Supplementary Information

for

Reductive Arene *ortho*-Silanolization of Aromatic Esters with Hydridosilyl Acetals

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Contents of Supporting Information page

Methods

NMR Spectra

General Experimental

^{1}H and ^{13}C NMR spectra were recorded on JEOL Eclipse Plus 500 (500 MHz) and JEOL ECX 300 (300 MHz) spectrometers. ^{1}H NMR chemical shifts are referenced to chloroform (7.26 ppm), and DMSO-d_6 (2.50 ppm). Non-first order multiplets are identified as "nfom". ^{13}C NMR chemical shifts are referenced to chloroform (77.23 ppm), and DMSO-d_6 (39.52 ppm). The following format was used to report peaks: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^{1}H NMR assignments are indicated by structure environment, e.g., CH_aH_b. Coupling constant analysis was guided by methods we have described elsewhere.[1] ^{1}H NMR and ^{13}C NMR were processed with iNMR software program.

Infrared (IR) spectra were recorded on a Bruker Alpha-P FT-IR spectrometer using neat (for liquid compound) or a thin film from a concentrated DCM solution. Absorptions are reported in cm^{-1}.

MPLC refers to medium pressure liquid chromatography (25-200 psi) using hand-packed columns of Silasorb silica gel (20-45 μm, spherical, 70 Å pore size), a Waters HPLC pump, and a Waters R401 differential refractive index detector.

Electrospray ionization (ESI) mass spectrometry was performed on a Shimadzu LCMS IT-TOF. All HRMS data were recorded in ESI mode. Samples were introduced as solutions in mixed solution of methanol and methylene chloride (DCM).

GCMS data were recorded either on a Varian 450-GC/Varian 240-MS System. The method used are noted parenthetically: 5029017 refers to: 2 min @ 50 °C – 20 °C/min – 3 min @ 290 °C.

Reactions requiring anhydrous conditions were performed under an atmosphere of nitrogen or argon in flame- or oven-dried glassware. Anhydrous toluene and methylene chloride were distilled from CaH_2. Anhydrous THF and diethyl ether were distilled from sodium and benzophenone. Triethylamine and pyridine were distilled from KOH. DMF and DMSO were stored over 4Å molecular sieves. The concentrations of anionic solutions (e.g., *n*-BuLi and Grignards) were titered by spectroscopic (No-D NMR) methods.[2]

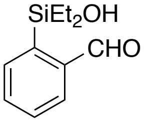
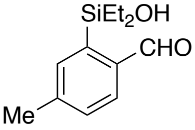
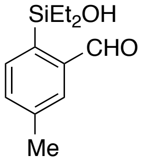
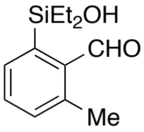
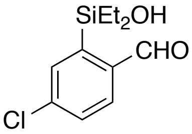
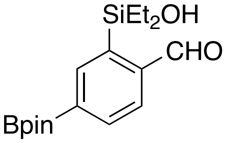
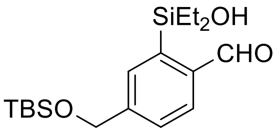
TLC experiments were performed on EMD Merck F254 plate, 250 μm thickness.

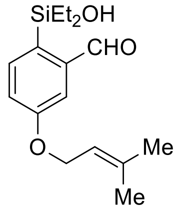
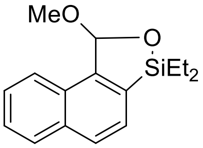
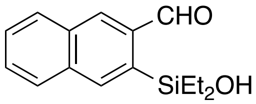
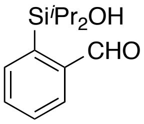
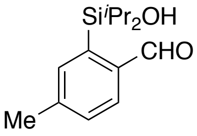
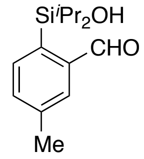
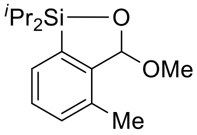
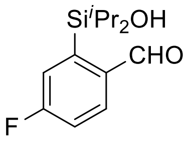
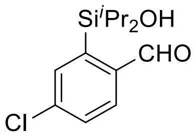
Abbreviations: coe = cyclooctene, nbd = norbornadiene, nbe = norbornene.

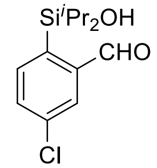
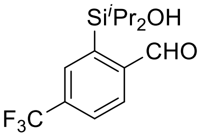
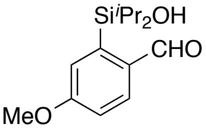
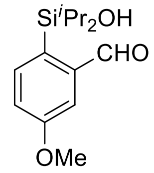
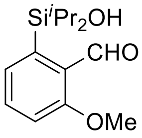
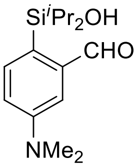
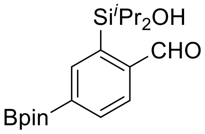
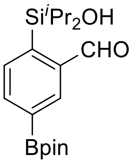
Supporting Information References

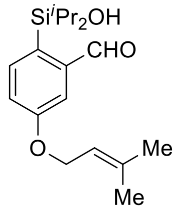
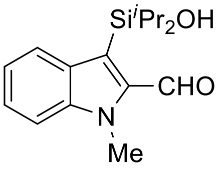
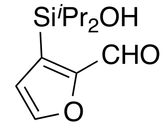
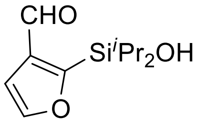
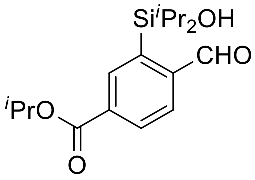
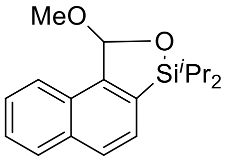
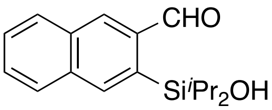
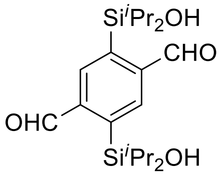
1. "A method for easily determining coupling constant (*J*) values: An addendum to 'A practical guide to first-order multiplet analysis in ^{1}H NMR spectroscopy'," Hoye, T. R.; Zhao, H. *J. Org. Chem.* **2002**, *67*, 4014-4016.
2. "No-D NMR spectroscopy as a convenient method for titering organolithium (RLi), RMgX, and LDA solutions," Hoye, T. R.; Eklov, B. M.; Voloshin, M. *Org. Lett.* **2004**, *6*, 2567-2570.
3. "Efficient Reduction of Esters to Aldehydes through Iridium-Catalyzed Hydrosilylation," Cheng, C.; Brookhart, M. *Angew. Chem. Int. Ed.* **2012***, 51,* 9422–9424.

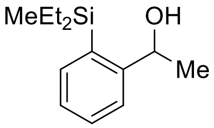
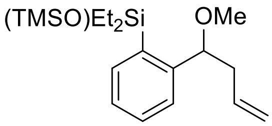
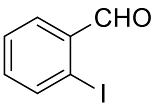
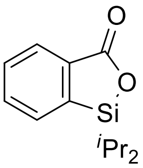
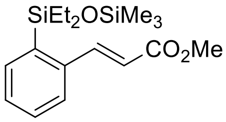
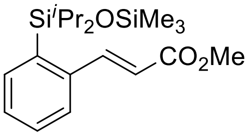
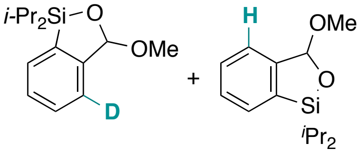
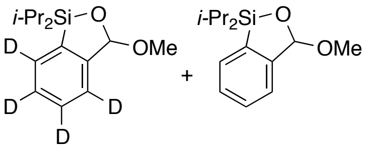
Table of Isolated Compounds

Structure	Compound #	Procedure begins on page:	Compound characterization begins on page:	NMR spectra on page:
	**2a**	9	10	40-41
	**2b**	9	11	42-43
	**2c**	9	11	44-45
	**2d**	9	12	46-47
	**2e**	9	12	48-49
	**2f**	9	13	50-51
	**2g**	9	13	52-53

	**2h**	9	14	54-55
	**6i**	9	15	56-57
	**2j**	9	15	58-59
	**3a**	9	16	60-61
	**3b**	9	17	62-63
	**3c**	9	17	64-65
	**7d**	9	18	66-67
	**3e**	9	19	68-69
	**3f**	9	19	70-71

	**3g**	9	20	72-73
	**3h**	9	21	74-75
	**3i**	9	22	76-77
	**3j**	9	22	78-79
	**3k**	9	23	80-81
	**3l**	9	24	82-83
	**3m**	9	24	84-85
	**3n**	9	25	86-87

	**3o**	9	26	88-89
	**3p**	9	27	90-91
	**3q**	9	27	92-93
	**3r**	9	28	94-95
	**3s**	9	28	96-97
	**7t**	9	29	98-99
	**3u**	9	30	100-101
	**3v**	9	31	102-103

	**8**	31	32	104-105
	**12**	33	34	106-107
	**13**	34	34	108-109
	**14**	35	35	110-111
	**15**	36	36	112-113
	**16**	37	36	114-115
	**7a**-D$_1$ + **7a**-H	37	--	116
	**7a**-D$_7$ + **7a**-H	38	--	117

General Procedure for Preparation of Diethylhydridosilyl Aetals (4):[3]

$[Ir(coe)_2Cl]_2$ (0.9 mg, 0.1 mol %) and ester **1** (1 mmol) were dissolved with CH_2Cl_2 (0.3 mL, 3.3 M). Diethylsilane (0.28 mL, 2 mmol) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was kept at rt and stirred for 3-12 h. The volatiles were removed *in vacuo* to afford the silyl acetals **4**, which were directly used for subsequent reactions without further purification.

General Procedure for Preparation of Hydridodiisopropylsilyl Aetals (5):[3]

$[Ir(coe)_2Cl]_2$ (0.9 mg, 0.1 mol %) and ester **1** (1 mmol) were dissolved with CH_2Cl_2 (0.3 mL, 3.3 M). Diisopropylsilane (0.38 mL, 2 mmol) was added to the mixture in one portion. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was kept at 45 °C and stirred for 24-36 h. The volatiles were removed *in vacuo* to afford the silyl acetals **5**, which were directly used for subsequent reactions without further purification.

General Procedure for Preparation of Cyclic Silyl Acetals (6/7):

$[Rh(nbd)Cl]_2$ (1.84 mg, 0.4 mol %), *tris*(4-methoxyphenyl)phosphine (8.45 mg, 2.4 mol %) and norbornene (188 mg, 2 mmol) were dissolved with THF (1 mL, 1 M), silyl acetal **4** or **5** (1 mmol) was added to the mixture in one portion. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 120 °C for 10 min. The reaction progress was monitored by GC/MS spectrometry. The yield of the cyclic silyl acetals **6** or **7** was determined by ^1H NMR spectroscopy by an addition of CH_2Br_2 (1 mmol) as an internal standard after the volatiles were removed *in vacuo*. Crude material was directly subjected to hydrolysis.

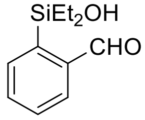
General Procedure for Preparation of 2-[Diethyl(hydroxy)silyl]benzaldehyde (2) and 2-(Hydroxydiisopropylsilyl)benzaldehyde (3)

The crude cyclic silyl acetals **6** or **7** (1 mmol) were dissolved by a 1:1 mixture (v/v) of actonitrile and pH 5 buffer (1 mL:1 mL, total concentration = 0.5 M) and stirred at rt for 10 h. The mixture was extracted with diethyl eher (5 mL×4). The combined organic layer was washed with water (10 mL) and brine (10 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo,* and the crude mixture was purified by MPLC to afford silanol aldehyde **2** (hexanes/EtOAc = 5:1, 7 mL/min, retention time 7-20 min) or **3** (hexanes/EtOAc = 10:1, 7 mL/min, retention time 10-25 min). Compound **3k** was purified by MPLC (hexanes/EtOAc = 3:1, 7 mL/min, retention time 7-8 min), and **3v** was obtained by recrystallization using DCM/hexanes.

Gram Scale Synthesis of 2-[Diethyl(hydroxy)silyl]benzaldehyde (2a)

$[Ir(coe)_2Cl]_2$ (10 mg, 0.1 mol %) and methyl benzoate **1a**-Me (1.5 mL, 12 mmol) were dissolved with CH_2Cl_2 (6 mL, 2 M). Diethylsilane (2.0 mL, 14.4 mmol, 1.2 equiv) was added to the mixture slowly (the reaction was exothermic). The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was stirred at rt for 10 h. The volatiles were removed *in vacuo* to afford the silyl acetal **4a**-Me, which was directly used for subsequent C–H silylation without further purification. $[Rh(nbd)Cl]_2$ (22.1 mg, 0.4 mol %), *tris*(4-methoxyphenyl)phosphine (101 mg, 2.4 mol %), and norbornene (2.26 g, 24 mmol) were dissolved with THF (6 mL, 2 M), the crude silyl acetal **4a**-Me was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 120 °C for 10 min. The yield of cyclic silyl acetal **6a**-Me was determined by ^1H NMR spectroscopy by an addition of CH_2Br_2 as an internal standard after the volatiles were removed *in vacuo*. The crude material **6a**-Me was dissolved by a 1:1 mixture (v/v) of actonitrile and pH 5 buffer (6 mL: 6 mL, total concentration = 1 M) and stirred at rt for 10 h. The mixture was extracted with diethyl eher (20 mL×4). The combined organic layer was washed with water (20 mL) and brine (20 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo,* and the crude mixture was purified by MPLC (hexanes/EtOAc = 5:1, 7 mL/min, retention time 8 min) to afford *ortho*-formyl arylsilanol **2a** (1.8 g, 72% yield) as a pale yellow liquid.

2-[Diethyl(hydroxy)silyl]benzaldehyde (2a)



2a

Yield: 1 mmol scale, 162 mg, 78%; 12 mmol scale, 1.80 g, 72%.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.0 (s, 1H, C*H*O), 7.89 (dd, *J* = 7.0, 1.6 Hz, 1H, CHOCC*H*), 7.79 (dd, *J* = 7.0, 1.6 Hz, 1H, SiCC*H*), 7.64 (ddd, *J* = 7.4, 7.4, 1.6 Hz, 1H, CHOCCHC*H* or SiCCHC*H*), 7.61 (ddd, *J* = 7.4, 7.4, 1.6 Hz, 1H, CHOCCHC*H* or SiCCHC*H*), 3.15 (br, 1H, SiO*H*), 0.99-0.95 [m, 6H, Si(CH$_2$C*H$_3$*)$_2$], and 0.92-0.89 [m, 4H, Si(C*H$_2$*CH$_3$)$_2$].

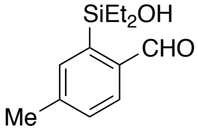
^{13}C NMR (CDCl$_3$, 75 MHz): δ 196.0, 141.2, 139.6, 136.1, 135.5, 133.8, 129.9, 7.1, and 6.5.

IR (neat): 3409 (br, m), 2955 (w), 1685 (s), 1200 (m), 1039 (s), 1003 (s), and 707 (s) cm^{-1}.

TLC: R$_f$ = 0.5 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+K)$^+$ ($C_{11}H_{16}KO_2Si$)$^+$: 247.0551. Found: 247.0568.

2-[Diethyl(hydroxy)silyl]-4-methylbenzaldehyde (2b)



2b

Yield: 1 mmol scale, 160 mg, 72%.

^{1}H NMR (CDCl$_3$, 500 MHz): δ 9.94 (s, 1H, C*H*O), 7.77 (d, *J* = 7.7 Hz, 1H, CHOCC*H*), 7.57 (d, *J* = 1.6 Hz, 1H, SiCC*H*), 7.39 (dd, *J* = 7.7, 1.6 Hz, 1H, CHOCCHC*H*), 3.14 (br s, 1H, SiO*H*), 0.98-0.95 [m, 6H, Si(CH$_2$C*H$_3$*)$_2$], and 0.91-0.88 [m, 4H, Si(C*H$_2$*CH$_3$)$_2$].

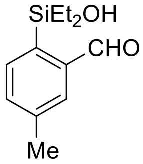
^{13}C NMR (CDCl$_3$, 75 MHz): δ 195.5, 144.8, 139.5, 139.0, 137.1, 136.2, 130.4, 22.2, 7.2, and 6.5.

IR (neat): 3372 (br, w), 2955 (m), 2874 (m), 1692 (m), 1592 (m), 1200 (m), 1039 (s), 1003 (s), 792 (s), and 704 (s) cm^{-1}.

TLC: R$_f$ = 0.5 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+Na)$^+$ ($C_{12}H_{18}NaO_2Si$)$^+$: 245.0968. Found: 245.0987.

2-[Diethyl(hydroxy)silyl]-5-methylbenzaldehyde (2c)



2c

Yield: 1 mmol scale, 140 mg, 63%.

^{1}H NMR (CDCl$_3$, 500 MHz): δ 9.98 (s, 1H, C*H*O), 7.68 (d, *J* = 1.6 Hz, 1H, CHOCC*H*), 7.66 (d,

J = 7.4 Hz, 1H, SiCC*H*), 7.57 (dd, J = 7.4, 1.6 Hz, 1H, CHOCCHC*H*), 3.00 (br s, 1H, SiO*H*), 0.98-0.94 [m, 6H, Si(CH_2CH_3)$_2$], and 0.92-0.89 [m, 4H, Si(CH_2CH_3)$_2$].

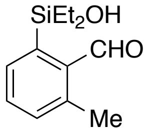
^{13}C NMR ($CDCl_3$, 125 MHz): δ 196.3, 141.5, 140.1, 136.7, 136.2, 136.0, 134.6, 21.2, 7.2, and 6.5.

IR (neat): 3407 (br, m), 2955 (m), 1684 (m), 1461 (m), 1189 (m), 1045 (s), 1015 (s), 977 (s), and 712 (s) cm^{-1}.

TLC: R_f = 0.45 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+Na)$^+$ ($C_{12}H_{18}NaO_2Si$)$^+$: 245.0968. Found: 245.0983.

2-[Diethyl(hydroxy)silyl]-6-methylbenzaldehyde (2d)



2d

Yield: 1 mmol scale, 191 mg, 86%.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.5 (s, 1H, C*H*O), 7.77 (d, J = 7.5 Hz, 1H, SiCC*H* or MeCC*H*), 7.41 (dd, J = 7.5, 7.5 Hz, 1H, SiCCHC*H*), 7.26 (d, J = 7.5 Hz, 1H, SiCC*H* or MeCC*H*), 2.68 (s, 3H, ArC*H*$_3$), 2.08 (br s, 1H, SiO*H*), 1.01-0.97 [m, 2H, Si(CH_2CH_3)$_2$], and 0.93-0.90 [m, 8H, Si(CH_2CH_3)$_2$ and Si(CH_2CH_3)$_2$].

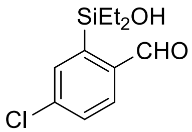
^{13}C NMR ($CDCl_3$, 125 MHz): δ 193.4, 141.7, 141.4, 139.3, 134.8, 133.1, 132.7, 20.4, 8.5, and 7.7.

IR (neat): 3407 (br, m), 2956 (m), 1683 (m), 1459 (m), 1179 (m), 1046 (s), 1004 (s), 978 (s), and 711 (s) cm^{-1}.

TLC: R_f = 0.45 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+Na)$^+$ ($C_{12}H_{18}NaO_2Si$)$^+$: 245.0968. Found: 245.0992.

4-Chloro-2-[diethyl(hydroxy)silyl]benzaldehyde (2e)



2e

Yield: 1 mmol scale, 179 mg, 74%.

^{1}**H NMR** ($\mathrm{CDCl_3}$, 500 MHz): δ 9.97 (s, 1H, $\mathrm{C}\mathit{H}\mathrm{O}$), 7.82 (d, *J* = 8.1 Hz, 1H, $\mathrm{CHOCC}\mathit{H}$), 7.76 (d, *J* = 2.1 Hz, 1H, $\mathrm{SiCC}\mathit{H}$), 7.57 (dd, *J* = 8.1, 2.1 Hz, 1H, $\mathrm{CHOCCHC}\mathit{H}$), 3.00 (br s, 1H, $\mathrm{SiO}\mathit{H}$), 0.98-0.94 [m, 6H, $\mathrm{Si(CH_2C}\mathit{H_3}\mathrm{)_2}$], and 0.92-0.89 [m, 4H, $\mathrm{Si(C}\mathit{H_2}\mathrm{CH_3)_2}$].

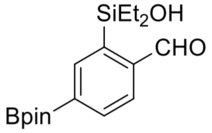
^{13}**C NMR** ($\mathrm{CDCl_3}$, 125 MHz): δ 194.3, 142.2, 141.0, 139.3, 136.39, 136.30, 129.9, 7.0, and 6.3.

IR (neat): 3440 (br, w), 2957 (m), 2876 (m), 1694 (s), 1547 (m), 1039 (s), 1003 (s), 728 (s), 698 (s), and 442 (s) cm^{-1}.

TLC: R_f = 0.45 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(\mathrm{M+Na})^+$ $(\mathrm{C_{11}H_{15}NaO_2Si})^+$: 265.0422. Found: 265.0437.

2-[Diethyl(hydroxy)silyl]-4-(4,4,5,5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)benzaldehyde (2f)



2f

Yield: 1 mmol scale, 250 mg, 75%.

^{1}**H NMR** ($\mathrm{CDCl_3}$, 500 MHz): δ 10.0 (s, 1H, $\mathrm{C}\mathit{H}\mathrm{O}$), 8.19 (d, *J* = 1.2 Hz, 1H, $\mathrm{SiCC}\mathit{H}$), 8.02 (dd, *J* = 7.4, 1.2 Hz, 1H, $\mathrm{CHOCCHC}\mathit{H}$), 7.86 (d, *J* = 7.4 Hz, 1H, $\mathrm{CHOCC}\mathit{H}$), 3.03 (br s, 1H, $\mathrm{SiO}\mathit{H}$), 1.36 {s, 12H, $\mathrm{B[OC(C}\mathit{H}_3\mathrm{)_2]_2}$}, 0.99-0.96 [m, 6H, $\mathrm{Si(CH_2C}\mathit{H_3}\mathrm{)_2}$], and 0.94-0.91 [m, 4H, $\mathrm{Si(C}\mathit{H_2}\mathrm{CH_3)_2}$].

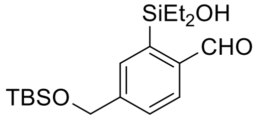
^{13}**C NMR** ($\mathrm{CDCl_3}$, 125 MHz): δ 196.2, 143.0, 142.1, 138.3, 136.3 (2), 134.4, 84.5, 25.1, 7.2, and 6.6.

IR (neat): 3441 (br, m), 2977 (m), 2875 (m), 1695 (s), 1473 (m), 1354 (s), 1141 (s), 1095 (s), 962 (s), 821 (s), 666 (s), and 430 (s) cm^{-1}.

TLC: R_f = 0.4 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(\mathrm{M+H})^+$ $(\mathrm{C_{17}H_{28}BO_4Si})^+$: 335.1844. Found: 335.1828.

4-{[(*tert*-Butyldimethylsilyl)oxy]methyl}-2-[diethyl(hydroxy)silyl]benzaldehyde (2g)



2g

Yield: 1 mmol scale, 274 mg, 78%.

^{1}H NMR ($\mathrm{CDCl_3}$, 500 MHz): δ 9.98 (s, 1H, C*H*O), 7.85 (d, *J* = 7.8 Hz, 1H, CHOCC*H*), 7.72 (s, 1H, SiCC*H*), 7.56 (d, *J* = 7.8 Hz, 1H, CHOCCHC*H*), 4.83 (s, 2H, $\mathrm{C}\mathit{H}_2\mathrm{OTBS}$), 3.29 (br s, 1H, SiO*H*), 0.98-0.95 [m, 6H, $\mathrm{Si(CH_2C}\mathit{H_3}\mathrm{)_2}$], 0.96 [s, 9H, $\mathrm{Si(CH_3)_2(C}\mathit{H_3}\mathrm{)_3}$], 0.92-0.89 [m, 4H, $\mathrm{Si(C}\mathit{H_2}\mathrm{CH_3)_2}$], and 0.12 [s, 6H, $\mathrm{Si(C}\mathit{H_3}\mathrm{)_2(CH_3)_3}$].

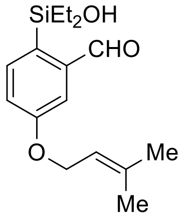
^{13}C NMR ($\mathrm{CDCl_3}$, 125 MHz): δ 195.7, 147.7, 140.2, 139.6, 136.1, 133.4, 127.0, 64.7, 26.1, 18.5, 7.2, 6.5, and 5.1.

IR (neat): 3449 (br, m), 2954 (m), 2877 (m), 1692 (s), 1462 (m), 1253 (m), 1098 (s), 834 (s), 776 (s), 731 (s), and 708 (s) $\mathrm{cm^{-1}}$.

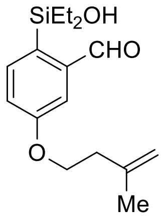
TLC: $R_f = 0.4$ in 10:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(\mathrm{C_{18}H_{32}NaO_3Si_2})^+$: 375.1782. Found: 375.1794.

2-[Diethyl(hydroxy)silyl]-5-[(3-methylbut-2-en-1-yl)oxy]benzaldehyde (2h)



2h



2h'

1,1-Disubstituted alkene **2h'** via alkene migration were isolated along with the desired product as an inseparable mixture. The ratio of **2h**: **2h'** is 1: 0.09.

Total Yield: 1 mmol scale, 223 mg, 78%.

^{1}H NMR ($\mathrm{CDCl_3}$, 500 MHz) for **2h**: δ 9.98 (s, 1H, C*H*O), 7.67 (d, *J* = 8.1 Hz, 1H, SiCC*H*), 7.42 (d, *J* = 2.6 Hz, 1H, CHOCC*H*), 7.14 (dd, *J* = 8.1, 2.6 Hz, 1H, SiCCHC*H*), 5.50 (app t, *J* = 6.8 Hz, 1H, $\mathrm{ArOCH_2C}\mathit{H}\mathrm{{=}CMe_2}$), 4.59 (d, *J* = 6.8 Hz, 2H, $\mathrm{ArOC}\mathit{H_2}\mathrm{CH{=}CMe_2}$), 3.06 (br s, 1H, SiO*H*), 1.81 [s, 3H, $\mathrm{ArOCH_2CH{=}C(C}\mathit{H_3}\mathrm{)_2)}$], 1.76 [s, 3H, $\mathrm{ArOCH_2CH{=}C(C}\mathit{H_3}\mathrm{)_2)}$], 0.97-0.94 [m, 6H, $\mathrm{Si(CH_2C}\mathit{H_3}\mathrm{)_2}$], and 0.89-0.86 [m, 4H, $\mathrm{Si(C}\mathit{H_2}\mathrm{CH_3)_2}$].

^{1}H NMR ($\mathrm{CDCl_3}$, 500 MHz) for **2h'**: 9.98 (s, 0.09H, C*H*O), 7.67 (d, *J* = 8.1 Hz, 0.09H, SiCC*H*), 7.42 (d, *J* = 2.6 Hz, 0.09H, CHOCC*H*), 7.14 (dd, *J* = 8.1, 2.6 Hz, 0.09H, SiCCHC*H*), 4.86 (app s, 0.09H, $\mathrm{C}\mathit{H_a}\mathrm{H_b{=}CMe_2}$), 4.81 (app s, 0.09H, $\mathrm{CH_a}\mathit{H_b}\mathrm{{=}CMe_2}$), 4.16 (t, *J* = 6.8 Hz, 0.18H, $\mathrm{ArOC}\mathit{H_2}\mathrm{CH_2}$), 2.53 (t, *J* = 6.8 Hz, 0.18H, $\mathrm{ArOCH_2C}\mathit{H_2}$), 1.81 [s, 0.27H, $\mathrm{CH_aH_b{=}CC}\mathit{H_3}$]. 0.97-0.94 [m, 0.54H, $\mathrm{Si(CH_2C}\mathit{H_3}\mathrm{)_2}$], and 0.89-0.86 [m, 0.36H, $\mathrm{Si(C}\mathit{H_2}\mathrm{CH_3)_2}$].

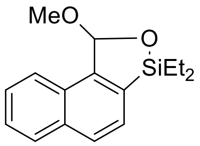
^{13}C NMR ($\mathrm{CDCl_3}$, 125 MHz) only for **2h**: δ 195.6, 160.4, 142.9, 139.2, 137.6, 130.2, 121.6, 119.6, 119.1, 65.1, 26.0, 18.4, 7.2, and 6.7.

