Thiol-ene Click Reaction as a General Route to Functional Trialkoxysilanes for Surface Coating Applications

Alexander K. Tucker-Schwartz, Richard A. Farrell, and Robin L.Garrell*

Department of Chemistry and Biochemistry and California NanoSystems Institute
University of California, Los Angeles
Box 951569
Los Angeles, CA 90095-1569
Tel.(+001) 310-825-2496
Fax: (+001) 310-206-2061
E-mail: garrell@chem.ucla.edu

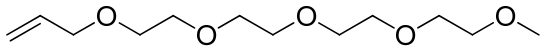
Table of Contents

1. General information

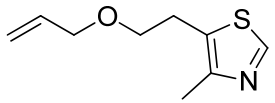
Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), ammonium hydroxide (NH_4OH), oleic acid, sodium sulfate (Na_2SO_4), magnesium sulfate ($MgSO_4$), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Fisher Scientific(Pittsburgh, PA). 3-mercaptopropyltriethoxysilane (MPTES), 3-mercaptopropyltrimethoxysilane (MPTMS), allyltriethoxysilane (ATES) were purchased at >95% purity from Gelest Inc.(Morrisville, PA). Diisopropylethylamine, potassium *tert*-butoxide (*t*-BuOK), and tetraethyleneglycol monomethyl ether were purchased from Acros Organics. Allyl bromide, 5-(2-hydroxyethyl)-4-methylthiazole, 10-undecenoic acid, di-*tert*-butyl dicarbonate, *N,N*-dimethylaminepyridine, *N*-Boc-trans-4-hydroxy-L-proline methyl ester, 4-penteneoic anhydride, 3-aminoquinuclidine dihydrochloride, dicyclohexylcarbodiimide (DCC), L-serine-*tert*-butyl ester, *tert*-butyl bromoacetate, benzyl hydrosulfide, 2,2-dimethoxy-1,2-diphenylethanone, Celite® 500 fine, and all other alkene substrates were purchased from Sigma Aldrich (St. Louis, MO). All solvents were HPLC grade and purchased from either EMD Biosciences, Inc. (Gibbstown, NJ) or Fisher. Dry THF, dioxane, and toluene were prepared by mixing the solvent with $MgSO_4$ and filtering into hot dry glassware just prior to use. All other solvents and chemicals were used as received.

Hand-held rare-earth magnets, recycled from computer hard drives, were used to separate magnetic nanoparticles from solution. Sonication was performed using a Branson 2510 ultrasonicator. Fourier transform infrared spectroscopy (FT-IR) was performed using pressed KBr pellets, or thin liquid films between AgCl plates on a Jasco FT/IR-420. Elemental analysis was performed on a Flash 1112 series elemental analyzer (Thermo Scientific). Magnetic measurements of particles were made using a Quantum Design MPMS 5XL Super Quantum Interference Device (SQUID) magnetometer. Transmission electron microscopy (TEM) images were obtained with an 80-300 kV tunable Titan TEM/STEM. ^{1}H, ^{13}CNMR spectra were obtained using either a Bruker AV300 spectrometer, or Bruker ARX400 spectrometer with a sample changer and $CDCl_3$ or CD_3CN as solvents. High resolution mass spectra were acquired on a Waters LCT Premier XE time-of-flight mass spectrometer; gas chromatography/mass spectrometry (GC/MS) was performed on a Agilent 6890-5975 GC-MS with autosampler, equipped with an HP-5 column.

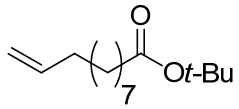
2. Alkene precursor synthesis



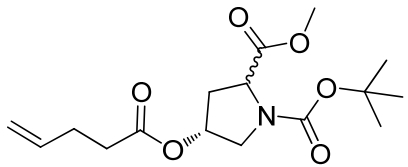
2,5,8,11,14-Pentaoxaheptadec-16-ene. An oven-dried 100 mL round bottom flask was charged with *t*-BuOK (13 mmol), dry THF (30 mL), purged with argon and cooled to 0°C in an ice bath. Tetraethyleneglycol monomethyl ether (10 mmol) was then added dropwise to the solution and the reaction stirred at 0°C for 1 h under argon. Allyl bromide (13 mmol) was added dropwise, and the solution was warmed to R.T. and allowed to stir for 24 h under argon. Deionized water (2 mL) was then added and the reaction stirred for 10 min. All liquid were then removed *in vacuo* and the residue redissolved in ethyl acetate (50 mL). The organic was washed three times with water (20 mL), dried over Na_2SO_4, filtered over Celite and then concentrated *in vacuo* to yield clear/light yellow oil (47%). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.90 (m, 1H), 5.23 (dd, 1H, $^3J_{HHtrans}$ = 17.3 Hz, , $^2J_{HHgem}$ = 1.7 Hz), 5.15 (dd, 1H, $^3J_{HH}$ = 10.4 Hz, , $^2J_{HHgem}$ = 1.5 Hz), 4.00 (dd, 2H, $^3J_{HH}$ = 5.89 Hz, , $^4J_{HH}$ = 1.5 Hz), 3.65 (m, 12H), 3.59 (m, 2H), 3.53 (m, 2H), 3.36 (s 3H) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ =134.8, 117.0, 72.2, 71.9, 70.6, 70.6, 70.6, 70.5, 69.4, 59.0 ppm. HRMS-ESI: Calculated $[M+Na]^+$: 271.1516; found: 271.1516.



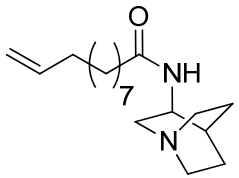
5-(2-(Allyloxy)ethyl)-4-methylthiazole. An oven-dried 100 mL round bottom flask was charged with *t*-BuOK (20.8 mmol), dry THF (25 mL), purged with argon and cooled to 0°C in an ice bath. 5-(2-Hydroxyethyl)-4-methylthiazole (16 mmol) was then added dropwise to the solution and the reaction stirred at 0 °C for 1 h under argon. Allyl bromide (20.8 mmol) was added dropwise, and the solution was warmed to R.T. and allowed to stir for 20 h under argon. Deionized water (4 mL) was then added and the reaction stirred for 10 min. All liquid were then removed *in vacuo* and the residue redissolved in ethyl acetate (50 mL). The organic phase was washed three times with water (20 mL), dried over Na_2SO_4, filtered over Celite, and then concentrated *in vacuo* to yield a yellow oil (96%).^{1}HNMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 1H), 5.89 (m, 1H), 5.23 (dd, 1H, $^3J_{HHtrans}$ = 17.4 Hz, $^2J_{HHgems}$ = 1.8 Hz), 5.13 (dd, 1H, $^3J_{HHcis}$ = 10.3 Hz, $^2J_{HHgems}$ = 1.6 Hz), 3.96 (dt, 2H, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 1.4 Hz), 3.57 (t, 2H, $^3J_{HH}$ = 6.9 Hz), 2.99 (t, 2H, $^3J_{HH}$ = 6.9 Hz), 2.37 (s, 3H) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 149.6, 149.2, 134.5, 127.9, 17.0, 71.9, 70.0, 27.0, 14.9 ppm. HRMS-ESI: Calculated $[M+H]^+$: 184.0791; found: 184.0787.



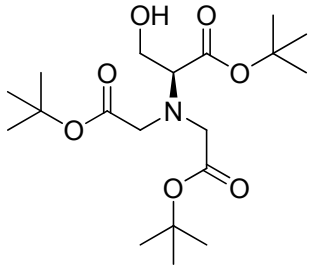
***tert*-Butyl undec-10-enoate**. An oven-dried 50 mL round bottom flask was charged with 10-undeceneoic acid (5 mmol), di-*tert*-butyl dicarbonate (10 mmol) and *tert*-butanol (10 mL). *N,N*-dimethylaminopyridine (1.5 mmol) was added to the stirred mixture and the reaction was allowed to stir for 20 h at R.T.. The reaction mixture was concentrated *in vacuo* and the residue purified by silica gel chromatography using ethyl acetate/hexanes (2:8) to afford the product as a light yellow oil (58%). R_f=0.98. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.81 (m, 1H), 4.96 (dq, 1H, $^3J_{HH}$ = 17.1 Hz, $^4J_{HH}$ = 1.6 Hz), 4.91 (dq, 1H, $^3J_{HH}$ = 10.2 Hz, $^4J_{HH}$ = 1.2 Hz), 2.19 (t, 2H, $^3J_{HH}$ = 7.7 Hz), 2.02 (q, 2H, $^3J_{HH}$ = 7.0 Hz), 1.28-1.56 (m, 21H) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 173.3, 139.2, 114.1, 79.9, 35.6, 33.8, 29.3, 29.2, 29.0, 28.9, 28.1, 25.1 ppm. GC/MS (EI): Calculated $[M-C_4H_9]^+$: 184.1; found: 184.1.



***N*-Boc 2-methyl (4R)-4-(pent-4-enoyloxy)pyrrolidine-1,2-dicarboxylate**. An oven-dried 50 mL round bottom flask was charged with *N*-Boc-trans-4-hydroxy-L-proline methyl ester (1 mmol), *N,N*-dimethylaminopyridine (0.15 mmol), pyridine (3 mmol), dry acetonitrile (5 mL), and placed under an argon atmosphere. 4-Pentenoic anhydride (3 mmol) was then added dropwise and the reaction was warmed to 50 °C and stirred under argon for 44 h. The reaction mixture was then concentrated *in vacuo*, and the residue dissolved in THF (5 mL), deionized water (3 mL), pyridine (0.5 mL) and allowed to stir an additional 24 h at 50 °C. The reaction mixture was then concentrated *in vacuo*, the residue dissolved in DCM (20 mL), and the DCM washed 1 M HCl (15 mL), water (15 mL), 1 M NaOH (15 mL), and finally with water (15 mL). The organic was dried over Na_2SO_4, filtered over Celite, and then concentrated *in vacuo* to yield a yellow oil (71%). Diastereomeric mixture (59:41). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.80 (m, 1H), 5.29 (m, 1H), 5.03 (m, 2H), 4.39 (dt, 1H, $^3J_{HH}$ = 8.7 Hz), 3.71 (s, 3H), 3.70-3.05 (m, 2H), 2.37 (m, 5H), 2.17 (m, 1H), 1.46 (s, 3H), 1.41 (s, 6H) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 172.9, 172.7, 172.3, 172.1, 154.0, 153.3, 136.2, 115.6, 80.3, 72.6, 71.8, 57.8, 57.4, 52.2, 52.0, 51.9, 36.5, 35.5, 33.2, 30.2, 29.6, 28.7, 28.2, 28.1 ppm. HRMS-ESI: Calculated $[M+Na]^+$: 350.1574; found: 350.1568.

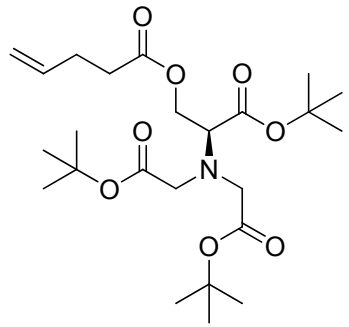


***N*-(quinuclidin-3-yl)undec-10-enamide**. An oven-dried 50 mL round bottom flask was charged with 3-aminoquinuclidine dihydrochloride (2 mmol), 10-undecenoic acid (2 mmol), *N,N*-dimethylaminopyridine (0.3 mmol), diisopropylethylamine (4 mmol), and dry DMF (15 mL). The flask was purged with argon and cooled to 0°C in an ice bath. Dicyclohexycarbodiimide (2.2 mmol) was than add to the solution, the flask repurged with argon, and the mixture warmed to R.T. and stirred for 46 h. The reaction mixture was concentrated *in vacuo* and 30 ml diethyl ether added to the residue. The solid was filtered off over Celite and the organic phase concentrated *in vacuo*. The residue was purified by silica gel chromatography using ethyl acetate/hexanes (3:7) to afford the product as a white solid (23%). R_f=0.44. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.73 (m, 1H), 4.93 (dd, 1H, $^3J_{HH}$ = 17.0 Hz, $^4J_{HH}$ = 1.5 Hz), 4.87 (d, 1H, $^3J_{HH}$ = 10.3 Hz), 3.71(m, 1H), 2.10 (t, 2H, $^3J_{HH}$ = 7.8 Hz), 1.97 (q, 2H, $^3J_{HH}$ = 7.3 Hz), 1.85 (m, 2H), 1.54-1.68 (m, 5H), 1.02-1.34 (m, 15H) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 172.2, 139.1, 114.1, 48.6, 48.0, 37.0, 34.0, 33.7, 33.2, 29.3, 29.2, 29.0, 28.8, 25.9, 25.7, 25.5, 25.0, 24.9 ppm. HRMS-ESI: Calculated $[M-C_2H_2]^+$: 266.2358; found: 266.2474.

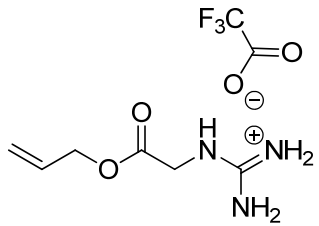


(S)-*tert*-Butyl-2-di(*tert*-butyloxycarbonylmethyl)amino-3-hydroxypropanoate. This material was prepared following a previously reported protocol (Meunier, S.; Cristau, P.; Taran, F. *Synth. Commun.* **(2005)**, *35*,2415-2425). An oven-dried 100 mL round bottom flask was charged with L-serine *tert*-butyl ester hydrochloride (4 mmol), diisopropylethylamine (24 mmol), and acetonitrile (25 mL). *tert*-butyl bromoacetate (16 mmol) was then added dropwise and the entire mixture refluxed in air for 24 h. The reaction mixture was concentrated *in vacuo* and ethyl acetate (40 mL) added and the resulting precipitate filtered off over Celite. The ethyl acetate was then concentrated *in vacuo* and the residue purified by silica gel chromatography using ethyl acetate/hexanes (2:8) to afford the product as a light yellow solid (68%). R_f=0.56. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.21 (d, 1H, $^3J_{HH}$ = 10.9 Hz), 3.69 (td, 1H, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$

= 13.6 Hz), 3.42 (m, 6H), 1.40 (s, 27H) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 171.3, 107.2, 81.7, 81.3, 68.2, 60.1, 54.9, 28.1, 28.0 ppm. HRMS-ESI: Calculated $[M+H]^+$: 390.2488; found: 390.2470.



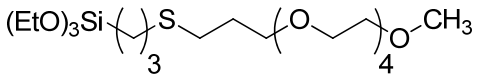
(S)-*tert*-Butyl-2-di(*tert*-butyloxycarbonylmethyl)amino-3-(pent-4-enoyloxy)-propanoate. An oven-dried 50 mL round bottom flask was charged with (S)-*tert*-butyl-2-di(*tert*-butyloxycarbonylmethyl)amino-3-hydroxypropanoate (1 mmol), *N,N*-dimethylaminopyridine (0.3 mmol), diisopropylethylamine (3 mmol), acetonitrile (5 mL), and purged with argon. 4-pentenoic anhydride (3 mmol) was then slowly added dropwise and the reaction mixture stirred under agron at 55 °C for 42 h. The reaction mixture was concentrated *in vacuo* and the residue dissolved in THF (5 mL), deionized water (1 mL), pyridine (0.5 mL), capped, and stirred at 55 °C for 24 h. Solvents were concentrated *in vacuo* and the residue purified by silica gel chromatography using ethyl acetate/hexanes (1:9) to afford the product as a light yellow oil (96%). R_f=0.49. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.80 (m, 1H), 5.05 (dq, 1H, $^3J_{HH}$ = 17.2 Hz, $^4J_{HH}$ = 1.6 Hz), 4.97 (dq, 1H, $^3J_{HH}$ = 10.2 Hz, $^4J_{HH}$ = 1.4 Hz), 4.42 (dd, 1H, $^2J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 5.9 Hz),4.29 (dd, 1H, $^2J_{HH}$ = 11.2 Hz, $^3J_{HH}$ = 6.7 Hz), 3.69 (t, 1H, $^3J_{HH}$ = 5.6 Hz), 3.55 (s, 2H), 3.54 (s, 2H), 2.36 (m, 4H), 1.45 (s, 9H), 1.44 (s, 18H) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 172.4, 170.6, 169.6, 136.6, 115.5, 81.7, 80.8, 63.8, 63.5, 54.3, 33.4, 28.7, 28.1 ppm. HRMS-ESI: Calculated $[M+H]^+$: 472.2905; found: 472.2924.



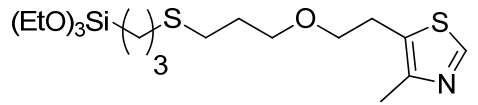
((2-(allyloxy)-2-oxoethyl)amino)(amino)methaniminium 2,2,2-trifluoroacetate. An oven-dried 100 mL round bottom flask was charged with guanidineacetic acid (4.32 mmol), trifluoroacetic acid (20 mL), and allyl alcohol (15 mL) and the reaction mixture refluxed 48 h. The reaction mixture was concentrated *in vacuo* and the residue purified by silica gel chromatography chloroform/methanol (7:3) to afford the product as a viscous yellow oil (52%). R_f=0.82 . ^{1}HNMR (400 MHz, CD_3CN): δ = 7.79 (bt, 1H, $^{3}J_{HH}$ = 5.3 Hz), 7.15 (bs, 1H), 5.90 (m, 1H), 5.33 (dd, 1H, $^{3}J_{HH}$ = 17.3 Hz, $^{4}J_{HH}$ = 1.4 Hz), 5.23 (dd, 1H, $^{3}J_{HH}$ = 10.3 Hz, $^{4}J_{HH}$ = 1.4 Hz), 4.61 (d, 2H, $^{3}J_{HH}$ = 5.6 Hz),4.01 (d, 2H, $^{3}J_{HH}$ = 6.1 Hz) ppm. ^{13}CNMR (400 MHz, CD_3CN): δ = 169.6, 159.2, 159.2, 159.1, 132.9, 132.8, 132.8, 119.0, 67.1, 67.0, 66.9, 43.7, 43.6 ppm. ^{13}CNMR (400 MHz, CD_3CN): δ = -77.5 ppm. HRMS-ESI: Calculated $[M]^+$: 158.0930; found: 158.0927.

3. Triethoxysilane synthesis

General procedure. A cooled oven-dried 10-mL round bottom was charged with MPTES (1 equiv.), alkene (1 equiv.) and 2 mol% 2,2-dimethoxy-1,2-diphenylethanone (0.02 equiv.), known commercially as Irgacure®651. The reaction was run neat unless the alkene did not fully dissolve, in which case a tiny amount of dry chloroform or methanol was added. The reaction mixture was then capped with a septum and purged briefly with argon or nitrogen. The flask was placed next to an 15 W, 18"-long blacklight having a total UV output of 2.6 W and λ_{max} = 368 nm. The flask was positioned so that one side rested against the center of the bulb. The UV flux at λ_{max} = 368 nm was measured to be 30% attenuated after passing through standard thickness Pyrex glass beaker. Both the flask and blacklight were wrapped in aluminum foil and the reaction mixture irradiated on average for 24 h with gentle stirring to yield product silanes in high purity. If solvent was added to the reaction, it was removed *in vacuo* upon completion of the reaction. Product conversion and purity were determined by ^{1}HNMR or GC/MS.

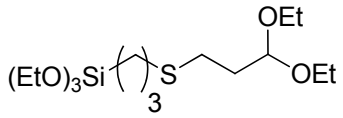


PEG triethoxysilane (1). Following the general procedure above, MPTES (2 mmol), 2,5,8,11,14-pentaoxaheptadec-16-ene (2 mmol), and Irgacure®651 (0.04 mmol) were mixed, purged with argon, and irradiated 24 h (>99% conversion, 96% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 3.78 (q, 2H, $^{3}J_{HH}$ = 6.7 Hz), 3.35-3.65 (m, 18H), 3.37 (s, 3H),2.56 (t, 2H, $^{3}J_{HH}$ = 7.6 Hz), 2.52 (t, 2H, $^{3}J_{HH}$ = 7.2 Hz), 1.82 (m, 2H), 1.68 (m, 2H), 0.726 (t, $^{3}J_{HH}$ = 8.5 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 70.6, 70.6, 70.6, 70.6, 70.5, 70.5, 70.2, 69.8, 59.0, 58.4, 35.2, 29.7, 28.6, 23.2, 18.3, 9.9 ppm. HRMS-ESI: Calculated $[M+Na]^{+}$: 509.2575; found: 509.2552.

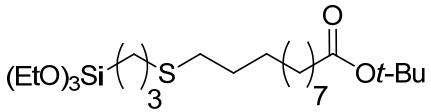


Thiazole triethoxysilane (2). Following the general procedure above, MPTES (5 mmol)**,** 5-(2-(allyloxy)ethyl)-4-methylthiazole (5 mmol), and Irgacure®651 (0.1 mmol) were mixed, purged with argon, and irradiated 24 h (>99% conversion, 95% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1H), 3.78 (q, 6H, $^{3}J_{HH}$ = 7.2 Hz), 3.56 (t, 2H, $^{3}J_{HH}$ = 6.6 Hz), 3.50 (t, 2H, $^{3}J_{HH}$ = 6.1 Hz), 2.98 (t, 2H, $^{3}J_{HH}$ = 6.4 Hz), 2.56 (t, 2H, $^{3}J_{HH}$ = 7.2 Hz), 2.50 (t, 2H, $^{3}J_{HH}$ = 7.2 Hz), 2.37 (s, 3H), 1.14 (t, 9H, $^{3}J_{HH}$ = 6.7 Hz), 0.71 (t, 2H, $^{3}J_{HH}$=7.7

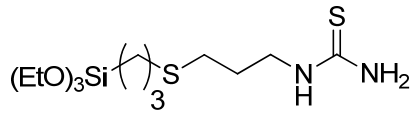
Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 149.6, 149.1, 128.0, 70.6, 69.5, 58.4, 35.1, 29.8, 28.6, 27.0, 23.0, 18.3, 14.9, 9.9 ppm. HRMS-ESI: Calculated $[M+H]^+$: 422.1850; found: 422.1850.



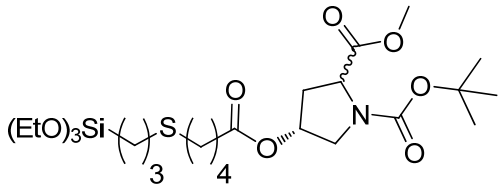
Diethyl acetal triethoxysilane (3). Following the general procedure above, MPTES (2 mmol)**,** acrolein diethyl acetal (2 mmol), and Irgacure®651 (0.04 mmol) were mixed, purged with argon, and irradiated 24 h (>99% conversion, 96% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.95 (t, 1H, $^3J_{HH}$ = 5.6 Hz), 3.80 (q, 6H, $^3J_{HH}$ = 7.1 Hz), 3.64 (m, 2H), 3.49 (m, 2H), 2.53 (q, 4H, $^3J_{HH}$ = 6.6 Hz), 1.88 (m, 2H), 1.70 (m, 2H), 1.20 (m, 15H), 0.72 (t, 2H, $^3J_{HH}$ = 8.1 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 101.17, 61.5, 58.4, 35.2, 33.9, 27.1, 23.2, 18.3, 15.3, 9.9 ppm. HRMS-ESI: Calculated $[M+Na]^+$: 391.1945; found: 391.1932.



***tert*-Butyl undecanoate triethoxysilane (4).** Following the general procedure above, MPTES (2 mmol)**,** *tert*-butyl undec-10-enoate (2 mmol), and Irgacure®651 (0.04 mmol) were mixed, purged with argon, and irradiated 24 h (>98% conversion, 96% pure). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (q, 6H, $^3J_{HH}$ = 6.9 Hz), 2.52 (t, 2H, $^3J_{HH}$ = 7.2 Hz), 2.48 (t, 2H, $^3J_{HH}$ = 7.2 Hz), 2.19 (t, 2H, $^3J_{HH}$ = 7.6 Hz), 1.68 (m, 2H), 1.56 (m, 4H), 1.43 (s, 9H), 1.36 (m, 12H), 1.22 (t, 9H, $^3J_{HH}$ = 7.2 Hz), 0.73 (t, 2H, $^3J_{HH}$ = 8.4 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 173.3, 79.9, 58.4, 35.6, 35.2, 32.0, 29.8, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.1, 25.1, 23.3, 18.3, 9.9 ppm. HRMS-ESI: Calculated $[M+Na]^+$: 501.3046; found: 501.3050.

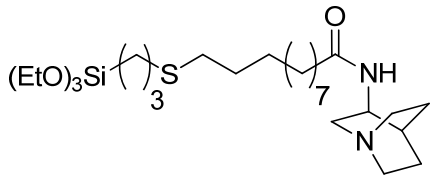


Thiourea triethoxysilane (5). Following the general procedure above, MPTES (2 mmol)**,** *N*-allylthiourea (2 mmol), Irgacure®651 (0.04 mmol), and dry MeOH (0.6 mL) were mixed, purged with argon, and irradiated 24 h (>99% conversion, 95% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 6.61 (bs, 1H), 5.94 (bs, 1H), 3.77 (q, 6H, $^{3}J_{HH}$ =6.6 Hz), 3.51 (bs, 1H), 2.51 (q, 4H, $^{3}J_{HH}$ = 7.3 Hz), 2.16 (s, 2H), 1.77 (m, 2H), 1.62 (m, 2H), 1.59 (t, 9H, $^{3}J_{HH}$ =7.4 Hz), 0.68 (t, 2H, $^{3}J_{HH}$ = 8.2 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 182.9, 58.2, 34.7, 28.9, 22.9 ppm. HRMS-ESI: Calculated $[M+Na]^{+}$: 377.1365; found: 377.1368.

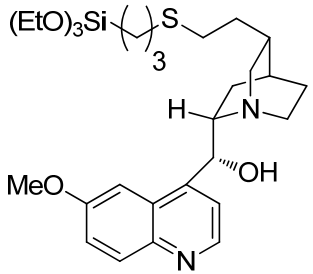


Mix of diestereomers (59:41)

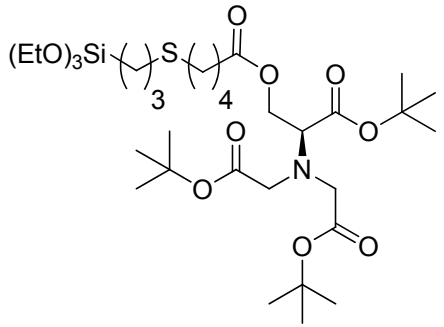
***N*-Boc-(4R)-4-hydroxy-L-proline methyl ester triethoxysilane (6).** Following the general procedure above, MPTES (0.66 mmol)**,** *N*-Boc 2-methyl (4R)-4-(pent-4-enoyloxy)pyrrolidine-1,2-dicarboxylate (0.66 mmol), and Irgacure®651 (0.013 mmol) were mixed, purged with argon, and irradiated 24 h (96% conversion, 94% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.28 (s, 1H), 4.34 (dt, 1H, $^{3}J_{HH}$ = 8.3 Hz), 3.82 (q, 6H, $^{3}J_{HH}$ = 6.9 Hz), 3.49-3.74 (m, 5H), 2.51 (q, 4H, $^{3}J_{HH}$ = 7.3 Hz), 2.36 (m, 1H 2.32 (t, 2H, $^{3}J_{HH}$ = 7.7 Hz), 2.19, (m, 1H), 1.68 (m, 6H), 1.45 (s, 3H), 1.41 (s, 6H), 1.22 (t, 9H, $^{3}J_{HH}$ = 7.2 Hz), 0.73 (t, 2H, $^{3}J_{HH}$ = 8.0) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 173.1, 172.8, 172.7, 154.2, 153.5, 80.5, 72.5, 71.8, 58.4, 57.9, 57.5, 52.3, 52.2, 52.1, 52.0, 36.6, 35.6, 35.1, 33.8, 31.4, 29.0, 28.3, 28.2, 24.0, 23.2, 18.3, 9.9 ppm. HRMS-ESI: Calculated $[M+Na]^{+}$: 588.2639; found: 588.2649.



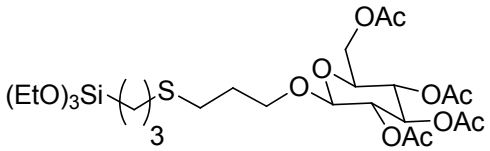
Quinuclidine triethoxysilane (7). Following the general procedure above, MPTES (0.41 mmol)**,** *N*-(quinuclidin-3-yl)undec-10-enamide (0.41 mmol), Irgacure®651 (0.008 mmol), and dry $CHCl_3$ (0.5 mL) were mixed, purged with argon, and irradiated 24 h (>98% conversion, 96% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.34 (s, 1H), 3.80 (m, 6H), 2.52 (t, 2H, $^3J_{HH}$ = 7.5 Hz), 2.48 (t, 2H, $^3J_{HH}$ = 7.5 Hz), 2.11 (t, 2H, $^3J_{HH}$ = 7.8 Hz), 1.57-1.89 (m, 12H), 1.23 (m, 26H), 0.73 (t, 2H, $^3J_{HH}$ = 8.2 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 172.1, 129.1, 77.2, 67.1, 58.4, 58.2, 48.0, 37.1, 35.2, 33.3, 32.0, 29.8, 29.5, 29.4, 29.3, 29.2, 29.0, 25.9, 25.6, 24.9, 23.2, 18.3, 9.9 ppm. HRMS-ESI: Calculated $[M\text{-}C_3H_6NO]^+$:458.3124; found: 458.3134.



Quinine triethoxysilane (8). Following the general procedure above, MPTES (1 mmol)**,** quinine (1 mmol), Irgacure®651 (0.02 mmol), and dry $CHCl_3$ (1 mL) were mixed, purged with argon, and irradiated 27 h (>98% conversion, 96% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 8.63 (d, 1H, $^3J_{HH}$ = 4.6 Hz), 7.95 (d, 1H, $^3J_{HH}$ = 9.2 Hz), 7.47 (d, 1H, $^3J_{HH}$ = 5.1 Hz), 7.31 (dd, 1H, $^3J_{HH}$ = 9.2 Hz, $^4J_{HH}$ = 2.6 Hz), 7.22 (d, 1H, $^4J_{HH}$ = 2.0 Hz), 5.51 (s, 1H), 3.98 (s, 3H), 3.78 (q, 6H, $^3J_{HH}$ = 7.1 Hz),3.58 (bs, 1H), 3.42 (bs, 1H), 3.06 (m, 2H), 2.65 (m, 1H), 2.45 (t, 2H, $^3J_{HH}$ = 7.1 Hz), 2.39 (t, 2H, $^3J_{HH}$ = 7.1 Hz), 1.42-1.75 (m, 10H), 1.19 (t, 9H, $^3J_{HH}$ = 6.6 Hz), 0.67 (t, 2H, $^3J_{HH}$ = 8.2 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 157.8, 147.6, 144.3, 131.6, 126.6, 121.5, 118.4, 117.5, 101.3, 77.2, 72.0, 59.8, 58.4, 43.2, 35.2, 34.7, 34.7, 30.0, 28.2, 25.7, 23.2, 21.7, 18.3, 9.9 ppm. HRMS-ESI: Calculated $[M+H]^+$: 563.2969; found: 563.2977.



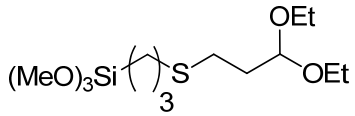
Nitrilotriacetate (NTA) triethoxysilanesilane (9). Following a similar procedure to the one described above, MPTES (0.5 mmol), (S)-*tert*-butyl-2-di(*tert*-butyloxycarbonylmethyl)amino-3-(pent-4-enoyloxy)propanoate (0.5 mmol), and Irgacure®651 (0.015 mmol, 3 mol %) were mixed, purged with argon, and then gently warmed in an oil bath until the Irgacure®651 dissolved. The mixture was then irradiated 45 h. Following, an additional amount of Irgacure®651 (0.01 mmol, 2 mol%) was added to the reaction, the flask purged, and the mixture irradiated an additional 22 h (94% conversion, 90% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.41 (dd, 1H, $^{2}J_{HH}$ = 10.9 Hz, $^{3}J_{HH}$ = 5.8 Hz),4.27 (dd, 1H, $^{2}J_{HH}$ = 10.9 Hz, $^{3}J_{HH}$ = 6.9 Hz), 3.81 (q, 6H, $^{3}J_{HH}$ = 6.9 Hz), 3.68 (t, 1H, $^{3}J_{HH}$ = 6.6 Hz), 3.54 (d, 3H, $^{4}J_{HH}$ = 2.8 Hz), 2.50 (m, 4H), 2.30 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz), 1.57-1.71 (m, 6H), 1.45 (m, 28H), 1.21 (t, 9H, $^{3}J_{HH}$ = 7.1 Hz), 0.72 (t, 2H, $^{3}J_{HH}$ = 8.3 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 172.7, 170.5, 169.6, 81.8, 80.8, 63.8, 63.4, 58.4, 54.2, 35.1, 33.6, 31.5, 29.1, 28.1, 24.0, 23.2, 18.3, 9.9 ppm. HRMS-ESI: Calculated $[M+H]^+$: 710.3964; found: 710.3981 ppm.



