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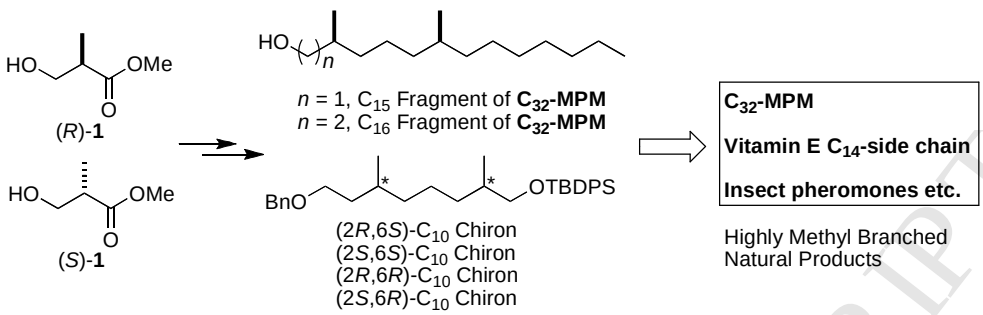
TOC/Graphical Abstract



Synthesis of Stereopure Acyclic 1,5-Dimethylalkane Chirons: Building Blocks of Highly Methyl Branched Natural Products

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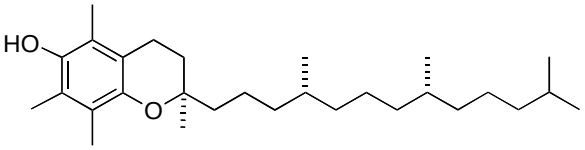
ABSTRACT: An efficient synthetic method towards stereopure acyclic 1,5-dimethylalkane building blocks from methyl (2*R*)-3-hydroxy-2-methylpropionate (*R*)-**1** (>99% ee) and methyl (2*S*)-3-hydroxy-2-methylpropionate (*S*)-**1** (>99% ee) through a series of chemical transformations, including Julia–Kocienski olefination and diimide reduction, is described. Through this strategy, two fragments of β-D-mannosyl phosphomycoketide (**C_{32}-MPM**) and four stereopure 1,5-dimethylalkane C_{10} chirons are prepared. These **C_{32}-MPM** fragments and C_{10} chirons have shown great potential application as building blocks for the synthesis of highly methyl-branched natural products containing chiral oligoisoprenoid-like chains.

KEYWORDS: Stereopure, Acyclic, 1,5-Dimethylalkane C_{10} Chiron, Highly Methyl Branched Natural Product, Oligoisoprenoid Chain.

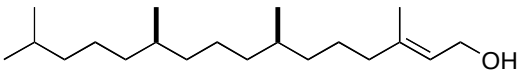
INTRODUCTION

The chiral 1,5-dimethylalkane subunit is ubiquitous among many biologically active natural products (Figure 1), such as vitamins,[1,2] phytol,[3] insect pheromones[4-12], marine natural

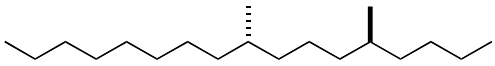
products,[13,14] archaeal lipids,[15-18] and the bacterial membrane lipids (β-D-mannosyl phosphomycoketides).[19,20] Total synthesis of these methyl-branched natural products has been an interesting and active subject for several decades due to their structural determinations and their increasing biological and biomedical applications.[21-28] For this purpose, a series of 1,5-dimethylalkane C_9 chirons (Figure 2A)[6,11,18,29-34] and 1,5-dimethylalkane C_{10} chirons (Figure 2B)[15,18,35-39] have been prepared. These C_9 chirons have been used to prepare a vitamin E C_{14}-side chain[29,31,34] and some insect pheromones (Figure 1, **III-VI**).[6,11,29,33] Not only have C_{10} chirons been used to prepare a vitamin E side chain[37] and insect pheromones,[36] but they have also been used to prepare highly methyl-branched archaeal lipids.[15,18] Additionally, van Summeren *et al.* reported the total synthesis of **C_{32}-MPM** using the C_{10} chiron: methyl (3*R*,7*S*)-3,7-dimethyl-8-hydroxyoctanoic ester (Figure 2B: **XVIa**).[40] However, this approach yielded **C_{32}-mycoketide**, the precursor of the final **C_{32}-MPM**, with only 70% stereopurity.[41] In a recently published report, we described a highly stereocontrolled total synthesis of **C_{32}-MPM** with >96% stereopurity starting from a single chiral source, (2*S*)-3-hydroxy-2-methylpropionate ((*S*)-**1**).[42] Here, we report the synthesis of a series of stereopure 1,5-dimethylalkane acyclic chirons (Figure 2C). Through a series of chemical transformations, including Julia–Kocienski olefination and diimide reduction, we developed an alternative synthesis of the C_{15} and C_{16} fragments of **C_{32}-MPM** beginning from (2*R*)-3-hydroxy-2-methylpropionate ((*R*)-**1**). We also prepared four stereopure 1,5-dimethylalkane C_{10} chirons (Figure 2C) from (*S*)-**1** and/or (*R*)-**1.** To further evaluate the synthetic value of these chirons in natural product synthesis, we prepared the vitamin E C_{14}-side chain (Figure 1, **I**) and the precursor of apple leaf miner pheromone (Figure 1, **III)** in a straightforward fashion.



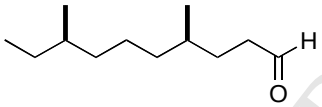
I:[1] **Vitamin E**



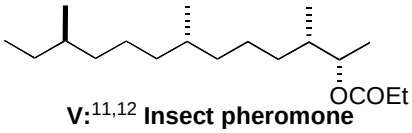
II:[3] **Phytol**



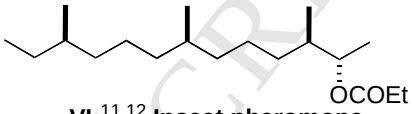
III:[4-8] **Insect pheromone**



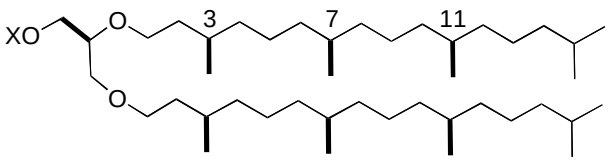
IV:[9,10] **Insect pheromone**



V:[11,12] **Insect pheromone**

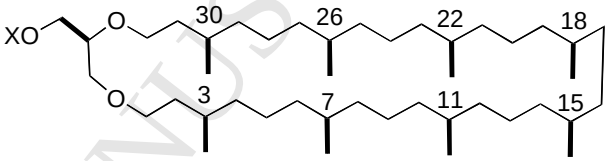


VI:[11,12] **Insect pheromone**



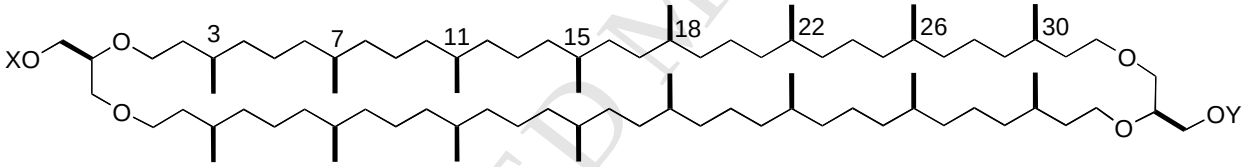
(3R, 7R, 11R)

VII:[15,16] **Archaeol lipid, a lipid isolated from *Methanobacterium thermoautotrophicum***



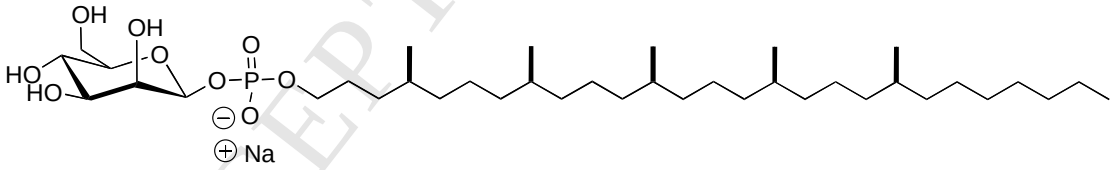
(3R, 7R, 11S, 15S, 18S, 22S, 26R, 30R)

VIII:[15] **Cyclic archaeol lipid, a lipid isolated from *Methanococcus jannaschii***



(3R, 7R, 11S, 15S, 18S, 22S, 26R, 30R)

IX:[17,18] **Caldarchaeol, an archaeal membrane lipid isolated from *Methanobacterium thermoautotrophicum***



X:[19,20] **β-D-mannosyl phosphomycoketide (C_{32}-MPM), a lipid isolated from *Mycobacterium Tuberculosis***

Figure 1. Examples of natural products containing 1,5-dimethylalkanesubunits.

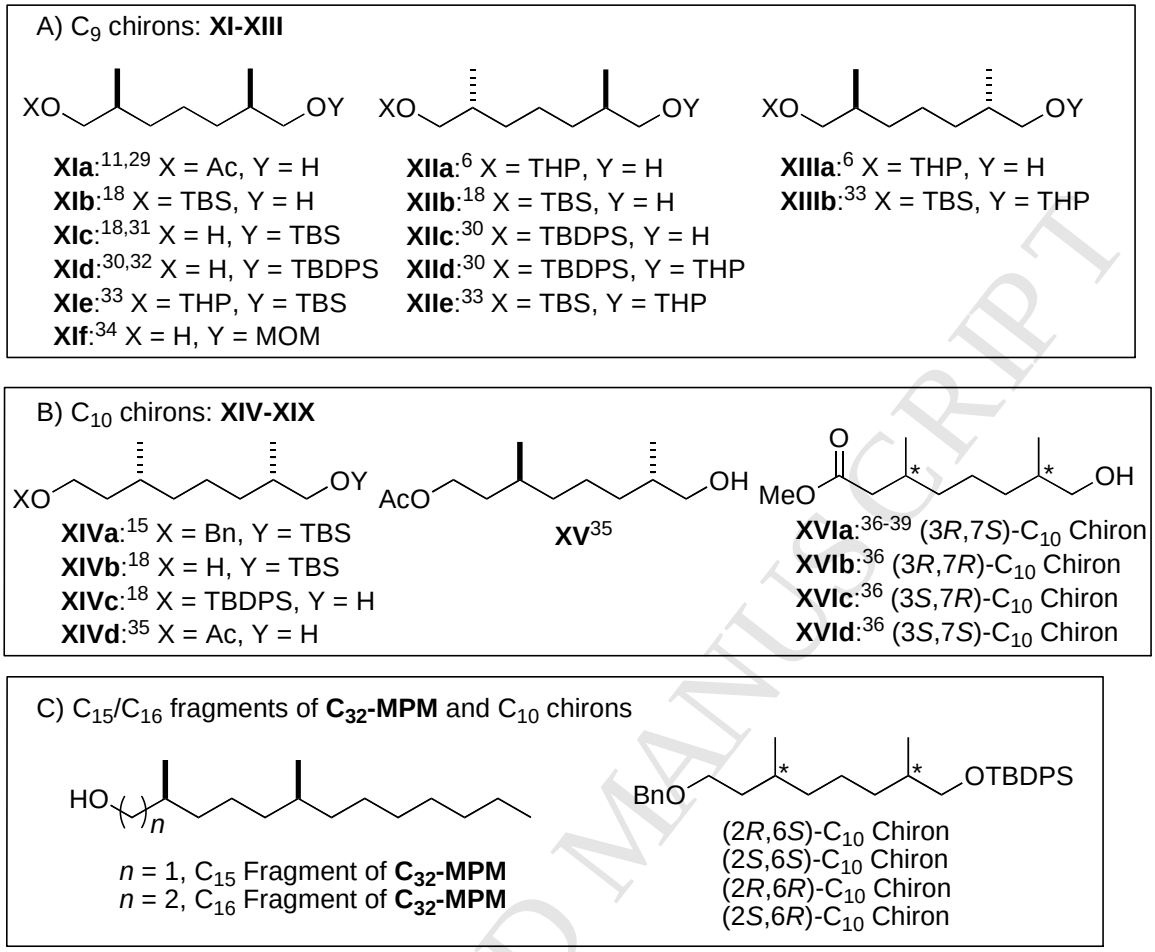


Figure 2. Structures of 1,5-dimethylalkane chirons. A) Examples of 1,5-dimethylalkane C_9 chirons reported in Literature;[6,11,18,29-34] B) Examples of 1,5-dimethylalkane C_{10} chirons reported in Literature.[18,35-39] C) Structures of C_{15}/C_{16} fragments of **C_{32}-MPM** and 1,5-dimethylalkane C_{10} chirons synthesized.

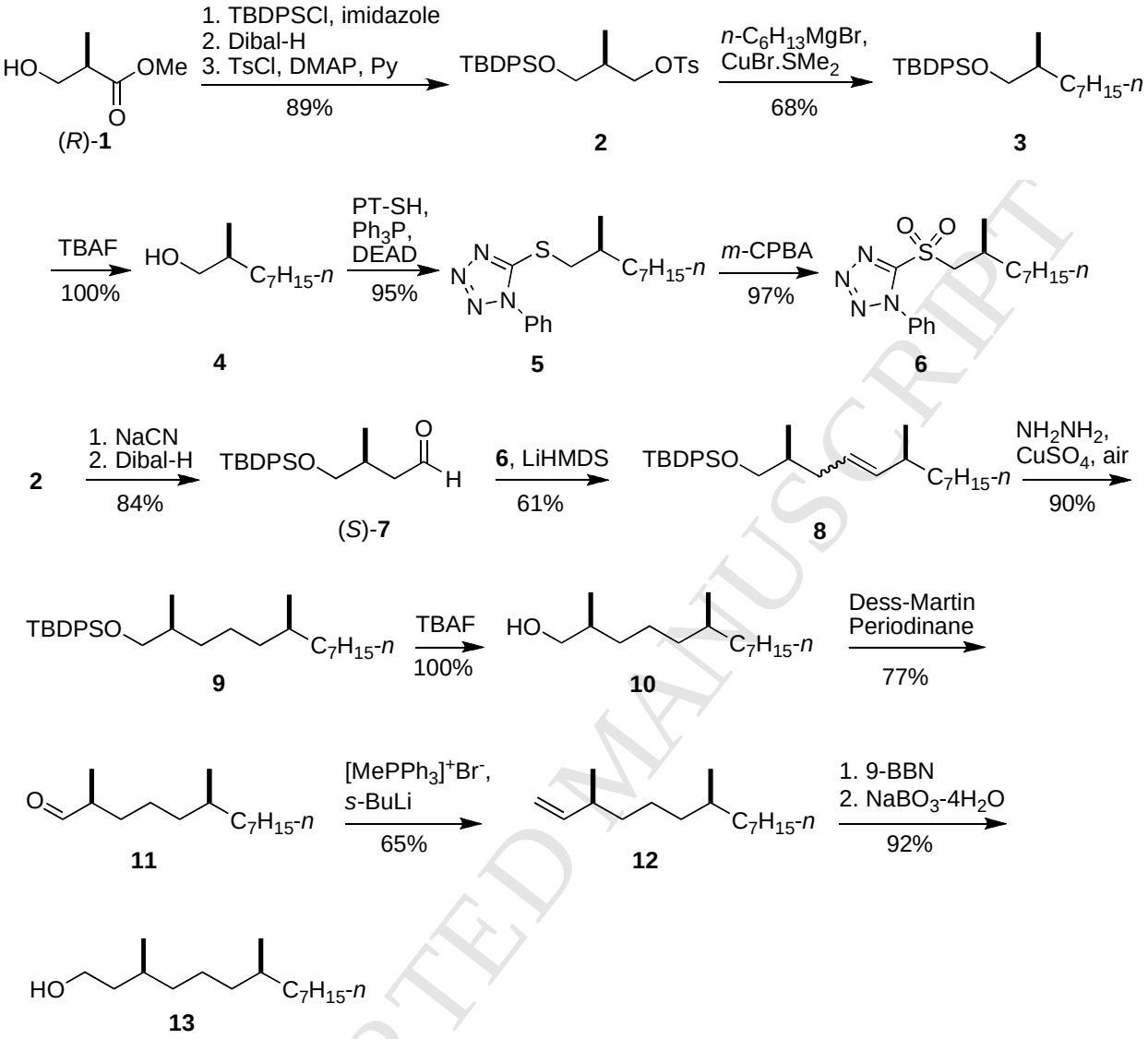
RESULTS AND DISCUSSION

A. Synthesis of the C_{15} and C_{16} fragments of **C_{32}-MPM** (Scheme 1), and the C_{15} diastereomer **15** (Scheme 2).

(2*R*)-3-(*tert*-Butyldiphenylsilyloxy)-2-methylpropyl tosylate (**2**) could be prepared from methyl (2*R*)-3-hydroxy-2-methylpropionate [(*R*)-**1**] in three steps (89% yield) via TBDPS

silylation, Dibal-H reduction and tosylation (Scheme 1). Tosylate **2** was then used as the common precursor to generate the two substrates needed in the Julia–Kocienski olefination reaction. *N*-Phenyltetrazolyl sulfone **6** was obtained from **2** in four steps (63% yield), and aldehyde (*S*)-**7** was prepared from **2** in two steps (84% yield). The Julia–Kocienski olefination[43] step was carried out by slow addition of lithium hexamethyldisilazide into a solution of sulfone **6** and (*S*)-**7** in THF at -78 ºC. Excess sulfone **6** could be used to improve the yield of olefination followed by recovery of the unreacted sulfone **6** by silica gel chromatography during the product purification. The reaction yielded alkene **8** in 61% yield as a mixture of (*E*/*Z*)-isomers (*E*/*Z* ~7:3). The relatively low *E*-selectivity of the reaction with these methyl branched substrates is consistent with our recently report with *E*/*Z* ~75:25.[42]

Scheme 1



Reduction of alkene **8** to compound **9** was then investigated using various reduction conditions. The results of these investigations are summarized in Table 1. The palladium-catalyzed hydrogenation approach afforded reduction product (67% yield) containing a 21% α-methyl epimerization along with a 15% recovery of its starting material (entry 1). Using platinum as a hydrogenation catalyst increased both the yield (90%) and stereopurity (*ca.* 9% α-methyl epimerization) of alkane **9** (entry 2). Iridium black, and osmium powder did not catalyze

the hydrogenation reaction (entries 3 and 4). The hydroboration/protonation procedure[44] could not be used to convert alkene **8** to compound **9** (entry 5). Reduction of **8** by Ashby's method[45] ($LiAlH_4$/Nickel(II) chloride), however, yielded **9** in 33% yield but the reaction was incomplete as 43% of **8** was recovered (entry 6). Diimide (HN=NH) offered an attractive alternative for alkene reduction as the proposed reaction mechanism involves a cyclic transition state that precludes epimerization.[46,47] Three additional methods for the *in situ* generation of diimide (A: $NH_2NH_2/NaIO_4$,[48] B: $TsNHNH_2$/NaOAc,[49] C: $NH_2NH_2/CuSO_4$[50]) were examined to reduce alkene **8**. Method A ($NH_2NH_2/NaIO_4$) gave stereopure **9** in 33% yield along with 14% recovery of **8**. On the other hand, Method B ($TsNHNH_2$/NaOAc) gave no reduced product, but Method C gave the best result. From the latter method, a 90% yield of the stereopure **9** was obtained when alkene **8** was reacted with 100 equivalent of hydrazine and ~10% copper(II) sulfate in ethanol at 70 ºC for 15 hours (Table 1, entry 15). Stereopure C_{15} fragment **9** of **C_{32}-MPM** was then obtained from (*R*)-**1** in nine steps with 31% overall yield. Additionally, C_{15} fragment **9** could be converted to the C_{16} fragment **13** in four steps with 46% overall yield (Scheme 1). This approach provides an alternative route leading to the C_{16} fragment from (*R*)-**1** in addition to our previously reported method beginning from (*S*)-**1**.[42] Both C_{15} and C_{16} fragments (**10** and **13**, respectively**)** have been used as intermediates to prepare β-D-mannosyl phosphomycoketide (**C_{32}-MPM**).[40,42]

Table 1. Reduction of alkene **8** to alkane **9**.

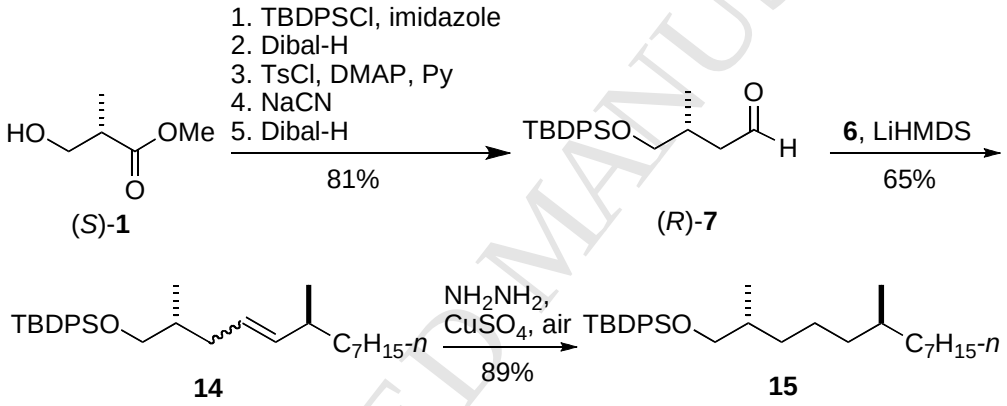
Entry	Reductive Reaction Conditions	Recovery of **8** (%)[a]	Yield (%)[b]
1[c,d]	10% Pd/C (0.2 equiv.), H_2, benzene, rt, overnight	15	67
2[c,e]	10% Pt/C (0.2 equiv.), H_2, benzene, rt, overnight	0	90
3	Iridium black (0.2 equiv.), H_2, benzene, rt, overnight	100	0
4	Osmium powder (0.2 equiv.), H_2, benzene, rt, overnight	100	0
5	i). 9-BBN/THF, rt, 24 h; ii). CH_3CO_2H, rt, 24 h	70	0
6	$NiCl_2$ (2.0 equiv.)/$LiAlH_4$ (2.0 equiv.), THF, -78 ºC-rt, 24 h	43	33
7	NH_2NH_2 (100 equiv.), $NaIO_4$ (2.5 equiv.), 75 ºC, 2 h	14	33
8	$TsNHNH_2$ (10 equiv.), NaOAc, dimethyl ethylene ether, reflux, 4 h	84	0
9	$CuSO_4$ (0.5 equiv.), NH_2NH_2 (140 equiv.), EtOH, rt, 63 h	10	64
10	$CuSO_4$ (0.5 equiv.), NH_2NH_2 (140 equiv.), EtOH, 70 ºC, 24 h	0	62
11	$CuSO_4$ (0.22 equiv.), NH_2NH_2 (140 equiv.), EtOH, 70 ºC, 24 h	0	63
12	$CuSO_4$ (0.22 equiv.), NH_2NH_2 (140 equiv.), EtOH, 70 ºC, 15 h	0	82
13	$CuSO_4$ (0.22 equiv.), NH_2NH_2 (70 equiv.), EtOH, 70 ºC, 15 h	5	73
14	$CuSO_4$ (0.22 equiv.), NH_2NH_2 (100 equiv.), EtOH, 70 ºC, 15 h	0	82
15	$CuSO_4$ (0.11 equiv.), NH_2NH_2 (100 equiv.), EtOH, 70 ºC, 15 h	0	90
16	$CuSO_4$ (0.10 equiv.), NH_2NH_2 (100 equiv.), EtOH, 70 ºC, 7.5 h	0	80
17	$CuSO_4$ (0.05equiv.), NH_2NH_2 (100 equiv.), EtOH, 70 ºC, 8 h	3	68

[a] Estimated by the ^{1}H NMR of the isolated product. [b] Isolated yield. [c] Epimerization estimated by the ^{13}C NMR of the isolated product. [d] 21% α-Methyl epimerization observed. [e] 9% α-Methyl epimerization observed.

Aldehyde (*R*)-**7** was prepared from (*S*)-**1** in five steps with 81% yield.[42] The Julia–Kocienski olefination of aldehyde (*R*)-**7** with sulfone **6** in the presence of lithium

hexamethyldisilazide gave alkene **14** in 65% yield (Scheme 2). Reduction of alkene **14** with diimide yielded *O*-silylated alkane **15** (a diastereomer of **9**) in 89% yield. Compound **15** could be used as an intermediate to prepare a modified **C_{32}-MPM** molecule with a change in chirality of single carbon from (*S*) to (*R*). We believe the efficient synthesis of natural and unnatural **C_{32}-MPMs** would allow further investigation into how the structure of **C_{32}-MPM** can influence its biological functions.

