Nickel-Catalyzed Reductive Conjugate Addition of Primary Alkyl Bromides to Enones to Form Silyl Enol Ethers

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Supporting Information

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I. General Information

Metals:
$NiCl_2$(1,2-dimethoxyethane) ($NiCl_2$(dme)) was synthesized according to the literature procedure.[1] The stoichiometry of the $NiCl_2$(dme) was found to be variable and the glyme is easily lost upon exposure to vacuum. The amount of glyme present in $NiCl_2$(dme) was determined by elemental analysis and the molecular weight of $NiCl_2$(dme) was calculated accordingly. Manganese powder -325 mesh (Aldrich) and zinc flake, -325 mesh (Alfa) were used as received. $NiCl_2$(glyme), manganese powder, and zinc flake were stored in a Vacuum Atmospheres nitrogen filled glove box.

Ligands:
6,6'-dibromo-2,2':6',2"-terpyridine (Aldrich) and 4,4',4"-tri-*tert*-butyl-2,2':6'2"-terpyridine (Aldrich) were used as received. 6,6'-Dimethyl-2,2':6',2"-terpyridine was synthesized according to the published procedure.[2] Other ligands tested were from commercial suppliers and used as received.

Solvents: Anhydrous *N*,*N*-dimethylacetamide (DMA), *N*,*N*-dimethylformamide (DMF), dimethoxyethane (DME), and tetrahydrofuran (THF) were obtained by passage of the ACS grade or better solvents through activated alumina and molecular sieves in a solvent purification system and were stored over 4 Å molecular sieves in a nitrogen filled glovebox.

Enones: 2-cyclohexen-1-one (Aldrich), 2-cyclopenten-1-one (Aldrich), 2-cyclohepten-1-one (Aldrich), 4-hexen-3-one (SAFC), 4,4-dimethyl-2-cyclohexen-1-one (Acros) were used as received.

Alkyl Halides: ethyl 4-bromobutyrate (Alfa), 1-bromooctane (Aldrich), 1-bromo-2-methylpropane (Aldrich), 4-bromobutyronitrile (TCI), 1-bromo-3-chloropropane (Aldrich), neopentyl bromide (Alfa), 1-(2-bromoethyl)-4-chlorobenzene (Combi), 2-(3-chlorophenyl)ethyl bromide (Combi), 1-phenyl-2-bromoethane (Acros), 3-bromopropionitrile (Alfa), 5-bromo-2-methyl-2-pentene (Aldrich), 2-(tert-butyldimethylsilyloxy)ethyl bromide (Oakwood), and 2-bromoethyl phenyl ether (Aldrich) were used as received. 3-bromopropylamine tert-butylcarbamate[3], 5-bromo-2-pentanone[4], benzyl N-(3-bromopropyl)carbamate[5], 4-methoxyphenethyl bromide[6], (5-bromopent-1-yn-1-yl)triisopropylsilane[7] were prepared according to literature procedures.

Silylating Reagents:
All silyl reagents were purchased from Gelest and stored in a Vacuum Atmospheres nitrogen filled glove box. For the large scale reaction set up on the benchtop, the required amount of silyl reagent was removed from glove box in a sealed vial before use.

Other Reagents:
Dodecane (Aldrich) was purchased commercially and used without further purification.

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[1] Ward, L. G. L.; Pipal, J. R., *Inorg. Synth*. **2007**, *13*, 154.
[2] Sato, Y.; Nakayama Y.; Yasuda, H. *J. Organomet. Chem.* **2004**, *689*, 744.
[3] Huang, A. Y.-T.; Tsai, C.-H.; Chen. H.-Y.; Chen, H.-T.; Lu, C.-Y.; Ling, Y.-T.; Kao, C.-L. *Chem. Commun.* **2013**, *49*, 5784.
[4] Yu, F.; Miller, D. J.; Allemann, R. K. *Chem. Commun.* **2007**, *40*, 4155.
[5] Robarge, M. J.; Husbands, S. M.; Kieltyka, A.; Brodbeck, R.; Thurkauf, A.; Newman, A. H. *J. Med. Chem.* **2001**, *44*, 3175.
[6] Pitts, A. K.; O'Hara, F.; Snell, R. H.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 5451.
[7] Chen, C.; Layton, M. E.; Sheehan, S. M.; Shair, M. D. *J. Am. Chem. Soc.* **2000**, *122*, 7424.

II. Methods

NMR Spectroscopy:
^{1}H and ^{13}C NMR spectra were acquired on 400 and 500 MHz Bruker NMR instruments. NMR chemical shifts are reported in ppm and are referenced to the residual solvent peak for $CDCl_3$ (δ = 7.26 ppm, ^{1}H NMR; δ = 77.16 ppm, ^{13}C NMR). Chemical shifts are reported in parts per million (ppm) and coupling constants (*J*) are reported in Hertz, and integration is provided and assignments are indicated.

Gas Chromatography:
GC analyses were performed on an Agilent 7890A GC equipped with dual DB-5 columns (20 m x 180 µm x 0.18 µm), dual FID detectors, and hydrogen as the carrier gas. A sample volume of 1 µL was injected at a temperature of 300 °C and a 100:1 split ratio. The initial inlet pressure was 20.3 psi but varied as the column flow was held constant at 1.8 mL/min for the duration of the run. The initial oven temperature of 50 °C was held for 0.46 min followed by a temperature ramp of 65 °C/min up to 300 °C. The temperature was held at 300 °C for 3 min. The total run time was ~7.3 min and the FID temperature was 325 °C. Dodecane was used as an internal standard for GC analysis of catalytic reactions.

Gas Chromatography / Mass Spectrometry:
GC/MS analyses were performed on a Shimadzu GCMS-QP2010 equipped with an RTX-XLB column (30 m x 0.25 mm x 0.28 µm) with a quadrupole mass analyzer using helium as a carrier gas. The analysis method used in all cases was 5 µL injection of sample, an injection temperature of 225 °C, and a 25:1 split ratio. The initial inlet pressure was 7.8 psi, but varied as the column flow was held constant at 1.0 mL/min for the duration of the run. The interface temperature was held at 250 °C, and the ion source (EI+, 30 eV) was held at 250 °C. The initial oven temperature was held at 50 °C for 3 min with the detector off, followed by a temperature ramp, with the detector on, at 280 °C at 40 °C/min. The temperature was held at 280 °C for 3 min. The total run time was 11.75 min. Data are reported in the form of m/z (intensity relative to the base peak = 100 ion).

Liquid Chromatography Mass Spectrometry:
LC/MS analyses were performed on a Shimadzu LC/MS 2010 equipped with an electrospray ionization (ESI) probe operating in positive ion mode (ESI+) with an ion trap mass analyzer. Direct injection analysis was employed in all cases with a sample solution in methanol.

High Resolution Mass Spectrometry:
High resolution mass spectra (HRMS) under electron impact (EI+) or electrospray (ESI+) ionization methods were obtained from Mass Spectrometry Laboratory at University of Illinois at Champaign Urbana. The 70-VSE mass spectrometer (EI+ HRMS) was purchased in part with a grant from the Division of Research Resources, National Institutes of Health (RR 04648). The Q-TOF Ultima (ESI HRMS) mass spectrometer was purchased in part with a grant from the National Science Foundation, Division of Biological Infrastructure (DBI-0100085).

Thin Layer / Column Chromatography:
Thin layer chromatography was performed on EMD Chemicals TLC Silica Gel 60 F254 plates. All plates used in isolation of silyl enol ethers were pre-treated with 0.1% trimethylamine. The remaining solvent was removed under reduced pressure. Visualization was accomplished with *p*-anisaldehyde (PNA) or potassium permanganate after inspection under UV light. Flash chromatography was performed using EMD silica gel 60, particle size 0.040-0.063 mm using standard flash techniques.

Elemental Analysis:
Elemental analysis data was obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

III. General Procedures for Reductive Addition of Primary Unhindered Alkyl Halides to Enones

(A) Procedure for reactions set up in a glove box and run under nitrogen

Reactions were set up in a Vacuum Atmospheres nitrogen filled glove box. To an oven-dried 1-dram vial containing a Teflon-coated stir-bar was added $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL, internal standard), enone (1.00 mmol, 1.00 equiv), alkyl bromide (1.10 mmol, 1.10 equiv), and silylating reagent (1.10 mmol, 1.10 equiv). The reaction vials were capped with a PTFE-faced silicone septum, removed from the glove box and heated in a reaction block set at 40 °C on the benchtop with stirring at 1200 rpm until the reaction was judged complete (<5% enone or alkyl bromide remaining) by GC analysis, typically 18–24 h.

GC Analysis.

After 18–24 h, a 10 µL aliquot of the reaction mixture was removed with a 50 µL gas-tight syringe. The aliquot was diluted with diethyl ether (1.5 mL), quenched with 10 µL of 1 M aqueous $NaHSO_4$, and filtered through a short silica plug (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography and percent yield was calculated versus dodecane as an internal standard.

Isolation and Purification.

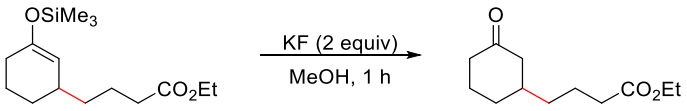
Upon completion (<5% enone or alkyl bromide remaining) by GC analysis the reaction mixture was filtered through a short plug of silica gel (1.5 cm wide × 2 cm high) to remove metal salts and eluted with diethyl ether (100 mL). The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography using silica gel that was pre-treated with 0.1% triethylamine.[8] The purity of the desired product was determined by gas chromatography and ^{1}H NMR spectroscopy.

(B) Large-Scale Procedure conducted on the benchtop in a round-bottom flask

To a flame-dried 50 mL round-bottom flask containing a Teflon-coated stir-bar was added $NiCl_2$(glyme) (49.4 mg, 0.240 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (188 mg, 0.48 mmol, 0.0800 equiv), Mn^0 (659 mg, 12 mmol, 2 equiv), THF (12 mL), 2-cyclohexene-1-one (618 µL, 6.00 mmol, 1.00 equiv), ethyl 4-bromobutyrate (945 µL, 6.6 mmol, 1.1 equiv), and triethylchlorosilane (1.1 mL, 6.6 mmol, 1.1 equiv). The reaction flask was sealed with a rubber septum, and the septum was fitted with a needle connected to an oil bubbler and a needle connected to a nitrogen manifold. The headspace of the reaction mixture was purged with nitrogen gas for ten minutes. The reaction mixture was warmed to 40 °C in an oil bath and stirred at that temperature under a positive flow of nitrogen. After the reaction was judged complete by GC analysis (~ 18 h), the reaction mixture was filtered through a plug of silica gel (1.5 cm wide × 3 cm high). The silica gel pad was washed with diethyl ether (300 mL) and combined filtrates were concentrated under reduced pressure. The resulting residue was purified by column chromatography using silica that was pre-treated with 0.1% triethylamine to yield 1.63 g of **4a** (83% yield). Characterization data matched those obtain on 1.0 mmol scale (vide infra).

[8] In several cases, we observed small amounts of isomerization of the silyl enol ether during column chromatography and storage. The other enol ether isomer is visible as a second vinyl hydrogen signal in the ^{1}H NMR spectrum and crude ^{1}H NMR spectra did not display this extra peak. We were unable to reproduce this phenomenon when we re-ran these reactions, but our working hypothesis is that this occurred with silica gel that had been insufficiently deactivated with triethylamine.

IV. Procedures for Deprotection of Silyl Enol Ether Products from a Crude Reaction Mixture[9] **(Scheme 1, 4c)**

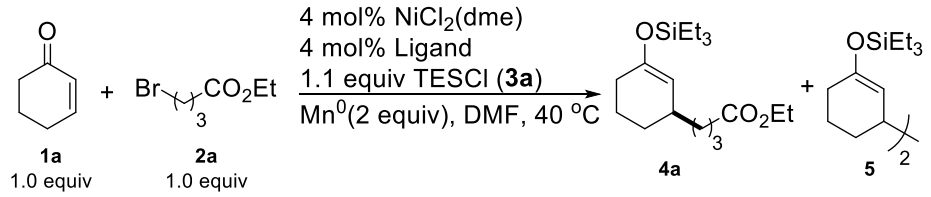


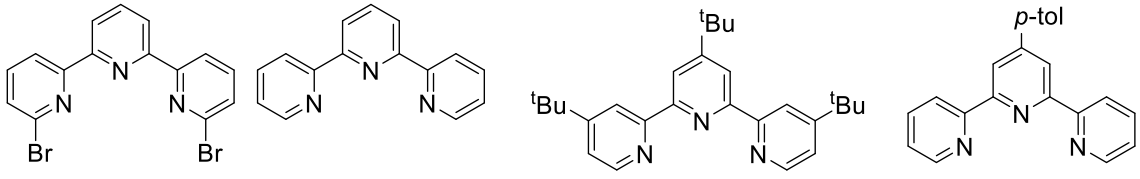
General procedure **A** was followed with 2-cyclohexene-1-one (103 µL, 1.00 mmol, 1.00 equiv), ethyl 4-bromobutyrate (157 µL, 1.10 mmol, 1.10 equiv), and trimethylsilylchloride (140 µL, 1.10 mmol, 1.10 equiv). Upon completion (judged as <5 Area % of starting materials remaining by GC analysis) the reaction mixture was filtered through a short plug of silica gel (1.5 cm wide × 2 cm high) and eluted with diethyl ether (100 mL). The filtrate was concentrated under reduced pressure. The resulting residue was dissolved in methanol (16 mL) and KF (116 mg, 2.00 mmol, 2.00 equiv) was added in small portions at room temperature. The resulting mixture was stirred for 30 minutes. Upon completion (judged as <1 Area% of silyl enol ether product remained by GC analysis) the solvent was removed under reduced pressure and the resulting residue was purified using silica gel chromatography.

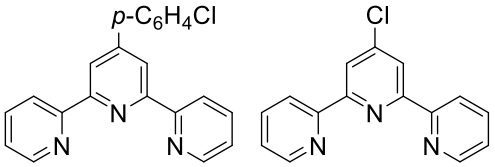
[9] (a) Shrestha, R.; Dorn, S. C. M.; Weix, D. J. *J. Am. Chem. Soc.* **2013**, *135,* 751; (b) Oppolzer, W.; Snowden, R. L. *Helv. Chim. Acta* **1981**, *64*, 2592.

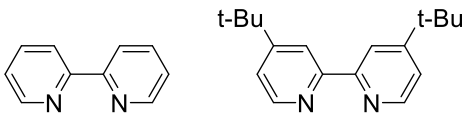
V. Additional Experiments

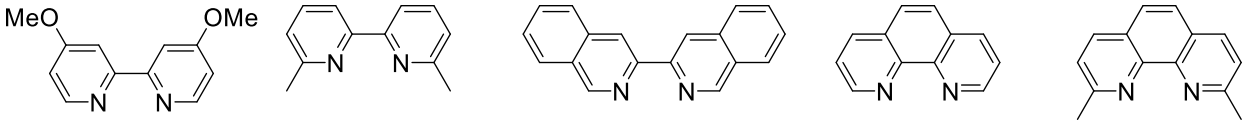
Table S1. Effect of Ligand on Addition of 4-Bromoethylbutyrate (**2a**) to 2-Cyclohexen-1-one (**1a**).[a]

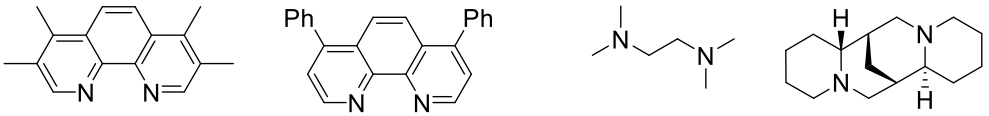






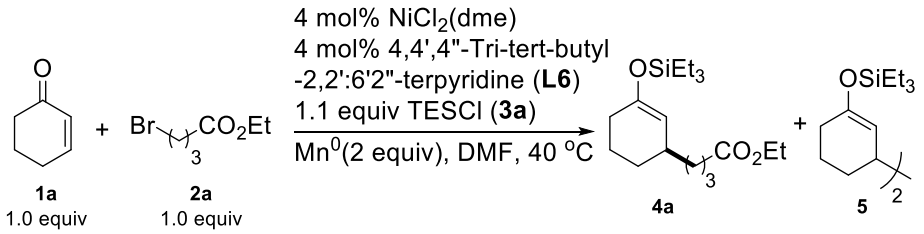






[a] General Procedure **A** was followed, reactions were run on a 0.5 mmol scale for 18 – 24 h in 1 mL of solvent, corrected GC yields of **4a** vs. dodecane as an internal standard. [b] All starting materials consumed, dimerized byproducts observed (**5**).

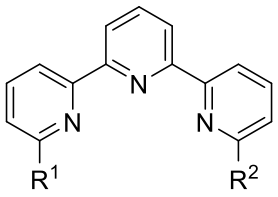
Table S2. Synergistic Effects of Solvent and M:L Ratio with **L6**[a]



entry	Solvent	mol % **L6**	yield **4a**[b] (%)	yield **5** (%)
1	DMF	4	0	71
2	DMF	8	<5	67
3	THF	4	11	61
4	THF	8	72	19

[a] General Procedure **A** was followed; reactions were run on a 0.5 mmol scale for 18 – 24 h in 1 mL of solvent. [b] Corrected GC yields of **4a** vs. dodecane as an internal standard.

Table S3. Analysis of **L7** by ESI+ MS after reaction is complete.

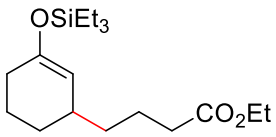


	LC/MS *m/z* (% relative intensity, ion)
L7: $R^1 = R^2 = Br$	414.10 (5.07, $M+Na^+$)
L9: $R^1 = H$, $R^2 = (CH_2)_3CO_2Et$	370.00 (9.67, $M+Na^+$)
L10: $R^1 = R^2 = (CH_2)_3CO_2Et$	485.05 (4.64, $M+Na^+$)

[a] General Procedure **A** was followed to form **4a**; reaction was run on a 0.5 mmol scale for 18 h in 1 mL of solvent (THF). A sample of the reaction mixture was diluted in methanol and infused into the mass spectrometer. The spectrum was searched for peaks with masses attributable to ligand derivatives.

VI. Characterization Data

Ethyl 4-(3-((triethylsilyl)oxy)cyclohex-2-en-1-yl)butanoate (Scheme 1, 4a)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), ethyl 4-bromobutyrate (157 µL, 1.10 mmol, 1.10 equiv), and chlorotriethylsilane (185 µL, 1.10 mmol, 1.10 equiv).

Yield: 265 mg, 81% yield, clear, colorless oil

TLC: R_f = 0.23 (3% Et_2O in hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]

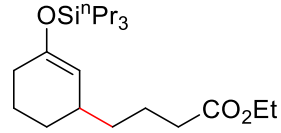
^{1}H NMR (400 MHz; $CDCl_3$): δ 4.78 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.12 (d, *J* = 0.7 Hz, 1H), 1.98 (s, 2H), 1.76-1.60 (m, 4H), 1.58-1.51 (m, 1H), 1.28 (dt, *J* = 19.4, 7.4 Hz, 5H), 1.09 (q, *J* = 10.9 Hz, 1H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.8, 150.8, 108.8, 60.2, 36.6, 34.7, 34.5, 30.1, 28.8, 22.6, 21.9, 14.3, 6.8, 5.2.

GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV): 326.20 (3.14, M^+), 211.15 (100.00, M^+- $C_6H_{11}O_2$), 115.10 (23.97, M^+- $C_{12}H_{23}OSi$), 87.00 (14.34, M^+- $C_{14}H_{27}OSi$)

HRMS (ESI+): $[M+Na]^+$ Calc. for $C_{18}H_{34}O_3Si$: 349.2169; found: 349.2180

Ethyl 4-(3-((tripropylsilyl)oxy)cyclohex-2-en-1-yl)butanoate (Scheme 1, 4b)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), ethyl 4-bromobutyrate (157 µL, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).

Yield: 361 mg, 98% yield, clear, colorless oil

TLC: R_f = 0.26 (3% Et_2O in hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]

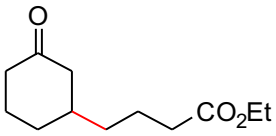
^{1}H NMR (400 MHz; $CDCl_3$): δ 4.75 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.13-2.11 (m, 1H), 1.99-1.92 (m, 2H), 1.75-1.50 (m, 6H), 1.43-1.21 (m, 13H), 1.04-0.96 (m, 9H), 0.64 (dd, *J* = 9.6, 7.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9, 150.9, 108.8, 60.3, 36.6, 34.8, 34.5, 30.2, 28.9, 22.7, 21.9, 18.5, 17.2, 16.6, 14.4.

GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 368.10 (5.48, M^+), 253.05 (100.00, M^+-$C_6H_{11}O_2$), 115.05 (47.05, M^+-$C_{15}H_{29}OSi$), 73.00 (22.25, $C_{18}H_{35}OSi$)

HRMS (ESI+): $[M+Na]^+$ Calc. for $C_{21}H_{40}O_3Si$: 391.2639; found: 391.2656

Ethyl 4-(3-oxocyclohexyl)butanoate (Scheme 1, 4c)



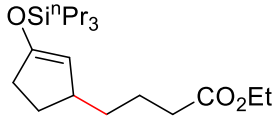
The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), ethyl 4-bromobutyrate (157 µL, 1.10 mmol, 1.10 equiv), and chlorotrimethylsilane (140 µL, 1.10 mmol, 1.10 equiv). General Deprotect Procedure IV was followed to afford the crude ketone product. Analytical data match those in the literature.[10]

Yield: 147 mg, 69% yield

[10] Blake, A. J.; Shannon, J.; Stephens, J. C.; Woodward, S. *Chem.-Eur. J.* **2007**, *13*, 2462.

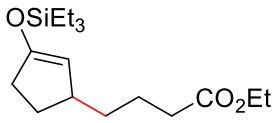
TLC: R_f = 0.33 (25% EtOAc in hexanes, potassium permanganate stain)
^{1}H NMR (500 MHz; $CDCl_3$): δ 4.13 (q, *J* = 7.1 Hz, 2H), 2.43-2.24 (m, 5H), 2.04-1.98 (m, 2H), 1.92-1.89 (m, 1H), 1.80-1.76 (m, 1H), 1.66-1.61 (m, 3H), 1.41-1.30 (m, 3H), 1.27-1.19 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 211.7, 176.8, 60.4, 48.2, 41.6, 38.9, 36.1, 34.4, 31.3, 25.3, 22.3, 14.4.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 212.10 (<1, M^+), 97.00 (100, M^+-$C_6H_{11}O_2$)
HRMS (ESI+): $[M+Na]^+$ Calc. for $C_{12}H_{20}O_3$: 235.1305; found: 235.1306

Ethyl 4-(3-((tripropylsilyl)oxy)cyclopent-2-en-1-yl)butanoate (Scheme 1, 4d)



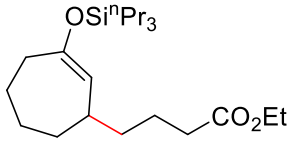
The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclopenten-1-one (83.8 µL, 1.00 mmol, 1.00 equiv), ethyl 4-bromobutyrate (157 µL, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).
Yield: 316 mg, 89% yield, clear, colorless oil
TLC: R_f = 0.27 (3% Et_2O in hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR (400 MHz; $CDCl_3$): 4.59 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.60-2.56 (m, 1H), 2.30-2.22 (m, 3H), 2.02 (dq, *J* = 13.1, 6.8 Hz, 1H), 1.65-1.55 (m, 2H), 1.41-1.34 (m, 8H), 1.26 (q, *J* = 8.7 Hz, 4H), 0.96 (t, *J* = 7.2 Hz, 9H), 0.66 (t, *J* = 8.3 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9, 155.3, 106.6, 60.3, 41.7, 36.9, 34.8, 33.3, 28.3, 23.2, 18.4, 16.82, 16.75, 14.4.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 354.10 (3.35, M^+), 239.05 (100.00, M^+-$C_6H_{11}O_2$), 87.00 (4.68, M^+-$C_{16}H_{31}OSi$)
HRMS (ESI+): $[M+Na]^+$ Calc. $C_{20}H_{38}O_3Si$: 355.2668; found: 355.2682

Ethyl 4-(3-((triethylsilyl)oxy)cyclopent-2-en-1-yl)butanoate (Scheme 1, 4e)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclopenten-1-one (83.8 µL, 1.00 mmol, 1.00 equiv), ethyl 4-bromobutyrate (157 µL, 1.10 mmol, 1.10 equiv), and chlorotriethylsilane (185 µL, 1.10 mmol, 1.10 equiv).
Yield: 200 mg, 64% yield, clear, colorless oil
TLC: R_f = 0.31 (3% Et_2O in hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR (400 MHz; $CDCl_3$): δ 4.61 (d, *J* = 1.6 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.58 (dd, *J* = 8.1, 3.8 Hz, 1H), 2.30-2.23 (m, 4H), 2.05-2.00 (m, 1H), 1.65-1.56 (m, 2H), 1.45-1.19 (m, 6H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9, 155.3, 106.7, 60.3, 41.7, 36.9, 34.7, 33.3, 28.3, 23.2, 14.4, 6.7, 4.9.
GC-MS *m/z* (% relative intensity, ion): (EI, 30 eV) 312.05 (2.53, M^+), 197.05 (100.00, M^+-$C_6H_{11}O_2$), 115.00 (42.39, M^+-$C_{11}H_{21}OSi$), 87.00 (20.41, M^+-$C_{13}H_{25}OSi$)
HRMS (ESI+): $[M+Na]^+$ Calc. for $C_{17}H_{32}O_3Si$: 335.2018; found: 335.2022

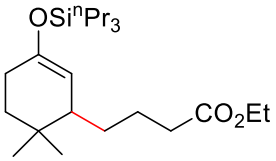
Ethyl 4-(3-((tripropylsilyl)oxy)cyclohept-2-en-1-yl)butanoate (Scheme 1, 4f)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cycloheptenone (112 µL, 1.00 mmol, 1.00 equiv), ethyl 4-bromobutyrate (157 µL, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).
Yield: 256 mg, 67% yield, clear, colorless oil
TLC: R_f = 0.20 (2% Et_2O in hexanes) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde]

^{1}H NMR (500 MHz; $CDCl_3$): δ 4.74 (d, *J* = 3.5 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.23-2.35 (m, 3H), 2.07 (dd, *J* = 14.9, 7.6 Hz, 2H), 1.87-1.85 (m, 1H), 1.61 (td, *J* = 15.3, 6.8 Hz, 4H), 1.52-1.24 (m, 14H), 0.96 (t, *J* = 7.1 Hz, 9H), 0.63 (t, *J* = 8.2 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9 155.1, 113.4, 60.3, 37.1, 36.1, 35.4, 30.1, 26.7, 25.4, 22.9, 18.5, 17.1, 17.1, 16.9, 14.4.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 382.05 (9.74, M^+), 267.05 (100.00, M^+-$C_6H_{11}O_2$), 225.00 (5.91, M^+-$C_9H_{21}Si$) 157.05 (13.93, M^+-$C_3H_{21}O_3$), 115.00 (36.33, M^+-$C_{16}H_{31}OSi$), 87.00 (8.48, M^+-$C_{18}H_{35}OSi$)
HRMS (ESI+): $[M+Na]^+$ Calc. $C_{22}H_{42}O_3Si$: 405.2801; found: 405.2804

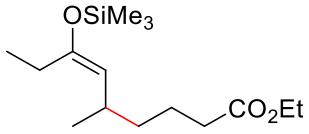
Ethyl 4-(6,6-dimethyl-3-((tripropylsilyl)oxy)cyclohex-2-en-1-yl)butanoate (Scheme 1, 4g)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 4,4-dimethyl-2-cyclohexen-1-one (131.55 µL, 1.00 mmol, 1.00 equiv), ethyl 4-bromobutyrate (157 µL, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).

Yield: 246, 62% yield, clear, colorless oil
TLC: R_f = 0.21 (3% Et_2O in hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR (400 MHz; $CDCl_3$): δ 4.76 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.30 (dt, *J* = 7.9, 6.3 Hz, 2H), 2.04-1.73 (m, 4H), 1.61-1.34 (m, 10H), 1.23 (dt, *J* = 17.9, 8.3 Hz, 4H), 0.95 (dd, *J* = 16.1, 8.8 Hz, 9H), 0.92 (s, 3H), 0.75 (s, 3H), 0.66-0.62 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 173.8, 149.8, 106.6, 60.3, 44.2, 36.6, 34.8, 31.7, 30.7, 28.5, 27.6, 23.6, 21.7, 18.5, 17.2, 16.9, 14.4.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 396.10 (5.43, M^+), 381.10 (3.47, M^+-CH_3) 353.10 (5.34, M^+-C_3H_7), 309.10 (5.46, M^+-$C_4H_7O_2$) 281.10 (100.00, M^+-$C_6H_{11}O_2$), 115.00 (39.60, M^+-$C_{17}H_{33}OSi$), 87.00 (13.15, M^+-$C_{19}H_{37}OSi$)
HRMS (EI+): $[M+H]^+$ Calc. for $C_{23}H_{44}O_3Si$: 397.3138; found: 397.3123

Ethyl-5-methyl-7-((trimethylsilyl)oxy)non-6-enoate (Scheme 1, 4h)



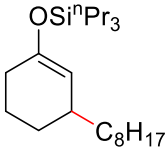
The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), *E*-4-hexen-3-one (115 µL, 1.00 mmol, 1.00 equiv), ethyl 4-bromobutyrate (157 µL, 1.10 mmol, 1.100 equiv), and trimethylchlorosilane (140 µL, 1.10 mmol, 1.10 equiv). The product was isolated as an inseparable mixture of E and Z isomers (1:4 by comparison of the 1H NMR spectrum to the closely related butyl addition products[11]).

