Enantioselective Hydroformylation of 1-Alkenes with Commercial Ph-BPE Ligand

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Supporting Information

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General Information:

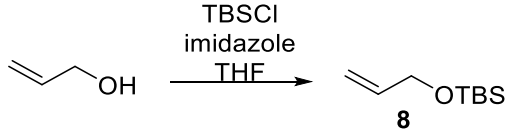
^{1}H-NMR spectra were recorded on a Varian Gemini-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as the following: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, app = apparent), and coupling constants (Hz). Coupling constants are reported to the nearest 0.5 Hz. ^{13}C NMR spectra were recorded on a Varian Gemini-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.23 ppm). Infrared (IR) spectra were recorded on a Burker alpha spectrophotometer, ν_{max} cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). High-resolution mass spectrometry (ESI) was performed at the Mass Spectrometry Facility, Boston College.

Liquid Chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230×450 Mesh) purchased from Silicycle. Thin Layer Chromatography was performed on 25 μm silica gel plates purchased from Silicycle. Visualization was performed using ultraviolet light (254 nm), potassium permanganate ($KMnO_4$) in water, 2,4-dinitrophenylhydrazine (2,4-DNP) in water/ethanol or phosphomolybdic acid (PMA) in ethanol. Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter. Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), toluene, diethyl ether (Et_2O) and dichloromethane (DCM) were purified using a Pure Solv MD-4 solvent purification system from Innovative Technology Inc. by passing through two activated alumina columns after being purged with argon. Hydroformylation reactions were performed in an Argonaut Technologies Endeavor® Catalyst Screening System or 100-600 mL pressure vessel by Parr Instrument Company with a gage block using 1:1 H_2/CO supplied by Airgas, Inc. (Acetylacetonato)dicarbonylrhodium (I) [$Rh(acac)(CO)_2$] and (−)-1,2-Bis((2*R*,5*R*)-2,5-diphenylphospholano)ethane [(*S,S*)-Ph-BPE] were purchased from Strem Chemicals, Inc. and used without further purification. All other reagents were purchased from Aldrich, Alfa Aesar, or Fisher and used without further purification.

I. Preparation of Terminal Olefins

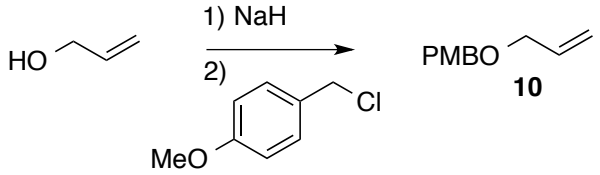
Preparation of (Allyloxy)(tert-butyl)dimethylsilane



8

t-Butyldimethylsilylallylether **8** (Table 1, entry 1) was prepared using a known procedure and all spectral data are in accordance with literature report.[1]

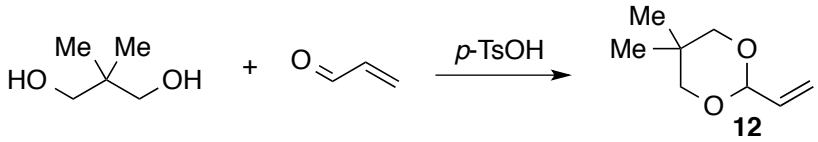
Preparation of 1-((allyloxy)methyl)-4-methoxybenzene



10

para-Methoxybenzyl allyl ether **10** (Table 1, entry 3) was prepared using a known procedure and all spectral data are in accordance with the literature report.[2]

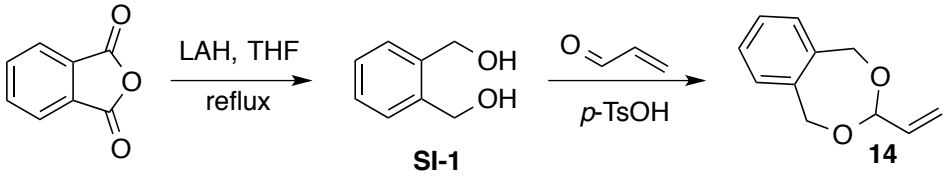
Preparation of 5,5-dimethyl-2-vinyl-1,3-dioxane



12

Acetal **12** (Table 1, entry 5) was prepared using a known procedure and all spectral data are in accordance with the literature report.[3]

Preparation of 3-vinyl-1,5-dihydrobenzo[e][1,3]dioxepine.



SI-1 **14**

1,2-Benzenedimethanol **SI-1** was prepared according to a literature procedure.[4]

Diol **SI-1** (3.3 g, 23.9 mmol) and catalytic (approximately 10 mg) *p*-TsOH were dissolved in dry CH_2Cl_2 (12 mL) in a 50 mL round bottom flask, and stirred with $MgSO_4$ under nitrogen. Acrolein (1.59 mL, 23.9 mmol) was added dropwise to the mixture at room temperature and stirred overnight. The resulting mixture was filtered and

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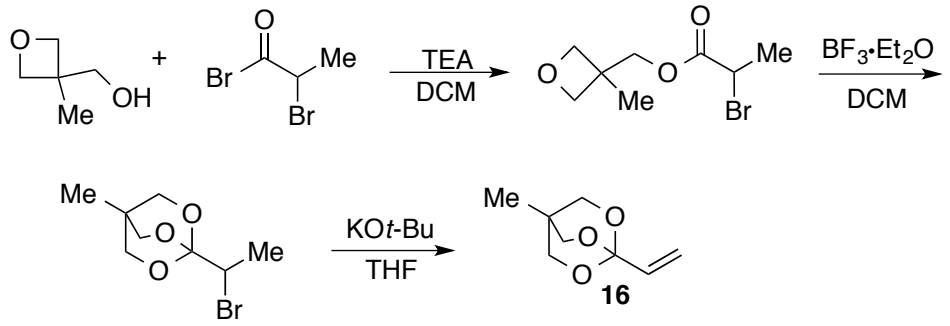
[1] Su, C. C.; Williard, P. G. *Org. Lett.* **2010**, *12*, 5378.
[2] Chênevert, R.; Dasser, M. *J. Org. Chem.* **2000**, *65*, 4529.
[3] Doumèche, B.; Archelas, A.; Furstoss, R. *Adv. Synth. Catal*. **2006**, *348*, 1948.
[4] Steffen, J.; Lei, X. G.; Li, W; Liu, Z. Q.; Turro, N. J.; Ottaviani, M. F.; Abrams, L. *J. Org. Chem*. **2002** , *67*, 2606.

concentrated. The residue was purified by silica gel chromatography to afford the titled compound **14** (Table 1, entry 6) as a colorless oil (3.3 g, 79% yield). All spectral data are in accordance with literature report.[5]

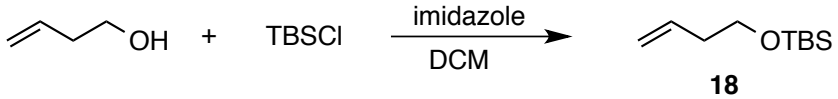
Preparation of 4-methyl-1-vinyl-2,6,7-trioxabicyclo[2.2.2]octane



16

Vinyl-trioxobicyclo[2.2.2.]octane **16** (Table 1, entry 6) was prepared using a known sequence from commercially available 3-methyl-3-oxetanemethanol and all spectral data are in accordance with the literature.[6]

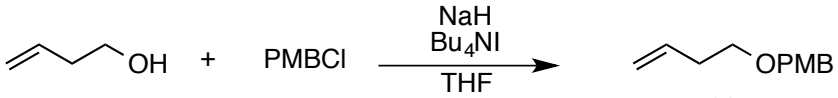
Preparation of (but-3-en-1-yloxy)(tert-butyl)dimethylsilane



18

Homoallylether **18** (Table 2, entry 1) was prepared using a known a procedure and all spectral data are in accordance with the literature.[7]

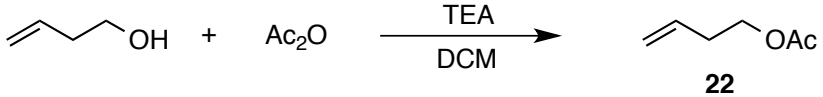
Preparation of 1-((but-3-en-1-yloxy)methyl)-4-methoxybenzene (20)



20

Homoallylether **20** (Table 2, entry 2) was prepared using known procedure and all spectral data are in accordance with the literature report.[8]

Preparation of 3-buten-1-yl acetate (22)



22

Homoallyl acetate **22** (Table 2, entry 3) was prepared by a known procedure and all spectral data are in accordance with the literature report.[9]

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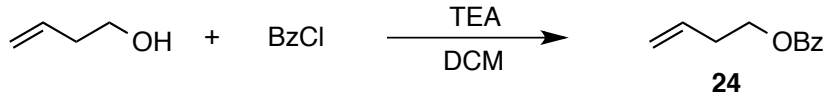
[5] Arab, K. E.; Hanan, A. Q,; Patrick, M. H. *J. Organomet. Chem.* **2002**, *656*, 168.
[6] Risi, R. M.; Burke, S. D. *Org. Lett*. **2012**, *14*, 2572.
[7] Ghosh, A. K.; Li, J. -F. *Org. Lett.* **2009**, *11*, 4164.
[8] Raghavan, S.; Krishnaiah, V. *J. Org. Chem.* **2010**, *75*, 748.

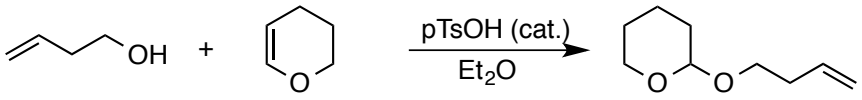
Preparation of but-3-en-1-yl benzoate (24)



24

Homoallyl benzoate **24** (Table 2, entry 4) was prepared by a known procedure and all spectral data are in accordance with the literature report.[10]

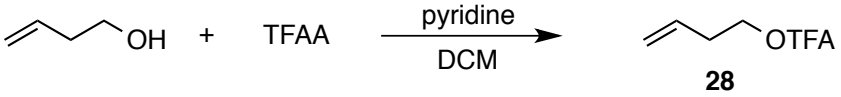
Preparation of 2-(but-3-en-1-yloxy)tetrahydro-2H-pyran (26)



26

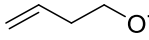
Tetrahydropyran **26** (Table 2, entry 5) was prepared using a known procedure and all spectral data are in accordance with the literature report.[11]

Preparation of but-3-en-1-yl 2,2,2-trifluoroacetate (28)



28

To a 25 mL round bottom flask equipped with a stir bar, was added 3-buten-1-ol (0.65 mL, 7.5 mmol) followed by dichloromethane (7.5 mL). The reaction was cooled to 0 °C in an ice bath and charged with pyridine (1.20 mL, 15.0 mmol) followed by drop-wise addition of trifluoroacetic anhydride (1.79 mL, 12.75 mmol). The reaction was allowed to stir at 0 °C for 14 hours. The reaction was then diluted with deionized water (10 mL) and extracted twice with diethyl ether (5 mL), the organic layers were combined and washed with 1M HCl (2 x 5 mL), saturated aqueous $NaHCO_3$, and saturated aqueous NaCl. The organic layer was then dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude product was purified by Kugelrohr distillation under N_2 at 100 °C to afford a light yellow oil (1.11g, 94 % yield).



But-3-en-1-yl 2,2,2-trifluoroacetate (28, Table 2): ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77 (1H, ddt, J = 17.0 Hz, 10.0 Hz, 7.0 Hz), 5.18 (1H, q, J = 1.5 Hz), 5.16-5.13 (1H, m), 4.40 (2H, t, J = 7.0 Hz), 2.50 (2H, dq, J = 7.0 Hz, 1.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.5 (q, J = 157.5), 132.3, 118.5, 114.5 (q, J = 283.9), 66.9, 32.5; ^{19}F (470 Hz, CDCl3): δ −75.2; IR (neat): 2958 (m), 2925 (s), 2871 (m), 2854 (m), 1734 (s), 1458 (m), 1262 (m), 1163 (m), 1029 (w) cm^{-1}; HRMS-(ESI+) for $C_6H_8F_3O_2$ [M+H]: calculated: 168.0476, found 167.0471.

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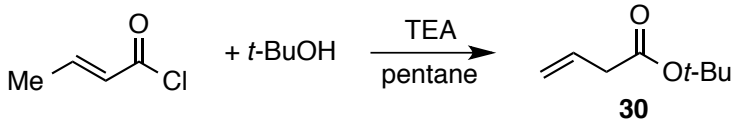
[9] Fürstner, A.; Müller, T. *Synlett.* **1997**, 1997, 1010.
[10] Zhang, M.; Vedanthanm, P.; Flynn, D. L.; Hanson, P. R. *J. Org. Chem.* **2004**, *69*, 8340.
[11] Hernandez, D.; Nielsen, L.; Lindsay, K. B.; Lopez-Garcia, A.; Bjerglund, K.; Skrydstrup, T.; *Org. Lett.* **2010**, *12*, 3528.

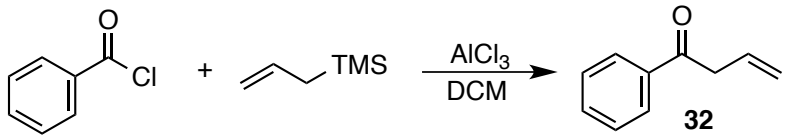
Preparation of but-3-enoic acid tert-butyl ester (30)



30

t-Butyl ester **30** (Table 2, entry 7) was prepared using a known procedure and all spectral data are in accordance with the literature report.[12]

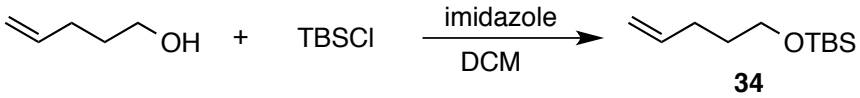
Preparation of 1-phenyl-but-3-en-1-one (32)



32

To an oven dried 50 mL round bottom flask with stir bar was added aluminum chloride (730.0 mg, 5.5 mmol). The flask was capped with a septa and purged with N_2. To this was added dichloromethane (20 mL) followed by dropwise addition of benzoyl chloride (0.58 mL, 5.0 mmol). The reaction was allowed to stir for 20 minutes prior to dropwise addition of allyltrimethylsilane (0.96 mL in 2.0 mL dichloromethane, 6.0 mmol). The reaction was allowed to stir for 4 hours at room temperature. The reaction mixture was quenched with ice-cold deionized water and washed three times with dichloromethane. The organic layers combined, dried over magnesium sulfate, concentrated *in vacuo* and purified on silica gel (30:1 pentane: diethyl ether) to afford **32** as a clear, colorless oil (866.4 mg, quantitative yield) (Table 2, entry 3). R_f= 0.31 (30:1 pentane: diethyl ether, stain in $KMnO_4$). All spectral data are in accordance with the literature.[13]

Preparation of (1,1-dimethylethyl)(dimethyl)(4-pentenyloxy)silane (34)

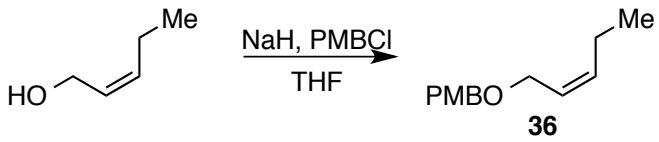


34

Bishomoallyl ether **34** (Table 2, entry 4) was prepared using literature procedure and all spectral data are in accordance with literature.[14]

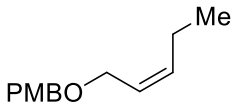
[12] Ramachandran, P.V.; Nicponski, D.; Kim, B. *Org. Lett.* **2013**, *15*, 1398.
[13] Moriyama, K.; Takemura, M.; Togo, H. *J. Org. Chem.* **2014**, *79*, 6094.
[14] (a) Kovtonyuk, V.N.; Kobrina, L.S.; Gatilov, Y.V.; Bagryanskaya, I.Y.; Fröhlich, R.; Haufe, G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1929. (b) Kwan, E.E.; Scheerer, J.R.; Evans, D.A. *J. Org. Chem.* **2013**, *78*, 175.

II. Preparation of p-Methoxybenzyl cis-2-pentenyl ether (36)



36

A flamed dried 100 mL round bottom flask with stir bar was charged with NaH (360 mg, 15 mmol) and 20 mL THF under N_2. After cooling to 0°C, *cis*-2-penten-1-ol (1.1 mL, 11 mmol) was added dropwise *via* syringe, which was allowed to stir at 0°C for 45 min. Then Bu_4NI (50 mg, catalytic) and PMBCl (1.4 mL, 10 mmol) were added sequentially at 0°C, and the solution was allowed to warm to room temperature and stir overnight. The reaction was quenched with NH_4Cl aqueous solution and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organics were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by silica gel chromatography (diethyl ether : hexanes = 1:10) to afford **36** as a clear, colorless oil. R_f = 0.53 (6:1 hexanes: diethyl ether, stain in $KMnO_4$).



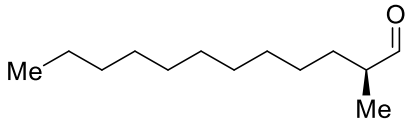
(*Z*)-1-Methoxy-4-((pent-2-en-1-yloxy)methyl)benzene (Scheme 4, 36). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (2H, d, *J* = 9.5 Hz), 6.88 (2H, d, *J* = 9.0 Hz), 5.60-5.54 (2H, m), 4.44 (2H, s), 4.04 (2H, d, *J* = 6.0 Hz), 3.81 (3H, s), 2.06 (2H, quin, *J* = 7.5 Hz), 0.97 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.4, 135.6, 130.8, 129.6, 125.7, 114.0, 71.9, 65.5, 55.5, 21.1, 14.4; IR (neat): 3011 (w), 2836 (w), 1613 (m), 1513 (s), 1463 (w), 1302 (m), 1247 (s), 1172 (m), 1082 (s), 1036 (s), 820 (s) cm^{-1}.

