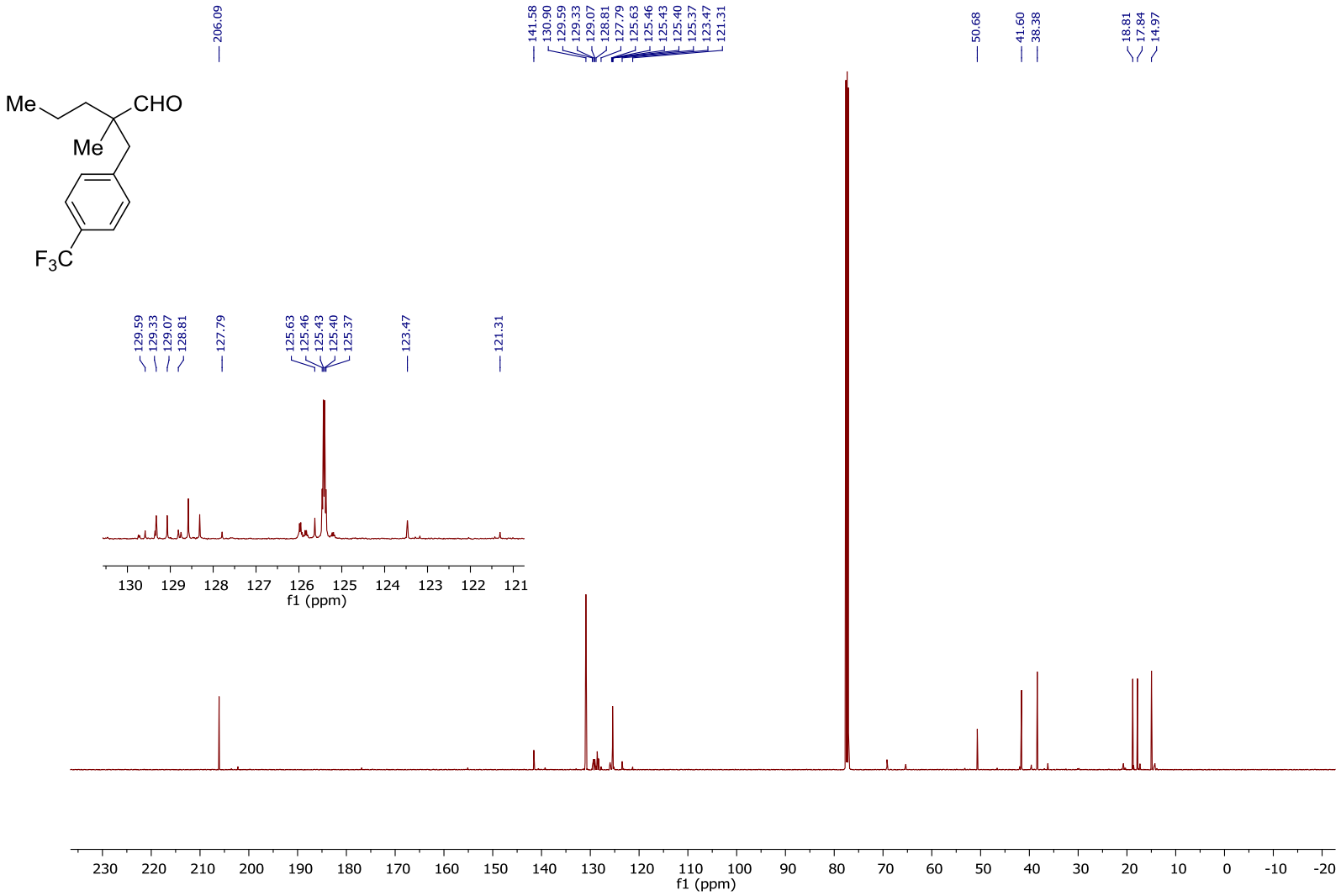
2-methyl-2-(4-(trifluoromethyl)benzyl)pentanal (3bh)

^{1}H NMR (400 MHz, $CDCl_3$):



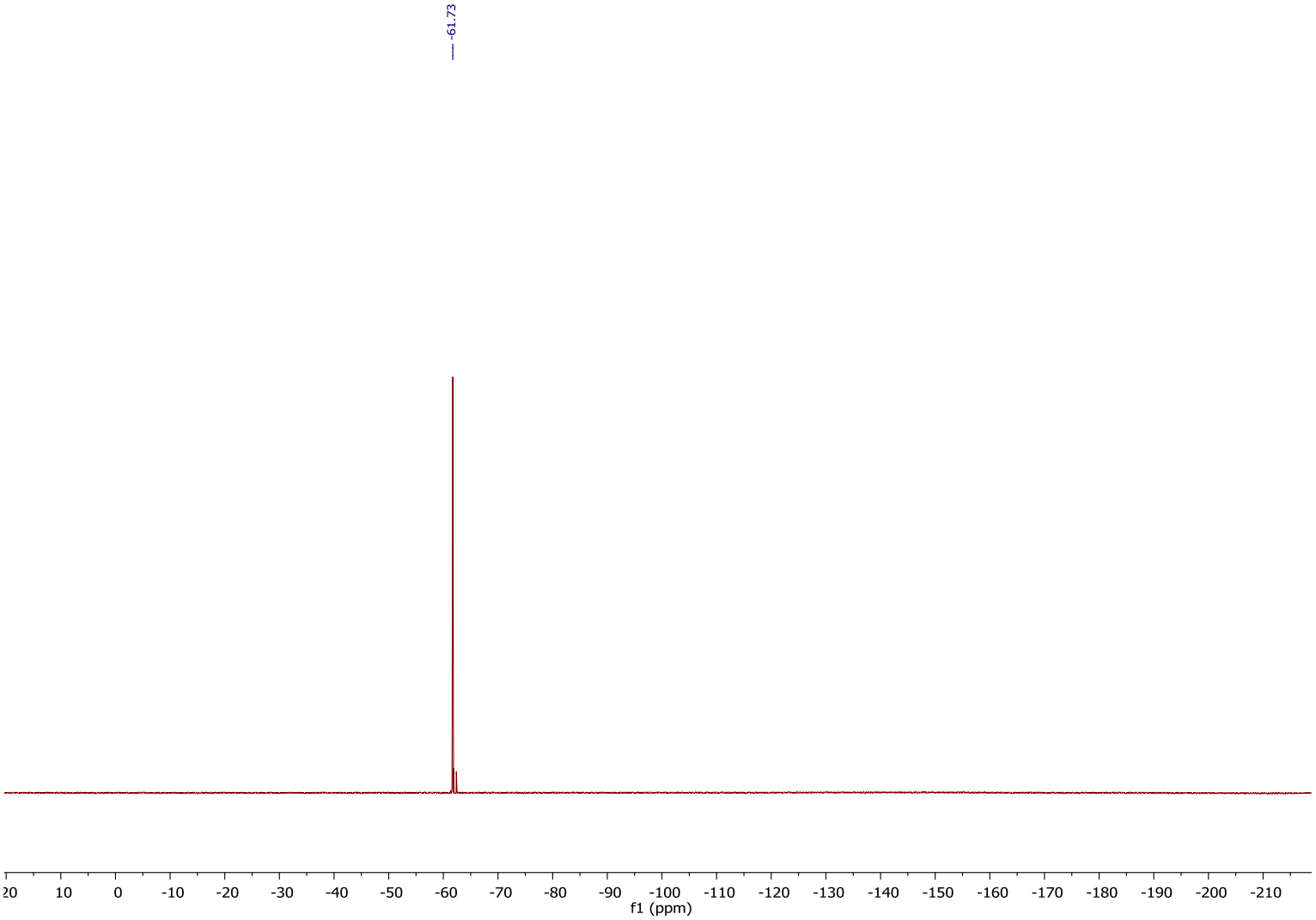
2-methyl-2-(4-(trifluoromethyl)benzyl)pentanal (3bh)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



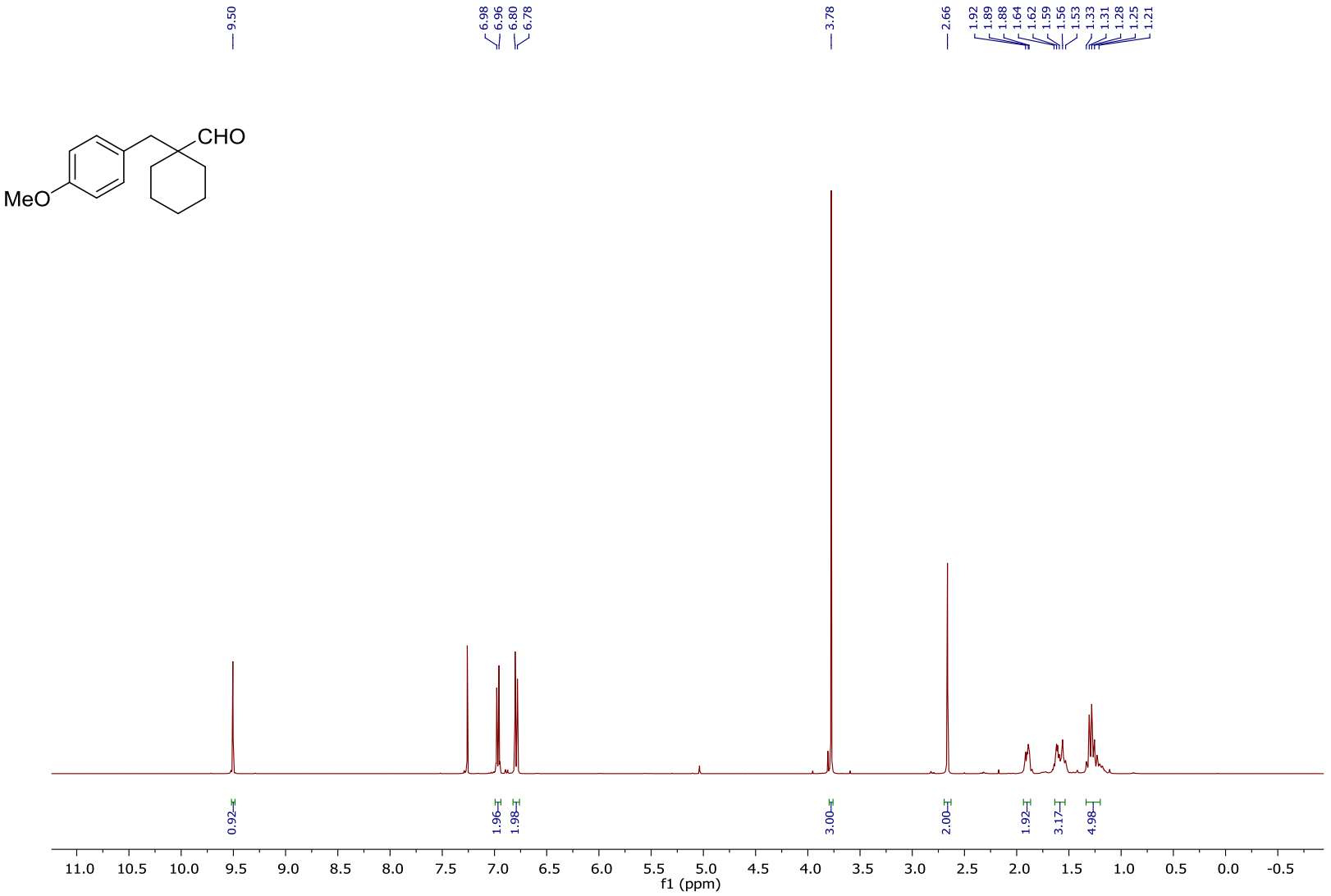
2-methyl-2-(4-(trifluoromethyl)benzyl)pentanal (3bh)

$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$):



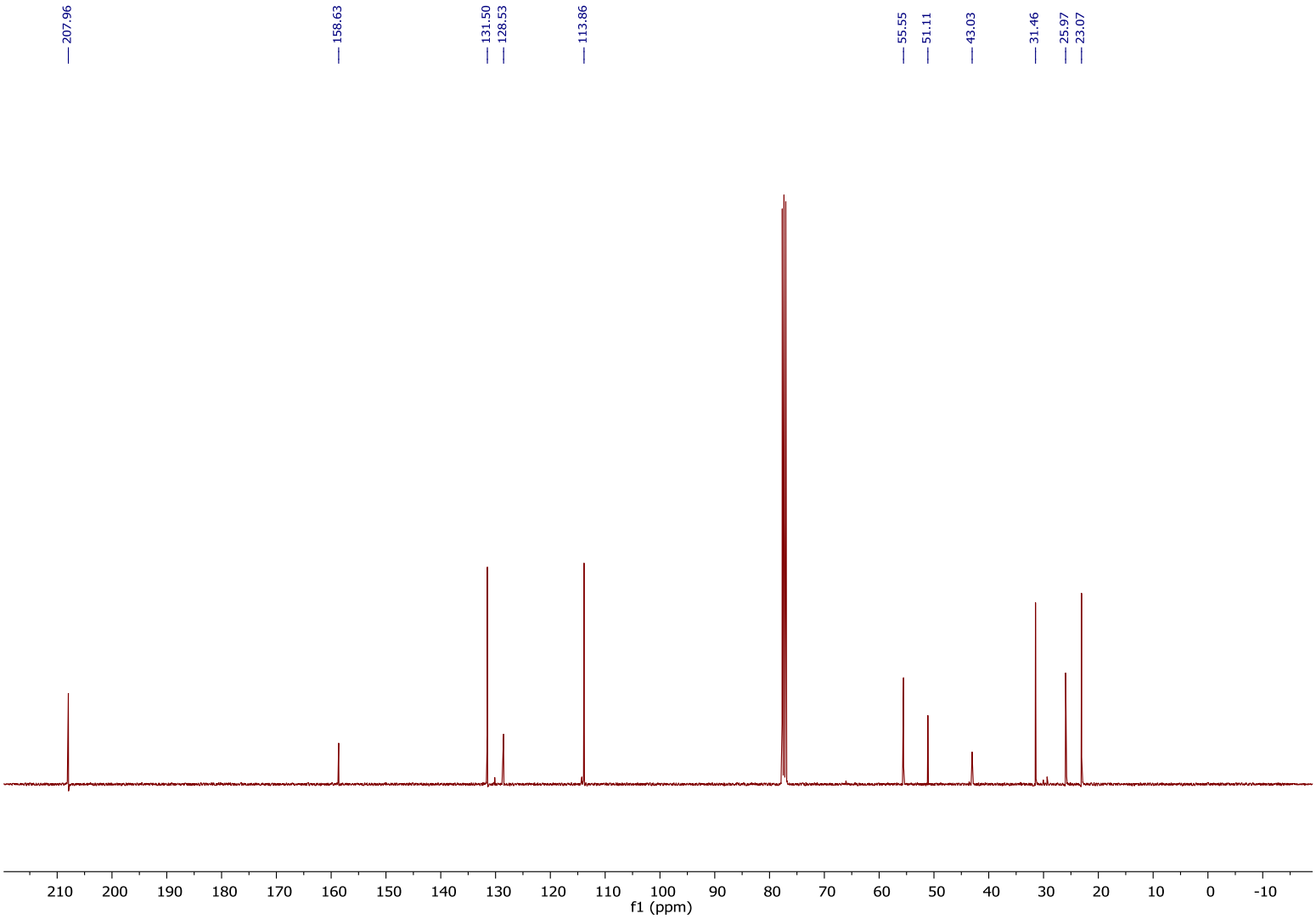
1-(4-methoxybenzyl)cyclohexanecarbaldehyde (3ca)

^{1}H NMR (400 MHz, $CDCl_3$):



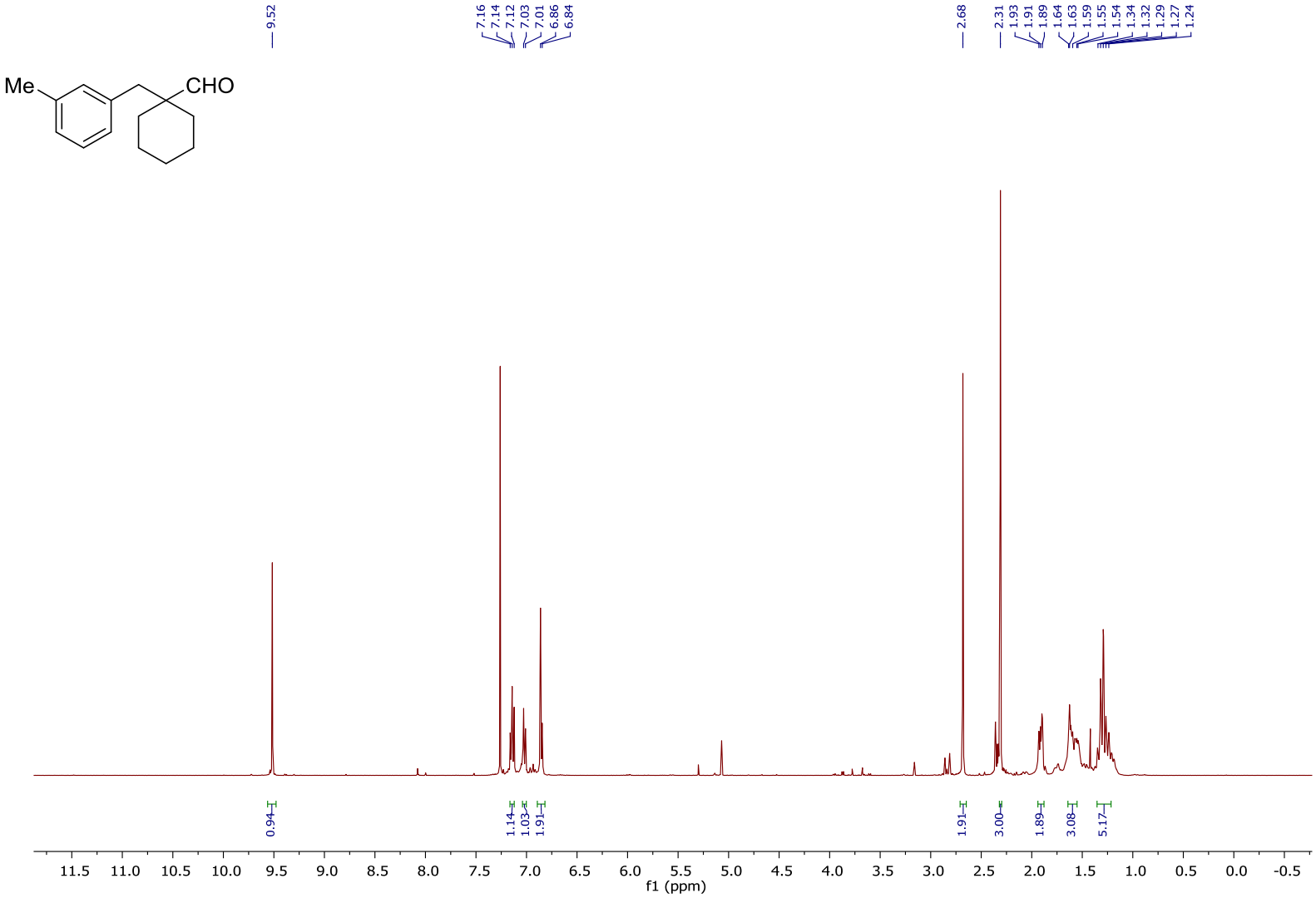
1-(4-methoxybenzyl)cyclohexanecarbaldehyde (3ca)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



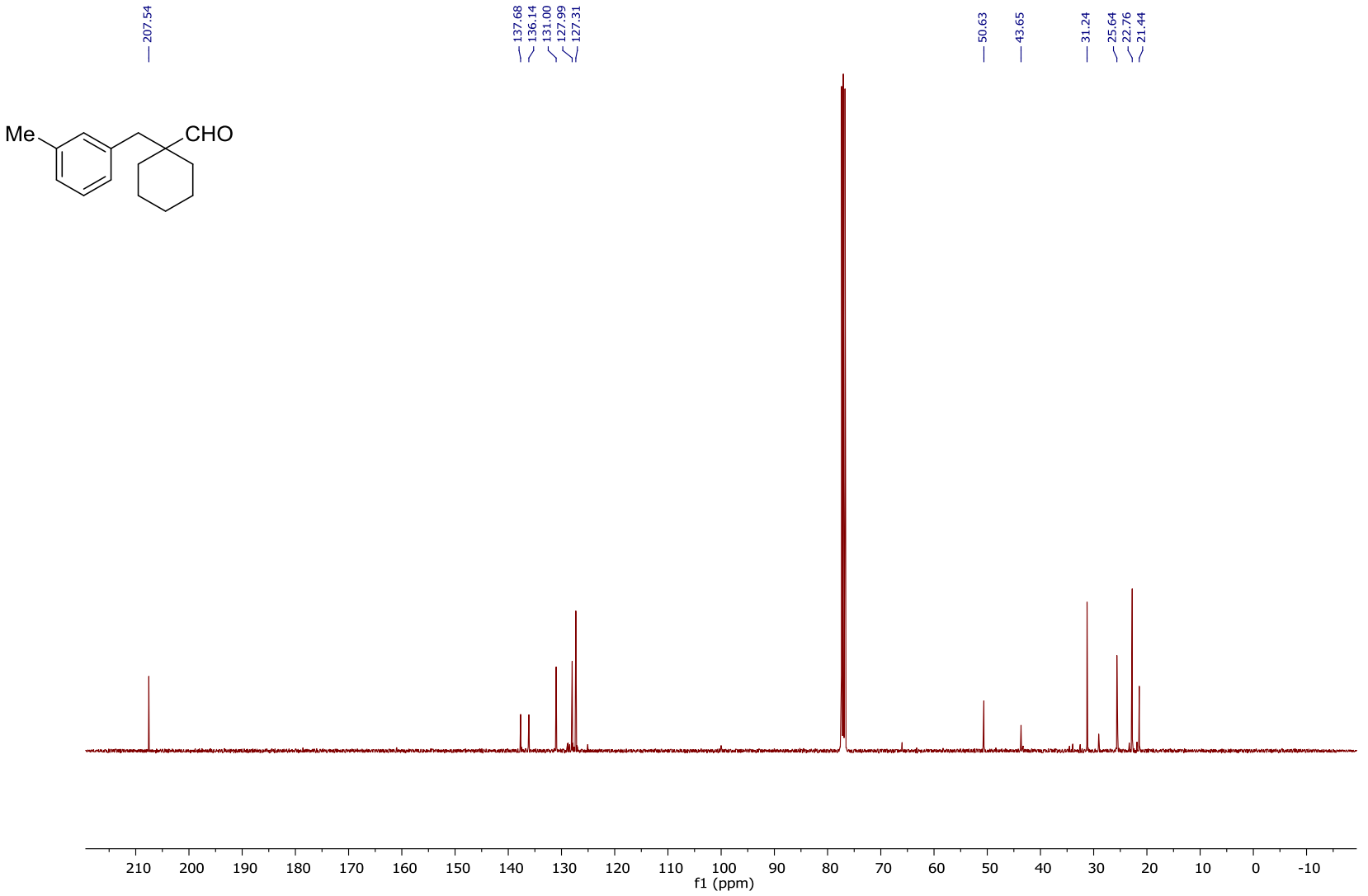
1-(3-methybenzyl)cyclohexanecarbaldehyde (3ce)

^{1}H NMR (400 MHz, $CDCl_3$):



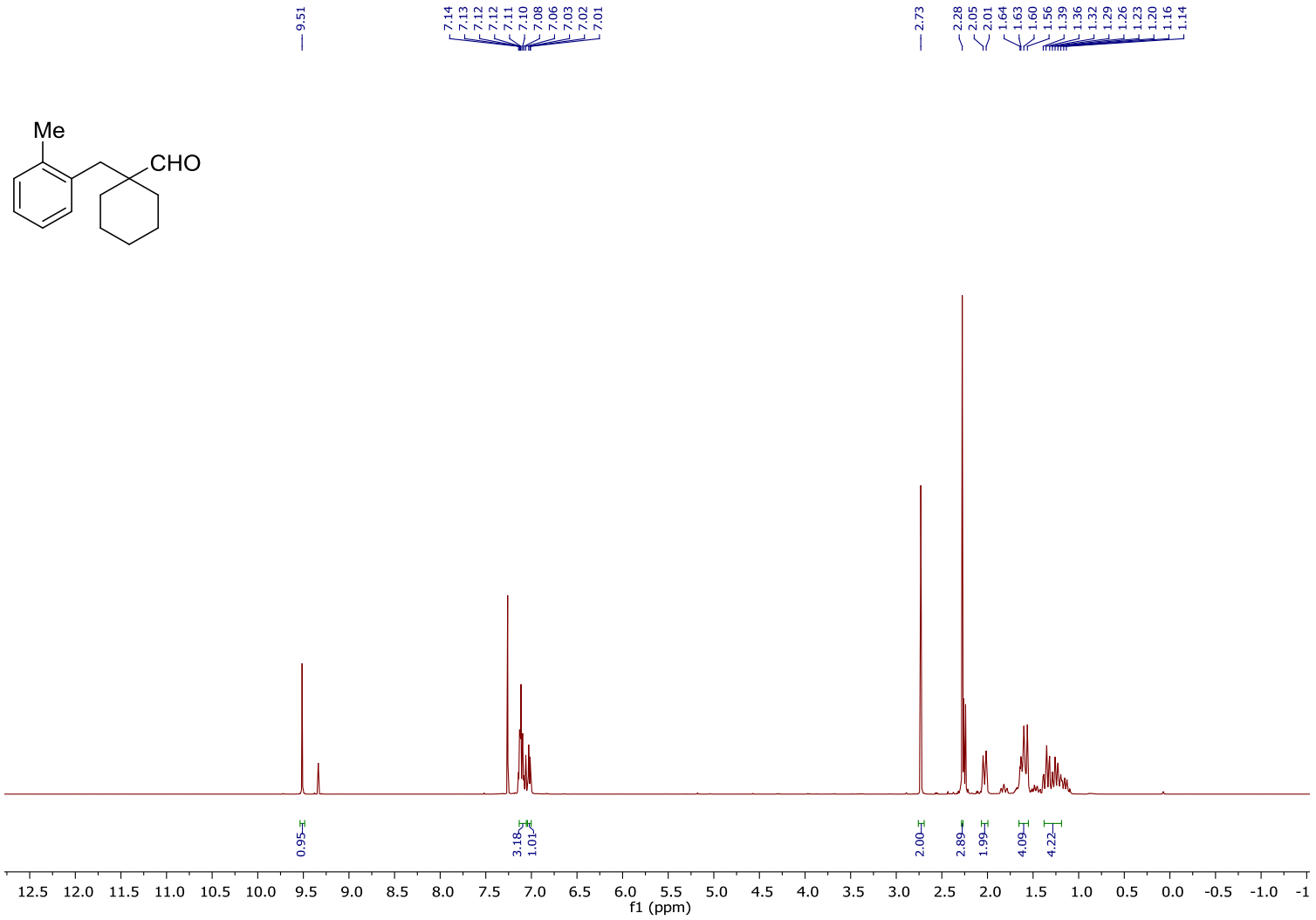
1-(3-methybenzyl)cyclohexanecarbaldehyde (3ce)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



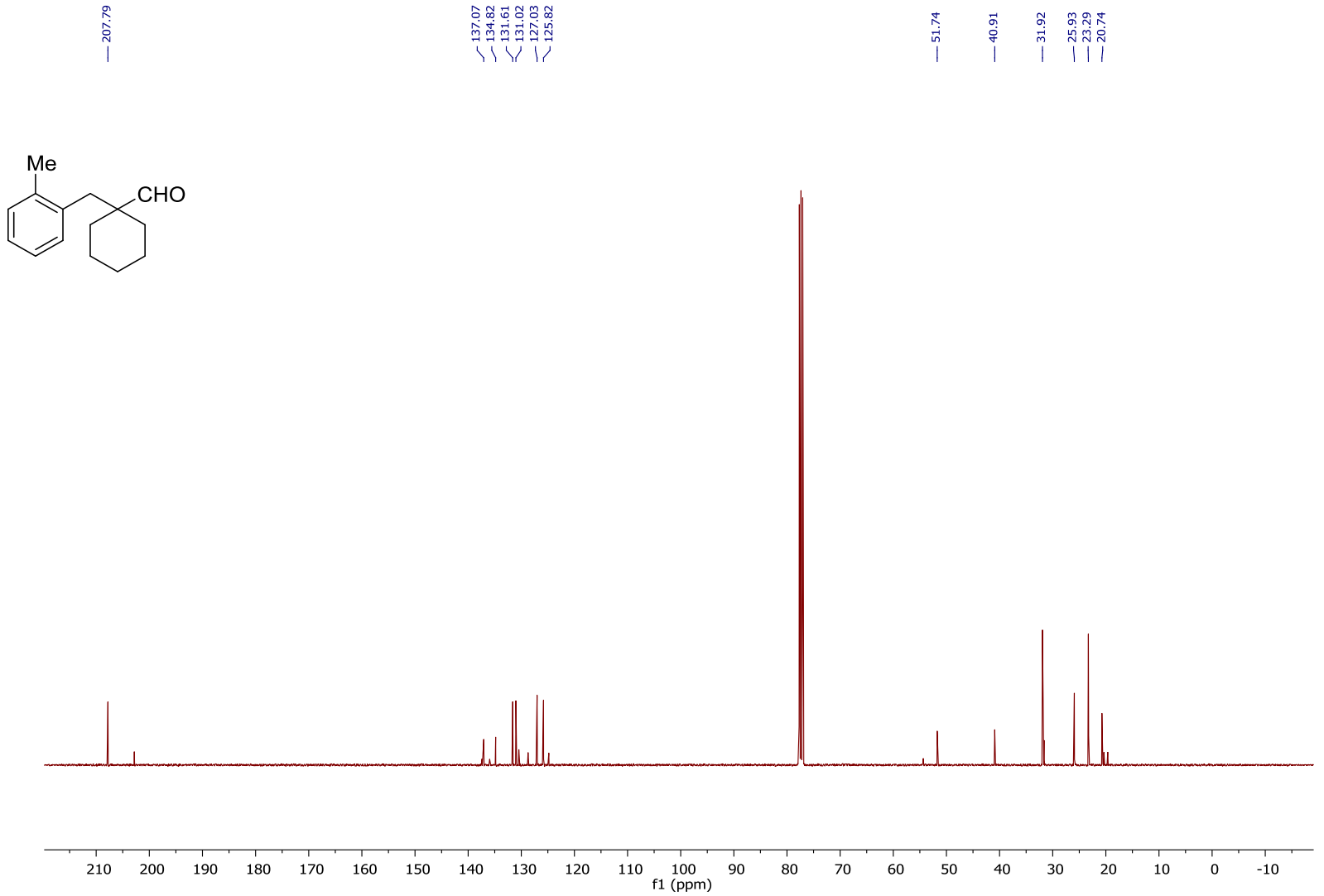
1-(2-methybenzyl)cyclohexanecarbaldehyde (3cf)

^{1}H NMR (400 MHz, $CDCl_3$):



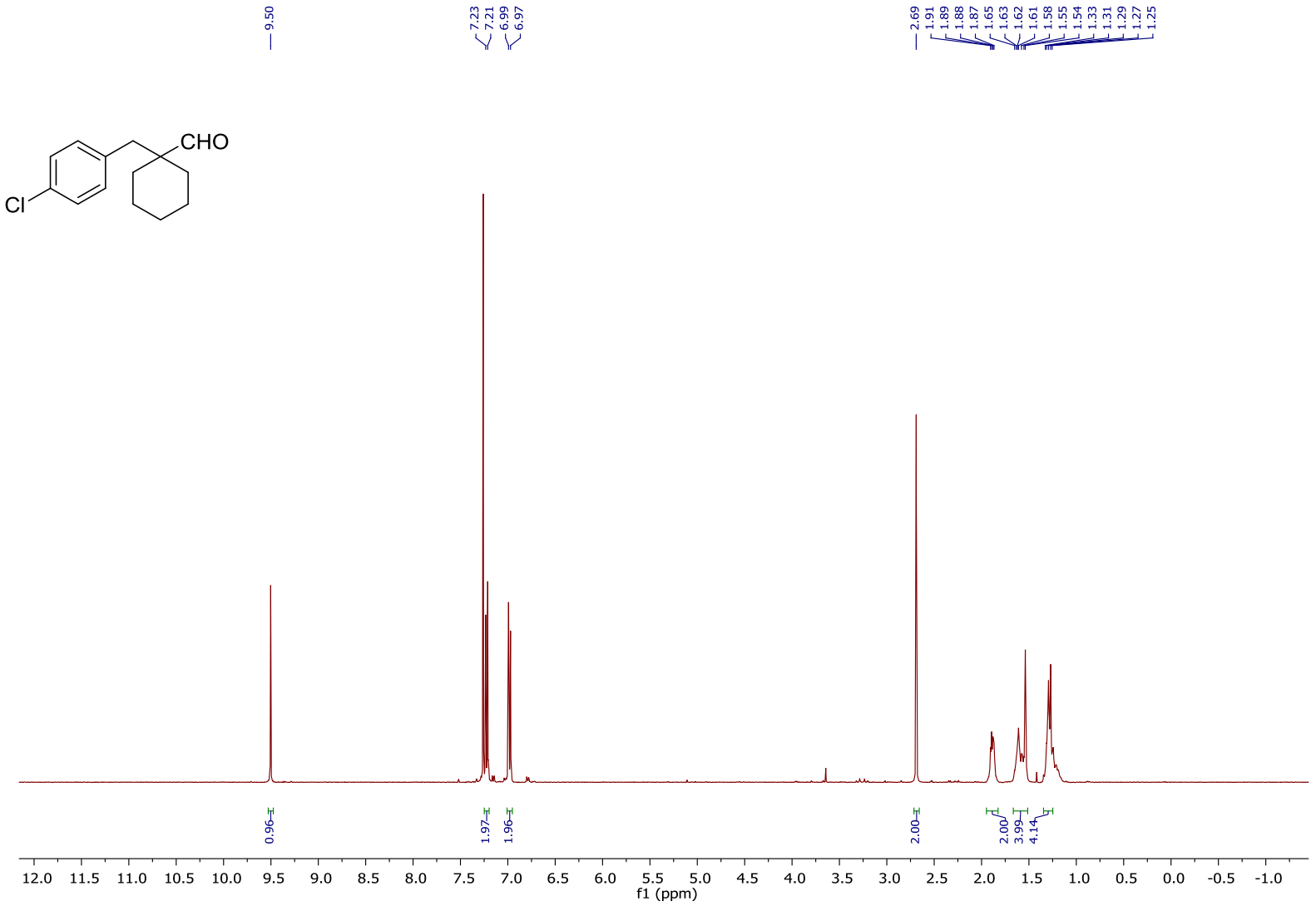
1-(2-methybenzyl)cyclohexanecarbaldehyde (3cf)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



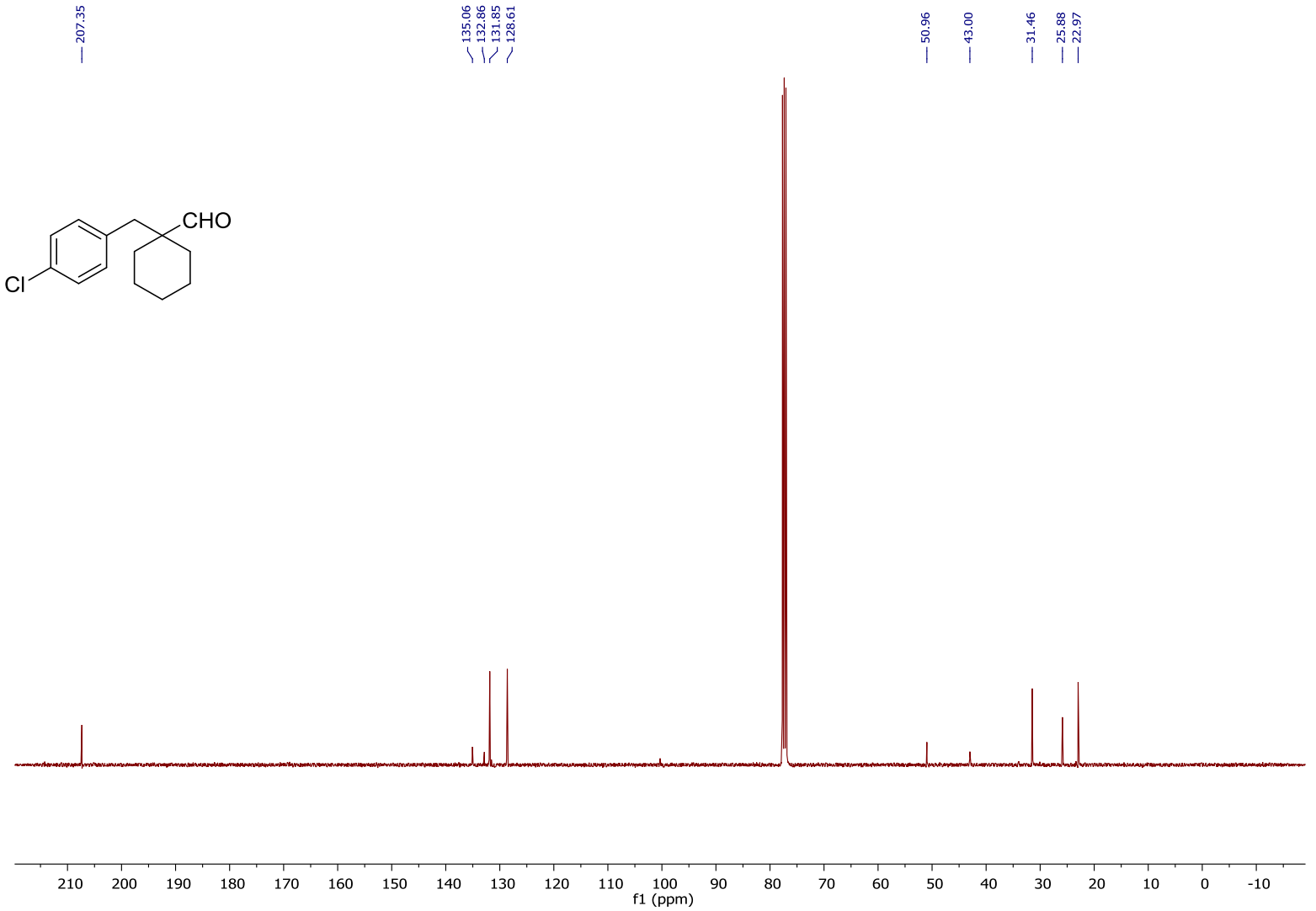
1-(4-chlorobenzyl)cyclohexanecarbaldehyde (3ci)

^{1}H NMR (400 MHz, $CDCl_3$):



