CHEMISTRY
A European Journal

Supporting Information

Two Enabling Strategies for the Stereoselective Conversion of Internal Alkynes into Trisubstituted Alkenes

Nikolas Huwyler, Karin Radkowski, Stephan M. Rummelt, and Alois Fürstner*[a]

chem_201702470_sm_miscellaneous_information.pdf

#ÈÅ Í ÉÃÁls ÁÎÄ 3ÏÌÖÅÎÔÓ¢ All chemicals and solvents were purchased from ABCR, ACROS, ALFA–AESAR, APOLLO SCIENTIFIC, FLUKA, FLUOROCHEM, MERCK, SIGMA-ALDRICH, TCI, or STREM CHEMICALS and used as received, unless mentioned otherwise.[1] Et_2O and THF were distilled from Mg/anthracene, CH_2Cl_2 and EtOAc from CaH_2, toluene from Na/K, and MeOH from Mg turnings under an inert atmosphere of nitrogen or argon. DMF, DMSO, MeCN, Et_3N and pyridine were dried by passage through molecular sieve colums (H_2O content < 30 ppm, KARL–FISCHER titration) using a VACUUM ATMOSPHERES COMPANY *Solvent Purifier* system.[2] Dry acetone was obtained by drying over B_2O_3, followed by filtration and distillation.[3] 2,6-Lutidine was distilled from CaH_2 under an inert atmosphere of argon. $[(Cp^*)RuCl_2]_n$ was prepared according to a literature procedure.[4] Copper(I) thiophene-2-carboxylate (CuTC) could either be prepared according to a literature procedure[5] or purchased from SIGMA-ALDRICH without noticeable differences in reactivity. $(Bu_4N)OP(O)Ph_2$ was prepared by a slightly adapted procedure (*vide infra)*.[6] All hygroscopic or air-sensitive chemicals were stored in SCHLENK-flasks under an atmosphere of argon at the appropriate temperature, as indicated by the supplier.

'ÅÎÅÒÁl 0ÒÏÃÅÄÕÒÅ¢ All non-aqueous reactions were performed under an inert atmosphere of dry argon at ca. 0.4 bar overpressure using flame dried glassware, unless otherwise noted. Reactions were stirred using magnetic stir-bars and monitored by thin layer chromatography (TLC). Analytical thin layer chromatography was performed using MACHEREY–NAGEL *POLYGRAM SIL G/UV* pre-coated polyester plates and visualized by ultraviolet light (UV). Additionally, TLC plates were stained with either aqueous potassium permanganate [1.5 g $KMnO_4$, 200 mL H_2O, 10 g K_2CO_3, 2.5 mL 1M NaOH aq.], cerium ammonium molybdate [0.5 g $Ce(NH_4)_2(NO_3)_6$, 12 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 235 mL H_2O, 15 mL conc. H_2SO_4] or ethanolic *p*-anisaldehyde [3.7 mL *p*-anisaldehyde, 135 mL EtOH, 5 mL conc. H_2SO_4, 1.5 mL AcOH]. Concentration under reduced pressure (= *in vacuo*) was performed using commercial rotator evaporators. Chromatographic

---

[1] For general information on purification of chemicals and reagents, see: W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals,* 7th ed., Elsevier, Amsterdam, **ςπρσ**.

[2] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **ρωωφ**, *15*, 1518-1520.

[3] D. R. Burfield, R. H. Smithers, *J. Org. Chem.* **ρωχψ**, *43*, 3966-3968.

[4] T. D. Tilley, R. H. Grubbs, J. E. Bercaw, *Organometallics* **ρωψτ**, *3*, 274-278.

[5] G. D. Allred, L. S. Liebeskind, *J. Am. Chem. Soc.* **ρωωφ**, *118*, 2748-2749.

[6] For the original procedure, see: J. Srogl, G. D. Allred, L. S. Liebeskind, *J. Am. Chem. Soc.* **ρωωχ**, *119,* 12376-12377.

purification was performed as flash chromatography[7] on MERCK 60 Å (40-63 µm) silica gel at ca. 0.4 bar overpressure. Purified compounds were dried under high vacuum (10^{-3} mbar).

! ÎÁÌÙÔÉÃal - ÅÔÈÏÄÓ¢ Nuclear Magnetic Resonance (NMR): NMR data were recorded on a BRUKER *AV 400* (Progeny cryoprobe) or BRUKER *AVIII* 600 (cryoprobe) spectrometer in the solvents indicated. Chemical shifts (δ) are reported in ppm with the residual solvent signal as internal standard ($CDCl_3$ at 7.26 and 77.00 ppm for ^1H and ^{13}C NMR spectroscopy, respectively; CD_3OD at 3.31 and 49.00 ppm for ^1H and ^{13}C NMR spectroscopy, respectively), unless otherwise noted. ^1H NMR data are reported as δ (ppm) (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet or unresolved, br = broad signal, app. = appearing as; coupling constant(s) (*J*) in Hz; integration). ^{13}C NMR spectra were recorded with broadband ^1H decoupling while *J*-coupling(s) to other NMR-active heteronuclei (*i.e.* ^{19}F and ^{31}P) are reported as (d = doublet, t = triplet, q = quartet, qui = quintet; coupling constant(s) in Hz). If HSQC or DEPT data were available the carbon atoms are denoted with (CH_3 = methyl, CH_2 = methylene, CH = methine, CR_4 = fully substituted carbon atom). ^{31}P NMR and ^{119}Sn NMR spectra were referenced to H_3PO_4 (85% in D_2O) and $SnMe_4$, respectively, as external standards.

Only experimentally observed and resolved signals are tabulated or compiled; therefore it is possible that the number of signals in the ^{13}C NMR spectra does not match the expected number of magnetically inequivalent C-atoms in a given molecule.

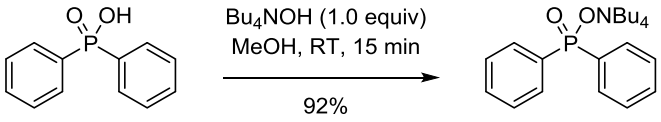
Fourier Transform Infrared Spectrometry (FTIR): FTIR spectra were recorded on a PERKIN ELMER *Spectrum One FT-IR (UATR)* instrument as thin films. Absorptions (ν) are given in wavenumbers (cm^{-1}).

High Resolution Mass Spectrometry (HRMS): HRMS analyses were performed as ESI measurements on a BRUKER *7T APEX III Fourier Transform Ion Cyclotron MS* or a FINNIGAN *MAT 95* instrument.

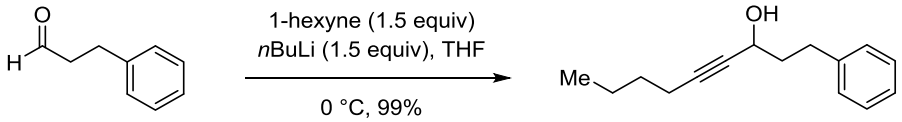
[7] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **ρωχψ**, *43*, 2923-2925.

3ÕÂÓÛÒÁÛÅs, 2ÅÁÇÅÎûÓ ÁÎd 2ÅÆÀÒÅÎÃe CÏ Í ÐÏÕÎÄÓ

Except for the compounds outlined below, all other substrates were prepared as previously described; their analytical and spectral data are contained in the Supporting Information of previous publications from this group.[8]



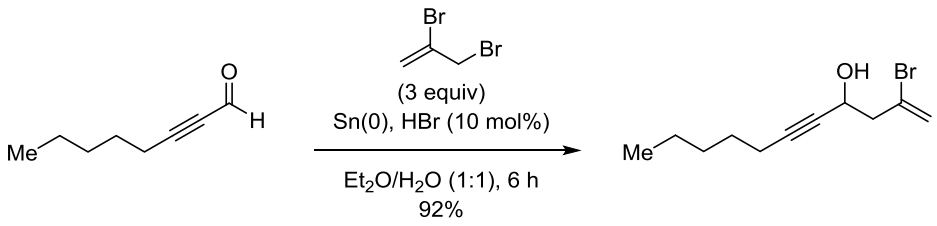
4ÅÛÒÁ*n*ÂÕÛÙÌÁ Í Ï ÎÉÕm ÄÉÐÈÅÎÙÌÐÈÏÓÐÈÉÎÁÛÅ. To a suspension of Ph_2PO_2H (5.50 g, 25.2 mmol) in dry MeOH (27.5 mL) at ambient temperature was added Bu_4NOH (1.0 M in MeOH, 25.2 mL, 25.2 mmol) and the resulting yellow solution was stirred at that temperature for another 15 min. The mixture was filtered through a short pad of Celite, eluting with dry MeOH (25 mL), and the combined filtrates were concentrated under reduced pressure (water bath at 60 °C). The resulting pale yellow oil was dried under high vacuum for 8 h to afford a solid yellow wax, which was re-dissolved in dry EtOAc and the solvent evaporated again to remove residual MeOH. Recrystallization of the residue from EtOAc/Et_2O (ca. 1:4, 50 mL; slow cooling from reflux to –20 °C) afforded $Ph_2PO_2NBu_4$ (10.6 g, 92%) as white crystalline needles. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.85 (m, 4H), 7.27-7.18 (m, 6H), 3.31 (app. t, J = 8.4 Hz, 8H), 1.57 (app. quintet, J = 7.9 Hz, 8H), 1.35 (sextet, J = 7.4 Hz, 8H), 0.92 (app. t, J = 7.3 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.7 (d, J = 8.6 Hz), 128.3 (br s), 127.2 (d, J = 11.3 Hz), 58.9 (s), 24.2 (s), 19.7 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$, ^{1}H-decoupled): δ 13.14.



---

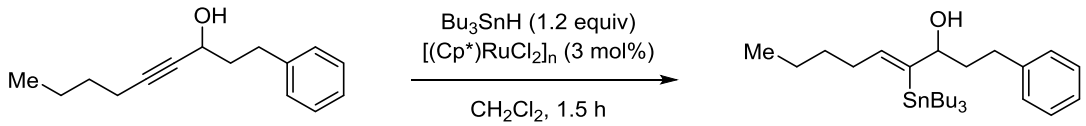
8 a) S. M. Rummelt, K. Radkowski, D.-A. Roşca, A. Fürstner, *J. Am. Chem. Soc.* **çπρυ**, *137*, 5506-5519; b) D.-A. Roşca, K. Radkowski, L. M. Wolf, M. Wagh, R. Goddard, W. Thiel, A. Furstner, *J. Am. Chem. Soc.* **çπρχ**, *139*, 2443-2455; c) H. Sommer, A. Fürstner, *Chem. Eur. J.* **çπρχ**, *23*, 558-562; d) H. Sommer, A. Fürstner, *Org. Lett.* **çπρφ**, *18*, 3210-3213; e) H. Sommer, J. Y. Hamilton, A. Fürstner, *Angew. Chem. Int. Ed.* **çπρχ**, in press (doi: 10.1021/anie.201701391).

ρζ0ÈÅÎÙÌÎ Ï Îζτζ ÙÎζσζ ÏÌ⁞ *n*BuLi, (1.6 M in hexanes, 21.5 mL, 34.4 mmol) was added to a solution of 1-hexyne (4.80 mL, 41.8 mmol) in THF (90 mL) at 0 °C and the resulting mixture was stirred at that temperature for 30 min. 3-Phenylpropanal (3.60 mL, 27.3 mmol) was added and the resulting mixture was allowed to reach ambient temperature over 2 hours. The reaction was quenched by the addition of NH_4Cl solution (50 mL, sat. aqueous) and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 100 mL). The combined extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 15:85) afforded the title compound (5.62 g, 99%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.27 (m, 2H), 7.24-7.17 (m, 3H), 4.37 (tt, J = 6.5, 2.0 Hz, 1H), 2.80 (t, J = 7.9 Hz, 2H), 2.24 (td, J = 7.0, 2.0 Hz, 2H), 2.07-1.93 (m, 2H), 1.84 (br s, 1H), 1.55-1.39 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.5 (CR_4), 128.5 (2 × CH_2), 128.4 (2 × CH_2), 125.9 (CH), 86.0 (CR_4), 80.9 (CR_4), 62.0 (CH), 39.7 (CH_2), 31.5 (CH_2), 30.7 (CH_2), 21.9 (CH_2), 18.3 (CH_2), 13.6 (CH_3); FTIR (thin film): ν 3334, 3063, 3027, 2955, 2931, 2862, 2229, 1604, 1496, 1455, 1379, 1328, 1133, 1053, 1030, 915, 746 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{15}H_{20}ONa$ [(M+Na)$^+$] 239.1406, found 239.1407.

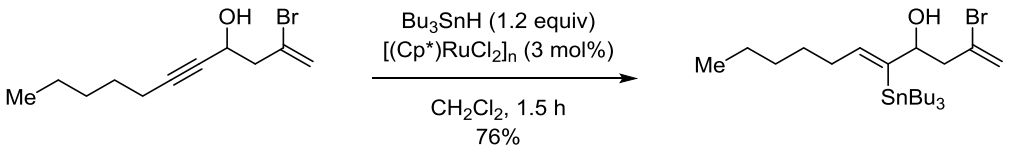


ςζ"ÒÏ Í ÏÕÎÄÅÃζρζÅÎζυζÙÎζτζ ÏÌ⁞ HBr (48% in H_2O, 0.05 mL, 0.4 mmol, 10 mol%) and 2-octynal (500 mg, 4.03 mmol) were successively added to a suspension of Sn powder (717 mg, 6.04 mmol) and 2,3-dibromopropene, 80 wt% (1.50 mL, 12.3 mmol) in Et_2O (8.0 mL) and H_2O (8.0 mL). The resulting mixture was stirred for 6 h before it was diluted with *tert*-butyl methyl ether (50 mL) and poured into H_2O (50 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (2 × 50 mL), the combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 10:90 to 20:80; step gradient) afforded the title compound (792 mg, 97%) as a colorless oil. ^{1}H NMR (400

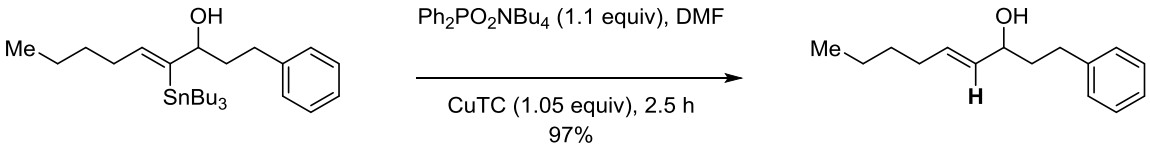
MHz, $CDCl_3$): δ 5.74 (dt, J = 2.0, 1.1 Hz, 1H), 5.55 (d, J = 1.7 Hz, 1H), 4.68 (ddt, J = 7.6, 5.5, 2.0 Hz, 1H), 2.81 (ddd, J = 14.5, 7.7, 0.9 Hz, 1H), 2.75 (ddd, J = 14.5, 5.6, 1.2 Hz, 1H), 2.20 (td, J = 7.1, 2.0 Hz, 2H), 1.83 (s, 1H), 1.54-1.46 (m, 2H), 1.39-1.26 (m, 4H), 0.90 (app. t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 128.7 (CR_4), 120.2 (CH_2), 86.7 (CR_4), 79.5 (CR_4), 60.6 (CH), 49.9 (CH_2), 31.0 (CH_2), 28.2 (CH_2), 22.2 (CH_2), 18.6 (CH_2), 14.0 (CH_3); FTIR (thin film): ν 3339, 2957, 2932, 2860, 2230, 1632, 1459, 1429, 1341, 1202, 1145, 1116, 1037, 890 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{11}H_{17}O(^{79}Br)Na$ [(M+Na)$^+$] 267.0355, found 267.0353.



j Z Q ζ ρ ζ 0 È Å Î Ù Ì ζ τ ζ j ô Ò É Â Õ ô Ù Ì Ó ô Á Î Î Ù Ì Q Î Ï Î ζ τ ζ Å Î ζ σ ζ Ï Ì 8 Bu_3SnH (3.75 mL, 13.9 mmol) was added dropwise over 1 h via syringe pump to a brown solution of 1-phenylnon-4-yn-3-ol (2.60 g, 12.0 mmol) and $[(Cp^*)RuCl_2]_n$ (110 mg, 0.358 mmol, 3 mol%) in CH_2Cl_2 (60 mL) at ambient temperature. The mixture was stirred for additional 0.5 h before it was concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 5:95 to 10:90; step gradient) afforded the title compound (5.62 g, 92%) as a faintly yellowish oil with a proximal/distal ratio of >99:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 2H), 7.22-7.17 (m, 3H), 6.18 (td, J = 7.2, 1.1 Hz, 1H), 4.15 (t, J = 6.8 Hz, 1H), 2.65 (qdd, J = 13.8, 9.8, 6.2 Hz, 2H), 2.05 (app. q, J = 7.2 Hz, 2H), 189-1.66 (m, 2H), 1.60-1.41 (m, 7H), 1.41-1.25 (m, 10H), 1.04-0.82 (m, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5 (CR_4), 142.2 (CR_4), 141.2 (CH), 128.5 (2 × CH), 128.3 (2 × CH), 125.7 (CH), 79.4 (CH), 39.3 (CH_2), 34.0 (CH_2), 32.3 (2 × CH_2), 29.3 (3 × CH_2), 27.4 (3 × CH_2), 22.6 (CH_2), 14.1 (CH_3), 13.7 (3 × CH_3), 11.1 (3 × CH_2); ^{119}Sn NMR (149 MHz, $CDCl_3$, ^{1}H decoupling): δ –55.1; FTIR (thin film): ν 3463, 3063, 3027, 2955, 2922, 2871, 2853, 1614, 1496, 1455, 1419, 1376, 1340, 1289, 1180, 1152, 1071, 1048, 1030, 1001, 961, 925, 863, 767 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{27}H_{48}OSnNa$ [(M+Na)$^+$] 531.2619, found 531.2618.



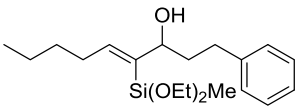
jZQzçz"ÒÏ Í ÏzuzjôÒÉÂÕôÙÌÓôÁÎ ÎÙÌQÕÎÄÅÃÁzρhuzÄÉÅÎzτzÏÌ8 Bu_3SnH (1.20 mL, 4.46 mmol) was added over 1 h via syringe pump to a dark brown solution of 2-bromoundec-1-en-5-yn-4-ol (973 mg, 3.97 mmol) and $[(Cp^*)RuCl_2]_n$ (36.0 mg, 0.117 mmol, 3 mol%) in CH_2Cl_2 (20 mL) at ambient temperature. The resulting mixture was stirred for additional 0.5 h before it was concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 2:98 to 5:95 to 10:90; step gradient) afforded the title compound (1.62 g, 76%) as colorless oil with a proximal/distal ratio of 92:8. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.27 (td, J = 7.2, 1.1 Hz, 1H), 5.65 (d, J = 1.3 Hz, 1H), 5.51 (d, J = 1.6 Hz, 1H), 4.50-4.46 (m, 1H), 2.57- 2.47 (m, 2H), 2.05-1.98 (m, 2H), 1.69 (d, J = 2.8 Hz, 1H), 1.55-1.42 (m, 6H), 1.39-1.24 (m, 12H), 1.01-0.95 (m, 6H), 0.89 (t, J = 7.3 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.5 (CR_4), 141.7 (CH), 130.8 (CR_4), 119.3 (CH_2), 76.4 (CH), 49.9 (CH_2), 34.3 (CH_2), 31.7 (CH_2), 29.7 (CH_2), 29.2 (3 × CH_2), 27.4 (3 × CH_2), 22.6 (CH_2) , 14.0 (CH_3), 13.7 (3 × CH_3), 11.1 (3 × CH_2; ^{119}Sn NMR (149 MHz, $CDCl_3$, ^{1}H decoupling): δ −54.0; FTIR (thin film): ν 3463, 2955, 2922, 2871, 2854, 1630, 1493, 1463, 1420, 1376, 1290, 1197, 1147, 1116, 1071, 1020, 961, 883, 745, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{23}H_{45}OBrSnNa$ [$(M+Na)^+$] 559.1567, found 559.1563.



jEQzρz0ÈÅÎÙÌÎ Ï ÎzτzÅÎzσzÏÌ jψQ8 CuTC (20.0 mg, 105 µmol) was added to a solution of (*Z*)-1-phenyl-4-(tributylstannyl)non-4-en-3-ol (**φ**) (50.0 mg, 98.5 µmol) and $Ph_2PO_2NBu_4$ (50.0 mg, 109 µmol) in DMF (0.50 mL) at ambient temperature and the resulting mixture was stirred for 2.5 h. The mixture was diluted with *tert*-butyl methyl ether (30 mL) and poured into a mixture of 25% aqueous NH_4OH/sat. aqueous NH_4Cl solution (1:9, 10 mL). The phases were separated and the aqueous layer extracted with *tert*-butyl methyl ether (2 × 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash

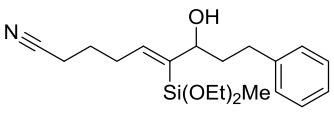
chromatography (EtOAc/hexane 20:80) afforded the title compound (20.8 mg, 97%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.25 (m, 2H), 7.22-7.17 (m, 3H), 5.66 (dtd, J = 15.4, 6.7, 0.9 Hz, 1H), 5.50 (ddt, J = 15.4, 7.0, 1.4 Hz, 1H), 4.08 (q, J = 6.7 Hz, 1H), 2.76-2.63 (m, 2H), 2.05 (q, J = 6.6 Hz, 2H), 1.93-1.76 (m, 2H), 1.46 (br s, 1H), 1.41- 1.26 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.0 (CR_4), 132.7 (CH), 132.6 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 125.8 (CH), 72.5 (CH), 38.8 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 31.3 (CH_2), 22.2 (CH_2), 13.9 (CH_3); FTIR (thin film): ν 3358, 3063, 3027, 2956, 2926, 2858, 1603, 1496, 1455, 1379, 1294, 1098, 1053, 1030, 970, 917, 746 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{15}H_{22}ONa$ [(M+Na)$^+$] 241.1563, found 241.1564.

2ÅÐÒÅÓÅÎÔÁÔÉÖÅ 0ÒÏÃÅÄÕre £Ïr ÔÈÅ ÔÒÁÎÓ(ÙÄÒÏÓÍÙÌÁÔÉÏn ÕÓÉÎg AÌËÏØÙÓÍÁÎÅÓ. (*Z***ζζτζ**



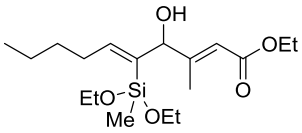
j$ÉÅÔÈÏØÙ Í ÅÔÈÙÌÓÉÌÙÌζρζÐÈÅÎÙÌÎÏÎζτζÅÎζσζÏÌ. Diethoxymethylsilane (650 mg, 4.8417 mmol) was added under argon to a stirred solution of 1-phenyldec-4-yn-3-ol (950 mg, 4.3916 mmol) and [Cp*RuCl]$_4$ (60 mg, 0.05520 mmol) in CH_2Cl_2 (22 mL). Once the reaction was complete (ca. 15 min, TLC), $CNCH_2COOK$ (120 mg, 0.97 mmol) was added as catalyst scavenger, and stirring was continued for 2 hours. Insoluble matrials were filtered off and rinsed with CH_2Cl_2, the combined filtrates were evaporated under reduced pressure, and the residue was purified by filtration through a short pad of silica using hexanes/ethyl acetate 15:1 as the eluent to give the title compound as a pale yellow oil (942 mg, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.21-7.15 (m, 3H), 6.12 (t, J = 7.6 Hz, 1H), 3.95 (m, 1H), 3.80 (m, 4H), 3.49 (d, J = 10.3 Hz, OH), 2.77-2.56 (m, 2H), 2.27-2.16 (m, 2H), 2.06-1.95 (m, 1H), 1.87-1.76 (m, 1H), 1.43-1.29 (m, 4H), 1.24 (td, J = 5.0, 0.9 Hz, 6H), 0.91 (m, 3H), 0.28 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 146.8, 142.5, 138.2, 128.4, 125.6, 79.6, 58.3, 40.5, 32.8, 31.8, 31.3, 22.5, 18.18, 18.13, 14.0, -2.1; FTIR (thin film): ν̃ 3496, 3026, 2958, 2926, 2874, 1613, 1496, 1481, 1454, 1410, 1390, 1364, 1294, 1257, 1214, 1165, 1101, 1071, 1031, 1006, 945, 876, 817, 792, 760, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{20}H_{34}O_3SiNa$ (M+Na$^+$) 373.2169, found 373.2173.

j*Z*ζζφζj$ÉÅÔÈÏØÙj Í ÅÔÈÙÌζÓÉÌÙÌζχζÈÙÄÒÏØÙζωζÐÈÅÎÙÌÎÏÎζυζÅÎÅÎÉÔÒÉÀ. Prepared analogously as a colorless oil (115 mg, 36 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.21-7.15 (m, 3H), 6.05 (t, J = 7.5 Hz,



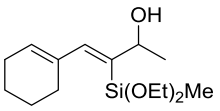
1H), 3.98 (m, 1H), 3.80 (m, 4H), 3.31 (d, *J* = 9.8 Hz, OH), 2.79-2.57 (m, 2H), 2.44-2.31 (m, 4H), 2.05-1.93 (m, 1H), 1.87-1.70 (m, 3H), 1.25 (td, *J* = 5.0, 0.9 Hz, 6H), 0.29 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 142.7, 142.1, 141.3, 128.4, 125.7, 119.3, 78.9, 58.3, 40.1, 32.6, 30.2, 25.4, 18.13, 18.11, 16.7, -2.2; FTIR (thin film): ν̃ 3493, 3026, 2972, 2926, 2246, 1615, 1496, 1454, 1424, 1390, 1365, 1293, 1259, 1164, 1101, 1069, 947, 792, 758, 699 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{20}H_{31}NO_3SiNa$ [(M+Na)$^+$] 384.1965, found 384.1966.

%ÔÈÙl jçEℏυZQζυζj$ÉÅÔÈÏØÙj Í ÅÔÈÙÌQÓÉÌÙÌQζτζÈÙÄÒÏØÙζσζ Í ÅÔÈÙÌÄÅÃÁζçℏυζÄÉÅÎÏÁÔÅ.

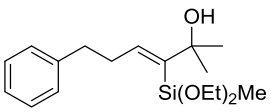


Prepared analogously as a pale yellow oil (207 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (t, *J* = 7.6 Hz, 1H), 6.05 (t, *J* = 1.4 Hz, 1H), 4.42 (d, *J* = 10.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.10 (d, *J* = 9.8 Hz, OH), 3.82-3.70 (m, 4H), 2.26 (m, 2H), 2.03 (s, 3H), 1.44-1.30 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.23 (td, *J* = 7.0, 0.9 Hz, 6H), 0.91 (m, 3H), 0.20 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 167.1, 159.8, 150.1, 134.9, 114.6, 83.1, 59.5, 58.5, 31.7, 31.3, 22.5, 18.0, 16.3, 14.3, 14.0, -2.4; FTIR (thin film): ν̃ 3466, 2973, 2926, 2875, 1716, 1651, 1612, 1443, 1390, 1366, 1342, 1258, 1207, 1142, 1100, 1071, 1044, 948, 876, 821, 801, 762, 681 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{18}H_{34}O_5SiNa$ [(M+Na)$^+$] 381.2068, found 381.2068.

jZQζτζj#ÙÃÌÏÈÅØζρζÅÎζρζÙÌQζσζjÄÉÅÔÈÏØÙj Í ÅÔÈÙÌQÓÉÌÙÌQÂÕÔζσζÅÎζçζÏÌ. Prepared analogously as a pale yellow oil (164 mg, 47 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (s, 1H), 5.75 (m, 1H), 4.24 (m, 1H), 3.85-3.74 (m, 5H), 2.06 (m, 2H), 2.00 (m, 2H), 1.68-1.50 (m, 4H), 1.36 (d, *J* = 6.6 Hz, 3H), 1.24 (m, 6H), 0.24 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 147.0, 139.5, 136.6, 126.6, 75.5, 58.3, 58.2, 28.1, 25.4, 24.7, 22.5, 21.9, 18.1, -2.5; FTIR (thin film): ν̃ 3448, 2971, 2925, 2833, 1597, 1438, 1390, 1364, 1294, 1255, 1164, 1102, 1070, 942, 895, 859, 838, 797, 756, 730, 684 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{15}H_{28}O_3SiNa$ [(M+Na)$^+$] 307.1700, found 307.1702.

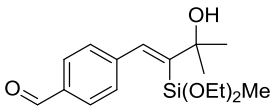


jZQζσζj$ÉÅÔÈÏØÙj Í ÅÔÈÙÌQÓÉÌÙÌQζçζ Í ÅÔÈÙÌζφζÐÈÅÎÙÌÈÅØζσζÅÎζçζÏÌ8 Prepared analogously as a colorless oil (180 mg, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.21-7.15 (m, 3H), 6.21 (t, *J* = 7.5 Hz, 1H), 4.32 (s, OH), 3.77 (m, 4H), 2.69 (m, 2H), 2.54 (m, 2H), 1.35 (s, 6H), 1.23 (t, *J* = 6.8 Hz, 6H), 0.22 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 143.9, 141.5, 140.7, 128.5,



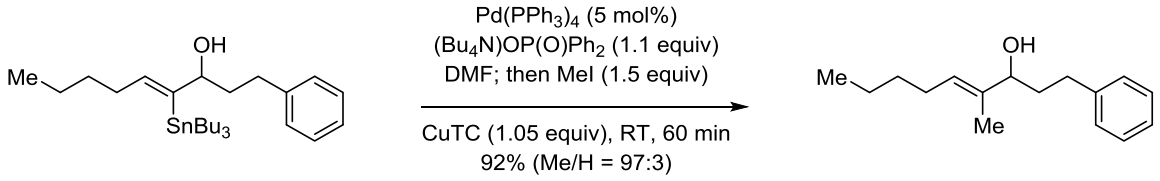
128.3, 125.9, 74.0, 58.2, 36.1, 33.2, 30.1, 18.1, -1.9; FTIR (thin film): ṽ 3497, 3086, 3063, 3027, 2972, 2926, 2883, 1605, 1496, 1482, 1454, 1390, 1369, 1294, 1258, 1209, 1163, 1100, 1069, 998, 944, 881, 790, 752, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{18}H_{30}O_3SiNa$ [(M+Na)$^+$] 345.1856, found 345.1857.

jZQZτZjçZj$ÉÅÔÈÏØÙj Í ÅÔÈÙÌQÓÉÌÙÌQZσZÈÙÄÒÏØÙZσZ Í ÅÔÈÙÌÂÕÔZρZÅÎZρZÙÌQÂÅÎÚÁÌÄÅÈÙÄÅ8



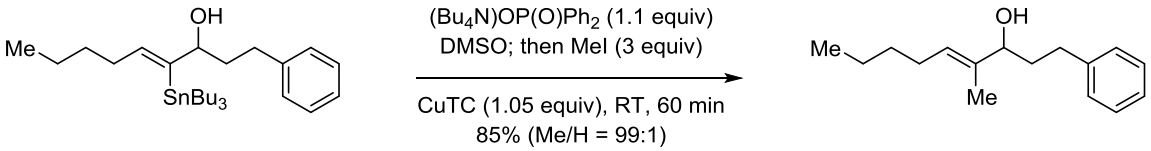
Prepared analogously as a yellow oil that has to be used without delay (118 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.83 (m, 2H), 7.47 (m, 2H), 7.31 (s, 1H), 4.44 (s, OH), 3.72 (m, 4H), 1.49 (s, 6H), 1.16 (t, *J* = 7.0 Hz, 6H), -0.05 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 191.8, 150.8, 145.6, 139.9, 135.2, 129.31, 129.16, 74.9, 58.4, 30.5, 18.0, -2.0; FTIR (thin film): ṽ 3483, 2973, 2927, 2884, 2838, 2733, 1697, 1602, 1565, 1482, 1443, 1389, 1363, 1305, 1260, 1208, 1166, 1102, 1067, 949, 889, 866, 813, 794, 777, 758, 688 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{17}H_{26}O_4SiNa$ [(M+Na)$^+$] 345.1493, found 345.1495.

#ÏÐÐÅÒj)QZ - ÅÄÉÁÔÅd - ÅÔÈÙÌÁÔÉÏÎ and !ÌÌÙÌÁÔÉÏn ÏÆ AlkeÎÙÌÓÔÁÎÎÁÎÅÓ



2ÅÐÒÅÅÎÔÁÔÉÖÅ 0ÒÏÃÅÄÕre ÆÏÒ ÔÈÅ #Z - ÅÔÈÙÌÁÔÉÏn ÏÆ !ÌËÅÎÙÌÓÔÁÎÎÁÎÅÓ8 - ÅÔÈÏÄ !j#ÏÐÐÅÒT0ÁÌÌÁÄÉÕm #ÏZ#ÁÔÁÌÙÓÉÓQ: jEQZτZ - ÅÔÈÙÌZρZÐÈÅÎÙÌ Ï ÎZτZÅÎZσZÏl jχQ8 To a clear, colorless solution of (*Z*)-1-phenyl-4-(tributylstannyl)non-4-en-3-ol (**φ**) (254 mg, 501 µmol) and $(Ph_2PO_2)NBu_4$ (250 mg, 544 µmol) in DMF (2.5 mL) at ambient temperature was added $Pd(PPh_3)_4$ (30.0 mg, 26 µmol, 5 mol%) and the resulting yellow mixture was stirred until complete dissolution had occurred, usually ca. 5 min. After that time, MeI (48 µL, 770 µmol) was added, immediately followed, *within max. 30 seconds*, by CuTC (100 mg, 524 µmol). The resulting black suspension was stirred for 0.5 h before the reaction was quenched by the addition

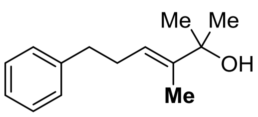
of Et_3N (ca. 0.1 mL). The mixture was diluted with *tert*-butyl methyl ether (30 mL), poured on a mixture of 25% aqueous NH_4OH/sat. aqueous NH_4Cl solution (1:9, 20 mL), the phases were separated and the bright blue aqueous phase extracted with *tert*-butyl methyl ether (2 × 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 10:90 to 20:80; step gradient) afforded the methylated product **χ** (107 mg, 92%) as a faintly yellowish oil with a methylation/protodestannation ratio of **χ**:**ψ** = 97:3, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.25 (m, 2H), 7.23-7.16 (m, 3H), 5.41 (t, J = 7.1 Hz, 1H), 4.02 (t, J = 6.7 Hz, 1H), 2.71-2.55 (m, 2H), 2.04 (q, J = 7.0 Hz, 2H), 1.95-1.79 (m, 2H), 1.63 (s, 3H), 1.46 (br s, 1H), 1.40-1.26 (m, 4H), 0.91 (app. t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.1 (CR_4), 136.7 (CR_4), 128.4 (2 × CH), 128.3 (2 × CH), 127.3 (CH), 125.7 (CH), 77.4 (CH), 36.5 (CH_2), 32.2 (CH_2), 31.7 (CH_2), 27.2 (CH_2), 22.4 (CH_2), 14.0 (CH_3), 11.2 (CH_3); FTIR (thin film): ν 3348, 3027, 2955, 2927, 2858, 1496, 1455, 1378, 1298, 1052, 1030, 998, 918, 851, 747, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{16}H_{24}ONa$ [(M+Na)$^+$] 255.1719, found 255.1719.



2ÅÐÒÅÓÅÂÎÔÁÔÉÖÅ 0ÒÏÃÅÄÕre ÆÏr ÔÈÅ -ÅÔÈÙÌÁÔÉÏn Ïf !ÌËÅÎÙÌÓÔÁÎÎÁÅ. -ÅÔÈÏÄ B j#ÕTC /ÎÌÙǫ ĵ*E*ǪǷτǷ -ÅÔÈÙÌǷρǷÐÈÅÎÙÌÎ Ï ÎǷτǷÅÎǷσǷÏl ĵχǪ. To a clear, colorless solution of (*Z*)-1-phenyl-4-(tributylstannyl)non-4-en-3-ol (**φ**) (254 mg, 501 µmol) and $(Ph_2PO_2)NBu_4$ (250 mg, 544 µmol) in DMSO (2.5 mL) at ambient temperature was added MeI (95 µL, 1500 µmol), immediately followed, *within maximum 30 seconds*, by CuTC (100 mg, 524 µmol). The resulting black suspension was stirred for 1 hour before the reaction was quenched by the addition of Et_3N (ca. 0.1 mL).

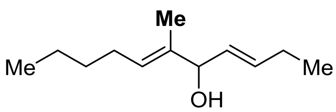
The mixture was diluted with *tert*-butyl methyl ether (30 mL) and poured on a mixture of 25% aqueous NH_4OH/sat. aqueous NH_4Cl solution (1:9, 20 mL). The phases were separated and the clear, bright blue aqueous phase was extracted with *tert*-butyl methyl ether (2 × 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 10:90 to 20:80; step gradient) afforded the desired methylated product **χ** (99.4 mg, 85%) as a colorless oil with a methylation/protodestannation ratio **χ**:ψ = 99:1, as determined by ^{1}H NMR and GCMS. Analytical and spectral data as described above.

j*E*qζςȟσζ$É Í ÅôÈÙÌζφζÐÈÅÎÙÌÈÅØζσζÅÎζςζÏÌ8 Prepared according to method " as a colorless oil (78.2 mg, 76%) with a methylation/protodestannation ratio of 94:6, as determined by ^{1}H NMR and GCMS.



The same product was prepared according to method ! as a colorless oil (89.8 mg, 88%) with a methylation/protodestannation ratio of 79:21, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.27 (m, 2H), 7.24-7.18 (m, 3H), 5.58 (td, J = 7.1, 1.3 Hz, 1H), 2.71 (dd, J = 8.8, 6.8 Hz, 2H), 2.36 (app. q, J = 7.4 Hz, 2H), 1.63 (br s, 4H), 1.33 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.1 (CR_4), 141.9 (CR_4), 128.4 (2 × CH), 128.1 (2 × CH), 125.6 (CH), 121.1 (CH), 73.3 (CR_4), 35.8 (CH_2), 29.8 (CH_2), 28.8 (2 × CH_3), 12.6 (CH_3); FTIR (thin film): ν 3384, 3026, 2974, 2927, 2858, 1603, 1496, 1453, 1370, 1258, 1136, 1075, 1030, 1001, 935, 850, 746, 697 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{14}H_{20}ONa$ [$(M+Na)^+$] 227.1406, found 227.1404.

jσ*E*ȟφ*E*qζφζ - ÅôÈÙÌÕÎÄÅÃÁζσȟφζÄÉÅÎζυζÏÌ8 Prepared according to method " as a colorless oil (65.8 mg, 72%) with a methylation/protodestannation ratio of 95:5, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.72 (dtd, J = 15.4, 6.3, 1.2 Hz, 1H), 5.46 (ddt, J = 15.4, 6.8, 1.5 Hz, 2H), 4.45 (d, J = 6.5 Hz, 1H), 2.13-1.98 (m, 4H), 1.59 (s, 3H), 1.56 (br s, 1H), 1.39-1.24 (m, 4H), 0.99 (t, J = 7.5 Hz, 3H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.3 (CR_4), 133.9 (CH), 130.0 (CH), 126.3 (CH), 78.2 (CH), 31.7 (CH_2), 27.3 (CH_2), 25.3 (CH_2), 22.4 (CH_2), 14.0 (CH_3), 13.4 (CH_3), 12.1 (CH_3); FTIR (thin film): ν 3352,



2959, 2926, 2872, 2857, 1459, 1378, 1297, 1084, 1004, 965, 850 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{12}H_{22}ONa$ [$(M+Na)^+$] 205.1563, found 205.1563.

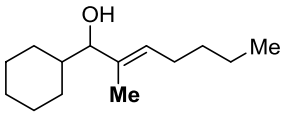
j*E*) ζ 1 ζ j#ÙÄÌÏÈÅØζρζÅÎζρζÙÌζ ζ ς,4 ζ ÄÉ Í ÅÔÈÙÌÐÅÎô ζ 1 ζ Ån ζσζÏÌ⁸ Prepared according to method " as a colorless oil (76.8 mg, 79%) with a methylation/proto-destannation ratio of 90:10, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73 (br s, 1H), 5.59 (app. dt, J = 3.9, 2.0 Hz, 1H), 3.58 (d, J = 8.1 Hz, 1H), 2.09 (dq, J = 6.6, 2.7 Hz, 4H), 1.82-1.72 (m, 1H), 1.74 (d, J = 1.2 Hz, 3H), 1.67-1.53 (m, 5H), 0.98 (d, J = 6.6 Hz, 3H), 0.80 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.1 (CR_4), 134.8 (CR_4), 129.9 (CH), 127.1 (CH), 84.7 (CH), 31.3 (CH), 29.3 (CH_2), 25.6 (CH_2), 22.9 (CH_2), 22.2 (CH_2), 19.5 (CH_3), 18.6 (CH_3), 13.2 (CH_3); FTIR (thin film): ν 3387, 2925, 2869, 2833, 1447, 1379, 1365, 1295, 1242, 1169, 1132, 1009, 923, 885, 801 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{13}H_{22}ONa$ [$(M+Na)^+$] 217.1563, found 217.1563.

j*E*ζτζjσζ (ÙÄÒÏØÙζς♄σζÄÉ Í ÅÔÈÙÌÂÕÔζρζÅÎζρζÙÌζ ÂÅÎÚÏ ÎÉÔÒÉÌÅ⁸ Prepared according to method " as a colorless oil (87.2 mg, 86%) with a methylation/protodestannation ratio of 99:1, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 6.69 (d, J = 1.6 Hz, 1H), 1.87 (d, J = 1.3 Hz, 3H), 1.70 (s, 1H), 1.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0 (CR_4), 143.4 (CR_4), 131.8 (2 × CH), 129.6 (2 × CH), 121.1 (CH), 119.1 (CR_4), 109.5 (CR_4), 73.9 (CR_4), 28.9 (2 × CH_3), 14.7 (CH_3); FTIR (thin film): ν 3430, 2975, 2931, 2871, 2226, 1642, 1603, 1502, 1462, 1446, 1408, 1363, 1240, 1211, 1170, 1115, 959, 941, 879, 821 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{13}H_{15}NONa$ [$(M+Na)^+$] 224.1046, found 224.1044.

j*E*ζχζ (ÙÄÒÏØÙζφζ Í ÅÔÈÙÌζωζÐÈÅÎÙÌÎ Îζυζ ÅÎÅÎÉÔÒÉÌÅ⁸ Prepared according to method " as a colorless oil (98.8 mg, 81%) with a methylation/protode-stannation ratio of 99:1, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.16 (m, 2H), 7.14-7.09 (m, 3H), 5.29 (app. tp, J = 7.3, 1.2 Hz,1H), 3.96 (t, J = 6.6 Hz, 1H), 2.62 (ddd, J = 13.8, 9.4, 6.4 Hz, 1H), 2.52 (ddd, J = 13.8, 9.1, 6.9 Hz, 1H), 2.27 (t, J = 7.1 Hz, 2H), 2.15 (app. q, J = 7.3 Hz, 2H), 1.79 (dddd, J = 9.2, 6.8, 6.1, 4.9 Hz, 2H), 1.67 (p, J = 7.2 Hz, 2H), 1.58 (app. t, J = 1.1 Hz, 3H), 1.48 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.8 (CR_4), 139.6 (CR_4), 128.4

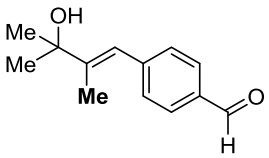
(4 × CH), 125.8 (CH), 123.7 (CH), 119.7 (CR_4), 76.9 (CH), 36.6 (CH_2), 32.1 (CH_2), 26.4 (CH_2), 25.1 (CH_2), 16.6 (CH_2), 11.7 (CH_3); FTIR (thin film): ν 3428, 3026, 2929, 2860, 2247, 1603, 1495, 1454, 1304, 1156, 1055, 1030, 1008, 918, 870, 749, 700 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{16}H_{21}NONa$ [(M+Na)$^+$] 266.1515, found 266.1514.

jE)ρ#ÙÃÌÏÈÅØÙÌçÍÅÔÈÙÌÈÅÐÔçÅÎρÏÌ Prepared according to method " as a



colorless oil (86.4 mg, 82%) with a methylation/protodestannation ratio of >99:1, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (ddq, J = 8.3, 5.8, 1.2 Hz, 1H), 3.61 (d, J = 8.3 Hz, 1H), 2.05-1.96 (m, 3H), 1.80-1.60 (m, 3H), 1.57 (app. q, J = 1.0 Hz, 3H), 1.48-1.07 (m, 10H), 0.99-0.78 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.9 (CR_4), 128.3 (CH), 83.3 (CH), 40.6 (CH), 31.7 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 27.2 (CH_2), 26.5 (CH_2), 26.2 (CH_2), 26.0 (CH_2), 22.4 (CH_2), 14.0 (CH_3), 11.1 (CH_3); FTIR (thin film): ν 3360, 2955, 2920, 2851, 1449, 1378, 1306, 1290, 1260, 1206, 1081, 1054, 1008, 891, 851 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{14}H_{26}ONa$ [(M+Na)$^+$] 233.1876, found 233.1873.

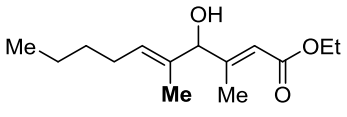
jE) 4 jσ(ÙÄÒÏxy 2,3 ÄÉÍÅÔÈÙÌÂÕÔρÅÎρÙÌQÂÅÎÚÁÌÄÅÈÙÄÅ Prepared according



to method " as a colorless oil (87.1 mg, 85%) with a methylation/protodestannation ratio of 98:2, as determined by ^{1}H NMR and GCMS.

The same compound was prepared according to method ! as a colorless oil (82.9 mg, 81%) with a methylation/protodestannation ratio of 98:2, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.80 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 6.71 (s, 1H), 1.97 (s, 1H), 1.89 (d, J = 1.4 Hz, 3H), 1.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.9 (CH), 147.7 (CR_4), 145.1 (CR_4), 134.1 (CR_4), 129.5 (4 × CH), 121.5 (CH), 73.8 (CR_4), 28.9 (2 × CH_3), 14.8 (CH_3); FTIR (thin film): ν 3434, 2974, 2930, 2831, 2735, 1687, 1646, 1599, 1563, 1462, 1445, 1416, 1362, 1306, 1212. 1166, 1112, 978, 959, 941, 879, 825, 788, 745 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{13}H_{16}O_2Na$ [(M+Na)$^+$] 227.1042, found 227.1041.

%ÔÈÙl jçEℏυEQζτζÈÙÄÒÏØÙζσℏυζÄÉÍÅÔÈÙÌÄÅÃÁζçℏυζÄÉÅÎÏÁÔÅ Prepared according to

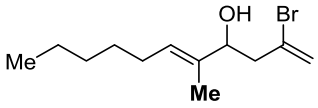


method " as a colorless oil (99.5 mg, 83%) with a methylation/protodestannation ratio of 97:3, as determined by

^{1}H NMR and GCMS.

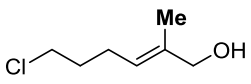
The same compound was prepared according to method **!** as a colorless oil (106 mg, 88%) with a methylation/protodestannation ratio of 95:5, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08 (p, J = 1.4 Hz, 1H), 5.53 (t, J = 7.2 Hz, 1H), 4.44 (s, 1H), 4.15 (qd, J = 7.1, 1.3 Hz, 2H), 2.04 (q, J = 7.3 Hz, 2H), 1.99 (d, J = 1.4 Hz, 3H), 1.87 (d, J = 2.6 Hz, 1H), 1.49 (d, J = 1.2 Hz, 3H), 1.41-1.22 (m, 7H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.9 (CR_4), 157.7 (CR_4), 133.7 (CR_4), 130.3 (CH), 115.0 (CH), 81.6 (CH), 59.7 (CH_2), 31.5 (CH_2), 27.4 (CH_2), 22.3 (CH_2), 15.5 (CH_3), 14.3 (CH_3), 13.9 (CH_3), 11.1 (CH_3); FTIR (thin film): ν 3475, 2957, 2928, 2859, 1716, 1698, 1446, 1367, 1342, 1280, 1211, 1144, 1042, 995, 892 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{14}H_{24}O_3Na$ [(M+Na)$^+$] 263.1618, found 263.1615.

jEQZ ç Z "0Ï Í ÏZ u Z Í ÅÔÈÙÌÕÎÄÅÃÁZ ρ ŭ u Z Ä É Å Î Z τ Z Ï Ì Prepared according to method " as a



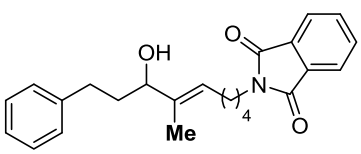
colorless oil (94.5 mg, 72%) with a methylation/protodestannation ratio of 97:3, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.68 (q, J = 1.2 Hz, 1H), 5.53-5.47 (m, 2H), 4.35 (dd, J = 8.1, 5.0 Hz, 1H), 2.68-2.56 (m, 2H), 2.01 (q, J = 7.2 Hz, 2H), 1.68 (br s, 1H), 1.63 (s, 3H), 1.40-1.22 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.2 (CR_4), 130.7 (CR_4), 127.8 (CH), 119.3 (CH_2), 74.9 (CH), 47.4 (CH_2), 31.5 (CH_2), 29.1 (CH_2), 27.5 (CH_2), 22.6 (CH_2), 14.1 (CH_3), 11.6 (CH_3); FTIR (thin film): ν 3379, 2956, 2924, 2856, 1632, 1458, 1378, 1300, 1200, 1115, 1017, 885, 570 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{12}H_{21}OBrNa$ [(M+Na)$^+$] 283.0668, found 283.0665.

jEQZ φ Z #ÈÌÏÒÏZ ç Z Í ÅÔÈÙÌÈÅØZ ç Z Å Î Z ρ Z Ï Ì Prepared according to method " as a colorless oil



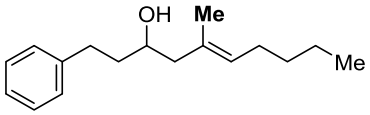
(49.8 mg, 67%) with a methylation/protodestannation ratio of 98:2, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37 (tdd, J = 7.3, 2.6, 1.3 Hz, 1H), 3.99 (s, 2H), 3.52 (t, J = 6.6 Hz, 2H), 2.19 (q, J = 7.1 Hz, 2H), 1.83 (p, J = 6.7 Hz, 2H), 1.68 (br s, 1H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.3 (CR_4), 123.9 (CH), 68.7 (CH_2), 44.5 (CH_2), 32.2 (CH_2), 24.7 (CH_2), 13.7 (CH_3); FTIR (thin film): ν 3322, 2935, 2917, 2862, 1443, 1385, 1346, 1308, 1287, 1230, 1065, 1038, 1007, 861, 844, 746, 723 cm^{-1}; HRMS (ESI): exact mass calculated for $C_7H_{13}O(^{35}Cl)Na$ [(M+Na)$^+$] 171.0547, found 171.0547.

jEQZ çZjχZ (ÙÄÒÏØÙZφZ Í ÅÔÈÙÌZωZÐÈÅÎÙÌÎÏÎZυZÅÎZρZÙÌQÉÓÏÉÎÄÏÌÉÎÅZρℓσZÄÉÏÎÅ Prepared



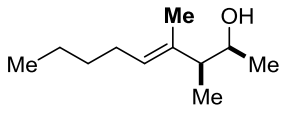
according to method " as a colorless oil (144 mg, 76%) with a methylation/protodestannation ratio of 96:4, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, J = 5.4, 3.1 Hz, 2H), 7.70 (dd, J = 5.5, 3.1 Hz, 2H), 7.29-7.24 (m, 2H), 7.20-7.14 (m, 3H), 5.37 (t, J = 7.1 Hz, 1H), 4.01 (t, J = 6.7 Hz, 1H), 3.68 (t, J = 7.3 Hz, 2H), 2.67 (ddd, J = 13.8, 9.8, 6.2 Hz, 1H), 2.57 (ddd, J = 13.9, 9.5, 6.5 Hz, 1H), 2.09 (br q, J = 7.4 Hz, 2H), 1.94-1.75 (m, 2H), 1.74-1.63 (m, 3H), 1.62 (s, 3H), 1.43 (p, J = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4 (2 × CR_4), 142.1 (CR_4), 137.6 (CR_4), 133.8 (2 × CR_4), 132.1 (2 × CH), 128.4 (2 × CH), 128.3 (2 × CH), 126.2 (CH), 125.7 (CH), 123.1 (2 × CH), 77.3 (CH), 37.8 (CH_2), 36.4 (CH_2), 32.1 (CH_2), 28.0 (CH_2), 26.9 (CH_2), 26.5 (CH_2), 11.3 (CH_3); FTIR (thin film): ν 3467, 3061, 3026, 2937, 2859, 1770, 1705, 1604, 1495, 1467, 1453, 1437, 1396, 1369, 1337,.1188, 1037, 920, 892, 867, 749, 719, 700 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{24}H_{27}NO_3Na$ [(M+Na)$^+$] 400.1883, found 400.1880.

jEQZ υZ - ÅÔÈÙÌZρZÐÈÅÎÙÌÄÅÃZυZÅÎZσZÏÌ Prepared from (Z)-1-phenyl-5-

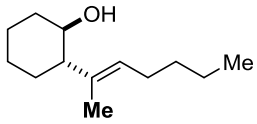


(tributylstannyl)dec-5-en-3-ol (86:15 mixture of proximal/distal vinyl stannane, 261 mg, 501 μmol) according to method ! as a faintly yellowish oil (85:15 mixture of proximal/distal product, 103 mg, 84%) with a methylation/protodestannation ratio of 92:8, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (87:13 mixture of proximal/distal product, only resonances of the major isomer are reported, 400 MHz, $CDCl_3$): δ 7.33-7.26 (m, 2H), 7.24-7.15 (m, 3H), 5.27 (tq, J = 7.2, 1.3 Hz, 1H), 3.71 (dtd, J = 9.6, 6.1, 3.7 Hz, 1H), 2.90-2.77 (m, 1H), 2.71 (dt, J = 13.7, 8.1 Hz, 1H), 2.23 (dd, J = 13.2, 3.3 Hz, 1H), 2.12-1.96 (m, 3H), 1.85-1.66 (m, 3H), 1.62 (d, J = 1.2 Hz, 3H), 1.40-1.24 (m, 4H), 0.95-0.85 (m, 3H); ^{13}C NMR (87:13 mixture of proximal/distal product, only resonances of the major isomer are reported,101 MHz, $CDCl_3$): δ 142.3 (CR_4), 131.6 (CR_4), 129.2 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 125.7 (CH), 67.7 (CH), 48.1 (CH_2), 38.7 (CH_2), 32.2 (CH_2), 31.9 (CH_2), 27.7 (CH_2), 22.4 (CH_2), 16.0 (CH_3), 14.0 (CH_3); FTIR (thin film): ν 3375, 3062, 3026, 2954, 2925, 2857, 1603, 1495, 1454, 1380, 1266, 1181, 1079, 1050, 1029, 929, 840, 745, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{17}H_{30}NO$ [(M+NH_4)$^+$] 264.2322, found 264.2318.

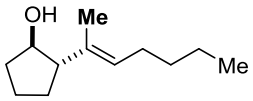
j ç*SR*ħσ*SR*ħ*E*QZ σħτZ $É Í ÅÔÈÙÌÎ Ï ÎZ τZ ÅÎZ çZ ÏÌ⁸ Prepared from (2*SR*,3*RS*,*Z*)-3-methyl-4-(tributylstannyl)non-4-en-2-ol (94:6 mixture of proximal/distal vinyl stannane, 224 mg, 503 μmol) according to method **!** as a faintly yellowish oil (94:6 mixture of proximal/distal product, 72.2 mg, 84%) with a methylation/protodestannation ratio of 94:6, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (94:6 mixture of proximal/distal product, only resonances of the major isomer are reported, 400 MHz, $CDCl_3$): δ 5.21 (tp, J = 7.1, 1.3 Hz, 1H), 3.72 (p, J = 6.3 Hz, 1H), 2.08-1.96 (m, 3H), 1.57 (s, 3H), 1.47 (br s, 1H), 1.37-1.26 (m, 4H), 1.13 (d, J = 6.3 Hz, 3H), 1.04 (d, J = 7.0 Hz, 3H), 0.94-0.83 (m, 3H); ^{13}C NMR (94:6 mixture of proximal/distal product, only resonances of the major isomer are reported, 101 MHz, $CDCl_3$): 137.0 (CR_4), 126.3 (CH), 69.2 (CH), 49.7 (CH), 31.9 (CH_2), 27.4 (CH_2), 22.4 (CH_2), 21.2 (CH_3), 14.4 (CH_3), 13.99 (CH_3), 13.95 (CH_3); FTIR (thin film): ν 3362, 2959, 2926, 2873, 2859, 1455, 1372, 1298, 1249, 1157, 1081, 1026, 972, 952, 908, 850, 727 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{11}H_{22}ONa$ [(M+Na)$^+$] 193.1563, found 193.1563.



j ρ*RS*ħ ç*SR*QZ çZ j j*E*QZ (ÅÐÔZ çZ ÅÎZ çZ ÙÌQÃÙÃÌÏÈÅØÁÎZ ρZ ÏÌ⁸ Prepared from (1*RS*,2*RS*)-2-((*Z*)-1-(tributylstannyl)hex-1-en-1-yl)cyclohexan-1-ol (85:15 mixture of proximal/ distal vinyl stannane, 236 mg, 501 μmol) according to method **!** as a faintly yellowish oil (87:13 mixture of proximal/distal product, 59.7 mg, 61%) with a methylation/protodestannation ratio of 94:6, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (87:13 mixture of proximal/distal product, only resonances of the major isomer are reported, 400 MHz, $CDCl_3$): δ 5.32 (ddd, J = 8.6, 6.3, 1.5 Hz, 1H), 3.40 (td, J = 10.0, 4.2 Hz, 1H), 2.12-1.97 (m, 3H), 1.88-1.59 (m, 5H), 1.56 (d, J = 1.3 Hz, 3H), 1.40-1.12 (m, 8H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (87:13 mixture of proximal/distal product, only resonances of the major isomer are reported, 101 MHz, $CDCl_3$): 135.3 (CR_4), 128.6 (CH), 70.2, 56.3, 34.0, 31.9, 30.0, 27.4, 25.7, 24.9, 22.4, 14.0, 12.5; δ 142.3 (CR_4), 131.6 (CR_4), 129.2 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 125.7 (CH), 67.7 (CH), 48.1 (CH_2), 38.7 (CH_2), 32.2 (CH_2), 31.9 (CH_2), 27.7 (CH_2), 22.4 (CH_2), 16.0 (CH_3), 14.0 (CH_3); FTIR (thin film): ν 3441, 2954, 2926, 2856, 1449, 1379, 1352, 1270, 1132, 1106, 1063, 1042, 1008, 945, 843 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{13}H_{25}O$ [(M+H)$^+$] 197.1900, found 197.1899.

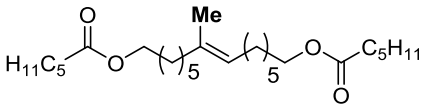


jρ*RS*ʰς*SR*ζςζjj*E*ζ(ÅÐôζςζÅÎζςζÙÌζÃÙÃÌÏÐÅÎôÁÎζρζÏÌ Prepared from (1*RS*,2*RS*)-2-((*Z*)-



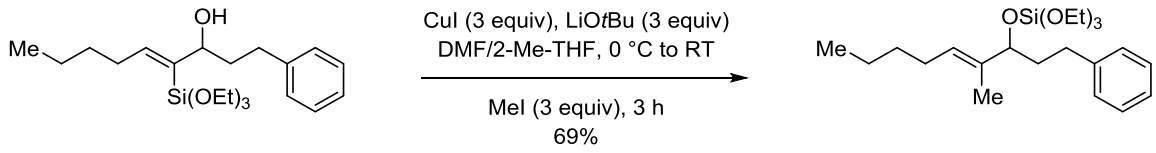
1-(tributylstannyl)hex-1-en-1-yl)cyclopentan-1-ol (85:15 mixture of proximal/ distal vinyl stannane, 229 mg, 501 μmol) according to method **!** as a faintly yellowish oil (86:14 mixture of proximal/distal product, 60.4 mg, 66%) with a methylation/protodestannation ratio of 98:2, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (86:14 mixture of proximal/distal product, only resonances of the major isomer are reported, 400 MHz, $CDCl_3$): δ 5.25 (tp, J = 7.1, 1.3 Hz, 1H), 3.96 (q, J = 7.4 Hz, 1H), 2.24 (dt, J = 10.3, 7.8 Hz, 1H), 1.99 (ddt, J = 12.8, 10.3, 7.3 Hz, 3H), 1.83-1.45 (m, 6H), 1.58 (s, 3H), 1.39-1.24 (m,4H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (86:14 mixture of proximal/distal product, only resonances of the major isomer are reported,101 MHz, $CDCl_3$): δ 134.7 (CR_4), 126.2 (CH), 75.7 (CH), 57.8 (CH), 33.6 (CH_2), 32.0 (CH_2), 28.2 (CH_2), 27.6 (CH_2), 22.4 (CH_2), 21.3 (CH_2), 14.0 (CH_3), 13.3 (CH_3); FTIR (thin film): ν 3336, 2955, 2926, 2871, 1453, 1378, 1341, 1299, 1247, 1151, 1086, 1050, 975, 937, 838, 727 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{12}H_{23}O$ [(M+H)$^+$] 183.1743, found 183.1743.

jEζχζ - ÅôÈÙÌôÅÔÒÁÄÅÃζχζÅÎÅζρʰρτζÄÉÙl ÄÉÈÅØÁÎÏÁÔÅ Prepared according to method **!**



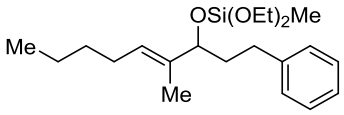
as a colorless oil (164 mg, 75%) with a methylation/protodestannation ratio of >99:1, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.08 (t, J = 6.7 Hz, 1H), 4.04 (t, J = 6.7 Hz, 4H), 2.27 (t, J = 7.5 Hz, 4H), 1.95 (app. q, J = 7.7 Hz, 4H), 1.60 (tt, J = 7.6, 4.1 Hz, 8H), 1.56 (s, 3H), 1.42-1.22 (m, 20H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.9 (2 × CR_4), 135.0 (CR_4), 124.4 (CH), 64.3 (2 × CH_2), 39.5 (CH_2), 34.3 (2 × CH_2), 31.3 (2 × CH_2), 29.7 (CH_2), 28.87 (CH_2), 28.83 (CH_2), 28.6 (2 × CH_2), 27.78 (CH_2), 27.74 (CH_2), 25.83 (CH_2), 25.80 (CH_2), 24.7 (2 × CH_2), 22.3 (2 × CH_2), 15.8 (CH_3), 13.9 (2 × CH_3); FTIR (thin film): ν 2954, 2928, 2857, 1735, 1463, 1381, 1355, 1244, 1169, 1099, 1067, 944, 889, 851, 729 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{27}H_{50}O_4Na$ [(M+Na)$^+$] 461.3601, found 461.3605.

#ÏÐÐÅÒj)ǫǯ - ÅÄɆÁÔÅd - ÅÔÈÙÌÁÔɆÏ Î and ! ÌÌÙÌÁÔɆÏn ÏÆ ! ÌËÅÎÙÌÓɆÌɆÃÁÔÅÅÓ *via* "ÒÏ ÏËǯ2ÅÁÒÒÁÎÇÅ Í ÅÎô



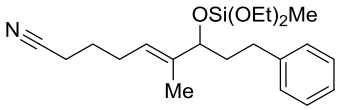
2ÅÐÒÅÓÅÎÔÁÔɆÖÅ 0ÒÏÃÅÄÕÒÅ: jƐǫǯ4ÒɆÅÔÈÙÌÏØÙjjτǯ Í ÅÔÈÙÌǯρǯÐÈÅÎÙÌÎÏÎǯτǯÅÎǯσǯ ÙÌǫÏØÙǫÓɆÌÁÎÅ jρπÄǫ§ LiO*t*Bu (0.9 M in 2-Me-THF, 0.33 mL, 300 µmol) was added to a suspension of CuI (58.0 mg, 305 µmol) in DMF (0.50 mL) at 0 °C, the cooling bath was removed and the resulting dark brown solution was stirred at ambient temperature for 30 min. A solution of (*Z*)-1-phenyl-4-(triethoxysilyl)non-4-en-3-ol (**ωÄ**) (38.0 mg, 99.8 µmol) in DMF (0.6 mL) was added, immediately followed by MeI (19.0 µL, 305 µmol). The resulting mixture was stirred until TLC control showed complete conversion of the substrate before the reaction was quenched with Et_3N (0.1 mL). The mixture was diluted with *tert*-butyl methyl ether (30 mL) and poured into a mixture of 25% aqueous NH_4OH/sat. aqueous NH_4Cl solution (1:9, 10 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (2 × 30 mL), the combined extracts were washed with brine (3 x) and then dried over Na_2SO_4, filtered and concentrated under reduced pressure, and the residue was purified by flash chromatography (EtOAc/hexane 2:98 to 10:90; step gradient) to give the title compound (27.2 mg, 69%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.24 (m, 2H), 7.22-7.14 (m, 3H), 5.39 (t, J = 7.1 Hz, 1H), 4.27 (t, J = 6.7 Hz, 1H), 3.82 (q, J = 7.0 Hz, 6H), 2.66-2.48 (m, 2H), 2.03 (q, J = 7.0 Hz, 2H), 1.99-1.89 (m, 1H), 1.82 (dddd, J = 13.3, 10.2, 6.5, 5.7 Hz, 1H), 1.61 (s, 3H), 1.39-1.28 (m, 4H), 1.21 (t, J = 7.0 Hz, 9H), 0.94-0.87 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.4 (CR_4), 135.7 (CR_4), 128.4 (2 × CH), 128.2 (2 × CH), 127.1 (CH), 125.6 (CH), 78.7 (CH), 59.1 (3 × CH_2), 37.3 (CH_2), 32.0 (CH_2), 31.7 (CH_2), 27.2 (CH_2), 22.4 (CH_2), 18.1 (3 × CH_3), 14.0 (CH_3), 10.9 (CH_3); FTIR (thin film): ν 3027, 2973, 2927, 1604, 1496, 1554, 1390, 1296, 1168, 1103, 1079, 965, 791 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{22}H_{38}O_4SiNa$ [(M+Na)$^+$] 417.2432, found 417.2424.

jEQZ$ÉÅÔÈÏØÙj Í ÅÔÈÙÌQjjτZ Í ÅÔÈÙÌZρZÐÈÅÎÙÌÎÏÎZτZÅÎZσZÙÌQÏØÙQÓÉÌÁÎÅ8 The reaction



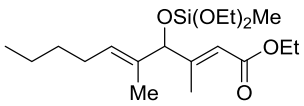
was performed analogously; the crude product was analytically pure (>98% by NMR, 54 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.14 (m, 3H), 5.37 (t, *J* = 7.2 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 1H), 3.78 (qd, *J* = 7.1, 2.8 Hz, 4H), 2.58 (m, 2H), 2.02 (m, 2H), 1.86 (m, 2H), 1.60 (s, 3H), 1.39-1.28 (m, 4H), 1.20 (t, *J* = 7.0 Hz, 6H), 0.90 (m, 3H), 0.09 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 142.4, 136.0, 128.4, 128.3, 127.0, 125.6, 78.1, 58.22, 58.19, 37.5, 32.1, 31.7, 27.2, 22.4, 18.24, 18.22, 14.0, 10.92, -6.44; FTIR (thin film): ṽ 3086, 3063, 3027, 2958, 2926, 2874, 1742, 1604, 1496, 1454, 1389, 1334, 1295, 1262, 1167, 1102, 1075, 984, 957, 888, 824, 790, 767, 748, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{21}H_{36}O_3SiNa$ [(M+Na)$^+$] 387.2326, found 387.2327.

jEQZχZjj$ÉÅÔÈÏØÙj Í ÅÔÈÙÌQÓÉÌÙÌQÏØÙQZφZ Í ÅÔÈÙÌZωZÐÈÅÎÙÌÎÏÎZυZÅÎÅÎÉÔÒÉÌÅ8 Prepared



according to the general procedure as a colorless oil (26 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.21-7.15 (m, 3H), 5.32 (t, *J* = 7.1 Hz, 1H), 4.23 (t, *J* = 6.5 Hz, 1H), 3.79 (m, 4H), 2.59 (m, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 2.21 (m, 2H), 1.98-1.76 (m, 2H), 1.74 (t, *J* = 7.2 Hz, 2H), 1.64 (s, 3H), 1.21 (td, *J* = 7.0, 0.8 Hz, 6H), 0.10 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 142.1, 139.0, 128.34, 128.29, 125.7, 123.4, 119.6, 77.5, 58.25, 58.22, 37.4, 32.0, 26.2, 25.2, 18.23, 16.5, 11.4, -6.5; FTIR (thin film): ṽ 3063, 3027, 2973, 2927, 2885, 2247, 1603, 1496, 1454, 1390, 1366, 1333, 1294, 1263, 1166, 1100, 1071, 985, 956, 889, 822, 788, 767, 750, 699 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{21}H_{33}NO_3SiNa$ [(M+Na)$^+$] 398.2122, found 398.2124.

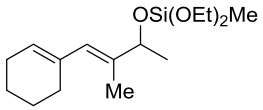
%ÔÈÙl jς%ћυ%QZτZjjÄÉÅÔÈÏØÙj Í ÅÔÈÙÌQÓÉÌÙÌQÏØÙQZσћυZÄÉ Í ÅÔÈÙÌÄÅÃÁZςћυZÄÉÅÎÏÁÔÅ.



Prepared according to the general procedure as a colorless oil (28 mg, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (qui, *J* = 1.4 Hz, 1H), 5.51 (t, *J* = 7.1 Hz, 1H), 4.59 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.77 (m, 4H), 2.03 (q, *J* = 7.1 Hz, 2H), 1.98 (s, 3H), 1.45 (s, 3H), 1.33 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.20 (td, *J* = 7.1, 1.9 Hz, 6H), 0.89 (m, 3H), 0.10 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 167.1, 157.9, 133.5, 129.6, 114.9, 81.7, 59.6, 58.37, 58.34, 31.5, 27.4, 22.3, 18.18, 15.3, 14.3, 13.9, 10.7, -6.5; FTIR (thin film): ṽ 2973, 2927, 2875, 1717, 1654, 1444, 1388, 1367, 1315, 1263, 1211, 1144,

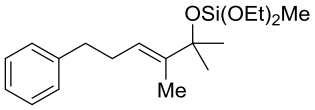
1073, 1004, 957, 887, 826, 792, 763, 734 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{19}H_{36}O_5SiNa$ [$(M+Na)^+$] 395.2224, found 395.2224.

jEQZjjτZj#ÙÃÌÏÈÅØZρZÅÎZρZÙÌQZσZ Í ÅÔÈÙÌÂÕÔZσZÅÎZçZÙÌQÏØÙQÄÉÅÔÈÏØÙj Í ÅÔÈÙÌQÓÉÌÁÎÅ.

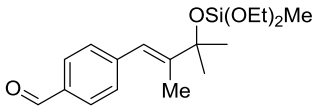


Prepared according to the general procedure as a colorless oil (26 mg, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (s (br), 1H), 5.58 (m, 1H), 4.39 (q, *J* = 6.4 Hz, 1H), 3.79 (qd, *J* = 7.0, 1.5 Hz, 4H), 2.09 (m, 4H), 1.76 (s, 3H), 1.60 (m, 4H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 6H), 0.11 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 137.5, 135.0, 127.1, 126.7, 74.4, 58.23, 58.21, 29.2, 25.6, 23.0, 22.8, 22.2, 18.24, 18.23, 13.1, -6.5; FTIR (thin film): ṽ 2973, 2927, 2835, 1650, 1439, 1390, 1369, 1334, 1312, 1294, 1262, 1199, 1167, 1102, 1074, 991, 956, 880, 865, 825, 779 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{16}H_{30}O_3SiNa$ [$(M+Na)^+$] 321.1856, found 321.1854.

jEQZjjçĥσZ$É Í ÅÔÈÙÌZφZÐÈÅÎÙÌÈÅØZσZÅÎZçZÙÌQÏØÙQÄÉÅÔÈÏØÙj Í ÅÔÈÙÌQÓÉÌÁÎÅ. Prepared according to the general procedure; the crude product was pure enough for further use (55 mg, 99 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.15 (m, 3H), 5.50 (tq, *J* = 7.0, 1.3 Hz, 1H), 3.77 (q, *J* = 7.0 Hz, 4H), 2.66 (m, 2H), 2.32 (m, 2H), 1.60 (s, 3H), 1.38 (s, 6H), 1.21 (t, *J* = 7.0 Hz, 6H), 0.10 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 142.3, 141.6, 128.5, 128.2, 125.7, 121.1, 76.6, 58.0, 35.8, 29.9, 29.2, 18.2, 12.5, -4.7; FTIR (thin film): ṽ 3086, 3063, 3027, 2974, 2926, 2882, 1604, 1496, 1454, 1388, 1376, 1364, 1294, 1262, 1160, 1104, 1076, 1048, 995, 815, 778, 747, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{19}H_{32}O_3SiNa$ [$(M+Na)^+$] 359.2013, found 359.2015.

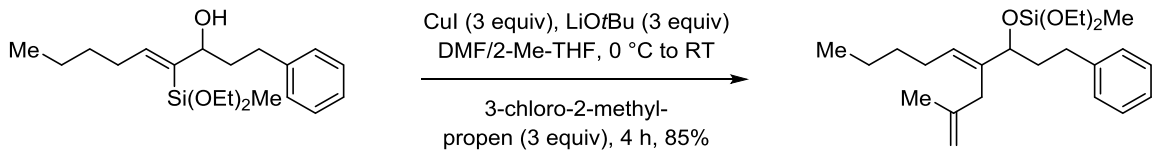


jEQZτZjσZjj$ÉÅÔÈÏØÙj Í ÅÔÈÙÌQÓÉÌÙÌQÏØÙQZçĥσZÄÉ Í ÅÔÈÙÌÂÕÔZρZÅÎZρZÙÌQÂÅÎÚÁÌÄÅÈÙÄÅ.



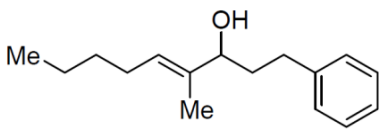
Prepared according to the general procedure as a colorless oil (20 mg, 48 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.84 (m, 2H), 7.40 (m, 2H), 6.67 (s, 1H), 3.82 (q, *J* = 7.0 Hz, 4H), 1.90 (d, *J* = 1.3 Hz, 3H), 1.52 (s, 6H), 1.23 (t, *J* = 6.9 Hz, 6H), 0.17 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 191.9, 147.5, 145.4, 134.2, 129.60, 129.54, 121.6, 77.0, 58.2, 29.2, 18.3, 14.6, -4.7; FTIR (thin film): ṽ 2975, 2927, 2881, 2825, 2734, 1720, 1698, 1649, 1602, 1566, 1507, 1482, 1443, 1415, 1388, 1364, 1304, 1263, 1246, 1212, 1165, 1102, 1075, 1045, 1003, 981, 951, 876,

817, 778, 732, 708, 650 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{18}H_{29}O_4Si$ [$(M+H)^+$] 337.1830, found 337.1831.

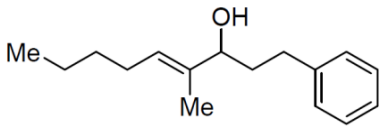


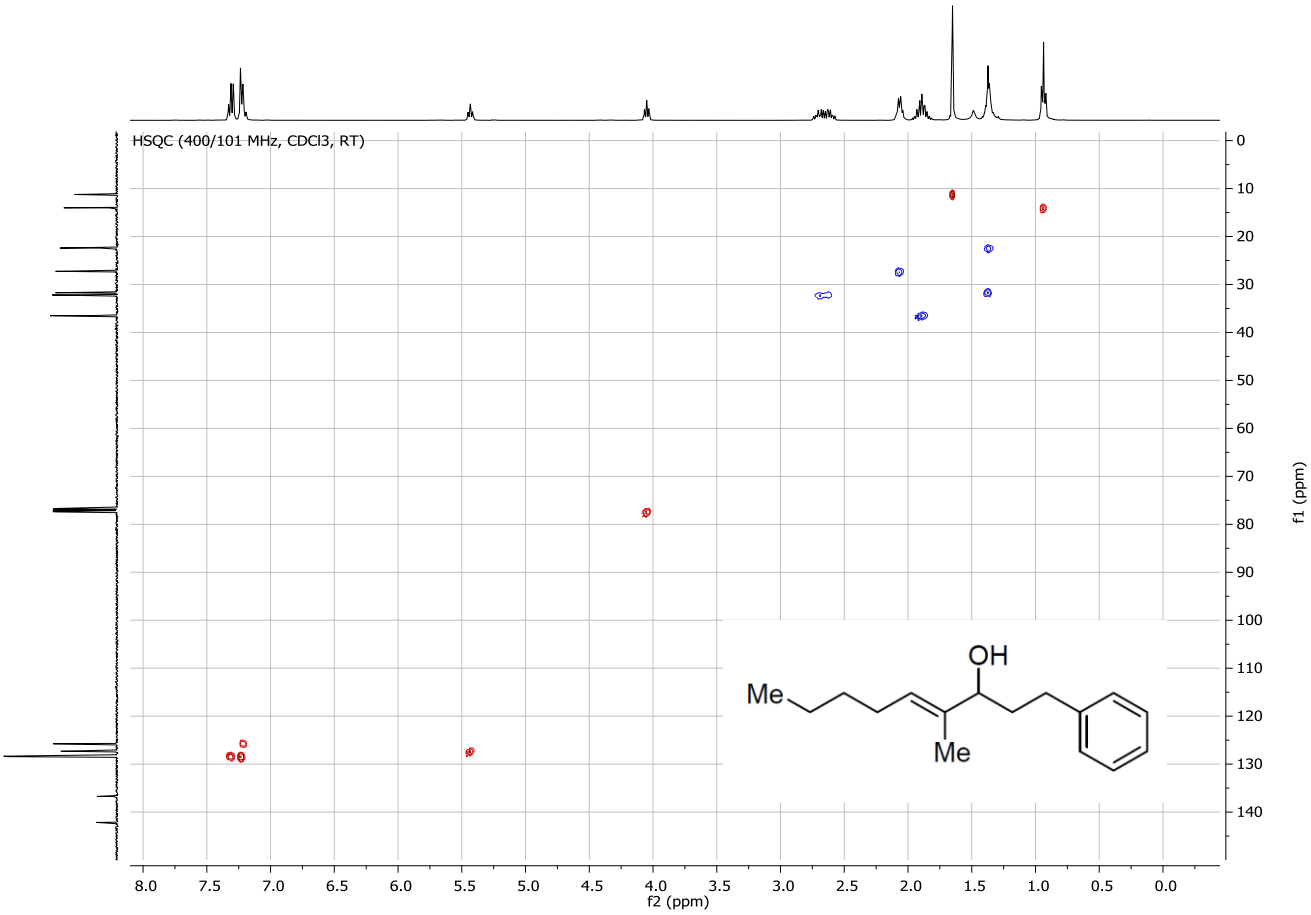
jEQZ $ÉÅÔÈÏØÙj Í ÅÔÈÙÌQjjτZjçZ Í ÅÔÈÙÌÁÌÌÙÌQZρZÐÈÅÎÙÌÎÏÎZτZÅÎZσZÙÌQÏØÙQÓÉÌÁÎÅ8 LiO*t*Bu (0.9 M solution in 2-Me-THF, 0.33 mL, 300 µmol) was added to a suspension of CuI (58.0 mg, 305 µmol) in DMF (0.50 mL) at 0 °C, the cooling bath was removed and the resulting dark brown solution was stirred at ambient temperature for 30 min. A solution of (*Z*)-4-(diethoxy(methyl)silyl)-1-phenylnon-4-en-3-ol (35.0 mg, 99.8 µmol) in DMF (0.6 mL) was added, followed – *within maximum 30 seconds* – by 3-chloro-2-methylpropene (30 µL, 304 µmol). The resulting mixture was stirred for 4 hours before the reaction was quenched with Et_3N (0.1 mL). The mixture was diluted with *tert*-butyl methyl ether (30 mL), poured on a mixture of 25% aqueous NH_4OH/sat. aqueous NH_4Cl solution (1:9, 10 mL), the phases were separated and the aqueous phase extracted with *tert*-butyl methyl ether (2 × 30 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 1:99 to 5:95; step gradient) afforded the title compound (34.2 mg, 85%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.23 (m, 2H), 7.20-7.14 (m, 3H), 5.62 (t, J = 7.1 Hz, 1H), 4.74 (s, 1H), 4.69 (s, 1H), 4.28 (t, J = 6.0 Hz, 1H), 3.81 (ttd, J = 7.0, 4.5, 2.3 Hz, 4H), 2.82 (d, J = 15.9 Hz, 1H), 2.71 (d, J = 15.9 Hz, 1H), 2.75-2.54 (m, 2H), 2.02 (td, J = 7.0, 3.4 Hz, 2H), 1.88-1.80 (m, 2H), 1.72 (s, 3H), 1.40-1.29 (m, 4H), 1.22 (td, J = 7.0, 1.6 Hz, 6H), 0.90 (t, J = 7.1 Hz, 3H), 0.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.3 (CR_4), 142.6 (CR_4), 137.2 (CR_4), 128.5 (CH), 128.4 (2 × CH), 128.2 (2 × CH), 125.6 (CH), 110.9 (CH_2), 75.9 (CH), 58.2 (2 × CH_2), 38.2 (CH_2), 35.5 (CH_2), 32.0 (CH_2), 31.8 (CH_2), 27.6 (CH_2), 22.9 (CH_3), 22.5 (CH_2), 18.3 (2 × CH_3), 14.0 (CH_3), −6.4 (CH_3); FTIR (thin film): ν 3027, 2969, 2925, 1646, 1604, 1496, 14454, 1389, 1262, 1167, 1077987, 957, 890, 823, 792, 767, 748 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{24}H_{40}O_3SiNa$ [$(M+Na)^+$] 427.2639, found 427.2636.

1H NMR (400MHz, CDCl3, RT)

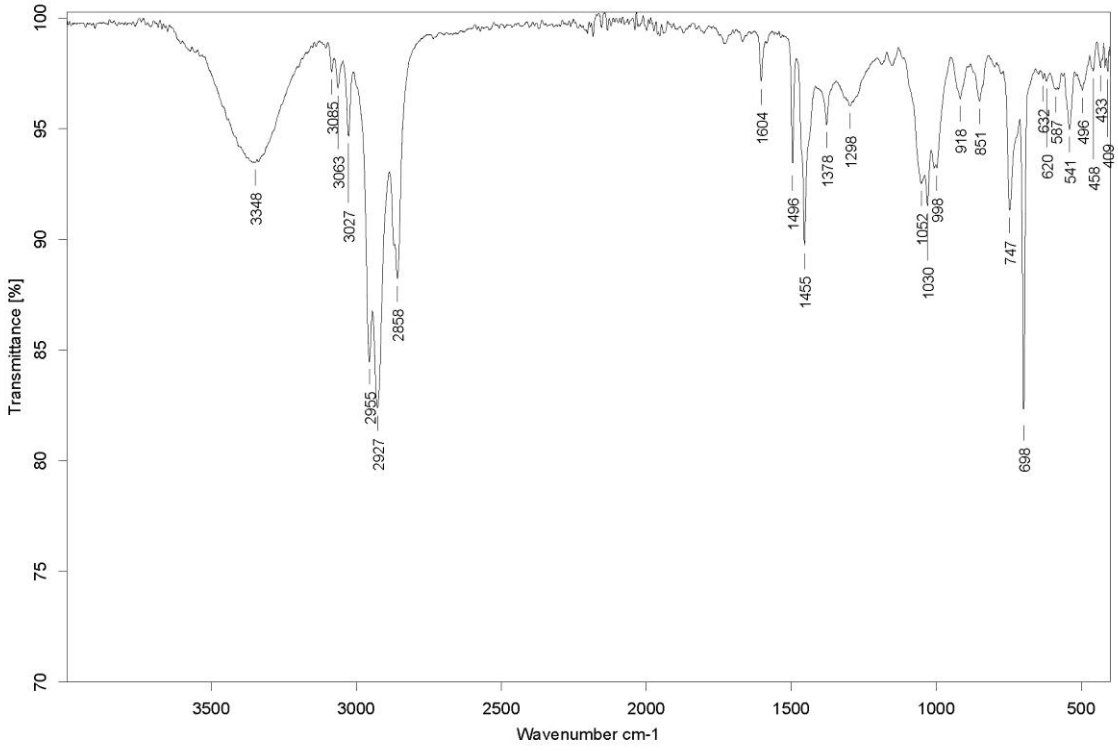


13C NMR (101 MHz, CDCl3, RT)

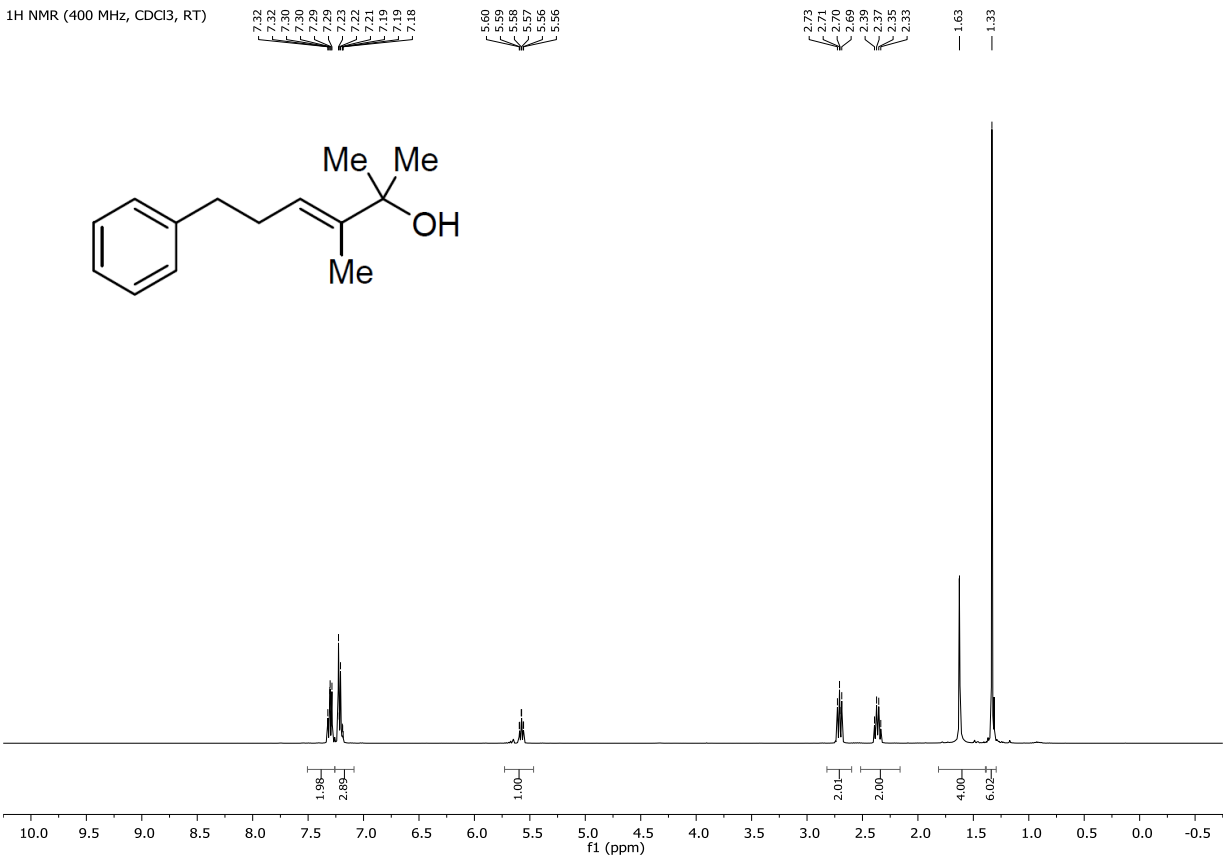




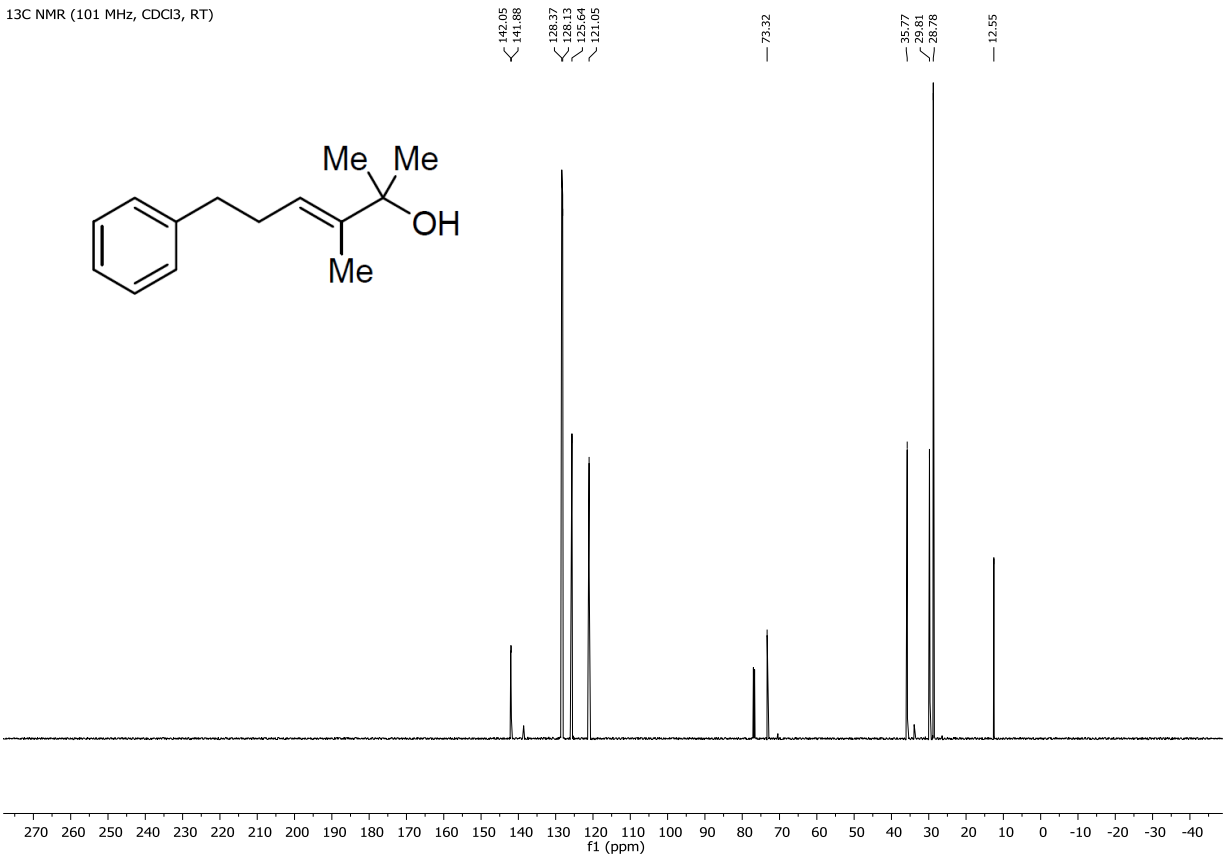
HUR-HA-003-10.0 **01.07.2016**

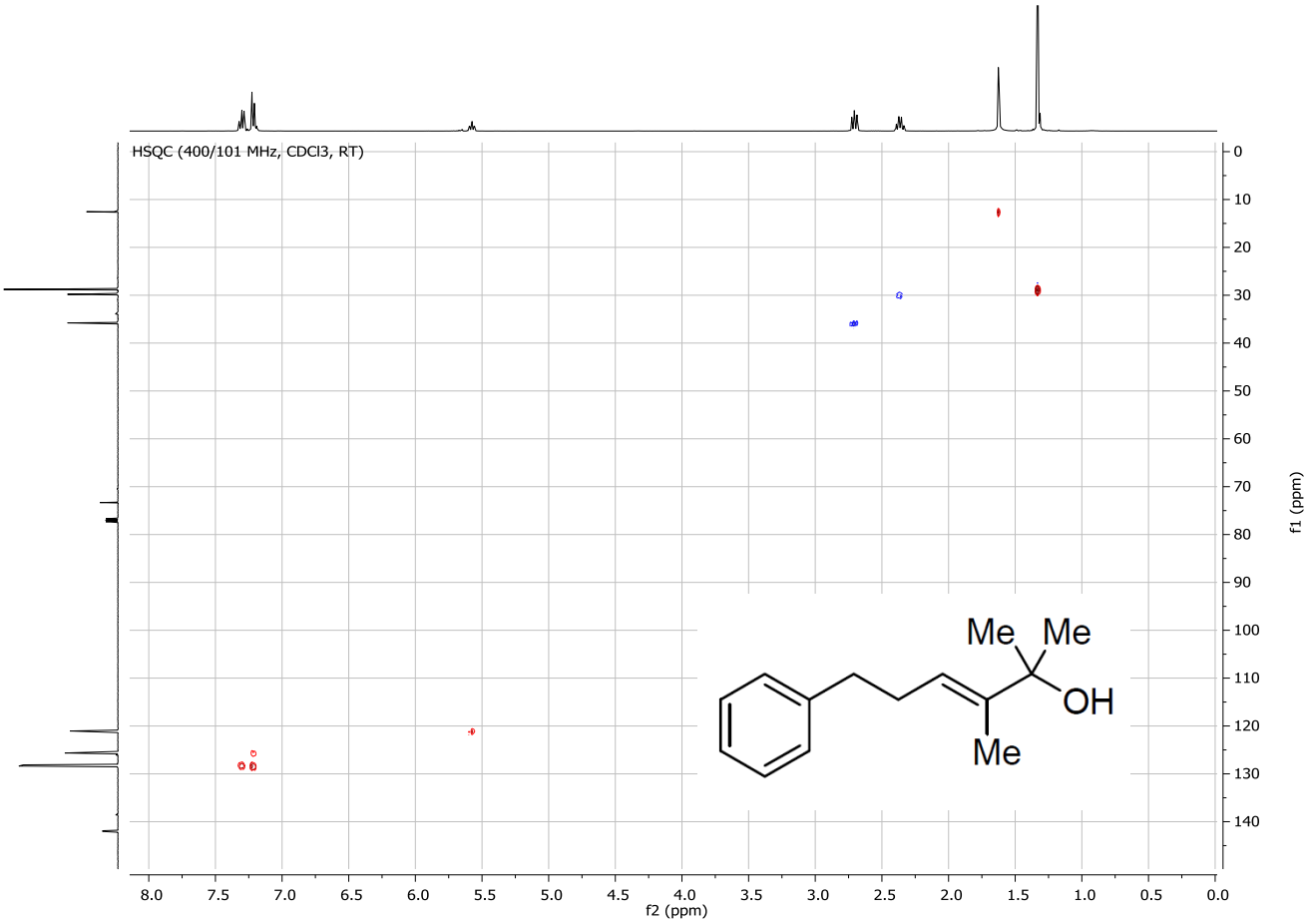


1H NMR (400 MHz, CDCl3, RT)

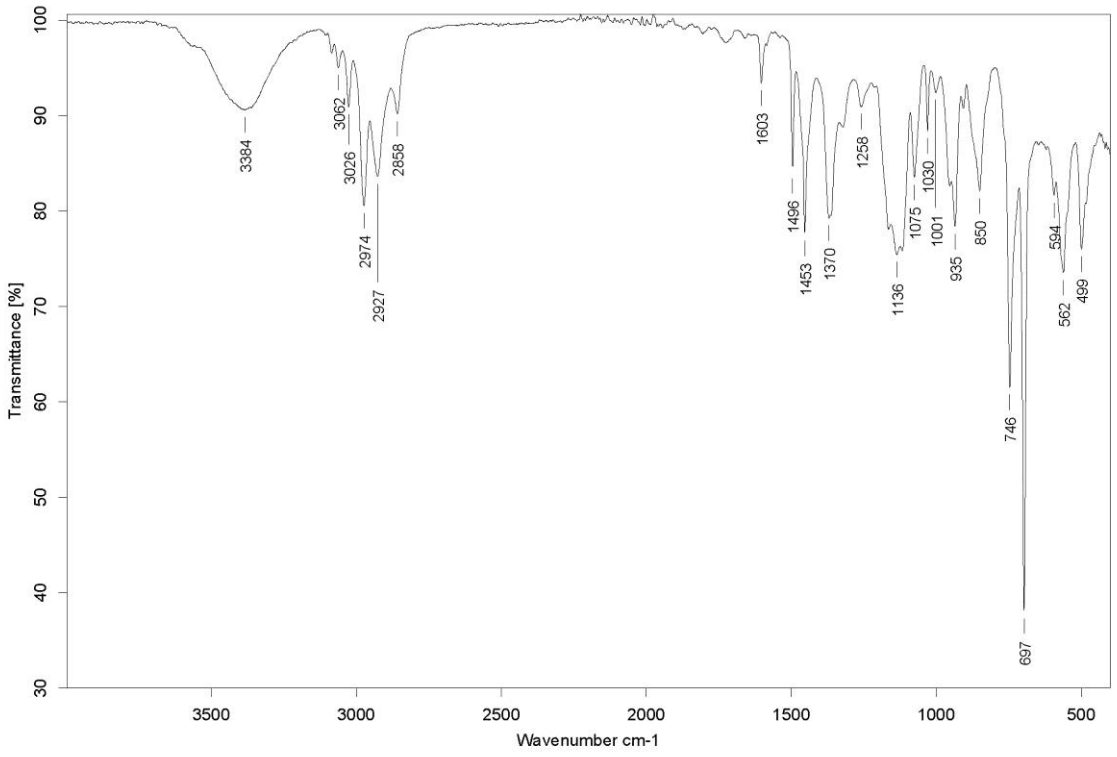


13C NMR (101 MHz, CDCl3, RT)

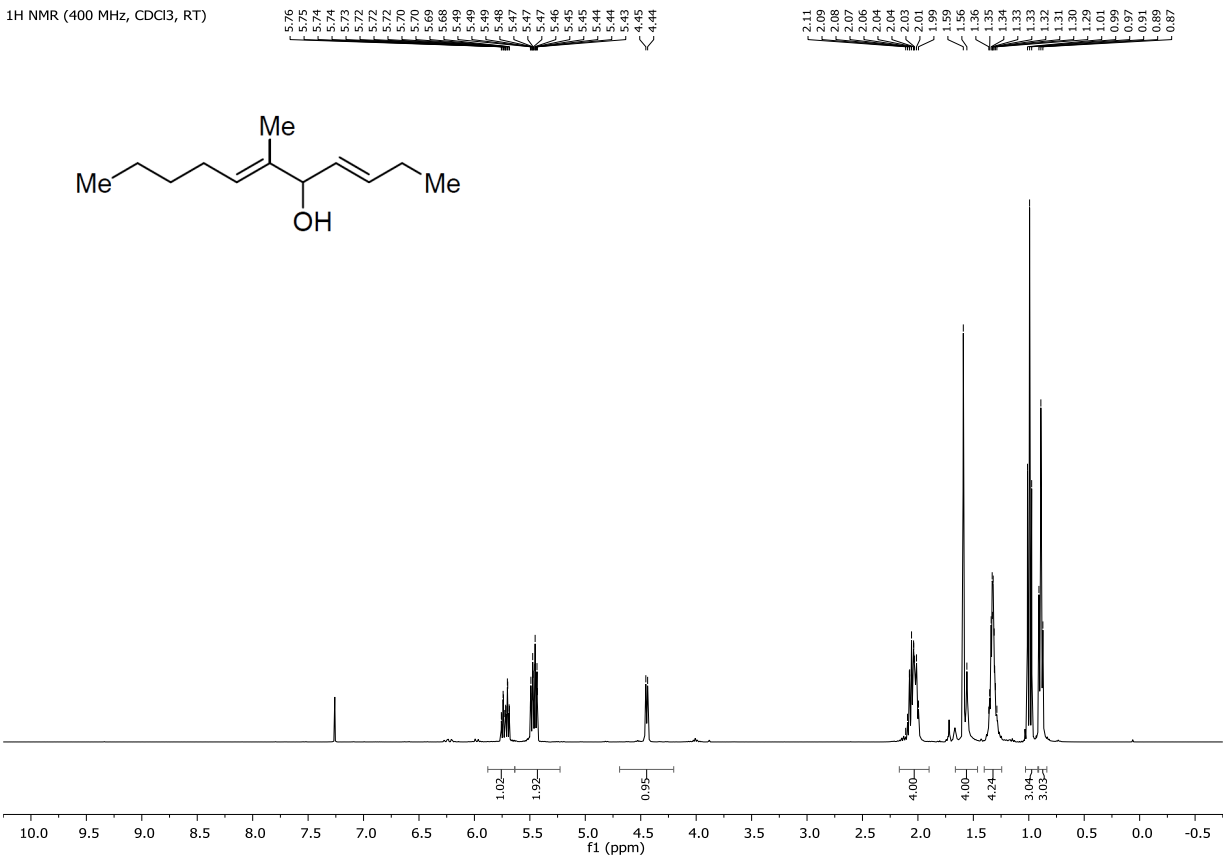




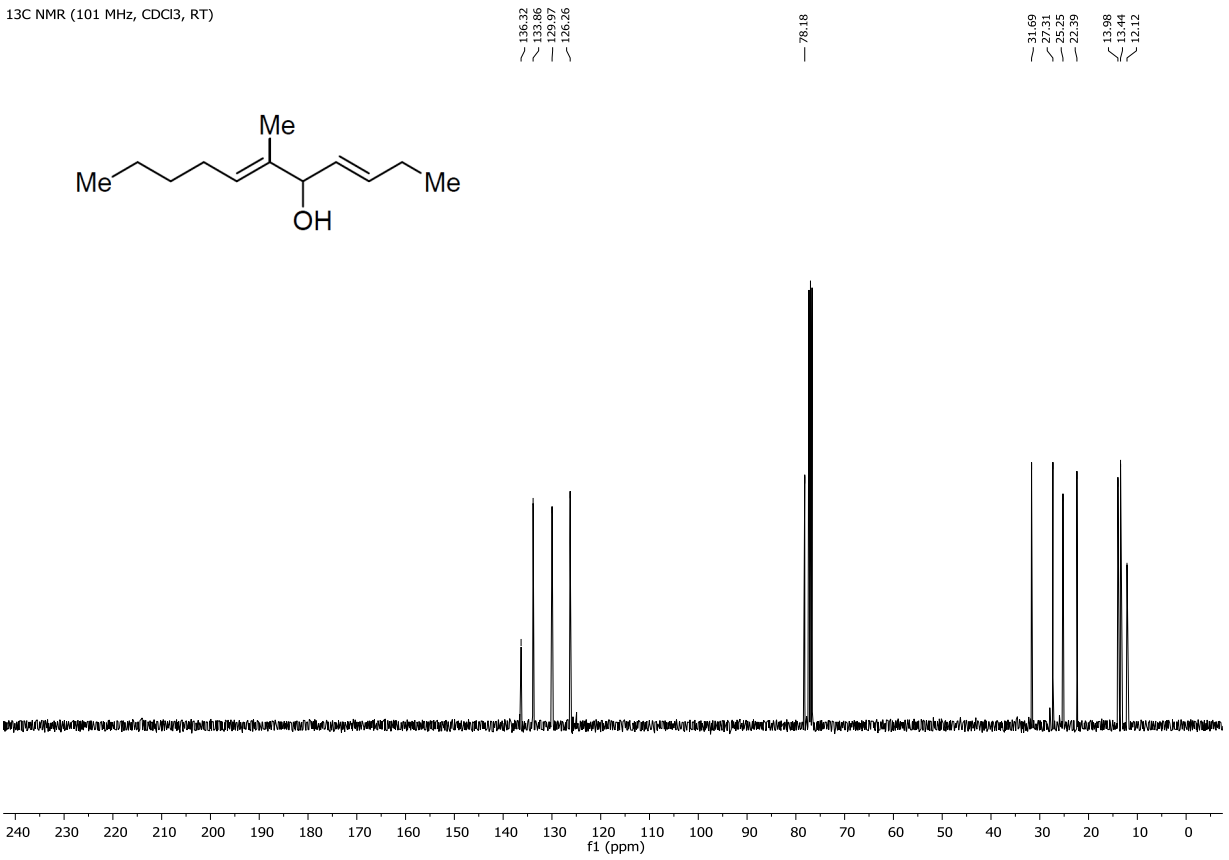
HUR-HA-084-11.0 **24.08.2016**

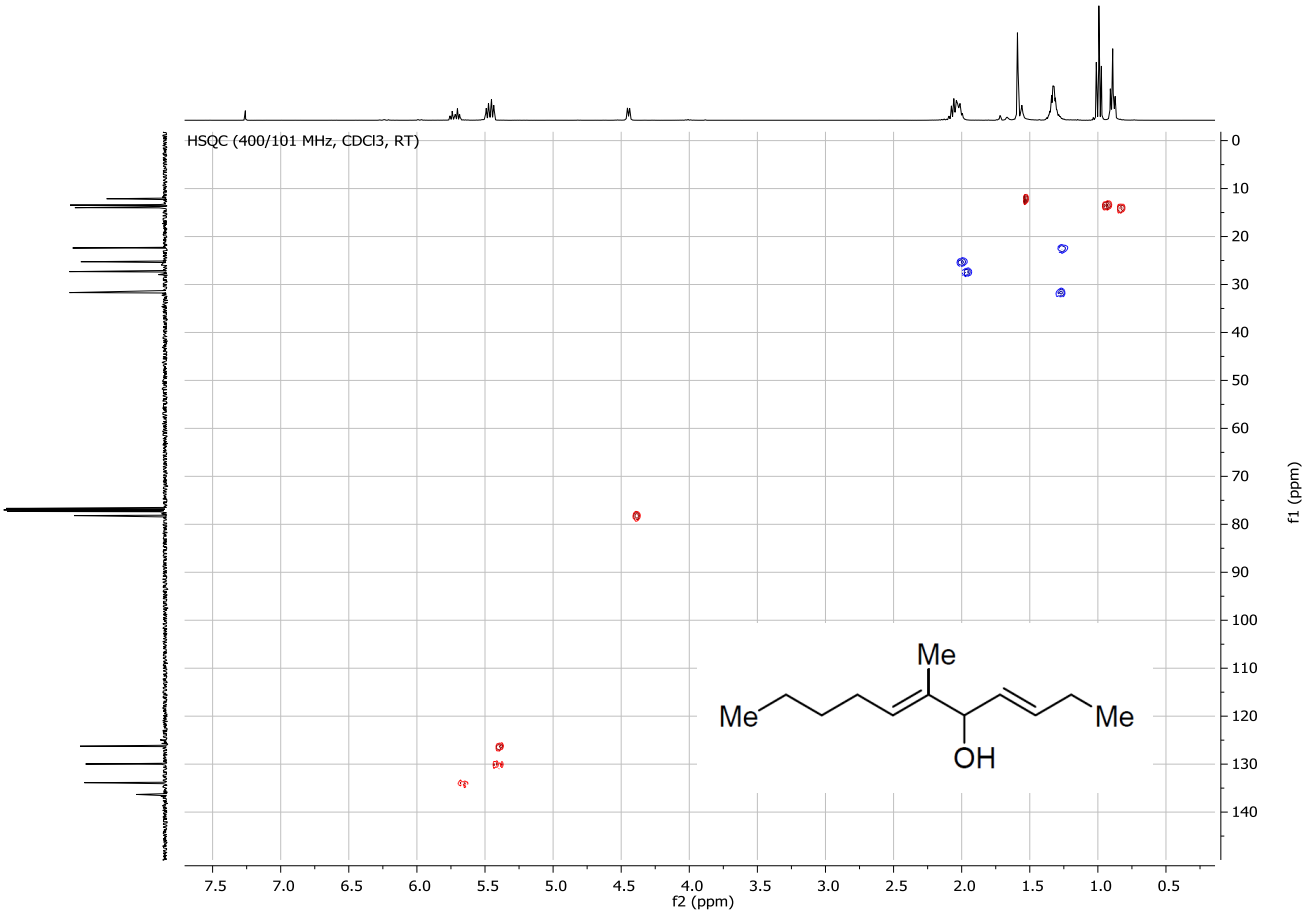


1H NMR (400 MHz, CDCl3, RT)

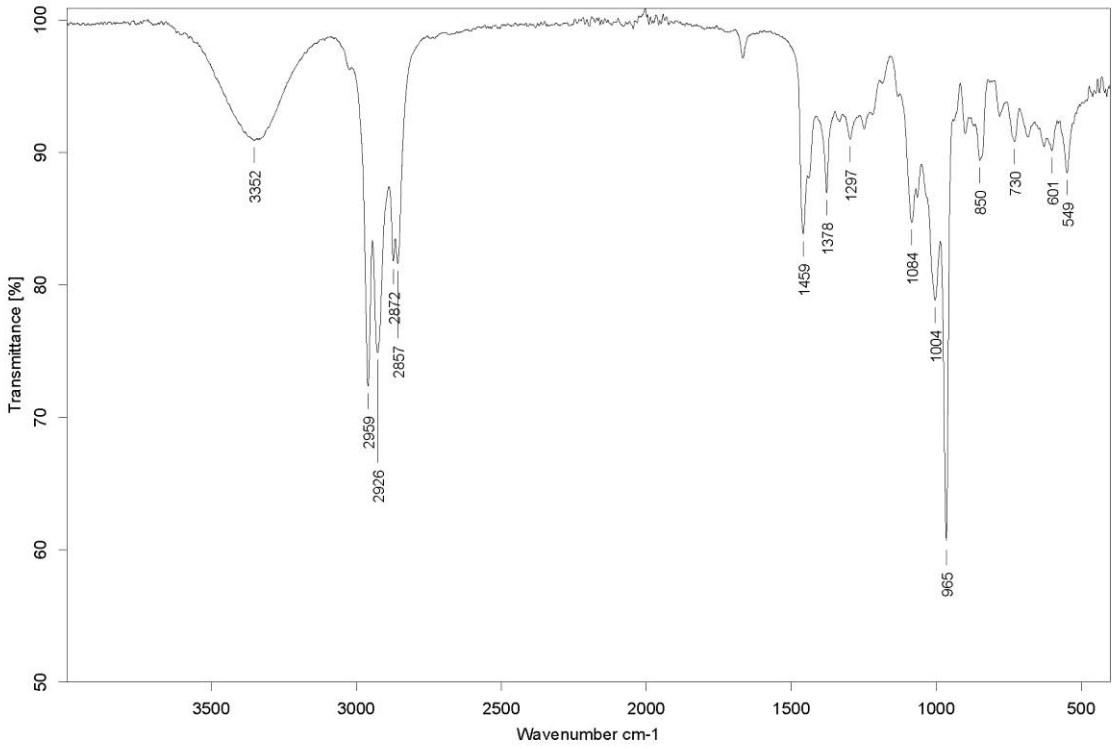


13C NMR (101 MHz, CDCl3, RT)

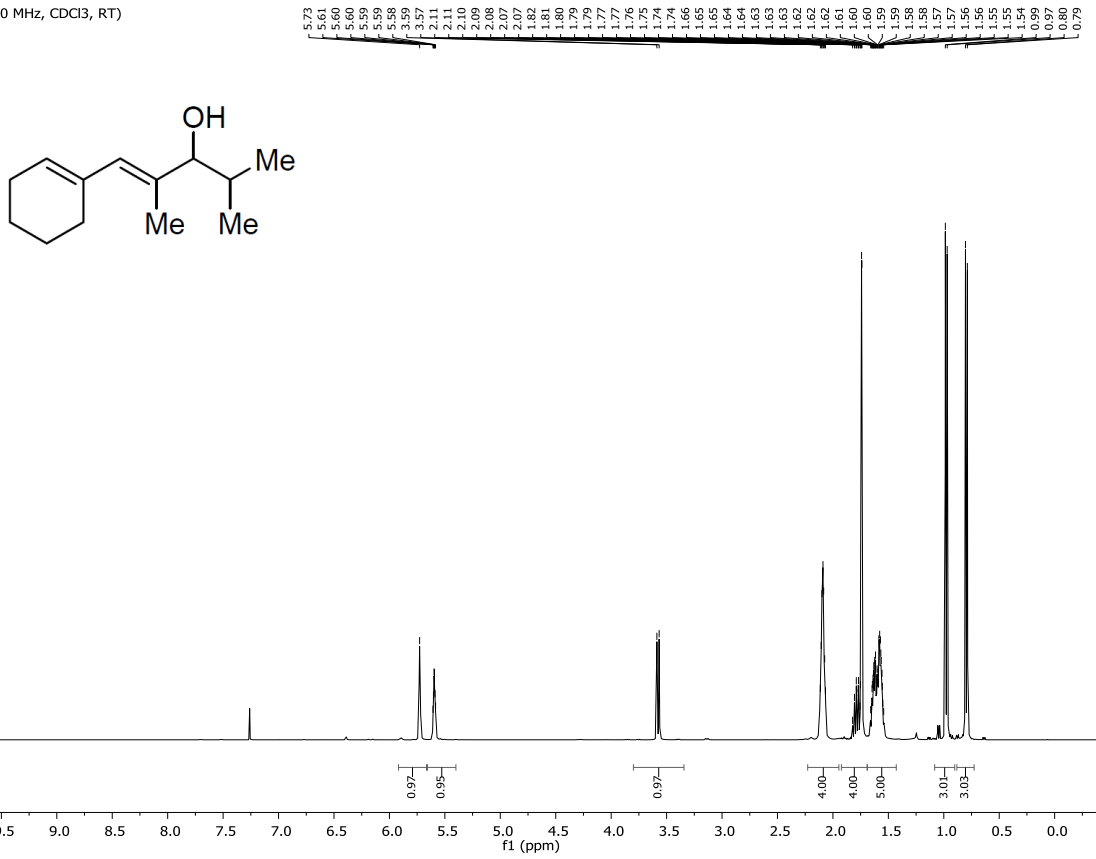




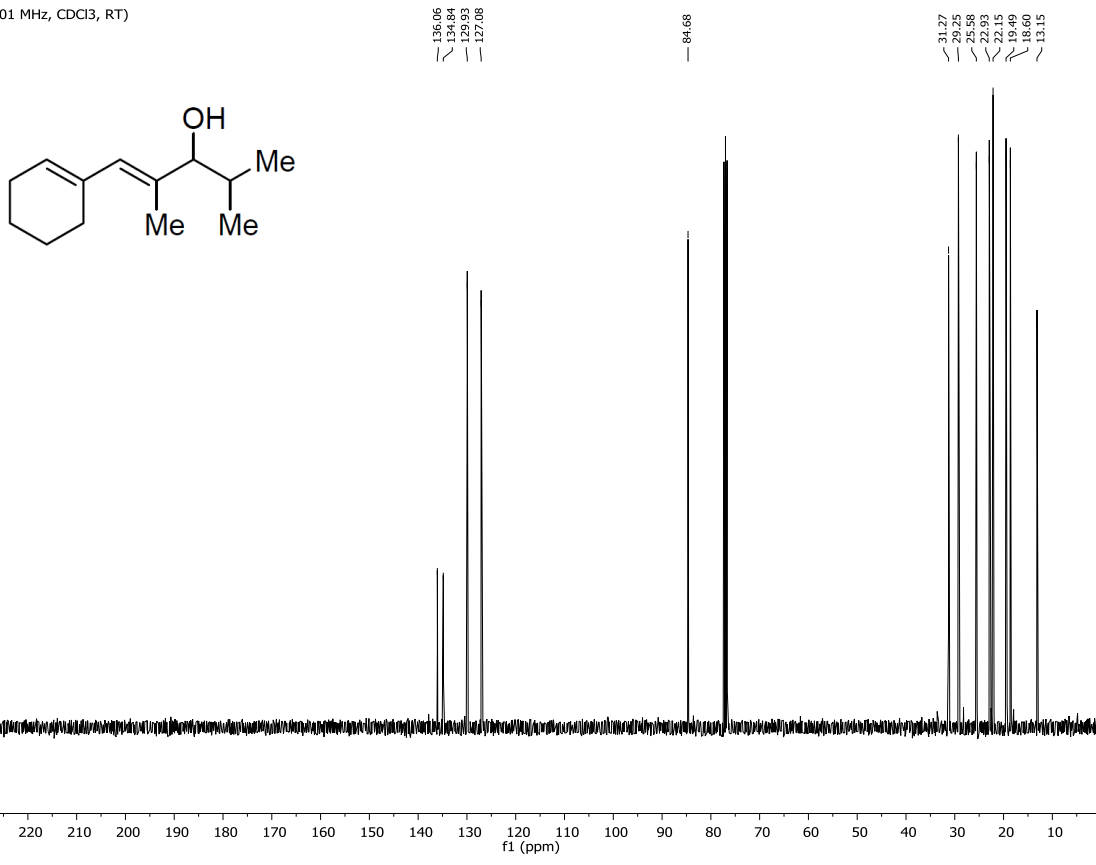
HUR-HA-090-11.0 **31.08.2016**

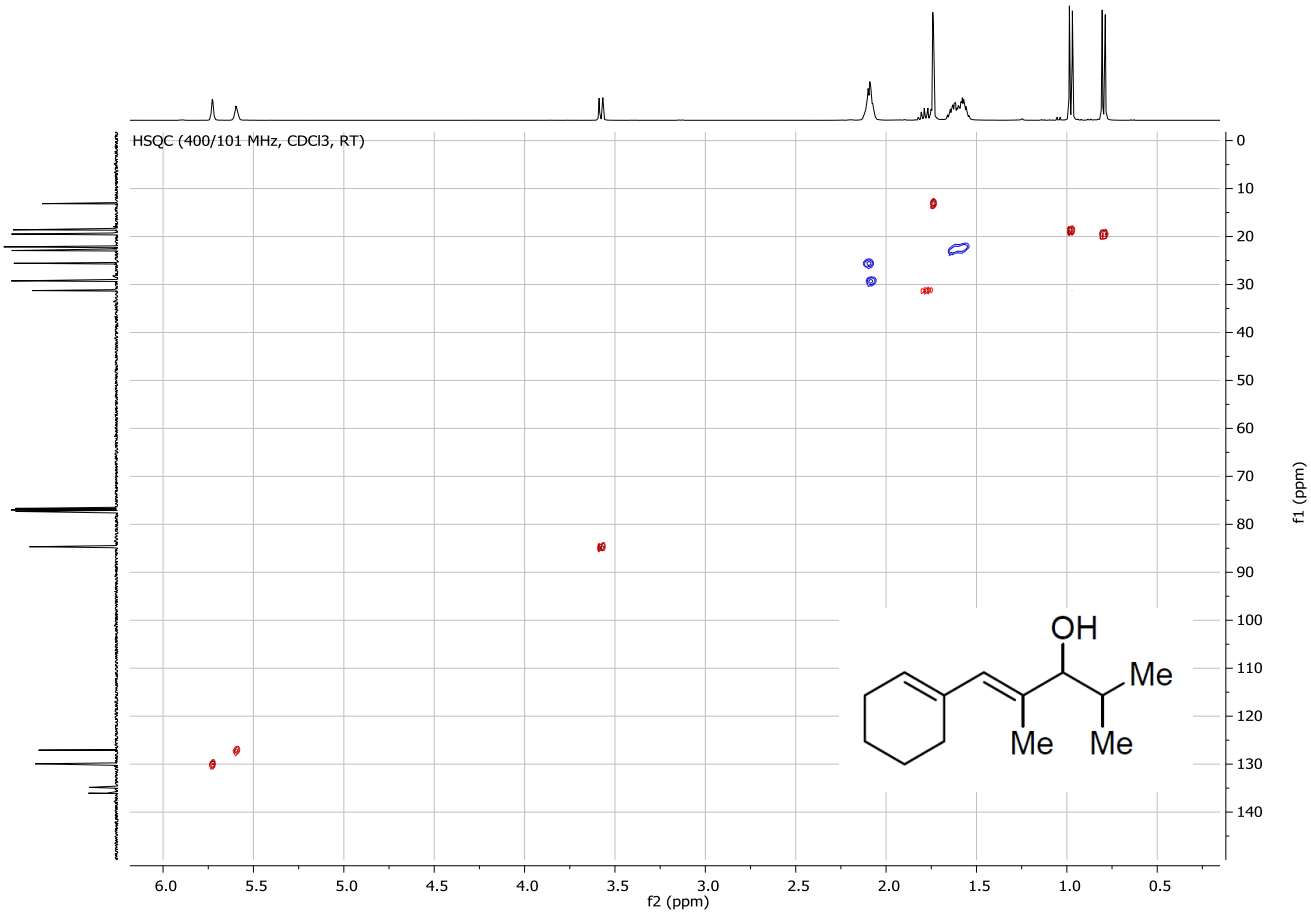


1H NMR (400 MHz, CDCl3, RT)

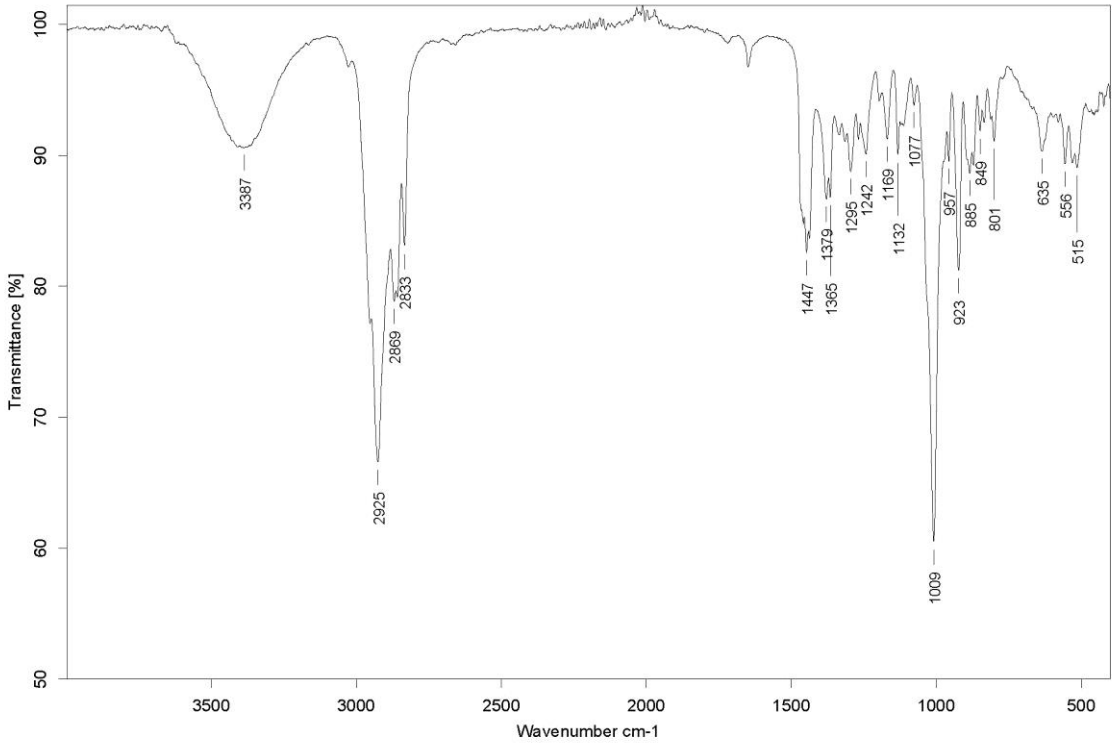


13C NMR (101 MHz, CDCl3, RT)

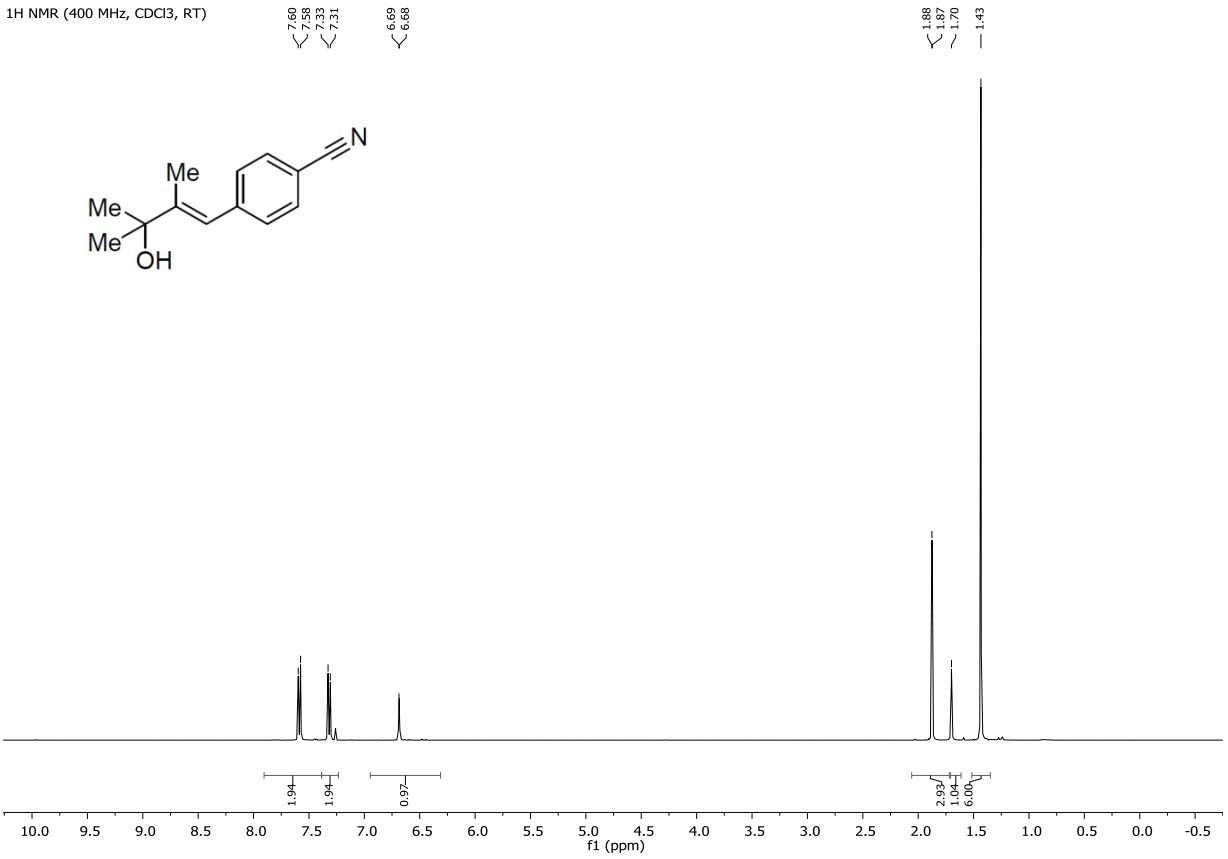




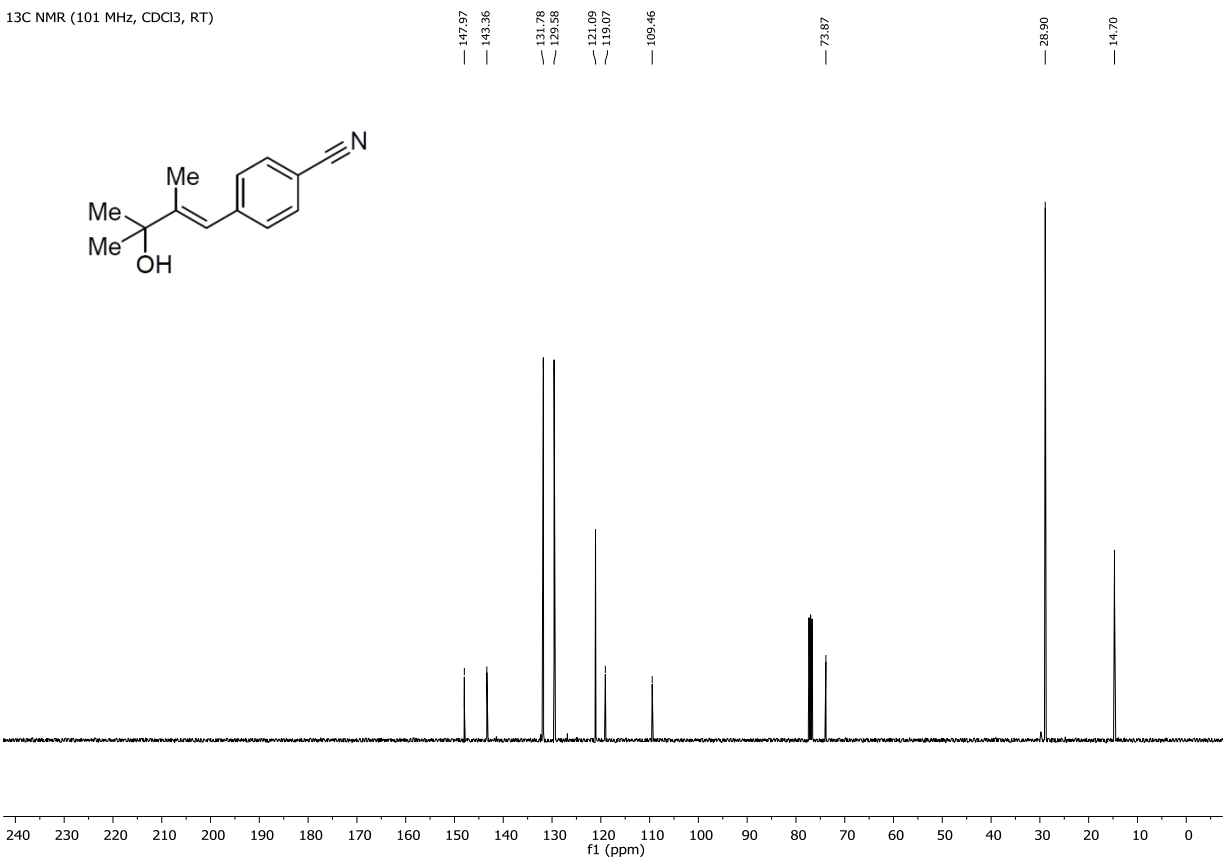
HUR-HA-088-12.0 **29.08.2016**

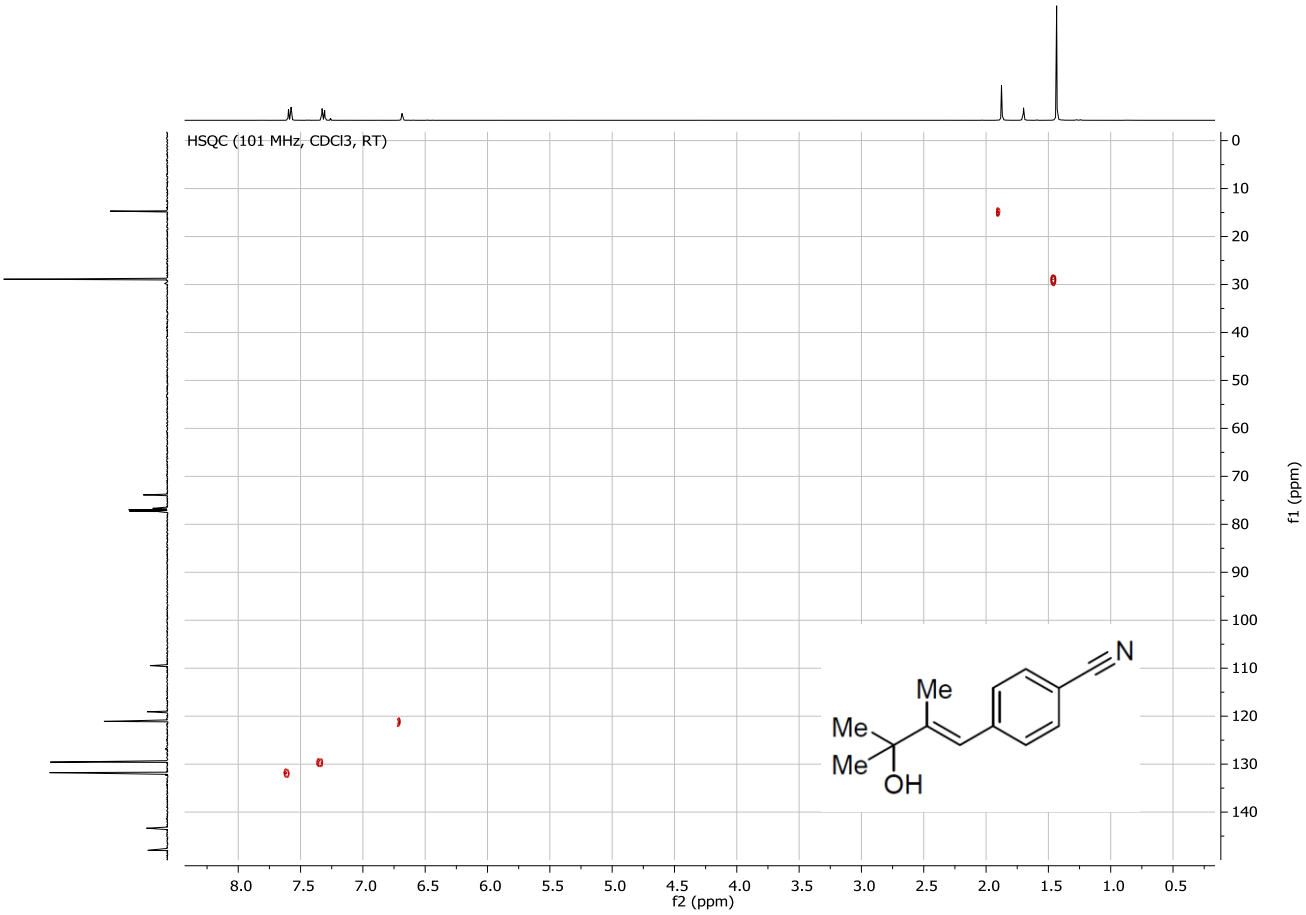


1H NMR (400 MHz, CDCl3, RT)