III. Procedure of Asymmetric Hydroformylation Reactions

Representative Procedure A: (Argonaut Technologies Endeavor®, 0.5% catalyst loading): Reactions were conducted in an Argonaut Endeavor® reactor system which has eight reactor wells. Each well to be used was charged with approximately 0.5 mL of toluene in an oven dried glass vial. The Endeavor was sealed and purged with nitrogen (4 x 100 psi). Meanwhile an oven-dried two dram-vial in dry box under an argon atmosphere was charged with alkene (1.0 mmol) and 0.5 mL of toluene followed by 0.5 mL of a rhodium/ligand stock solution (0.010 M $Rh(acac)(CO)_2$/0.011M (*S,S*)-PhBPE in toluene). The reaction mixture was then taken up in a syringe, removed from dry box and injected into the Endeavor. After injection the Endeavor was purged with nitrogen (1 x 100 psi), stirred at 250 rpm, and heated to 80 °C for 10 min. Stirring was stopped and the Endeavor charged with 150 psi of syngas (1:1 CO/H_2), stirring was brought to 700 rpm and heated to desired reaction temperature (80 °C). When the reaction was complete (indicated by syngas uptake) the Endeavor was vented, cooled and the vials were removed before the solvent evaporated *in vacuo.*

Representative Procedure B: (Parr Reactor, 0.5% catalyst loading): To an oven-dried two dram vial with stir bar in dry box under an argon atmosphere was added alkene (1.0 mmol) and 0.5 mL of toluene. The vial was then charged with 0.5 mL of a rhodium/ligand stock solution (0.010 M $Rh(CO)_2acac$/0.011M (*S,S)*-PhBPE in toluene) and sealed with a septum cap and removed from dry box. At this time the reaction vial was brought to the pressure vessel and the septa cap pierced with a 22-gauge sterile needle and then the reactor was sealed and pressurized with 500 psi of Synthesis gas (1:1 CO/H_2). Once pressurized the gas was slowly allowed to vent until the parr reactor gauge read 0 psi, the parr reactor was then pressurized and vented two more times in the same manner before pressurizing to the final desired reaction pressure. Following this purging process the parr reaction was placed in an oil bath, heated to the desired temperature and allowed to stir at 800 rpm for the desired reaction time. At the end of the reaction the oil bath was removed and parr reactor allowed to cool and then placed in an ice bath before venting. The vial was removed and the solvent evaporated *in vacuo.*

IV. Characterization of Reaction Products and Analysis of Stereochemistry

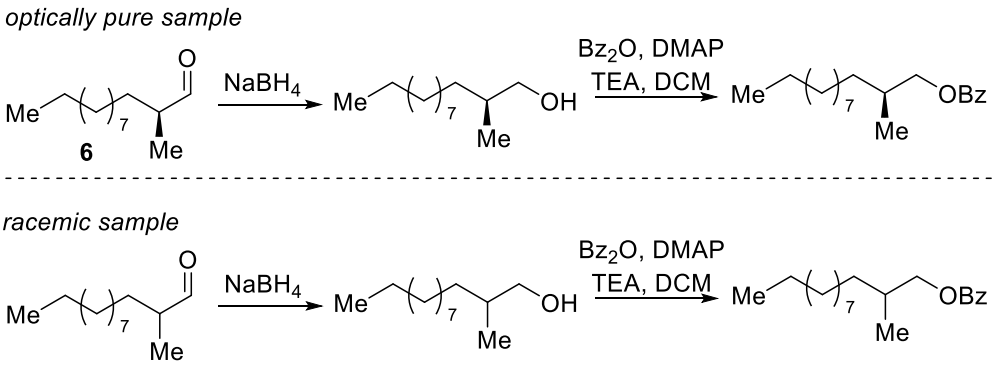


(*S*)-2-Methyldodecanal (6, Scheme 2): The title compound was prepared *via* Representative Procedure **A** with 1-dodecene **5**. The crude reaction mixture was purified on silica gel (100% pentane to 40:1 pentane:

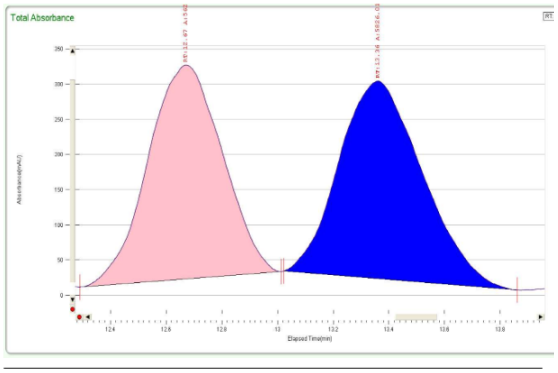
diethyl ether) to afford a clear, colorless oil (mixture of branched and linear isomers, 196 mg, 99% yield). R_f = 0.07 (40:1 pentane: diethyl ether, stain in 2,4-DNP). $[\alpha]^{22}_D$ = +38.667 (*c* = 0.421, $CHCl_3$, *l* = 50 mm). Spectral data are in accordance with literature.[15]

Analysis of Stereochemistry:

The titled compound **6** was subjected to $NaBH_4$ reduction followed by benzoate protection, as depicted below. The analogous racemic material was prepared *via* the same route, using triphenylphoshine as achiral ligand in the hydroformylation reaction. Optical purity was determined by SFC analysis of the derived benzoate. Absolute stereochemistry was determined by analogy to the optical rotation of (*S*)-2-methyldecanal reported in the literature.[16]



Chiral SFC (Chiralpak, AD-H, 35 °C, 3 mL/min, 2% mixed solvent (Isopropanol:hexane = 1:1) 100 bar, 210-270 nm) – analysis of benzoate.



Enatnioenriched Sample

Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
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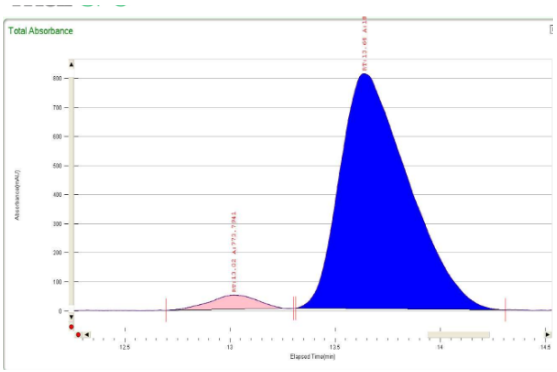
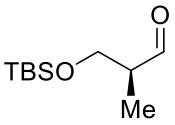
2	50.8977	5826.0112	13.36
Total:	100	11446.5076	



Racemic Sample

Peak Info			
Peak No	**% Area**	**Area**	**RT (min)**
1	4.057	773.7941	13.02
2	95.943	18299.1306	13.64
Total:	100	19072.9247	

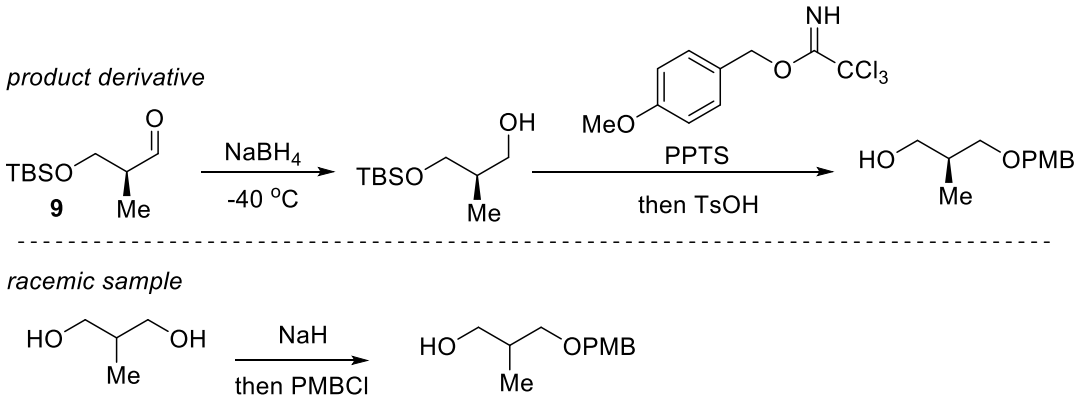
[15] Wakabayashi, T.; Mori, K.; Kobayashi, S. *J. Am. Chem. Soc.* **2001**, *123*, 1372.
[16] Oppolzer, W.; Darcel, C.; Rochet, P.; Rosset, S.; Brabander, J. D. *Helv. Chim Acta* **1997**, *80*, 1319.



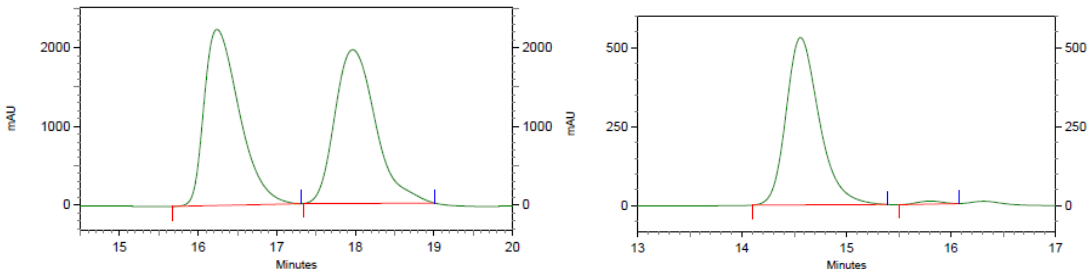
(*S*)-3-((*tert*-Butyldimethylsilyl)oxy)-2-methylpropanal. (9, Table 1). Representative procedure **A** was used with the following modifications. Olefin **8** (7.7 g, 45 mmol), $Rh(acac)(CO)_2$ (4.6 mg, 0.018 mmol), (*S,S*)-Ph-BPE (17.4 mg, 0.022 mmol) and toluene (5.1 mL). The reaction was stopped with full conversion observed after 8 h. The crude reaction mixture was purified on silica gel (hexane: diethyl ether = 20:1) to afford a clear colorless oil (6.54 g, 72% yield). $[\alpha]^{21}_D$ = +31.942 (*c* = 0.72, $CHCl_3$, *l* = 50 mm). All spectral data are in accordance with literature.[17]

Analysis of Stereochemistry

The titled compound **9** was converted to the corresponding *p*-methoxybenzyl ether as shown below. The resulting benzyl ether was compared to racemic material prepared from 2-methyl-propan-1,3-diol. Absolute stereochemistry was assigned by comparing optical rotation to literature $[\alpha]^{22}_D$ = +19.5 (*c* = 1.00, $CHCl_3$, *l* = 50 mm).[17]



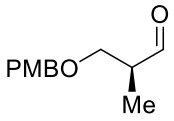
Chiral HPLC (Chiralpak, AD-H, 25 °C, 3 mL/min, 5% Isopropanol in hexane, 220 nm) – analysis of benzyl ether.



VWD: Signal A, 220 nm Results

Retention Time	Area	Area %	Height	Height %
14.560	196559679	98.65	8892358	98.20
15.803	2689437	1.35	163313	1.80
Totals	199249116	100.00	9055671	100.00

[17] Altendorfer, M.; Raja, A.; Sasse, F.; Irschikc, H.; Menche, D. *Org. Biomol. Chem.* **2013**, *11*, 2116.

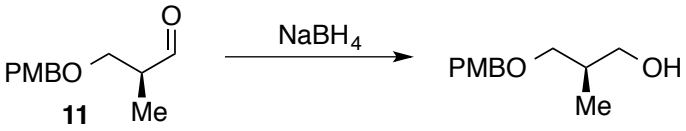


(*S*)-3-((4-Methoxybenzyl)oxy)-2-methylpropanal (11, Table 1). The title compound was prepared *via* representative procedure **B** using olefin **10**. The crude reaction mixture was purified on silica gel (2:1 pentane: diethyl ether) to afford a clear, colorless oil (136 mg, 78% yield). R_f = 0.78 (1:1 pentane: diethyl ether, stain in $KMnO_4$). $[\alpha]^{21}_D$ = +28.886 (*c* = 0.72, $CHCl_3$, *l* = 50 mm). All spectral data are in accordance with literature report.[17]

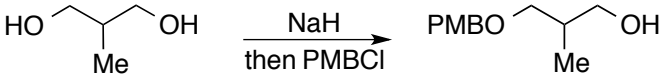
Analysis of Stereochemistry:

The titled compound **11** was reduced to the corresponding *p*-methoxybenzyl ether as shown below. The resulting benzyl ether was compared to racemic material prepared from 2-methyl-1,3-propanediol as shown below. Absolute stereochemistry was assigned by comparing optical rotation to literature $[\alpha]^{22}_D$ = +30.5 (*c* = 1.00, $CHCl_3$).[17]

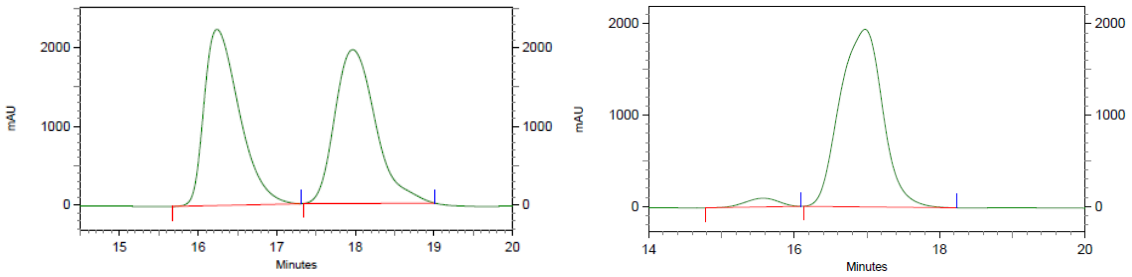
optically pure sample



racemic sample

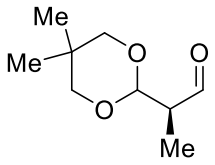


Chiral HPLC (Chiralpak, AD-H, 25 °C, 3 mL/min, 5% Isopropanol in hexane, 220 nm) – analysis of benzyl ether.



VWD: Signal A, 220 nm Results

Retention Time	Area	Area %	Height	Height %
15.573	50852879	3.68	1602594	4.69
16.977	1332416422	96.32	32587530	95.31
Totals	1383269301	100.00	34190124	100.00

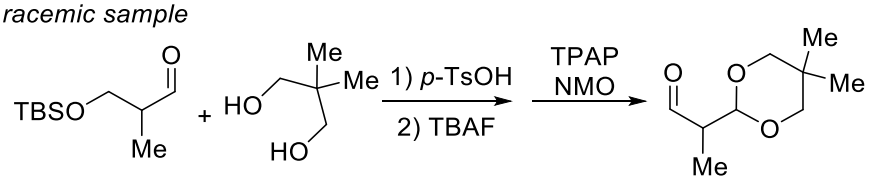


(*R*)-2-(5,5-Dimethyl-1,3-dioxan-2-yl)propanal (13, Table 1). The title compound was prepared *via* representative procedure **B** using olefin **12**. The crude reaction mixture was purified on silica gel (4:1 pentane: diethyl ether) to afford a yellow oil (157 mg, 92% yield). R_f = 0.57 (4:1 pentane: diethyl ether, stain in $KMnO_4$) $[\alpha]^{21}_D$ = +53.630 (*c* = 0.88, $CHCl_3$, *l* = 50 mm). All spectral data are in accordance with literature report.[18]

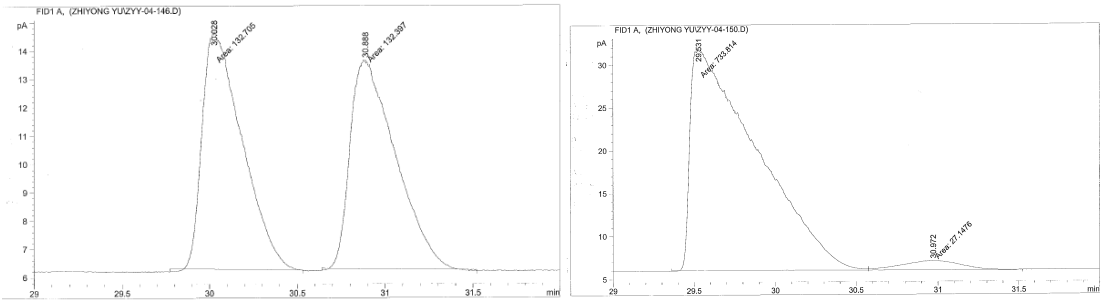
Analysis of Stereochemistry:

The titled compound **13** was compared to racemic material. Absolute stereochemistry was assigned by analogy.

racemic sample

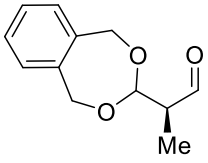


*Chiral GC (β-dex-120, supelco, 100 °C, 20 psi)-analysis of **13**.*



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.531	MF	0.4738	733.81372	25.81345	96.43245
2	30.972	FM	0.4149	27.14764	1.09051	3.56755

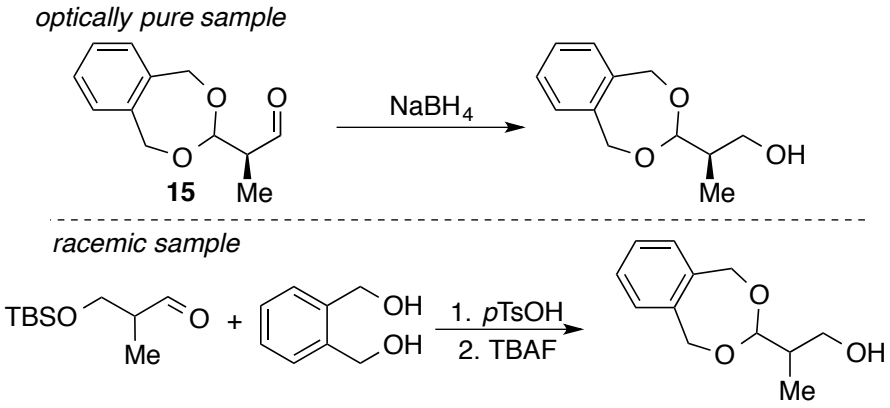
[18] Tanaka, K.; Fujimori, Y.; Saikawa, Y; Nakata, M. *J. Org. Chem.* **2008**, *73*, 6292.