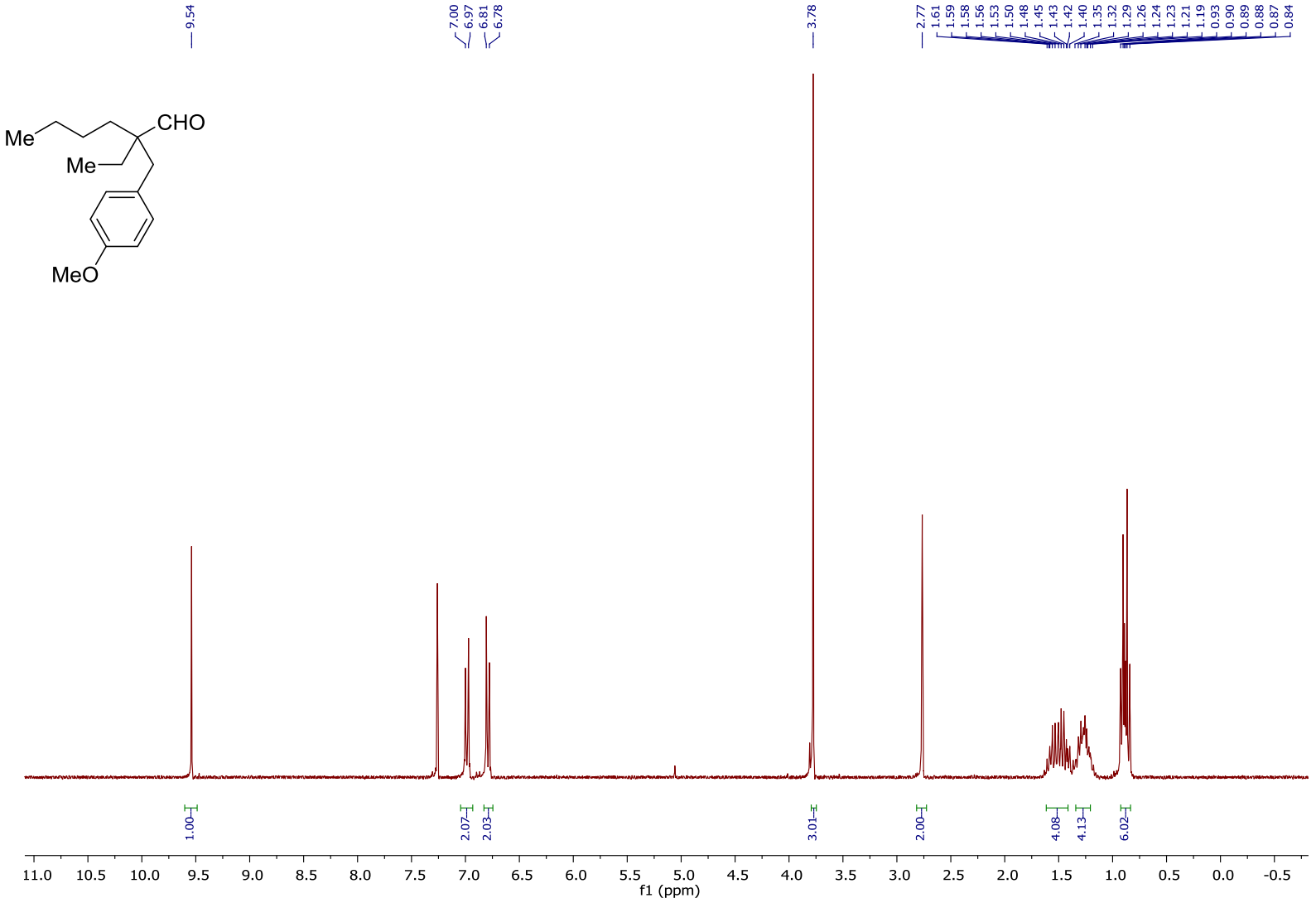
1-(4-chlorobenzyl)cyclohexanecarbaldehyde (3ci)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



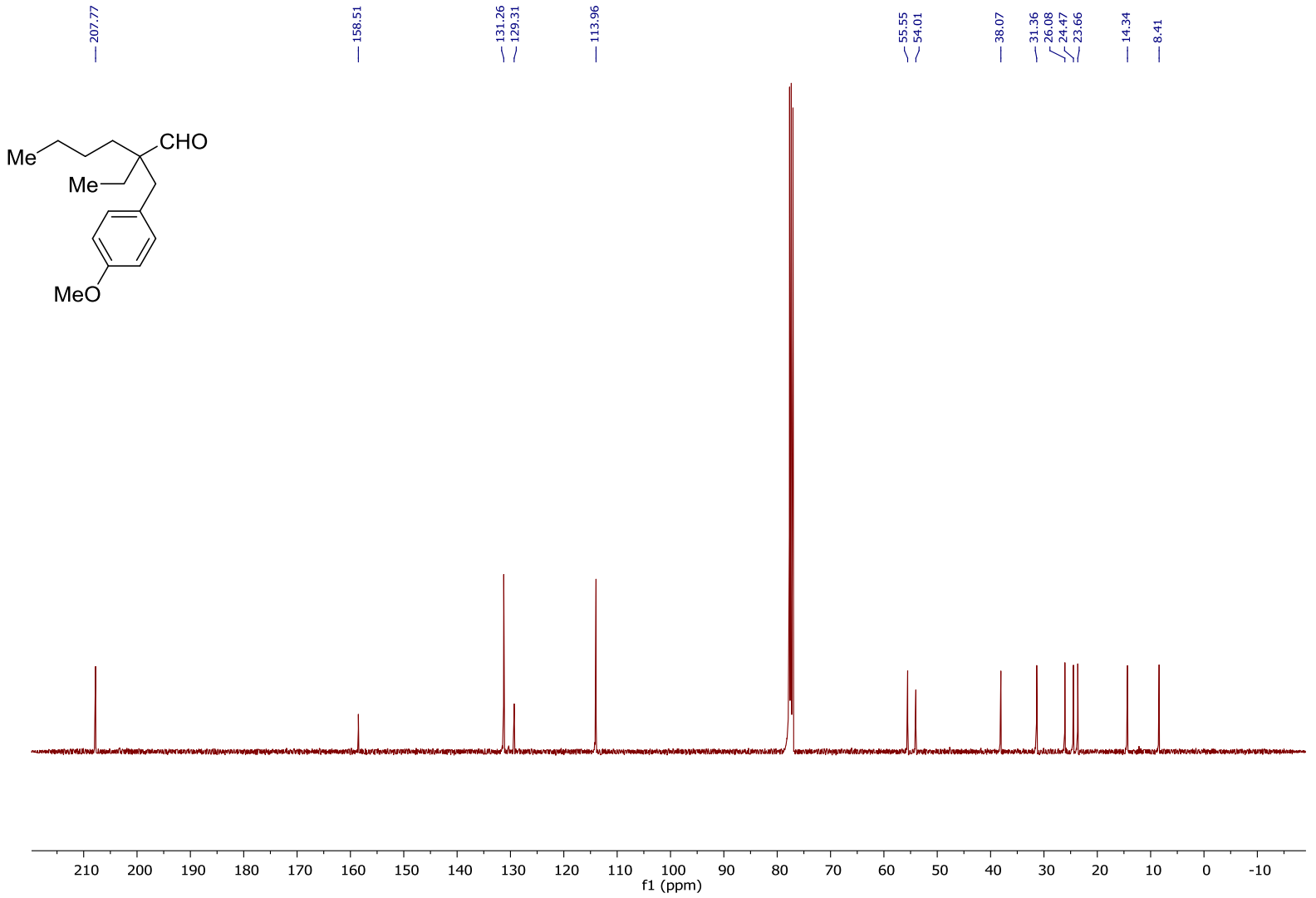
2-ethyl-2-(4-methoxybenzyl)hexanal (3da)

^{1}H NMR (400 MHz, $CDCl_3$):



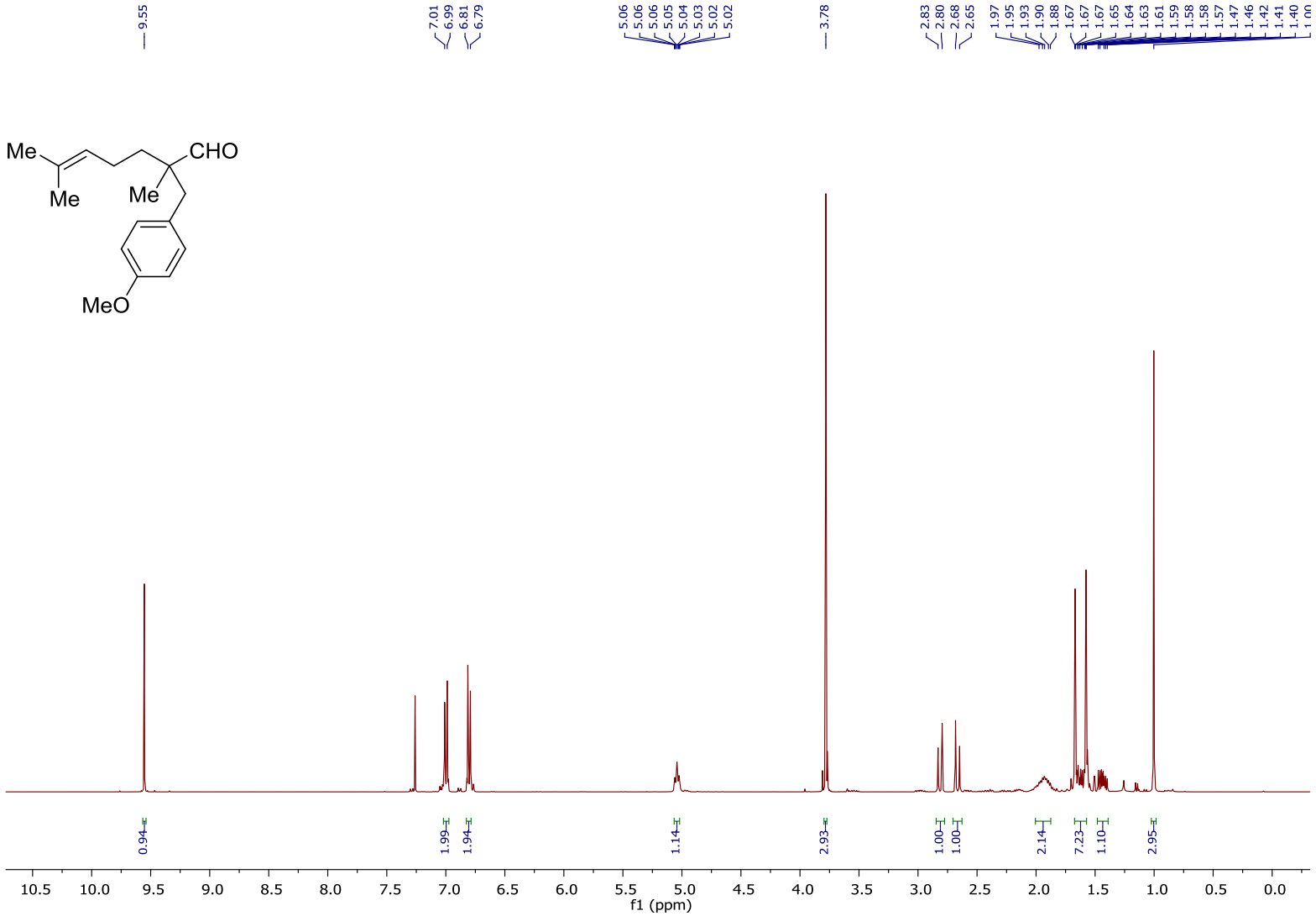
2-ethyl-2-(4-methoxybenzyl)hexanal (3da)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



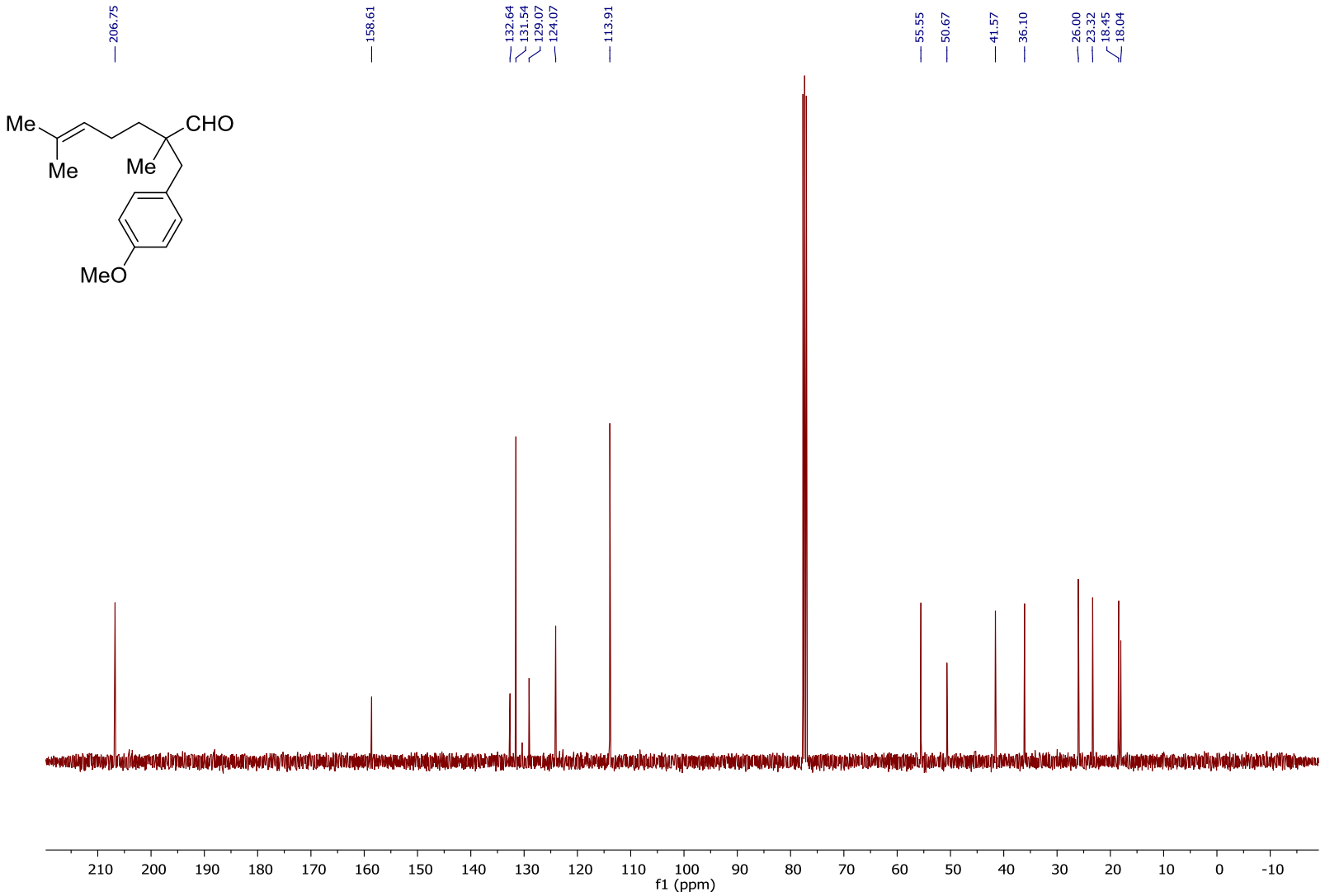
2-(4-methoxybenzyl)-2,6-dimethylhept-5-enal (3ea)

^{1}H NMR (400 MHz, $CDCl_3$):



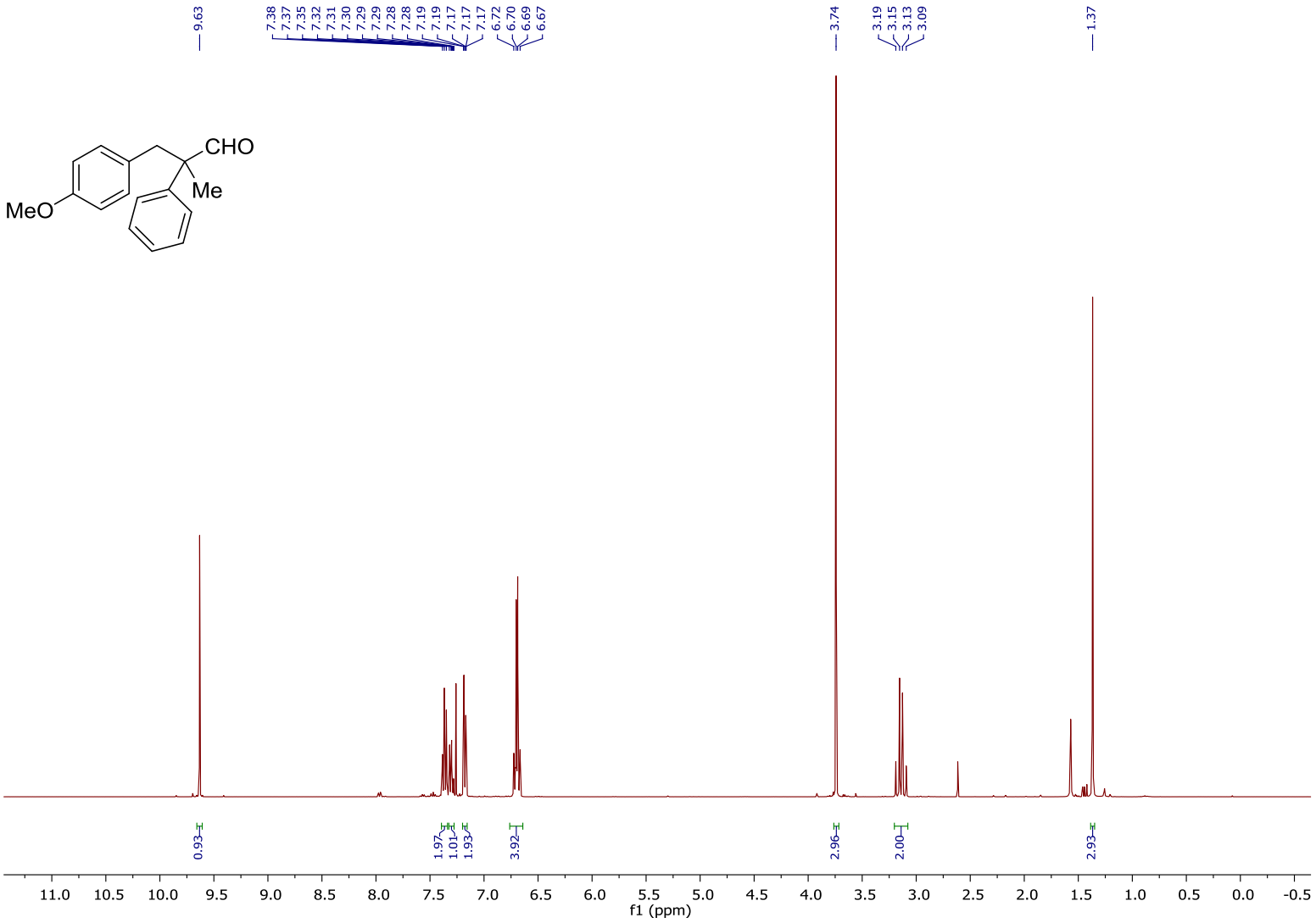
2-(4-methoxybenzyl)-2,6-dimethylhept-5-enal (3ea)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



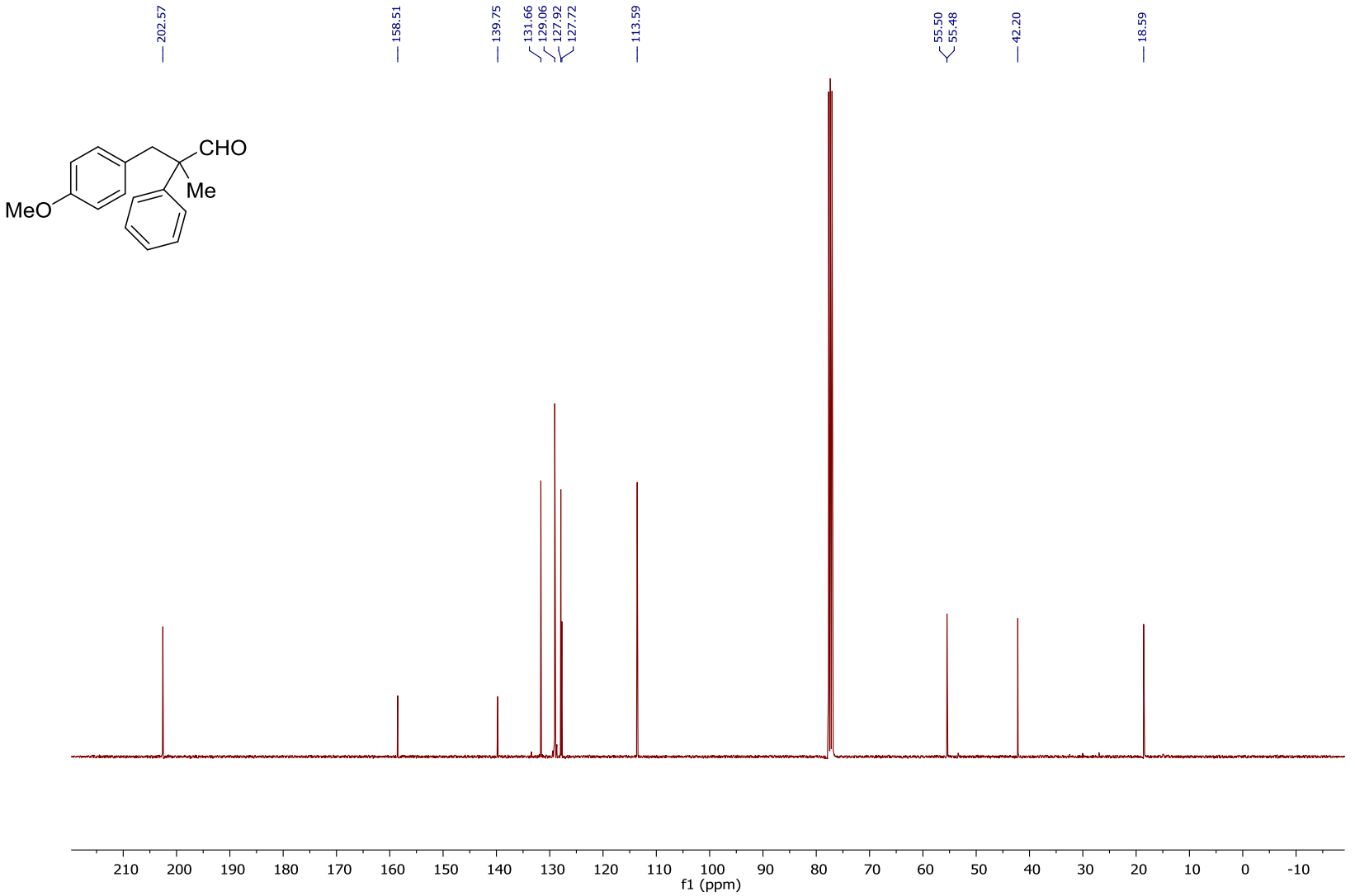
3-(4-methoxyphenyl)-2-methyl-2-phenylpropanal (7aa)

^{1}H NMR (400 MHz, $CDCl_3$):



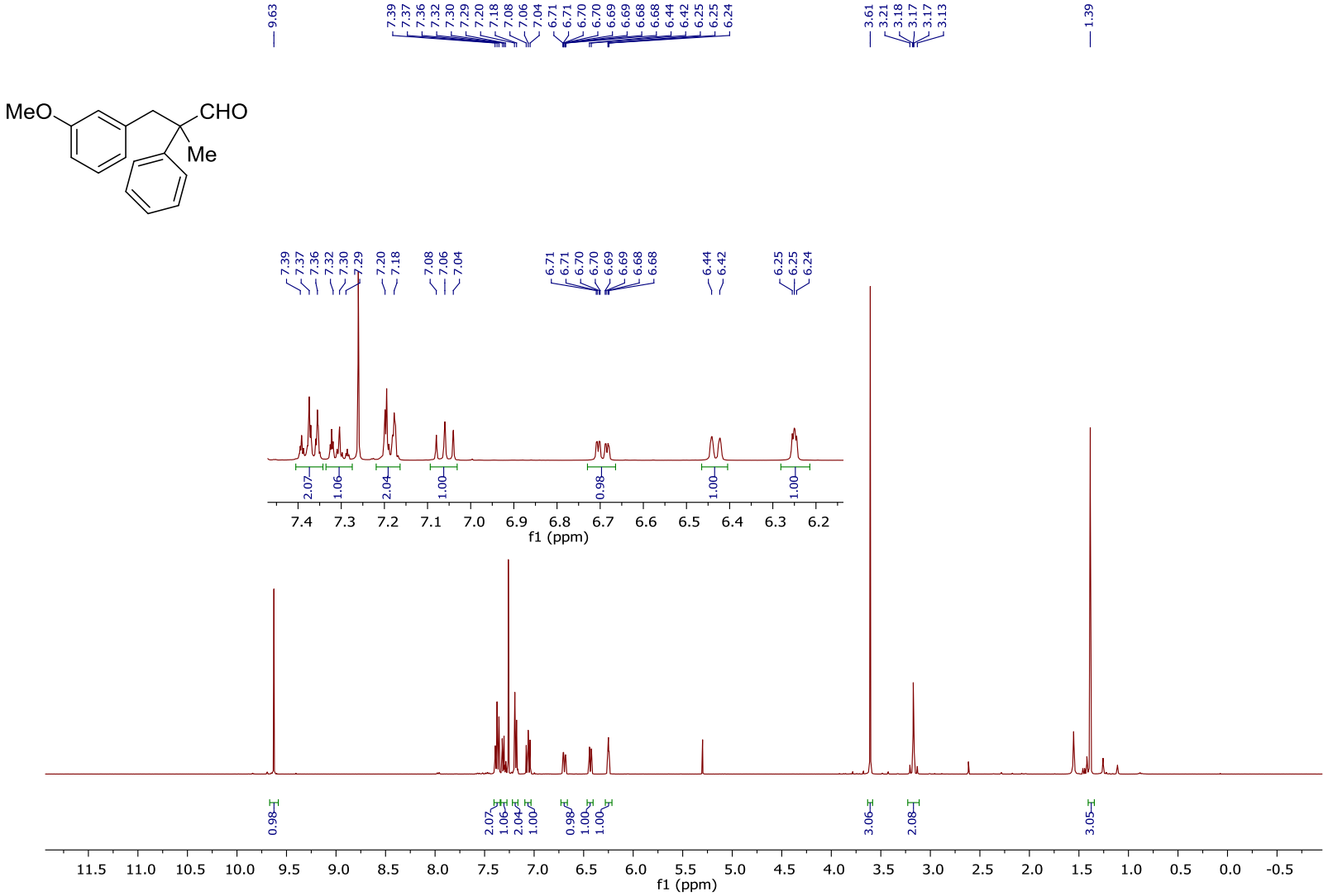
3-(4-methoxyphenyl)-2-methyl-2-phenylpropanal (7aa)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



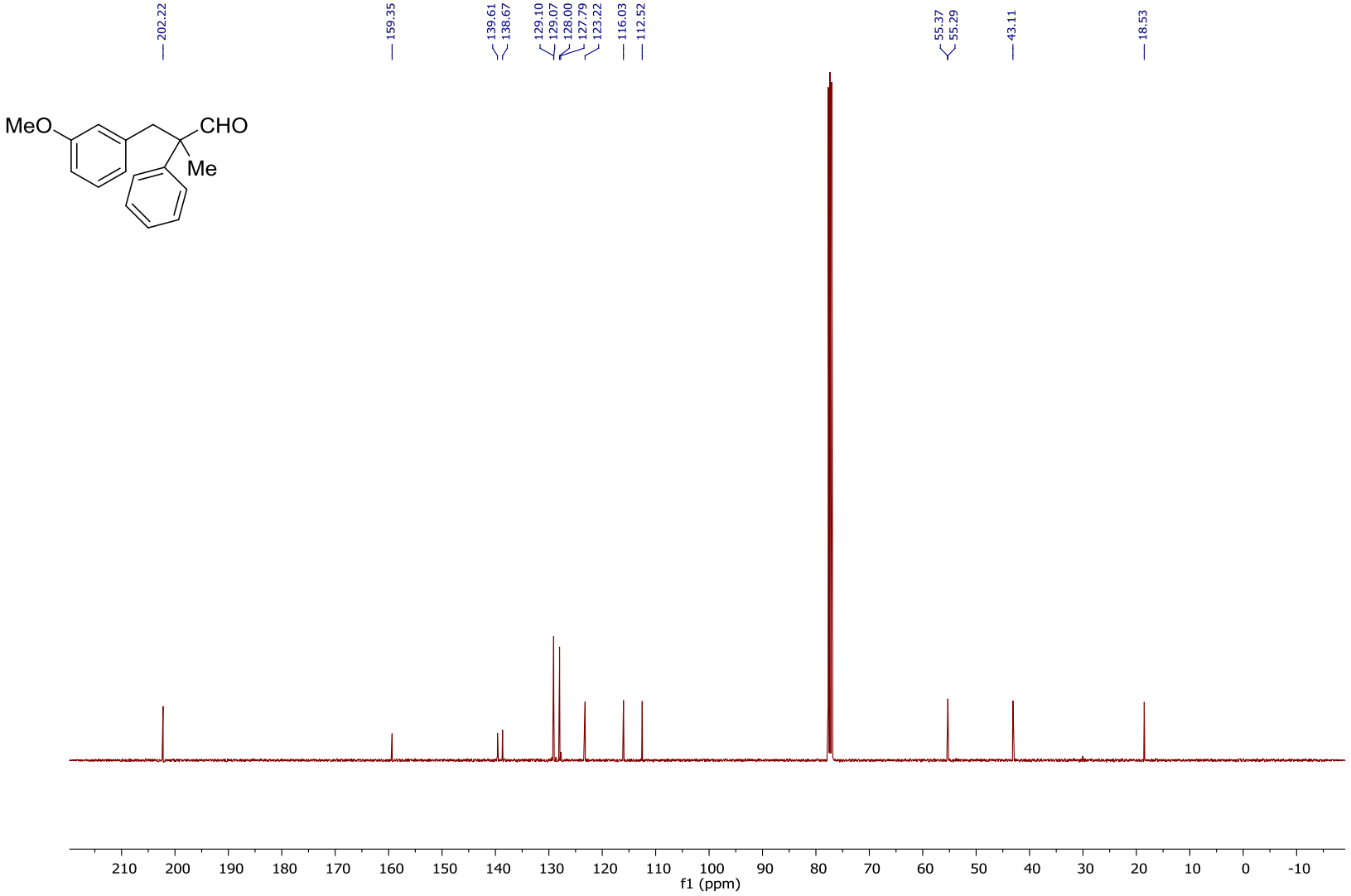
3-(3-methoxyphenyl)-2-methyl-2-phenylpropanal (7ab)

^{1}H NMR (400 MHz, $CDCl_3$):



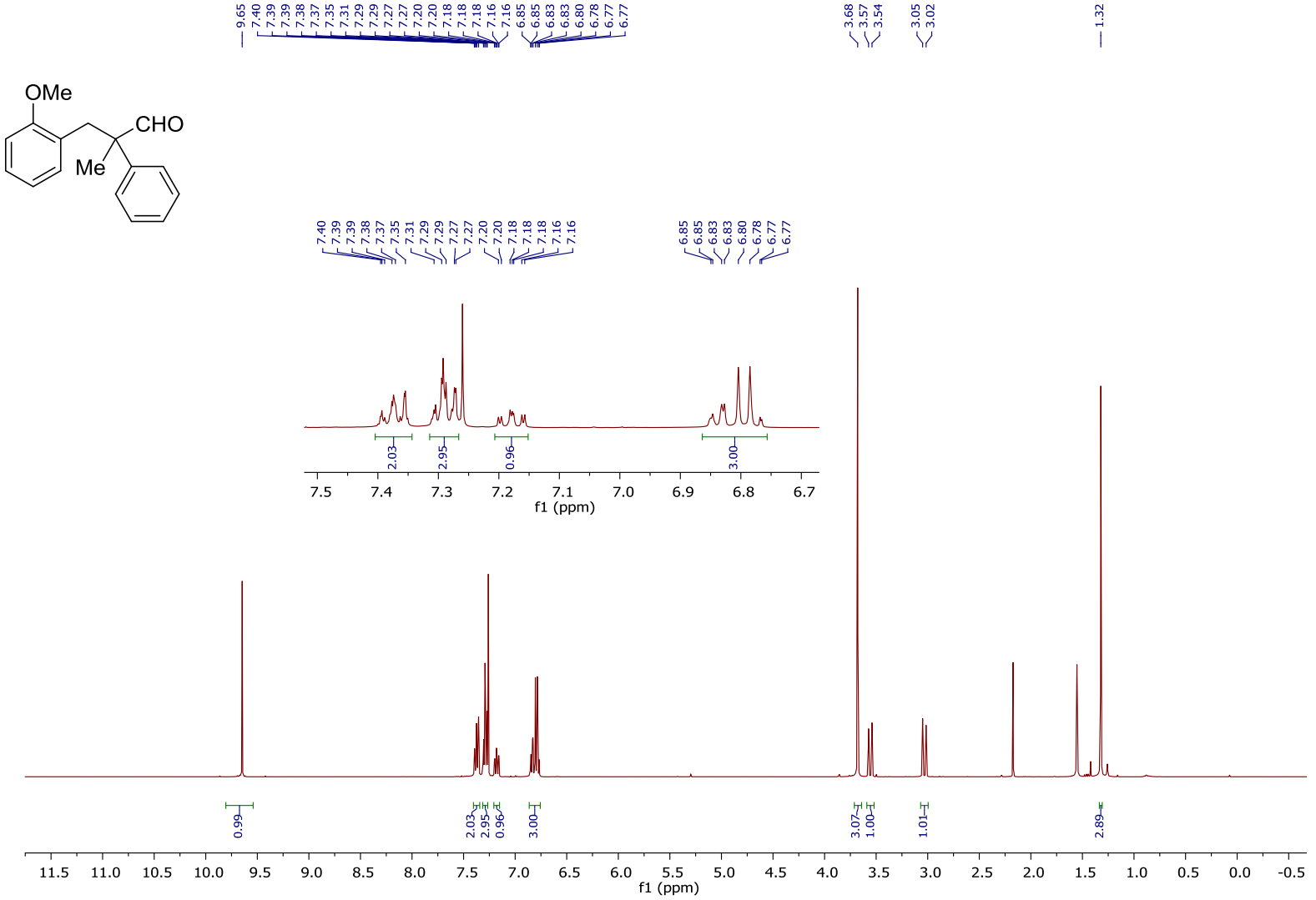
3-(3-methoxyphenyl)-2-methyl-2-phenylpropanal (7ab)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



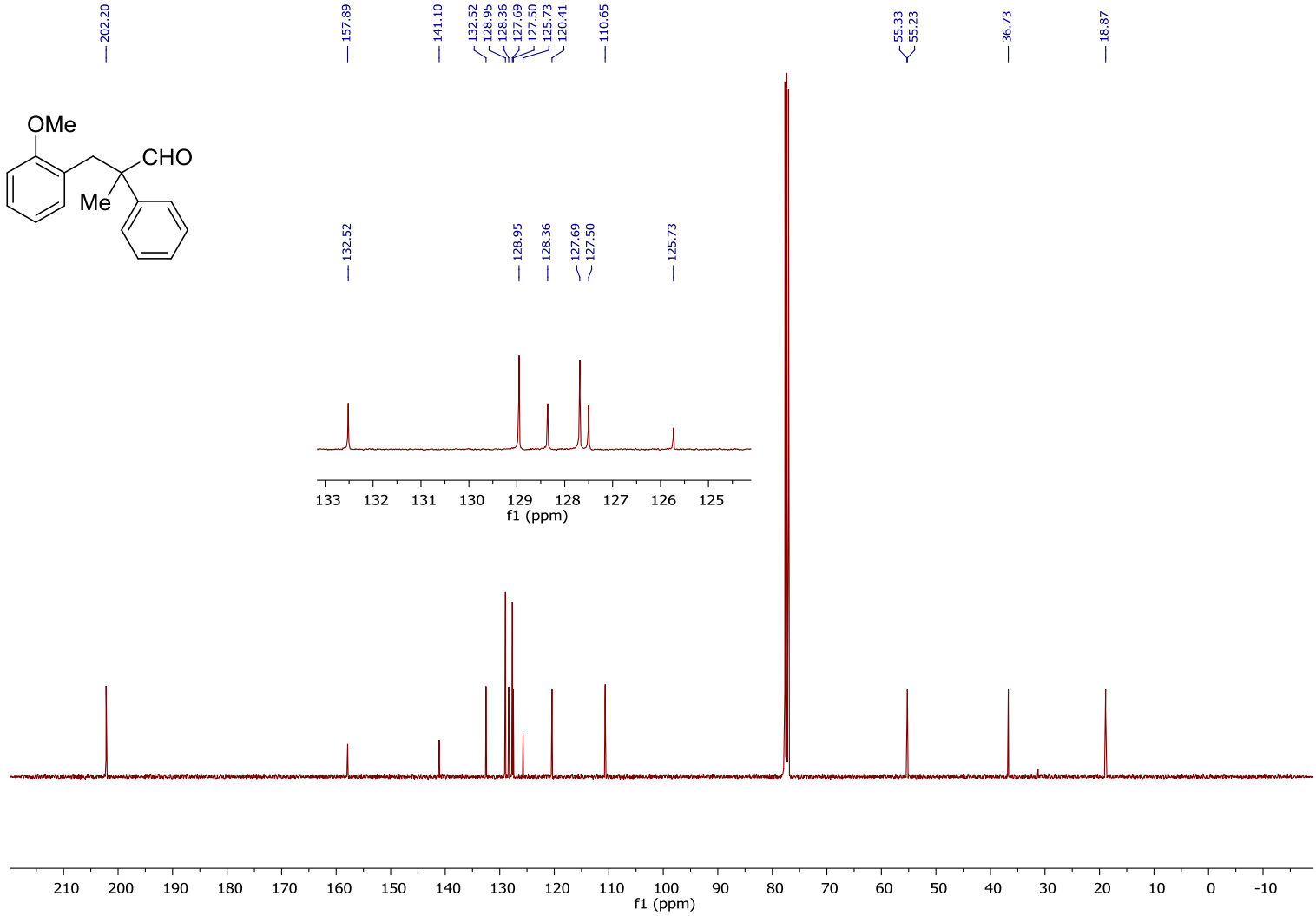
3-(2-methoxyphenyl)-2-methyl-2-phenylpropanal (7ac)

^{1}H NMR (400 MHz, $CDCl_3$):



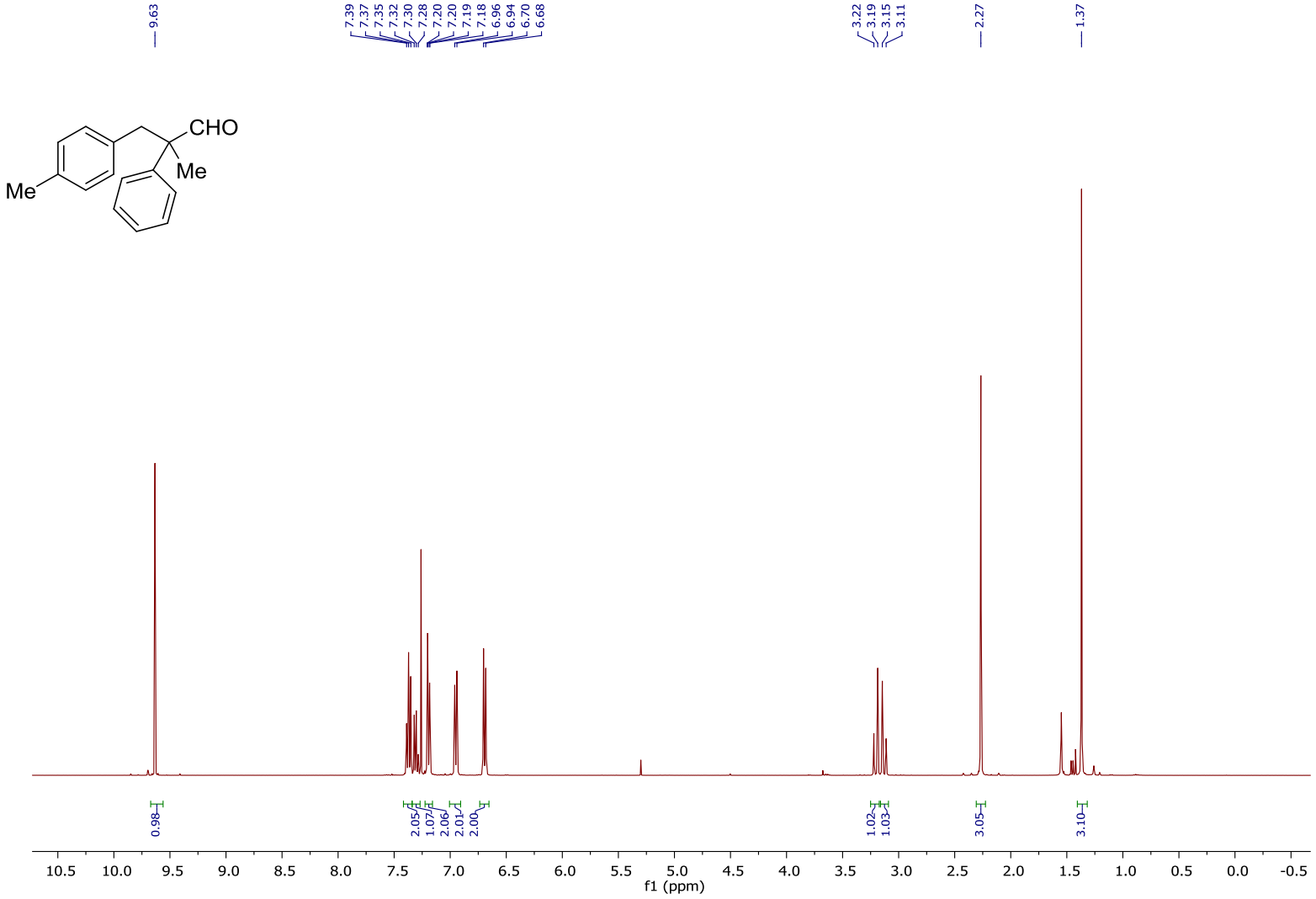
3-(2-methoxyphenyl)-2-methyl-2-phenylpropanal (7ac)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