Yield: 240 mg, 84% yield, clear, colorless oil (*Z*/*E* ratio = 3.8:1)
TLC: R_f = 0.21 (3% Et_2O in hexanes) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde]
^{1}H NMR (500 MHz; $CDCl_3$): **[(*Z*)-4h]:** δ 4.21 (d, *J* = 3.0 Hz, 1 H) 4.11 (q, *J* = 7.1 Hz, 2H), 2.50-2.42 (m, 1H), 2.26 (t, *J* = 15.1 Hz, 2H), 2.00 (q, *J* = 21.8 Hz, 2H), 1.60 (dt, *J* = 56.5, 12.8 Hz, 2H), 1.33-1.14 (m, 5H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.18 (s, 9H); **[(*E*)-4h]:** 4.34 (d, *J* = 2.1 Hz, 1 H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.48-2.44 (m, 1H), 2.26 (t, *J* = 15.0 Hz, 2H), 2.05 (q, *J* = 14.6 Hz, 2H), 1.60 (dt, *J* = 56.5, 12.8 Hz, 2H), 1.33-1.14 (m, 5H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.93 (d, *J* = 6.67 Hz, 3H), 0.18 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$): **[(*Z*)-4h]:** δ 174.1 151.2, 113.2, 60.2, 37.4, 34.69, 31.9, 29.6, 23.2, 21.3, 14.4, 12.0, 0.84; **[(*E*)-4h]:** 174.1, 151.2, 113.8, 60.2, 37.8, 34.61, 31.9, 29.6, 24.9, 23.3, 22.5, 12.2, 0.55.

[11] Bergdahl, M.; Eriksson, M.; Nilsson, M.; Olsson, T. *J. Org. Chem.* **1993**, *58*, 7238-7244.

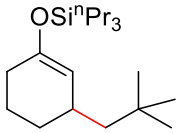
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 286.20 (4.09, M^+), 257.15 (3.43, M^+-C_2H_5), 171.15 (100.00, M^+-$C_6H_{11}O_2$), 144.10 (12.36, M^+-$C_7H_{15}OSi$), 129.05 (3.14, M^+-$C_9H_{16}O_2$), 73.05 (47.75, M^+-$C_{12}H_{21}O_3$)
HRMS (EI+): $[M+H]^+$ Calc. for $C_{15}H_{30}O_3Si$: 287.2042; found: 287.2043

((3-octylcyclohex-1-en-1-yl)oxy)tripropylsilane (Scheme 2, 6a)



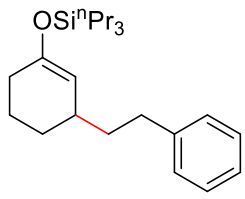
The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), bromooctane (190 µL, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).
Yield: 349 mg, 95% yield, clear, colorless oil
TLC: R_f = 0.69 (100% hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR (400 MHz; $CDCl_3$): δ 4.78 (s, 1H), 2.10-2.06 (m, 1H), 2.01-1.92 (m, 2H), 1.75-1.66 (m, 2H), 1.53 (q, *J* = 7.7 Hz, 1H), 1.48-1.34 (m, 7H), 1.27 (s, 14H), 1.07 (dd, *J* = 21.2, 10.2 Hz, 1H), 0.96 (t, *J* = 7.2 Hz, 9H), 0.88 (t, *J* = 6.6 Hz, 3H), 0.64 (t, *J* = 8.3 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.2, 109.2, 37.0, 34.5, 31.8, 29.9, 29.8, 29.6, 29.3, 28.9, 26.9, 22.6, 21.8, 18.3, 16.9, 16.6, 14.0.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 366.15 (6.07, M^+), 253.05 (100.00, M^+-C_8H_{17}), 157.05 (8.91, M^+-$C_{14}H_{25}O$)
HRMS (EI+): $[M+H]^+$ Calc. for $C_{23}H_{46}OSi$: 367.3396; found: 367.3398

((3-neopentylcyclohex-1-en-1-yl)oxy)tripropylsilane (Scheme 2, 6b)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), neopentyl bromide (139 µL 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv). Analytical data match those in the literature.[12]
Yield: 247 mg, 76% yield, clear, colorless oil
TLC: R_f = 0.52 (100% hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR (500 MHz; $CDCl_3$): δ 4.82 (d, *J* = 1.3 Hz, 1H), 2.19 (ddd, *J* = 7.9, 5.2, 2.7 Hz, 1H), 1.98-1.93 (m, 2H), 1.75-1.66 (m, 2H), 1.59-1.51 (m, 1H), 1.44-1.36 (m, 6H), 1.26-1.09 (m, 3H), 0.97 (t, *J* = 7.3 Hz, 9H), 0.91 (s, 9H), 0.66-0.63 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 149.7, 111.4, 51.5, 31.6, 31.2, 31.1, 30.1, 29.7, 21.9, 18.4, 17.1, 16.8.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 324.10 (7.07, M^+), 253.05 (100.00, M^+-C_5H_{11}), 157.00 (12.81, M^+-$C_{11}H_{19}O$)
HRMS (EI+): $[M+H]^+$ Calc. for $C_{20}H_{40}OSi$: 325.2927; found: 325.2925

((3-phenethylcyclohex-1-en-1-yl)oxy)tripropylsilane (Scheme 2, 6c)

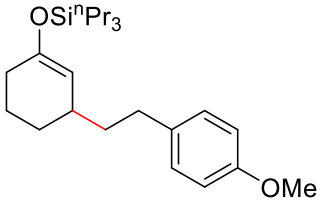


The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), 1-phenyl-2-bromoethane (150 µL 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).
Yield: 334 mg, 93% yield, clear, colorless oil
TLC: R_f = 0.3 (100% hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]

[12] Shrestha, R.; Weix, D. J. *Org. Lett.* **2011**, *13*, 2766.

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.27 (t, *J* = 7.0 Hz, 2H), 7.8 (t, *J* = 8.2 Hz, 3H), 4.83 (s, 1H), 2.66-2.62 (m, 2H), 2.18-2.17 (m, 1H), 2.01-1.97 (m, 2H), 1.74-1.73 (m, 2H), 1.61-1.55 (m, 3H), 1.40 (dt, *J* = 15.9, 7.8 Hz, 6H), 1.26-1.14 (m, 1H), 0.97 (td, *J* = 7.2, 2.7 Hz, 9H), 0.66 (ddd, *J* = 9.7, 6.8, 2.7 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.9, 143.1, 128.5, 128.4, 125.7, 108.8, 39.2, 34.4, 33.6, 30.2, 29.1, 21.9, 18.5, 17.2, 16.9.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 358.10 (9.53, M^+), 315.05 (14.04, M^+-C_3H_7), 253.05 (100.00, M^+-C_8H_9), 157.05 (12.84, M^+-$C_{14}H_{17}O$)
HRMS (EI+): $[M]^+$ Calc. for $C_{23}H_{38}OSi$: 358.2692; found: 358.2690

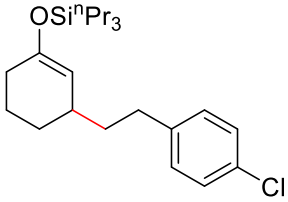
((3-(4-methoxyphenethyl)cyclohex-1-en-1-yl)oxy)tripropylsilane (Scheme 2, 6d)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv) 4-methoxyphenethyl bromide (237 mg, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).

Yield: 353 mg, 91% yield, clear, colorless oil
TLC: R_f = 0.264 (5% Et_2O in hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR: (400 MHz; $CDCl_3$): δ 7.10 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.83 (d, *J* = 0.8 Hz, 1H), 3.79 (s, 3H), 2.58 (t, *J* = 8.0 Hz, 1H), 2.16-2.15 (m, 1H), 2.02-1.98 (m, 2H), 1.78-1.72 (m, 2H), 1.60-1.53 (m, 3H), 1.45-1.36 (m, 7H), 0.98 (t, *J* = 7.2 Hz, 9H), 0.68-0.64 (m, 6H).
^{13}C NMR: (126 MHz, $CDCl_3$): δ 157.8, 150.9, 135.1, 129.4, 113.9, 108.8, 55.4, 39.4, 34.3, 32.6, 30.2, 29.0, 21.9, 18.5, 17.2, 16.9.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 388.10 (5.18, M^+), 345.10 (17.57, M^+-C_3H_7), 253.10 (100.00, M^+-$C_9H_{11}O$), 215.00, (4.25, M^+-$C_9H_{21}OSi$)
HRMS (EI+): $[M+H]^+$ Calc. for $C_{24}H_{40}O_2Si$: 389.2876; found: 389.2873

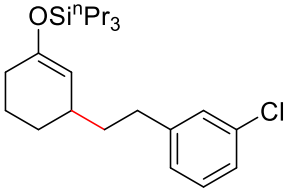
((3-(4-chlorophenethyl)cyclohex-1-en-1-yl)oxy)tripropylsilane (Scheme 2, 6e)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), 1-(2-bromoethyl)-4-chlorobenzene (160 µL 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).

Yield: 362 mg, 92% yield, clear, colorless oil
TLC: R_f = 0.47 (100% hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR (500 MHz; $CDCl_3$): (500 MHz; $CDCl_3$): δ 7.24 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 4.80 (s, 1H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.17-2.14 (m, 1H), 2.01-1.94 (m, 2H), 1.79-1.72 (m, 2H), 1.58-1.53 (m, 3H), 1.40 (dq, *J* = 15.7, 7.7 Hz, 6H), 1.16-1.14 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 9H), 0.66 (dd, *J* = 9.9, 6.7 Hz, 6H)
^{13}C NMR (126 MHz, $CDCl_3$): δ 151.1, 141.5, 131.5, 129.9, 128.5, 108.5, 39.0, 34.3, 32.9, 30.2, 29.0, 21.9, 18.5, 17.2, 16.9.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 392.00 (11.56, M^+), 349.00 (12.24, M^+-C_3H_7), 253.10 (100.00, M^+-C_8H_8Cl), 157.05 (12.42, M^+-$C_{14}H_{16}ClO$)
HRMS (EI+): $[M]^+$ Calc. for $C_{23}H_{37}ClOSi$: 392.2329; found: 392.2324

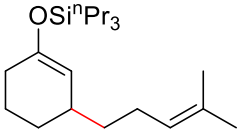
((3-(3-chlorophenethyl)cyclohex-1-en-1-yl)oxy)tripropylsilane (Scheme 2, 6f)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), 2-(3-chlorophenyl)ethyl bromide (242 mg, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).

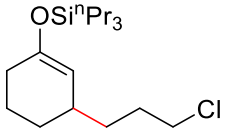
Yield: 295 mg, 75% yield, clear, colorless oil
TLC: R_f = 0.44 (100% hexanes) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde]
^{1}H NMR (500 MHz; $CDCl_3$): δ 7.18 (dq, *J* = 12.8, 6.8 Hz, 3H), 7.06 (d, *J* = 7.5 Hz, 1H), 4.81 (s, 1H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.17-2.15 (m, 1H), 2.04-1.95 (m, 2H), 1.79-1.72 (m, 2H), 1.57 (tq, *J* = 14.5, 7.3 Hz, 3H), 1.41 (dq, *J* = 15.9, 7.8 Hz, 6H), 1.27-1.11 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 9H), 0.66 (t, *J* = 8.3 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 151.2, 145.1, 134.2, 129.7, 128.7, 126.7, 125.9, 108.4, 38.8, 34.4, 33.3, 30.2, 28.9, 21.9, 18.5, 17.2, 16.9.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 392.00 (12.05, M^+), 349.00 (10.62, M^+-C_3H_7), 253.10 (100.00, M^+-C_8H_8Cl), 157.05 (12.42, M^+-$C_{14}H_{16}ClO$)
HRMS (EI+): $[M]^+$ Calc. for $C_{23}H_{37}ClOSi$: 392.2329; found: 392.2320

((3-(4-methylpent-3-en-1-yl)cyclohex-1-en-1-yl)oxy)tripropylsilane (Scheme 2, 6g)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv) 5-bromo-2-methyl-2-pentene (147 µL, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).
Yield: 290 mg, 86% yield, clear, colorless oil
TLC: R_f = 0.55 (100% hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR (400 MHz; $CDCl_3$): δ 5.12 (s, 1H), 4.79 (s, 1H), 2.12 (s, 1H), 2.03-1.97 (m, 4H), 1.76-1.69 (m, 5H), 1.61 (s, 3H), 1.56-1.51 (m, 1H), 1.40 (dq, *J* = 15.9, 7.7 Hz, 6H), 1.30 (t, *J* = 7.5 Hz, 2H), 1.09 (d, *J* = 10.8 Hz, 1H), 0.97 (t, *J* = 7.2 Hz, 9H), 0.65 (dd, *J* = 10.0, 6.7 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.6, 131.3, 124.9, 109.1, 37.3, 34.4, 30.2, 29.1, 25.9, 25.7, 22.0, 18.5, 17.8, 17.2, 16.9.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 336.30 (37.05, M^+), 293.25 (21.42, M^+-C_3H_7), 279.25 (M^+-C_4H_9) 253.20 (62.08, M^+-C_6H_{11}) 157.15 (M^+-$C_{12}H_{19}O$).
HRMS (EI+): $[M+H]^+$ Calc. for $C_{21}H_{40}OSi$: 337.2927; found: 337.2919

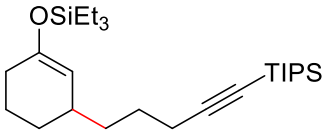
((3-(2-chloroethyl)cyclohex-1-en-1-yl)oxy)tripropylsilane (Scheme 2, 6h)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), 1-bromo-3-chloropropane (120 µL, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).
Yield: 276 mg, 83% yield, clear, colorless oil
TLC: R_f = 0.52 (100% hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR (400 MHz; $CDCl_3$): δ 4.75 (s, 1H), 3.53 (t, *J* = 6.7 Hz, 2H), 2.15-2.12 (m, 1H), 2.03-1.92 (m, 2H), 1.83-1.68 (m, 4H), 1.59-1.49 (m, 1H), 1.39 (dd, *J* = 15.5, 7.4 Hz, 8H), 1.26 (s, 1H), 1.14-1.08 (m, 1H), 0.97 (t, *J* = 7.2 Hz, 9H), 0.64 (t, *J* = 8.3 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 151.1, 108.5, 45.5, 34.38, 34.25, 30.4, 30.1, 28.9, 21.9, 18.5, 17.2, 16.9.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 330.10 (7.94, M^+), 253.05 (100.00, M^+-C_3H_6Cl), 157.10 (14.56, M^+-$C_9H_{14}ClO$)

HRMS (EI+): $[M]^+$ Calc. for $C_{18}H_{35}ClOSi$: 330.2146; found: 330.2149

Triethyl(5-(3-((tripropylsilyl)oxy)cyclohex-2-en-1-yl)pent-1-yn-1-yl)silane (Scheme 2, 6i)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv) (5-bromopent-1-yn-1-yl)triisopropylsilane (332 mg, 1.10 mmol, 1.10 equiv), and chlorotriethylsilane (185 µL, 1.10 mmol, 1.10 equiv).

Yield: 395 mg, 91% yield, clear, colorless oil

TLC: R_f = 0.44 (100% hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]

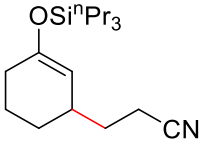
^{1}H NMR (400 MHz; $CDCl_3$): δ 4.78 (s, 1H), 2.25 (t, *J* = 6.9 Hz, 2H), 2.14 (dd, *J* = 5.0, 2.2 Hz, 1H), 2.05-1.94 (m, 2H), 1.78-1.66 (m, 2H), 1.60-1.49 (m, 3H), 1.49-1.35 (m, 2H), 1.11-1.03 (m, 21H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 150.7, 109.3, 109.1, 80.3, 36.2, 34.4, 30.1, 28.9, 26.5, 21.9, 20.2, 18.8, 11.5, 6.9, 5.2.

GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 434.40 (1.26, M^+), 391.30 (7.73, M^+-C_3H_7), 277.20 (3.09, M^+-$C_9H_{21}Si$), 237.20 (100.00, M^+-$C_{11}H_{21}OSi$).

HRMS (EI+): $[M]^+$ Calc. for $C_{26}H_{50}OSi_2$ 434.3400; found: 434.3398

3-(3-((tripropylsilyl)oxy)cyclohex-2-en-1-yl)propanenitrile (Scheme 2, 6j)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), 3-bromopropionitrile (91.3 µL 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv). Analytical data matches those in the literature.[13]

Yield: 280 mg, 91% yield, clear, colorless oil

TLC: R_f = 0.18 (5% Et_2O in hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]

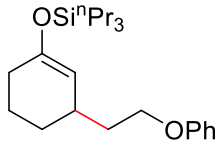
^{1}H NMR (500 MHz; $CDCl_3$): δ 4.68 (s, 1H), 2.33 (q, *J* = 8.3 Hz, 3H), 2.00-1.98 (m, 2H), 1.78-1.55 (m, 5H), 1.42-1.34 (m, 6H), 1.12 (t, *J* = 9.5 Hz, 1H), 0.96 (t, *J* = 7.3 Hz, 9H), 0.64 (dd, *J* = 9.9, 6.8 Hz, 6H).

^{13}C NMR (126 MHz; CDCl3): δ 151.1, 119.5, 107.5, 35.8, 33.9, 29.8, 28.5, 22.8, 21.5, 18.1, 16.9, 16.6.

GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 307.10 (16.58, M^+), 264.05 (100.00, M^+-C_3H_7), 222.05 (69.34, M^+-C_6H_{14}), 157.10 (22.60, M^+-$C_9H_{12}NO$)

HRMS (ESI+): $[M+Na]^+$ Calc. for $C_{18}H_{33}NOSi$: 330.2229; found: 330.2238

((3-(2-phenoxyethyl)cyclohex-1-en-1-yl)oxy)tripropylsilane (Scheme 2, 6k)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv) 2-bromoethyl phenyl ether (362 mg, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).

Yield: 273 mg, 73% yield, clear, colorless oil

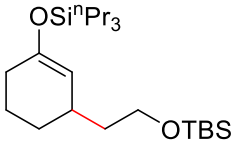
TLC: R_f = 0.29 (100% hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.30-7.26 (m, 2H), 6.93 (dd, *J* = 15.2, 7.6 Hz, 3H), 4.83 (d, *J* = 1.2 Hz, 1H), 4.02 (t, *J* = 6.6 Hz, 2H), 2.43-2.42 (m, 1H), 2.02-1.95 (m, 2H), 1.86-1.70 (m, 4H), 1.63-1.54 (m, 1H), 1.41 (quintet, *J* = 8.9 Hz, 6H), 1.23-1.18 (m, 1H), 0.99-0.95 (m, 9H), 0.68-0.64 (m, 6H).

[13] Streuff, J. *Chem.-Eur. J.* **2011**, *17*, 5507.

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2, 151.2, 129.5, 120.6, 114.6, 108.3, 66.1, 36.4, 31.8, 30.1, 28.9, 21.8, 18.5, 17.2, 16.9.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 374.10 (2.98, M^+), 331.10 (39.87, M^+-C_3H_7), 253.10 (100.00, M^+-C_8H_9O) 157.10 (19.20, M^+-$C_{14}H_{17}O_2$)
HRMS (EI+): $[M+H]^+$ Calc. for $C_{23}H_{38}O_2Si$: 375.2719; found: 375.2729

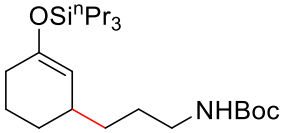
Tert-butyldimethyl(2-(3-((tripropylsilyl)oxy)cyclohex-2-en-1-yl)ethoxy)silane (Scheme 2, 6l)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv) 2-(tert-butyldimethylsilyloxy)ethyl bromide (236 µL, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).

Yield: 281 mg, 68% yield, clear, colorless oil
TLC: R_f = 0.24 (100% hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR (400 MHz; $CDCl_3$): δ 4.77 (s, 1H), 3.66 (td, *J* = 6.6, 2.5 Hz, 2H), 2.27-2.26 (m *J* = 1.7 Hz, 1H), 1.97 -1.96(m, *J* = 2.1 Hz, 2H), 1.75-1.65 (m, 2H), 1.58-1.46 (m, 3H), 1.42-1.36 (m, 7H), 0.96 (td, *J* = 7.2, 2.5 Hz, 10H), 0.89 (d, *J* = 2.5 Hz, 8H), 0.64 (dt, *J* = 8.2, 4.1 Hz, 6H), 0.05 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.8, 108.8, 61.4, 40.1, 31.3, 30.2, 29.1, 26.1, 21.8, 18.5, 17.2, 16.9, -5.1
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV)
HRMS (EI+): $[M+H]^+$ Calc. for $C_{23}H_{48}O_2Si_2$: 413.3271; found: 413.3271

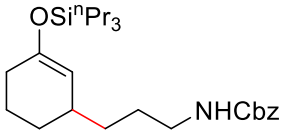
Tert-butyl (3-(3-((tripropylsilyl)oxy)cyclohex-2-en-1-yl)propyl)carbamate (Scheme 2, 6m)



The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), 3-bromopropylamine tert-butylcarbamate (262 mg, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).

Yield: 375 mg, 91% yield, clear, colorless oil
TLC: R_f = 0.225 (5% Et_2O in hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR (400 MHz; $CDCl_3$): δ 4.74 (s, 1H), 4.49 (td, *J* = 2.0, 0.8 Hz, 1H), 3.10-3.09 (m, 2H), 2.12-1.67 (m, 5H), 1.51-1.25 (m, 21H), 0.98-0.94 (m, 9H), 0.64 (td, *J* = 7.7, 3.5 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.1, 150.9, 108.8, 79.1, 41.0, 34.5, 34.3, 30.2, 28.9, 28.6, 27.7, 21.9, 18.5, 17.2, 16.8
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 411.00 (<1.00, M^+), 354.10 (62.73, M^+-C_4H_9), 338.10 (3.07, M^+-C_4H_9O), 295.10 (3.25, M^+-$C_5H_{10}NO_2$), 253.10 (100.00, M^+-$C_8H_{16}NO_2$), 157.10 (25.37, M^+-$C_{14}H_{24}NO_3$), 116.05 (81.30, M^+-$C_{18}H_{36}OSi$)
HRMS (ESI+): $[M+Na]^+$ Calc. for $C_{23}H_{45}NO_3Si$: 434.3066, found: 434.3062

Benzyl (3-(3-((tripropylsilyl)oxy)cyclohex-2-en-1-yl)propyl)carbamate (Scheme 2, 6n)

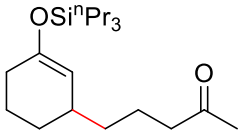


The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv) benzyl N-(3-bromopropyl)carbamate (299 mg, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).

Yield: 388 mg, 87% yield, clear, colorless oil
TLC: R_f = 0.19 (5% Et_2O in hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]

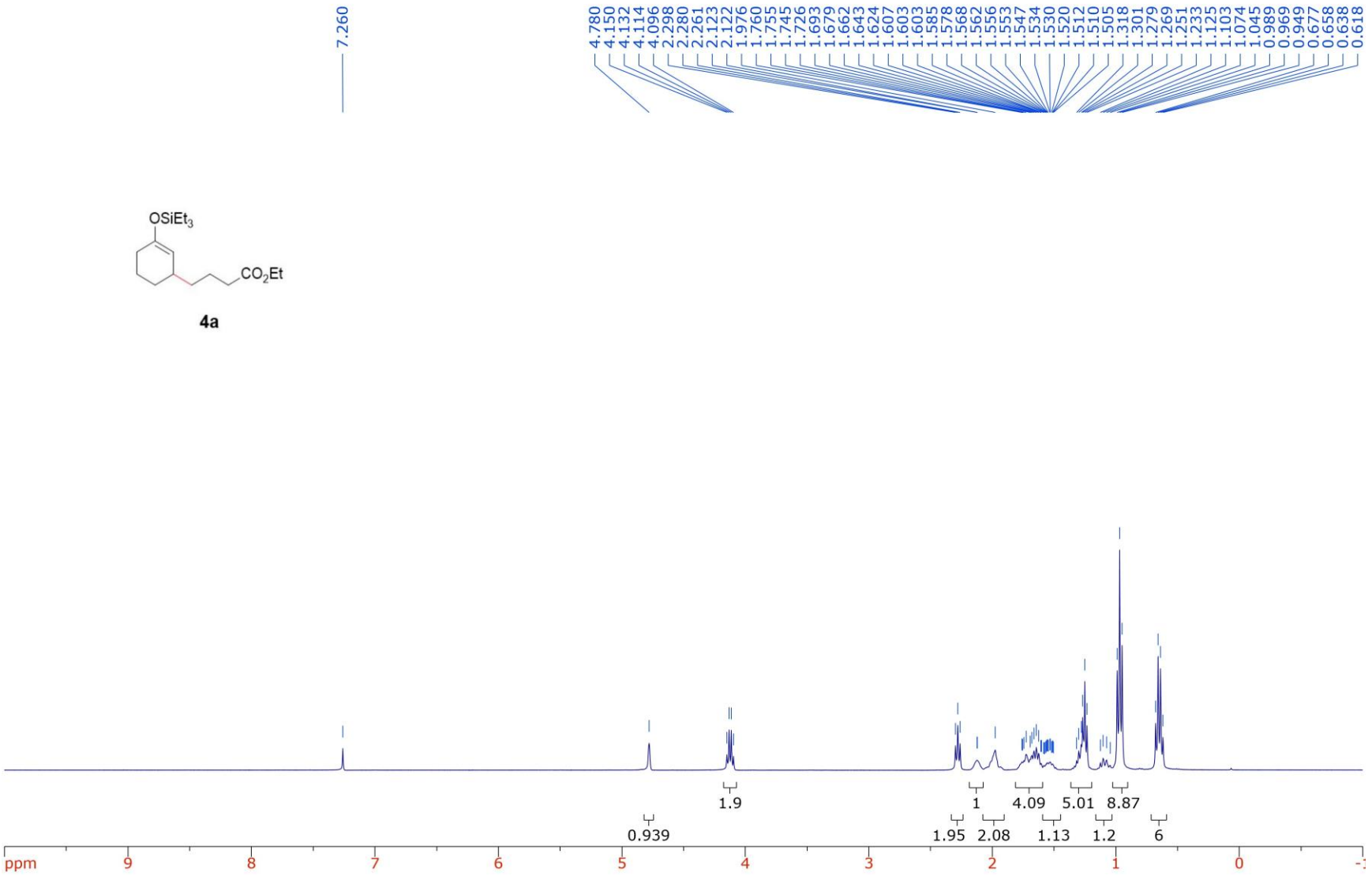
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.36-7.32 (m, 5H), 5.09 (s, 2H), 4.73 (s, 2H), 3.19 (d, *J* = 5.7 Hz, 2H), 2.11 (dd, *J* = 2.9, 1.0 Hz, 1H), 1.96 (s, 2H), 1.75-1.67 (m, 2H), 1.52-1.50 (m, 3H), 1.42-1.36 (m, 6H), 1.27 (t, *J* = 7.3 Hz, 2H), 1.08 (t, *J* = 10.5 Hz, 1H), 0.98-0.94 (m, 9H), 0.64 (dd, *J* = 10.3, 6.1 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.4, 150.9, 136.8, 128.6, 128.2, 128.2, 108.7, 66.7, 41.5, 34.4, 34.2, 30.1, 28.9, 27.6, 21.8, 18.4, 17.1, 16.8.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 445.10 (<1.00, M^+), 338.10 (7.21, M^+-C_7H_7O), 253.05 (100.0, M^+-$C_{11}H_{14}NO_2$), 157.10 (17.42, M^+-$C_{17}H_{22}NO_2$) 115.00 (57.70, M^+-$C_{21}H_{34}OSi$)
HRMS (ESI+): $[M+Na]^+$ Calc. for $C_{26}H_{43}NO_3Si$: 446.3090, 446.3085

5-(3-((tripropylsilyl)oxy)cyclohex-2-en-1-yl)pentan-2-one (Scheme 2, 6o)
The general procedure was followed with $NiCl_2$(glyme) (8.24 mg, 0.0400 mmol, 0.0400 equiv), 6,6'-dibromo-2,2':6',2"-terpyridine (31.3 mg, 0.0800 mmol, 0.0800 equiv), Mn^0 (110 mg, 2.00 mmol, 2.00 equiv), THF (2 mL), dodecane (10.0 µL internal standard), 2-cyclohexen-1-one (103 µL, 1.00 mmol, 1.00 equiv), 5-bromo-2-pentanone (182 mg, 1.10 mmol, 1.10 equiv), and tri-*n*-propylchlorosilane (240 µL, 1.10 mmol, 1.10 equiv).



