Reductive Conjugate Addition of Haloalkanes to Enones to Form Silyl Enol Ethers

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Supporting Information

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I. Chemicals:

Nickel Sources:

$Ni(acac)_2$ (Strem Chemicals) and $Ni(cod)_2$ (Strem Chemicals) were used as received. $NiCl_2$(glyme) (Aldrich) was purchased commercially or synthesized according to the literature procedure[1]. The stoichiometry of the $NiCl_2$(glyme) was found to be variable and the glyme is easily lost upon exposure to vacuum. Molecular weight of $NiCl_2$(glyme) was corrected for the actual amount of glyme present as determined by elemental analysis. In cases of unknown stoichiometry of $NiCl_2$(glyme) 1:1 adduct of nickel:glyme (molecular weight = 219.71) may be assumed. A slight excess of either nickel or ligand does not diminish yields. The nickel salts were either stored in a Vacuum Atmospheres nitrogen filled glove box or stored on benchtop in a desiccator over drierite.

Ligands:

Pyridine, anhydrous, 99.8% (Aldrich), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (Aldrich) and 4,4′,4″-tri-tert-butyl-2,2′:6′,2″-terpyridine (Aldrich) were purchased from Aldrich and used as received or synthesized according to the literature procedures[2]. The ligands were either stored in a Vacuum Atmospheres nitrogen filled glove box or stored on benchtop in a desiccator over drierite.

Reducing Agents: Manganese powder -325 mesh (Aldrich), zinc dust -325 mesh (Aldrich), and tetrakis(dimethylamino)ethylene (Aldrich) were used as received.

Enones/enals:

2-cyclohexen-1-one (Alfa Aesar), 2-cyclopenten-1-one (Aldrich), 2-cyclohepten-1-one (Aldrich), *trans*-2-methyl-2-butenal (TCI America), 3-methyl-3-penten-2-one (TCI America) were used as received. 2-bromo-cyclohexen-1-one was prepared using literature procedure[3] and stored under nitrogen at -30 ^{o}C.

Alkyl halides:

2-bromoheptane (Aldrich), bromocyclooctane (Aldrich), bromocycloheptane (Aldrich), 4-bromo-tetrahydropyran (Frontier Scientific), 2-bromo-2-methylpropane (Aldrich), were used as received. 2-iodoheptane[4], 2-bromoethylbutyrate[5], 3-bromoheptane[6], 2-bromopentanenitrile[7] were prepared using literature procedures. 2-iodoheptane, and 1-iodo-2,2-dimethylpropane (Aldrich) were filtered through a short, dry, activated basic alumina pad (1.5 cm) under nitrogen before use.

Silylating Reagents:

All silyl reagents were purchased from Gelest and stored in a Vacuum Atmospheres nitrogen filled glove box. For reactions set up on benchtop, the required amount of silyl reagent was removed from glove box in a sealed vial every time before use.

Solvents:

Anhydrous solvents: 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, Aldrich), *N,N*-dimethylacetamide (DMAc, Aldrich), dimethyl sulfoxide (DMSO, Aldrich), 1-methyl-2-pyrrolidinone (NMP, Fluka) were used as received. Anhydrous tetrahydrofuran and pentane were prepared from ACS grade, inhibitor free solvents by passage through activated alumina and molecular sieves in a Vacuum Atmospheres solvent purification system. Anhydrous *N,N*-dimethylformamide (DMF) and acetonitrile were prepared from ACS grade, inhibitor free solvent by passage though activated alumina and molecular sieves in a Glass Contour solvent purification system. All solvents were stored in a Vacuum Atmospheres glove box in an amber bottle over 4 Å molecular sieves. Water content was routinely measured using Karl-Fisher titration (Metrohm) and was less than 30 ppm.

Other Reagents:

Dodecane (Aldrich) was purchased commercially and used without further purification, *p*-Tolualdehyde (Aldrich) was freshly distilled and stored under nitrogen.

II. Methods

NMR Spectroscopy:

^{1}H and ^{13}C NMR spectra were recorded on a Bruker model Avance-500 MHz (126 MHz, ^{13}C) NMR spectrometers operating at 500.13 MHz proton NMR frequency, and data analysis was performed using the iNMR software package (version 3.6.0, Nucleomatica, September 2010). NMR chemical shifts are reported in ppm and referenced to the residual solvent peak $CDCl_3$ (δ = 7.26 ppm, ^{1}H; δ = 77.16 ppm ^{13}C) as an internal standard unless otherwise noted. Chemical shifts are reported in parts per million (ppm), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), dm (doublet of multiplet), td (triplet of doublets), qd (quartet of doublets), dq (doublet of quartet), ddd (doublet of doublet of doublet), m (multiplet) and br (broad). 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 with hydrogen as the carrier gas. The analysis method used in all cases was 1 µL inj. of sample, inj. temp of 300 ºC, 100:1 split ratio, 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. Initial oven temperature of 50 ºC was held for 0.46 min followed by a temperature ramp up to 300 ºC at 65 ºC/min and finally the temperature was held at 300 ºC for 0.69 min. Total run time was ~ 5 min. FID temperature was 325 ºC.

Gas Chromatography Mass Spectroscopy:

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 the carrier gas. The analysis method used in all cases was 5 µL inj. of sample, inj. temp of 225 ºC, 25:1 split ratio, 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 ºC, and the electron impact (EI, 30 eV) ion source was held at 250 ºC. Initial oven temperature was held at 50 ºC for 3 min with the detector off followed by a temperature ramp, with the detector on, to 280 ºC at 40 ºC/min, and finally the temperature was held at 280 ºC for 3 min. Total run time was 11.75 min. Data are reported in the form of m/z (intensity relative to the base peak = 100, ion).

High Resolution Mass Spectrometry:

High resolution mass spectra (HRMS) under chemical ionization methods using methane gas were obtained from Chemistry Mass Spectrometry Facility at SUNY at Buffalo.

Thin Layer / Column Chromatography:

Thin layer chromatography was performed on EMD Chemcials TLC Silica Gel 60 F_{254} plates. Visualization was accomplished with *p*-anisaldehyde or phosphomolybdic acid (PMA) stains.

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 for complex **10** 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 Haloalkanes to Electrophilic Olefins

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

This procedure was used for optimization experiments and control reactions (Table 1 and other optimization experiments).

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 the required amount of appropriate metal complex and ligand followed by solvent, haloalkane, electrophilic olefin, silylating reagent, Mn^0, and dodecane (10.0 µL internal standard). The reaction vials were capped with a PTFE-faced silicone septum, removed from the glove box and heated in a reaction block on the benchtop with stirring at 1200 rpm. After 17-24 h reaction time, 10 µL aliquots of reaction mixture were removed with a 50 µL gas-tight syringe and quenched with 10 µL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography and percent yield was calculated versus the dodecane internal standard.

(B) Procedure for reactions set up on bench and run under air.

This procedure was used for isolation purposes (Scheme 1)

No precautions were taken to exclude air from the reaction vessel but anhydrous DMF was used as the solvent. Reactions were set up in oven-dried 1-dram vials and a dry gas-tight syringe was used.

On the benchtop, $Ni(acac)_2$ (10.3 mg, 0.04 mmol, 0.04 equiv), 2,2':6',2''-tri-*tert*-butyl-terpyridine (16.1 mg, 0.04 mmol, 0.04 equiv), solid substrates and manganese powder (110 mg, 2.00 mmol, 2.00 equiv) were weighed directly into an oven-dried 1 dram vial equipped with an oven-dried teflon-coated stir bar. DMF (2 mL), haloalkane and electrophilic olefin were added using an automatic pipet. The vial was then capped with a PTFE-faced silicone septum, and silylating reagent was injected into the vial using a dry 250 µL gas-tight syringe. The reaction vial was placed in a 40 ºC reaction block with stirring at 1200 rpm.

The reaction progress was followed by GC analysis. At appropriate times 10 µL aliquots of reaction mixture were removed with a 50 µL gas-tight syringe and quenched with 10 µL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography.

Upon completion (judged as <1 Area % of starting materials remaining by GC analysis) the reaction mixture was filtered though a short plug of silica gel treated with 0.1% Et_3N to remove metal salts, eluted with diethyl ether, concentrated under reduced pressure, and purified by column chromatography (SiO_2). Column fractions were analyzed by TLC using *p*-anisaldehyde or phosphomolybdic acid stain for visualization. In cases where mixed fractions of the desired product were obtained, the mixed fractions were combined, concentrated under reduced pressure and the residue was resubjected to column chromatography. The purity of the desired product was determined by gas chromatography and ^1H NMR spectroscopy.

IV. Procedures for Deprotection of Silyl Enol Ether Products

(A) Procedure for deprotection of pure silyl enol ether product.

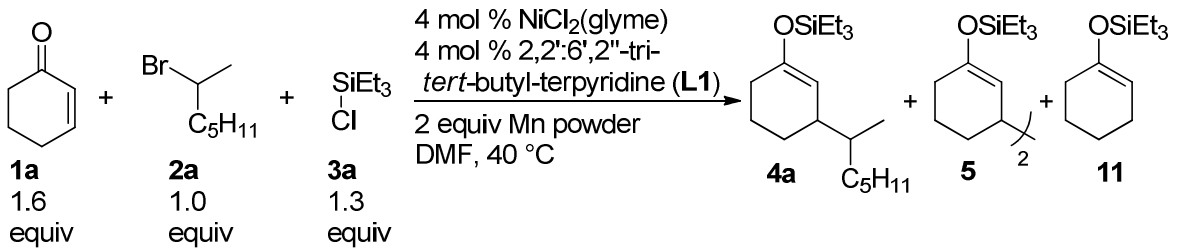
General procedure **B** was followed to obtain pure silyl enol ether product. The pure product obtained was treated with 2 mL of 2 M HCl and heated to 40 ºC with stirring at 1200 rpm for 8 h. The reaction mixture was extracted with diethyl ether (3 x 5 mL). Organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography. Column fractions were analyzed by TLC using phosphomolybdic acid stain for visualization. The purity of the desired product was determined by gas chromatography and ^{1}H NMR spectroscopy.

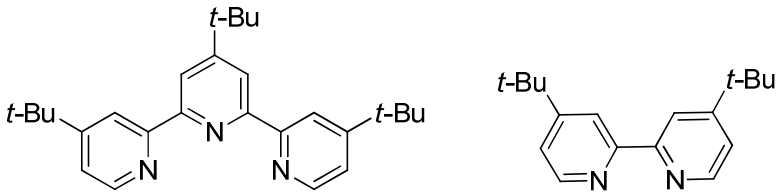
(B) Procedure for deprotection of silyl enol ether product from a crude reaction mixture.

General procedure **B** was followed with the desired olefin, haloalkane and a trialkylsilyl chloride reagent. Upon completion (judged as <1 Area % of starting materials remaining by GC analysis) the reaction mixture was filtered though a short plug of silica gel (5 cm x 1 cm) treated with 0.1% Et_3N and eluted with diethyl ether. The filtrate was concentrated under reduced pressure. The resulting residue was treated with 2 mL of 2 M HCl and heated to 40 ºC with stirring at 1200 rpm for 8 h. The reaction mixture was extracted with diethyl ether (3 x 5 mL). Organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography (SiO_2). Column fractions were analyzed by TLC using phosphomolybdic acid stain for visualization. The purity of the desired product was determined by gas chromatography and ^{1}H NMR spectroscopy

V. Optimization Experiments and Control Reactions

Table S1: Reductive Coupling of 2-Cyclohexen-1-one (**1a**) with 2-Bromoheptane (**2a**).[a]

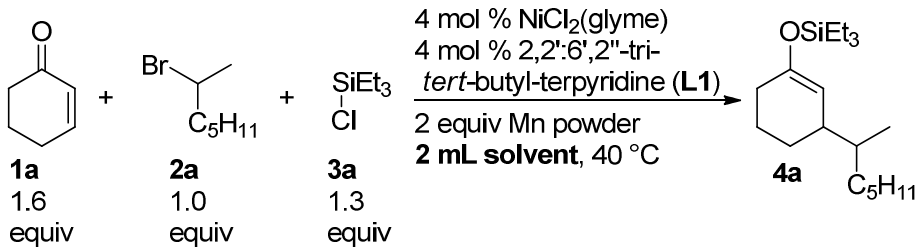




Entry	Change From Optimal Conditions	Yield **4a** (%)[b]	Amount of SM left[c]		Ratio
			% **1a**	% **2a**	**4a**:**5**:**11**[d]
1	none	76	8	0	72:22:6
2	no ligand (omit **L1**)	6	76	85	25:25:50
3	4-12 mol % pyridine in place of **L1**	5 – 7	36	83	14:56:30
4	4 mol % **L2** in place of **L1**	15	10	25	30:60:10
5	no triethylsilyl chloride (**3a**)	4[e]	3	0	--
6	no nickel	3	86	87	50:0:50
7	$Ni(acac)_2$ in place of $NiCl_2$(glyme)	77	20	0	73:18:9
8	no Mn powder	No reaction	--	--	--
9	1.2 – 1.4 equiv of **1a** to 1.0 equiv of **2a**	66 – 74	0-10	0	69:25:6
10	1.2 – 1.6 equiv of **2a** to 1.0 equiv of **1a**	65 – 68	0	0	67:25:8
11	1 mol % $NiCl_2$(glyme) and **L1**	77	0	0	72:16:12
12	10 mol% $NiCl_2$(glyme) and **L1**	33	0	0	29:34:19

[a] General procedure **A** was followed, reactions were run on 0.5 mmol scale for 14-36 h.
[b] Uncorrected GC yield vs the dodecane internal standard, mixture of region- and stereo-isomers.
[c] Corrected GC% vs the dodecane internal standard. [d] Ratio of products by GC analysis, uncorrected. [e] Ketone product obtained instead of enol ether **4a**.

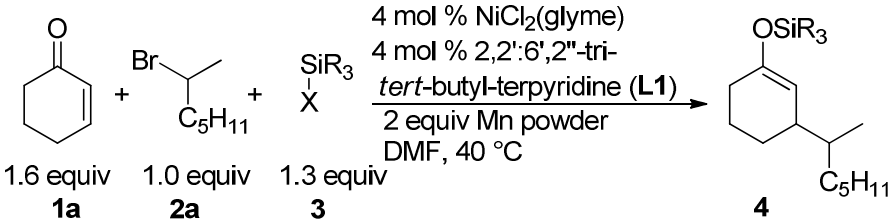
Table S2: Solvent Effects[a]



Entry	Solvent	Yield **4a** (%)[b]
1	DMF (Standard Condition)	76
2	DMPU	51
3	DMI	47
4	DMAc	69
5	DMSO	0
6	NMP	8
7	THF	46
8	MeCN	5
9	1,4-dioxane	11

[a] General procedure **A** was followed, reactions were run on 0.5 mmol scale for 24 h and monitored by GC analysis. [b] Uncorrected GC yield vs the dodecane internal standard.

Table S3: Effect of Silylating Reagent on Reductive Conjugate Addition[a]

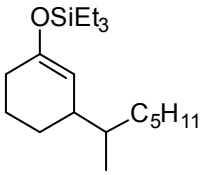


Entry	Silyl Reagent R_3SiX (**3**)	Yield **4** (%)[b]
1	Me_3SiOTf	<5
2	Me_3SiCl	35
3	$(Me_3Si)_2NH$	<5
4	$(Me_3Si)NHCHOSiMe_3$	<5
5	$Et(Me)_2SiCl$	42
6	*n*-$Bu(Me)_2SiCl$	58
7	Et_3SiCl (Standard Condition)	76
8	Et_3SiOTf	13
9	*i*-$Pr(Me)_2SiCl$	71
10	*n*-Pr_3SiCl	95
11	*t*-$Bu(Me)_2SiCl$	39
12	*t*-$Bu(Me)_2SiOTf$	27
13	*i*-Pr_3SiCl	45
14	*i*-Pr_3SiOTf	52
15	*t*-$Bu(Ph)_2SiCl$	34

[a] General procedure **A** was followed, reactions were run on 0.5 mmol scale for 24 h and monitored by GC analysis. [b] Uncorrected GC yield vs the dodecane internal standard.

VI. Reductive Coupling Reactions (Isolations and Characterizations)

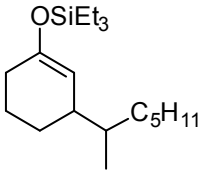
Triethyl((3-heptan-2-yl)cyclohex-1-en-1-yl)oxy)silane (4a) (Scheme 1)



General procedure **B** was followed with 2-cyclohexen-1-one (155 µL, 1.60 mmol, 1.60 equiv), 2-bromoheptane (188 µL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (218 µL, 1.30 mmol, 1.30 equiv). After 17 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil as a mixture of regio- and stereoisomers. The minor regioisomer was determined to be triethyl((3-heptan-3-yl)cyclohex-1-en-1-yl)oxy)silane.

Data for **4a**, Scheme 1
Yield: Run 1 (224 mg, 72%)
Yield: Run 2 (220 mg, 71%)
Average yield: 72%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 4.74 (d, *J* = 7.4 Hz, 1H), 2.15-1.78 (m, 4H), 1.59-1.49 (m, 2H), 1.39-1.04 (m, 10H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.81 (dd, *J* = 6.7, 9.4 Hz, 3H), 0.68-0.64 (q, *J* = 7.9 Hz, 6H)
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 151.1, 150.8, 108.8, 107.5, 40.3, 40.0, 37.8, 37.7, 34.3, 33.9, 32.4, 30.2 (2C), 27.5, 27.4, 26.1, 24.4, 22.9, 22.8, 16.7, 16.2, 14.3, 6.9, 5.2
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
309.25 (0.96, M^+), 211.10 (100, M^+- C_7H_{15}), 115.05 (20.55, M^+- $C_{13}H_{23}O$), 87.00 (29.15, M^+-$C_{13}H_{23}OSi$)
TLC: R_f 0.6 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde stain]
HRMS (CI):
Calc. for $C_{19}H_{39}OSi$ $[M + 1]^+$: 311.2765; Found: 311.2767

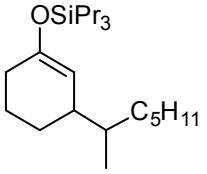
Triethyl((3-heptan-2-yl)cyclohex-1-en-1-yl)oxy)silane (4a) (Scheme 1, gram scale)



General procedure **B** was followed. On the benchtop, $Ni(acac)_2$ (103 mg, 0.40 mmol, 0.04 equiv), 2,2':6',2''-tri-*tert*-butyl-terpyridine (161 mg, 0.40 mmol, 0.04 equiv), and manganese powder (1.10 g, 20.0 mmol, 2.00 equiv) were added to an oven-dried 20 mL scintillation vial equipped with an oven-dried teflon-coated stir bar. DMF (15 mL), 2-cyclohexen-1-one (1.54 mL, 16.0 mmol, 1.60 equiv), 2-bromoheptane (1.88 mL, 10.0 mmol, 1.00 equiv) and chlorotriethylsilane (2.18 mL, 13.0 mmol, 1.30 equiv) were added. The vial was then capped with a polyseal cap and heated to 40 ºC in an oil bath with stirring at 1200 rpm. After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 5 cm) and eluted with ether (250 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (20 cm x 7 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil (2.27 g, 73% yield) as a mixture of regio- and stereoisomers. Data matched those reported for **4a**, Scheme 1. The minor regioisomer was determined to be triethyl((3-heptan-3-yl)cyclohex-1-en-1-

yl)oxy)silane.

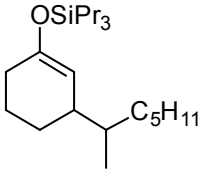
((3-(Heptan-2-yl)cyclohex-1-en-1-yl)oxy)tripropylsilane (4b) (Scheme 1).



General procedure **B** was followed with 2-cyclohexen-1-one (155 µL, 1.60 mmol, 1.60 equiv), 2-bromoheptane (188 µL, 1.00 mmol, 1.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 17 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil as a mixture of regio- and stereoisomers. The minor regioisomer was determined to be ((3-(heptan-3-yl)cyclohex-1-en-1-yl)oxy)tripropylsilane by independent synthesis of authentic product and comparison of GC and NMR data (page S23).

Data for **4b**, Scheme 1
Yield: Run 1 (289 mg, 82%)
Yield: Run 2 (302 mg, 86%)
Average yield: 84%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 4.72-4.71 (m, 1H), 2.30-1.76 (m, 4H), 1.59-1.49 (m, 2H), 1.41 (dt, *J* = 16.1, 7.8 Hz, 6H), 1.36-1.07 (m, 10H), 0.970 (t, *J* = 7.3 Hz, 9H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 7.1 Hz, 3H), 0.67-0.63 (m, 6H).
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 151.2, 150.9, 108.6, 107.4, 40.3, 40.0, 37.8, 37.7, 34.3, 33.9, 32.4, 30.3, 30.2 , 27.5 (2C), 26.1, 24.5, 22.9 (2C), 22.7, 18.5, 17.2, 16.9, 16.7, 16.3, 14.3
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
352.32 (<1.00, M^+), 253.10 (100, M^+- C_7H_{15}), 157.10 (13.55, M^+- $C_{13}H_{23}O$), 99.00 (2.02, M^+-$C_{15}H_{29}OSi$), 87.00 (11.46, $C_{13}H_{23}OSi$)
TLC: R_f 0.5 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde stain]
HRMS (CI):
Calc. for $C_{22}H_{45}OSi$ $[M + 1]^+$: 353.3234; Found: 353.3239

((3-(Heptan-2-yl)cyclohex-1-en-1-yl)oxy)tripropylsilane (4b) (Scheme 1, from R^1-I).

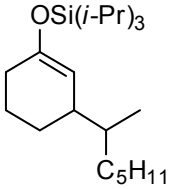


General procedure **B** was followed with 2-cyclohexen-1-one (155 µL, 1.60 mmol, 1.60 equiv), 2-iodoheptane (226 mg, 1.00 mmol, 1.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 2 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil as a mixture of regio- and stereoisomers. The minor regioisomer was determined to be ((3-(heptan-3-yl)cyclohex-1-en-1-yl)oxy)tripropylsilane by independent synthesis of authentic product and comparison of GC and NMR data.

Data for **4b**, Scheme 1
Yield: Run 1 (250 mg, 71 %)

Yield: Run 2 (250 mg, 71 %)
Average yield: 71%
Characterization data matched those reported for **4b**, Scheme 1.

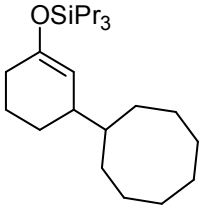
((3-(Heptan-2-yl)cyclohex-1-en-1-yl)oxy)triisopropylsilane (4c) (Scheme 1).



General procedure **B** was followed with 2-cyclohexen-1-one (155 µL, 1.60 mmol, 1.60 equiv), 2-bromoheptane (188 µL, 1.00 mmol, 1.00 equiv) and triisopropylsilyl triflate (349 µL, 1.30 mmol, 1.30 equiv). After 17 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil as a mixture of regio and stereoisomers.

Data for **4c**, Scheme 1
Yield: Run 1 (183 mg, 52%)
Yield: Run 2 (186 mg, 53%)
Average yield: 53%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 4.75 (d, *J* = 3.0 Hz, 1H), 2.13-1.77 (m, 4H), 1.60-1.49 (m, 2H), 1.38-1.13 (m, 13H), 1.09-1.04 (m, 19H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.81 (dd, *J* = 7.8, 6.8 Hz, 2H).
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 151.3, 151.0, 108.2, 107.0, 40.4, 40.1, 37.9, 37.7, 34.3, 33.9, 32.4, 30.2 (2C), 27.5, 27.4, 26.1, 24.5, 22.9, 22.8 (2C), 18.2, 16.7, 16.3, 14.3, 12.8
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
352.32 (<1.00, M^+), 253.10 (100, M^+- C_7H_{15}), 157.10 (14.44, M^+- $C_{13}H_{23}O$), 99.00 (1.65, M^+-$C_{15}H_{29}OSi$), 87.00 (11.68, $C_{13}H_{23}OSi$)
TLC: R_f 0.5 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde stain]
HRMS (CI):
Calc. for $C_{22}H_{45}OSi$ $[M + 1]^+$: 353.3234; Found: 353.3239

((3-Cyclooctylcyclohex-1-en-1-yl)oxy)tripropylsilane (4d) (Scheme 1)

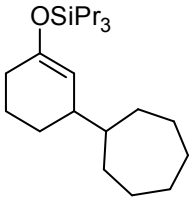


General procedure **B** was followed with 2-cyclohexen-1-one (155 µL, 1.60 mmol, 1.60 equiv), bromocyclooctane (148 µL, 1.00 mmol, 1.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil.

Data for **4d**, Scheme 1
Yield: Run 1 (227 mg, 62%)
Yield: Run 2 (242 mg, 66%)
Average yield: 64%
^{1}H NMR: (500 MHz, $CDCl_3$)

δ 4.69 (s, br, 1H), 2.12-1.89 (m, 3H), 1.81-1.36 (m, 22H), 1.33-1.23 (m, 2H), 1.13-1.05 (m, 1H), 0.97 (t, *J* = 7.2 Hz, 9H), 0.66-0.63 (m, 6H)
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 151.4, 108.4, 42.7, 42.1, 31.2, 30.5, 30.3, 27.1, 27.0, 26.9, 26.7, 25.6, 22.8, 18.5, 17.2, 16.9
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
364.68 (<1.00, M^+), 253.20 (100, M^+- C_8H_{15}), 206.90 (20.97, M^+- $C_{14}H_{23}O$)
TLC: R_f 0.5 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde stain]
HRMS (CI):
Calc. for $C_{23}H_{45}OSi$ $[M + 1]^+$: 365.3234; Found: 365.3227

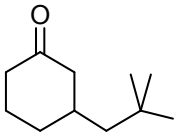
((3-Cycloheptylcyclohex-1-en-1-yl)oxy)tripropylsilane (4e) (Scheme 1)



General procedure **B** was followed with 2-cyclohexen-1-one (155 µL, 1.60 mmol, 1.60 equiv), bromocycloheptane (137 µL, 1.00 mmol, 1.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil.