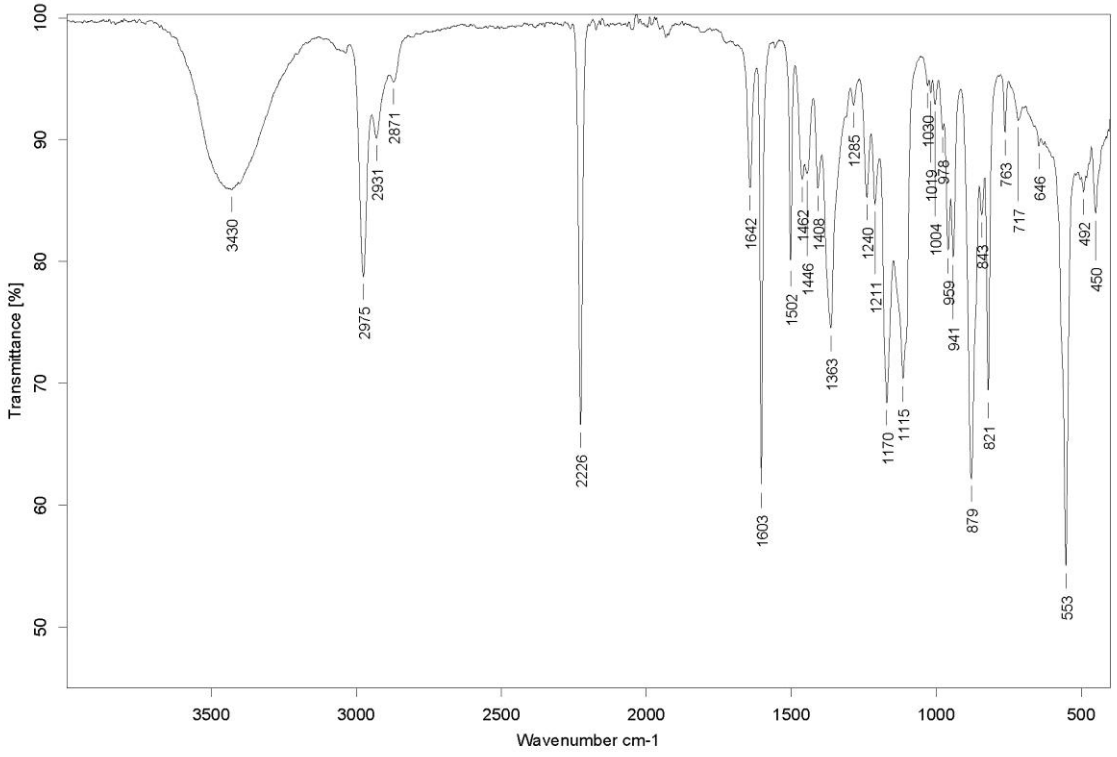


13C NMR (101 MHz, CDCl3, RT)

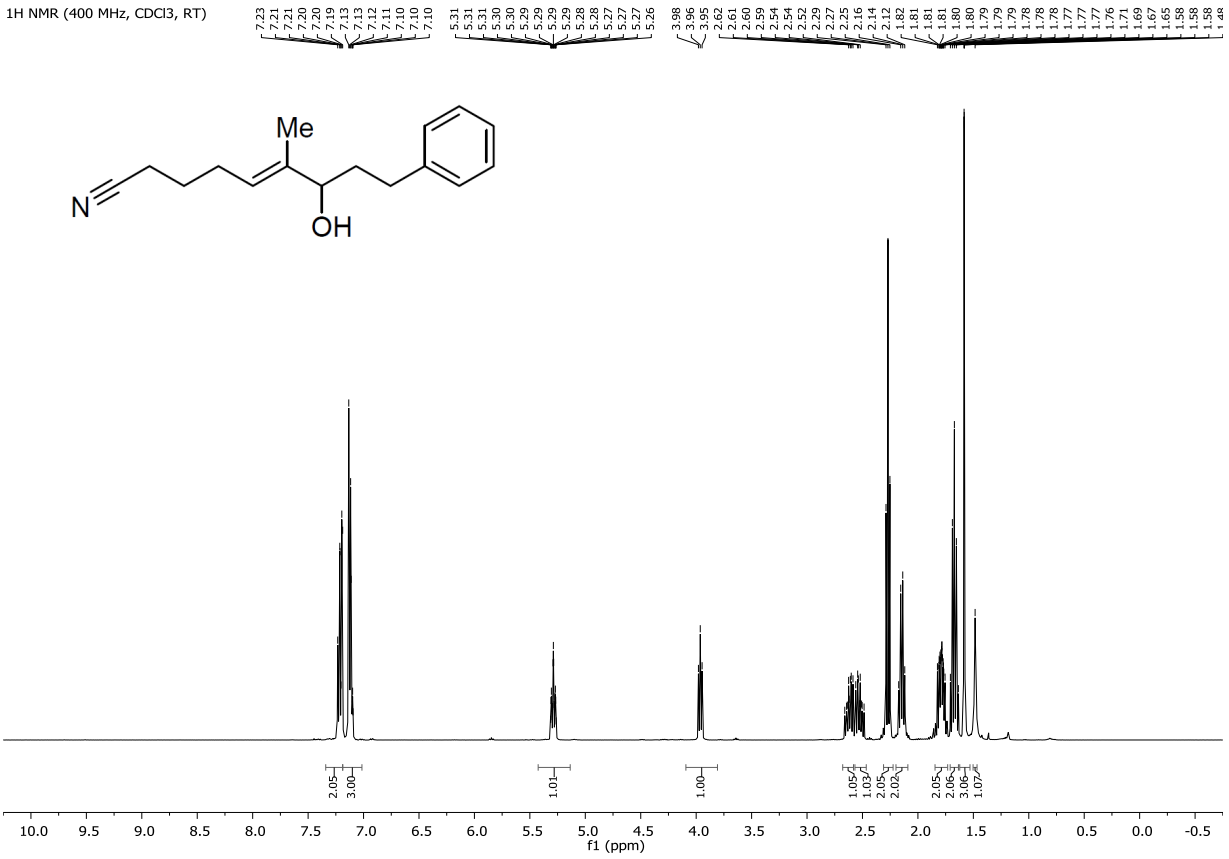




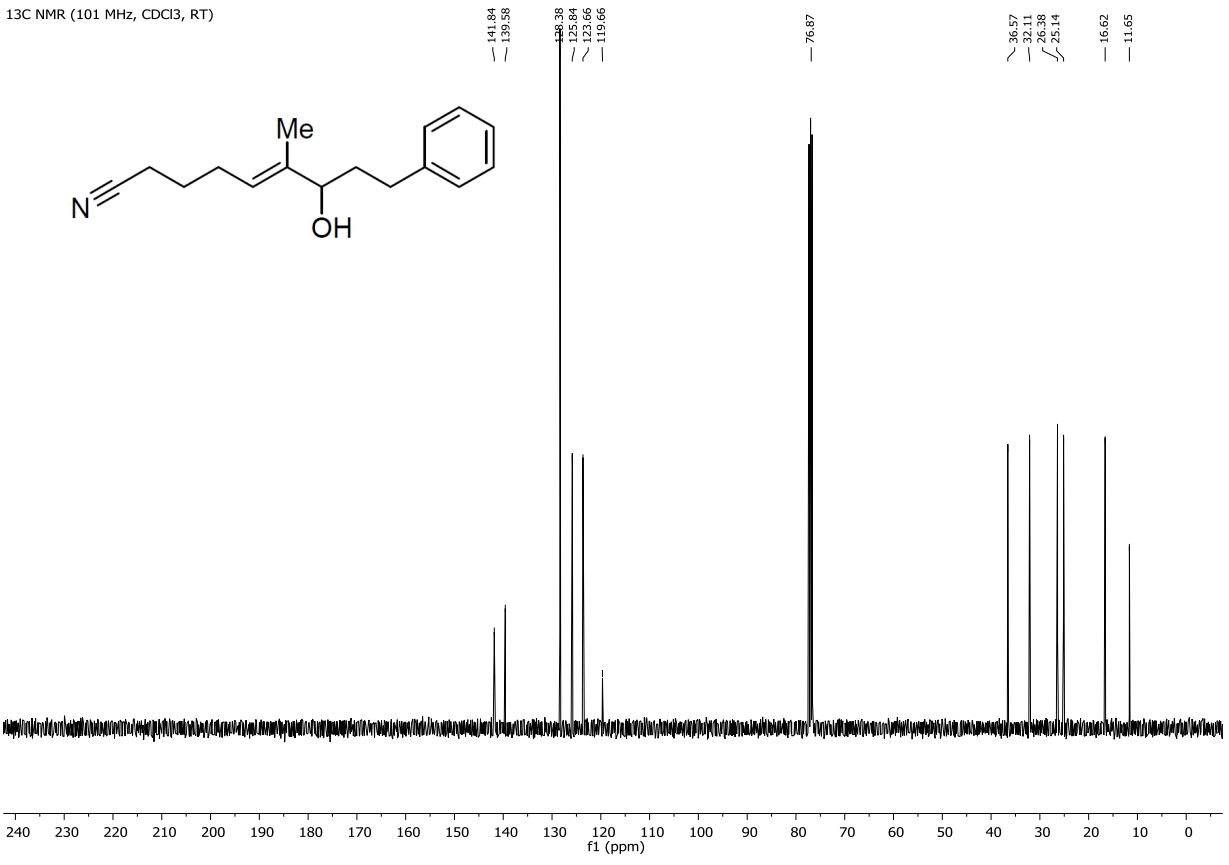
HUR-HA-081-12.0 **22.08.2016**

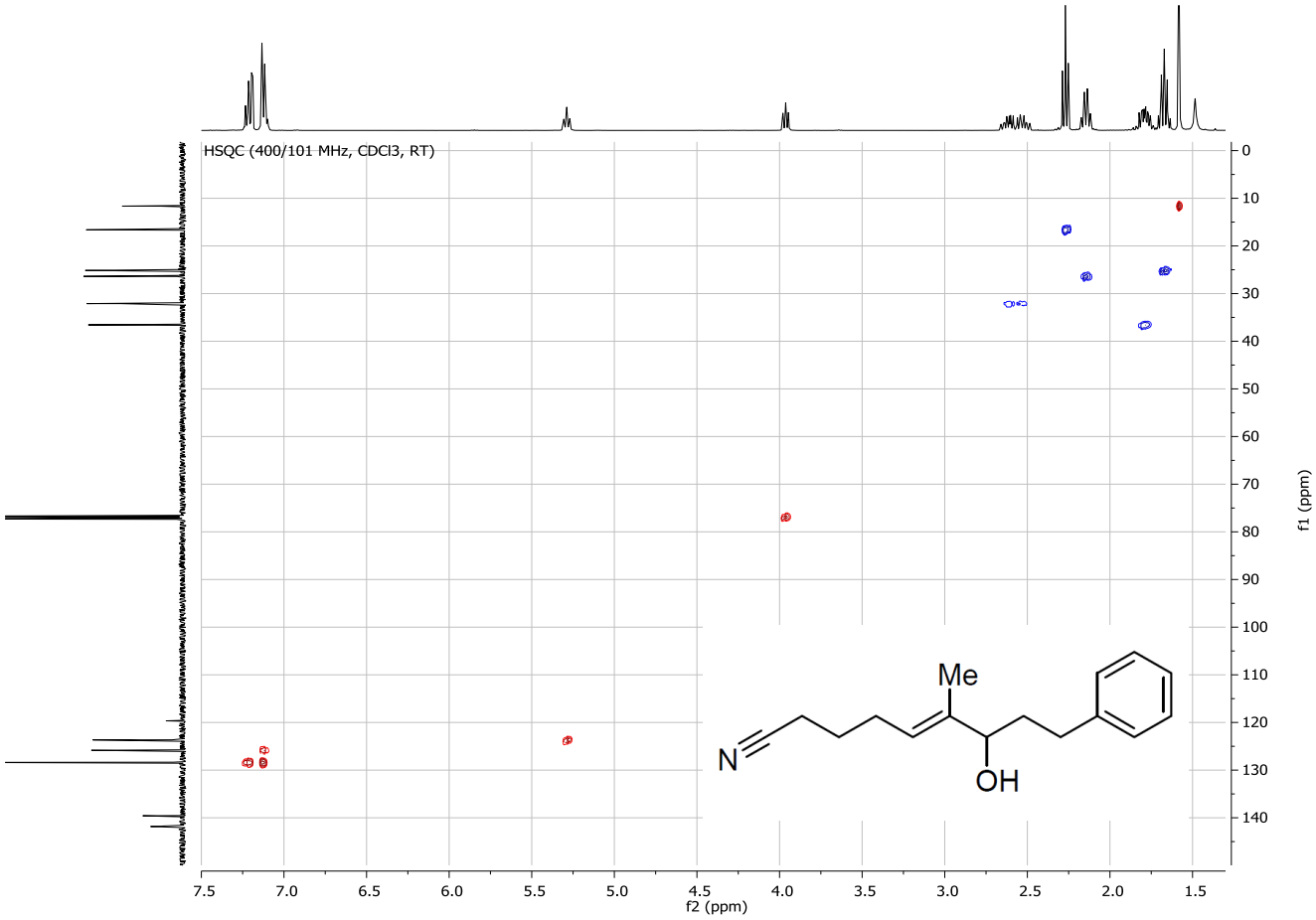


1H NMR (400 MHz, CDCl3, RT)

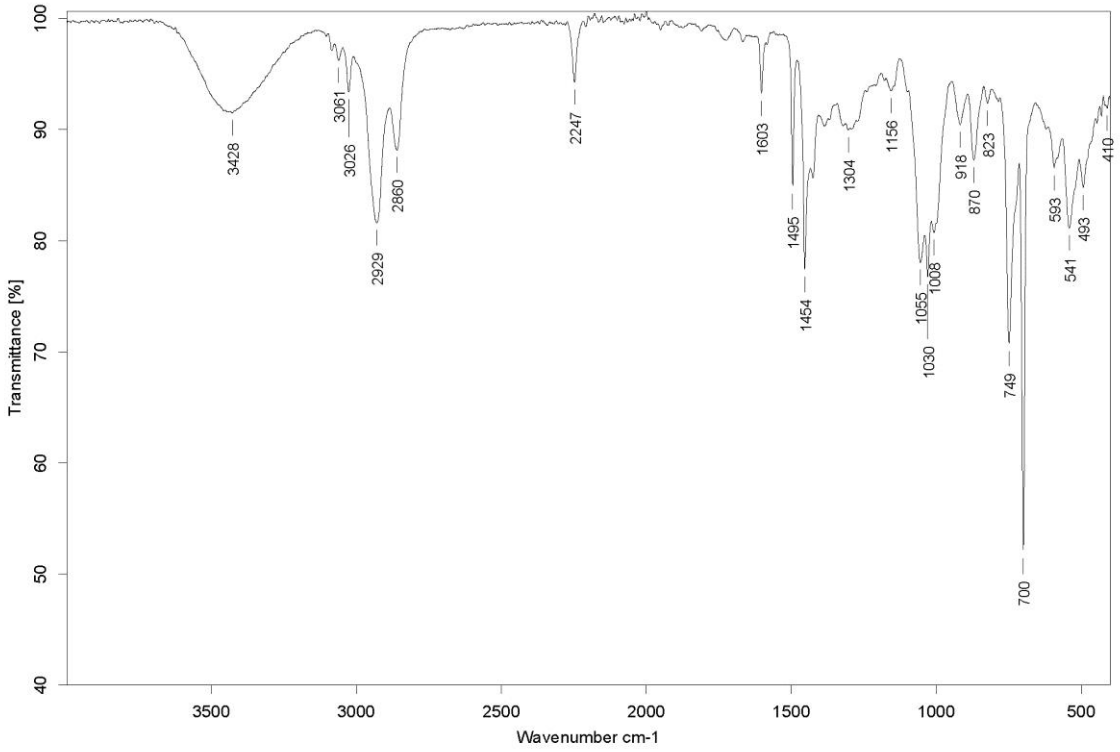


13C NMR (101 MHz, CDCl3, RT)

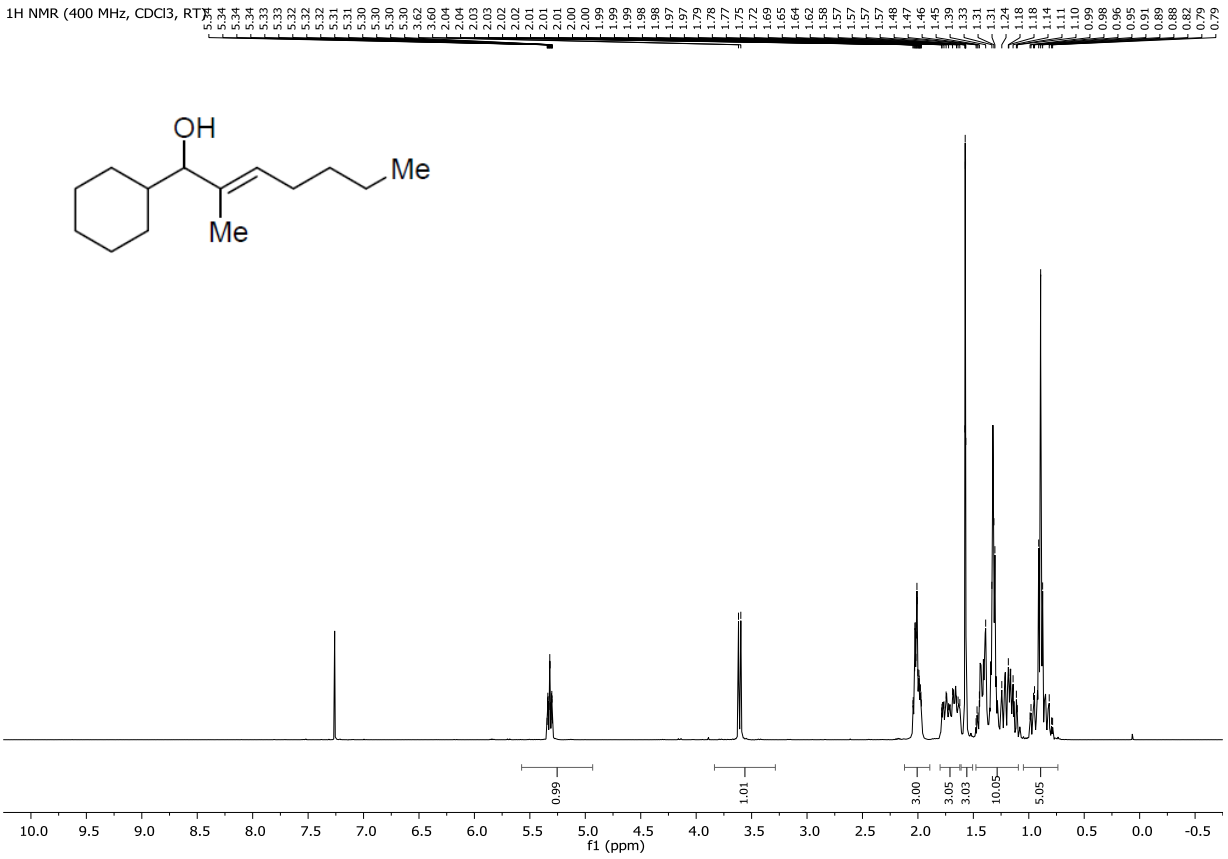




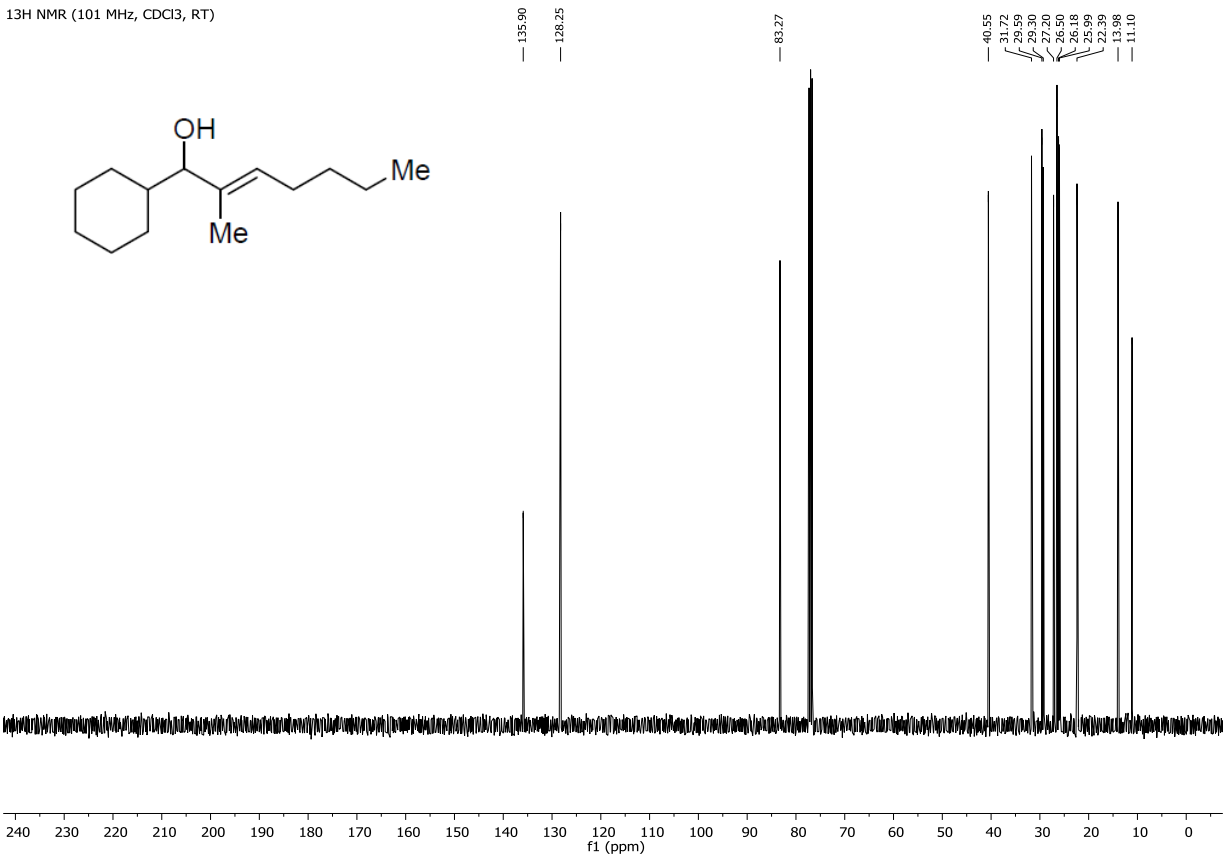
HUR-HA-091-12 FTIR.0 **02.09.2016**

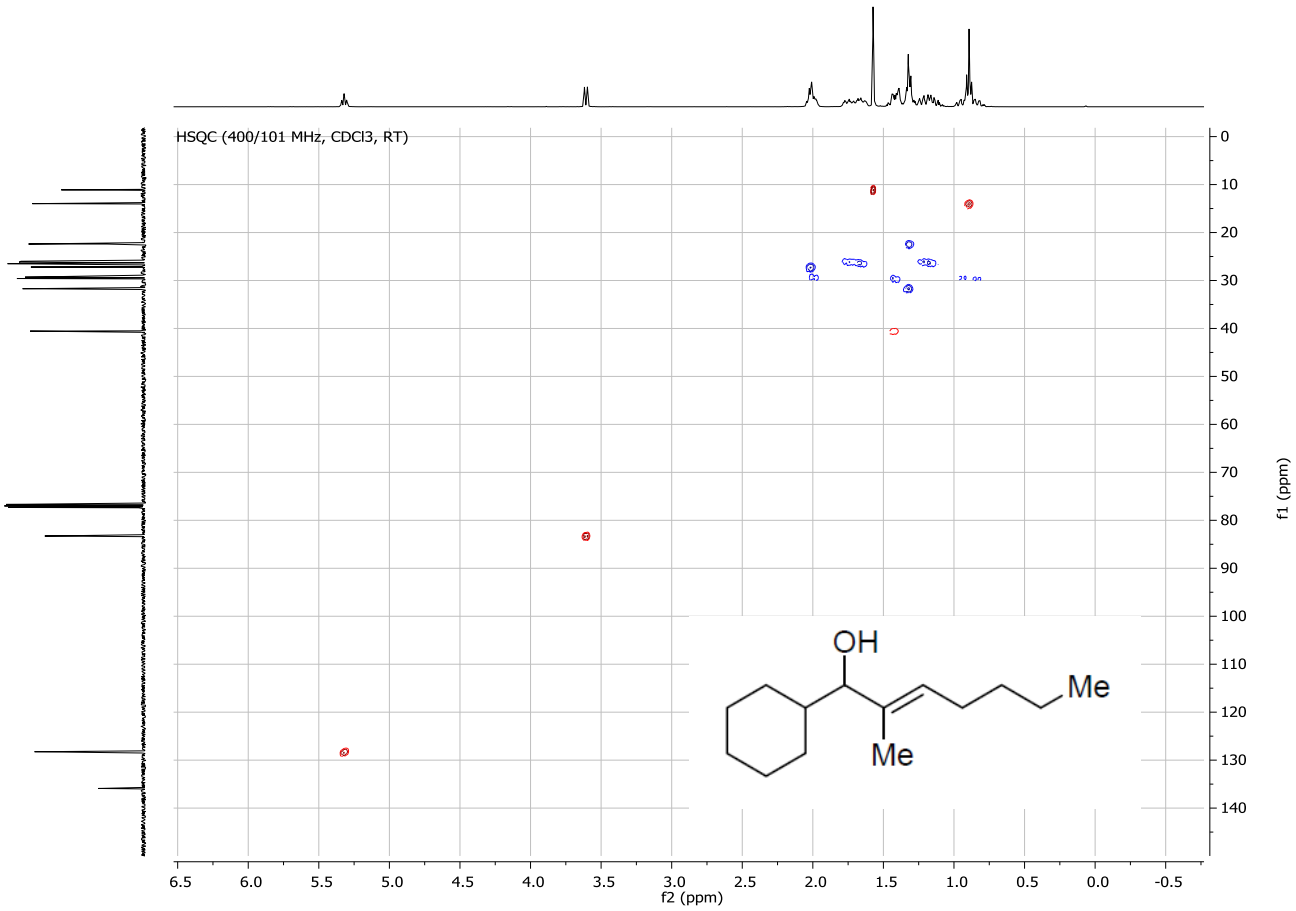


1H NMR (400 MHz, CDCl3, RT)

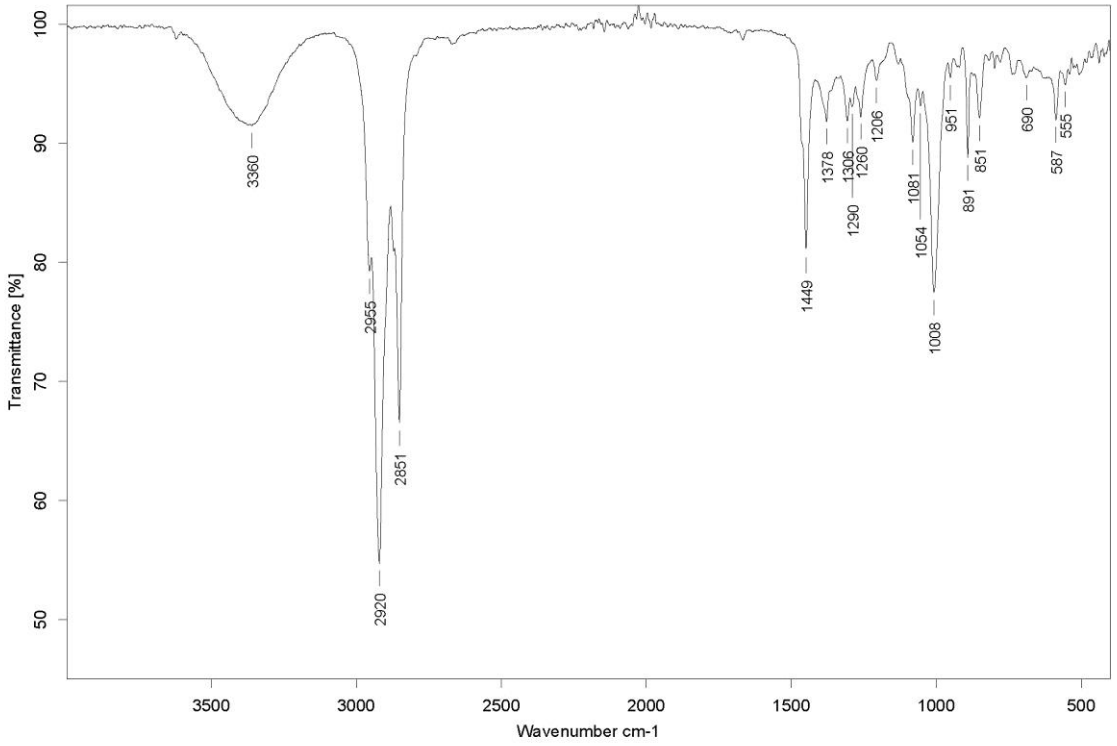


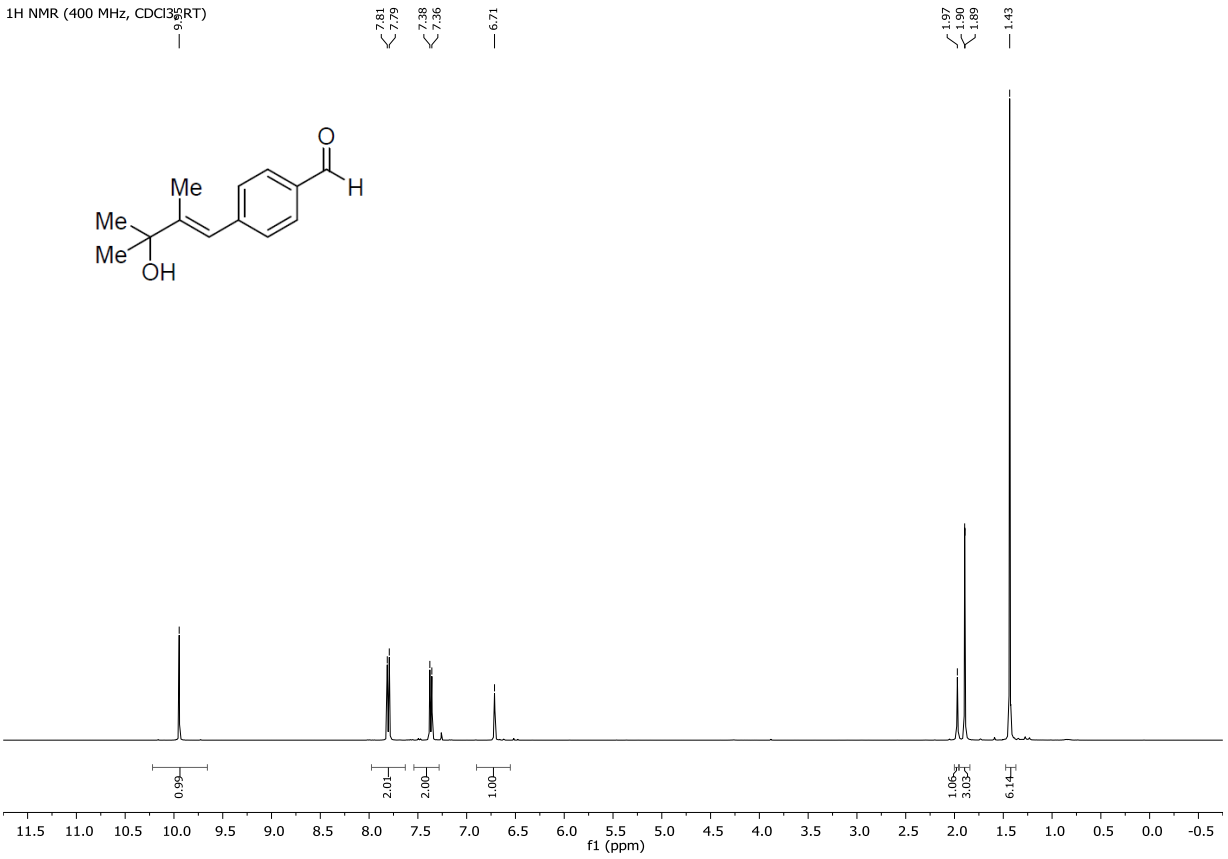
13H NMR (101 MHz, CDCl3, RT)

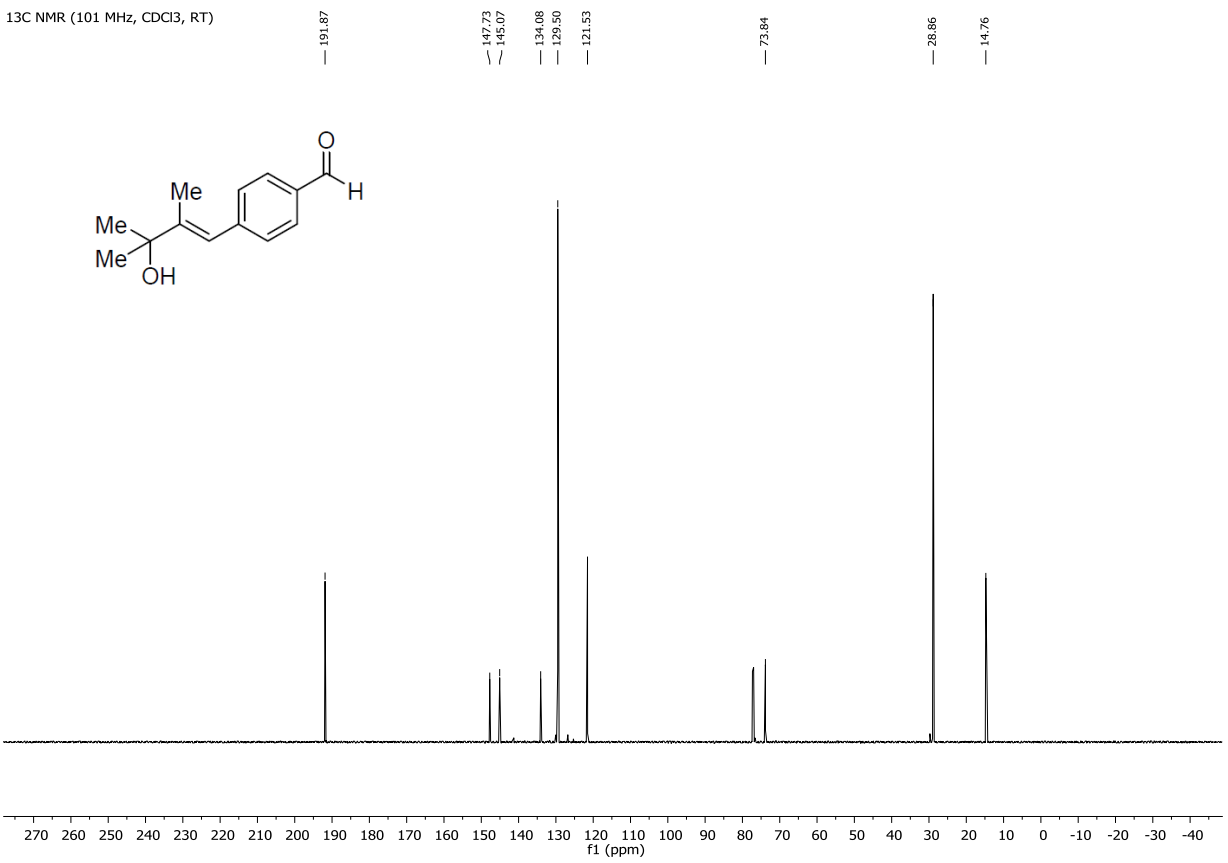


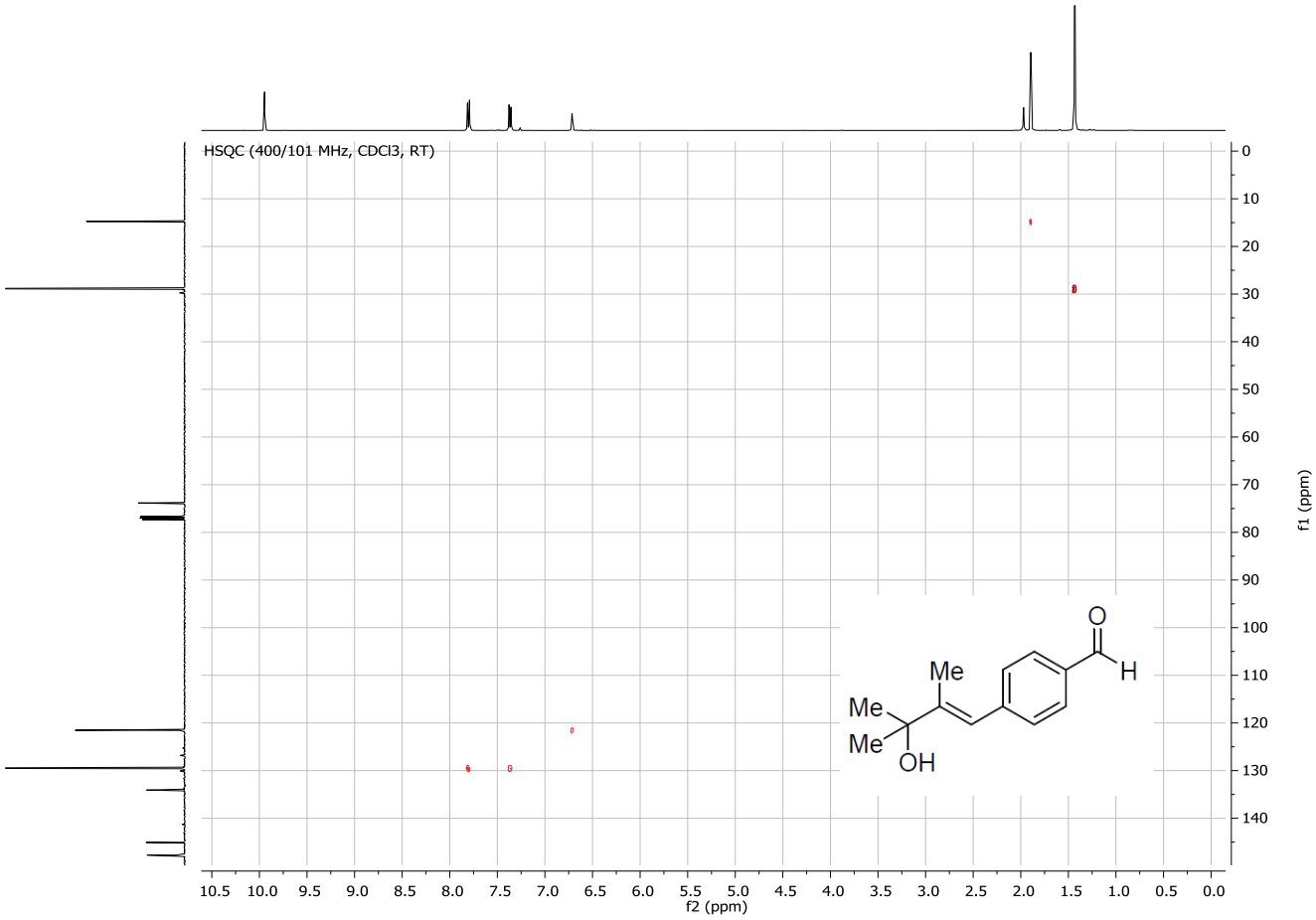


HUR-HA-119-12.0 **08.11.2016**

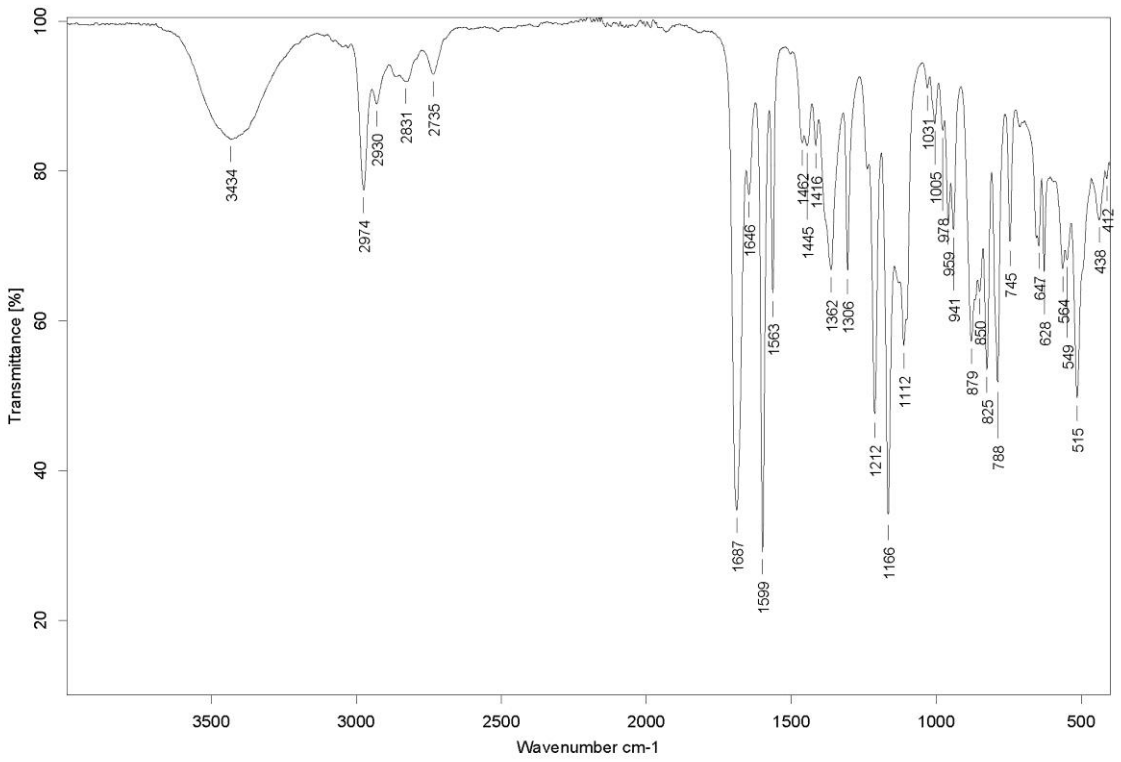



1H NMR (400 MHz, CDCl3, RT)
9.95
7.81
7.79
7.38
7.36
6.71
1.97
1.90
1.89
1.43
O
H
Me
Me
Me
OH
0.99
2.01
2.00
1.00
1.06
3.03
6.14
f1 (ppm)

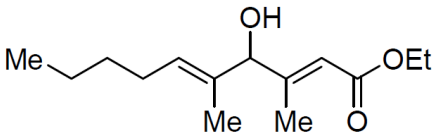

13C NMR (101 MHz, CDCl3, RT)
191.87
147.73
145.07
134.08
129.50
121.53
73.84
28.86
14.76
O
H
Me
Me
Me
OH
f1 (ppm)

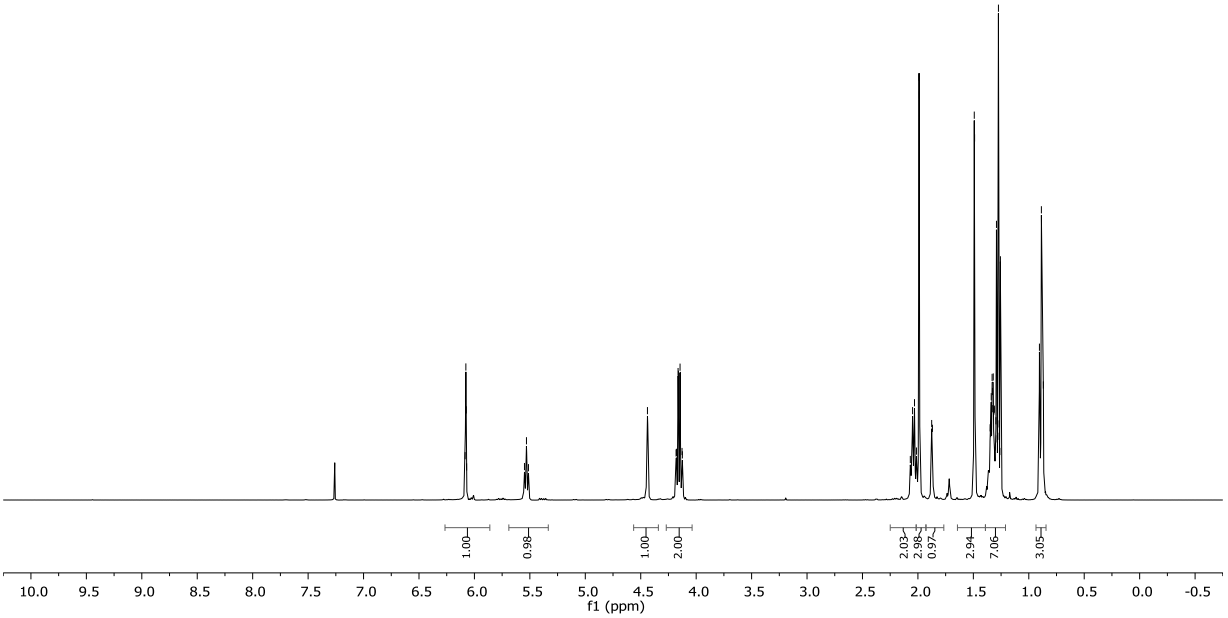


HUR-HA-082-11.0 **23.08.2016**

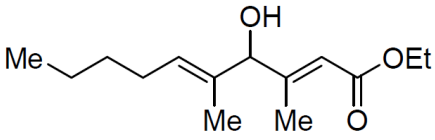


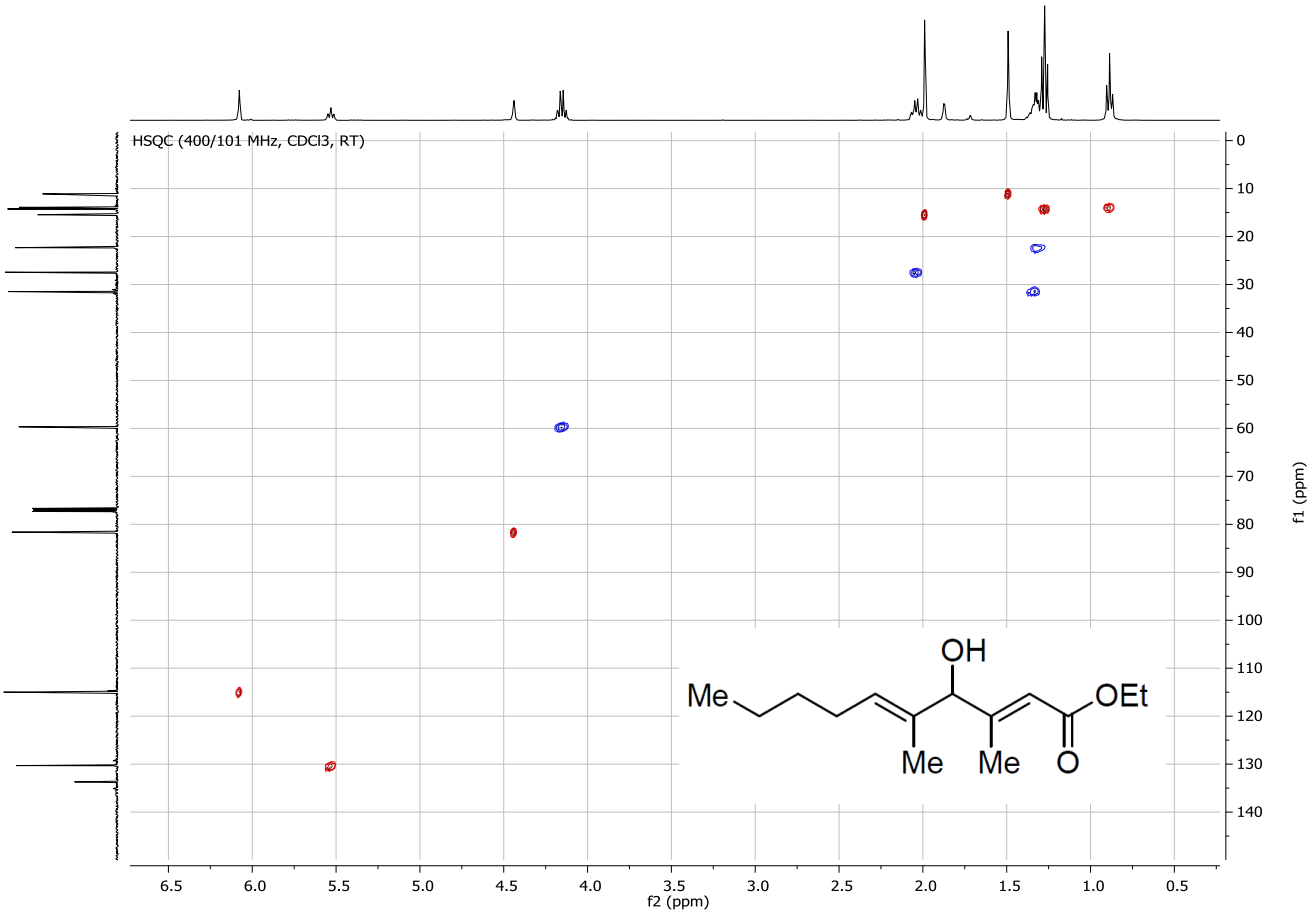
1H NMR (400 MHz, CDCl3, RT)



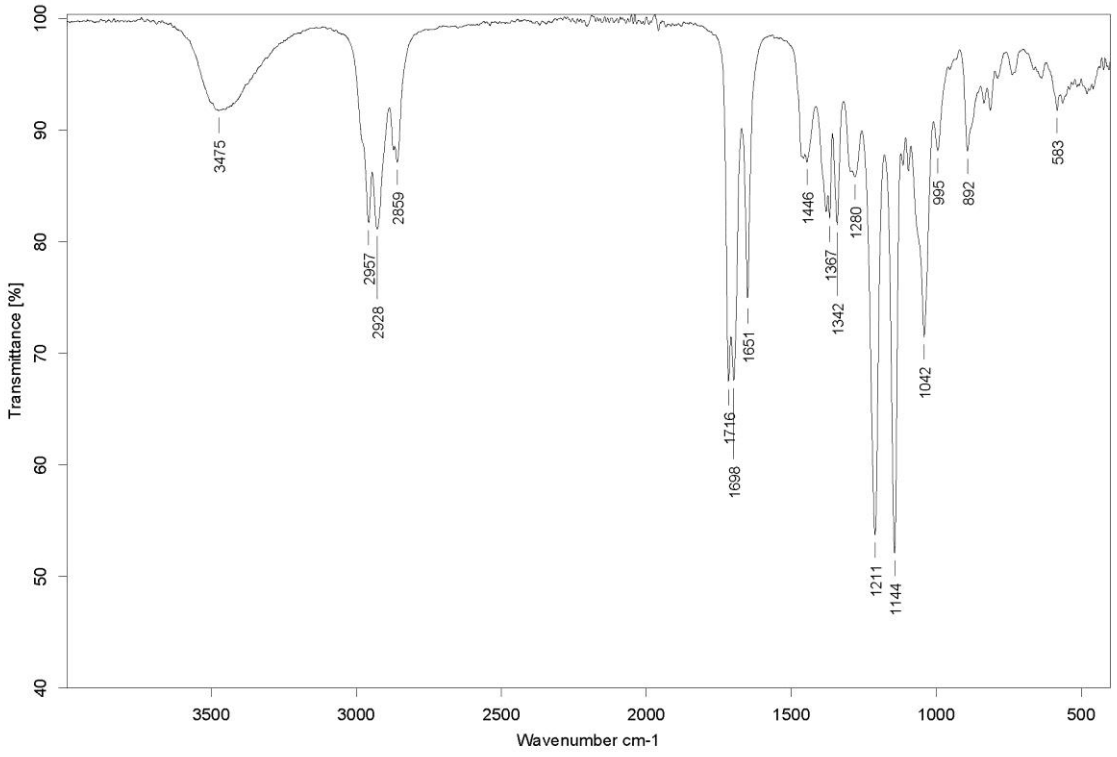


13C NMR (101 MHz, CDCl3, RT)

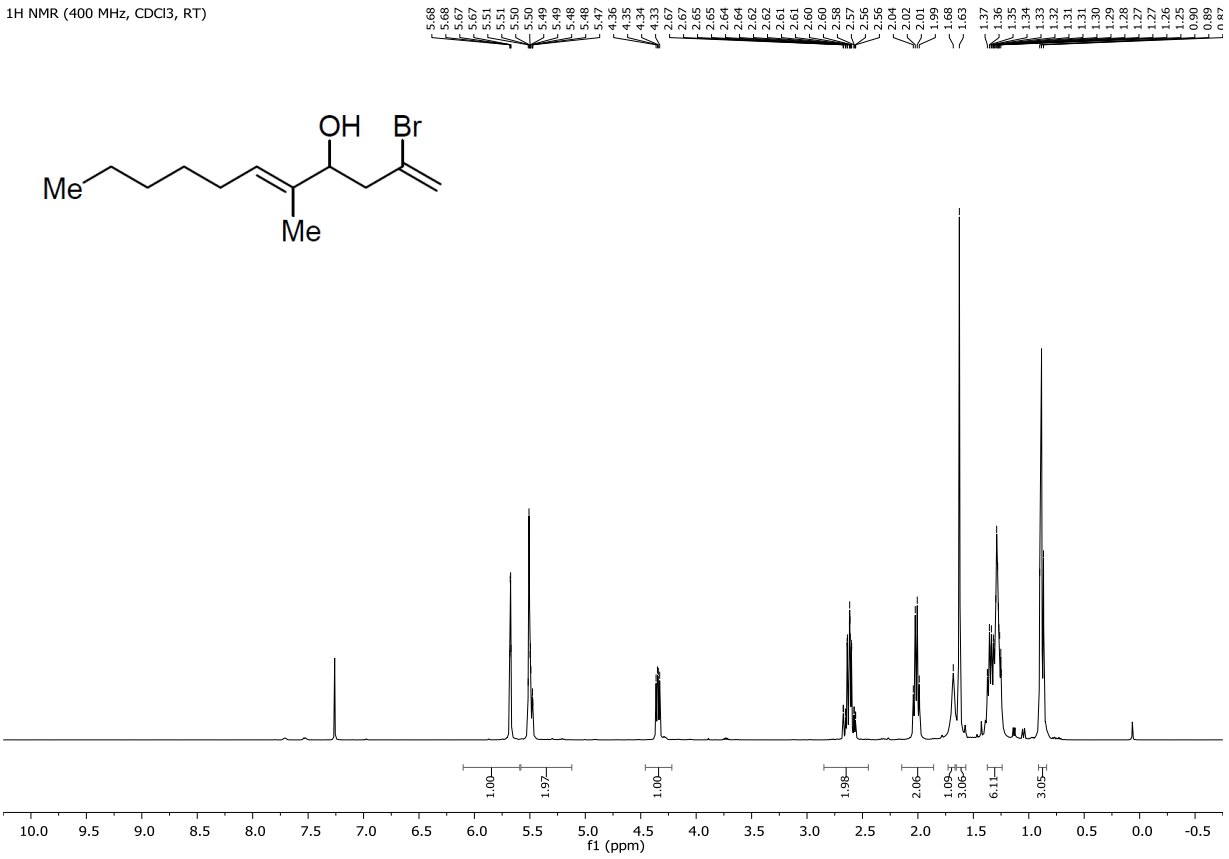




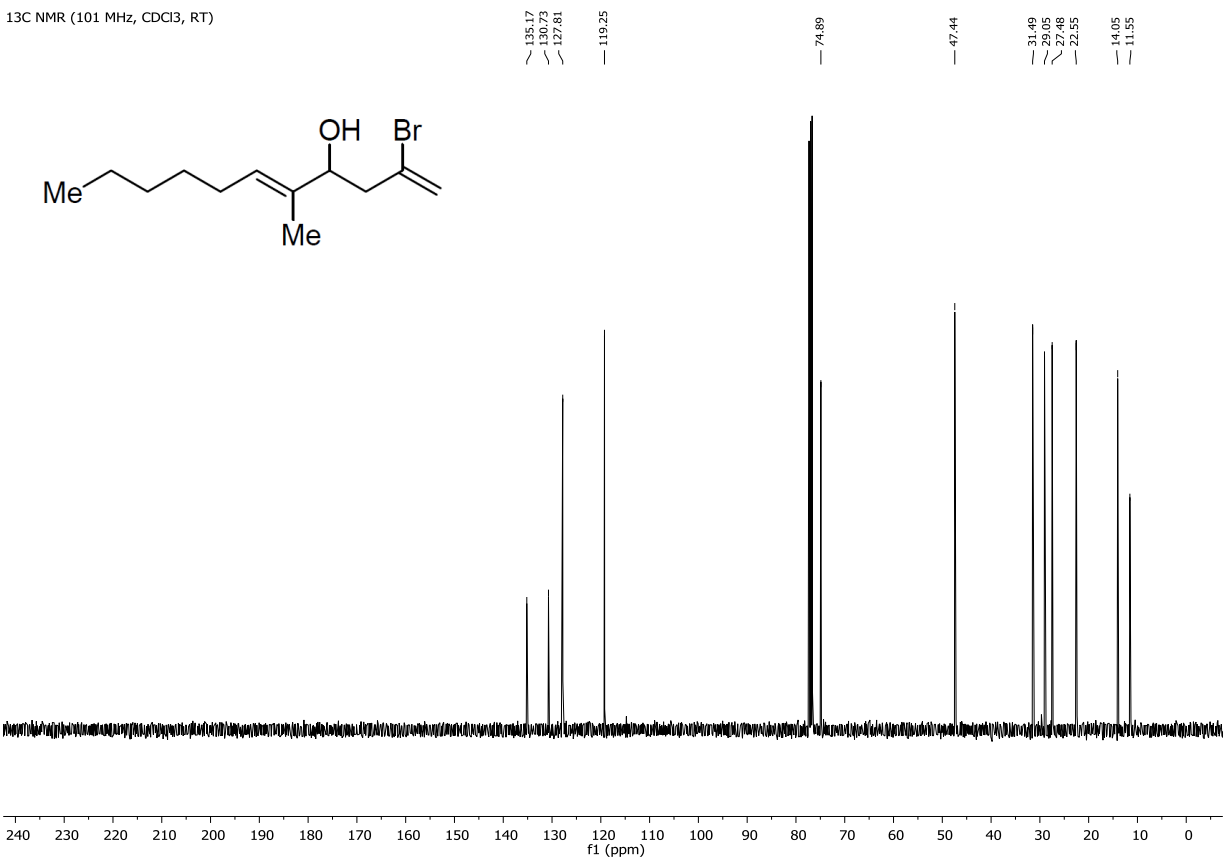
HUR-HA-085-11.0 **24.08.2016**

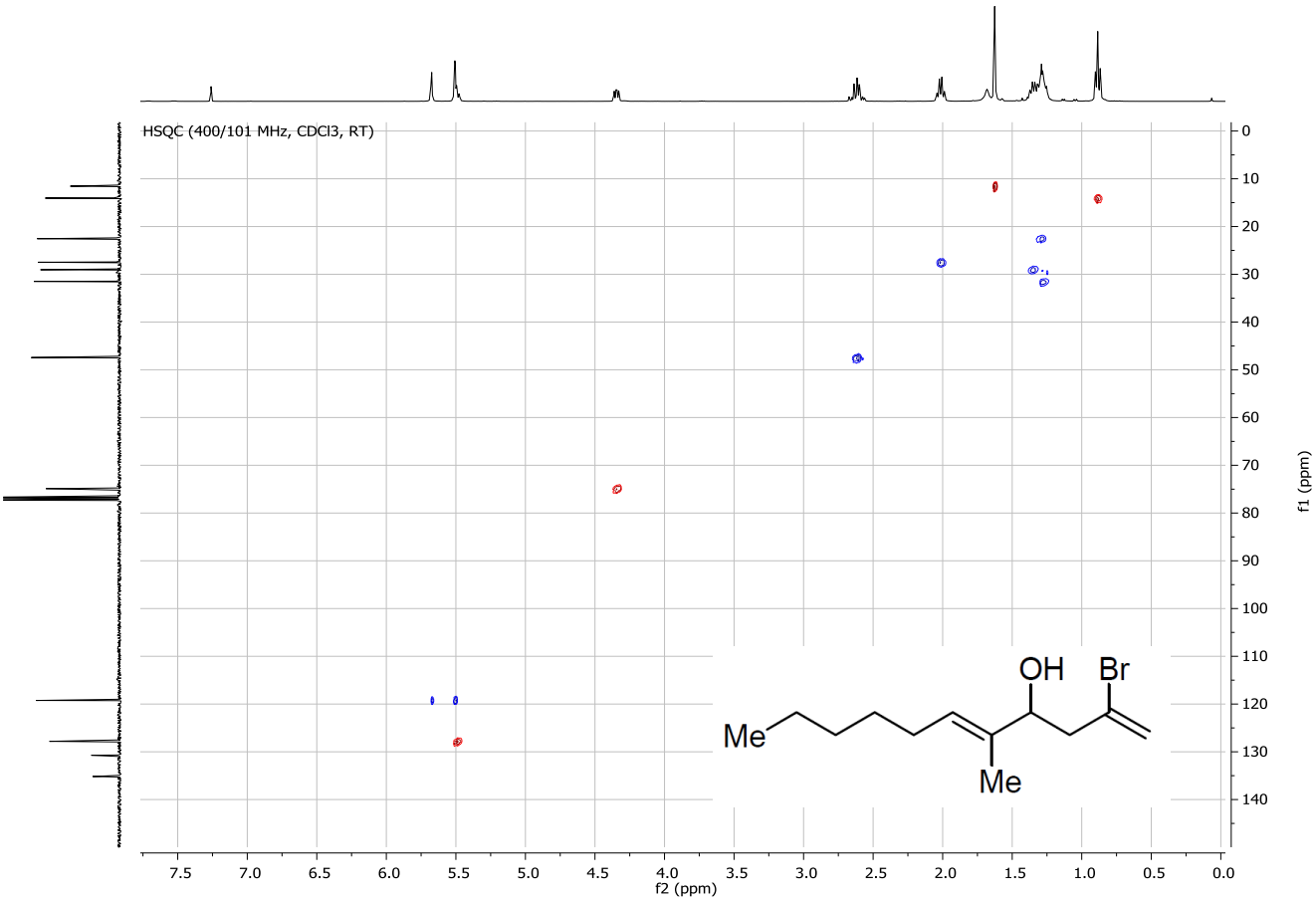


1H NMR (400 MHz, CDCl3, RT)

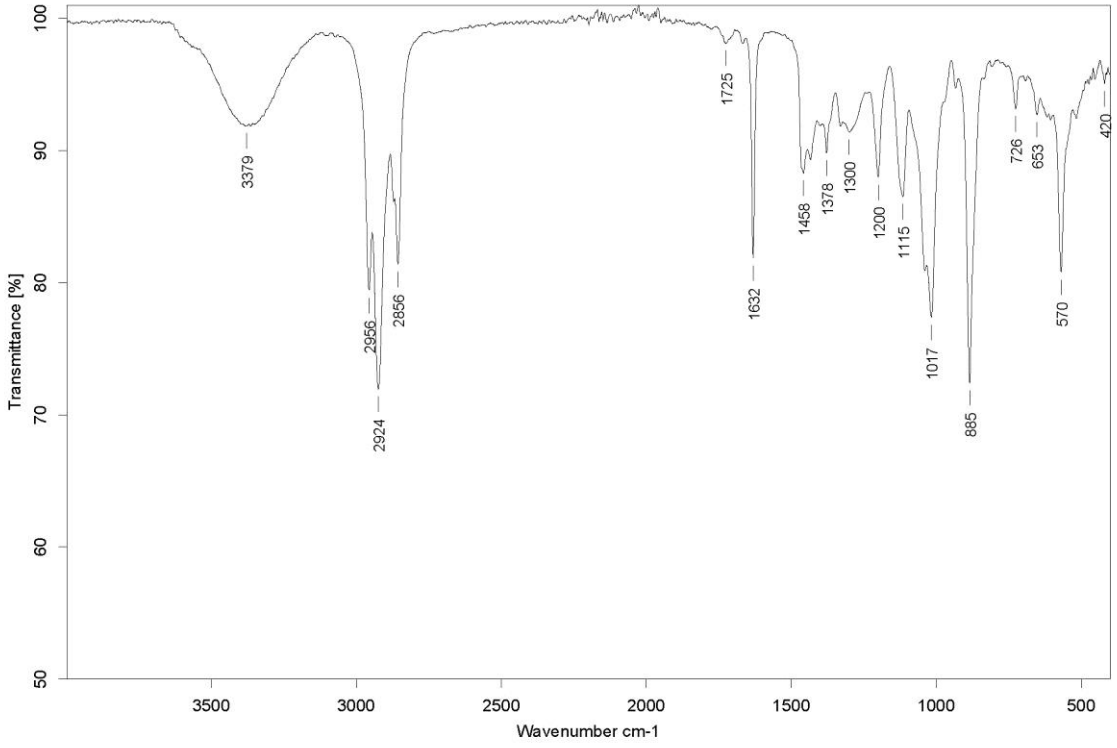


13C NMR (101 MHz, CDCl3, RT)

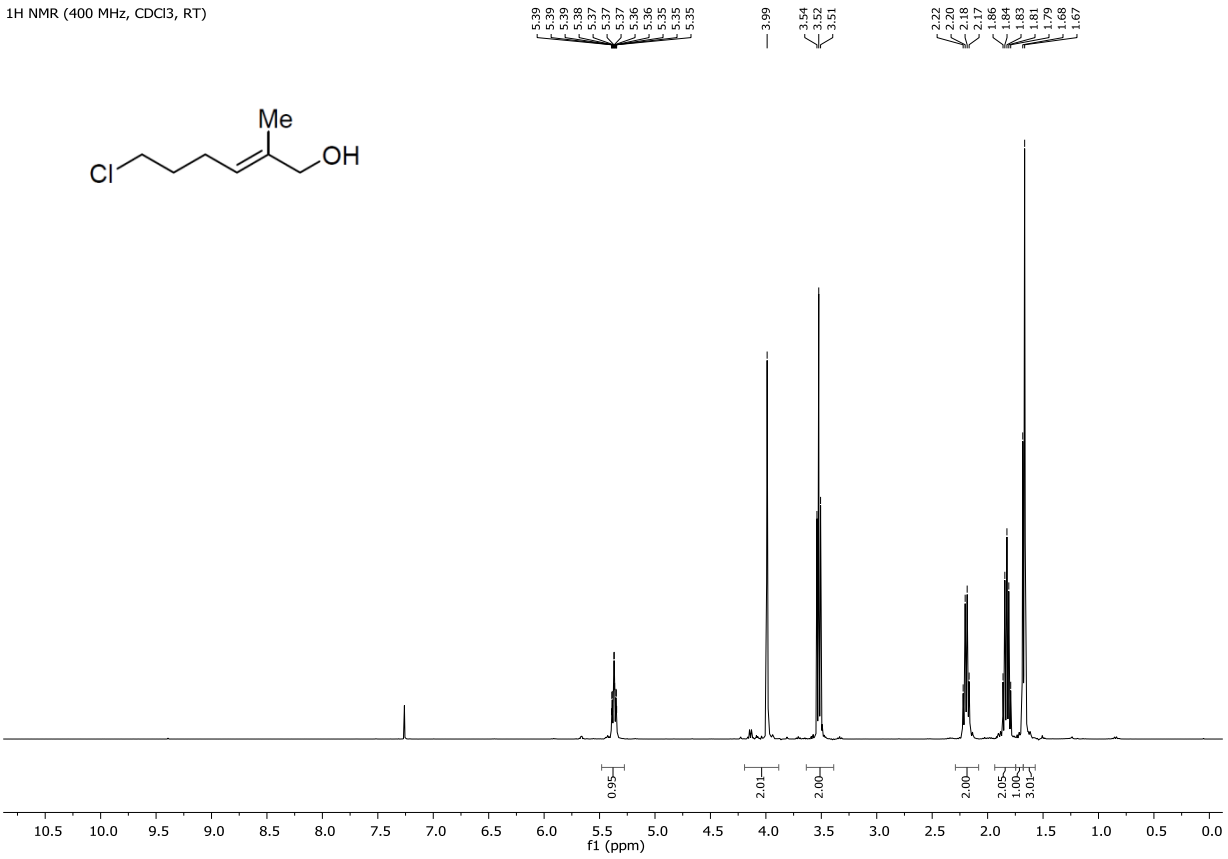




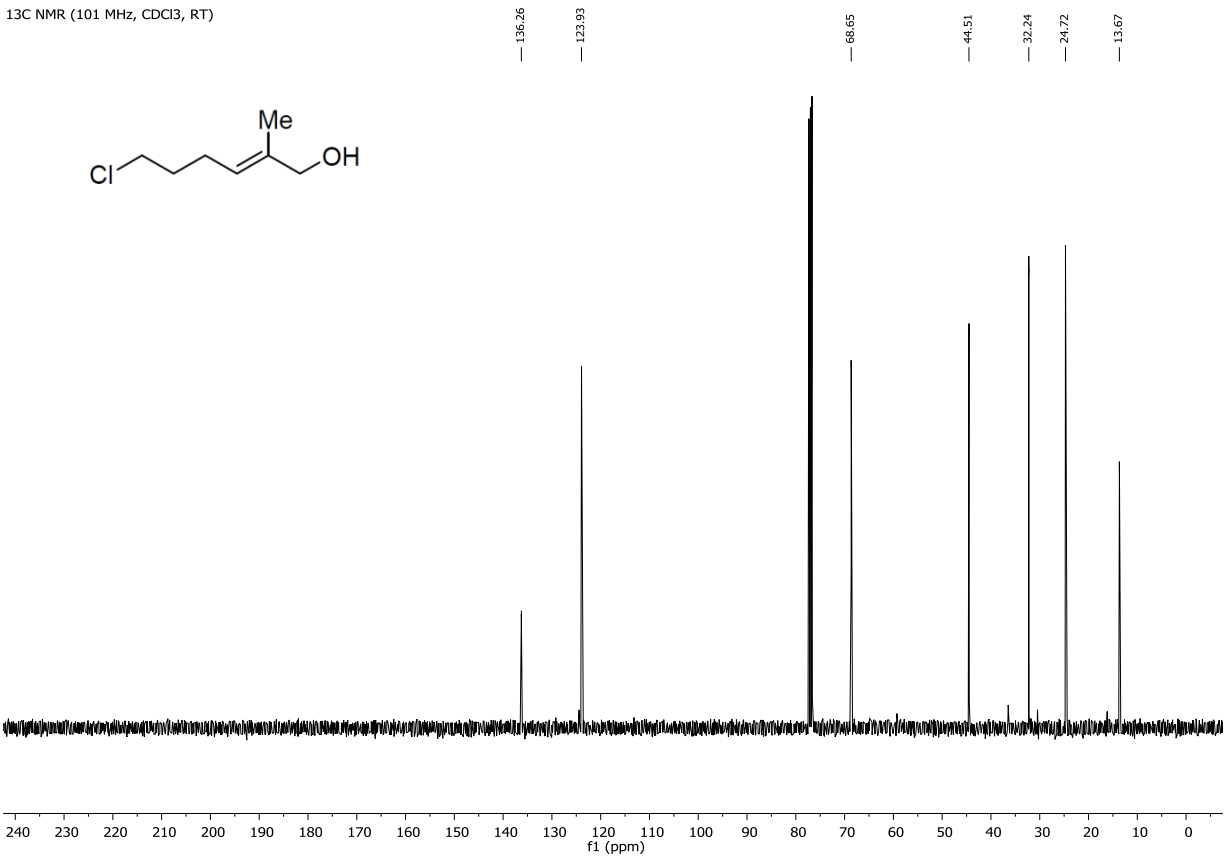
HUR-HA-096-11.0 **22.09.2016**

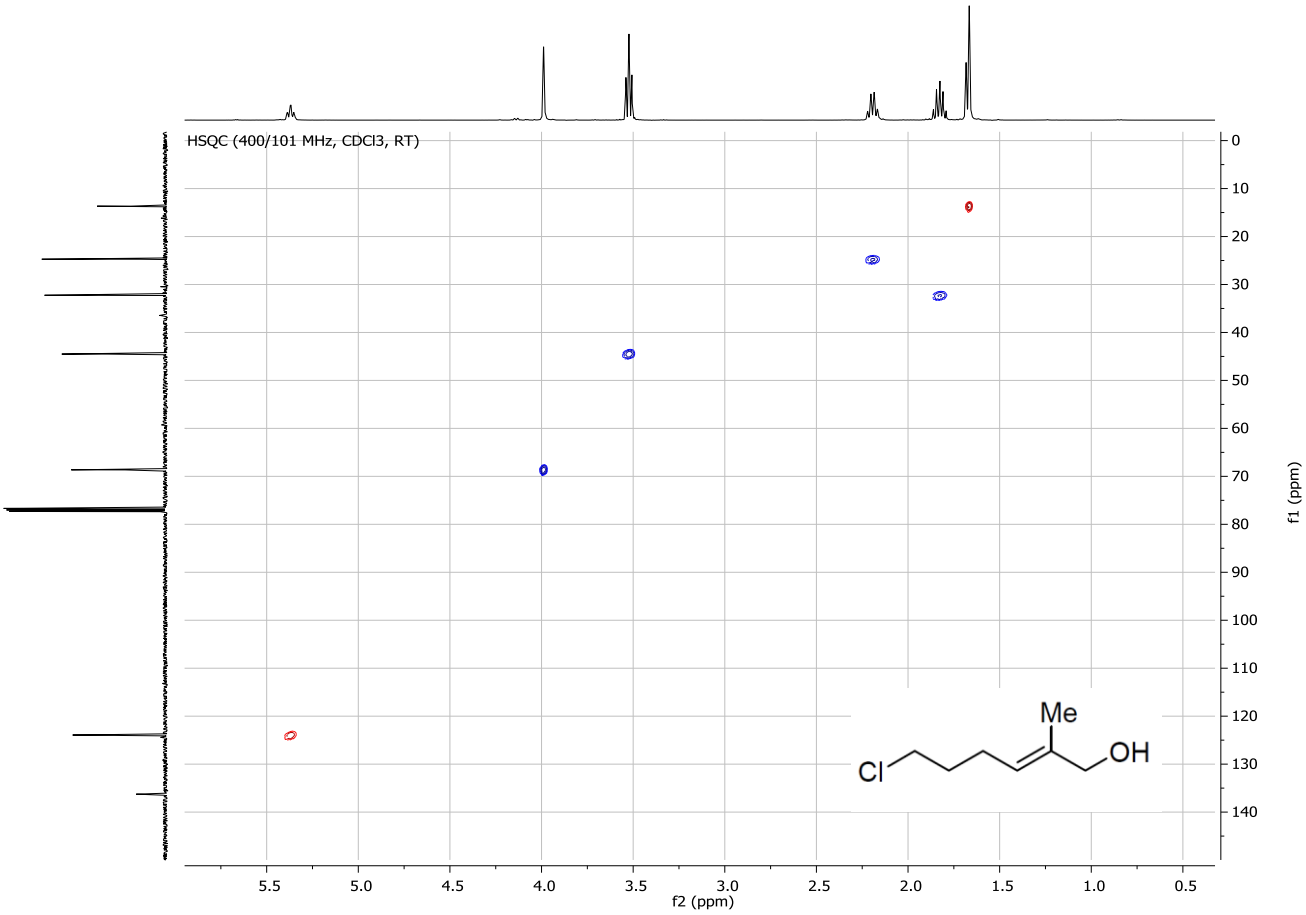


1H NMR (400 MHz, CDCl3, RT)

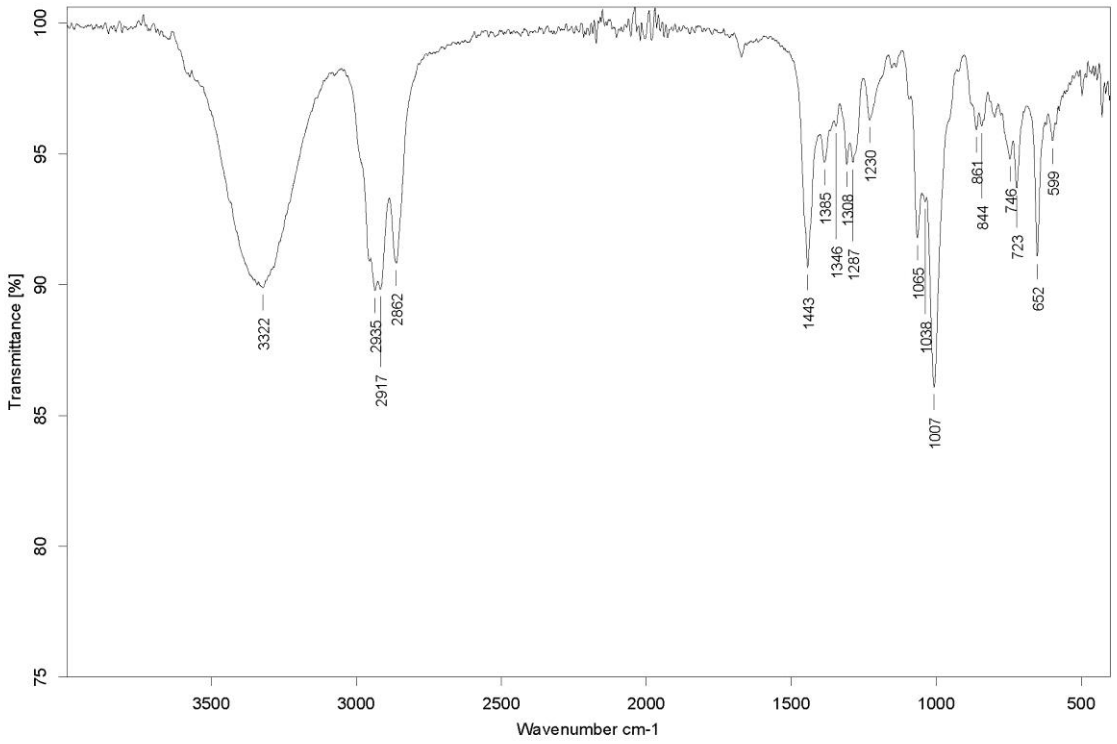


13C NMR (101 MHz, CDCl3, RT)

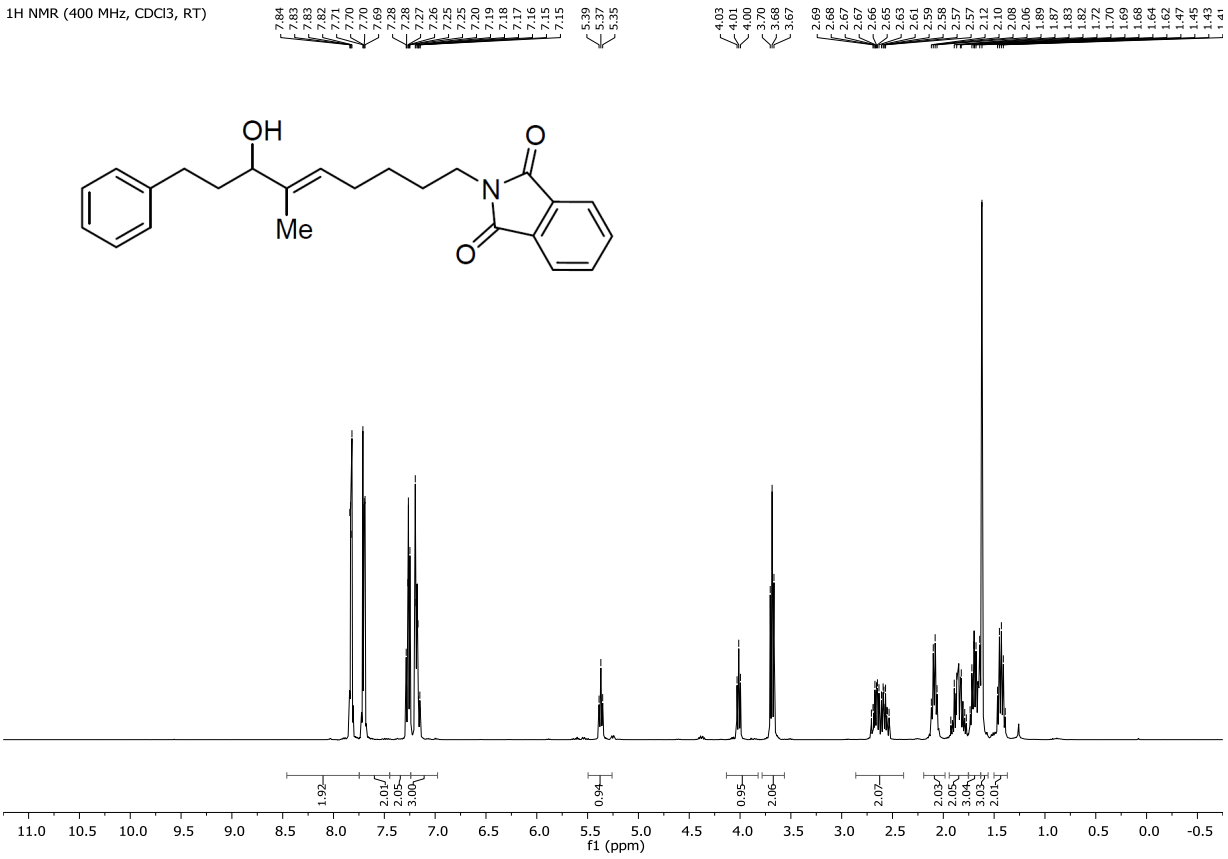




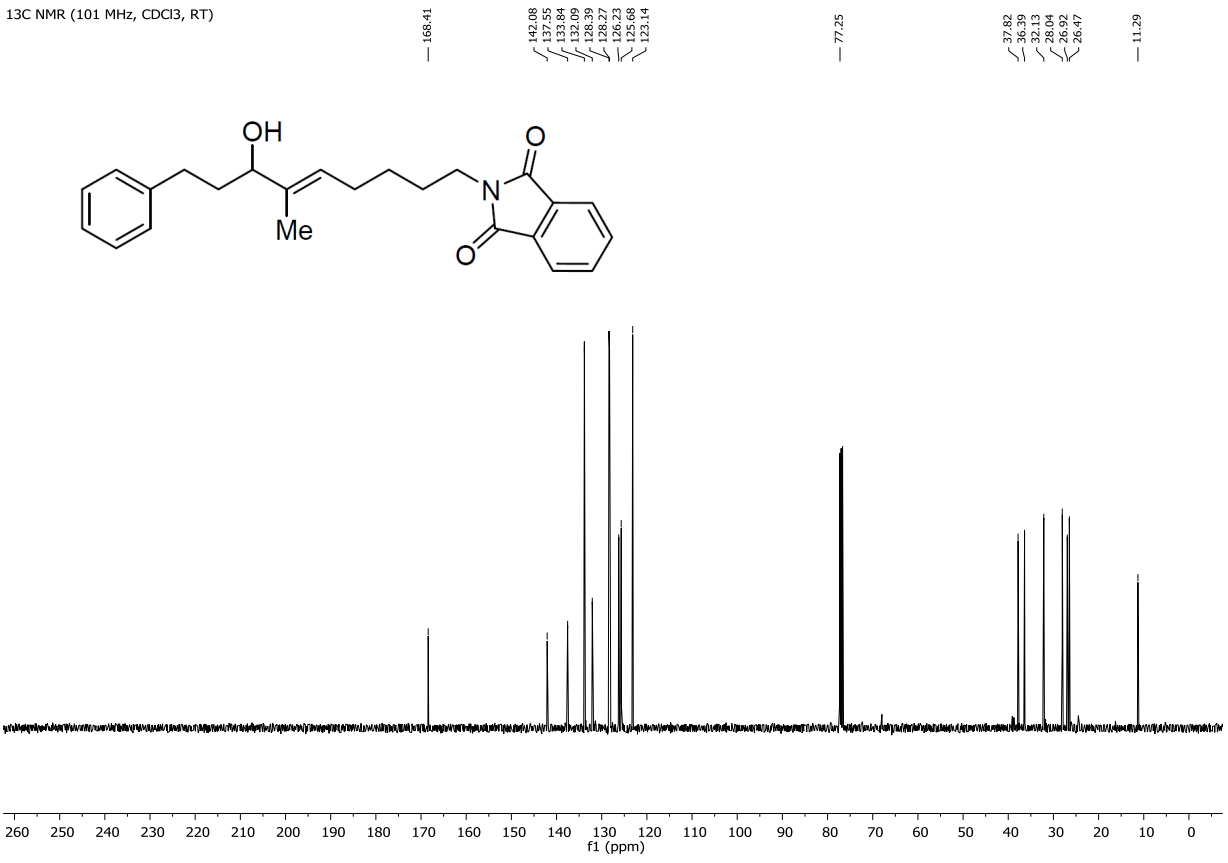
HUR-HA-118-12.0 **27.10.2016**

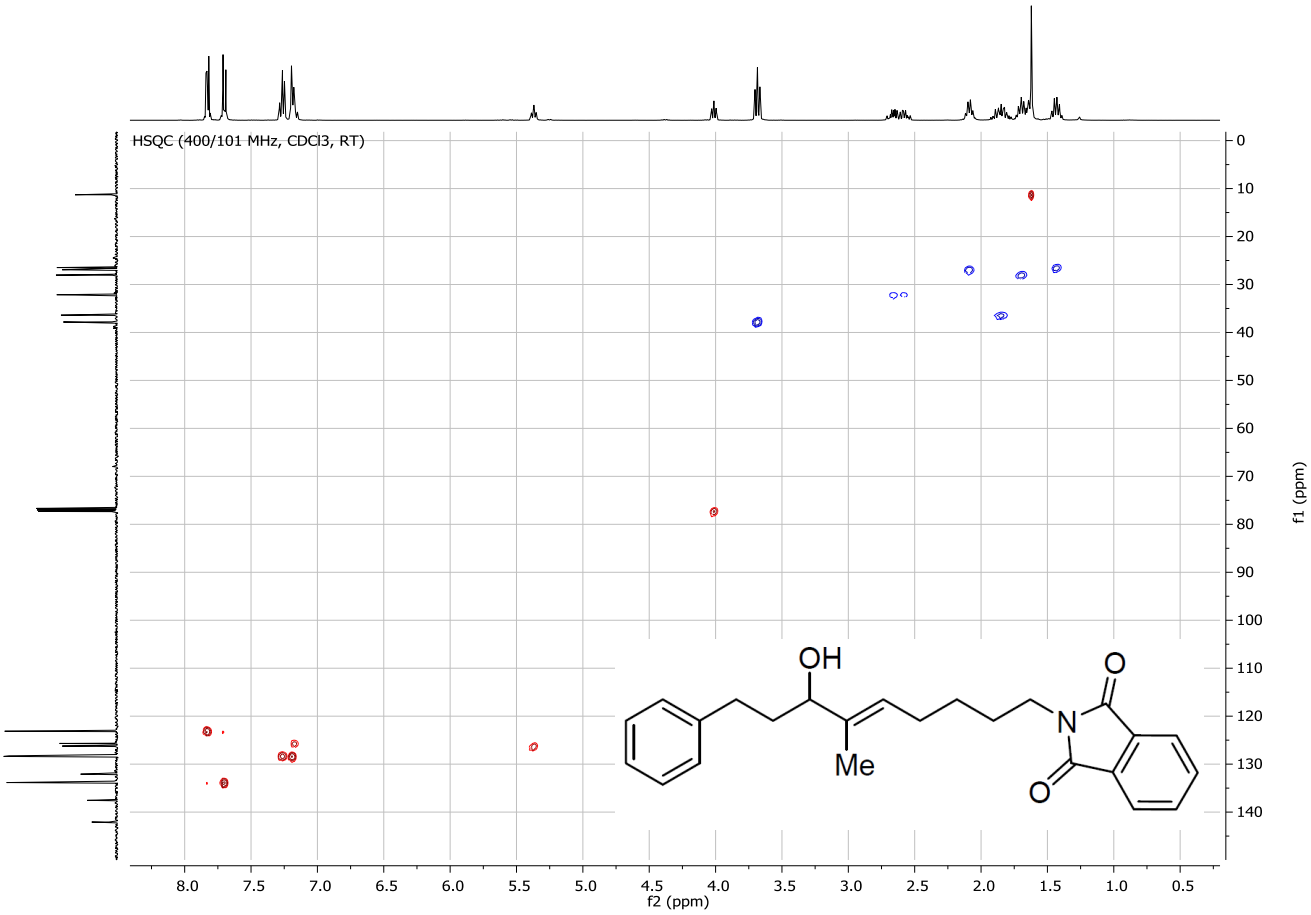


1H NMR (400 MHz, CDCl3, RT)

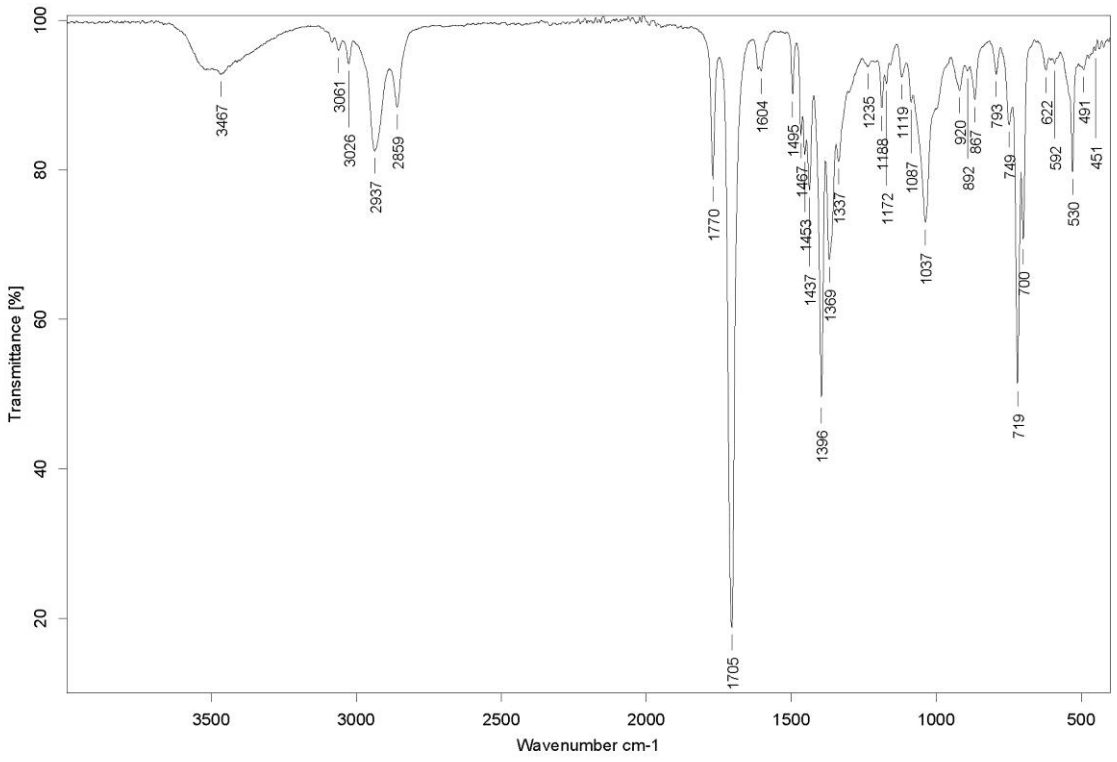


13C NMR (101 MHz, CDCl3, RT)

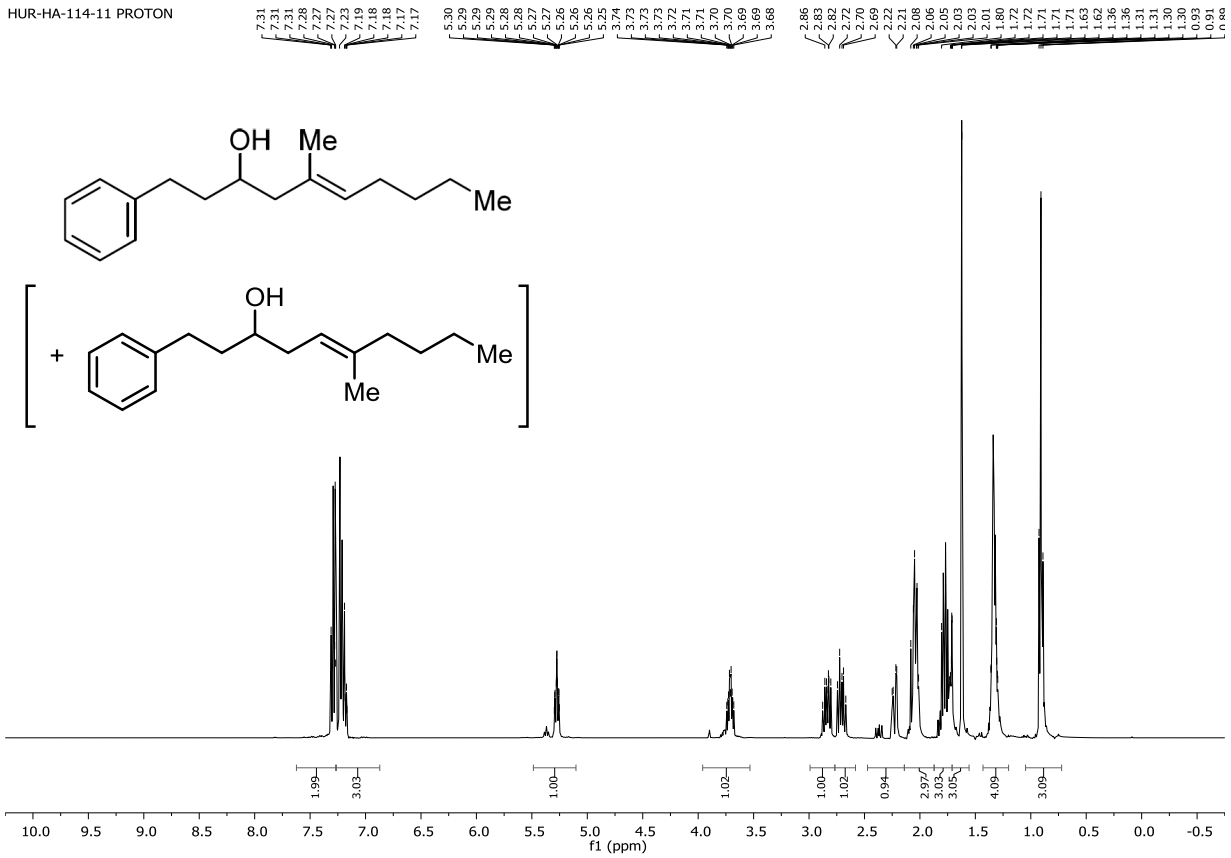




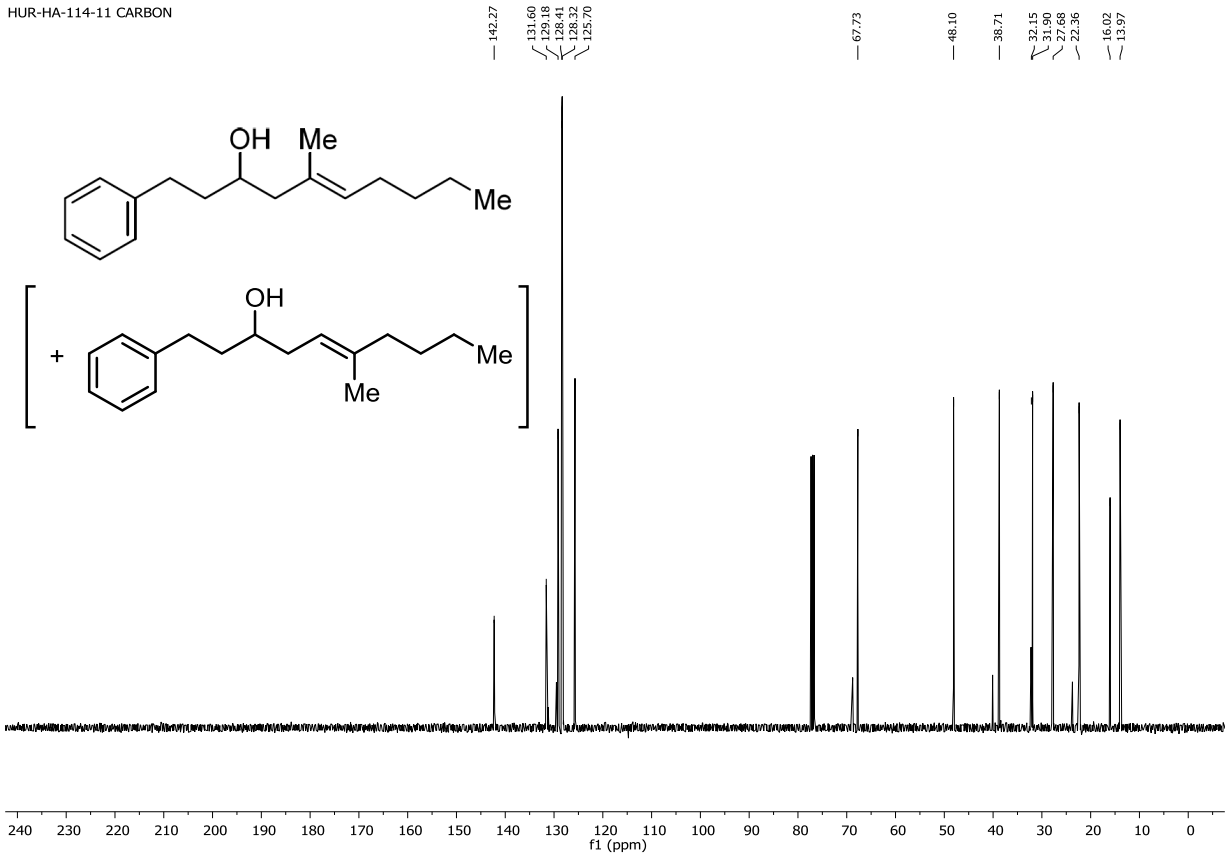
HUR-HA-120-11.0 **04.11.2016**

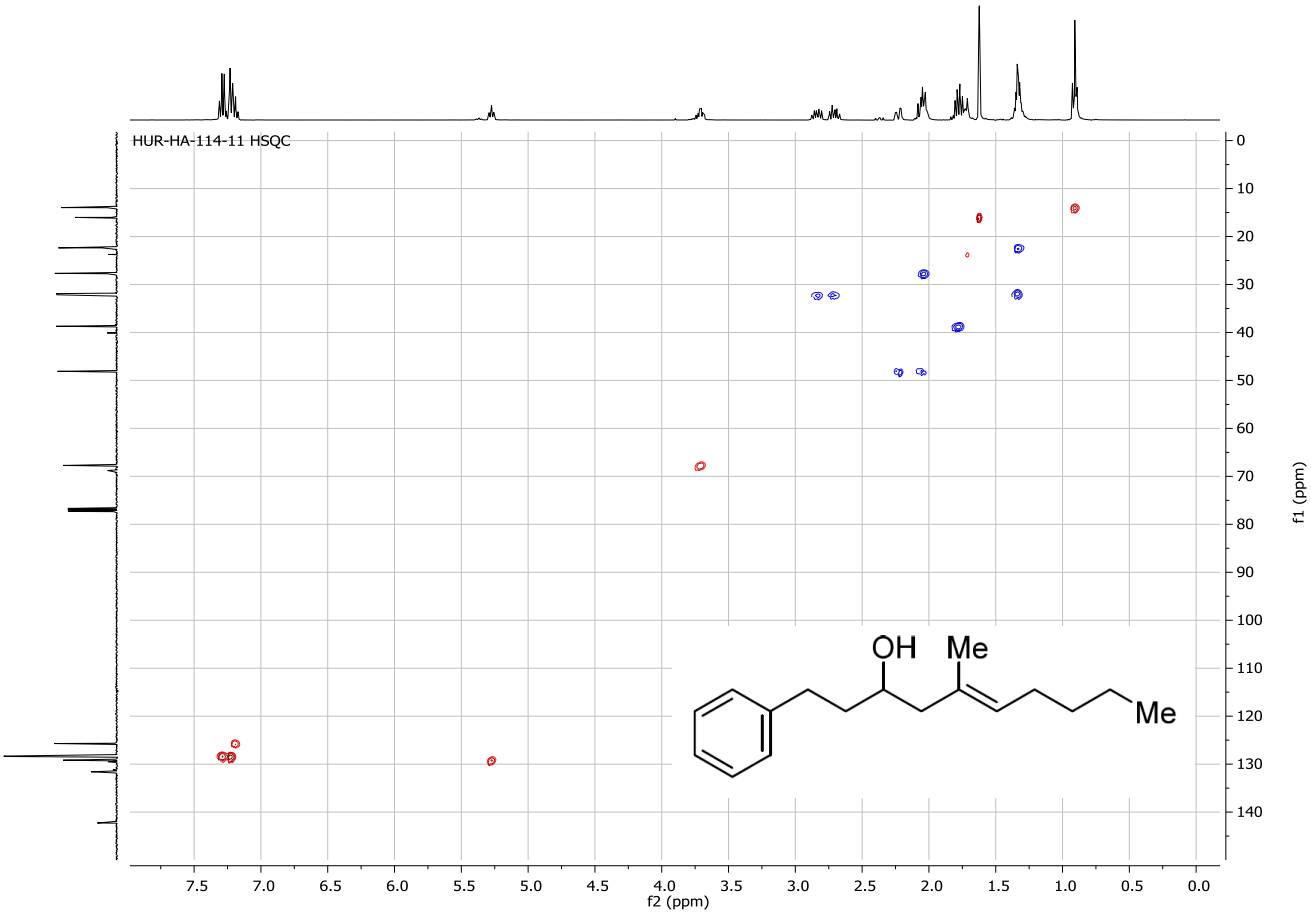


HUR-HA-114-11 PROTON

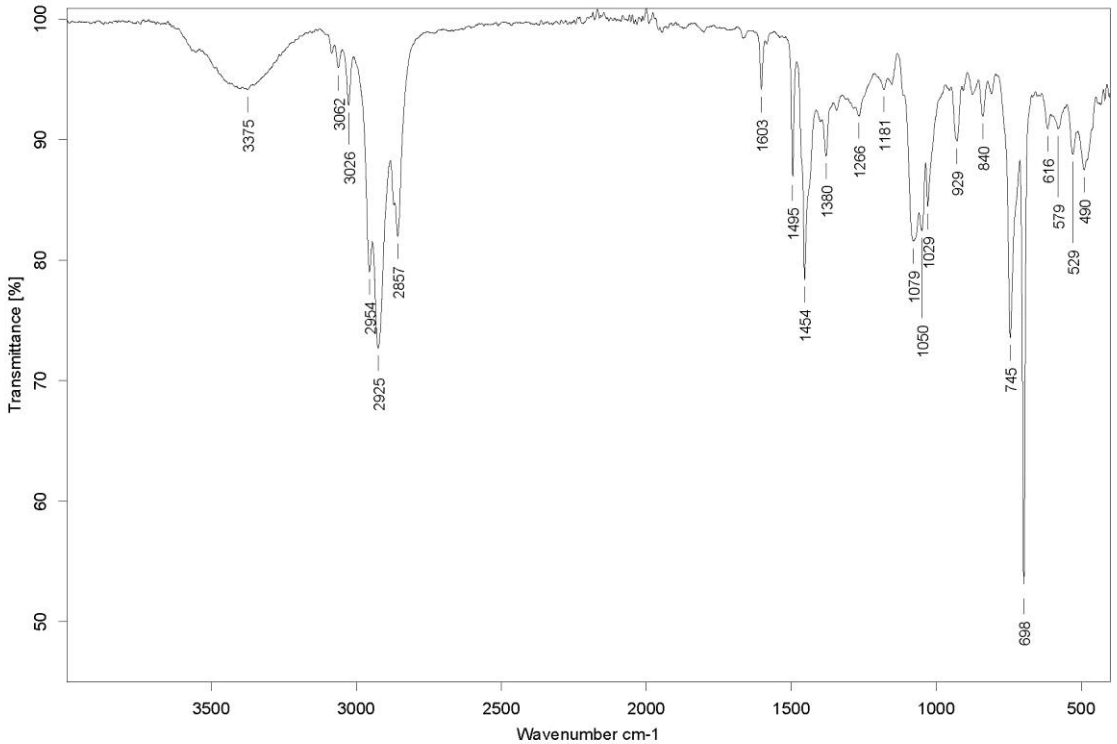


HUR-HA-114-11 CARBON

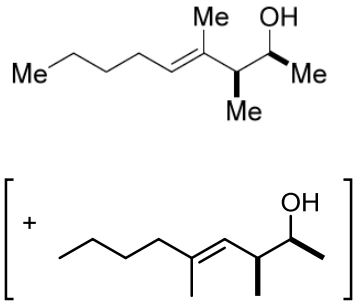




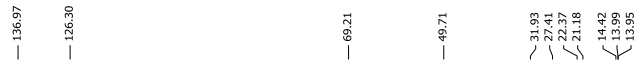
HUR-HA-114-11.0 **25.10.2016**

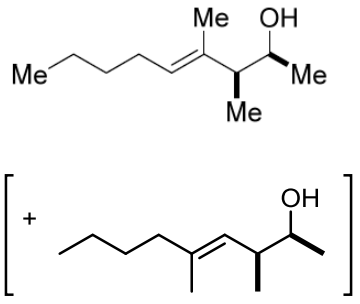


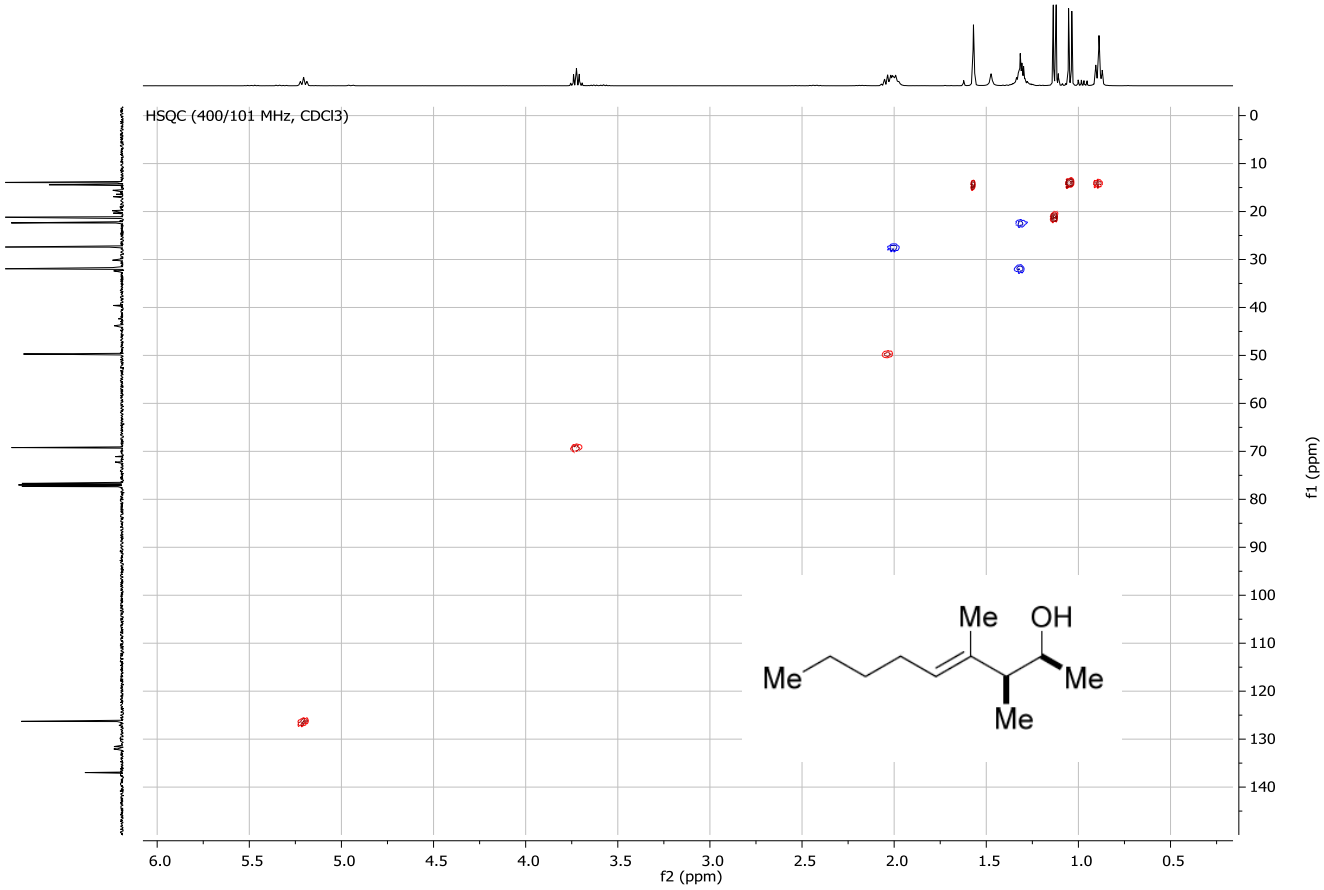
1H NMR (400 MHz, CDCl3)



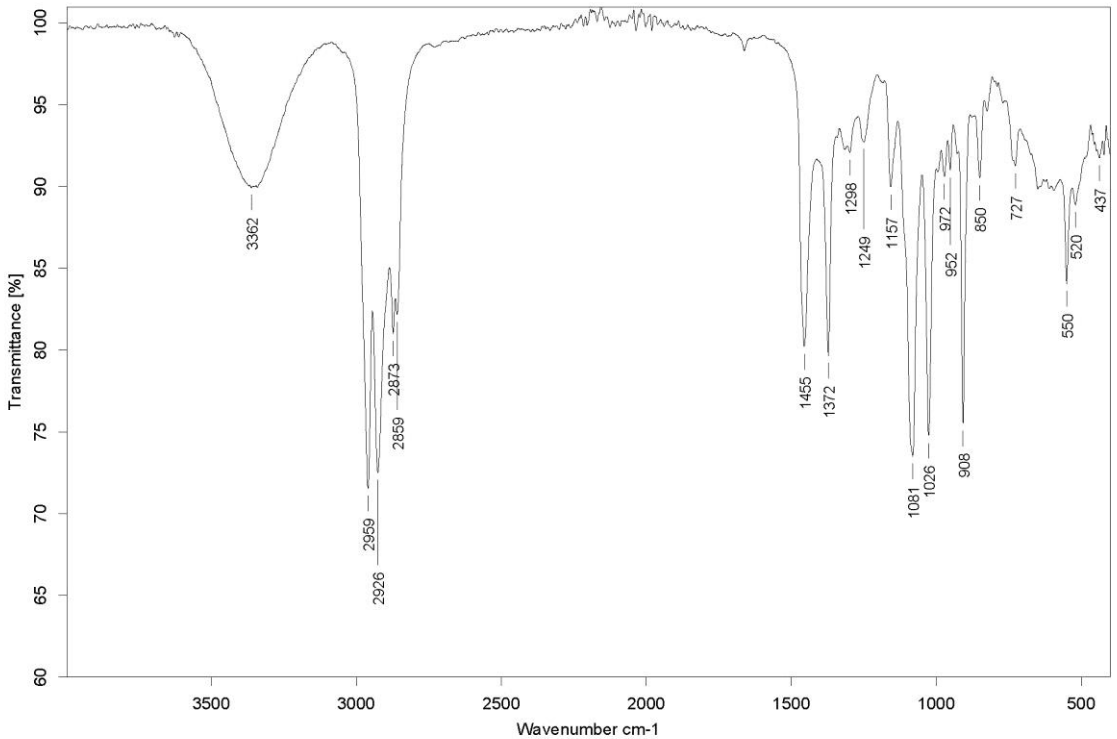
13C NMR (101 MHz, CDCl3)



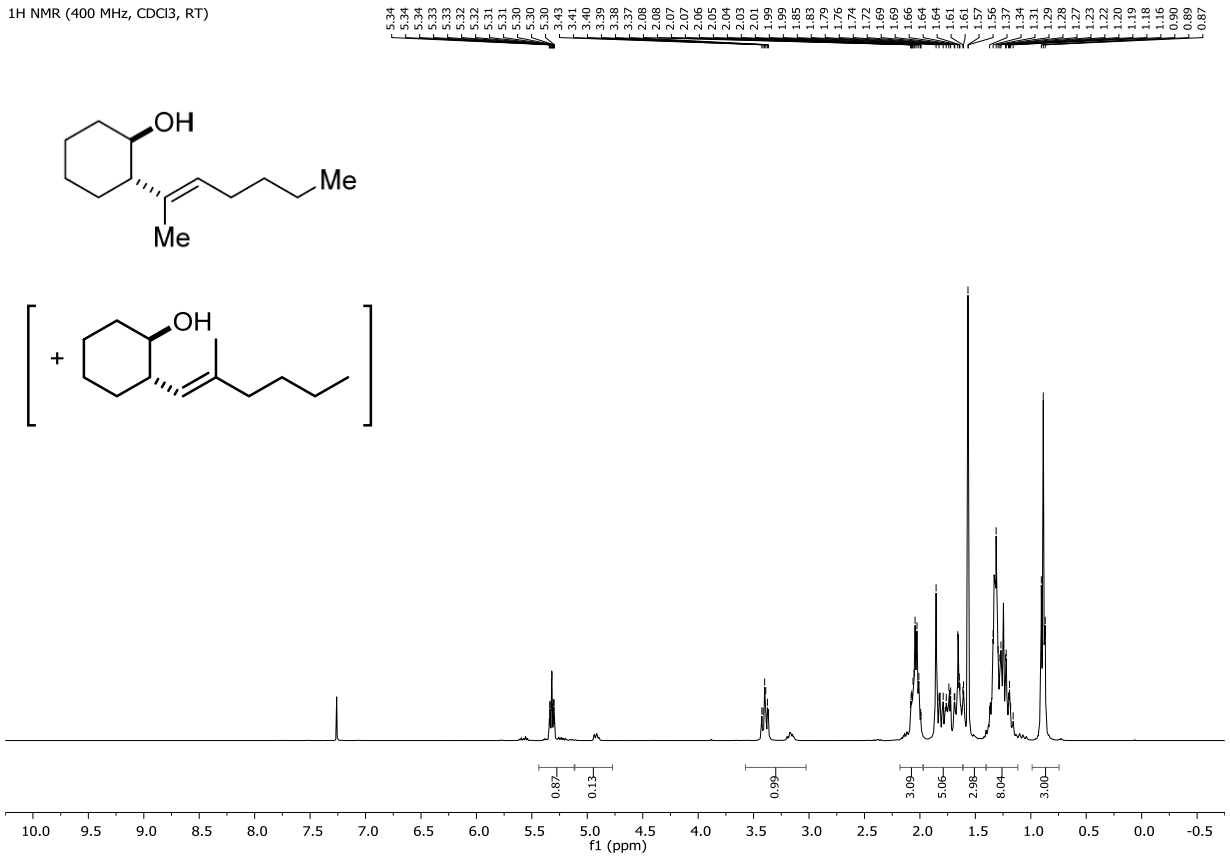




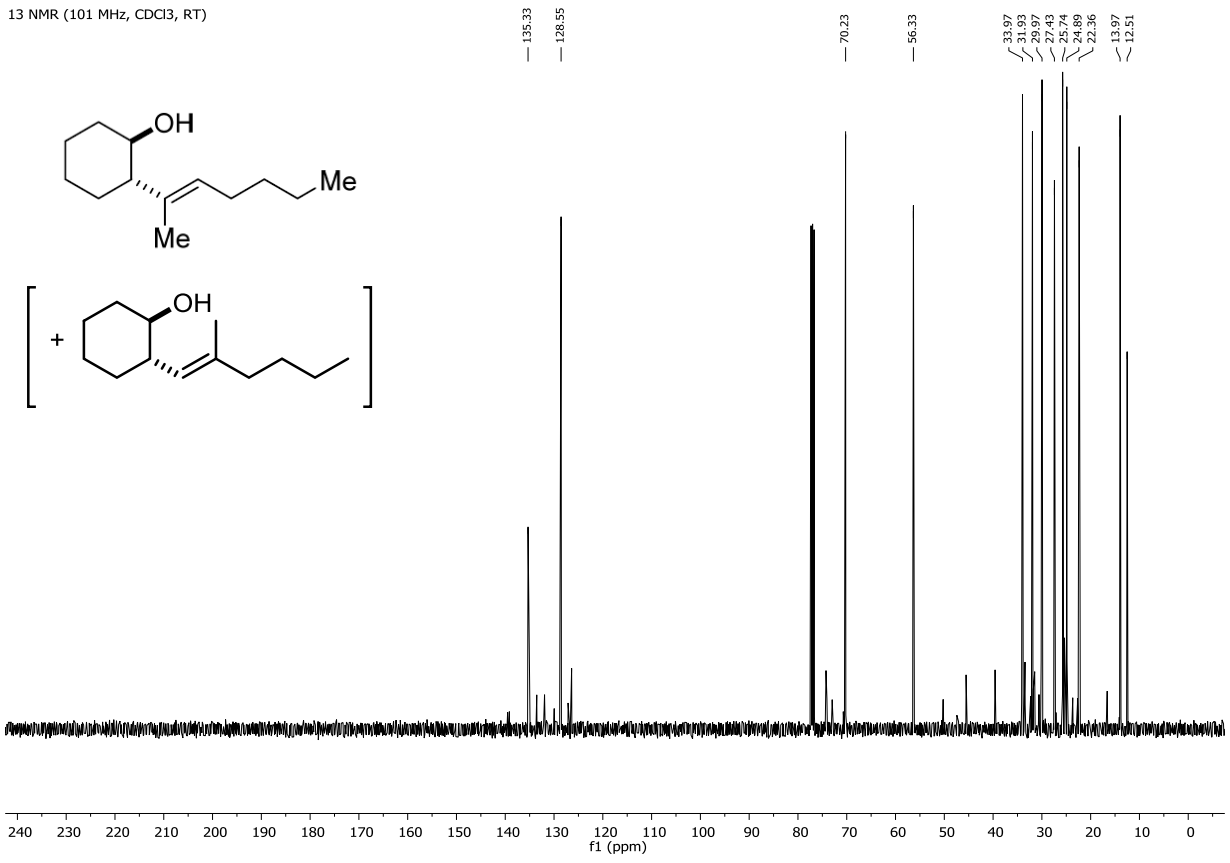
HUR-HA-100-12.0 **14.11.2016**

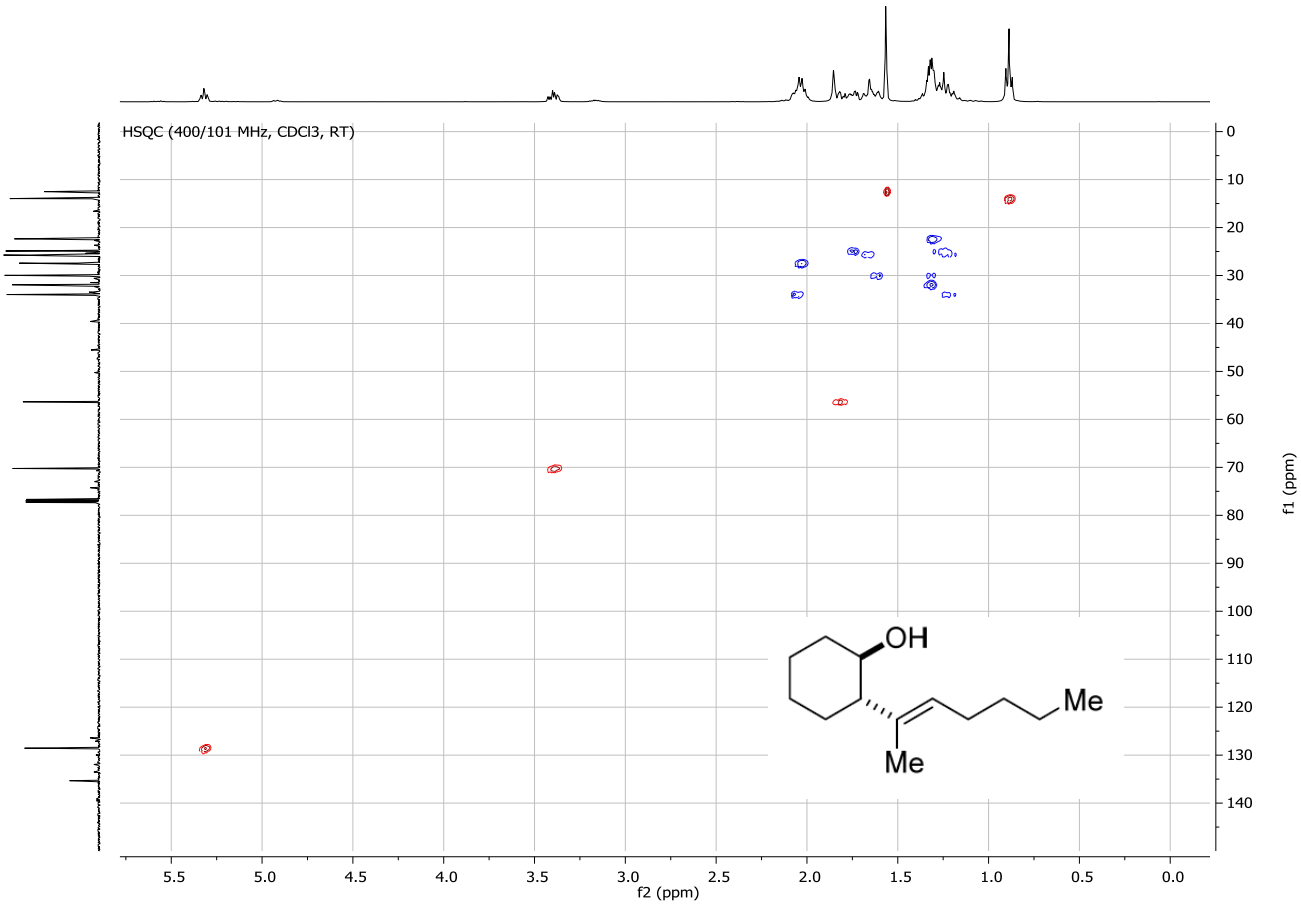


1H NMR (400 MHz, CDCl3, RT)