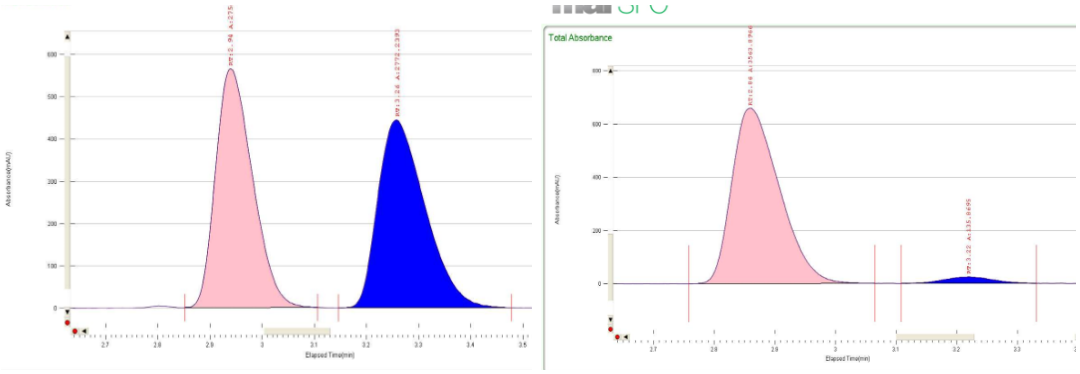
(*R*)-2-(1,5-Dihydrobenzo[e][1,3]dioxepin-3-yl)propanal (15, Table 1). The title compound was prepared *via* representative procedure **B** using olefin **14**. The crude reaction mixture was purified on silica gel (4:1 pentane: diethyl ether) to afford a white solid (185 mg, 90% yield). R_f= 0.17 (4:1 pentane: diethyl ether, stain in CAM). $[\alpha]^{21}_D$= +46.492 (*c* = 0.90, $CHCl_3$, *l* = 50 mm). All spectral data are in accordance with the literature.[19]

Analysis of Stereochemistry:

The titled compound **15** was converted to the corresponding alcohol as shown below. The resulting alcohol was compared to racemic material prepared from racemic aldehyde as shown below. Absolute stereochemistry was assigned by analogy.



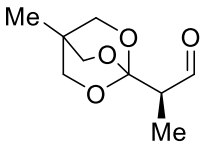
Chiral SFC (Chiralpak, AS-H, 35 °C, 5 mL/min, 5% Isopropanol, 100 bar, 210-270 nm) – analysis of alcohol.



Peak Info			
Peak No	% Area	Area	RT (min)
1	49.8582	2756.5624	2.94
2	50.1418	2772.2393	3.26
Total:	100	5528.8017	

Peak Info			
Peak No	% Area	Area	RT (min)
1	96.3276	3563.8966	2.86
2	3.6724	135.8695	3.22
Total:	100	3699.7661	

[19] Yu, Z, -Y., Ely, R. J.; Morken, J. P. *Angew. Chem. Int. Ed*. **2014**, *53*, 9632.

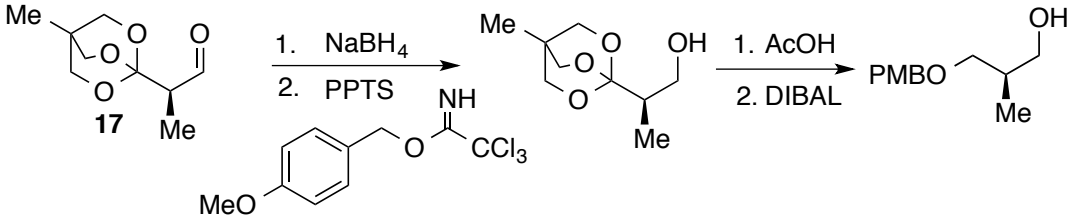


(*R*)-2-(4-Methyl-2,6,7-trioxabicyclo[2.2.2]octan-1-yl)propanal (17, Table 1). The title compound was prepared *via* representative procedure **B** using olefin **16**. The crude reaction mixture was purified on silica gel (1:1 pentane: diethyl ether) to afford a white solid (185 mg, 90% yield). R_f=0.8 (1:1 pentane: diethyl ether, stain in 2,4-DNP). $[\alpha]^{21}_D$ = +65.933 (c = 0.72, $CHCl_3$, l = 50 mm). All spectral data are in accordance with literature report.[20]

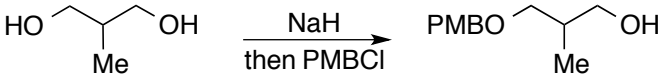
Analysis of Stereochemistry:

The titled compound **17** was converted to corresponding *p*-methoxybenzyl ether as shown below. The resulting benzyl ether was compared to racemic material prepared from 2-methyl-1,3-propanediol as shown below.

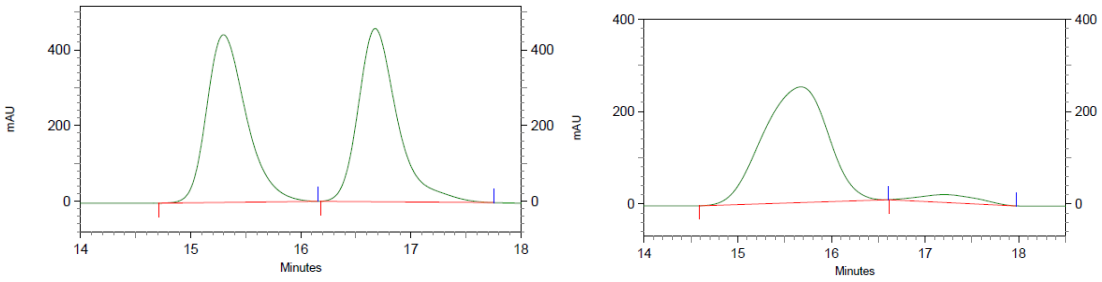
optically pure sample



racemic sample



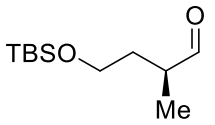
Chiral HPLC (Chiralpak, AD-H, 25 °C, 1 mL/min, 5% Isopropanol in hexane, 220 nm) – analysis of benzyl ether.



VWD: Signal A, 220 nm Results

Retention Time	Area	Area %	Height	Height %
15.673	203707854	94.27	4201524	93.65
17.203	12373743	5.73	284950	6.35
Totals	216081597	100.00	4486474	100.00

[20] Risi, R. M.; Burke, S. D. *Org. Lett.* **2012**, *14*, 2572.

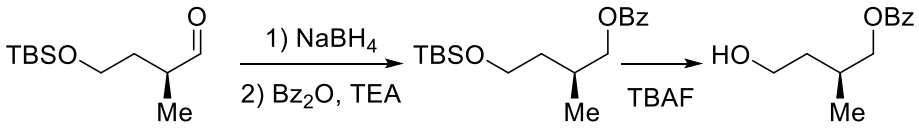


(*S*)-4-((*tert*-Butyldimethylsilyl)oxy)-2-methylbutanal (19, Table 2). The titled compound was prepared via representative procedure **A** with olefin **18**. The crude reaction mixture was purified on silica gel (20:1 hexane: diethyl ether) to afford a clear, colorless oil (138 mg, 64% yield). $[\alpha]^{22}_{D}$ = +18.347 (*c* = 1.0, $CHCl_3$. *l* = 50 mm). All spectral data are in accordance with literature.[21]

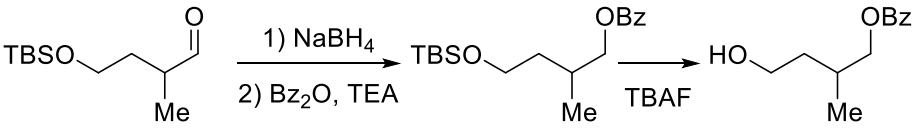
Analysis of Stereochemistry:

The titled compound was subjected to $NaBH_4$ reduction followed by benzoate protection and TBS removal. The analogous racemic material was prepared by employing PPh_3 as ligand in hydroformylation of olefin **18**. Optical purity was determined by chiral HPLC analysis of the derived alcohol. Absolute stereochemistry was determined by analogy the optical rotation reported in the literature.[21]

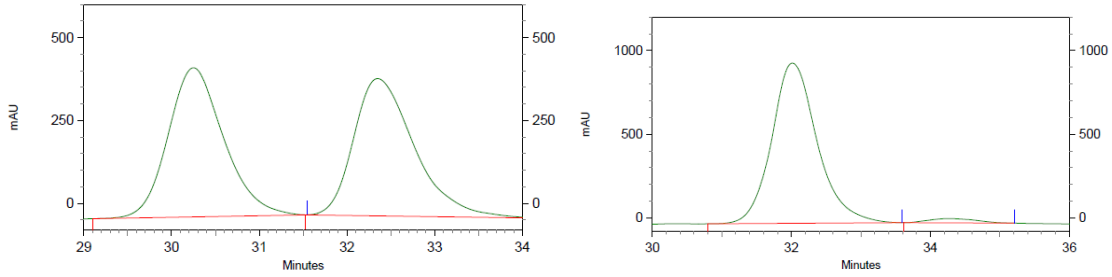
optically pure sample



racemic sample



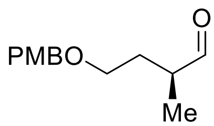
Chiral HPLC (Chiralpak, AD-H, 25 °C, 1 mL/min, 3 % Isopropanol in hexane, 220 nm) – analysis of alcohol.



VWD: Signal A, 220 nm Results

Retention Time	Area	Area %	Height	Height %
32.013	730462339	97.33	16051857	97.44
34.263	20002090	2.67	422068	2.56
Totals	750464429	100.00	16473925	100.00

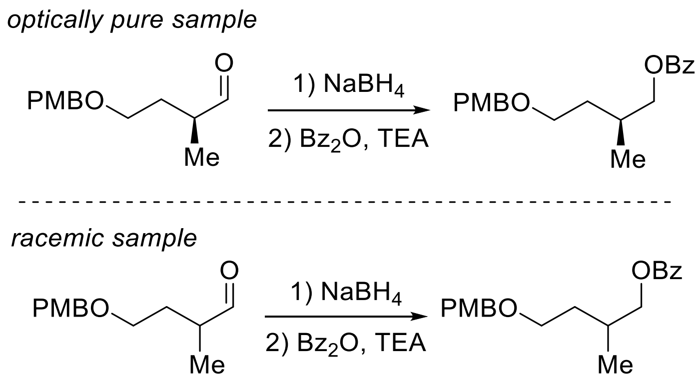
[21] (a) Fürst, R.; Rinner, U. *J. Org. Chem*. **2013**, *78*, 8748. (b) Enders, D.; Vicario, J. L.; Job, A.; Wolberg, M.; Müller, M. *Chem. Eur. J*. **2002**, *8*, 4272.



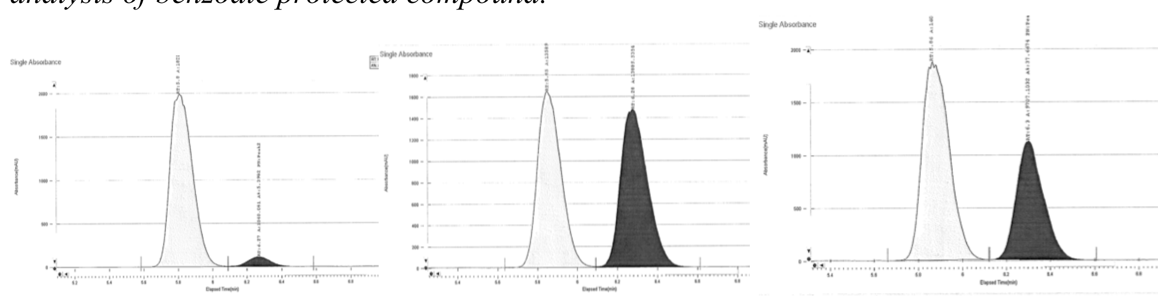
(*S*)-4-((4-Methoxybenzyl)oxy)-2-methylbutanal (21, Table 2): The titled compound was prepared *via* Representative Procedure **A** with olefin **20**. The crude reaction mixture was purified on silica gel (10:1 pentane: diethyl ether) to afford a clear, colorless oil (133 mg, 60% yield). R_f=0.17 (5:1 pentane: diethyl ether, stain $KMnO_4$). $[\alpha]^{22}_{D}$ = +15.453 (c = 0.522, $CHCl_3$, l = 50 mm). All spectral data are in accordance with the literature.[22]

Analysis of Stereochemistry:

The title compound was subjected to $NaBH_4$ reduction followed by benzoate protection, as depicted below. The analogous racemic material was prepared *via* the same route, using triphenylphoshine as achiral ligand in the hydroformylation reaction. Optical purity was determined by SFC analysis of the derived compound as compared to racemic product. Absolute stereochemistry was determined by comparing to the optical rotation reported in the literature.[23]



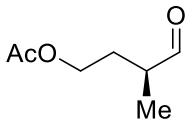
Chiral SFC (OD-H, Chiralpak, 215nm, 3.0 mL/min, 10% i-PrOH, 100 bar, 35°C)-analysis of benzoate protected compound.



Enatnioenriched Sample *Racemic Sample* *Co-injection*

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	94.6018	18227.1122	5.8	1988.7641	0.008
2	5.3982	1040.081	6.27	114.1512	0.0087
Total:	100	19267.1932			

[22] Takagi, R.; Tsuyumine, S.; Nishitani, H.; Miyanaga, W.; Ohkata, K. *Aust. J. Chem.* **2004**, *57*, 439.
[23] Chen, J. L.-Y.; Brimble, M. A. *J. Org. Chem.* **2011**, *76*, 9417.

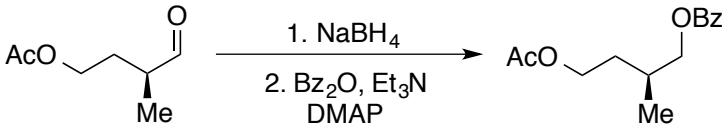


(*S*)-4-Acetoxy-2-methyl butanal (23, Table 2): The title compound was prepared with Representative Procedure **A** with olefin **22**. The crude reaction mixture was purified on silica gel (7:1 pentane: diethyl ether) to afford a clear, colorless oil (54 mg, 63% yield). R_f = 0.26 (7:1 pentane: diethyl ether, stain in $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.63 (1H, d, *J* = 1.5 Hz), 4.14-4.11 (2H, m), 2.48 (1H, dd, *J* = 14.0 Hz, 7.0 Hz), 2.11-2.04 (1H, m), 2.02 (3H, m), 1.73-1.66 (1H, m) 1.14 (3H, dd, *J* = 7.5 Hz, 2.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.7, 170.9, 61.8, 43.5, 29.3, 20.8, 13.2; IR (neat): 2968 (w), 2932 (w), 1737 (s), 1459 (w), 1388 (w), 1367 (w), 1237 (s), 1052 (w) cm^{-1}; HRMS-(ESI+) for $C_7H_{12}O_3$ $[M+NH_4]^+$: calculated: 162.1130, found 162.1134. $[\alpha]^{22}_D$ = +2.245 (*c* = 0.481, $CHCl_3$, *l* = 50 mm).

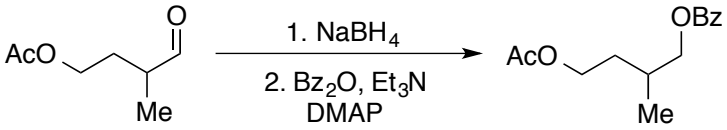
Analysis of Stereochemistry:

The title compound was subjected to $NaBH_4$ reduction followed by benzoate protection, as depicted below. The analogous racemic material was prepared *via* the same route, using triphenylphoshine as achiral ligand in the hydroformylation reaction. Optical purity was determined by SFC analysis of the derived compound as compared to racemic product. Absolute stereochemistry was determined by analogy.

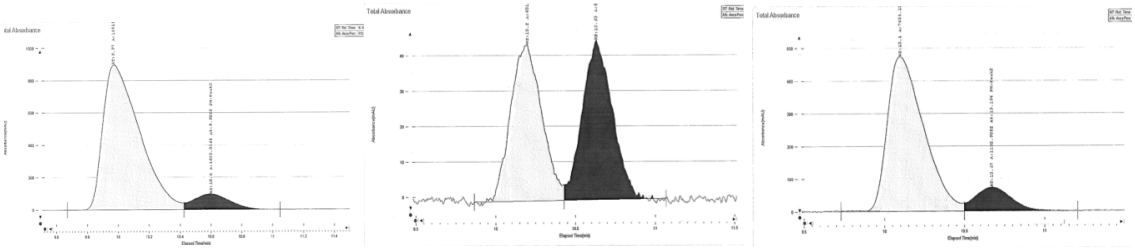
optically pure sample



racemic sample



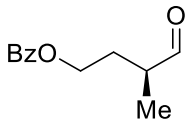
Chiral SFC (OD-H, Chiralpak, 215nm, 3.0 mL/min, 1% i-PrOH, 100 bar, 35°C)-analysis of benzoate.



Enantioenriched Sample *Racemic Sample* *Co-injection*

Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	90.0712	14814.2417	9.97	898.8523	0.0099
2	9.9288	1633.0064	10.6	99.1684	0.0105
Total:	100	16447.2481			

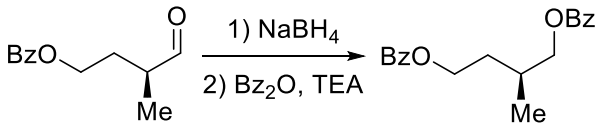


(*S*)-3-Methyl-4-oxobutyl benzoate (25, Table 2): The title compound was prepared with representative procedure **A** with olefin **24**. The crude reaction mixture was purified on silica gel (3:1 pentane: diethyl ether) to afford a clear, colorless oil (142 mg, 69% yield). R_f = 0.19 (3:1 pentane: diethyl ether, stain in 2,4-DNP). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.71 (1H, d, *J* = 1.5 Hz), 8.10-8.00 (2H, m), 7.56 (1H, tt, *J* = 7.5 Hz, 1.5 Hz), 7.44 (2H, t, *J* = 8.0 Hz), 4.44-4.37 (2H, m), 2.59 (1H, tt, *J* = 7.0 Hz, 1.5 Hz), 2.25 (1H, dq, *J* = 14.5 Hz, 6.5 Hz), 1.85 (1H, dq, *J* = 14.5 Hz, 6.5 Hz), 1.21 (3H, d, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.8, 166.4, 133.0, 129.6, 128.4, 62.4, 29.5, 13.3; IR (neat): 2968 (m), 2931 (m), 1717 (s), 1452 (m), 1272 (s), 1070 (m), 936 (w), 711 (m) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{15}O_3$ [M+H]: calculated: 207.1021, found 207.1015. $[\alpha]^{22}_D$ = +38.947 (*c* = 0.723, $CHCl_3$).