Data for **4e**, Scheme 1
Yield: Run 1 (217 mg, 62%)
Yield: Run 2 (212 mg, 61%)
Average yield: 62%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 4.69 (s, br, 1H), 2.16 (s, br, 1H), 2.03-1.90 (m, 2H), 1.79-1.77 (m, 1H), 1.69-1.46 (m, 10H), 1.43-1.36 (m, 9H), 1.31-1.22 (m, 2H), 1.16-1.09 (m, 1H), 0.96 (t, *J* = 7.2 Hz, 9H), 0.66-0.63 (m, 6H)
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 151.2, 108.5, 44.3, 42.1, 32.0, 31.1, 30.2, 28.6, 28.3, 27.9, 27.8, 25.3, 22.9, 18.5, 17.2, 16.9
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
350.35 (3.60, M^+), 253.10 (100, M^+- C_7H_{13}), 157.00 (10.49, M^+- $C_{13}H_{21}O$)
TLC: R_f 0.6 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde]
HRMS (CI):
Calc. for $C_{22}H_{43}OSi$ $[M + 1]^+$: 351.3078; Found: 351.3067

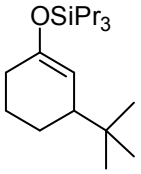
3-Neopentylcyclohexanone (4f) (Scheme 1)



General procedure **B** was followed with 2-cyclohexen-1-one (96.3 µL, 1.00 mmol, 1.00 equiv), 1-iodo-2,2-dimethylpropane (265 µL, 2.00 mmol, 2.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The crude silyl enol ether product obtained was subjected to deprotection protocol **B**. Pure ketone product was obtained by silica gel chromatography (16 cm x 3 cm, 5% EtOAc in hexanes with 0.1% Et_3N) to afford a clear, colorless oil.

Data for **4f**, Scheme 1
Yield: Run 1 (89 mg, 53%)
Yield: Run 2 (92 mg, 55%)
Average yield: 54%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 2.38 (dm, *J* = 4.1, 1H), 2.31-2.25 (m, 1H), 2.22-2.14 (m, 1H), 2.03-1.93 (m, 2H), 1.87-1.75 (m, 2H), 1.67-1.56 (m, 1H), 1.38-1.31 (m, 1H), 1.24 (dt, *J* = 13.7, 6.7 Hz, 1H), 1.11 (dd, *J* = 14.1, 5.0 Hz, 1H), 0.85 (s, 9H).
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 212.1, 50.7, 50.5, 41.2, 35.6, 33.9, 31.1, 29.9, 25.5
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
168.18 (<1.00, M^+), 97.00 (100, M^+- C_5H_{11})
TLC: R_f 0.3 (5% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, phosphomolybdic acid stain]
HRMS (CI):
Calc. for $C_{11}H_{21}O$ $[M + 1]^+$: 168.1520; Found: 168.1508

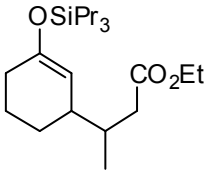
((3-(*Tert*-butyl)cyclohex-1-en-1-yl)oxy)tripropylsilane (4g) (Scheme 1)



General procedure **B** was followed with 2-cyclohexen-1-one (96.3 µL, 1.00 mmol, 1.00 equiv), 2-bromo-2-methylpropane (224 µL, 2.00 mmol, 2.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil.

Data for **4g**, Scheme 1
Yield: Run 1 (233 mg, 75%)
Yield: Run 2 (215 mg, 69%)
Average yield: 72%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 4.88 (s, 1H), 2.02-1.68 (m, 5H), 1.55-1.48 (m, 1H), 1.40 (dq, *J* = 15.9, 7.8 Hz, 6H), 1.11-1.03 (m, 1H), 0.96 (t, *J* = 7.2 Hz, 9H), 0.85 (s, 9H), 0.67-0.64 (m, 6H)
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 151.5, 106.4, 45.8, 33.1, 30.0, 27.5, 24.3, 23.2, 18.5, 17.2, 16.9
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
310.27 (<1.00, M^+), 253.10 (100, M^+- C_4H_9), 98.95 (2.49, M^+- $C_{15}H_{29}OSi$), 157.10 (13.97, M^+- $C_{10}H_{17}O$), 57.00 (10.94, M^+- $C_{15}H_{29}OSi$)
TLC: R_f 0.5 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde stain]
HRMS (CI):
Calc. for $C_{19}H_{39}OSi$ $[M + 1]^+$: 311.2765; Found: 311.2754

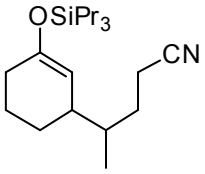
Ethyl 3-(3-((triisopropylsilyl)oxy)cyclohex-2-en-1-yl)butanoate (4h) (Scheme 1)



General procedure **B** was followed with 2-cyclohexen-1-one (96.3 µL, 1.00 mmol, 1.00 equiv), ethyl 3-bromobutanoate (390 mg, 2.00 mmol, 2.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, 95:5 hexanes:EtOAc with 0.1% Et_3N) to afford a clear, colorless oil as a mixture of regio and stereoisomers.

Data for **4h**, Scheme 1
Yield: Run 1 (231 mg, 63%)
Yield: Run 2 (256 mg, 69%)
Average yield: 66%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 4.69 (d, *J* = 5.6 Hz, 1H), 4.12 (qd, *J* = 7.1, 0.9 Hz, 2H), 2.35 (ddd, *J* = 14.4, 9.4, 4.8 Hz, 1H), 2.19-2.17 (m, 1H), 2.11-1.90 (m, 4H), 1.81-1.78 (m, 1H), 1.60-1.47 (m, 2H), 1.39 (dq, *J* = 16.1, 7.9 Hz, 7H), 1.25 (td, *J* = 7.1, 0.7 Hz, 3H), 0.96 (td, *J* = 7.3, 0.8 Hz, 9H), 0.90 (dd, *J* = 12.8, 6.8 Hz, 3H), 0.66-0.63 (m, 6H).
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 173.9, 173.8, 152.0, 151.8, 107.1, 106.5, 60.3, 40.1, 39.8, 39.3, 38.8, 35.1, 35.0, 30.2, 30.1, 25.5, 24.5, 22.6, 22.5, 18.5, 17.2, 16.9, 16.8, 16.3, 14.4
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
368.25 (1.83, M^+), 253.15 (100, M^+- $C_{15}H_{29}OSi$), 73.00 (25.97, M^+- $C_{18}H_{35}OSi$)
TLC: R_f 0.3 (5% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde]
HRMS (CI):
Calc. for $C_{21}H_{41}O_3Si$ $[M + 1]^+$: 369.2819; Found: 369.2812

4-(3-((tripropylsilyl)oxy)cyclohex-2-en-1-yl)pentanenitrile (4i) (Scheme 1)

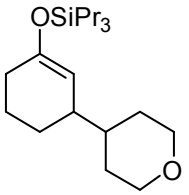


General procedure **B** was followed with 2-cyclohexen-1-one (155 µL, 1.60 mmol, 1.60 equiv), 4-bromopentanenitrile (162 mg, 1.00 mmol, 1.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, 95:5 hexanes:EtOAc with 0.1% Et_3N) to afford a clear, colorless oil as a mixture of regio and stereoisomers.

Data for **4i**, Scheme 1
Yield: (150.5 mg, 45%)
Yield: (153.6 mg, 46%)
Average yield: 45%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 4.63 (d, *J* = 2.0 Hz, 1H), 2.41-2.25 (m, 2H), 2.18 (d, *J* = 9.8 Hz, 1H), 2.04-1.89 (m, 2H), 1.82-

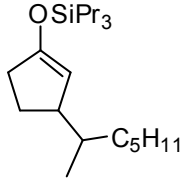
1.70 (m, 2H), 1.51 (m, 4H), 1.38 (dq, *J* = 16.1, 7.8 Hz, 6H), 1.12 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 9H), 0.86 (dd, *J* = 10.7, 6.8 Hz, 3H), 0.65-0.62 (m, 6H).
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 152.1, 151.8, 119.96, 119.93, 106.9, 105.9, 39.8, 39.5, 36.83, 36.79, 30.07, 30.03, 29.7, 29.3, 25.6, 24.1, 22.53, 22.41, 18.4, 17.1, 16.8, 15.9, 15.58, 15.54, 15.2.
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
335.3 (<1.00, M^+), 253.10 (100, M^+- C_5H_8N).
TLC: R_f 0.3 (5% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde]
HRMS (CI):
Calc. for $C_{20}H_{38}NOSi$ $[M + 1]^+$: 336.2717; Found: 336.2726

Tripropyl((3-(tetrahydro-2*H*-pyran-4-yl)cyclohex-1-en-1-yl)oxy)silane (4j) (Scheme 1)



General procedure **B** was followed with 2-cyclohexen-1-one (96.3 µL, 1.00 mmol, 1.00 equiv), 4-tetrahydropyran (225 µL, 2.00 mmol, 2.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, 150 mL hexanes with 0.1% Et_3N, followed by eluting with 100 mL of 95:5 hexanes:TBME) to afford a clear, colorless oil.
Data for **4j**, Scheme 1
Yield: Run 1 (213 mg, 63%)
Yield: Run 2 (227 mg, 67%)
Average yield: 65%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 4.81 (s, br, 1H), 4.00-3.97 (m, 1H), 3.35 (td, *J* = 11.5, 2.1 Hz, 1H), 2.03-1.74 (m, 4H), 1.66-1.49 (m, 4H), 1.43-1.35 (m, 9H), 1.30-1.16 (m, 2H), 0.98-0.95 (m, 10H), 0.67-0.63 (m, 6H)
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 151.4, 106.6, 68.6 (2C), 40.6, 40.1, 30.6, 30.5, 30.2, 25.7, 22.2, 18.5, 17.2, 16.9
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
338.26 (<1.00, M^+), 253.10 (100, M^+- C_5H_9O).
HRMS (CI):
Calc. for $C_{20}H_{39}O_2Si$ $[M + 1]^+$: 339.2714; Found: 339.2703

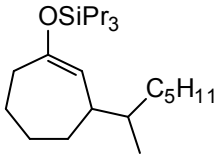
((3-Heptan-2-yl)cyclopent-1-en-1-yl)oxy)tripropylsilane (4k) (Scheme 1)



General procedure **B** was followed with 2-cyclopenten-1-one (134 µL, 1.60 mmol, 1.60 equiv), 2-bromoheptane (188 µL, 1.00 mmol, 1.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil as a mixture of regio and stereoisomers.

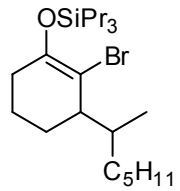
Data for **4k**, Scheme 1
Yield: Run 1 (170 mg, 61%)
Yield: Run 2 (223 mg, 66%)
Average yield: 64%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 4.57 (dd, *J* = 1.69, 7.20 Hz, 1H), 2.55-2.52 (m, 1H), 2.27-2.19 (m, 2H), 1.97-1.83 (m, 1H), 1.54-1.47 (m, 1H), 1.46-1.36 (m, 6H), 1.35-1.01 (m, 9H), 0.97 (t, *J* = 7.25 Hz, 9H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.80 (t, *J* = 6.6 Hz, 3H), 0.69-0.66 (m, 6H)
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 155.2, 155.0, 105.9, 105.0, 47.7, 47.6, 38.6, 38.2, 34.6, 34.5, 33.7, 33.6, 32.4, 27.3, 27.2, 25.9, 24.8, 22.9, 18.4, 16.8 (3C), 16.5, 14.3
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
338.30 (<1.00, M^+), 239.05 (100, M^+- C_7H_{15}), 157.10 (14.90, M^+- $C_{12}H_{21}O$)
TLC: R_f 0.6 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde stain]
HRMS (CI):
Calc. for $C_{21}H_{43}OSi$ $[M + 1]^+$: 339.3078; Found: 339.3067

((3-(Heptan-2-yl)cyclohept-1-en-1-yl)oxy)tripropylsilane (4l) (Scheme 1)



General procedure **B** was followed with 2-cyclohepten-1-one (178 µL, 1.60 mmol, 1.60 equiv), 2-bromoheptane (188 µL, 1.00 mmol, 1.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil as a mixture of regio and stereoisomers.
Data for **4l**, Scheme 1
Yield: Run 1 (223 mg, 61%)
Yield: Run 2 (209 mg, 62%)
Average yield: 62%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 4.80 (d, *J* = 4.4 Hz, 1H), 2.37-2.30 (m, 1H), 2.15-2.04 (m, 2H), 1.93-1.89 (m, 1H), 1.71-1.65 (m, 1H), 1.57-1.07 (m, 19H), 0.97 (t, *J* = 7.2 Hz, 9H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 7.1 Hz, 3H), 0.66-0.63 (m, 6H)
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 155.0, 154.5, 112.8, 110.6, 41.2, 40.6, 38.9, 38.8, 35.2, 35.1, 34.6, 33.6, 32.4, 32.3, 30.8, 30.3, 30.1, 27.5, 27.3, 25.4, 25.3, 22.7, 18.4, 17.0, 16.7, 16.6, 15.6, 14.1
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
366.38 (<1.00, M^+), 267.15 (100, M^+- C_7H_{15}), 157.05 (10.96, M^+- $C_{14}H_{25}O$)
TLC: R_f 0.6 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde stain]
HRMS (CI):
Calc. for $C_{23}H_{47}OSi$ $[M + 1]^+$: 367.3391; Found: 367.3380

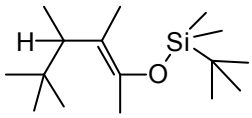
((2-Bromo-3-(heptan-2-yl)cyclohex-1-en-1-yl)oxy)tripropylsilane (4m) (Scheme 1)



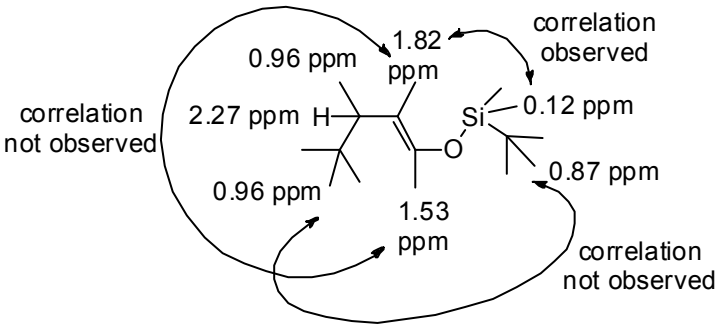
General procedure **B** was followed with 2-bromocyclohex-2-enone (280 mg, 1.60 mmol, 1.60 equiv), 2-bromoheptane (188 µL, 1.00 mmol, 1.00 equiv) and tri-*n*-propylchlorosilane (285 µL, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil as a mixture of regio and stereoisomers.

Data for **4m**, Scheme 1
Yield: Run 1 (302 mg, 70%)
Yield: Run 2 (294 mg, 68%)
Average yield: 69%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 2.44 (dm, *J* = 30.3, 7.2 Hz, 1H), 2.19-2.08 (m, 3H), 1.88-1.48 (m, 4H), 1.42 (dt, *J* = 15.9, 7.7 Hz, 6H), 1.39-1.15 (m, 8H), 0.97 (td, *J* = 7.2, 1.9 Hz, 9H), 0.93-0.86 (m, 5H), 0.70 (dd, *J* = 11.7, 5.2 Hz, 7H).
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 148.3, 110.0, 47.3, 45.0, 35.6, 35.3, 35.0, 32.4, 32.3 (3C), 30.6, 28.1, 27.6, 24.5, 23.7, 22.9 (2C), 22.1, 18.6 (2C), 17.9, 17.6, 16.9, 14.3, 13.9
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
432.45 (4.21, $[M+2]^+$), 430.20 (3.74, M^+), 335.10 (4.66, $[M+2]^+$-C_7H_{15}), 333.10 (87.69, M^+-C_7H_{15}), 157.10 (72.43, M^+- $C_{13}H_{22}BrO$)
TLC: R_f 0.4 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde stain]
HRMS (CI):
Calc. for $C_{22}H_{44}BrOSi$ $[M + 1]^+$: 433.2319; Found: 433.2299

***(E)-Tert*-butyldimethyl((3,4,5,5-tetramethylhex-2-en-2-yl)oxy)silane (4n) (Scheme 1)**



General procedure **B** was followed with 3-methyl-3-penten-2-one (181 µL, 1.60 mmol, 1.60 equiv), *tert*-butyl bromide (112 µL, 1.00 mmol, 1.00 equiv) and *tert*-butyl(chloro)dimethylsilane (196 mg, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil. The stereochemistry of **4n** was determined by 1D-NOE ^{1}H NMR.

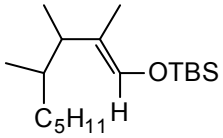


Data for **4n**, Scheme 1

Yield: Run 1 (137.9 mg, 51%)
Yield: Run 2 (135.3 mg, 50%)
Average yield: 51%

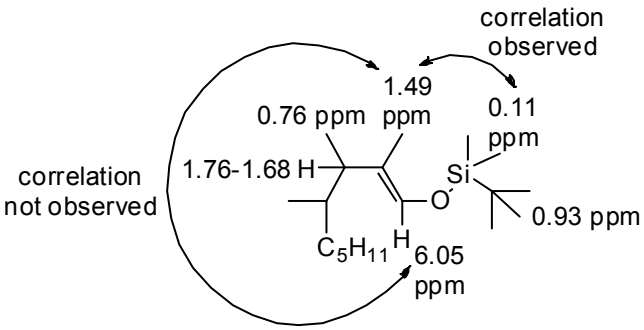
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 2.27 (q, J = 7.1 Hz, 1H), 1.82 (d, J = 1.4 Hz, 3H), 1.53 (d, J = 1.4 Hz, 3H), 0.96 (m, 12 H), 0.87 (s, 9H), 0.12 (d, J = 3.0 Hz, 6H)
NOE ^{1}H NMR: (500 MHz, $CDCl_3$)
Irradiation at 0.12 ppm enhanced signal at 1.82 ppm
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 142.0, 117.7, 44.2, 35.1, 28.7, 26.2, 19.5, 18.4, 14.2, 12.8, -3.4, -3.6.
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
270.27 (<1.00, M^+), 57.05 (100, M^+- C_4H_9)
TLC: R_f 0.5 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde stain]
HRMS (CI):
Calc. for $C_{16}H_{33}OSi$ $[M - 1]^+$: 269.2295; Found: 269.2292

***E-Tert*-butyldimethyl((2,3,4-trimethylnon-1-en-yl)oxy)silane (4o) (Scheme 1)**



General procedure **B** was followed with *trans*-2-methyl-2-butenal (155 µL, 1.60 mmol, 1.60 equiv), 2-bromoheptane (188 µL, 1.00 mmol, 1.00 equiv) and *tert*-butyl(chloro)dimethylsilane (196 mg, 1.30 mmol, 1.30 equiv). After 24 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil as a mixture of regio and stereoisomers. The stereochemistry of **4o** was determined by 1D-NOE ^{1}H NMR.

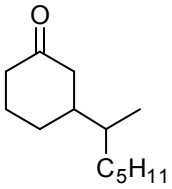
Data for **4o**, Scheme 1



Yield: Run 1 (167 mg, 56%)
Yield: Run 2 (181 mg, 61%)
Average yield: 59%
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 6.05 (s, br, 1H), 1.76-1.68 (m, 1H), 1.49 (s, 3H), 1.46-1.14 (m, 8H), 0.96 (dd, J = 6.9, 11.7 Hz, 4H), 0.93 (s, 9H), 0.91-0.79 (m, 6H), 0.76 (d, J = 6.7 Hz, 1H), 0.11 (s, 6H).
NOE ^{1}H NMR: (500 MHz, $CDCl_3$)
Irradiation at 0.11 ppm enhanced signal at 1.49 ppm
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 134.3, 121.8, 42.8, 35.7, 35.4, 35.3, 33.8, 32.5, 32.4, 26.9, 26.7, 25.9, 22.9, 18.5, 18.2, 17.4,

16.9, 16.6, 14.3, 9.8, 9.5
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
298.27 (<1.00, M^+), 199.05 (100, M^+- C_7H_{15}), 127.00 (10.78, M^+- $C_9H_{19}OSi$)
TLC: R_f 0.5 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde stain]
HRMS (CI):
Calc. for $C_{18}H_{37}OSi$ $[M - 1]^+$: 297.2608; Found: 297.2615

3-(Heptan-2-yl)cyclohexanone



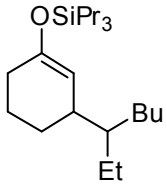
General procedure **B** was followed with 2-cyclohexen-1-one (155 µL, 1.60 mmol, 1.60 equiv), 2-bromoheptane (188 µL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (218 µL, 1.30 mmol, 1.30 equiv). After 17 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The crude silyl enol ether product obtained was subjected to deprotection protocol **B**. Pure ketone product was obtained by silica gel chromatography (16 cm x 3 cm, 5% EtOAc in hexanes with 0.1% Et_3N) to afford a clear, colorless oil.

Following deprotection protocol **A**, ketone product could be isolated in 92% yield.

Data for **3-(Heptan-2-yl)cyclohexanone**
Yield: (74 mg, 75%)
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 2.36-2.19 (m, 3H), 2.16-2.04 (m, 2H), 1.80-1.75 (m, 1H), 1.73-1.64 (m, 1H), 1.59-1.53 (m, 1H), 1.47-1.07 (m, 10H), 0.88-0.84 (m, 6H).
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 212.9, 212.8, 46.2, 44.3, 44.1, 43.9, 41.7, 37.5, 37.4, 33.9 (2C), 32.3, 29.2, 27.3, 27.1 (2C), 25.8 (2C), 22.8, 16.0, 15.8, 14.2
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
196.18 (<1.00, M^+), 97.00 (100, M^+- C_7H_{15}), 125.05 (1.31, M^+- C_5H_{11})
TLC: R_f 0.3 (5% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, phosphomolybdic acid stain]
HRMS (CI):
Calc. for $C_{13}H_{25}O$ $[M + 1]^+$: 197.1900; Found: 197.1904

VII. Independent Synthesis of Minor Regioisomer of 4b

Triethyl((3-heptan-3-yl)cyclohex-1-en-1-yl)oxy)silane (4b regioisomer)



General procedure **B** was followed with 2-cyclohexen-1-one (155 µL, 1.60 mmol, 1.60 equiv), 3-bromoheptane (188 µL, 1.00 mmol, 1.00 equiv) and chlorotripropylsilane (284 µL, 1.30 mmol, 1.30 equiv). After 17 h, the reaction mixture was quickly filtered through silica gel (5 cm x 1 cm) and eluted with ether (100 mL). The filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel chromatography (16 cm x 3 cm, hexanes with 0.1% Et_3N) to afford a clear, colorless oil. The GC retention time and NMR chemical shifts matched those observed for minor peaks for **4b**.

Data for **Regioisomer of 4b**
Yield: Run 1 (263 mg, 75%)
^{1}H NMR: (500 MHz, $CDCl_3$)
δ 4.68 (d, *J* = 6.1 Hz, 1H), 2.28 (s, 1H), 2.01 (m, 1H), 1.92 (dd, *J* = 17.1, 5.9 Hz, 1H), 1.82-1.77 (m, 1H), 1.58-1.50 (m, 2H), 1.44-1.36 (m, 6H), 1.31-1.23 (m, 7H), 1.15 (s, 1H), 1.06 (s, 2H), 0.97 (t, *J* = 7.3 Hz, 9H), 0.90-0.86 (m, 6H), 0.67-0.63 (m, 6H)
^{13}C NMR: (126 MHz, $CDCl_3$)
δ 151.02, 150.99, 108.4, 108.2, 44.83, 44.74, 37.29, 37.15, 30.66, 30.55, 30.38, 30.27, 25.6, 25.2, 23.95, 23.86, 23.38, 23.37, 22.9, 18.5, 17.22, 17.2, 16.9, 14.34, 14.31, 12.61, 12.47
MS *m/z* (% relative intensity, ion): (EI, 30 eV)
352.32 (<1, M^+), 253.15 (100, M^+- C_7H_{15}), 115.05 (35.93, M^+- $C_{13}H_{23}O$), 87.05 (12.55, M^+- $C_{13}H_{23}OSi$)
TLC: R_f 0.6 (hexanes, 100%) [silica gel treated with 0.1% Et_3N, *p*-anisaldehyde stain]
HRMS (CI):
Calc. for $C_{22}H_{45}OSi$ $[M + 1]^+$: 353.3234; Found: 353.3219

VIII. Mechanistic Studies

(A) Synthesis of (pyridine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (10)[8]

In a nitrogen filled glove box, $Ni(cod)_2$ (500 mg, 1.80 mmol, 1.00 equiv) was added to an oven-dried scintillation vial containing a teflon-coated stir-bar. A solution of 2-cyclohexen-1-one (176 µL, 1.80 mmol, 1.00 equiv) and pyridine (294 µL, 3.60 mmol, 2.00 equiv) in 4 mL THF was added to the $Ni(cod)_2$, followed by addition of triethylchlorosilane (306 µL, 1.80 mmol, 1.00 equiv). The mixture was stirred to obtain a deep red solution. The resulting solution was concentrated under reduced pressure to obtain a deep-red residue. The resulting residue was dissolved in 5 mL of pentane, filtered through a short celite pad (1.5 cm) in a pipette packed with glass wool. The filtrate was stored in a freezer at -30 ^{o}C to induce crystallization. The supernatant was removed and deep red crystals obtained were dried under vacuum to obtain **10** (365 mg, 1.10 mmol, 61% yield).