Yield: 295 mg, 87% yield, clear, colorless oil
TLC: R_f = 0.19 (5% Et_2O in hexanes) [plate pre-treated with 0.1% Et_3N, *p*-anisaldehyde stain]
^{1}H NMR (400 MHz; $CDCl_3$): δ 4.74 (s, 1H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.13 (s, 4H), 1.98-1.90 (m, 2H), 1.76-1.65 (m, 2H), 1.63-1.49 (m, 3H), 1.42-1.33 (m, 6H), 1.29-1.18 (m, 2H), 1.07 (dd, *J* = 22.1, 10.1 Hz, 1H), 0.95 (t, *J* = 7.3 Hz, 9H), 0.65-0.61 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 209.1, 150.8, 108.7, 44.1, 36.7, 34.6, 30.1, 29.9, 28.9, 21.9, 21.5, 18.4, 17.1, 16.8.
GC-MS *m/z* (% relative intensity, ion): (EI+, 30 eV) 338.10 (8.17, M^+), 295.10 (4.50, M^+-C_3H_7), 253.10 (100.00, M^+-C_5H_9O), 157.10 (14.75, M^+-$C_{11}H_{17}O_2$)
HRMS (ESI+): $[M+Na]^+$ Calc. for $C_{20}H_{38}O_2Si$: 361.2539; found: 361.2544

VI. Spectra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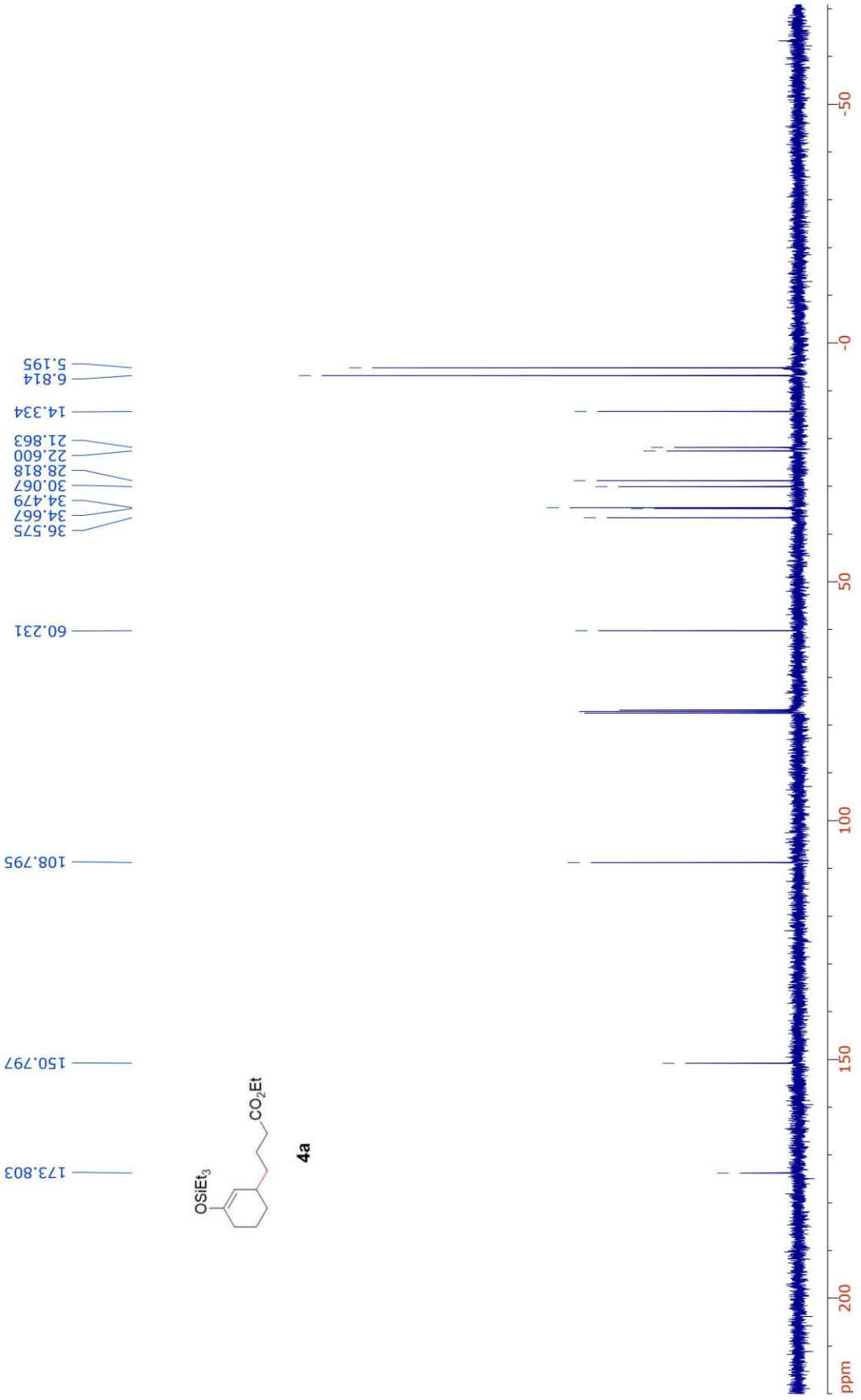
4.150
4.132
4.114
4.096
2.298
2.280
2.261
2.123
2.122
1.976
1.760
1.755
1.745
1.726
1.693
1.679
1.662
1.643
1.624
1.607
1.603
1.603
1.585
1.578
1.568
1.562
1.556
1.553
1.547
1.534
1.530
1.520
1.512
1.510
1.505
1.318
1.301
1.279
1.269
1.251
1.233
1.125
1.103
1.074
1.045
0.989
0.969
0.949
0.677
0.658
0.638
0.618
OSiEt3
CO2Et
4a
0.939
1.9
1.95
2.08
1
4.09
1.13
5.01
1.2
8.87
6
ppm
9
8
7
6
5
4
3
2
1
0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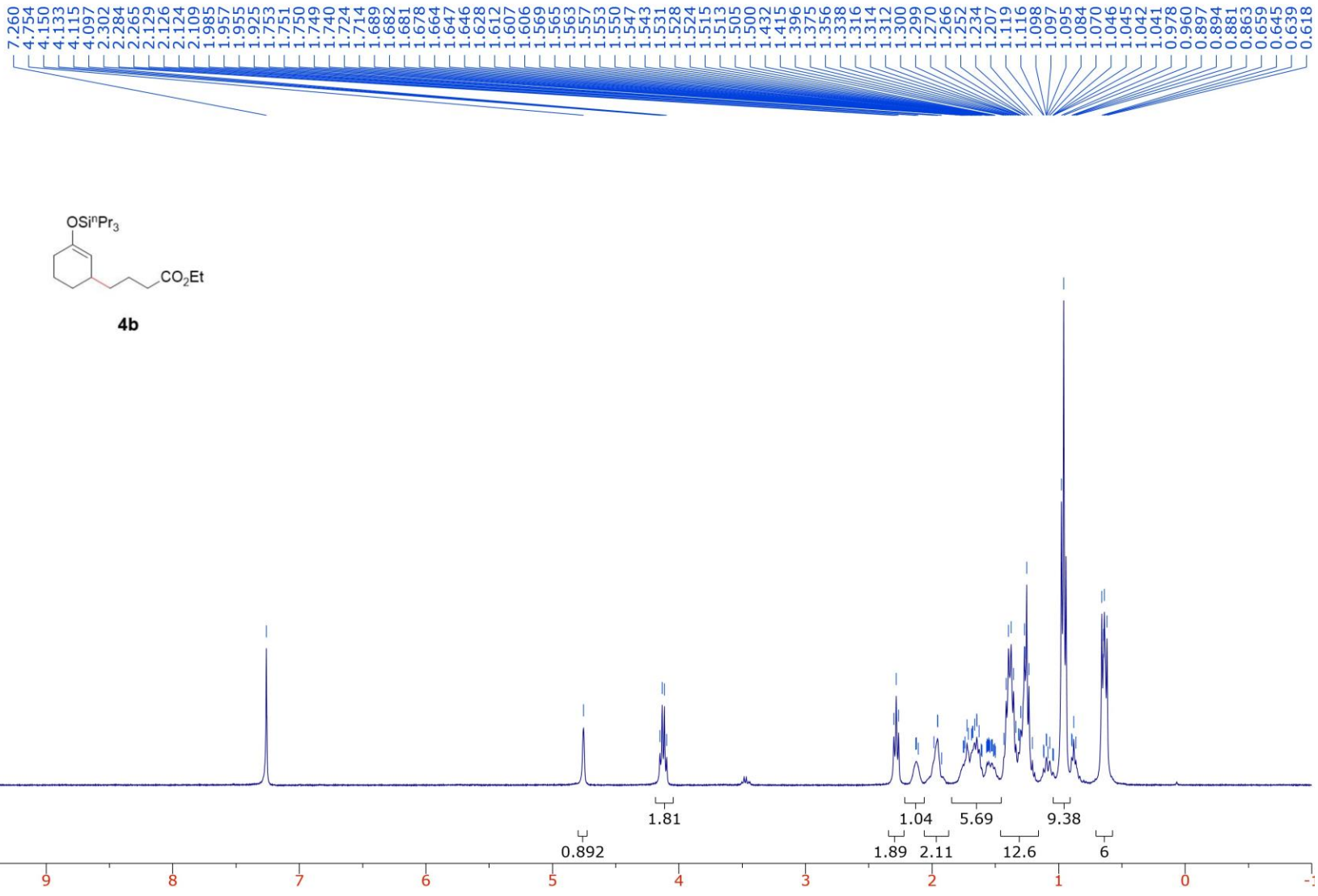
6.814
14.334
21.863
22.600
28.818
30.067
34.479
34.667
36.575
60.231
108.795
150.797
173.803
OSiEt3
CO2Et
4a
ppm
200
150
100
50
-0
-50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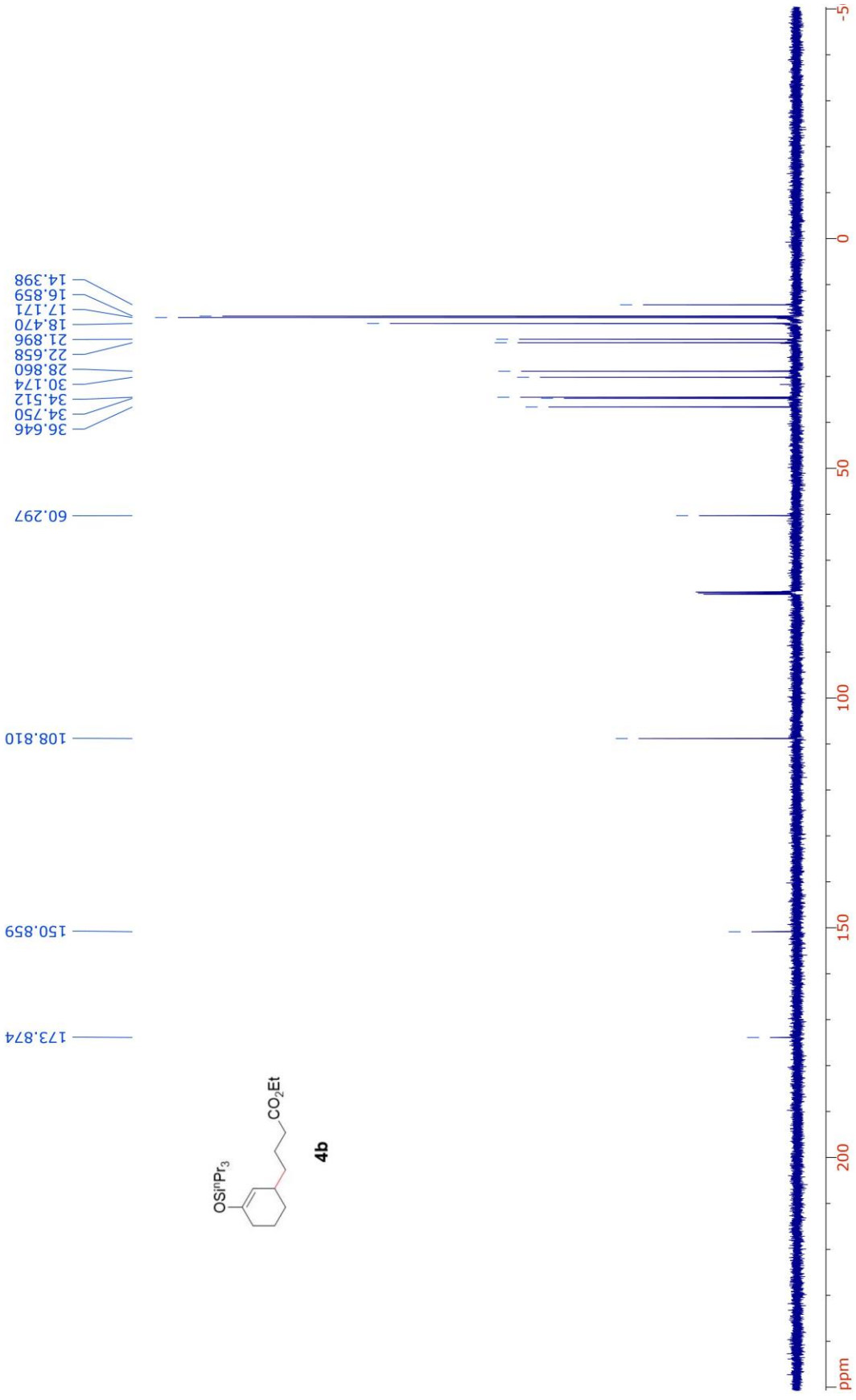
4.150
4.133
4.115
4.097
2.302
2.284
2.265
2.129
2.126
2.124
2.109
1.985
1.957
1.955
1.925
1.753
1.751
1.750
1.749
1.740
1.724
1.714
1.689
1.682
1.681
1.678
1.664
1.647
1.646
1.628
1.612
1.607
1.606
1.569
1.565
1.563
1.557
1.553
1.550
1.547
1.543
1.531
1.528
1.524
1.515
1.513
1.505
1.500
1.432
1.415
1.396
1.375
1.356
1.338
1.316
1.314
1.312
1.300
1.299
1.270
1.266
1.252
1.234
1.207
1.119
1.116
1.098
1.097
1.095
1.084
1.070
1.046
1.045
1.042
1.041
0.978
0.960
0.897
0.894
0.881
0.863
0.659
0.645
0.639
0.618
OSi^{n}Pr$_3$
CO$_2$Et
4b
1.81
1.04
5.69
9.38
0.892
1.89
2.11
12.6
6
ppm
9
8
7
6
5
4
3
2
1
0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16.859
17.171
18.470
21.896
22.658
28.860
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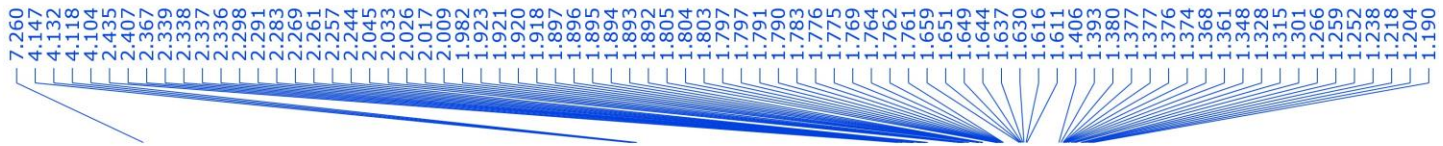
34.750
36.646
60.297
108.810
150.859
173.874
OSiⁱPr3
CO2Et
4b
ppm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4.132
4.118
4.104
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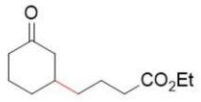
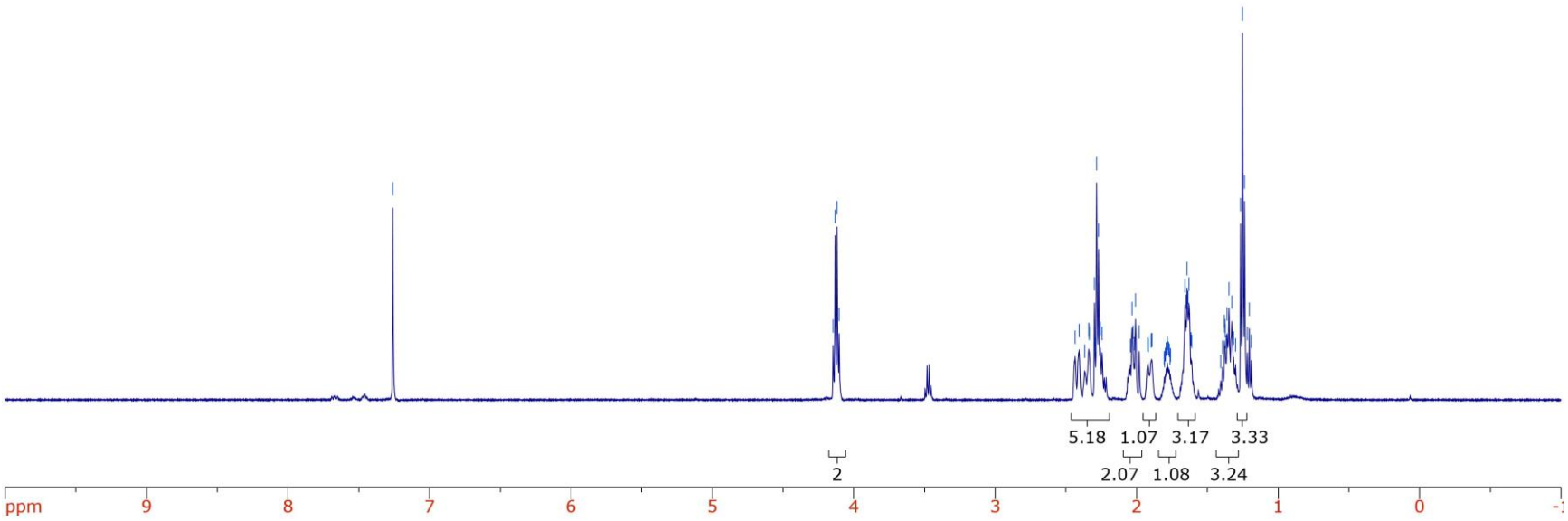
2.407
2.367
2.339
2.338
2.337
2.336
2.298
2.291
2.283
2.269
2.261
2.257
2.244
2.045
2.033
2.026
2.017
2.009
1.982
1.923
1.921
1.920
1.918
1.897
1.896
1.895
1.894
1.893
1.892
1.805
1.804
1.803
1.797
1.797
1.791
1.790
1.783
1.776
1.775
1.769
1.764
1.762
1.761
1.659
1.651
1.649
1.644
1.637
1.630
1.616
1.611
1.406
1.393
1.380
1.377
1.377
1.376
1.374
1.368
1.361
1.348
1.328
1.315
1.301
1.266
1.259
1.252
1.238
1.218
1.204
1.190


O
CO2Et

4c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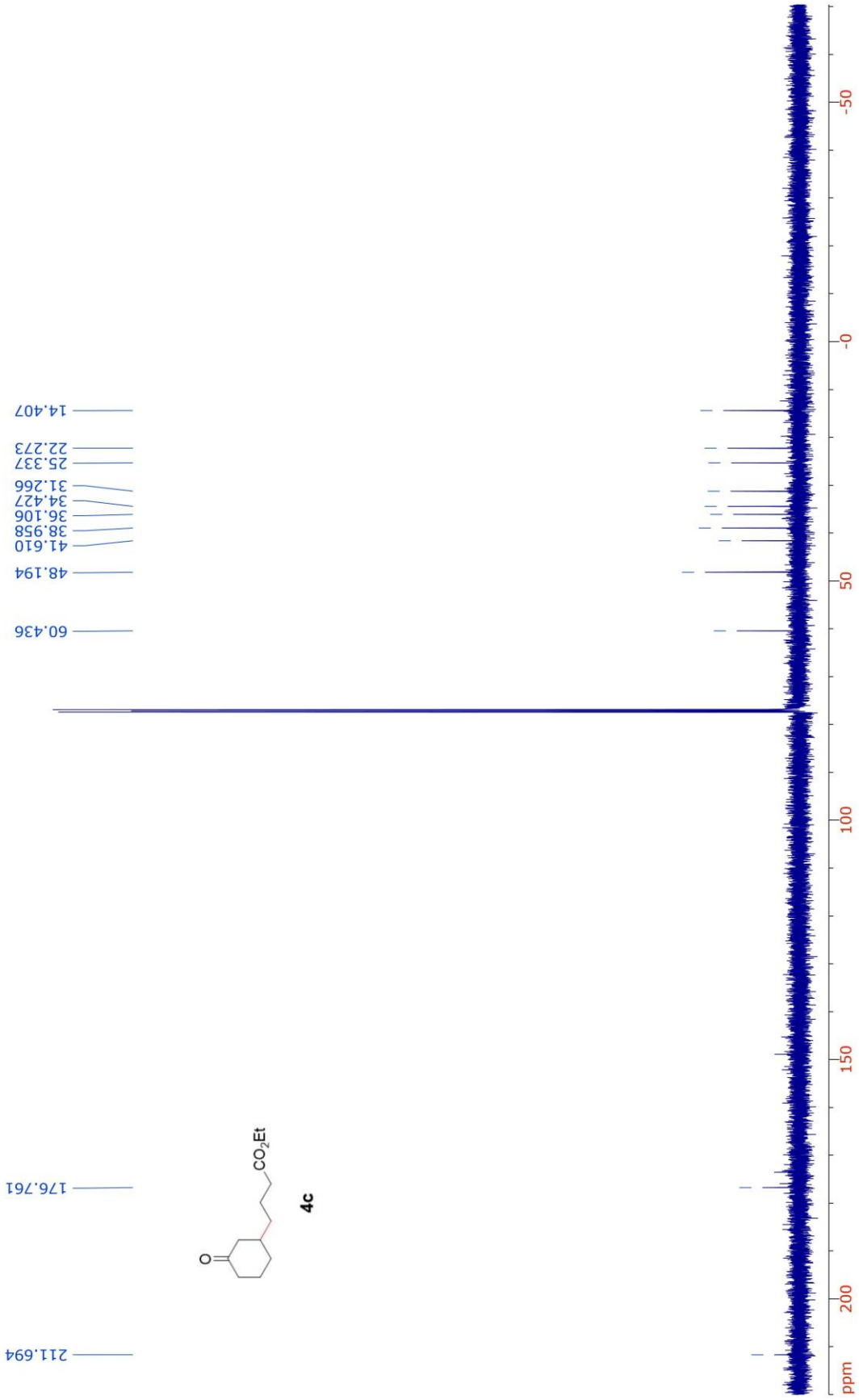
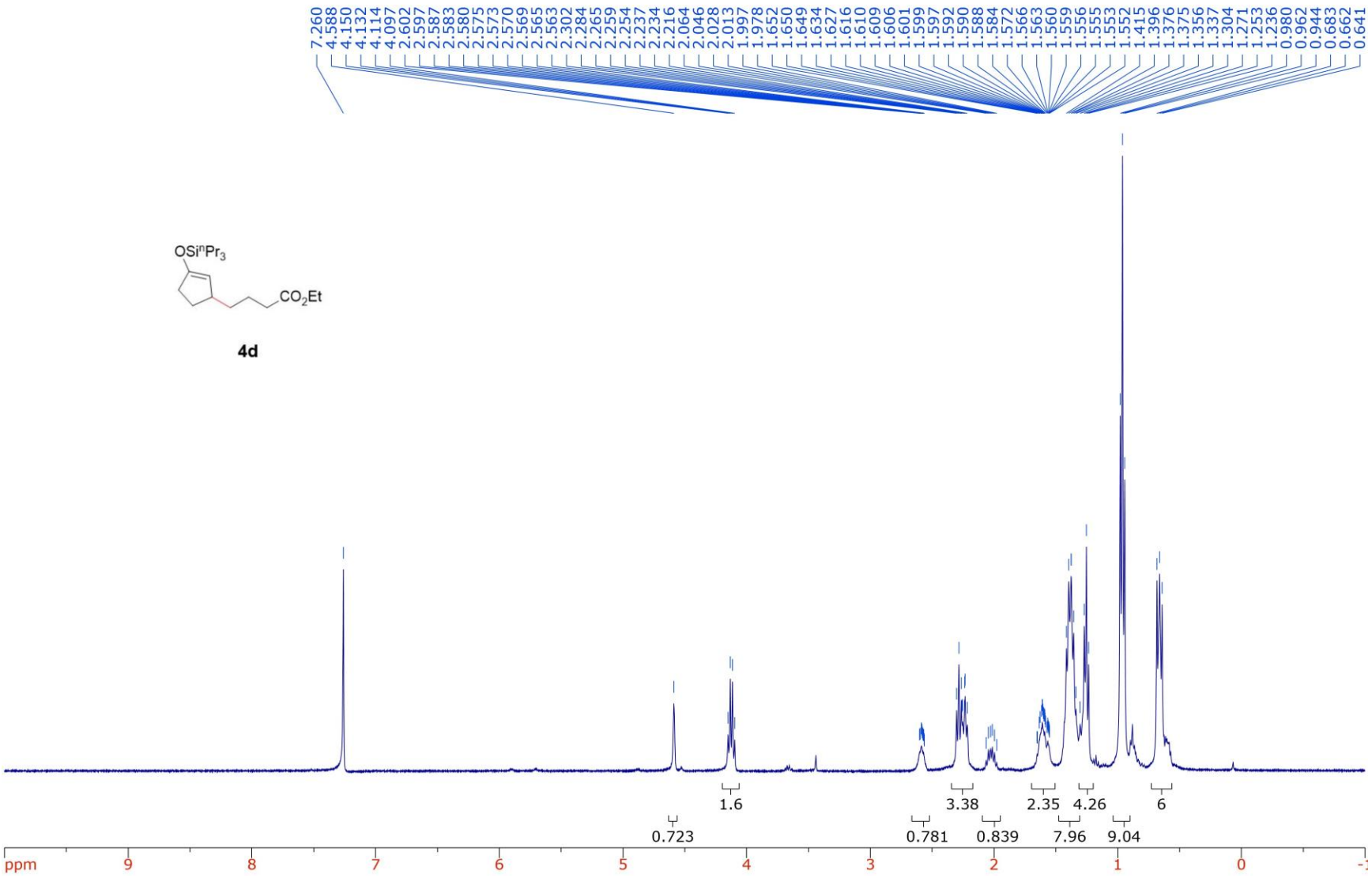
1.07
3.17
3.33
2
2.07
1.08
3.24
ppm
9
8
7
6
5
4
3
2
1
0


