Supporting Information

Efficient and Stereodivergent Synthesis of Unsaturated Acyclic Fragments Bearing Contiguous Stereogenic Elements

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General information

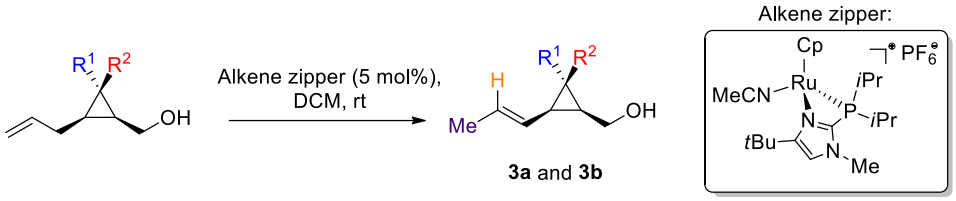
Unless stated otherwise, reactions were conducted in flame-dried glassware under a positive pressure of argon. Ether and THF were dried from Pure-Solv® Purification System (Innovative Technology©). DMF was distilled over CaH_2 and stored over activated 4 Å molecular sieves under argon. $[Pd(OTs)_2(MeCN)_2]$ was freshly prepared and stored under a dry atmosphere.[1] Grignard reagents (to the exception of MeMgBr) were prepared in solution in Et_2O and freshly titrated with menthol and 1,10-phenanthroline as indicator prior use. All other commercially obtained reagents were used as received. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm), and visualized by exposure to UV light (254 nm) or stained with anisaldehyde, phosphomolybdic acid, or potassium permanganate solutions. Column chromatography was performed using Fluka silica gel 60 Å (40-63mm, 230-400 mesh). NMR spectra were recorded on Bruker spectrometers (AVIII400) and are reported relative to deuterated solvent signals. Chemical shifts are reported in parts per million (ppm) with respect to the residual solvent signal $CDCl_3$ (^{1}H NMR: δ = 7.26; ^{13}C NMR: δ = 77.16). Peak multiplicities are reported as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were obtained by the mass spectrometry facility at the Technion. Reactions were monitored by gas chromatography spectrometry (GC) using an Agilent Technologies 7820A GC with an Agilent Technologies 19091J-413 (30 m × 0.3 mm) column. Enantiomeric excesses were determined by chiral-HPLC using Agilent©1100 Series line and CHIRALPAK®AY-H (0.46 cm Ø×25 cm) and CHIRALPAK® AZ-H (0.46 cm Ø×25 cm).

[1] Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *41*, 235.

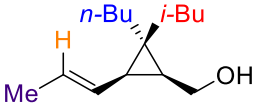
Procedures for the syntheses of starting materials

General procedure for the preparation of **1a** and **1b**

(*E*)-vinylcyclopropyl carbinols **1a** and **1b** (R^3=Me, R^4=H) were synthesized according to a previously reported strategy.[2]



The characterization and preparation of compound **1a** (R^1=*n*Bu, R^2=Me, R^3=Me, R^4=H) was previously reported.2



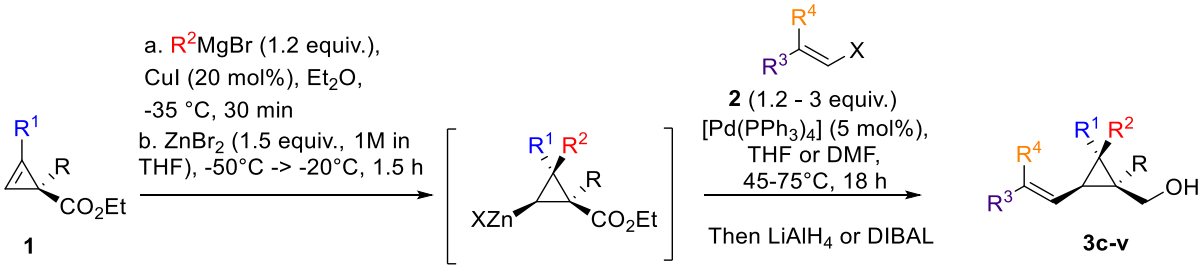
3b

M_w = 224.4 g.mol^{-1}

((1S*,2R*,3R*)-2-butyl-2-isobutyl-3-((*E*)-prop-1-en-1-yl)cyclopropyl)methanol (3b). From allylcyclopropylcarbinol (R^1=*n*Bu, R^2=*i*Bu).2 Yield = 397 mg (94%). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.62 (dq, *J* = 14.9, 6.4 Hz, 1H), 5.28 (ddq, *J* = 14.9, 9.8, 1.5 Hz, 1H), 3.80 (dt, *J* = 11.6, 7.0 Hz, 1H), 3.61 (ddd, *J* = 11.6, 9.4, 3.8 Hz, 1H), 1.76 (dt, *J* = 13.7, 6.8 Hz, 1H), 1.69 (dd, *J* = 6.5, 1.6 Hz, 3H), 1.45 – 1.11 (m, 9H), 1.04 (td, *J* = 9.1, 6.6 Hz, 1H), 0.94 – 0.85 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 126.9, 126.8, 60.4, 39.0, 34.6, 31.5, 29.7, 28.3, 28.2, 25.0, 23.1, 23.0, 22.8, 18.4, 14.2. **HRMS** (APCI-MS ES$^+$): $[M\text{-}OH]^+$, calculated for $C_{15}H_{27}$ 207.2107; found 207.2107.

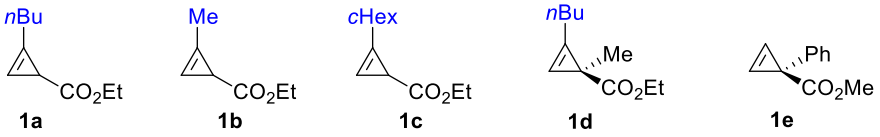
General procedures for the preparation of **3c-v**

Except for **3a** and **3b**, all other vinylcyclopropyl carbinols were synthesized according to the following strategy.

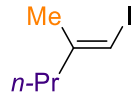


[2] Bruffaerts, J.; Vasseur, A.; Marek, I. *Adv. Synth. Catal.* **2018**, DOI 10.1002/adsc.201701481

Racemic cyclopropenes ethyl esters **1a**,[3] **1b**,[4] **1c**,[5] **1d**[6] and **1e**[7] were synthesized according to previously reported procedures. (*Z*)-1-bromoprop-1-ene (**2a**) was used as received from commercial sources. (*Z*)-1-iodohex-1-ene (**2b**) was prepared following the works of Brown and coworkers.[8] (*E*)-1-bromohex-1-ene (**2c**), (*E*)-1-bromo-3-methylbut-1-ene (**2d**), (*E*)-(3-bromoallyl)benzene (**2e**), (*E*)-1-bromo-3,3-dimethylbut-1-ene (**2f**) and (*E*)-1-bromo-5-chloropent-1-ene (**2g**) were prepared following the general procedure described by Alexakis and coworkers,[9] and were consistent with the literature.



The typical procedure (zirconocene-catalyzed methylalumination of alkynes) previously described[10] was followed to prepare **2h**.

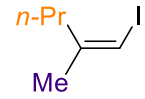


2h

M_w = 210.1 g.mol^{-1}

(*E*)-1-iodo-2-methylpent-1-ene (2h). From 1-pentyne (50 mmol scale). Yield = 10.5 g (76%). Pale yellow liquid. *E*/*Z* > 99:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.84 (d, *J* = 1.0 Hz, 1H), 2.16 (t, *J* = 14.8 Hz, 2H), 1.80 (s, 3H), 1.44 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.86 (dt, *J* = 7.4, 1.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.58, 74.90, 41.72, 23.89, 21.02, 13.70. **HRMS** (TOF-MS ES$^+$) $[M+H]^+$, calculated for $C_6H_{12}I$; 210.9884; found 210.9981.

The typical procedure (carbocupration of alkynes) previously described[11] was followed to prepare **4i** and **4j**.



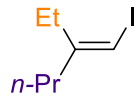
2i

M_w = 210.1 g.mol^{-1}

(*Z*)-1-iodo-2-methylpent-1-ene (2i). From propylmagnesium bromide (30 mmol) and an excess of 1-propyne. Yield = 6.3 g (82%). Pale yellow liquid.

[3] Li, C.; Zhang, H.; Feng, J.; Zhang, Y.; Wang, J. *Org. Lett.* **2010**, *12*, 3082.
[4] Lia, L.; Zhang, F.; Yan, N.; Golen, J. A.; Fox, J. M. *Tetrahedron* **2004**, *60*, 1803.
[5] Masatumi, U.; Nobuyoshi, D.; Miyagawa, H.; Sugita, S.; Takeda, N.; Shinada, T.; Miyata, O. *Chem. Commun.* **2015**, *51*, 4204.
[6] Mueller, P.; Gaenicher, C. *Helv. Chim. Acta* **1995**, *78*, 129.
[7] Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2003**, *125*, 7198.
[8] Brown, H. C.; Blue, C. D.; Nelson, D. J.; Bhat, N. G. *J. Org. Chem.* **1989**, *54*, 6064.
[9] D. Müller, A. Alexakis, *Chem. Eur. J.***2013**, *19*, 15226-15239
[10] Wipf, P.; Lim, S. *Angew. Chem. Int. Ed.* **1993**, *32*, 1068.
[11] Lipshutz, B. H.; Sengupta, S. *Org. React.*, Organocopper Reagents: Substitution, Conjugate Addition, Carbo/Metallocupration, and Other Reactions, John Wiley & Sons, Inc., **2004**.

Z/E > 99:1. **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (d, *J* = 1.3 Hz, 1H), 2.26 – 2.13 (m, 2H), 1.87 (d, *J* = 1.4 Hz, 3H), 1.51 – 1.38 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.6, 74.0, 40.5, 23.3, 20.3, 13.8. **HRMS** (TOF-MS ES$^+$) $[M+H]^+$, calculated for $C_6H_{12}I$; 210.9884; found 210.9975.



2j

M_w = 224.1 g.mol^{-1}

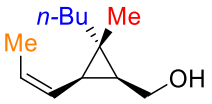
(*E*)-1-iodo-2-ethylpent-1-ene (2j). From 1-pentyne (30 mmol scale). Yield = 6.7 g (78%). Pale yellow liquid. *E/Z* > 99:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.80 (s, 1H), 2.30 – 2.07 (m, 4H), 1.52 – 1.37 (m, 2H), 0.99 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.9, 73.6, 38.8, 30.4, 21.0, 13.7, 11.7. **HRMS** (TOF-MS ES$^+$) $[M+H]^+$, calculated for $C_7H_{14}I$; 225.0140; found 225.0149.

*Procedure A (**3c-v**)*

In a flamed-dried three-neck flask under Ar, CuI (10 mol%) and a cyclopropene **3** (1 equiv) were dissolved into Et_2O (8 mL / mmol substrate) and this solution was cooled down to -45°C. Then, the Grignard reagent (1.5 equiv, in solution in Et_2O) was added dropwise and the resulting solution was let to stir from -35°C to -25°C (conversion monitored by TLC and/or GC). Following the complete conversion of **3**, the reactional mixture was then cooled to -50°C and a solution of flame-dried $ZnBr_2$ (1 M in THF, 1.5 equiv.) and anhydrous THF (20 mL) were successively added and the resulting white suspension was let to warm-up until -20°C (*c.a.* 1.5 h) under vigorous stirring. At room temperature. $[Pd(PPh_3)_4]$ (10 mol%) and the 1-alkenyl halide 4 (1.5 equiv, 1.5 mmol) were added. The reaction mixture was heated at 50 °C for 16 hours. Upon completion, the reaction was quenched with a saturated solution of ammonium chloride and the aqueous phase was extracted with Et_2O three times. The combined organic phases were dried over anhydrous $MgSO_4$, filtered over a pad of celite (washed with Et_2O) and concentrated under reduced pressure. The resulting crude mixture was directly engaged into the next reduction step.

In a flamed dried three-neck flask under Ar, to a solution of the vinycyclopropylcarbinol ester (1 equiv.) in THF (10 mL/mmol substrate) was dropwisely added to a suspension of DIBAL (1.0 M in hexane, 2.5 equiv, 2.5 mmol) (or diisobutyl aluminium deuteride in the case of **3n**) under stirring at 0°C. The reaction was warmed up to room temperature and run for 2 hours. After completion of the reaction, the reactional mixture was quenched with EtOAc, then, after 1h, a saturated aqueous solution of Rochelle salt (5 mL/mmol substrate) was carefully added

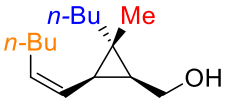
and the suspension was vigorously stirred for 1h at 0°C. The mixture was stirred until complete dissolution of the aluminium salts. The phases were separated and the aqueous phase was extracted with Et_2O three times. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. A column chromatography (15% Et_2O in hexane) afforded the desired alcohol as a pure compound.



3c

Mw = 182.31 g.mol^{-1}

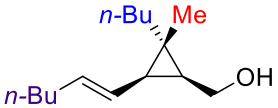
((1S*,2S*,3R*)-2-butyl-2-methyl-3-((*Z*)-prop-1-en-1-yl)cyclopropyl)methanol (3c). From **1a** (12 mmol scale) and **2a**.Yield = 1219 mg (56%). Colorless oil. *Z/E* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.71 – 5.52 (m, 1H), 5.22 (ddd, *J* = 10.8, 9.1, 1.7 Hz, 1H), 3.75 – 3.59 (m, 1H), 1.71 (dd, *J* = 6.8, 1.6 Hz, 1H), 1.50 (t, *J* = 9.0 Hz, 1H), 1.44 – 1.22 (m, 3H), 1.12 (dd, *J* = 16.3, 8.2 Hz, 1H), 1.03 (s, 1H), 0.89 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 126.6, 125.4, 60.3, 42.6, 31.0, 28.8, 25.4, 24.9, 22.8, 14.2, 13.3, 12.8. **HRMS** (TOF-MS ES$^+$) $[M\text{-}OH]^+$, calculated for $C_{12}H_{21}$ 165.1652; found 165.1643.



3d

Mw = 224.4 g.mol^{-1}

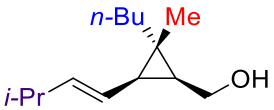
((1S*,2S*,3R*)-2-butyl-3-((*Z*)-hex-1-en-1-yl)-2-methylcyclopropyl)methanol (3d). From **1a** (5 mmol scale) and **2b**. Yield = 626 mg (57%). Colorless oil. *Z/E* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.52 (dtd, *J* = 10.8, 7.3, 1.1 Hz, 1H), 5.18 (ddt, *J* = 10.8, 9.3, 1.5 Hz, 1H), 3.75 – 3.60 (m, 2H), 2.13 (ddd, *J* = 9.0, 7.9, 4.3 Hz, 2H), 1.50 (td, *J* = 9.2, 0.9 Hz, 1H), 1.43 – 1.19 (m, 11H), 1.10 (dd, *J* = 16.7, 8.0 Hz, 2H), 1.03 (s, 3H), 0.97 – 0.83 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.8, 124.3, 60.4, 42.6, 31.9, 31.1, 28.8, 27.5, 25.5, 25.1, 22.9, 22.4, 14.2, 14.0, 12.8. **HRMS** (TOF-MS ES$^+$) $[M+H]^+$, calculated for $C_{15}H_{29}O$, 225.2218; found 225.2190.



3e

Mw = 224.4 g.mol^{-1}

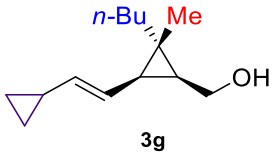
((1S*,2S*,3R*)-2-butyl-3-((*E*)-hex-1-en-1-yl)-2-methylcyclopropyl)methanol (3e). From **1a** (11.8 mmol scale) and **2c**.Yield = 1959 mg (74%). Colorless oil. *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.61 (dt, *J* = 14.9, 6.8 Hz, 1H), 5.21 (ddt, *J* = 15.1, 9.3, 1.3 Hz, 1H), 3.78 – 3.59 (m, 2H), 2.01 (q, *J* = 6.9 Hz, 2H), 1.43 – 1.12 (m, 11H), 1.04 (s, 3H), 1.03 (q, *J* = 8.0 Hz, 1H), 0.88 (dd, *J* = 7.1, 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.0, 125.1, 60.4, 42.5, 32.7, 31.9, 30.9, 29.6, 28.7, 25.3, 22.9, 22.2, 14.2, 14.0, 12.9. **HRMS** (TOF-MS ES$^+$) $[M+H]^+$, calculated for $C_{15}H_{29}O$, 225.2218; found 225.2220.



3f

Mw = 210.4 g.mol^{-1}

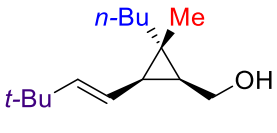
((1S*,2S*,3R*)-2-butyl-2-methyl-3-((*E*)-3-methylbut-1-en-1-yl)cyclopropyl)methanol (3f). From **1a** (4 mmol scale) and **2d**. Yield = 564 mg (67%). Colorless oil. *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.52 (dd, *J* = 15.3, 6.7 Hz, 1H), 5.10 (ddd, *J* = 15.3, 9.3, 1.3 Hz, 1H), 3.73 – 3.52 (m, 2H), 2.20 (dqd, *J* = 13.4, 6.7, 1.2 Hz, 1H), 1.36 – 1.03 (m, 7H), 0.97 (s, 3H), 0.96 – 0.92 (m, 1H), 0.91 (d, *J* = 1.7 Hz, 3H), 0.89 (d, *J* = 1.7 Hz, 3H), 0.82 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.3, 122.1, 60.5, 42.5, 31.5, 30.8, 29.6, 28.7, 25.3, 22.9, 22.8, 22.8, 14.2, 12.9. **HRMS** (APCI ES$^+$) [M-OH]$^+$, calculated for $C_{14}H_{25}$, 193.1951; found 193.2000.



3g

Mw = 208.4 g.mol^{-1}

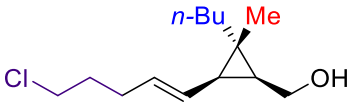
((1S*,2S*,3R*)-2-butyl-3-((*E*)-2-cyclopropylvinyl)-2-methylcyclopropyl)methanol (3g). From **1a** (2.1 mmol scale) and **2e**. Yield = 178 mg (40%). Colorless oil. *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.32 (dd, *J* = 15.1, 9.5 Hz, 1H), 5.12 (dd, *J* = 15.1, 8.7 Hz, 1H), 3.77 – 3.67 (m, 2H), 1.48 – 1.10 (m, 7H), 1.05 (s, 3H), 1.10 – 0.97 (m, 1H), 0.95 – 0.80 (m, 1H), 0.88 (t, *J* = 7.0 Hz, 1H), 0.67 (dd, *J* = 8.1, 1.9 Hz, 2H), 0.39 – 0.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 123.0, 60.4, 42.5, 31.0, 29.8, 28.7, 25.4, 22.9, 14.9, 14.2, 12.9, 6.7, 6.7. **HRMS** (APCI ES$^+$) [M-OH]$^+$, calculated for $C_{14}H_{25}$, 191.1794; found 191.1812.



3h

Mw = 224.4 g.mol^{-1}

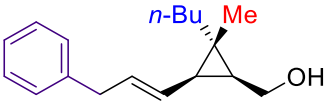
((1S*,2S*,3R*)-2-butyl-3-((*E*)-3,3-dimethylbut-1-en-1-yl)-2-methylcyclopropyl)methanol (3h). From **1a** (4 mmol scale) and **2f**. Yield = 606 mg (68%). Colorless oil. *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.66 (dd, *J* = 15.5, 0.6 Hz, 1H), 5.12 (dd, *J* = 15.5, 9.1 Hz, 1H), 3.70 (ddd, *J* = 8.0, 5.8, 2.3 Hz, 2H), 1.42 – 1.09 (m, 7H), 1.04 (s, 3H), 1.08 – 1.01 (m, 1H), 0.99 (s, 9H), 0.88 (td, *J* = 7.0, 2.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 119.6, 60.5, 42.5, 33.3, 30.7, 29.8, 29.6, 28.7, 25.3, 22.9, 14.2, 12.9. **HRMS** (APCI ES$^+$) [M-OH]$^+$, calculated for $C_{15}H_{27}$, 207.2004; found 207.2113.



3i

M_w = 244.8 g.mol^{-1}

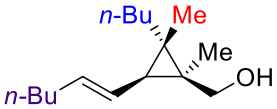
((1S*,2S*,3R*)-2-butyl-3-((*E*)-5-chloropent-1-en-1-yl)-2-methylcyclopropyl)methanol (3i). From **1a** (4.6 mmol scale) and **2g**. Yield = 614 mg (54%). Colorless oil. *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.55 (dt, *J* = 14.3, 6.9 Hz, 1H), 5.28 (dd, *J* = 15.1, 9.4 Hz, 1H), 3.69 (qd, *J* = 11.6, 7.9 Hz, 2H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.17 (q, *J* = 7.0 Hz, 2H), 1.86 – 1.77 (m, 2H), 1.45 – 1.10 (m, 7H), 1.08 – 1.00 (m, 1H), 1.03 (s, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 130.4, 127.2, 60.3, 44.4, 42.5, 32.3, 31.0, 30.0, 29.6, 28.7, 25.4, 22.8, 14.2, 12.9. **HRMS** (APCI ES$^+$) $[M+Na]^+$, calculated for $C_{14}H_{27}OClNa$, 267.1492; found 267.2316.



3j

M_w = 258.4 g.mol^{-1}

((1S*,2S*,3R*)-2-butyl-2-methyl-3-((*E*)-3-phenylprop-1-en-1-yl)cyclopropyl)methanol (3j). From **1a** (3.3 mmol scale) and **2h**. Yield = 442 mg (52%). Colorless oil. *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 8.7 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 5.77 (dt, *J* = 14.3, 6.9 Hz, 1H), 5.33 (ddt, *J* = 15.0, 9.4, 1.3 Hz, 1H), 3.72 (dq, *J* = 3.8, 8.4 Hz, 2H), 3.37 (d, *J* = 6.9 Hz, 2H), 1.42 (t, *J* = 9.2 Hz, 1H), 1.38 – 1.13 (m, 6H), 1.07 (q, *J* = 7.9 Hz, 1H), 1.06 (s, 3H), 0.89 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 131.2, 128.5, 128.4, 127.1, 126.0, 60.4, 42.5, 39.4, 31.1, 29.6, 28.7, 25.5, 22.9, 14.2, 13.0. **HRMS** (APCI ES$^+$) $[M-H_2O+Na]^+$, calculated for $C_{18}H_{24}Na$, 263.1776; found 263.0227.



3k

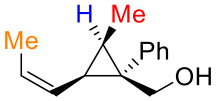
M_w = 238.4 g.mol^{-1}

((1S*,2S*,3S*)-2-butyl-3-((*E*)-hex-1-en-1-yl)-1,2-dimethylcyclopropyl)methanol (3k). From **1d** (4 mmol scale) and **2c**. Yield = 326 mg (34%). Colorless oil. *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.51 (dt, *J* = 14.7, 6.8 Hz, 1H), 5.18 (dd, *J* = 15.1, 9.3 Hz, 1H), 3.57 (qd, *J* = 11.5, 5.9 Hz, 2H), 1.94 (q, *J* = 6.7 Hz, 2H), 1.44 – 1.12 (m, 14H), 1.02 (s, 3H), 1.00 (dd, *J* = 14.6, 7.8 Hz, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.9, 125.8, 65.8, 37.5, 37.2, 32.7, 31.9, 31.1, 29.5, 29.2, 23.1, 22.2, 18.4, 14.3, 14.2, 14.0. **HRMS** (APCI ES$^+$) $[M-OH]^+$, calculated for $C_{16}H_{29}$, 221.2264; found 221.2280.

3l

M_w = 238.4 g.mol^{-1}

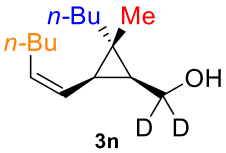
((1S*,2S*,3S*)-2-butyl-3-((*Z*)-hex-1-en-1-yl)-1,2-dimethylcyclopropyl)methanol (3l). From **1d** (6 mmol scale) and **2b**. Yield = 608 mg (43%). Colorless oil. *Z*/*E* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.45 (dtd, *J* = 10.8, 7.3, 1.2 Hz, 1H), 5.17 (ddt, *J* = 10.5, 9.0, 1.5 Hz, 1H), 3.54 (qd, *J* = 11.6, 5.7 Hz, 2H), 2.09 – 1.95 (m, 2H), 1.47 – 1.13 (m, 13H), 1.11 (dd, *J* = 9.0, 0.7 Hz, 1H), 1.01 (s, 3H), 0.84 (td, *J* = 7.1, 1.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.7, 125.0, 65.8, 37.6, 32.7, 31.9, 31.4, 29.8, 29.4, 27. 6, 23.1, 22.4, 18.5, 14.2, 14.2, 14.1. **HRMS** (APCI ES$^+$) [M-OH]$^+$, calculated for $C_{16}H_{29}$, 221.2264; found 221.2294.



3m

M_w = 202.3 g.mol^{-1}

((1R*,2R*,3S*)-2-methyl-1-phenyl-3-((*Z*)-prop-1-en-1-yl)cyclopropyl)methanol (3m). From **1e** (12 mmol scale) and **2a**. Yield = 653 mg (27%). Colorless oil. *Z*/*E* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 5.68 (dqd, *J* = 10.8, 6.8, 1.2 Hz, 1H), 5.35 (ddq, *J* = 10.5, 9.1, 1.6 Hz, 1H), 3.95 – 3.70 (m, 2H), 1.95 (t, *J* = 9.0 Hz, 1H), 1.72 (dd, *J* = 6.8, 1.7 Hz, 3H), 1.53 (dq, *J* = 9.0, 6.6 Hz, 1H), 1.21 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 129.0, 128.6, 127.9, 126.6, 124.3, 63.4, 36.3, 25.7, 23.5, 13.6, 9.0.



3n

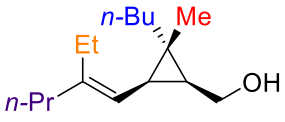
Mw = 226.4 g.mol^{-1}

((1S*,2S*,3R*)-2-butyl-3-((*Z*)-hex-1-en-1-yl)-2-methylcyclopropyl)methan-D$_2$-ol (3n). From **1a** (0.5 mmol scale) and **2b**. Yield = 59 mg (57%). Colorless oil. *Z*/*E* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.52 (dtd, *J* = 10.8, 7.3, 1.1 Hz, 1H), 5.18 (ddt, *J* = 10.8, 9.3, 1.5 Hz, 1H), 2.18 – 2.07 (m, 2H), 1.50 (td, *J* = 9.1, 1.1 Hz, 1H), 1.42 – 1.18 (m, 11H), 1.09 (dd, *J* = 7.4, 2.8 Hz, 2H), 1.03 (s, 3H), 0.94 – 0.82 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.8, 124.3, 42.6, 31.9, 30.9, 28.8, 27.5, 25.5, 25.1, 22.9, 22.4, 14.2, 14.1, 12.9. **HRMS** (APCI ES$^+$) [M-OD]$^+$, calculated for $C_{15}H_{26}D$, 209.2254; found 209.2280.

*Procedure B (**3o-v**)*

In a flamed-dried three-neck flask under Ar, CuI (10 mol%) and a cyclopropene **3** (1 equiv) were dissolved into Et_2O (8 mL / mmol substrate) and this solution was cooled down to -45°C. Then, the Grignard reagent (1.5 equiv, in solution in Et_2O) was added dropwise and the resulting solution was let to stir from -35°C to -25°C (conversion monitored by TLC and/or GC). Following the complete conversion of **3**, the reactional mixture was then cooled to -50°C and a solution of flame-dried $ZnBr_2$ (1 M in THF, 1.5 equiv.) was slowly added and the resulting white suspension was let to warm-up until -20°C (*c.a.* 1.5 h) under vigorous stirring. Then, in a separate flask, [$Pd(PPh_3)_4$] (5 mol%) and the vinylhalide **2** (1.2 equiv) were dissolved into DMF (4 mL / mmol cyclopropene) and transferred to the reactional mixture at -20°C. The resulting orange suspension was heated until 75°C and stirred overnight (monitored by GC). The reaction was quenched with brine and the aqueous phase was extracted with Et_2O three times. The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. A column chromatography (gradient eluent: 100% hexane to 2% Et_2O/hexane, stain: phosphomolybdic acid solution) afforded the desired vinylcyclopropane ester as the major product. In all cases, remaining hydrolysed cyclopropane derivative (*c.a.* 5-10%) could not be avoided and this mixture was directly engaged into the next reduction step.

In a flamed dried three-neck flask under Ar, a solution of the vinycyclopropylcarbinol ester (1 equiv.) in THF (5 mL/mmol substrate) was slowly added to a suspension of $LiAlH_4$ (3 equiv.) in THF (5 mL/mmol substrate) under stirring at 0°C. After completion of the reaction, the reactional mixture was quenched with EtOAc, then carefully a saturated aqueous solution of Rochelle salt (5 mL/mmol substrate) was added and the suspension was vigorously stirred for 1h at 0°C. The phases were separated and the aqueous phase was extracted with Et_2O three times. The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. A column chromatography (gradient eluent: 10 – 20% Et_2O/hexane) afforded the desired alcohol as a pure compound.

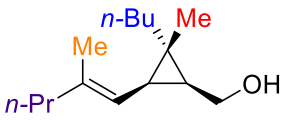


3o

M_w = 238.4 g.mol^{-1}

((1S*,2S*,3R*)-2-butyl-3-((*E*)-2-ethylpent-1-en-1-yl)-2-methylcyclopropyl)methanol (3o). From **1a** (10 mmol scale) and **2j**. Yield = 1039 mg (44%). Colorless oil. *E/Z* > 99:1. dr = 98:2:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.89 (d, *J* = 8.5 Hz, 1H), 3.67 – 3.60 (m, 2H), 2.19 – 2.02 (m, 2H), 1.97 (t, *J* = 7.4 Hz, 2H), 1.44 – 1.11 (m, 11H), 0.98 (m, 8H), 0.86 (m,

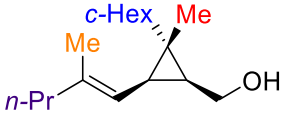
6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 118.3, 60.4, 42.7, 38.9, 30.5, 28.8, 25.2, 25.0, 23.5, 22.9, 21.3, 14.1, 13.8, 13.0, 12.8. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{16}H_{30}ONa$; 261.2194; found 261.2189.



3p

M_w = 224.4 g.mol^{-1}

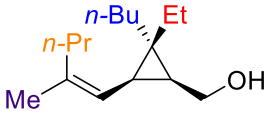
((1S*,2S*,3R*)-2-butyl-2-methyl-3-((*E*)-2-methylpent-1-en-1-yl)cyclopropyl)methanol (3p). From **1a** (15 mmol scale) and **2h**. Yield = 1895 mg (57%). Colorless oil. *E/Z* > 99:1. dr = 98:2:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.92 (dd, *J* = 8.0, 1.1 Hz, 1H), 3.59 (d, *J* = 7.7 Hz, 2H), 1.94 (t, *J* = 7.4 Hz, 2H), 1.76 (bs, 1H), 1.63 (s, 3H), 1.44 – 1.13 (m, 9H), 1.04 – 0.97 (m, 1H), 0.96 (s, 3H), 0.83 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.6, 118.9, 60.2, 42.6, 41.8, 30.3, 28.8, 25.5, 24.8, 22.8, 21.0, 16.4, 14.1, 13.5, 12.8. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{15}H_{28}ONa$; 247.2037; found 247.2034.



3q

M_w = 250.4 g.mol^{-1}

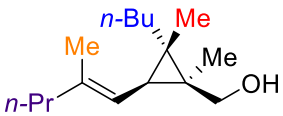
((1S*,2S*,3R*)-2-cyclohexyl-2-methyl-3-((*E*)-2-methylpent-1-en-1-yl)cyclopropyl)methanol (3q). From **1c** (3 mmol scale) and **2h**. Yield = 340 mg (46%). Colorless oil. *E/Z* > 99:1. dr = 98:2:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.90 (dd, *J* = 8.0, 1.1 Hz, 1H), 3.68 – 3.50 (m, 2H), 1.94 – 1.86 (m, 3H), 1.78 – 1.66 (m, 2H), 1.62 (t, *J* = 6.6 Hz, 6H), 1.34 (m, 3H), 1.24 – 1.01 (m, 6H), 0.93 (m, 1H), 0.81 (m, 6H), 0.41 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.3, 119.0, 59.9, 50.4, 41.9, 30.4, 29.6, 29.4, 29.2, 26.9, 26.8, 26.6, 25.5, 21.0, 16.4, 13.5, 9.0. **HRMS** (TOF-MS ES$^+$) $[M+H]^+$, calculated for $C_{17}H_{31}O$; 251.2375; found 251.2366.



3r

M_w = 238.4 g.mol^{-1}

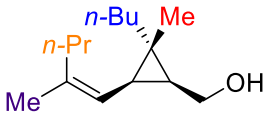
((1S*,2S*,3R*)-2-butyl-2-ethyl-3-((*Z*)-2-methylpent-1-en-1-yl)cyclopropyl)methanol (3r). From **1a** (3 mmol scale) and **2i**. Yield = 239 mg (34%). Colorless oil. *E/Z* > 99:1. dr = 98:2:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.00 (d, *J* = 9.1 Hz, 1H), 3.79 – 3.70 (m, 1H), 3.69 – 3.58 (m, 1H), 2.19 – 1.98 (m, 2H), 1.69 (s, 3H), 1.52 – 1.13 (m, 10H), 1.09 – 0.98 (m, 1H), 0.96 – 0.83 (m, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 119.3, 60.1, 38.1, 34.3, 31.4, 30.0, 28.3, 25.6, 23.7, 22.9, 21.1, 18.9, 14.2, 14.1, 10.6. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{16}H_{30}ONa$; 261.2194; found 261.2211.



3s

M_w = 238.4 g.mol^{-1}

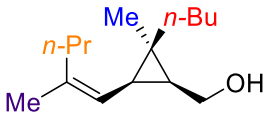
((1S*,2S*,3S*)-2-butyl-1,2-dimethyl-3-((*E*)-2-methylpent-1-en-1-yl)cyclopropyl)methanol (3s). From **1d** (3 mmol scale) and **2h**. Yield = 285 mg (57%). Colorless oil. *E*/*Z* > 99:1. dr = 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4δ 5.05 – 4.94 (m, 1H), 3.57 (q, *J* = 11.6 Hz, 2H), 1.97 (t, *J* = 7.5 Hz, 2H), 1.64 (d, *J* = 1.0 Hz, 3H), 1.49 – 1.22 (m, 12H), 1.08 – 1.03 (m, 4H), 0.92 – 0.82 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.9, 119.8, 66.0, 41.9, 37.8, 33.4, 30.7, 29.5, 29.2, 23.2, 21.2, 18.6, 16.8, 14.4, 14.3, 13.8. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{15}H_{28}ONa$; 247.2037; found 247.2034.



3t

M_w = 224.4 g.mol^{-1}

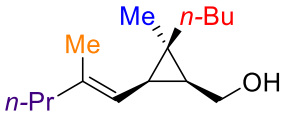
((1S*,2S*,3R*)-2-butyl-2-methyl-3-((*Z*)-2-methylpent-1-en-1-yl)cyclopropyl)methanol (3t). From **1a** (3 mmol scale) and vinyl halide **2i**. Yield = 233 mg (35%). Colorless oil. *Z*/*E* > 99:1. dr = 98:2:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.92 (d, *J* = 8.4 Hz, 1H), 3.60 (d, *J* = 7.7 Hz, 2H), 2.12 – 1.96 (m, 2H), 1.81 (bs, 1H), 1.66 (s, 3H), 1.48 – 1.12 (m, 9H), 1.03 – 0.92 (m, 4H), 0.86 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 119.5, 60.1, 42.7, 34.3, 30.4, 28.7, 25.4, 24.9, 23.5, 22.8, 21.0, 14.1, 14.0, 12.8. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{15}H_{28}ONa$; 247.2037; found 247.2045.



3u

M_w = 224.4 g.mol^{-1}

((1S*,2R*,3R*)-2-butyl-2-methyl-3-((*Z*)-2-methylpent-1-en-1-yl)cyclopropyl)methanol (3u). From **1a** (3 mmol scale) and **2i**. Yield = 147 mg (22%). Colorless oil. *Z*/*E* > 99:1. dr = 98:2:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.00 (d, *J* = 8.8 Hz, 1H), 3.76 (d, *J* = 6.9 Hz, 1H), 3.61 (t, *J* = 10.0 Hz, 1H), 2.23 – 1.97 (m, 2H), 1.70 (s, 3H), 1.52 – 1.15 (m, 11H), 1.07 (s, 3H), 0.98 – 0.82 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 119.6, 60.4, 34.5, 32.2, 29.7, 29.1, 26.5, 26.2, 25.5, 23.9, 23.3, 21.2, 14.3, 14.2. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{15}H_{28}ONa$; 247.2037; found 247.2033.



3v

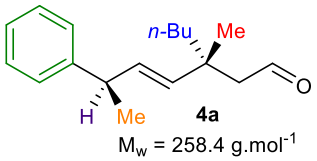
M_w = 224.4 g.mol^{-1}

((1S*,2R*,3R*)-2-butyl-2-methyl-3-((*E*)-2-methylpent-1-en-1-yl)cyclopropyl)methanol (3v). From **1a** (3 mmol scale) and **2h**. Yield = 206 mg (31%). Colorless liquid. *E*/*Z* > 99:1. dr = 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.98 (dd, *J* = 8.6, 1.1 Hz, 1H), 3.75 (dd, *J* = 11.6,

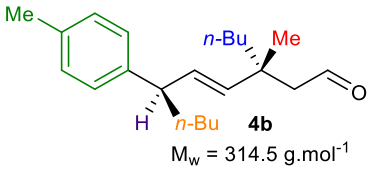
7.0 Hz, 1H), 3.59 (dd, *J* = 11.5, 8.6 Hz, 1H), 1.96 (t, *J* = 7.4 Hz, 2H), 1.66 (s, 3H), 1.47 – 1.16 (m, 12H), 1.13 – 0.98 (m, 4H), 0.92 – 0.78 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.5, 119.1, 60.3, 42.0, 32.0, 29.7, 29.0, 26.5, 26.2, 25.3, 23.3, 21.2, 16.6, 14.2, 13.7. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{15}H_{28}ONa$; 247.2037; found 247.2045.

General procedure for the Heck arylation of vinylcyclopropylcarbinols with arylboronic acids

In a dry one-neck flask under O_2 (balloon, 1 atm), 5-(2-pyridyl)-1,3-oxazole (9 mol%), $[Pd(MeCN)_2(OTs)_2]$ (7.5 mol%), $Cu(OTf)_2$ (5 mol%), molecular sieves 3 Å (100% w/w substrate) and vinylcyclopropyl carbinol (1 equiv., 0.25 mmol except mentioned otherwise) were dissolved into DMA (8 mL/mmol substrate). The corresponding arylboronic acid (3 equiv.) was then rapidly poured into the reactional mixture which was set on stirring at 55°C for 18 h. After completion of the reaction, the reactional mixture was diluted with brine and EtOAc. The phases were separated and the aqueous phase was successively washed three times with EtOAc. The combined organic phases were then dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. A column chromatography (typically, gradient eluent 100% hexane / 5% Et_2O/hexane) afforded the desired aldehyde.

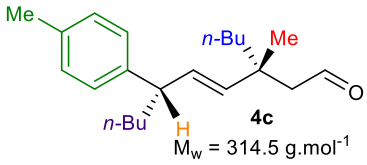


(3R*,6R*,4*E*)-3-butyl-3-methyl-6-phenylhept-4-enal (4a). From **3c** and phenylboronic acid. Yield = 50 mg (78%). Colorless liquid. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (t, *J* = 3.2 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.22 – 7.16 (m, 3H), 5.57 (dd, *J* = 15.8, 6.4 Hz, 1H), 5.49 (d, *J* = 16.2 Hz, 1H), 3.47 (p, *J* = 6.8 Hz, 1H), 2.33 (ddd, *J* = 35.7, 14.7, 3.1 Hz, 3H), 1.37 (dd, *J* = 17.3, 7.4 Hz, 6H), 1.35 (d, *J* = 7.0 Hz, 4H), 1.31 – 1.15 (m, 7H), 1.12 (s, 4H), 0.88 (t, *J* = 7.1 Hz, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.8, 146.0, 135.9, 133.5, 128.4, 127.1, 126.1, 53.7, 42.3, 41.8, 38.1, 26.1, 24.2, 23.2, 21.5, 14.0. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{18}H_{27}O$; 259.2062; found 259.2015.

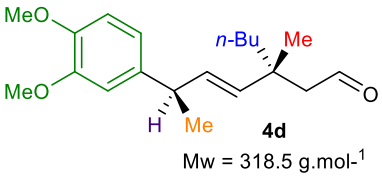


(3R*,6R*,4*E*)-3-butyl-3-methyl-6-(*p*-tolyl)dec-4-enal (4b). From **3d** and *p*-tolylboronic acid. Yield = 49 mg (63%). Colorless liquid. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.70 (t, *J* = 3.2 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 5.50 (d, *J* = 15.8 Hz, 1H), 5.45 (d, *J* = 15.6 Hz, 1H), 3.19 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.36 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.32 (s, 3H), 2.27 (dd, *J* = 14.7, 3.5 Hz, 1H), 1.65 (ddd, *J* = 9.3, 7.3, 2.4 Hz, 2H), 1.41 – 1.13 (m, 10H), 1.10 (s, 3H), 0.86 (t, *J* = 6.9 Hz, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.0, 142.2, 136.5, 135.5, 132.8, 129.1, 127.3, 53.7, 48.4, 41.9,

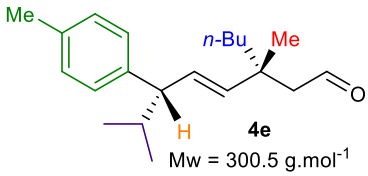
38.2, 35.8, 29.9, 26.1, 24.3, 23.3, 22.7, 21.0, 14.1. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{22}H_{35}O$; 315.2682; found 315.2686.



(3R*,6S*,4*E*)-3-butyl-3-methyl-6-(*p*-tolyl)dec-4-enal (4c). From **3e** and *p*-tolylboronic acid. Yield = 36 mg (46%). Colorless liquid. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.76 – 9.53 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 5.55 – 5.36 (m, 2H), 3.19 (dd, *J* = 12.9, 5.9 Hz, 1H), 2.32 (s, 3H), 2.29 (qd, *J* = 14.8, 3.2 Hz, 2H), 1.65 (ddd, *J* = 13.6, 7.0, 2.2 Hz, 2H), 1.46 – 1.13 (m, 10H), 1.10 (s, 3H), 0.92 – 0.84 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.0, 142.2, 136.5, 135.5, 132.9, 129.1, 127.32, 54.0, 48.5, 41.8, 38.2, 35.8, 29.9, 26.2, 24.0, 23.3, 22.7, 21.0, 14.1, 14.1. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{22}H_{35}O$; 315.2682; found 315.2688.

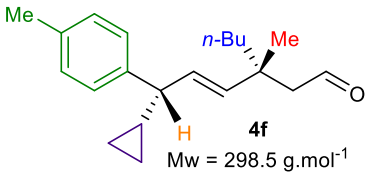


(3R*,6R*,4*E*)-3-butyl-6-(3,4-dimethoxyphenyl)-3-methylhept-4-enal (4d). From **3c** and 3,4-dimethoxybenzeneboronic acid. Yield = 56 mg (70%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, *J* = 3.1 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.77 – 6.66 (m, 2H), 5.54 (dd, *J* = 15.8, 6.1 Hz, 1H), 5.47 (d, *J* = 16.1 Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 3.42 (dt, *J* = 13.4, 6.8 Hz, 1H), 2.33 (ddd, *J* = 35.6, 14.7, 3.1 Hz, 2H), 1.33 (d, *J* = 7.0 Hz, 3H), 1.46 – 1.15 (m, 6H), 1.13 (s, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.7, 148.8, 147.3, 138.6, 135.7, 133.7, 118.8, 111.2, 110.6, 55.9, 55.8, 53.8, 41.8, 38.1, 26.1, 24.1, 23.2, 21.5, 14.1. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{20}H_{31}O_3$; 319.2273; found 319.2267.

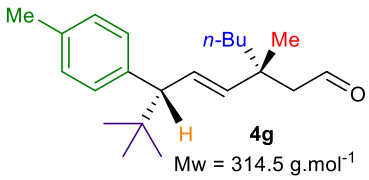


(3R*,6S*,4*E*)-3-butyl-3,7-dimethyl-6-(*p*-tolyl)oct-4-enal (4e). From **3f** and *p*-tolylboronic acid. Yield = 45 mg (60%). Colorless liquid. *E/Z* > 99:1. dr = 89:11. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.60 (dd, *J* = 3.6, 2.8 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 5.56 (dd, *J* = 15.6, 8.7 Hz, 1H), 5.47 (d, *J* = 15.7 Hz, 1H), 2.86 (t, *J* = 8.6 Hz, 1H), 2.36 – 2.29 (dd, *J* = 14.8, 2.7 Hz, 1H), 2.31 (s, 3H), 2.23 (dd, *J* = 14.8, 3.7 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.41 – 1.32 (m, 2H), 1.32 – 1.14 (m, 4H), 1.10 (s, 3H), 0.91 (d, *J* =

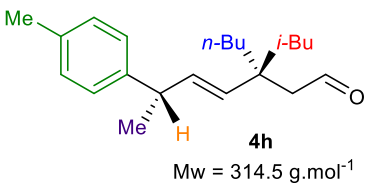
6.7 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.1, 141.6, 137.5, 135.3, 131.4, 129.0, 127.6, 56.8, 53.9, 41.8, 38.3, 33.0, 26.2, 24.2, 23.3, 21.2, 21.0, 20.7, 14.1. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{21}H_{33}O$; 301.2526; found 301.2572.



(3R*)-3-((3S*,1*E*)-3-cyclopropyl-3-(*p*-tolyl)prop-1-en-1-yl)-3-methylheptanal (4f). From **3g** and *p*-tolylboronic acid. Yield = 39 mg (52%). Colorless liquid. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.71 (t, *J* = 3.2 Hz, 1H), 7.19 – 7.10 (m, 4H), 5.56 (d, *J* = 2.8 Hz, 2H), 2.57 (dt, *J* = 8.8, 2.9 Hz, 1H), 2.34 (s, 3H), 2.45 – 2.23 (m, 2H), 1.46 – 1.35 (m, 2H), 1.34 – 1.19 (m, 4H), 1.13 (s, 3H), 1.03 (ddd, *J* = 11.9, 8.1, 3.2 Hz, 1H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.64 – 0.48 (m, 2H), 0.29 – 0.15 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.0, 141.5, 136.9, 135.7, 131.6, 129.1, 127.6, 54.0, 52.5, 41.8, 38.3, 26.2, 24.1, 23.3, 21.1, 16.3, 14.1, 4.4. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{21}H_{31}O$; 299.2369; found 299.2379.

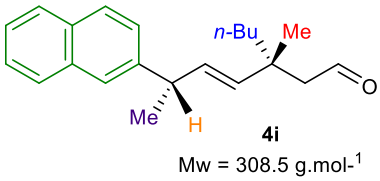


(3R*,6R*,4*E*)-3-butyl-3,7,7-trimethyl-6-(*p*-tolyl)oct-4-enal (4g). From **3h** and *p*-tolylboronic acid. Yield = 45 mg (50%). Colorless oil. *E/Z* > 99:1. dr = 91:9. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.52 (dd, *J* = 3.5, 2.8 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 5.77 (dd, *J* = 15.6, 9.8 Hz, 1H), 5.41 (d, *J* = 15.6 Hz, 1H), 2.91 (d, *J* = 9.7 Hz, 1H), 2.26 (dd, *J* = 10.7, 4.3 Hz, 1H), 2.24 (s, 3H), 2.16 (dd, *J* = 14.8, 3.7 Hz, 1H), 1.38 – 1.08 (m, 6H), 1.05 (s, 3H), 0.86 – 0.75 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.1, 140.1, 138.6, 135.3, 129.3, 129.0, 128.4, 59.8, 53.9, 41.7, 38.4, 34.1, 31.6, 28.1, 26.2, 24.3, 23.3, 22.7, 21.0, 14.2, 14.1. **HRMS** (APCI-MS ES+) $[M+Na]^+$, calculated for $C_{22}H_{34}ONa$; 337.2507; found 337.2501.



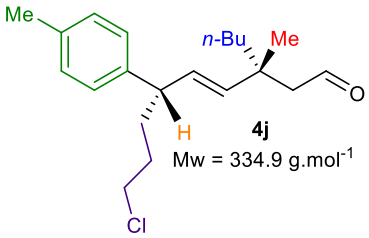
(3S*,6S*,4*E*)-3-butyl-3-isobutyl-6-(*p*-tolyl)hept-4-enal (4h). From **3b** and *p*-tolylboronic acid. Yield = 54 mg (69%). Colorless liquid. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 (t, *J* = 3.1 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.08

(d, *J* = 8.2 Hz, 2H), 5.50 (dd, *J* = 16.0, 6.3 Hz, 1H), 5.43 (d, *J* = 16.3 Hz, 1H), 3.46 (p, *J* = 6.8 Hz, 1H), 2.39 (d, *J* = 3.1 Hz, 3H), 2.33 (s, 3H), 1.75 – 1.58 (m, 2H), 1.53 – 1.41 (m, 2H), 1.40 – 1.32 (m, 5H), 1.31 – 1.14 (m, 3H), 0.89 (dt, *J* = 7.0, 4.0 Hz, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.0, 142.9, 136.3, 135.6, 133.5, 129.1, 127.0, 50.1, 47.8, 42.1, 41.4, 37.8, 25.8, 25.1, 25.1, 24.0, 23.3, 21.4, 21.0, 14.1 (CH_3). **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{22}H_{35}O$; 315.2681; found 315.2681.



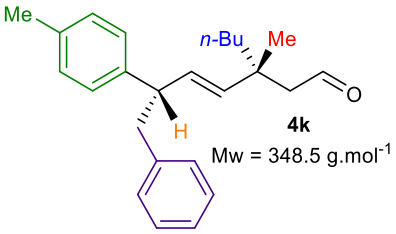
4i
Mw = 308.5 g.mol^{-1}

(3R*,6S*,4*E*)-3-butyl-3-methyl-6-(2-naphthalenyl)hept-4-enal (4i). From **3a** and 2-napthylboronic acid. Yield = 48 mg (61%). Colorless liquid. *E*/*Z* > 99:1. dr = 91:9. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.71 (t, *J* = 3.1 Hz, 1H), 7.83 – 7.76 (m, 3H), 7.63 (s, 1H), 7.52 – 7.39 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 1H), 5.64 (dd, *J* = 15.8, 6.4 Hz, 1H), 5.54 (d, *J* = 15.9 Hz, 1H), 3.64 (p, *J* = 6.9 Hz, 1H), 2.38 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.29 (dd, *J* = 14.7, 3.5 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 3H), 1.50 – 1.35 (m, 2H), 1.34 – 1.18 (m, 4H), 1.14 (s, 3H), 0.90 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.8, 143.4, 136.3, 133.7, 133.5, 132.2, 128.0, 127.7, 127.6, 126.3, 126.0, 125.4, 125.1, 53.8, 42.4, 41.8, 38.2, 26.2, 24.2, 23.3, 21.4, 14.1. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{22}H_{29}O$; 309.2213; found 309.2273.

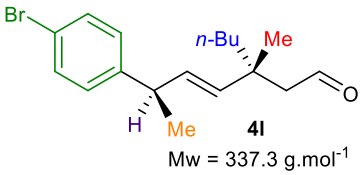


4j
Mw = 334.9 g.mol^{-1}

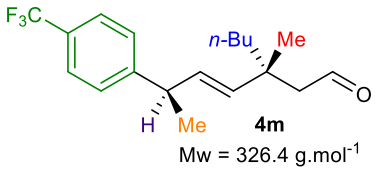
(3R*,6S*,4*E*)-3-butyl-9-chloro-3-methyl-6-(*p*-tolyl)non-4-enal (4j). From **3i** and *p*-tolylboronic acid. Yield = 46 mg (55%). Colorless oil. *E*/*Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.65 (dd, *J* = 3.3, 2.9 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 5.55 – 5.45 (m, 2H), 3.52 (dt, *J* = 6.4, 3.1 Hz, 2H), 3.22 (dd, *J* = 7.1, 3.5 Hz, 1H), 2.35 (dd, *J* = 15.0, 2.9 Hz, 1H), 2.32 (s, 3H), 2.26 (dd, *J* = 14.8, 3.5 Hz, 1H), 1.89 – 1.57 (m, 4H), 1.36 (s, 3H), 1.46 – 1.13 (m, 6H), 1.11 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.7, 141.2, 137.1, 135.9, 132.3, 129.3, 127.3, 53.8, 47.9, 45.1, 41.7, 38.3, 33.2, 30.8, 26.2, 24.0, 23.3, 21.0, 14.1. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{21}H_{34}OCl$; 337.2298; found 337.2264.



(3R*,6S*,4*E*)-3-butyl-3-methyl-7-phenyl-6-(*p*-tolyl)hept-4-enal (4k). From **3j** and *p*-tolylboronic acid. Yield = 52 mg (60%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.49 (dd, *J* = 3.5, 2.9 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.14 – 7.07 (m, 6H), 5.52 (dd, *J* = 15.7, 8.1 Hz, 1H), 5.32 (dd, *J* = 15.7, 0.7 Hz, 1H), 3.56 (td, *J* = 8.7, 6.2 Hz, 1H), 3.07 (dd, *J* = 13.5, 5.9 Hz, 1H), 2.92 (dd, *J* = 13.5, 9.4 Hz, 1H), 2.34 (s, 3H), 2.27 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.17 (dd, *J* = 14.7, 3.6 Hz, 1H), 1.25 (ddd, *J* = 6.7, 5.5, 2.6 Hz, 2H), 1.22 – 1.17 (m, 2H), 1.03 (s, 3H), 1.11 – 0.92 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.9, 140.3, 139.2, 136.6, 134.7, 130.3, 128.2, 128.1, 127.1, 126.2, 124.9, 52.7, 49.3, 41.8, 40.6, 37.0, 24.8, 23.0, 22.1, 20.0, 13.0. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{25}H_{33}O$; 349.2526; found 349.2575.

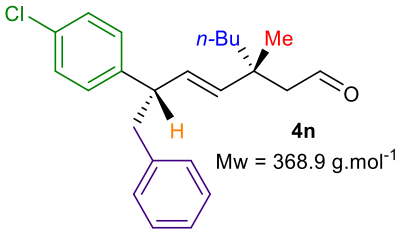


(3R*,6R*,4*E*)-6-(4-bromophenyl)-3-butyl-3-methylhept-4-enal (4l). From **3c** and 4-bromobenzeneboronic acid. Yield = 41 mg (49%). Orange oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.71 (t, *J* = 3.1 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 5.58 – 5.41 (m, 2H), 3.47 – 3.38 (m, 1H), 2.32 (qd, *J* = 14.7, 3.1 Hz, 2H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.41 – 1.15 (m, 6H), 1.12 (s, 3H), 0.88 (t, *J* = 3.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.6, 145.0, 136.5, 133.0, 131.5, 128.9, 119.8, 53.7, 41.8, 41.8, 38.2, 26.1, 24.1, 23.2, 21.4, 14.1. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{18}H_{26}BrO$; 337.1162; found 337.1192.

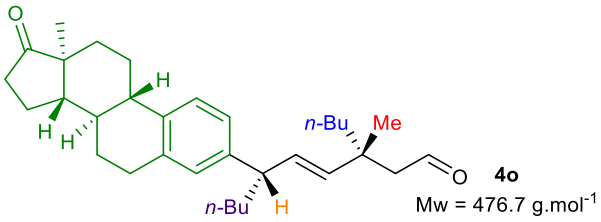


(3R*,6R*,4*E*)-3-butyl-3-methyl-6-(4-(trifluoromethyl)phenyl)hept-4-enal (4m). From **3c** and 4-trifluoromethylbenzeneboronic acid. Yield = 31 mg (38%). Colorless liquid. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (t, *J* = 3.1 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.62 – 5.45 (m, 2H), 3.60 – 3.46 (m, 1H), 2.34 (qd, *J* = 14.7, 3.1 Hz, 2H), 1.38 (dd, *J* = 14.6, 7.5 Hz, 3H), 1.36 (d, *J* = 7.0 Hz, 4H), 1.32 – 1.14 (m, 4H), 1.13 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.5, 150.1, 136.9, 132.6, 128.6, 128.3, 127.5, 125.7, 125.4 (q, *J* = 3.8

Hz, CF_3), 123.0, 53.7, 42.0, 41.7, 38.2, 26.1, 24.1, 23.2, 21.4, 14.1. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{19}H_{26}F_3O$; 327.1930; found 327.1969.

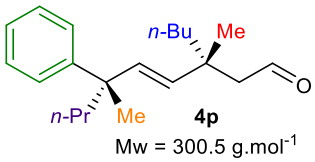


(3R*,6S*,4*E*)-3-butyl-6-(4-chlorophenyl)-3-methyl-7-phenylhept-4-enal (4n). From **3j** and 4-chlorobenzeneboronic acid. Yield = 37 mg (40%). Colorless liquid. *E/Z* > 99:1. dr > 95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (t, *J* = 3.1 Hz, 1H), 7.41 – 6.82 (m, 9H), 5.41 (dd, *J* = 15.7, 7.8 Hz, 1H), 5.26 (dd, *J* = 15.7, 0.7 Hz, 1H), 3.48 (dd, *J* = 15.2, 7.9 Hz, 1H), 2.93 (dd, *J* = 13.5, 6.6 Hz, 1H), 2.84 (dd, *J* = 13.4, 8.7 Hz, 1H), 2.19 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.11 (dd, *J* = 14.7, 3.5 Hz, 1H), 1.24 – 1.05 (m, 6H), 0.96 (s, 3H), 0.77 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.6, 142.8, 139.7, 138.2, 132.0, 130.8, 129.2, 128.9, 128.6, 128.2, 126.1, 53.7, 50.2, 42.7, 41.6, 38.2, 25.9, 24.0, 23.2, 14.1. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{24}H_{30}ClO$; 369.1980; found 369.2014.



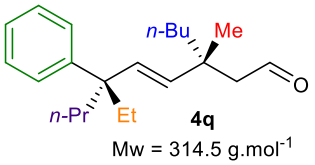
(3R*,6S*,4*E*)-3-butyl-3-methyl-6-(17-oxo-estra-1,3,5(10)-trienyl)dec-4-enal (4o). From **3e** and the boronic acid derived from estrone prepared according to a reported protocol.[12] Yield = 61 mg (51%). Colorless oil. *E/Z* > 99:1. dr = 2:1:0:0. Mixture of diastereoisomers: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.7 (t, *J* = 3.1 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.88 (s, 1H), 5.67 – 5.56 (m, 1H), 5.50 (d, *J* = 14.7 Hz, 1H), 5.45 (d, *J* = 15.9 Hz, 1H), 5.22 (dd, *J* = 15.2, 9.3 Hz, 1H), 3.78 – 3.63 (m, 1H), 3.16 (dd, *J* = 13.7, 6.8 Hz, 1H), 2.97 – 2.79 (m, 2H), 2.50 (dd, *J* = 18.7, 8.7 Hz, 1H), 2.30 (ddd, *J* = 18.3, 14.7, 3.1 Hz, 4H), 2.20 – 1.91 (m, 6H), 0.93 – 0.83 (m, 14H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.0, 142.8, 142.8, 137.4, 137.4, 136.6, 136.4, 133.0, 132.7, 128.0, 128.0, 125.4, 125.3, 125.1, 124.8, 124.8, 60.4, 54.0, 50.6, 48.4, 48.1, 44.4, 42.5, 41.8, 38.3, 38.2, 35.9, 35.8, 35.7, 32.7, 31.9, 31.7, 30.9, 30.0, 29.6, 29.5, 28.7 , 26.6, 26.2, 25.7 , 25.3, 24.0, 23.3, 22.9, 22.6, 22.2, 21.6, 14.2, 14.1, 14.1, 14.0, 13.9, 12.9. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{33}H_{49}O_2$; 477.3733; found 477.3750.

[12] Baek, Y.; Kim, S.; Jeon, B.; Lee, P. H. *Org. Lett.* **2016**, *18*, 104.



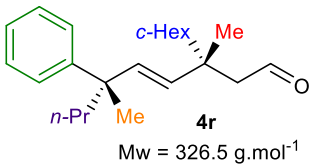
4p
Mw = 300.5 g.mol^{-1}

(3R*,6S*,4*E*)-3-butyl-3,6-dimethyl-6-phenylnon-4-enal (4p). From **3p** and phenylboronic acid. Yield = 54 mg (73%). Colorless oil. *E*/*Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, *J* = 3.1 Hz, 1H), 7.36 – 7.10 (m, 6H), 5.59 (d, *J* = 16.2 Hz, 1H), 5.43 (d, *J* = 16.2 Hz, 1H), 2.39 (dd, *J* = 14.7, 2.7 Hz, 1H), 2.30 (dd, *J* = 14.7, 3.5 Hz, 1H), 1.78 – 1.61 (m, 2H), 1.45 – 1.37 (m, 2H), 1.35 (s, 3H), 1.32 – 1.17 (m, 6H), 1.14 (s, 3H), 0.94 – 0.82 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.9, 148.3, 137.7, 134.2, 128.2, 126.7, 125.8, 54.1, 44.2, 43.7, 42.1, 38.3, 26.3, 26.0, 24.3, 23.4, 18.0, 14.9, 14.2. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{21}H_{32}ONa$; 323.2351; found 323.2350.



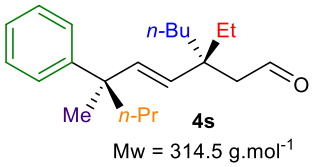
4q
Mw = 314.5 g.mol^{-1}

(3R*,6S*,4*E*)-3-butyl-6-ethyl-3-methyl-6-phenylnon-4-enal (4q). From **3o** and phenylboronic acid. Yield = 61 mg (78%). Colorless oil. *E*/*Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, *J* = 3.1 Hz, 1H), 7.31 – 7.08 (m, 5H), 5.45 (d, *J* = 1.5 Hz, 2H), 2.39 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.29 (dd, *J* = 14.7, 3.5 Hz, 1H), 1.85 – 1.59 (m, 4H), 1.44 – 1.34 (m, 2H), 1.32 – 1.16 (m, 4H), 1.16 – 0.92 (m, 5H), 0.85 (dt, *J* = 14.5, 7.0 Hz, 6H), 0.66 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.9, 146.8, 136.3, 135.1, 128.0, 127.5, 125.7, 54.2, 47.2, 42.2, 40.1, 38.6, 30.4, 26.4, 24.3, 23.4, 17.4, 15.0, 14.2, 8.7. **HRMS** (APCI-MS ES$^+$) $[M+H]^+$, calculated for $C_{22}H_{35}O$; 315.2682; found 315.2652.

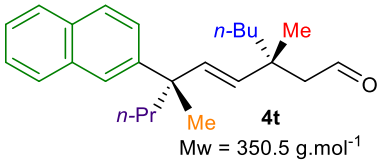


4r
Mw = 326.5 g.mol^{-1}

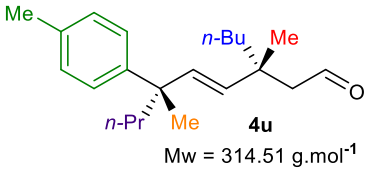
(3S*,6S*,4*E*)-3-cyclohexyl-3,6-dimethyl-6-phenylnon-4-enal (4r). From **3q** and phenylboronic acid. Yield = 60 mg (75%). Colorless oil. *E*/*Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.81 – 9.59 (m, 1H), 7.35 – 7.11 (m, 5H), 5.59 (d, *J* = 16.3 Hz, 1H), 5.44 (d, *J* = 16.3 Hz, 1H), 2.41 (dd, *J* = 14.6, 2.5 Hz, 1H), 2.33 (dd, *J* = 14.6, 3.6 Hz, 1H), 1.87 – 1.61 (m, 7H), 1.35 (s, 3H), 1.28 – 1.03 (m, 9H), 1.00 – 0.91 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.4, 148.2, 138.3, 133.3, 128.1, 126.6, 125.7, 52.1, 48.0, 44.2, 43.8, 40.9, 27.5, 27.3, 26.9, 26.6, 25.9, 20.8, 17.9, 14.8. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{23}H_{34}ONa$; 349.2507; found 349.2498.



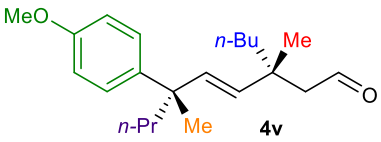
(3R*,6R*,4*E*)-3-butyl-3-ethyl-6-methyl-6-phenylnon-4-enal (4s). From **3r** and phenylboronic acid. Yield = 63 mg (81%). Colorless oil. *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 – 9.72 (m, 1H), 7.37 – 7.08 (m, 5H), 5.57 (d, *J* = 16.4 Hz, 1H), 5.33 (d, *J* = 16.4 Hz, 1H), 2.36 (s, 2H), 1.70 (ddd, *J* = 21.9, 13.5, 7.5 Hz, 2H), 1.59 – 1.05 (m, 13H), 1.00 – 0.77 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.9, 148.3, 138.3, 133.8, 128.2, 126.7, 125.8, 50.0, 44.3, 43.9, 41.3, 37.4, 30.6, 26.1, 25.8, 23.4, 18.0, 14.9, 14.2, 8.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ.-118.09. **HRMS** (APCI-MS ES$^+$) $[M+H]^+$, calculated for $C_{22}H_{35}O$; 315.2682; found 315.2704.



(3R*,6S*,4*E*)-3-butyl-3,6-dimethyl-6-(2-naphthalenyl)non-4-enal (4t). From **3p** and 2-naphtylboronic acid. Yield = 56 mg (64%). White oily wax. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.76 (t, J = 3.2 Hz, 1H), 7.86 – 7.75 (m, 3H), 7.70 (d, J = 1.6 Hz, 1H), 7.53 – 7.38 (m, 3H), 5.67 (d, J = 16.2 Hz, 1H), 5.47 (d, J = 16.2 Hz, 1H), 2.42 (dd, J = 14.7, 2.8 Hz, 1H), 2.32 (dd, J = 14.7, 3.5 Hz, 1H), 1.92 – 1.74 (m, 2H), 1.48 – 1.08 (m, 14H), 0.95 – 0.88 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.79, 145.54, 137.74, 134.50, 133.34, 131.82, 127.98, 127.56, 127.41, 125.90, 125.88, 125.46, 124.65, 54.06, 43.95, 43.86, 42.00, 38.31, 26.28, 25.77, 24.19, 23.31, 17.94, 14.87, 14.16. **HRMS** (APCI-MS ES$^+$) $[M+H]^+$, calculated for $C_{25}H_{34}O$; 351.2688; found 351.2676.



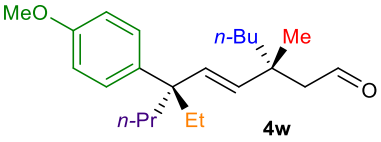
(3R*,6S*,4*E*)-3-butyl-3,6-dimethyl-6-(p-tolyl)non-4-enal (4u). From **3p** and p-tolylboronic acid. Yield = 36 mg (47%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (t, *J* = 3.2 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 5.57 (d, *J* = 16.2 Hz, 1H), 5.41 (d, *J* = 16.2 Hz, 1H), 2.41 – 2.36 (m, 1H), 2.33 – 2.24 (m, 4H), 1.76 – 1.57 (m, 2H), 1.44 – 1.35 (m, 2H), 1.34 – 1.05 (m, 12H), 0.93 – 0.82 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.96, 145.34, 137.87, 135.21, 133.97, 128.87, 126.59, 54.14, 44.23, 43.38, 42.06, 38.31, 26.33, 26.01, 24.31, 23.37, 20.99, 18.01, 14.93, 14.20. **HRMS** (APCI-MS ES$^+$) $[M+H]^+$, calculated for $C_{22}H_{35}O$; 315.2682; found 315.2688.



4v

Mw = 330.5 g.mol^{-1}

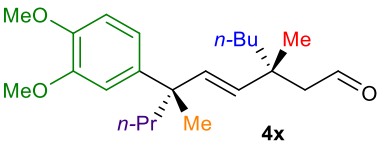
(3R*,6S*,4*E*)-3-butyl-6-(4-methoxyphenyl)-3,6-dimethylnon-4-enal (4v). From **3p** and 4-methoxybenzeneboronic acid. Yield = 62 mg (75%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (t, *J* = 3.2 Hz, 1H), 7.17 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 5.56 (d, *J* = 16.2 Hz, 1H), 5.40 (d, *J* = 16.2 Hz, 1H), 3.79 (s, 3H), 2.39 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.29 (dd, *J* = 14.7, 3.5 Hz, 1H), 1.74 – 1.62 (m, 2H), 1.45 – 1.04 (m, 14H), 0.92 – 0.83 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.9, 157.6, 140.4, 138.0, 133.9, 127.7, 113.5, 55.3, 54.1, 44.3, 43.1, 42.1, 38.3, 26.3, 26.1, 24.3, 23.4, 18.0, 14.9, 14.2. **HRMS** (APCI-MS ES^{+}) $[M+H]^{+}$, calculated for $C_{22}H_{35}O_2$; 331.2632; found 331.2682.



4w

Mw = 344.5 g.mol^{-1}

(3R*,6S*,4*E*)-3-butyl-6-ethyl-6-(4-methoxyphenyl)-3-methylnon-4-enal (4w). From **3o** and 4-methoxybenzeneboronic acid. Yield = 66 mg (78%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.76 (t, *J* = 3.1 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.45 (s, 2H), 3.79 (s, 4H), 2.42 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.32 (dd, *J* = 14.7, 3.4 Hz, 1H), 1.83 – 1.62 (m, 4H), 1.46 – 1.39 (m, 3H), 1.35 – 1.21 (m, 5H), 1.15 (s, 3H), 0.92 – 0.84 (m, 6H), 0.69 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.9, 157.5, 138.8, 136.6, 134.9, 128.5, 113.3, 55.3, 54.2, 46.5, 42.2, 40.2, 38.5, 30.5, 26.4, 24.3, 23.4, 17.4, 14.9, 14.2, 8.7. **HRMS** (APCI-MS ES^{+}) $[M+H]^{+}$, calculated for $C_{23}H_{37}O_2$; 345.2788; found 345.2757.

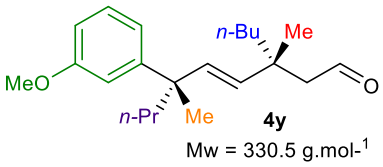


4x

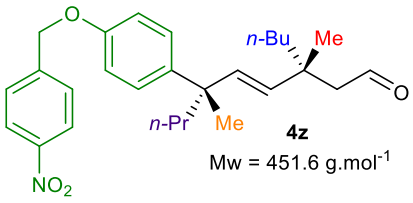
Mw = 360.5 g.mol^{-1}

(3R*,6S*,4*E*)-3-butyl-6-(3,4-dimethoxyphenyl)-3,6-dimethylnon-4-enal (4x). From **3p** and 3,4-dimethoxybenzeneboronic acid. Yield = 77 mg (87%). Pale yellow oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 (t, *J* = 3.1 Hz, 1H), 6.80 (s, 2H), 6.77 (s, 1H), 5.56 (d, *J* = 16.2 Hz, 1H), 5.41 (d, *J* = 16.2 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 2.40 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.31 (dd, *J* = 14.7, 3.4 Hz, 1H), 1.76 – 1.57 (m, 3H), 1.41 (dd, *J* = 9.3, 6.2 Hz, 3H), 1.35 – 1.18 (m, 12H), 1.15 (s, 3H), 0.92 – 0.84 (m,

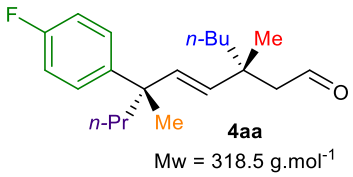
6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.7, 148.6, 147.1, 141.0, 137.9, 134.0, 118.5, 110.7, 110.7, 56.0, 55.9, 54.15, 44.2, 43.5, 42.1, 38.4, 26.4, 26.1, 24.3, 23.4, 18.0, 14.9, 14.2. **HRMS** (APCI-MS ES$^+$) $[M+H]^+$, calculated for $C_{23}H_{37}O_3$; 361.2737; found 361.2760.



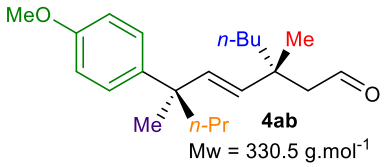
(3R*,6S*,4*E*)-3-butyl-6-(3-methoxyphenyl)-3,6-dimethylnon-4-enal (4y). From **3p** and 3-methoxybenzeneboronic acid. Yield = 43 mg (52%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, J = 3.2 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 6.86 (ddd, J = 7.8, 1.6, 0.8 Hz, 1H), 6.83 – 6.81 (m, 1H), 6.72 (ddd, J = 8.1, 2.5, 0.7 Hz, 1H), 5.58 (d, J = 16.2 Hz, 1H), 5.43 (d, J = 16.2 Hz, 1H), 3.79 (s, 3H), 2.39 (dd, J = 14.7, 2.8 Hz, 1H), 2.30 (dd, J = 14.7, 3.5 Hz, 1H), 1.69 (m, 2H), 1.44 – 1.05 (m, 14H), 0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.86, 159.50, 150.17, 137.57, 134.18, 129.02, 119.21, 113.21, 110.57, 55.22, 54.12, 44.16, 43.81, 42.06, 38.34, 26.35, 25.94, 24.31, 23.38, 18.00, 14.92, 14.19. **HRMS** (APCI-MS ES$^+$) $[M+H]^+$, calculated for $C_{22}H_{35}O_2$; 331.2637; found 331.2648.



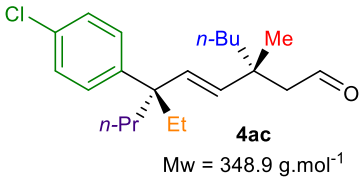
(3R*,6S*,4*E*)-3-butyl-3,6-dimethyl-6-(4-((4-nitrobenzyl)oxy)phenyl)non-4-enal (4z). From **3p** (0.15 mmol) and 1.5 equiv. of arylboronic acid [prepared by treating 4-hydroxyboronic acid (1 equiv., 0.25 mmol) with 4-nitrobenzyl bromide (1 equiv., 0.25 mmol) in the presence of anhydrous K_2CO_3 (2 equiv.) in acetone (5 mL) under vigorous stirring for 48h]. After reaction, the suspension was diluted with water and extracted three times with EtOAc. The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated. The crude solid was used without further purification in the following reaction.] Yield = 26 mg (40%). Yellow oily wax. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ δ 9.72 (t, *J* = 3.1 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 5.55 (d, *J* = 16.2 Hz, 1H), 5.40 (d, *J* = 16.2 Hz, 1H), 5.15 (s, 2H), 2.39 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.30 (dd, *J* = 14.7, 3.5 Hz, 1H), 1.75 – 1.53 (m, 4H), 1.40 (dd, *J* = 10.0, 5.9 Hz, 2H), 1.34 – 1.17 (m, 9H), 1.14 (s, 3H), 0.93 – 0.83 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.9, 156.2, 147.7, 144.9, 141.5, 137.8, 134.1, 127.9, 127.7, 124.0, 114.4, 68.8, 54.1, 44.3, 43.2, 42.1, 38.3, 26.3, 26.1, 24.3, 23.4, 18.0, 14.9, 14.2. **HRMS** (TOF-MS ES$^+$) $[M+H]^+$, calculated for $C_{28}H_{37}NO_4$; 452.2801; found 452.2751.



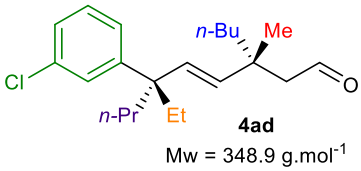
(3R*,6S*,4*E*)-3-butyl-6-(4-fluorophenyl)-3,6-dimethylnon-4-enal (4aa). From **3p** and 4-fluorobenzeneboronic acid. Yield = 59 mg (76%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (t, *J* = 3.1 Hz, 1H), 7.20 (dd, *J* = 8.9, 5.4 Hz, 2H), 6.96 (t, *J* = 8.8 Hz, 2H), 5.55 (d, *J* = 16.2 Hz, 1H), 5.40 (d, *J* = 16.2 Hz, 1H), 2.39 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.30 (dd, *J* = 14.7, 3.4 Hz, 1H), 1.76 – 1.58 (m, 2H), 1.46 – 1.00 (m, 14H), 0.90 – 0.84 (m 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.5, 161.2, 158.7, 142.8, 142.8, 136.4, 133.2, 127.0 (d, *J* = 7.7 Hz), 113.6 (d, *J* = 20.8 Hz), 52.9, 43.2, 42.2, 40.9, 37.2, 25.2, 25.0, 23.1, 22.2, 16.8, 13.7, 13.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.1. **HRMS** (APCI-MS ES$^+$) $[M+H]^+$, calculated for $C_{21}H_{32}OF$; 319.2437; found 319.2475.



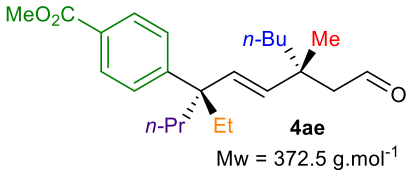
(3R*,6R*,4*E*)-3-butyl-6-(4-methoxyphenyl)-3,6-dimethylnon-4-enal (4ab). From **3p** and 4-methoxybenzeneboronic acid. Yield = 70 mg (85%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, *J* = 3.2 Hz, 1H), 7.18 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 5.57 (d, *J* = 16.2 Hz, 1H), 5.40 (d, *J* = 16.2 Hz, 1H), 3.79 (s, 3H), 2.39 (dd, *J* = 14.7, 2.7 Hz, 1H), 2.30 (dd, *J* = 14.7, 3.5 Hz, 1H), 1.68 (ddt, *J* = 19.9, 13.5, 6.8 Hz, 2H), 1.45 – 1.36 (m, 2H), 1.35 – 1.07 (m, 12H), 0.94 – 0.82 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.9, 157.5, 140.3, 137.9, 133.9, 127.6, 113.3, 65.9, 55.2, 54.0, 44.2, 43.0, 42.0, 38.2, 26.2, 26.1, 24.2, 23.3, 17.9, 15.3, 14.8, 14.1. **HRMS** (APCI-MS ES$^+$) $[M+K]^+$, calculated for $C_{22}H_{35}O_2K$; 370.2273; found 370.2321.



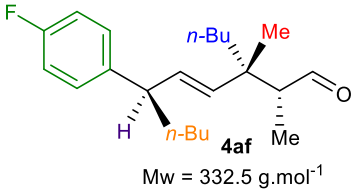
(3R*,6S*,4*E*)-3-butyl-6-(4-chlorophenyl)-6-ethyl-3-methylnon-4-enal (4ac). From **3o** and 4-chlorobenzeneboronic acid. Yield = 38 mg (44%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 (t, *J* = 3.1 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 5.44 (s, 2H), 2.45 – 2.37 (m, 1H), 2.32 (dd, *J* = 14.7, 3.3 Hz, 1H), 1.84 – 1.62 (m, 5H), 1.47 – 1.38 (s, 3H), 1.31 – 1.21 (m, 5H), 1.15 (s, 3H), 0.87 (m, 6H), 0.68 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.6, 145.4, 135.9, 135.6, 131.5, 128.9, 128.1, 54.1, 47.0, 42.1, 40.1, 38.6, 30.4, 26.4, 24.3, 23.4, 17.4, 14.9, 14.2, 8.6. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{22}H_{33}OClNa$; 371.2117; found 371.2098.



(3R*,6S*,4*E*)-3-butyl-6-(3-chlorophenyl)-6-ethyl-3-methylnon-4-enal (4ad). From **3o** and 3-chlorobenzeneboronic acid. Yield = 20 mg (23%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 (t, *J* = 3.1 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 5.44 (s, 2H), 2.45 – 2.37 (m, 1H), 2.32 (dd, *J* = 14.7, 3.3 Hz, 1H), 1.84 – 1.62 (m, 5H), 1.47 – 1.38 (s, 3H), 1.31 – 1.21 (m, 5H), 1.15 (s, 3H), 0.87 (m, 6H), 0.68 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.6, 145.4, 135.9, 135.6, 131.5, 128.9, 128.1, 54.1, 47.0, 42.1, 40.1, 38.6, 30.4, 26.4, 24.3, 23.4, 17.4, 14.9, 14.2, 8.6. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{22}H_{33}OClNa$; 371.2117; found 371.2105.

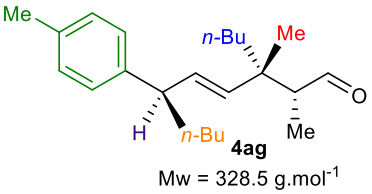


methyl 4-((4S*,7R*,5*E*)-4-ethyl-7-methyl-7-(2-oxoethyl)undec-5-en-4-yl)benzoate (4ae). From **3o** and 4-methylcarboxylatebenzeneboronic acid. Yield = 22 mg (25%). Pale yellow oil. *E/Z* > 99:1. dr > 95:5. $\mathbf{R_f}$ = 0.3 (10:90 Et_2O/Hex, stain: phosphomolybdic acid solution) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.75 (t, *J* = 3.1 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.46 (s, 2H), 3.90 (s, 3H), 2.41 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.33 (dd, *J* = 14.7, 3.3 Hz, 1H), 1.87 – 1.67 (m, 4H), 1.43 (t, *J* = 7.8 Hz, 3H), 1.31 – 1.21 (m, 5H), 1.16 (s, 3H), 0.91 – 0.83 (dt, *J* = 14.5, 7.0 Hz, 6H), 0.68 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.5, 167.3, 152.5, 135.9, 135.6, 129.4, 127.6, 54.1, 52.1, 47.6, 42.1, 40.1, 38.6, 30.4, 26.4, 24.3, 23.4, 17.4, 14.9, 14.2, 8.6. **HRMS** (APCI-MS ES$^+$) $[M+H]^+$, calculated for $C_{24}H_{37}O_3$; 373.2737; found 373.2701.

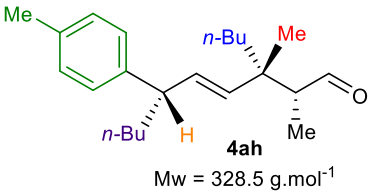


(2R*,3S*,6R*,4*E*)-3-butyl-6-(4-fluorophenyl)-2,3-dimethyldec-4-enal (4af). From **3l** and 4-fluorobenzeneboronic acid. Yield = 45 mg (54%). Colorless oil. *E/Z* > 99:1. dr = 86:14:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 2.5 Hz, 1H), 7.15 – 7.06 (m, 2H), 6.97 (dd, *J* = 12.1, 5.3 Hz, 2H), 5.50 – 5.44 (m, 2H), 3.24 (dd, *J* = 4.4, 2.4 Hz, 1H), 2.31 (dd, *J* = 6.9, 2.4 Hz, 1H), 1.66 (dd, *J* = 15.1, 7.6 Hz, 2H), 1.41 – 1.04 (m, 10H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.98 (s, 3H), 0.91 – 0.78 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.3, 161.3 (d, *J* = 243.6 Hz), 140.9 (d, *J* = 3.1 Hz), 135.9, 133.6, 128.8 (d, *J* = 7.7 Hz),

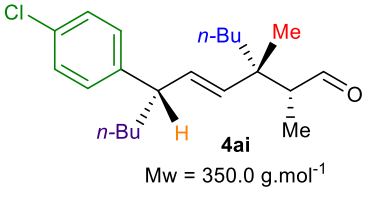
115.1 (d, *J* = 21.0 Hz), 53.8, 48.2, 40.8, 39.7, 35.7, 29.9, 25.9, 23.3, 22.6, 20.1, 14.1, 14.1, 8.7. **HRMS** (APCI-MS ES$^+$) [M+H]$^+$, calculated for $C_{22}H_{34}OF$; 333.2588; found 333.2599.



(2R*,3S*,6R*,4*E*)-3-butyl-2,3-dimethyl-6-(*p*-tolyl)dec-4-enal (4ag). From **3l** and *p*-tolylboronic acid. Yield = 47 mg (57%). Colorless oil. *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (d, *J* = 2.5 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 5.54 (d, *J* = 15.8 Hz, 1H), 5.48 (d, *J* = 15.5 Hz, 2H), 3.24 (dd, *J* = 13.5, 7.1 Hz, 1H), 2.39 – 2.30 (m, 1H), 2.33 (s, 3H), 1.72 – 1.59 (m, 2H), 1.47 – 1.07 (m, 10H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.99 (s, 3H), 0.93 – 0.83 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.5, 142.2, 135.5, 135.4, 134.0, 129.1, 127.4, 53.9, 48.6, 40.8, 39.8, 35.7, 30.0, 25.9, 23.3, 22.9, 22.7, 21.0, 20.1, 14.1, 14.1, 8.7. **HRMS** (APCI-MS ES$^+$) [M+H]$^+$, calculated for $C_{23}H_{37}O$; 329.2844; found 329.2843.