Data for **10**
Yield: 365 mg, 61%
Stability: Complex **10** was found to be air and moisture sensitive. The complex is stable in solid state and in solution at -30 ^{o}C for over a month. In cases where decomposition of the complex is observed, pure material can be obtained by recrystallization procedure as described above.
^{1}H NMR: (500 MHz, DMF-d_7, -10 ^{o}C)
δ 8.74 (s, 2H), 7.99 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 6.8 Hz, 2H), 5.51 (d, J = 7.1 Hz, 1H), 3.32 (t, J = 4.5 Hz, 1H), 2.30 (dq, J = 16.7, 4.7 Hz, 1H), 2.19 (dd, J = 11.2, 5.2 Hz, 1H), 1.75 (d, J = 16.5 Hz, 1H), 1.41 (s, br, 1H), 1.12 (s, br, 2H), 085 (t, J = 6.7 Hz, 9H), 0.63-0.56 (m, 6H).
^{13}C NMR: (126 MHz, DMF-d_7, -10 ^{o}C)
δ 151.9, 138.4, 125.4, 114.0, 89.0, 55.3, 36.7, 27.2, 20.8, 7.1, 5.4
Elemental Analysis:
Calc. for $C_{17}H_{28}ClNNiOSi$: C 53.08%, H 7.34%, N 3.64%; Found: C 52.75%, H 7.14%, N 3.61%.
X-Ray Analysis: Available as a CIF file

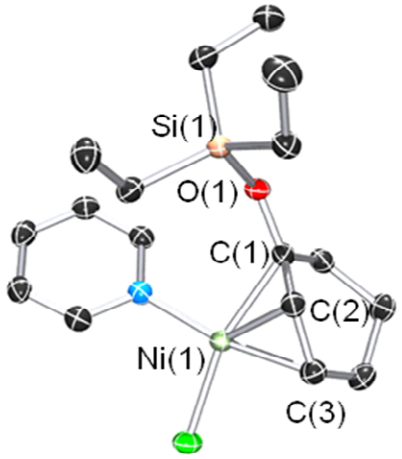
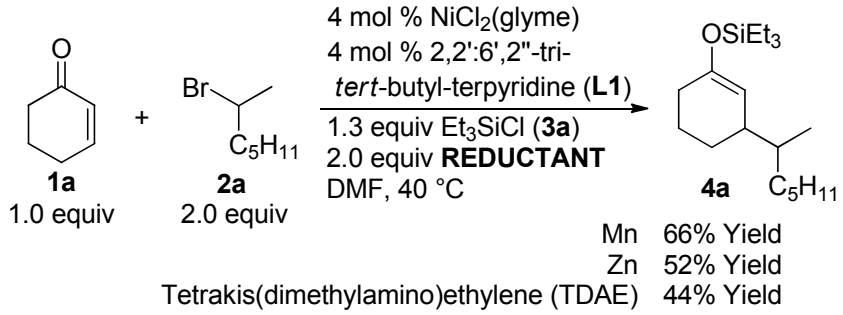


Figure S1. ORTEP diagram of **10** (H atoms are omitted for clarity).

Table S4: Crystal data and structure refinement for $C_{17}H_{28}ClNNiOSi$ (**10**)

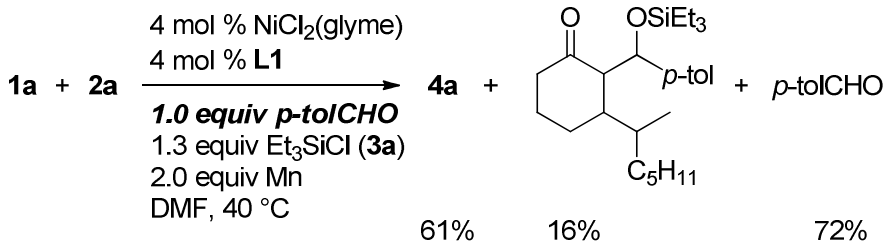
Identification code	weixrs03	
Empirical formula	C17 H28 Cl N Ni O Si	
Formula weight	384.65	
Temperature	100.0(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.287(2) Å	α = 90°
	b = 10.884(2) Å	β = 107.092(3)°
	c = 15.828(3) Å	γ = 90°
Volume	1858.5(6) $Å^3$	
Z	4	
Density (calculated)	1.375 Mg/m^3	
Absorption coefficient	1.253 mm^{-1}	
F(000)	816	
Crystal color, morphology	orange, needle	
Crystal size	0.28 x 0.14 x 0.12 mm^3	
Theta range for data collection	1.97 to 28.28°	
Index ranges	$-15 \leq h \leq 15$, $-14 \leq k \leq 14$, $-21 \leq l \leq 21$	
Reflections collected	27522	
Independent reflections	4605 [R(int) = 0.1110]	
Observed reflections	2885	
Completeness to theta = 28.28°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.8642 and 0.7204	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4605 / 0 / 234	
Goodness-of-fit on F^2	1.002	
Final R indices [I>2sigma(I)]	$R1$ = 0.0447, $wR2$ = 0.0823	
R indices (all data)	$R1$ = 0.0934, $wR2$ = 0.0965	
Largest diff. peak and hole	0.484 and -0.466 e.$Å^{-3}$	

(B) Procedure for reactions used to study in-situ-formation of organomanganese reagent (Figure 1, Mechanism A)



Reactions were set up in a nitrogen filled glove box. To an oven-dried 1-dram vial containing a teflon-coated stir-bar were added $NiCl_2$(0.41 glyme) (3.33 mg, 0.02 mmol, 0.04 equiv), 2,2':6',2"-tri-*tert*-butylterpyridine (8.1 mg, 0.02 mmol, 0.04 equiv), 2 mL DMF, 2-cyclohexen-1-one (**1a**) (48 µL, 0.50 mmol, 1.00 equiv), 2-bromoheptane (**2a**) (188 µL, 1.00 mmol, 2.00 equiv), triethylchlorosilane (**3a**) (109 µL, 0.65 mmol, 1.30 equiv), the desired reducing agent (1.0 mmol, 2.00 equiv) and dodecane (10.0 µL internal standard). The reaction vials were capped with a PTFE-faced silicone septum, removed from the glove box and heated to 40 ^{o}C in a reaction block on the benchtop with stirring at 1200 rpm for 17 h. After 17 h reaction time, a 10 µL aliquot of the reaction mixture was removed with a 50 µL gas-tight syringe and quenched with 10 µL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography and the percent yield was calculated versus the dodecane internal standard.

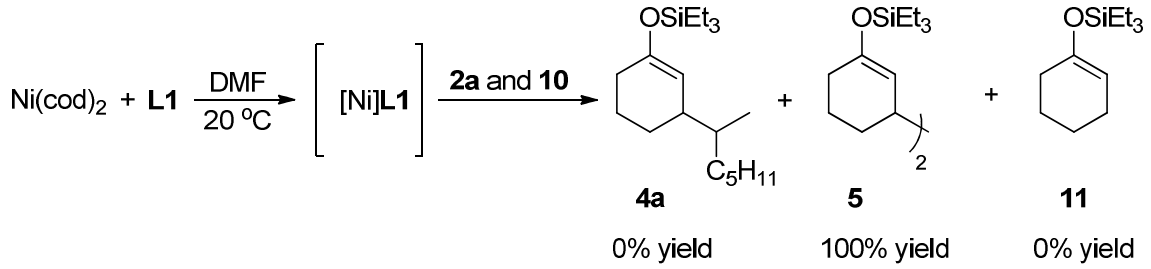
(C) Procedure used for conjugate addition reaction in presence of *p*-tolualdehyde (Figure 1, Mechanism A)



Reactions were set up in a nitrogen filled glove box. To an oven-dried 1-dram vial containing a teflon-coated stir-bar were added $NiCl_2$(0.41 glyme) (3.33 mg, 0.02 mmol, 0.04 equiv), 2,2':6',2"-tri-*tert*-butylterpyridine (8.1 mg, 0.02 mmol, 0.04 equiv), 2 mL DMF, 2-cyclohexen-1-one (**1a**) (48 µL, 0.50 mmol, 1.00 equiv), 2-bromoheptane (**2a**) (188 µL, 1.00 mmol, 2.00 equiv), triethylchlorosilane (**3a**) (109 µL, 0.65 mmol, 1.30 equiv), *p*-tolualdehyde (58 µL, 0.50 mmol, 1.00 equiv), Mn powder (55 mg, 1.0 mmol, 2.00 equiv) and dodecane (10.0 µL internal standard). The reaction vials were capped with a PTFE-faced silicone septum, removed from the glove box and heated to 40 ^{o}C in a reaction block on the benchtop with stirring at 1200 rpm for 12 h. After 12 h reaction time, 10 µL aliquot of reaction mixture was removed

with a 50 µL gas-tight syringe and quenched with 10 µL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography and percent yield was calculated versus the dodecane internal standard.

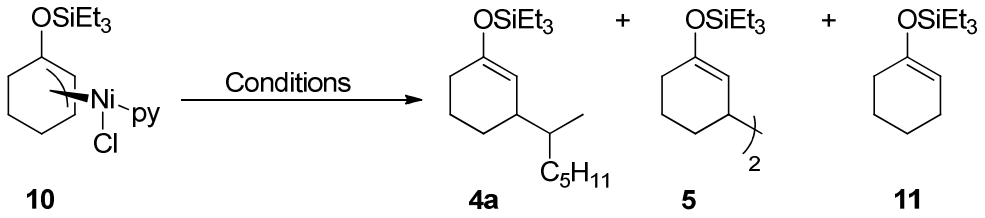
(D) Procedure for reaction used to study disproportionation mechanism (Figure 1, Mechanism B and Table 2, entry 1)



*Consumption of 2-bromoheptane (**2a**) led to quantitative formation of heptenes.

Reactions were set up in a nitrogen filled glove box. To an oven-dried 1-dram vial containing a teflon-coated stir-bar was added $Ni(cod)_2$ (28.0 mg, 0.10 mmol, 1.00 equiv), 2,2':6',2"-tri-*tert*-butylterpyridine (40.2 mg, 0.10 mmol, 1.00 equiv), and 3 mL of DMF and stirred at room temperature until a homogeneous green solution was obtained. To the mixture was added 2-bromoheptane (**2a**) (19.0 µL, 0.10 mmol, 1.00 equiv), a solution of complex **10** (35 mg, 0.1 mmol, 1.0 equiv) in 200 µl of DMF and dodecane (10.0 µL internal standard). The reaction vial was capped with a PTFE-faced silicone septum, removed from the glove box and heated to 40 °C in a reaction block on the benchtop with stirring at 1200 rpm for 1 h. After 1 h reaction time, 10 µL aliquot of reaction mixture was removed with a 50 µL gas-tight syringe and quenched with 10 µL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography and percent yield was calculated versus the dodecane internal standard.

(E) Procedure for reactions used to study order of oxidative addition of electrophiles (Figure 1, Mechanisms C and D and Table 3)

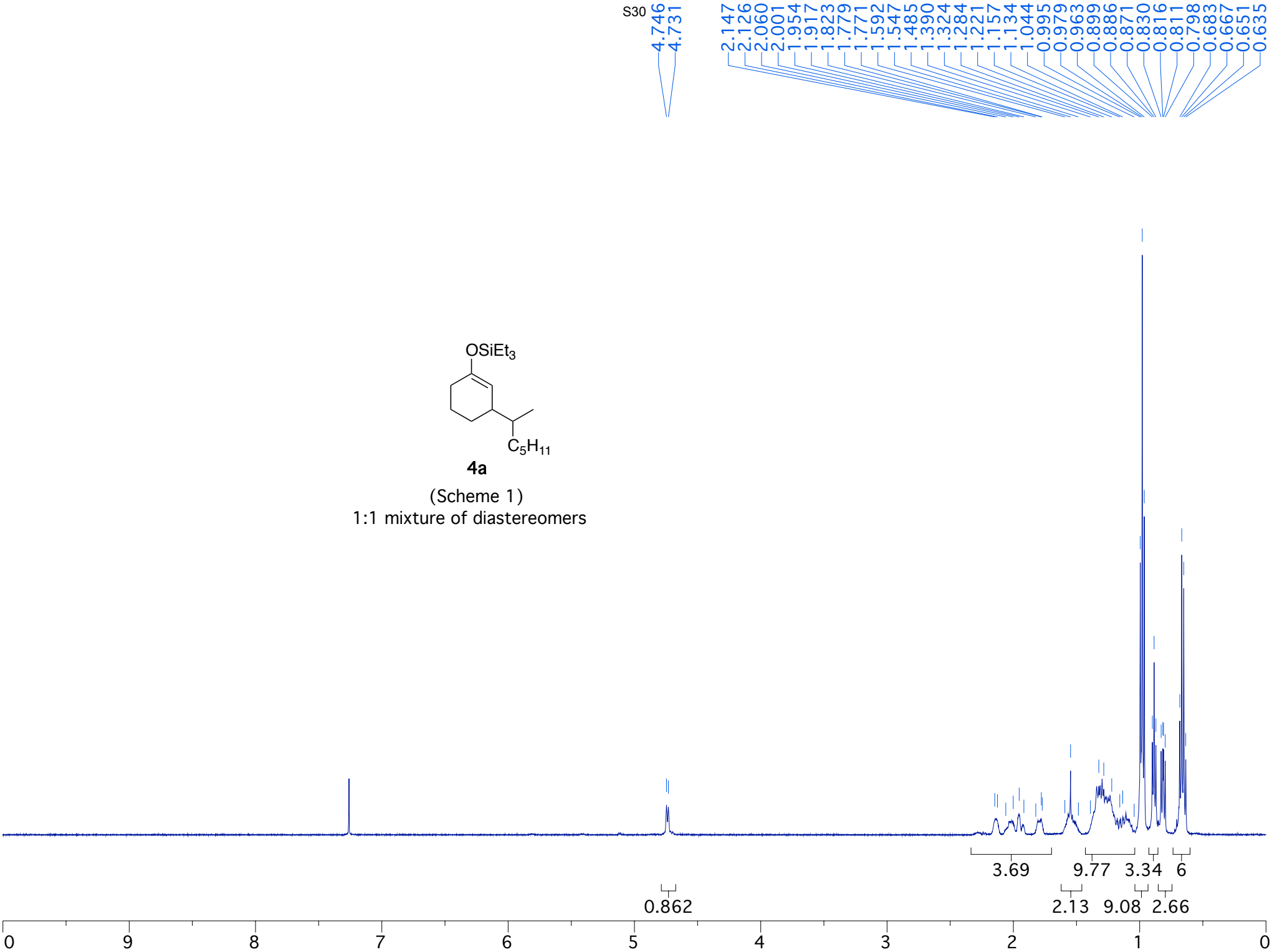


Reactions were set up in a nitrogen filled glove box. To an oven-dried 1-dram vial containing a teflon-coated stir-bar was added the required amount of (pyridine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (**10**), followed by 2 mL DMF, and 2-cyclohexen-1-one (**1a**), 2-bromoheptane (**2a**), triethylchlorosilane (**3a**), Mn powder, and dodecane (10.0 µL internal standard). The reaction vials were capped with a PTFE-faced silicone septum, removed from the glove box and heated in a reaction block to 40 °C on the benchtop with stirring at 1200 rpm .

After 17-24 h reaction time, 10 μL aliquots of reaction mixture were removed with a 50 μL gas-tight syringe and quenched with 10 μL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography and percent yield was calculated versus the dodecane internal standard.

IX. References

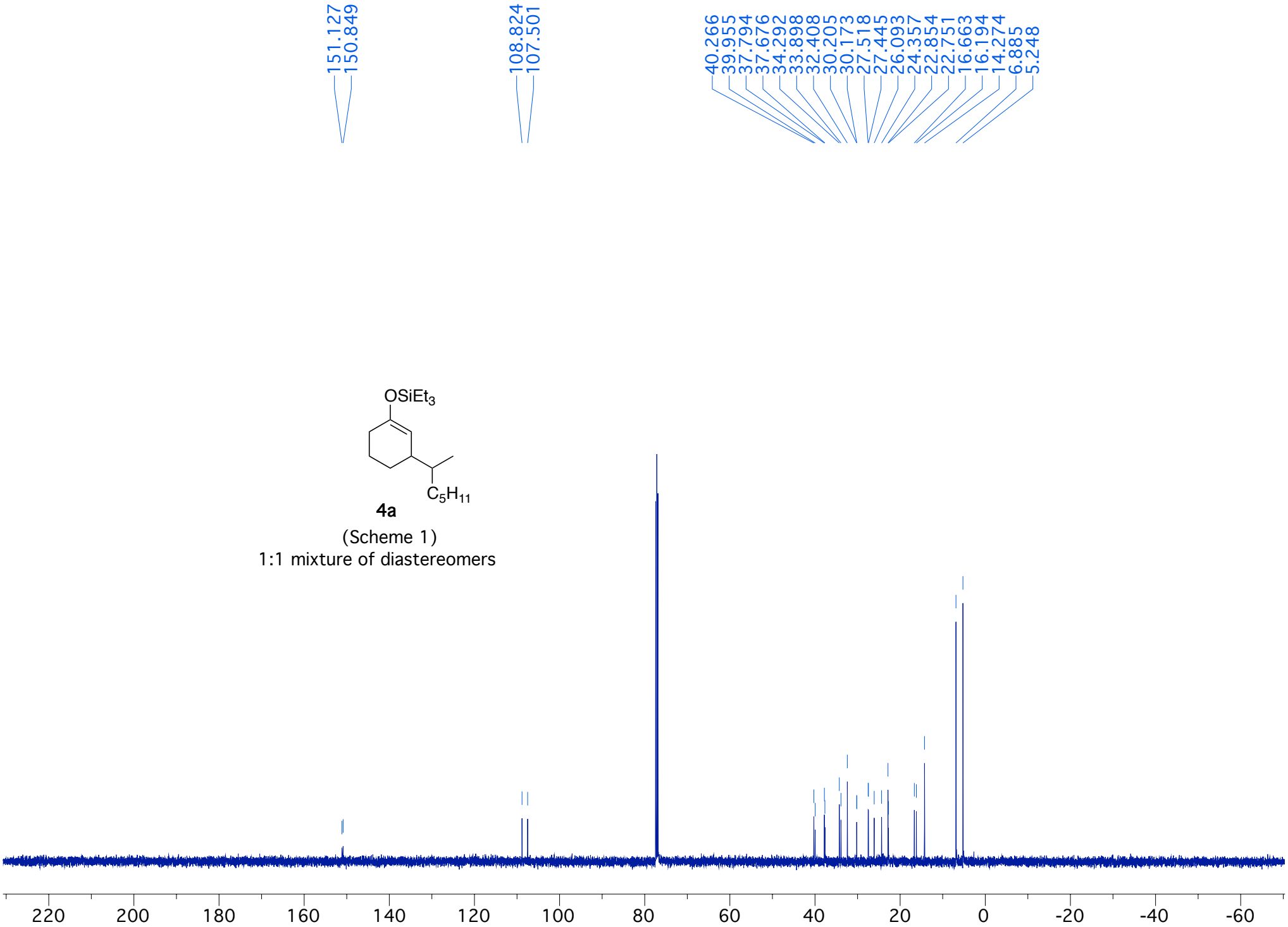
[1] Ward, L. G. L and Pipal, J. R., *Inorg. Synth.* **2007**, *13*, 154.
[2] Rosevear, P. E. and Sasse, W. H. F. *J. Heterocycl. Chem.* **1971**, *8*, 483 and Hadda, T. B. and Le Bozec, H. *Polyhedron*, **1988**, *7*, 575.
[3] Buckley, D. J.; McKervey, M. A. *J. Chem. Soc. Perkin Trans. 1*, **1985**, 2193.
[4] Schirm, M.; Besendorf, H. *Arch. der Pharm.* **1942**, *280*, 74.
[5] Lease, M.; *J. Am. Chem. Soc.* **1933**, *55*, 807.
[6] Glacet, G.l *Bull. Soc. Chim. Franc.* **1956**, 1425.
[7] Strilko, P. S.; Morita, H.; Oae, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2165.
[8] Johnson, J. R.; Tully, P. S.; Mackenzie, P. B.; Sabat, M. *J. Am. Chem. Soc.* **1991**, *113*, 6172.



4a

(Scheme 1)