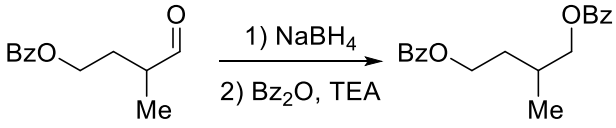
Analysis of Stereochemistry:

The title compound was subjected to $NaBH_4$ reduction followed by benzoate protection, as depicted below. The analogous racemic material was prepared *via* the same route, using triphenylphoshine as achiral ligand in the hydroformylation reaction. Optical purity was determined by SFC analysis of the derived compound as compared to racemic product. Absolute stereochemistry was determined by analogy.

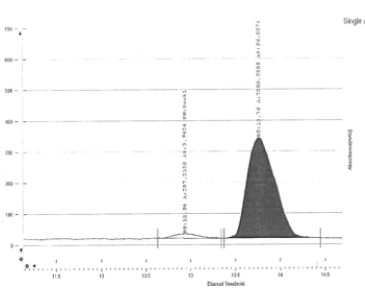
optically pure sample



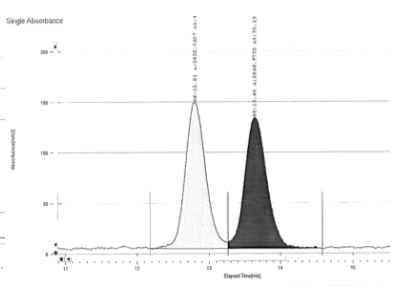
racemic sample



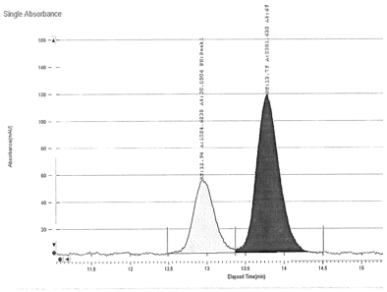
Chiral SFC (OJ-H, Chiralpak, 215nm, 3.0 mL/min, 2% i-PrOH, 100 bar, 35°C)-analysis of bis-benzoate.



Enatnioenriched Sample

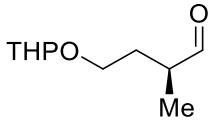


Racemic Sample



Co-injection

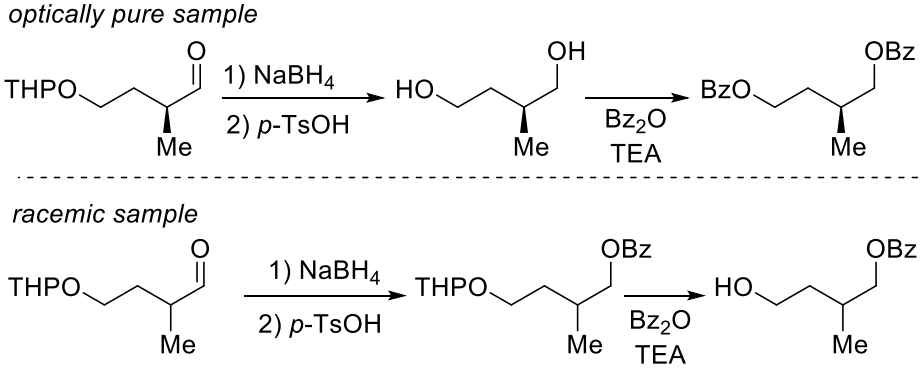
Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	3.9424	287.3358	12.94	15.8878	0.0199
2	96.0576	7000.9285	13.76	323.7626	0.0212
Total:	100	7288.2643			



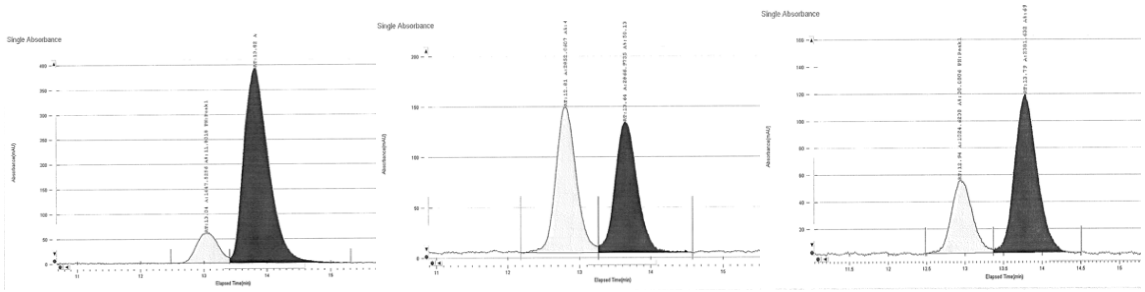
(2*S*)-2-Methyl-4-((tetrahydro-2*H*-pyran-2-yl)oxy)butanal (27, Table 2): The title compound **27** was prepared using representative procedure **A** with olefin **26**. The crude reaction mixture was purified on silica gel (20:1 pentane: diethyl ether) to afford a colorless oil as a 1:1 mixture of inseparable diastereomers (114 mg, 35% yield). R_f= 0.17 (10:1 pentane: diethyl ether, stain in 2,4-DNP). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.65 (1H, d, *J* = 1.5 Hz), 9.64 (1H, d, *J* = 2.0 Hz), 4.56-4.55 (2H, m), 3.52-3.48 (2H, m), 3.43 (2H, dddd, *J* = 22.0 Hz, 12.5 Hz, 7.0 Hz, 6.0 Hz), 2.56-2.47 (2H, m), 2.03 (2H, ddt, *J* = 14.0 Hz, 7.5 Hz, 5.5 Hz), 1.80-1.66 (6H, m), 1.58-1.49 (8H, m), 1.13 (3H, d, *J* = 1.5 Hz), 1.12 (3H, d, *J* = 2.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.7, 98.9, 98.8, 64.8, 64.5, 62.2, 44.0, 43.8, 31.0, 30.8, 30.5, 25.4, 19.4, 13.3, 13.1; IR (neat): 2939 (m), 2872 (m), 2714 (w), 1723 (s), 1120 (m), 1022 (m), 973 (s), 732 (m), cm^{-1}; HRMS-(ESI+) for $C_{10}H_{19}O_3$ [M+H]: calculated: 187.1334, found 187.1344. $[\alpha]_D^{22}$ = +26.258 (*c* = 0.646, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

The title compound was subjected to $NaBH_4$ reduction, followed by removal of the tetrahydropyranyl ether group and bis-benzoyl protection, as depicted below. The analogous racemic material was prepared *via* the same route, using tricylcohexylphoshine as achiral ligand in the hydroformylation reaction. Optical purity was determined by SFC analysis of the derived compound. Absolute stereochemistry was determined by analogy.

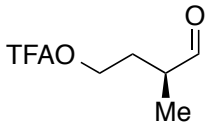


Chiral SFC (OJ-H, Chiralpak, 215nm, 3.0 mL/min, 2% i-PrOH, 100 bar, 35°C)-analysis of benzoate protected compound.

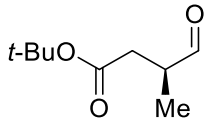


Enantioenriched Sample *Racemic Sample* *Co-injection*

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	11.8018	1447.5256	13.04	60.7848	0.0125
2	88.1982	10817.8139	13.82	393.3788	0.0133
Total:	100	12265.3395			



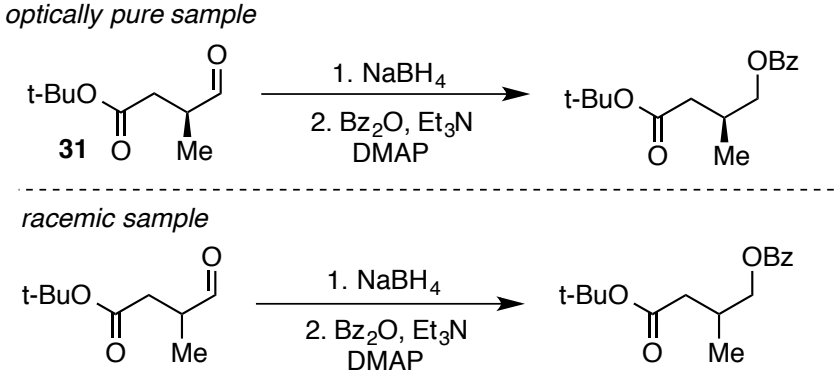
(*S*)-3-methyl-4-oxobutyl 2,2,2-trifluoroacetate (29, Table 2): The title compound was prepared using representative procedure **A** with olefin **28**. The crude reaction was purified on silica gel (7:1 pentane: diethyl ether) to afford a yellow oil (124 mg, 63% yield). R_f = 0.25 (7:1 pentane: diethyl ether, stain in 2,4-DNP).). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.67 (1H, s), 4.43 (2H, t, *J* = 6.0 Hz), 2.50 (1H, dd, *J* = 15.0 Hz, 7.5 Hz), 2.20 (1H, dd, *J* = 13.5 Hz, 6.5 Hz), 1.79 (1H, dd, *J* = 12.5 Hz, 6.0 Hz), 1.21 (3H, d, *J* = 7.5 Hz). ^{19}F (470 Hz, CDCl3): δ −75.0; IR (neat): 2975 (w), 1768 (m), 1711 (m), 1219 (m), 1158 (s), 816 (w). $[\alpha]^{22}_D$ = +16.553 (*c* = 0.252, $CHCl_3$, *l* = 50 mm).



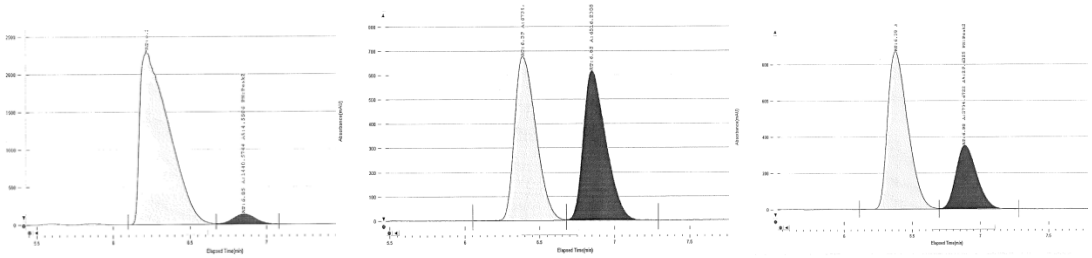
***tert*-Butyl-(*S*)-3-methyl-4-oxobutyl (31, Table 2)**: The title compound was prepared using representative procedure **A** with olefin **30**. The crude reaction mixture was purified on silica gel (10:1 pentane: diethyl ether) to afford a clear, colorless oil (93 mg, 54% yield). R_f = 0.12 (10:1 pentane: diethyl ether, stain in $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.69 (1H, d, *J* = 1.0 Hz), 2.78 (1H, dq, *J* = 14.0 Hz, 7.0 Hz), 2.64 (1H, dd, *J* = 16.0 Hz, 7.0 Hz), 2.34 (1H, dd, *J* = 16.5 Hz, 6.5 Hz), 1.44 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.9, 170.9, 81.0, 42.8, 36.4, 28.0, 13.2; IR (neat): 2978 (w), 2933 (w), 2717 (w), 1727 (s), 1367 (w), 1156 (w) cm^{-1}; HRMS-(ESI+) for $C_9H_{16}O_3$ [M+H]: calculated: 173.1178, found 173.1184. $[\alpha]^{22}_D$ = −98.065 (*c* = 0.153, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

The title compound **25** was subjected to $NaBH_4$ reduction followed by benzoate protection, as depicted below. The analogous racemic material was prepared *via* the same route, using triphenylphoshine as achiral ligand in the hydroformylation reaction. Optical purity was determined by SFC analysis of the derived compound as compared to racemic product. Absolute stereochemistry was determined by analogy.



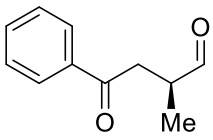
Chiral SFC (OD-H, Chiralpak, 215nm, 3.0 mL/min, 1% i-PrOH, 100 bar, 35°C)-analysis of benzoate protected compound.



Enantioenriched Sample *Racemic Sample* *Co-injection*

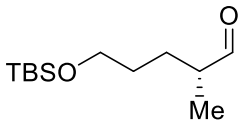
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	95.4414	30160.4156	6.22	2319.5375	0.0057
2	4.5586	1440.5744	6.85	138.464	0.0062
Total:	100	31600.99			



(*S*)-2-Methyl-4-oxo-4-phenylbutanal (33, Table 2). The title compound was prepared using representative procedure **A** with olefin **32**. The crude reaction mixture was purified on silica gel (6:1 pentane: diethyl ether) to afford a clear, colorless oil (116 mg, 66% yield). R_f = 0.17 (5:1 pentane: diethyl ether, stain in $KMnO_4$). All spectral data are in accordance with the literature.[24]

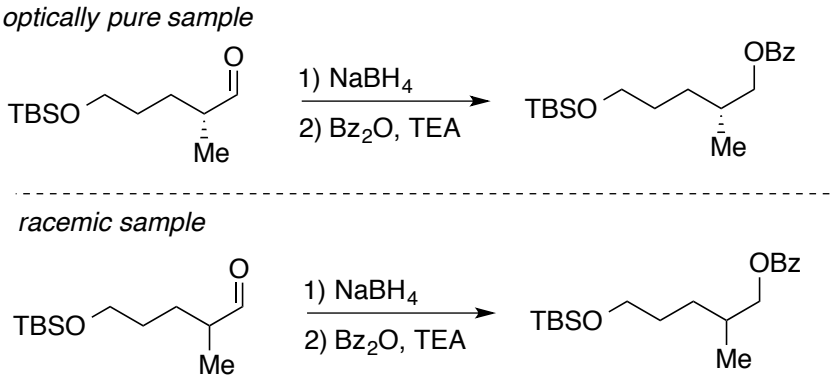
[24] Zhang, J.; Xing, C.; Tiwari, B.; Chi, Y. *J. Am. Chem. Soc*. **2013**, *135*, 8113.



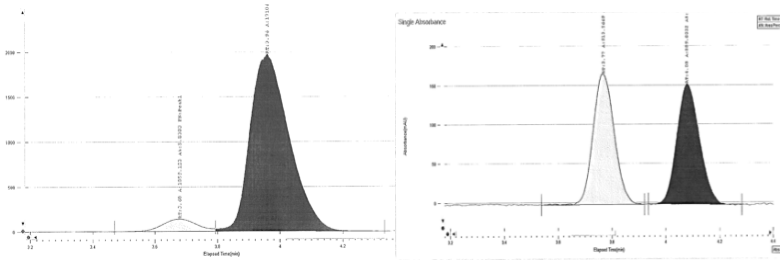
(*S*)-5-((*tert*-Butyldimethylsilyl)oxy)-2-methylpentanal (compound 35, Table 2): The titled compound **35** was prepared with representative procedure **A** (using (*R,R*)-Ph-BPE ligand) with olefin **34**. The crude reaction mixture was purified on silica gel (10:1 pentane: diethyl ether) to afford a clear, colorless oil (97 mg, 42 % yield). R_f = 0.26 (10:1 pentane: diethyl ether, stain in $KMnO_4$). $[\alpha]^{22}_D$ = −46.830 (*c* = 0.556, *l* = 50 mm, $CHCl_3$). All spectral data were in accordance with the literature.[25]

Analysis of Stereochemistry:

The titled compound **35** was subjected to $NaBH_4$ reduction followed by benzoate protection, as depicted below. The analogous racemic material was prepared *via* the same route, using triphenylphoshine as achiral ligand in the hydroformylation reaction. Optical purity was determined by SFC analysis of the derived compound as compared to racemic product. Absolute stereochemistry was determined by comparison with literature.[25]



Chiral SFC (OD-H, Chiralpak, 215nm, 3.0 mL/min, 3% i-PrOH, 100 bar, 35°C)-analysis of benzoate.

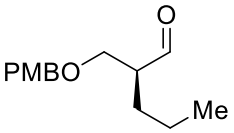


Enantioenriched Sample *Racemic Sample*

Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	5.8303	1059.123	3.68	138.5669	0.0067
2	94.1697	17106.7375	3.96	1972.3598	0.0072
Total:	100	18165.8605			

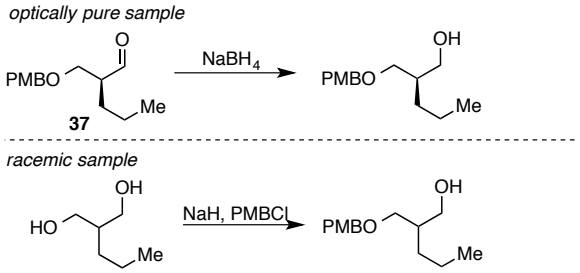
[25] Rentsch, A.; Kalesse, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 11381.