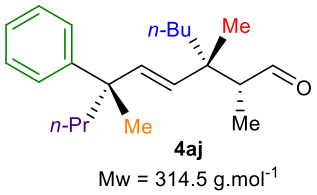


(2R*,3S*,6S*,4*E*)-3-butyl-2,3-dimethyl-6-(*p*-tolyl)dec-4-enal (4ah). From **3k** and *p*-tolylboronic acid. Yield = 53 mg (64%). Colorless oil. *E/Z* > 99:1. dr = 92:8:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.56 (d, *J* = 2.3 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 5.42 (s, 1H), 5.41 (s, 1H), 3.21 – 3.03 (m, 1H), 2.24 (s, 3H), 2.22 (dd, *J* = 7.0, 2.3 Hz, 1H), 1.65-1.55 (m, 2H), 1.42 – 1.00 (m, 10H), 0.92-0.87 (m, 6H), 0.82 (t, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.6, 142.2, 135.5, 135.4, 133.9, 129.1, 127.3, 54.1, 48.6, 40.9, 39.8, 35.7, 30.0, 26.1, 23.4, 22.7, 21.0, 19.9, 14.2, 14.1, 8.6. **HRMS** (APCI-MS ES$^+$) [M+Na]$^+$, calculated for $C_{23}H_{36}ONa$; 351.2664; found 351.2651.

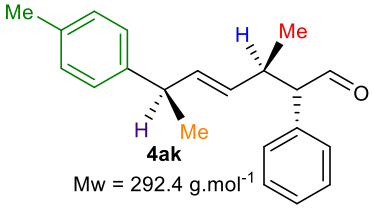


(2R*,3S*,6S*,4*E*)-3-butyl-6-(4-chlorophenyl)-2,3-dimethyldec-4-enal (4ai). From **3k** and 4-chlorobenzeneboronic acid. Yield = 29 mg (33%). Colorless oil. *E/Z* > 99:1. dr = 92:8:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 2.4 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.12 – 7.04 (m, 2H), 5.48 (d, *J* = 15.1 Hz, 1H), 5.43 (d, *J* = 13.1 Hz, 1H), 3.22 (dd, *J* = 13.5, 7.1 Hz, 1H), 2.28 (qd, *J* = 6.9, 2.5 Hz, 1H), 1.65 (dd,

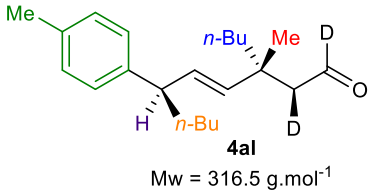
J = 15.1, 7.6 Hz, 2H), 1.48 – 1.07 (m, 10H), 0.97 (s, 3H), 0.95 (d, *J*=7.7 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.2, 143.7, 136.2, 133.3, 131.7, 128.8, 128.6, 54.0, 48.4, 40.9, 39.7, 35.6, 29.9, 26.0, 23.4, 22.6, 19.9, 14.1, 14.1, 8.6. **HRMS** (APCI-MS ES$^+$) $[M+H]^+$, calculated for $C_{22}H_{35}OCl$; 351.2376; found 351.2100.



(2R*,3S*,6S*,4*E*)-3-butyl-2,3,6-trimethyl-6-phenylnon-4-enal (4aj). From **3v** and phenylboronic acid. Yield = 26 mg (36%). Colorless oil. *E/Z* > 99:1. dr = 92:8:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 2.5 Hz, 1H), 7.24 – 7.16 (dd, *J* = 8.2, 6.0 Hz, 5H), 5.54 (d, *J* = 16.3 Hz, 1H), 5.37 (d, *J* = 16.3 Hz, 1H), 2.27 (qd, *J* = 6.9, 2.5 Hz, 1H), 1.73 – 1.56 (m, 2H), 1.49 (s, 1H), 1.39 – 1.32 (m, 3H), 1.29 (s, 3H), 1.25 – 0.98 (m, 8H), 0.96 – 0.93 (m, 6H), 0.85 – 0.78 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.5, 148.3, 138.7, 133.2, 128.2, 126.8, 125.8, 54.4, 44.3, 44.0, 41.0, 40.0, 26.2, 26.0, 23.5, 20.2, 18.0, 14.9, 14.2, 8.9. **HRMS** (APCI-MS ES$^+$) $[M+OH]^+$, calculated for $C_{22}H_{35}O_2$; 331.2637; found 331.2634.

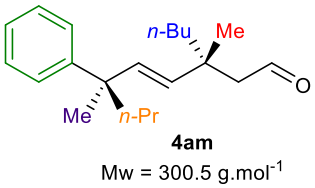


(2S*,3R*,6R*,4*E*)-3-methyl-2-phenyl-6-(*p*-tolyl)hept-4-enal (4ak). From **3m** and *p*-tolylboronic acid. Yield = 42 mg (58%). Colorless oil. *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 (d, *J* = 2.9 Hz, 1H), 7.33 (m, 3H), 7.14 (d, *J* = 6.7 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 5.42 (dd, *J* = 15.4, 6.8 Hz, 1H), 5.12 (dd, *J* = 15.4, 8.1 Hz, 1H), 3.37 (dd, *J* = 8.9, 2.8 Hz, 1H), 3.23 (p, *J* = 6.9 Hz, 1H), 3.08 – 2.94 (m, 1H), 2.31 (s, 3H), 1.18 (d, *J* = 7.0 Hz, 3H), 1.12 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.9, 142.7, 136.2, 135.3, 135.1, 130.8, 129.8, 128.9, 128.8, 127.4, 127.0, 65.4, 41.4, 37.4, 21.1, 21.0, 19.2.



(2S*,3R*,6R*,4*E*)-3-butyl-3-methyl-6-(*p*-tolyl)dec-4-enal-1,2-d$_2$ (4al). From **3n** and *p*-tolylboronic acid. Yield = 45 mg (57%). Colorless oil. *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 5.50 (d, *J* = 15.8 Hz, 1H), 5.45 (d, *J* = 15.7 Hz, 1H), 3.19 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.32 (s, 3H), 2.25 (s, 1H), 1.65 (ddd, *J* = 9.3, 7.3, 2.5 Hz, 2H), 1.40 – 1.12 (m, 10H), 1.10 (s, 3H),

0.86 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.2, 136.5, 135.5, 132.8, 129.1, 127.3, 48.4, 41.8, 38.1, 35.8, 29.9, 26.1, 24.3, 23.3, 22.7, 21.0, 14.1, 14.1. **HRMS** (APCI-MS ES$^+$) $[M+H]^+$, calculated for $C_{22}H_{33}OD_2$; 317.2808; found 317.2812.



4am

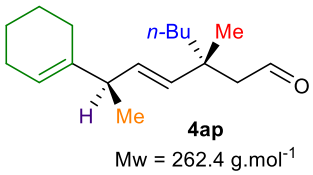
Mw = 300.5 g.mol^{-1}

(3R*,6R*,4*E*)-3-butyl-3,6-dimethyl-6-phenylnon-4-enal (4am). From **3t** and phenylboronic acid. Yield = 60 mg (81%). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, *J* = 3.2 Hz, 1H), 7.18 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 5.57 (d, *J* = 16.2 Hz, 1H), 5.40 (d, *J* = 16.2 Hz, 1H), 3.79 (s, 3H), 2.39 (dd, *J* = 14.7, 2.7 Hz, 1H), 2.30 (dd, *J* = 14.7, 3.5 Hz, 1H), 1.78 – 1.54 (m, 3H), 1.46 – 1.05 (m, 16H), 0.88 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.9, 148.4, 137.7, 134.3, 128.2, 126.7, 125.8, 54.1, 44.3, 43.8, 42.1, 38.3, 26.3, 26.0, 24.3, 23.4, 18.0, 14.9, 14.2. **HRMS** (TOF-MS ES$^+$) $[M+Na]^+$, calculated for $C_{21}H_{32}ONa$; 323.2351; found 323.2372.

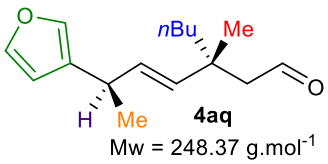
Racemic stereoisomers **4an** (prepared from **3u**) and **4ao** (prepared from **3v**) present similar characterization data than with **4p** and **4am** respectively.

Typical procedure for the Heck vinylation of vinylcyclopropyl carbinol 3c with cyclohexenyl triflate

In a dry one-neck flask under O_2 (balloon, 1 atm), 5-(2-pyridyl)-1,3-oxazole (9 mol%), [$Pd(MeCN)_2(OTs)_2$] (7.5 mol%), $Cu(OTf)_2$ (5 mol%), molecular sieves 3 Å (100% w/w substrate) and vinylcyclopropyl carbinol **3c** (1 equiv., 0.25 mmol) were dissolved into DMA (8 mL/mmol substrate). Cyclohexenyl triflate[13] (3 equiv.) was then rapidly added into the reactional mixture which was set on stirring at 55°C for 18 h. After completion of the reaction, the reactional mixture was diluted with brine and EtOAc. The phases were separated and the aqueous phase was successively washed three times with EtOAc. The combined organic phases were then dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. A column chromatography (gradient eluent 100% hexane / 5% Et_2O/hexane) afforded the desired aldehyde **4ap**.



(3R*,6R*,4*E*)-3-butyl-6-(cyclohex-1-en-1-yl)-3-methylhept-4-enal (4ap). From **3c**. Yield = 35 mg (53%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.71 (t, *J* = 3.2 Hz, 1H), 5.41 (br, 1H), 5.39 (d, *J* = 15.3 Hz, 1H), 5.29 (dd, *J* = 15.8, 7.0 Hz, 1H), 2.66 (p, *J* = 6.9 Hz, 1H), 2.35 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.25 (dd, *J* = 14.7, 3.5 Hz, 1H), 2.11 – 1.96 (m, 2H), 1.96 – 1.73 (m, 2H), 1.66 – 1.45 (m, 4H), 1.41 – 1.31 (m, 2H), 1.23 (m, 4H), 1.10 (s, 3H), 1.07 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.2, 141.1, 135.7, 133.3, 120.2, 53.8, 43.9, 41.9, 38.1, 26.6, 26.1, 25.3, 24.2, 23.3, 23.1, 22.7, 18.7, 14.1. **HRMS** [Found (APCI-MS ES+) : $[C_{18}H_{31}O]^+$ 263.2387, $C_{18}H_{31}O$ calcul 263.2369].



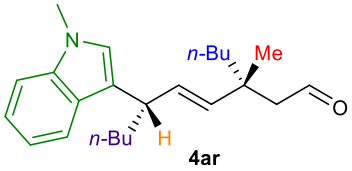
(3R*,6R*,4*E*)-3-butyl-6-(furan-3-yl)-3-methylhept-4-enal (4aq). From **3c**. Yield = 19 mg (30%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (t, J = 3.1 Hz, 1H), 7.35 (t, J = 1.5 Hz, 1H), 7.17 (s, 1H), 6.23 (s, 1H), 5.50 (d, J = 15.8 Hz, 1H), 5.46 (d, J = 6.4 Hz, 1H), 3.39 – 3.23 (m, 1H), 2.37 (dd, J = 14.7, 2.8 Hz, 1H), 2.28 (dd, J = 14.7, 3.4 Hz, 1H), 1.28 (d, J = 7.0 Hz, 3H), 1.46 – 1.16 (m, 6H), 1.13 (s, 3H), 0.89 (t, J = 7.1

[13] Garcia Martinez, Herrera, A.; Martinez, R.; Teso, E.; Garcia, A.; Osio, J.; Pargada, L.; Unanue, R. *J. Heter. Chem.* **1988**, *25*, 1237.

Hz, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 203.8, 143.0, 138.3, 136.3, 133.1, 129.8, 110.2, 53.6, 41.9, 38.2, 33.8, 26.2, 24.3, 23.4, 21.1, 14.2.

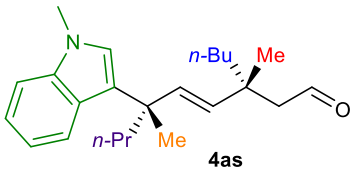
General procedure for the Fujiwara-Moritani insertion of *N*-methylindole on vinylcyclopropyl carbinols

In a dry one-neck flask under O_2 (balloon, 1 atm), 5-(2-pyridyl)-1,3-oxazole (9 mol%), [$Pd(MeCN)_2(OTs)_2$] (7.5 mol%), anhydrous $CuSO_4$ (5 mol%), molecular sieves 3 Å (100% w/w substrate) and vinylcyclopropyl carbinol (1 equiv.) were dissolved into DMA (8 mL/mmol substrate). *N*-methylindole (5 equiv.) was then rapidly added into the reactional mixture which was set on stirring at 55°C for 18 h. After completion of the reaction, the reactional mixture was diluted with brine (50 mL/mmol) and EtOAc (50 mL/mmol). The phases were separated and the aqueous phase was successively washed three times with EtOAc. The combined organic phases were then dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. A column chromatography (gradient eluent 100% hexane / 10% Et_2O/hexane) afforded the desired aldehyde.



4ar
Mw = 353.5 g.mol^{-1}

(3R*,6S*,*4E*)-3-butyl-3-methyl-6-(1-methyl-1H-indol-3-yl)dec-4-enal (4ar). From **3e**. Yield = 49 mg (56%). Colorless oil. *E/Z* > 99:1. dr > 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.65 (t, *J* = 3.1 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.09 – 7.02 (m, 1H), 6.79 (s, 1H), 5.57 (d, *J* = 15.7 Hz, 1H), 5.50 (dd, *J* = 15.7, 7.4 Hz, 1H), 3.73 (s, 3H), 3.53 (dd, *J* = 14.4, 7.4 Hz, 1H), 2.35 (dd, *J* = 14.7, 2.7 Hz, 1H), 2.23 (dd, *J* = 14.7, 3.6 Hz, 1H), 1.94 – 1.80 (m, 1H), 1.77 – 1.63 (m, 1H), 1.42 – 1.16 (m, 10H), 1.10 (s, 3H), 0.88 (dt, *J* = 14.1, 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.2, 137.2, 136.4 (CH), 132.7, 127.3, 125.2, 121.5, 119.6, 118.5, 118.3, 109.2, 53.9, 41.9, 40.3, 38.3, 35.1, 32.7, 30.1, 26.3, 24.2, 23.3, 22.7, 14.2, 14.1. **HRMS** [Found (APCI+): $[C_{24}H_{36}NO]^+$ 354.2802, $C_{24}H_{36}NO$ calcul 354.2797].



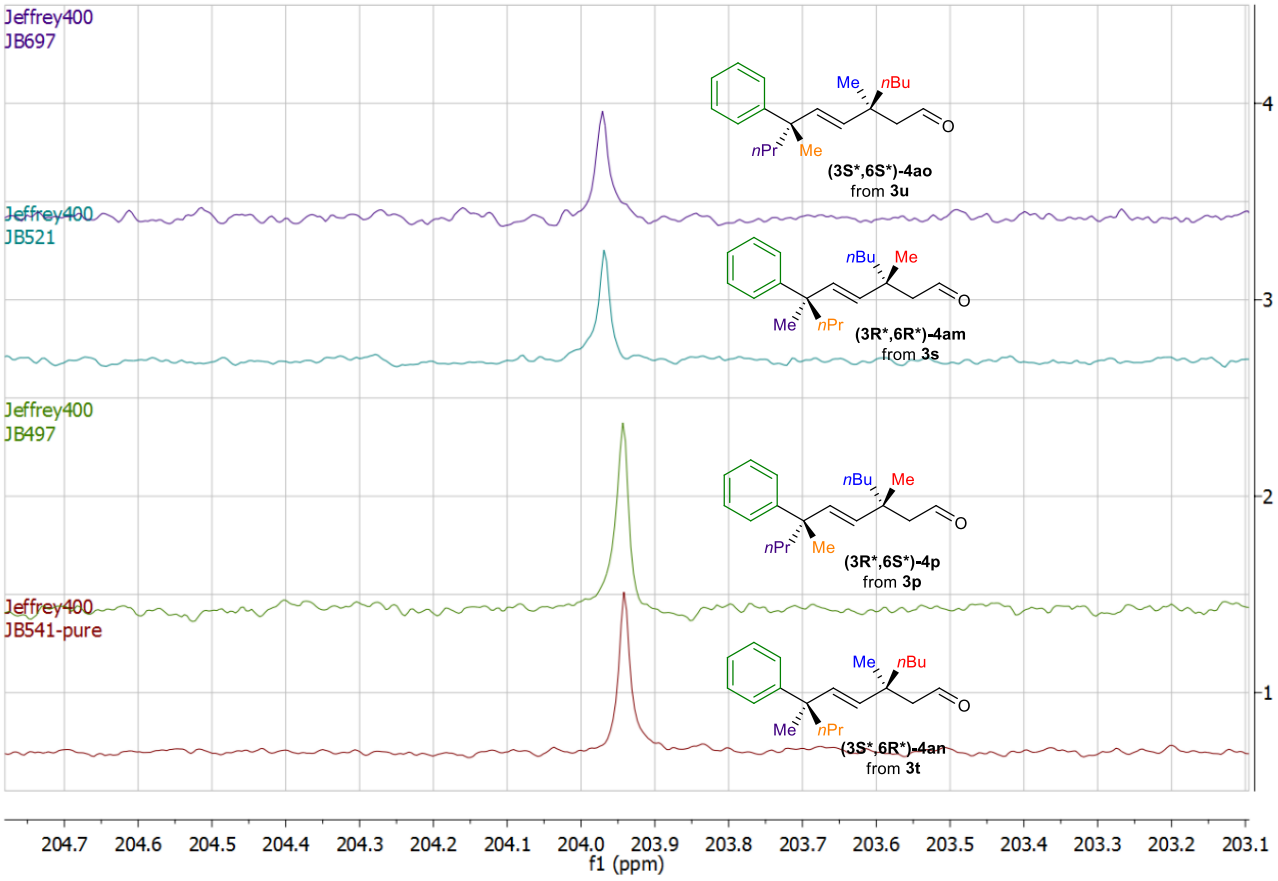
4as
Mw = 353.5 g.mol^{-1}

(3R*,6S*,4*E*)-3-butyl-3,6-dimethyl-6-(1-methyl-1H-indol-3-yl)non-4-enal (4as). From **3p** using 5-(2-pyridyl)-1,3-oxazole (18 mol%), [$Pd(MeCN)_2(OTs)_2$] (15 mol%), anhydrous $CuSO_4$ (10 mol%). Yield = 49 mg (56%). Yellow oil. R_f = 0.5 (40:60 Et_2O/Hex, *p*-anisaldehyde). *E/Z* > 99:1. dr > 95:5:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.69 (t, *J* = 3.2 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.04 – 6.99 (m, 1H), 6.78 (s, 1H), 5.66 (d, *J* = 16.2 Hz, 1H), 5.43 (d, *J* = 16.2 Hz, 1H), 3.75 (s, 4H),

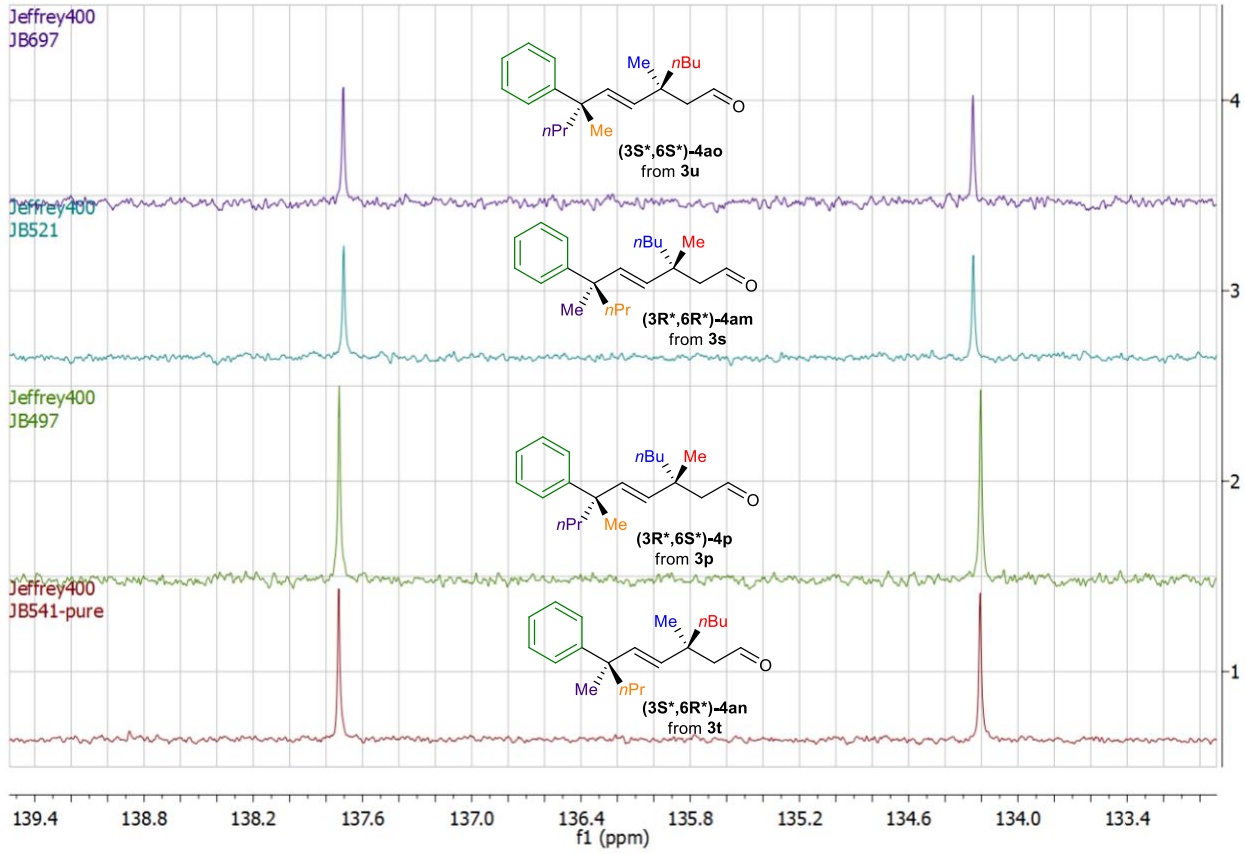
2.35 (dd, *J* = 14.7, 2.8 Hz, 1H), 2.28 – 2.21 (m, 1H), 1.98 – 1.89 (m, 1H), 1.74 (td, *J* = 12.6, 4.5 Hz, 1H), 1.43 (s, 4H), 1.39 – 1.15 (m, 23H), 1.11 (s, 4H), 0.91 – 0.82 (m, *J* = 7.1, 3.9 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.2, 137.7, 137.5, 133.8, 126.4, 125.8, 121.7, 121.5, 121.1, 118.1, 109.2, 53.9, 43.4, 41.9, 40.2, 38.1, 32.7, 29.7, 26.2, 25.9, 24.3, 23.3, 17.8, 14.8, 14.1. **HRMS** (APCI-MS ES+) $[M+H]^+$, calculated for $C_{24}H_{36}NO$; 354.2797; found 354.2779.

Comparison of the ^{13}C NMR spectra of stereoisomers 4p, 4am, 4an and 4ao

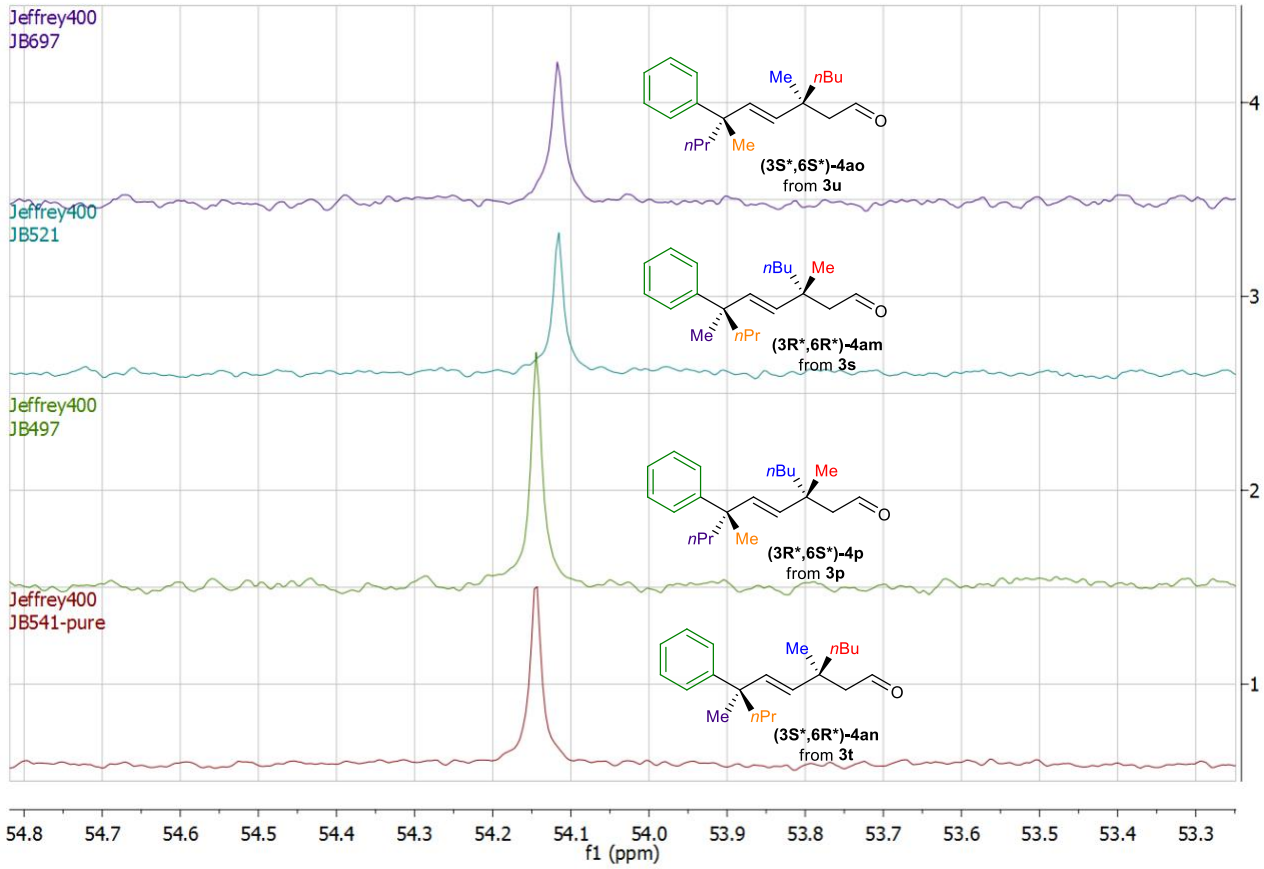
Zoom from 203 – 205 ppm:



Zoom from 133 –140 ppm:

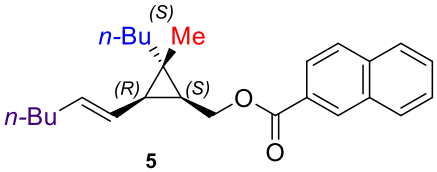


Zoom from 53 – 55 ppm:



Determination of the enantiospecificity

The determination of the enantiospecificity was assessed by comparing the enantiomeric ratio of **3e** and **4c** after the palladium-catalyzed oxidative Heck reaction. As the enantiomers of **1e** could not be directly separated on chiral HPLC columns, it was derivatized to **6**. Enantioenriched **3e** was synthesized following the similar protocol than the racemic mixture using substrate **1a** enantioenriched through a previously described protocol.[14]

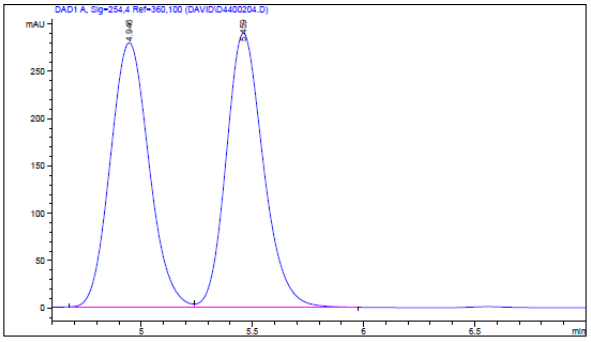


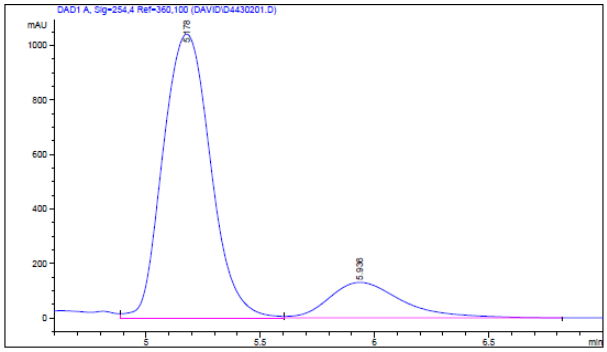
5

M_w = 378.6 g.mol^{-1}

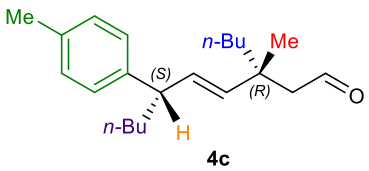
((1S,2S,3R)-2-butyl-3-((*E*)-hex-1-en-1-yl)-2-methylcyclopropyl)methyl 2-naphthoate (5). 2-naphtoyl chloride (65 mg, 0.34 mmol, 1.1 equiv) was added to a mixture of **3h** (70 mg, 0.31 mmol, 1.0 equiv), triethylamine (35 mg, 0.34 mmol, 1.1 equiv) and N,N-dimethyl-4-aminopyridine (2 mg, 0.02 mmol, 5 mol%) in anhydrous tetrahydrofuran (0.1M). The mixture was stirred overnight and quenched by the addition of a saturated aqueous ammonium chloride solution. The aqueous phase was extracted with diethyl ether. The combined organics were dried over anhydrous sodium sulfate, filtered and concentrated to a yellow liquid which was purified by silica chromatography using 5% diethyl ether in hexane. The desired product was obtained as a colorless liquid (91 mg, 77% yield). *E/Z* > 99:1. dr > 98:2:0:0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.07 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.57 (ddd, *J* = 14.9, 13.5, 6.7 Hz, 2H), 5.63 (dt, *J* = 14.8, 6.9 Hz, 1H), 5.28 (dd, *J* = 15.2, 9.1 Hz, 1H), 4.51 (dd, *J* = 11.8, 7.3 Hz, 1H), 4.40 (dd, *J* = 11.8, 9.0 Hz, 1H), 2.02 (dd, *J* = 13.3, 6.7 Hz, 2H), 1.49 (t, *J* = 9.0 Hz, 1H), 1.46 – 1.16 (m, 11H), 1.11 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 135.5, 133.3, 132.6, 131.0, 129.4, 128.2, 128.1, 127.9, 127.8, 126.6, 125.4, 125.0, 63.6, 42.3, 32.7, 31.9, 30.1, 28.7, 26.6, 25.2, 22.8, 22.2, 14.3, 14.0, 13.0. **HRMS** (APCI-ES$^+$) $[M+H]^+$, calculated for $C_{26}H_{35}O_2$; 379.2632; found 379.2620. **HPLC** analyses (CHIRALPAK®AY-H (0.46 cm Ø×25 cm, elution with hexane/isopropanol (99:1), 1 mL/minute) er = 85:15.

[14] Lou, Y.; Horikawa, M.; Kloster, A.; Hawryluk, N. A.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 8916.

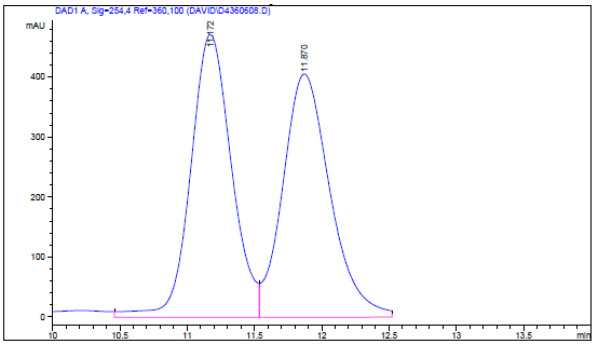


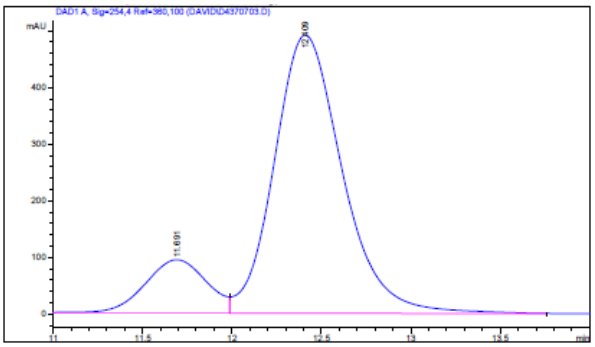


Enantioenriched compound (3*R*,6*S*)-**4c** was synthesized from enantioenriched **3e** and *p*-tolylboronic acid using the general procedure (see p. 15). **HPLC** analyses (CHIRALPAK® AZ-H (0.46 cm Ø×25 cm) with elution of hexane/isopropanol (99:1), flow: 1 mL/minute) er = 85:15.



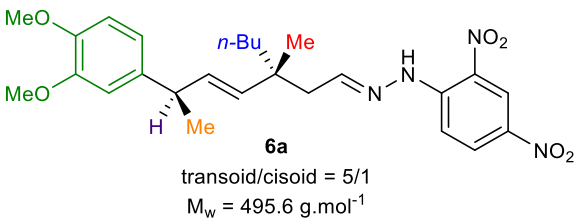
4c





Determination of the relative configuration

The relative configurations of aldehydes **4d** and **4ah** were respectively determined by the X-Ray analysis of their hydrazine derivative **6a** and **6b**, prepared according to the following procedures.

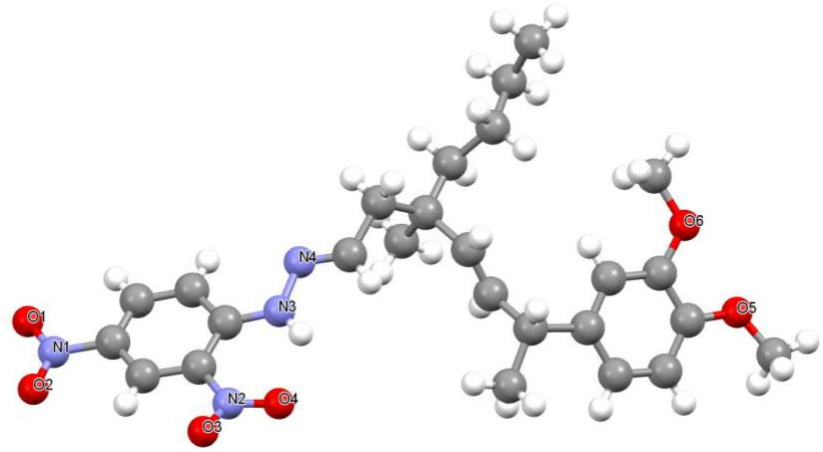


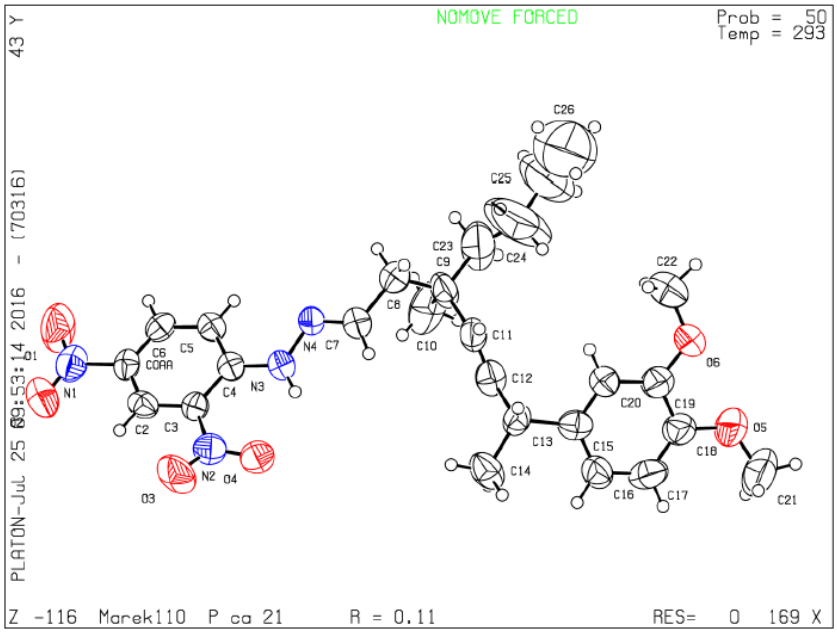
6a

transoid/cisoid = 5/1

M_w = 495.6 g.mol^{-1}

(3R*,6R*,4*E*)-3-butyl-6-(3,4-dimethoxyphenyl)-3-methylhept-4-enal-2-(2,4-dinitrophenyl)hydrazone (6a). 2,4-dinitrophenyl hydrazine (19 mg, 0.9 mmol, 1.0 equiv) in ethanol (3 mL) was added to the aldehyde **4d** (30 mg, 0.9 mmol, 1.0 equiv). One drop of concentrated sulfuric acid was added. The reaction was stirred for 24 h. Ethyl acetate and water were then added. The organic fraction was washed with aqueous saturated solutions of sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered and concentrated in vacuo to an orange oil. The purification was done by silica chromatography using 15% diethyl ether in hexane. The product was obtained as an orange solid which was recrystallised using dichloromethane and hexane (1:5). **6a** was obtained as an orange solid in a 1:4 ratio of cisoid and transoid isomers. (38 mg, 81% yield). Mp = 180-182 °C (deg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.99 (s, 1H), 9.10 (d, *J* = 2.4 Hz, 1H), 8.35 – 8.19 (m, 1H), 7.91 (dd, *J* = 14.6, 8.6 Hz, 1H), 7.54 – 7.32 (m, 1H), 6.74 (dt, *J* = 32.1, 10.7 Hz, 3H), 5.54 (dd, *J* = 15.8, 6.5 Hz, 1H), 5.42 (d, *J* = 15.8 Hz, 1H), 3.84 (d, *J* = 1.7 Hz, 6H), 3.52 – 3.33 (m, 1H), 2.57 – 2.25 (m, 2H), 2.25 – 2.01 (m, 1H), 1.65 – 0.69 (m, 15H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1, 148.8, 147.4, 145.1, 138.6, 137.8, 135.9, 133.9, 129.9, 128.8, 123.5, 118.7, 116.5, 111.1, 110.8, 55.9, 55.8, 43.5, 41.8, 41.5, 39.0, 31.6, 29.7, 26.3, 24.0, 23.3, 22.7, 21.5, 14.1.





Crystal structure determination of product 6a (CDCC 1813305)

Single crystals suitable for X-ray diffraction were grown by dissolving compound **6a** in hexane/dichloromethane (2:1) and allowing it to evaporate slowly at room temperature. The single-crystal material was immersed in Paratone–N oil and mounted on a Kappa CCD diffractometer at temperature 293(2) K. Data collection was performed using monochromated Mo Kα radiation, λ = 0.71073 Å, using φ and ω scans to cover the Ewald sphere.[1] Accurate cell parameters were obtained with the amount of indicated reflections.[2] The structure was solved by direct methods (SHELXS-97)[3] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for

terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Software used for molecular graphics: Mercury 3.7.[5]

1. Kappa CCD Server Software, Nonius BV, Delft, The Netherlands, 1997.

2. Z. Otwinowski and W. Minor, Methods Enzymol., 1997, 276, 307.

3. G. M. Sheldrick, Acta Crystallogr., Sect. A: Fundam. Crystallogr.,1990, 46, 467.

4. ORTEP, TEXSAN Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1999.

5. Mercury Software from CCDC: http://www.ccdc.cam.ac.uk/ Solutions/CSDSystem/Pages/Mercury.aspx.

Table 1 Crystal data and structure refinement for 6a.

Identification code	marek110
Empirical formula	$C_{26}H_{25}N_4O_6$
Formula weight	489.50
Temperature/K	293.15
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	6.690(5)
b/Å	24.410(4)
c/Å	16.2140(17)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2648(2)
Z	4
$\rho_{calc}g/cm^3$	1.228
μ/mm^{-1}	0.089
F(000)	1028.0
Crystal size/mm^3	0.45 × 0.24 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.024 to 48.28
Index ranges	$0 \leq h \leq 7$, $-27 \leq k \leq 0$, $0 \leq l \leq 18$
Reflections collected	2018
Independent reflections	2018 [R_{int} = 0.0890, R_{sigma} = 0.0428]
Data/restraints/parameters	2018/106/226
Goodness-of-fit on F^2	1.337
Final R indexes [I>=2σ (I)]	R_1 = 0.1018, wR_2 = 0.2205
Final R indexes [all data]	R_1 = 0.1124, wR_2 = 0.2258
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.14

Flack parameter 0.0

Alert level B

THETM01_ALERT_3_B The value of sine(theta_max)/wavelength is less than 0.575
Calculated sin(theta_max)/wavelength = 0.5619
Author Response: Weak diffracted crystal

PLAT220_ALERT_2_B Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 7.8 Ratio
Author Response: Partly disordered n-butyl group in the molecule

PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C24 Check
Author Response: Partly disordered n-butyl group in the molecule

PLAT242_ALERT_2_B Low 'MainMol' Ueq as Compared to Neighbors of C25 Check
Author Response: Partly disordered n-butyl group in the molecule

PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.01937 Ang.
Author Response: Partly disordered n-butyl group in the molecule

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 6a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
C1	-5146(12)	610(4)	-4527(11)	55.7(19)
C2	-4755(12)	734(3)	-3722(12)	55.0(19)
C3	-4475(12)	315(3)	-3166(11)	50.5(18)
C4	-4637(12)	-248(3)	-3408(11)	50.4(18)
C5	-5010(12)	-347(3)	-4253(11)	54(2)
C6	-5227(12)	72(4)	-4799(11)	56(2)
C7	-4780(14)	-1566(4)	-2601(12)	71(3)
C8	-5334(17)	-2140(4)	-2769(12)	84(3)
C9	-3620(20)	-2546(4)	-2640(12)	89(3)
C10	-1940(30)	-2410(5)	-3246(12)	121(4)
C11	-4340(40)	-3132(5)	-2846(14)	176(8)
C12	-3780(50)	-3596(9)	-2550(20)	159(13)
C12A	-5540(70)	-3364(15)	-2450(40)	184(12)
C14	-6880(90)	-4062(18)	-2480(50)	210(20)
C13	-5050(40)	-4052(10)	-2881(12)	160(12)
C13A	-5370(80)	-4266(15)	-2740(40)	181(19)
C14A	-6660(60)	-4377(14)	-2460(20)	190(20)
C15	-2870(19)	-2507(3)	-1777(11)	72(3)
C16	-1100(18)	-2435(4)	-1491(11)	70(2)
C17	-462(16)	-2397(4)	-613(11)	70(2)
C18	462(19)	-1841(4)	-424(12)	96(3)
C19	869(14)	-2889(3)	-368(11)	63(2)
C20	147(15)	-3413(4)	-543(11)	70(2)
C21	1214(16)	-3875(4)	-329(12)	73(3)
C22	3050(16)	-3824(4)	47(12)	78(2)
C23	3762(17)	-3311(4)	217(12)	85(3)
C24	2680(17)	-2845(4)	6(11)	77(2)
C25	5620(30)	-4295(7)	789(15)	149(6)
C26	-1060(20)	-4485(5)	-989(14)	117(5)
N1	-5423(13)	1050(4)	-5130(11)	77(2)
N2	-4121(12)	477(3)	-2316(11)	68(2)
N3	-4462(11)	-669(3)	-2872(11)	60.1(18)
N4	-4960(11)	-1190(3)	-3143(11)	61.0(19)
O1	-5807(19)	934(4)	-5829(11)	132(4)
O2	-5338(13)	1518(3)	-4875(11)	107(3)
O3	-4426(15)	940(3)	-2109(10)	107(3)
O4	-3435(12)	121(3)	-1854(10)	82(2)

O5	4008(15)	-4307(3)	234(12)	124(3)
O6	628(14)	-4399(3)	-469(11)	113(3)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 6a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C1	37(4)	61(4)	69(4)	15(4)	5(4)	6(4)
C2	41(5)	49(4)	75(4)	-2(4)	4(4)	-1(4)
C3	43(4)	54(4)	55(4)	-1(3)	6(4)	5(4)
C4	37(4)	54(4)	60(4)	3(3)	9(4)	2(4)
C5	45(5)	55(4)	62(4)	-3(3)	8(4)	4(4)
C6	43(5)	72(5)	54(4)	4(4)	4(4)	1(4)
C7	80(7)	57(4)	76(6)	12(5)	-12(5)	5(4)
C8	111(7)	66(5)	74(6)	15(5)	-25(6)	-11(5)
C9	154(9)	51(4)	63(5)	0(4)	-25(5)	9(5)
C10	176(11)	140(10)	47(5)	-7(6)	-1(6)	59(8)
C11	360(30)	54(6)	117(11)	0(6)	-98(13)	-20(8)
C12	230(20)	55(8)	200(30)	18(15)	-80(30)	-29(12)
C12A	190(30)	101(16)	260(40)	0(20)	-130(20)	-43(14)
C14	230(30)	120(20)	270(60)	-100(30)	-10(30)	-50(20)
C13	250(30)	84(13)	150(30)	42(17)	-20(20)	-100(20)
C13A	220(40)	84(13)	240(50)	40(20)	50(30)	-66(18)
C14A	250(40)	110(20)	210(50)	40(30)	60(30)	-70(30)
C15	110(7)	53(5)	53(5)	7(4)	-7(4)	6(5)
C16	96(6)	60(5)	54(4)	5(4)	7(4)	12(5)
C17	87(7)	65(5)	56(5)	-4(4)	-1(4)	7(4)
C18	131(10)	63(5)	94(8)	-14(6)	-1(7)	1(6)
C19	70(5)	66(4)	52(5)	-4(4)	4(4)	-4(4)
C20	73(6)	67(4)	71(6)	1(5)	-7(5)	-5(4)
C21	76(6)	61(5)	82(7)	-2(5)	-13(5)	-2(4)
C22	80(6)	75(5)	78(6)	-4(5)	-13(5)	8(4)
C23	74(6)	91(6)	89(7)	-12(6)	-21(6)	-4(5)
C24	89(6)	73(5)	69(6)	-5(5)	-11(5)	-9(5)
C25	128(13)	163(14)	157(14)	17(11)	-53(10)	48(10)
C26	124(11)	77(7)	151(12)	-18(7)	-37(9)	-21(7)
N1	73(5)	74(5)	84(5)	18(4)	0(4)	3(4)
N2	68(5)	72(5)	62(4)	-9(4)	5(4)	-1(4)
N3	69(5)	49(4)	62(4)	3(3)	-2(4)	-5(3)
N4	61(5)	54(3)	68(5)	7(3)	-8(4)	-1(3)
O1	212(12)	108(6)	76(5)	23(4)	-15(6)	19(7)

O2	128(7)	67(4)	126(6)	21(4)	-12(6)	-5(4)
O3	166(8)	69(4)	87(5)	-32(4)	1(5)	10(5)
O4	111(6)	79(4)	56(4)	-6(3)	-15(4)	-9(4)
O5	126(7)	88(5)	156(8)	-18(6)	-55(6)	34(5)
O6	132(7)	60(4)	149(8)	7(5)	-51(6)	-7(4)

Table 4 Bond Lengths for 6a.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
C1	C2	1.365(12)	C14	C13A	1.21(7)
C1	C6	1.387(12)	C14	C14A	0.78(5)
C1	N1	1.463(11)	C13	C13A	0.61(3)
C2	C3	1.377(12)	C13	C14A	1.5000(13)
C3	C4	1.433(10)	C13A	C14A	1.01(5)
C3	N2	1.454(11)	C15	C16	1.284(15)
C4	C5	1.414(12)	C16	C17	1.489(13)
C4	N3	1.350(10)	C17	C18	1.522(14)
C5	C6	1.360(12)	C17	C19	1.548(13)
C7	C8	1.475(13)	C19	C20	1.396(12)
C7	N4	1.276(11)	C19	C24	1.359(14)
C8	C9	1.528(15)	C20	C21	1.380(13)
C9	C10	1.528(19)	C21	C22	1.377(13)
C9	C11	1.546(17)	C21	O6	1.356(11)
C9	C15	1.490(14)	C22	C23	1.367(13)
C11	C12	1.29(3)	C22	O5	1.376(12)
C11	C12A	1.18(6)	C23	C24	1.390(13)
C12	C12A	1.32(6)	C25	O5	1.402(17)
C12	C13	1.5000(12)	C26	O6	1.422(15)
C12	C13A	1.98(4)	N1	O1	1.195(12)
C12A	C14	1.93(5)	N1	O2	1.218(11)
C12A	C13	1.85(5)	N2	O3	1.196(9)
C12A	C13A	2.26(6)	N2	O4	1.235(9)
C14	C13	1.39(7)	N3	N4	1.387(9)

Table 5 Bond Angles for 6a.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C2	C1	C6	121.4(8)	C14	C13	C12A	71(3)
C2	C1	N1	120.0(8)	C14	C13	C14A	31(2)
C6	C1	N1	118.5(9)	C13A	C13	C12	135(7)

C1	C2	C3	119.2(8)	C13A	C13	C12A	125(7)
C2	C3	C4	121.5(7)	C13A	C13	C14	60(6)
C2	C3	N2	116.2(7)	C13A	C13	C14A	29(7)
C4	C3	N2	122.2(7)	C14A	C13	C12A	100(3)
C5	C4	C3	116.2(7)	C12	C13A	C12A	35.4(16)
N3	C4	C3	123.2(8)	C14	C13A	C12	93(4)
N3	C4	C5	120.6(7)	C14	C13A	C12A	59(3)
C6	C5	C4	121.5(8)	C13	C13A	C12	33(5)
C5	C6	C1	120.0(8)	C13	C13A	C12A	42(6)
N4	C7	C8	122.2(9)	C13	C13A	C14	94(8)
C7	C8	C9	113.6(9)	C13	C13A	C14A	134(9)
C8	C9	C11	109.6(12)	C14A	C13A	C12	127(5)
C10	C9	C8	108.8(8)	C14A	C13A	C12A	97(5)
C10	C9	C11	106.9(12)	C14A	C13A	C14	40(3)
C15	C9	C8	109.9(9)	C14	C14A	C13	67(5)
C15	C9	C10	110.0(11)	C14	C14A	C13A	84(5)
C15	C9	C11	111.5(9)	C13A	C14A	C13	17(3)
C12	C11	C9	130.0(17)	C16	C15	C9	131.2(11)
C12A	C11	C9	123(3)	C15	C16	C17	128.2(10)
C12A	C11	C12	64(2)	C16	C17	C18	111.4(8)
C11	C12	C12A	54(2)	C16	C17	C19	111.2(7)
C11	C12	C13	111(2)	C18	C17	C19	114.0(9)
C11	C12	C13A	121(3)	C20	C19	C17	117.4(8)
C12A	C12	C13	82(3)	C24	C19	C17	124.5(8)
C12A	C12	C13A	84(3)	C24	C19	C20	118.1(9)
C13	C12	C13A	13(2)	C21	C20	C19	121.3(9)
C11	C12A	C12	62(3)	C22	C21	C20	119.9(9)
C11	C12A	C14	137(5)	O6	C21	C20	125.4(9)
C11	C12A	C13	96(4)	O6	C21	C22	114.7(9)
C11	C12A	C13A	108(4)	C23	C22	C21	118.9(9)
C12	C12A	C14	92(3)	C23	C22	O5	125.3(10)
C12	C12A	C13	53.3(19)	O5	C22	C21	115.8(9)
C12	C12A	C13A	60(2)	C22	C23	C24	121.1(10)
C14	C12A	C13A	32(2)	C19	C24	C23	120.7(9)
C13	C12A	C14	43(2)	O1	N1	C1	119.2(10)
C13	C12A	C13A	12.6(16)	O1	N1	O2	123.6(9)
C13	C14	C12A	66(3)	O2	N1	C1	117.1(9)
C13A	C14	C12A	89(4)	O3	N2	C3	119.7(8)
C13A	C14	C13	26(2)	O3	N2	O4	123.9(8)
C14A	C14	C12A	141(7)	O4	N2	C3	116.4(7)
C14A	C14	C13	82(6)	C4	N3	N4	118.3(7)

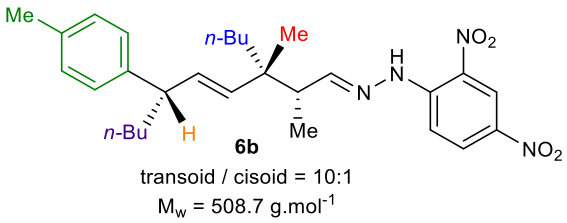
C14A	C14	C13A	56(4)	C7	N4	N3	114.8(7)
C12	C13	C12A	44.7(19)	C22	O5	C25	118.8(10)
C12	C13	C14A	129(3)	C21	O6	C26	117.9(9)
C14	C13	C12	110(3)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6a.

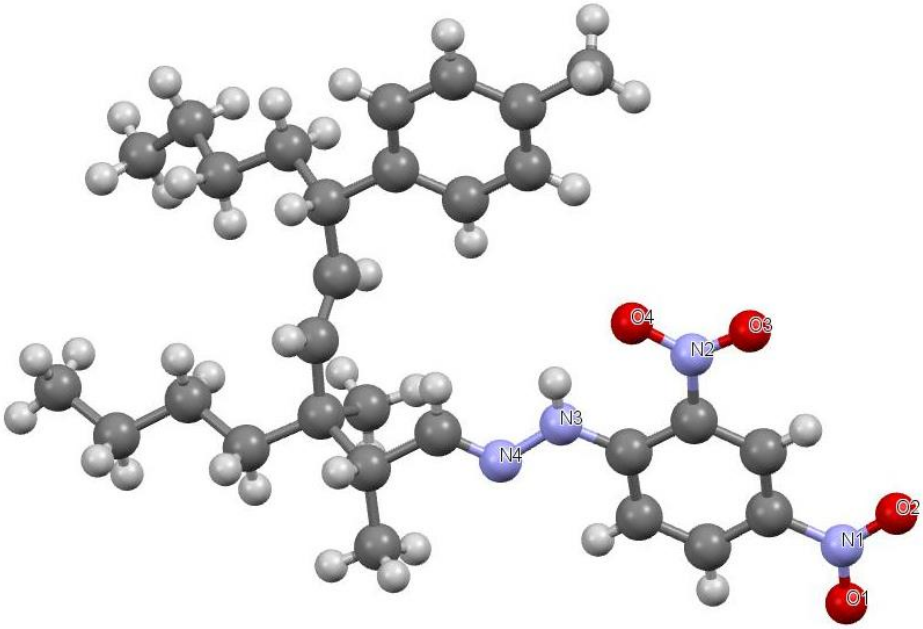
Atom	***x***	***y***	***z***	**U(eq)**
H2	-4679	1097	-3552	66
H5	-5109	-706	-4440	65
H6	-5429	-3	-5356	68
H7	-4283	-1475	-2083	85
H8A	-5797	-2169	-3335	101
H8B	-6436	-2242	-2412	101
H10A	-2455	-2418	-3799	181
H10B	-890	-2674	-3191	181
H10C	-1431	-2051	-3129	181
H15	-3855	-2541	-1375	86
H16	-89	-2402	-1881	84
H17	-1680	-2423	-279	83
H18A	1750	-1816	-683	144
H18B	610	-1800	161	144
H18C	-390	-1556	-632	144
H20	-1077	-3451	-809	84
H23	4991	-3273	479	102
H24	3202	-2501	121	92
H25A	6713	-4100	545	224
H25B	6023	-4663	912	224
H25C	5212	-4115	1288	224
H26A	-760	-4355	-1534	176
H26B	-2185	-4290	-773	176
H26C	-1357	-4869	-1010	176
H3	-4052	-615	-2376	72

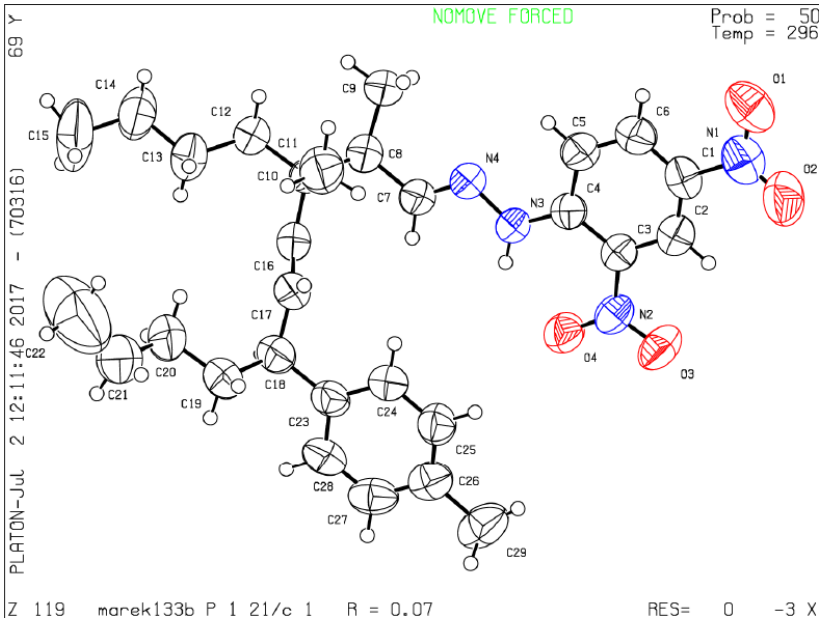
Table 7 Atomic Occupancy for 6a.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C12	0.5	C12A	0.5	C14	0.5
C13	0.5	C13A	0.5	C14A	0.5



(2R*,3S*,6S*,4*E*)-3-butyl-2,3-dimethyl-6-(*p*-tolyl)dec-4-enal-2-(2,4-dinitrophenyl)hydrazone (6b). 2,4-dinitrophenyl hydrazine (28 mg, 0.14 mmol, 1.0 equiv) in ethanol (3 mL) was added to the aldehyde **4ah** (47 mg, 0.14 mmol, 1.0 equiv). One drop of concentrated sulfuric acid was added. After 10 minutes TLC showed the complete conversion of the aldehyde. Ethyl acetate and water were added. The organic fraction was washed with aqueous saturated solutions of sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered and concentrated in vacuo to an orange oil. The purification was done by silica chromatography using 15% diethyl ether in hexane. The product was obtained as an orange solid which was recrystallised using dichloromethane and hexane (1:5). **6b** was obtained as an orange solid in a 1:10 ratio of cisoid and transoid isomers. (72 mg, 98% yield). Mp = 197-199 °C (deg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.96 (s, 1H), 9.10 (d, *J* = 2.5 Hz, 1H), 8.27 (dd, *J* = 9.6, 2.1 Hz, 1H), 7.89 – 7.85 (m, 3H), 7.40 (t, *J* = 6.1 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 5.53 (dd, *J* = 15.8, 6.6 Hz, 1H), 5.42 (d, *J* = 16.4 Hz, 1H), 3.88 (s, 3H), 3.51 (dq, *J* = 14.2, 6.9 Hz, 1H), 2.41 (dd, *J* = 8.5, 6.3 Hz, 2H), 1.36 (d, *J* = 7.0 Hz, 3H), 1.51 – 1.11 (m, 12H), 1.07 (s, 3H), 0.96 – 0.79 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 151.4, 150.8, 145.0, 137.8, 136.8, 132.9, 129.9, 129.7, 128.8, 128.1, 127.1, 127.0, 123.5, 116.4, 77.3, 52.0, 43.5, 42.4, 41.3, 39.1, 31.6, 26.2, 24.0, 23.3, 21.2, 14.1.





Crystal structure determination of product 6b (CDCC 1813312)

Single crystals suitable for X-ray diffraction were grown by dissolving compound **6b** in dichloromethane/hexane (1:4) and allowing it to evaporate slowly at room temperature. The single-crystal material was immersed in Paratone–N oil and mounted on an APEX2 v2010.7-0 (Bruker AXS) diffractometer at temperature 296.15(2) K. Data collection was performed using monochromated Mo Kα radiation, λ = 0.71073 Å, using φ and ω scans to cover the Ewald sphere.[1] Accurate cell parameters were obtained with the amount of indicated reflections.[2] The structure was solved by direct methods (SHELXS-97)[3] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Software used for molecular graphics: Mercury 3.7.[5]

1. 'APEX2 v2010.7-0 (Bruker AXS)'

2. Z. Otwinowski and W. Minor, Methods Enzymol., 1997, 276, 307.

3. G. M. Sheldrick, Acta Crystallogr., Sect. A: Fundam. Crystallogr., 1990, 46, 467.

4. ORTEP, TEXSAN Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1999.

5. Mercury Software from CCDC: http://www.ccdc.cam.ac.uk/Solutions/CSDSystem/Pages/Mercury.aspx.

Table 1 Crystal data and structure refinement for 6b.

Identification code	Marek133b
Empirical formula	$C_{29}O_4N_4H_{40}$
Formula weight	508.65
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.036(2)
b/Å	23.049(7)
c/Å	18.453(6)
α/°	90
β/°	96.995(4)
γ/°	90
Volume/Å^3	2970.4(17)
Z	4
ρ_{calc}g/cm^3	1.137
μ/mm^{-1}	0.076
F(000)	1096.0
Crystal size/mm^3	0.3 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.84 to 48.282
Index ranges	$-7 \leq h \leq 7$, $-25 \leq k \leq 25$, $-20 \leq l \leq 20$
Reflections collected	35171
Independent reflections	4371 [R_{int} = 0.0431, R_{sigma} = 0.0224]
Data/restraints/parameters	4371/0/339
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0736, wR_2 = 0.1245
Final R indexes [all data]	R_1 = 0.1043, wR_2 = 0.1490
Largest diff. peak/hole / e Å^{-3}	0.67/-0.22

Alert level B

THETM01_ALERT_3_B The value of sine(theta_max)/wavelength is less than 0.575
Calculated sin(theta_max)/wavelength = 0.5612

Author Response: Weak diffracted crystal

PLAT230_ALERT_2_B Hirshfeld Test Diff for C21 --C22 . 12.3 s.u.

Author Response: Disordered n-butyl group in the molecule

PLAT430_ALERT_2_B Short Inter D...A Contact O4 ..O4 2.81 Ang.

Author Response: Disordered nitro group in the molecule

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 6b. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	2968(5)	6063.8(17)	9072(2)	120.4(12)
O2	2970(6)	6728.3(17)	8254(2)	127.8(13)
O3	1557(4)	6287.9(12)	5769.3(16)	97.5(9)
O4	1224(4)	5414.7(12)	5369.5(15)	86.8(8)
N1	2795(5)	6223(2)	8434(3)	97.2(11)
N2	1500(4)	5763.3(14)	5878.6(19)	72.9(8)
N3	1305(4)	4541.3(12)	6272.8(16)	68.8(8)
N4	1123(5)	3973.4(13)	6488.7(17)	78.2(9)
C1	2392(5)	5790.6(17)	7863(2)	72.2(10)
C2	2128(5)	5961.9(16)	7159(2)	68.3(9)
C3	1755(4)	5553.0(14)	6612.7(19)	61.0(9)
C4	1647(5)	4954.4(15)	6776.6(19)	62.2(9)
C5	1929(5)	4805.7(17)	7527(2)	77.6(10)
C6	2293(5)	5213.6(18)	8057(2)	79.5(11)
C7	731(6)	3610.1(16)	5984(2)	78.4(11)
C8	420(7)	2984.0(16)	6133(2)	93.0(13)
C9	116(9)	2872.1(18)	6906(2)	115.4(18)
C10	1754(6)	2594.8(15)	5769.3(19)	76.0(11)
C11	3840(8)	2708(2)	6210(3)	111.8(16)
C12	1321(7)	1959.6(16)	5854(2)	89.9(12)
C13	2233(7)	1520.8(17)	5415(3)	102.9(14)
C14	1785(9)	902.2(18)	5545(3)	122.3(18)
C15	2594(11)	470(3)	5088(5)	179(3)
C16	1881(7)	2756.1(15)	5004(2)	80.9(11)
C17	3120(6)	2954.4(16)	4636(2)	77.7(11)
C18	3179(7)	3082.2(17)	3868(2)	85.8(12)
C19	4711(7)	2740.3(19)	3539(2)	103.4(15)
C20	4809(11)	2098(2)	3692(3)	152(3)
C21	6530(16)	1795(3)	3450(5)	214(5)
C22	6984(18)	1256(6)	3770(6)	281(6)
C23	3256(5)	3723.8(17)	3688(2)	73.5(10)
C24	3582(6)	4147.8(17)	4217(2)	82.2(11)
C25	3624(6)	4731.3(18)	4032(2)	85.0(11)
C26	3336(5)	4913.5(19)	3332(3)	80.9(11)
C27	2993(5)	4491(2)	2806(2)	87.4(12)
C28	2960(6)	3913(2)	2976(2)	83.1(11)
C29	3393(7)	5543.4(19)	3131(3)	114.9(17)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 6b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	118(3)	151(3)	90(2)	-30(2)	7.1(19)	-9(2)
O2	154(3)	100(3)	131(3)	-37(2)	21(2)	-19(2)
O3	113(2)	65.4(18)	107(2)	19.5(15)	-14.4(17)	-1.8(15)
O4	109(2)	73.3(17)	75.5(17)	5.8(15)	-1.5(15)	2.2(15)
N1	80(2)	110(3)	101(3)	-22(3)	10(2)	-8(2)
N2	66.3(19)	63(2)	87(2)	10.5(18)	0.5(16)	4.1(15)
N3	88(2)	55.0(18)	64.6(18)	4.8(14)	13.4(15)	7.2(14)
N4	105(2)	61.6(19)	71(2)	4.4(16)	22.4(17)	6.7(16)
C1	56(2)	81(3)	79(3)	-18(2)	9.1(18)	-2.6(18)
C2	47.5(19)	69(2)	89(3)	0(2)	7.7(17)	2.0(16)
C3	49.6(18)	63(2)	70(2)	3.5(18)	3.6(15)	6.0(15)
C4	54.9(19)	65(2)	67(2)	4.2(18)	9.1(15)	9.3(16)
C5	85(3)	73(2)	75(3)	6(2)	11(2)	7(2)
C6	80(3)	89(3)	69(2)	2(2)	9.5(19)	3(2)
C7	100(3)	65(2)	75(3)	6(2)	28(2)	11(2)
C8	129(4)	65(2)	93(3)	-1(2)	45(3)	1(2)
C9	190(5)	75(3)	94(3)	5(2)	72(3)	2(3)
C10	106(3)	60(2)	64(2)	7.8(17)	21(2)	19(2)
C11	138(4)	101(3)	92(3)	2(3)	-4(3)	26(3)
C12	128(4)	63(2)	84(3)	1(2)	31(2)	2(2)
C13	129(4)	68(3)	114(3)	-7(2)	20(3)	17(2)
C14	149(5)	70(3)	153(5)	-15(3)	36(4)	1(3)
C15	192(7)	93(4)	259(9)	-66(5)	53(6)	14(4)
C16	108(3)	59(2)	80(3)	-6.7(19)	29(2)	-3(2)
C17	97(3)	70(2)	68(2)	-1.7(19)	19(2)	7(2)
C18	105(3)	81(3)	77(3)	-9(2)	32(2)	-13(2)
C19	136(4)	89(3)	94(3)	-10(2)	50(3)	0(3)
C20	246(8)	80(3)	151(5)	-13(3)	110(5)	5(4)
C21	374(13)	109(5)	192(7)	31(5)	164(9)	92(7)
C22	321(15)	326(15)	195(9)	-40(10)	34(9)	146(13)
C23	75(2)	79(2)	70(2)	-4(2)	24.5(18)	-7.8(19)
C24	102(3)	78(3)	70(2)	3(2)	23(2)	-5(2)
C25	92(3)	74(3)	91(3)	-9(2)	21(2)	-7(2)
C26	60(2)	90(3)	96(3)	17(3)	21(2)	9(2)
C27	67(2)	117(4)	79(3)	25(3)	14(2)	8(2)
C28	76(3)	108(3)	68(3)	-4(2)	18.9(19)	-4(2)
C29	98(3)	94(3)	159(5)	40(3)	40(3)	18(3)

Table 4 Bond Lengths for 6b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.224(5)	C10	C12	1.508(5)
O2	N1	1.223(5)	C10	C16	1.474(5)
O3	N2	1.227(4)	C12	C13	1.489(5)
O4	N2	1.234(4)	C13	C14	1.486(6)
N1	C1	1.452(5)	C14	C15	1.463(7)
N2	C3	1.429(4)	C16	C17	1.254(5)
N3	N4	1.379(4)	C17	C18	1.453(5)
N3	C4	1.332(4)	C18	C19	1.521(6)
N4	C7	1.258(5)	C18	C23	1.518(5)
C1	C2	1.349(5)	C19	C20	1.508(6)
C1	C6	1.381(5)	C20	C21	1.511(9)
C2	C3	1.382(5)	C21	C22	1.397(12)
C3	C4	1.417(5)	C23	C24	1.381(5)
C4	C5	1.416(5)	C23	C28	1.376(5)
C5	C6	1.359(5)	C24	C25	1.389(5)
C7	C8	1.490(5)	C25	C26	1.350(6)
C8	C9	1.490(6)	C26	C27	1.375(6)
C8	C10	1.513(5)	C26	C29	1.500(6)
C10	C11	1.610(6)	C27	C28	1.370(6)

Table 5 Bond Angles for 6b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	N1	C1	118.7(4)	C12	C10	C11	106.7(3)
O2	N1	O1	123.0(4)	C16	C10	C8	112.9(3)
O2	N1	C1	118.3(4)	C16	C10	C11	106.5(3)
O3	N2	O4	121.5(3)	C16	C10	C12	112.4(3)
O3	N2	C3	119.1(3)	C13	C12	C10	119.8(4)
O4	N2	C3	119.4(3)	C14	C13	C12	116.8(4)
C4	N3	N4	119.5(3)	C15	C14	C13	117.1(5)
C7	N4	N3	116.0(3)	C17	C16	C10	137.5(4)
C2	C1	N1	119.3(4)	C16	C17	C18	134.9(4)
C2	C1	C6	121.7(4)	C17	C18	C19	113.0(4)
C6	C1	N1	119.0(4)	C17	C18	C23	114.7(3)
C1	C2	C3	119.7(3)	C23	C18	C19	111.8(3)
C2	C3	N2	116.8(3)	C20	C19	C18	116.9(4)
C2	C3	C4	121.3(3)	C19	C20	C21	114.7(5)

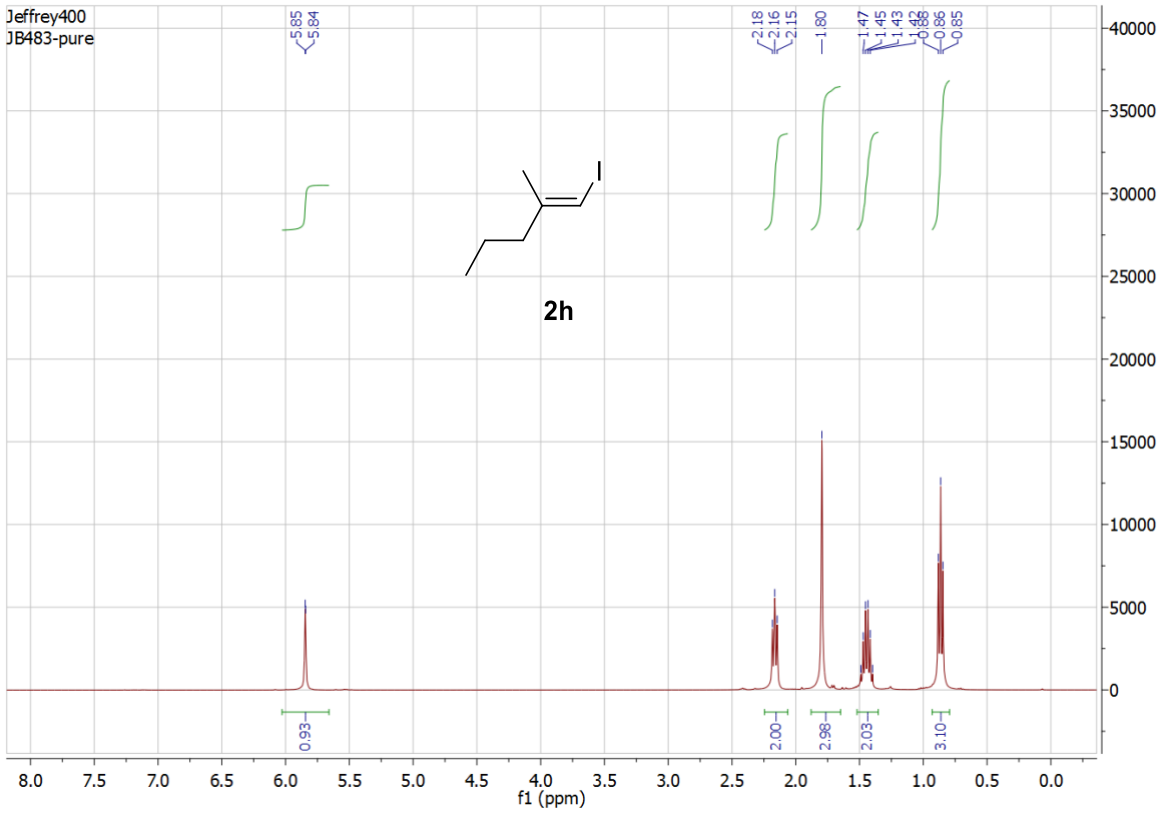
C4	C3	N2	121.9(3)	C22	C21	C20	115.8(7)
N3	C4	C3	123.9(3)	C24	C23	C18	122.8(4)
N3	C4	C5	120.1(3)	C28	C23	C18	120.8(4)
C5	C4	C3	116.1(3)	C28	C23	C24	116.4(4)
C6	C5	C4	121.9(4)	C23	C24	C25	121.2(4)
C5	C6	C1	119.4(4)	C26	C25	C24	122.1(4)
N4	C7	C8	122.1(4)	C25	C26	C27	116.6(4)
C7	C8	C10	112.3(3)	C25	C26	C29	122.1(5)
C9	C8	C7	112.7(3)	C27	C26	C29	121.2(4)
C9	C8	C10	119.4(4)	C28	C27	C26	122.2(4)
C8	C10	C11	104.8(3)	C27	C28	C23	121.4(4)
C12	C10	C8	112.7(3)				

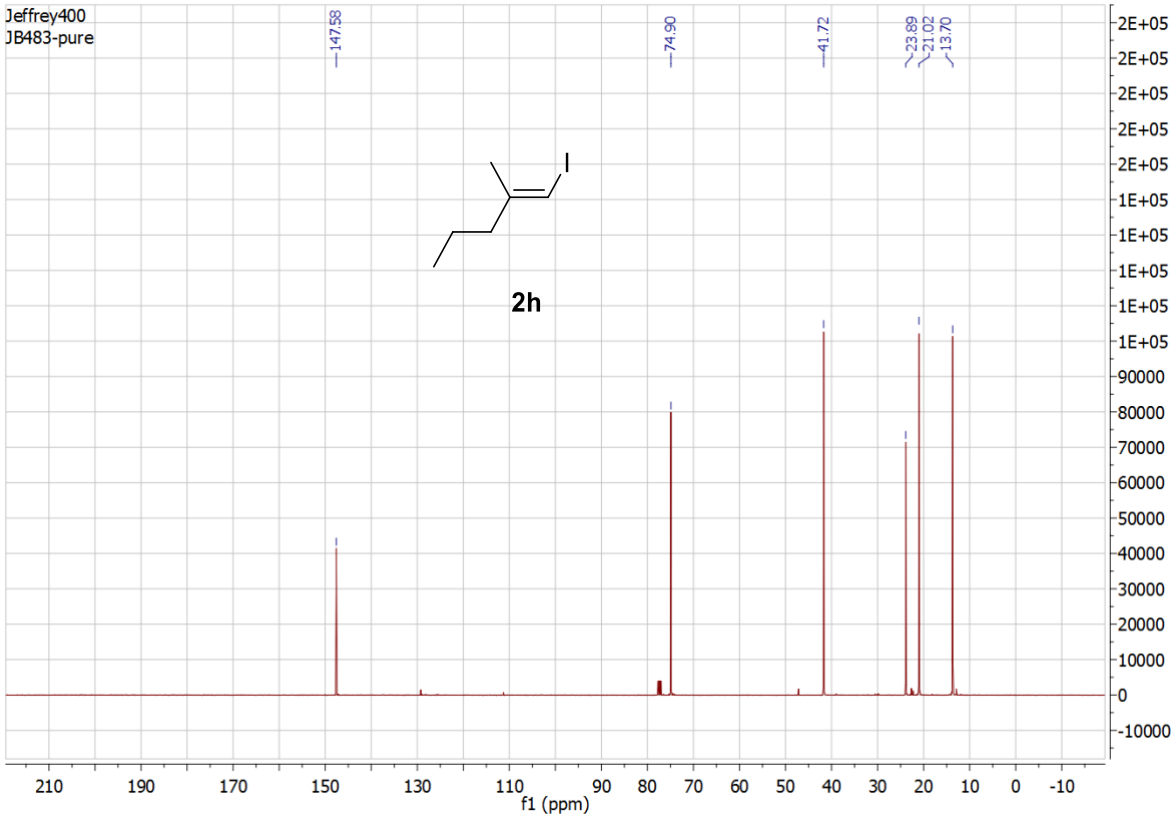
Table 6 Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 6b.