1:1 mixture of diastereomers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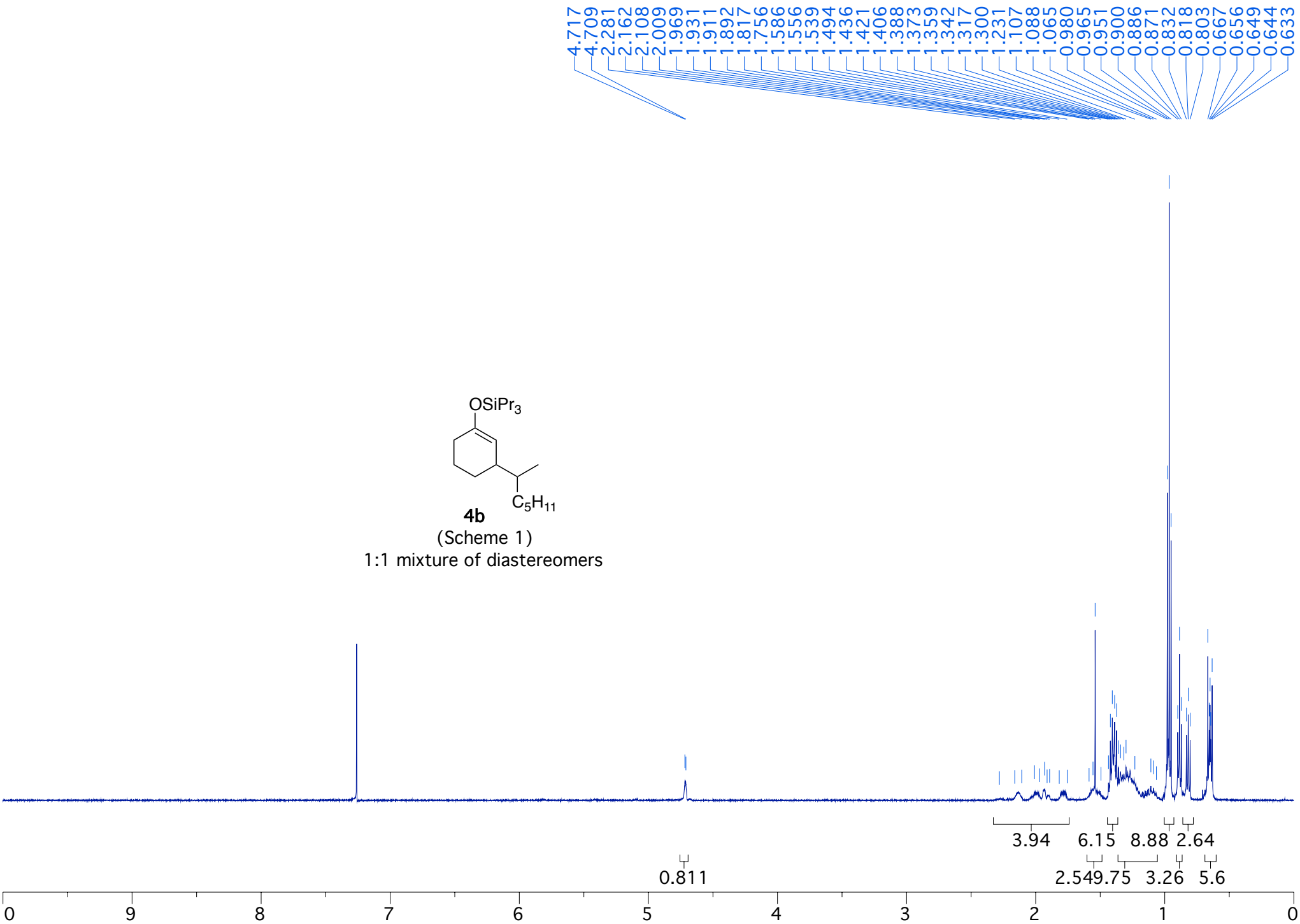
150.849
108.824
107.501
40.266
39.955
37.794
37.676
34.292
33.898
32.408
30.205
30.173
27.518
27.445
26.093
24.357
22.854
22.751
16.663
16.194
14.274
6.885
5.248
OSiEt3
C5H11
4a
(Scheme 1)
1:1 mixture of diastereomers
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60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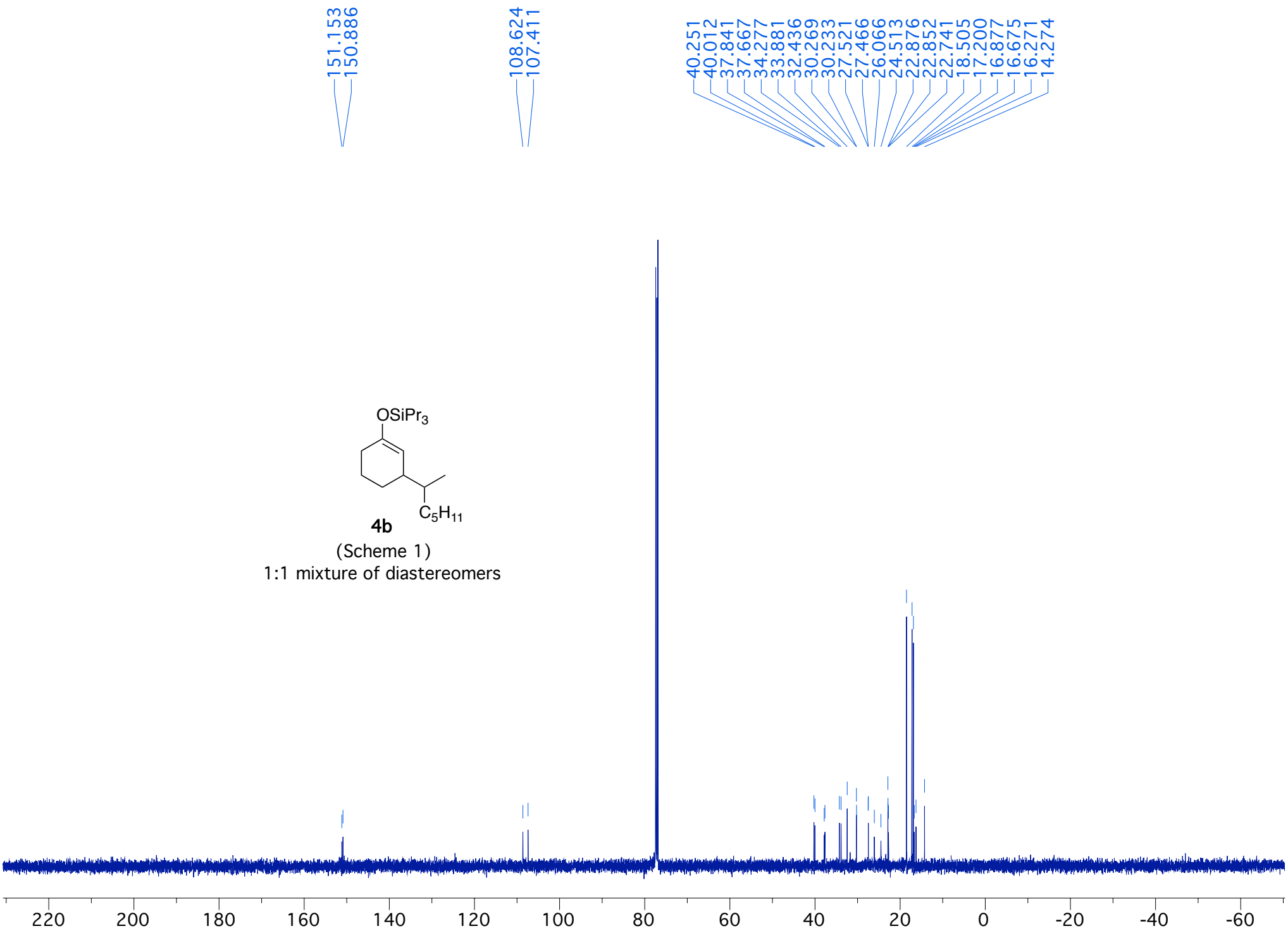
4.709
2.281
2.162
2.108
2.009
1.969
1.931
1.911
1.892
1.817
1.756
1.586
1.556
1.539
1.494
1.436
1.421
1.406
1.388
1.373
1.359
1.342
1.317
1.300
1.231
1.107
1.088
1.065
0.980
0.965
0.951
0.900
0.886
0.871
0.832
0.818
0.803
0.667
0.656
0.649
0.644
0.633
OSiPr3
C5H11
4b
(Scheme 1)
1:1 mixture of diastereomers
3.94
6.15
8.88
2.64
0.811
2.54
9.75
3.26
5.6
0
9
8
7
6
5
4
3
2
1
0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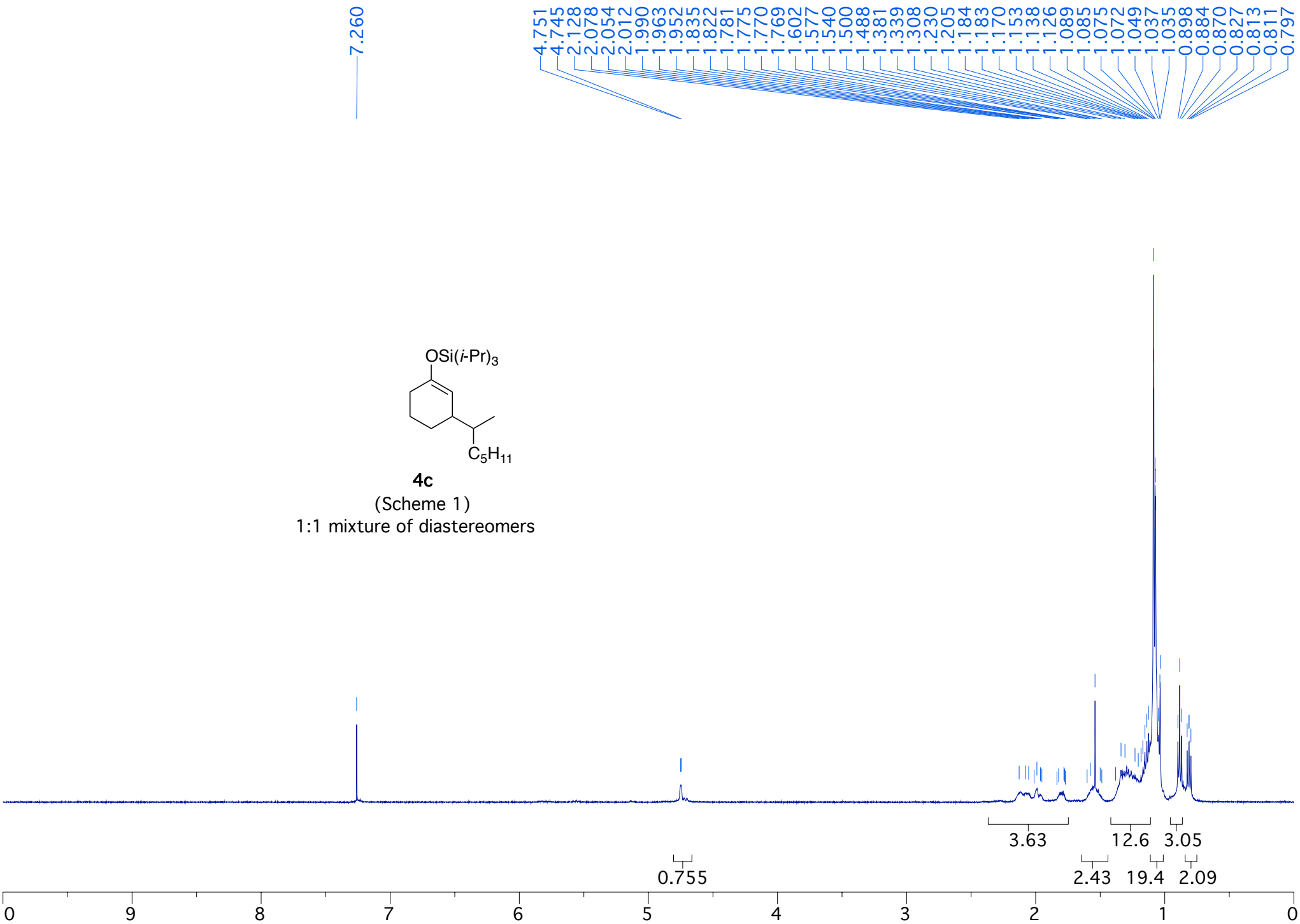
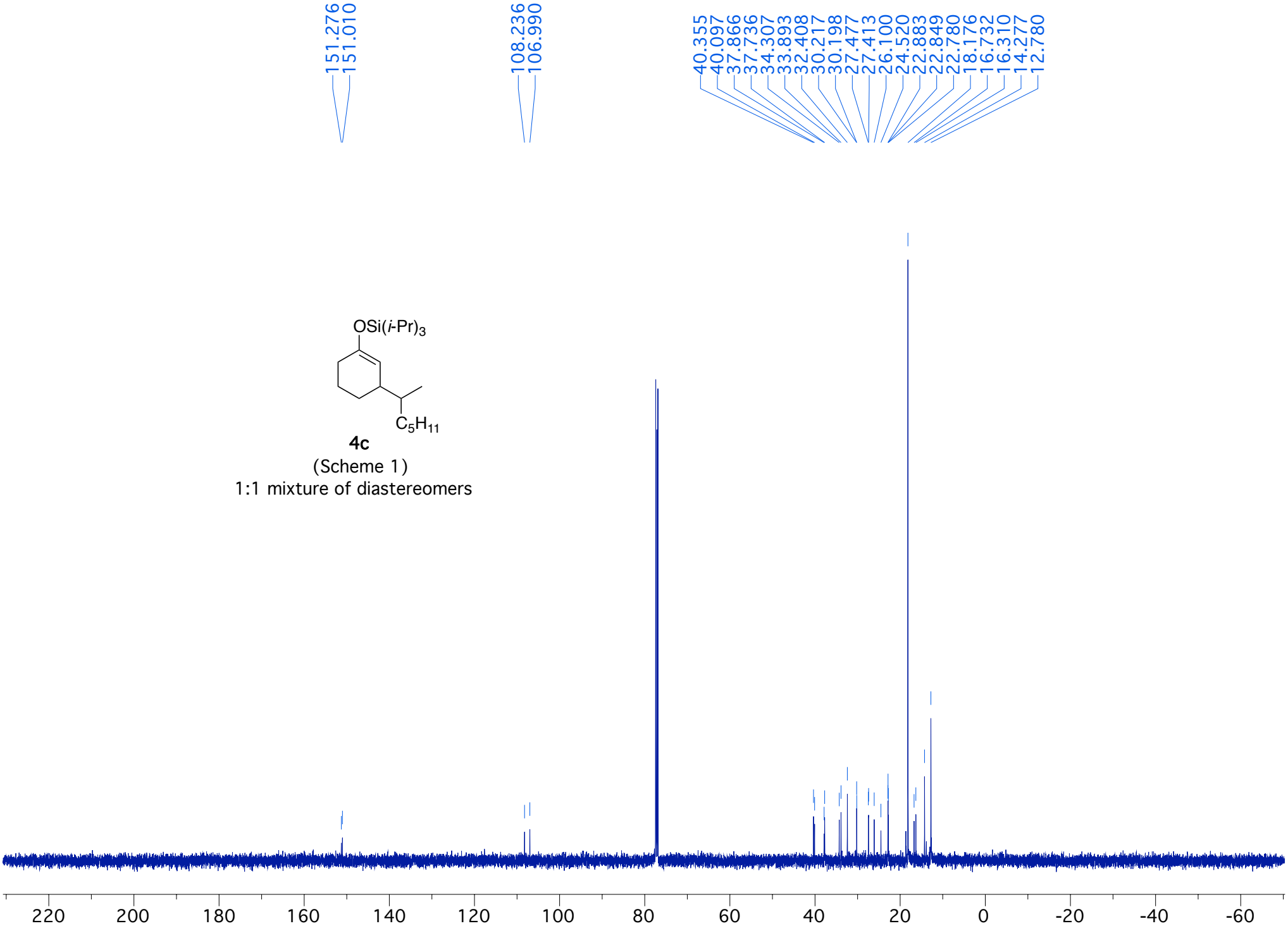
150.886
108.624
107.411
40.251
40.012
37.841
37.667
34.277
33.881
32.436
30.269
30.233
27.521
27.466
26.066
24.513
22.876
22.852
22.741
18.505
17.200
16.877
16.675
16.271
14.274
OSiPr3
C5H11
4b
(Scheme 1)
1:1 mixture of diastereomers
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60


7.260
4.751
4.745
2.128
2.078
2.054
2.012
1.990
1.963
1.952
1.835
1.822
1.781
1.775
1.770
1.769
1.602
1.577
1.540
1.500
1.488
1.381
1.339
1.308
1.230
1.205
1.184
1.183
1.170
1.153
1.138
1.126
1.089
1.085
1.075
1.072
1.049
1.037
1.035
0.898
0.884
0.870
0.827
0.813
0.811
0.797
OSi(i-Pr)3
C5H11
4c
(Scheme 1)
1:1 mixture of diastereomers
3.63
12.6
3.05
0.755
2.43
19.4
2.09
0
9
8
7
6
5
4
3
2
1
0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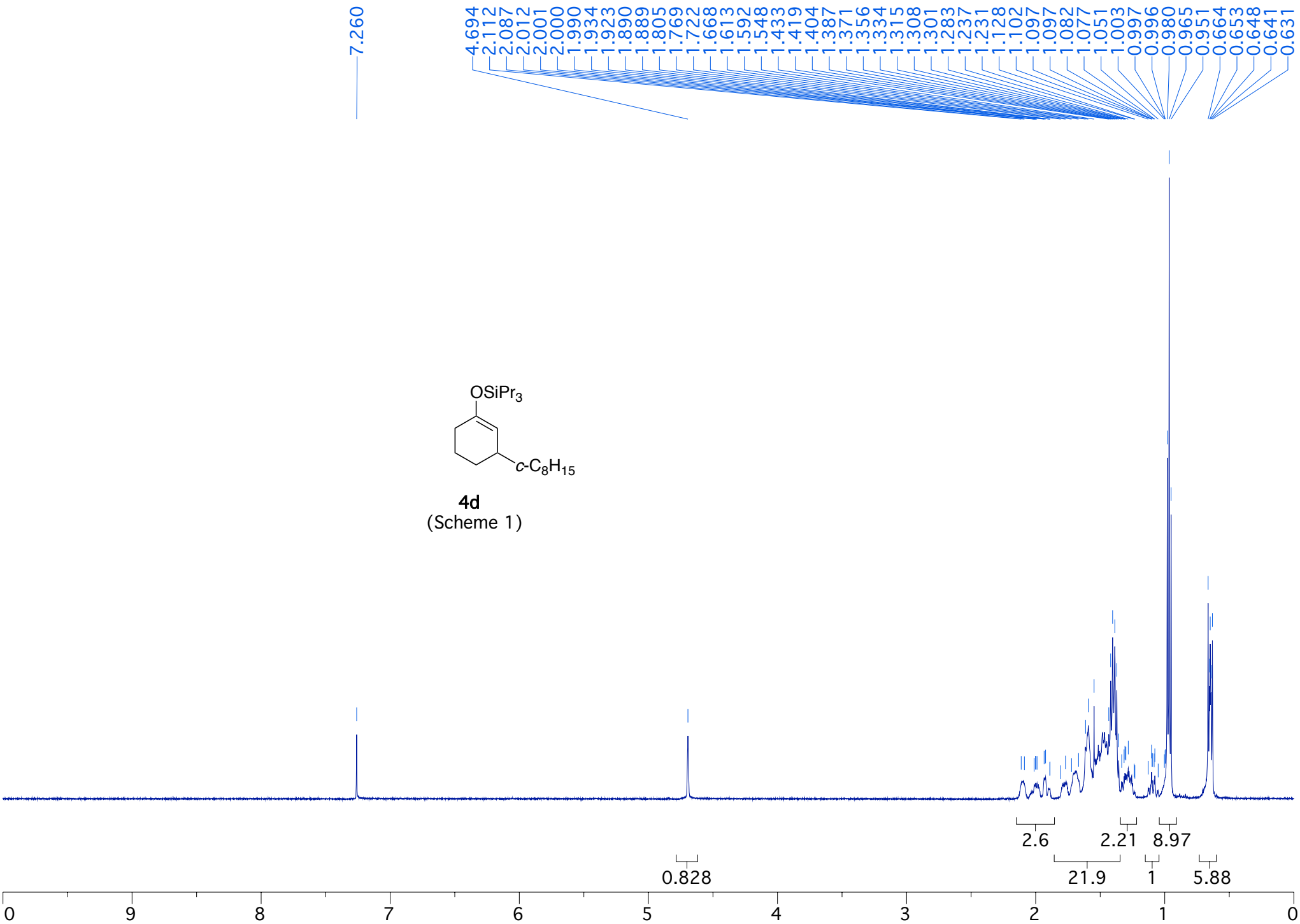
151.010
108.236
106.990
40.355
40.097
37.866
37.736
34.307
33.893
32.408
30.217
30.198
27.477
27.413
26.100
24.520
22.883
22.849
22.780
18.176
16.732
16.310
14.277
12.780
OSi(i-Pr)3
C5H11
4c
(Scheme 1)
1:1 mixture of diastereomers
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60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4.694
2.112
2.087
2.012
2.001
2.000
1.990
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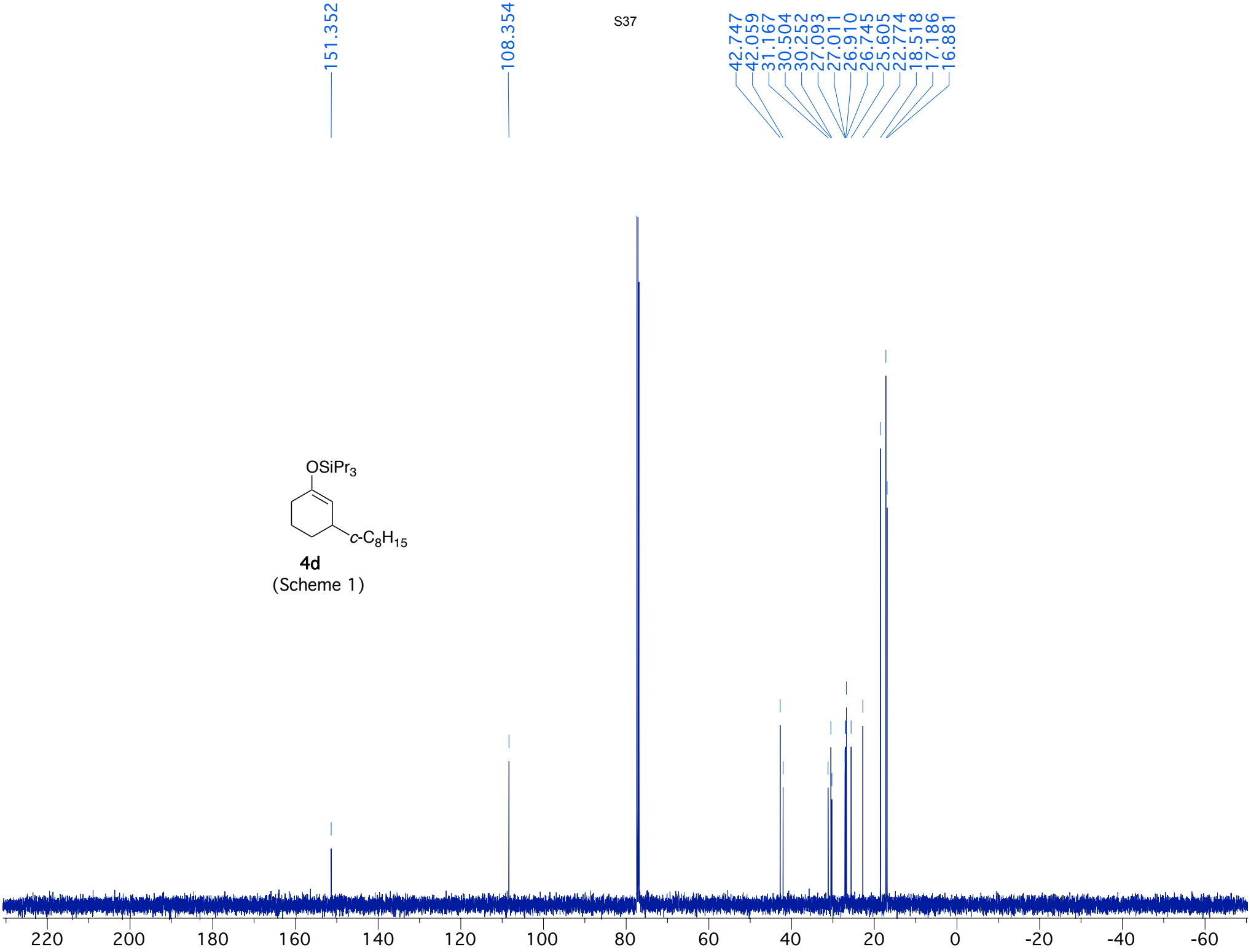
1.923
1.890
1.889
1.805
1.769
1.722
1.668
1.613
1.592
1.548
1.433
1.419
1.404
1.387
1.371
1.356
1.334
1.315
1.308
1.301
1.283
1.237
1.231
1.128
1.102
1.097
1.082
1.077
1.051
1.003
0.997
0.996
0.980
0.965
0.951
0.664
0.653
0.648
0.641
0.631
OSiPr3
c-C8H15
4d
(Scheme 1)
2.6
2.21
8.97
0.828
21.9
1
5.88
0
9
8
7
6
5
4
3
2
1
0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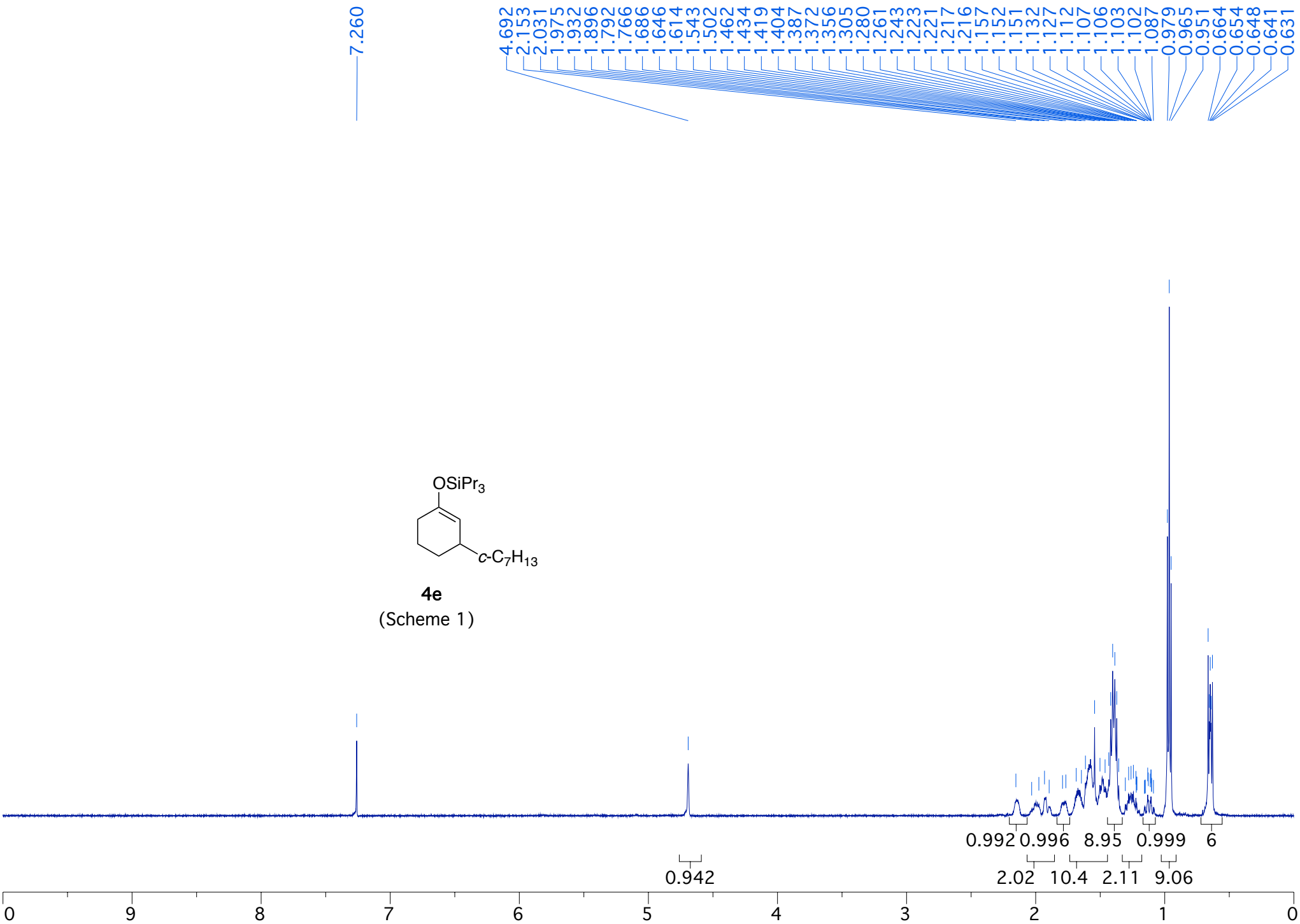
42.059
31.167
30.504
30.252
27.093
27.011
26.910
26.745
25.605
22.774
18.518
17.186
16.881
OSiPr3
c-C8H15
4d
(Scheme 1)
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60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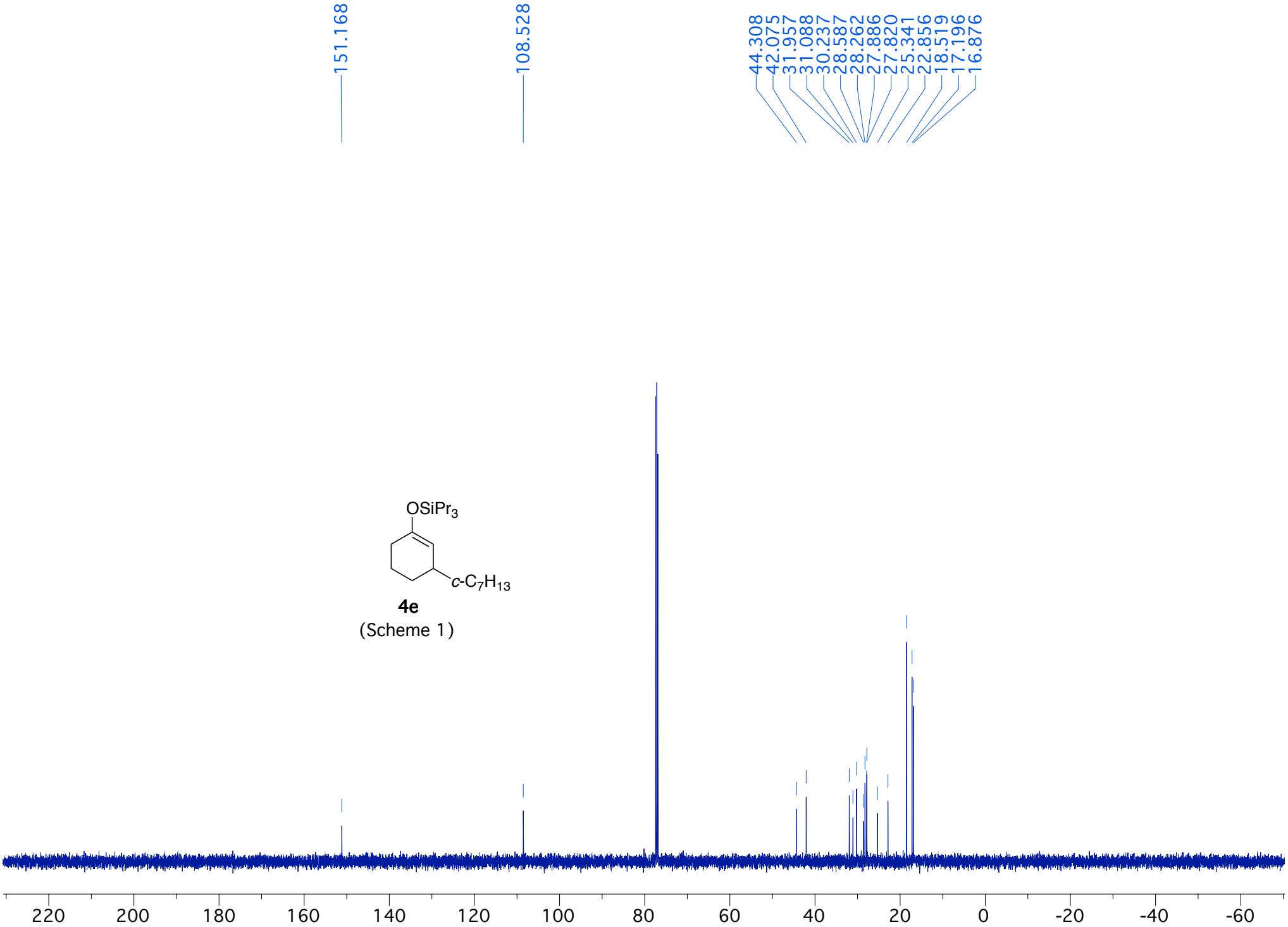
1.792
1.766
1.686
1.646
1.614
1.543
1.502
1.462
1.434
1.419
1.404
1.387
1.372
1.356
1.305
1.280
1.261
1.243
1.223
1.221
1.217
1.216
1.157
1.152
1.151
1.132
1.127
1.112
1.107
1.106
1.103
1.102
1.087
0.979
0.965
0.951
0.664
0.654
0.648
0.641
0.631
OSiPr3
c-C7H13
4e
(Scheme 1)
0.992
0.996
8.95
0.999
6
0.942
2.02
10.4
2.11
9.06
0
9
8
7
6
5
4
3
2
1
0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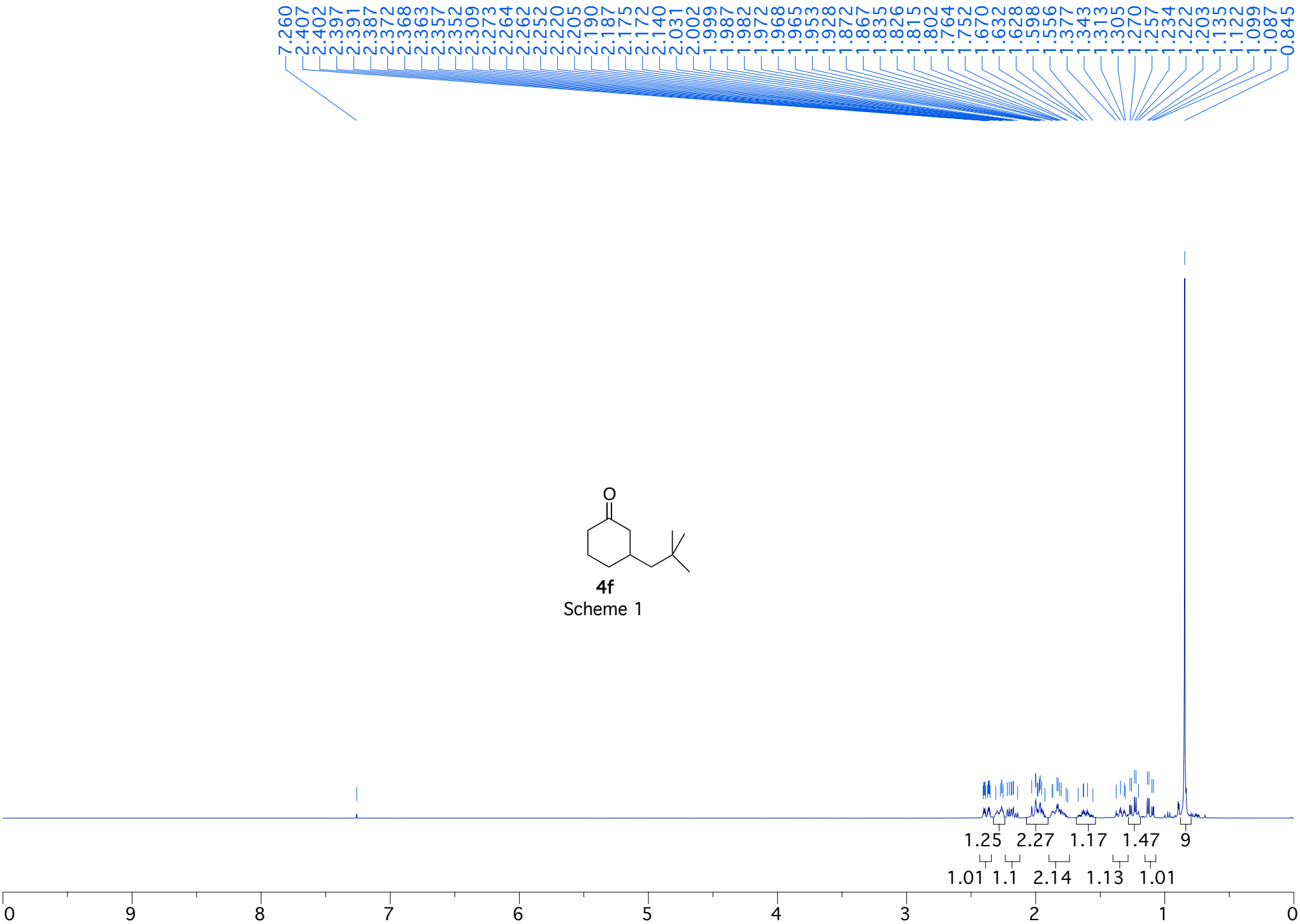
44.308
42.075
31.957
31.088
30.237
28.587
28.262
27.886
27.820
25.341
22.856
18.519
17.196
16.876
OSiPr3
c-C7H13
4e
(Scheme 1)
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60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2.397
2.391
2.387
2.372
2.368
2.363
2.357
2.352
2.309
2.273
2.264
2.262
2.252
2.220
2.205
2.190
2.187
2.175
2.172
2.140
2.031
2.002
1.999
1.987
1.982
1.972
1.968
1.965
1.953
1.928
1.872
1.867
1.835
1.826
1.815
1.802
1.764
1.752
1.670
1.632
1.628
1.598
1.556
1.537
1.343
1.313
1.305
1.270
1.257
1.234
1.222
1.203
1.135
1.122
1.099
1.087
0.845
O
4f
Scheme 1
1.25
2.27
1.17
1.47
9
1.01
1.1
2.14
1.13
1.01
0
9
8
7
6
5
4
3
2
1
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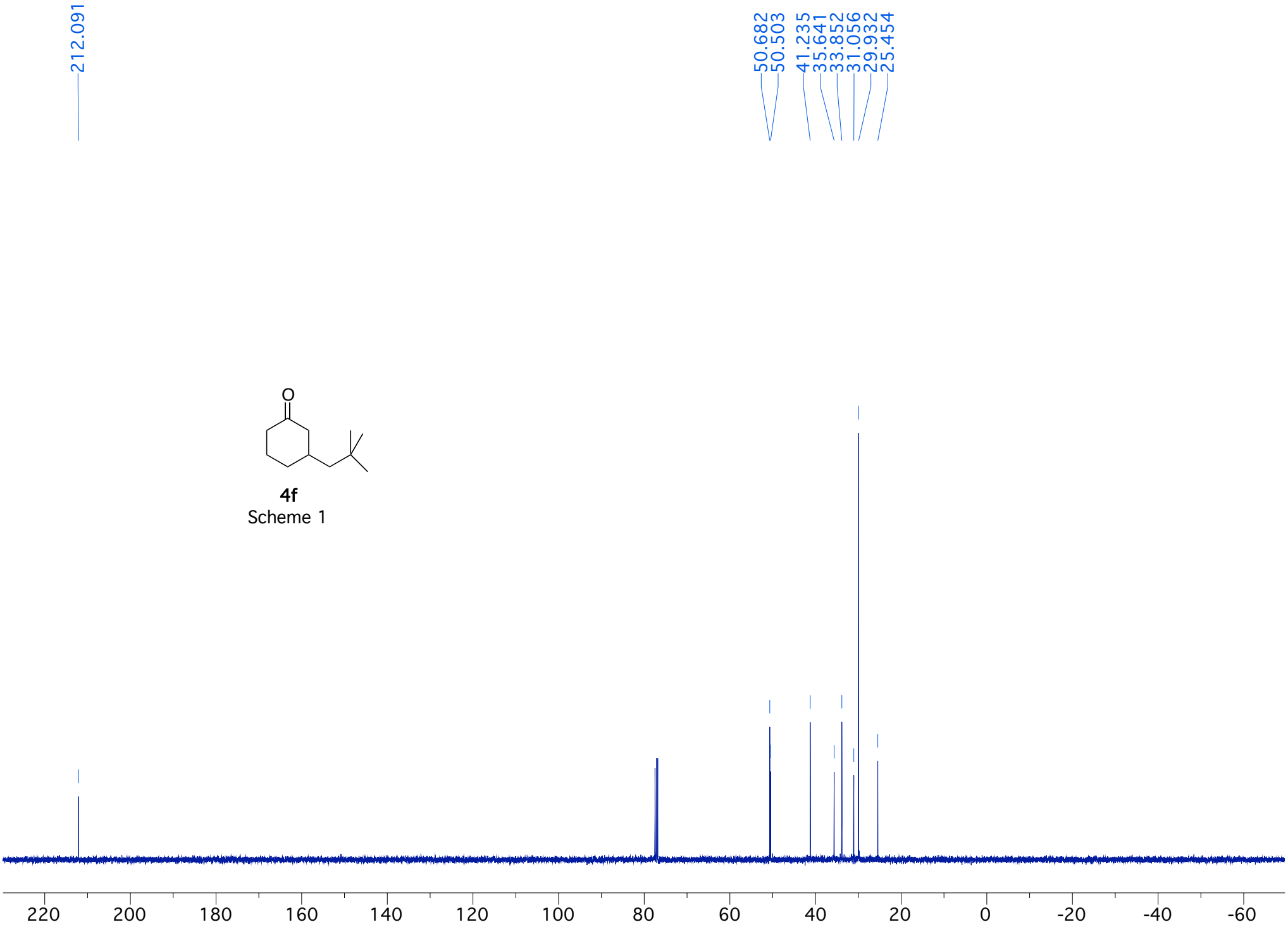
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50.503
41.235
35.641
33.852
31.056
29.932
25.454
O
220
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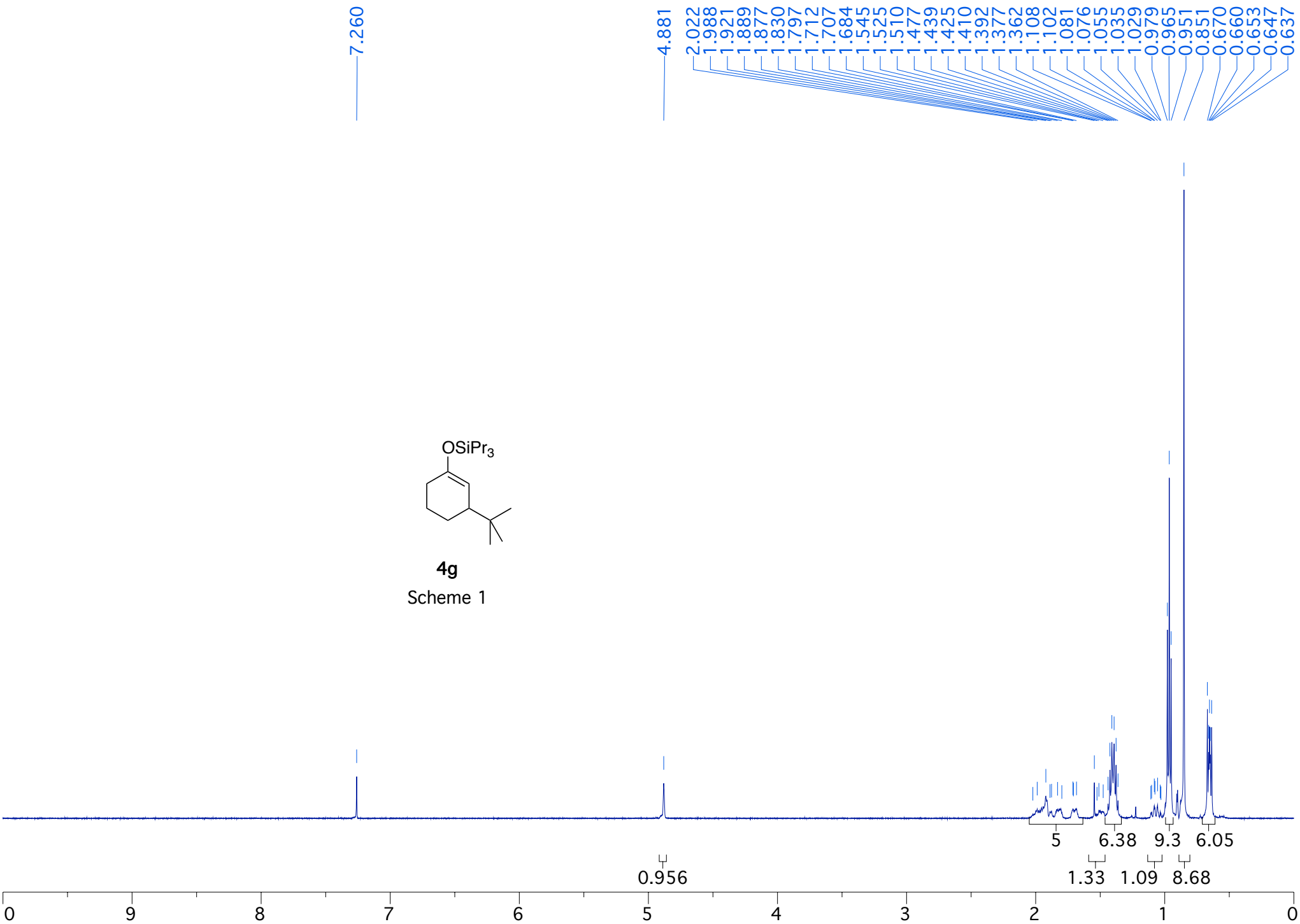
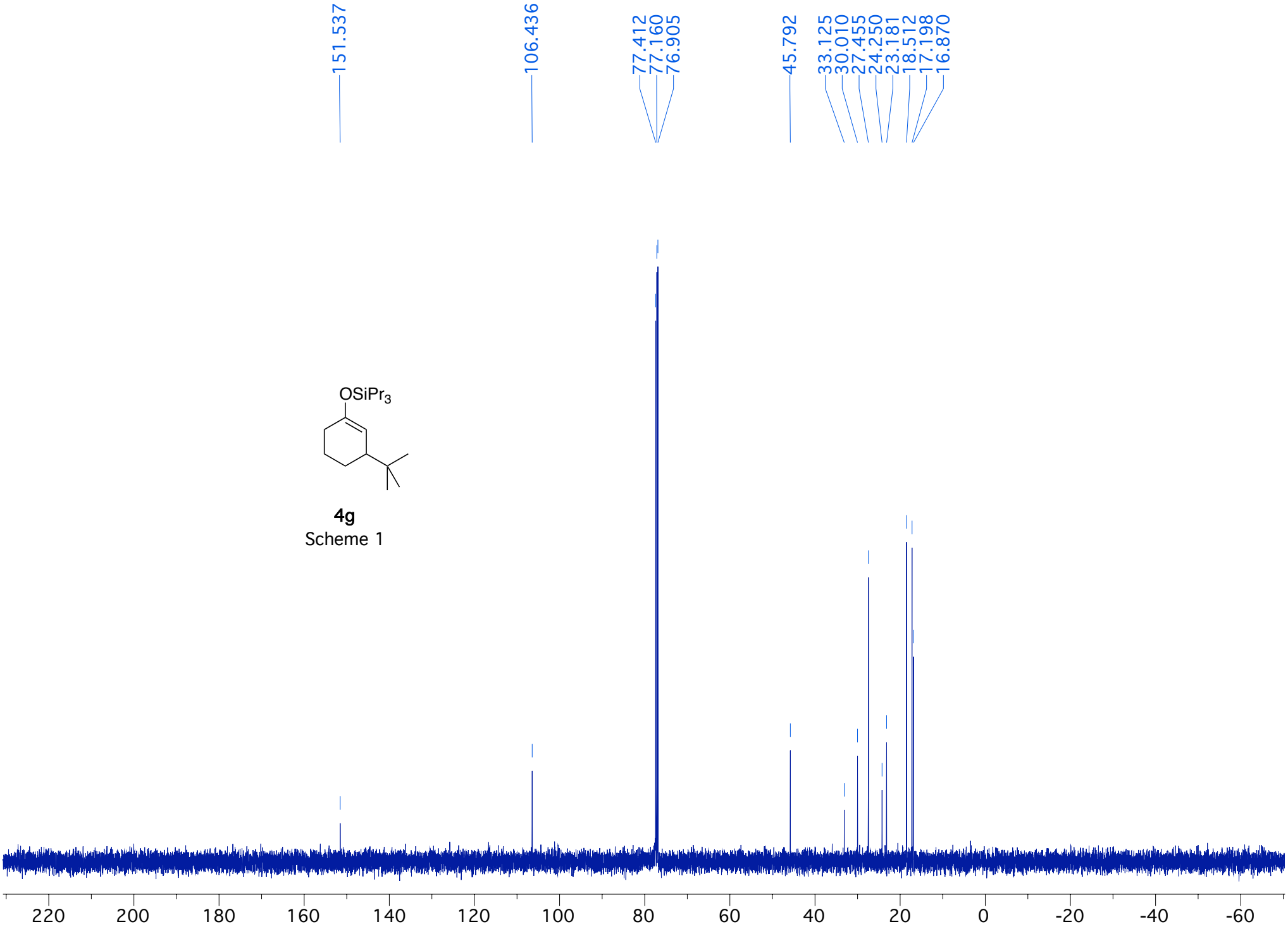
180
160
140
120
100
80
60
40
20
0
-20
-40
-60