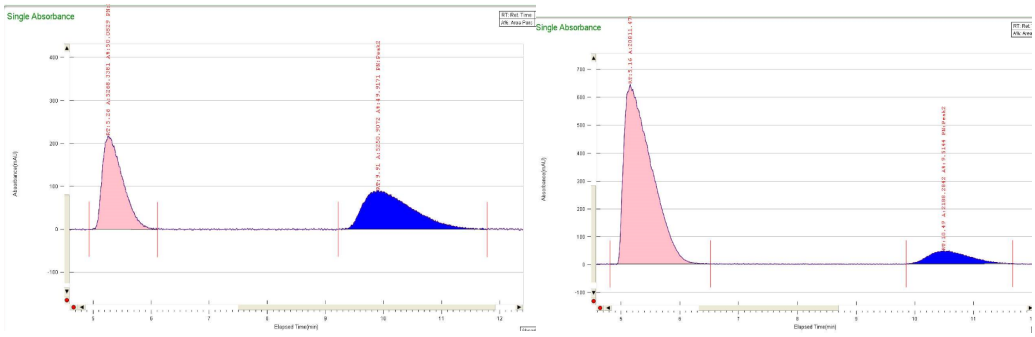
(*S*)-2-(((4-Methoxybenzyl)oxy)methyl)pentanal (37, Scheme 4). The title compound was prepared using representative procedure **A** with olefin **36** The crude reaction mixture was purified on silica gel (12:1 hexane: diethyl ether) to afford a clear, colorless oil (132 mg, 56% yield). R_f = 0.35 (6:1 hexane:diethyl ether, stain in $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.68 (1H, d, *J* = 2.5 Hz), 7.23 (2H, d, *J* = 9.0 Hz), 6.88 (2H, d, *J* = 8.5 Hz), 4.43 (2H, m), 3.80 (3H, s), 3.66 (1H, dd, *J* = 9.0 Hz, 7.0 Hz), 3.61 (1H, dd, *J* = 9.5 Hz, 5.0 Hz), 2.55 (1H, m), 1.65 (1H, ddt, *J* = 14.5 Hz, 7.5 Hz, 7.5 Hz), 1.45 (1H, ddt, *J* = 14.5 Hz, 7.0 Hz, 7.0 Hz), 1.33 (2H, 2H, qt, *J* = 7.0 Hz, 7.0 Hz), 0.91 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.4, 159.5, 130.2, 129.4, 114.0, 73.1, 68.5, 55.5, 52.2, 28.2, 20.4, 14.3; IR (neat): 2958 (w), 2933 (w), 2864 (w), 1725 (s), 1612 (m), 1513 (s), 1465 (w), 1247 (s), 1086 (s), 1034 (s), 819 (s) cm^{-1}; HRMS-(ESI+) for $C_{14}H_{19}O_3$ [M+H]: calculated: 235.1334, found: 235.1343. $[\alpha]_D^{22} = -17.033$ (c = 0.95, $CHCl_3$).

Analysis of Stereochemistry:

The titled compound **37** was converted to the corresponding alcohol as shown below. The resulting alcohol was compared to racemic material prepared from 2-propyl-propan-1,3-diol. Absolute stereochemistry was assigned by comparing optical rotation of the alcohol to literature [lit. $[\alpha]_D^{22} = -14.0$ (*c* = 1.1, $CHCl_3$)].[26]



Chiral SFC (AS-H, Chiralpak, 215nm, 3.0 mL/min, 15% i-PrOH, 100 bar, 35°C)-analysis of alcohol.



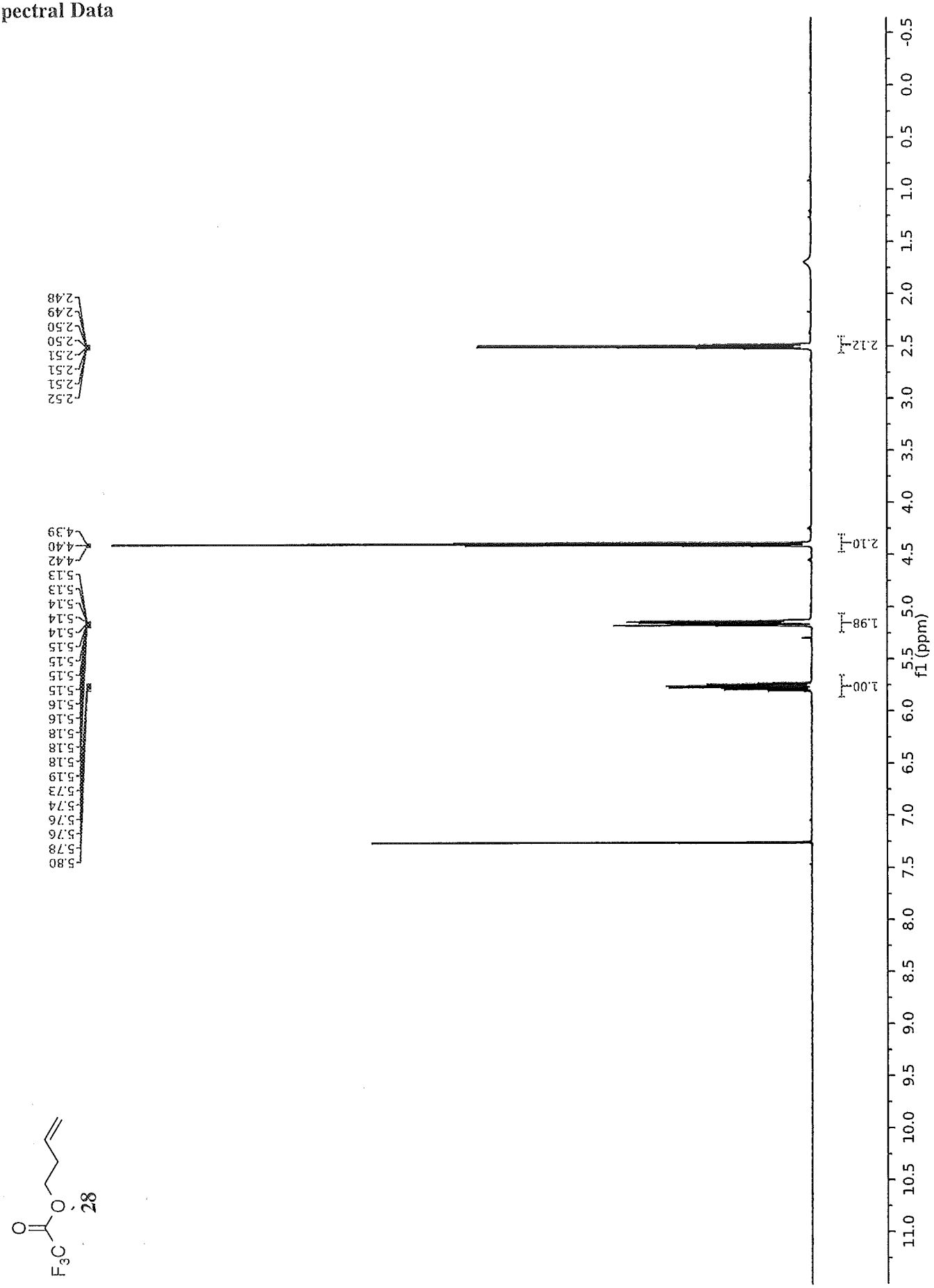
Peak Info

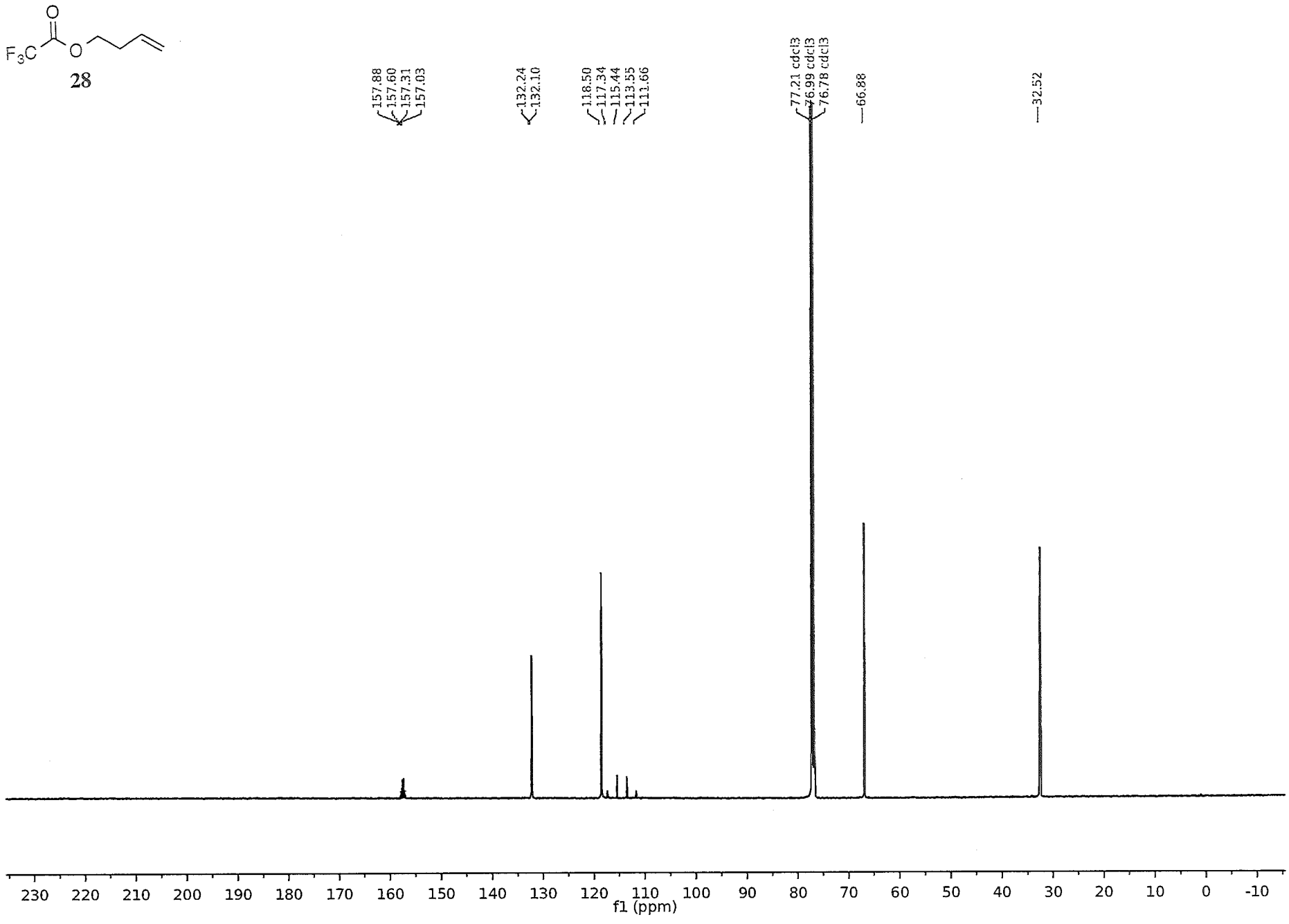
Peak Name	Number	Concentration	Area %	Area
Peak1	1	0	90.4856	20811.4749
Peak2	2	0	9.5144	2188.2842

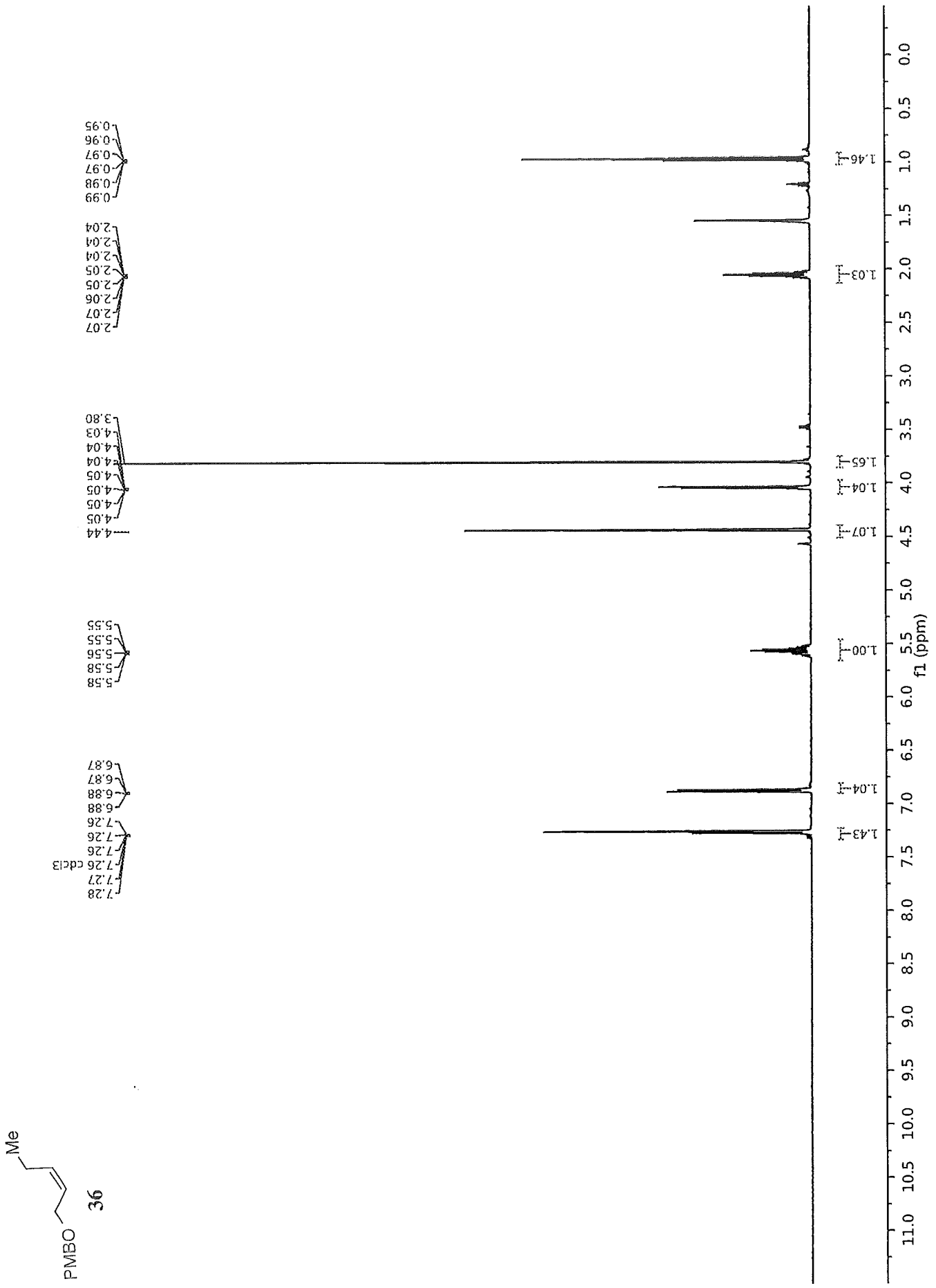
Area Sum	RT (min)	St. (min)	End (min)	Height	Width (min)
	5.16	4.8145	6.5227	644.6855	1.7099
22999.7591	10.49	9.8513	11.6601	46.2777	1.8104

[26] Yadav, J. S.; Nanda, S. *Tetrahedron: Asymmetry*, **2001**, *12*, 3223.