Scheme 2

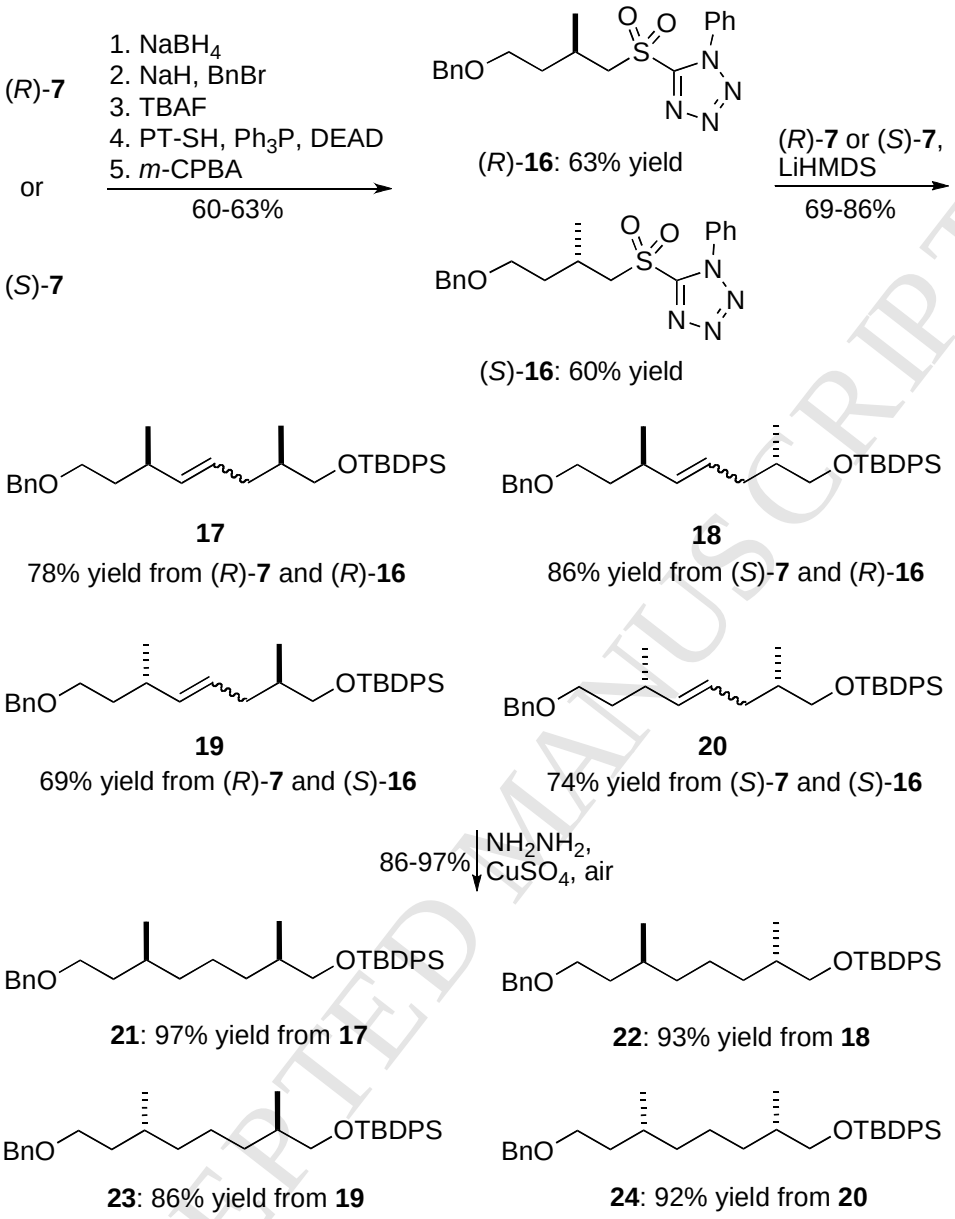


B. Synthesis of C_{10} chirons (**21-24**)

Enantiomeric aldehydes (*R*)-**7** and (*S*)-**7** were converted to the corresponding *N*-phenyltetrazolyl sulfones (*R*)-**16** and (*S*)-**16** in five steps with 60%-63% yield (Scheme 3). The Julia–Kocienski olefinations of (*R*)-**7** to (*R*)-**16**, (*S*)-**7** to (*R*)-**16**, (*R*)-**7** to (*S*)-**16,** and (*S*)-**7** to (*S*)-**16** in the presence of lithium hexylmethyldisilazide yielded alkenes **17** (78% yield), **18** (86%), **19** (69%) and **20** (74%), respectively. Reduction of the latter set of alkenes with hydrazine in the presence of copper(II) sulfate produced C_{10} chirons **21-24** in 86-97% yields. Each of these chirons contained a benzyl and a TBDPS protective group. Compounds with these two protective groups underwent the most common reaction conditions, such as treatment with acids, bases,

oxidants, reductants, and organometallic reagents but they could be selectively removed either by TBAF or by palladium-catalyzed hydrogenation to generate up to eight partially protected alcohols. Therefore, C_{10} chirons **21-24** (Figure 2C) are expected to be more versatile and flexible than any other of the C_9 and C_{10} chirons previously reported (Figures 2A and 2B). These partially protected alcohols are expected to be very useful for the synthesis of a range of methyl-branched natural products (Figure 1). The C_{10} chiron, **21,** has been synthesized and applied towards the total synthesis of **C_{32}-MPM**.[42]

Scheme 3

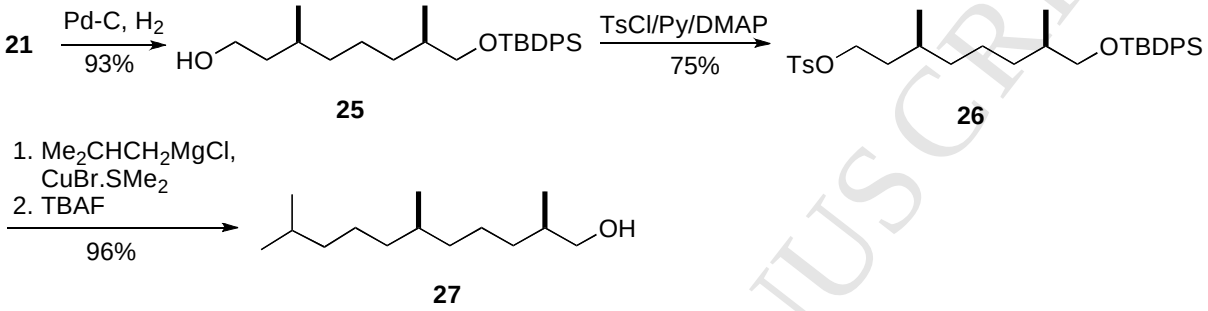


C. Application of C_{10} chirons to the synthesis of vitamin E C_{14}-side chain and the precursor of apple leaf miner pheromone (**III**)

To further evaluate the synthetic value of these chirons, the vitamin E C_{14}-side chain (**27**) was prepared from chiron **21** (Scheme 4). Removal of the benzyl group of **21** by palladium-catalyzed hydrogenation gave **25** in 93% yield. Reaction of **25** with TsCl in pyridine gave the tosylate **26** in 75% yield. The coupling reaction of tosylate **26** with isobutylmagnesium chloride

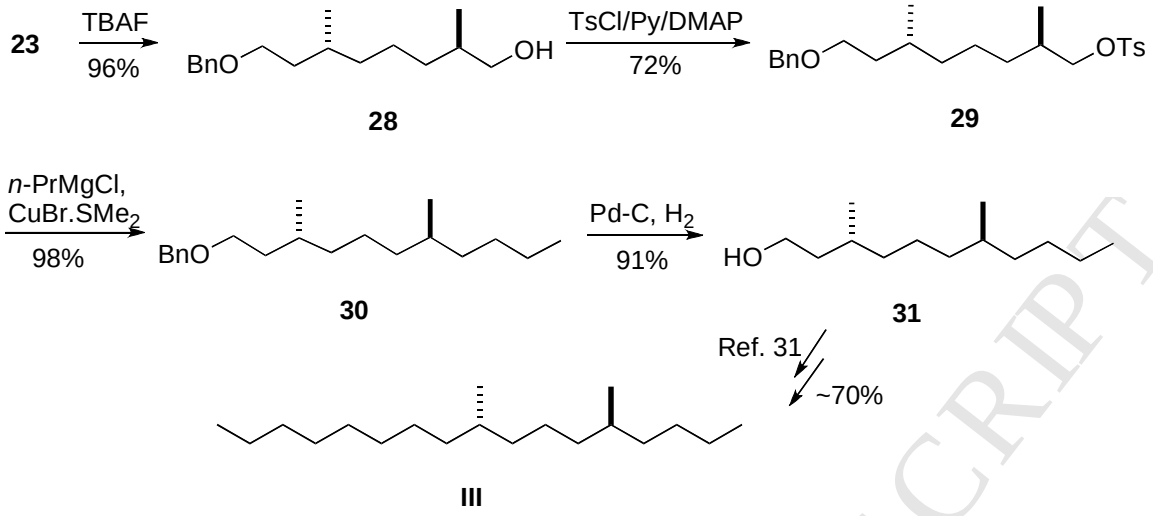
in the presence of copper (I) bromide dimethyl sulfide followed by desilylation with TBAF gave the vitamin E C_{14}-side chain (**27**)[29,31,34] in 96% yield.

Scheme 4



Chiron **23** was treated with TBAF to give alcohol **28** in 96% yield. Reaction of **28** with TsCl in pyridine gave tosylate **29** in 72% yield. Coupling of tosylate **29** with propylmagnesium chloride in the presence of copper (I) bromide-dimethyl sulfide complex provided **30** in 98% yield. Finally, catalytic hydrogenation of **30** produced alcohol **31** in 91% yield. The apple leafminer pheromone (Figure 1, **III**) was prepared from **31** in two steps with ~70% yield.[36]

Scheme 5



In summary, through a series of classic chemical transformations, including the Julia–Kocienski olefination and diimide reduction, we have developed an alternative synthesis of C_{15}/C_{16} fragments of **C_{32}-MPM** (**10** and **13** respectively) from (2*R*)-3-hydroxy-2-methylpropionate ((*R*)-**1**) in addition to our recently reported method beginning from (*S*)-**1**.[42] We further prepared four stereopure 1,5-dimethylalkane acyclic C_{10} building blocks (**21-24**) from (*R*)-**1** and (*S*)-**1**. These C_{10} chirons could be partially deprotected using either TBAF or Pd/H_2, and are expected to be more versatile and flexible than other C_9 and C_{10} chirons reported (Figure 2, A and B). The synthesis of vitamin E C_{14}-side chain, the precursor of insect pheromone, and **C_{32}-MPM**[42] has clearly demonstrated these 1,5-dimethyl fragments and chirons as very useful intermediates for the efficient synthesis of highly methyl-branched natural and unnatural products containing oligoisopenoid-like chains (Figure 1).

EXPERIMENTAL SECTION

Methyl (2*R*)-3-hydroxy-2-methylpropionate (*R*)-**1** (>99% ee) and methyl (2*S*)-3-hydroxy-2-methylpropionate (*S*)-**1** (>99% ee) were purchased from TCI America. All other reagents and anhydrous solvents were purchased from Aldrich; other solvents were purchased from Fisher.

(2*R*)-3-(*tert*-Butyldiphenylsilyloxy)-2-methylpropyl *p*-toluenesulfonate (2): To a solution of (*R*)-**1** (11.8 g, 100 mmol) and imidazole (15.0 g, 220 mmol) in dry dichloromethane (100 mL) at 0 ºC was added dropwise TBDPSCl (28.2 mL, 110 mmol). After the mixture was stirred at rt for 1 h, the reaction was quenched with water (40 mL). The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was co-evaporated with dry toluene (2 × 10 mL) and then dried under vacuum.

To a solution of dried crude co-evaporated mixture (methyl (2*R*)-3-(*tert*-butyldiphenylsilyloxy)-2-methylpropionate (~100 mmol)) in anhydrous dichloromethane (200 mL) under an argon atmosphere at -78 ºC was added dropwise Dibal-H (1.0 M in hexane, 270 mL, 270 mmol). After the reaction mixture was stirred at -40 ºC then warmed to -10 ºC for 1 h, the mixture was poured into a cooled aqueous potassium sodium tartrate solution (1.0 M, 300 mL) and allowed to stir at rt overnight. The reaction mixture was extracted with diethyl ether, then the combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and solvent removal, the residue was co-evaporated with dry toluene (2 × 10 mL) and dried *in vacuo*.

To a solution of the dried crude (2*S*)-3-(*tert*-butyldiphenylsilyloxy)-2-methylpropanol (~100 mmol) and DMAP (20 mg) in dry pyridine (150 mL) under argon at 0 ºC was added *p*-TsCl (22.88 g, 120 mmol). After stirrirng at rt overnight, the reaction mixture was quenched with

water (150 mL). The reaction mixture was then extracted with ether (3 × 150 mL), and the combined organic layers were washed successively with 1 *N* HCl (150 mL), saturated aqueous $NaHCO_3$ (100 mL) and brine (150 mL). The organic layer was dried over $MgSO_4$. After filtration and solvent removal, the residue was purified by silica gel chromatography, eluting with 10% ethyl acetate in hexane to give **2**:[51,52] 42.8 g (89% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.78 (d, 2H, *J* = 8.0 Hz), 7.60-7.55 (m, 4H), 7.45-7.25 (m, 8H), 4.12 (dd, 1H, *J* = 5.6, 9.2 Hz), 4.00 (dd, 1H, *J* = 6.0, 9.2 Hz), 3.50 (dd, 1H, *J* = 4.8, 10.4 Hz), 3.46 (dd, 1H, *J* = 6.8, 10.4 Hz), 2.42 (s, 3H), 2.01 (m, 1H), 0.97 (s, 9H), 0.86 (d, 1H, *J* = 6.8); ^{13}C NMR ($CDCl_3$) δ 144.7, 135.7, 135.6, 134.9, 133.49, 133.46, 129.9, 129.8, 128.1, 127.8, 72.3, 64.6, 35.8, 26.9, 21.8, 19.3, 13.4.

1-(*tert*-Butyldiphenylsilyloxy)-(2*S*)-2-methyl-nonane (3): Under argon, hexylmagnesium bromide (2.0 M in diethyl ether, 40 mL, 80 mmol) was added slowly over 2 h to a solution of **2** (4.83 g, 10.0 mmol), copper (I) bromide-dimethyl sulfide complex (514 mg, 2.50 mmol) in anhydrous THF (130 mL) at -78 ºC. After the mixture was stirred in cold for 2 h, the reaction mixture was allowed to warm up to 0 ºC and stir overnight. The reaction was quenched with saturated ammonium chloride, followed by extraction with ether. The organic layers were combined, washed with brine and dried over $MgSO_4$. After filtration and solvent removal, the residue was purified by silica gel chromatography, eluting with hexane to give **3** as an oil: 2.72 g (68% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.69-7.64 (m, 4H), 7.45-7.30 (m, 6H), 3.51 (dd, 1H, *J* = 6.0, 10.0 Hz), 3.43 (dd, 1H, *J* = 6.4, 10.0 Hz), 1.64 (m, 1H), 1.42 (m, 1H), 1.33 -1.77 (m, 11H), 1.06 (s, 9H), 0.91 (d, 3H, *J* = 6.8 Hz), 0.88 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 135.8, 134.3, 129.6, 127.7, 69.1, 35.9, 33.3, 32.1, 30.1, 29.5, 27.1, 27.0, 22.9, 19.5, 17.1, 14.3; HRMS (ESI/APCl) calcd for $C_{26}H_{41}OSi$ [MH^+] 397.2921, found 391.2918.

(2*S*)-2-Methyl-1-nonanol (4): To a solution of **3** (2.72 g, 6.85 mmol) in THF (15 mL) was added TBAF (1.0 M in THF, 10.0 mL, 10.0 mmol). After the mixture was stirred at rt overnight, the solvent was removed, and the residue was purified by silica gel chromatography, eluting with 10% ethyl acetate in hexane to give **4** as an oil:[53] 1.08 g (100% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 3.44 (m, 1H), 3.36 (m, 1H), 1.56 (m, 1H), 1.40-1.15 (m, 12H), 0.90-0.85 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 68.5, 35.8, 33.2, 32.0, 30.0, 29.4, 27.1, 22.8, 16.7, 14.2.

5-[(2*S*)-2-Methyl-nonylsulfanyl]-1-phenyl-1*H*-tetrazole (5): To a solution of **4** (1.08 g, 6.85 mmol), 1-phenyl-1*H*-tetrazole-5-thiol (1.46 g, 8.22 mmol), PPh_3 (2.16 g, 8.22 mmol) in anhydrous THF (20 mL) under argon at 0 ºC was added DEAD (1.32 mL, 8.22 mmol). After the mixture was warmed to rt and stirred for 1 h, the reaction was quenched with water and extracted with diethyl ether. The organic layers were combined and the solvent was removed, the residue was purified by silica gel chromatography, eluting with 5% ethyl acetate in hexane to give **5** as an oil: 2.08 g (95% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.65-7.50 (m, 5H), 3.46 (dd, 1H, J = 6.8, 12.4 Hz), 3.26 (dd, 1H, J = 12.4, 7.6 Hz), 1.93 (m, 1H), 1.47 (m, 1H), 1.41-1.18 (m, 11H), 1.04 (d, 3H, J = 6.5 Hz), 0.88 (t, 3H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 154.8, 133.9, 130.1, 129.8, 123.9, 40.6, 36.0, 33.0, 31.9, 29.8, 29.3, 26.9, 22.7, 19.2, 14.2; HRMS (ESI/APCl) calcd for $C_{17}H_{27}N_4S$ [MH^+] 319.1951, found 319.1953.

5-[(2*S*)-2-Methyl-nonane-1-sulfonyl]-1-phenyl-1*H*-tetrazole (6): To a solution of **5** (1.75 g, 5.48 mmol) in dichloromethane (65 mL) at 0 ºC was added *m*-CPBA (77%, 6.15 g, 27.4 mmol) was added. After the reaction mixture was stirred at rt overnight, 10% aqueous $Na_2S_2O_3$ (10 mL)

and saturated aqueous sodium bicarbonate (15 mL) were added, stirred for an additional 30 min, then extracted with dichloromethane multiple times. The organic layers were combined and washed successively with 10% aqueous $Na_2S_2O_3$ (10 mL), saturated aqueous sodium bicarbonate (2 × 10 mL) and brine. After solvent removal, the residue was purified by silica gel chromatography, eluting with 5% ethyl acetate in hexane to give **6** an oil: 1.87 g (97% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.73-7.56 (m, 5H), 3.81 (dd, 1H, *J* = 4.8, 14.4 Hz), 3.58 (dd, 1H, *J* = 14.4, 8.0 Hz), 2.33 (m, 1H), 1.53 (m, 1H), 1.43-1.20 (m, 11H), 1.15 (d, 3H, *J* = 6.8 Hz), 0.88 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 154.2, 133.2, 131.6, 129.8, 125.3, 62.0, 36.7, 31.9, 29.5, 29.3, 28.4, 26.4, 22.7, 19.8, 14.2; HRMS (ESI/APCl) calcd for $C_{17}H_{27}N_4O_2S$ [MH^+] 351.1849, found 351.1855.

(3*S*)-4-(*tert*-Butyldiphenylsilyloxy)-3-methylbutanal [(*S*)-7)]: A solution mixture of **2** (14.6 g, 30.3 mmol) and sodium cyanide (1.78 g, 95%, 36.4 mmol) in DMF (35 mL) was heated and stirred at 60 ºC for 24 h. After quenching the reaction with water (30 mL), the crude product was extracted with hexane (4 × 35 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. Following filtration and solvent removal, the residue was purified by silica gel chromatography, eluting with 5% ethyl acetate in hexane to give (3*S*)-4-(*tert*-butyldiphenylsilyloxy)-3-methylbutanenitrile:[32] 9.86 g (96% yield). ^{13}C NMR ($CDCl_3$) δ 135.67, 135.64, 133.32, 133.26, 130.0, 127.9, 119.0, 67.0, 33.4, 27.0, 21.2, 19.4, 16.0.

To a solution of (3*S*)-4-(*tert*-butyldiphenylsilyloxy)-3-methylbutanenitrile (1.14 g, 3.39 mmol) in anhydrous dichloromethane (4.0 mL) stirring at -78 ºC under argon was added dropwise Dibal-H (1.0 M in hexane, 3.7 mL, 3.7 mmol). After stirring at -78 ºC for 1 h, the reaction was quenched and acidified to pH 3 by slow addition of 1 *N* HCl. To the mixture,

diethyl ether (10 mL) and aqueous potassium sodium tartrate solution (1.0 M, 5.0 mL) were added, then the entire mixture was stirred at rt for an additional 2 h. The aqueous layer was extracted with diethyl ether (3 × 10 mL) and the combined organic layers were washed with brine then dried over $MgSO_4$. After filtration and solvent removal, the residue was purified by silica gel chromatography, eluting with 5% ethyl acetate in hexane to give (*S*)-**7**:[32,54] 1.014 g (88% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 9.78 (s, 1H), 7.70-7.60 (m, 4H), 7.48-7.30 (m, 6H), 3.57 (dd, 1H, *J* = 5.2, 10.0 Hz), 3.45 (dd, 1H, *J* = 7.2, 10.0 Hz), 2.60 (m, 1H), 2.40-2.20 (m, 2H), 1.05 (s, 9H), 0.94 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 202.8, 135.73, 135.71, 133.6, 129.8, 127.8, 68.5, 48.3, 31.4, 27.0, 19.4, 16.9.

1-(*tert*-Butyldiphenylsilyloxy)-(2*S*,6*S*)-2,6-dimethyl-(*Z*/*E*)-4-tridecene (8): Standard procedure for Julia–Kocienski olefination reaction: Under argon, LiHMDS (0.50 M in THF, 4.0 mL, 2.0 mmol) was added in a dropwise fashion over 15 min. to a solution of **6** (700 mg, 2.00 mmol) and (*S*)-**7** (0.448 g, 1.32 mmol) in anhydrous THF (15 mL) at -78 ºC. The resulting yellow solution was stirred at -78 ºC for 3 h and then allowed to warm to rt overnight. The reaction was quenched with aqueous saturated NH_4Cl and the aqueous layer was extracted with Et_2O. After solvent removal, the residue was purified by silica gel chromatography, eluting with hexane to give **8** as an oil: 0.374 g (61% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.70-7.60 (m, 4H), 7.45-7.30 (m, 6H), 5.26 (m, 2H), 3.49 (m, 2H), 2.45-1.95 (m, 2H), 1.84 (m, 1H), 1.70 (m, 1H), 1.34-1.25 (m, 12H), 1.06 (s, 9H), 0.94-0.83 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 138.3, 137.7, 135.8, 134.28, 134.25, 129.6, 127.7, 126.5, 126.4, 68.8, 68.5, 37.7, 37.3, 36.9, 36.8, 36.4, 36.3, 32.1, 31.8, 31.2, 30.0, 29.9, 29.5, 27.7, 27.5, 27.0, 22.8, 21.4, 21.1, 19.5, 16.8, 16.6, 14.3; HRMS (ESI/APCl) calcd for $C_{31}H_{49}OSi$ [MH^+] 465.3547, found 465.3555.

1-(*tert*-Butyldiphenylsilyloxy)-(2*S*,6*S*)-2,6-dimethyl-tridecane (9): Standard procedure for diimide reduction reaction: $CuSO_4$ (1.4 mg, 0.0086 mmol) was added to a solution of **8** (40 mg, 0.086 mmol) and hydrazine (0.27 mL, 8.6 mmol) in ethanol (5 mL). After the mixture was bubbled with air and stirred at 70 ºC for 15 h, the solvent was removed, and the residue was purified by silica gel chromatography, eluting with hexane to give product **9**:[40] 36 mg (90% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.70-7.60 (m, 4H), 7.45-7.30 (m, 6H), 3.51 (dd, 1H, *J* = 5.6, 9.6 Hz), 3.43 (dd, 1H, *J* = 6.4, 9.6 Hz), 1.65 (m, 1H), 1.45-1.00 (m, 19H), 1.05 (s, 9H), 0.92 (d, 3H, *J* = 6.8 Hz), 0.88 (t, 3H, *J* = 6.4 Hz), 0.83 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 135.8, 134.3, 129.6, 127.7, 69.1, 37.5, 37.2, 35.9, 33.6, 32.9, 32.1, 30.1, 29.5, 27.2, 27.0, 24.5, 22.8, 19.9, 19.5, 17.1, 14.3.

(2*S*,6*S*)-2,6-Dimethyl-1-tridecanol (10): TBAF (1.0 M, 1.66 mL, 1.66 mmol) was added to a solution of **9** (388 mg, 0.83 mmol) in THF (3.0 mL). After the mixture was stirred at rt overnight, the solvent was removed, and the residue was purified by silica gel chromatograph, eluting with 8% ethyl acetate in hexane to give product **10**:[40] 189 mg (100%). ^{1}H NMR ($CDCl_3$/TMS) δ 3.50 (dd, 1H, *J* = 6.0, 10.4 Hz), 3.40 (dd, 1H, *J* = 6.4, 10.4 Hz), 1.72 (brs, 1H), 1.60 (m, 1H), 1.45-1.17 (m, 16H), 1.17-1.00 (m, 3H), 0.92 (d, 3H, *J* = 6.8 Hz), 0.88 (t, 3H, *J* = 7.2 Hz), 0.84 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 68.3, 37.3, 37.0, 35.8, 33.5, 32.7, 31.9, 30.0, 29.4, 27.1, 24.4, 22.7, 19.7, 16.6, 14.1.

(2*S*,6*S*)-2,6-Dimethyl-tridecanal (11): Under argon, Dess-Martin periodinane (662 mg, 1.56 mmol) was added to a solution of **10** (297 mg, 1.30 mmol) in dichloromethane (10 mL) at 0 ºC. After stirring at 0 ºC to rt for 3 h, TLC showed the reaction was complete. The mixture was

diluted with ether (100 mL), the solid filtered off, and rinsed with ether. The filtrate was washed subsequently with 10% aqueous $Na_2S_2O_3$ (20 mL), aqueous $NaHCO_3$ (20 mL), brine (20 mL) and dried over $MgSO_4$. After filtration and solvent removal, the residue was purified by silica gel chromatography, eluting with 3% ethyl acetate in hexane to give **11**:[40] 0.228 g (77% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 9.61 (m, 1H), 2.33 (m, 1H), 1.70 (m, 1H), 1.45-1.16 (m, 17H), 1.16-1.03 (m, 1H), 1.09 (d, 3H, *J* = 8.4 Hz), 0.88 (t, 3H, *J* = 7.2 Hz), 0.84 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 205.5, 46.5, 37.2, 37.1, 32.8, 32.1, 31.0, 30.1, 29.5, 27.2, 24.6, 22.8, 19.8, 14.2, 13.5.

(3*S*,7*S*)-3,7-dimethyl-1-tetradecene (12): Under argon *s*-BuLi (1.4 M in cyclohexane, 2.1 mL, 3.0 mmol) was added slowly to a suspension of triphenylmethylphosphonium bromide (1.07 g, 3.00 mmol) in anhydrous THF (6 mL) at -78 ºC. After stirring at -78 ºC for 30 min, a solution of **11** (226 mg, 1.00 mmol) in anhydrous THF (3 mL) was added to the mixture under argon. The mixture was allowed to warm to rt overnight. The reaction was quenched with saturated aqueous ammonium chloride followed by extraction with ether, and drying the organic layers over magnesium sulfate. After solvent removal, the residue was purified by silica gel chromatography, eluting with hexane to give **12** as an oil: 146 mg (65% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 5.69 (m, 1H), 4.98-4.86 (m, 2H), 2.10 (m, 1H), 1.40-1.16 (m, 17H), 1.13-1.00 (m, 2H), 0.97 (d, 3H, *J* = 5.2 Hz), 0.88 (t, 3H, *J* = 5.2 Hz), 0.83 (d, 3H, *J* = 5.2 Hz); ^{13}C NMR ($CDCl_3$) δ 145.2, 112.3, 37.9, 37.29, 37.28, 37.1, 32.9, 32.1, 30.1, 29.6, 27.3, 24.8, 22.9, 20.4, 19.8, 14.3; HRMS (ESI/APCl) calcd for $C_{16}H_{32}$ [M^+] 224.2499, found 224.2500.

(3*S*,7*S*)-3,7-Dimethyl-1-tetradecanol (13): Under argon, 9-BBN (226 mg, 0.93 mmol) was added to a solution of **12** (104 mg, 0.46 mmol) in anhydrous THF (5 mL). After the reaction

mixture was stirred at rt overnight, water (3 mL) and $NaBO_3$-$4H_2O$ (859 mg, 5.58 mmol) were added, the mixture was stirred at rt for an additional 2 h. The mixture was extracted with diethyl ether (3 × 10 mL), the organic layers combined, and washed with brine. After solvent removal, the residue was purified by silica gel chromatography, eluting with 10% ethyl acetate in hexane to give **13** as an oil:[42] 103 mg (92% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 3.67 (m, 2H), 1.63 (brs, 1H), 1.59 (m, 2H), 1.42-1.00 (m, 20H), 0.92-0.82 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 61.3, 40.1, 37.6, 37.5, 37.2, 32.9, 32.1, 30.1, 29.7, 29.5, 27.2, 24.5, 22.8, 19.84, 19.78, 14.2; HRMS (EI-GCMS) calcd for $C_{16}H_{33}O$ $[M-H]^+$ 241.2531, found 241.2534.

1-(*tert*-Butyldiphenylsilyloxy)-(2*R*,6*S*)-2,6-dimethyl-(*Z*/*E*)-4-tridecene (14): Compound **14** was prepared according to standard procedure, as described for the synthesis of **8**. LiHMDS (0.50 M in THF, 3.06 mL, 1.53 mmol) was slowly added to a solution of **6** (536 mg, 1.53 mmol) and (*R*)-**7** (0369 mg, 1.08 mmol) in anhydrous THF (10 mL) at -78 ºC for 15 min. The reaction afforded **14** as an oil: 0.326 g (65% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.83-7.73 (m, 4H), 7.53-7.42 (m, 6H), 5.45-5.20 (m, 2H), 3.70-3.50 (m, 2H), 2.51 (m, 0.3H), 2.29 (m, 1H), 2.14 (m, 0.7H), 1.98 (m, 1H), 1.87 (m, 1H), 1.43-1.28 (m, 12H), 1.18 (s, 9H), 1.04-0.93 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 138.3, 137.7, 135.8, 134.26, 134.24, 129.6, 127.7, 126.5, 126.4, 69.0, 68.6, 37.8, 37.4, 37.0, 36.7, 36.5, 36.3, 32.1, 31.8, 31.2, 30.0, 29.9, 29.5, 27.7, 27.6, 27.1, 22.9, 21.4, 21.2, 19.50, 19.48, 16.84, 16.68, 14.3; HRMS (ESI/APCl) calcd for $C_{31}H_{49}OSi$ $[MH^+]$ 465.3547, found 465.3558.