211.694
176.761
60.436
48.194
41.610
38.958
36.106
34.427
31.266
25.337
22.273
14.407
4c
O
CO2Et
ppm
200
150
100
50
-0
-50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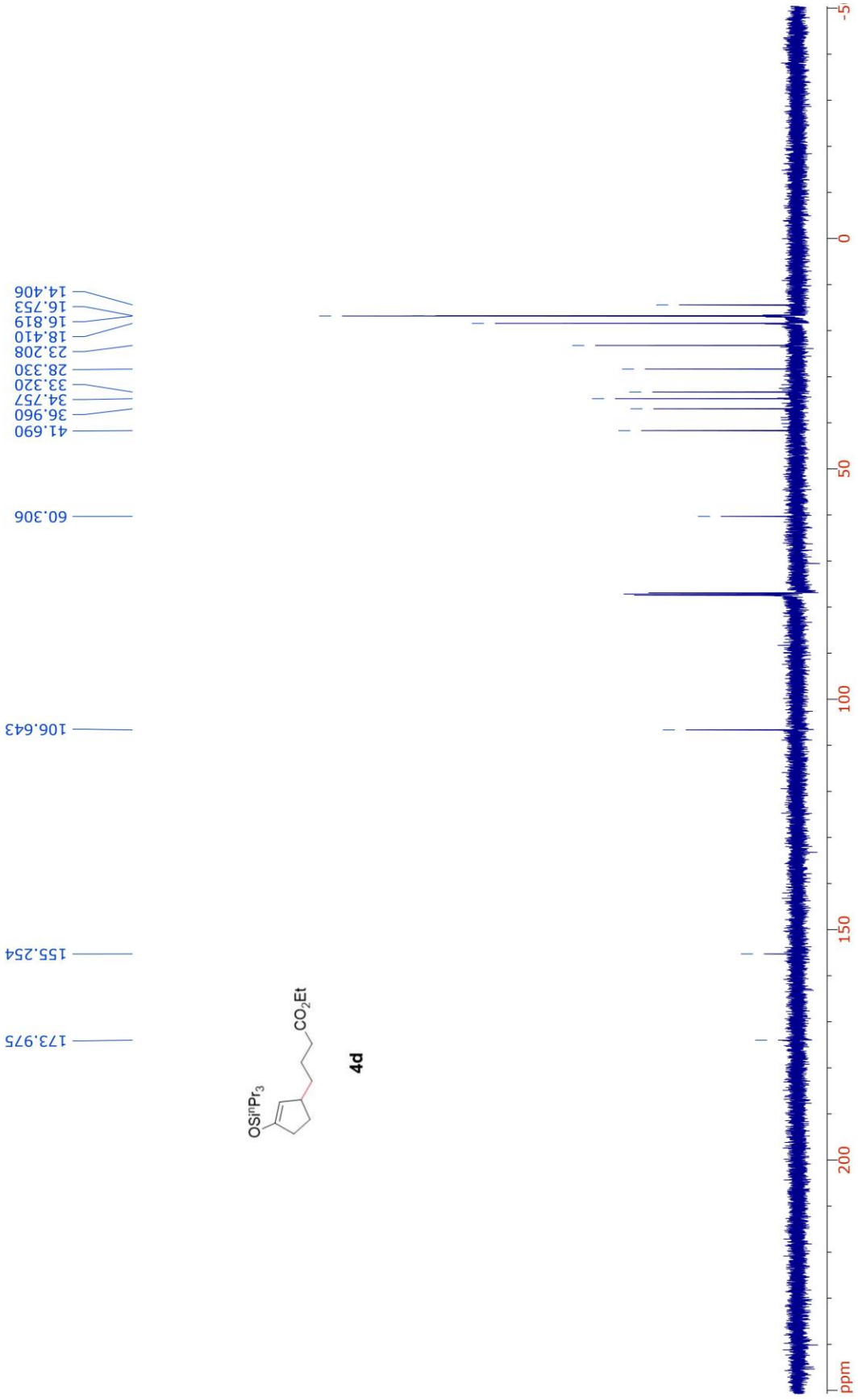
4.588
4.150
4.132
4.114
4.097
2.602
2.597
2.587
2.583
2.580
2.575
2.573
2.570
2.569
2.565
2.563
2.302
2.284
2.265
2.259
2.254
2.237
2.234
2.216
2.064
2.046
2.028
2.013
1.997
1.978
1.652
1.650
1.649
1.634
1.627
1.616
1.610
1.609
1.606
1.601
1.599
1.597
1.592
1.590
1.588
1.584
1.572
1.566
1.563
1.560
1.559
1.556
1.555
1.553
1.552
1.415
1.396
1.376
1.375
1.356
1.337
1.304
1.271
1.253
1.236
0.980
0.962
0.944
0.683
0.662
0.641
OSi^{n}Pr$_3$
CO$_2$Et
4d
1.6
3.38
2.35
4.26
6
0.723
0.781
0.839
7.96
9.04
ppm
9
8
7
6
5
4
3
2
1
0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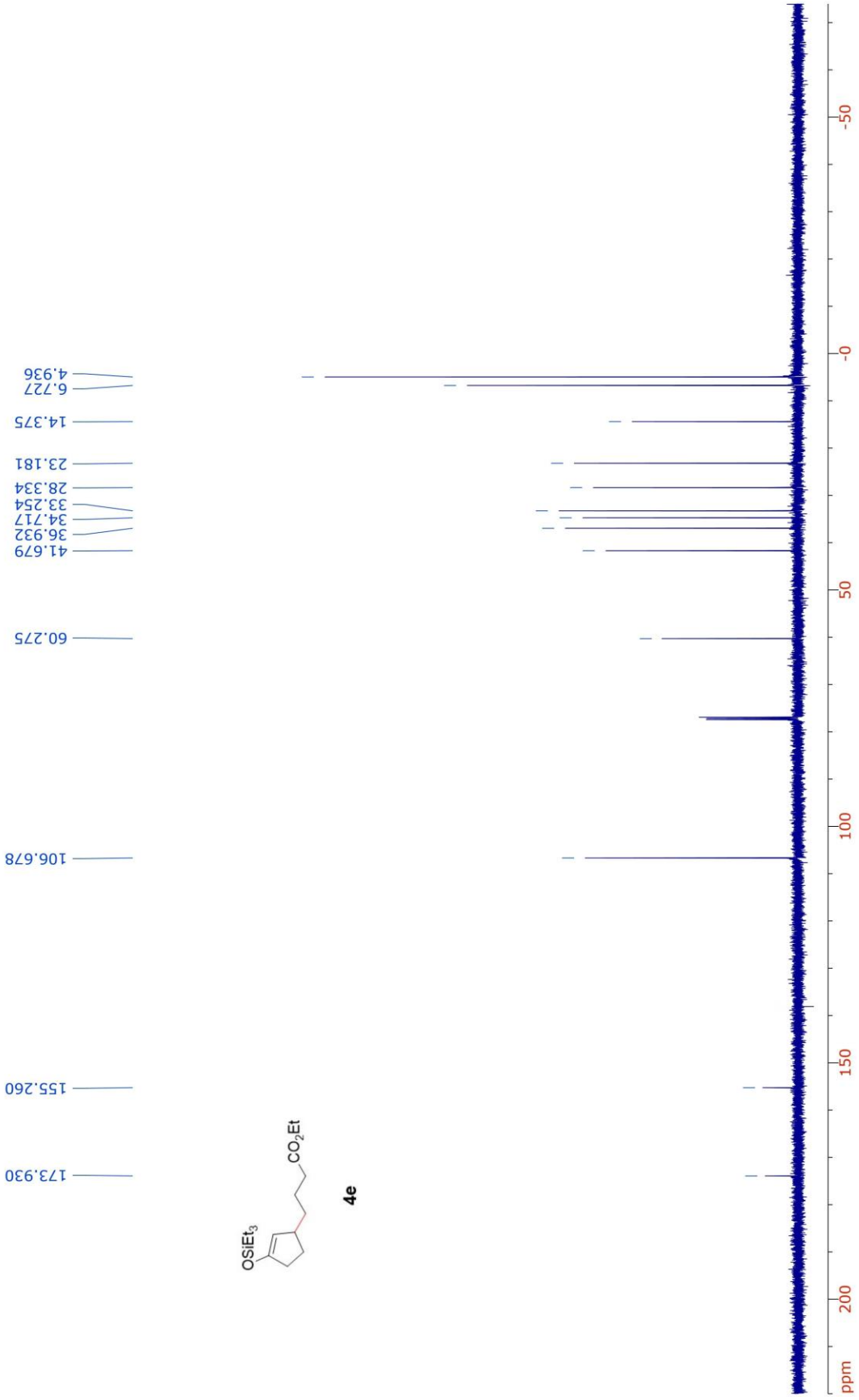
16.753
16.819
18.410
23.208
28.330
33.320
34.757
36.960
41.690
60.306
106.643
155.254
173.975
OSiiPr3
CO2Et
4d
ppm
-5
0
50
100
150
200

0.637
0.657
0.677
0.697
0.946
0.966
0.986
1.221
1.231
1.249
1.267
1.281
1.303
1.324
1.342
1.348
1.364
1.382
1.396
1.403
1.409
1.416
1.427
1.448
1.562
1.586
1.597
1.604
1.611
1.621
1.623
1.639
1.646
1.998
1.999
2.016
2.030
2.049
2.233
2.251
2.259
2.277
2.297
2.567
2.574
2.584
2.597
4.092
4.109
4.127
4.145
4.604
4.608
7.260
OSiEt3
CO2Et
4e
0.974
2
1.04
4.23
1.09
2.3
6.55
9.15
6
ppm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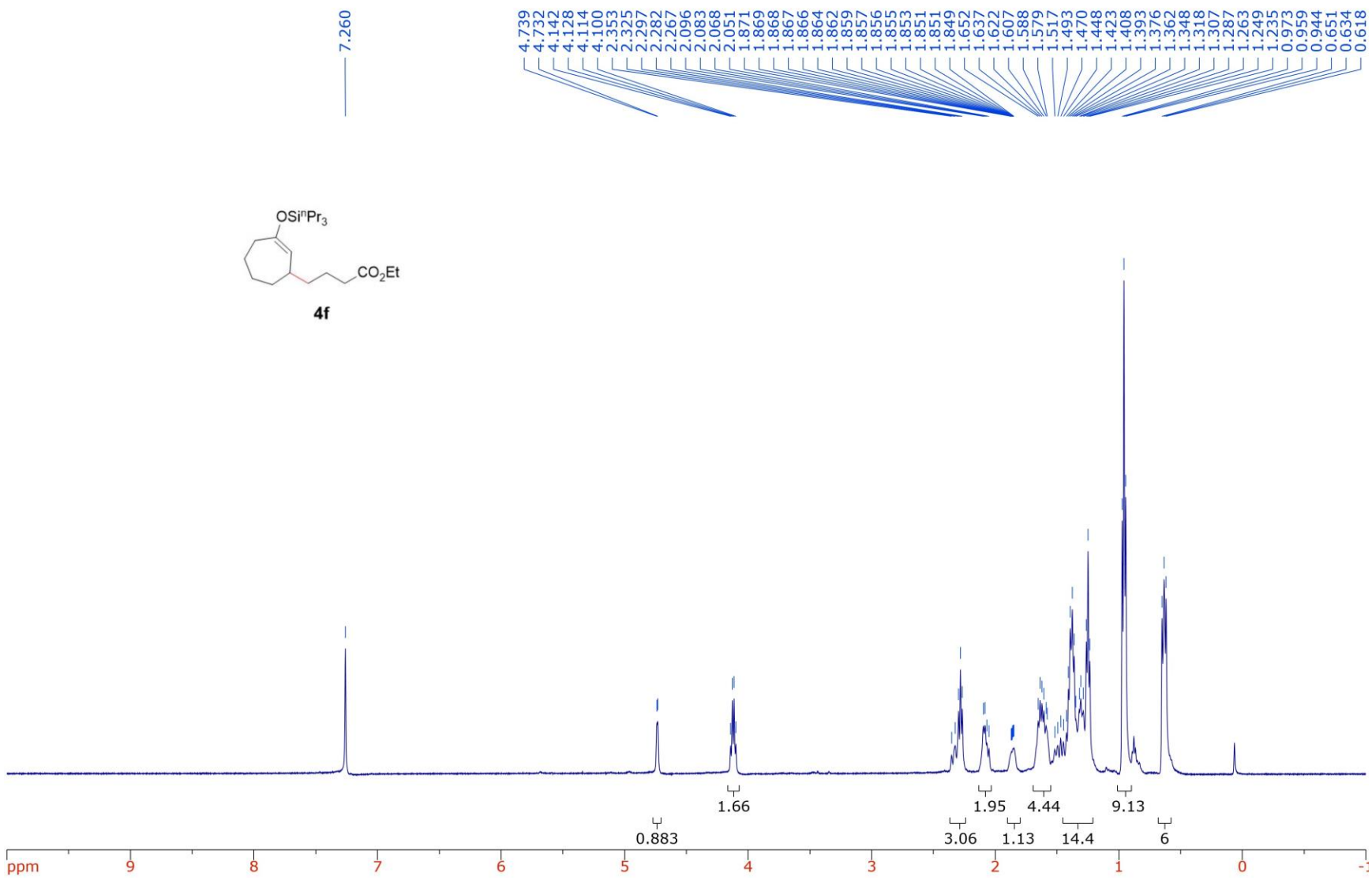
155.260
106.678
60.275
41.679
36.932
34.717
33.254
28.334
23.181
14.375
6.727
4.936
OSiEt3
CO2Et
4e
ppm
200
150
100
50
-0
-50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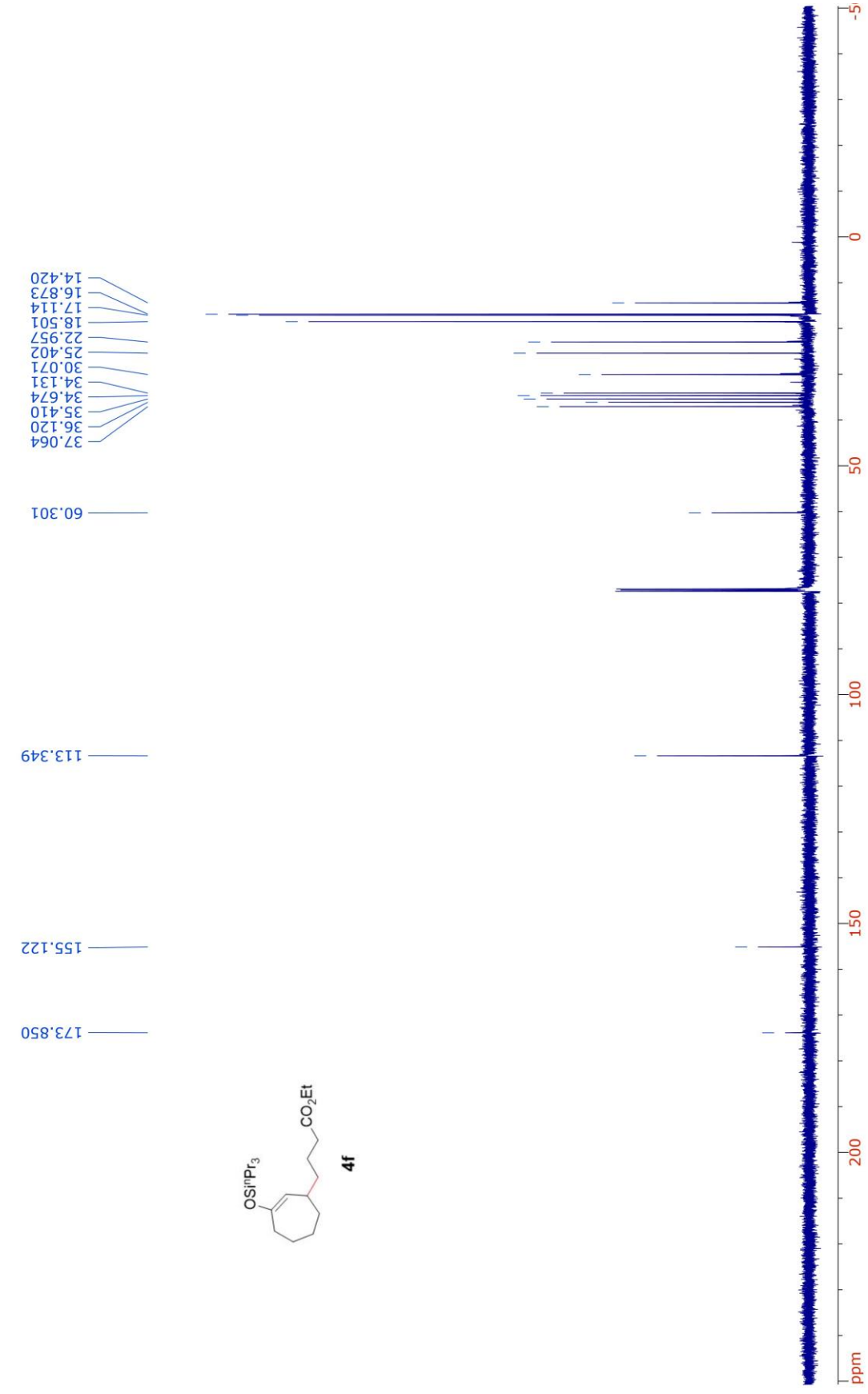
4.739
4.732
4.142
4.128
4.114
4.100
2.353
2.325
2.297
2.282
2.267
2.096
2.083
2.068
2.051
1.871
1.869
1.868
1.867
1.866
1.864
1.862
1.859
1.857
1.856
1.855
1.853
1.851
1.849
1.652
1.637
1.622
1.607
1.588
1.579
1.517
1.493
1.470
1.448
1.423
1.408
1.393
1.376
1.362
1.348
1.318
1.307
1.287
1.263
1.249
1.235
0.973
0.959
0.944
0.651
0.634
0.618
OSi^{n}Pr$_3$
CO$_2$Et
4f
0.883
1.66
3.06
1.95
1.13
4.44
14.4
9.13
6
ppm
9
8
7
6
5
4
3
2
1
0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16.873
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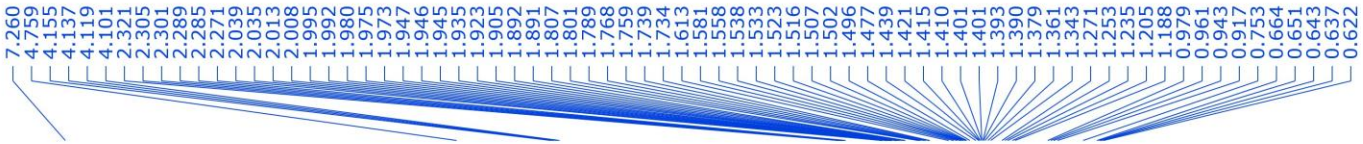
18.501
22.957
25.402
30.071
34.131
34.674
35.410
36.120
37.064
60.301
113.349
155.122
173.850
ppm
-5
0
50
100
150
200
OSiiPr3
CO2Et
4f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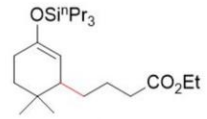
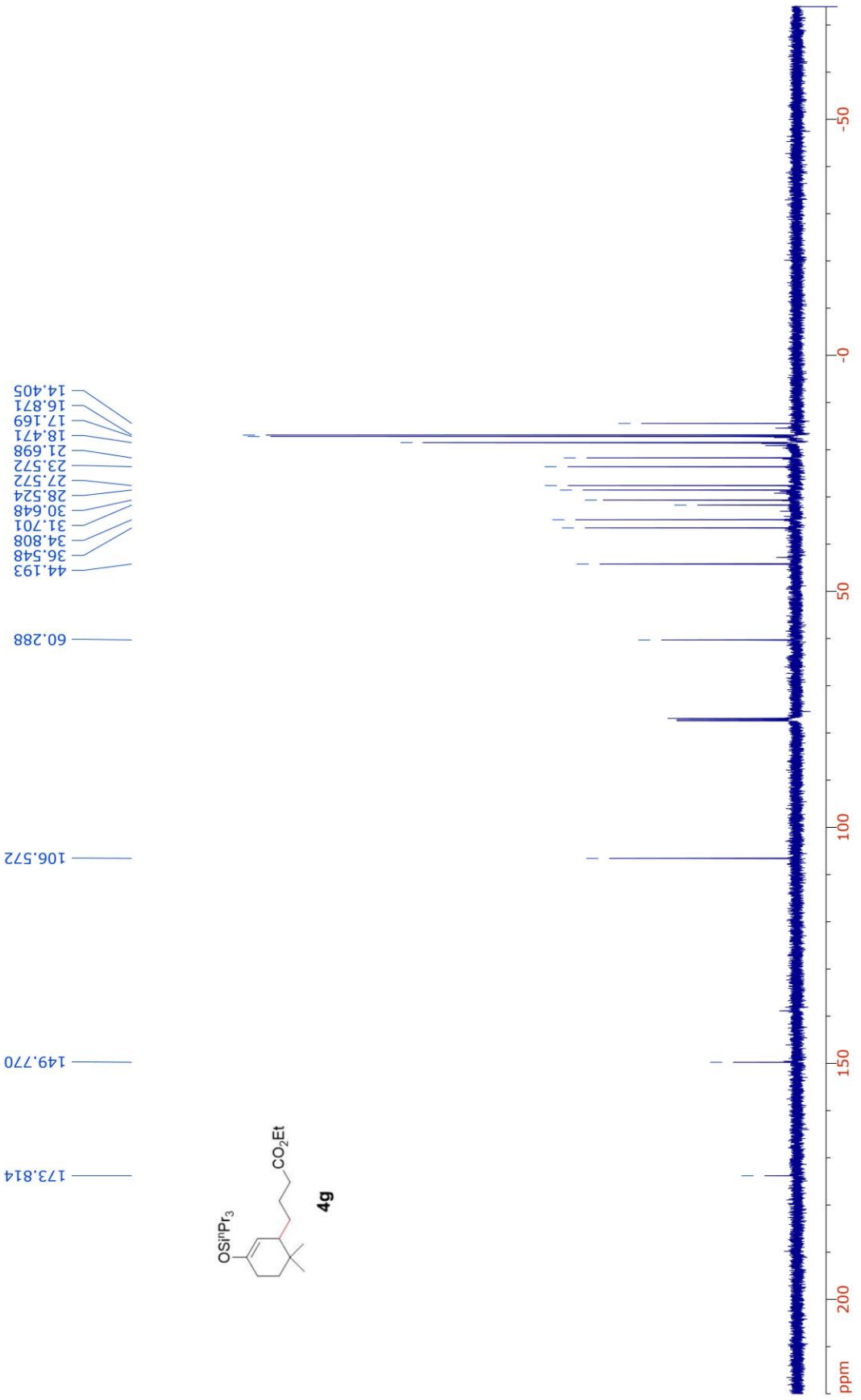
4.155
4.137
4.119
4.101
2.321
2.305
2.301
2.289
2.285
2.271
2.039
2.035
2.013
2.008
1.995
1.992
1.980
1.975
1.973
1.947
1.946
1.945
1.935
1.923
1.905
1.892
1.891
1.807
1.801
1.789
1.768
1.759
1.739
1.734
1.613
1.581
1.558
1.538
1.533
1.523
1.516
1.507
1.502
1.496
1.477
1.439
1.421
1.415
1.410
1.401
1.401
1.393
1.390
1.379
1.361
1.343
1.271
1.253
1.235
1.205
1.188
0.979
0.961
0.943
0.917
0.753
0.664
0.651
0.643
0.637
0.622