IR (neat): 3408 (br, m), 2955 (m), 2875 (m), 1688 (s), 1591 (s), 1267 (s), 1231 (m), 1071 (s), 1002 (s), 825 (s), and 707 (s) cm^{-1}.

TLC: R_f = 0.45 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+H)^+$ $(C_{16}H_{25}O_3Si)^+$: 293.1567. Found: 293.1578.

3,3-Diethyl-1-methoxy-1,3-dihydronaphtho[2,1-*c*][1,2]oxasilole (6i)



6i

Yield: 1 mmol scale, 247 mg, 91%.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.14 (dddd, *J* = 8.1, 1.5, 0.6, 0.6 Hz, 1H, naphthalene-*H5*), 7.92 (ddd, *J* = 8.1, 1.5, 0.6 Hz, 1H, naphthalene-*H8*), 7.89 (dd, *J* = 8.0, 0.6 Hz, 1H, naphthalene-*H4*), 7.62 (d, *J* = 8.0 Hz, 1H, naphthalene-*H3*), 7.60 (ddd, *J* = 8.1, 6.9, 1.5 Hz, 1H, naphthalene-*H6* or naphthalene-*H7*), 7.56 (ddd, *J* = 8.1, 6.9, 1.5 Hz, 1H, naphthalene-*H6* or naphthalene-*H7*), 6.60 (s, 1H, SiOC*H*OMe), 3.64 (s, 3H, O*Me*), 1.11-1.07 [m, 3H, $Si(CH_2CH_3)_2$)], 1.03-0.94 [m, 7H, $Si(CH_2CH_3)_2$ and $Si(CH_2CH_3)_2$].

^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.3, 134.8, 132.7, 129.5, 129.2, 128.6, 126.79, 126.75(2), 124.3, 104.2, 54.4, 7.1, 6.7, 6.64 and 6.61.

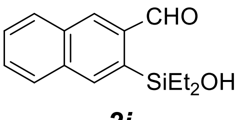
IR (neat): 3047 (w), 2955 (m), 2875 (m), 1507 (m), 1234 (m), 1097 (s), 1045 (s), 862 (s), 728 (s), 705 (s), and 435 (s) cm^{-1}.

TLC: R_f = 0.4 in 10:1 hexanes: EtOAc.

GCMS (5029017): t_R=12.08 min, m/z 272 (M^+, 20), 271 [$(M-H)^+$, 25], and 241 [$(M-OMe)^+$, 100].

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{16}H_{20}NaO_2Si)^+$: 295.1125. Found: 295.15138.

3-[Diethyl(hydroxy)silyl]-2-naphthaldehyde (2j)



2j

Yield: 1 mmol scale, 186 mg, 72%.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.1 (s, 1H, C*H*O), 8.37 (s, 1H, naphthalene-*H1* or naphthalene-*H4*), 8.22 (s, 1H, naphthalene-*H1* or naphthalene-*H4*), 8.00 (dd, *J* = 8.1, 1.3 Hz, 1H, naphthalene-*H8* or naphthalene-*H5*), 7.93 (dd, *J* = 8.1, 1.3 Hz, 1H, naphthalene-*H8* or naphthalene-*H5*), 7.69 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H, naphthalene-*H6* or naphthalene-*H7*), 7.62 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H, naphthalene-*H6* or naphthalene-*H7*), 3.25 (br s, 1H, SiO*H*), 1.03-0.96 [m, 10H, $Si(CH_2CH_3)_2$ and $Si(CH_2CH_3)_2$].

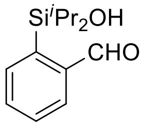
^{13}C NMR ($CDCl_3$, 125 MHz): δ 195.7, 139.4, 138.6, 137.7, 135.7, 133.3, 132.9, 129.9, 129.3, 128.7, 128.0, 7.3, and 6.6.

IR (neat): 3441 (br, m), 2954 (m), 2873 (m), 1688 (s), 1450 (m), 1212 (m), 1141 (m), 1031 (s), 746 (s), 702 (s), and 477 (s) cm^{-1}.

TLC: $R_f = 0.4$ in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+H)^+$ $(C_{15}H_{19}O_2Si)^+$: 259.1149. Found: 259.1157.

2-(Hydroxydiisopropylsilyl)benzaldehyde (3a)



3a

The ratio of aldehyde and silyl hemiacetal is 1:0.07.

Yield: 1 mmol scale, 215 mg, 91%; 6 mmol scale, 1.19 g, 84%.

^{1}H NMR ($CDCl_3$, 500 MHz) for **3a**: δ 10.0 (s, 1H, C*H*O), 7.90 (dd, *J* = 7.3, 1.6 Hz, 1H, CHOCC*H*), 7.81 (dd, *J* = 7.3, 1.6 Hz, 1H, SiCC*H*), 7.62 (ddd, *J* = 7.3, 7.3, 1.6 Hz, 1H, CHOCCHC*H* or SiCCHC*H*), 7.59 (ddd, *J* = 7.3, 7.3, 1.6 Hz, 1H, CHOCCHC*H* or SiCCHC*H*), 3.51 (br s, 1H, SiO*H*), 1.34 [septet, *J* = 7.4 Hz, 2H, $CH(CH_3)_2$], 1.08 [d, *J* = 7.4 Hz, 6H, $CH(CH_3)_2$], and 0.90 [d, *J* = 7.4 Hz, 6H, $CH(CH_3)_2$].

^{1}H NMR ($CDCl_3$, 500 MHz) for silyl hemiacetal: 7.55 [dd, *J* = 7.0, 1.2 Hz, 0.07H, C(OSi)CC*H* or SiCC*H*], 7.50 (dd, *J* = 7.6, 1.2 Hz, 0.07H, C(OSi)CC*H* or SiCC*H*], 7.47 [ddd, *J* = 7.6, 7.0, 1.2 Hz, 0.07H, C(OSi)CC*H* or SiCCHC*H*], 7.39 (ddd, *J* = 7.0, 7.0, 1.2 Hz, 0.07H, C(OSi)CC*H* or SiCCHC*H*], 6.36 (br s, 0.07H, SiOC*H*OH), 1.37 [septet, *J* = 7.4 Hz, 0.07H, $CH(CH_3)_2$], 1.30 [septet, *J* = 7.4 Hz, 0.07H, $CH(CH_3)_2$], 1.06 [d, *J* = 7.4 Hz, 0.21H, $CH(CH_3)_2$], 1.04 [d, *J* = 7.4 Hz, 0.21H, $CH(CH_3)_2$], 1.00 [d, *J* = 7.4 Hz, 0.21H, $CH(CH_3)_2$], and 0.98 [d, *J* = 7.4 Hz, 0.21H, CH(C*H*$_3$)$_2$].

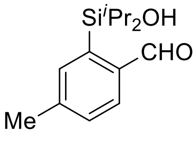
^{13}C NMR (CDCl$_3$, 125 MHz) only for **3a**: δ 196.2, 141.8, 139.0, 136.4, 135.6, 133.5, 129.7, 17.9, 17.7, and 13.3.

IR (neat): 3441 (br, m), 2944 (m), 2864 (m), 1686 (s), 1462 (s), 1202 (s), 1076 (m), 879 (s), 755 (s), 661 (s), and 505 (s) cm^{-1}.

TLC: R$_f$ = 0.5 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+K)$^+$ ($C_{13}H_{20}KO_2Si$)$^+$: 275.0864. Found: 275.0844.

2-(Hydroxydiisopropylsilyl)-4-methylbenzaldehyde (3b)



3b

The ratio of aldehyde and silyl hemiacetal is 1:0.02.

Yield: 1 mmol scale, 225 mg, 90%.

^{1}H NMR (CDCl$_3$, 500 MHz) only for **3b**: δ 9.94 (s, 1H, C*H*O), 7.78 (d, *J* = 7.7 Hz, 1H, CHOCC*H*), 7.59 (s, 1H, SiCC*H*), 7.37 (d, *J* = 7.7 Hz, 1H, CHOCCHC*H*), 3.61 (br s, 1H, SiO*H*), 2.44 (s, 3H, ArC*H*$_3$), 1.33 [septet, *J* = 7.4 Hz, 2H, C*H*(CH$_3$)$_2$], 1.07 [d, *J* = 7.4 Hz, 6H, CH(C*H*$_3$)$_2$], and 0.89 [d, *J* = 7.4 Hz, 6H, CH(C*H*$_3$)$_2$].

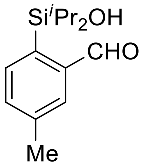
^{13}C NMR (CDCl$_3$, 125 MHz) only for **3b**: δ 195.5, 144.4, 139.4, 138.9, 137.3, 136.0, 120.2, 22.2, 18.0, 17.7, and 13.3.

IR (neat): 3443 (br, m), 2944 (m), 2864 (m), 1685 (s), 1462 (s), 880 (s), 817 (s), 790 (s), and 485 (s) cm^{-1}.

TLC: R$_f$ = 0.5 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+K)$^+$ ($C_{14}H_{22}KO_2Si$)$^+$: 289.1021. Found: 289.1011.

2-(Hydroxydiisopropylsilyl)-5-methylbenzaldehyde (3c)



3c

The ratio of aldehyde and silyl hemiacetal is 1:0.04.

Yield: 1 mmol scale, 167 mg, 67%.

^{1}**H NMR** ($CDCl_3$, 500 MHz) only for **3c**: δ 9.99 (s, 1H, C*H*O), 7.71 (d, *J* = 1.6 Hz, 1H, CHOCC*H*), 7.67 (d, *J* = 7.5 Hz, 1H, SiCC*H*), 7.44 (dd, *J* = 7.5, 1.6 Hz, 1H, SiCCHC*H*), 3.47 (br s, 1H, SiO*H*), 2.45 (s, 3H, ArCH_3), 1.34 [septet, *J* = 7.4 Hz, 2H, C*H*(CH_3)$_2$], 1.07 [d, *J* = 7.4 Hz, 6H, CH(CH_3)$_2$], and 0.90 [d, *J* = 7.4 Hz, 6H, CH(CH_3)$_2$].

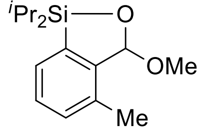
^{13}**C NMR** ($CDCl_3$, 125 MHz) only for **3c**: δ 196.4, 142.0, 139.8, 136.5 (2), 135.3, 134.3, 21.2, 17.9, 17.6, and 13.3.

IR (neat): 3450 (br, m), 2944 (m), 2864 (m), 1681 (s), 1462 (s), 880 (s), 823 (s), 660 (s), and 479 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{14}H_{22}NaO_2Si)^+$: 273.1281. Found: 273.1269.

1,1-Diisopropyl-3-methoxy-4-methyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (7d)



7d

Yield: 1 mmol scale, 238 mg, 90%.

^{1}**H NMR** ($CDCl_3$, 500 MHz): δ 7.36 (d, *J* = 7.4 Hz, 1H, MeCC*H or* SiCC*H*), 7.27 (dd, *J* = 7.4, 7.4 Hz, 1H, MeCCHC*H*), 7.21 (d, *J* = 7.4 Hz, 1H, MeCC*H or* SiCC*H*), 6.00 (s, 1H, SiOC*H*OMe), 3.56 (s, 3H, OCH_3), 2.36 (s, 3H, ArCH_3), 1.25 [septet, *J* = 7.4 Hz, 1H, C*H*(CH_3)$_2$], 1.21 [septet, *J* = 7.4 Hz, 1H, C*H*(CH_3)$_2$], 1.08 [d, *J* = 7.4 Hz, 3H, CH(CH_3)$_2$], 1.06 [d, *J* = 7.4 Hz, 3H, CH(CH_3)$_2$], 1.01[d, *J* = 7.4 Hz, 3H, CH(CH_3)$_2$] and 0.95 [d, *J* = 7.4 Hz, 3H, CH(CH_3)$_2$].

^{13}**C NMR** ($CDCl_3$, 125 MHz): δ 147.8, 134.4, 132.9, 132.0, 129.3, 128.8, 104.5, 55.1, 18.6, 17.41, 17.37, 17.19, 17.13, 12.76 and 12.67.

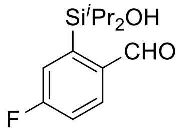
IR (neat): 2943 (m), 2864 (m), 1461 (s), 1071 (s), 1019 (m), 880 (s), 708 (s), and 471 (s) cm^{-1}.

TLC: R_f = 0.6 in 10:1 hexanes: EtOAc.

GCMS (5029017): t_R = 10.01 min, m/z 264 (M^+, 5), 263 [$(M-H)^+$, 20], 233 [$(M-OMe)^+$, 100], and 221[$(M-^iPr)^+$, 10].

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{15}H_{24}NaO_2Si)^+$: 287.1438. Found: 287.1449.

4-Fluoro-2-(hydroxydiisopropylsilyl)benzaldehyde (3e)



3e

The ratio of aldehyde and silyl hemiacetal is 1:0.04.

Yield: 1 mmol scale, 216 mg, 85%.

^{1}H NMR ($CDCl_3$, 500 MHz) only for **3e**: δ 9.96 (s, 1H, C*H*O), 7.92 [dd, *J* = 8.3, 5.3 ($J^4_{F\text{-}H}$) Hz, 1H, CHOCC*H*], 7.54 [dd, 1H, *J* = 9.3 ($J^3_{F\text{-}H}$), 2.5 Hz, SiCC*H*], 7.24 [ddd, *J* = 8.3, 8.3 ($J^3_{F\text{-}H}$), 2.5 Hz, 1H, CHOCCHC*H*], 3.12 (br s, 1H, SiO*H*), 1.35 [septet, *J* = 7.4 Hz, 2H, C*H*(CH_3)$_2$], 1.09 [d, *J* = 7.4 Hz, 6H, CH(CH_3)$_2$], and 0.88 [d, *J* = 7.4 Hz, 6H, CH(CH_3)$_2$].

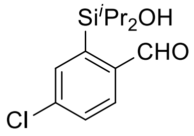
^{13}C NMR ($CDCl_3$, 125 MHz) only for **3e**: δ 193.9, 166.0 (d, $J^1_{F\text{-}C}$ = 260.3 Hz), 143.8 (d, $J^3_{F\text{-}C}$ = 5.8 Hz), 138.1 (d, $J^4_{F\text{-}C}$ = 2.1 Hz), 137.9 (d, $J^3_{F\text{-}C}$ = 9.3 Hz), 123.9 (d, $J^2_{F\text{-}C}$ = 20.4 Hz), 116.5 (d, $J^2_{F\text{-}C}$ = 21.7 Hz), 18.0, 17.7, and 13.2.

IR (neat): 3453 (br, m), 2945 (m), 2866 (m), 1689 (s), 1566 (s), 1464 (m), 1257(m), 1210 (s), 880 (s), 798 (s), 680 (s), and 456 (s) cm^{-1}.

TLC: R_f = 0.55 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{13}H_{19}FNaO_2Si)^+$: 277.1031. Found: 277.1047.

4-Chloro-2-(hydroxydiisopropylsilyl)benzaldehyde (3f)



3f

The ratio of aldehyde and silyl hemiacetal is 1:0.08.

Total Yield: 1 mmol scale, 203 mg, 75%.

^{1}H NMR ($CDCl_3$, 500 MHz) for **3f**: δ 9.99 (s, 1H, C*H*O), 7.83 (d, *J* = 8.2 Hz, 1H, CHOCC*H*), 7.82 (d, *J* = 2.2 Hz, 1H, SiCC*H*CCl), 7.55 (dd, *J* = 8.2, 2.2 Hz, 1H, ClCC*H*CHCCHO), 3.08 (br s, 1H, SiO*H*), 1.35 [septet, *J* = 7.4 Hz, 2H, C*H*(CH_3)$_2$], 1.08 [d, *J* = 7.4 Hz, 6H, CH(CH_3)$_2$], and 0.87 [d, *J* = 7.4 Hz, 6H, CH(CH_3)$_2$].

^{1}H NMR ($CDCl_3$, 500 MHz) for silyl hemiacetal: 7.48 (s, 0.08H, SiCC*H*), 7.419-7.417 (m, 0.16H, ClCCHC*H*CHO and ClCC*H*CHCHO], 6.33 (s, 0.08H, SiOC*H*OH), 1.25 [septet, *J* = 7.4

Hz, 0.08H, C*H*(CH_3)$_2$], 1.23 [septet, *J* = 7.4 Hz, 0.08H, C*H*(CH_3)$_2$], 1.05 [d, *J* = 7.4 Hz, 0.24H, CH(C*H₃*)$_2$], 1.03 [d, *J* = 7.4 Hz, 0.24H, CH(C*H₃*)$_2$], 0.99 [d, *J* = 7.4 Hz, 0.24H, CH(C*H₃*)$_2$], and 0.97 [d, *J* = 7.4 Hz, 0.24H, CH(C*H₃*)$_2$].

^{13}C NMR ($CDCl_3$, 125 MHz) for **3f**: δ 194.3, 141.9, 140.9, 139.8, 136.6, 136.0, 129.8, 18.0, 17.7, and 13.2.

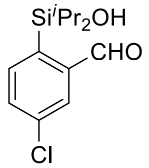
^{13}C NMR ($CDCl_3$, 125 MHz) for silyl hemiacetal: 139.1, 137.9, 135.3, 131.4, 130.6, 125.8, 98.3, 17.23, 17.12, 16.99, 16.98, 12.5, and 12.4.

IR (neat): 3456 (br, m), 2945 (m), 2865 (m), 1692 (s), 1546 (m), 1462 (m), 1138 (s), 821 (s), 665 (s), and 483 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+H)^+$ $(C_{13}H_{20}ClO_2Si)^+$: 271.0916. Found: 271.0947.

5-Chloro-2-(hydroxydiisopropylsilyl)benzaldehyde (3g)



3g

The ratio of aldehyde and silyl hemiacetal is 1:0.22.

Total Yield: 1 mmol scale, 211 mg, 78%.

^{1}H NMR ($CDCl_3$, 500 MHz) for **3g**: δ 10.0 (s, 1H, C*H*O), 7.87 (d, *J* = 2.1 Hz, 1H, CHOCC*H*), 7.77 (d, *J* = 7.9 Hz, 1H, SiCC*H*), 7.59 (dd, *J* = 7.9, 2.1 Hz, 1H, SiCCHC*H*CCl), 2.96 (br s, 1H, SiO*H*), 1.33 [septet, *J* = 7.4 Hz, 2H, C*H*(CH_3)$_2$], 1.08 [d, *J* = 7.4 Hz, 6H, CH(C*H₃*)$_2$], and 0.87 [d, *J* = 7.4 Hz, 6H, CH(C*H₃*)$_2$].

^{1}H NMR ($CDCl_3$, 500 MHz) for silyl hemiacetal: 7.48 (d, *J* = 1.8 Hz, 0.22H, CHOCC*H*), 7.46 (d, *J* = 7.7 Hz, 0.22H, SiCC*H*), 7.36 (dd, *J* = 7.7, 1.8 Hz, 0.22H, SiCCHC*H*CCl), 6.31 (s, 0.22H, SiOC*H*OH), 1.25 [septet, *J* = 7.4 Hz, 0.22H, C*H*(CH_3)$_2$], 1.22 [septet, *J* = 7.4 Hz, 0.22H, C*H*(CH_3)$_2$], 1.04 [d, *J* = 7.4 Hz, 0.66H, CH(C*H₃*)$_2$], 1.03 [d, *J* = 7.4 Hz, 0.66H, CH(C*H₃*)$_2$], 0.98 [d, *J* = 7.4 Hz, 0.66H, CH(C*H₃*)$_2$], and 0.97 [d, *J* = 7.4 Hz, 0.66H, CH(C*H₃*)$_2$].

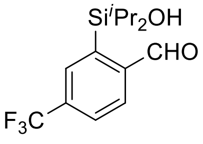
^{13}C NMR ($CDCl_3$, 125 MHz) for **3g**: δ 194.4, 143.3, 137.9, 136.4, 134.2, 133.4, 124.8, 17.9, 17.7, and 13.3. For partial assignment of silyl hemiacetal: 137.3, 136.9, 133.0, 129.3, 98.2, 17.27, 17.15, 17.09, 17.03, 12.55, and 12.40.

IR (neat): 3450 (br, m), 2945 (m), 2865 (m), 1698 (m), 1587 (m), 1462 (m), 1191 (s), 1058 (s), 978 (s), 801 (s), 774 (s), and 497 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+H)$^+$ ($C_{13}H_{20}ClO_2Si$)$^+$: 271.0916. Found: 271.0958.

2-(Hydroxydiisopropylsilyl)-4-(trifluoromethyl)benzaldehyde (3h)



3h

The ratio of aldehyde and silyl hemiacetal is 1:0.55.

Total Yield: 1 mmol scale, 219 mg, 72%.

^{1}H NMR ($CDCl_3$, 500 MHz) for **3h**: δ 10.1 (s, 1H, C*H*O), 8.13 (d, *J* = 1.9 Hz, 1H, SiCC*H*CCF$_3$), 8.01 (d, *J* = 7.9 Hz, 1H, CHOCC*H*), 7.84 (dd, *J* = 7.9, 1.9 Hz, 1H, CF$_3$CC*H*CHCCHO), 2.72 (br s, 1H, SiO*H*), 1.38 [septet, *J* = 7.4 Hz, 2H, C*H*(CH$_3$)$_2$], 1.11 [d, *J* = 7.4 Hz, 6H, CH(C*H$_3$*)$_2$], and 0.86 [d, *J* = 7.5 Hz, 6H, CH(C*H$_3$*)$_2$].

^{1}H NMR ($CDCl_3$, 500 MHz) for silyl hemiacetal: 7.78 (d, *J* = 1.6 Hz, 0.55H, SiCC*H*), 7.72 (dd, *J* = 8.1, 1.6 Hz, 0.55H, CHOCC*H*), 7.61 (d, *J* = 8.1 Hz, 0.55H, CF$_3$CC*H*CHCCHO), 6.39 (d, *J* = 6.7 Hz, 0.55H, SiOC*H*OH), 2.98 (d, *J* = 6.7 Hz, 0.55H, SiOCHO*H*)， 1.29 [septet, *J* = 7.4 Hz, 0.55H, C*H*(CH$_3$)$_2$], 1.23 [septet, *J* = 7.4 Hz, 0.55H, C*H*(CH$_3$)$_2$], 1.06 [d, *J* = 7.4 Hz, 1.65 H, CH(C*H$_3$*)$_2$], 1.05 [d, *J* = 7.4 Hz, 1.65H, CH(C*H$_3$*)$_2$], 1.00 [d, *J* = 7.4 Hz, 1.65H, CH(C*H$_3$*)$_2$], and 0.99 [d, *J* = 7.4 Hz, 1.65H, CH(C*H$_3$*)$_2$].

^{13}C NMR ($CDCl_3$, 125 MHz) for **3h**: δ 194.5, 140.9, 134.0, 133.1 (q, $J^3_{F\text{-}C}$ = 3.6 Hz), 131.1 (q, $J^2_{F\text{-}C}$ = 32.1 Hz), 126.7 (q, $J_{F\text{-}C}$ = 3.7 Hz), 126.0 (q, $J^1_{F\text{-}C}$ = 273.1 Hz), 124.9, 18.0, 17.7, 13.2.

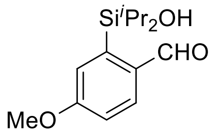
^{13}C NMR ($CDCl_3$, 125 MHz) for silyl hemiacetal: 154.5, 134.4, 131.1 (q, $J^2_{F\text{-}C}$ = 31.3 Hz), 128.5 (q, $J_{F\text{-}C}$ = 3.6 Hz), 127.6 (q, $J_{F\text{-}C}$ = 3.0 Hz), 125.0, 124.5 (q, $J^1_{F\text{-}C}$ = 262.1 Hz), 98.4, 17.22, 17.13, 17.00 (2), 12.5, and 12.4.

IR (neat): 3460 (br, w), 2947 (m), 2868 (m), 1754 (w), 1706 (w), 1463 (m), 1321 (s), 1124 (s), 1075 (s), 977 (s), 802 (s), 639 (s), and 486 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+H)$^+$ ($C_{14}H_{20}F_3O_2Si$)$^+$: 305.1179. Found: 305.1199.

2-(Hydroxydiisopropylsilyl)-4-methoxybenzaldehyde (3i)



3i

The ratio of aldehyde and silyl hemiacetal is 1:0.01.

Yield: 1 mmol scale, 149 mg, 56%.

^{1}H NMR ($CDCl_3$, 500 MHz) only for **3i**: δ 9.83 (s, 1H, C*H*O), 7.85 (d, *J* = 8.5 Hz, 1H, CHOCC*H*), 7.30 (d, 1H, *J* = 2.6 Hz, SiCC*H*), 7.01 (dd, *J* = 8.5, 2.6 Hz, 1H, CHOCCHC*H*), 3.90 (s, 3H, OCH_3), 3.82 (br s, 1H, SiO*H*), 1.32 [septet, *J* = 7.4 Hz, 2H, C*H*(CH_3)$_2$], 1.07 [d, *J* = 7.4 Hz, 6H, CH(CH_3)$_2$], and 0.91 [d, *J* = 7.4 Hz, 6H, CH(CH_3)$_2$].

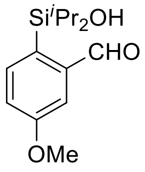
^{13}C NMR ($CDCl_3$, 125 MHz) only for **3i**: δ 194.3, 163.7, 141.7, 139.1, 134.9, 123.4, 113.2, 55.7, 17.9, 17.6, and 13.2.

IR (neat): 3453 (br, m), 2943 (m), 2864 (m), 1680 (s), 1582 (m), 1555 (m), 1462 (s), 1230 (s), 1212 (s), 881 (s), 665 (s), and 486 (s) cm^{-1}.

TLC: R_f = 0.4 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+Na)$^+$ ($C_{14}H_{22}NaO_3Si$)$^+$: 289.1230. Found: 289.1252.

2-(Hydroxydiisopropylsilyl)-5-methoxybenzaldehyde (3j)



3j

The ratio of aldehyde and silyl hemiacetal is 1:0.05.

Yield: 1 mmol scale, 205 mg, 77%.

^{1}H NMR ($CDCl_3$, 500 MHz) only for **3j**: δ 10.0 (s, 1H, C*H*O), 7.70 (d, *J* = 8.2 Hz, 1H, SiCC*H*), 7.44 (d, 1H, *J* = 2.6 Hz, CHOCC*H*), 7.15 (dd, *J* = 8.2, 2.6 Hz, 1H, SiCCHC*H*), 3.89 (s, 3H, ArOCH_3), 3.15 (br s, 1H, SiO*H*), 1.30 [septet, *J* = 7.4 Hz, 2H, C*H*(CH_3)$_2$], 1.07 [d, *J* = 7.4 Hz, 6H, CH(CH_3)$_2$], and 0.90 [d, *J* = 7.4 Hz, 6H, CH(CH_3)$_2$].

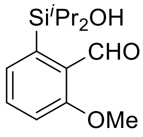
^{13}C NMR ($CDCl_3$, 125 MHz) only for **3j**: δ 195.7, 160.9, 143.6, 137.9, 129.6, 120.1, 119.0, 55.6, 17.9, 17.6, and 13.4.

IR (neat): 3400 (br, m), 2943 (m), 2865 (m), 1738 (m), 1686 (m), 1593 (m), 1462 (s), 1238 (s), 1048 (s), 1025 (s), 880 (s), 662 (s), and 464 (s) cm^{-1}.

TLC: R_f = 0.4 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{14}H_{22}NaO_3Si)^+$: 289.1230. Found: 289.1260.

2-(Hydroxydiisopropylsilyl)-6-methoxybenzaldehyde (3k)



3k

The ratio of aldehyde and corresponding silyl hemiacetal is 1:0.45.

Total Yield: 1 mmol scale, 96 mg, 36%.

^{1}H NMR ($CDCl_3$, 500 MHz) for **3k**: δ 10.5 (s, 1H, C*H*O), 7.56 (dd, *J* = 8.3, 7.4 Hz, 1H, SiCCHC*H*), 7.42 (d, *J* = 7.4 Hz, 1H, SiCC*H*), 7.03 (d, *J* = 8.3 Hz, 1H, MeOCC*H*), 3.92 (s, 3H, ArOC*H$_3$*), 3.16 (br s, 1H, SiO*H*), 1.34 [septet, *J* = 7.4 Hz, 2H, C*H*$(CH_3)_2$], 1.08 [d, *J* = 7.4 Hz, 6H, CH(C*H$_3$*)$_2$], and 0.85 [d, *J* = 7.4 Hz, 6H, CH(C*H$_3$*)$_2$].