1-(*tert*-Butyldiphenylsilyloxy)-(2*R*,6*S*)-2,6-dimethyl-tridecane (15): Following the standard procedure described for the synthesis of **9**, compound **15** was prepared from the reaction of **14**

(216 mg, 0.465 mmol) and hydrazine (1.46 mL, 46.5 mmol) in the presence of $CuSO_4$ (7.4 mg, 0.047 mmol) in ethanol (25 mL) while bubbling air flow and stirring at 70 ºC for 15 h. The reaction afforded product **15** as an oil: 194 mg (89% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.70-7.62 (m, 4H), 7.45-7.30 (m, 6H), 3.51 (dd, 1H, *J* = 5.6, 10.0 Hz), 3.44 (dd, 1H, *J* = 6.4, 10.0 Hz), 1.64 (m, 1H), 1.45-1.00 (m, 19H), 1.06 (s, 9H), 0.92 (d, 3H, *J* = 6.8 Hz), 0.88 (t, 3H, *J* = 6.4 Hz), 0.83 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 135.8, 134.3, 129.6, 127.7, 69.2, 37.5, 37.3, 35.9, 33.6, 32.9, 32.1, 30.2, 29.6, 27.3, 27.1, 24.6, 22.9, 19.9, 17.1, 14.3; HRMS (ESI/APCl) calcd for $C_{31}H_{51}OSi$ [MH^+] 467.3704, found 467.3714.

5-[(2*S*)-4-Benzyloxy-2-methyl-butane-1-sulfonyl]-1-phenyl-1*H*-tetrazole [(*S*)-16)]: (*S*)-**16** was prepared from [(*S*)-**7**] in five steps with 60% overall yield according to the procedure described for the synthesis of (*R*)-**16**.[42] ^{1}H NMR ($CDCl_3$/TMS) δ 7.70-7.50 (m, 5H), 7.36-7.23 (m, 5H), 4.48 (s, 2H), 3.98 (dd, 1H, *J* = 14.4, 4.4 Hz), 3.60 (dd, 1H, *J* = 14.4, 8.0 Hz), 3.58-3.51 (m, 2H), 2.54 (m, 1H), 1.83 (m, 1H), 1.68 (m, 1H), 1.17 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 154.1, 138.2, 133.1, 131.5, 129.7, 128.5, 127.72, 127.71, 125.3, 73.1, 67.3, 61.8, 36.1, 26.4, 19.8.

8-Benzyloxy-1-(*tert*-butyldiphenylsilyloxy)-(2*S*,6*R*)-2,6-dimethyl-(*Z*/*E*)-4-octene (18): Compound **18** was prepared according to the standard procedure described for the synthesis of **8.** LiHMDS (1.0 M in THF, 2.4 mL, 2.4 mmol) was slowly added to a solution of (*R*)-**16**[42] (918 mg, 2.38 mmol) and (*S*)-**7** (317 mg, 0.931 mmol) in anhydrous THF (10 mL) at -78 ºC for 15 min. The reaction yielded **18** as an oil: 399 mg (86% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.70-7.20 (m, 15H), 5.40-5.10 (m, 2H), 4.50-4.40 (m, 2H), 3.51-3.30 (m, 4H), 2.60 (m, 0.3H), 2.30-2.10 (m,

1.7H), 2.00-1.40 (m, 4H), 1.06 (s, 9H), 0.97-0.85 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 138.8, 138.7, 137.3, 136.6, 135.7, 134.13, 134.11, 129.6, 128.39, 128.37, 127.7, 127.53, 127.50, 127.3, 127.2, 73.03, 72.99, 68.88, 68.83, 68.7, 68.4, 37.3, 37.0, 36.5, 36.4, 36.2, 33.9, 31.1, 28.9, 27.0, 21.5, 21.2, 19.43, 19.41, 16.9, 16.6; HRMS (ESI/APCl) calcd for $C_{33}H_{44}O_2Si$ [MNH_4^+] 518.3449, found 518.3462.

8-Benzyloxy-1-(*tert*-butyldiphenylsilyloxy)-(2*R*,6*S*)-2,6-dimethyl-(*Z*/*E*)-4-octene (19): Compound **19** was prepared according to the standard procedure described for the synthesis of **8.** LiHMDS (1.0 M in THF, 1.5 mL, 1.5 mmol) was slowly added to a solution of (*S*)-**16** (563 mg, 1.46 mmol) and (*R*)-**7**[42] (341 mg, 1.00 mmol) in anhydrous THF (10 mL) at -78 ºC for 15 min. The reaction yielded **19** as an oil: 345 mg (69% yield). The ^{1}H and ^{13}C NMR data of **18** and **19** are consistent.

8-Benzyloxy-1-(*tert*-butyldiphenylsilyloxy)-(2*S*,6*S*)-2,6-dimethyl-(*Z*/*E*)-4-octene (20): Compound **20** was prepared according to the standard procedure described for the synthesis of **8.** LiHMDS (1.0 M in THF, 1.5 mL, 1.5 mmol) was slowly added to a solution of (*S*)-**16** (386 mg, 1.00 mmol) and (*S*)-**7** (170 mg, 0.500 mmol) in anhydrous THF (5 mL) at -78 ºC for 15 min. The reaction yielded **20** as an oil: 185 mg (74% yield). The ^{1}H and ^{13}C NMR data are consistent with that of its enantiomer **17**.[42]

8-Benzyloxy-1-(*tert*-butyldiphenylsilyloxy)-(2*S*,6*S*)-2,6-dimethyl-octane (22): According to the standard procedure described for the synthesis of **9**, compound **22** was prepared from **18** (397 mg, 0.793 mmol) and hydrazine (2.66 mL, 79.7 mmol) in the presence of $CuSO_4$ (12.7 mg, 0.0797 mmol) in ethanol (40 mL) while bubbling air and stirring at 70 ºC for 15 h. The reaction

yielded **22** as an oil: 0.370 g (93% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.70-7.60 (m, 4H), 7.45-7.20 (m, 11H), 4.49 (s, 2H), 3.55-3.35 (m, 4H), 1.70-1.00 (m, 10H), 1.05 (s, 9H), 0.91 (d, 3H, *J* = 6.4 Hz), 0.86 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 138.9, 135.8, 134.3, 129.6, 128.5, 127.73, 127.69, 127.6, 73.0, 69.1, 68.9, 37.5, 37.0, 35.8, 33.6, 30.0, 27.0, 24.4, 19.8, 19.5, 17.1; HRMS (ESI/APCl) calcd for $C_{33}H_{50}NO_2Si$ $[MNH_4]^+$ 520.3605, found 520.3612.

8-Benzyloxy-1-(*tert*-butyldiphenylsilyloxy)-(2*R*,6*R*)-2,6-dimethyl-octane (23): According to the standard procedure described for the synthesis of **9**, compound **23** was prepared from **19** (339 mg, 0.793 mmol) and hydrazine (2.26 mL, 67.7 mmol) in the presence of $CuSO_4$ (10.8 mg, 0.0677 mmol) in ethanol (35 mL) while bubbling air and stirring at 70 ºC for 15 h. The reaction yielded **23** as an oil: 0.293 g (86% yield). The ^{1}H and ^{13}C NMR data of **22** and **23** are consistent.

8-Benzyloxy-1-(*tert*-butyldiphenylsilyloxy)-(2*S*,6*R*)-2,6-dimethyl-octane (24): According to the standard procedure described for the synthesis of **9**, compound **24** was prepared from **20** (178 mg, 0.355 mmol) and hydrazine (1.19 mL, 35.5 mmol) in the presence of $CuSO_4$ (5.7 mg, 0.036 mmol) in ethanol (18 mL) while bubbling air and stirring at 70 ºC for 15 h. The reaction yielded **24** as an oil: 0.164 g (92% yield). The ^{1}H and ^{13}C NMR data are consistent with that of its enantiomer **21**.[42]

8-(*tert*-Butyldiphenylsilyloxy)-(3*S*,7*R*)-3,7-dimethyl-octyl *p*-toluenesulfonate (26): DMAP (2.0 mg) and TsCl (132 mg, 0.694 mmol) were added to a solution of **25**[42] (191 mg, 0.463 mmol) in pyridine (5.0 mL) at 0 ºC. After the reaction mixture was stirred at rt overnight, the reaction was quenched with water (1.0 mL) and extracted with ether. The organic layer was washed with 1 *N* HCl, water, followed by saturated aqueous $NaHCO_3$, and brine, and then dried over $MgSO_4$.

After filtration and solvent removal, the residue was purified by silica gel chromatography, eluting with 5% ethyl acetate in hexane to give **26** as an oil: (197 mg, 75% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.79 (m, 2H), 7.70-7.62 (m, 4H), 7.45-7.28 (m, 8H), 4.10-4.00 (m, 2H), 3.48 (dd, 1H, *J* = 10.0, 5.6 Hz), 3.42 (dd, 1H, *J* = 10.0, 6.4 Hz), 2.43 (s, 3H), 1.70-1.00 (m, 10H), 1.05 (s, 9H), 0.90 (d, 3H, *J* = 6.4 Hz), 0.78 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 144.7, 135.7, 134.2, 133.4, 129.9, 129.6, 128.0, 127.7, 69.2, 68.9, 37.1, 35.81, 35.78, 33.4, 29.3, 27.0, 24.2, 21.8, 19.5, 19.3, 17.1; HRMS (ESI/APCl) calcd for $C_{33}H_{46}O_4NaSiS$ [MNa^+] 589.2778, found 589.2793.

(2*R*,6*R*)-2,6,10-Trimethyl-undecanol-1 (27): Under argon to the solution of **26** (99.0 mg, 0.175 mmol), copper(I) bromide-dimethyl sulfide complex (20 mg, 0.097 mmol) in anhydrous THF (5 mL) at -78 ºC was added isobutylmagnesium chloride (2.0 M in diethyl ether, 2.0 mL, 4.0 mmol). After stirring at -78 ºC for 2 h, the reaction mixture was allowed to warm to 0 ºC and stir overnight. The reaction was quenched with saturated ammonium chloride, the organic layer was separated and the aqueous layer was extracted with ether. The organic layers were combined and washed with brine and dried over $MgSO_4$. After filtration and solvent removal, and the residue was treated with a TBAF solution (1.0 M in THF, 1.0 mL, 1.0 mmol) and allowed to at rt overnight. After solvent removal, the residue was purified by silica gel chromatography, eluting with 10% ethyl acetate hexane to give **27**:[29] 36 mg (96% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 3.55-3.47 (m, 2H), 1.62 (m, 1H), 1.52 (m, 1H), 1.42-1.00 (m, 13H), 0.92 (d, 3H, *J* = 6.8 Hz), 0.90-0.82 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 68.6, 39.5, 37.5, 37.4, 35.9, 33.6, 32.9, 28.1, 24.9, 24.6, 22.9, 22.8, 19.9, 16.8.

(2*R*,6*R*)-8-Benzyloxy-2,6-dimethyloctanol-1 (28): A TBAF solution (1.0 M solution, 0.50 mL, 0.50 mmol) was added to a solution of **23** (100 mg, 0.200 mmol) in THF (1.0 mL). After the mixture was stirred at rt overnight, the solvent was removed, and the residue was purified by silica gel chromatography, eluting with 15% ethyl acetate in hexane to give **28** as an oil: 51 mg (96% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.40-7.20 (m, 5H), 4.50 (s, 2H), 3.60-3.30 (m, 4H), 1.70-1.10 (m, 10H), 0.91 (d, 3H, *J* = 6.8 Hz), 0.87 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 138.8, 128.4, 127.7, 127.6, 73.0, 68.8, 68.4, 37.4, 36.9, 35.8, 33.4, 29.9, 24.4, 19.7, 16.7; HRMS (ESI/APCl) calcd for $C_{17}H_{29}O_2$ [MH^+] 265.2162, found 265.2162.

(2*R*,6*R*)-8-Benzyloxy-2,6-dimethyloctyl *p*-toluenesulfonate (29): To a solution of **28** (49.0 mg, 0.185 mmol) in pyridine (2.0 mL) at 0 ºC were added DMAP (1.0 mg) and TsCl (71 mg, 0.372 mmol). After the reaction mixture was stirred at rt overnight, the reaction was quenched with water then extracted with ether. The organic layer was washed successively with 1 N HCl, water, saturated aqueous $NaHCO_3$, and brine, and then dried over $MgSO_4$. After filtration and solvent removal, the residue was purified by silica gel chromatography, eluting with 5% ethyl acetate in hexane to give **29** as an oil: 56 mg, 72% yield. ^{1}H NMR ($CDCl_3$/TMS) δ 7.78 (d, 2H, *J* = 9.6 Hz), 7.40-7.20 (m, 7H), 4.49 (s, 2H), 3.87 (dd, 1H, *J* = 6.0, 9.2 Hz), 3.79 (m, 1H, *J* = 6.4, 9.2 Hz), 3.54-3.40 (m, 2H), 2.44 (s, 3H), 1.85-0.95 (m, 10H), 0.87 (d, 3H, *J* = 6.8 Hz), 0.84 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 144.7, 138.8, 133.3, 129.9, 128.5, 128.0, 127.7, 127.6, 75.3, 73.0, 68.7, 37.2, 36.9, 33.0, 32.9, 29.9, 24.0, 21.7, 19.7, 16.5; HRMS (ESI/APCl) calcd for $C_{24}H_{35}O_4S$ [MH^+] 419.2251, found 419.2259.

(3*R*,7*S*)-1-Benzyloxy-3,5-dimethylundecane (30): Under argon to a solution of **29** (55 mg, 0.13 mmol), copper (I) bromide-dimethyl sulfide complex (26.7 mg, 0.13 mmol) in anhydrous THF (5 mL) at -78 ºC was added *n*-propylmagnesium chloride (2.0 M in diethyl ether, 1.3 mL, 2.6 mmol). After the mixture was allowed to stir at -78 ºC then warm up to 0 ºC overnight, the reaction was quenched with saturated aqueous ammonium chloride. The organic layer was separated, and the aqueous layer was extracted with ether. After solvent removal, the residue was purified by silica gel chromatography, eluting with 10% ethyl acetate in hexane to give **30** as an oil: 37 mg (98% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 7.40-7.20 (m, 5H), 4.50 (s, 2H), 3.60-3.40 (m, 2H), 1.70-1.00 (m, 16H), 0.92-0.80 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 138.8, 128.5, 127.7, 127.6, 73.0, 68.9, 37.6, 37.5, 36.99, 36.97, 32.9, 30.0, 29.5, 24.5, 23.2, 19.82, 19.80, 14.3; HRMS (ESI/APCl) calcd for $C_{20}H_{33}O$ $[M-H]^+$ 289.2526, found 289.2518.

(3*R*,7*S*)-3,5-Dimethylundecanol-1 (31): 10% Pd on carbon (5.0 mg, 0.047 mmol) was added in a single portion to a solution of **30** (33 mg, 0.11 mmol) in ethyl acetate (5 mL). The resulting suspension was saturated with hydrogen gas by 5 vacuum-hydrogen cycles. After stirring at rt overnight under an H_2 atmosphere, TLC showed the reaction was complete. The catalyst was filtered off, the solvent from the filtrate was removed, and the filtrate residue was purified by silica gel chromatography, eluting with 10% ethyl acetate in hexane to give **31** as an oil:[36] 20 mg (91% yield). ^{1}H NMR ($CDCl_3$/TMS) δ 3.80-3.60 (m, 2H), 1.58 (m, 2H), 1.43-1.02 (m, 14H), 0.92-0.82 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 61.4, 40.2, 37.6, 37.4, 37.0, 32.9, 29.6, 29.5, 24.5, 23.2, 19.8, 19.7, 14.3.

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SUPPORTING INFORMATION

^{1}H and ^{13}C NMR spectra for all new compounds.

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Synthesis of Stereopure Acyclic 1,5-Dimethylalkyl Chirons: Building Blocks of Highly Methyl Branched Natural Products

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Supporting Information

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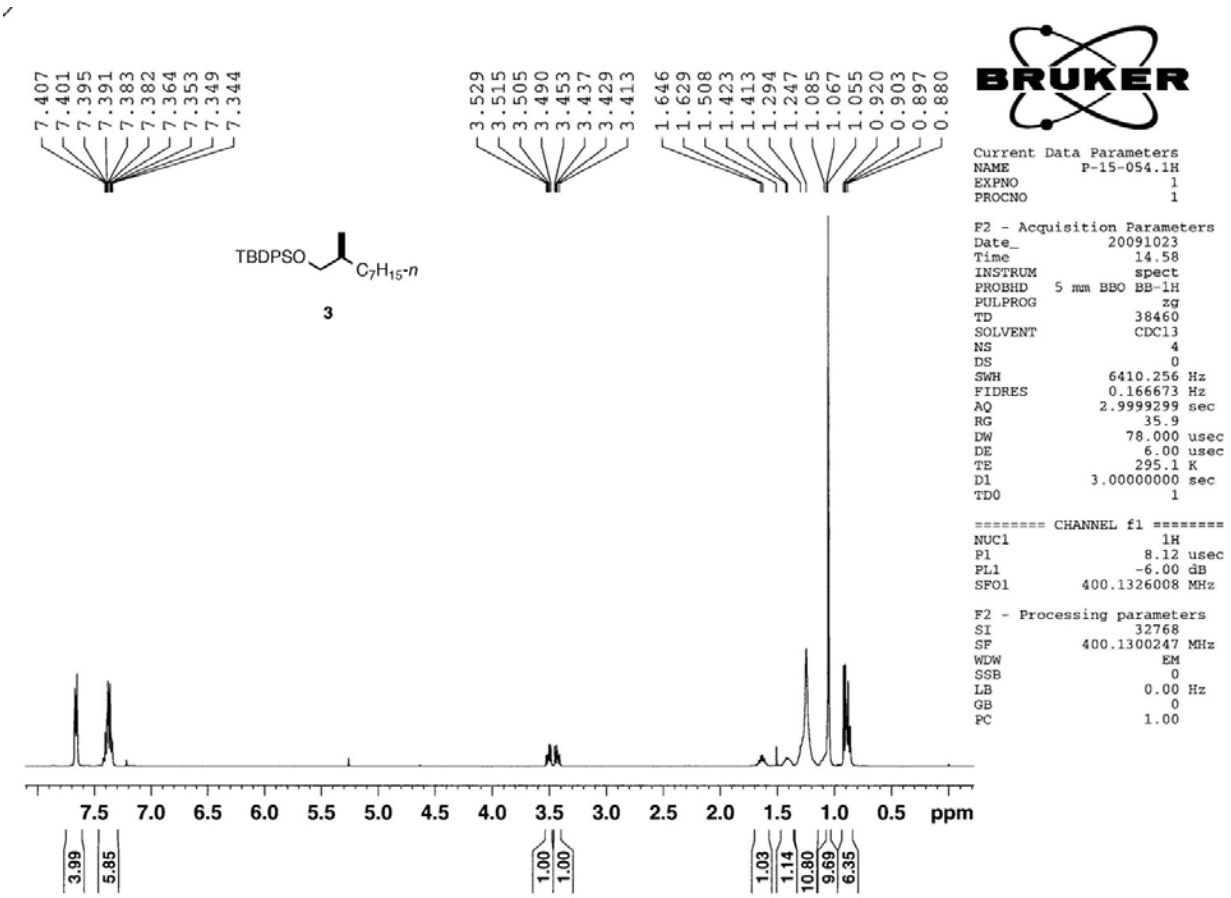


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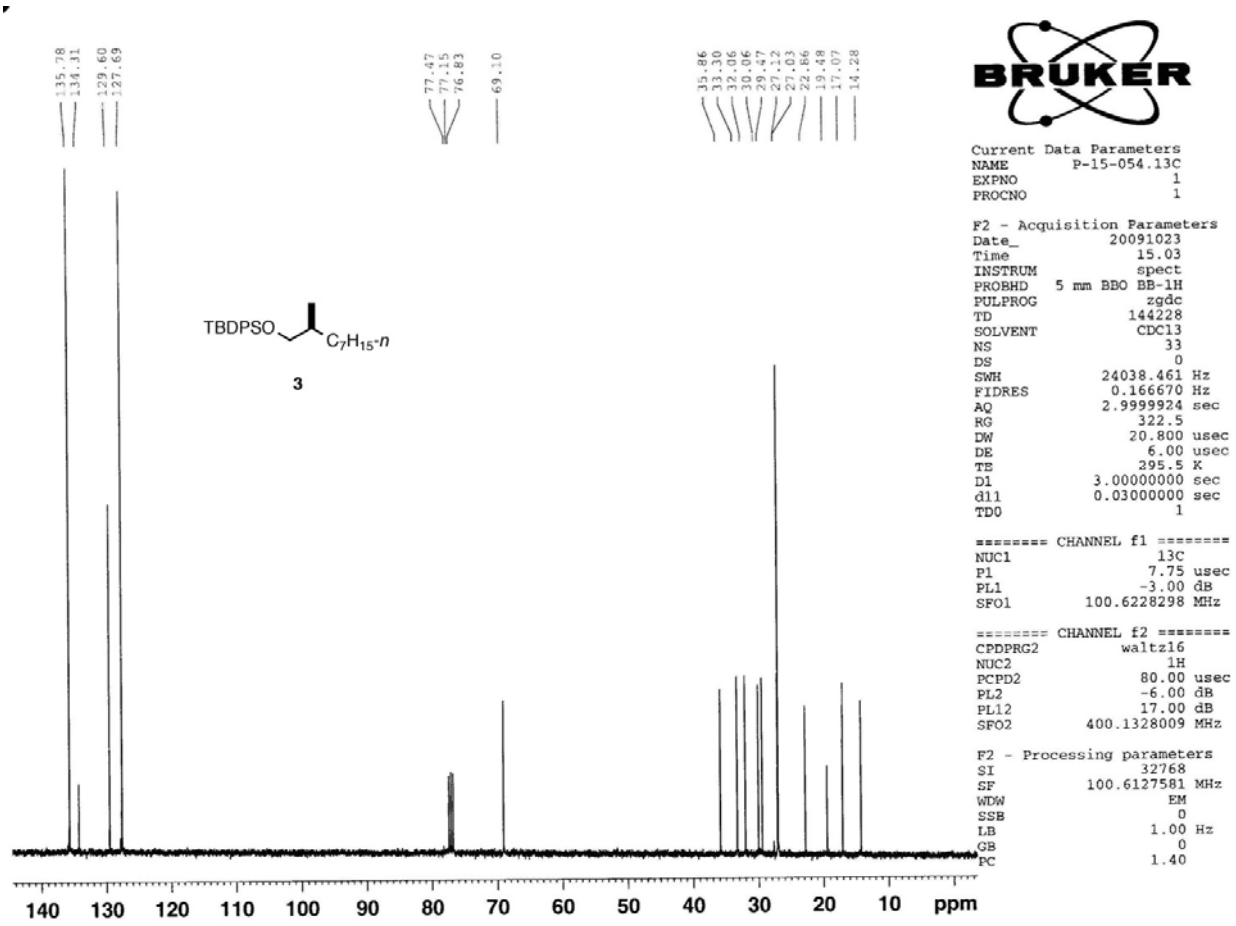