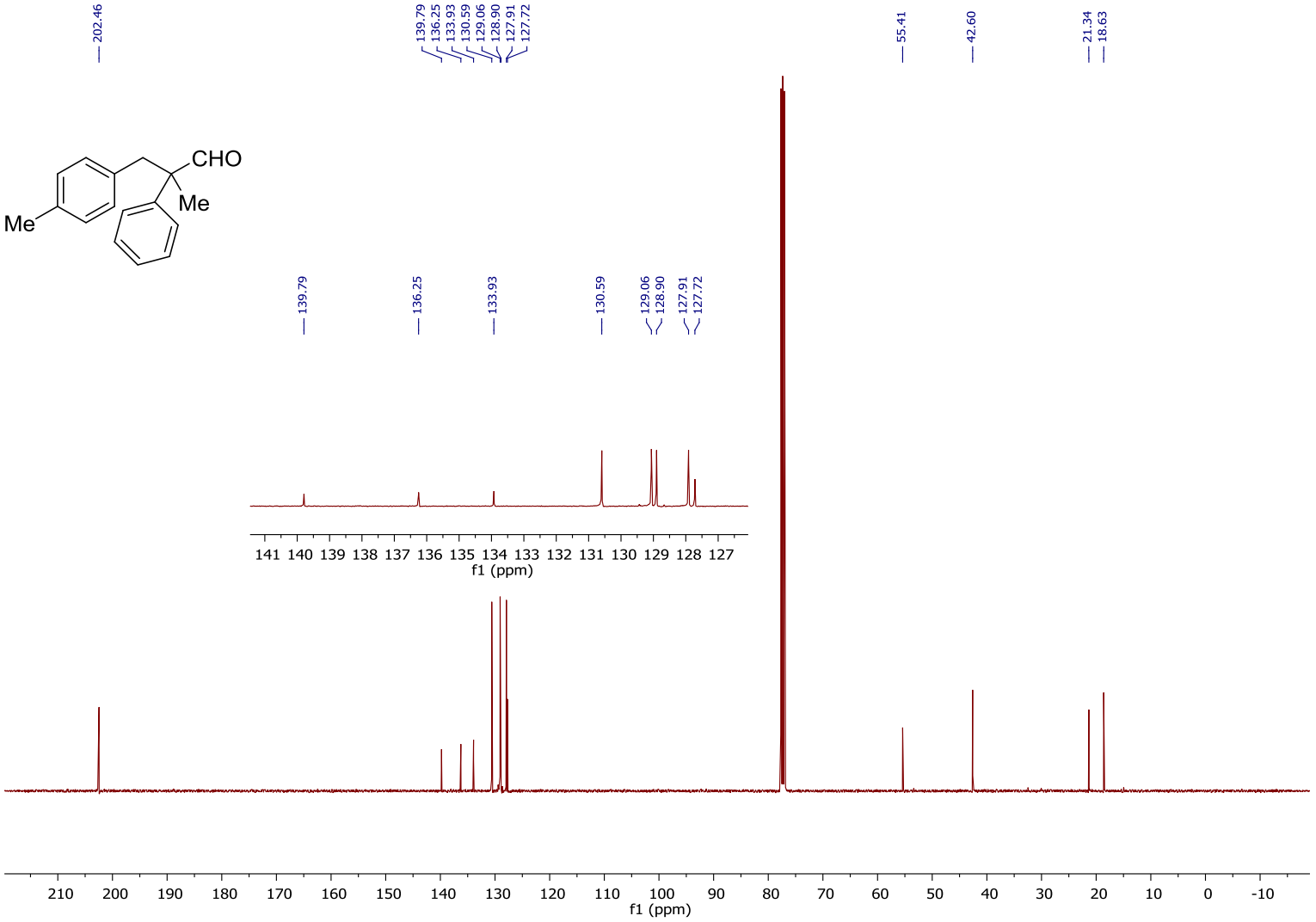
2-methyl-2-phenyl-3-(p-tolyl)propanal (7ad)

^{1}H NMR (400 MHz, $CDCl_3$):



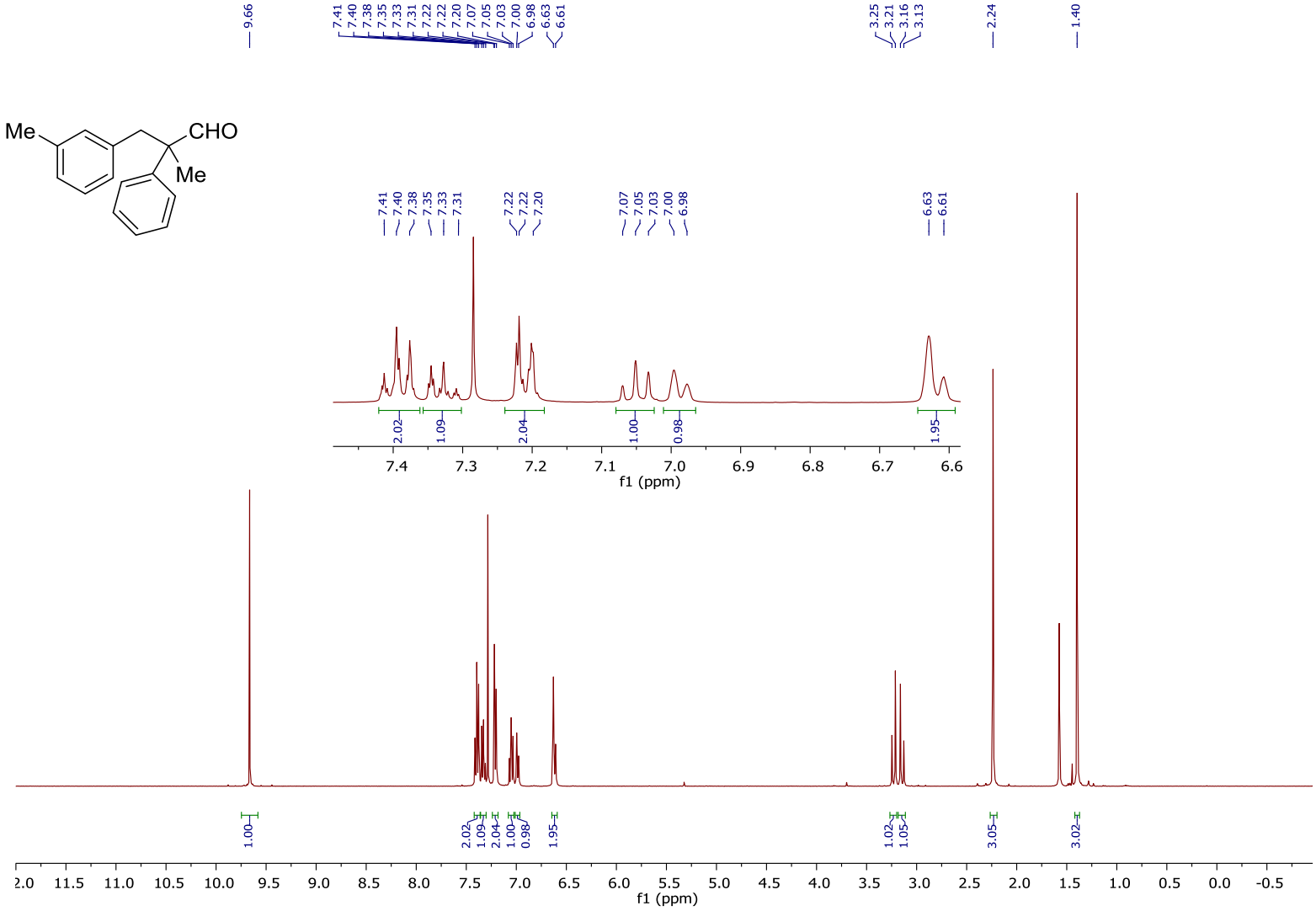
2-methyl-2-phenyl-3-(p-tolyl)propanal (7ad)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



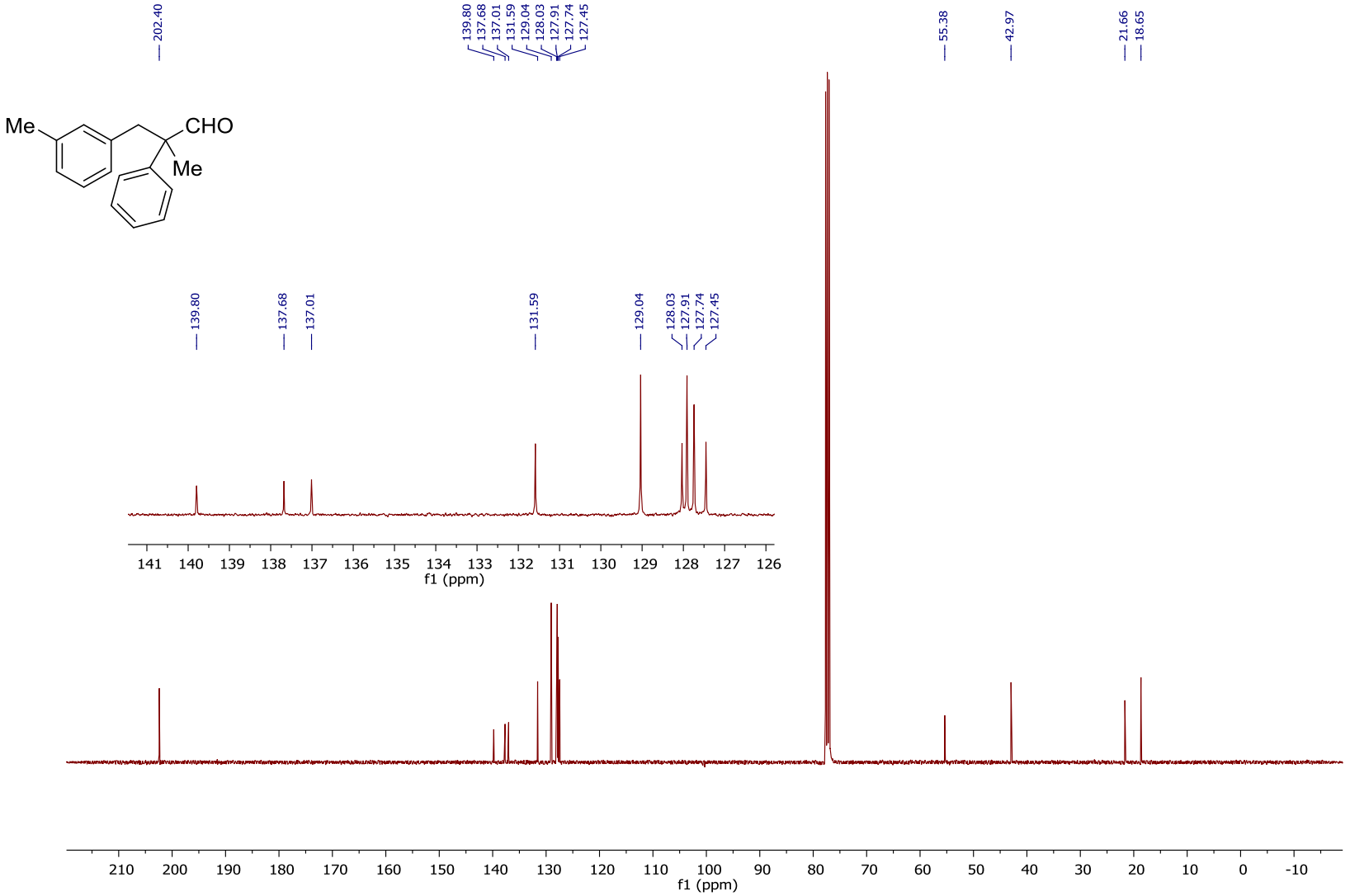
2-methyl-2-phenyl-3-(m-tolyl)propanal (7ae)

^{1}H NMR (400 MHz, $CDCl_3$):



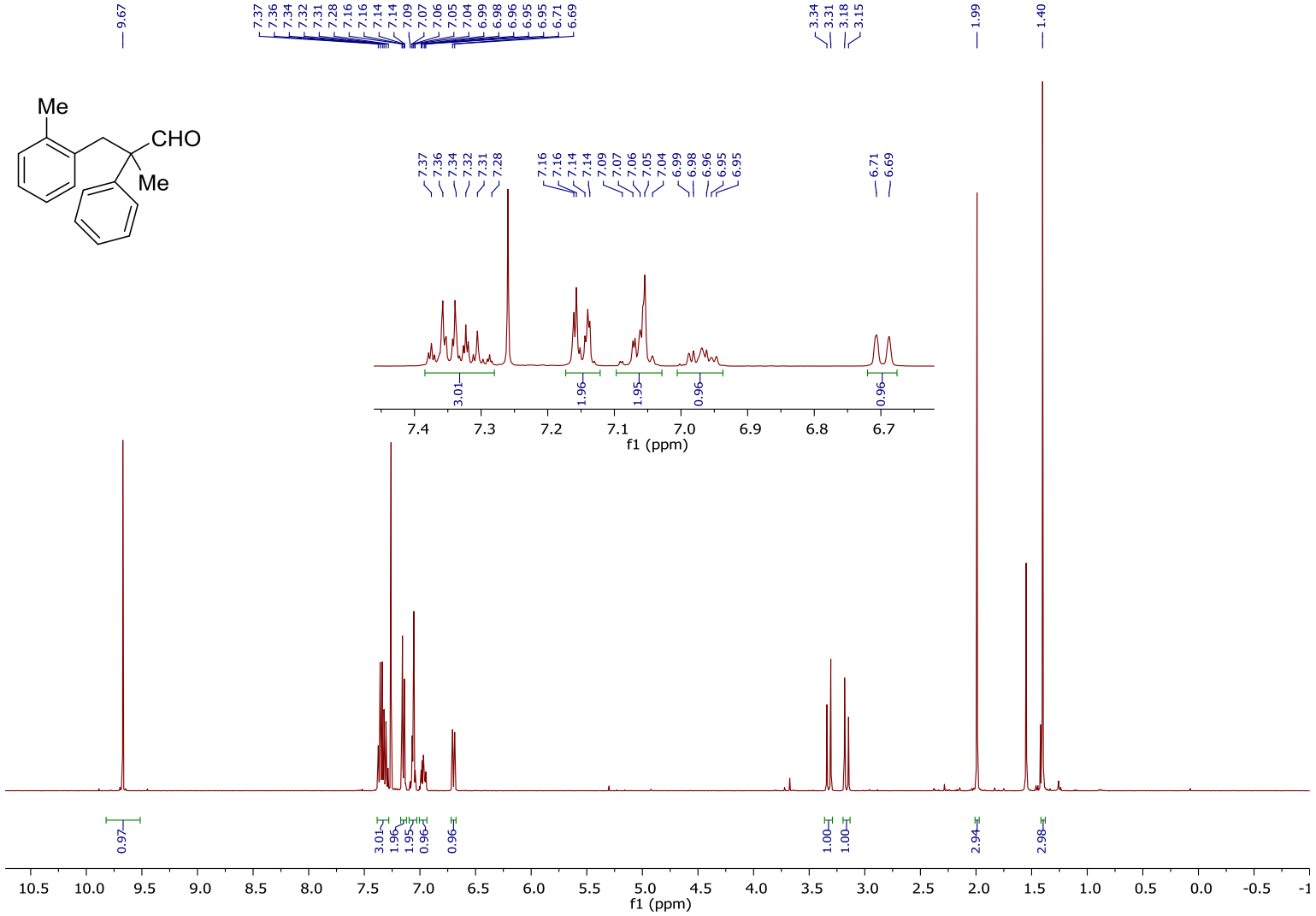
2-methyl-2-phenyl-3-(m-tolyl)propanal (7ae)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



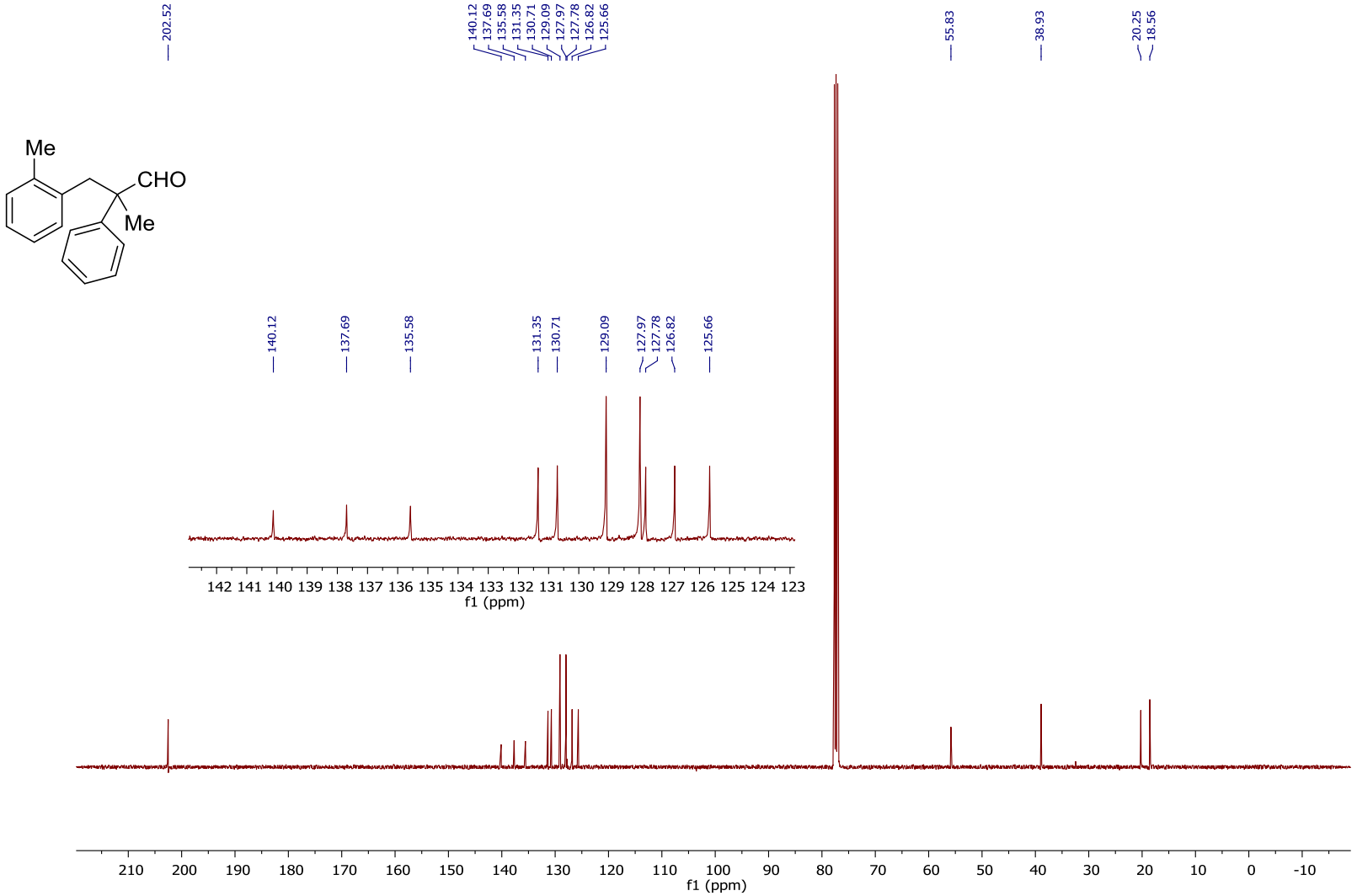
2-methyl-2-phenyl-3-(o-tolyl)propanal (7af)

^{1}H NMR (400 MHz, $CDCl_3$):



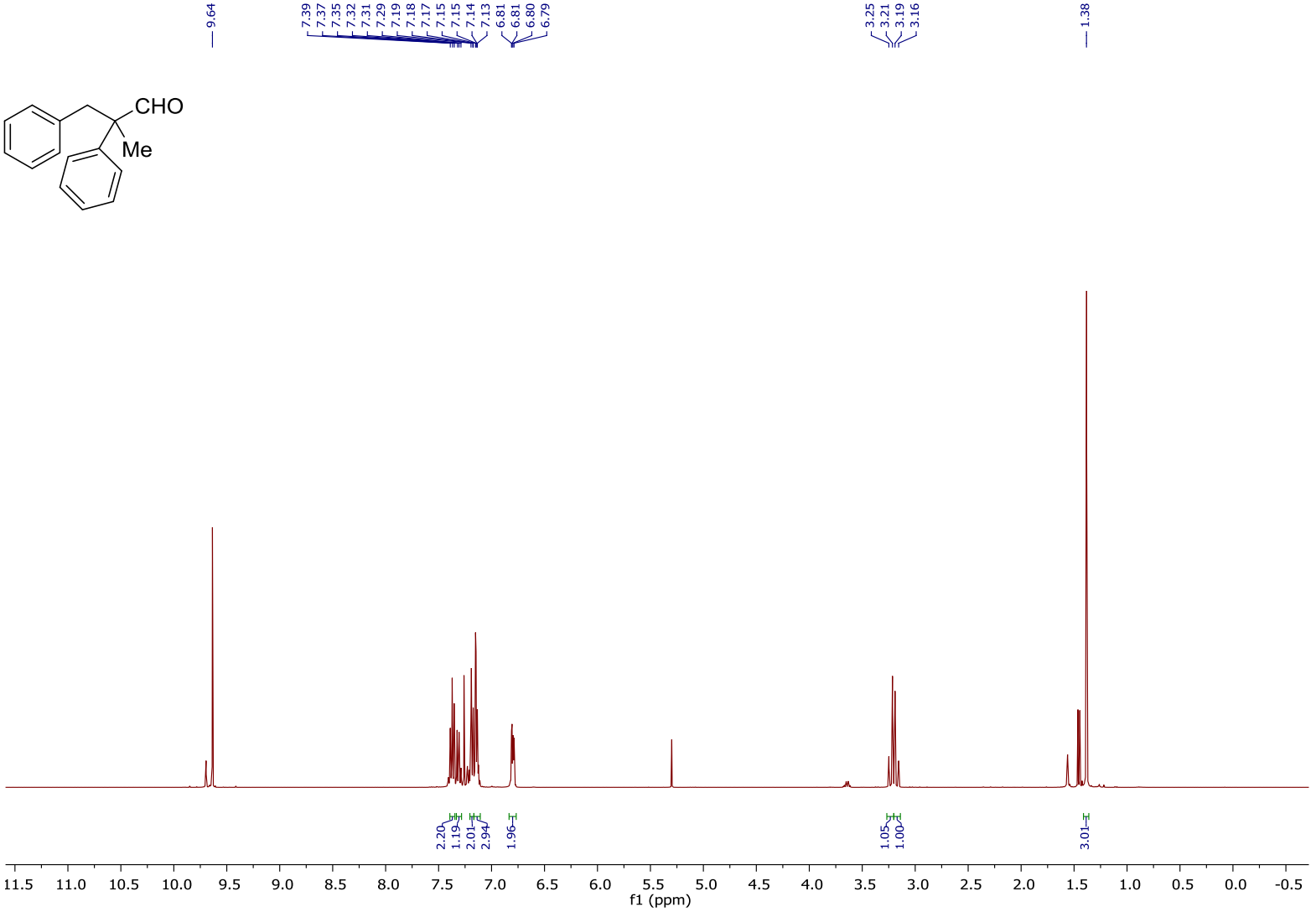
2-methyl-2-phenyl-3-(o-tolyl)propanal (7af)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



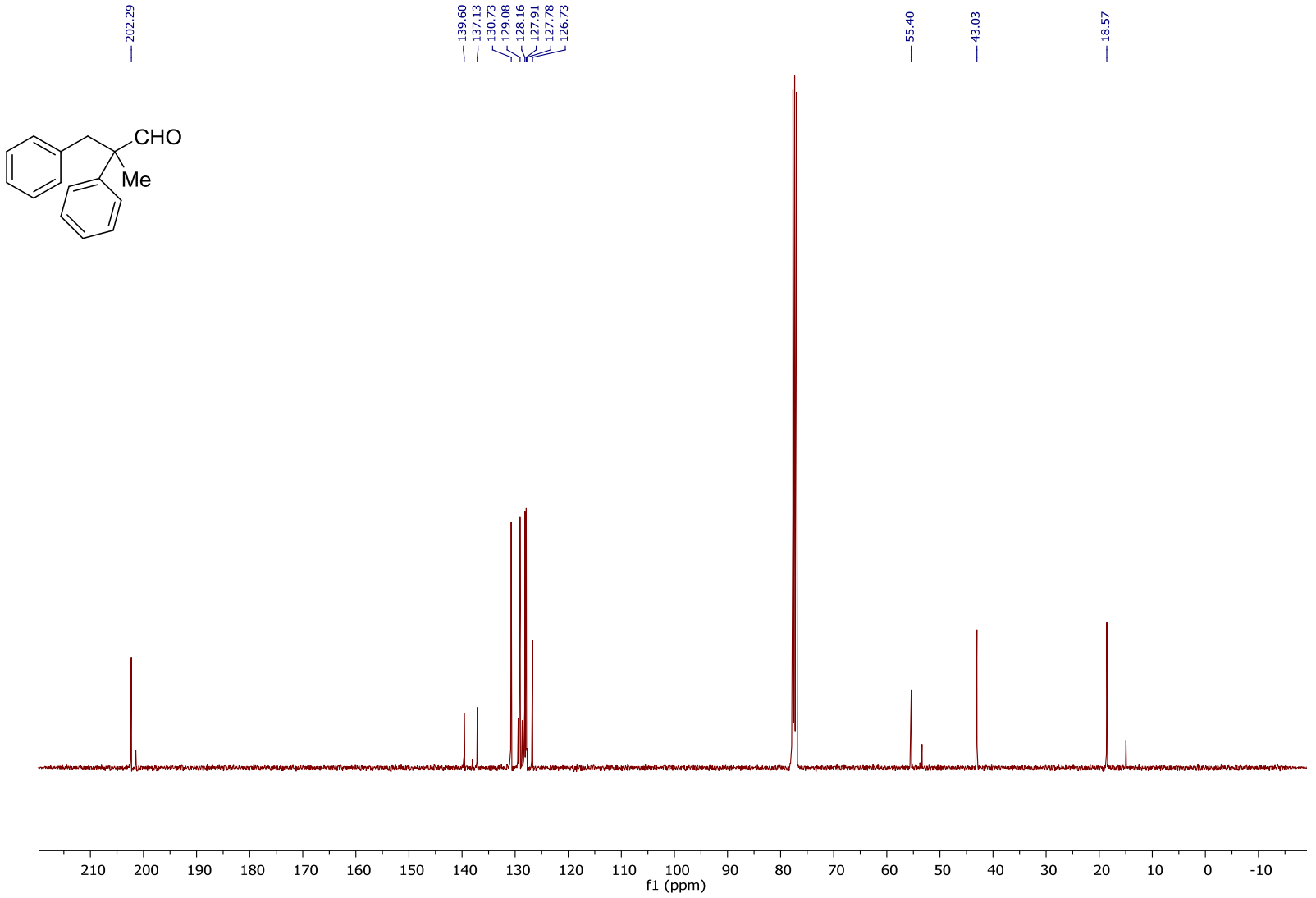
2-methyl-2,3-diphenylpropanal (7ag)

^{1}H NMR (400 MHz, $CDCl_3$):



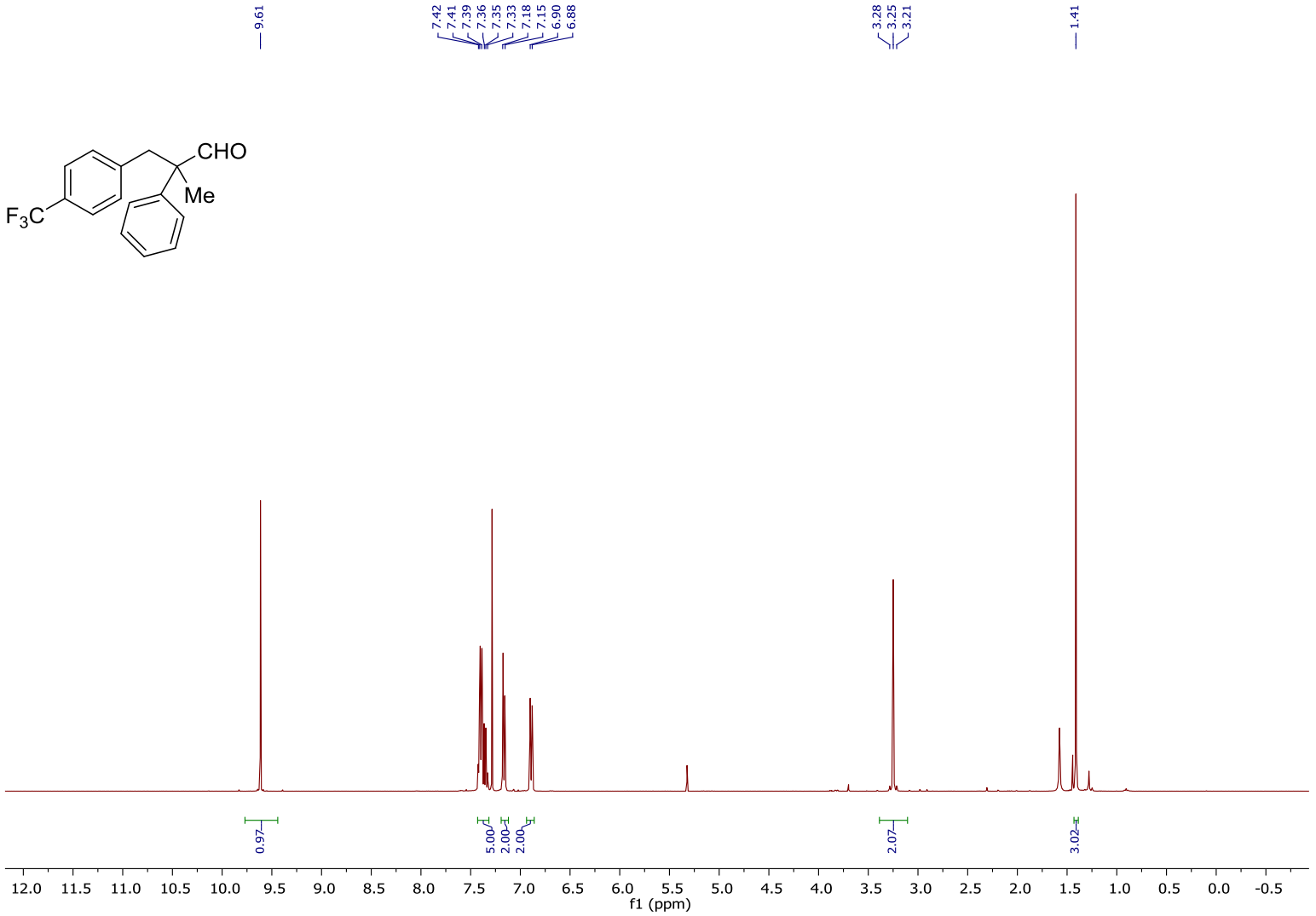
2-methyl-2,3-diphenylpropanal (7ag)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



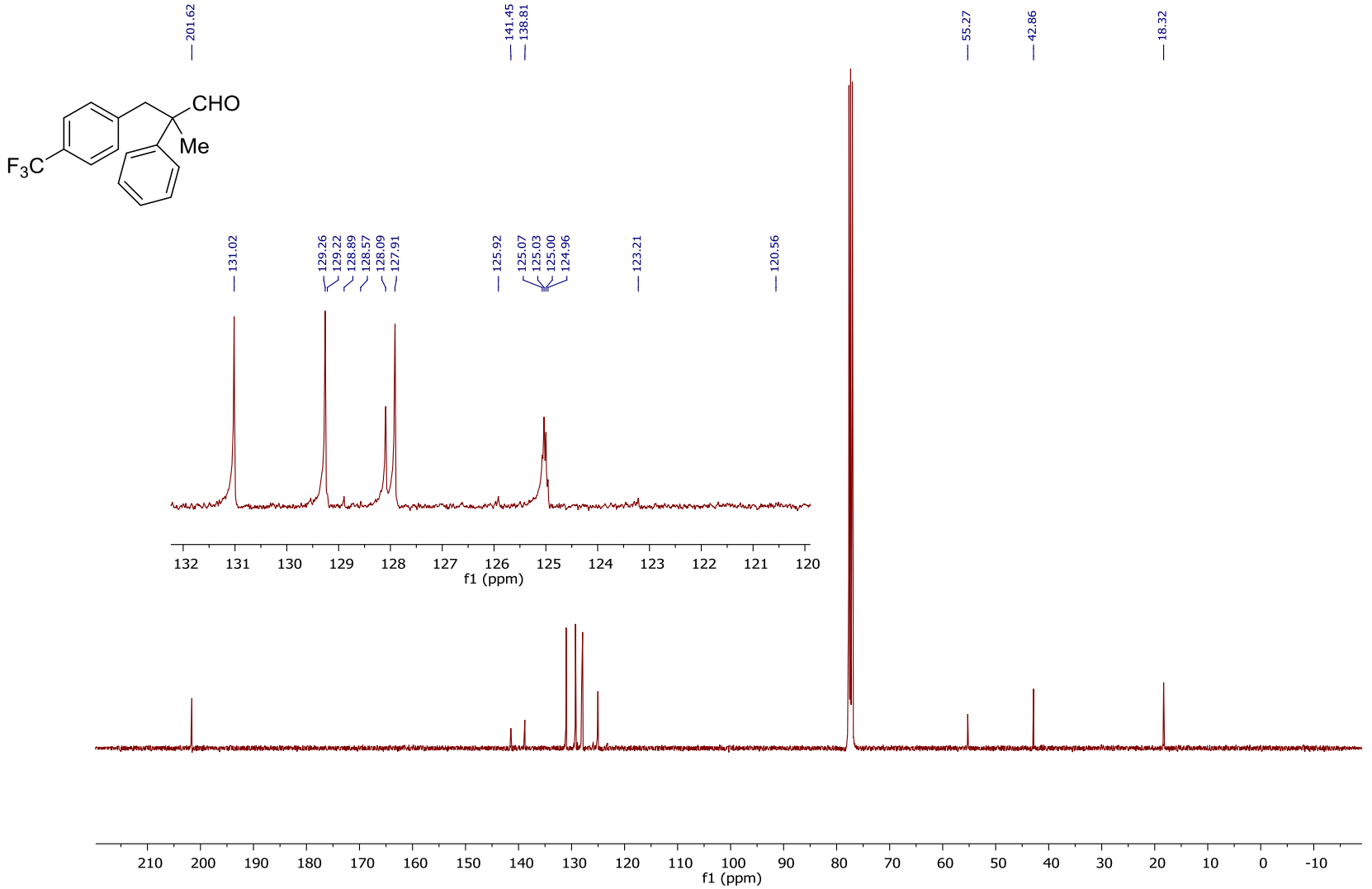
2-methyl-2-phenyl-3-(4-(trifluoromethyl)phenyl)propanal (7ah)

^{1}H NMR (400 MHz, $CDCl_3$):



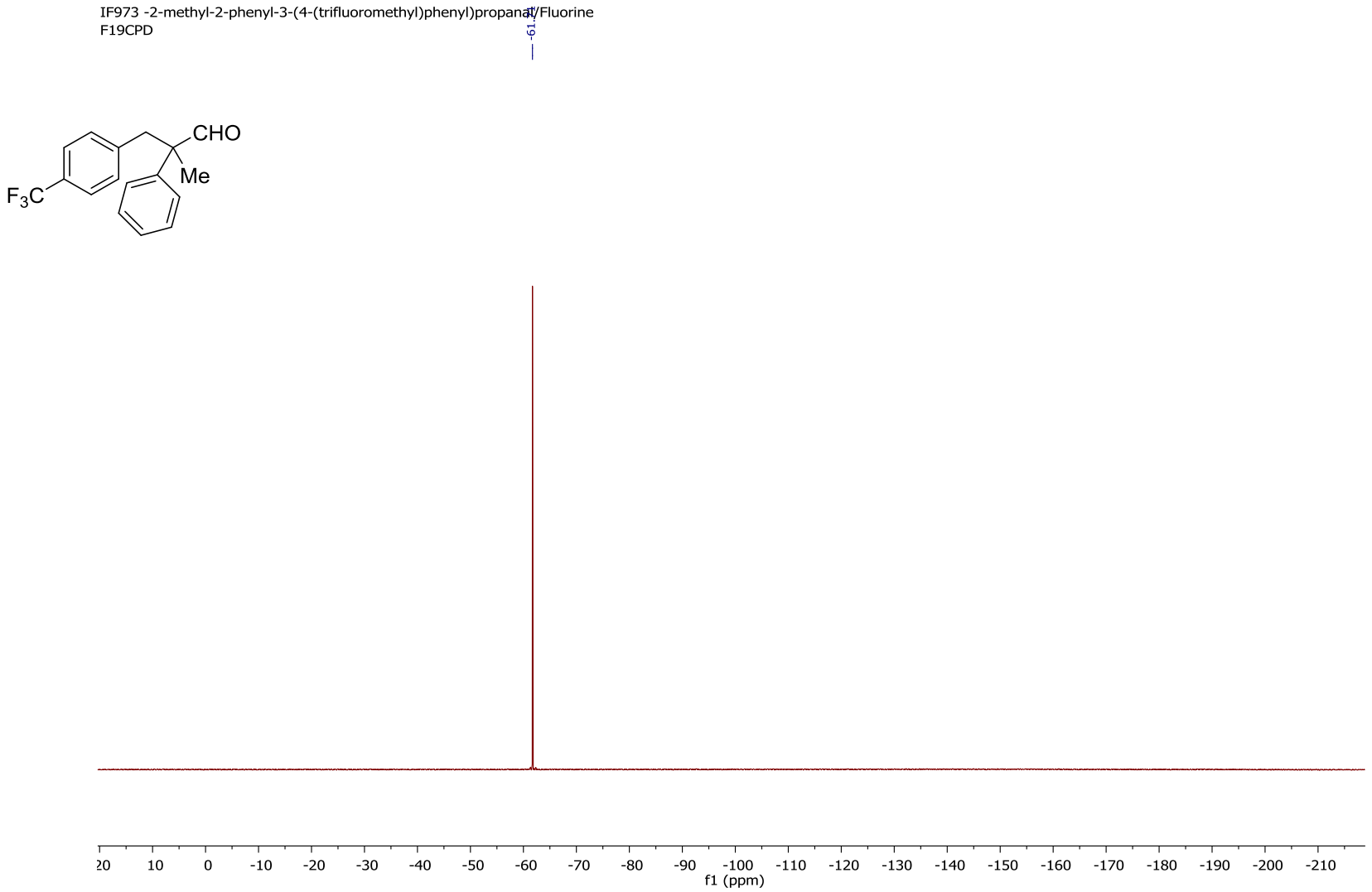
2-methyl-2-phenyl-3-(4-(trifluoromethyl)phenyl)propanal (7ah)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