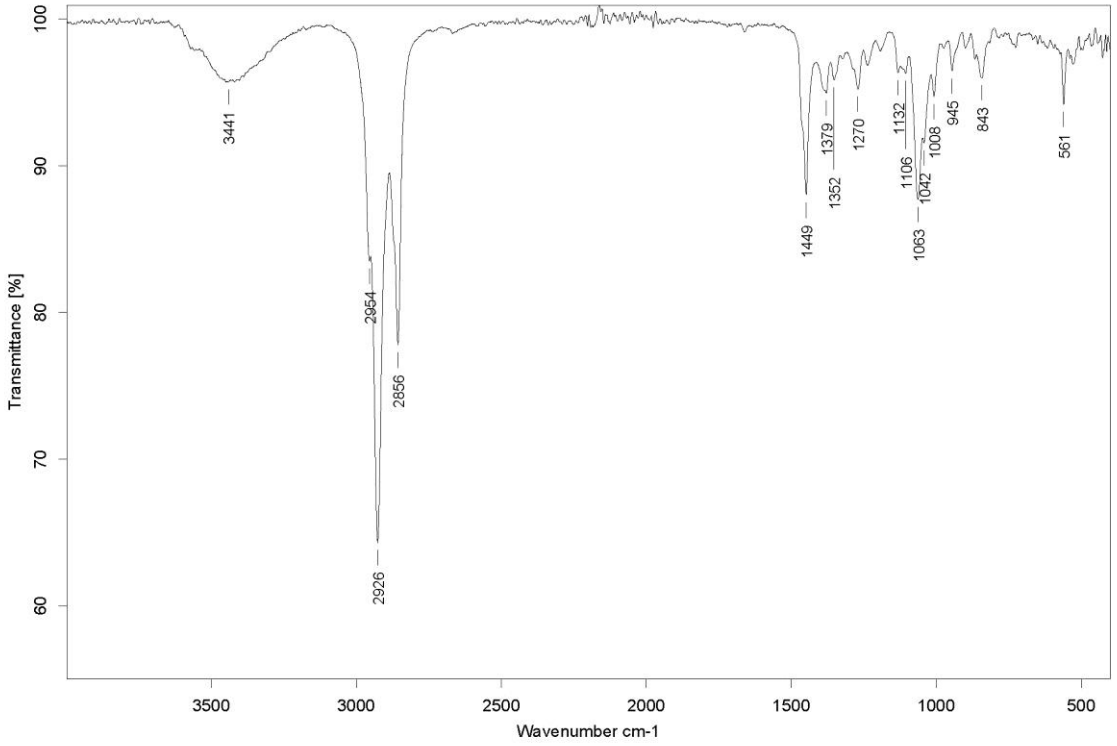


13 NMR (101 MHz, CDCl3, RT)

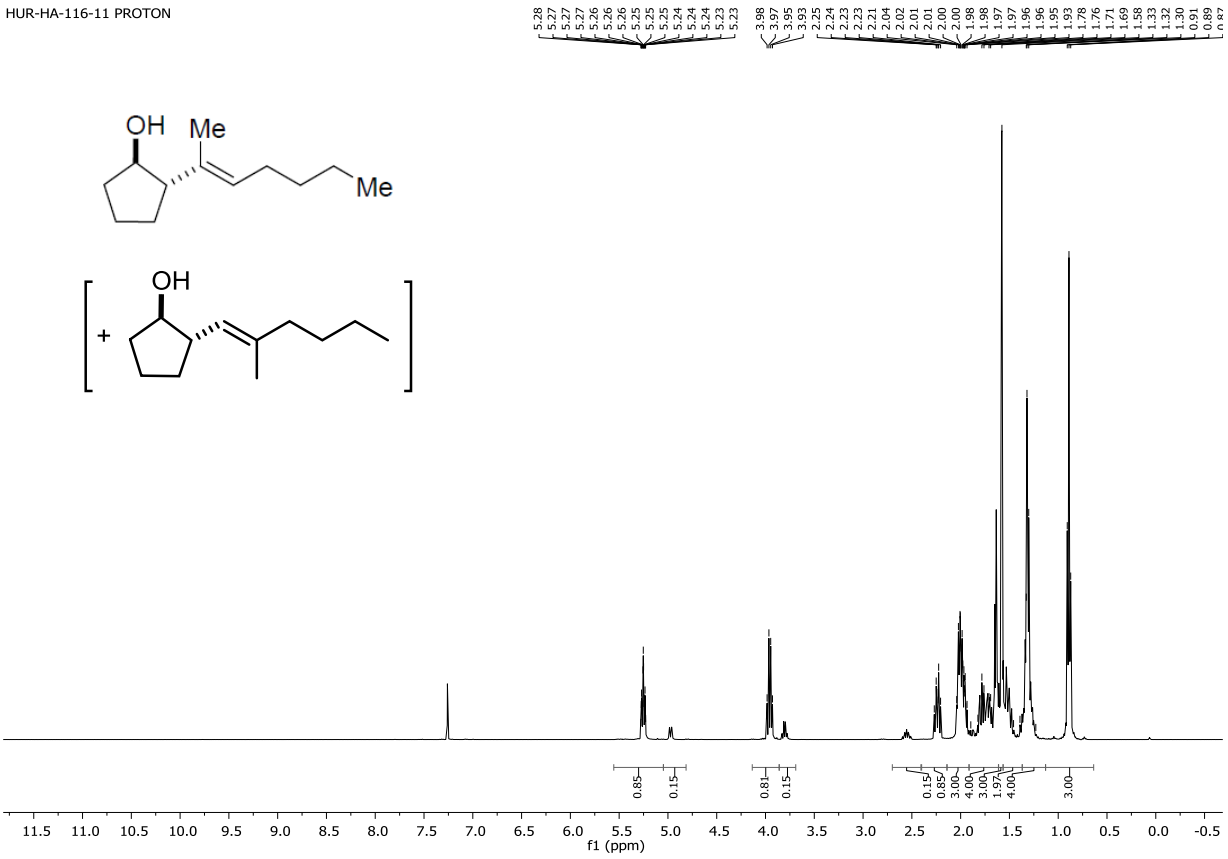




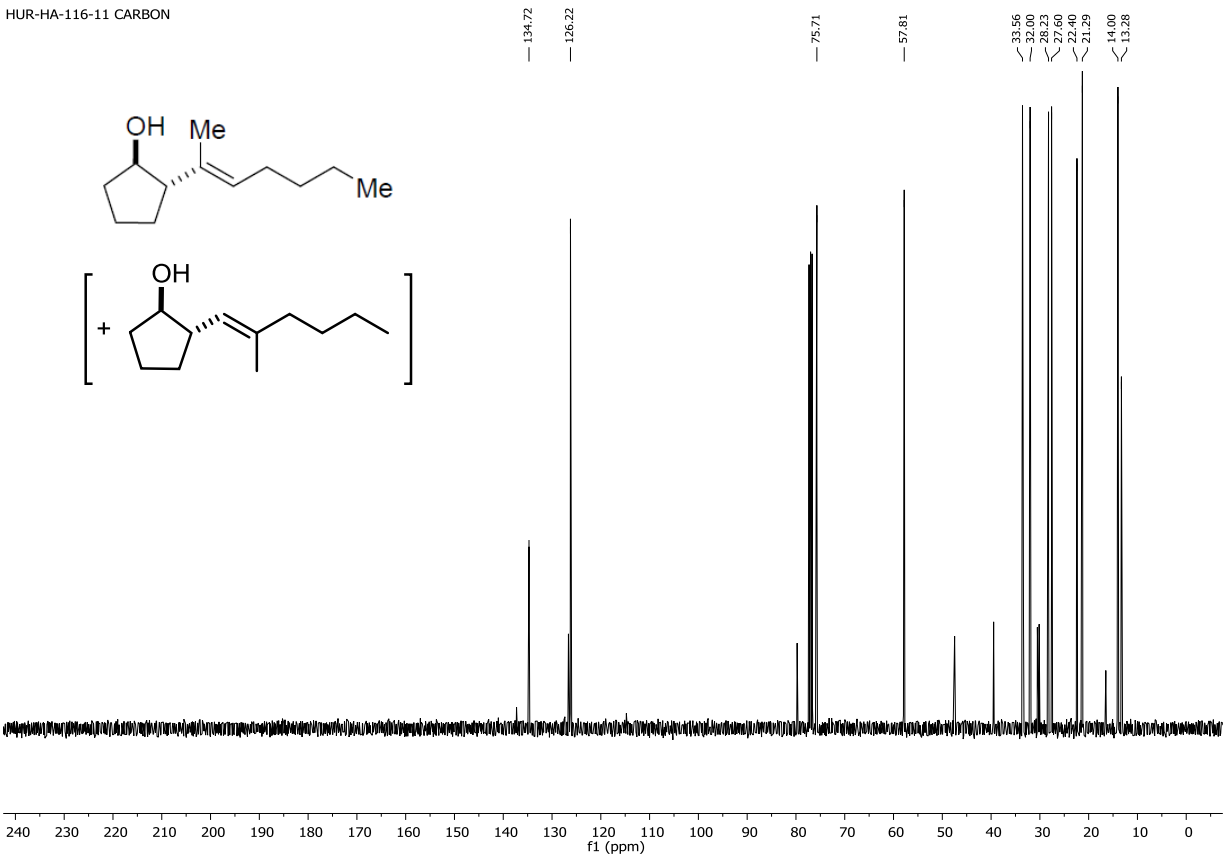
HUR-HA-115-13.0 **02.11.2016**

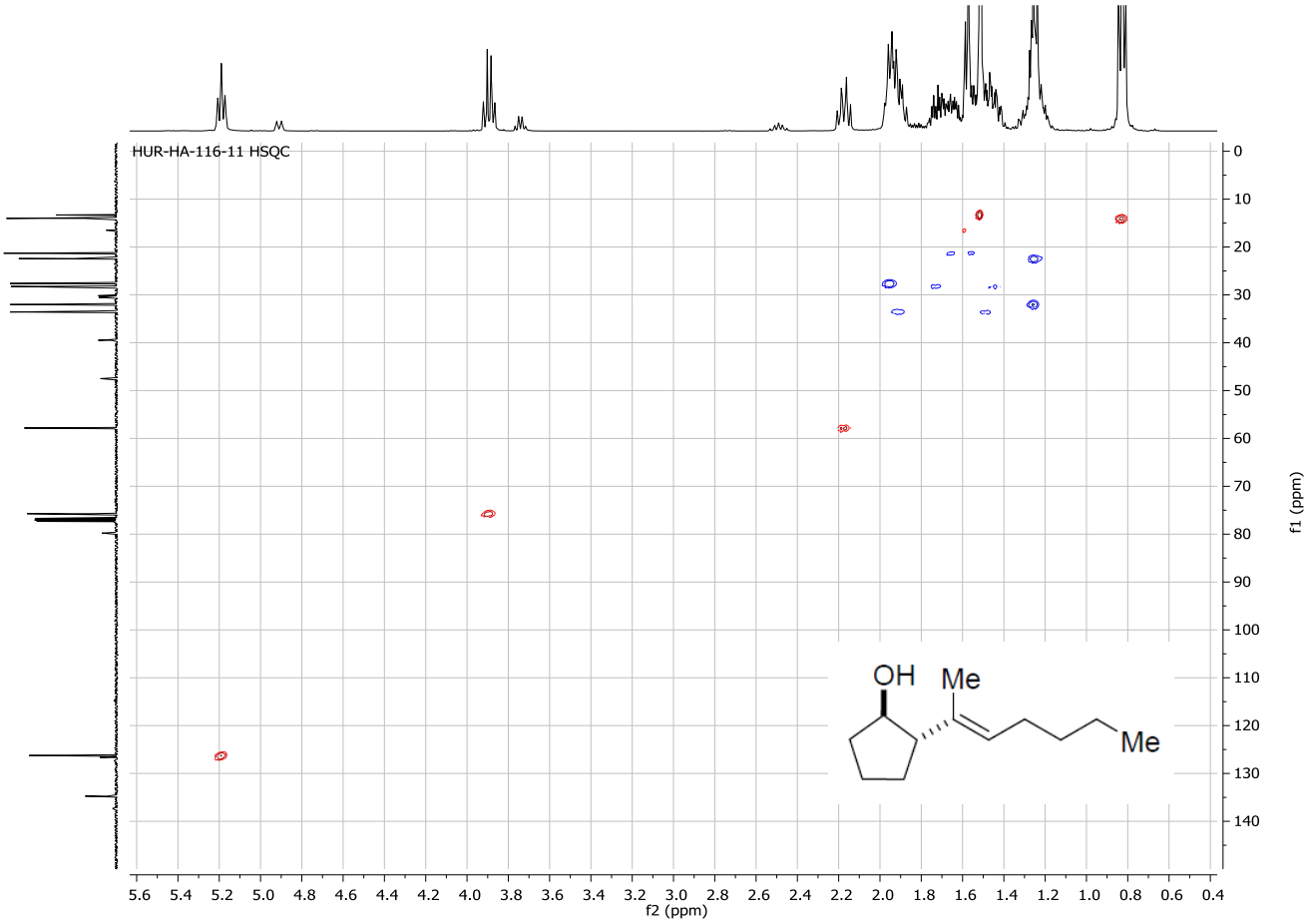


HUR-HA-116-11 PROTON

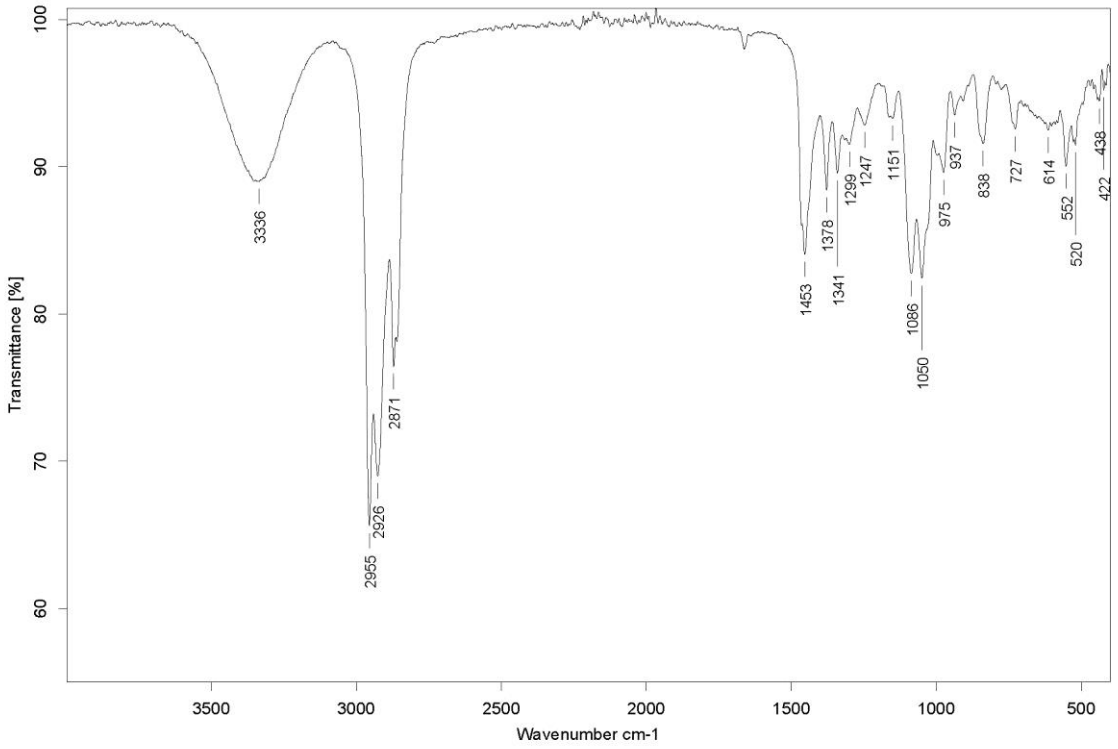


HUR-HA-116-11 CARBON

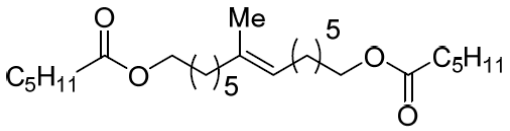


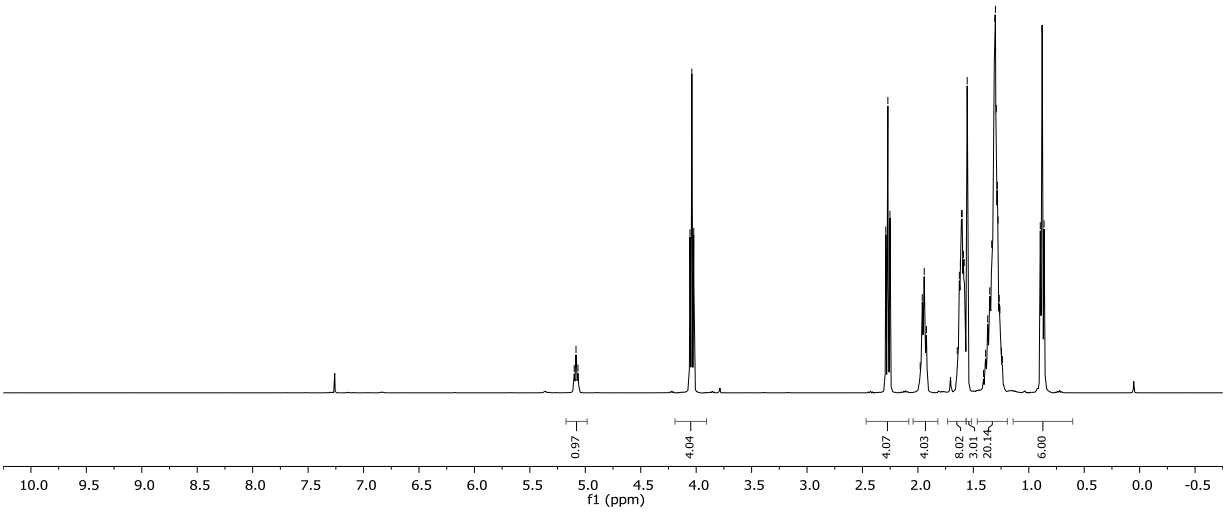


HUR-HA-116-11.0 **02.11.2016**

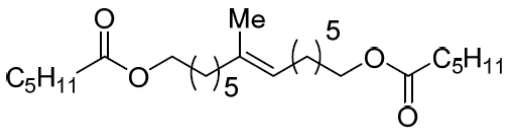


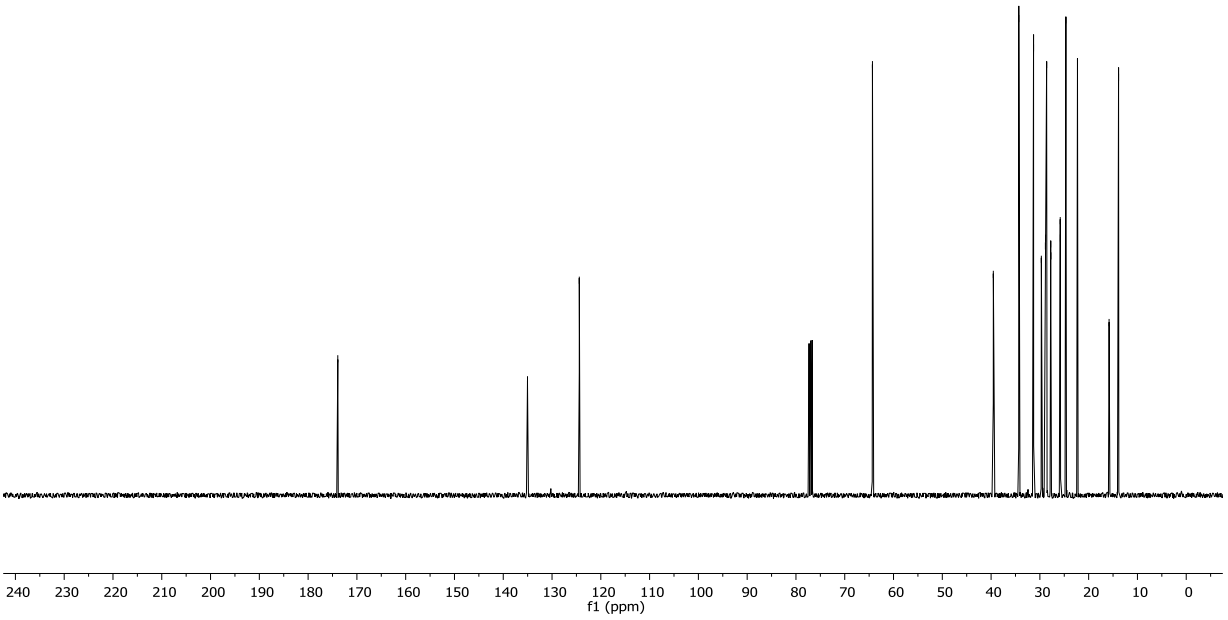
1H NMR (400 MHz, CDCl3, RT)

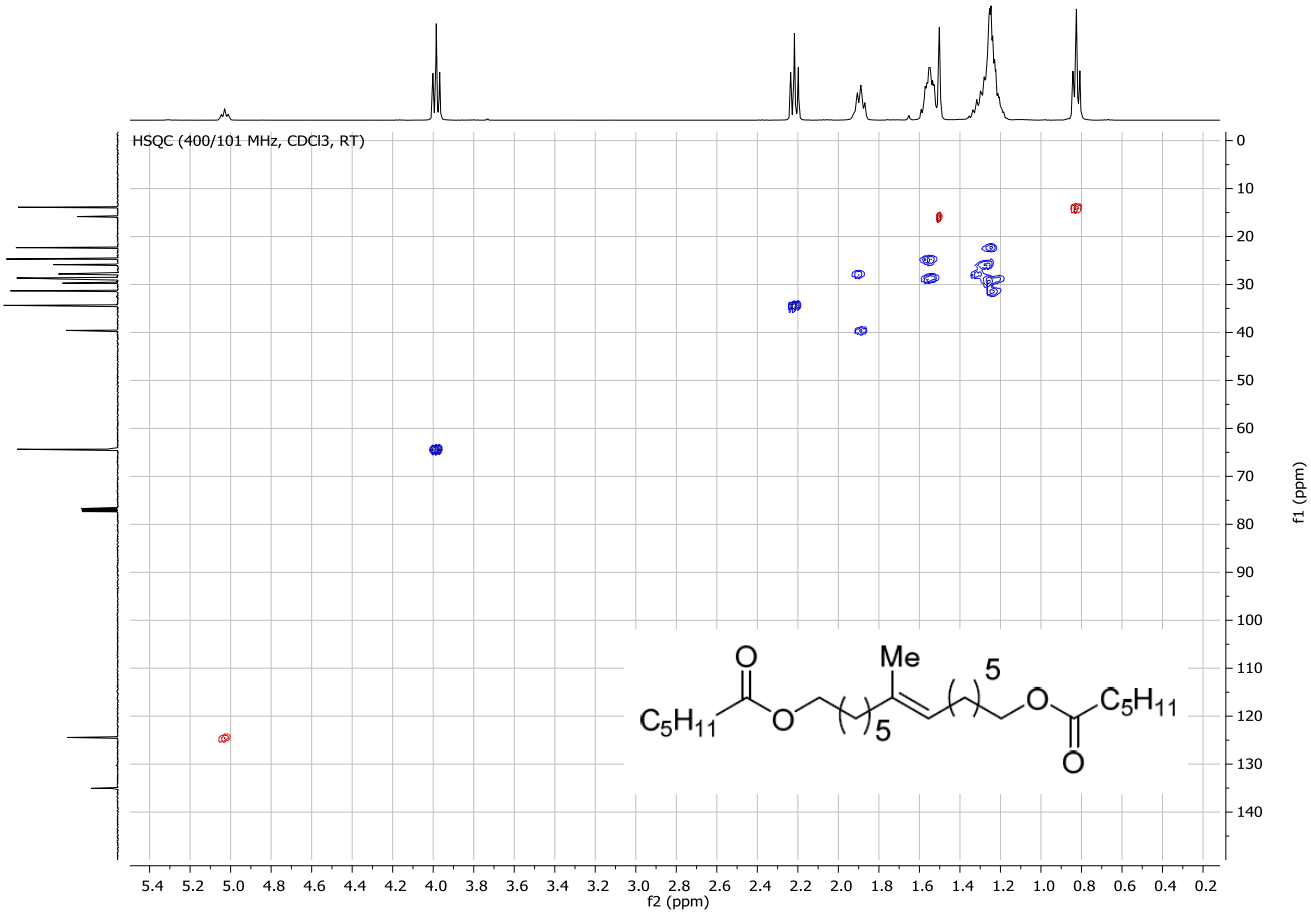




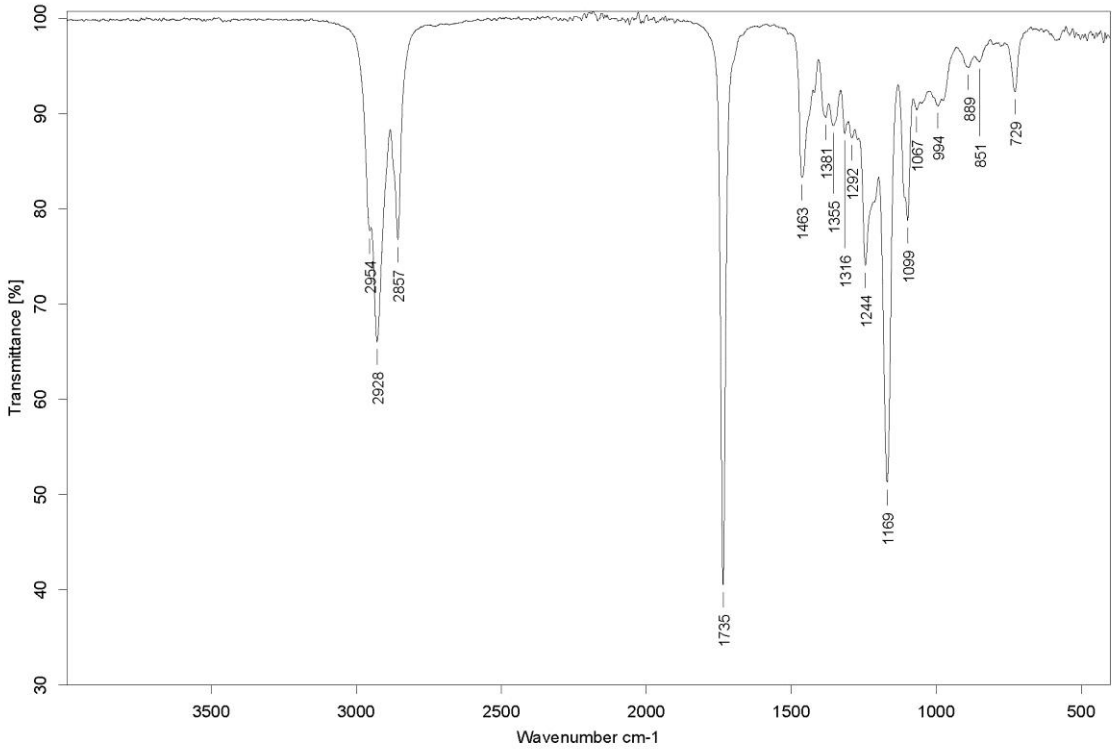
13C NMR (101 MHz, CDCl3, RT)



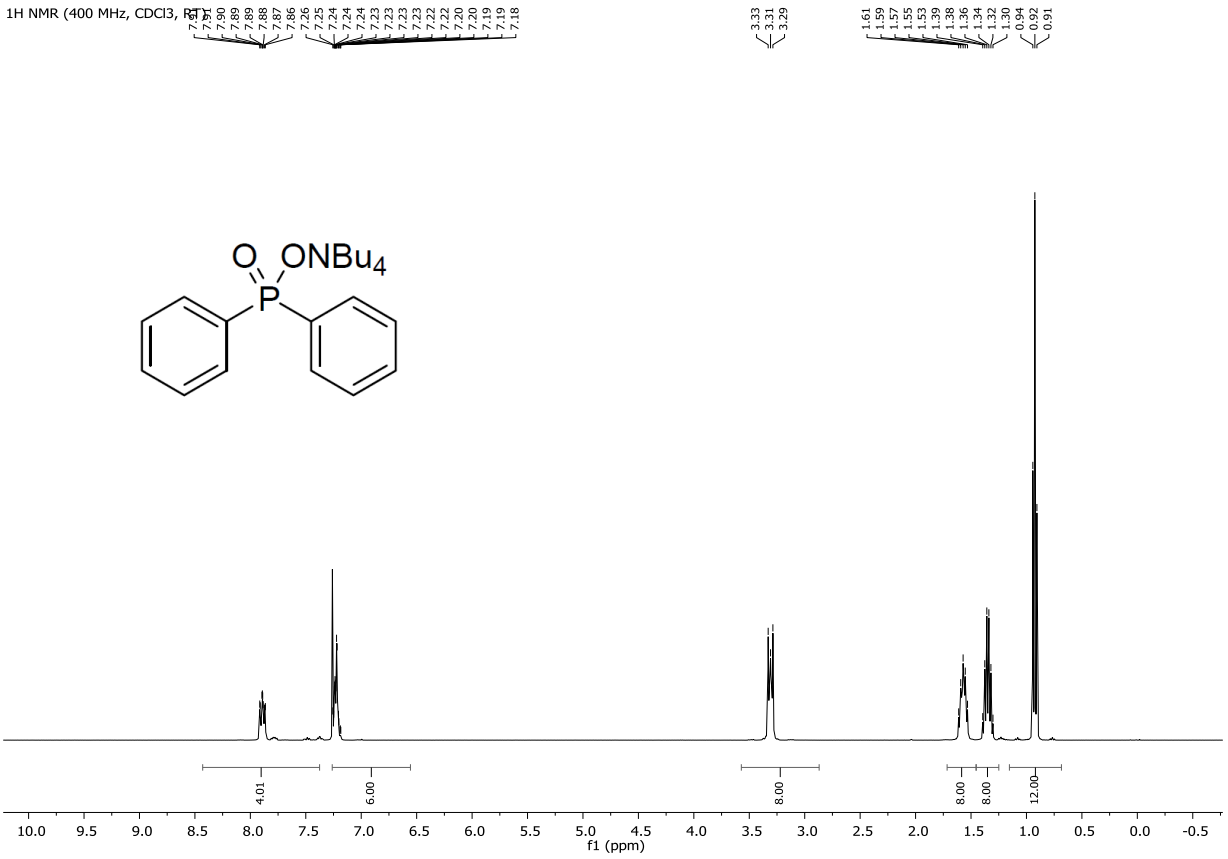




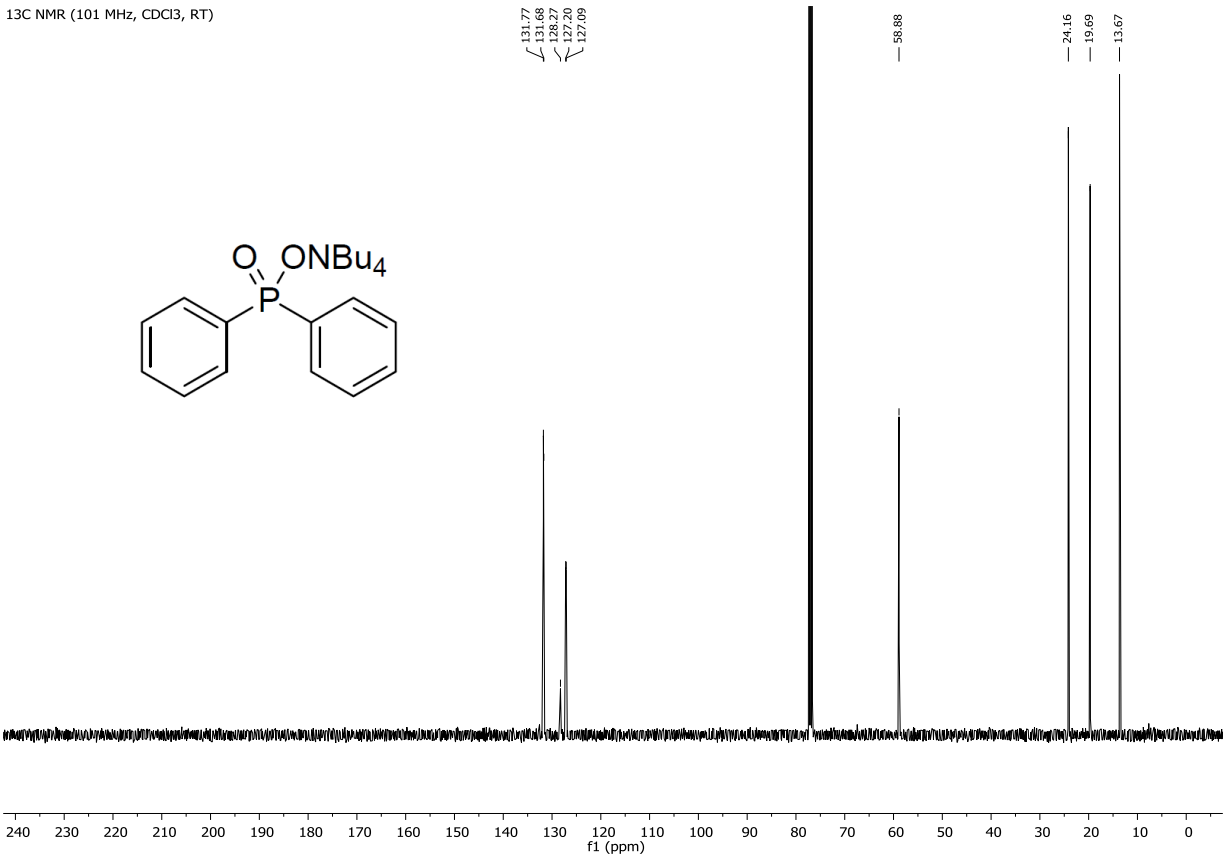
HUR-HA-105-13.1 **17.10.2016**



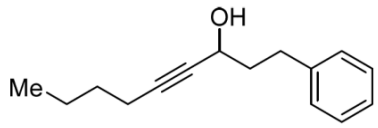
1H NMR (400 MHz, CDCl3, RT)

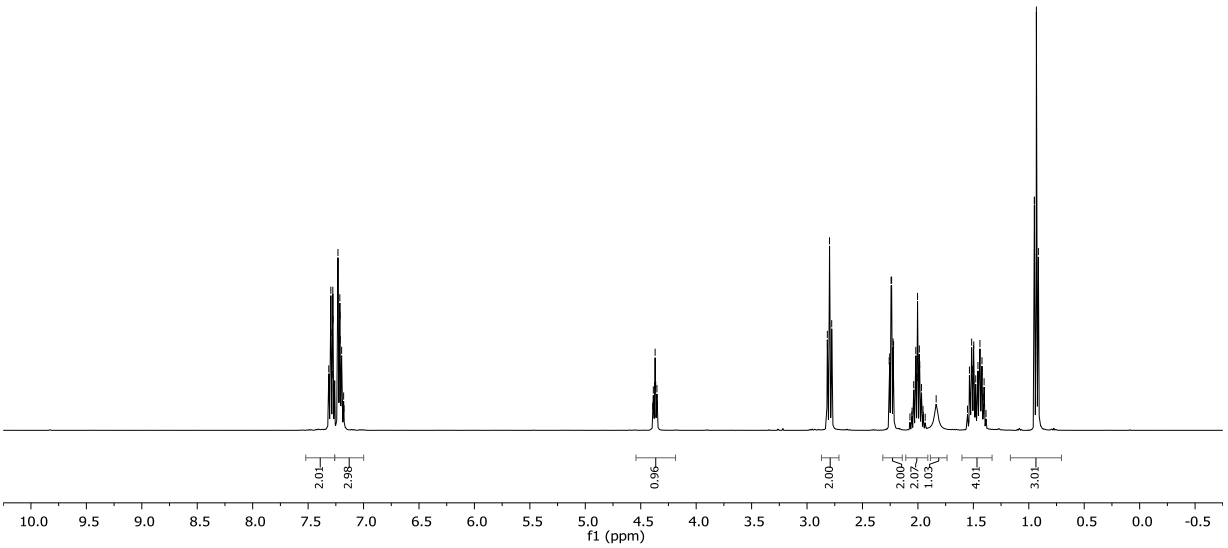


13C NMR (101 MHz, CDCl3, RT)

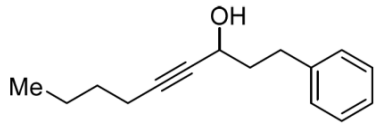


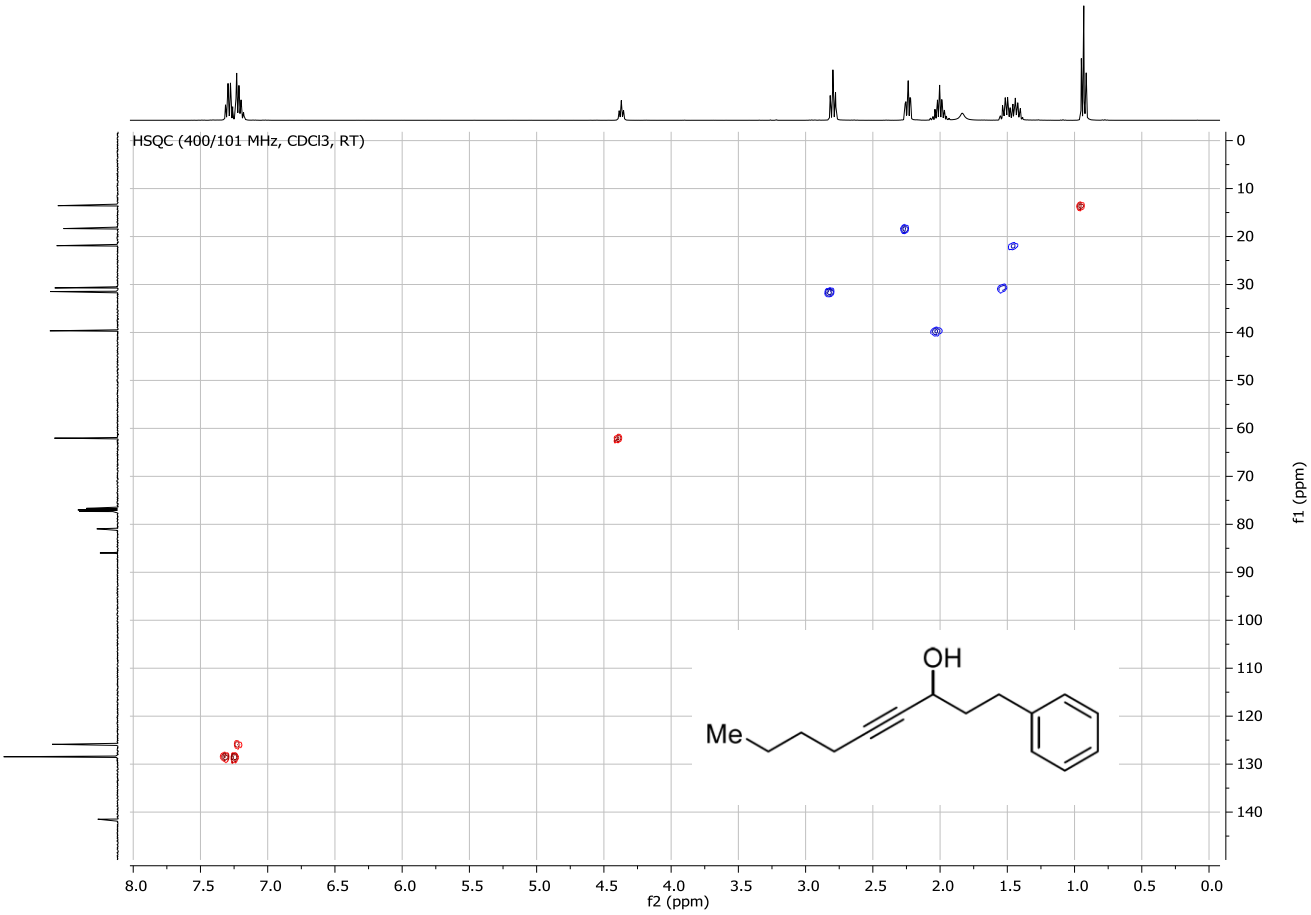
1H NMR (400 MHz, CDCl3, RT)



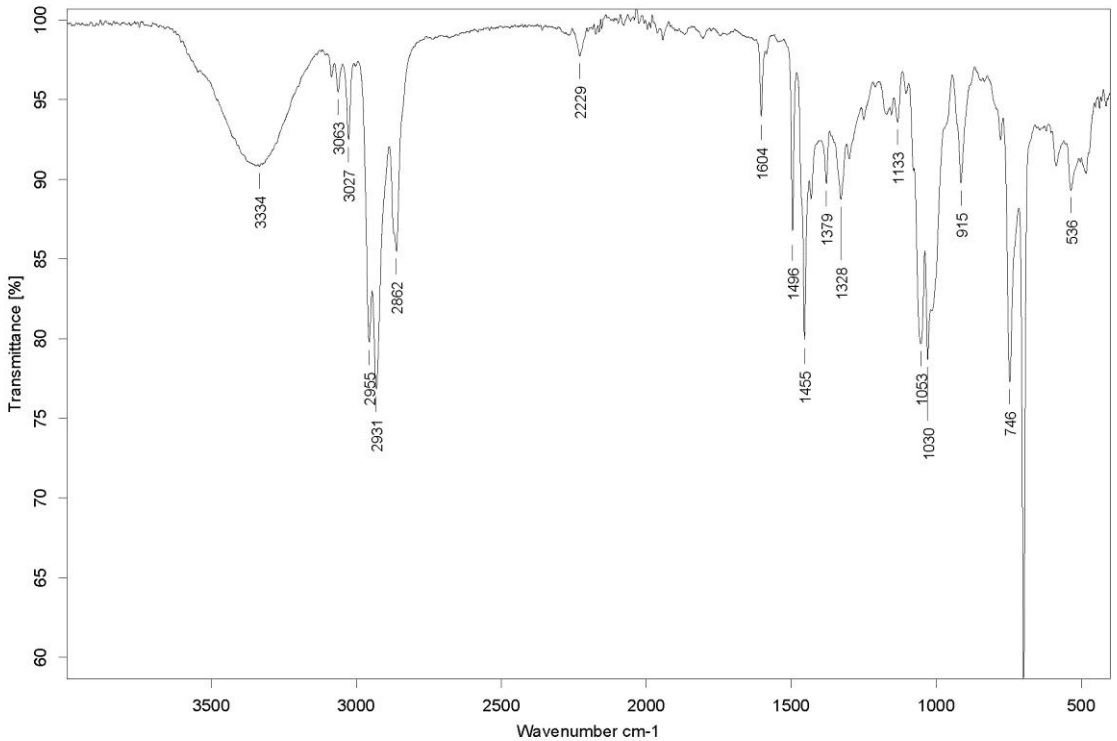


13C NMR (101 MHz, CDCl3, RT)

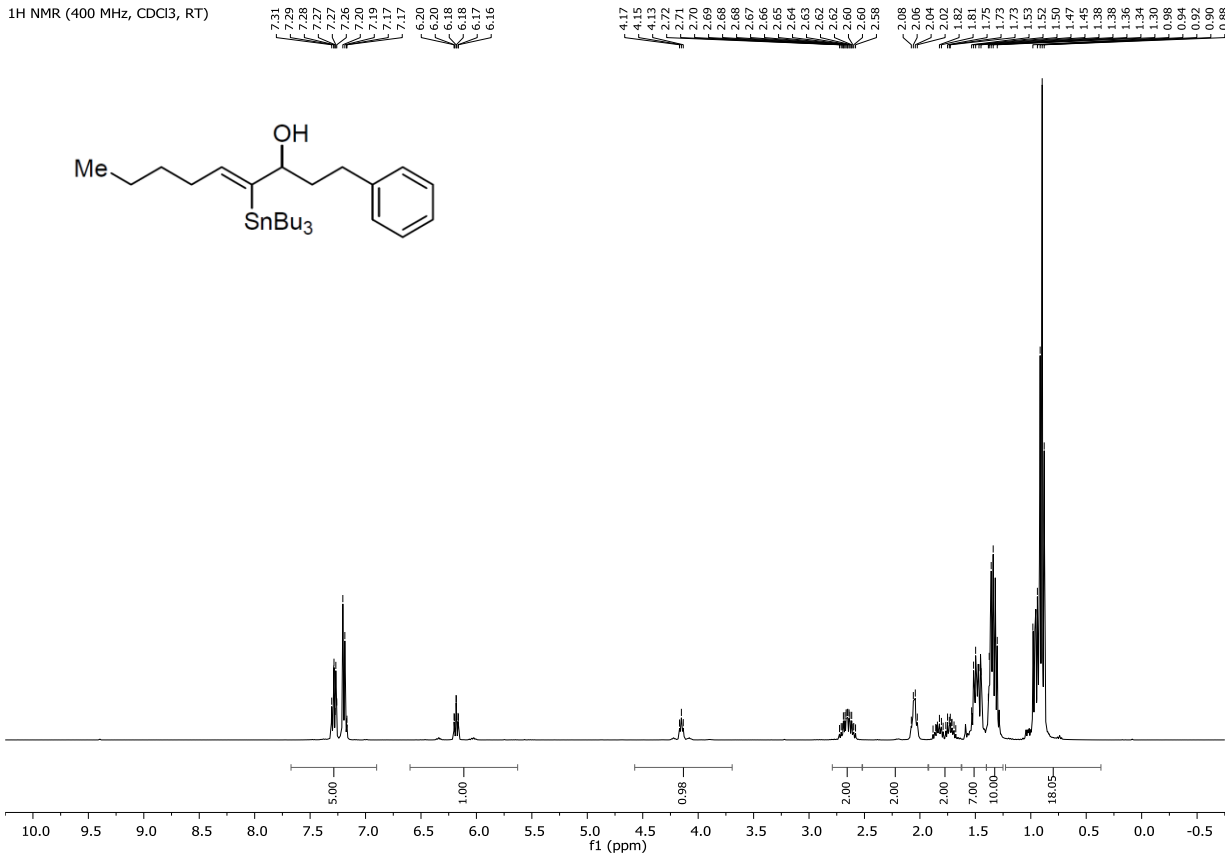




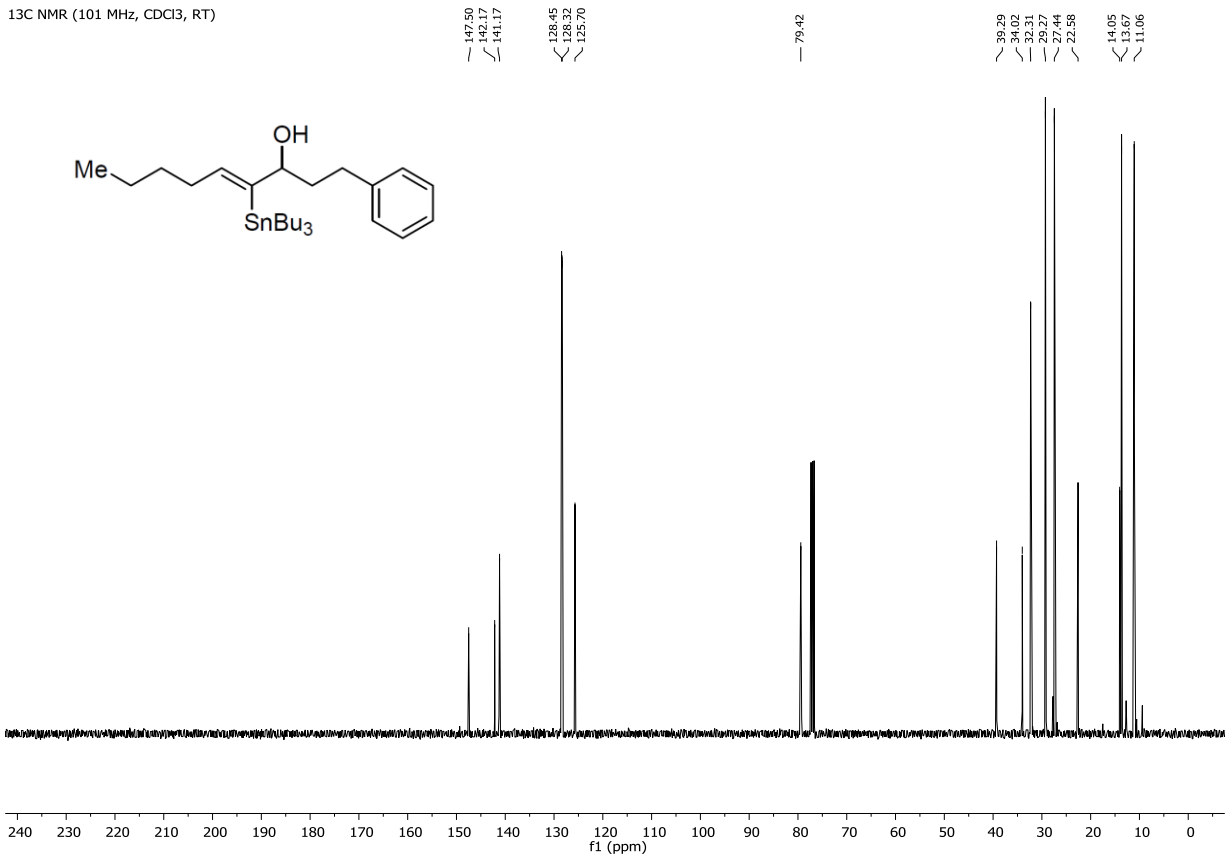
HUR-HA-031-12.0 **06.07.2016**



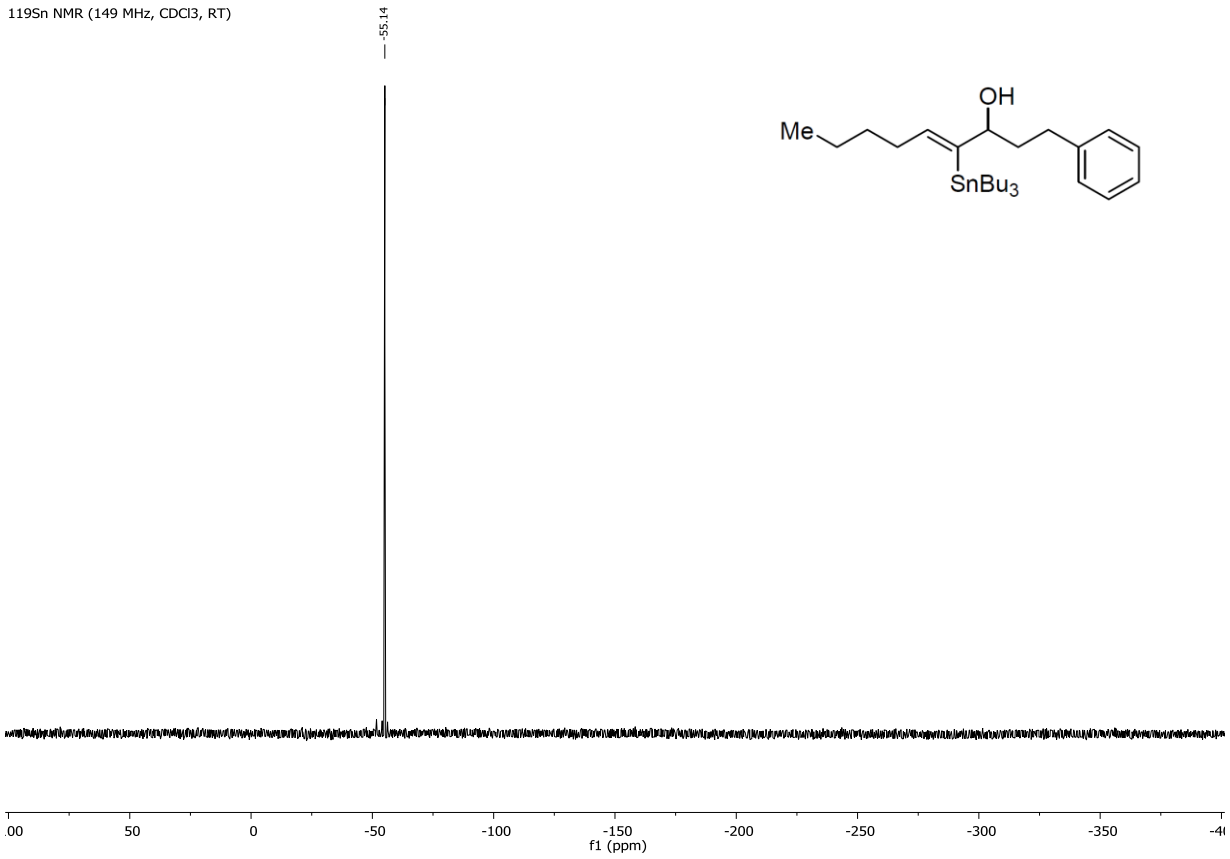
1H NMR (400 MHz, CDCl3, RT)



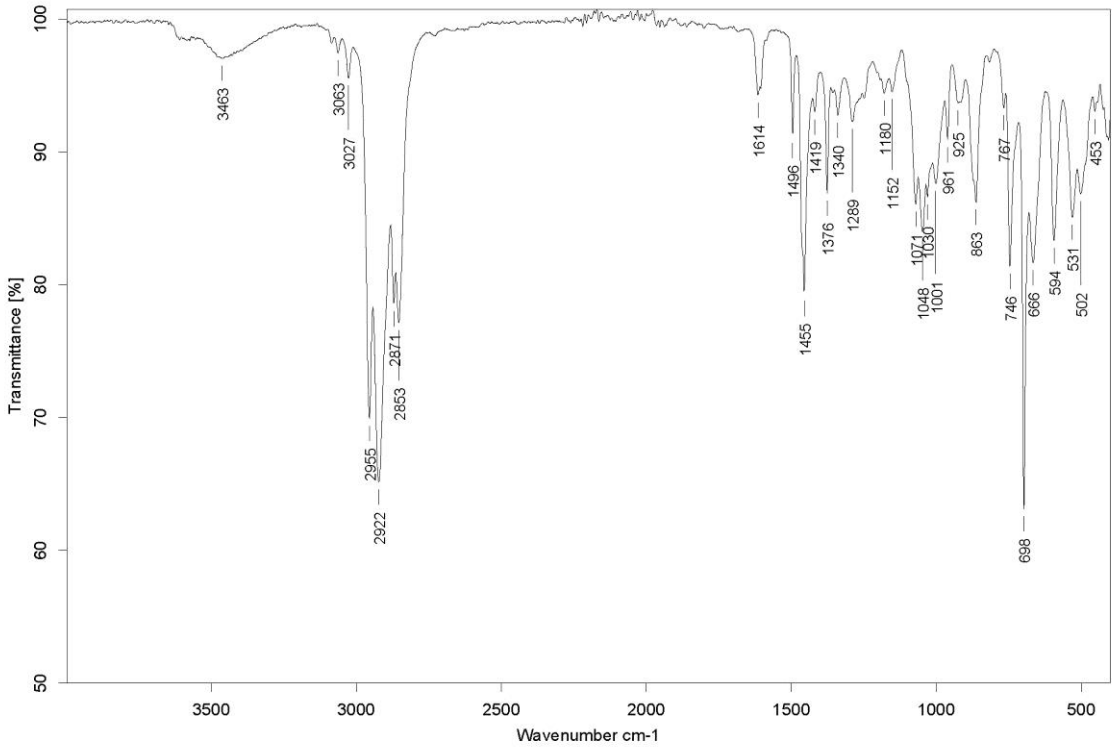
13C NMR (101 MHz, CDCl3, RT)



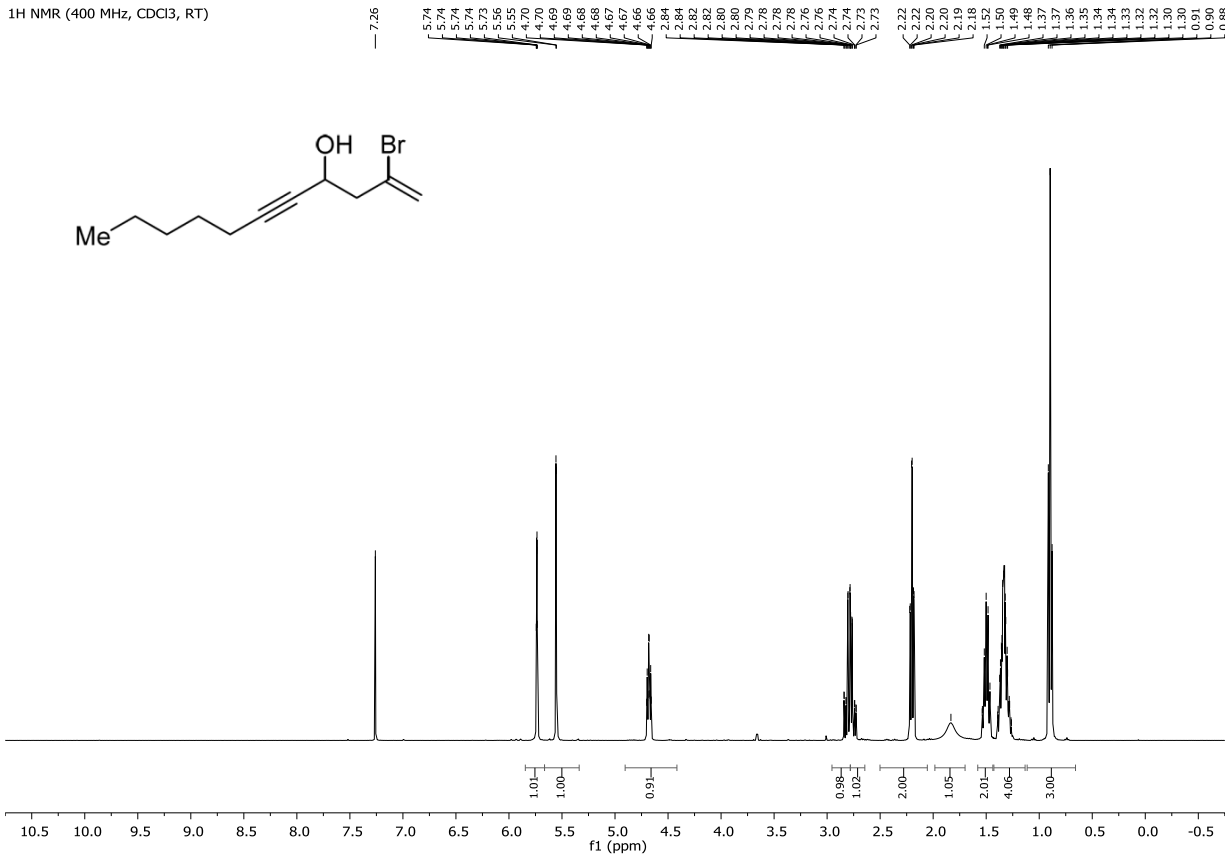
119Sn NMR (149 MHz, CDCl3, RT)



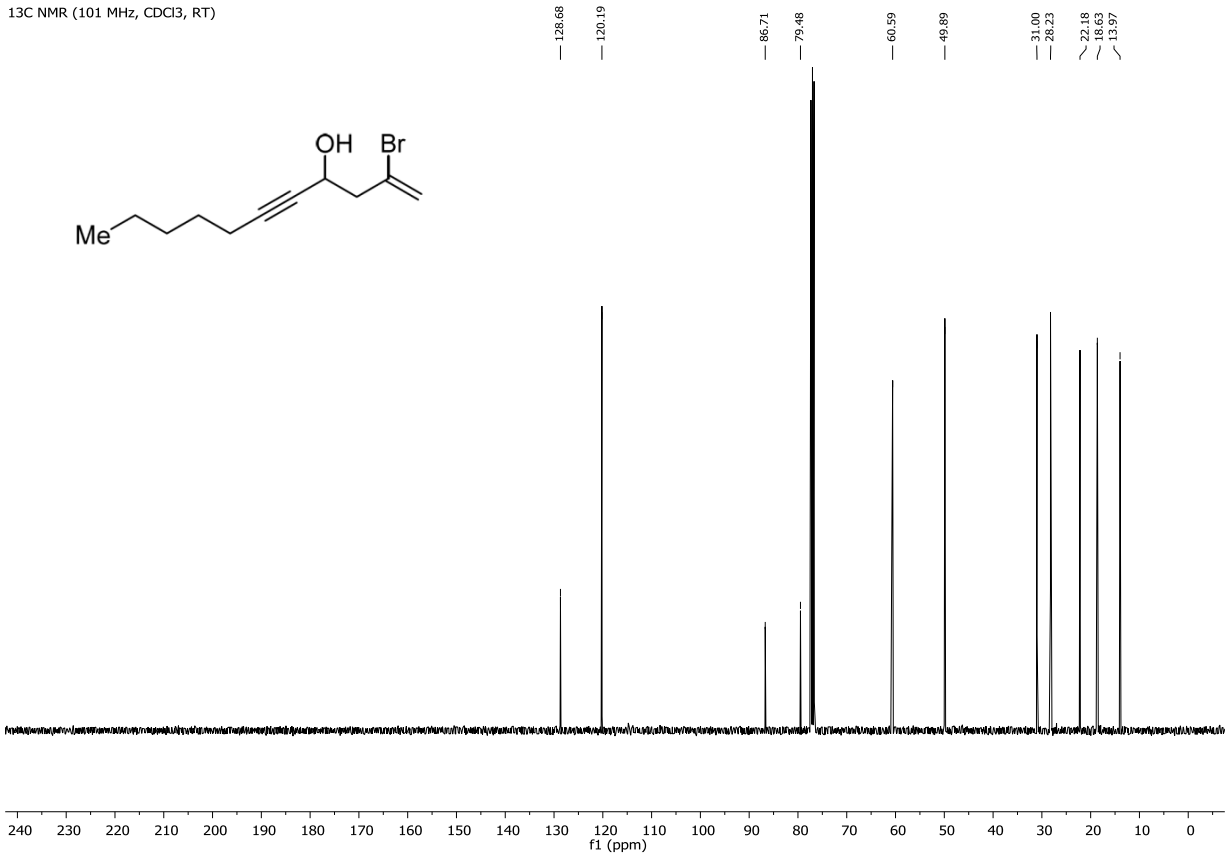
HUR-HA-076-12.0 **15.08.2016**

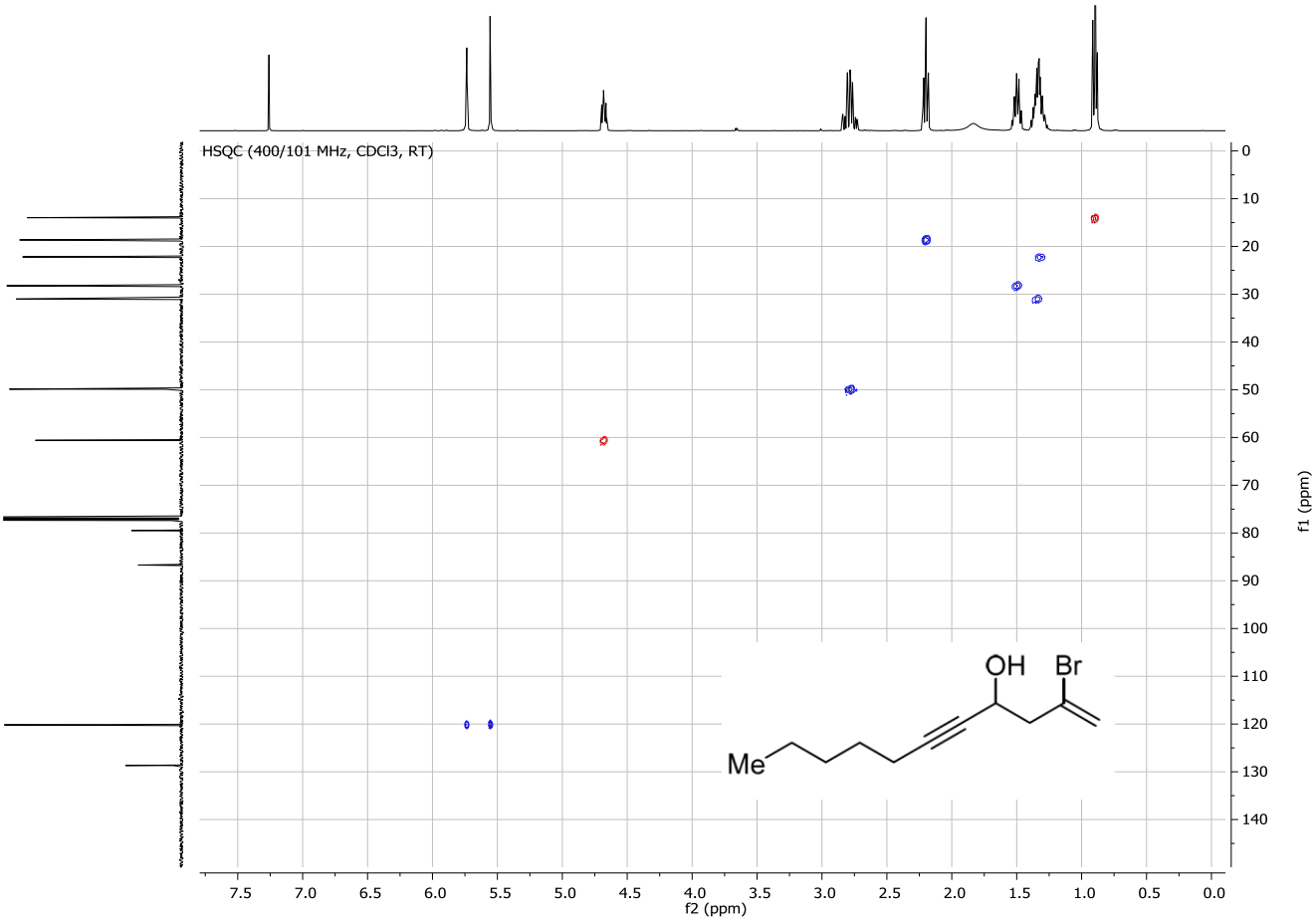


1H NMR (400 MHz, CDCl3, RT)

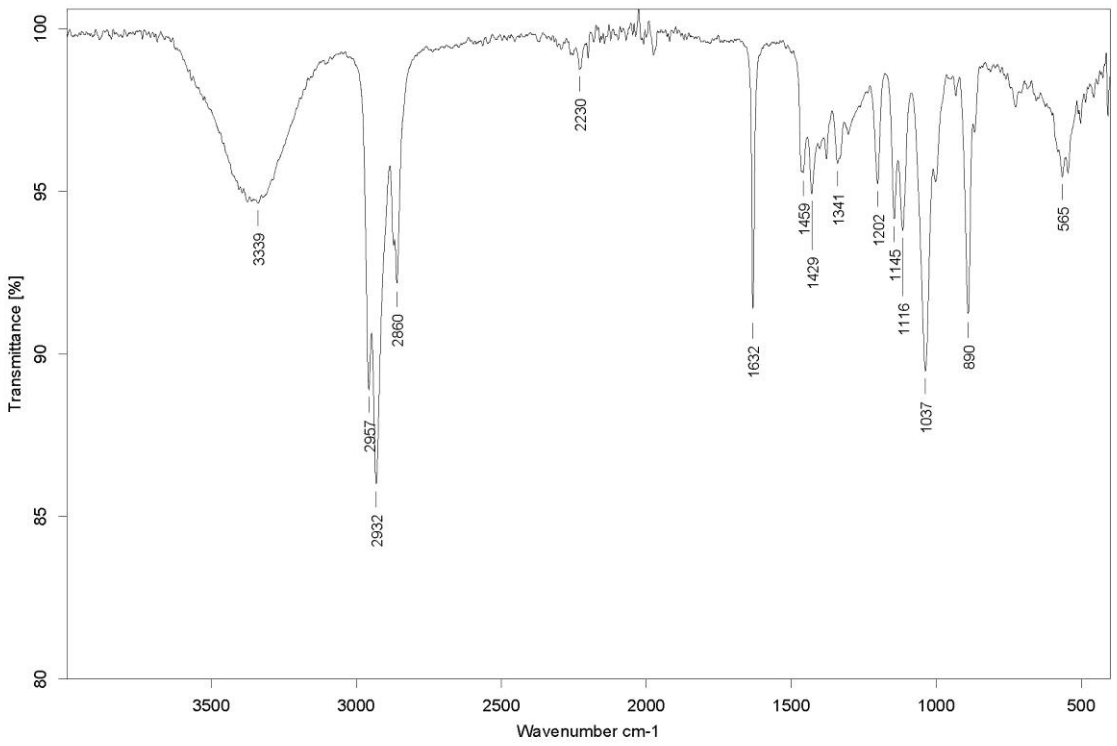


13C NMR (101 MHz, CDCl3, RT)

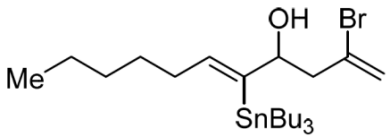




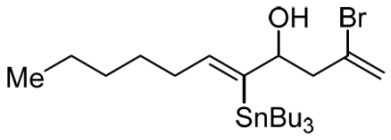
HUR-HA-074-12.0 **16.08.2016**



1H NMR (400 MHz, CDCl3, RT)

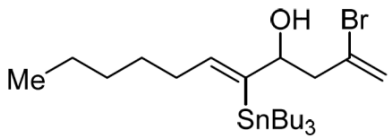


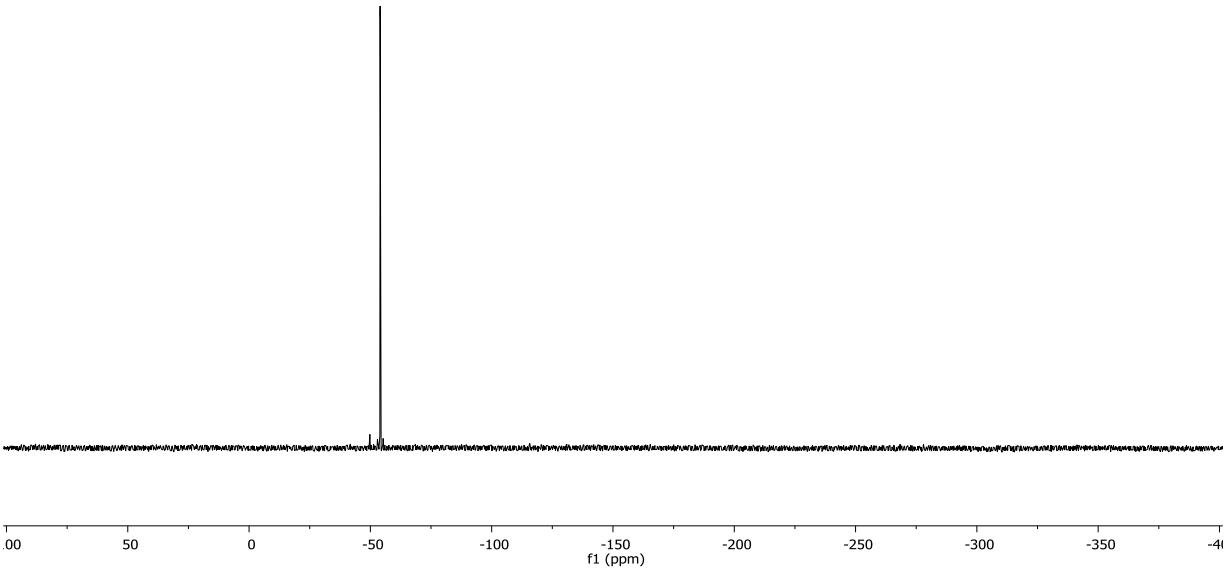
13C NMR (101 MHz, CDCl3, RT)

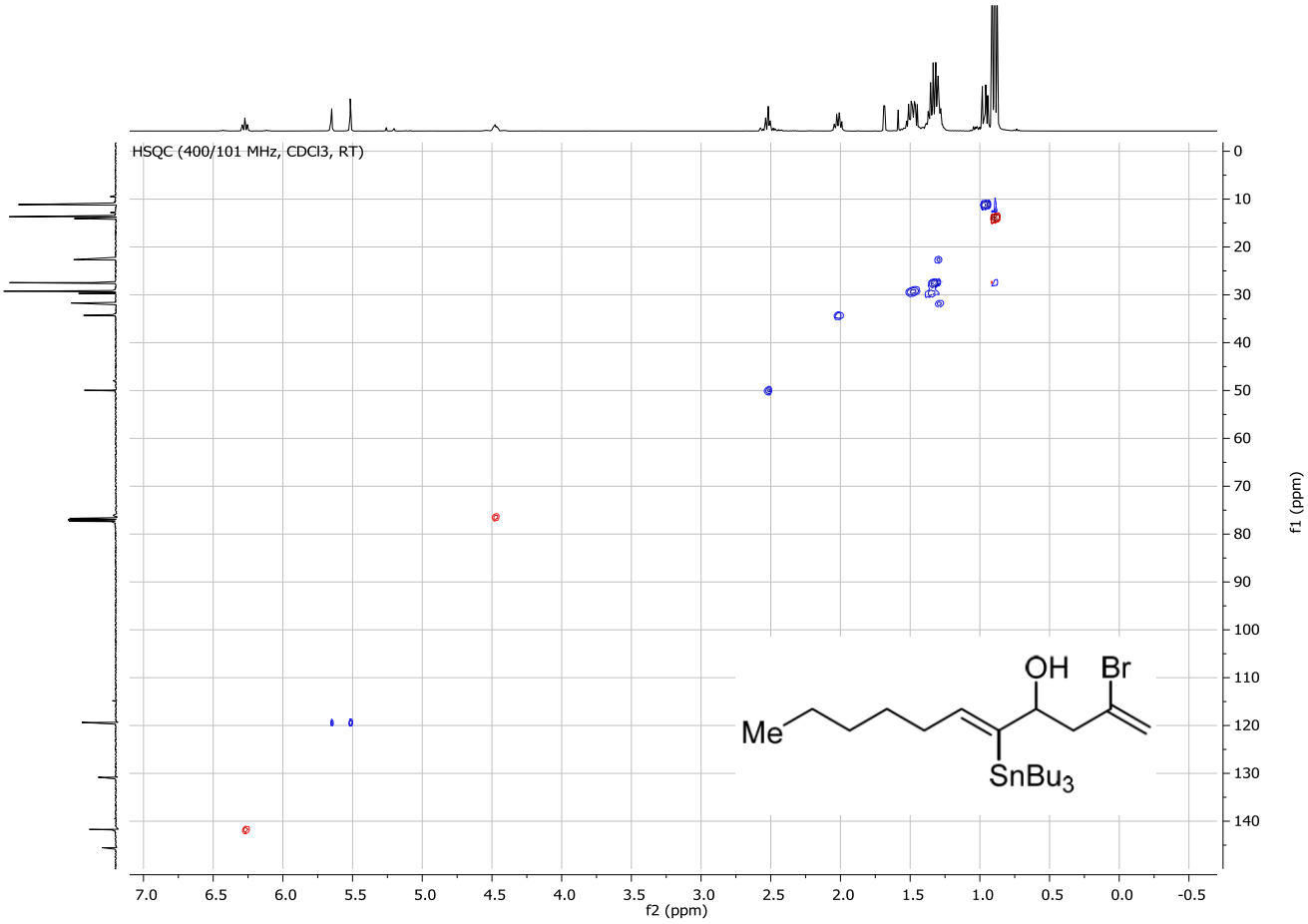


119Sn NMR (149 MHz, CDCl3, RT)

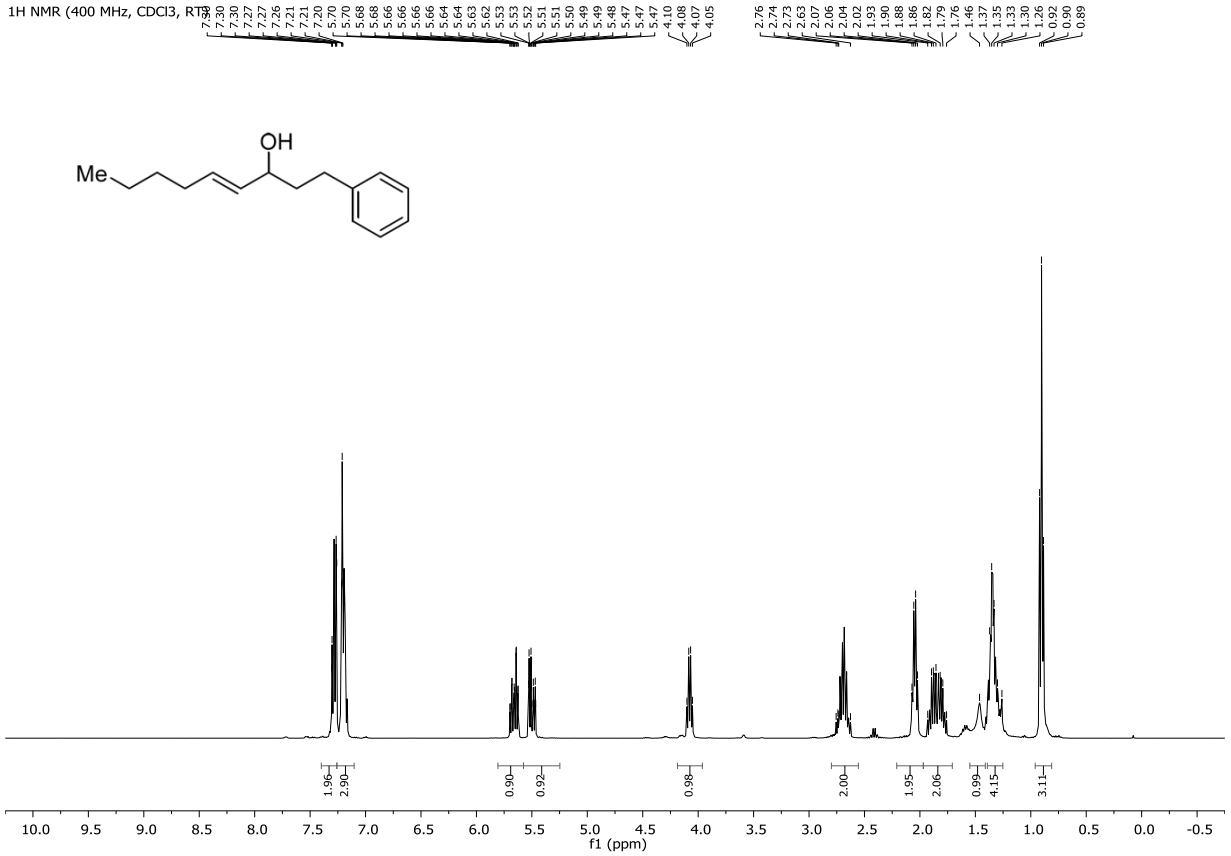
-54.02



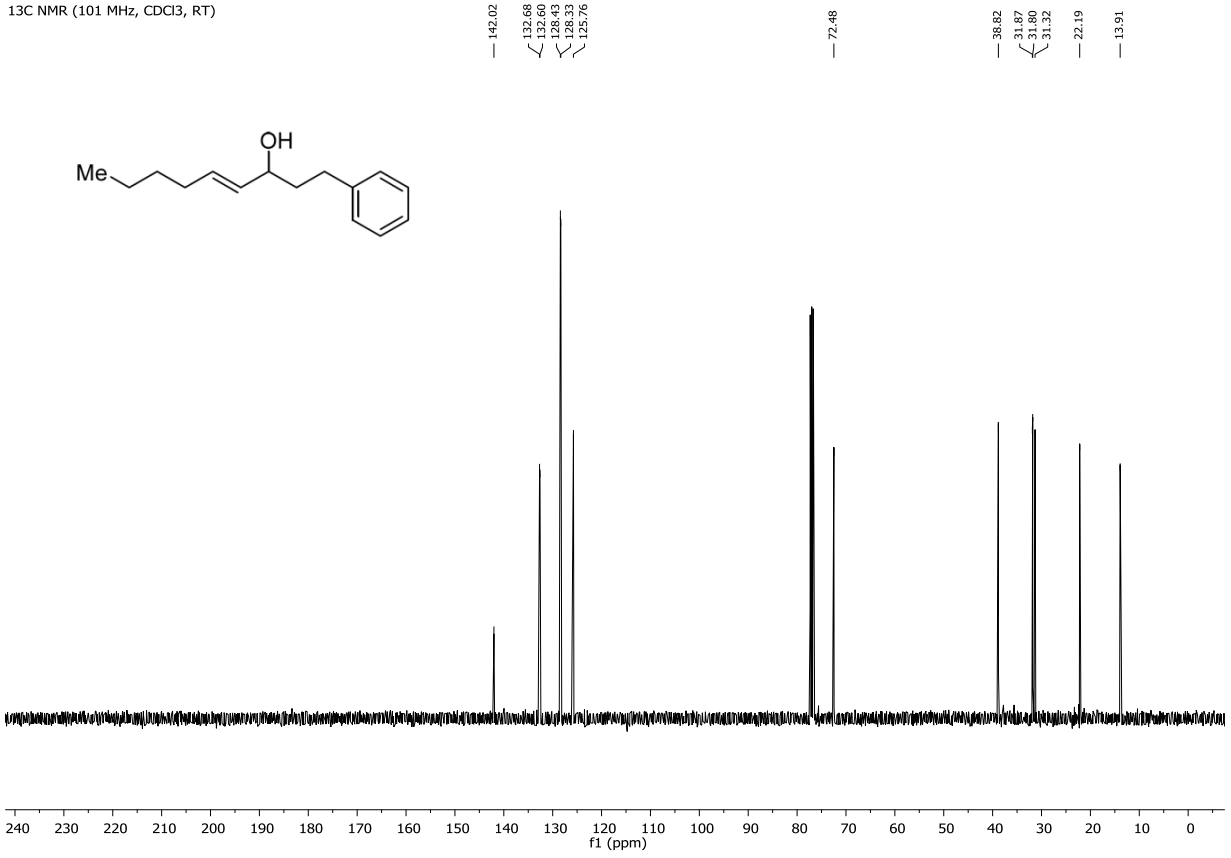


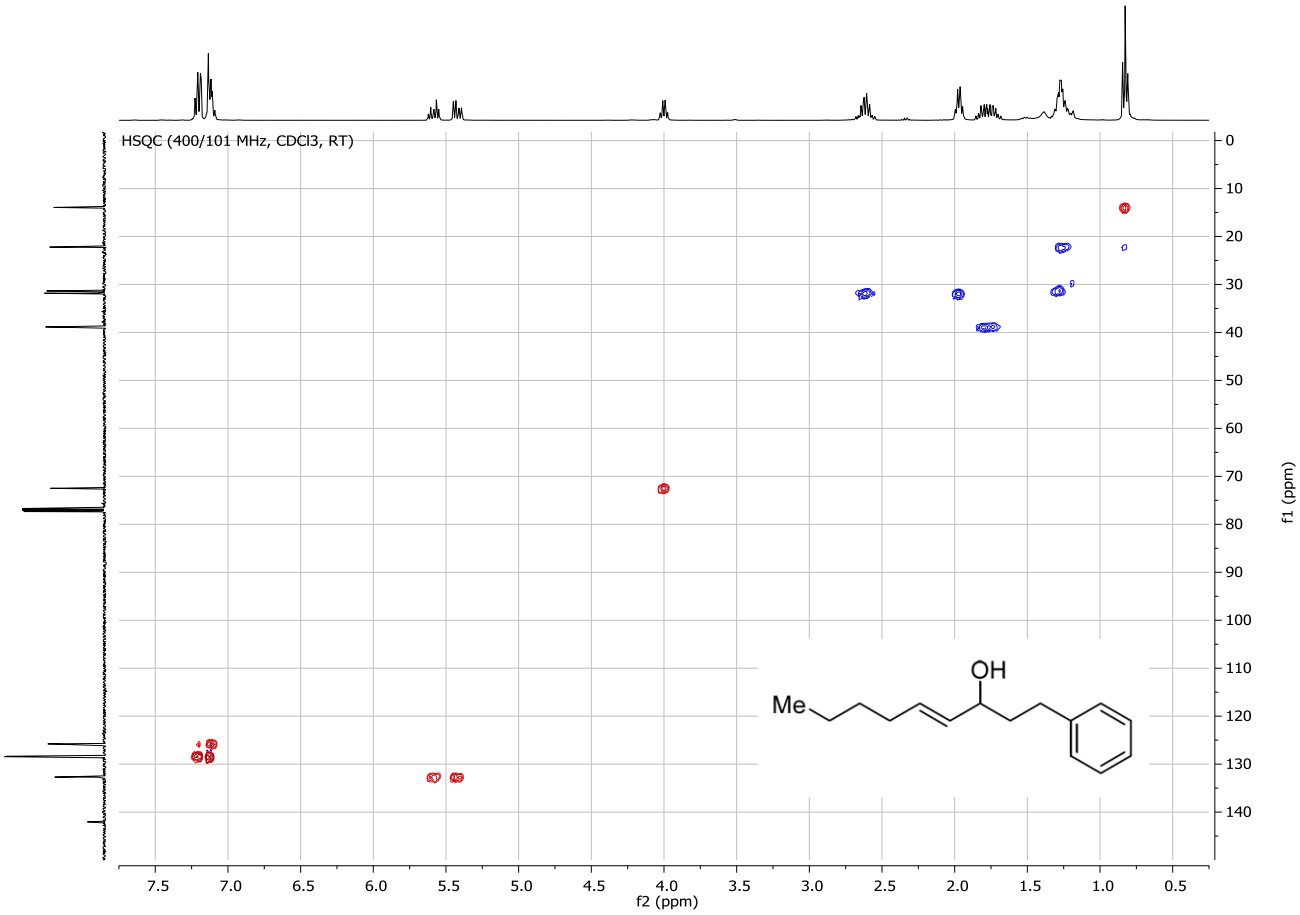


1H NMR (400 MHz, CDCl3, RT)

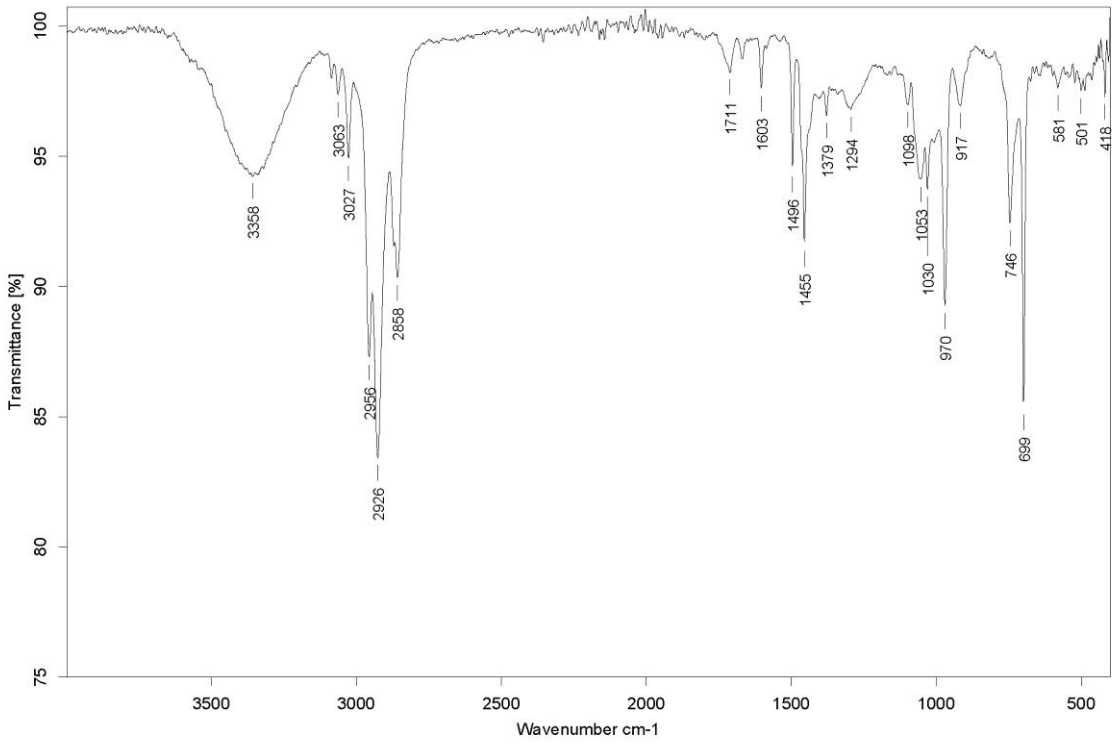


13C NMR (101 MHz, CDCl3, RT)

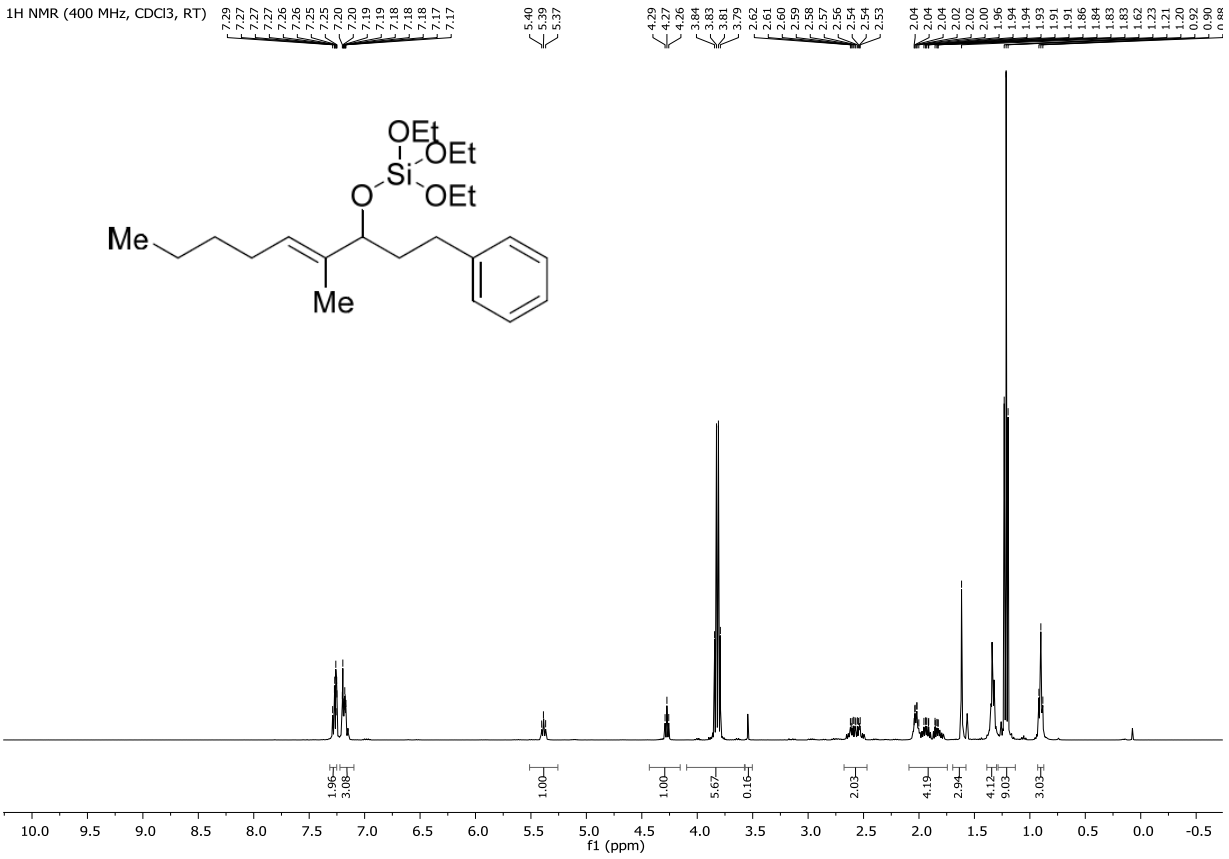




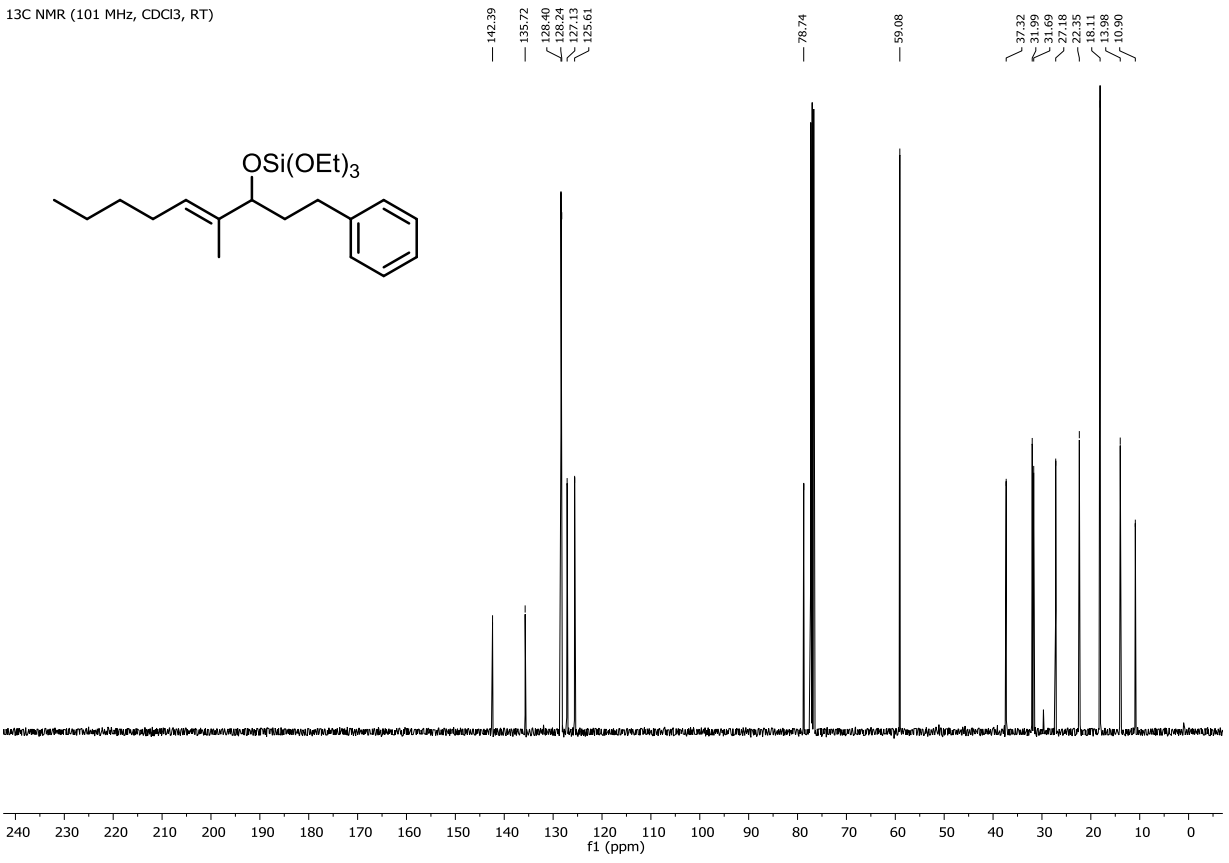
HUR-HA-002-20.0 **01.07.2016**

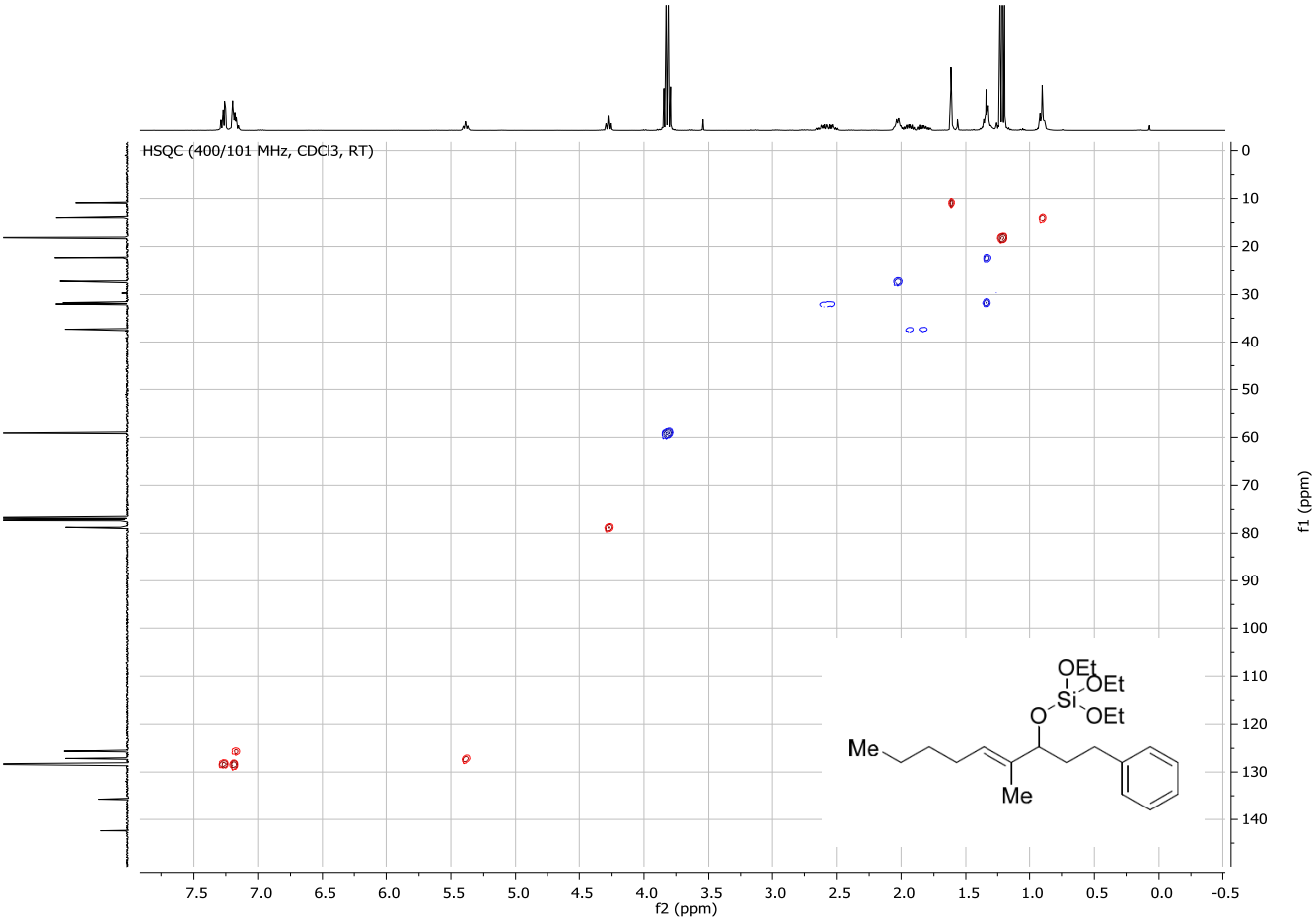


1H NMR (400 MHz, CDCl3, RT)

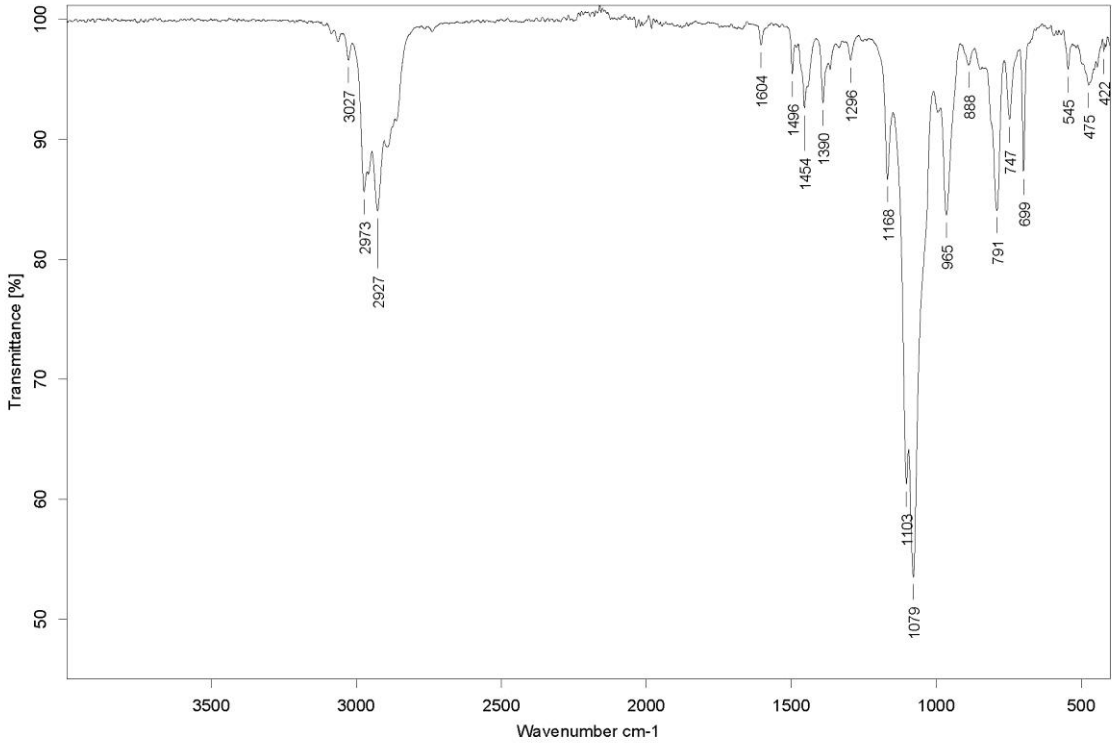


13C NMR (101 MHz, CDCl3, RT)

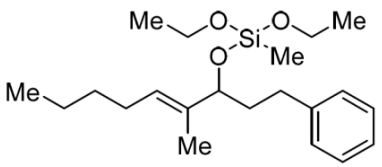




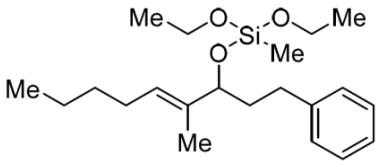
HUR-HA-123-11.0 **09.11.2016**

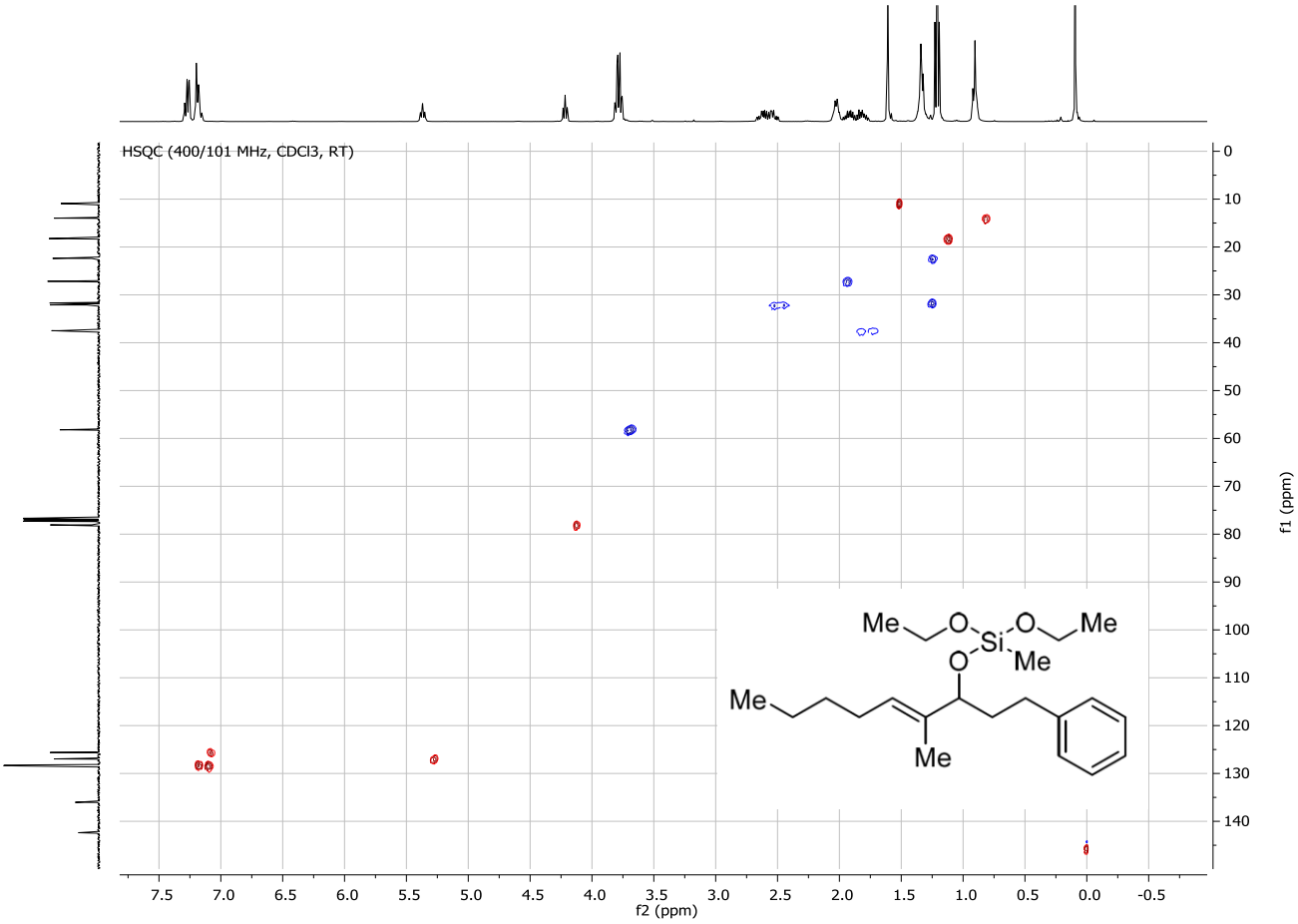


1H NMR (400 MHz, CDCl3, RT)

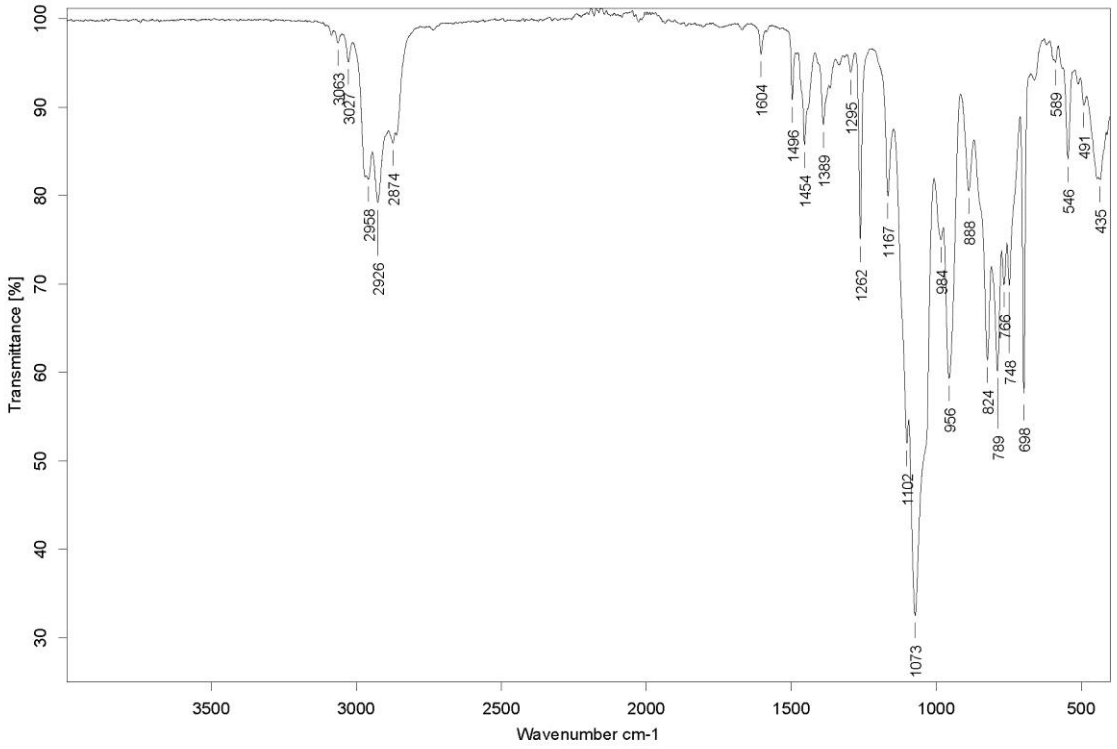


13C NMR (101 MHz, CDCl3, RT)

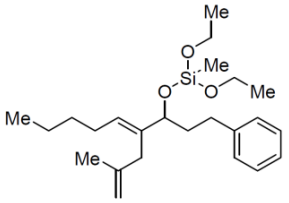




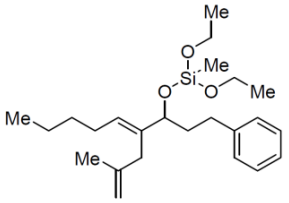
HUR-HA-146-11.0 **15.12.2016**

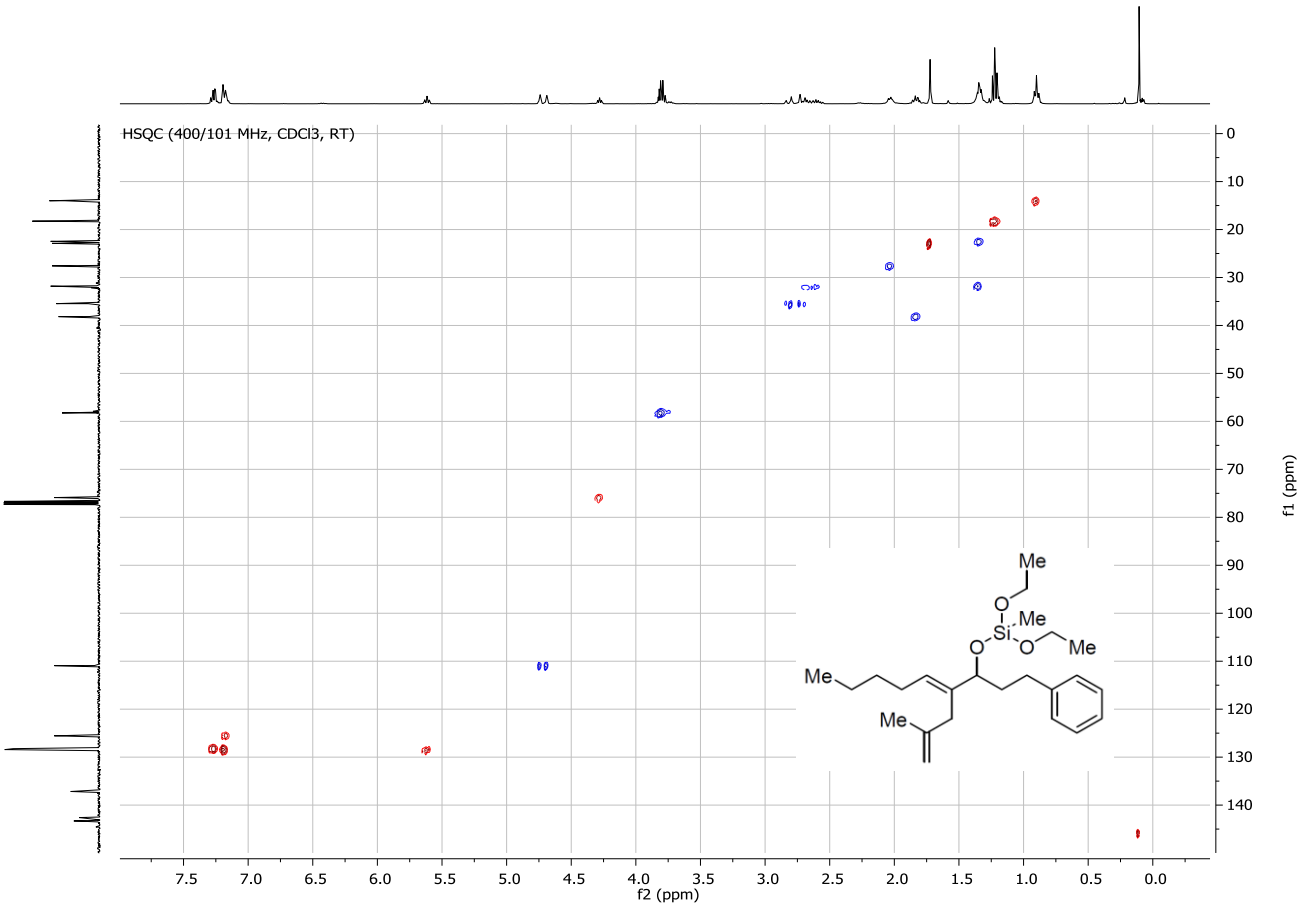


1H NMR (400 MHz, CDCl3, RT)

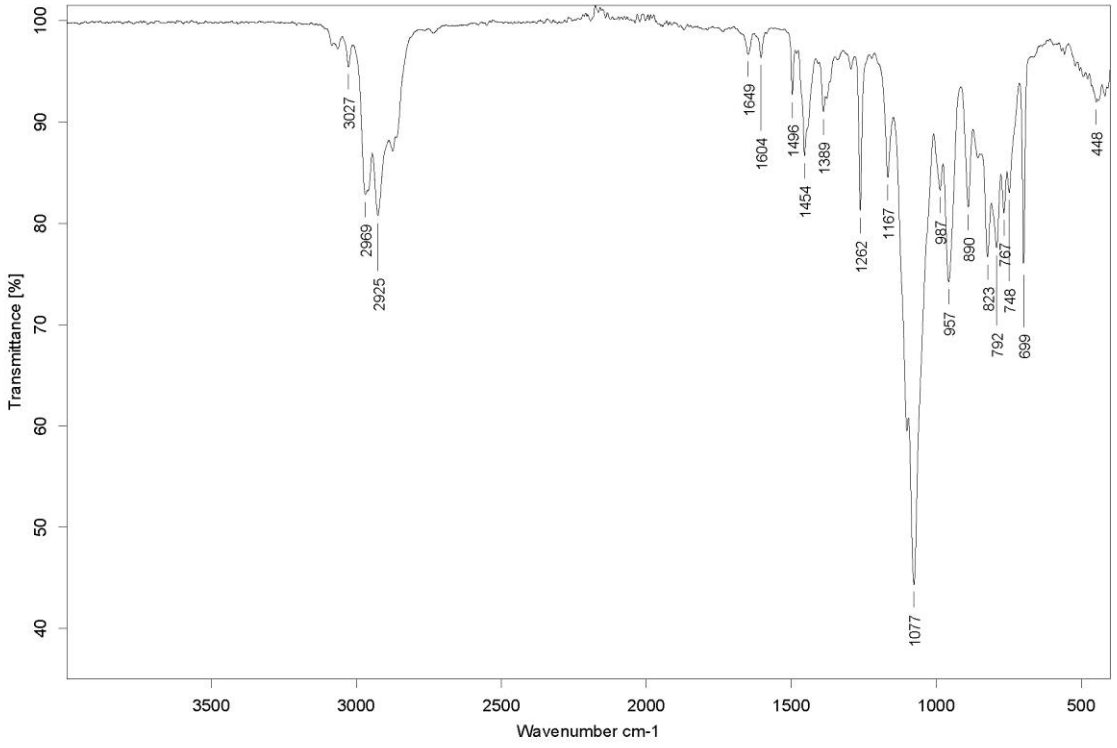


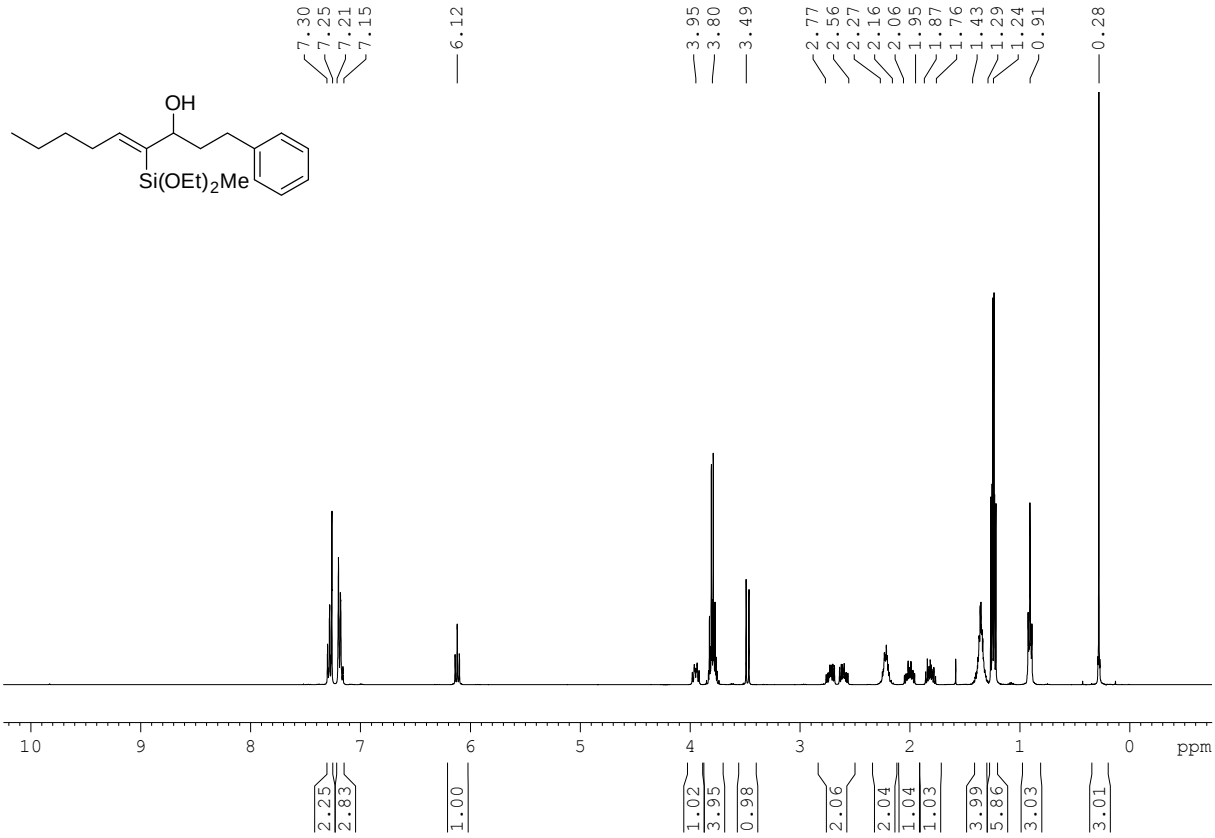
13C NMR (101 MHz, CDCl3, RT)

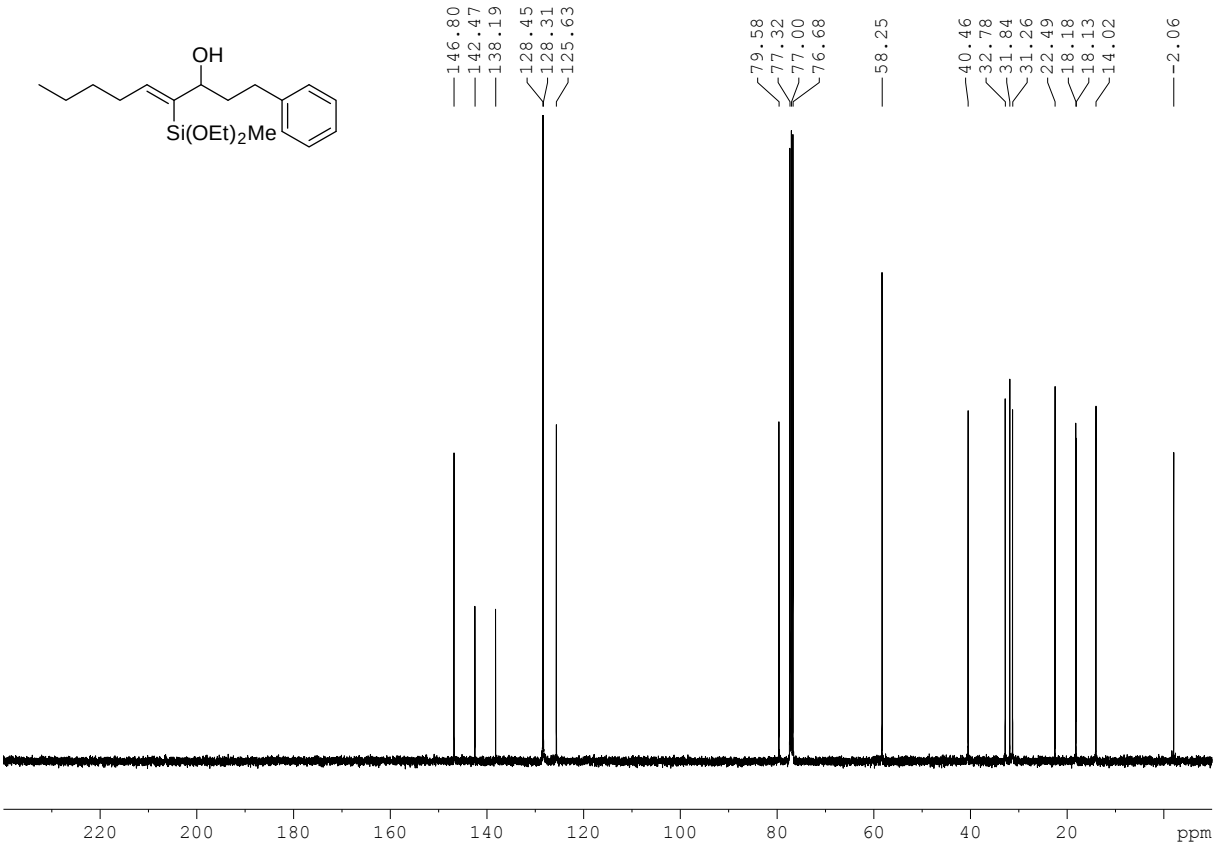


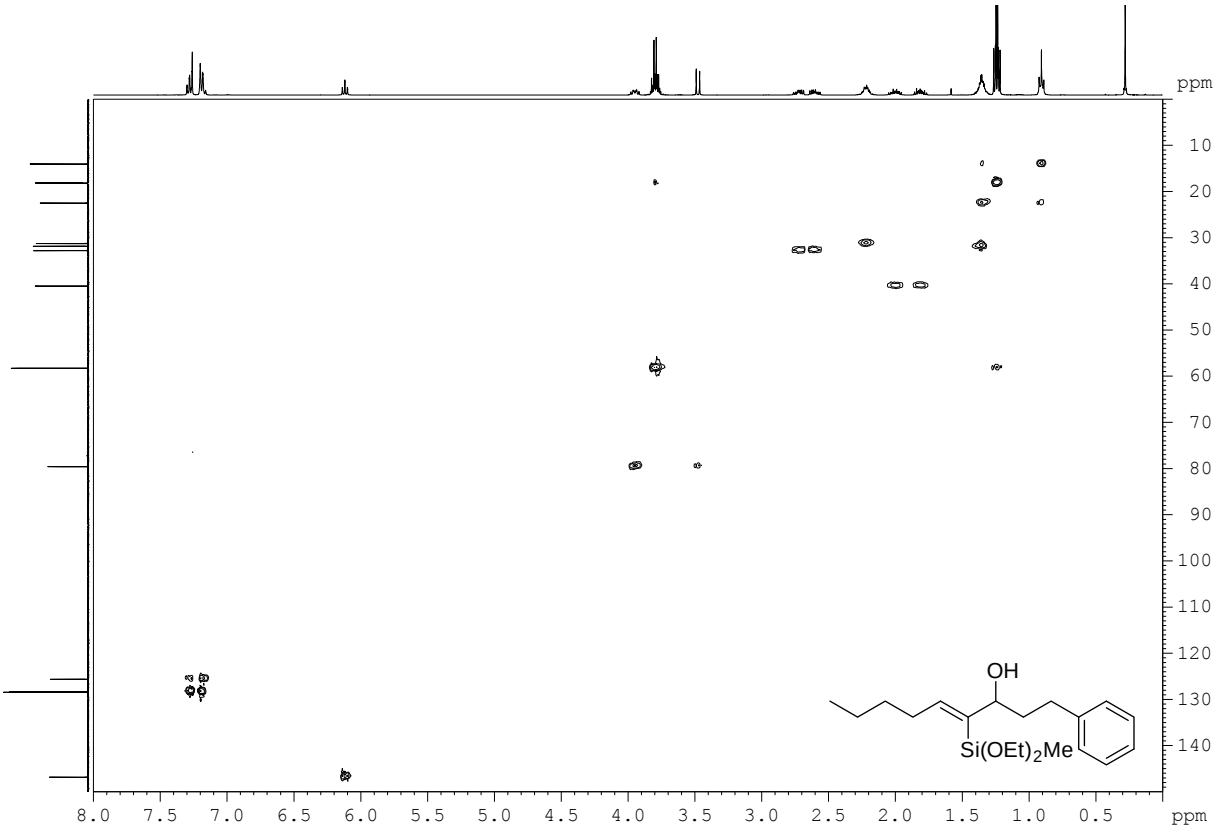


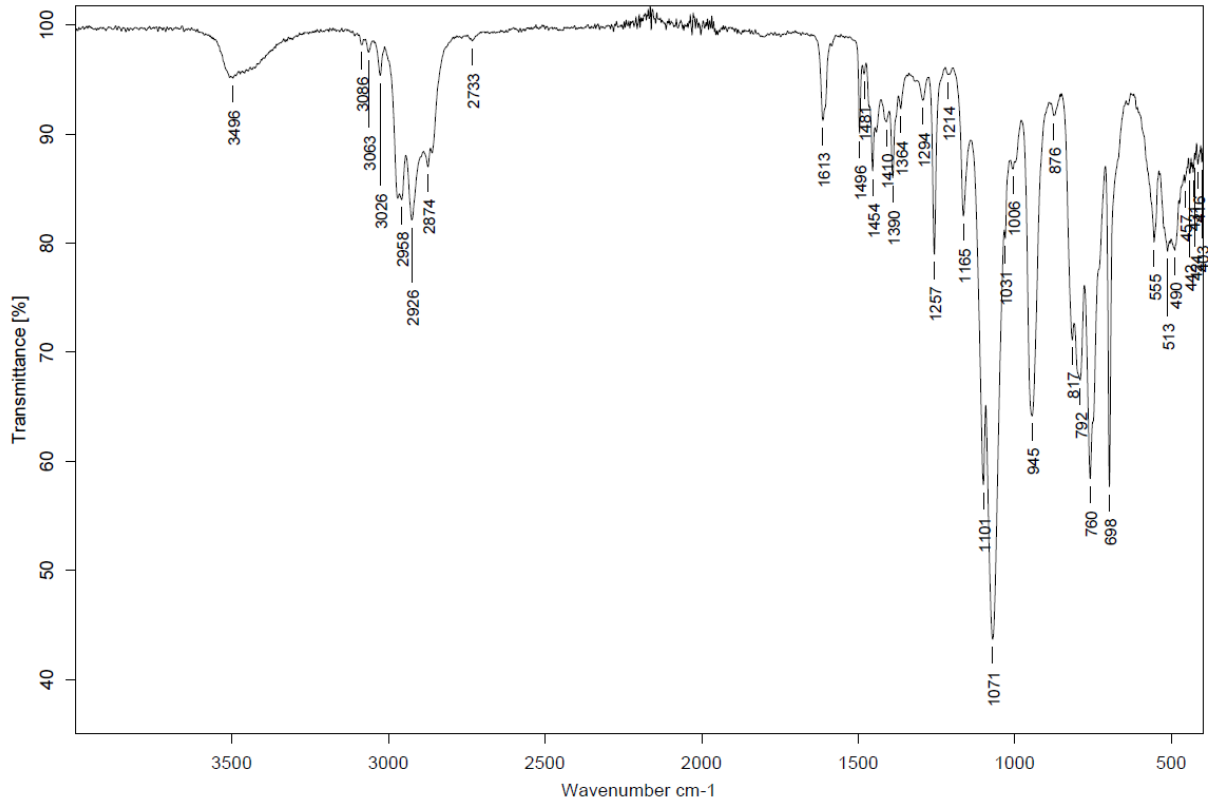
HUR-HA-150-12.0 **20.12.2016**

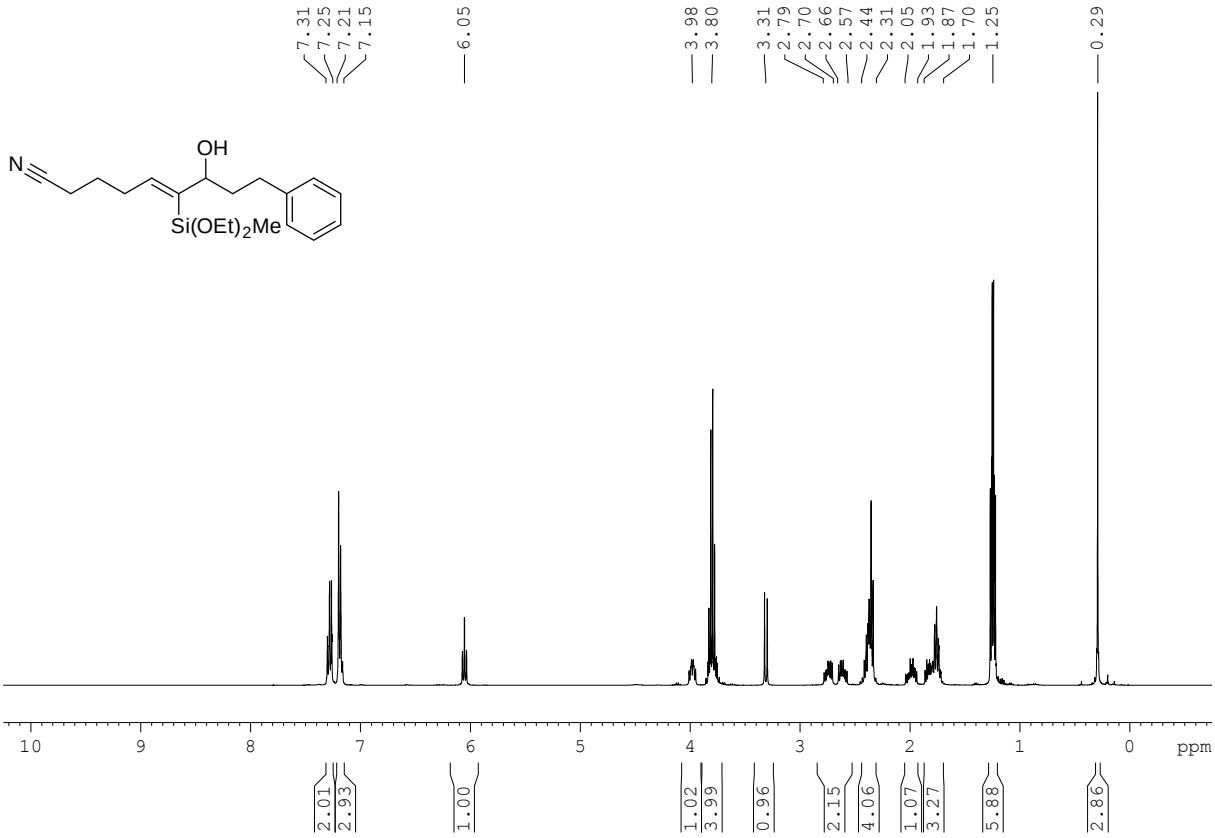


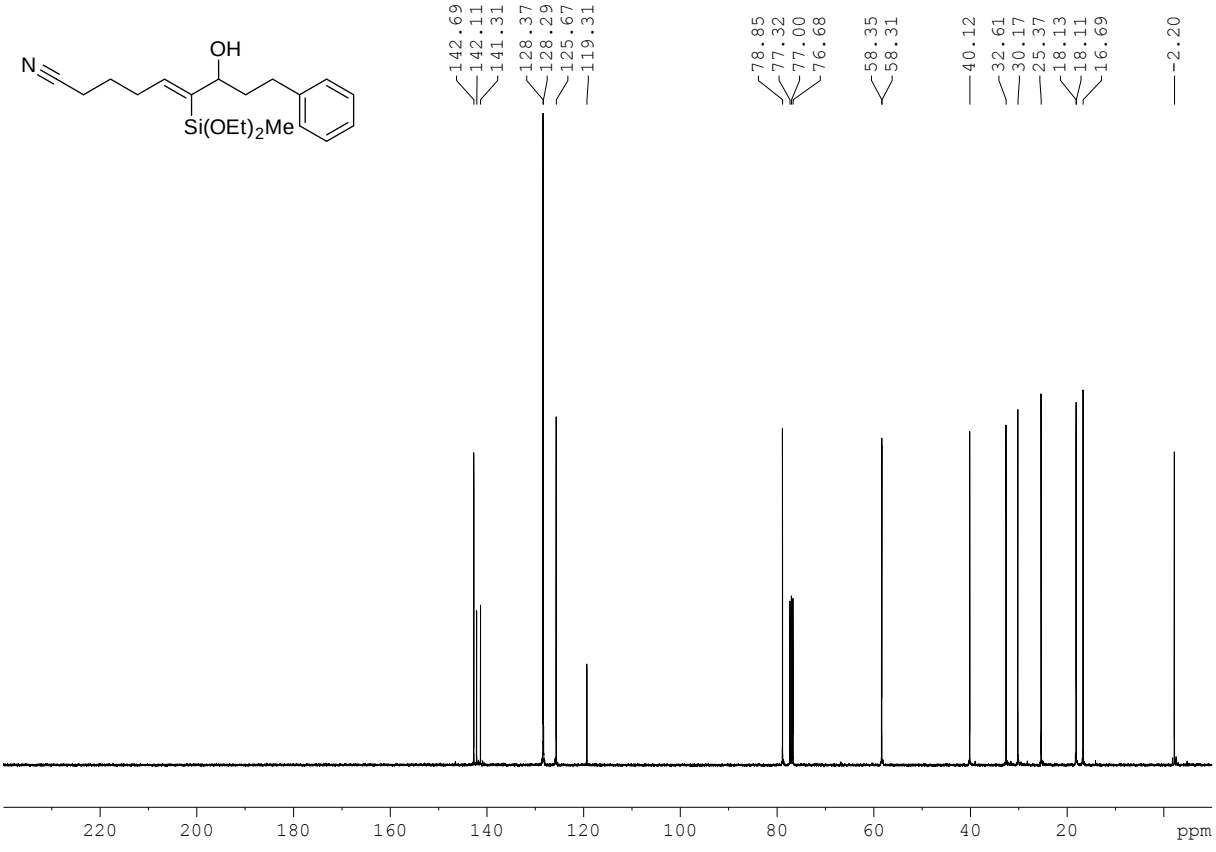

7.30
7.25
7.21
7.15
6.12
3.95
3.80
3.49
2.77
2.56
2.27
2.16
2.06
1.95
1.87
1.76
1.43
1.29
1.24
0.91
0.28
OH
Si(OEt)2Me
10
9
8
7
6
5
4
3
2
1
0
ppm
2.25
2.83
1.00
1.02
3.95
0.98
2.06
2.04
1.04
1.03
3.99
5.86
3.03
3.01

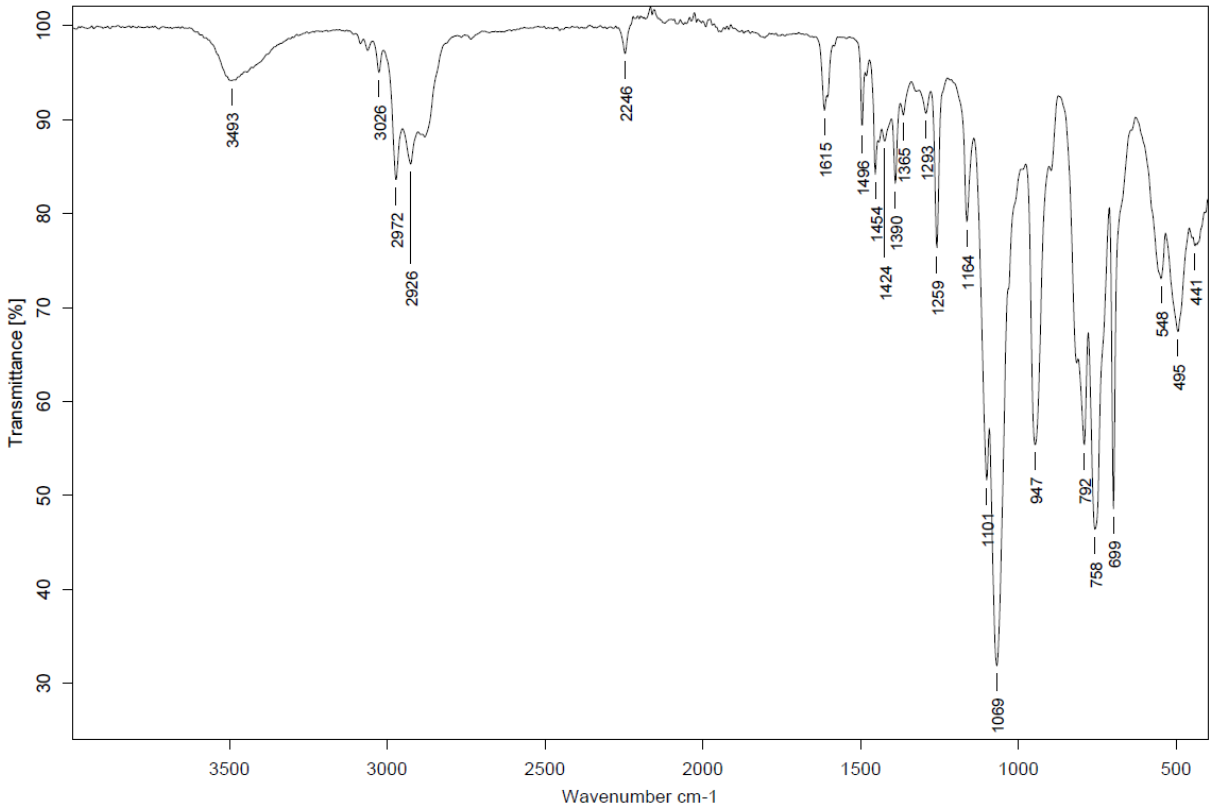

146.80
142.47
138.19
128.45
128.31
125.63
79.58
77.32
77.00
76.68
58.25
40.46
32.78
31.84
31.26
22.49
18.18
18.13
14.02
-2.06
OH
Si(OEt)2Me
220
200
180
160
140
120
100
80
60
40
20
ppm