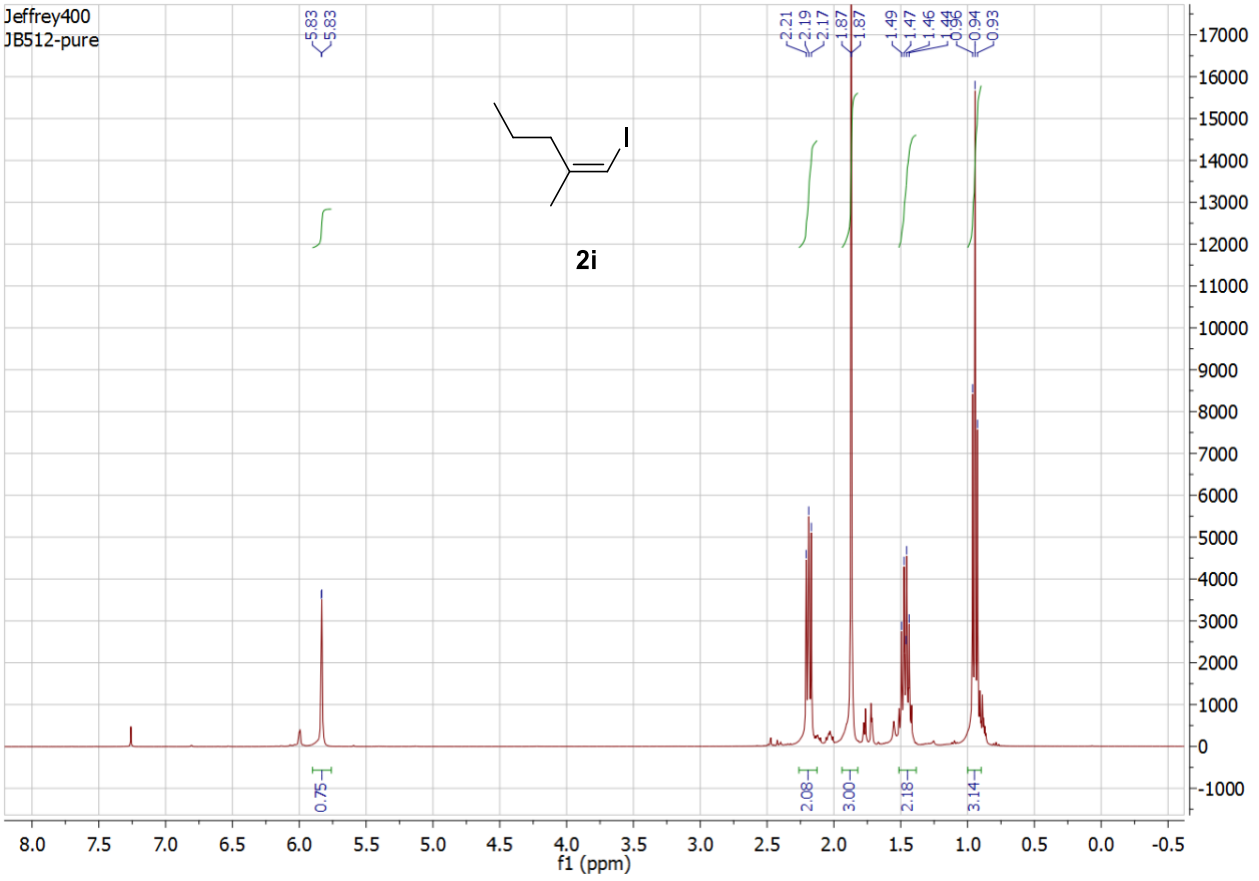
Atom	***x***	***y***	***z***	**U(eq)**
H3	1198	4628	5816	83
H2	2196	6353	7042	82
H5	1864	4418	7660	93
H6	2472	5105	8546	95
H7	632	3736	5502	94
H8	-837	2904	5861	112
H9A	1185	3020	7225	173
H9B	1	2462	6981	173
H9C	-1035	3062	7009	173
H11A	4139	3114	6195	168
H11B	4780	2490	5989	168
H11C	3844	2588	6708	168
H12A	1662	1861	6365	108
H12B	-54	1912	5749	108
H13A	1857	1605	4902	123
H13B	3610	1570	5508	123
H14A	2225	813	6051	147
H14B	404	858	5478	147
H15A	1884	470	4610	269
H15B	2518	93	5304	269
H15C	3908	563	5052	269
H16	724	2694	4713	97
H17	4268	3039	4921	93
H18	1956	2944	3617	103

H19A	4512	2794	3013	124
H19B	5946	2908	3714	124
H20A	3659	1917	3449	182
H20B	4817	2038	4213	182
H21A	6309	1744	2925	257
H21B	7632	2048	3555	257
H22A	8015	1084	3549	421
H22B	5882	1007	3697	421
H22C	7366	1305	4284	421
H24	3778	4041	4706	99
H25	3859	5005	4402	102
H27	2775	4602	2318	105
H28	2733	3642	2601	100
H29A	2142	5666	2920	172
H29B	4288	5599	2784	172
H29C	3784	5769	3561	172

NMR spectra of vinyl halides 2h-j



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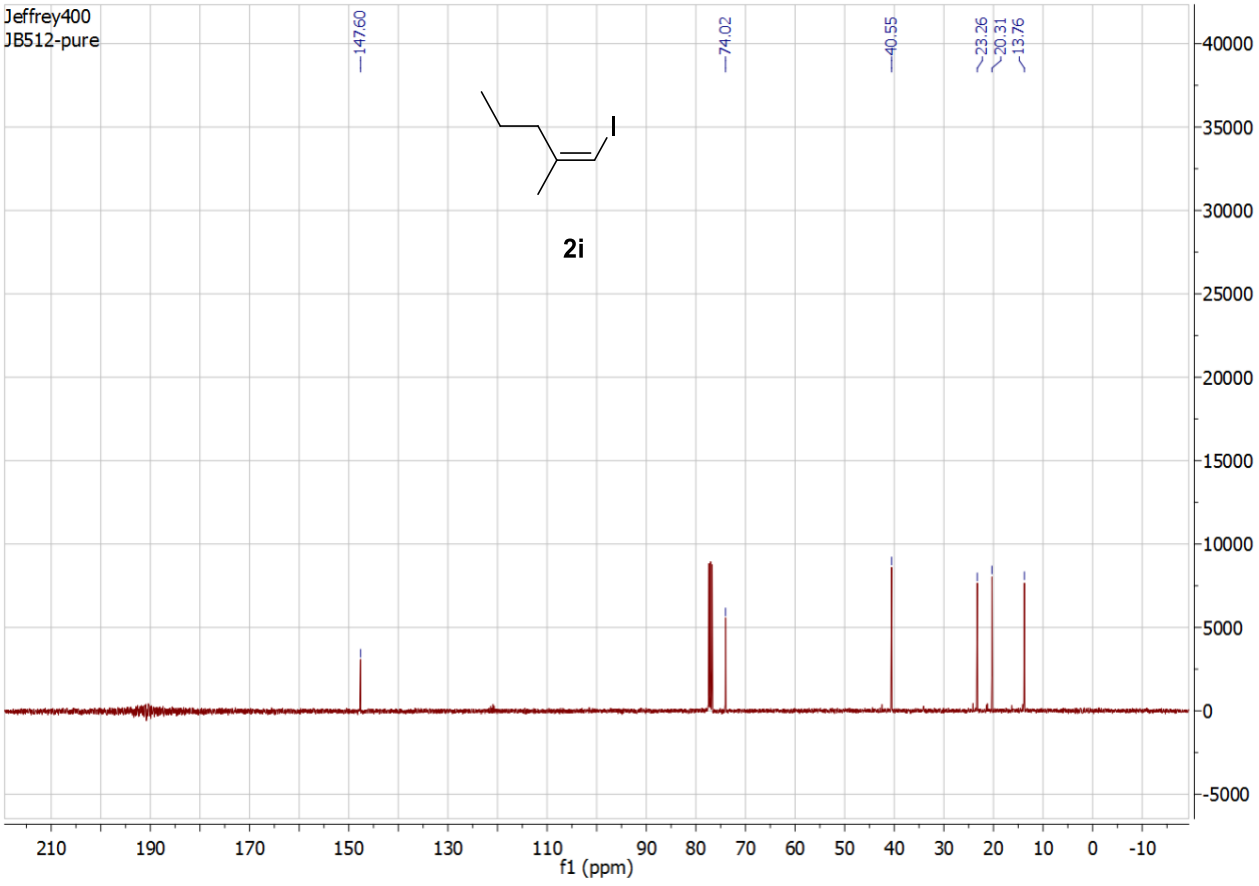
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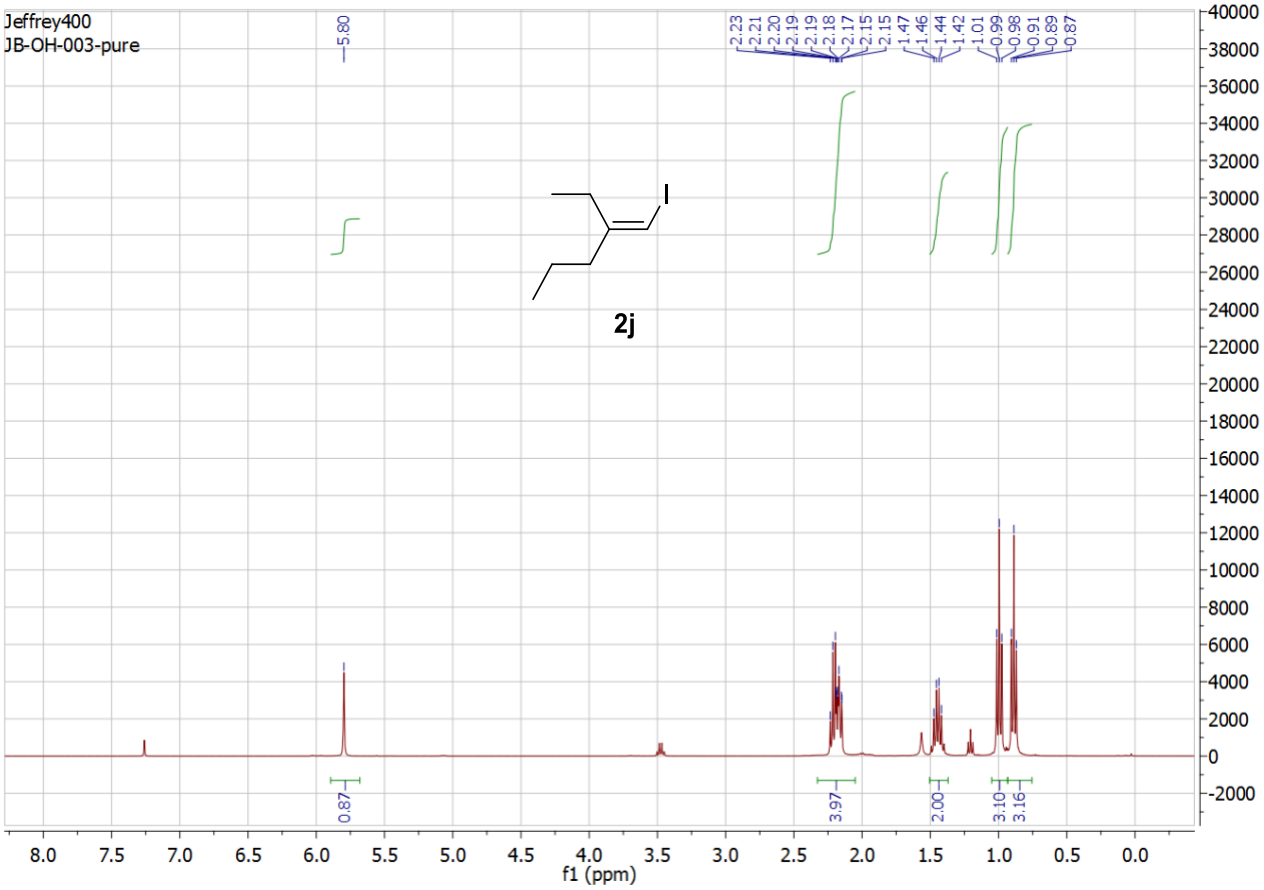
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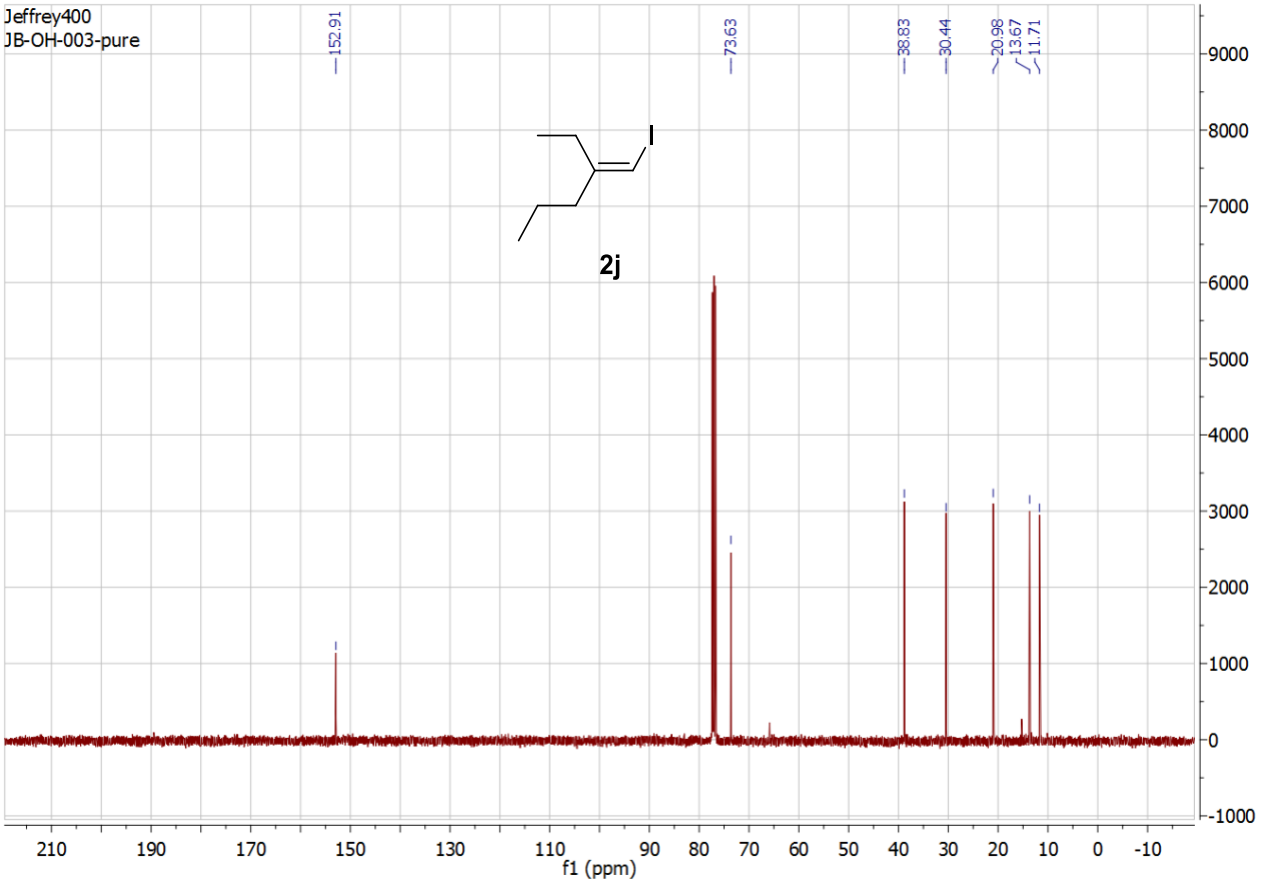
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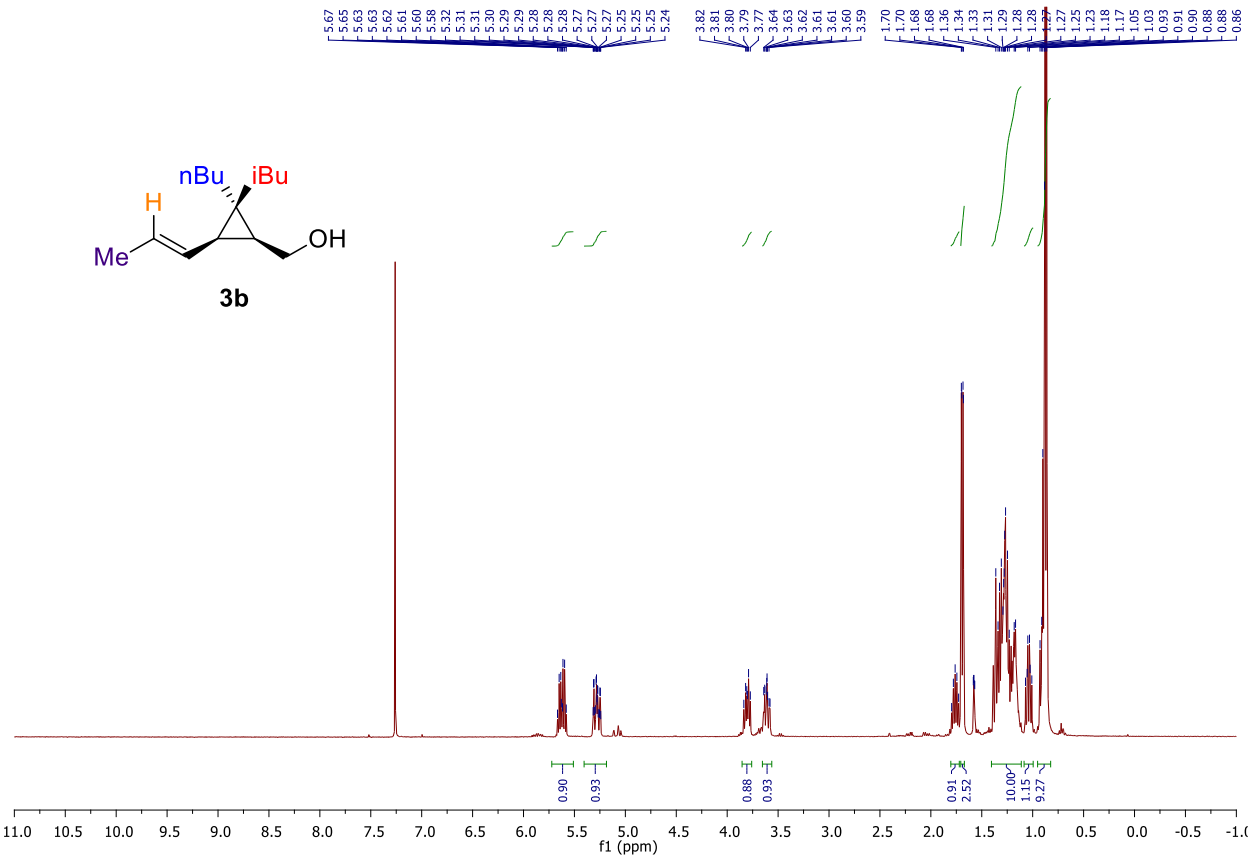
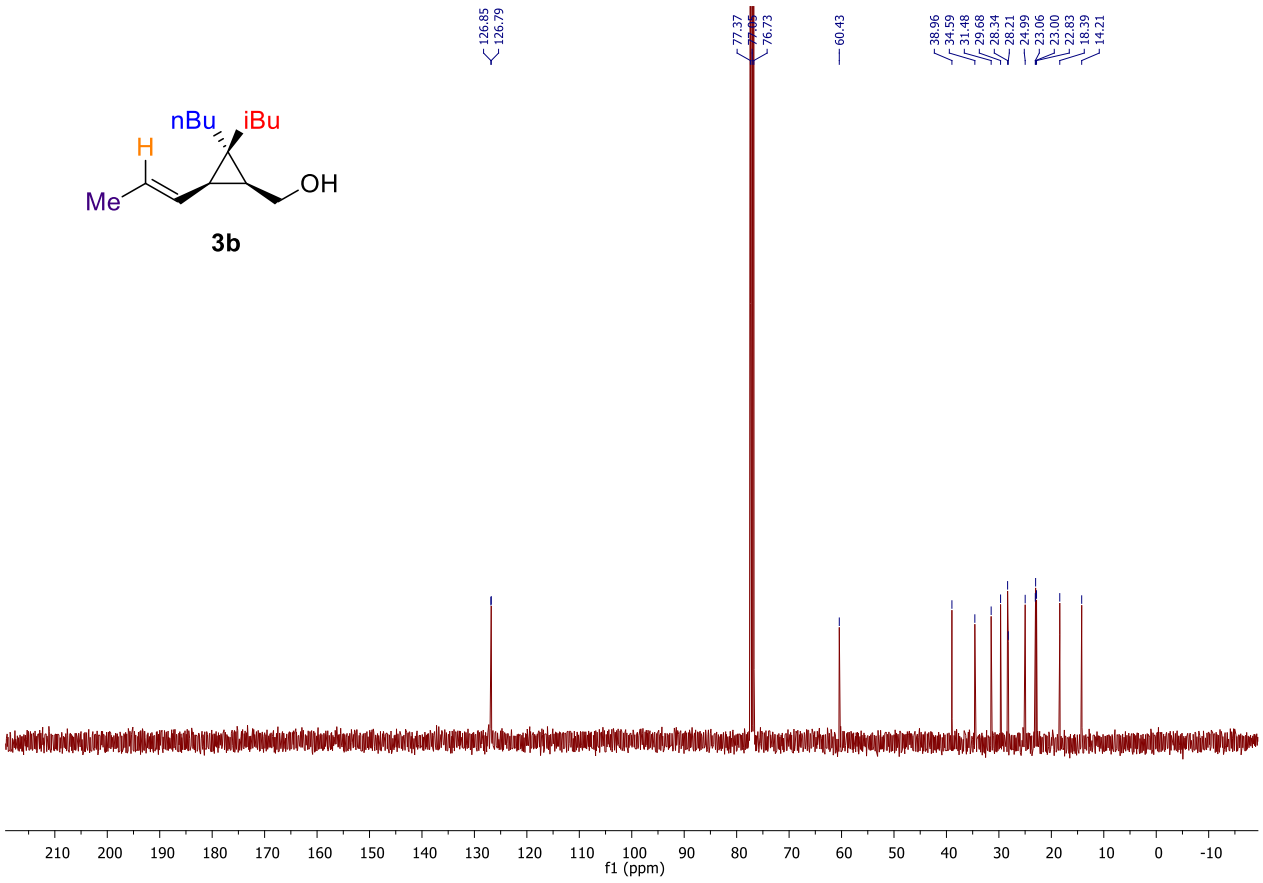
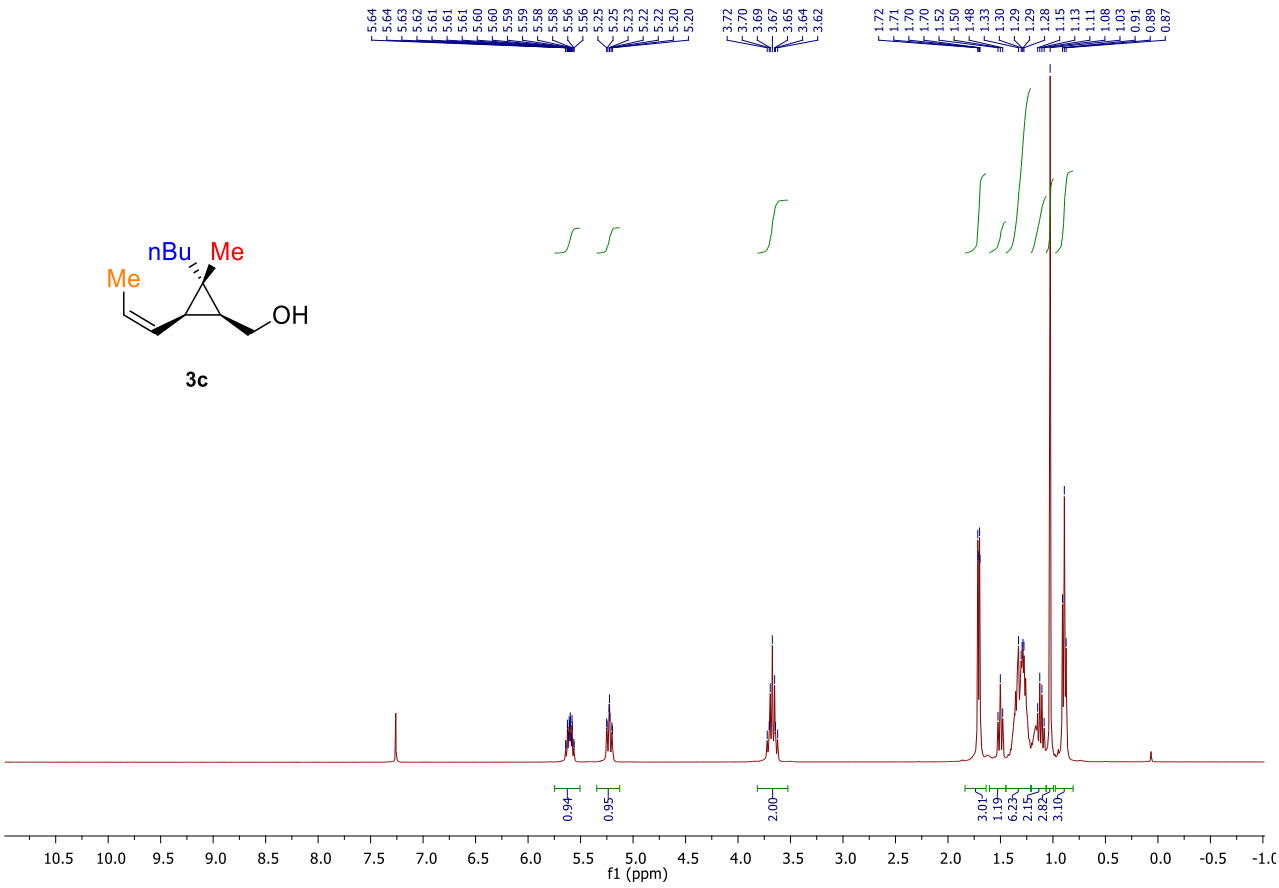
f1 (ppm)

NMR spectras of vinylcyclopropylcarbinols 3b-v



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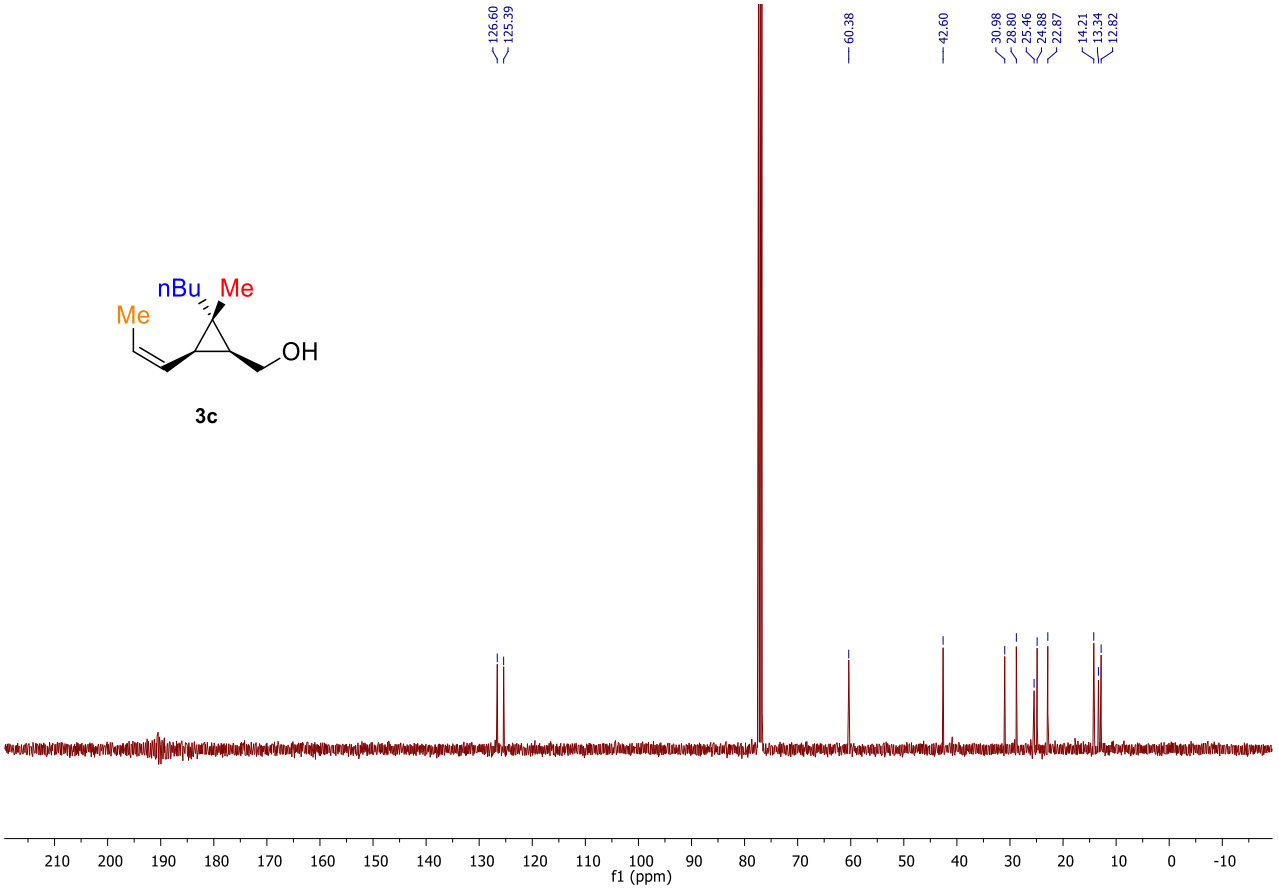
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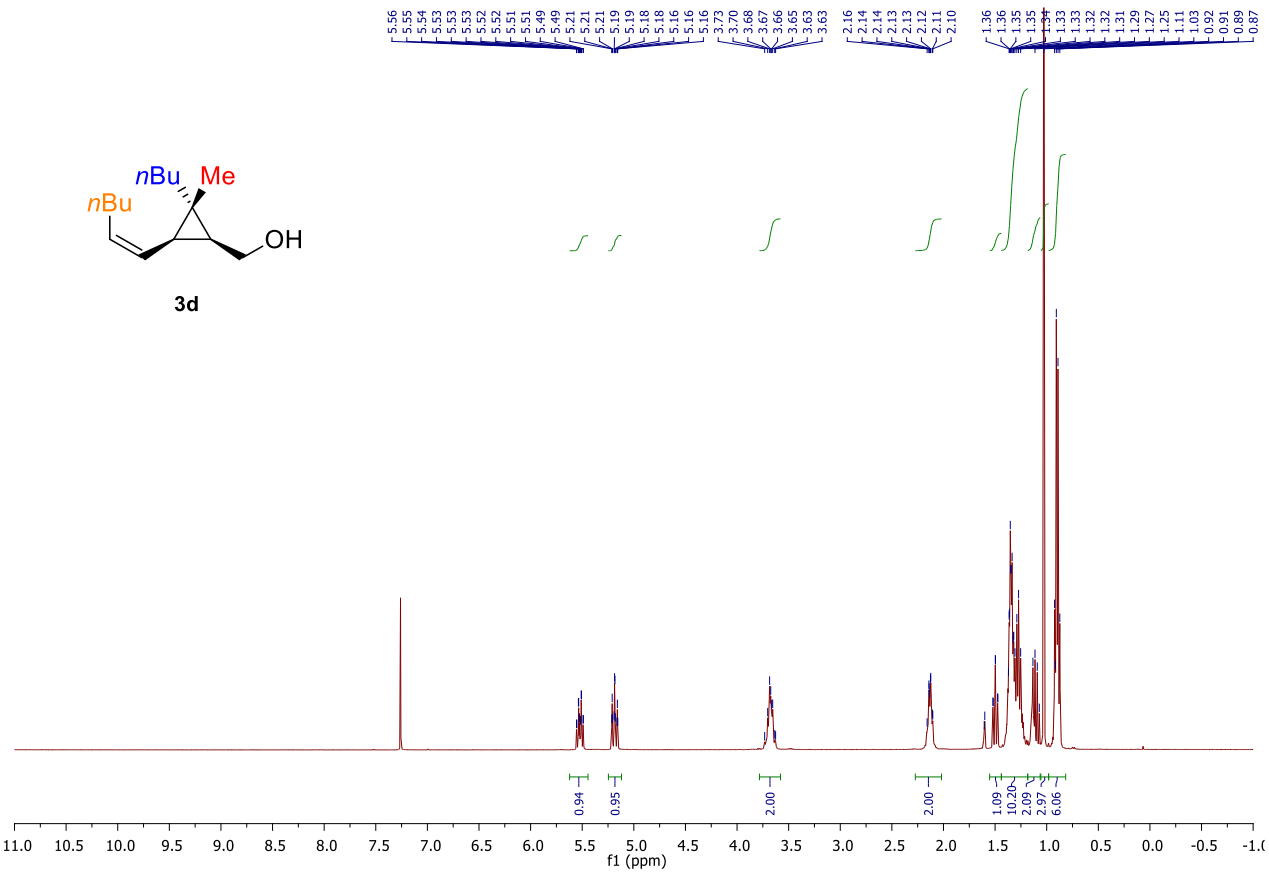
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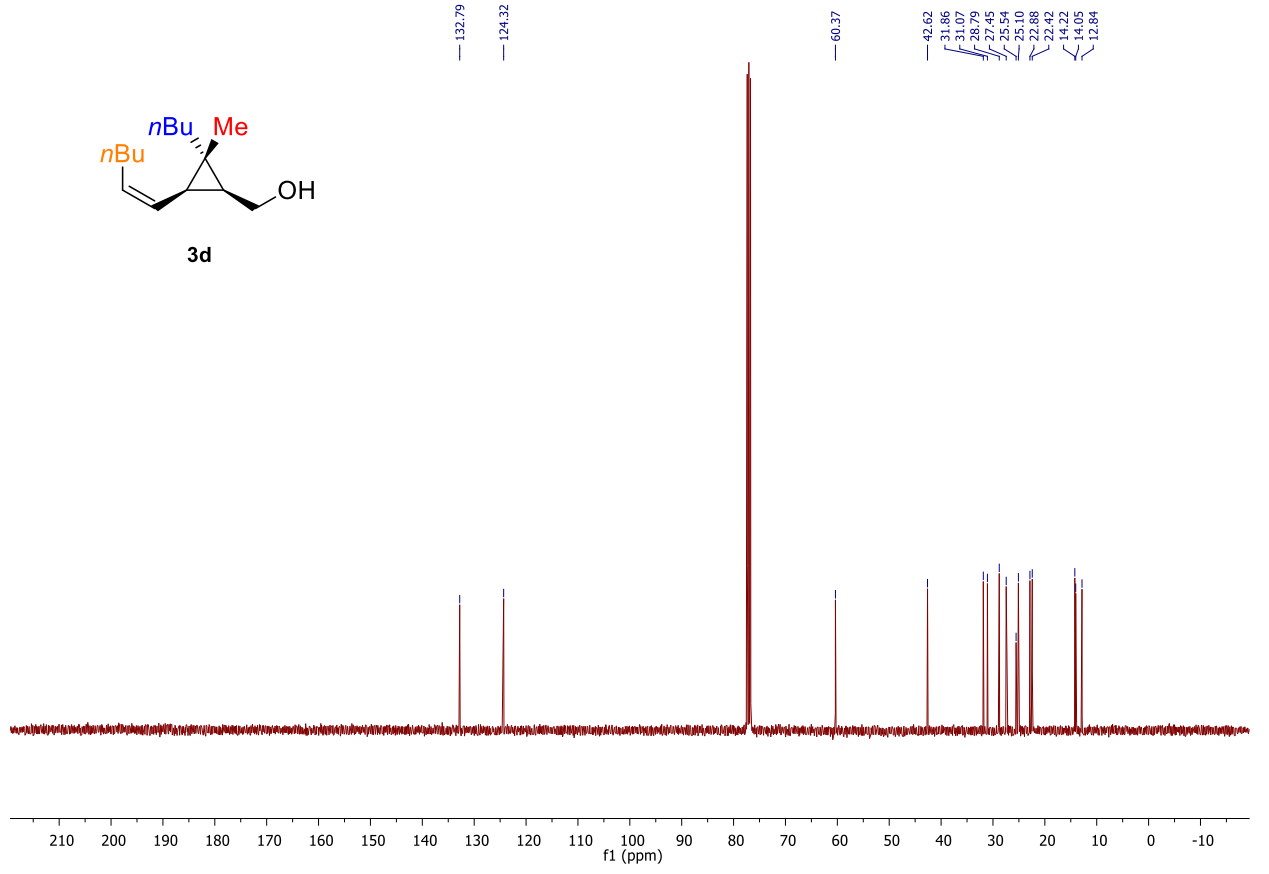
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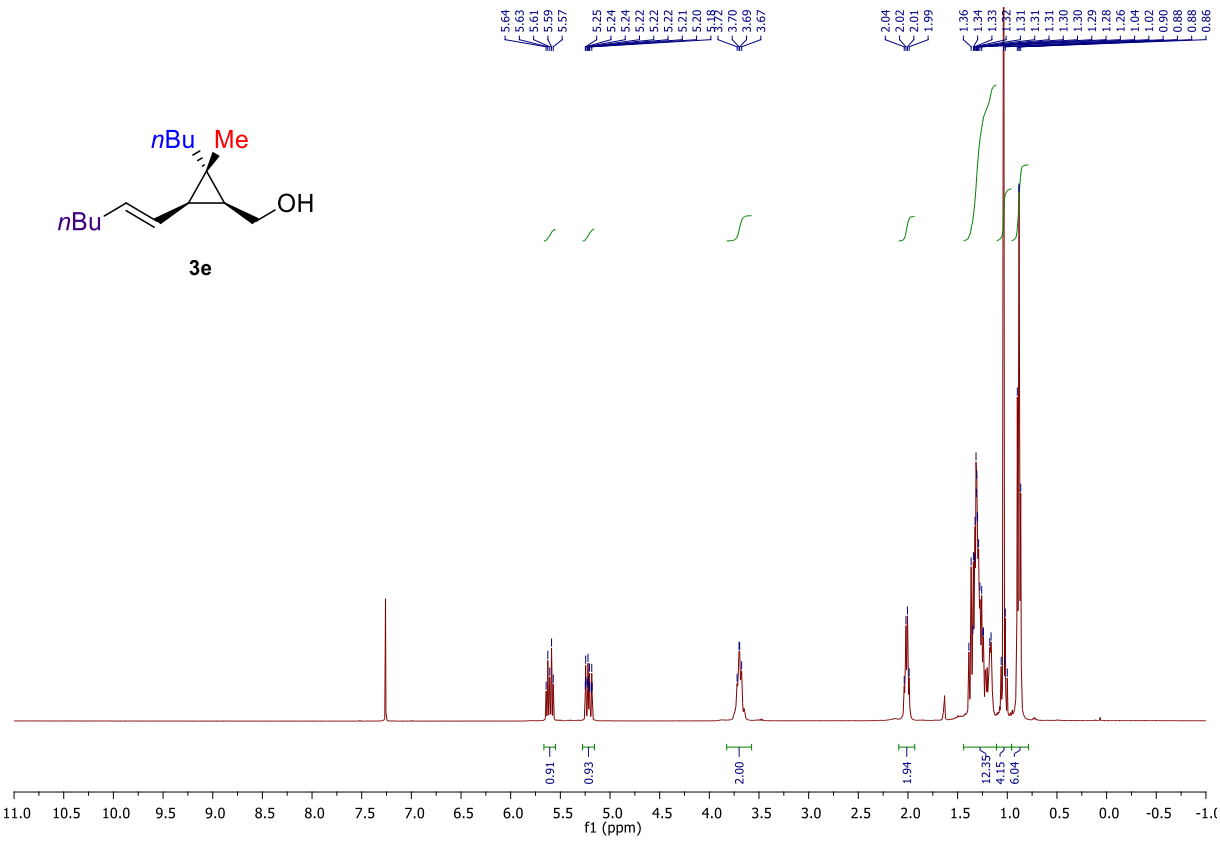
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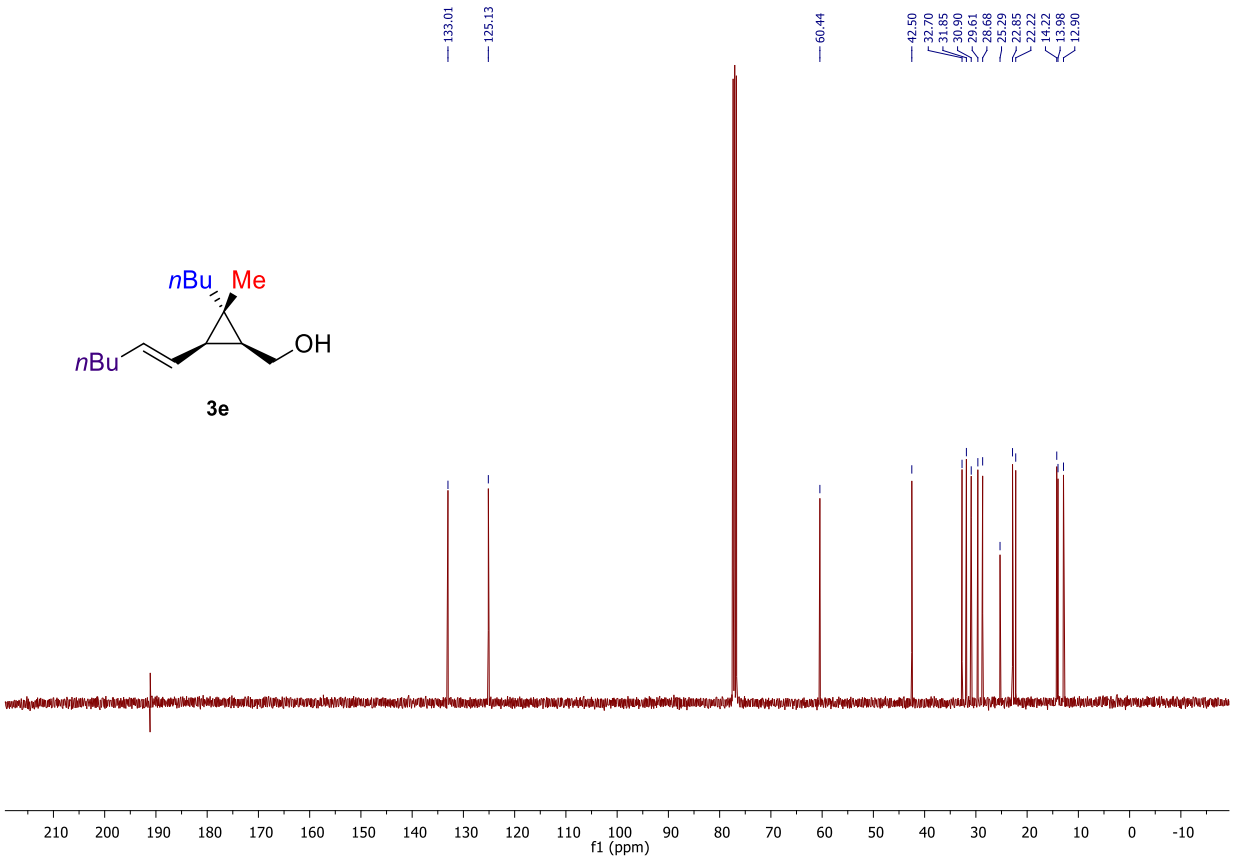
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3e
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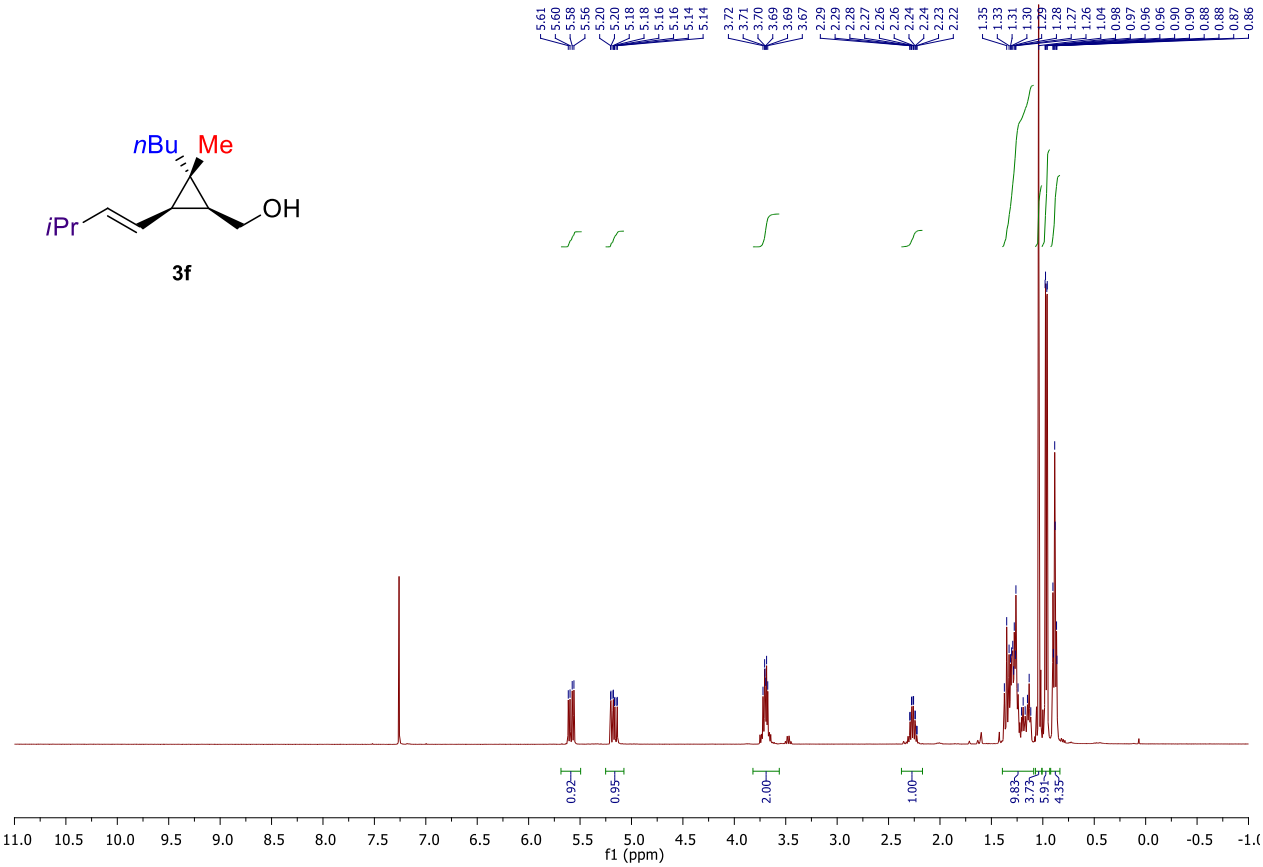
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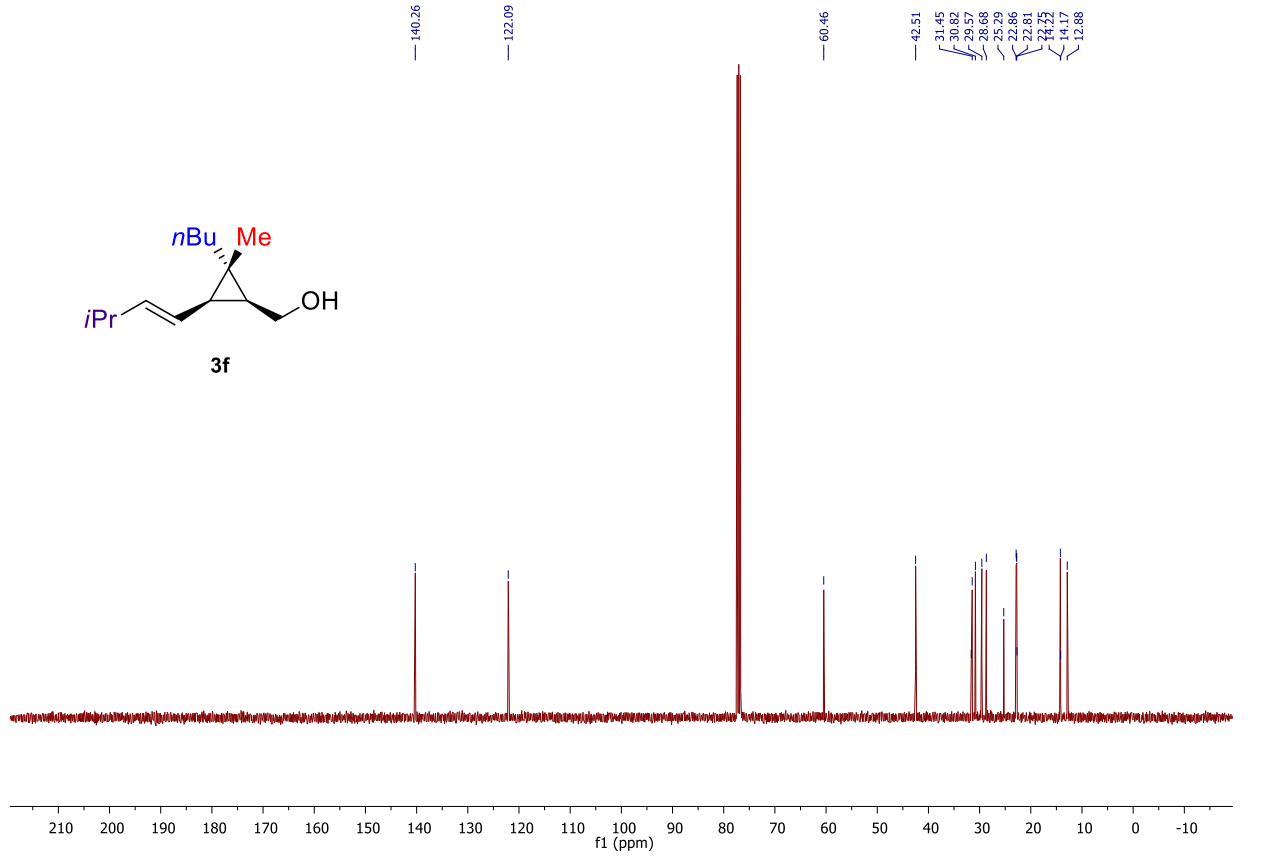
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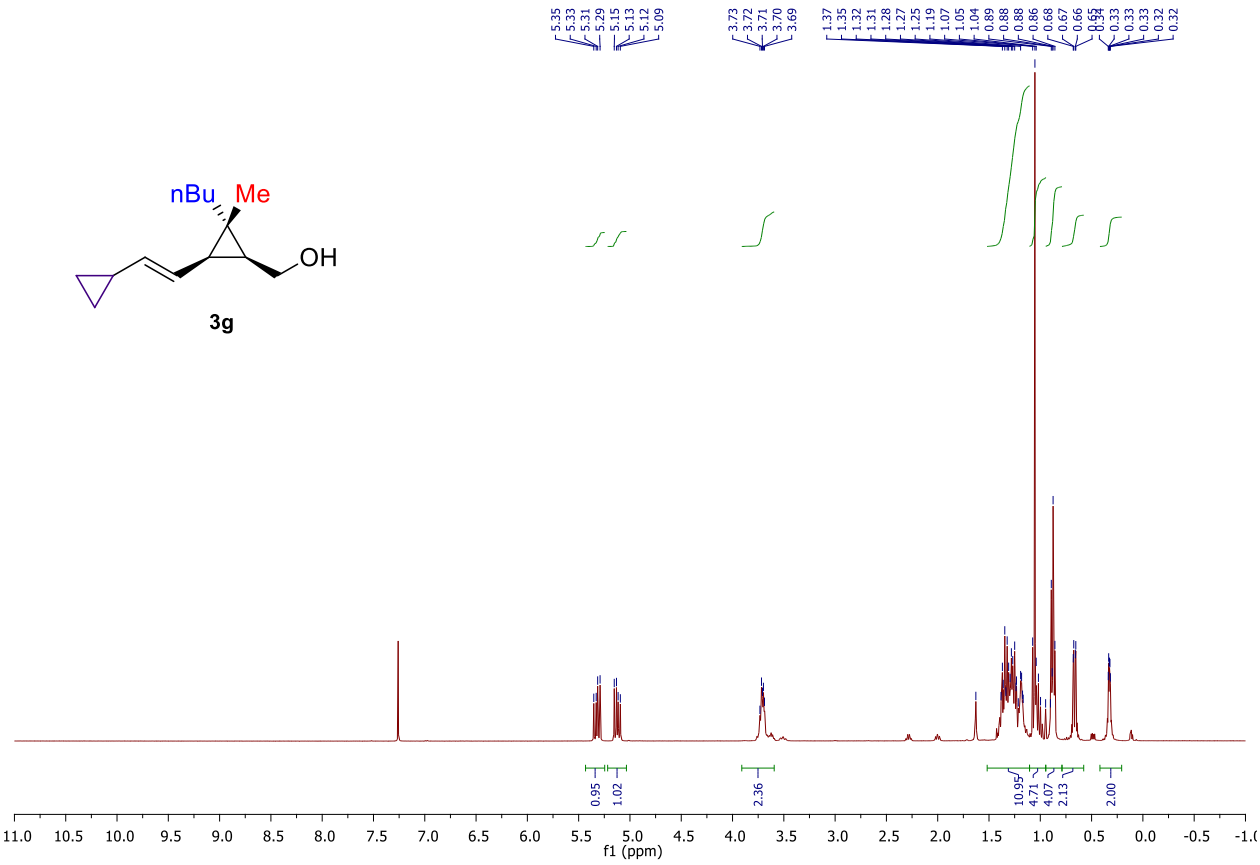
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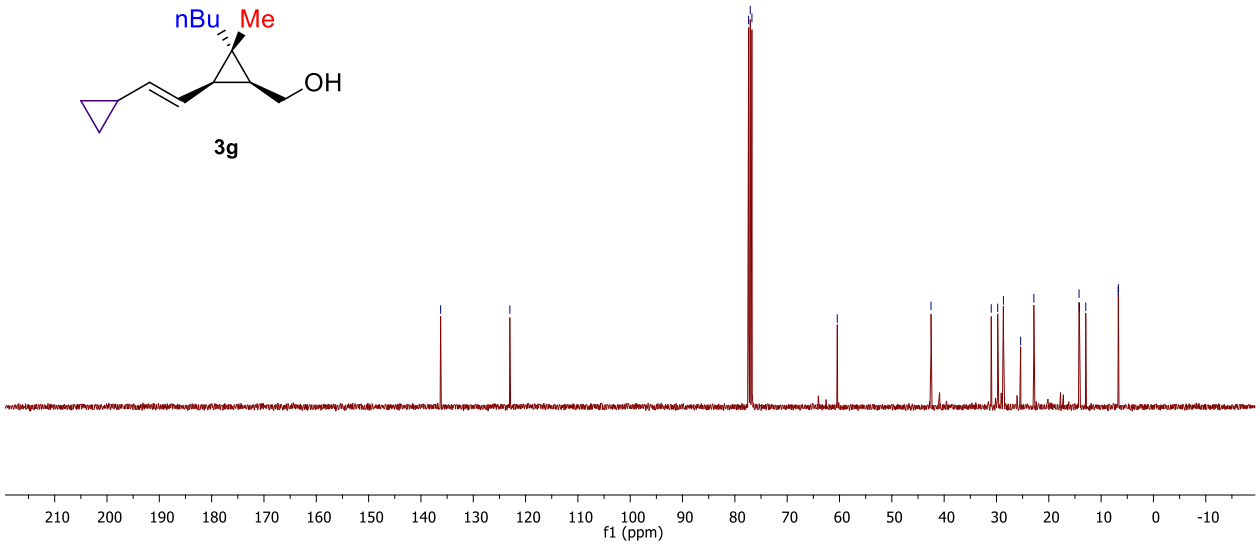
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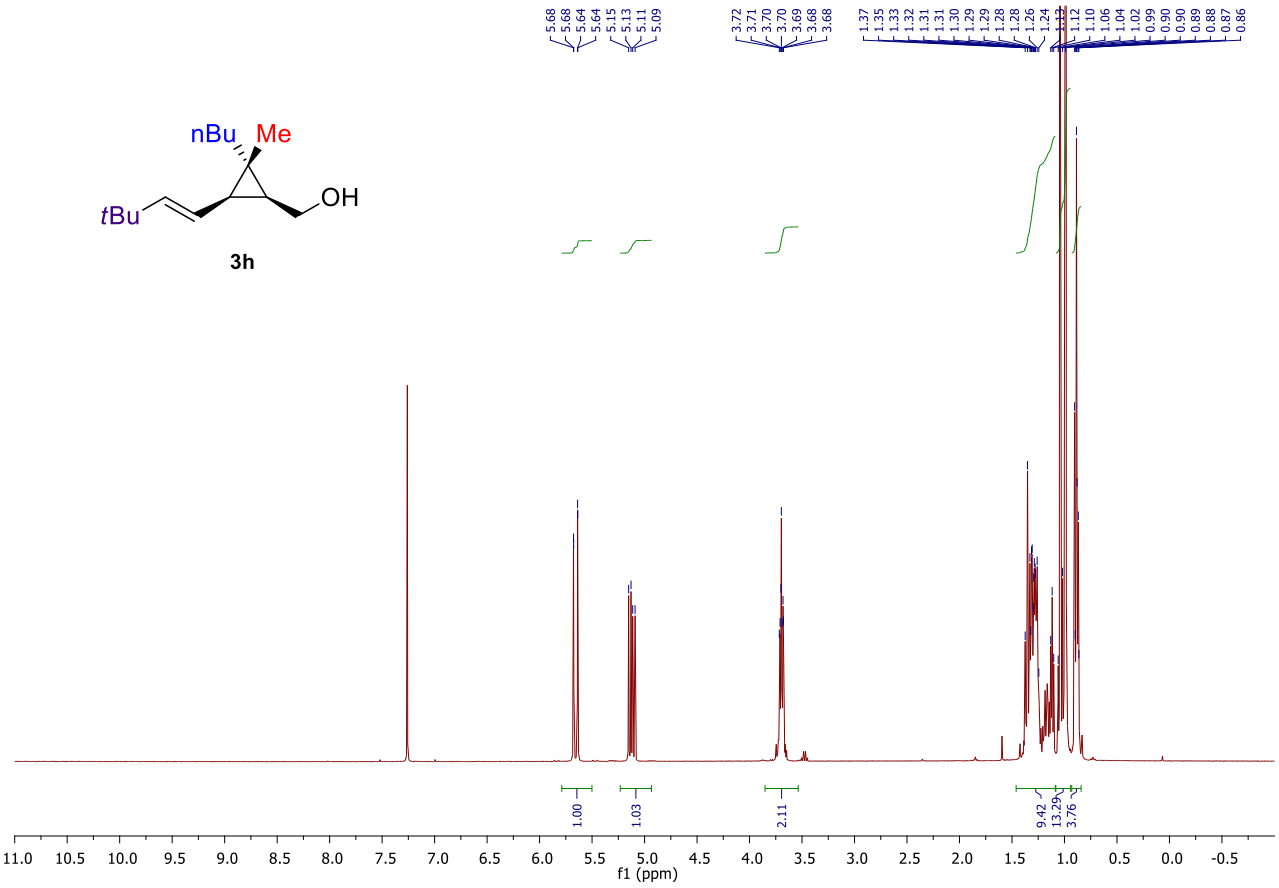
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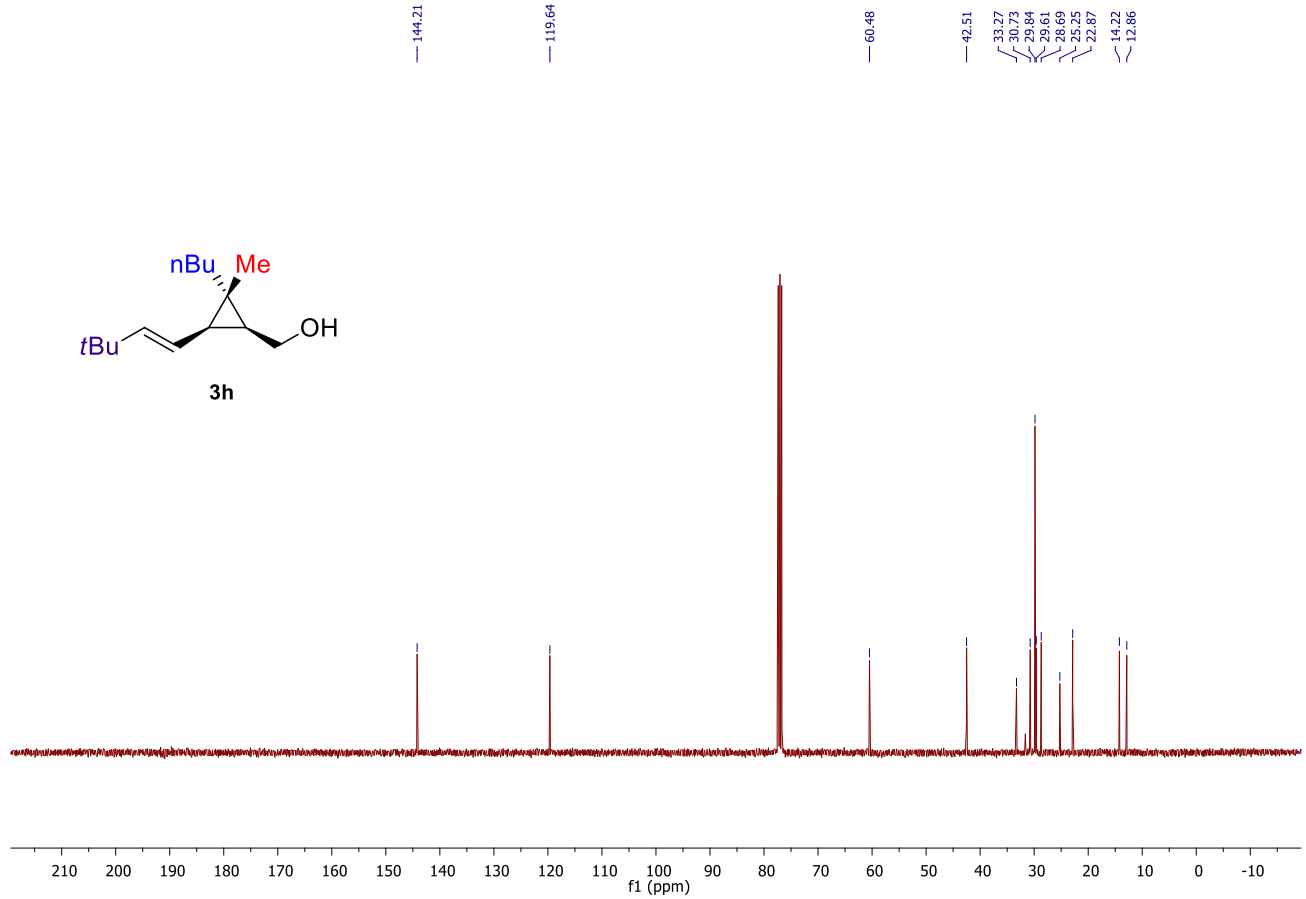
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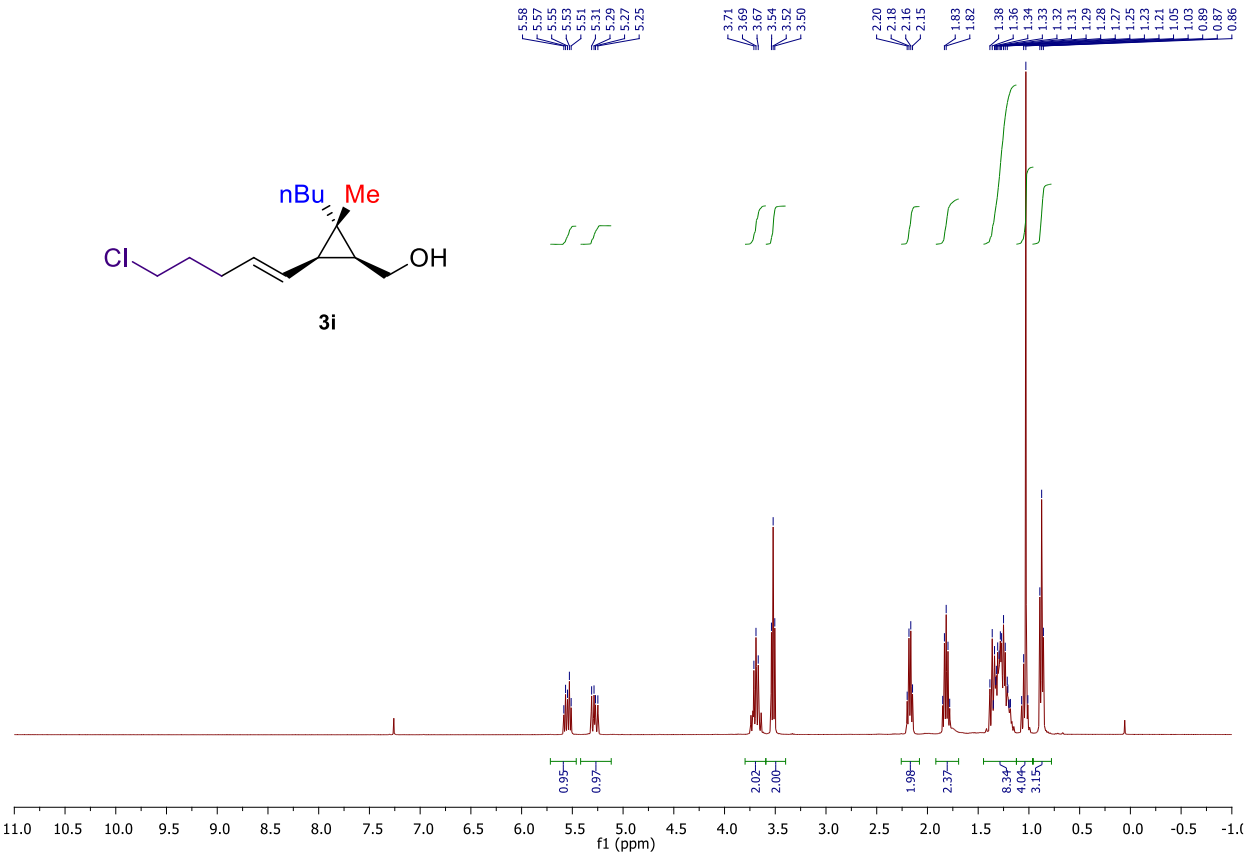
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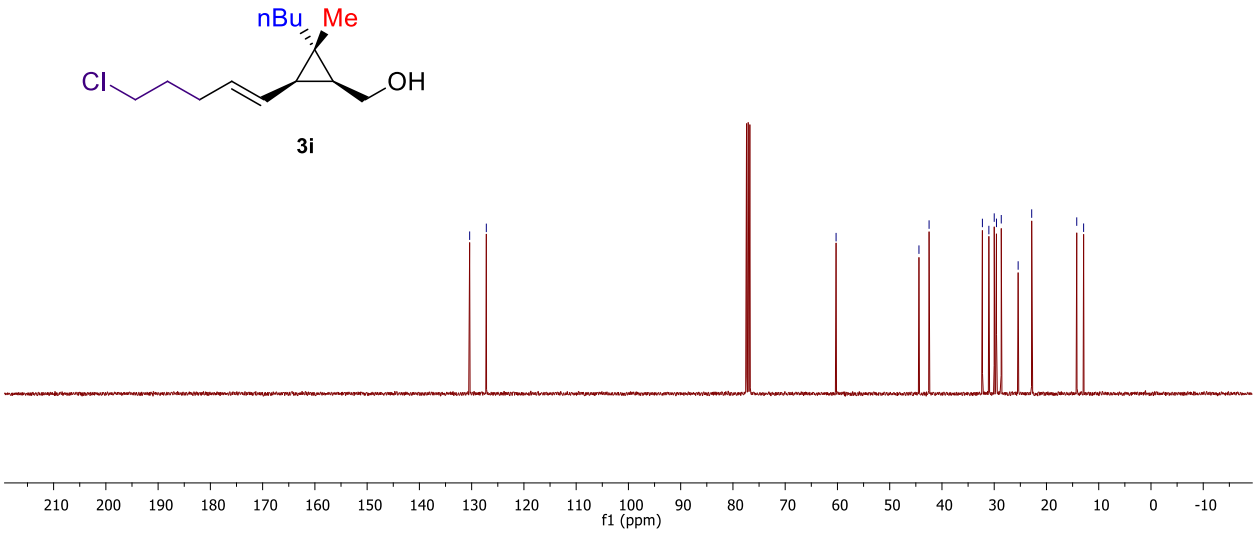
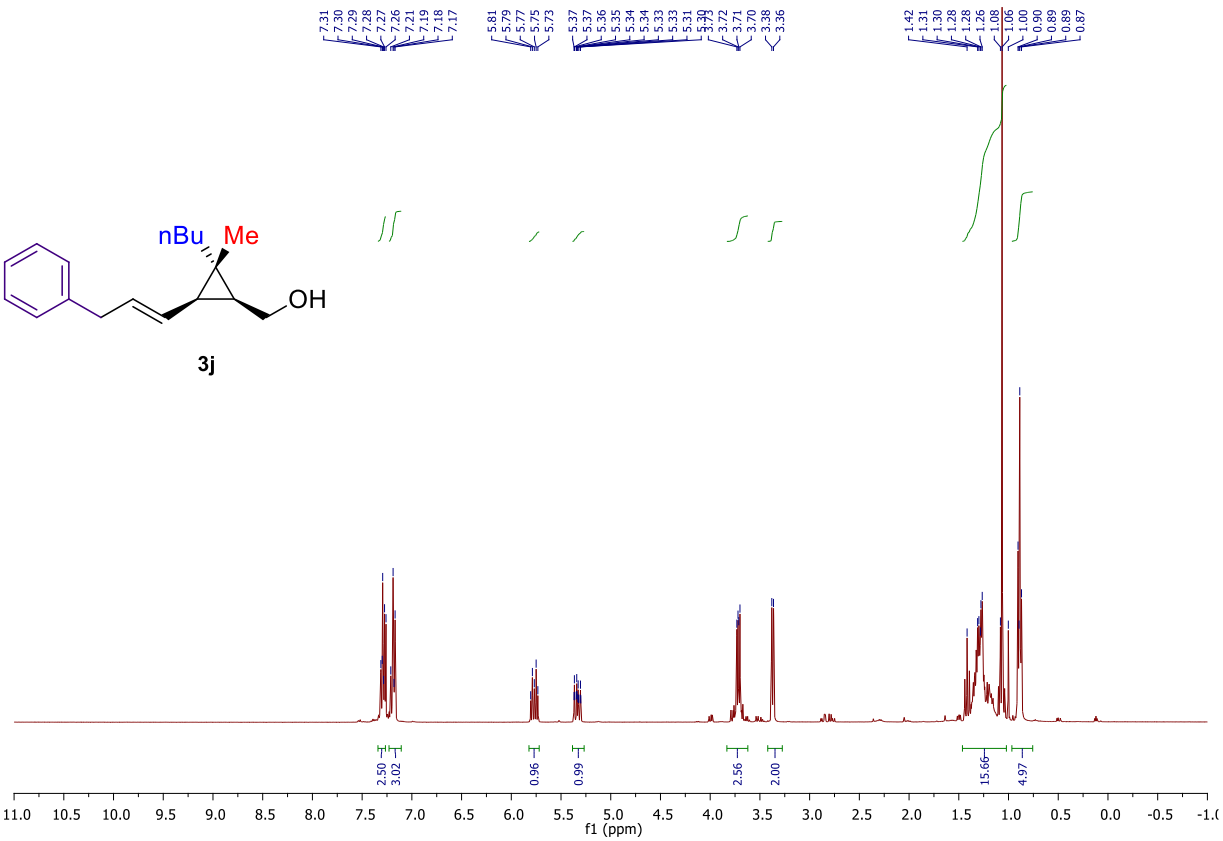
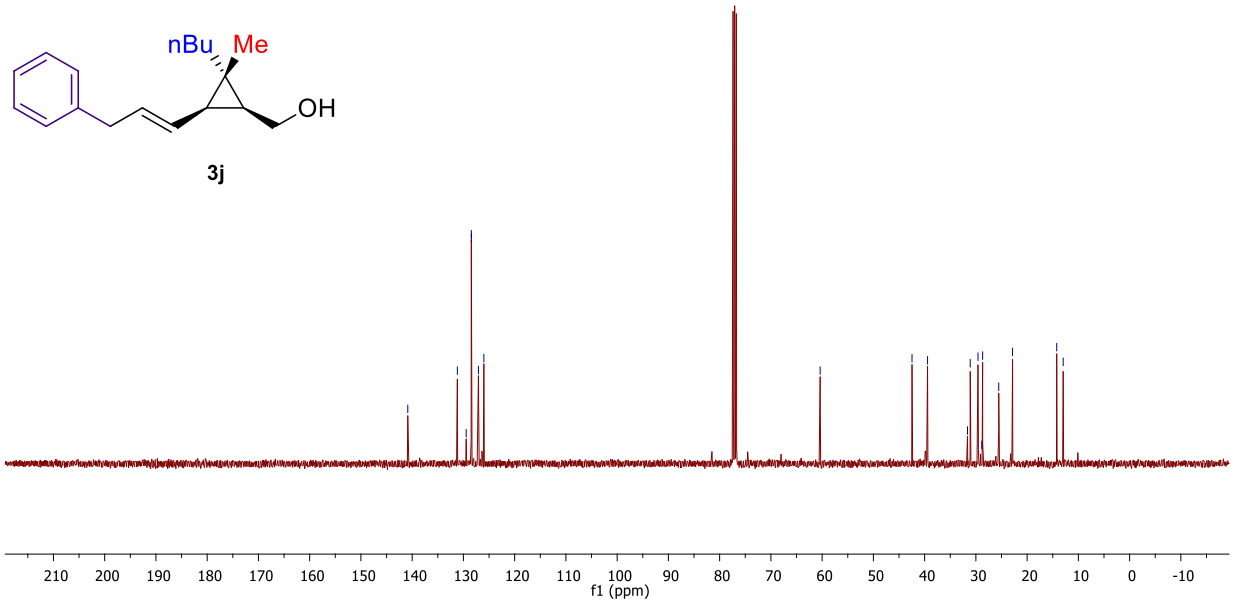
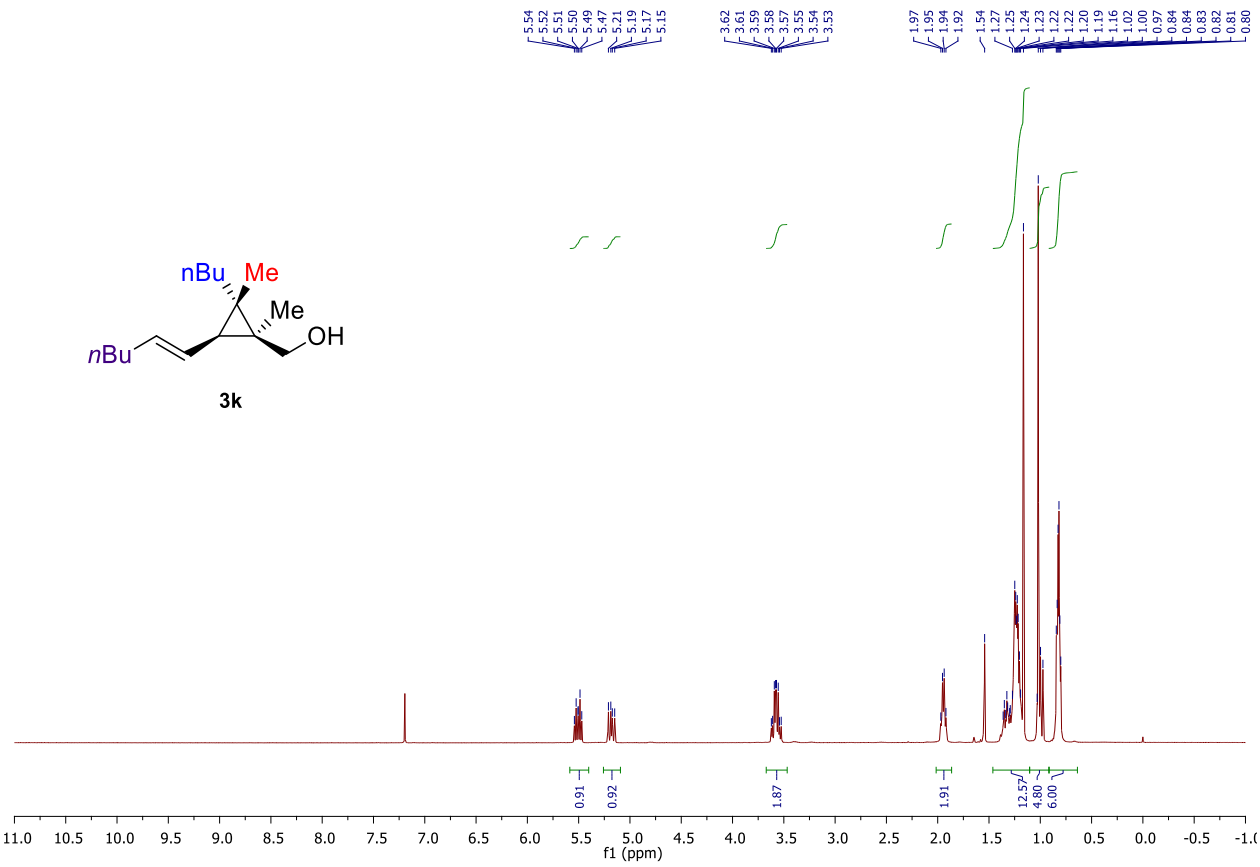
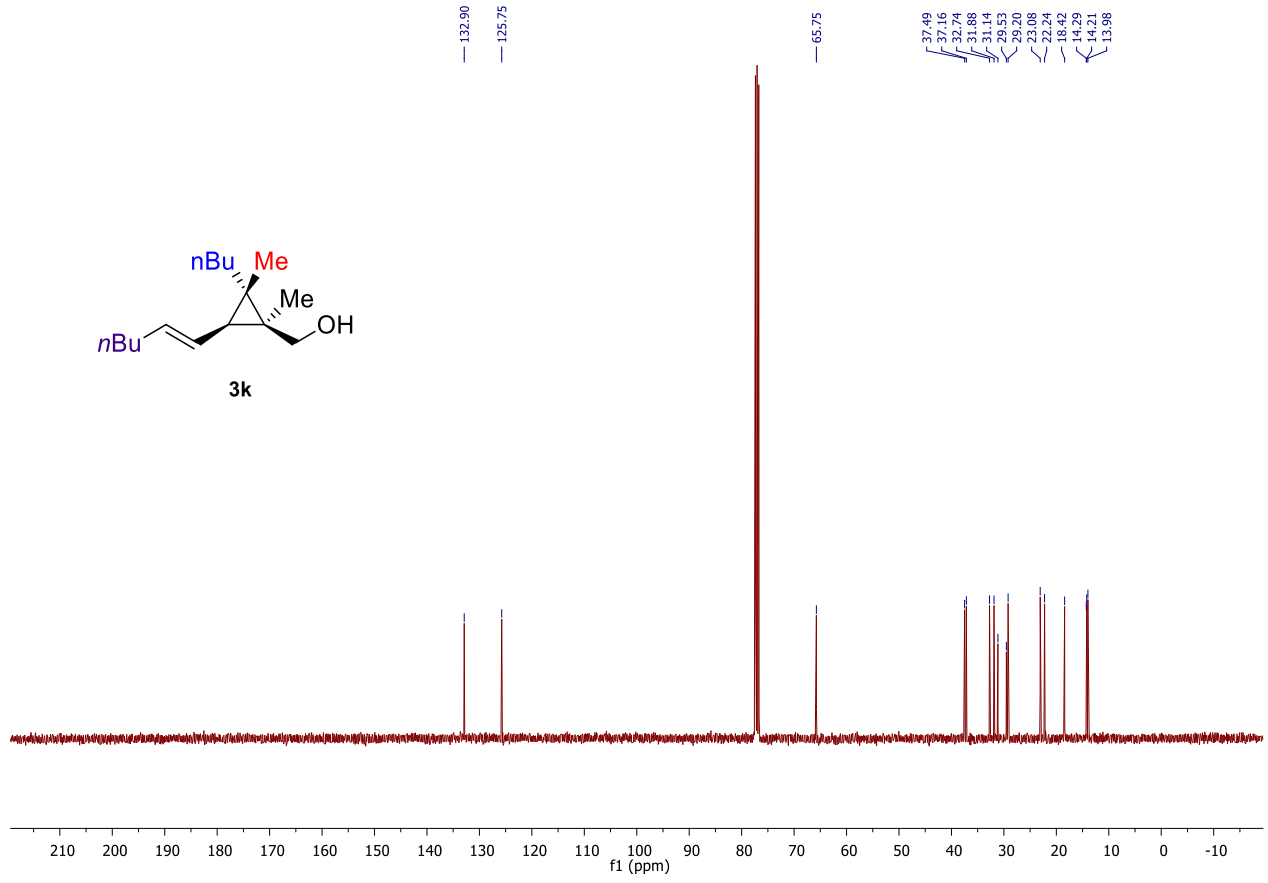

nBu
Me
Cl
OH
3i
f1 (ppm)


nBu
Me
OH
3j
f1 (ppm)


nBu
Me
OH
3j
f1 (ppm)


nBu
Me
Me
OH
nBu
3k
f1 (ppm)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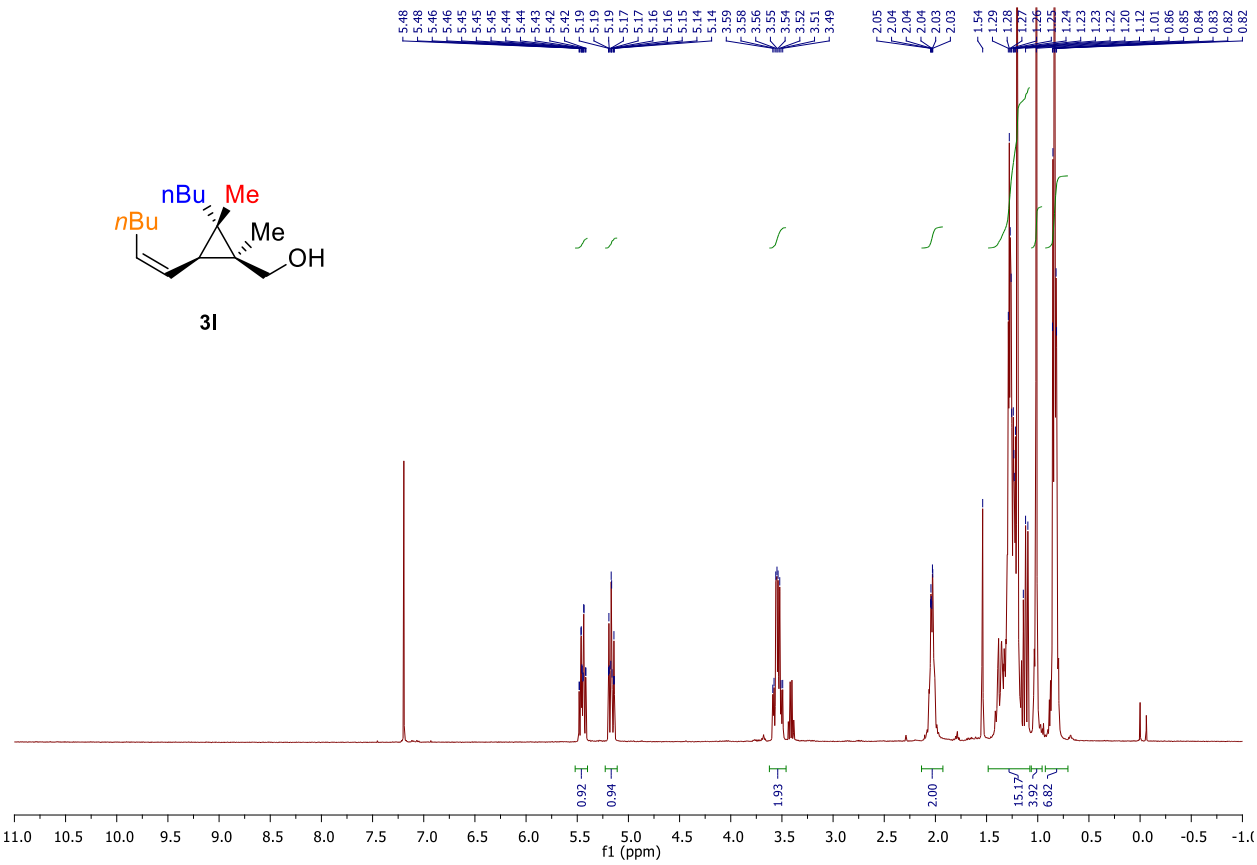
Me
Me
OH
nBu
3k
f1 (ppm)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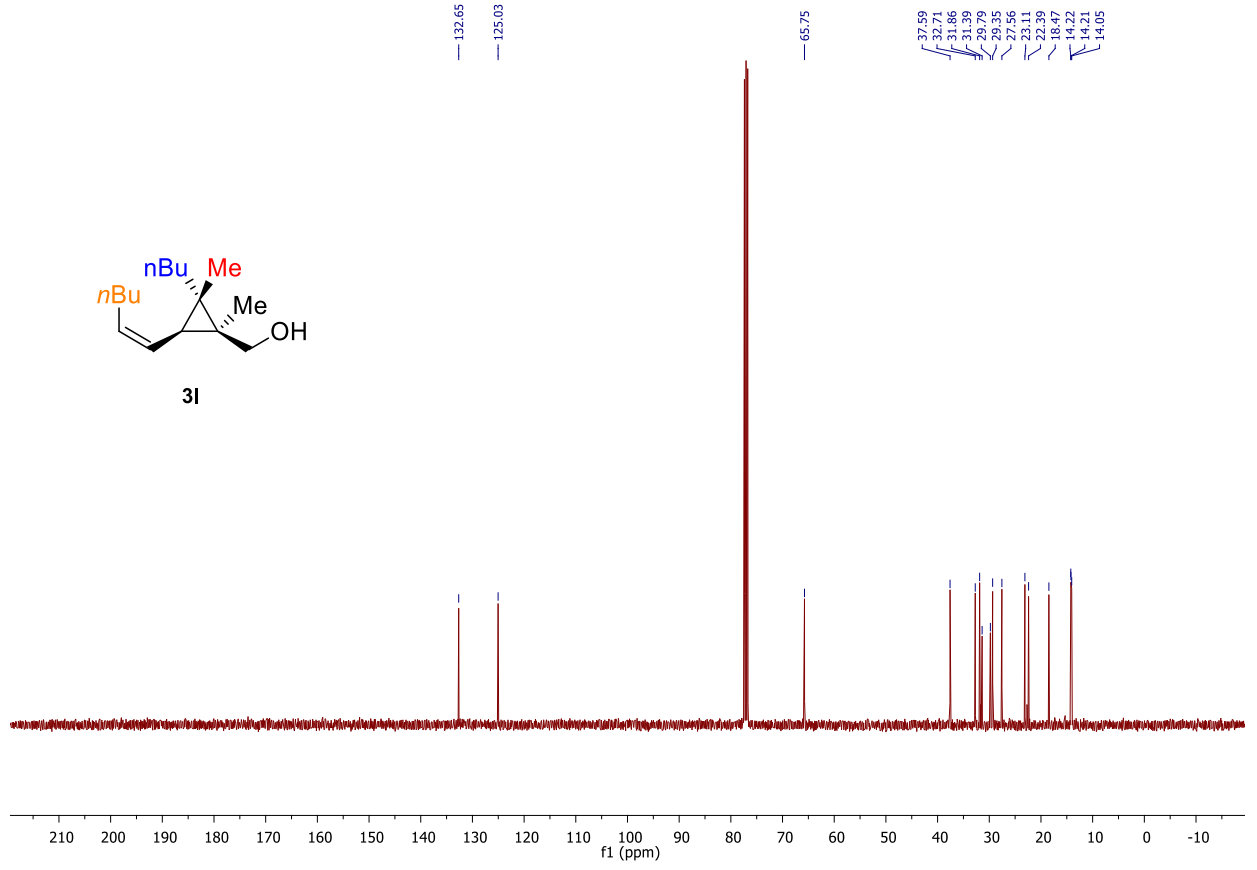
Me
nBu
Me
OH
3l
f1 (ppm)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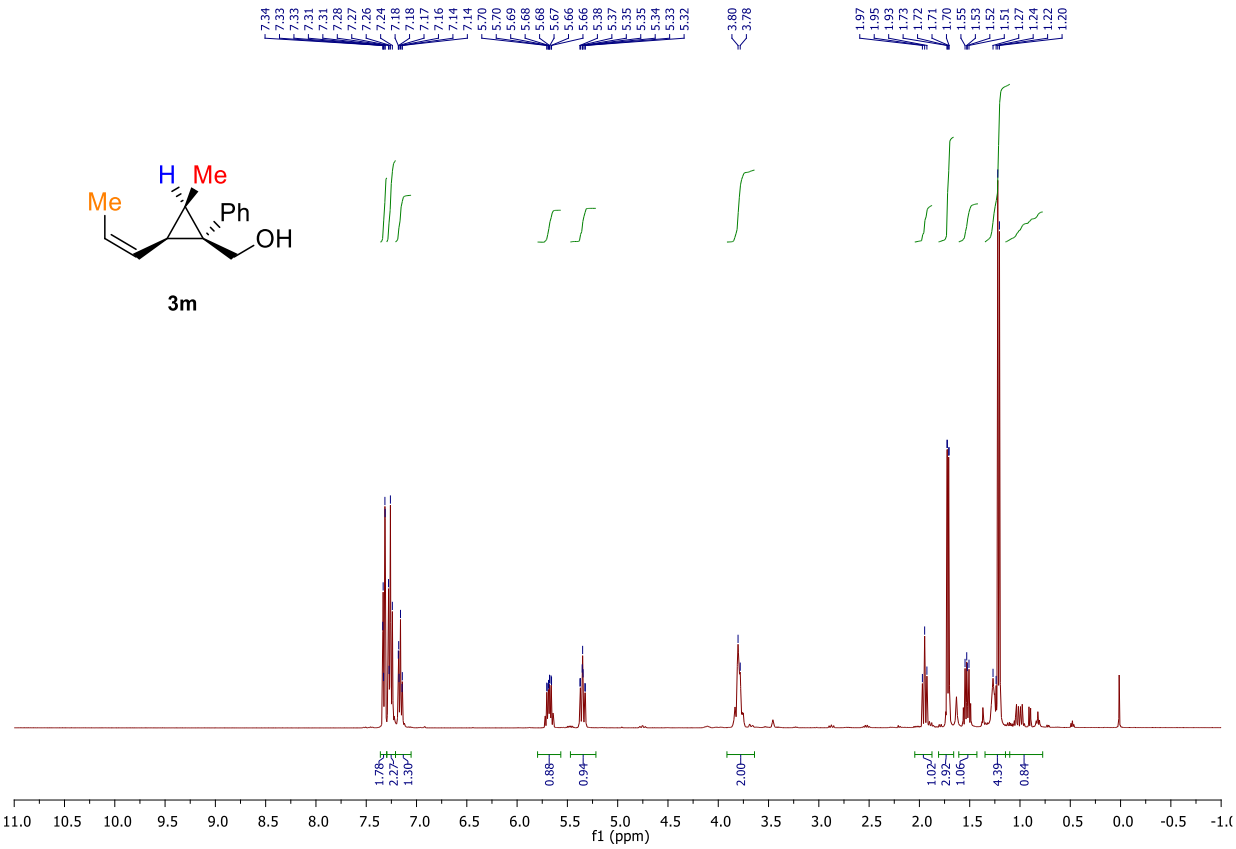
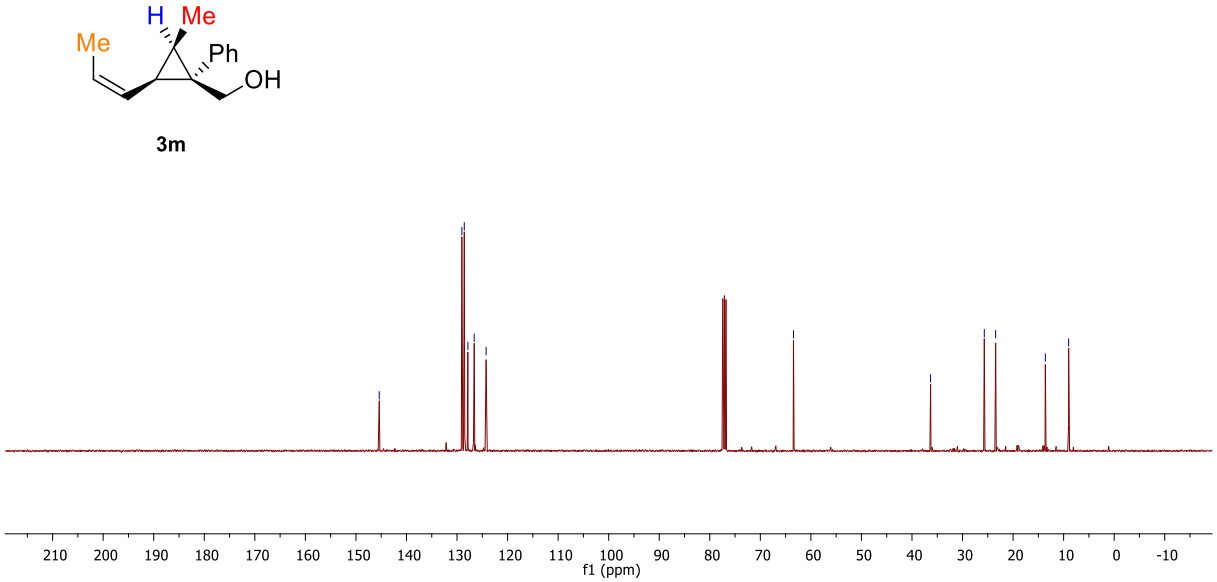
Me
nBu
Me
OH
3l
f1 (ppm)