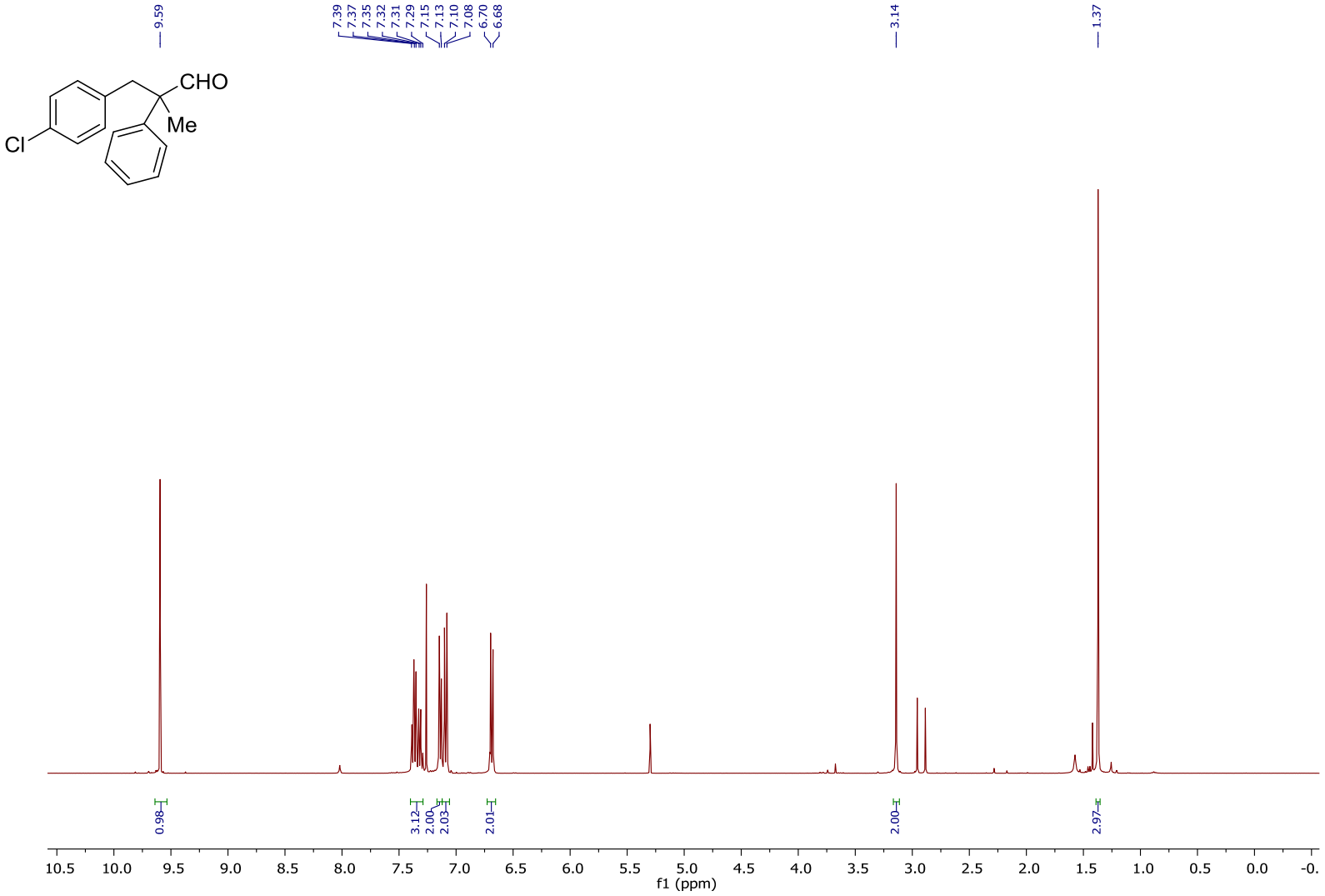
2-methyl-2-phenyl-3-(4-(trifluoromethyl)phenyl)propanal (7ah)

$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$):



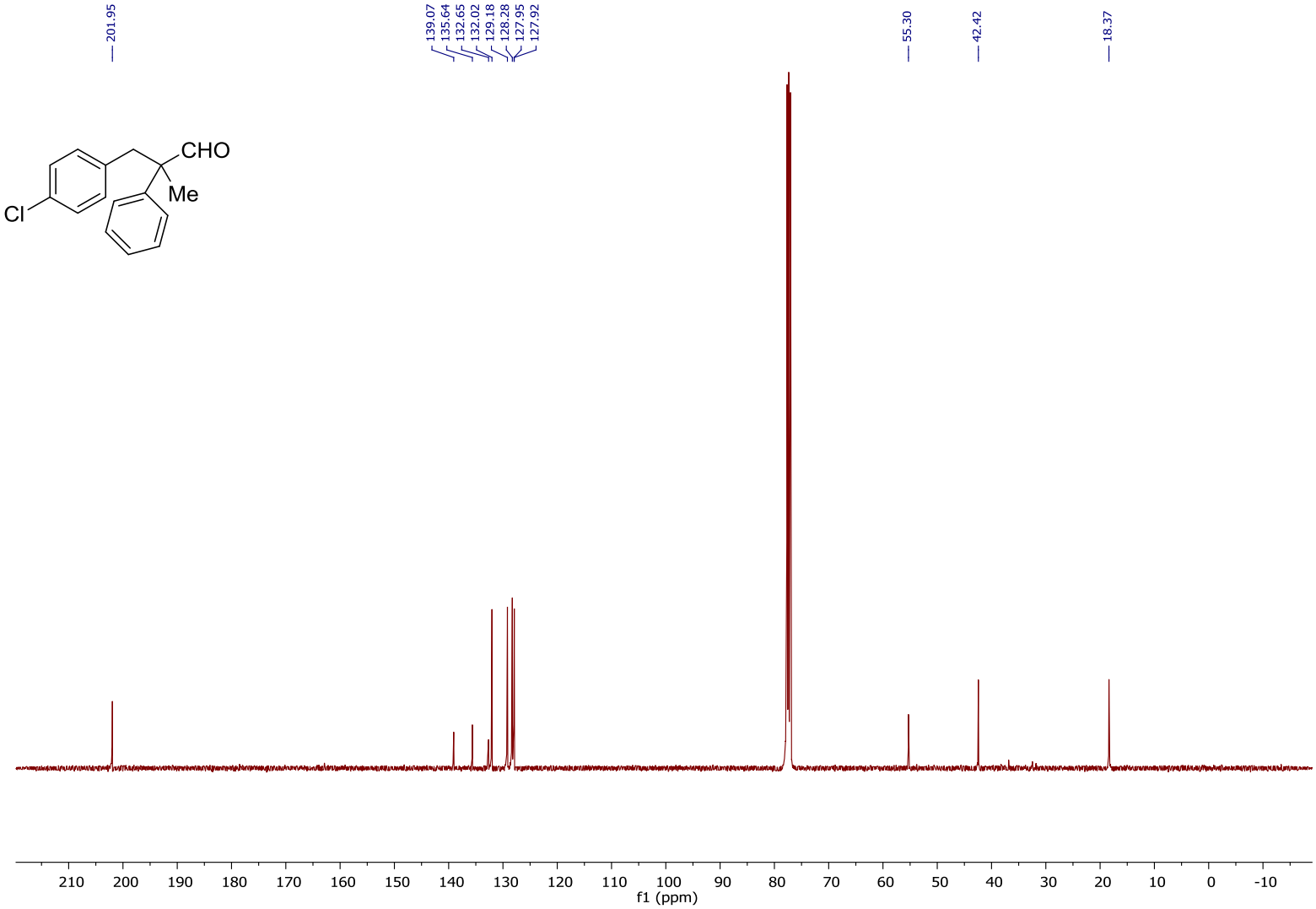
3-(4-chlorophenyl)-2-methyl-2-phenylpropanal (7ai)

^{1}H NMR (400 MHz, $CDCl_3$):



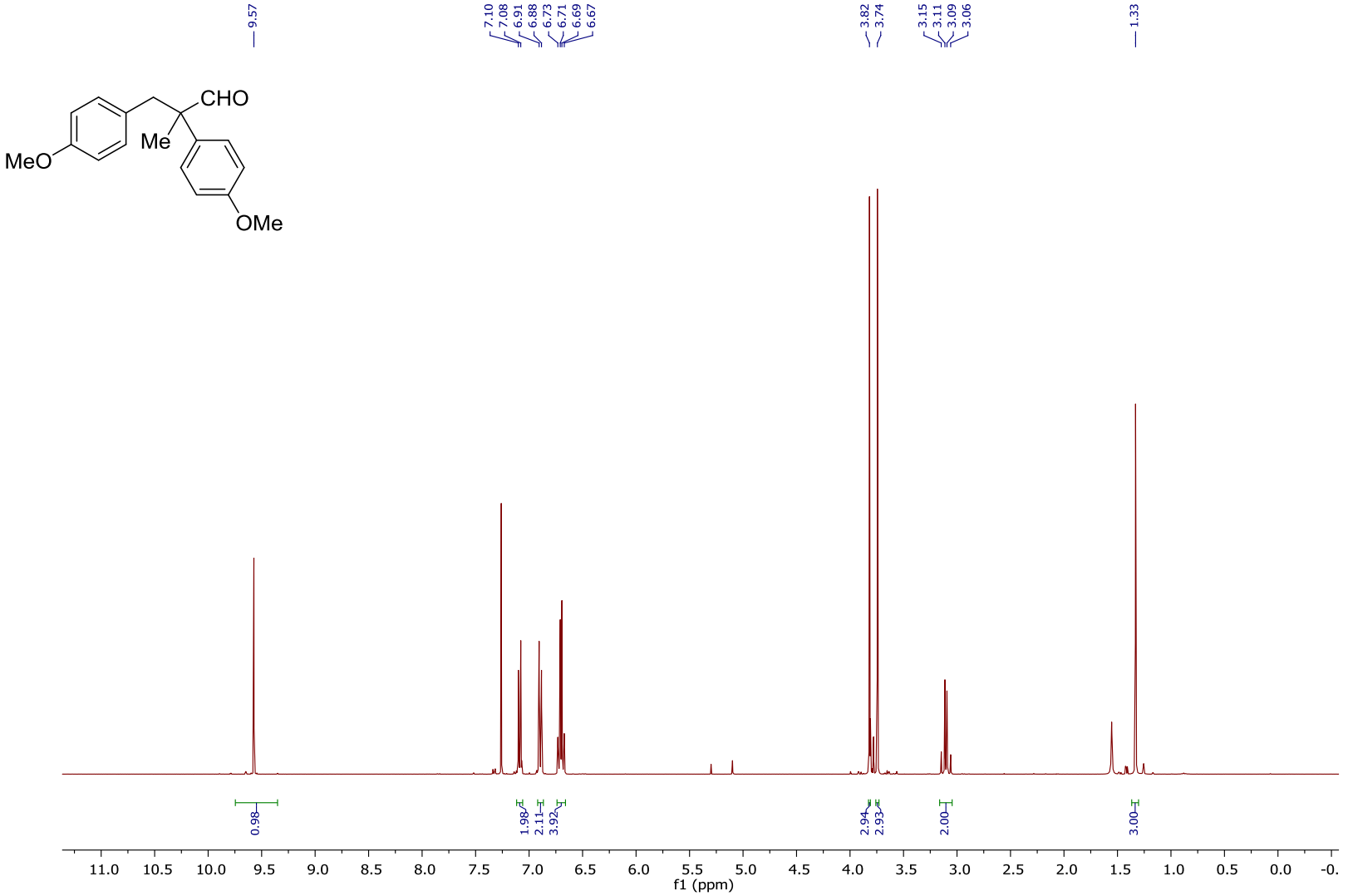
3-(4-chlorophenyl)-2-methyl-2-phenylpropanal (7ai)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



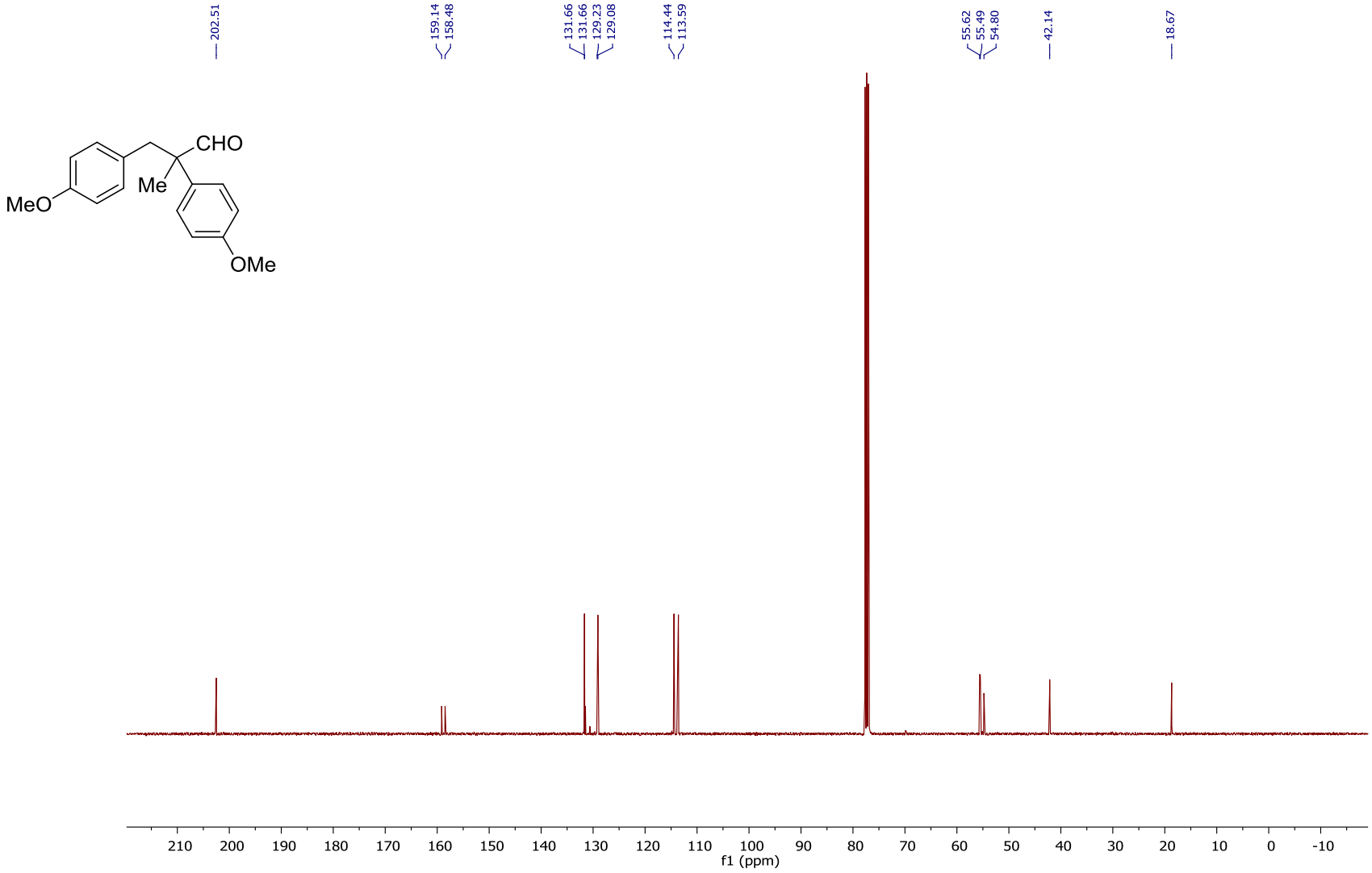
2,3-bis(4-methoxyphenyl)-2-methylpropanal (7ba)

^{1}H NMR (400 MHz, $CDCl_3$):



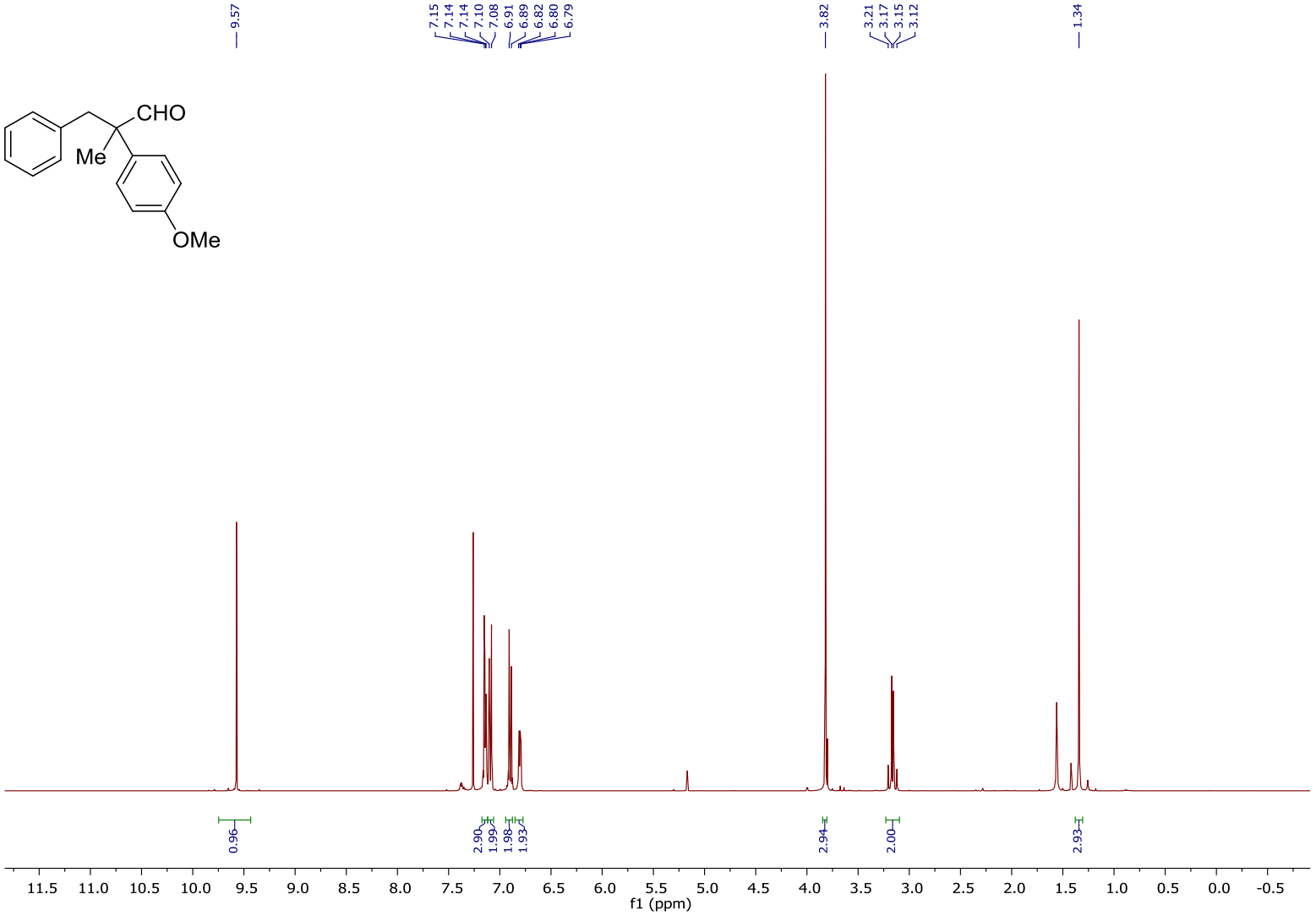
2,3-bis(4-methoxyphenyl)-2-methylpropanal (7ba)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



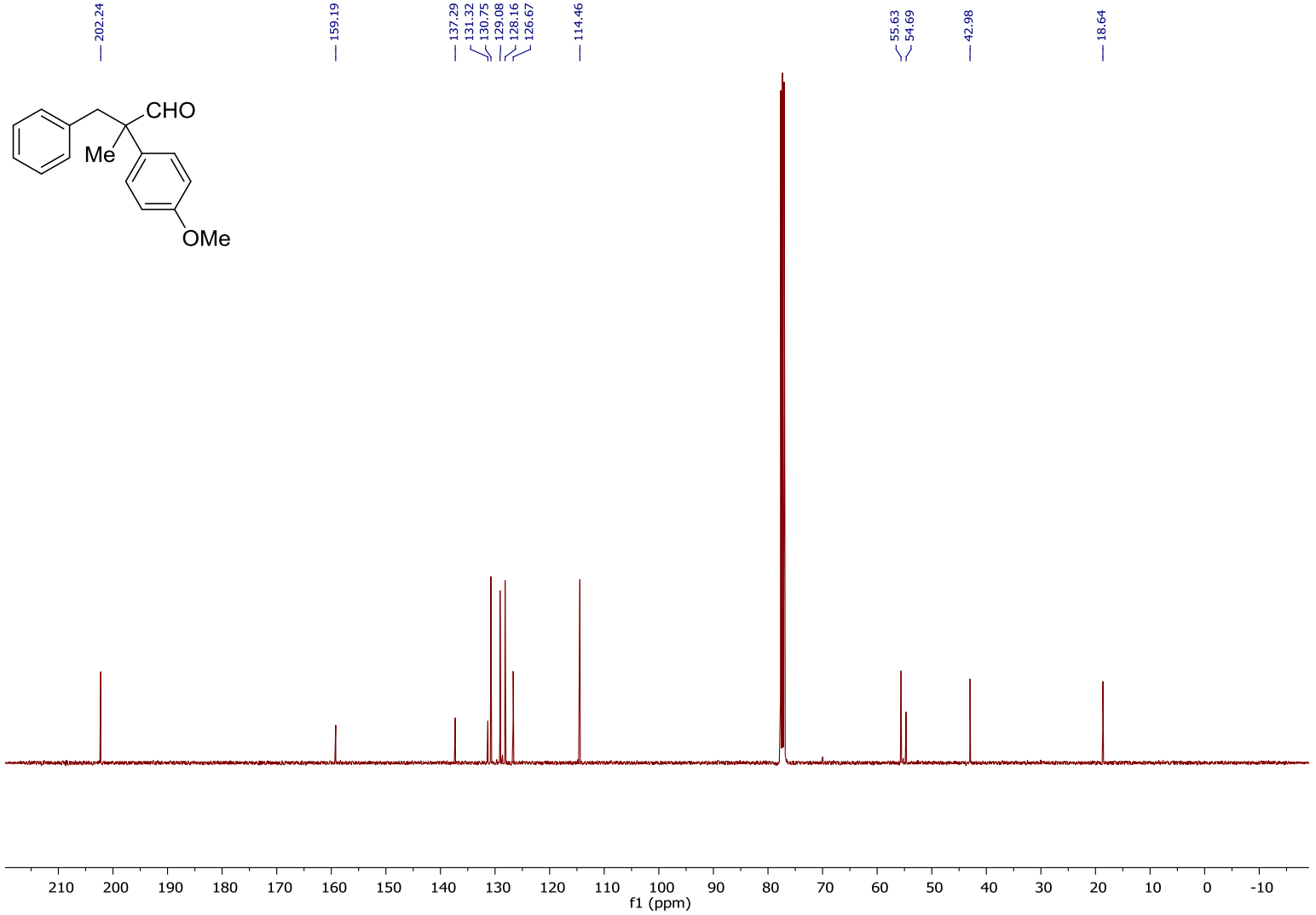
2-(4-methoxyphenyl)-2-methyl-3-phenylpropanal (7bg)

^{1}H NMR (400 MHz, $CDCl_3$):



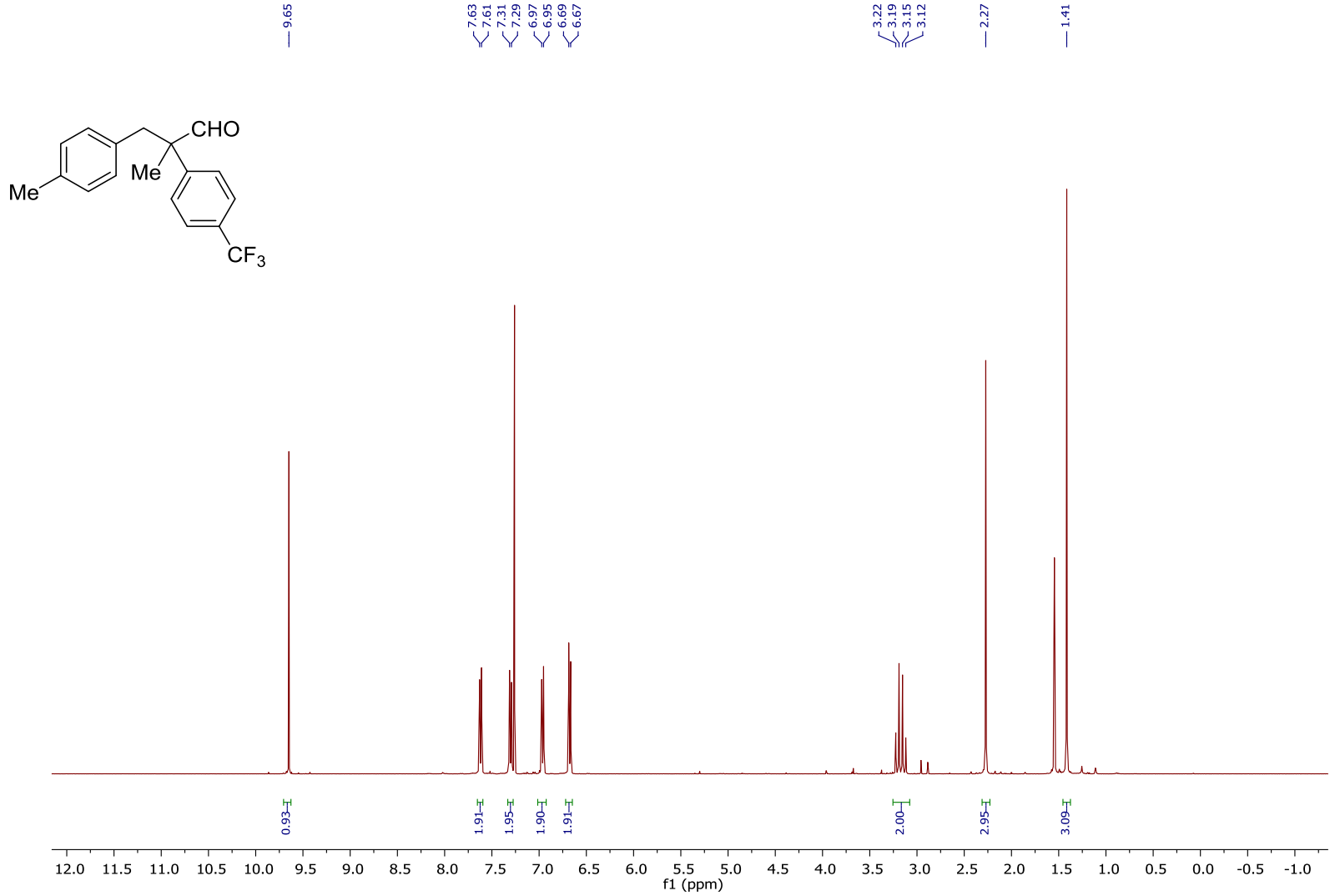
2-(4-methoxyphenyl)-2-methyl-3-phenylpropanal (7bg)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



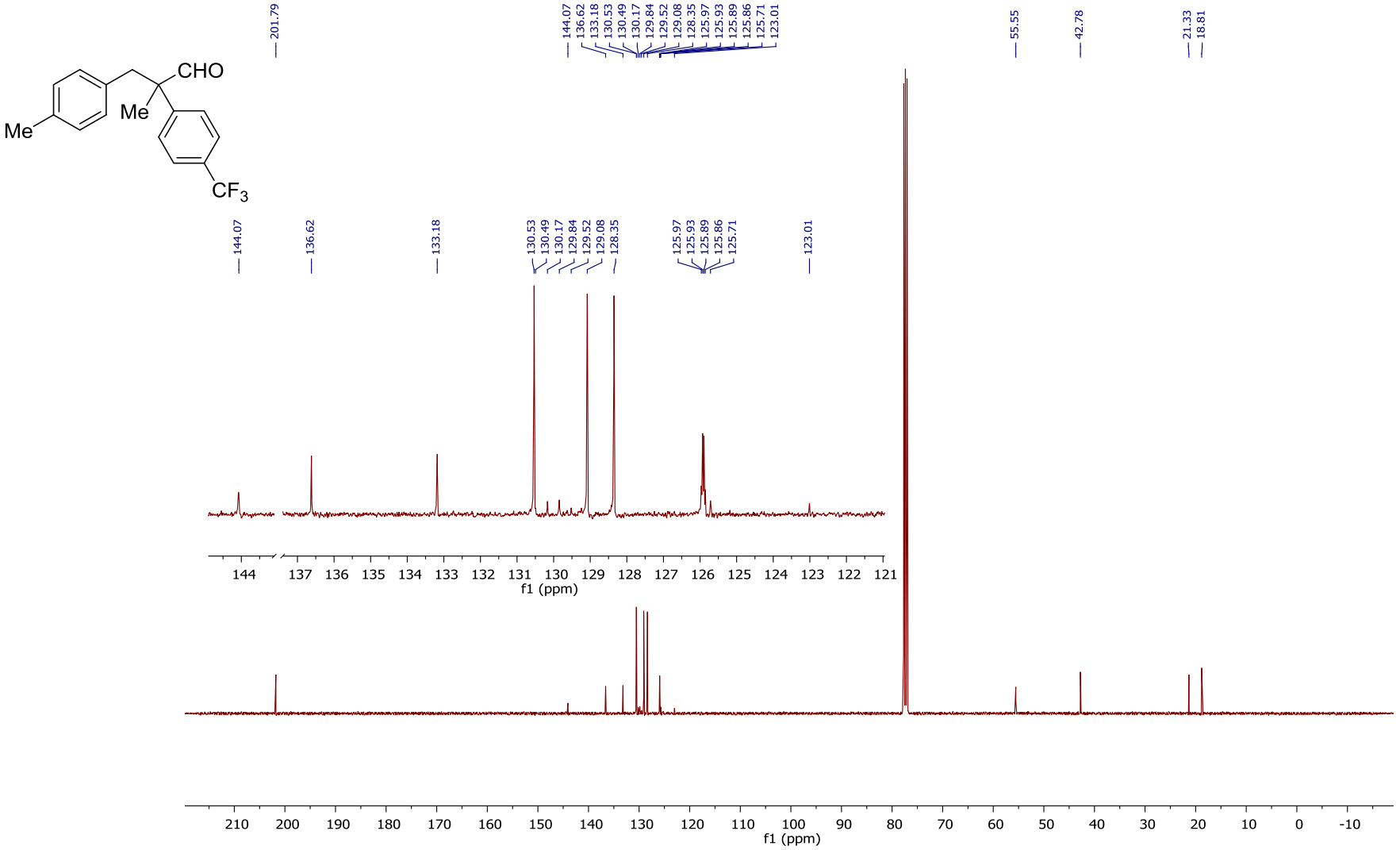
2-methyl-3-(p-tolyl)-2-(4-(trifluoromethyl)phenyl)propanal (7cd)

^{1}H NMR (400 MHz, $CDCl_3$):



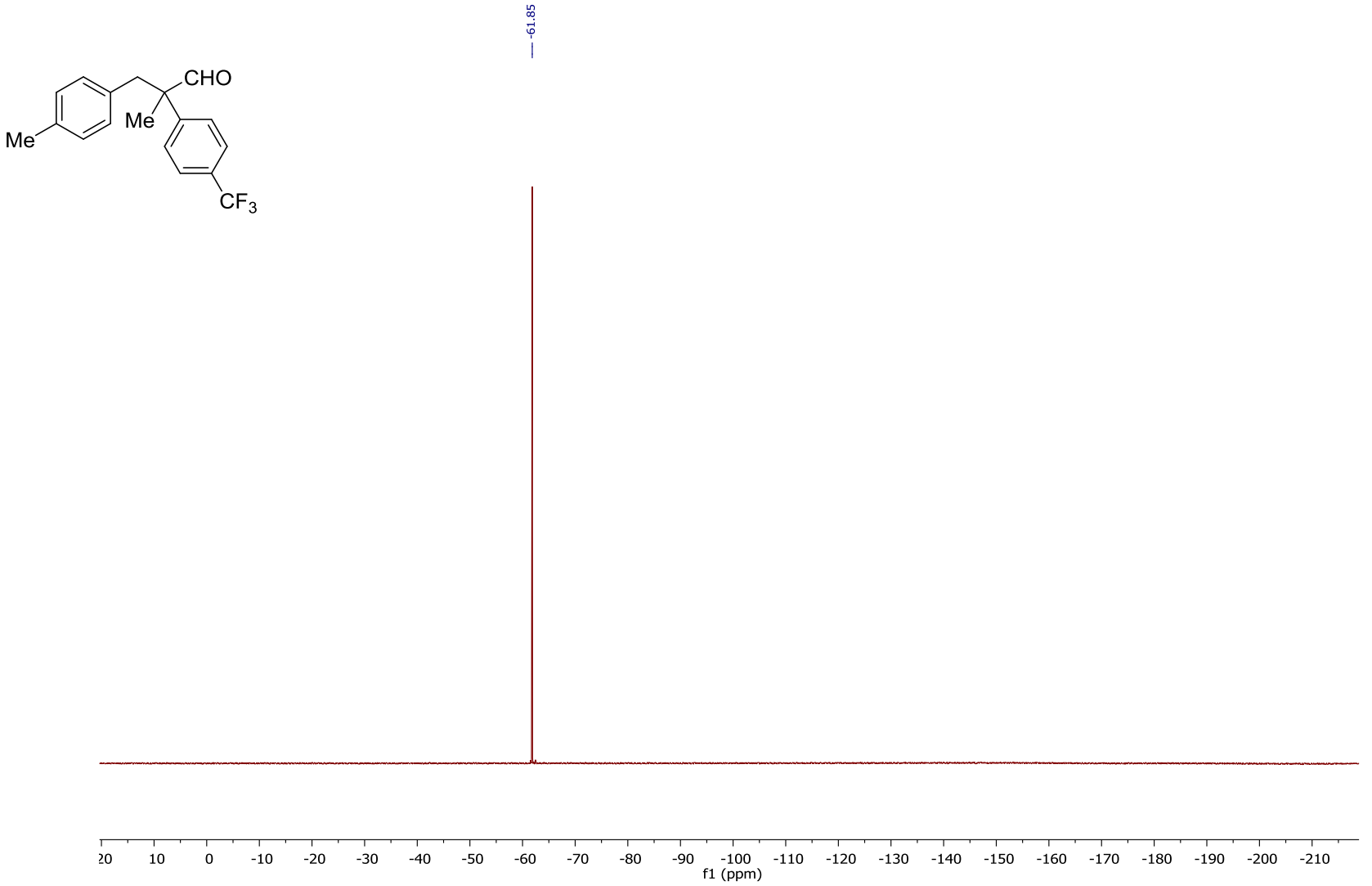
2-methyl-3-(p-tolyl)-2-(4-(trifluoromethyl)phenyl)propanal (7cd)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



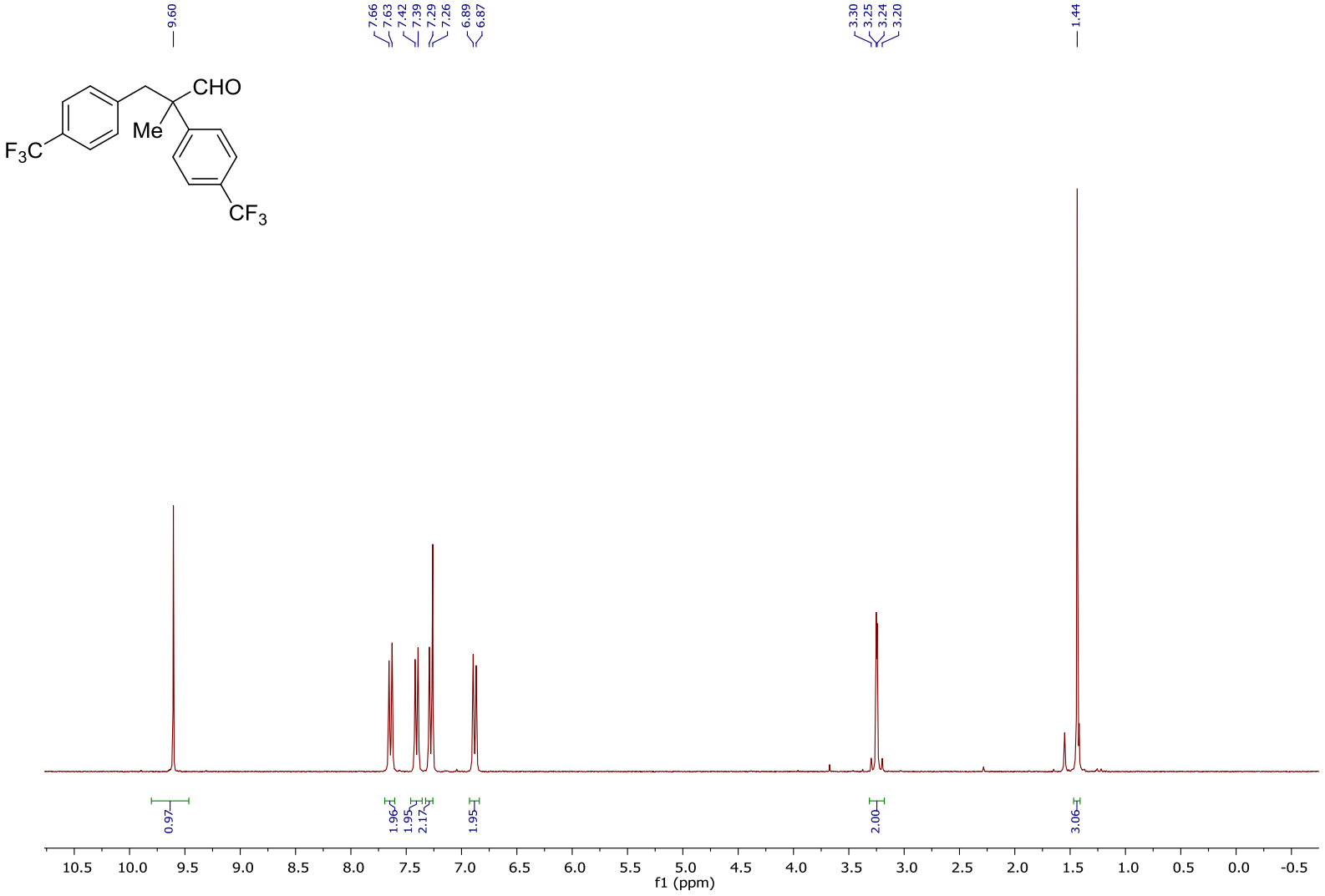
2-methyl-3-(p-tolyl)-2-(4-(trifluoromethyl)phenyl)propanal (7cd)

$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$):