^{1}H NMR ($CDCl_3$, 500 MHz) for silyl hemiacetal: 7.36 (dd, *J* = 8.0, 7.2 Hz, 0.45H, SiCCHC*H*), 7.10 (d, *J* = 7.4 Hz, 0.45H, SiCC*H*), 6.92 (d, *J* = 8.0 Hz, 0.45H, MeOCC*H*), 6.49 (s, 0.45H, SiOC*H*OH), 3.88 (s, 1.35H, ArOC*H$_3$*), 1.26 [septet, *J* = 7.4 Hz, 0.45H, C*H*$(CH_3)_2$], 1.20 [septet, *J* = 7.4 Hz, 0.45H, C*H*$(CH_3)_2$], 1.07 [d, *J* = 7.4 Hz, 1.35H, CH(C*H$_3$*)$_2$], 1.06 [d, *J* = 7.4 Hz, 1.35H, CH(C*H$_3$*)$_2$], 0.97 [d, *J* = 7.4 Hz, 1.35H, CH(C*H$_3$*)$_2$], and 0.96 [d, *J* = 7.4 Hz, 1.35H, CH(C*H$_3$*)$_2$].

^{13}C NMR ($CDCl_3$, 125 MHz) for **3k**: δ 193.0, 163.6, 141.1, 135.4, 128.5, 123.7, 112.8, 55.8, 18.3, 18.1, and 13.3.

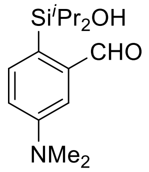
^{13}C NMR ($CDCl_3$, 125 MHz) for silyl hemiacetal: 155.8, 138.8, 134.7, 130.7, 129.5, 112.0, 97.0, 55.3, 17.37, 17.24, 17.05 (2), 12.52, and 12.48.

IR (neat): 3435 (br, m), 2943 (m), 2864 (m), 1738 (m), 1676 (m), 1570 (m), 1466 (s), 1258 (s), 1024 (s), 963 (s), 786 (s), 668 (s), and 502 (s) cm^{-1}.

TLC: R_f = 0.4 in 3:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{14}H_{22}NaO_3Si)^+$: 289.1230. Found: 289.1257.

5-(Dimethylamino)-2-(hydroxydiisopropylsilyl)benzaldehyde (3l)



3l

The ratio of aldehyde and silyl hemiacetal is 1:0.04.

Yield: 1 mmol scale, 254 mg, 91%.

^{1}H NMR (CDCl$_3$, 500 MHz) only for **3l**: δ 9.99 (s, 1H, C*H*O), 7.59 (d, *J* = 8.3 Hz, 1H, SiCC*H*), 7.22 (d, 1H, *J* = 2.7 Hz, CHOCC*H*), 6.91 (dd, *J* = 8.3, 2.7 Hz, 1H, SiCCHC*H*), 3.34 (br s, 1H, SiO*H*), 3.05 [s, 6H, N(C*H$_3$*)$_2$], 1.28 [septet, *J* = 7.4 Hz, 2H, C*H*(CH$_3$)$_2$], 1.06 [d, *J* = 7.4 Hz, 6H, CH(C*H$_3$*)$_2$], and 0.91 [d, *J* = 7.4 Hz, 6H, CH(C*H$_3$*)$_2$].

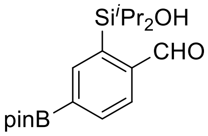
^{13}C NMR (CDCl$_3$, 125 MHz) only for **3l**: δ 197.0, 151.1, 143.0, 137.5 (2), 119.2, 116.3, 40.2, 17.9, 17.7, and 13.5.

IR (neat): 3436 (br, m), 2942 (m), 2863 (m), 1682 (s), 1595 (s), 1359 (m), 1208 (m), 1061 (s), 816 (s), 662 (s), and 485 (s) cm^{-1}.

TLC: R$_f$ = 0.35 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+H)$^+$ ($C_{15}H_{26}NO_2Si$)$^+$: 280.1727. Found: 280.1746.

2-(Hydroxydiisopropylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (3m)



3m

The ratio of aldehyde and silyl hemiacetal is 1:0.22.

Total Yield: 1 mmol scale, 279 mg, 77%.

^{1}H NMR (CDCl$_3$, 500 MHz) for **3m**: δ 10.0 (s, 1H, C*H*O), 8.21 (app s, 1H, SiCC*H*CBpin), 8.01 (dd, *J* = 7.5, 1.1 Hz, 1H, pinBCC*H*CHCCHO), 7.87 (d, *J* = 7.5 Hz, 1H, CHOCC*H*), 3.17 (br s, 1H, SiO*H*), 1.38 [septet, *J* = 7.4 Hz, 2H, C*H*(CH$_3$)$_2$], 1.36 {s, 12H, B[OC(C*H$_3$*)$_2$]$_2$}, 1.09 [d, *J* = 7.4 Hz, 6H, CH(C*H$_3$*)$_2$], and 0.88 [d, *J* = 7.5 Hz, 6H, CH(C*H$_3$*)$_2$].

^{1}H NMR (CDCl$_3$, 500 MHz) for silyl hemiacetal: 7.98 (app s, 0.22H, SiCC*H*CBpin), 7.91 (dd, *J*

= 7.7, 1.1 Hz, 0.22H, pinBCC*H*CHCCHO), 7.49 (d, *J* = 7.7 Hz, 0.22H, CHOCC*H*), 6.35 (s, 0.22H, SiOC*H*OH), 1.36 {s, 2.6H, $B[OC(C\mathit{H}_3)_2]_2$}, 1.27 [septet, *J* = 7.4 Hz, 0.22H, $C\mathit{H}(CH_3)_2$], 1.24 [septet, *J* = 7.4 Hz, 0.22H, $C\mathit{H}(CH_3)_2$], 1.053 [d, *J* = 7.4 Hz, 0.66 H, $CH(C\mathit{H}_3)_2$], 1.046 [d, *J* = 7.4 Hz, 0.66H, $CH(C\mathit{H}_3)_2$], 0.987 [d, *J* = 7.4 Hz, 0.66H, $CH(C\mathit{H}_3)_2$], and 0.984 [d, *J* = 7.4 Hz, 0.66H, $CH(C\mathit{H}_3)_2$].

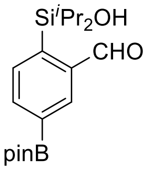
^{13}C NMR ($CDCl_3$, 125 MHz) for **3m**: δ 196.2, 143.5, 142.4, 137.7, 137.0, 136.1, 134.1, 84.5, 25.1, 18.1, 17.8, and 13.3. For partial assignment of silyl hemiacetal: 138.5, 123.6, 98.8, 84.1, 24.9, 17.35, 17.27, 17.10 (2), 12.6, and 12.4.

IR (neat): 3442 (br, w), 2945 (m), 2866 (m), 1696 (w), 1464 (m), 1356 (s), 1260 (s), 1094 (s), 1011 (s), 795 (s), 736 (s), and 482 (s) cm^{-1}.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+H)^+$ $(C_{19}H_{32}BO_4Si)^+$: 363.2157. Found: 363.2189.

2-(Hydroxydiisopropylsilyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (3n)



3n

The ratio of aldehyde and silyl hemiacetal is 1:0.05.

Yield: 1 mmol scale, 261 mg, 72%.

^{1}H NMR ($CDCl_3$, 500 MHz) only for **3n**: δ 10.0 (s, 1H, C*H*O), 8.31 (app s, 1H, CHOCC*H*), 8.03 (dd, *J* = 7.2, 1.2 Hz, 1H, SiCCHC*H*), 7.81 (d, *J* = 7.2 Hz, 1H, SiCC*H*), 3.53 (br s, 1H, SiO*H*), 1.37 {s, 12H, $B[OC(C\mathit{H}_3)_2]_2$}, 1.34 [septet, *J* = 7.4 Hz, 2H, $C\mathit{H}(CH_3)_2$], 1.07 [d, *J* = 7.4 Hz, 6H, $CH(C\mathit{H}_3)_2$], and 0.87 [d, *J* = 7.4 Hz, 6H, $CH(C\mathit{H}_3)_2$].

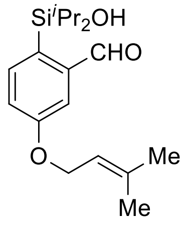
^{13}C NMR ($CDCl_3$, 125 MHz) only for **3n**: δ 196.6, 142.5, 142.2, 141.1, 139.6 (2), 135.9, 84.6, 25.1, 17.9, 17.7, and 13.2.

IR (neat): 3443 (br, w), 2943 (m), 2865 (m), 1690 (w), 1463 (m), 1356 (s), 1141 (s), 881 (s), 673 (s), and 497 (m) cm^{-1}.

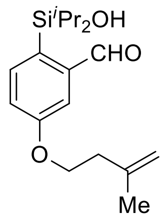
TLC: R_f = 0.4 in 10:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{19}H_{31}BNaO_4Si)^+$: 385.1977. Found: 385.1997.

2-(Hydroxydiisopropylsilyl)-5-[(3-methylbut-2-en-1-yl)oxy]benzaldehyde (3o)



3o



3o'

1,1-Disubstituted alkene **3o'** via alkene migration were isolated along with the desired product as an inseparable mixture. The ratio of three compounds (**3o**: **3o'**: silyl hemiacetal of **3o**) is 1:0.18:0.08.

Total Yield: 1 mmol scale, 227 mg, 71%.

^{1}H NMR (CDCl$_3$, 500 MHz) for **3o**: δ 10.04 (s, 1H, C*H*O), 7.683 (d, *J* = 8.2 Hz, 1H, SiCC*H*), 7.448 (d, *J* = 2.6 Hz, 1H, CHOCC*H*), 7.150 (dd, *J* = 8.2, 2.6 Hz, 1H, SiCCHC*H*), 5.51 (app t, *J* = 6.8 Hz, 1H, ArOCH$_2$C*H*=CMe$_2$), 4.59 (d, *J* = 6.8 Hz, 2H, ArOC*H*$_2$CH=CMe$_2$), 3.16 (br s, 1H, SiO*H*), 1.81 [s, 3H, ArOCH$_2$CH=C(C*H*$_3$)$_2$], 1.77 [s, 3H, ArOCH$_2$CH=C(C*H*$_3$)$_2$)], 1.30 [septet, *J* = 7.4 Hz, 2H, C*H*(CH$_3$)$_2$], 1.06 [d, *J* = 7.4Hz, 6H, CH(C*H*$_3$)$_2$], and 0.901 [d, *J* = 7.4 Hz, 6H, CH(C*H*$_3$)$_2$],

^{1}H NMR (CDCl$_3$, 500 MHz) for **3o'**: 10.05 (s, 0.18H, C*H*O), 7.685 (d, *J* = 8.2 Hz, 0.18H, SiCC*H*), 7.439 (d, *J* = 2.6 Hz, 0.18H, CHOCC*H*), 7.142 (dd, *J* = 8.2, 2.6 Hz, 0.18H, SiCCHC*H*), 4.87 (app s, 0.18H, C*H*$_a$H$_b$=CMe), 4.82 (app s, 0.18H, CH$_a$*H*$_b$=CMe), 4.16 (t, *J* = 6.8 Hz, 0.36H, ArOC*H*$_2$CH$_2$), 2.54 (t, *J* = 6.8 Hz, 0.36H, ArOCH$_2$C*H*$_2$), 2.25 (br s, 0.18H, SiCHO*H*), 1.81 [s, 0.54H, ArOCH$_2$CH=C(C*H*$_3$)$_2$], 1.32-1.17 [m, 0.36H, C*H*(CH$_3$)$_2$], 1.038 [d, *J* = 7.4Hz, 1.08H, CH(C*H*$_3$)$_2$], and 0.898 [d, *J* = 7.4 Hz, 1.08H, CH(C*H*$_3$)$_2$].

^{1}H NMR (CDCl$_3$, 500 MHz) for silyl hemiacetal of **3o**: 7.427 (d, *J* = 8.0 Hz, 0.08H, SiCC*H*), 7.02 (d, *J* = 2.2 Hz, 0.08H, CH$_2$OCC*H*CCHO), 6.96 (dd, *J* = 8.0, 2.2 Hz, 0.08H, SiCCHC*H*), 6.29 (d, *J* = 7.4 Hz, 0.08H, SiC*H*OH), 5.51 (app t, *J* = 6.8 Hz, 0.08H, ArOCH$_2$C*H*=CMe$_2$), 4.57-4.50 (m, 0.16H, ArOC*H*$_2$CH=CMe$_2$), 2.88 (d, *J* = 7.4 Hz, 0.08H, SiCHO*H*), 1.80 [s, 0.24H, ArOCH$_2$CH=C(C*H*$_3$)$_2$], 1.32-1.17 [m, 0.16H, C*H*(CH$_3$)$_2$], 1.75 [s, 0.24H, ArOCH$_2$CH=C(C*H*$_3$)$_2$], 1.046 [d, *J* = 7.4 Hz, 0.24H, CH(C*H*$_3$)$_2$], 1.028 [d, *J* = 7.4 Hz, 0.24H, CH(C*H*$_3$)$_2$], 0.989 [d, *J* = 7.4 Hz, 0.24H, CH(C*H*$_3$)$_2$], and 0.969 [d, *J* = 7.4 Hz, 0.24H, CH(C*H*$_3$)$_2$].

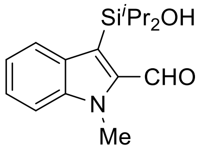
^{13}C NMR (CDCl$_3$, 125 MHz) only for **3o**: δ 195.7, 160.2, 143.5, 139.3, 137.9, 129.4, 120.9, 119.7, 119.2, 65.1, 26.1, 18.5, 17.9, 17.6, and 13.4.

IR (neat): 3457 (br, w), 2942 (m), 2864 (m), 1686 (s), 1591 (s), 1462 (m), 1297 (s), 1267 (s), 1232 (s), 1069 (s), 995 (s), 826 (s), 662 (s), and 487 (m) cm^{-1}.

TLC: $R_f = 0.4$ in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{18}H_{28}NaO_3Si)^+$: 343.1700. Found: 343.1735.

3-(Hydroxydiisopropylsilyl)-1-methyl-1*H*-indole-2-carbaldehyde (3p)



3p

Yield: 1 mmol scale, 118 mg, 41%.

^{1}H NMR (CDCl$_3$, 500 MHz): δ 10.3 (s, 1H, C*H*O), 7.94 (ddd, *J* = 8.1, 0.9, 0.9 Hz, 1H, Ar*H*), 7.44-7.40 (nfom, 2H, Ar*H*), 7.17 (ddd, *J* = 8.1, 4.9, 3.0 Hz, 1H, Ar*H*), 4.12 (s, 3H, NC*H$_3$*), 3.25 (br s, 1H, SiO*H*), 1.39 [septet, *J* = 7.4 Hz, 2H, C*H*(CH$_3$)$_2$], 1.12 [d, *J* = 7.4 Hz, 6H, CH(C*H$_3$*)$_2$], and 0.99 [d, *J* = 7.4 Hz, 6H, CH(C*H$_3$*)$_2$].

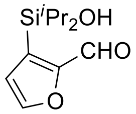
^{13}C NMR (CDCl$_3$, 125 MHz): δ 186.6, 141.4, 141.0, 132.2, 126.7, 125.2, 121.5, 121.2, 110.6, 32.2, 17.4, 17.1, and 14.4.

IR (neat): 3382 (br, w), 3052 (w), 2943 (m), 2864 (m), 1642 (s), 1465 (m), 1385 (m), 1346 (m), 878 (s), and 488 (m) cm^{-1}.

TLC: $R_f = 0.6$ in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{16}H_{23}NNaO_2Si)^+$: 312.1390. Found: 312.1412.

3-(Hydroxydiisopropylsilyl)furan-2-carbaldehyde (3q)



3q

The ratio of aldehyde and silyl hemiacetal is 1:0.04.

Yield: 1 mmol scale, 140 mg, 62%.

^{1}H NMR (CDCl$_3$, 500 MHz) only for **3q**: δ 9.78 (d, *J* = 0.7 Hz, 1H, C*H*O), 7.76 (d, *J* = 1.5 Hz, 1H, Ar*H*), 6.62 (dd, J = 1.5, 0.7 Hz, 1H, Ar*H*), 4.82 (br s, 1H, SiO*H*), 1.15 [septet, *J* = 7.2 Hz, 2H, C*H*(CH$_3$)$_2$], 1.04 [d, *J* = 7.2 Hz, 6H, CH(C*H$_3$*)$_2$], and 0.96 [d, *J* = 7.3 Hz, 6H, CH(C*H$_3$*)$_2$].

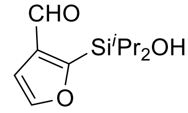
^{13}C NMR (CDCl$_3$, 125 MHz) only for **3q**: δ 182.6, 157.8, 148.1, 128.9, 118.0, 17.1, 16.8, and 13.2.

IR (neat): 3397 (br, w), 2945 (m), 2866 (m), 1734 (m), 1664 (s), 1460 (s), 1353 (m), 821 (s), 762 (s), and 493 (m) cm^{-1}.

TLC: R$_f$ = 0.5 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+Na)$^+$ (C$_{11}$H$_{18}$NaO$_3$Si)$^+$: 249.0917. Found: 249.0937.

2-(Hydroxydiisopropylsilyl)furan-3-carbaldehyde (3r)



3r

The ratio of aldehyde and silyl hemiacetal is 1:0.05.

Yield: 1 mmol scale, 160 mg, 71%.

^{1}H NMR (CDCl$_3$, 500 MHz) only for **3r**: δ 9.88 (d, *J* = 0.7 Hz, 1H, C*H*O), 8.23 (d, *J* = 1.3 Hz, 1H, Ar*H*), 7.42 (dd, J = 1.3, 0.7 Hz, 1H, Ar*H*), 4.74 (br s, 1H, SiO*H*), 1.09 [septet, *J* = 7.2 Hz, 2H, C*H*(CH$_3$)$_2$], 1.02 [d, *J* = 7.2 Hz, 6H, CH(C*H$_3$*)$_2$], and 0.96 [d, *J* = 7.2 Hz, 6H, CH(C*H$_3$*)$_2$].

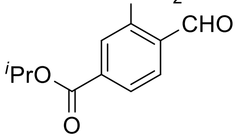
^{13}C NMR (CDCl$_3$, 125 MHz) only for **3r**: δ 187.1, 155.9, 149.9, 133.1, 113.3, 17.2, 17.0, and 13.5.

IR (neat): 3382 (br, w), 2945 (m), 2867 (m), 1734 (m), 1670 (s), 1463 (s), 996 (s), 882 (s), 674 (s), and 479 (m) cm^{-1}.

TLC: R$_f$ = 0.5 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+Na)$^+$ (C$_{11}$H$_{18}$NaO$_3$Si)$^+$: 249.0917. Found: 249.0940.

Isopropyl 4-formyl-3-(hydroxydiisopropylsilyl)benzoate (3s)



3s

The ratio of aldehyde and silyl hemiacetal is 1:0.40.

Total Yield: 1 mmol scale, 184 mg, 57%.

^{1}H NMR (CDCl$_3$, 500 MHz) for **3s**: δ 10.1 (s, 1H, C*H*O), 8.46 (d, *J* = 1.7 Hz, 1H, SiCC*H*), 8.20 (dd, *J* = 7.9, 1.7 Hz, 1H, CHOCCHC*H*CCO$_2$^{i}Pr), 7.96 (d, *J* = 7.9 Hz, 1H, CHOCC*H*), 5.27

[septet, *J* = 6.3 Hz, 1H, ArCO$_2$C*H*(CH$_3$)$_2$], 3.35 (br s, 1H, SiO*H*), 1.39 [d, *J* = 6.3 Hz, 6H, ArCO$_2$CH(C*H*$_3$)$_2$], 1.35 {septet, *J* = 7.4 Hz, 2H, Si[C*H*(CH$_3$)$_2$]$_2$},1.09 [d, *J* = 7.4 Hz, 6H, SiCH(C*H*$_3$)$_2$], and 0.89 [d, *J* = 7.4 Hz, 6H, SiCH(C*H*$_3$)$_2$].

^{1}H NMR (CDCl$_3$, 500 MHz) for silyl hemiacetal: 8.19 (d, *J* = 1.6 Hz, 0.4H, SiCC*H*), 8.11 (dd, *J* = 8.0, 1.6 Hz, 0.4H, CHOCCHC*H*CCO$_2{}^i$Pr), 7.54 (d, *J* = 8.0 Hz, 1H, CHOCC*H*), 6.38 (s, 0.4H, SiOC*H*OH), 5.26 [septet, *J* = 6.3 Hz, 0.4H, ArCO$_2$C*H*(CH$_3$)$_2$], 1.38 [d, *J* = 6.3 Hz, 2.4H, ArCO$_2$CH(C*H*$_3$)$_2$], 1.27 {septet, *J* = 7.4 Hz, 0.4H, Si[C*H*(CH$_3$)$_2$]$_2$}, 1.25 {septet, *J* = 7.4 Hz, 0.4H, Si[C*H*(CH$_3$)$_2$]$_2$}, 1.05 [d, *J* = 7.4 Hz, 1.2H, SiCH(C*H*$_3$)$_2$], 1.04 [d, *J* = 7.4 Hz, 1.2H, SiCH(C*H*$_3$)$_2$], 0.99 [d, *J* = 7.4 Hz, 1.2H, SiCH(C*H*$_3$)$_2$], and 0.98 [d, *J* = 7.4 Hz, 1.2H, SiCH(C*H*$_3$)$_2$].

^{13}C NMR (CDCl$_3$, 125 MHz) for **3s**: δ 195.3, 165.6, 139.6, 137.2, 134.6, 134.1, 131.7, 130.7, 69.5, 22.09, 18.0, 17.7, and 13.3.

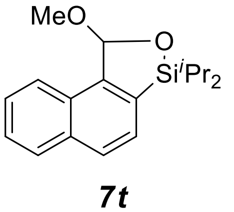
^{13}C NMR (CDCl$_3$, 125 MHz) for silyl hemiacetal: 166.3, 155.4, 144.5, 133.2, 131.4, 126.6, 124.3, 98.5, 68.8, 22.14 (2), 17.24, 17.15, 17.02 (2), 12.5, and 12.4.

IR (neat): 3492 (br, w), 2944 (m), 2866 (m), 1716 (s), 1463 (m), 1276 (m), 1244 (m), 1099 (s), 806 (s), and 483 (m) cm^{-1}.

TLC: R$_f$ = 0.3 in 10:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for (M+Na)$^+$ (C$_{17}$H$_{26}$NaO$_4$Si)$^+$: 345.1493. Found: 345.1515.

3,3-Diisopropyl-1-methoxy-1,3-dihydronaphtho[2,1-*c*][1,2]oxasilole (7t)



7t

Yield: 1 mmol scale, 273 mg, 91%.

^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.11 (dddd, *J* = 8.1, 1.5, 0.6, 0.6 Hz, 1H, naphthalene-*H5*), 7.91 (ddd, *J* = 8.1, 1.5, 0.6 Hz, 1H, naphthalene-*H8*), 7.87 (dd, *J* = 8.0, 0.6 Hz, 1H, naphthalene-*H4*), 7.60 (d, *J* = 8.0 Hz, 1H, naphthalene-*H3*), 7.58 (ddd, *J* = 8.1, 6.9, 1.5 Hz, 1H, naphthalene-*H6* or naphthalene-*H7*), 7.54 (ddd, *J* = 8.1, 6.9, 1.5 Hz, 1H, naphthalene-*H6* or naphthalene-*H7*), 6.54 (s, 1H, SiOC*H*OMe), 3.68 (s, 3H, OC*H*$_3$), 1.35 [septet, *J* = 7.4 Hz, 1H, C*H*(CH$_3$)$_2$], 1.31 [septet, *J*

= 7.4 Hz, 1H, C*H*(CH_3)$_2$], 1.15 [d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$], 1.13 [d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$], 1.06 [d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$], and 1.01 [d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$].

^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.7, 134.9, 131.4, 129.32, 129.22, 128.6, 127.4, 126.74, 126.72, 124.4, 104.4, 54.9, 17.51, 17.41, 17.21, 17.19, and 12.8 (2).

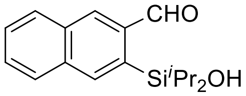
IR (neat): 3047 (w), 2943 (m), 2864 (m), 1461 (m), 1244 (m), 1065 (s), 801 (s), 671 (s), and 435 (m) cm^{-1}.

TLC: R_f = 0.4 in 10:1 hexanes: EtOAc.

GCMS (5029017): t_R = 12.48 min, m/z 300 (M^+, 18), 299 [$(M-H)^+$, 10], 269 [$(M-OMe)^+$, 100], and 257 [$(M-{}^iPr)^+$, 15].

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ ($(C_{18}H_{24}NaO_2Si)^+$): 323.1438. Found: 323.1456.

3-(Hydroxydiisopropylsilyl)-2-naphthaldehyde (3u)



3u

The ratio of aldehyde and silyl hemiacetal is 1:0.01.

Yield: 1 mmol scale, 220 mg, 77%.

^{1}H NMR ($CDCl_3$, 500 MHz) only for **3u**: δ 10.1 (s, 1H, C*H*O), 8.38 (s, 1H, naphthalene-*H1* or naphthalene –*H4*), 8.26 (s, 1H, naphthalene-*H1* or naphthalene –*H4*), 8.00 (dd, *J* = 8.1, 1.3 Hz, 1H, naphthalene-*H8* or naphthalene-*H5*), 7.93 (dd, *J* = 8.1, 1.3 Hz, 1H, naphthalene-*H8* or naphthalene-*H5*), 7.68 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H, naphthalene-*H6* or naphthalene-*H7*), 7.62 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H, naphthalene-*H6* or naphthalene-*H7*), 3.39 (br s, 1H, SiO*H*), 1.44 [septet, *J* = 7.2 Hz, 2H, C*H*(CH_3)$_2$], 1.12 [d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$], and 0.92 [d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$].

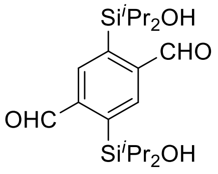
^{13}C NMR ($CDCl_3$, 125 MHz) only for **3u**: δ 195.8, 139.6, 138.9, 138.0, 135.6, 132.8, 132.5, 129.9, 129.3, 128.7, 128.0, 18.2, 17.9, and 13.4.

IR (neat): 3455 (br, w), 2943 (m), 2863 (m), 1686 (s), 1461 (m), 1211 (s), 881 (s), 744 (s), and 477 (m) cm^{-1}.

TLC: R_f = 0.4 in 10:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+H)^+$ ($(C_{17}H_{23}O_2Si)^+$): 287.1462. Found: 287.1488.

2,5-Bis(hydroxydiisopropylsilyl)terephthalaldehyde (3v)



3v

Yield: 1 mmol scale, 295 mg, 75%.

^{1}H NMR (DMSO-d6, 500 MHz): δ 10.4 (s, 2H, C*H*O), 8.39 (s, 2H, SiCC*H*), 6.15 (s, 2H, SiO*H*), 3.33 (H_2O) , 1.30 [septet, *J* = 7.4 Hz, 4H, C*H*(CH_3)$_2$], 1.03 [d, *J* = 7.4 Hz, 12H, CH(CH_3)$_2$], and 0.76 [d, *J* = 7.4 Hz, 12H, CH(CH_3)$_2$].

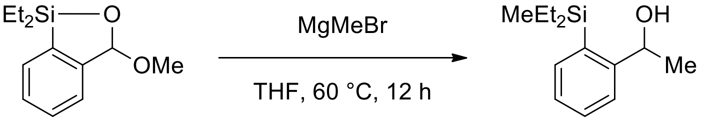
^{13}C NMR (DMSO-d6, 125 MHz): δ 195.3, 143.5, 141.2, 137.9, 17.9, 17.5, and 12.7.

IR (neat): 3489 (br, w), 2944 (s), 2865 (s), 1694 (s), 1463 (s), 1086 (s), 1018 (s), 880 (s), and 672 (m) cm^{-1}.

TLC: R_f = 0.2 in 5:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+H)^+$ $(C_{20}H_{35}O_4Si_2)^+$: 395.2068. Found: 395.2089.

Procedure for Preparation of 1-{2-[Diethyl(methyl)silyl]phenyl}ethanol (8):



6a ***8***

Crude cyclic silyl acetal **6a** (1 mmol) was dissolved with THF (1 mL, 1 M). Methylmagnesium bromide (3 M in diethyl ether, 1 mL, 3 mmol) was added to the mixture in one portion. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was kept at 60 °C and stirred for 12 h. The reaction was quenched by adding saturated aqueous ammonium chloride (5 mL) and extracted with ditheyl ether (8 mL×4). The combined organic layer was washed with water (10 mL) and brine (10 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo,* and the crude mixture was purified by MPLC (hexanes/EtOAc = 20:1, 7 mL/min, retention time 9 min) to afford **8** (202 mg, 91%) as a colorless liquid.