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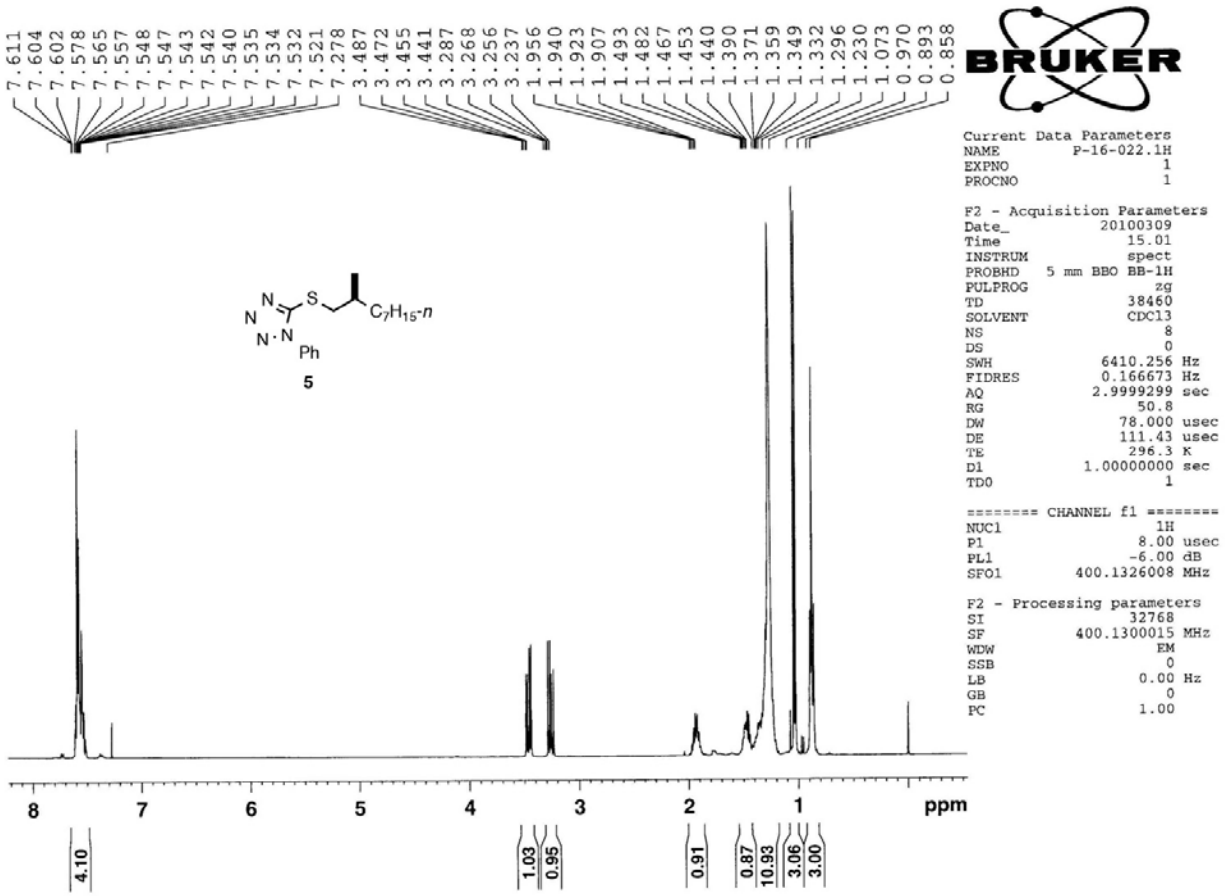
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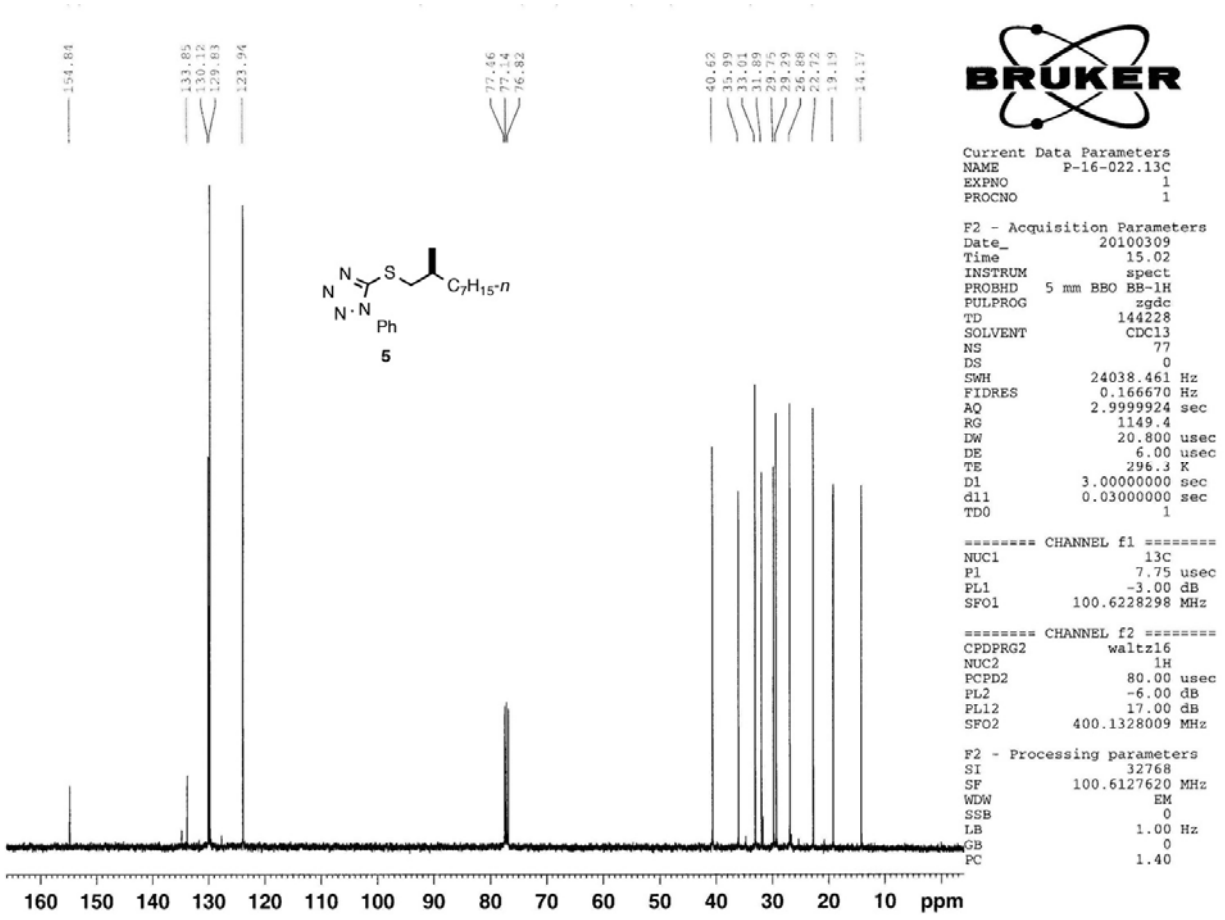
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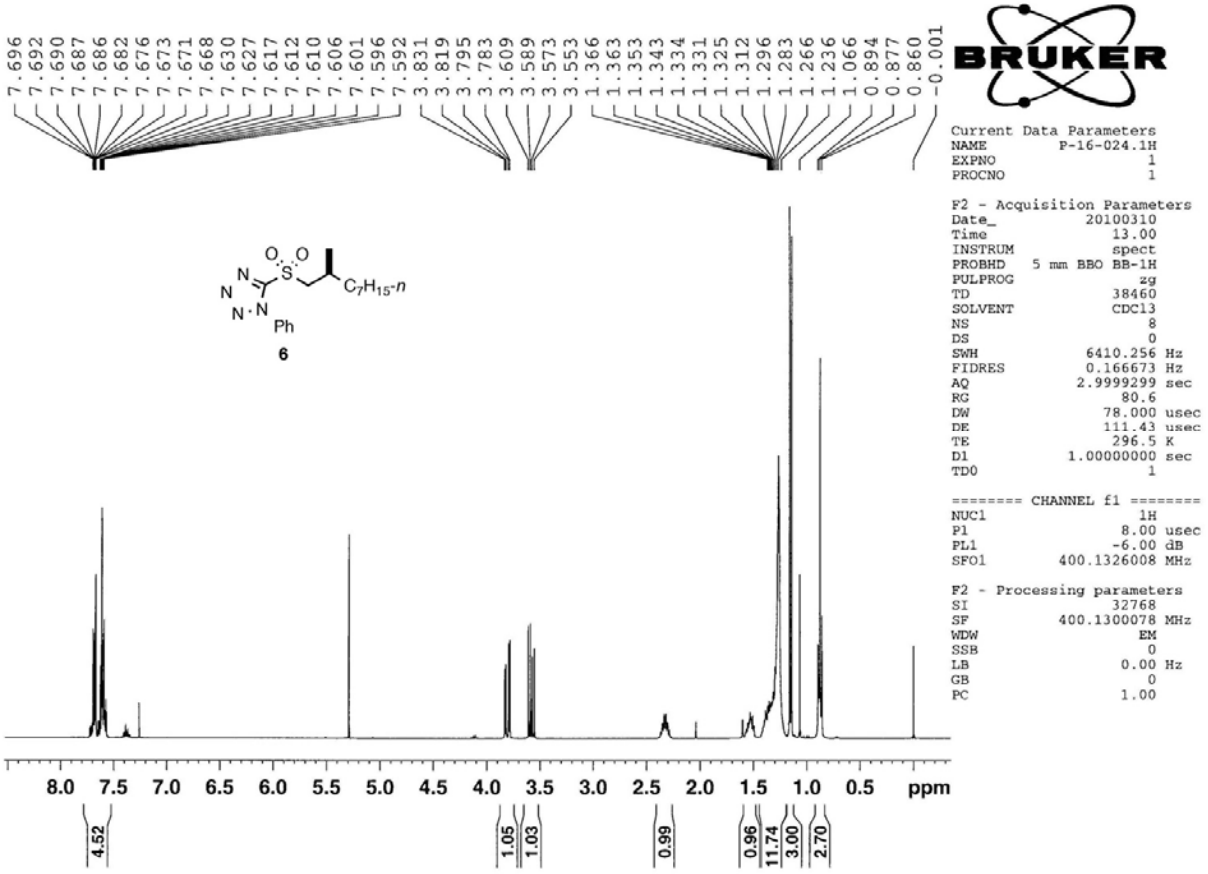
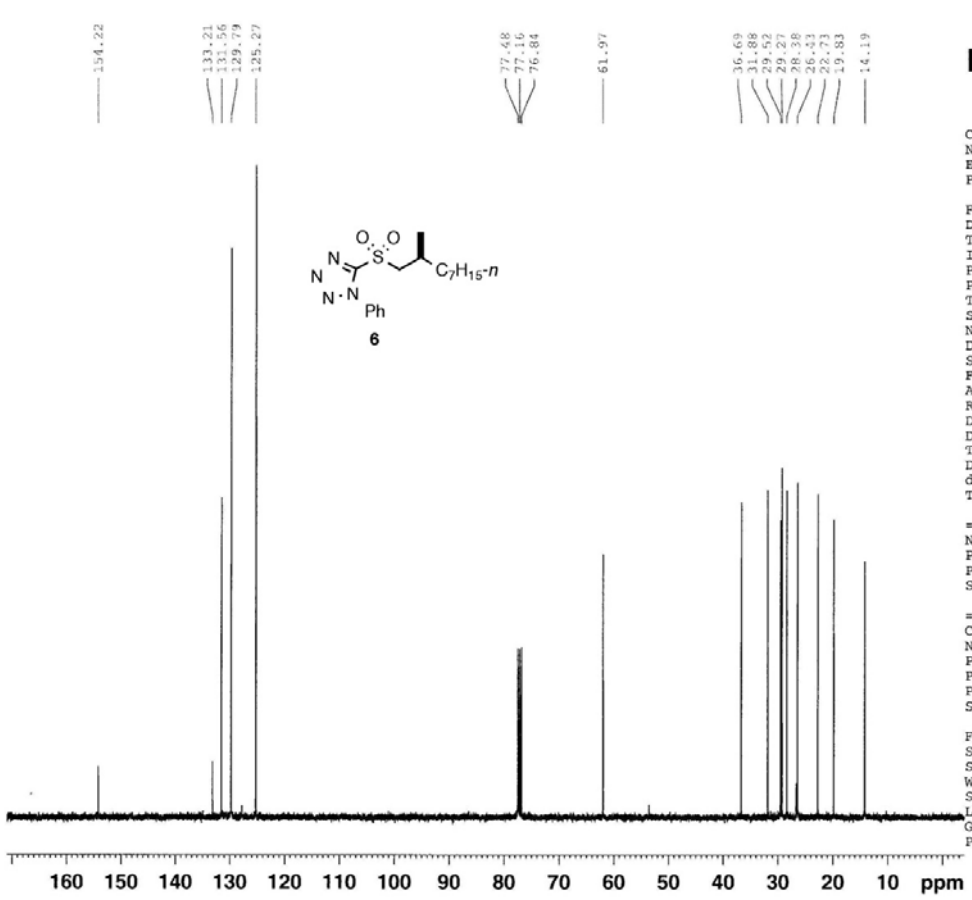
PL12 17.00 dB
SFO2 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 100.6127620 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.696
7.692
7.690
7.687
7.686
7.682
7.676
7.673
7.671
7.668
7.630
7.627
7.617
7.612
7.610
7.606
7.601
7.596
7.592
3.831
3.819
3.795
3.783
3.609
3.589
3.573
3.553
1.366
1.363
1.353
1.343
1.334
1.331
1.325
1.312
1.296
1.283
1.266
1.236
1.066
0.894
0.877
0.860
-0.001
BRUKER
Current Data Parameters
NAME P-16-024.1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100310
Time 13.00
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 38460
SOLVENT CDCl3
NS 8
DS 0
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 80.6
DW 78.000 usec
DE 111.43 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -6.00 dB
SFO1 400.1326008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300078 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
O
O
S
N
N
N
N
Ph
C7H15-n
6
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
ppm
4.52
1.05
1.03
0.99
0.96
11.74
3.00
2.70



BRUKER

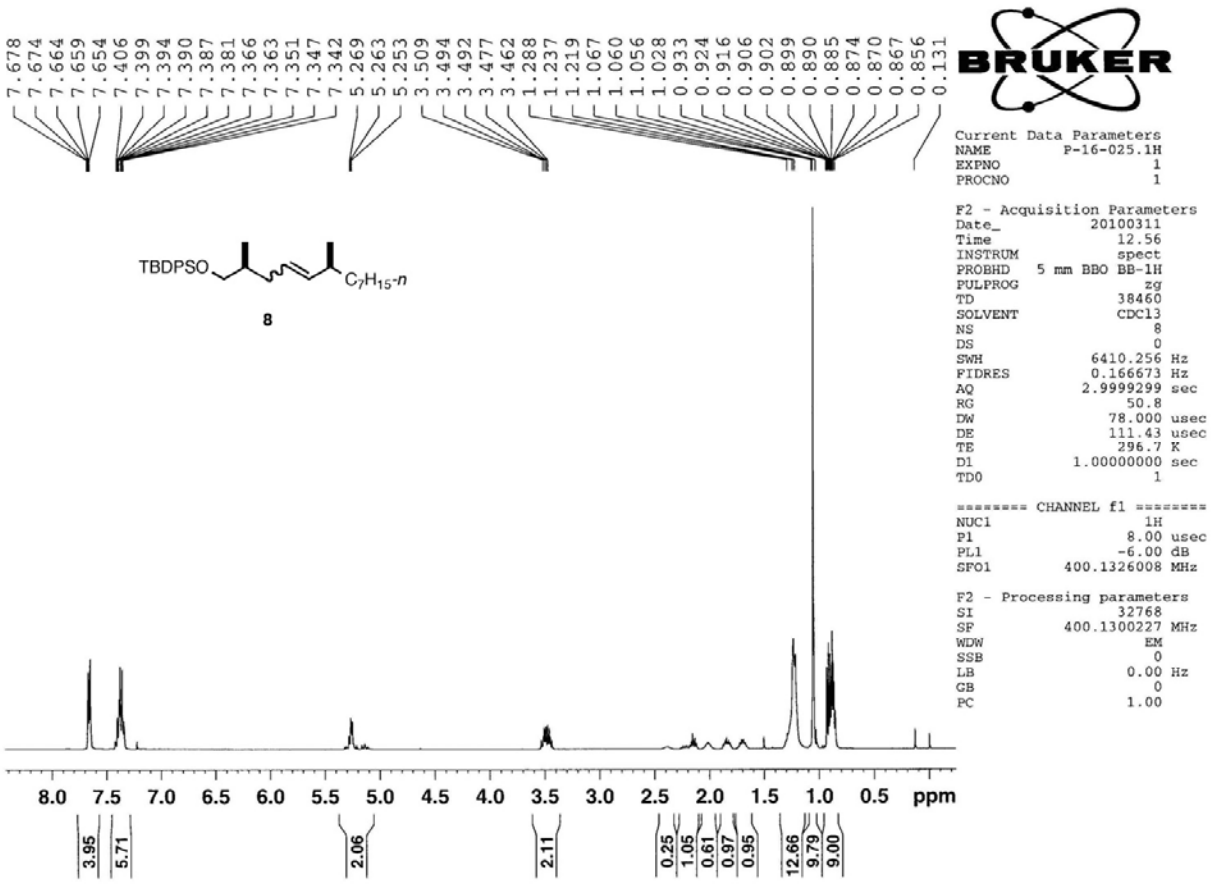
Current Data Parameters
NAME P-16-024.13C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100310
Time 13.02
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 144228
SOLVENT CDCl3
NS 95
DS 0
SWH 24038.461 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 406.4
DW 20.800 usec
DE 6.00 usec
TE 296.6 K
D1 3.00000000 sec
d11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.75 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 17.00 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 32768
SF 100.6127583 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



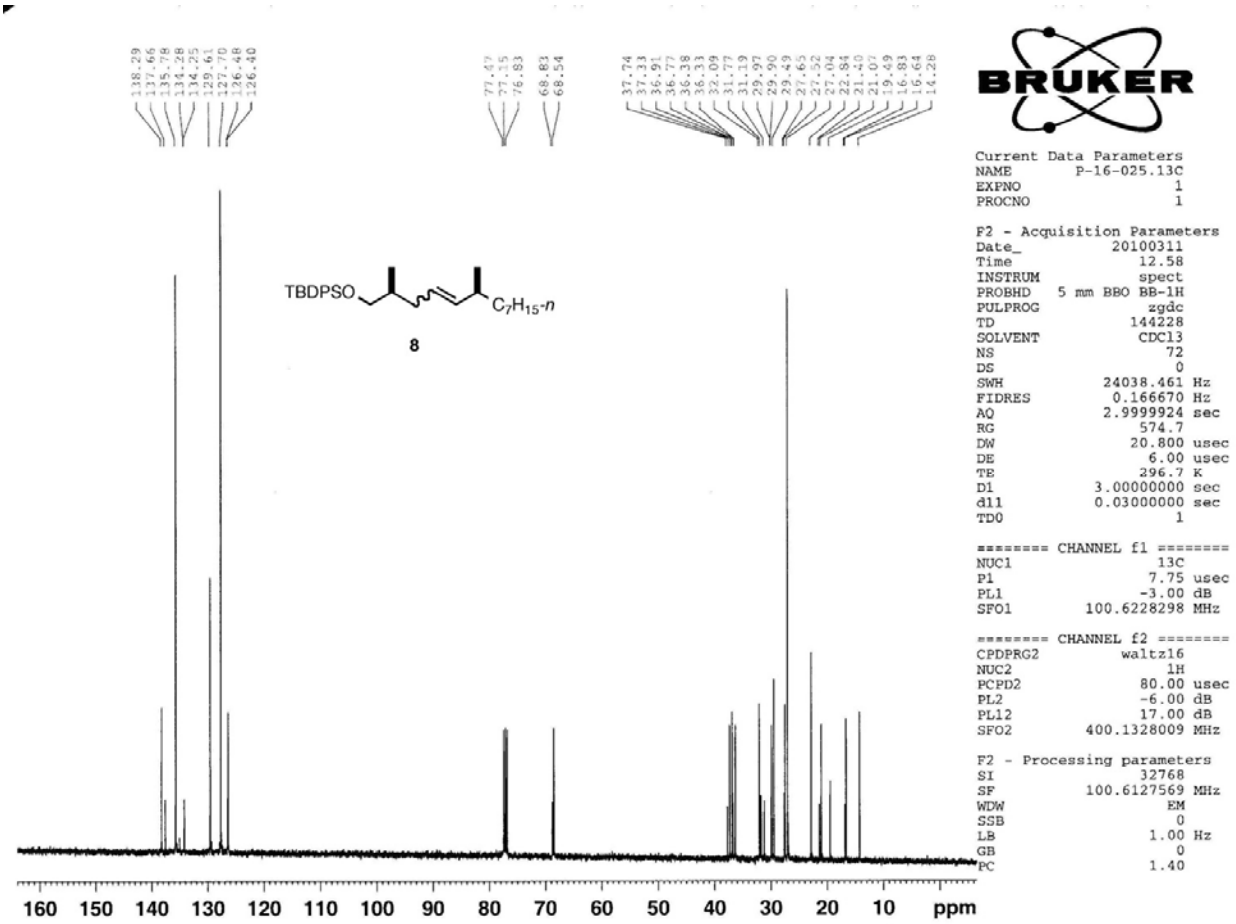
BRUKER

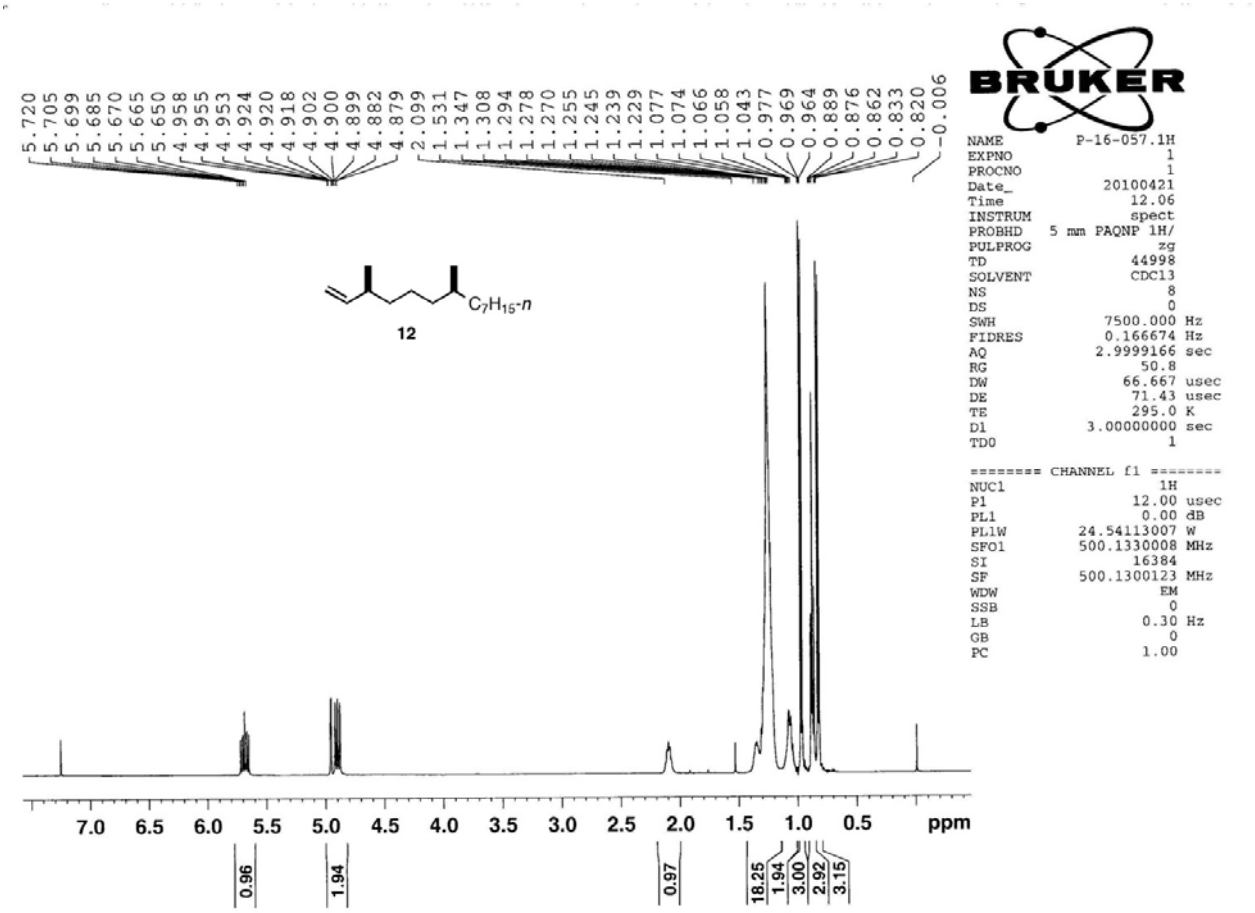
Current Data Parameters
NAME P-16-025.1H
EXPNO 1
PROCNO 1

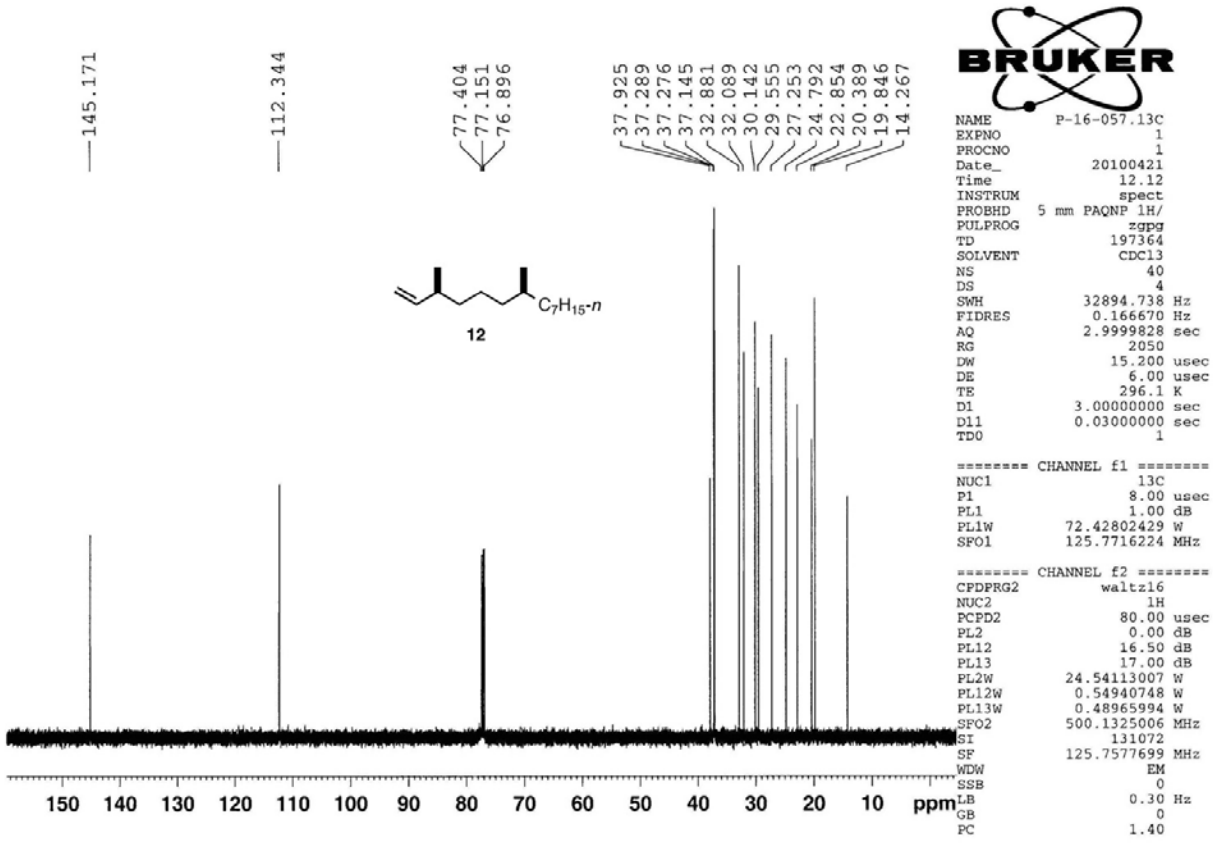
F2 - Acquisition Parameters
Date_ 20100311
Time 12.56
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 38460
SOLVENT CDCl3
NS 8
DS 0
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 50.8
DW 78.000 usec
DE 111.43 usec
TE 296.7 K
D1 1.00000000 sec
TD0 1

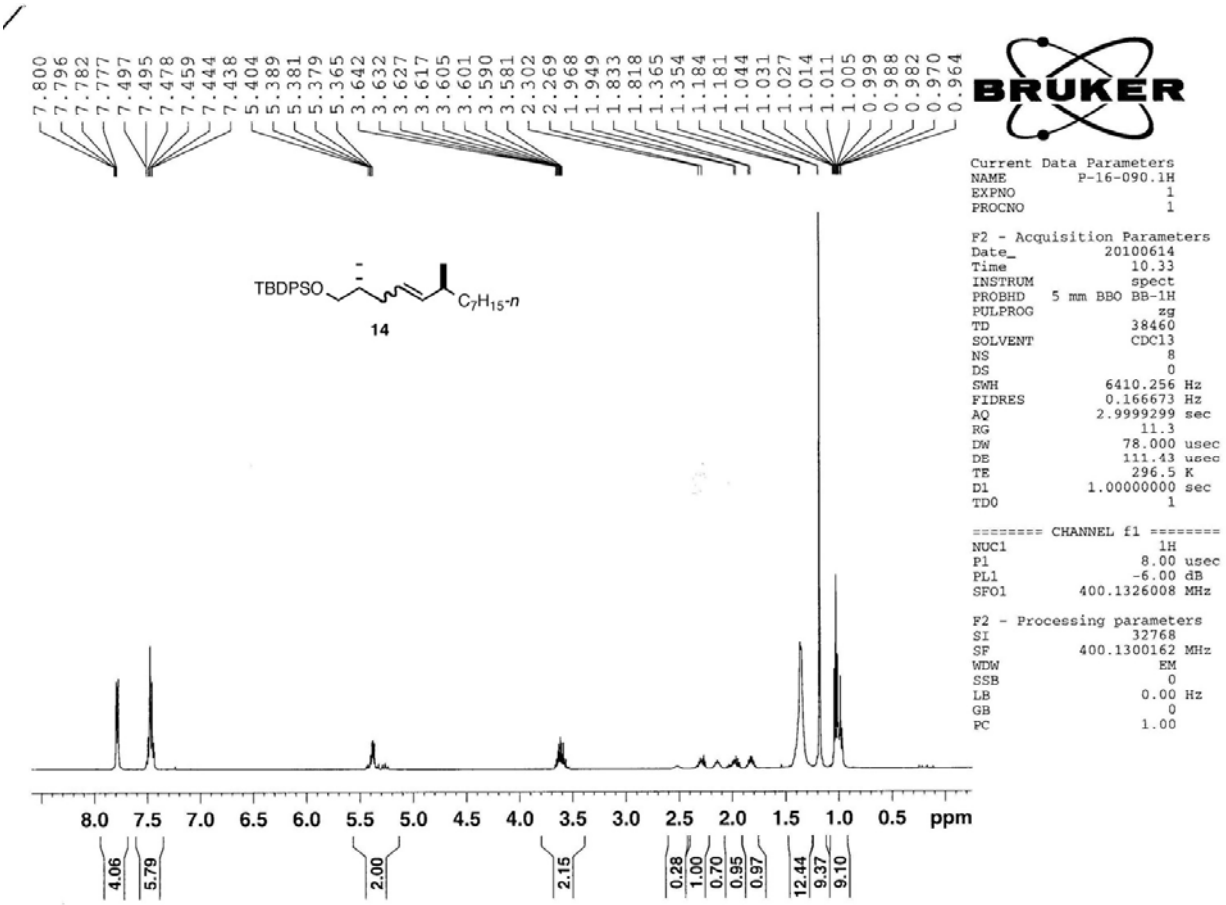
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -6.00 dB
SFO1 400.1326008 MHz

F2 - Processing parameters
SI 32768
SF 400.1300227 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00