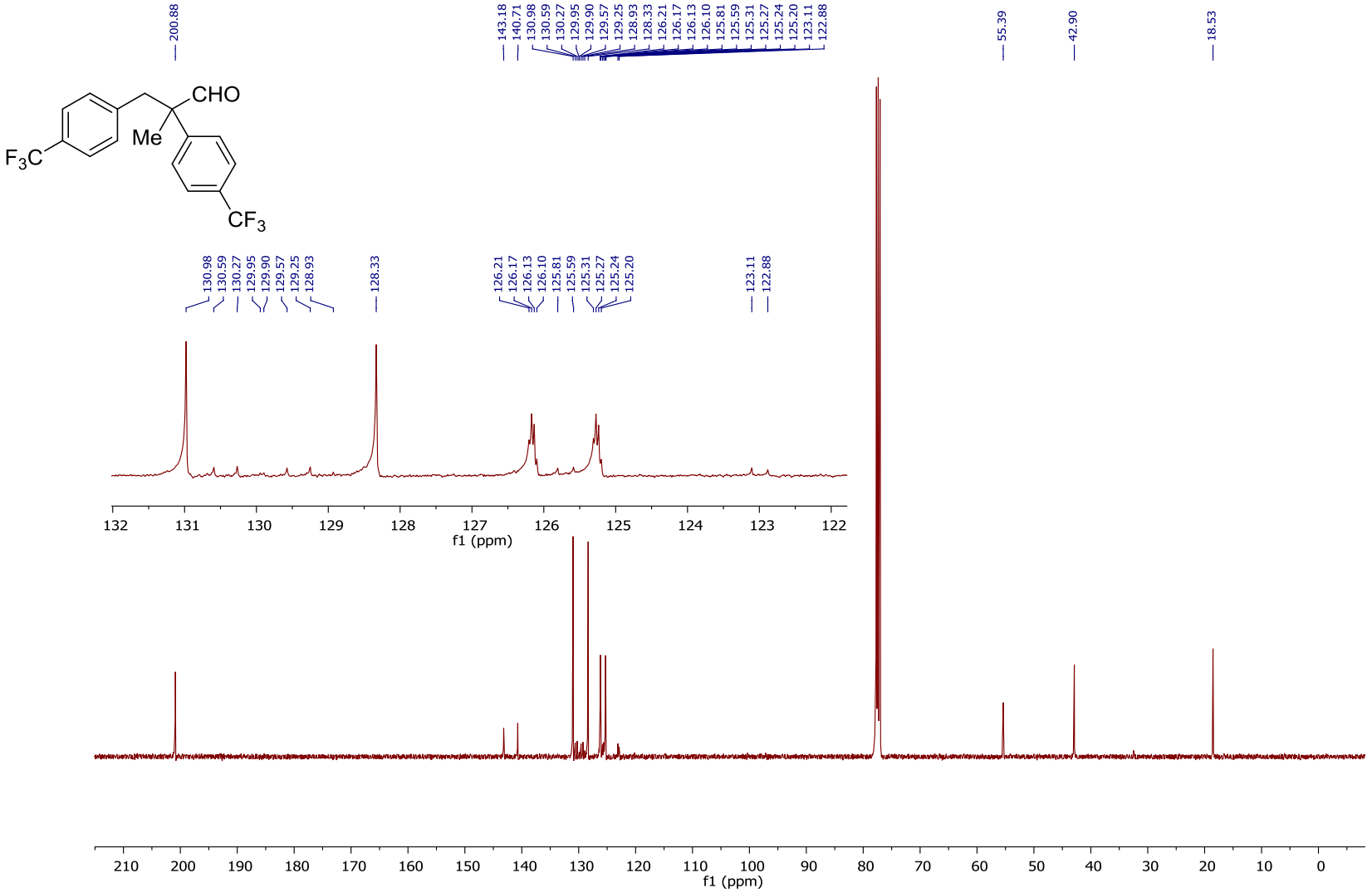
2-methyl-2,3-bis(4-(trifluoromethyl)phenyl)propanal (7ch)

^{1}H NMR (400 MHz, $CDCl_3$):



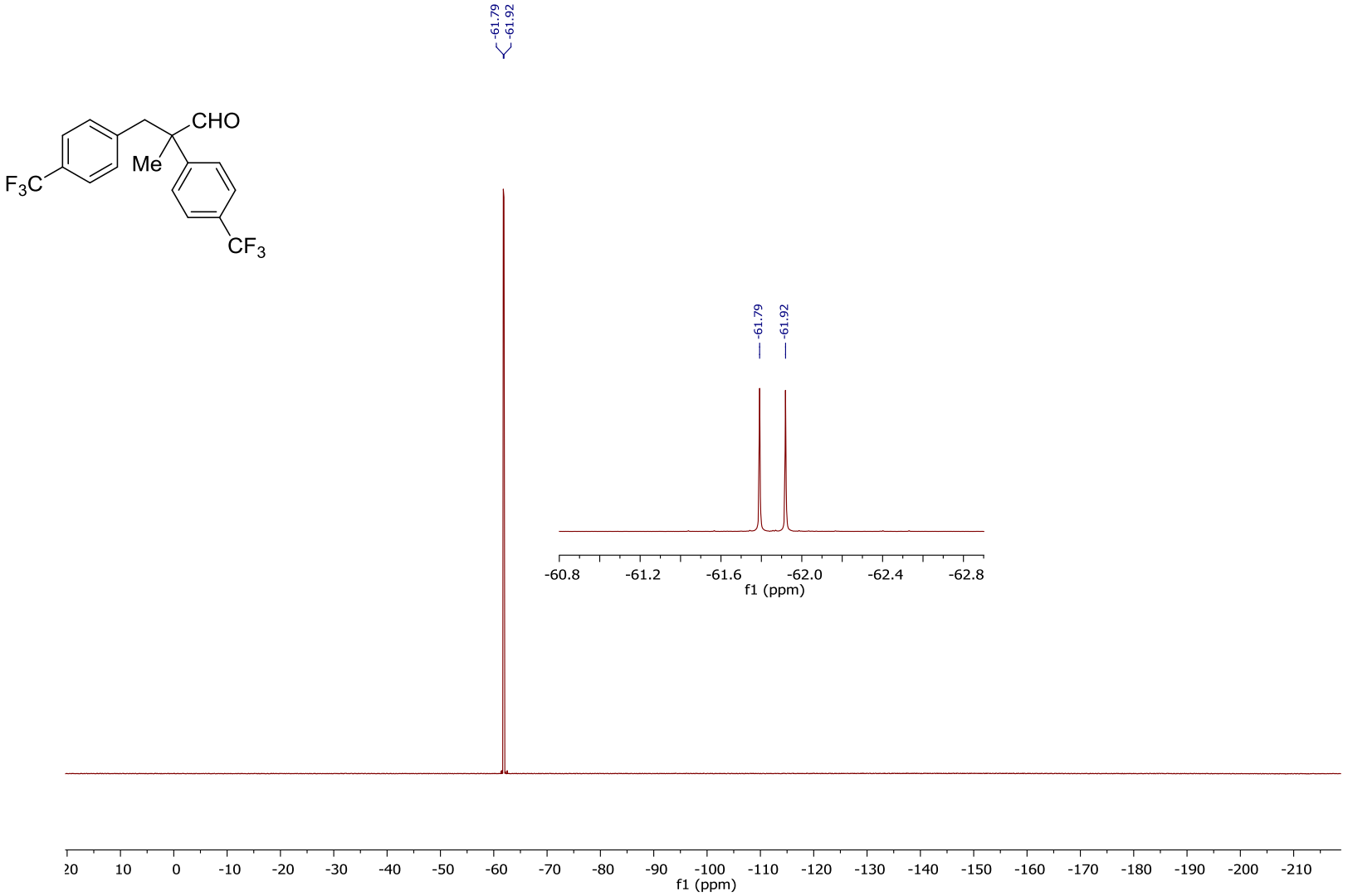
2-methyl-2,3-bis(4-(trifluoromethyl)phenyl)propanal (7ch)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



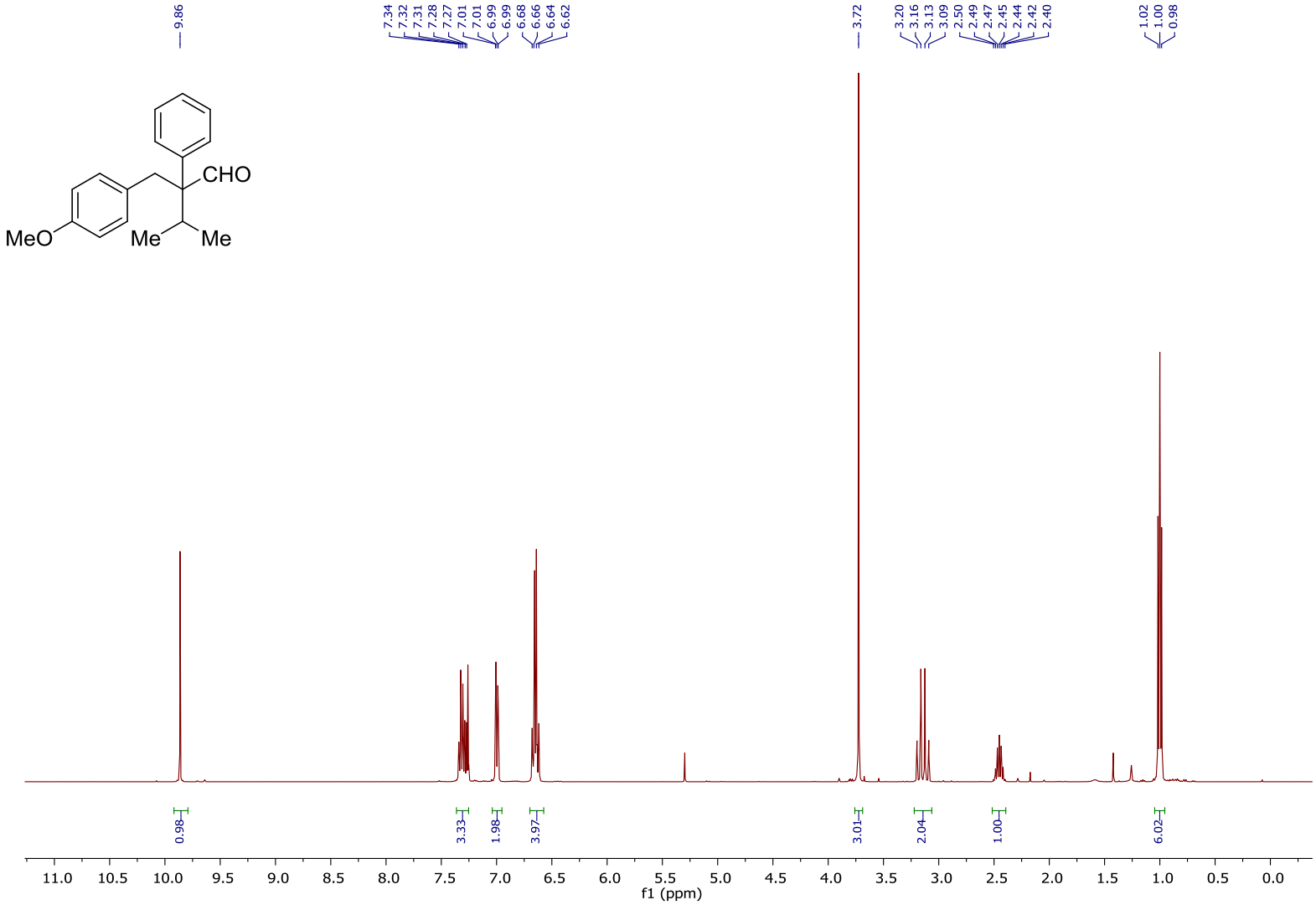
2-methyl-2,3-bis(4-(trifluoromethyl)phenyl)propanal (7ch)

$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$):



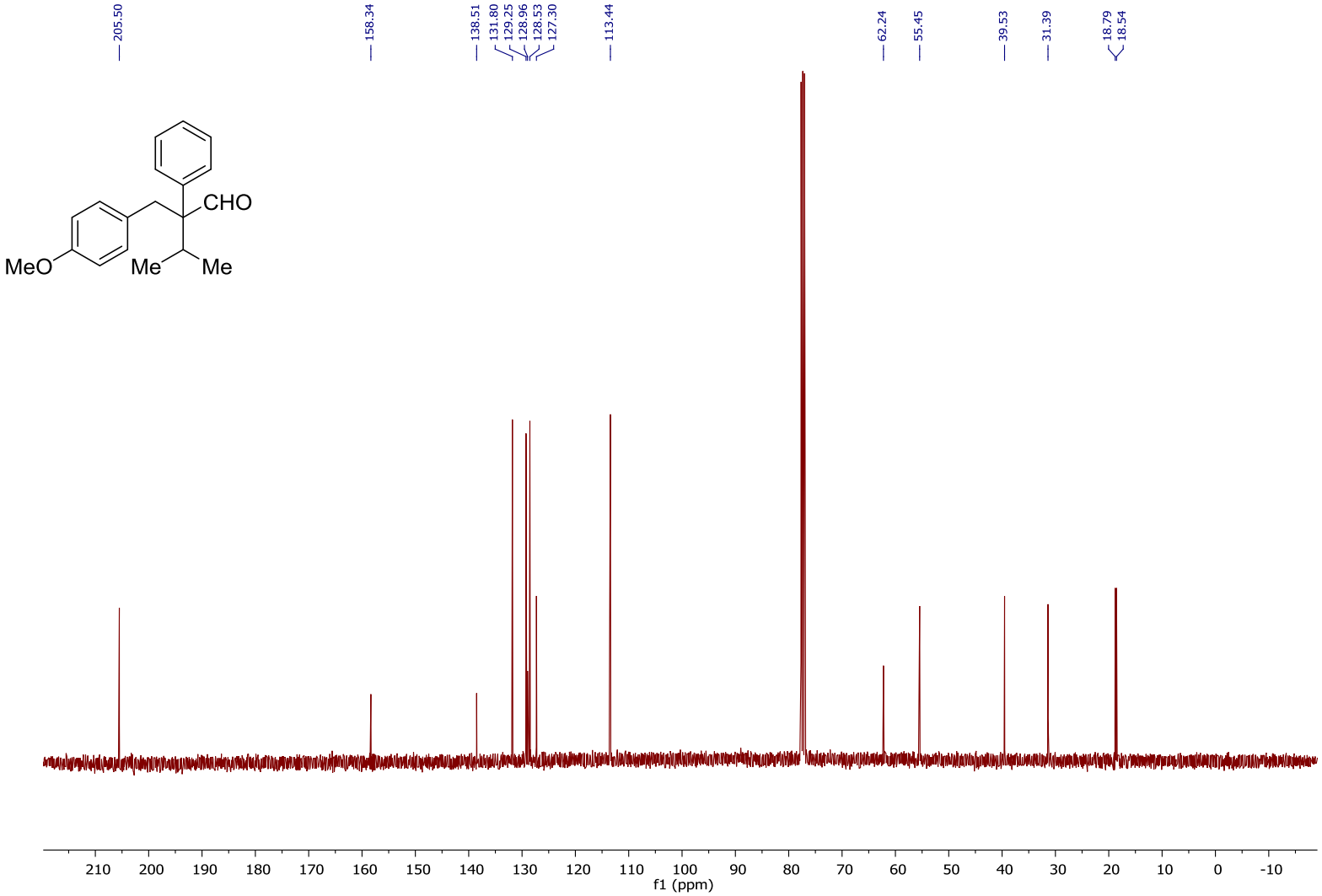
2-(4-methoxybenzyl)-3-methyl-2-phenylbutanal (7da)

^{1}H NMR (400 MHz, $CDCl_3$):



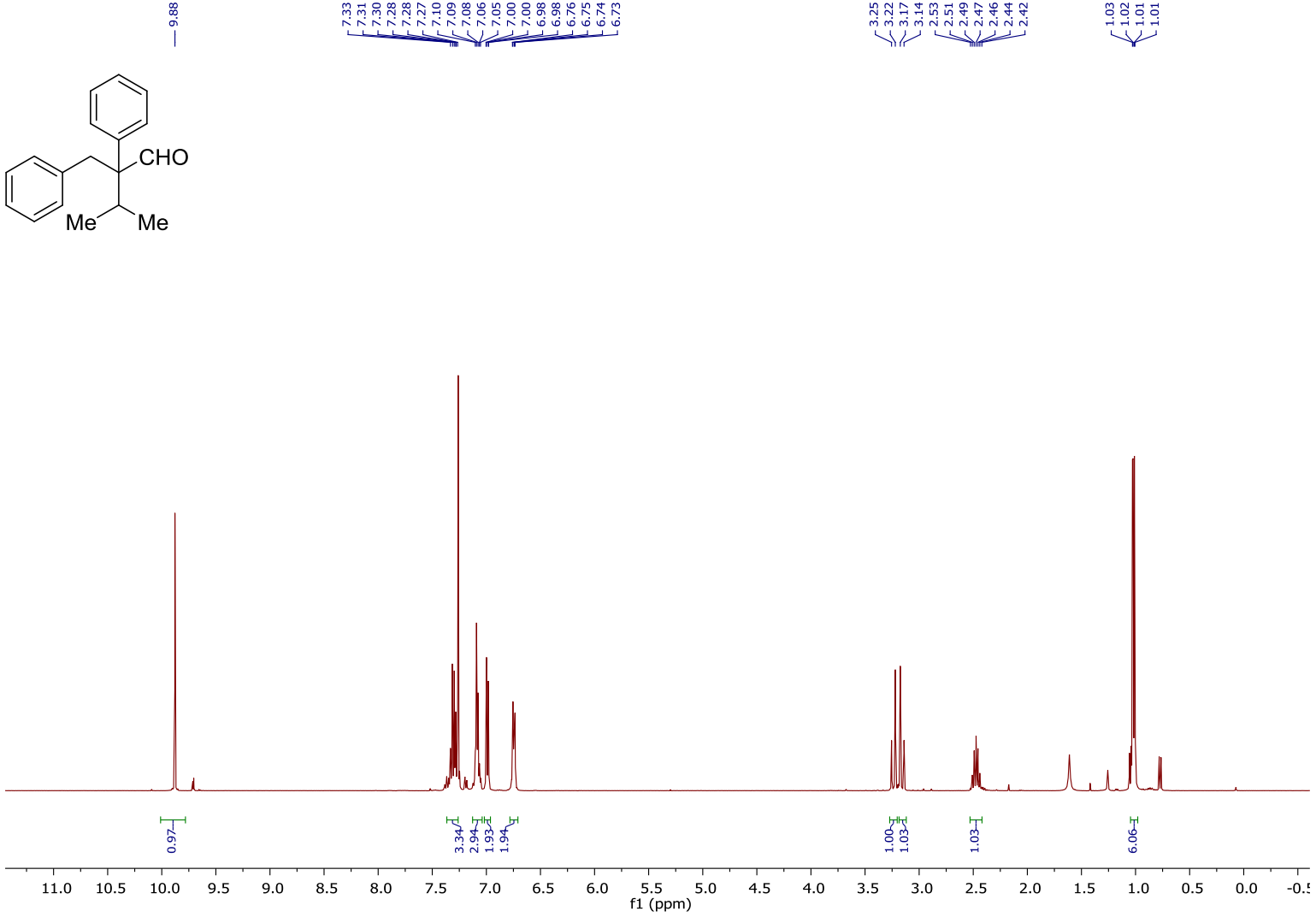
2-(4-methoxybenzyl)-3-methyl-2-phenylbutanal (7da)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



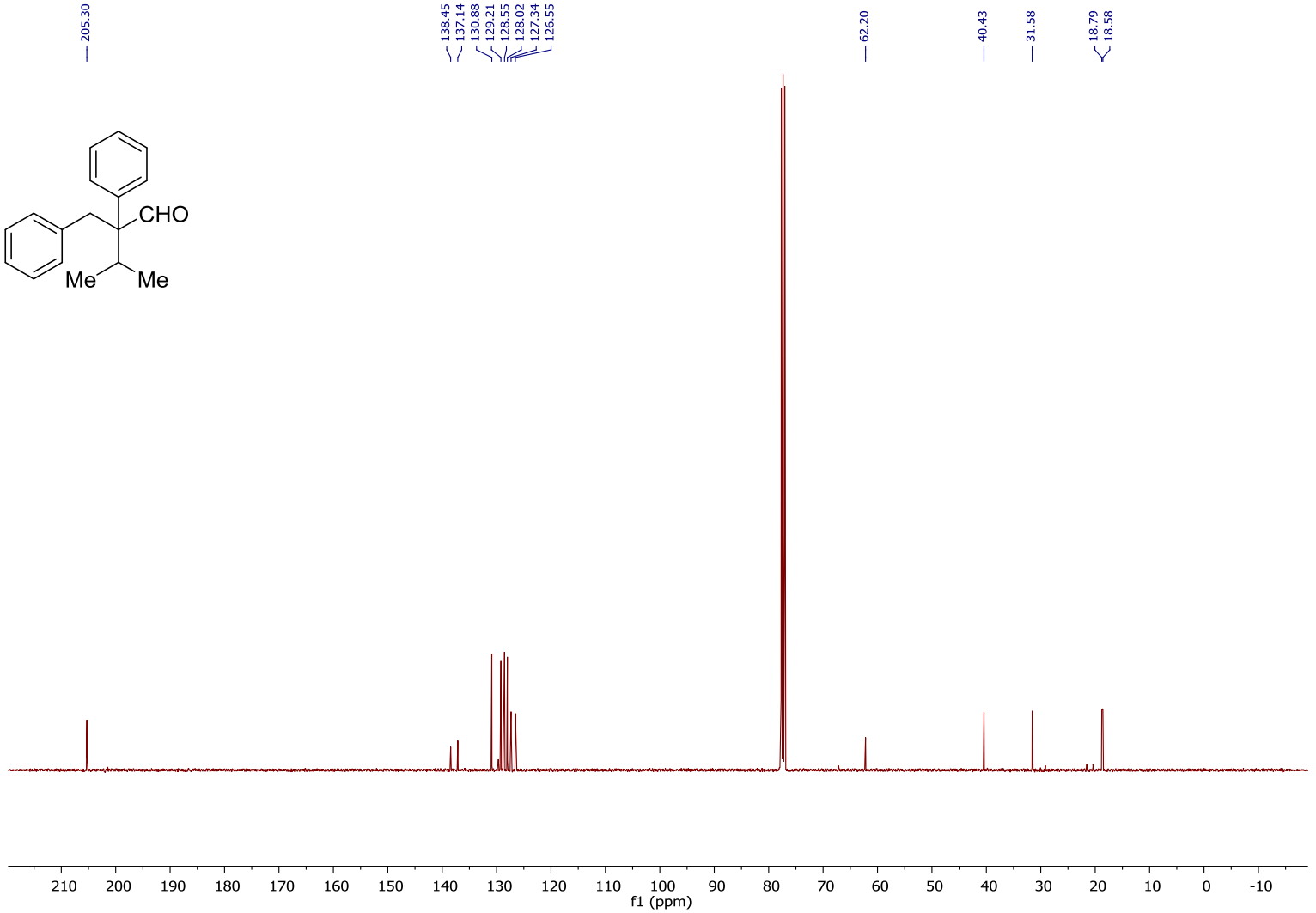
2-benzyl-3-methyl-2-phenylbutanal (7dg)

^{1}H NMR (400 MHz, $CDCl_3$):



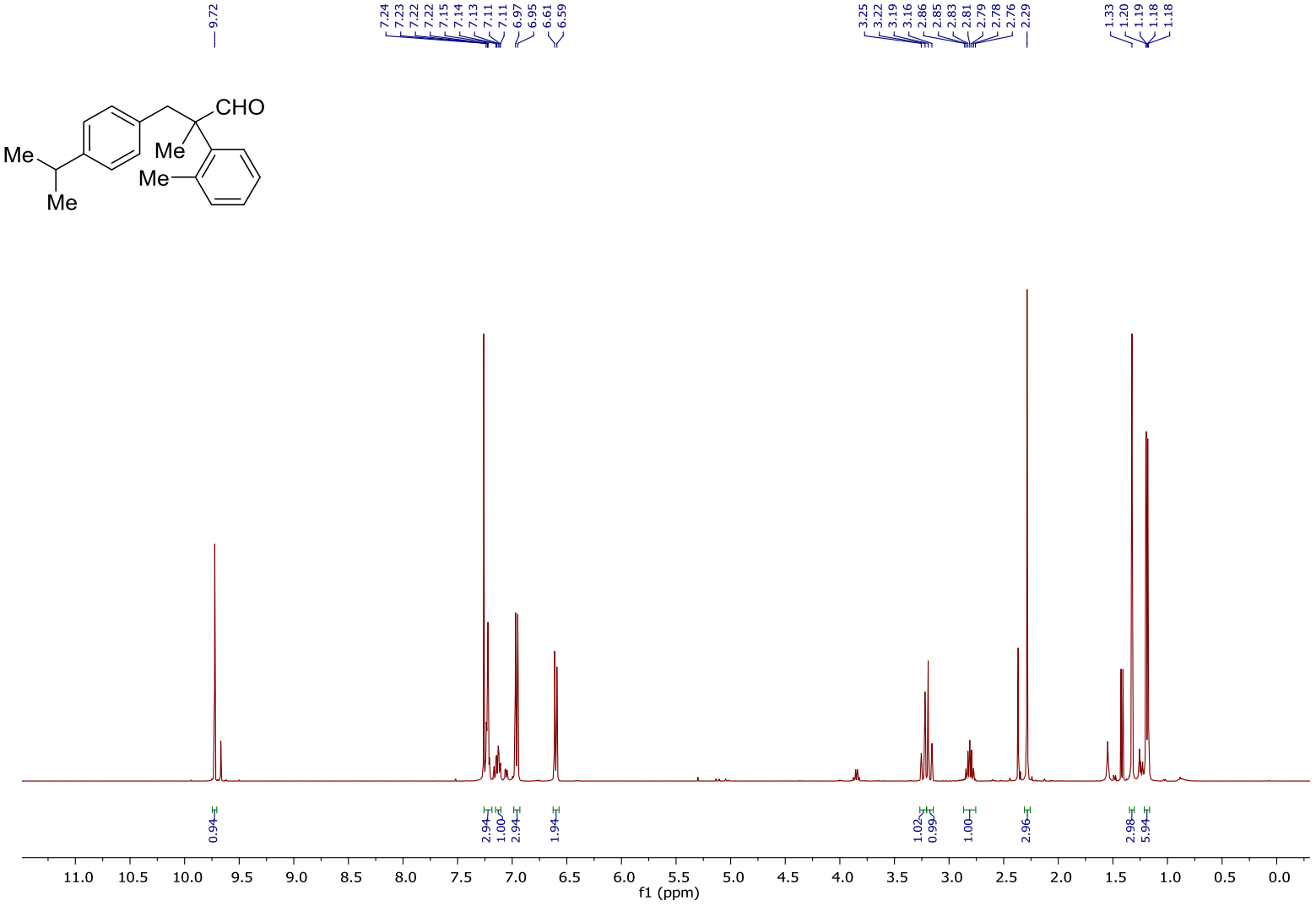
2-benzyl-3-methyl-2-phenylbutanal (7dg)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



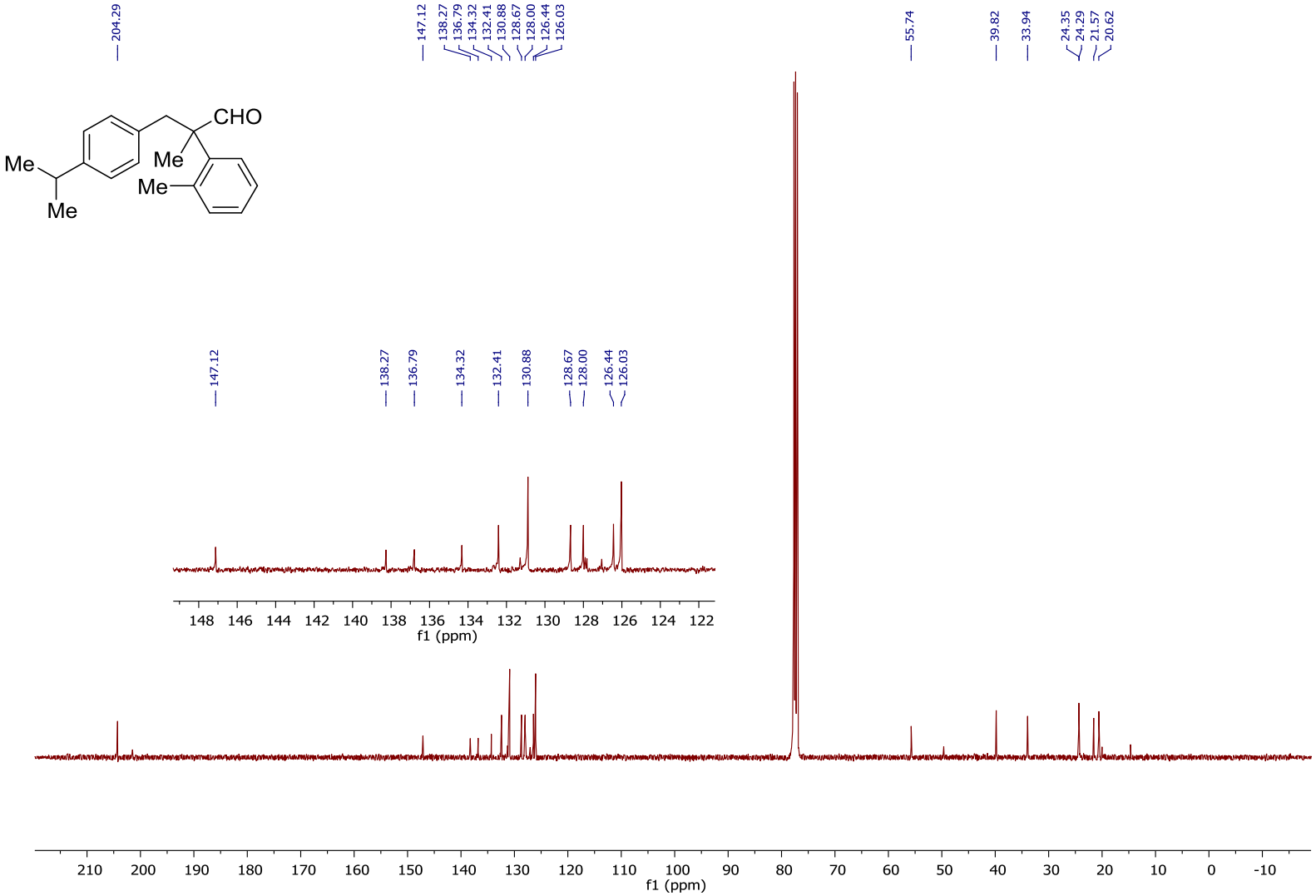
3-(4-isopropylphenyl)-2-methyl-2-(o-tolyl)propanal (7ej)

^{1}H NMR (400 MHz, $CDCl_3$):



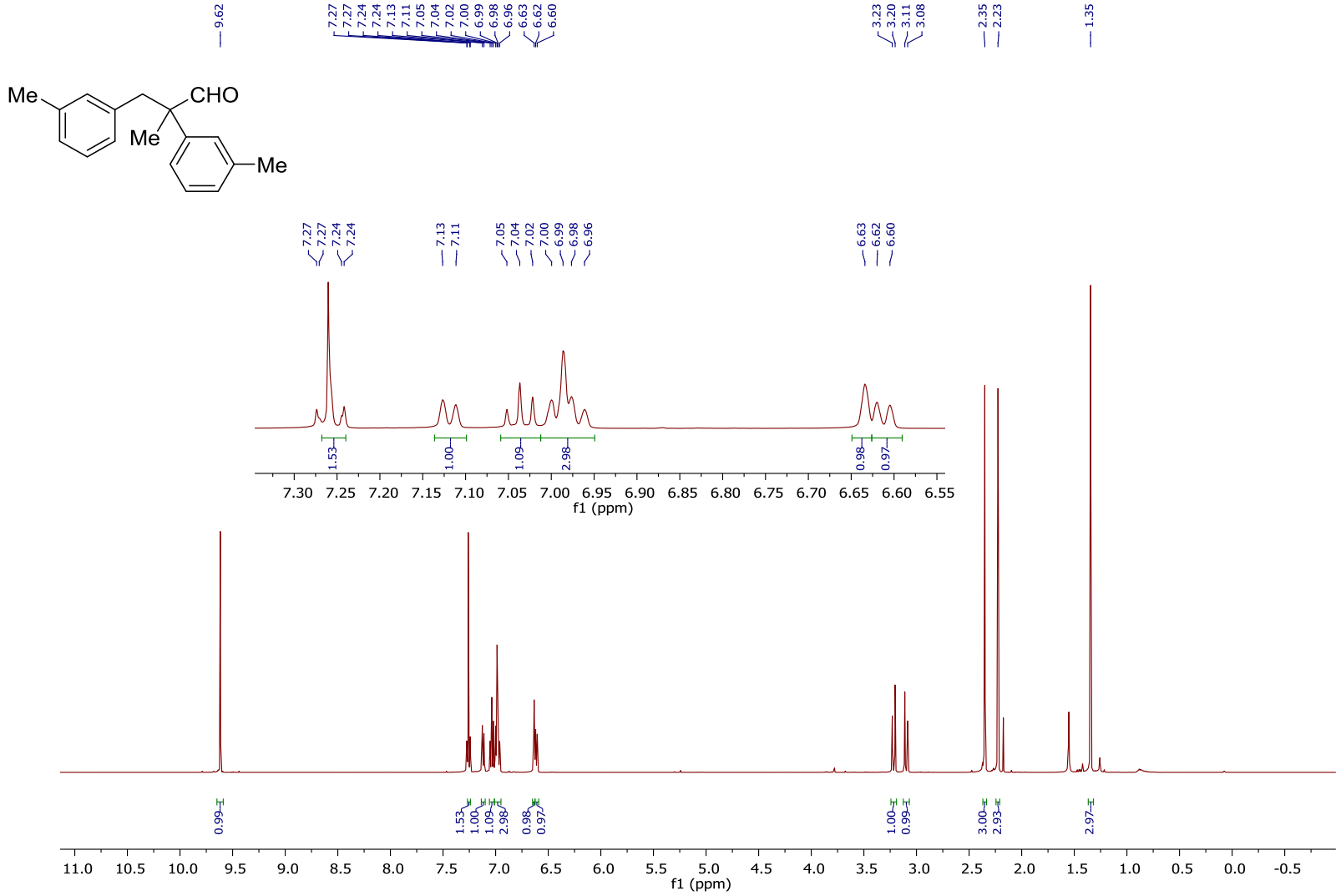
3-(4-isopropylphenyl)-2-methyl-2-(o-tolyl)propanal (7ej)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



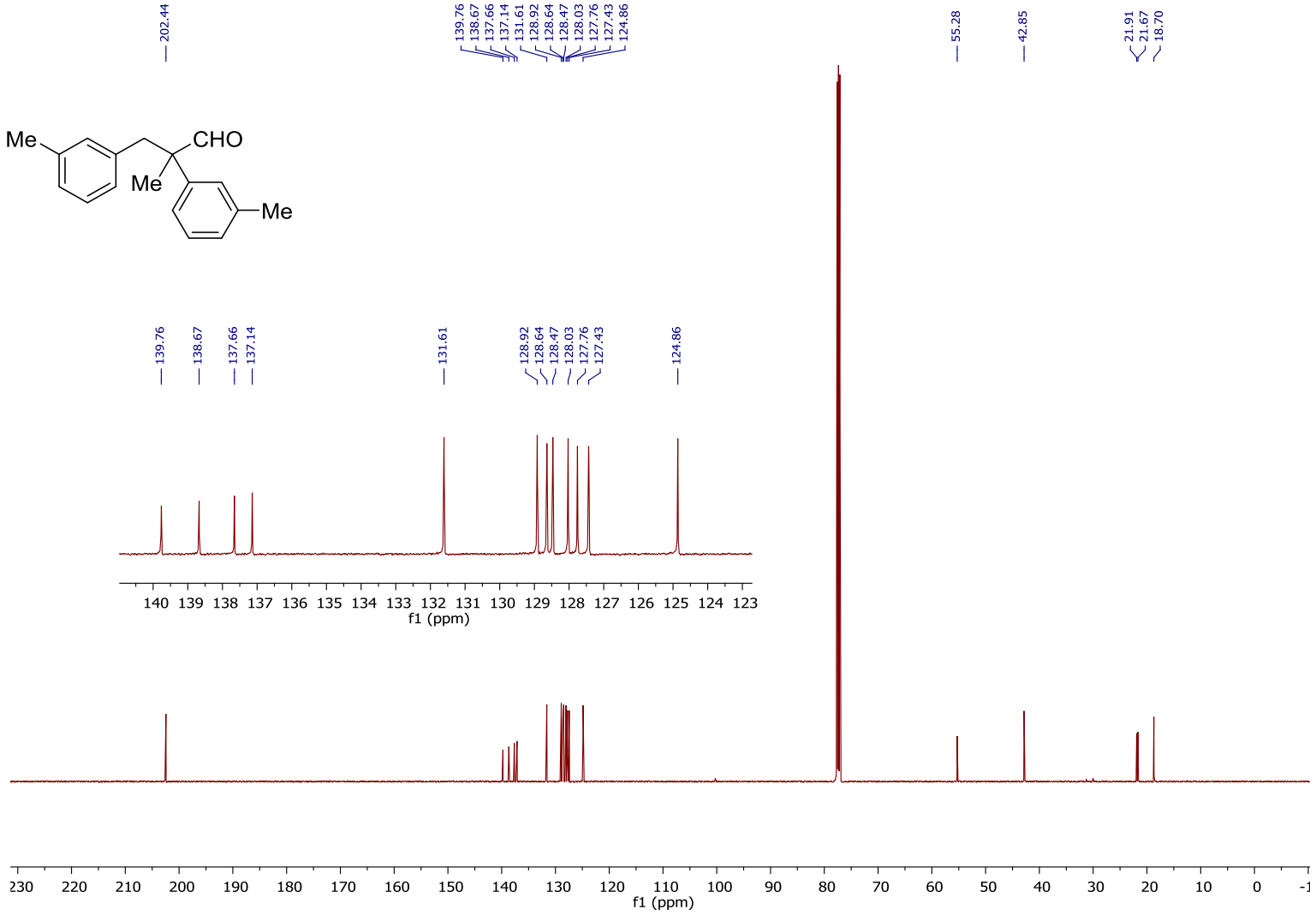
2-methyl-2,3-di-m-tolylpropanal (7fe)

^{1}H NMR (400 MHz, $CDCl_3$):