OSi^{n}Pr$_3$
CO$_2$Et

4g

0.978
2
2.25
2.24
2.12
2.69
8.85
4.14
14.8
3.03
6.28
ppm
9
8
7
6
5
4
3
2
1
0
-1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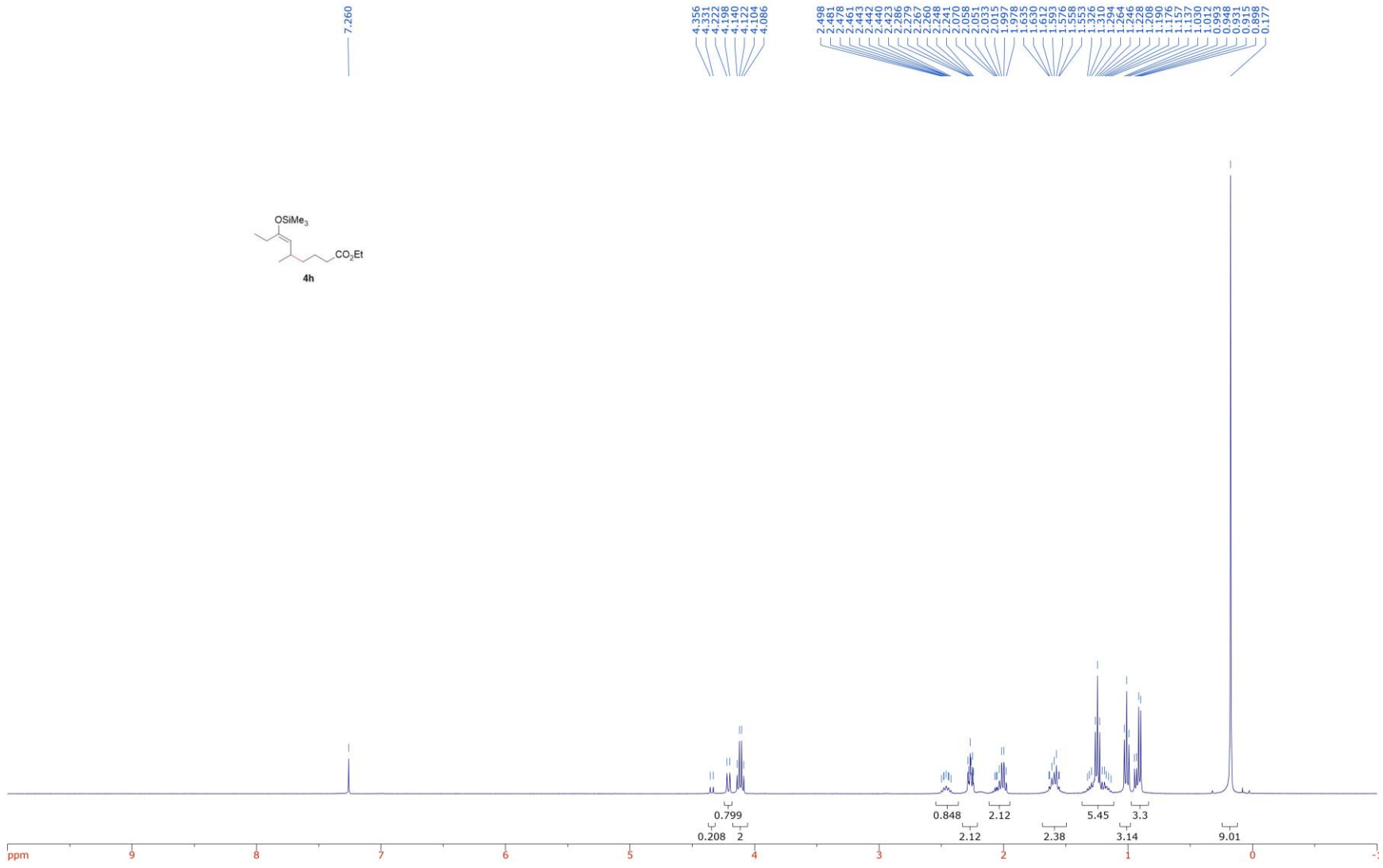
17.169
18.471
21.698
23.572
27.572
28.524
30.648
31.701
34.808
36.548
44.193
60.288
106.572
149.770
173.814
OSiiPr3
CO2Et
4g
ppm
200
150
100
50
-0
-50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4.222
4.198
4.140
4.122
4.104
4.086
2.498
2.481
2.478
2.461
2.443
2.442
2.440
2.423
2.276
2.279
2.267
2.260
2.248
2.241
2.070
2.058
2.051
2.033
2.015
1.997
1.978
1.635
1.630
1.592
1.593
1.576
1.558
1.553
1.326
1.310
1.294
1.264
1.246
1.228
1.208
1.190
1.176
1.157
1.137
1.130
1.012
0.993
0.948
0.931
0.915
0.898
0.177
OSiMe3
CO2Et
4h
0.799
0.208
2
0.848
2.12
2.12
2.38
5.45
3.14
3.3
9.01
ppm
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8
7
6
5
4
3
2
1
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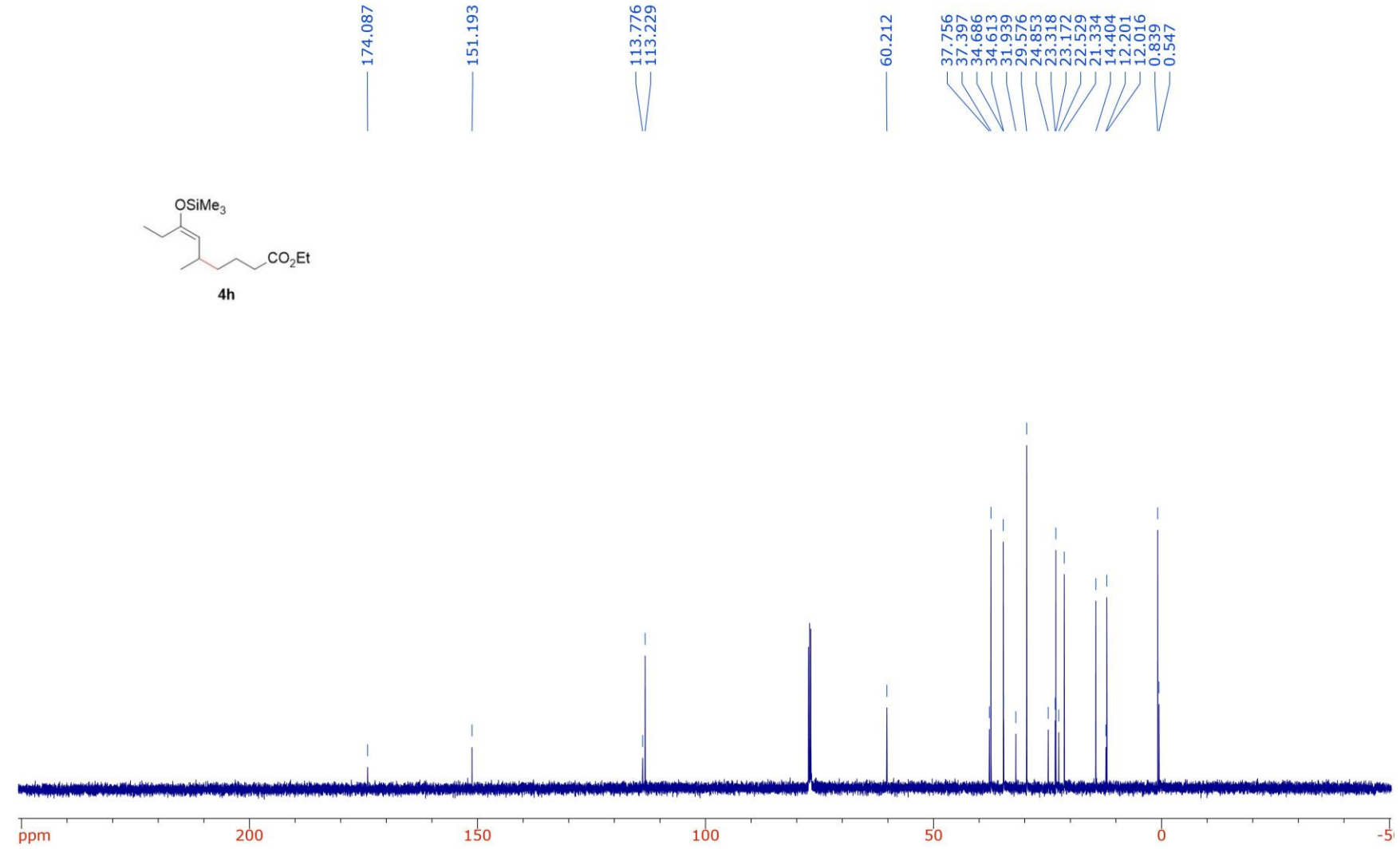
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151.193
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113.229
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37.756
37.397
34.686
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31.939
29.576
24.853
23.318
23.172
22.529
21.334
14.404
12.201
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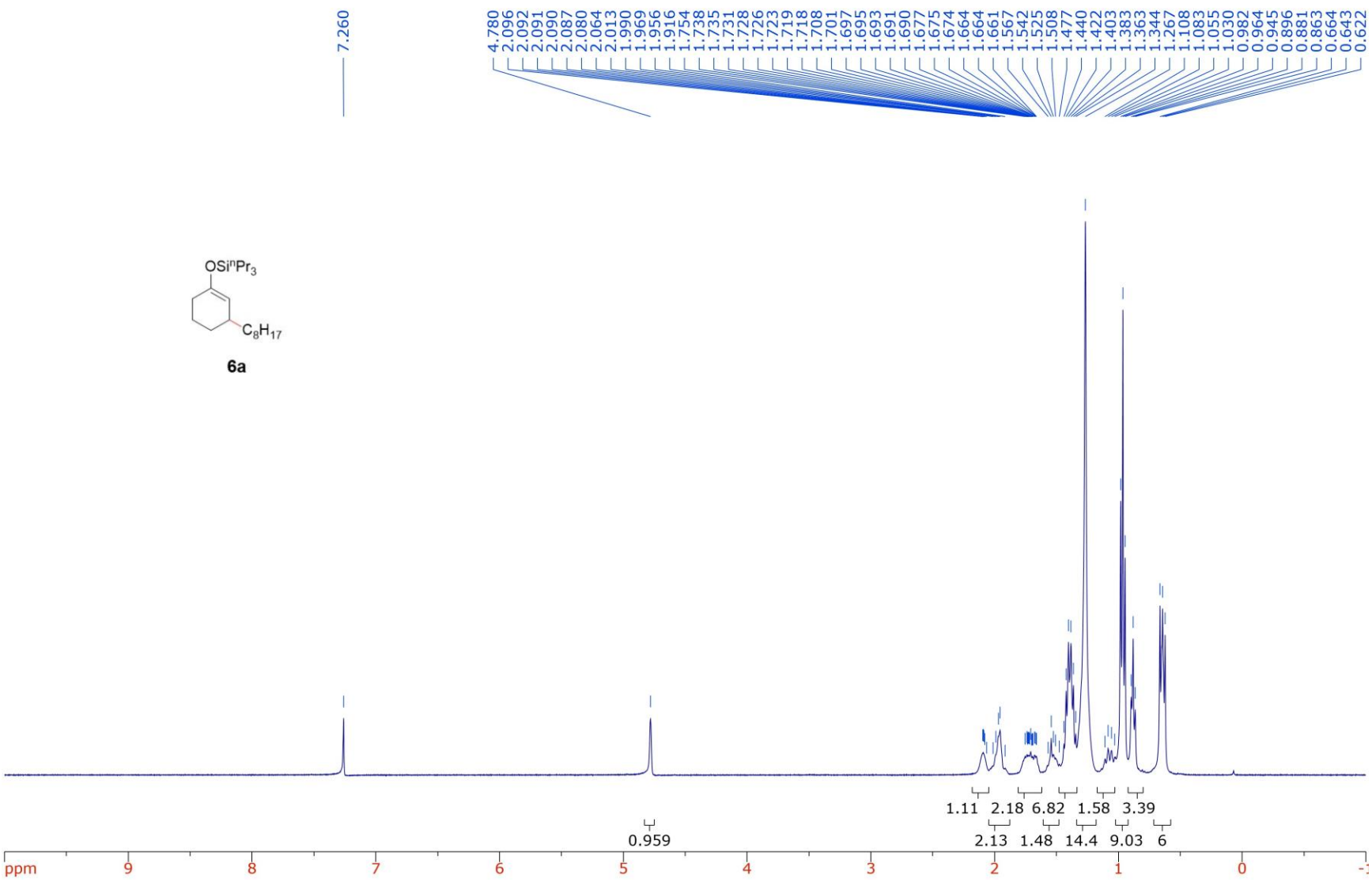
0.839
0.547
OSiMe3
CO2Et
4h
ppm
200
150
100
50
0
-5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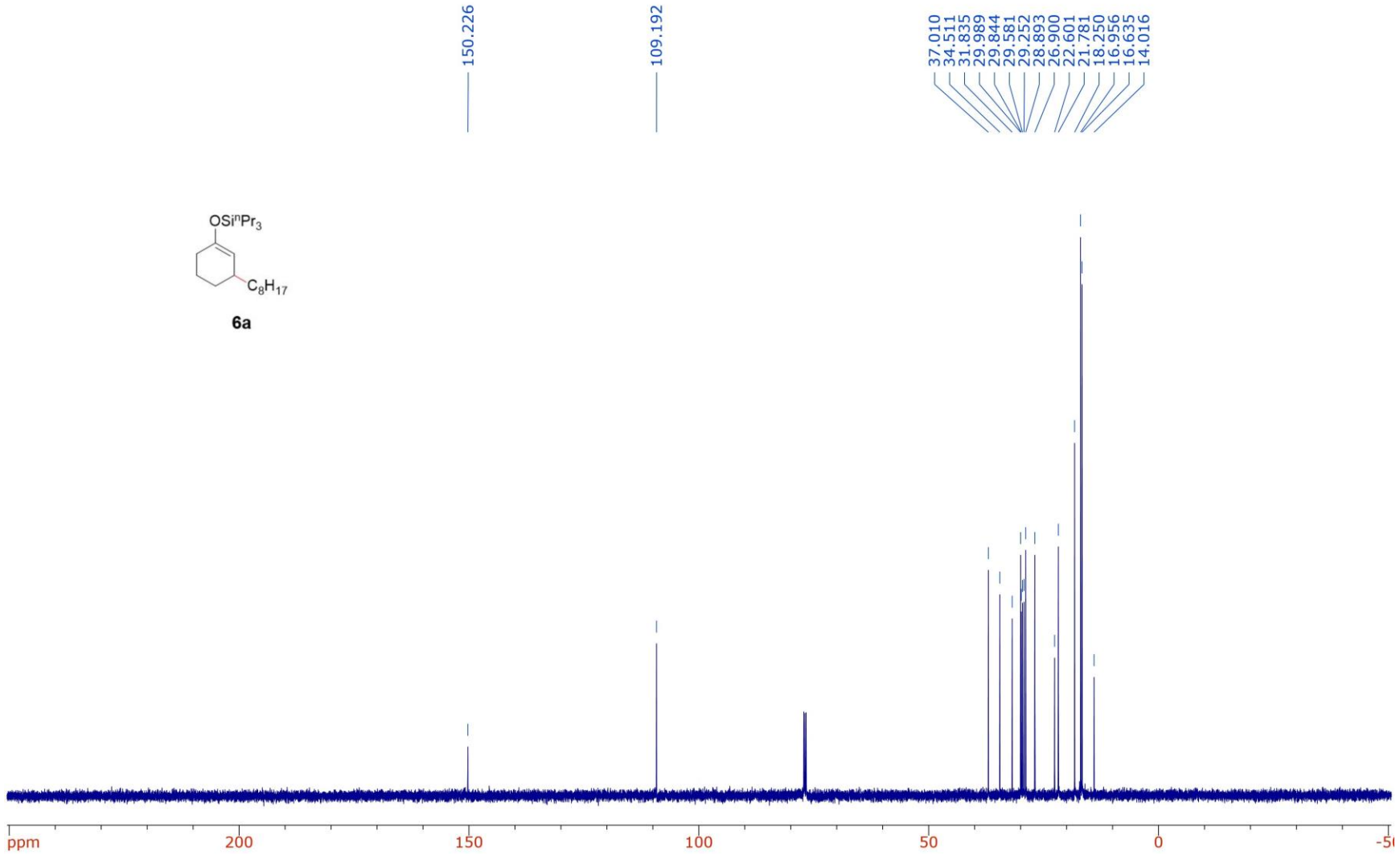
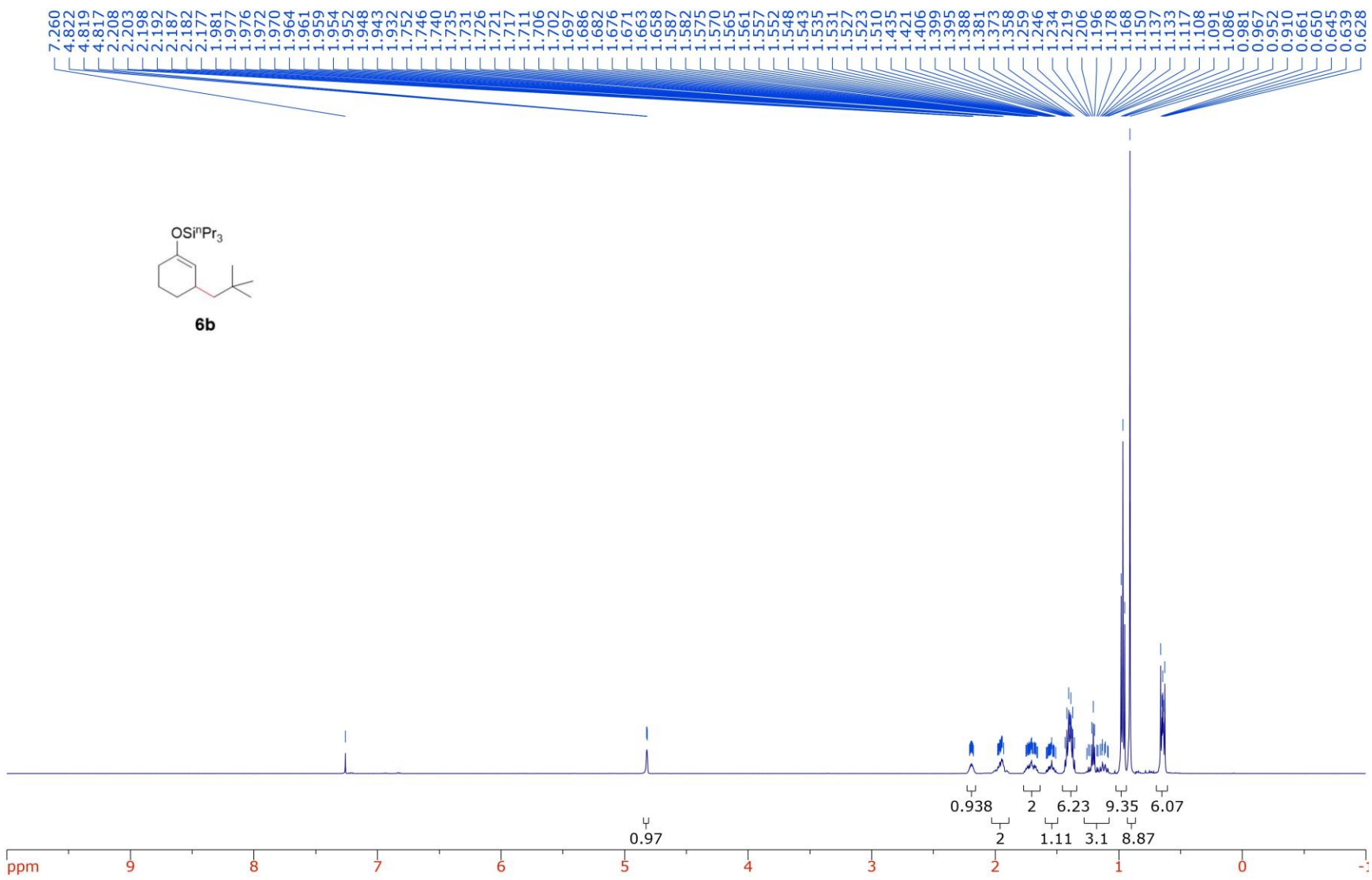
4.780
2.096
2.092
2.091
2.090
2.087
2.080
2.064
2.013
1.990
1.969
1.956
1.916
1.754
1.738
1.735
1.731
1.728
1.726
1.723
1.719
1.718
1.708
1.701
1.697
1.695
1.693
1.691
1.690
1.677
1.675
1.674
1.664
1.664
1.661
1.567
1.542
1.525
1.508
1.477
1.440
1.422
1.403
1.383
1.363
1.344
1.267
1.108
1.083
1.055
1.030
0.982
0.964
0.945
0.896
0.881
0.863
0.664
0.643
0.622
OSi^{n}Pr$_3$
C$_8$H$_{17}$
6a
1.11
2.18
6.82
1.58
3.39
0.959
2.13
1.48
14.4
9.03
6
ppm
9
8
7
6
5
4
3
2
1
0


150.226
109.192
37.010
34.511
31.835
29.989
29.844
29.581
29.252
28.893
26.900
22.601
21.781
18.250
16.956
16.635
14.016
OSi^{n}Pr$_3$
C$_8$H$_{17}$
6a
ppm
200
150
100
50
0


7.260
4.822
4.819
4.817
2.208
2.203
2.198
2.192
2.187
2.182
2.177
1.981
1.977
1.976
1.972
1.970
1.964
1.961
1.959
1.954
1.952
1.948
1.943
1.932
1.752
1.746
1.740
1.735
1.731
1.726
1.721
1.717
1.711
1.706
1.702
1.697
1.686
1.682
1.676
1.671
1.663
1.658
1.587
1.582
1.575
1.570
1.565
1.561
1.557
1.552
1.548
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1.535
1.531
1.527
1.523
1.510
1.435
1.421
1.406
1.399
1.395
1.388
1.381
1.373
1.358
1.259
1.246
1.234
1.219
1.206
1.196
1.178
1.168
1.150
1.137
1.133
1.117
1.108
1.091
1.086
0.981
0.967
0.952
0.910
0.661
0.650
0.645
0.639
0.628
OSi^{n}Pr$_3$
6b
0.938
2
6.23
9.35
6.07
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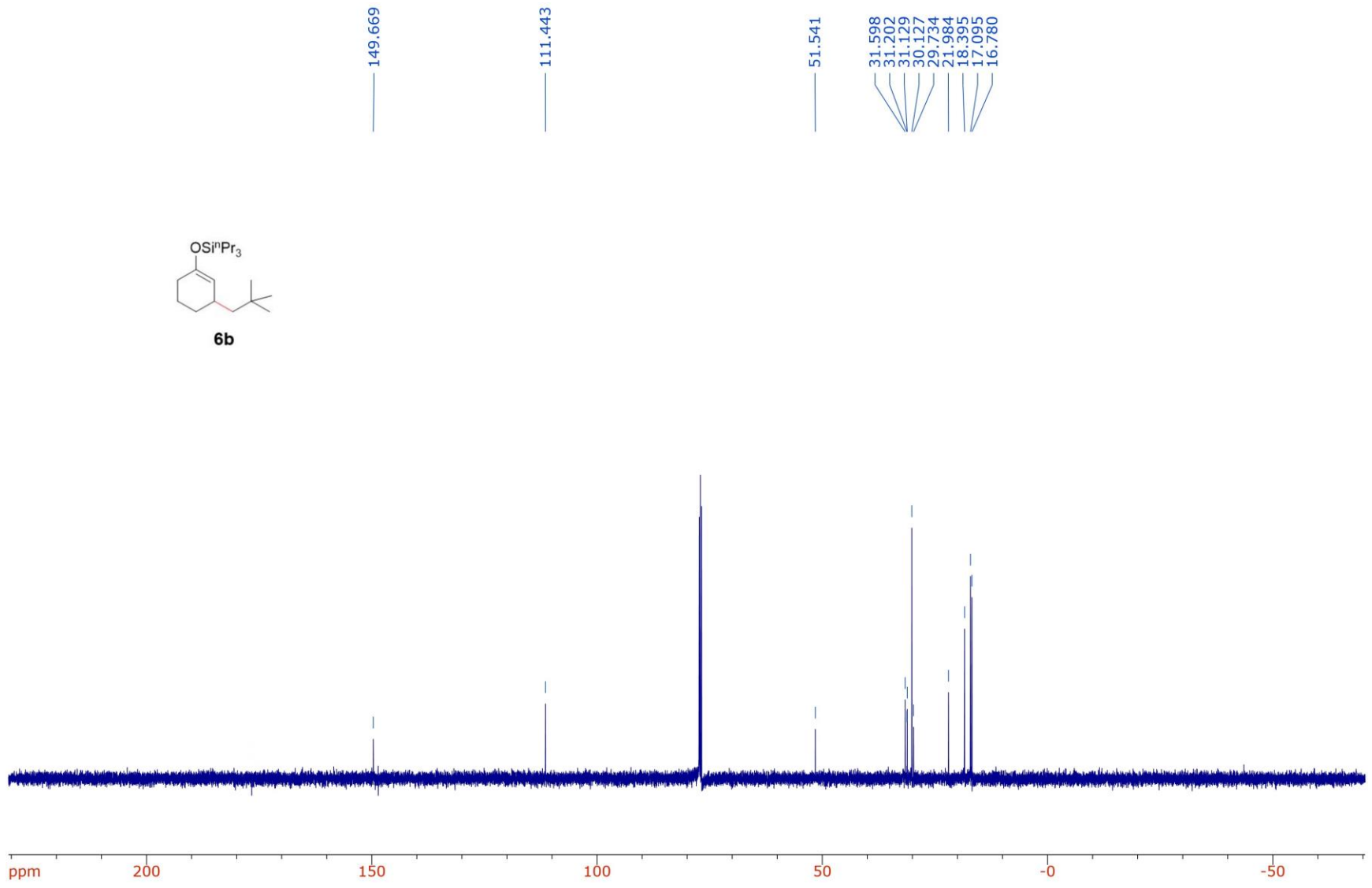
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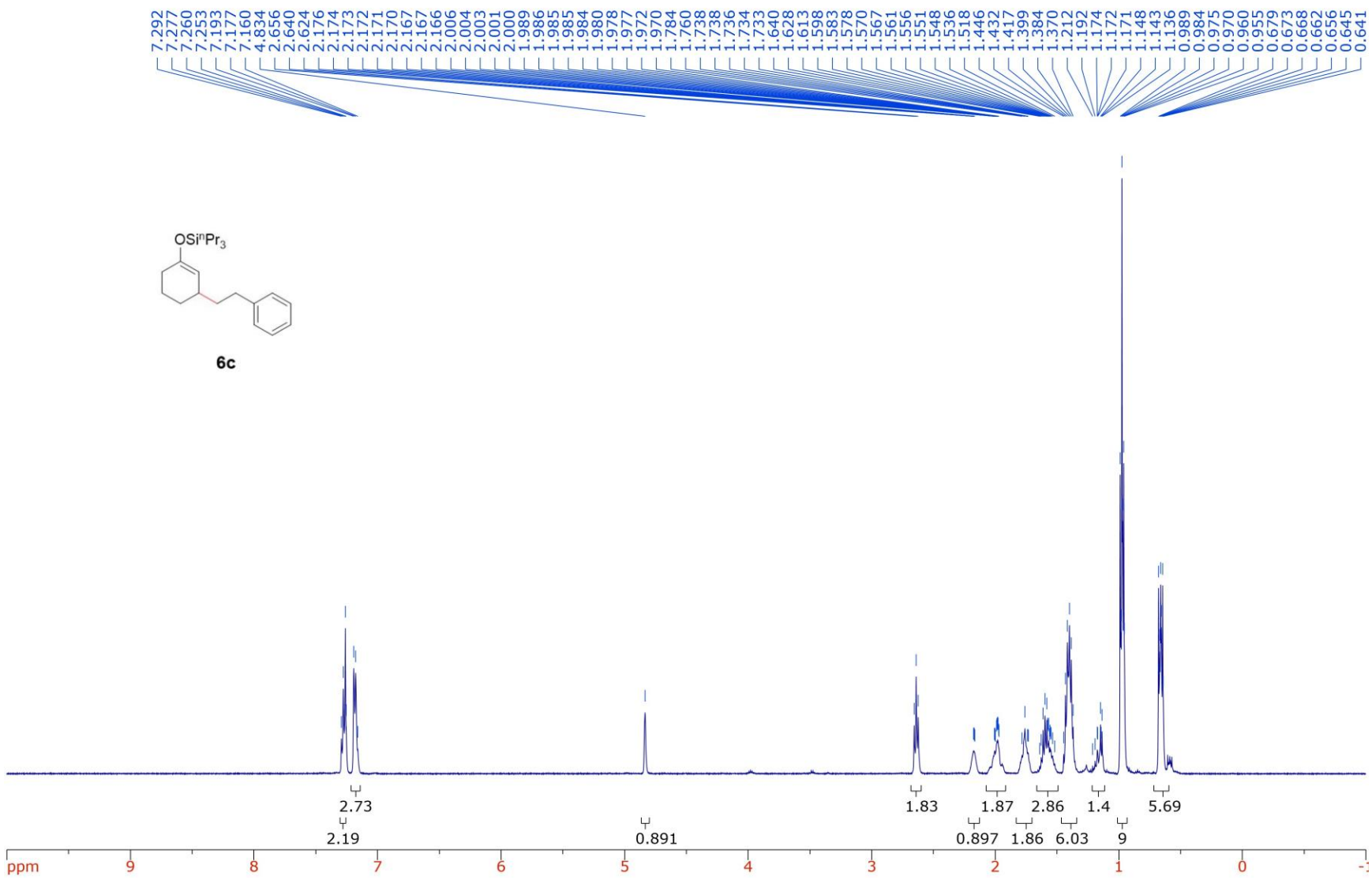
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2.176
2.174
2.173
2.172
2.171
2.170
2.167
2.167
2.166
2.006
2.004
2.003
2.001
2.000
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1.986
1.985
1.985
1.984
1.980
1.978
1.977
1.972
1.970
1.784
1.760
1.738
1.736
1.734
1.733
1.640
1.628
1.613
1.598
1.583
1.578
1.570
1.567
1.561
1.556
1.551
1.548
1.536
1.518
1.446
1.432
1.417
1.399
1.384
1.370
1.212
1.192
1.174
1.172
1.171
1.148
1.143
1.136
0.989
0.984
0.975
0.970
0.960
0.955
0.679
0.673
0.668
0.662
0.656
0.645
0.641
OSi^{n}Pr$_3$
6c
2.73
2.19
0.891
1.83
1.87
0.897
2.86
1.86
1.4
6.03
5.69
9
ppm
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8
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6
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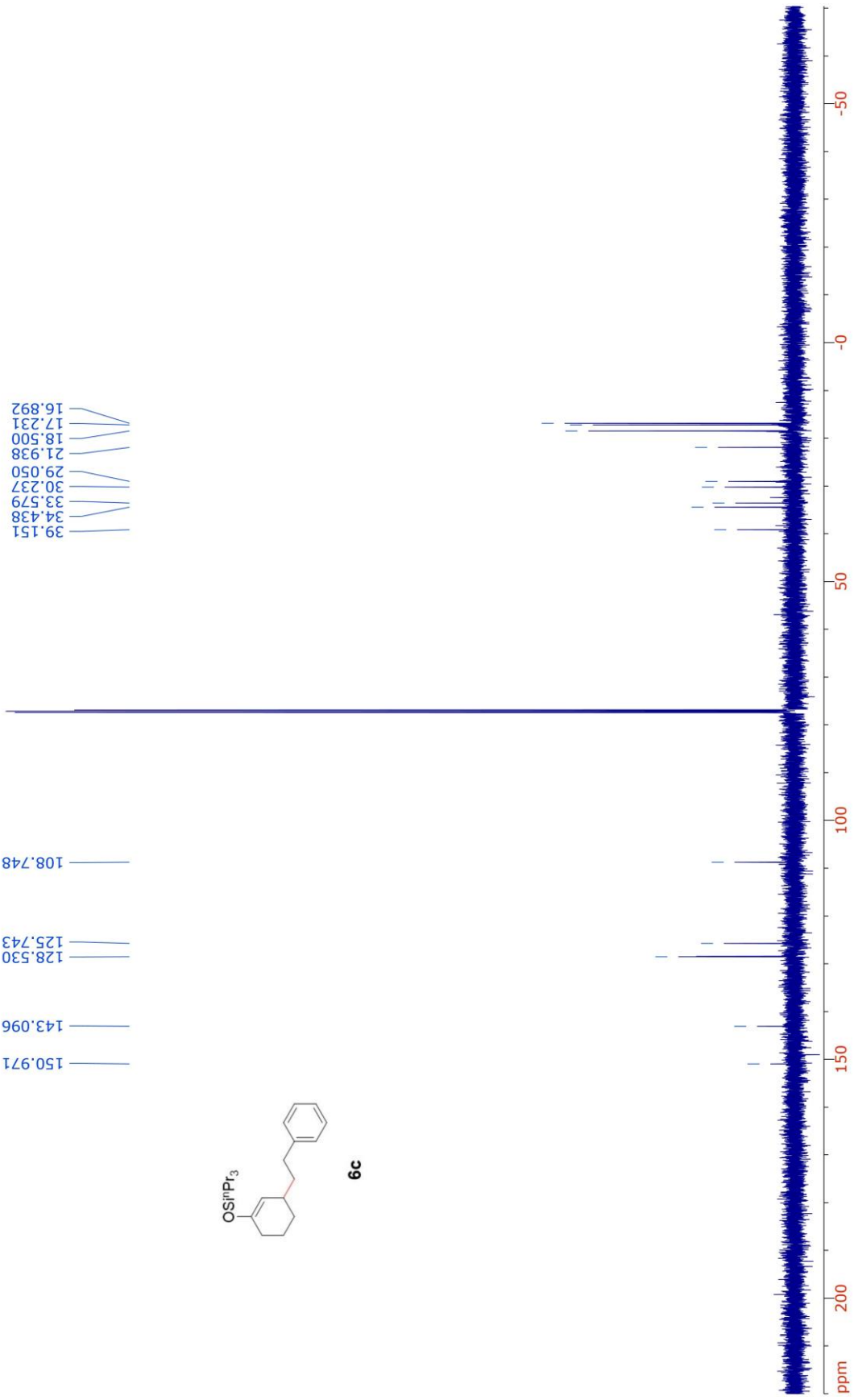
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150.971
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6c
ppm
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100
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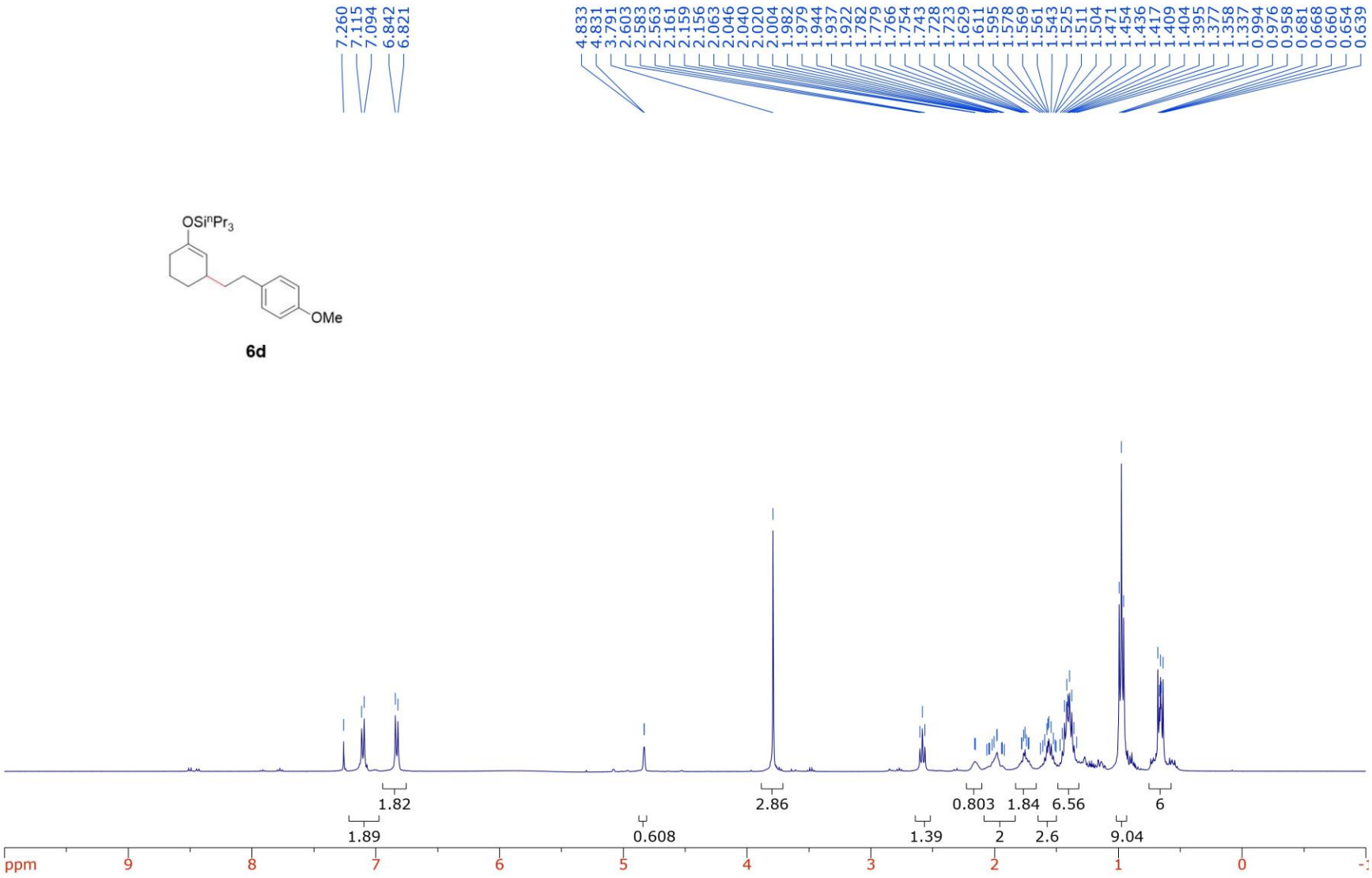
-0
-50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2.563
2.161
2.159
2.156
2.063
2.046
2.040
2.020
2.004
1.982
1.979
1.944
1.937
1.922
1.782
1.779
1.766
1.754
1.743
1.728
1.723
1.629
1.611
1.595
1.578
1.569
1.561
1.543
1.525
1.511
1.504
1.471
1.454
1.436
1.417
1.409
1.404
1.395
1.377
1.358
1.337
0.994
0.976
0.958
0.681
0.668
0.660
0.654
0.639
OSi^{n}Pr$_3$
OMe
6d
1.82
2.86
0.803
1.84
6.56
6
1.89
0.608
1.39
2
2.6
9.04
ppm
9
8
7
6
5
4
3
2
1
0
-1