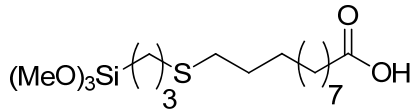
Tetra-*O*-acetyl-β-D-glucopyranoside triethoxysilane (10). Following the general procedure above, MPTES (1 mmol)**,** allyl-tetra-*O*-acetyl-β-D-glucopyranoside (1 mmol), Irgacure®651 (0.02 mmol), and dry $CHCl_3$ (0.6 mL) were mixed, purged, and irradiated 25 h (>99% conversion, 97% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.30 (s, 2H), 5.20 (t, 1H, $^{3}J_{HH}$ = 8.9 Hz), 5.07 (t, 1H, $^{3}J_{HH}$ = 9.5 Hz), 4.97 (t, 1H, $^{3}J_{HH}$ = 8.9 Hz), 4.50 (d, 1H, $^{3}J_{HH}$ = 8.9 Hz), 4.28 (dd, 1H, $^{3}J_{HH}$ = 12.5 Hz, $^{3}J_{HH}$ = 4.8 Hz), 4.14 (dd, 1H, $^{3}J_{HH}$ = 12.5 Hz, $^{3}J_{HH}$ = 2.4 Hz), 3.70 (dt, 1H, $^{3}J_{HH}$ = 10.1 Hz, $^{3}J_{HH}$ = 5.4 Hz), 3.82 (q, 6H, $^{3}J_{HH}$ = 7.2 Hz), 3.62 (m, 2H), 2.53 (q, 4H, $^{3}J_{HH}$ = 7.7 Hz), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.80 (m, 2H), 1.67 (m, 2H), 1.22 (t, 9H, $^{3}J_{HH}$=7.1 Hz) 0.73 (t, 2H, $^{3}J_{HH}$=8.3 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 170.7, 170.3, 169.4, 169.3, 101.0, 72.9, 71.8, 71.3, 68.5, 62.0, 58.4, 53.4, 53.1, 29.4, 28.2, 23.2, 20.8, 20.7, 20.6, 20.6, 18.3, 10.0 ppm. HRMS-ESI: Calculated $[M+Na]^+$: 422.1850; found: 422.1850.

4. Silane synthesis using MPTMS or thiol/ATES.

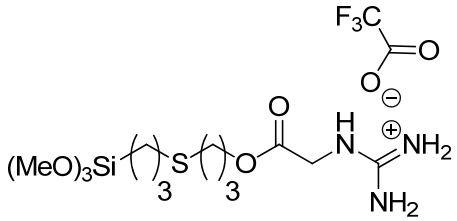
General procedure. A cooled oven-dried 10-mL round bottom was charged with either MPTMS, alkene (1 equiv.) and 2 mol% Irgacure®651, or ATES (1 equiv.), or thiol (1 equiv.) and 2 mol% Irgacure®651. The reaction was run neat unless one of the reactants did not fully dissolve; in which case a tiny amount of dry chloroform, or methanol was added. The reaction mixture was then capped with a septum and purged briefly with argon or nitrogen. The flask was placed next to an 18" 15 W blacklight, with total UV output of 2.6 W and λ_{max} = 368 nm, so that the flask's side rested against the center of the bulb. The UV flux at λ_{max} = 368 nm was measured to be attenuated ~30% after passing through standard thickness Pyrex glass. Both the flask and UV blacklight were wrapped in aluminum foil and the reaction mixture irradiated for 24 hours with gentle stirring to yield products in high purity. If solvent was added to the reaction, it was removed upon reaction completion *in vacuo*.



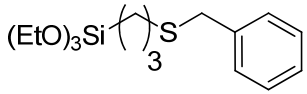
Acetal trimethoxysilane (11). Following the general procedure above, MPTMS (2 mmol)**,** acrolein diethyl acetal (2 mmol), Irgacure®651 (0.04 mmol), were mixed, purged, and irradiated 24 h (>99% conversion, 96% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.59 (t, 1H, $^{3}J_{HH}$ = 5.5 Hz), 3.64 (m, 2H), 3.54 (s, 9H), 3.49 (m, 2H), 2.52 (q, 4H, $^{3}J_{HH}$ = 7.5 Hz), 1.86 (m, 2H), 1.69 (m, 2H), 1.19 (t, 6H, $^{3}J_{HH}$ = 7.0 Hz), 0.74 (t, 2H, $^{3}J_{HH}$ = 8.1 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 101.7, 61.5, 50.5, 35.1, 33.8, 27.1, 22.9, 15.3, 8.6 ppm. HRMS-ESI: Calculated $[M+Na]^+$: 349.1475; found: 349.1478.



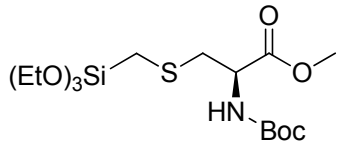
Undecanoic acid trimethoxysilane (12). Following the general procedure above, MPTMS (2.5 mmol)**,** 10-undecenoic acid (2.5 mmol), Irgacure®651 (0.05 mmol), and dry $CHCl_3$ (0.5 mL) were mixed, purged, and irradiated 24 h (>99% conversion, 96% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 3.56 (s, 9H), 2.50 (m, 4H), 2.34 (t, 2H, $^{3}J_{HH}$ = 7.8 Hz), 1.60 (m, 6H), 1.32 (m, 12H), 0.75 (t, 2H, $^{3}J_{HH}$ = 8.1 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 179.5, 117.7, 50.5, 35.1, 34.0, 32.0, 29.7, 29.4, 29.3, 29.2, 29.0, 28.9, 24.7, 23.0, 8.6 ppm. HRMS-ESI: Calculated $[M-H]^-$: 379.1980; found: 379.1992.



Guanidinum triethoxysilane (13). Following the general procedure above, MPTMS (1.0 mmol)**,** ((2-(allyloxy)-2-oxoethyl)amino)(amino)methaniminium 2,2,2-trifluoroacetate (1.0 mmol), Irgacure®651 (0.05 mmol), and dry CH_3CN (0.7 mL) were mixed, purged, and irradiated 24 h (>99% conversion, 95% pure). The final product contained some dimerized silane due to reaction of **13** with small amounts of water trapped in the guanidinium salt. Formation of the dimer was determined from analysis of the high resolution mass spectrum, ^{1}HNMR, and ^{13}CNMR spectra. ^{1}HNMR (400 MHz, CD_3CN): δ = 7.81 (bs, 1H), 7.16 (bs, 4H), 4.20 (t, 2H, $^3J_{HH}$ = 6.4 Hz), 3.96 (bs, 2H), 3.49 (s, 5H), 2.52 (m, 4H), 1.87 (m, 2H), 1.62 (m, 2H), 0.72 (t, 2H, $^3J_{HH}$ = 7.9 Hz) ppm. ^{13}CNMR (400 MHz, CD_3CN): δ = 168.7, 168.6, 168.6, 158.2, 64.2, 7, 42.7, 34.2, 28.4, 27.5, 22.9, 22.8, 9.5, 9.4, 8.0 ppm. ^{13}FNMR (400 MHz, CD_3CN): δ = -76.6 ppm. HRMS-ESI: Calculated $[M\text{-}C_2O_2F_3]^+$: 354.1519; found: 354.1518. Calculated for dimer $[2M\text{-}2C_2O_2F_3\text{-}2MeO\text{-}H]^+$: 661.2535; found: 661.2549.



Benzyl triethoxysilane (14). Following the general procedure above, ATES (2 mmol)**,** benzyl hydrosulfide (2 mmol), Irgacure®651 (0.04 mmol), were mixed, purged, and irradiated 24 h (>99% conversion, 97% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.30 (m, 4H), 7.23 (m, 1H), 3.80 (q, 6H, $^3J_{HH}$ = 7.0 Hz), 3.70 (s, 2H), 2.44 (t, 2H, $^3J_{HH}$ = 7.3 Hz), 1.66 (m, 2H), 1.22 (t, 9H, $^3J_{HH}$ = 7.0 Hz), 0.70 (t, 2H, $^3J_{HH}$ = 8.3 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 138.7, 128.8, 128.4, 126.9, 58.4, 36.1, 34.4, 22.8, 18.3, 9.9 ppm. HRMS-ESI: Calculated $[M\text{-}C_4H_9O]^+$: 255.0870; found: 255.0874.



Boc-cysteine-OMe triethoxysilane (15). Following the general procedure above, ATES (2 mmol)**,** *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester (2 mmol), Irgacure®651 (0.04 mmol), were mixed, purged, and irradiated 24 h (>99% conversion, 97% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.43 (d, 1H, $^{3}J_{HH}$= 7.7 Hz), 4.51 (q, 1H, $^{2}J_{HH}$ = 14.5 Hz, $^{3}J_{HH}$ = 4.9 Hz), 3.80 (q, 6H, $^{3}J_{HH}$ = 7.0 Hz), 3.74 (s, 3H), 2.93 (d, 2H, $^{3}J_{HH}$ = 4.6 Hz), 2.52 (t, 2H, $^{3}J_{HH}$ = 7.3 Hz), 1.65 (m, 2H), 1.43(s, 9H), 1.20 (t, 9H, $^{3}J_{HH}$ = 6.6 Hz), 0.69 (t, 2H, $^{3}J_{HH}$ = 8.4 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 171.6, 155.1, 80.0, 58.3, 53.2, 52.4, 35.6, 34.3, 28.3, 23.1, 18.3, 9.8 ppm. HRMS-ESI: Calculated $[M+H]^{+}$: 440.2138; found: 440.2123.

5. Large-scale synthesis of 3

A cooled oven-dried Pyrex glass tube (7.5" tall, 1" diameter) with a 29/42 joint was charged with MPTES (107 mmol), acrolein diethyl acetal (107 mmol), Irgacure®651 (2.1 mmol), and then capped with a septum purged briefly with argon. The small tube diameter made it possible for the maximum amount of light to illuminate the reaction mixture. The tube was placed next to two 15 W, 18" long blacklights, each having a total UV output of 2.6 W (λ_{max} = 368 nm). The tube was positioned so that each blacklight just rested against each side of the tube, (See Figure S1 below.) The flask and blacklights were wrapped in aluminum foil and the reaction mixture irradiated for 24 h with gentle stirring to yield product silanes in high purity (>99% conversion, 93% pure). ^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.95 (t, 1H, $^{3}J_{HH}$ = 5.6 Hz), 3.80 (q, 6H, $^{3}J_{HH}$ = 7.1 Hz), 3.64 (m, 2H), 3.49 (m, 2H), 2.53 (q, 4H, $^{3}J_{HH}$ = 6.6 Hz), 1.88 (m, 2H), 1.70 (m, 2H), 1.20 (m, 15H), 0.72 (t, 2H, $^{3}J_{HH}$ = 8.1 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$): δ = 101.17, 61.5, 58.4, 35.2, 33.9, 27.1, 23.2, 18.3, 15.3, 9.9 ppm.

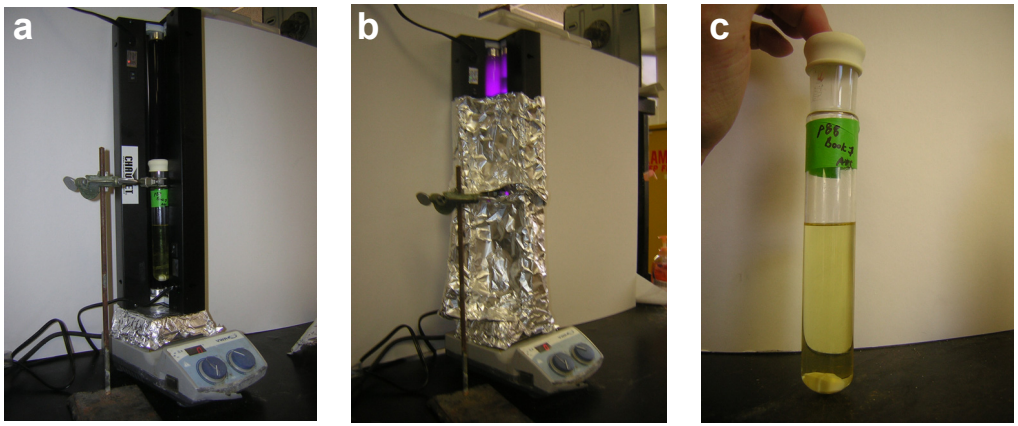


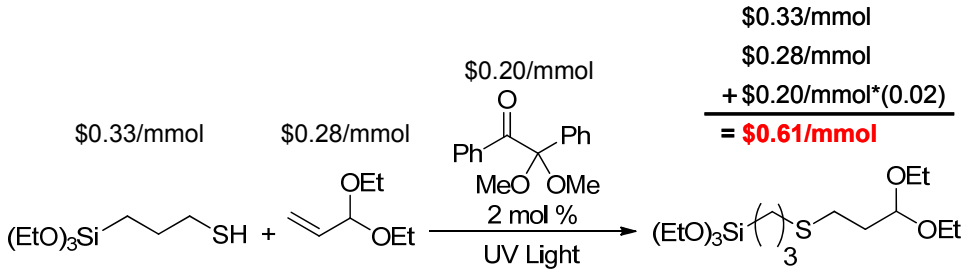
Figure S1. Images of setup for large-scale synthesis of **3:** a) prior to, and b) during reaction. c) Image of reaction tube containing product **3** after the reaction was complete.

6. Cost analysis for synthesizing triethoxysilanes 3 and 7

The estimates provided here of the material cost to produce triethoxysilanes **3** and **7** via the thiol-ene reaction were simplified by only considering the cost of the chemicals. [The blacklights, stir plate, glassware, and energy required to power the lamps were not included because the equipment is reusable and the blacklights we used are very inexpensive.]

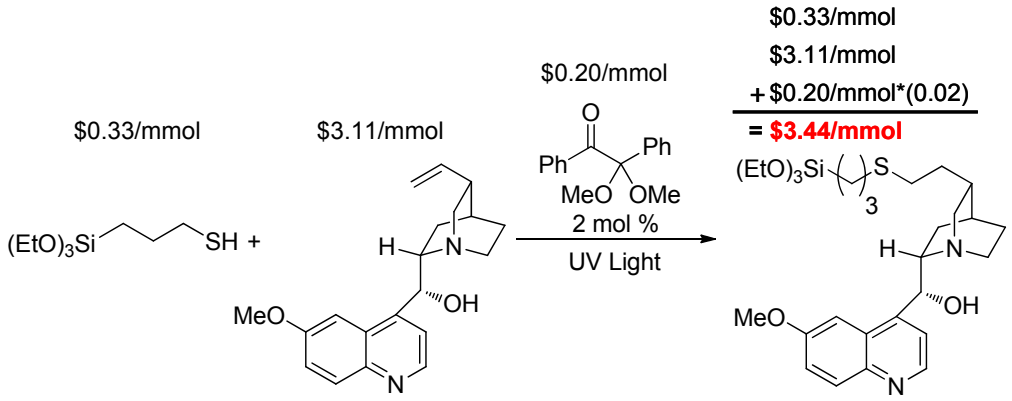
The cost estimates for producing **3** and **7** per mmol material are shown below in Schemes S1 and S2, respectively. Starting materials to prepare **3** and **7** included 25 g acrolein diethyl acetal (≥96%), 5 g quinine (suitable for fluorescence, anhydrous, ≥98.0%), 50 g 2,2-dimethoxy-1,2-diphenylethanone (>99%) purchased from Sigma Aldrich, and 25g MPTES (≥95%) purchased from Gelest Inc.

The estimated cost to prepare **3** is $0.61/mmol **3.** The retail price of the chemically similar, commercially available triethoxysilylundecanal ethylene glycol acetal (Gelest catalog #: SIT8194.5) is 13 times higher.



Scheme S1. Synthesis of diethyl acetal triethoxysilane **3** and cost of materials.

The estimated cost to prepare **7** is $3.44/mmol. For comparison, the price of (R)-*N*-triethoxysilylpropyl quinine urethane (Gelest catalog #: SIT8192.4) is 4 times higher.



Scheme S2. Synthesis of quinine triethoxysilane **7** and cost of materials.

7. UV-visible spectra of silane 9 and photoinitiator.

Figure S2 shows an overlay of the UV-visible spectra of silane **9** (0.3 M) and the Irgacure® 651 photoinitiator (0.003 M). At 368 nm, λ_{max} for the blacklight used to drive the thiol-ene reaction, there is a little overlap of the absorption bands of the photoinitiator and product. Despite the large difference in molar extinction coefficients at 368 nm, one must remember that the photoinitiator is present at only at 2 mol% while the silane is extremely concentrated. Consequently, there is significant absorbance overlap at 365 nm. This absorbance overlap is believed to be a factor that prevents the reaction of MPTES (0.5 mmol) and (S)-*tert*-butyl-2-di(*tert*-butyloxycarbonylmethyl)amino-3-(pent-4-enoyloxy)propanoate from reaching completion. The other contributing factor is thought to be the increase in the solution viscosity of the reaction as it proceeds, which limits mass transport.

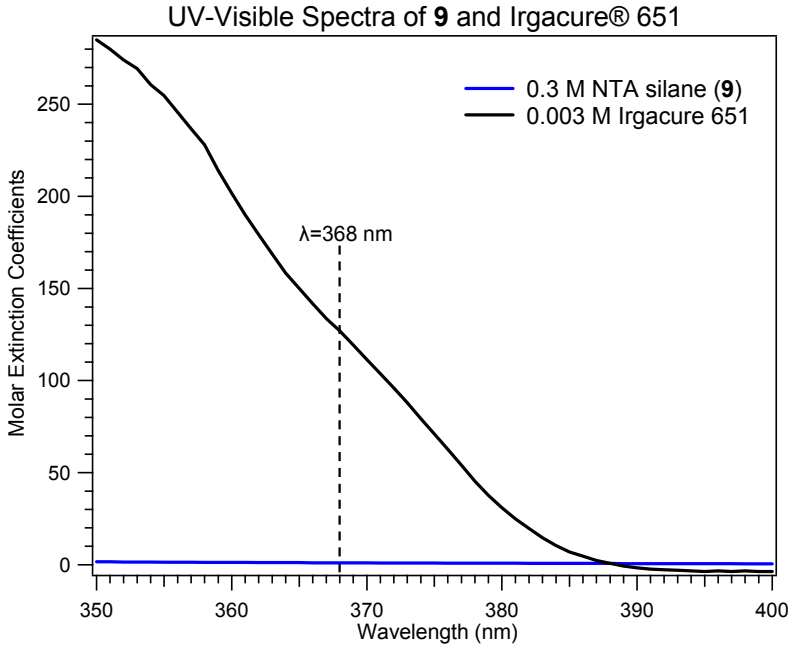


Figure S2. UV-visible spectra of 0.3 M NTA silane **9** in chloroform (black line) and 0.003 M Irgacure® 651 in chloroform (blue line) with the y-axis normalized to concentration and sample path length..

8. Nanoparticle synthesis and silane surface coating procedure.

8.1-Preparation of oleic acid-coated Fe_3O_4 superparamagnetic nanoparticles (SPNs). Core magnetite SPNs were synthesized by the method previously described.[1] Briefly, 1 mL of an aqueous 3.0 M $FeCl_2$, 2 M HCl solution was mixed with 4 mL of 1.5 M $FeCl_3$, 2 M HCl on a magnetic stir plate at R.T. The iron chloride solution was then slowly titrated dropwise with 50 mL of 1.05 M NH_4OH over a period of about 30 min, producing a deep black particle suspension. The superparamagnetic magnetite nanoparticles were separated using a hand-held neodymium rare-earth magnet and washed three times with water, three times with acetone, and then air-dried for at least 3 h. The collected particles were crushed, weighed and placed in a screw-cap glass vial. An equal weight of oleic acid was added to the vial along with 1 mL ethyl acetate *per 0.1 g SPNs*. The vial was capped and sonicated for 2 h at 60 °C. The suspension was cooled, and the particles were magnetically separated, washed three times with excess ethyl acetate, three times with methanol, and then dried under vacuum. The final product was crushed to yield a black/dark brown powder.

8.2- General procedure for functionalizing Fe_3O_4 SPNs with triethoxysilanes 1–10. The goal of these experiments was simply to determine whether the triethoxysilanes **1–10** could be covalently attached to magnetite SPN surfaces and detected. Because we were not concerned with the relative surface reactivities of the silanes, the amount of silane used in the reaction was not tightly controlled. In most cases, the triethoxysilanes were made on ≥1 mmol scale, and 1 mmol was used to coat the SPNs. In a few cases, <1 mmol was synthesized, and all of the product was used to coat the SPNs.

Oleic acid-coated SPNs (120 mg), and either toluene or dioxane (60 mL), passed over $MgSO_4$ just prior to use, were added to a hot, oven-dried 100 mL round bottom flask. The flask was immediately capped and purged with argon for 5 min. The flask was then placed in an ultrasonication bath at R.T. and sonicated for 20 min to redisperse the oleic acid-coated SPNs. Then a stir bar was quickly added to the flask, which was immediately capped and purged 5 min with argon while vigorously stirring the particle suspension to prevent the SPNs from sticking to the stir bar. An argon balloon was placed on the flask and a triethoxysilane (0.4 to 1 mmol; see Table S1 for exact quantity of added silane) was added to the flask dropwise. The flask was placed in a 75 °C oil bath and heated for 24 h with vigorous stirring. The stir bar was removed and the particles were separated using a hand-held rare-earth magnet, washed three times with either diethyl ether or $CHCl_3$, and then dried under vacuum.

9. Nanoparticle spectroscopic data.

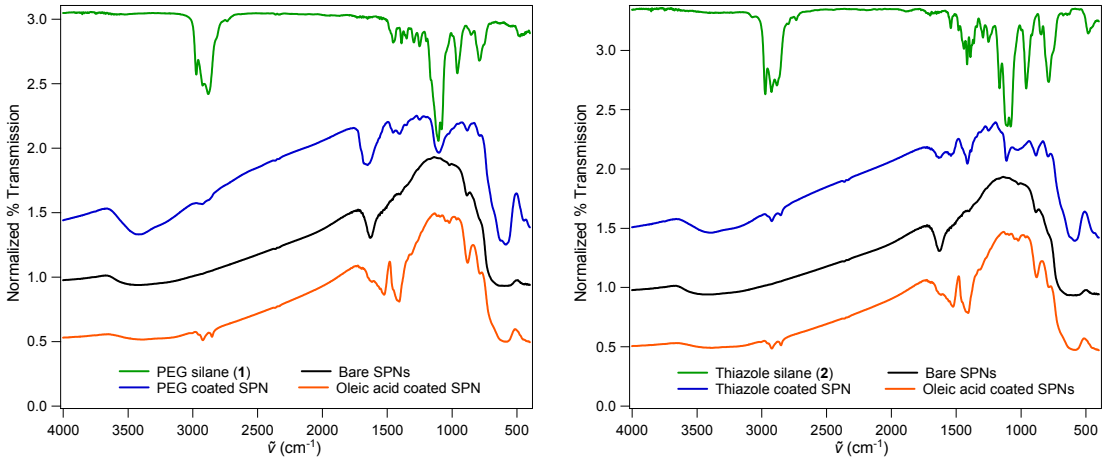
9.1- Elemental analysis of silane loadings on coated SPNs. All triethoxysilanes used to coat the SPNs contained at least one sulfur atom present in the thioether bridge formed during synthesis of the silane. This allowed quantification of silane loadings on coated SPNs by sulfur elemental analysis. The experimentally-determined loadings are given in Table S1. Nearly all of the thiol-ene reactions used to produce these silanes reached ≥98% conversion. The crude products contained virtually no MPTES, which, if present, could bind to the surface and contribute to the measured sulfur content. Hence, for the reactions with >98% reactant conversions, we have assumed that the measured SPN sulfur content of the silane-coated particles derived only from the *functional triethoxysilane*. For the two cases in which the reactions reached only 94% or 96% conversion (**6**, **9**), we have assumed that the percentage of the measured sulfur content that is attributable to surface-bound functional triethoxysilane is at best equal to the percent purity of the as-synthesized crude silane .

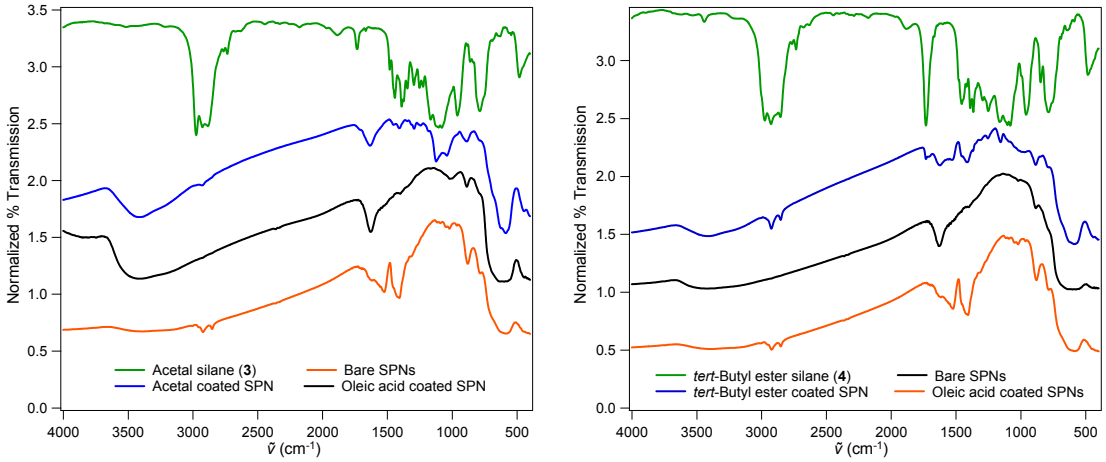
Table S1. Triethoxysilane loadings on SPNs.[a]

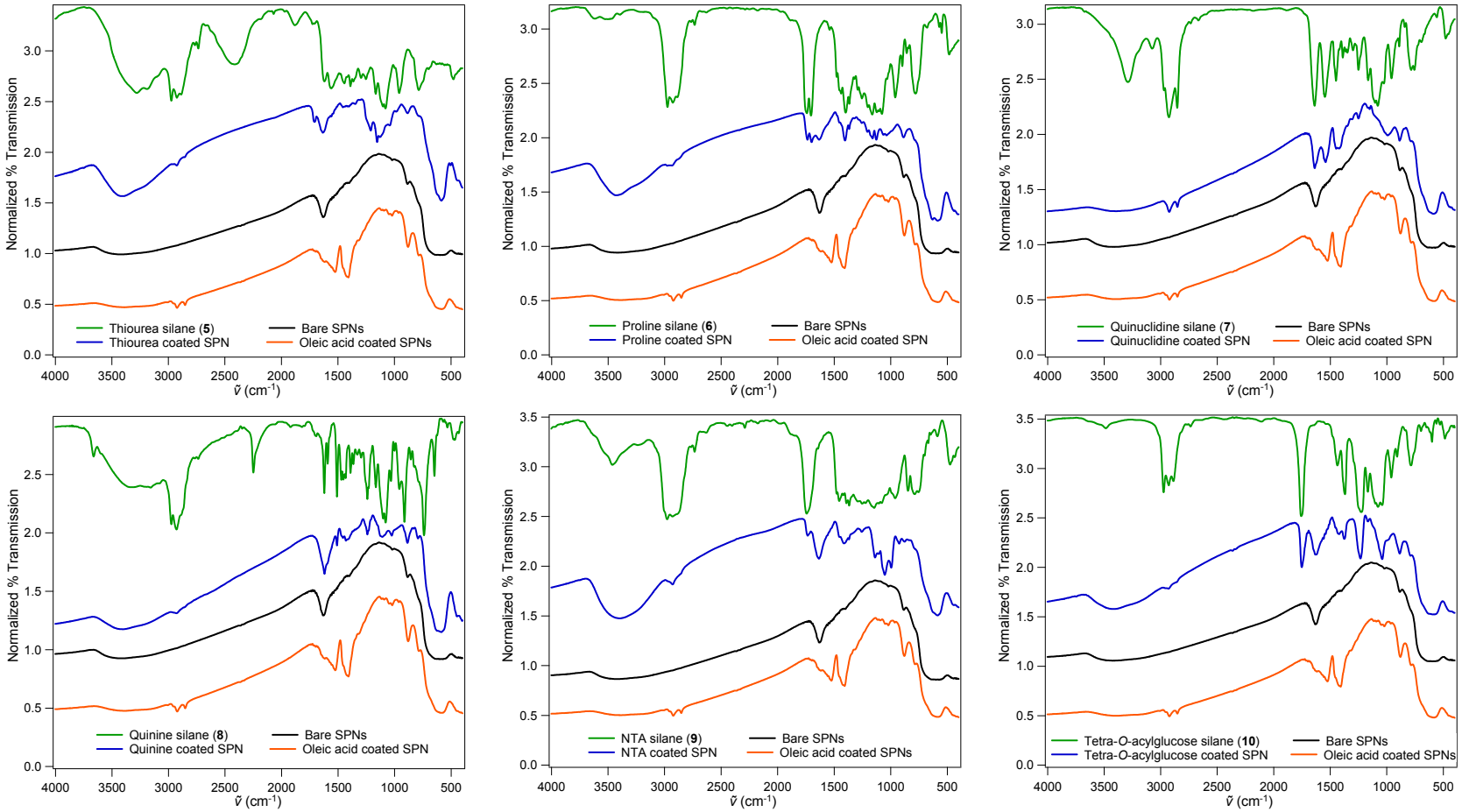
Coated silane	Quantity used (mmol)	Silane loading (mmol/g SPN)
1	1.0	0.23
2	1.0	0.34
3	1.0	0.79
4	1.0	0.16
5	1.0	0.31
6	0.5	0.23[b]
7	0.4	0.27
8	1.0	0.27
9	0.5	0.13[c]
10	1.0	0.15

[a]Loadings determined by sulfur elemental analysis.
[b]Silane loading assuming 94% of the SPN sulfur content is from the functional silane and the rest from MPTES.
[c]Silane loading assuming 90% of the SPN sulfur content is from the functional silane and the rest from MPTES.

9.2- FT-IR spectroscopic analysis of silane-coated SPNs. FT-IR spectra of silane-coated SPNs pressed into KBr pellets were obtained to confirm that that silanes had been immobilized on the particle surfaces. The figures shown below depict overlaid FT-IR spectra of the pure silanes, silane-coated SPNs, oleic acid-coated SPNs, and bare magnetite SPNs. The spectra verify that all of the triethoxysilanes **1**–**10** were successfully immobilized onto the surface of oleic-acid coated SPNs. A key indication that silanes have been covalently immobilized on the nanoparticle surface is the presence of a new Si-O-Si stretching vibration between 1060 and 1140 cm^{-1}.




Normalized % Transmission
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
4000
3500
3000
2500
2000
1500
1000
500
ṽ (cm-1)
Acetal silane (3)
Acetal coated SPN
Bare SPNs
Oleic acid coated SPN
Normalized % Transmission
3.0
2.5
2.0
1.5
1.0
0.5
0.0
4000
3500
3000
2500
2000
1500
1000
500
ṽ (cm-1)
tert-Butyl ester silane (4)
tert-Butyl ester coated SPN
Bare SPNs
Oleic acid coated SPNs


Normalized % Transmission
ṽ (cm-1)
Thiourea silane (5)
Thiourea coated SPN
Bare SPNs
Oleic acid coated SPNs
Proline silane (6)
Proline coated SPN
Bare SPNs
Oleic acid coated SPN
Quinuclidine silane (7)
Quinuclidine coated SPN
Bare SPNs
Oleic acid coated SPN
Quinine silane (8)
Quinine coated SPN
Bare SPNs
Oleic acid coated SPN
NTA silane (9)
NTA coated SPN
Bare SPNs
Oleic acid coated SPNs
Tetra-O-acylglucose silane (10)
Tetra-O-acylglucose coated SPN
Bare SPNs
Oleic acid coated SPNs

9.3- Magnetic properties of SPNs. The magnetic properties of the synthesized SPNs were measured at R.T. on a supercritical quantum interference device (SQUID). Figure S3 shows magnetic hysteresis curves for all of the SPNs: the bare magnetite, the oleic acid-coated particles, and the silane-modified SPNs. All of the particles exhibit low coercivity, <20 Oe, indicating that they are superparamagnetic. Both the coated and uncoated particles have excellent saturation magnetizations, >34 emu/g, which means they are strongly attracted to magnetic fields produced by standard rare-earth magnets.