Spectral Data




28
157.88
157.60
157.31
157.03
132.24
132.10
118.50
117.34
115.44
113.55
111.66
77.21 cdcl3
76.99 cdcl3
76.78 cdcl3
66.88
32.52
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
PMBO
36
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7.27
7.26 cdcl3
7.26
7.26
7.26
6.88
6.88
6.87
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5.56
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5.55
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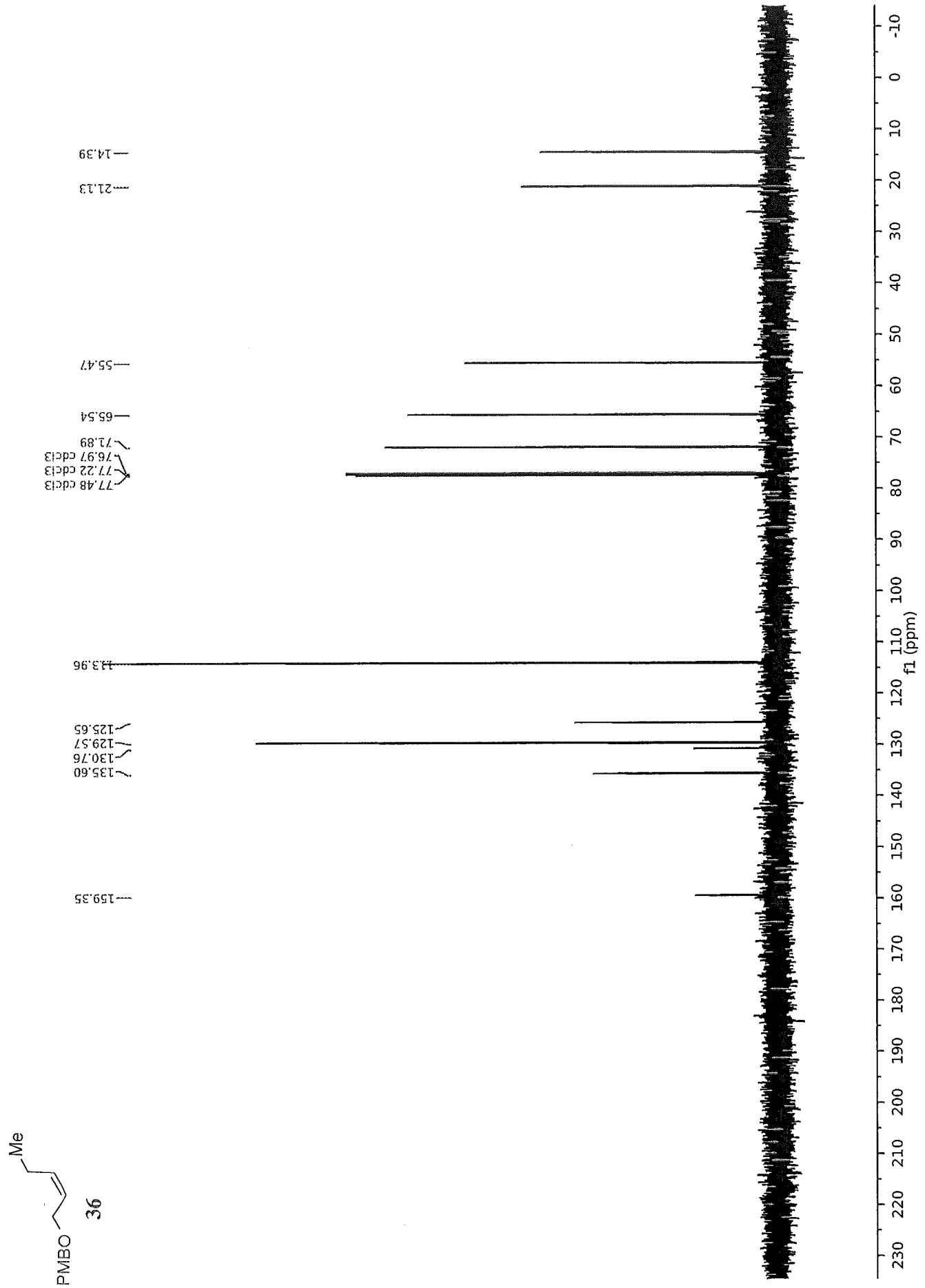
4.04
4.04
4.03
3.80
2.07
2.07
2.06
2.05
2.05
2.04
2.04
2.04
0.99
0.98
0.97
0.97
0.96
0.95
1.46
1.03
1.65
1.04
1.07
1.00
1.04
1.43
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Me
PMBO
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130.76
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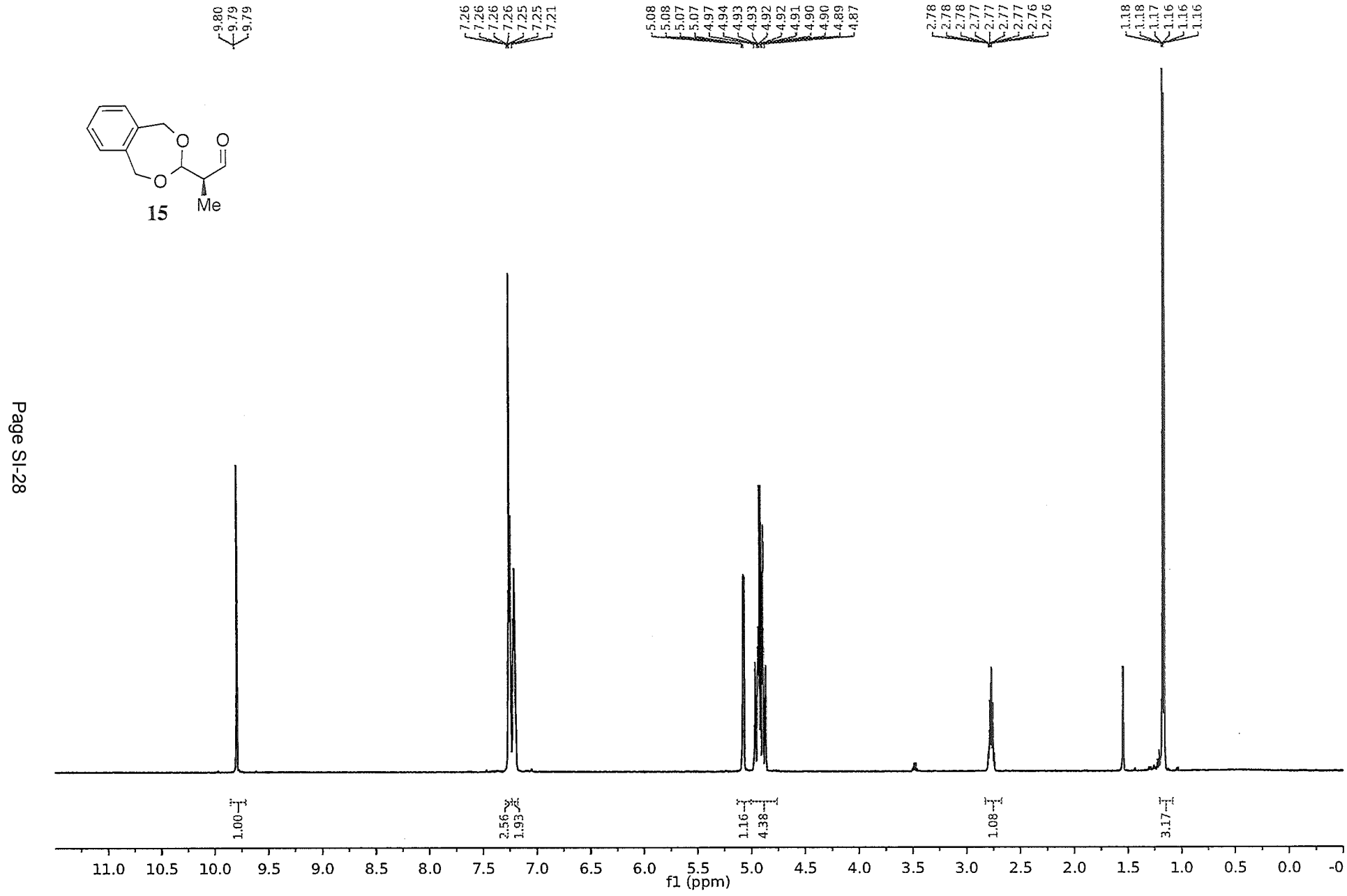
159.35
f1 (ppm)


9.80
9.79
9.79
7.26
7.26
7.26
7.26
7.25
7.25
7.21
5.08
5.08
5.07
5.07
4.97
4.94
4.93
4.93
4.92
4.92
4.91
4.90
4.90
4.89
4.87
2.78
2.78
2.78
2.77
2.77
2.77
2.76
2.76
1.18
1.18
1.17
1.16
1.16
1.16
O
O
O
O
Me
15
1.00
2.56
1.93
1.16
4.38
1.08
3.17
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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1.5
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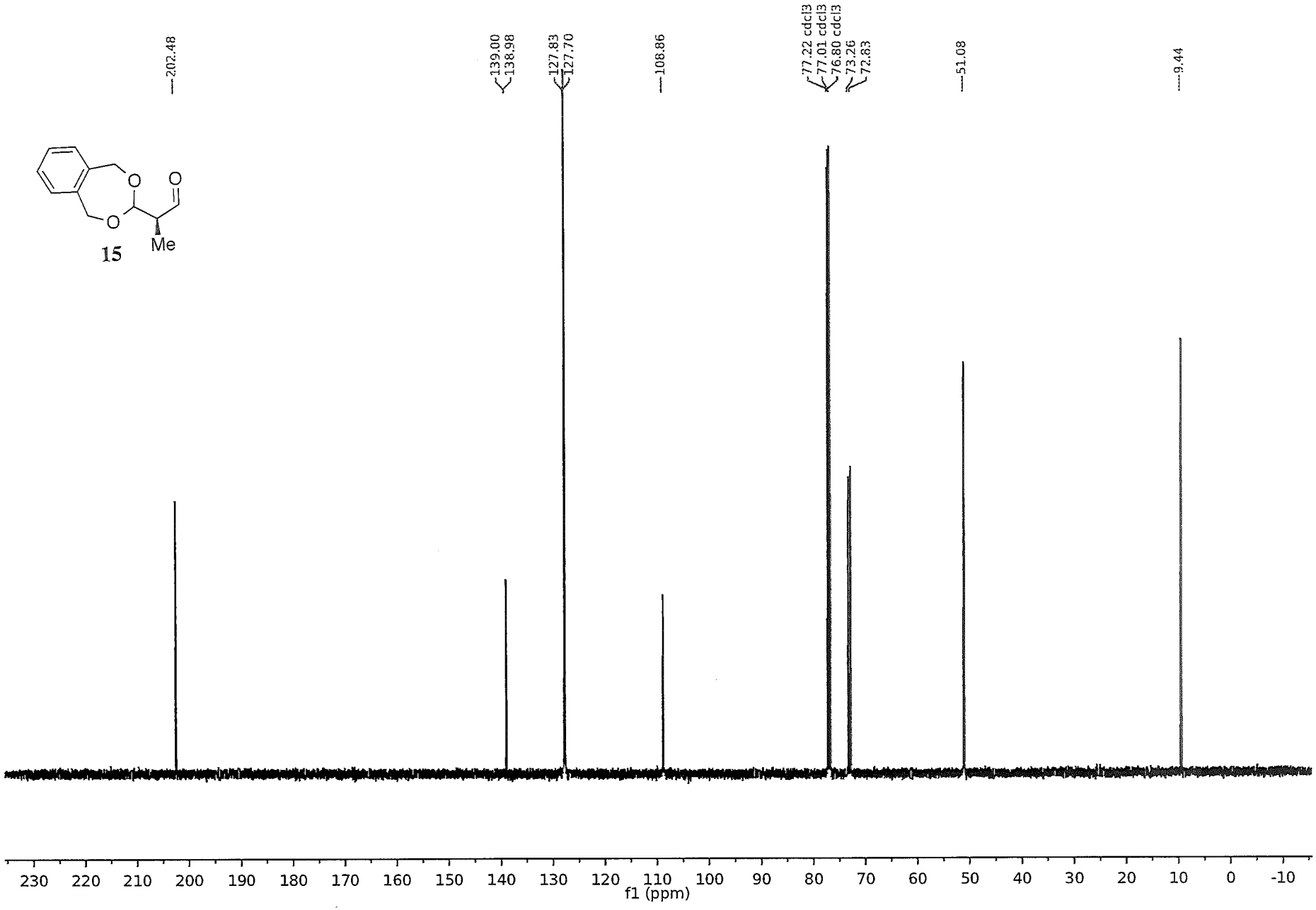
-0
f1 (ppm)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138.98
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127.70
108.86
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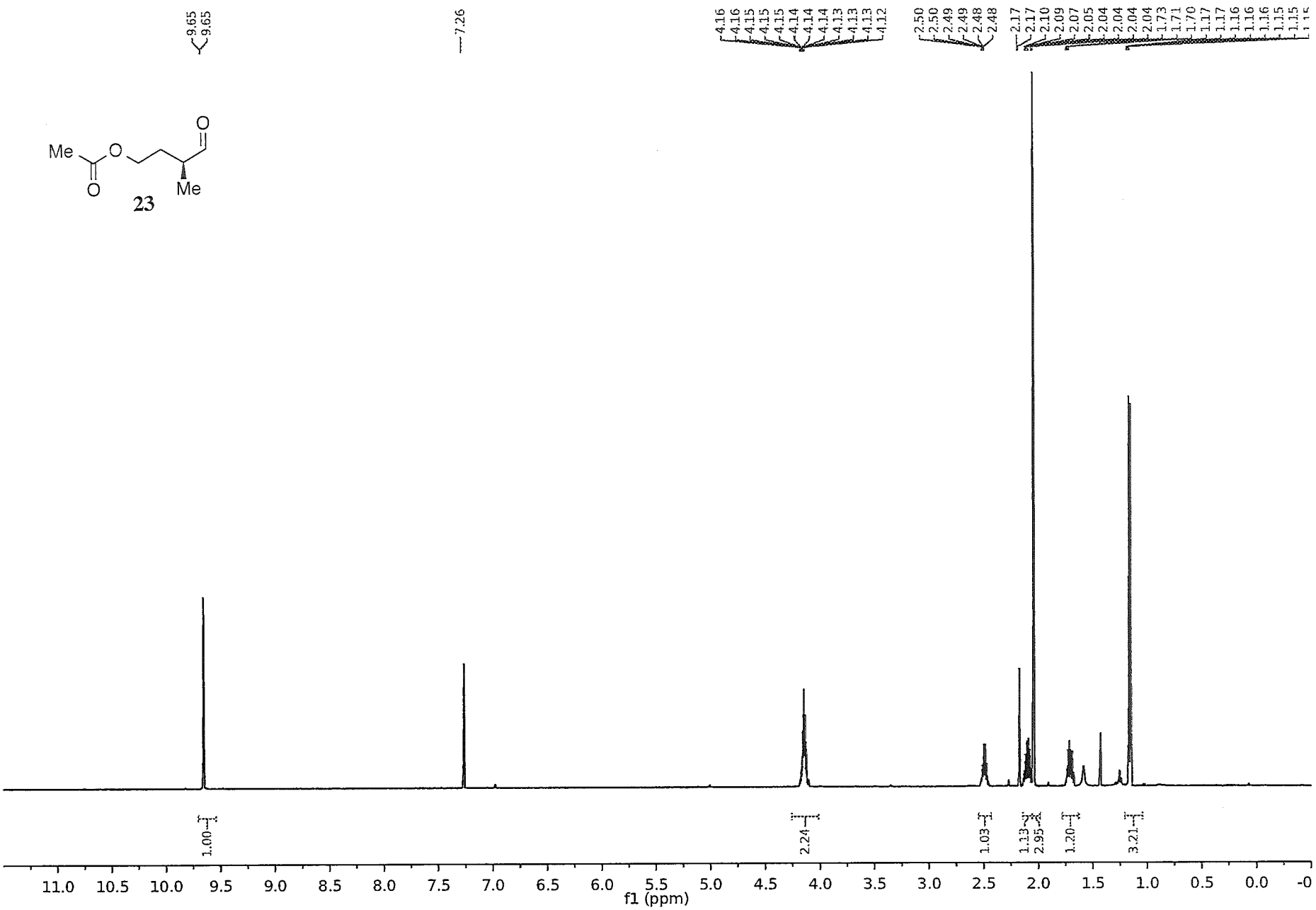
77.01 cdcl3
76.80 cdcl3
73.26
72.83
51.08
9.44
O
O
O
Me
15
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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9.65
7.26
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4.16
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4.15
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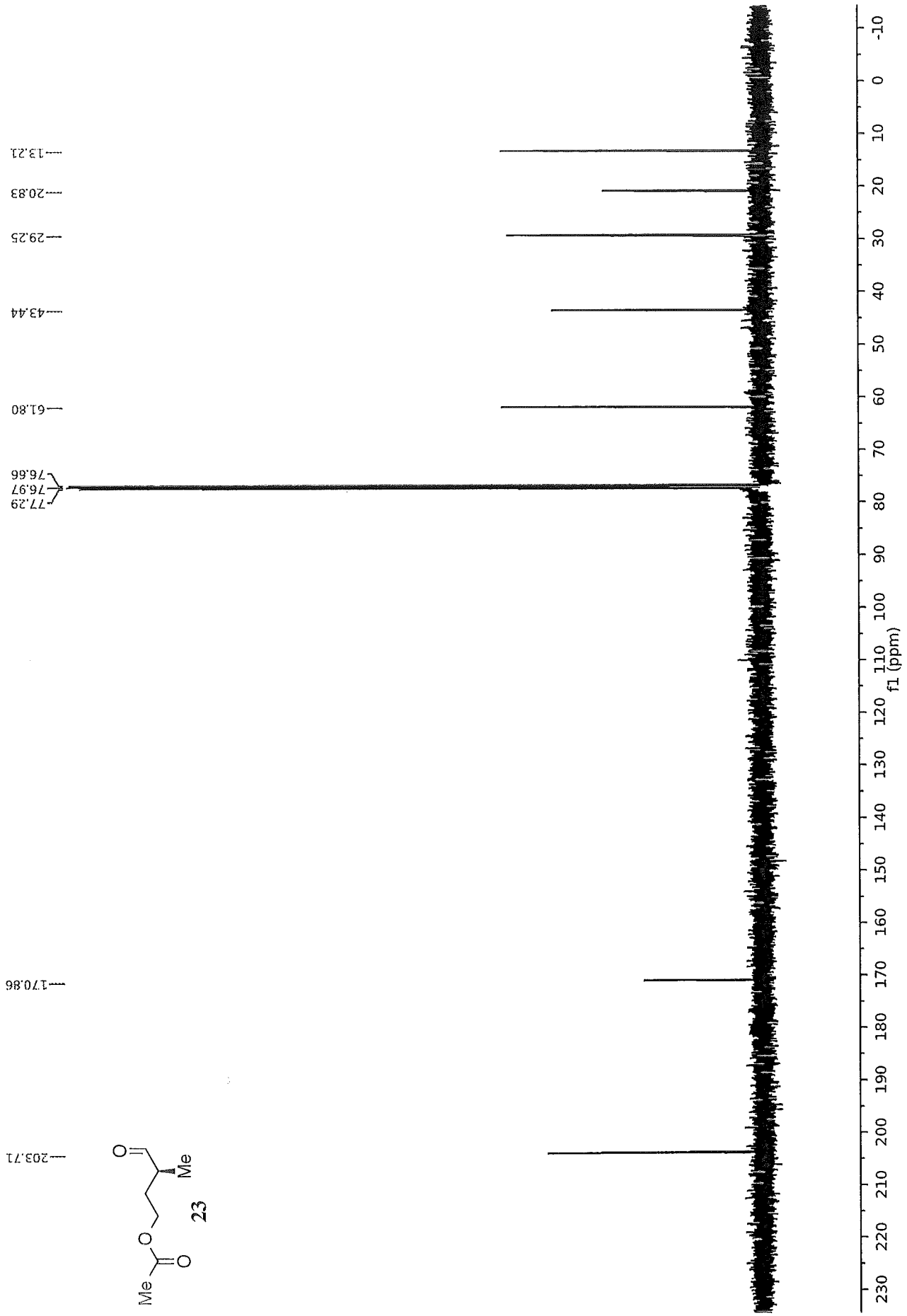
4.14
4.14
4.13
4.13
4.12
2.50
2.50
2.49
2.49
2.48
2.48
2.17
2.17
2.10
2.09
2.07
2.05
2.04
2.04
2.04
2.04
1.73
1.71
1.70
1.17
1.17
1.16
1.16
1.16
1.15
1.15
Me
O
O
O
Me
23
1.00
2.24
1.03
1.13
2.95
1.20
3.21
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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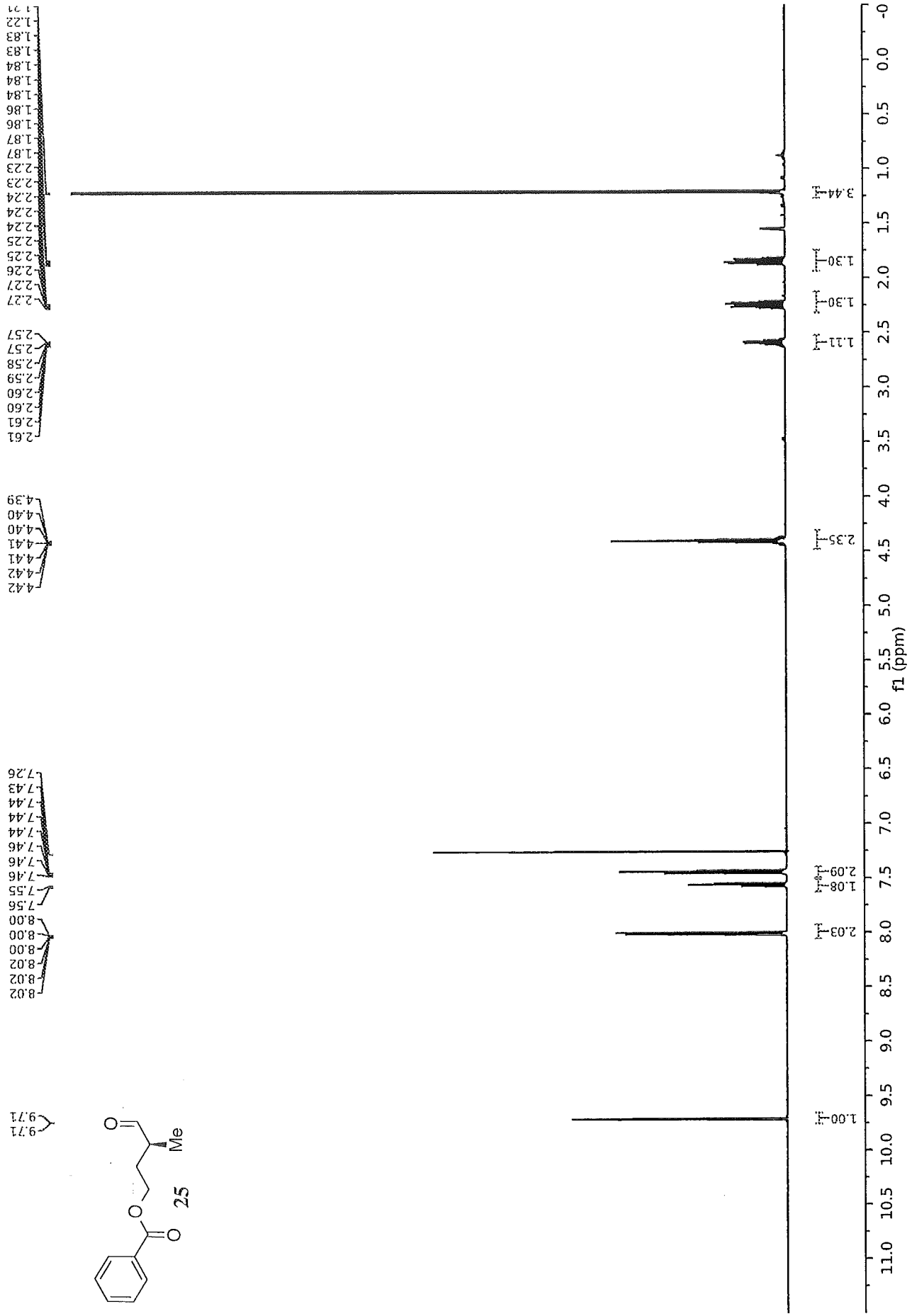
170.86
77.29
76.97
76.66
61.80
43.44
29.25
20.83
13.21
Me
O
Me
O
O
23
f1 (ppm)