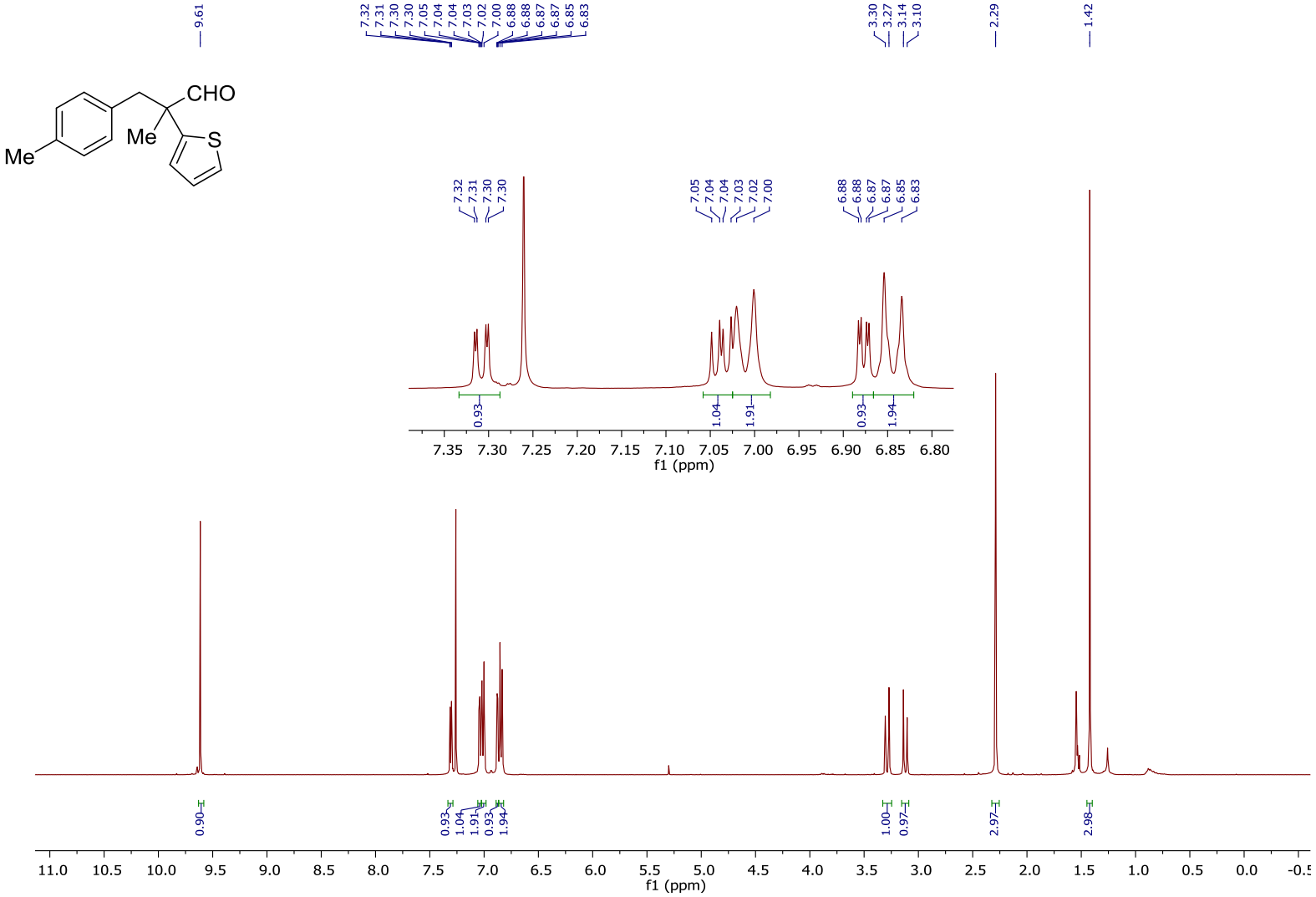
2-methyl-2,3-di-m-tolylpropanal (7fe)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



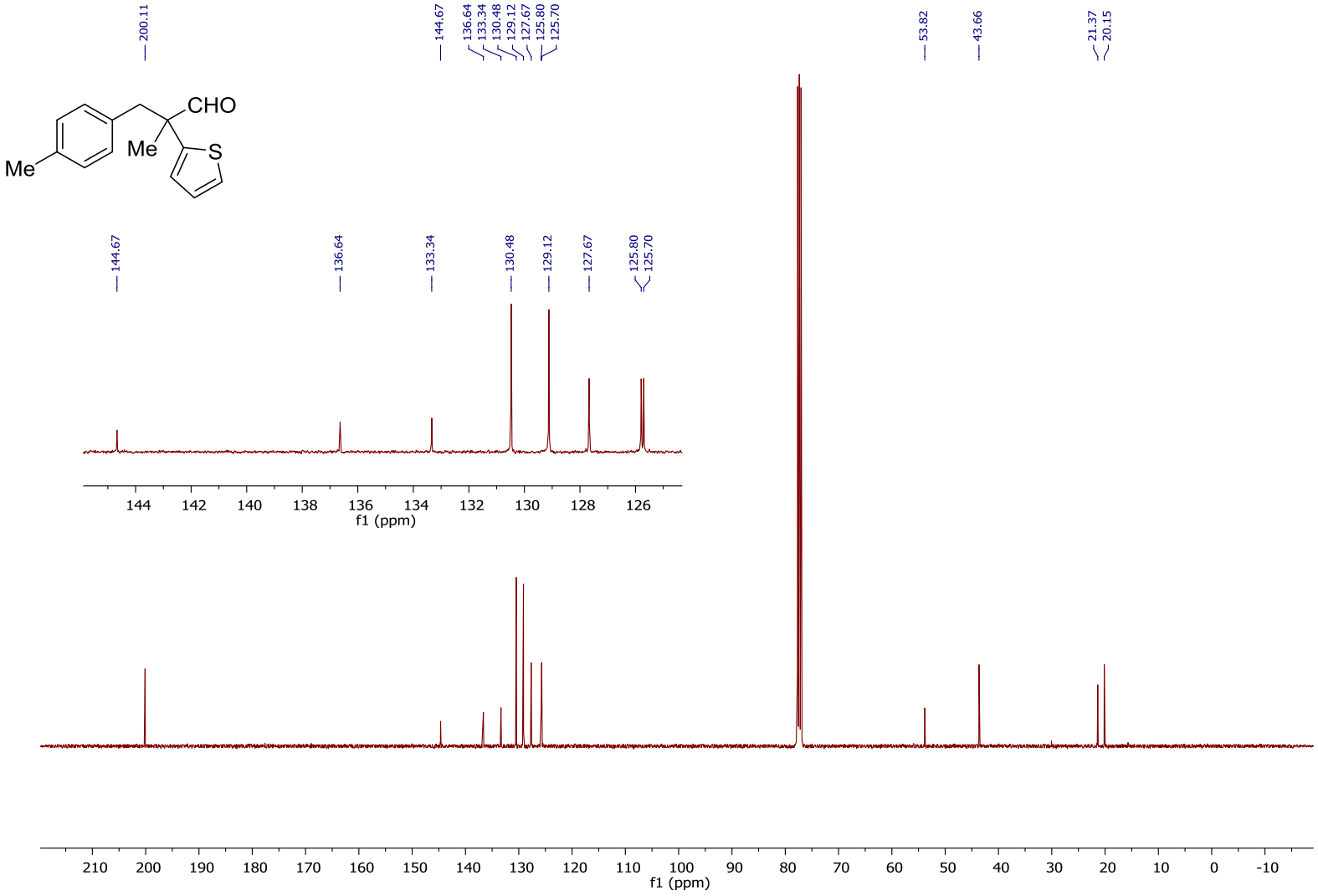
2-methyl-2-(thiophen-2-yl)-3-(p-tolyl)propanal (7ge)

^{1}H NMR (400 MHz, $CDCl_3$):



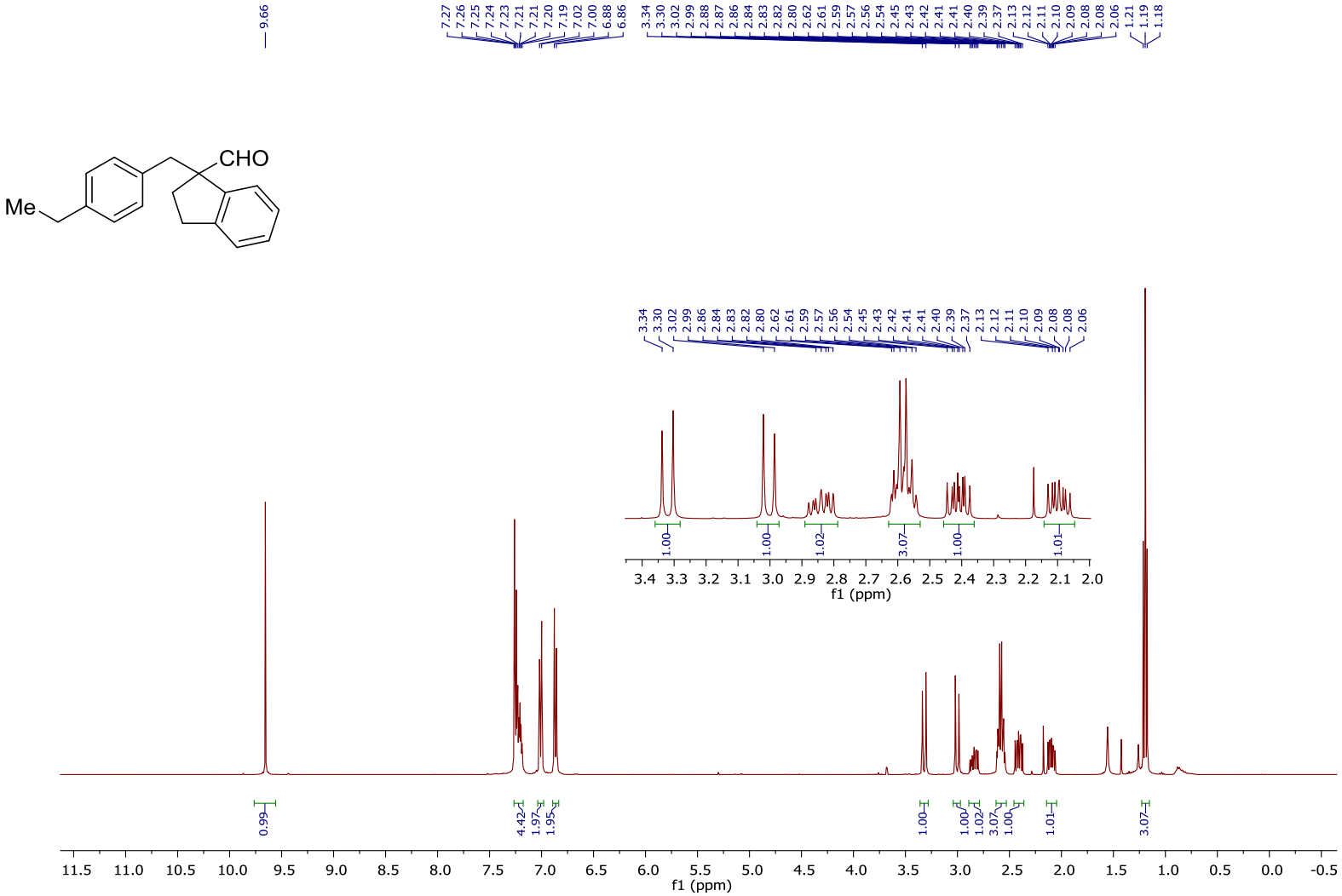
2-methyl-2-(thiophen-2-yl)-3-(p-tolyl)propanal (7ge)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



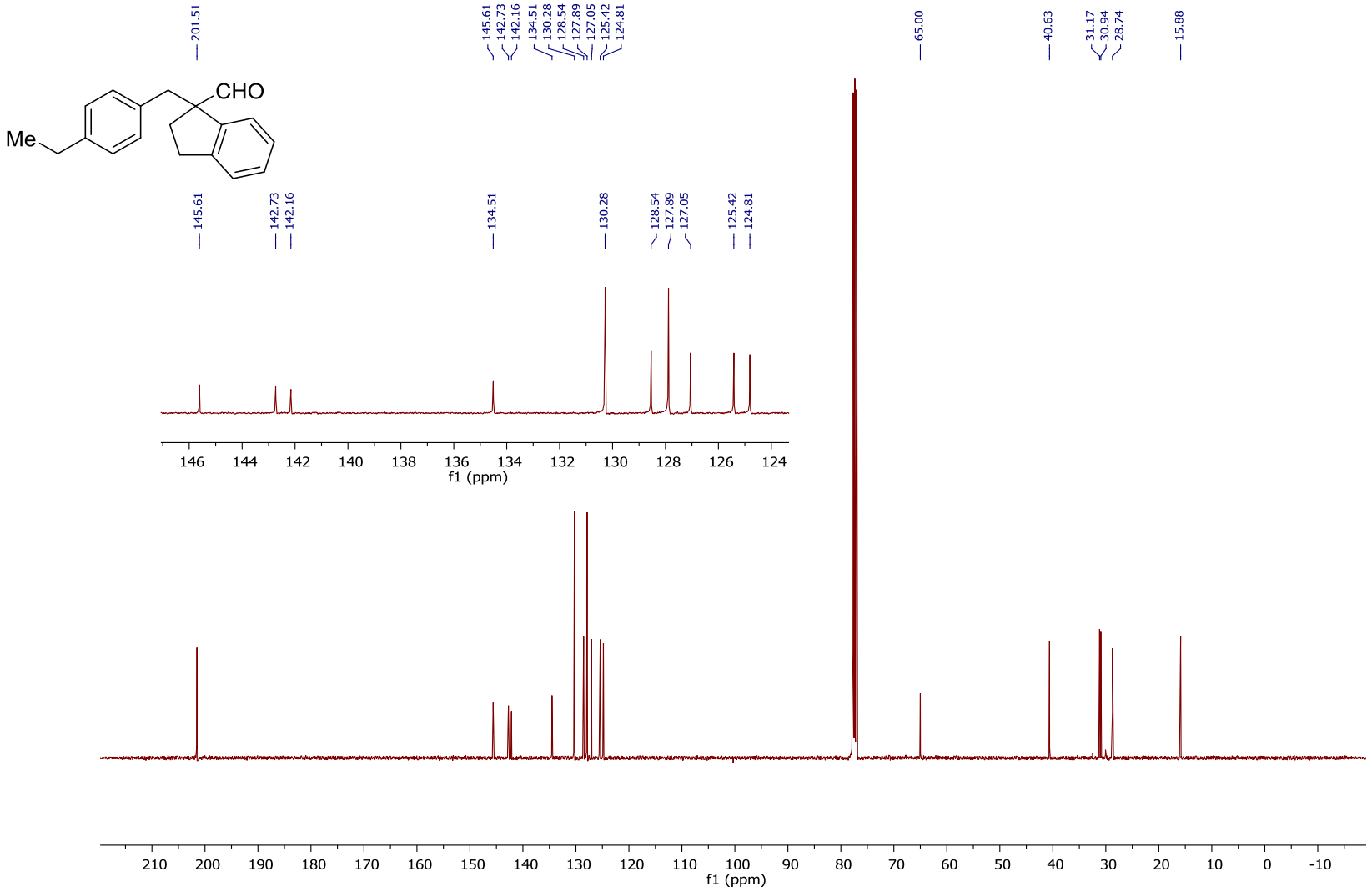
1-(4-ethylbenzyl)-2,3-dihydro-1H-indene-1-carbaldehyde (7hk)

^{1}H NMR (400 MHz, $CDCl_3$):



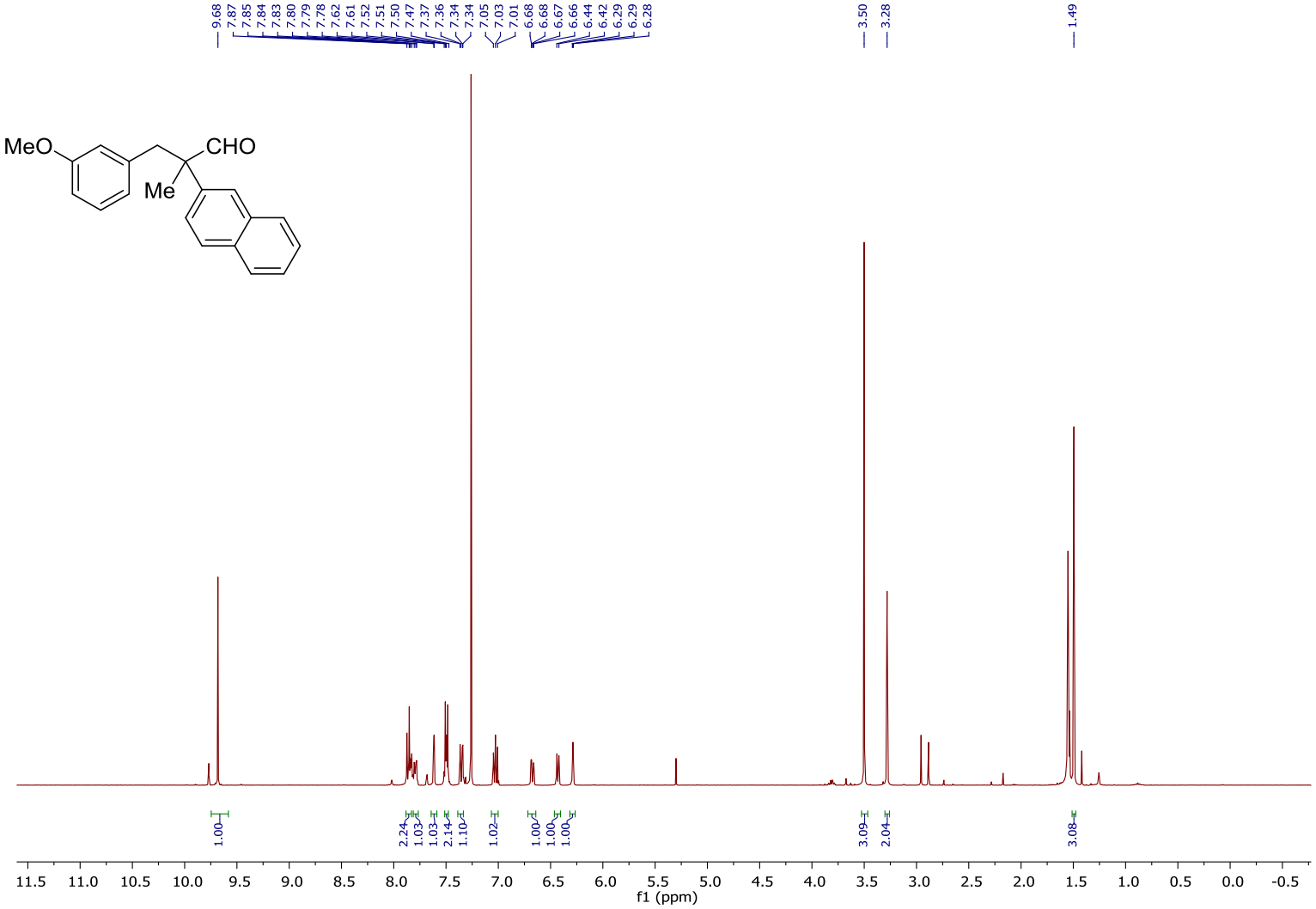
1-(4-ethylbenzyl)-2,3-dihydro-1H-indene-1-carbaldehyde (7hk)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



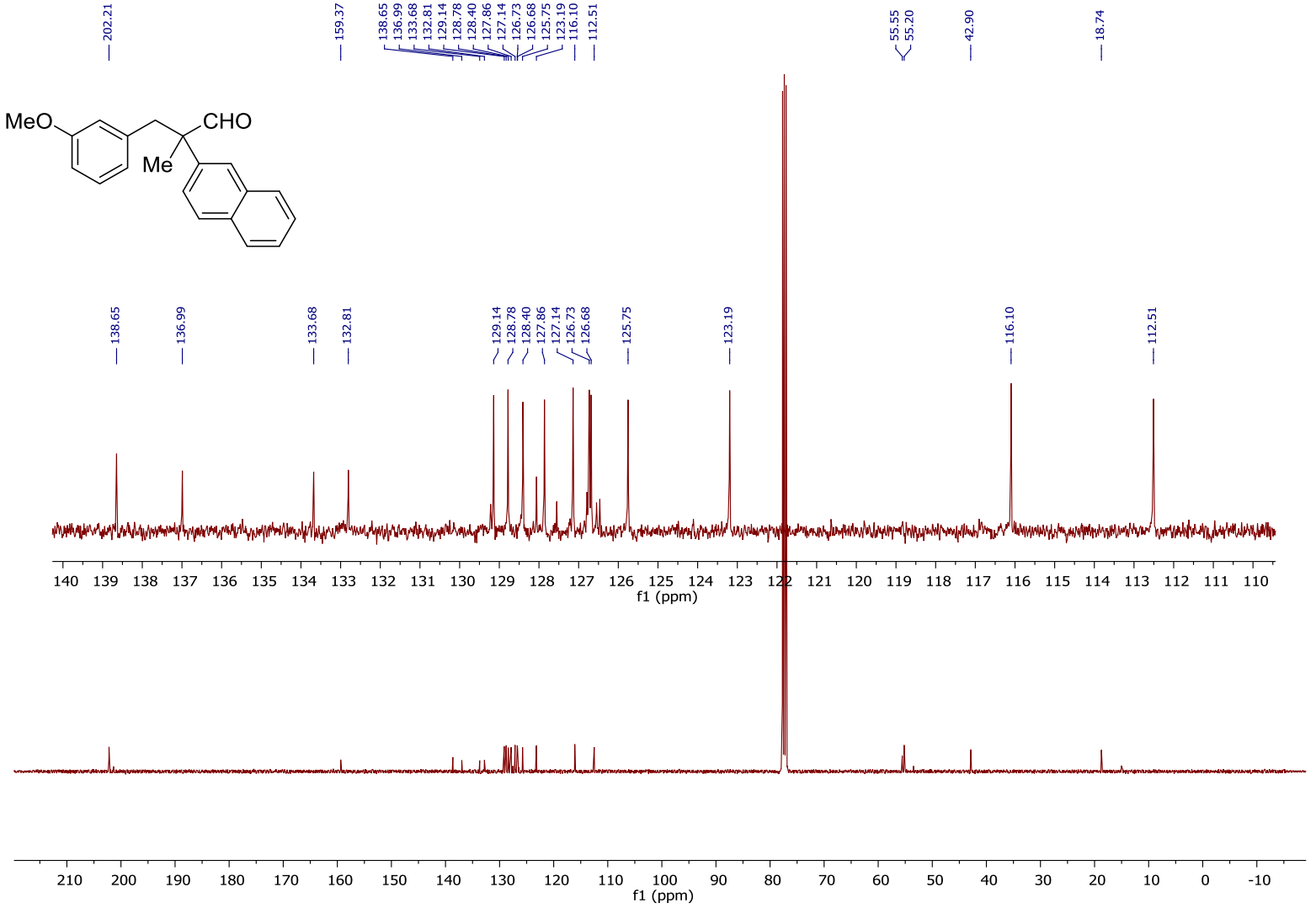
3-(3-methoxyphenyl)-2-methyl-2-(naphthalen-2-yl)propanal (7ib)

^{1}H NMR (400 MHz, $CDCl_3$):



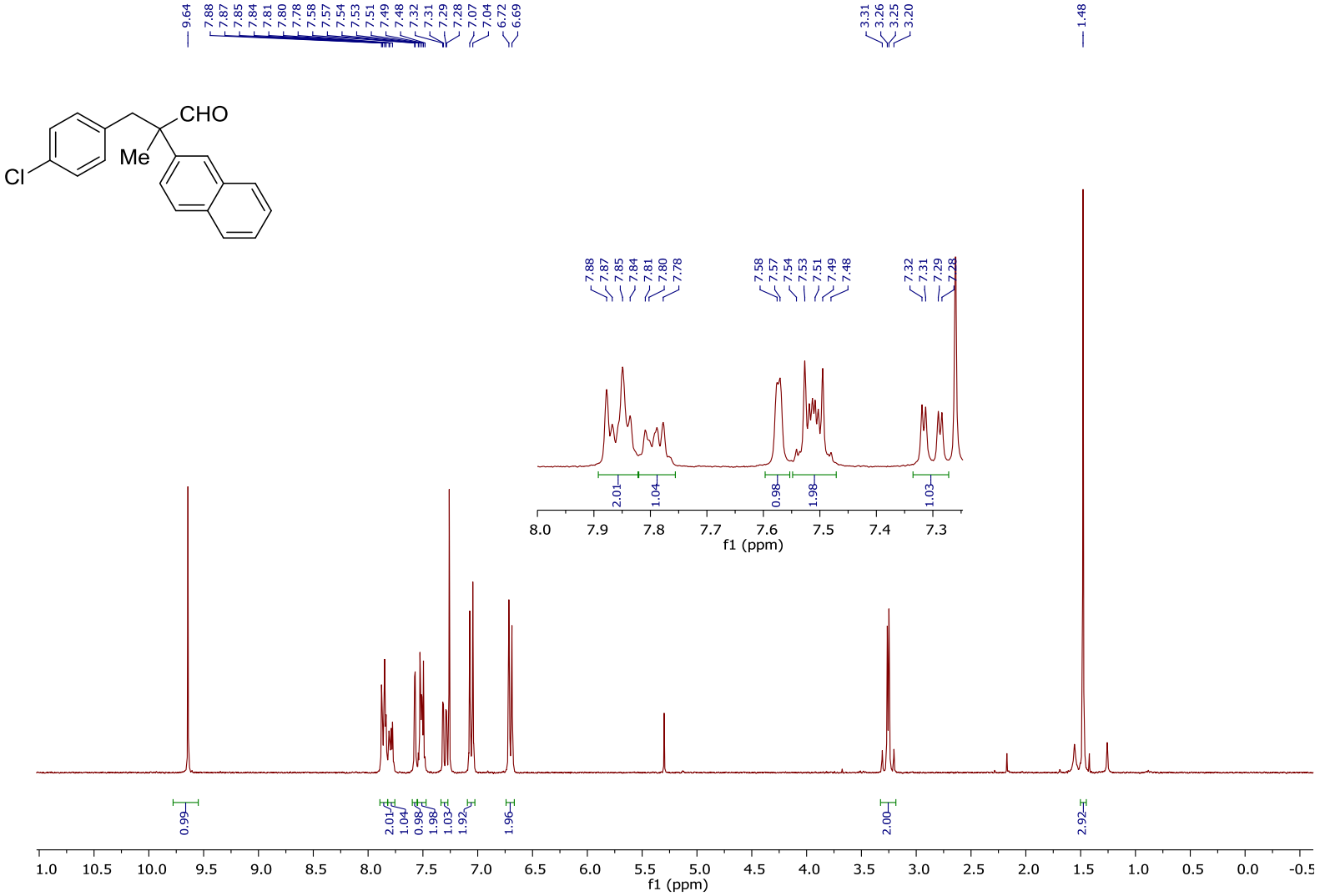
3-(3-methoxyphenyl)-2-methyl-2-(naphthalen-2-yl)propanal (7ib)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



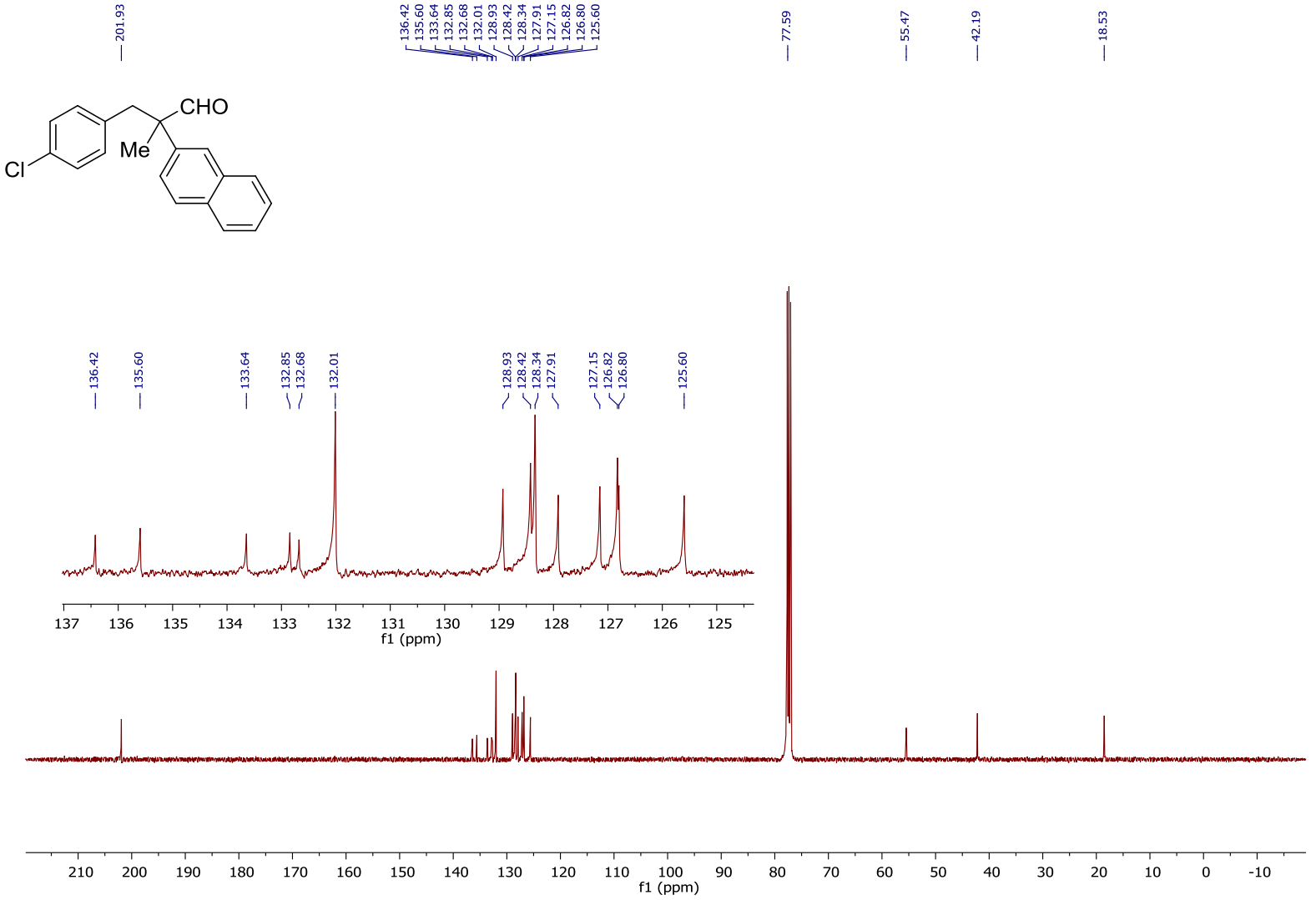
3-(4-chlorophenyl)-2-methyl-2-(naphthalen-2-yl)propanal (7ii)

^{1}H NMR (400 MHz, $CDCl_3$):



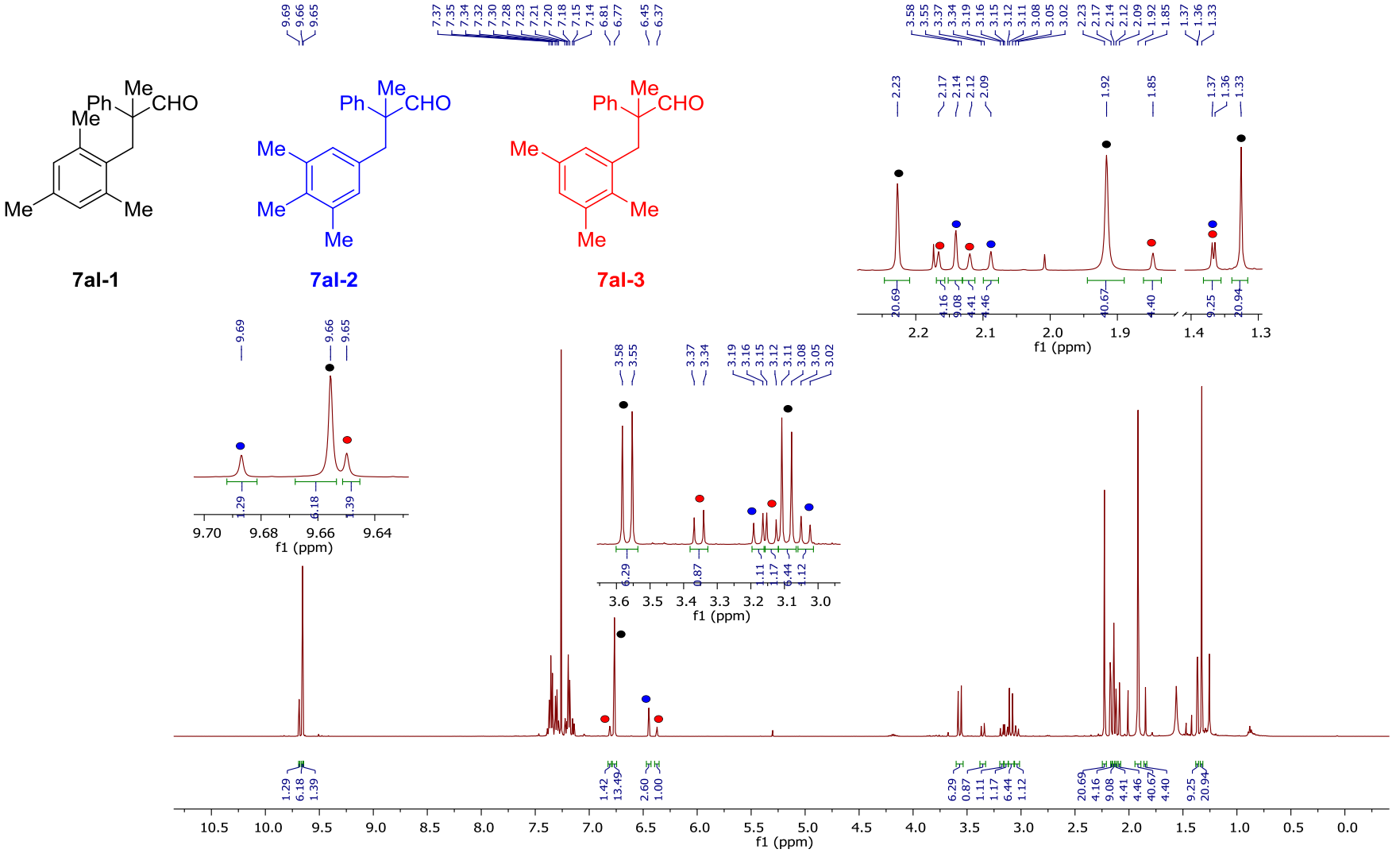
3-(4-chlorophenyl)-2-methyl-2-(naphthalen-2-yl)propanal (7ii)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



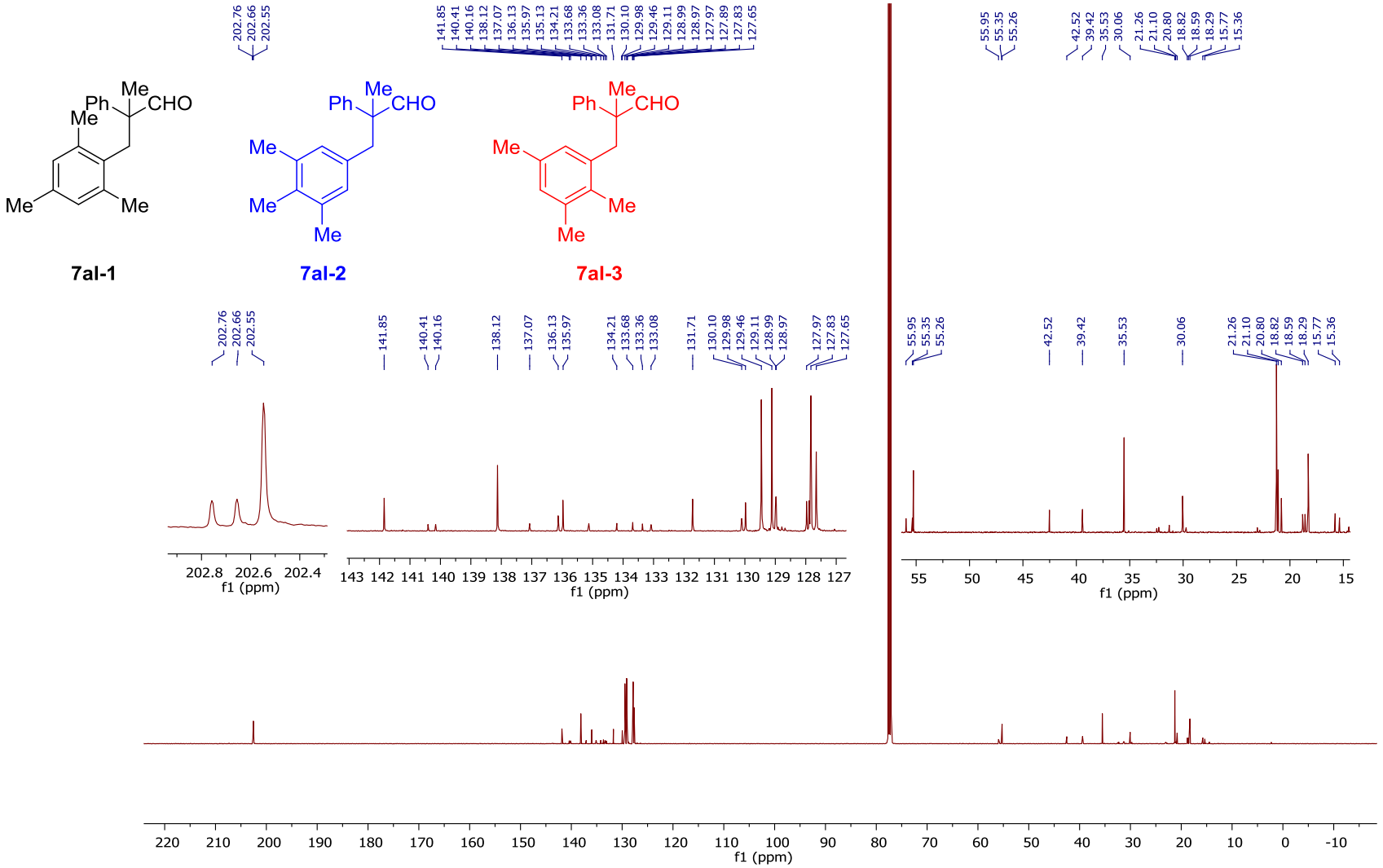
Mixture of isomers (7al-1, 7al-2, 7al-3)

^{1}H NMR (500 MHz, $CDCl_3$):



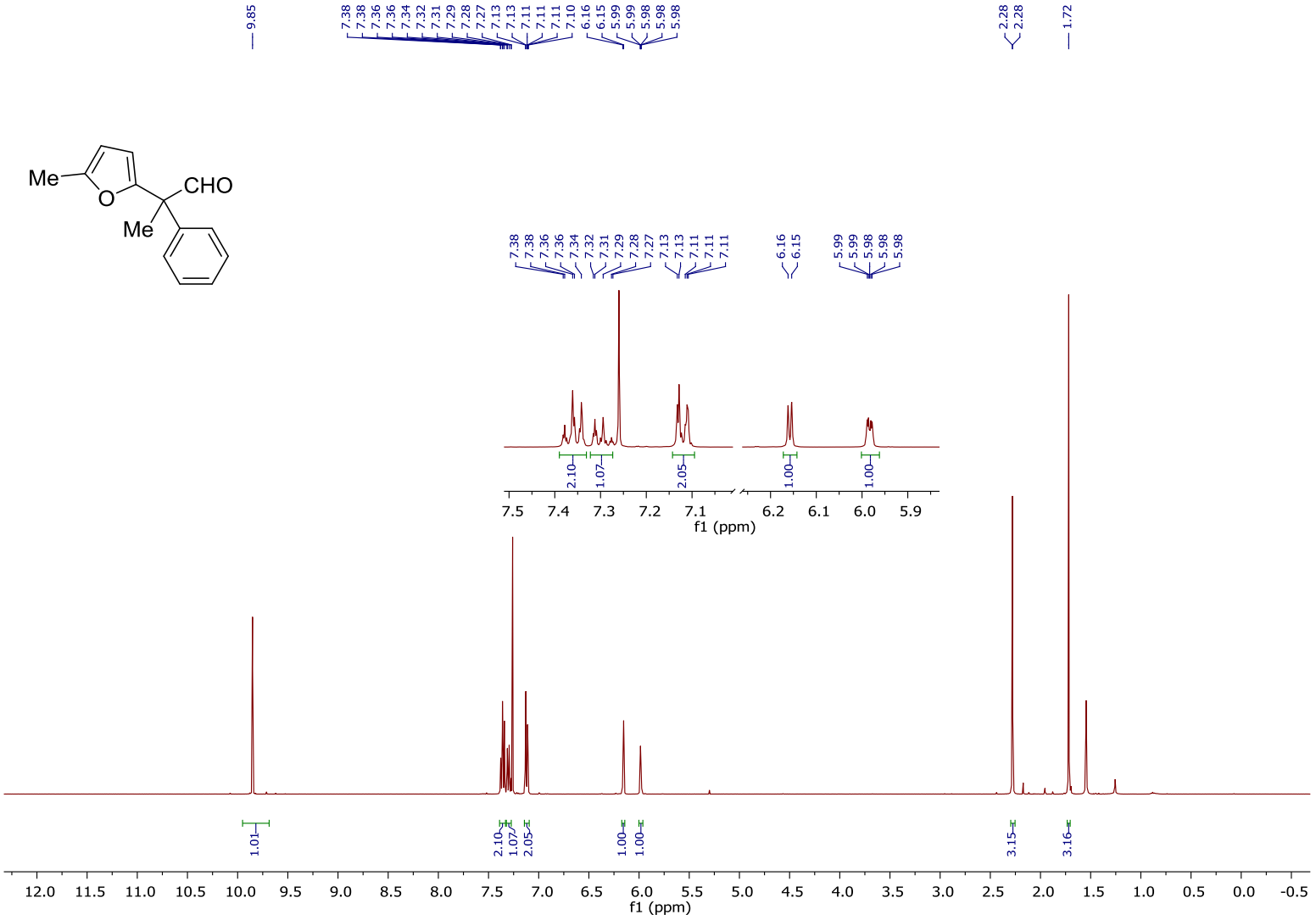
Mixture of isomers (7al-1, 7al-2, 7al-3)