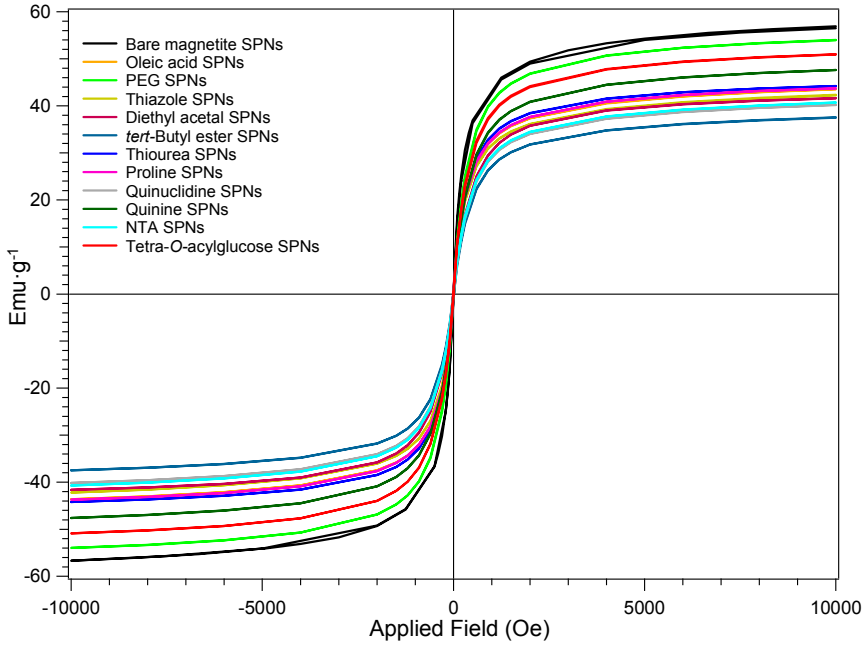


Figure S3. Magnetic hysteresis curves of all synthesized SPNs.

9.4- Transmission electron microscopy (TEM) of SPNs. The TEM images in Figure S4 show silane-coated SPNs ranging in size from ~10 to 25 nm. This polydispersity is expected from the protocol that was used to prepare these Fe_3O_4 nanoparticles. Single particles, clusters and large aggregates are typically present. We did not systematically investigate the reasons for the varying extent of particle aggregation, because many factors can influence this process and some are interdependent. These factors include: a) the composition of the surface coating; b) the surface coverage of the silane coating; c) the uniformity of silane coating; d) interactions between the particles, which are solvent-dependent; e) the dispersing solvent; and f) the cleanliness and surface charge of the carbon grids onto which the particle suspensions are deposited for TEM analysis.

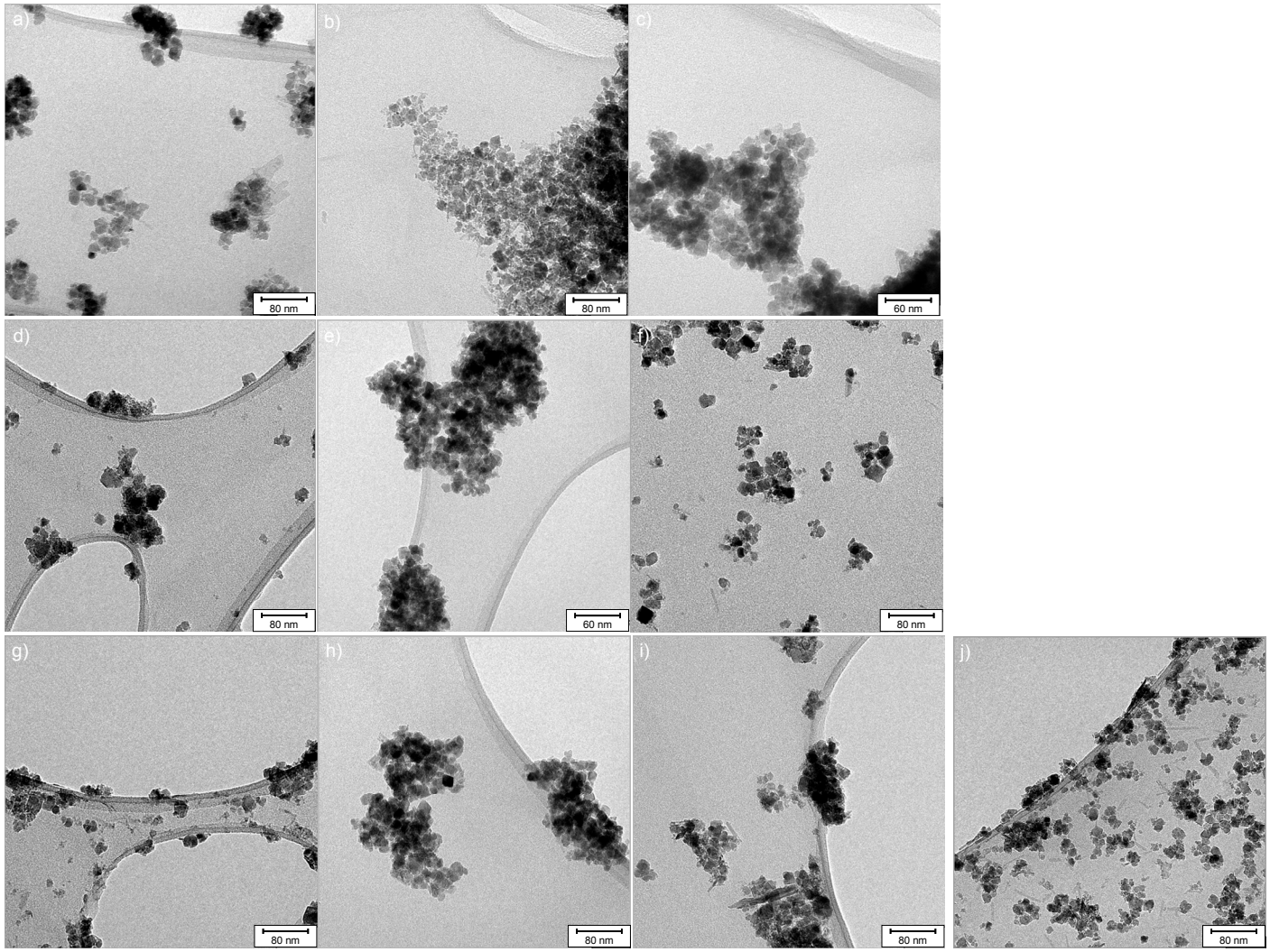
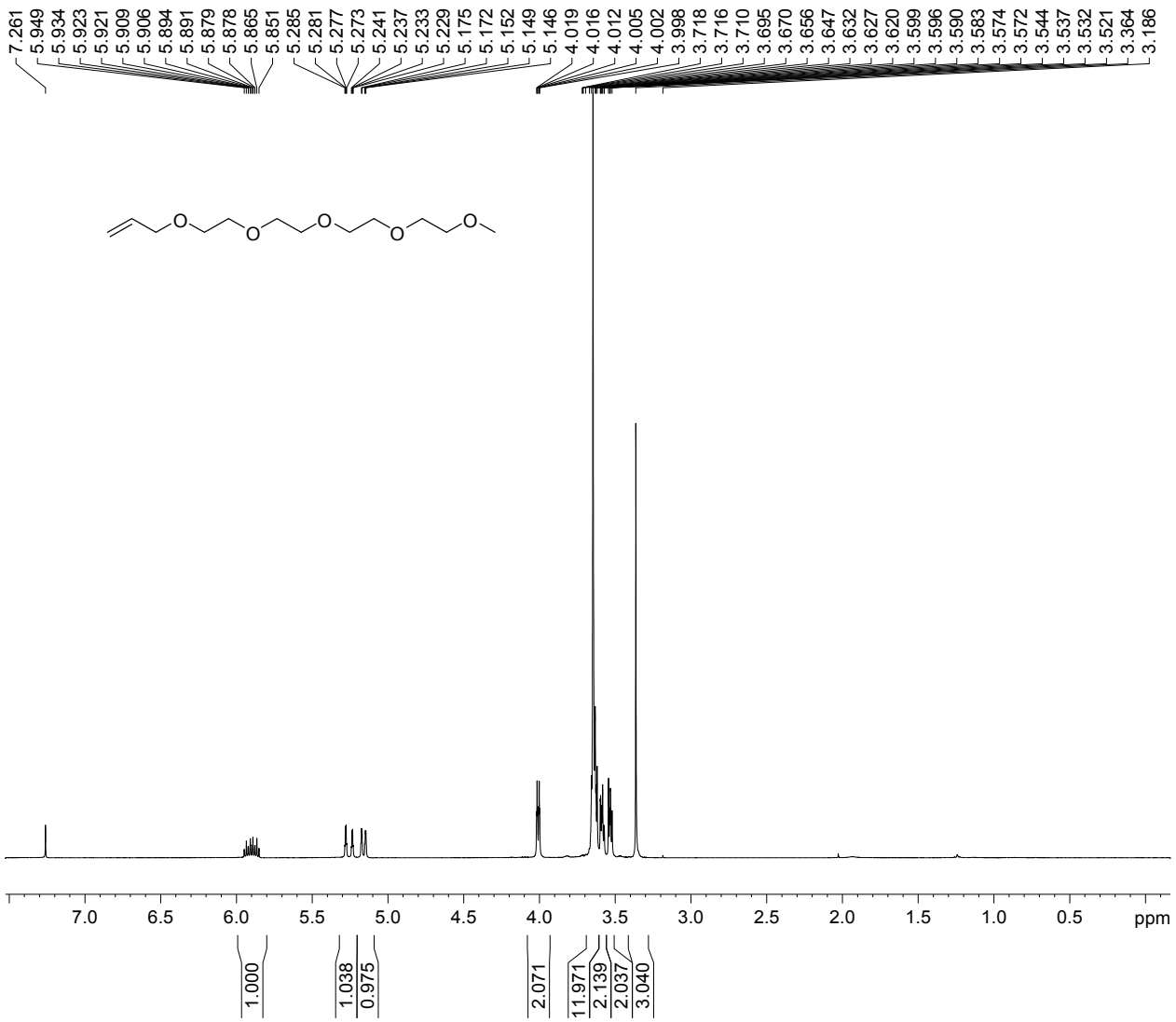


Figure S4. TEM images of a) PEG SPNs, **1**, b) thiazole SPNs, **2**, c) aectal SPNs, **3**, d) *tert*-butyl ester SPNs, **4**, e) thiourea SPNs, **5**, f) proline SPNs, **6**, g) quinuclidine SPNs, **7**, h) quinine SPNs, **8**, i) NTA SPNs, **9**, j) tetra-*O*-acylglucose, **10**, SPNs.

10. ^{1}H and ^{13}CNMR spectra of synthesized compounds.

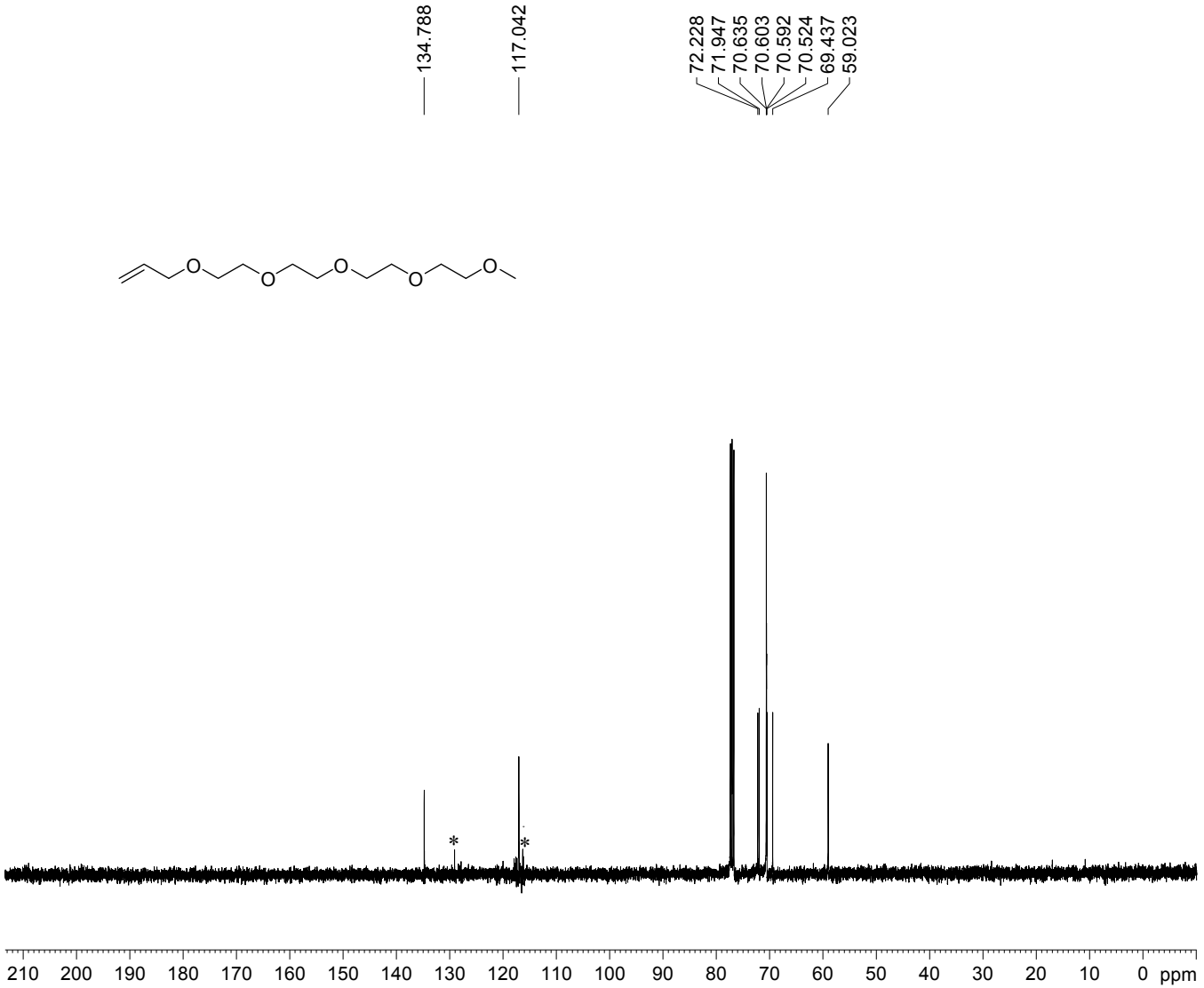
Shown below are ^{1}HNMR and ^{13}CNMR spectra of the synthesized compounds. Note that ^{13}CNMR spectra obtained with our 400 MHz spectrometer sometimes showed a significant amount of noise at ~118 and 129 ppm. Although this noise may look like one or more real spectral features, it is an artifact produced by the spectrometer, and cannot be corrected or compensated for, due to the instrument's age. These artifacts, denoted with asterisks (*) in the ^{13}CNMR spectra, are more noticeable when the signal-to-noise ratio is low. We have verified that the features are not assignable to vinyl carbons from unreacted alkenes by observing that ^{1}HNMR spectra of the same samples usually have extremely weak or no signals from the vinyl protons. Most importantly, high resolution mass spectra of the synthesized compounds confirm their identities.

2,5,8,11,14-Pentaoxaheptadec-16-ene



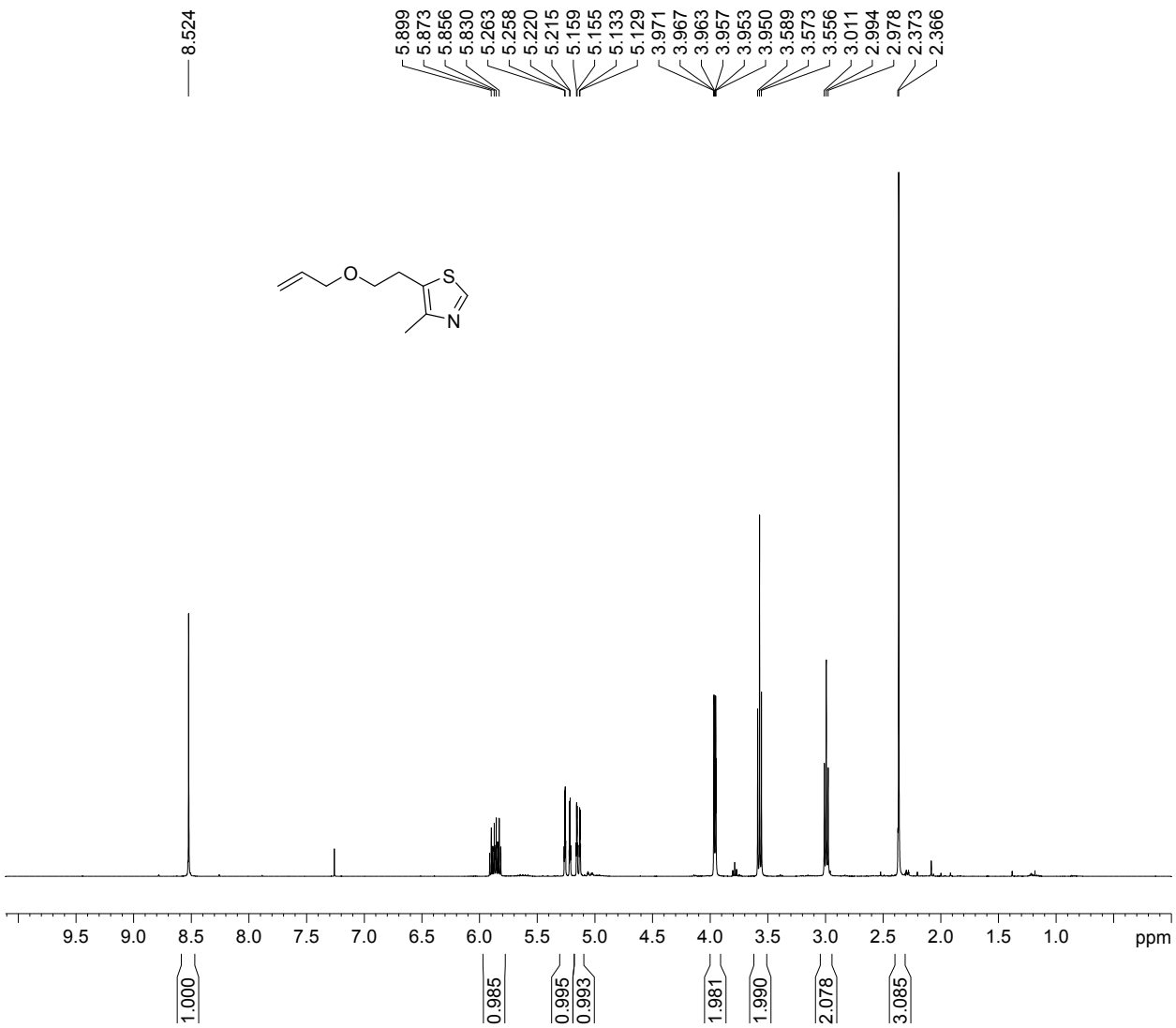
NAME	June1-2010
EXPNO	151
PROCNO	1
Date_	20100601
Time	13.58
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	512
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

2,5,8,11,14-Pentaoxaheptadec-16-ene



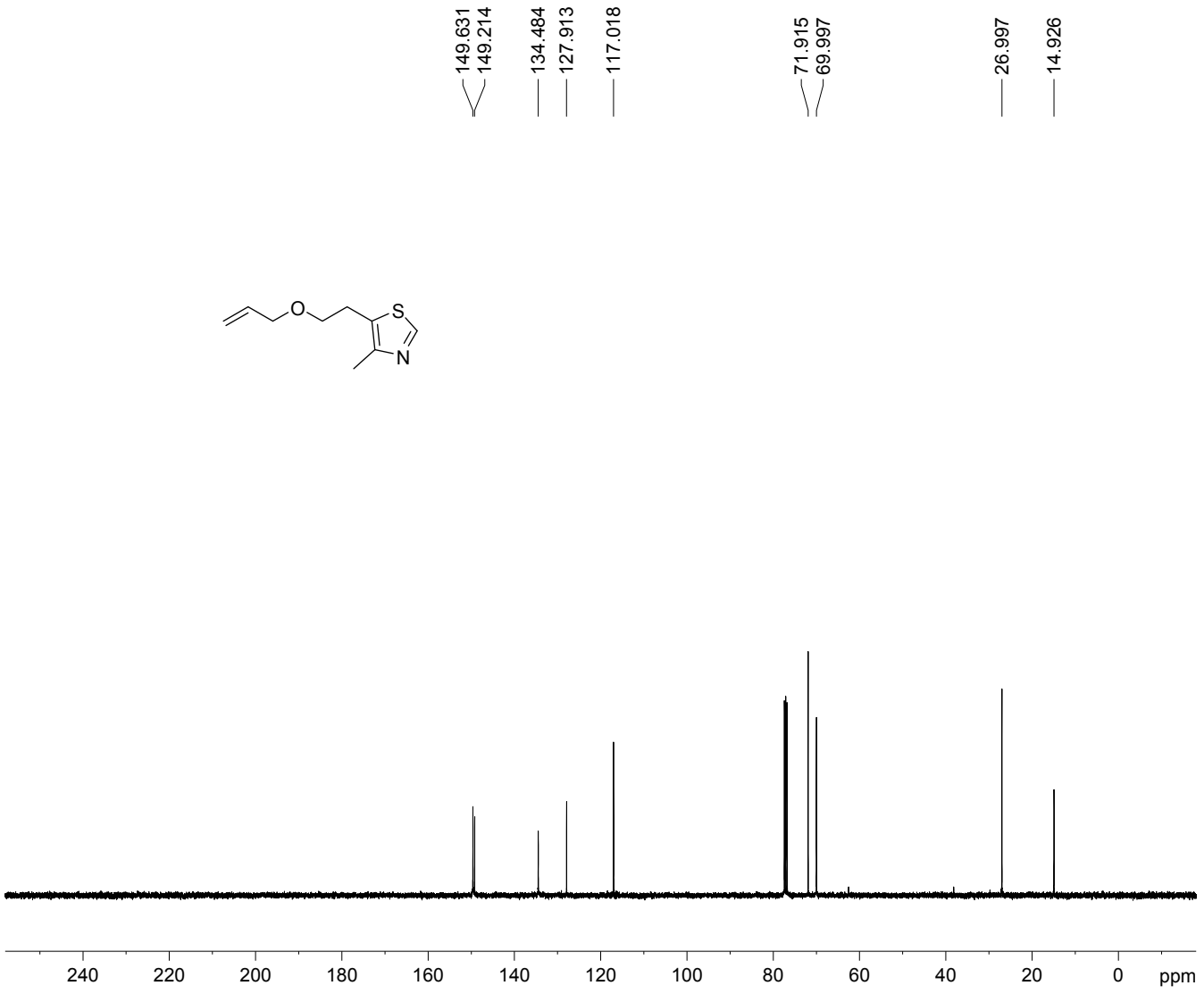
NAME	June1-2010
EXPNO	152
PROCNO	1
Date_	20100601
Time	14.06
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	128
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

5-(2-(Allyloxy)ethyl)-4-methylthiazole



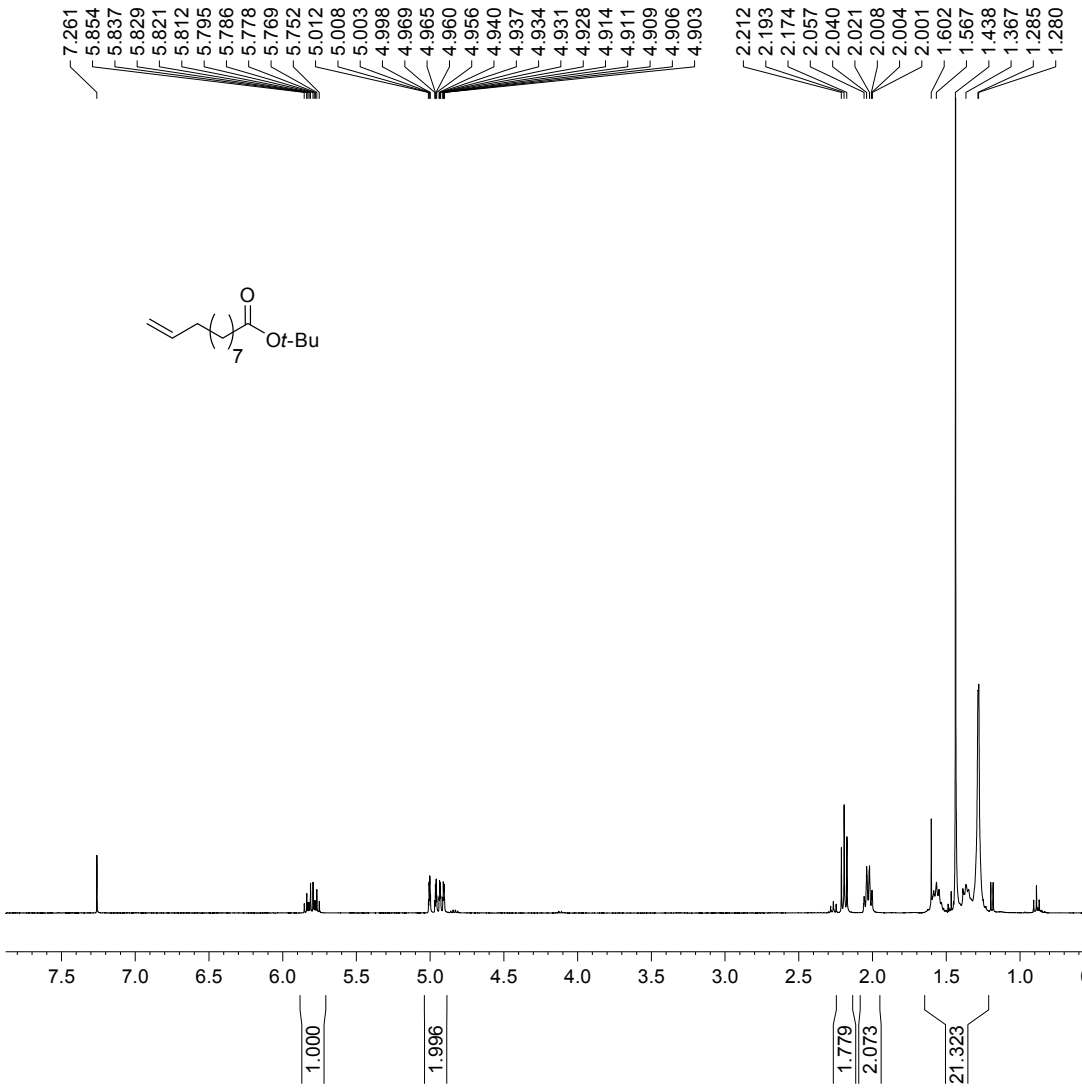
NAME	Dec4-2009
EXPNO	231
PROCNO	1
Date_	20091204
Time	16.07
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	256
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