5.720
5.705
5.699
5.685
5.670
5.665
5.650
4.958
4.955
4.953
4.924
4.920
4.918
4.902
4.900
4.899
4.882
4.879
2.099
1.531
1.347
1.308
1.294
1.278
1.270
1.255
1.245
1.239
1.229
1.077
1.074
1.066
1.058
1.043
0.977
0.969
0.964
0.889
0.876
0.862
0.833
0.820
0.006
C7H15-n
12
BRUKER
NAME P-16-057.1H
EXPNO 1
PROCNO 1
Date_ 20100421
Time 12.06
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDC13
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 sec
RG 50.8
DW 66.667 usec
DE 71.43 usec
TE 295.0 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1330008 MHz
SI 16384
SF 500.1300123 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
ppm
0.96
1.94
0.97
18.25
1.94
3.00
2.92
3.15


145.171
112.344
77.404
77.151
76.896
37.925
37.289
37.276
37.145
32.881
32.089
30.142
29.555
27.253
24.792
22.854
20.389
19.846
14.267
C7H15-n
12
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
BRUKER
NAME P-16-057.13C
EXPNO 1
PROCNO 1
Date_ 20100421
Time 12.12
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 197364
SOLVENT CDCl3
NS 40
DS 4
SWH 32894.738 Hz
FIDRES 0.166670 Hz
AQ 2.9999828 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 296.1 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7716224 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7577699 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



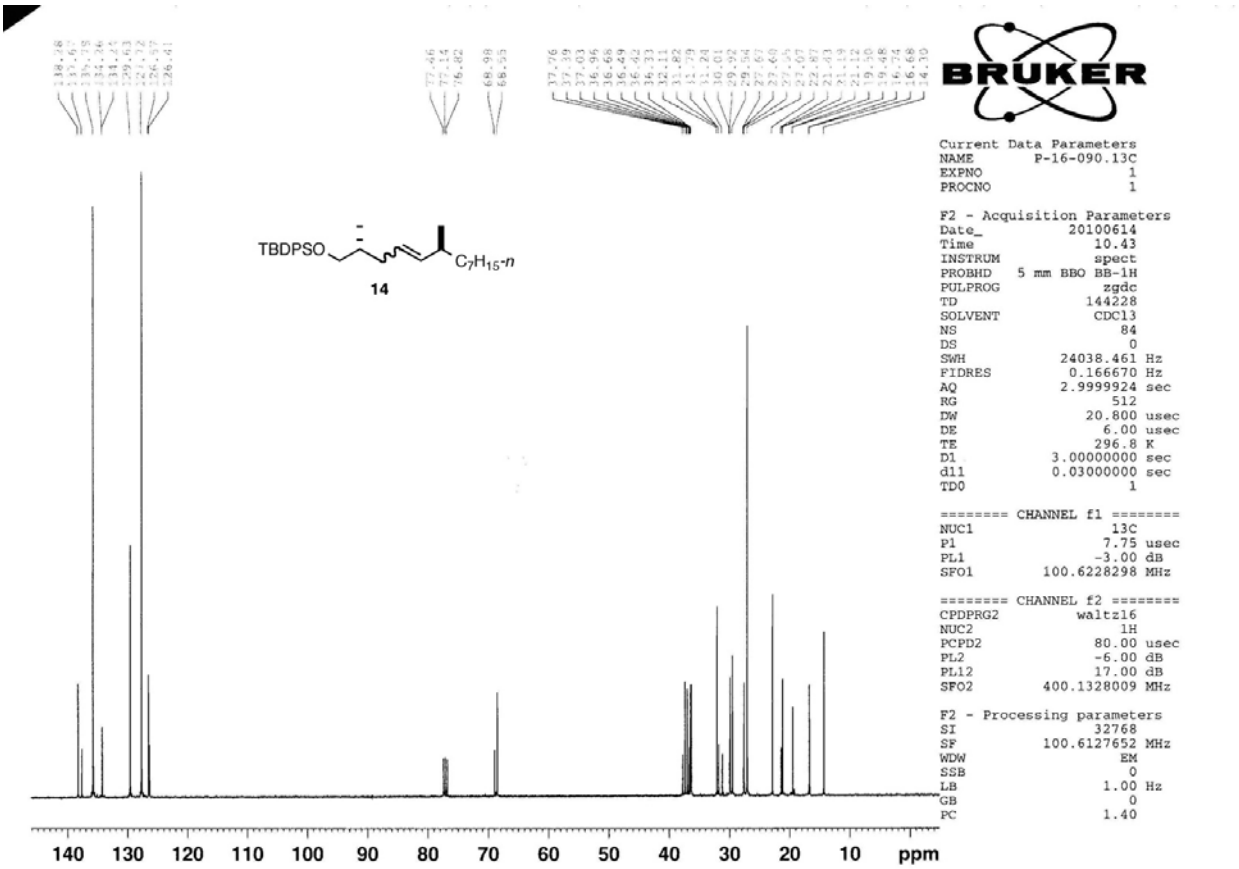
BRUKER

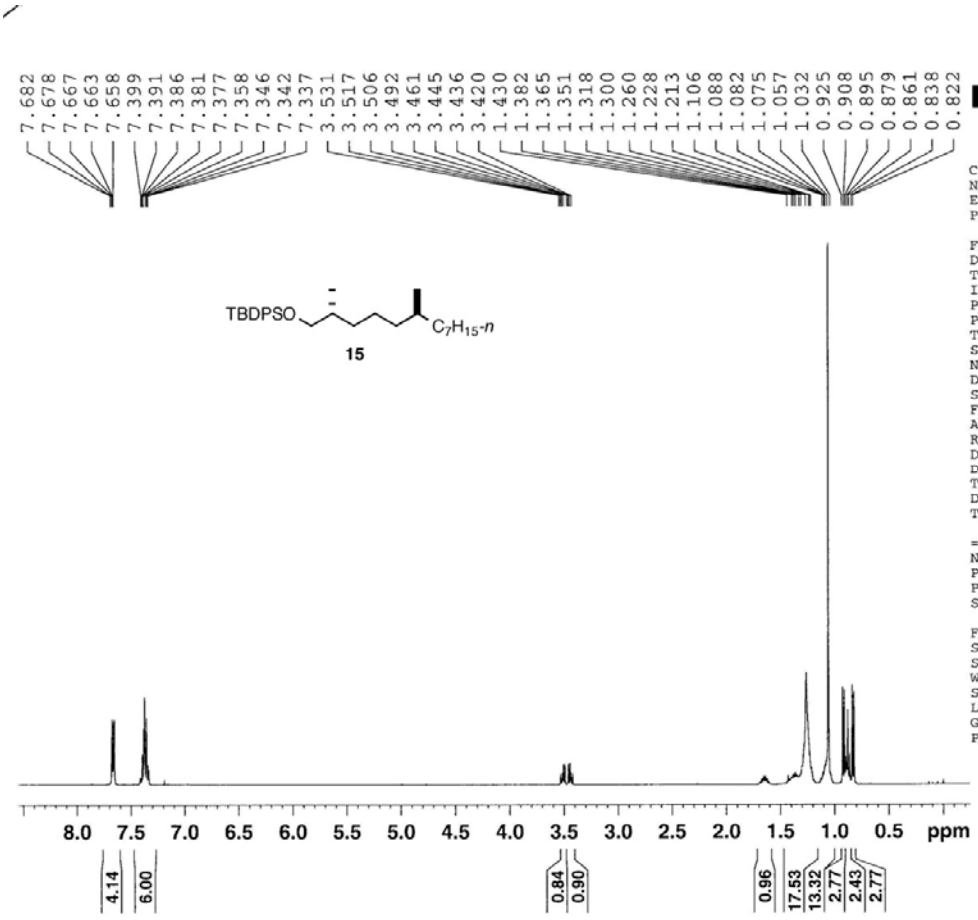
Current Data Parameters
NAME P-16-090.1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100614
Time 10.33
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 38460
SOLVENT CDCl3
NS 8
DS 0
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 11.3
DW 78.000 usec
DE 111.43 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -6.00 dB
SFO1 400.1326008 MHz

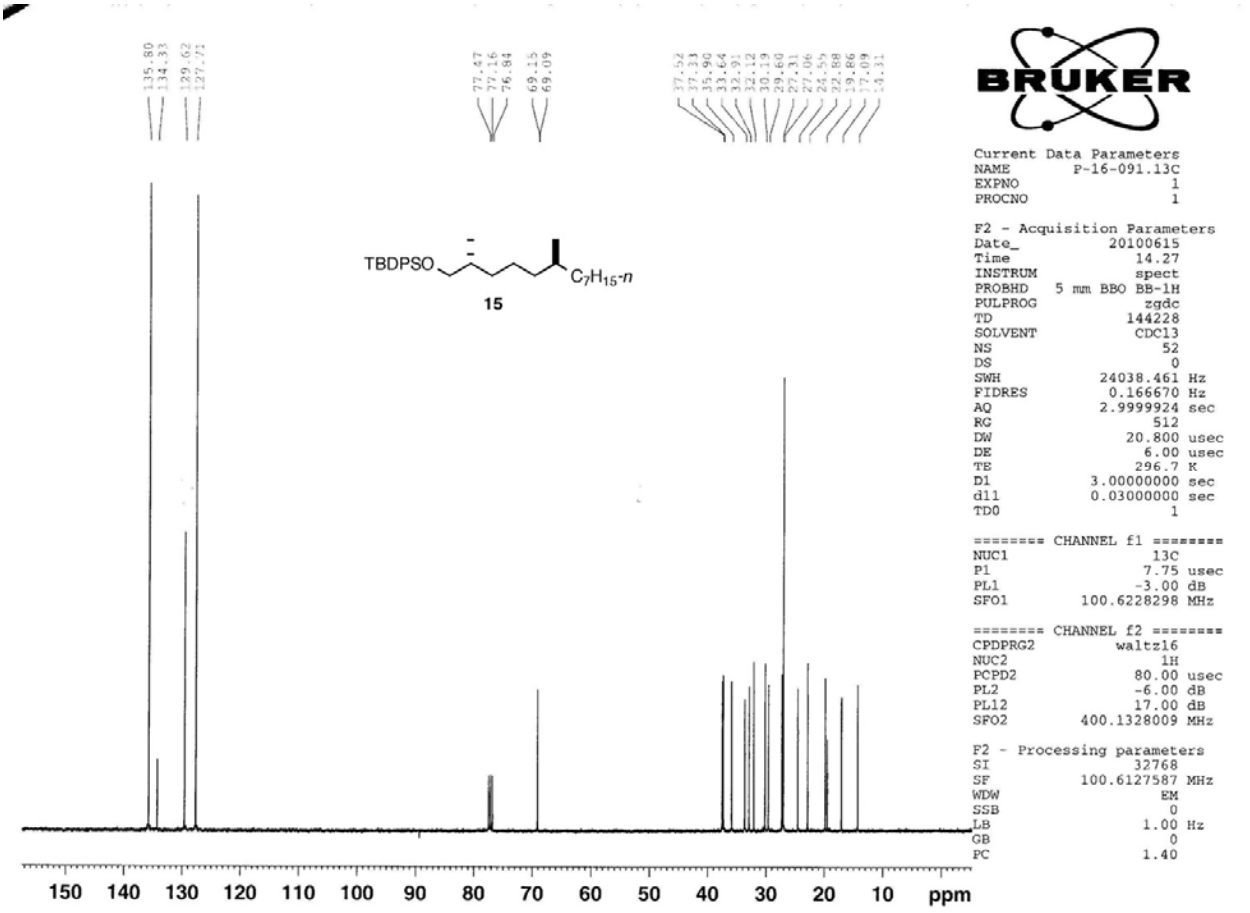
F2 - Processing parameters
SI 32768
SF 400.1300162 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00


TBDPSO
C_7H_{15}-n
14
BRUKER
Current Data Parameters
NAME P-16-090.13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100614
Time 10.43
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 144228
SOLVENT CDCl3
NS 84
DS 0
SWH 24038.461 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 512
DW 20.800 usec
DE 6.00 usec
TE 296.8 K
D1 3.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.75 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 17.00 dB
SFO2 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 100.6127652 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



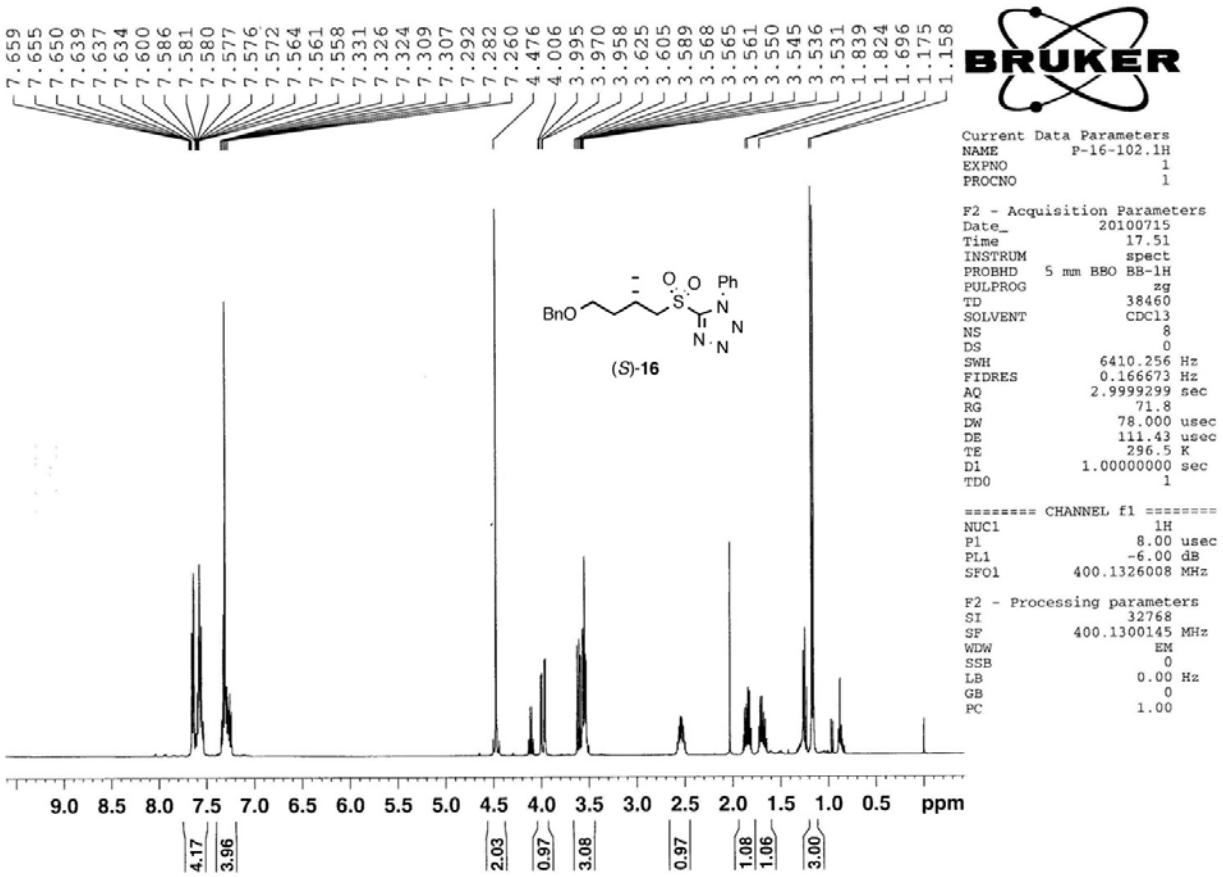
BRUKER

```
Current Data Parameters
NAME          P-16-091.1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20100615
Time                14.21
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg
TD                  38460
SOLVENT             CDCl3
NS                      4
DS                      0
SWH              6410.256 Hz
FIDRES           0.166673 Hz
AQ               2.9999299 sec
RG                   20.2
DW                 78.000 usec
DE                 111.43 usec
TE                  296.3 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  8.00 usec
PL1                -6.00 dB
SFO1          400.1326008 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300361 MHz
WDW                    EM
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```



BRUKER

```
Current Data Parameters
NAME          P-16-091.13C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20100615
Time                 14.27
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zgdc
TD                  144228
SOLVENT              CDCl3
NS                      52
DS                       0
SWH              24038.461 Hz
FIDRES           0.166670 Hz
AQ               2.9999924 sec
RG                     512
DW                20.800 usec
DE                 6.00 usec
TE                296.7 K
D1            3.00000000 sec
d11           0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.75 usec
PL1                  -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                  -6.00 dB
PL12                 17.00 dB
SFO2          400.1328009 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127587 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```



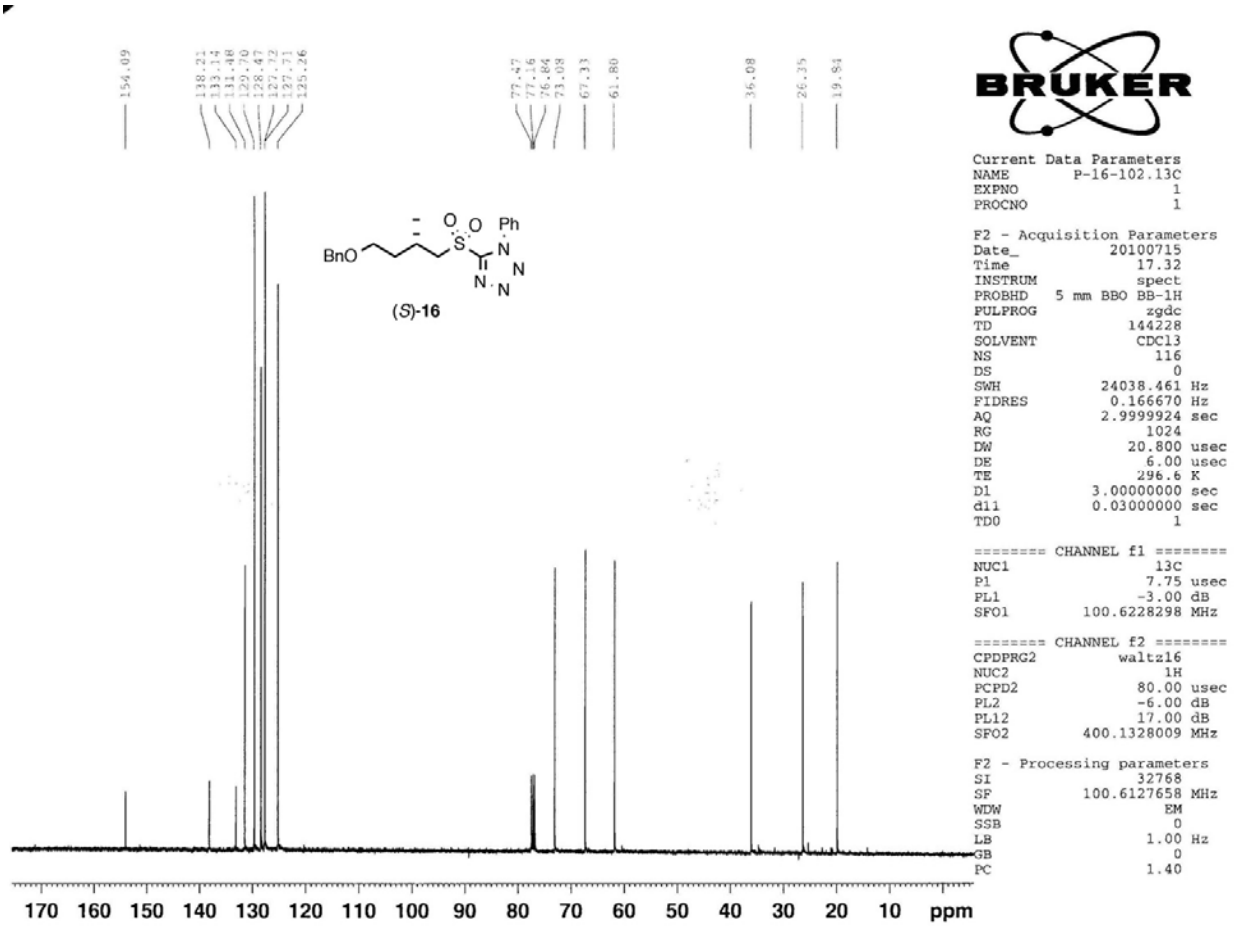
BRUKER

Current Data Parameters
NAME P-16-102.1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100715
Time 17.51
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 38460
SOLVENT CDCl3
NS 8
DS 0
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 71.8
DW 78.000 usec
DE 111.43 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -6.00 dB
SFO1 400.1326008 MHz

F2 - Processing parameters
SI 32768
SF 400.1300145 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



BRUKER

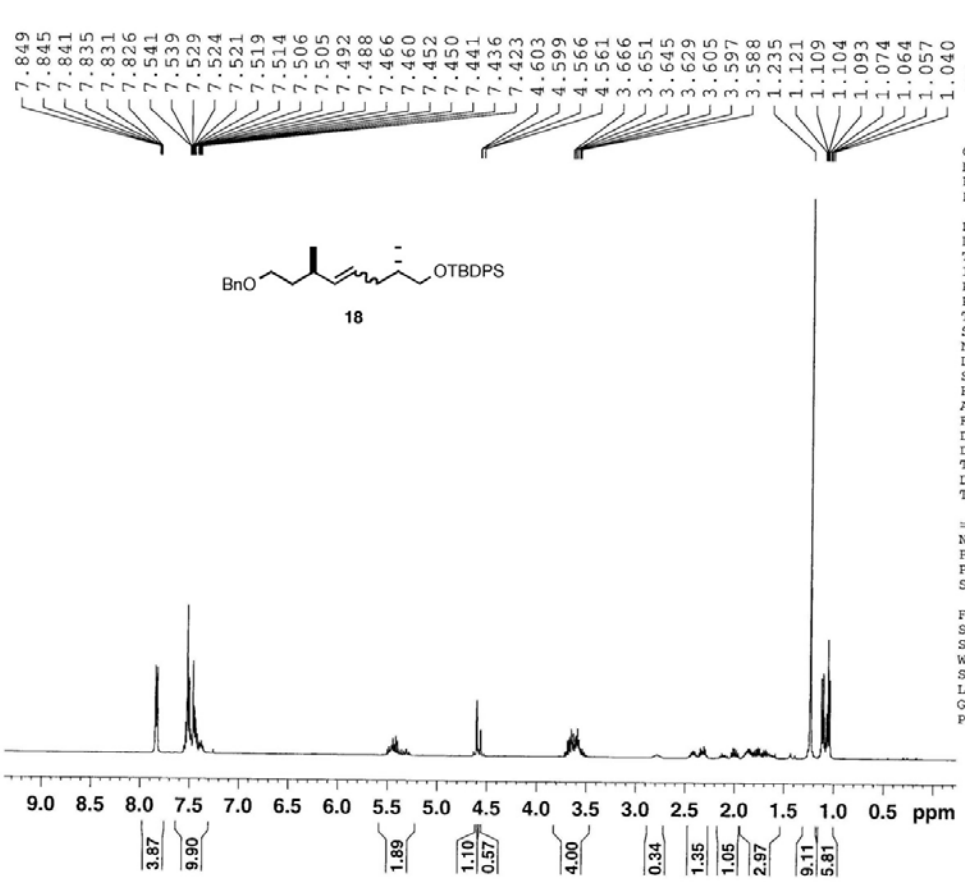
Current Data Parameters
NAME P-16-102.13C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100715
Time 17.32
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 144228
SOLVENT CDCl3
NS 116
DS 0
SWH 24038.461 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 1024
DW 20.800 usec
DE 6.00 usec
TE 296.6 K
D1 3.00000000 sec
d11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.75 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

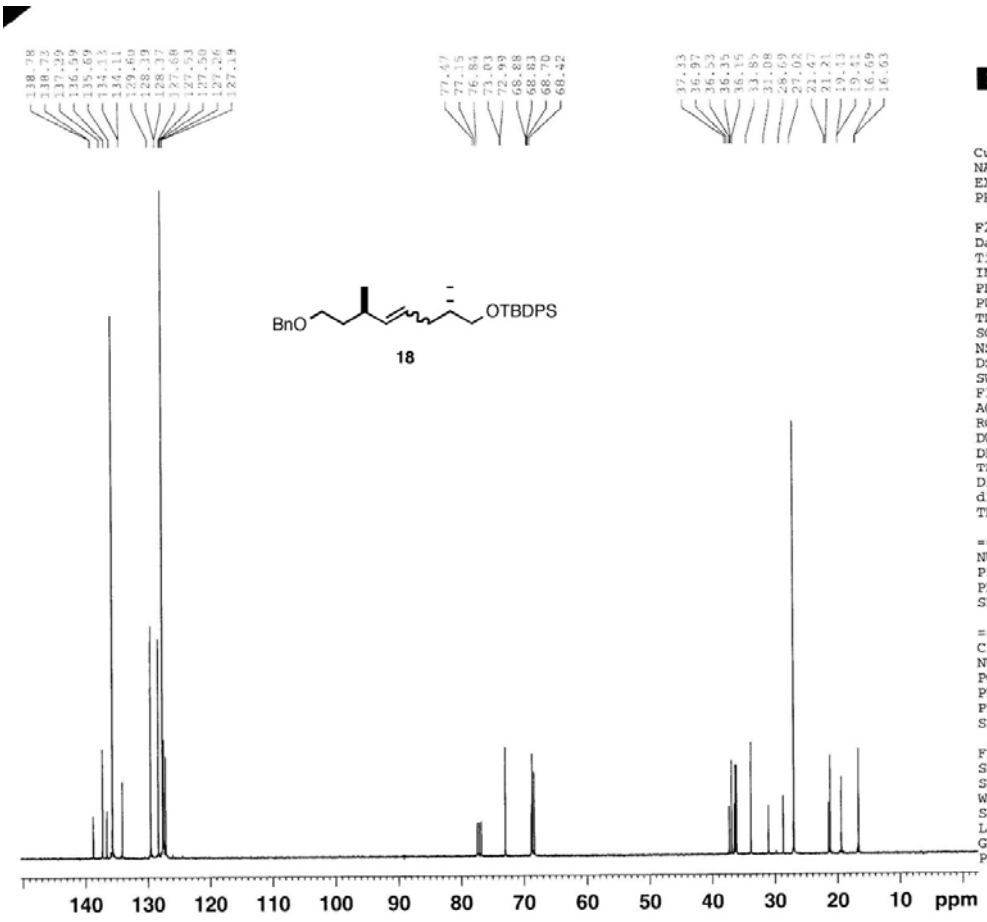
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 17.00 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 32768
SF 100.6127658 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