H
Me
Me
Ph
OH
3m
f1 (ppm)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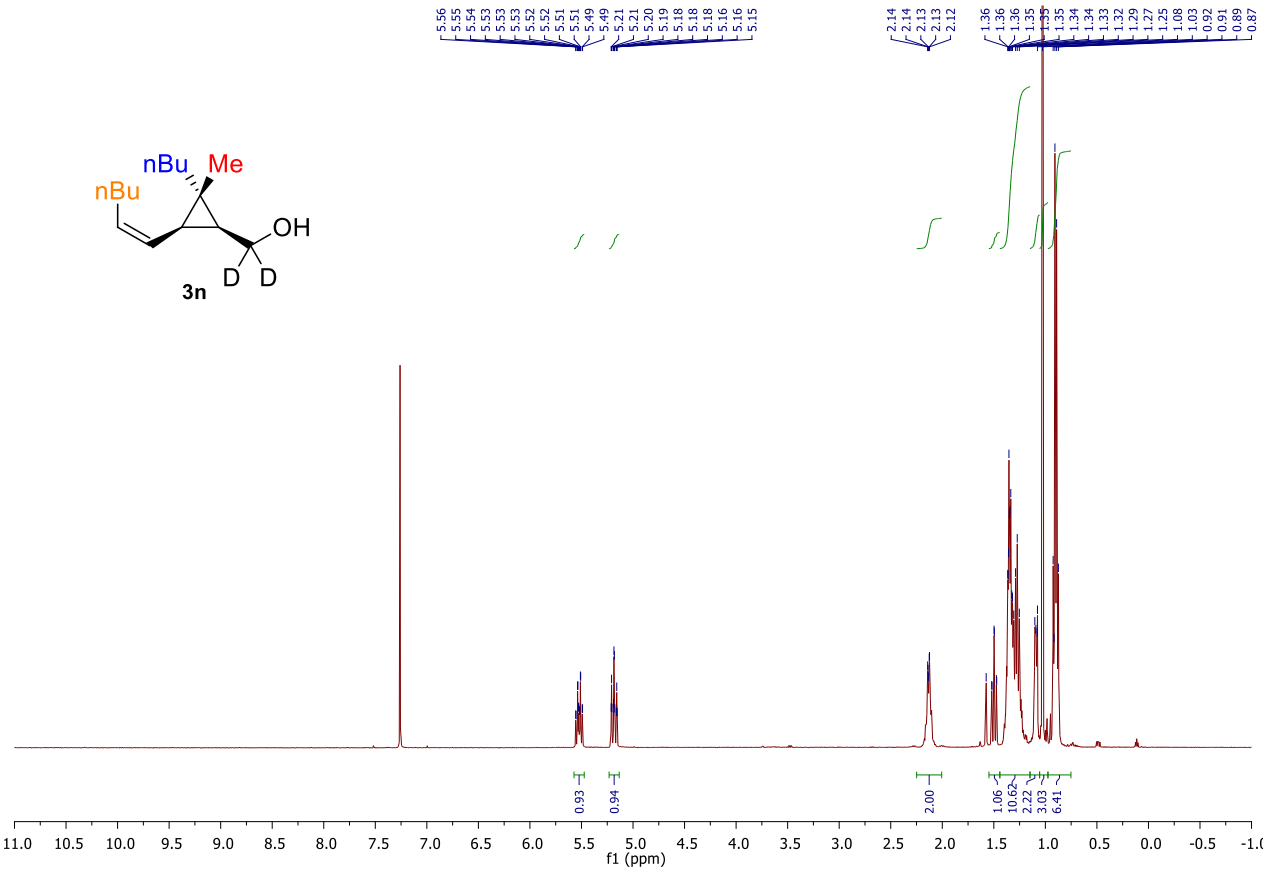
Me
Me
Ph
OH
3m
f1 (ppm)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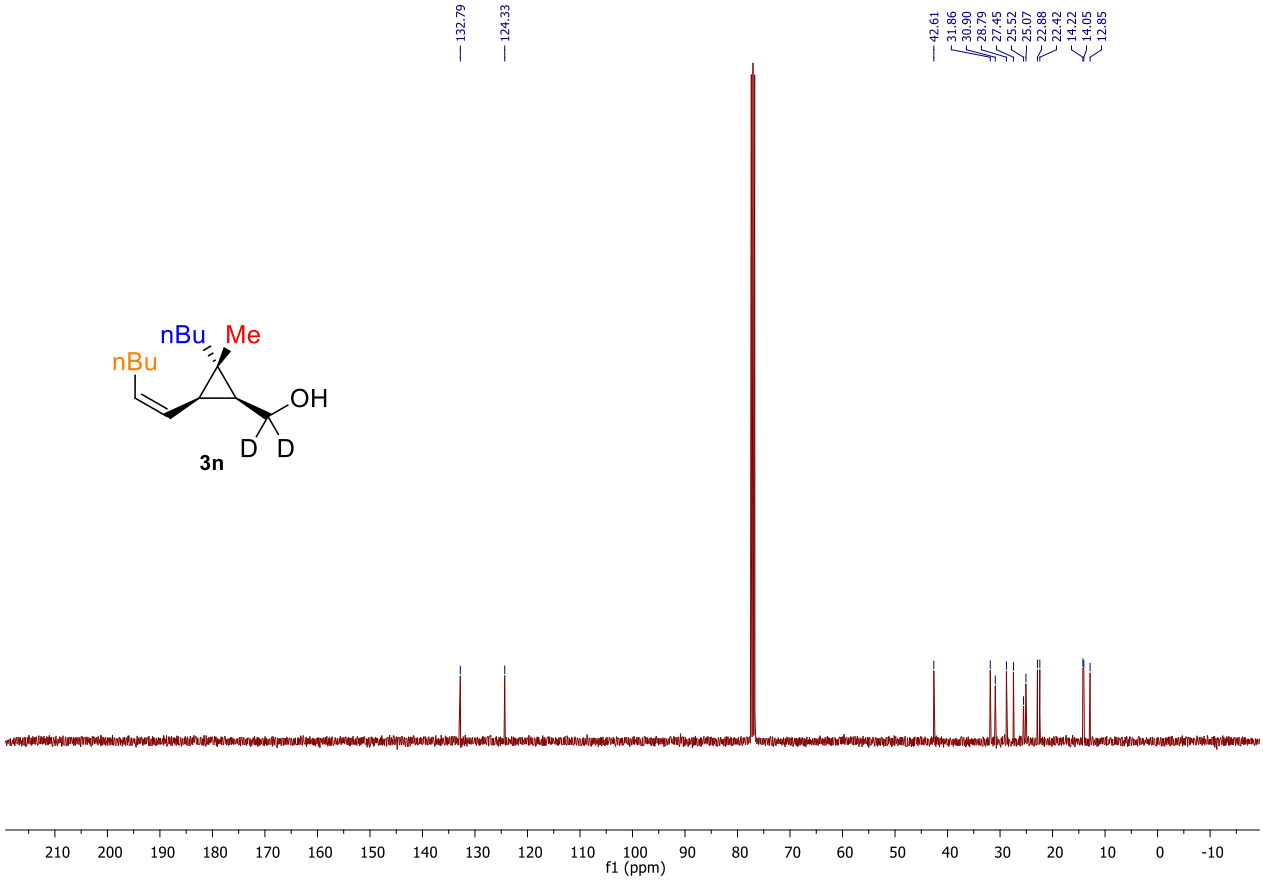
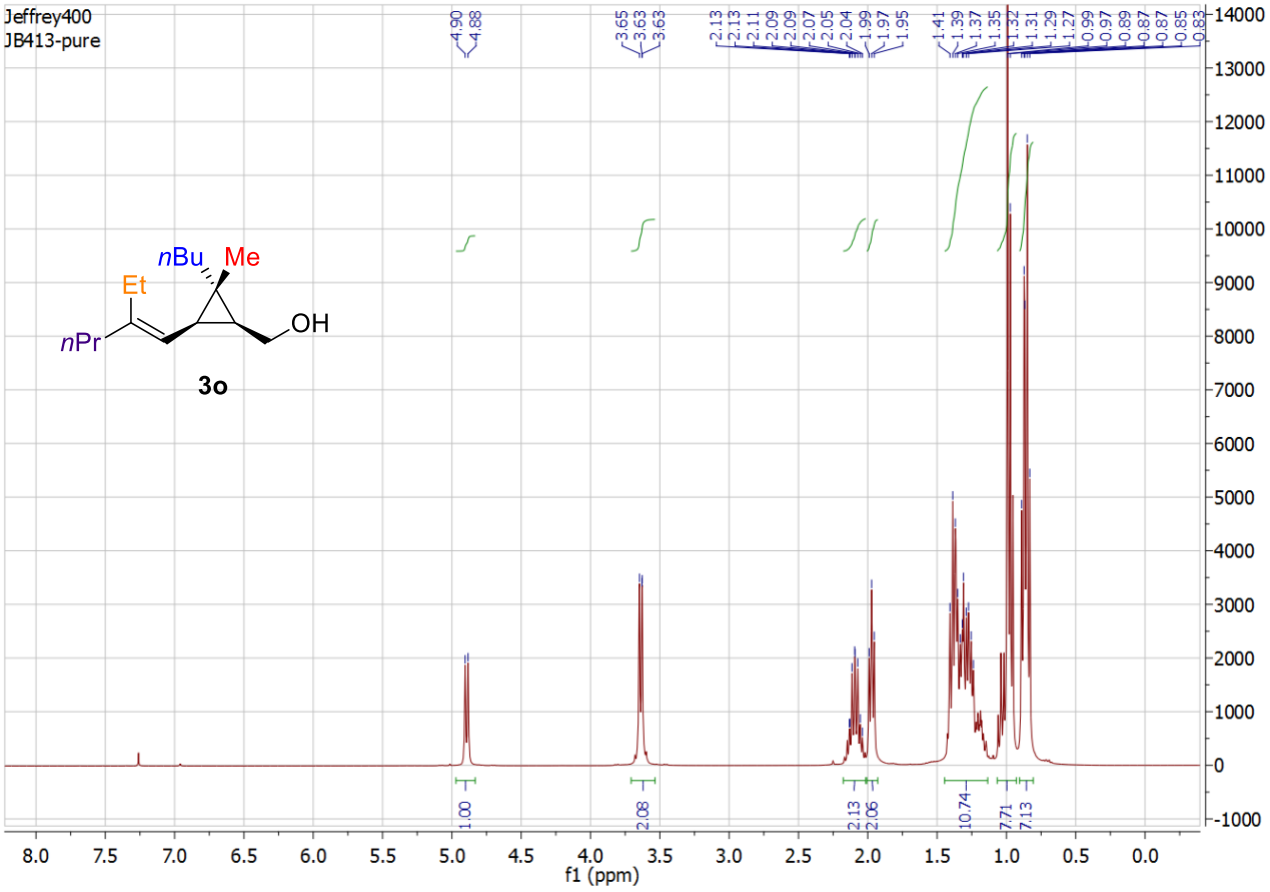
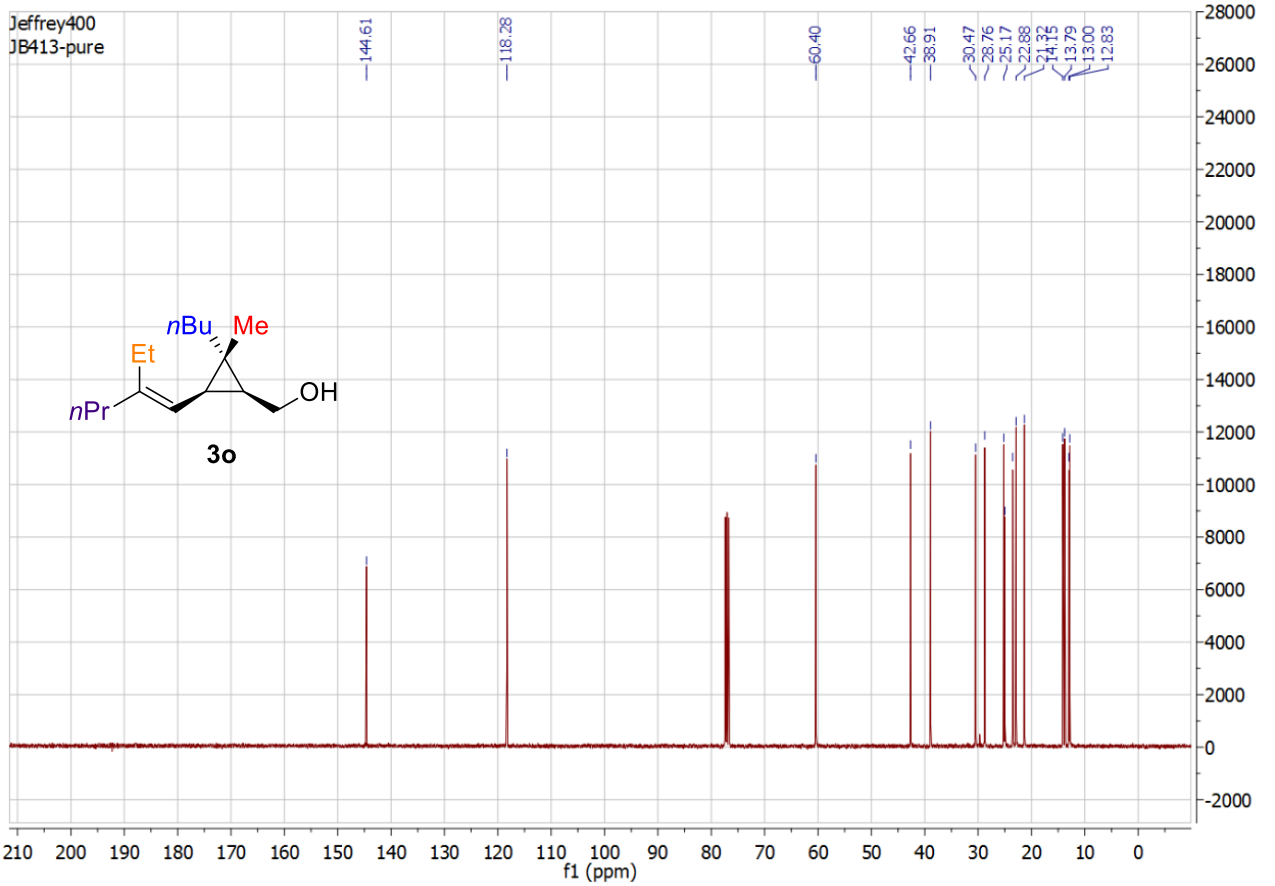
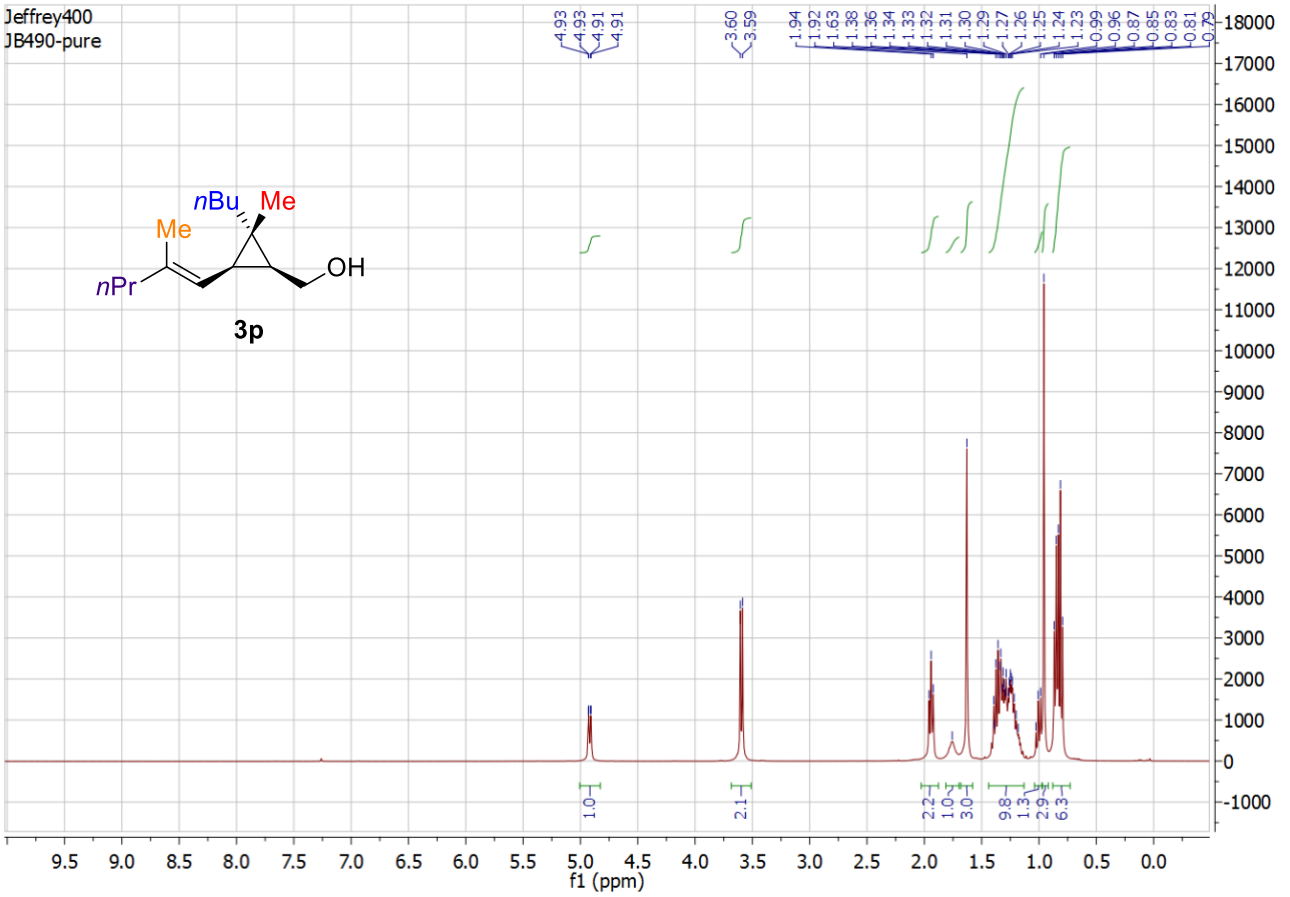
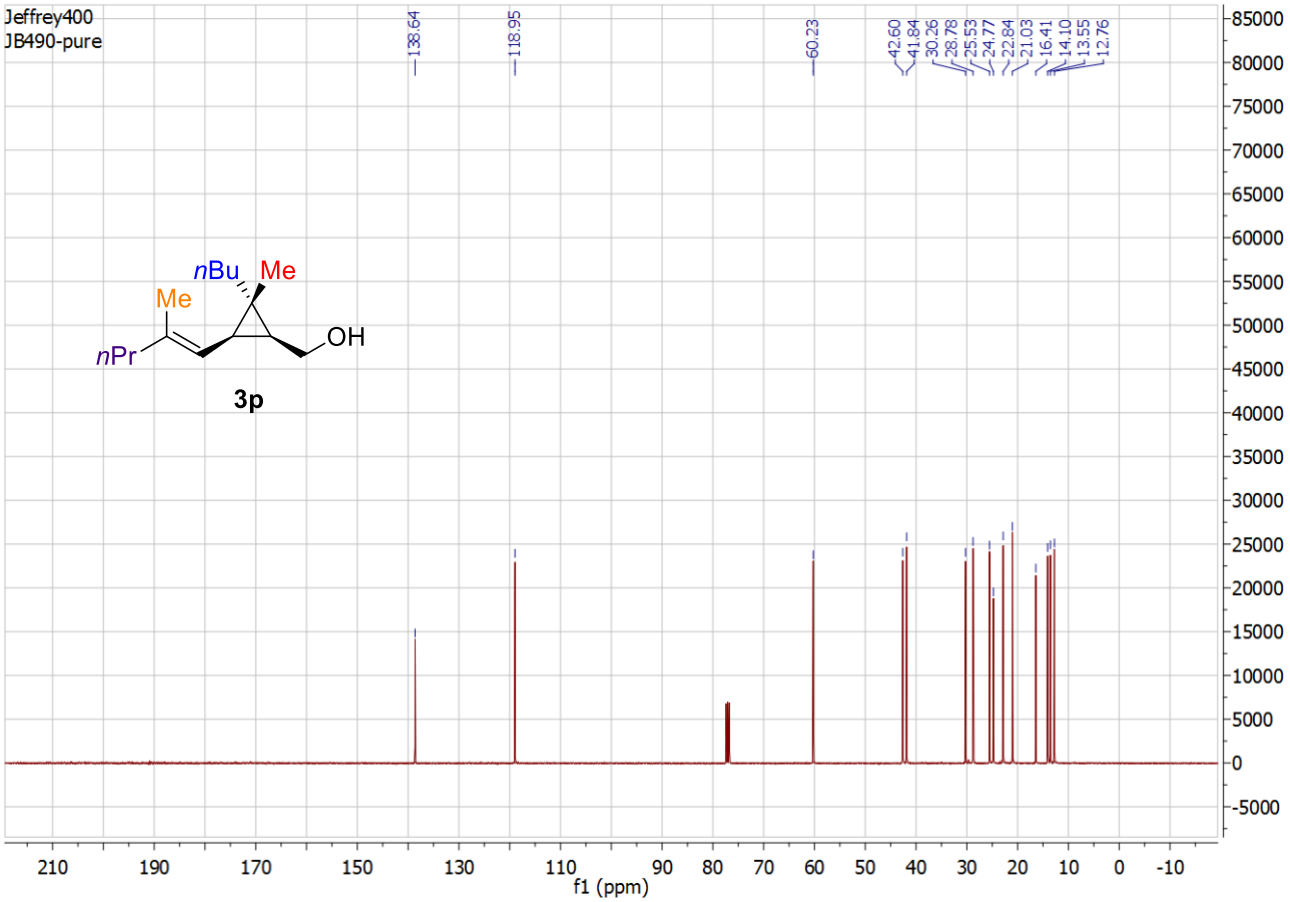
Me
nBu
OH
D D
3n
f1 (ppm)

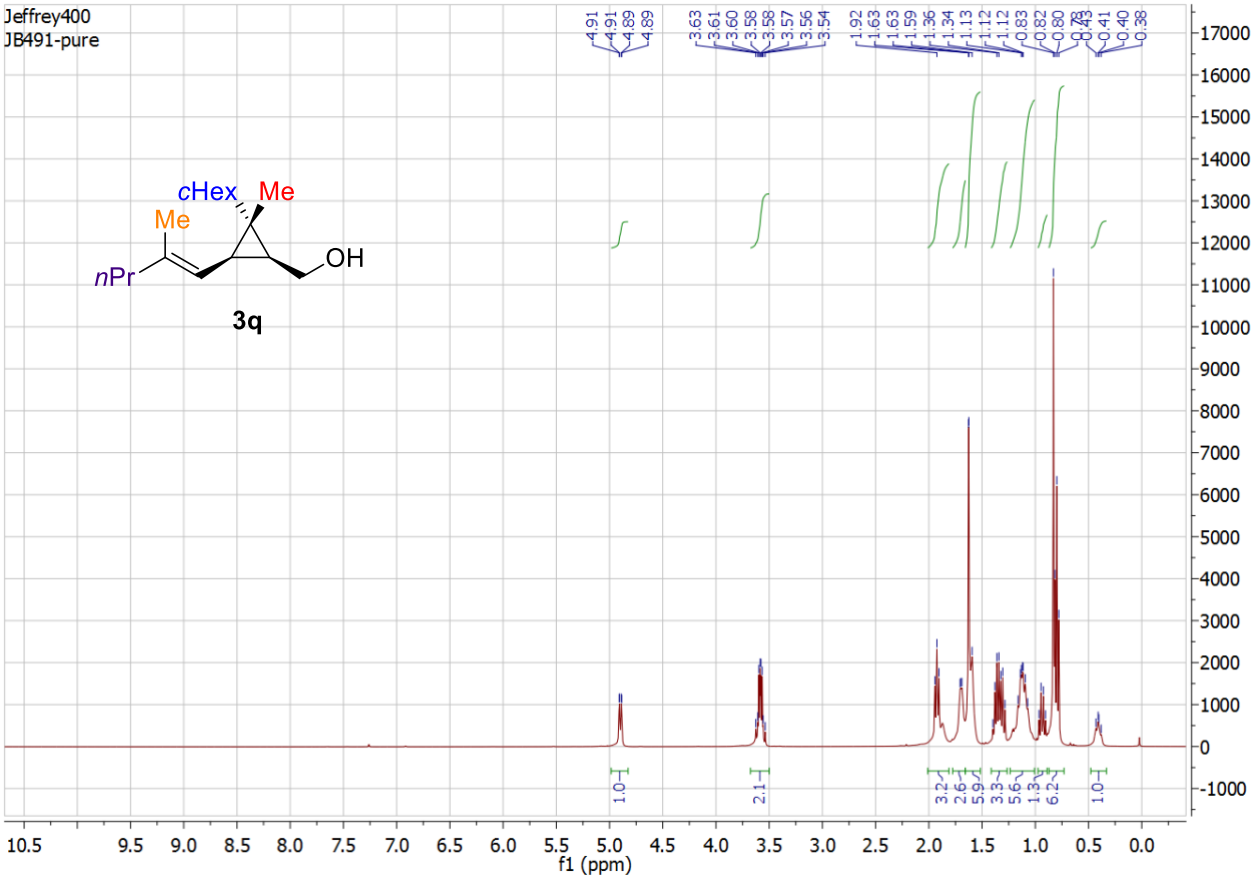

nBu
Me
nBu
OH
D D
3n
f1 (ppm)


Jeffrey400
JB413-pure
nBu
Me
Et
nPr
OH
3o
f1 (ppm)


Jeffrey400
JB413-pure
nBu
Me
Et
nPr
OH
3o
f1 (ppm)


Jeffrey400
JB490-pure
nBu
Me
Me
nPr
OH
3p
f1 (ppm)


Jeffrey400
JB490-pure
nBu
Me
Me
nPr
OH
3p
f1 (ppm)


Jeffrey400
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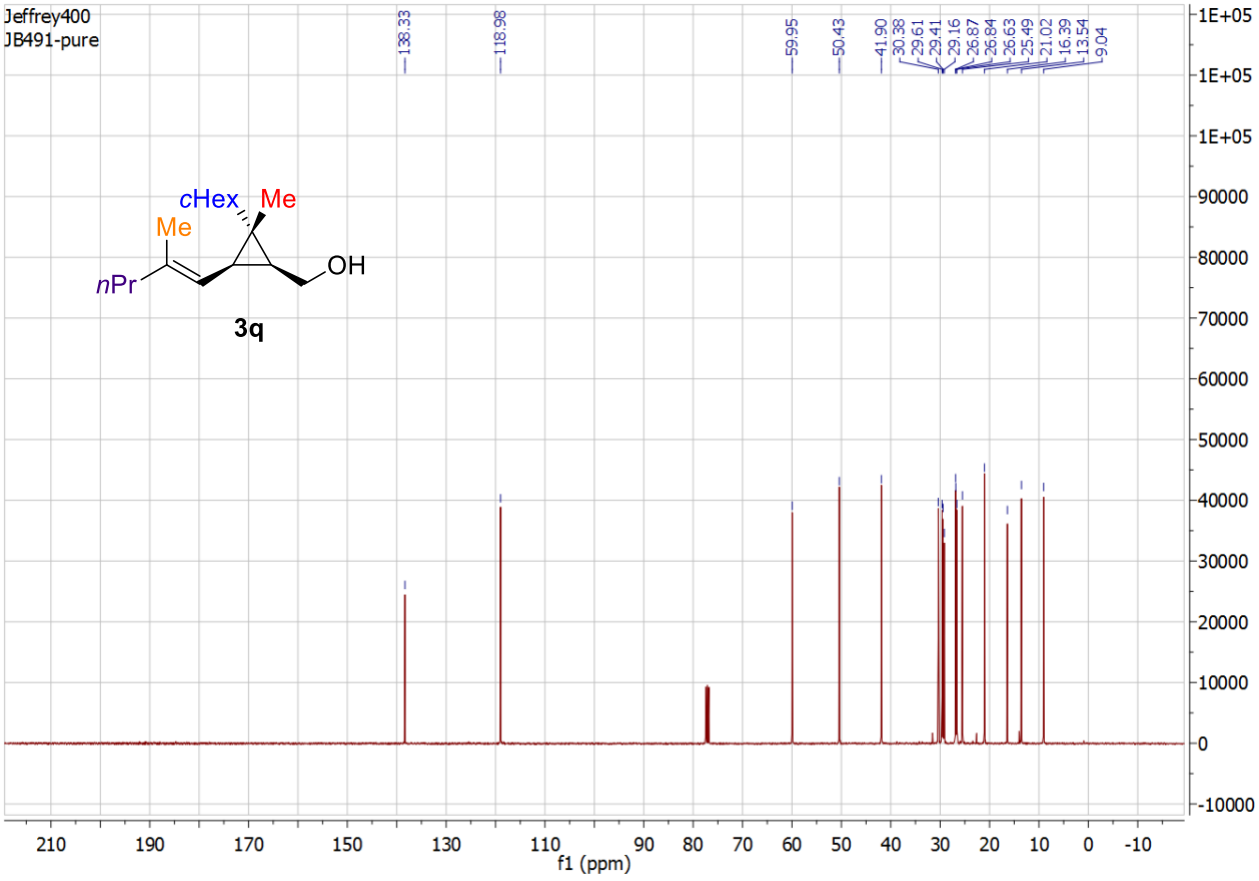
cHex
Me
Me
nPr
OH
3q
f1 (ppm)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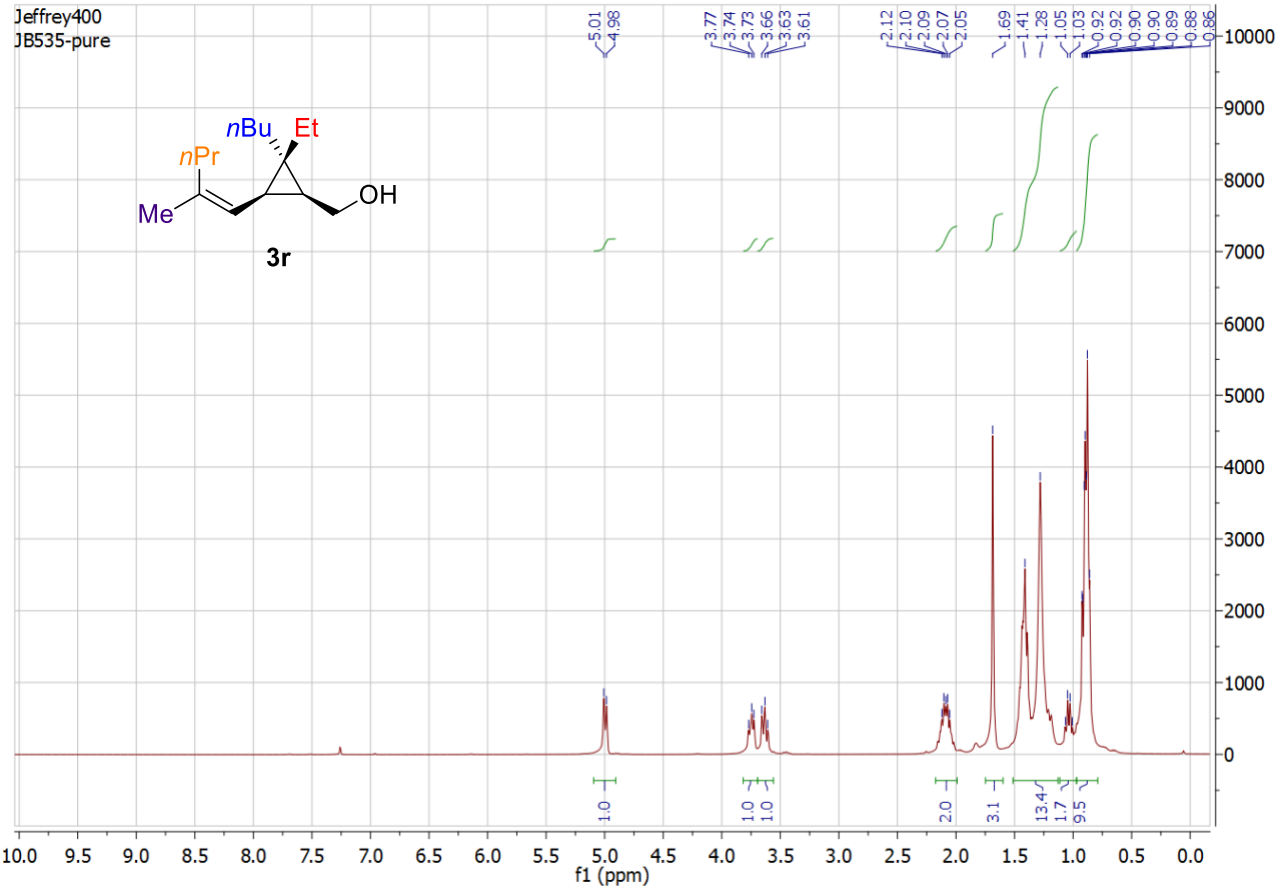
cHex
Me
Me
nPr
OH
3q
f1 (ppm)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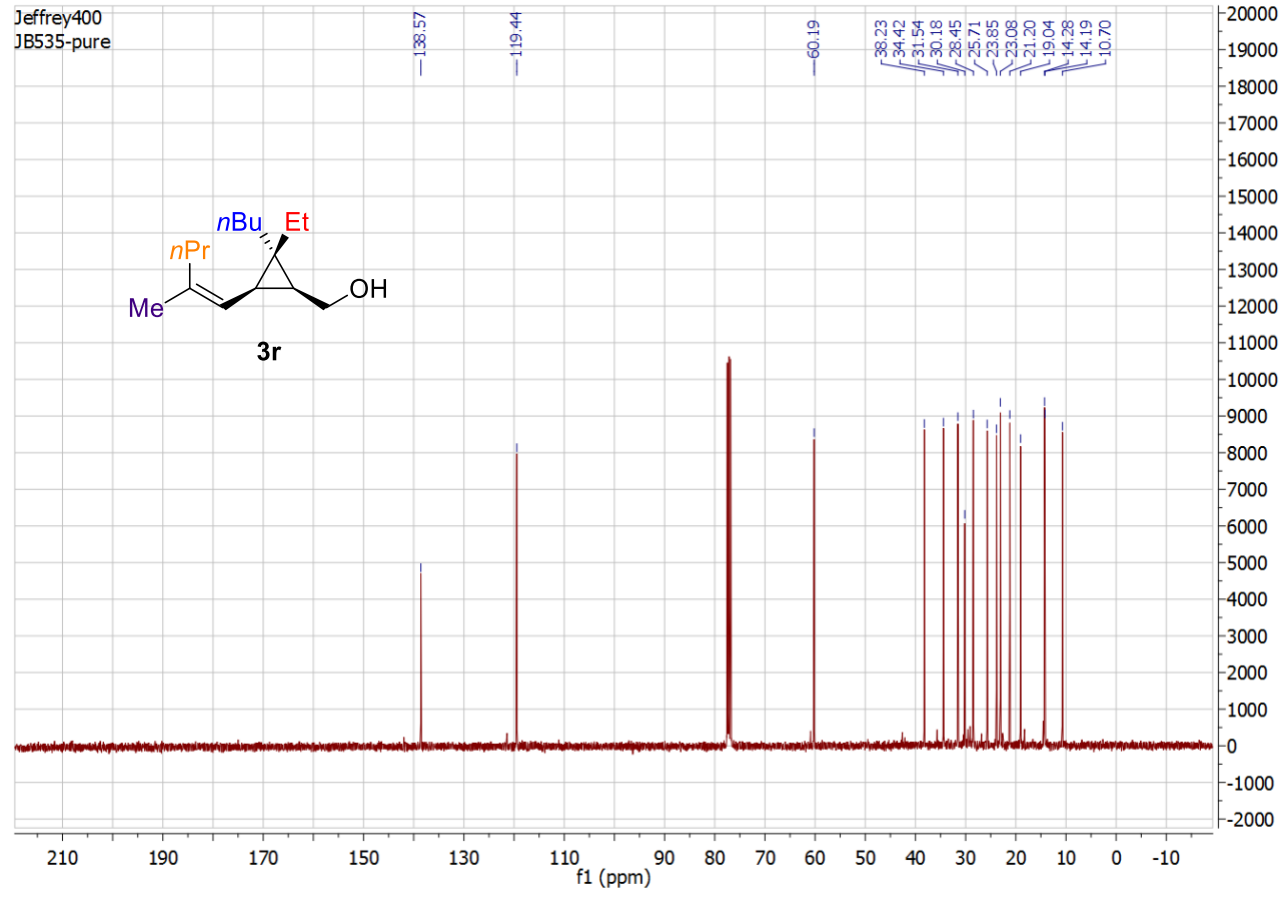
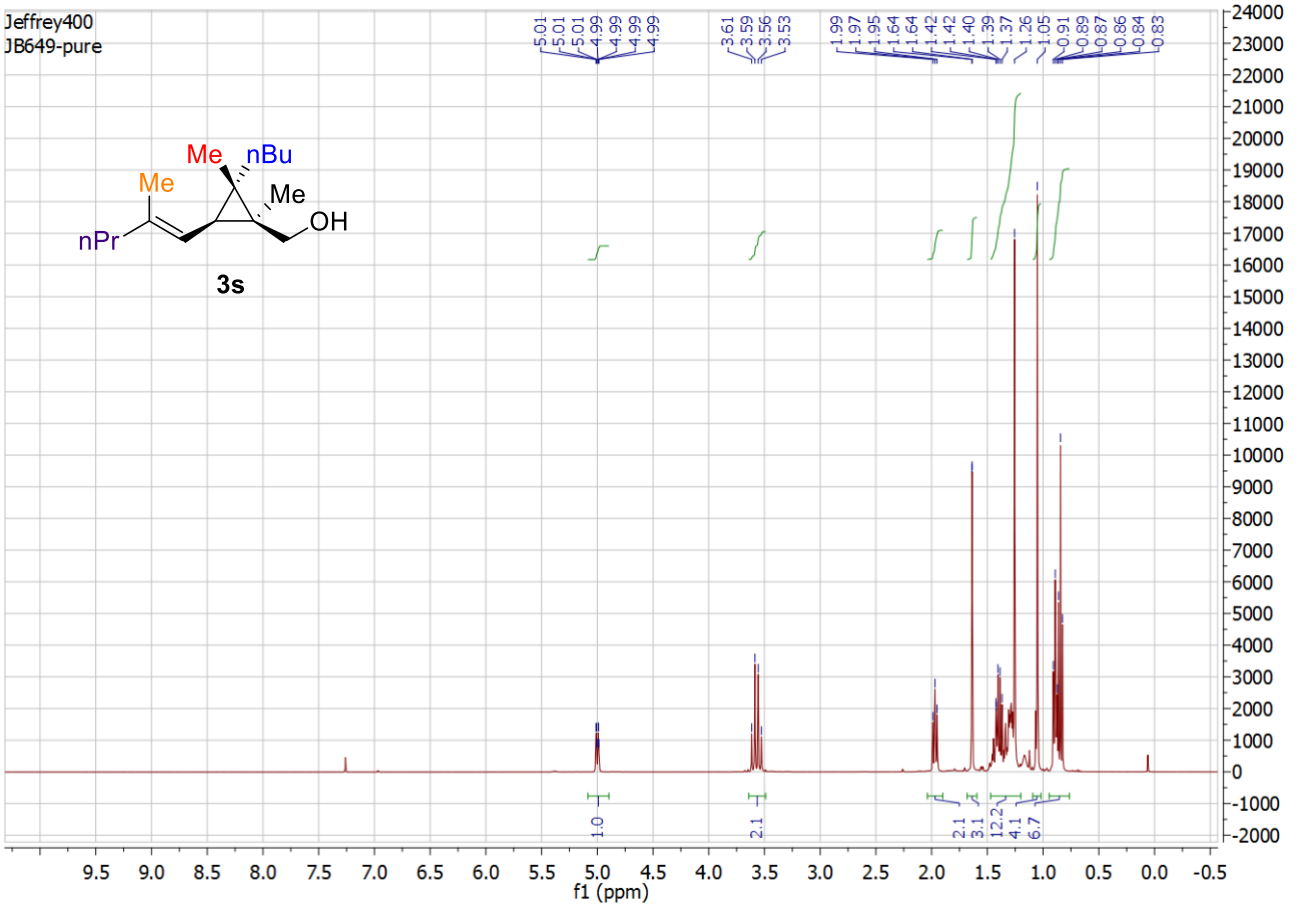
JB535-pure
nBu
Et
nPr
Me
OH
3r
f1 (ppm)


Jeffrey400
JB535-pure
nBu
Et
nPr
Me
OH
3r
f1 (ppm)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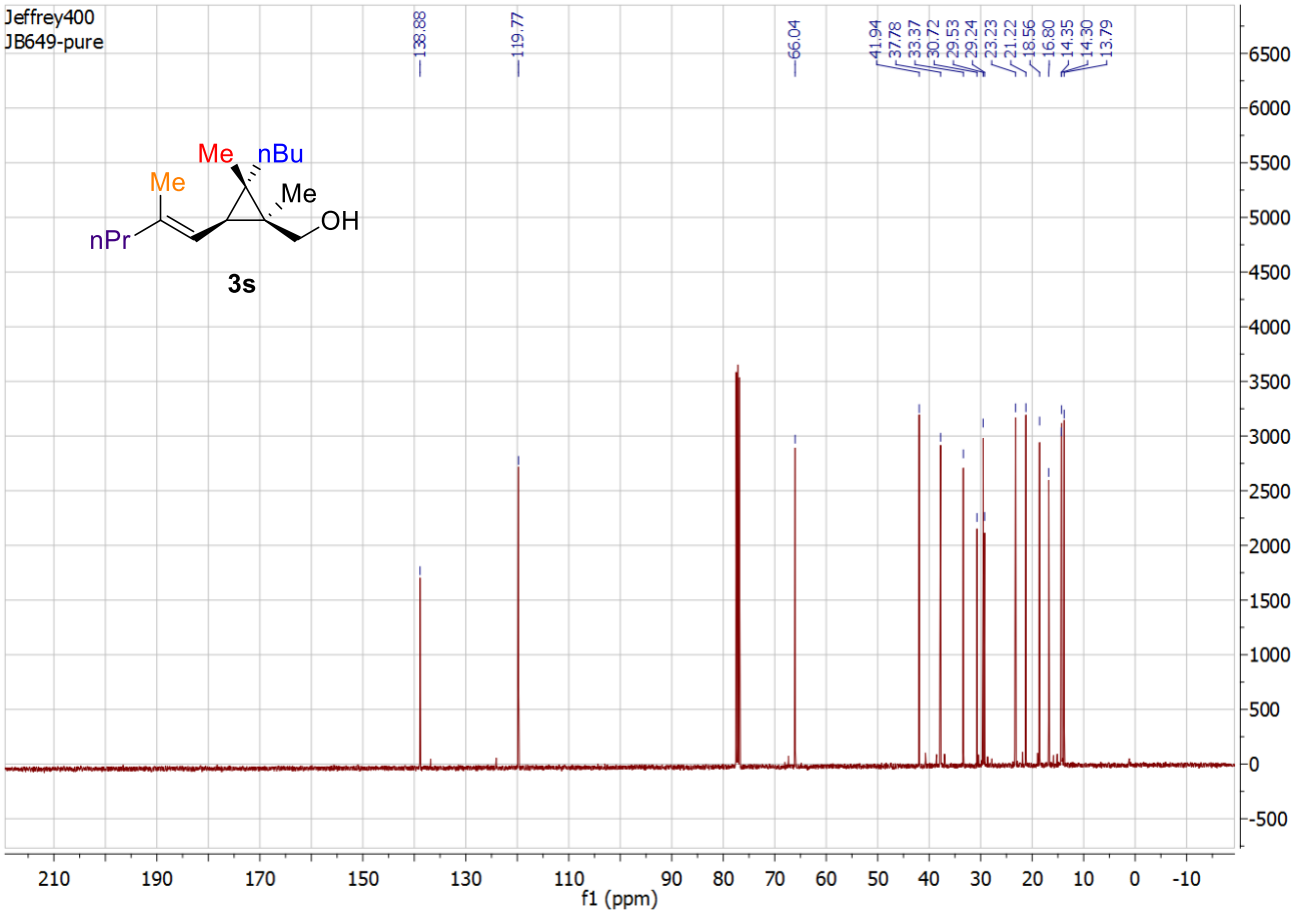
JB649-pure
Me
nBu
Me
Me
nPr
OH
3s
f1 (ppm)


Jeffrey400
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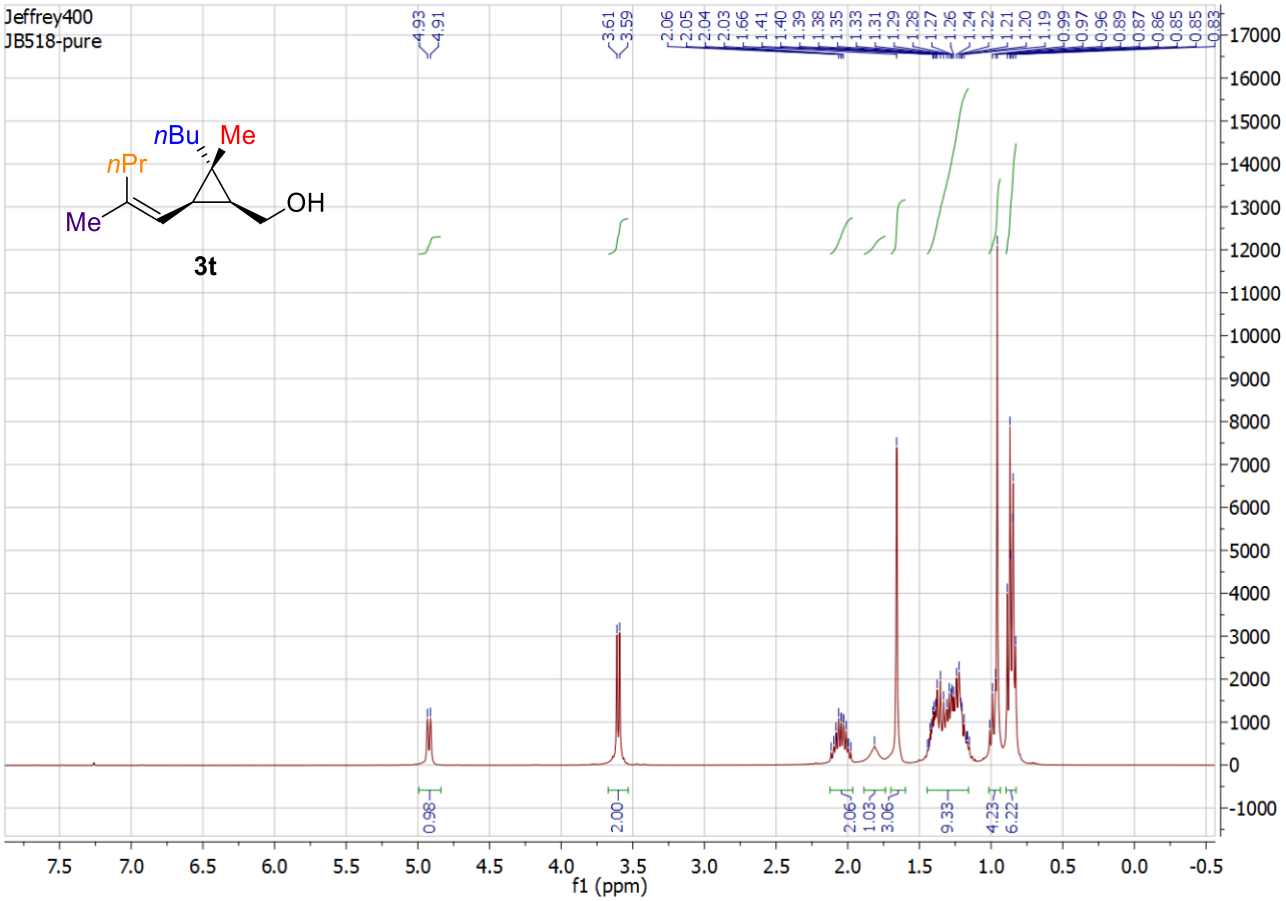
Me
nBu
Me
Me
nPr
OH
3s
f1 (ppm)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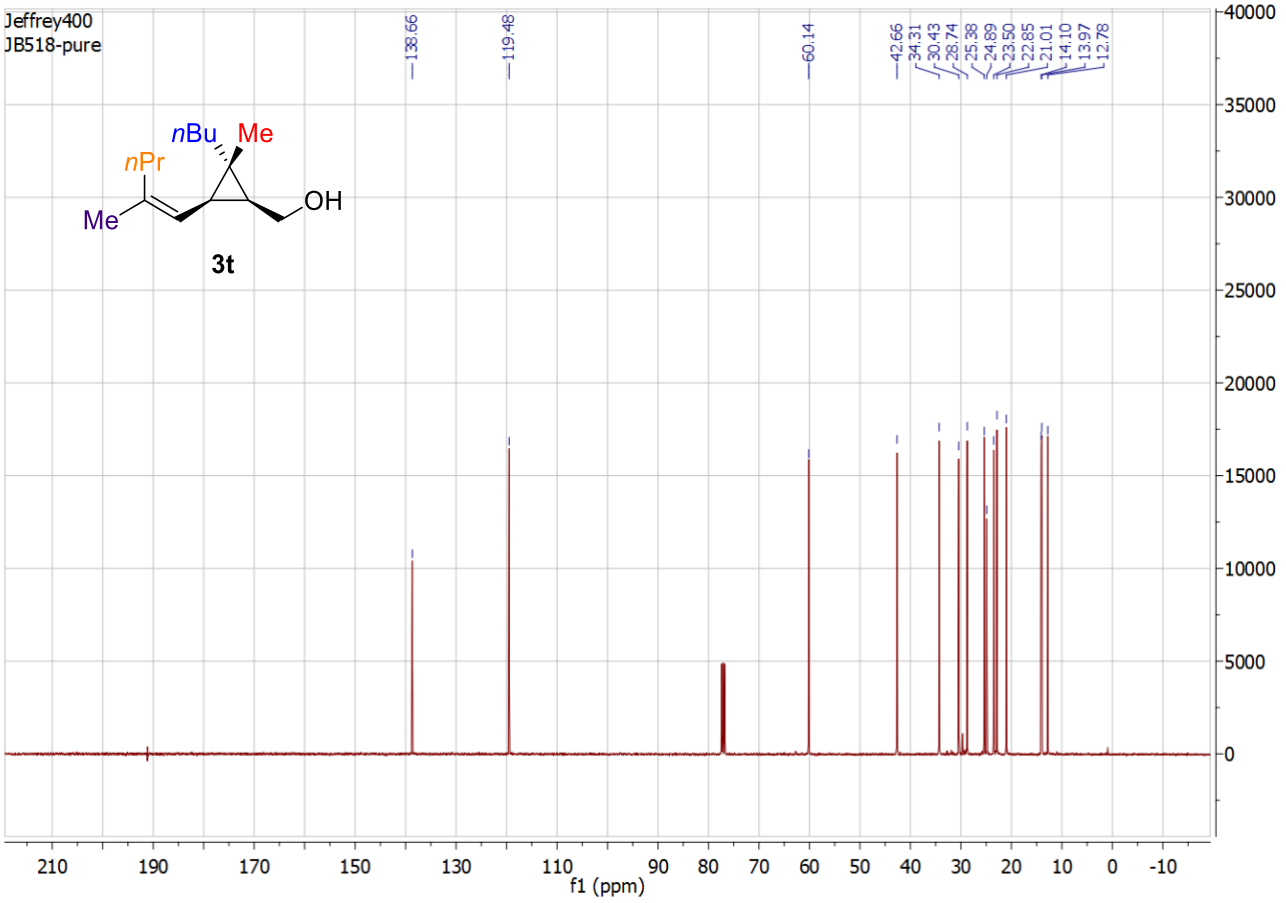
JB518-pure
nBu
Me
nPr
Me
OH
3t
f1 (ppm)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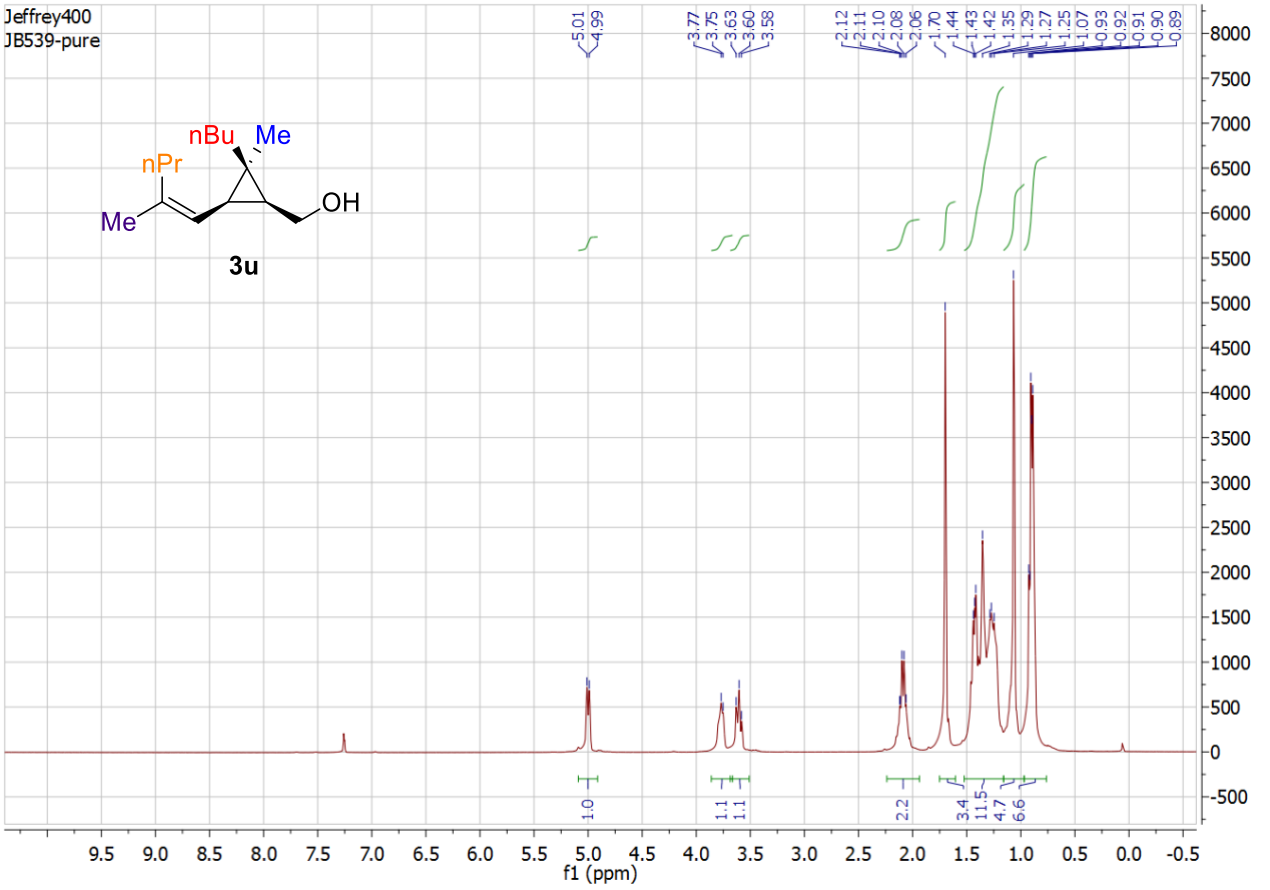
JB518-pure
nBu
Me
nPr
Me
OH
3t
f1 (ppm)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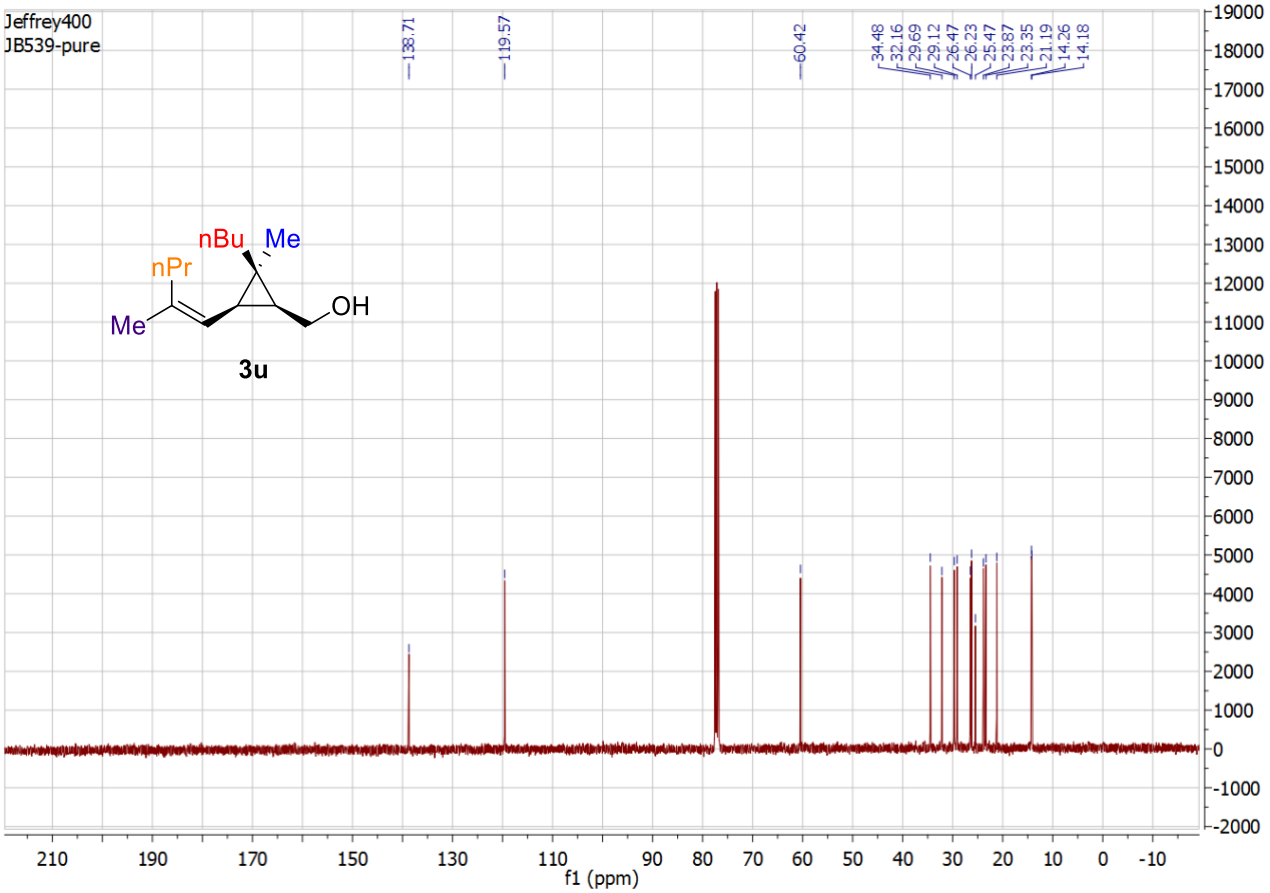
JB539-pure
nBu
Me
nPr
Me
OH
3u
f1 (ppm)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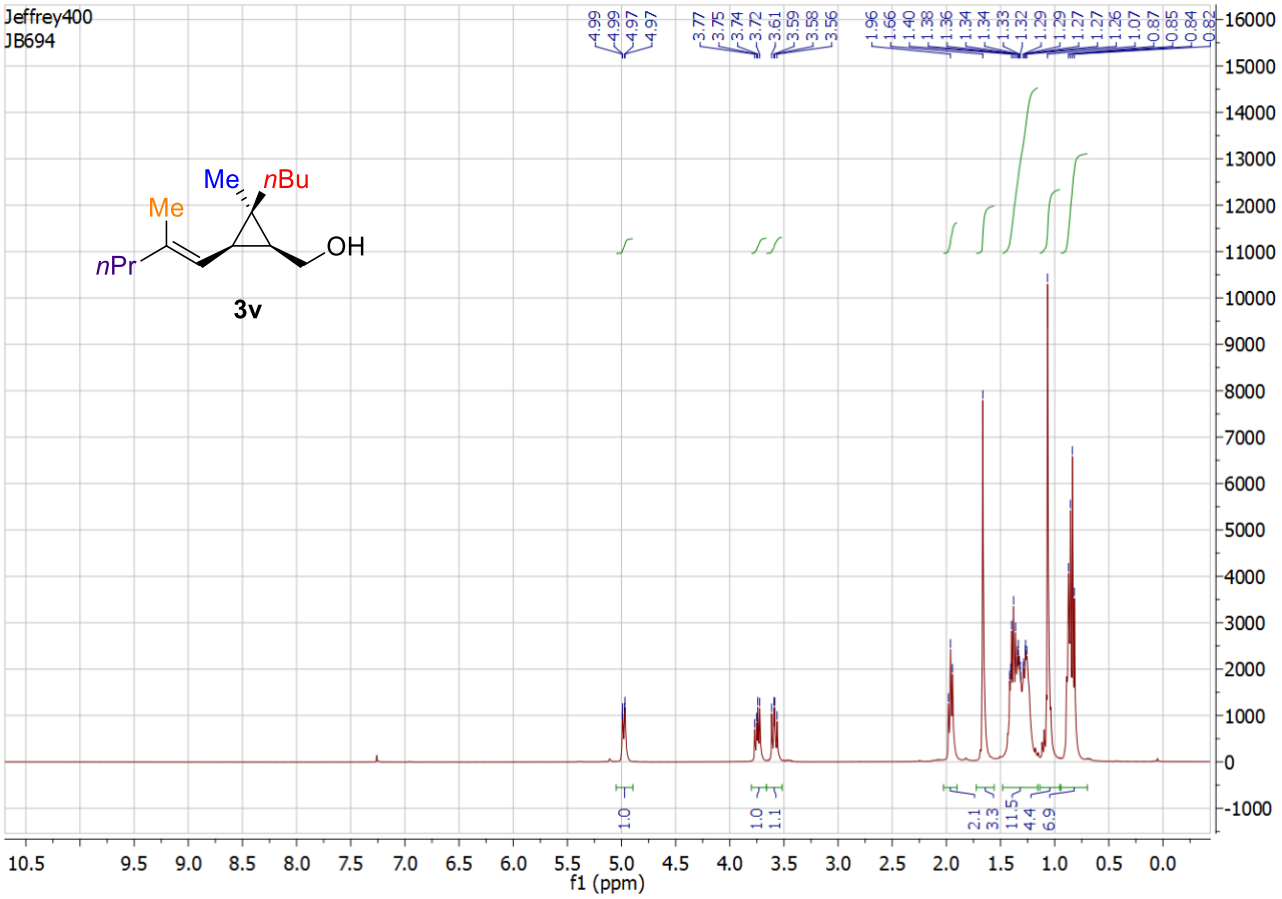
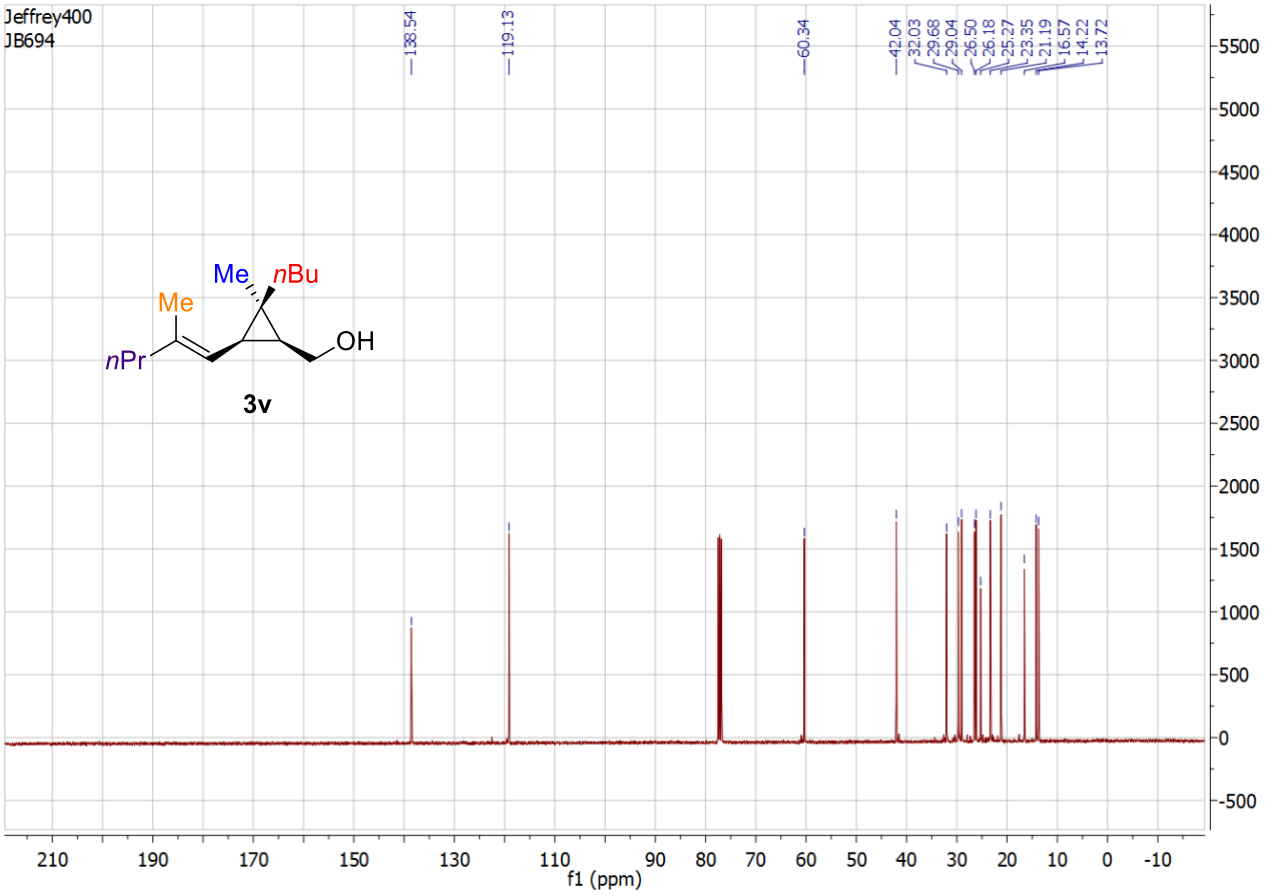
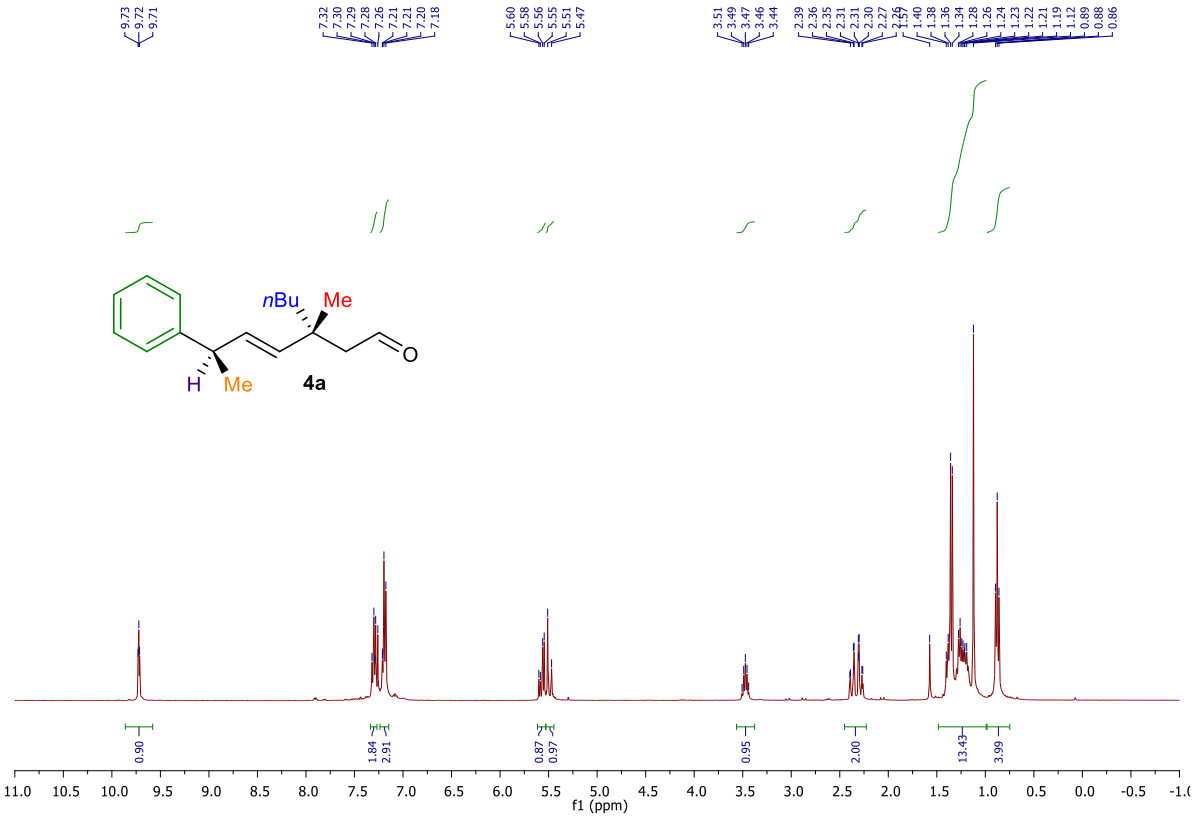
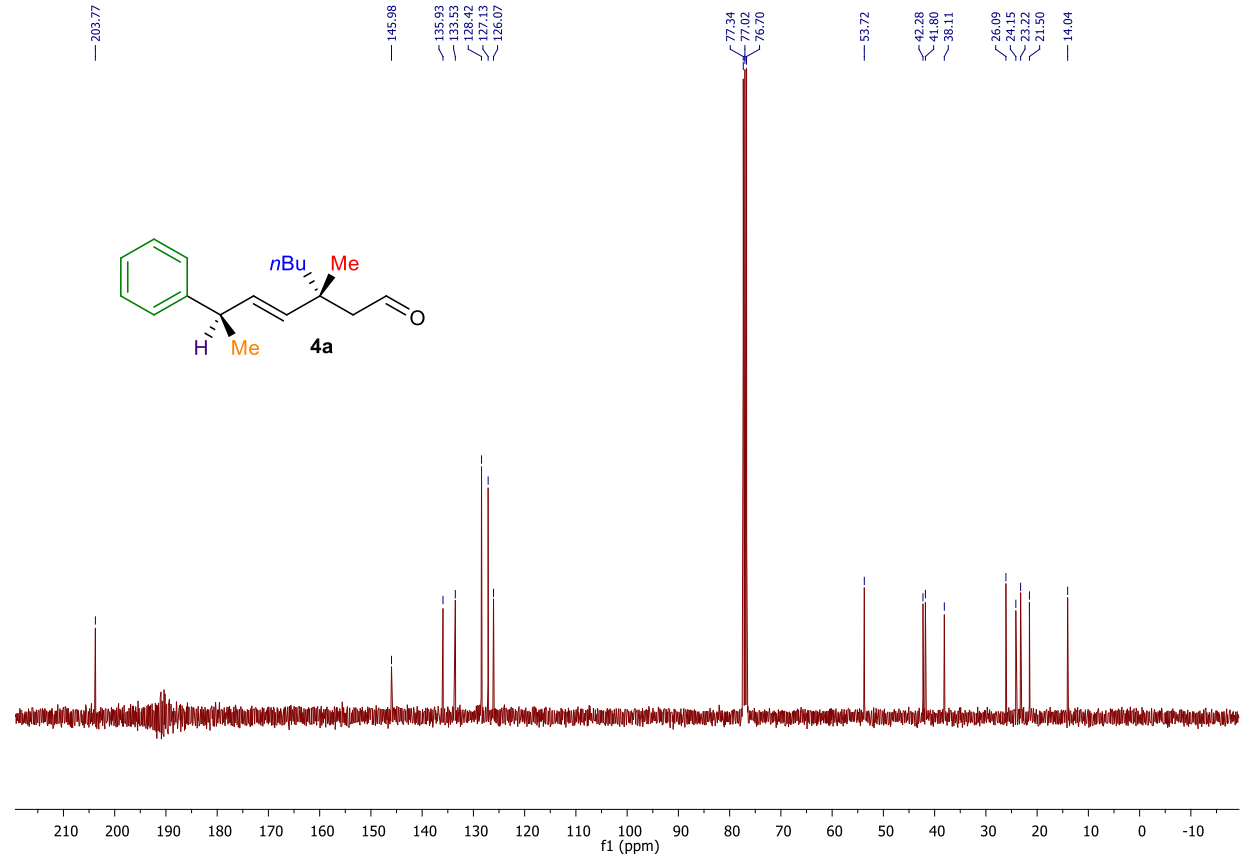
JB539-pure
nBu
Me
nPr
Me
OH
3u
f1 (ppm)

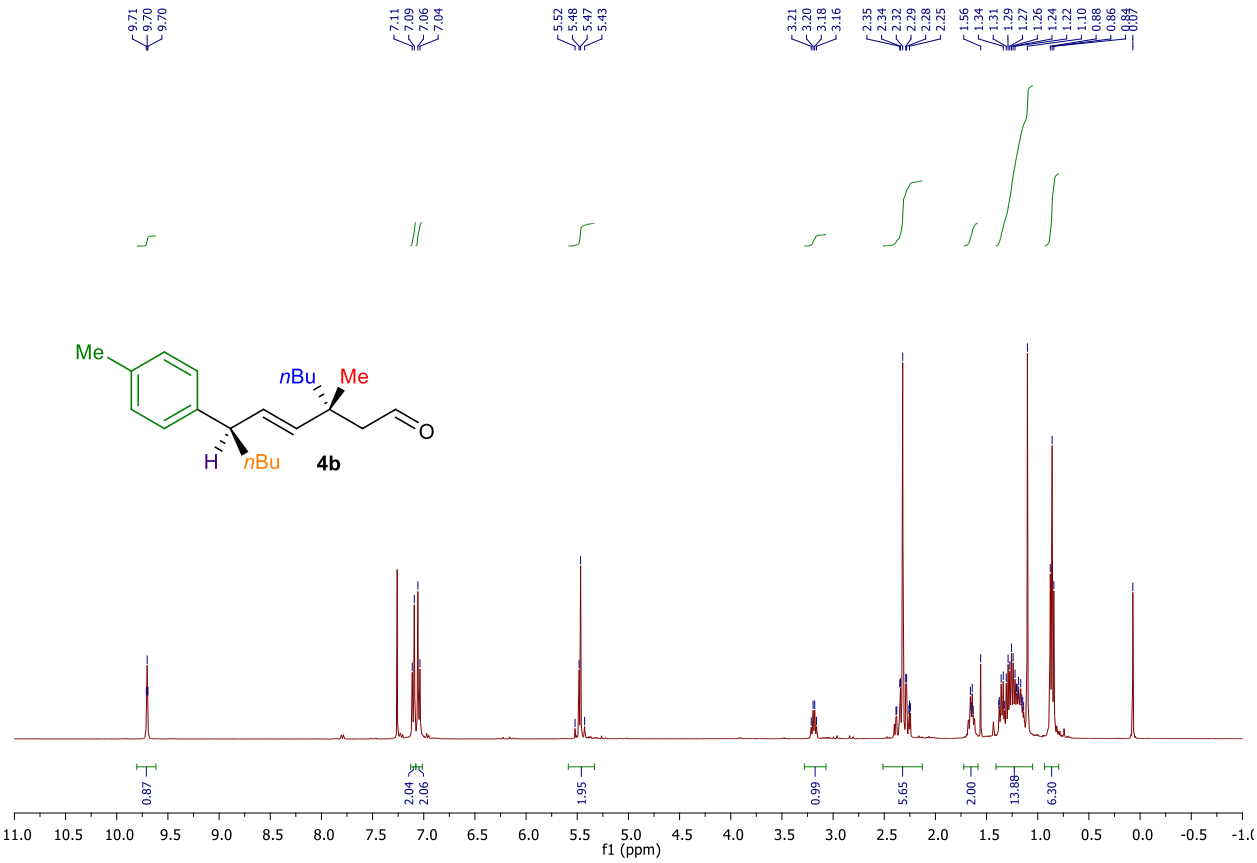

Jeffrey400
JB694
Me
nBu
Me
nPr
OH
3v
f1 (ppm)

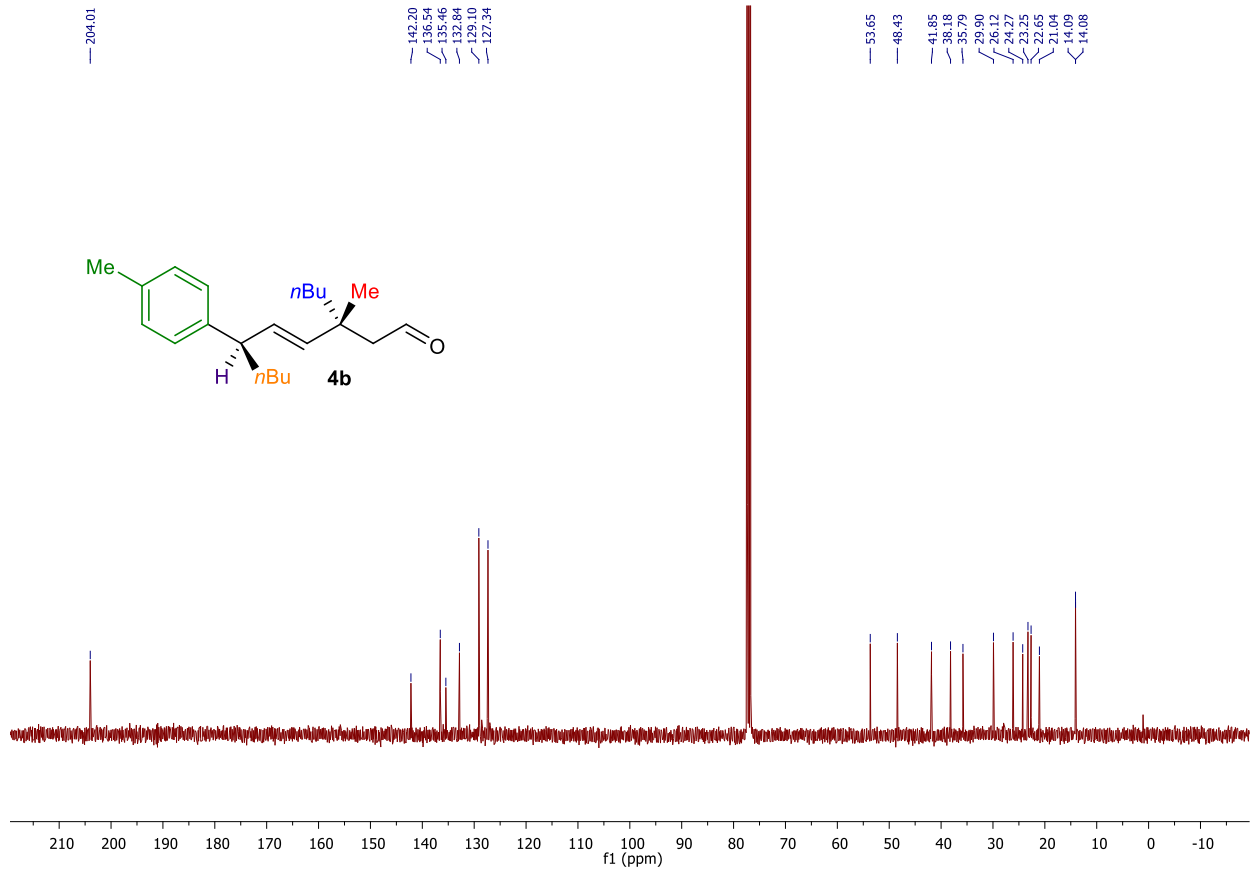

Jeffrey400
JB694
Me
nBu
Me
nPr
OH
3v
f1 (ppm)