5-(2-(Allyloxy)ethyl)-4-methylthiazole



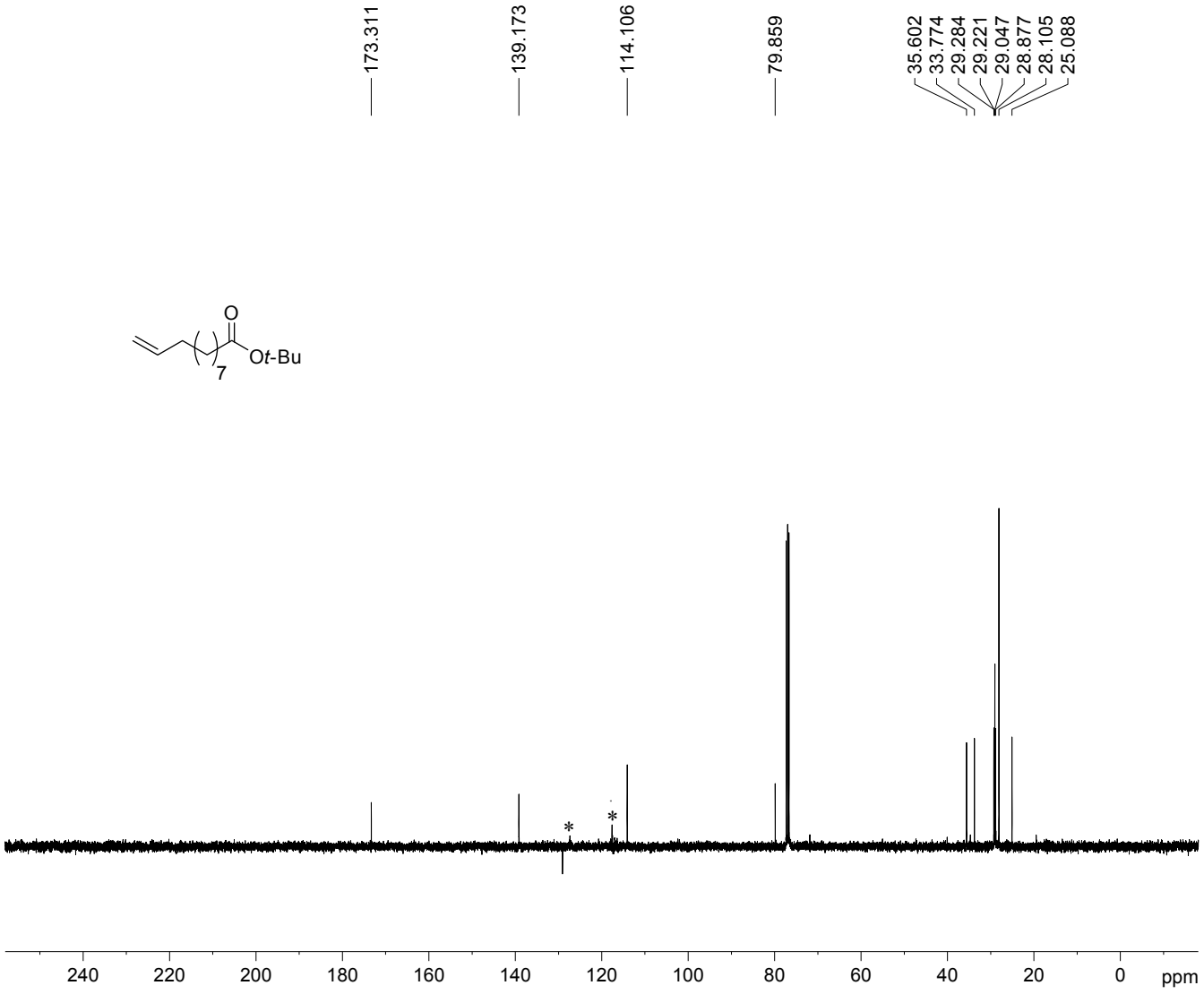
NAME	Dec4-2009
EXPNO	232
PROCNO	1
Date_	20091204
Time	16.16
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	160
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	23.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.25 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

tert-Butyl undec-10-enoate



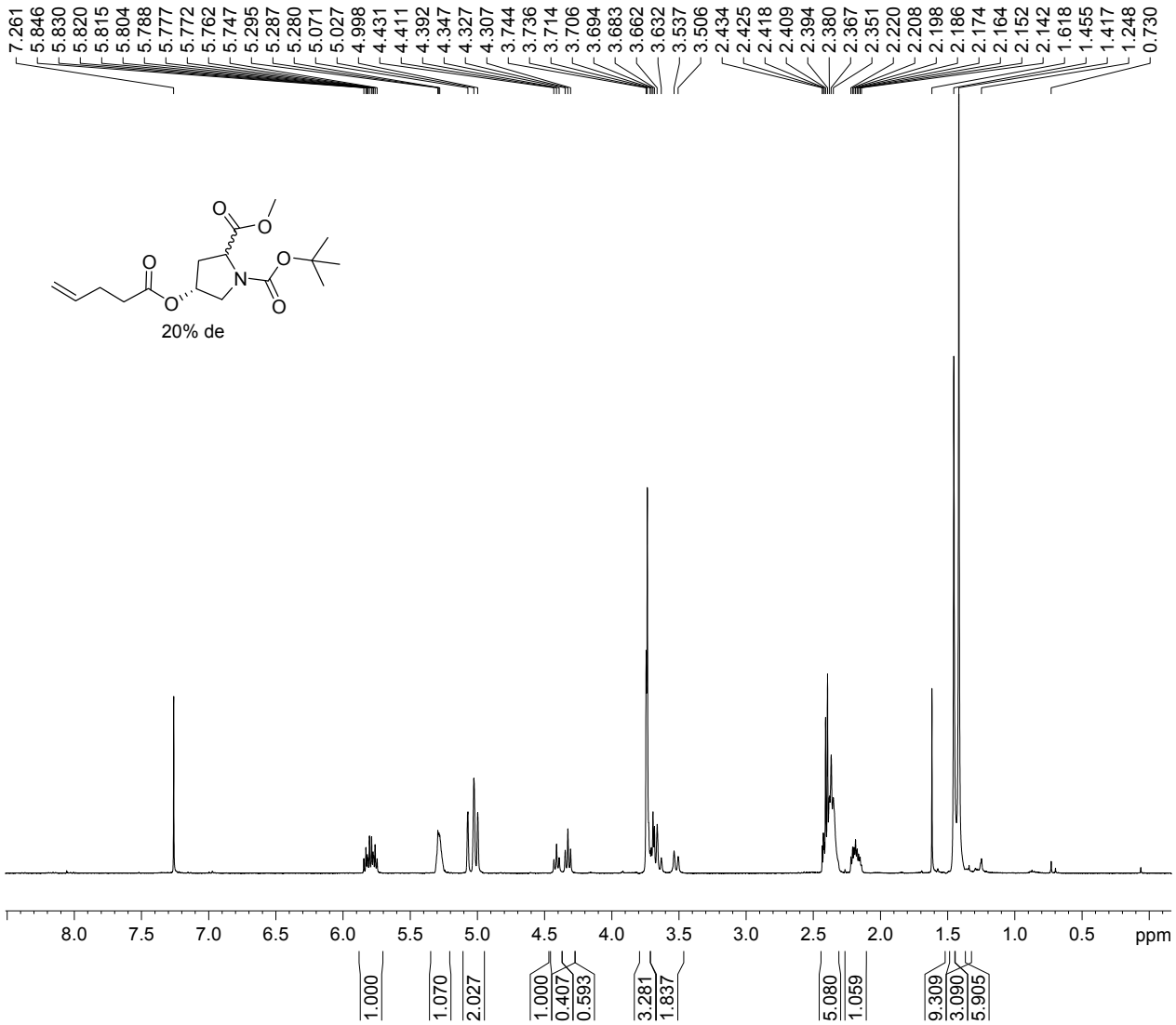
NAME	Sept8-2010
EXPNO	290
PROCNO	1
Date_	20100908
Time	18.02
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	360
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

tert-Butyl undec-10-enoate



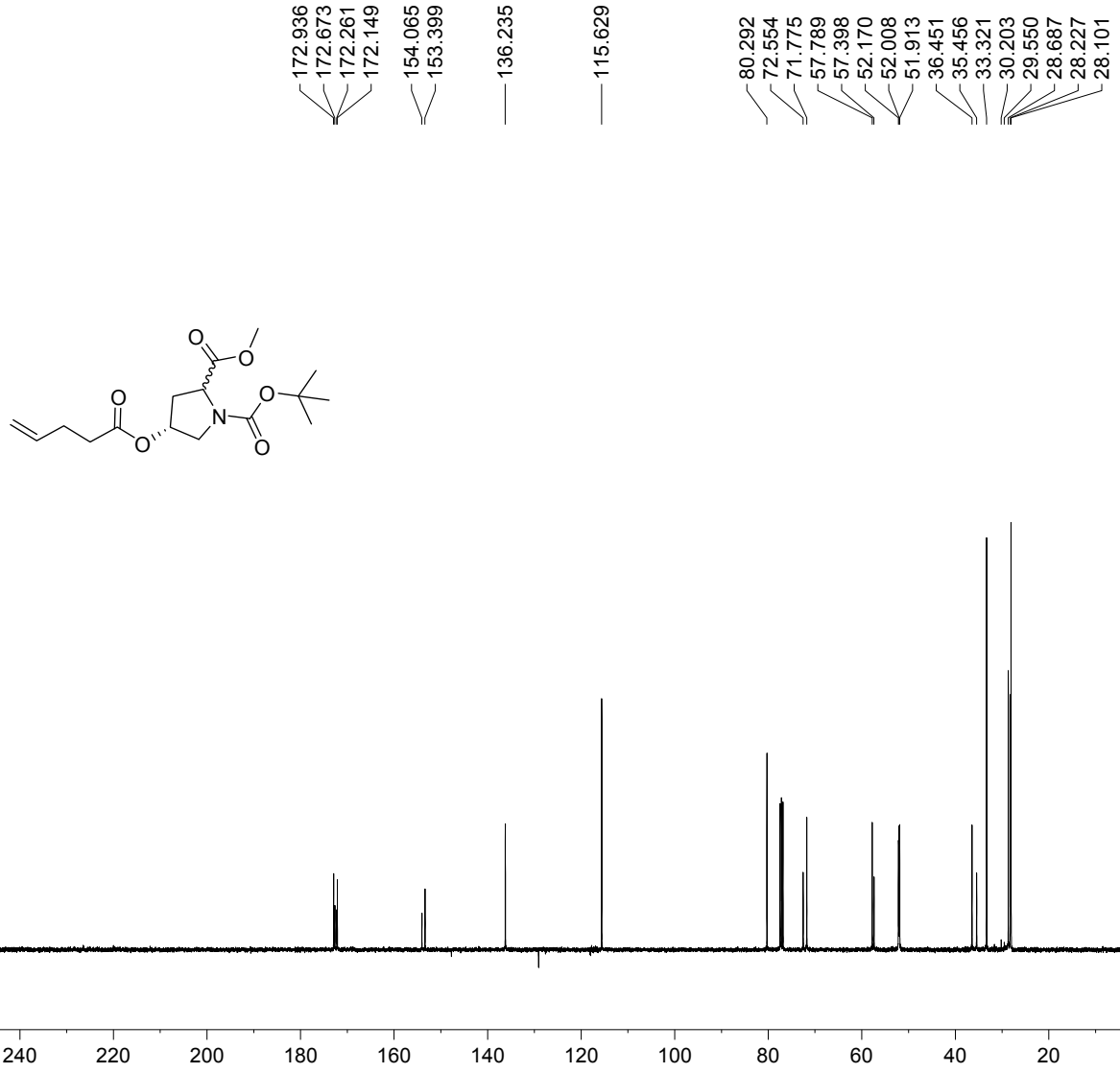
NAME	Sept8-2010
EXPNO	291
PROCNO	1
Date_	20100908
Time	18.11
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	160
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

N-Boc 2-methyl (4R)-4-(pent-4-enoyloxy)pyrrolidine-1,2-dicarboxylate



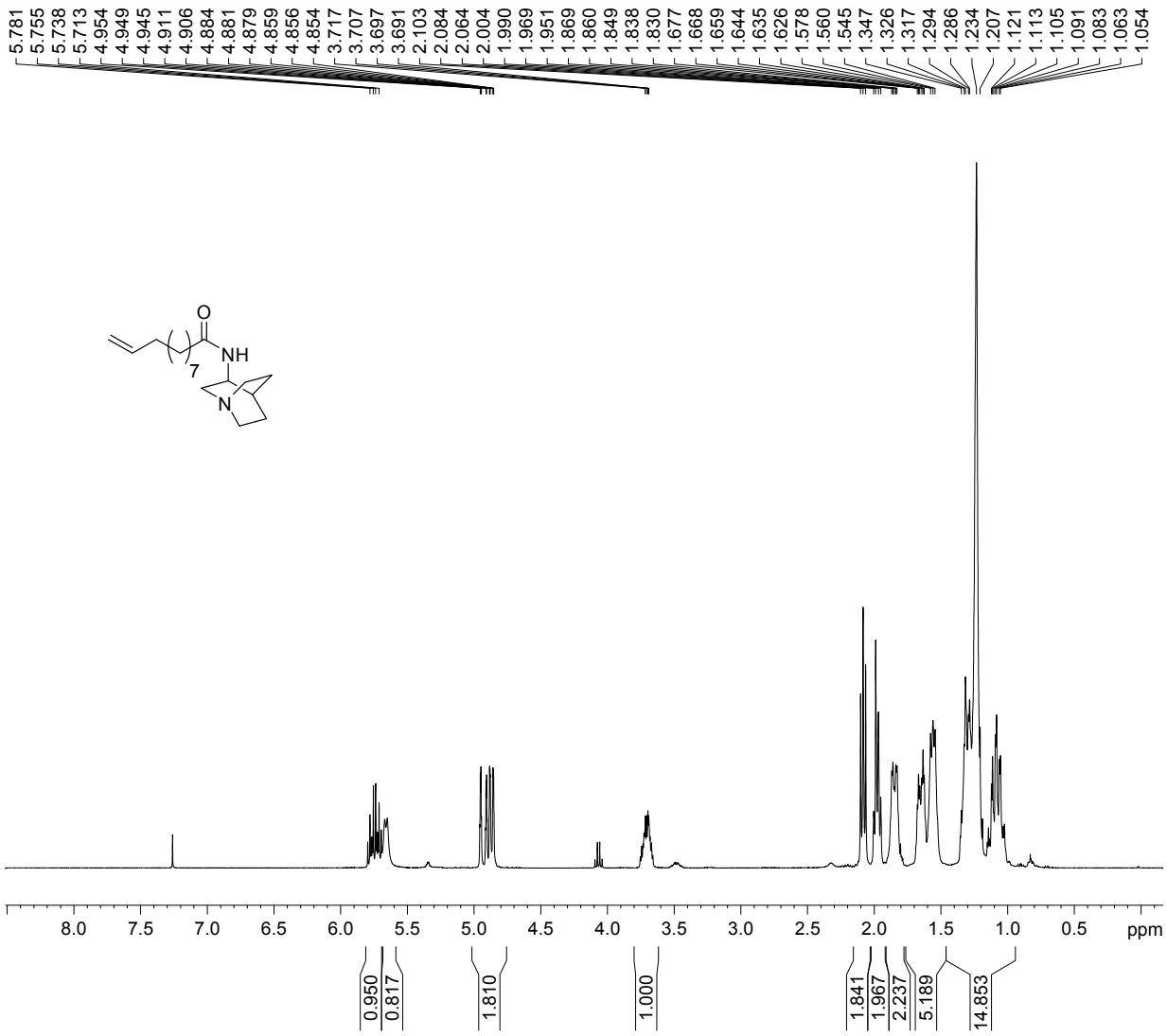
NAME June24-2010
EXPNO 110
PROCNO 1
Date_ 20100624
Time 11.50
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 715
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

N-Boc 2-methyl (4R)-4-(pent-4-enoyloxy)pyrrolidine-1,2-dicarboxylate



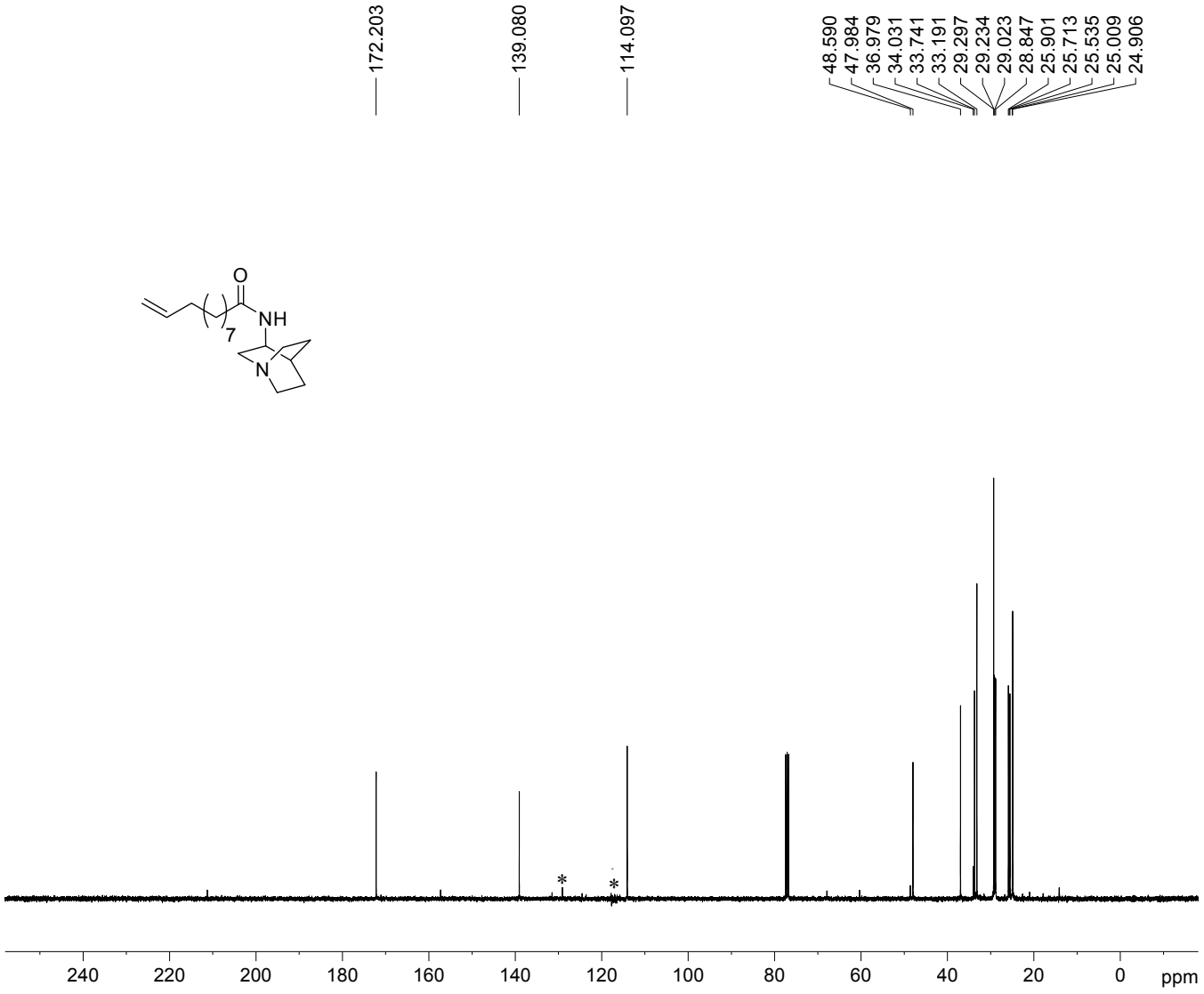
NAME	June24-2010
EXPNO	220
PROCNO	1
Date_	20100624
Time	16.13
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	184
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

N-(quinuclidin-3-yl)undec-10-enamide



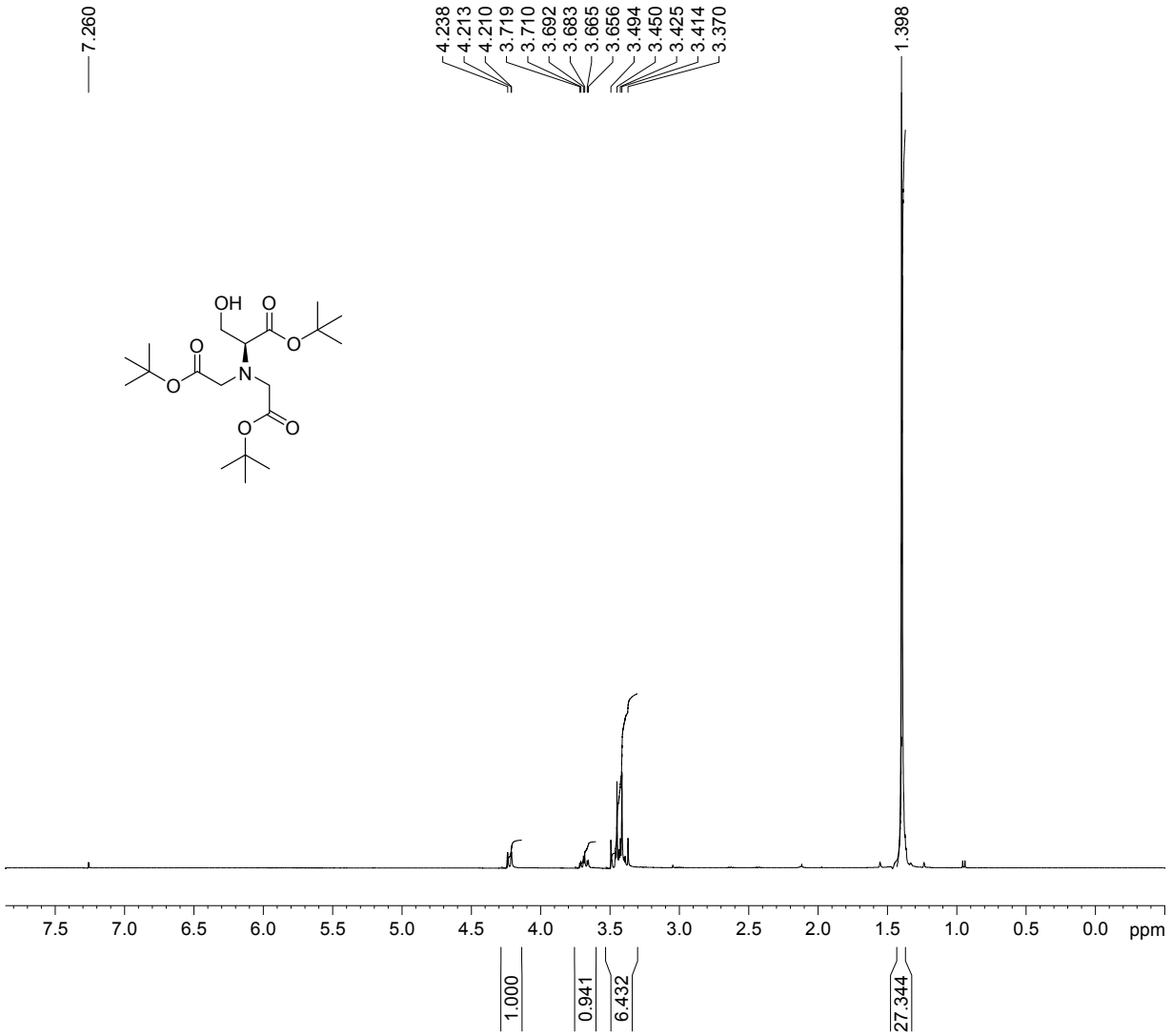
NAME	Aug5-2010
EXPNO	70
PROCNO	1
Date_	20100805
Time	9.35
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	90
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

N-(quinuclidin-3-yl)undec-10-enamide



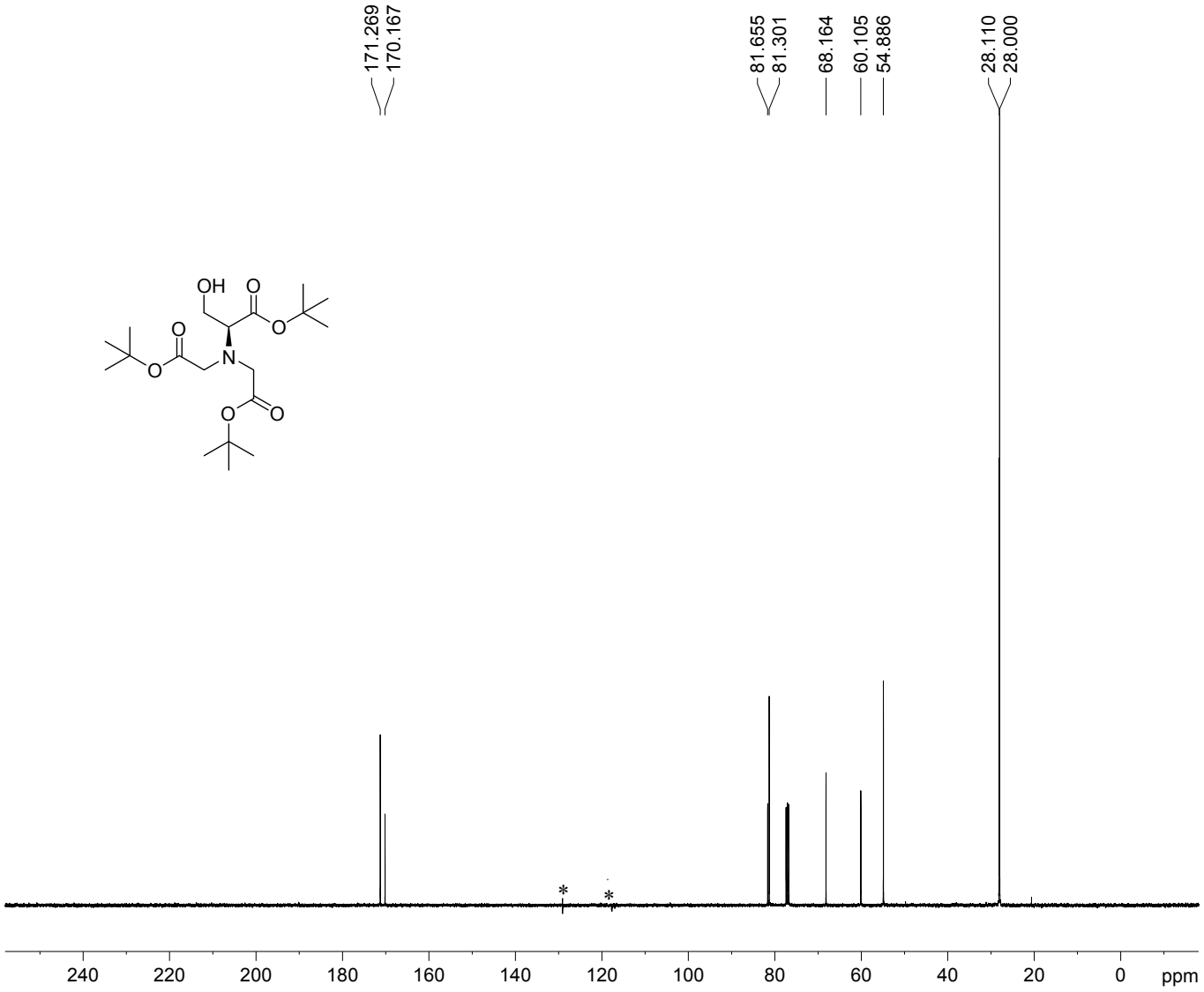
NAME	Aug5-2010
EXPNO	71
PROCNO	1
Date_	20100805
Time	9.45
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	168
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

(S)-tert-Butyl-2-di(tert-butyloxycarbonylmethyl)amino-3-hydroxypropanoate



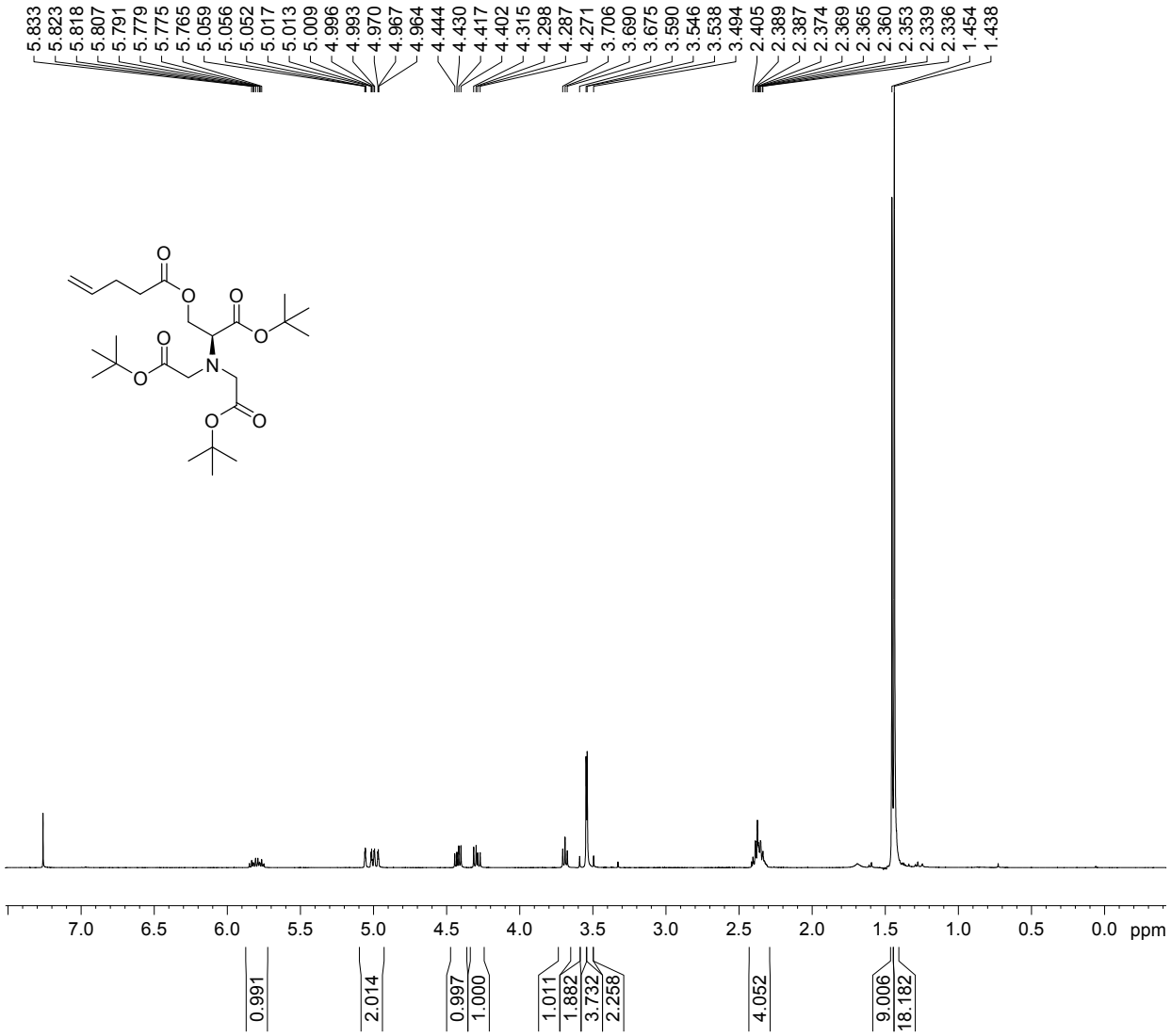
NAME	Aug30-2010
EXPNO	10
PROCNO	1
Date_	20100830
Time	8.36
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	90
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

(S)-tert-Butyl-2-di(tert-butyloxycarbonylmethyl)amino-3-hydroxypropanoate



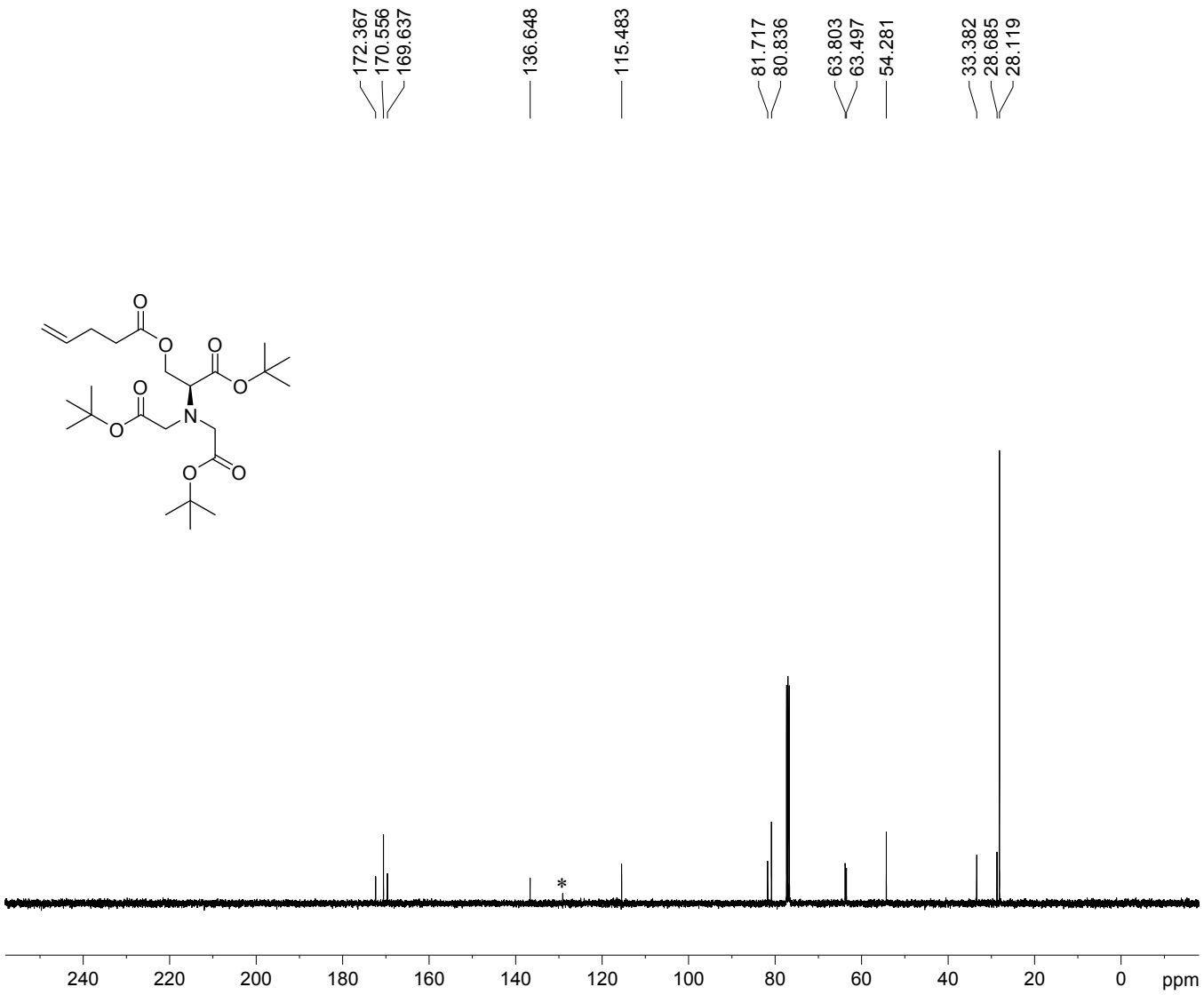
NAME	Aug30-2010
EXPNO	11
PROCNO	1
Date_	20100830
Time	8.46
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	168
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

(S)-tert-Butyl-2-di(tert-butyloxycarbonylmethyl)amino-3-(pent-4-enoyloxy)-propanoate