f1 (ppm)
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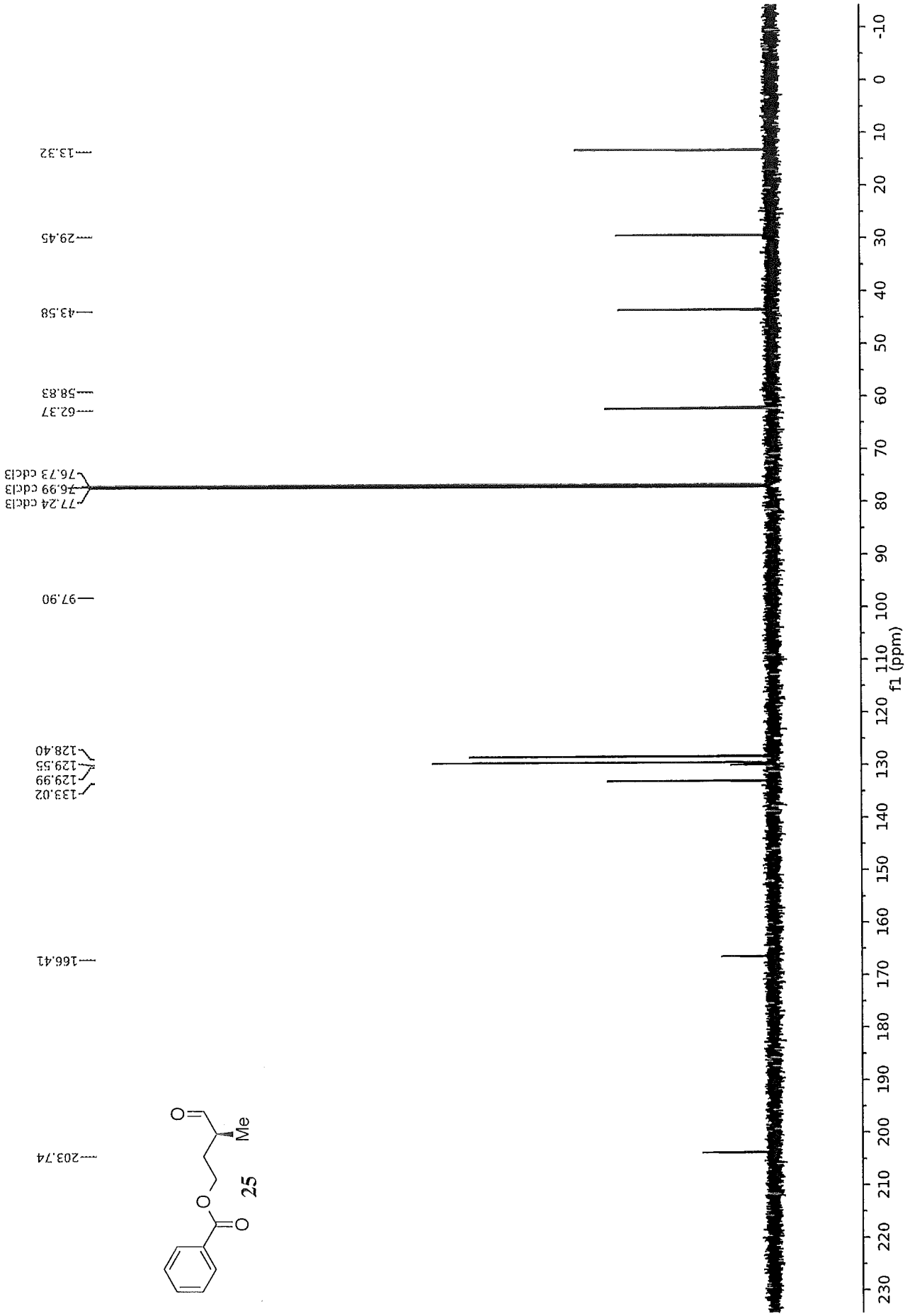
O
O
O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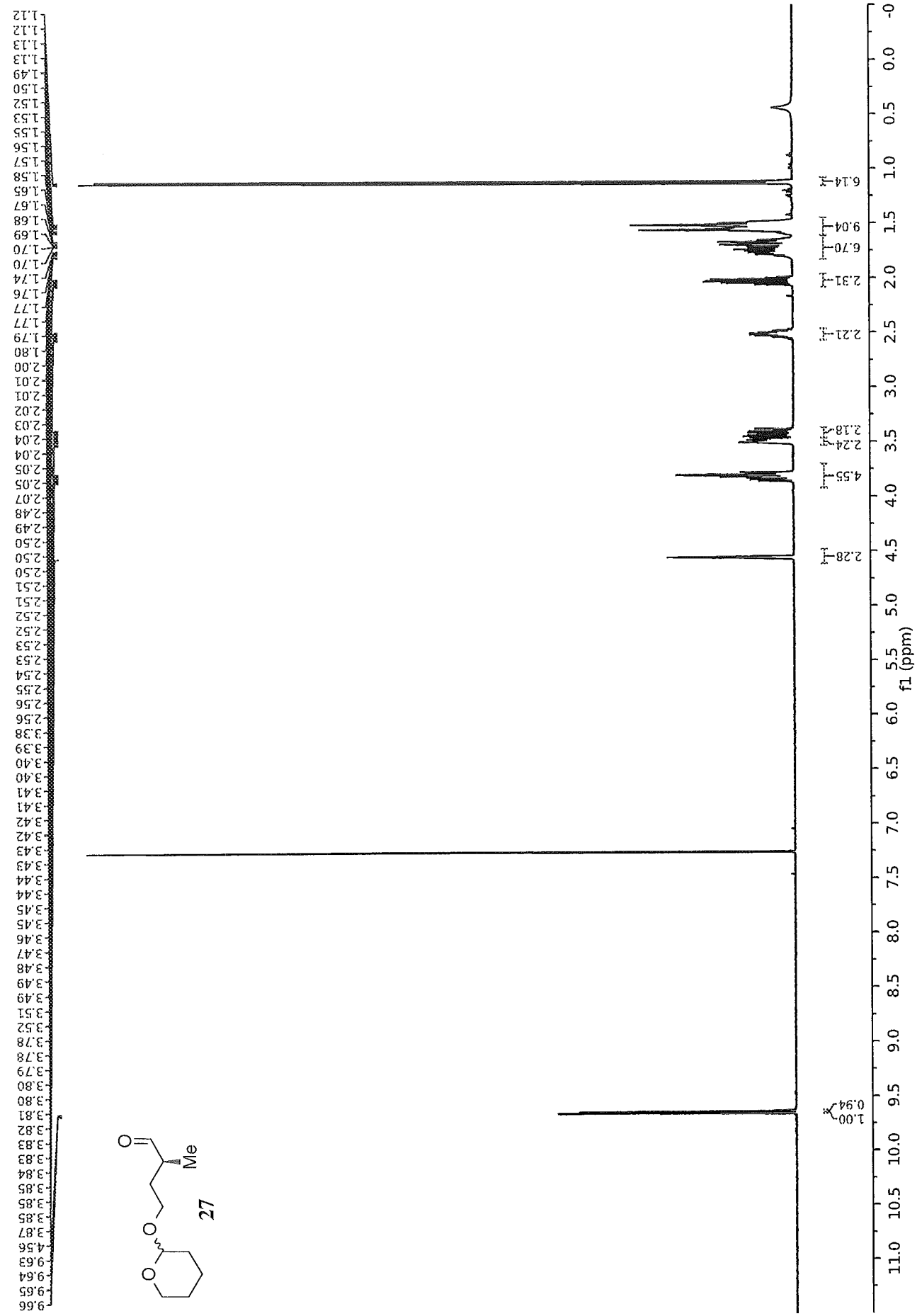
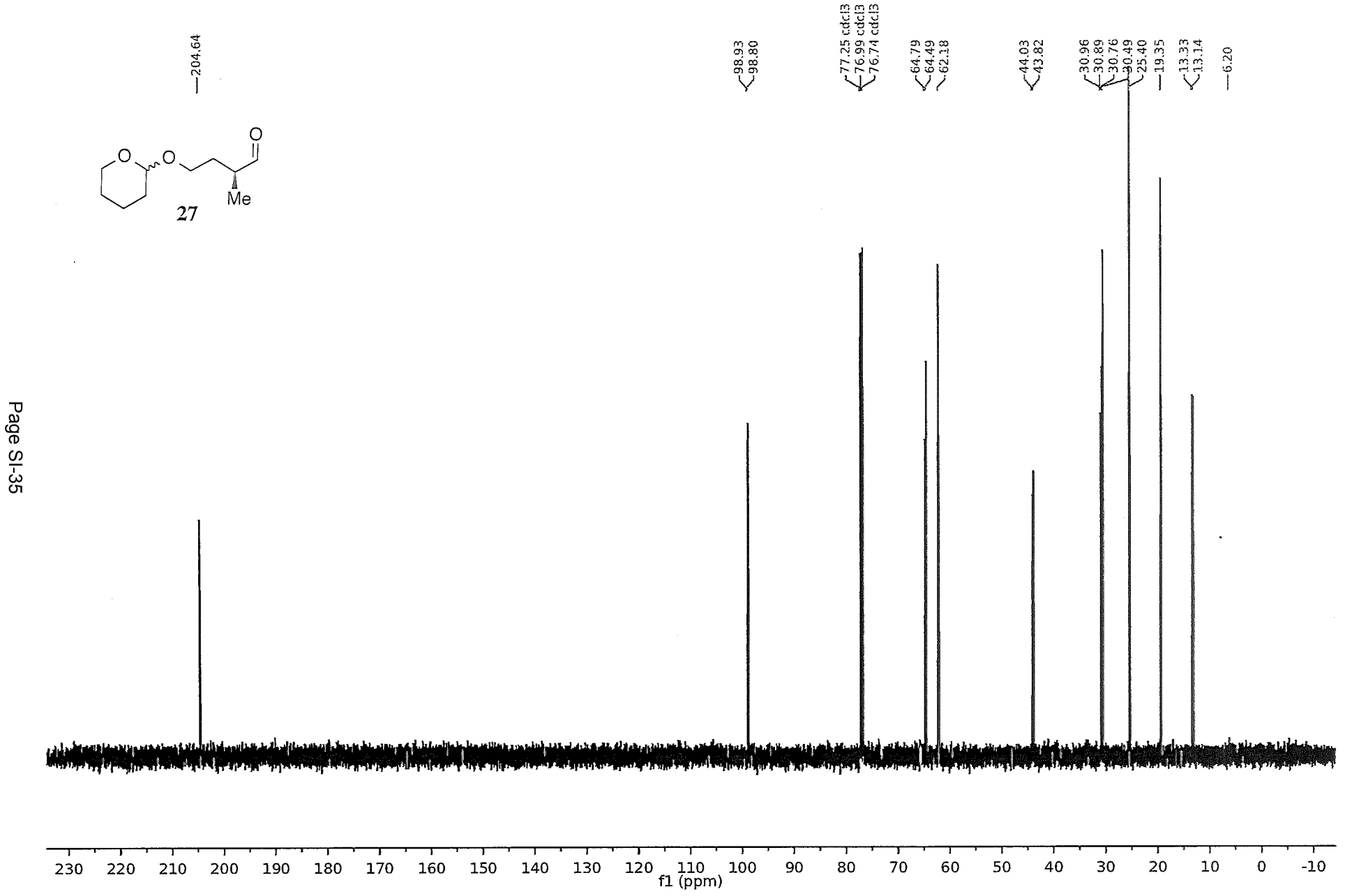
166.41
133.02
129.99
129.55
128.40
97.90
77.24 cdcl3
76.99 cdcl3
76.73 cdcl3
62.37
58.83
43.58
29.45
13.32
Me
O
O
O
25
f1 (ppm)