16.882
17.188
18.505
21.927
29.031
30.216
32.598
34.320
39.384
55.376
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113.863
129.354
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157.764
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OMe
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ppm
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150
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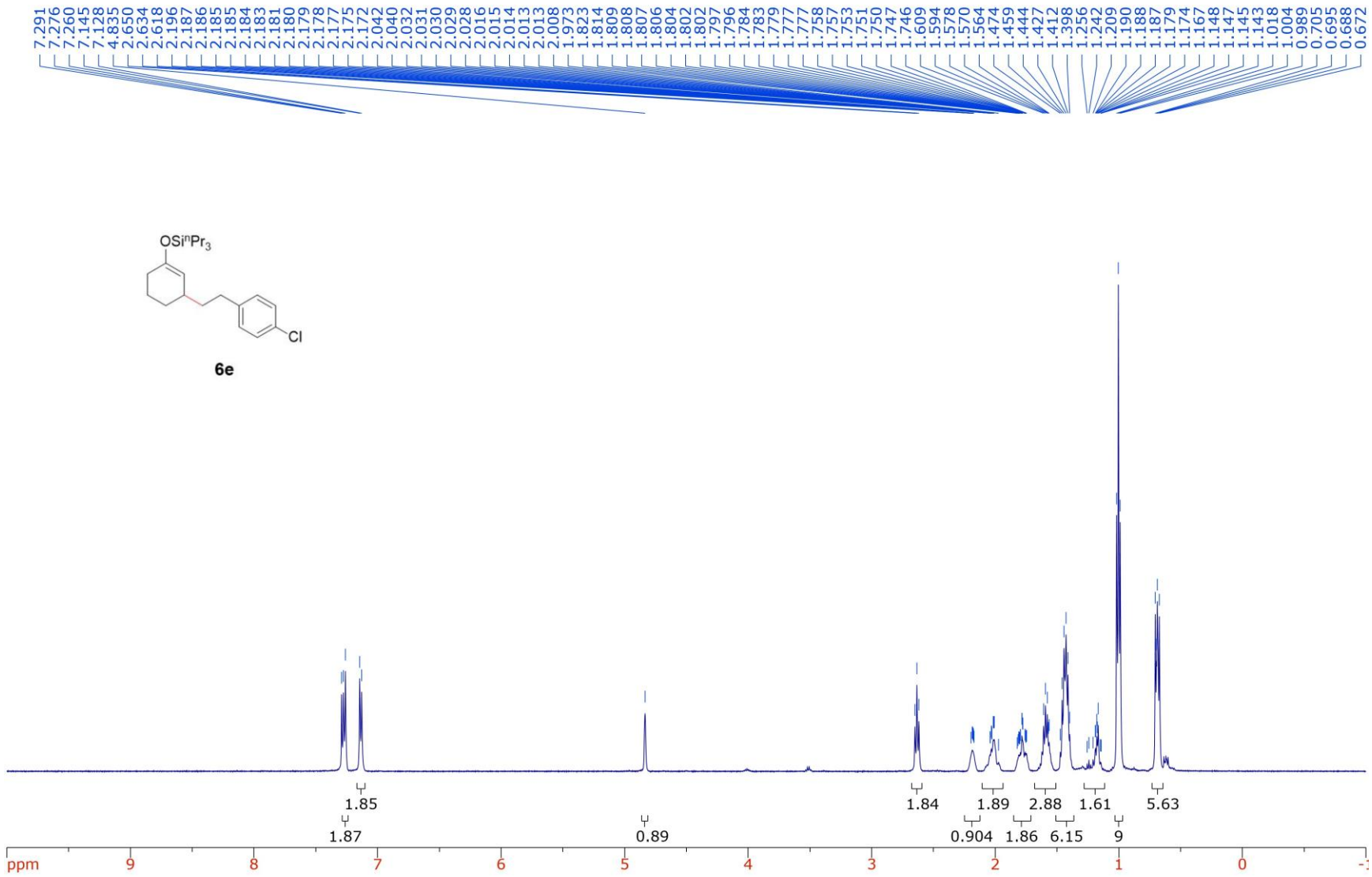
-50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2.634
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2.186
2.185
2.185
2.184
2.183
2.181
2.180
2.179
2.178
2.177
2.175
2.172
2.042
2.040
2.032
2.031
2.030
2.029
2.028
2.016
2.015
2.014
2.013
2.008
1.973
1.823
1.814
1.809
1.808
1.807
1.806
1.804
1.802
1.802
1.797
1.796
1.784
1.783
1.779
1.777
1.777
1.758
1.757
1.753
1.751
1.750
1.747
1.746
1.609
1.594
1.578
1.570
1.564
1.474
1.459
1.444
1.427
1.412
1.398
1.256
1.242
1.209
1.190
1.188
1.187
1.179
1.174
1.167
1.148
1.147
1.145
1.143
1.018
1.004
0.989
0.705
0.695
0.688
0.672
OSi^{n}Pr$_3$
Cl
6e
1.85
1.87
0.89
1.84
1.89
0.904
2.88
1.86
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6.15
5.63
9
ppm
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8
7
6
5
4
3
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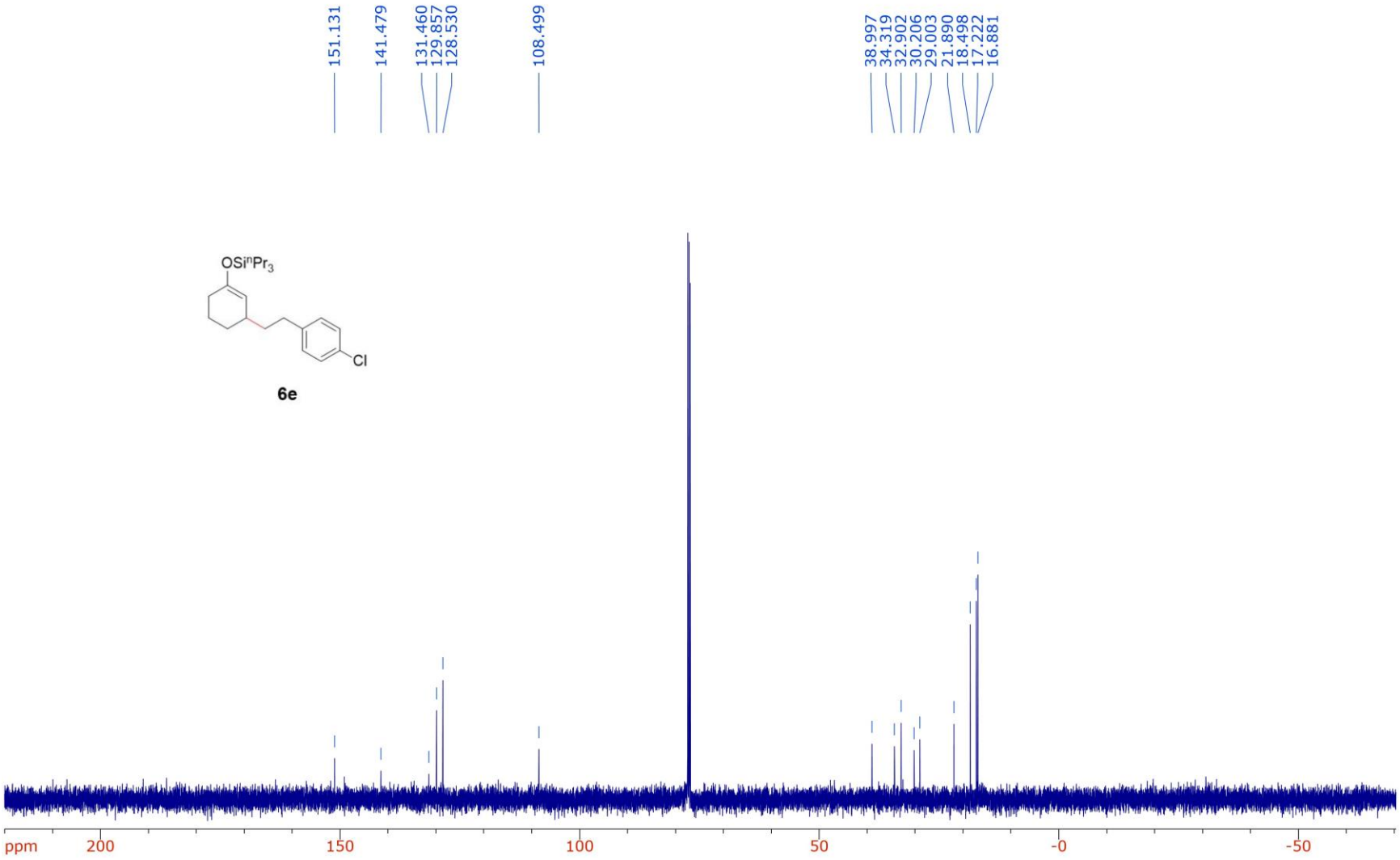
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131.460
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128.530
108.499
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32.902
30.206
29.003
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18.498
17.222
16.881
OSi^{n}Pr$_3$
Cl
6e
ppm
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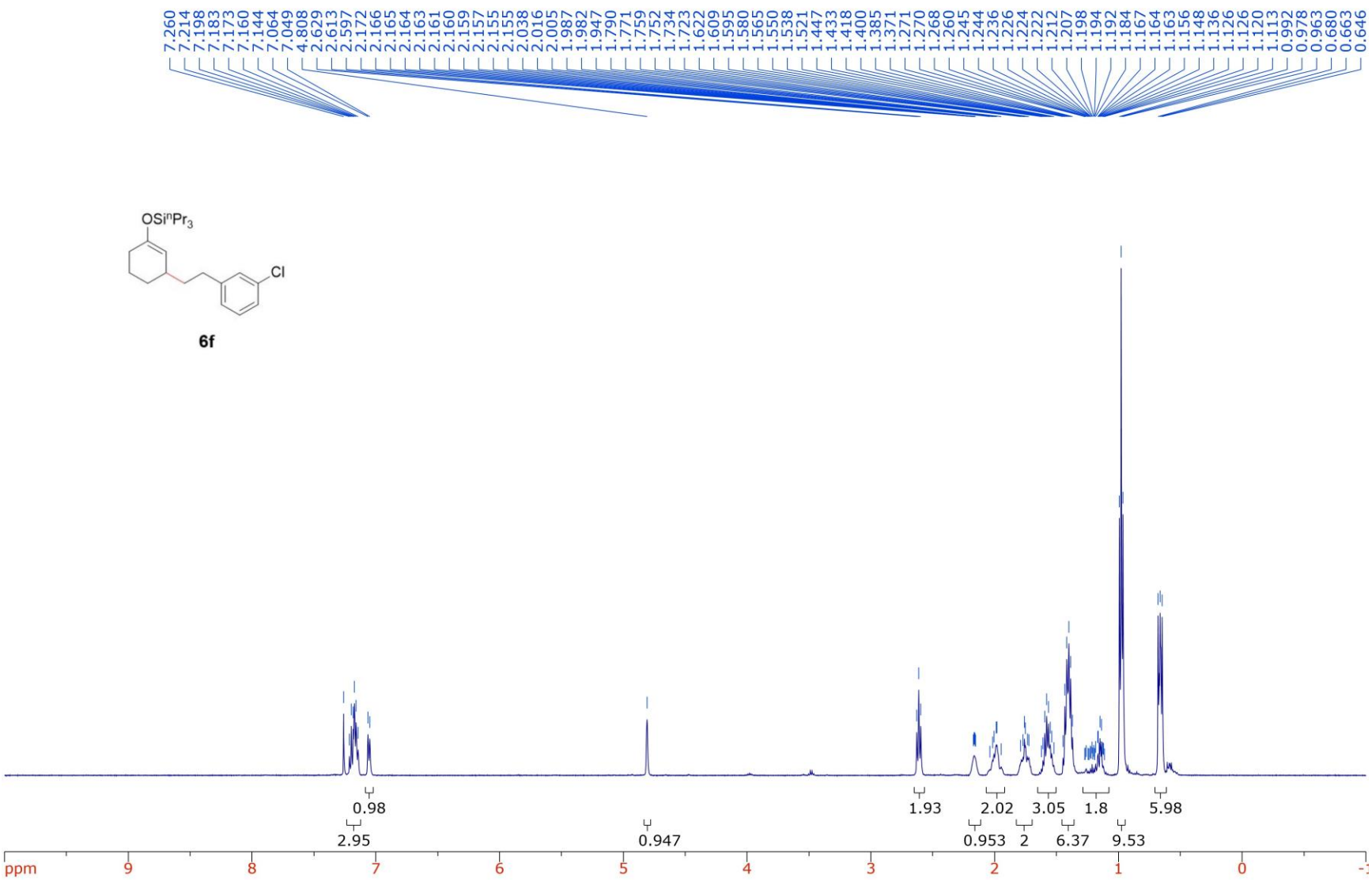
150
100
50
-0
-50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7.198
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7.173
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7.144
7.064
7.049
4.808
2.629
2.613
2.597
2.172
2.166
2.165
2.164
2.163
2.161
2.160
2.159
2.157
2.155
2.155
2.038
2.016
2.005
1.987
1.982
1.947
1.790
1.771
1.759
1.752
1.734
1.723
1.622
1.609
1.595
1.580
1.565
1.550
1.538
1.521
1.447
1.433
1.418
1.400
1.385
1.371
1.271
1.270
1.268
1.260
1.245
1.244
1.236
1.226
1.224
1.222
1.212
1.207
1.198
1.194
1.192
1.184
1.167
1.164
1.163
1.156
1.148
1.136
1.126
1.126
1.120
1.113
0.992
0.978
0.963
0.680
0.663
0.646
OSi^{n}Pr$_3$
Cl
6f
0.98
2.95
0.947
1.93
2.02
0.953
3.05
2
1.8
6.37
5.98
9.53
ppm
9
8
7
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5
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3
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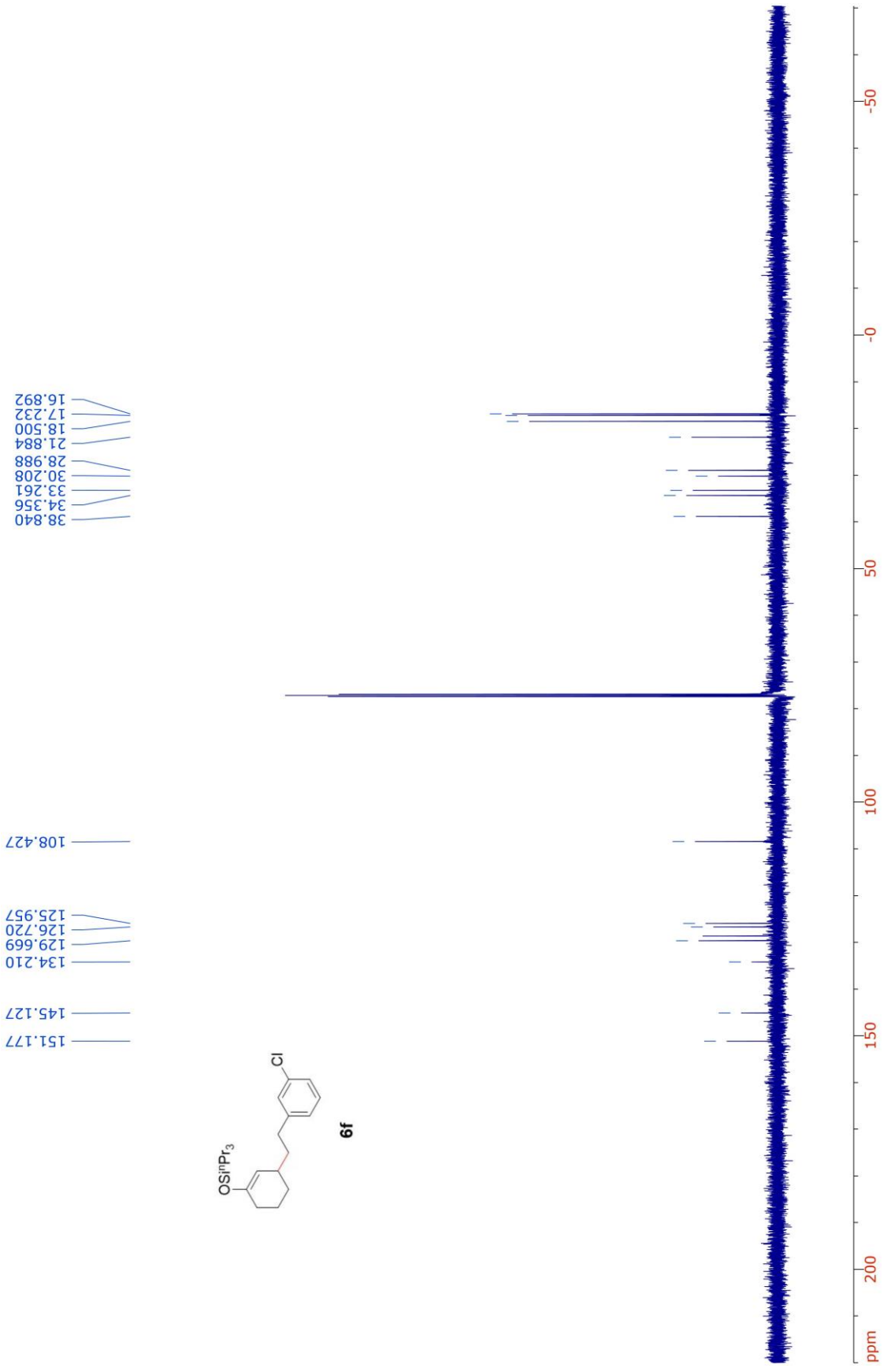
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34.356
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125.957
126.720
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151.177
ppm
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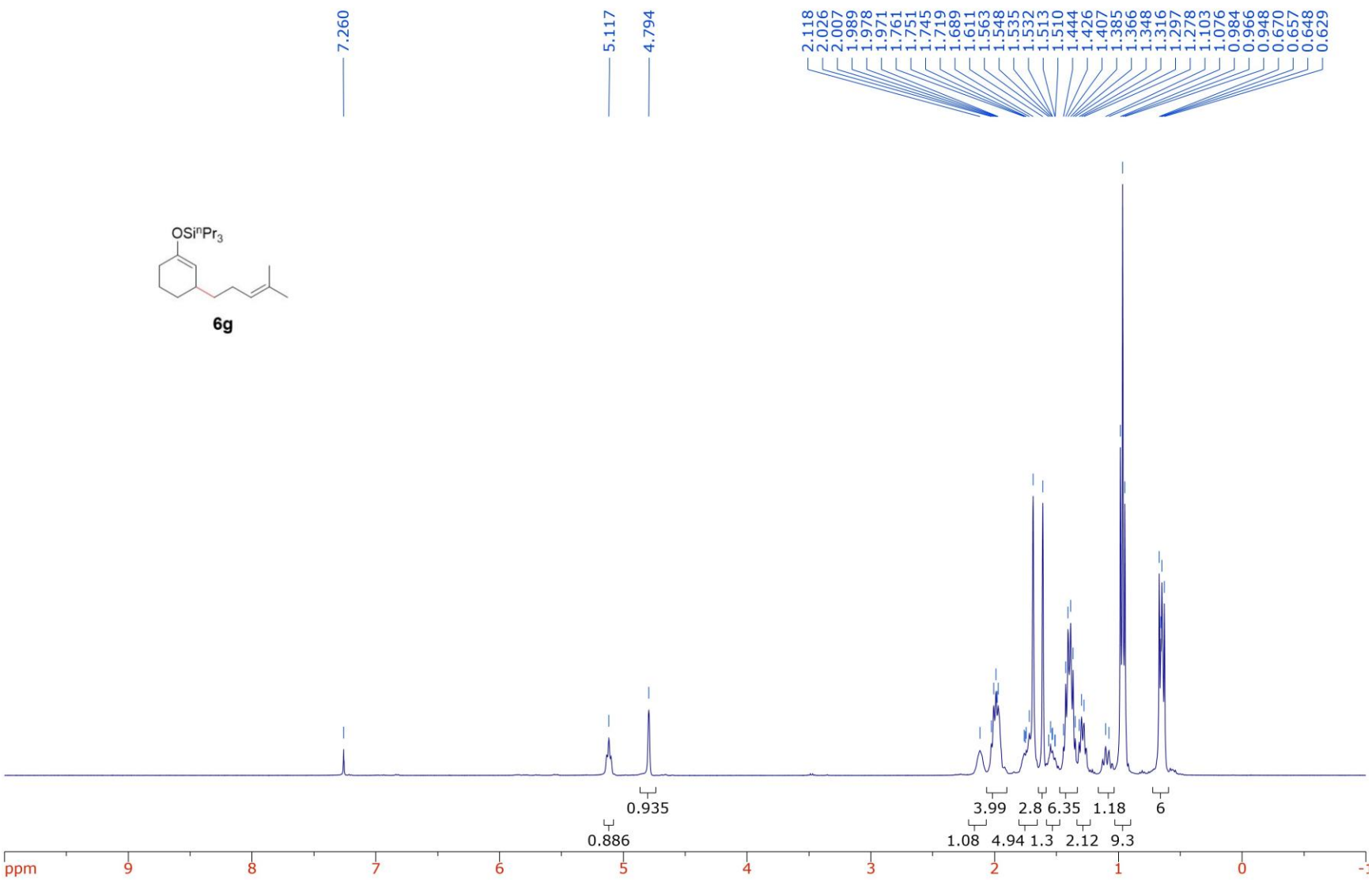
-0
50
100
150
200
Cl
OSi^{i}Pr$_3$
6f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1.978
1.971
1.761
1.751
1.745
1.719
1.689
1.611
1.563
1.548
1.535
1.532
1.513
1.510
1.444
1.426
1.407
1.385
1.366
1.348
1.316
1.297
1.278
1.103
1.076
0.984
0.966
0.948
0.670
0.657
0.648
0.629
OSi^{n}Pr$_3$
6g
0.935
3.99
2.8
6.35
1.18
6
0.886
1.08
4.94
1.3
2.12
9.3
ppm
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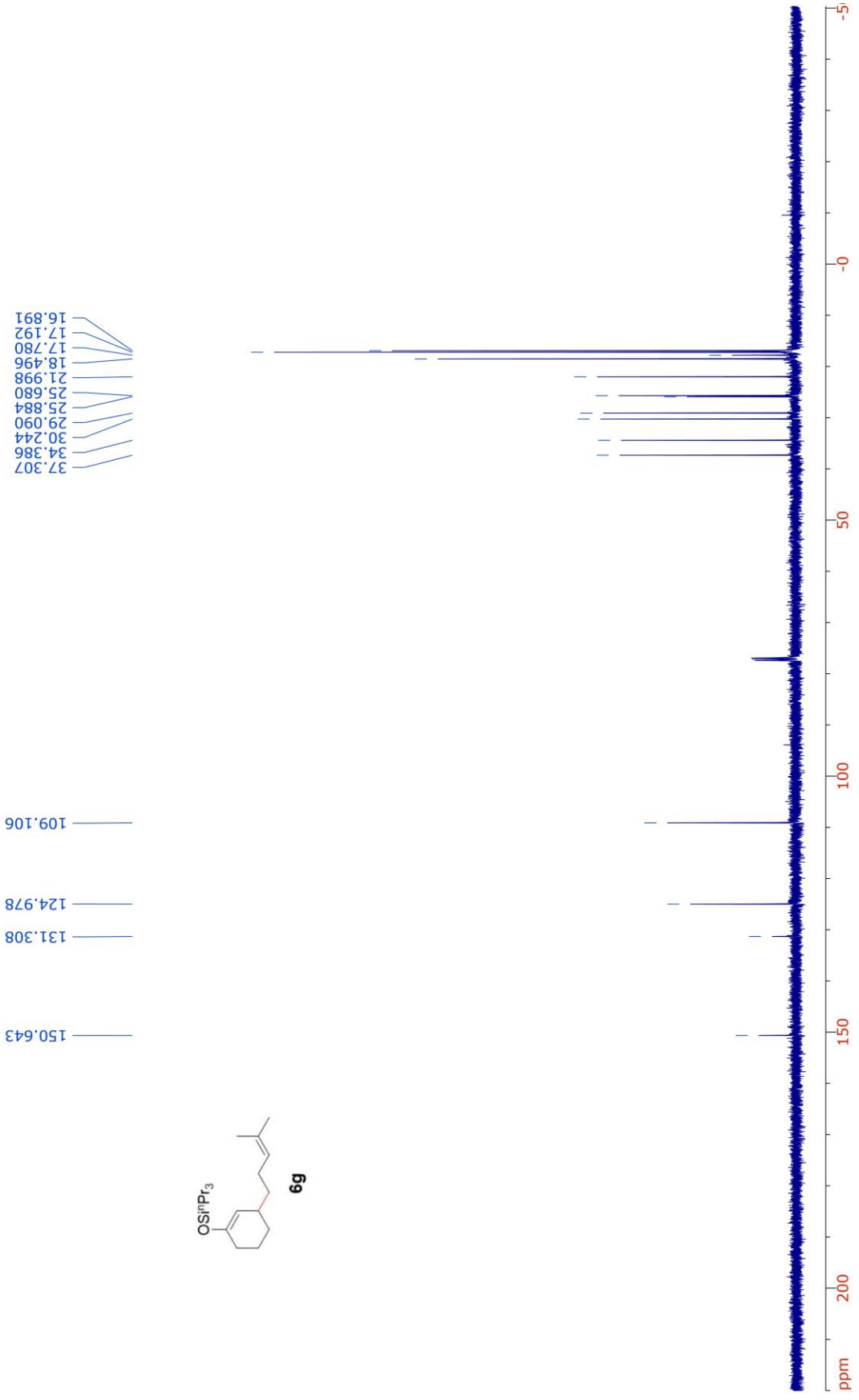
8
7
6
5
4
3
2
1
0
-1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17.780
18.496
21.998
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25.884
29.090
30.244
34.386
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124.978
131.308
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OSiⁿPr3
6g
ppm
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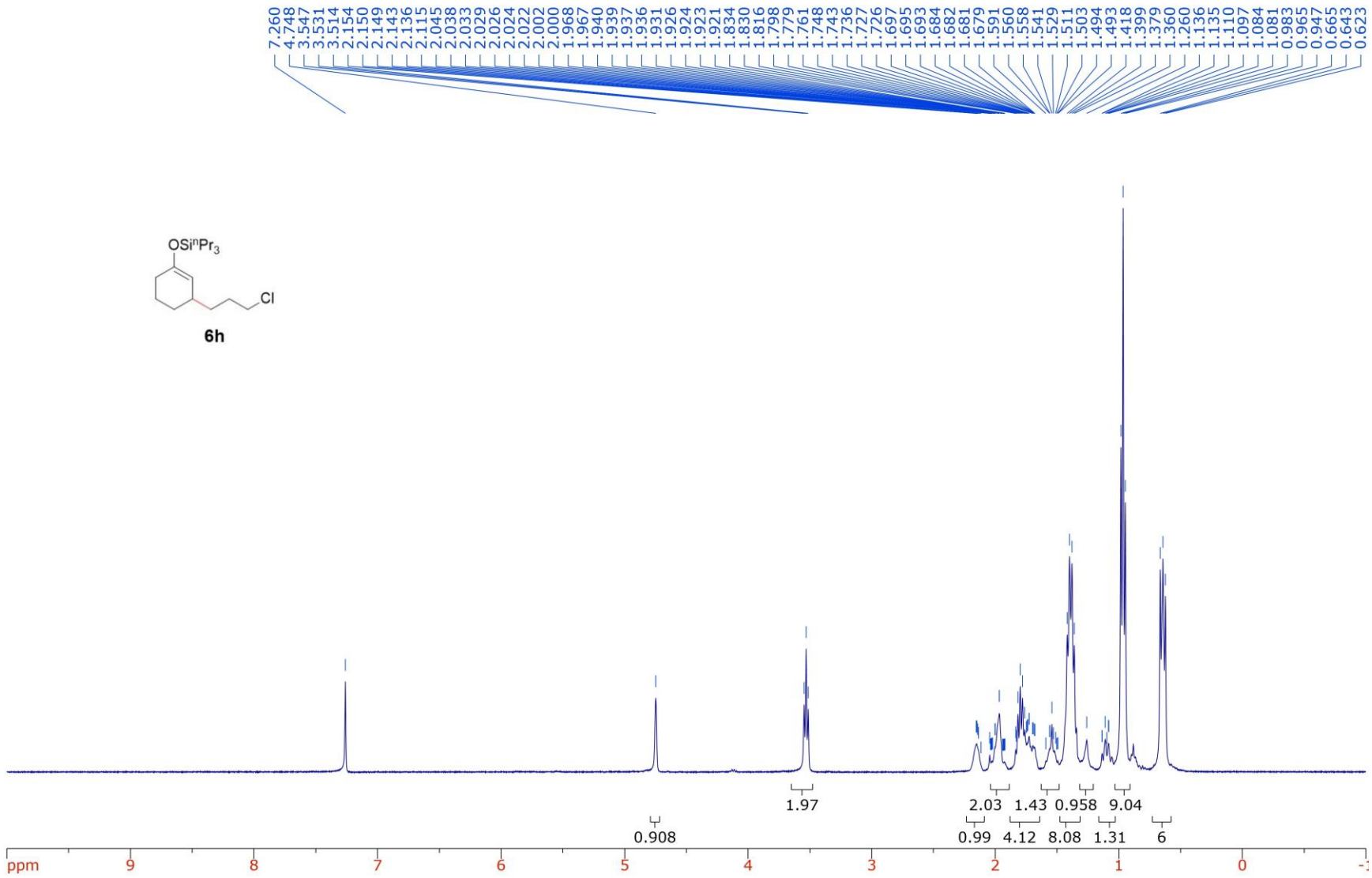
150
100
50
0
-5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2.150
2.149
2.143
2.136
2.115
2.045
2.038
2.033
2.029
2.026
2.024
2.022
2.002
2.000
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1.967
1.940
1.939
1.937
1.936
1.931
1.926
1.924
1.923
1.921
1.834
1.830
1.816
1.798
1.779
1.761
1.748
1.743
1.736
1.727
1.726
1.697
1.695
1.693
1.684
1.682
1.681
1.679
1.591
1.560
1.558
1.541
1.529
1.511
1.503
1.494
1.493
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1.399
1.379
1.360
1.260
1.136
1.135
1.110
1.097
1.084
1.081
0.983
0.965
0.947
0.665
0.643
0.623
OSi^{n}Pr$_3$
Cl
6h
0.908
1.97
0.99
2.03
4.12
1.43
8.08
0.958
1.31
9.04
6
ppm
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8
7
6
5
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3
2
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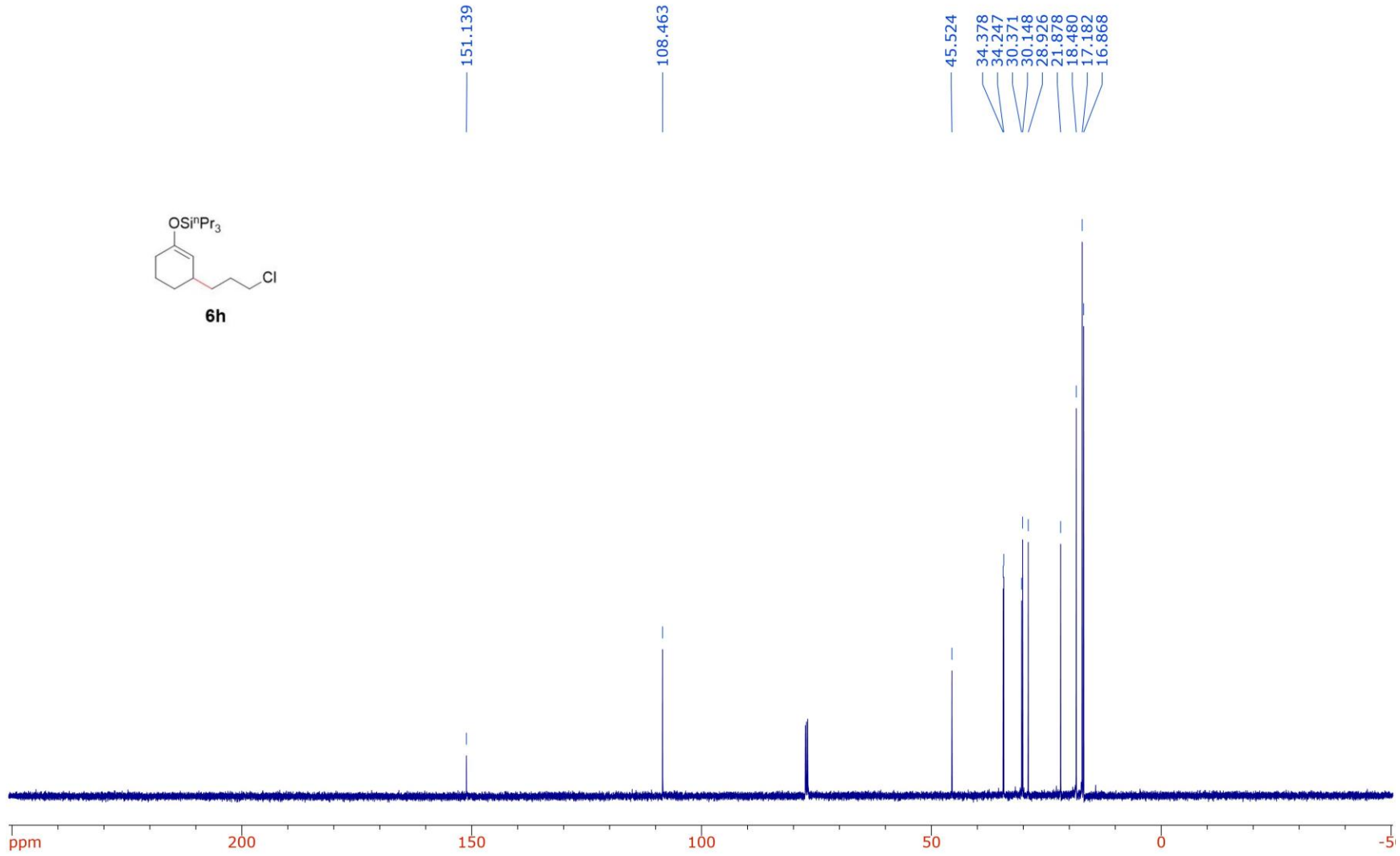
0
-1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28.926
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17.182
16.868
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Cl
6h
ppm
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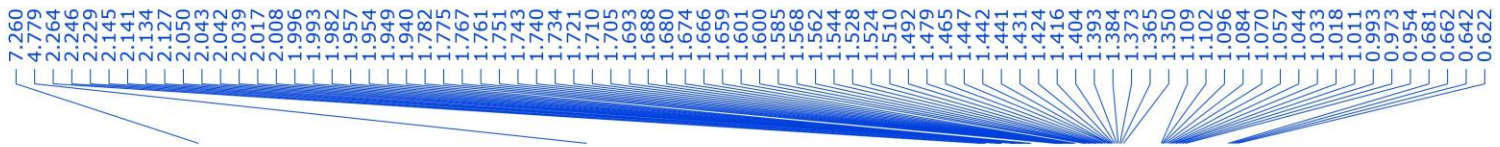
150
100
50
0
-5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2.229
2.145
2.141
2.134
2.127
2.050
2.043
2.042
2.039
2.017
2.008
1.996
1.993
1.982
1.957
1.954
1.949
1.940
1.782
1.775
1.767
1.761
1.751
1.743
1.740
1.734
1.721
1.710
1.705
1.693
1.688
1.680
1.674
1.666
1.659
1.601
1.600
1.585
1.568
1.562
1.544
1.528
1.524
1.510
1.492
1.479
1.465
1.447
1.442
1.441
1.431
1.424
1.416
1.404
1.393
1.384
1.373
1.365
1.350
1.109
1.102
1.096
1.084
1.070
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1.044
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1.018
1.011
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0.954
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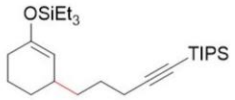
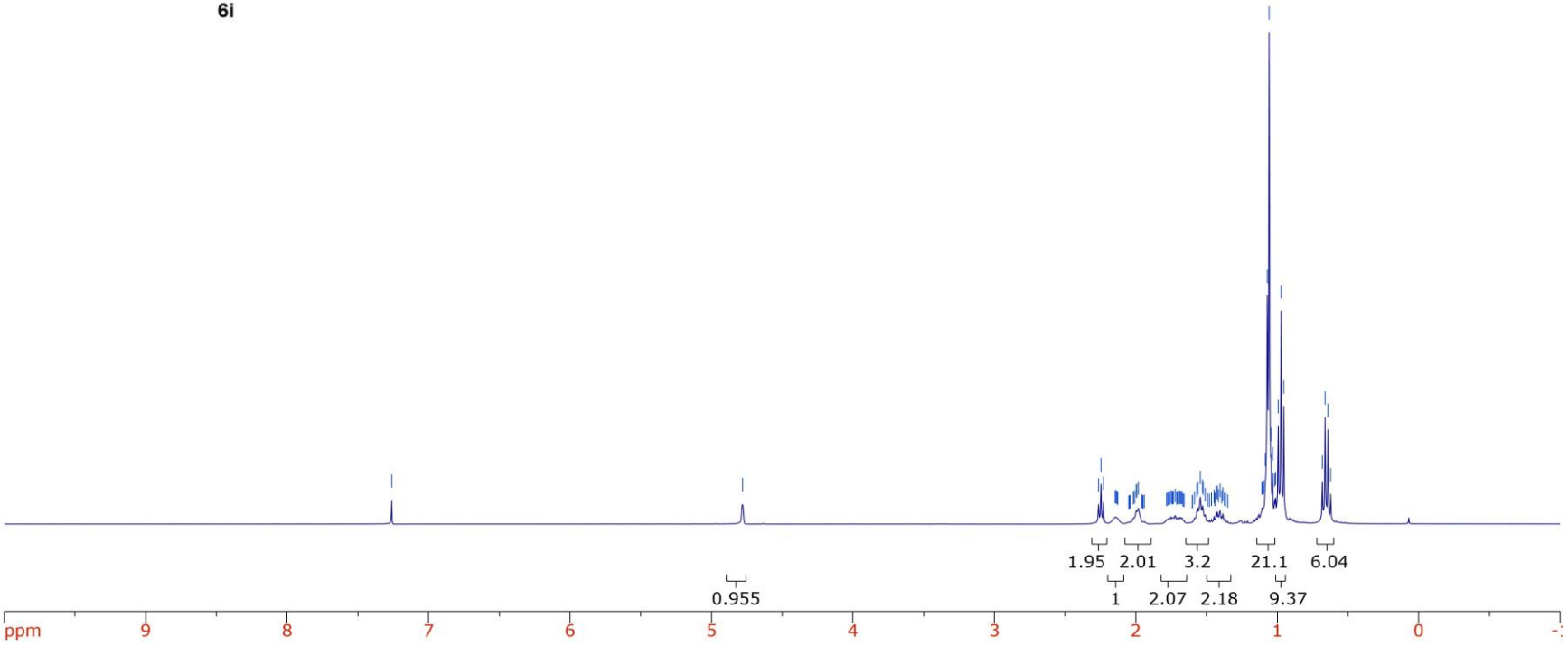
0.662
0.642
0.622