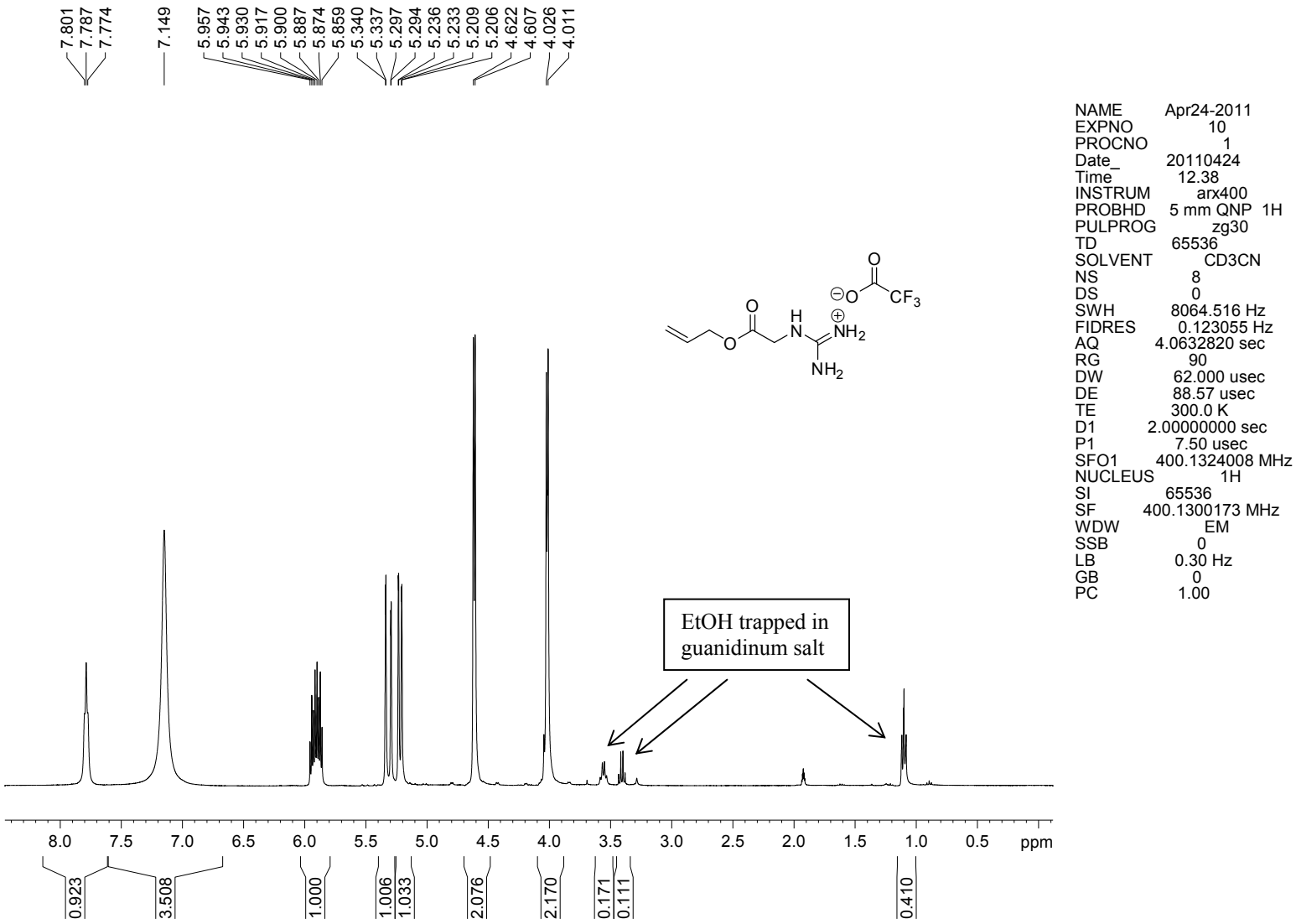
NAME	Sept16-2010
EXPNO	270
PROCNO	1
Date_	20100916
Time	16.20
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	512
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

(S)-tert-Butyl-2-di(tert-butyloxycarbonylmethyl)amino-3-(pent-4-enoyloxy)-propanoate



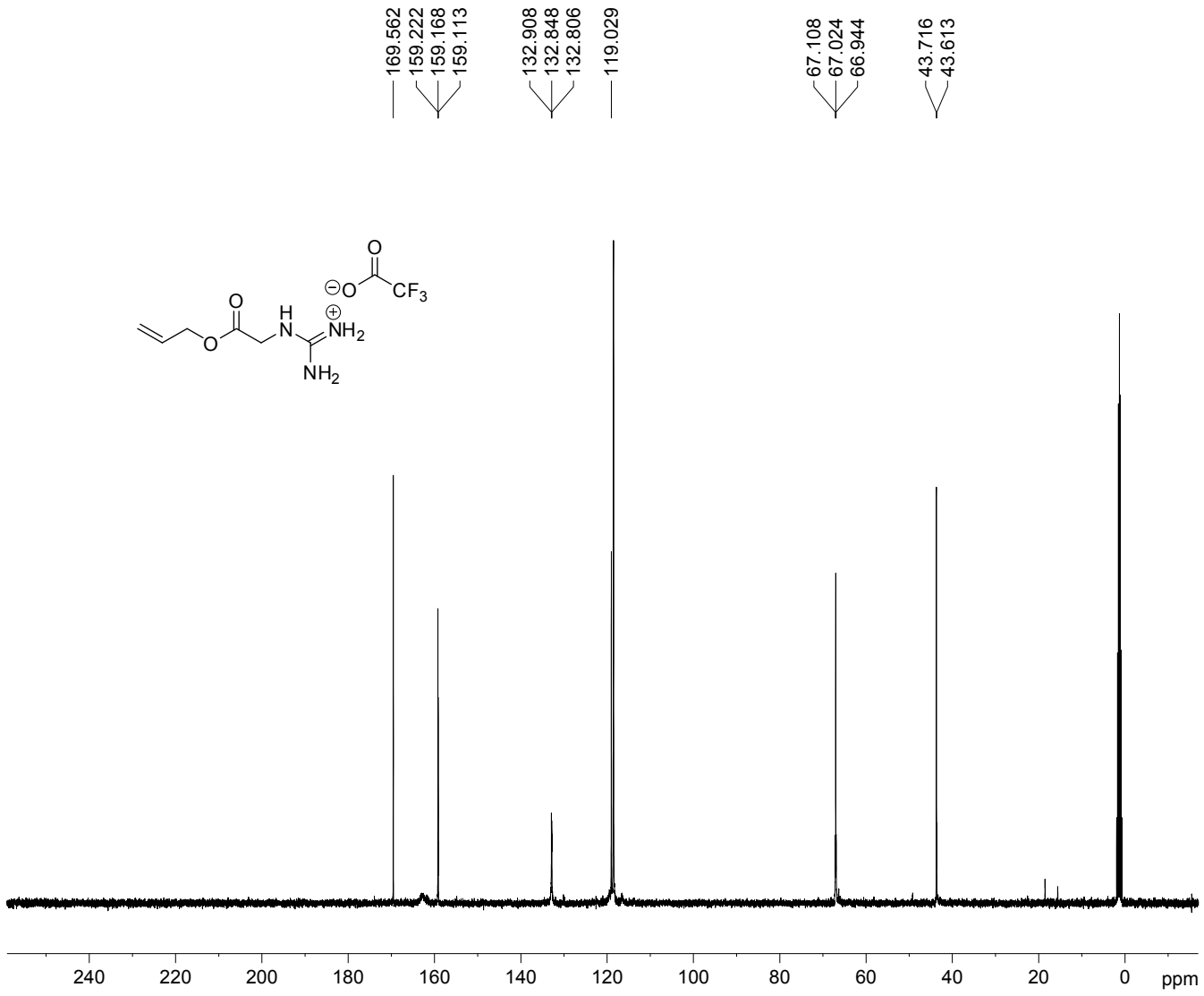
NAME	Sept16-2010
EXPNO	271
PROCNO	1
Date_	20100916
Time	16.30
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	168
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

(2-(allyloxy)-2-oxoethylamino)(amino)methaniminium 2,2,2-trifluoroacetate



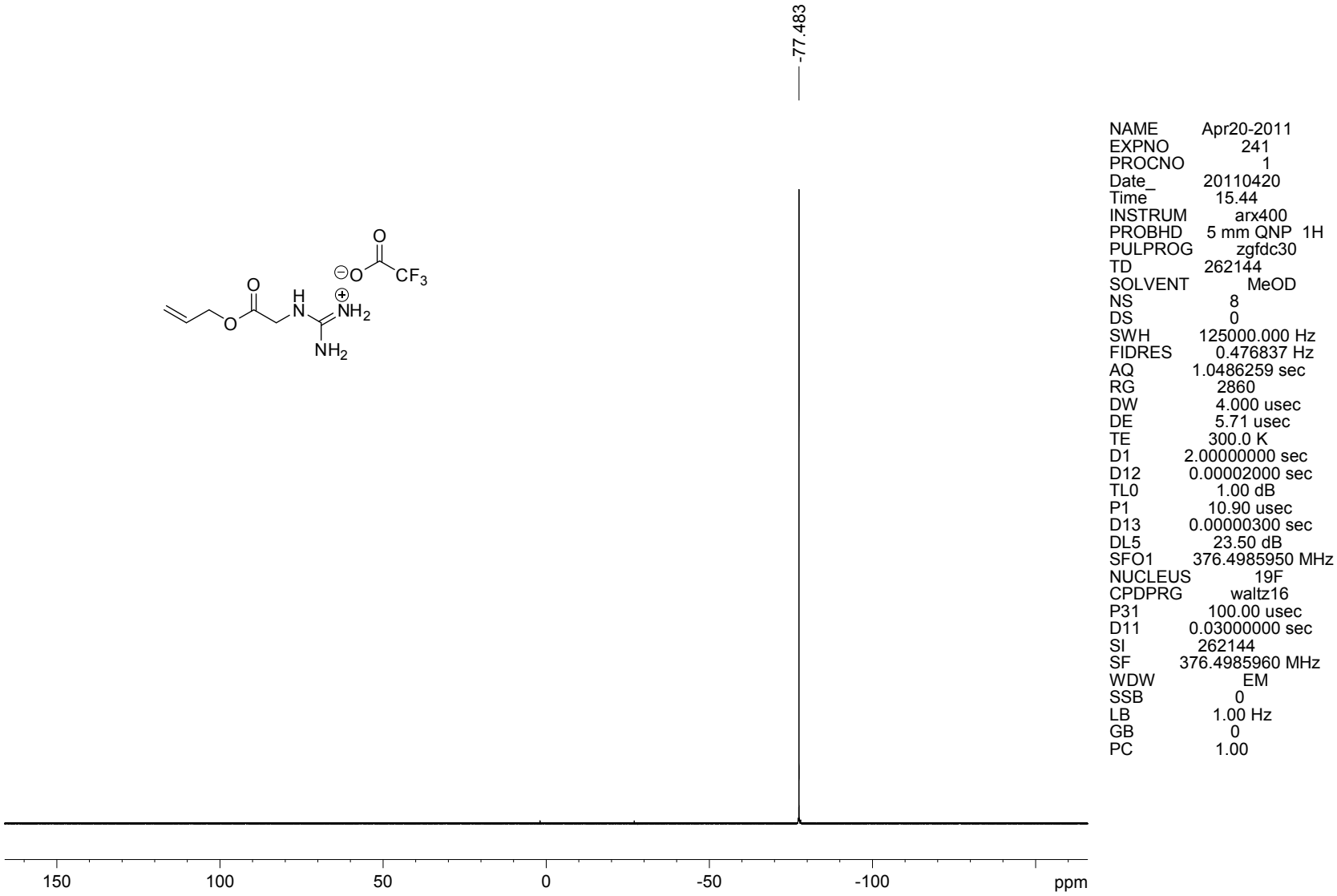
NAME	Apr24-2011
EXPNO	10
PROCNO	1
Date_	20110424
Time	12.38
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CD3CN
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	90
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

(2-(allyloxy)-2-oxoethylamino)(amino)methaniminium 2,2,2-trifluoroacetate



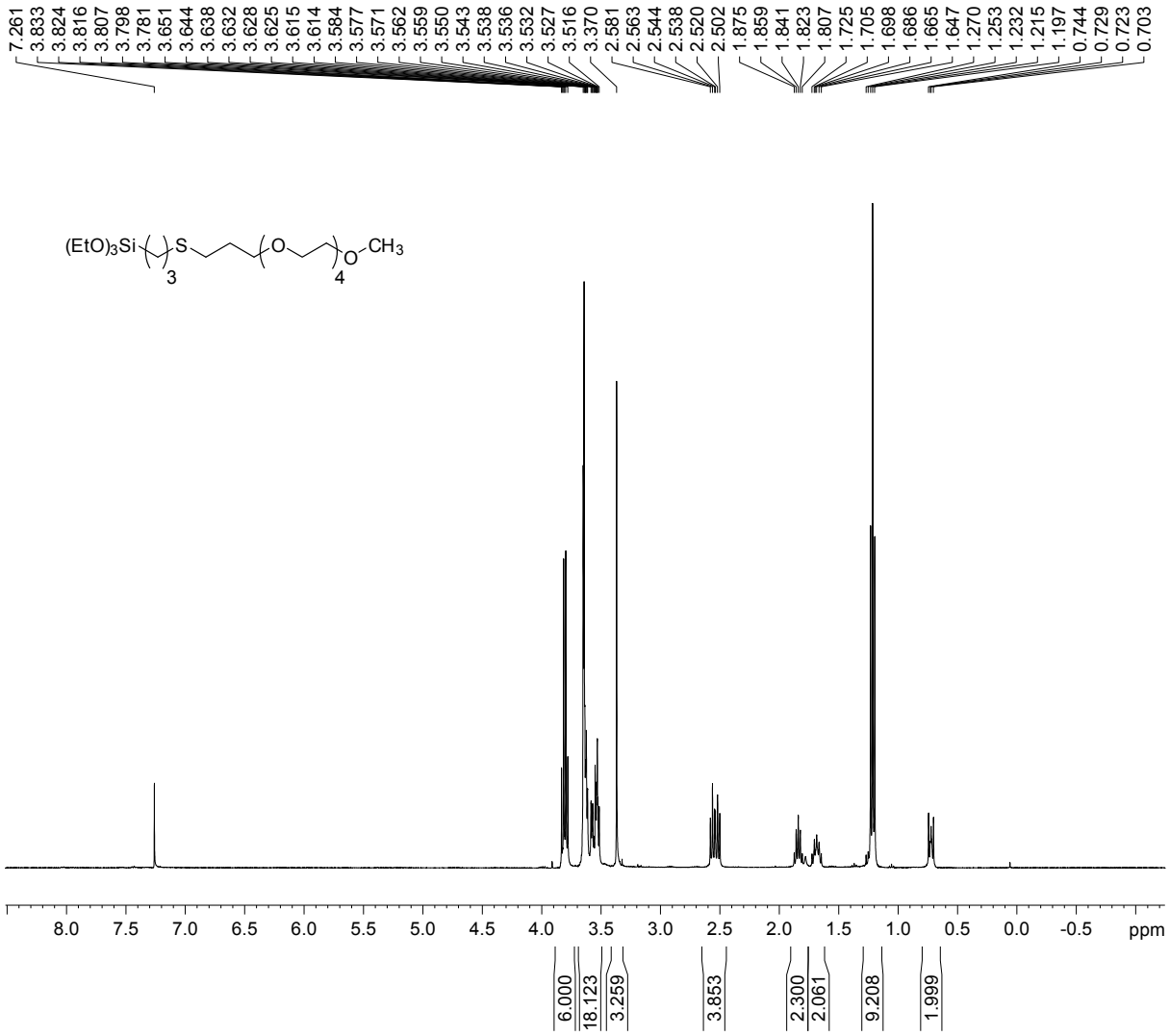
NAME	Apr24-2011
EXPNO	11
PROCNO	1
Date_	20110424
Time	12.48
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CD3CN
NS	168
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	23.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.25 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6126671 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

(2-(allyloxy)-2-oxoethylamino)(amino)methaniminium 2,2,2-trifluoroacetate



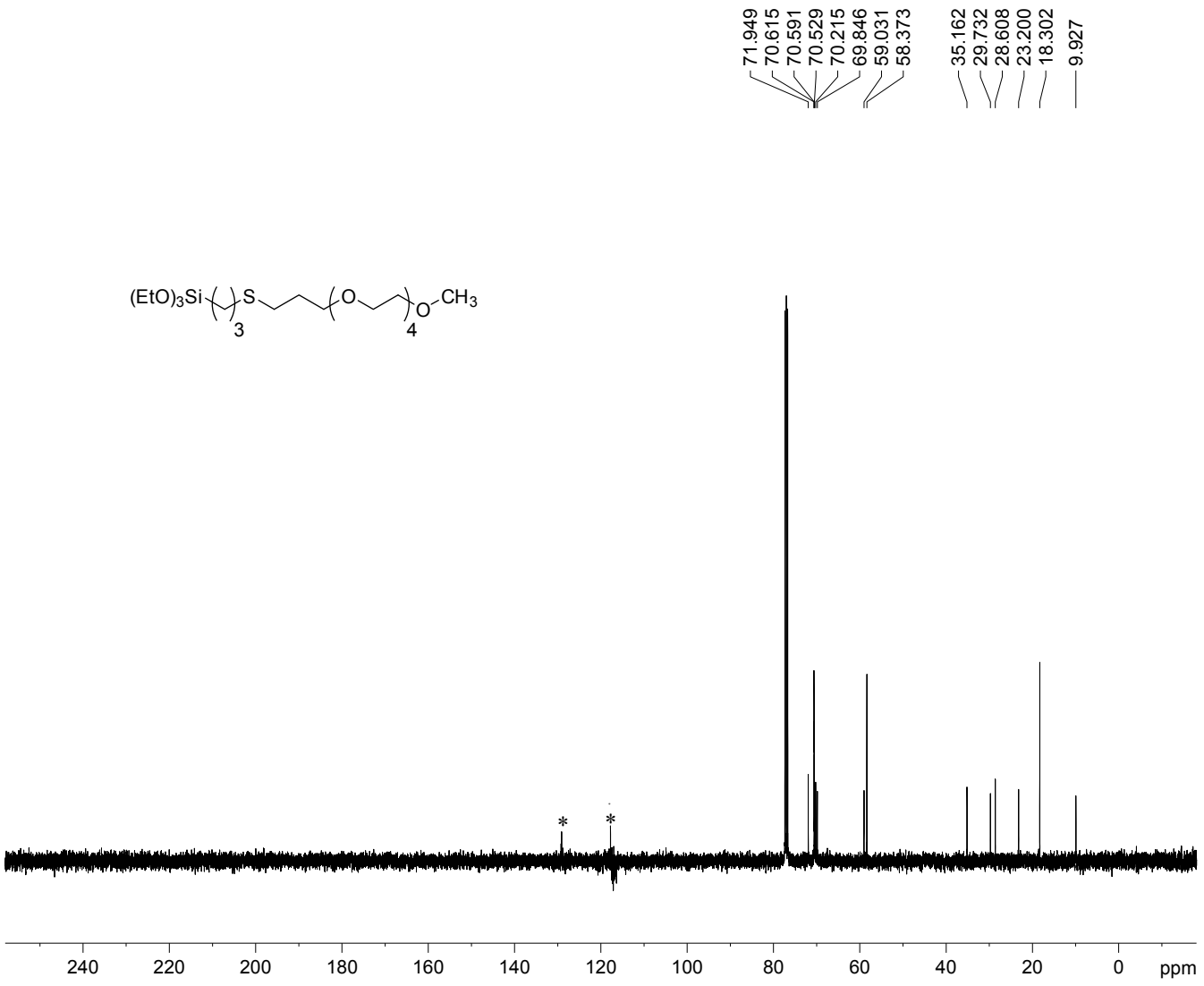
NAME	Apr20-2011
EXPNO	241
PROCNO	1
Date_	20110420
Time	15.44
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgfdc30
TD	262144
SOLVENT	MeOD
NS	8
DS	0
SWH	125000.000 Hz
FIDRES	0.476837 Hz
AQ	1.0486259 sec
RG	2860
DW	4.000 usec
DE	5.71 usec
TE	300.0 K
D1	2.00000000 sec
D12	0.00002000 sec
TL0	1.00 dB
P1	10.90 usec
D13	0.00000300 sec
DL5	23.50 dB
SFO1	376.4985950 MHz
NUCLEUS	19F
CPDPRG	waltz16
P31	100.00 usec
D11	0.03000000 sec
SI	262144
SF	376.4985960 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

PEG triethoxysilane (1)



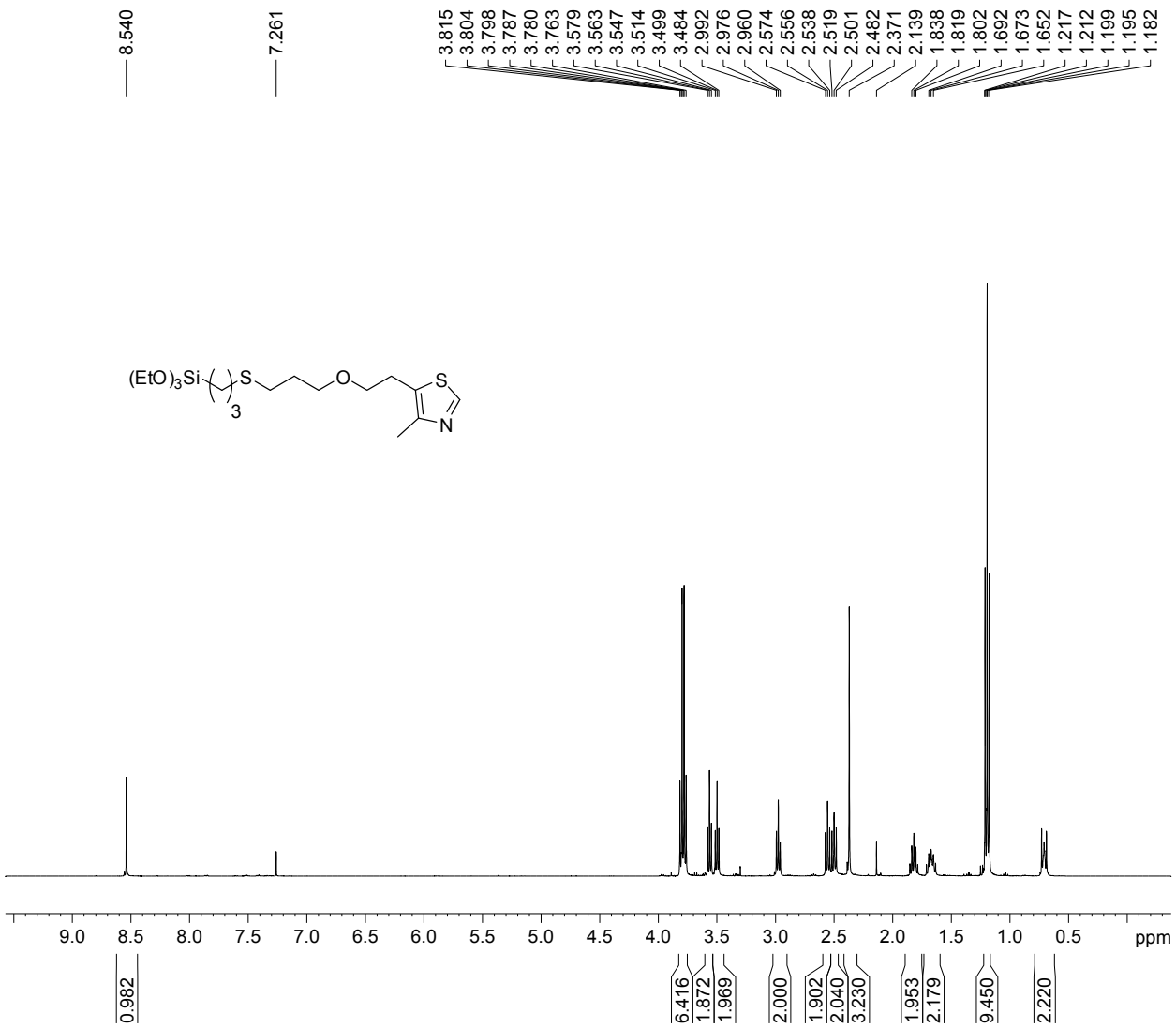
NAME	June2-2010
EXPNO	60
PROCNO	1
Date_	20100602
Time	10.18
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	512
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

PEG triethoxysilane (1)



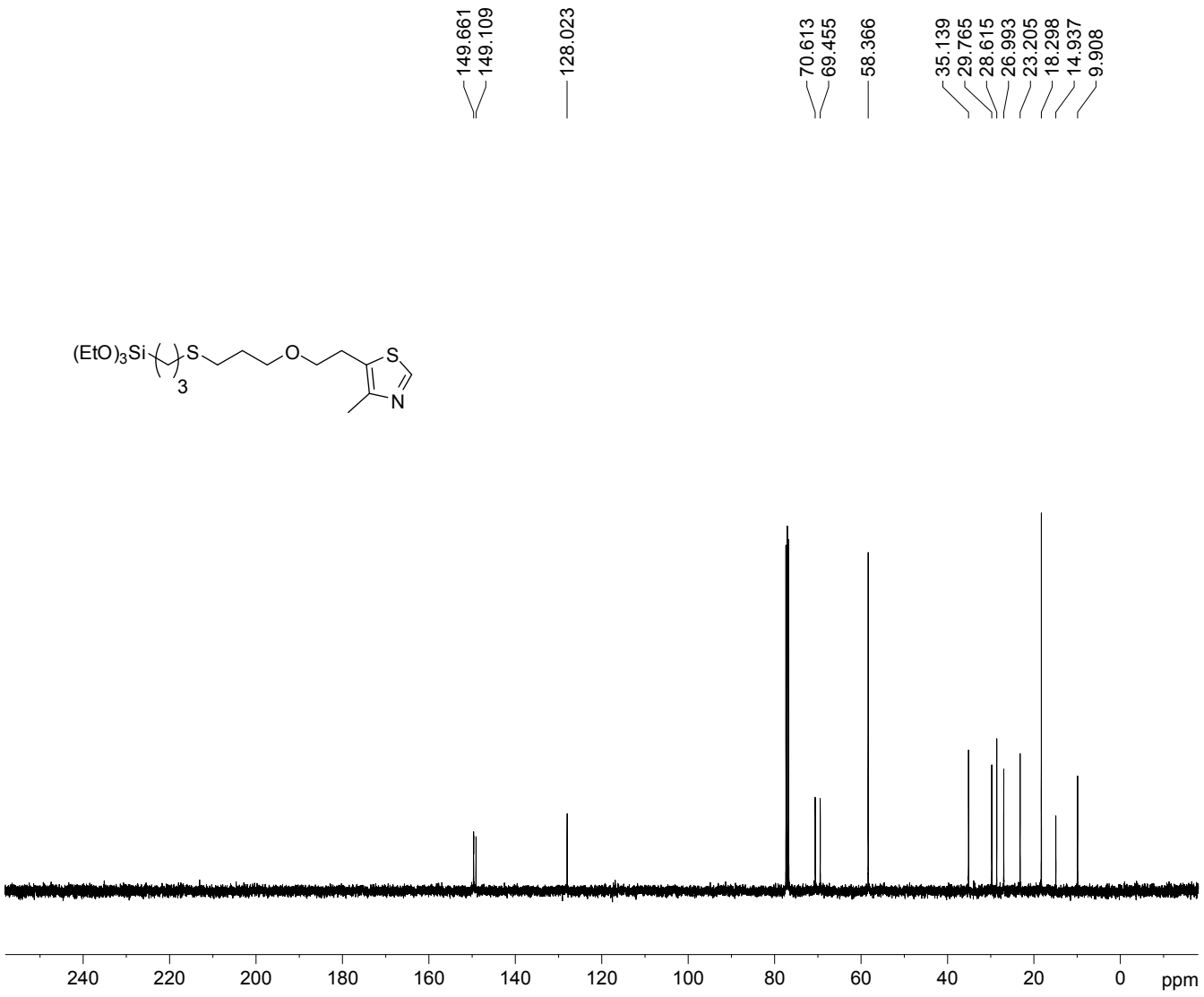
NAME	June2-2010
EXPNO	61
PROCNO	1
Date_	20100602
Time	10.27
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	160
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Thiazole triethoxysilane (2)



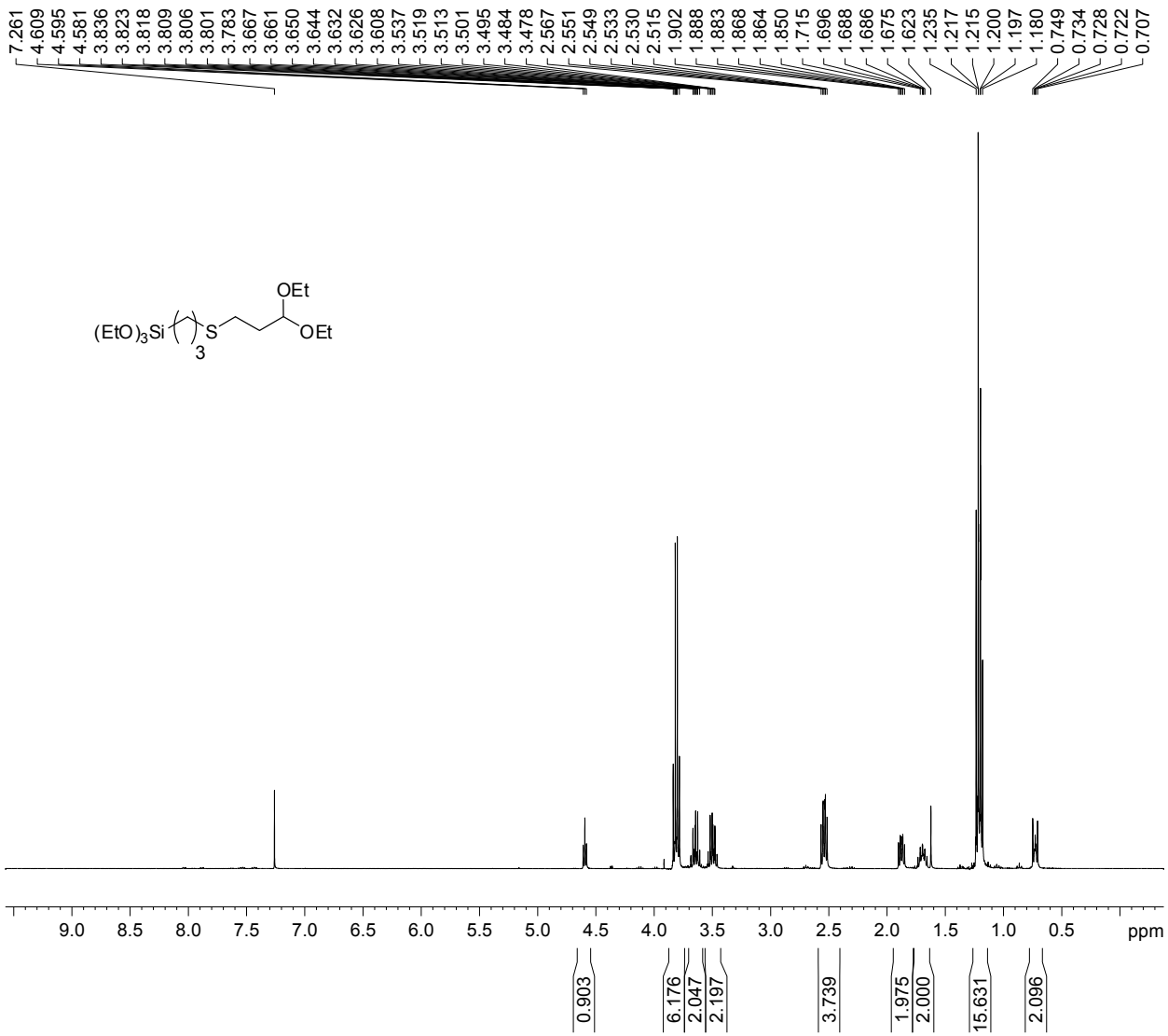
NAME Dec7-2009
EXPNO 70
PROCNO 1
Date_ 20091207
Time 9.58
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 256
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Thiazole triethoxysilane (2)