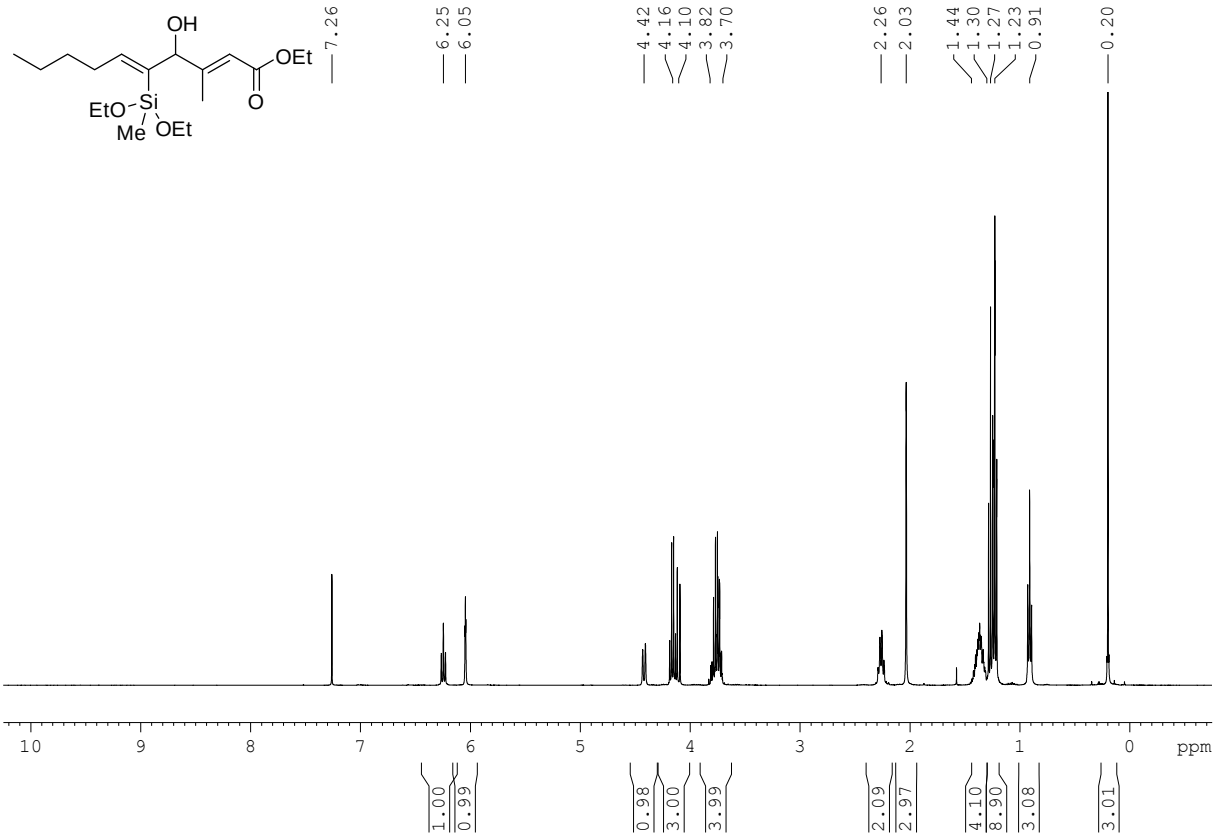

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
OH
Si(OEt)2Me

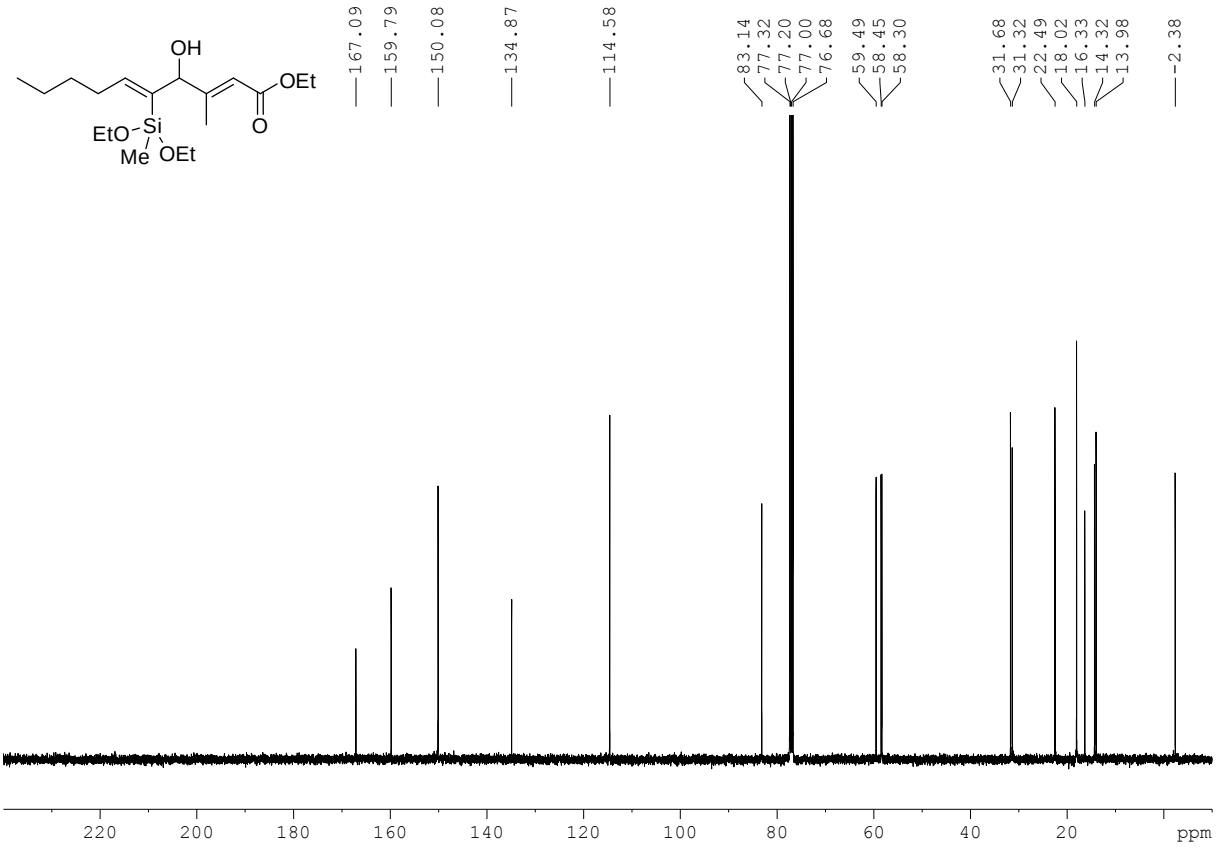

Transmittance [%]
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3496
3086
3063
3026
2958
2926
2874
2733
1613
1496
1481
1454
1410
1390
1364
1294
1257
1214
1165
1101
1071
1031
1006
945
876
817
792
760
698
555
513
490
457

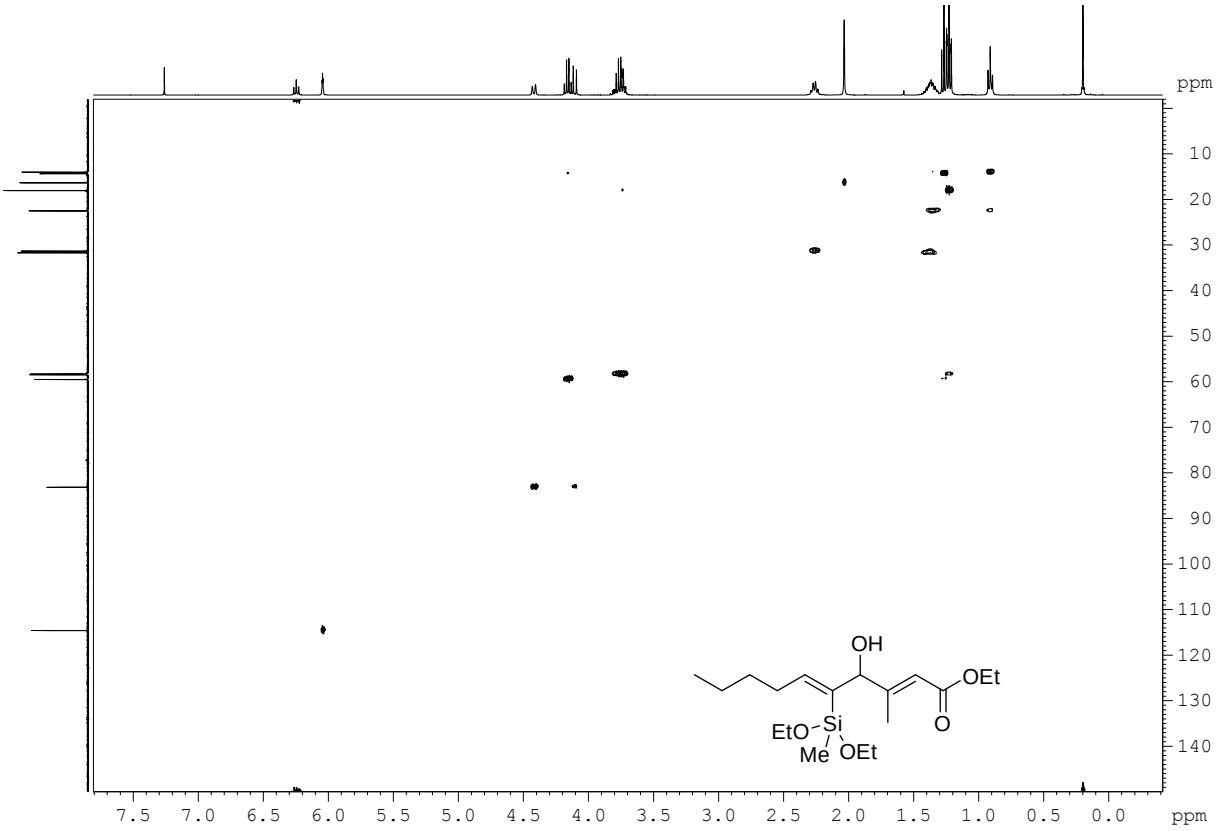

7.31
7.25
7.21
7.15
6.05
3.98
3.80
3.31
2.79
2.70
2.66
2.57
2.44
2.31
2.05
1.93
1.87
1.70
1.25
0.29
OH
N
Si(OEt)2Me
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
2.93
1.00
1.02
3.99
0.96
2.15
4.06
1.07
3.27
5.88
2.86

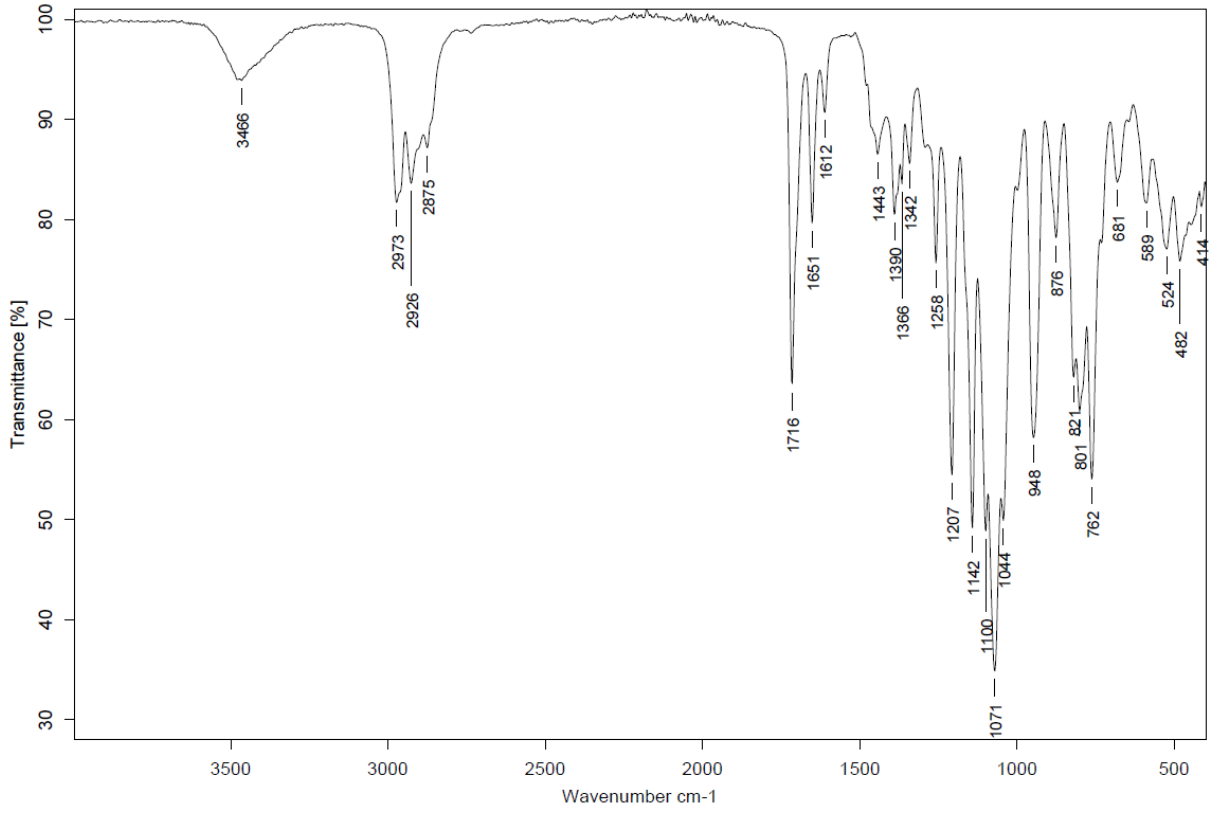

142.69
142.11
141.31
128.37
128.29
125.67
119.31
78.85
77.32
77.00
76.68
58.35
58.31
40.12
32.61
30.17
25.37
18.13
18.11
16.69
-2.20
OH
N
Si(OEt)2Me
220
200
180
160
140
120
100
80
60
40
20
ppm

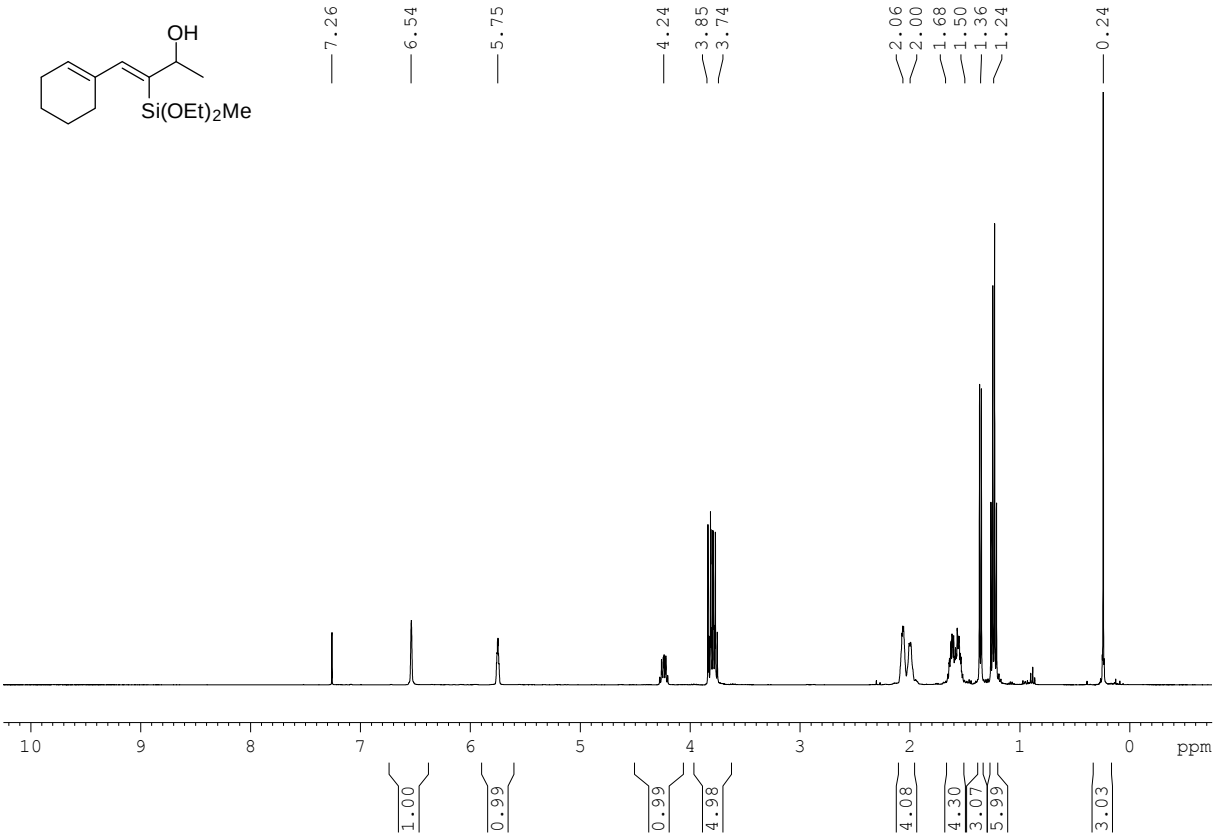

Transmittance [%]
100
90
80
70
60
50
40
30
3493
3026
2972
2926
2246
1615
1496
1454
1424
1390
1365
1293
1259
1164
1101
1069
947
792
758
699
548
495
441
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

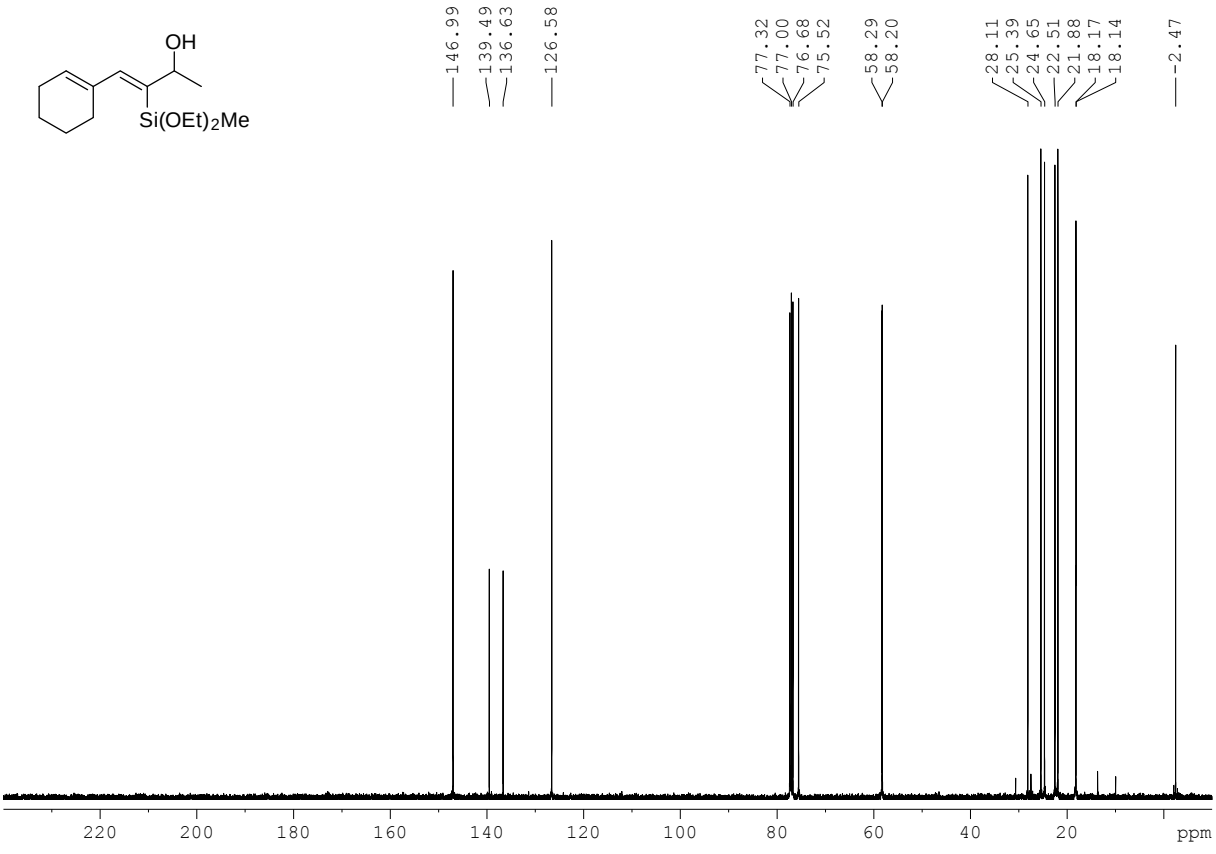

OH
OEt
O
EtO
Si
Me
OEt
7.26
6.25
6.05
4.42
4.16
4.10
3.82
3.70
2.26
2.03
1.44
1.30
1.27
1.23
0.91
0.20
ppm
1.00
0.99
0.98
3.00
3.99
2.09
2.97
4.10
8.90
3.08
3.01

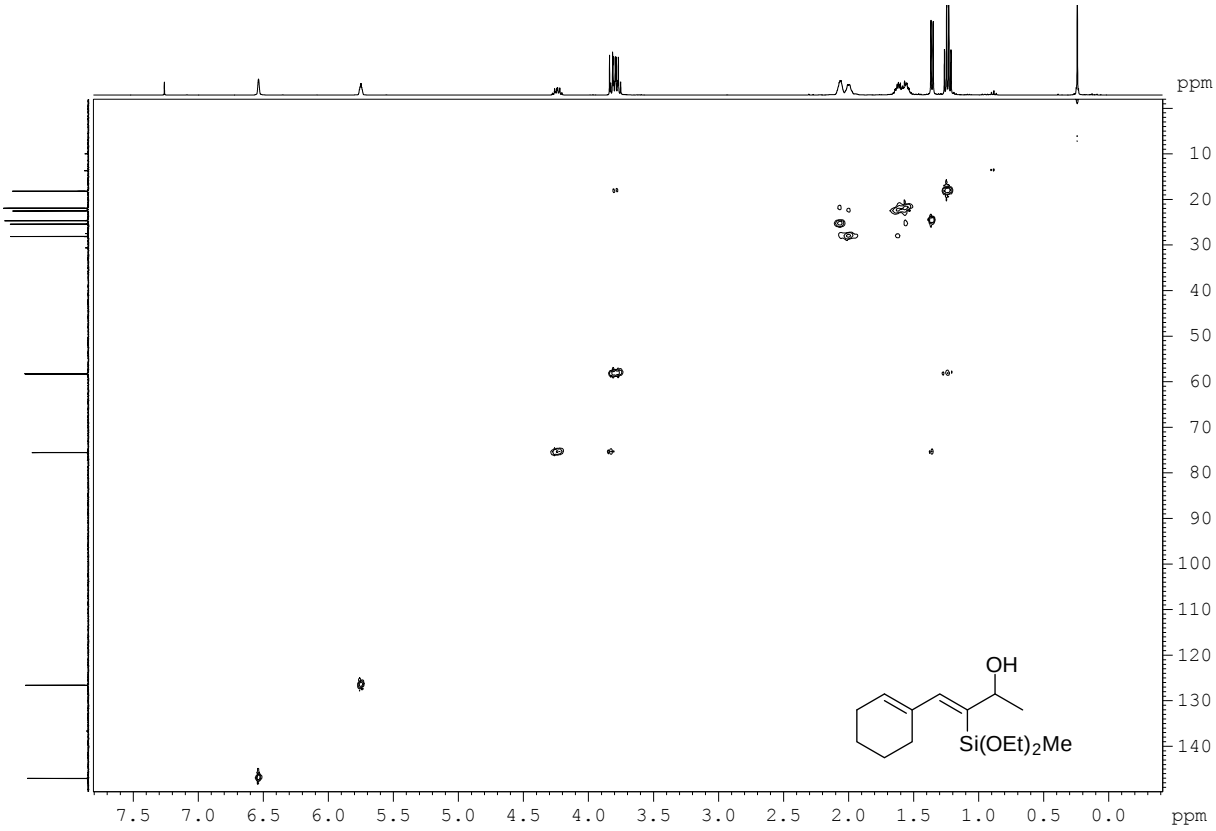

OH
OEt
O
EtO
Si
Me
OEt
167.09
159.79
150.08
134.87
114.58
83.14
77.32
77.20
77.00
76.68
59.49
58.45
58.30
31.68
31.32
22.49
18.02
16.33
14.32
13.98
-2.38
ppm

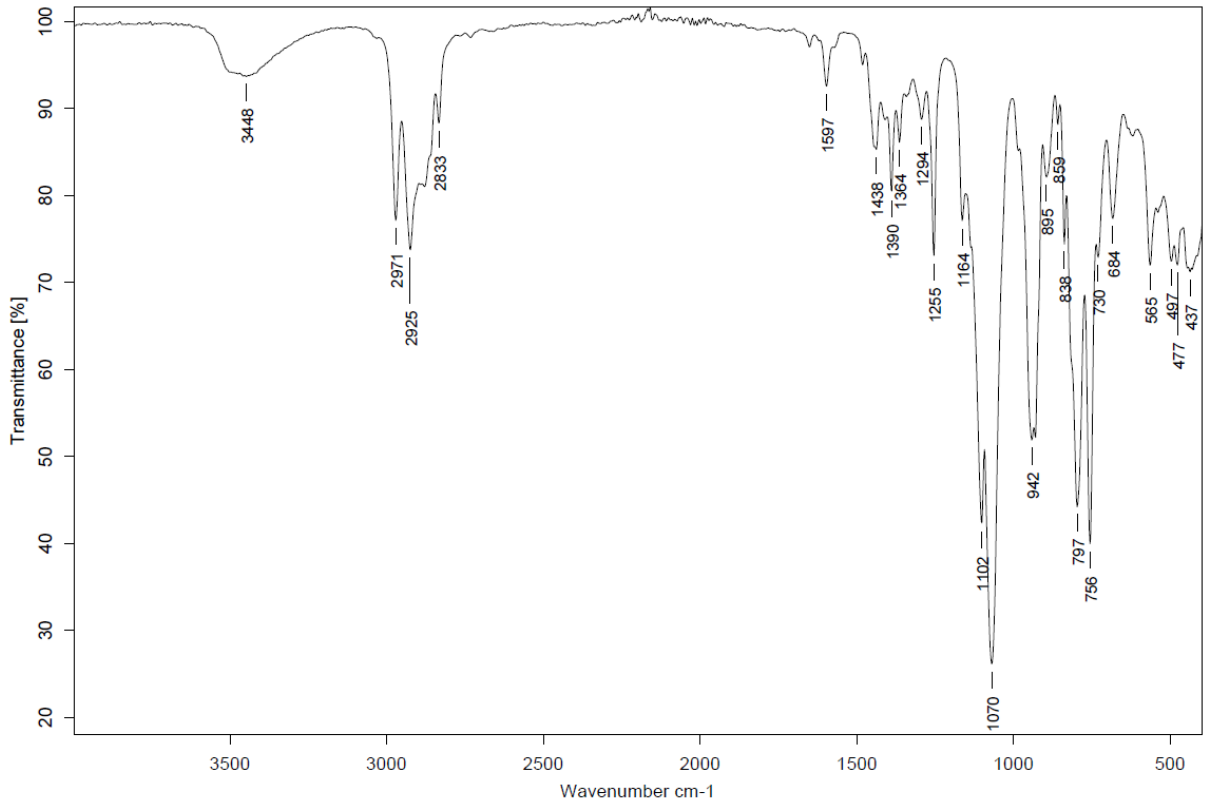

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
OH
OEt
O
EtO
Si
Me
OEt

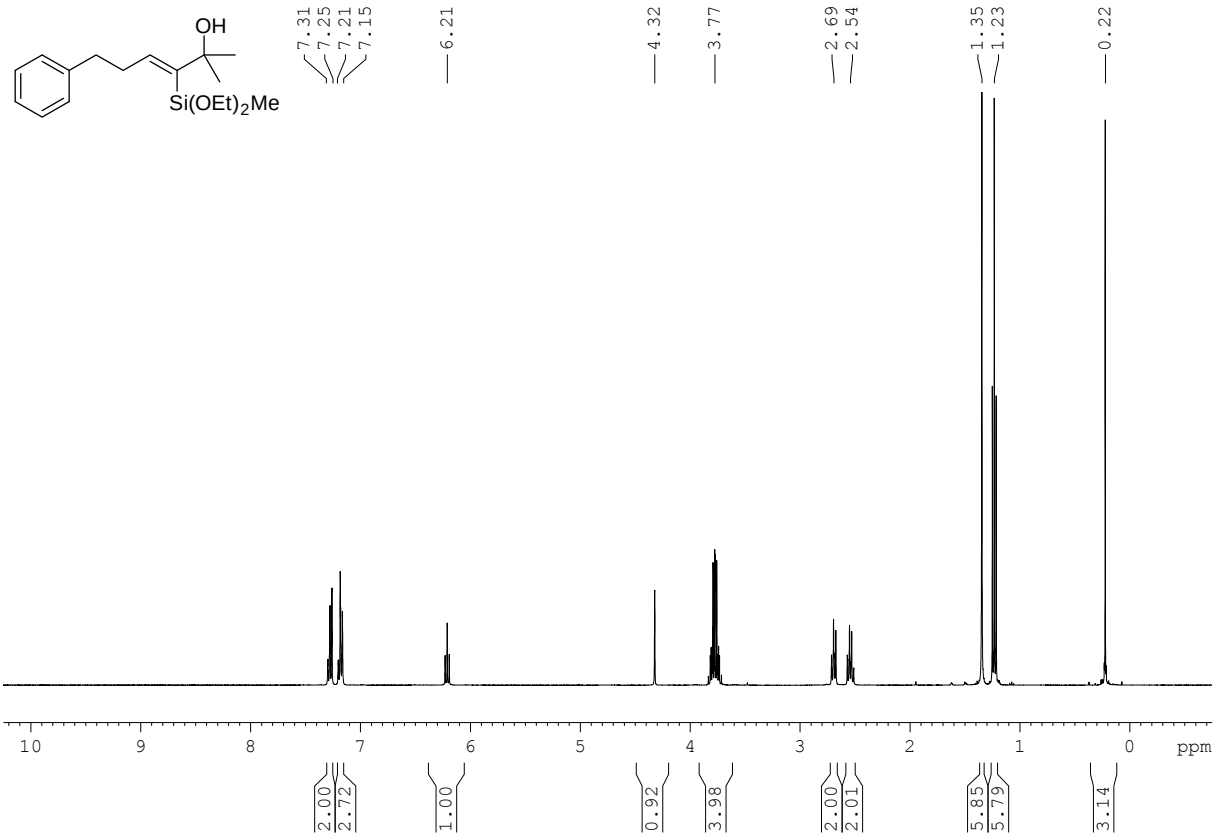

Transmittance [%]
100
90
80
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3466
2973
2926
2875
1716
1651
1612
1443
1390
1366
1342
1258
1207
1142
1100
1071
1044
948
876
821
801
762
681
589
524
482
414

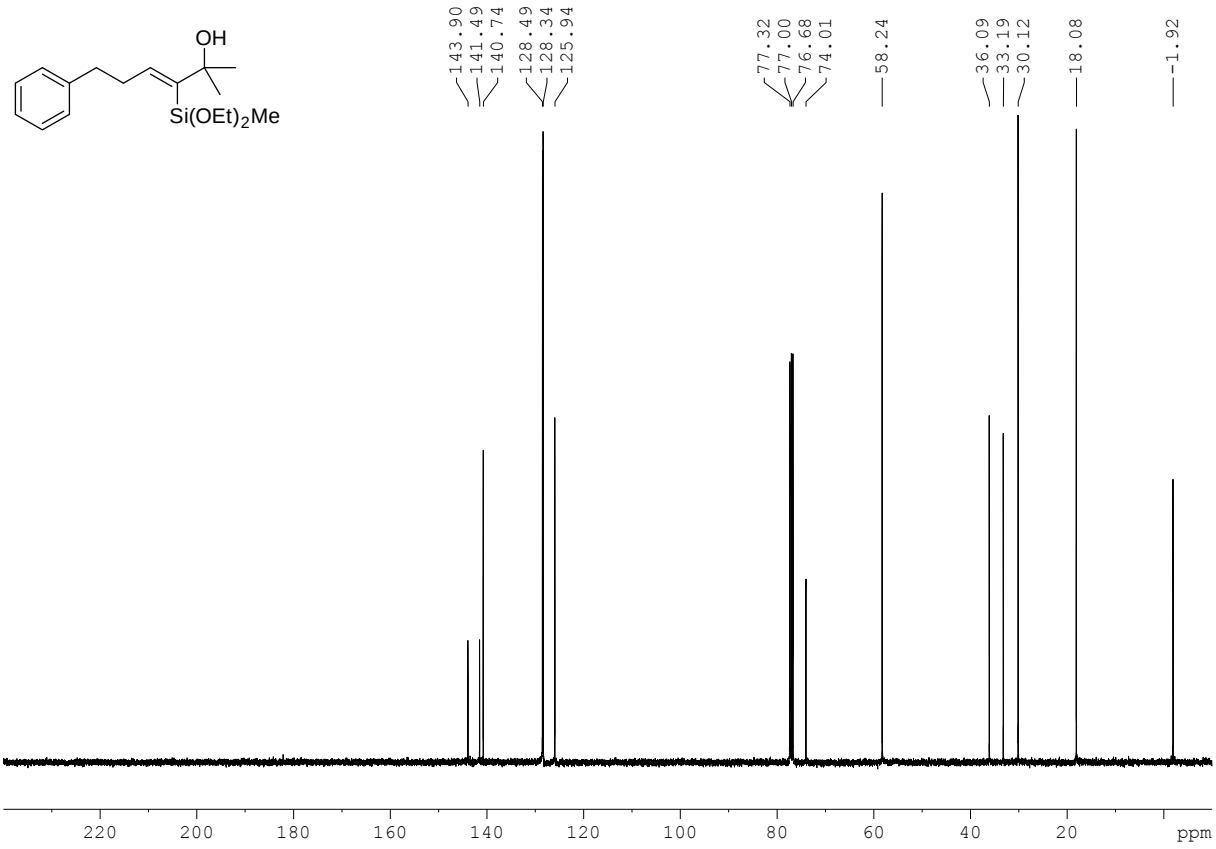

OH
Si(OEt)2Me
7.26
6.54
5.75
4.24
3.85
3.74
2.06
2.00
1.68
1.50
1.36
1.24
0.24
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
0.99
4.98
4.08
4.30
3.07
5.99
3.03

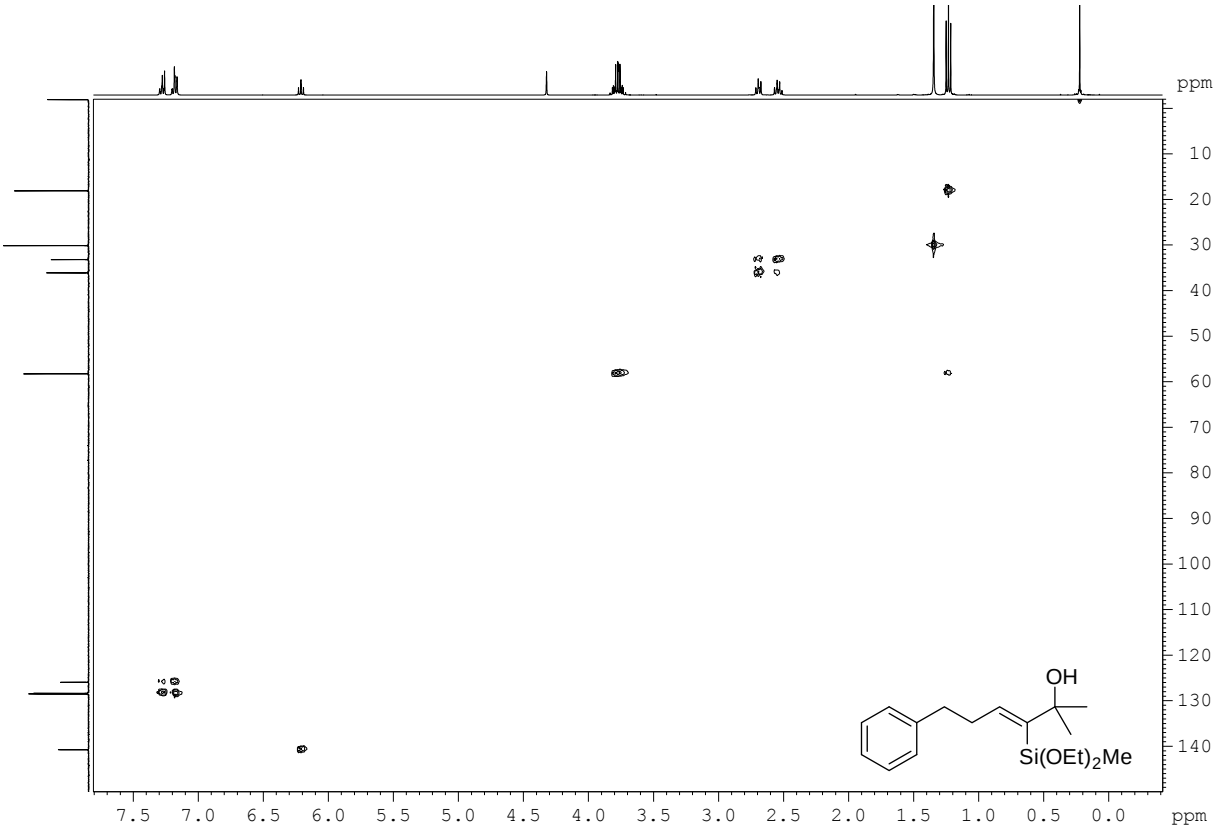

OH
Si(OEt)2Me
146.99
139.49
136.63
126.58
77.32
77.00
76.68
75.52
58.29
58.20
28.11
25.39
24.65
22.51
21.88
18.17
18.14
-2.47
220
200
180
160
140
120
100
80
60
40
20
ppm

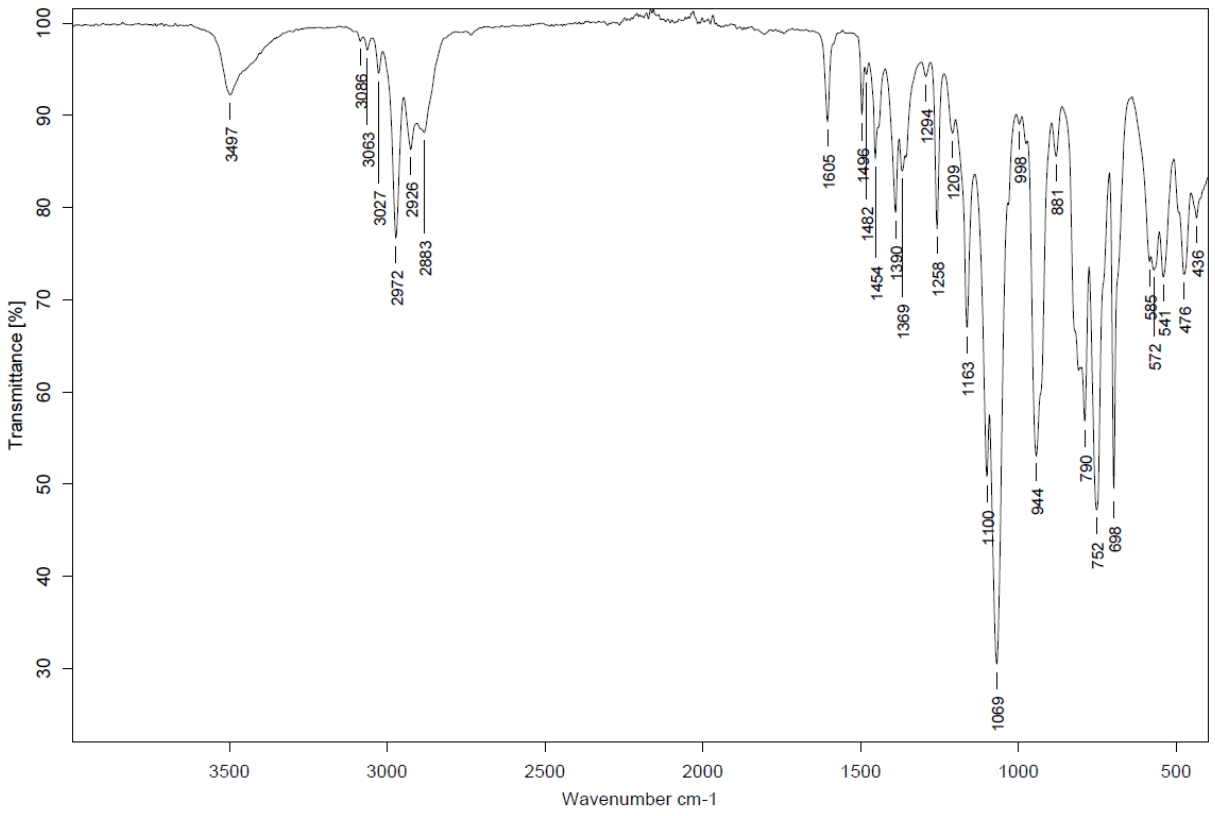

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
OH
Si(OEt)2Me

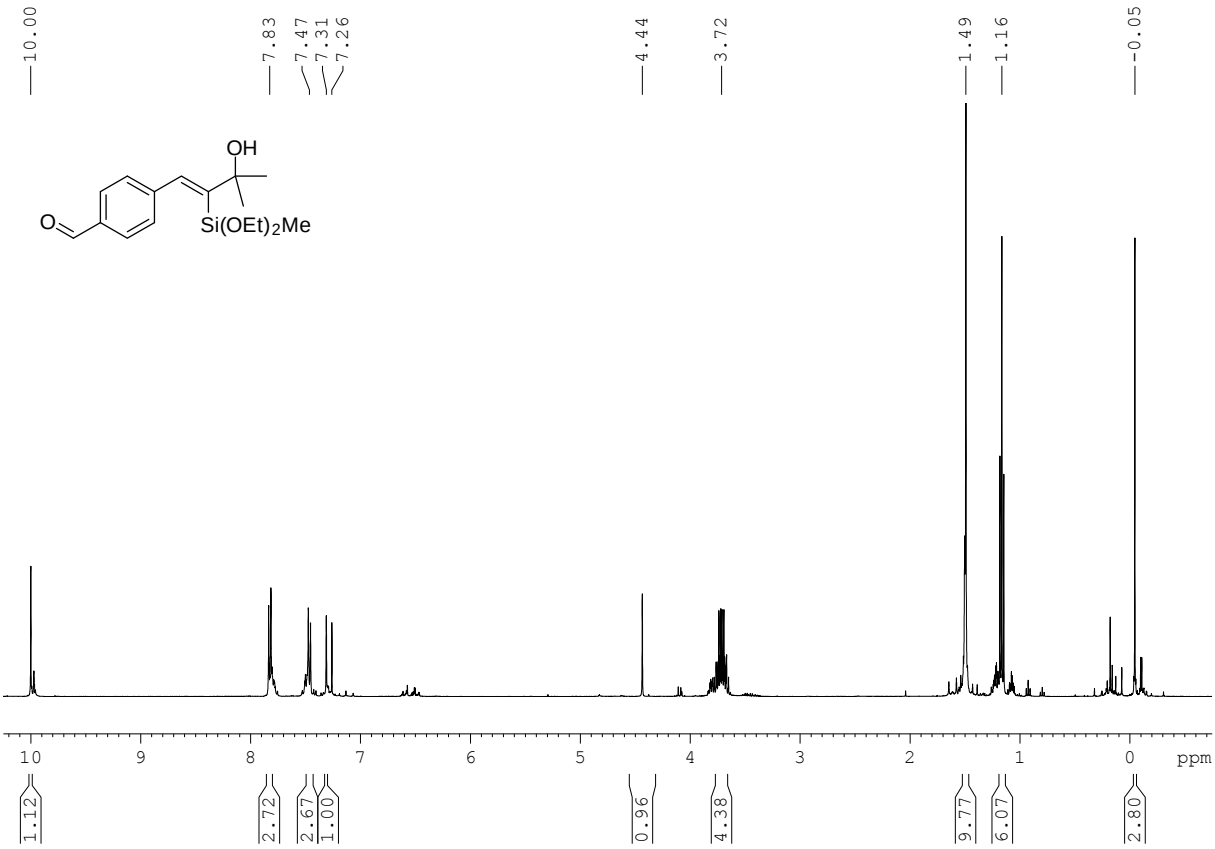

Transmittance [%]
100
90
80
70
60
50
40
30
20
3448
2971
2925
2833
1597
1438
1390
1364
1294
1255
1164
1102
1070
942
895
859
838
797
756
730
684
565
497
477
437
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

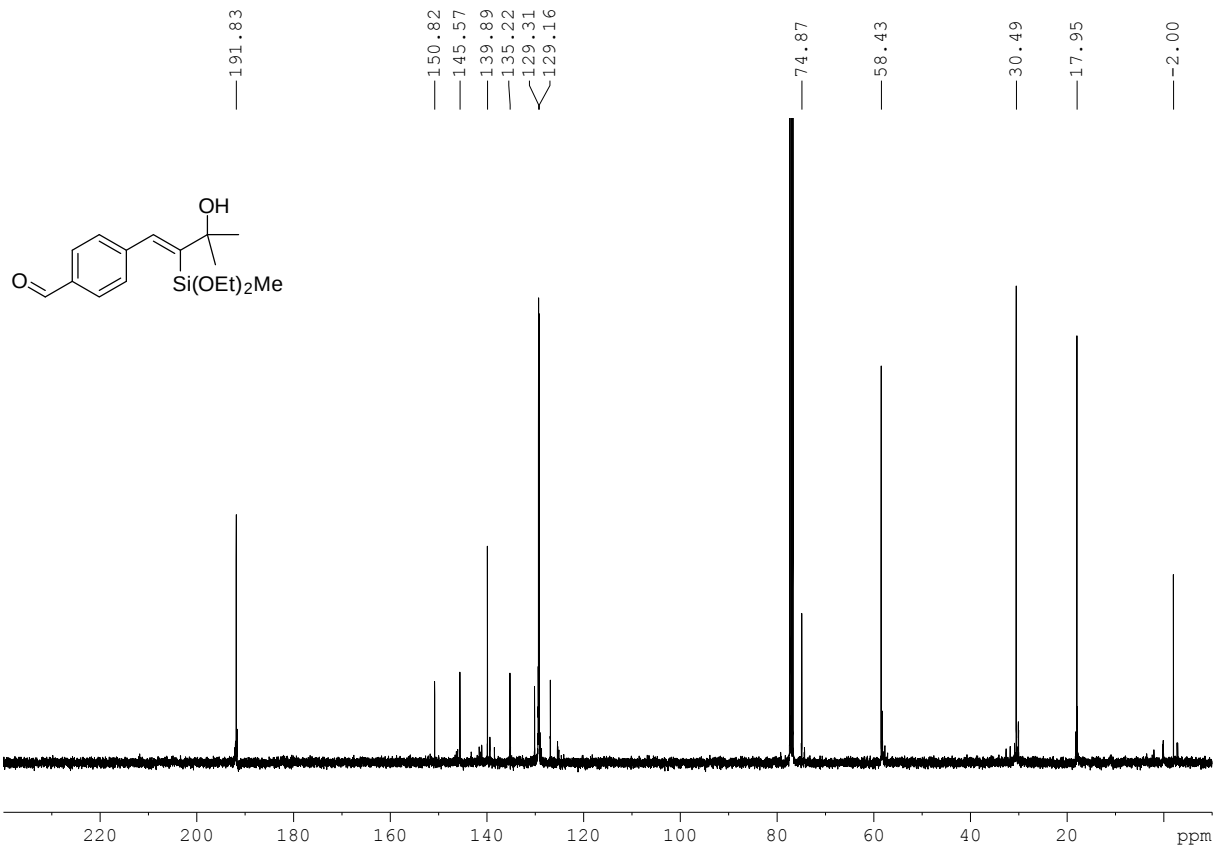

OH
Si(OEt)2Me
7.31
7.25
7.21
7.15
6.21
4.32
3.77
2.69
2.54
1.35
1.23
0.22
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.72
1.00
0.92
3.98
2.00
2.01
5.85
5.79
3.14

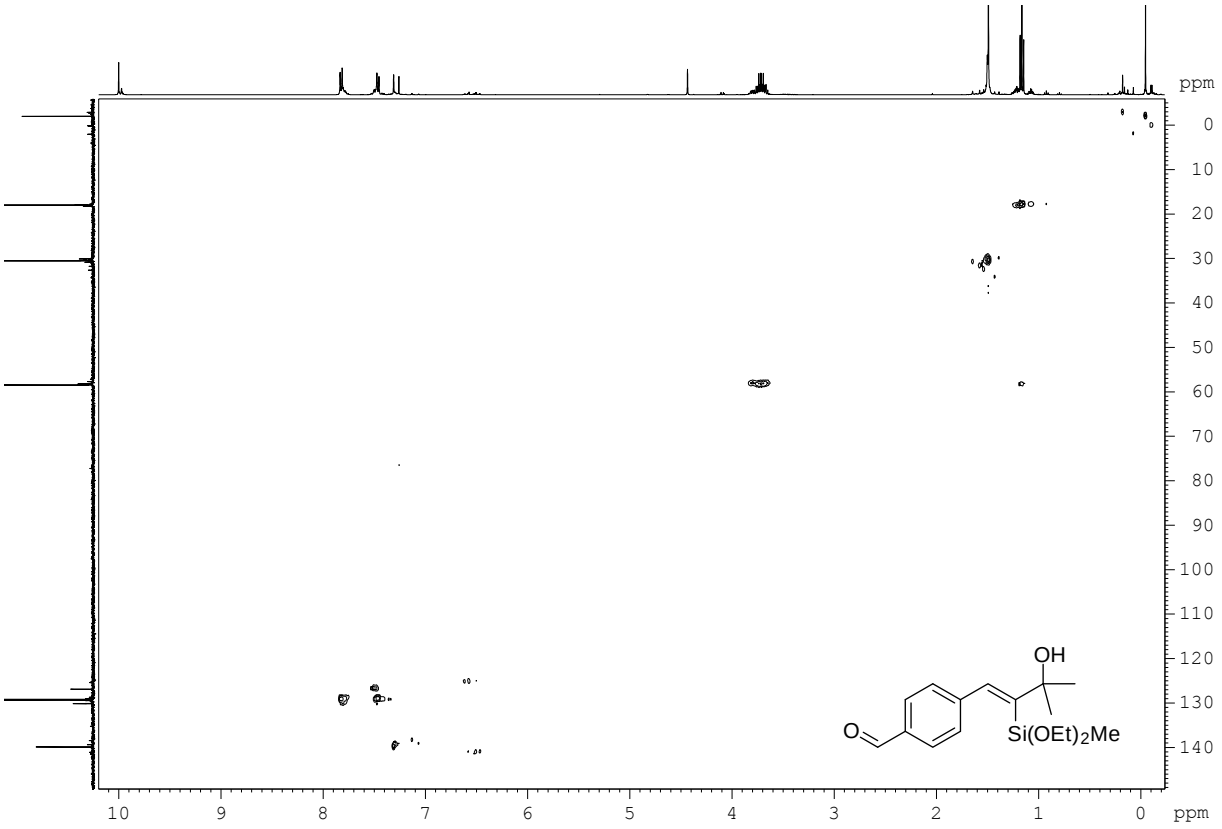

OH
Si(OEt)2Me
143.90
141.49
140.74
128.49
128.34
125.94
77.32
77.00
76.68
74.01
58.24
36.09
33.19
30.12
18.08
-1.92
220
200
180
160
140
120
100
80
60
40
20
ppm

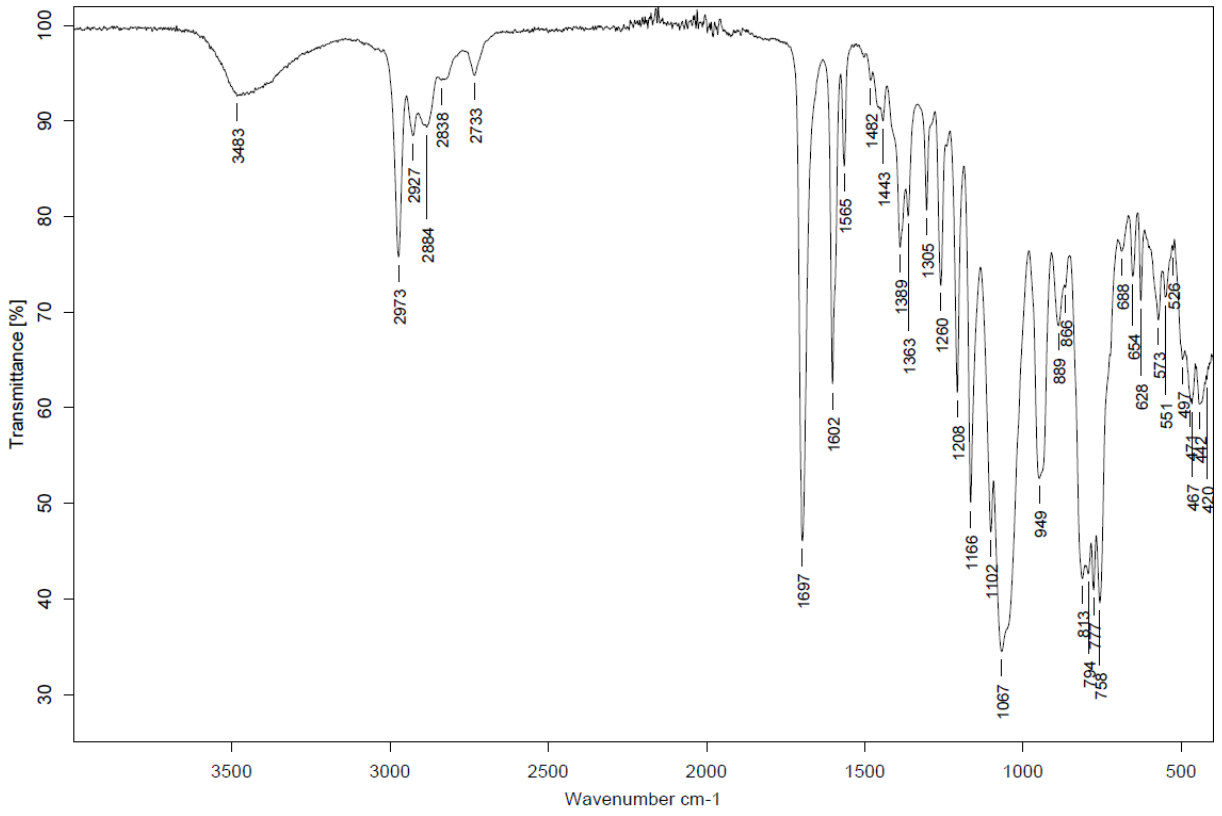

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
OH
Si(OEt)2Me

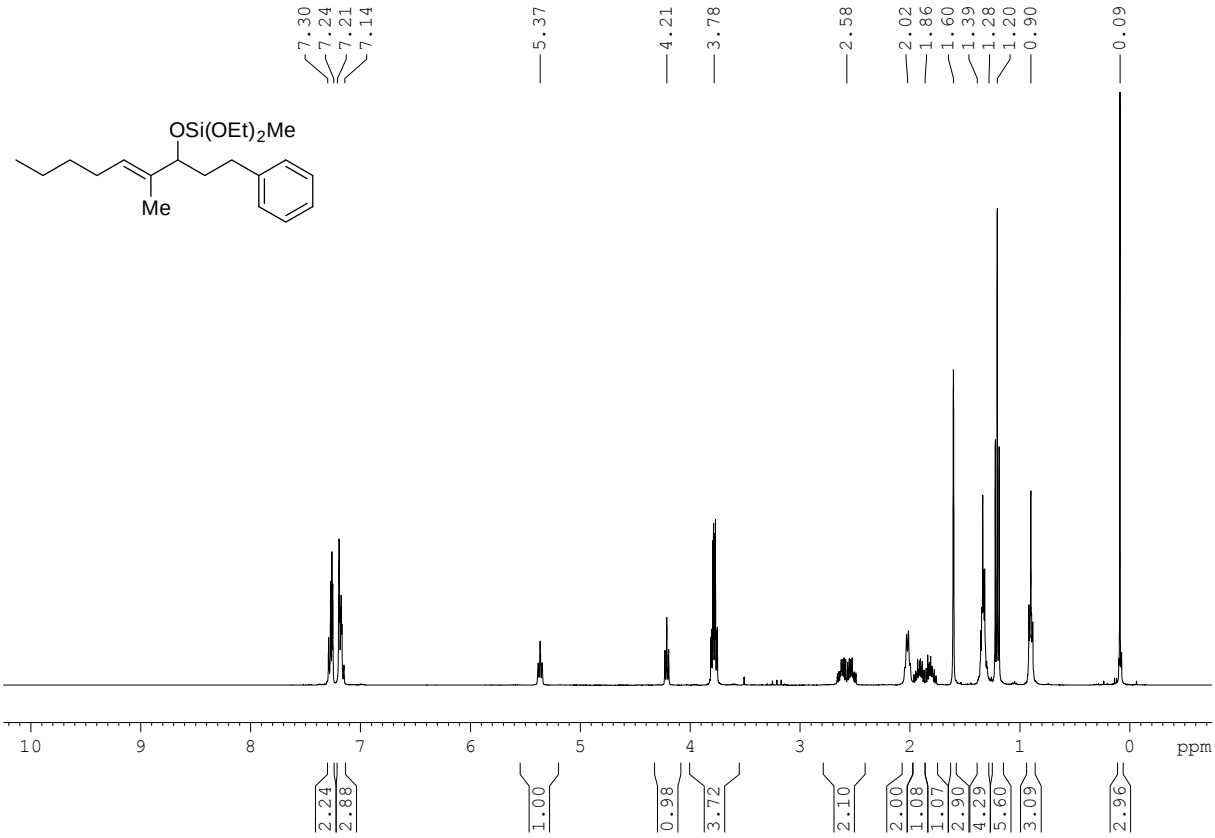

Transmittance [%]
100
90
80
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3497
3086
3063
3027
2972
2926
2883
1605
1496
1482
1454
1390
1369
1294
1258
1209
1163
1100
1069
998
944
881
790
752
698
572
585
541
476
436

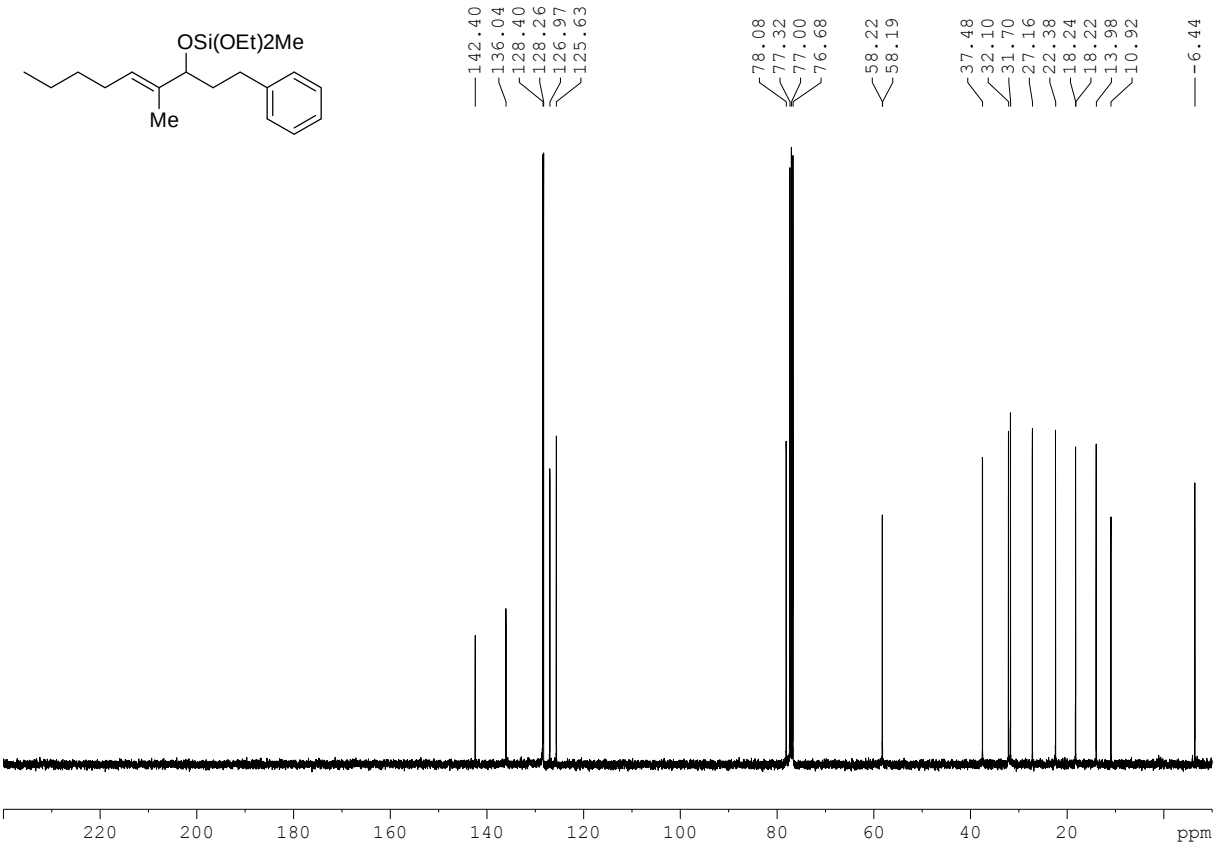

10.00
7.83
7.47
7.31
7.26
4.44
3.72
1.49
1.16
-0.05
OH
O
Si(OEt)2Me
10
9
8
7
6
5
4
3
2
1
0
ppm
1.12
2.72
2.67
1.00
0.96
4.38
9.77
6.07
2.80

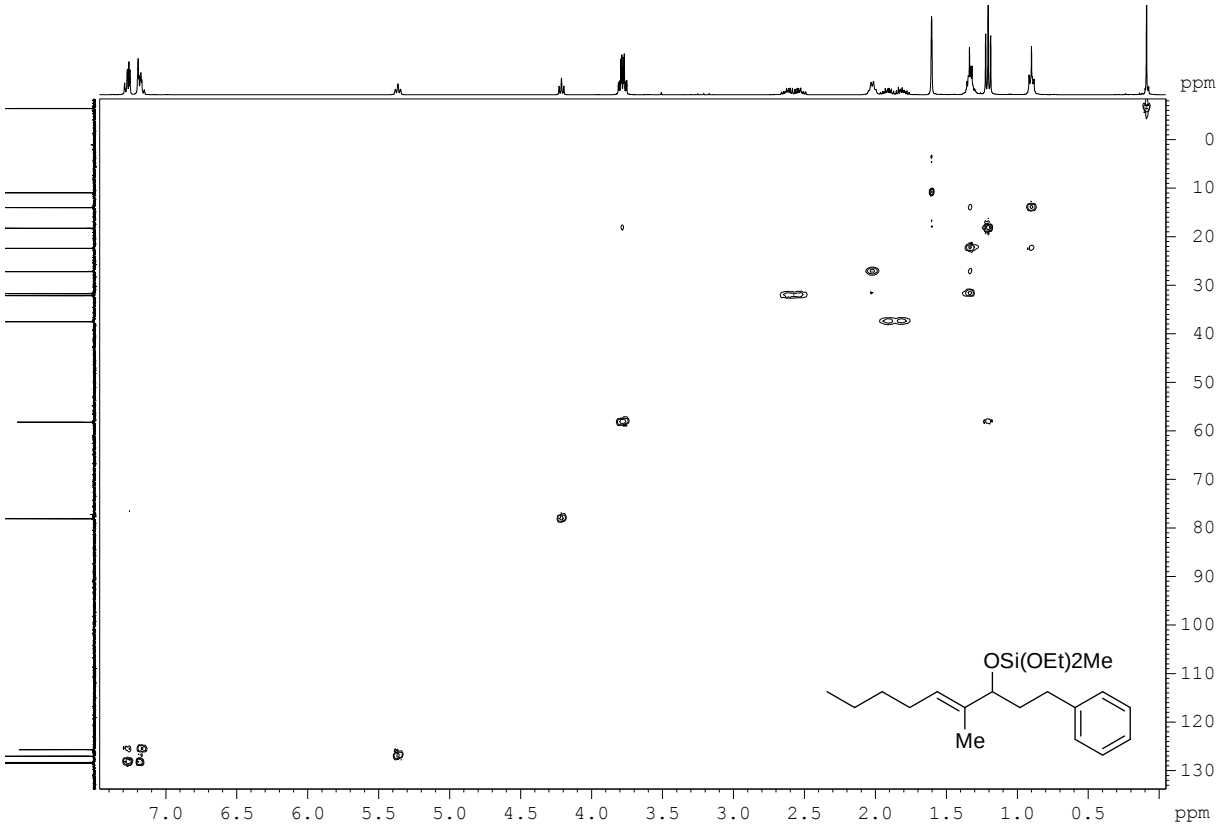

191.83
150.82
145.57
139.89
135.22
129.31
129.16
74.87
58.43
30.49
17.95
-2.00
OH
O
Si(OEt)2Me
220
200
180
160
140
120
100
80
60
40
20
ppm

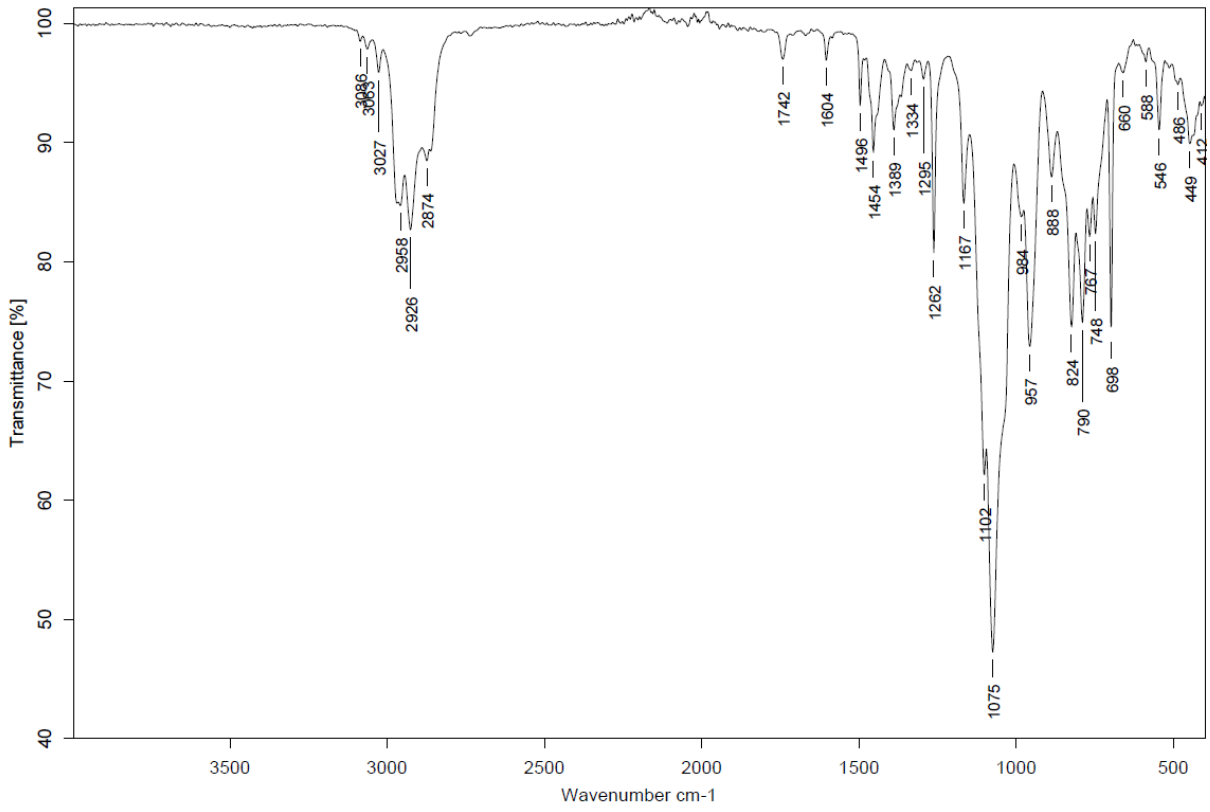

ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
10
9
8
7
6
5
4
3
2
1
0
ppm
OH
O
Si(OEt)2Me

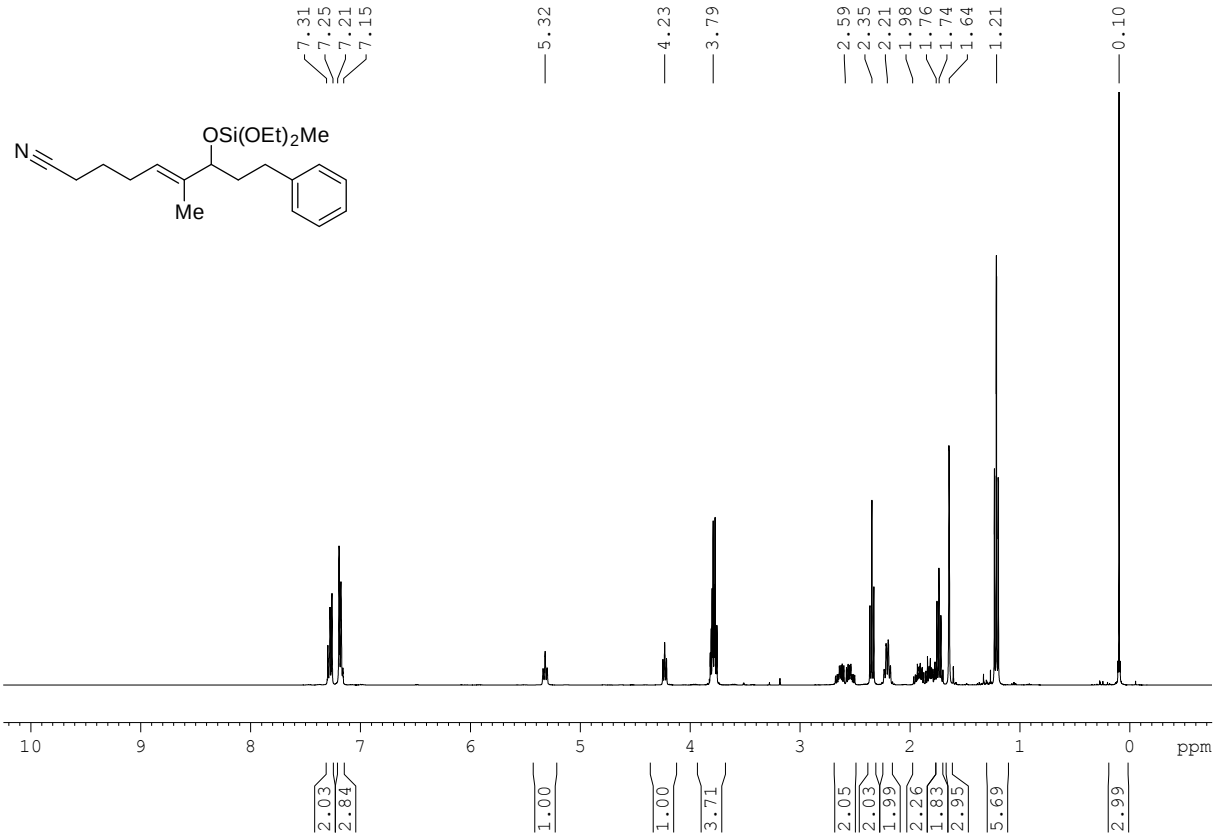

Transmittance [%]
100
90
80
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3483
2973
2927
2884
2838
2733
1697
1602
1565
1482
1443
1389
1363
1305
1260
1208
1166
1102
1067
949
889
866
813
794
758
688
654
628
573
551
526
497
471
467
442
420

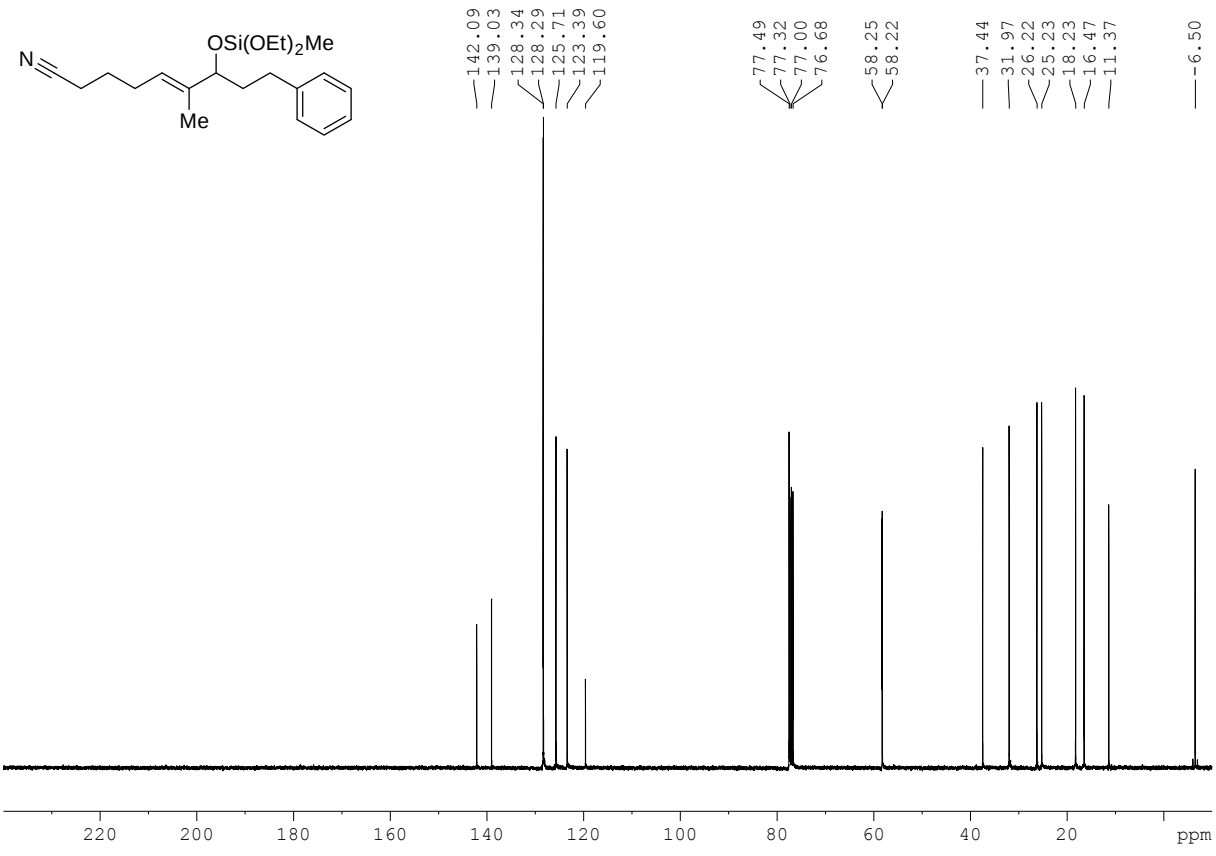

OSi(OEt)2Me
Me
7.30
7.24
7.21
7.14
5.37
4.21
3.78
2.58
2.02
1.86
1.60
1.39
1.28
1.20
0.90
0.09
ppm
2.24
2.88
1.00
0.98
3.72
2.10
2.00
1.08
1.07
2.90
4.29
5.60
3.09
2.96

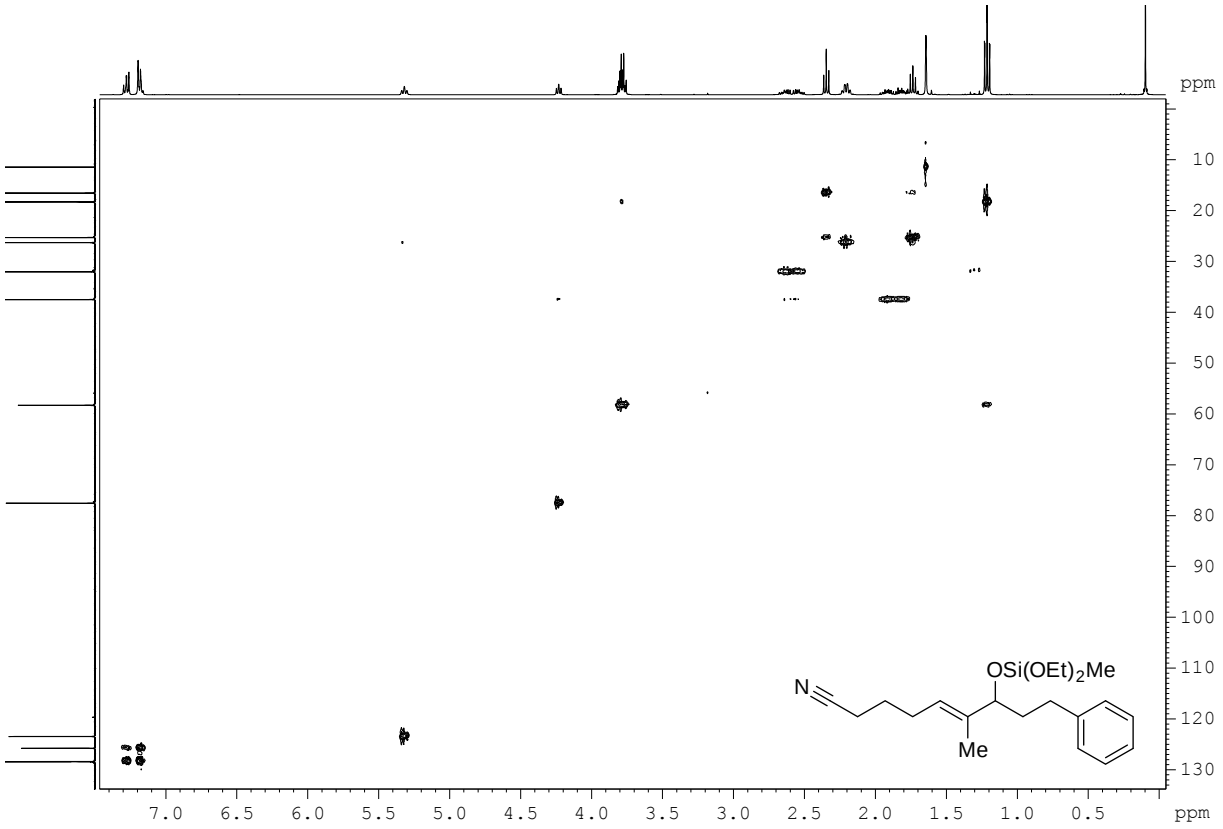

OSi(OEt)2Me
Me
142.40
136.04
128.40
128.26
126.97
125.63
78.08
77.32
77.00
76.68
58.22
58.19
37.48
32.10
31.70
27.16
22.38
18.24
18.22
13.98
10.92
-6.44
ppm

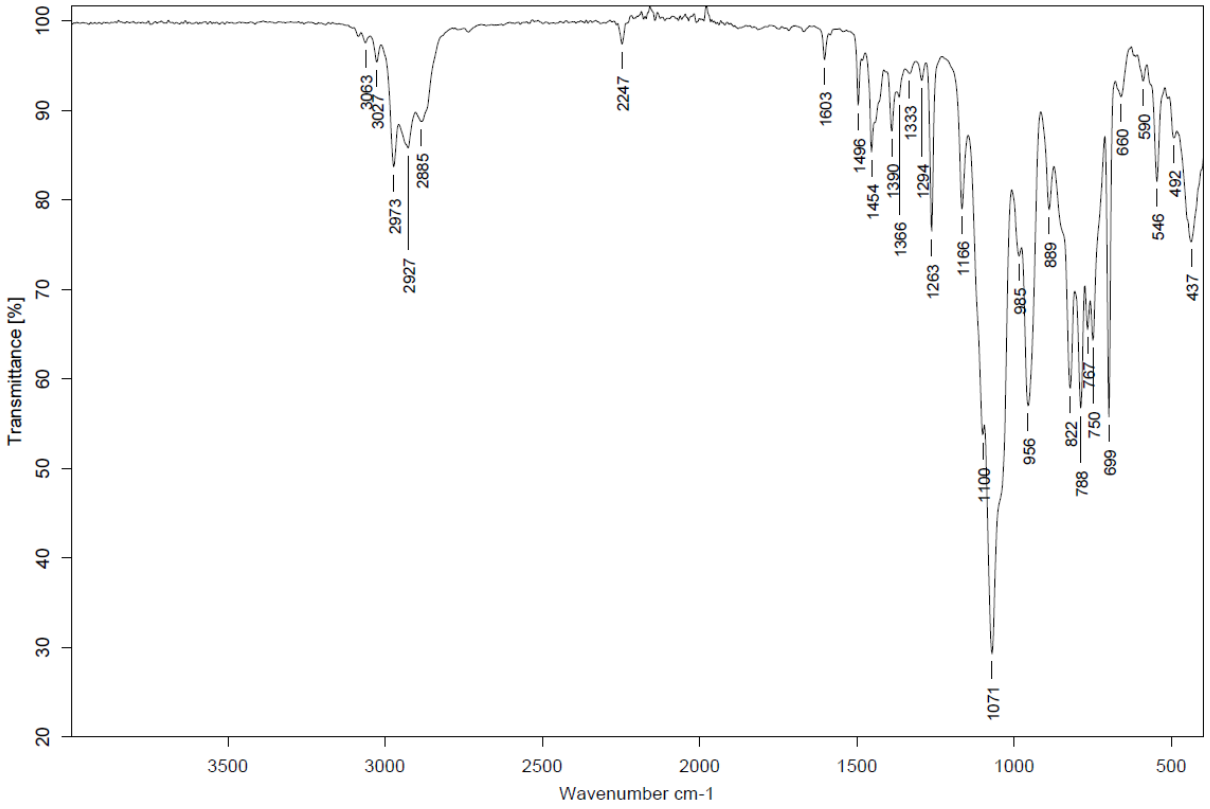

ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
OSi(OEt)2Me
Me

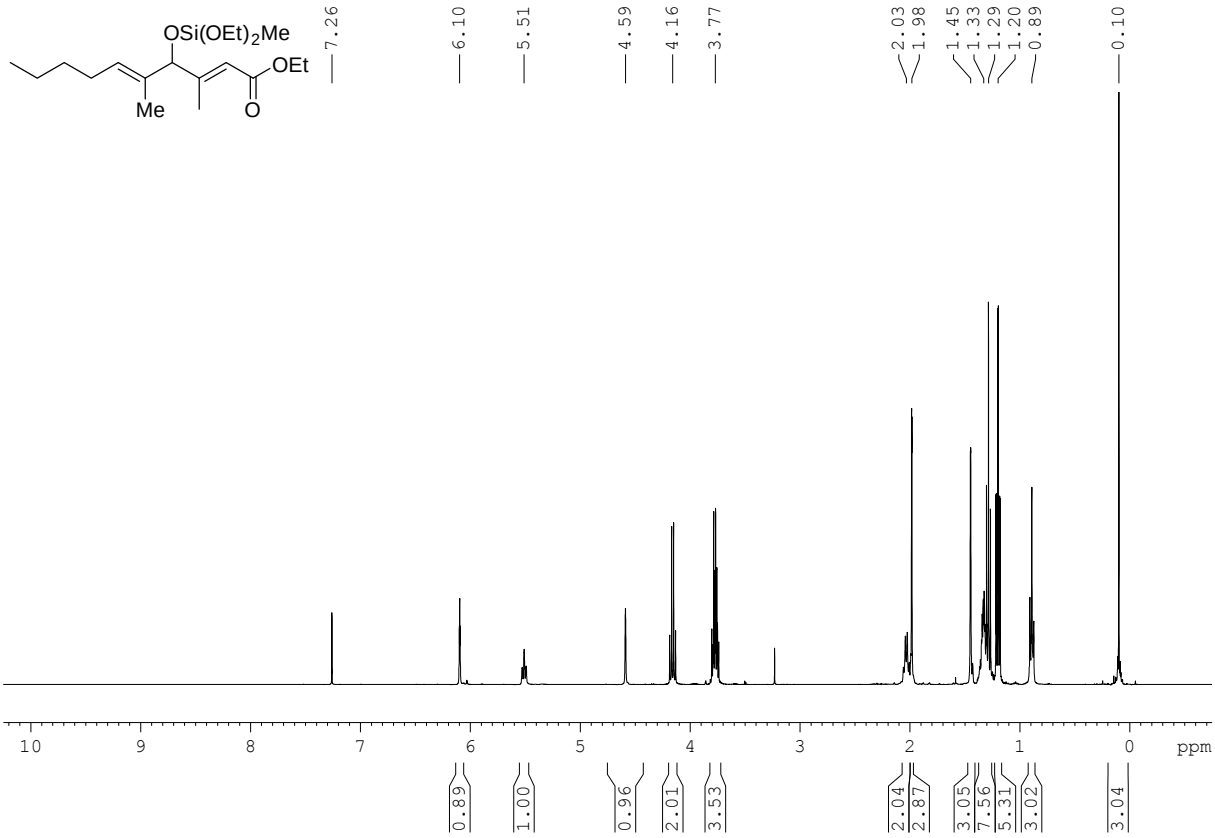

Transmittance [%]
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3086
3063
3027
2958
2926
2874
1742
1604
1496
1454
1389
1334
1295
1262
1167
1102
1075
984
957
888
824
790
767
748
698
660
588
546
486
449
412

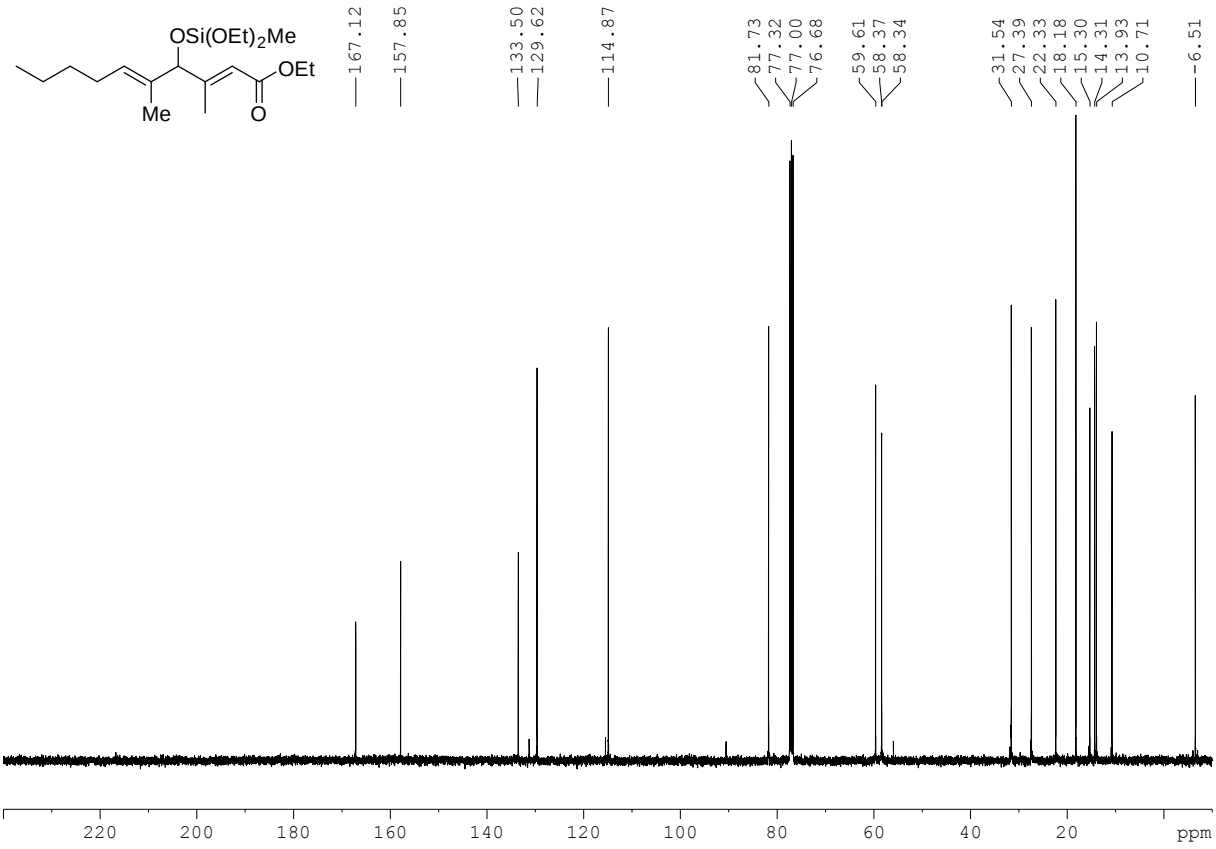

7.31
7.25
7.21
7.15
5.32
4.23
3.79
2.59
2.35
2.21
1.98
1.76
1.74
1.64
1.21
0.10
N
OSi(OEt)2Me
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
2.84
1.00
1.00
3.71
2.05
2.03
1.99
2.26
1.83
2.95
5.69
2.99

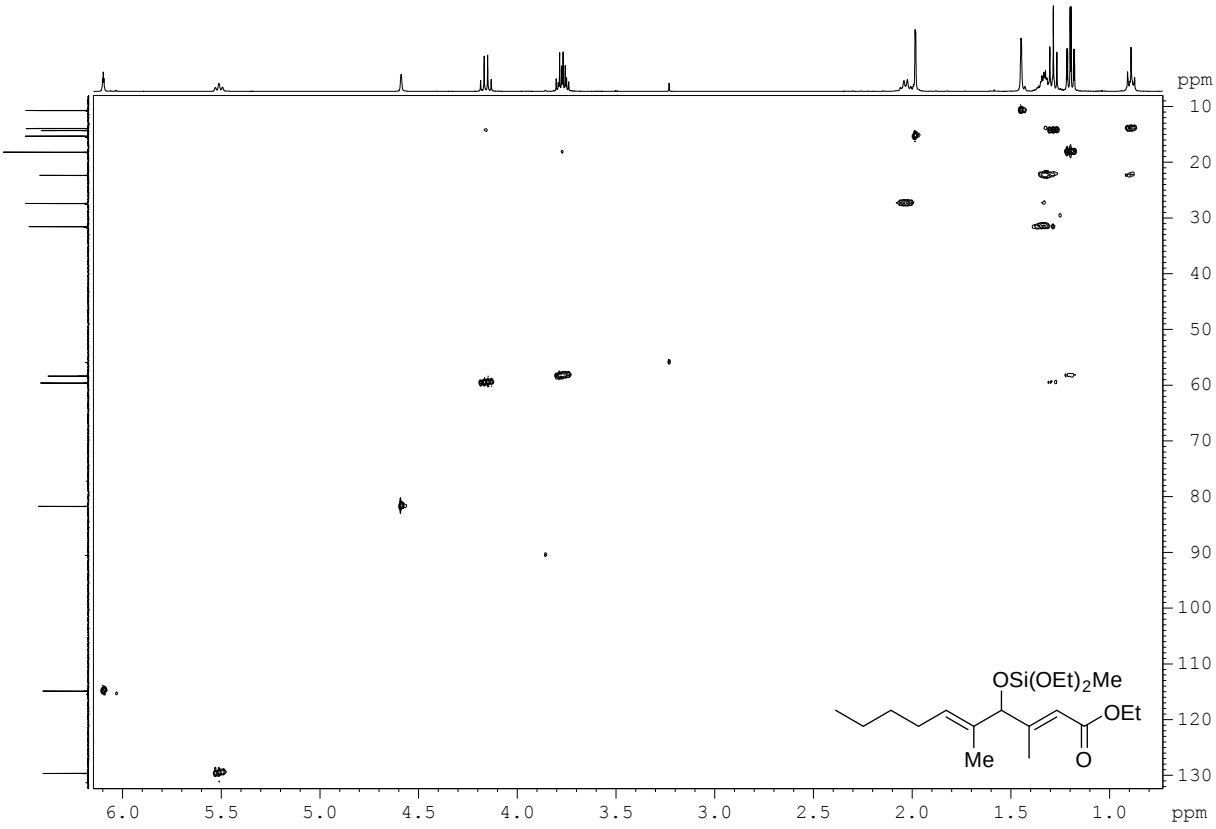

142.09
139.03
128.34
128.29
125.71
123.39
119.60
77.49
77.32
77.00
76.68
58.25
58.22
37.44
31.97
26.22
25.23
18.23
16.47
11.37
-6.50
N
OSi(OEt)2Me
Me
220
200
180
160
140
120
100
80
60
40
20
ppm

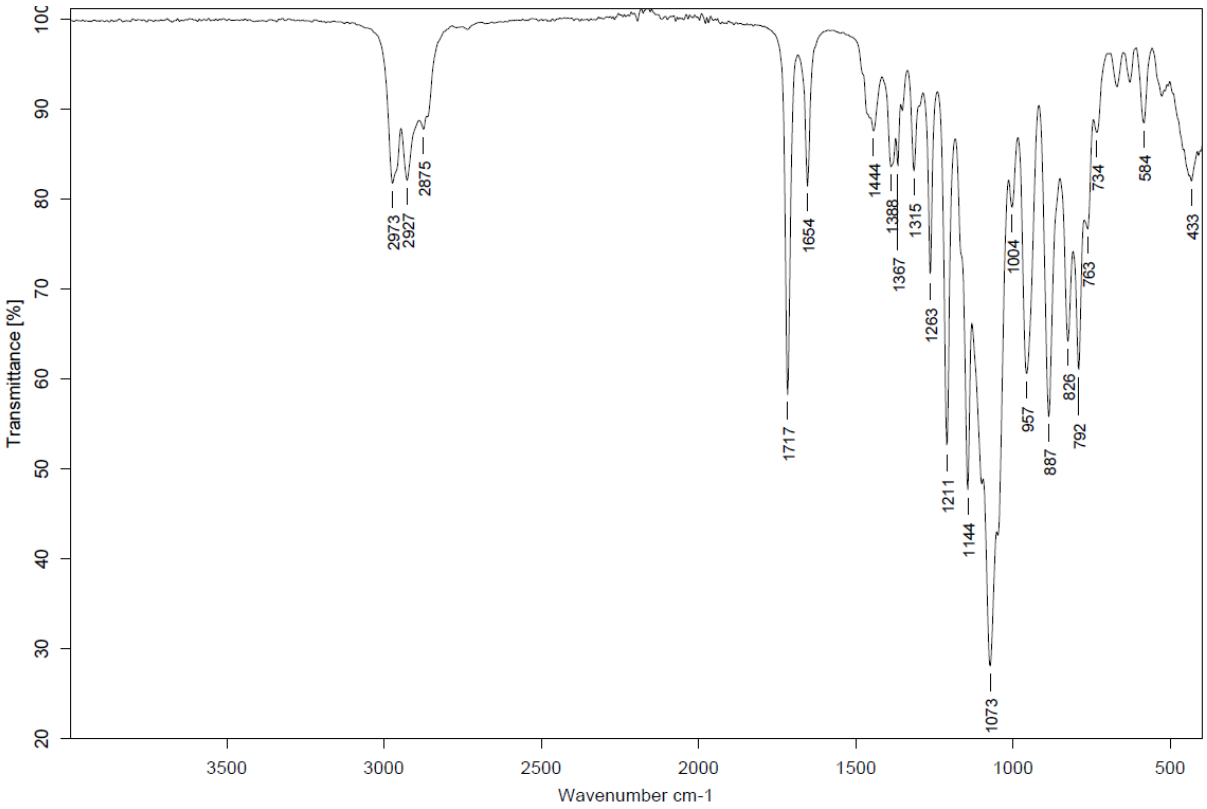

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
N
OSi(OEt)2Me
Me

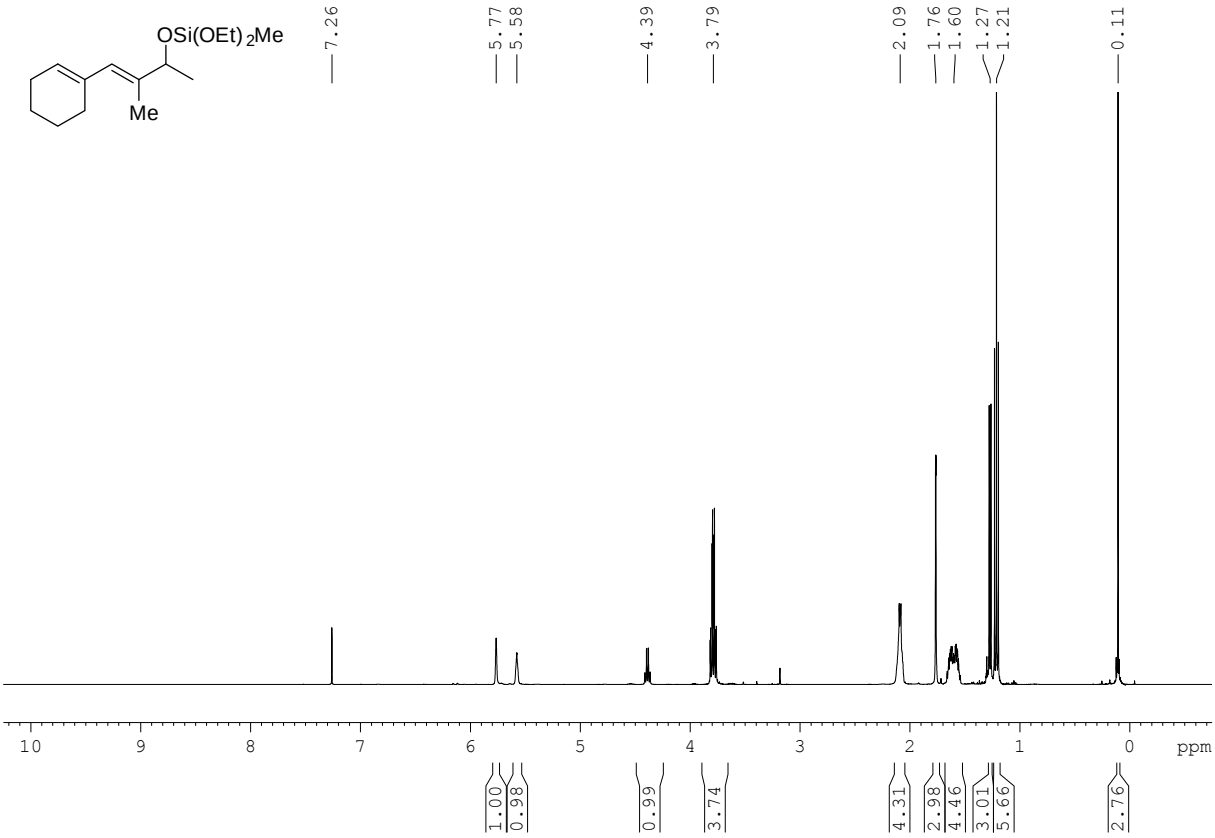

Transmittance [%]
100
90
80
70
60
50
40
30
20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3063
3027
2973
2927
2885
2247
1603
1496
1454
1390
1366
1333
1294
1263
1166
1100
1071
985
956
889
822
788
767
750
699
660
590
546
492
437

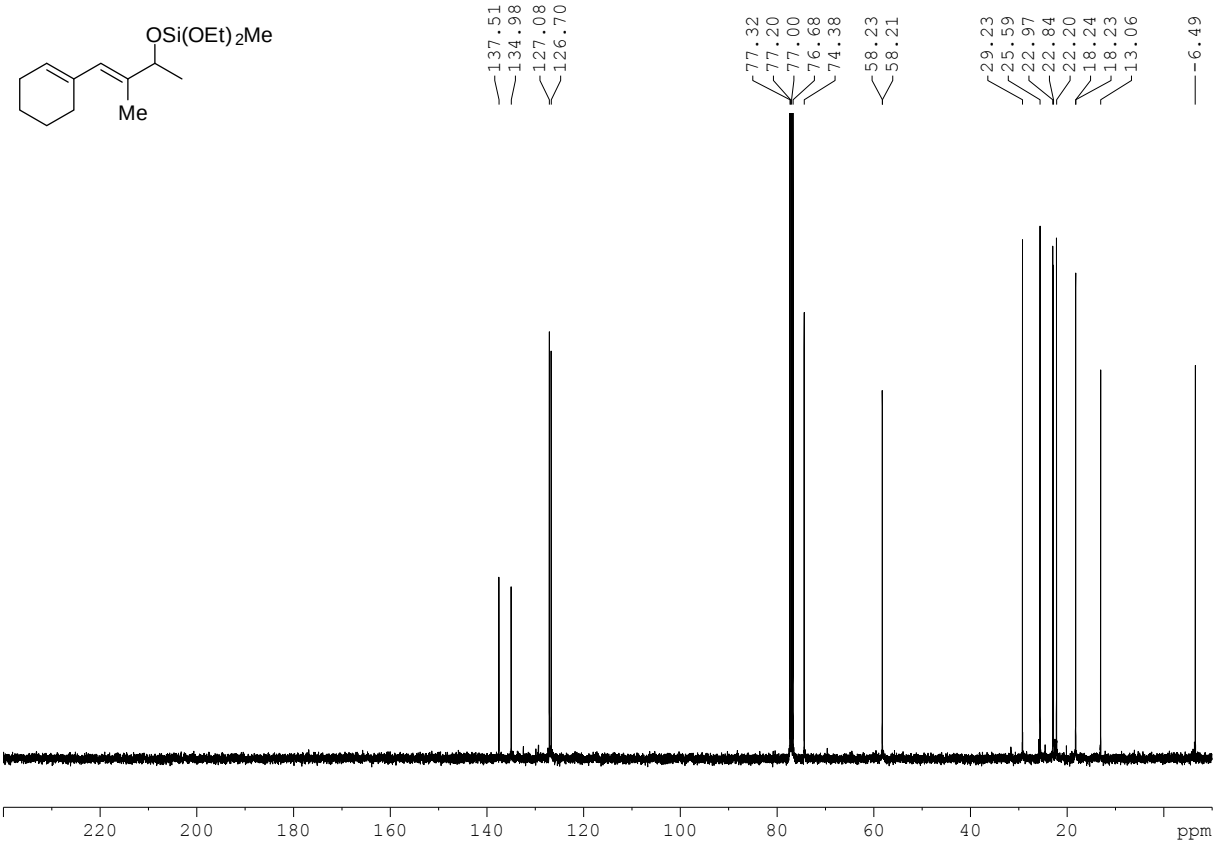

OSi(OEt)2Me
OEt
Me
O
7.26
6.10
5.51
4.59
4.16
3.77
2.03
1.98
1.45
1.33
1.29
1.20
0.89
0.10
10
9
8
7
6
5
4
3
2
1
0
ppm
0.89
1.00
0.96
2.01
3.53
2.04
2.87
3.05
7.56
5.31
3.02
3.04

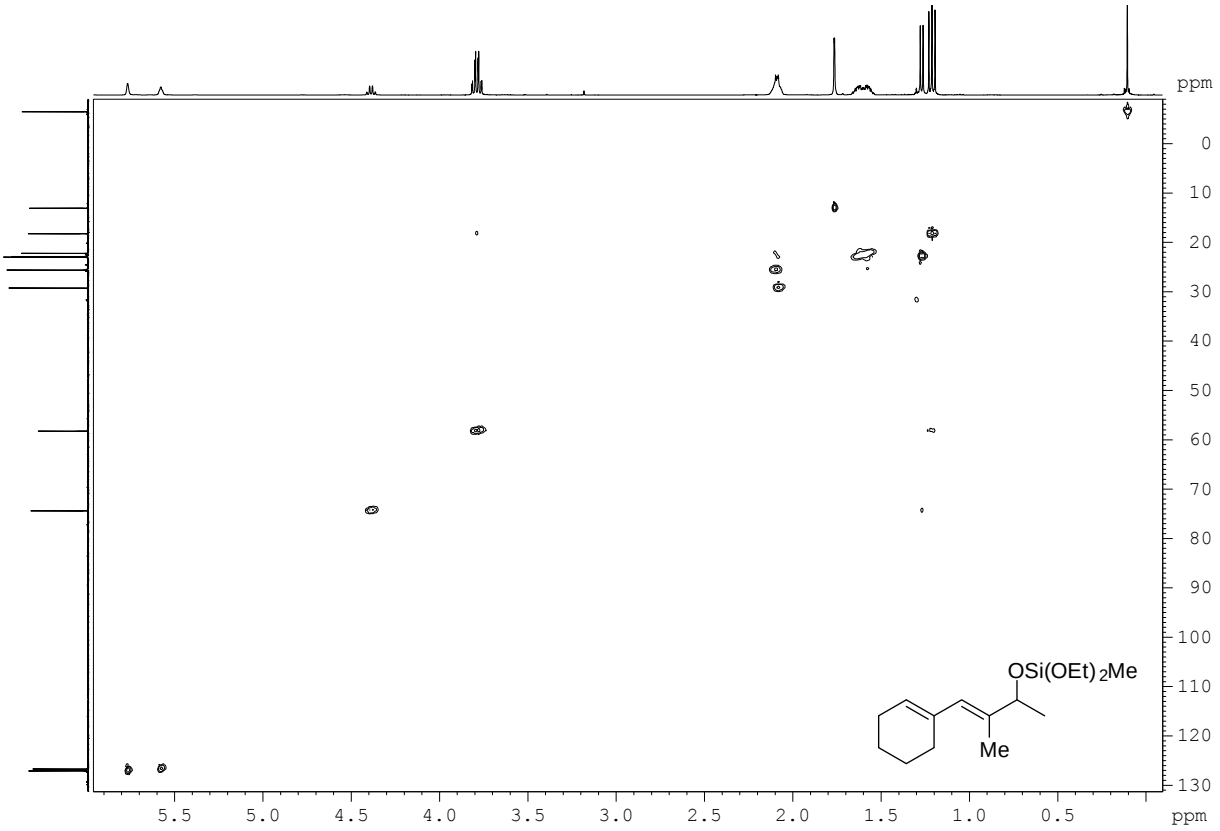

OSi(OEt)2Me
OEt
Me
O
167.12
157.85
133.50
129.62
114.87
81.73
77.32
77.00
76.68
59.61
58.37
58.34
31.54
27.39
22.33
18.18
15.30
14.31
13.93
10.71
-6.51
220
200
180
160
140
120
100
80
60
40
20
ppm

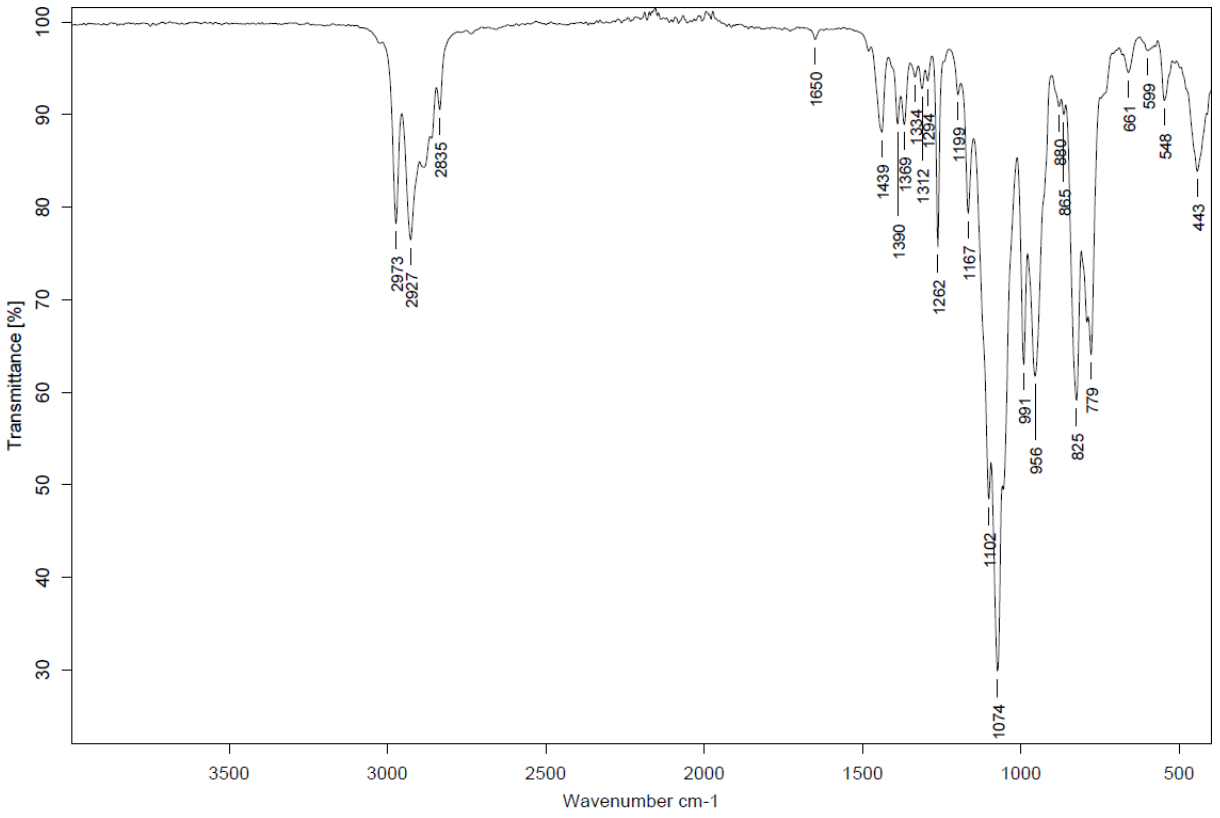

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
OSi(OEt)2Me
OEt
Me
O

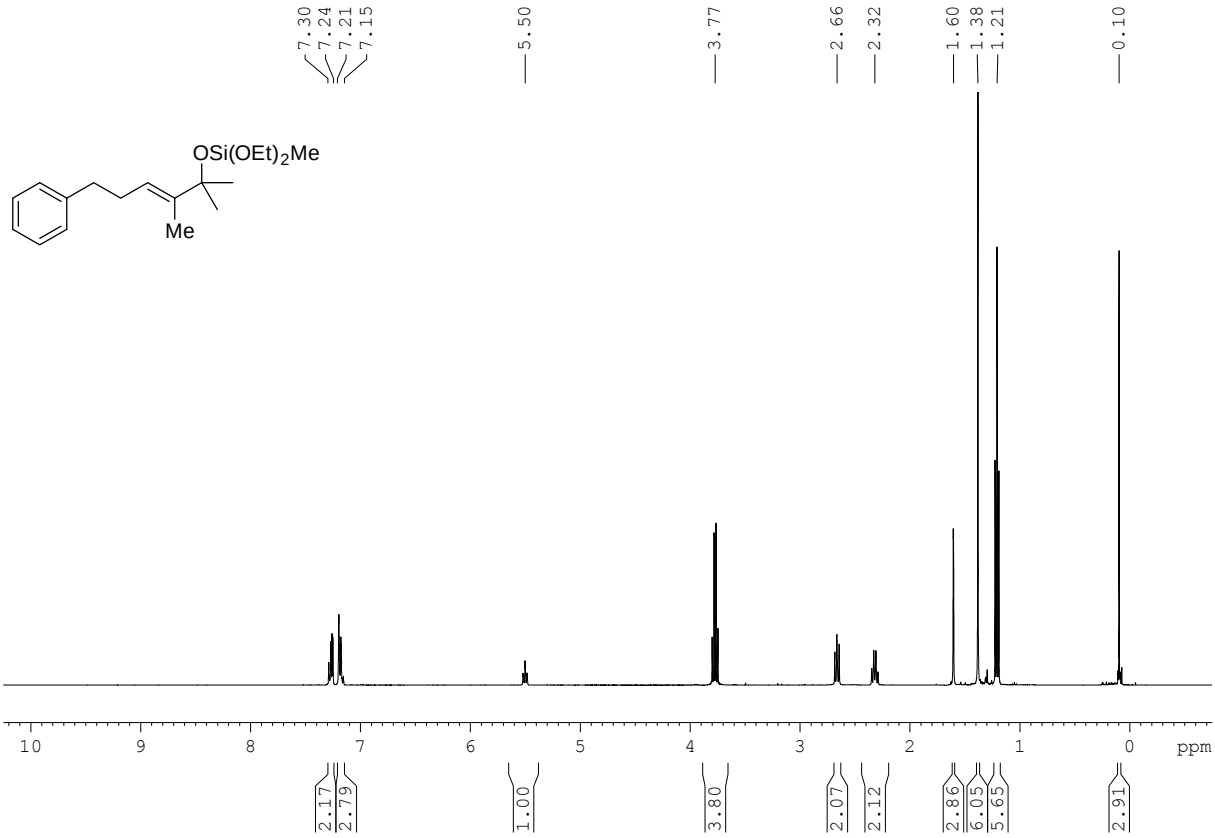

Transmittance [%]
100
90
80
70
60
50
40
30
20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
2973
2927
2875
1717
1654
1444
1388
1367
1315
1263
1211
1144
1073
1004
957
887
826
792
763
734
584
433

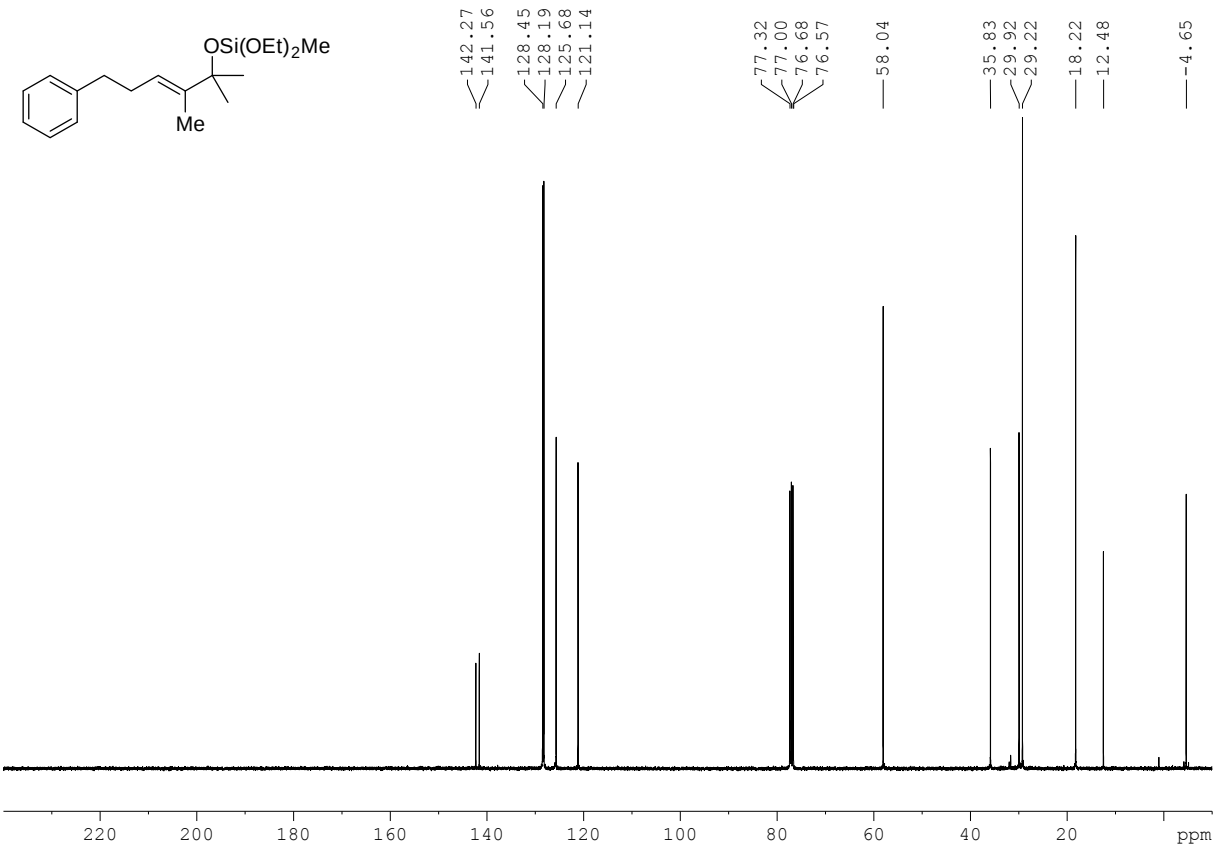

OSi(OEt)2Me
Me
7.26
5.77
5.58
4.39
3.79
2.09
1.76
1.60
1.27
1.21
0.11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
0.99
3.74
4.31
2.98
4.46
3.01
5.66
2.76

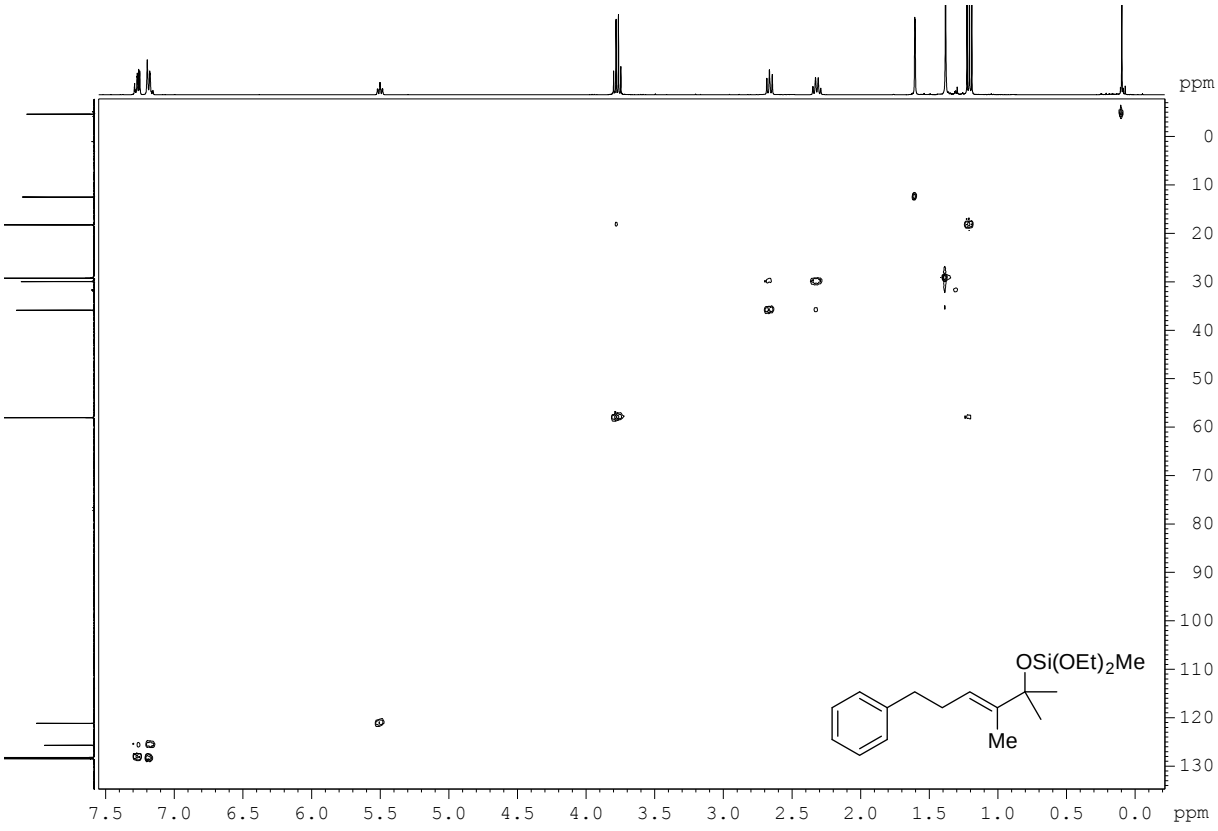

OSi(OEt)2Me
Me
137.51
134.98
127.08
126.70
77.32
77.20
77.00
76.68
74.38
58.23
58.21
29.23
25.59
22.97
22.84
22.20
18.24
18.23
13.06
-6.49
220
200
180
160
140
120
100
80
60
40
20
ppm

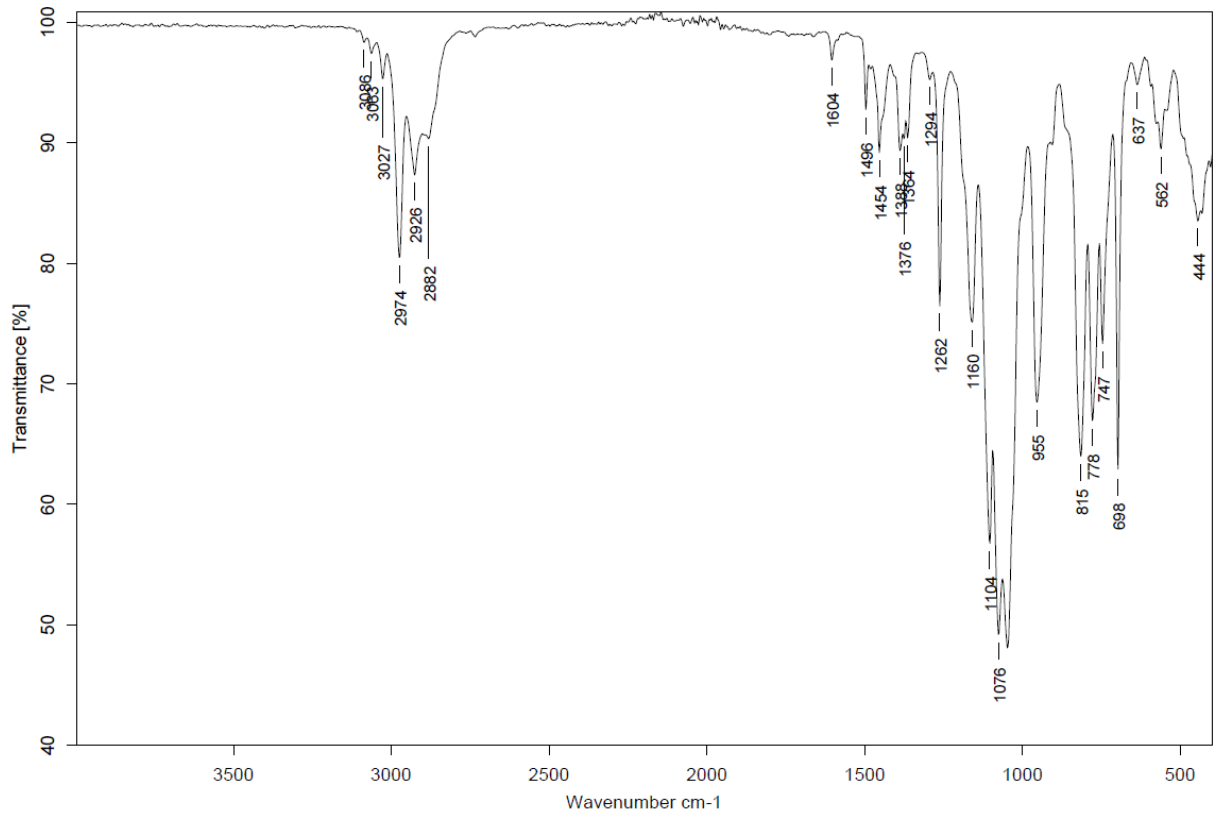

ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
OSi(OEt)2Me
Me

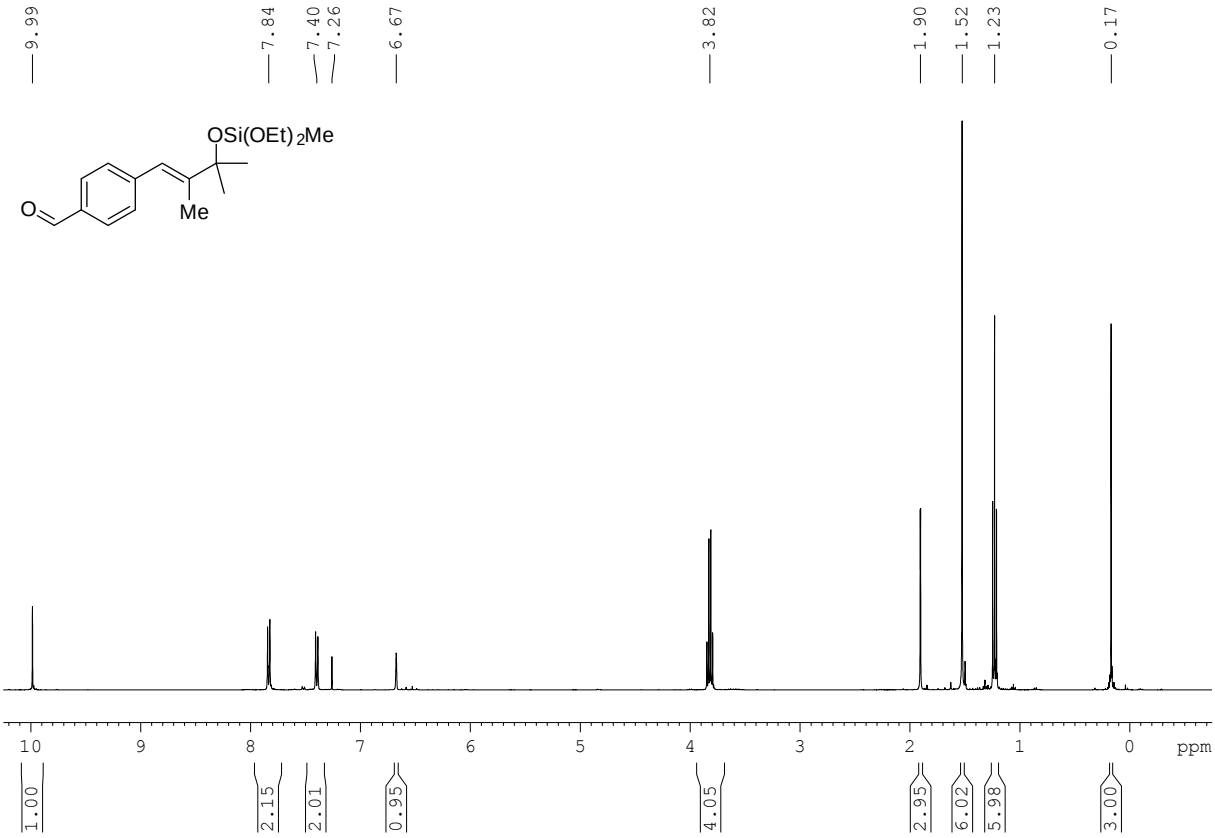

Transmittance [%]
100
90
80
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
2973
2927
2835
1650
1439
1390
1369
1334
1312
1284
1262
1199
1167
1102
1074
991
956
880
865
825
779
661
599
548
443

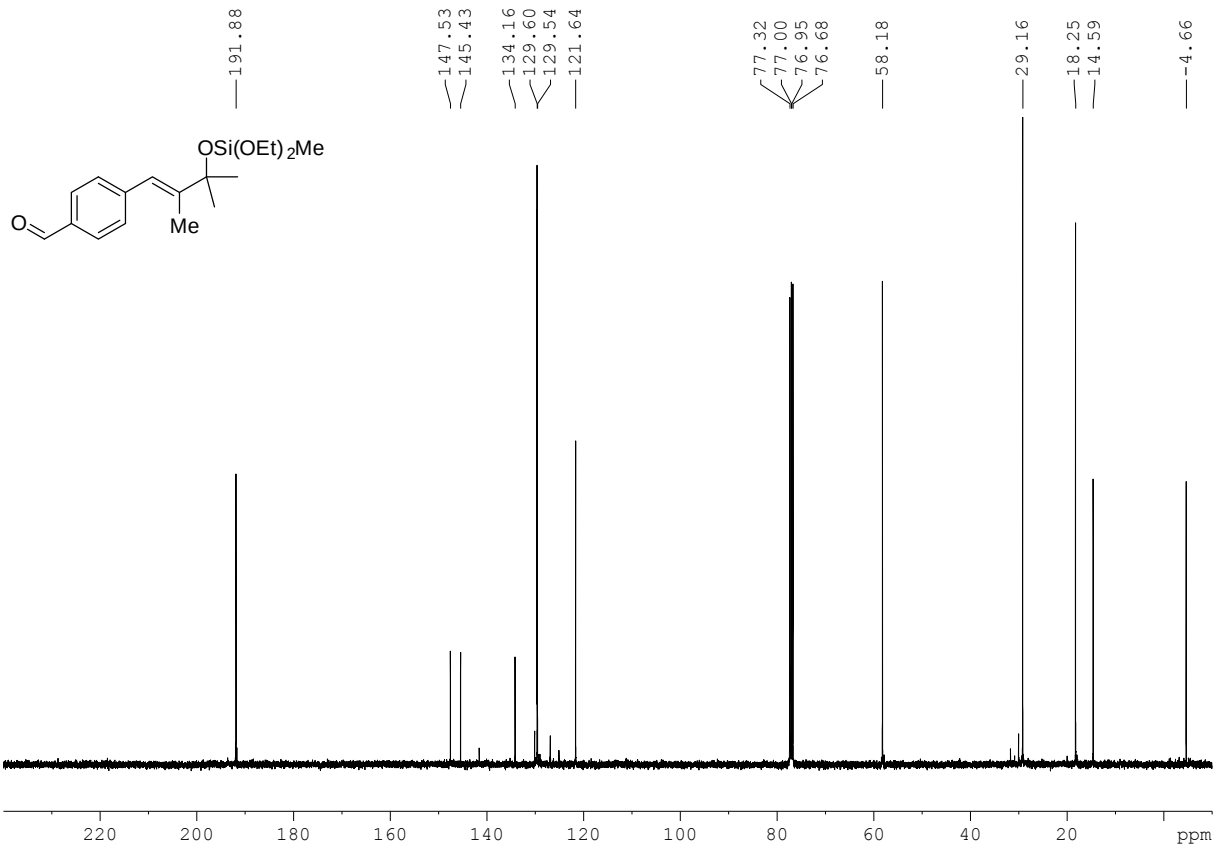

7.30
7.24
7.21
7.15
5.50
3.77
2.66
2.32
1.60
1.38
1.21
0.10
OSi(OEt)2Me
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
2.17
2.79
1.00
3.80
2.07
2.12
2.86
6.05
5.65
2.91

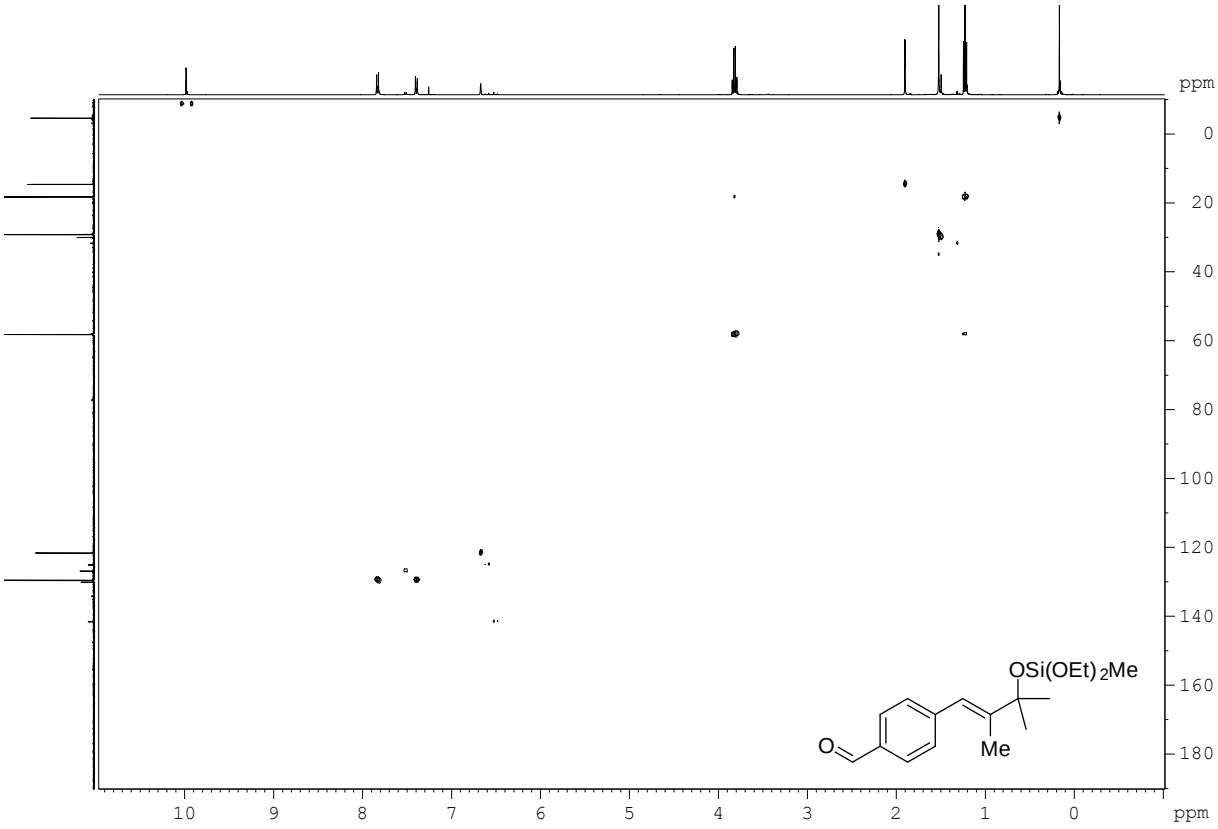

OSi(OEt)2Me
Me
142.27
141.56
128.45
128.19
125.68
121.14
77.32
77.00
76.68
76.57
58.04
35.83
29.92
29.22
18.22
12.48
-4.65
220
200
180
160
140
120
100
80
60
40
20
ppm

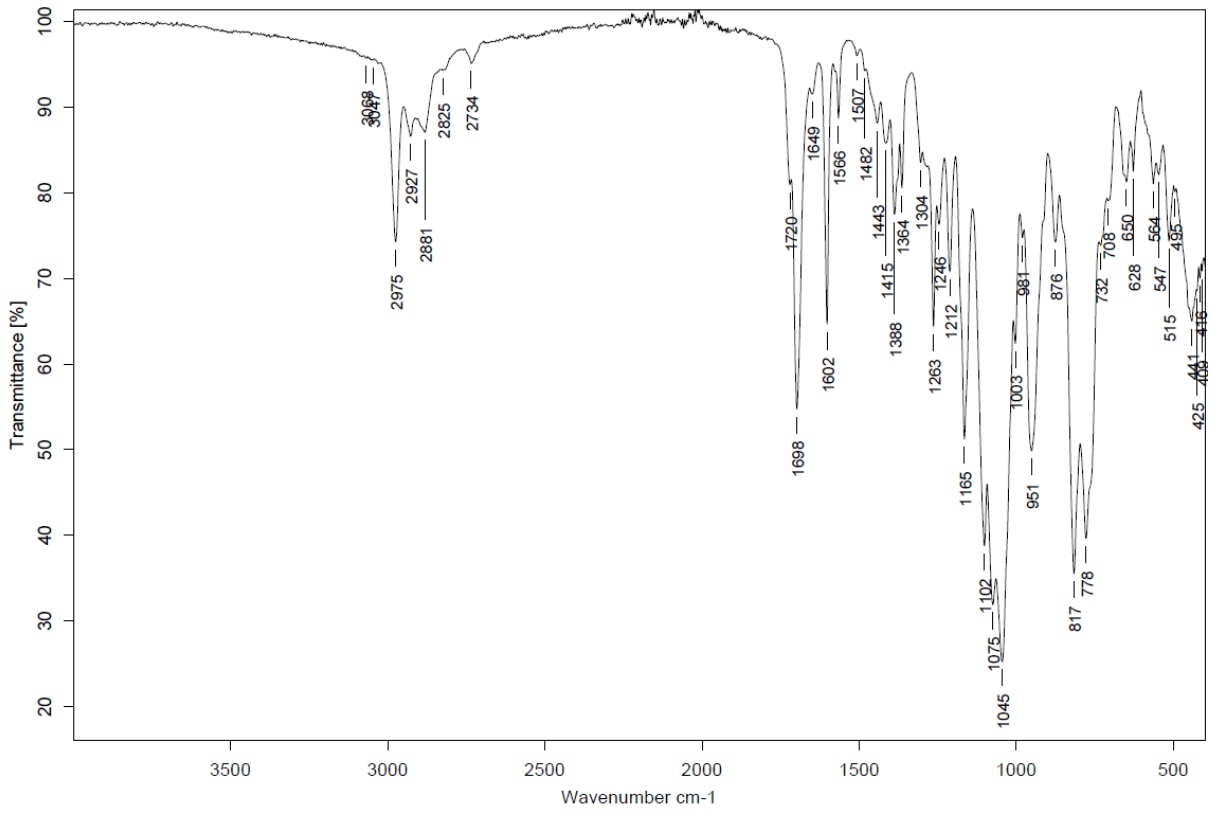

ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
OSi(OEt)2Me
Me


Transmittance [%]
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3086
3063
3027
2974
2926
2882
1604
1496
1454
1388
1364
1376
1294
1262
1160
1104
1076
955
815
778
747
698
637
562
444


9.99
7.84
7.40
7.26
6.67
3.82
1.90
1.52
1.23
0.17
OSi(OEt)2Me
O
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.15
2.01
0.95
4.05
2.95
6.02
5.98
3.00


191.88
147.53
145.43
134.16
129.60
129.54
121.64
77.32
77.00
76.95
76.68
58.18
29.16
18.25
14.59
-4.66
OSi(OEt)2Me
O
Me
220
200
180
160
140
120
100
80
60
40
20
ppm


ppm
0
20
40
60
80
100
120
140
160
180
10
9
8
7
6
5
4
3
2
1
0
ppm
OSi(OEt)2Me
O
Me


Transmittance [%]
100
90
80
70
60
50
40
30
20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3068
3047
2975
2927
2881
2825
2734
1720
1698
1649
1602
1566
1507
1482
1443
1415
1388
1364
1304
1263
1246
1212
1165
1102
1075
1045
1003
981
951
876
817
778
732
708
650
628
564
547
515
495
441
425

Chemicals and Solvents: All chemicals and solvents were purchased from ABCR, ACROS, ALFA–AESAR, APOLLO SCIENTIFIC, FLUKA, FLUOROCHEM, MERCK, SIGMA-ALDRICH, TCI, or STREM CHEMICALS and used as received, unless mentioned otherwise.[1] Et_2O and THF were distilled from Mg/anthracene, CH_2Cl_2 and EtOAc from CaH_2, toluene from Na/K, and MeOH from Mg turnings under an inert atmosphere of nitrogen or argon. DMF, DMSO, MeCN, Et_3N and pyridine were dried by passage through molecular sieve colums (H_2O content < 30 ppm, KARL–FISCHER titration) using a VACUUM ATMOSPHERES COMPANY *Solvent Purifier* system.[2] Dry acetone was obtained by drying over B_2O_3, followed by filtration and distillation.[3] 2,6-Lutidine was distilled from CaH_2 under an inert atmosphere of argon. $[(Cp^*)RuCl_2]_n$ was prepared according to a literature procedure.[4] Copper(I) thiophene-2-carboxylate (CuTC) could either be prepared according to a literature procedure[5] or purchased from SIGMA-ALDRICH without noticeable differences in reactivity. $(Bu_4N)OP(O)Ph_2$ was prepared by a slightly adapted procedure (*vide infra)*.[6] All hygroscopic or air-sensitive chemicals were stored in SCHLENK-flasks under an atmosphere of argon at the appropriate temperature, as indicated by the supplier.