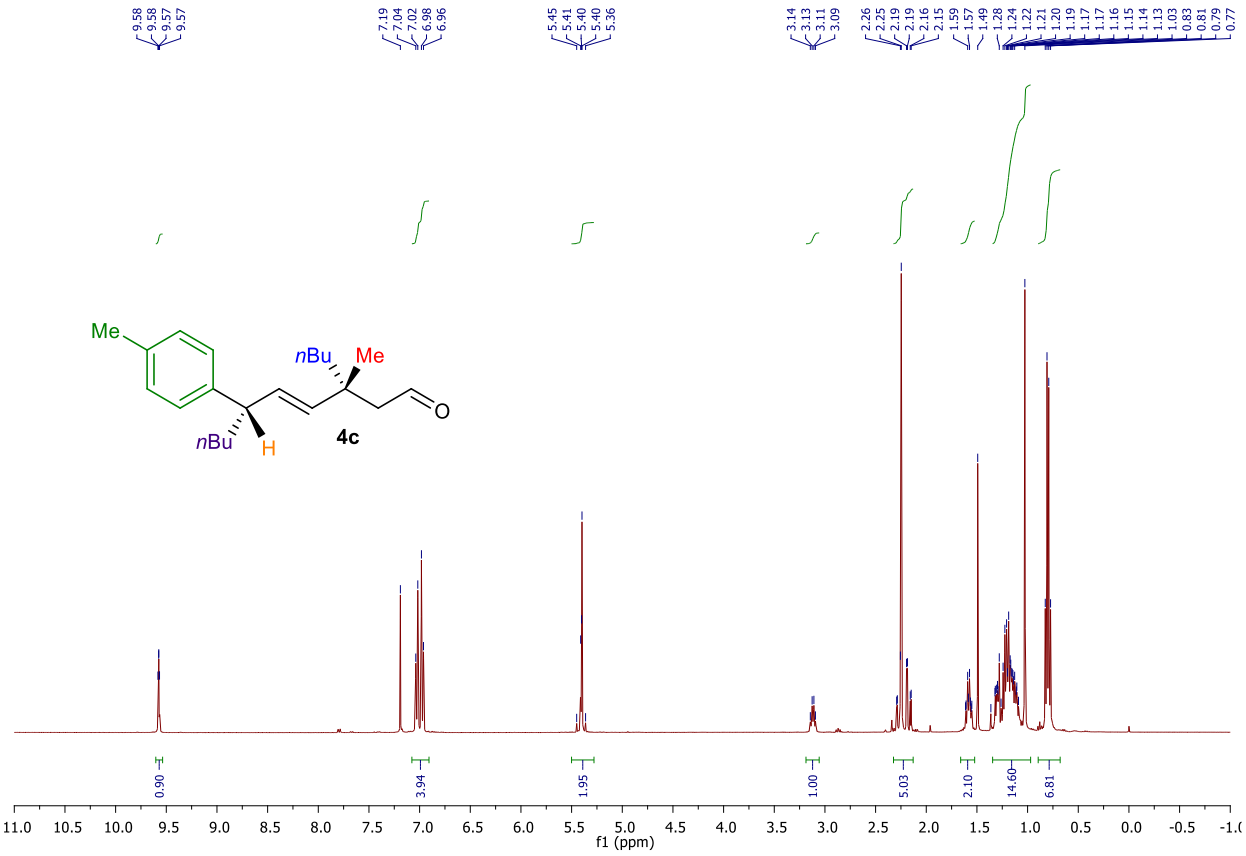
NMR spectras of aldehydes 4a-4ar

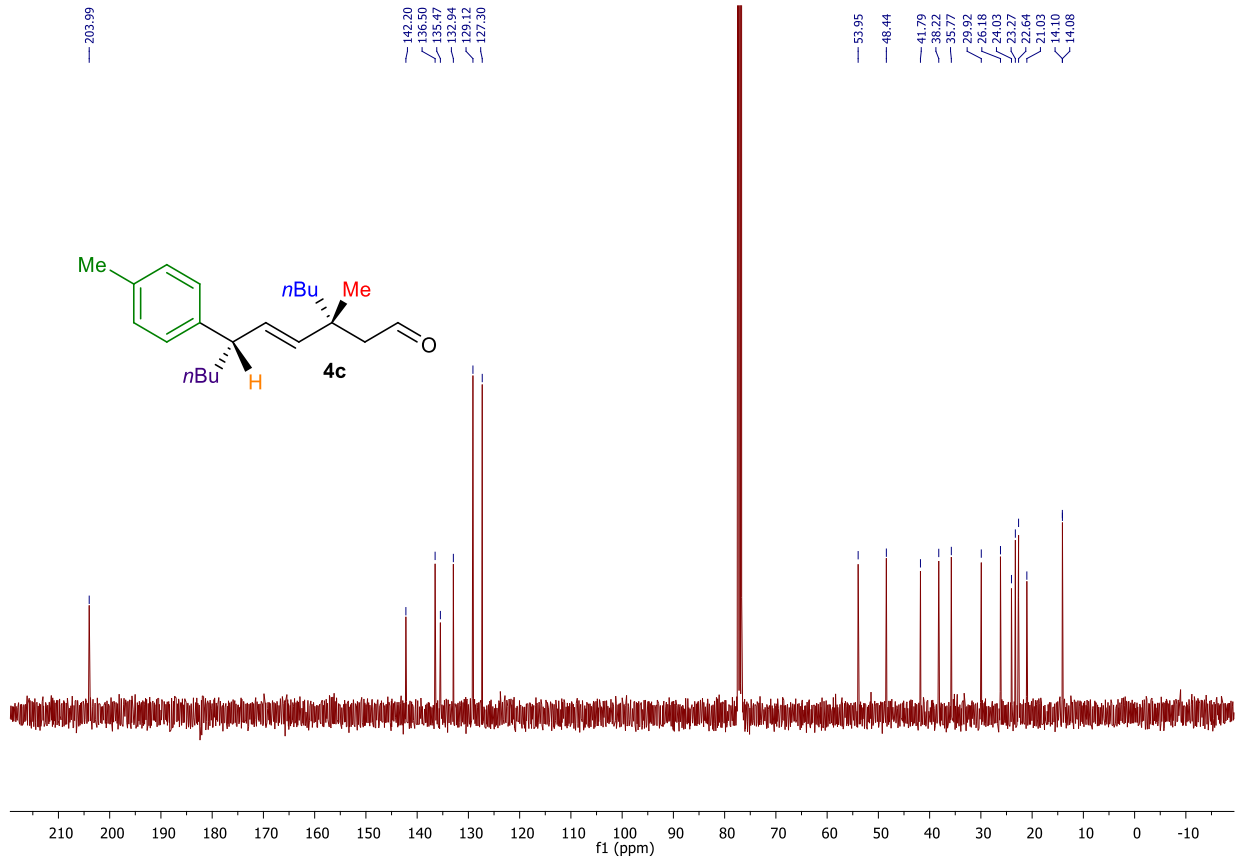


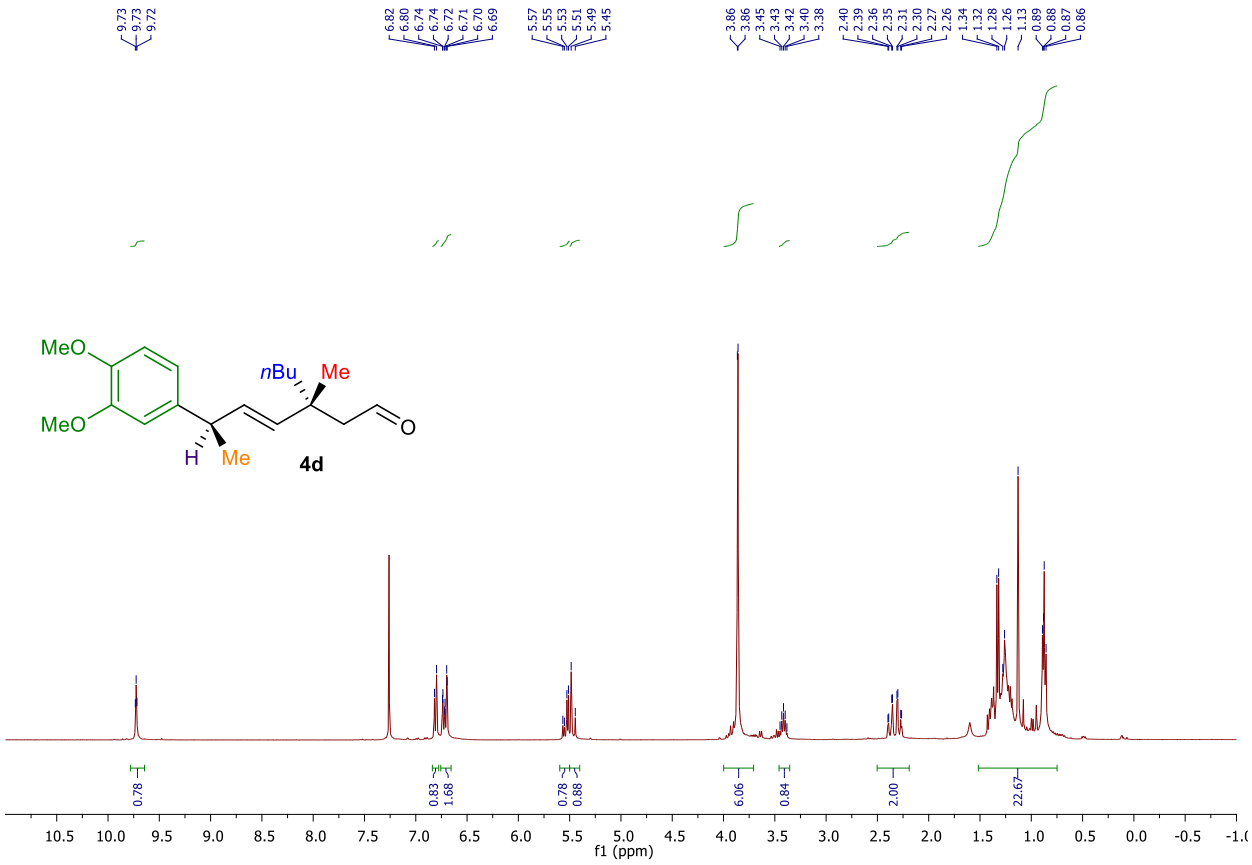


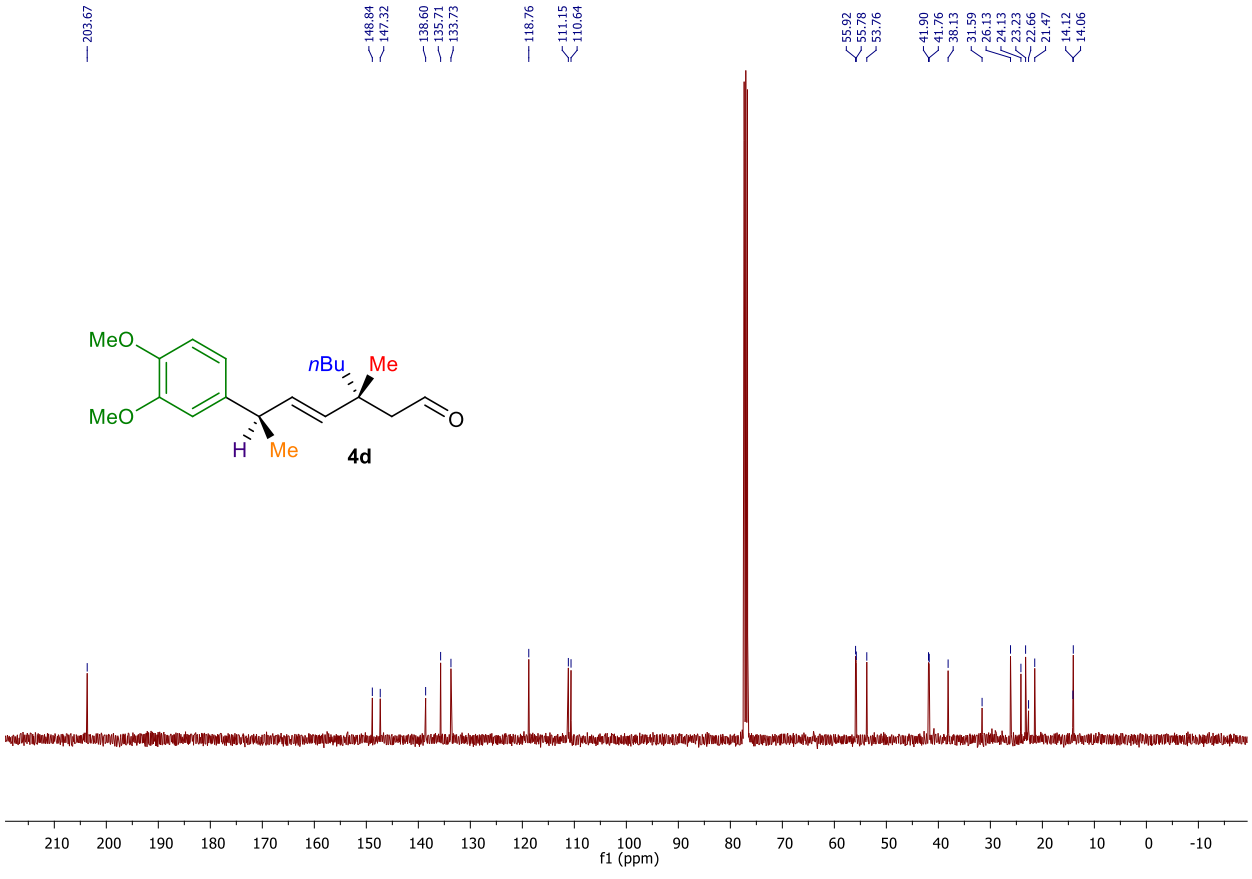

9.71
9.70
9.70
7.11
7.09
7.06
7.04
5.52
5.48
5.47
5.43
3.21
3.20
3.18
3.16
2.35
2.34
2.32
2.29
2.28
2.25
1.56
1.34
1.31
1.29
1.27
1.26
1.24
1.22
1.10
0.88
0.86
Me
nBu
Me
H
nBu
4b
O
0.87
2.04
2.06
1.95
0.99
5.65
2.00
13.88
6.30
f1 (ppm)


204.01
142.20
136.54
135.46
132.84
129.10
127.34
53.65
48.43
41.85
38.18
35.79
29.90
26.12
24.27
23.25
22.65
21.04
14.09
14.08
Me
nBu
Me
H
nBu
4b
O
f1 (ppm)


9.58
9.58
9.57
9.57
7.19
7.04
7.02
6.98
6.96
5.45
5.41
5.40
5.40
5.36
3.14
3.13
3.11
3.09
2.26
2.25
2.19
2.19
2.16
2.15
1.59
1.57
1.49
1.28
1.24
1.22
1.21
1.20
1.19
1.17
1.17
1.16
1.15
1.14
1.13
1.03
0.83
0.81
0.79
0.77
Me
nBu
Me
nBu
H
O
4c
0.90
3.94
1.95
1.00
5.03
2.10
14.60
6.81
f1 (ppm)


203.99
142.20
136.50
135.47
132.94
129.12
127.30
53.95
48.44
41.79
38.22
35.77
29.92
26.18
24.03
23.27
22.64
21.03
14.10
14.08
Me
nBu
Me
nBu
H
O
4c
f1 (ppm)


9.73
9.73
9.72
6.82
6.80
6.74
6.72
6.71
6.70
6.69
5.57
5.55
5.53
5.51
5.49
5.45
3.86
3.86
3.45
3.43
3.42
3.40
3.38
2.40
2.39
2.36
2.35
2.31
2.30
2.27
2.26
1.34
1.32
1.28
1.26
1.13
0.89
0.88
0.87
0.86
MeO
MeO
nBu
Me
H
Me
O
4d
0.78
0.83
1.68
0.78
0.88
6.06
0.84
2.00
22.67
f1 (ppm)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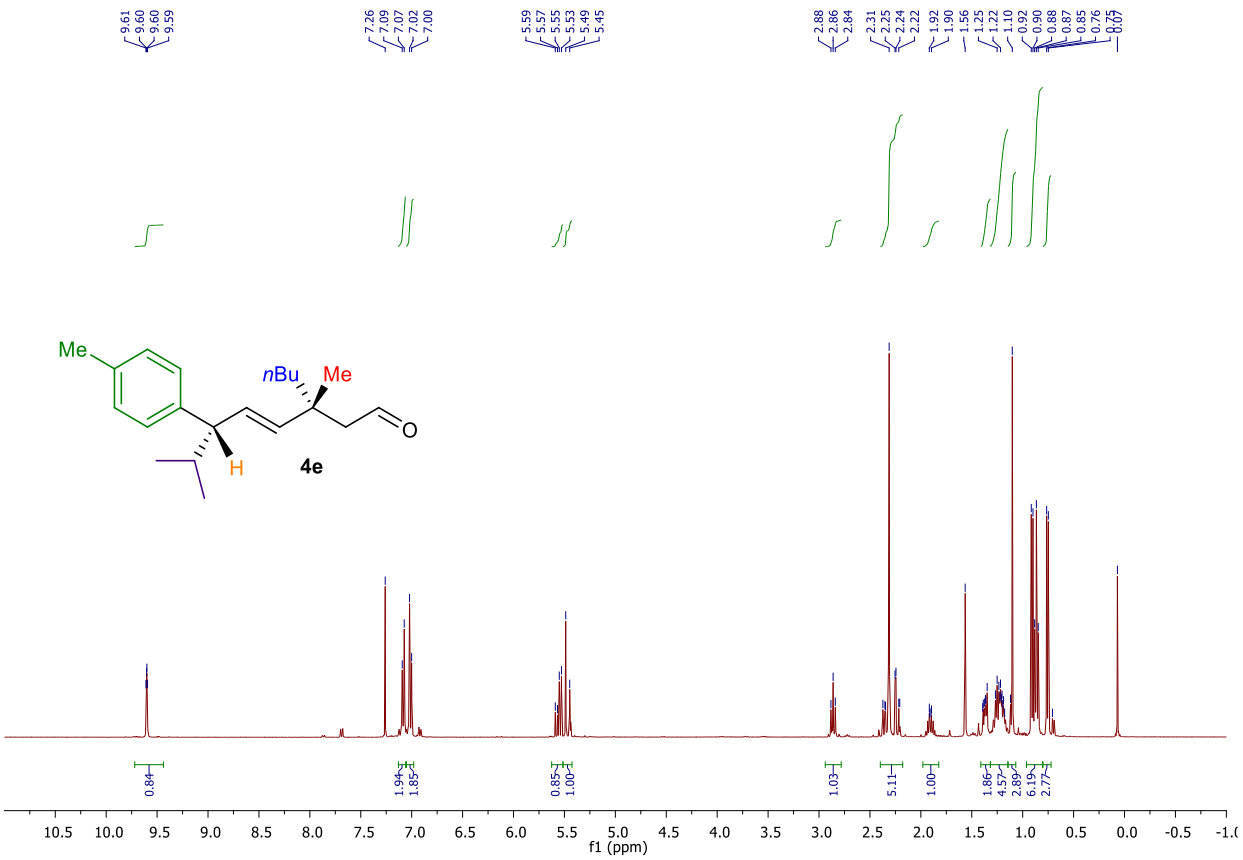
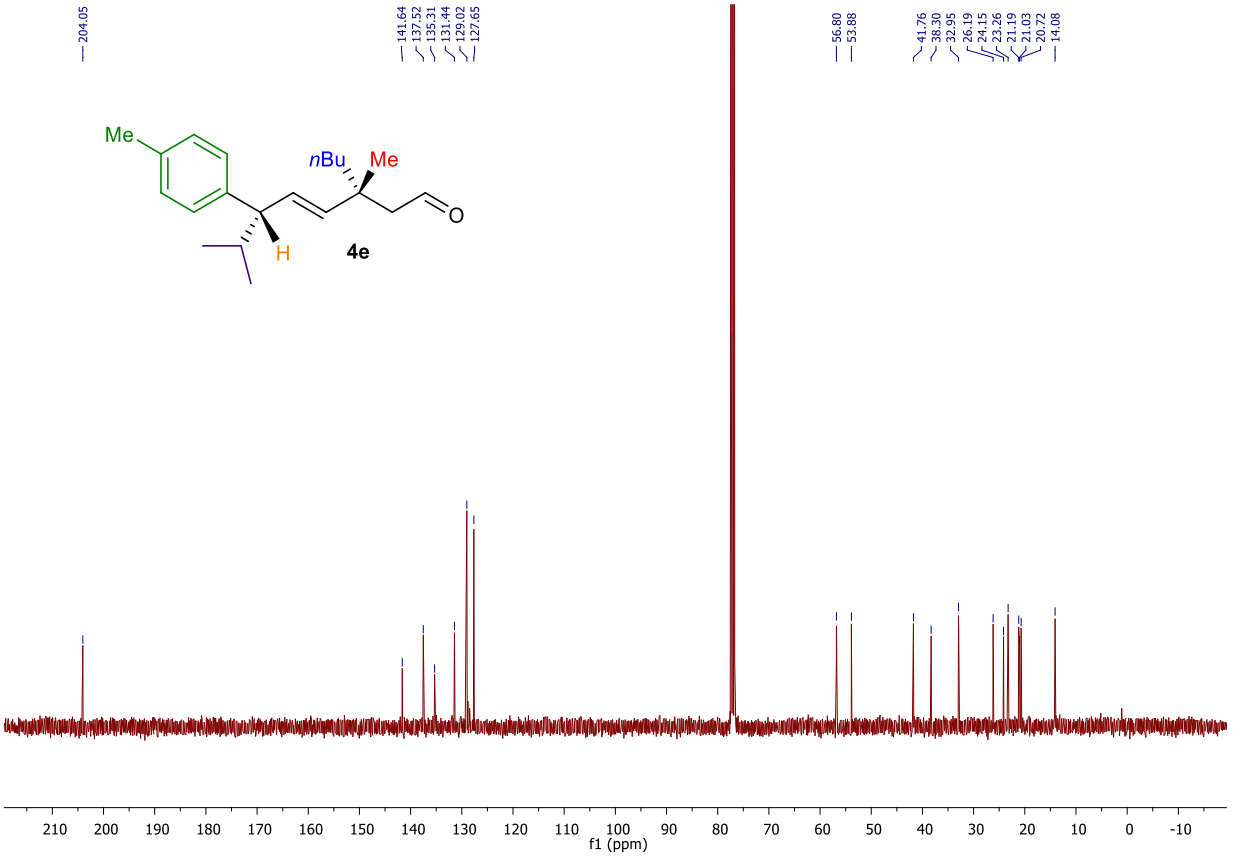
147.32
138.60
135.71
133.73
118.76
111.15
110.64
55.92
55.78
53.76
41.90
41.76
38.13
31.59
26.13
24.13
23.23
22.66
21.47
14.12
14.06
MeO
MeO
nBu
Me
H
Me
O
4d
f1 (ppm)


9.61
9.60
9.60
9.59
7.26
7.09
7.07
7.02
7.00
5.59
5.57
5.55
5.53
5.49
5.45
2.88
2.86
2.84
2.31
2.25
2.24
2.22
1.92
1.90
1.56
1.25
1.22
1.10
0.92
0.90
0.88
0.87
0.85
0.76
0.07
0.00
Me
nBu
Me
O
H
4e
0.84
1.94
1.85
0.85
1.00
1.03
5.11
1.00
1.86
4.57
2.89
6.19
2.77
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 -0.5
f1 (ppm)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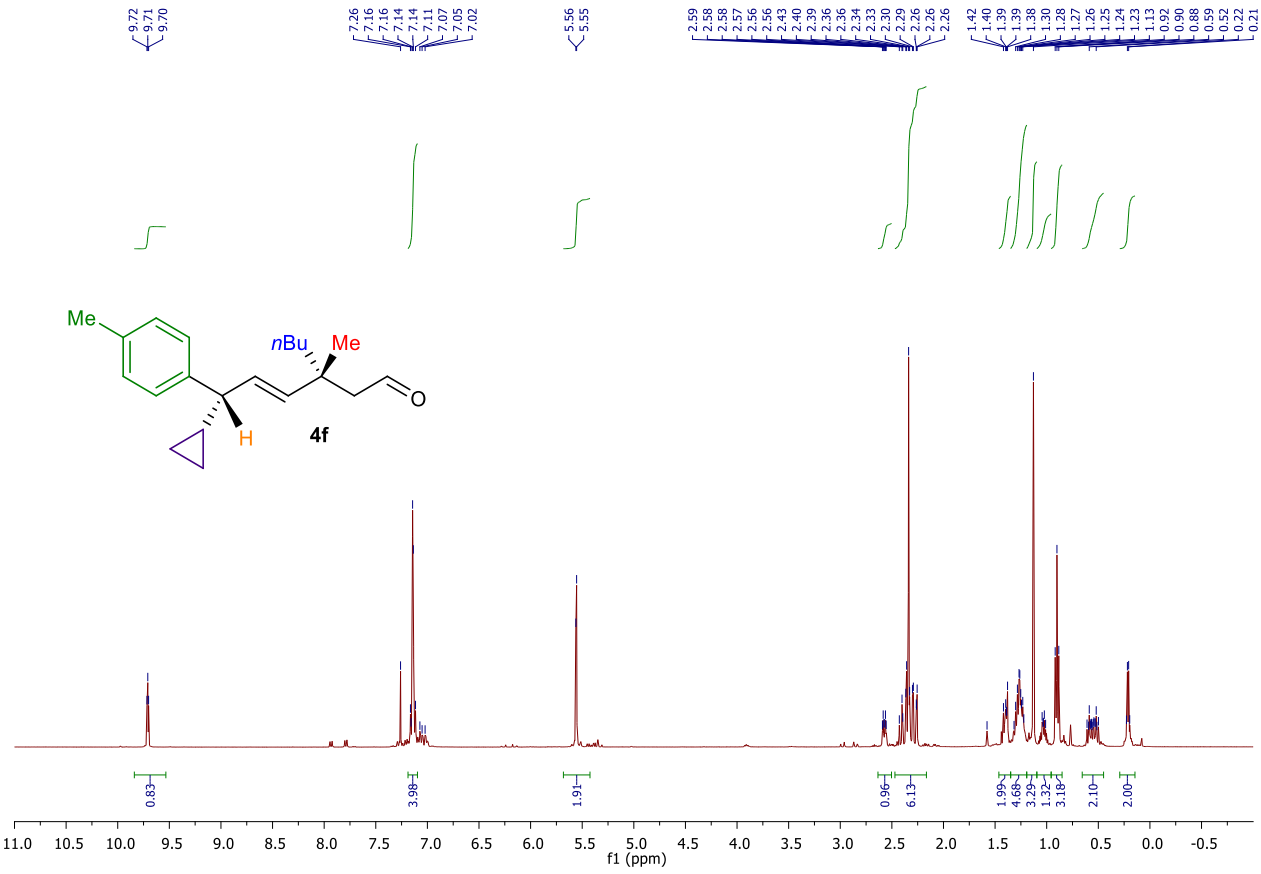
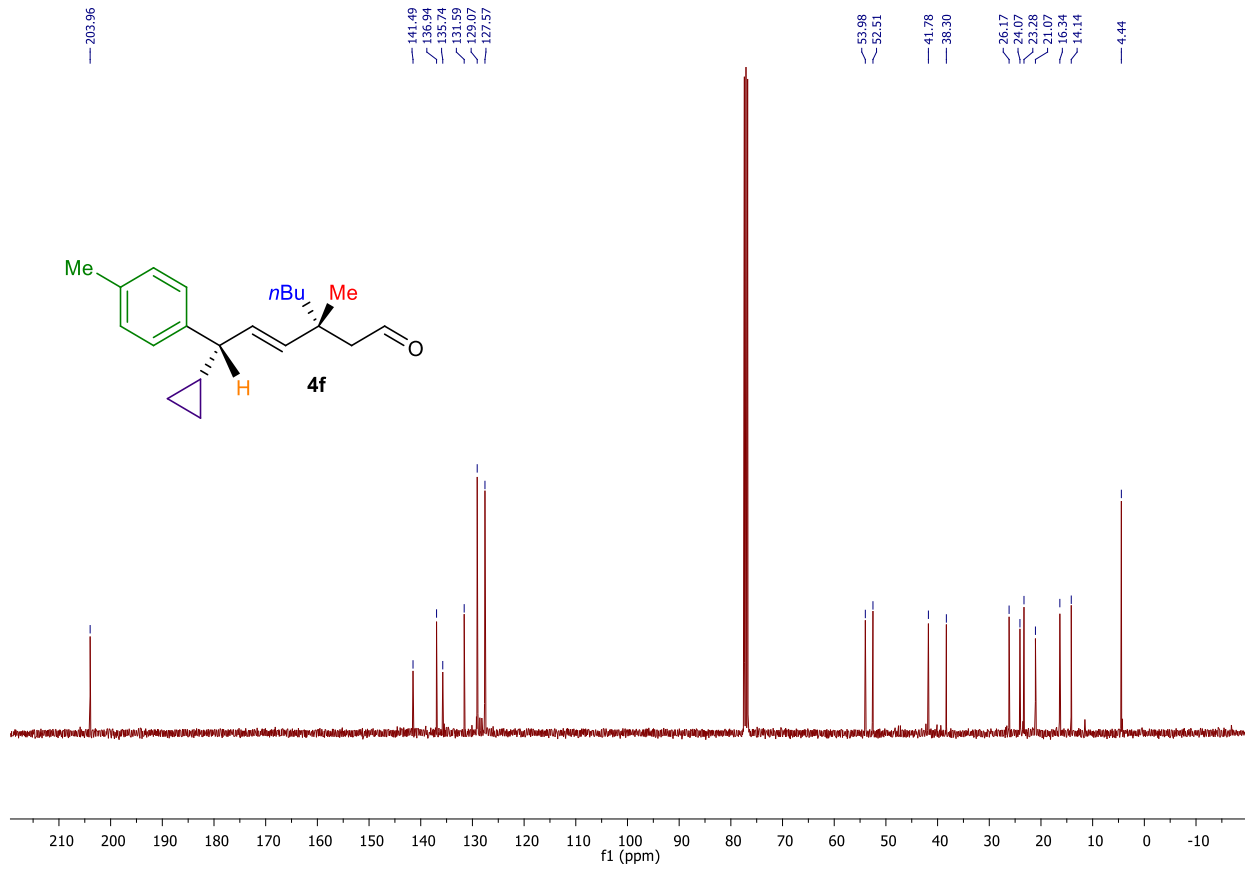
137.52
135.31
131.44
129.02
127.65
56.80
53.88
41.76
38.30
32.95
26.19
24.15
23.26
21.19
21.03
20.72
14.08
Me
nBu
Me
O
H
4e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.72
9.71
9.70
7.26
7.16
7.16
7.14
7.14
7.14
7.11
7.07
7.05
7.02
5.56
5.55
2.59
2.58
2.58
2.57
2.56
2.56
2.43
2.40
2.39
2.36
2.36
2.34
2.33
2.30
2.29
2.26
2.26
2.26
1.42
1.40
1.39
1.39
1.38
1.30
1.28
1.27
1.26
1.25
1.24
1.23
1.13
0.92
0.90
0.88
0.59
0.52
0.22
0.21
Me
nBu
Me
O
H
4f
0.83
3.98
1.91
0.96
6.13
1.99
4.68
3.29
1.32
3.18
2.10
2.00
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
-0.5
f1 (ppm)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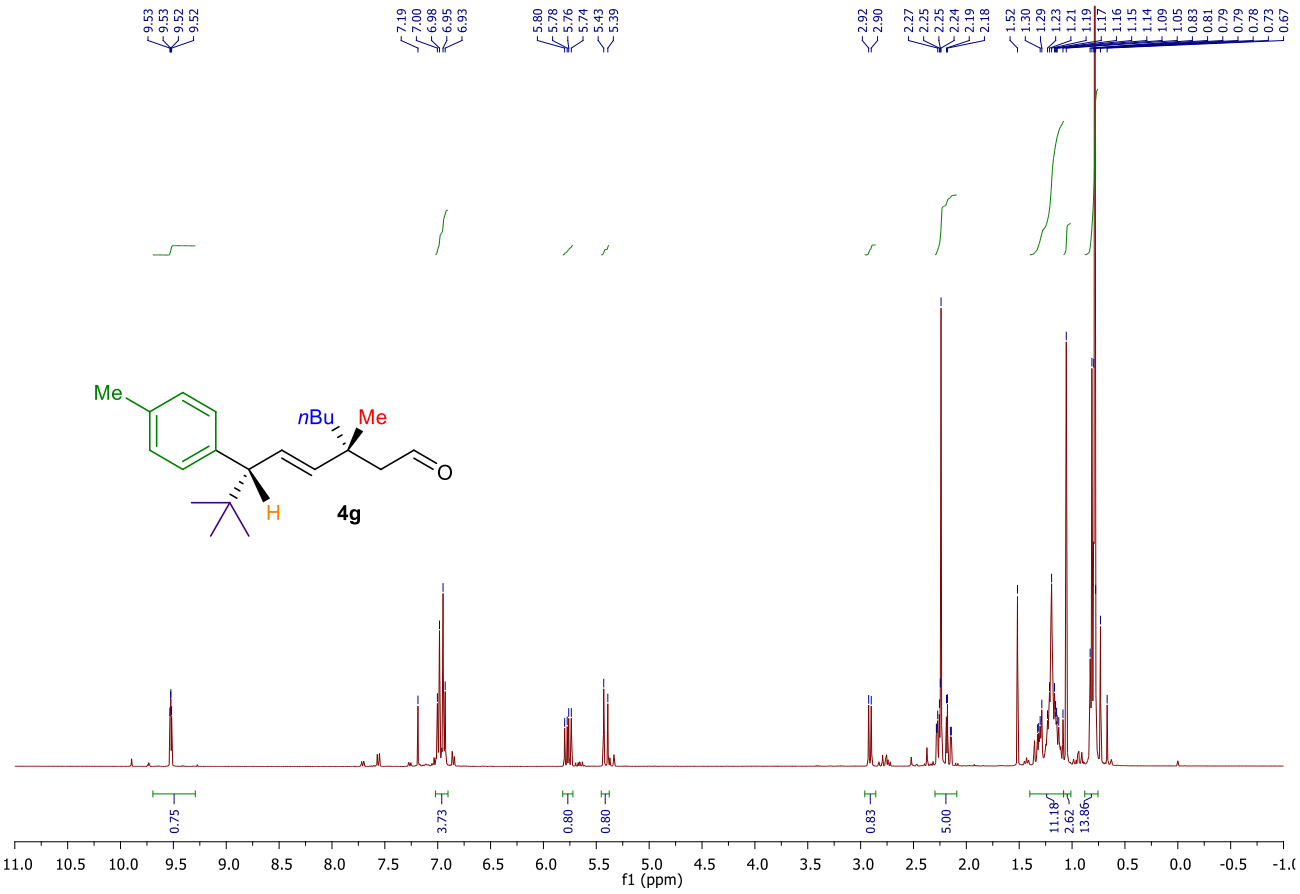
136.94
135.74
131.59
129.07
127.57
53.98
52.51
41.78
38.30
26.17
24.07
23.28
21.07
16.34
14.14
4.44
Me
nBu
Me
O
H
4f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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9.52
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6.98
6.95
6.93
5.80
5.78
5.76
5.74
5.43
5.39
2.92
2.90
2.27
2.25
2.25
2.24
2.19
2.18
1.52
1.30
1.29
1.23
1.21
1.19
1.17
1.16
1.15
1.14
1.09
1.05
0.83
0.81
0.79
0.79
0.78
0.73
0.67
Me
nBu
Me
O
H
4g
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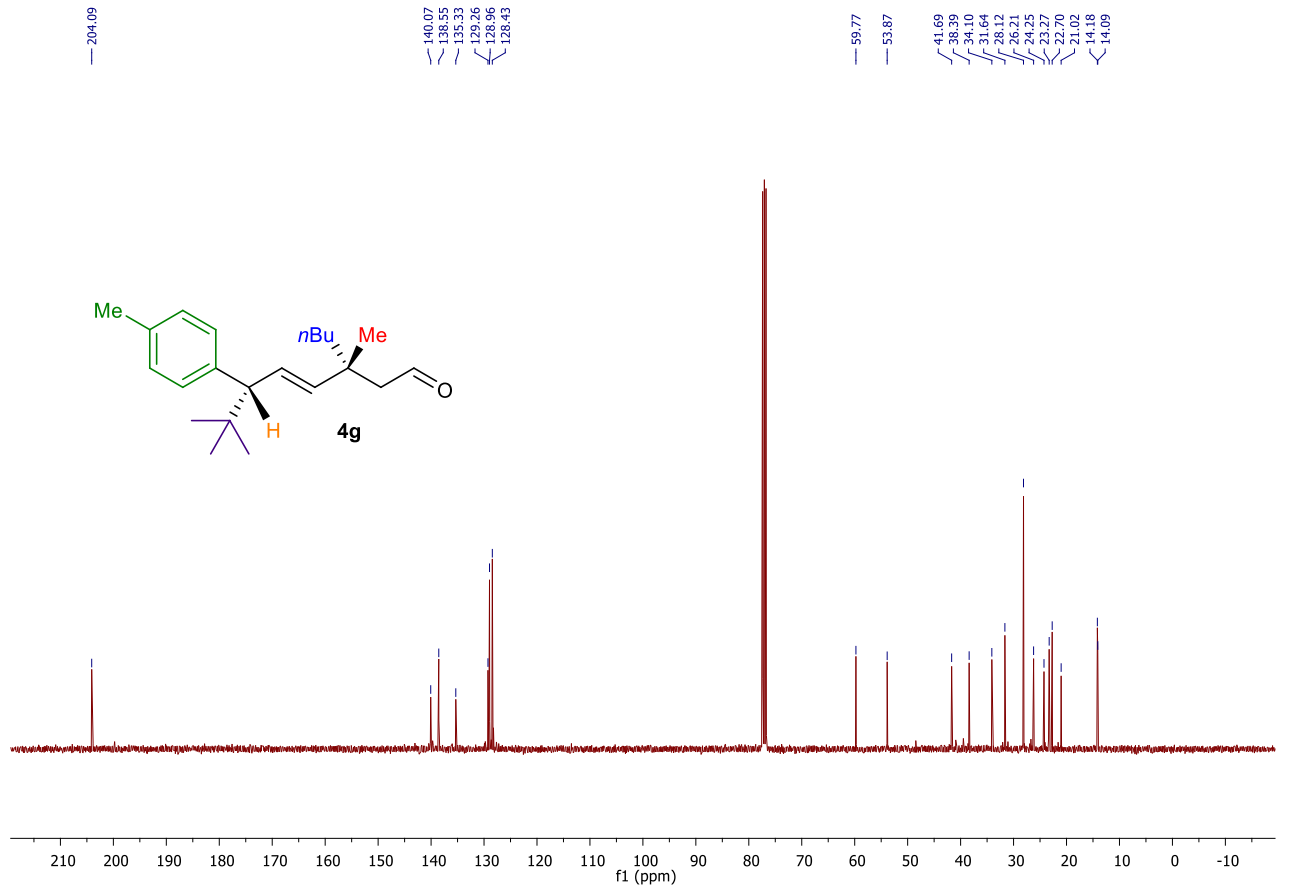
3.73
0.80
0.80
0.83
5.00
11.18
2.62
13.86
f1 (ppm)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128.43
59.77
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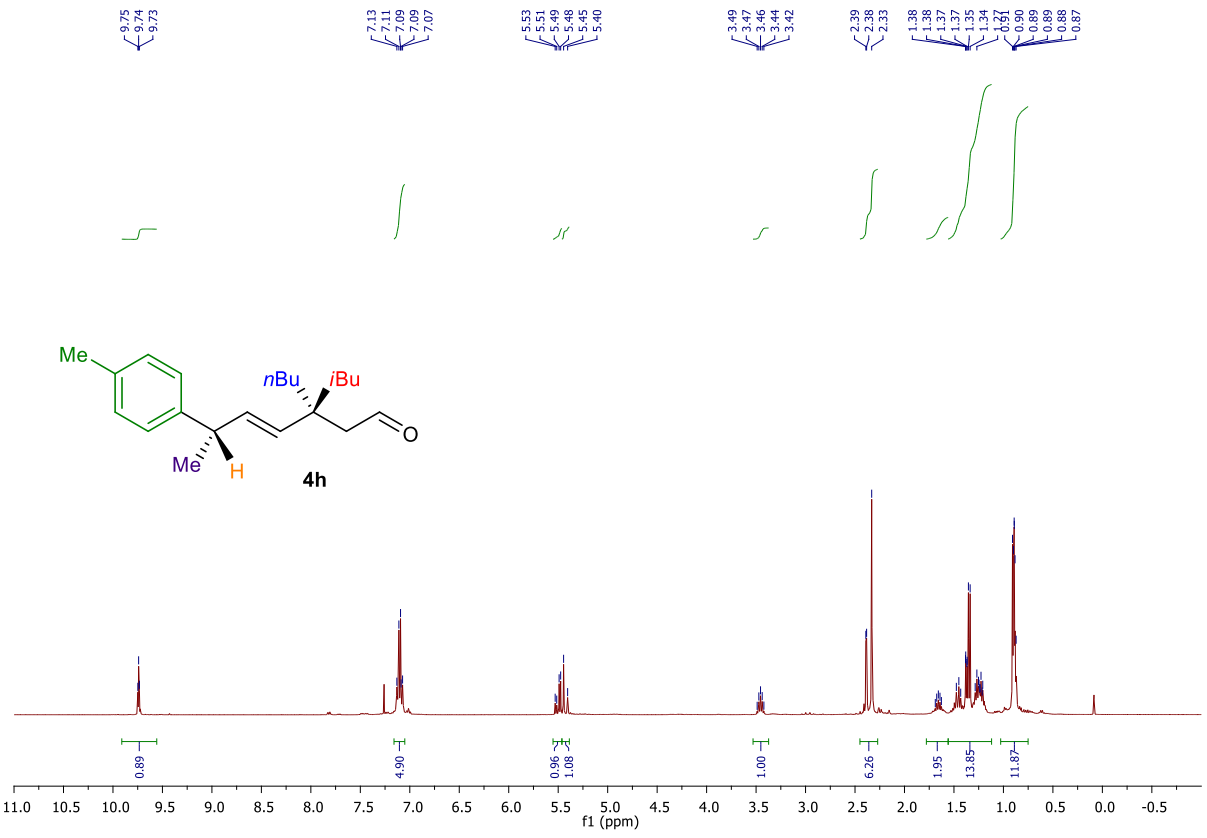
41.69
38.39
34.10
31.64
28.12
26.21
24.25
23.27
22.70
21.02
14.18
14.09
Me
nBu
Me
O
H
4g
f1 (ppm)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9.73
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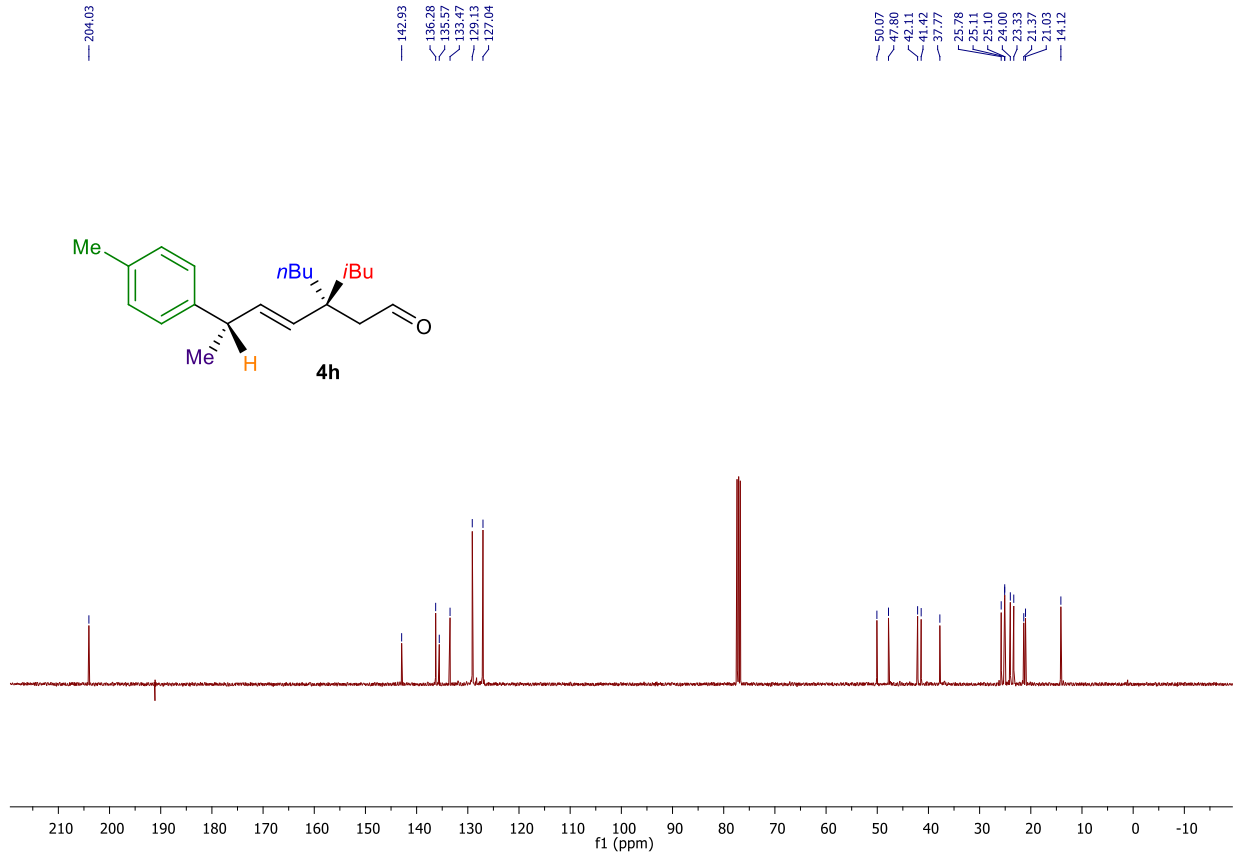
7.09
7.09
7.07
5.53
5.51
5.49
5.48
5.45
5.40
3.49
3.47
3.46
3.44
3.42
2.39
2.38
2.33
1.38
1.38
1.37
1.37
1.35
1.34
1.27
0.91
0.90
0.89
0.89
0.88
0.87
Me
nBu
iBu
O
Me
H
4h
0.89
4.90
0.96
1.08
1.00
6.26
1.95
13.85
11.87
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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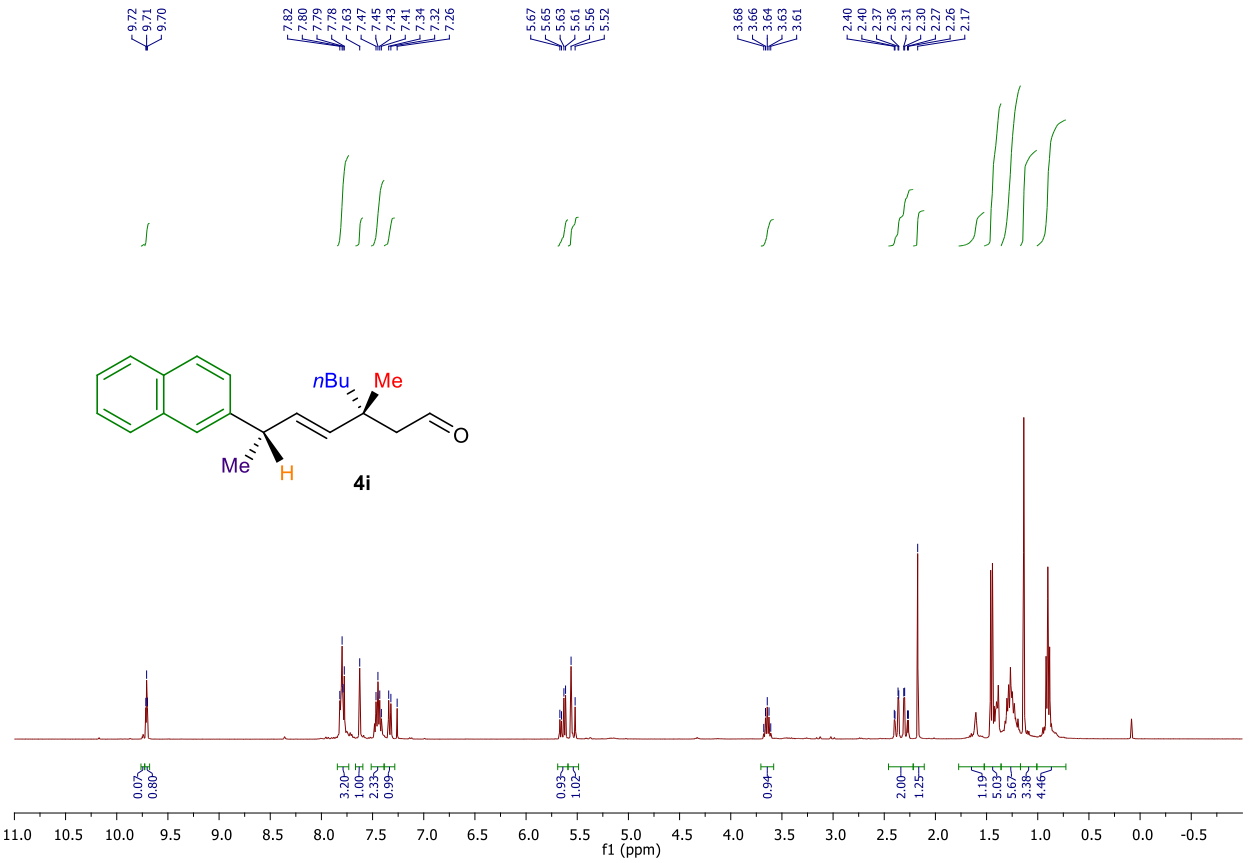
142.93
136.28
135.57
133.47
129.13
127.04
50.07
47.80
42.11
41.42
37.77
25.78
25.11
25.10
24.00
23.33
21.37
21.03
14.12
Me
nBu
iBu
O
Me
H
4h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.72
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7.80
7.79
7.78
7.63
7.47
7.45
7.43
7.41
7.34
7.32
7.26
5.67
5.65
5.63
5.61
5.56
5.52
3.68
3.66
3.64
3.63
3.61
2.40
2.40
2.37
2.36
2.31
2.30
2.27
2.26
2.17
nBu
Me
Me
H
O
4i
0.07
0.80
3.20
1.00
2.33
0.99
0.93
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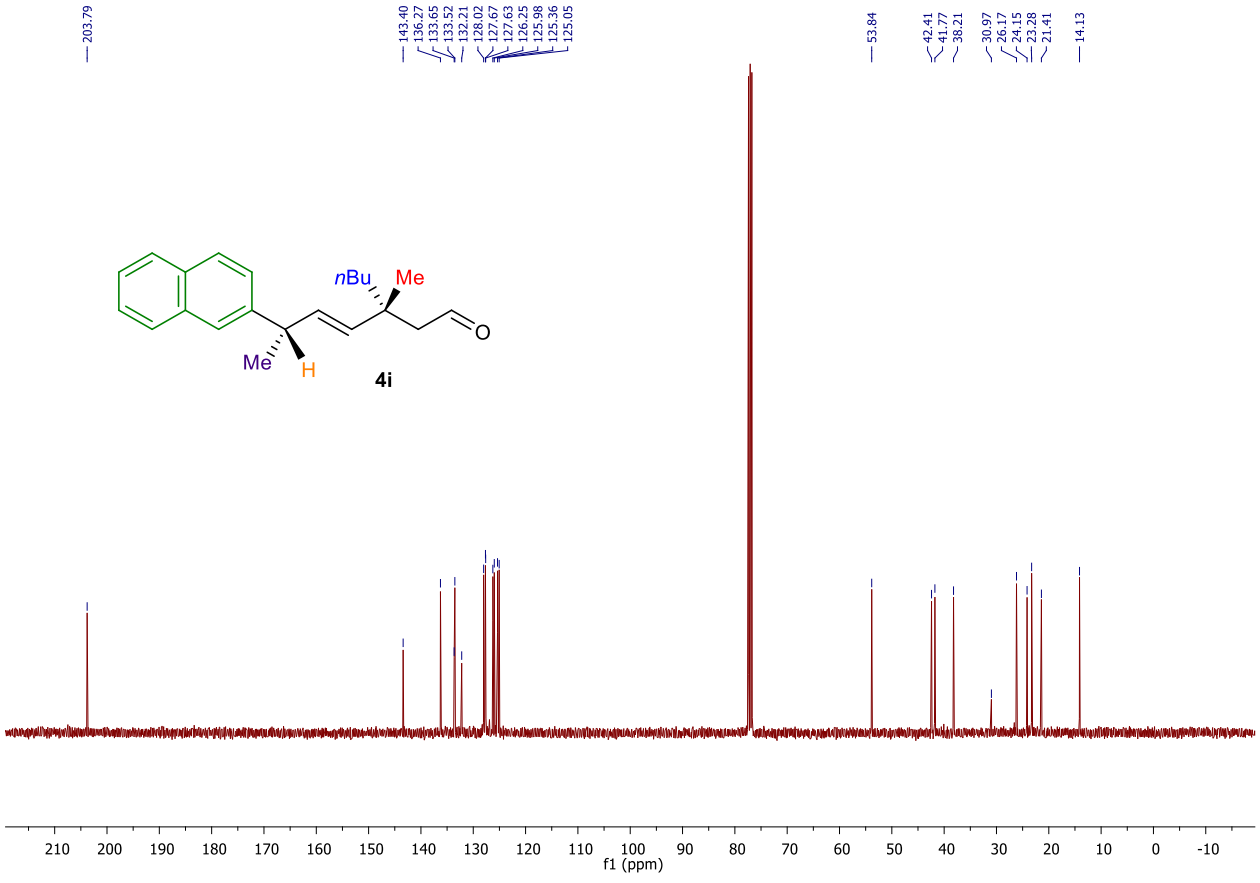
0.94
2.00
1.25
1.19
5.03
5.67
3.38
4.46
f1 (ppm)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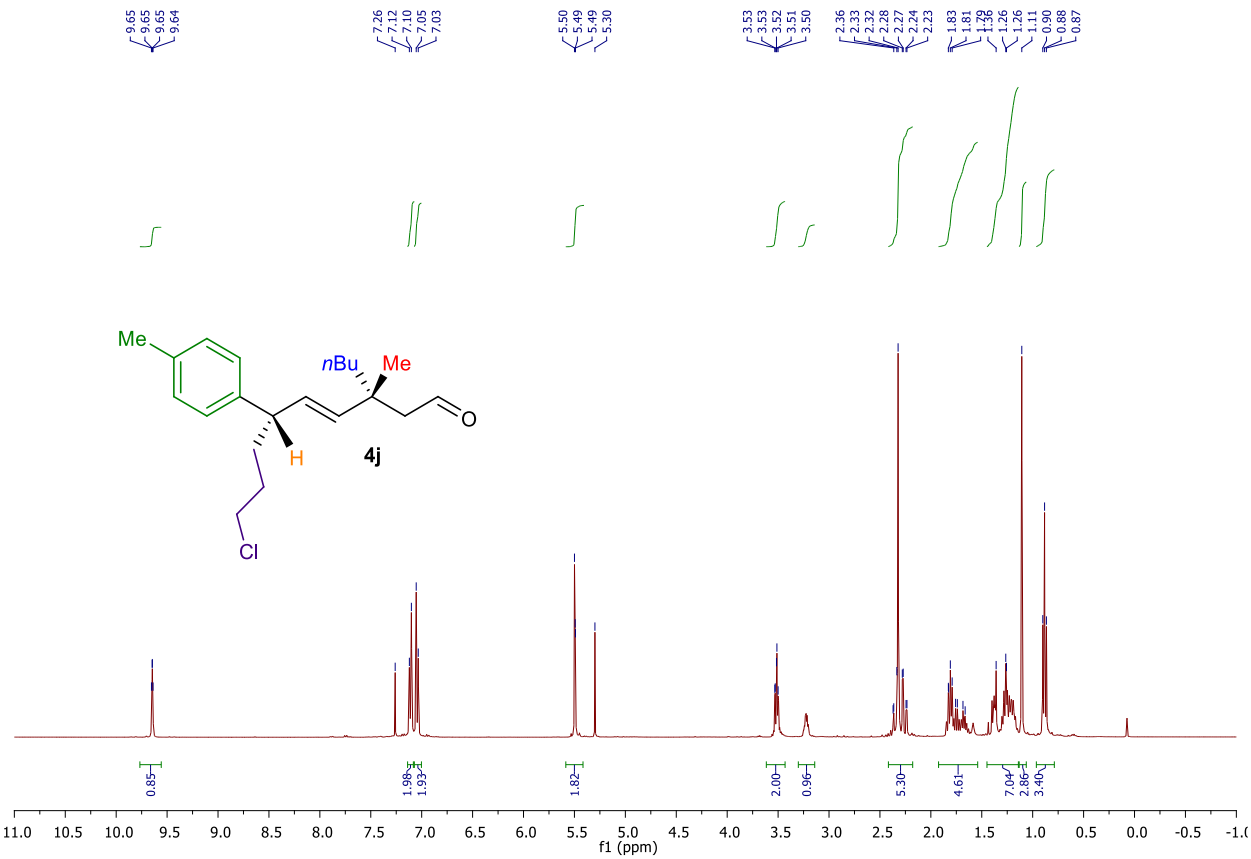
143.40
136.27
133.65
133.52
132.21
128.02
127.67
127.63
126.25
125.98
125.36
125.05
53.84
42.41
41.77
38.21
30.97
26.17
24.15
23.28
21.41
14.13
nBu
Me
Me
H
O
4i
f1 (ppm)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9.65
9.65
9.64
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7.12
7.10
7.05
7.03
5.50
5.49
5.49
5.30
3.53
3.53
3.52
3.51
3.50
2.36
2.33
2.32
2.28
2.27
2.24
2.23
1.83
1.81
1.79
1.36
1.26
1.26
1.11
0.90
0.88
0.87
Me
nBu
Me
O
H
4j
Cl
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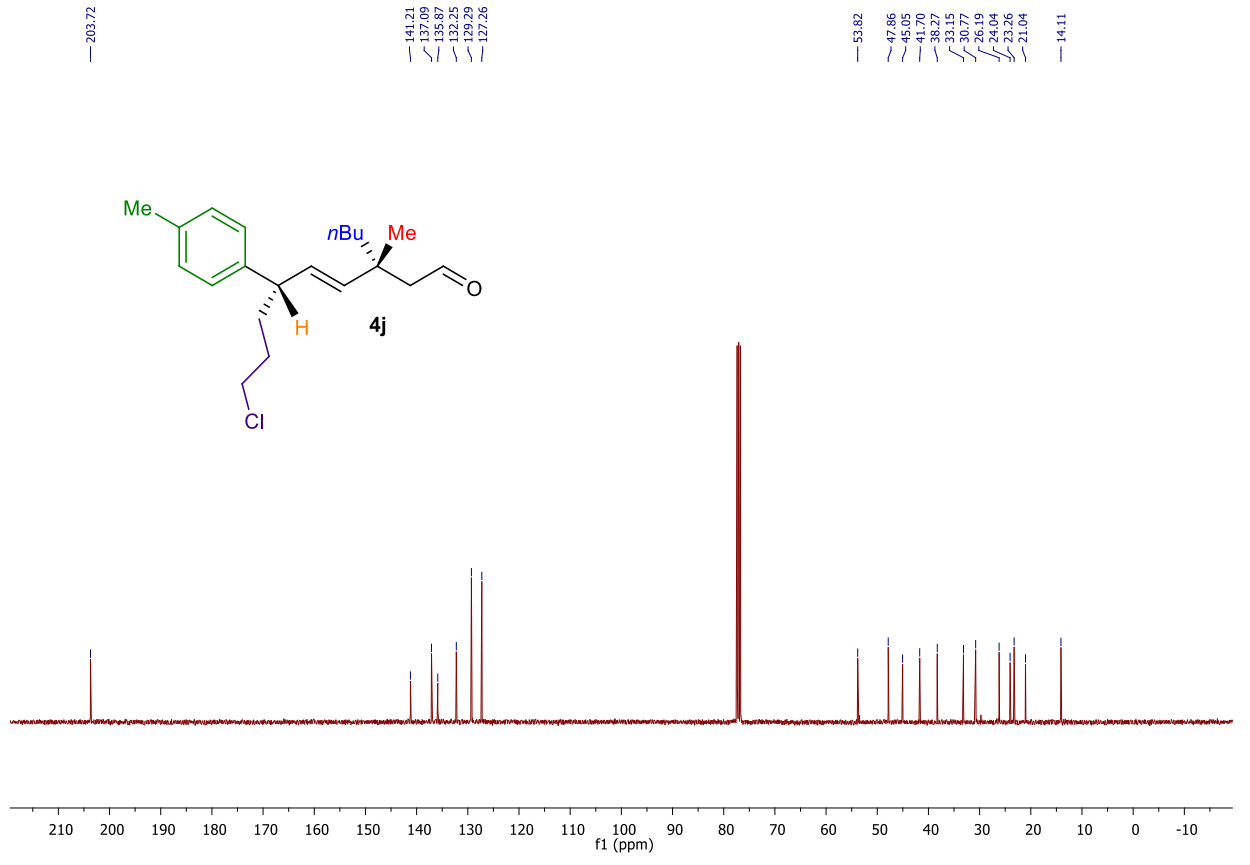
1.93
1.82
2.00
0.96
5.30
4.61
7.04
2.86
3.40
f1 (ppm)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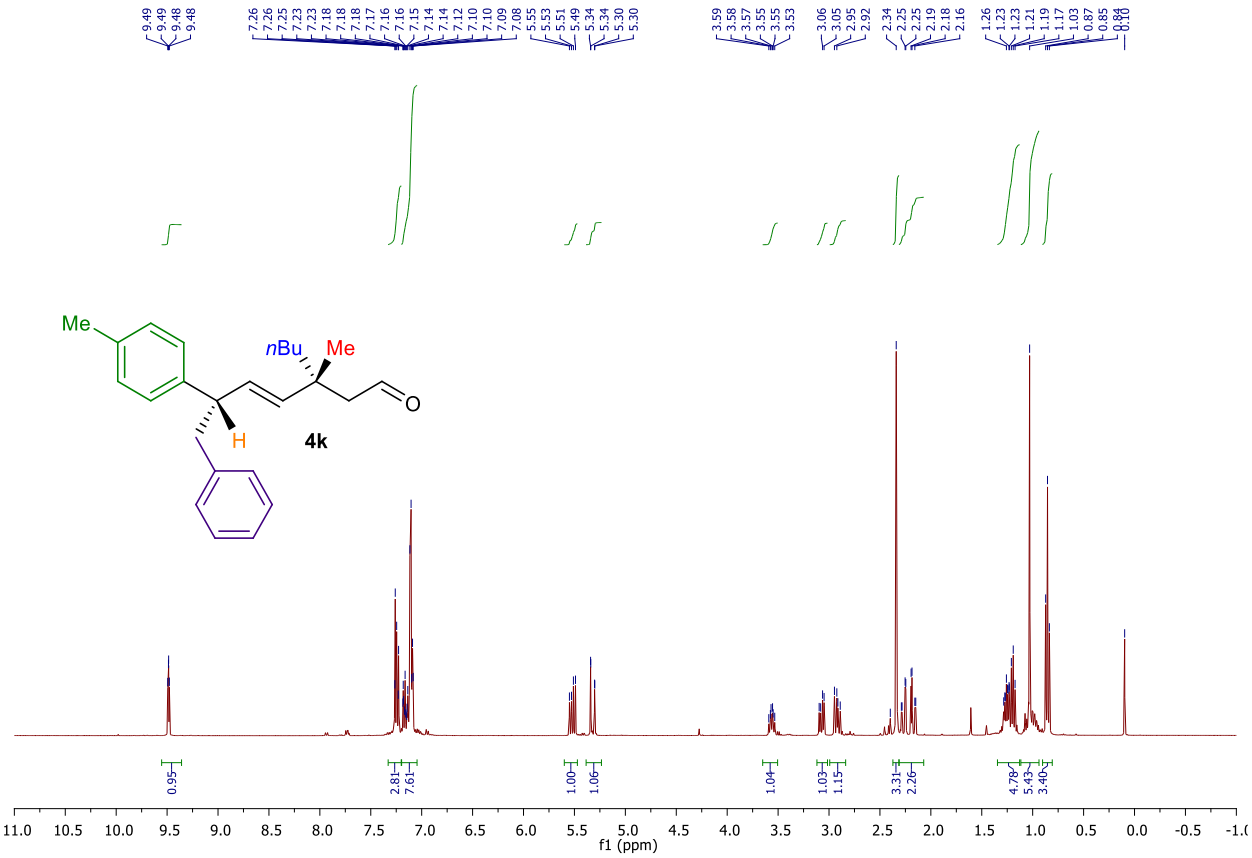
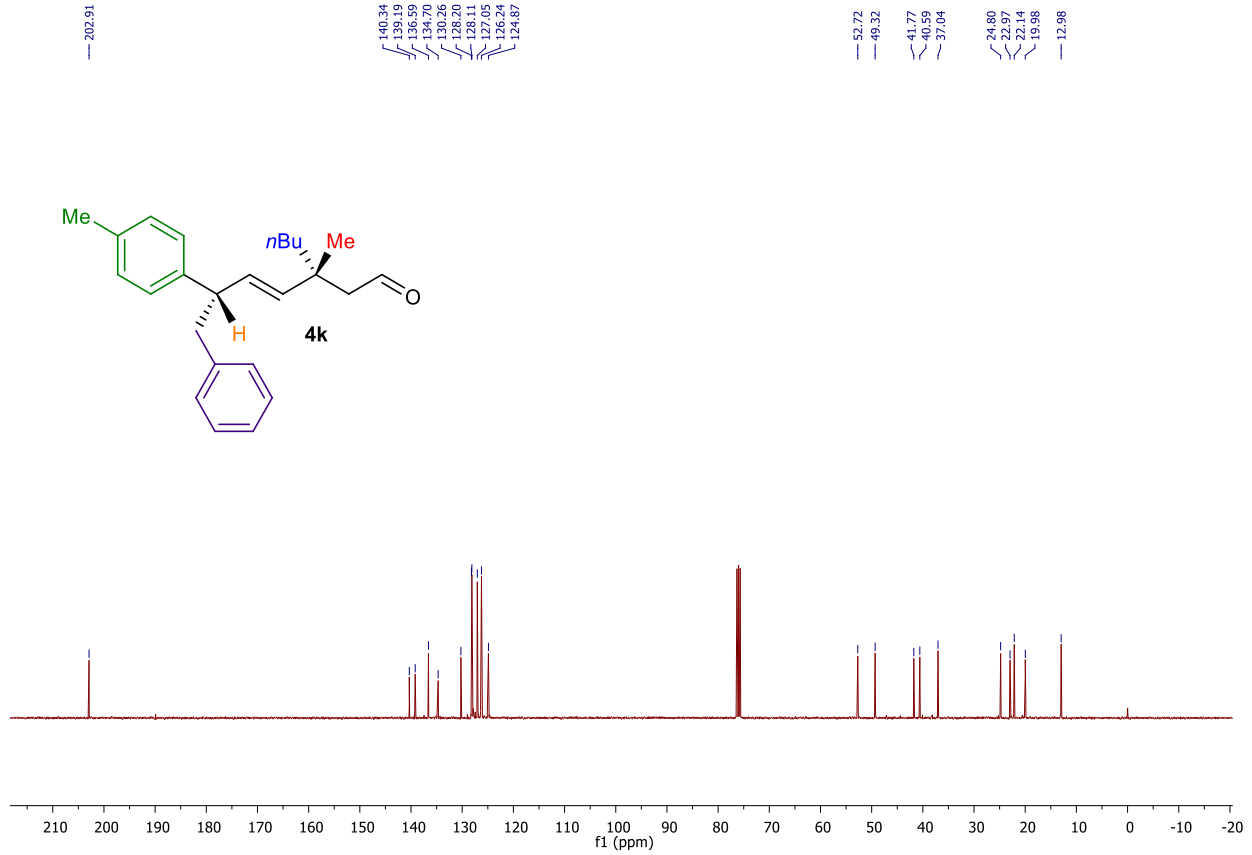
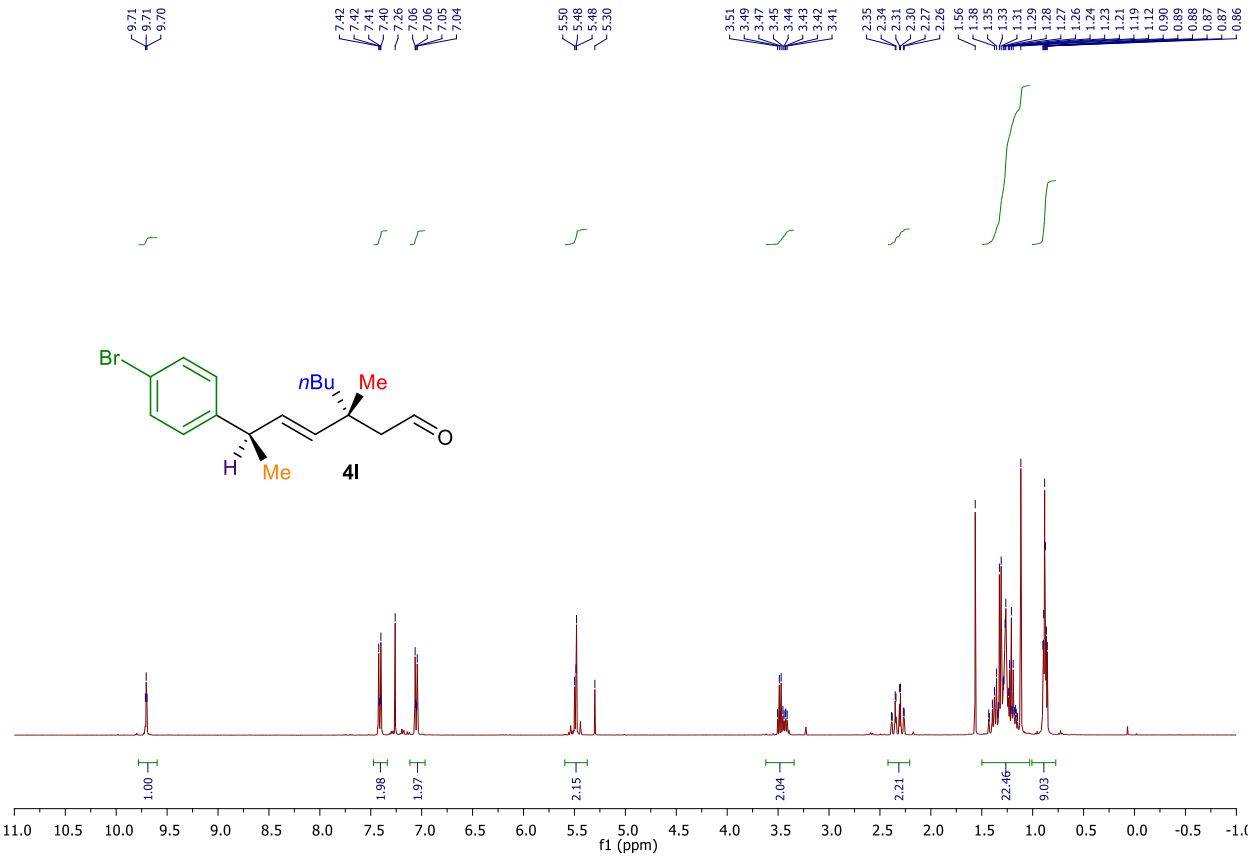
137.09
135.87
132.25
129.29
127.26
53.82
47.86
45.05
41.70
38.27
33.15
30.77
26.19
24.04
23.26
21.04
14.11
Me
nBu
Me
O
H
4j
Cl
f1 (ppm)


Me
nBu
Me
O
H
4k
f1 (ppm)


Me
nBu
Me
O
H
4k
f1 (ppm)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9.71
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7.40
7.26
7.06
7.06
7.05
7.04
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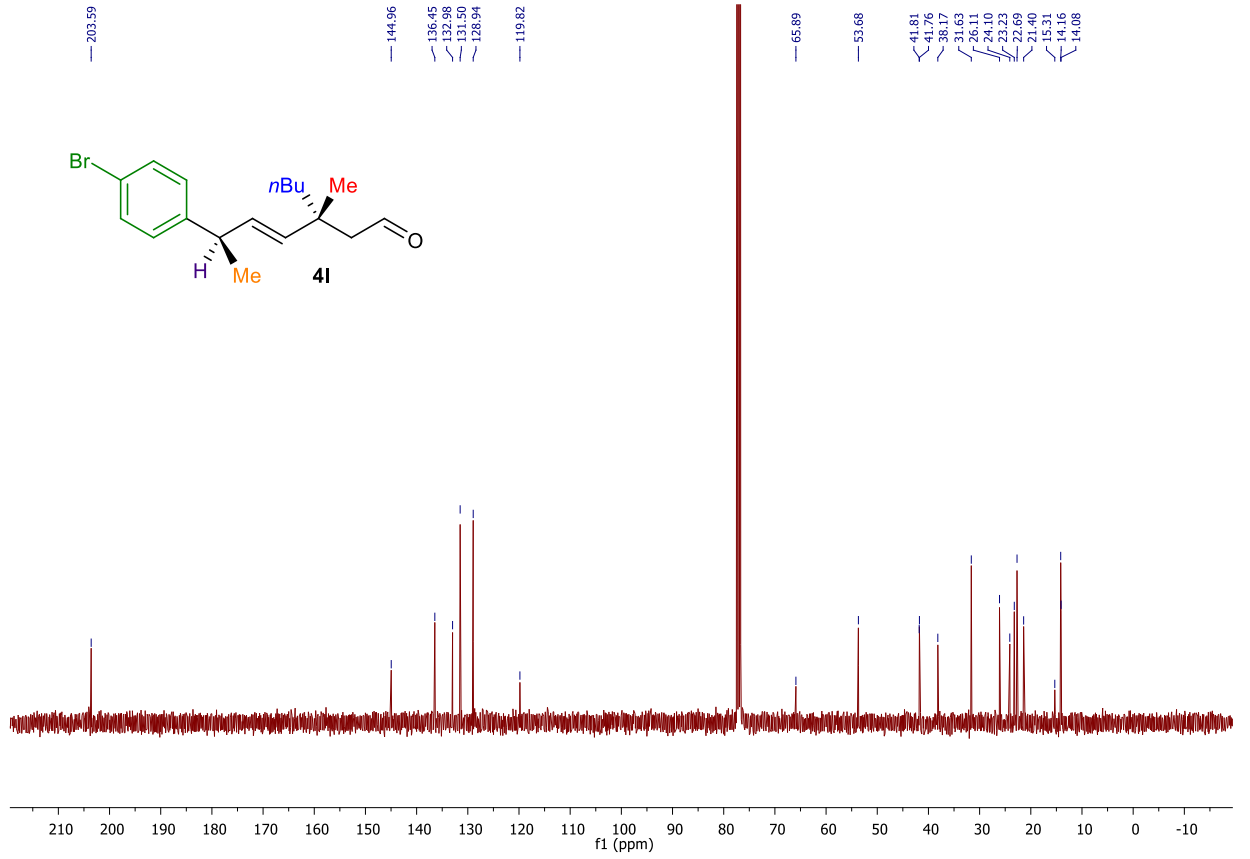
5.48
5.48
5.30
3.51
3.49
3.47
3.45
3.44
3.43
3.42
3.41
2.35
2.34
2.31
2.30
2.27
2.26
1.56
1.38
1.35
1.33
1.31
1.29
1.28
1.27
1.26
1.24
1.23
1.21
1.19
1.12
0.90
0.89
0.88
0.87
0.87
0.86
Br
nBu
Me
H
Me
O
4l
1.00
1.98
1.97
2.15
2.04
2.21
22.46
9.03
f1 (ppm)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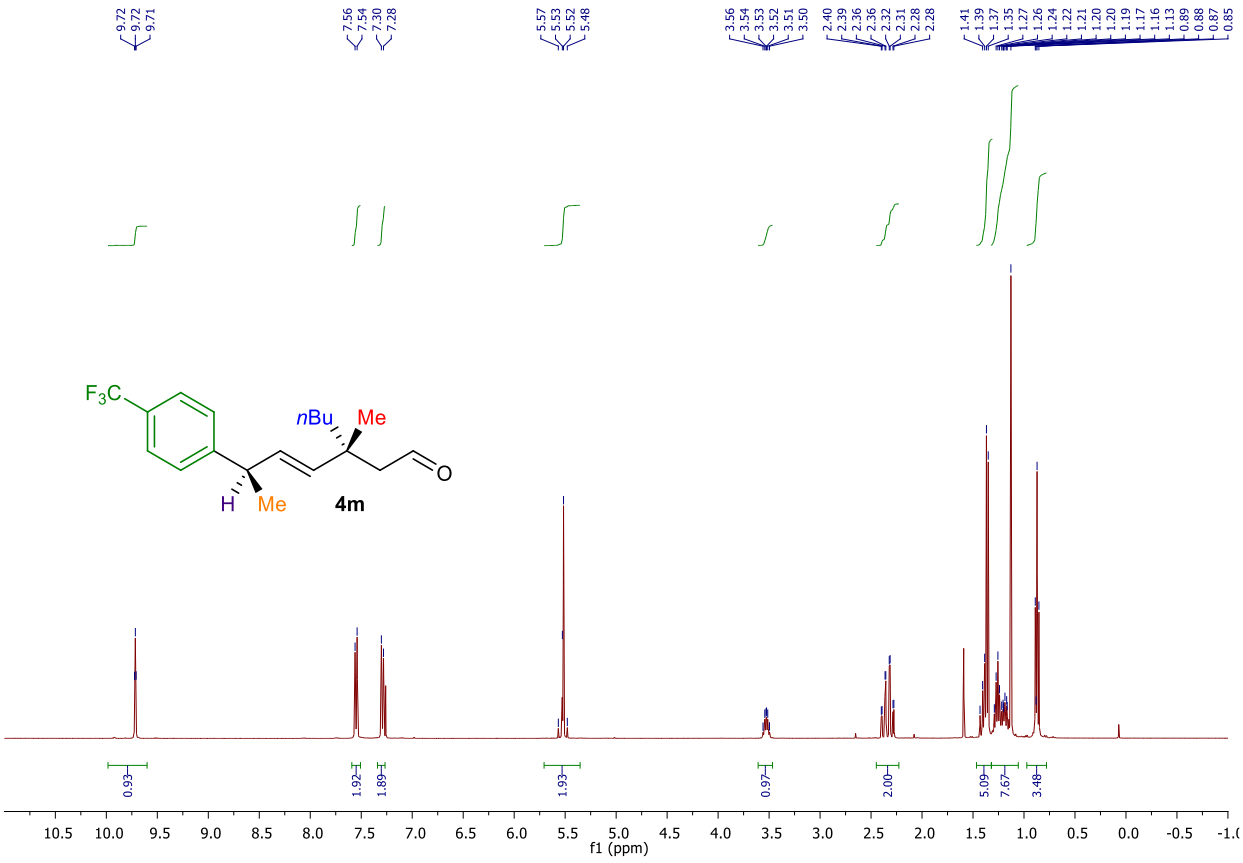
41.76
38.17
31.63
26.11
24.10
23.23
22.69
21.40
15.31
14.16
14.08
Br
nBu
Me
H
Me
O
4l
f1 (ppm)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9.72
9.71
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7.54
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7.28
5.57
5.53
5.52
5.48
3.56
3.54
3.53
3.52
3.51
3.50
2.40
2.39
2.36
2.36
2.32
2.31
2.28
2.28
1.41
1.39
1.37
1.35
1.27
1.26
1.24
1.22
1.21
1.20
1.20
1.19
1.17
1.16
1.13
0.89
0.88
0.87
0.85
F3C
nBu
Me
H
Me
4m
O
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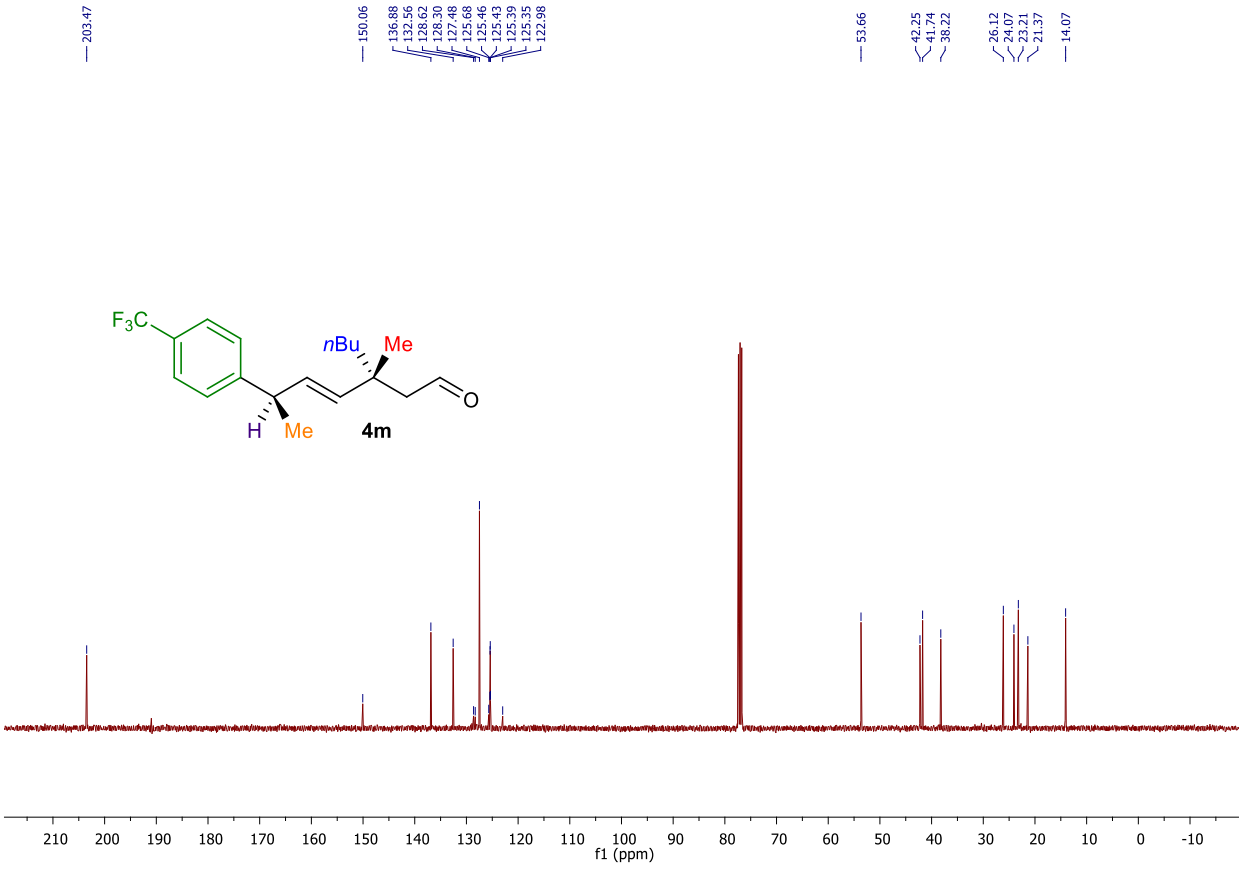
1.92
1.89
1.93
0.97
2.00
5.09
7.67
3.48
f1 (ppm)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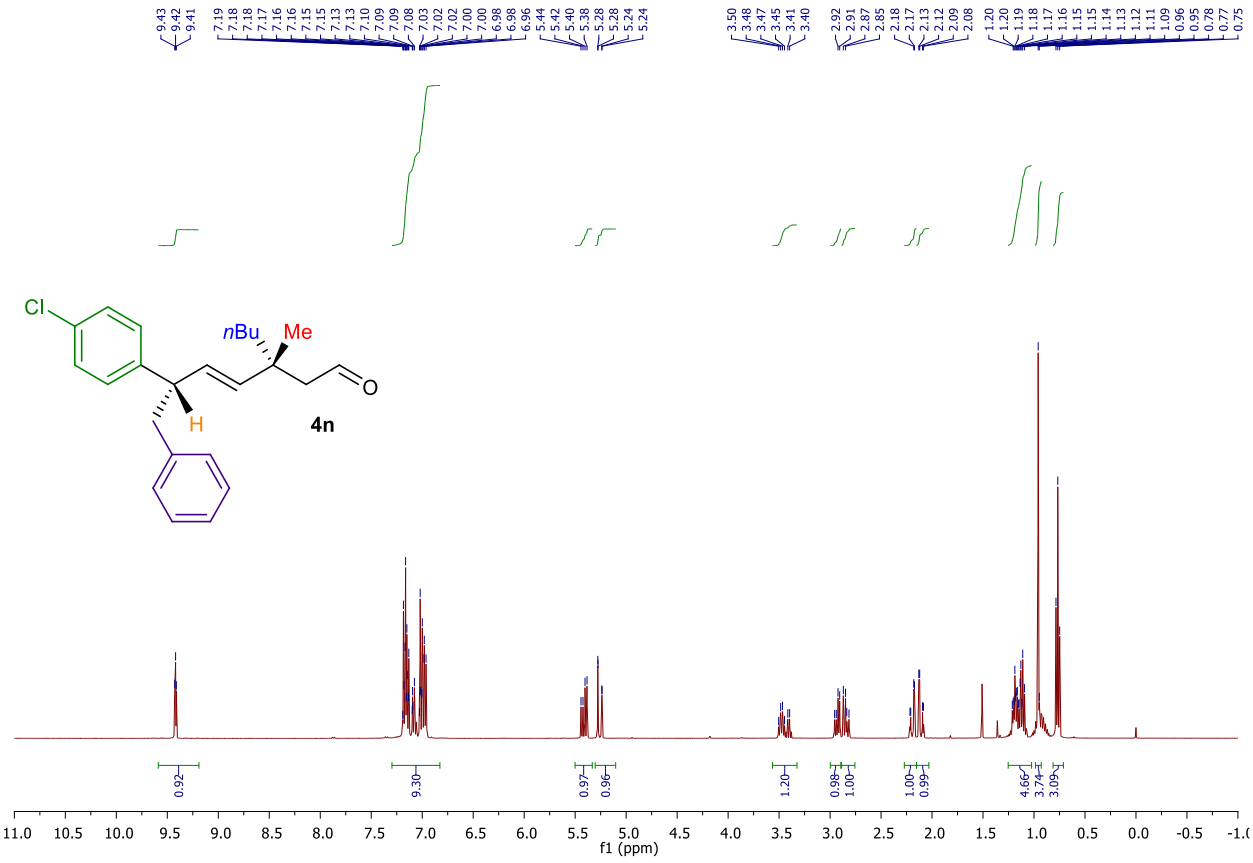
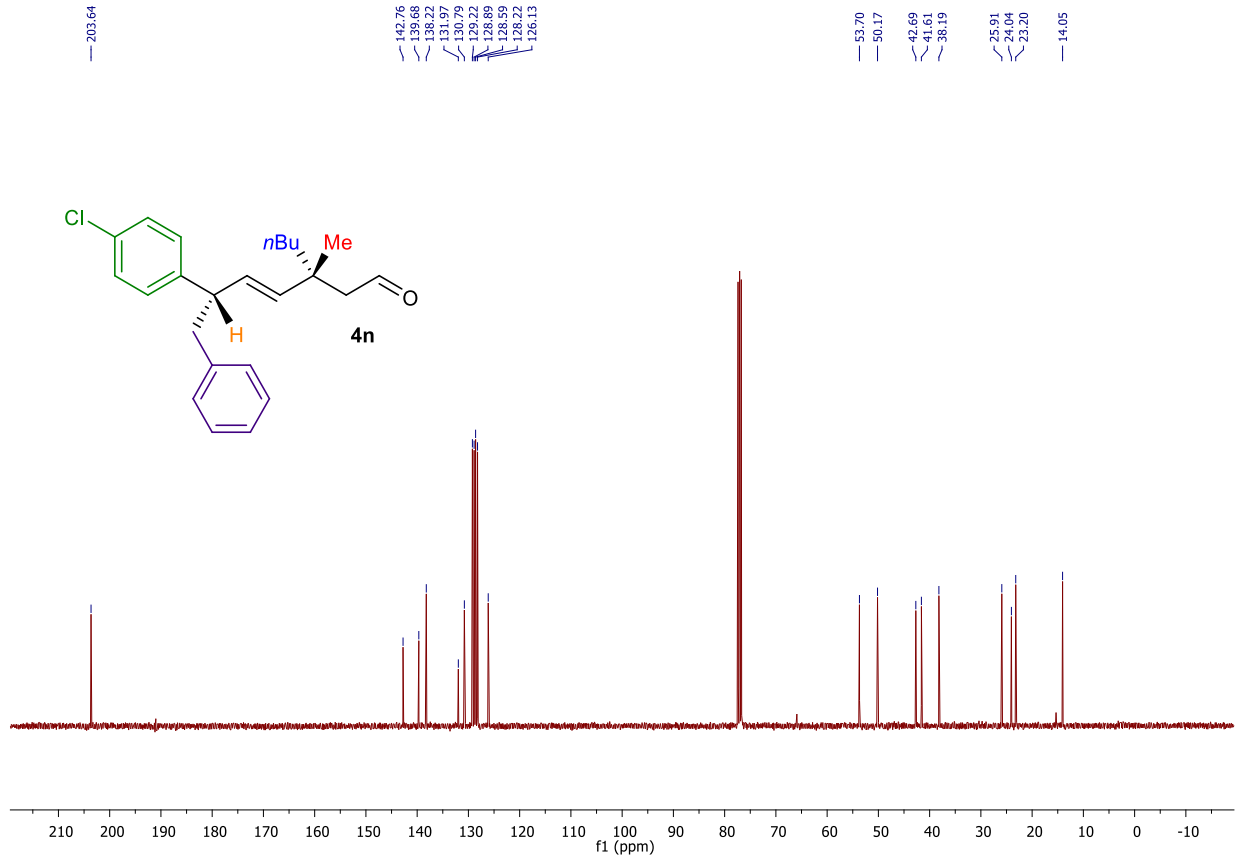
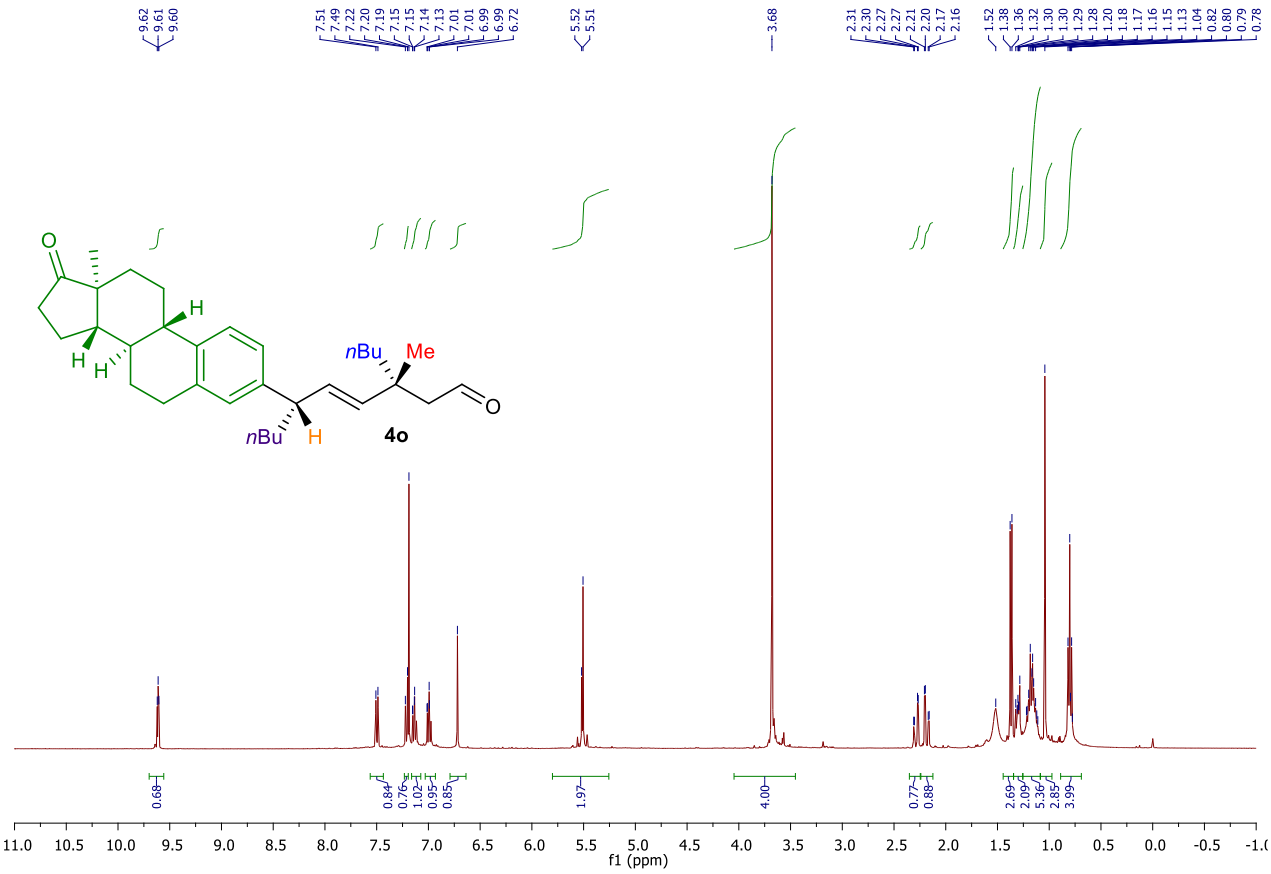
127.48
125.68
125.46
125.43
125.39
125.35
122.98
53.66
42.25
41.74
38.22
26.12
24.07
23.21
21.37
14.07
F3C
nBu
Me
H
Me
4m
O
f1 (ppm)