OSiEt3
TIPS

6i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3.2
21.1
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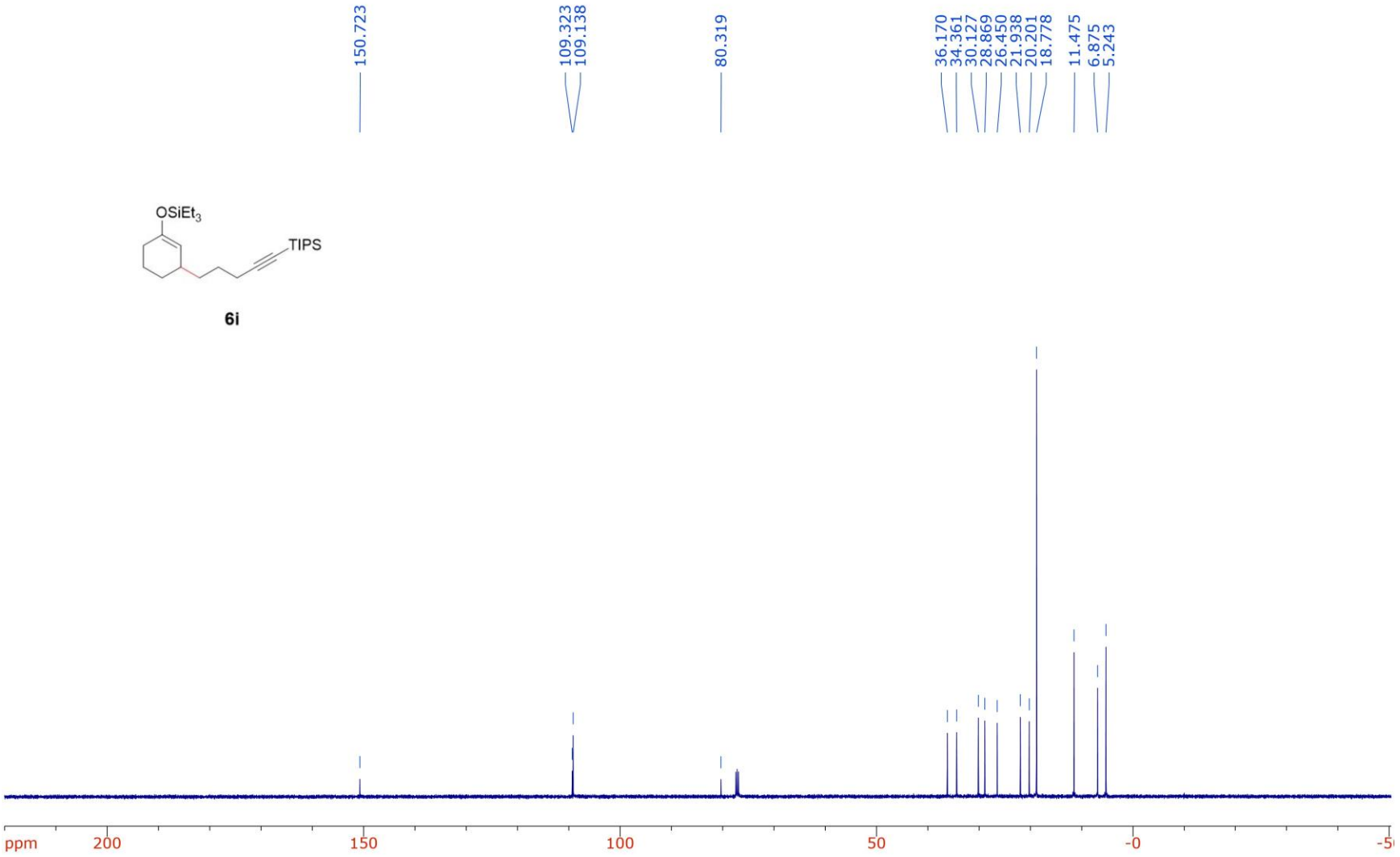
1
2.07
2.18
9.37
ppm
9
8
7
6
5
4
3
2
1
0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36.170
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30.127
28.869
26.450
21.938
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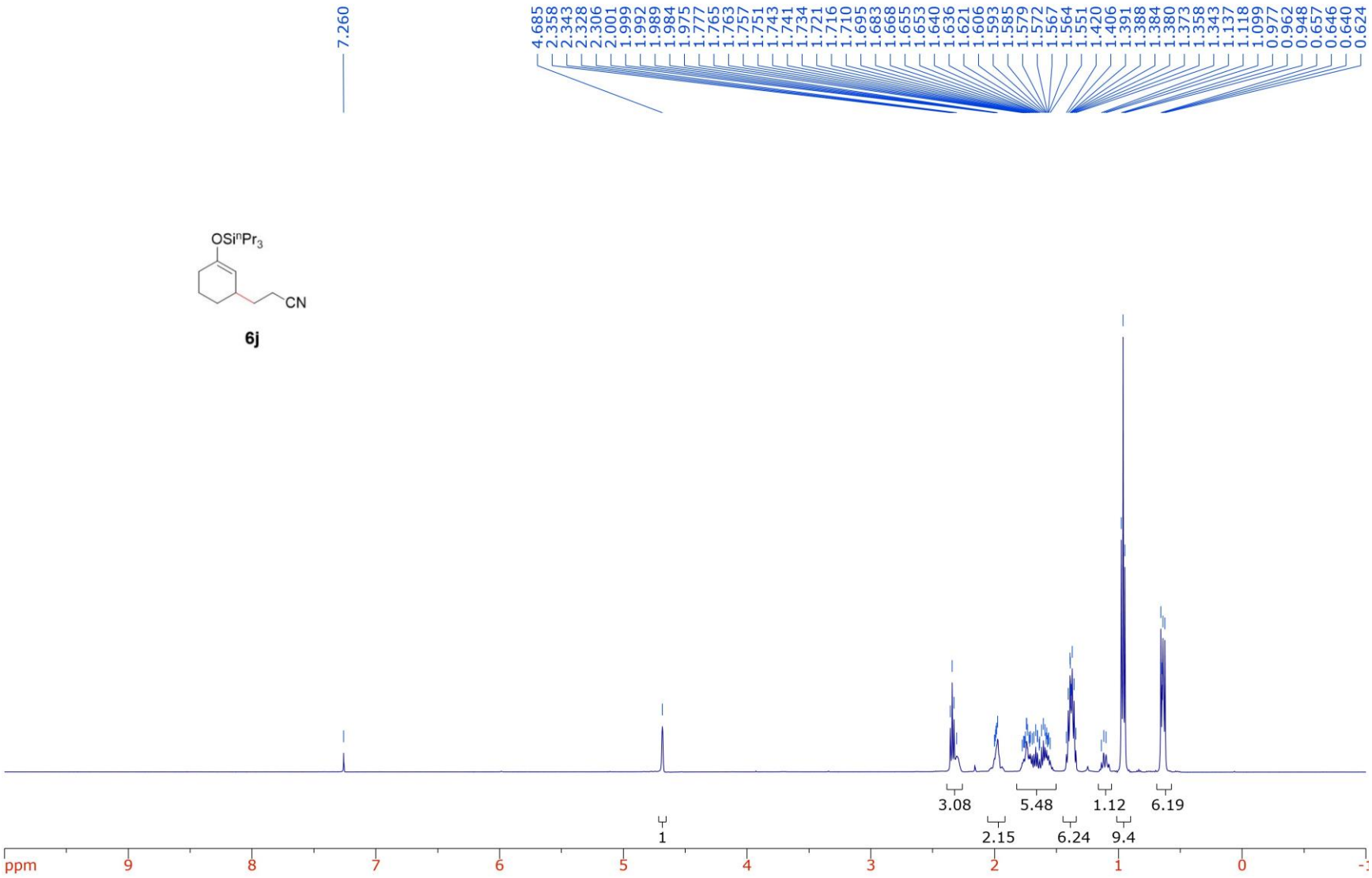
11.475
6.875
5.243
OSiEt3
TIPS
6i
ppm
200
150
100
50
-0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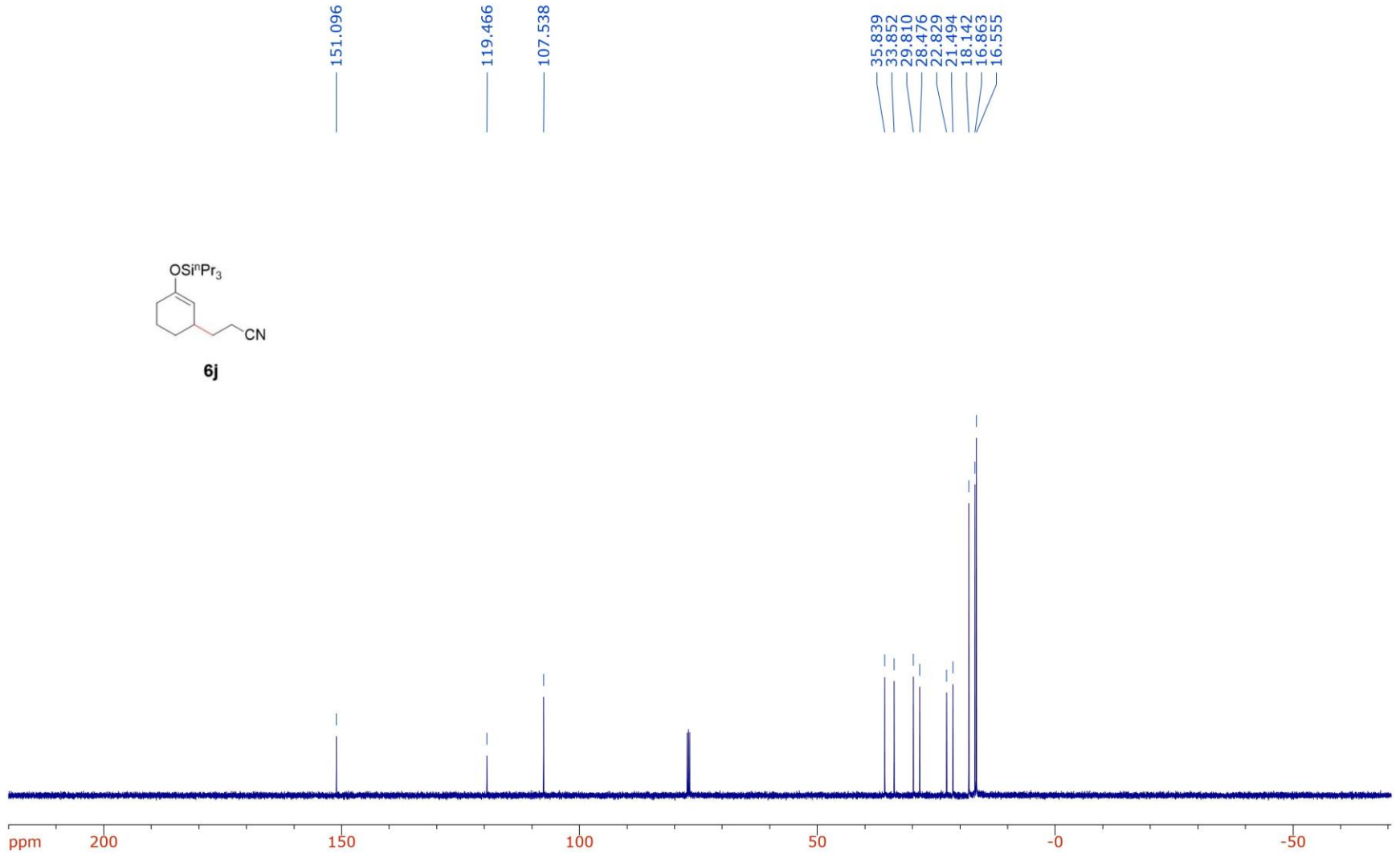
1.989
1.984
1.975
1.777
1.765
1.763
1.757
1.751
1.743
1.741
1.734
1.721
1.716
1.710
1.695
1.683
1.668
1.655
1.653
1.640
1.636
1.621
1.606
1.593
1.585
1.579
1.572
1.567
1.564
1.551
1.420
1.406
1.391
1.388
1.384
1.380
1.373
1.358
1.343
1.137
1.118
1.099
0.977
0.962
0.948
0.657
0.646
0.640
0.624
OSi^{n}Pr$_3$
CN
6j
3.08
5.48
1.12
6.19
1
2.15
6.24
9.4
ppm
9
8
7
6
5
4
3
2
1
0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35.839
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22.829
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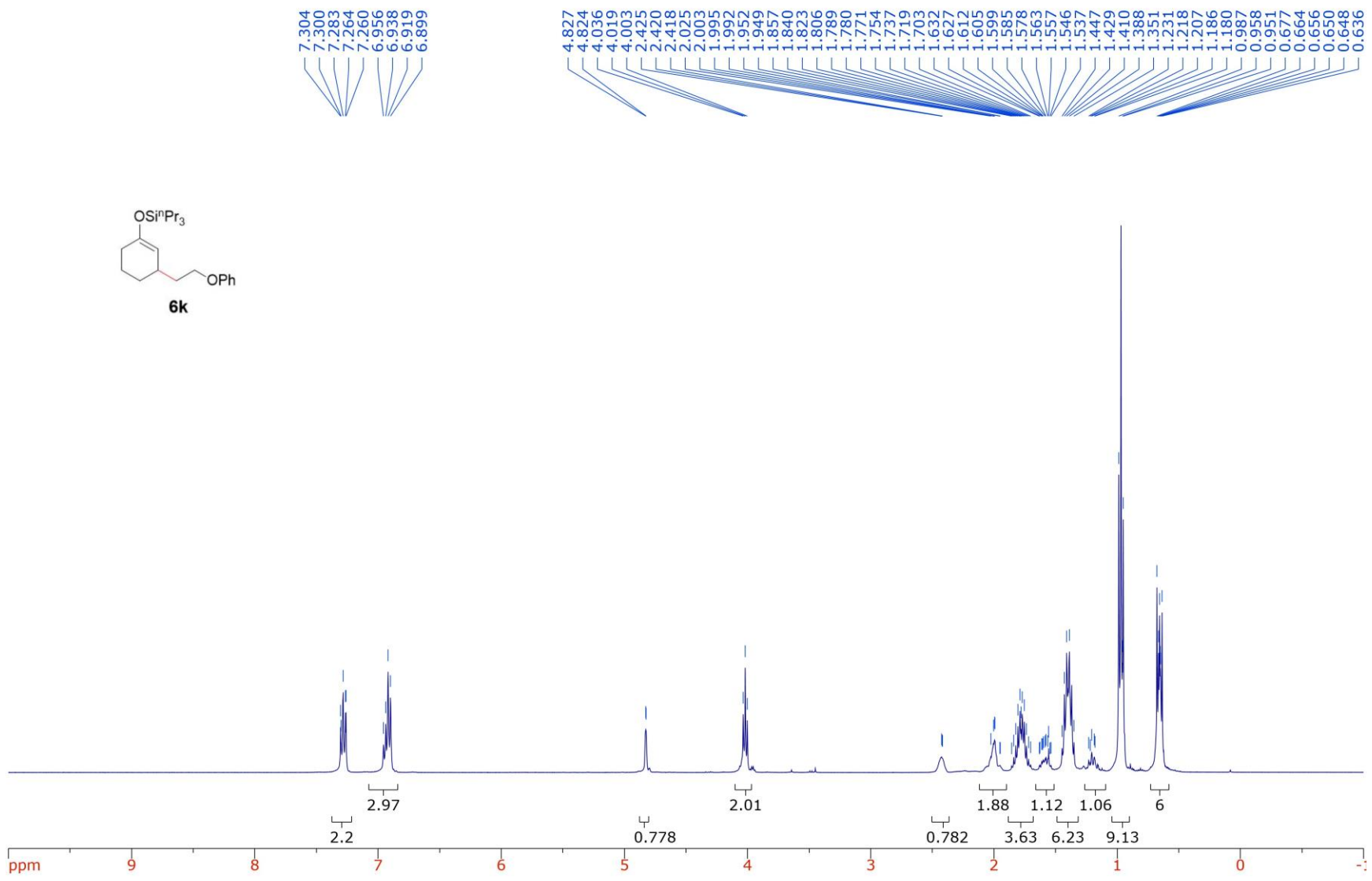
16.555
OSi^{n}Pr$_3$
CN
6j
ppm
200
150
100
50
-0
-50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4.019
4.003
2.425
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1.780
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0.677
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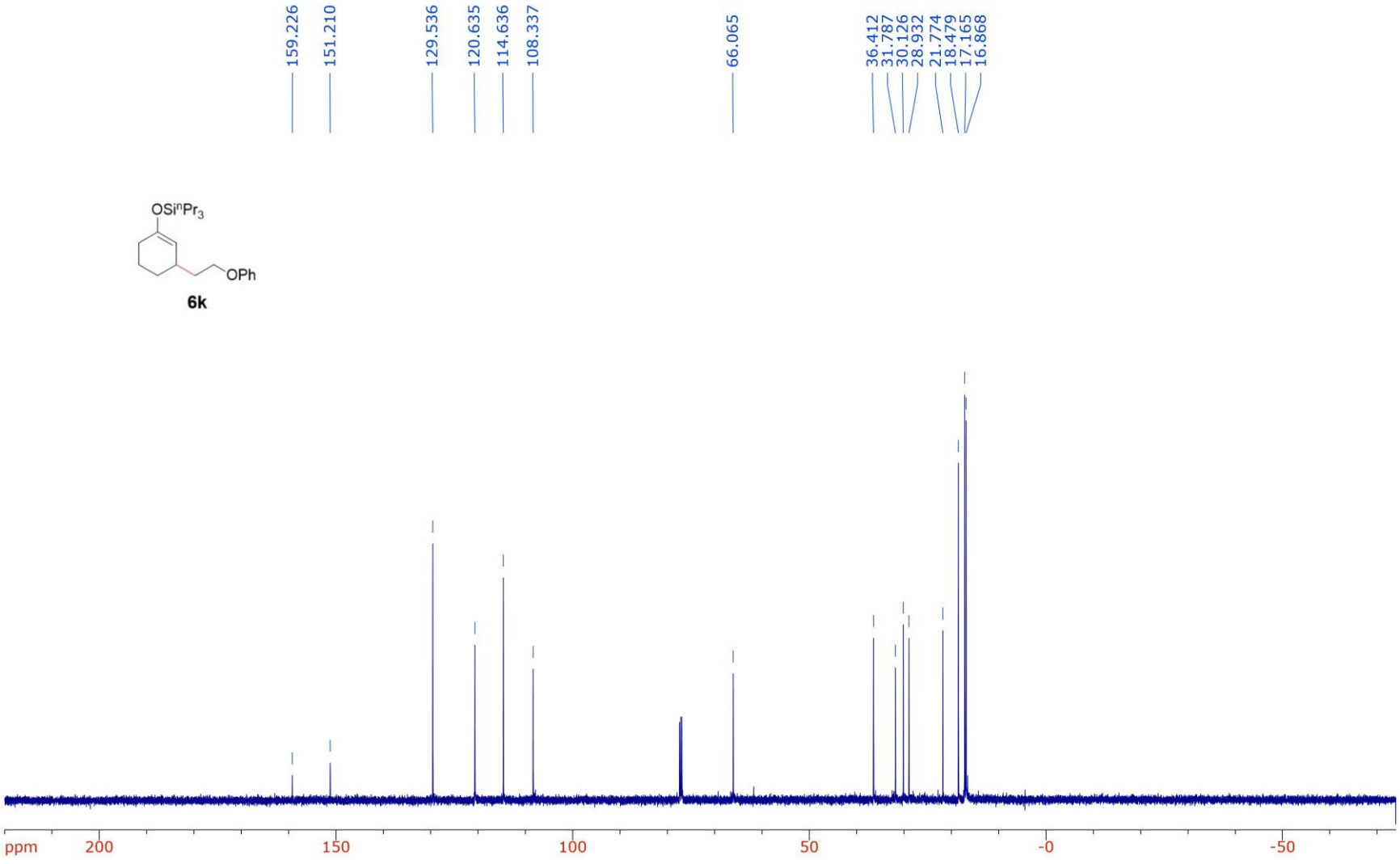
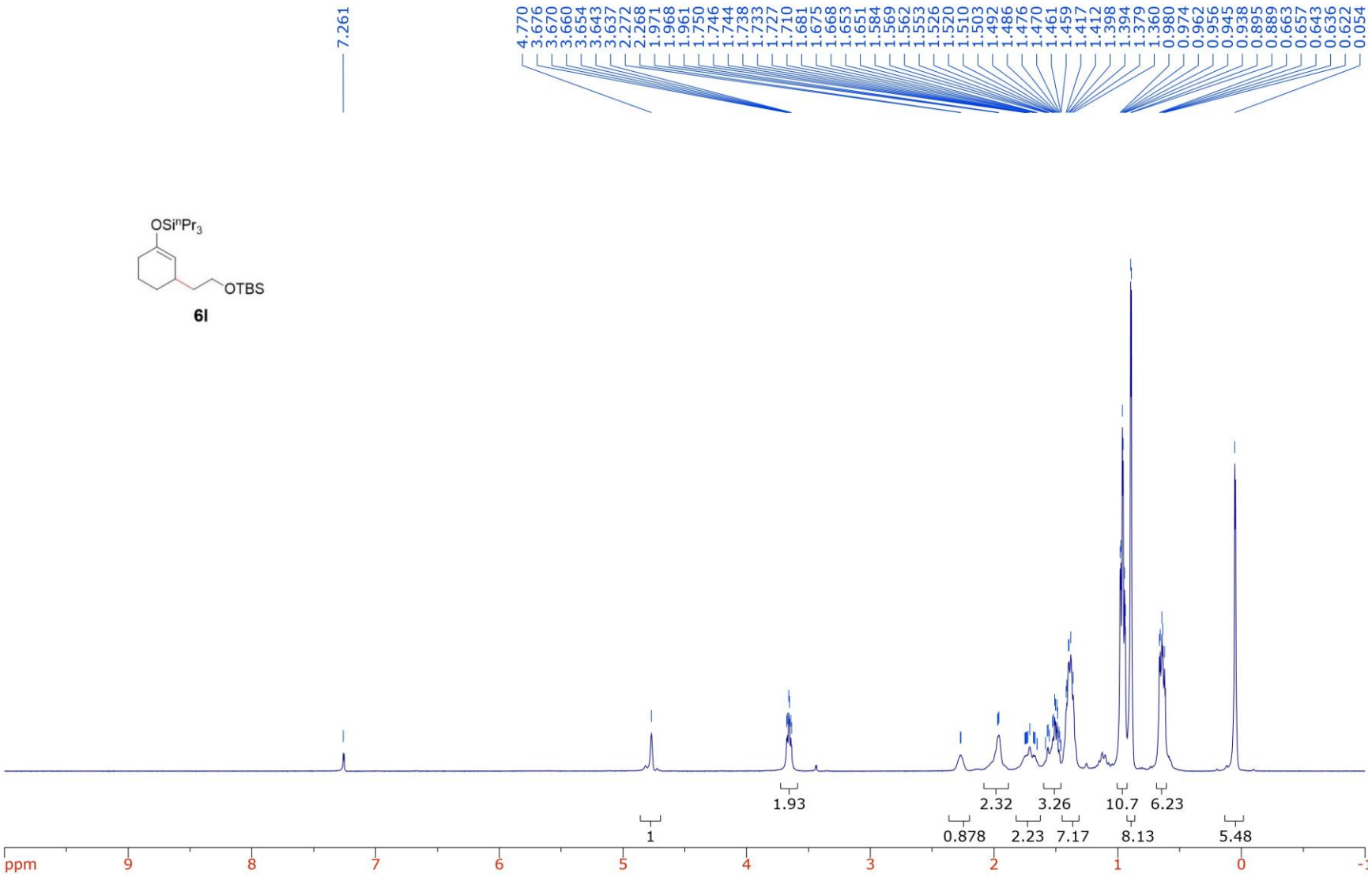
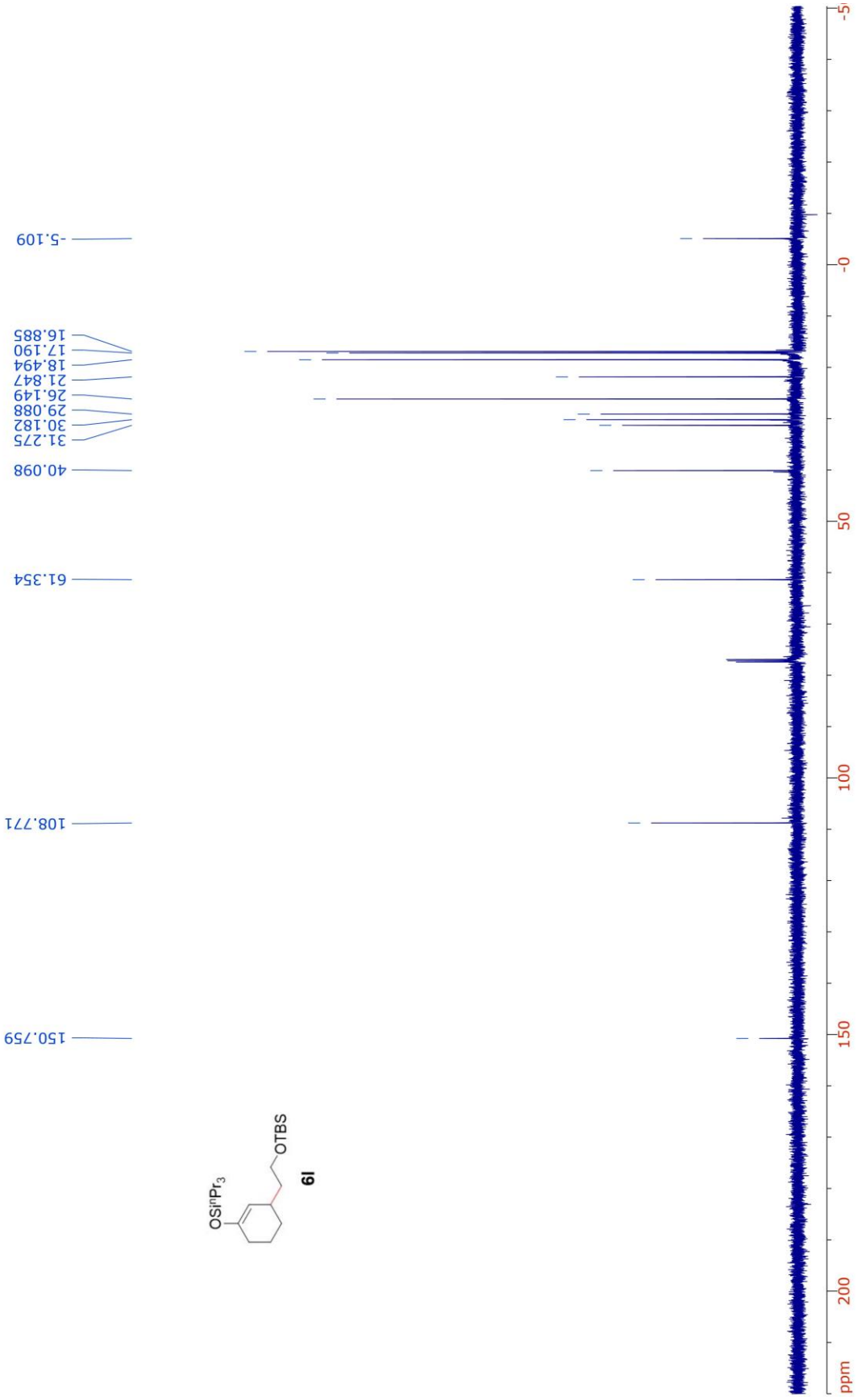
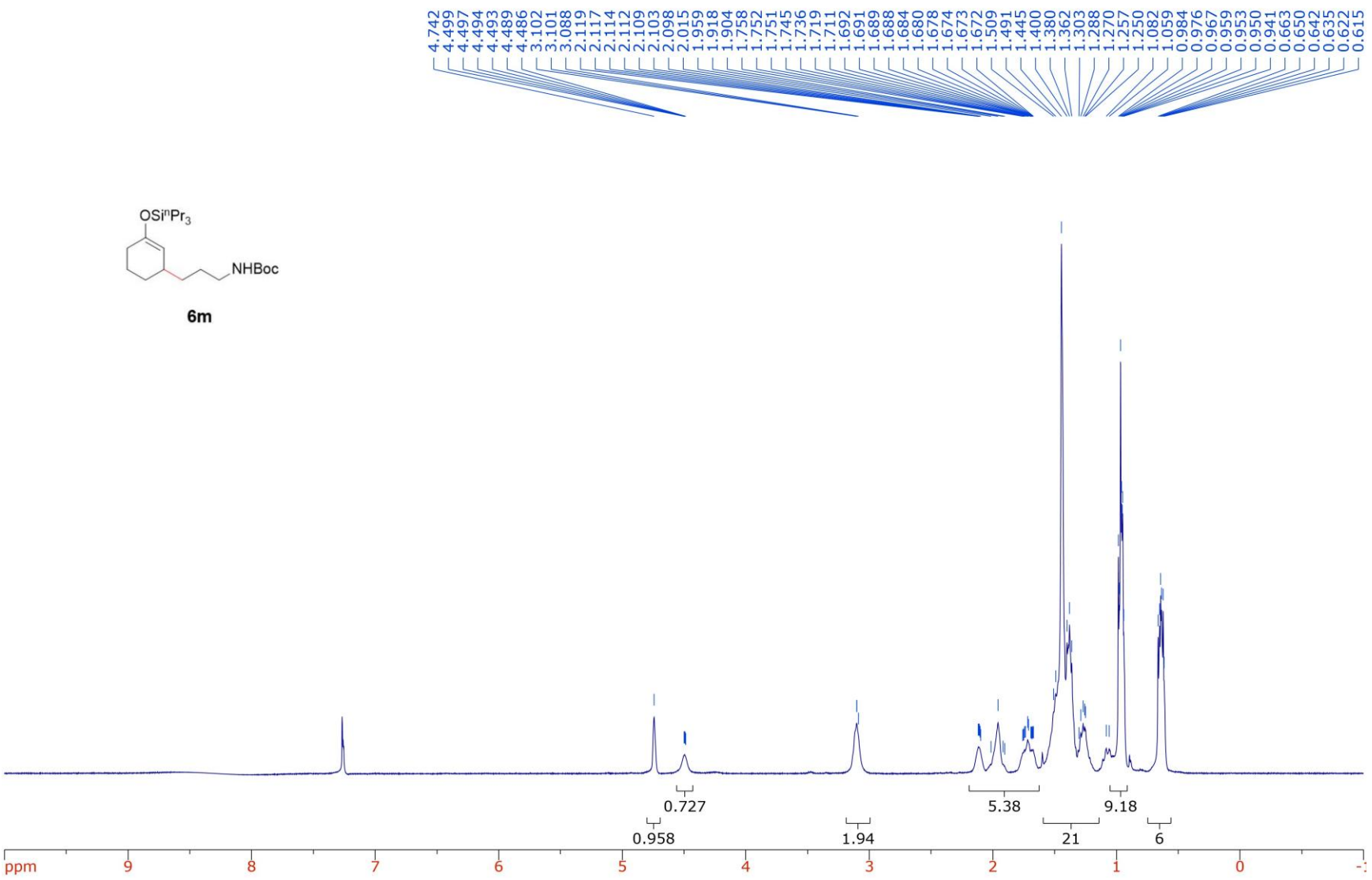
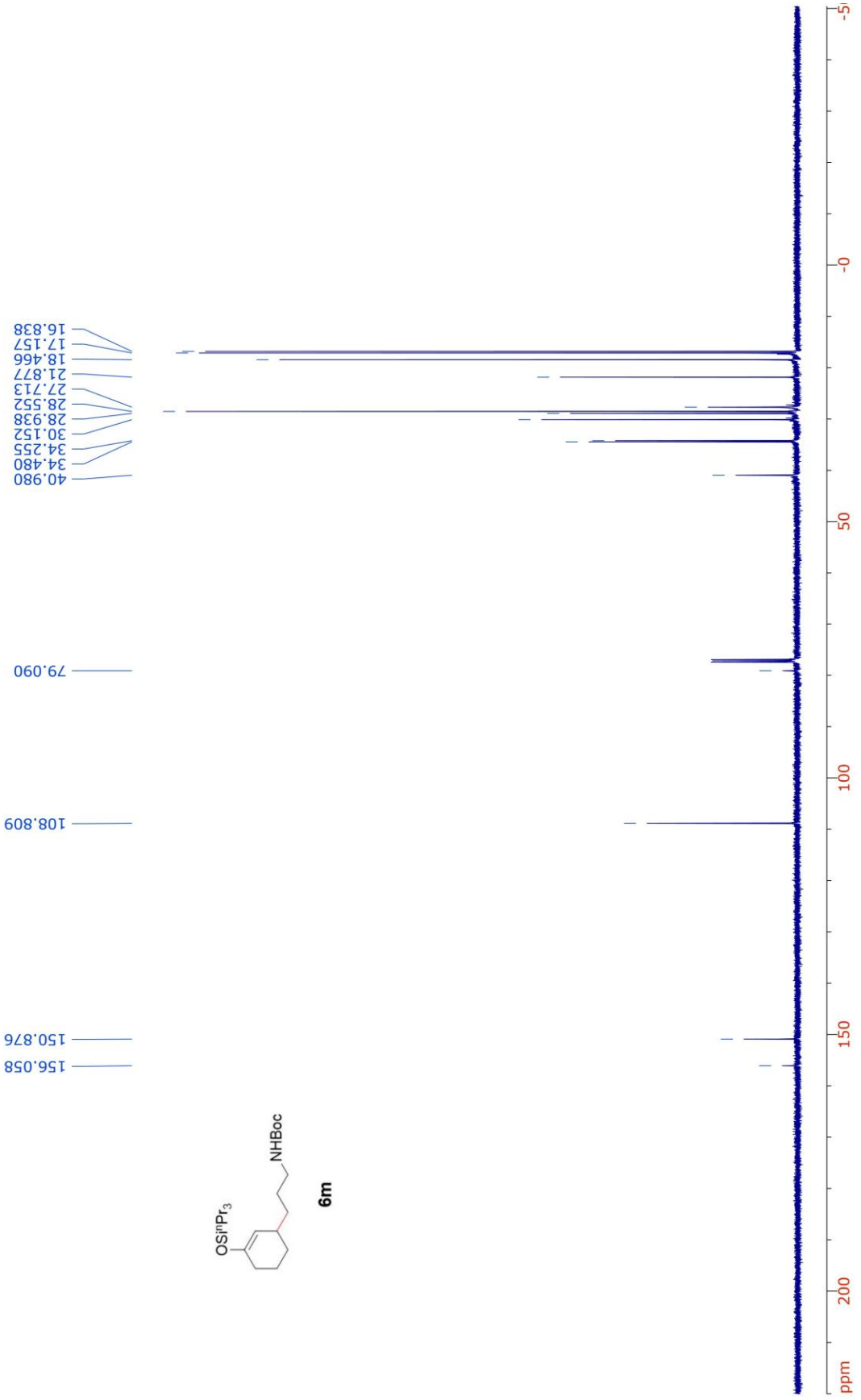
0.656
0.650
0.648
0.636
OSi^{n}Pr$_3$
OPh
6k
2.97
2.01
1.88
1.12
1.06
6
2.2
0.778
0.782
3.63
6.23
9.13
ppm
9
8
7
6
5
4
3
2
1
0
-1