General Procedures: All non-aqueous reactions were performed under an inert atmosphere of dry argon at ca. 0.4 bar overpressure using flame dried glassware, unless otherwise noted. Reactions were stirred using magnetic stir-bars and monitored by thin layer chromatography (TLC). Analytical thin layer chromatography was performed using MACHEREY–NAGEL *POLYGRAM SIL G/UV* pre-coated polyester plates and visualized by ultraviolet light (UV). Additionally, TLC plates were stained with either aqueous potassium permanganate [1.5 g $KMnO_4$, 200 mL H_2O, 10 g K_2CO_3, 2.5 mL 1M NaOH aq.], cerium ammonium molybdate [0.5 g $Ce(NH_4)_2(NO_3)_6$, 12 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 235 mL H_2O, 15 mL conc. H_2SO_4] or ethanolic *p*-anisaldehyde [3.7 mL *p*-anisaldehyde, 135 mL EtOH, 5 mL conc. H_2SO_4, 1.5 mL AcOH]. Concentration under reduced pressure (= *in vacuo*) was performed using commercial rotator evaporators. Chromatographic

---

[1] For general information on purification of chemicals and reagents, see: W. L. F. Armarego, C. L. L. Chai in *"Purification of Laboratory Chemicals"* 7th Edition, Elsevier, Amsterdam, **2013**.
[2] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518-1520.
[3] D. R. Burfield, R. H. Smithers, *J. Org. Chem.* **1978**, *43*, 3966-3968.
[4] T. D. Tilley, R. H. Grubbs, J. E. Bercaw, *Organometallics* **1984**, *3*, 274-278.
[5] G. D. Allred, L. S. Liebeskind, *J. Am. Chem. Soc.* **1996**, *118*, 2748-2749.
[6] For the original procedure, see: J. Srogl, G. D. Allred, L. S. Liebeskind, *J. Am. Chem. Soc.* **1997**, *119,* 12376-12377.

purification was performed as flash chromatography[7] on MERCK 60 Å (40-63 µm) silica gel at ca. 0.4 bar overpressure. Purified compounds were dried under high vacuum (10^{-3} mbar).

Analytical Methods: Nuclear Magnetic Resonance (NMR): NMR data were recorded on a BRUKER *AV 400* (Progeny cryoprobe) or BRUKER *AVIII* 600 (cryoprobe) spectrometer in the solvents indicated. Chemical shifts (δ) are reported in ppm with the residual solvent signal as internal standard ($CDCl_3$ at 7.26 and 77.00 ppm for ^1H and ^{13}C NMR spectroscopy, respectively; CD_3OD at 3.31 and 49.00 ppm for ^1H and ^{13}C NMR spectroscopy, respectively), unless otherwise noted. ^1H NMR data are reported as δ (ppm) (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet or unresolved, br = broad signal, app. = appearing as; coupling constant(s) (J) in Hz; integration). ^{13}C NMR spectra were recorded with broadband ^1H decoupling while J-coupling(s) to other NMR-active heteronuclei (*i.e.* ^{19}F and ^{31}P) are reported as (d = doublet, t = triplet, q = quartet, qui = quintet; coupling constant(s) in Hz). If HSQC or DEPT data were available the carbon atoms are denoted with (CH_3 = methyl, CH_2 = methylene, CH = methine, CR_4 = fully substituted carbon atom). ^{31}P NMR and ^{119}Sn NMR spectra were referenced to H_3PO_4 (85% in D_2O) and $SnMe_4$, respectively, as external standards.

Only experimentally observed and resolved signals are tabulated or compiled; therefore it is possible that the number of signals in the ^{13}C NMR spectra does not match the expected number of magnetically inequivalent C-atoms in a given molecule.

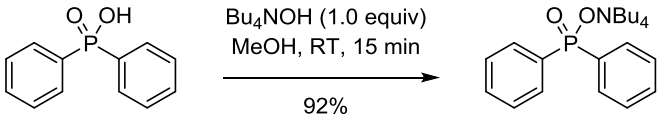
Fourier Transform Infrared Spectrometry (FTIR): FTIR spectra were recorded on a PERKIN ELMER *Spectrum One FT-IR (UATR)* instrument as thin films. Absorptions (ν) are given in wavenumbers (cm^{-1}).

High Resolution Mass Spectrometry (HRMS): HRMS analyses were performed as ESI measurements on a BRUKER *7T APEX III Fourier Transform Ion Cyclotron MS* or a FINNIGAN *MAT 95* instrument.

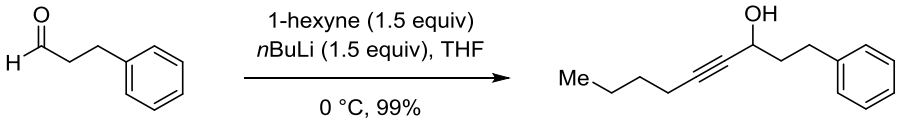
[7] W. C. Still, M. Kahn, A. J. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.

Substrates, Reagents and Reference Compounds

Except for the compounds outlined below, all other substrates were prepared as previously described; their analytical and spectral data are contained in the Supporting Information of previous publications from this group.[8]



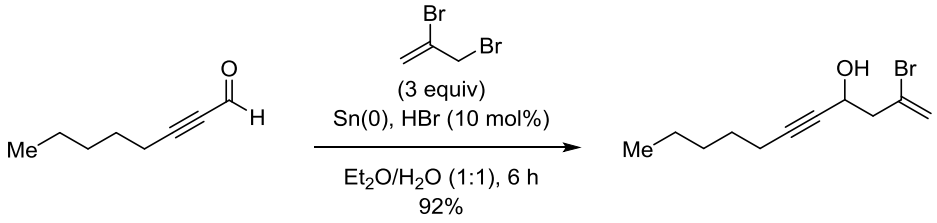
Tetra-*n*-butylammonium diphenylphosphinate. To a suspension of Ph_2PO_2H (5.50 g, 25.2 mmol) in dry MeOH (27.5 mL) at ambient temperature was added Bu_4NOH (1.0 M in MeOH, 25.2 mL, 25.2 mmol) and the resulting yellow solution was stirred at that temperature for another 15 min. The mixture was filtered through a short pad of Celite, eluting with dry MeOH (25 mL), and the combined filtrates were concentrated under reduced pressure (water bath at 60 °C). The resulting pale yellow oil was dried under high vacuum for 8 h to afford a solid yellow wax, which was re-dissolved in dry EtOAc and the solvent evaporated again to remove residual MeOH. Recrystallization of the residue from EtOAc/Et_2O (ca. 1:4, 50 mL; slow cooling from reflux to –20 °C) afforded $Ph_2PO_2NBu_4$ (10.6 g, 92%) as white crystalline needles. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.85 (m, 4H), 7.27-7.18 (m, 6H), 3.31 (app. t, J = 8.4 Hz, 8H), 1.57 (app. quintet, J = 7.9 Hz, 8H), 1.35 (sextet, J = 7.4 Hz, 8H), 0.92 (app. t, J = 7.3 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.7 (d, J = 8.6 Hz), 128.3 (br s), 127.2 (d, J = 11.3 Hz), 58.9 (s), 24.2 (s), 19.7 (s), 13.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$, ^{1}H-decoupled): δ 13.14.



---

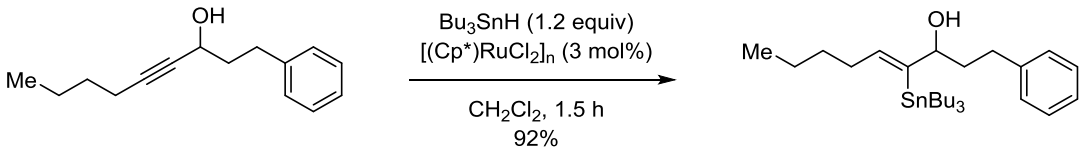
8 a) S. M. Rummelt, K. Radkowski, D.-A. Roşca, A. Fürstner, *J. Am. Chem. Soc.* **2015**, *137*, 5506-5519; b) D.-A. Rosca, K. Radkowski, L. M. Wolf, M. Wagh, R. Goddard, W. Thiel, A. Fürstner, *J. Am. Chem. Soc*. **2017**, *139*, 2443-2455; c) a) H. Sommer, A. Fürstner, *Chem. Eur. J*. **2017**, *23*, 558-562; b) H. Sommer, A. Fürstner, *Org. Lett*. **2016**, *18*, 3210-3212; c) H. Sommer, J. Y. Hamilton, A. Fürstner, *Angew. Chem. Int. Ed*. **2017**, in press (doi: 10.1021/anie.201701391).

1-Phenylnon-4-yn-3-ol. *n*BuLi, (1.6 M in hexanes, 21.5 mL, 34.4 mmol) was added to a solution of 1-hexyne (4.80 mL, 41.8 mmol) in THF (90 mL) at 0 °C and the resulting mixture was stirred at that temperature for 30 min. 3-Phenylpropanal (3.60 mL, 27.3 mmol) was added and the resulting mixture was allowed to reach ambient temperature over 2 hours. The reaction was quenched by the addition of NH_4Cl solution (50 mL, sat. aqueous) and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 100 mL). The combined extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 15:85) afforded the title compound (5.62 g, 99%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.27 (m, 2H), 7.24-7.17 (m, 3H), 4.37 (tt, J = 6.5, 2.0 Hz, 1H), 2.80 (t, J = 7.9 Hz, 2H), 2.24 (td, J = 7.0, 2.0 Hz, 2H), 2.07-1.93 (m, 2H), 1.84 (br s, 1H), 1.55-1.39 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.5 (CR_4), 128.5 (2 × CH_2), 128.4 (2 × CH_2), 125.9 (CH), 86.0 (CR_4), 80.9 (CR_4), 62.0 (CH), 39.7 (CH_2), 31.5 (CH_2), 30.7 (CH_2), 21.9 (CH_2), 18.3 (CH_2), 13.6 (CH_3); FTIR (thin film): ν 3334, 3063, 3027, 2955, 2931, 2862, 2229, 1604, 1496, 1455, 1379, 1328, 1133, 1053, 1030, 915, 746 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{15}H_{20}ONa$ [(M+Na)$^+$] 239.1406, found 239.1407.

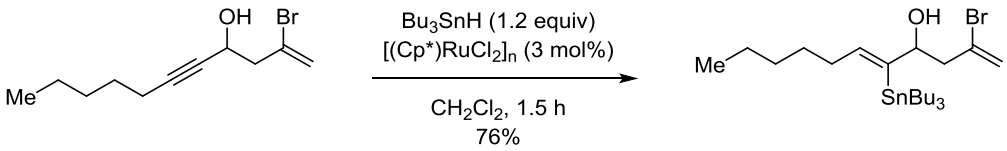


2-Bromoundec-1-en-5-yn-4-ol. HBr (48% in H_2O, 0.05 mL, 0.4 mmol, 10 mol%) and 2-octynal (500 mg, 4.03 mmol) were successively added to a suspension of Sn powder (717 mg, 6.04 mmol) and 2,3-dibromopropene, 80 wt% (1.50 mL, 12.3 mmol) in Et_2O (8.0 mL) and H_2O (8.0 mL). The resulting mixture was stirred for 6 h before it was diluted with *tert*-butyl methyl ether (50 mL) and poured into H_2O (50 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (2 × 50 mL), the combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 10:90 to 20:80; step gradient) afforded the title compound (792 mg, 97%) as a colorless oil. ^{1}H NMR (400

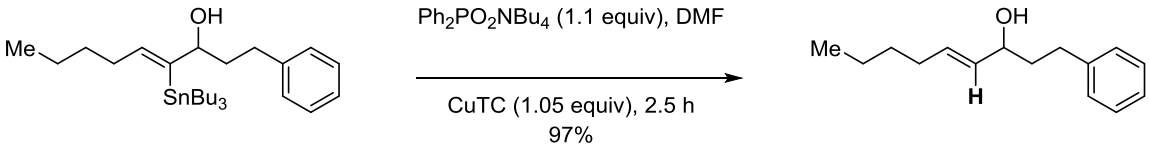
MHz, $CDCl_3$): δ 5.74 (dt, J = 2.0, 1.1 Hz, 1H), 5.55 (d, J = 1.7 Hz, 1H), 4.68 (ddt, J = 7.6, 5.5, 2.0 Hz, 1H), 2.81 (ddd, J = 14.5, 7.7, 0.9 Hz, 1H), 2.75 (ddd, J = 14.5, 5.6, 1.2 Hz, 1H), 2.20 (td, J = 7.1, 2.0 Hz, 2H), 1.83 (s, 1H), 1.54-1.46 (m, 2H), 1.39-1.26 (m, 4H), 0.90 (app. t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 128.7 (CR_4), 120.2 (CH_2), 86.7 (CR_4), 79.5 (CR_4), 60.6 (CH), 49.9 (CH_2), 31.0 (CH_2), 28.2 (CH_2), 22.2 (CH_2), 18.6 (CH_2), 14.0 (CH_3); FTIR (thin film): ν 3339, 2957, 2932, 2860, 2230, 1632, 1459, 1429, 1341, 1202, 1145, 1116, 1037, 890 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{11}H_{17}O(^{79}Br)Na$ [(M+Na)$^+$] 267.0355, found 267.0353.



(*Z*)-1-Phenyl-4-(tributylstannyl)non-4-en-3-ol. Bu_3SnH (3.75 mL, 13.9 mmol) was added dropwise over 1 h via syringe pump to a brown solution of 1-phenylnon-4-yn-3-ol (2.60 g, 12.0 mmol) and $[(Cp^*)RuCl_2]_n$ (110 mg, 0.358 mmol, 3 mol%) in CH_2Cl_2 (60 mL) at ambient temperature. The mixture was stirred for additional 0.5 h before it was concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 5:95 to 10:90; step gradient) afforded the title compound (5.62 g, 92%) as a faintly yellowish oil with a proximal/distal ratio of >99:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 2H), 7.22-7.17 (m, 3H), 6.18 (td, J = 7.2, 1.1 Hz, 1H), 4.15 (t, J = 6.8 Hz, 1H), 2.65 (qdd, J = 13.8, 9.8, 6.2 Hz, 2H), 2.05 (app. q, J = 7.2 Hz, 2H), 189-1.66 (m, 2H), 1.60-1.41 (m, 7H), 1.41-1.25 (m, 10H), 1.04-0.82 (m, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5 (CR_4), 142.2 (CR_4), 141.2 (CH), 128.5 (2 × CH), 128.3 (2 × CH), 125.7 (CH), 79.4 (CH), 39.3 (CH_2), 34.0 (CH_2), 32.3 (2 × CH_2), 29.3 (3 × CH_2), 27.4 (3 × CH_2), 22.6 (CH_2), 14.1 (CH_3), 13.7 (3 × CH_3), 11.1 (3 × CH_2); ^{119}Sn NMR (149 MHz, $CDCl_3$, ^{1}H decoupling): δ –55.1; FTIR (thin film): ν 3463, 3063, 3027, 2955, 2922, 2871, 2853, 1614, 1496, 1455, 1419, 1376, 1340, 1289, 1180, 1152, 1071, 1048, 1030, 1001, 961, 925, 863, 767 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{27}H_{48}OSnNa$ [(M+Na)$^+$] 531.2619, found 531.2618.



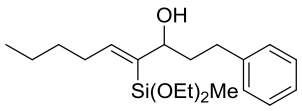
(*Z*)-2-Bromo-5-(tributylstannyl)undeca-1,5-dien-4-ol. Bu_3SnH (1.20 mL, 4.46 mmol) was added over 1 h via syringe pump to a dark brown solution of 2-bromoundec-1-en-5-yn-4-ol (973 mg, 3.97 mmol) and $[(Cp^*)RuCl_2]_n$ (36.0 mg, 0.117 mmol, 3 mol%) in CH_2Cl_2 (20 mL) at ambient temperature. The resulting mixture was stirred for additional 0.5 h before it was concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 2:98 to 5:95 to 10:90; step gradient) afforded the title compound (1.62 g, 76%) as colorless oil with a proximal/distal ratio of 92:8. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.27 (td, J = 7.2, 1.1 Hz, 1H), 5.65 (d, J = 1.3 Hz, 1H), 5.51 (d, J = 1.6 Hz, 1H), 4.50-4.46 (m, 1H), 2.57- 2.47 (m, 2H), 2.05-1.98 (m, 2H), 1.69 (d, J = 2.8 Hz, 1H), 1.55-1.42 (m, 6H), 1.39-1.24 (m, 12H), 1.01-0.95 (m, 6H), 0.89 (t, J = 7.3 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.5 (CR_4), 141.7 (CH), 130.8 (CR_4), 119.3 (CH_2), 76.4 (CH), 49.9 (CH_2), 34.3 (CH_2), 31.7 (CH_2), 29.7 (CH_2), 29.2 (3 × CH_2), 27.4 (3 × CH_2), 22.6 (CH_2) , 14.0 (CH_3), 13.7 (3 × CH_3), 11.1 (3 × CH_2; ^{119}Sn NMR (149 MHz, $CDCl_3$, ^{1}H decoupling): δ −54.0; FTIR (thin film): ν 3463, 2955, 2922, 2871, 2854, 1630, 1493, 1463, 1420, 1376, 1290, 1197, 1147, 1116, 1071, 1020, 961, 883, 745, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{23}H_{45}OBrSnNa$ [$(M+Na)^+$] 559.1567, found 559.1563.



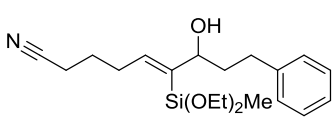
(*E*)-1-Phenylnon-4-en-3-ol (8). CuTC (20.0 mg, 105 µmol) was added to a solution of (*Z*)-1-phenyl-4-(tributylstannyl)non-4-en-3-ol (**6**) (50.0 mg, 98.5 µmol) and $Ph_2PO_2NBu_4$ (50.0 mg, 109 µmol) in DMF (0.50 mL) at ambient temperature and the resulting mixture was stirred for 2.5 h. The mixture was diluted with *tert*-butyl methyl ether (30 mL) and poured into a mixture of 25% aqueous NH_4OH/sat. aqueous NH_4Cl solution (1:9, 10 mL). The phases were separated and the aqueous layer extracted with *tert*-butyl methyl ether (2 × 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash

chromatography (EtOAc/hexane 20:80) afforded the title compound (20.8 mg, 97%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.25 (m, 2H), 7.22-7.17 (m, 3H), 5.66 (dtd, J = 15.4, 6.7, 0.9 Hz, 1H), 5.50 (ddt, J = 15.4, 7.0, 1.4 Hz, 1H), 4.08 (q, J = 6.7 Hz, 1H), 2.76-2.63 (m, 2H), 2.05 (q, J = 6.6 Hz, 2H), 1.93-1.76 (m, 2H), 1.46 (br s, 1H), 1.41- 1.26 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.0 (CR_4), 132.7 (CH), 132.6 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 125.8 (CH), 72.5 (CH), 38.8 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 31.3 (CH_2), 22.2 (CH_2), 13.9 (CH_3); FTIR (thin film): ν 3358, 3063, 3027, 2956, 2926, 2858, 1603, 1496, 1455, 1379, 1294, 1098, 1053, 1030, 970, 917, 746 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{15}H_{22}ONa$ [(M+Na)$^+$] 241.1563, found 241.1564.

Representative Procedure for the trans-Hydrosilylation using Alkoxysilanes. (*Z*)-4-(Diethoxymethylsilyl)-1-phenylnon-4-en-3-ol. Diethoxymethylsilane (650 mg, 4.8417 mmol) was added under argon to a stirred solution of 1-phenyldec-4-yn-3-ol (950 mg, 4.3916 mmol) and $[Cp^*RuCl]_4$ (60 mg, 0.05520 mmol) in CH_2Cl_2 (22 mL). Once the reaction was complete (ca. 15 min, TLC), $CNCH_2COOK$ (120 mg, 0.97 mmol) was added as catalyst scavenger, and stirring was continued for 2 hours. Insoluble matrials were filtered off and rinsed with CH_2Cl_2, the combined filtrates were evaporated under reduced pressure, and the residue was purified by filtration through a short pad of silica using hexanes/ethyl acetate 15:1 as the eluent to give the title compound as a pale yellow oil (942 mg, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.21-7.15 (m, 3H), 6.12 (t, J = 7.6 Hz, 1H), 3.95 (m, 1H), 3.80 (m, 4H), 3.49 (d, J = 10.3 Hz, OH), 2.77-2.56 (m, 2H), 2.27-2.16 (m, 2H), 2.06-1.95 (m, 1H), 1.87-1.76 (m, 1H), 1.43-1.29 (m, 4H), 1.24 (td, J = 5.0, 0.9 Hz, 6H), 0.91 (m, 3H), 0.28 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 146.8, 142.5, 138.2, 128.4, 125.6, 79.6, 58.3, 40.5, 32.8, 31.8, 31.3, 22.5, 18.18, 18.13, 14.0, -2.1; FTIR (thin film): ṽ 3496, 3026, 2958, 2926, 2874, 1613, 1496, 1481, 1454, 1410, 1390, 1364, 1294, 1257, 1214, 1165, 1101, 1071, 1031, 1006, 945, 876, 817, 792, 760, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{20}H_{34}O_3SiNa$ (M+Na$^+$) 373.2169, found 373.2173.

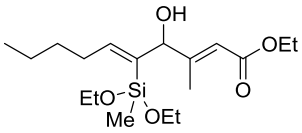


(*Z*)-6-(Diethoxy(methyl)silyl)-7-hydroxy-9-phenylnon-5-enenitrile. Prepared analogously as a colorless oil (115 mg, 36 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.21-7.15 (m, 3H), 6.05 (t, J = 7.5 Hz,



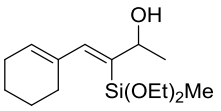
1H), 3.98 (m, 1H), 3.80 (m, 4H), 3.31 (d, *J* = 9.8 Hz, OH), 2.79-2.57 (m, 2H), 2.44-2.31 (m, 4H), 2.05-1.93 (m, 1H), 1.87-1.70 (m, 3H), 1.25 (td, *J* = 5.0, 0.9 Hz, 6H), 0.29 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 142.7, 142.1, 141.3, 128.4, 125.7, 119.3, 78.9, 58.3, 40.1, 32.6, 30.2, 25.4, 18.13, 18.11, 16.7, -2.2; FTIR (thin film): ṽ 3493, 3026, 2972, 2926, 2246, 1615, 1496, 1454, 1424, 1390, 1365, 1293, 1259, 1164, 1101, 1069, 947, 792, 758, 699 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{20}H_{31}NO_3SiNa$ [(M+Na)$^+$] 384.1965, found 384.1966.

Ethyl (2*E*,5*Z*)-5-(Diethoxy(methyl)silyl)-4-hydroxy-3-methyldeca-2,5-dienoate.



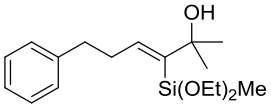
Prepared analogously as a pale yellow oil (207 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (t, *J* = 7.6 Hz, 1H), 6.05 (t, *J* = 1.4 Hz, 1H), 4.42 (d, *J* = 10.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.10 (d, *J* = 9.8 Hz, OH), 3.82-3.70 (m, 4H), 2.26 (m, 2H), 2.03 (s, 3H), 1.44-1.30 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.23 (td, *J* = 7.0, 0.9 Hz, 6H), 0.91 (m, 3H), 0.20 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 167.1, 159.8, 150.1, 134.9, 114.6, 83.1, 59.5, 58.5, 31.7, 31.3, 22.5, 18.0, 16.3, 14.3, 14.0, -2.4; FTIR (thin film): ṽ 3466, 2973, 2926, 2875, 1716, 1651, 1612, 1443, 1390, 1366, 1342, 1258, 1207, 1142, 1100, 1071, 1044, 948, 876, 821, 801, 762, 681 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{18}H_{34}O_5SiNa$ [(M+Na)$^+$] 381.2068, found 381.2068.

(*Z*)-4-(Cyclohex-1-en-1-yl)-3-(diethoxy(methyl)silyl)but-3-en-2-ol. Prepared



analogously as a pale yellow oil (164 mg, 47 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (s, 1H), 5.75 (m, 1H), 4.24 (m, 1H), 3.85-3.74 (m, 5H), 2.06 (m, 2H), 2.00 (m, 2H), 1.68-1.50 (m, 4H), 1.36 (d, *J* = 6.6 Hz, 3H), 1.24 (m, 6H), 0.24 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 147.0, 139.5, 136.6, 126.6, 75.5, 58.3, 58.2, 28.1, 25.4, 24.7, 22.5, 21.9, 18.1, -2.5; FTIR (thin film): ṽ 3448, 2971, 2925, 2833, 1597, 1438, 1390, 1364, 1294, 1255, 1164, 1102, 1070, 942, 895, 859, 838, 797, 756, 730, 684 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{15}H_{28}O_3SiNa$ [(M+Na)$^+$] 307.1700, found 307.1702.

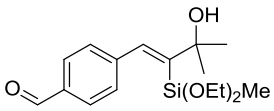
(*Z*)-3-(Diethoxy(methyl)silyl)-2-methyl-6-phenylhex-3-en-2-ol. Prepared



analogously as a colorless oil (180 mg, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.21-7.15 (m, 3H), 6.21 (t, *J* = 7.5 Hz, 1H), 4.32 (s, OH), 3.77 (m, 4H), 2.69 (m, 2H), 2.54 (m, 2H), 1.35 (s, 6H), 1.23 (t, *J* = 6.8 Hz, 6H), 0.22 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 143.9, 141.5, 140.7, 128.5,

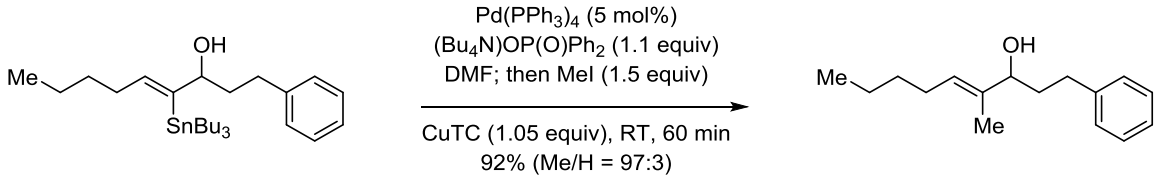
128.3, 125.9, 74.0, 58.2, 36.1, 33.2, 30.1, 18.1, -1.9; FTIR (thin film): ṽ 3497, 3086, 3063, 3027, 2972, 2926, 2883, 1605, 1496, 1482, 1454, 1390, 1369, 1294, 1258, 1209, 1163, 1100, 1069, 998, 944, 881, 790, 752, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{18}H_{30}O_3SiNa$ [(M+Na)$^+$] 345.1856, found 345.1857.

(*Z*)-4-(2-(Diethoxy(methyl)silyl)-3-hydroxy-3-methylbut-1-en-1-yl)benzaldehyde.



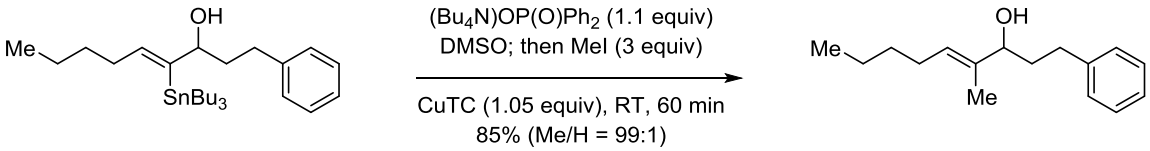
Prepared analogously as a yellow oil that has to be used without delay (118 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.83 (m, 2H), 7.47 (m, 2H), 7.31 (s, 1H), 4.44 (s, OH), 3.72 (m, 4H), 1.49 (s, 6H), 1.16 (t, *J* = 7.0 Hz, 6H), -0.05 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 191.8, 150.8, 145.6, 139.9, 135.2, 129.31, 129.16, 74.9, 58.4, 30.5, 18.0, -2.0; FTIR (thin film): ṽ 3483, 2973, 2927, 2884, 2838, 2733, 1697, 1602, 1565, 1482, 1443, 1389, 1363, 1305, 1260, 1208, 1166, 1102, 1067, 949, 889, 866, 813, 794, 777, 758, 688 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{17}H_{26}O_4SiNa$ [(M+Na)$^+$] 345.1493, found 345.1495.

Copper(I)-Mediated Methylation and Allylation of Alkenylstannanes



Representative Procedure for the C-Methylation of Alkenylstannanes. Method A (Copper/Palladium Co-Catalysis): (*E*)-4-Methyl-1-phenylnon-4-en-3-ol (7). To a clear, colorless solution of (*Z*)-1-phenyl-4-(tributylstannyl)non-4-en-3-ol (**6**) (254 mg, 501 µmol) and $(Ph_2PO_2)NBu_4$ (250 mg, 544 µmol) in DMF (2.5 mL) at ambient temperature was added $Pd(PPh_3)_4$ (30.0 mg, 26 µmol, 5 mol%) and the resulting yellow mixture was stirred until complete dissolution had occurred, usually ca. 5 min. After that time, MeI (48 µL, 770 µmol) was added, immediately followed, *within max. 30 seconds*, by CuTC (100 mg, 524 µmol). The resulting black suspension was stirred for 0.5 h before the reaction was quenched by the addition

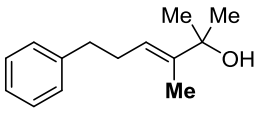
of Et_3N (ca. 0.1 mL). The mixture was diluted with *tert*-butyl methyl ether (30 mL), poured on a mixture of 25% aqueous NH_4OH/sat. aqueous NH_4Cl solution (1:9, 20 mL), the phases were separated and the bright blue aqueous phase extracted with *tert*-butyl methyl ether (2 × 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 10:90 to 20:80; step gradient) afforded the methylated product **7** (107 mg, 92%) as a faintly yellowish oil with a methylation/protodestannation ratio of **7**:**8** = 97:3, as determined by ^1H NMR and GCMS. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32-7.25 (m, 2H), 7.23-7.16 (m, 3H), 5.41 (t, J = 7.1 Hz, 1H), 4.02 (t, J = 6.7 Hz, 1H), 2.71-2.55 (m, 2H), 2.04 (q, J = 7.0 Hz, 2H), 1.95-1.79 (m, 2H), 1.63 (s, 3H), 1.46 (br s, 1H), 1.40-1.26 (m, 4H), 0.91 (app. t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.1 (CR_4), 136.7 (CR_4), 128.4 (2 × CH), 128.3 (2 × CH), 127.3 (CH), 125.7 (CH), 77.4 (CH), 36.5 (CH_2), 32.2 (CH_2), 31.7 (CH_2), 27.2 (CH_2), 22.4 (CH_2), 14.0 (CH_3), 11.2 (CH_3); FTIR (thin film): ν 3348, 3027, 2955, 2927, 2858, 1496, 1455, 1378, 1298, 1052, 1030, 998, 918, 851, 747, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{16}H_{24}ONa$ [$(M+Na)^+$] 255.1719, found 255.1719.



Representative Procedure for the Methylation of Alkenylstannanes. Method B (CuTC Only): (*E*)-4-Methyl-1-phenylnon-4-en-3-ol (7). To a clear, colorless solution of (*Z*)-1-phenyl-4-(tributylstannyl)non-4-en-3-ol (**6**) (254 mg, 501 μmol) and $(Ph_2PO_2)NBu_4$ (250 mg, 544 μmol) in DMSO (2.5 mL) at ambient temperature was added MeI (95 μL, 1500 μmol), immediately followed, *within maximum 30 seconds*, by CuTC (100 mg, 524 μmol). The resulting black suspension was stirred for 1 hour before the reaction was quenched by the addition of Et_3N (ca. 0.1 mL).

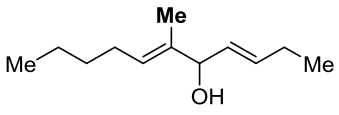
The mixture was diluted with *tert*-butyl methyl ether (30 mL) and poured on a mixture of 25% aqueous NH_4OH/sat. aqueous NH_4Cl solution (1:9, 20 mL). The phases were separated and the clear, bright blue aqueous phase was extracted with *tert*-butyl methyl ether (2 × 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 10:90 to 20:80; step gradient) afforded the desired methylated product **7** (99.4 mg, 85%) as a colorless oil with a methylation/protodestannation ratio **7**:**8** = 99:1, as determined by ^{1}H NMR and GCMS. Analytical and spectral data as described above.

(*E*)-2,3-Dimethyl-6-phenylhex-3-en-2-ol. Prepared according to method **B** as a colorless oil (78.2 mg, 76%) with a methylation/protodestannation ratio of 94:6, as determined by ^{1}H NMR and GCMS.



The same product was prepared according to method **A** as a colorless oil (89.8 mg, 88%) with a methylation/protodestannation ratio of 79:21, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.27 (m, 2H), 7.24-7.18 (m, 3H), 5.58 (td, J = 7.1, 1.3 Hz, 1H), 2.71 (dd, J = 8.8, 6.8 Hz, 2H), 2.36 (app. q, J = 7.4 Hz, 2H), 1.63 (br s, 4H), 1.33 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.1 (CR_4), 141.9 (CR_4), 128.4 (2 × CH), 128.1 (2 × CH), 125.6 (CH), 121.1 (CH), 73.3 (CR_4), 35.8 (CH_2), 29.8 (CH_2), 28.8 (2 × CH_3), 12.6 (CH_3); FTIR (thin film): ν 3384, 3026, 2974, 2927, 2858, 1603, 1496, 1453, 1370, 1258, 1136, 1075, 1030, 1001, 935, 850, 746, 697 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{14}H_{20}ONa$ [(M+Na)$^+$] 227.1406, found 227.1404.

(3*E*,6*E*)-6-Methylundeca-3,6-dien-5-ol. Prepared according to method **B** as a colorless oil (65.8 mg, 72%) with a methylation/protodestannation ratio of 95:5, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.72 (dtd, J = 15.4, 6.3, 1.2 Hz, 1H), 5.46 (ddt, J = 15.4, 6.8, 1.5 Hz, 2H), 4.45 (d, J = 6.5 Hz, 1H), 2.13-1.98 (m, 4H), 1.59 (s, 3H), 1.56 (br s, 1H), 1.39-1.24 (m, 4H), 0.99 (t, J = 7.5 Hz, 3H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.3 (CR_4), 133.9 (CH), 130.0 (CH), 126.3 (CH), 78.2 (CH), 31.7 (CH_2), 27.3 (CH_2), 25.3 (CH_2), 22.4 (CH_2), 14.0 (CH_3), 13.4 (CH_3), 12.1 (CH_3); FTIR (thin film): ν 3352,



2959, 2926, 2872, 2857, 1459, 1378, 1297, 1084, 1004, 965, 850 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{12}H_{22}ONa$ [$(M+Na)^+$] 205.1563, found 205.1563.

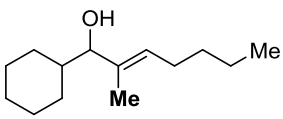
(*E*) - 1 - (Cyclohex-1-en-1-yl) - 2,4 - dimethylpent - 1 - en -3-ol. Prepared according to method **B** as a colorless oil (76.8 mg, 79%) with a methylation/proto-destannation ratio of 90:10, as determined by ^1H NMR and GCMS. ^1H NMR (400 MHz, $CDCl_3$): δ 5.73 (br s, 1H), 5.59 (app. dt, J = 3.9, 2.0 Hz, 1H), 3.58 (d, J = 8.1 Hz, 1H), 2.09 (dq, J = 6.6, 2.7 Hz, 4H), 1.82-1.72 (m, 1H), 1.74 (d, J = 1.2 Hz, 3H), 1.67-1.53 (m, 5H), 0.98 (d, J = 6.6 Hz, 3H), 0.80 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.1 (CR_4), 134.8 (CR_4), 129.9 (CH), 127.1 (CH), 84.7 (CH), 31.3 (CH), 29.3 (CH_2), 25.6 (CH_2), 22.9 (CH_2), 22.2 (CH_2), 19.5 (CH_3), 18.6 (CH_3), 13.2 (CH_3); FTIR (thin film): ν 3387, 2925, 2869, 2833, 1447, 1379, 1365, 1295, 1242, 1169, 1132, 1009, 923, 885, 801 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{13}H_{22}ONa$ [$(M+Na)^+$] 217.1563, found 217.1563.

(*E*)-4-(3-Hydroxy-2,3-dimethylbut-1-en-1-yl) benzonitrile. Prepared according to method **B** as a colorless oil (87.2 mg, 86%) with a methylation/protodestannation ratio of 99:1, as determined by ^1H NMR and GCMS. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 6.69 (d, J = 1.6 Hz, 1H), 1.87 (d, J = 1.3 Hz, 3H), 1.70 (s, 1H), 1.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0 (CR_4), 143.4 (CR_4), 131.8 (2 × CH), 129.6 (2 × CH), 121.1 (CH), 119.1 (CR_4), 109.5 (CR_4), 73.9 (CR_4), 28.9 (2 × CH_3), 14.7 (CH_3); FTIR (thin film): ν 3430, 2975, 2931, 2871, 2226, 1642, 1603, 1502, 1462, 1446, 1408, 1363, 1240, 1211, 1170, 1115, 959, 941, 879, 821 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{13}H_{15}NONa$ [$(M+Na)^+$] 224.1046, found 224.1044.

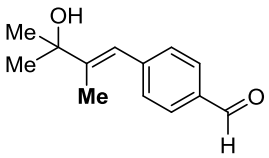
(*E*)-7-Hydroxy-6-methyl-9-phenylnon-5-enenitrile. Prepared according to method **B** as a colorless oil (98.8 mg, 81%) with a methylation/protode-stannation ratio of 99:1, as determined by ^1H NMR and GCMS. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24-7.16 (m, 2H), 7.14-7.09 (m, 3H), 5.29 (app. tp, J = 7.3, 1.2 Hz,1H), 3.96 (t, J = 6.6 Hz, 1H), 2.62 (ddd, J = 13.8, 9.4, 6.4 Hz, 1H), 2.52 (ddd, J = 13.8, 9.1, 6.9 Hz, 1H), 2.27 (t, J = 7.1 Hz, 2H), 2.15 (app. q, J = 7.3 Hz, 2H), 1.79 (dddd, J = 9.2, 6.8, 6.1, 4.9 Hz, 2H), 1.67 (p, J = 7.2 Hz, 2H), 1.58 (app. t, J = 1.1 Hz, 3H), 1.48 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.8 (CR_4), 139.6 (CR_4), 128.4

(4 × CH), 125.8 (CH), 123.7 (CH), 119.7 (CR_4), 76.9 (CH), 36.6 (CH_2), 32.1 (CH_2), 26.4 (CH_2), 25.1 (CH_2), 16.6 (CH_2), 11.7 (CH_3); FTIR (thin film): ν 3428, 3026, 2929, 2860, 2247, 1603, 1495, 1454, 1304, 1156, 1055, 1030, 1008, 918, 870, 749, 700 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{16}H_{21}NONa$ [$(M+Na)^+$] 266.1515, found 266.1514.

(*E*)-1-Cyclohexyl-2-methylhept-2-en-1-ol. Prepared according to method **B** as a colorless oil (86.4 mg, 82%) with a methylation/protodestannation ratio of >99:1, as determined by ^1H NMR and GCMS. ^1H NMR (400 MHz, $CDCl_3$): δ 5.32 (ddq, J = 8.3, 5.8, 1.2 Hz, 1H), 3.61 (d, J = 8.3 Hz, 1H), 2.05-1.96 (m, 3H), 1.80-1.60 (m, 3H), 1.57 (app. q, J = 1.0 Hz, 3H), 1.48-1.07 (m, 10H), 0.99-0.78 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.9 (CR_4), 128.3 (CH), 83.3 (CH), 40.6 (CH), 31.7 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 27.2 (CH_2), 26.5 (CH_2), 26.2 (CH_2), 26.0 (CH_2), 22.4 (CH_2), 14.0 (CH_3), 11.1 (CH_3); FTIR (thin film): ν 3360, 2955, 2920, 2851, 1449, 1378, 1306, 1290, 1260, 1206, 1081, 1054, 1008, 891, 851 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{14}H_{26}ONa$ [$(M+Na)^+$] 233.1876, found 233.1873.

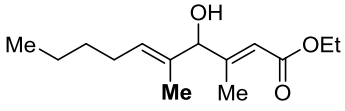


(*E*) - 4 - (3-Hydroxy - 2,3 - dimethylbut-1-en-1-yl)benzaldehyde. Prepared according to method **B** as a colorless oil (87.1 mg, 85%) with a methylation/protodestannation ratio of 98:2, as determined by ^1H NMR and GCMS.



The same compound was prepared according to method **A** as a colorless oil (82.9 mg, 81%) with a methylation/protodestannation ratio of 98:2, as determined by ^1H NMR and GCMS. ^1H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.80 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 6.71 (s, 1H), 1.97 (s, 1H), 1.89 (d, J = 1.4 Hz, 3H), 1.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.9 (CH), 147.7 (CR_4), 145.1 (CR_4), 134.1 (CR_4), 129.5 (4 × CH), 121.5 (CH), 73.8 (CR_4), 28.9 (2 × CH_3), 14.8 (CH_3); FTIR (thin film): ν 3434, 2974, 2930, 2831, 2735, 1687, 1646, 1599, 1563, 1462, 1445, 1416, 1362, 1306, 1212. 1166, 1112, 978, 959, 941, 879, 825, 788, 745 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{13}H_{16}O_2Na$ [$(M+Na)^+$] 227.1042, found 227.1041.

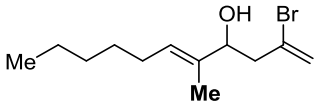
Ethyl (2*E*,5*E*)-4-hydroxy-3,5-dimethyldeca-2,5-dienoate. Prepared according to method **B** as a colorless oil (99.5 mg, 83%) with a methylation/protodestannation ratio of 97:3, as determined by



^{1}H NMR and GCMS.

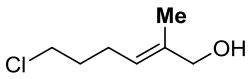
The same compound was prepared according to method **A** as a colorless oil (106 mg, 88%) with a methylation/protodestannation ratio of 95:5, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08 (p, J = 1.4 Hz, 1H), 5.53 (t, J = 7.2 Hz, 1H), 4.44 (s, 1H), 4.15 (qd, J = 7.1, 1.3 Hz, 2H), 2.04 (q, J = 7.3 Hz, 2H), 1.99 (d, J = 1.4 Hz, 3H), 1.87 (d, J = 2.6 Hz, 1H), 1.49 (d, J = 1.2 Hz, 3H), 1.41-1.22 (m, 7H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.9 (CR_4), 157.7 (CR_4), 133.7 (CR_4), 130.3 (CH), 115.0 (CH), 81.6 (CH), 59.7 (CH_2), 31.5 (CH_2), 27.4 (CH_2), 22.3 (CH_2), 15.5 (CH_3), 14.3 (CH_3), 13.9 (CH_3), 11.1 (CH_3); FTIR (thin film): ν 3475, 2957, 2928, 2859, 1716, 1698, 1446, 1367, 1342, 1280, 1211, 1144, 1042, 995, 892 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{14}H_{24}O_3Na$ [(M+Na)$^+$] 263.1618, found 263.1615.

(*E*)-2-Bromo-5-methylundeca-1,5-dien-4-ol. Prepared according to method **B** as a



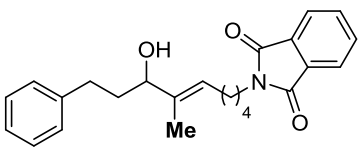
colorless oil (94.5 mg, 72%) with a methylation/protodestannation ratio of 97:3, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.68 (q, J = 1.2 Hz, 1H), 5.53-5.47 (m, 2H), 4.35 (dd, J = 8.1, 5.0 Hz, 1H), 2.68-2.56 (m, 2H), 2.01 (q, J = 7.2 Hz, 2H), 1.68 (br s, 1H), 1.63 (s, 3H), 1.40-1.22 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.2 (CR_4), 130.7 (CR_4), 127.8 (CH), 119.3 (CH_2), 74.9 (CH), 47.4 (CH_2), 31.5 (CH_2), 29.1 (CH_2), 27.5 (CH_2), 22.6 (CH_2), 14.1 (CH_3), 11.6 (CH_3); FTIR (thin film): ν 3379, 2956, 2924, 2856, 1632, 1458, 1378, 1300, 1200, 1115, 1017, 885, 570 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{12}H_{21}OBrNa$ [(M+Na)$^+$] 283.0668, found 283.0665.

(*E*)-6-Chloro-2-methylhex-2-en-1-ol. Prepared according to method **B** as a colorless oil



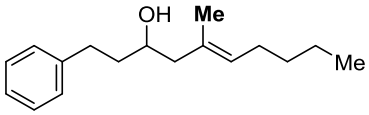
(49.8 mg, 67%) with a methylation/protodestannation ratio of 98:2, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37 (tdd, J = 7.3, 2.6, 1.3 Hz, 1H), 3.99 (s, 2H), 3.52 (t, J = 6.6 Hz, 2H), 2.19 (q, J = 7.1 Hz, 2H), 1.83 (p, J = 6.7 Hz, 2H), 1.68 (br s, 1H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.3 (CR_4), 123.9 (CH), 68.7 (CH_2), 44.5 (CH_2), 32.2 (CH_2), 24.7 (CH_2), 13.7 (CH_3); FTIR (thin film): ν 3322, 2935, 2917, 2862, 1443, 1385, 1346, 1308, 1287, 1230, 1065, 1038, 1007, 861, 844, 746, 723 cm^{-1}; HRMS (ESI): exact mass calculated for $C_7H_{13}O(^{35}Cl)Na$ [(M+Na)$^+$] 171.0547, found 171.0547.

(*E*)-2-(7-Hydroxy-6-methyl-9-phenylnon-5-en-1-yl)isoindoline-1,3-dione. Prepared



according to method **B** as a colorless oil (144 mg, 76%) with a methylation/protodestannation ratio of 96:4, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, J = 5.4, 3.1 Hz, 2H), 7.70 (dd, J = 5.5, 3.1 Hz, 2H), 7.29-7.24 (m, 2H), 7.20-7.14 (m, 3H), 5.37 (t, J = 7.1 Hz, 1H), 4.01 (t, J = 6.7 Hz, 1H), 3.68 (t, J = 7.3 Hz, 2H), 2.67 (ddd, J = 13.8, 9.8, 6.2 Hz, 1H), 2.57 (ddd, J = 13.9, 9.5, 6.5 Hz, 1H), 2.09 (br q, J = 7.4 Hz, 2H), 1.94-1.75 (m, 2H), 1.74-1.63 (m, 3H), 1.62 (s, 3H), 1.43 (p, J = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4 (2 × CR_4), 142.1 (CR_4), 137.6 (CR_4), 133.8 (2 × CR_4), 132.1 (2 × CH), 128.4 (2 × CH), 128.3 (2 × CH), 126.2 (CH), 125.7 (CH), 123.1 (2 × CH), 77.3 (CH), 37.8 (CH_2), 36.4 (CH_2), 32.1 (CH_2), 28.0 (CH_2), 26.9 (CH_2), 26.5 (CH_2), 11.3 (CH_3); FTIR (thin film): ν 3467, 3061, 3026, 2937, 2859, 1770, 1705, 1604, 1495, 1467, 1453, 1437, 1396, 1369, 1337,.1188, 1037, 920, 892, 867, 749, 719, 700 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{24}H_{27}NO_3Na$ [(M+Na)$^+$] 400.1883, found 400.1880.

(*E*)-5-Methyl-1-phenyldec-5-en-3-ol. Prepared from (Z)-1-phenyl-5-



(tributylstannyl)dec-5-en-3-ol (86:15 mixture of proximal/distal vinyl stannane, 261 mg, 501 μmol) according to method **A** as a faintly yellowish oil (85:15 mixture of proximal/distal product, 103 mg, 84%) with a methylation/protodestannation ratio of 92:8, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (87:13 mixture of proximal/distal product, only resonances of the major isomer are reported, 400 MHz, $CDCl_3$): δ 7.33-7.26 (m, 2H), 7.24-7.15 (m, 3H), 5.27 (tq, J = 7.2, 1.3 Hz, 1H), 3.71 (dtd, J = 9.6, 6.1, 3.7 Hz, 1H), 2.90-2.77 (m, 1H), 2.71 (dt, J = 13.7, 8.1 Hz, 1H), 2.23 (dd, J = 13.2, 3.3 Hz, 1H), 2.12-1.96 (m, 3H), 1.85-1.66 (m, 3H), 1.62 (d, J = 1.2 Hz, 3H), 1.40-1.24 (m, 4H), 0.95-0.85 (m, 3H); ^{13}C NMR (87:13 mixture of proximal/distal product, only resonances of the major isomer are reported,101 MHz, $CDCl_3$): δ 142.3 (CR_4), 131.6 (CR_4), 129.2 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 125.7 (CH), 67.7 (CH), 48.1 (CH_2), 38.7 (CH_2), 32.2 (CH_2), 31.9 (CH_2), 27.7 (CH_2), 22.4 (CH_2), 16.0 (CH_3), 14.0 (CH_3); FTIR (thin film): ν 3375, 3062, 3026, 2954, 2925, 2857, 1603, 1495, 1454, 1380, 1266, 1181, 1079, 1050, 1029, 929, 840, 745, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{17}H_{30}NO$ [(M+NH_4)$^+$] 264.2322, found 264.2318.

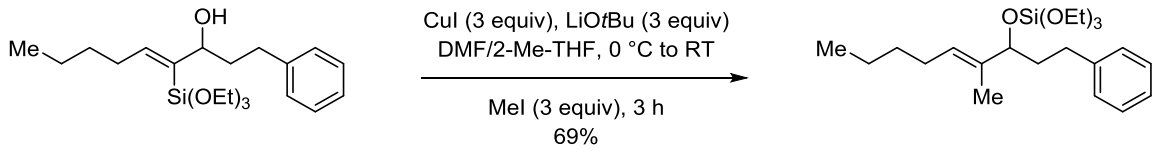
(2*SR*,3*SR*,*E*)-3,4-Dimethylnon-4-en-2-ol. Prepared from (2*SR*,3*RS*,*Z*)-3-methyl-4-(tributylstannyl)non-4-en-2-ol (94:6 mixture of proximal/distal vinyl stannane, 224 mg, 503 μmol) according to method **A** as a faintly yellowish oil (94:6 mixture of proximal/distal product, 72.2 mg, 84%) with a methylation/protodestannation ratio of 94:6, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (94:6 mixture of proximal/distal product, only resonances of the major isomer are reported, 400 MHz, $CDCl_3$): δ 5.21 (tp, J = 7.1, 1.3 Hz, 1H), 3.72 (p, J = 6.3 Hz, 1H), 2.08-1.96 (m, 3H), 1.57 (s, 3H), 1.47 (br s, 1H), 1.37-1.26 (m, 4H), 1.13 (d, J = 6.3 Hz, 3H), 1.04 (d, J = 7.0 Hz, 3H), 0.94-0.83 (m, 3H); ^{13}C NMR (94:6 mixture of proximal/distal product, only resonances of the major isomer are reported, 101 MHz, $CDCl_3$): 137.0 (CR_4), 126.3 (CH), 69.2 (CH), 49.7 (CH), 31.9 (CH_2), 27.4 (CH_2), 22.4 (CH_2), 21.2 (CH_3), 14.4 (CH_3), 13.99 (CH_3), 13.95 (CH_3); FTIR (thin film): ν 3362, 2959, 2926, 2873, 2859, 1455, 1372, 1298, 1249, 1157, 1081, 1026, 972, 952, 908, 850, 727 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{11}H_{22}ONa$ [(M+Na)$^+$] 193.1563, found 193.1563.

(1*RS*,2*SR*)-2-((*E*)-Hept-2-en-2-yl)cyclohexan-1-ol. Prepared from (1*RS*,2*RS*)-2-((*Z*)-1-(tributylstannyl)hex-1-en-1-yl)cyclohexan-1-ol (85:15 mixture of proximal/ distal vinyl stannane, 236 mg, 501 μmol) according to method **A** as a faintly yellowish oil (87:13 mixture of proximal/distal product, 59.7 mg, 61%) with a methylation/protodestannation ratio of 94:6, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (87:13 mixture of proximal/distal product, only resonances of the major isomer are reported, 400 MHz, $CDCl_3$): δ 5.32 (ddd, J = 8.6, 6.3, 1.5 Hz, 1H), 3.40 (td, J = 10.0, 4.2 Hz, 1H), 2.12-1.97 (m, 3H), 1.88-1.59 (m, 5H), 1.56 (d, J = 1.3 Hz, 3H), 1.40-1.12 (m, 8H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (87:13 mixture of proximal/distal product, only resonances of the major isomer are reported, 101 MHz, $CDCl_3$): 135.3 (CR_4), 128.6 (CH), 70.2, 56.3, 34.0, 31.9, 30.0, 27.4, 25.7, 24.9, 22.4, 14.0, 12.5; δ 142.3 (CR_4), 131.6 (CR_4), 129.2 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 125.7 (CH), 67.7 (CH), 48.1 (CH_2), 38.7 (CH_2), 32.2 (CH_2), 31.9 (CH_2), 27.7 (CH_2), 22.4 (CH_2), 16.0 (CH_3), 14.0 (CH_3); FTIR (thin film): ν 3441, 2954, 2926, 2856, 1449, 1379, 1352, 1270, 1132, 1106, 1063, 1042, 1008, 945, 843 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{13}H_{25}O$ [(M+H)$^+$] 197.1900, found 197.1899.

(1*RS*,2*SR*)-2-((*E*)-Hept-2-en-2-yl)cyclopentan-1-ol. Prepared from (1*RS*,2*RS*)-2-((*Z*)-1-(tributylstannyl)hex-1-en-1-yl)cyclopentan-1-ol (85:15 mixture of proximal/ distal vinyl stannane, 229 mg, 501 μmol) according to method **A** as a faintly yellowish oil (86:14 mixture of proximal/distal product, 60.4 mg, 66%) with a methylation/protodestannation ratio of 98:2, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (86:14 mixture of proximal/distal product, only resonances of the major isomer are reported, 400 MHz, $CDCl_3$): δ 5.25 (tp, J = 7.1, 1.3 Hz, 1H), 3.96 (q, J = 7.4 Hz, 1H), 2.24 (dt, J = 10.3, 7.8 Hz, 1H), 1.99 (ddt, J = 12.8, 10.3, 7.3 Hz, 3H), 1.83-1.45 (m, 6H), 1.58 (s, 3H), 1.39-1.24 (m,4H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (86:14 mixture of proximal/distal product, only resonances of the major isomer are reported,101 MHz, $CDCl_3$): δ 134.7 (CR_4), 126.2 (CH), 75.7 (CH), 57.8 (CH), 33.6 (CH_2), 32.0 (CH_2), 28.2 (CH_2), 27.6 (CH_2), 22.4 (CH_2), 21.3 (CH_2), 14.0 (CH_3), 13.3 (CH_3); FTIR (thin film): ν 3336, 2955, 2926, 2871, 1453, 1378, 1341, 1299, 1247, 1151, 1086, 1050, 975, 937, 838, 727 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{12}H_{23}O$ [$(M+H)^+$] 183.1743, found 183.1743.

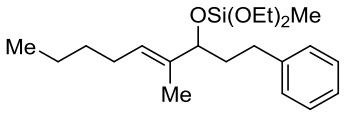
(*E*)-7-Methyltetradec-7-ene-1,14-diyl dihexanoate. Prepared according to method **A** as a colorless oil (164 mg, 75%) with a methylation/protodestannation ratio of >99:1, as determined by ^{1}H NMR and GCMS. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.08 (t, J = 6.7 Hz, 1H), 4.04 (t, J = 6.7 Hz, 4H), 2.27 (t, J = 7.5 Hz, 4H), 1.95 (app. q, J = 7.7 Hz, 4H), 1.60 (tt, J = 7.6, 4.1 Hz, 8H), 1.56 (s, 3H), 1.42-1.22 (m, 20H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.9 (2 × CR_4), 135.0 (CR_4), 124.4 (CH), 64.3 (2 × CH_2), 39.5 (CH_2), 34.3 (2 × CH_2), 31.3 (2 × CH_2), 29.7 (CH_2), 28.87 (CH_2), 28.83 (CH_2), 28.6 (2 × CH_2), 27.78 (CH_2), 27.74 (CH_2), 25.83 (CH_2), 25.80 (CH_2), 24.7 (2 × CH_2), 22.3 (2 × CH_2), 15.8 (CH_3), 13.9 (2 × CH_3); FTIR (thin film): ν 2954, 2928, 2857, 1735, 1463, 1381, 1355, 1244, 1169, 1099, 1067, 944, 889, 851, 729 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{27}H_{50}O_4Na$ [$(M+Na)^+$] 461.3601, found 461.3605.

Copper(I)-Mediated Methylation and Allylation of Alkenylsilicates *via* Brook-Rearrangement



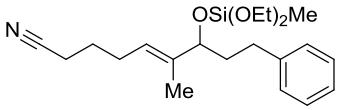
Representative Procedure: (*E*)-Triethyloxy((4-methyl-1-phenylnon-4-en-3-yl)oxy)silane (10d). LiO*t*Bu (0.9 M in 2-Me-THF, 0.33 mL, 300 µmol) was added to a suspension of CuI (58.0 mg, 305 µmol) in DMF (0.50 mL) at 0 °C, the cooling bath was removed and the resulting dark brown solution was stirred at ambient temperature for 30 min. A solution of (*Z*)-1-phenyl-4-(triethoxysilyl)non-4-en-3-ol (**9d**) (38.0 mg, 99.8 µmol) in DMF (0.6 mL) was added, immediately followed by MeI (19.0 µL, 305 µmol). The resulting mixture was stirred until TLC control showed complete conversion of the substrate before the reaction was quenched with Et_3N (0.1 mL). The mixture was diluted with *tert*-butyl methyl ether (30 mL) and poured into a mixture of 25% aqueous NH_4OH/sat. aqueous NH_4Cl solution (1:9, 10 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (2 × 30 mL), the combined extracts were washed with brine (3 x) and then dried over Na_2SO_4, filtered and concentrated under reduced pressure, and the residue was purified by flash chromatography (EtOAc/hexane 2:98 to 10:90; step gradient) to give the title compound (27.2 mg, 69%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.24 (m, 2H), 7.22-7.14 (m, 3H), 5.39 (t, J = 7.1 Hz, 1H), 4.27 (t, J = 6.7 Hz, 1H), 3.82 (q, J = 7.0 Hz, 6H), 2.66-2.48 (m, 2H), 2.03 (q, J = 7.0 Hz, 2H), 1.99-1.89 (m, 1H), 1.82 (dddd, J = 13.3, 10.2, 6.5, 5.7 Hz, 1H), 1.61 (s, 3H), 1.39-1.28 (m, 4H), 1.21 (t, J = 7.0 Hz, 9H), 0.94-0.87 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.4 (CR_4), 135.7 (CR_4), 128.4 (2 × CH), 128.2 (2 × CH), 127.1 (CH), 125.6 (CH), 78.7 (CH), 59.1 (3 × CH_2), 37.3 (CH_2), 32.0 (CH_2), 31.7 (CH_2), 27.2 (CH_2), 22.4 (CH_2), 18.1 (3 × CH_3), 14.0 (CH_3), 10.9 (CH_3); FTIR (thin film): ν 3027, 2973, 2927, 1604, 1496, 1554, 1390, 1296, 1168, 1103, 1079, 965, 791 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{22}H_{38}O_4SiNa$ [$(M+Na)^+$] 417.2432, found 417.2424.

(*E*)-Diethoxy(methyl)((4-methyl-1-phenylnon-4-en-3-yl)oxy)silane. The reaction



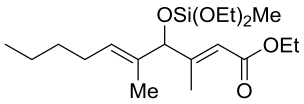
was performed analogously; the crude product was analytically pure (>98% by NMR, 54 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.14 (m, 3H), 5.37 (t, *J* = 7.2 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 1H), 3.78 (qd, *J* = 7.1, 2.8 Hz, 4H), 2.58 (m, 2H), 2.02 (m, 2H), 1.86 (m, 2H), 1.60 (s, 3H), 1.39-1.28 (m, 4H), 1.20 (t, *J* = 7.0 Hz, 6H), 0.90 (m, 3H), 0.09 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 142.4, 136.0, 128.4, 128.3, 127.0, 125.6, 78.1, 58.22, 58.19, 37.5, 32.1, 31.7, 27.2, 22.4, 18.24, 18.22, 14.0, 10.92, -6.44; FTIR (thin film): ṽ 3086, 3063, 3027, 2958, 2926, 2874, 1742, 1604, 1496, 1454, 1389, 1334, 1295, 1262, 1167, 1102, 1075, 984, 957, 888, 824, 790, 767, 748, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{21}H_{36}O_3SiNa$ [(M+Na)$^+$] 387.2326, found 387.2327.

(*E*)-7-((Diethoxy(methyl)silyl)oxy)-6-methyl-9-phenylnon-5-enenitrile. Prepared



according to the general procedure as a colorless oil (26 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.21-7.15 (m, 3H), 5.32 (t, *J* = 7.1 Hz, 1H), 4.23 (t, *J* = 6.5 Hz, 1H), 3.79 (m, 4H), 2.59 (m, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 2.21 (m, 2H), 1.98-1.76 (m, 2H), 1.74 (t, *J* = 7.2 Hz, 2H), 1.64 (s, 3H), 1.21 (td, *J* = 7.0, 0.8 Hz, 6H), 0.10 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 142.1, 139.0, 128.34, 128.29, 125.7, 123.4, 119.6, 77.5, 58.25, 58.22, 37.4, 32.0, 26.2, 25.2, 18.23, 16.5, 11.4, -6.5; FTIR (thin film): ṽ 3063, 3027, 2973, 2927, 2885, 2247, 1603, 1496, 1454, 1390, 1366, 1333, 1294, 1263, 1166, 1100, 1071, 985, 956, 889, 822, 788, 767, 750, 699 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{21}H_{33}NO_3SiNa$ [(M+Na)$^+$] 398.2122, found 398.2124.

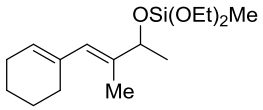
Ethyl (2E,5E)-4-((diethoxy(methyl)silyl)oxy)-3,5-dimethyldeca-2,5-dienoate.



Prepared according to the general procedure as a colorless oil (28 mg, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (qui, *J* = 1.4 Hz, 1H), 5.51 (t, *J* = 7.1 Hz, 1H), 4.59 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.77 (m, 4H), 2.03 (q, *J* = 7.1 Hz, 2H), 1.98 (s, 3H), 1.45 (s, 3H), 1.33 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.20 (td, *J* = 7.1, 1.9 Hz, 6H), 0.89 (m, 3H), 0.10 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 167.1, 157.9, 133.5, 129.6, 114.9, 81.7, 59.6, 58.37, 58.34, 31.5, 27.4, 22.3, 18.18, 15.3, 14.3, 13.9, 10.7, -6.5; FTIR (thin film): ṽ 2973, 2927, 2875, 1717, 1654, 1444, 1388, 1367, 1315, 1263, 1211, 1144,

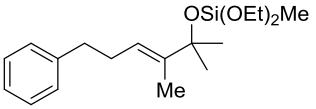
1073, 1004, 957, 887, 826, 792, 763, 734 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{19}H_{36}O_5SiNa$ [$(M+Na)^+$] 395.2224, found 395.2224.

(*E*)-((4-(Cyclohex-1-en-1-yl)-3-methylbut-3-en-2-yl)oxy)diethoxy(methyl)silane.

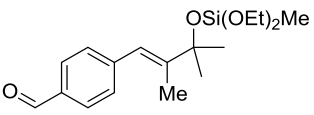


Prepared according to the general procedure as a colorless oil (26 mg, 80 %). ^1H NMR (400 MHz, $CDCl_3$) δ 5.77 (s (br), 1H), 5.58 (m, 1H), 4.39 (q, *J* = 6.4 Hz, 1H), 3.79 (qd, *J* = 7.0, 1.5 Hz, 4H), 2.09 (m, 4H), 1.76 (s, 3H), 1.60 (m, 4H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 6H), 0.11 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 137.5, 135.0, 127.1, 126.7, 74.4, 58.23, 58.21, 29.2, 25.6, 23.0, 22.8, 22.2, 18.24, 18.23, 13.1, -6.5; FTIR (thin film): ṽ 2973, 2927, 2835, 1650, 1439, 1390, 1369, 1334, 1312, 1294, 1262, 1199, 1167, 1102, 1074, 991, 956, 880, 865, 825, 779 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{16}H_{30}O_3SiNa$ [$(M+Na)^+$] 321.1856, found 321.1854.

(*E*)-((2,3-Dimethyl-6-phenylhex-3-en-2-yl)oxy)diethoxy(methyl)silane. Prepared according to the general procedure; the crude product was pure enough for further use (55 mg, 99 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.15 (m, 3H), 5.50 (tq, *J* = 7.0, 1.3 Hz, 1H), 3.77 (q, *J* = 7.0 Hz, 4H), 2.66 (m, 2H), 2.32 (m, 2H), 1.60 (s, 3H), 1.38 (s, 6H), 1.21 (t, *J* = 7.0 Hz, 6H), 0.10 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 142.3, 141.6, 128.5, 128.2, 125.7, 121.1, 76.6, 58.0, 35.8, 29.9, 29.2, 18.2, 12.5, -4.7; FTIR (thin film): ṽ 3086, 3063, 3027, 2974, 2926, 2882, 1604, 1496, 1454, 1388, 1376, 1364, 1294, 1262, 1160, 1104, 1076, 1048, 995, 815, 778, 747, 698 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{19}H_{32}O_3SiNa$ [$(M+Na)^+$] 359.2013, found 359.2015.

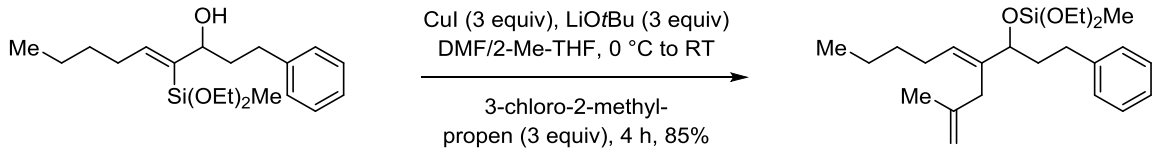


(*E*)-4-(3-((Diethoxy(methyl)silyl)oxy)-2,3-dimethylbut-1-en-1-yl)benzaldehyde.



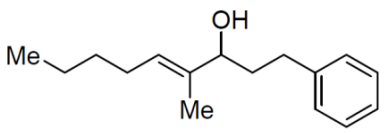
Prepared according to the general procedure as a colorless oil (20 mg, 48 %). ^1H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.84 (m, 2H), 7.40 (m, 2H), 6.67 (s, 1H), 3.82 (q, *J* = 7.0 Hz, 4H), 1.90 (d, *J* = 1.3 Hz, 3H), 1.52 (s, 6H), 1.23 (t, *J* = 6.9 Hz, 6H), 0.17 (s, 3H); ^{13}C (101 MHz, $CDCl_3$) δ 191.9, 147.5, 145.4, 134.2, 129.60, 129.54, 121.6, 77.0, 58.2, 29.2, 18.3, 14.6, -4.7; FTIR (thin film): ṽ 2975, 2927, 2881, 2825, 2734, 1720, 1698, 1649, 1602, 1566, 1507, 1482, 1443, 1415, 1388, 1364, 1304, 1263, 1246, 1212, 1165, 1102, 1075, 1045, 1003, 981, 951, 876,

817, 778, 732, 708, 650 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{18}H_{29}O_4Si$ [$(M+H)^+$] 337.1830, found 337.1831.

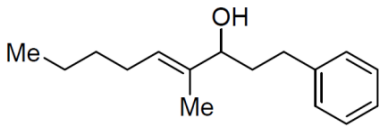


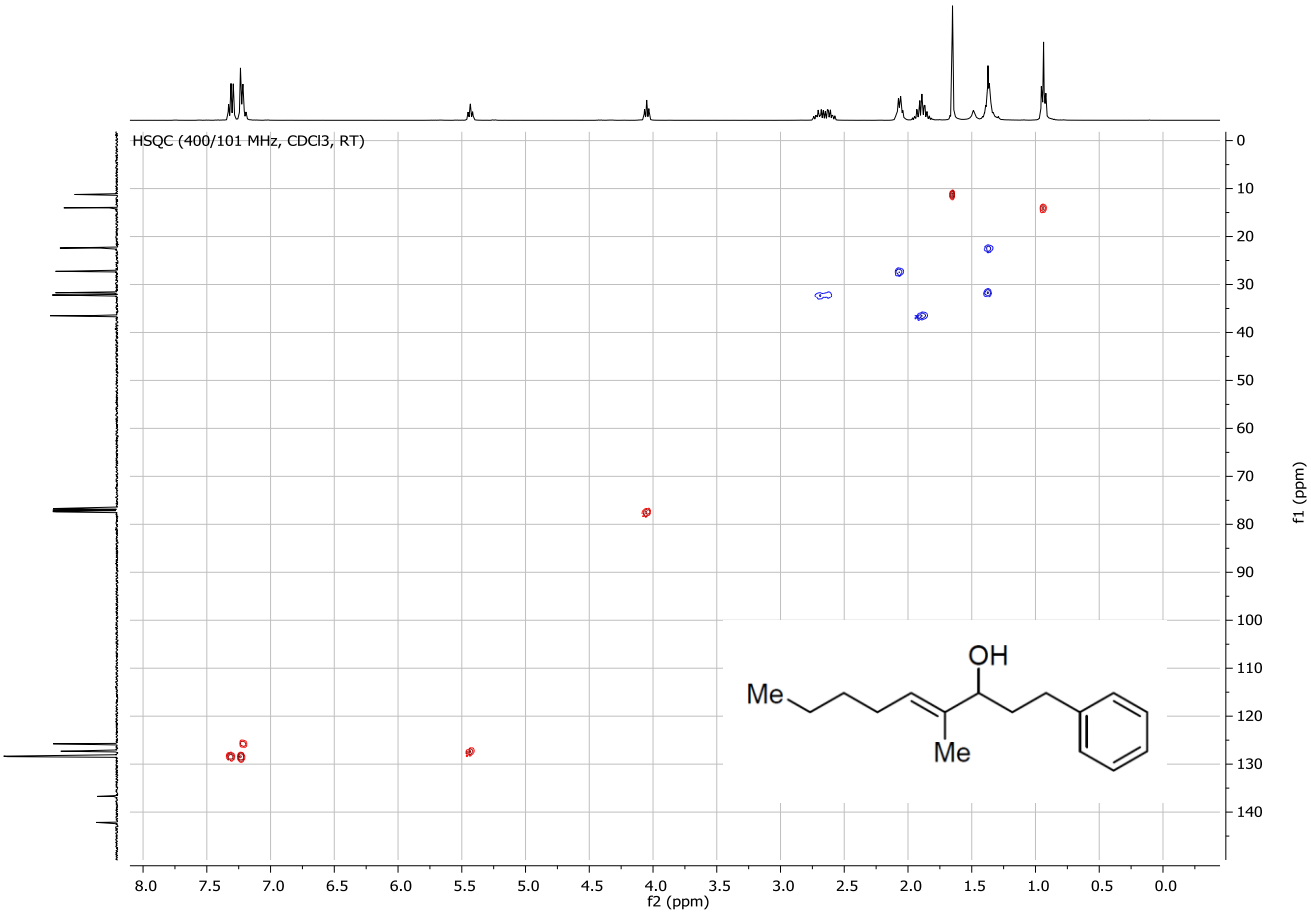
(*E*)-Diethoxy(methyl)((4-(2-methylallyl)-1-phenylnon-4-en-3-yl)oxy)silane. Li*O*t*Bu* (0.9 M solution in 2-Me-THF, 0.33 mL, 300 µmol) was added to a suspension of CuI (58.0 mg, 305 µmol) in DMF (0.50 mL) at 0 °C, the cooling bath was removed and the resulting dark brown solution was stirred at ambient temperature for 30 min. A solution of (*Z*)-4-(diethoxy(methyl)silyl)-1-phenylnon-4-en-3-ol (35.0 mg, 99.8 µmol) in DMF (0.6 mL) was added, followed – *within maximum 30 seconds* – by 3-chloro-2-methylpropene (30 µL, 304 µmol). The resulting mixture was stirred for 4 hours before the reaction was quenched with Et_3N (0.1 mL). The mixture was diluted with *tert*-butyl methyl ether (30 mL), poured on a mixture of 25% aqueous NH_4OH/sat. aqueous NH_4Cl solution (1:9, 10 mL), the phases were separated and the aqueous phase extracted with *tert*-butyl methyl ether (2 × 30 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (EtOAc/hexane 1:99 to 5:95; step gradient) afforded the title compound (34.2 mg, 85%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.23 (m, 2H), 7.20-7.14 (m, 3H), 5.62 (t, J = 7.1 Hz, 1H), 4.74 (s, 1H), 4.69 (s, 1H), 4.28 (t, J = 6.0 Hz, 1H), 3.81 (ttd, J = 7.0, 4.5, 2.3 Hz, 4H), 2.82 (d, J = 15.9 Hz, 1H), 2.71 (d, J = 15.9 Hz, 1H), 2.75-2.54 (m, 2H), 2.02 (td, J = 7.0, 3.4 Hz, 2H), 1.88-1.80 (m, 2H), 1.72 (s, 3H), 1.40-1.29 (m, 4H), 1.22 (td, J = 7.0, 1.6 Hz, 6H), 0.90 (t, J = 7.1 Hz, 3H), 0.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.3 (CR_4), 142.6 (CR_4), 137.2 (CR_4), 128.5 (CH), 128.4 (2 × CH), 128.2 (2 × CH), 125.6 (CH), 110.9 (CH_2), 75.9 (CH), 58.2 (2 × CH_2), 38.2 (CH_2), 35.5 (CH_2), 32.0 (CH_2), 31.8 (CH_2), 27.6 (CH_2), 22.9 (CH_3), 22.5 (CH_2), 18.3 (2 × CH_3), 14.0 (CH_3), −6.4 (CH_3); FTIR (thin film): ν 3027, 2969, 2925, 1646, 1604, 1496, 14454, 1389, 1262, 1167, 1077987, 957, 890, 823, 792, 767, 748 cm^{-1}; HRMS (ESI): exact mass calculated for $C_{24}H_{40}O_3SiNa$ [$(M+Na)^+$] 427.2639, found 427.2636.

1H NMR (400MHz, CDCl3, RT)

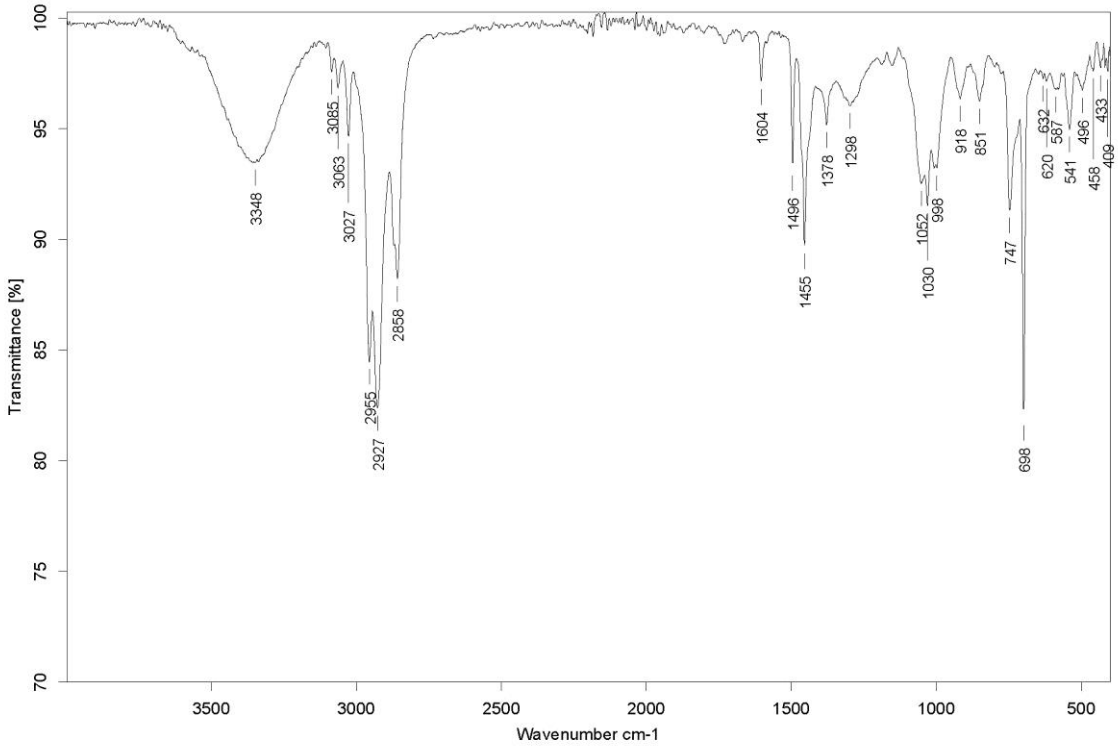


13C NMR (101 MHz, CDCl3, RT)

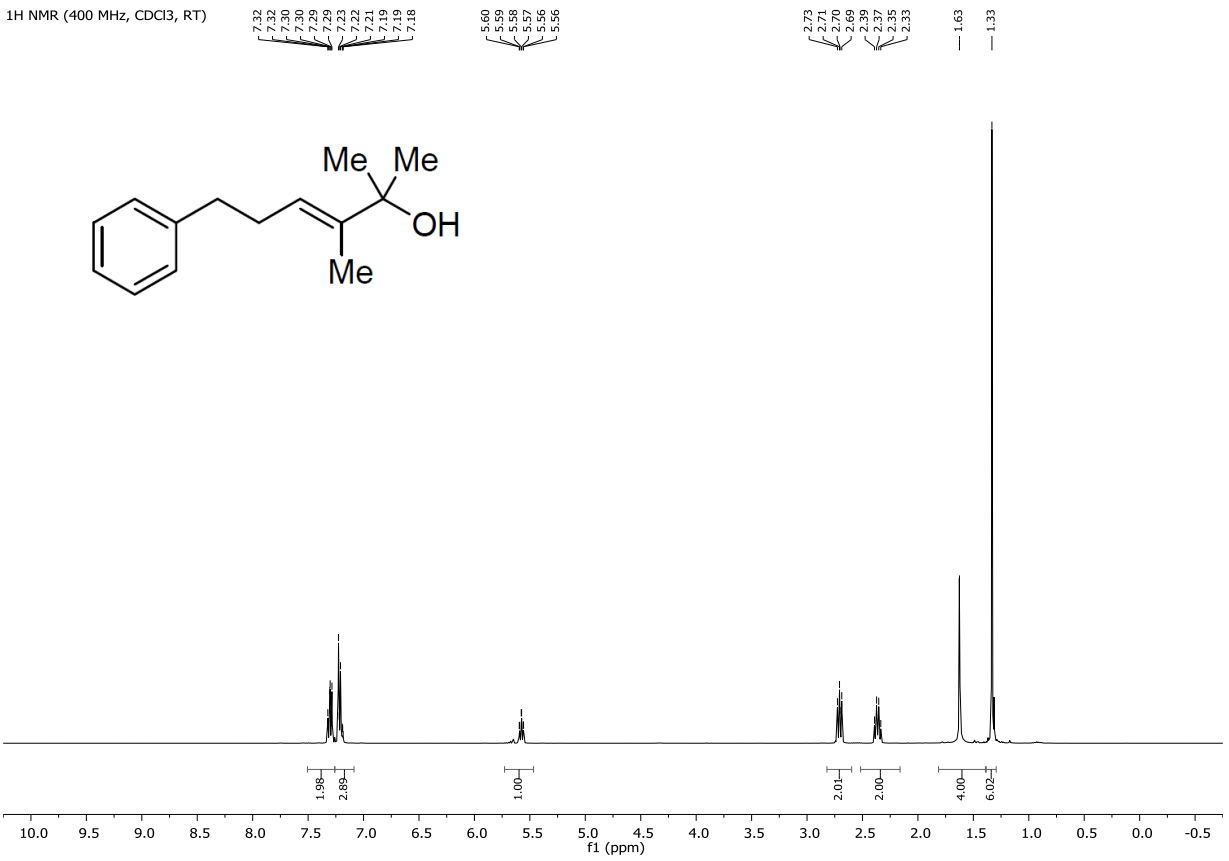




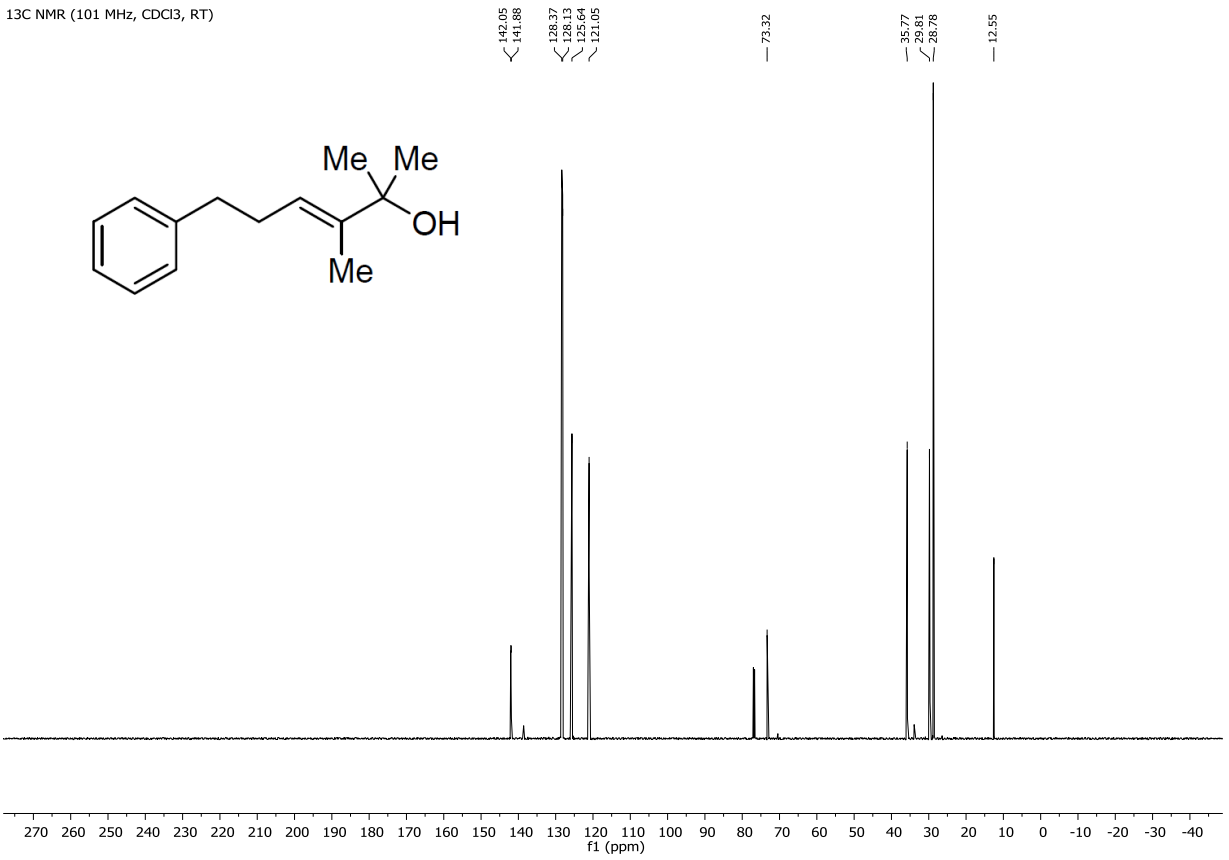
HUR-HA-003-10.0 **01.07.2016**

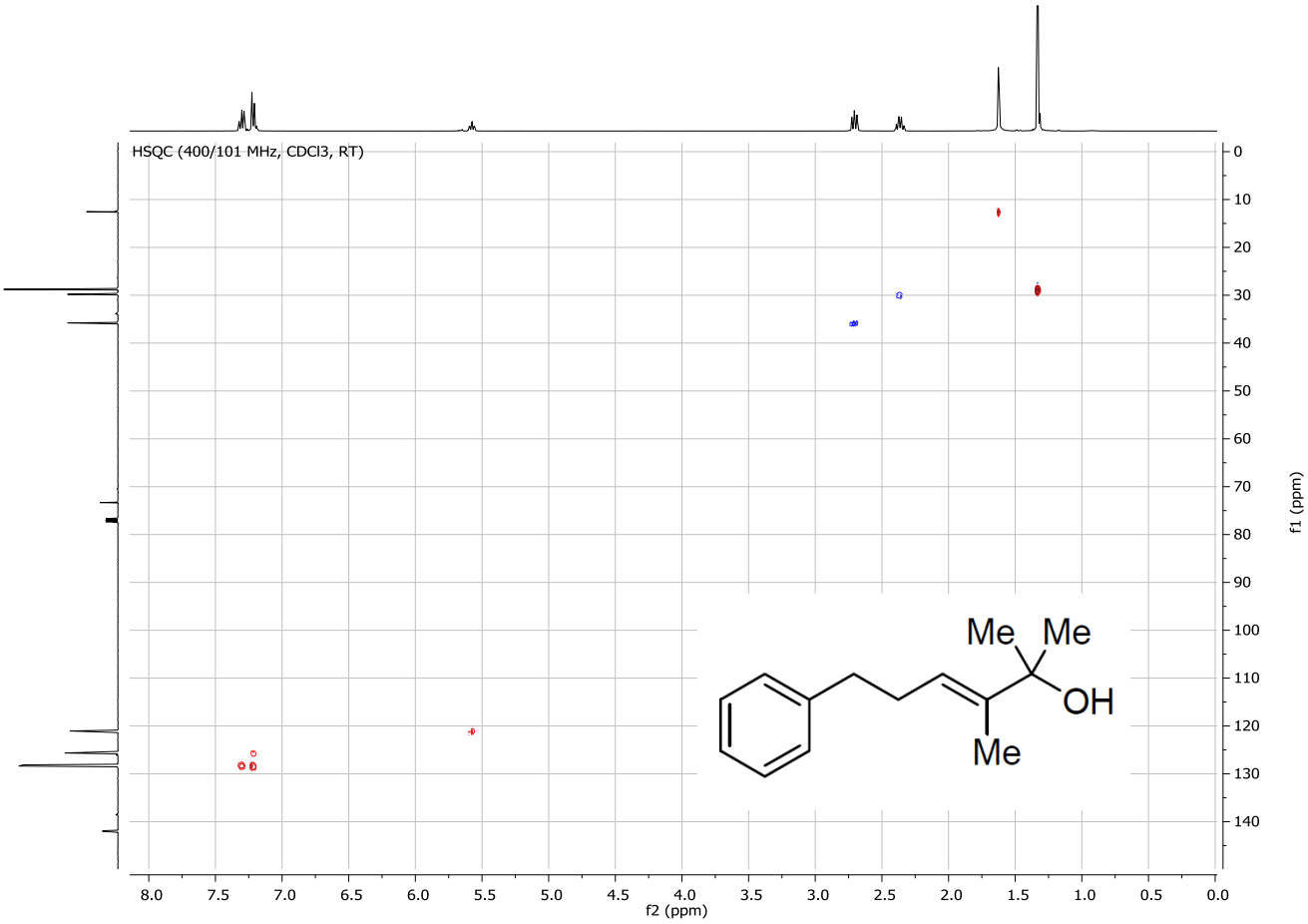


1H NMR (400 MHz, CDCl3, RT)

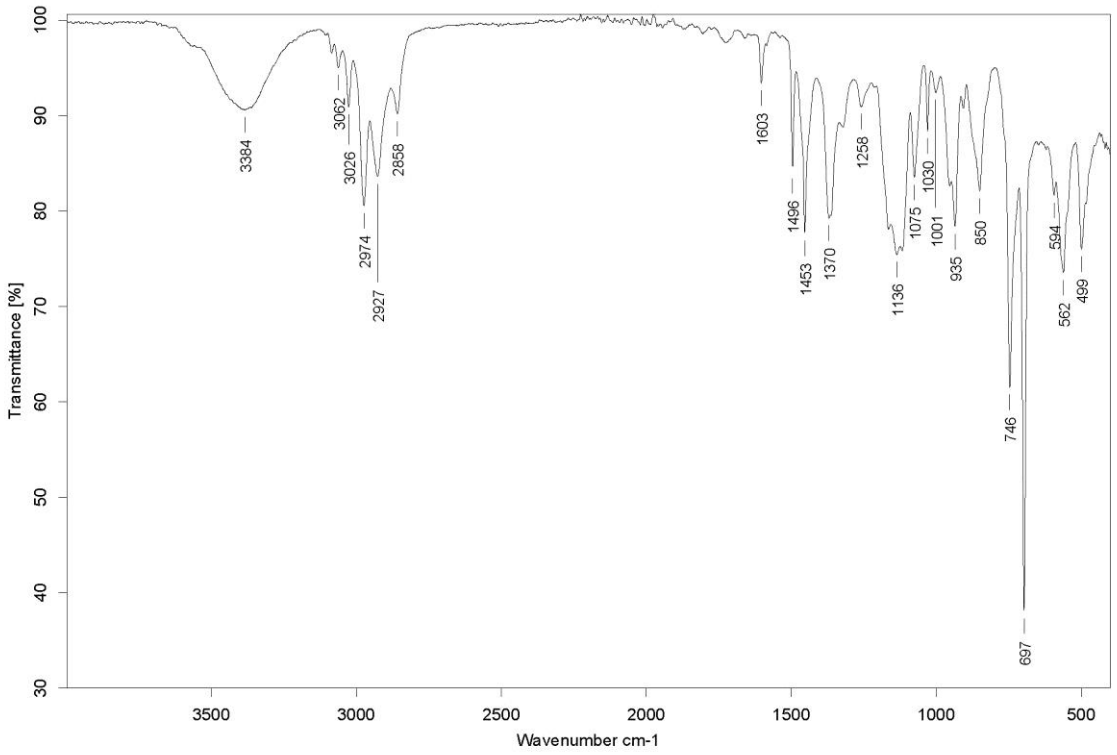


13C NMR (101 MHz, CDCl3, RT)

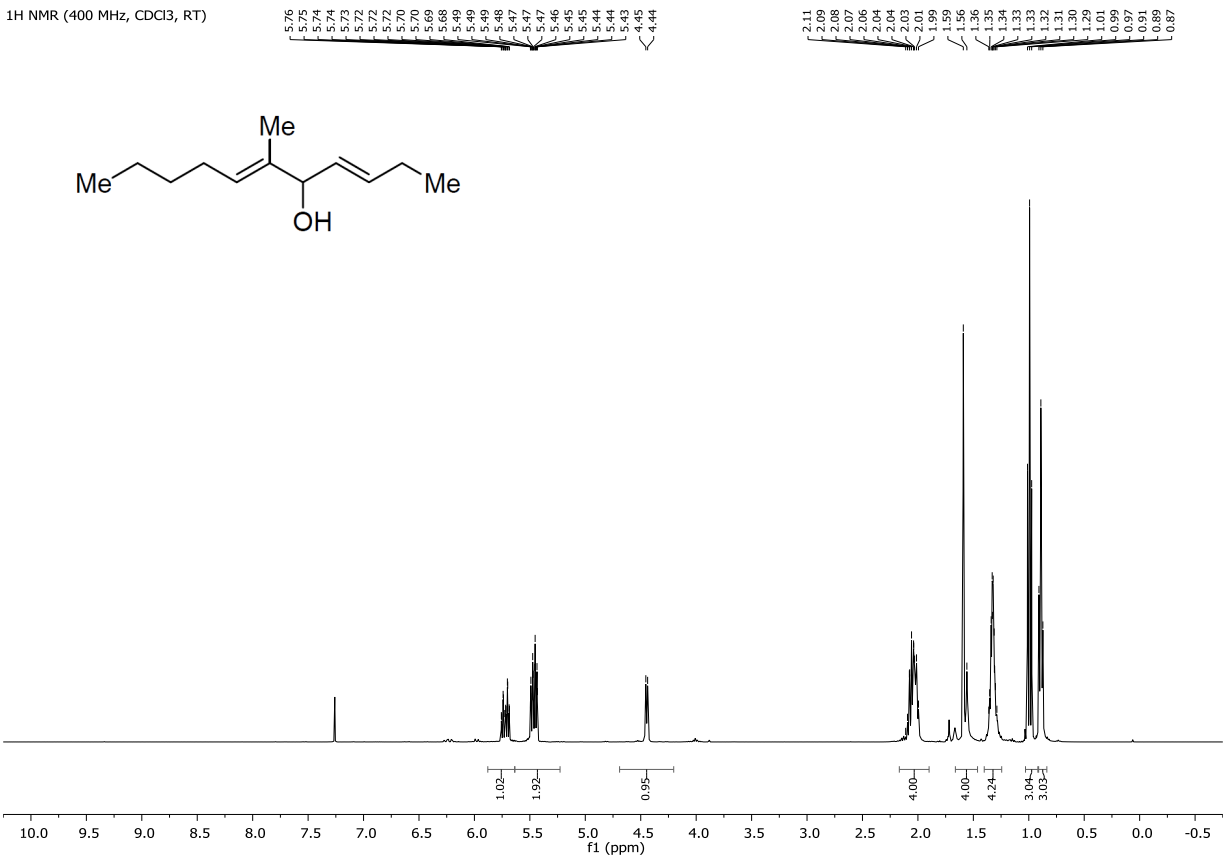




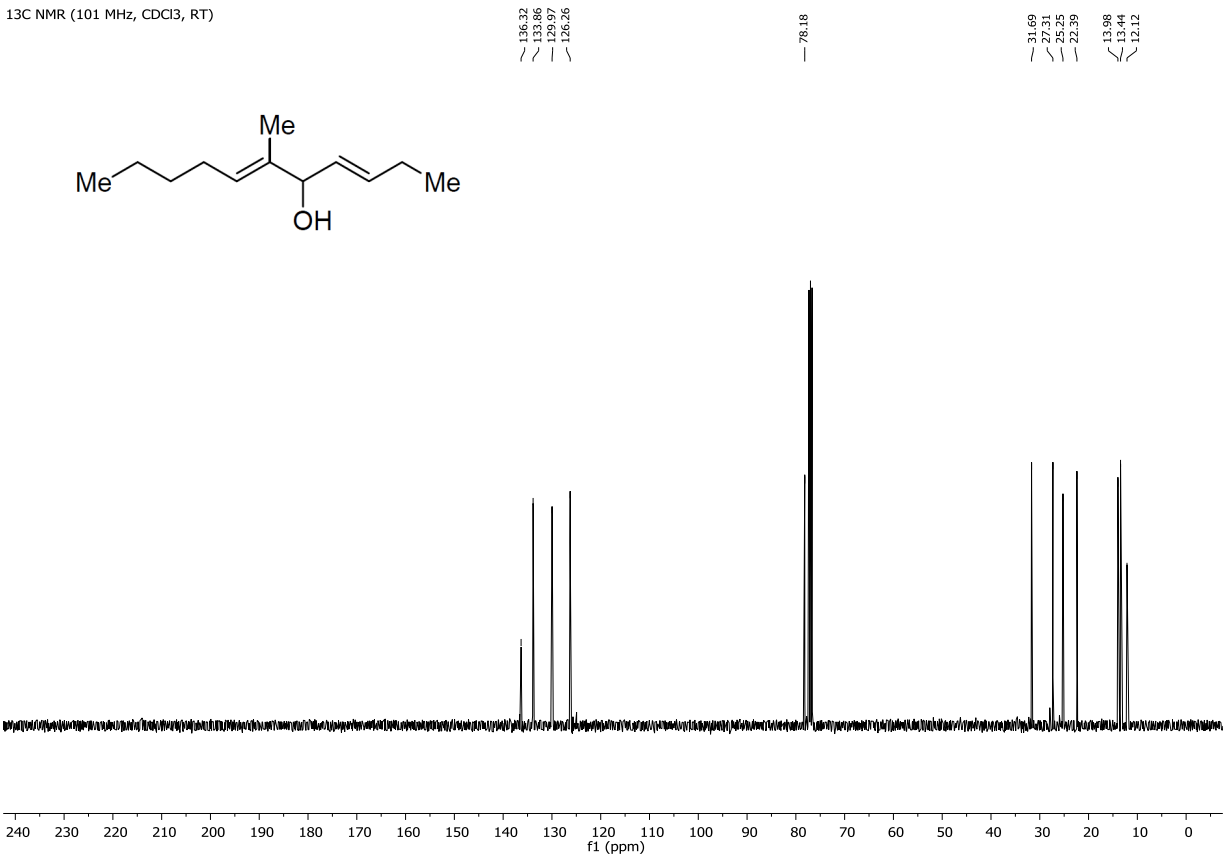
HUR-HA-084-11.0 **24.08.2016**

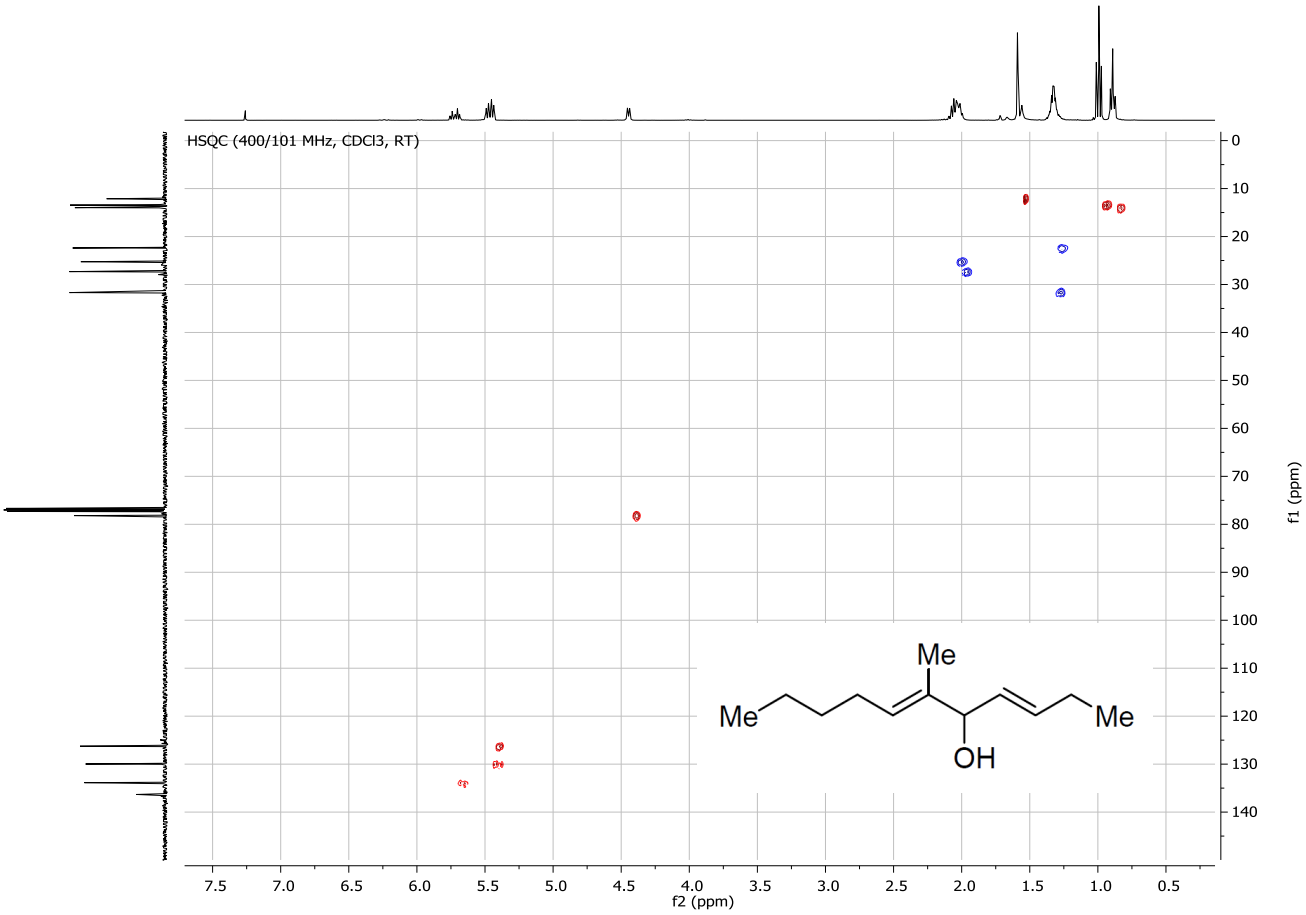


1H NMR (400 MHz, CDCl3, RT)

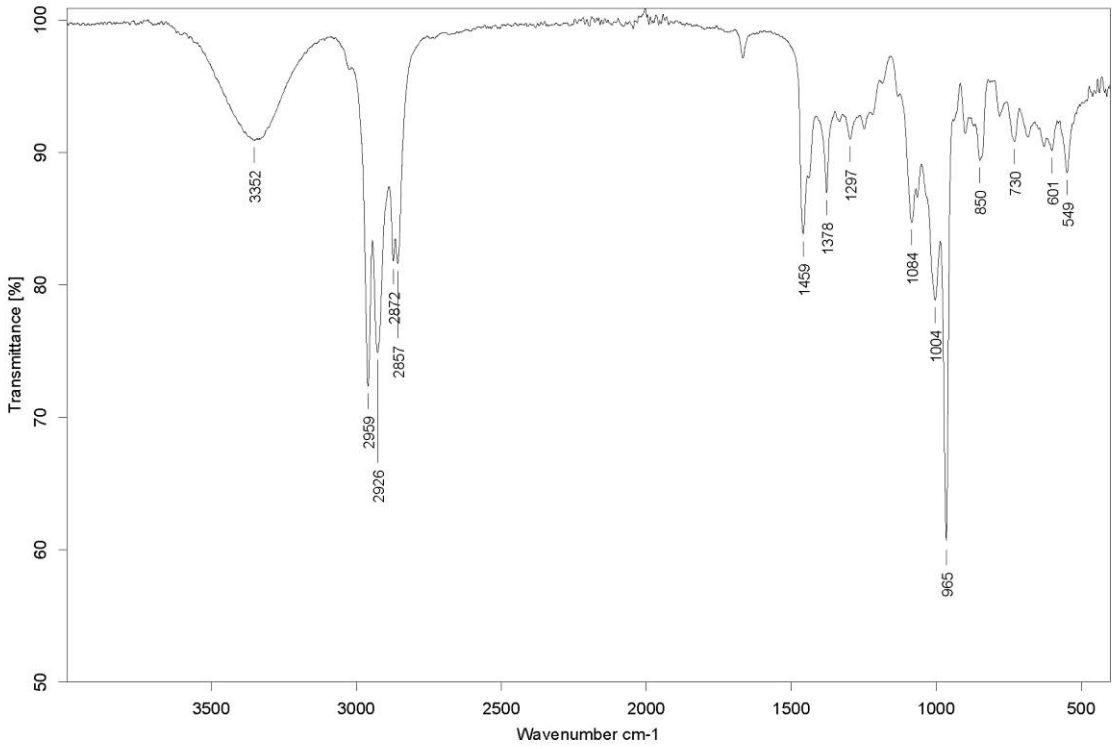


13C NMR (101 MHz, CDCl3, RT)

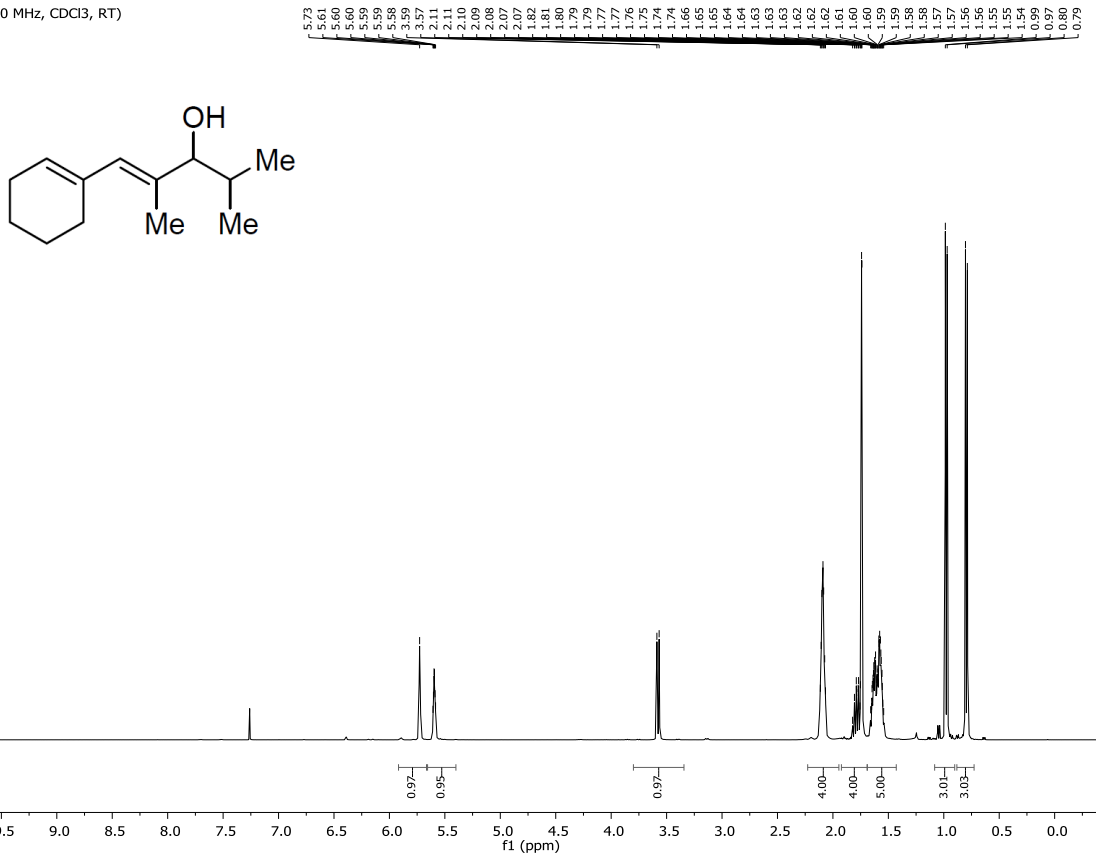




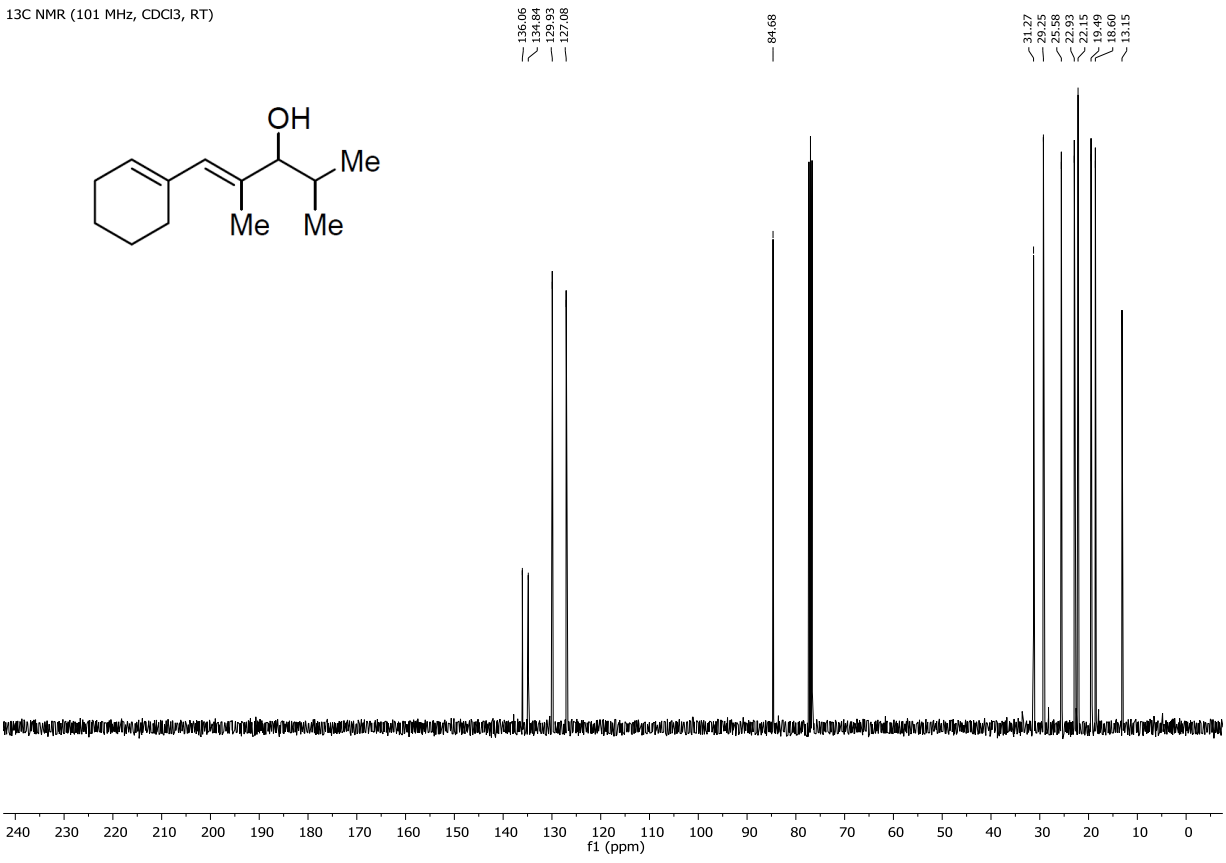
HUR-HA-090-11.0 **31.08.2016**

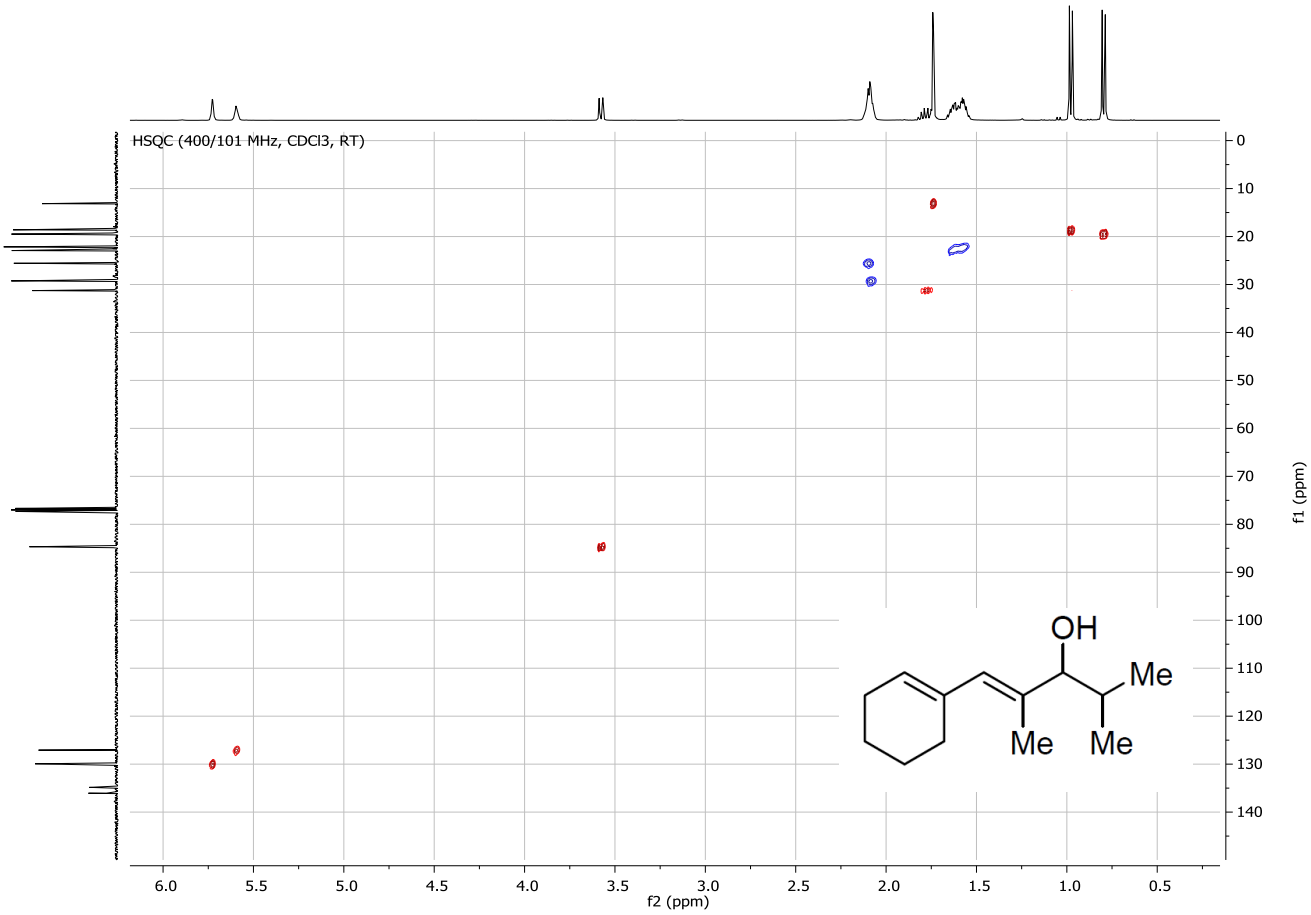


1H NMR (400 MHz, CDCl3, RT)

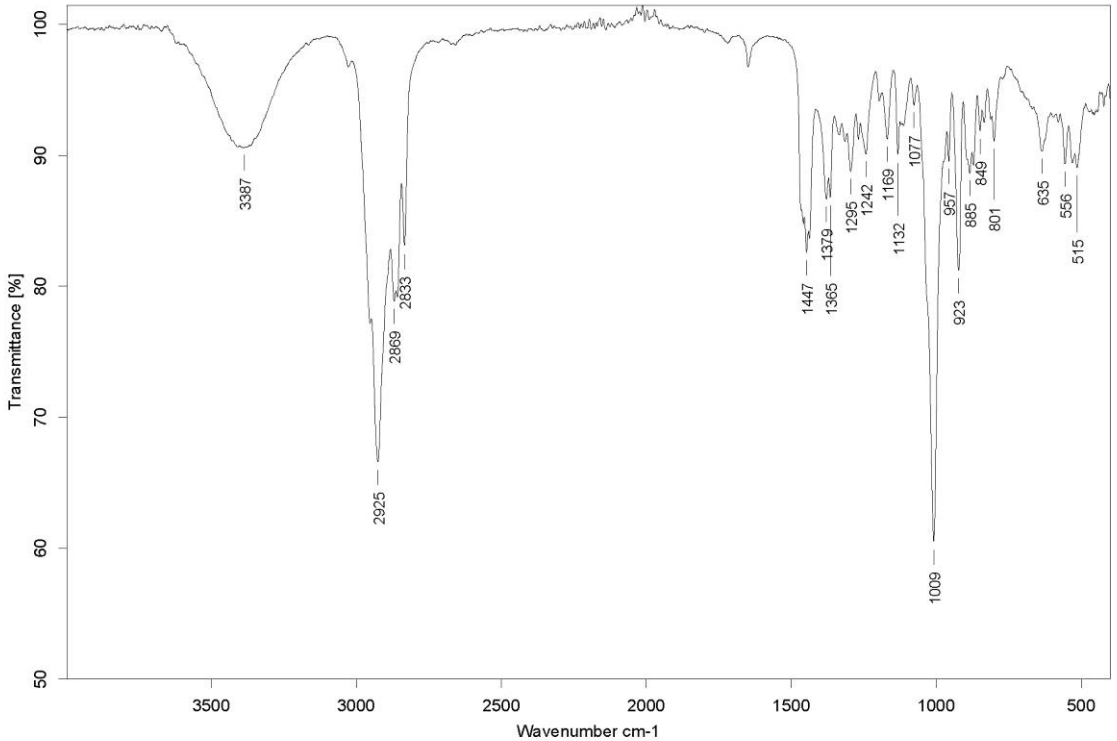


13C NMR (101 MHz, CDCl3, RT)

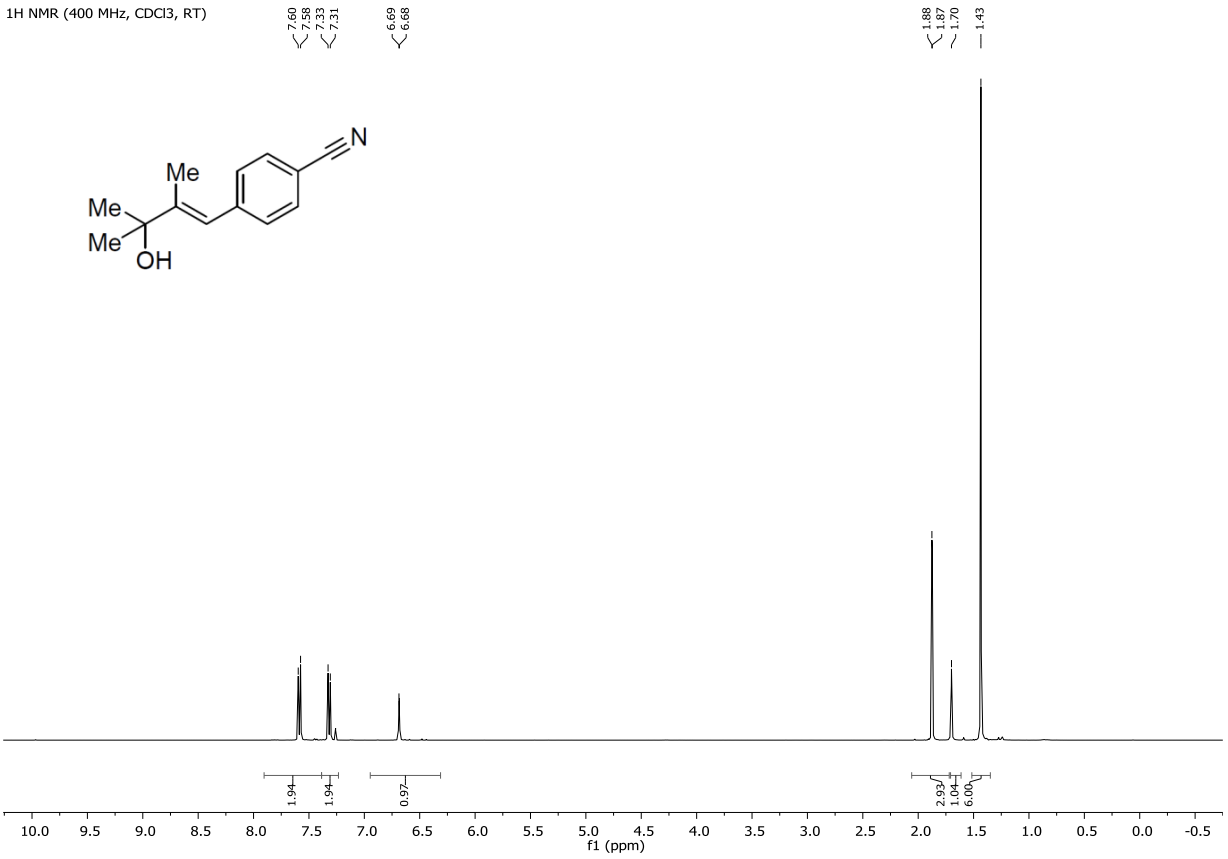




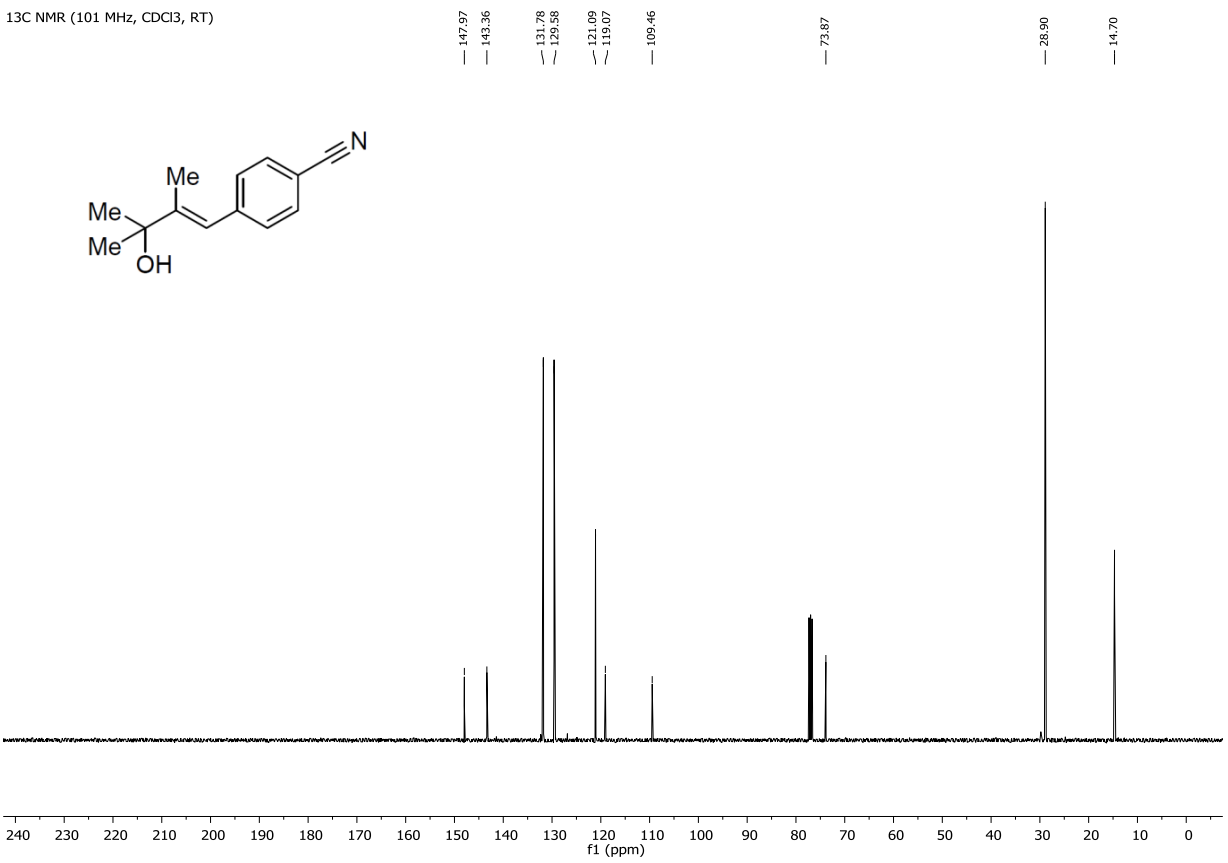
HUR-HA-088-12.0 **29.08.2016**

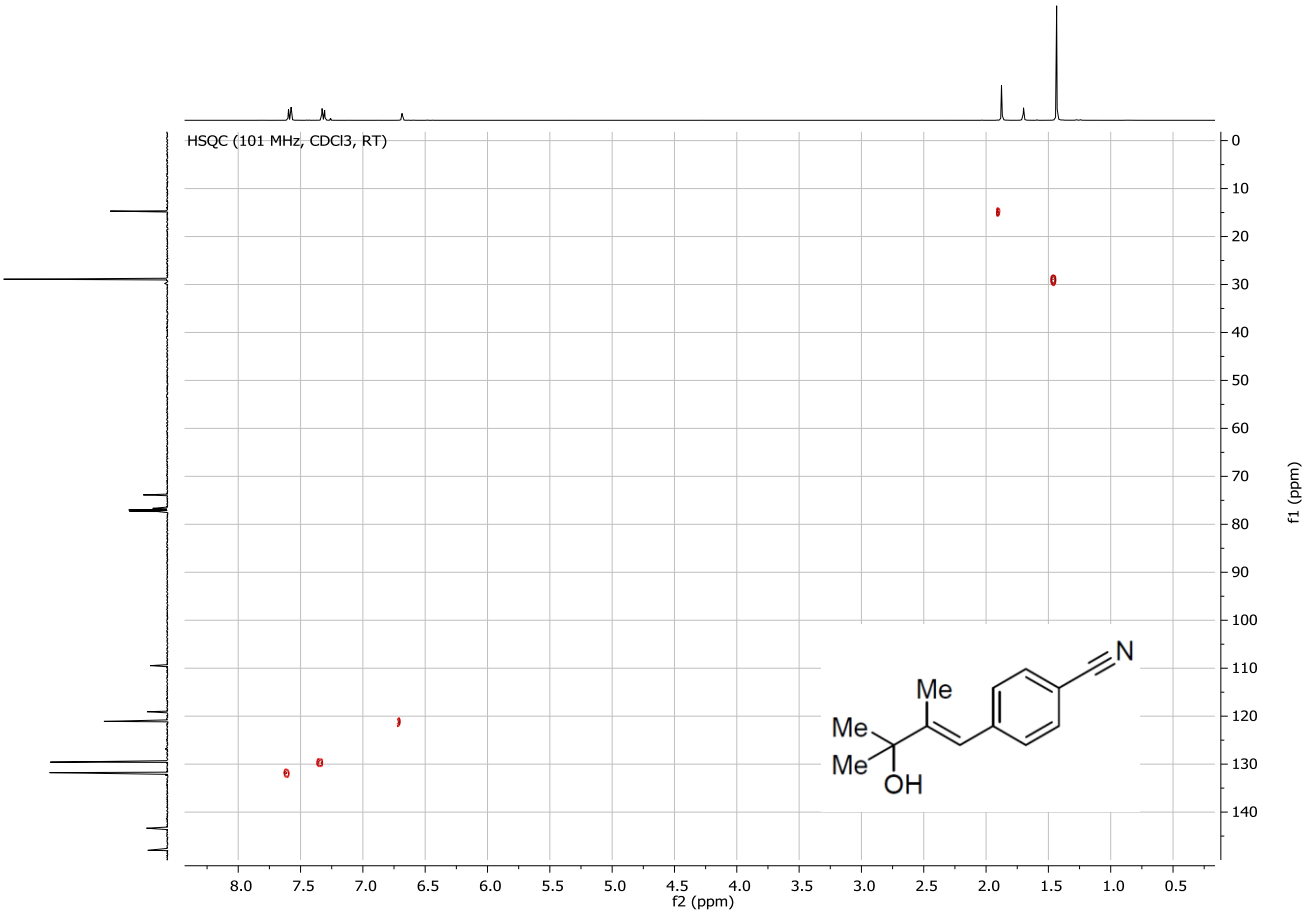


1H NMR (400 MHz, CDCl3, RT)