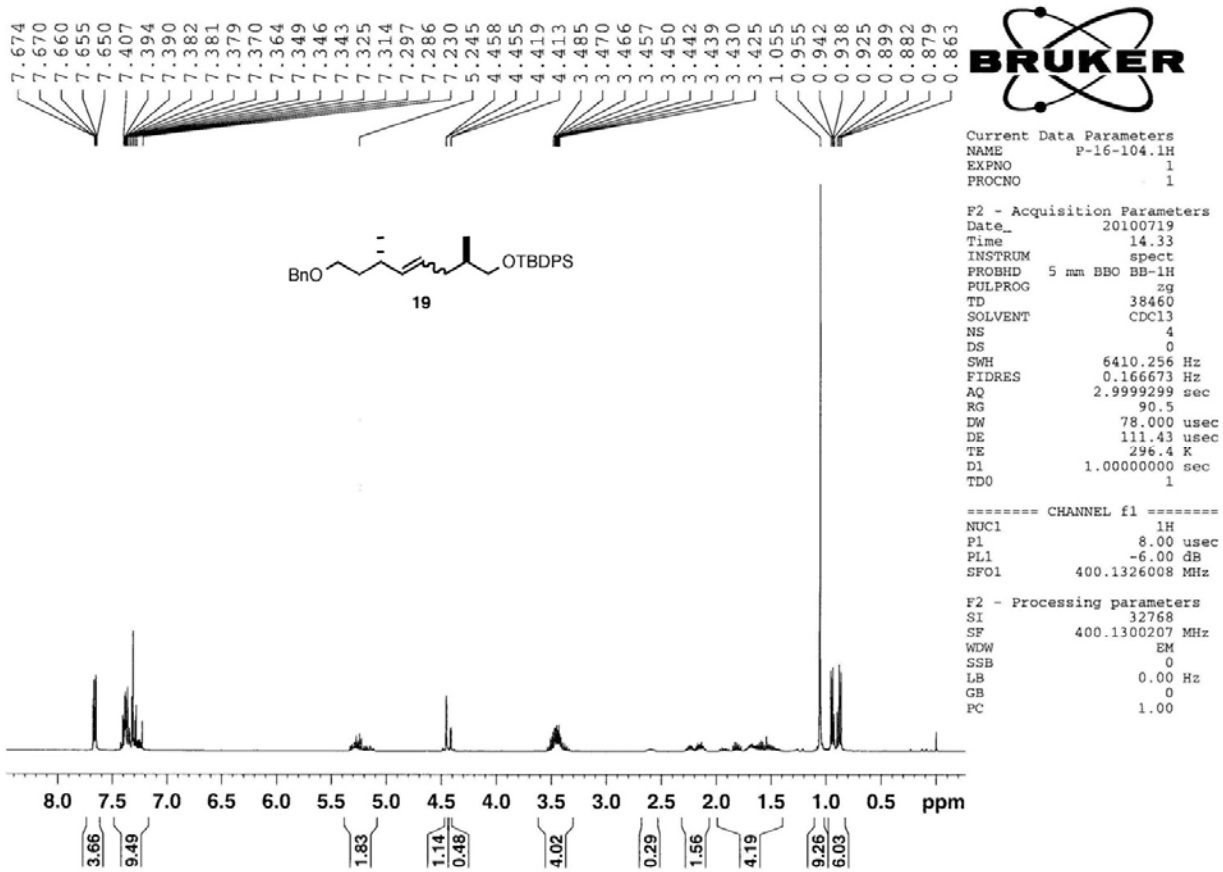
BRUKER

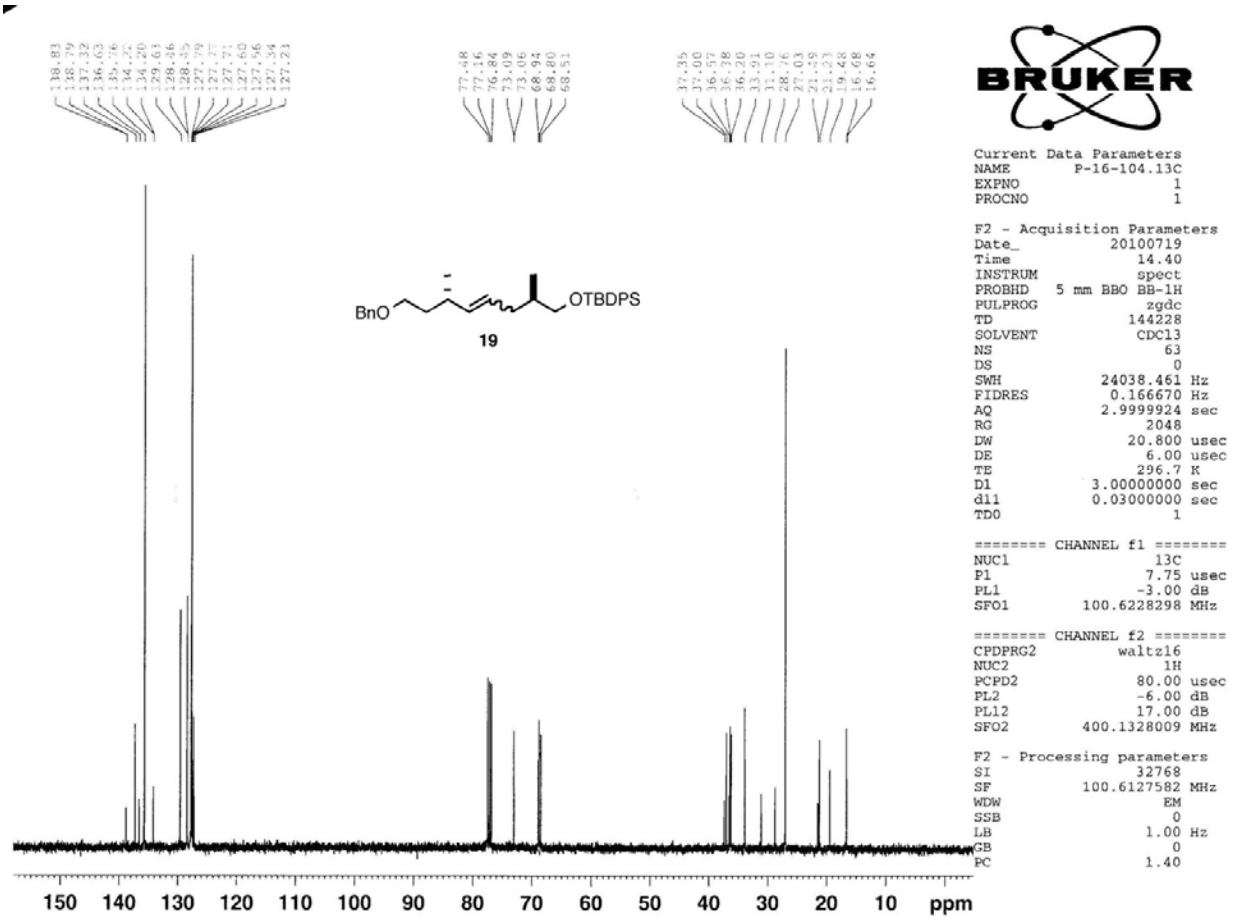
```
Current Data Parameters
NAME          P-16-092.1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20100616
Time                14.21
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg
TD                  38460
SOLVENT             CDCl3
NS                      4
DS                      0
SWH              6410.256 Hz
FIDRES           0.166673 Hz
AQ               2.9999299 sec
RG                   20.2
DW                 78.000 usec
DE                 111.43 usec
TE                  296.3 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  8.00 usec
PL1                -6.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300080 MHz
WDW                    EM
SSB                     0
LB                 0.00 Hz
GB                      0
PC                   1.00
```



BRUKER

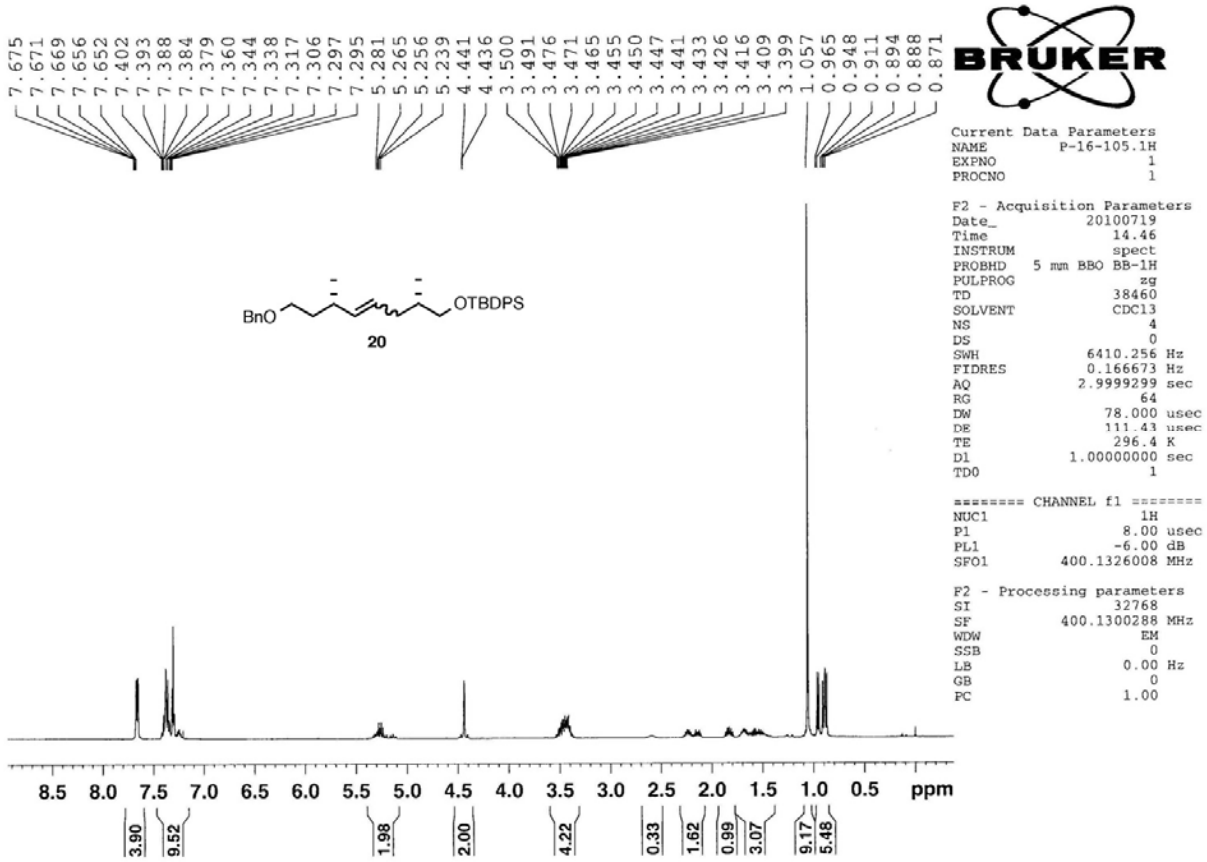
```
Current Data Parameters
NAME         P-16-092.13C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_             20100616
Time                 14.30
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zgdc
TD                  144228
SOLVENT              CDCl3
NS                      83
DS                       0
SWH              24038.461 Hz
FIDRES           0.166670 Hz
AQ               2.9999924 sec
RG                  1290.2
DW                  20.800 usec
DE                   6.00 usec
TE                  296.8 K
D1             3.00000000 sec
d11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.75 usec
PL1                  -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                  -6.00 dB
PL12                 17.00 dB
SFO2          400.1328009 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127774 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```


7.674
7.670
7.660
7.655
7.650
7.407
7.394
7.390
7.382
7.381
7.379
7.370
7.364
7.349
7.346
7.343
7.325
7.314
7.297
7.286
7.230
5.245
4.458
4.455
4.419
4.413
3.485
3.470
3.466
3.457
3.450
3.442
3.439
3.430
3.425
1.055
0.955
0.942
0.938
0.925
0.899
0.882
0.879
0.863
BnO
OTBDPS
19
BRUKER
Current Data Parameters
NAME P-16-104.1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100719
Time 14.33
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 38460
SOLVENT CDCl3
NS 4
DS 0
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 90.5
DW 78.000 usec
DE 111.43 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -6.00 dB
SFO1 400.1326008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300207 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
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 ppm
3.66
9.49
1.83
1.14
0.48
4.02
0.29
1.56
4.19
9.26
6.03



BRUKER

```
Current Data Parameters
NAME          P-16-104.13C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20100719
Time                 14.40
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                 144228
SOLVENT             CDCl3
NS                     63
DS                      0
SWH            24038.461 Hz
FIDRES          0.166670 Hz
AQ              2.9999924 sec
RG                   2048
DW                20.800 usec
DE                 6.00 usec
TE                296.7 K
D1           3.00000000 sec
d11          0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.75 usec
PL1                 -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                   32768
SF           100.6127582 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



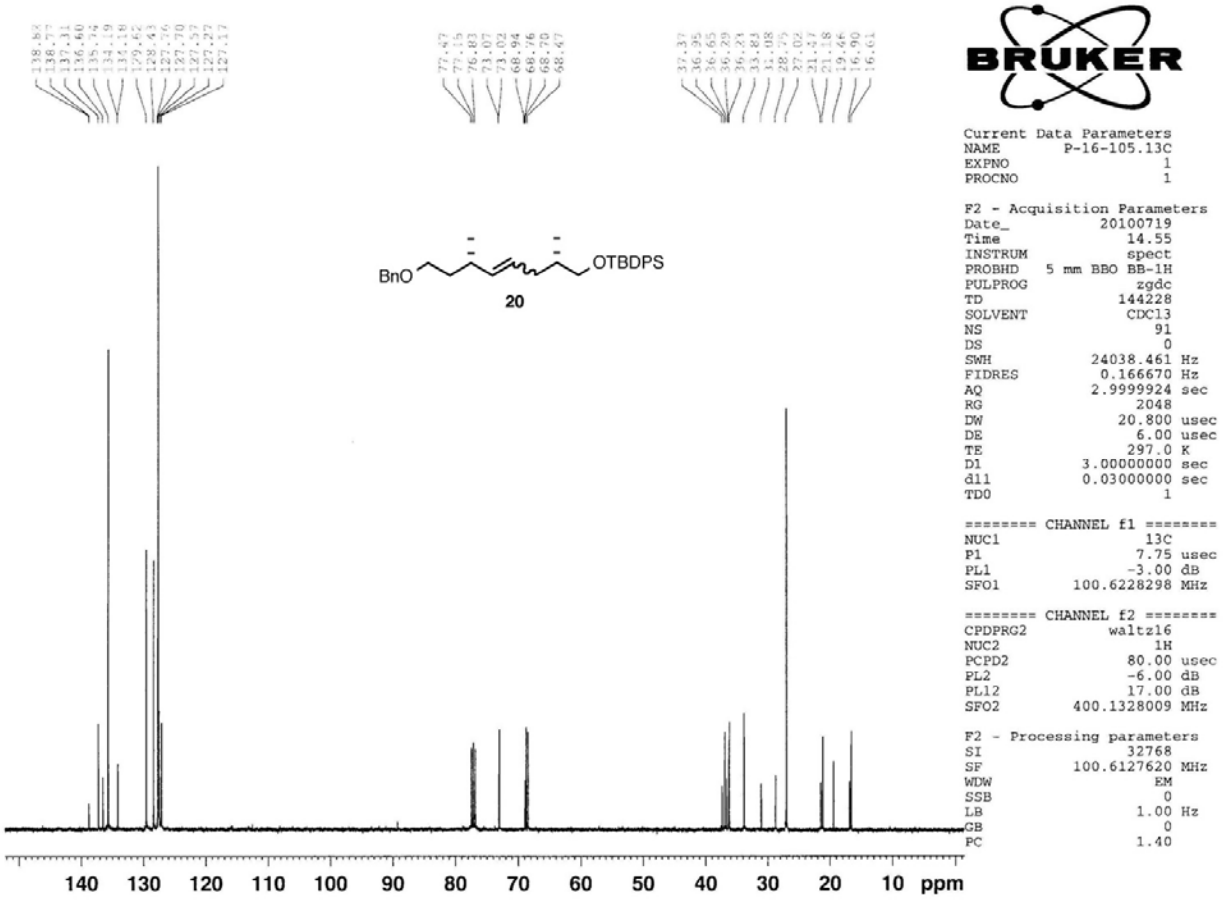
BRUKER

Current Data Parameters
NAME P-16-105.1H
EXPNO 1
PROCNO 1

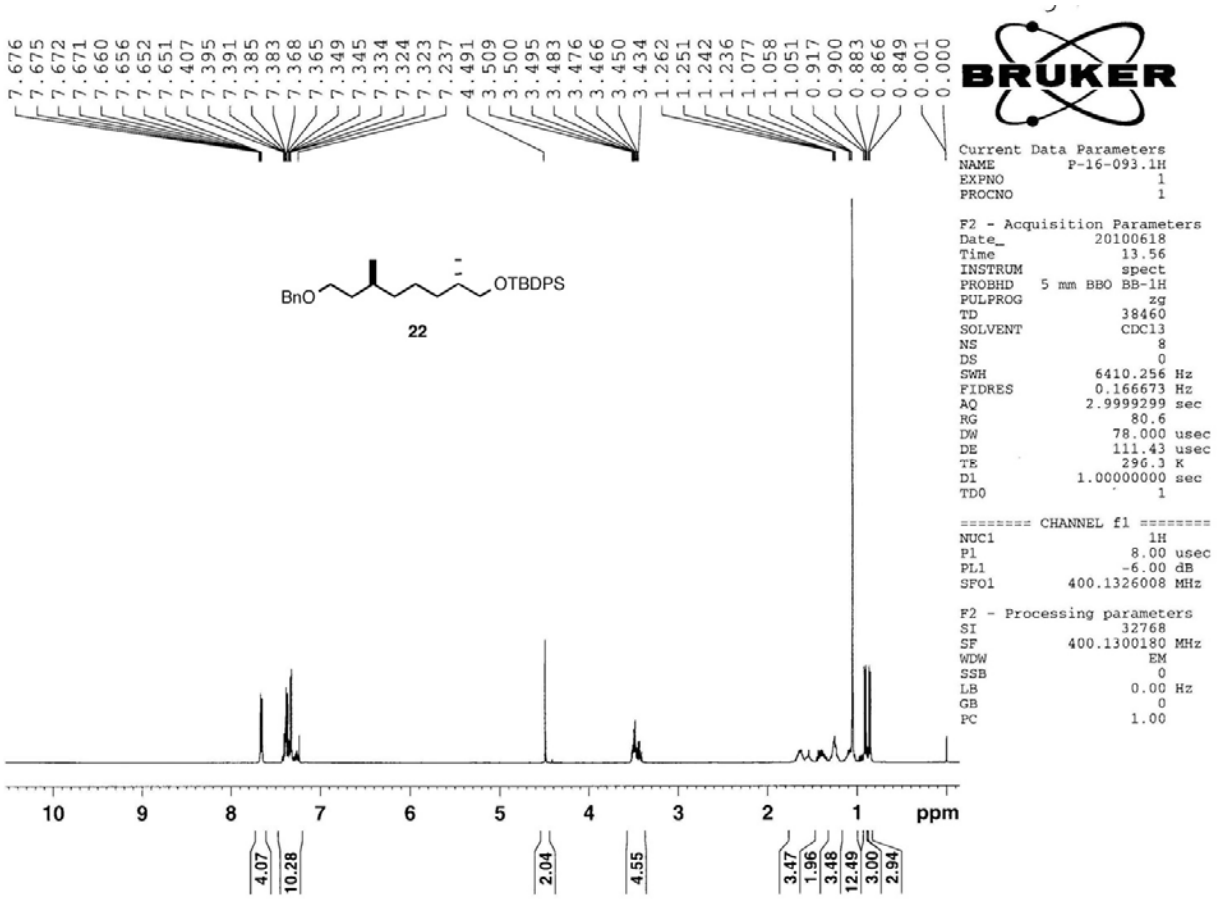
F2 - Acquisition Parameters
Date_ 20100719
Time 14.46
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 38460
SOLVENT CDC13
NS 4
DS 0
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 64
DW 78.000 usec
DE 111.43 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1

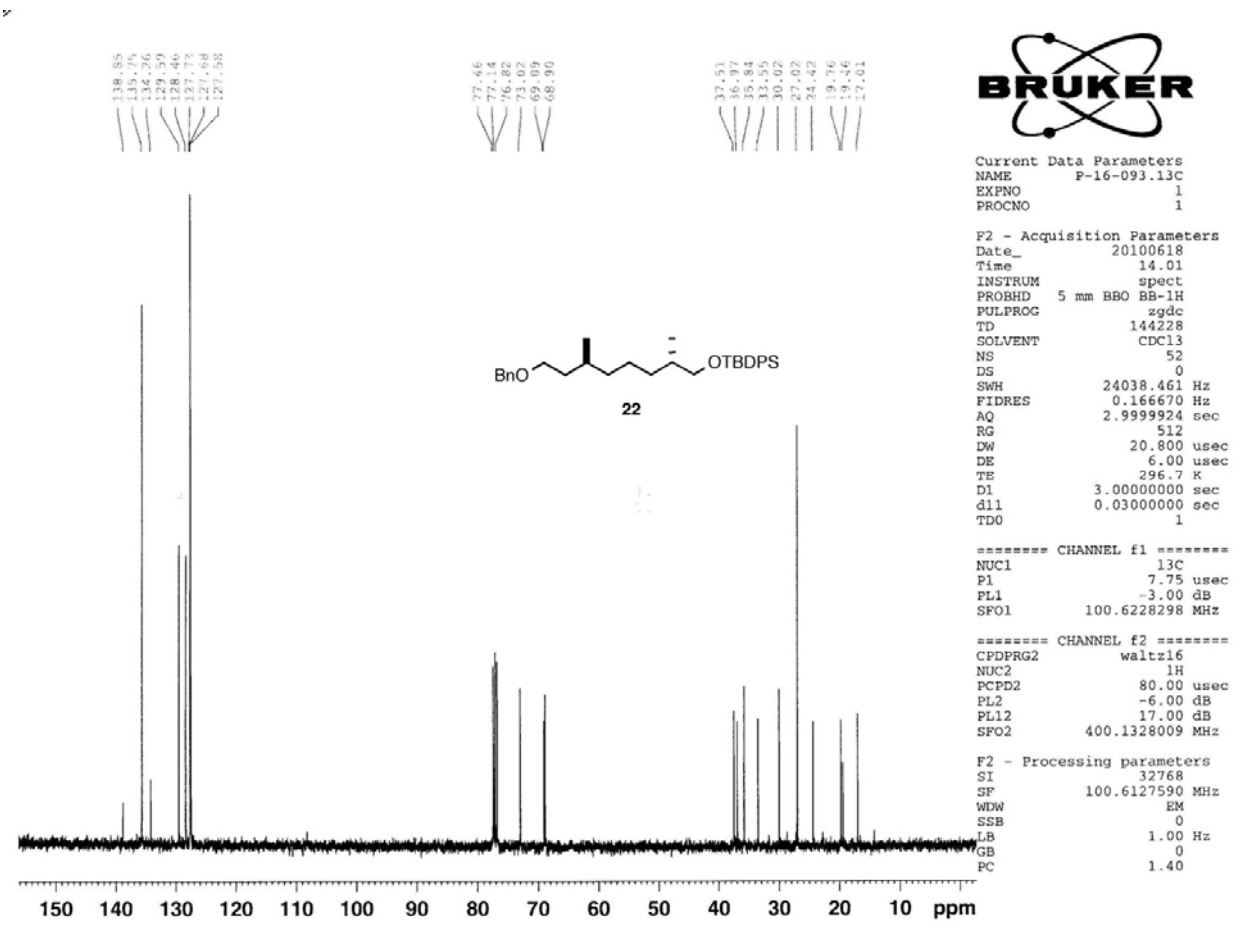
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -6.00 dB
SFO1 400.1326008 MHz