4f
Scheme 1

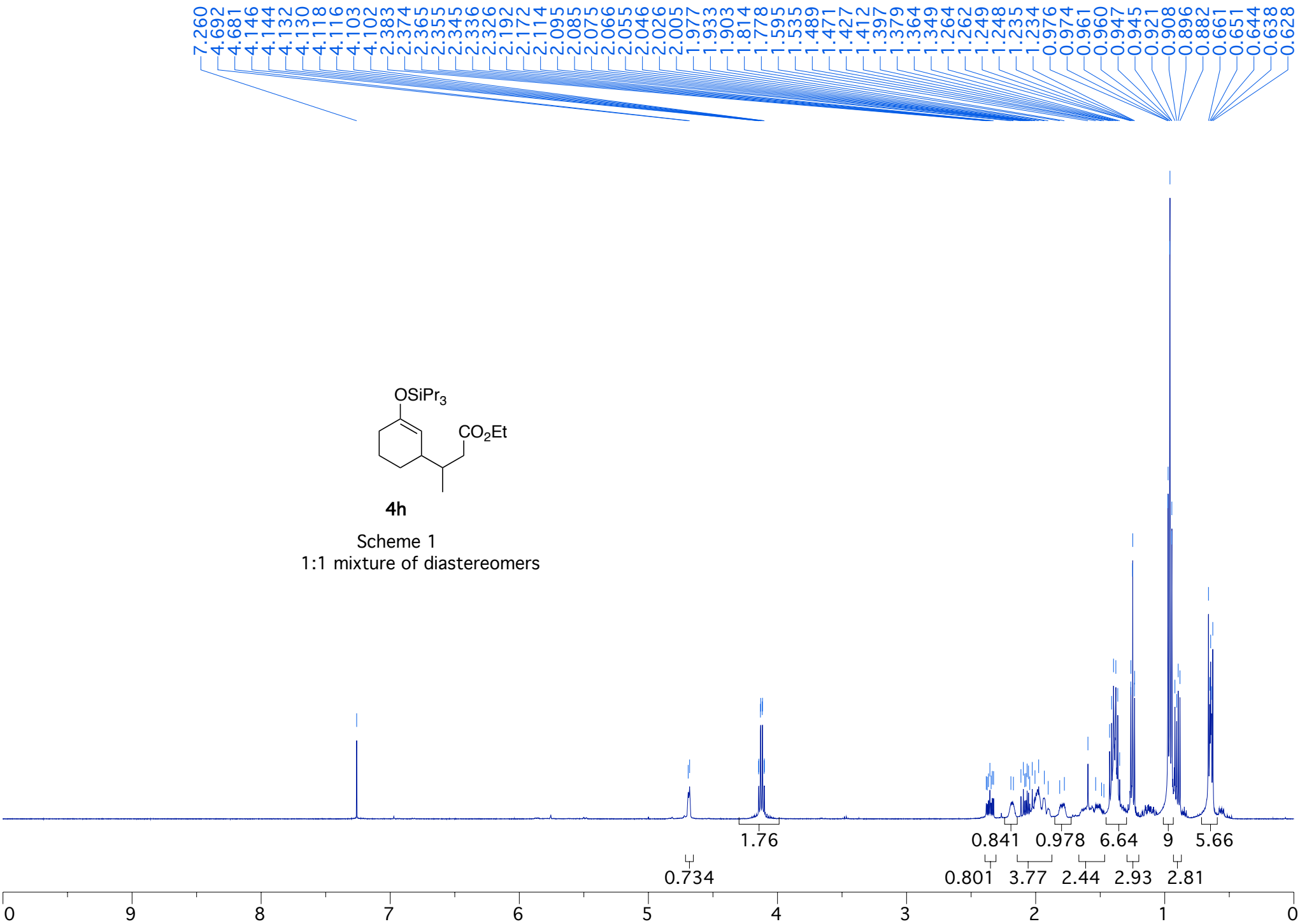

7.260
4.881
2.022
1.988
1.921
1.889
1.877
1.830
1.797
1.712
1.707
1.684
1.545
1.525
1.510
1.477
1.439
1.425
1.410
1.392
1.377
1.362
1.108
1.102
1.081
1.076
1.055
1.035
1.029
0.979
0.965
0.951
0.851
0.670
0.660
0.653
0.647
0.637
OSiPr3
5
6.38
9.3
6.05
0.956
1.33
1.09
8.68
0
9
8
7
6
5
4
3
2
1
0

4g

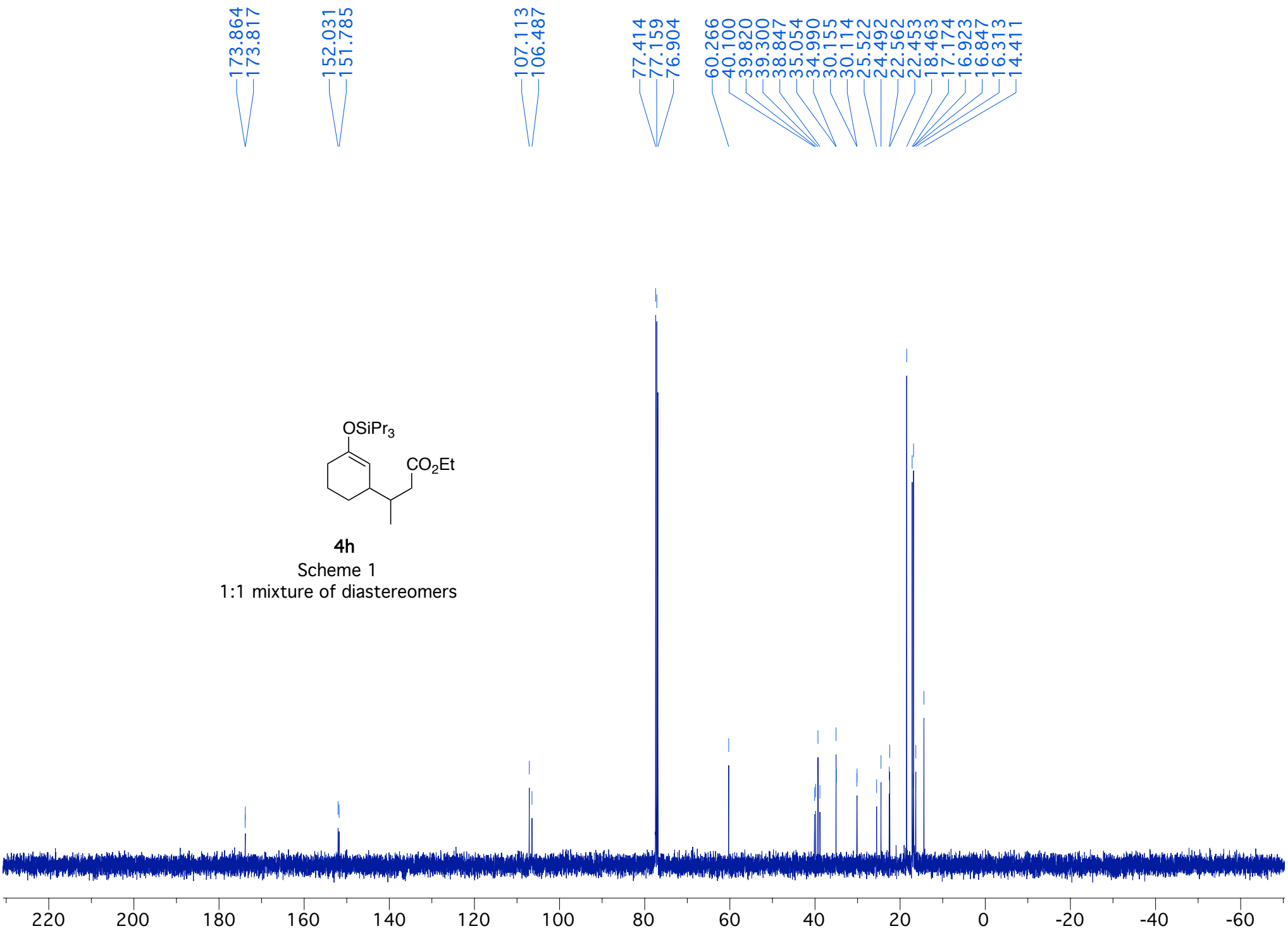
Scheme 1


151.537
106.436
77.412
77.160
76.905
45.792
33.125
30.010
27.455
24.250
23.181
18.512
17.198
16.870
OSiPr3
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60