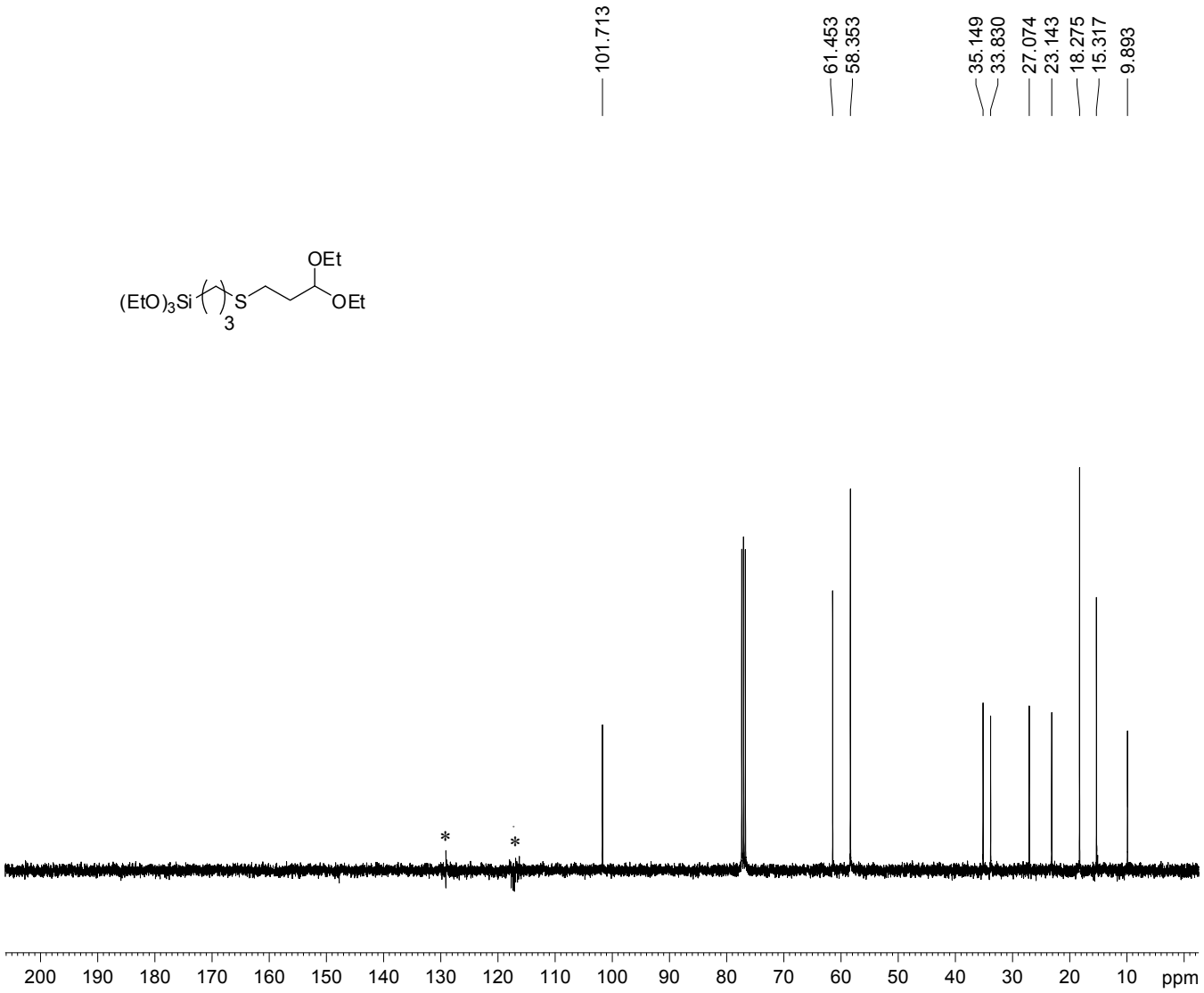
NAME	Dec7-2009
EXPNO	71
PROCNO	1
Date_	20091207
Time	10.05
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	120
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	23.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.25 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Diethyl acetal triethoxysilane (3)



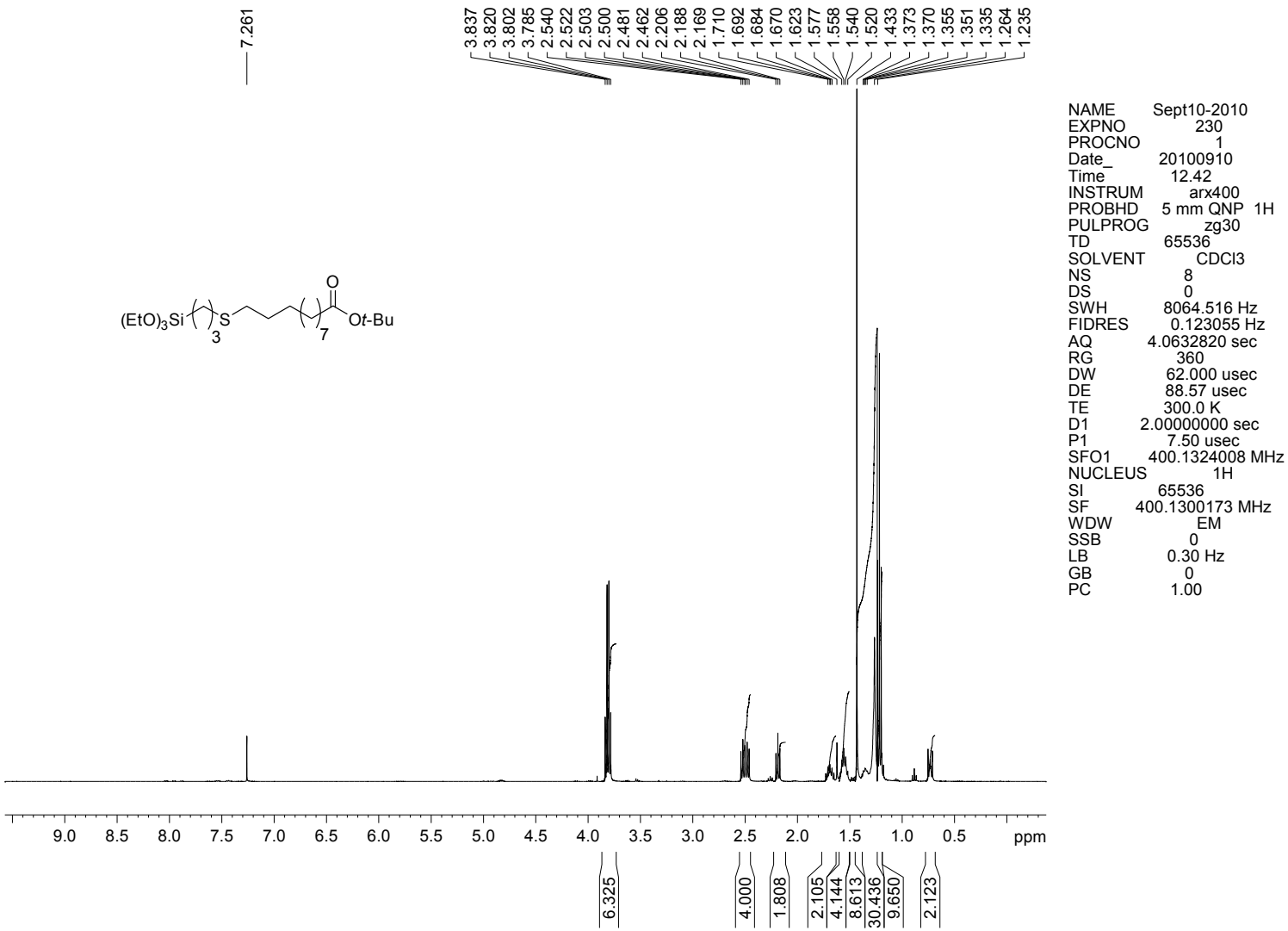
NAME	Aug31-2010
EXPNO	50
PROCNO	1
Date_	20100831
Time	9.15
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	512
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Diethyl acetal triethoxysilane (3)



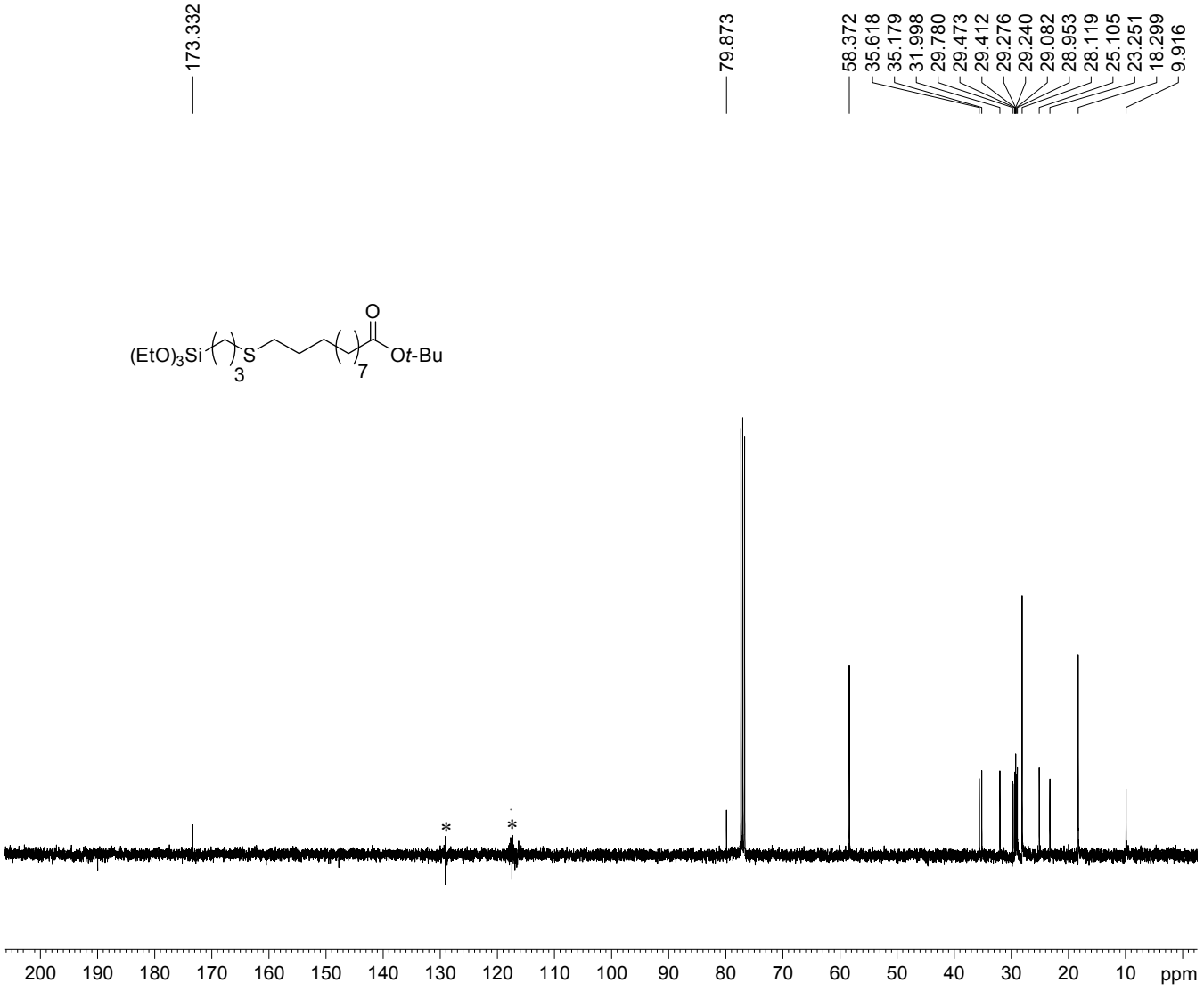
NAME Aug30-2010
EXPNO 361
PROCNO 1
Date_ 20100830
Time 17.40
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 80
DS 0
SWH 27777.777 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 32768
DW 18.000 usec
DE 25.71 usec
TE 300.0 K
D12 0.0000200 sec
DL5 21.50 dB
CPDPRG waltz16
P31 100.00 usec
D1 2.00000000 sec
P1 8.50 usec
SFO1 100.6248445 MHz
NUCLEUS 13C
D11 0.0300000 sec
SI 65536
SF 100.6127710 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

tert-Butyl undecanoate triethoxysilane (4)



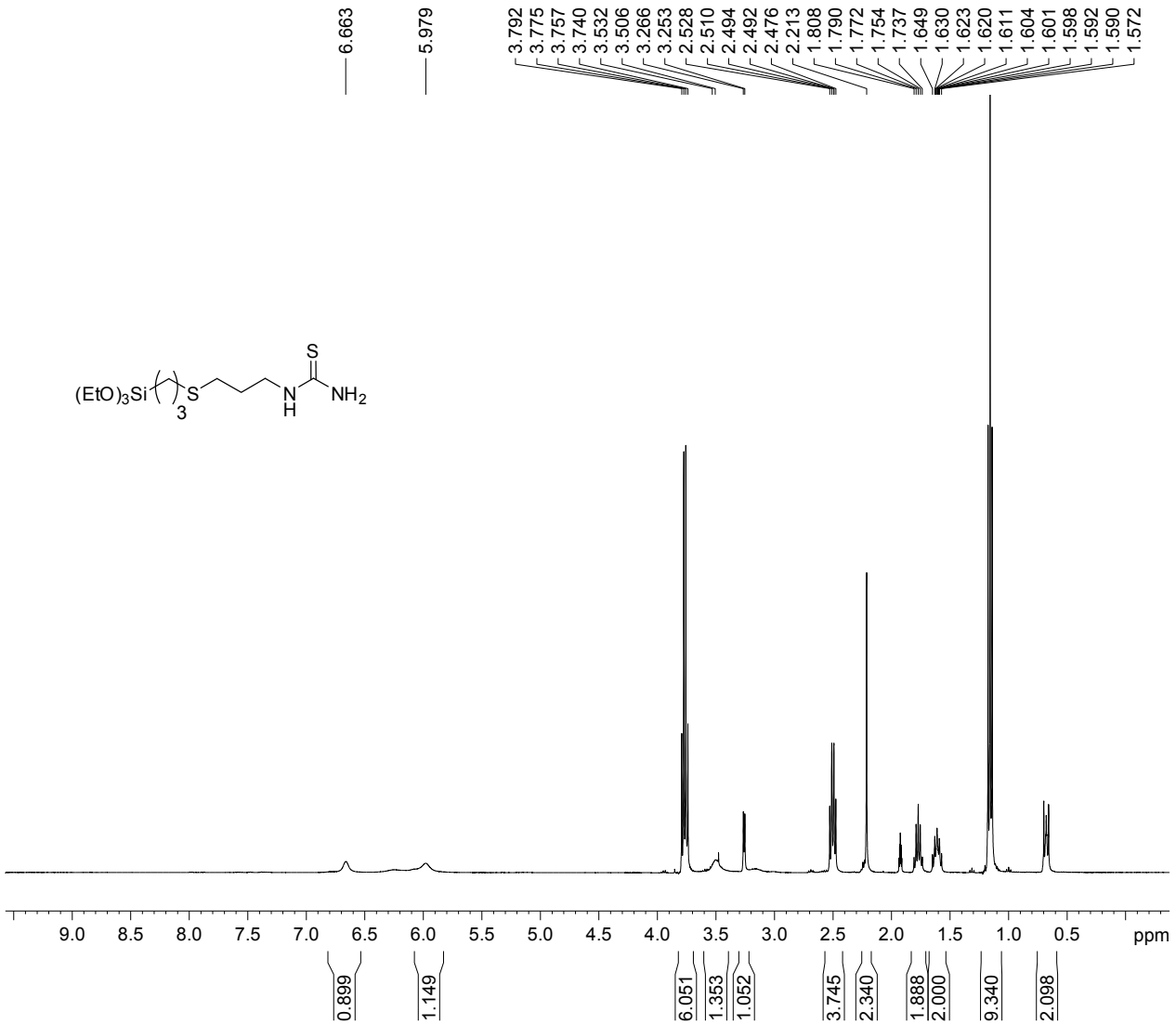
NAME Sept10-2010
EXPNO 230
PROCNO 1
Date_ 20100910
Time 12.42
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 360
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

tert-Butyl undecanoate triethoxysilane (4)



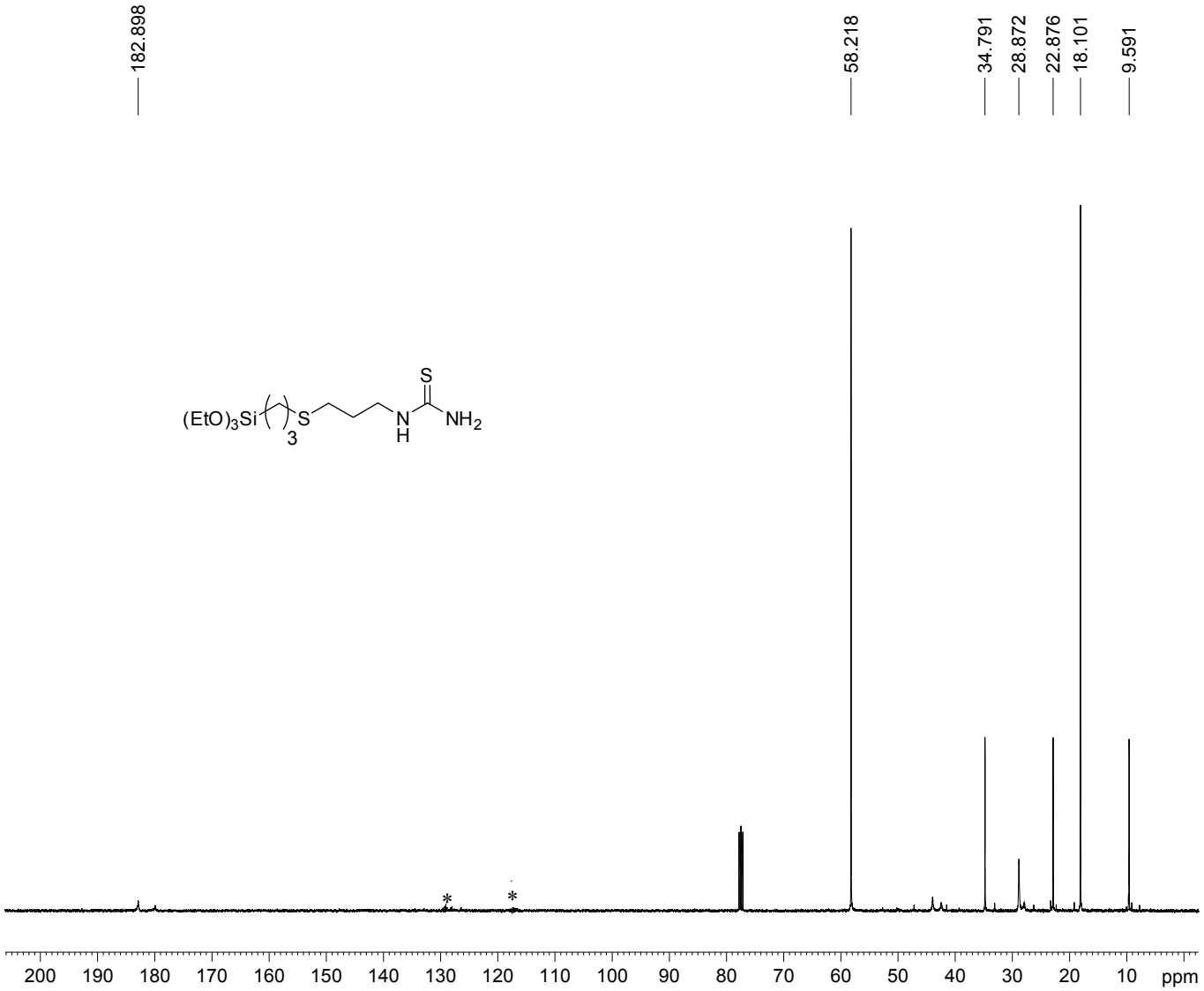
NAME	Sept10-2010
EXPNO	231
PROCNO	1
Date_	20100910
Time	12.52
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	160
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Thiourea triethoxysilane (5)



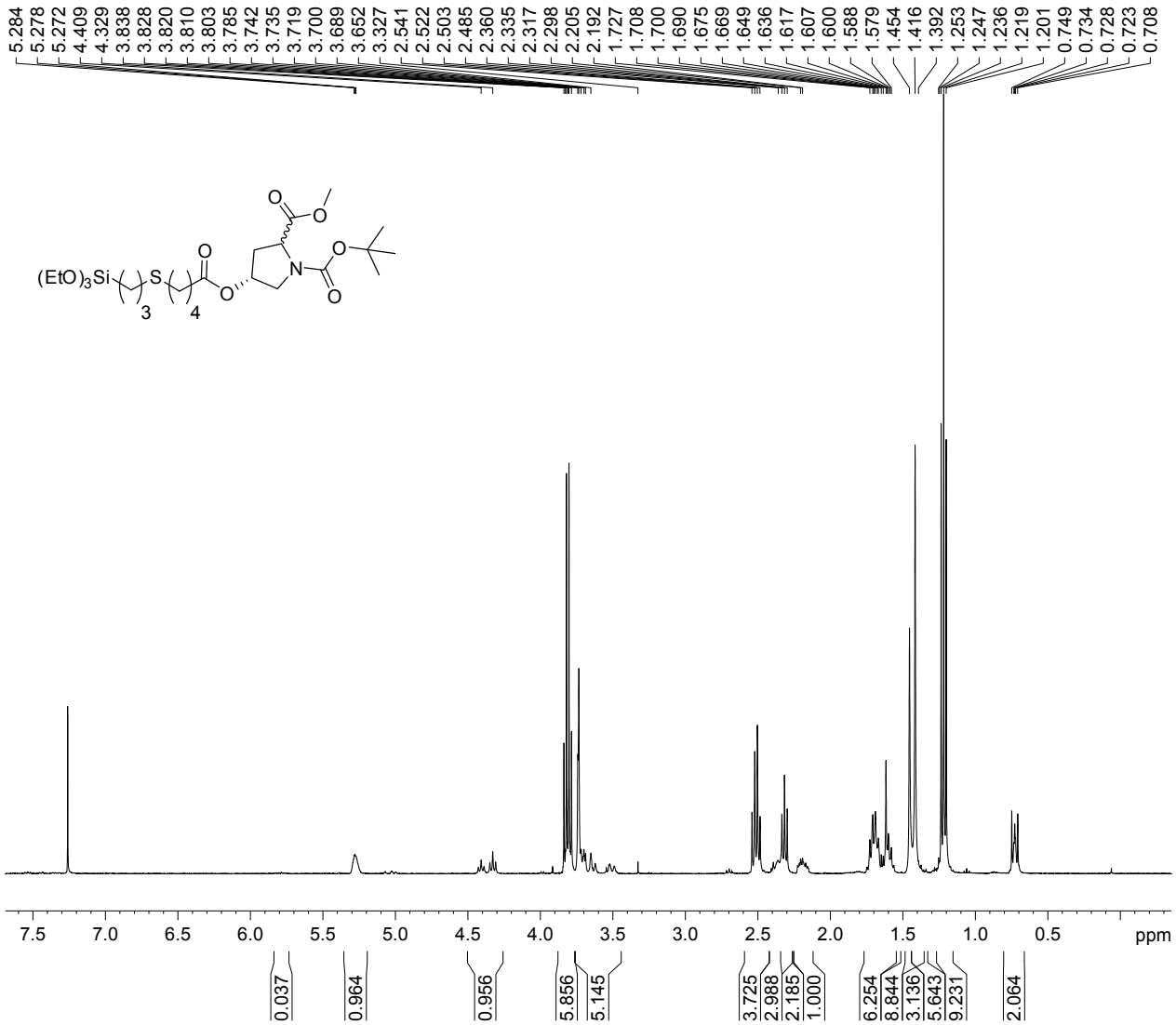
NAME Oct6-2010
EXPNO 340
PROCNO 1
Date_ 20101006
Time 15.05
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 256
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Thiourea triethoxysilane (5)



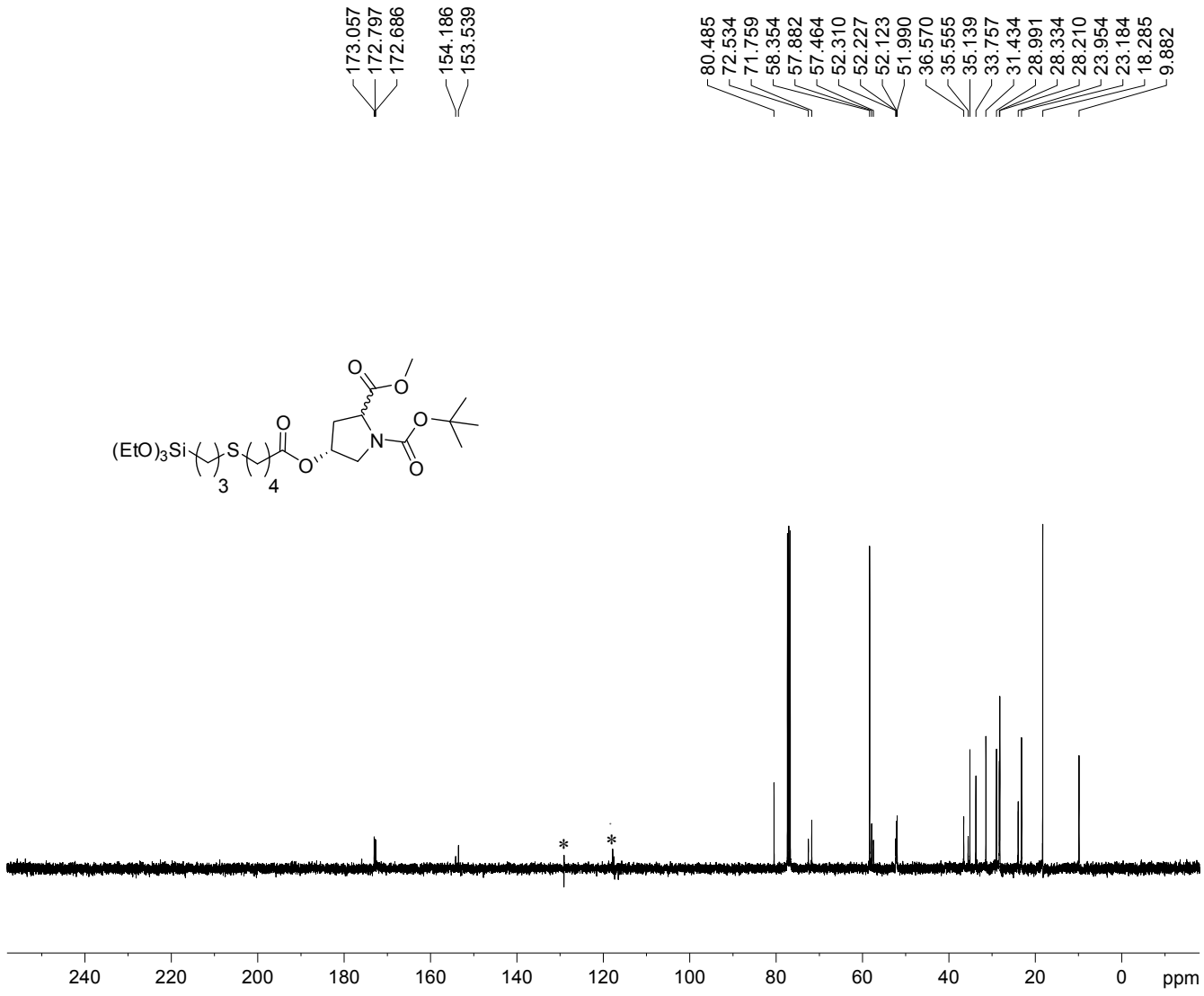
NAME	July1-2010
EXPNO	240
PROCNO	1
Date_	20100701
Time	16.36
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	176
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

N-Boc-(4R)-4-hydroxy-L-proline methyl ester triethoxysilane (6)



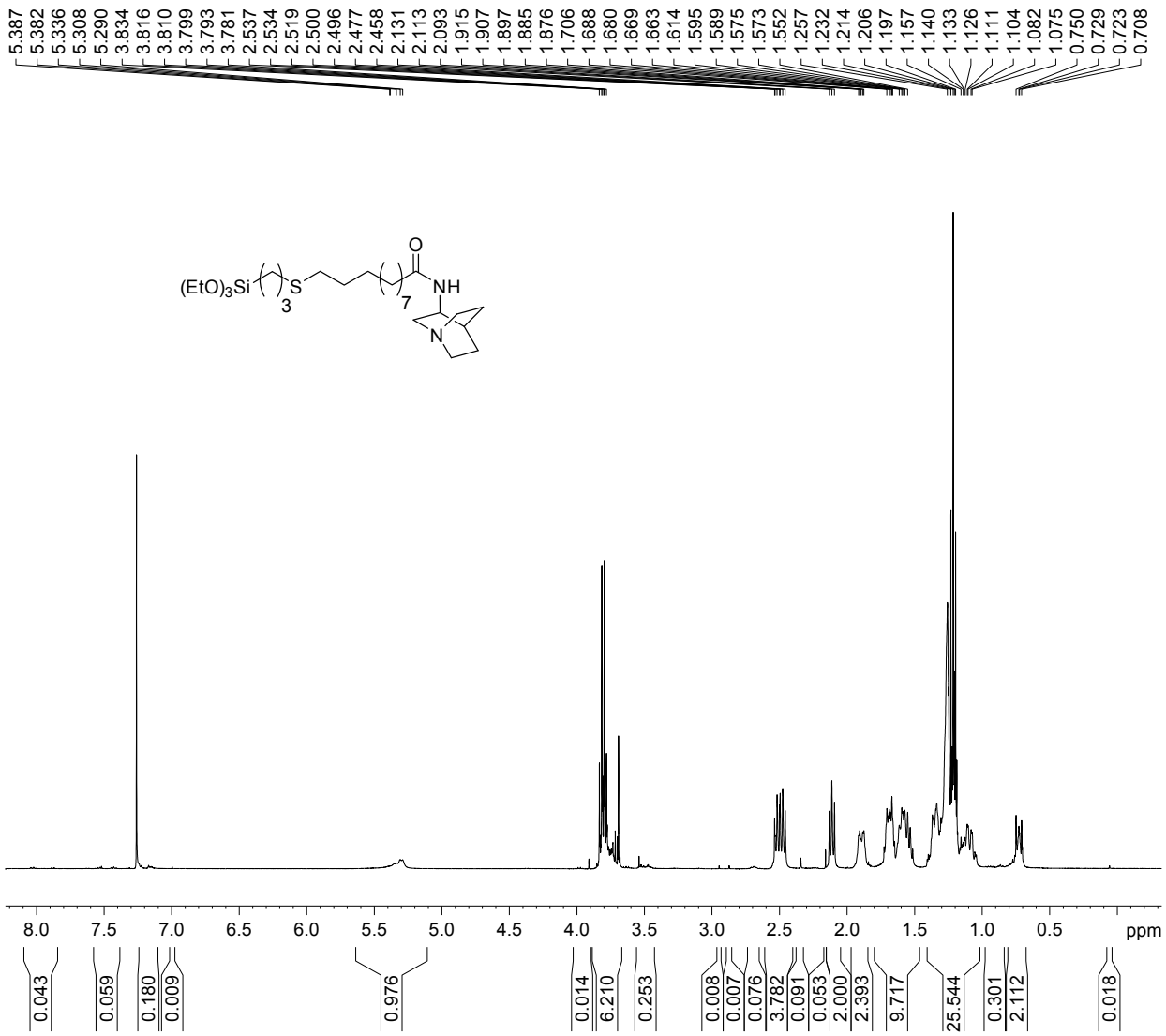
NAME	June29-2010
EXPNO	81
PROCNO	1
Date_	20100629
Time	10.49
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	715
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

N-Boc-(4R)-4-hydroxy-L-proline methyl ester triethoxysilane (6)