^{1}**H NMR** ($CDCl_3$, 500 MHz): δ 7.62 [dd, *J* = 7.5, 1.5 Hz, 1H, CH(OH)CC*H* or SiCC*H*], 7.47 [dd, *J* = 7.5, 1.5 Hz, 1H, CH(OH)CC*H* or SiCC*H*], 7.43 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H, SiCCHC*H* or SiCCHCHC*H*), 7.27 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H, SiCCHC*H* or SiCCHCHC*H*), 5.12 [q, *J* = 6.3 Hz, 1H, C*H*(OH)CH$_3$], 2.12 (br s, 1H, O*H*), 1.49 (d, *J* = 6.3 Hz, 3H, CH(OH)C*H*$_3$], 1.00-0.96 [m, 6H, Si(CH$_2$C*H*$_3$)$_2$], 0.88-0.83 [m, 4H, Si(C*H*$_2$CH$_3$)$_2$], and 0.34 (s, 3H, SiC*H*$_3$).

^{13}**C NMR** ($CDCl_3$, 125 MHz): δ 152.0, 135.06, 135.00, 129.9, 127.1, 125.4, 69.8, 25.4, 7.84, 7.81, 6.94, 6.85, and 3.9.

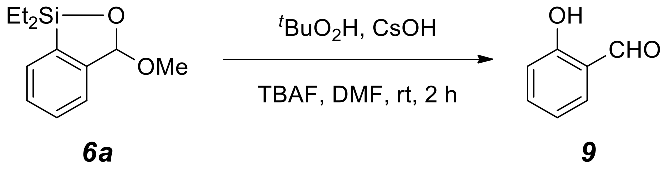
IR (neat): 3466 (br, w), 2954 (w), 2875 (w), 1077 (s), 1006 (s), and 732 (m) cm^{-1}.

TLC: R_f = 0.6 in 20:1 hexanes: EtOAc.

GCMS (5029017): t_R = 9.68 min, m/z 207 [(M-Me)$^+$, 10], 193 [(M-Et)$^+$, 12], and 177 [(M-CH(OH)Me)$^+$, 100].

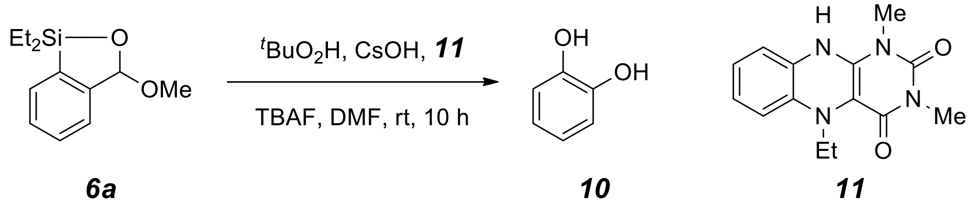
HRMS (ESI/TOF): Calcd for (M+H)$^+$ ($C_{13}H_{23}OSi$)$^+$: 223.1513. Found: 223.1530.

Procedure for Oxidation of 6a to Salicylic aldehyde (9):



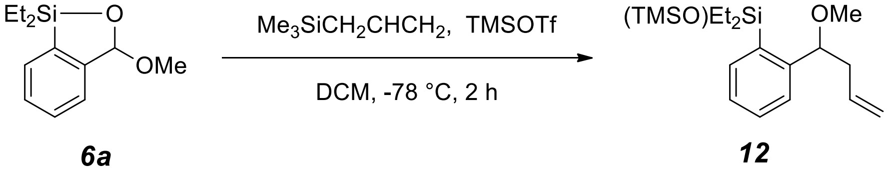
Crude cyclic silyl acetal **6a** (0.2 mmol), cesium hydroxide (45 mg, 0.3 mmol), and TBAF•3H_2O (126 mg, 0.4 mmol) were dissolved with DMF (0.2 mL, 1 M). *tert*-Butyl hydrogen peroxide (70% in water, 1 mL, 7 mmol) was added to the mixture. The reaction mixture was kept at rt and stirred for 2 h. The reaction was quenched by adding saturated aqueous sodium thiosulfate (5 mL) and acidified by HCl (1 N) and extracted with ditheyl ether (8 mL×4). The combined organic layer was washed with water (10 mL) and brine (10 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo,* and the crude mixture was purified by MPLC (hexanes/EtOAc = 5:1, 7 mL/min, retention time 8 min) to provide salicylic aldehyde **9** (21.5 mg, 88%) as a colorless liquid.

Procedure for Oxidation of 6a to Catechol (10):



Crude cyclic silyl acetal **6a** (0.2 mmol), cesium hydroxide (45 mg, 0.3 mmol), flavin **11** (5.4 mg, 10 mol %) and TBAF•3H$_2$O (126 mg, 0.4 mmol) were dissolved with DMF (0.2 mL, 1 M). *tert*-Butyl hydrogen peroxide (70% in water, 1 mL, 7 mmol) was added to the mixture. The reaction mixture was kept at rt and stirred for 10 h. The reaction was quenched by adding saturated aqeous sodium thiosulfate (5 mL) and acidified by HCl (1 N) and extracted with ditheyl ether (8 mL×4). The combined organic layer was washed with water (10 mL) and brine (10 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo,* and the crude mixture was purified by MPLC (hexanes/EtOAc = 3:1, 7 mL/min, retention time 6 min) to provide catechol **10** (14.5 mg, 66%).

Procedure for Allylation of 6a to 1,1-Diethyl-1-[2-(1-methoxybut-3-en-1-yl)phenyl]-3,3,3-trimethyldisiloxane (12):



Crude cyclic silyl acetal **6a** (12 mmol) and allyltrimethylsilane (2.4 mL, 15 mmol) were dissolved with CH$_2$Cl$_2$ (6 mL, 2 M), and the solution was cooled to –78 °C. Trimethylsilyl trifluoromethanesulfonate (TMSOTf, 0.18 mL, 1 mmol) was added into the reaction mixture. The reaction was kept at –78 °C for 2 h. The reaction was warmed to rt and quenched by adding saturated aqueous ammonium chloride (20 mL) extracted with ditheyl ether (20 mL×4). The combined organic layer was washed with water (20 mL) and brine (20 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo,* and the crude mixture was purified by MPLC (hexanes/EtOAc = 20:1, 7 mL/min, retention time 7 min) to provide **12** (2.90 g, 72% yield) as a colorless liquid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55 [dd, *J* = 7.4, 1.3 Hz, 1H, SiCC*H* or C(OMe)CC*H*], 7.52 [dd, *J* = 7.4, 1.3 Hz, 1H, SiCC*H* or C(OMe)CC*H*], 7.42 [ddd, *J* = 7.4, 7.4, 1.3 Hz, 1H, SiCCHC*H* or C(OMe)CCHC*H*], 7.28 [ddd, *J* = 7.4, 7.4, 1.3 Hz, 1H, SiCCHC*H* or C(OMe)CCHC*H*], 5.94 (dddd, *J* = 17.0, 10.3, 6.7, 6.7 Hz, 1H, $CH_2CH{=}CH_2$), 5.11 (dddd, *J* = 17.0, 2.0, 1.3, 1.3 Hz, 1H, $CH_2CH{=}CH_{cis}H_{trans}$), 5.08 (dddd, *J* = 10.3, 2.0, 1.3, 1.3 Hz, 1H, $CH_2CH{=}CH_{cis}H_{trans}$), 4.66 (dd, *J* = 8.9, 3.6 Hz, 1H, MeOC*H*), 3.22 (s, 3H, OCH_3), 2.46 (ddddd, *J* = 14.7, 8.9, 6.7, 1.3, 1.3, 1H, $MeOCHCH_aH_b$), 2.37 (ddddd, *J* = 14.7, 6.7, 3.6, 1.3, 1.3, 1H, $MeOCHCH_aH_b$), 0.99-0.94 [m, 6H, $Si(CH_2CH_3)_2$], 0.88-0.81 [m, 4H, $Si(CH_2CH_3)_2$], and 0.21 [s, 9H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.6, 135.7, 135.5, 134.8, 129.9, 126.7, 125.8, 116.6, 81.4, 56.5, 43.5, 9.14, 9.03, 7.1 (2) and 2.3.

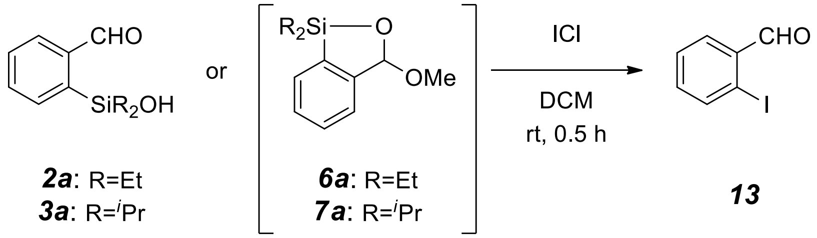
IR (neat): 3059 (w), 2954 (w), 2876 (w), 1252 (s), 1047 (s), 837 (s), and 719 (m) cm^{-1}.

TLC: $R_f = 0.6$ in 20:1 hexanes: EtOAc.

GCMS (5029017): $t_R = 10.79$ min, m/z 335 [$(M-H)^+$, 5], 295 [$(M\text{-allyl})^+$, 100], 234, and 192.

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{18}H_{32}NaO_2Si_2)^+$: 359.1833. Found: 359.1854.

Procedure for Iodo *ipso*-Desilylation of 2a/3a or 6a/7a to 2-Iodobenzaldehyde (13):



ortho-Formyl arylsilanols **2a**/**3a**, or cyclic silyl acetals **6a**/**7a** (0.2 mmol) and iodine chloride (65 mg, 0.4 mmol) were dissolved with DCM (1 mL, 0.2 M). The reaction mixture was stirred at rt for 2 h. The reaction was quenched by adding saturated aqueous sodium chloride (2 mL) and extracted with ditheyl ether (4 mL×4). The combined organic layer was washed with water (4 mL) and brine (4 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo,* and the crude mixture was purified by flash column (hexanes as eluent) to afford 2-iodobenzaldehdye **13** (43.6 mg, 94% from **2a**; 41.8 mg, 90% from **6a**; 41.3 mg, 89% from **3a**; 39.4 mg, 85% from **7a**).

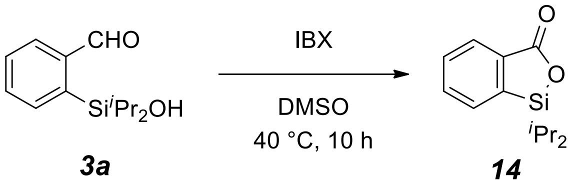
^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.1 [d, *J* = 1.0 Hz (coupled with CHOCCHC*H*), 1H, C*H*O], 7.95 (dd, *J* = 7.9, 1.0 Hz, 1H, ICC*H*), 7.88 (dd, *J* = 7.7, 1.8 Hz, 1H, CHOCC*H*), 7.46 [dddd, *J* = 7.7, 7.4, 1.0 (coupled with CHO), 1.0 Hz, 1H, CHOCCHC*H*], and 7.29 (ddd, *J* = 7.9, 7.4, 1.8 Hz, 1H, ICCHC*H*).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 196.0, 140.9, 135.7, 135.3, 130.5, 128.9, and 100.9.

TLC: R_f = 0.7 in 20:1 hexanes: EtOAc.

GCMS (5029017): t_R = 8.52 min, m/z 232 (M^+, 100), 231 [$(M-H)^+$, 35], and 104 [$(M-I)^+$, 40].

Procedure for Oxidative Lactonization of 3a to 1,1-Diisopropylbenzo[*c*][1,2]oxasilol-3-one (14):



ortho-Formyl phenylsilanol **3a** (1 mmol) and 2-iodoxybenzoic acid (IBX, 560 mg, 2 mmol) were mixed with DMSO (2 mL, 0.5 M). The suspension was warmed to 40 °C and stirred for 10 h. The reaction was quenched by adding saturated aqueous sodium chloride (5 mL) and extracted with ditheyl ether (8 mL×4). The combined organic layer was washed with water (10 mL) and brine (10 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo,* and the crude mixture was purified by MPLC (hexanes/EtOAc = 5:1, 7 mL/min, retention time 6 min) to afford silalactone **14** (212 mg, 91%) as a colorless liquid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08 [dd, *J* = 7.2, 1.3 Hz, 1H, SiCC*H* or C(O)CC*H*], 7.68 [dd, *J* = 7.2, 1.3 Hz, 1H, SiCC*H* or C(O)CC*H*], 7.64 [ddd, *J* = 7.2, 7.2, 1.3 Hz, 1H, C(O)CCHC*H* or SiCCHC*H*], 7.60 [ddd, *J* = 7.2, 7.2, 1.3 Hz, 1H, C(O)CCHC*H* or SiCCHC*H*], 1.41 [septet, *J* = 7.5 Hz, 2H, C*H*$(CH_3)_2$], 1.08 [d, *J* = 7.5 Hz, 6H, CH$(CH_3)_2$], and 1.04 [d, *J* = 7.5 Hz, 6H, CH$(CH_3)_2$].

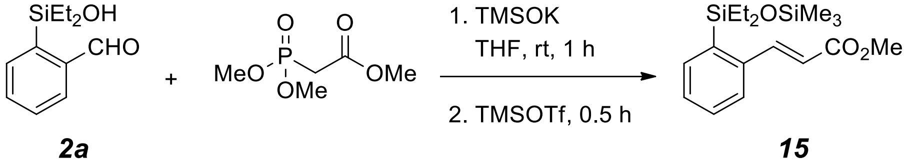
^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.1, 138.4, 138.0, 133.2, 132.1, 131.3, 127.8, 16.8 (2), and 11.7.

TLC: R_f = 0.5 in 5:1 hexanes: EtOAc.

GCMS (5029017): t_R = 10.58 min, m/z 235 [$(M+H)^+$, 5], 234 (M^+, 5), and 191 [$(M-{}^iPr)^+$, 100].

HRMS (ESI/TOF): Calcd for $(M+H)^+$ $(C_{13}H_{19}O_2Si)^+$: 235.1149. Found: 235.1170.

Procedure for Horner-Wadsworth-Emmons Homologatin of 2a into (*E*)-Methyl 3-[2-(1,1-diethyl-3,3,3-trimethyldisiloxanyl)phenyl]acrylate (15):



ortho-Formyl phenylsilanol **2a** (1 mmol) and trimethyl phosphonoacetate (0.19 mL, 1.2 mmol) were dissolved with THF (2 mL, 0.5 M). Potassium trimethylsilanolate (141 mg, 1 mmol) was added into the reaction mixture. After being stirred for 1h at rt, the reaction was quenched by adding saturated aqueous ammonium chloride (5 mL), and extracted with ditheyl ether (8 mL×4). The combined organic layer was washed with water (10 mL) and brine (10 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo*. The crude mixture was dissolved with CH_2Cl_2 (2 mL, 0.5 M). TMSOTf (0.09 mL, 0.5 mmol) was added into the reaction mixture. After being stirred for 0.5 h at rt, the reaction was quenched by adding saturated aqueous sodium bicarbonate (5 mL), and extracted with ditheyl ether (8 mL×4). The combined organic layer was washed with water (10 mL) and brine (10 mL), and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo*, and the crude mixture was purified by MPLC (hexanes/EtOAc = 10:1, 7 mL/min, retention time 6 min) to afford enoate **15** (312 mg, 93%, *E/Z* >20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.17 (d, *J* = 15.7 Hz, 1H, ArC*H*=CHCO$_2$Me), 7.66 [dd, *J* = 7.4, 1.3 Hz, 1H, SiCC*H* or (MeO$_2$CCH=CH)CC*H*], 7.60 [dd, *J* = 7.4, 1.3 Hz, 1H, SiCC*H* or (MeO$_2$CCH=CH)CC*H*], 7.39 [ddd, *J* = 7.4, 7.4, 1.3 Hz, 1H, SiCCHC*H* or (MeO$_2$CCH=CH)CCHC*H*], 7.36 [ddd, *J* = 7.4, 7.4, 1.3 Hz, 1H, SiCCHC*H* or (MeO$_2$CCH=CH)CCHC*H*], 6.36 (d, *J* = 15.7 Hz, 1H, ArCH=C*H*CO$_2$Me), 3.81 (s, 3H, OC*H$_3$*), 0.98-0.91 [m, 6H, Si(CH$_2$C*H$_3$*)$_2$], 0.88-0.82 [m, 4H, Si(C*H$_2$*CH$_3$)$_2$] and 0.15 [s, 9H, Si(C*H$_3$*)$_3$].

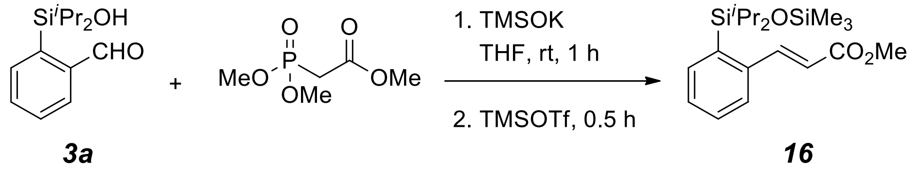
^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 146.2, 140.2, 139.5, 135.3, 129.8, 129.1, 126.2, 118.6, 51.8, 8.4, 7.0 and 2.1.

IR (neat): 3055 (w), 2954 (w), 2877 (w), 1720 (m), 1052 (s), 836 (s), and 719 (m) cm^{-1}.

TLC: R_f = 0.4 in 10:1 hexanes: EtOAc.

HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{17}H_{28}NaO_3Si_2)^+$: 359.1469. Found: 359.1482.

(*E*)-Methyl 3-(2-(1,1-diisopropyl-3,3,3-trimethyldisiloxanyl)phenyl)acrylate (16)



The procedure for the preparation of **16** is the same as one of **15**. The crude reaction mixture was purified by MPLC (hexanes/EtOAc = 20:1, 7 mL/min, retention time 5 min) to afford product **16** (298 mg, 82%, *E/Z* >20:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.07 (d, *J* = 15.7 Hz, 1H, ArC*H*=CHCO$_2$Me), 7.66 [dd, *J* = 7.4, 1.3 Hz, 1H, SiCC*H* or (MeO$_2$CCH=CH)CC*H*], 7.62 [dd, *J* = 7.4, 1.3 Hz, 1H, SiCC*H* or (MeO$_2$CCH=CH)CC*H*], 7.38 [ddd, *J* = 7.4, 7.4, 1.3 Hz, 1H, SiCCHC*H* or (MeO$_2$CCH=CH)CCHC*H*], 7.36 [ddd, *J* = 7.4, 7.4, 1.3 Hz, 1H, SiCCHC*H* or (MeO$_2$CCH=CH)CCHC*H*], 6.36 (d, *J* = 15.7 Hz, 1H, ArCH=C*H*CO$_2$Me), 3.80 (s, 3H, OC*H$_3$*), 1.25 [septet, 2H, *J* = 7.4 Hz, C*H*(CH$_3$)$_2$], 1.05 [d, *J* = 7.4 Hz, 6H, CH(C*H$_3$*)$_2$], and 0.92 [d, *J* = 7.4 Hz, 6H, CH(C*H$_3$*)$_2$].

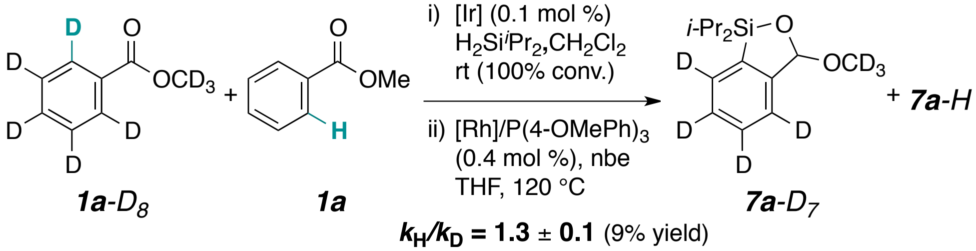
^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 146.9, 140.3, 138.8, 136.0, 129.5, 128.9 126.2, 118.4, 51.8, 17.709, 17.689, 14.5 and 2.4.

IR (neat): 3057 (w), 2944 (w), 2877 (w), 1721 (m), 1048 (s), 838 (s), and 714 (m) cm^{-1}.

TLC: R_f = 0.4 in 20:1 hexanes: EtOAc.

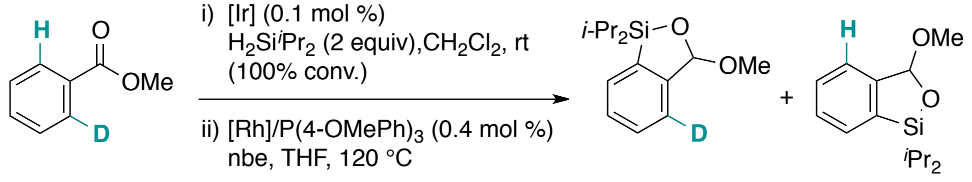
HRMS (ESI/TOF): Calcd for $(M+Na)^+$ $(C_{19}H_{32}NaO_3Si_2)^+$: 387.1782. Found: 387.1798.

Procedure for intermolecular KIE:



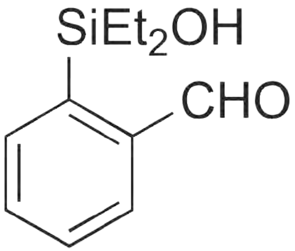
$[Ir(coe)_2Cl]_2$ (0.45 mg, 0.1 mol %), ester **1a** (0.25 mmol, 31.5 uL) and ester **1a**-D_8 (0.25 mmol, 30.5 uL) were dissolved with CH_2Cl_2 (0.2 mL, 2.5 M). Diisopropylsilane (0.2 mL, 1 mmol) was added to the mixture in one portion. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was kept at 45 °C and stirred for 24 h. The volatiles were removed *in vacuo* to afford the silyl acetals, which were directly used for subsequent reaction without further purification. $[Rh(nbd)Cl]_2$ (1 mg, 0.4 mol %), *tris*(4-methoxyphenyl)phosphine (4.2 mg, 2.4 mol %) and norbornene (94 mg, 1 mmol) were dissolved with THF (0.5 mL, 1 M), the previous prepared silyl acetals mixture (0.5 mmol) was added to the mixture in one portion. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 120 °C for 50 s. The yield of the cyclic silyl acetals (9%) was determined by ^{1}H NMR spectroscopy by an addition of CH_2Br_2 (0.5 mmol) as an internal standard after the volatiles were removed *in vacuo*. The crude mixture was purified by MPLC (hexanes/EtOAc = 40:1, 7 mL/min, retention time 7 min) to provide **7a**-D_7 and **7a**-H as a colorless liquid. The isolated cyclic silyl acetal products were analyzed by ^{1}H NMR using $CDCl_3$ as solvent and 20s relaxation delay on a 500 MHz NMR spectrometer. The reactions were run 6 times, the average KIE was **1.3** ± **0.1**.

Procedure for intramolecular KIE:

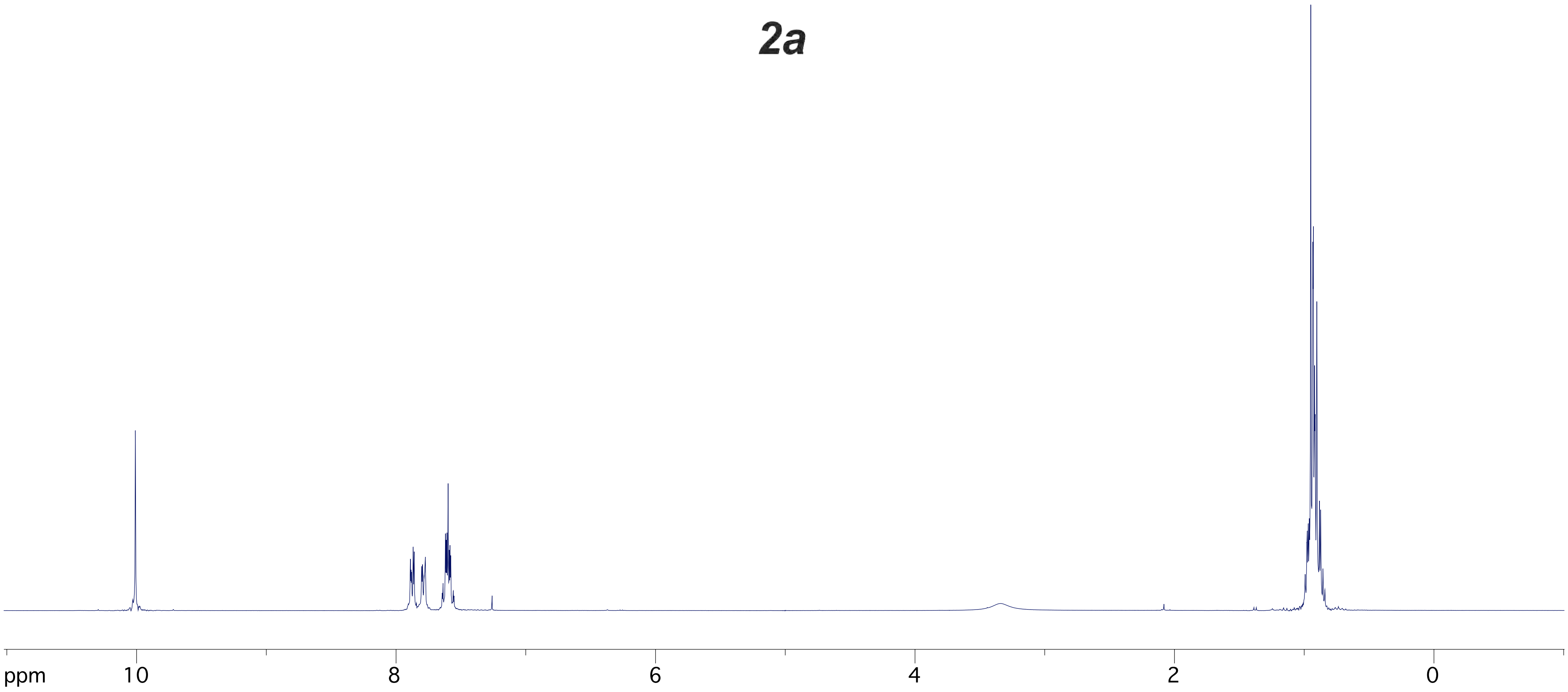


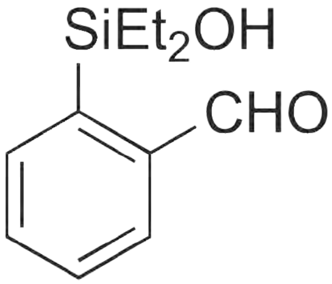
***1a**-D* **k_H/k_D = 2.1 ± 0.1** ***7a**-D_1* (68%) ***7a**-H* (32%)

$[Ir(coe)_2Cl]_2$ (0.23 mg, 0.1 mol %) and ester **1a**-D (0.25 mmol, 34.2 mg) were dissolved with CH_2Cl_2 (0.1 mL, 2.5 M). Diisopropylsilane (0.1 mL, 0.5 mmol) was added to the mixture in one portion. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was kept at 45 °C and stirred for 24 h. The volatiles were removed *in vacuo* to afford the silyl acetals, which were directly used for subsequent reaction without further purification. $[Rh(nbd)Cl]_2$ (0.5 mg, 0.4 mol %), *tris*(4-methoxyphenyl)phosphine (2.1 mg, 2.4 mol %) and norbornene (47 mg, 0.5 mmol) were dissolved with THF (0.5 mL, 1 M), the silyl acetals mixture (0.25 mmol) was added to the mixture in one portion. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 120 °C for 1h. The yield of the cyclic silyl acetals was determined by ^{1}H NMR spectroscopy by an addition of CH_2Br_2 (0.25 mmol) as an internal standard after the volatiles were removed *in vacuo*. The crude mixture was purified by MPLC (hexanes/EtOAc = 40:1, 7 mL/min, retention time 7 min) to provide **7a**-D_1 and **7a**-H as a colorless liquid. The conditions for ^{1}H NMR are: 500 MHz NMR; $CDCl_3$ as solvent; 20s relaxation delay. The reactions were run 3 times, the average KIE was **2.1** ± **0.1**.