4g
Scheme 1



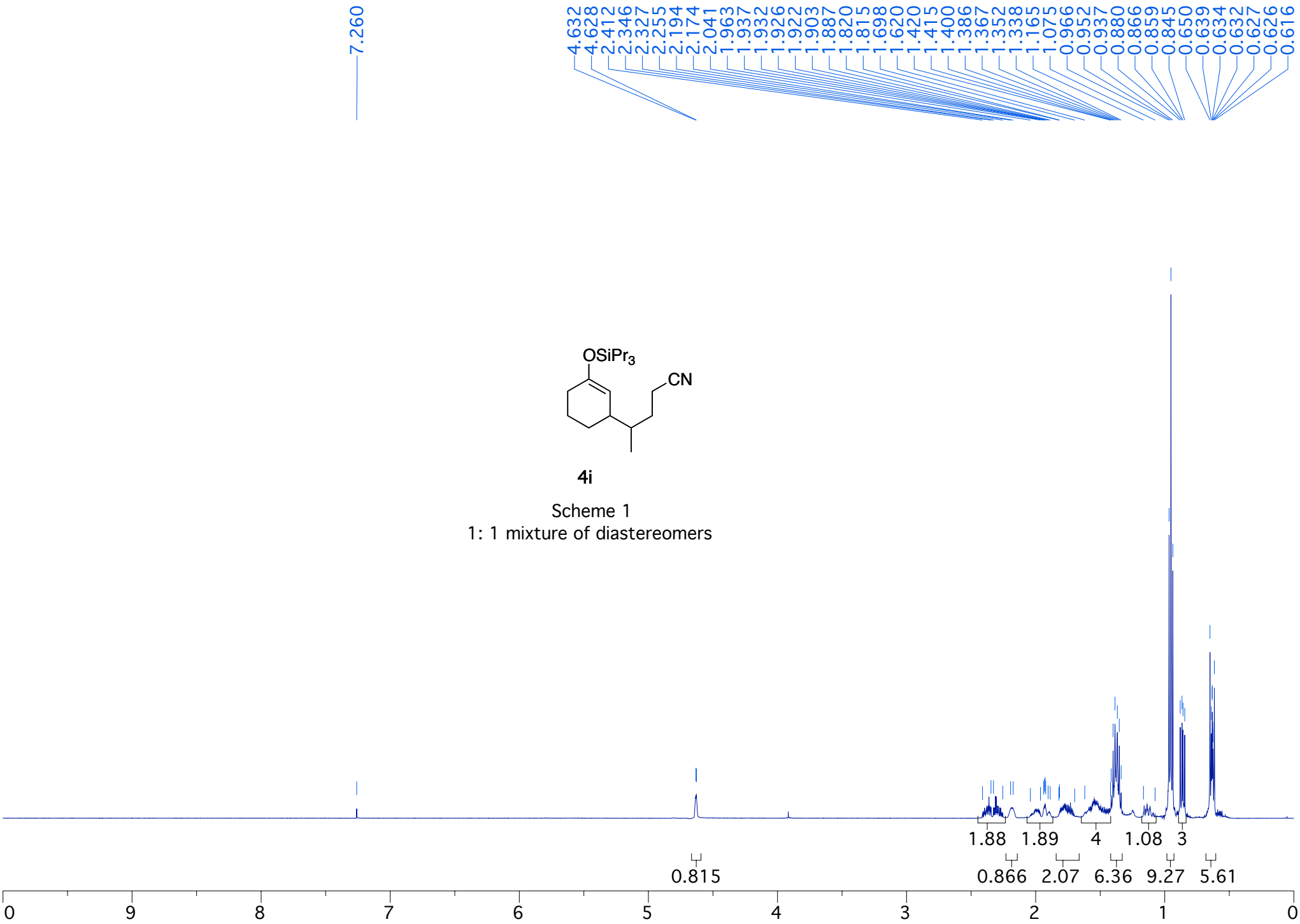
Scheme 1
1:1 mixture of diastereomers



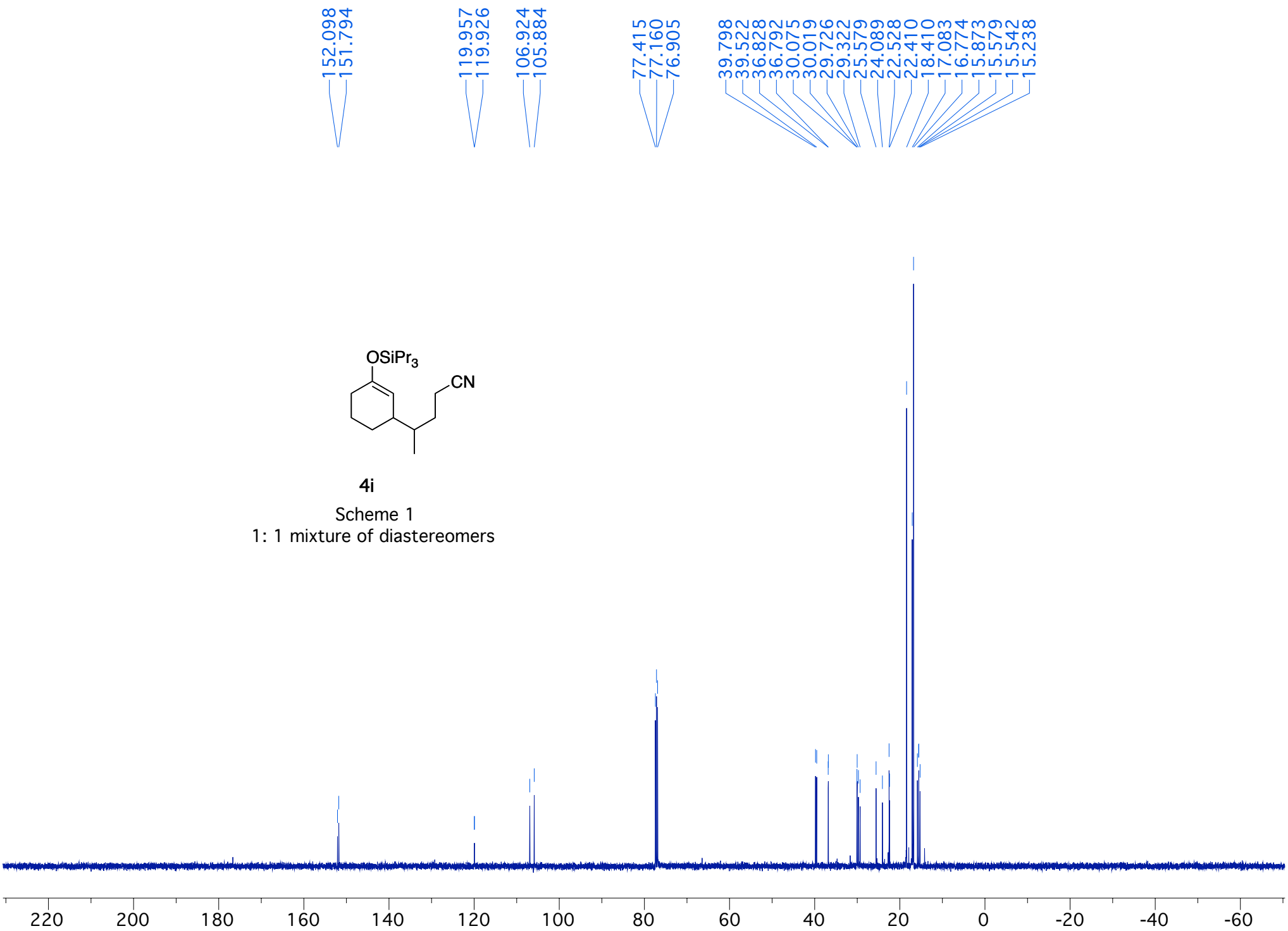
4h

Scheme 1

1:1 mixture of diastereomers



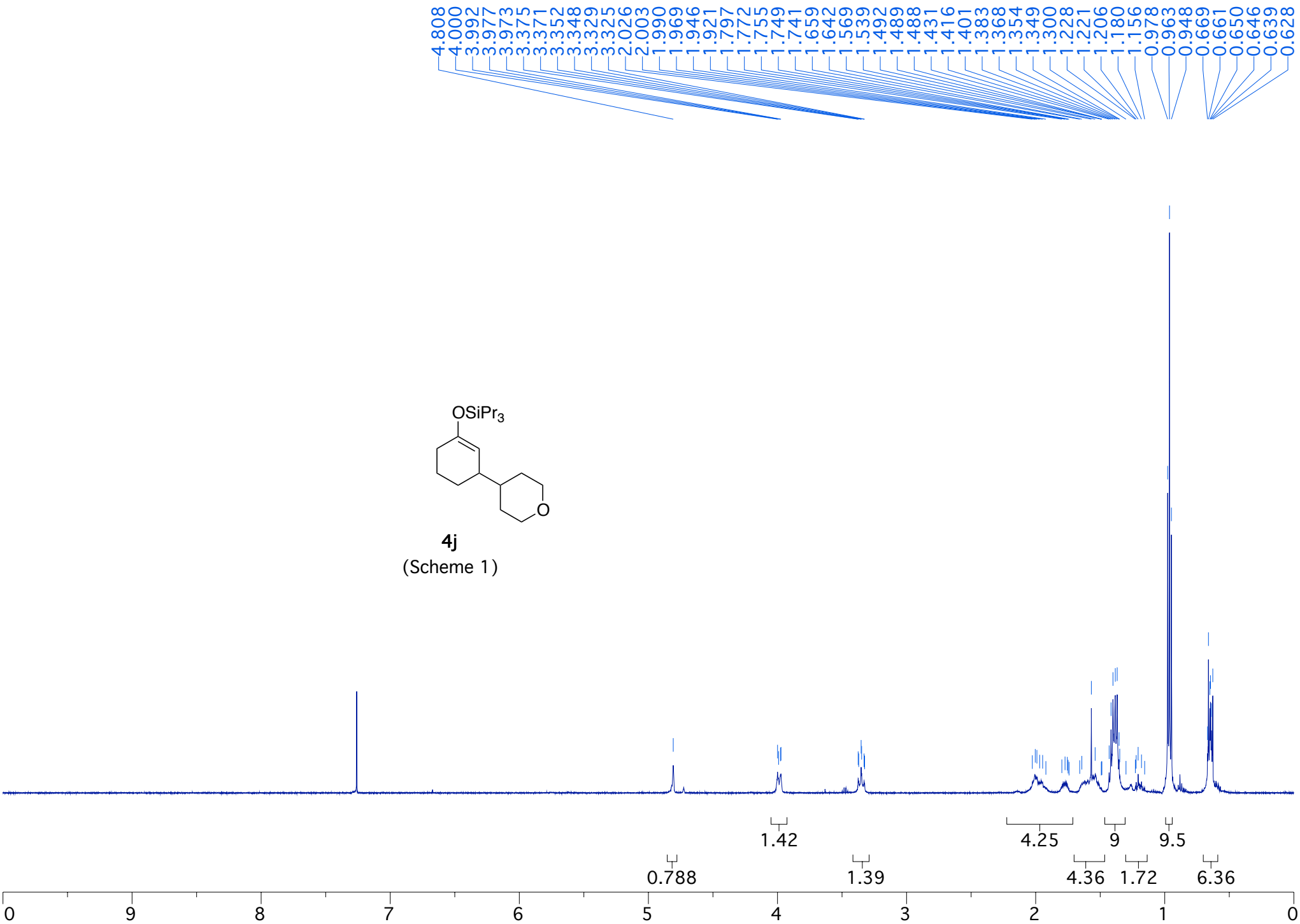
Scheme 1
1: 1 mixture of diastereomers

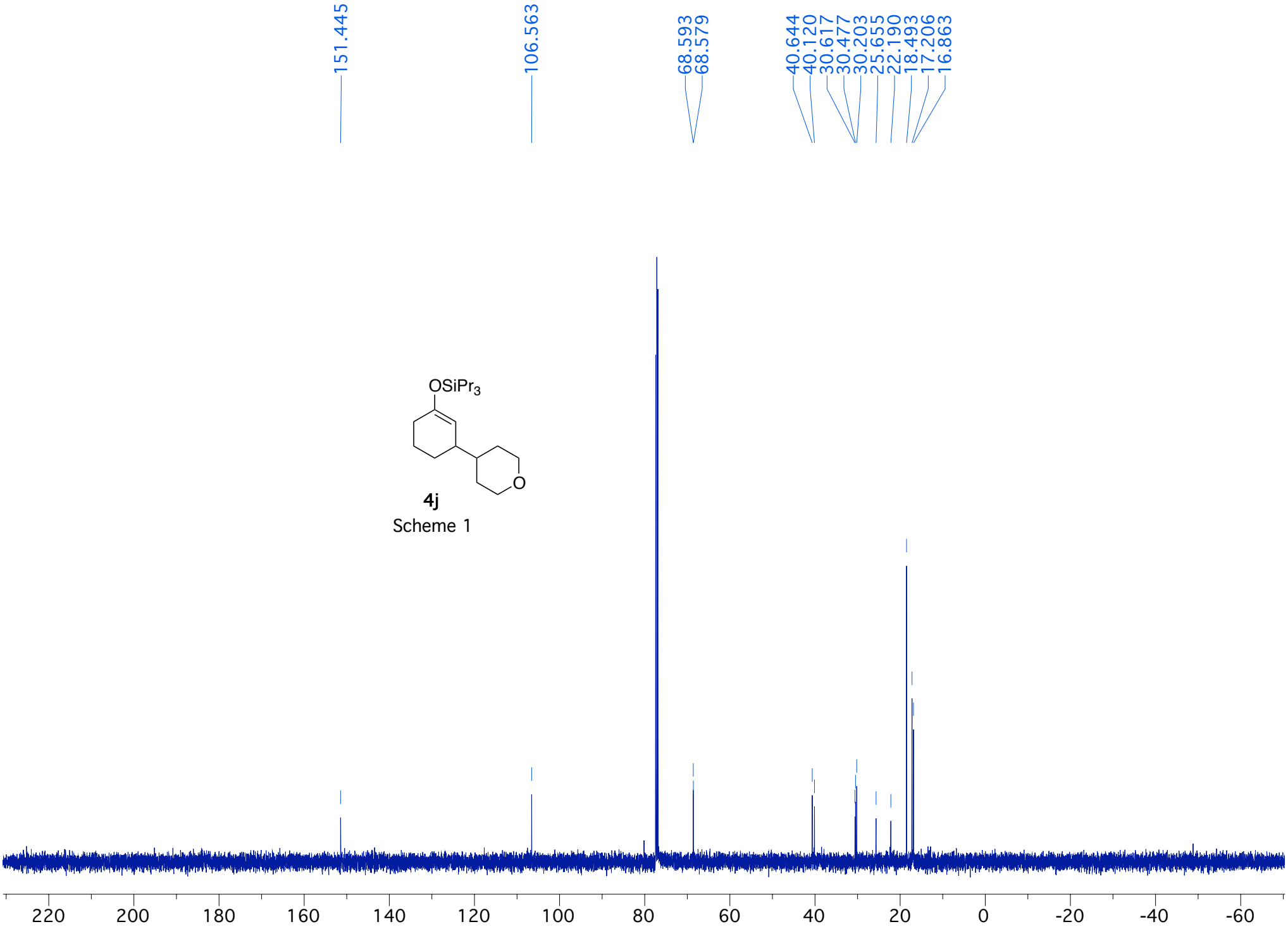


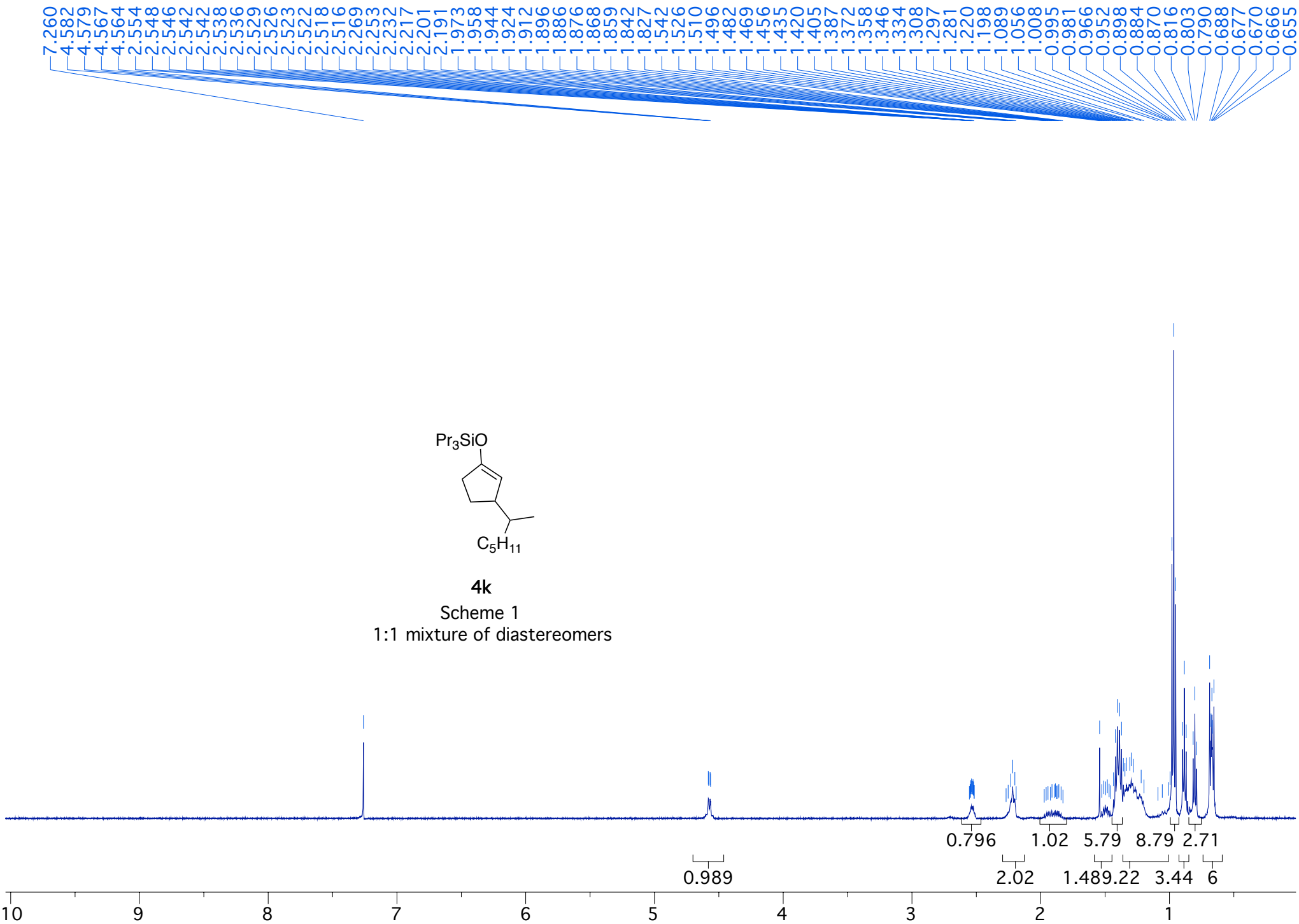
4i

Scheme 1

1: 1 mixture of diastereomers


4.808
4.000
3.992
3.977
3.973
3.375
3.371
3.352
3.348
3.329
3.325
2.026
2.003
1.990
1.969
1.946
1.921
1.797
1.772
1.755
1.749
1.741
1.659
1.642
1.569
1.539
1.492
1.489
1.488
1.431
1.416
1.401
1.383
1.368
1.354
1.349
1.300
1.228
1.221
1.206
1.180
1.156
0.978
0.963
0.948
0.669
0.661
0.650
0.646
0.639
0.628
OSiPr3
O
4j
(Scheme 1)
1.42
4.25
9
9.5
0.788
1.39
4.36
1.72
6.36
0
9
8
7
6
5
4
3
2
1
0


151.445
106.563
68.593
68.579
40.644
40.120
30.617
30.477
30.203
25.655
22.190
18.493
17.206
16.863
OSiPr3
O
4j
Scheme 1
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60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4.567
4.564
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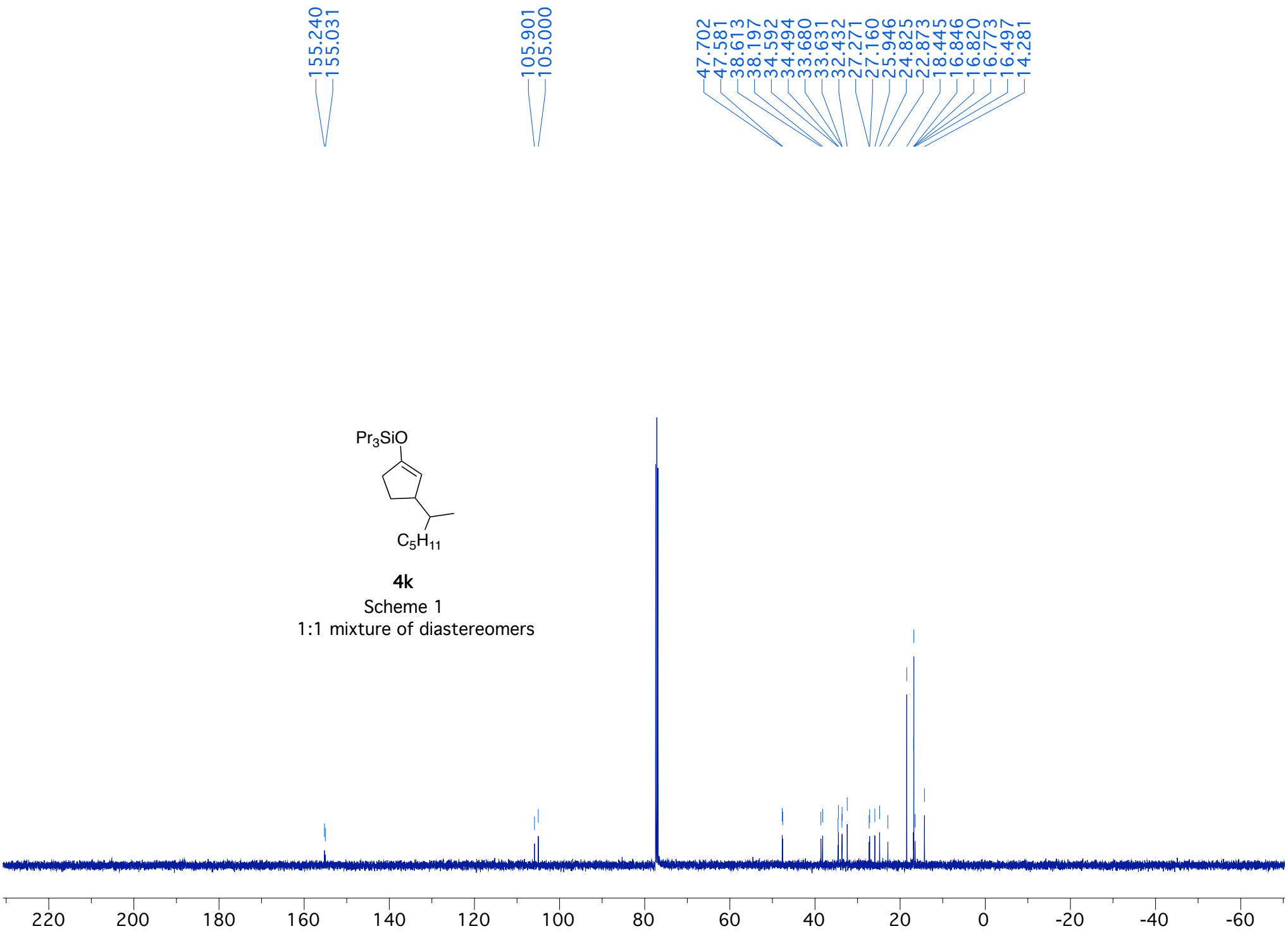
2.548
2.546
2.542
2.542
2.538
2.536
2.529
2.526
2.523
2.522
2.518
2.516
2.269
2.253
2.232
2.217
2.201
2.191
1.973
1.958
1.944
1.924
1.912
1.896
1.886
1.876
1.868
1.859
1.842
1.827
1.542
1.526
1.510
1.496
1.482
1.469
1.456
1.435
1.420
1.405
1.387
1.372
1.358
1.346
1.334
1.308
1.297
1.281
1.220
1.198
1.089
1.056
1.008
0.995
0.981
0.966
0.952
0.898
0.884
0.870
0.816
0.803
0.790
0.688
0.677
0.670
0.666
0.655
Pr3SiO
C5H11
4k
Scheme 1
1:1 mixture of diastereomers
0.989
0.796
1.02
2.02
5.79
1.48
9.22
8.79
3.44
2.71
6
10
9
8
7
6
5
4
3
2
1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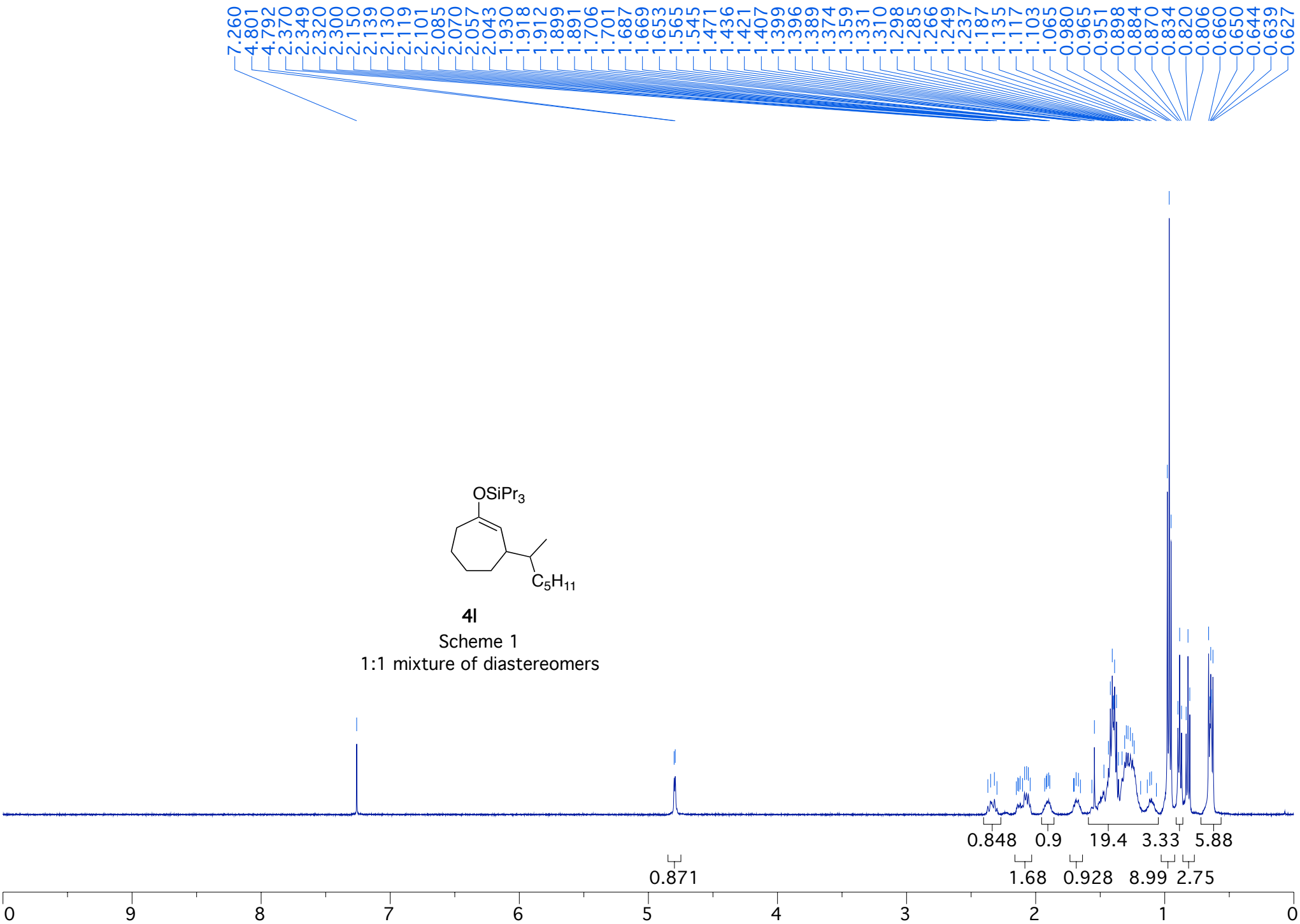
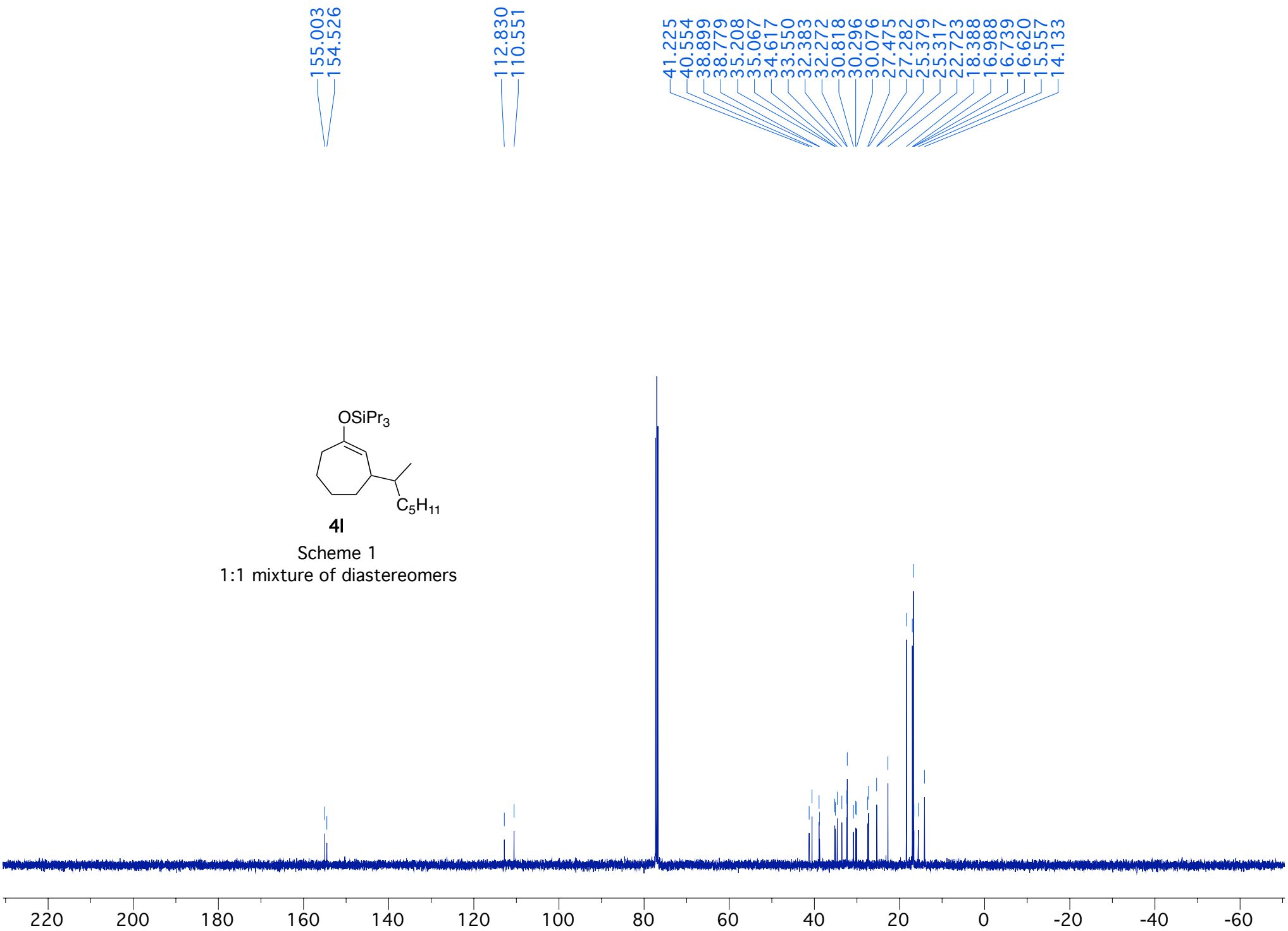
155.031
105.901
105.000
47.702
47.581
38.613
38.197
34.592
34.494
33.680
33.631
32.432
27.271
27.160
25.946
24.825
22.873
18.445
16.846
16.820
16.773
16.497
14.281
Pr3SiO
C5H11
4k
Scheme 1
1:1 mixture of diastereomers
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60