F2 - Processing parameters
SI 32768
SF 400.1300288 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00




```
Current Data Parameters
NAME        P-16-105.13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100719
Time               14.55
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                144228
SOLVENT             CDCl3
NS                     91
DS                      0
SWH          24038.461 Hz
FIDRES        0.166670 Hz
AQ            2.9999924 sec
RG                  2048
DW                20.800 usec
DE                 6.00 usec
TE                297.0 K
D1           3.00000000 sec
d11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.75 usec
PL1                 -3.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               17.00 dB
SFO2        400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127620 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```


7.676
7.675
7.672
7.671
7.660
7.656
7.652
7.651
7.407
7.395
7.391
7.385
7.383
7.368
7.365
7.349
7.345
7.334
7.324
7.323
7.237
4.491
3.509
3.500
3.495
3.483
3.476
3.466
3.450
3.434
1.262
1.251
1.242
1.236
1.077
1.058
1.051
0.917
0.900
0.883
0.866
0.849
0.001
0.000
BnO
OTBDPS
22
10
9
8
7
6
5
4
3
2
1
ppm
4.07
10.28
2.04
4.55
3.47
1.96
3.48
12.49
3.00
2.94
BRUKER
Current Data Parameters
NAME P-16-093.1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100618
Time 13.56
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 38460
SOLVENT CDC13
NS 8
DS 0
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 80.6
DW 78.000 usec
DE 111.43 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -6.00 dB
SFO1 400.1326008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300180 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



BRUKER

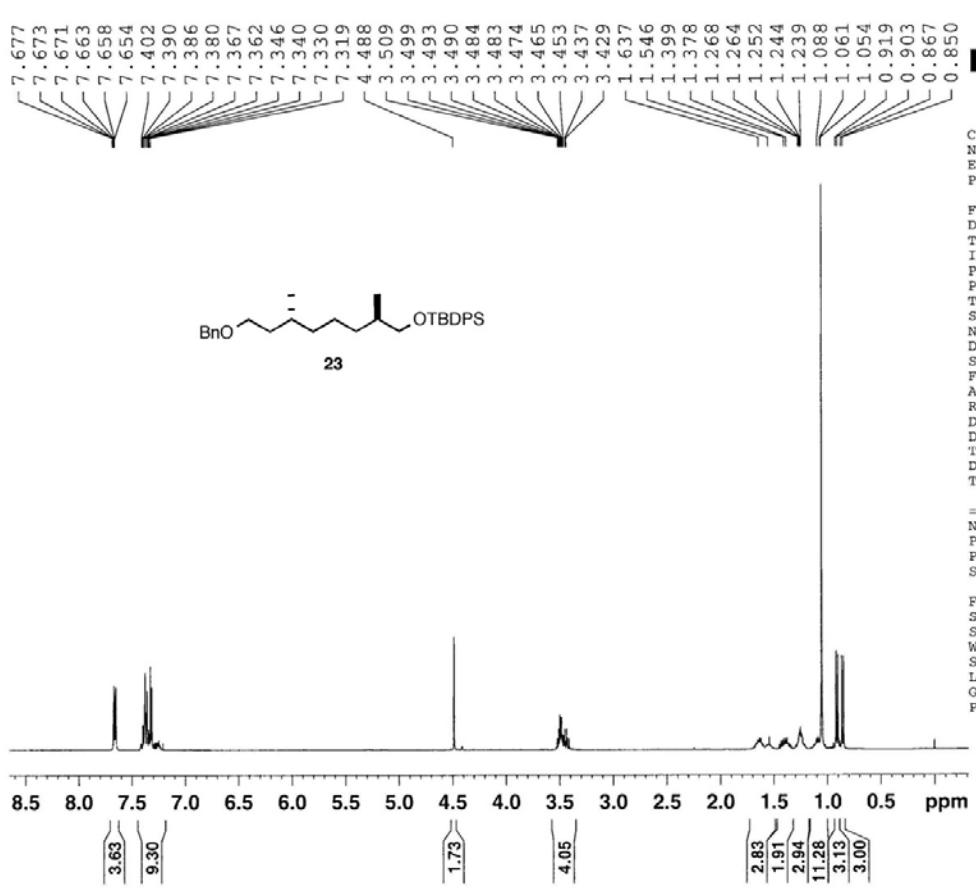
Current Data Parameters
NAME P-16-093.13C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100618
Time 14.01
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 144228
SOLVENT CDCl3
NS 52
DS 0
SWH 24038.461 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 512
DW 20.800 usec
DE 6.00 usec
TE 296.7 K
D1 3.00000000 sec
d11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.75 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 17.00 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 32768
SF 100.6127590 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



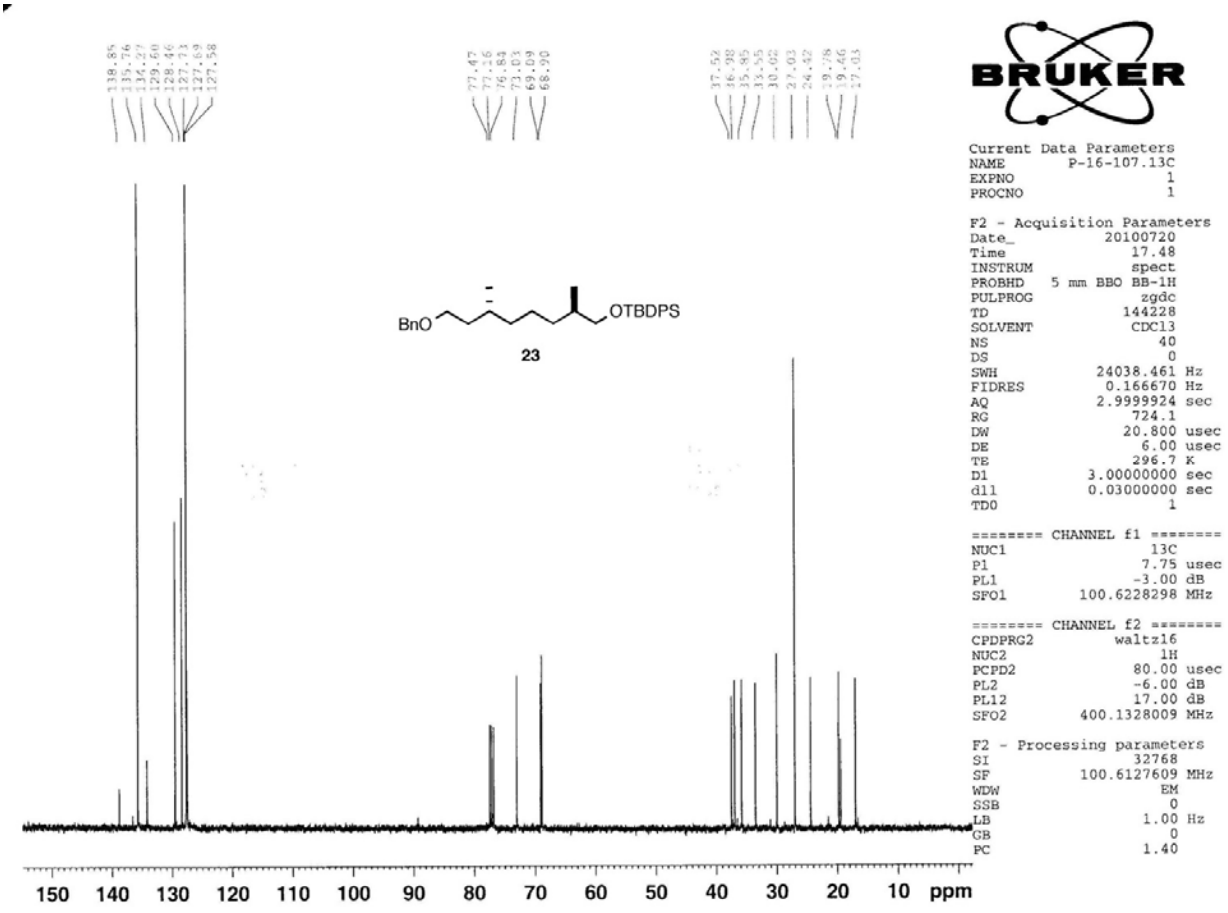
BRUKER

Current Data Parameters
NAME P-16-107.1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100720
Time 17.42
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 38460
SOLVENT CDCl3
NS 4
DS 0
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 64
DW 78.000 usec
DE 111.43 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1

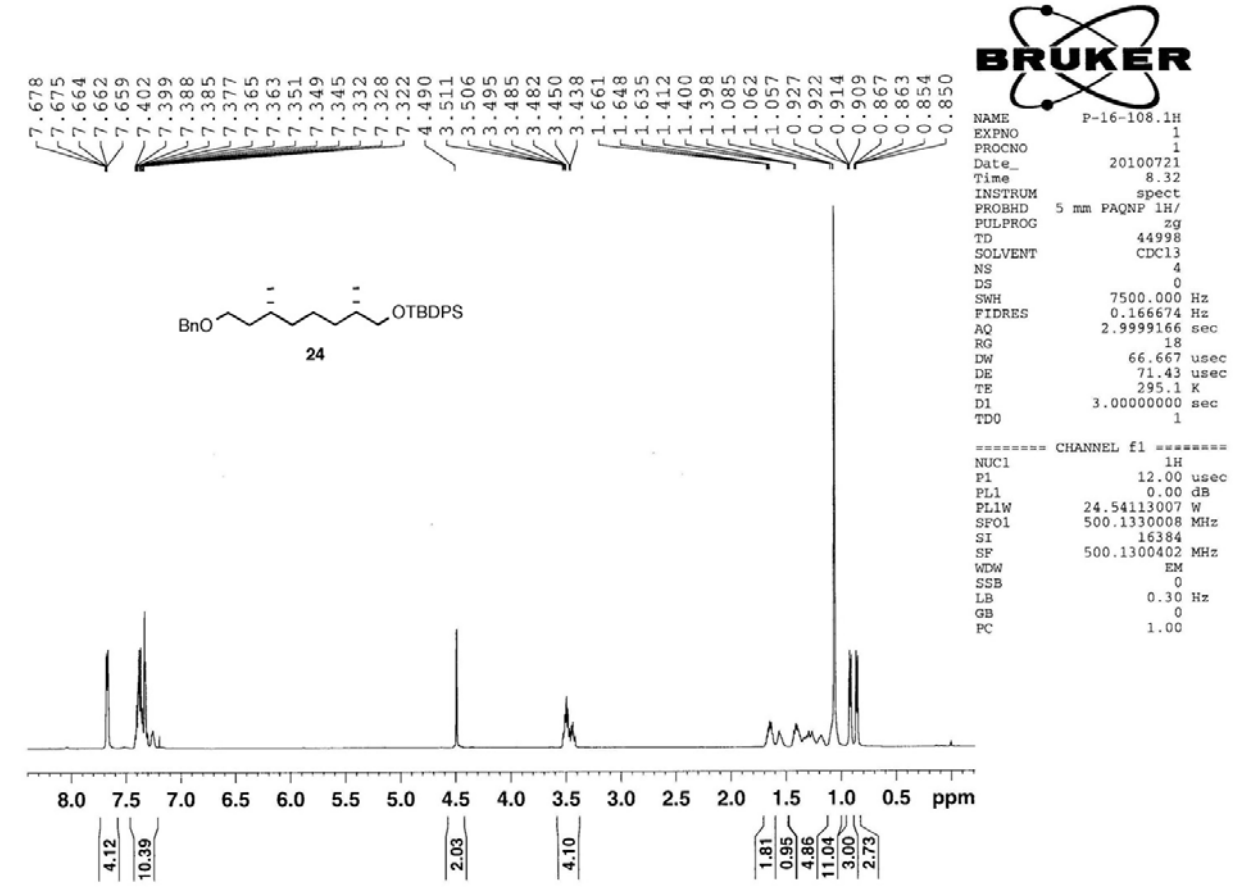
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -6.00 dB
SFO1 400.1326008 MHz

F2 - Processing parameters
SI 32768
SF 400.1300278 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



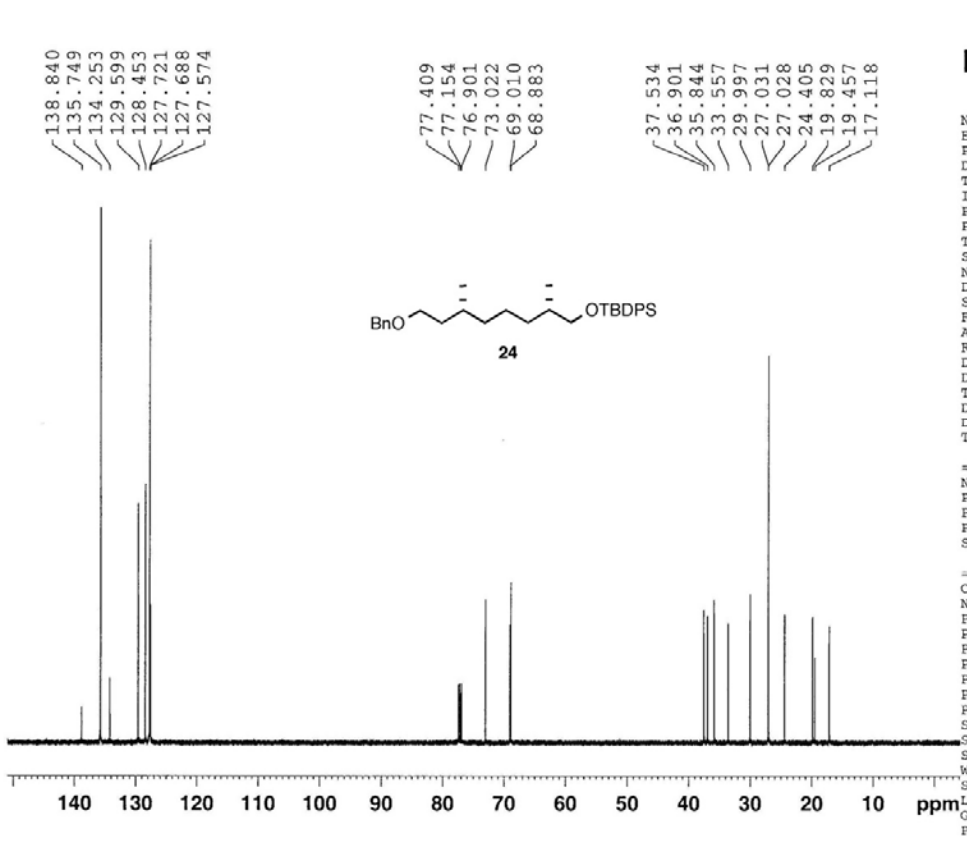
BRUKER

```
Current Data Parameters
NAME        P-16-107.13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100720
Time               17.48
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgdc
TD               144228
SOLVENT           CDCl3
NS                   40
DS                    0
SWH           24038.461 Hz
FIDRES         0.166670 Hz
AQ             2.9999924 sec
RG                724.1
DW               20.800 usec
DE                6.00 usec
TE               296.7 K
D1            3.00000000 sec
d11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.75 usec
PL1                -3.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              17.00 dB
SFO2        400.1328009 MHz

F2 - Processing parameters
SI                32768
SF          100.6127609 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



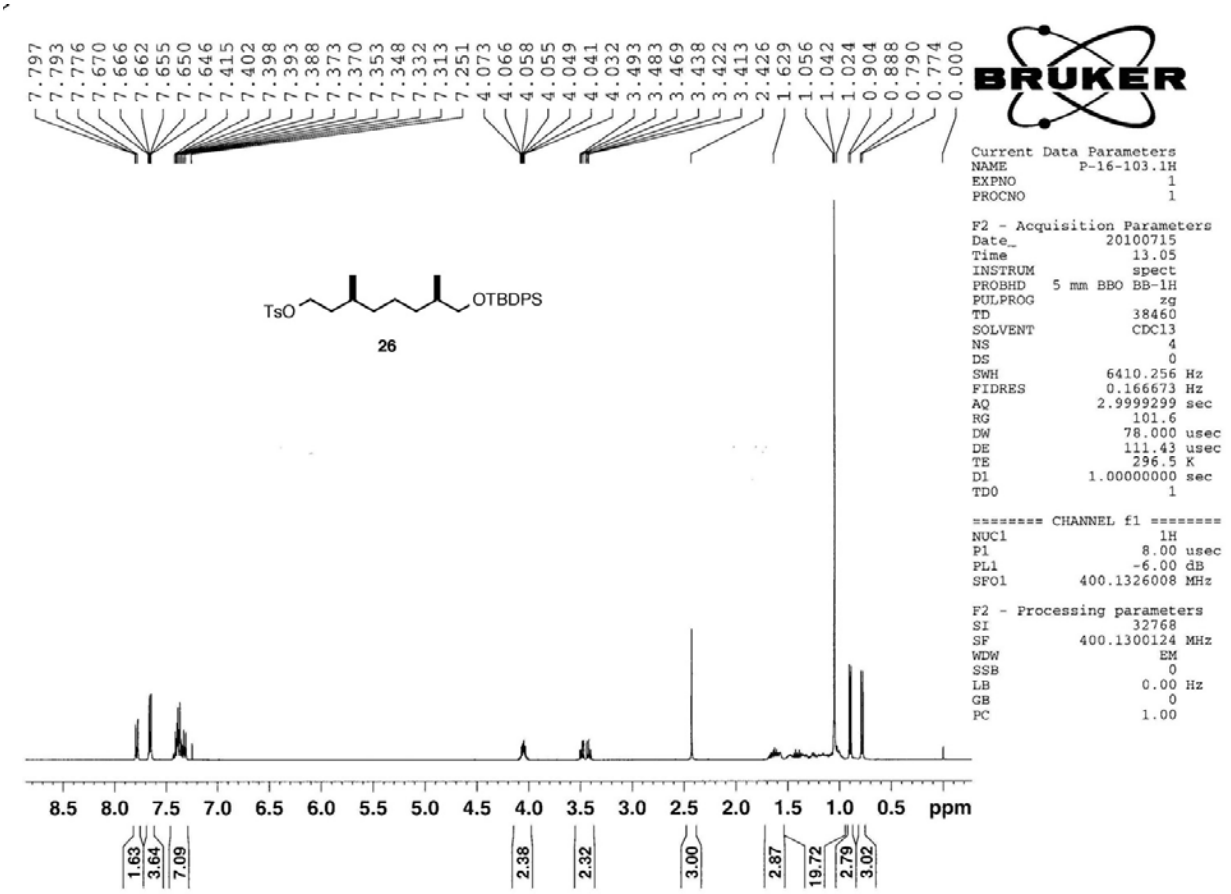
BRUKER

NAME	P-16-108.1H
EXPNO	1
PROCNO	1
Date_	20100721
Time	8.32
INSTRUM	spect
PROBHD	5 mm PAQNP 1H/
PULPROG	zg
TD	44998
SOLVENT	CDCl3
NS	4
DS	0
SWH	7500.000 Hz
FIDRES	0.166674 Hz
AQ	2.9999166 sec
RG	18
DW	66.667 usec
DE	71.43 usec
TE	295.1 K
D1	3.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.00 usec
PL1	0.00 dB
PL1W	24.54113007 W
SFO1	500.1330008 MHz
SI	16384
SF	500.1300402 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



BRUKER

NAME	P-16-108.13C
EXPNO	1
PROCNO	1
Date_	20100721
Time	8.39
INSTRUM	spect
PROBHD	5 mm PAQNP 1H/
PULPROG	zgpg
TD	197364
SOLVENT	CDCl3
NS	40
DS	4
SWH	32894.738 Hz
FIDRES	0.166670 Hz
AQ	2.9999828 sec
RG	2050
DW	15.200 usec
DE	6.00 usec
TE	296.0 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	1.00 dB
PL1W	72.42802429 W
SFO1	125.7716224 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	16.50 dB
PL13	17.00 dB
PL2W	24.54113007 W
PL12W	0.54940748 W
PL13W	0.48965994 W
SFO2	500.1325006 MHz
SI	131072
SF	125.7577818 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40



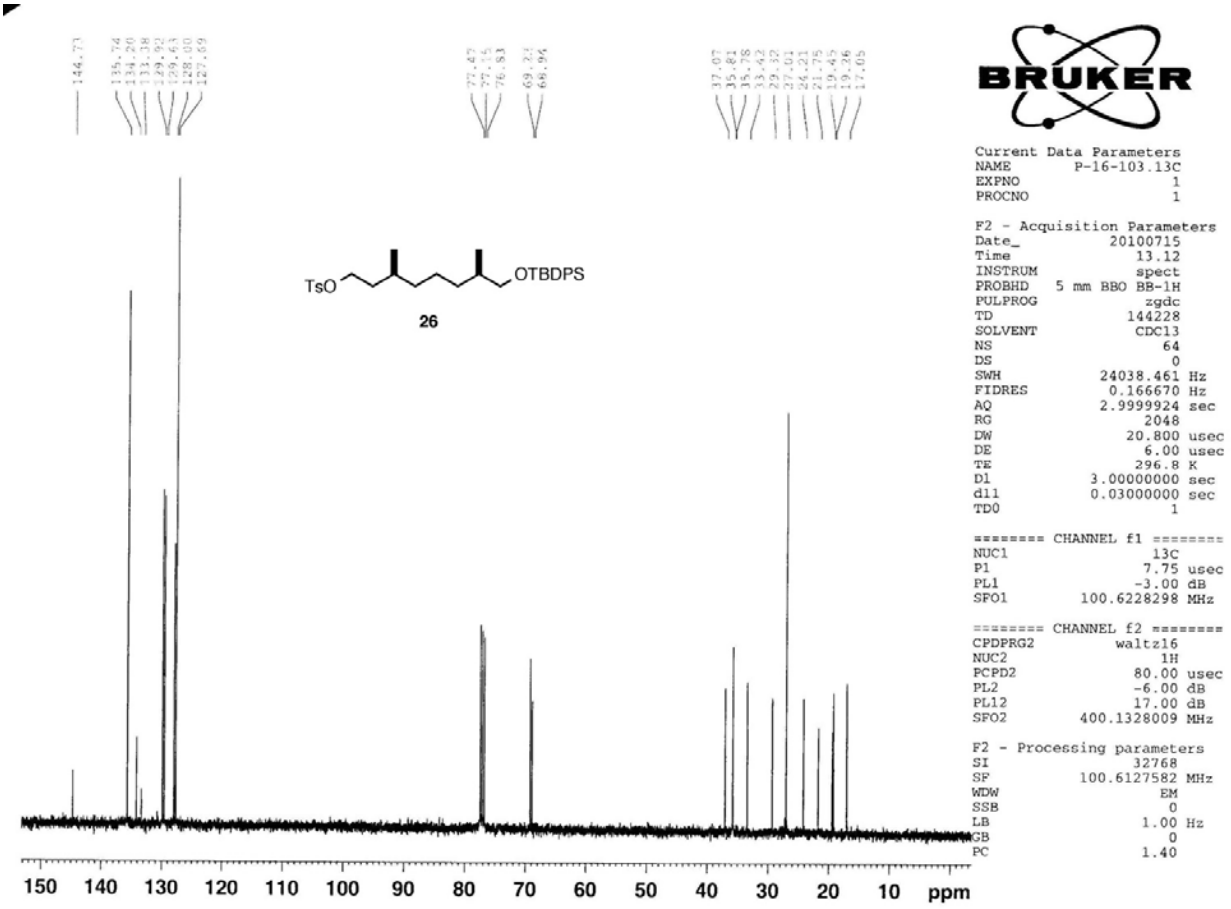
BRUKER

Current Data Parameters
NAME P-16-103.1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100715
Time 13.05
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 38460
SOLVENT CDCl3
NS 4
DS 0
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 101.6
DW 78.000 usec
DE 111.43 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -6.00 dB
SFO1 400.1326008 MHz

F2 - Processing parameters
SI 32768
SF 400.1300124 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



BRUKER

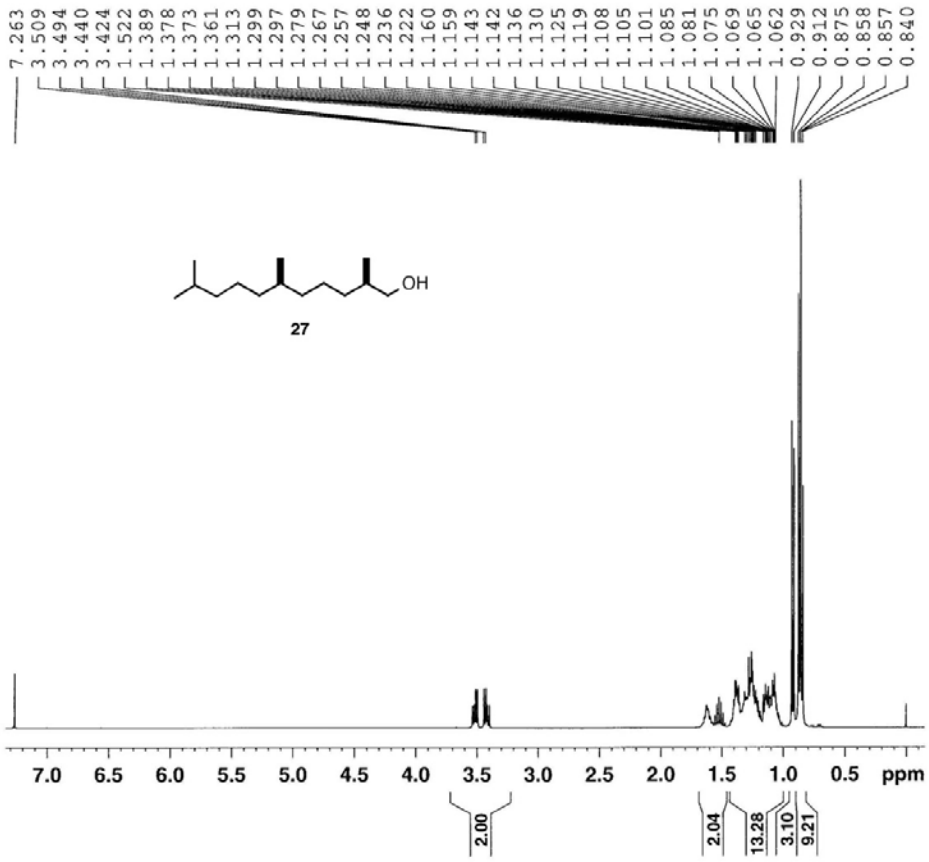
Current Data Parameters
NAME P-16-103.13C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100715
Time 13.12
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 144228
SOLVENT CDC13
NS 64
DS 0
SWH 24038.461 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 2048
DW 20.800 usec
DE 6.00 usec
TE 296.8 K
D1 3.00000000 sec
d11 0.03000000 sec
TD0 1