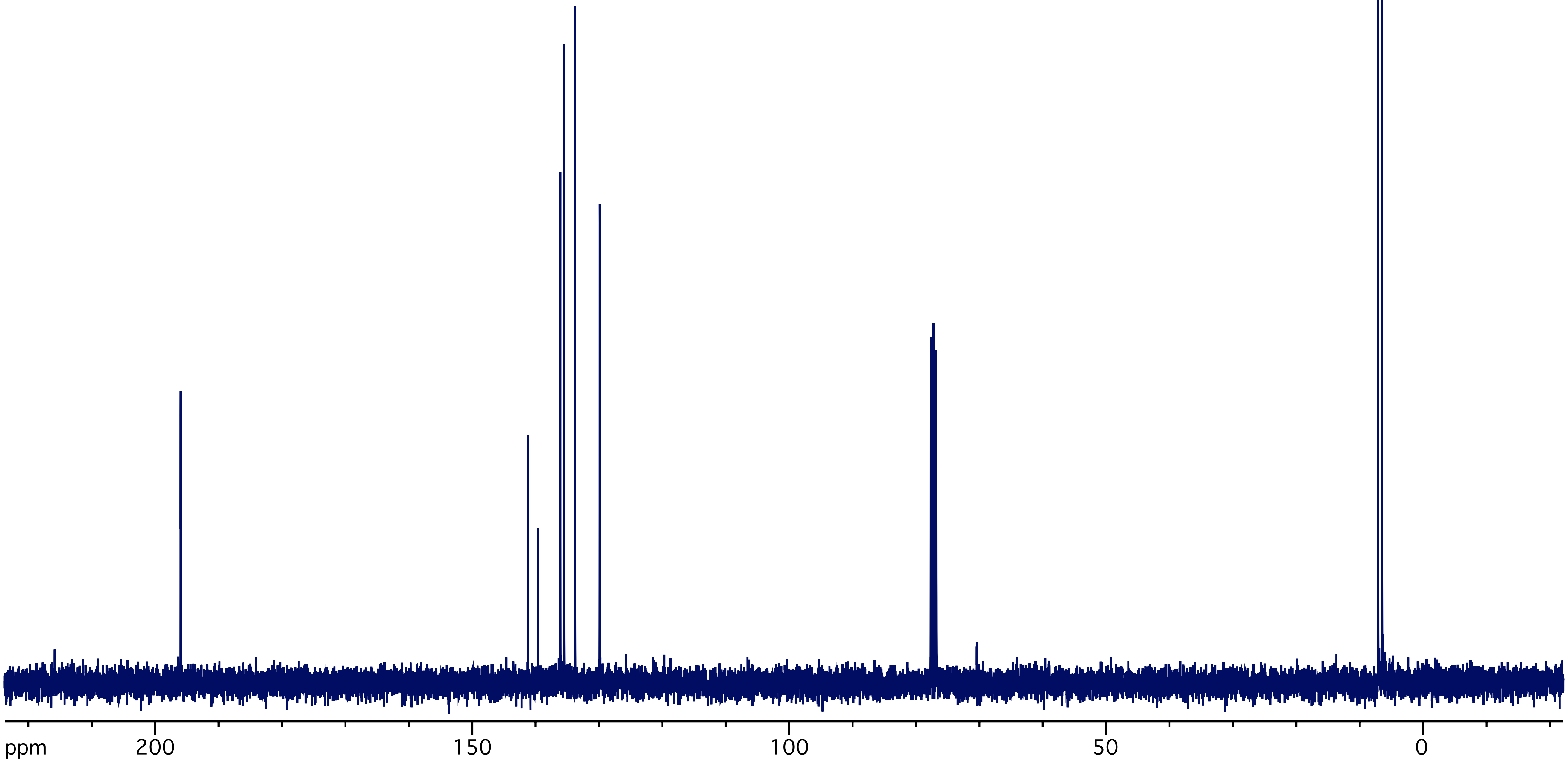


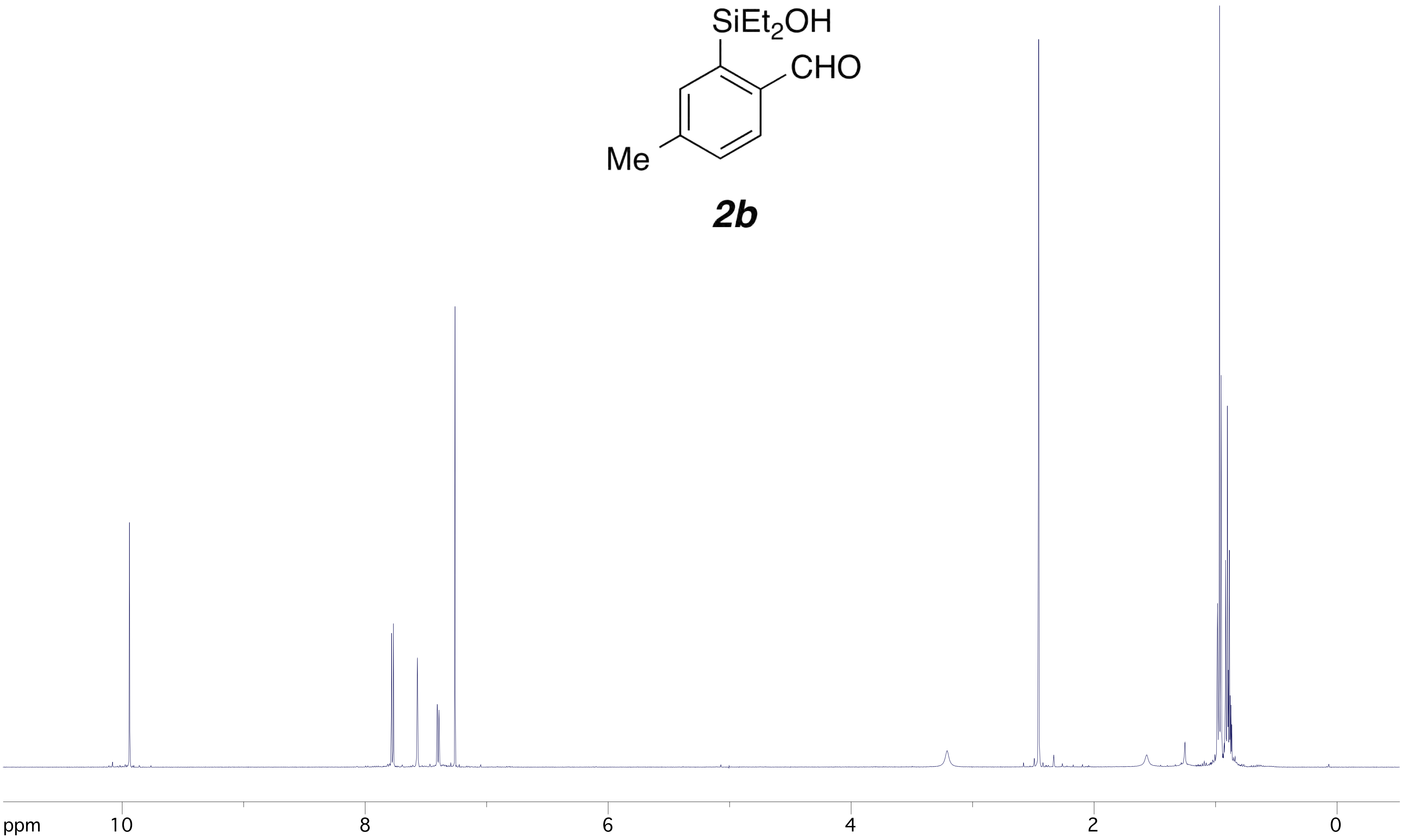
2a



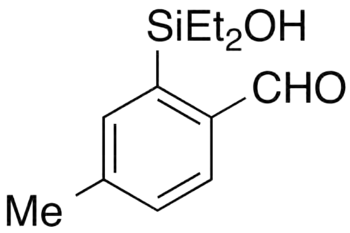


2a





2b



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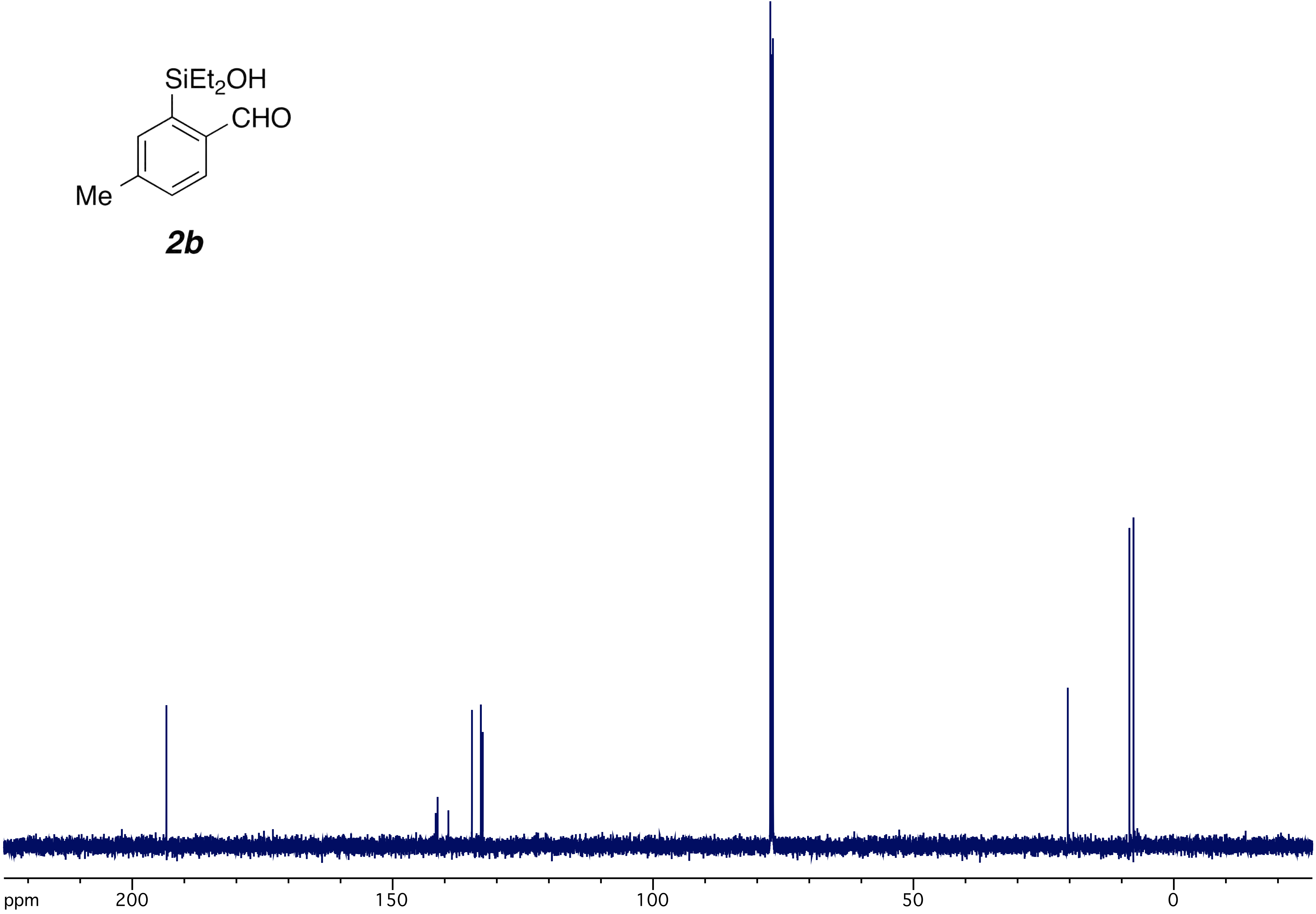

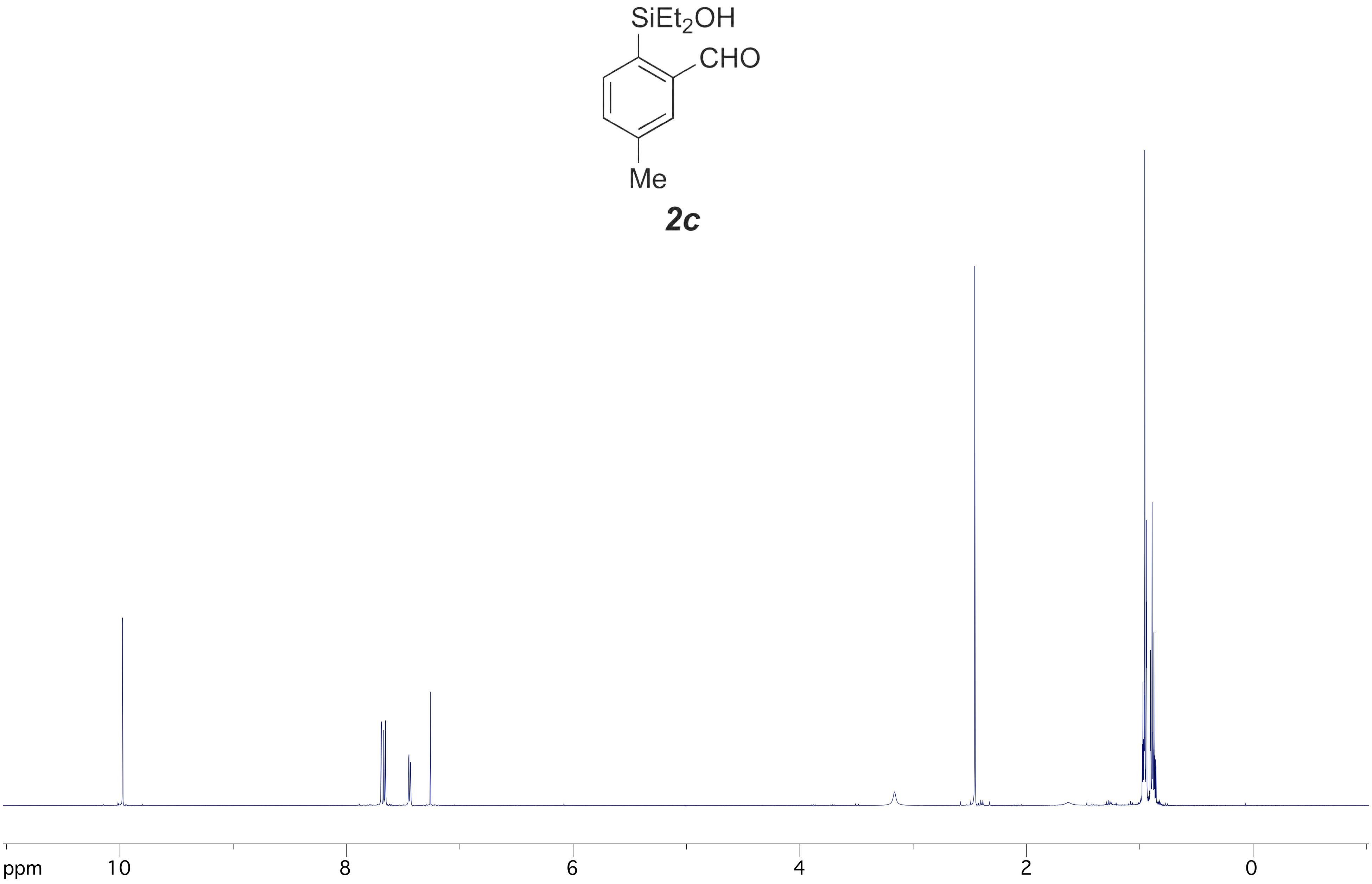

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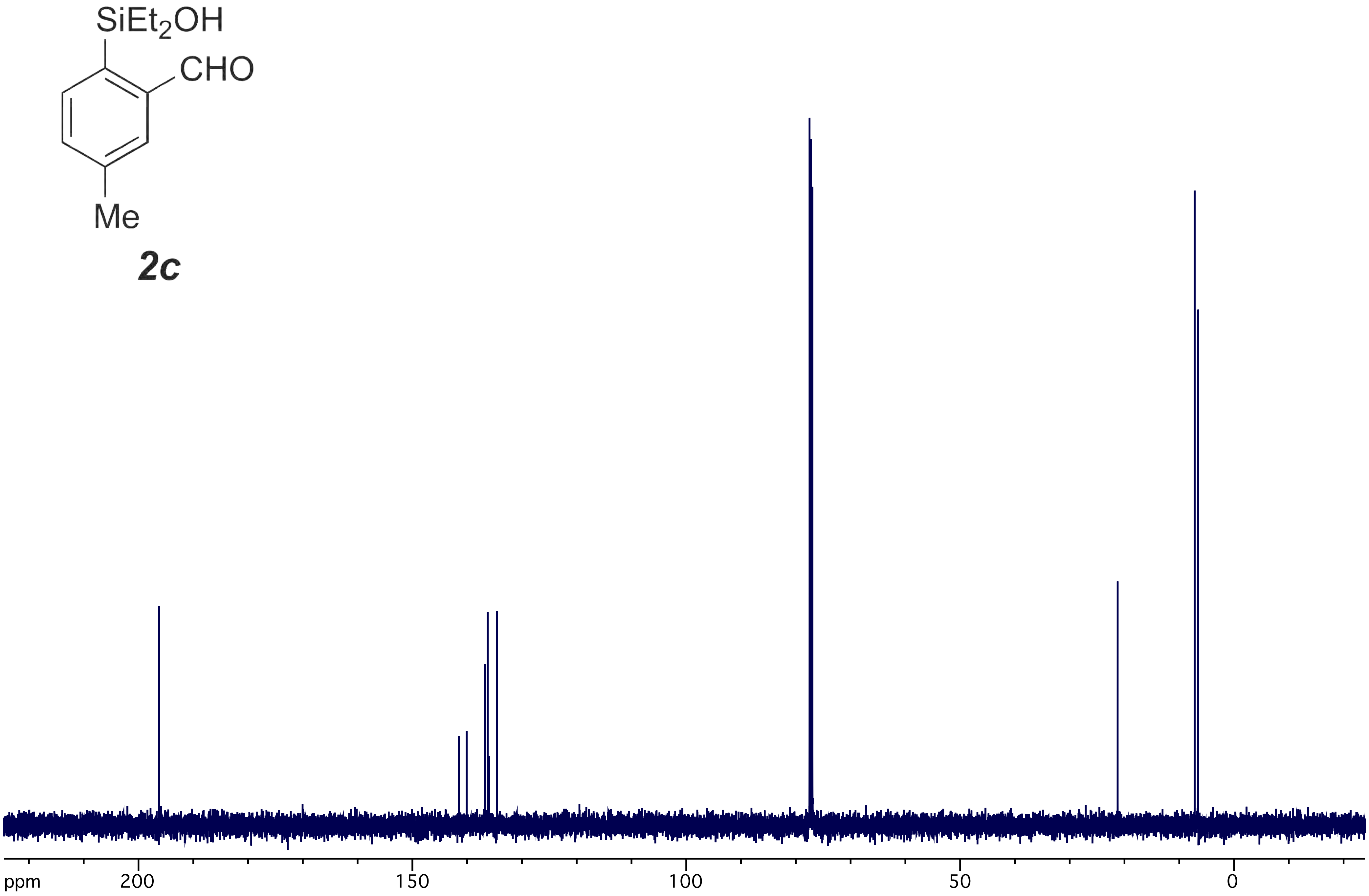

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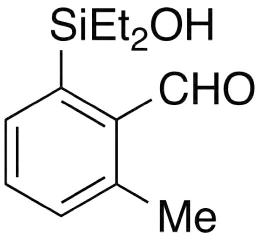

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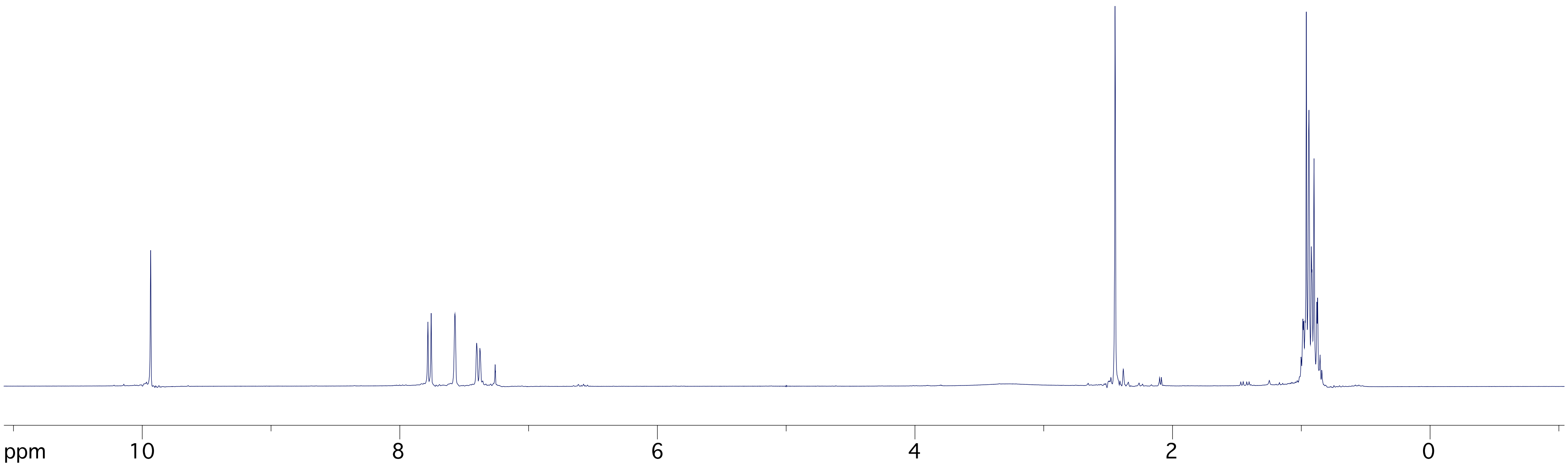

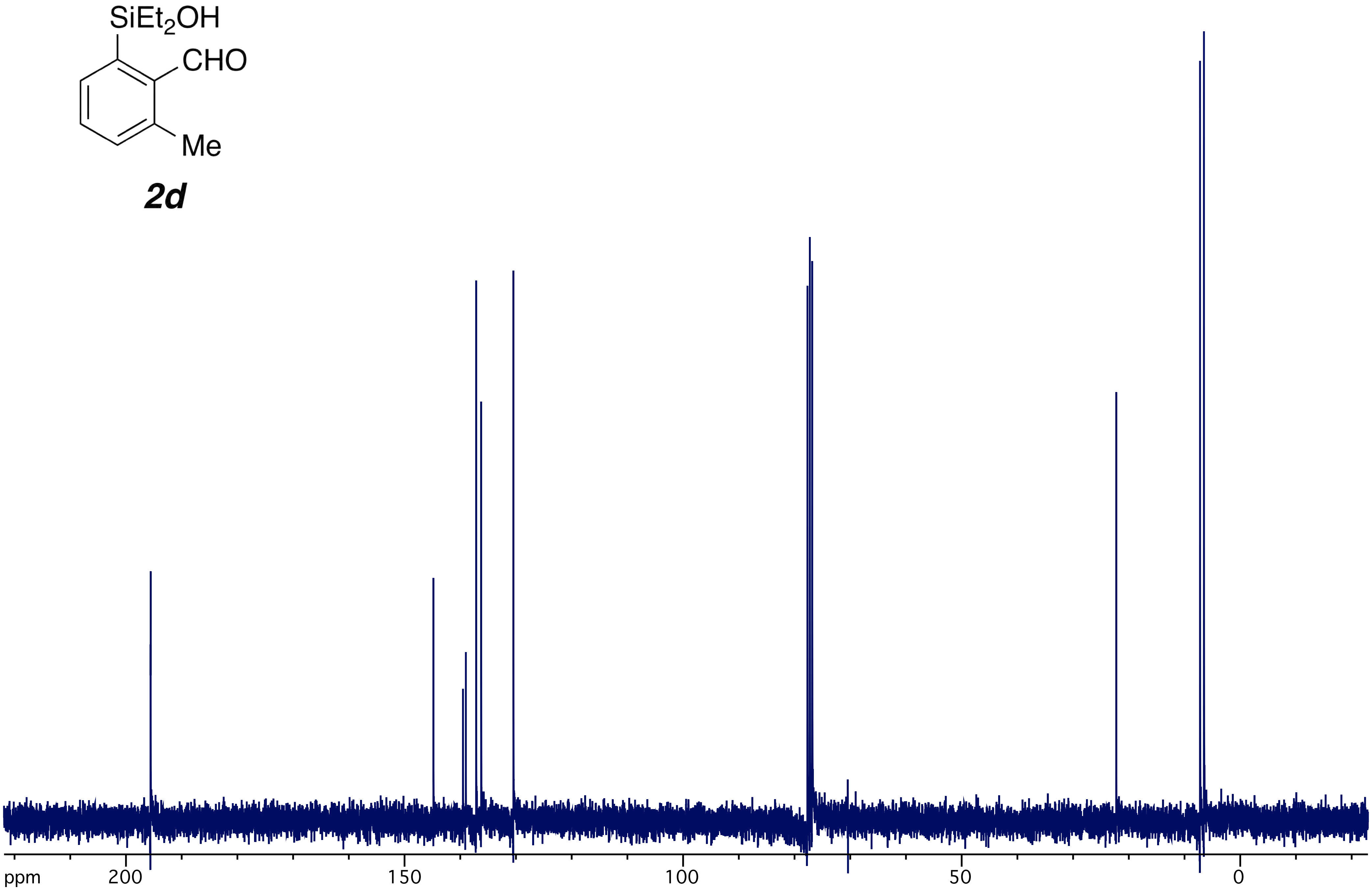

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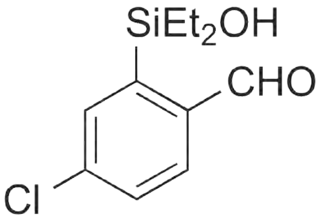

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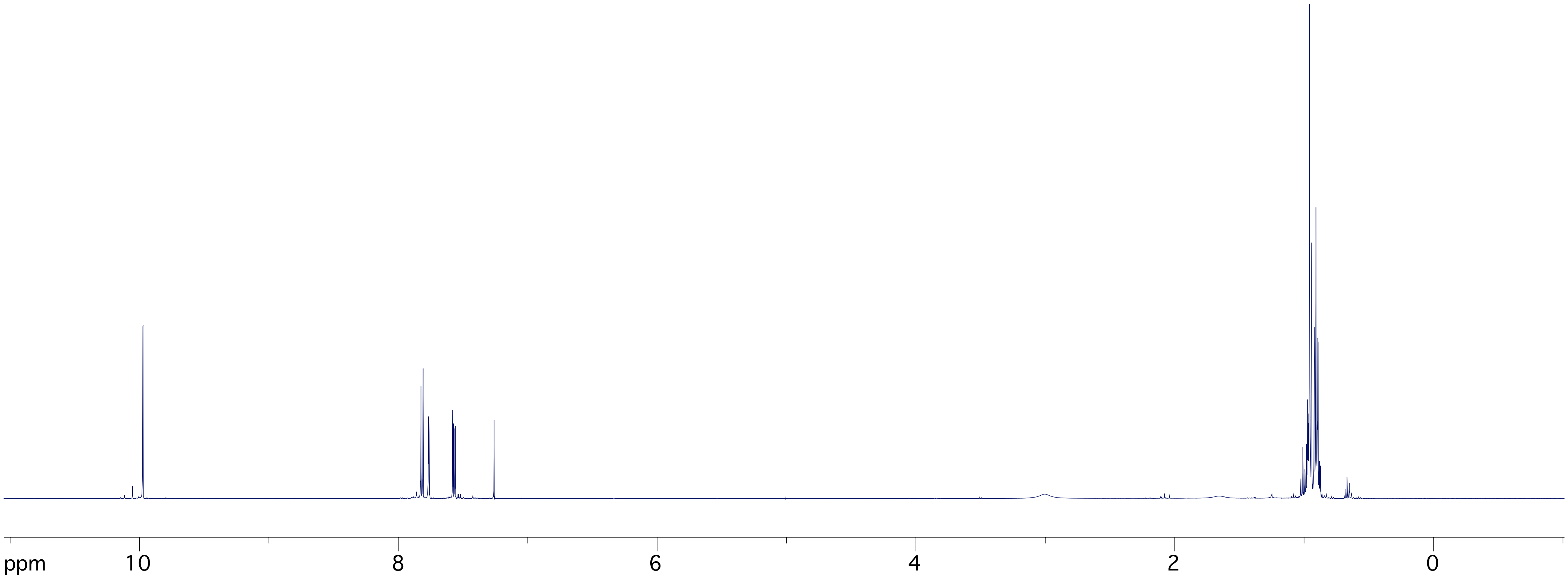