Cl
nBu
Me
H
O
4n
f1 (ppm)


Cl
nBu
Me
H
O
4n
f1 (ppm)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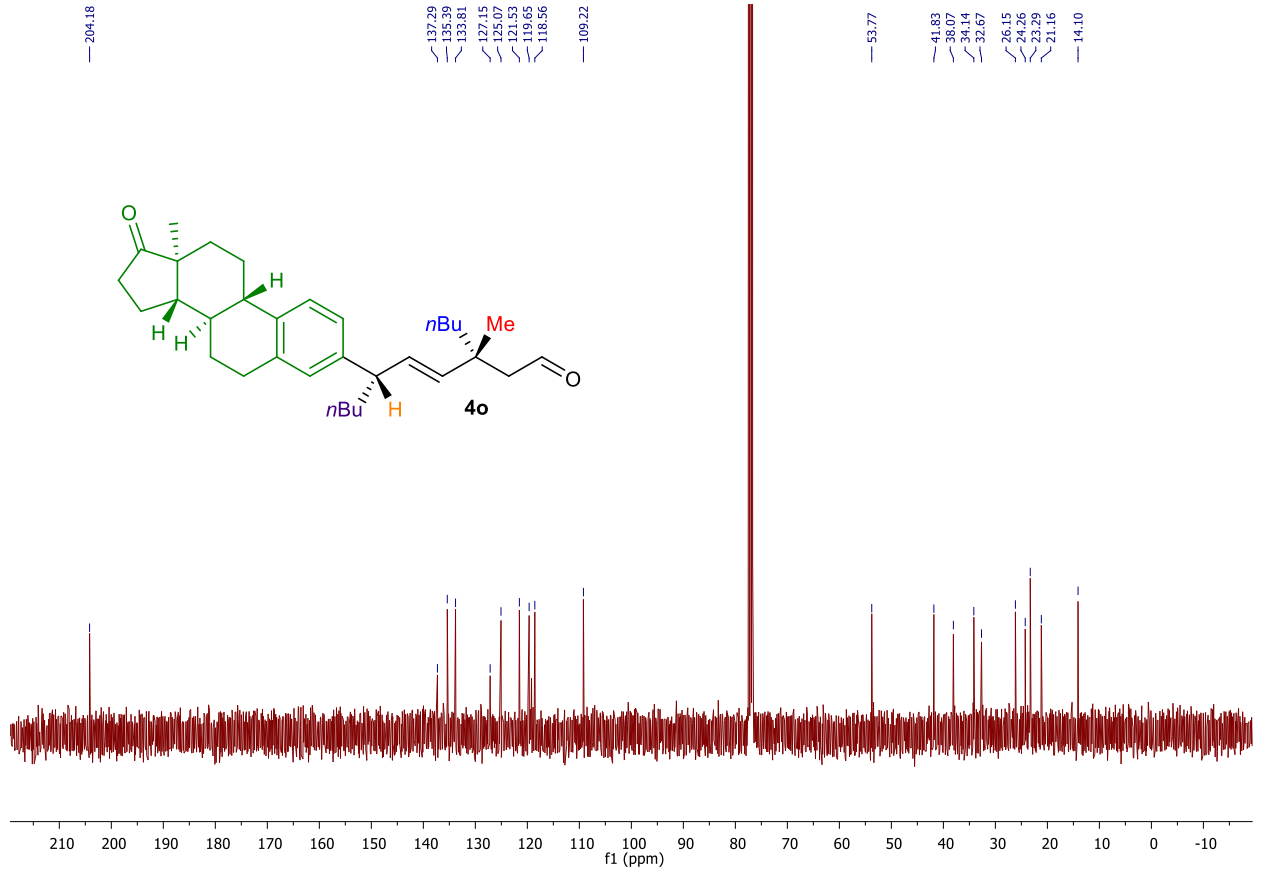
7.15
7.14
7.13
7.01
7.01
6.99
6.99
6.72
5.52
5.51
3.68
2.31
2.30
2.27
2.27
2.21
2.20
2.17
2.16
1.52
1.38
1.36
1.32
1.30
1.30
1.29
1.28
1.20
1.18
1.17
1.16
1.15
1.13
1.04
0.82
0.80
0.79
0.78
O
H
H
H
nBu
Me
nBu
H
O
4o
0.68
0.84
0.76
1.02
0.95
0.85
1.97
4.00
0.77
0.88
2.69
2.09
5.36
2.85
3.99
11.0
10.5
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
-0.5
f1 (ppm)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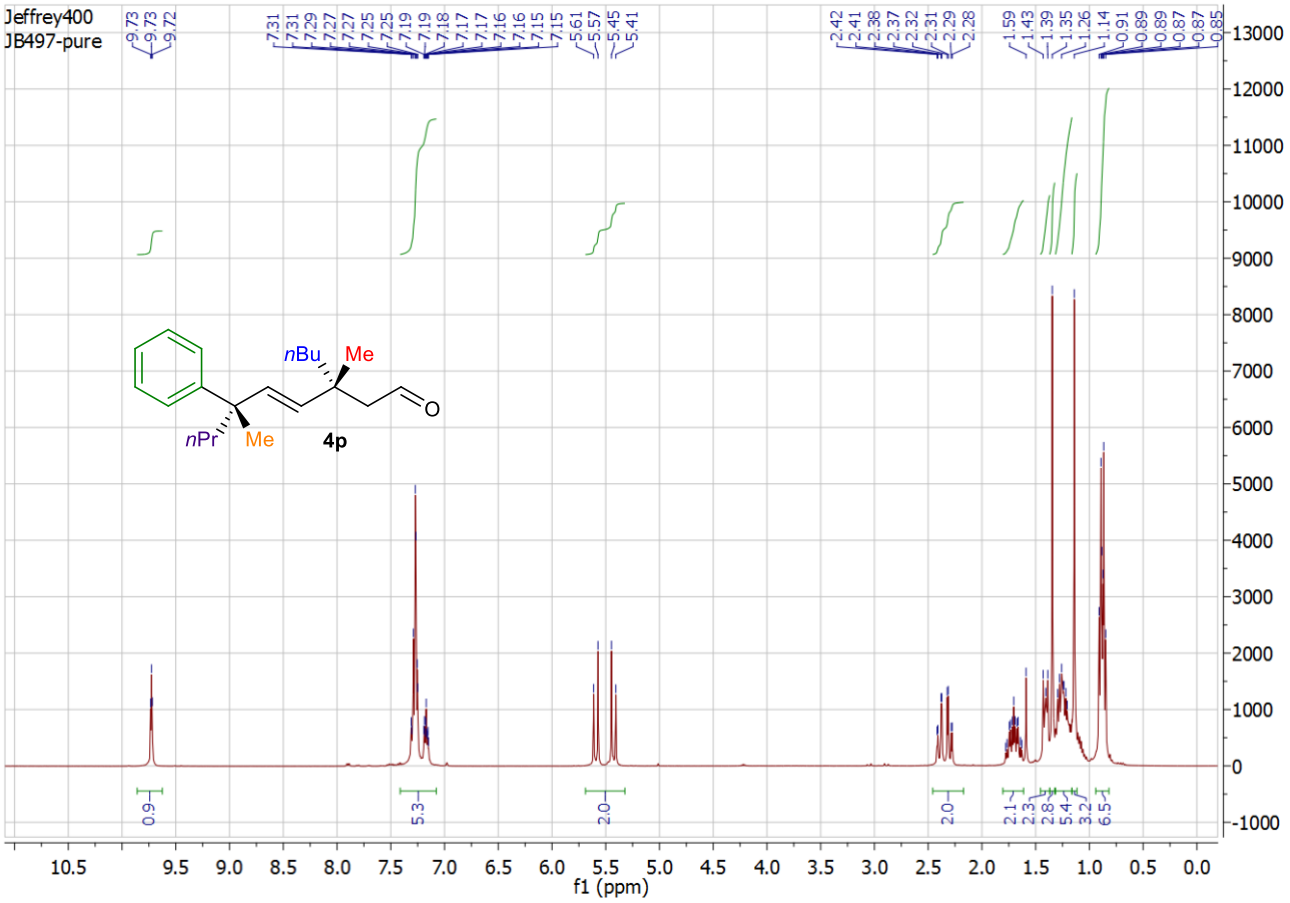
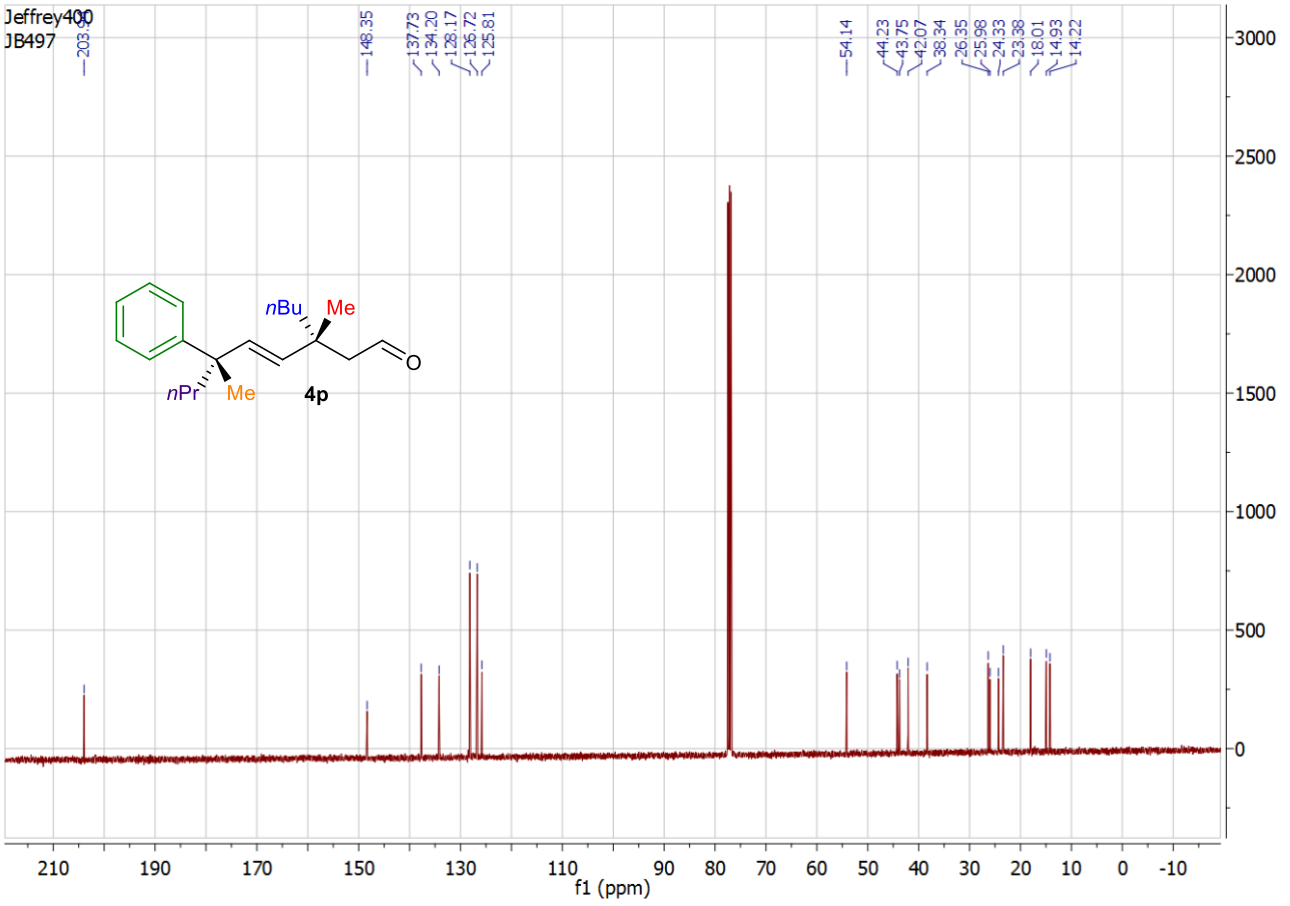
121.53
119.65
118.56
109.22
53.77
41.83
38.07
34.14
32.67
26.15
24.26
23.29
21.16
14.10
O
H
H
H
nBu
Me
nBu
H
O
4o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Jeffrey400
JB497-pure
nBu
Me
nPr
Me
4p
f1 (ppm)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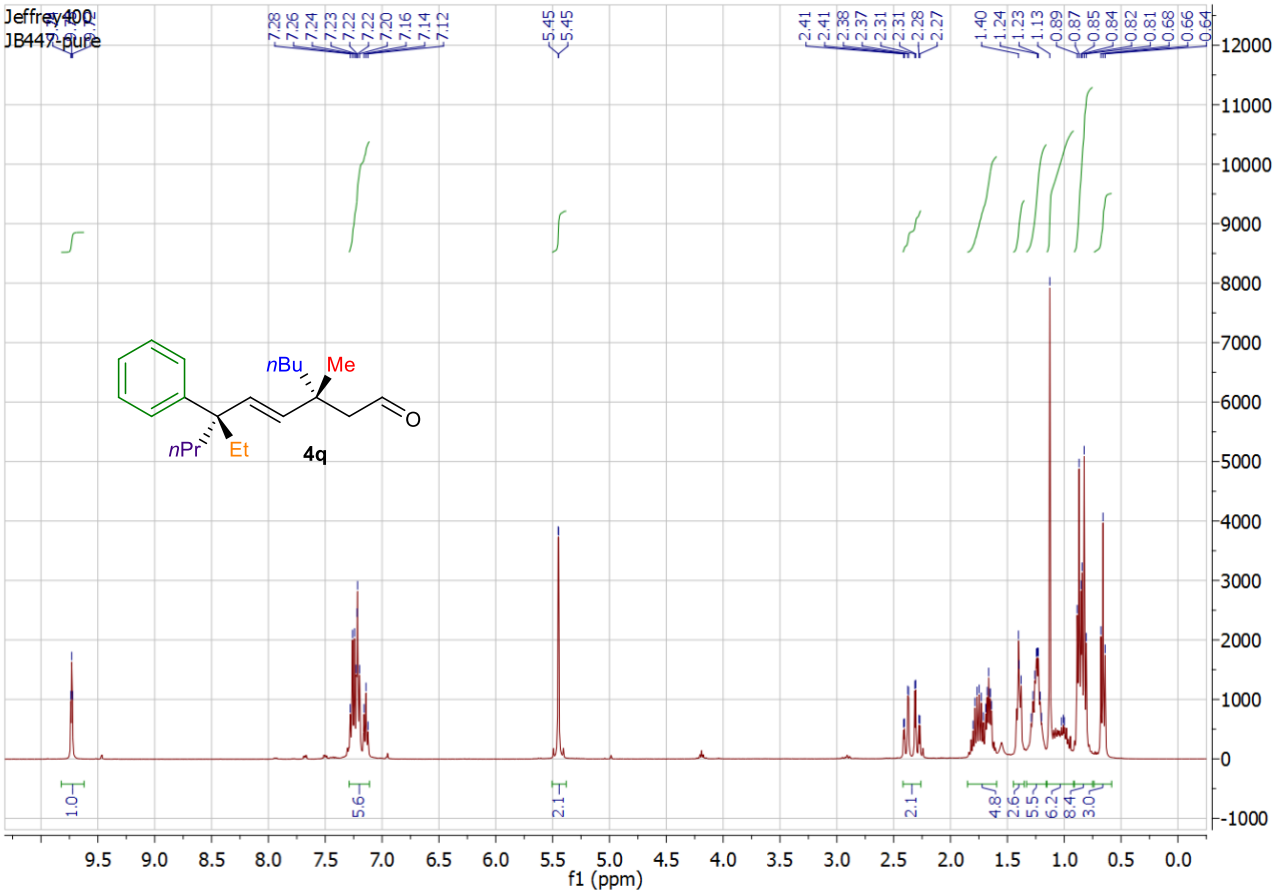
JB497
nBu
Me
nPr
Me
4p
f1 (ppm)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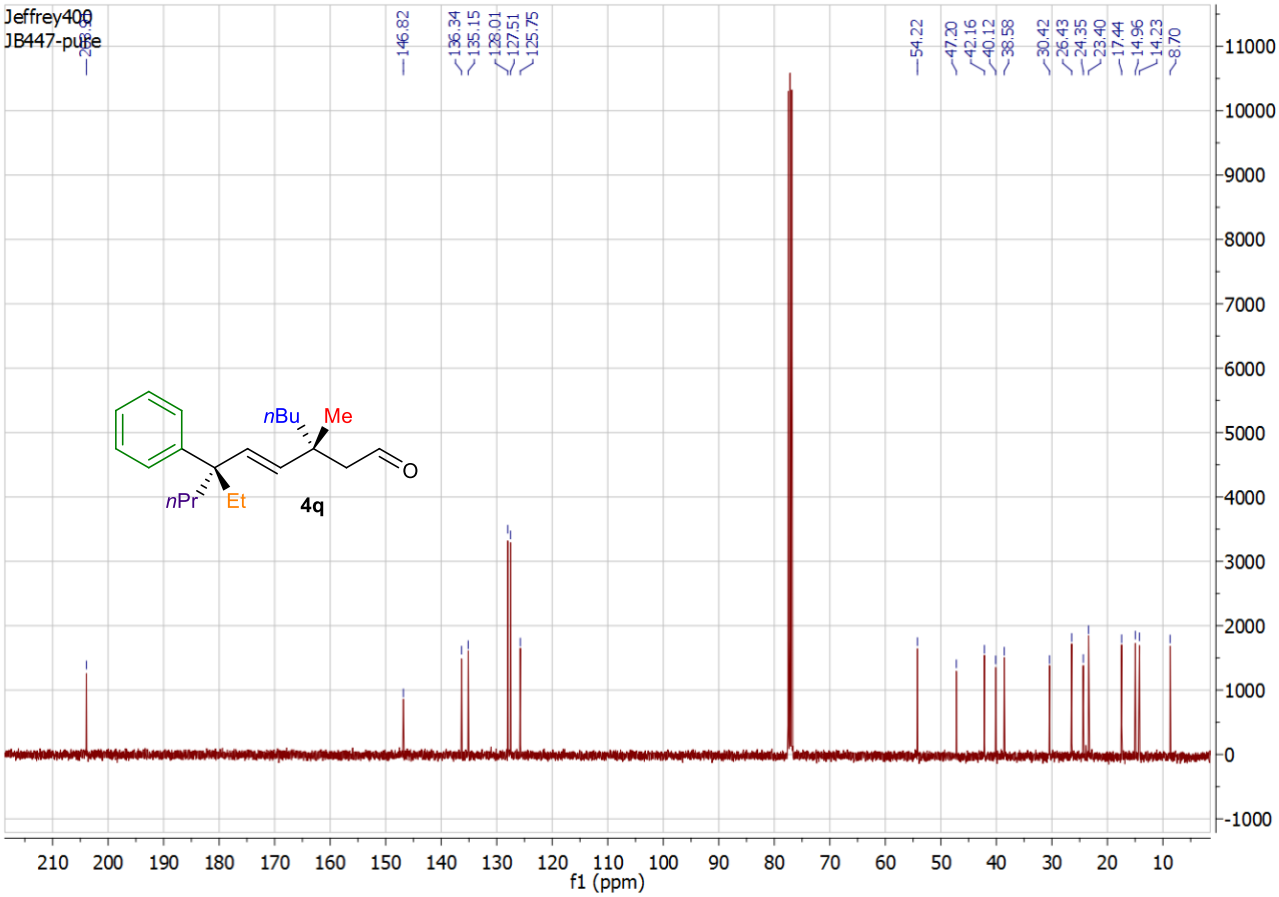
JB447-pure
nBu
Me
nPr
Et
4q
f1 (ppm)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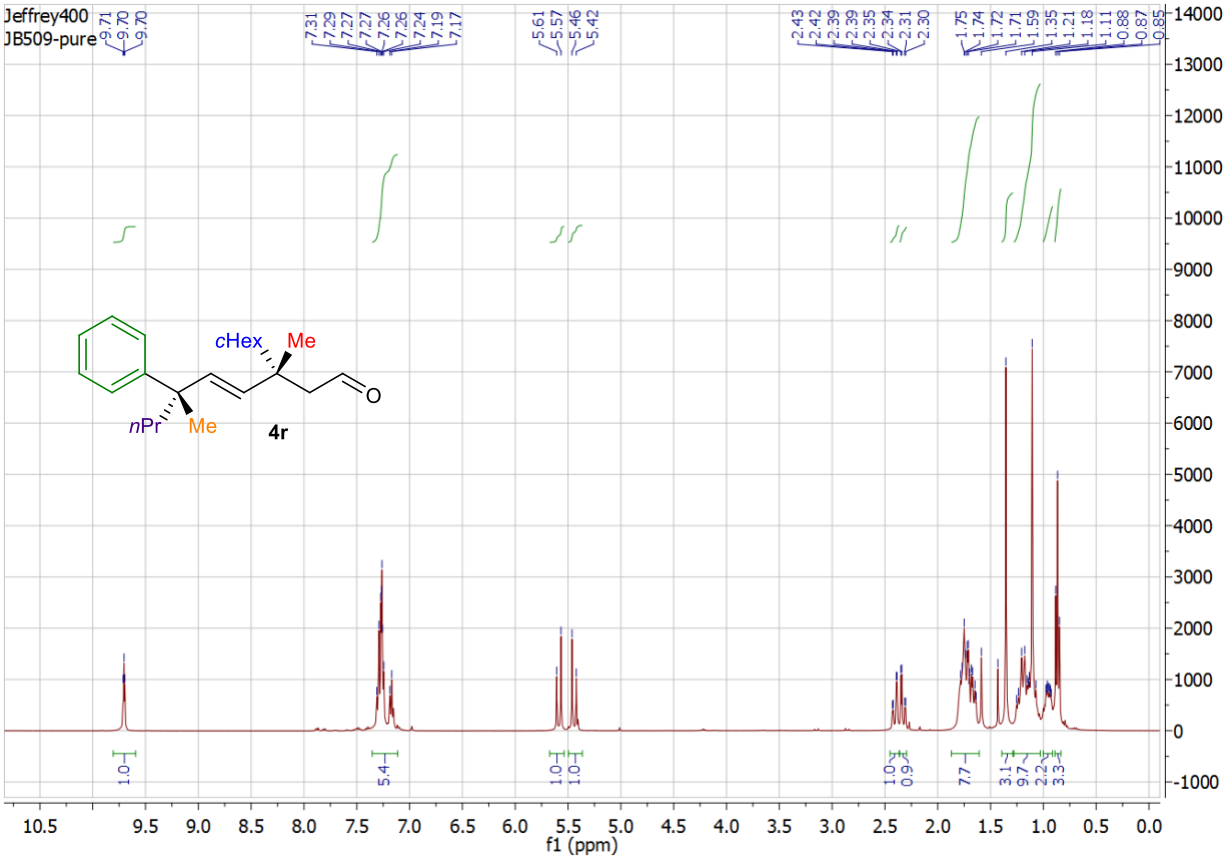
JB447-pure
nBu
Me
nPr
Et
4q
f1 (ppm)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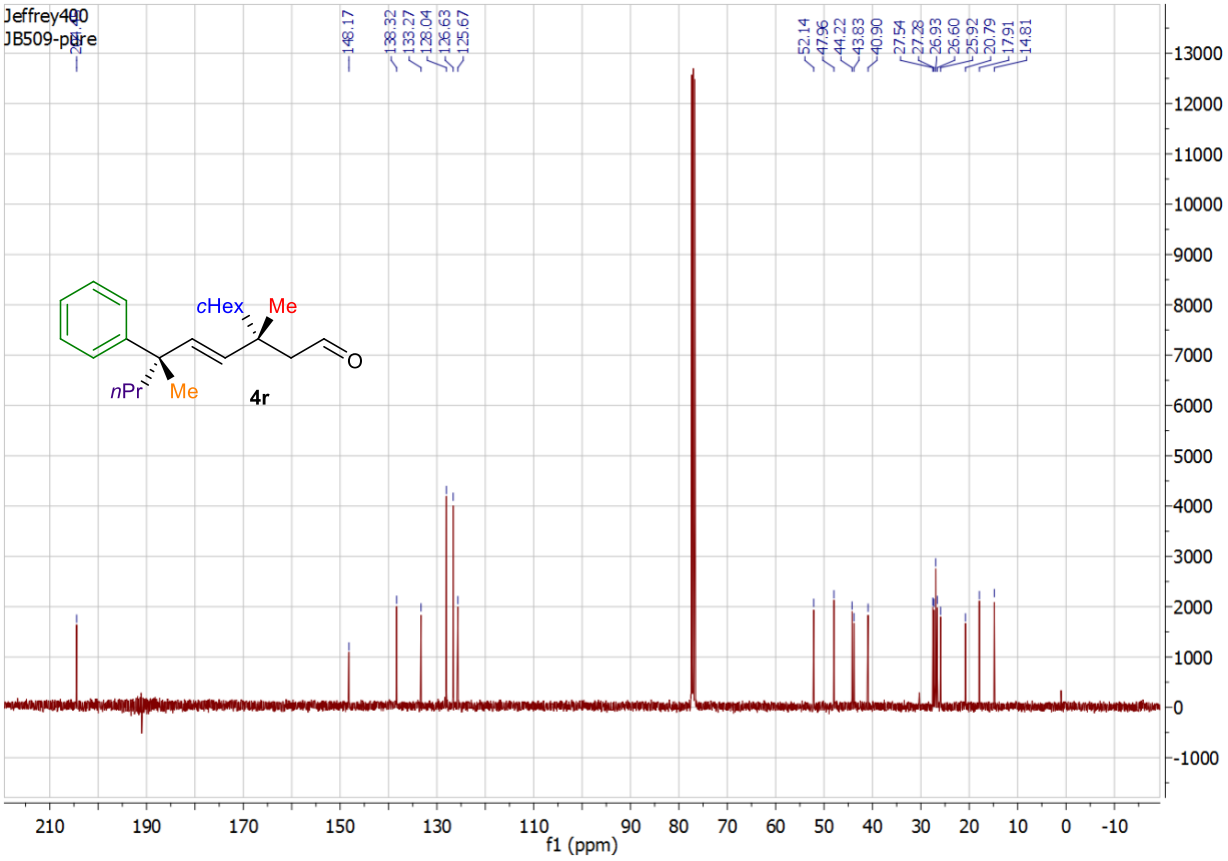
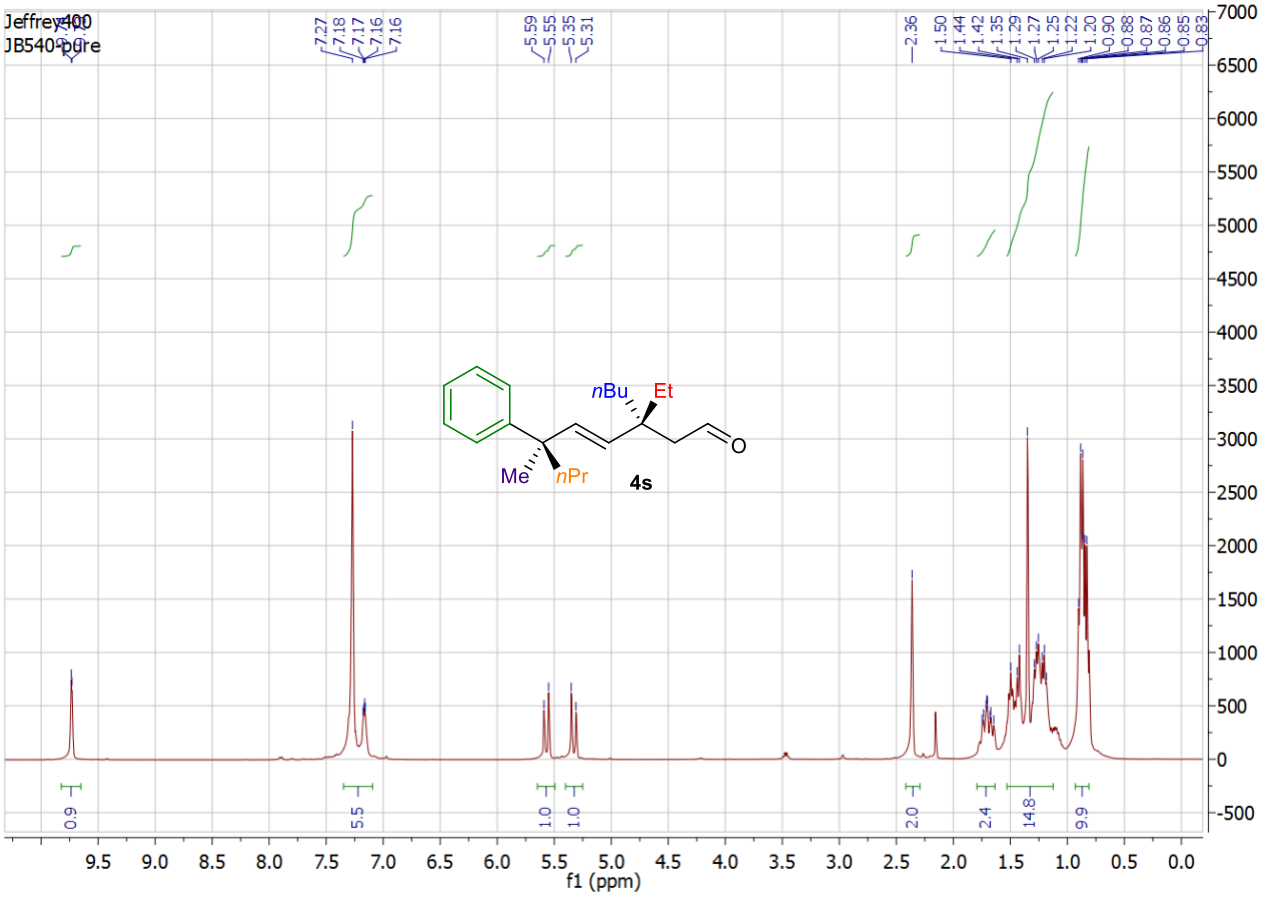
JB509-pure
cHex
Me
nPr
Me
4r
f1 (ppm)


Jeffrey400
JB509-pure
cHex
Me
nPr
Me
4r
f1 (ppm)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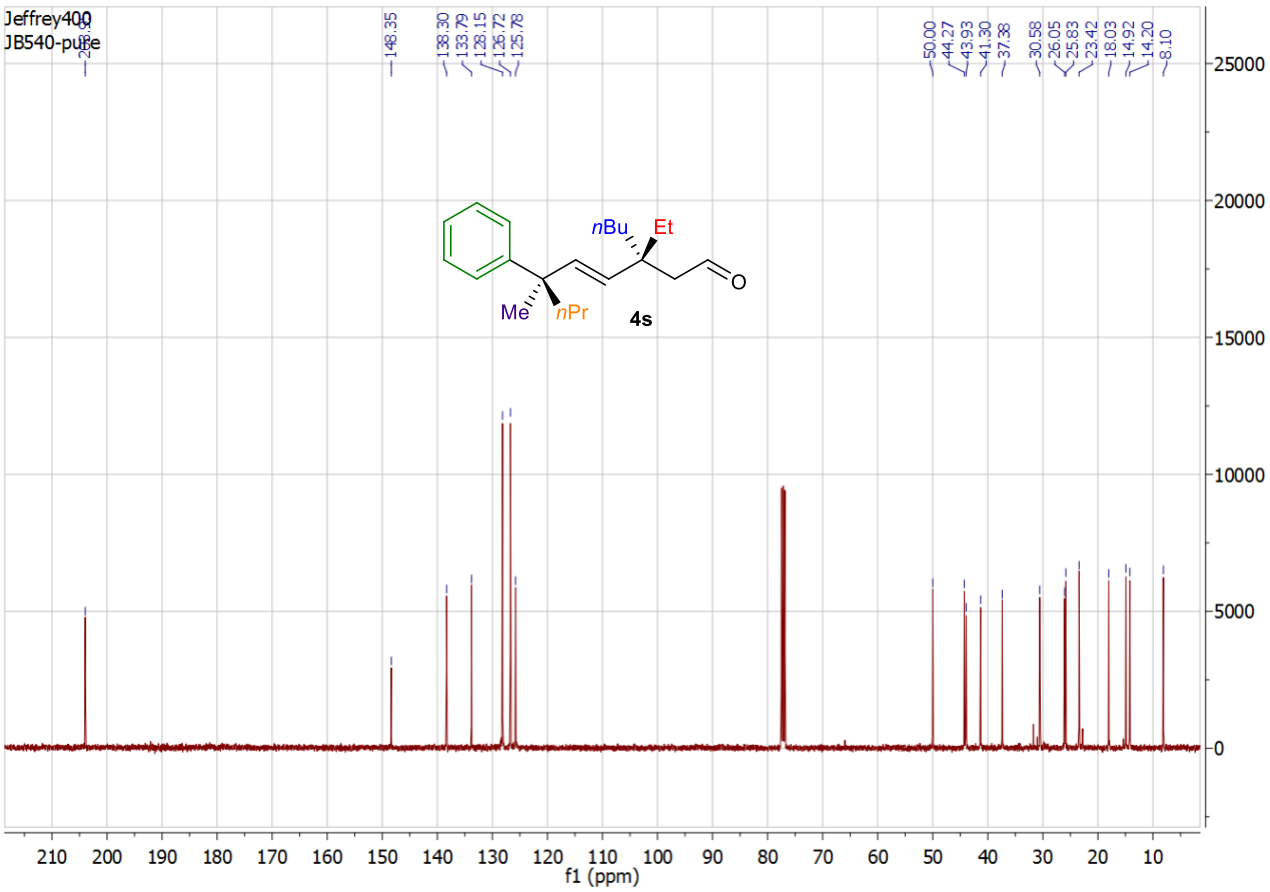
f1 (ppm)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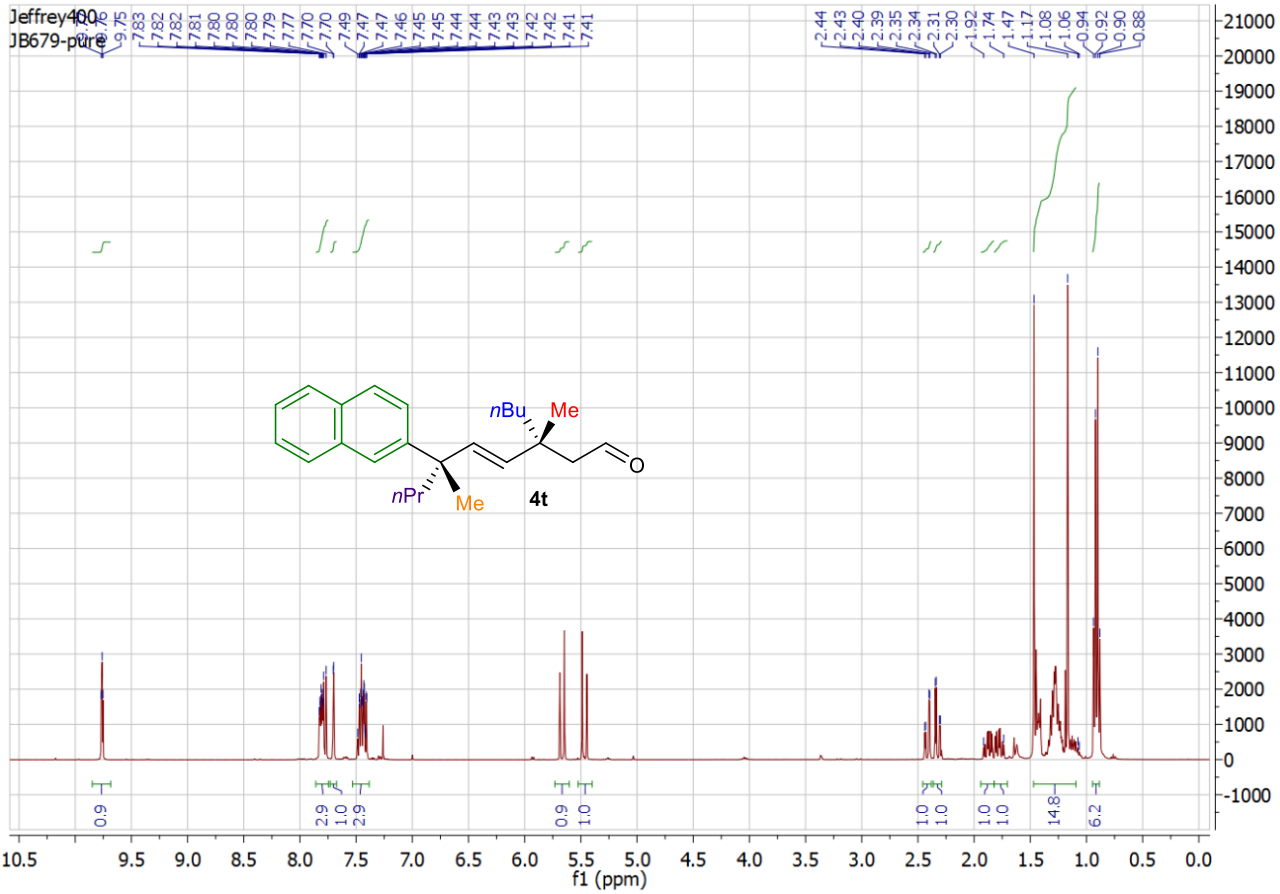
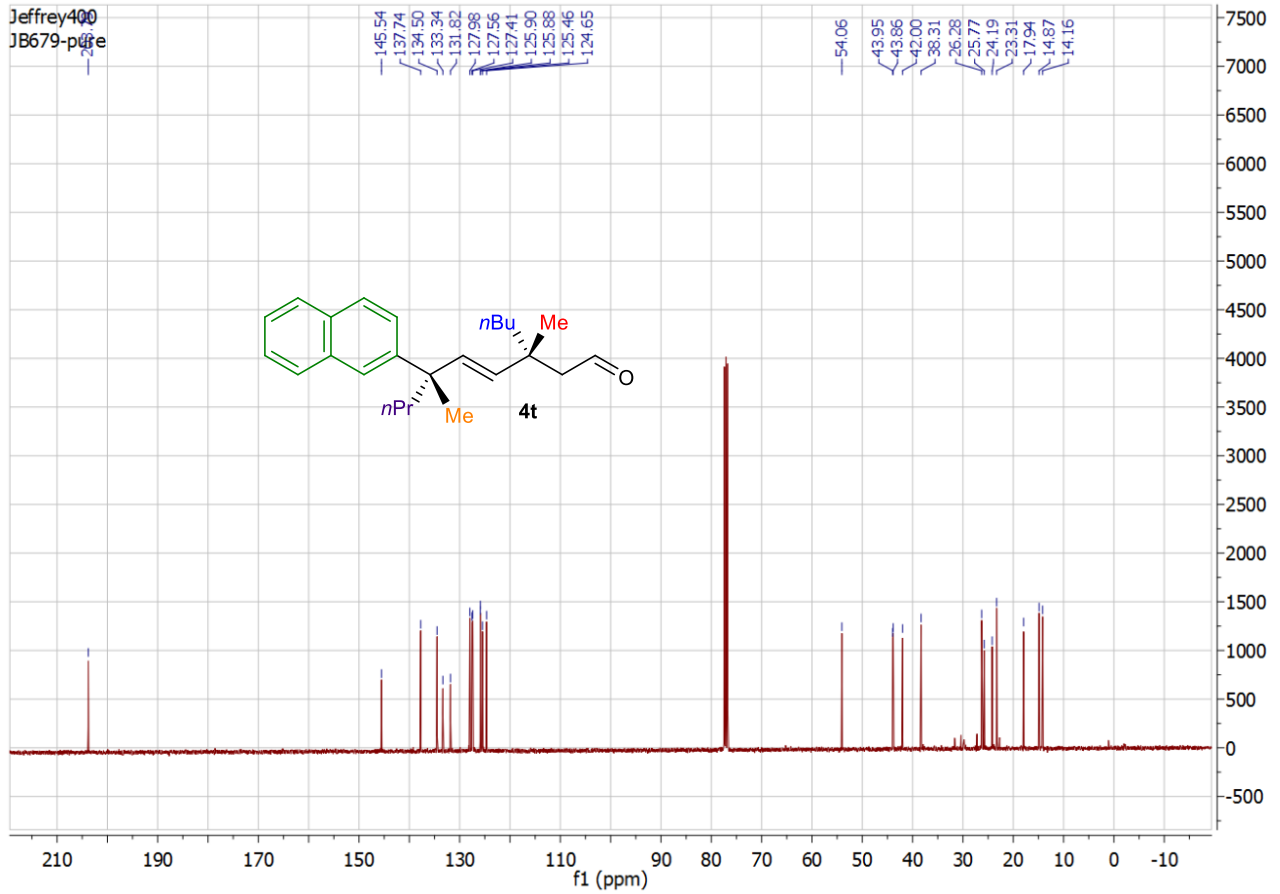
nBu
Et
Me
nPr
4s
f1 (ppm)


Jeffrey400
JB679-pure
nBu
Me
nPr
Me
4t
f1 (ppm)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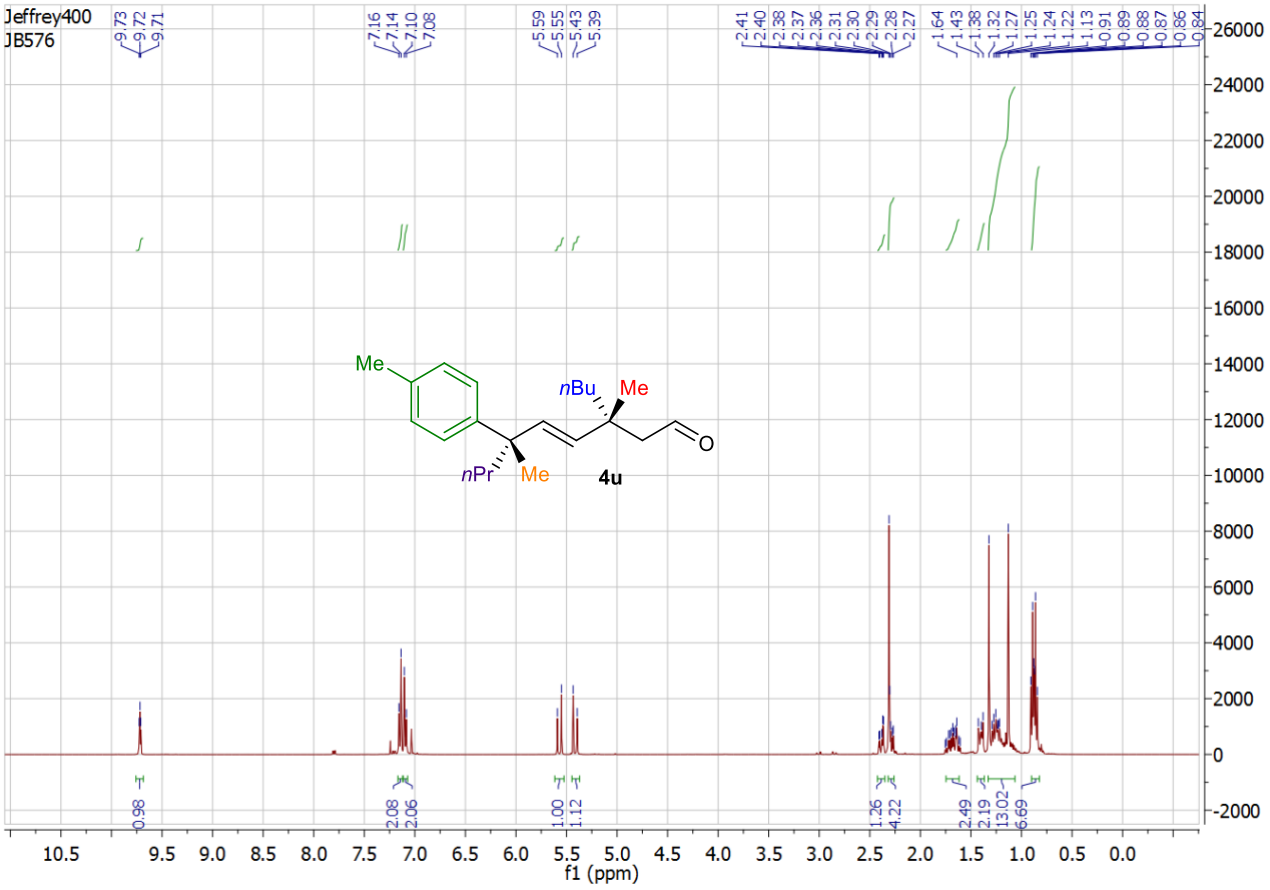
JB679-pure
nBu
Me
nPr
Me
4t
f1 (ppm)


Jeffrey400
JB576
Me
nBu
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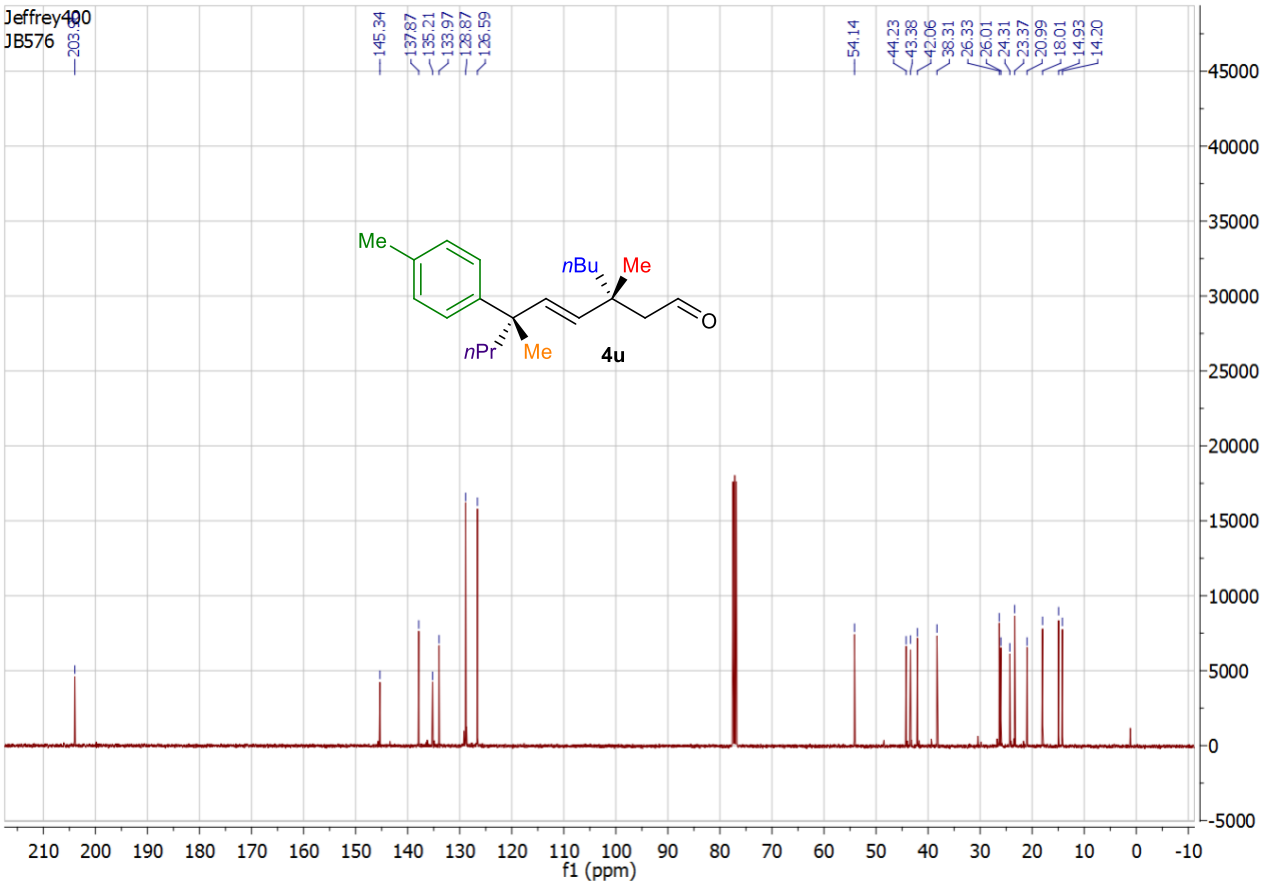
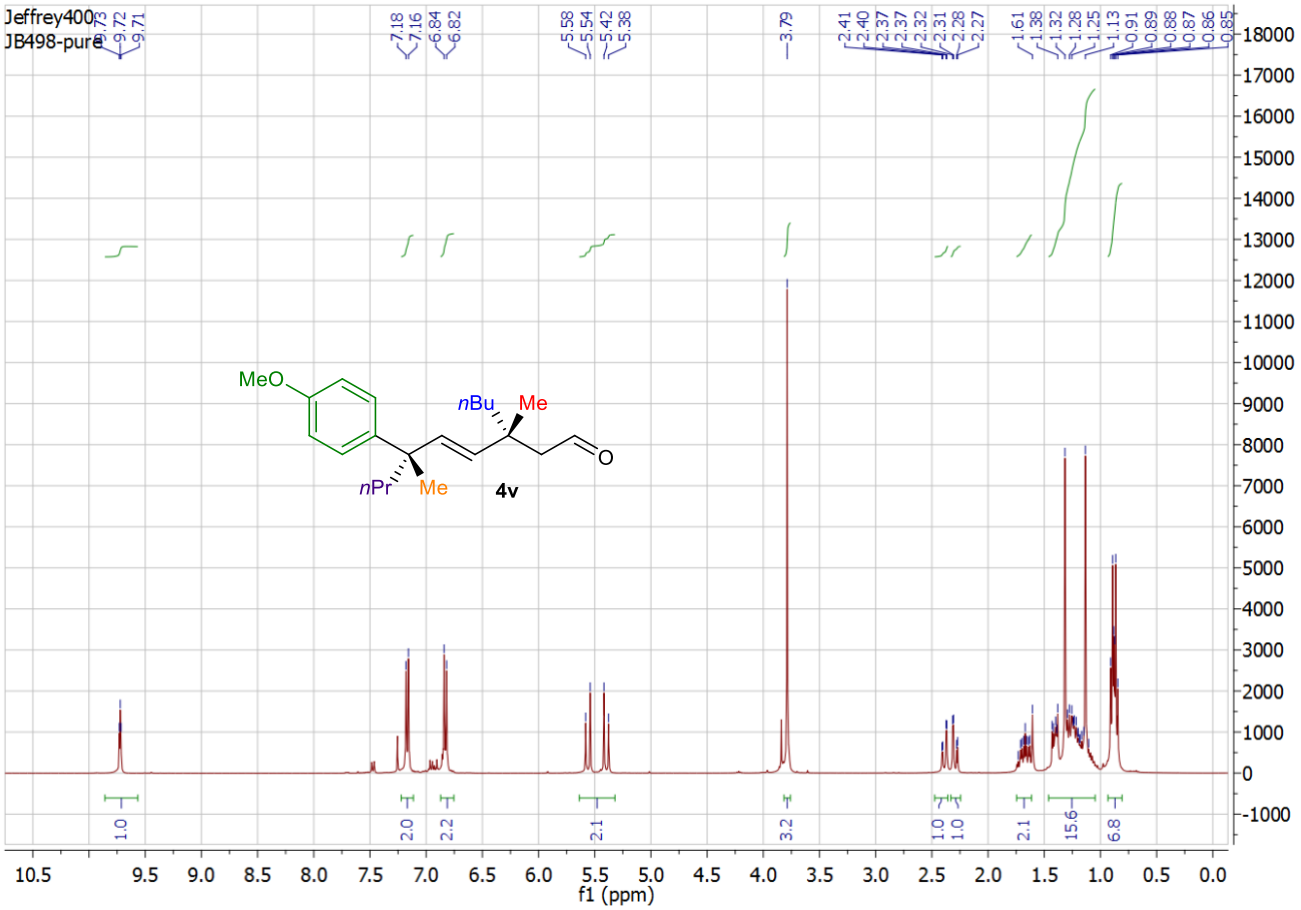
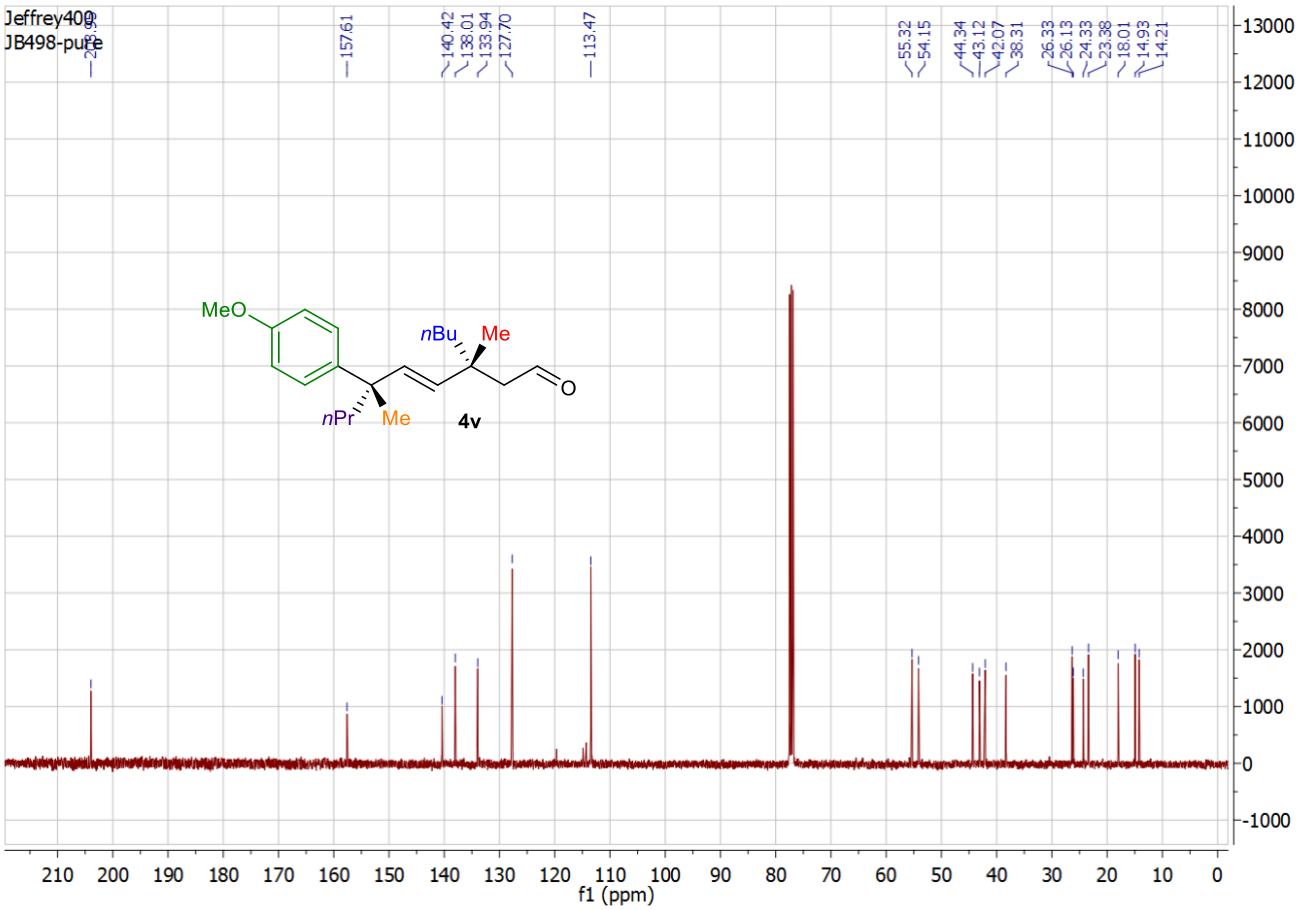
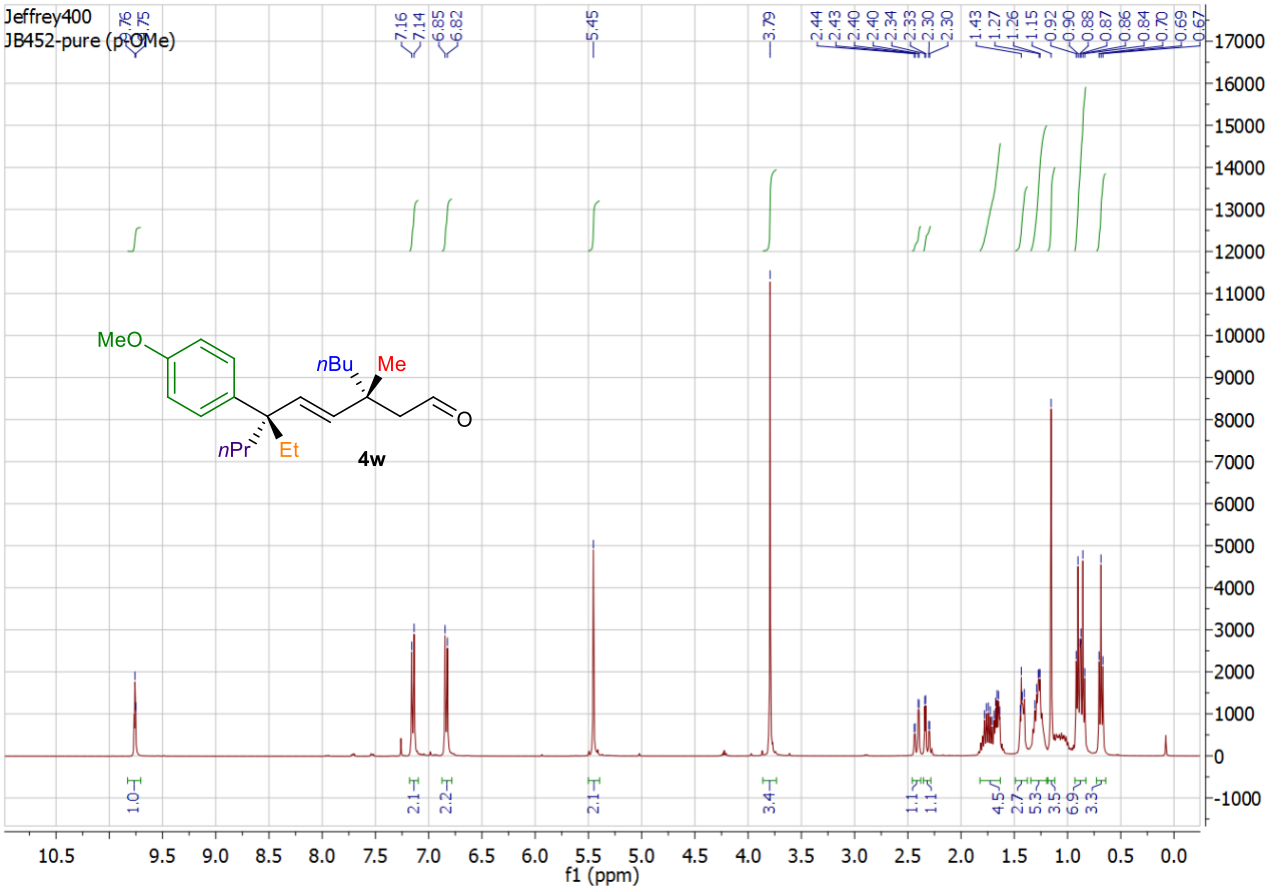
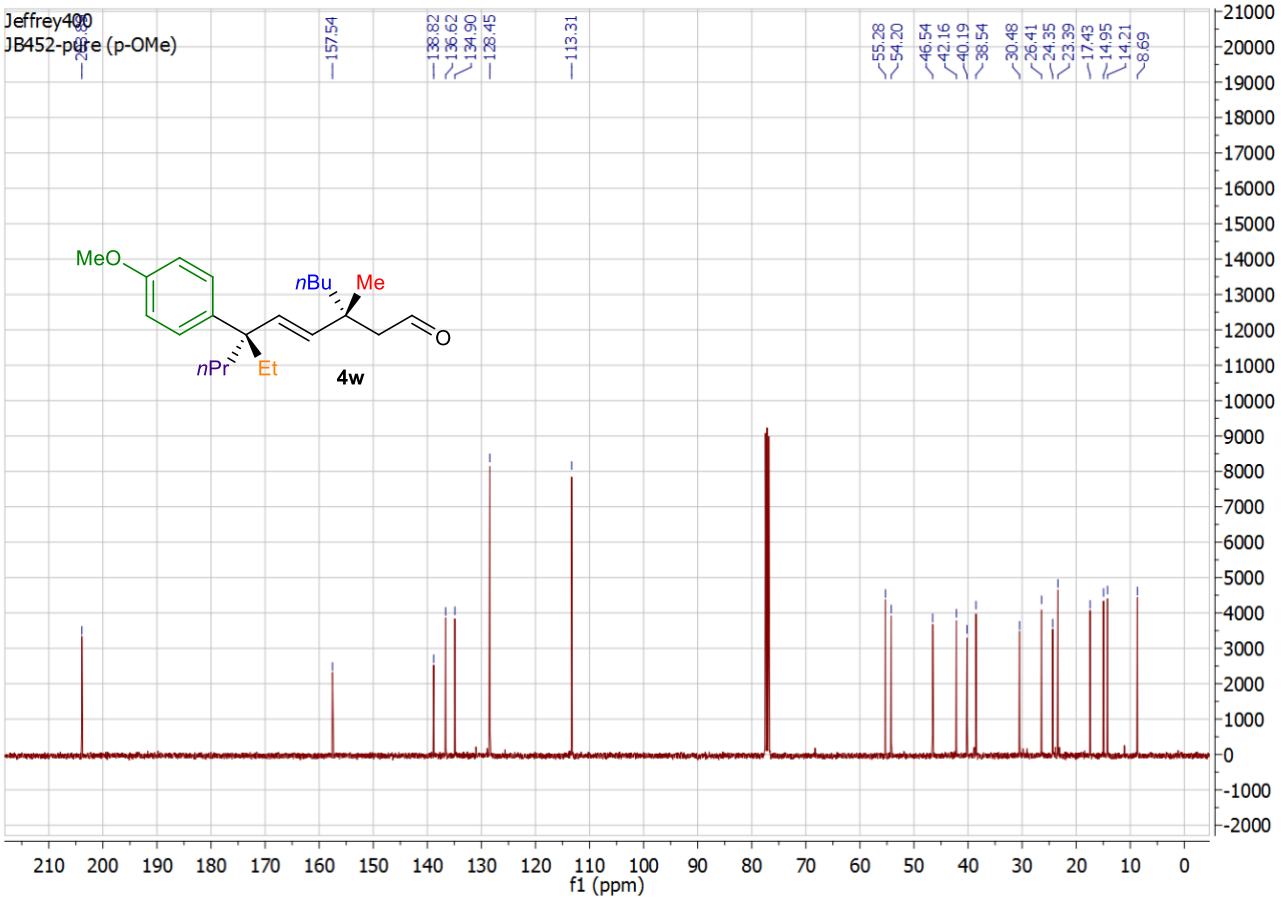
nPr
Me
4u
f1 (ppm)

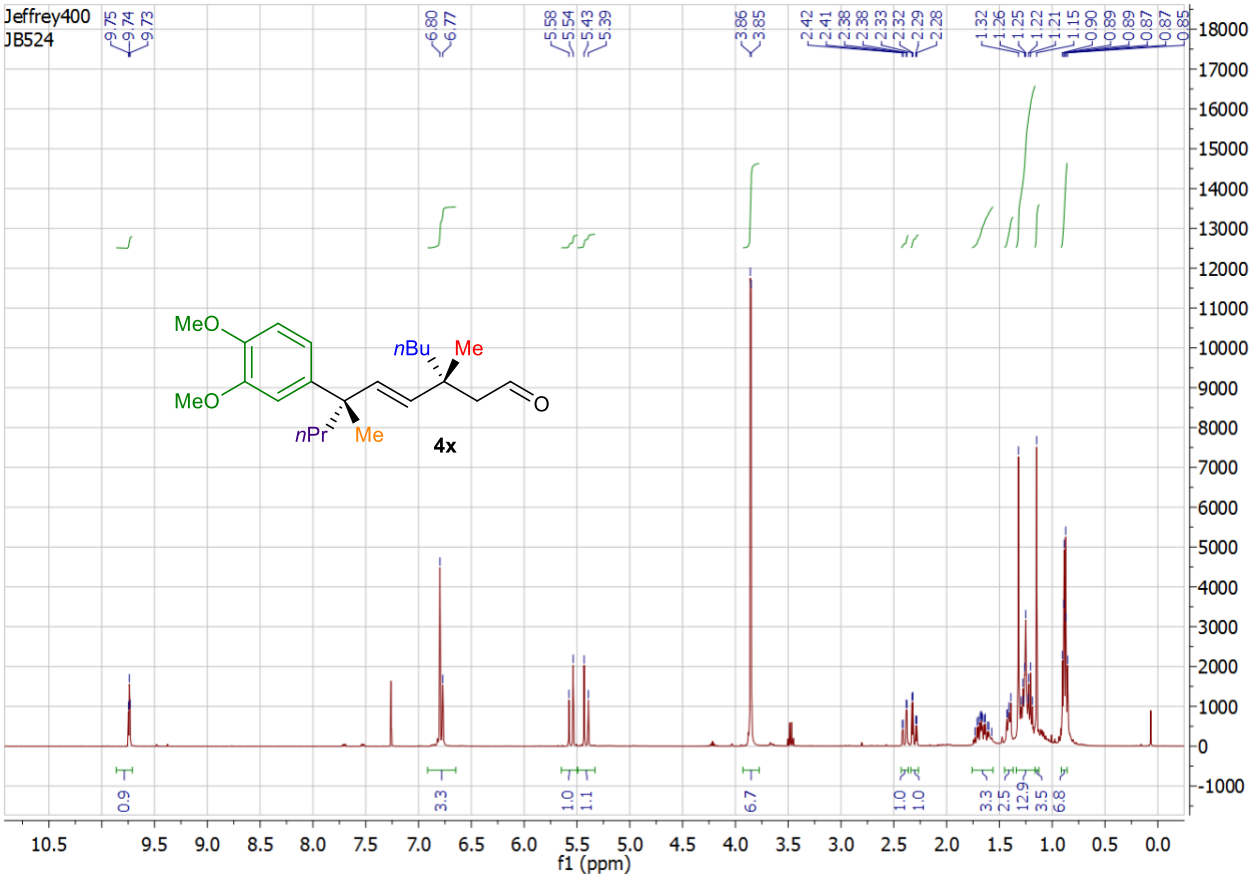

Jeffrey400
JB576
Me
nBu
Me
nPr
Me
4u
f1 (ppm)

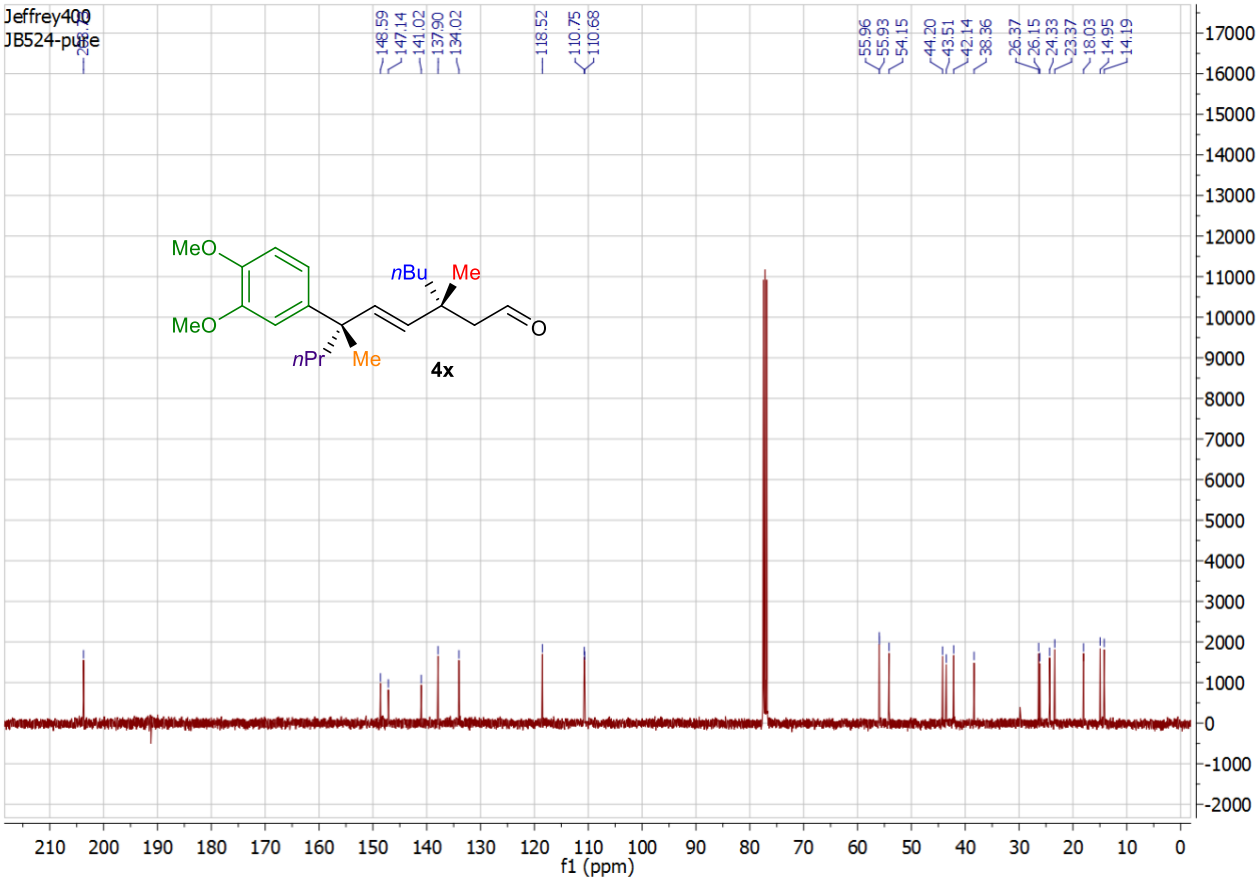

Jeffrey400
JB498-pure
MeO
nBu
Me
nPr
Me
4v
f1 (ppm)

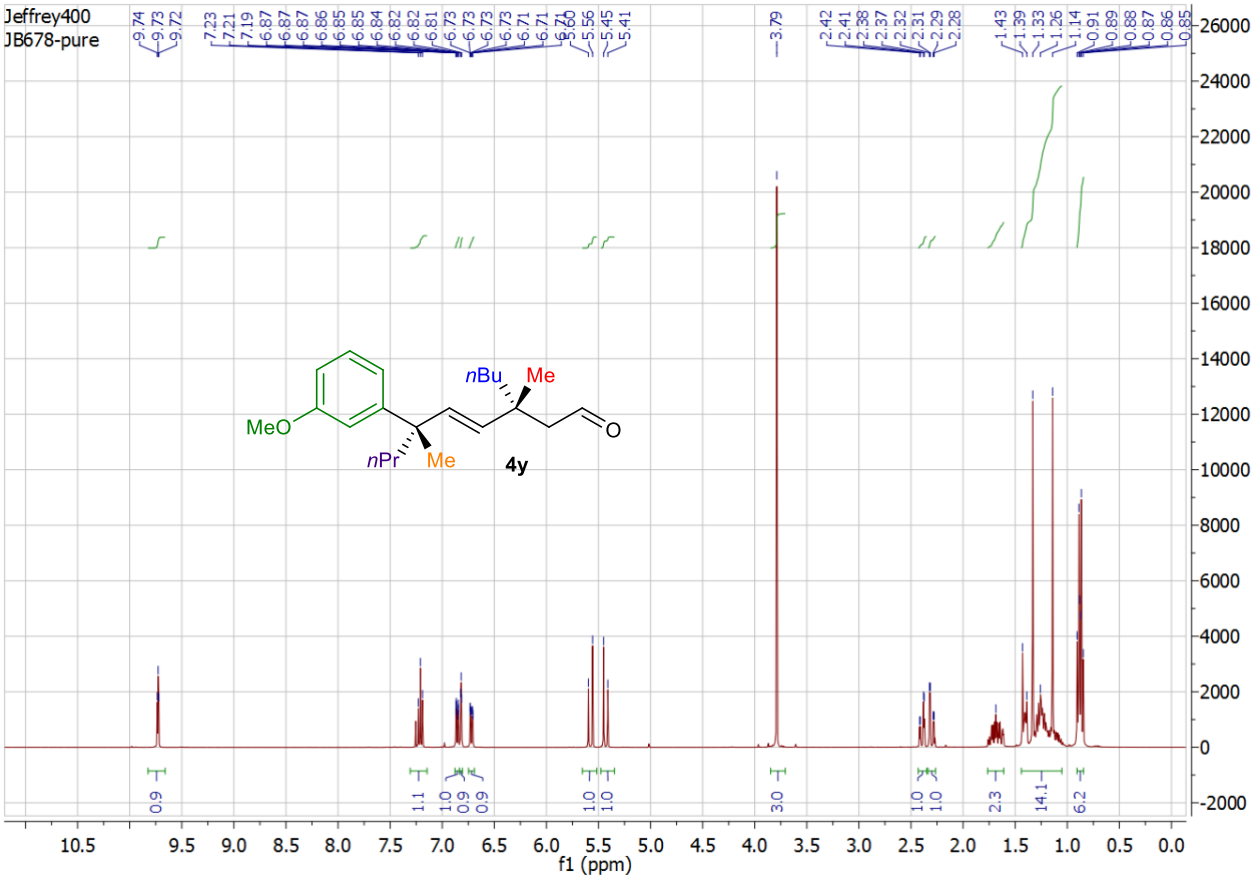

Jeffrey400
JB498-pure
MeO
nBu
Me
nPr
Me
4v
f1 (ppm)

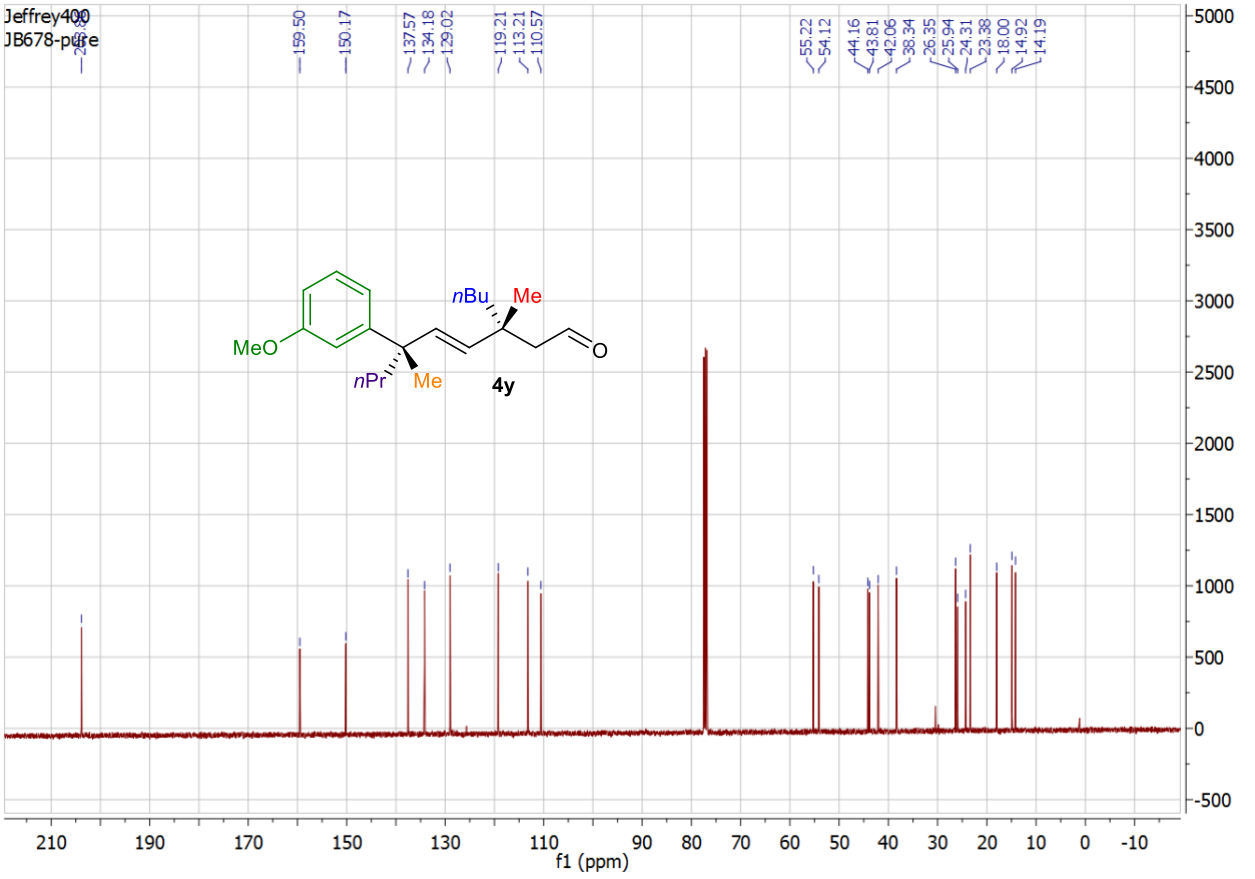

Jeffrey400
JB452-pure (p-OMe)
MeO
nBu
Me
nPr
Et
4w
f1 (ppm)

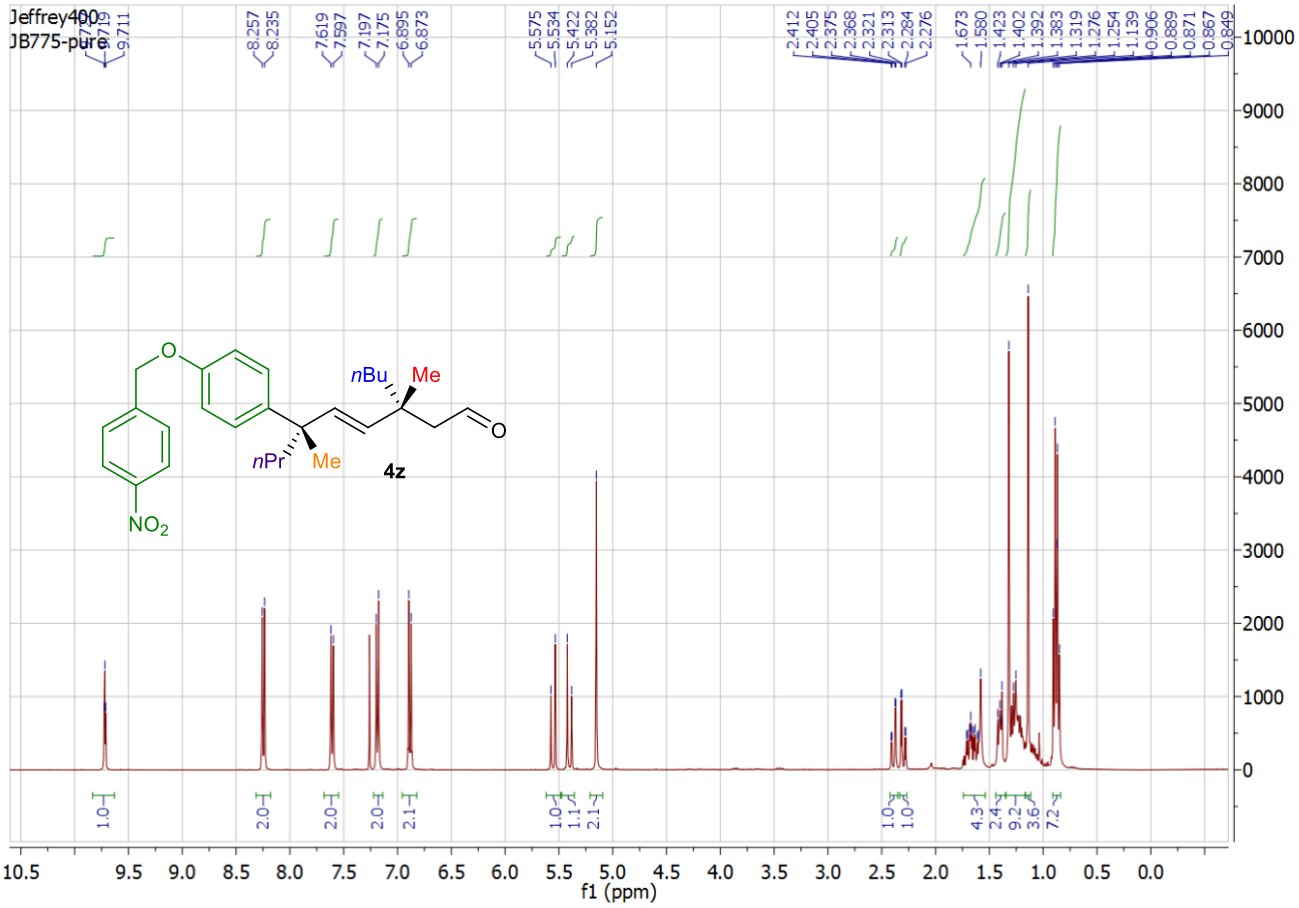

Jeffrey400
JB452-pure (p-OMe)
MeO
nBu
Me
nPr
Et
4w
f1 (ppm)