4l

Scheme 1

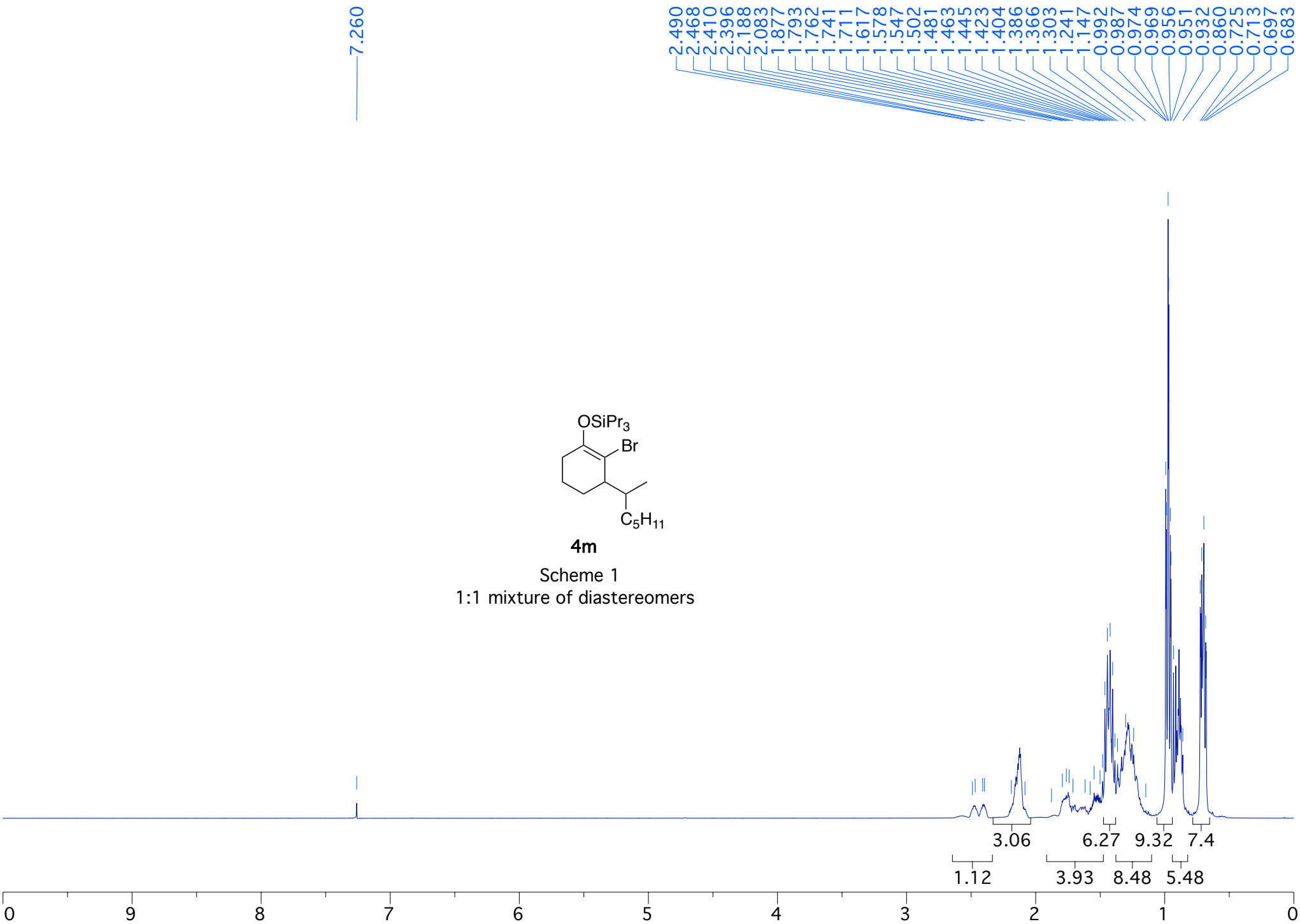
1:1 mixture of diastereomers



4l

Scheme 1

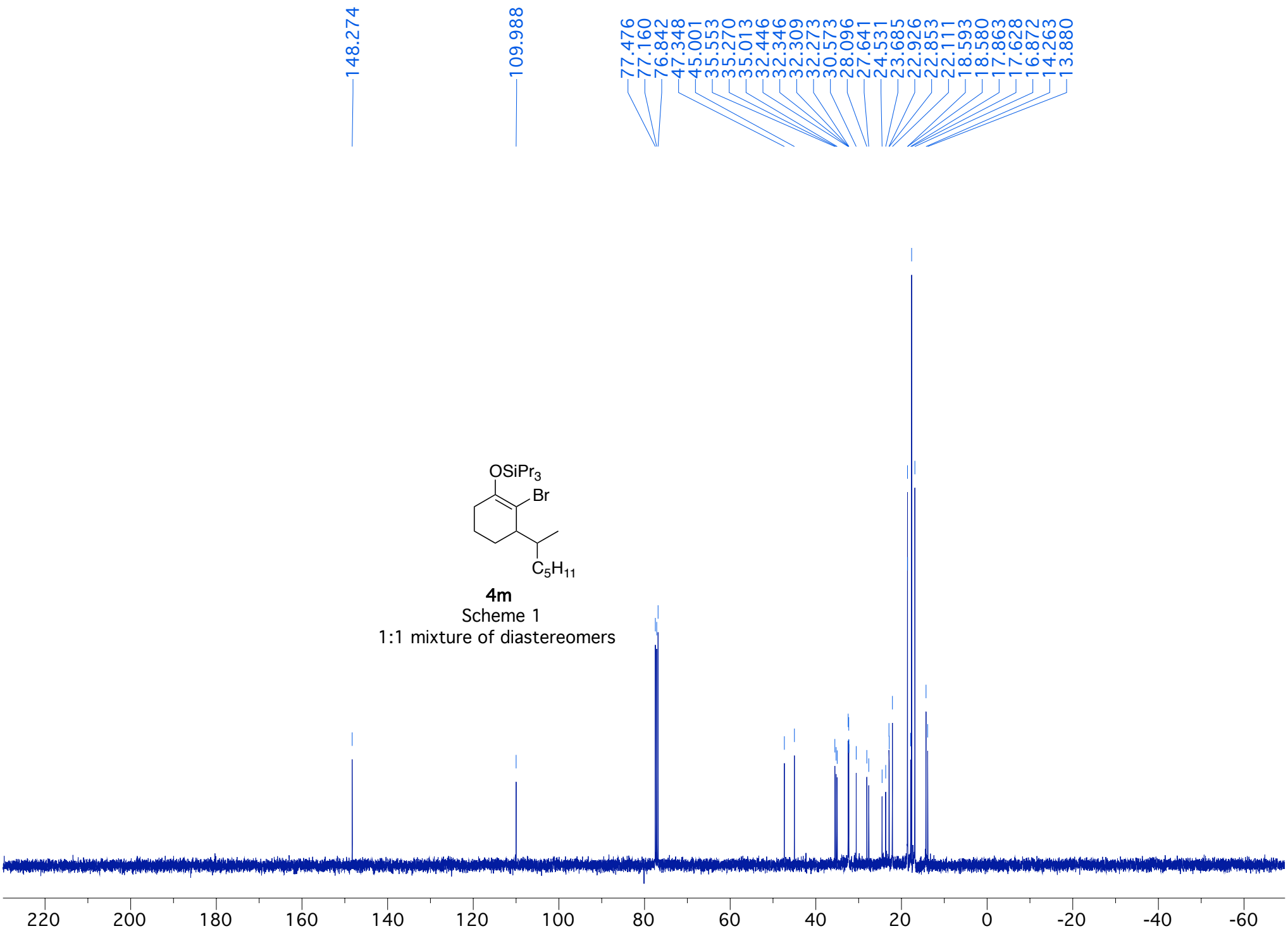
1:1 mixture of diastereomers

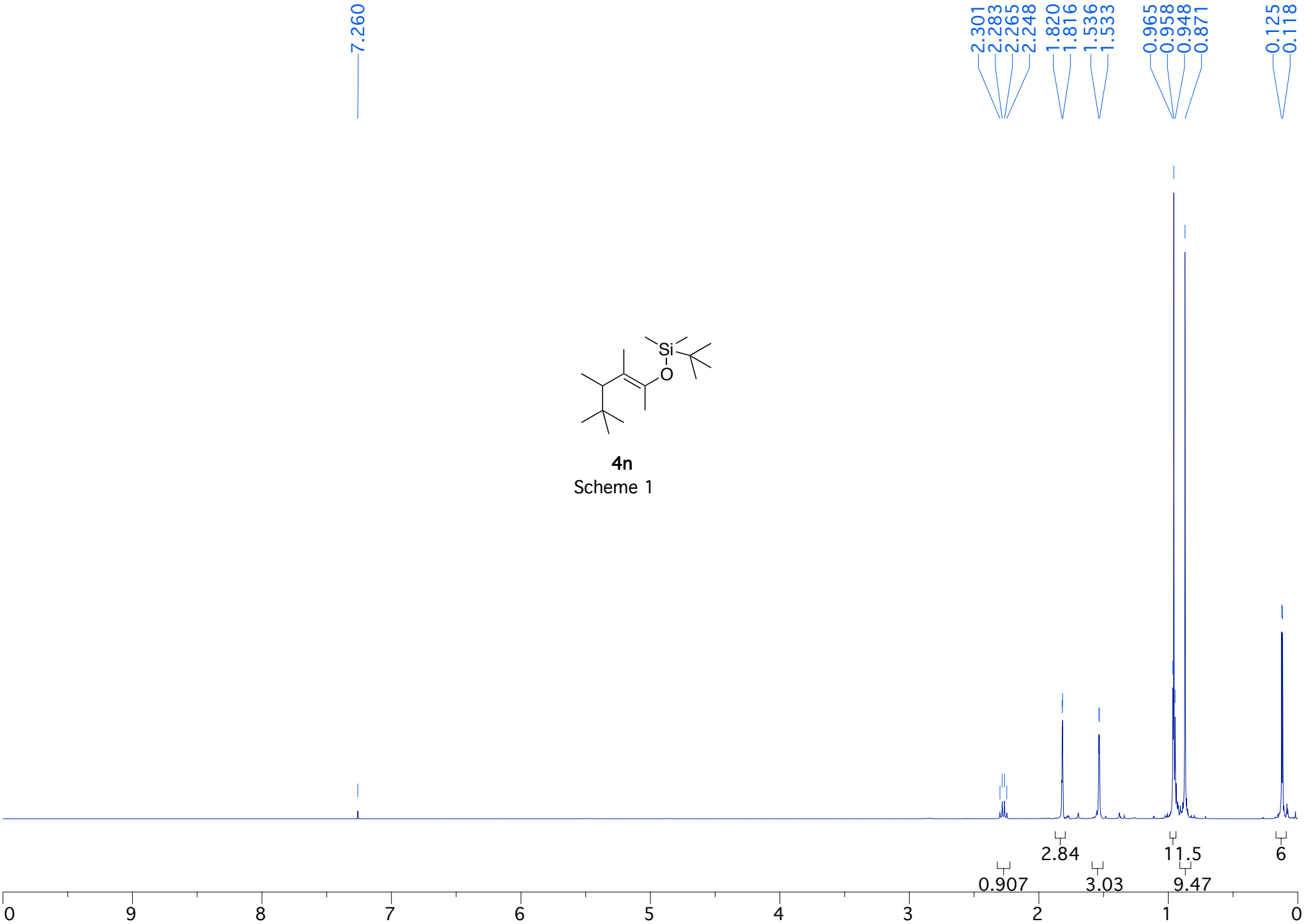


4m

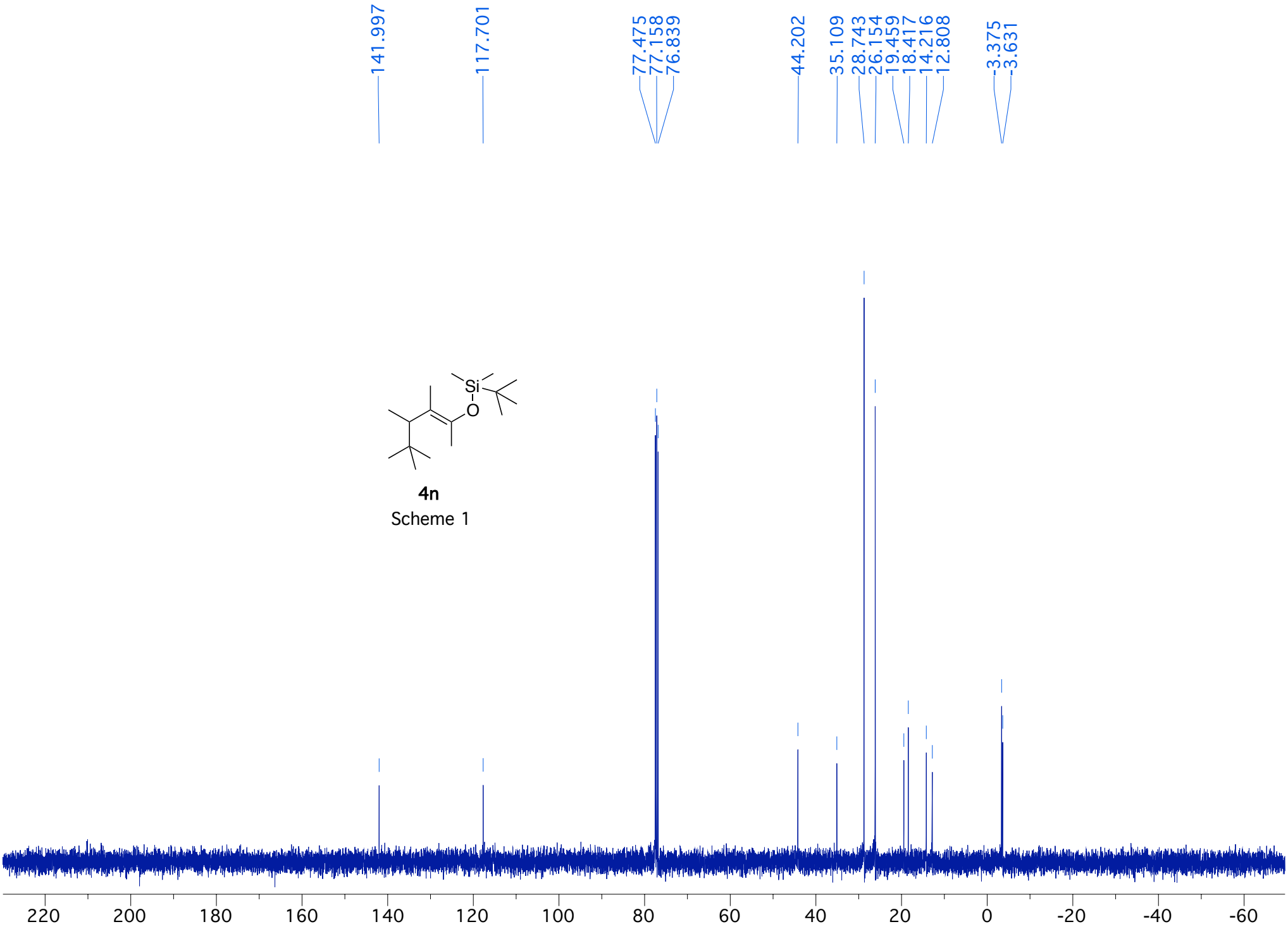
Scheme 1

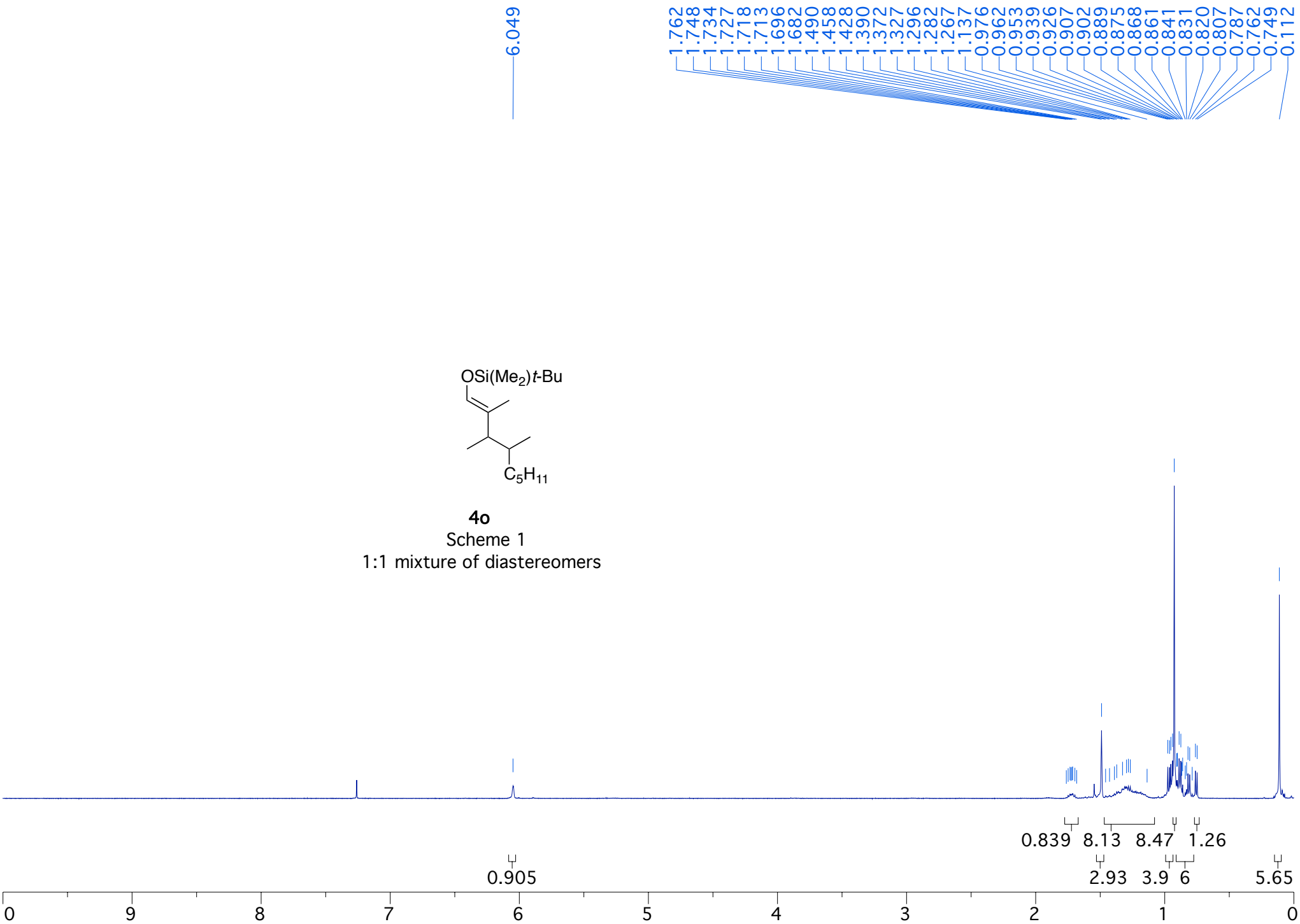
1:1 mixture of diastereomers


148.274
109.988
77.476
77.160
76.842
47.348
45.001
35.553
35.270
35.013
32.446
32.346
32.309
32.273
30.573
28.096
27.641
24.531
23.685
22.926
22.853
22.111
18.593
18.580
17.863
17.628
16.872
14.263
13.880
OSiPr3
Br
C5H11
4m
Scheme 1
1:1 mixture of diastereomers
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60

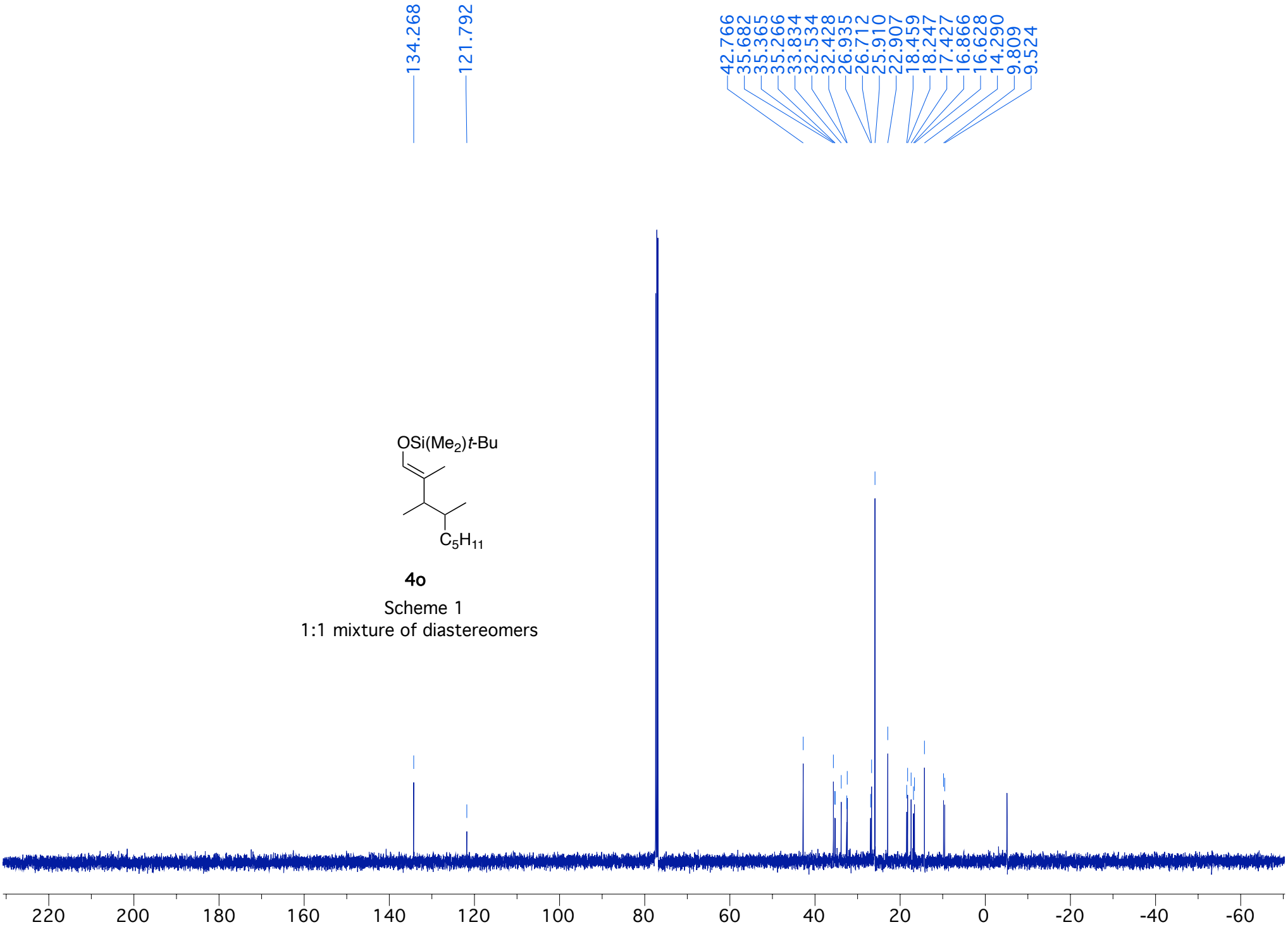

7.260
2.301
2.283
2.265
2.248
1.820
1.816
1.536
1.533
0.965
0.958
0.948
0.871
0.125
0.118
Si
O
2.84
11.5
6
0.907
3.03
9.47
0
9
8
7
6
5
4
3
2
1
0