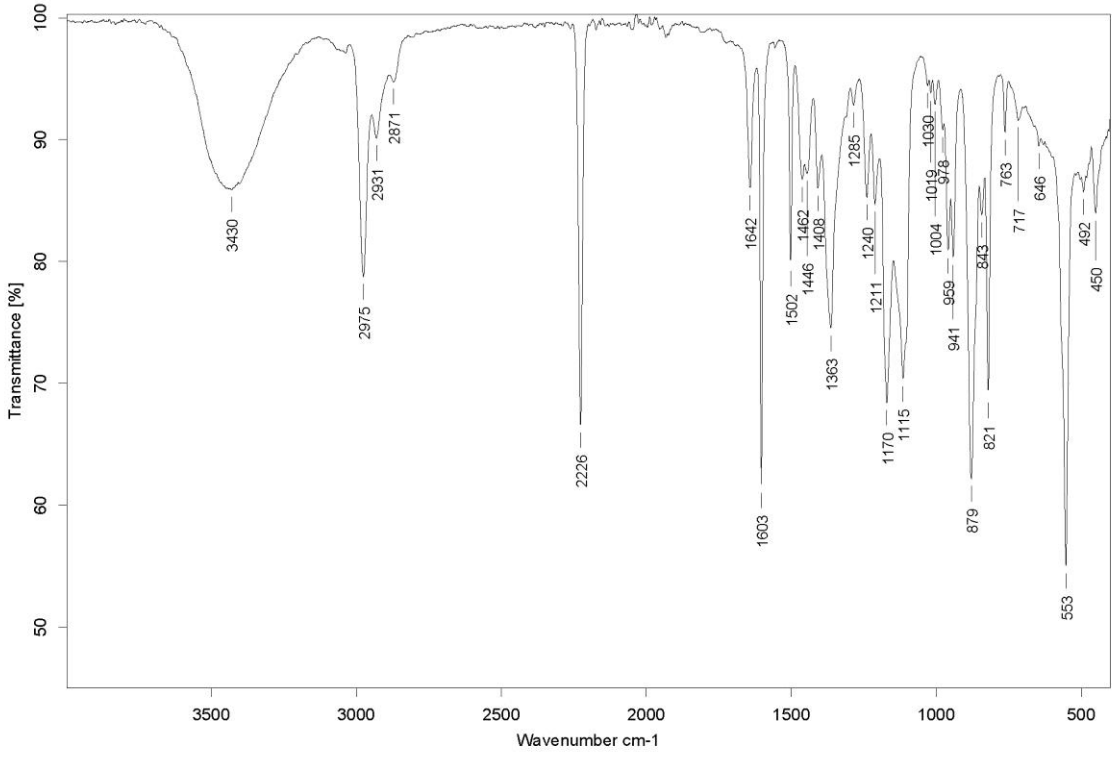


13C NMR (101 MHz, CDCl3, RT)

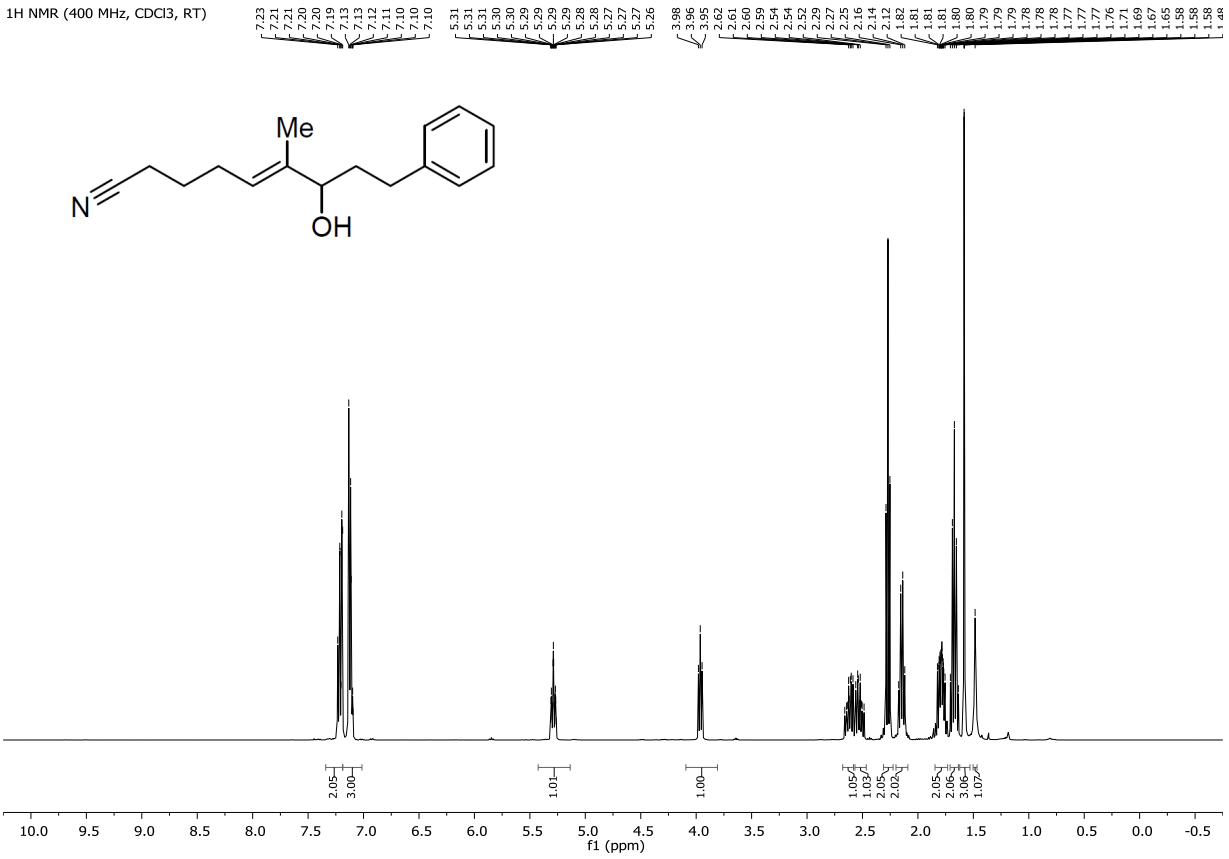




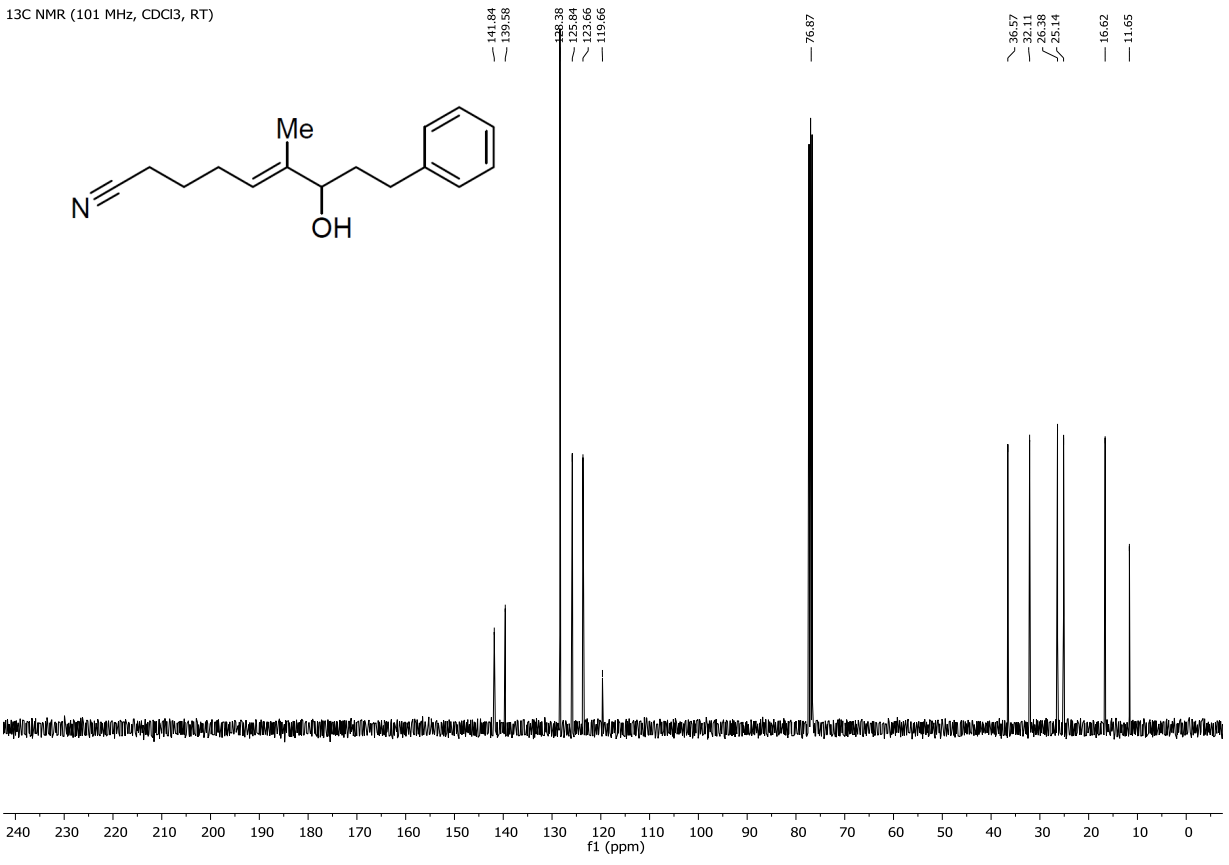
HUR-HA-081-12.0 **22.08.2016**

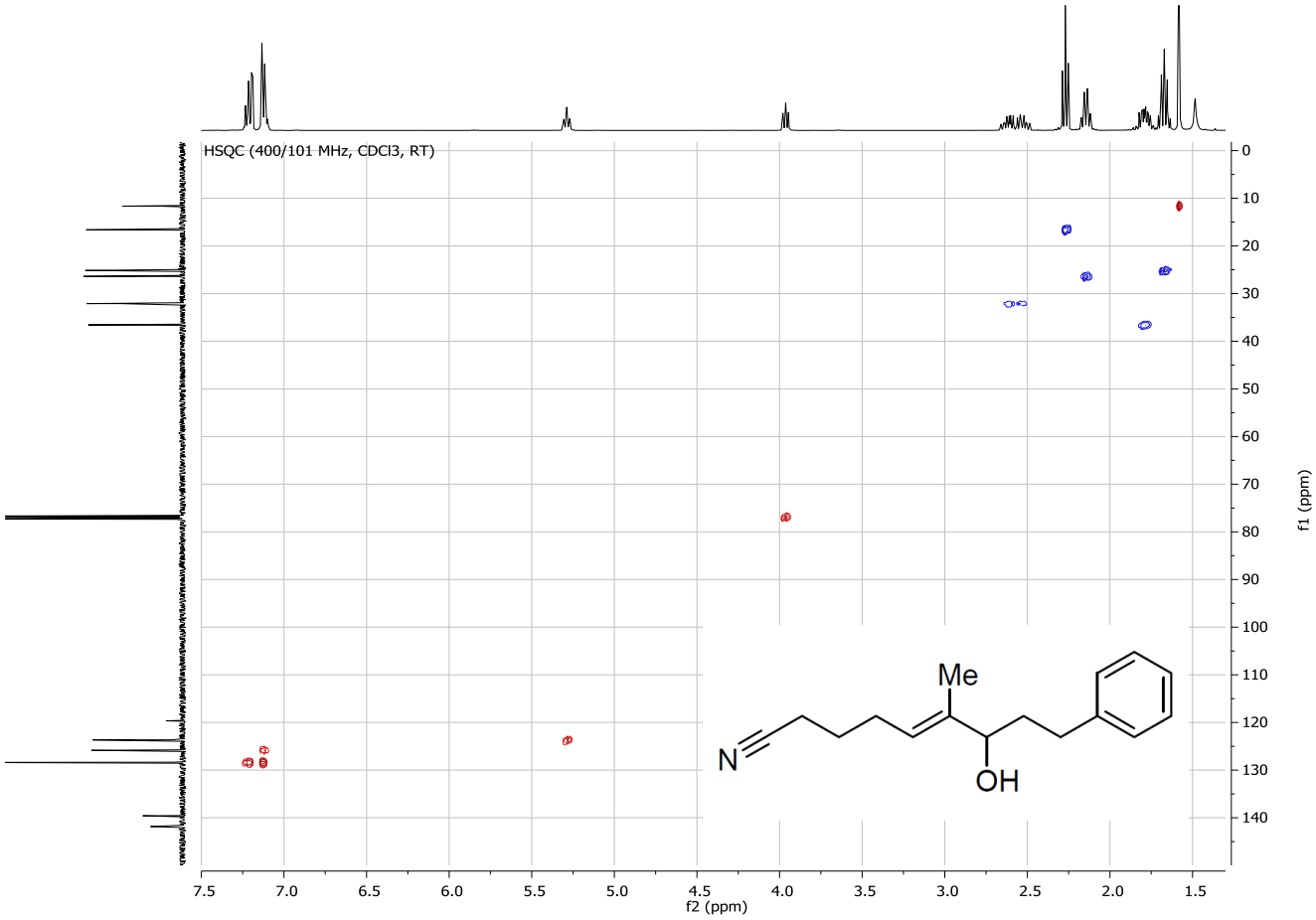


1H NMR (400 MHz, CDCl3, RT)

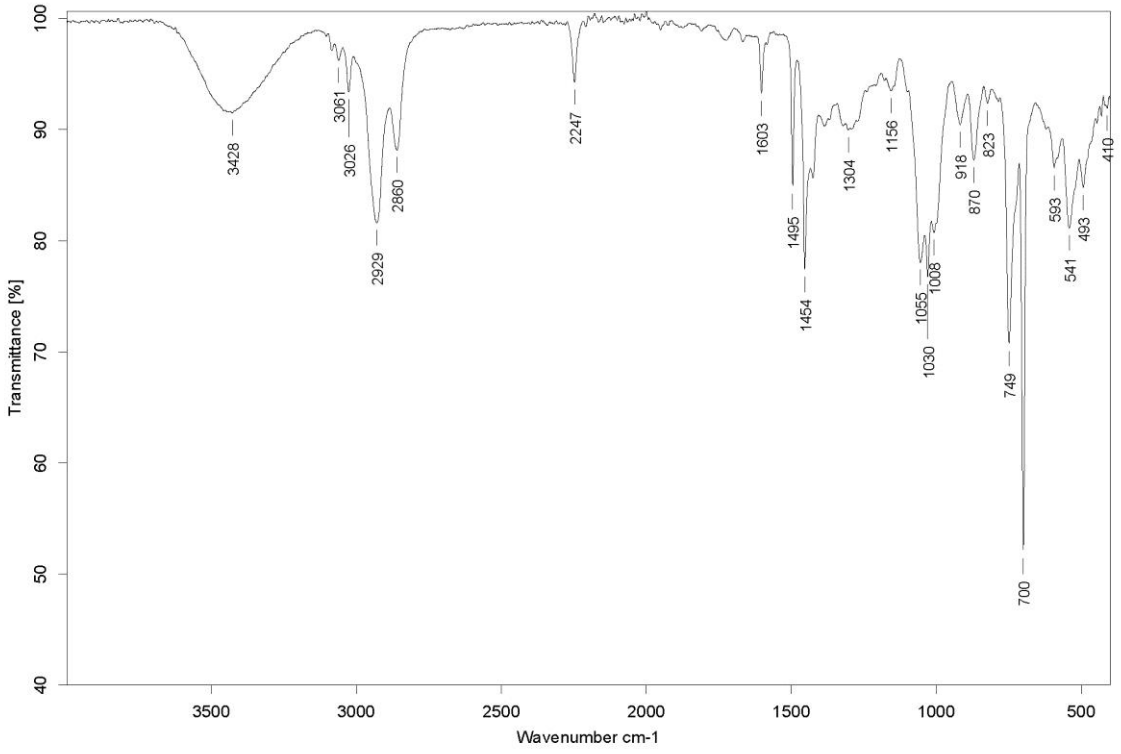


13C NMR (101 MHz, CDCl3, RT)

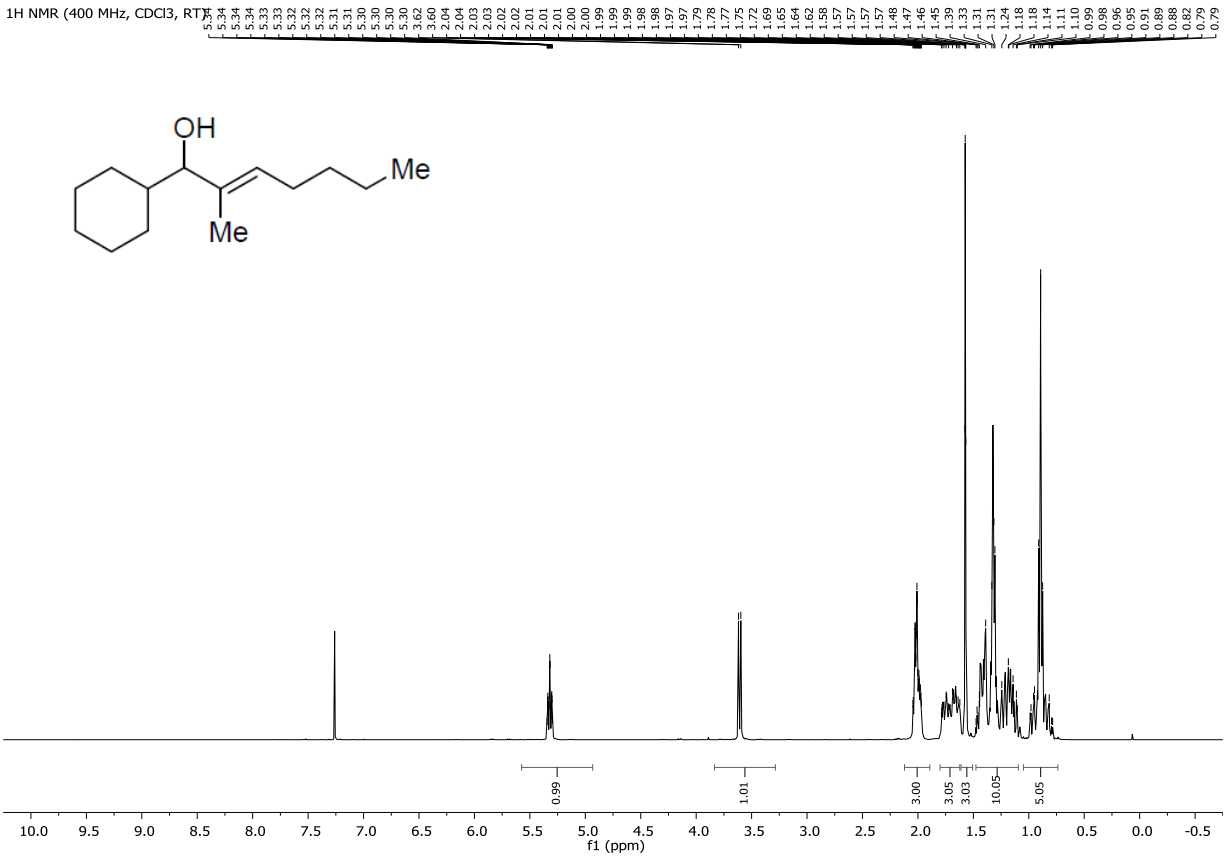




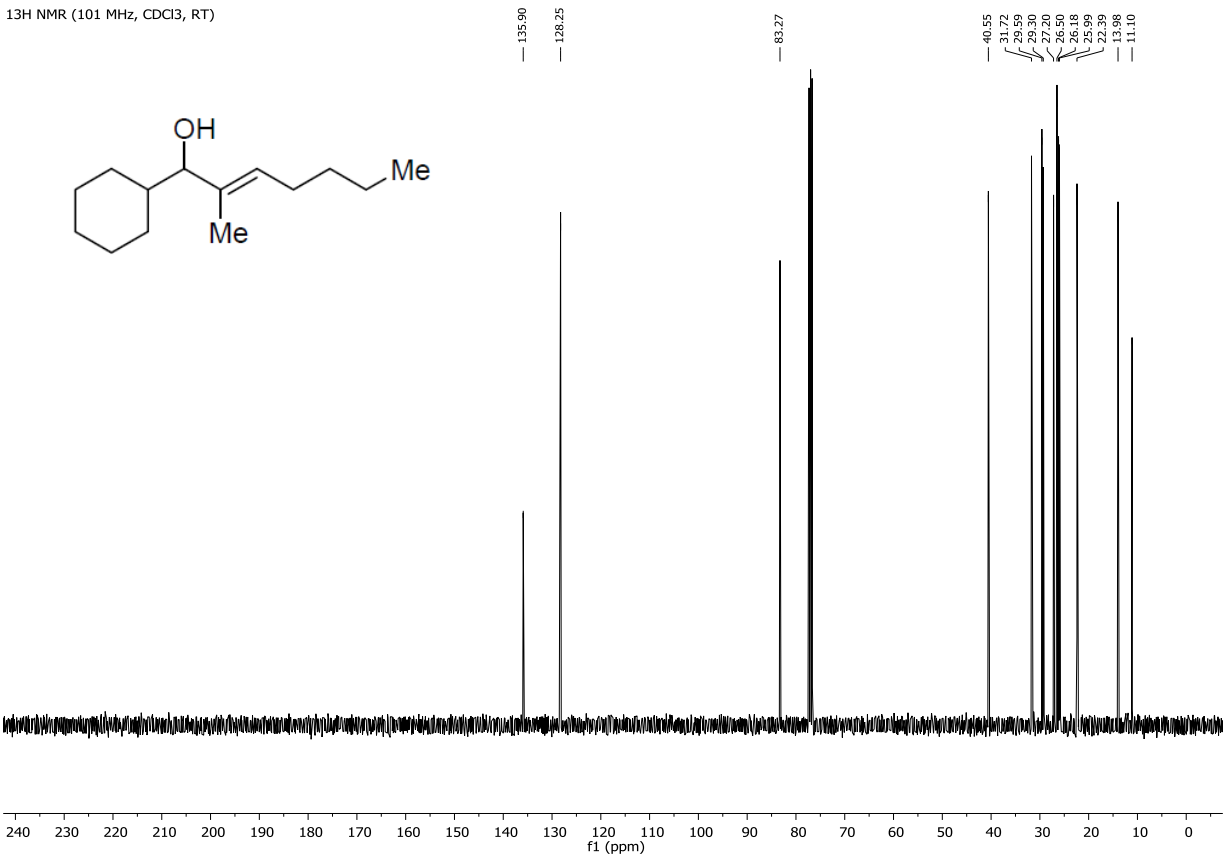
HUR-HA-091-12 FTIR.0 **02.09.2016**

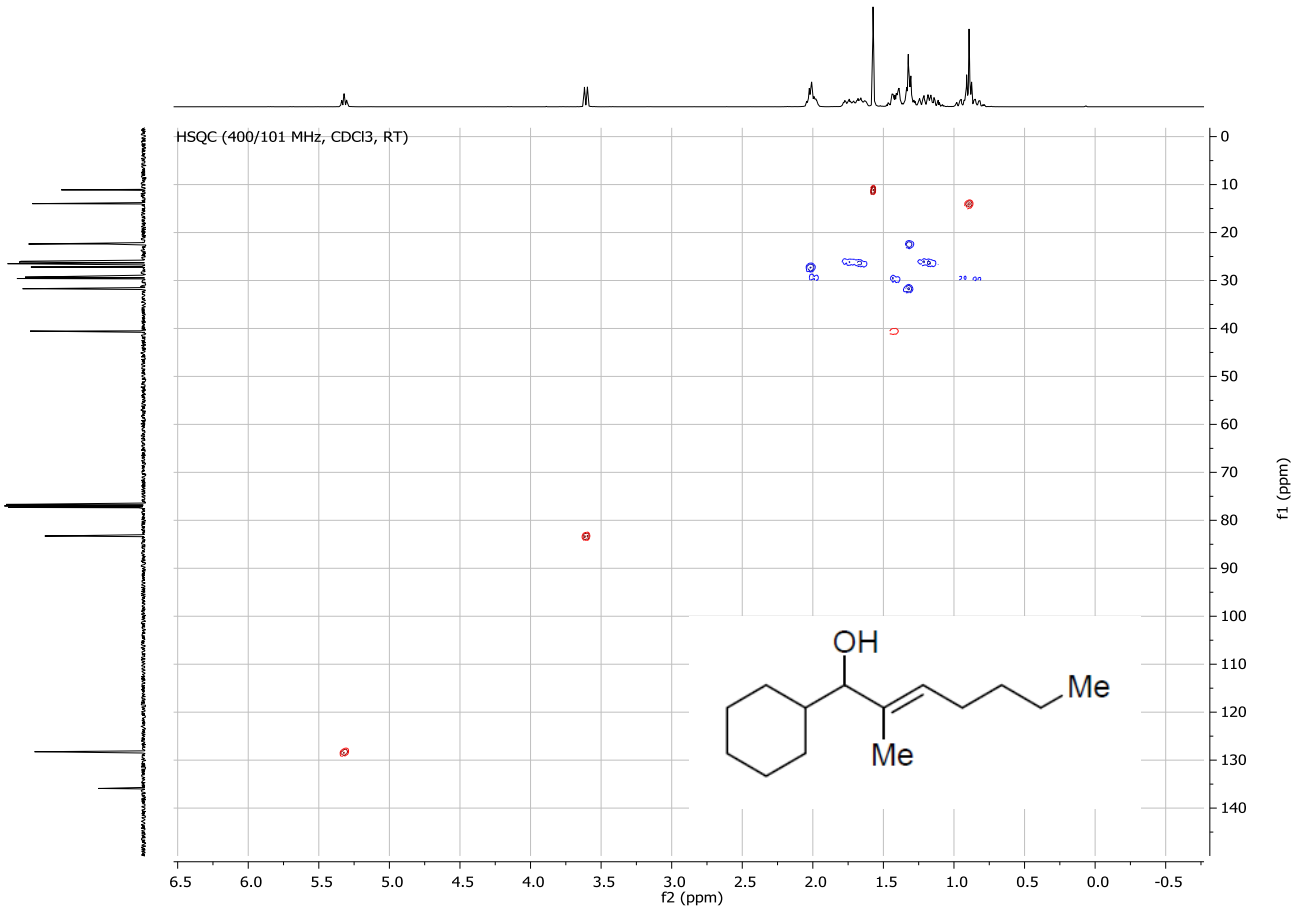


1H NMR (400 MHz, CDCl3, RT)

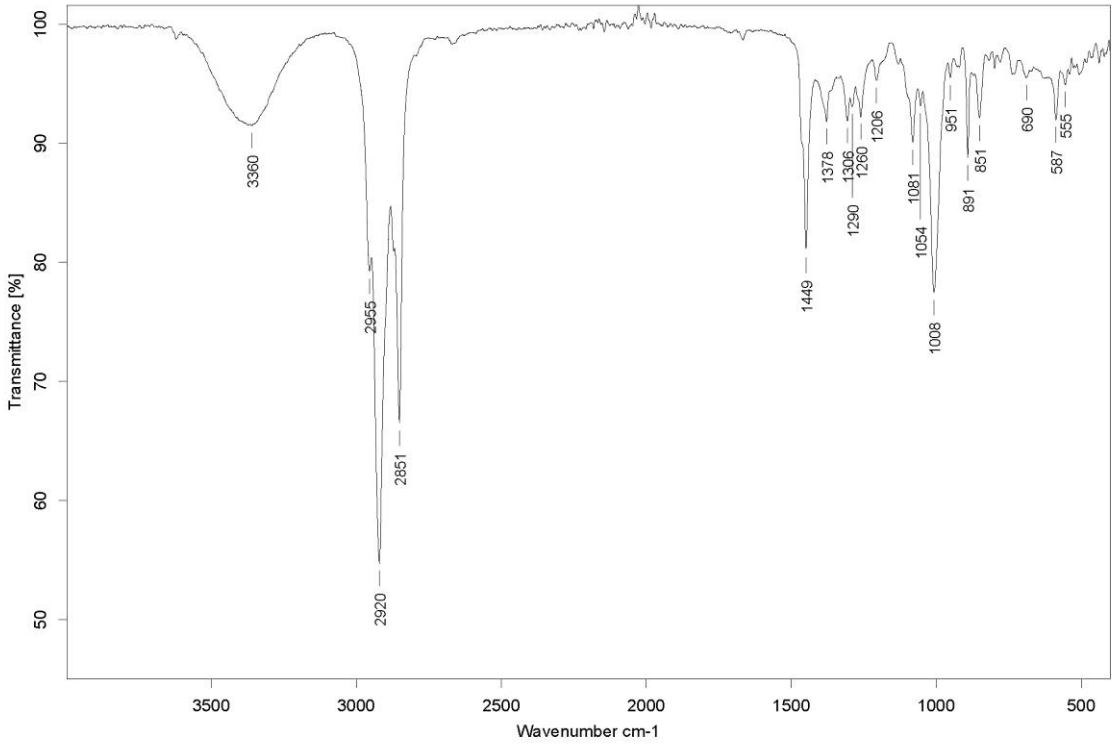


13H NMR (101 MHz, CDCl3, RT)

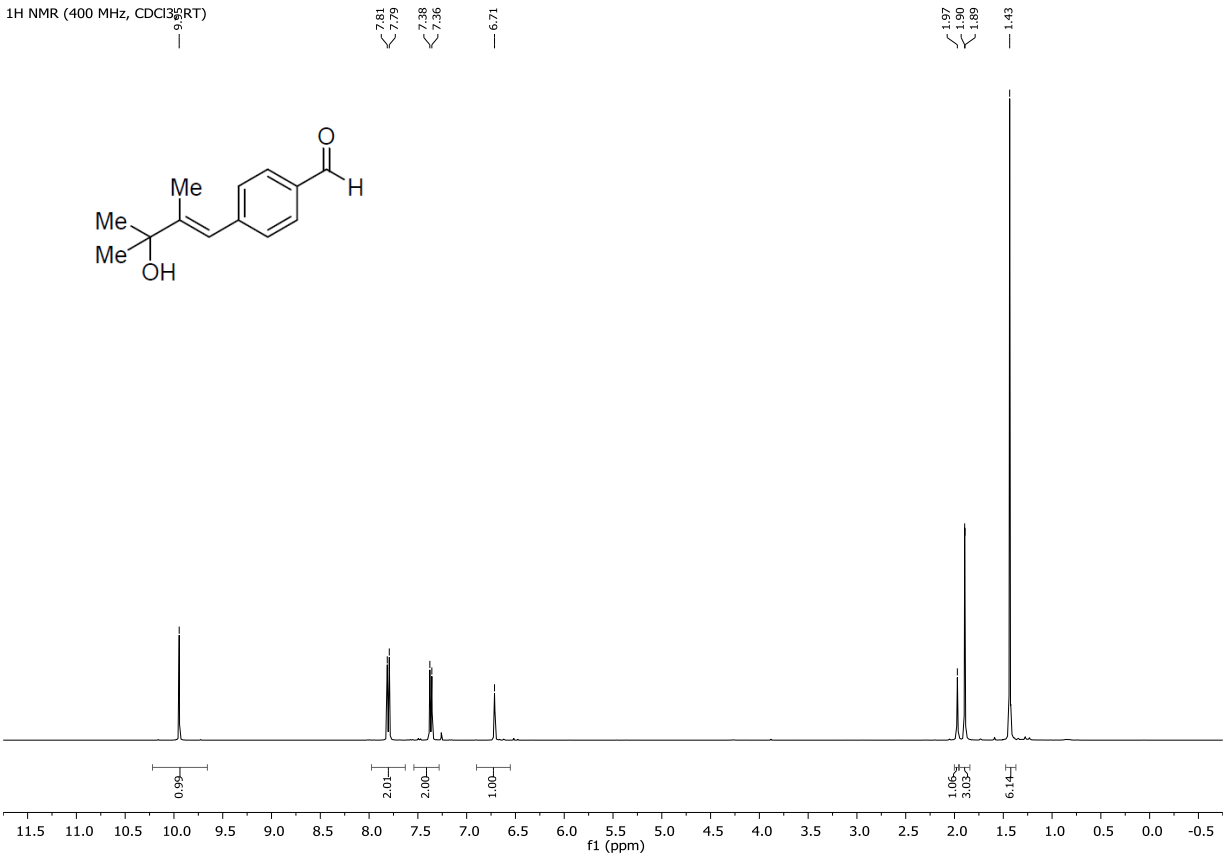




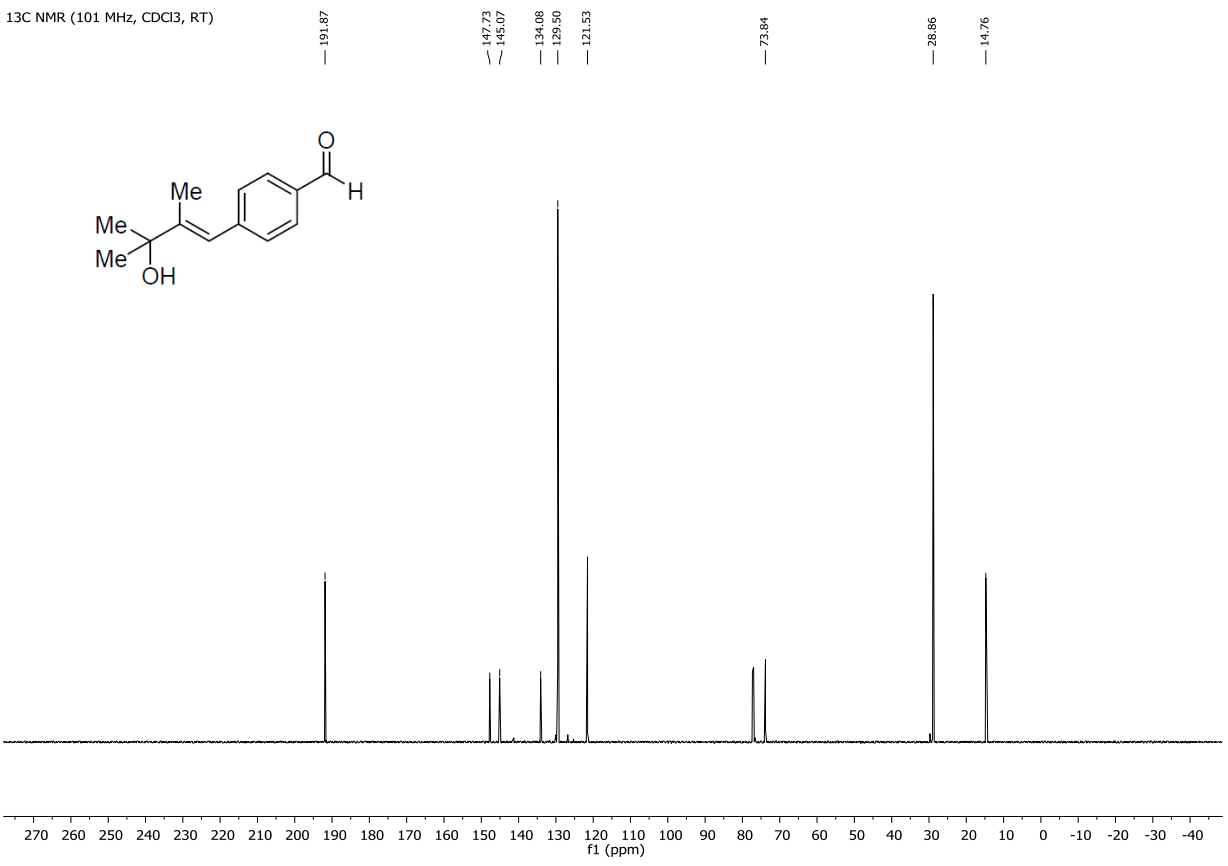
HUR-HA-119-12.0 **08.11.2016**

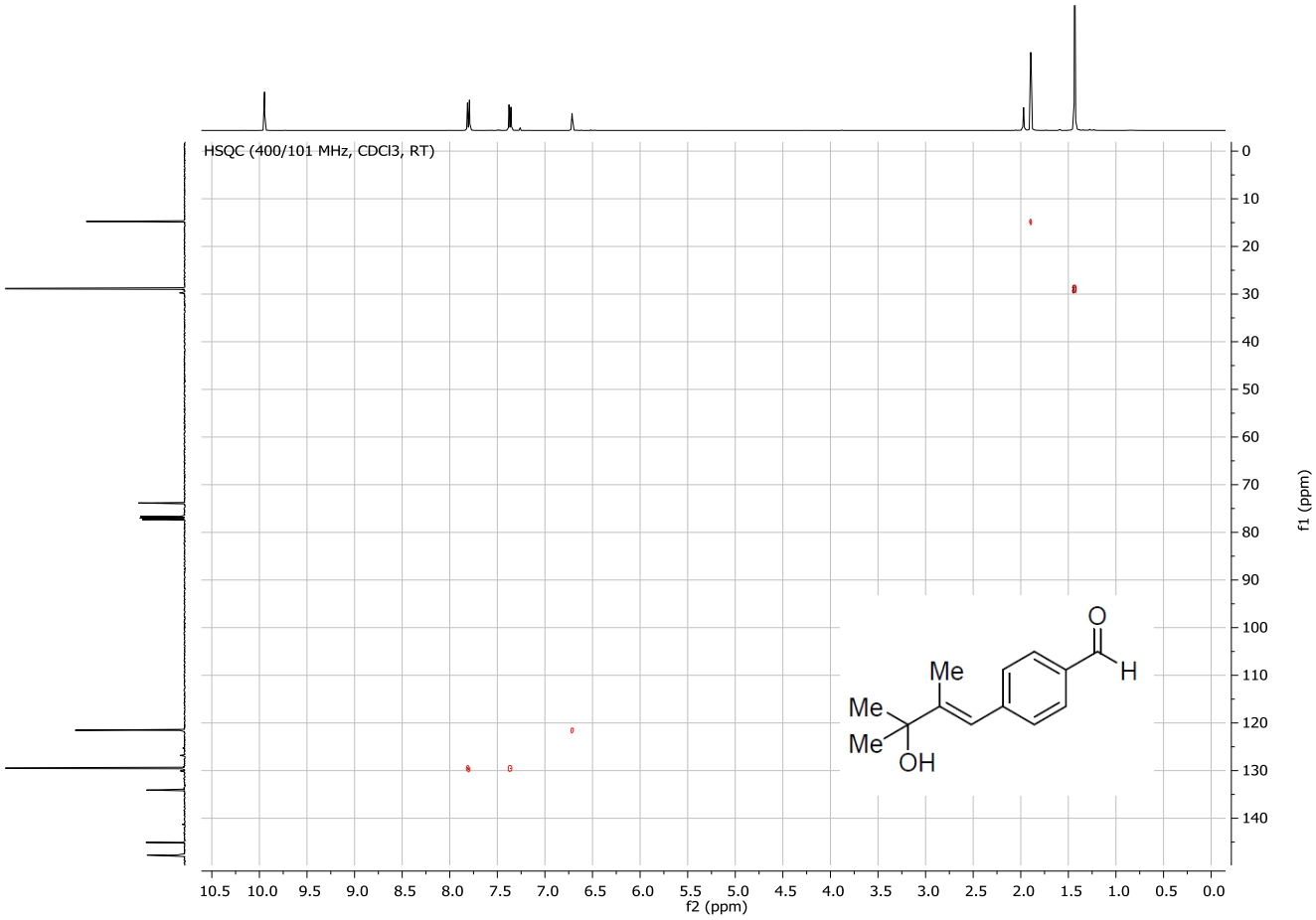


1H NMR (400 MHz, CDCl3, RT)

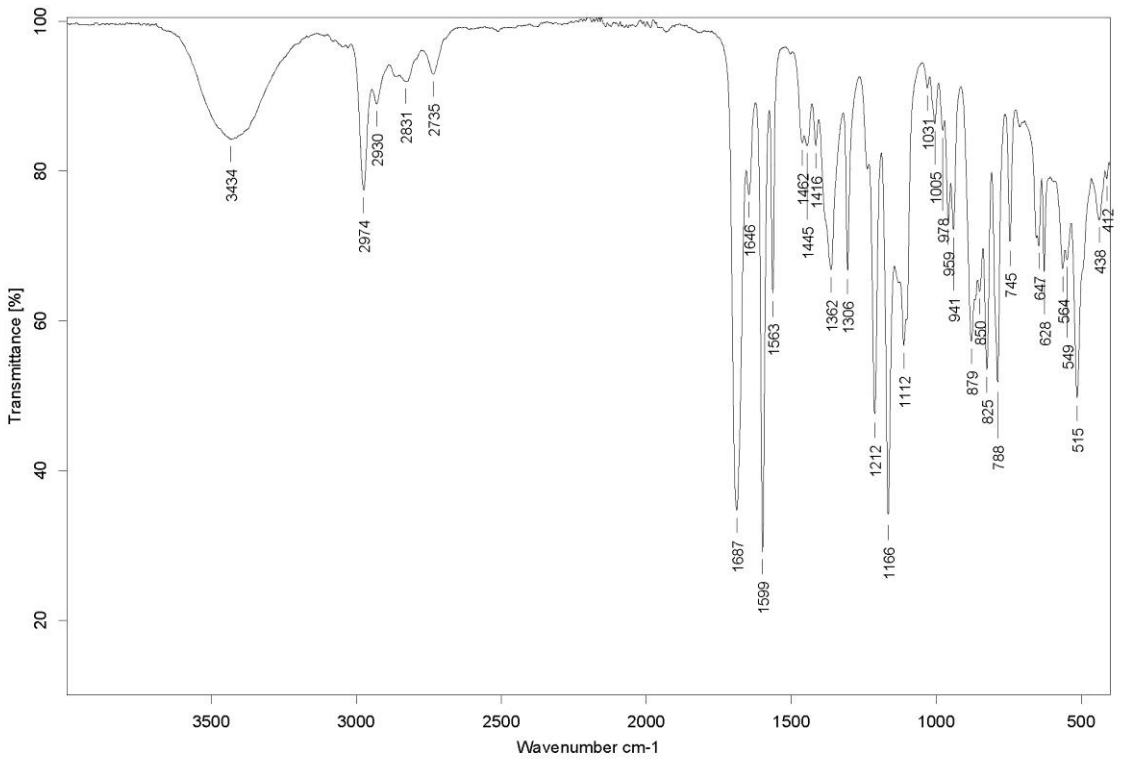


13C NMR (101 MHz, CDCl3, RT)

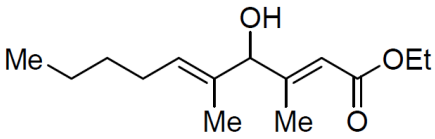


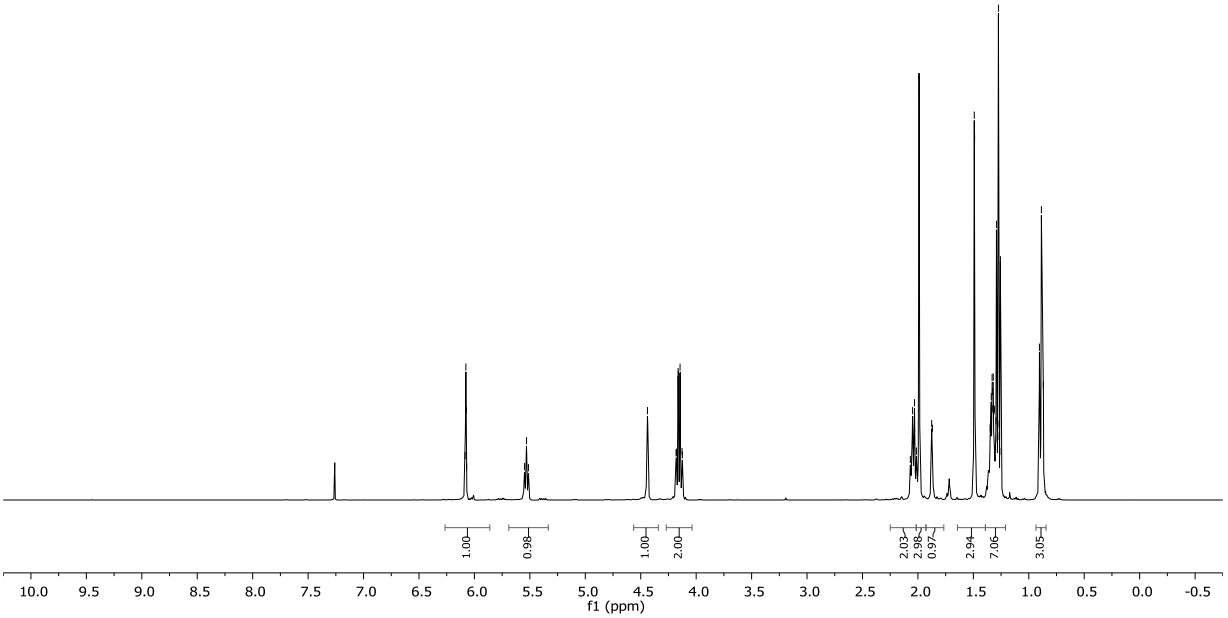


HUR-HA-082-11.0 **23.08.2016**

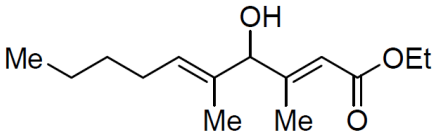


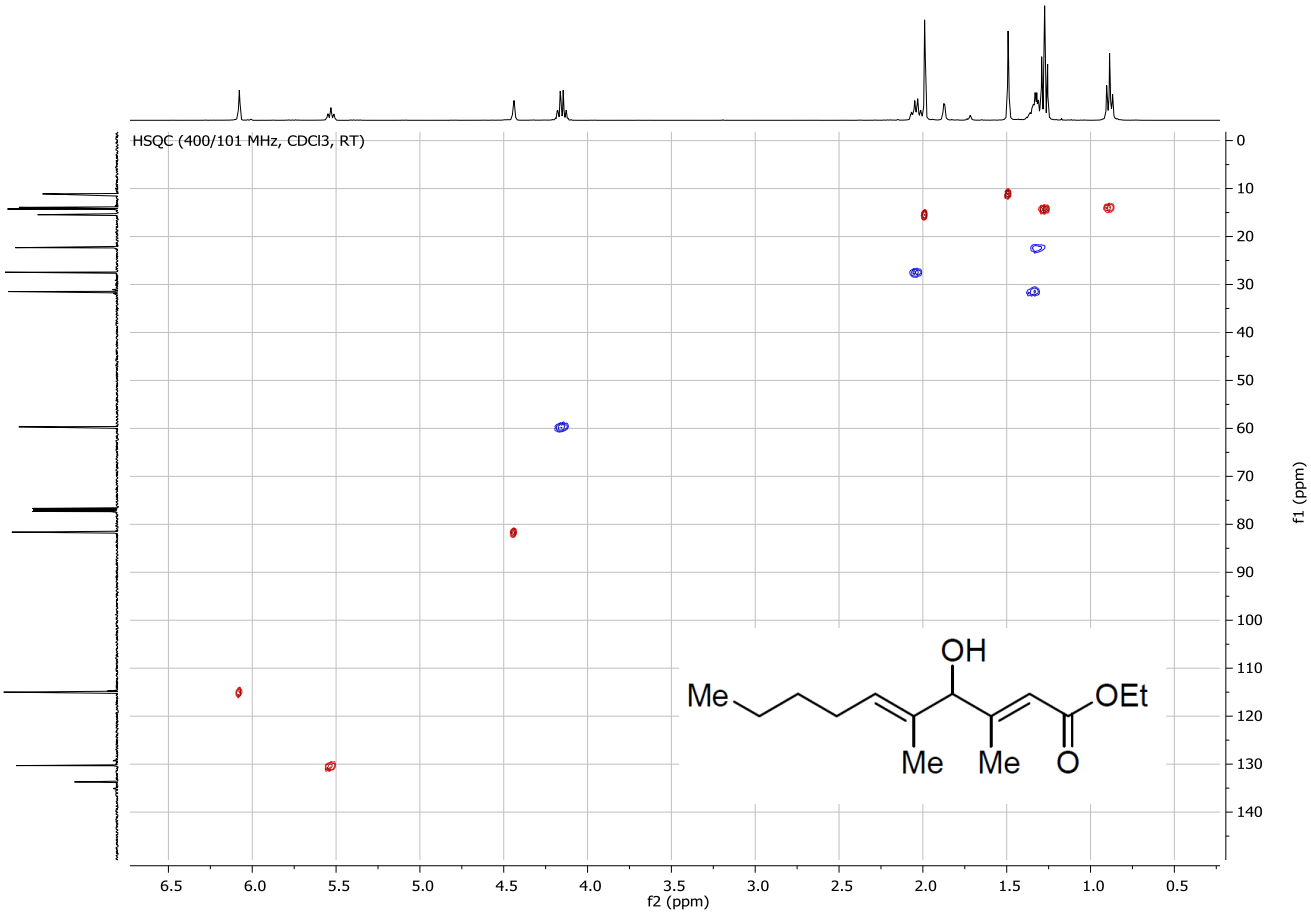
1H NMR (400 MHz, CDCl3, RT)



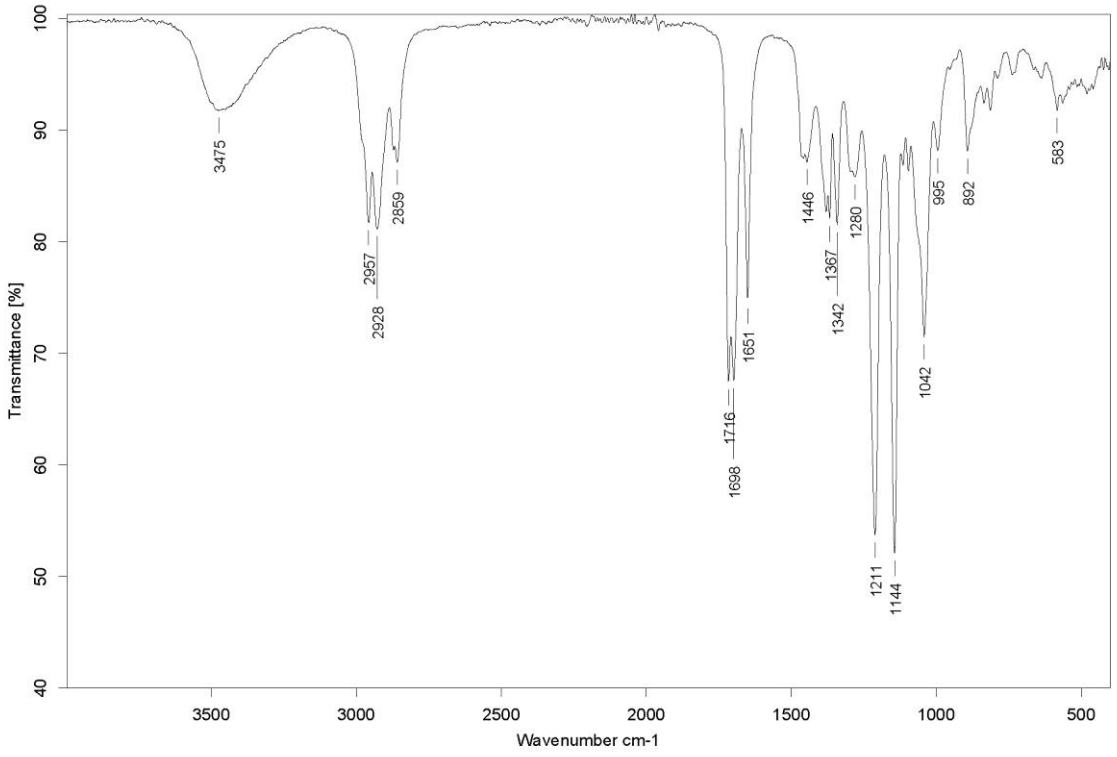


13C NMR (101 MHz, CDCl3, RT)

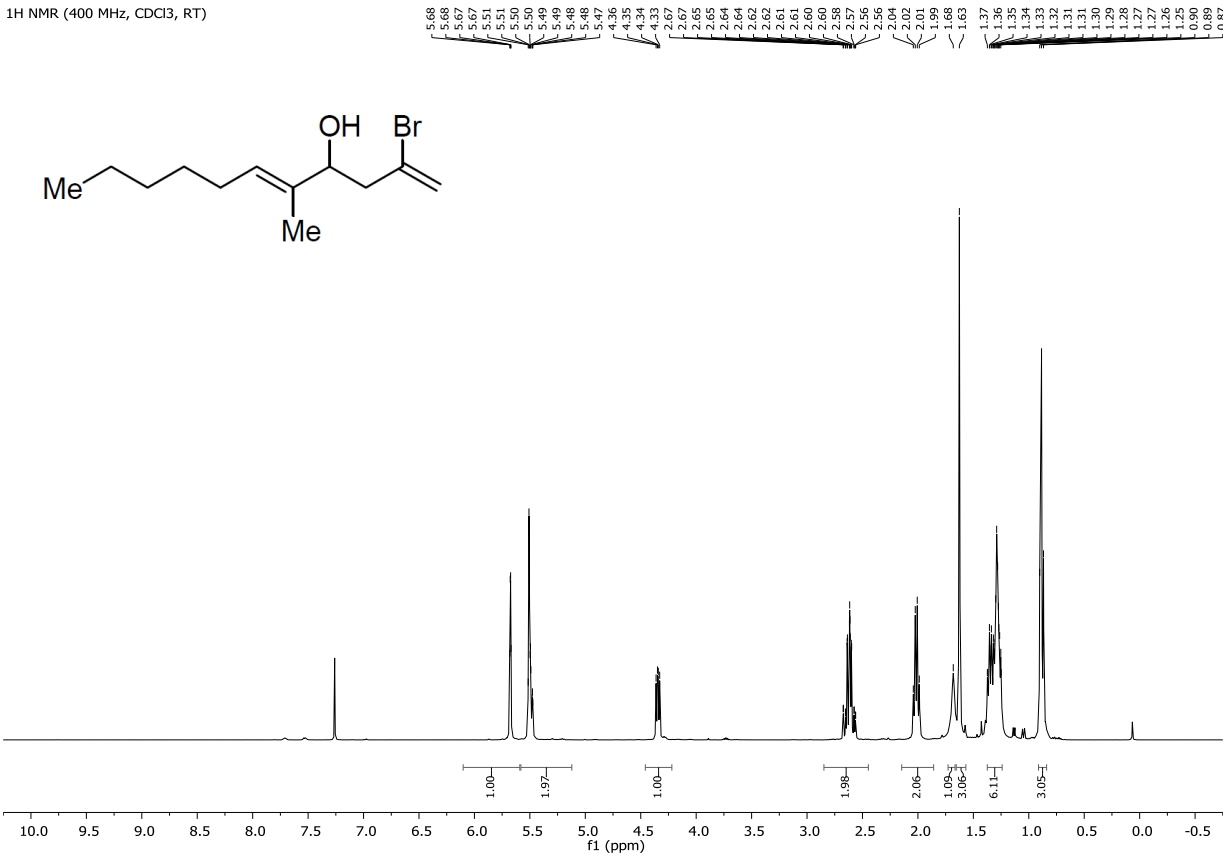




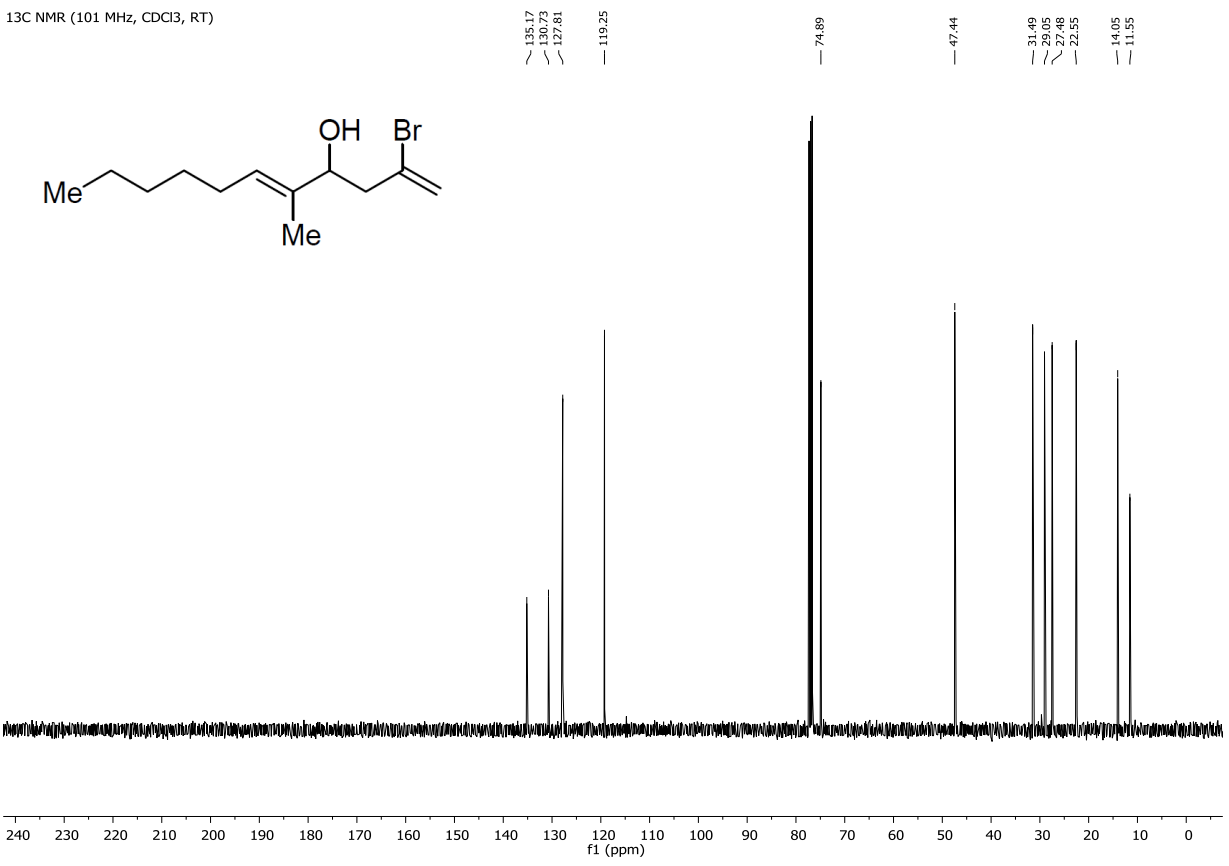
HUR-HA-085-11.0 **24.08.2016**

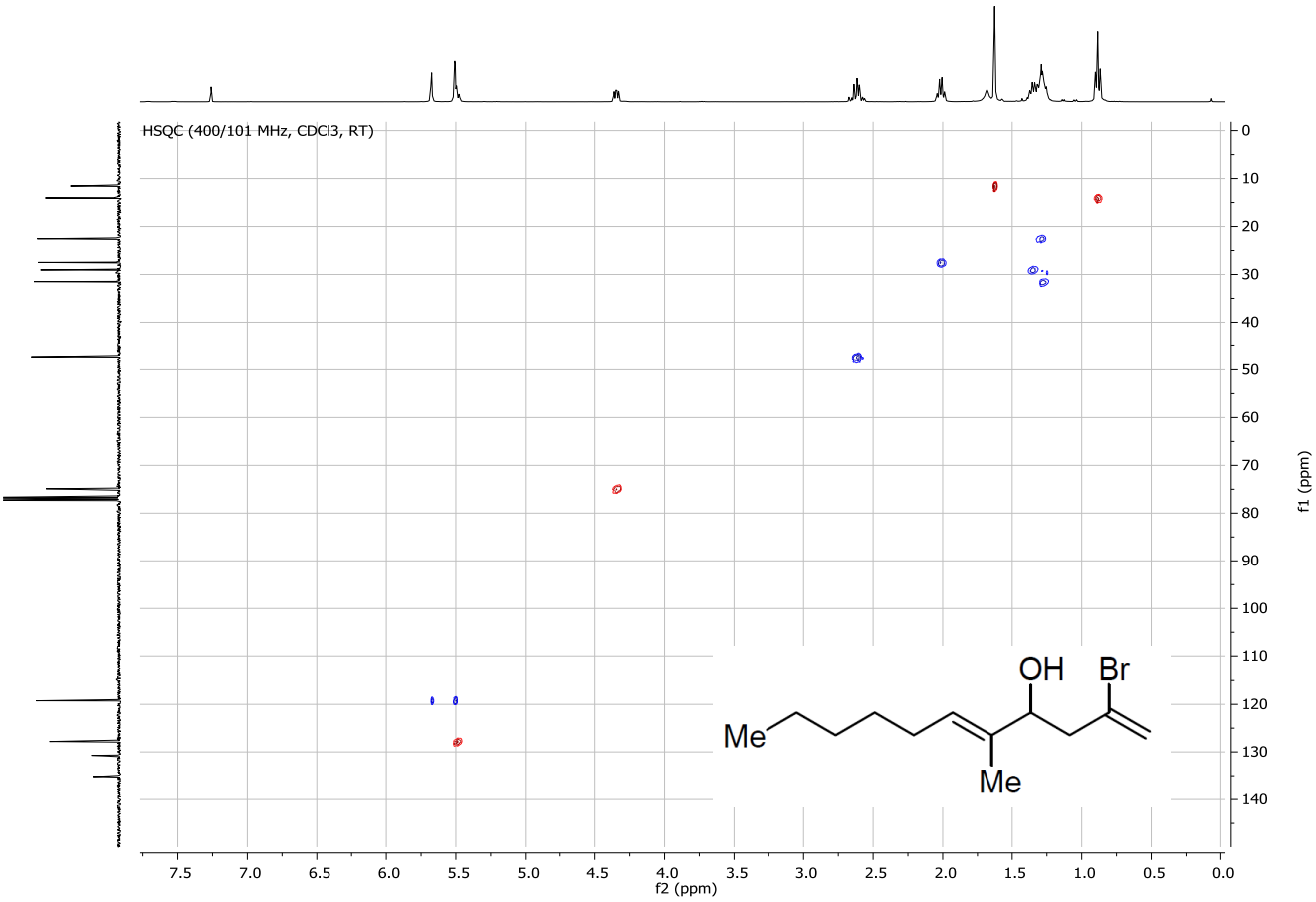


1H NMR (400 MHz, CDCl3, RT)

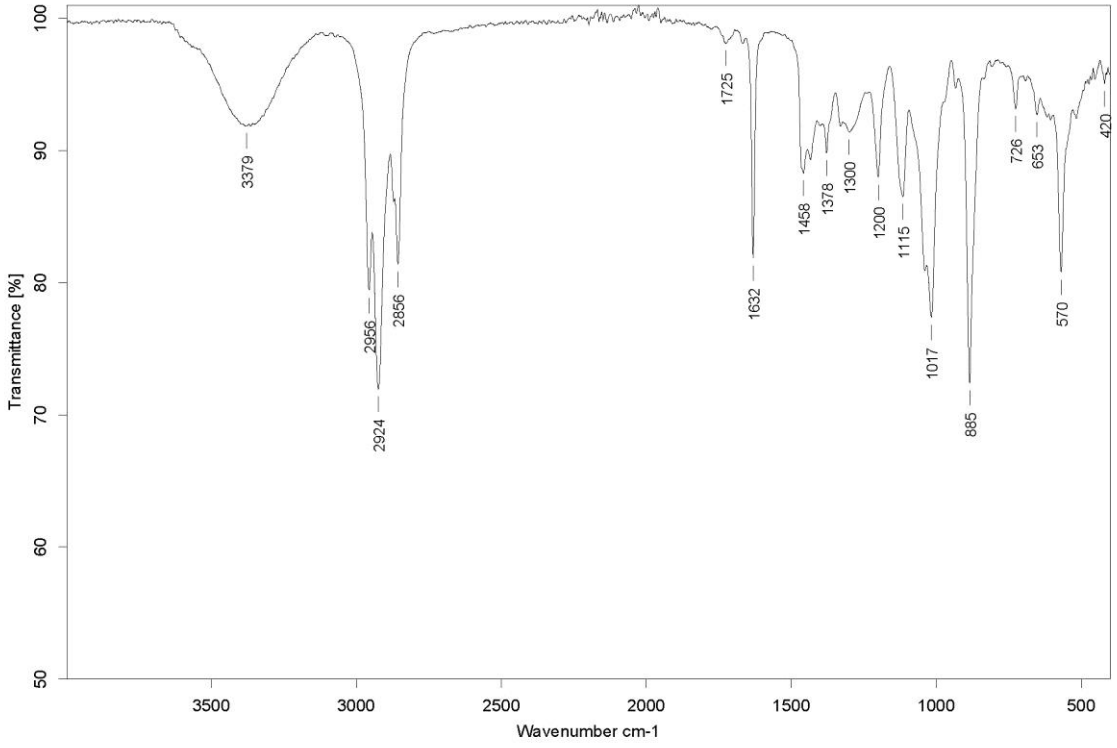


13C NMR (101 MHz, CDCl3, RT)

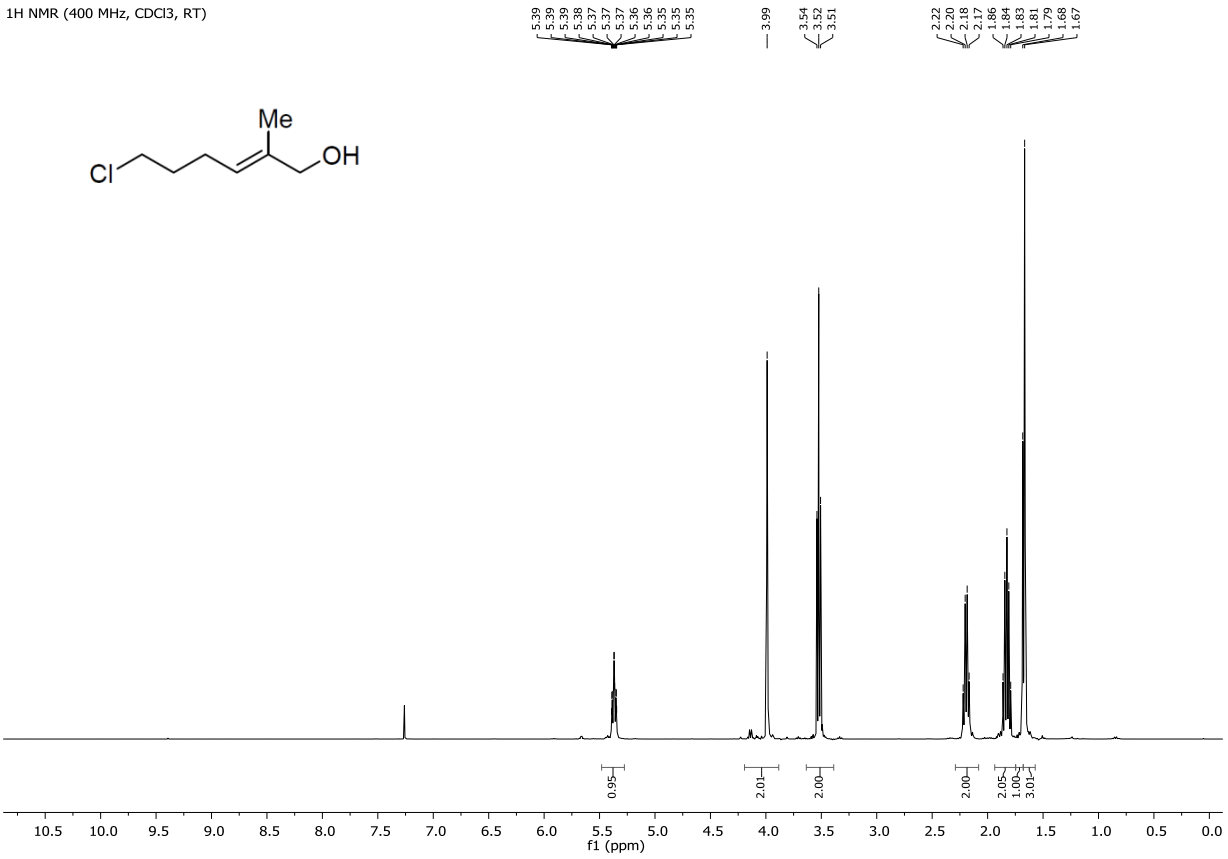




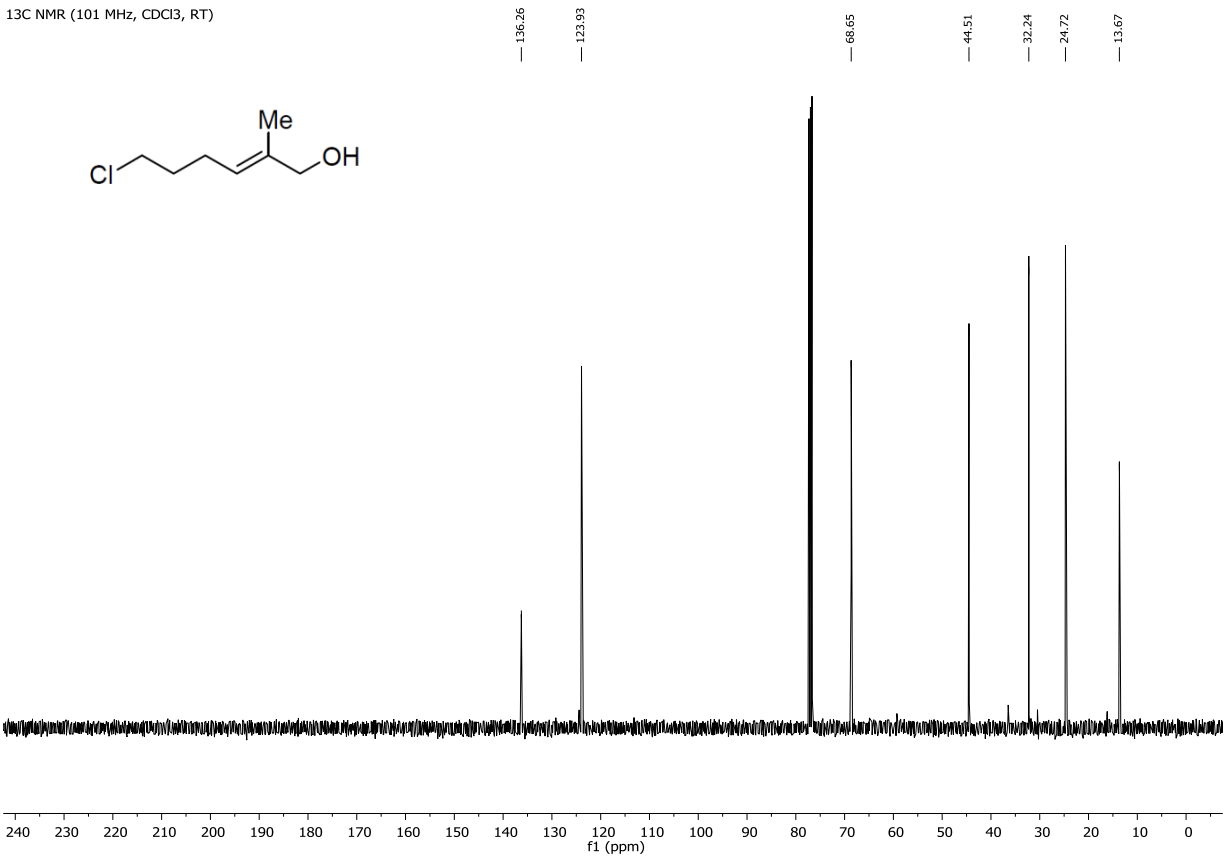
HUR-HA-096-11.0 **22.09.2016**

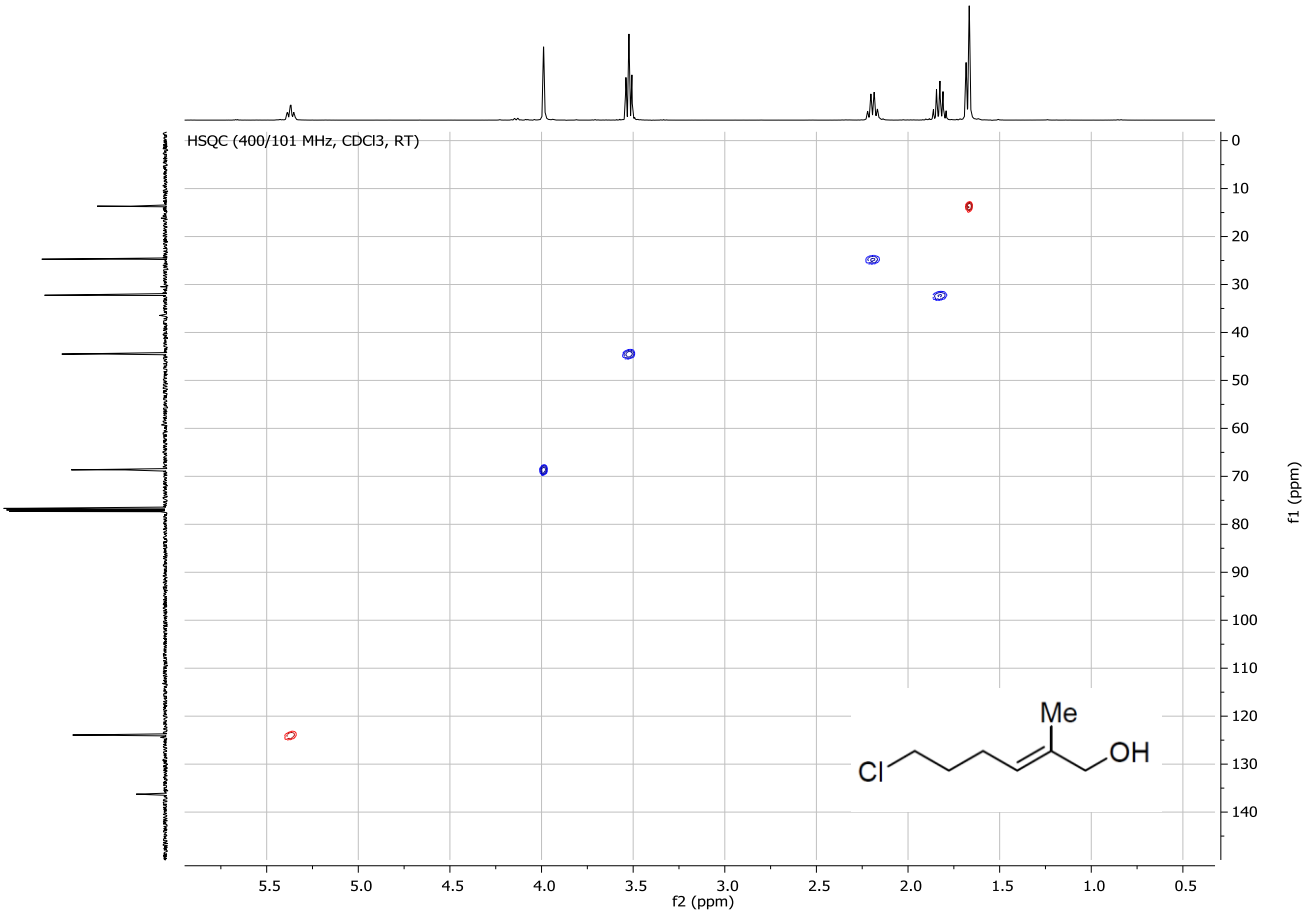


1H NMR (400 MHz, CDCl3, RT)

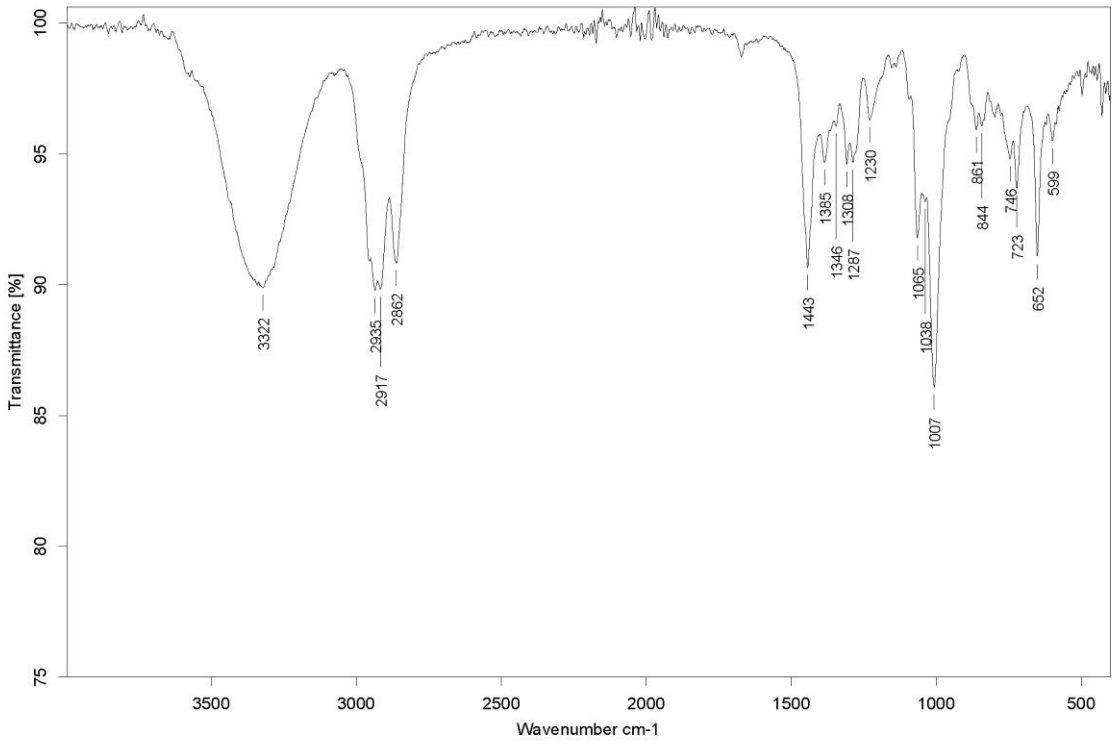


13C NMR (101 MHz, CDCl3, RT)

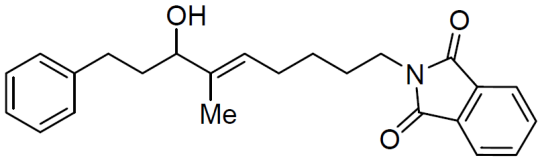




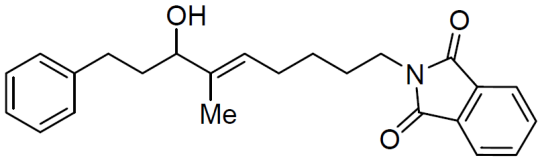
HUR-HA-118-12.0 **27.10.2016**

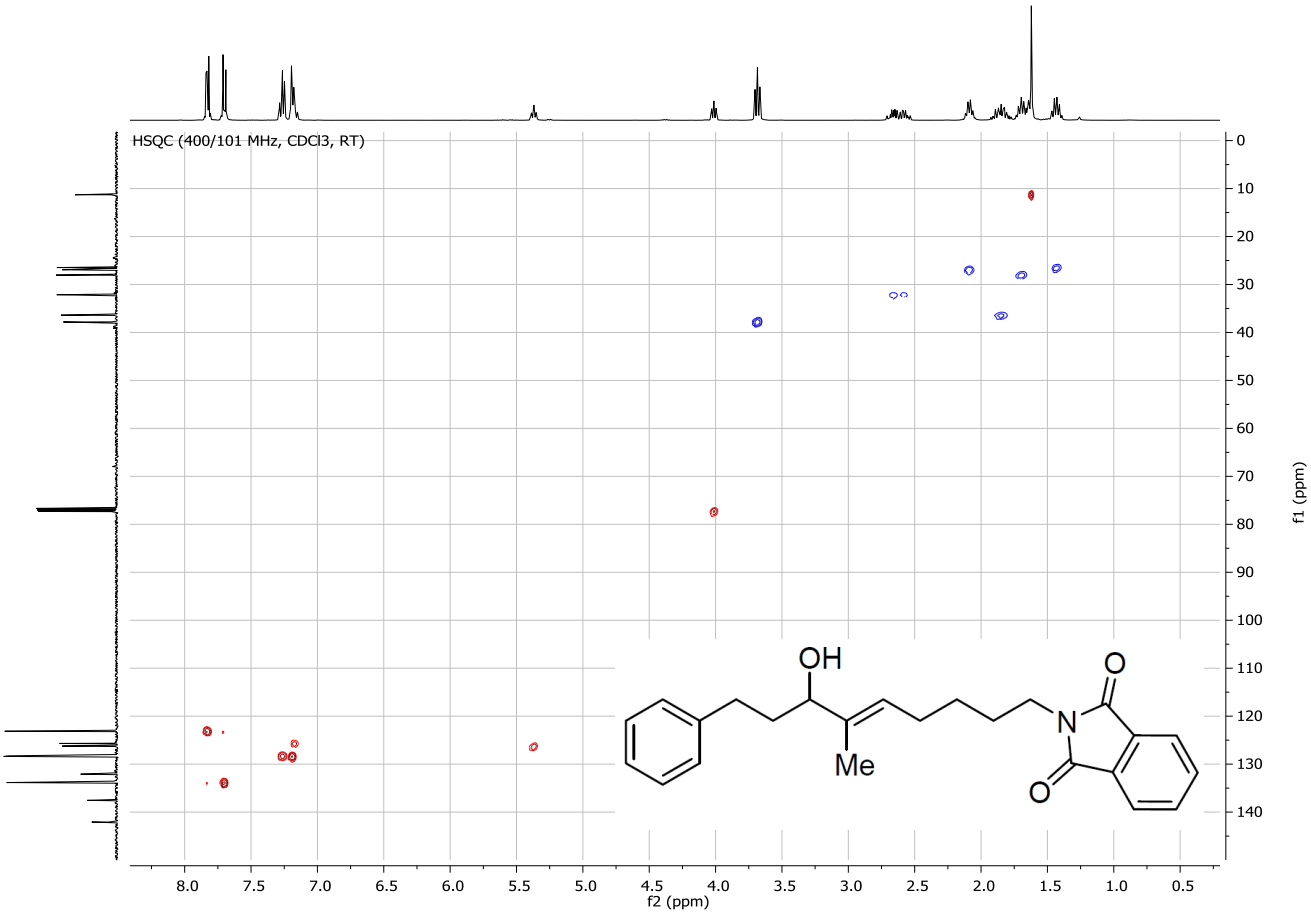


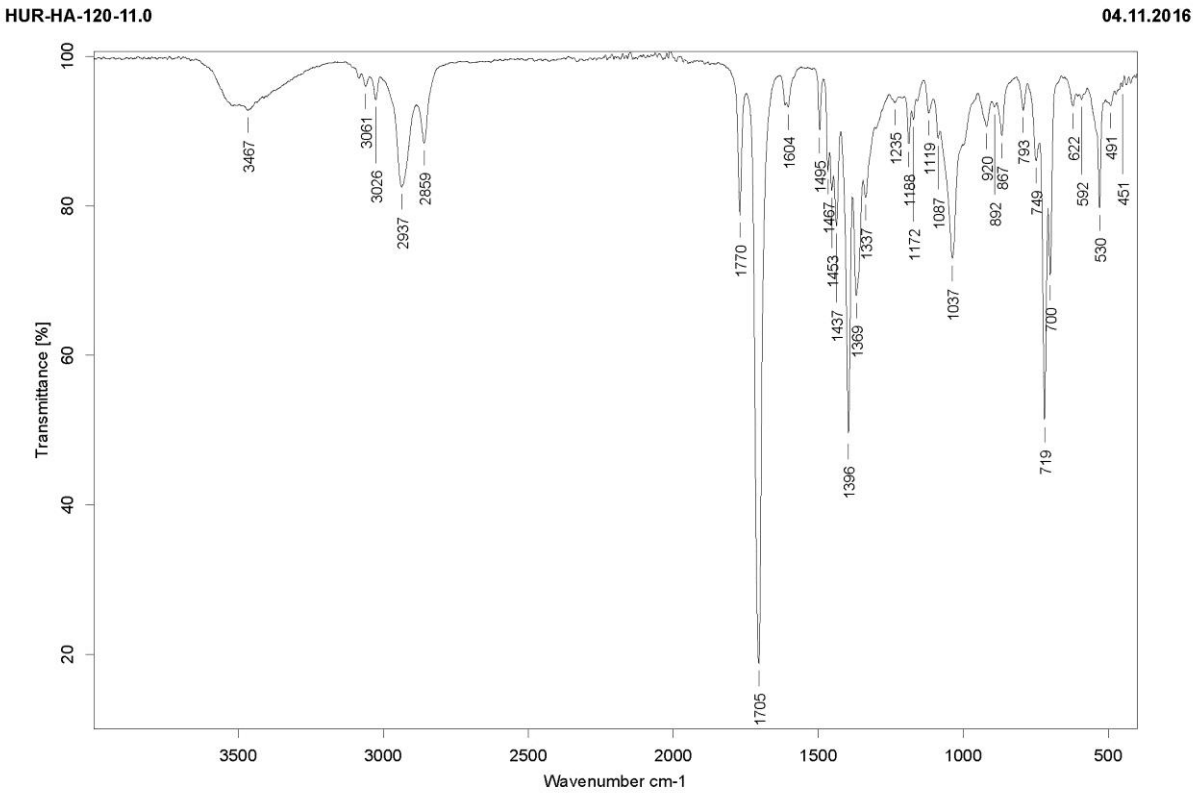
1H NMR (400 MHz, CDCl3, RT)



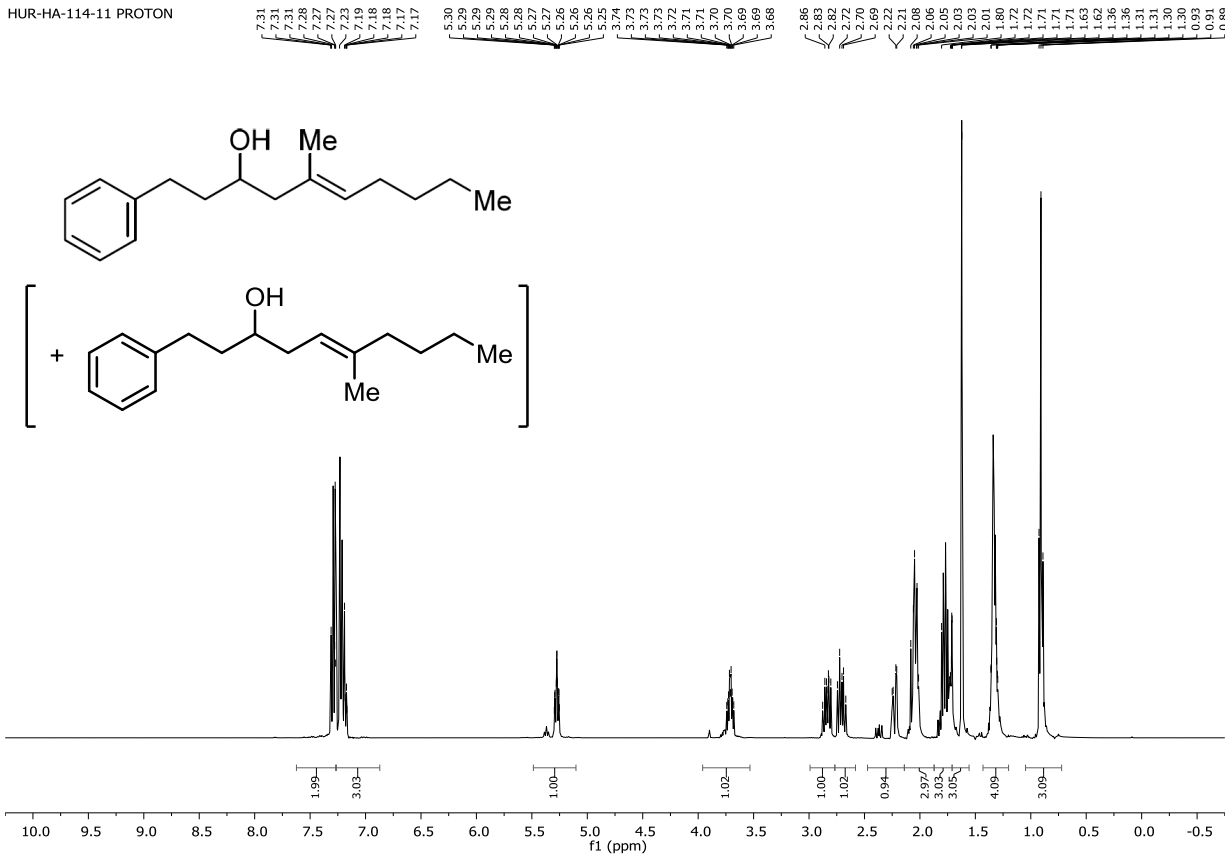
13C NMR (101 MHz, CDCl3, RT)



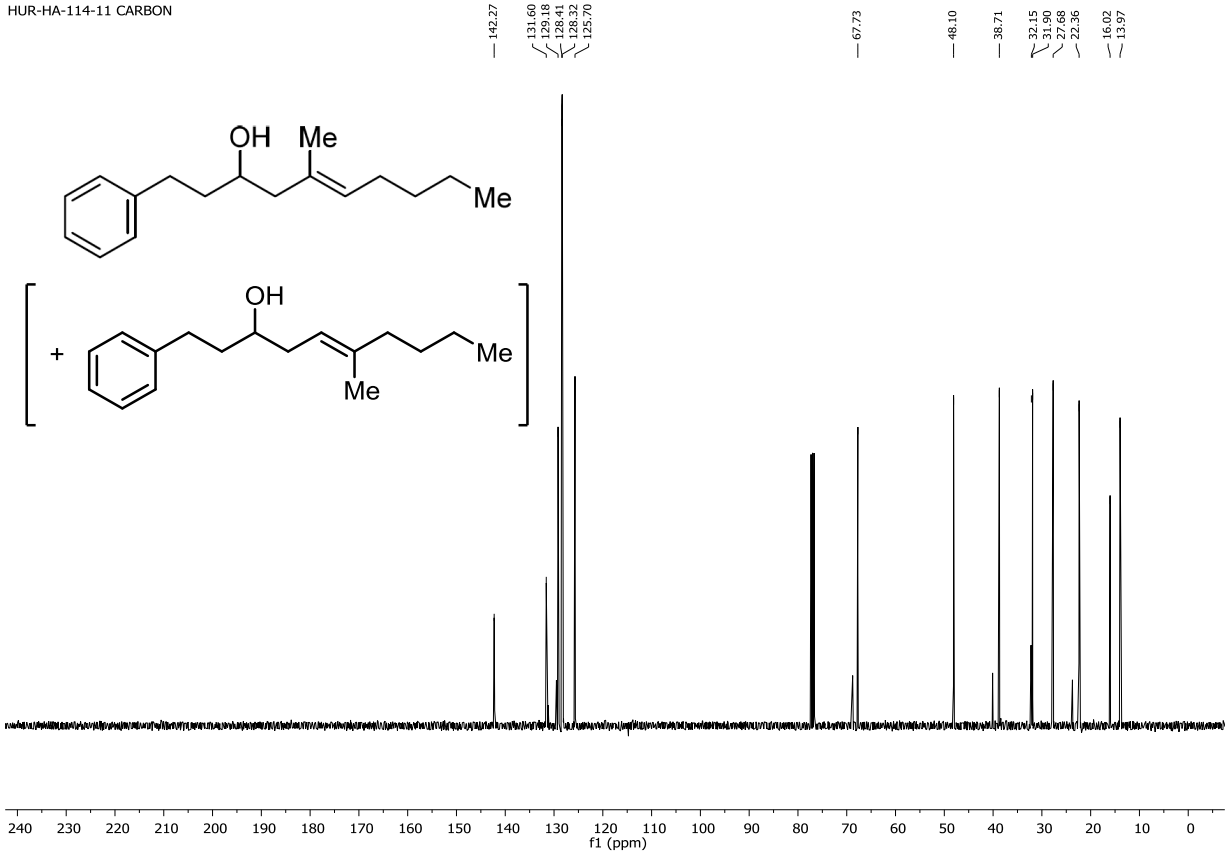

HSQC (400/101 MHz, CDCl3, RT)
f2 (ppm)
f1 (ppm)
OH
Me
N
O
O

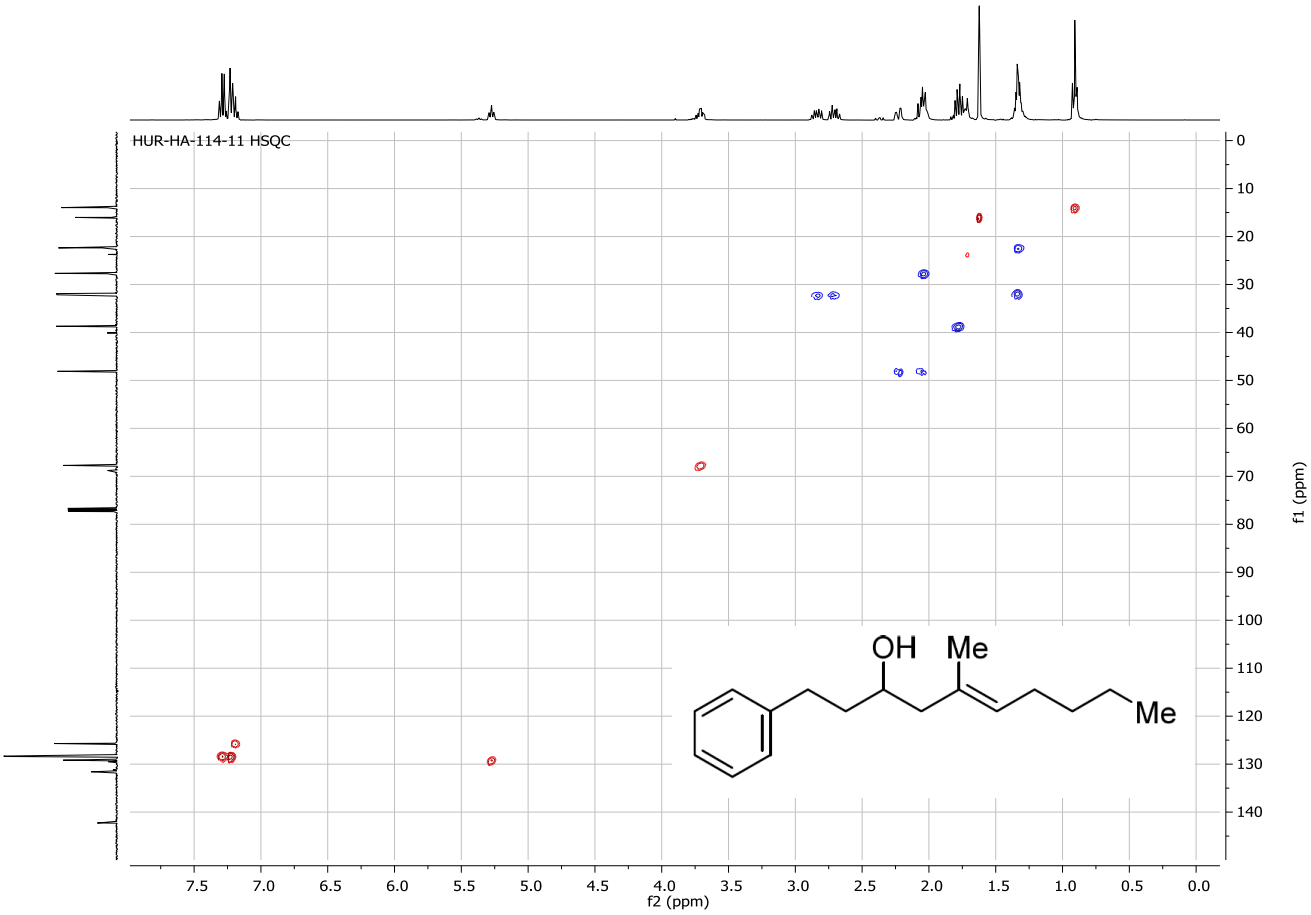

HUR-HA-120-11.0
04.11.2016
Transmittance [%]
Wavenumber cm-1
3467
3061
3026
2937
2859
1770
1705
1604
1495
1467
1453
1437
1396
1369
1337
1235
1188
1172
1119
1087
1037
920
892
867
793
749
719
700
622
592
530
491
451

HUR-HA-114-11 PROTON

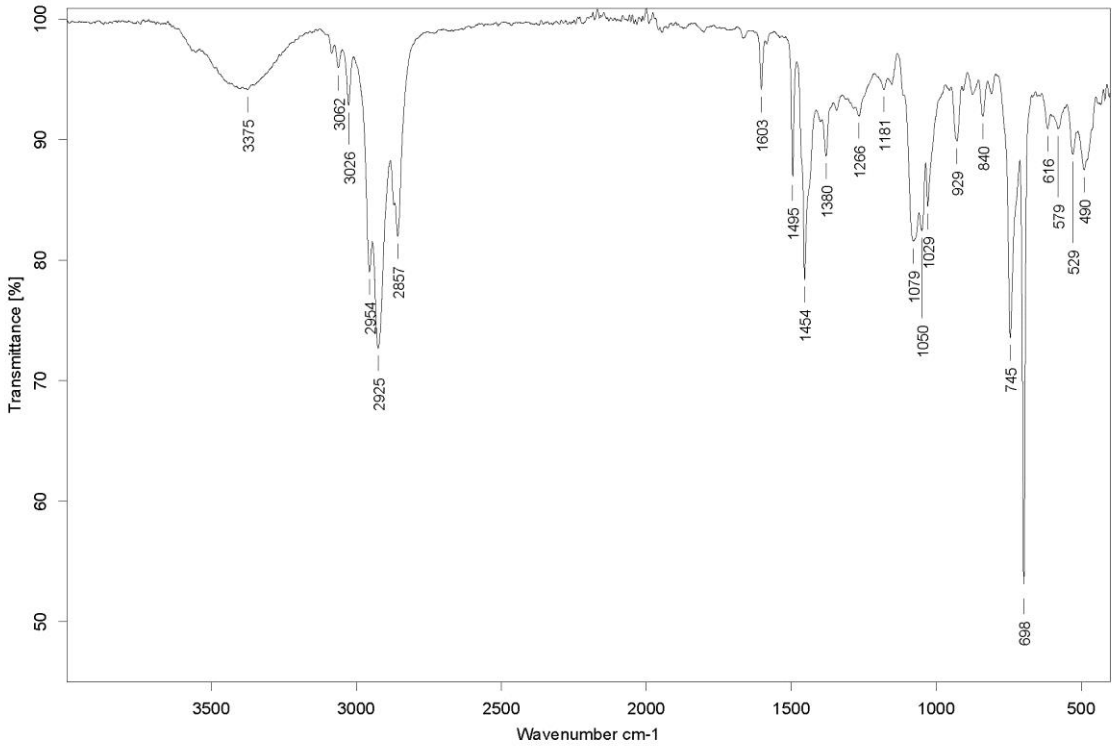


HUR-HA-114-11 CARBON

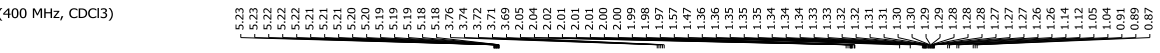


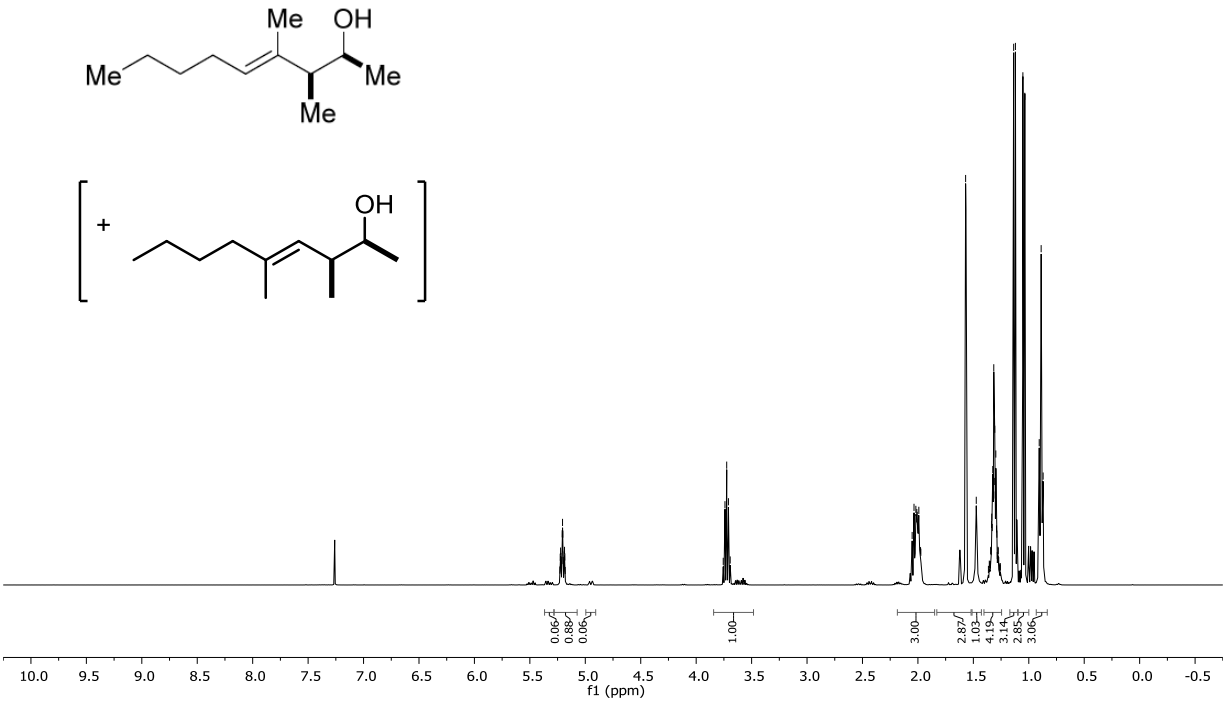


HUR-HA-114-11.0 **25.10.2016**

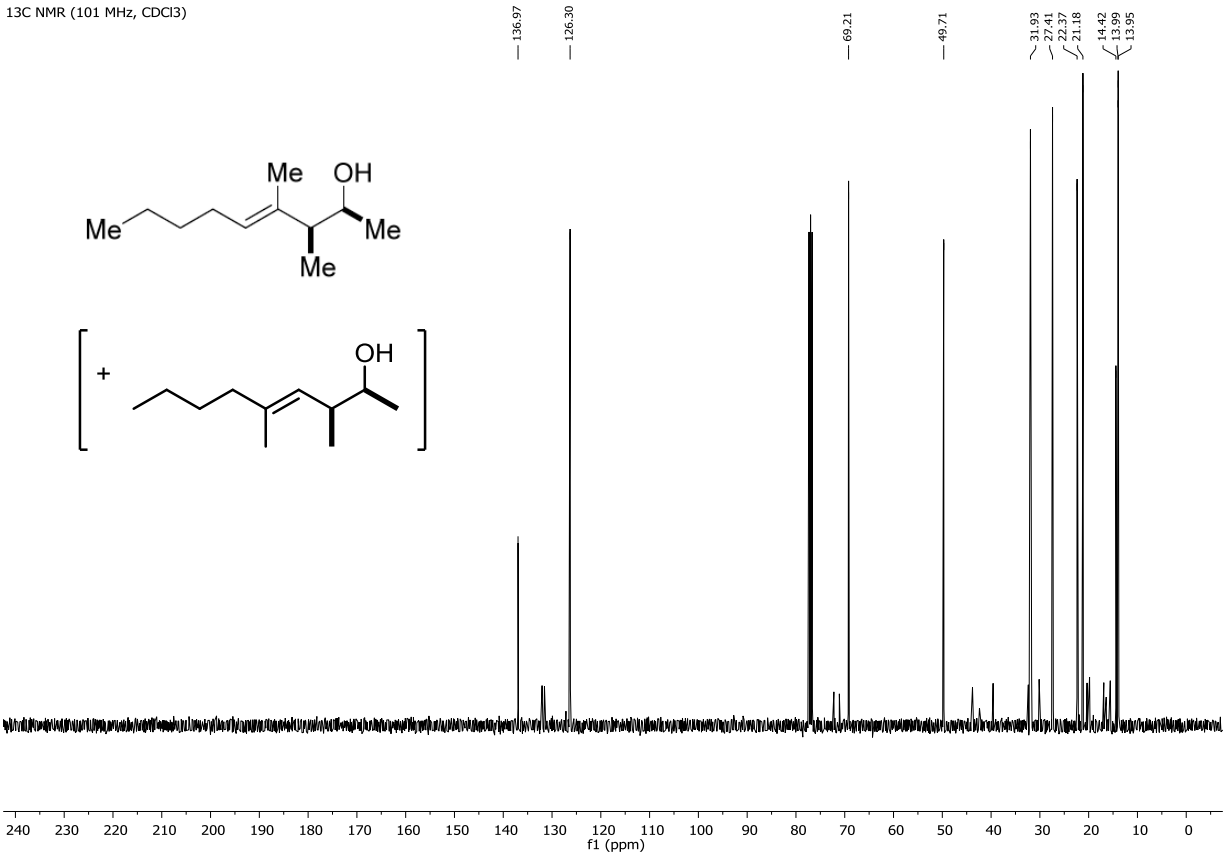


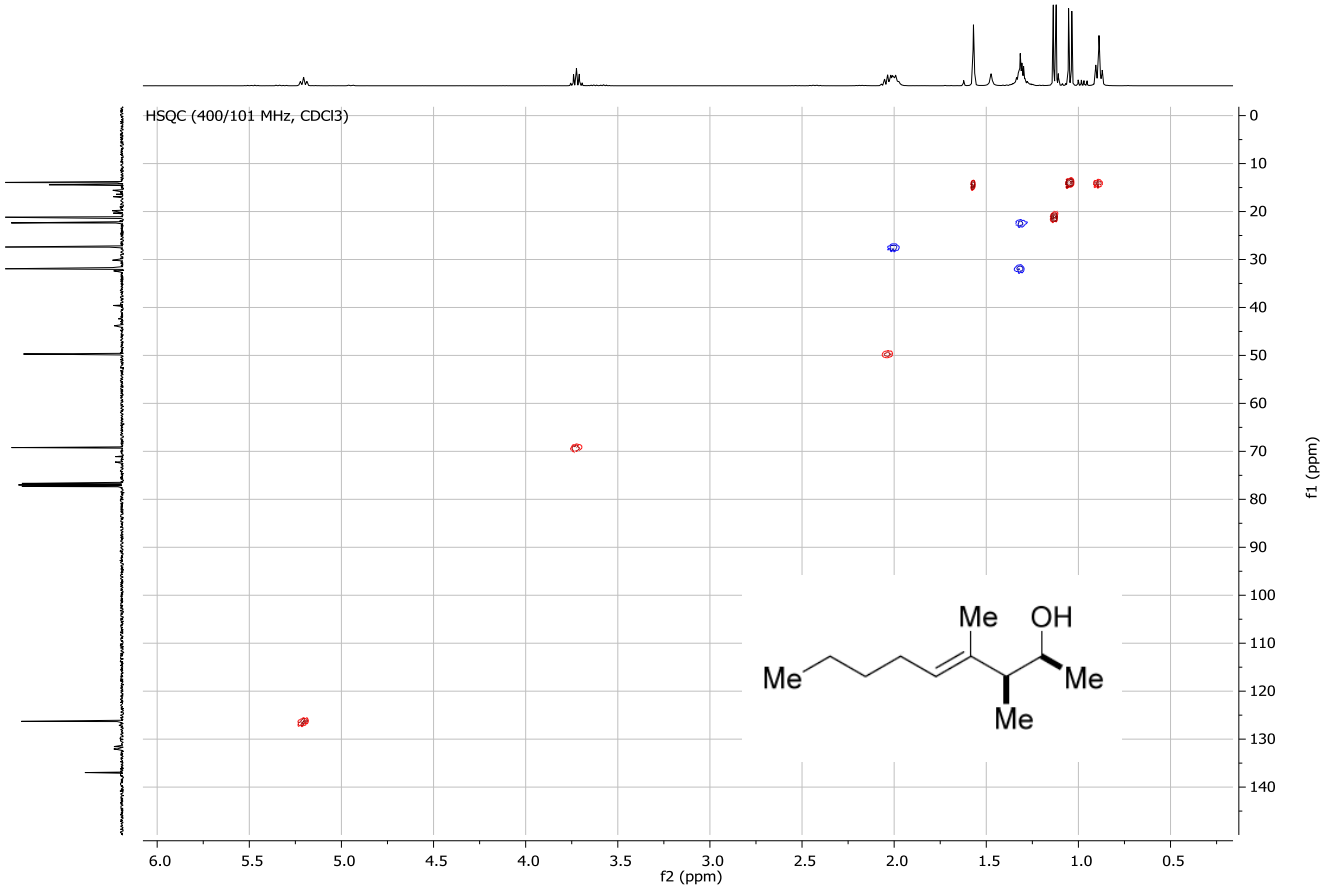
1H NMR (400 MHz, CDCl3)



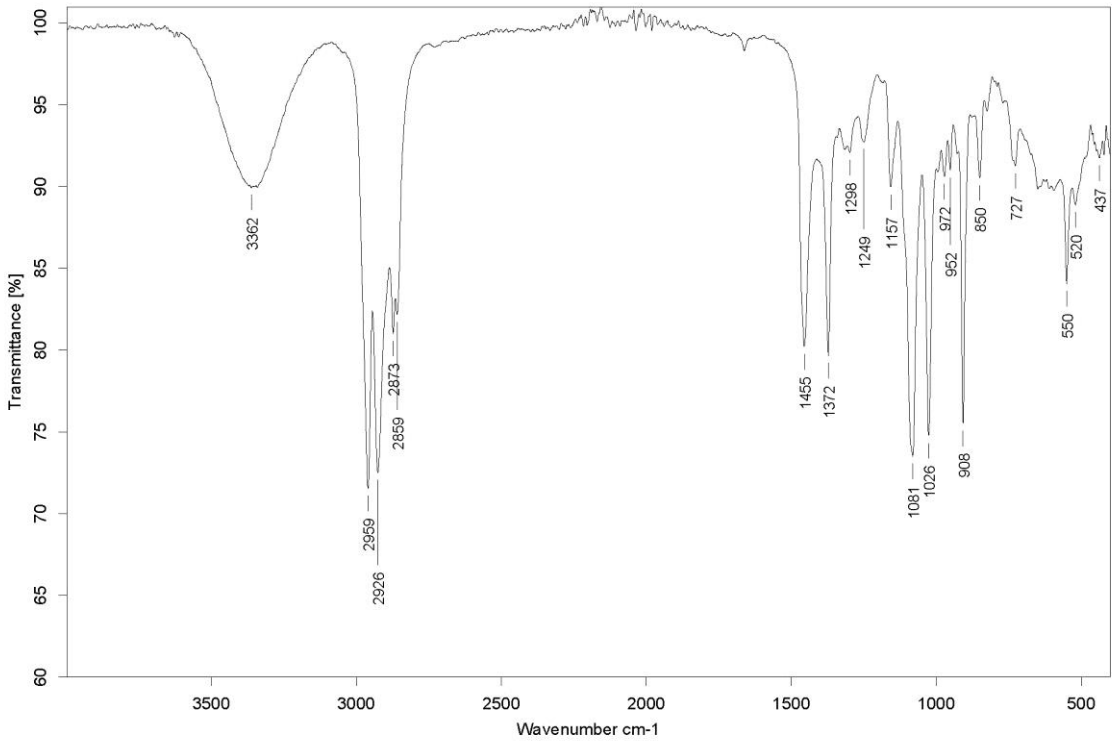


13C NMR (101 MHz, CDCl3)

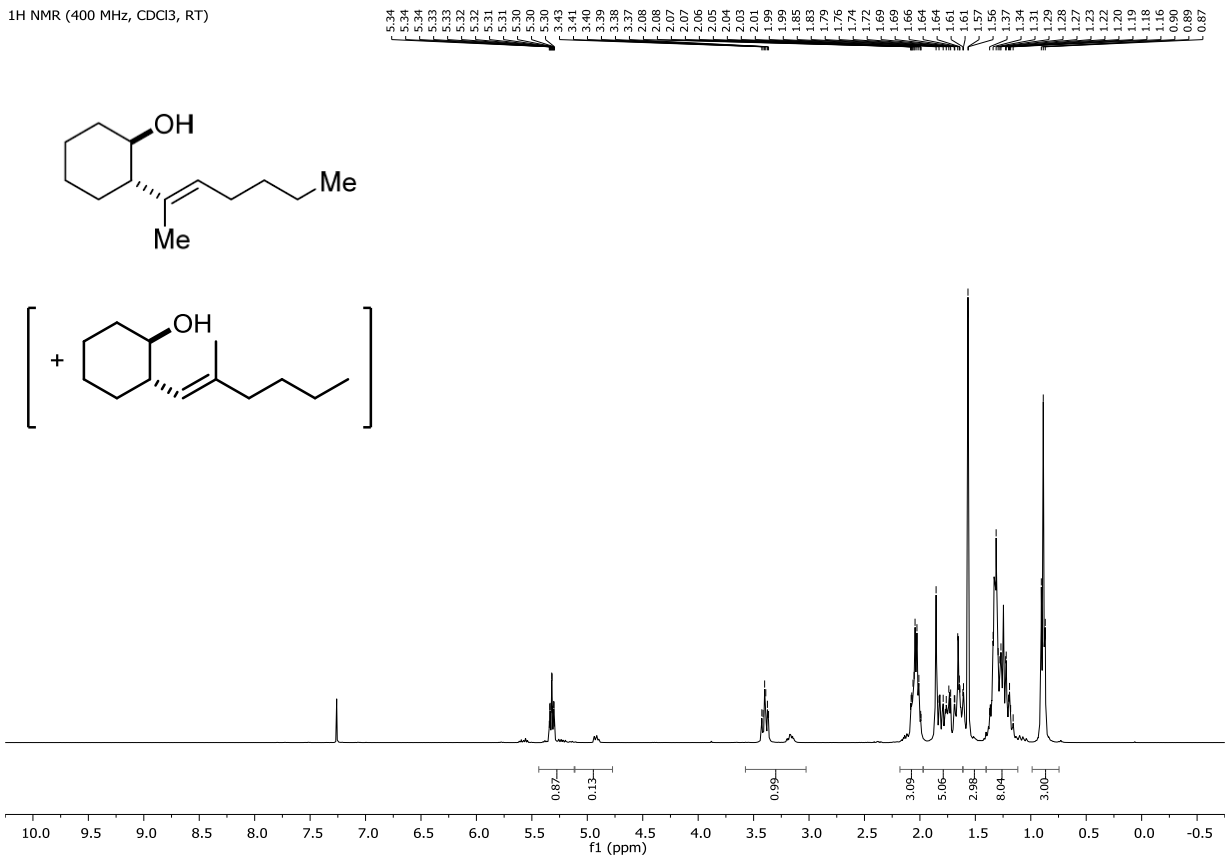




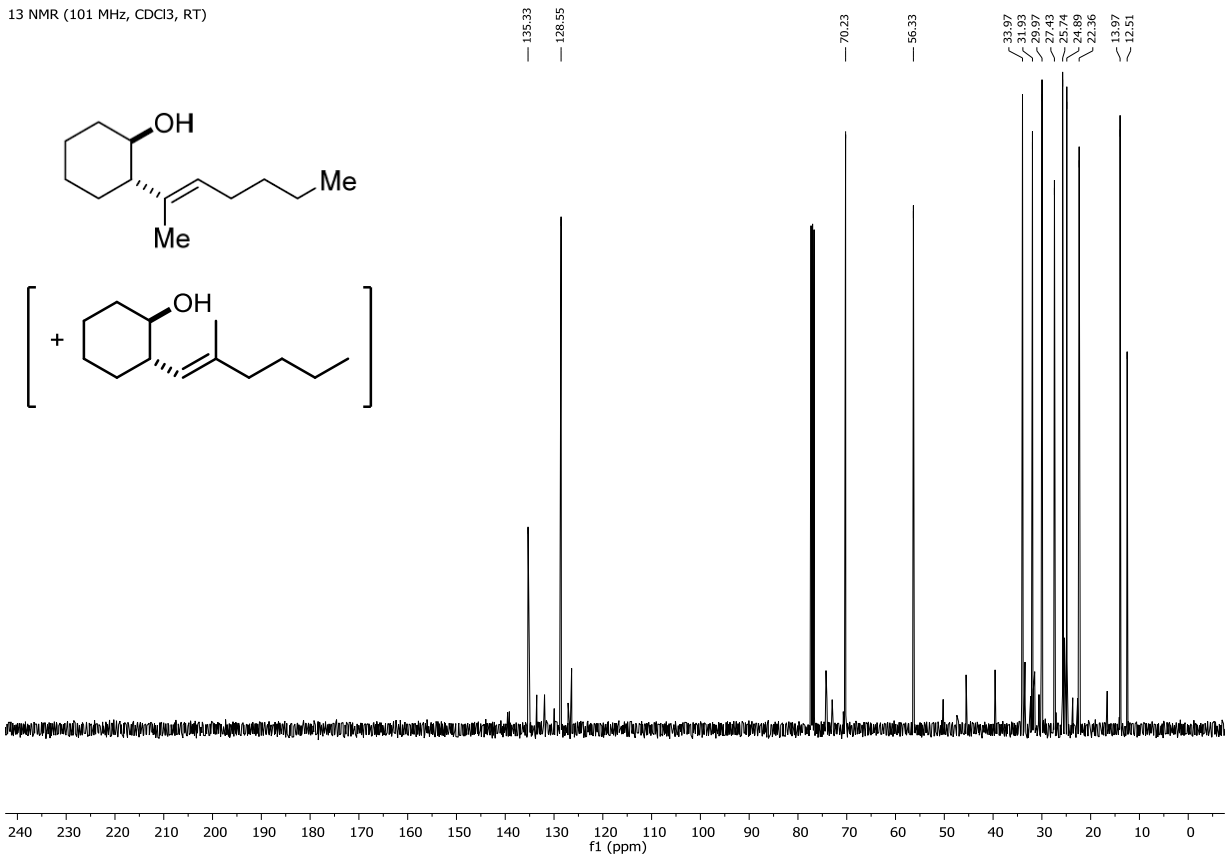
HUR-HA-100-12.0 **14.11.2016**

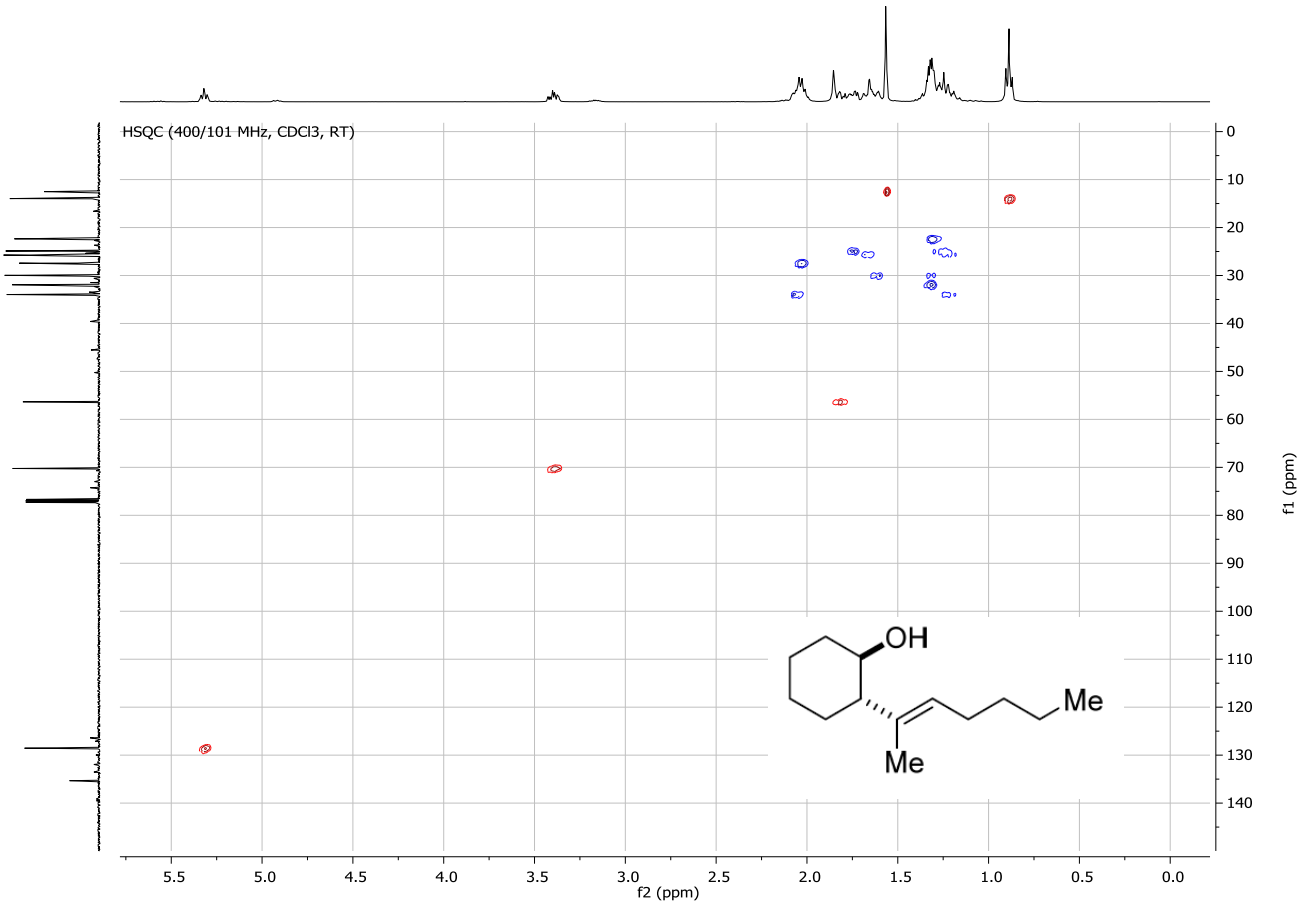


1H NMR (400 MHz, CDCl3, RT)