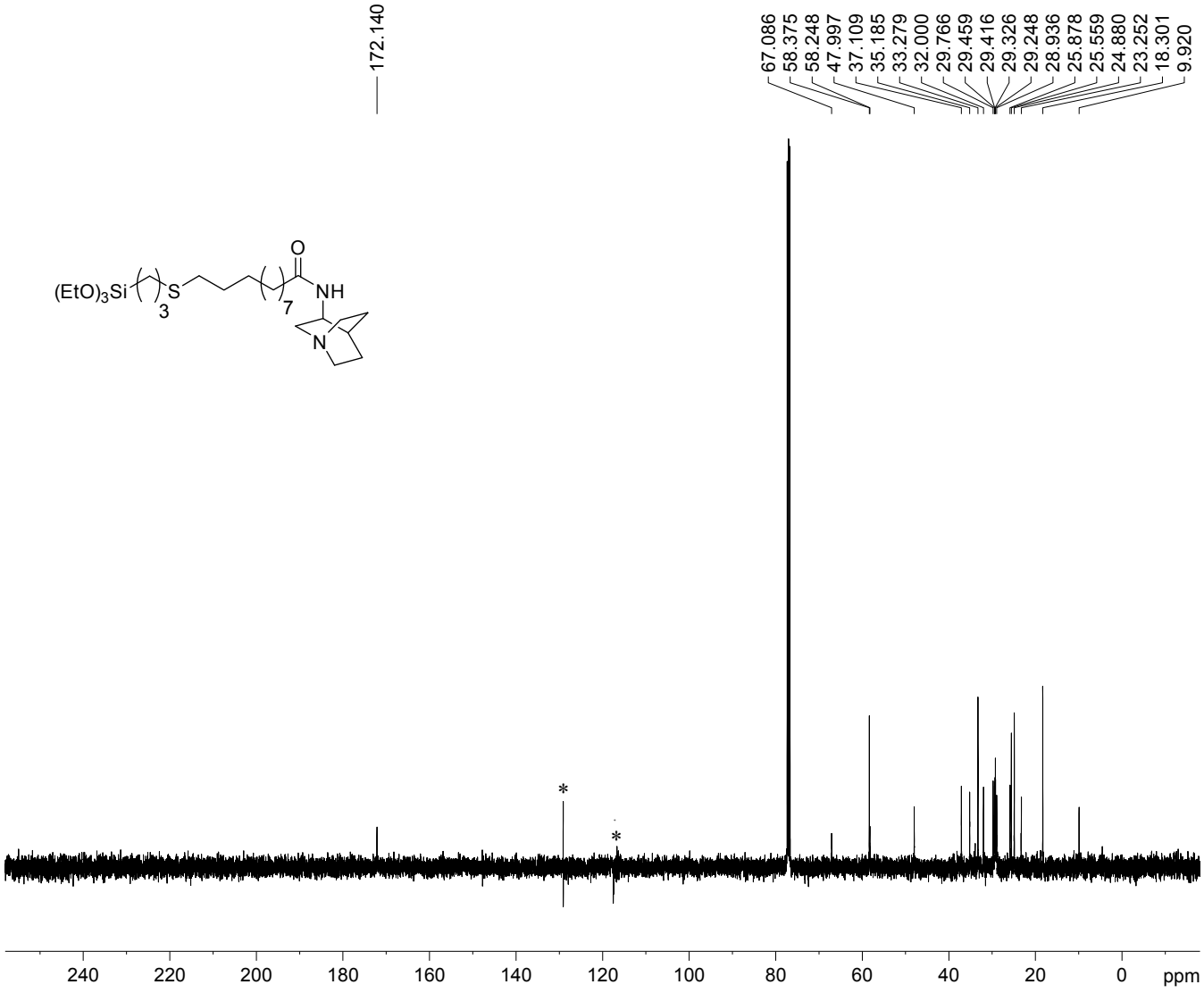
NAME July1-2010
EXPNO 230
PROCNO 1
Date_ 20100701
Time 16.19
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 176
DS 0
SWH 27777.777 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 32768
DW 18.000 usec
DE 25.71 usec
TE 300.0 K
D12 0.0000200 sec
DL5 21.50 dB
CPDPRG waltz16
P31 100.00 usec
D1 2.00000000 sec
P1 8.50 usec
SFO1 100.6248445 MHz
NUCLEUS 13C
D11 0.0300000 sec
SI 65536
SF 100.6127710 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Quinuclidine triethoxysilane (7)



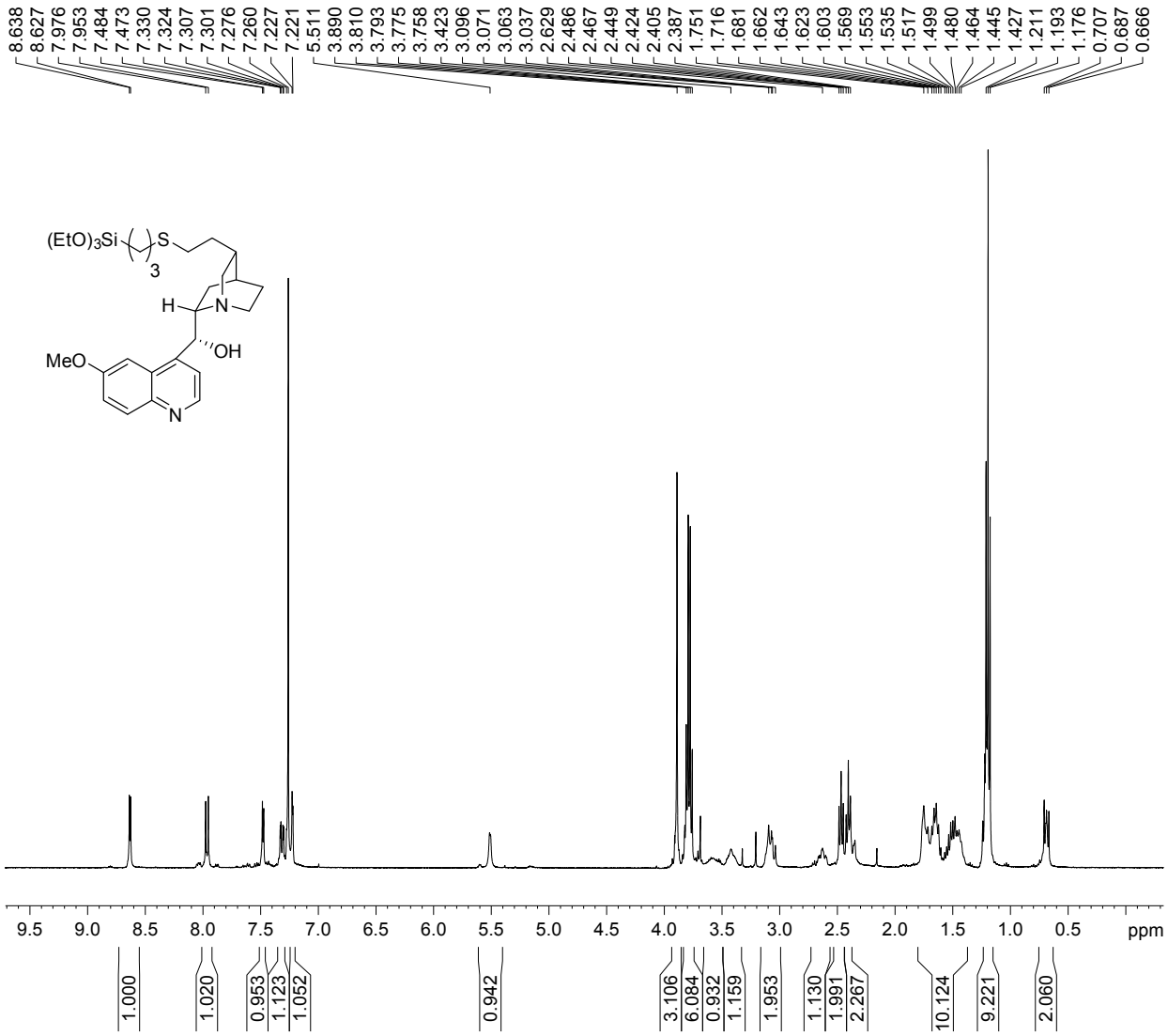
NAME	Aug28-2010
EXPNO	32
PROCNO	1
Date_	20100828
Time	18.00
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	24
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	360
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Quinuclidine triethoxysilane (7)



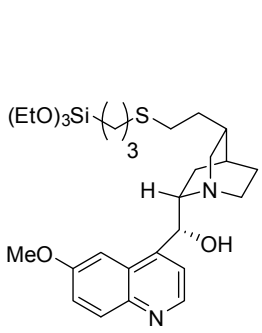
NAME	Aug28-2010
EXPNO	31
PROCNO	1
Date_	20100828
Time	17.38
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	160
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Quinine triethoxysilane (8)

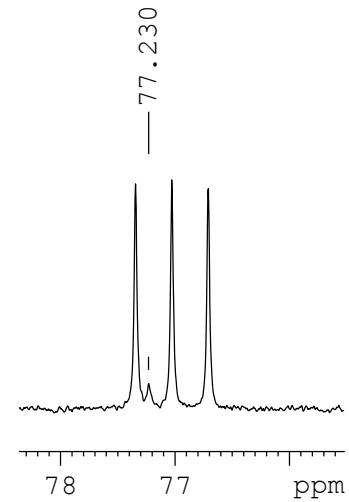


NAME July15-2010
EXPNO 240
PROCNO 1
Date_ 20100715
Time 14.55
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 715
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Quinine triethoxysilane (8)

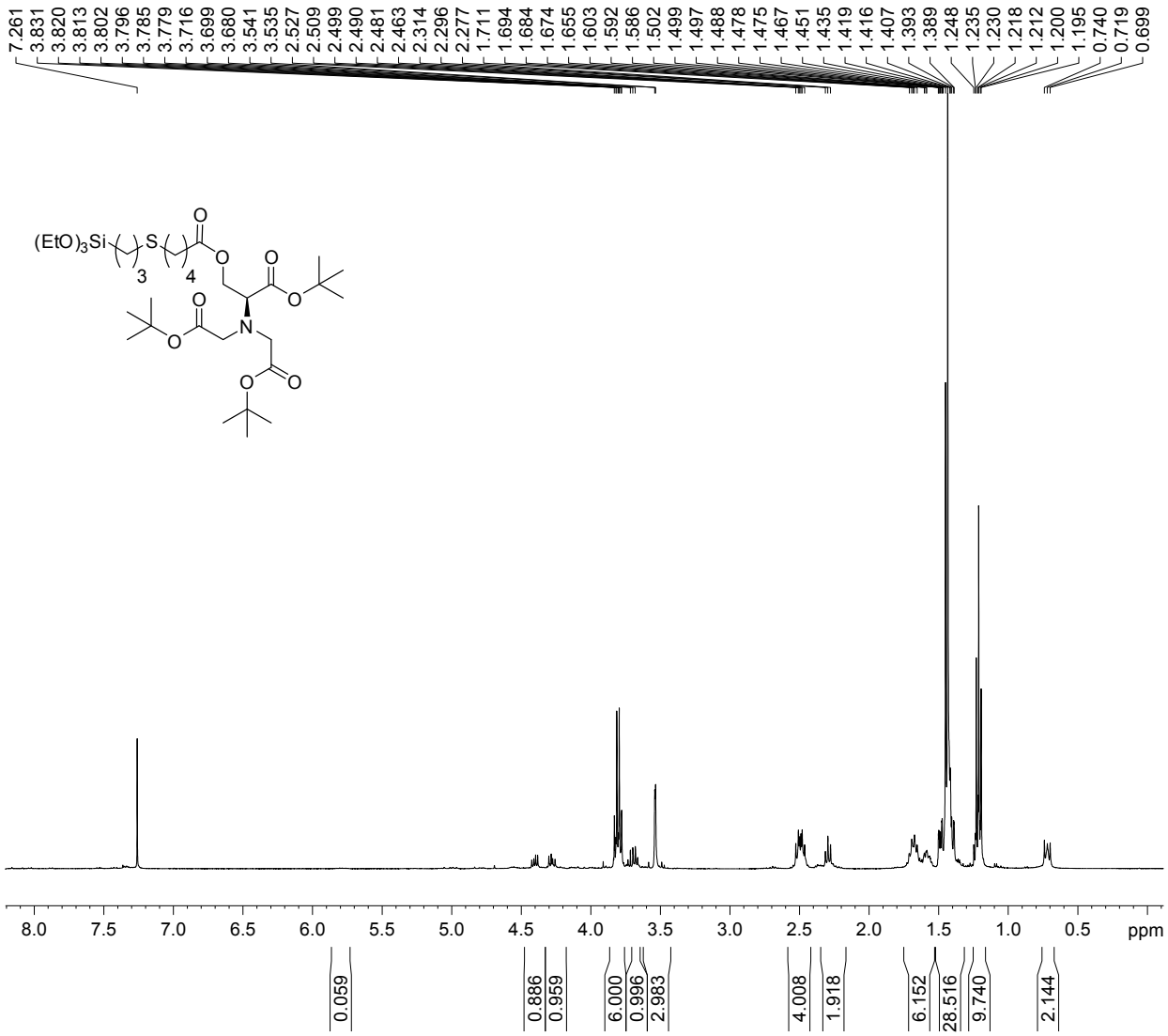


157.761
147.563
144.292
131.621
126.646
121.477
118.382
117.528
101.338
77.230
72.100
59.840
58.373
55.716
43.232
35.243
34.744
34.704
29.965
28.164
25.693
23.172
21.662
18.293
9.891



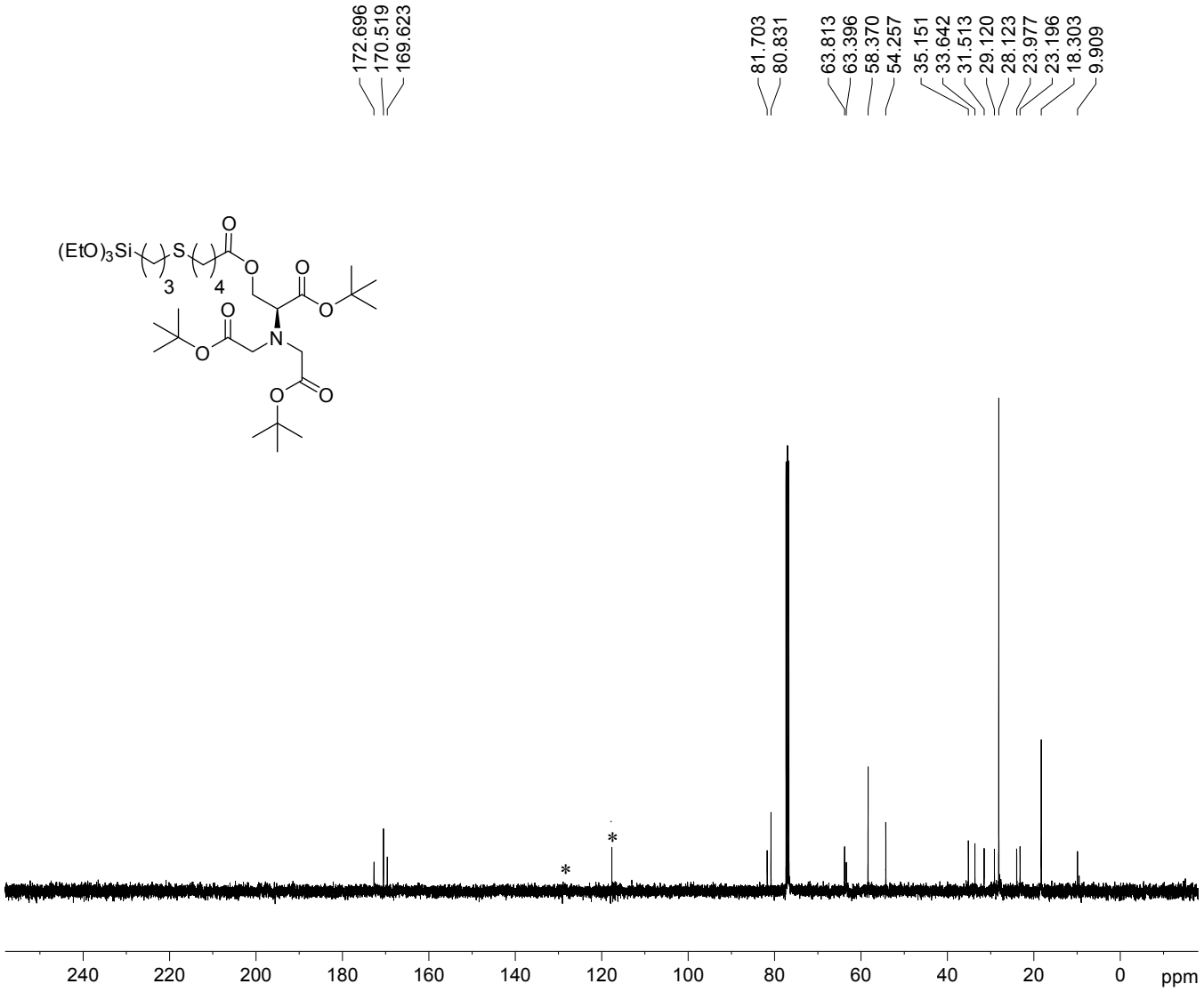
NAME	July15-2010
EXPNO	241
PROCNO	1
Date_	20100715
Time	15.04
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	168
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Nitrilotriacetate (NTA) triethoxysilanesilane (9)



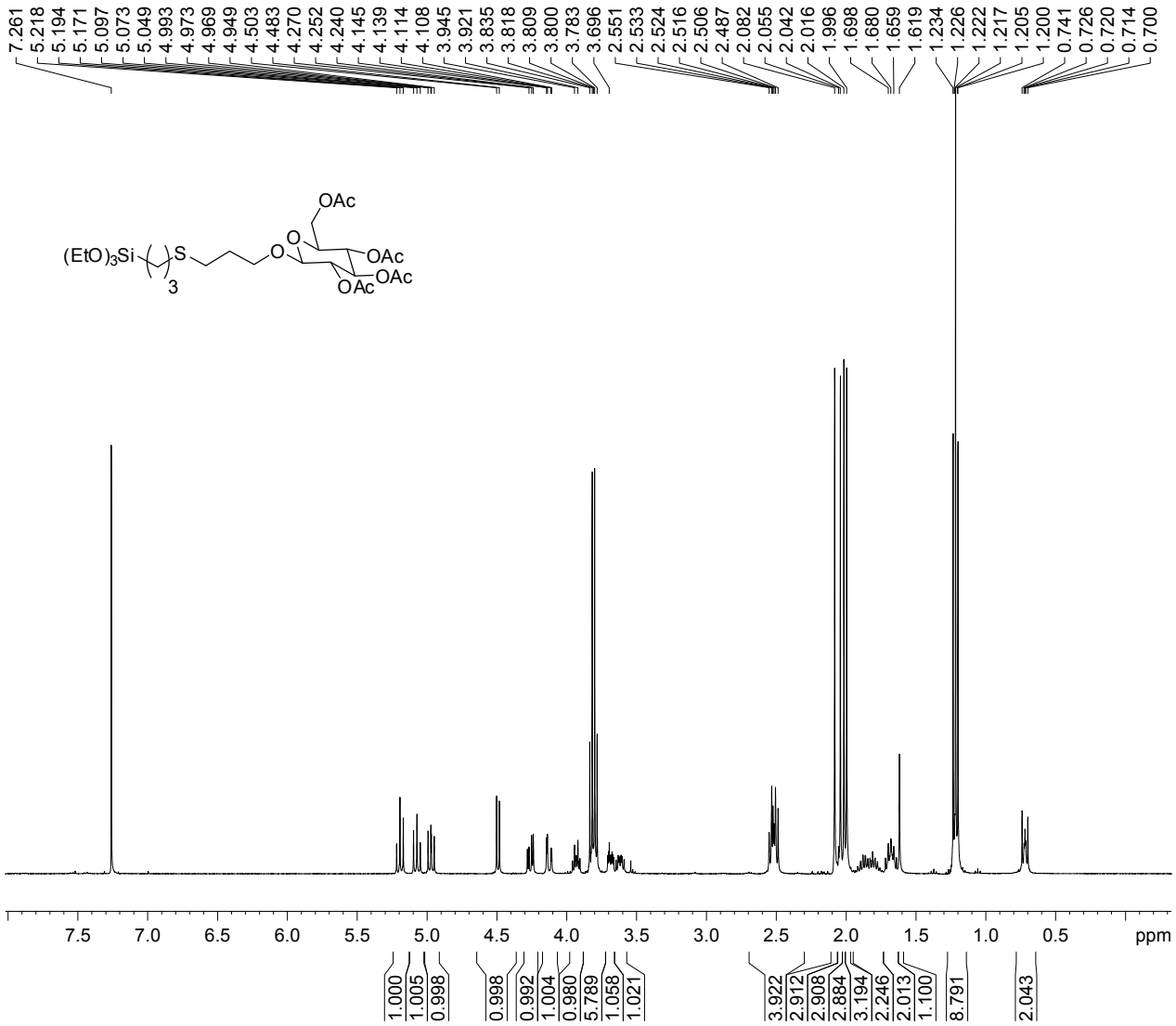
NAME	Oct4-2010
EXPNO	80
PROCNO	1
Date_	20101004
Time	9.42
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	360
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Nitrilotriacetate (NTA) triethoxysilanesilane (9)



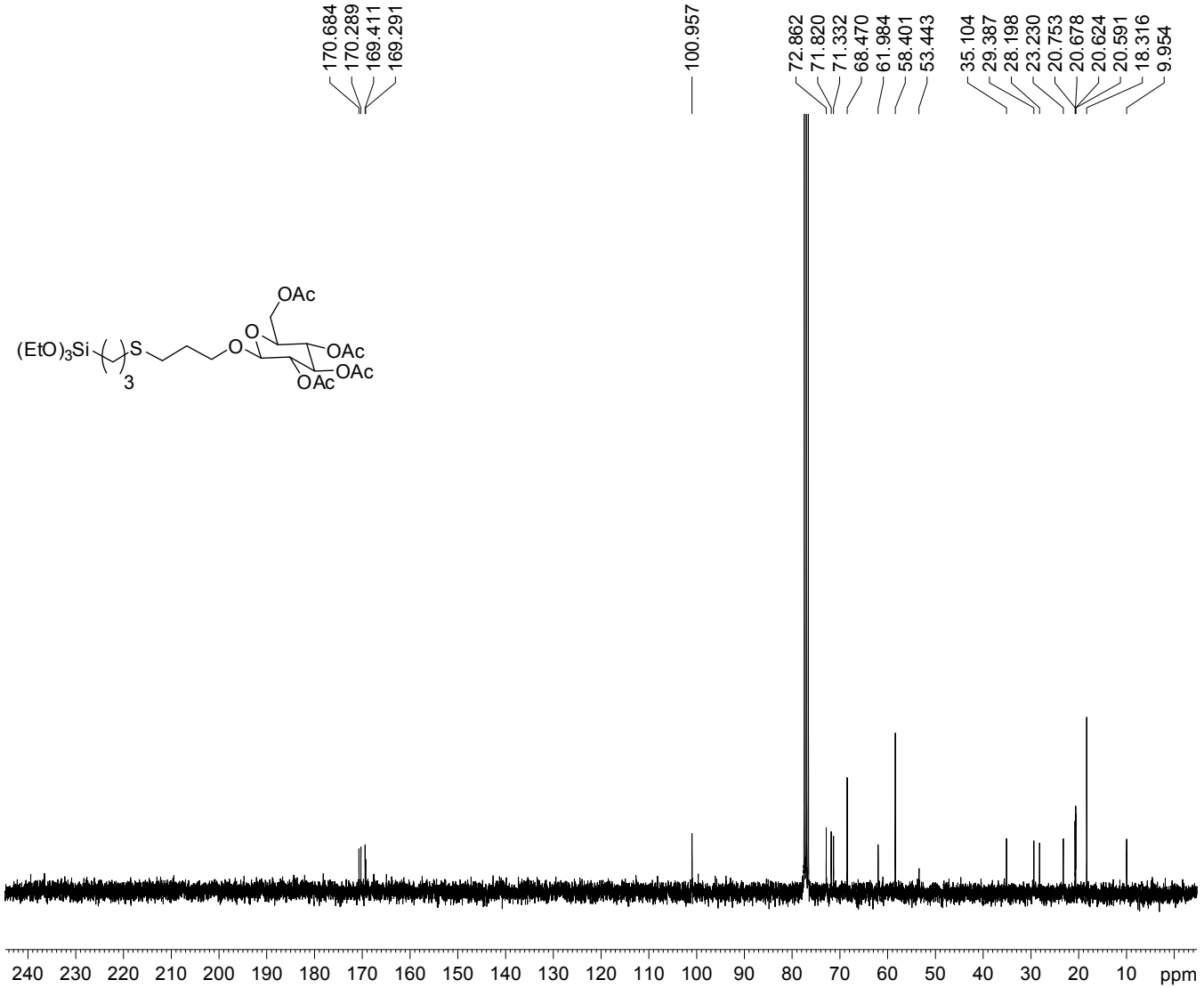
NAME	Oct2-2010
EXPNO	51
PROCNO	1
Date_	20101002
Time	13.10
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	160
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Tetra-O-acetyl-(beta)-D-glucopyranoside triethoxysilane (10)



NAME	Sept13-2010
EXPNO	230
PROCNO	1
Date_	20100913
Time	16.38
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	24
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	715
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Tetra-O-acetyl-(beta)-D-glucopyranoside triethoxysilane (10)

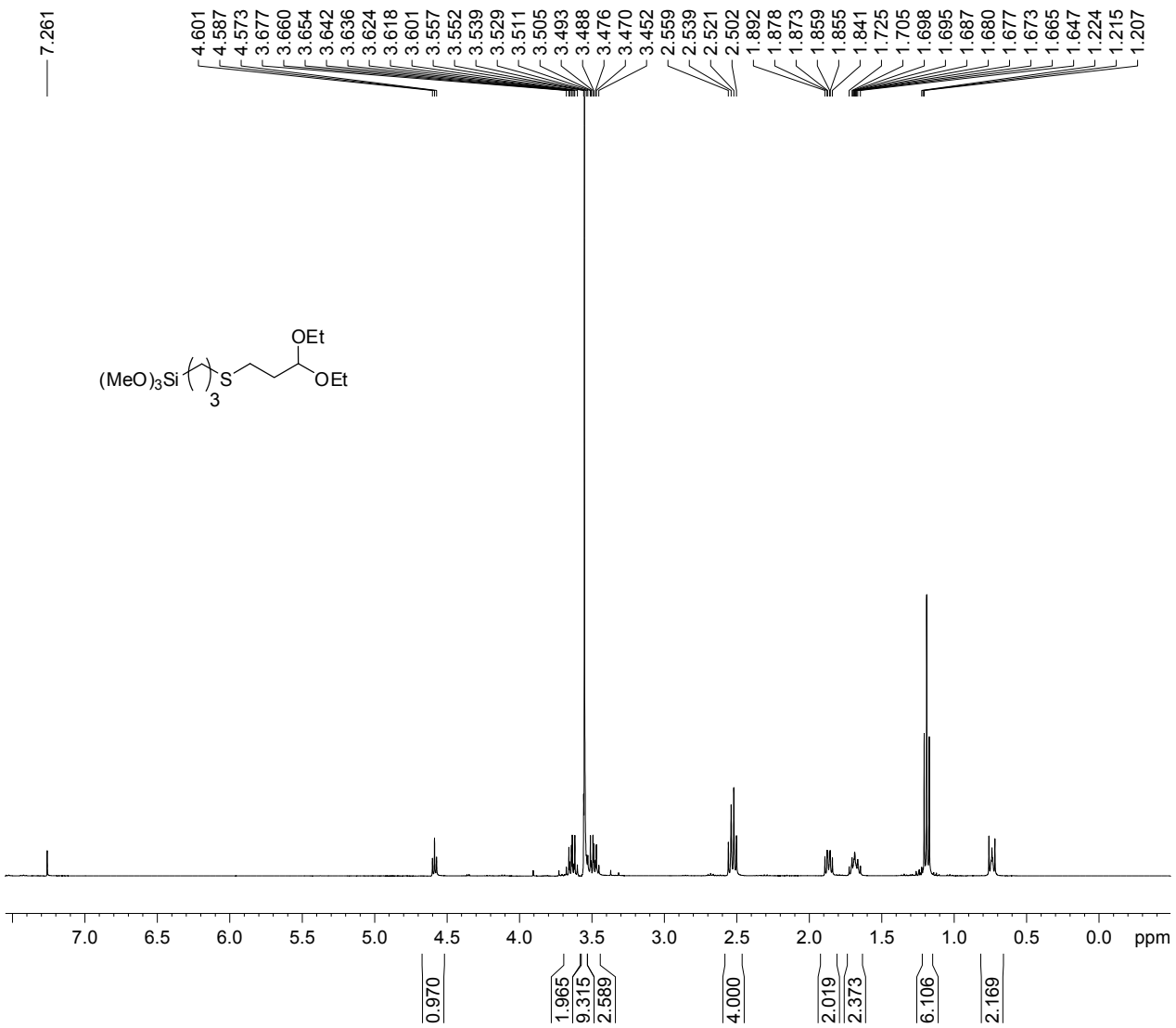


NAME silane Thio-enes
EXPNO 6
PROCNO 1
Date_ 20100607
Time 10.32
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 320
DS 0
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 32768
DW 26.550 usec
DE 6.00 usec
TE 299.7 K
D1 2.00000000 sec
d11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 -4.00 dB
SFO1 75.4768051 MHz

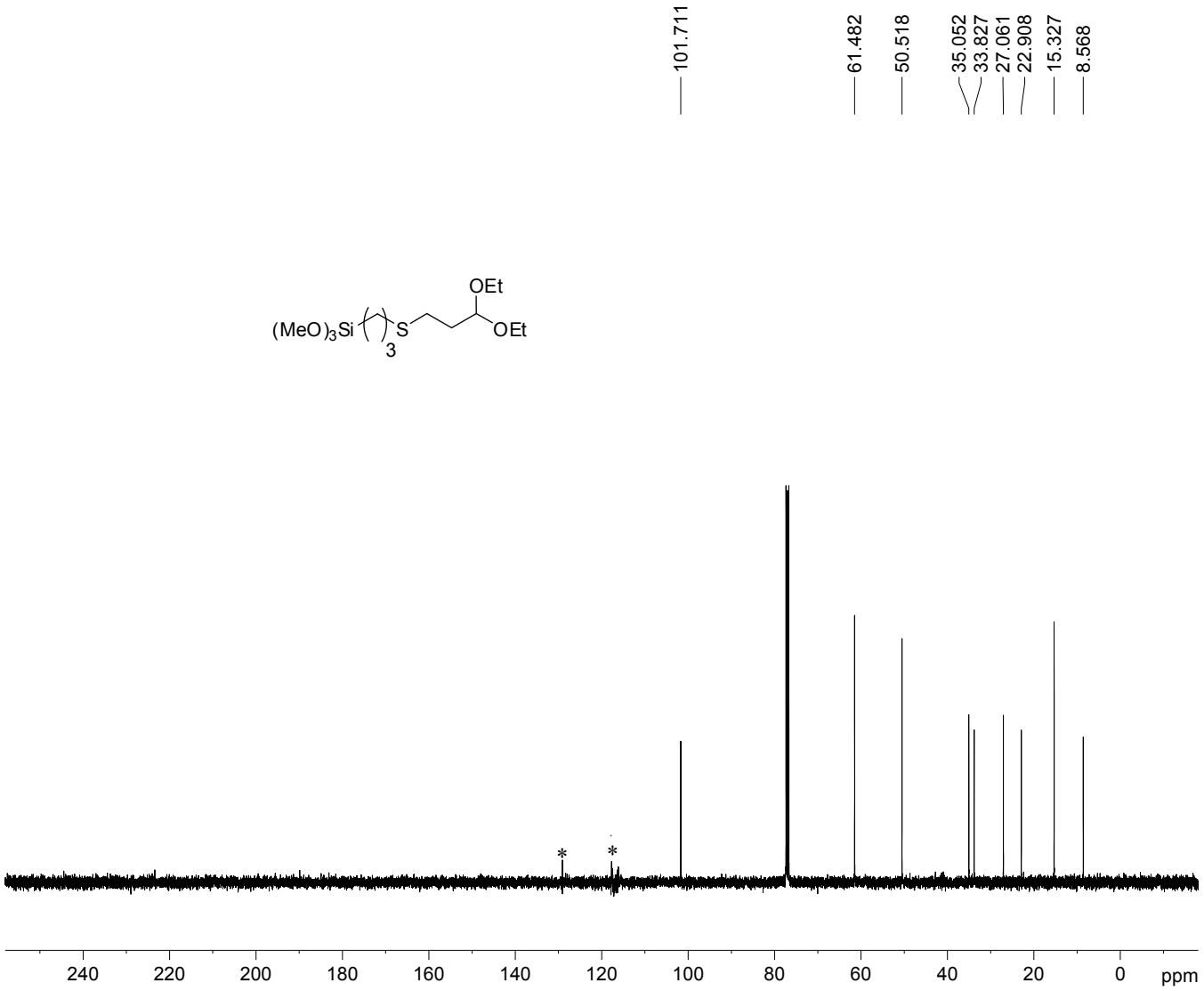
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 14.85 dB
SFO2 300.1318008 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Acetal trimethoxysilane (11)