4n
Scheme 1


141.997
117.701
77.475
77.158
76.839
44.202
35.109
28.743
26.154
19.459
18.417
14.216
12.808
-3.375
-3.631
Si
O
4n
Scheme 1
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60



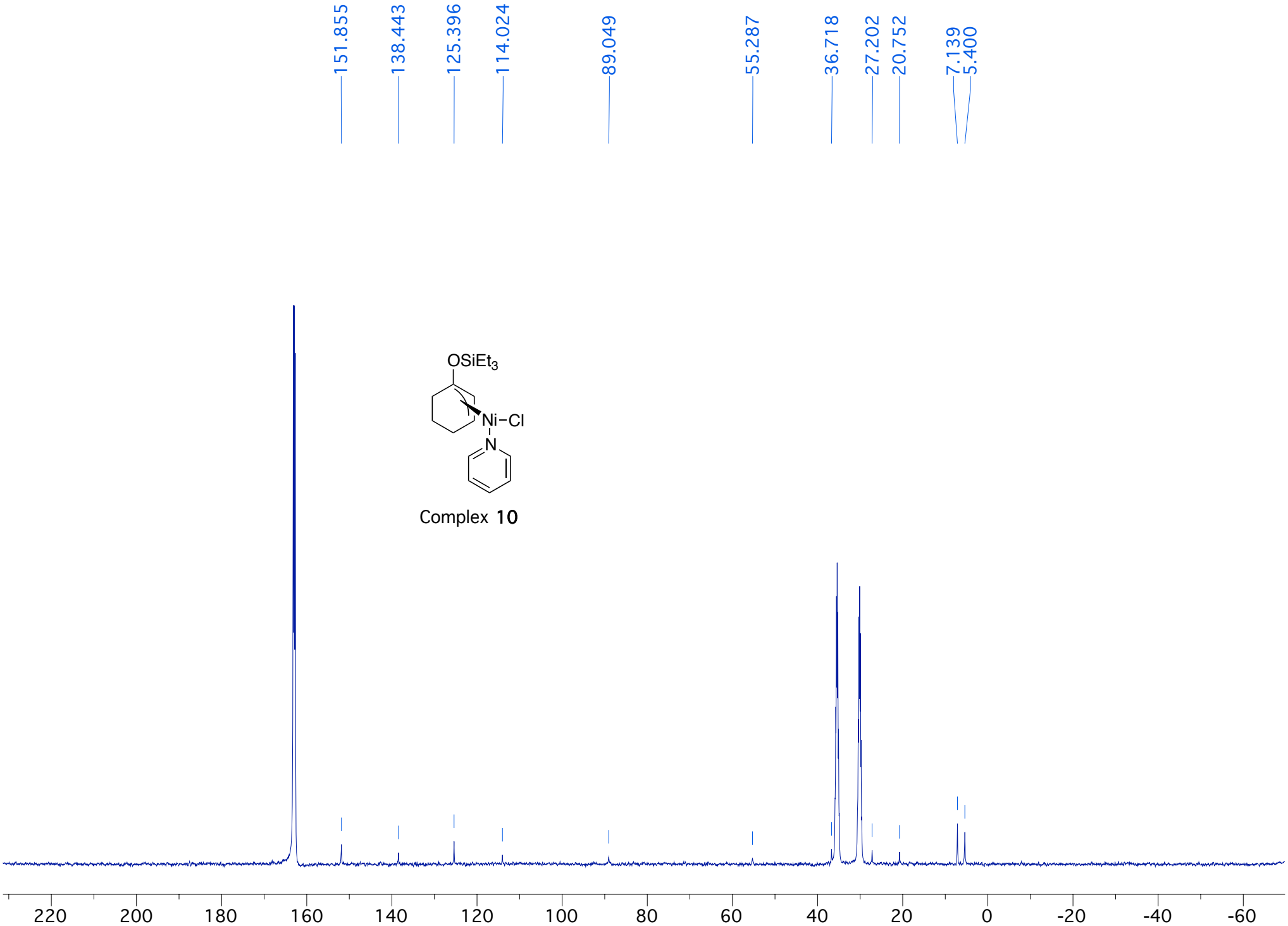
4o
Scheme 1
1:1 mixture of diastereomers

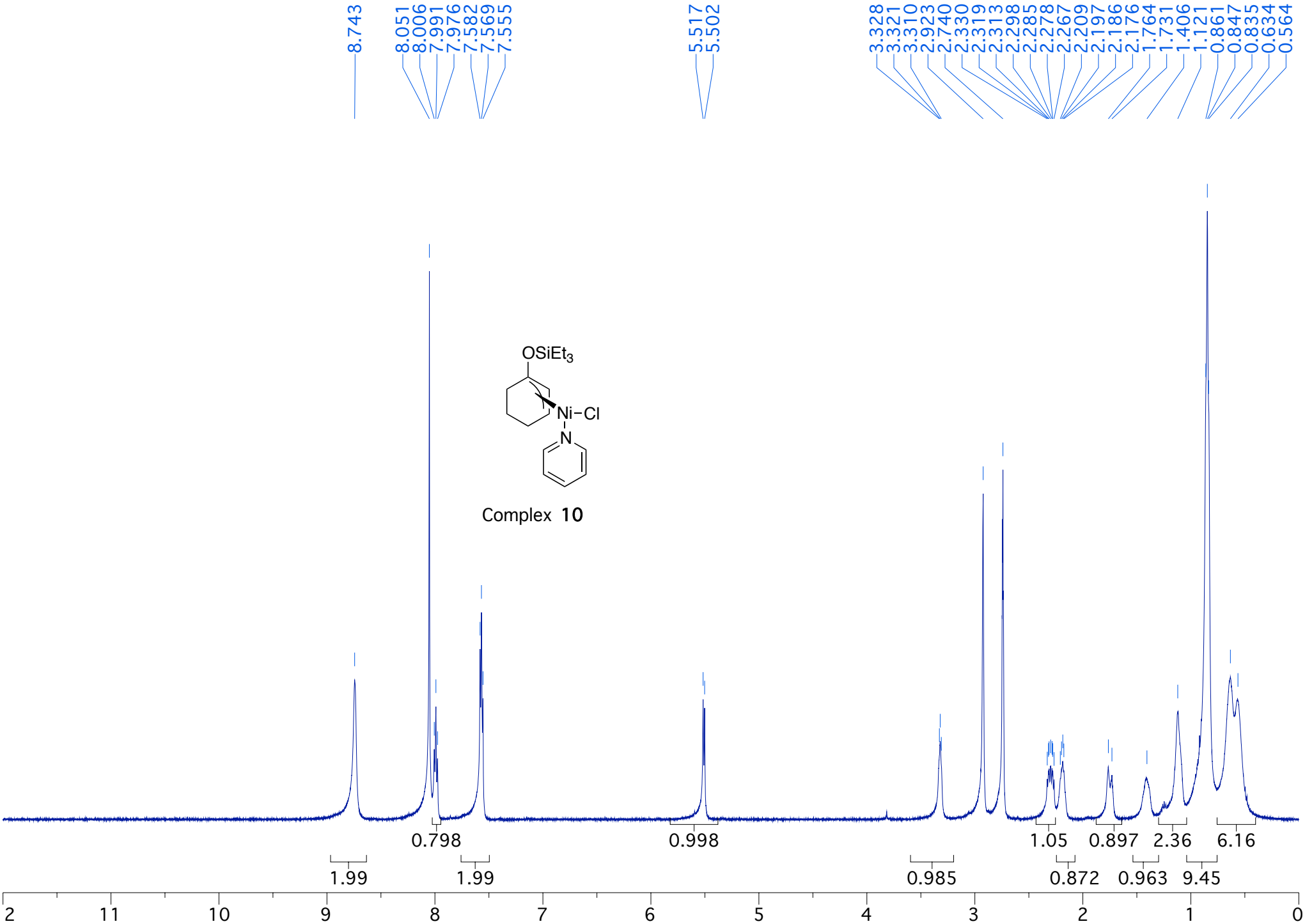


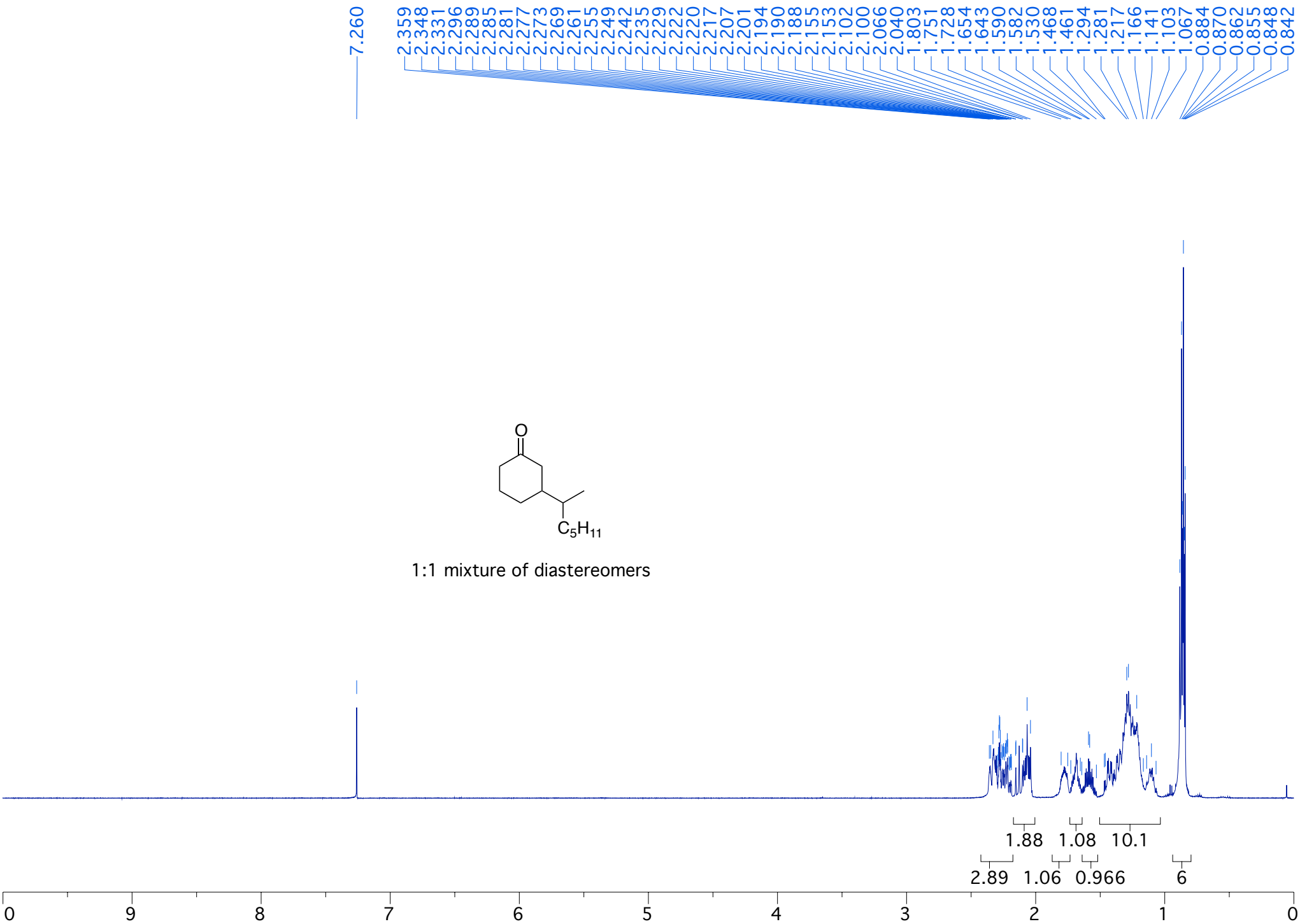
4o

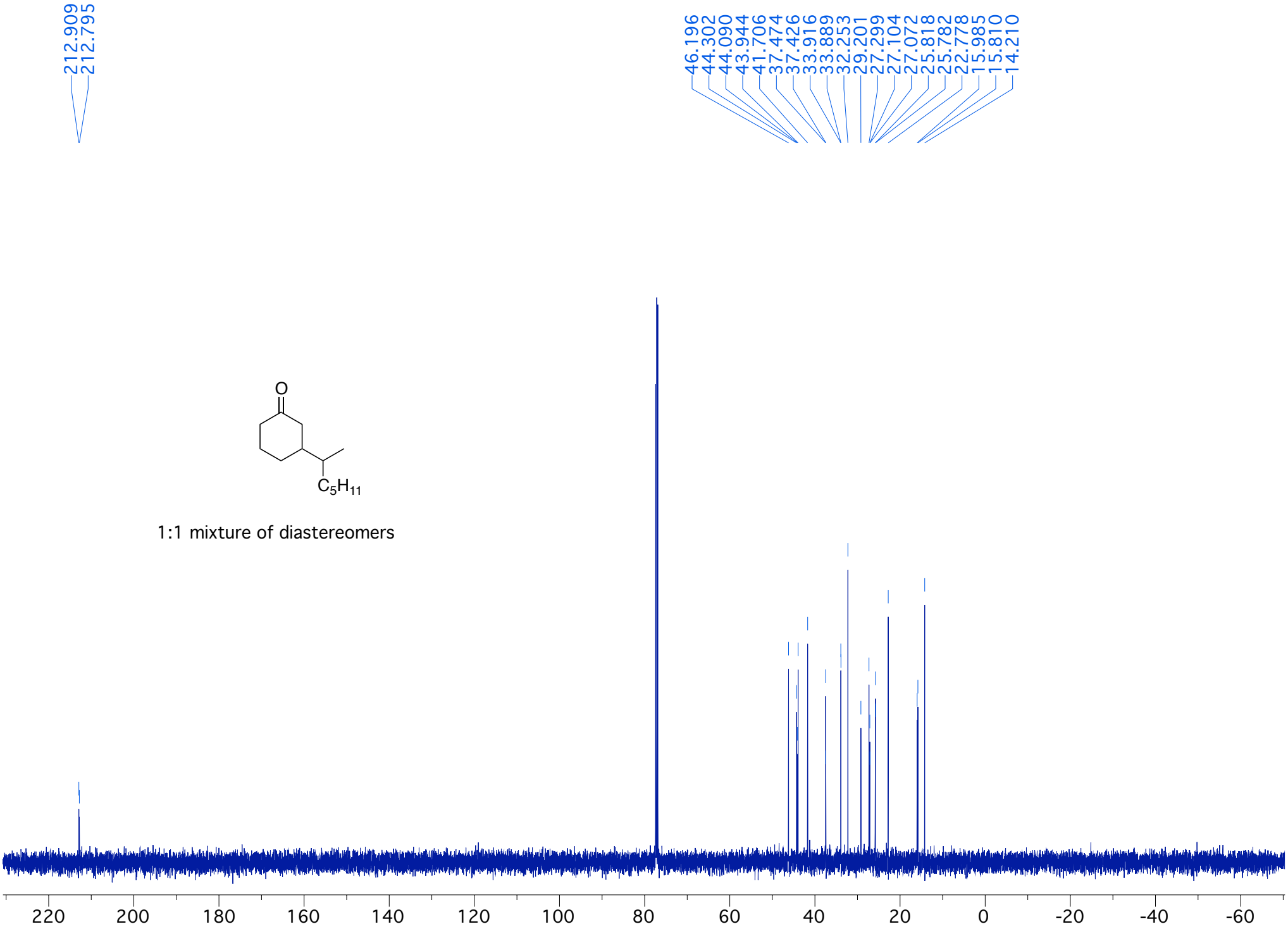
Scheme 1

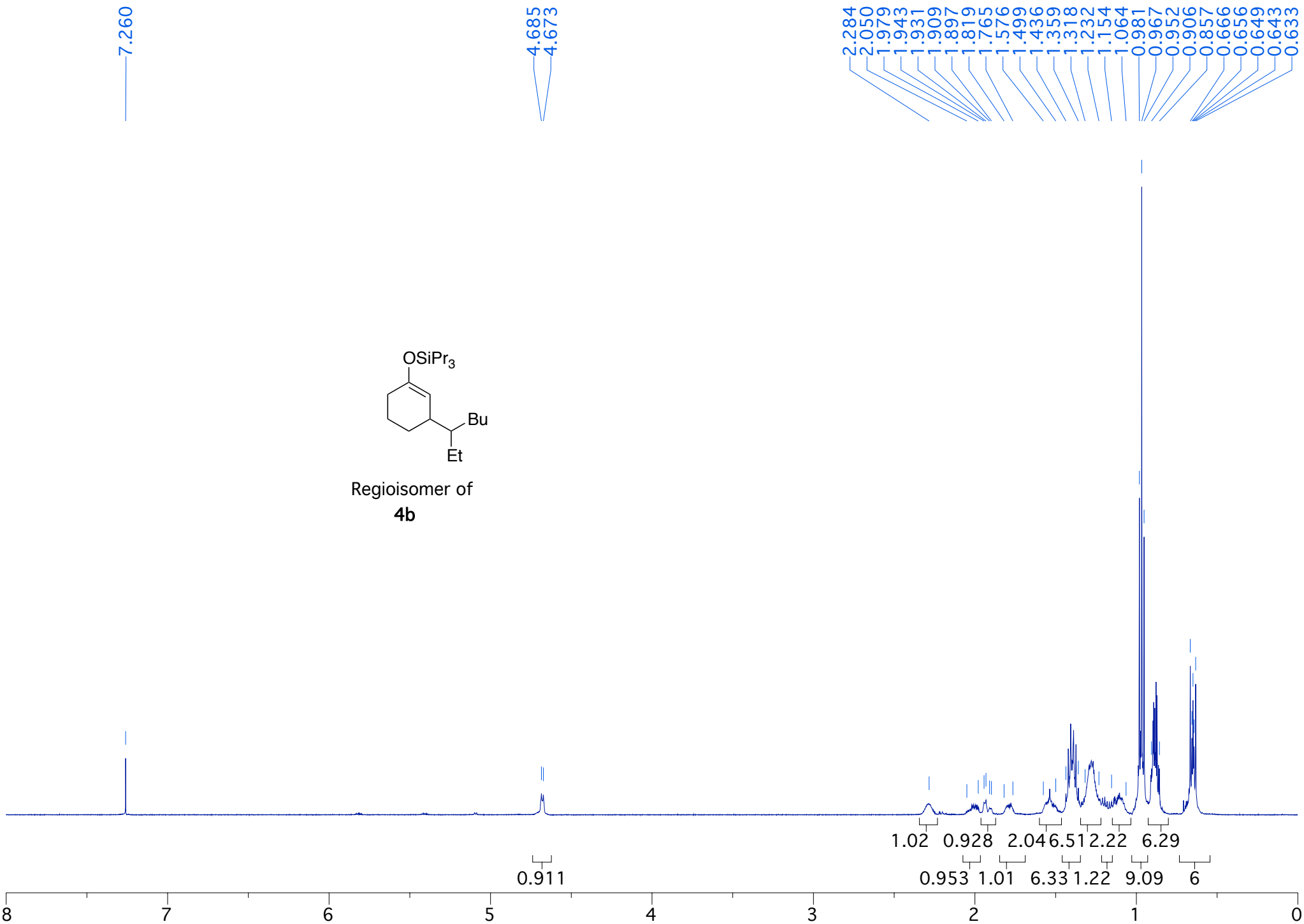
1:1 mixture of diastereomers

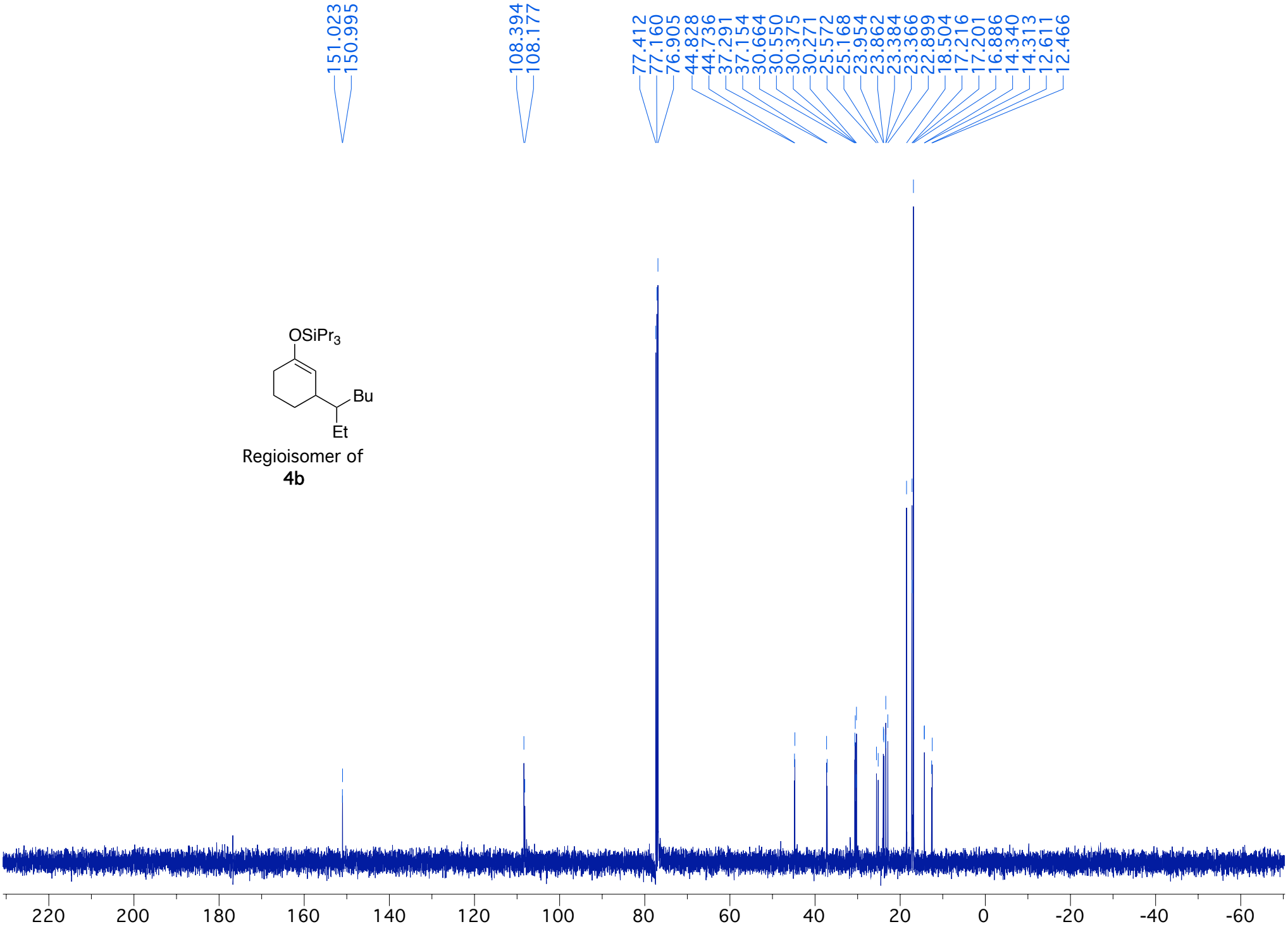

151.855
138.443
125.396
114.024
89.049
55.287
36.718
27.202
20.752
7.139
5.400
OSiEt3
Ni–Cl
N
Complex 10
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60


8.743
8.051
8.006
7.991
7.976
7.582
7.569
7.555
5.517
5.502
3.328
3.321
3.310
2.923
2.740
2.330
2.319
2.313
2.298
2.285
2.278
2.267
2.209
2.197
2.186
2.176
1.764
1.731
1.406
1.121
0.861
0.847
0.835
0.634
0.564
OSiEt3
Ni–Cl
N
Complex 10
0.798
0.998
1.05
0.897
2.36
6.16
1.99
1.99
0.985
0.872
0.963
9.45
12
11
10
9
8
7
6
5
4
3
2
1
0


7.260
2.359
2.348
2.331
2.296
2.289
2.285
2.281
2.277
2.273
2.269
2.261
2.255
2.249
2.242
2.235
2.229
2.222
2.220
2.217
2.207
2.201
2.194
2.190
2.188
2.155
2.153
2.102
2.100
2.066
2.040
1.803
1.751
1.728
1.654
1.643
1.590
1.582
1.530
1.468
1.461
1.294
1.281
1.217
1.166
1.141
1.103
1.067
0.884
0.870
0.862
0.855
0.848
0.842
O
C_5H_{11}
1:1 mixture of diastereomers
1.88
1.08
10.1
2.89
1.06
0.966
6
0
9
8
7
6
5
4
3
2
1
0


212.909
212.795
46.196
44.302
44.090
43.944
41.706
37.474
37.426
33.916
33.889
32.253
29.201
27.299
27.104
27.072
25.818
25.782
22.778
15.985
15.810
14.210
O
C_5H_{11}
1:1 mixture of diastereomers
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60


7.260
4.685
4.673
2.284
2.050
1.979
1.943
1.931
1.909
1.897
1.819
1.765
1.576
1.499
1.436
1.359
1.318
1.232
1.154
1.064
0.981
0.967
0.952
0.906
0.857
0.666
0.656
0.649
0.643
0.633
OSiPr3
Bu
Et
Regioisomer of
4b
1.02
0.928
2.04
6.51
2.22
6.29
0.911
0.953
1.01
6.33
1.22
9.09
6
8
7
6
5
4
3
2
1
0


151.023
150.995
108.394
108.177
77.412
77.160
76.905
44.828
44.736
37.291
37.154
30.664
30.550
30.375
30.271
25.572
25.168
23.954
23.862
23.384
23.366
22.899
18.504
17.216
17.201
16.886
14.340
14.313
12.611
12.466
OSiPr3
Bu
Et
Regioisomer of
4b
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60