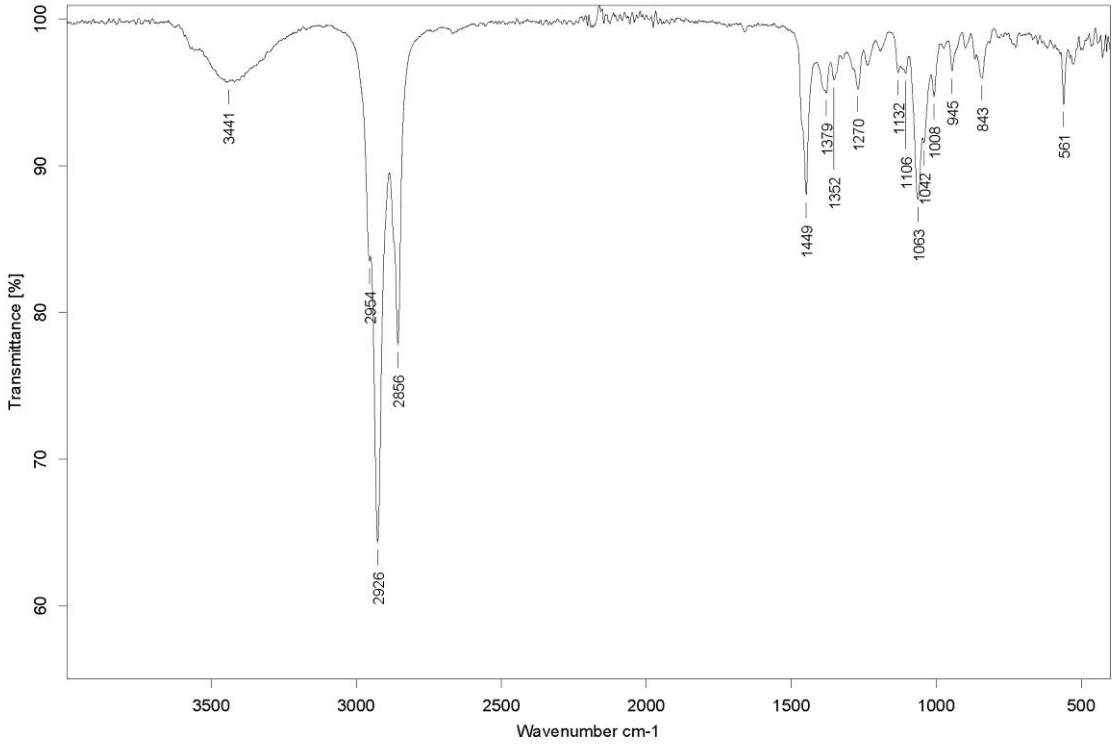


13 NMR (101 MHz, CDCl3, RT)

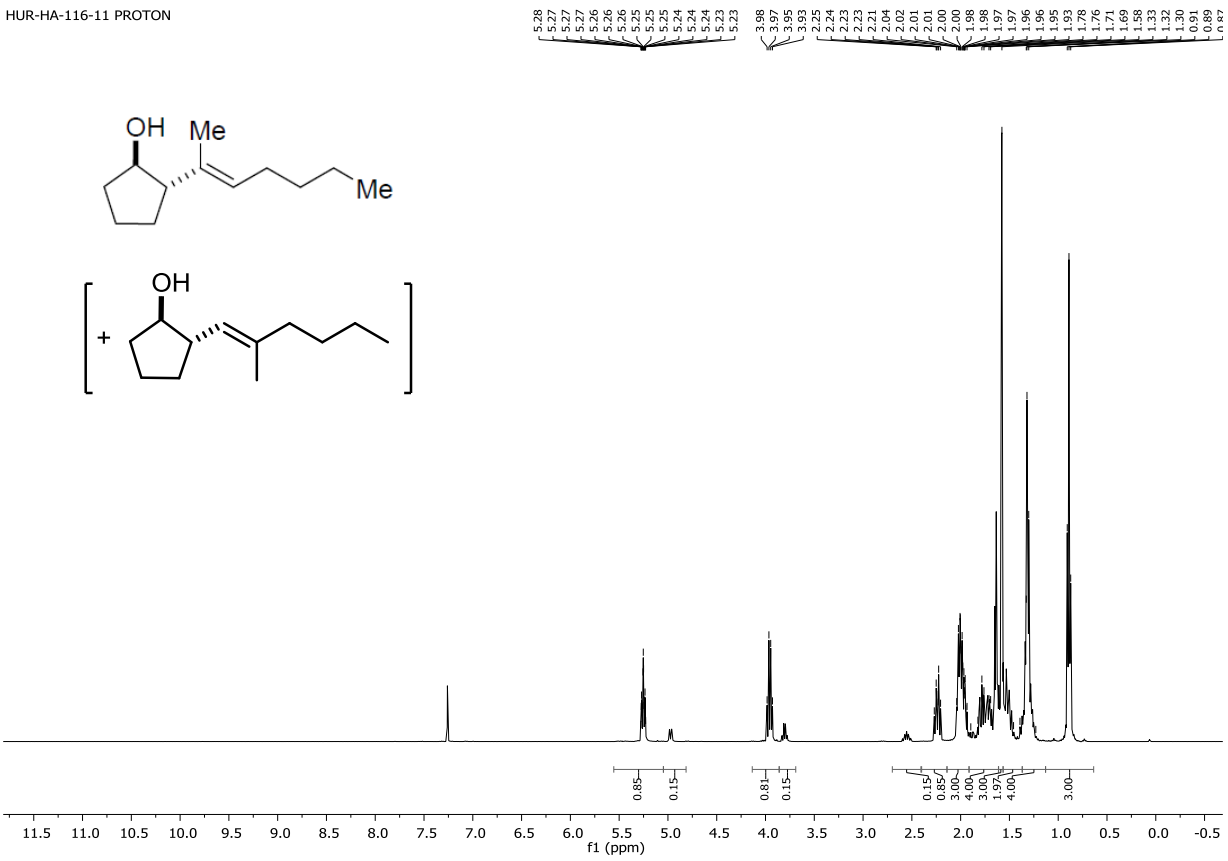




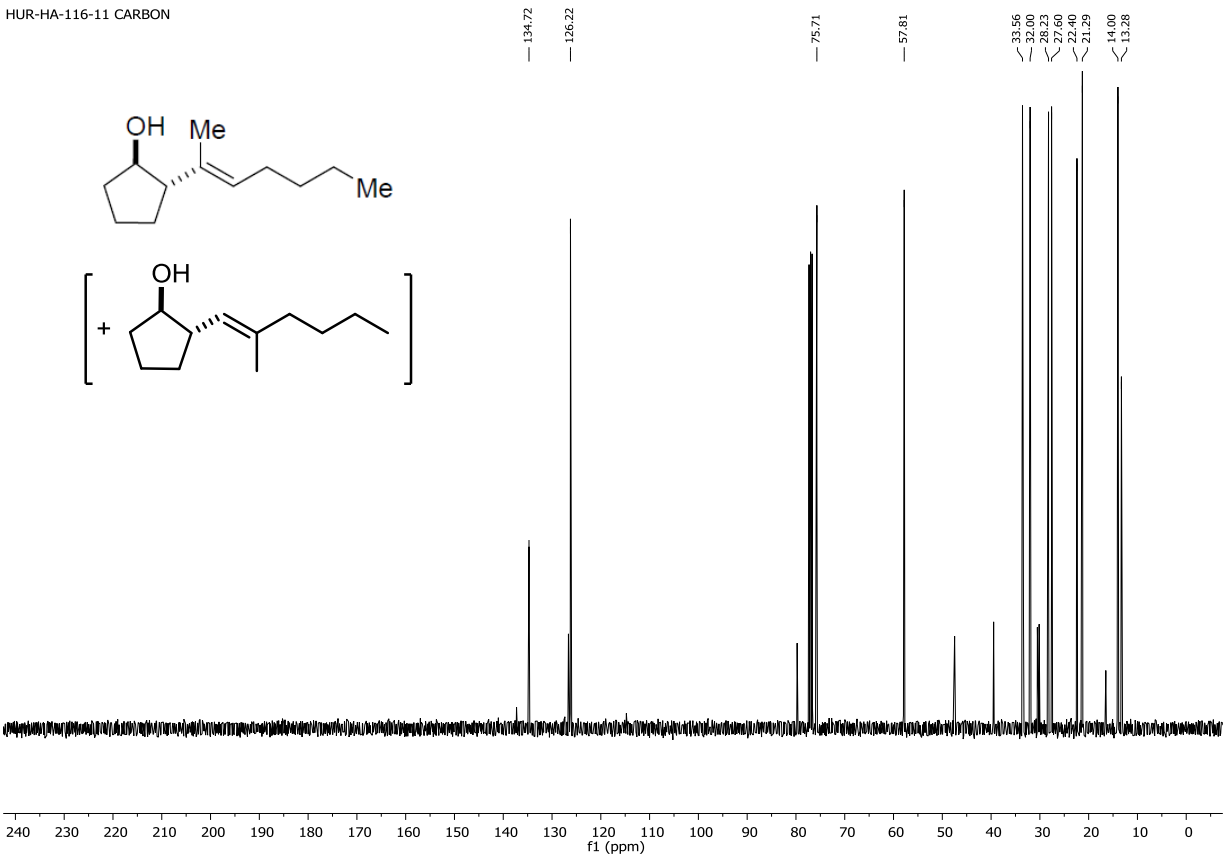
HUR-HA-115-13.0 **02.11.2016**

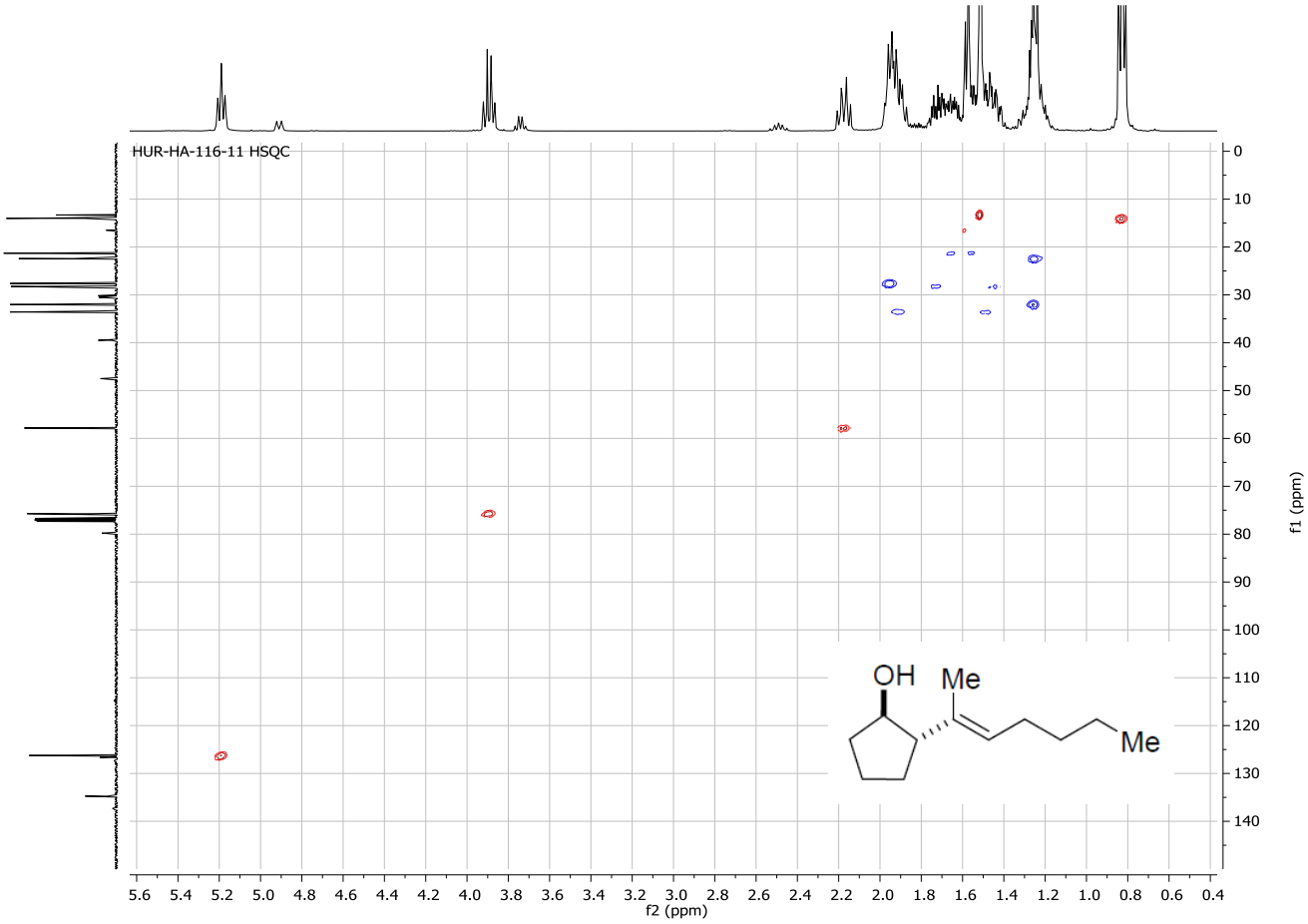


HUR-HA-116-11 PROTON

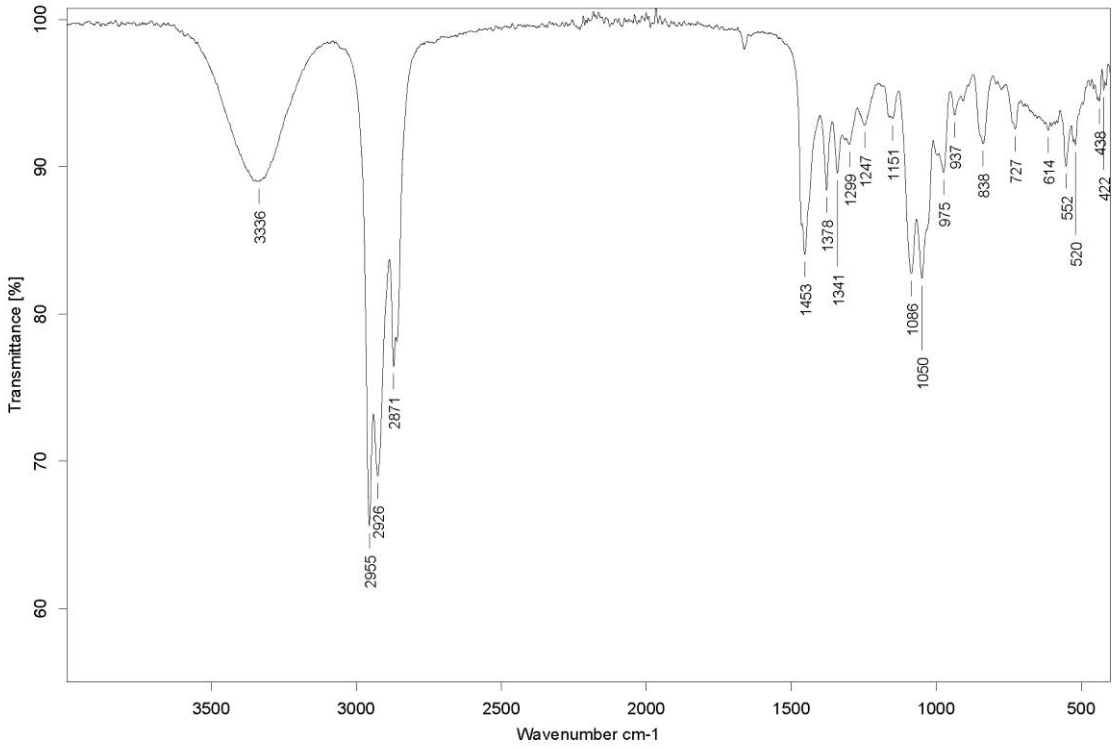


HUR-HA-116-11 CARBON

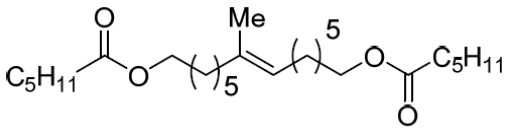




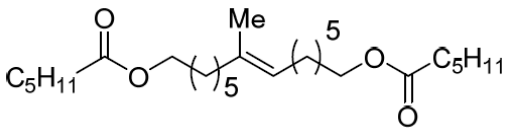
HUR-HA-116-11.0 **02.11.2016**

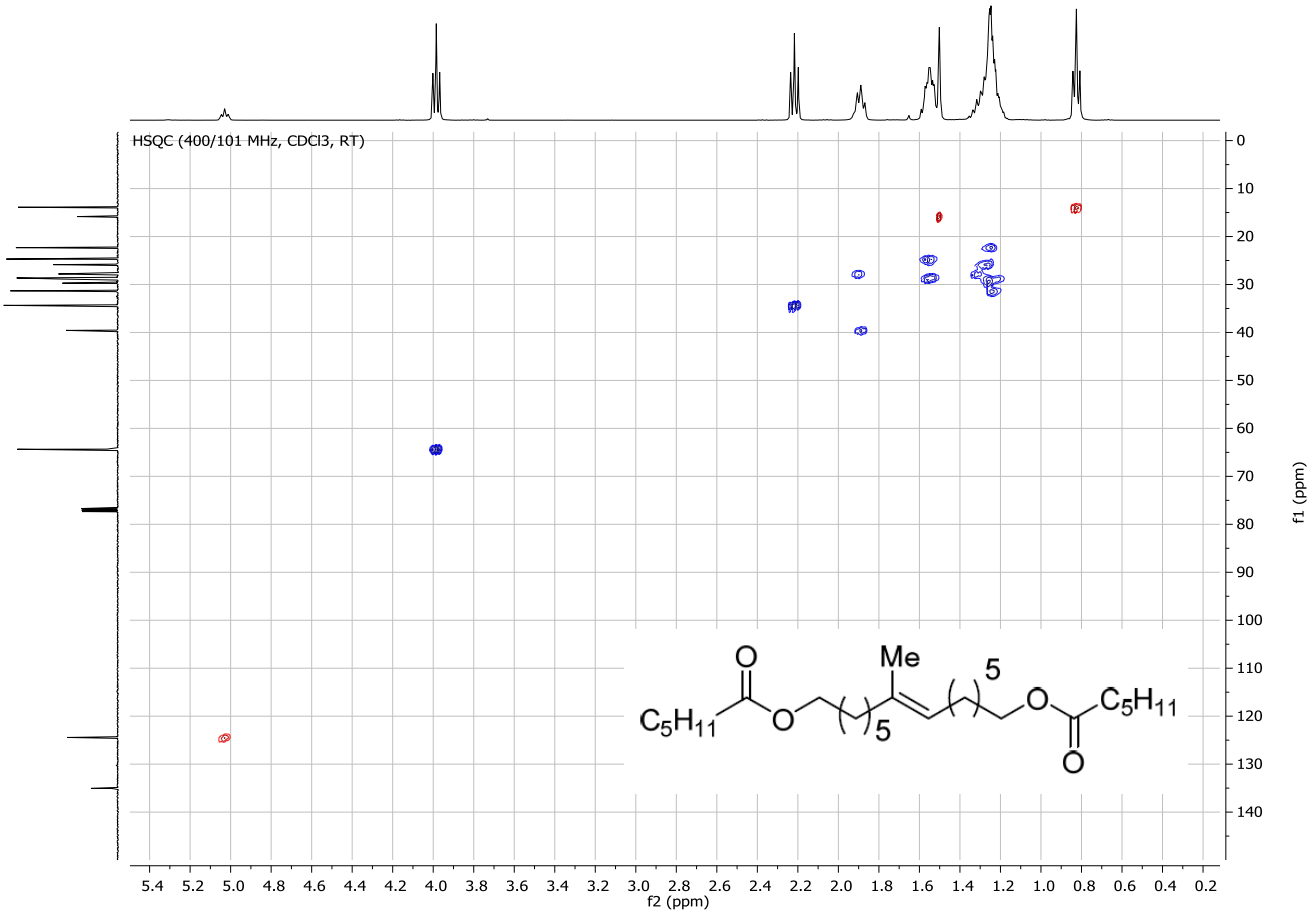


1H NMR (400 MHz, CDCl3, RT)

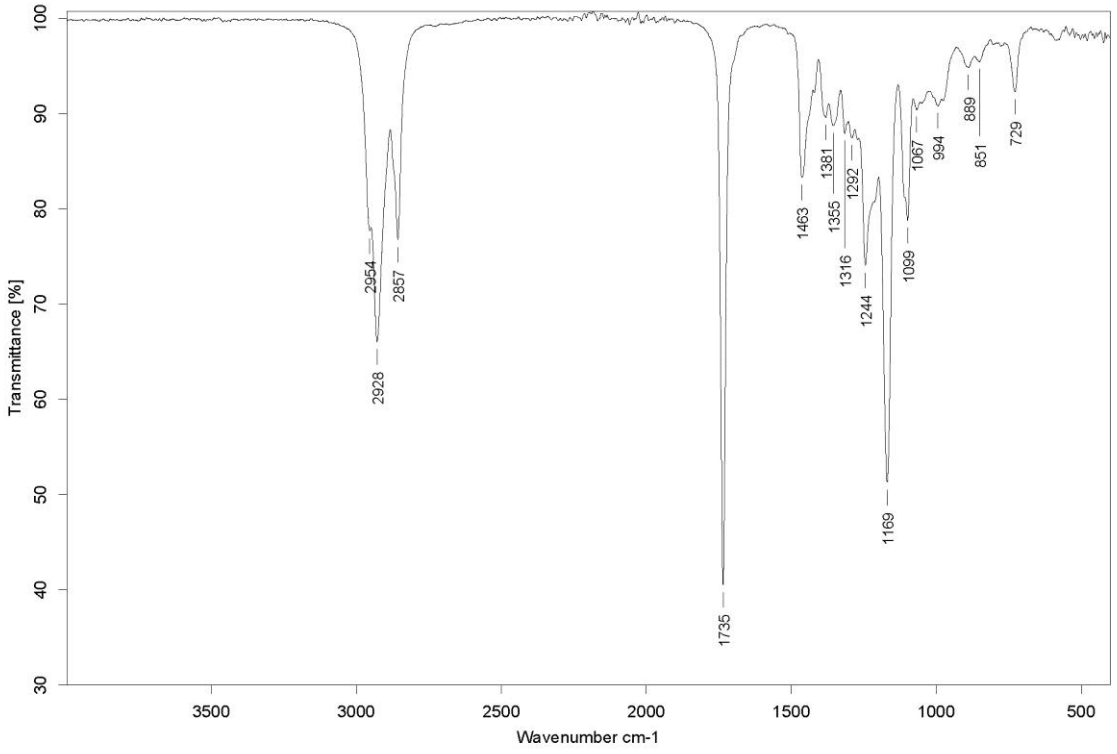


13C NMR (101 MHz, CDCl3, RT)

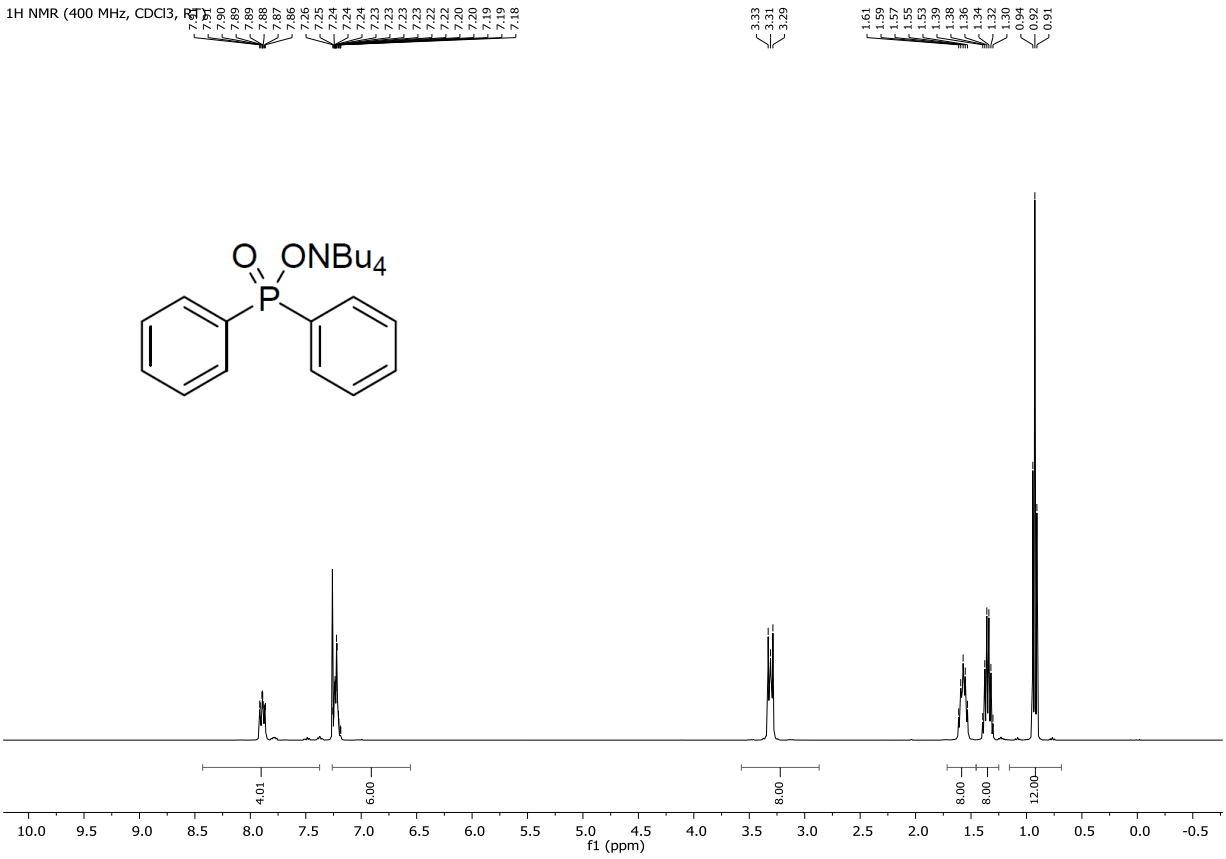




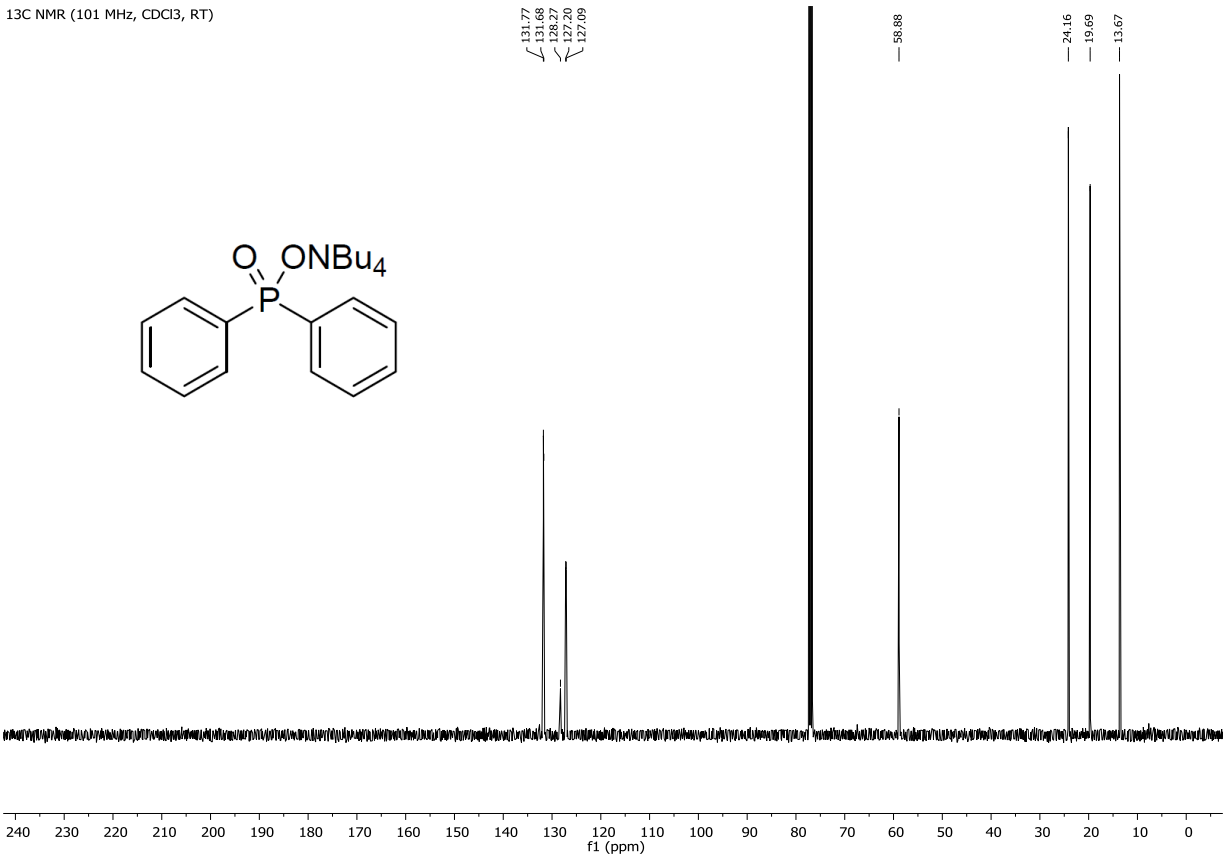
HUR-HA-105-13.1 **17.10.2016**



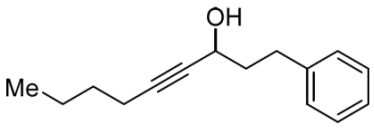
1H NMR (400 MHz, CDCl3, RT)

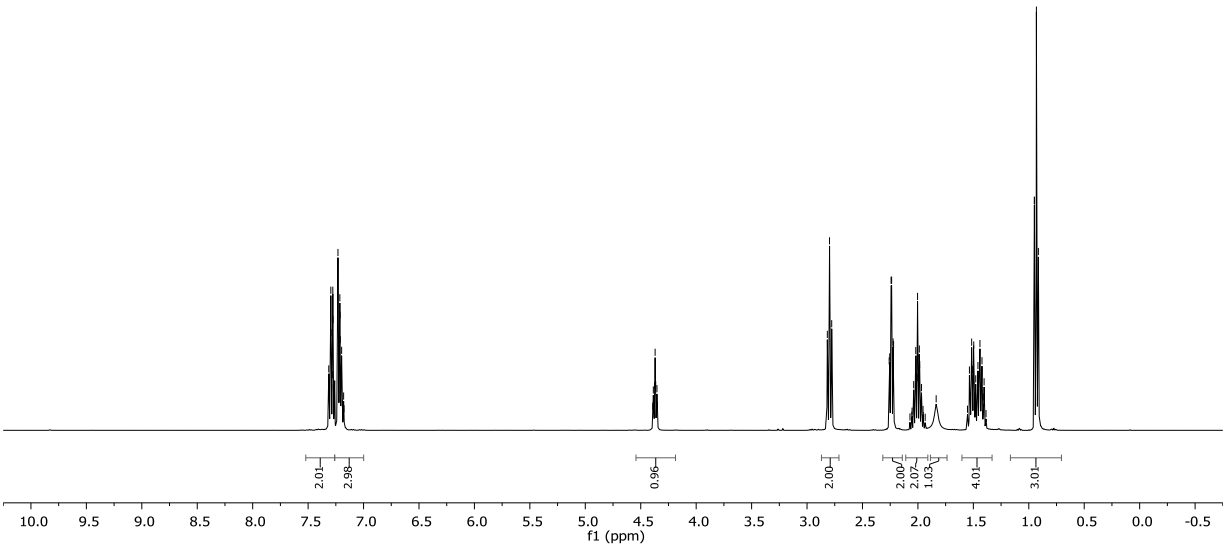


13C NMR (101 MHz, CDCl3, RT)

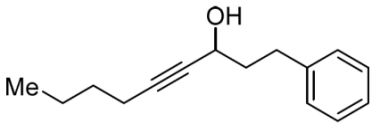


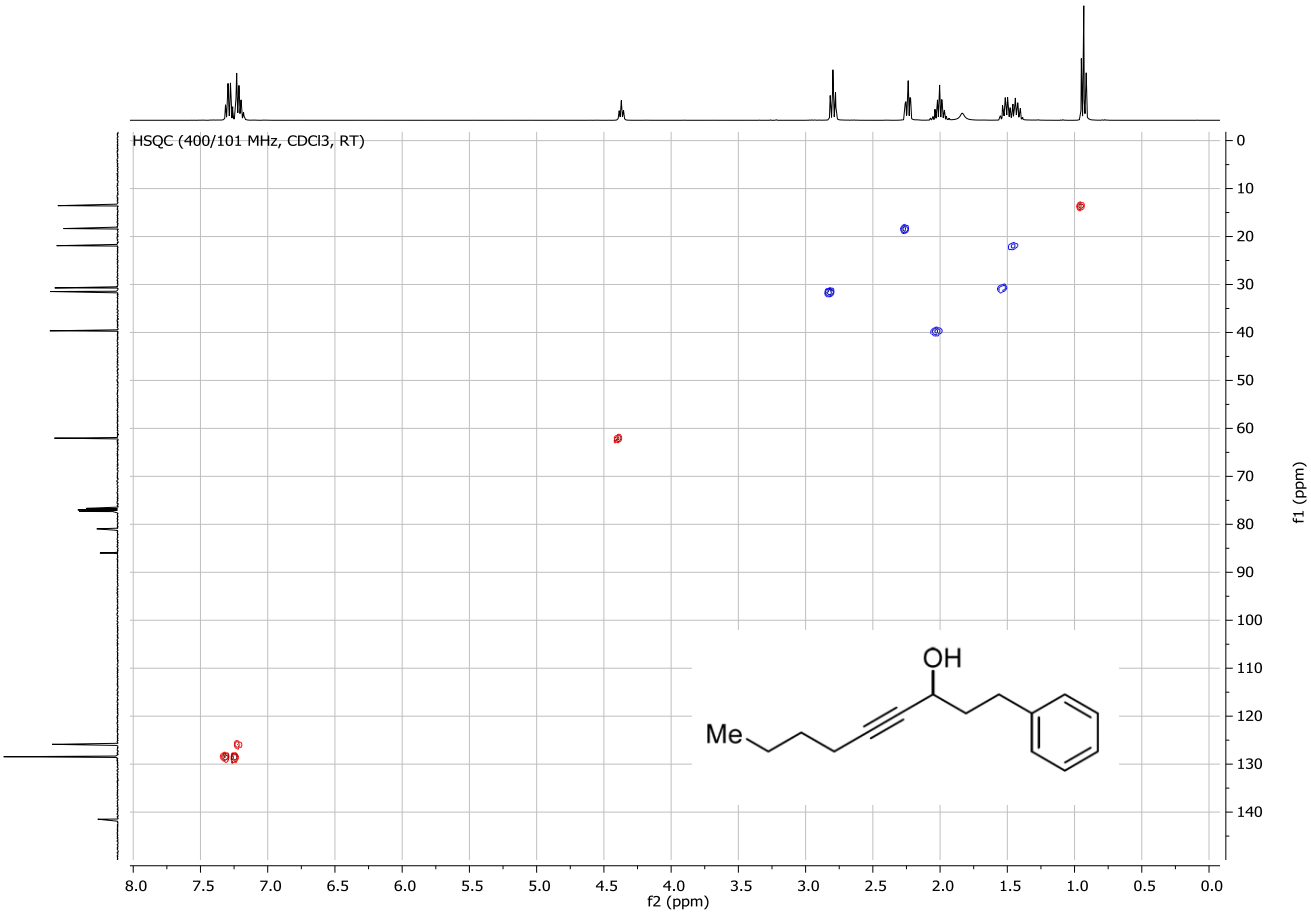
1H NMR (400 MHz, CDCl3, RT)



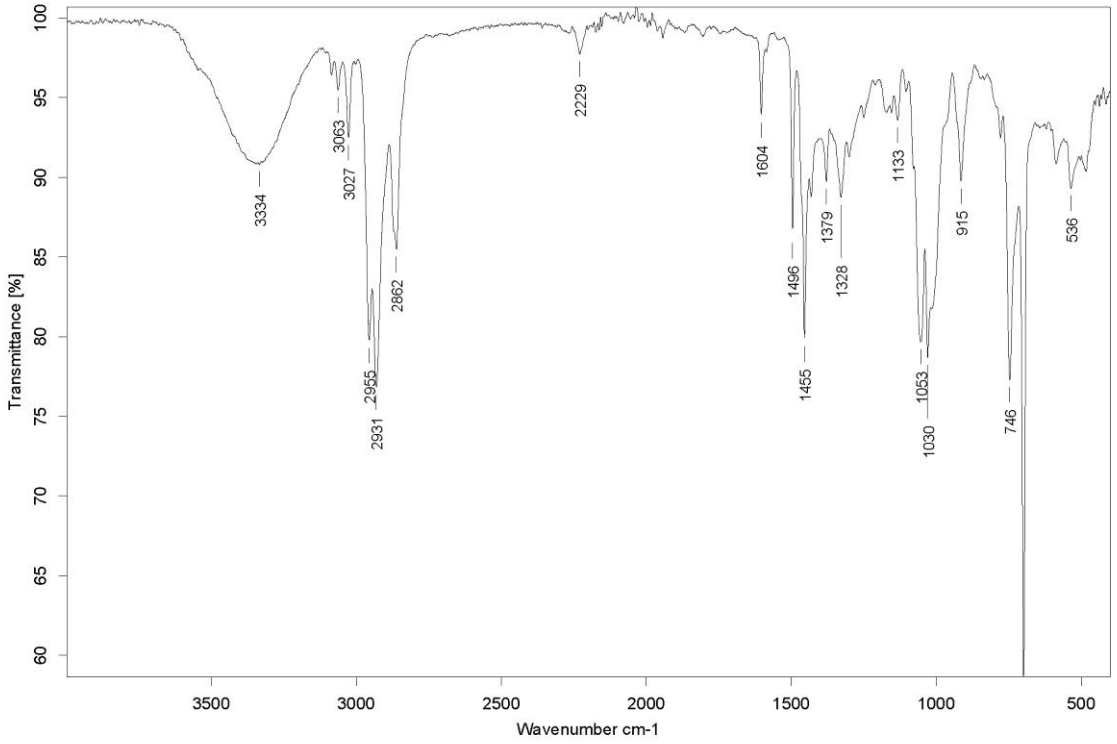


13C NMR (101 MHz, CDCl3, RT)

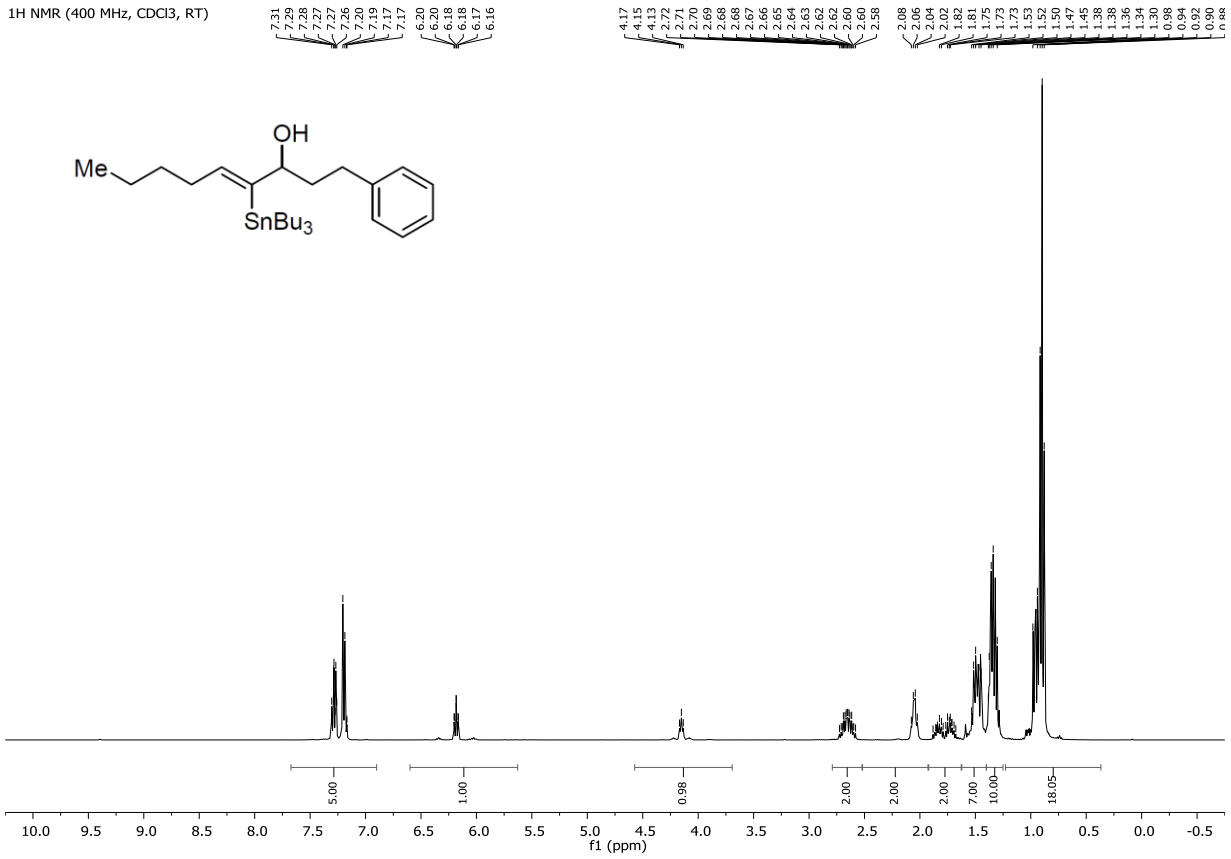




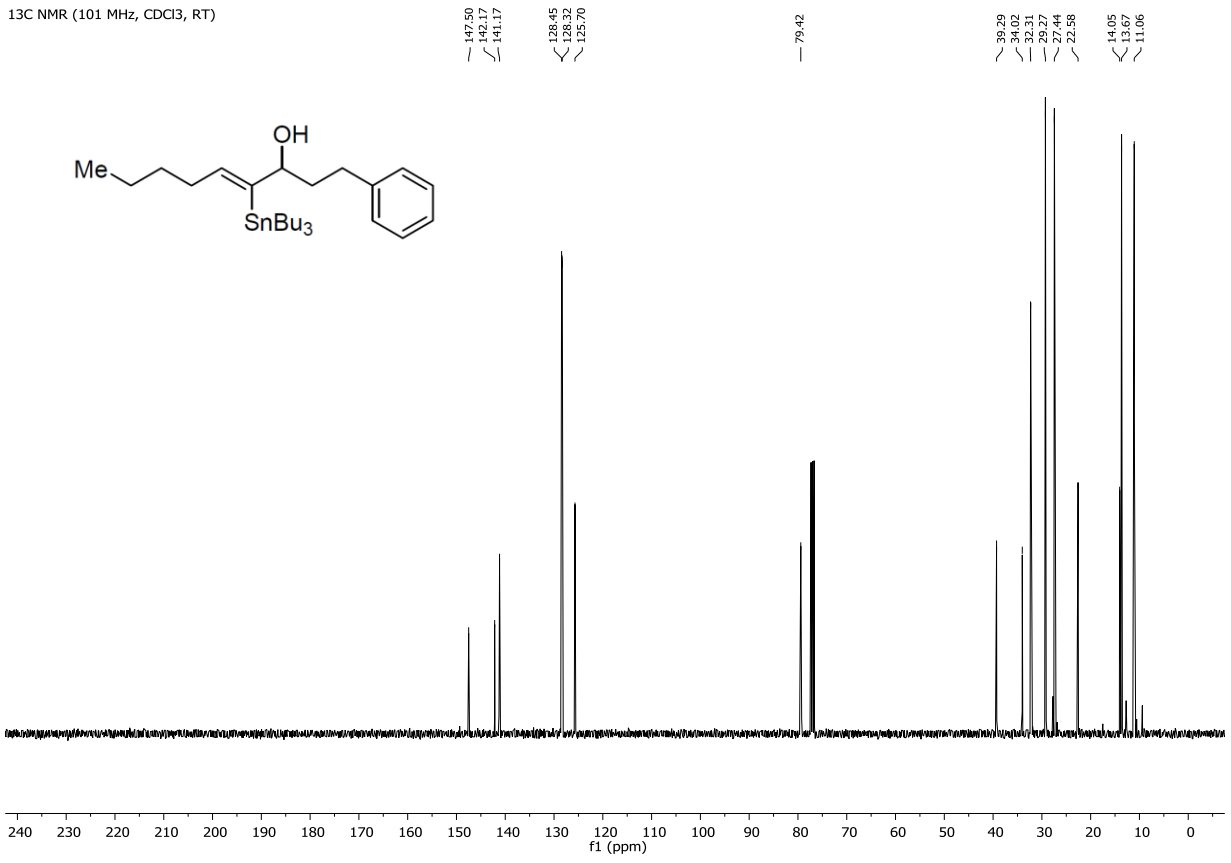
HUR-HA-031-12.0 **06.07.2016**



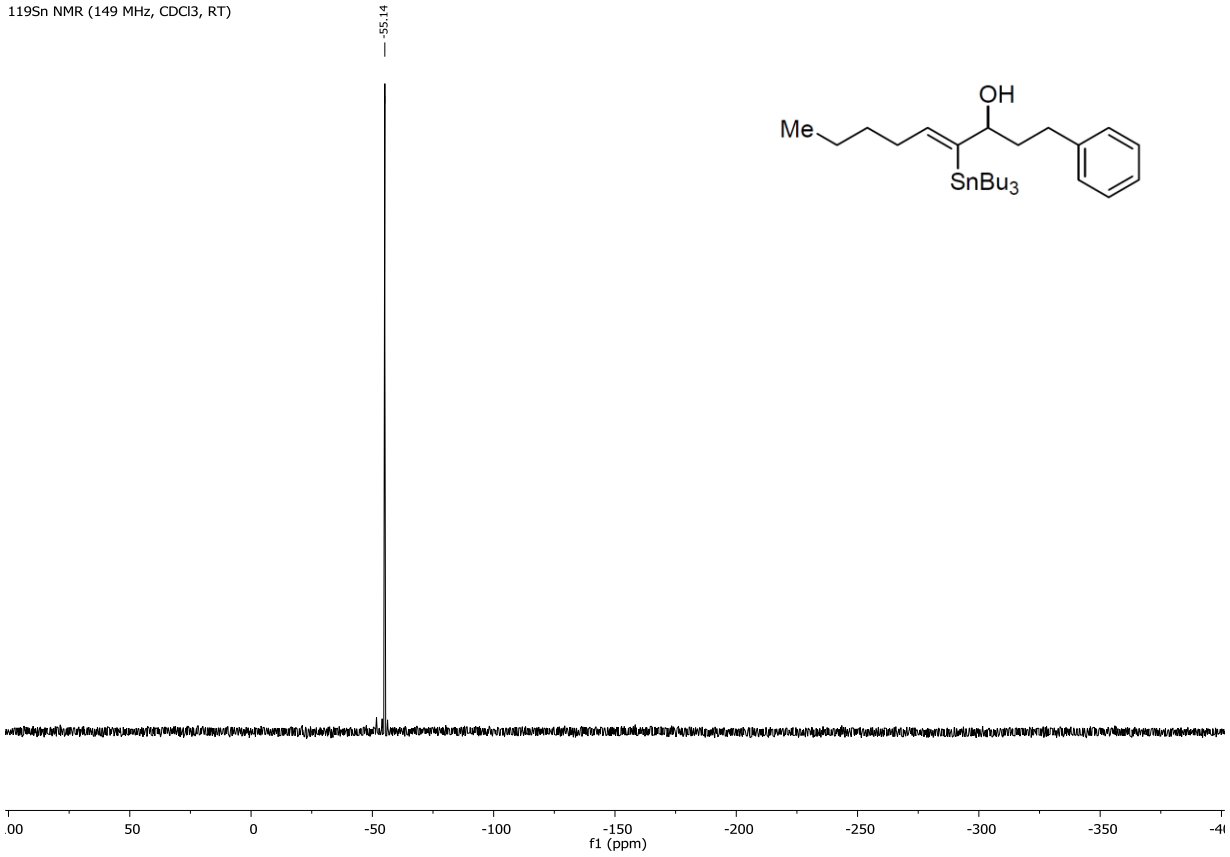
1H NMR (400 MHz, CDCl3, RT)



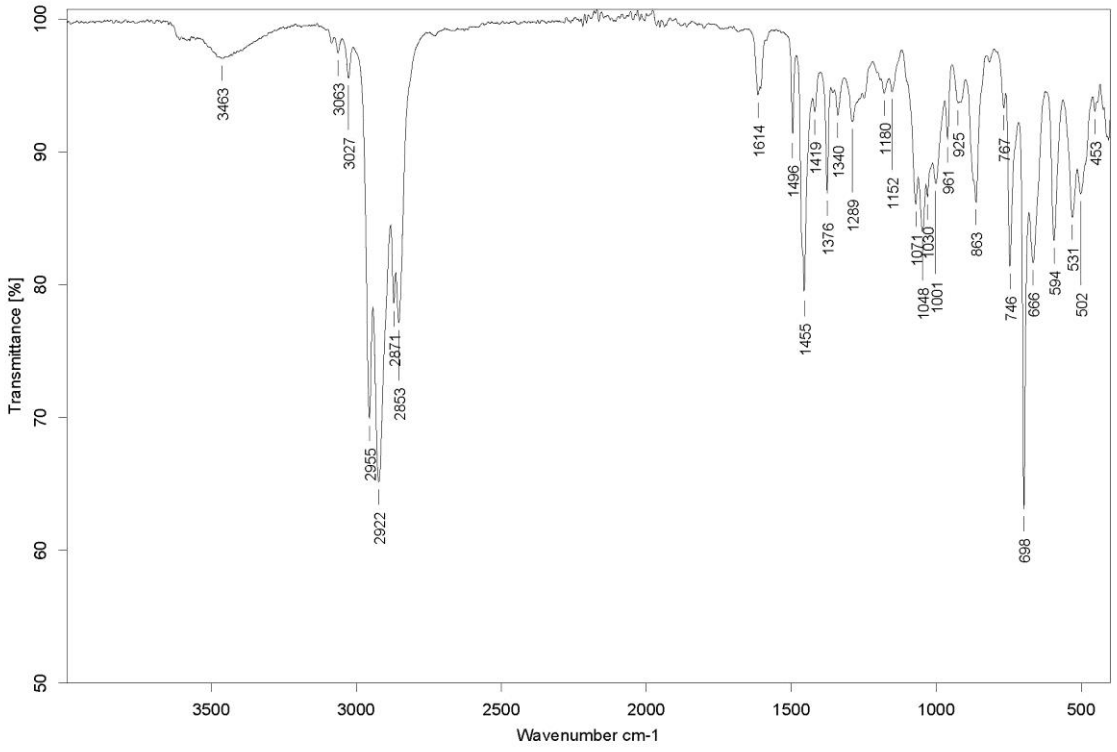
13C NMR (101 MHz, CDCl3, RT)



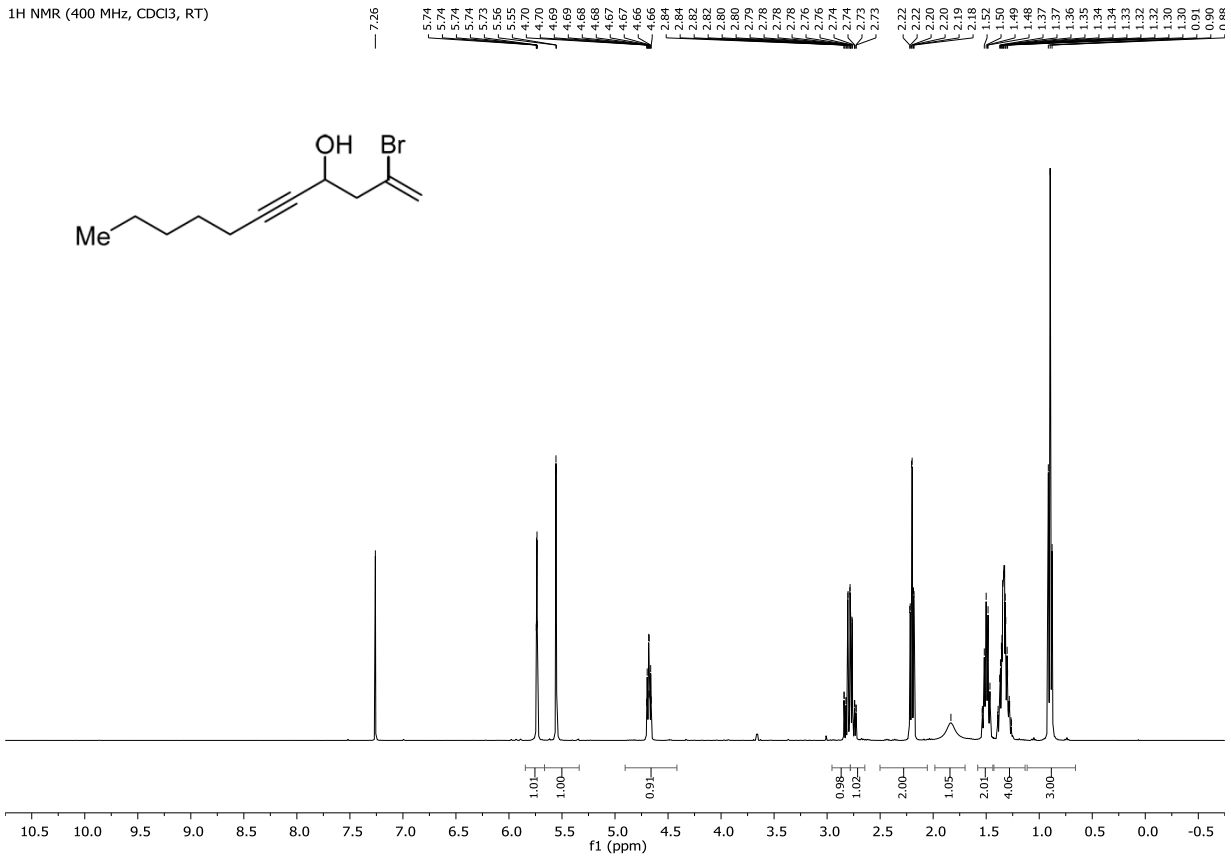
119Sn NMR (149 MHz, CDCl3, RT)



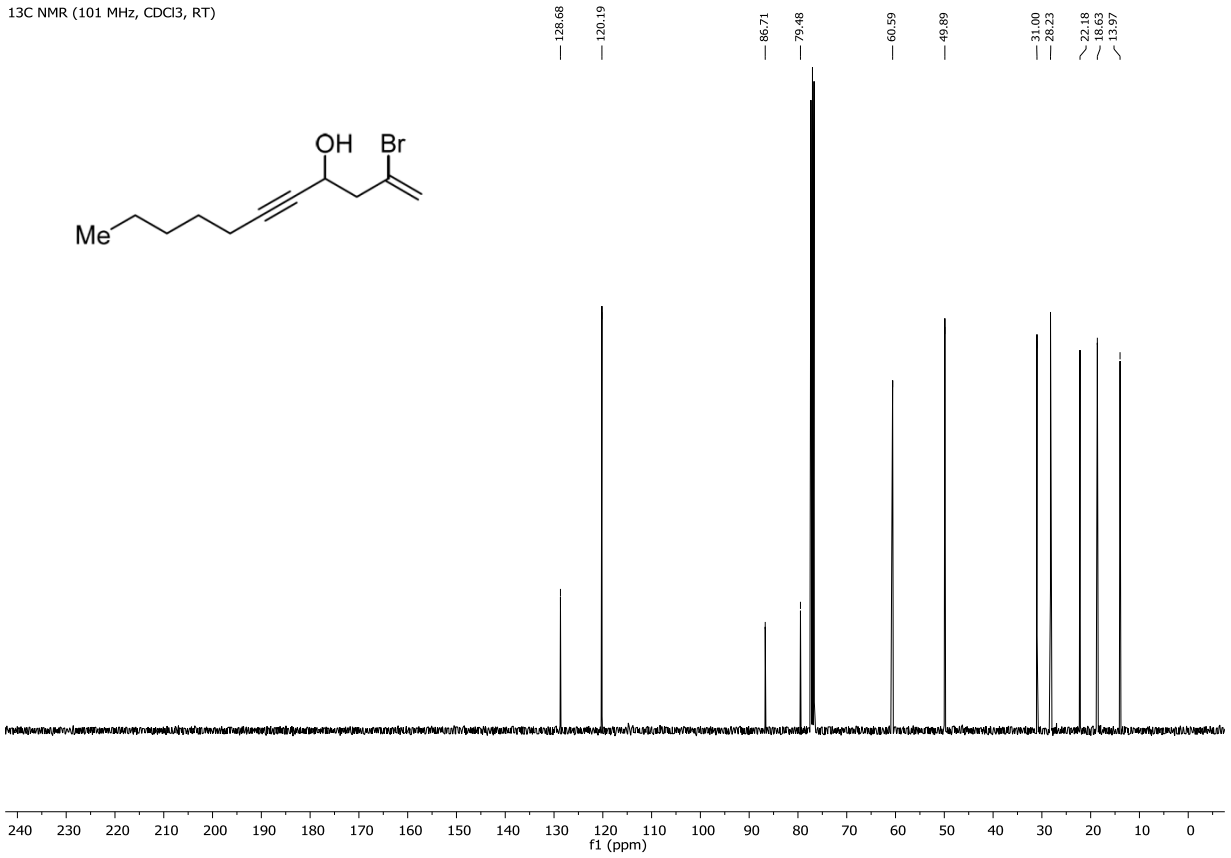
HUR-HA-076-12.0 **15.08.2016**

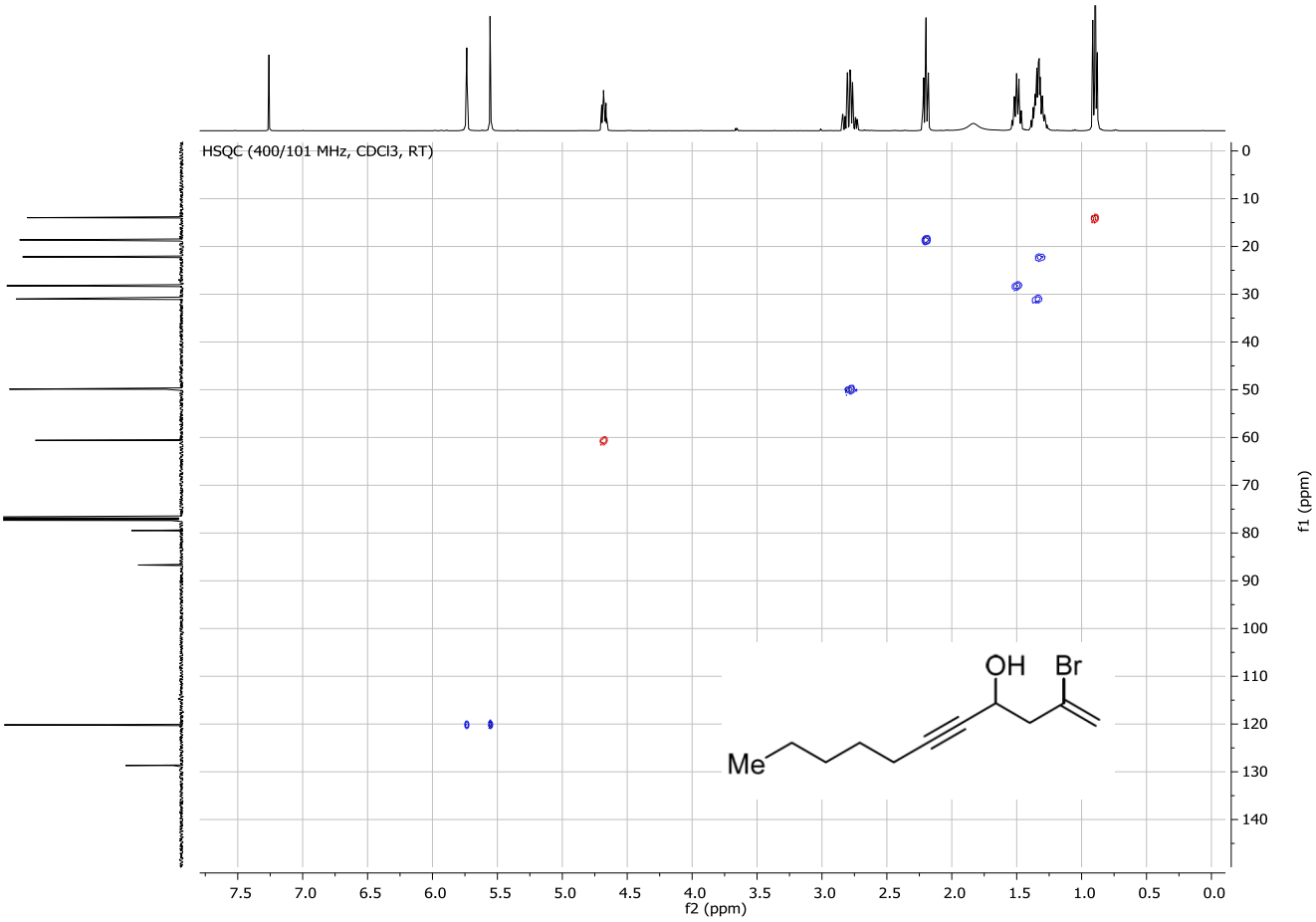


1H NMR (400 MHz, CDCl3, RT)

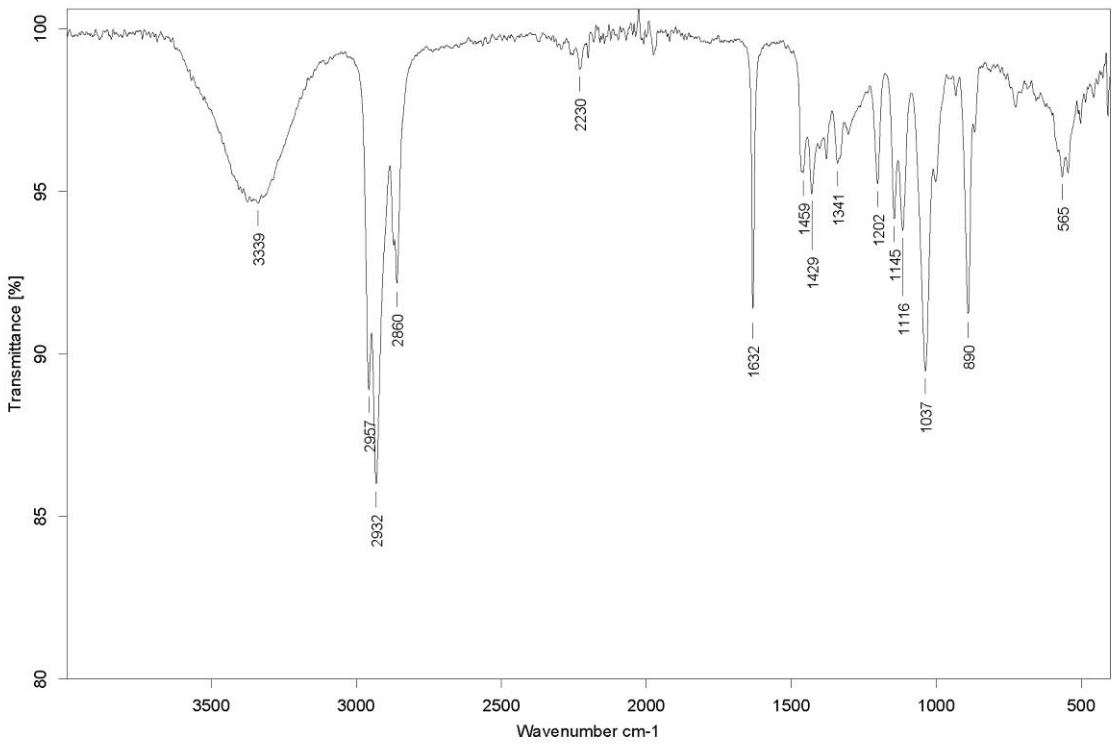


13C NMR (101 MHz, CDCl3, RT)

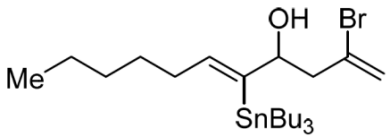




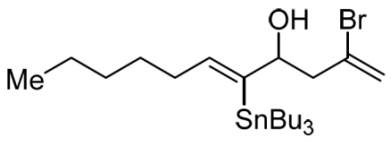
HUR-HA-074-12.0 **16.08.2016**



1H NMR (400 MHz, CDCl3, RT)

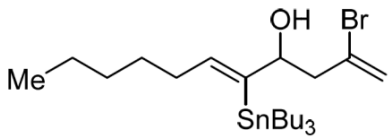


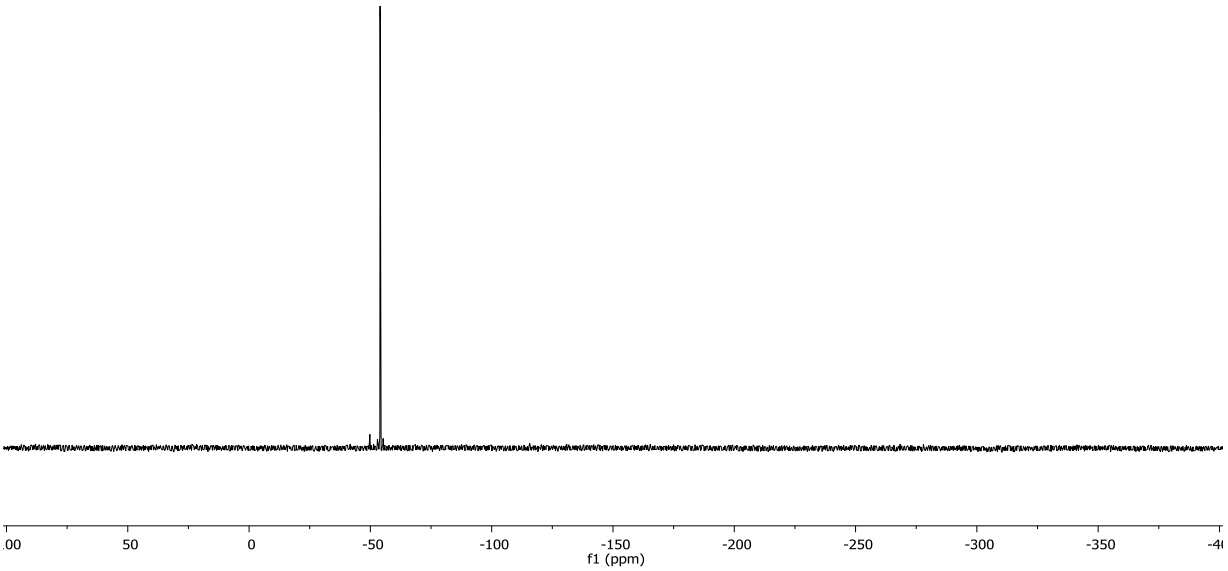
13C NMR (101 MHz, CDCl3, RT)

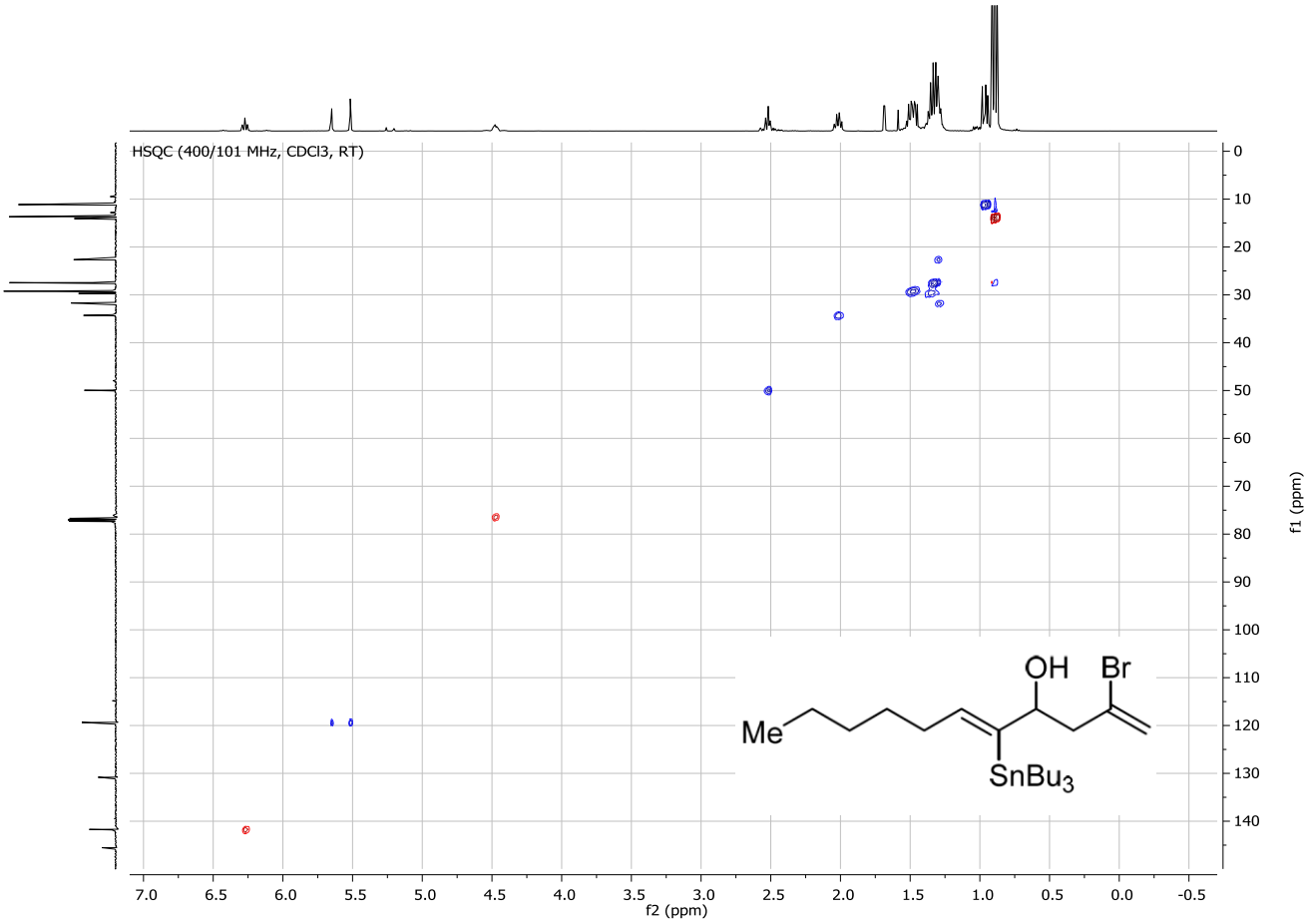


119Sn NMR (149 MHz, CDCl3, RT)

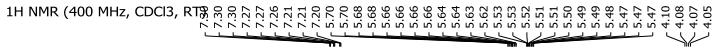
-54.02

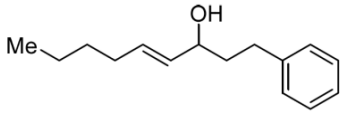


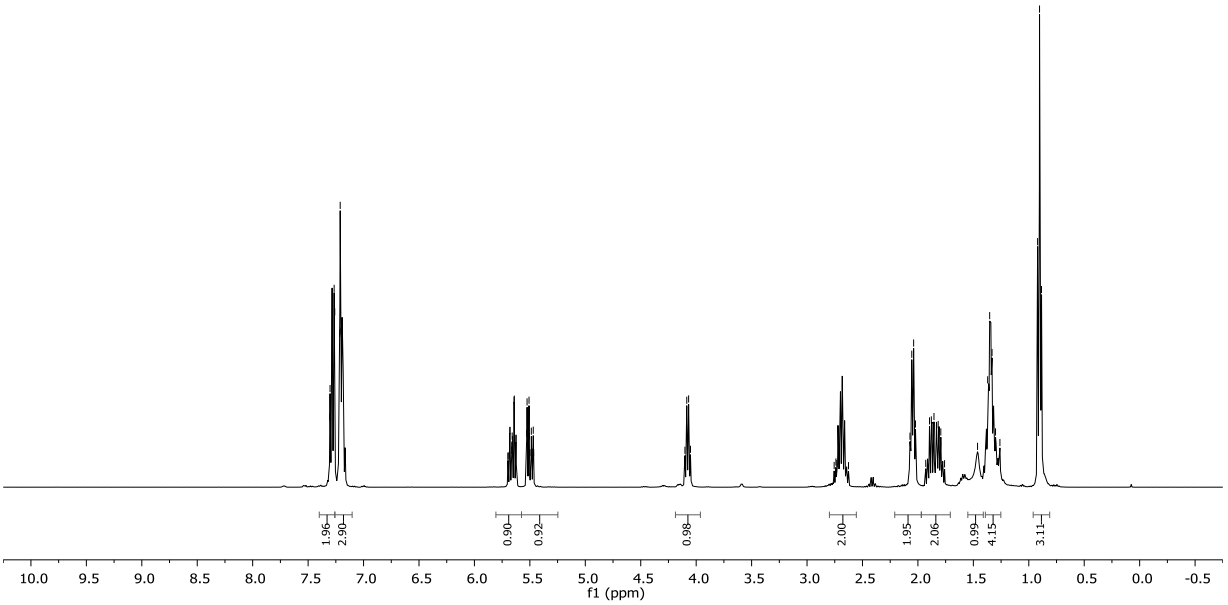




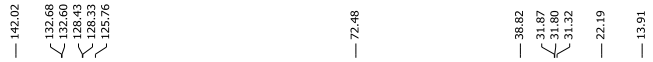
1H NMR (400 MHz, CDCl3, RT)

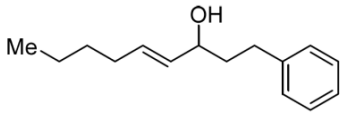


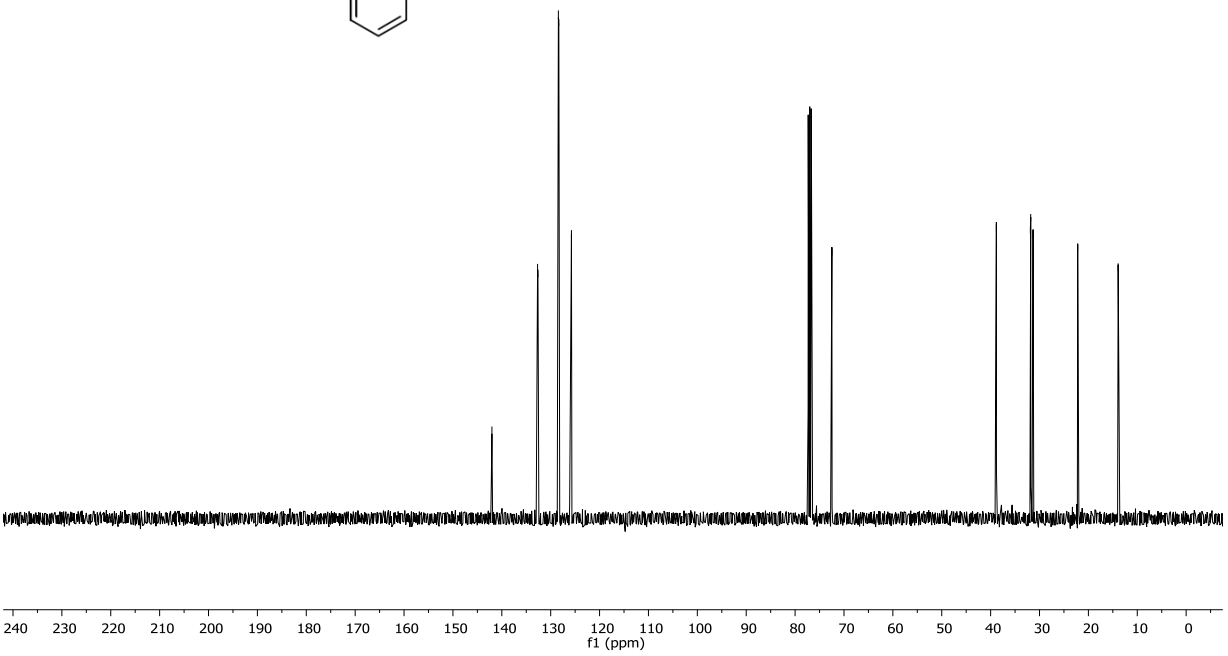


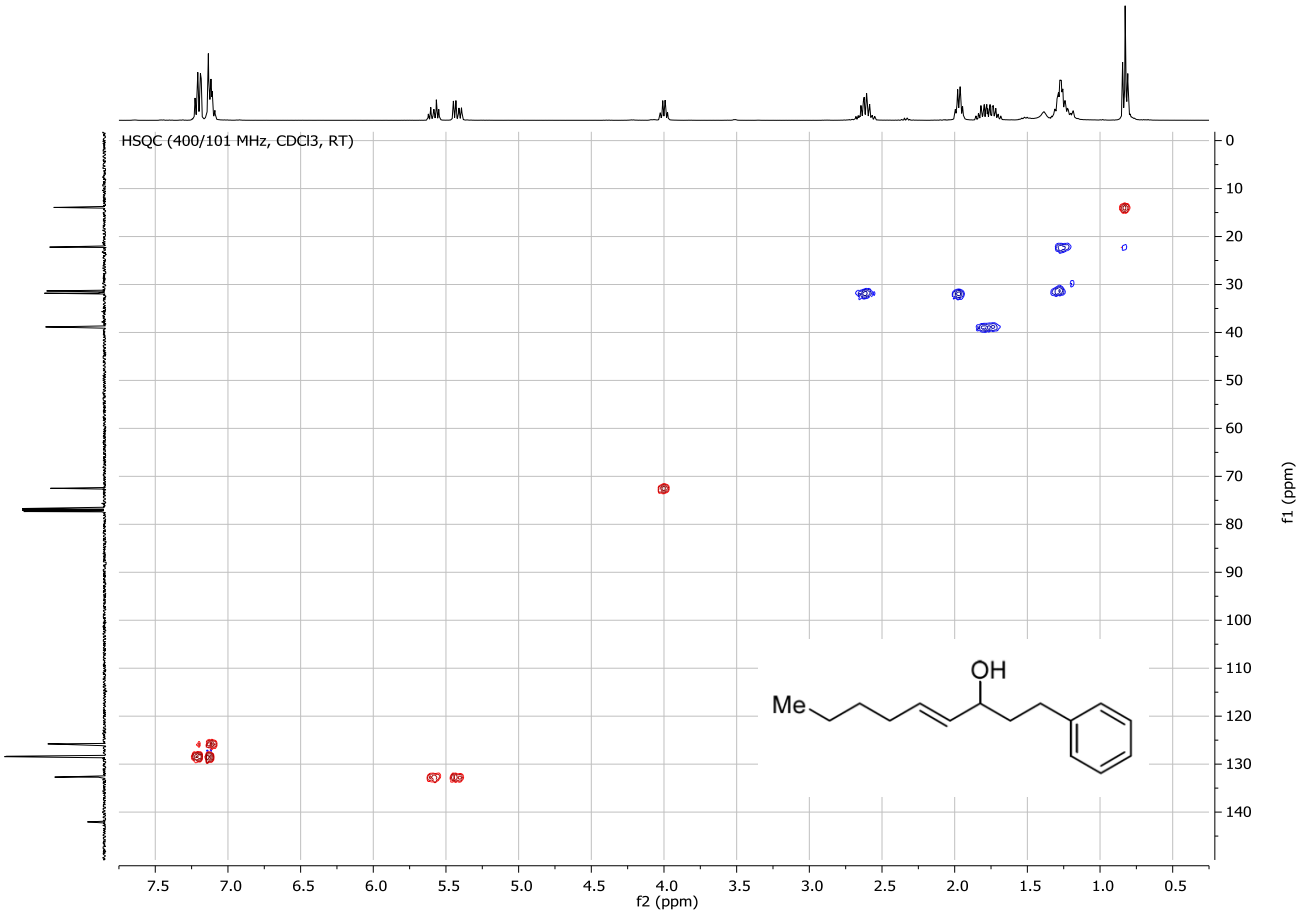


13C NMR (101 MHz, CDCl3, RT)

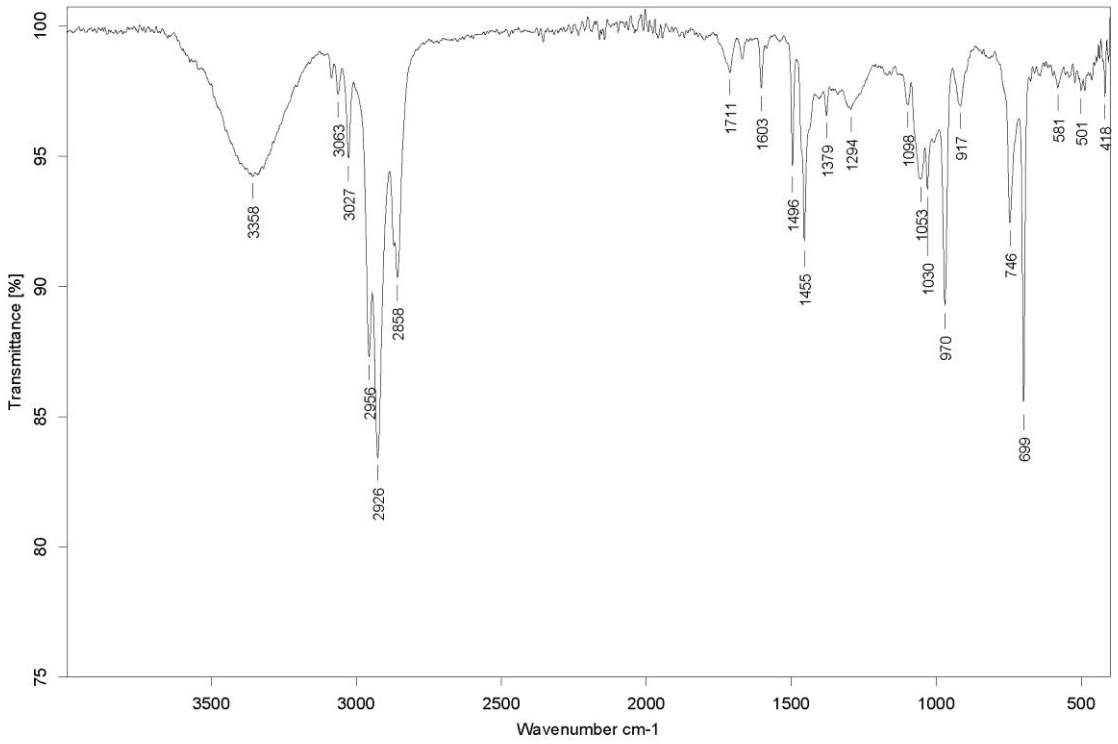




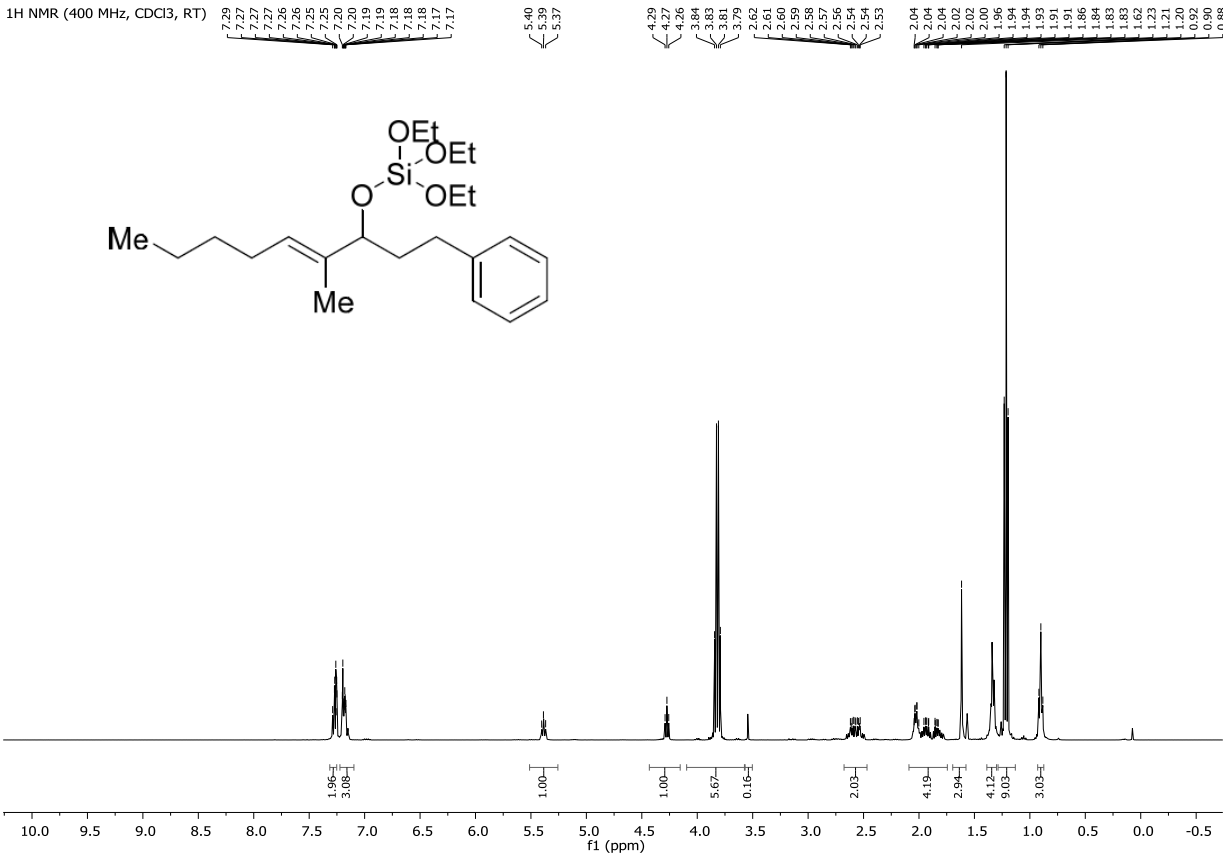




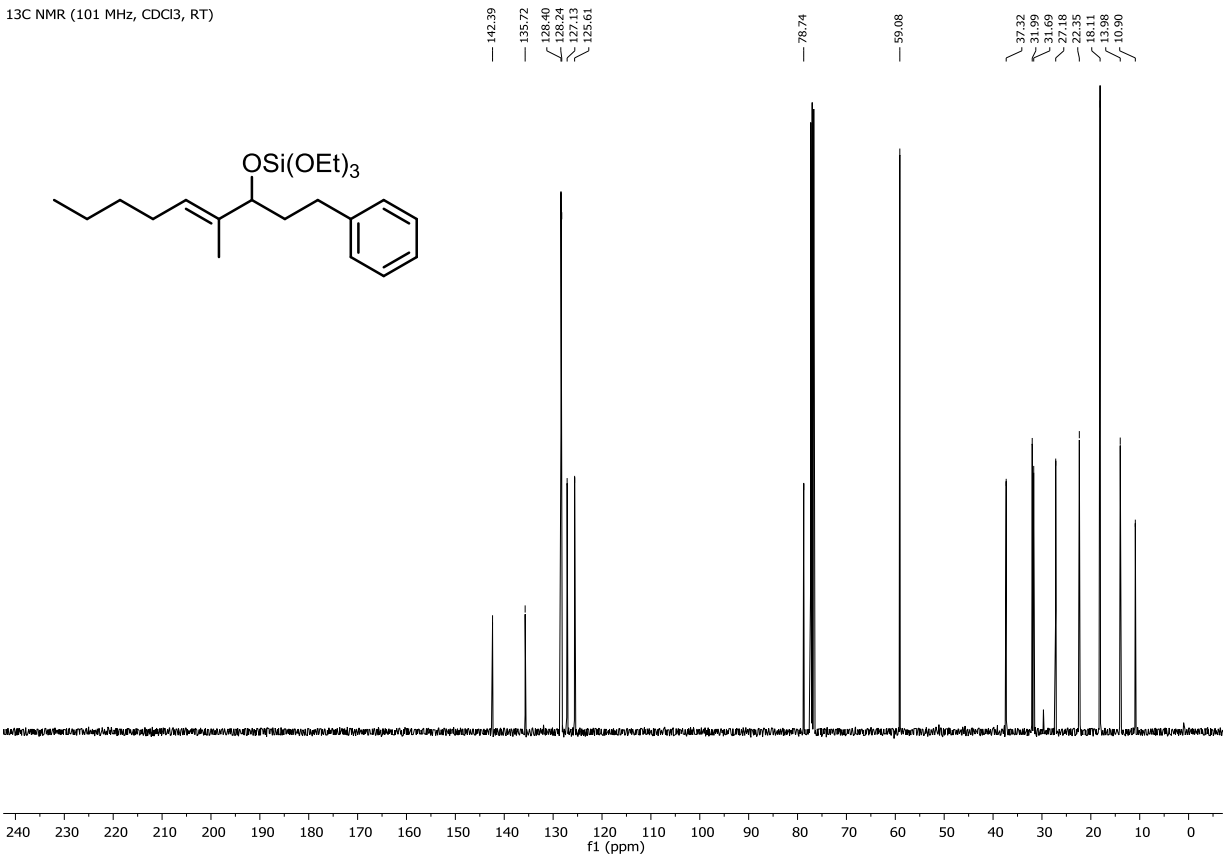
HUR-HA-002-20.0 **01.07.2016**

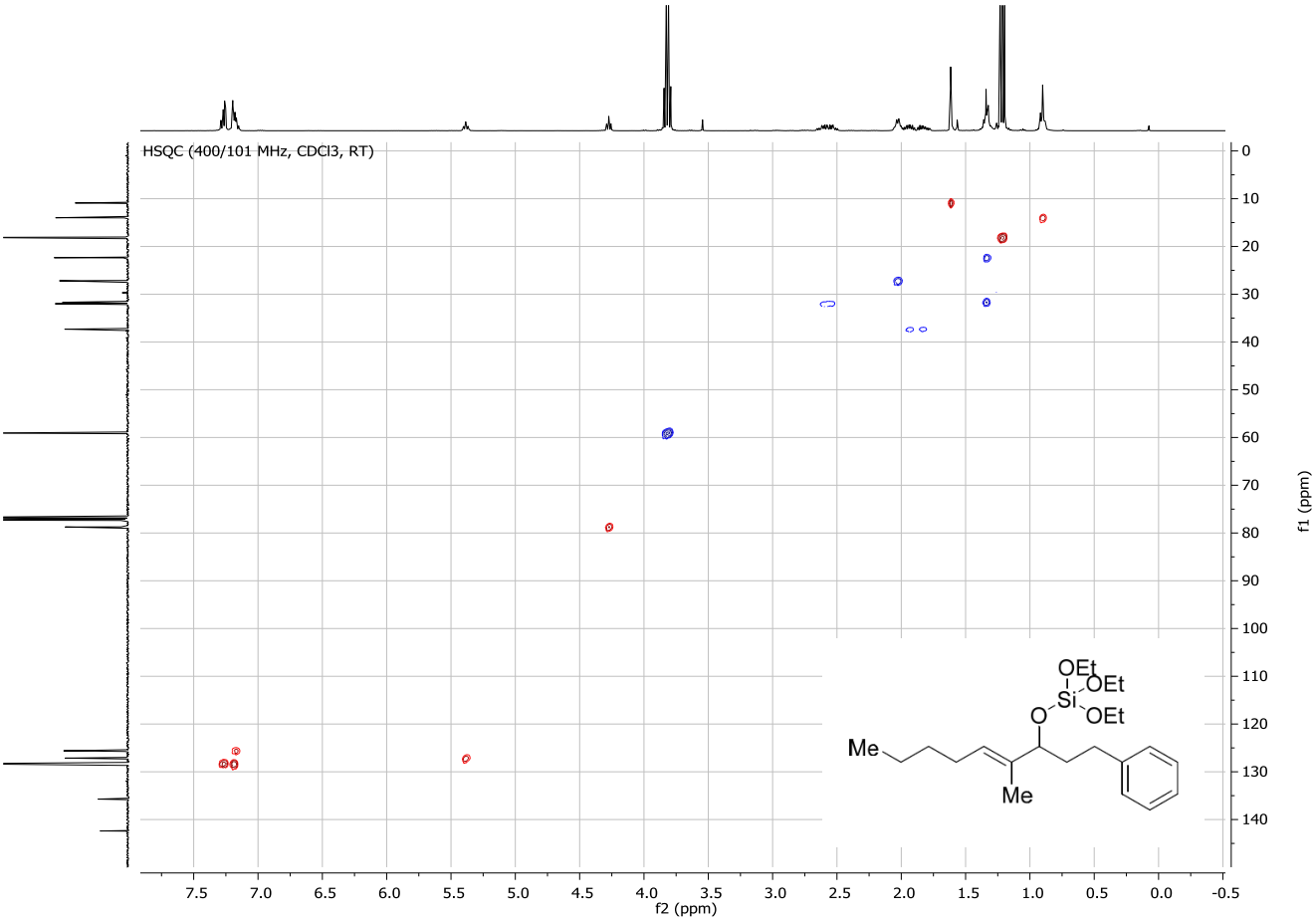


1H NMR (400 MHz, CDCl3, RT)

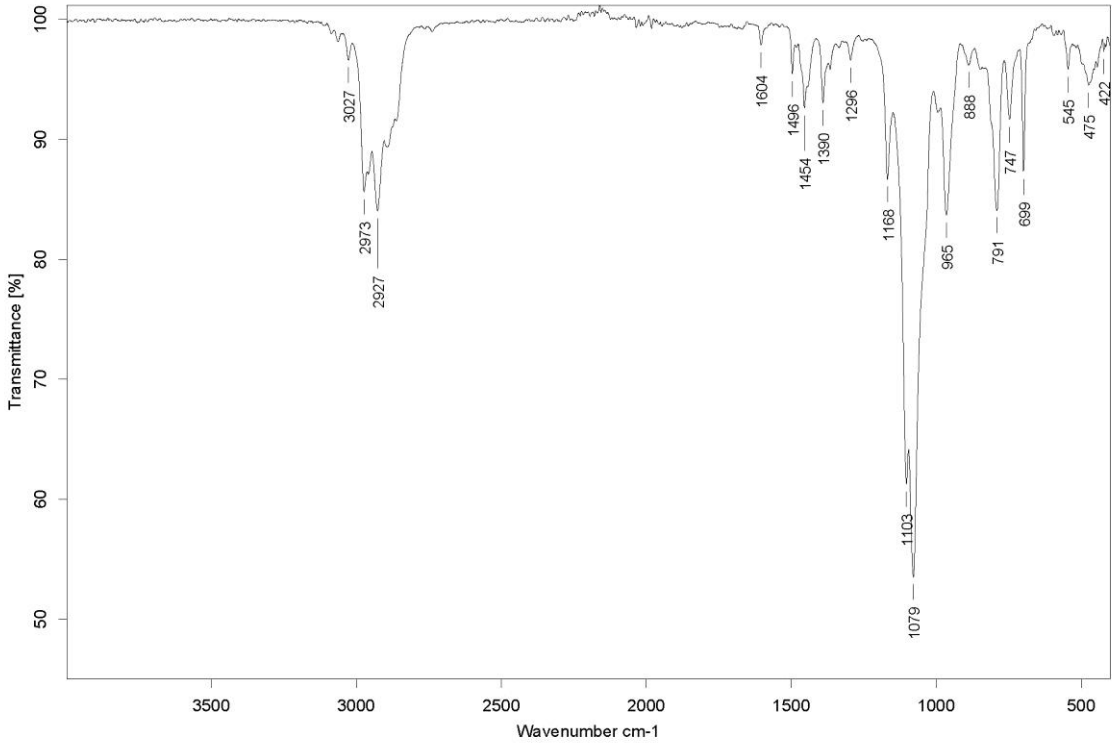


13C NMR (101 MHz, CDCl3, RT)

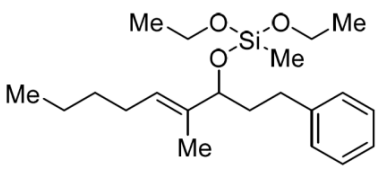




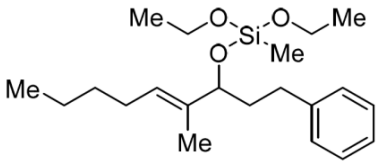
HUR-HA-123-11.0 **09.11.2016**

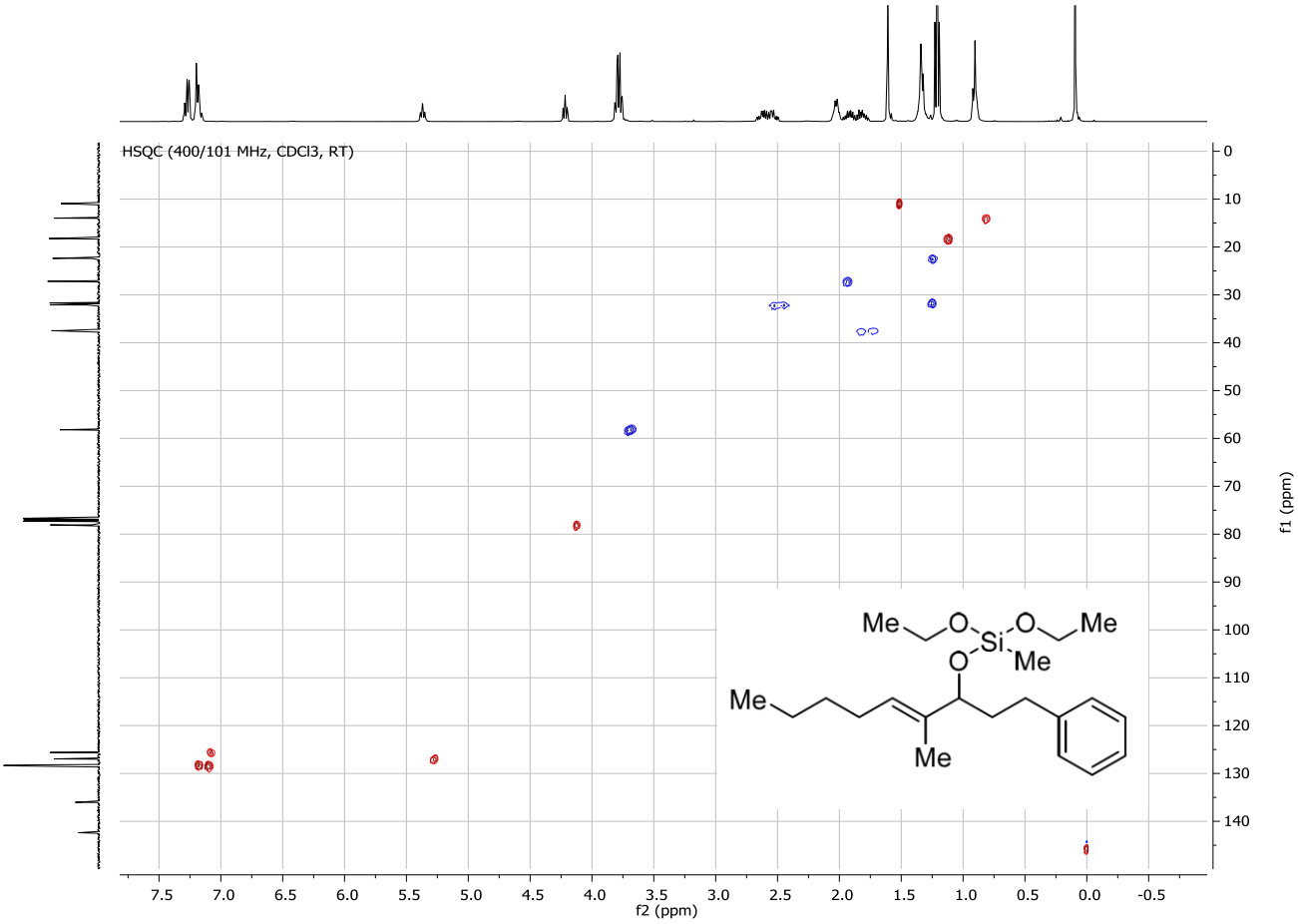


1H NMR (400 MHz, CDCl3, RT)

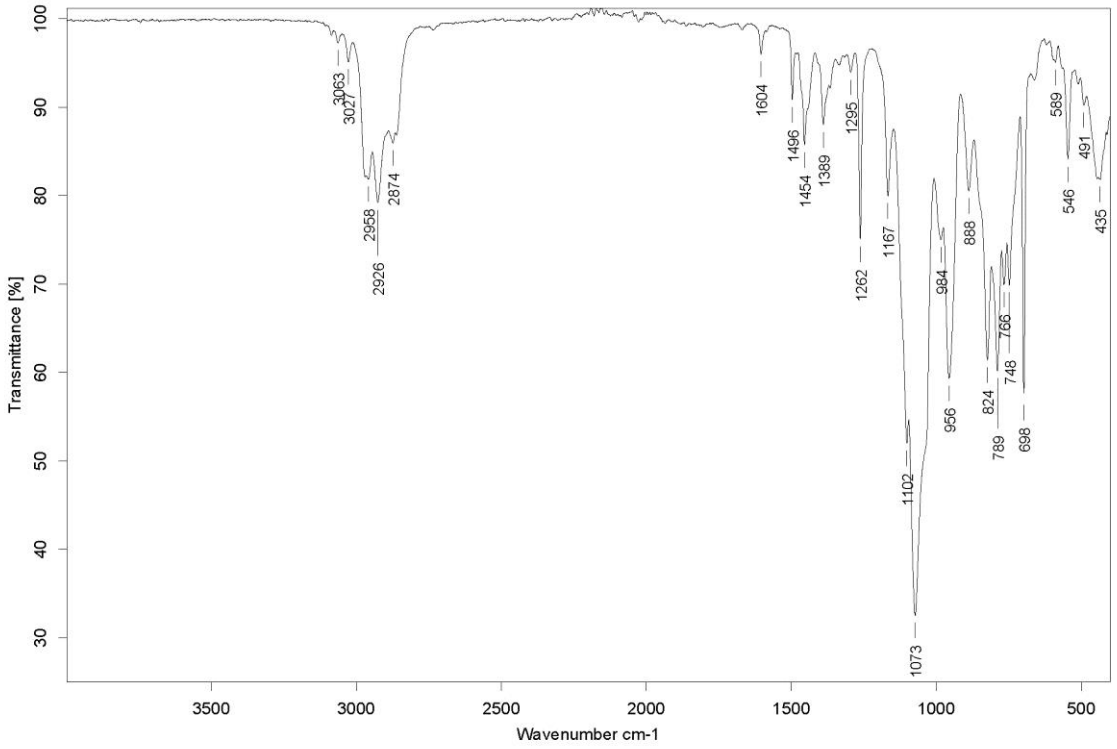


13C NMR (101 MHz, CDCl3, RT)

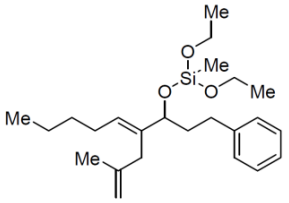




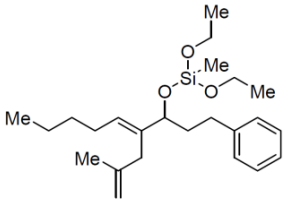
HUR-HA-146-11.0 **15.12.2016**

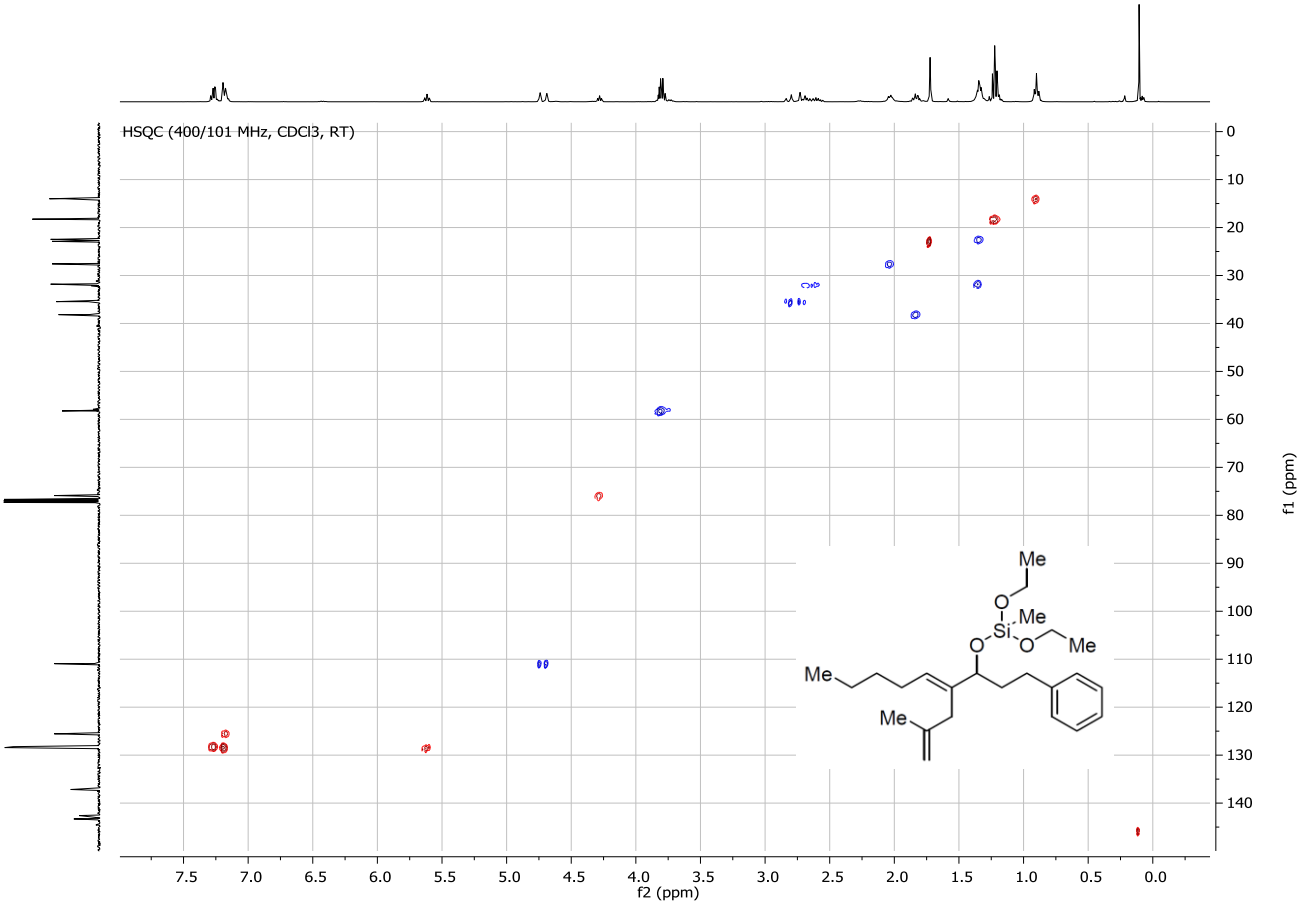


1H NMR (400 MHz, CDCl3, RT)

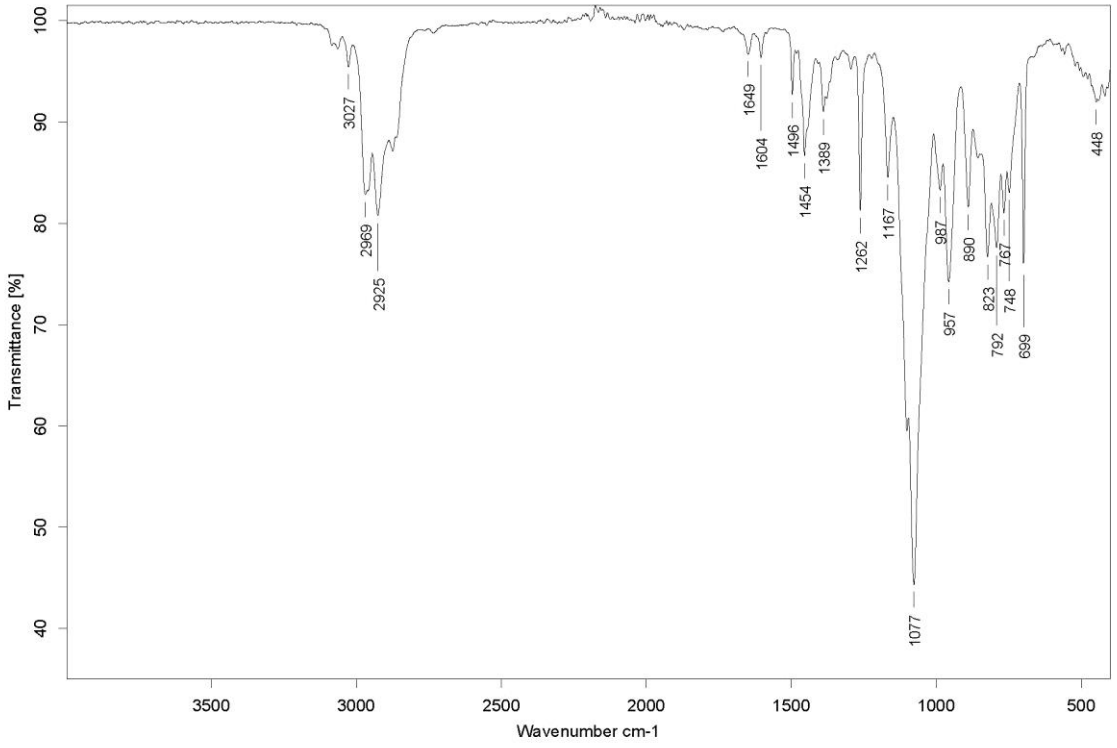


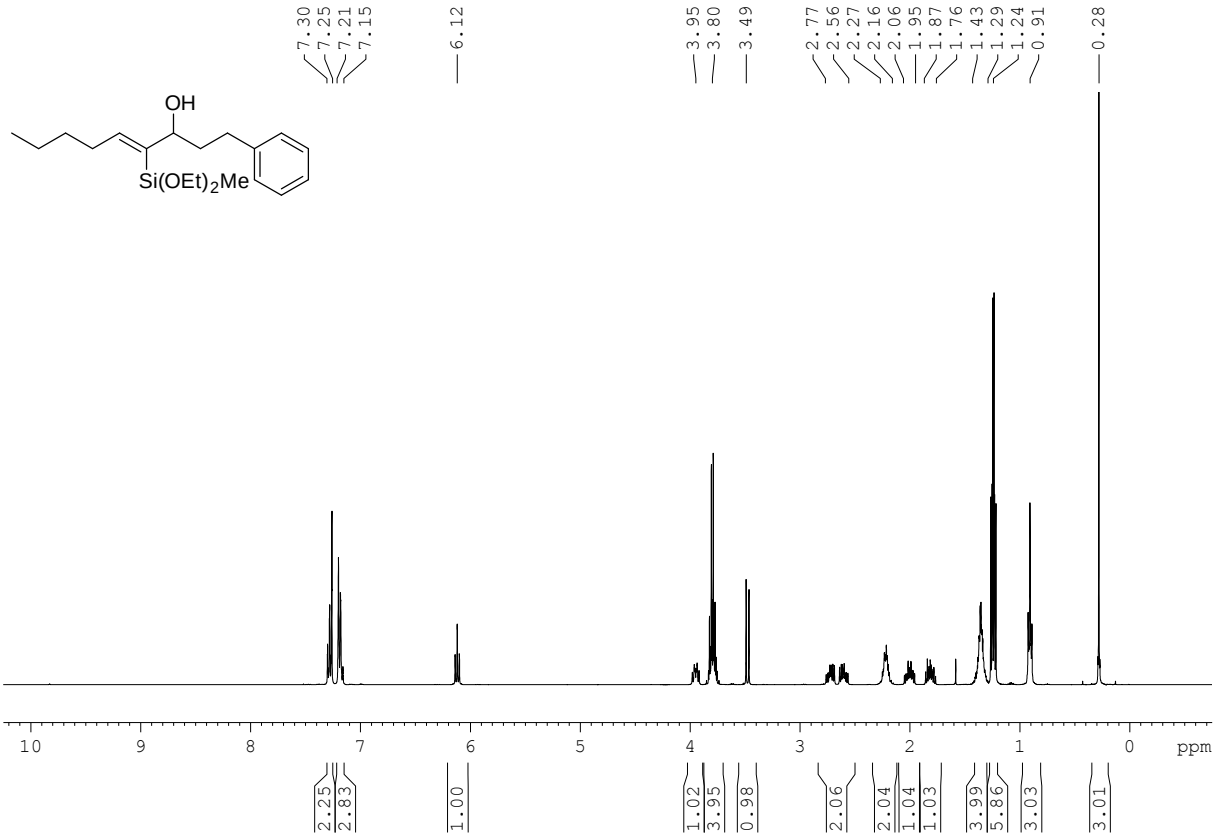
13C NMR (101 MHz, CDCl3, RT)

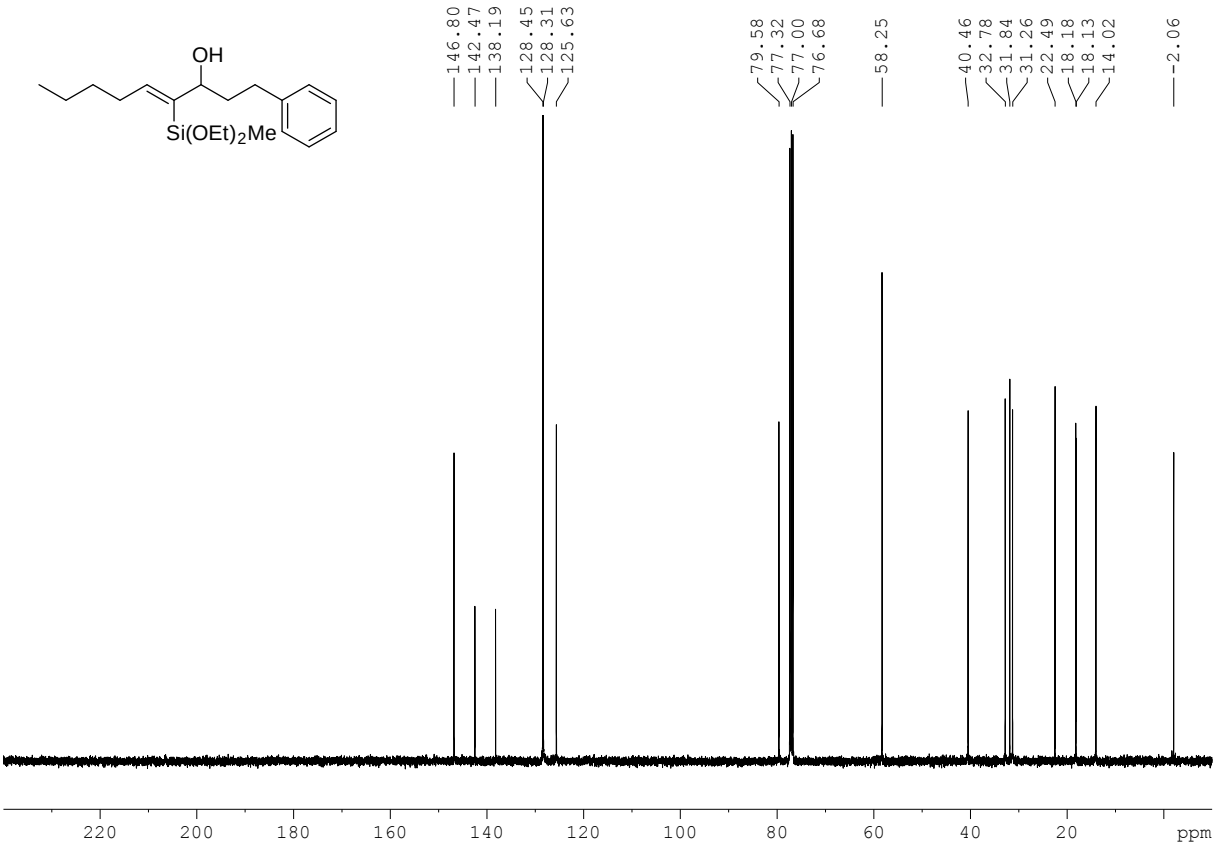


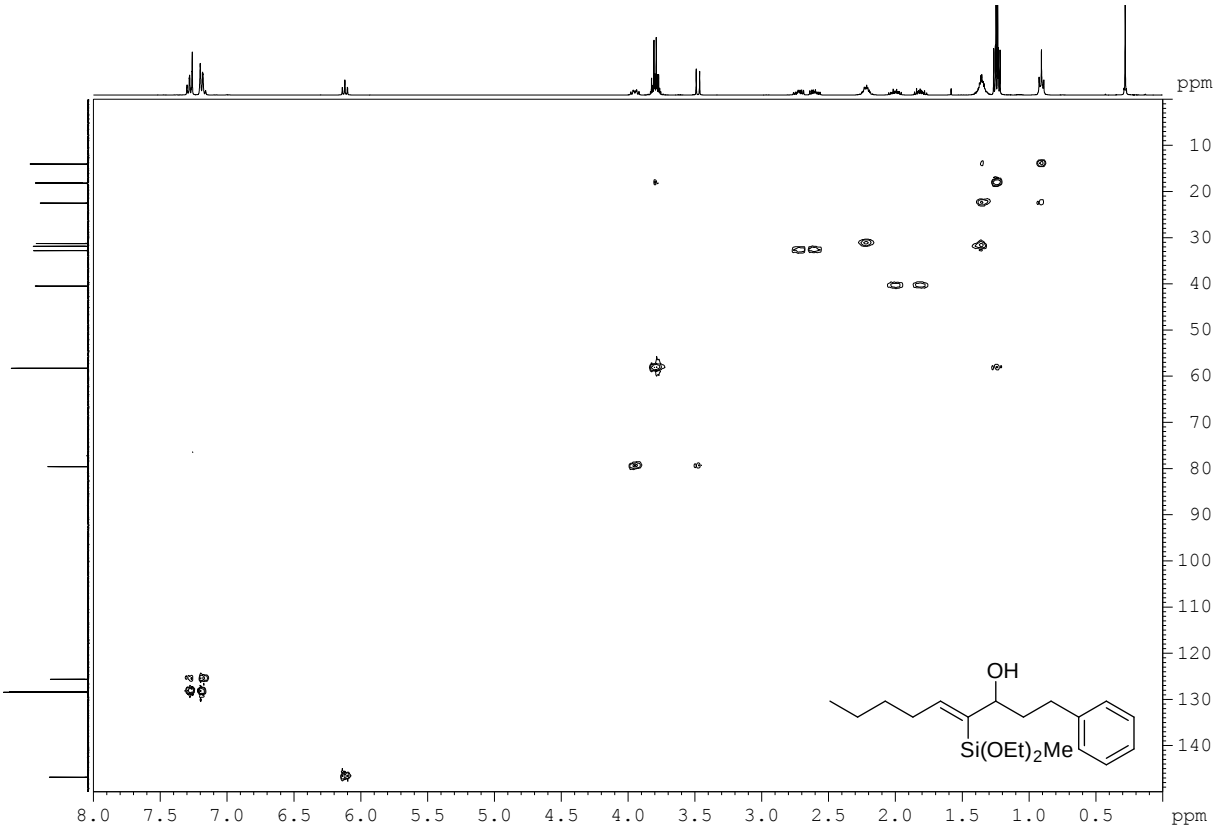


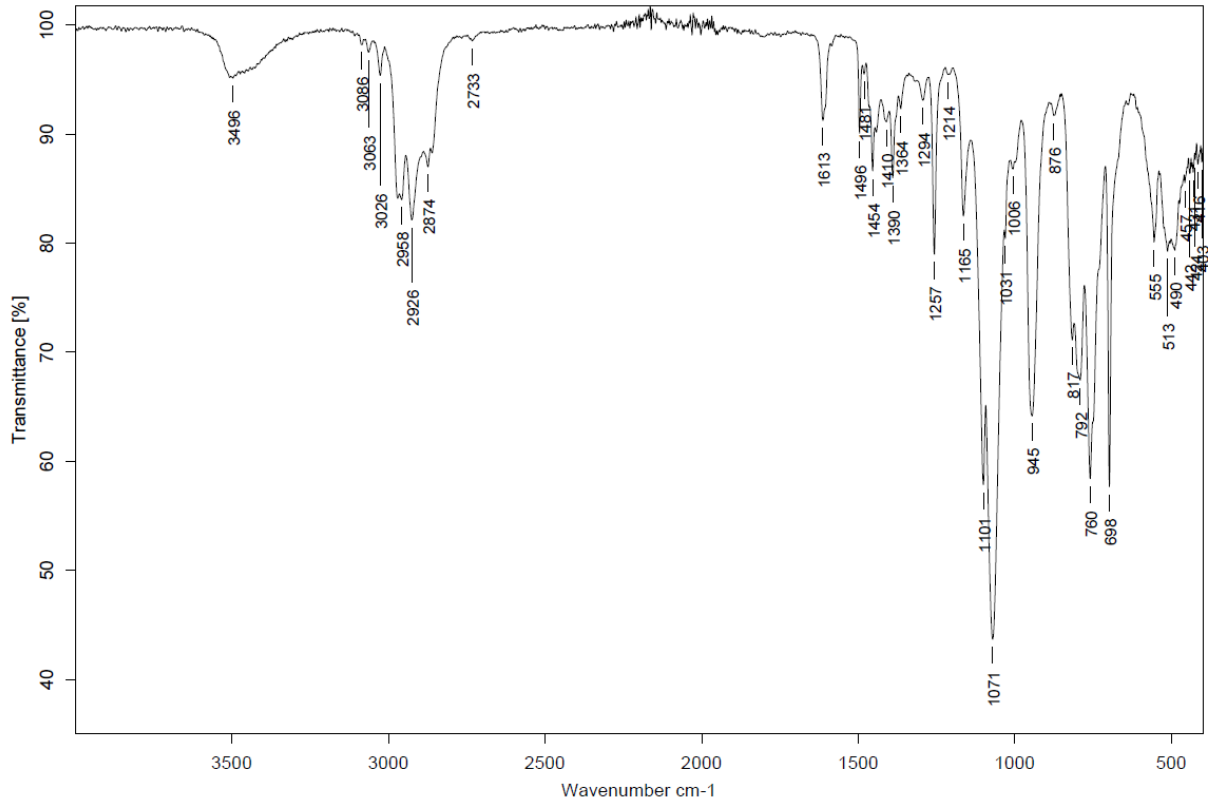
HUR-HA-150-12.0 **20.12.2016**

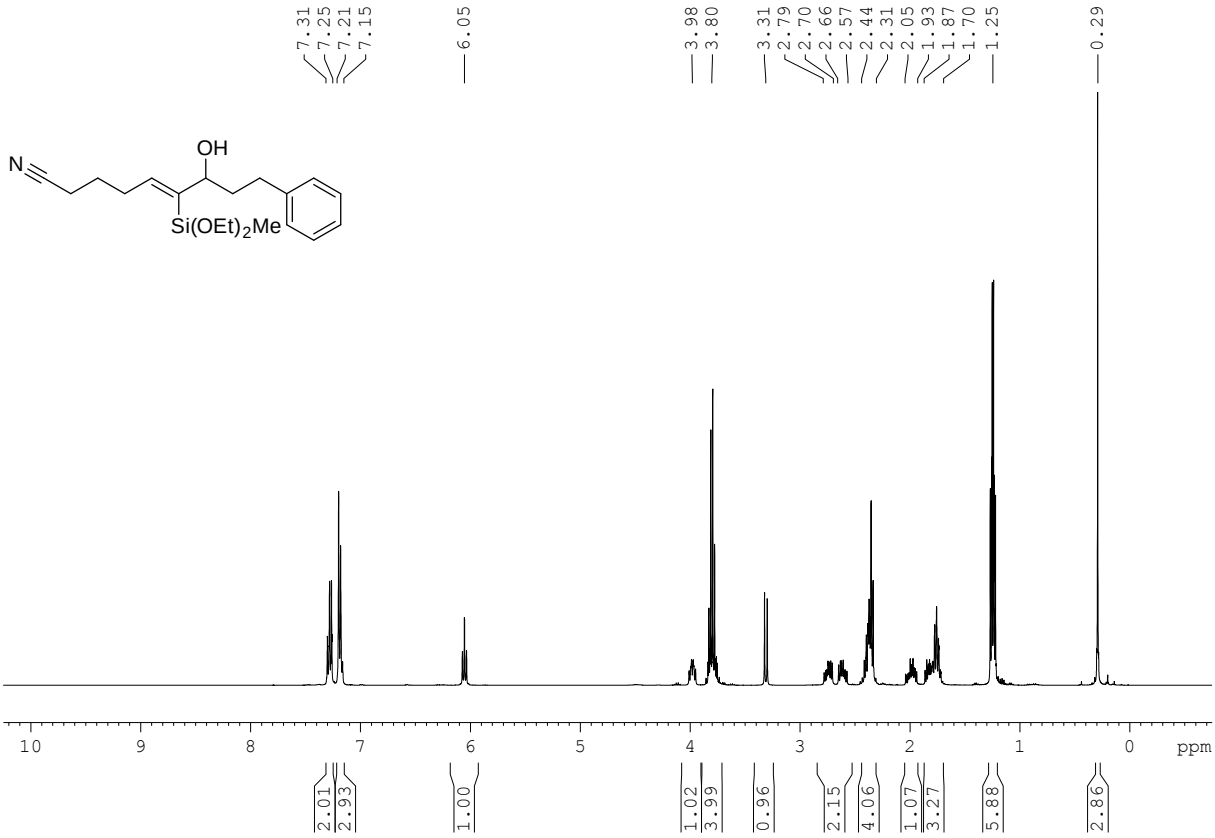


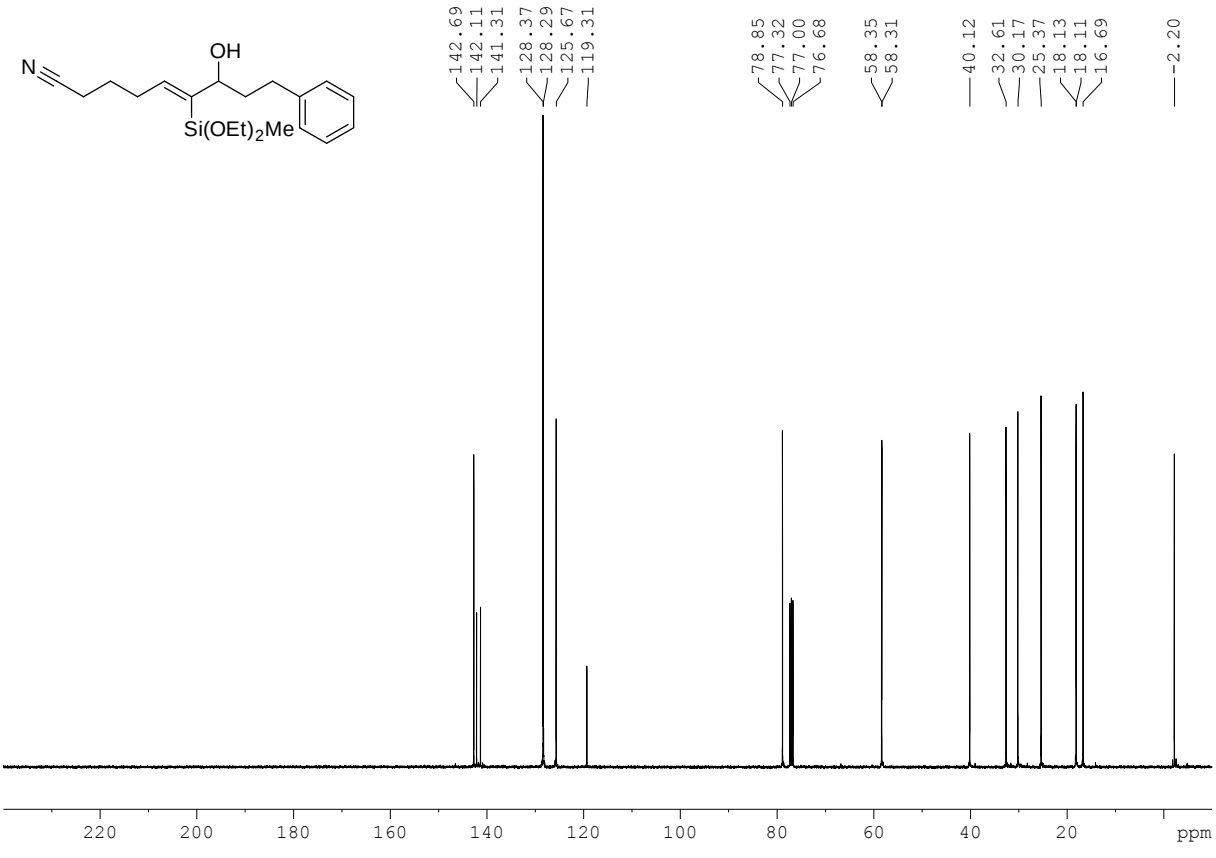

7.30
7.25
7.21
7.15
6.12
3.95
3.80
3.49
2.77
2.56
2.27
2.16
2.06
1.95
1.87
1.76
1.43
1.29
1.24
0.91
0.28
OH
Si(OEt)2Me
10
9
8
7
6
5
4
3
2
1
0
ppm
2.25
2.83
1.00
1.02
3.95
0.98
2.06
2.04
1.04
1.03
3.99
5.86
3.03
3.01

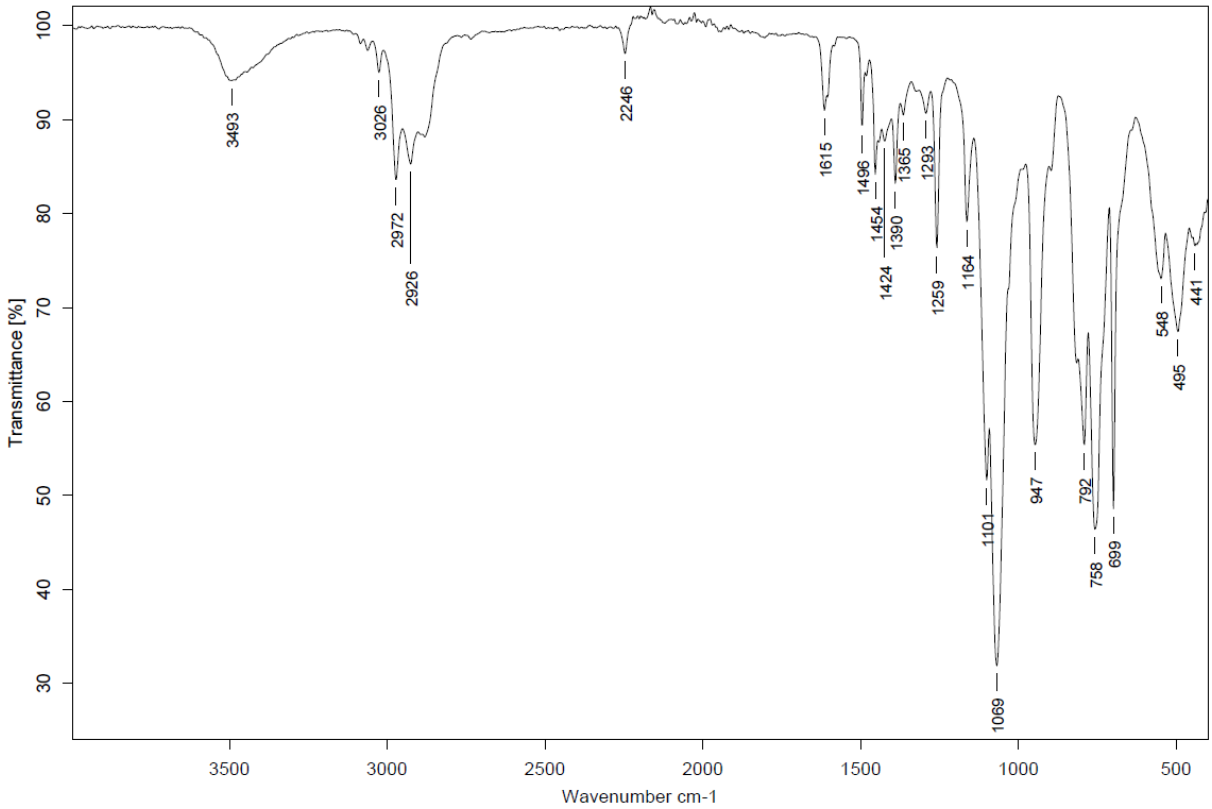

146.80
142.47
138.19
128.45
128.31
125.63
79.58
77.32
77.00
76.68
58.25
40.46
32.78
31.84
31.26
22.49
18.18
18.13
14.02
-2.06
OH
Si(OEt)2Me
220
200
180
160
140
120
100
80
60
40
20
ppm

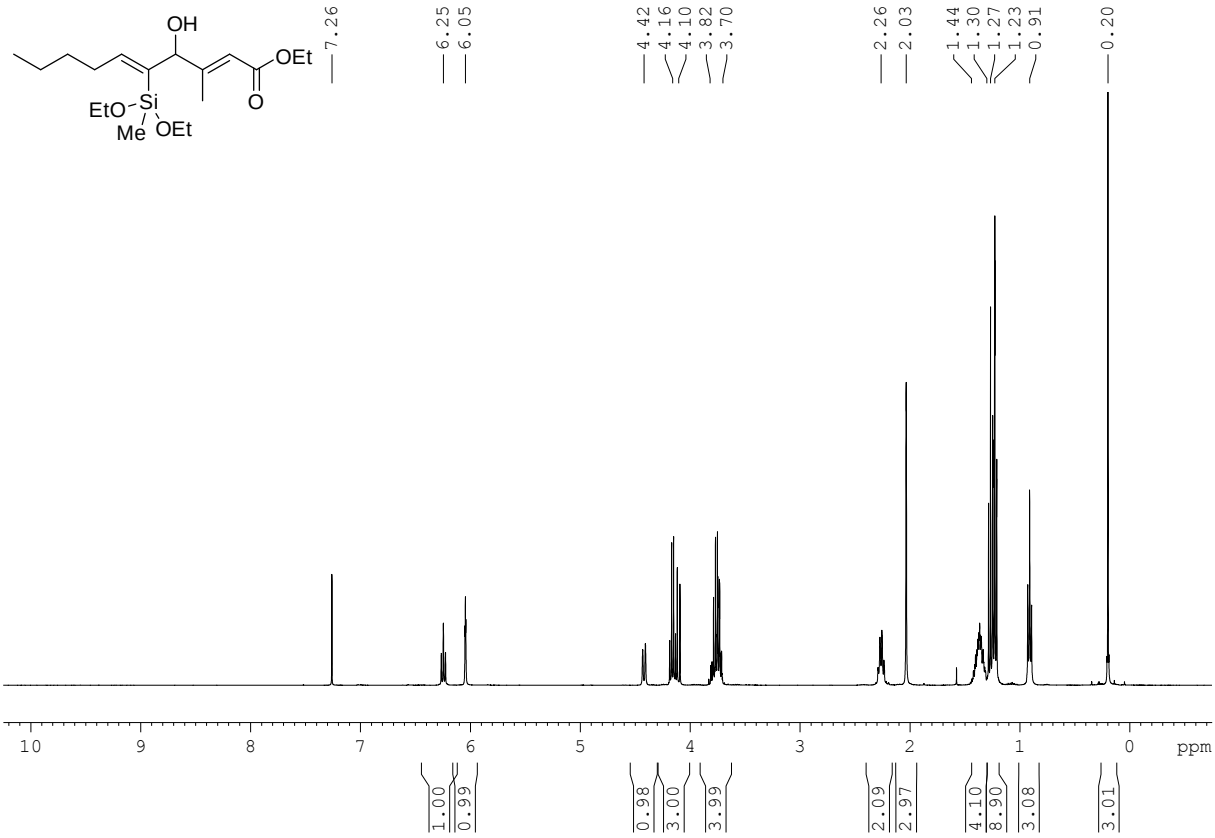

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
OH
Si(OEt)2Me

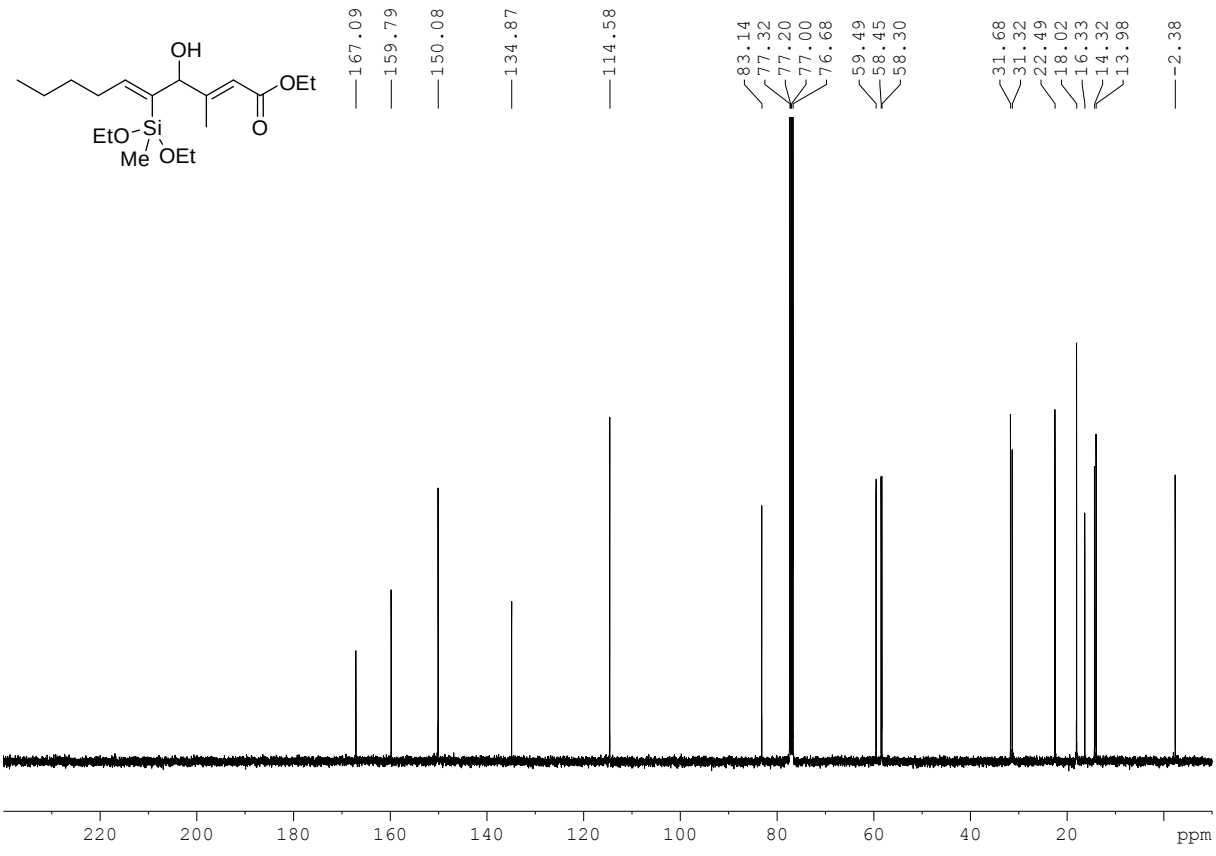

Transmittance [%]
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3496
3086
3063
3026
2958
2926
2874
2733
1613
1496
1481
1454
1410
1390
1364
1294
1257
1214
1165
1101
1071
1031
1006
945
876
817
792
760
698
555
513
490
457