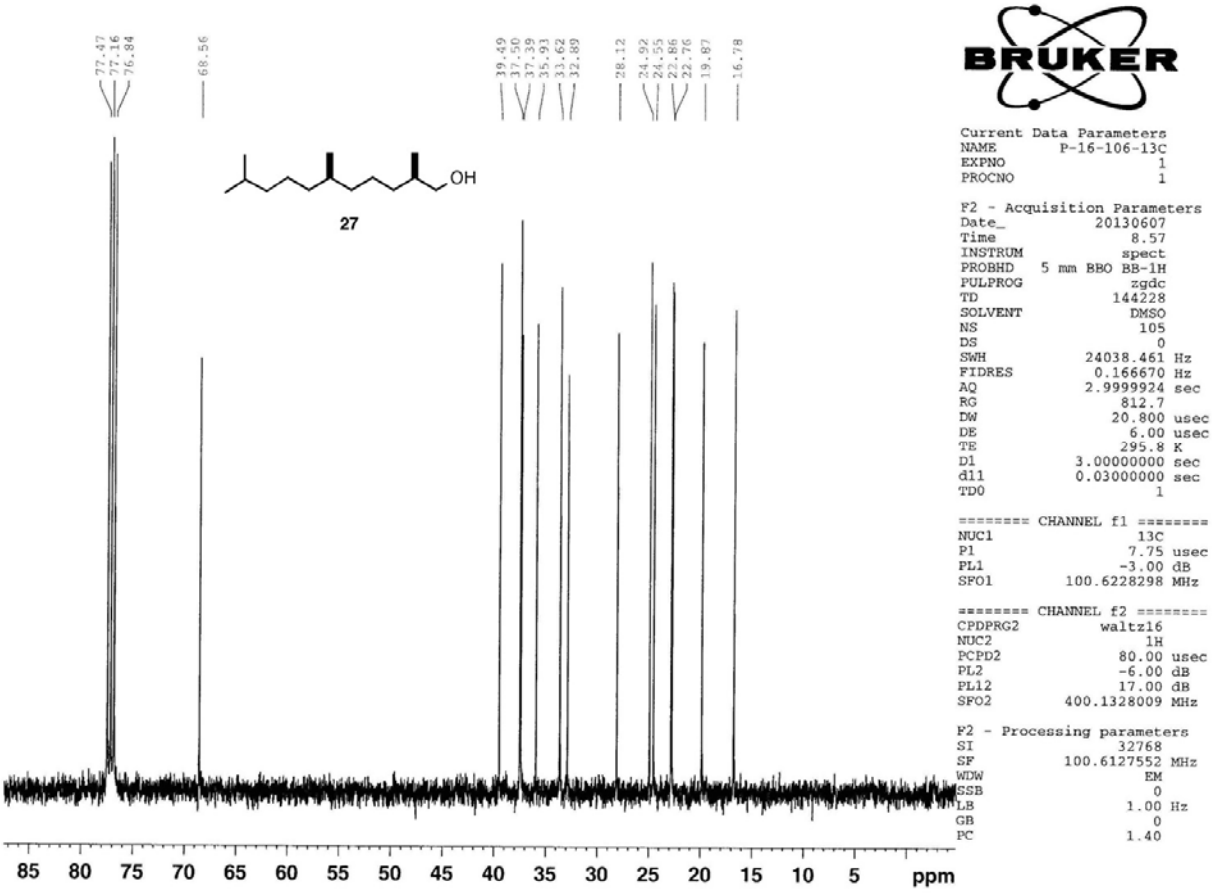
======== CHANNEL f1 ========
NUC1 13C
P1 7.75 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 17.00 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 32768
SF 100.6127582 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
Current Data Parameters
NAME         P-16-106-1H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130607
Time                8.55
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg
TD                 38460
SOLVENT            CDCl3
NS                    12
DS                     0
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ              2.9999299 sec
RG                 143.7
DW                78.000 usec
DE                111.43 usec
TE                 295.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1               -6.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300069 MHz
WDW                   EM
SSB                    0
LB                0.00 Hz
GB                     0
PC                1.00
```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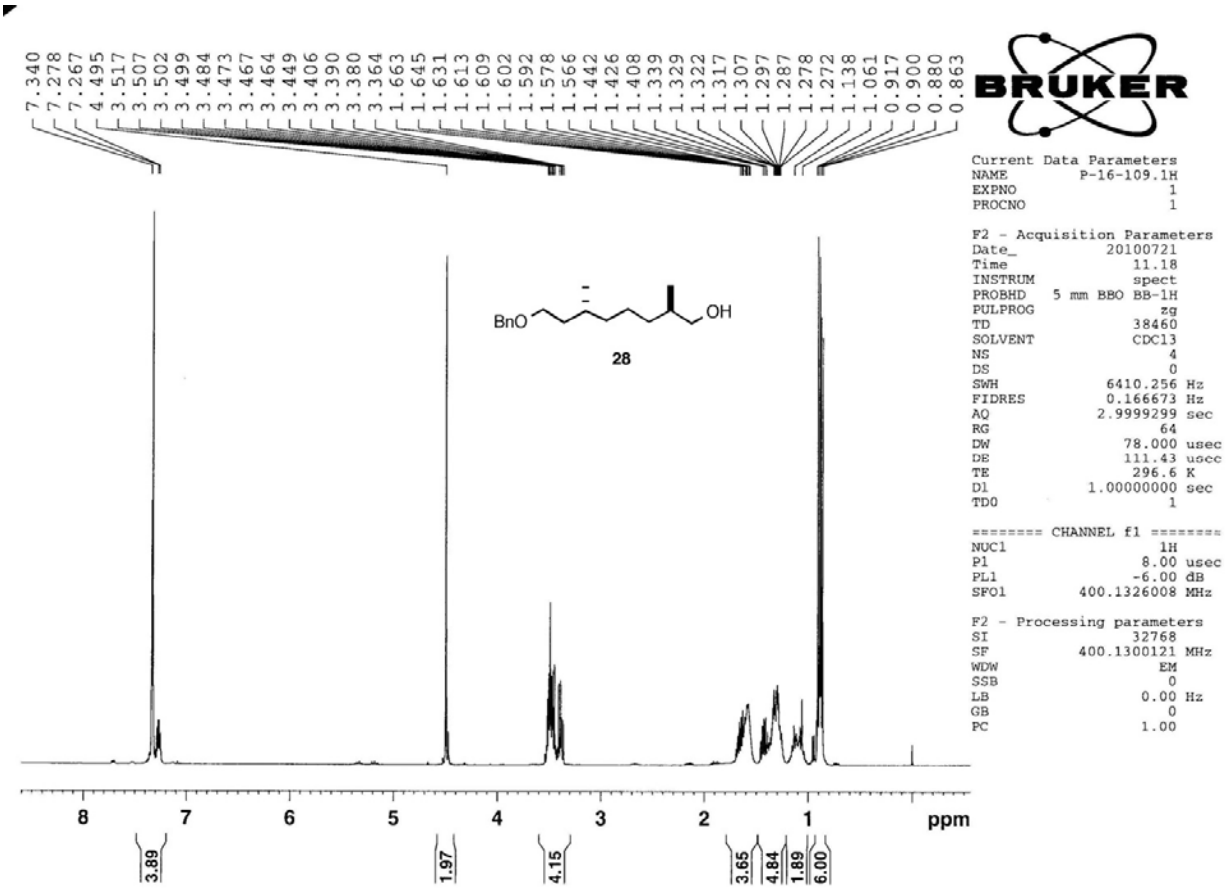
76.84
68.56
39.49
37.50
37.39
35.93
33.62
32.89
28.12
24.92
24.55
22.86
22.76
19.87
16.78
OH
27
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm
BRUKER
Current Data Parameters
NAME P-16-106-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130607
Time 8.57
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 144228
SOLVENT DMSO
NS 105
DS 0
SWH 24038.461 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 812.7
DW 20.800 usec
DE 6.00 usec
TE 295.8 K
D1 3.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.75 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 17.00 dB
SFO2 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 100.6127552 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.340
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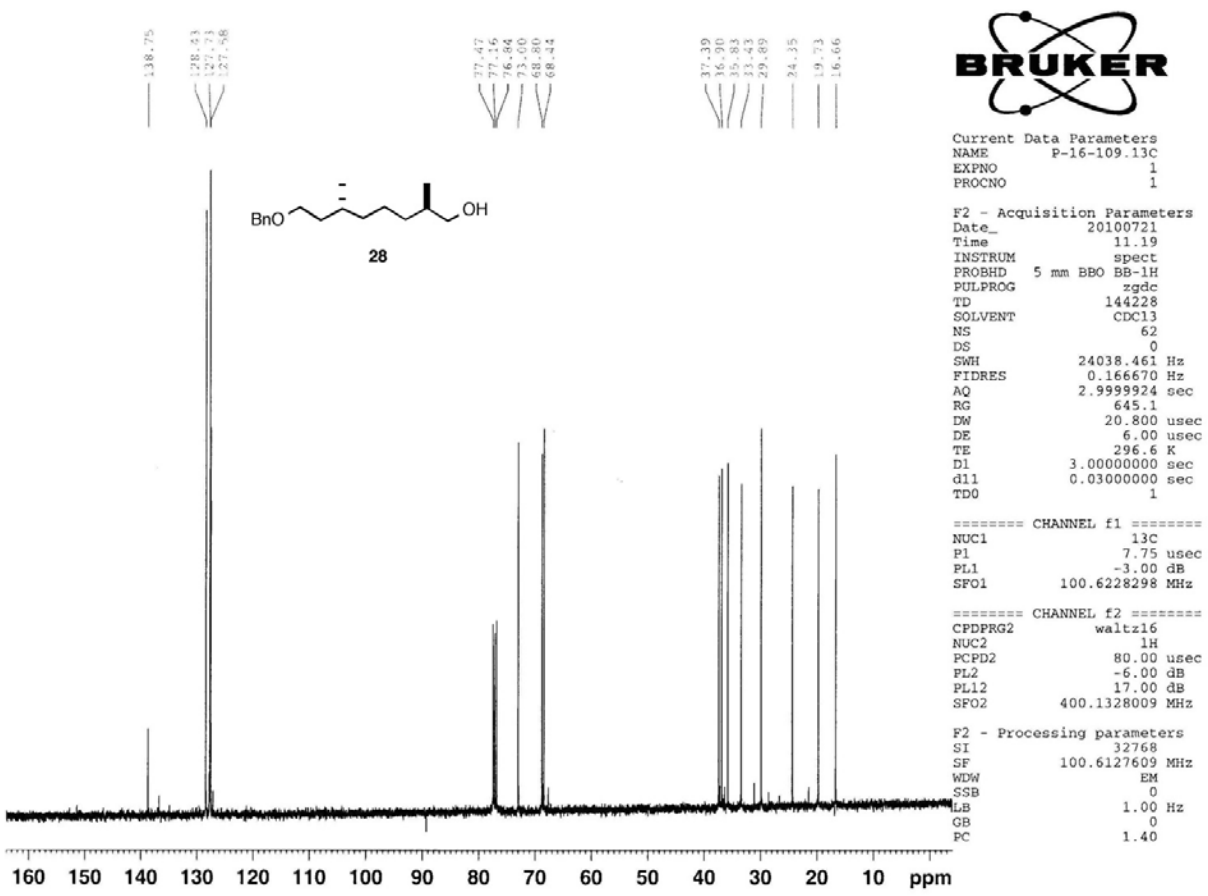
3.473
3.467
3.464
3.449
3.406
3.390
3.380
3.364
1.663
1.645
1.631
1.613
1.609
1.602
1.592
1.578
1.566
1.442
1.426
1.408
1.339
1.329
1.322
1.317
1.307
1.297
1.287
1.278
1.272
1.138
1.061
0.917
0.900
0.880
0.863
BnO
OH
28
8
7
6
5
4
3
2
1
ppm
3.89
1.97
4.15
3.65
4.84
1.89
6.00
BRUKER
Current Data Parameters
NAME P-16-109.1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100721
Time 11.18
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 38460
SOLVENT CDCl3
NS 4
DS 0
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 64
DW 78.000 usec
DE 111.43 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 -6.00 dB
SFO1 400.1326008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300121 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



BRUKER

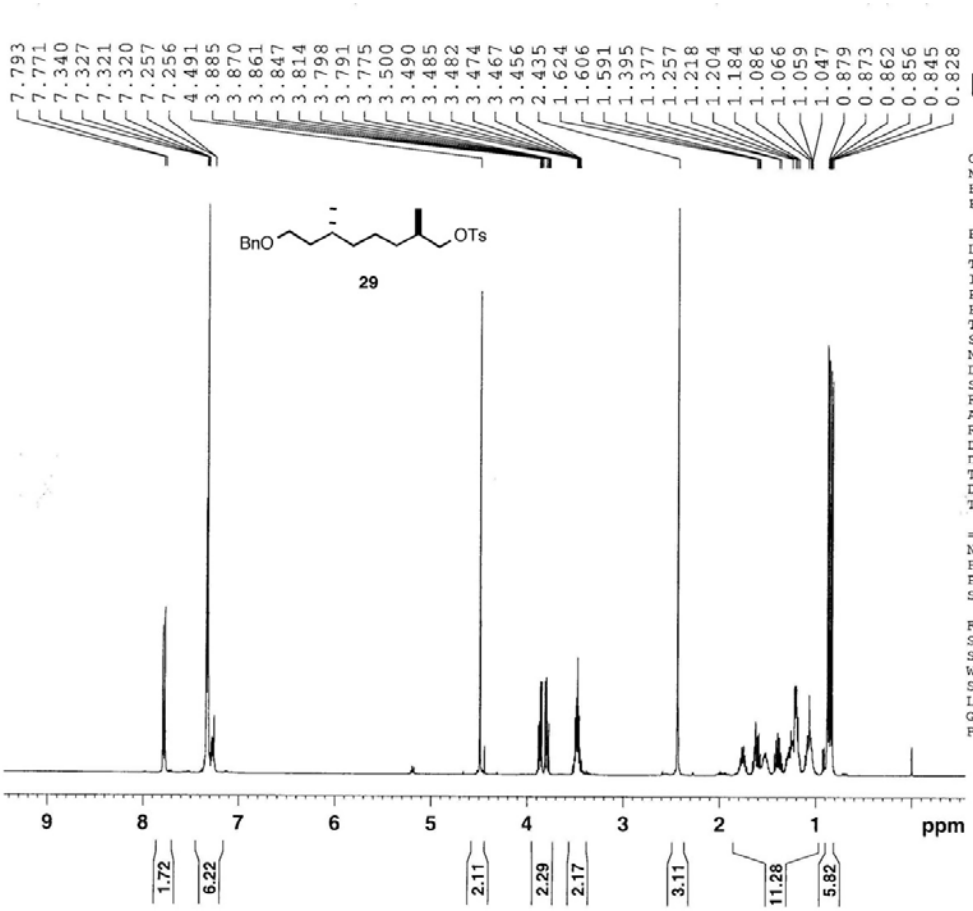
Current Data Parameters
NAME P-16-109.13C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100721
Time 11.19
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 144228
SOLVENT CDC13
NS 62
DS 0
SWH 24038.461 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 645.1
DW 20.800 usec
DE 6.00 usec
TE 296.6 K
D1 3.00000000 sec
d11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.75 usec
PL1 -3.00 dB
SFO1 100.6228298 MHz

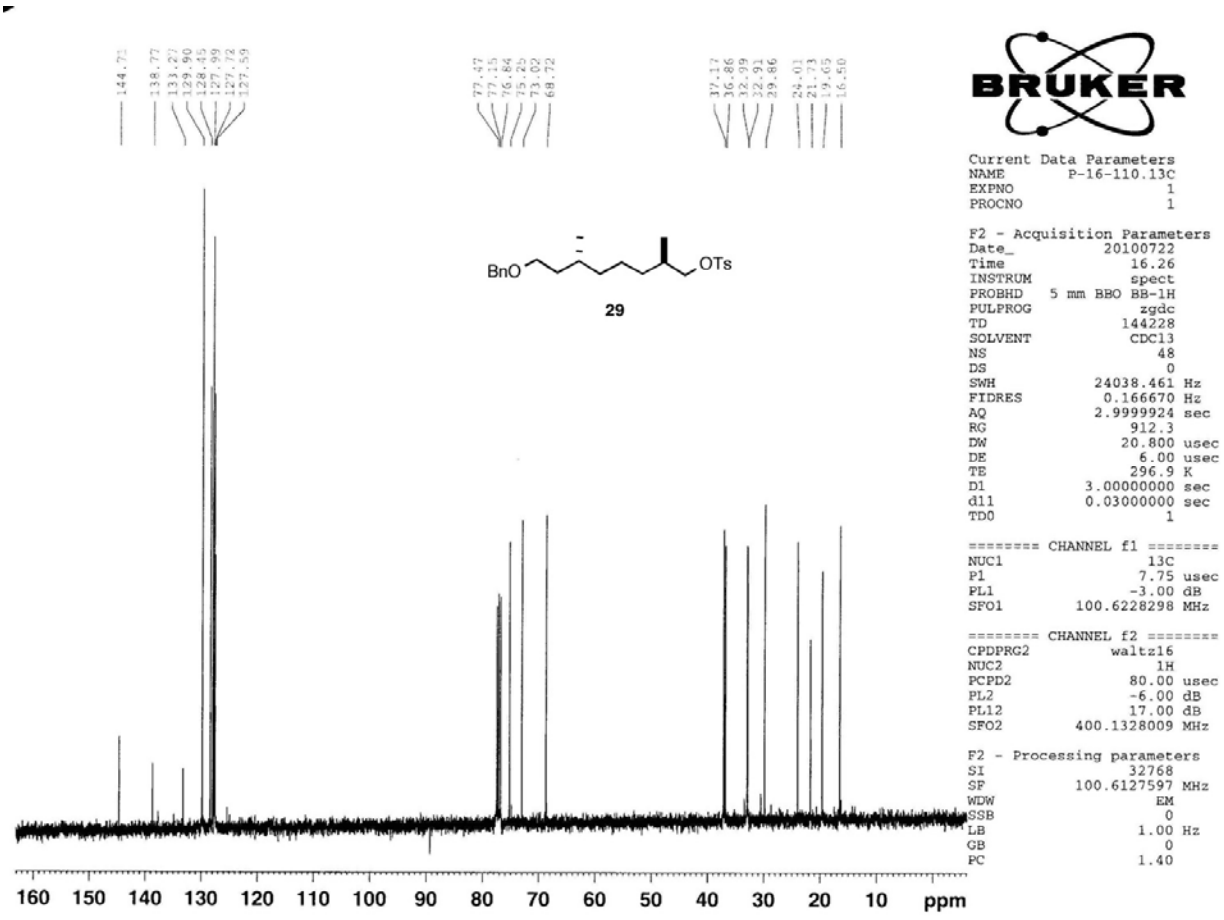
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 17.00 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 32768
SF 100.6127609 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



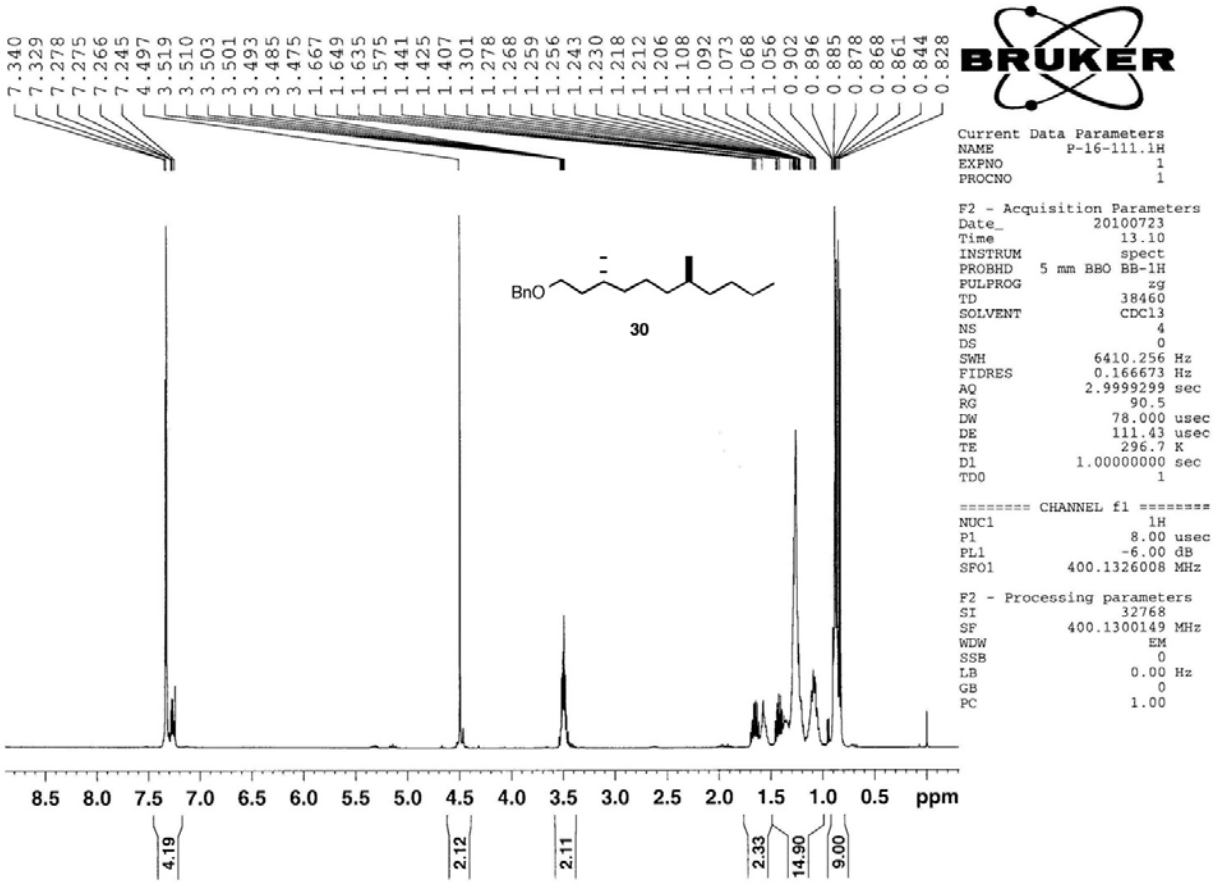
BRUKER

```
Current Data Parameters
NAME          P-16-110.1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20100722
Time                16.20
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg
TD                  38460
SOLVENT             CDCl3
NS                      4
DS                      0
SWH              6410.256 Hz
FIDRES          0.166673 Hz
AQ              2.9999299 sec
RG                  101.6
DW                 78.000 usec
DE                 111.43 usec
TE                 296.6 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.00 usec
PL1                 -6.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300101 MHz
WDW                    EM
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```



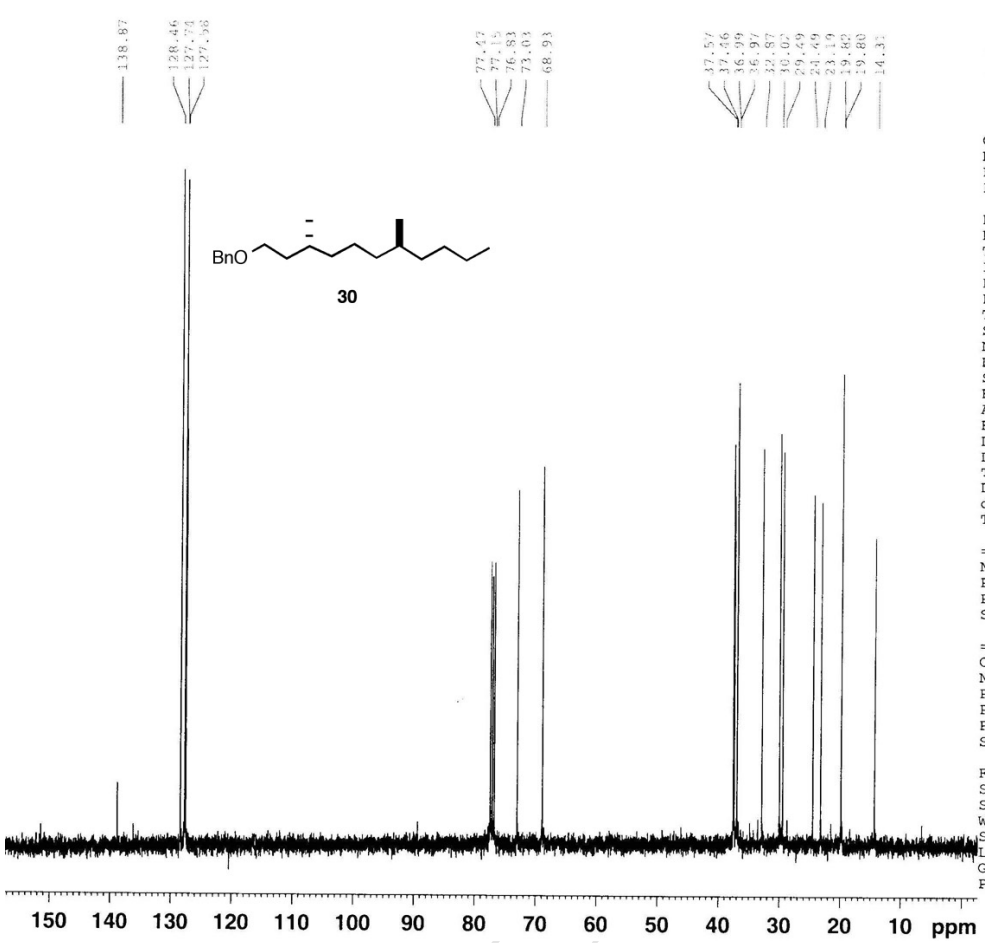
BRUKER

```
Current Data Parameters
NAME         P-16-110.13C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20100722
Time               16.26
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                144228
SOLVENT            CDCl3
NS                    48
DS                     0
SWH            24038.461 Hz
FIDRES          0.166670 Hz
AQ              2.9999924 sec
RG                 912.3
DW                20.800 usec
DE                 6.00 usec
TE                296.9 K
D1             3.00000000 sec
d11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.75 usec
PL1                -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127597 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

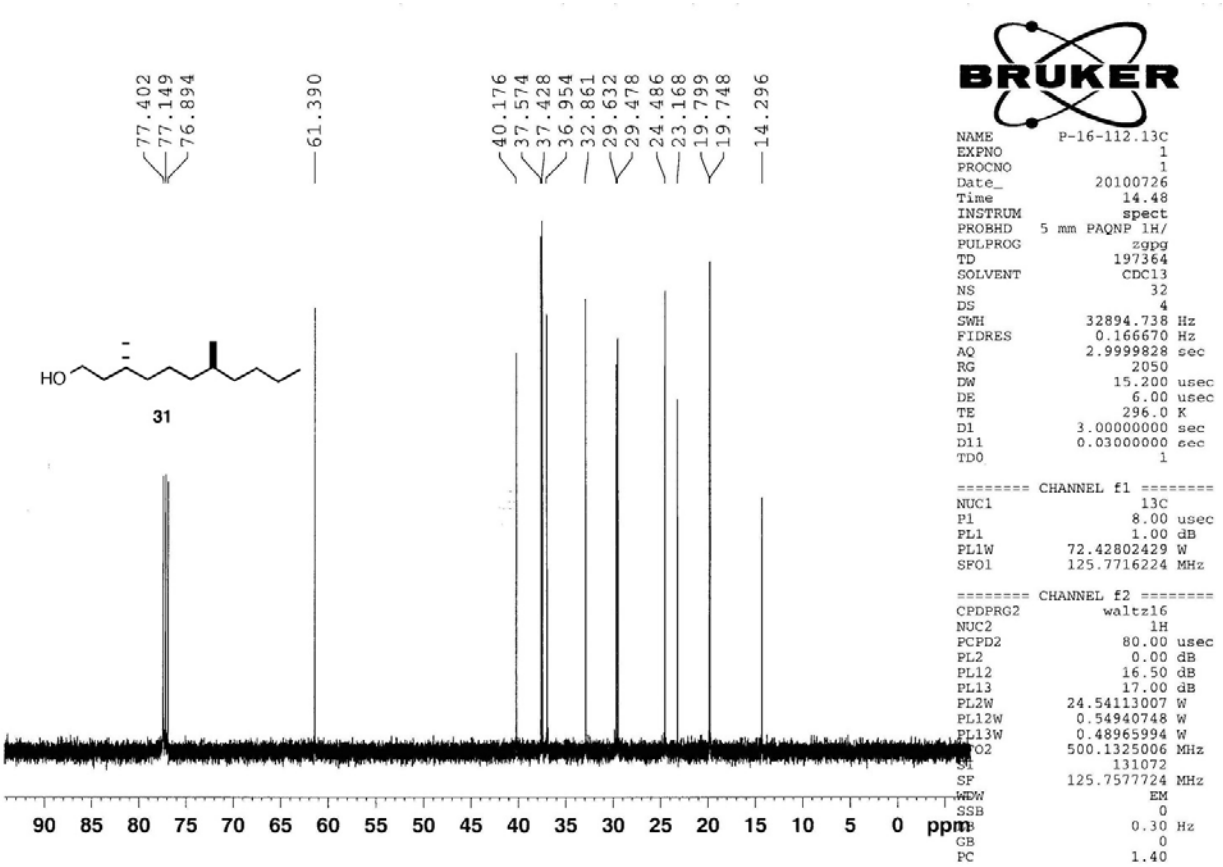


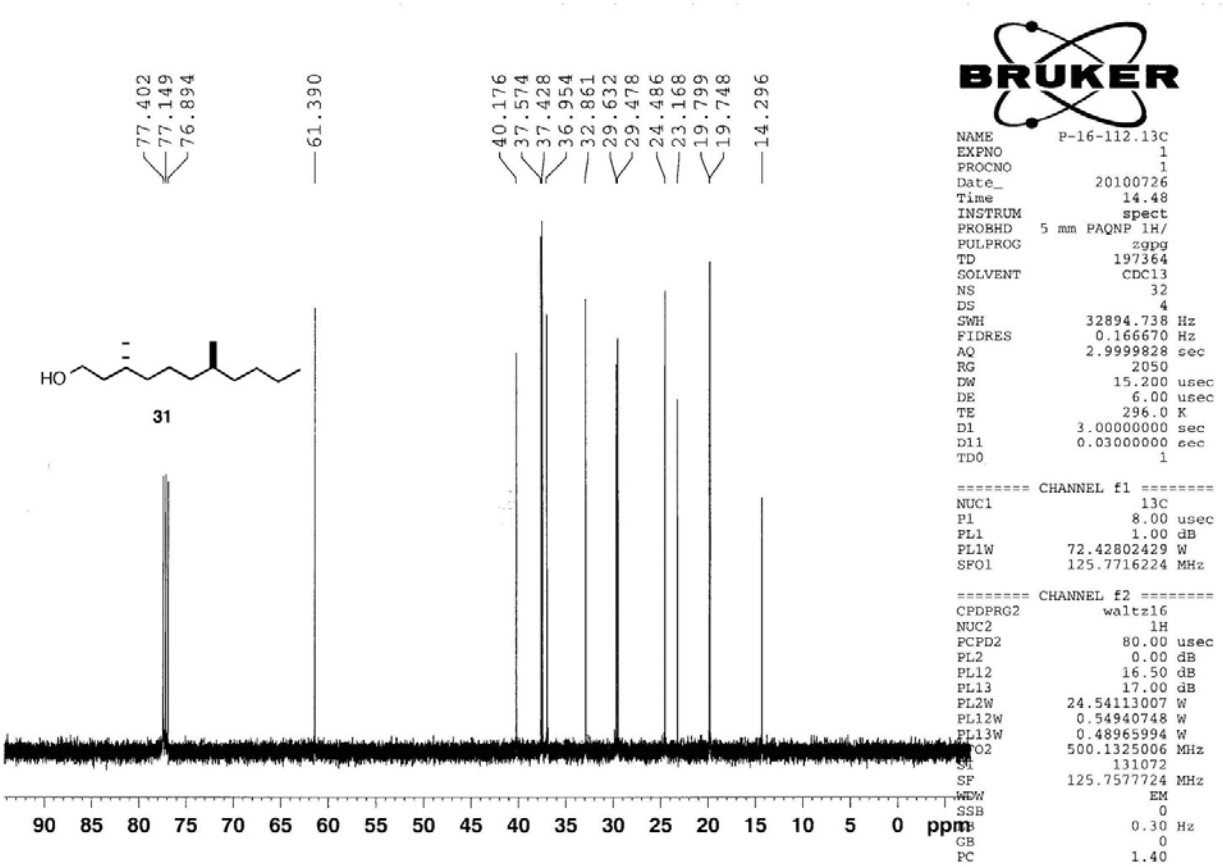
BRUKER

```
Current Data Parameters
NAME          P-16-111.1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20100723
Time                13.10
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg
TD                  38460
SOLVENT             CDCl3
NS                      4
DS                      0
SWH              6410.256 Hz
FIDRES           0.166673 Hz
AQ               2.9999299 sec
RG                   90.5
DW                 78.000 usec
DE                 111.43 usec
TE                  296.7 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  8.00 usec
PL1                -6.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300149 MHz
WDW                    EM
SSB                     0
LB                 0.00 Hz
GB                      0
PC                 1.00
```




```
Current Data Parameters
NAME        P-16-111.13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100723
Time               13.11
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                144228
SOLVENT             CDCl3
NS                     46
DS                      0
SWH            24038.461 Hz
FIDRES          0.166670 Hz
AQ              2.9999924 sec
RG                 812.7
DW                20.800 usec
DE                 6.00 usec
TE                296.8 K
D1             3.00000000 sec
d11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 7.75 usec
PL1               -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127569 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```


77.402
77.149
76.894
61.390
40.176
37.574
37.428
36.954
32.861
29.632
29.478
24.486
23.168
19.799
19.748
14.296
HO
31
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm
BRUKER
NAME P-16-112.13C
EXPNO 1
PROCNO 1
Date_ 20100726
Time 14.48
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 197364
SOLVENT CDCl3
NS 32
DS 4
SWH 32894.738 Hz
FIDRES 0.166670 Hz
AQ 2.9999828 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 296.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7716224 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7577724 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



BRUKER

NAME	P-16-112.13C
EXPNO	1
PROCNO	1
Date_	20100726
Time	14.48
INSTRUM	spect
PROBHD	5 mm PAQNP 1H/
PULPROG	zgpg
TD	197364
SOLVENT	CDCl3
NS	32
DS	4
SWH	32894.738 Hz
FIDRES	0.166670 Hz
AQ	2.9999828 sec
RG	2050
DW	15.200 usec
DE	6.00 usec
TE	296.0 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	1.00 dB
PL1W	72.42802429 W
SFO1	125.7716224 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	16.50 dB
PL13	17.00 dB
PL2W	24.54113007 W
PL12W	0.54940748 W
PL13W	0.48965994 W
SFO2	500.1325006 MHz
SI	131072
SF	125.7577724 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40