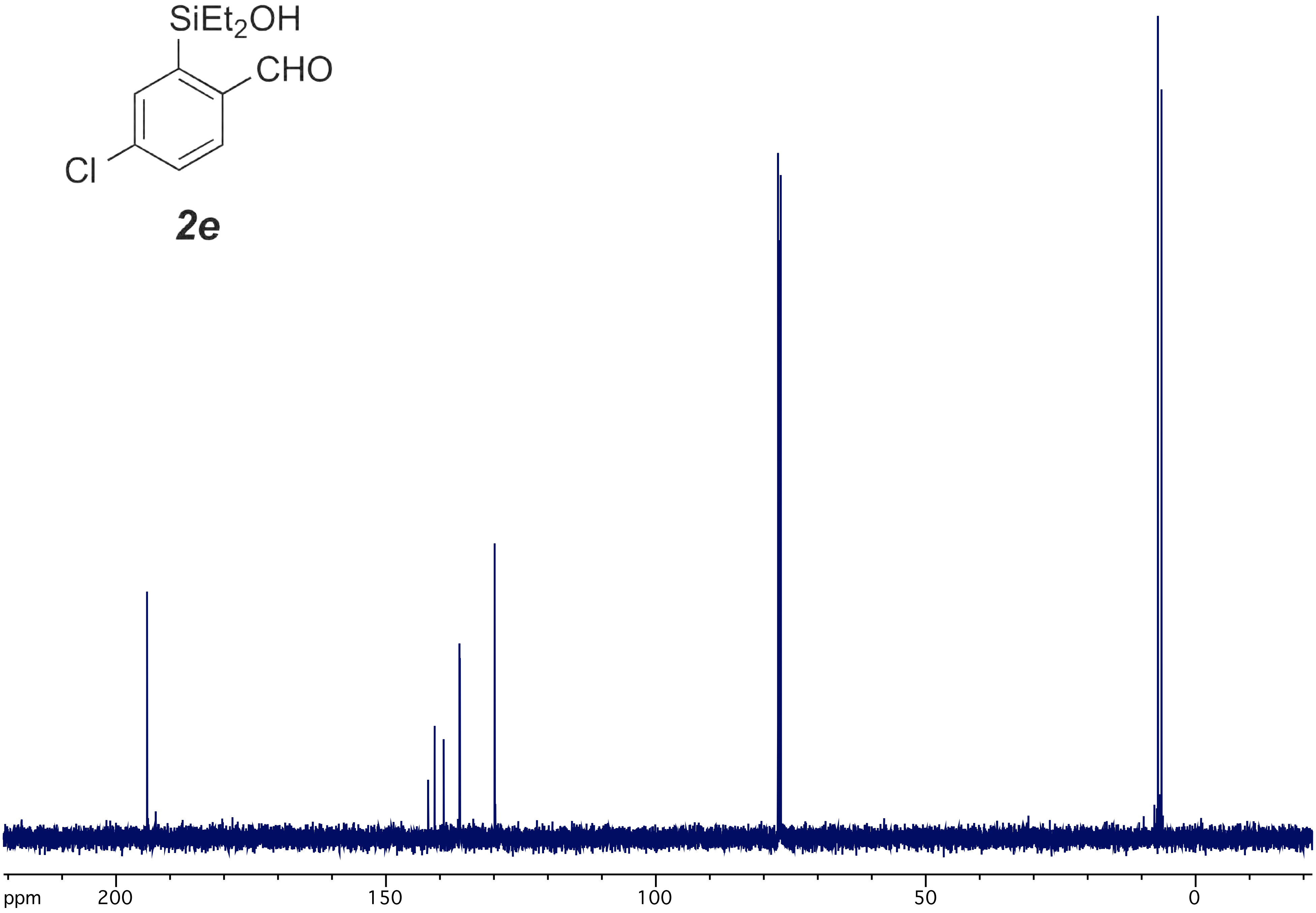

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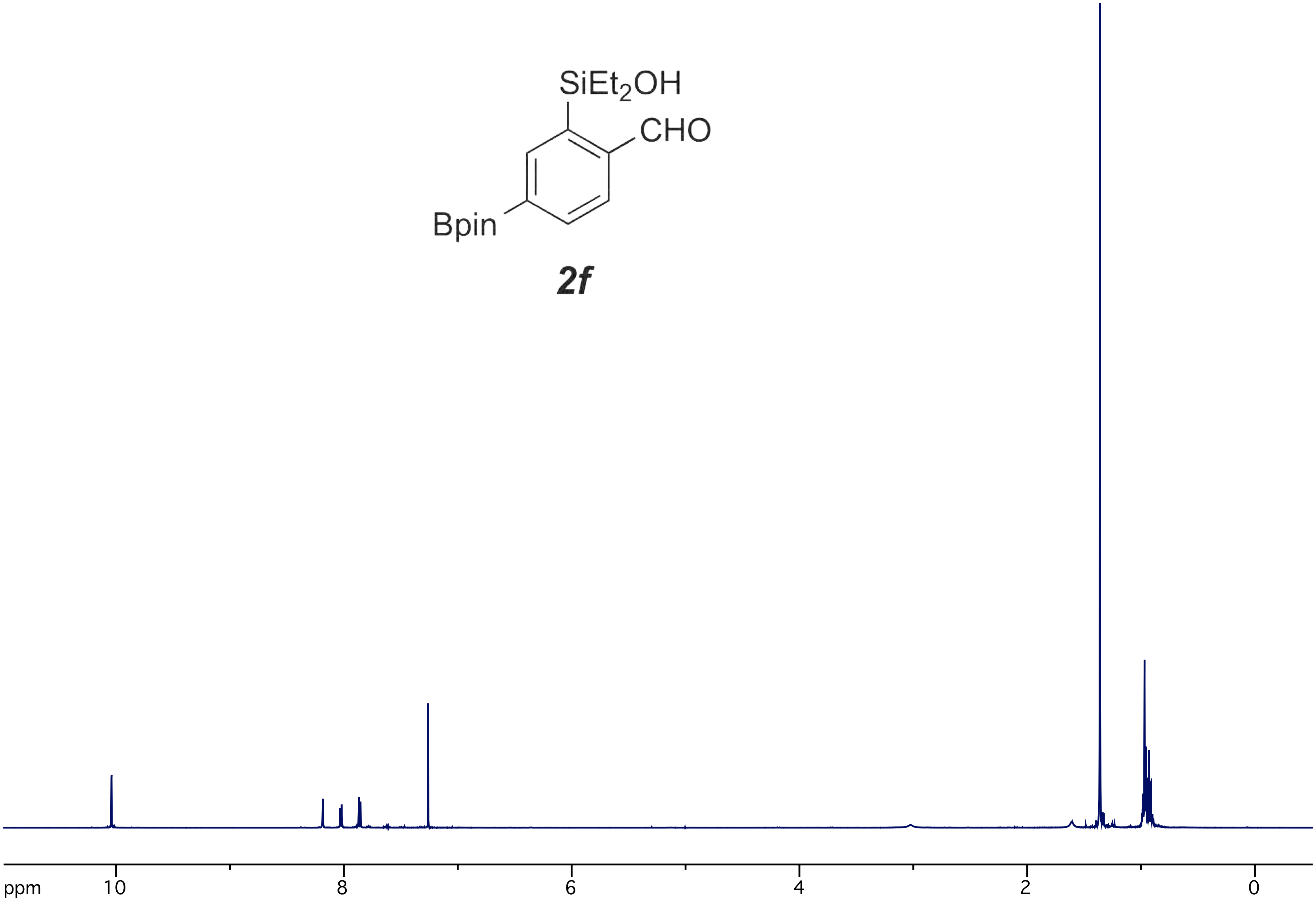

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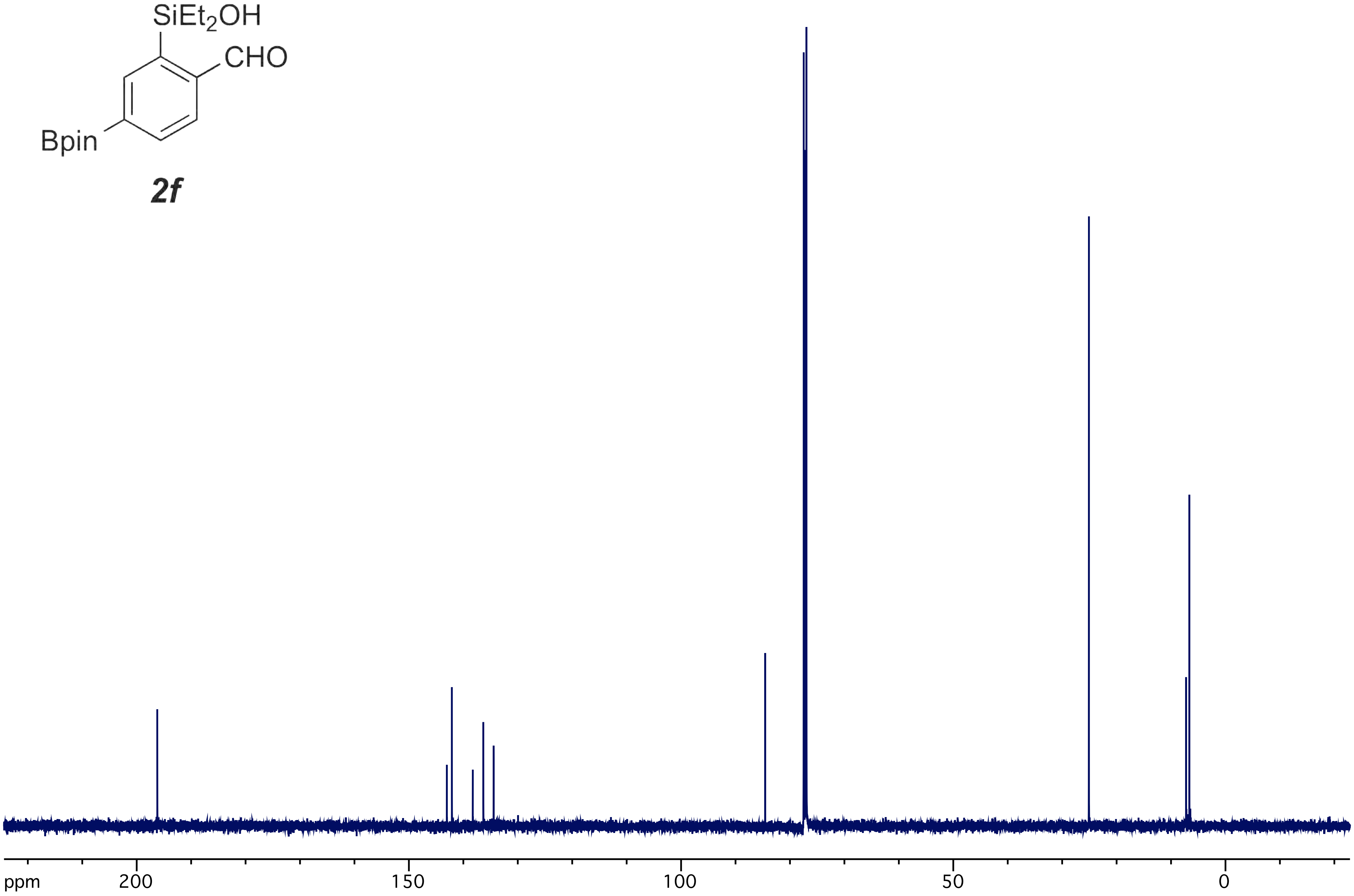

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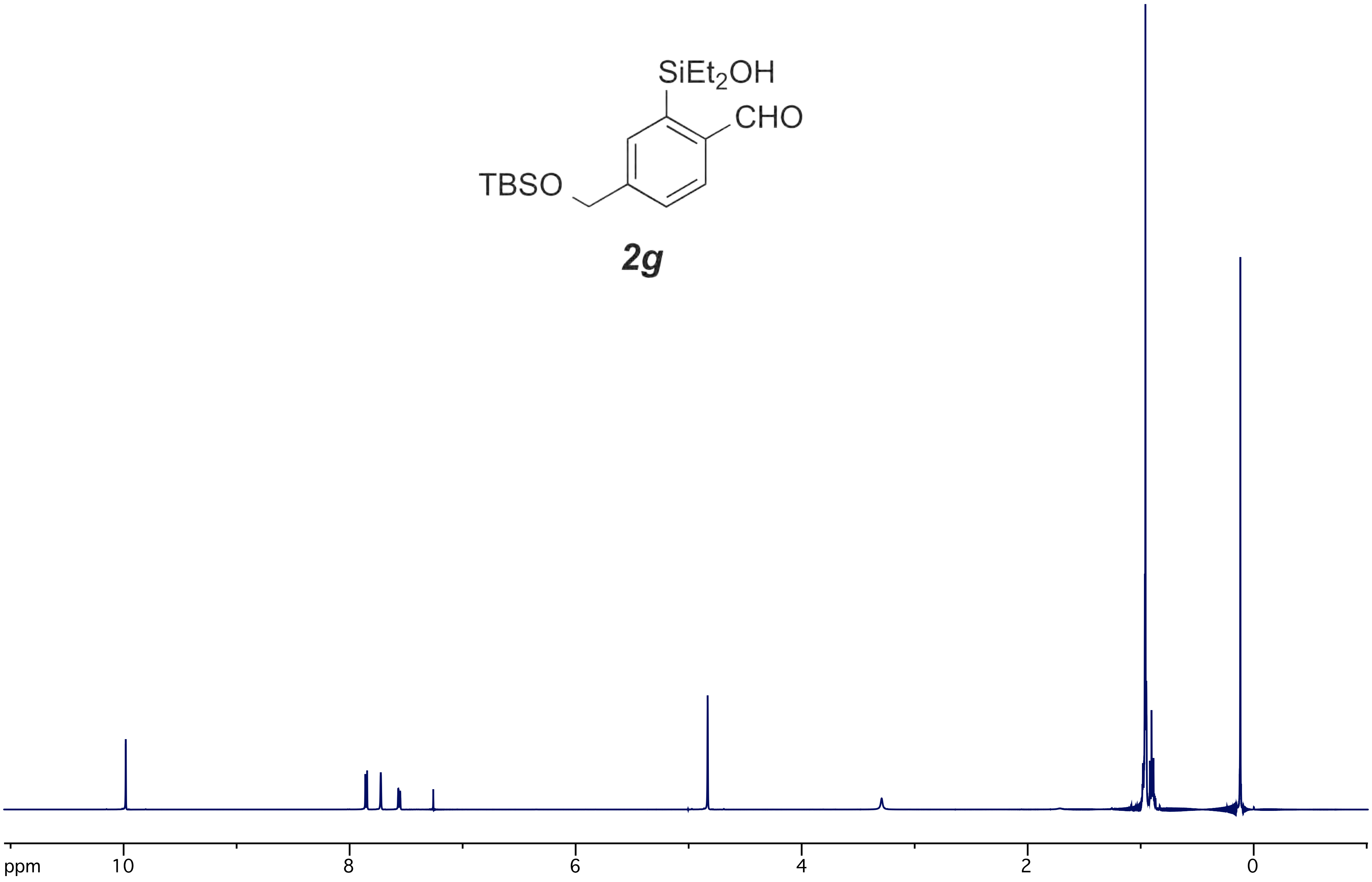
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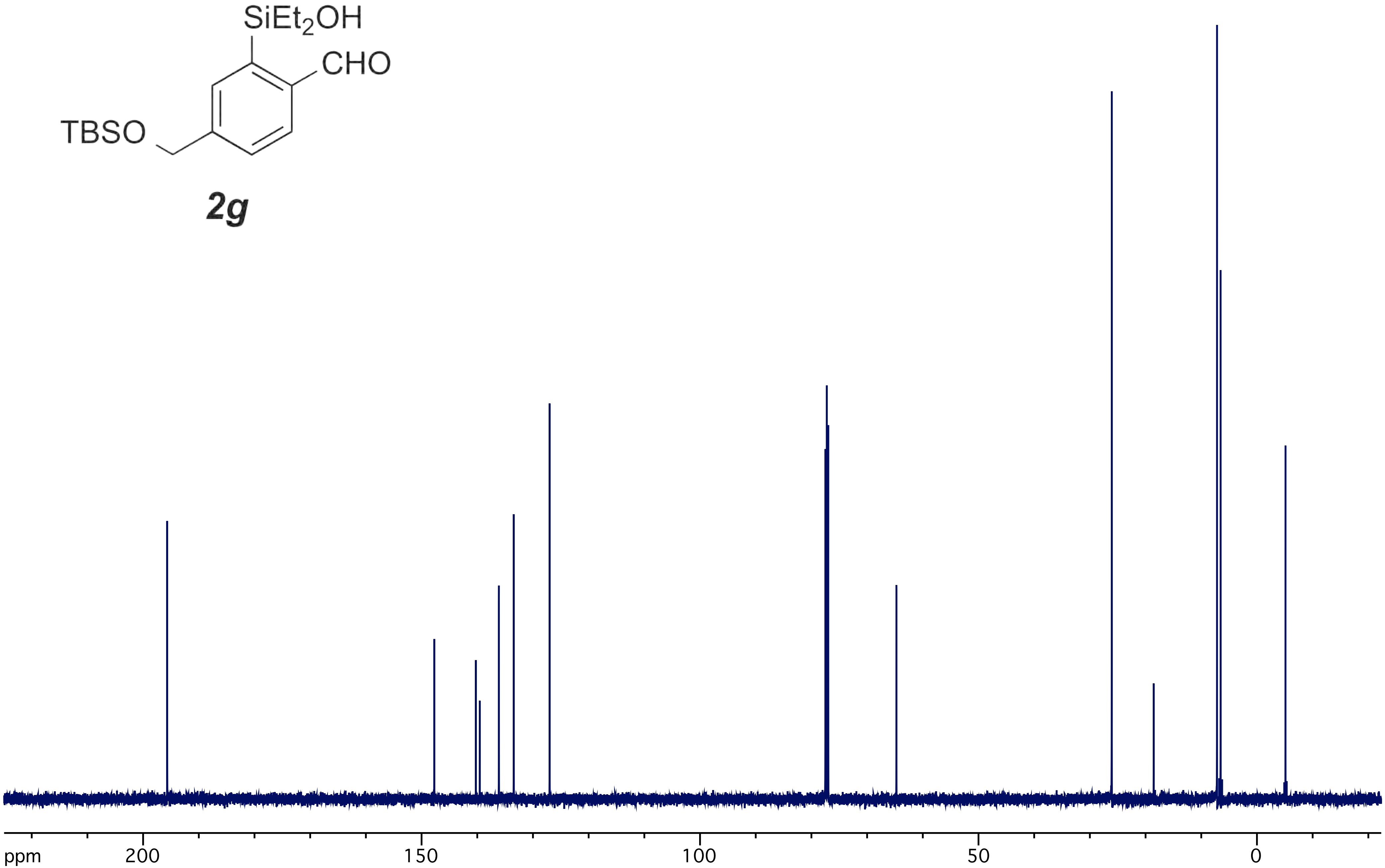

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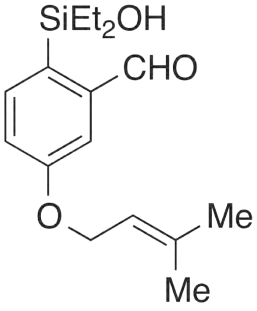

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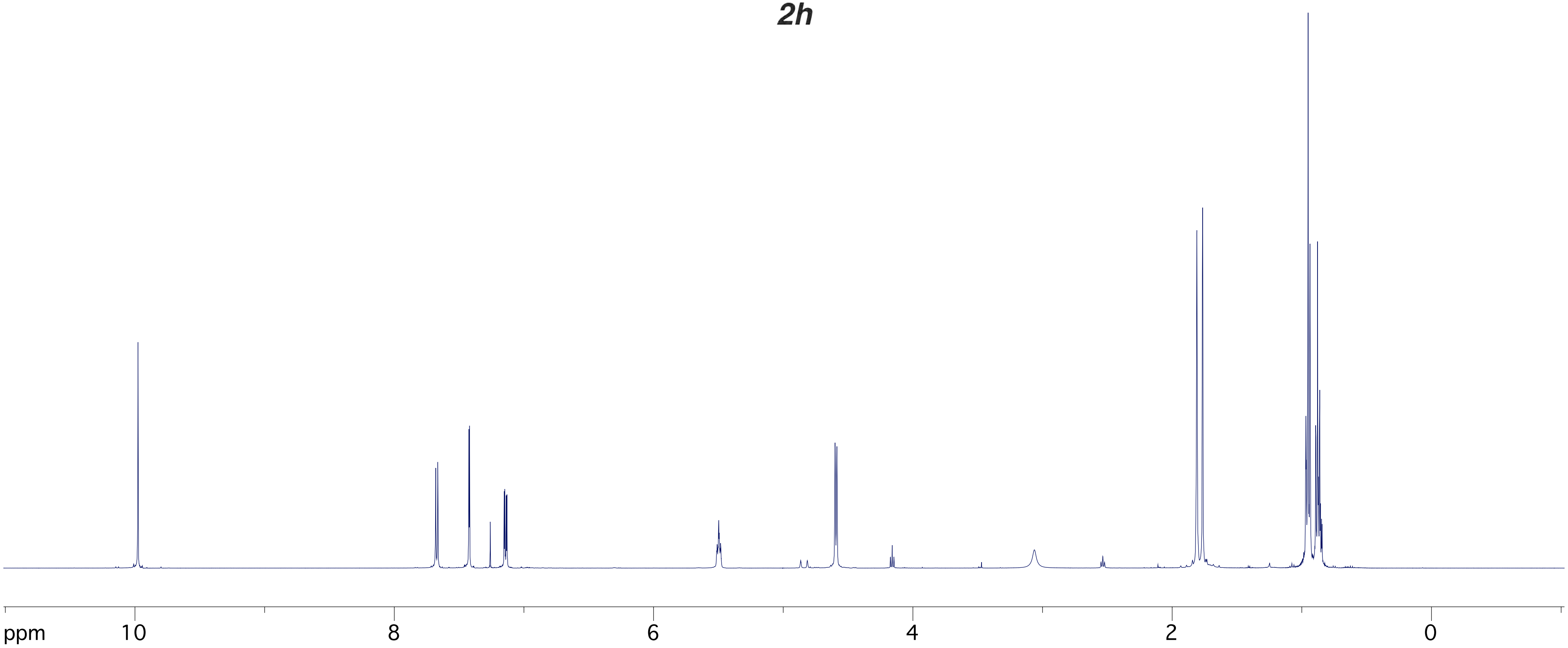

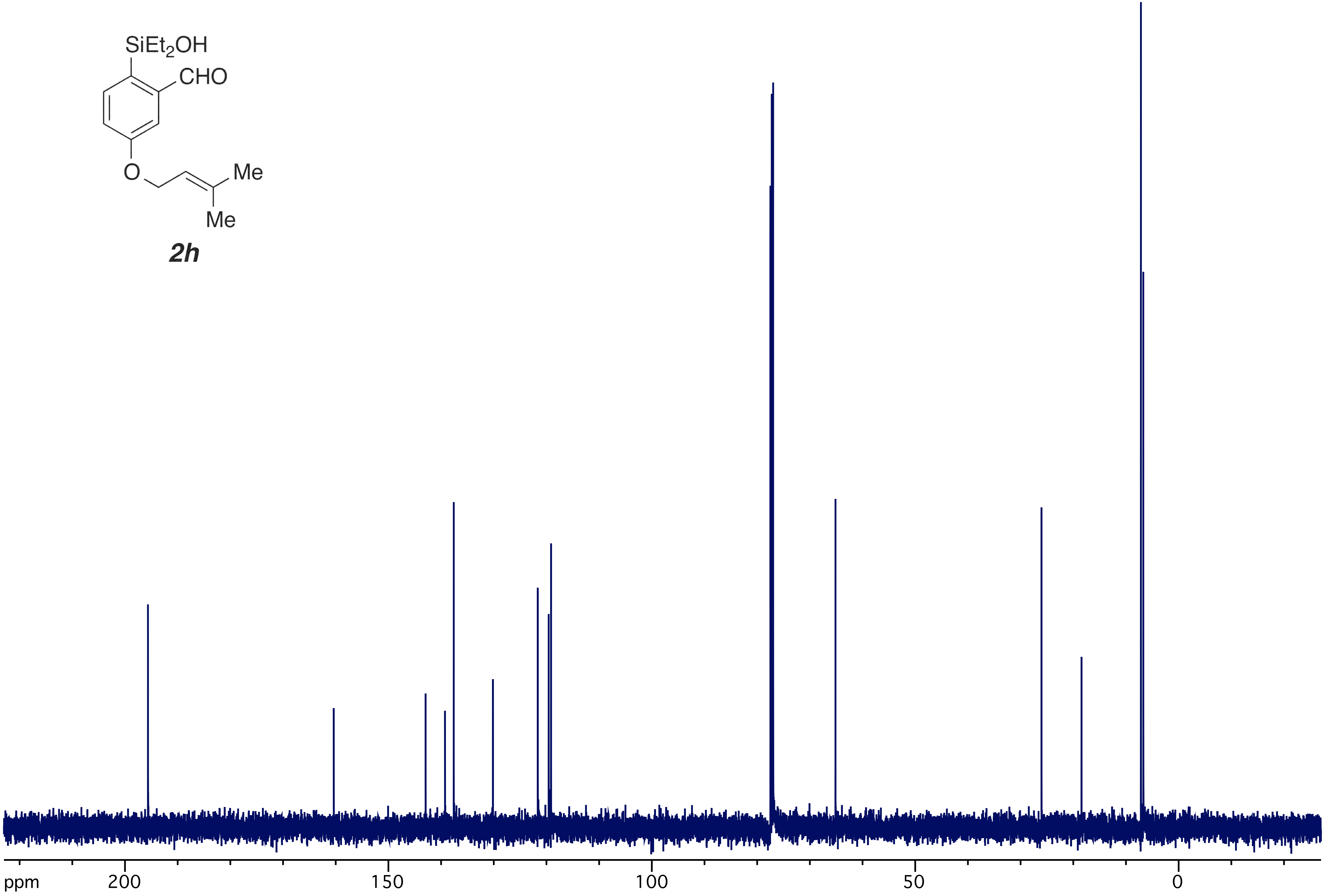

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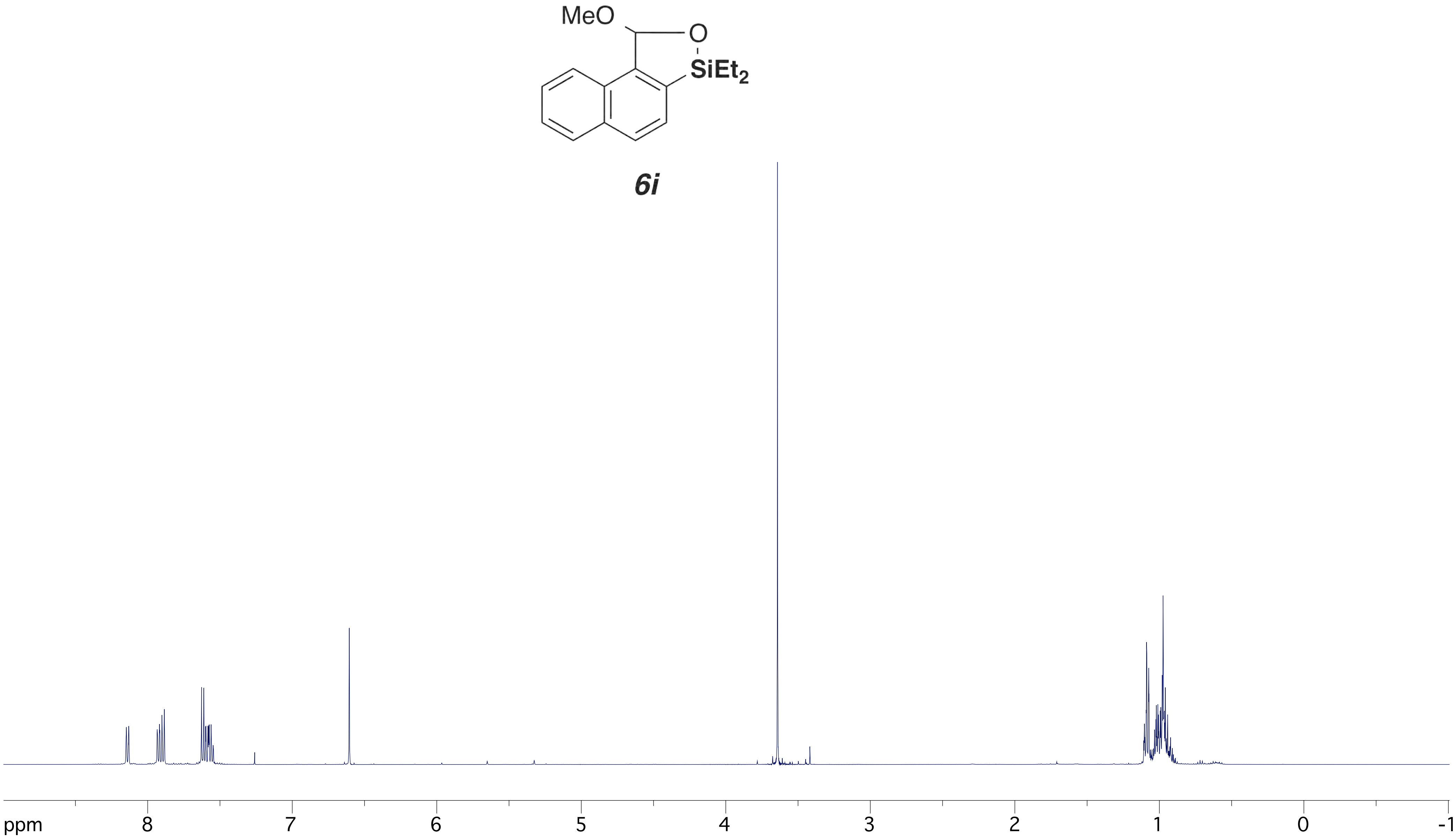