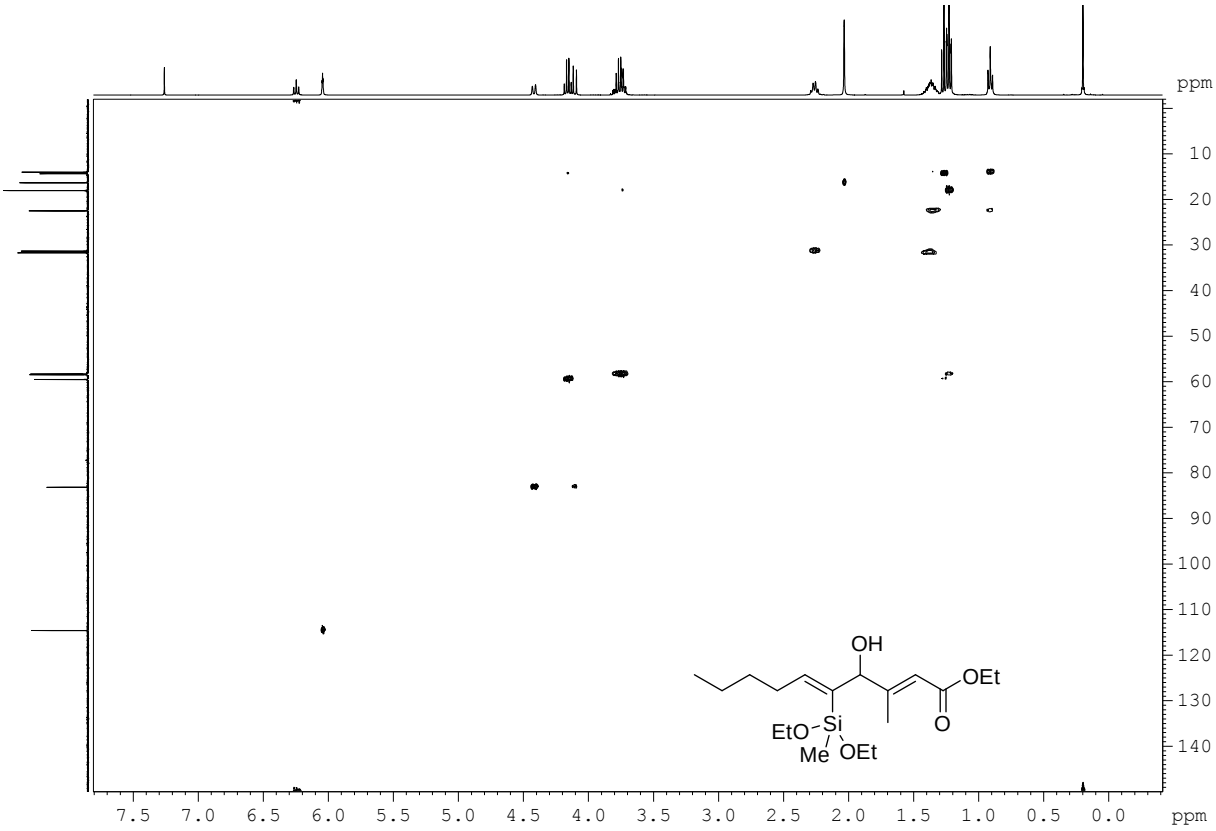

7.31
7.25
7.21
7.15
6.05
3.98
3.80
3.31
2.79
2.70
2.66
2.57
2.44
2.31
2.05
1.93
1.87
1.70
1.25
0.29
OH
N
Si(OEt)2Me
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
2.93
1.00
1.02
3.99
0.96
2.15
4.06
1.07
3.27
5.88
2.86

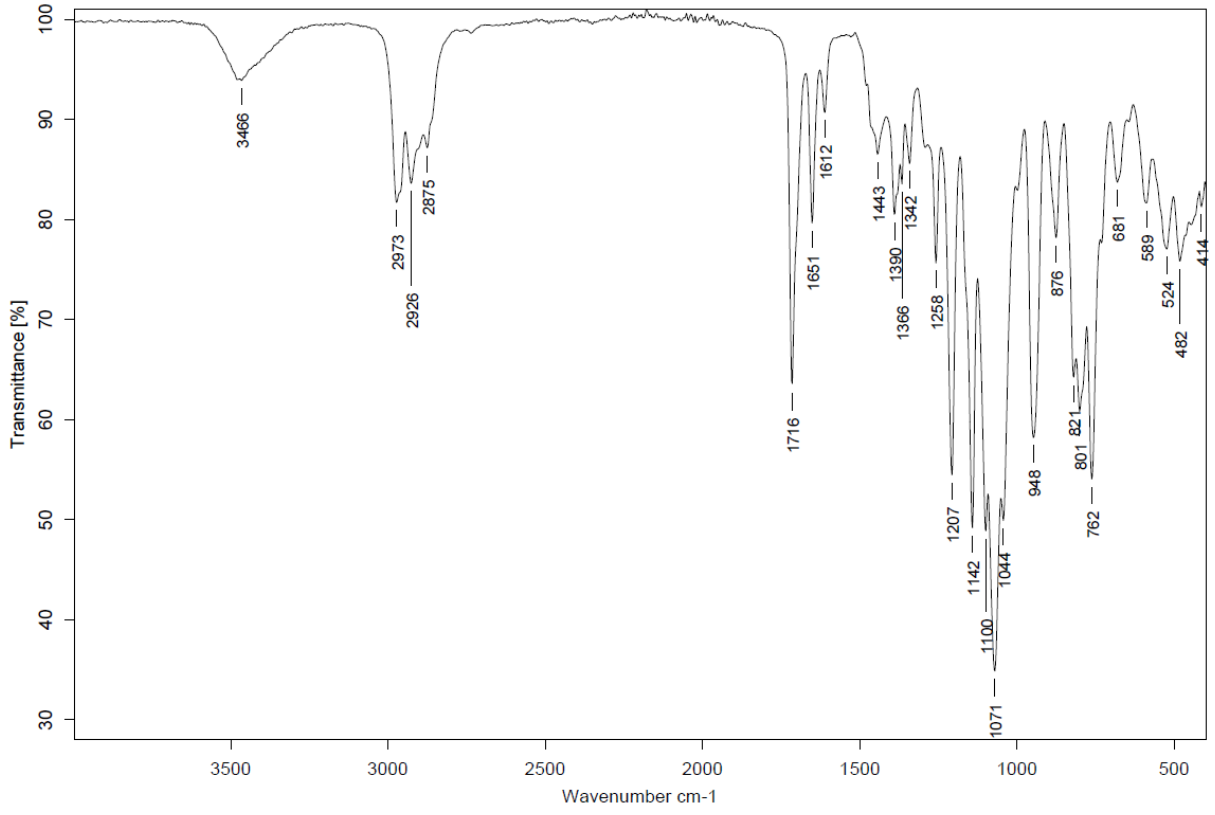

142.69
142.11
141.31
128.37
128.29
125.67
119.31
78.85
77.32
77.00
76.68
58.35
58.31
40.12
32.61
30.17
25.37
18.13
18.11
16.69
-2.20
OH
N
Si(OEt)2Me
220
200
180
160
140
120
100
80
60
40
20
ppm

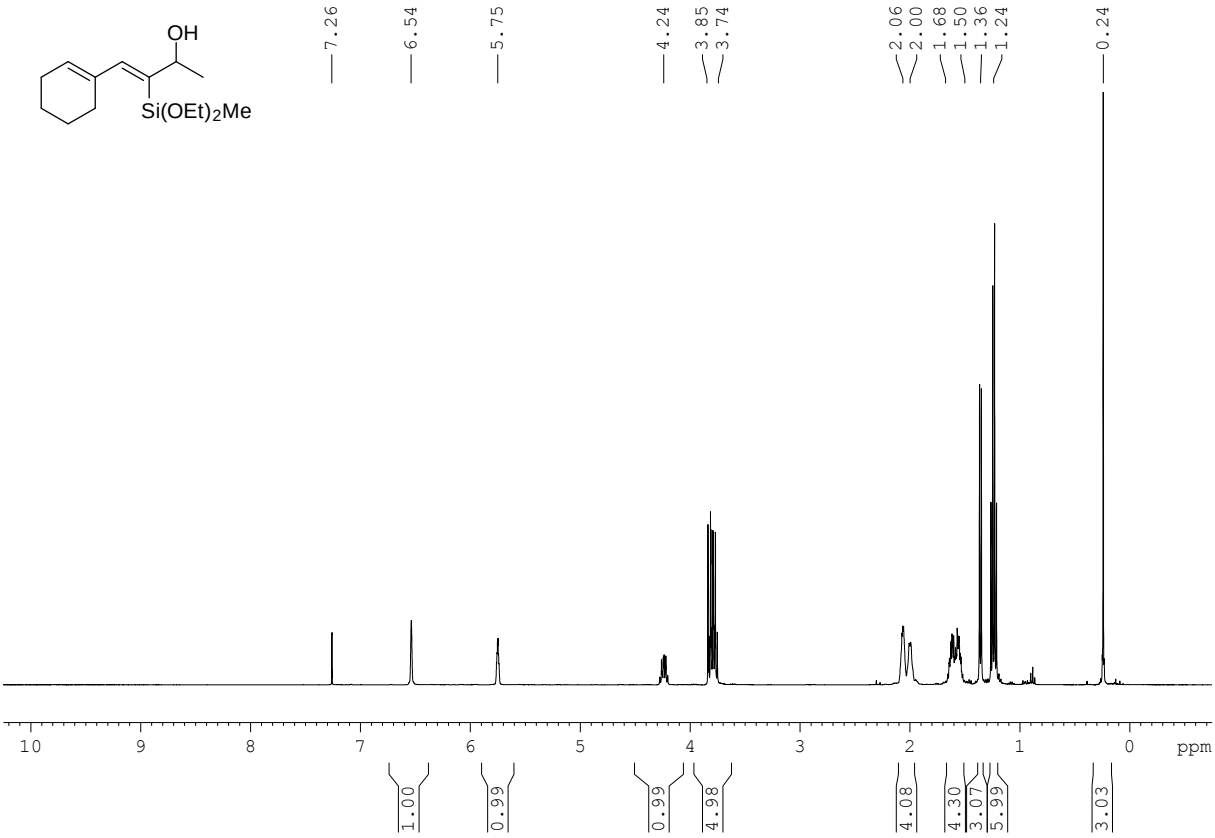

Transmittance [%]
100
90
80
70
60
50
40
30
3493
3026
2972
2926
2246
1615
1496
1454
1424
1390
1365
1293
1259
1164
1101
1069
947
792
758
699
548
495
441
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

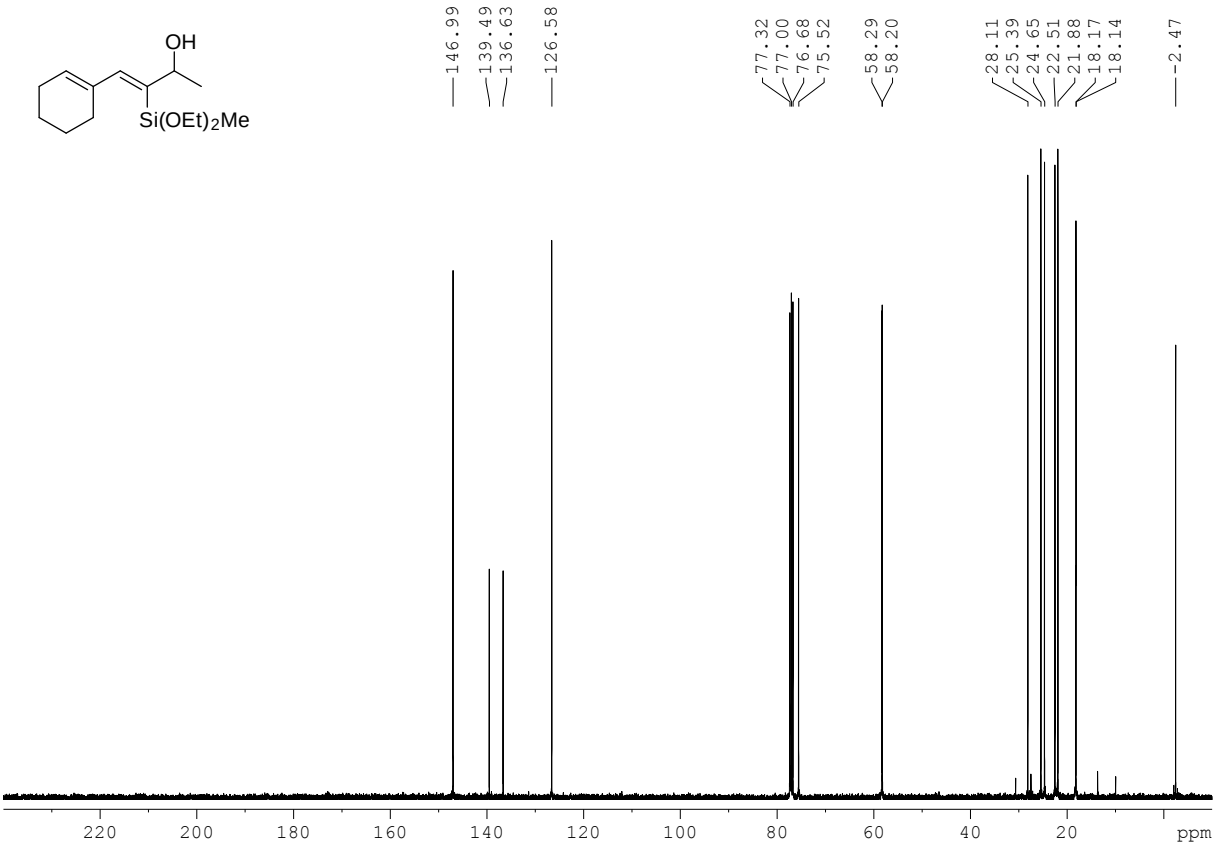

OH
OEt
O
EtO
Si
Me
OEt
7.26
6.25
6.05
4.42
4.16
4.10
3.82
3.70
2.26
2.03
1.44
1.30
1.27
1.23
0.91
0.20
ppm
1.00
0.99
0.98
3.00
3.99
2.09
2.97
4.10
8.90
3.08
3.01

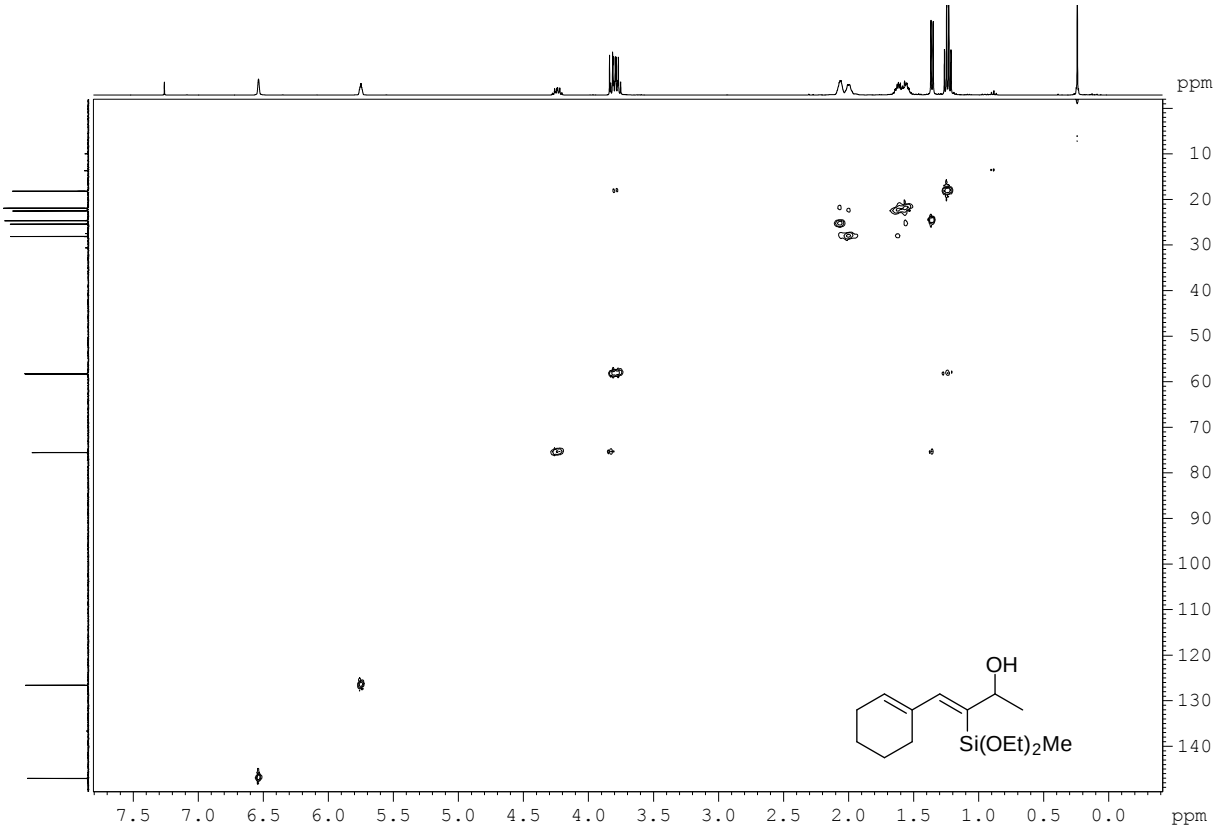

OH
OEt
O
EtO
Si
Me
OEt
167.09
159.79
150.08
134.87
114.58
83.14
77.32
77.20
77.00
76.68
59.49
58.45
58.30
31.68
31.32
22.49
18.02
16.33
14.32
13.98
-2.38
ppm

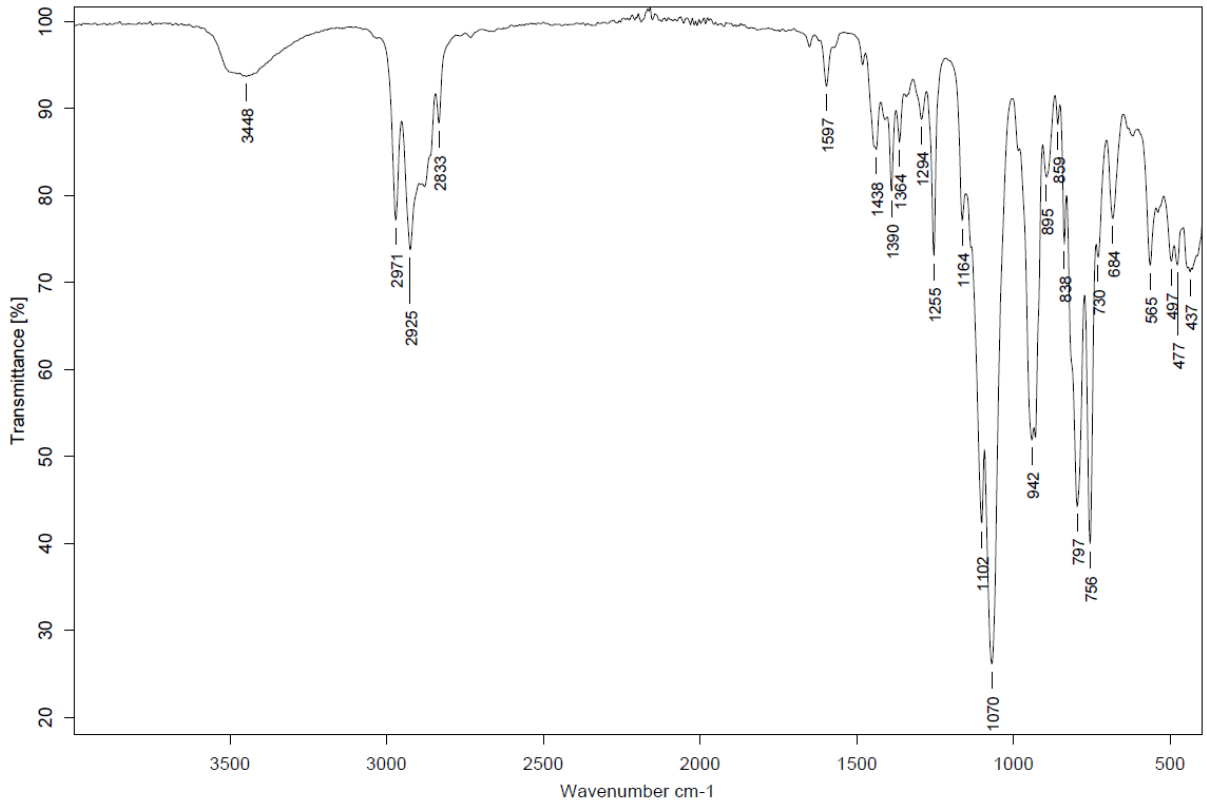

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
OH
OEt
O
EtO
Si
Me
OEt

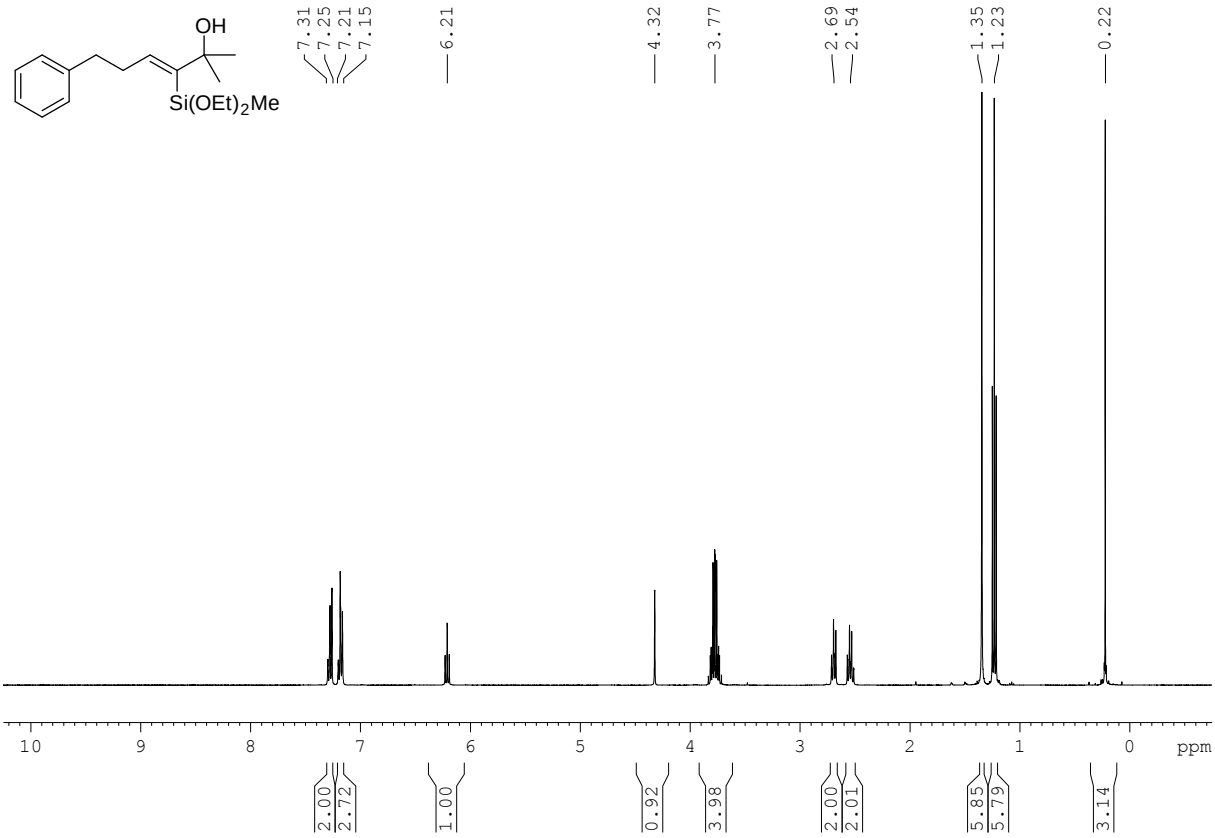

Transmittance [%]
100
90
80
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3466
2973
2926
2875
1716
1651
1612
1443
1390
1366
1342
1258
1207
1142
1100
1071
1044
948
876
821
801
762
681
589
524
482
414

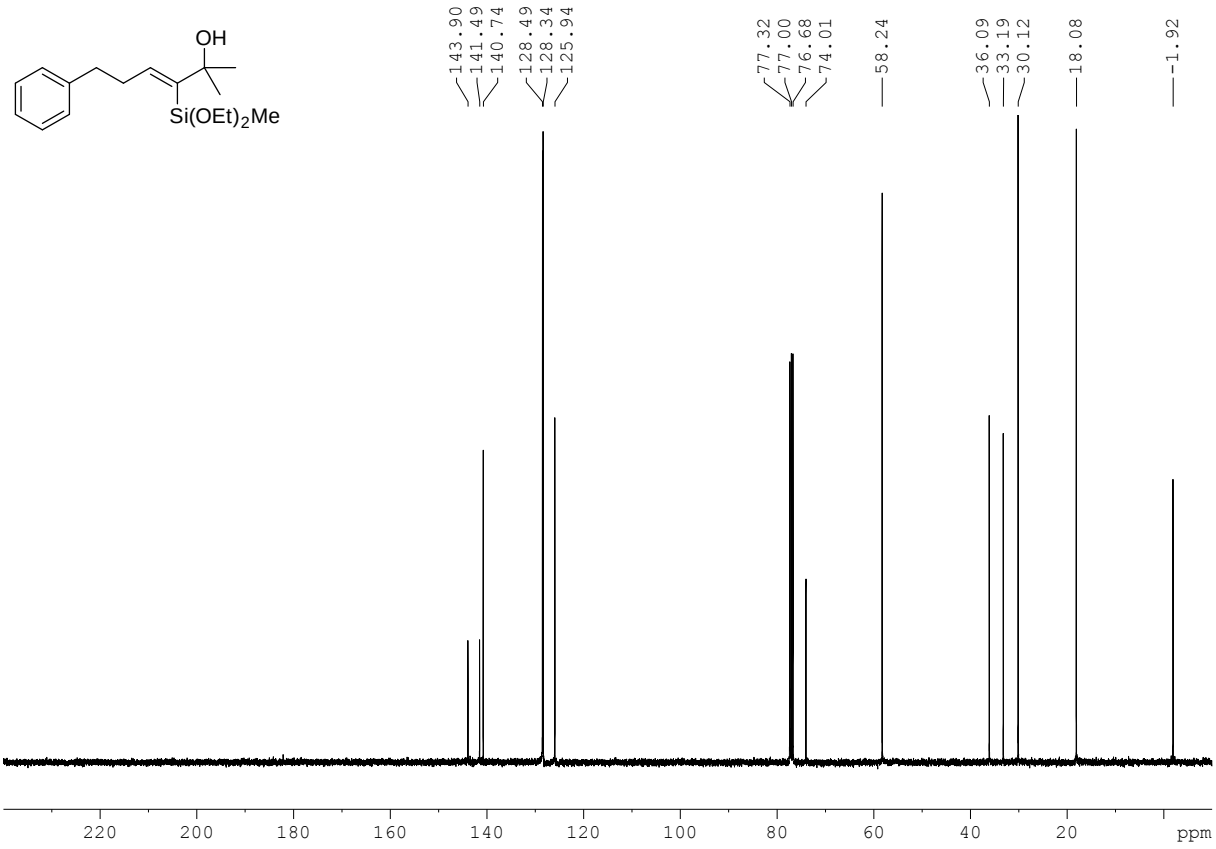

OH
Si(OEt)2Me
7.26
6.54
5.75
4.24
3.85
3.74
2.06
2.00
1.68
1.50
1.36
1.24
0.24
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
0.99
4.98
4.08
4.30
3.07
5.99
3.03

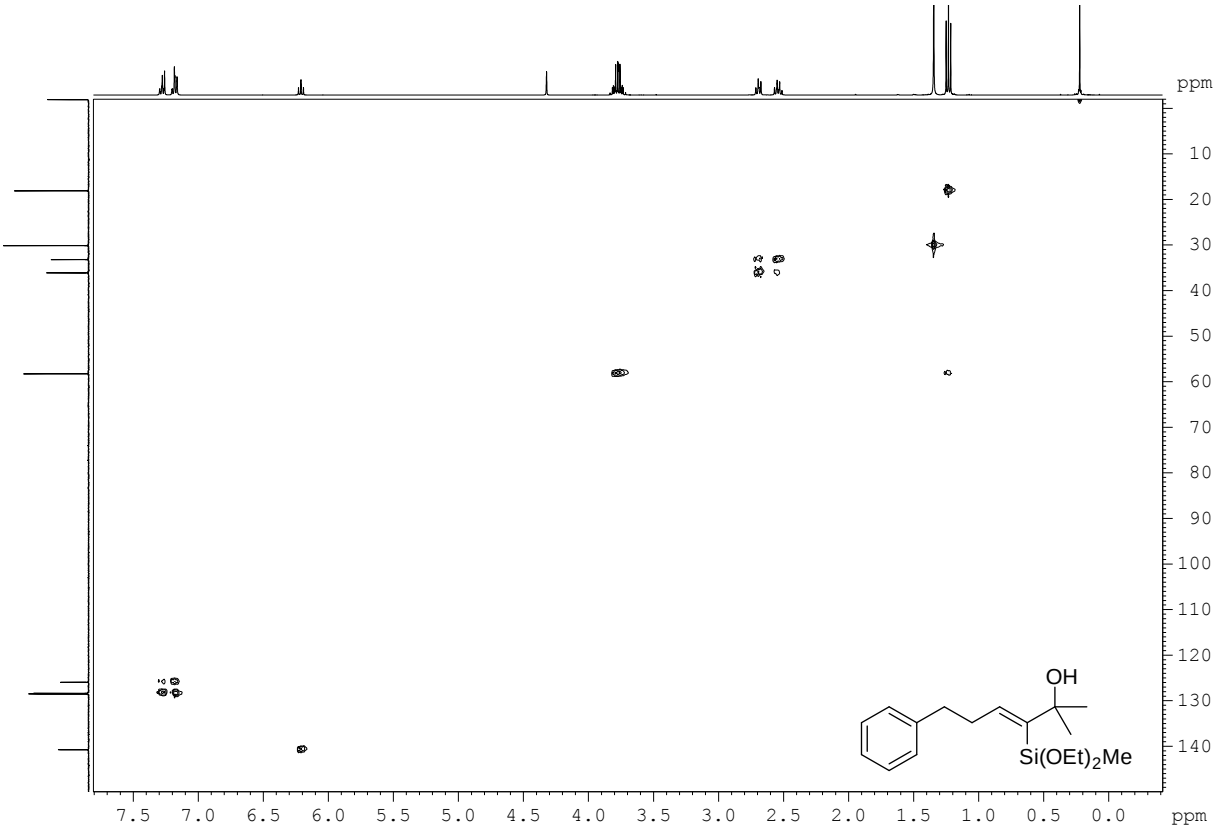

OH
Si(OEt)2Me
146.99
139.49
136.63
126.58
77.32
77.00
76.68
75.52
58.29
58.20
28.11
25.39
24.65
22.51
21.88
18.17
18.14
-2.47
220
200
180
160
140
120
100
80
60
40
20
ppm

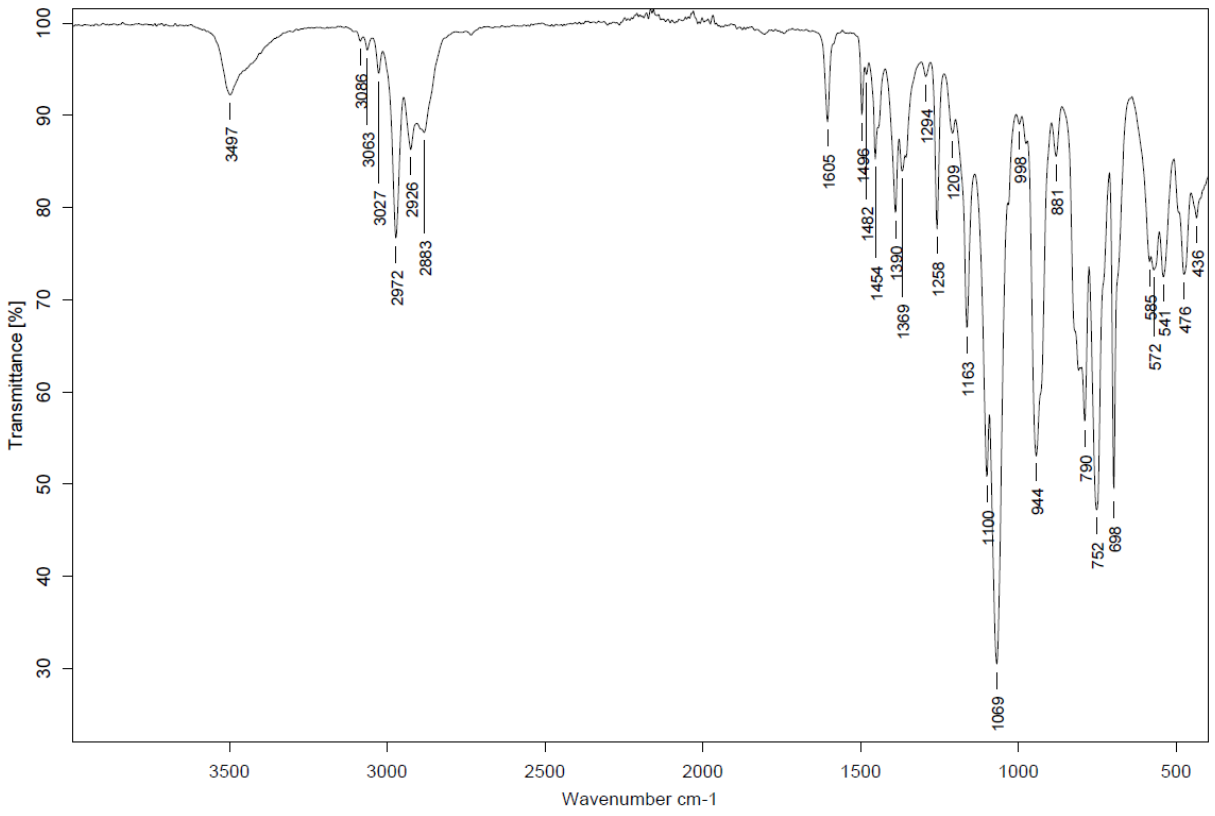

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
OH
Si(OEt)2Me

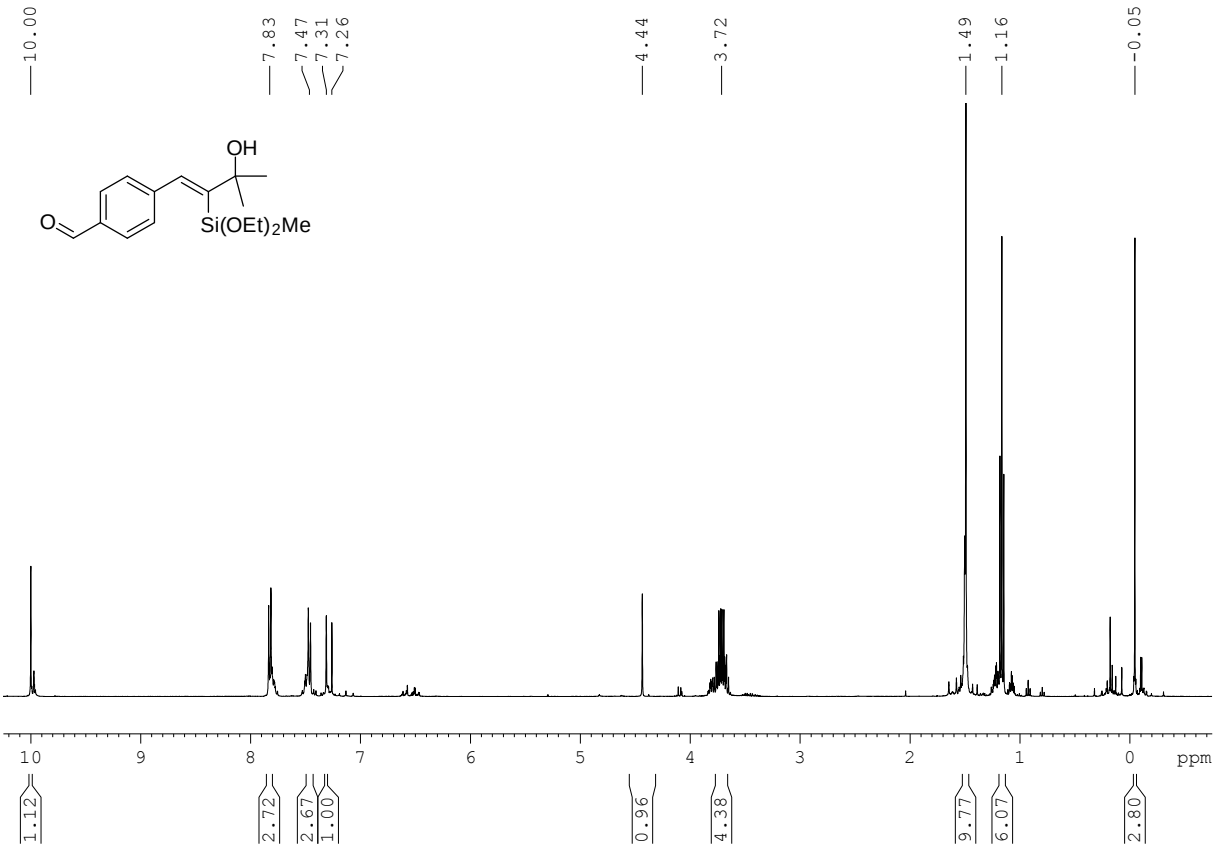

Transmittance [%]
100
90
80
70
60
50
40
30
20
3448
2971
2925
2833
1597
1438
1390
1364
1294
1255
1164
1102
1070
942
895
859
838
797
756
730
684
565
497
477
437
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

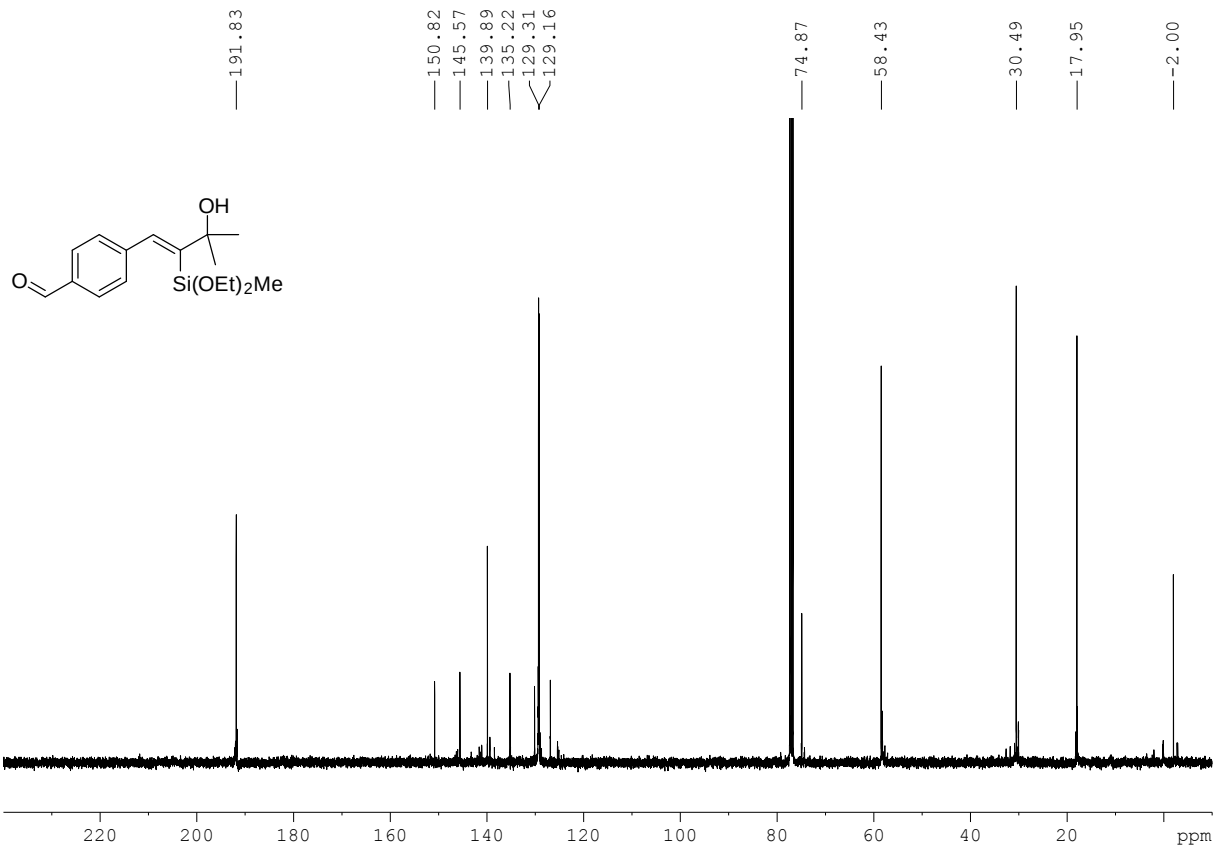

OH
Si(OEt)2Me
7.31
7.25
7.21
7.15
6.21
4.32
3.77
2.69
2.54
1.35
1.23
0.22
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.72
1.00
0.92
3.98
2.00
2.01
5.85
5.79
3.14

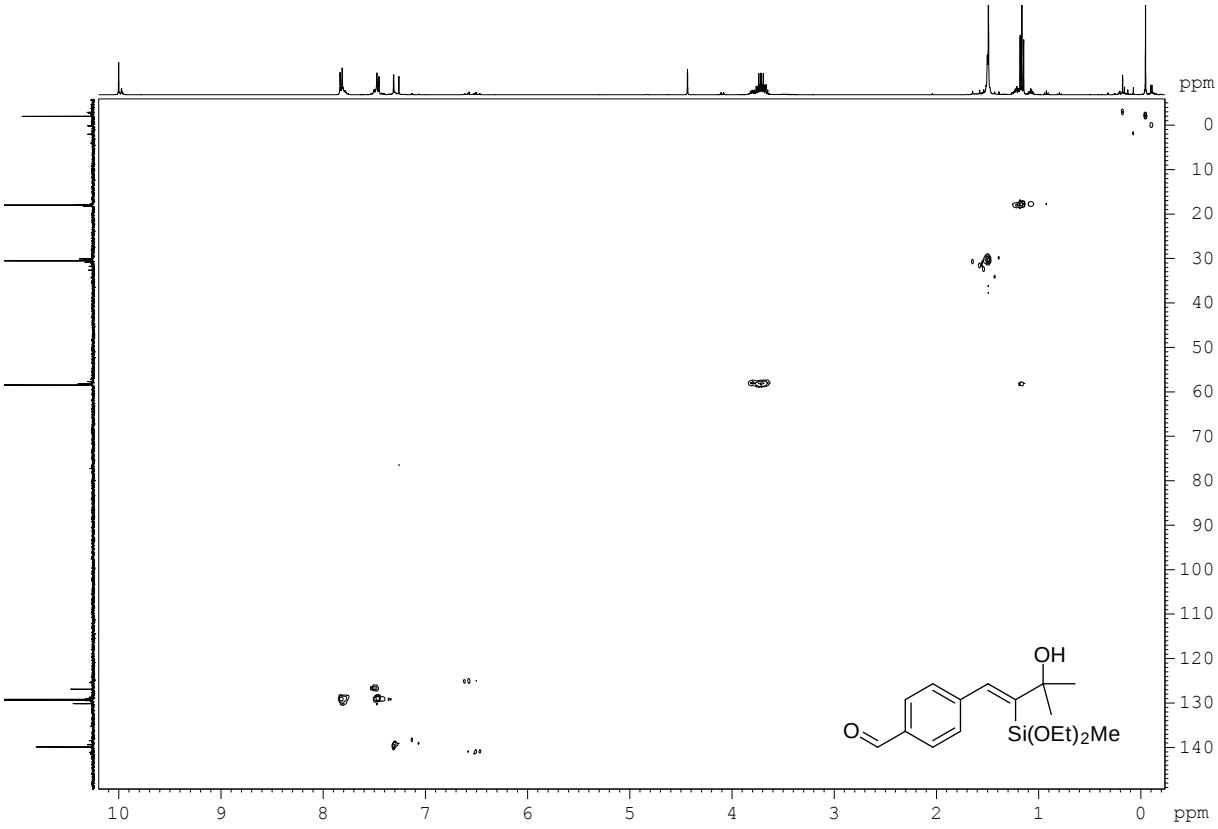

OH
Si(OEt)2Me
143.90
141.49
140.74
128.49
128.34
125.94
77.32
77.00
76.68
74.01
58.24
36.09
33.19
30.12
18.08
-1.92
220
200
180
160
140
120
100
80
60
40
20
ppm

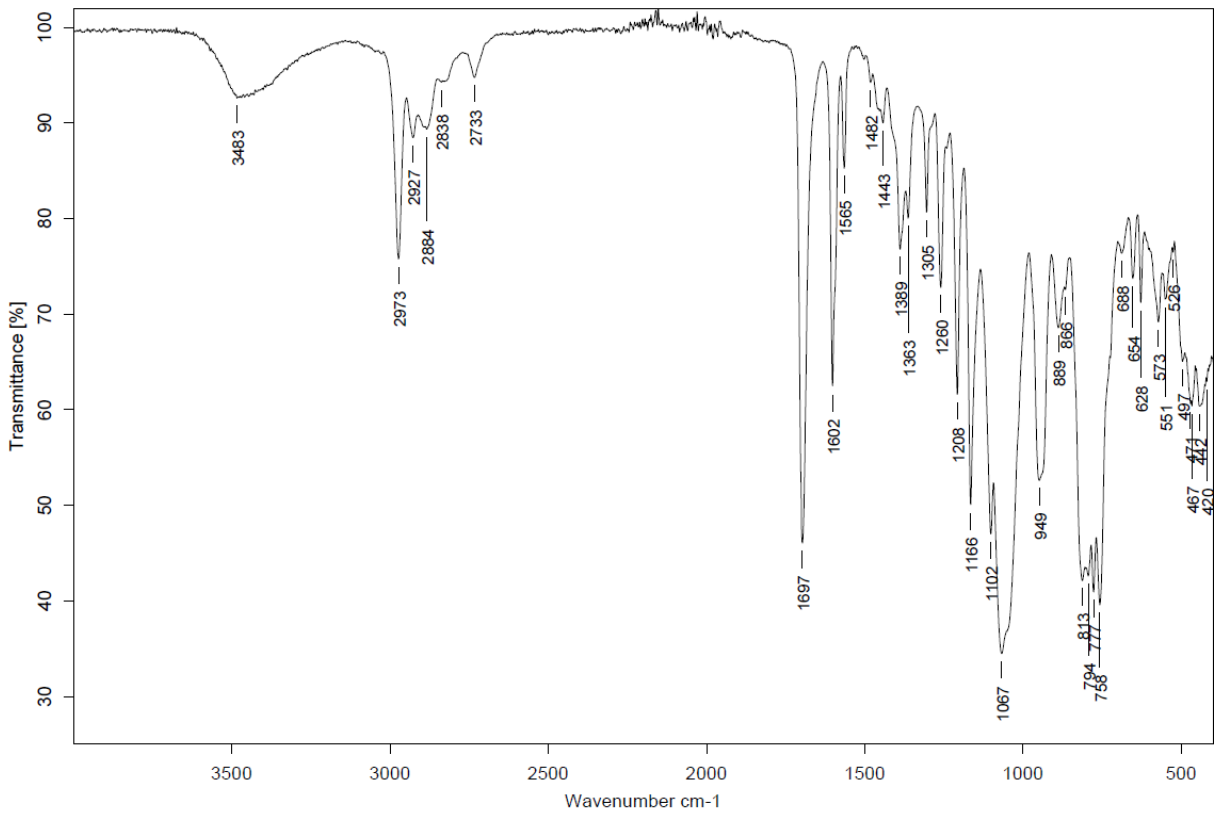

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
OH
Si(OEt)2Me

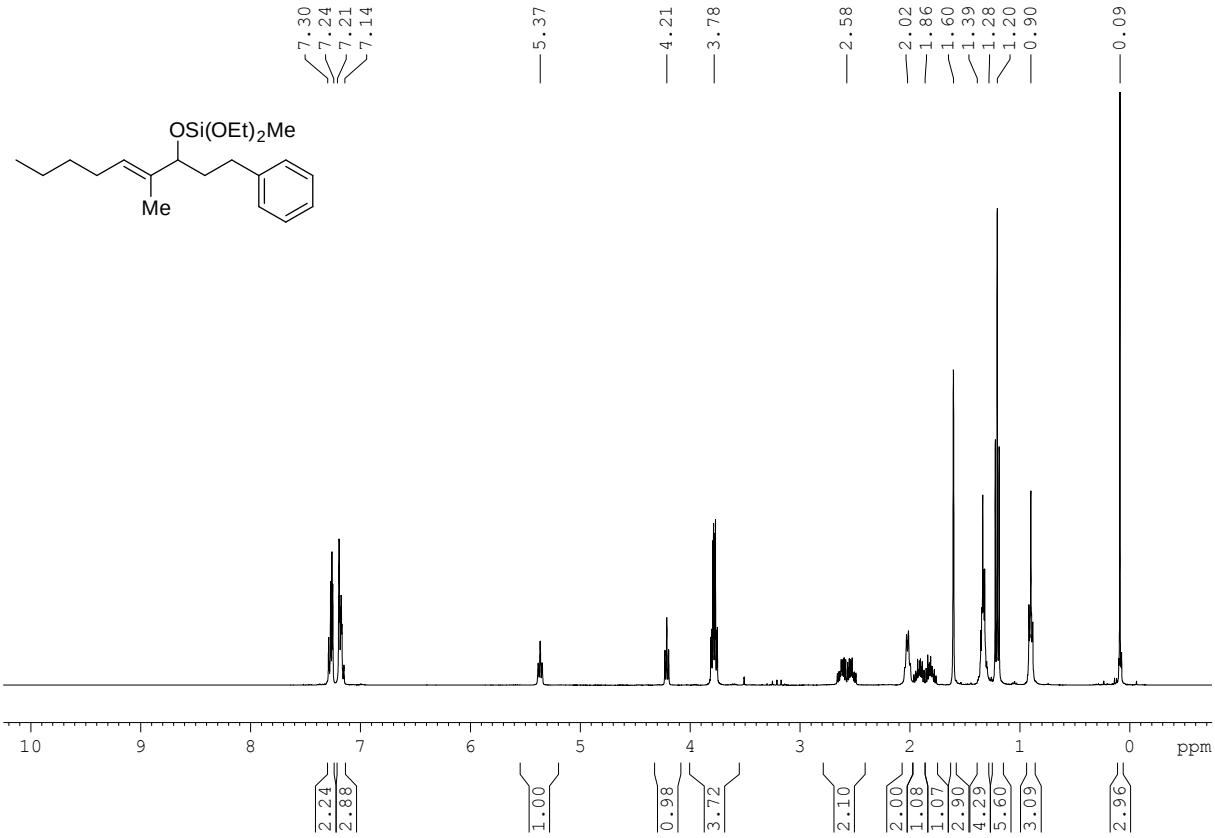

Transmittance [%]
100
90
80
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3497
3086
3063
3027
2972
2926
2883
1605
1496
1482
1454
1390
1369
1294
1258
1209
1163
1100
1069
998
944
881
790
752
698
585
572
541
476
436

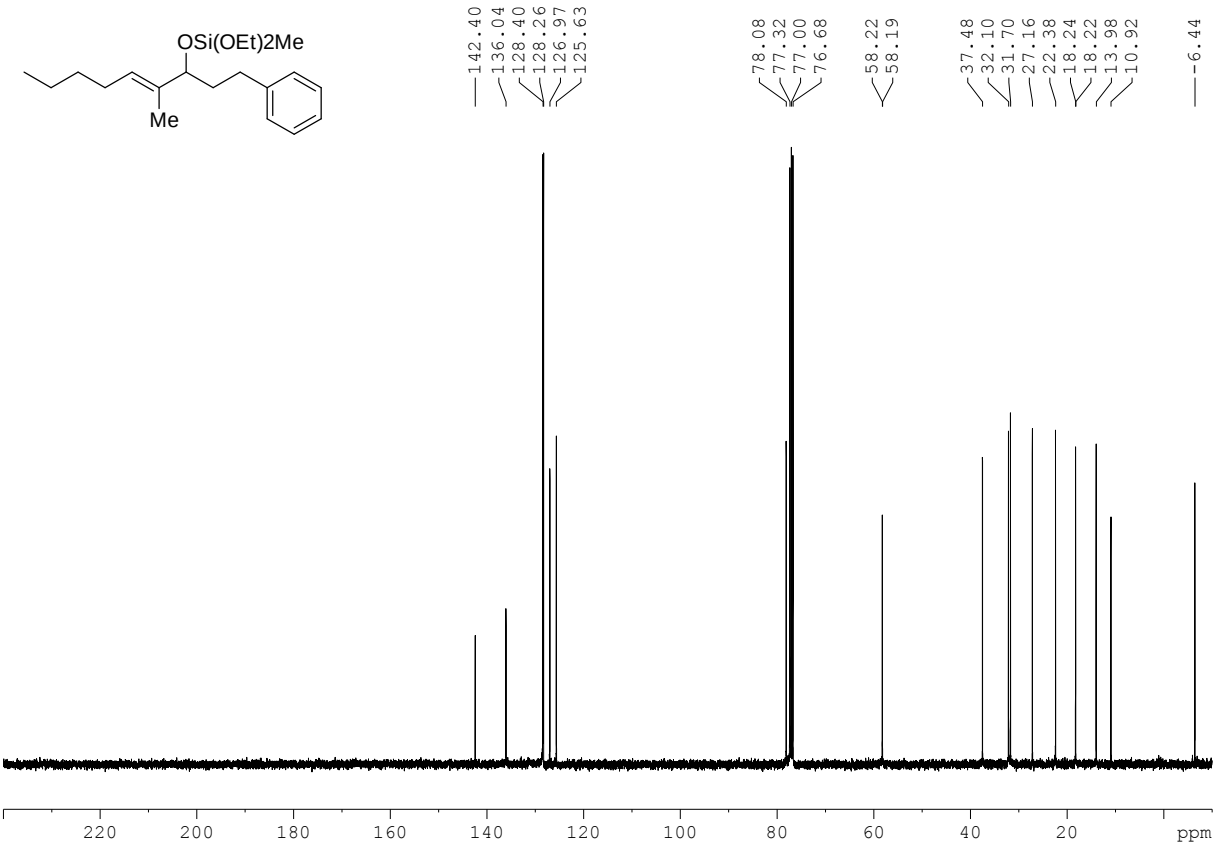

10.00
7.83
7.47
7.31
7.26
4.44
3.72
1.49
1.16
-0.05
OH
O
Si(OEt)2Me
10
9
8
7
6
5
4
3
2
1
0
ppm
1.12
2.72
2.67
1.00
0.96
4.38
9.77
6.07
2.80

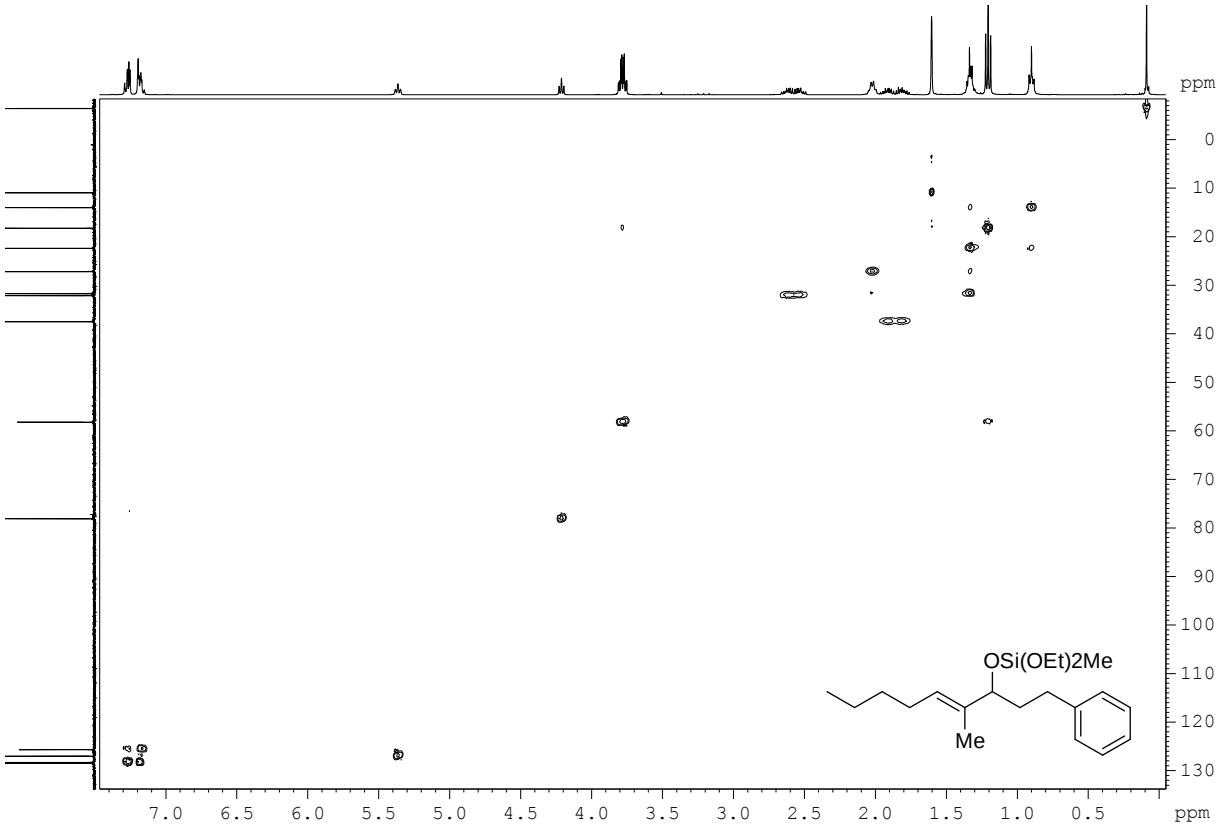

191.83
150.82
145.57
139.89
135.22
129.31
129.16
74.87
58.43
30.49
17.95
-2.00
OH
O
Si(OEt)2Me
220
200
180
160
140
120
100
80
60
40
20
ppm

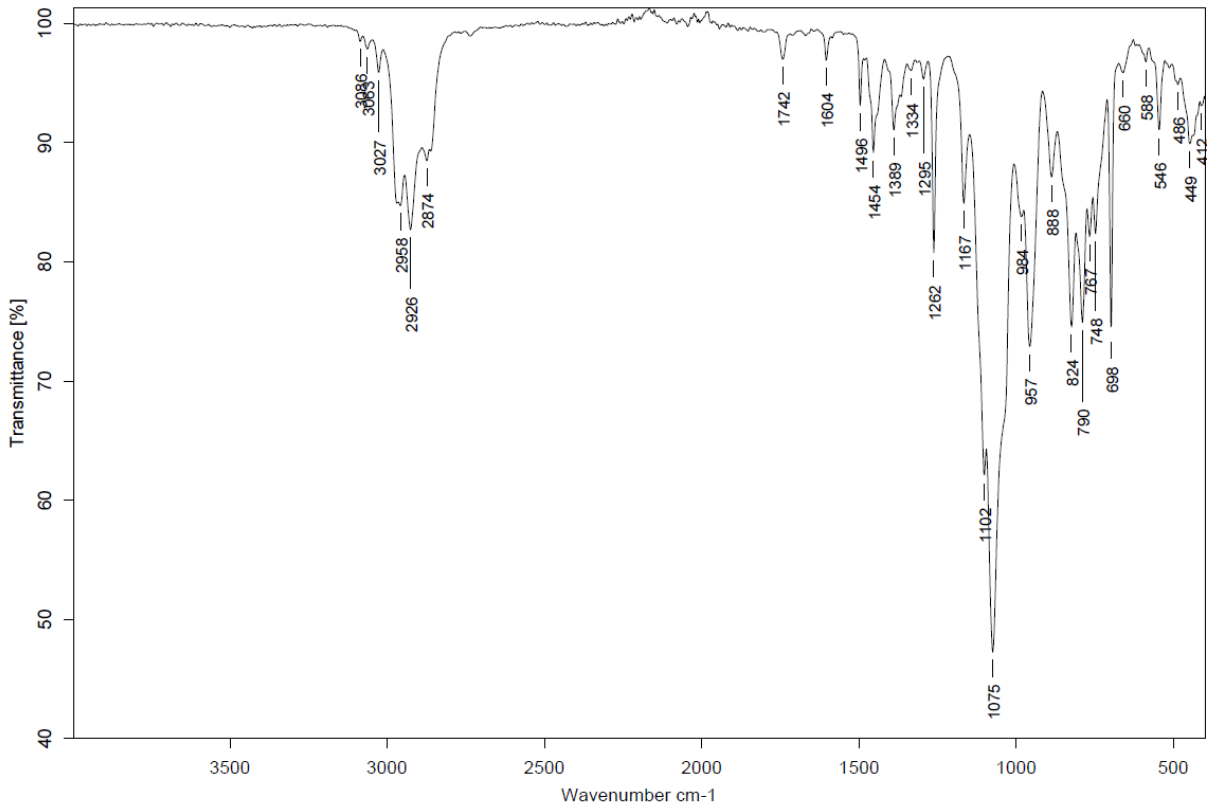

ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
10
9
8
7
6
5
4
3
2
1
0
ppm
OH
O
Si(OEt)2Me

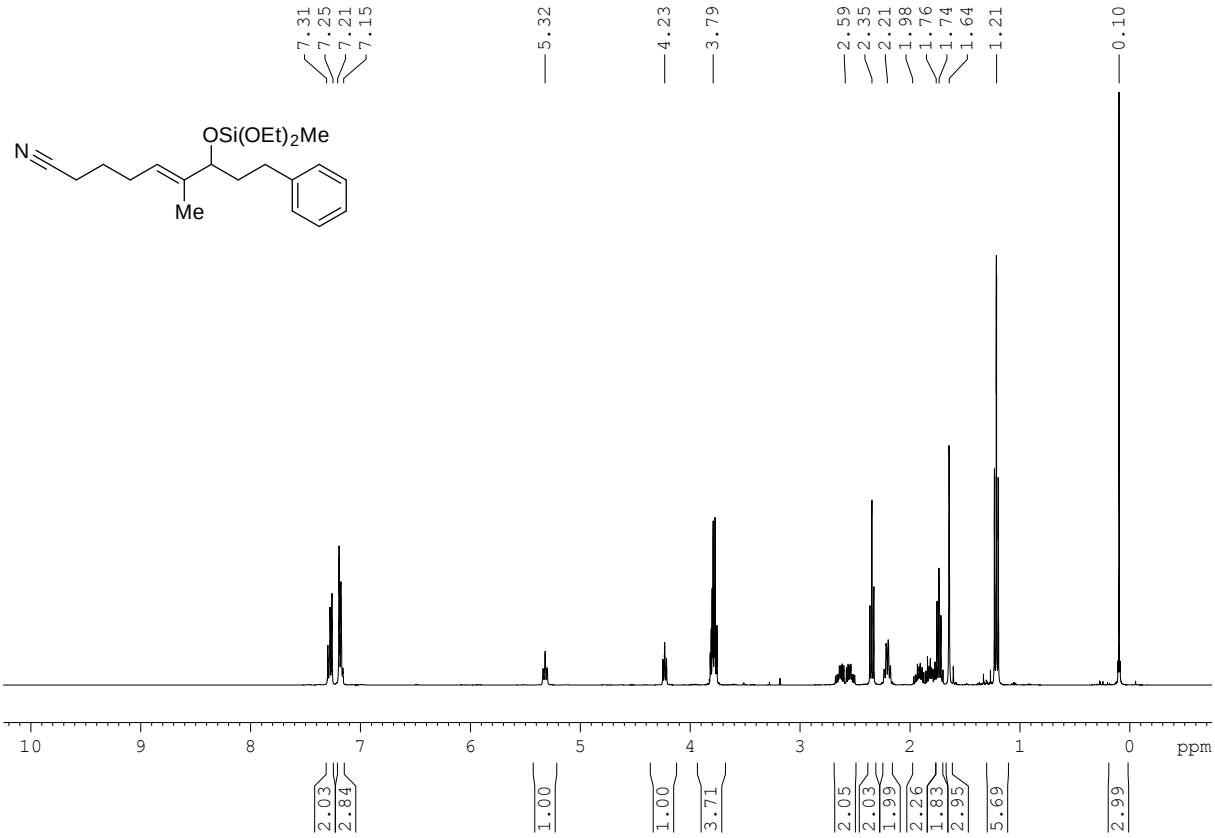

Transmittance [%]
100
90
80
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3483
2973
2927
2884
2838
2733
1697
1602
1565
1482
1443
1389
1363
1305
1260
1208
1166
1102
1067
949
889
866
813
794
758
688
654
628
573
551
526
497
471
467
442
420

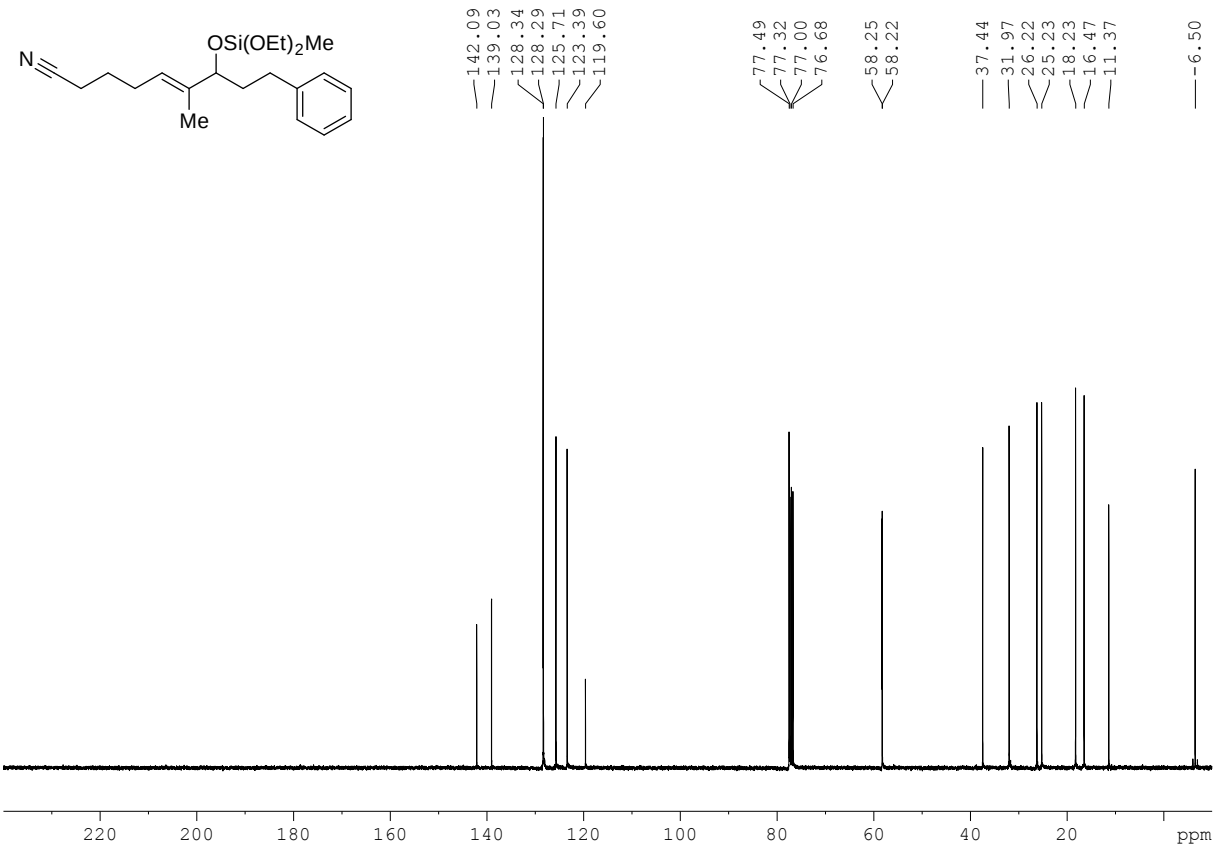

7.30
7.24
7.21
7.14
5.37
4.21
3.78
2.58
2.02
1.86
1.60
1.39
1.28
1.20
0.90
0.09
OSi(OEt)2Me
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
2.24
2.88
1.00
0.98
3.72
2.10
2.00
1.08
1.07
2.90
4.29
5.60
3.09
2.96

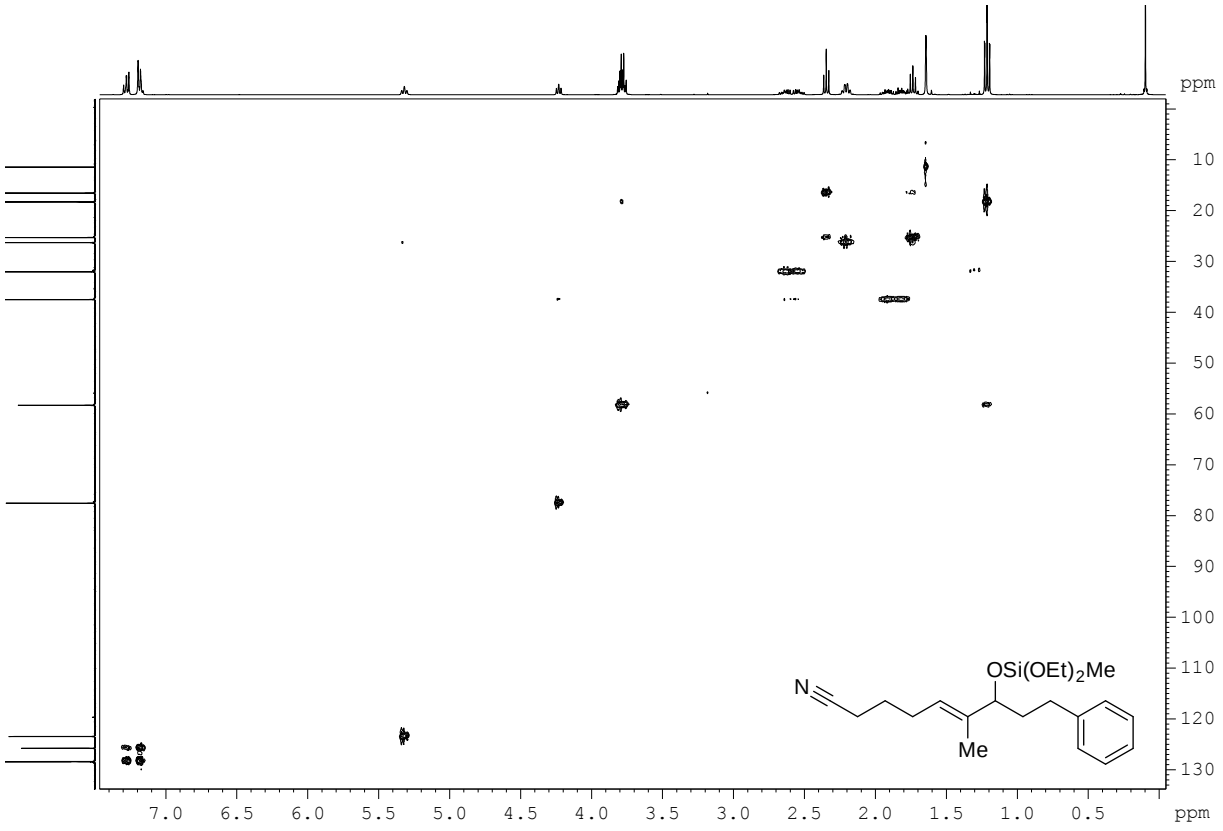

OSi(OEt)2Me
Me
142.40
136.04
128.40
128.26
126.97
125.63
78.08
77.32
77.00
76.68
58.22
58.19
37.48
32.10
31.70
27.16
22.38
18.24
18.22
13.98
10.92
-6.44
220
200
180
160
140
120
100
80
60
40
20
ppm

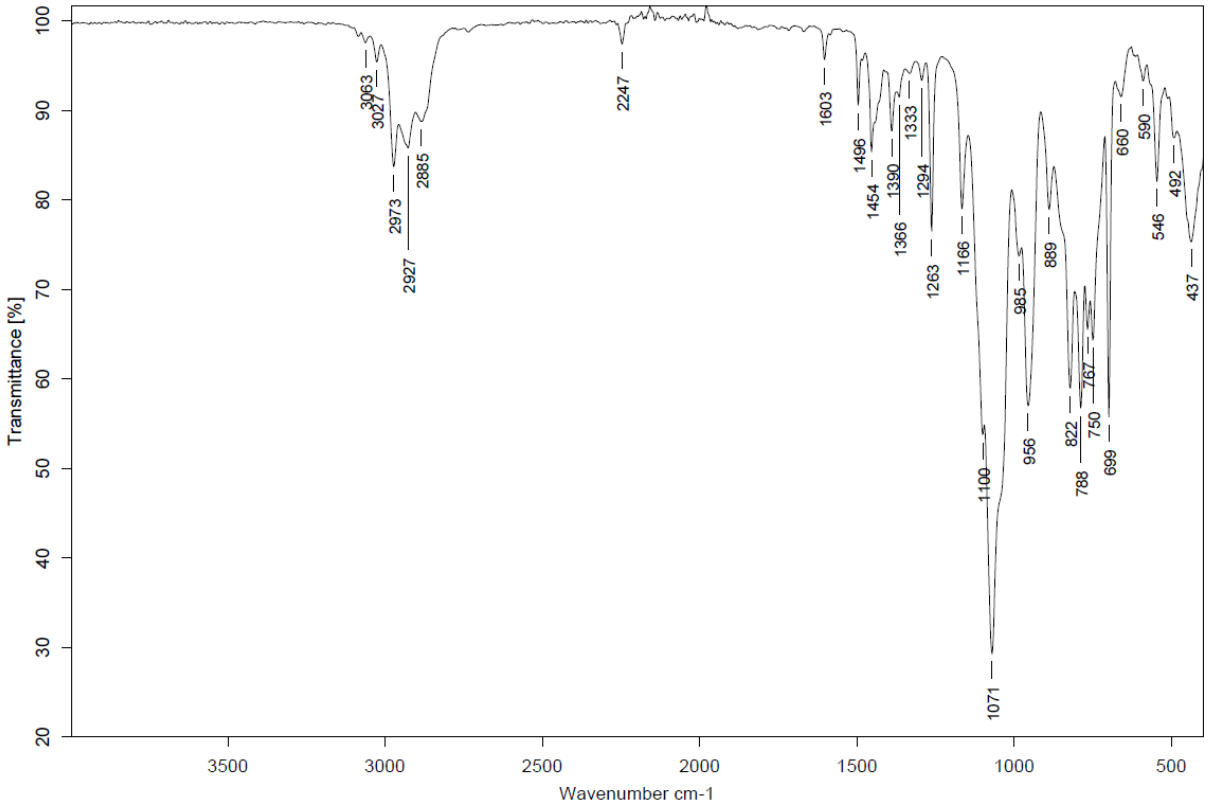

ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
OSi(OEt)2Me
Me

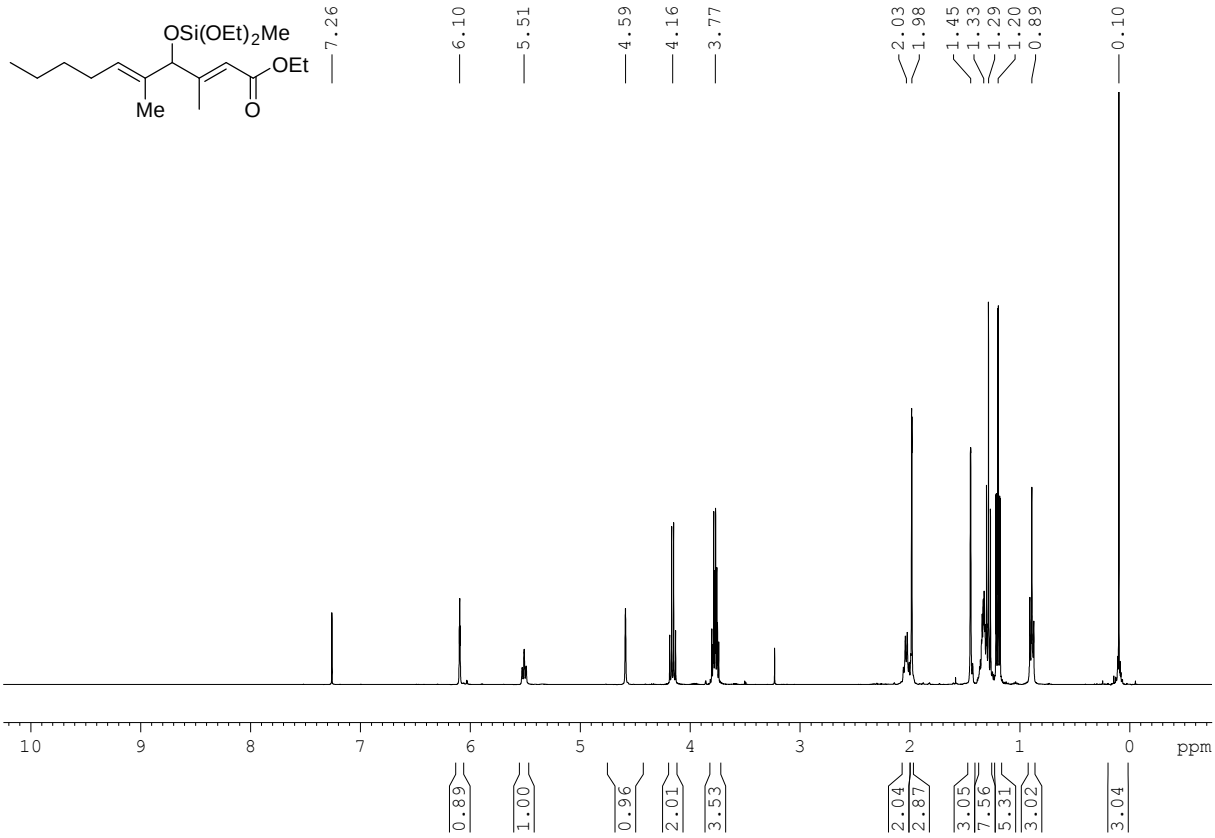

Transmittance [%]
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3086
3063
3027
2958
2926
2874
1742
1604
1496
1454
1389
1334
1295
1262
1167
1102
1075
984
957
888
824
790
767
748
698
660
588
546
486
449
412

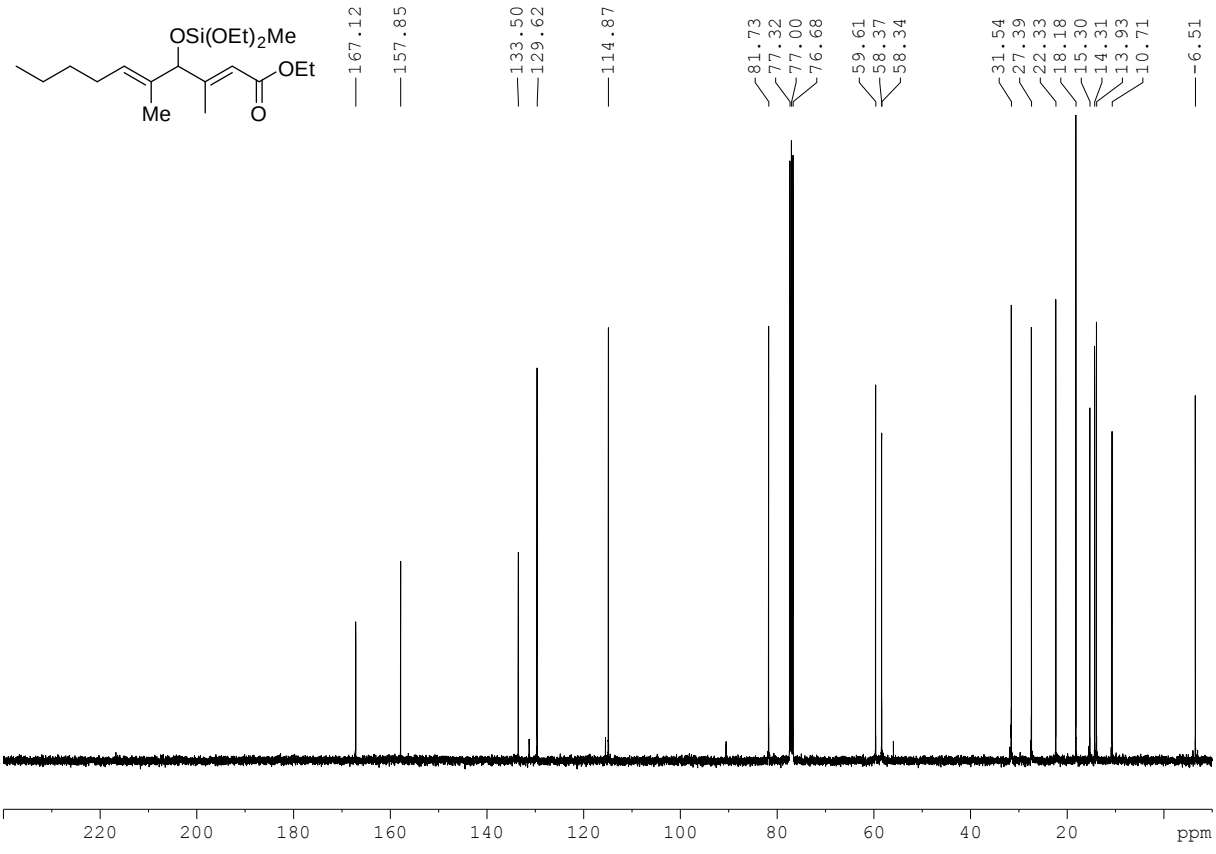

7.31
7.25
7.21
7.15
5.32
4.23
3.79
2.59
2.35
2.21
1.98
1.76
1.74
1.64
1.21
0.10
N
OSi(OEt)2Me
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
2.84
1.00
1.00
3.71
2.05
2.03
1.99
2.26
1.83
2.95
5.69
2.99

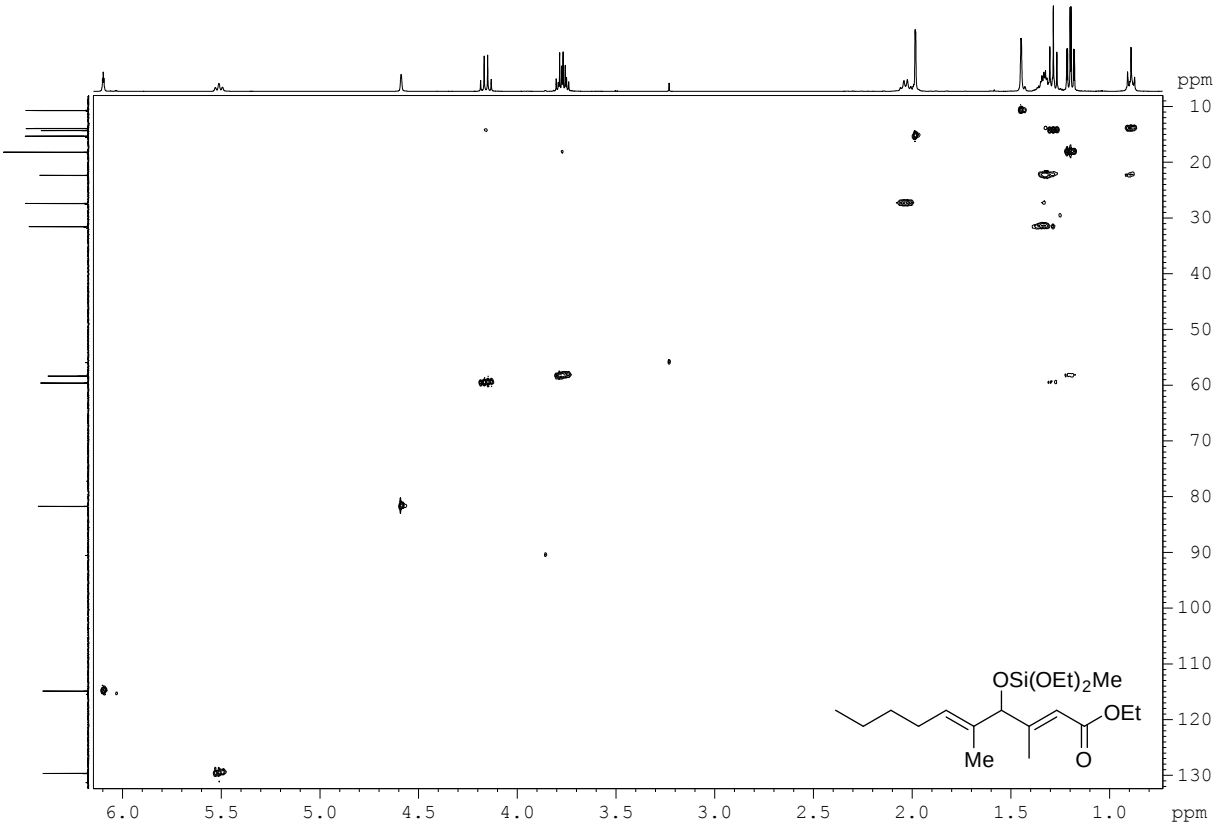

142.09
139.03
128.34
128.29
125.71
123.39
119.60
77.49
77.32
77.00
76.68
58.25
58.22
37.44
31.97
26.22
25.23
18.23
16.47
11.37
-6.50
N
OSi(OEt)2Me
Me
220
200
180
160
140
120
100
80
60
40
20
ppm

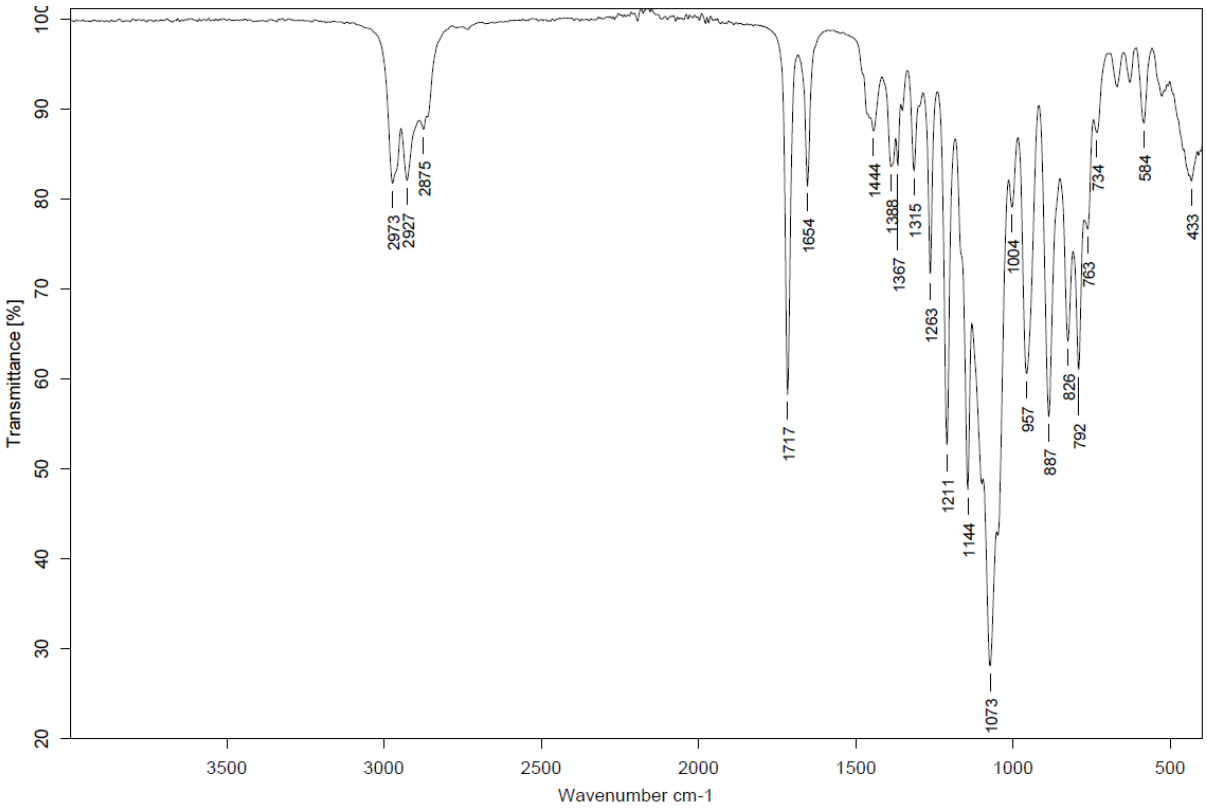

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
N
OSi(OEt)2Me
Me

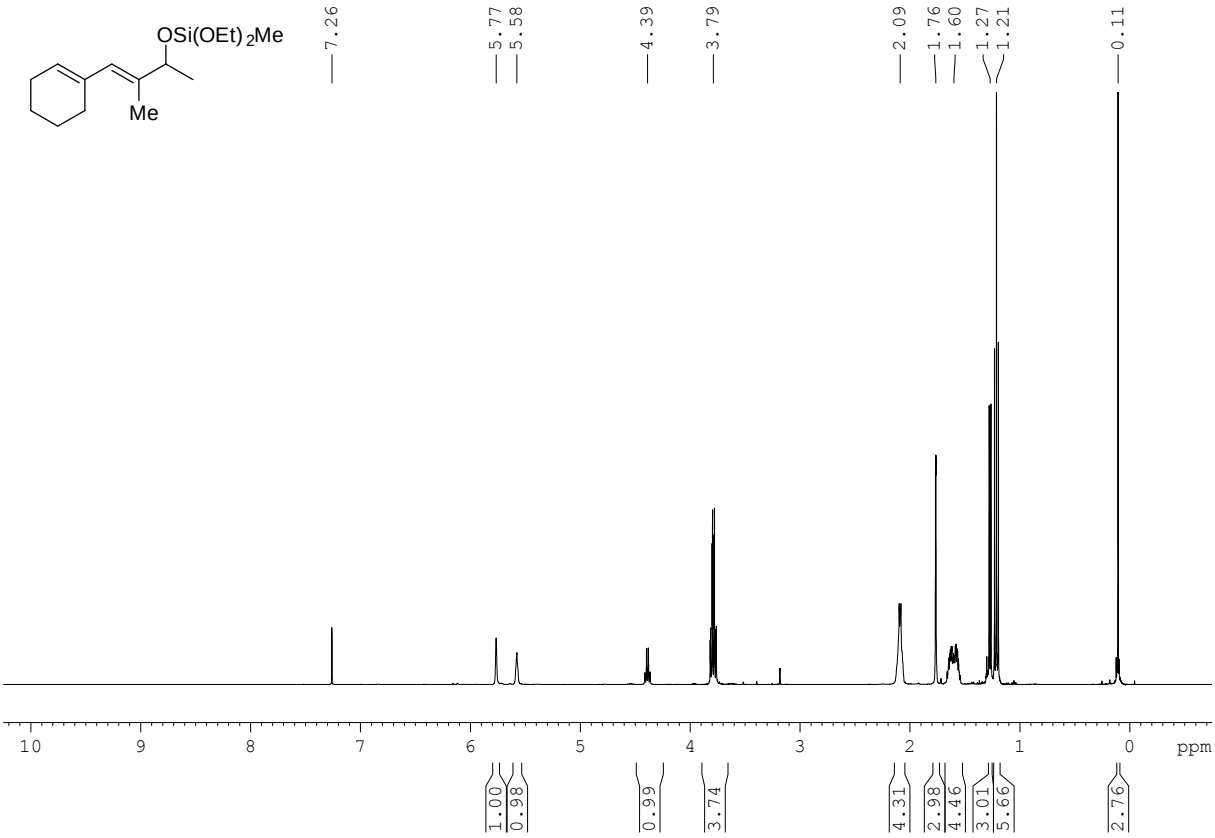

Transmittance [%]
100
90
80
70
60
50
40
30
20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3063
3027
2973
2927
2885
2247
1603
1496
1454
1390
1366
1333
1294
1263
1166
1100
1071
985
956
889
822
788
767
750
699
660
590
546
492
437

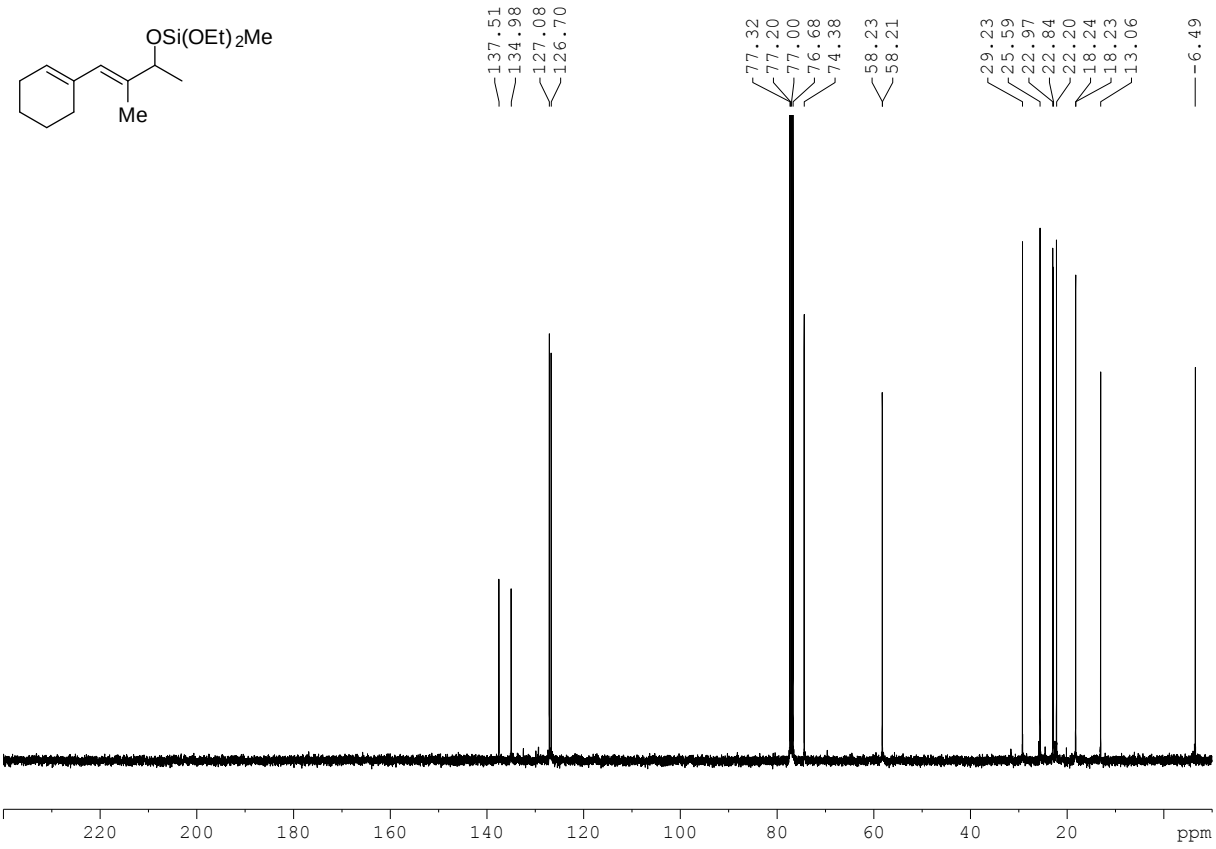

OSi(OEt)2Me
OEt
Me
O
7.26
6.10
5.51
4.59
4.16
3.77
2.03
1.98
1.45
1.33
1.29
1.20
0.89
0.10
10
9
8
7
6
5
4
3
2
1
0
ppm
0.89
1.00
0.96
2.01
3.53
2.04
2.87
3.05
7.56
5.31
3.02
3.04

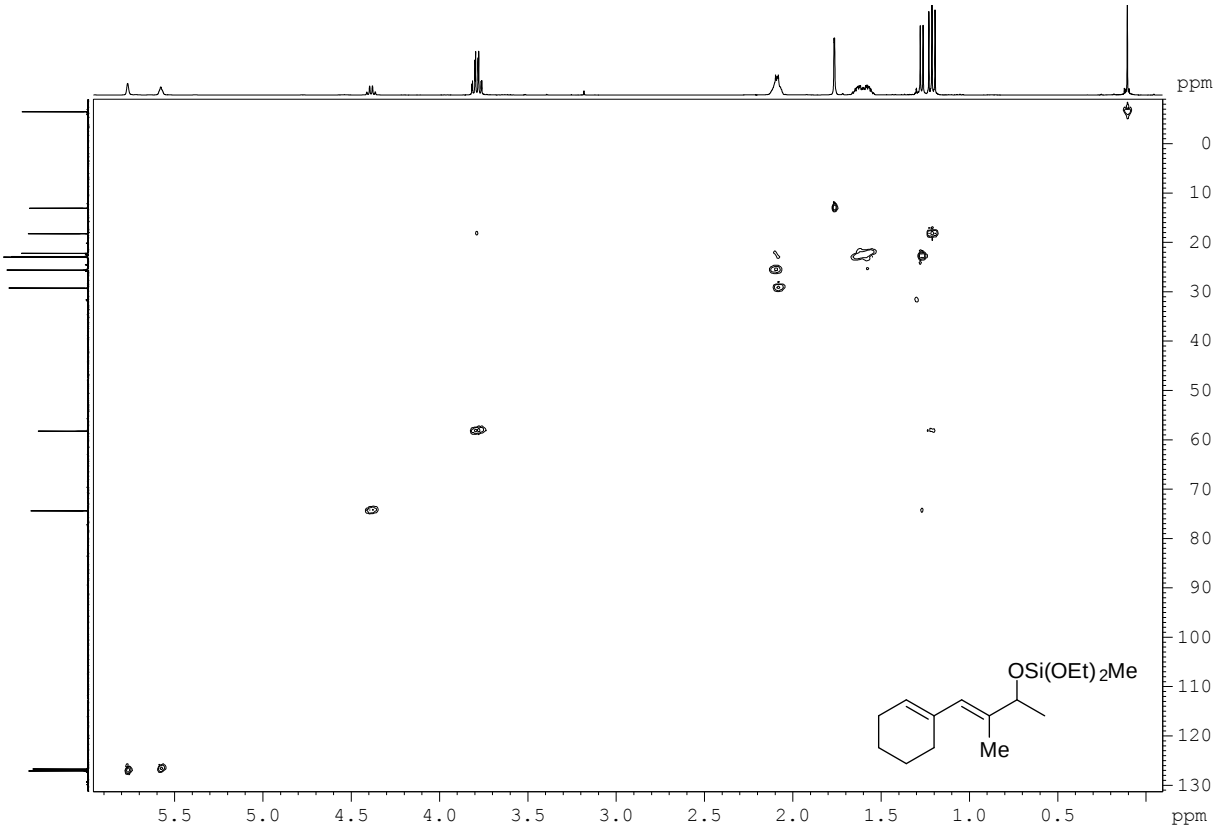

OSi(OEt)2Me
OEt
Me
O
167.12
157.85
133.50
129.62
114.87
81.73
77.32
77.00
76.68
59.61
58.37
58.34
31.54
27.39
22.33
18.18
15.30
14.31
13.93
10.71
-6.51
220
200
180
160
140
120
100
80
60
40
20
ppm

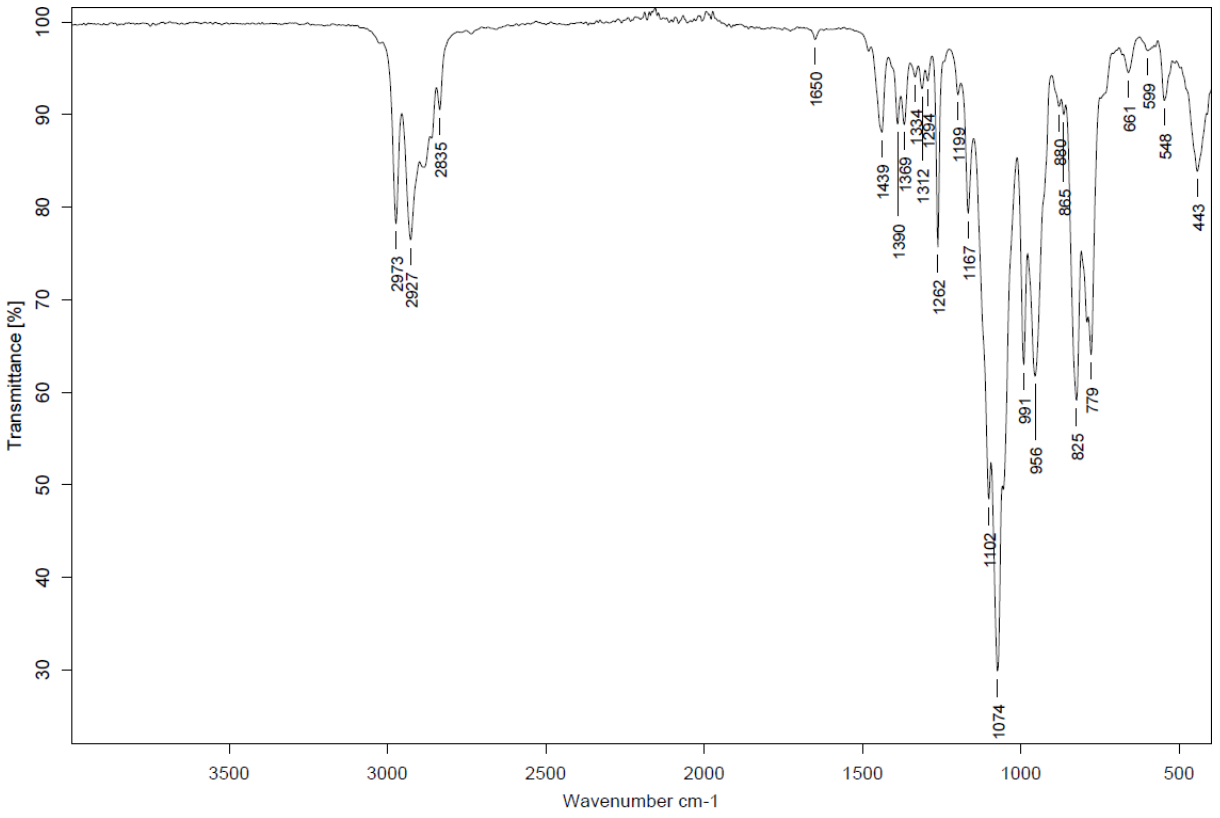

ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
OSi(OEt)2Me
OEt
Me
O

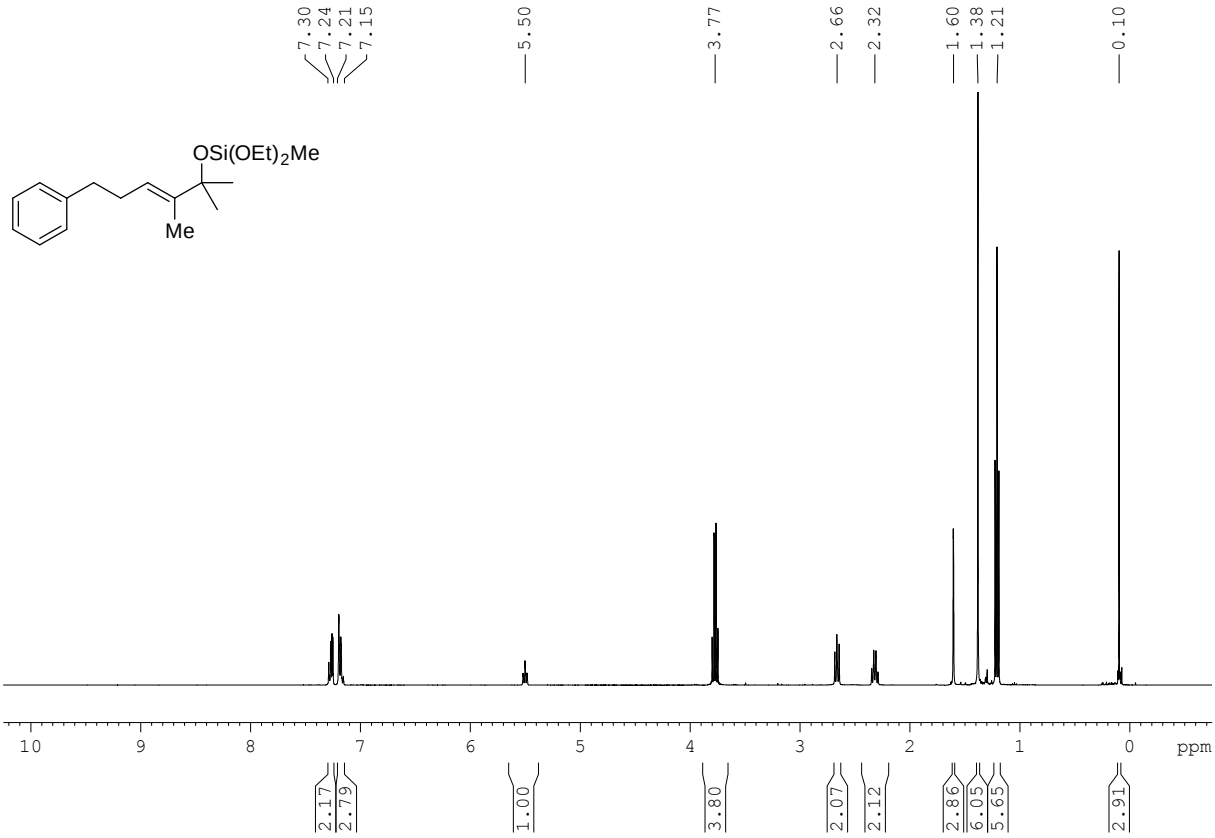

Transmittance [%]
100
90
80
70
60
50
40
30
20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
2973
2927
2875
1717
1654
1444
1388
1367
1315
1263
1211
1144
1073
1004
957
887
826
792
763
734
584
433

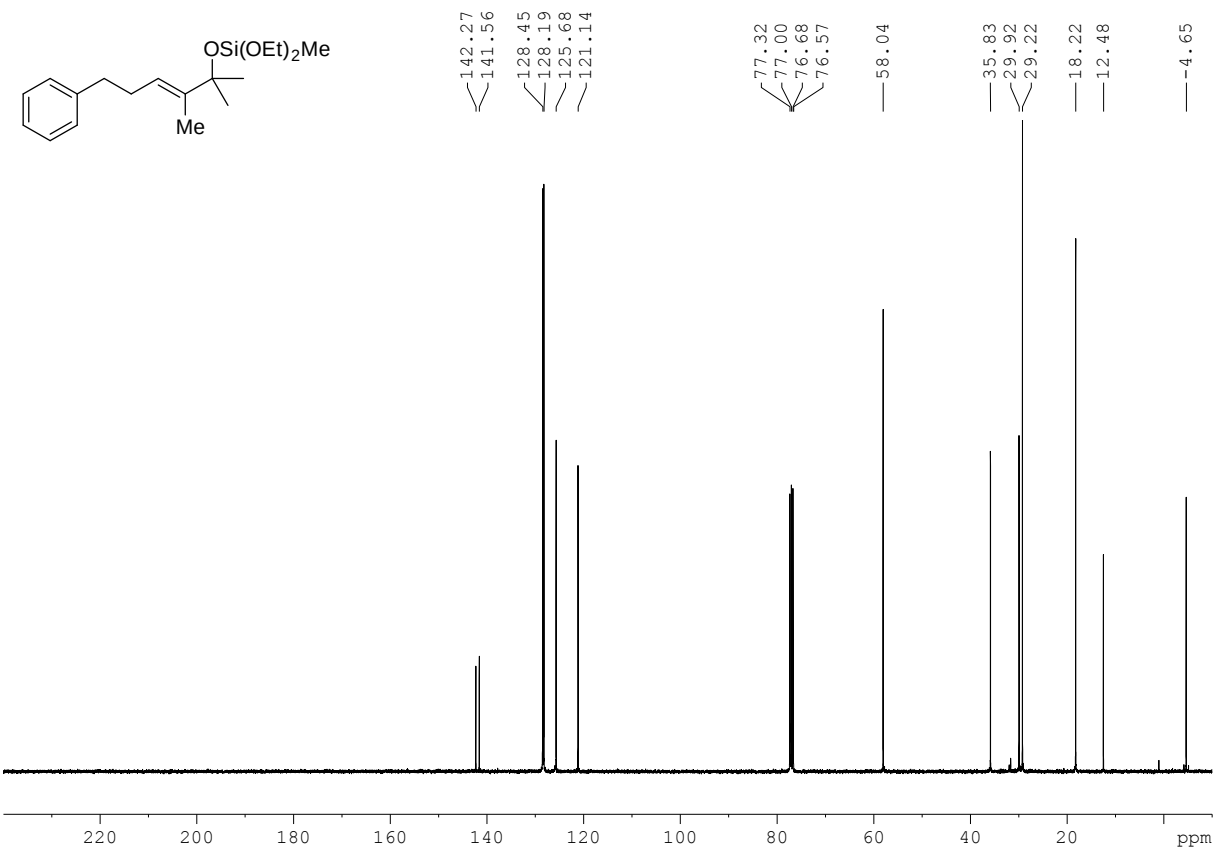

OSi(OEt)2Me
Me
7.26
5.77
5.58
4.39
3.79
2.09
1.76
1.60
1.27
1.21
0.11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
0.99
3.74
4.31
2.98
4.46
3.01
5.66
2.76

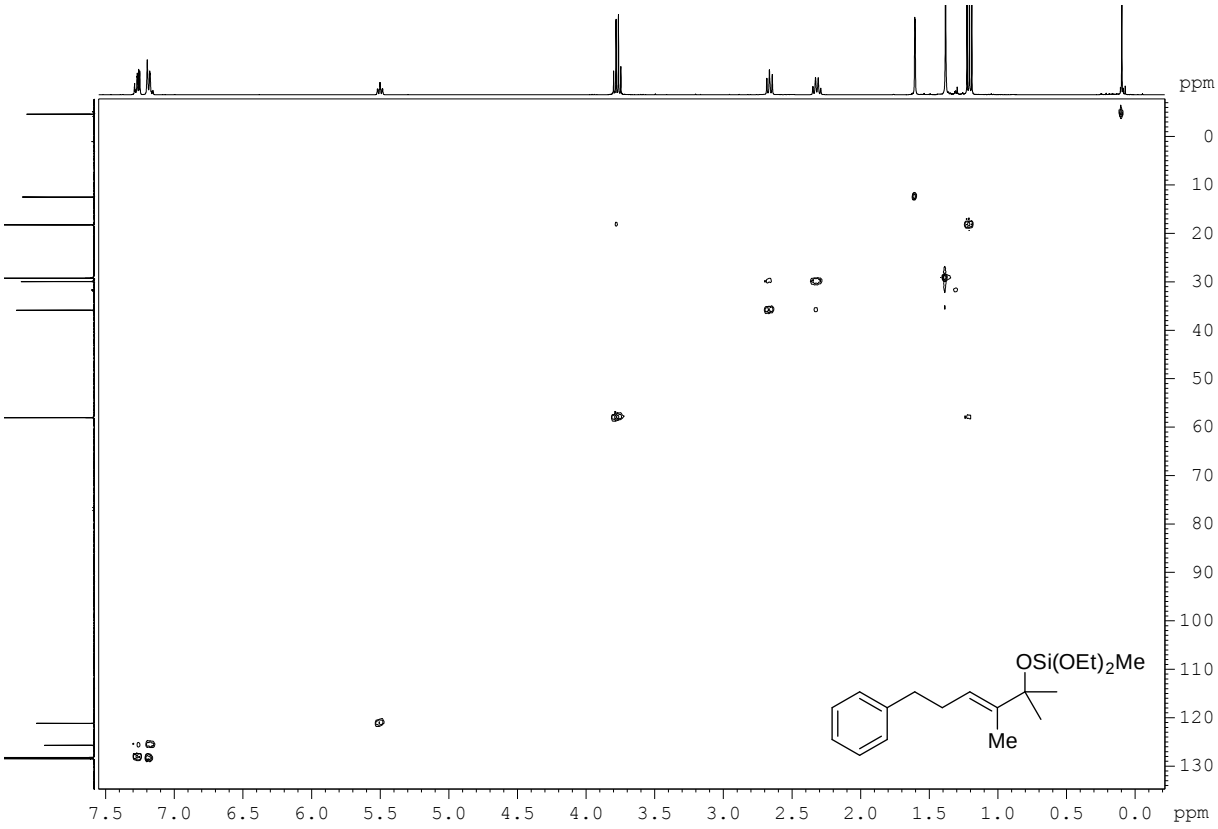

OSi(OEt)2Me
Me
137.51
134.98
127.08
126.70
77.32
77.20
77.00
76.68
74.38
58.23
58.21
29.23
25.59
22.97
22.84
22.20
18.24
18.23
13.06
-6.49
220
200
180
160
140
120
100
80
60
40
20
ppm

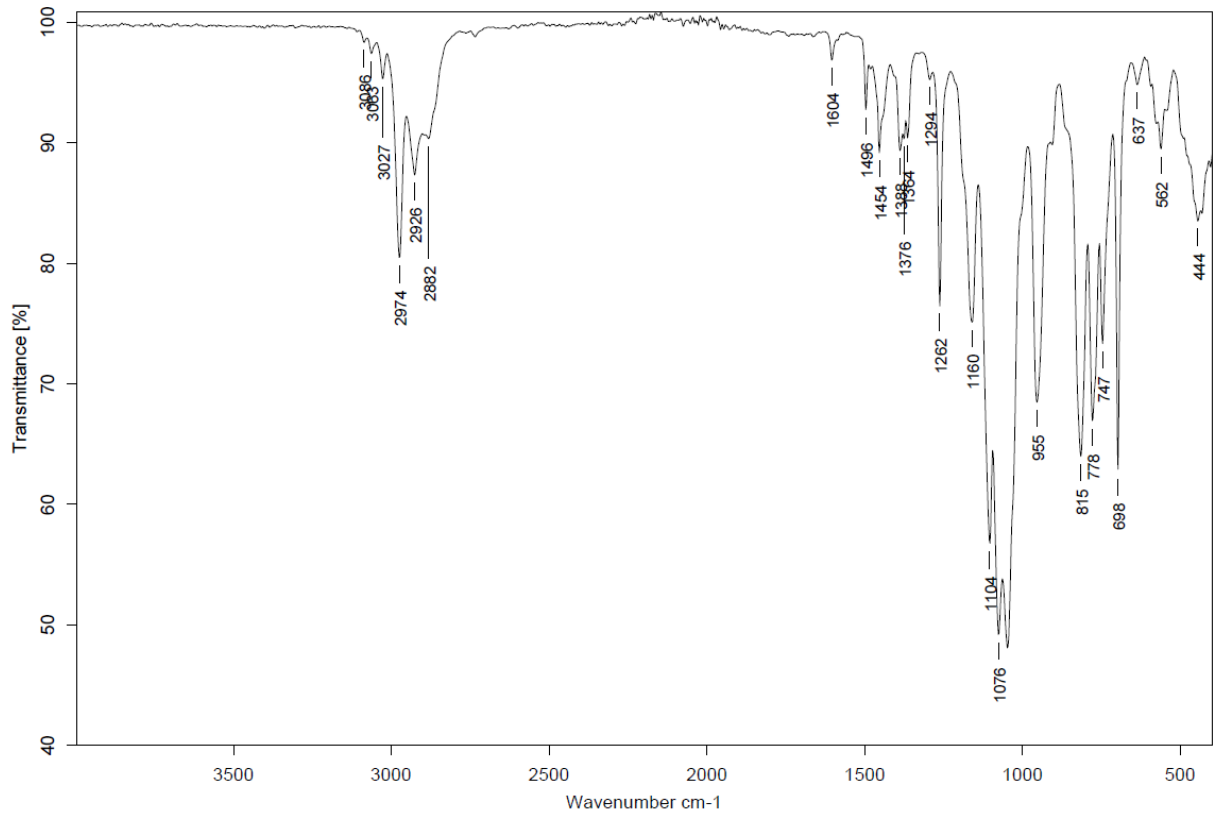

ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
OSi(OEt)2Me
Me

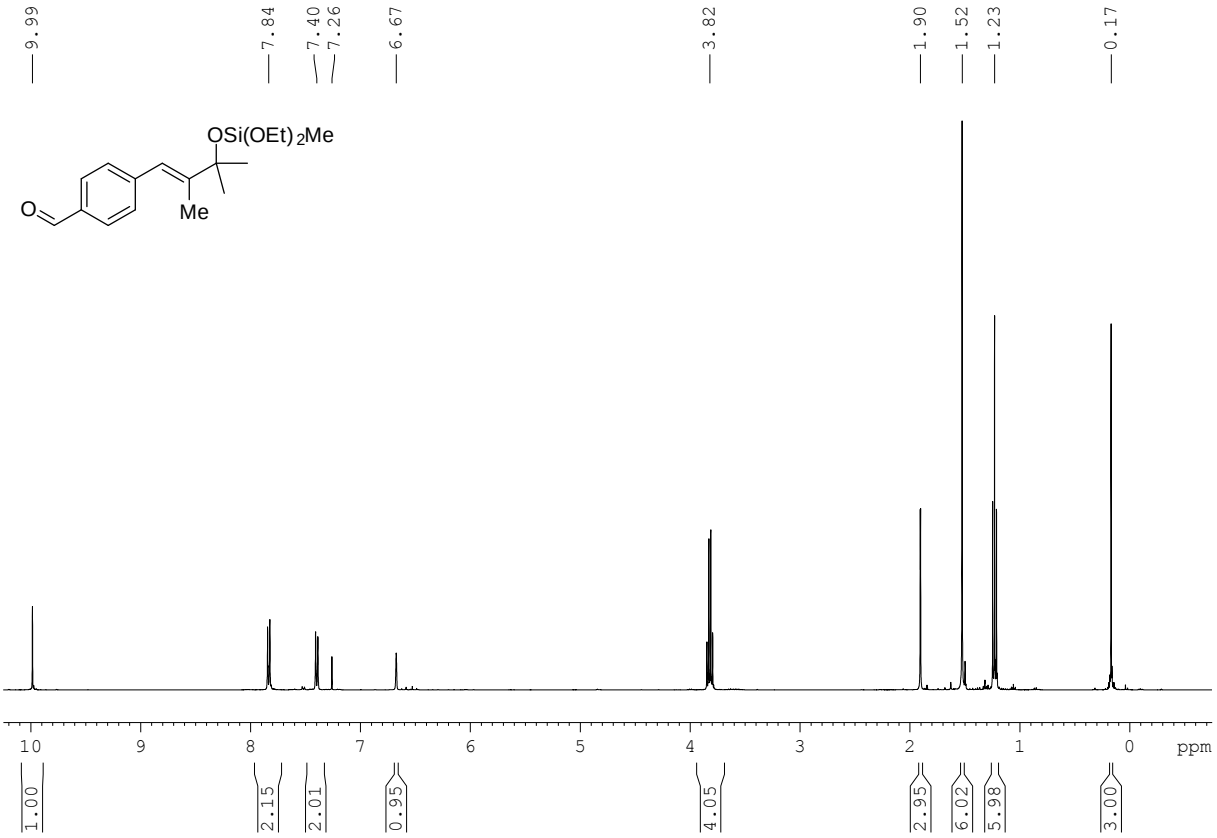

Transmittance [%]
100
90
80
70
60
50
40
30
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
2973
2927
2835
1650
1439
1390
1369
1334
1312
1284
1262
1199
1167
1102
1074
991
956
880
865
825
779
661
599
548
443

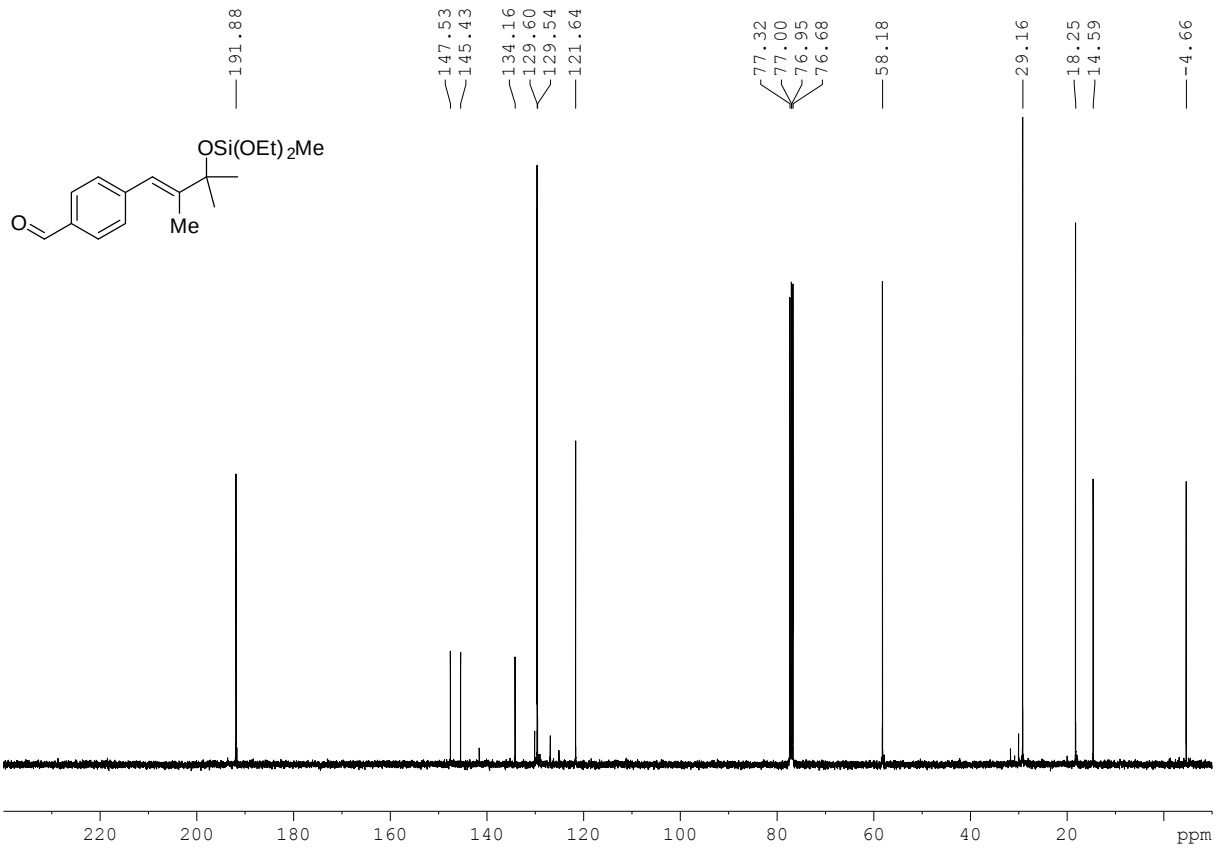

7.30
7.24
7.21
7.15
5.50
3.77
2.66
2.32
1.60
1.38
1.21
0.10
OSi(OEt)2Me
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
2.17
2.79
1.00
3.80
2.07
2.12
2.86
6.05
5.65
2.91

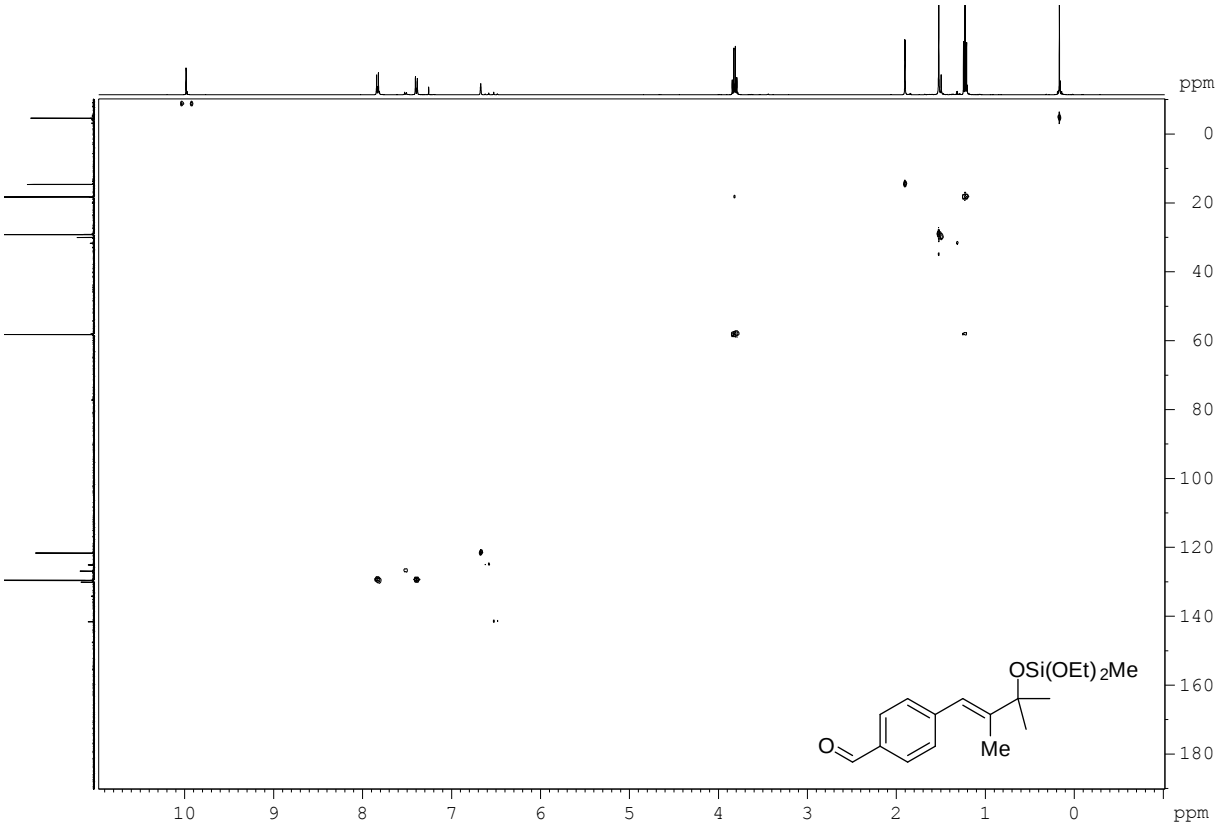

142.27
141.56
128.45
128.19
125.68
121.14
77.32
77.00
76.68
76.57
58.04
35.83
29.92
29.22
18.22
12.48
-4.65
OSi(OEt)2Me
Me
220
200
180
160
140
120
100
80
60
40
20
ppm

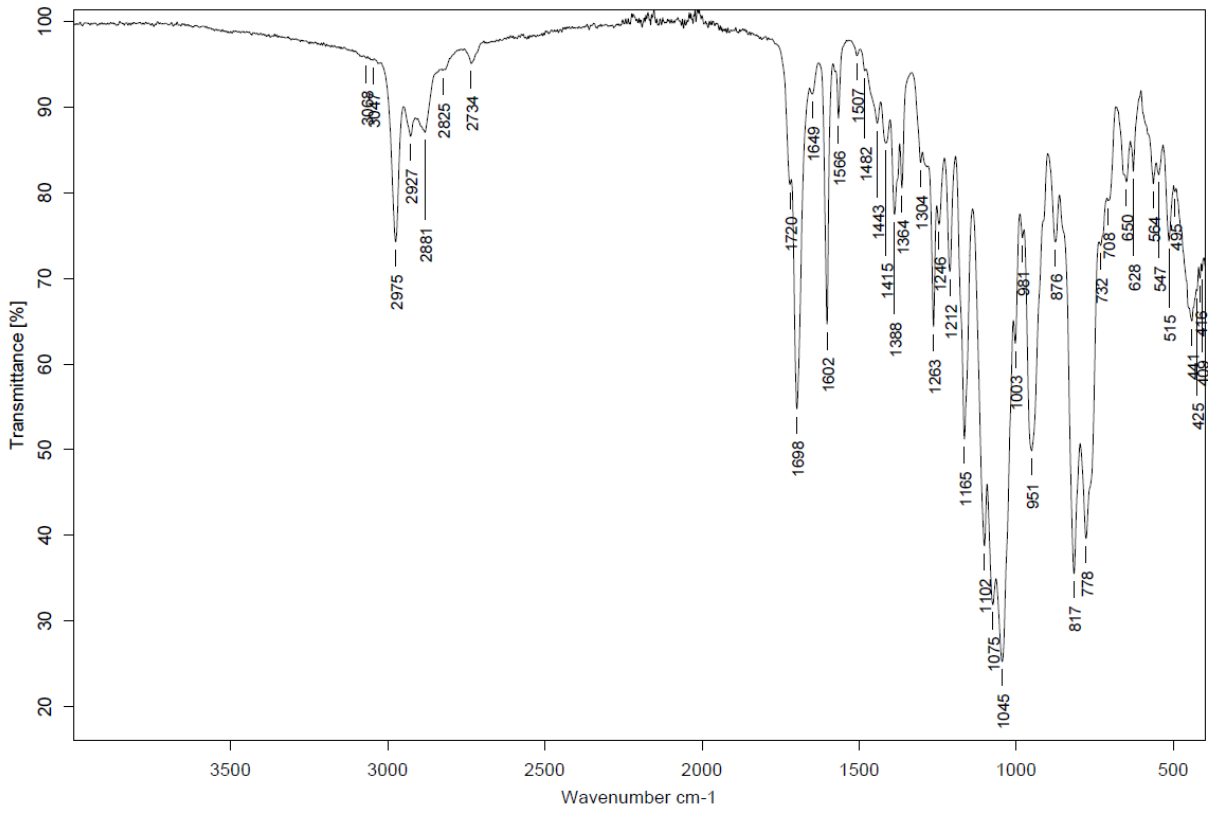

ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
OSi(OEt)2Me
Me


Transmittance [%]
100
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3086
3063
3027
2974
2926
2882
1604
1496
1454
1388
1364
1376
1294
1262
1160
1104
1076
955
815
778
747
698
637
562
444


9.99
7.84
7.40
7.26
6.67
3.82
1.90
1.52
1.23
0.17
OSi(OEt)2Me
O
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.15
2.01
0.95
4.05
2.95
6.02
5.98
3.00


191.88
147.53
145.43
134.16
129.60
129.54
121.64
77.32
77.00
76.95
76.68
58.18
29.16
18.25
14.59
-4.66
OSi(OEt)2Me
O
Me
220
200
180
160
140
120
100
80
60
40
20
ppm


ppm
0
20
40
60
80
100
120
140
160
180
10
9
8
7
6
5
4
3
2
1
0
ppm
OSi(OEt)2Me
O
Me


Transmittance [%]
100
90
80
70
60
50
40
30
20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3068
3047
2975
2927
2881
2825
2734
1720
1698
1649
1602
1566
1507
1482
1443
1415
1388
1364
1304
1263
1246
1212
1165
1102
1075
1045
1003
981
951
876
817
778
732
708
650
628
564
547
515
495
441
425