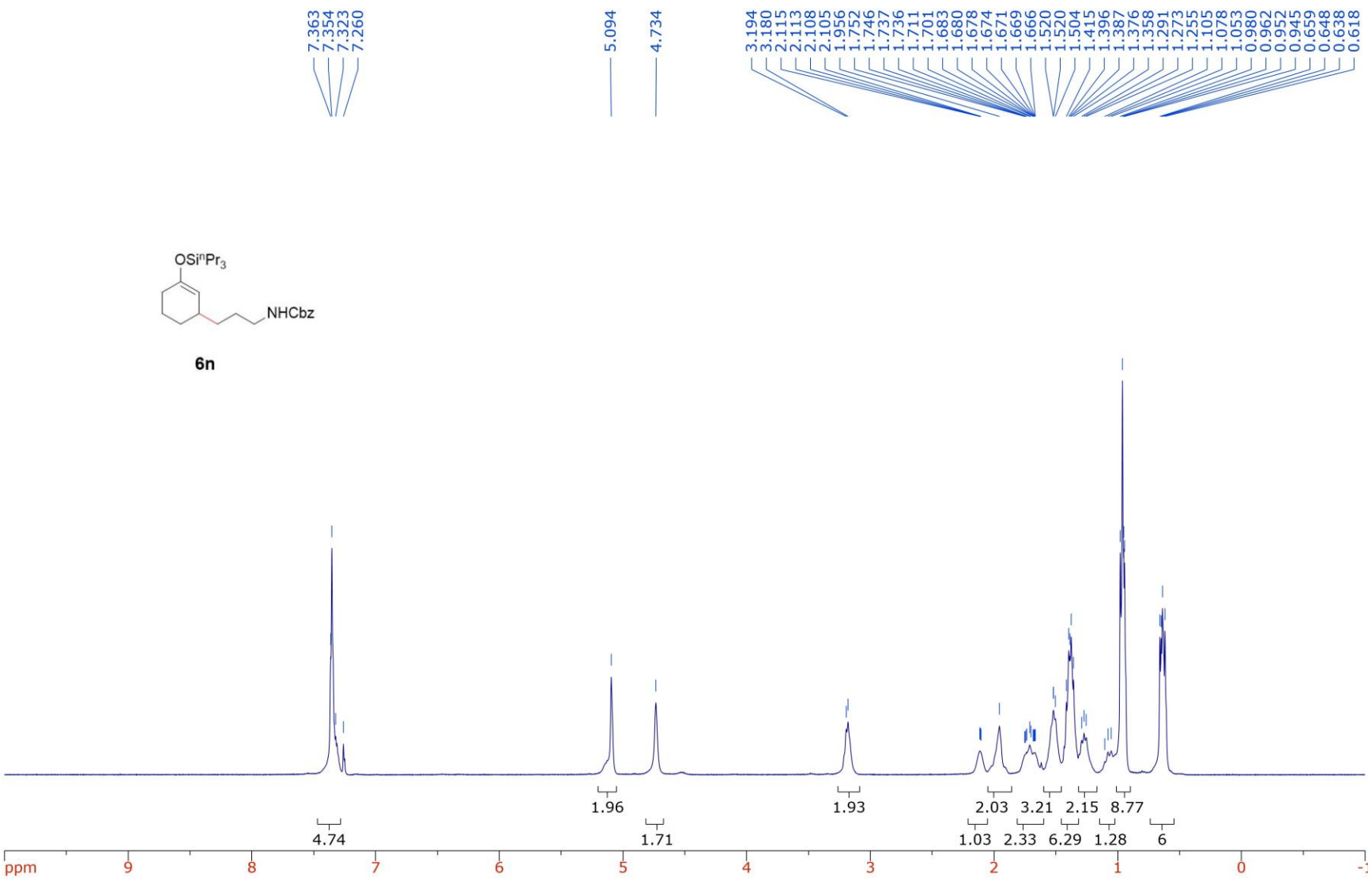

159.226
151.210
129.536
120.635
114.636
108.337
66.065
36.412
31.787
30.126
28.932
21.774
18.479
17.165
16.868
OSi^{n}Pr$_3$
OPh
6k
ppm
200
150
100
50
-0
-50

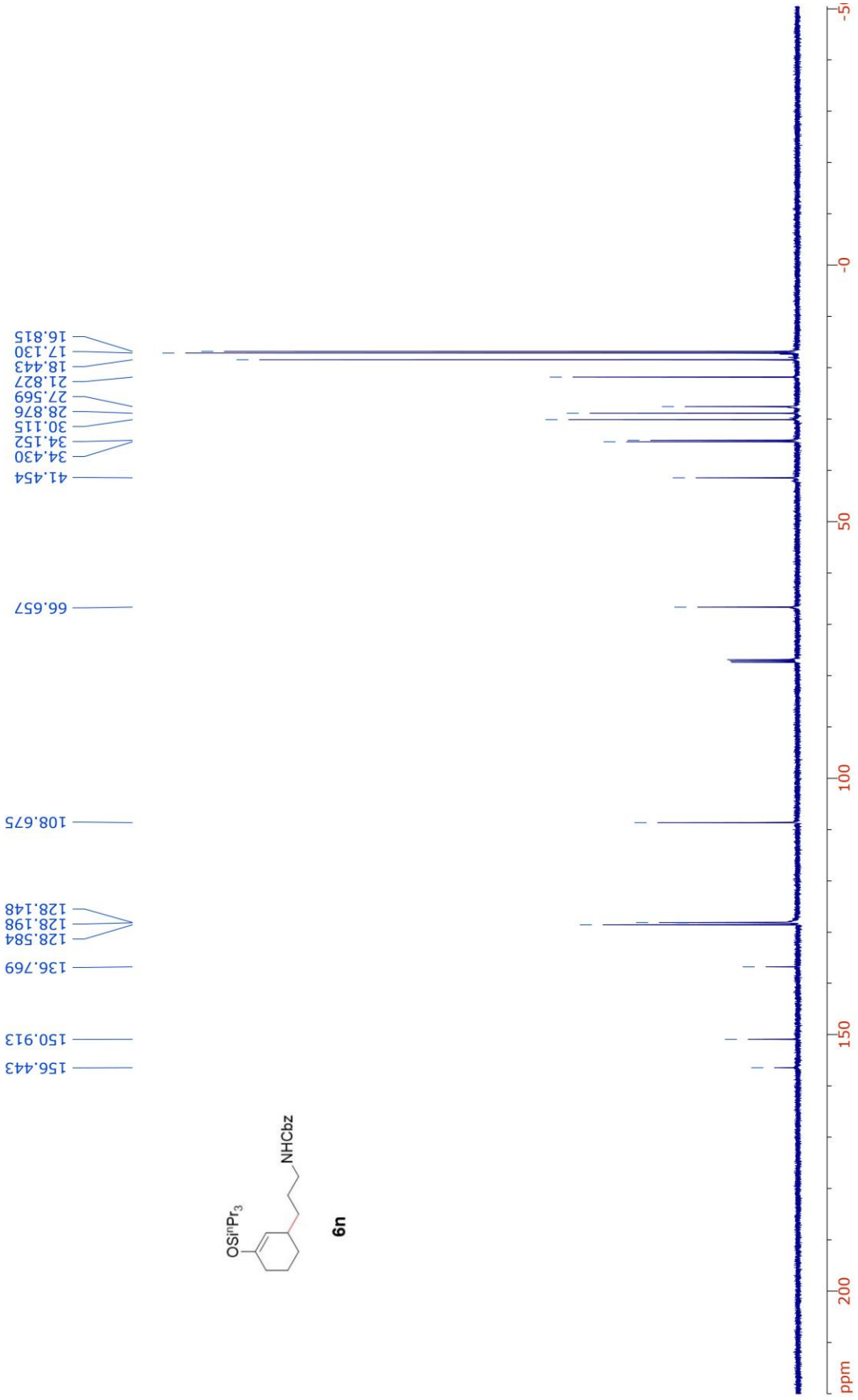

7.261
4.770
3.676
3.670
3.660
3.654
3.643
3.637
2.272
2.268
1.971
1.968
1.961
1.750
1.746
1.744
1.738
1.733
1.727
1.710
1.681
1.675
1.668
1.653
1.651
1.584
1.569
1.562
1.553
1.526
1.520
1.510
1.503
1.492
1.486
1.476
1.470
1.461
1.459
1.417
1.412
1.398
1.394
1.379
1.360
0.980
0.974
0.962
0.956
0.945
0.938
0.895
0.889
0.663
0.657
0.643
0.636
0.622
0.054
OSi^{n}Pr$_3$
OTBS
6l
1.93
2.32
3.26
10.7
6.23
1
0.878
2.23
7.17
8.13
5.48
ppm
9
8
7
6
5
4
3
2
1
0

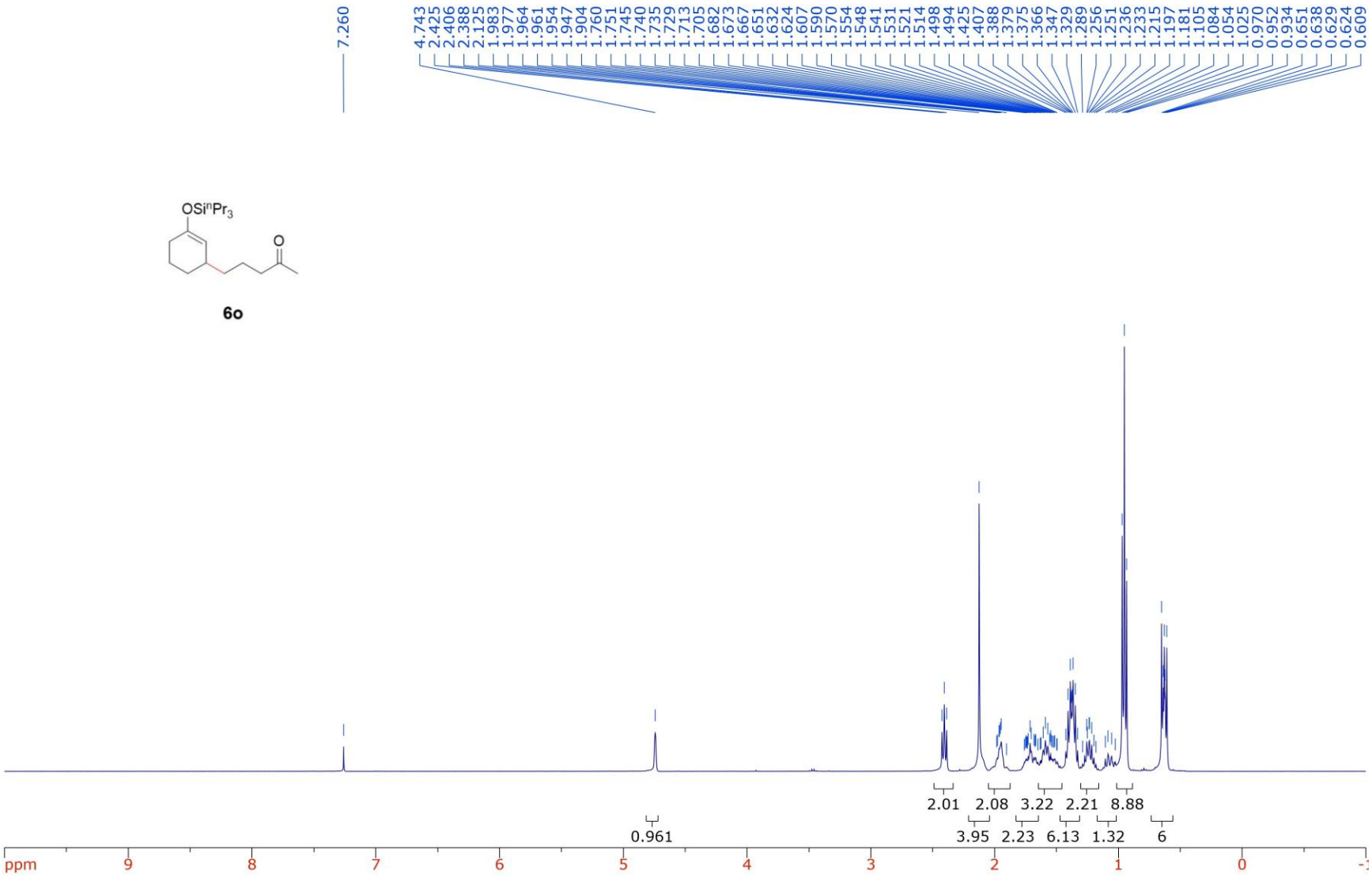

-5.109
16.885
17.190
18.494
21.847
26.149
29.088
30.182
31.275
40.098
61.354
108.771
150.759
OTBS
OSiiPr3
6l
ppm


4.742
4.499
4.497
4.494
4.493
4.489
4.486
3.102
3.101
3.088
2.119
2.117
2.114
2.112
2.109
2.103
2.098
2.015
1.959
1.918
1.904
1.758
1.752
1.751
1.745
1.736
1.719
1.711
1.692
1.691
1.689
1.688
1.684
1.680
1.678
1.674
1.673
1.672
1.509
1.491
1.445
1.400
1.380
1.362
1.303
1.288
1.270
1.257
1.250
1.082
1.059
0.984
0.976
0.967
0.959
0.953
0.950
0.941
0.663
0.650
0.642
0.635
0.622
0.615
OSi^{n}Pr$_3$
NHBoc
6m
0.727
5.38
9.18
0.958
1.94
21
6
ppm
9
8
7
6
5
4
3
2
1
0


16.838
17.157
18.466
21.877
27.713
28.552
28.938
30.152
34.255
34.480
40.980
79.090
108.809
150.876
156.058
NHBoc
OSiiPr3
6m
ppm


7.363
7.354
7.323
7.260
5.094
4.734
3.194
3.180
2.115
2.113
2.108
2.105
1.956
1.752
1.746
1.737
1.736
1.711
1.701
1.683
1.680
1.678
1.674
1.671
1.669
1.666
1.520
1.520
1.504
1.415
1.396
1.387
1.376
1.358
1.291
1.273
1.255
1.105
1.078
1.053
0.980
0.962
0.952
0.945
0.659
0.648
0.638
0.618
OSi^{n}Pr$_3$
NHCbz
6n
1.96
1.93
2.03
3.21
2.15
8.77
4.74
1.71
1.03
2.33
6.29
1.28
6
ppm
9
8
7
6
5
4
3
2
1
0


16.815
17.130
18.443
21.827
27.569
28.876
30.115
34.152
34.430
41.454
66.657
108.675
128.148
128.198
128.584
136.769
150.913
156.443
ppm
-5
0
50
100
150
200
NHCbz
OSiiPr3
6n


7.260
4.743
2.425
2.406
2.388
2.125
1.983
1.977
1.964
1.961
1.954
1.947
1.904
1.760
1.751
1.745
1.740
1.735
1.729
1.713
1.705
1.682
1.673
1.667
1.651
1.632
1.624
1.607
1.590
1.570
1.554
1.548
1.541
1.531
1.521
1.514
1.498
1.494
1.425
1.407
1.388
1.379
1.375
1.366
1.347
1.329
1.289
1.256
1.251
1.236
1.233
1.215
1.197
1.181
1.105
1.084
1.054
1.025
0.970
0.952
0.934
0.651
0.638
0.629
0.624
0.609
OSi^{n}Pr$_3$
O
6o
2.01
2.08
3.22
2.21
8.88
0.961
3.95
2.23
6.13
1.32
6
ppm
9
8
7
6
5
4
3
2
1
0
-1

209.123
150.836
108.738
44.089
36.657
34.566
30.142
29.920
28.855
21.854
21.458
18.433
17.134
16.821
ppm
200
150
100
50
-0
-50
OSiiPr3
O
6o