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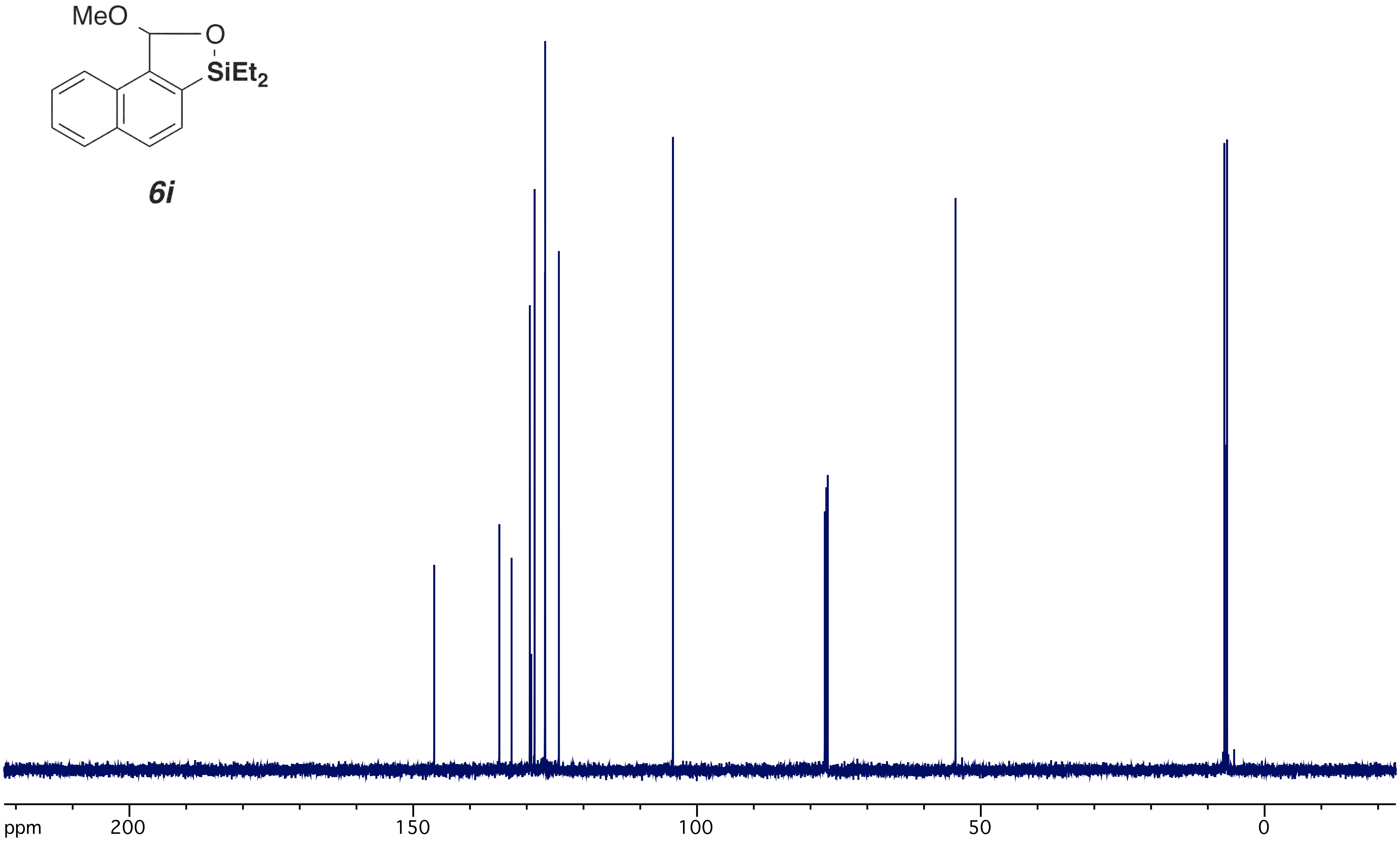

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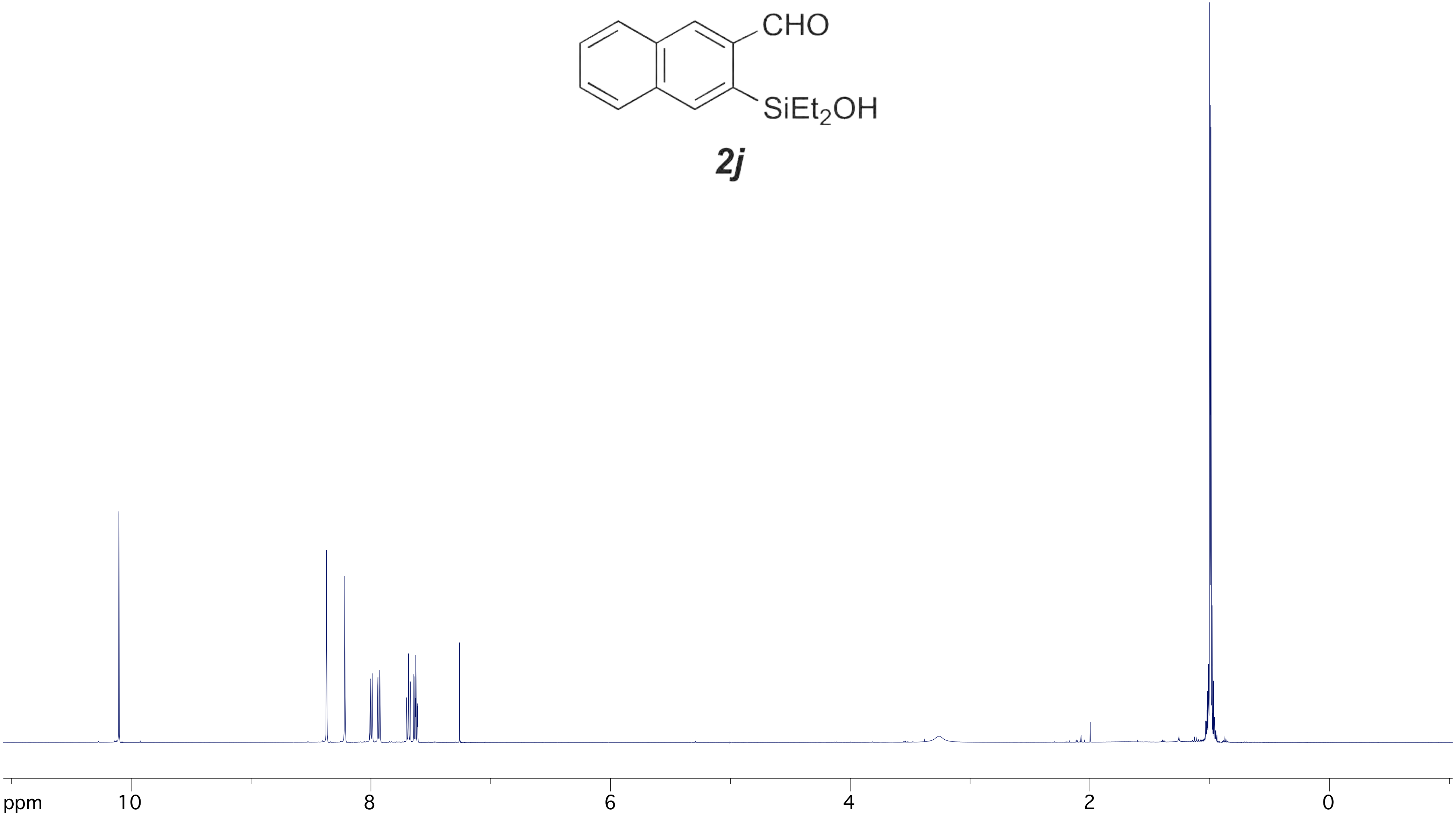

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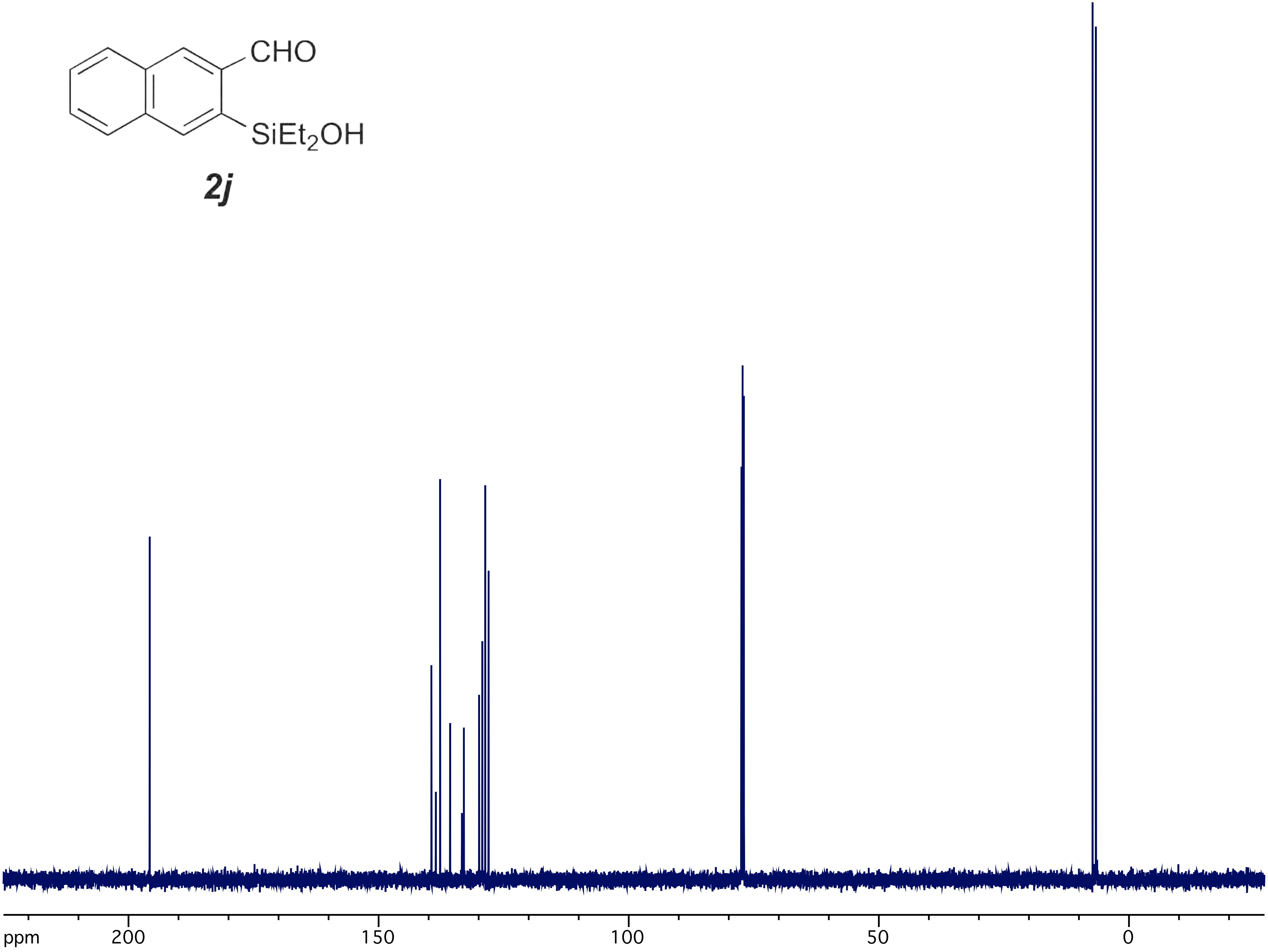

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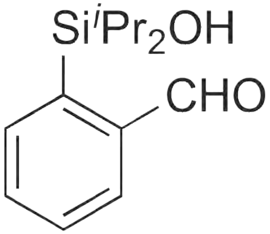

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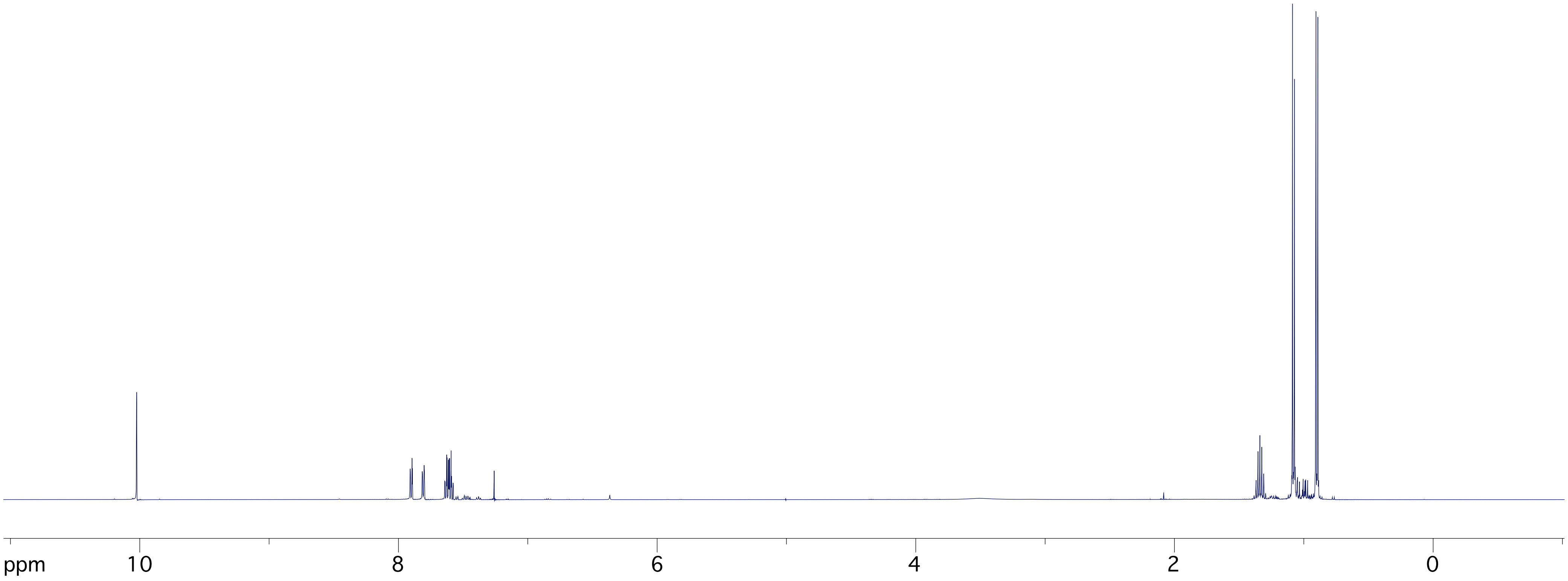

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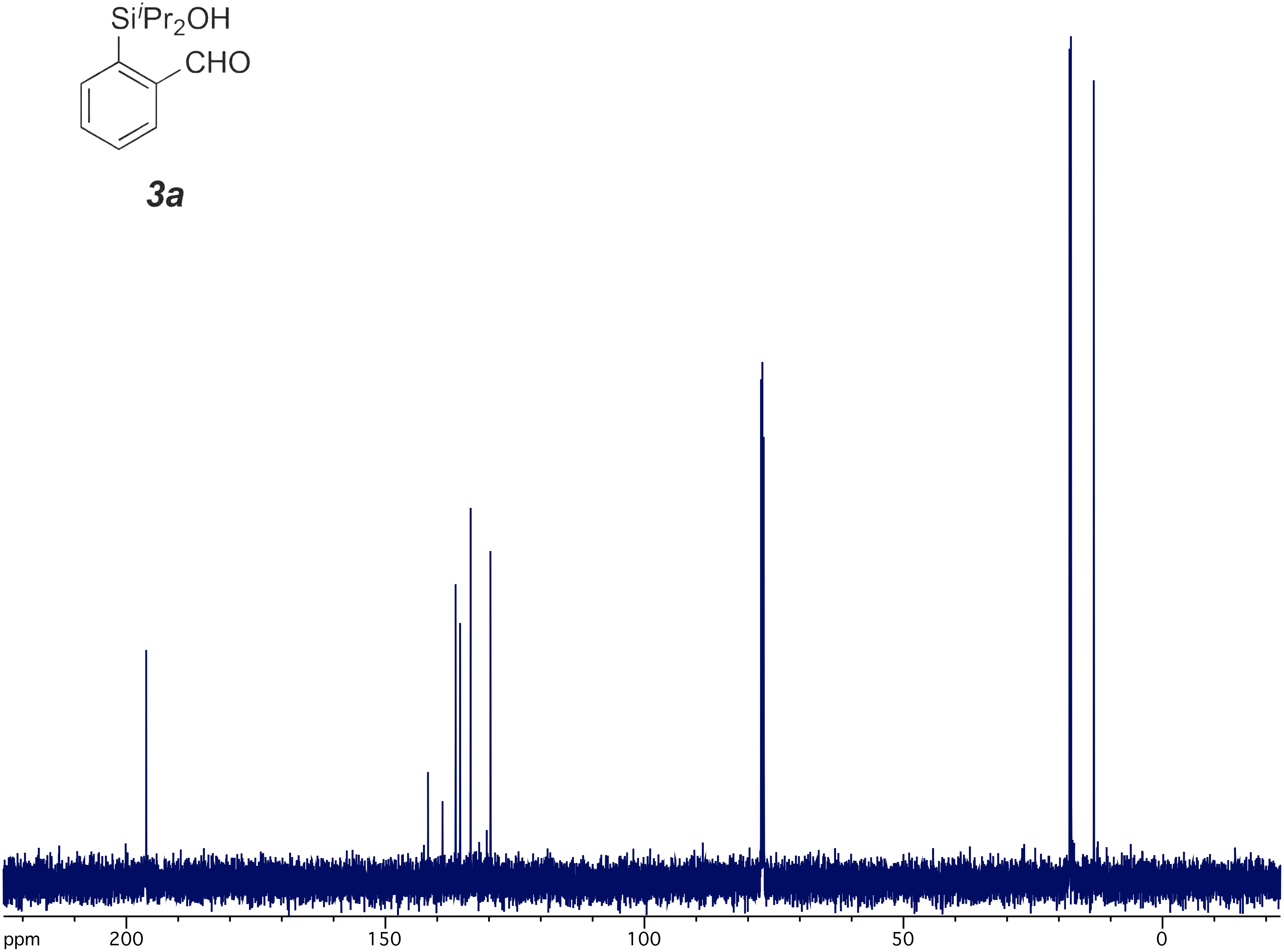

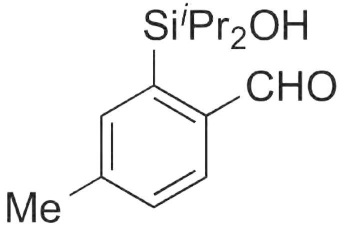

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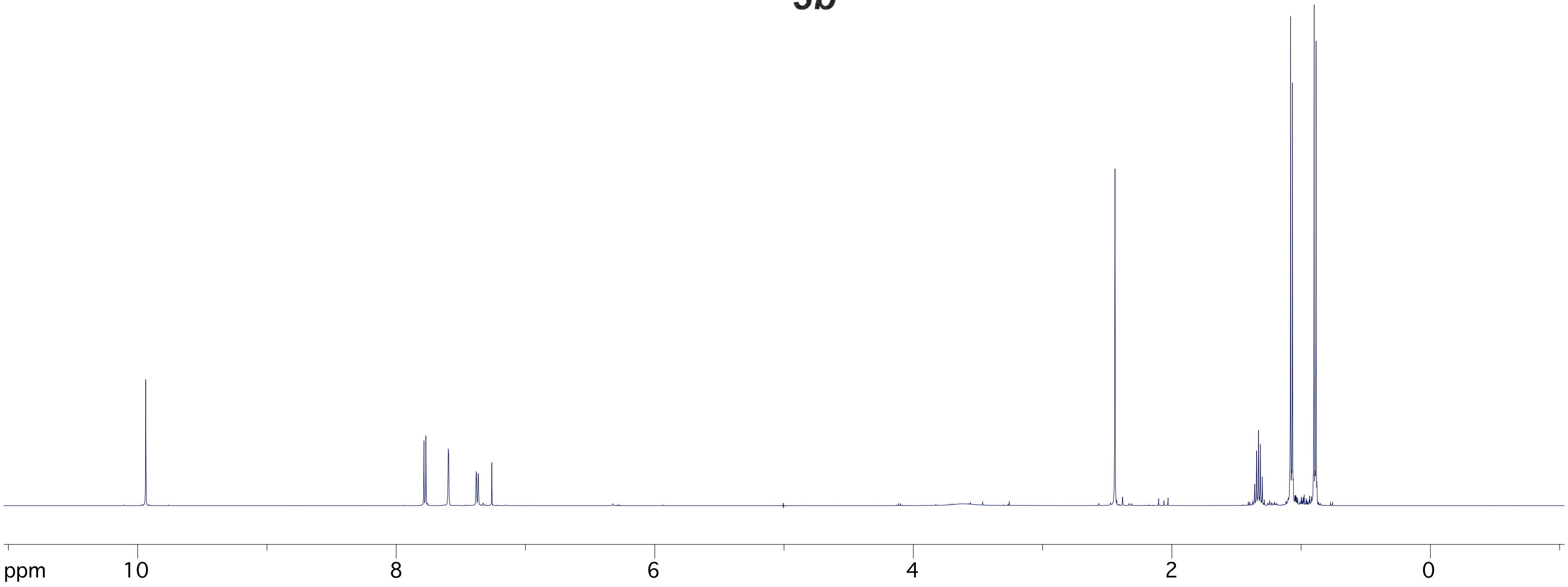

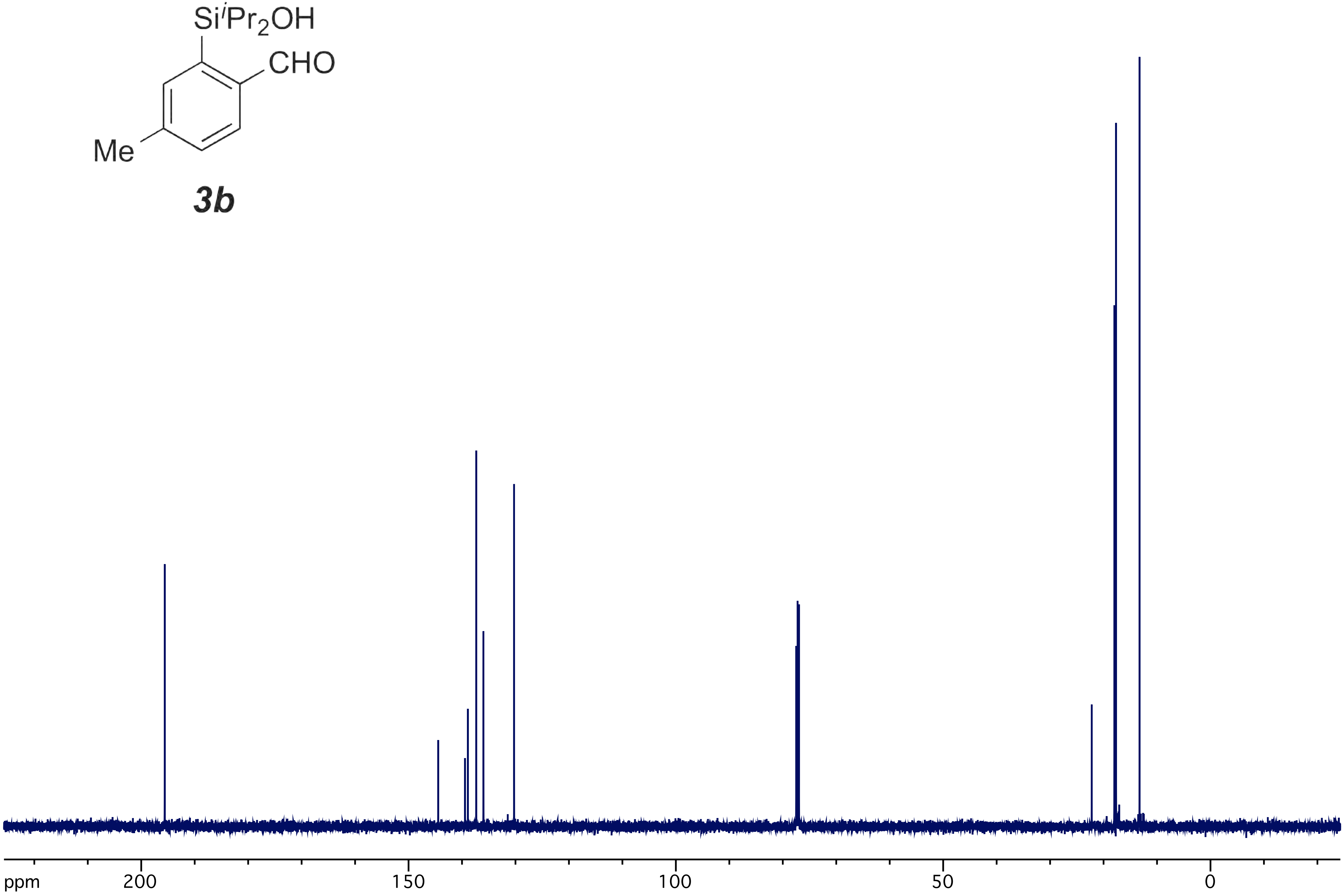

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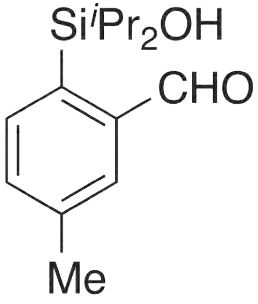

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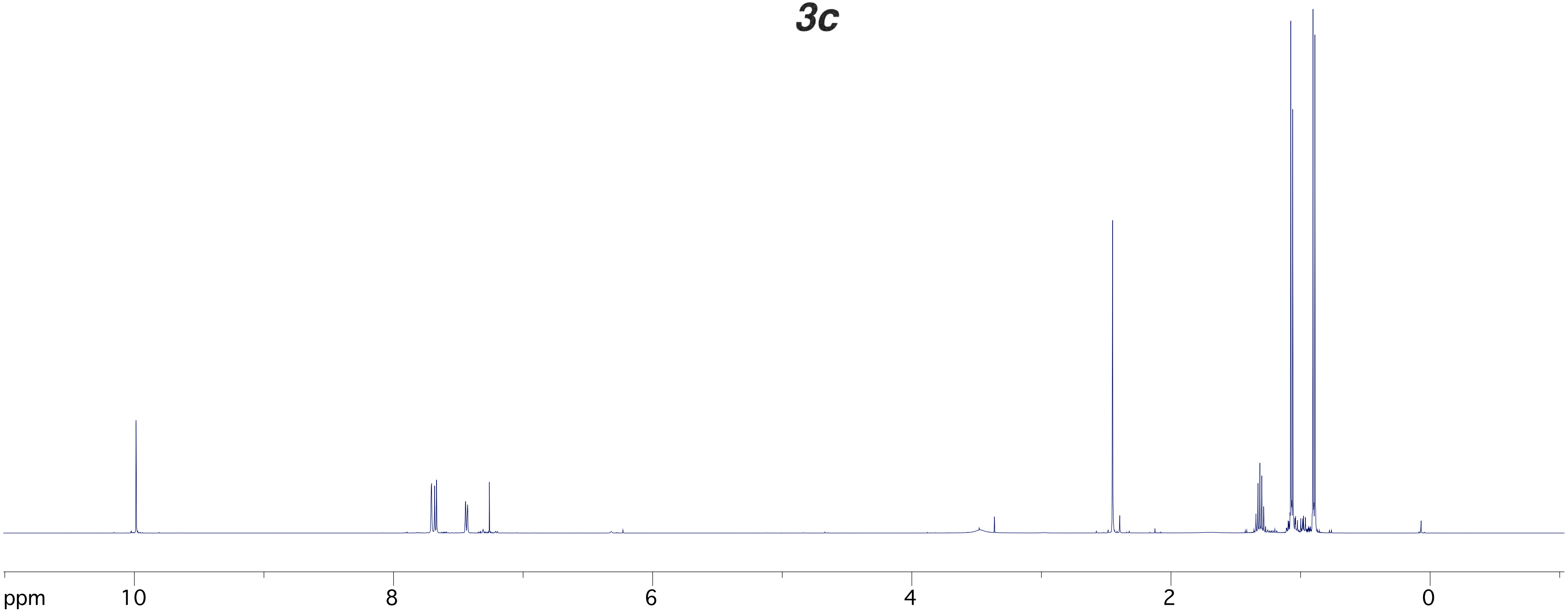