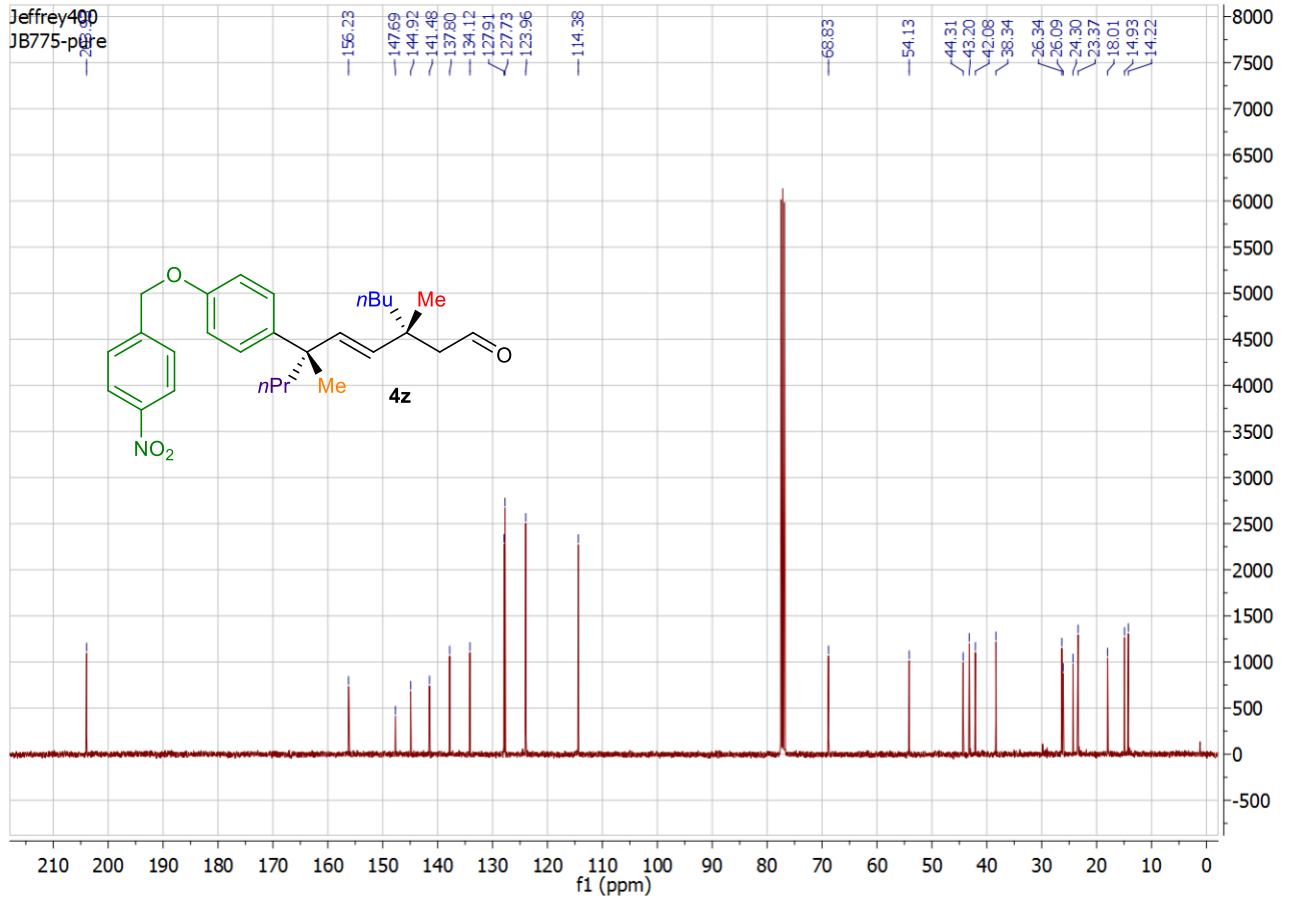

Jeffrey400
JB524
MeO
MeO
nBu
Me
nPr
Me
O
4x
f1 (ppm)

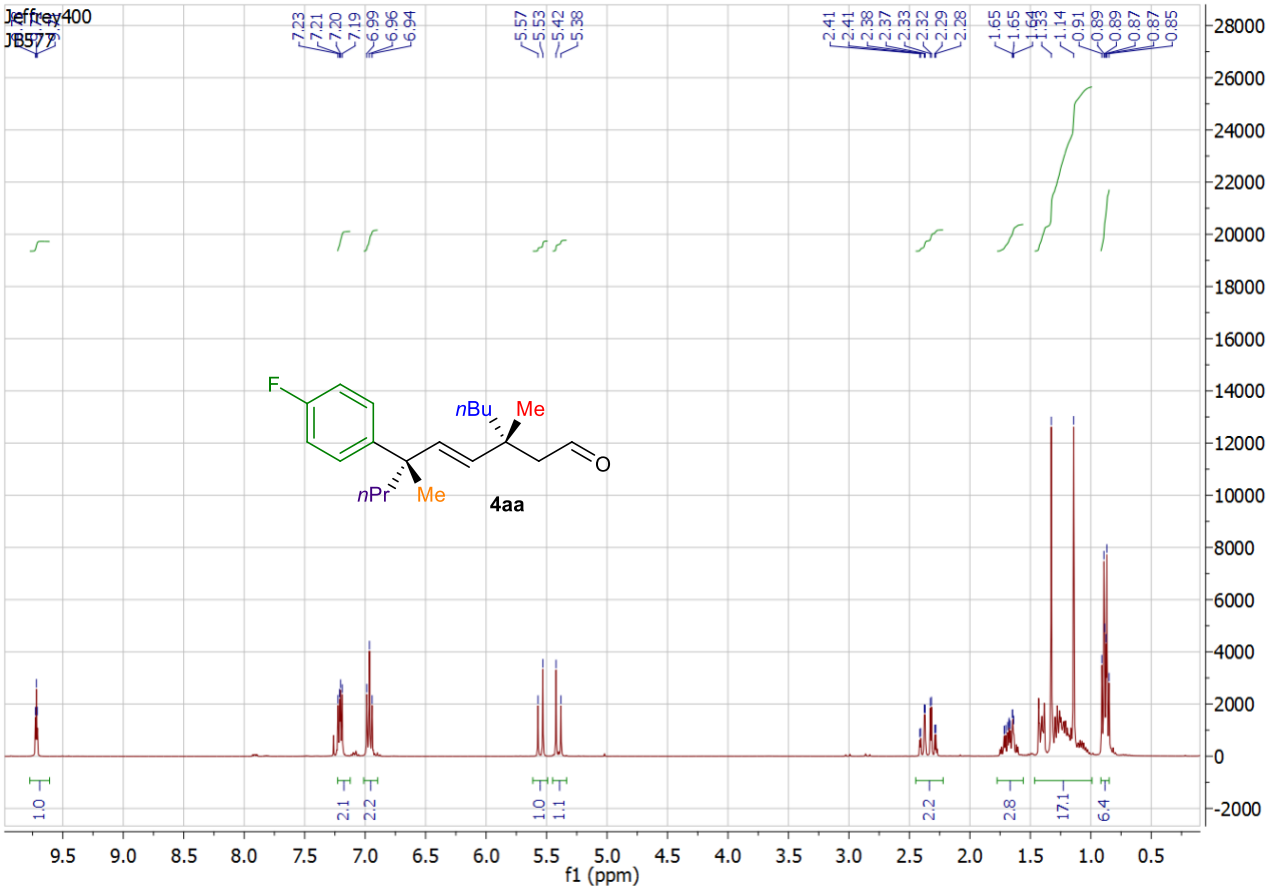

Jeffrey400
JB524-pure
MeO
MeO
nBu
Me
nPr
Me
O
4x
f1 (ppm)

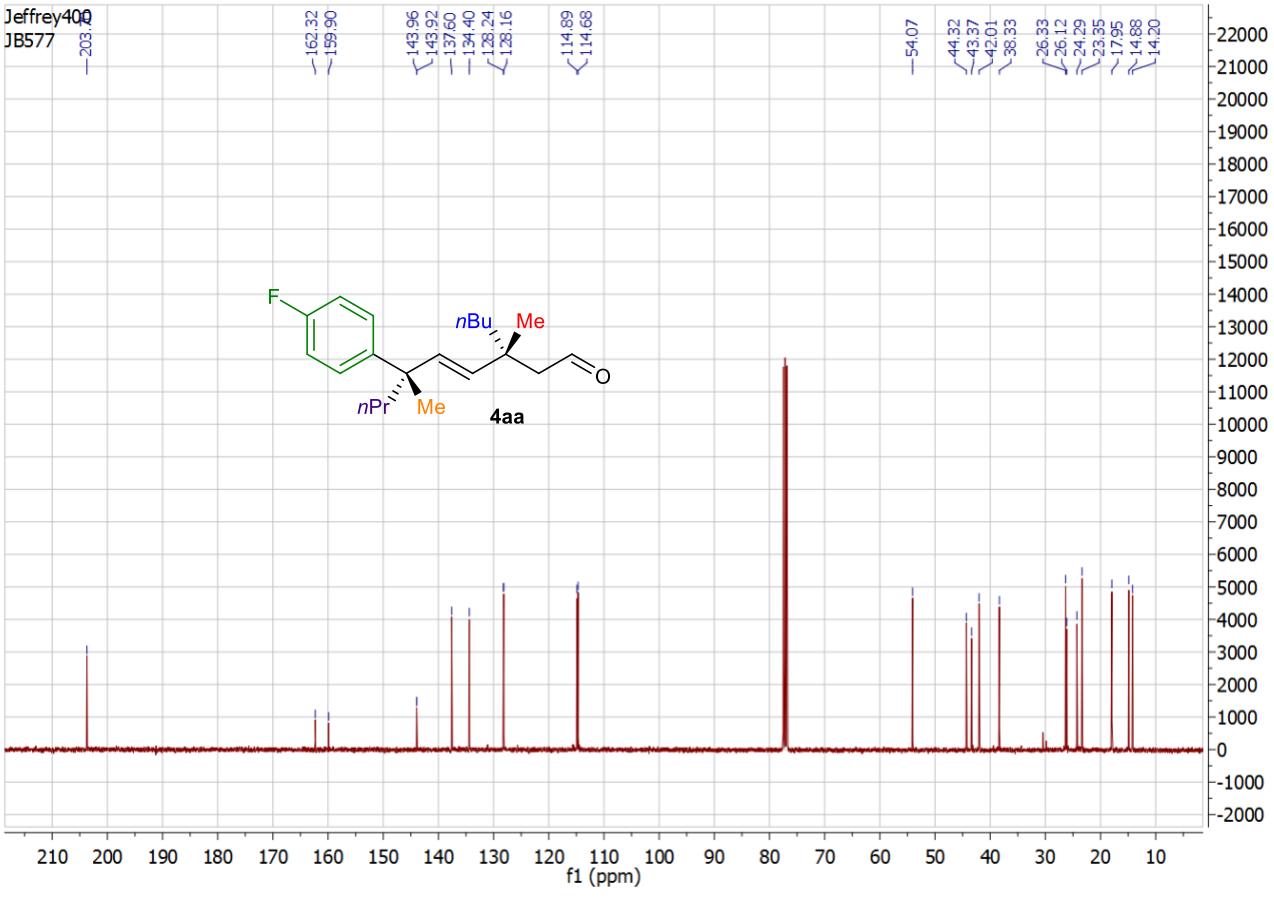

Jeffrey400
JB678-pure
MeO
nPr
Me
nBu
Me
O
4y
f1 (ppm)

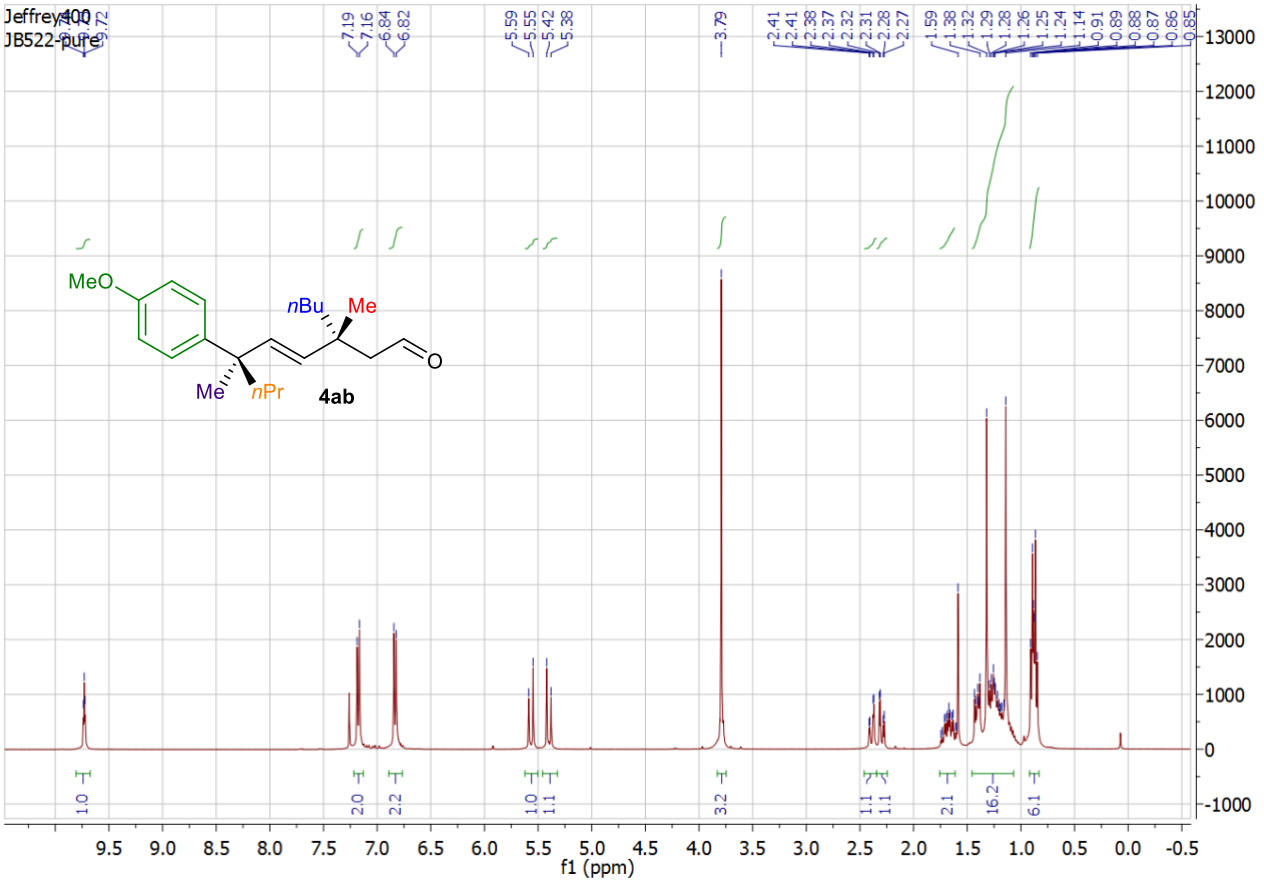

Jeffrey400
JB678-pure
MeO
nPr
Me
nBu
Me
O
4y
f1 (ppm)

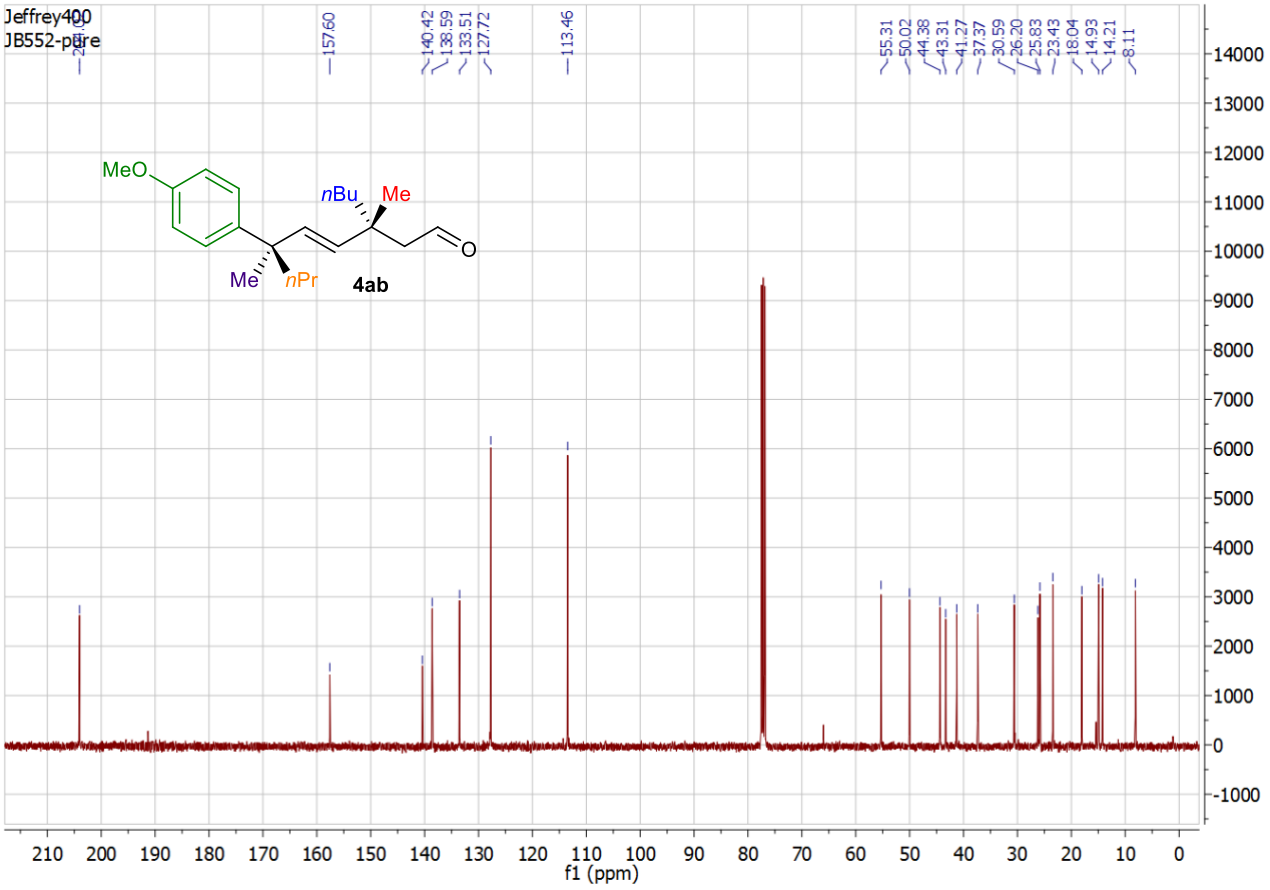

Jeffrey400
JB775-pure
f1 (ppm)
nBu
Me
nPr
Me
4z
NO2

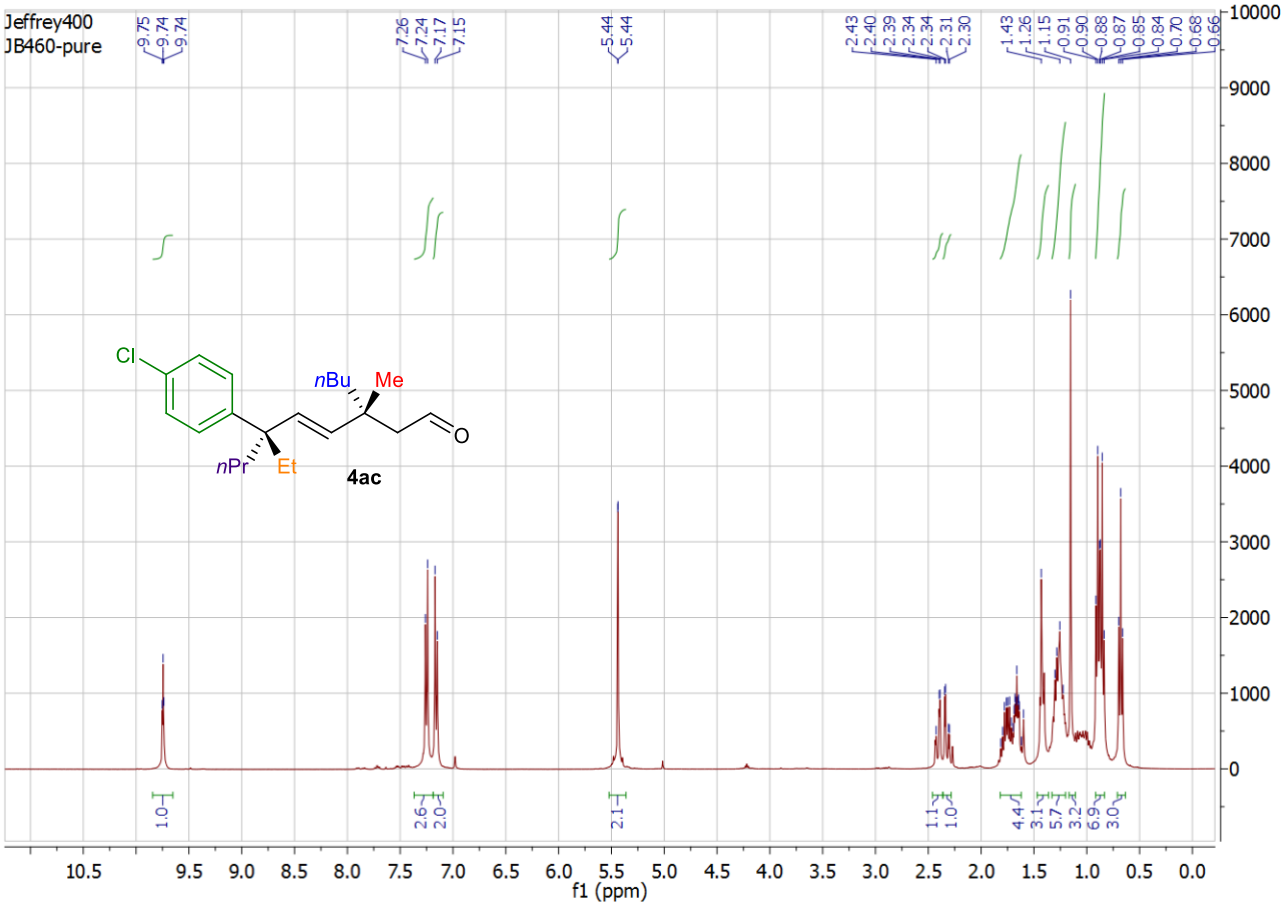

Jeffrey400
JB775-pure
f1 (ppm)
nBu
Me
nPr
Me
4z
NO2

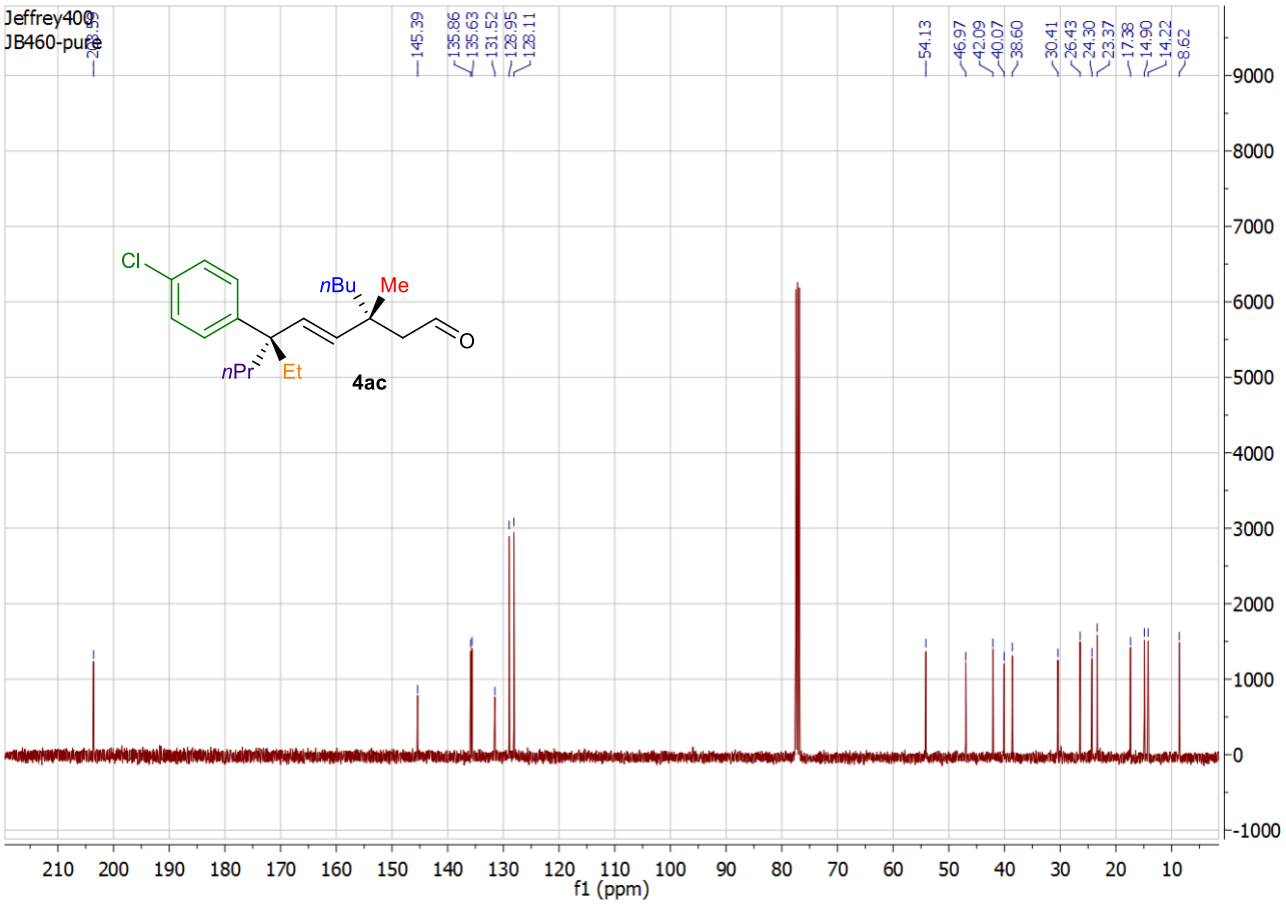

Jeffrey400
JB577
F
nBu
Me
nPr
Me
O
4aa
f1 (ppm)

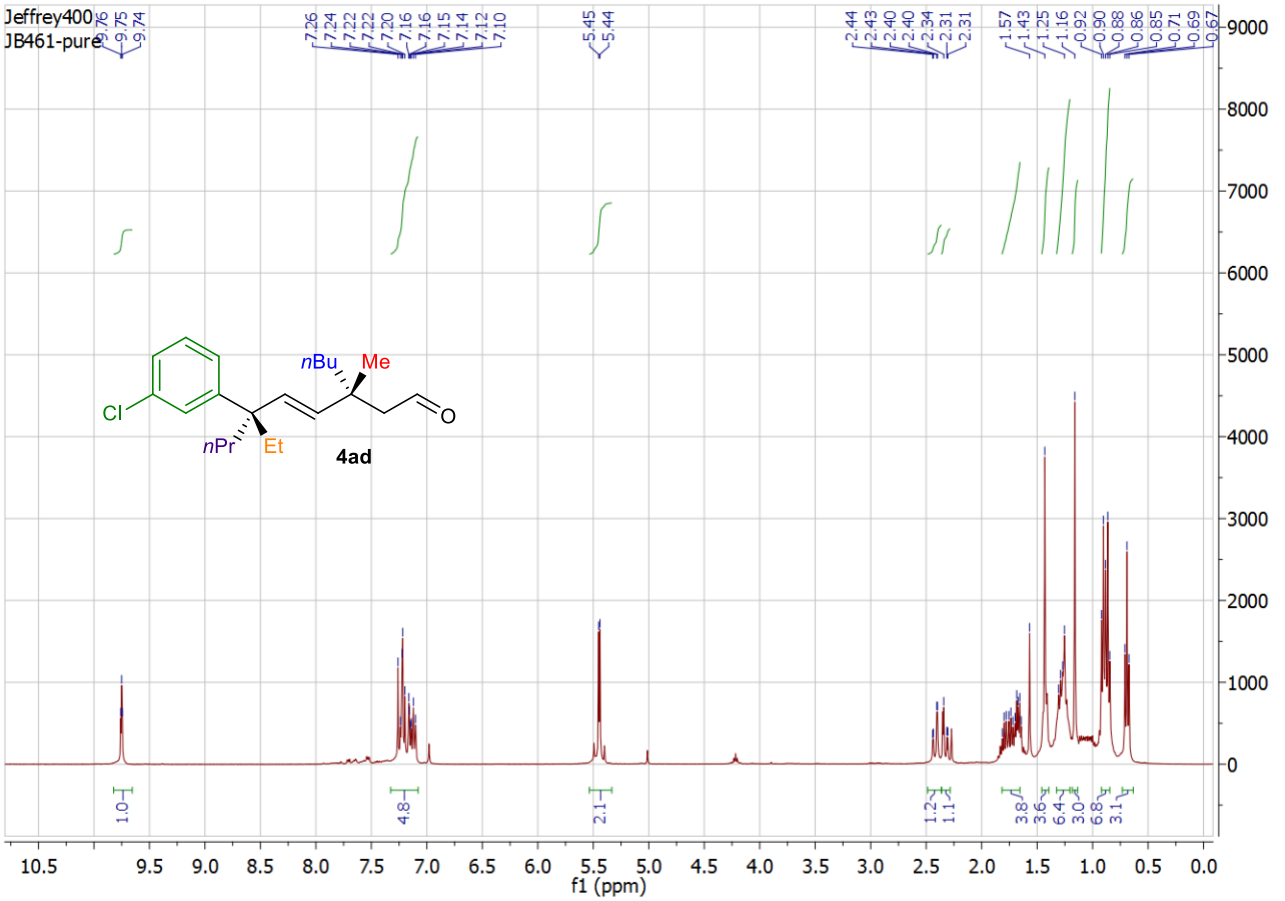

Jeffrey400
JB577
F
nBu
Me
nPr
Me
O
4aa
f1 (ppm)

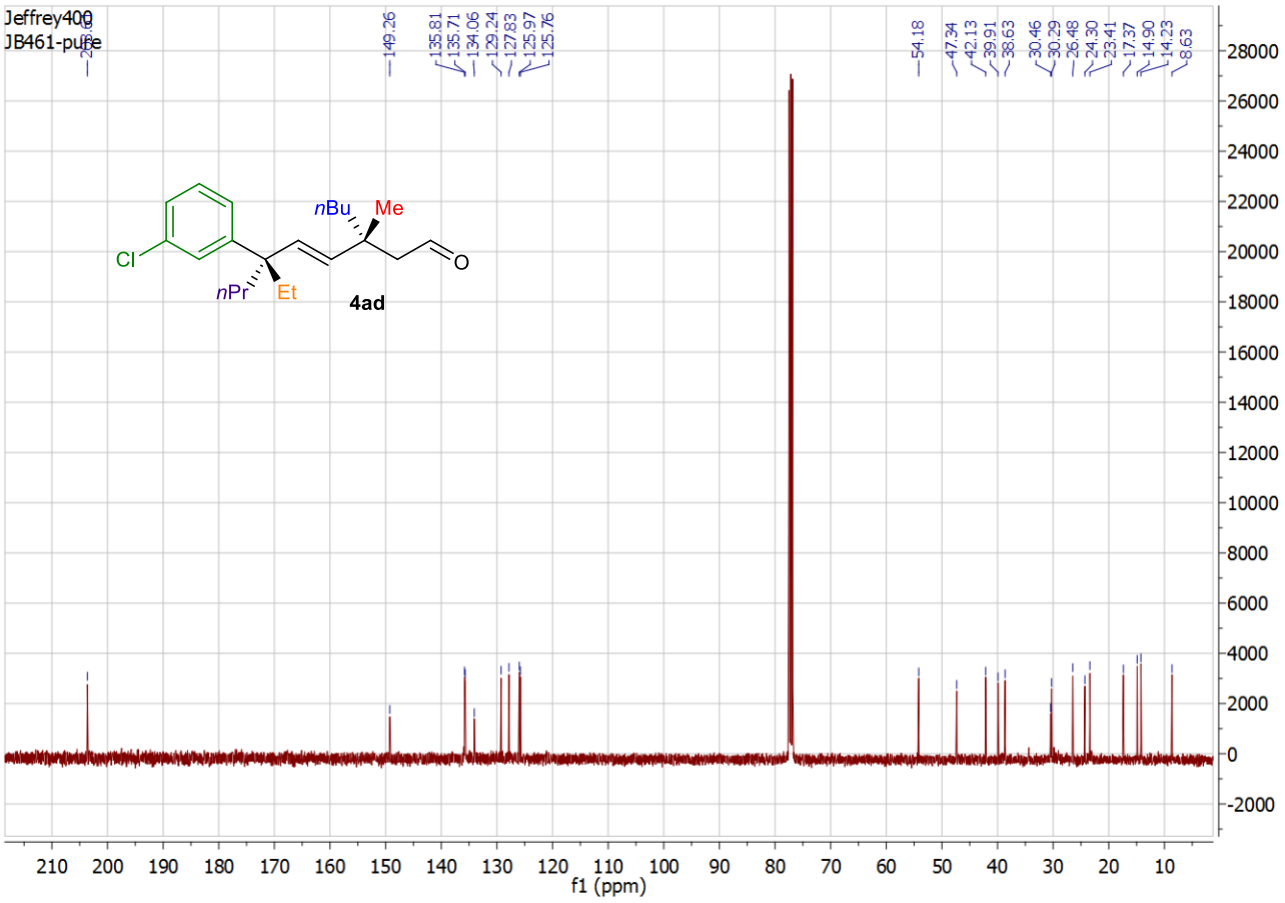

Jeffrey400
JB522-pure
MeO
nBu
Me
Me
nPr
4ab
f1 (ppm)

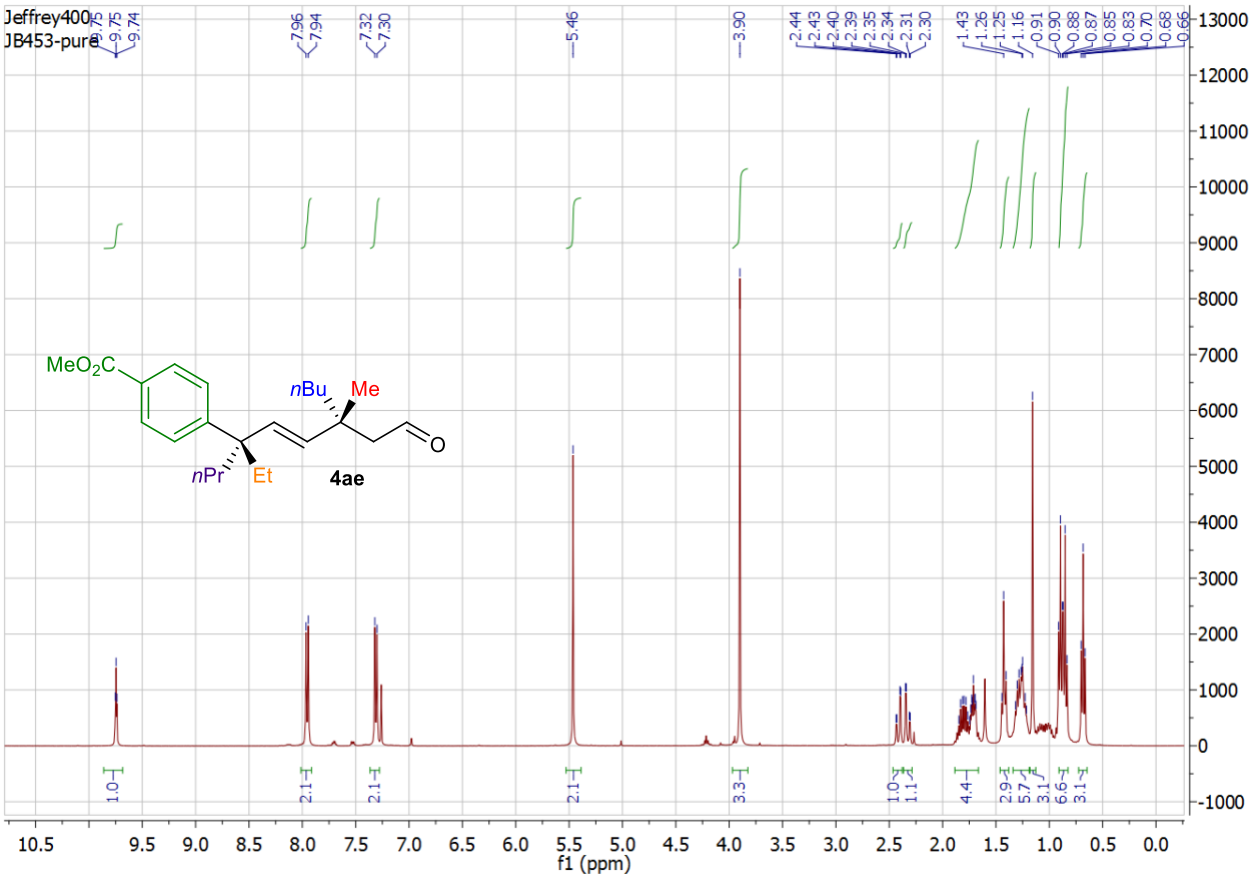

Jeffrey400
JB552-pure
MeO
nBu
Me
Me
nPr
4ab
f1 (ppm)

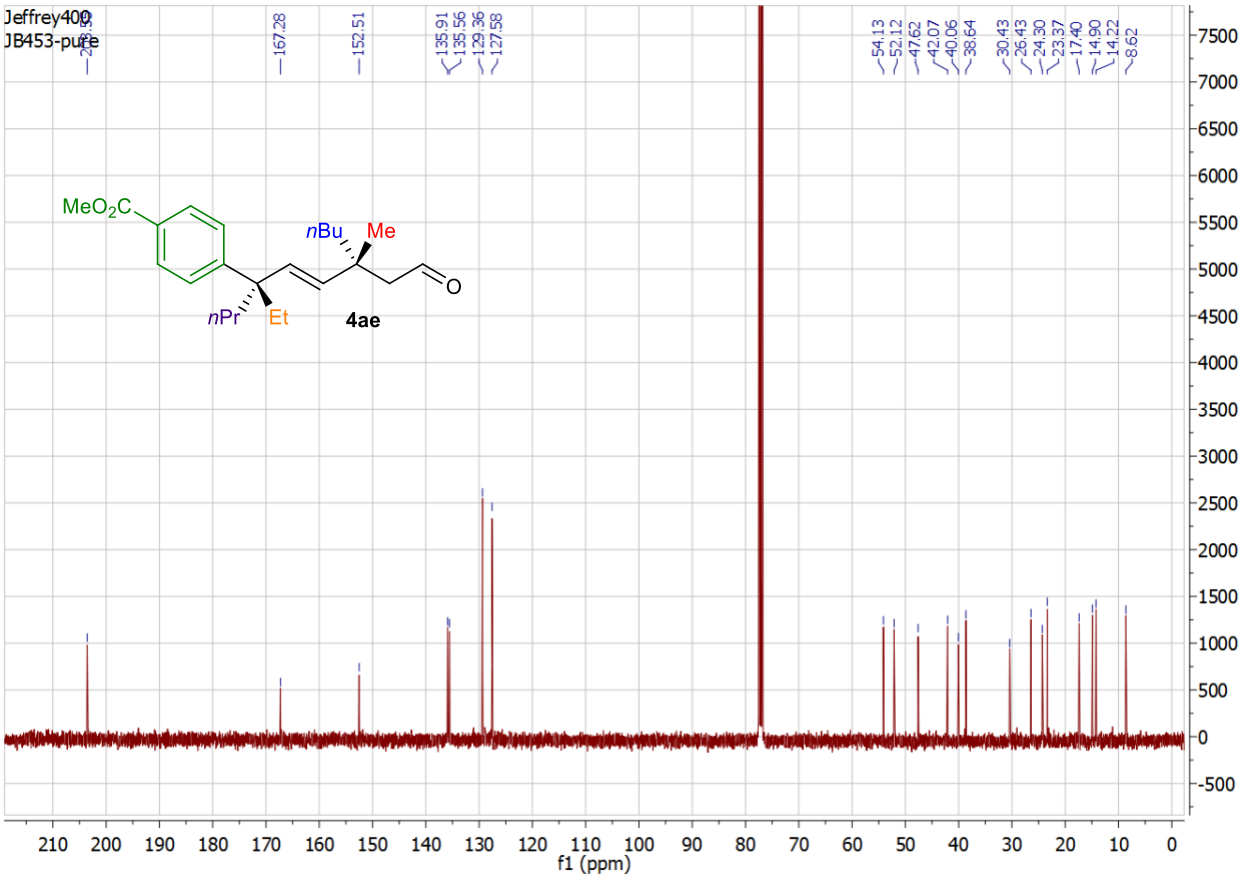

Jeffrey400
JB460-pure
Cl
nBu
Me
nPr
Et
O
4ac
f1 (ppm)

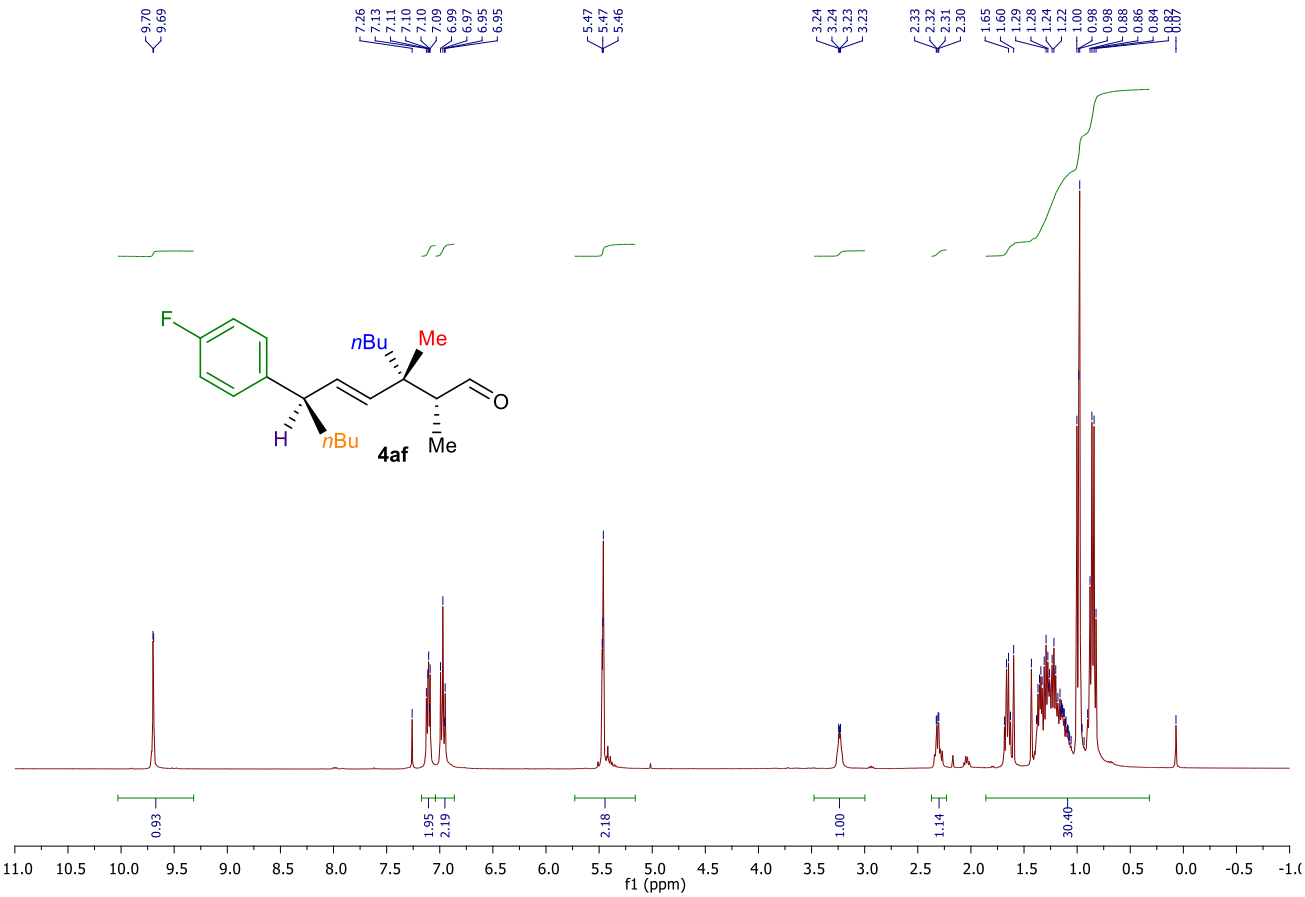

Jeffrey400
JB460-pure
Cl
nBu
Me
nPr
Et
O
4ac
f1 (ppm)

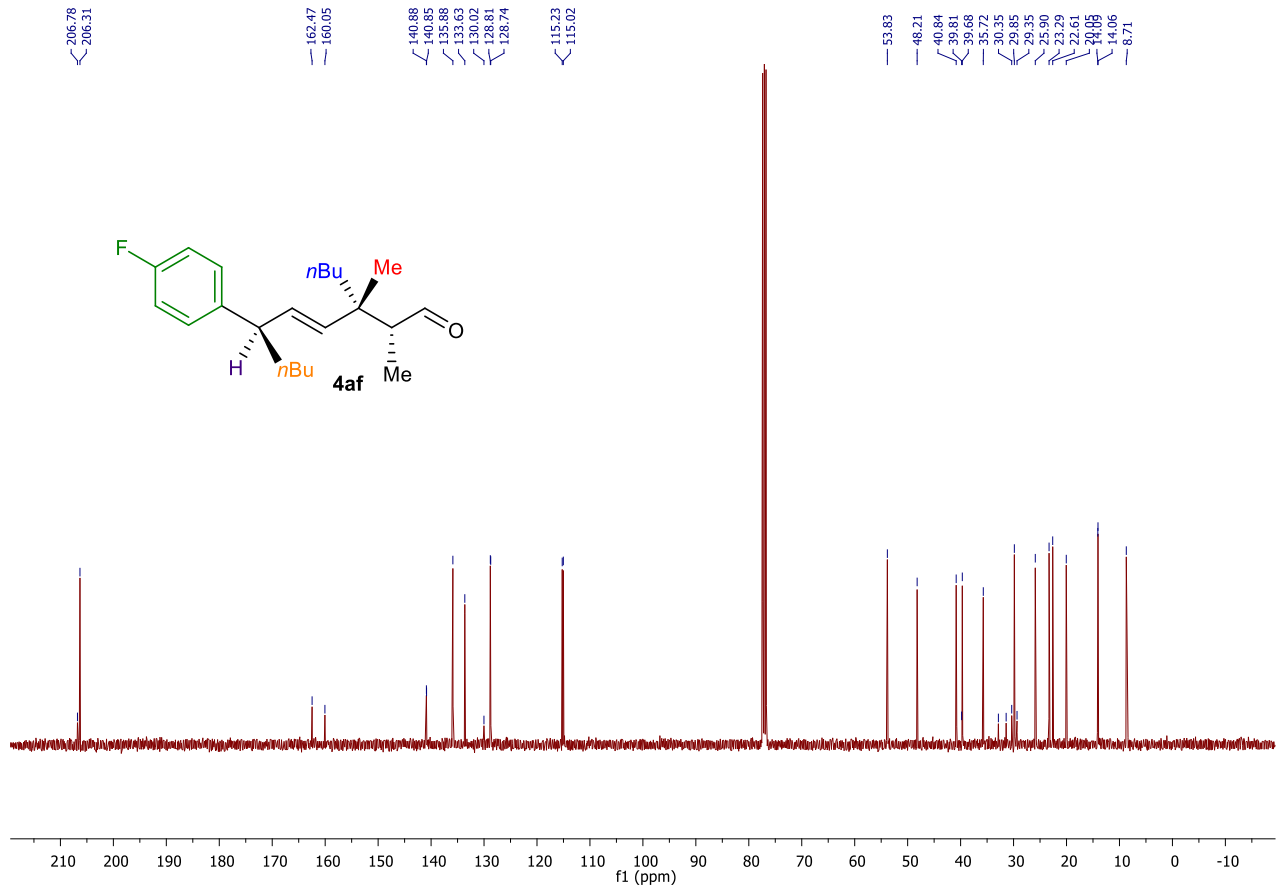

Jeffrey400
JB461-pure
nBu
Me
Cl
nPr
Et
4ad
f1 (ppm)

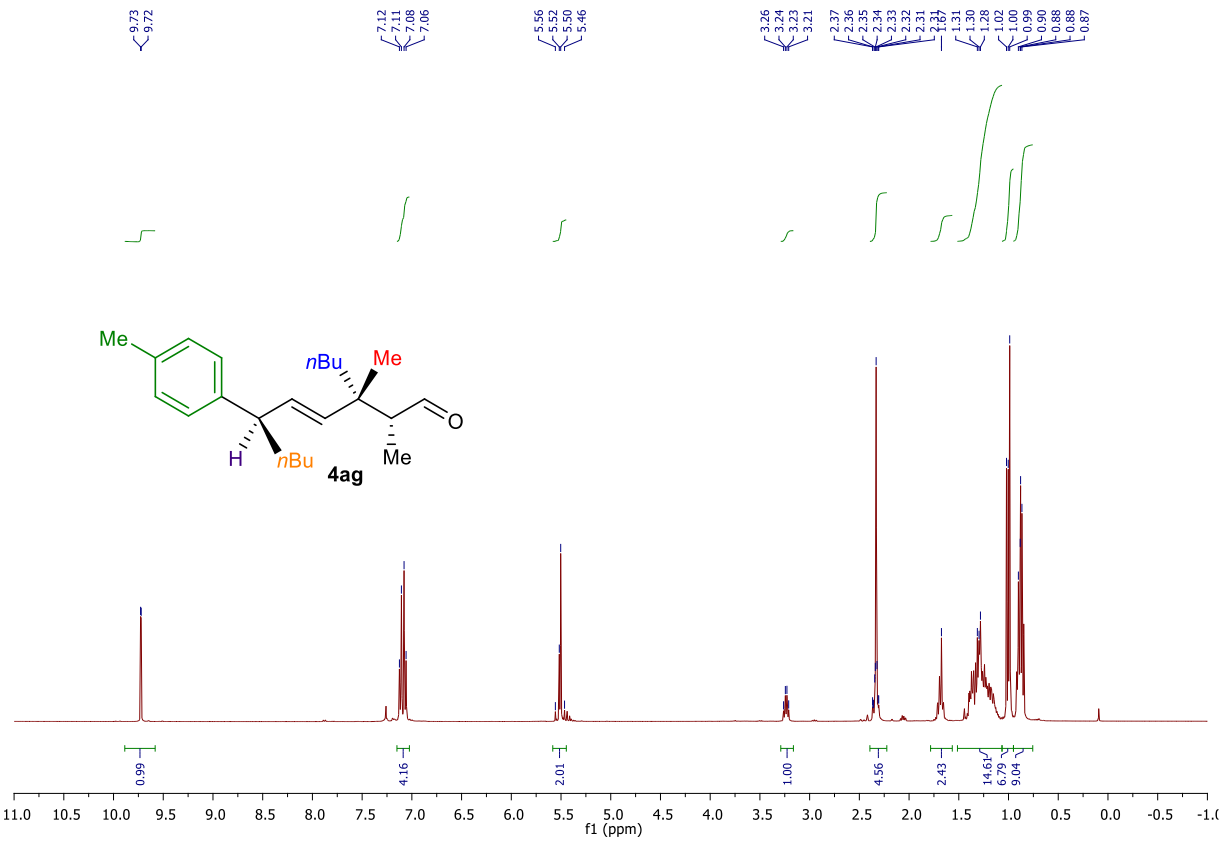

Jeffrey400
JB461-pure
nBu
Me
Cl
nPr
Et
4ad
f1 (ppm)

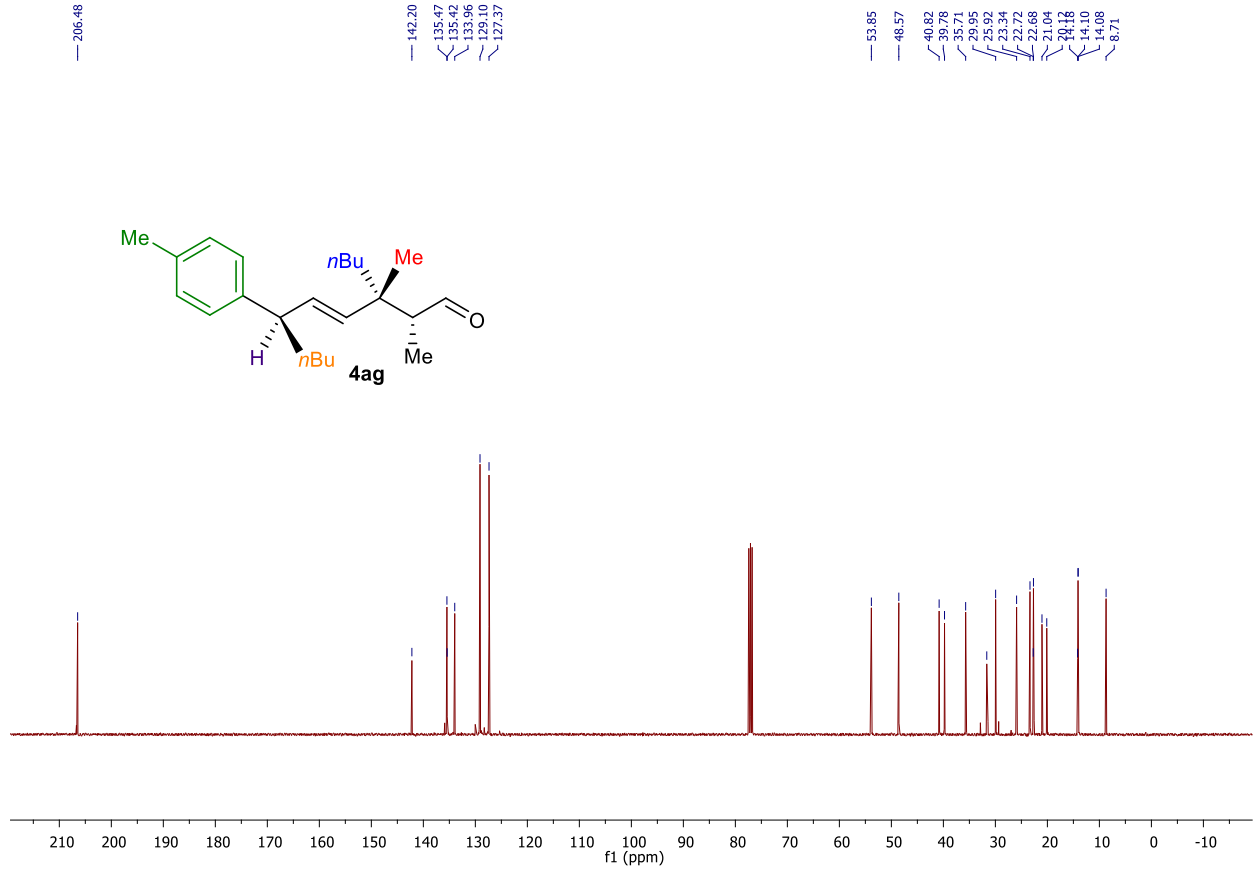

Jeffrey400
JB453-pure
MeO2C
nBu
Me
nPr
Et
4ae
f1 (ppm)

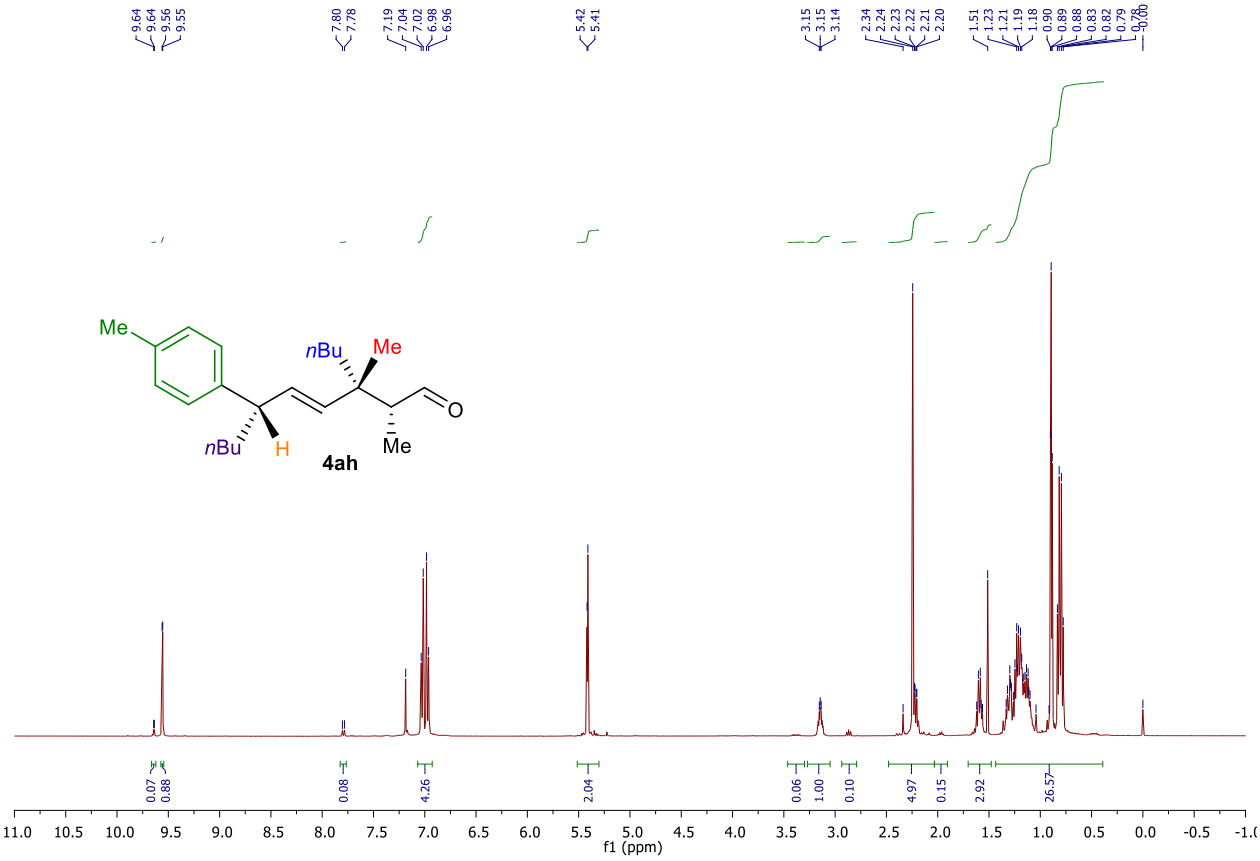

Jeffrey400
JB453-pure
MeO2C
nBu
Me
nPr
Et
4ae
f1 (ppm)

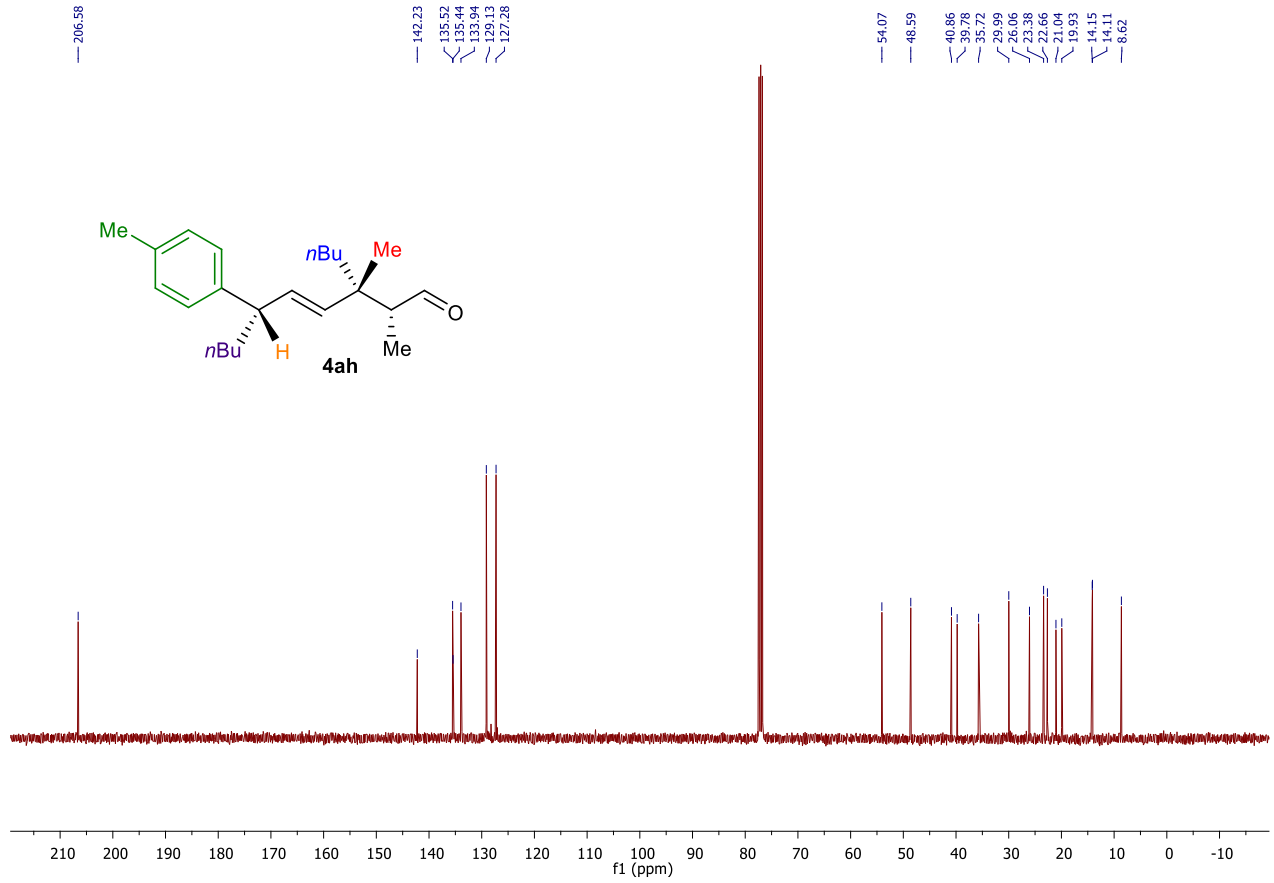

F
nBu
Me
H
nBu
O
Me
4af
f1 (ppm)

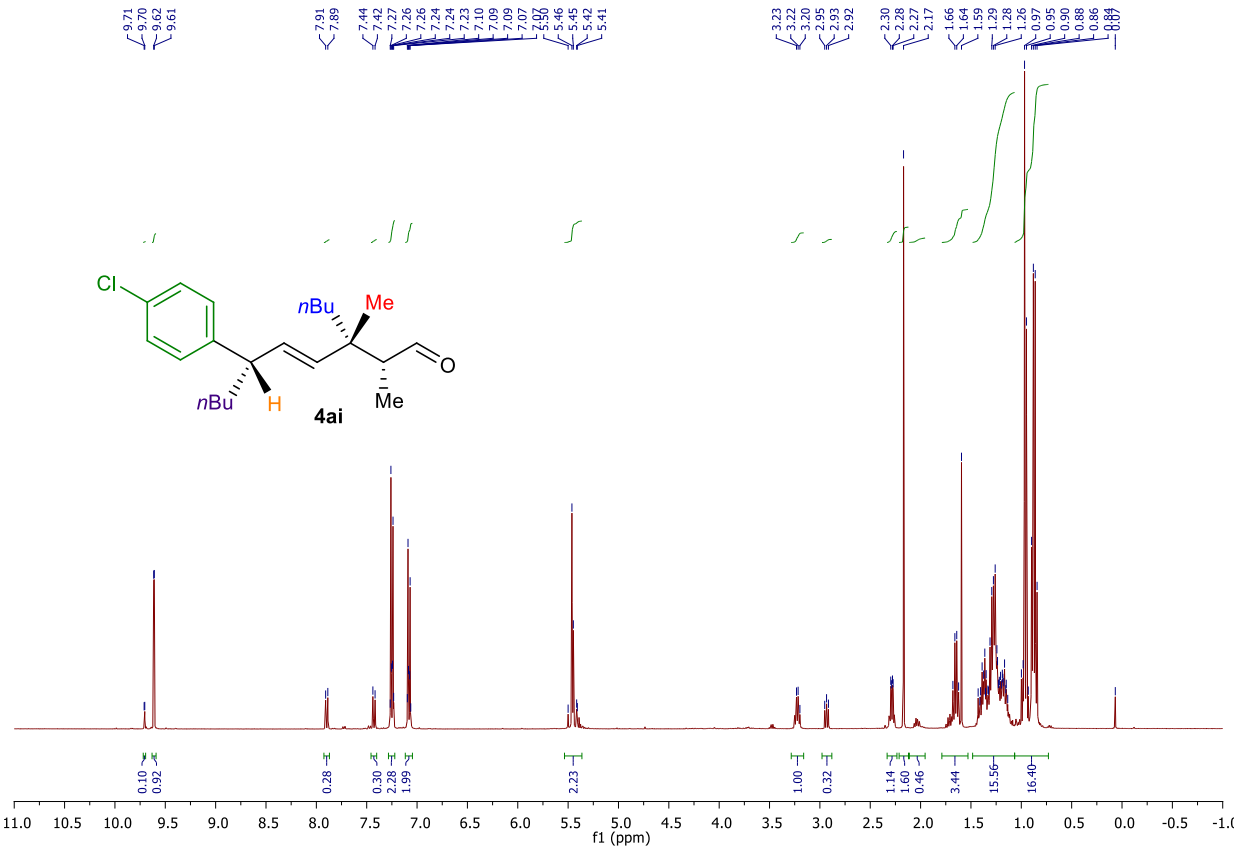

F
nBu
Me
H
nBu
O
Me
4af
f1 (ppm)

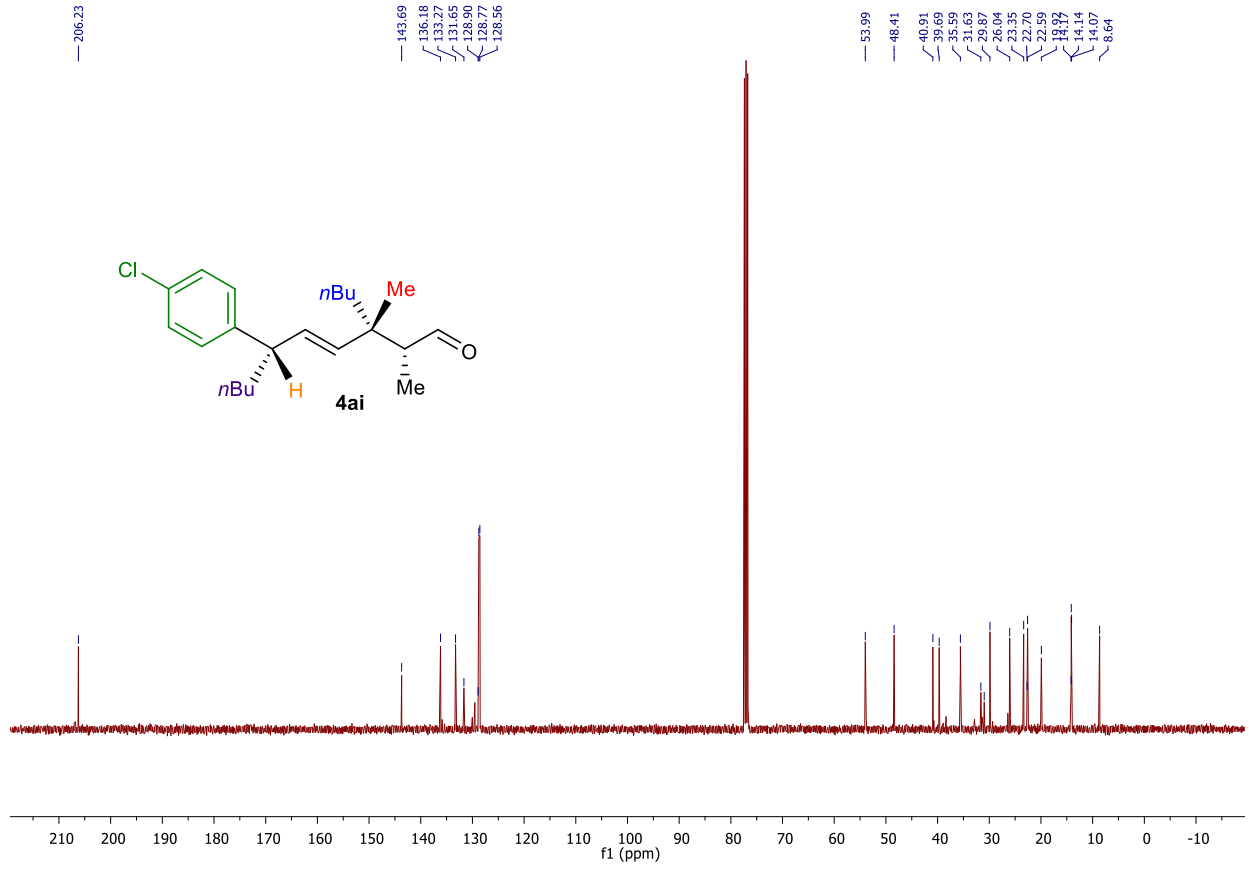

9.73
9.72
7.12
7.11
7.08
7.06
5.56
5.52
5.50
5.46
3.26
3.24
3.23
3.21
2.37
2.36
2.35
2.34
2.33
2.32
2.31
1.31
1.30
1.28
1.02
1.00
0.99
0.90
0.88
0.87
Me
nBu
Me
O
H
nBu
Me
4ag
0.99
4.16
2.01
1.00
4.56
2.43
14.61
6.79
9.04
f1 (ppm)

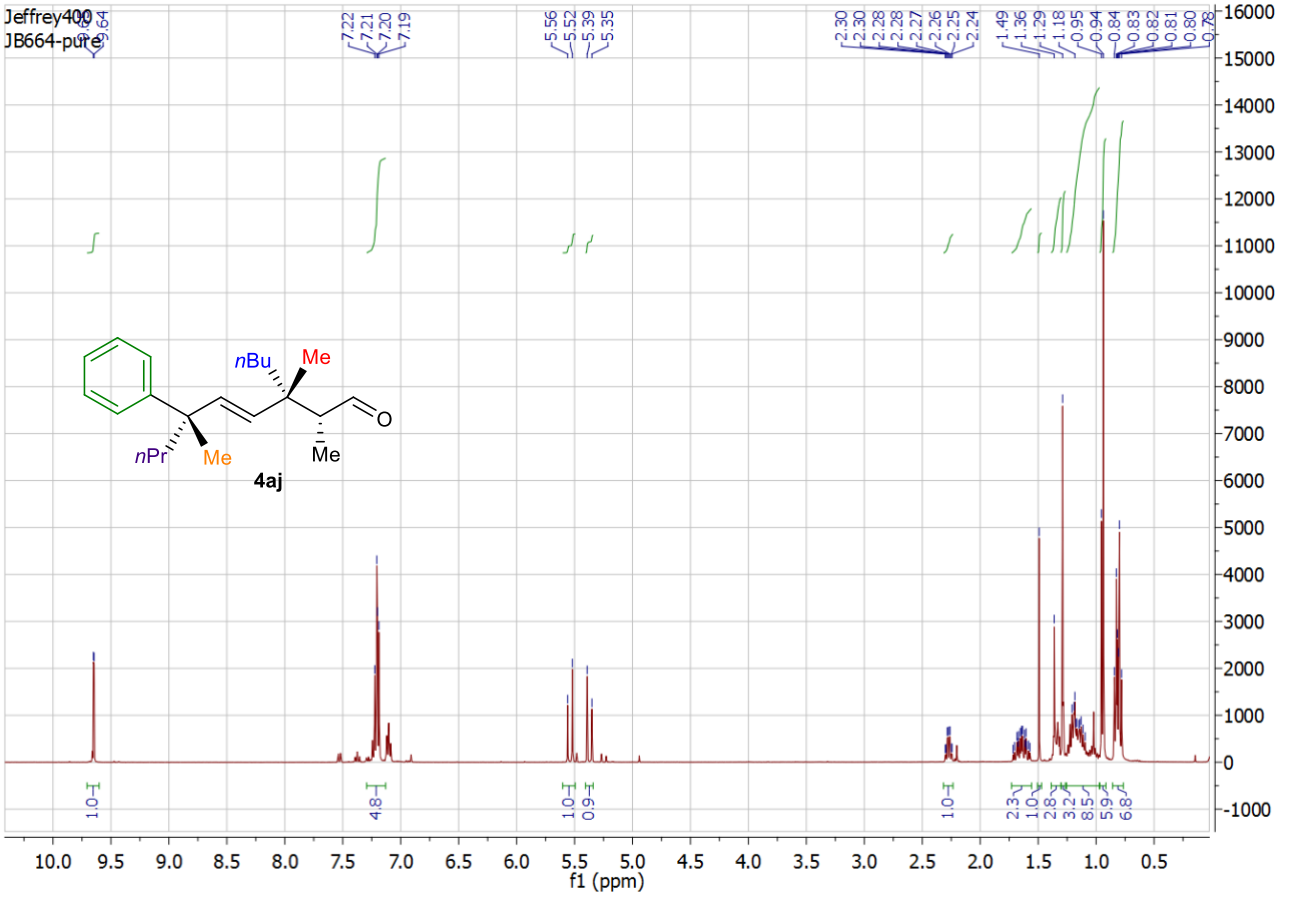

206.48
142.20
135.47
135.42
133.96
129.10
127.37
53.85
48.57
40.82
39.78
35.71
29.95
25.92
23.34
22.72
22.68
21.04
14.18
14.10
14.08
8.71
Me
nBu
Me
O
H
nBu
Me
4ag
f1 (ppm)

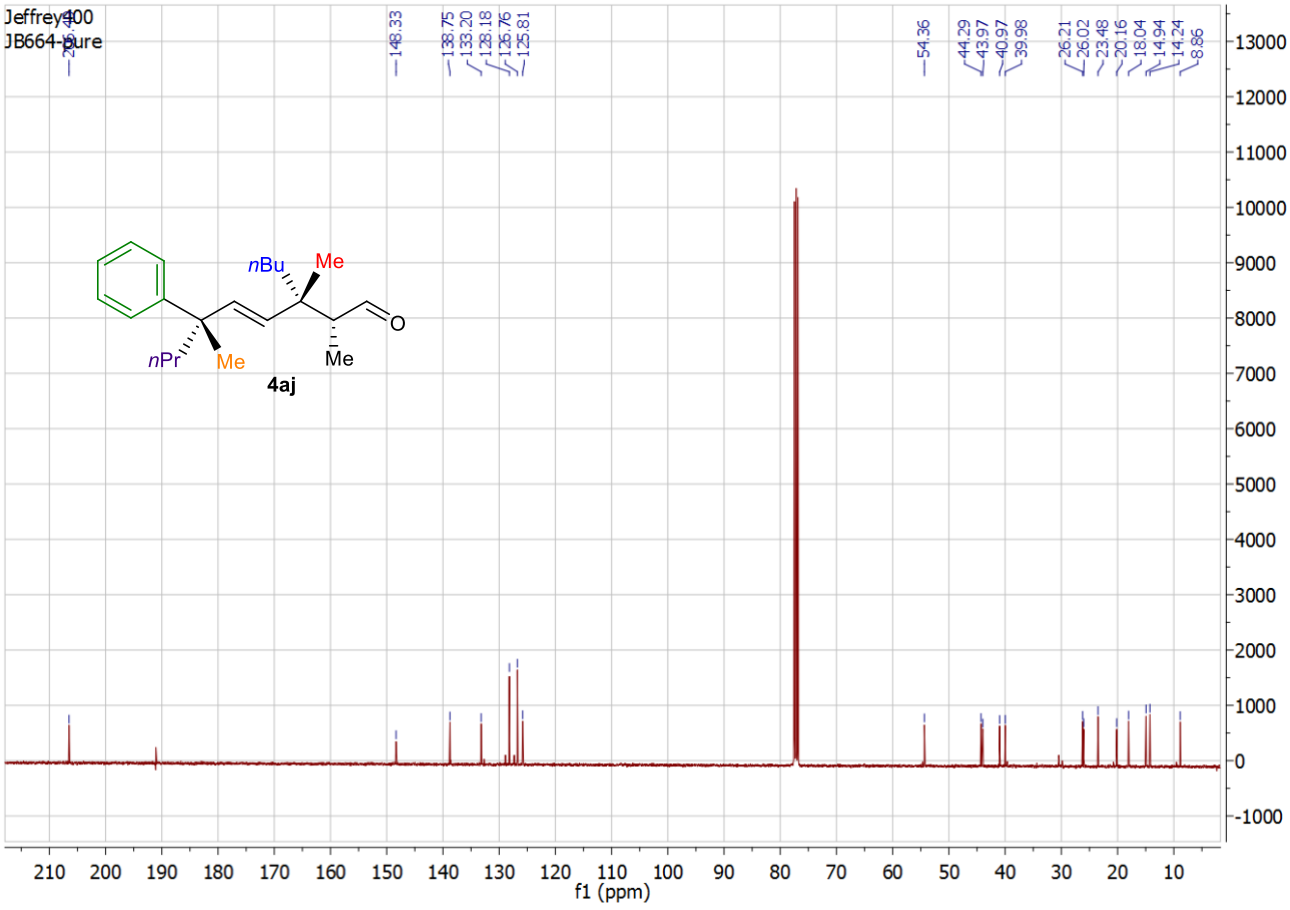

Me
nBu
Me
O
nBu
H
Me
4ah
f1 (ppm)

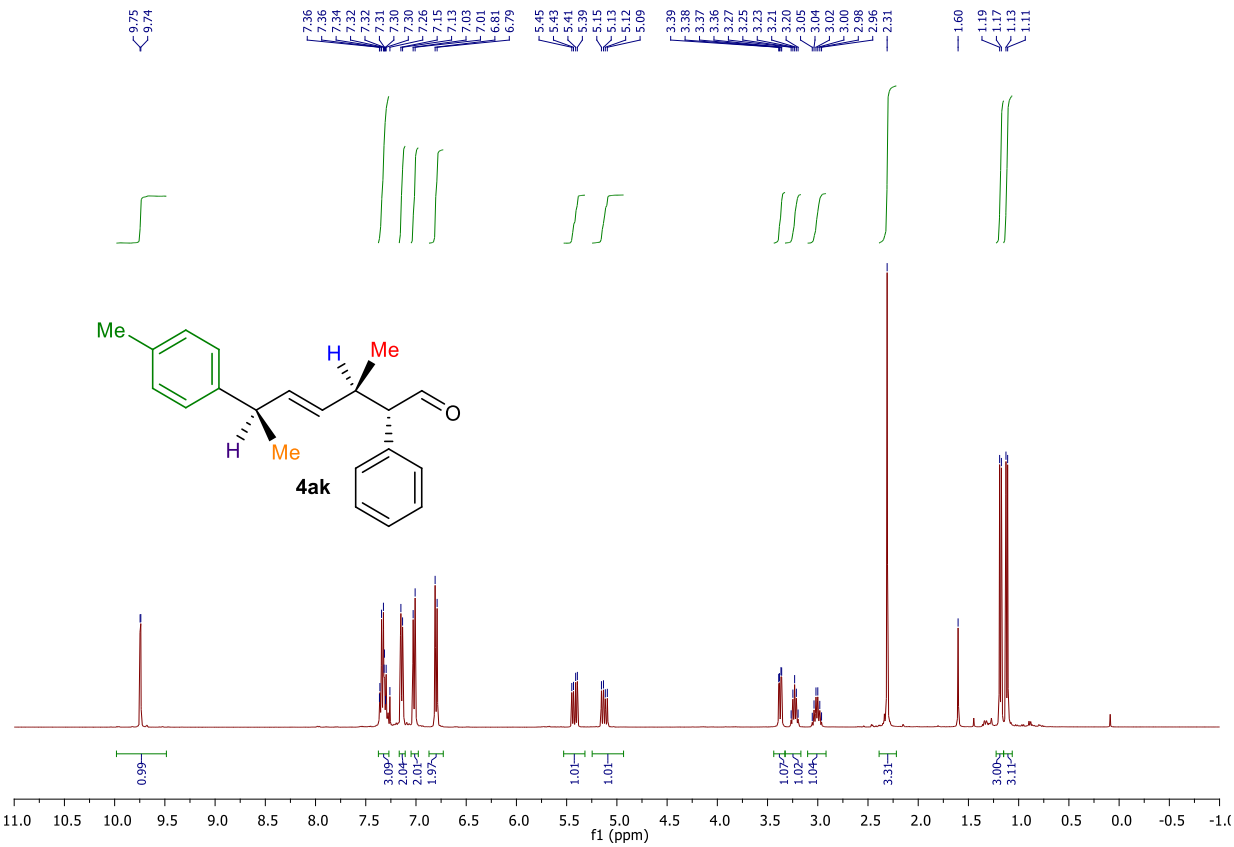

Me
nBu
Me
O
nBu
H
Me
4ah
f1 (ppm)

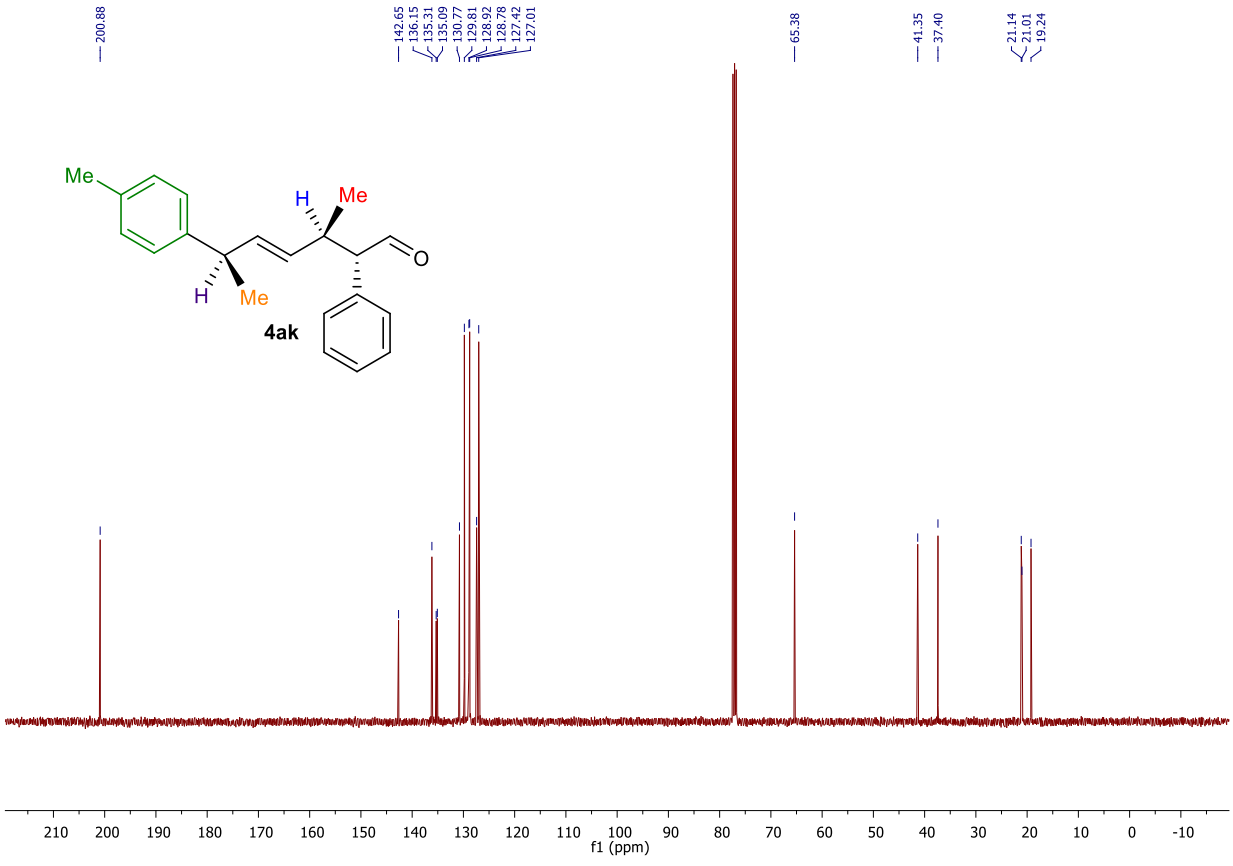

Cl
nBu
Me
nBu
H
Me
O
4ai
f1 (ppm)