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$):



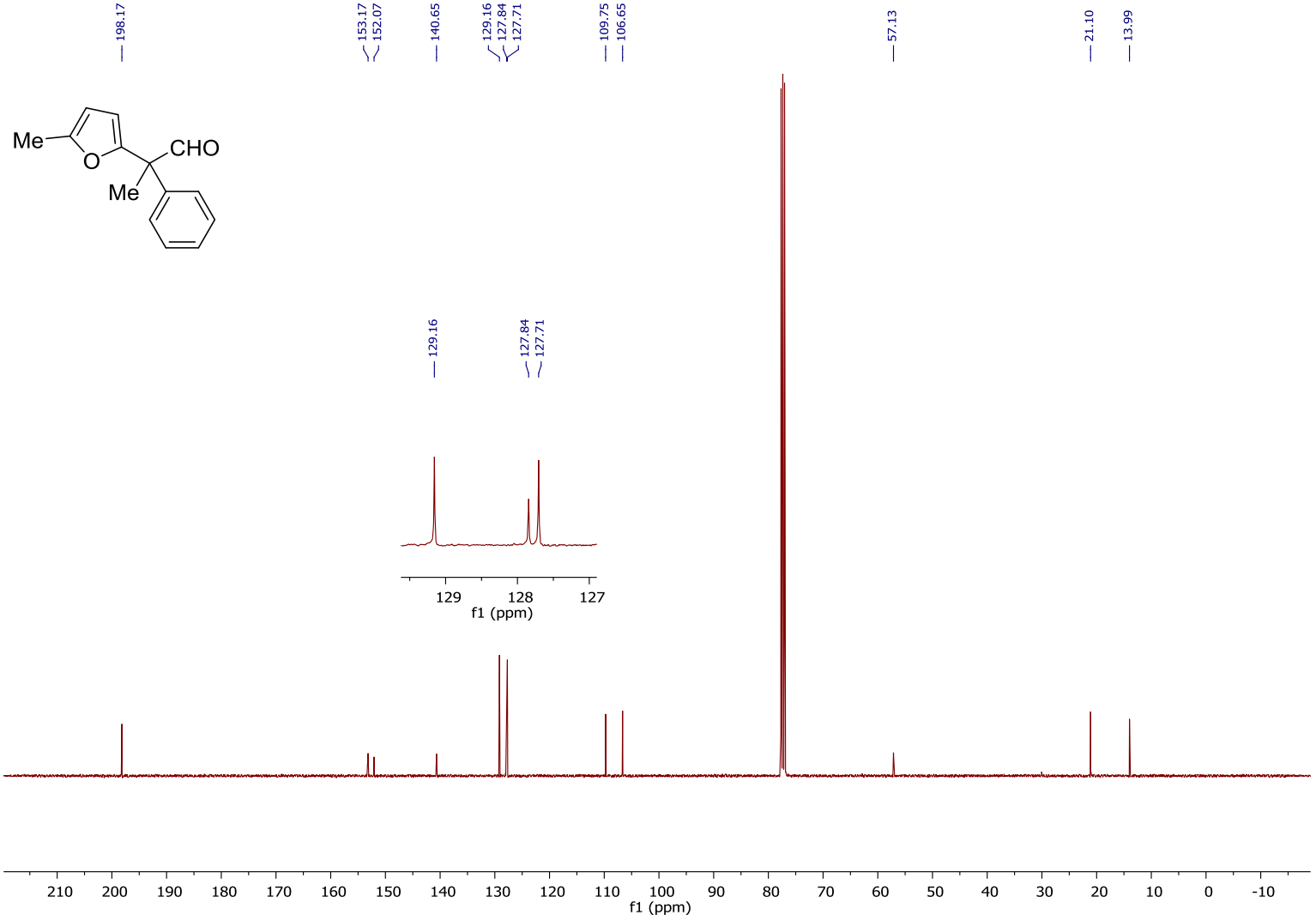
2-(5-methylfuran-2-yl)-2-phenylpropanal (7am)

^{1}H NMR (400 MHz, $CDCl_3$):



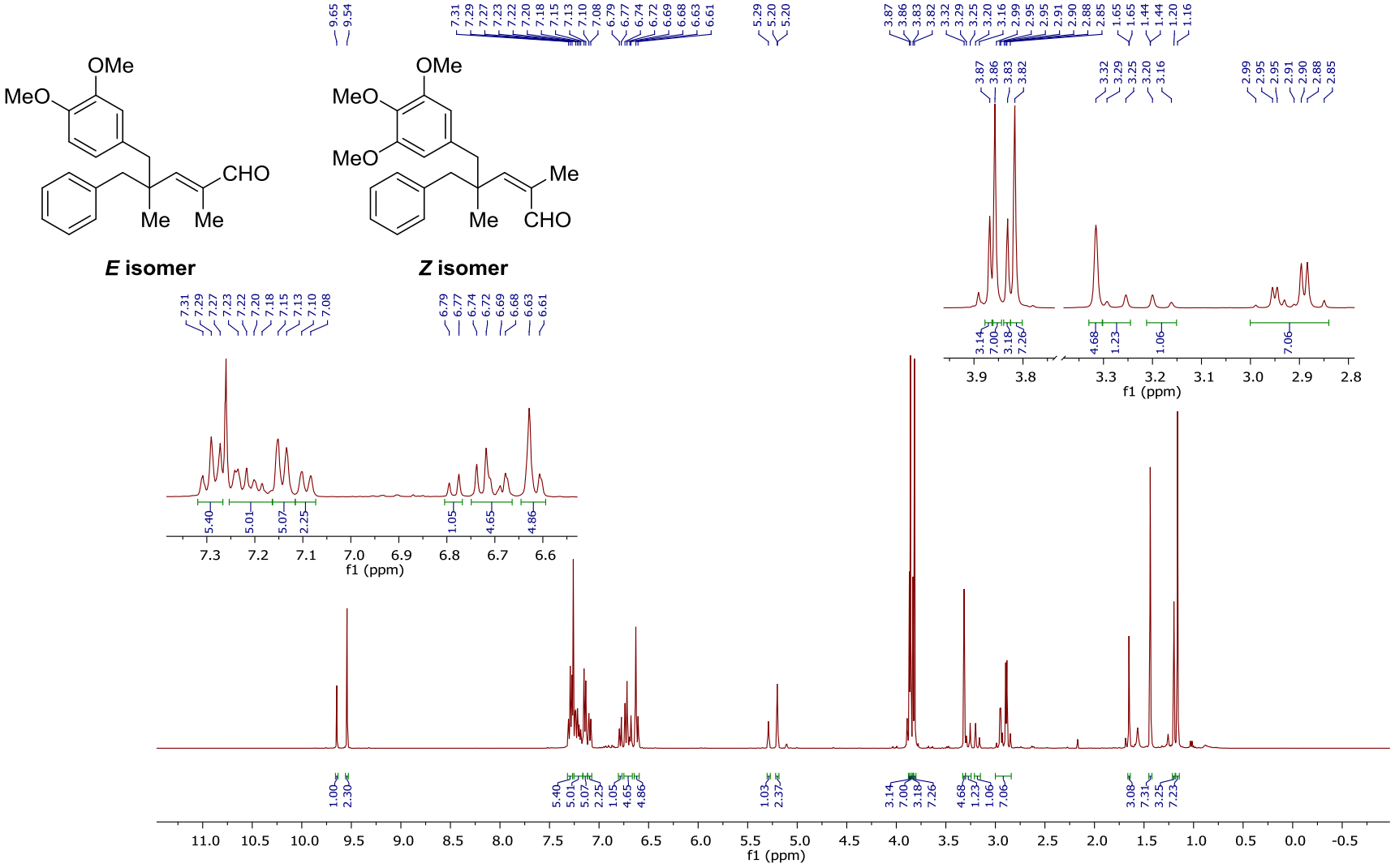
2-(5-methylfuran-2-yl)-2-phenylpropanal (7am)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



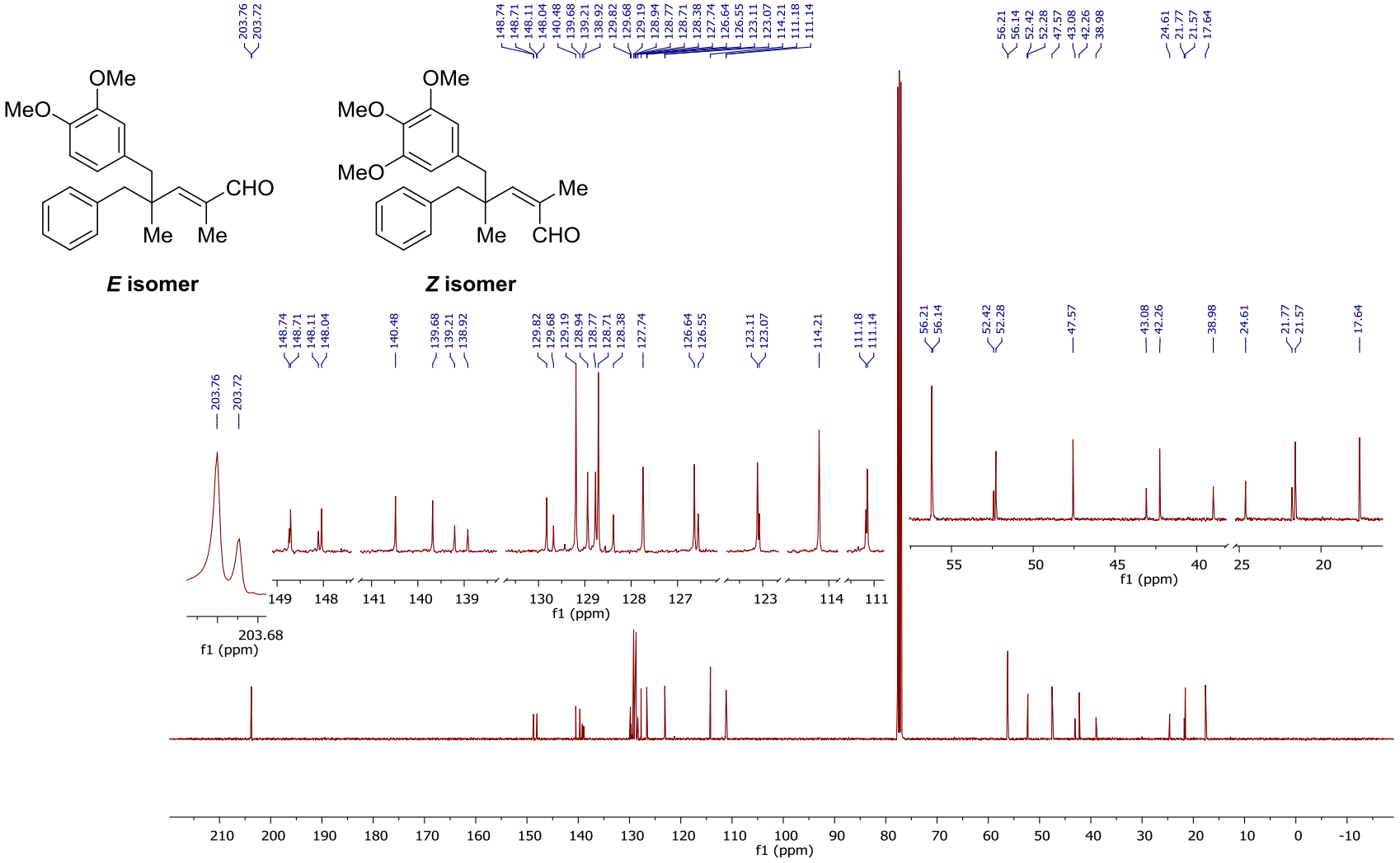
(*E*/*Z*)-4-benzyl-2,4-dimethyl-5-(3,4-dimethoxyphenyl)pent-2-enal (12an)

^{1}H NMR (400 MHz, $CDCl_3$):



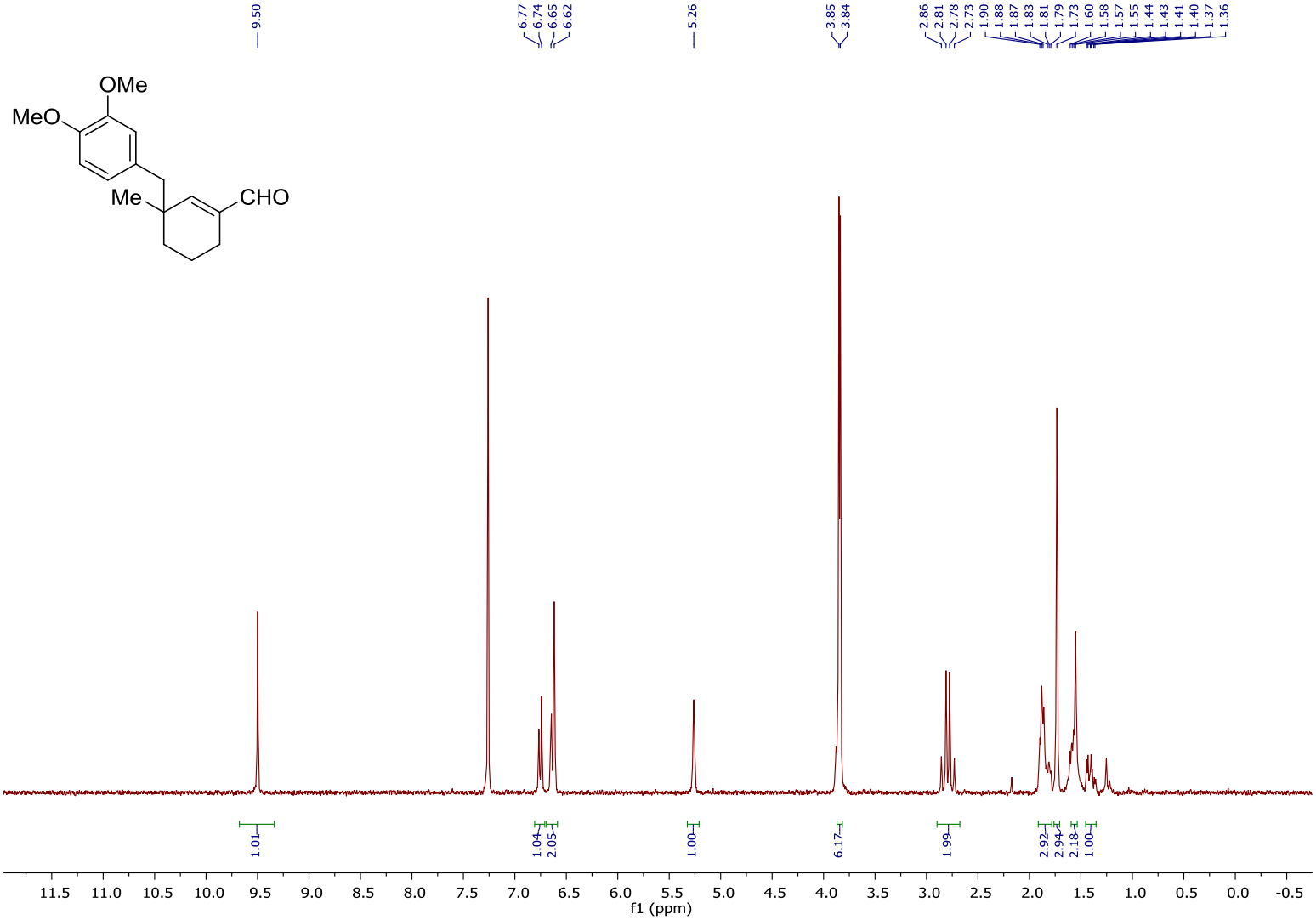
(*E*/*Z*)-4-benzyl-2,4-dimethyl-5-(3,4-dimethoxyphenyl)pent-2-enal (12an)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



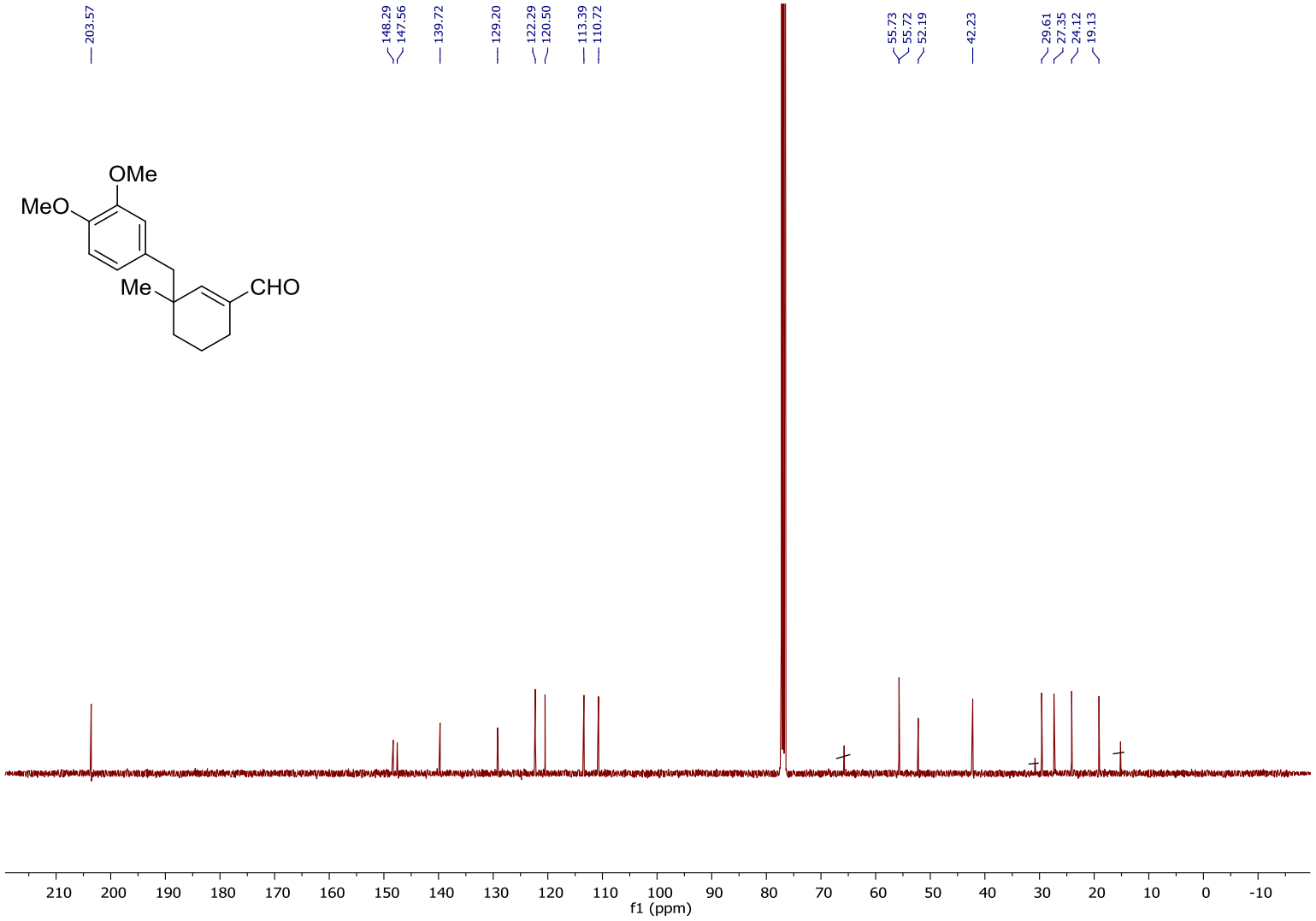
3-(3,4-dimethoxybenzyl)-3-methylcyclohex-1-enecarbaldehyde (12bn)

^{1}H NMR (400 MHz, $CDCl_3$):



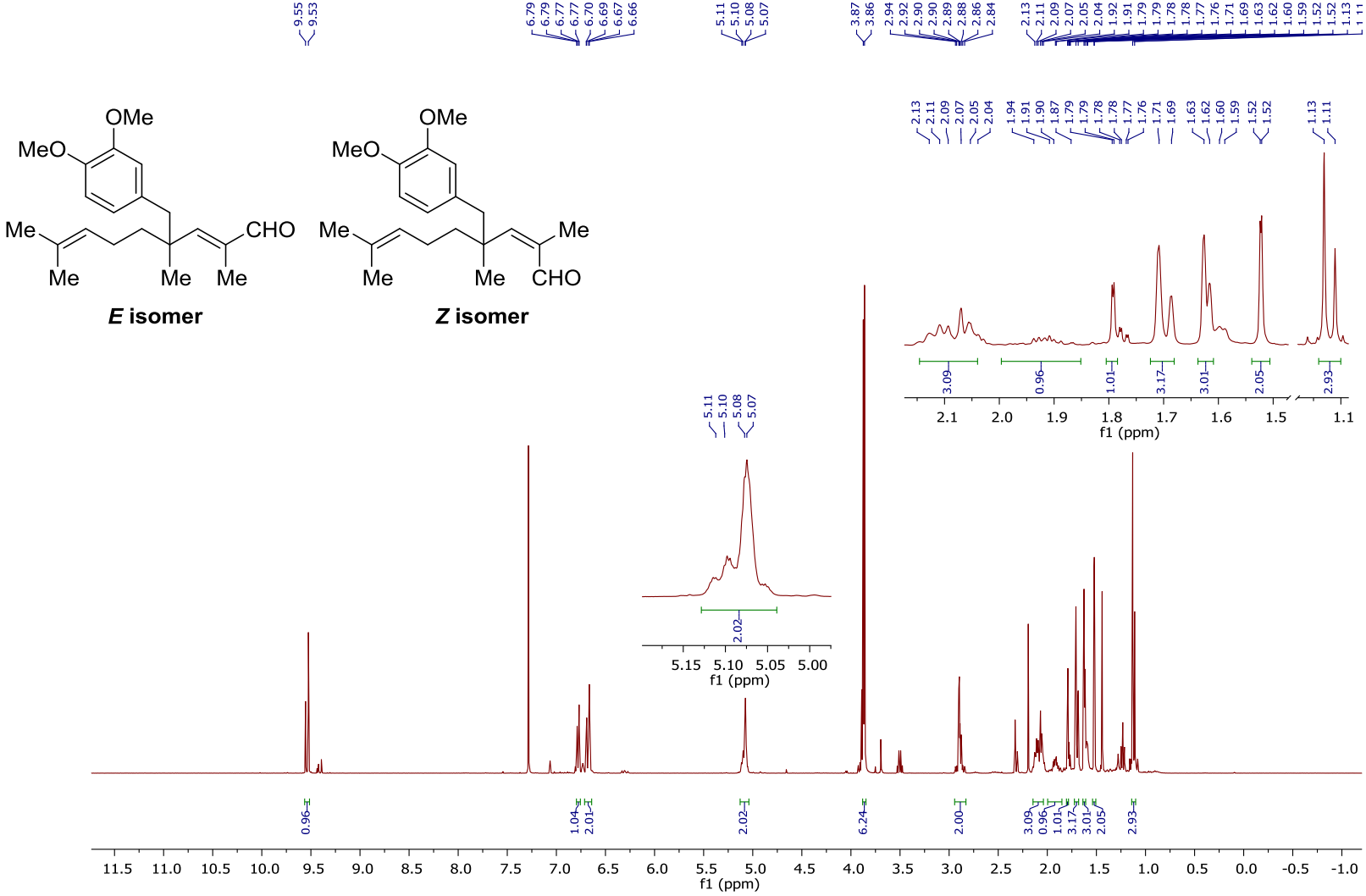
3-(3,4-dimethoxybenzyl)-3-methylcyclohex-1-enecarbaldehyde (12bn)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



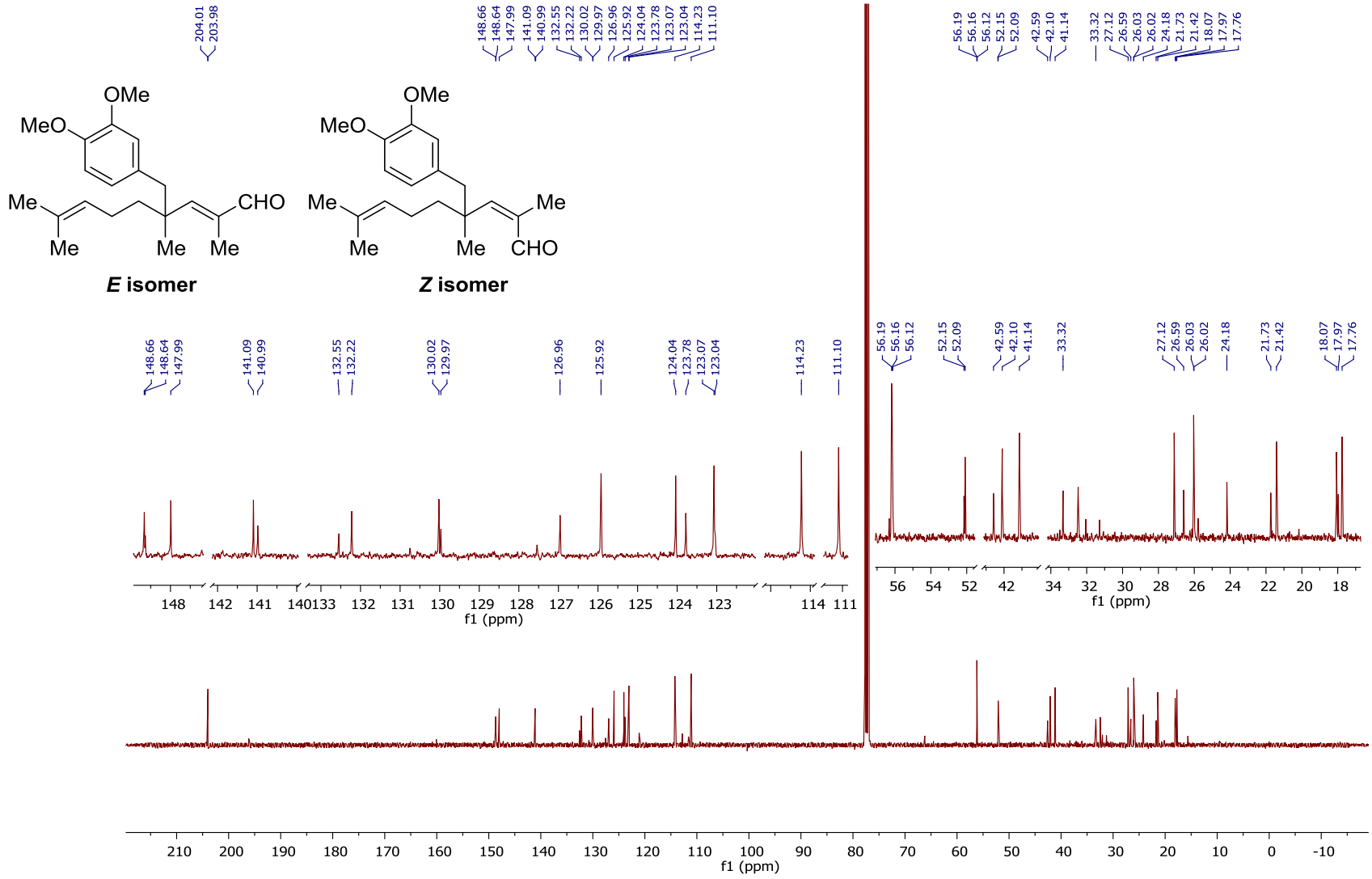
(*E*/*Z*)-4-(3,4-dimethoxybenzyl)-2,4,8-trimethylnona-2,7-dienal (12cn)

^{1}H NMR (400 MHz, $CDCl_3$):



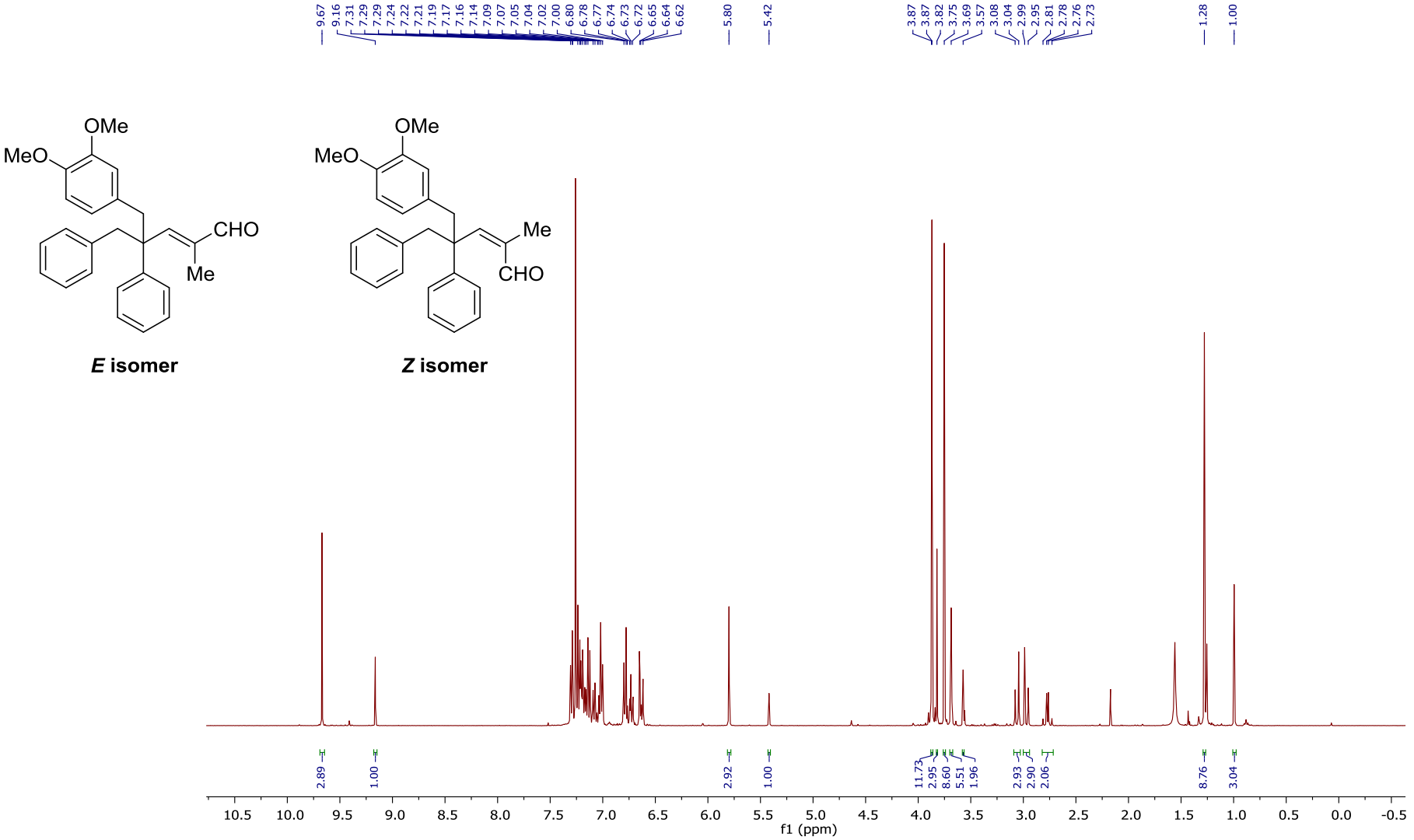
(*E*/*Z*)-4-(3,4-dimethoxybenzyl)-2,4,8-trimethylnona-2,7-dienal (12cn)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



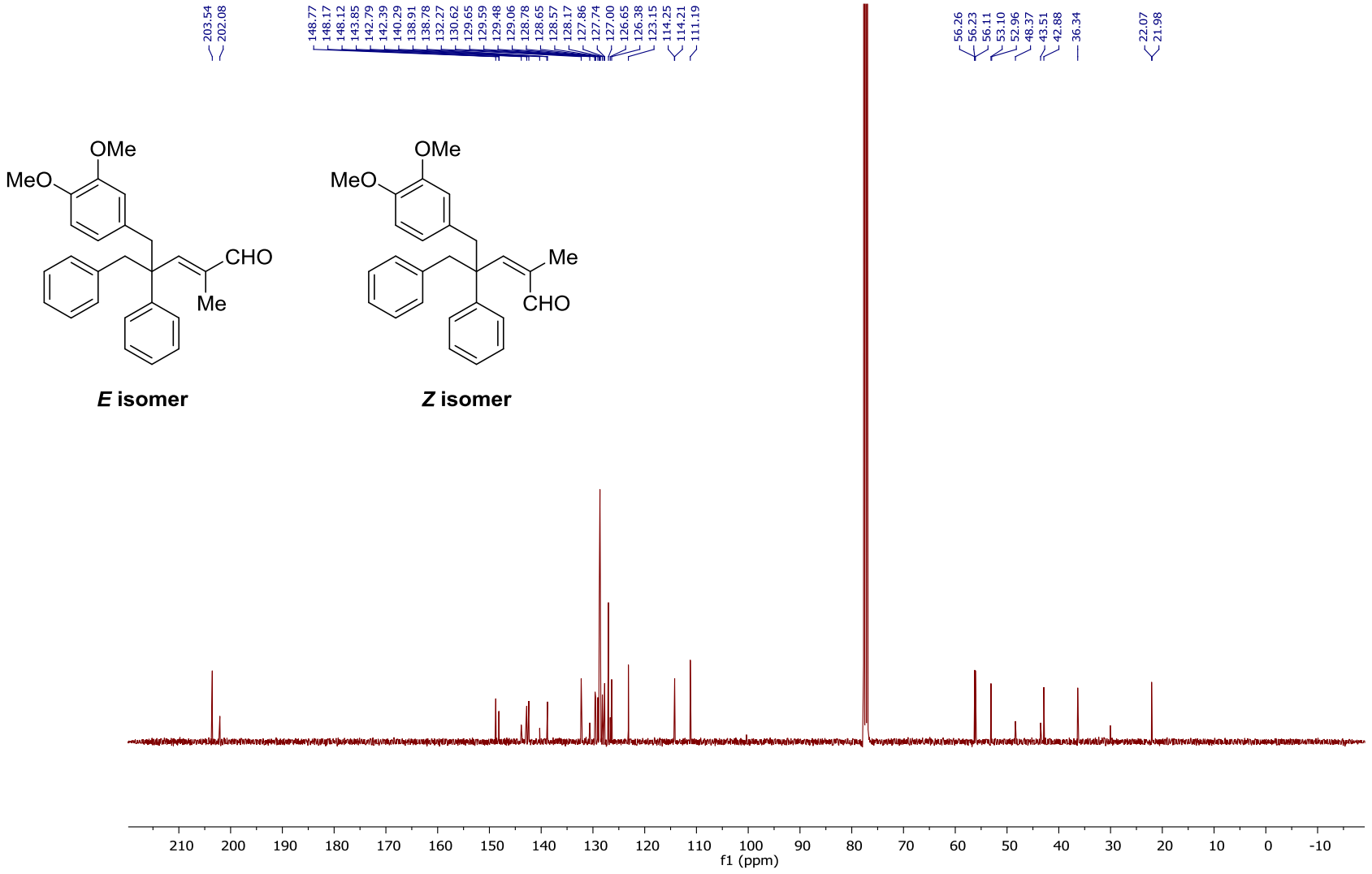
(*E*/*Z*)-4-benzyl-5-(3,4-dimethoxyphenyl)-2-methyl-4-phenylpent-2-enal (12dn)

^{1}H NMR (400 MHz, $CDCl_3$):



(*E/Z*)-4-benzyl-5-(3,4-dimethoxyphenyl)-2-methyl-4-phenylpent-2-enal (12dn)

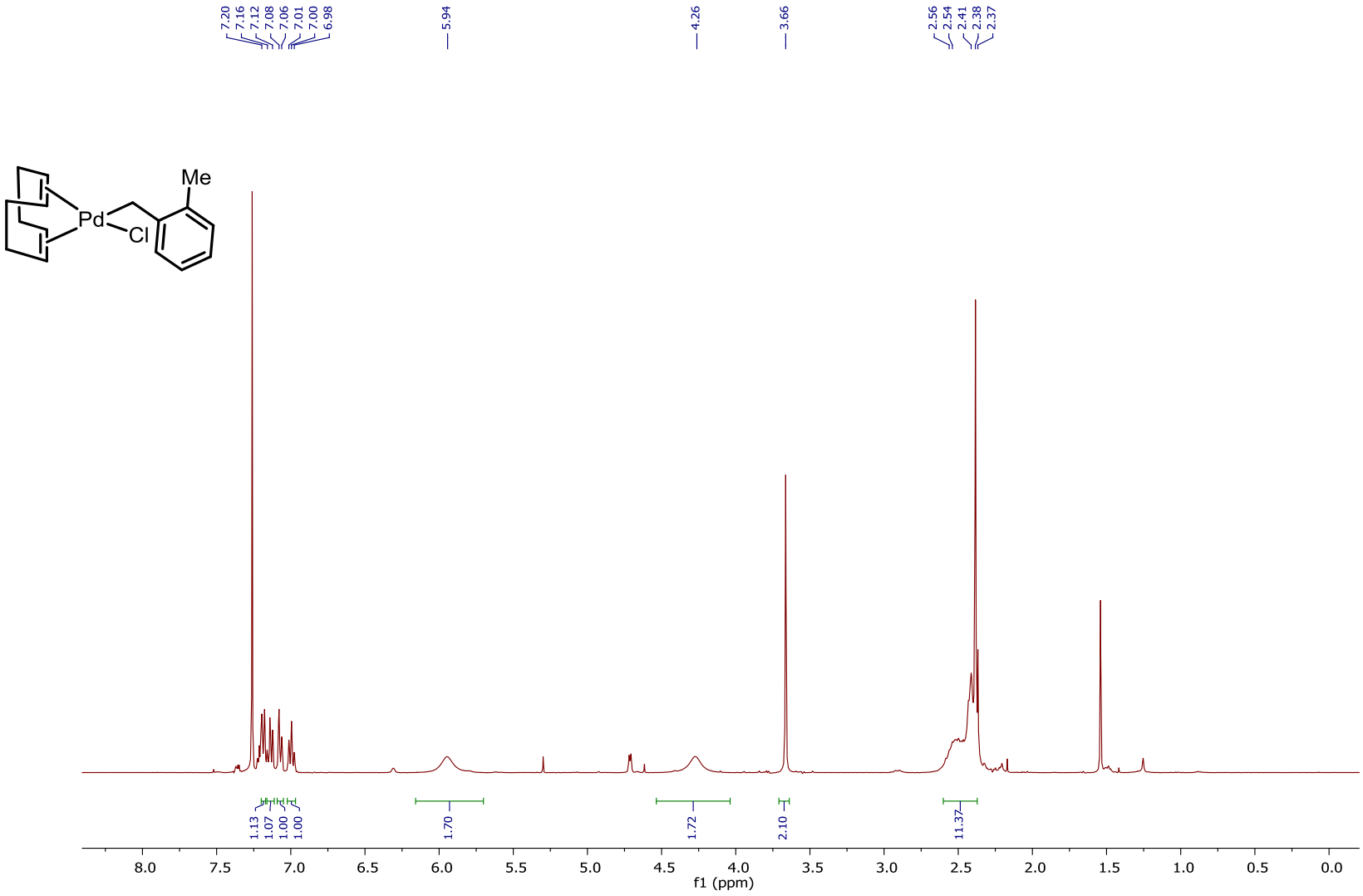
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