O
Me
O
O
27
f1 (ppm)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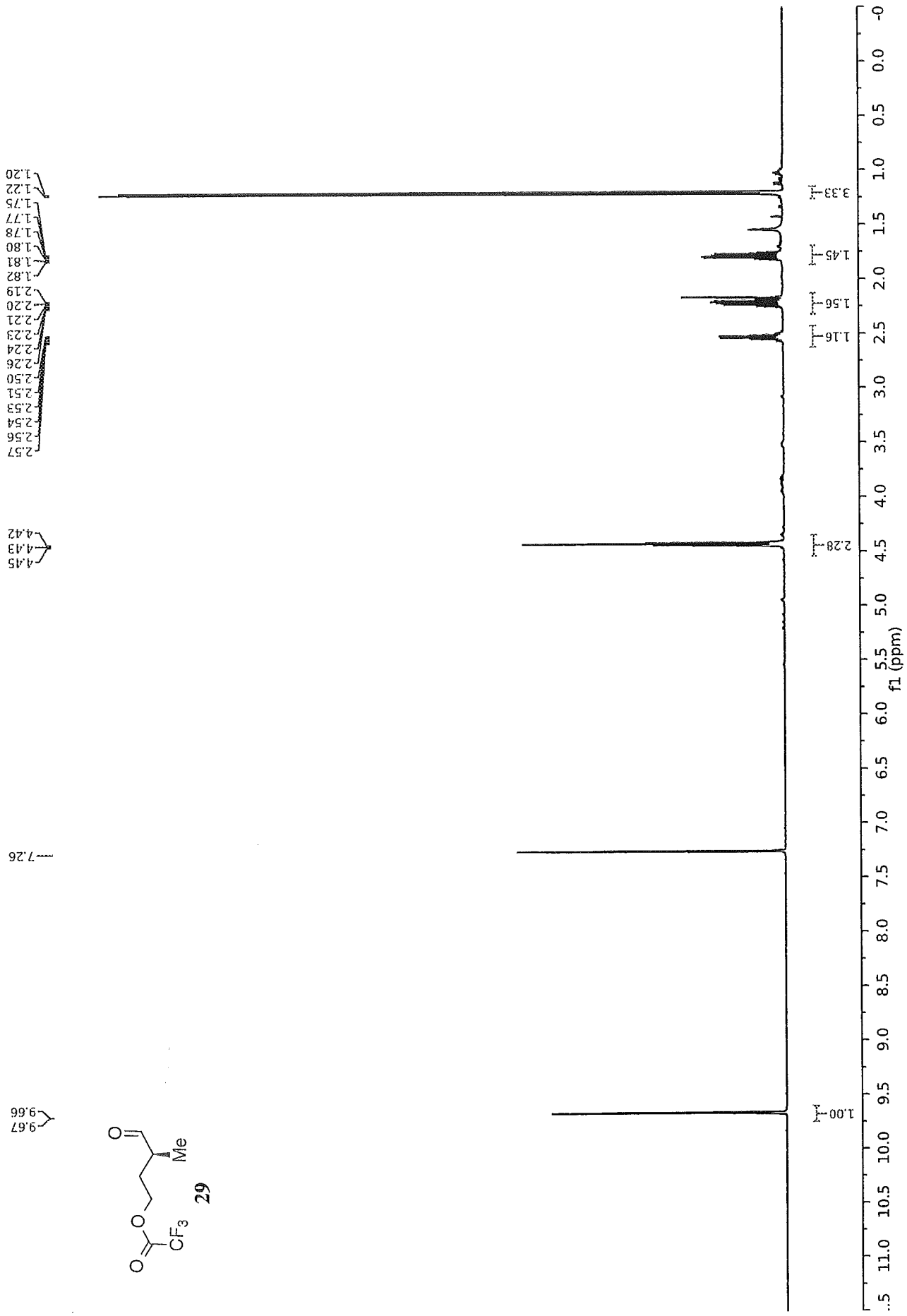
98.93
98.80
77.25 cdcl3
76.99 cdcl3
76.74 cdcl3
64.79
64.49
62.18
44.03
43.82
30.96
30.89
30.76
30.49
25.40
19.35
13.33
13.14
6.20
O
O
O
Me
27
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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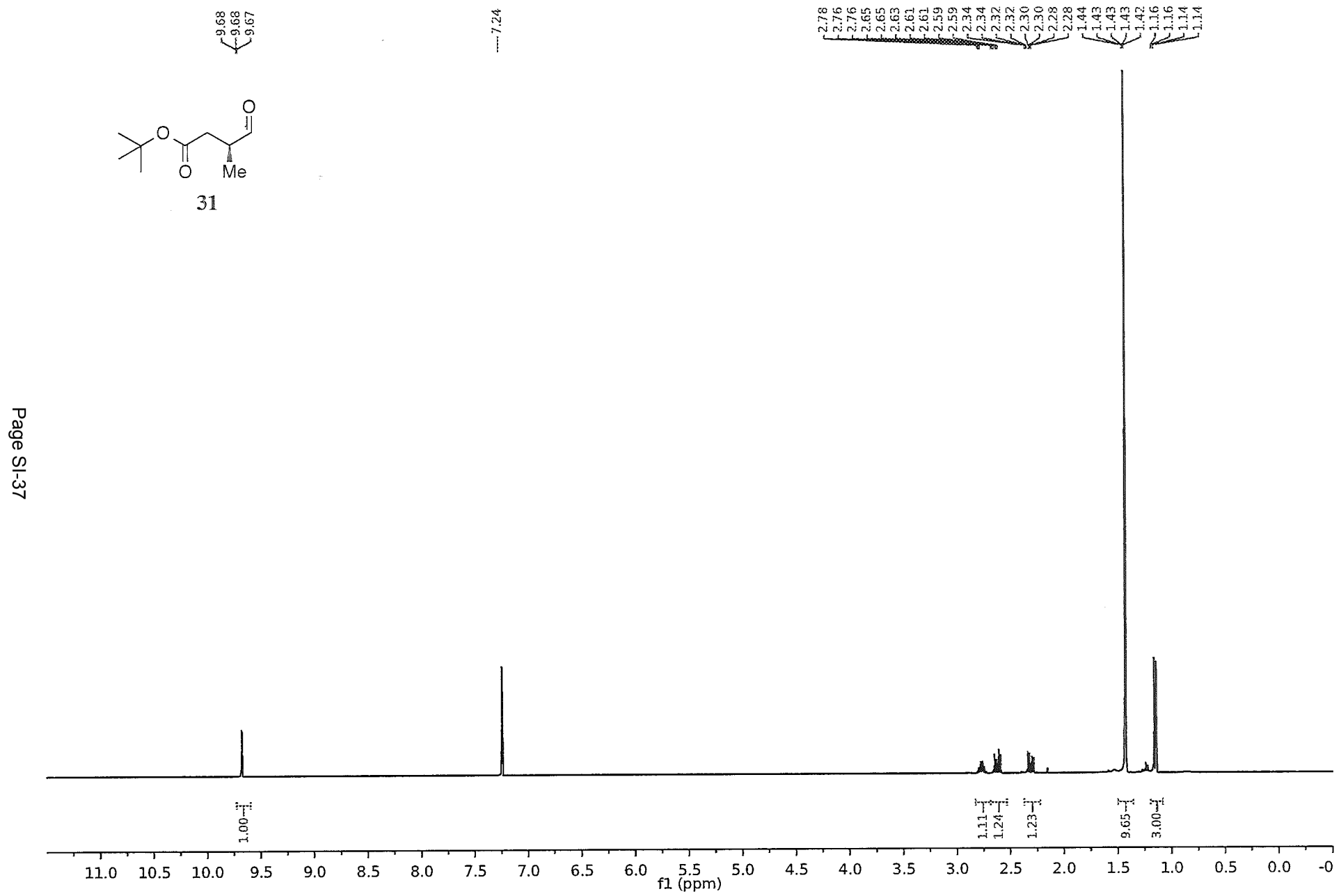
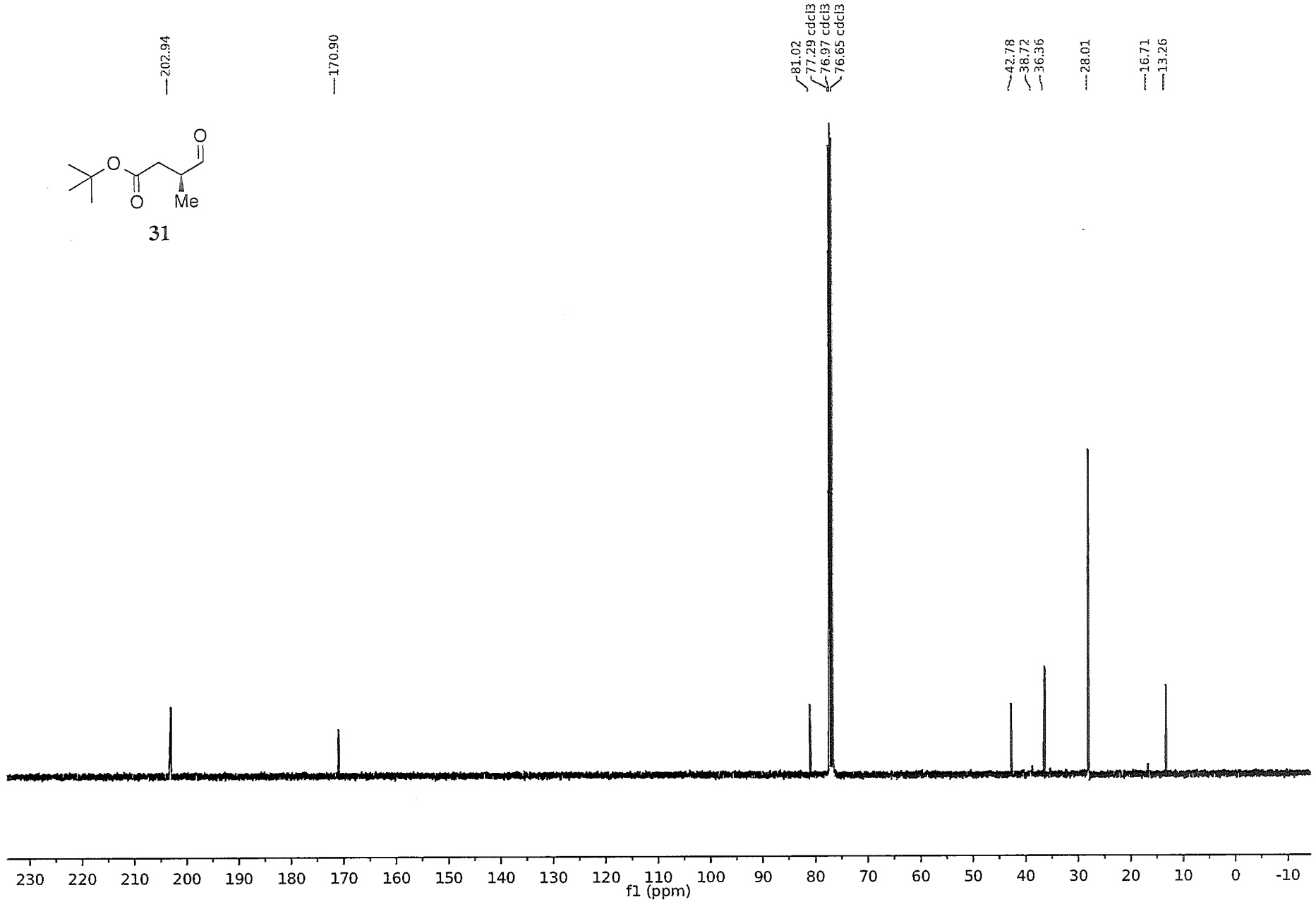
4.42
2.57
2.56
2.54
2.53
2.51
2.50
2.26
2.24
2.23
2.21
2.20
2.19
1.82
1.81
1.80
1.78
1.77
1.75
1.22
1.20
1.00
2.28
1.16
1.56
1.45
3.33
f1 (ppm)
O
Me
O
O
CF3
29


9.68
9.68
9.67
7.24
2.78
2.76
2.76
2.65
2.63
2.61
2.61
2.59
2.59
2.34
2.34
2.32
2.32
2.30
2.30
2.28
2.28
1.44
1.43
1.43
1.43
1.42
1.16
1.16
1.14
1.14
O
O
O
Me
31
1.00
1.11
1.24
1.23
9.65
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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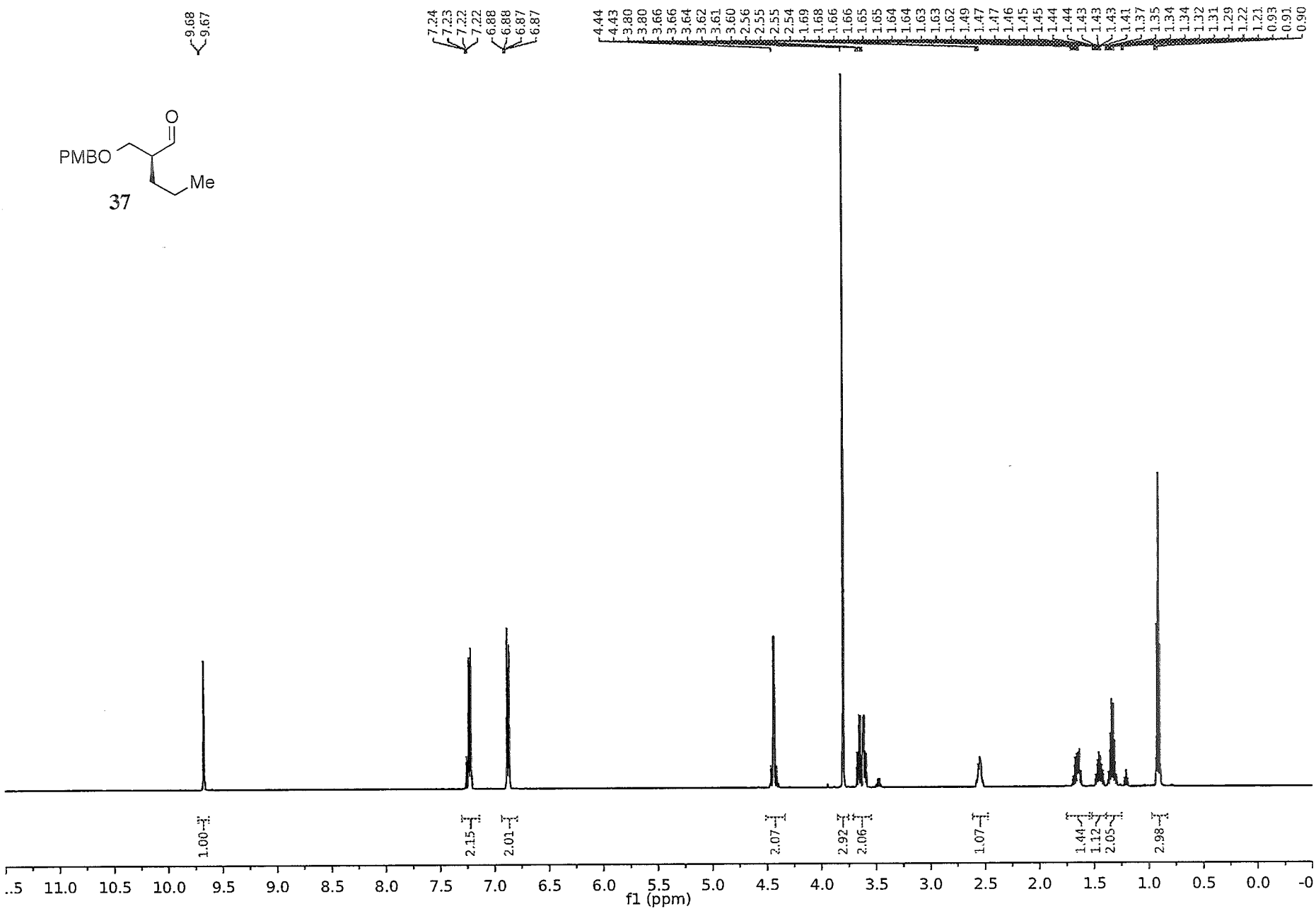
170.90
81.02
77.29 cdcl3
76.97 cdcl3
76.65 cdcl3
42.78
38.72
36.36
28.01
16.71
13.26
O
O
O
Me
31
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.22
7.22
6.88
6.88
6.87
6.87
4.44
4.43
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3.66
3.66
3.64
3.62
3.61
3.60
2.56
2.55
2.55
2.54
1.69
1.68
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1.64
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1.63
1.63
1.62
1.49
1.47
1.47
1.46
1.45
1.45
1.44
1.44
1.43
1.43
1.43
1.41
1.37
1.35
1.34
1.34
1.32
1.31
1.29
1.22
1.21
0.93
0.91
0.90
PMBO
Me
O
37
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2.15
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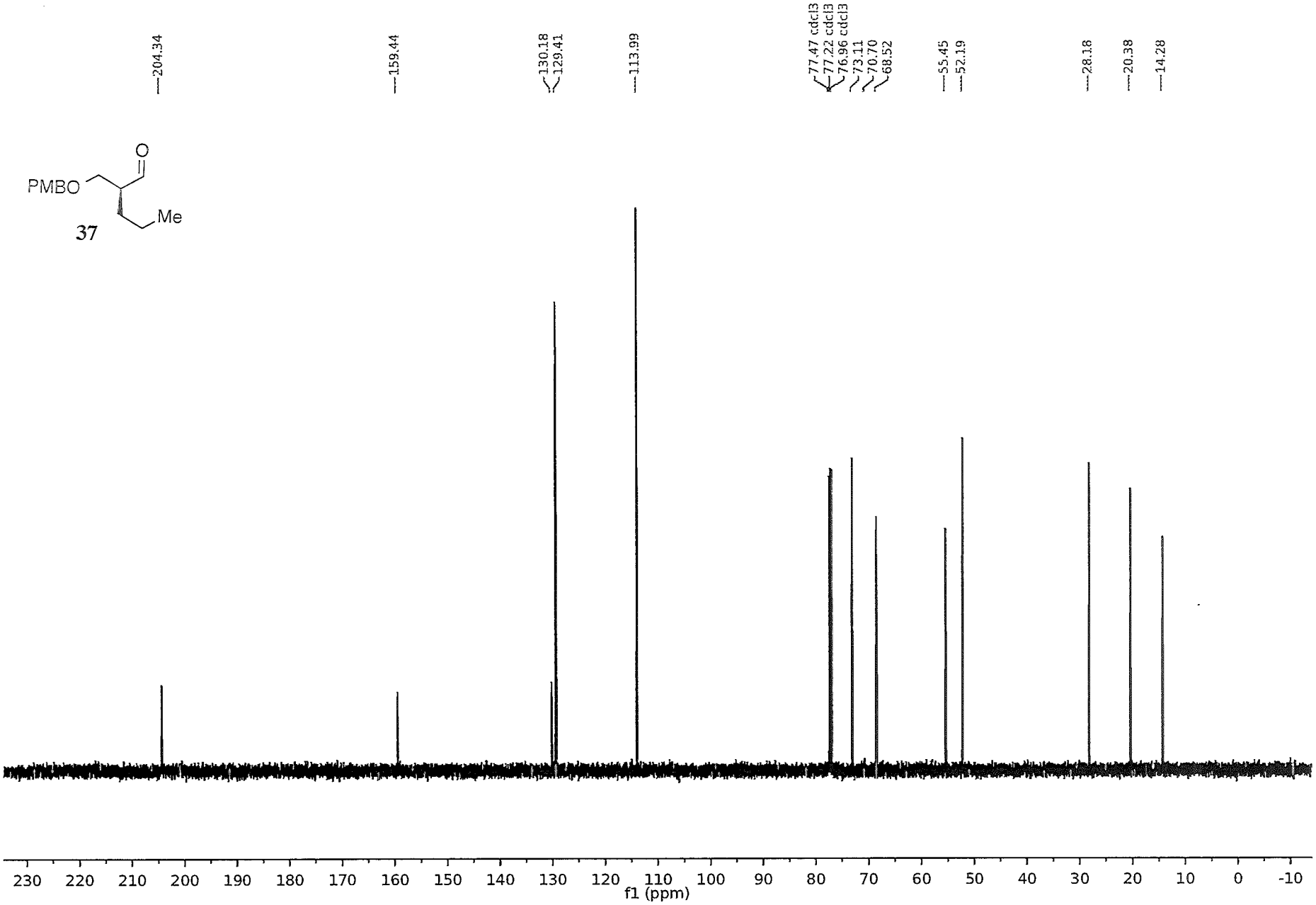
2.07
2.92
2.06
1.07
1.44
1.12
2.05
2.98
f1 (ppm)


204.34
159.44
130.18
129.41
113.99
77.47 cdcl3
77.22 cdcl3
76.96 cdcl3
73.11
70.70
68.52
55.45
52.19
28.18
20.38
14.28
PMBO
O
Me
37
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)