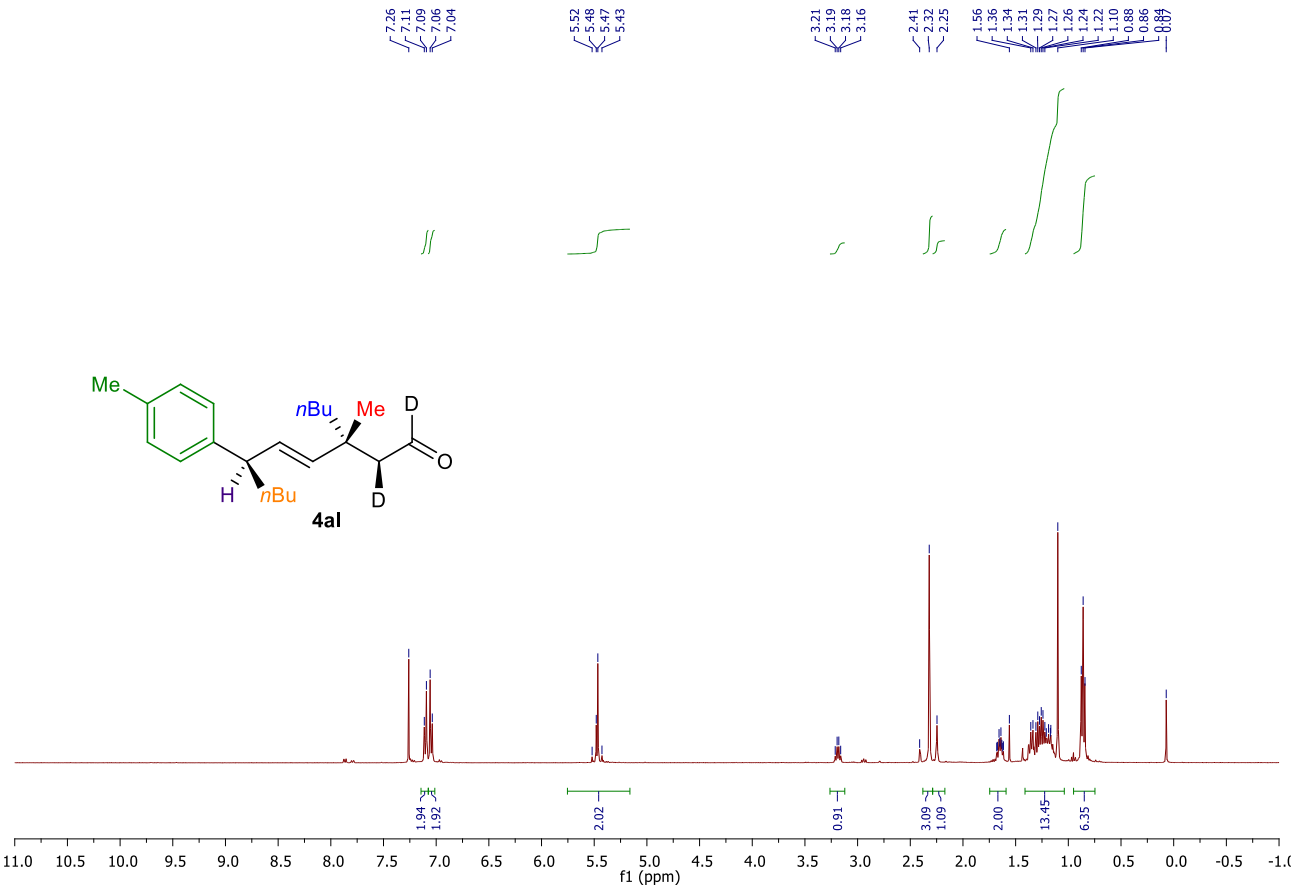

Cl
nBu
Me
nBu
H
Me
O
4ai
f1 (ppm)

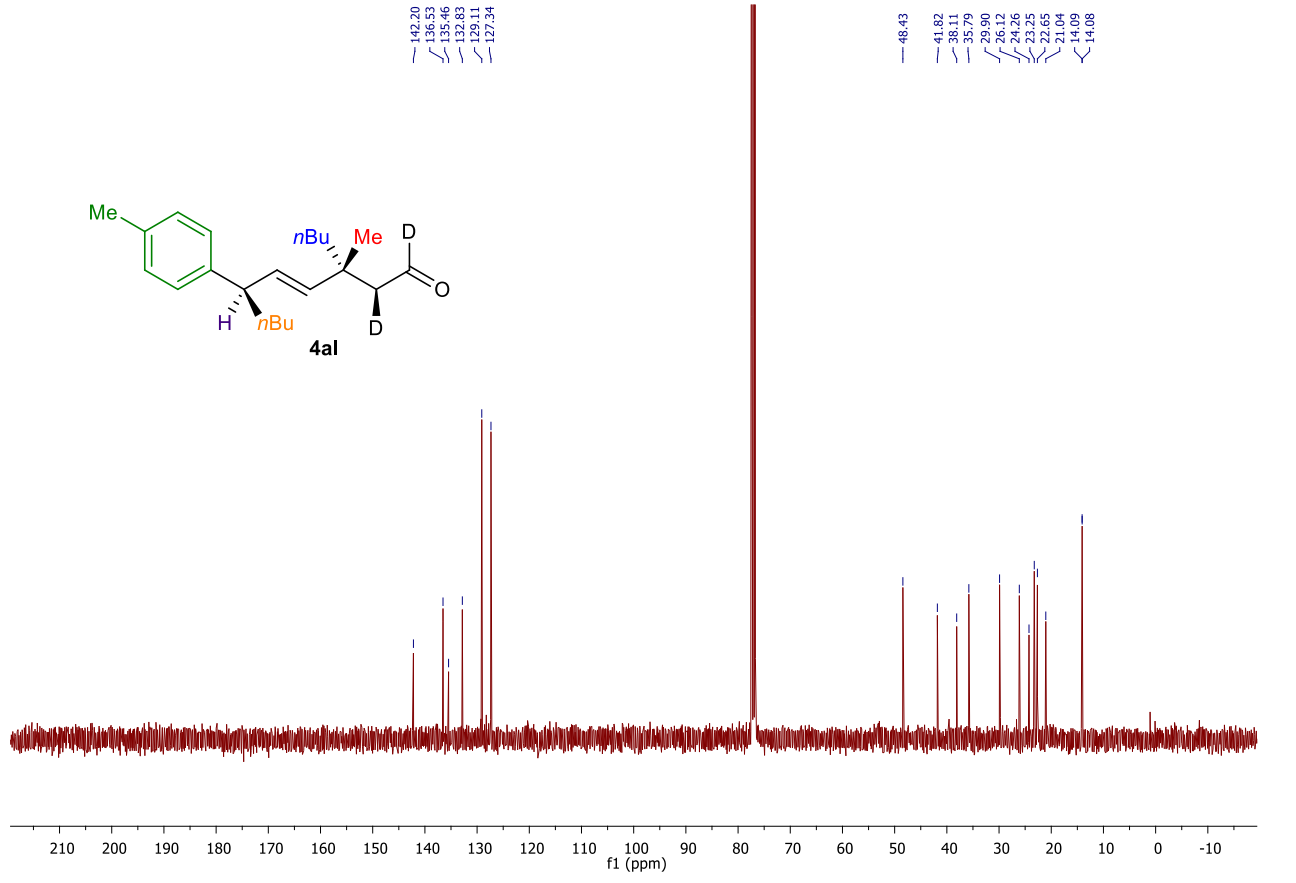

Jeffrey400
JB664-pure
nBu
Me
nPr
Me
Me
O
4aj
f1 (ppm)

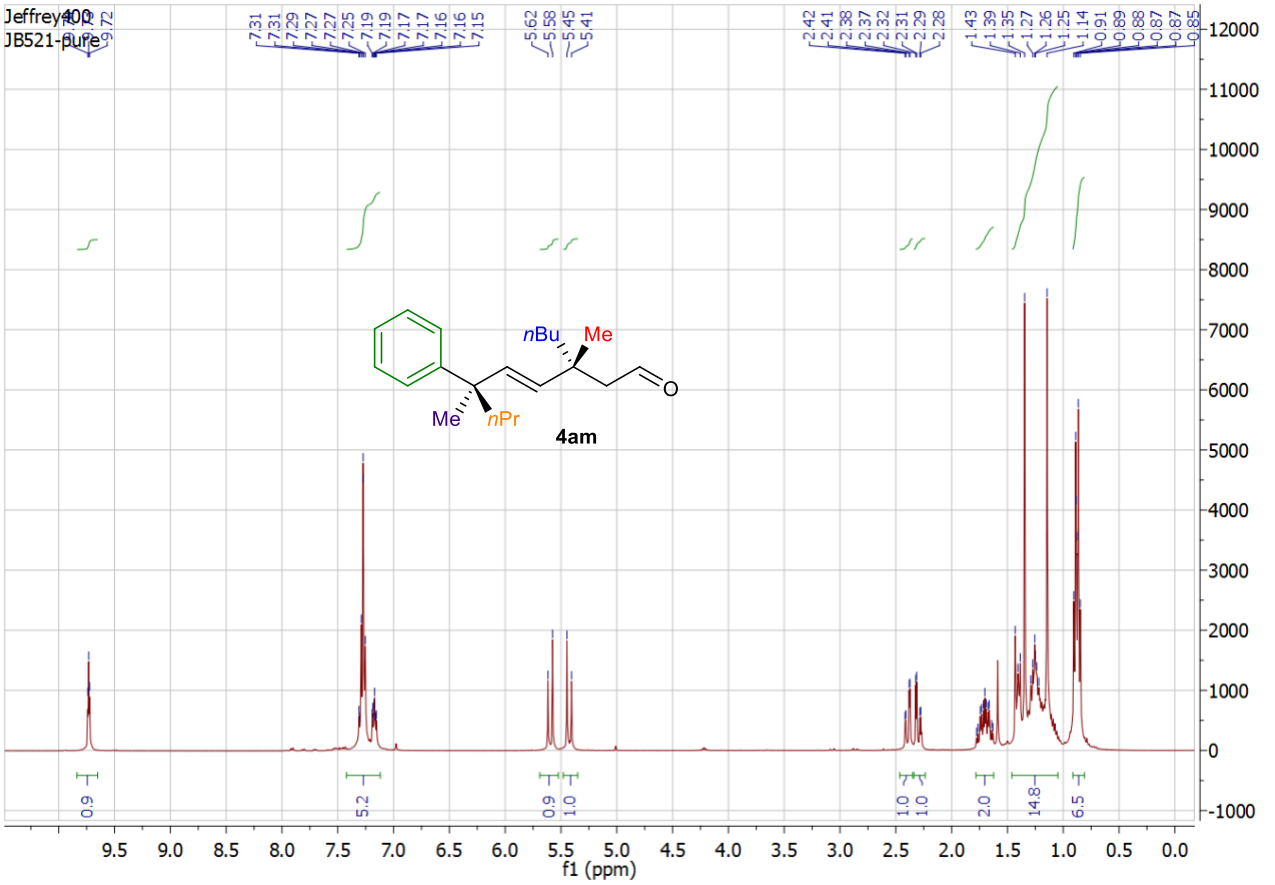

Jeffrey400
JB664-pure
nBu
Me
nPr
Me
Me
O
4aj
f1 (ppm)

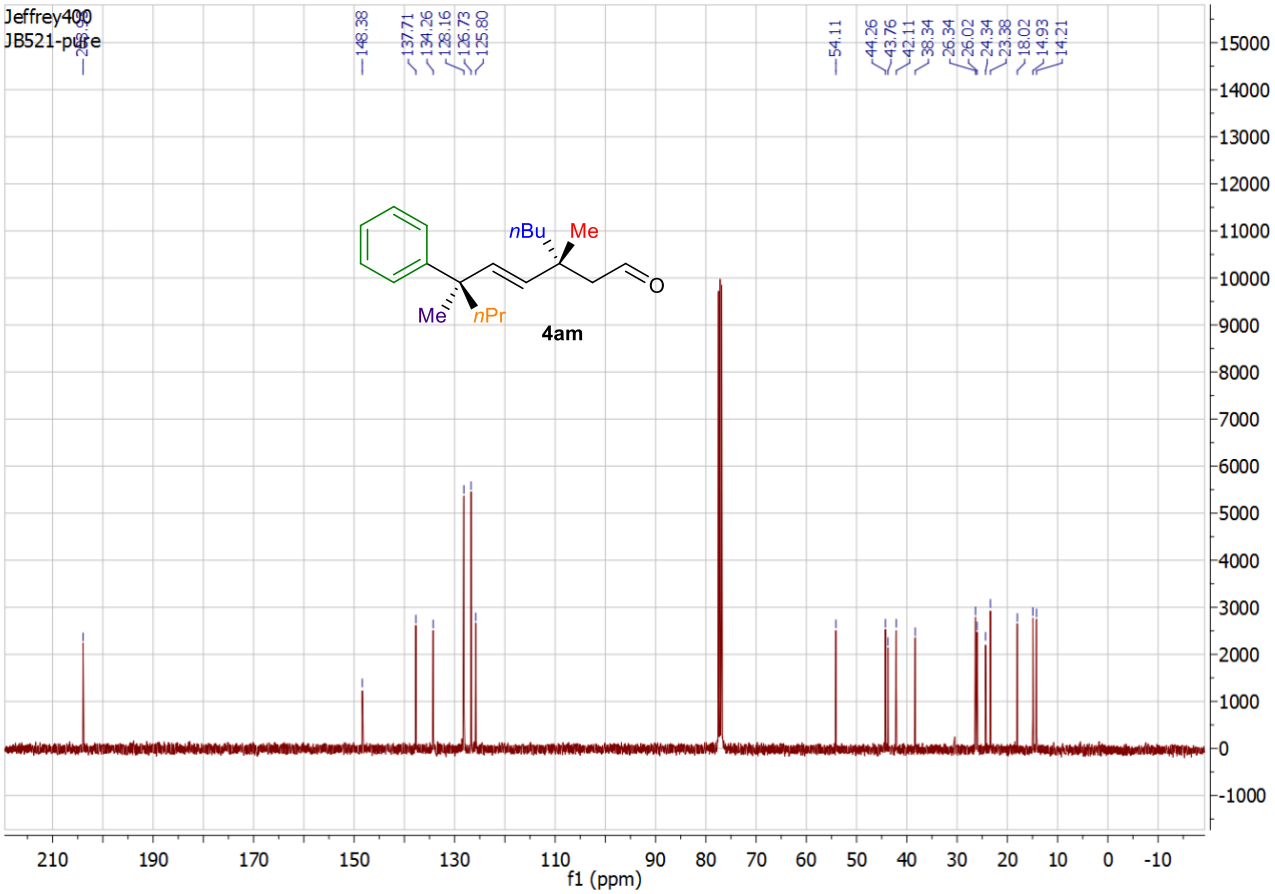

9.75
9.74
7.36
7.36
7.34
7.32
7.32
7.31
7.30
7.30
7.26
7.15
7.13
7.03
7.01
6.81
6.79
5.45
5.43
5.41
5.39
5.15
5.13
5.12
5.09
3.39
3.38
3.37
3.36
3.27
3.25
3.23
3.21
3.20
3.05
3.04
3.02
3.00
2.98
2.96
2.31
1.60
1.19
1.17
1.13
1.11
Me
H
Me
O
H
Me
4ak
0.99
3.09
2.04
2.01
1.97
1.01
1.01
1.07
1.02
1.04
3.31
3.00
3.11
f1 (ppm)

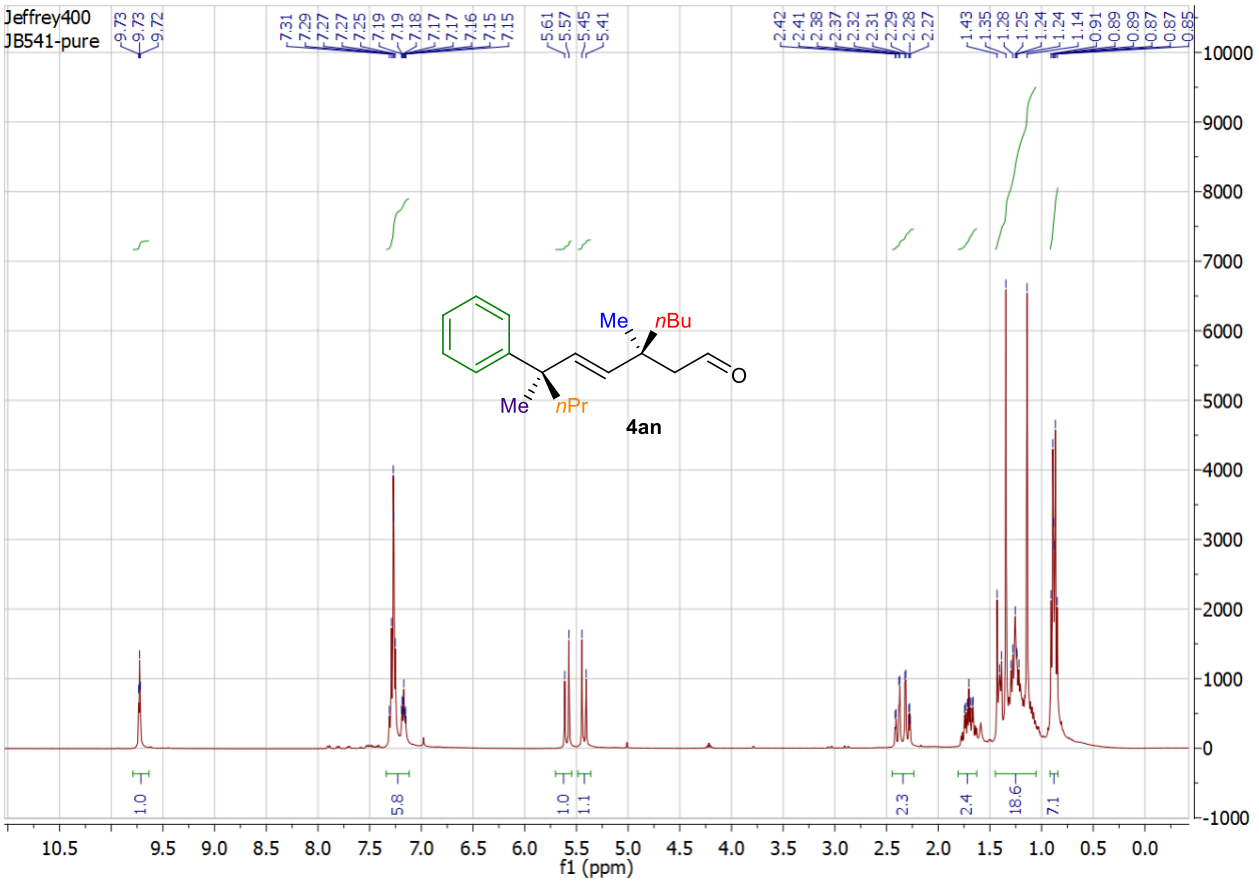

200.88
142.65
136.15
135.31
135.09
130.77
129.81
128.92
128.78
127.42
127.01
65.38
41.35
37.40
21.14
21.01
19.24
Me
H
Me
O
H
Me
4ak
f1 (ppm)

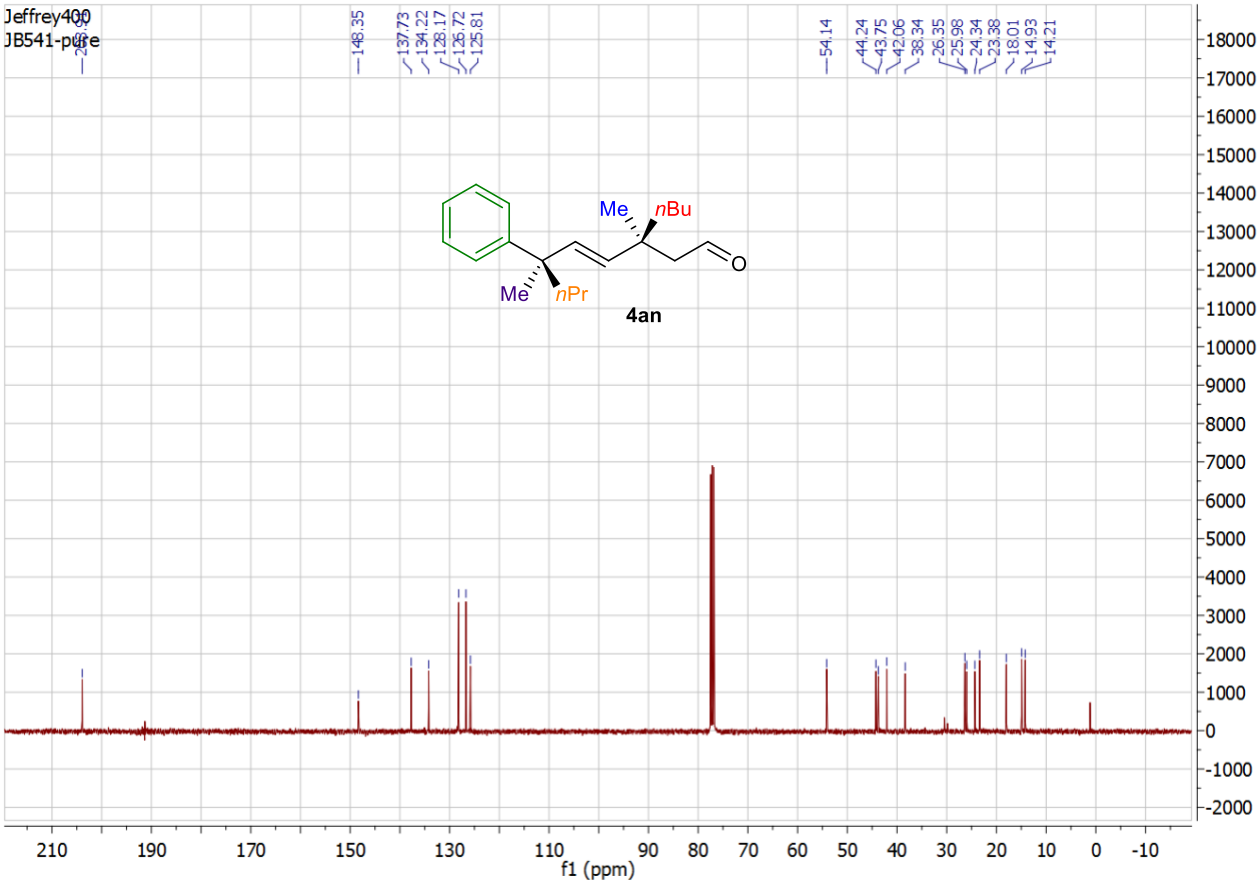

7.26
7.11
7.09
7.06
7.04
5.52
5.48
5.47
5.43
3.21
3.19
3.18
3.16
2.41
2.32
2.25
1.56
1.36
1.34
1.31
1.29
1.27
1.26
1.24
1.22
1.10
0.88
0.86
0.84
0.83
Me
nBu
Me
D
O
H
nBu
D
4al
1.94
1.92
2.02
0.91
3.09
1.09
2.00
13.45
6.35
f1 (ppm)

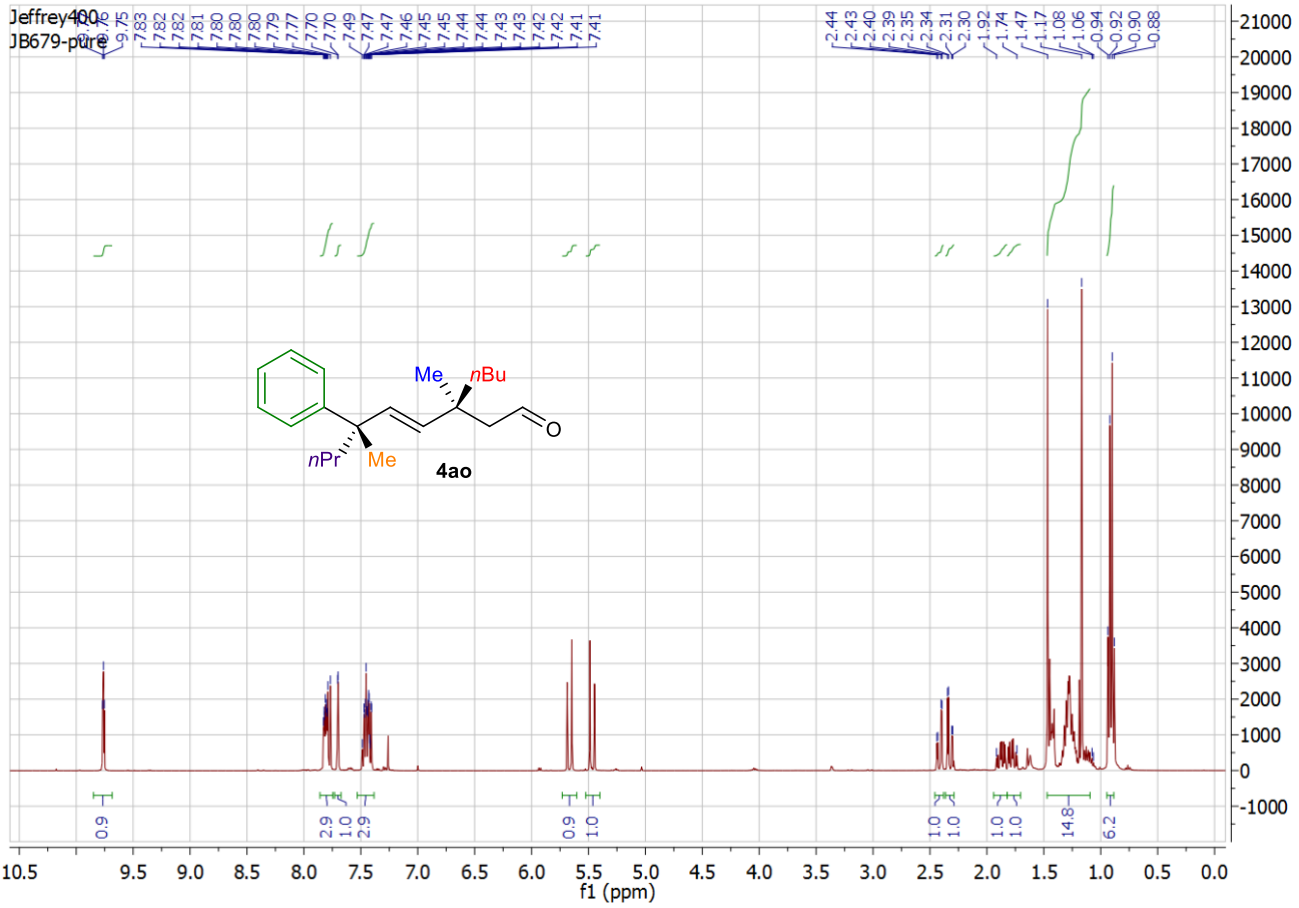

142.20
136.53
135.46
132.83
129.11
127.34
48.43
41.82
38.11
35.79
29.90
26.12
24.26
23.25
22.65
21.04
14.09
14.08
Me
nBu
Me
D
O
H
nBu
D
4al
f1 (ppm)

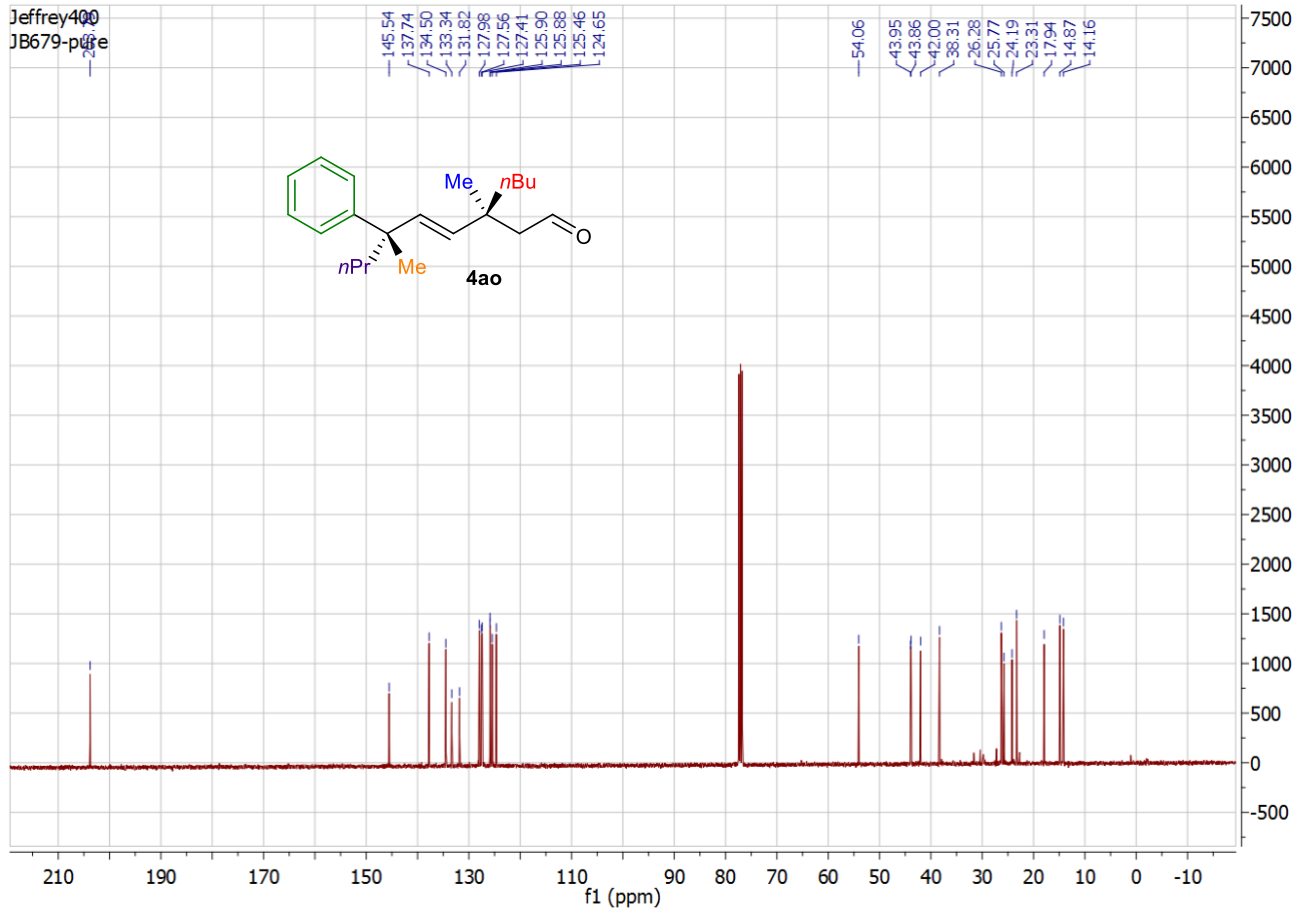

Jeffrey400
JB521-pure
nBu
Me
Me
nPr
4am
f1 (ppm)

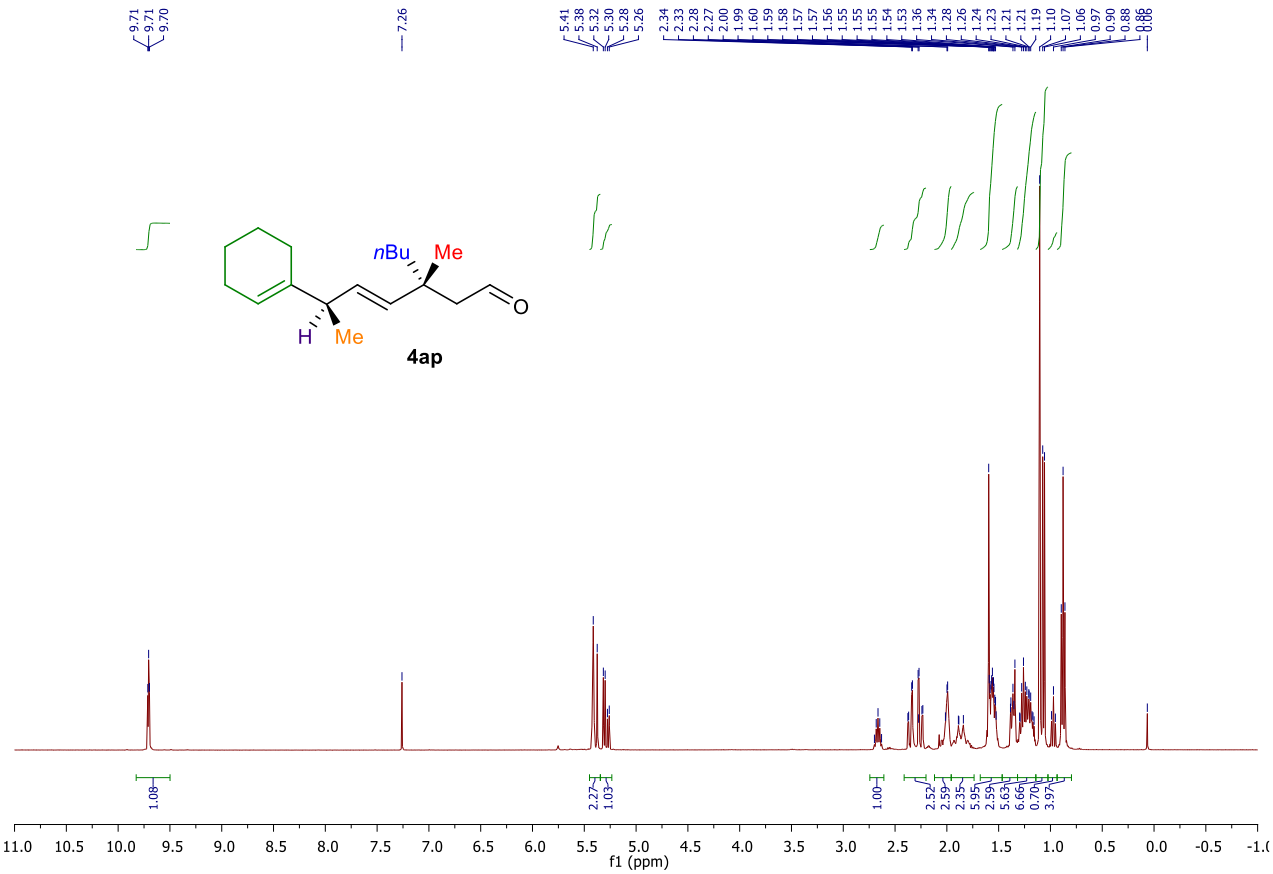

Jeffrey400
JB521-pure
nBu
Me
Me
nPr
4am
f1 (ppm)


Jeffrey400
JB541-pure
Me
nBu
Me
nPr
4an
f1 (ppm)


Jeffrey400
JB541-pure
Me
nBu
Me
nPr
4an
f1 (ppm)


Jeffrey400
JB679-pure
Me
nBu
nPr
Me
4ao
f1 (ppm)


Jeffrey400
JB679-pure
Me
nBu
nPr
Me
4ao
f1 (ppm)


9.71
9.71
9.70
7.26
5.41
5.38
5.32
5.30
5.28
5.26
2.34
2.33
2.28
2.27
2.00
1.99
1.60
1.59
1.58
1.57
1.57
1.56
1.55
1.55
1.55
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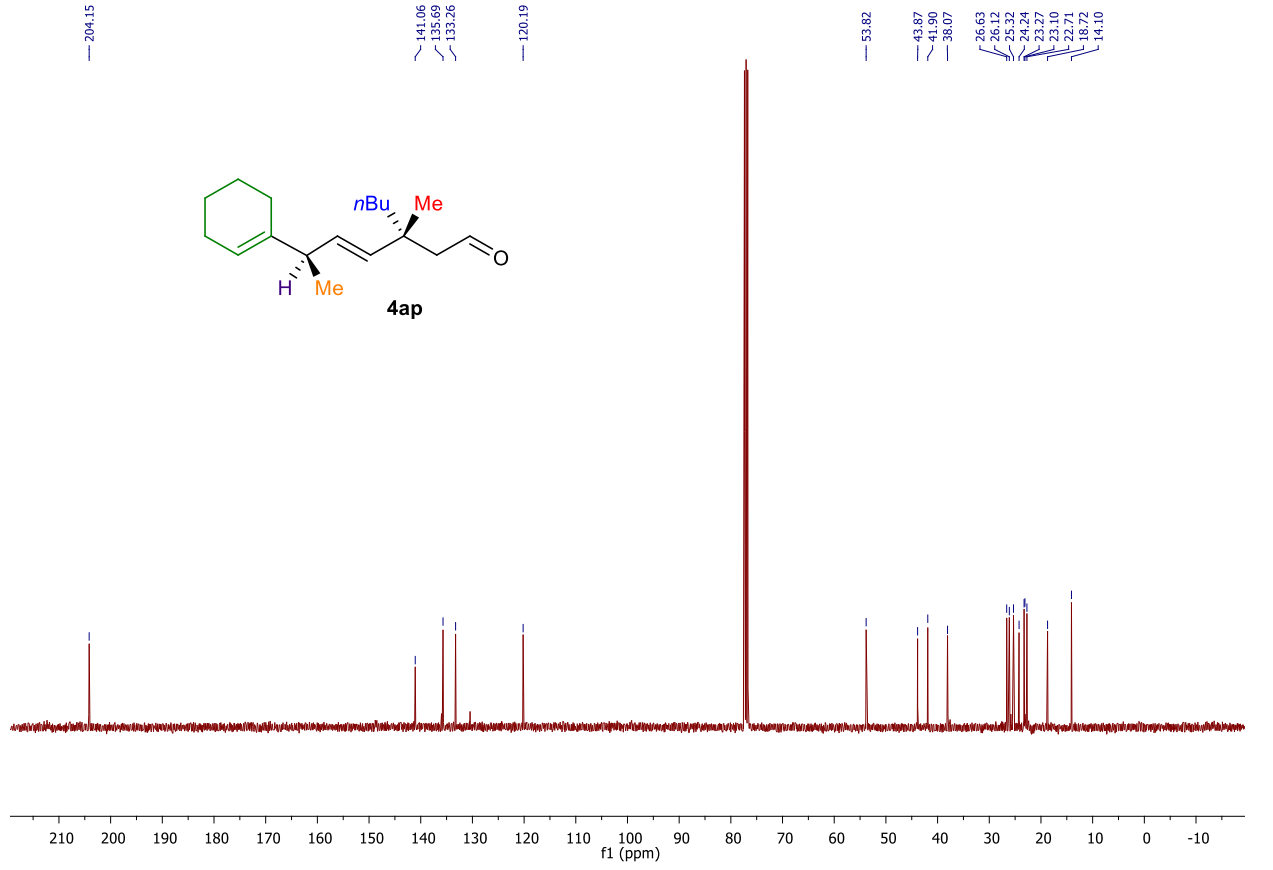
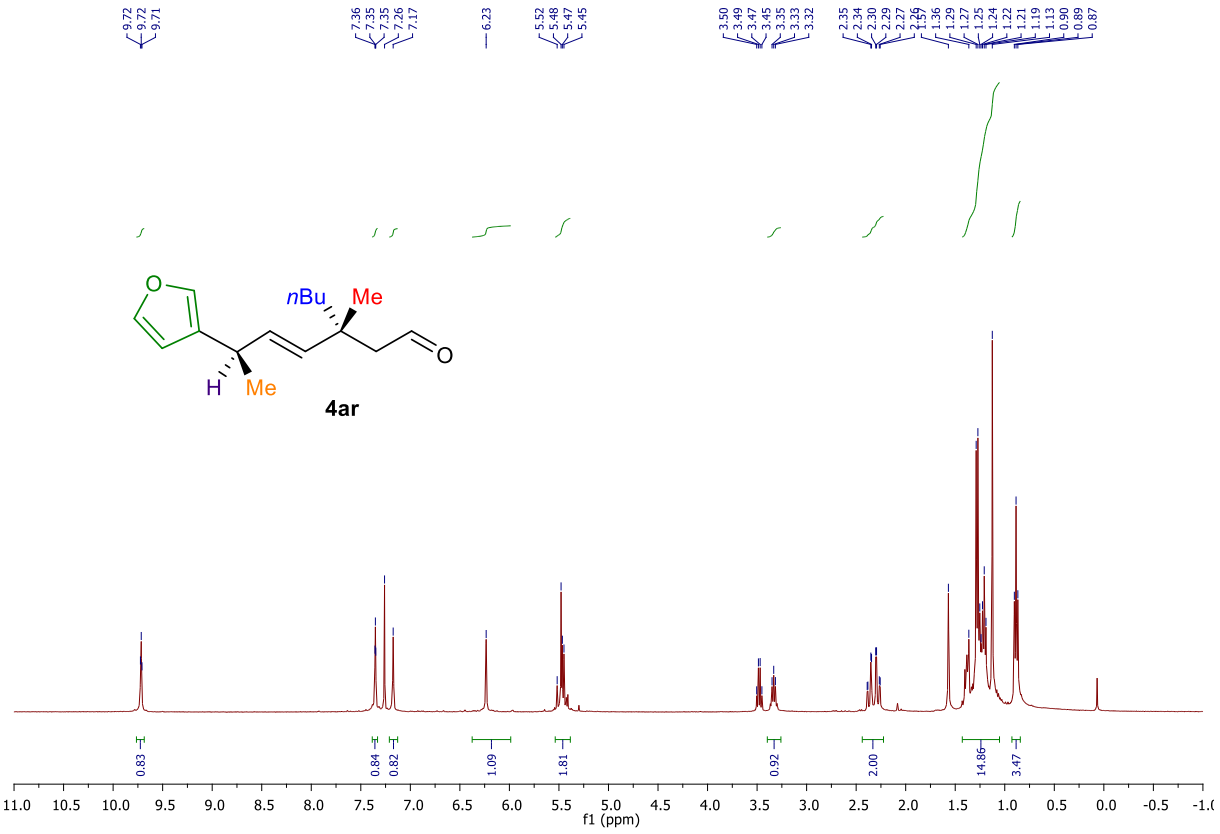
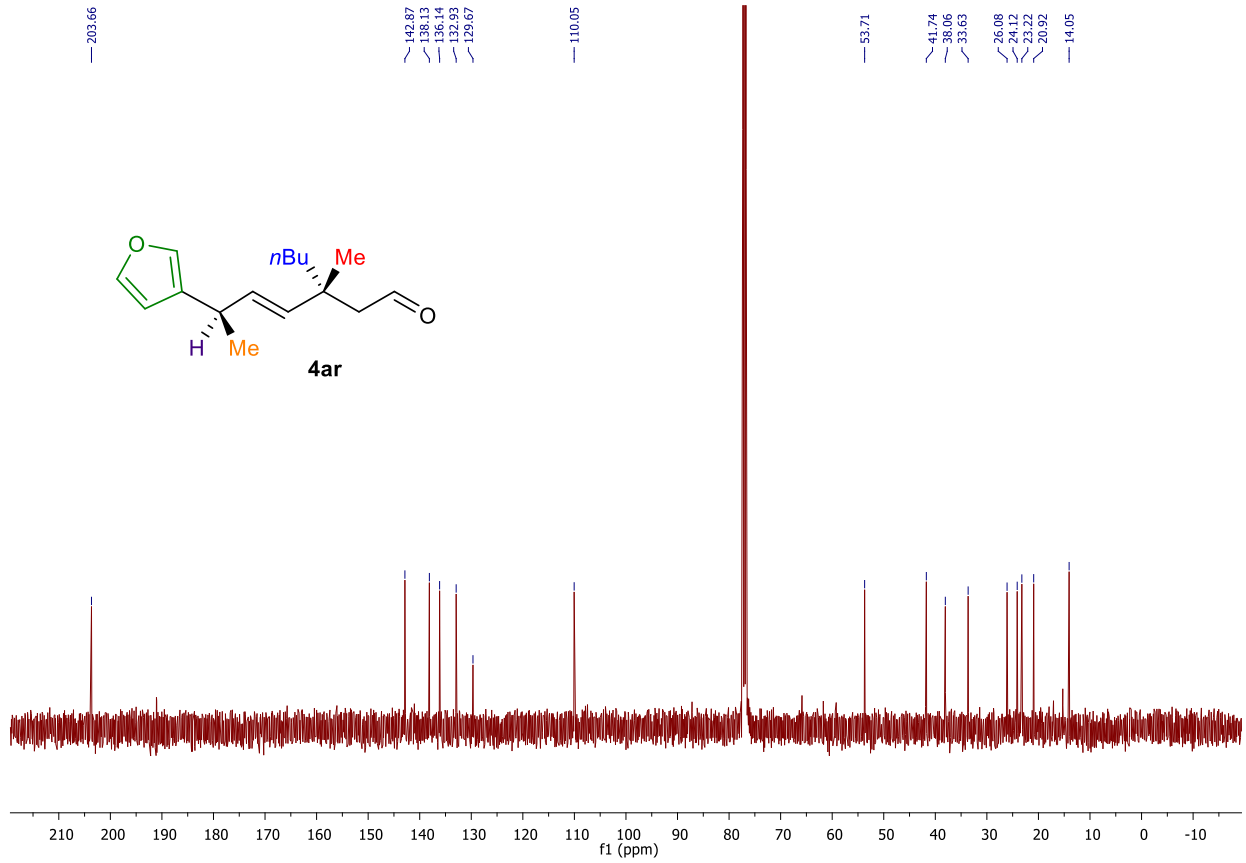
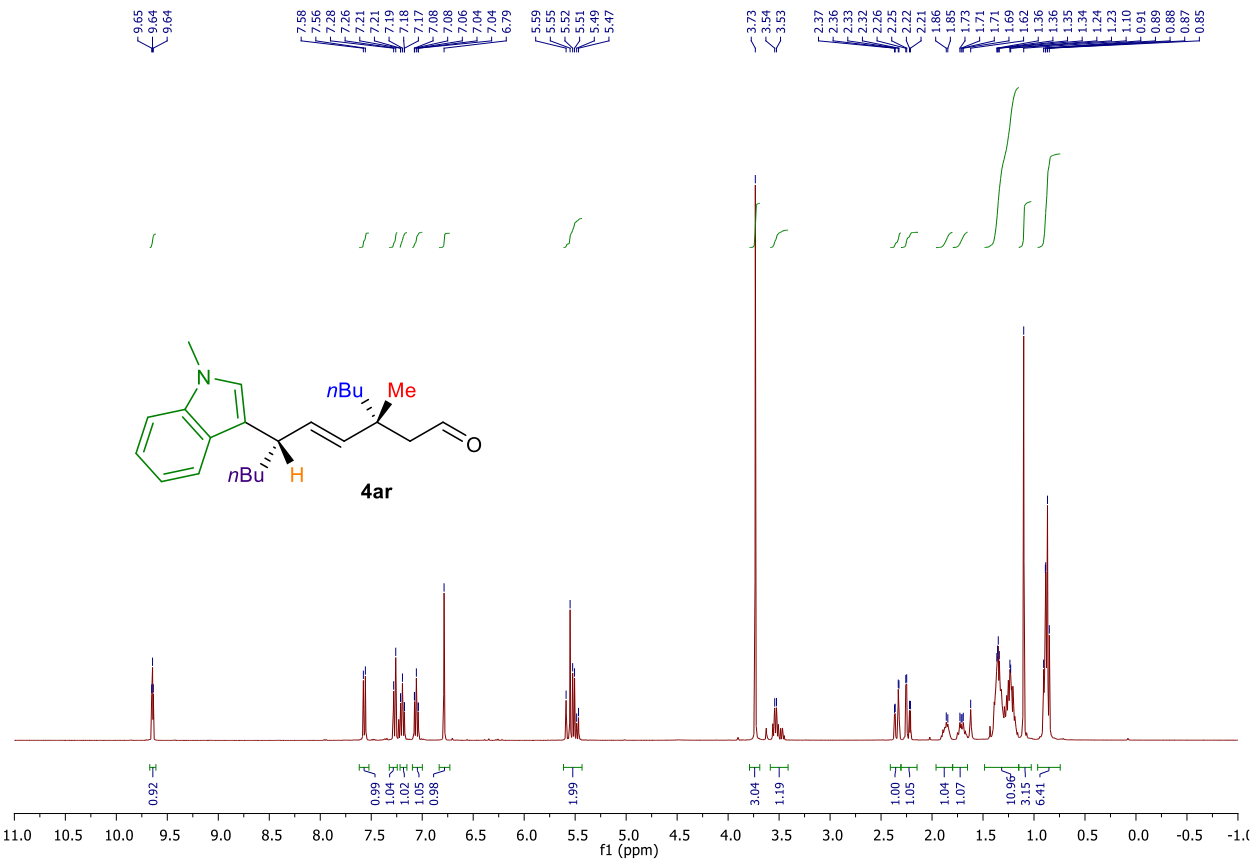
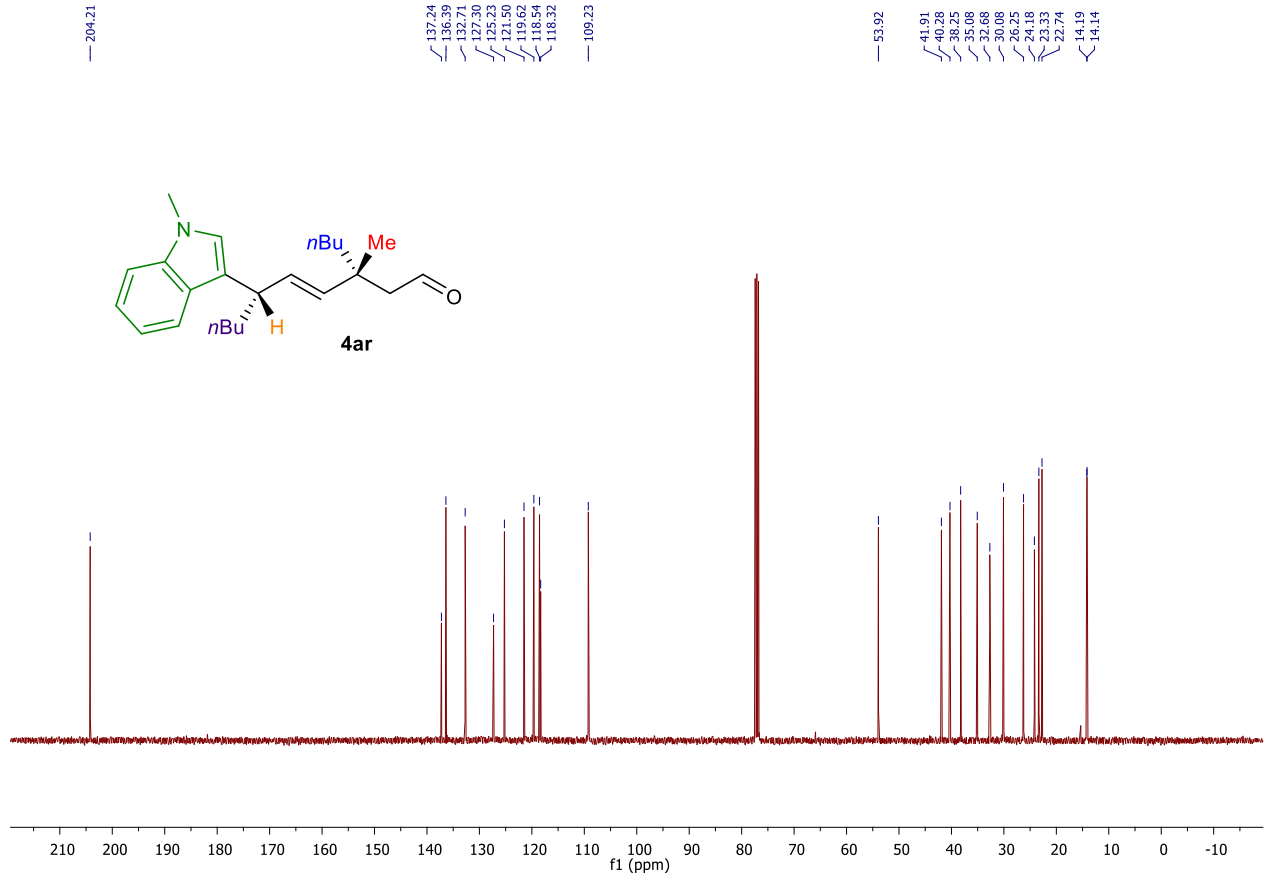
1.53
1.36
1.34
1.28
1.26
1.24
1.23
1.21
1.21
1.19
1.10
1.07
1.06
0.97
0.90
0.88
nBu
Me
H
Me
O
4ap
1.08
2.27
1.03
1.00
2.52
2.59
2.35
5.95
5.63
6.66
0.70
3.97
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

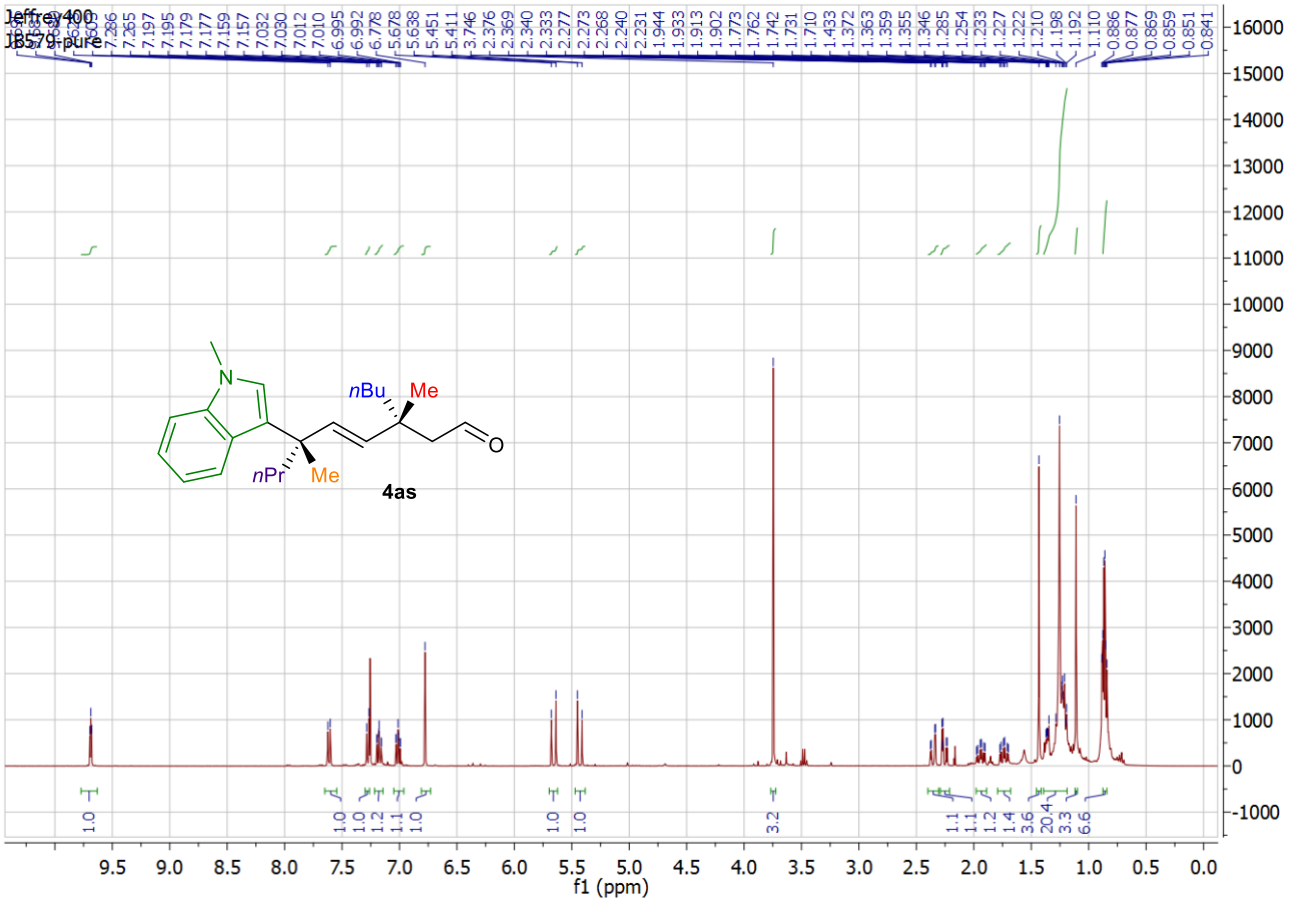

204.15
141.06
135.69
133.26
120.19
53.82
43.87
41.90
38.07
26.63
26.12
25.32
24.24
23.27
23.10
22.71
18.72
14.10
nBu
Me
H
Me
O
4ap
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

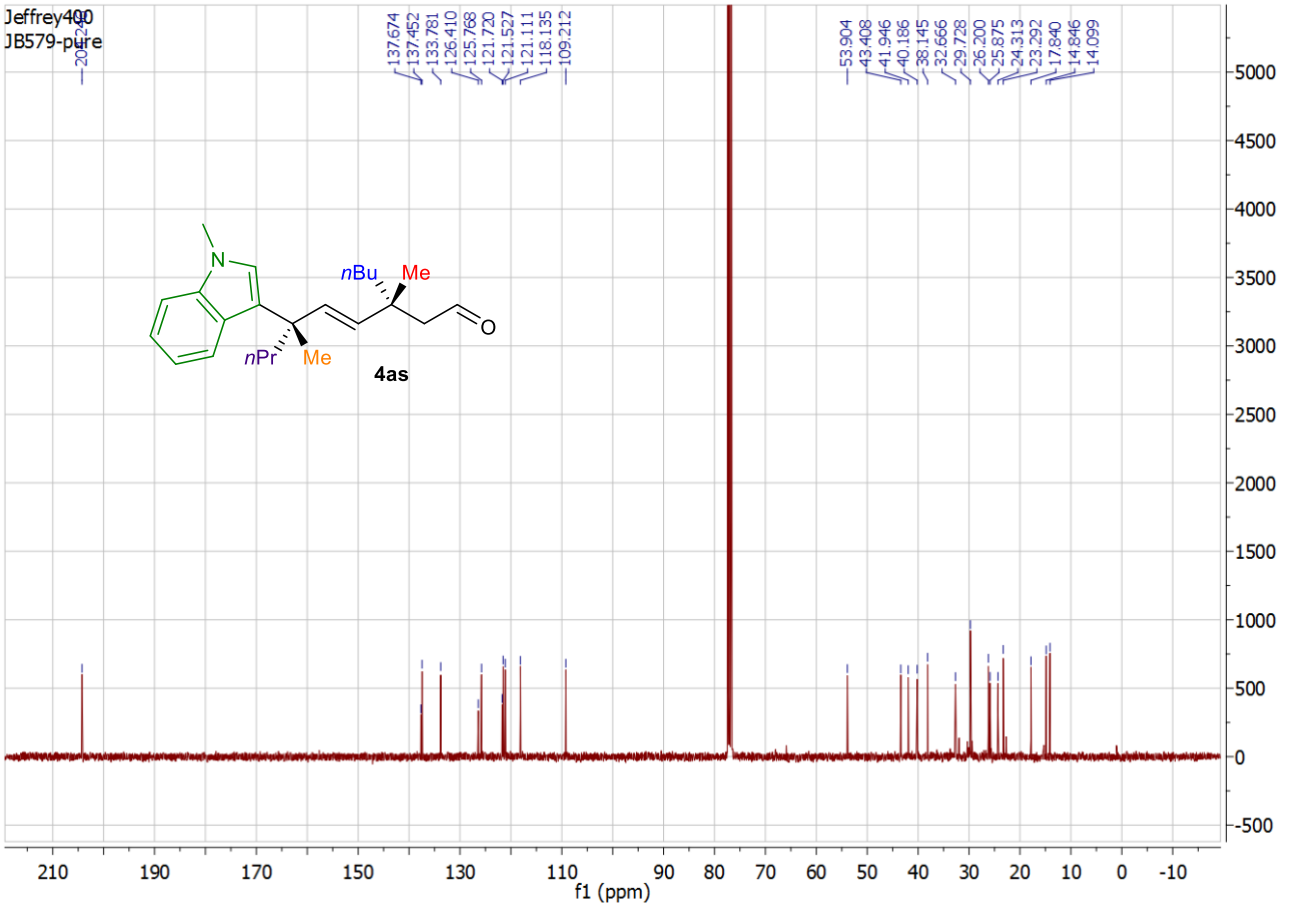

9.72
9.72
9.71
7.36
7.35
7.35
7.26
7.17
6.23
5.52
5.48
5.47
5.45
3.50
3.49
3.47
3.45
3.35
3.33
3.32
2.35
2.34
2.30
2.29
2.27
2.26
1.37
1.36
1.29
1.27
1.25
1.24
1.22
1.21
1.19
1.13
0.90
0.89
0.87
O
nBu
Me
H
Me
O
4ar
0.83
0.84
0.82
1.09
1.81
0.92
2.00
14.86
3.47
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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 -0.5 -1.0
f1 (ppm)


203.66
142.87
138.13
136.14
132.93
129.67
110.05
53.71
41.74
38.06
33.63
26.08
24.12
23.22
20.92
14.05
O
nBu
Me
H
Me
O
4ar
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)

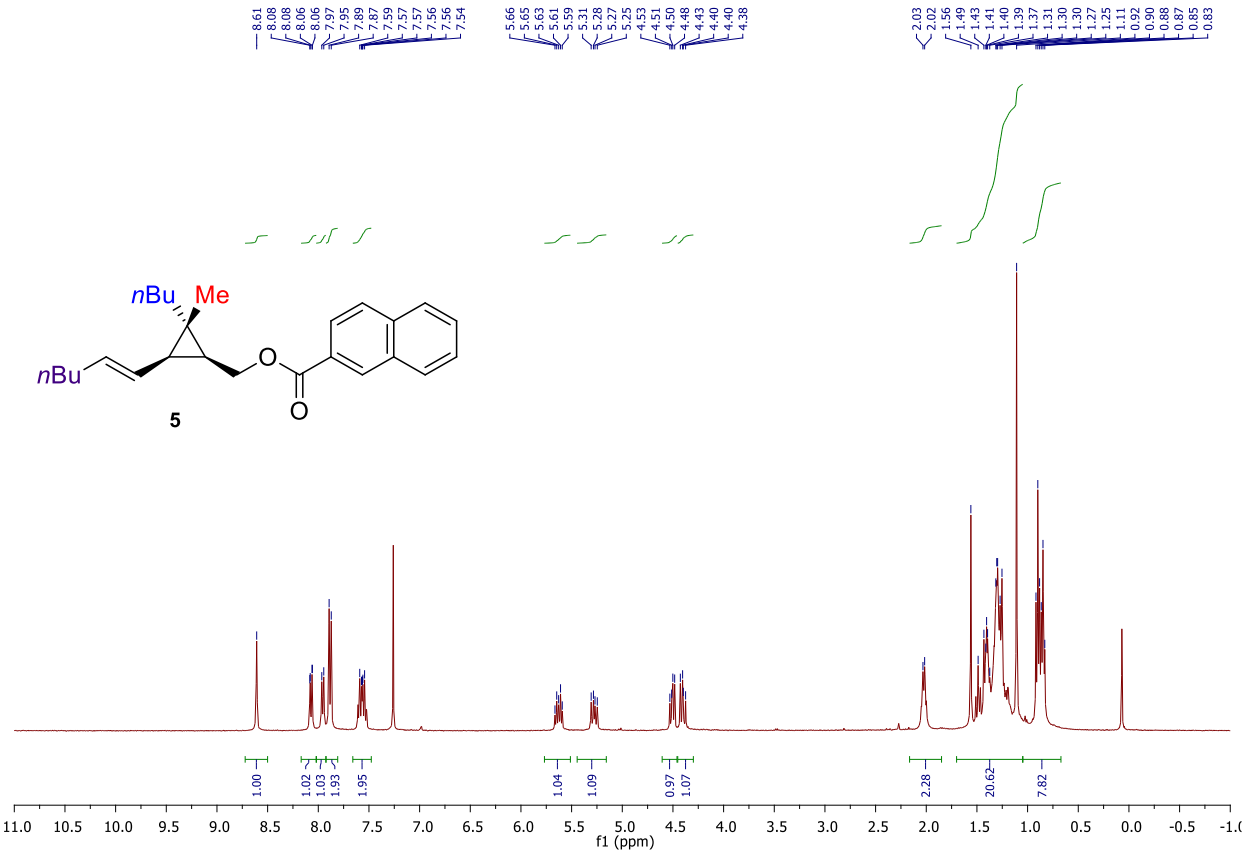

9.65
9.64
9.64
7.58
7.56
7.28
7.26
7.21
7.21
7.19
7.18
7.17
7.08
7.08
7.06
7.04
7.04
6.79
5.59
5.55
5.52
5.51
5.49
5.47
3.73
3.54
3.53
2.37
2.36
2.33
2.32
2.26
2.25
2.22
2.21
1.86
1.85
1.73
1.71
1.71
1.69
1.62
1.36
1.36
1.35
1.34
1.24
1.23
1.10
0.91
0.89
0.88
0.87
0.85
N
nBu
Me
O
nBu
H
4ar
0.92
0.99
1.04
1.02
1.05
0.98
1.99
3.04
1.19
1.00
1.05
1.04
1.07
10.96
3.15
6.41
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
-0.5
f1 (ppm)

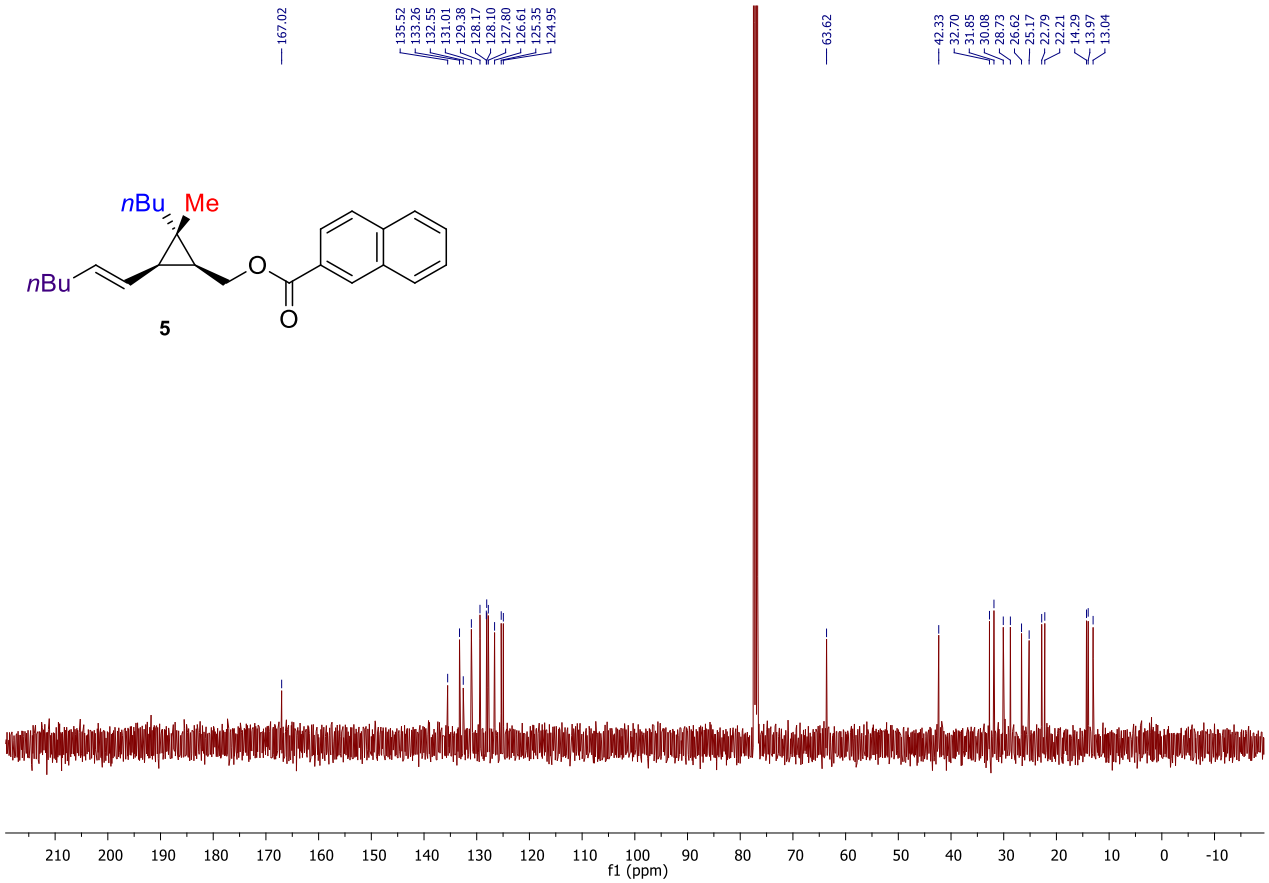

204.21
137.24
136.39
132.71
127.30
125.23
121.50
119.62
118.54
118.32
109.23
53.92
41.91
40.28
38.25
35.08
32.68
30.08
26.25
24.18
23.33
22.74
14.19
14.14
N
nBu
Me
O
nBu
H
4ar
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

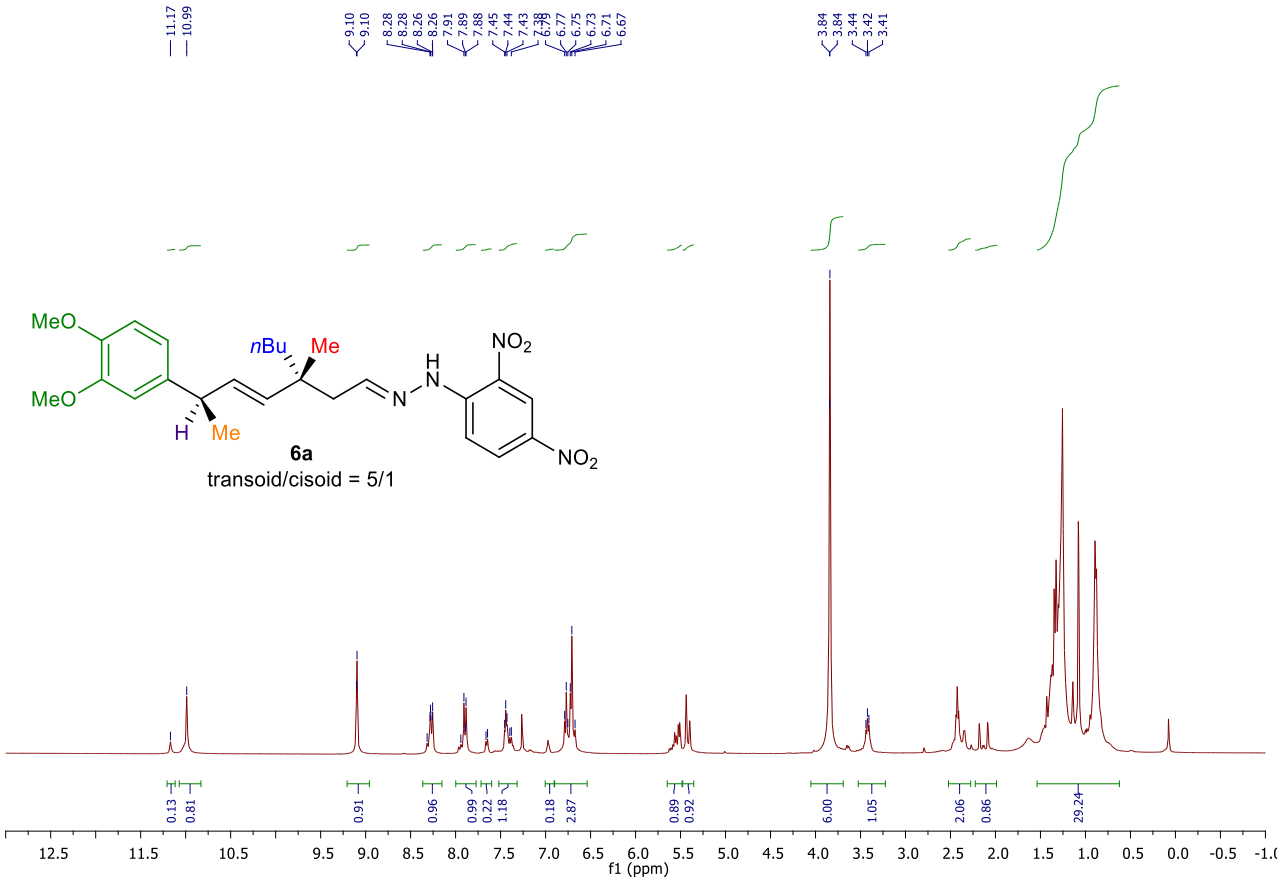

Jeffrey400
JB579-pure
nBu
Me
nPr
Me
4as
f1 (ppm)

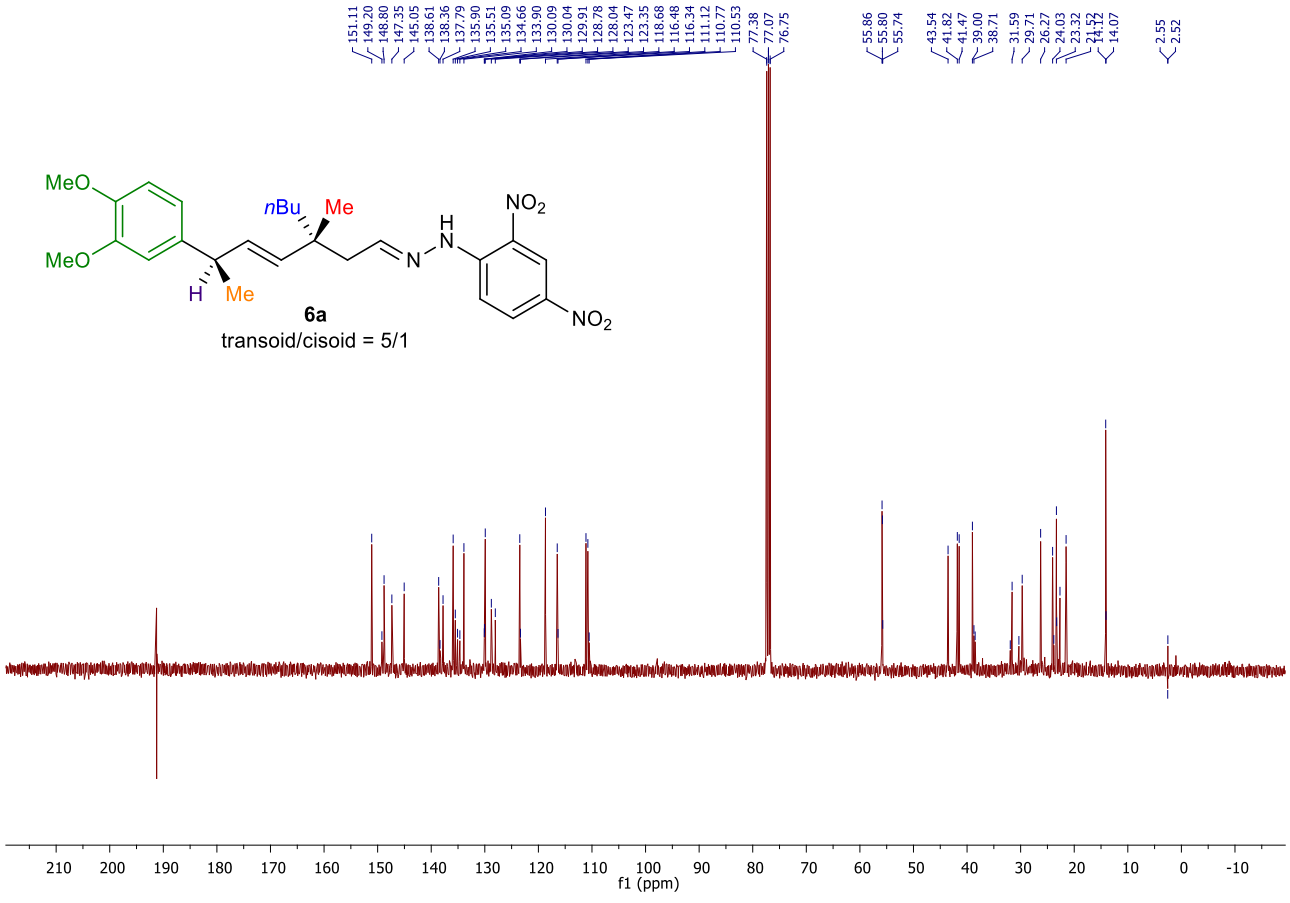

Jeffrey400
JB579-pure
nBu
Me
nPr
Me
4as
f1 (ppm)

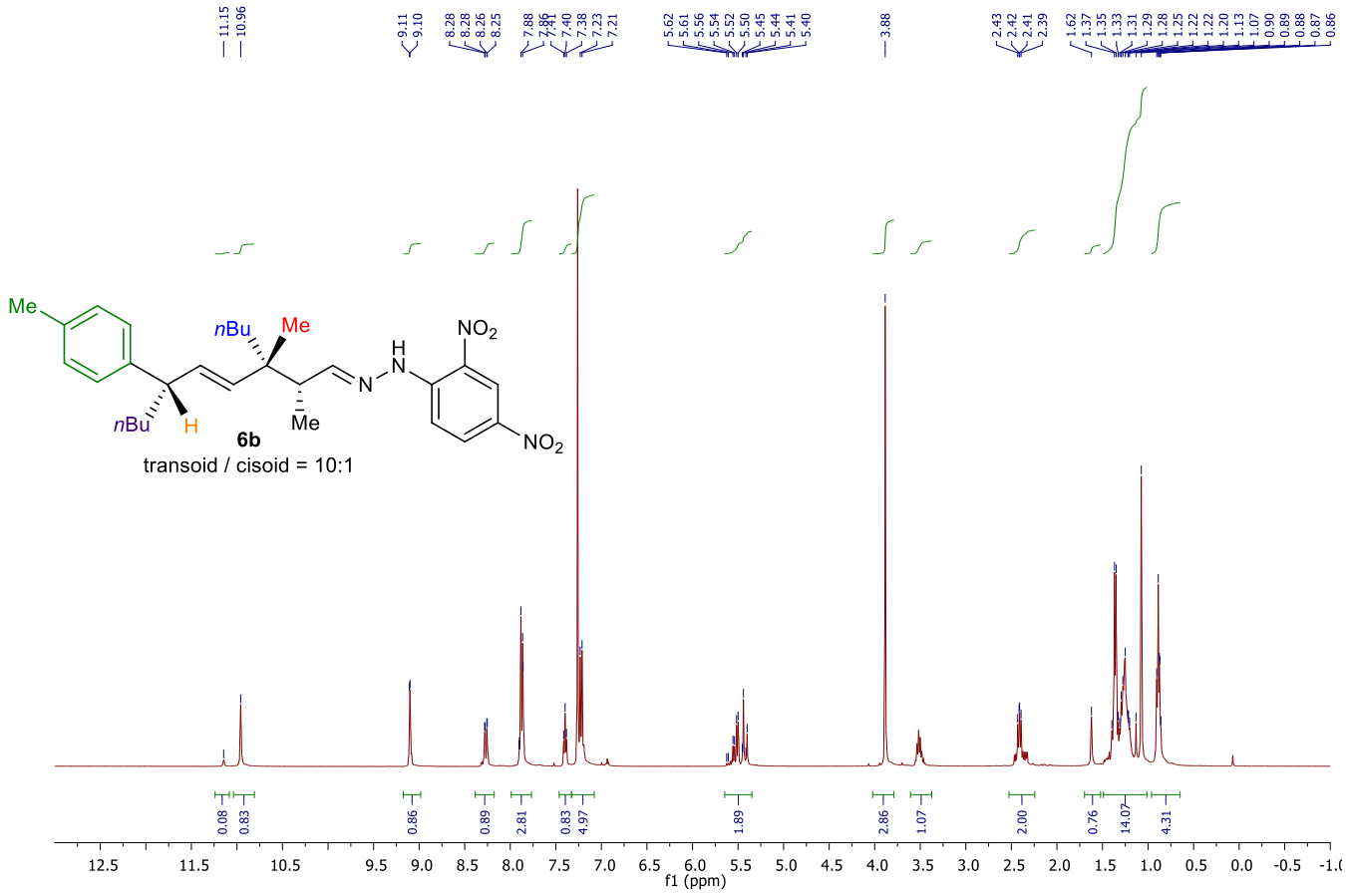
NMR spectras of derivatives 5, 6a and 6b

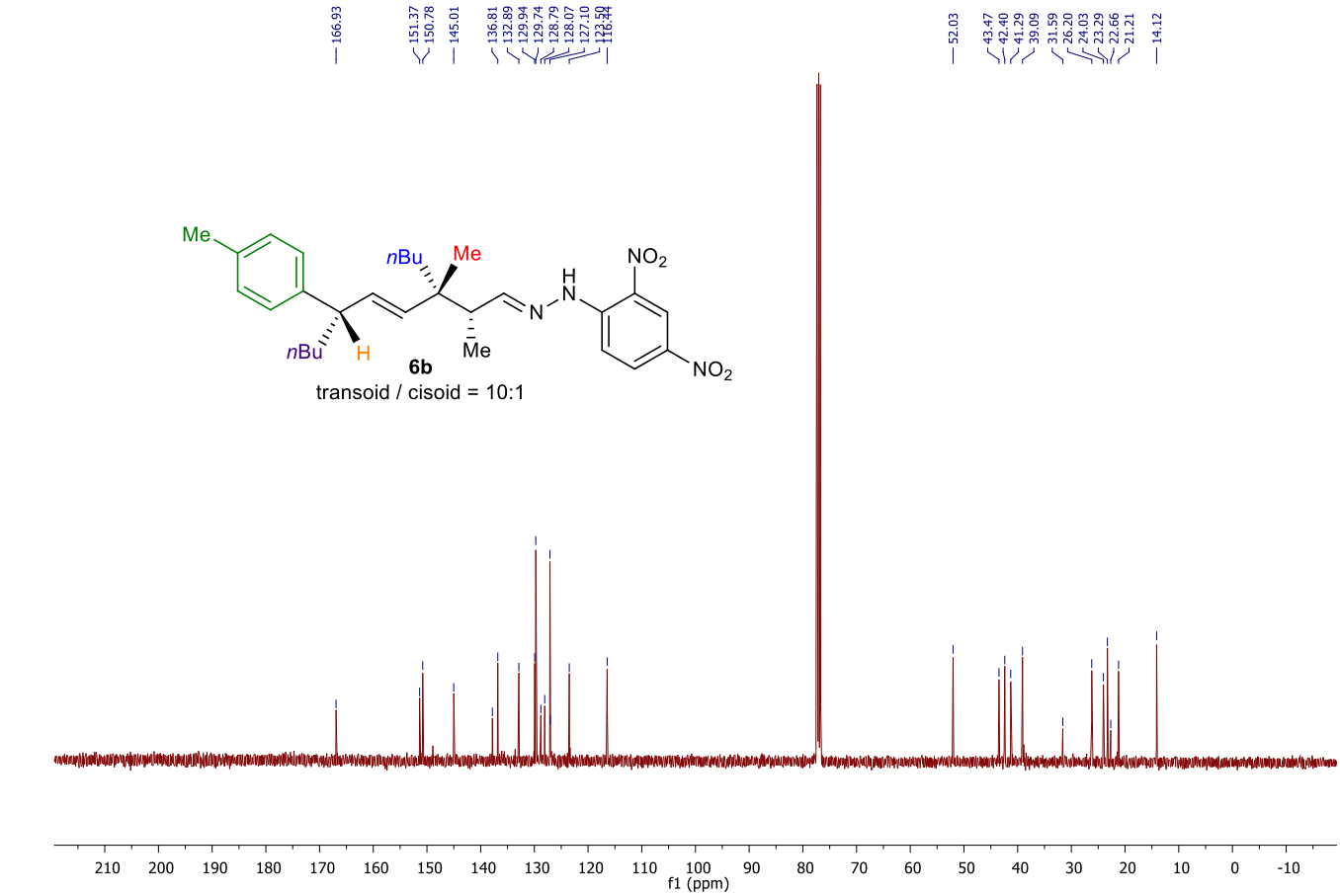





MeO
MeO
nBu
Me
H
Me
NO2
NO2
6a
transoid/cisoid = 5/1
f1 (ppm)


MeO
MeO
nBu
Me
H
Me
NO2
NO2
6a
transoid/cisoid = 5/1
f1 (ppm)


Me
nBu
Me
NO2
H
N
N
H
nBu
H
Me
NO2
6b
transoid / cisoid = 10:1
f1 (ppm)


Me
nBu
Me
NO2
H
N
N
H
nBu
H
Me
NO2
6b
transoid / cisoid = 10:1
f1 (ppm)