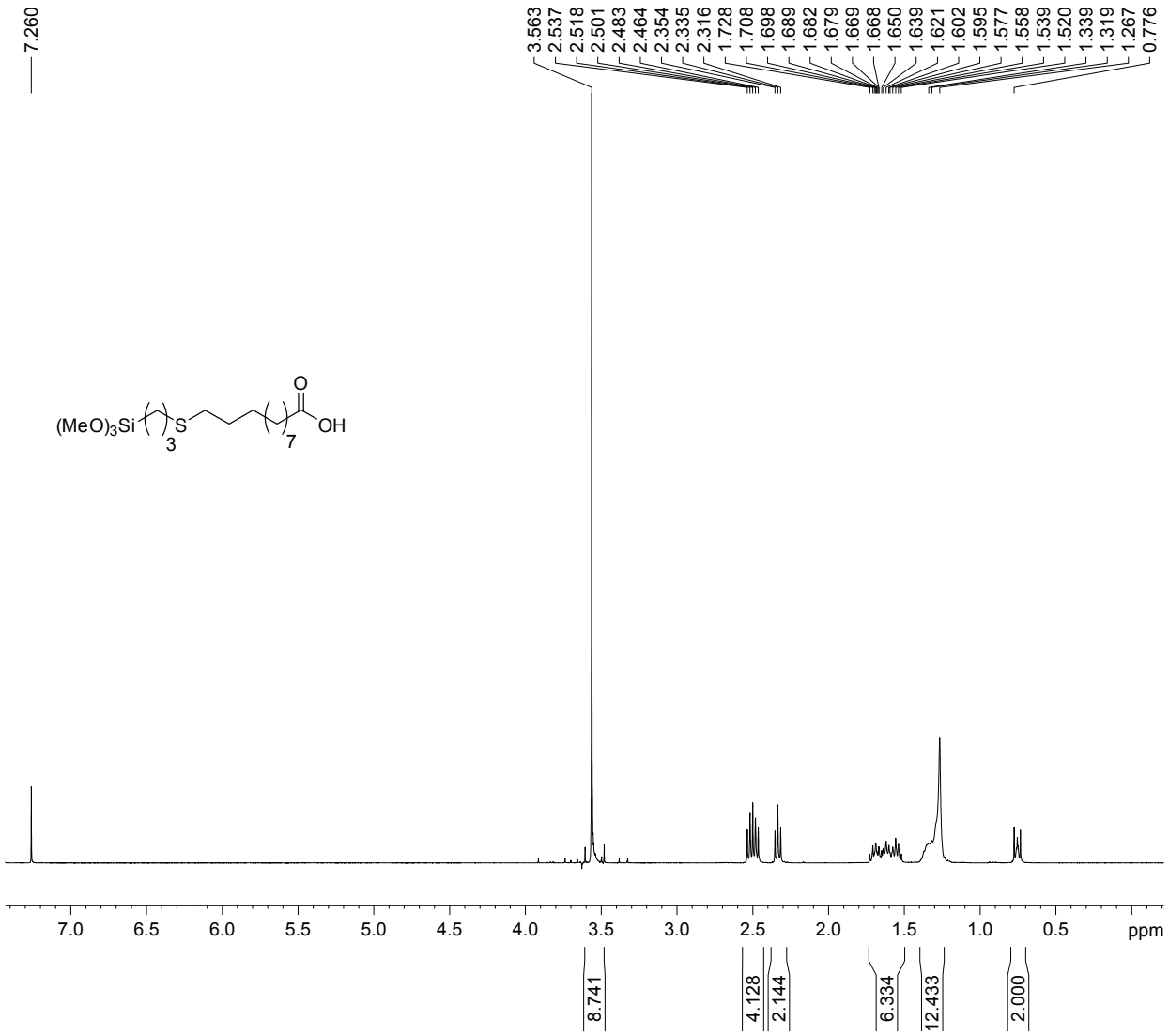
NAME	Sept3-2010
EXPNO	80
PROCNO	1
Date_	20100903
Time	10.08
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	360
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Acetal trimethoxysilane (11)



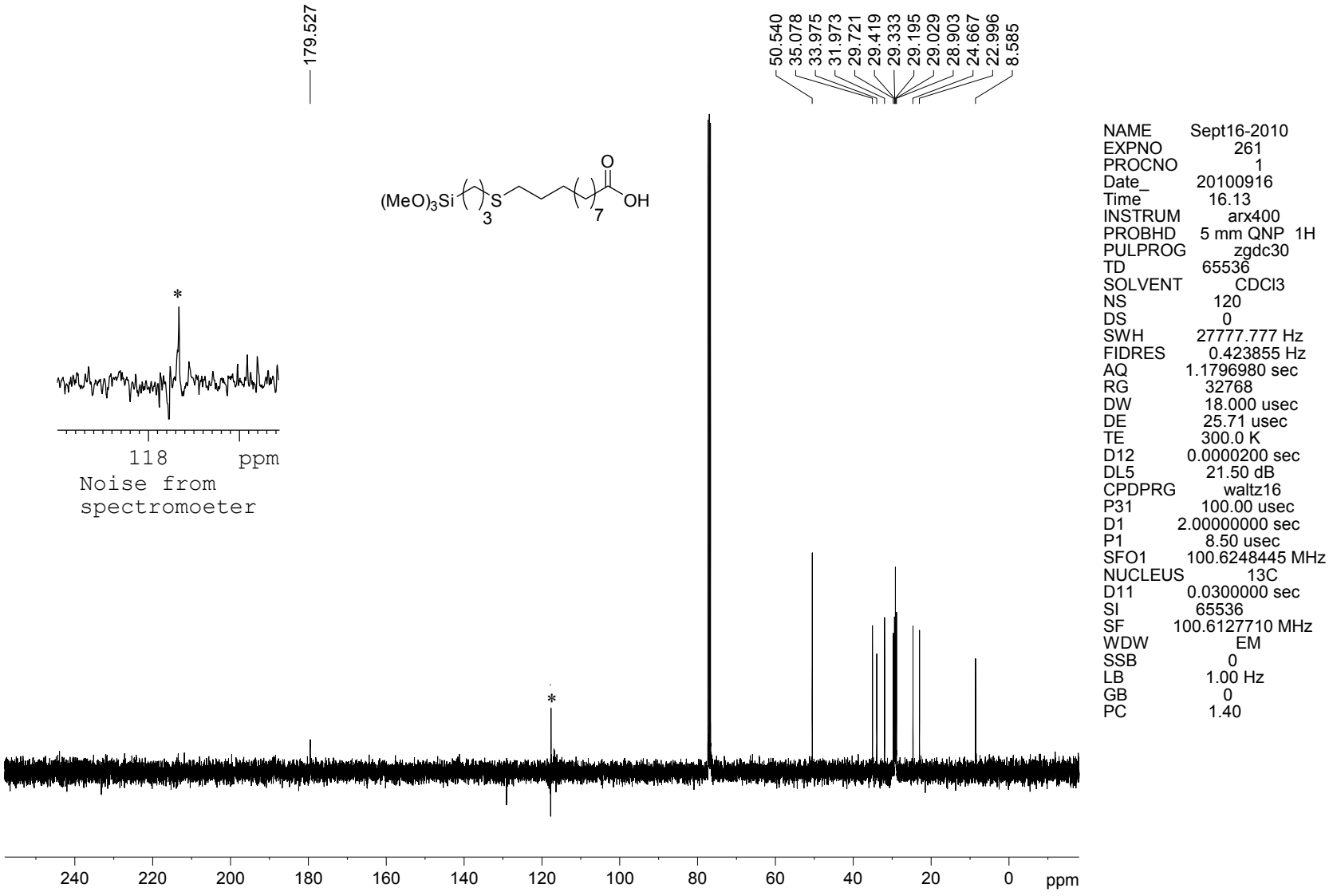
NAME	Sept3-2010
EXPNO	81
PROCNO	1
Date_	20100903
Time	10.17
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	160
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Undecanoic acid trimethoxysilane (12)



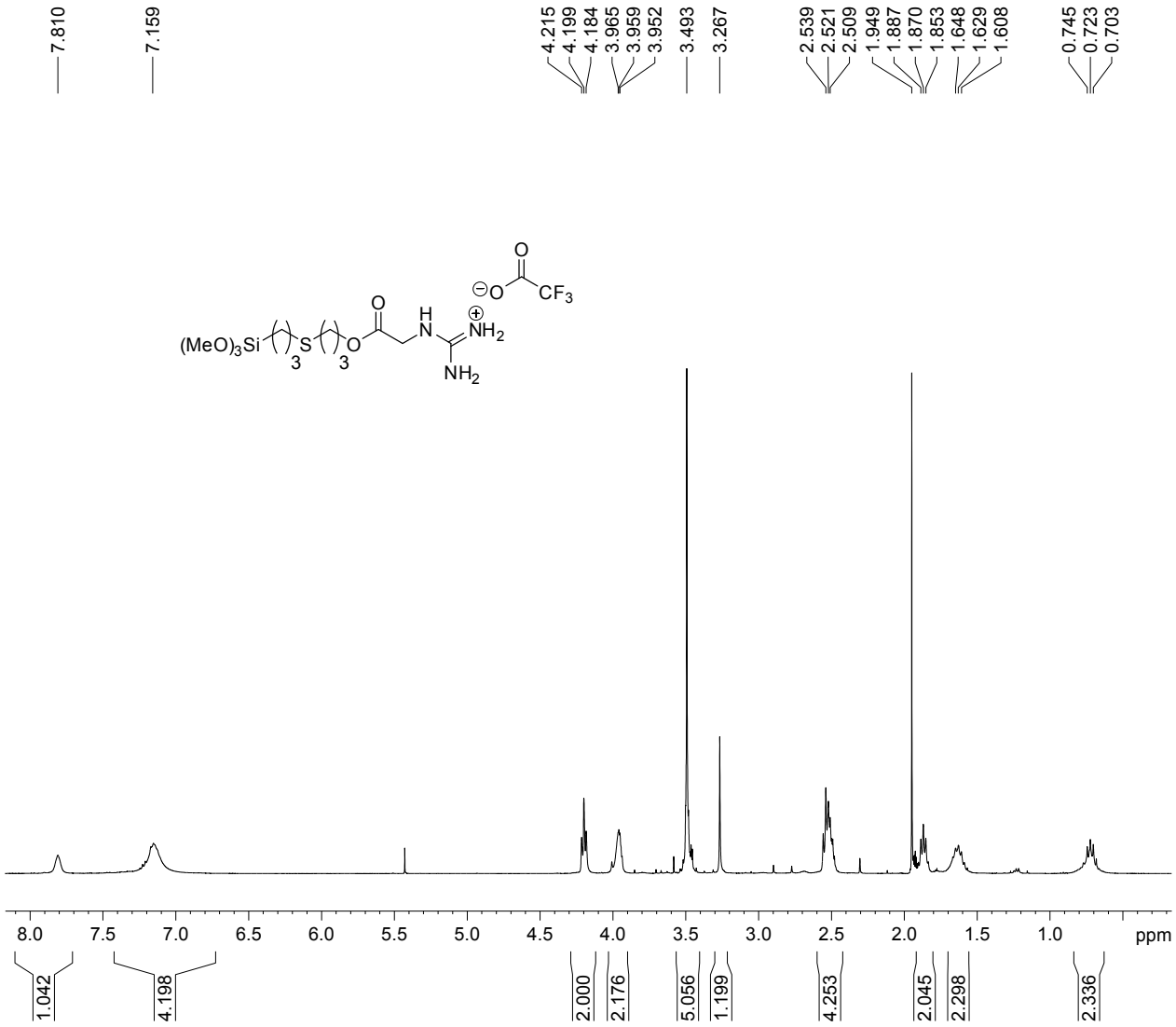
NAME Sept16-2010
EXPNO 260
PROCNO 1
Date_ 20100916
Time 16.05
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 360
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Undecanoic acid trimethoxysilane (12)



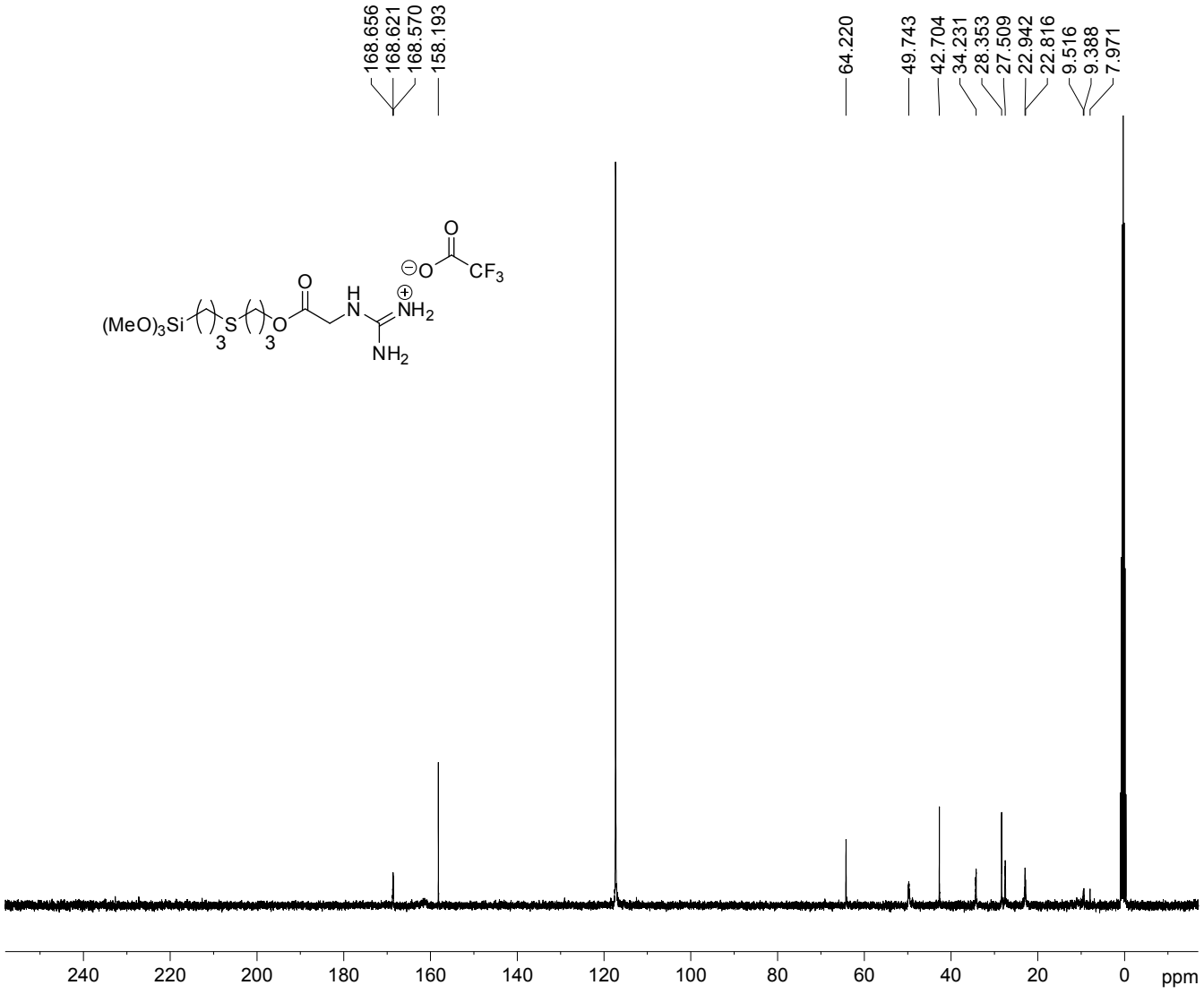
NAME	Sept16-2010
EXPNO	261
PROCNO	1
Date_	20100916
Time	16.13
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	120
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Guanidinium trimethoxysilane (13)



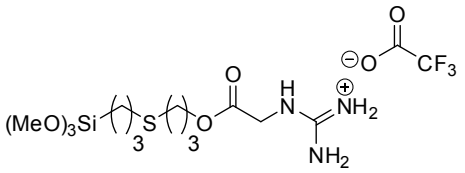
NAME May26-2011
EXPNO 210
PROCNO 1
Date_ 20110526
Time 15.47
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 180
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Guanidinium trimethoxysilane (13)



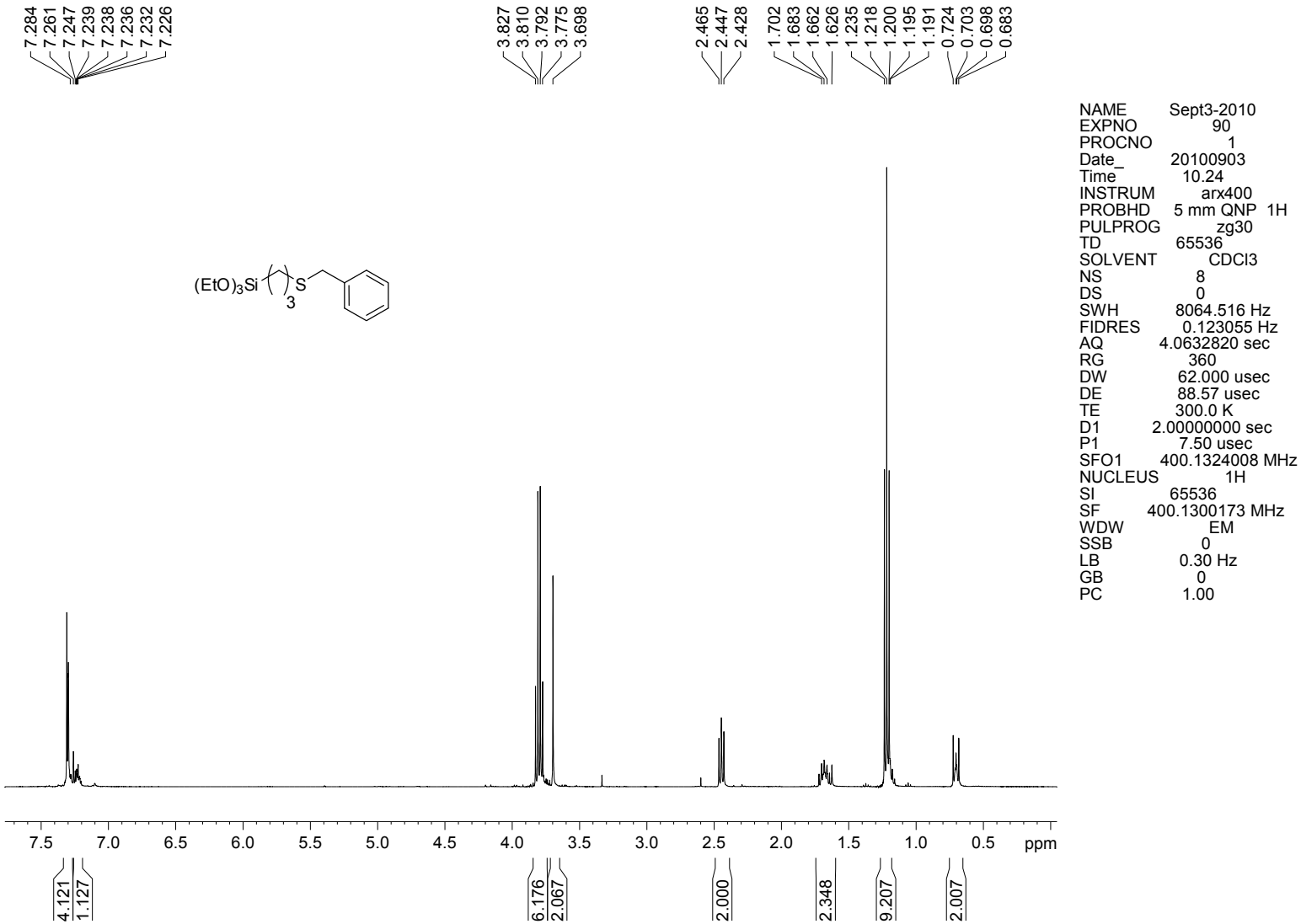
NAME	May26-2011
EXPNO	211
PROCNO	1
Date_	20110526
Time	15.59
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CD3CN
NS	200
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	23.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.25 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Guanidinium trimethoxysilane (13)



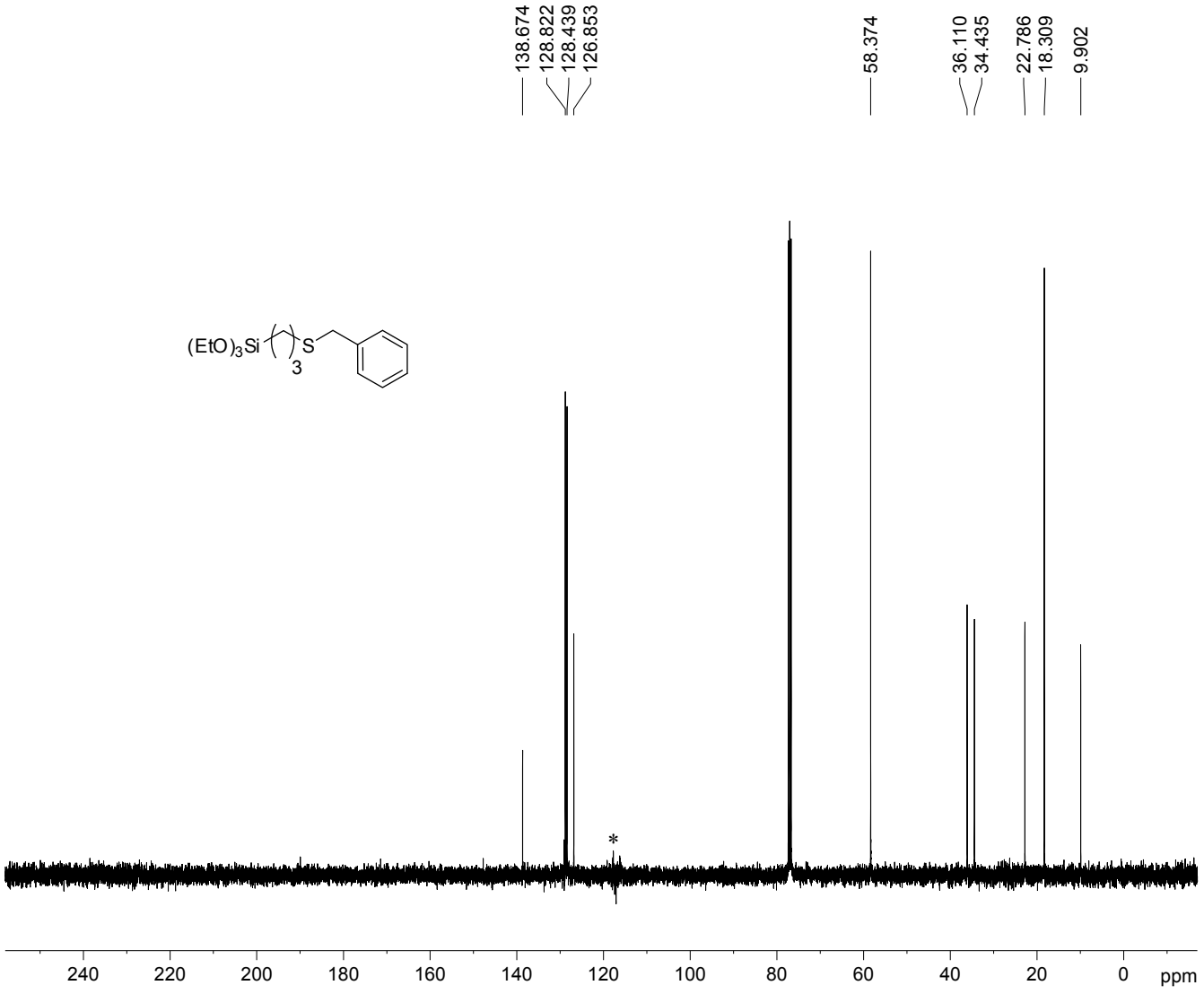
NAME	May27-2011
EXPNO	60
PROCNO	1
Date_	20110527
Time	9.23
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgfdc30
TD	262144
SOLVENT	CD3CN
NS	8
DS	0
SWH	125000.000 Hz
FIDRES	0.476837 Hz
AQ	1.0486259 sec
RG	2860
DW	4.000 usec
DE	5.71 usec
TE	300.0 K
D1	2.00000000 sec
D12	0.00002000 sec
TL0	1.00 dB
P1	10.90 usec
D13	0.00000300 sec
DL5	23.50 dB
SFO1	376.4985950 MHz
NUCLEUS	19F
CPDPRG	waltz16
P31	100.00 usec
D11	0.03000000 sec
SI	262144
SF	376.4985960 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

Benzyl triethoxysilane (14)



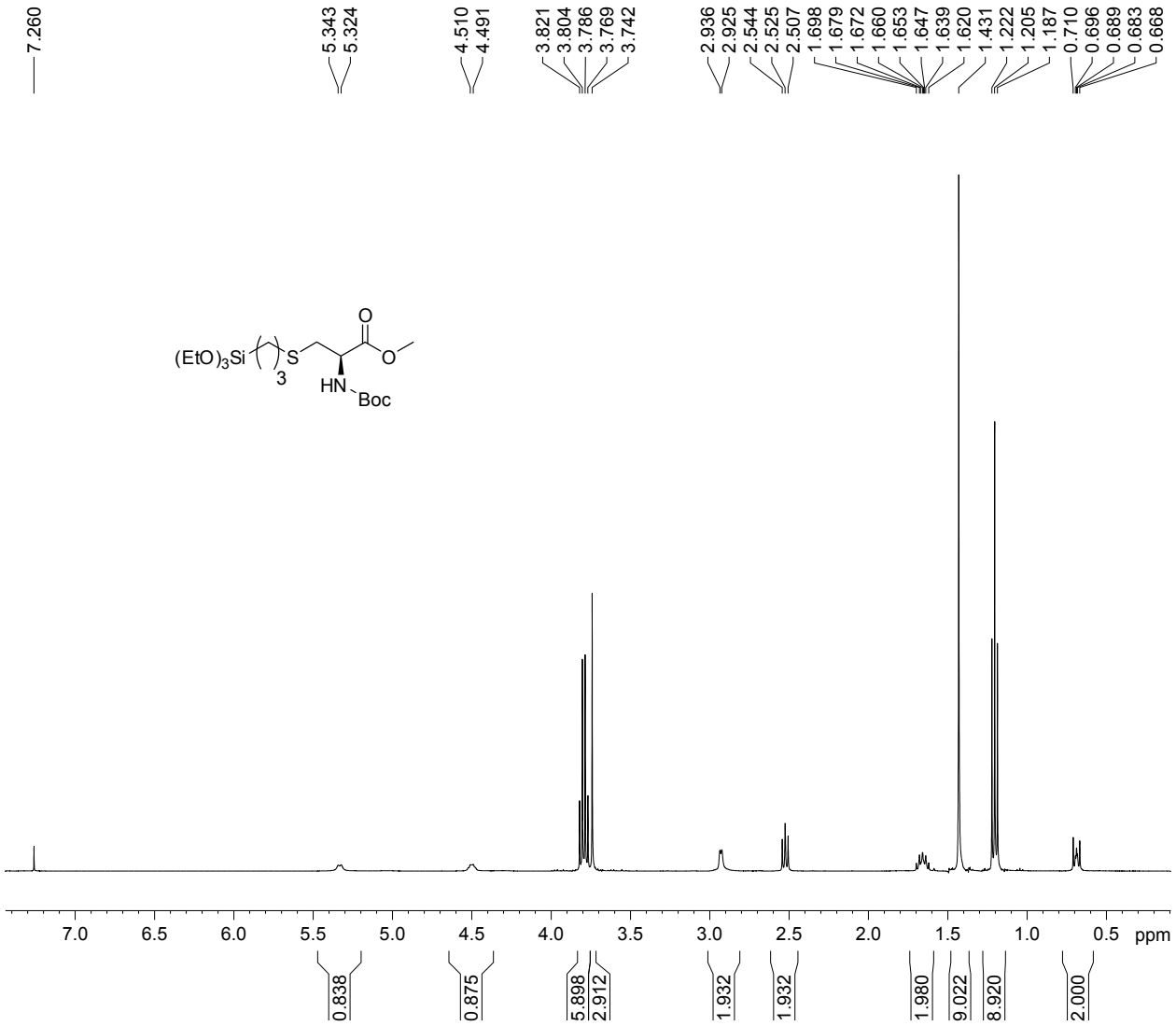
NAME Sept3-2010
EXPNO 90
PROCNO 1
Date_ 20100903
Time 10.24
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 360
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Benzyl triethoxysilane (14)



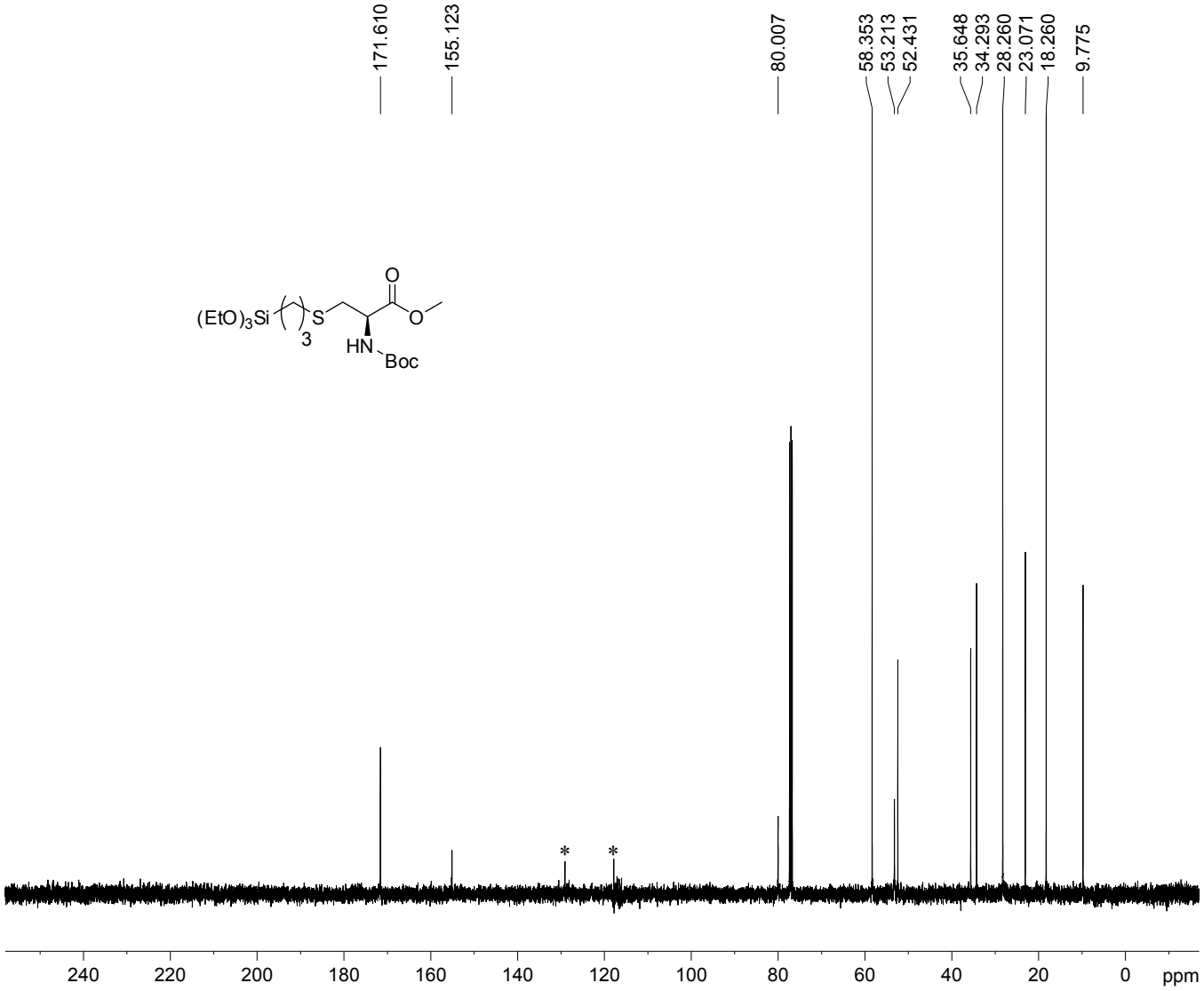
NAME	Sept3-2010
EXPNO	91
PROCNO	1
Date_	20100903
Time	10.33
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	160
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Boc-cysteine-OMe triethoxysilane (15)



NAME	Oct28-2010
EXPNO	50
PROCNO	1
Date_	20101028
Time	9.29
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	256
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	7.50 usec
SFO1	400.1324008 MHz
NUCLEUS	1H
SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Boc-cysteine-OMe triethoxysilane (15)



NAME	Oct28-2010
EXPNO	130
PROCNO	1
Date_	20101028
Time	14.04
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	120
DS	0
SWH	27777.777 Hz
FIDRES	0.423855 Hz
AQ	1.1796980 sec
RG	32768
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DL5	21.50 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	8.50 usec
SFO1	100.6248445 MHz
NUCLEUS	13C
D11	0.0300000 sec
SI	65536
SF	100.6127710 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40