***E* isomer** ***Z* isomer**

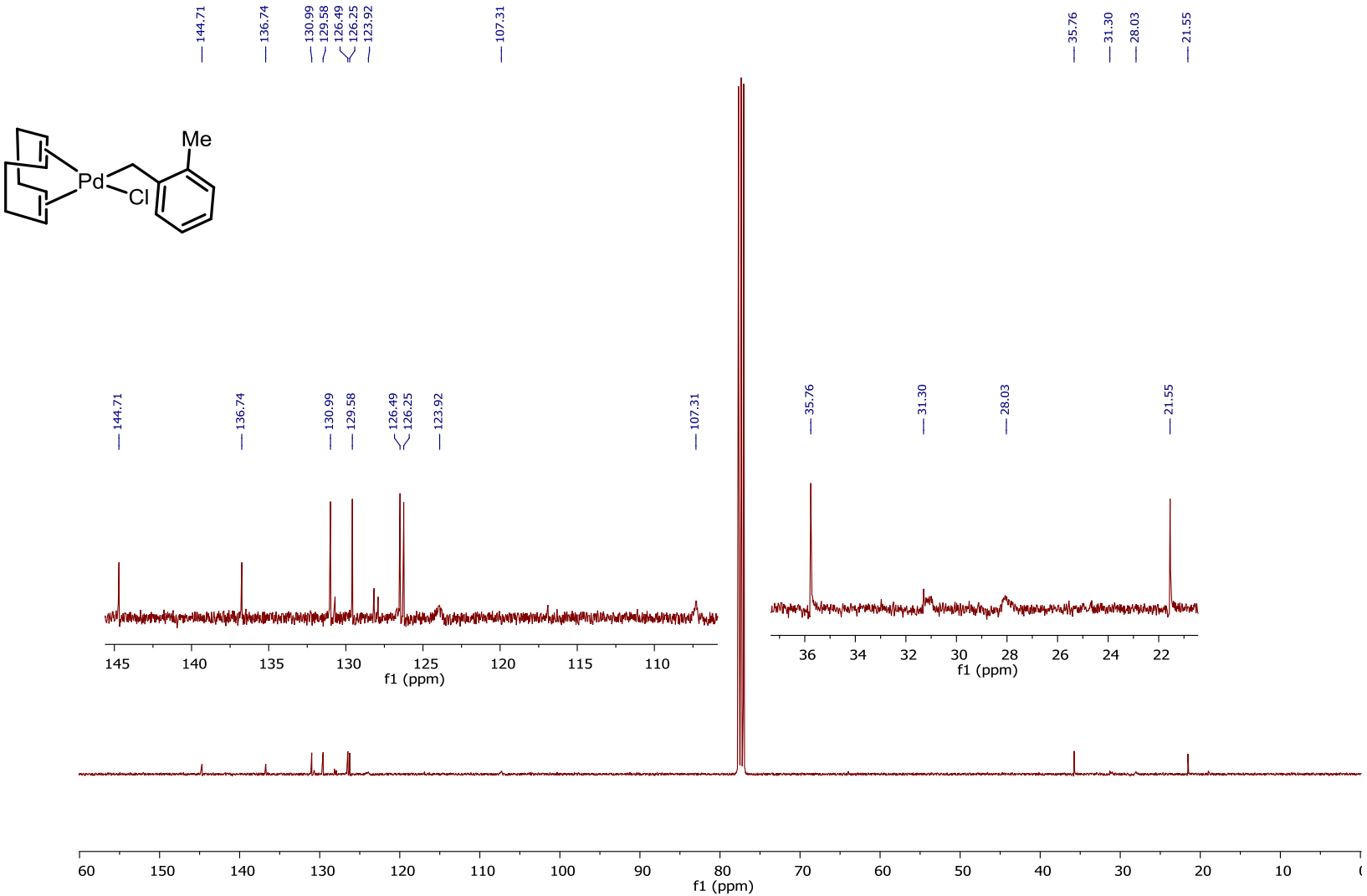
Chloro[(1,2,5,6-η)-1,5-cyclooctadiene][(2-methylphenyl)methyl]-palladium (9)

^{1}H NMR (400 MHz, $CDCl_3$):



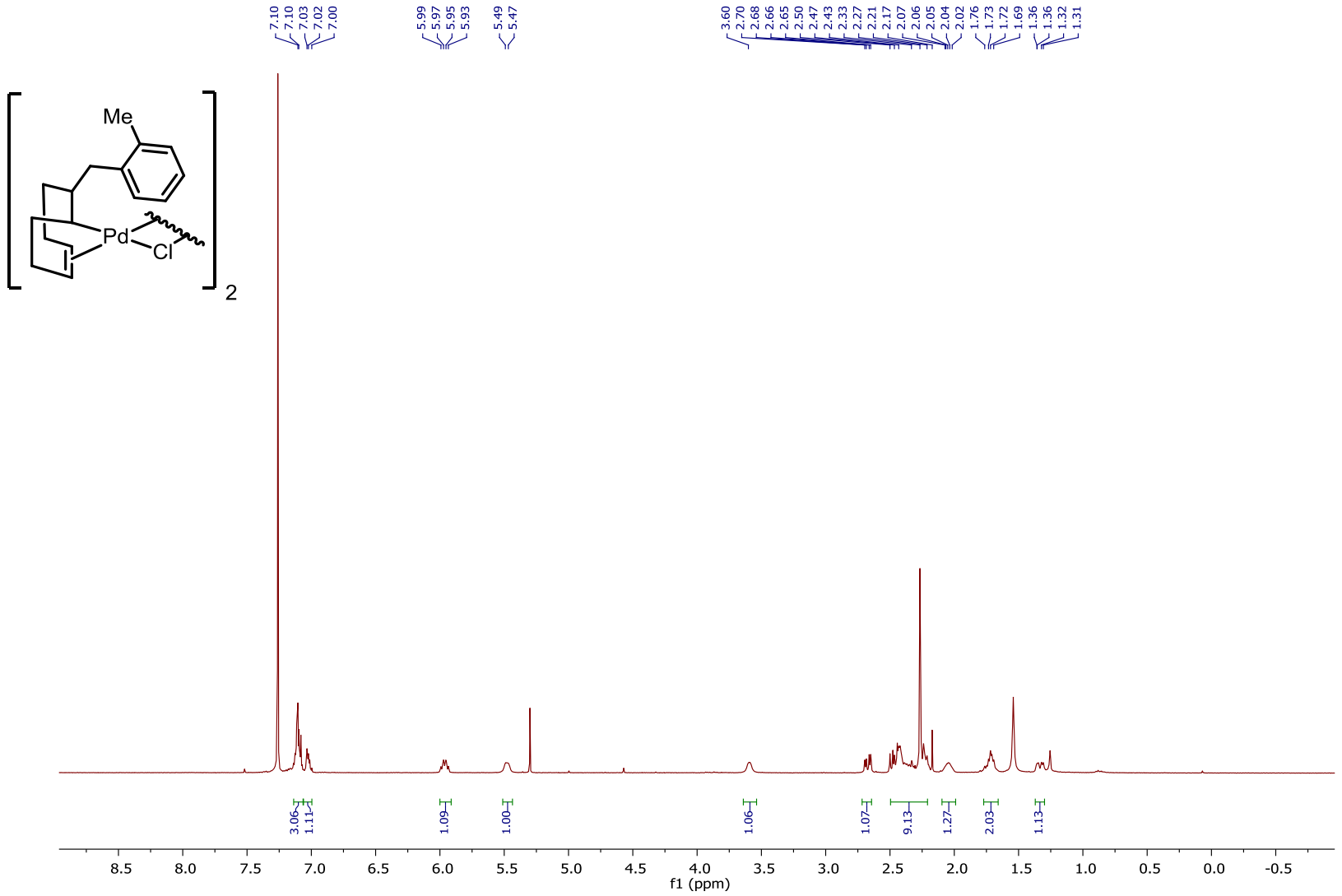
Chloro[(1,2,5,6-η)-1,5-cyclooctadiene][(2-methylphenyl)methyl]-palladium (9)

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



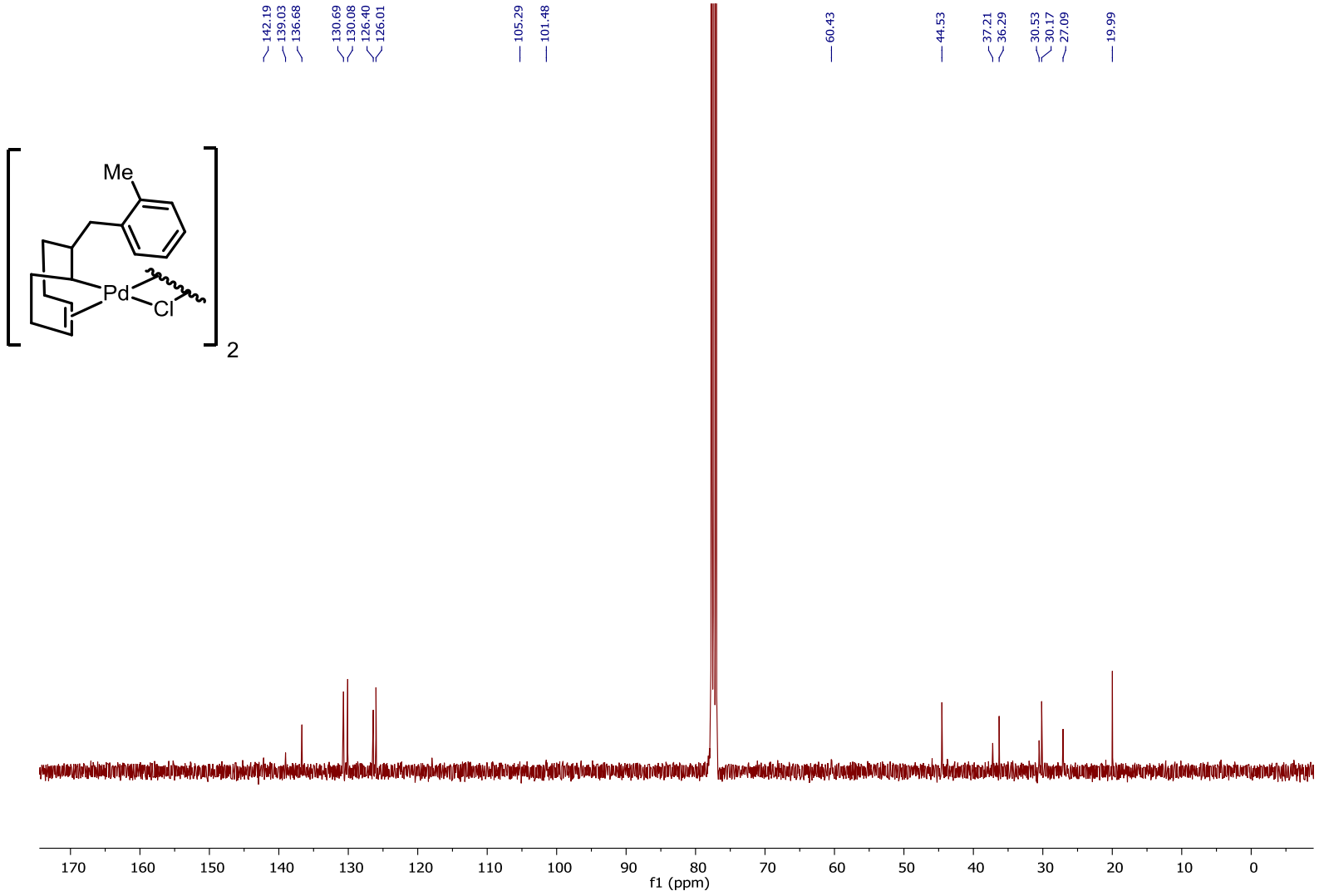
Di-μ-chloro[(1,4,5-η)-8-(2-methylbenzyl)-4-cycloocten-1-yl]dipalladium

^{1}H NMR (400 MHz, $CDCl_3$):



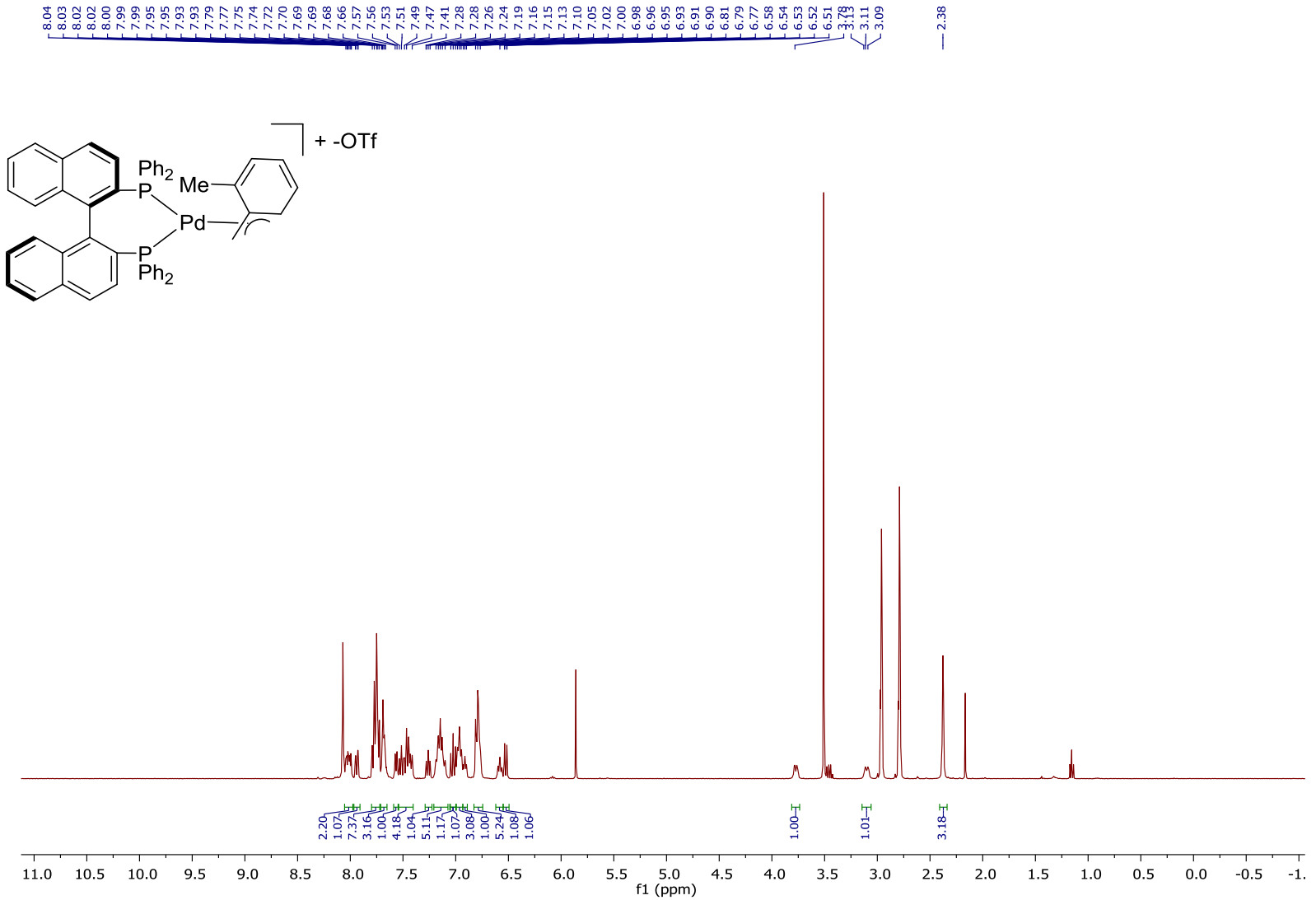
Di-μ-chloro[(1,4,5-η)-8-(2-methylbenzyl)-4-cycloocten-1-yl]dipalladium

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):



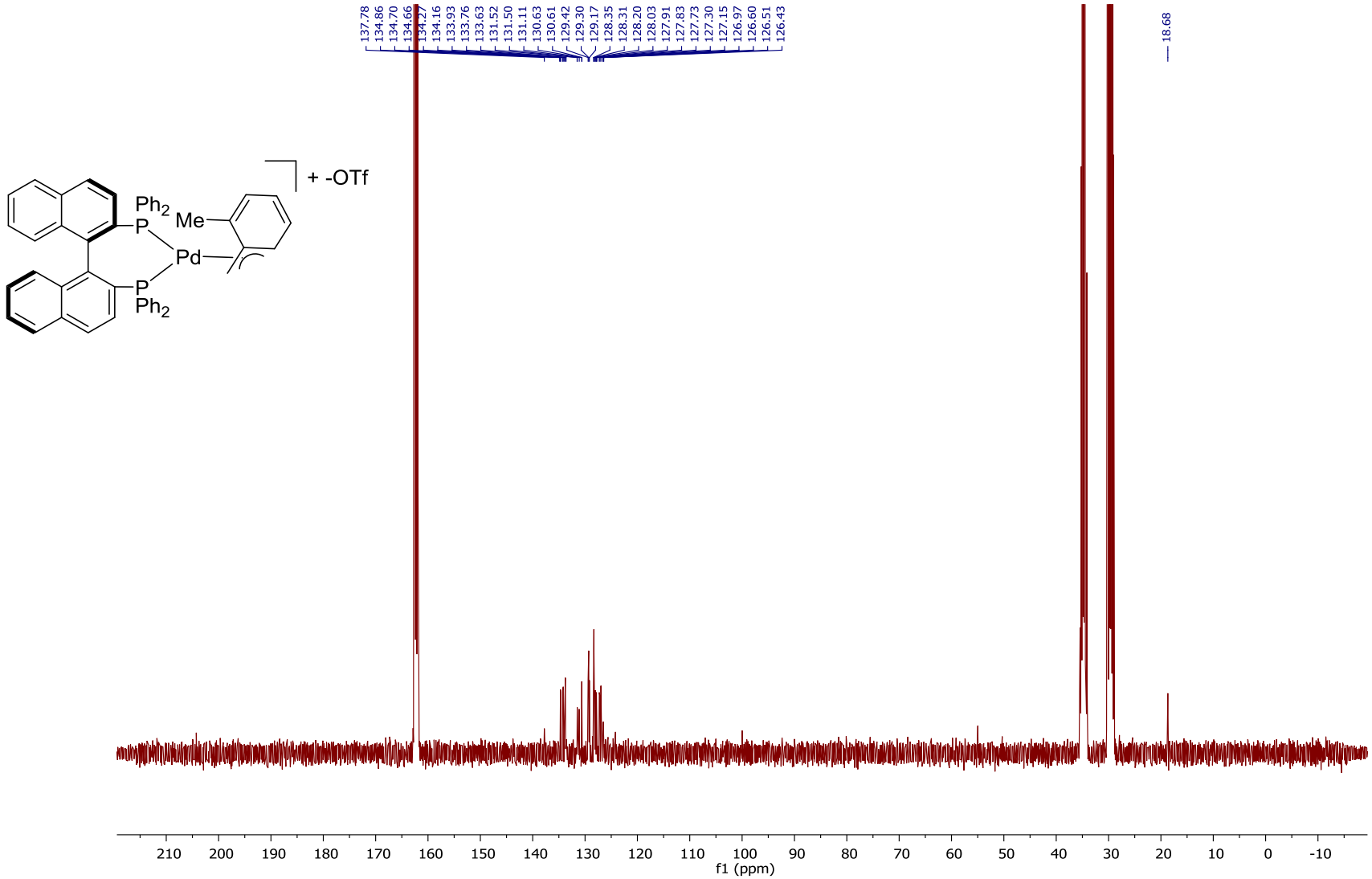
[(*R*)-(BINAP)Pd(2-methylbenzyl)]OTf (10)

^{1}H NMR (400 MHz, DMF-d_7):



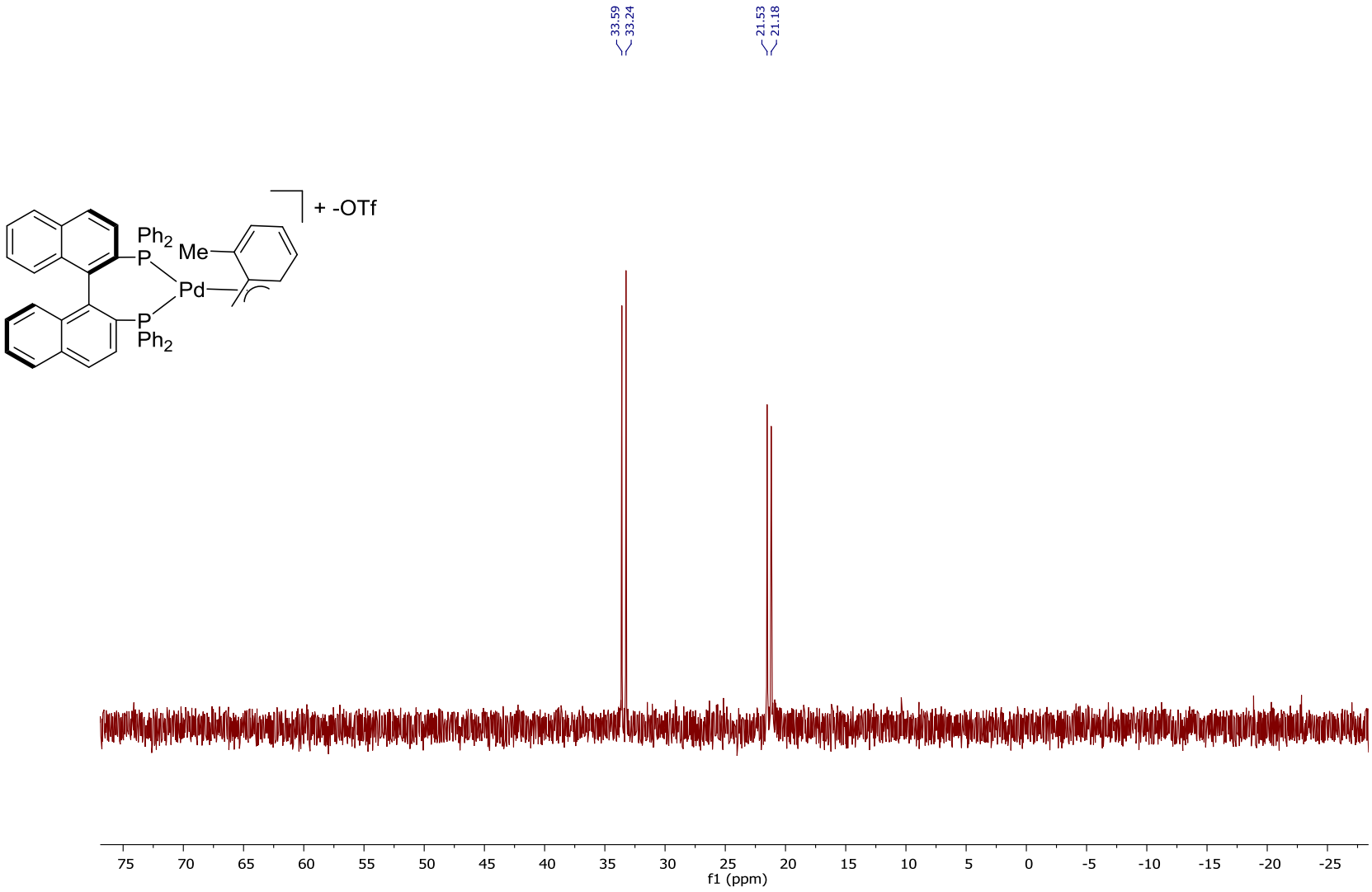
[(*R*)-(BINAP)Pd(2-methylbenzyl)]OTf (10)

$^{13}C\{^{1}H\}$ NMR (100 MHz, DMF-d_7):



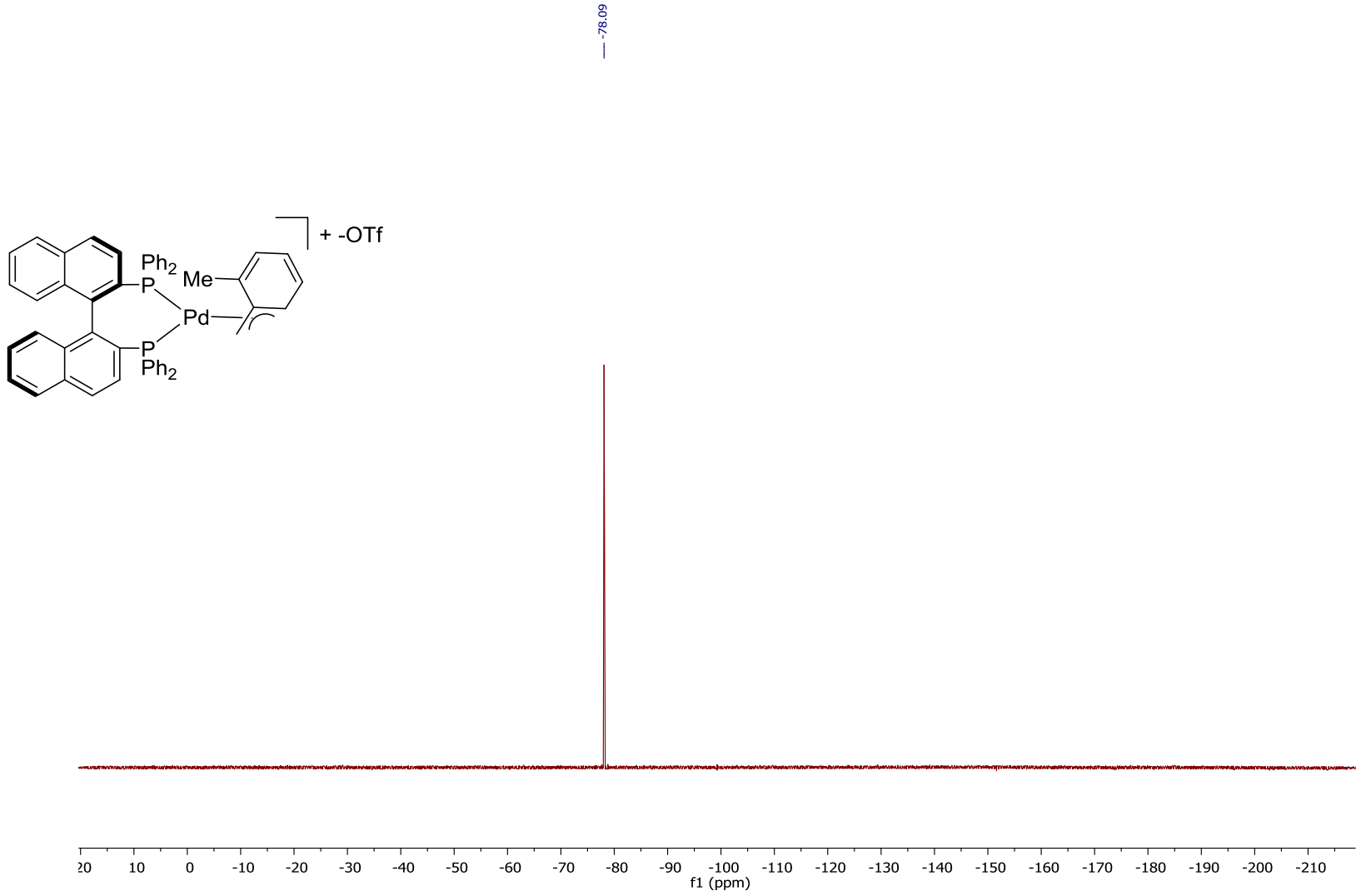
[(*R*)-(BINAP)Pd(2-methylbenzyl)]OTf (10)

$^{31}P\{^{1}H\}$ NMR (162 MHz, DMF-d_7):



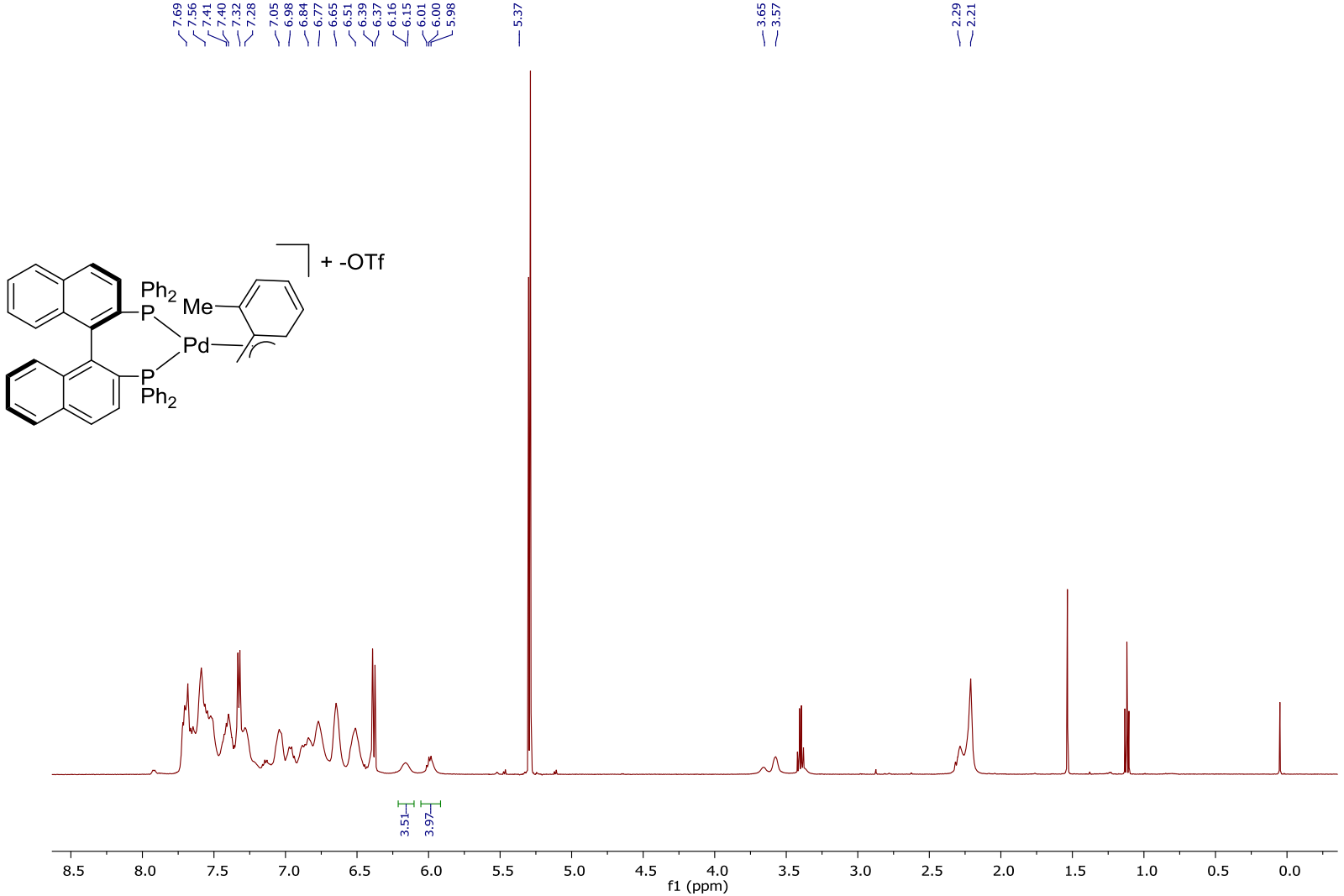
[(*R*)-(BINAP)Pd(2-methylbenzyl)]OTf (10)

$^{19}F\{^{1}H\}$ NMR (282 MHz, CD_2Cl_2):



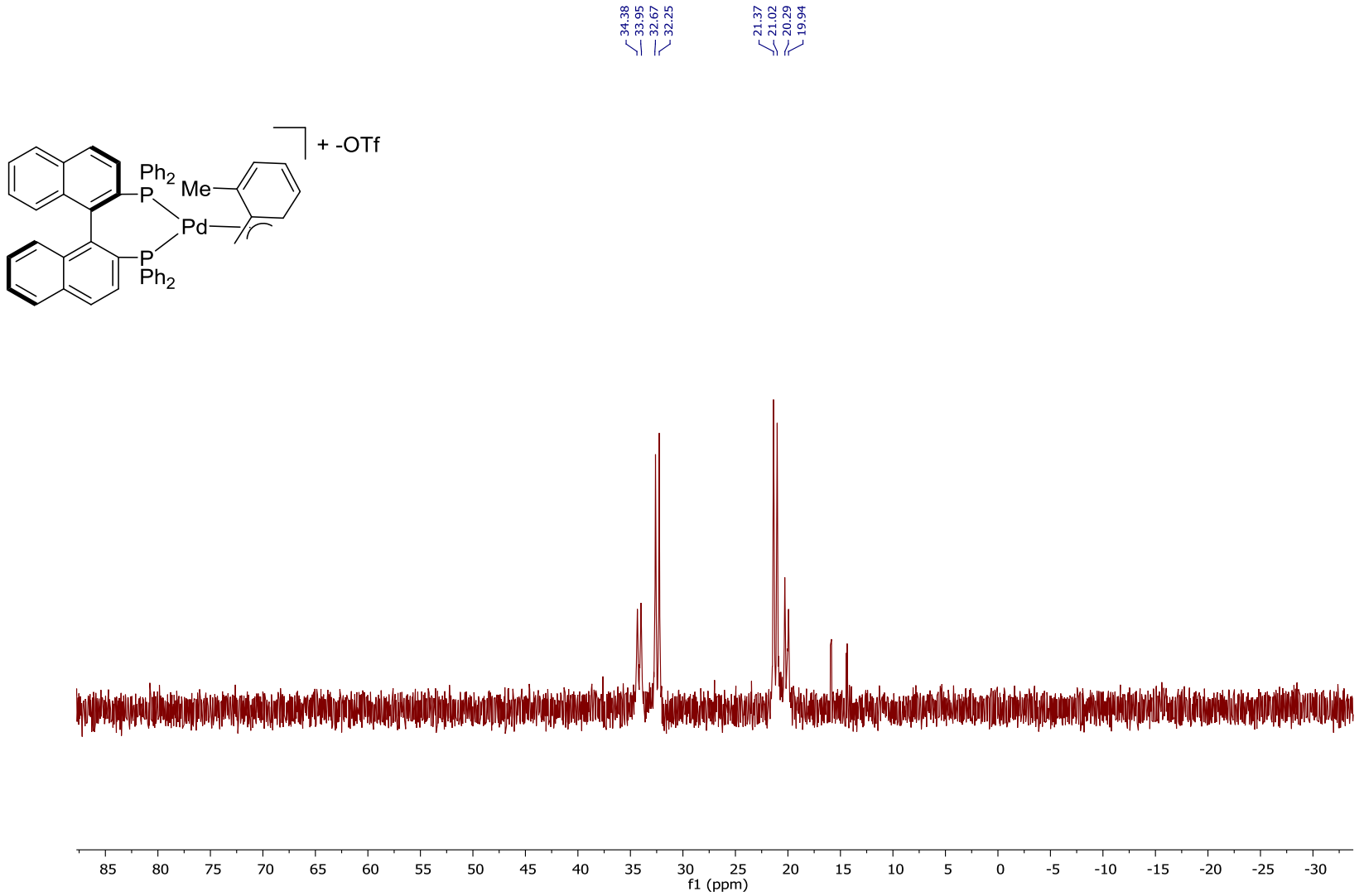
[(*R*)-(BINAP)Pd(2-methylbenzyl)]OTf (10)

^{1}HNMR (500 MHz, CD_2Cl_2, 298K):



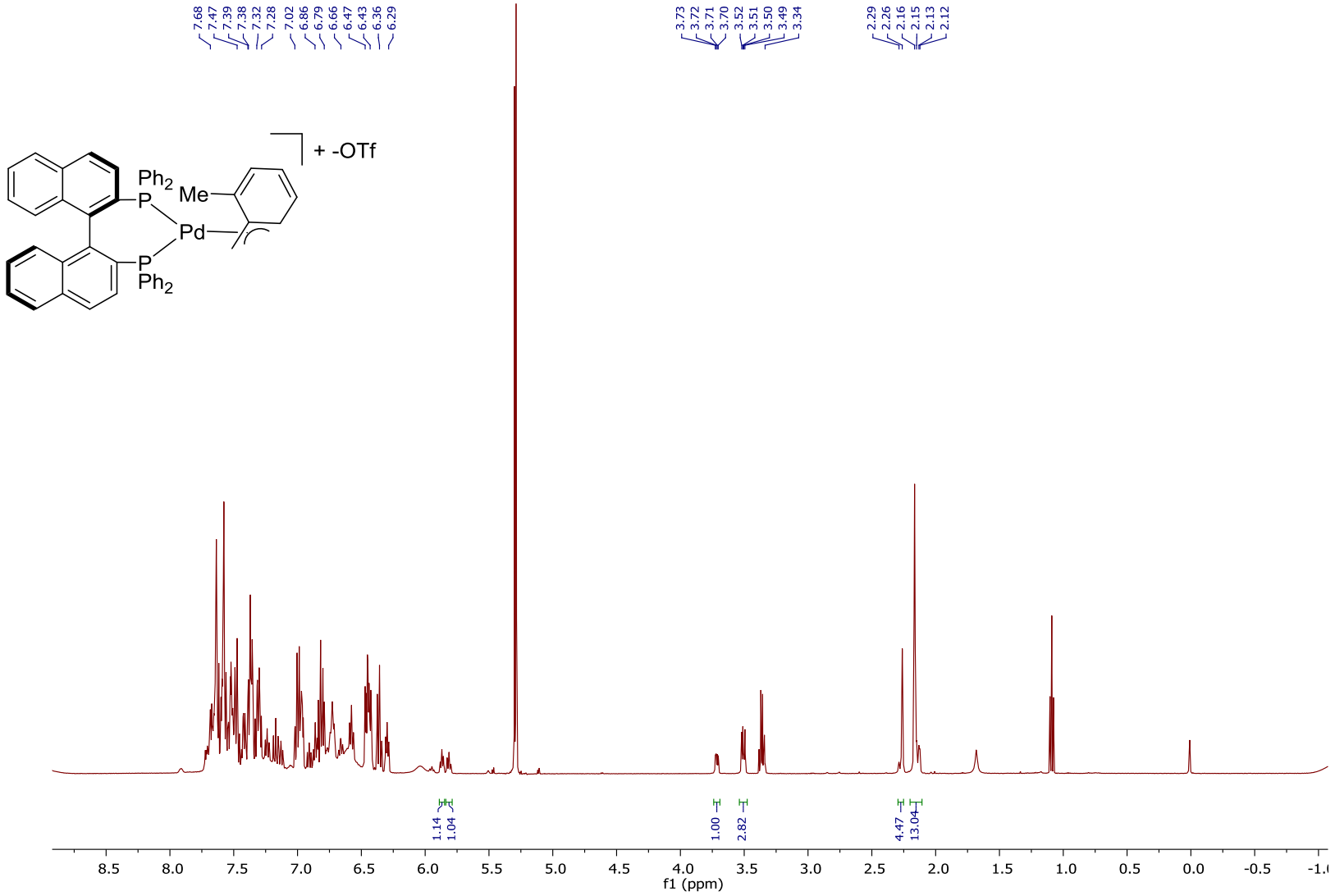
[(*R*)-(BINAP)Pd(2-methylbenzyl)]OTf (10)

$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2, 298K):



[(*R*)-(BINAP)Pd(2-methylbenzyl)]OTf (10)

^{1}HNMR (500 MHz, CD_2Cl_2, 243K):



[(*R*)-(BINAP)Pd(2-methylbenzyl)]OTf (10)

$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2, 243K):