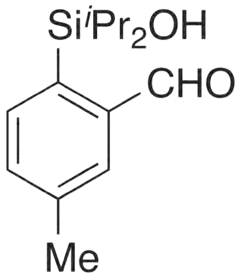

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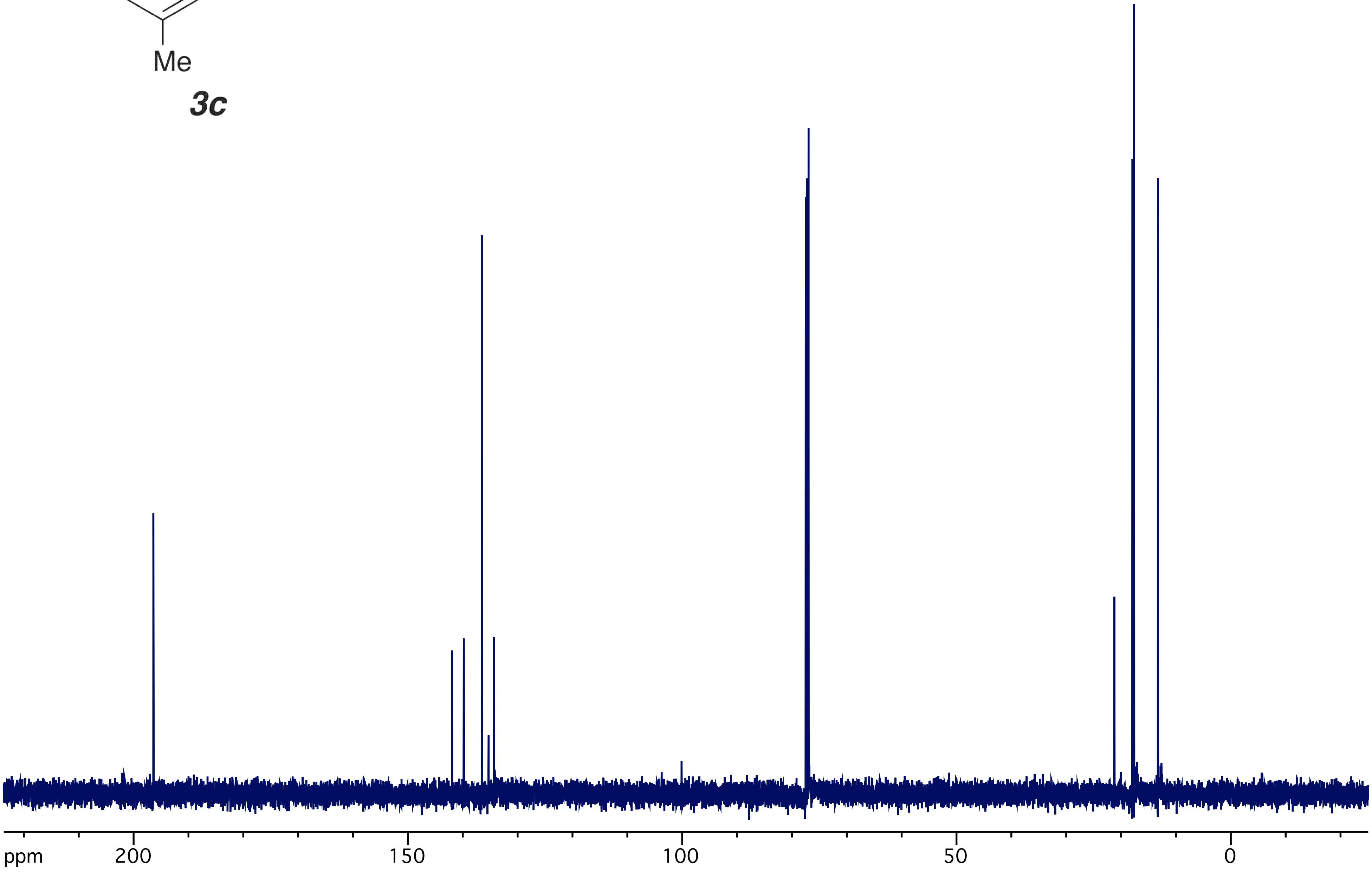

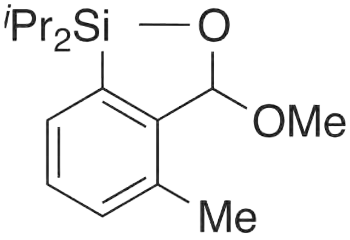

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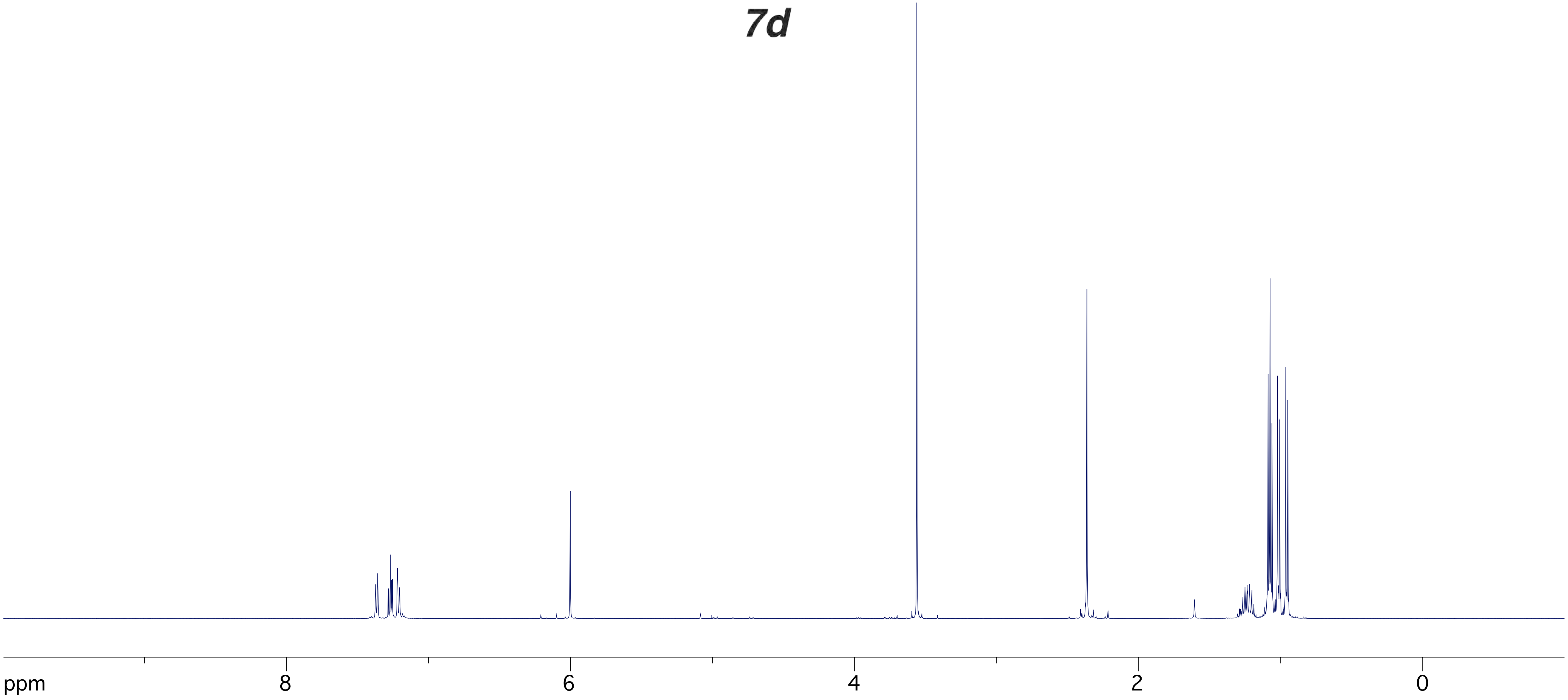

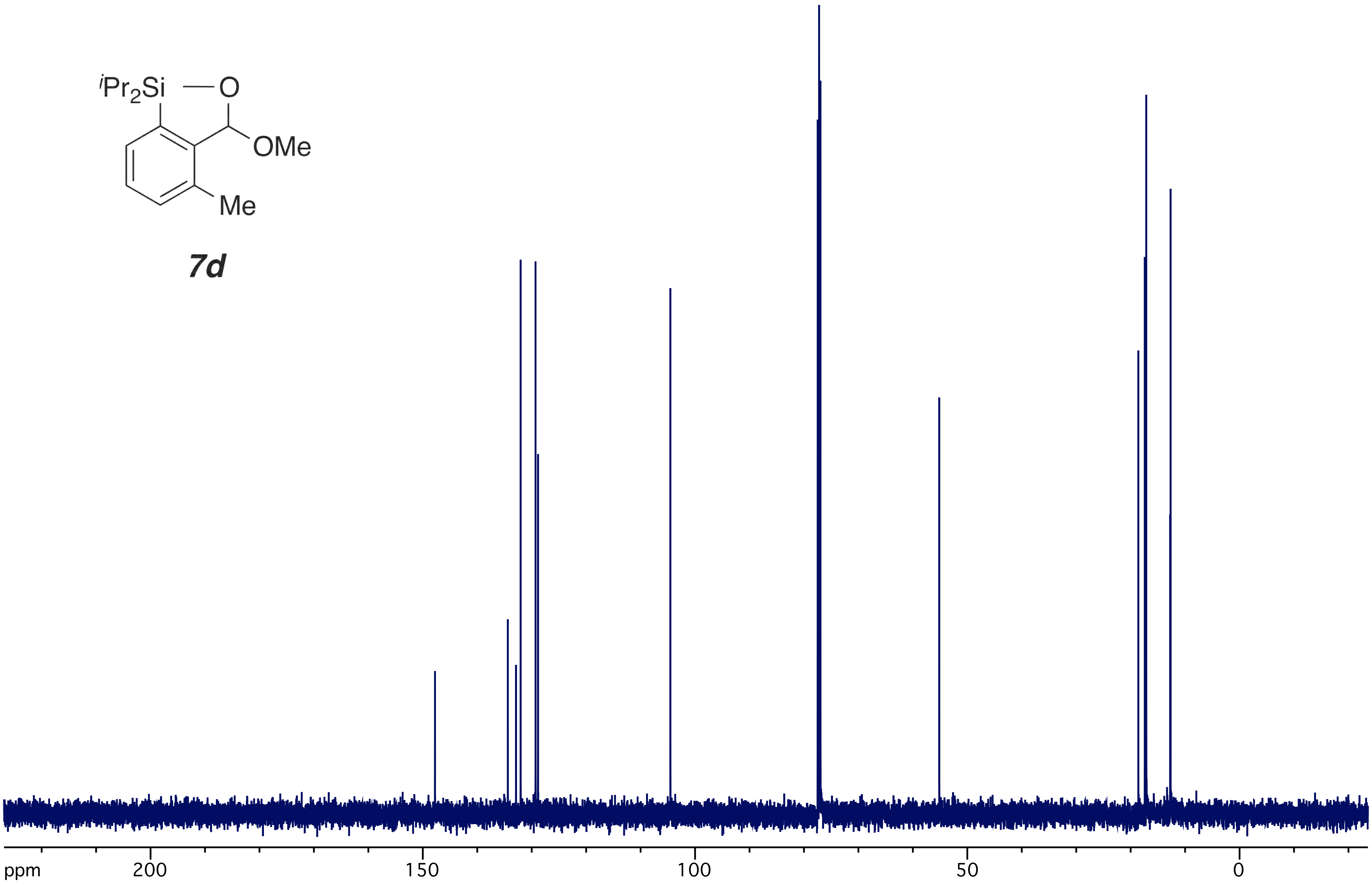

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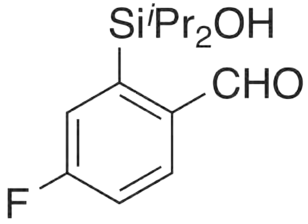

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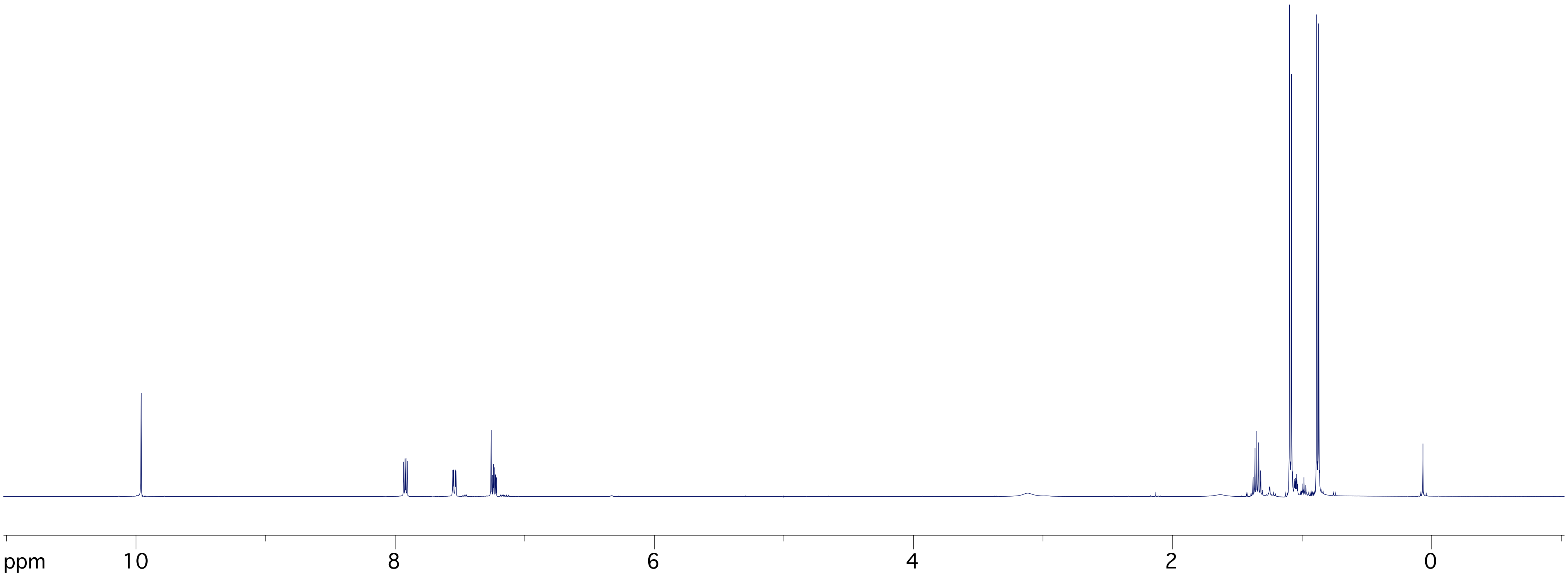

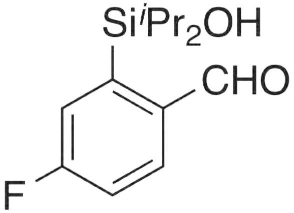

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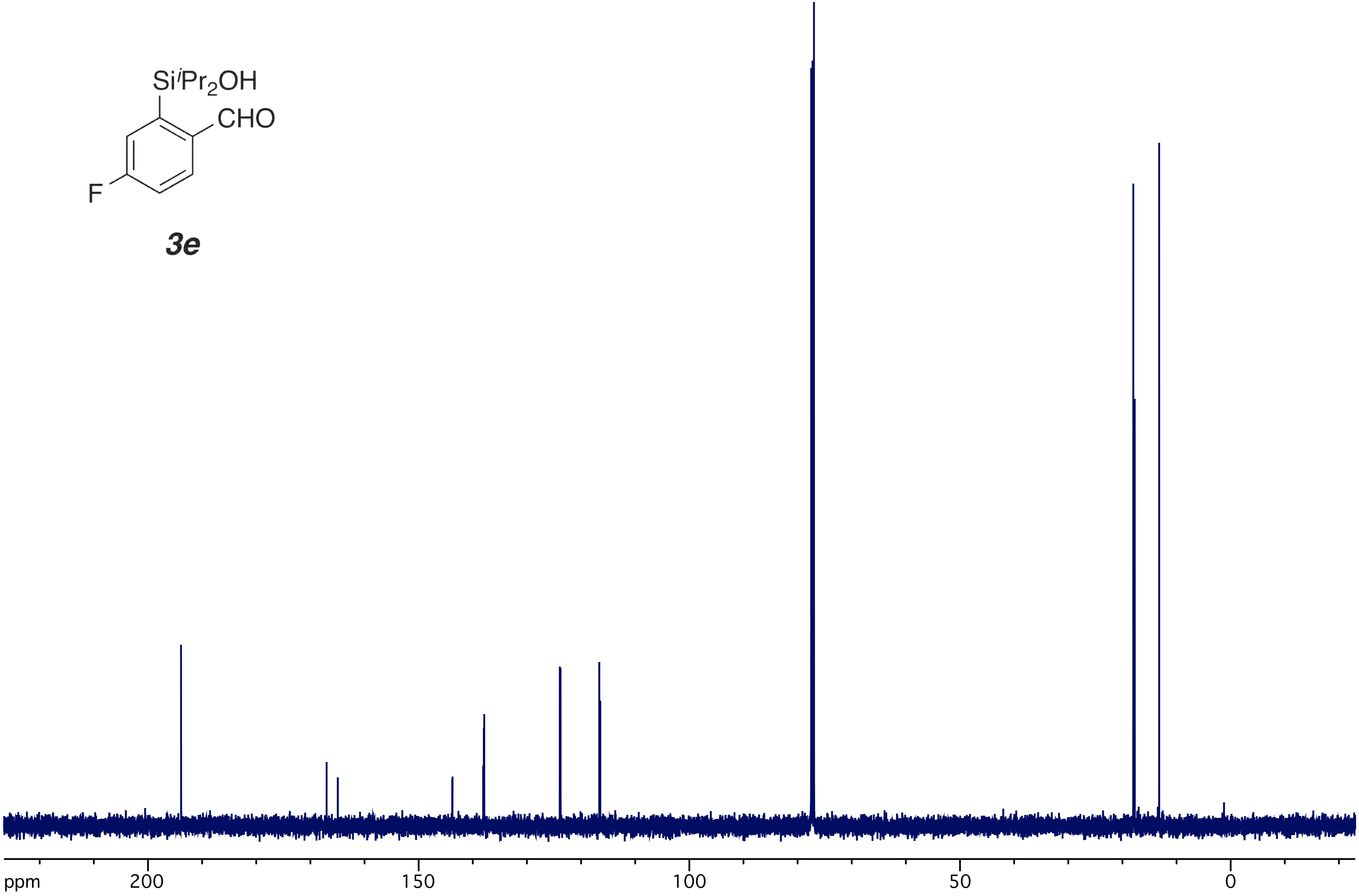

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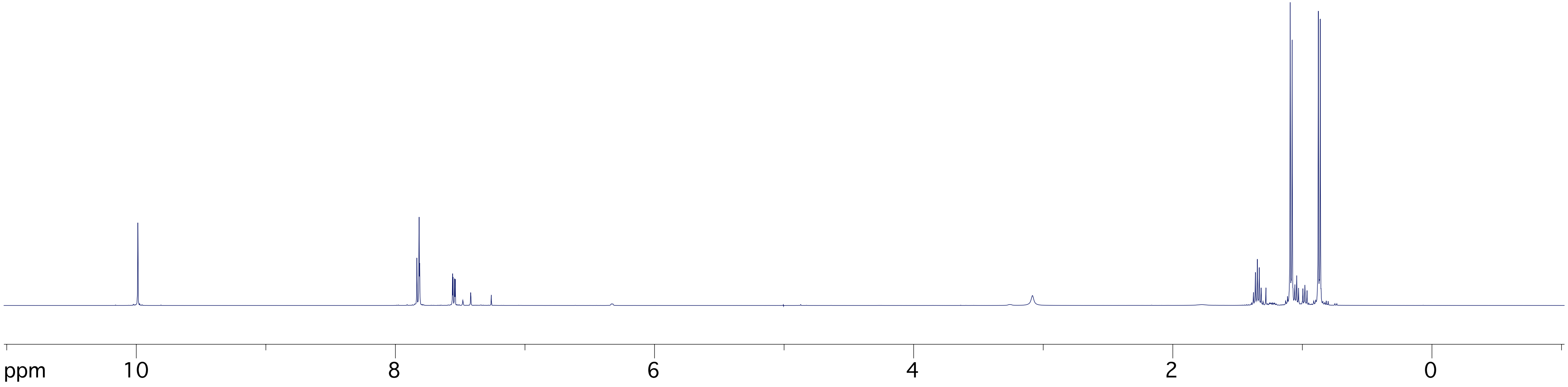

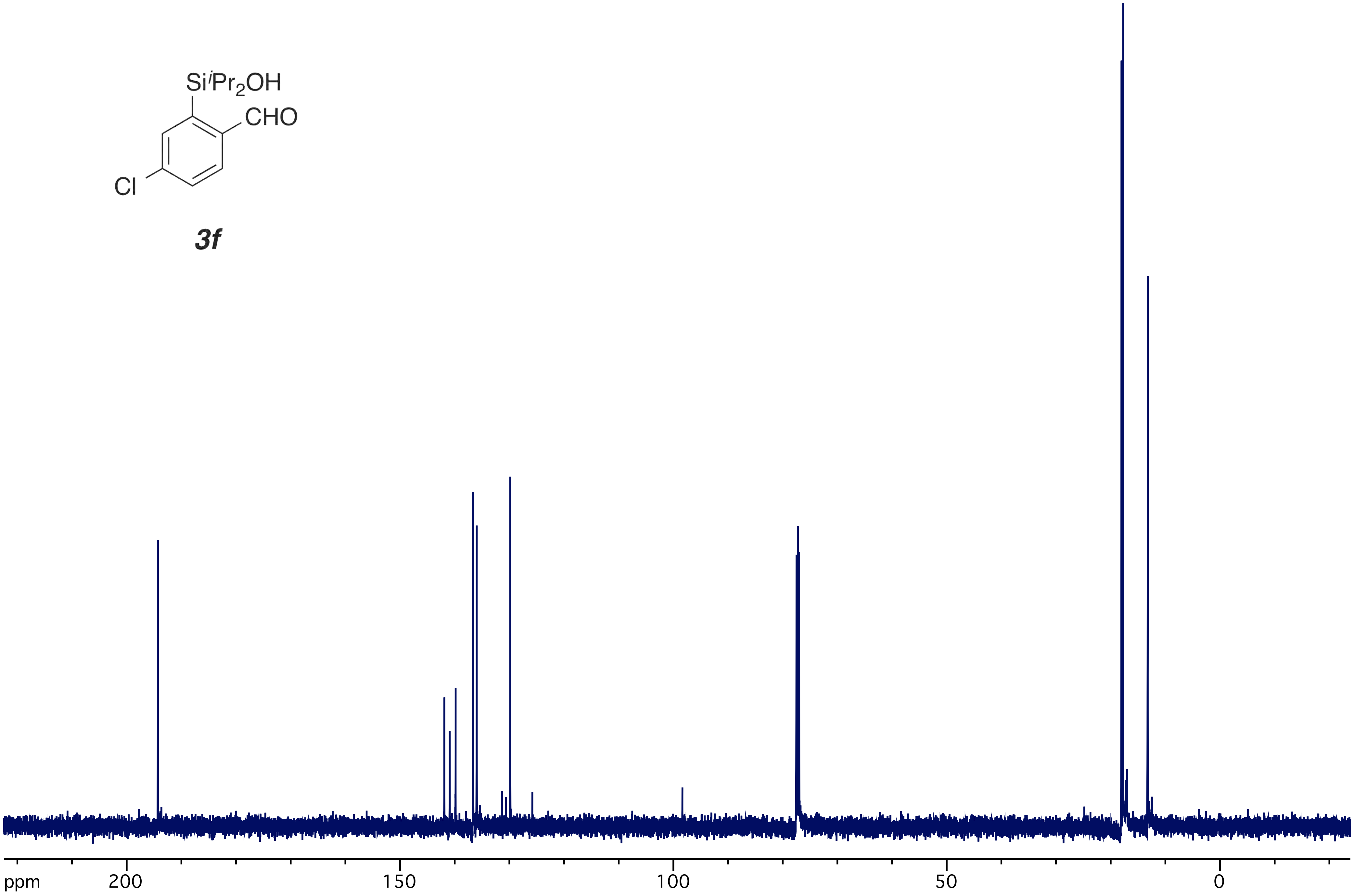

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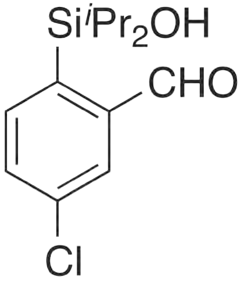

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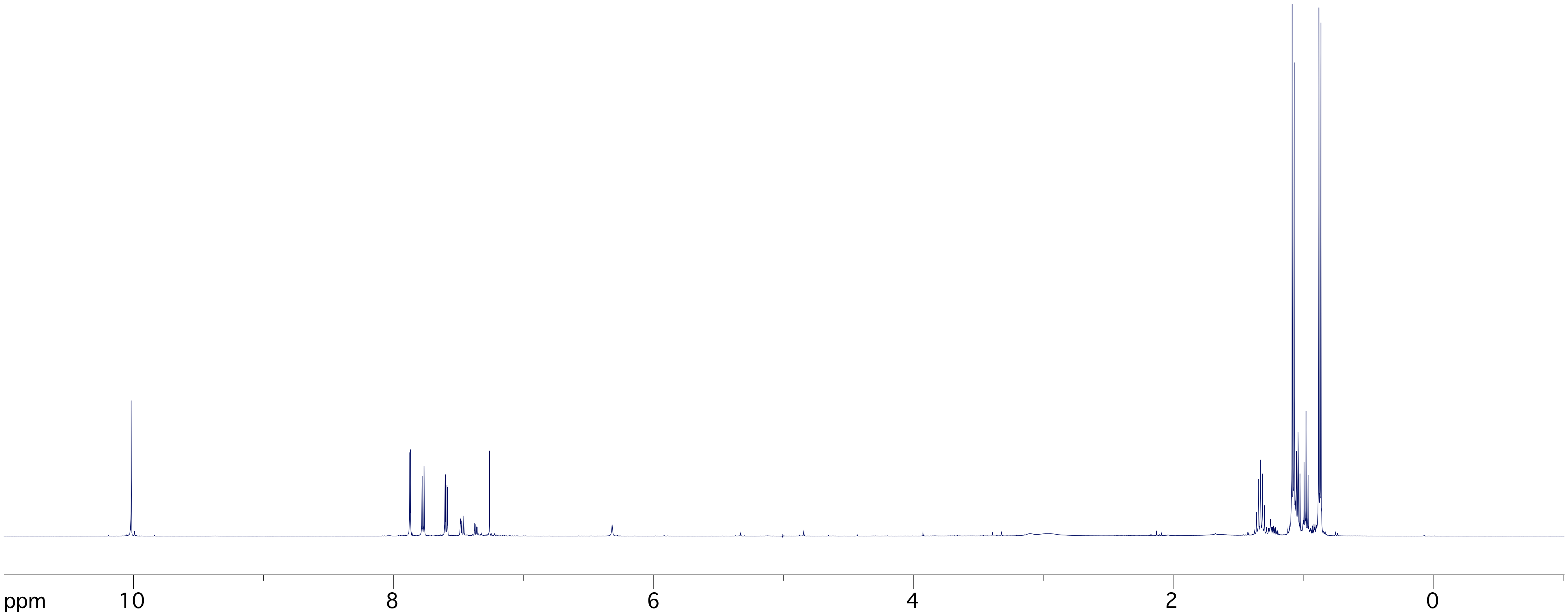

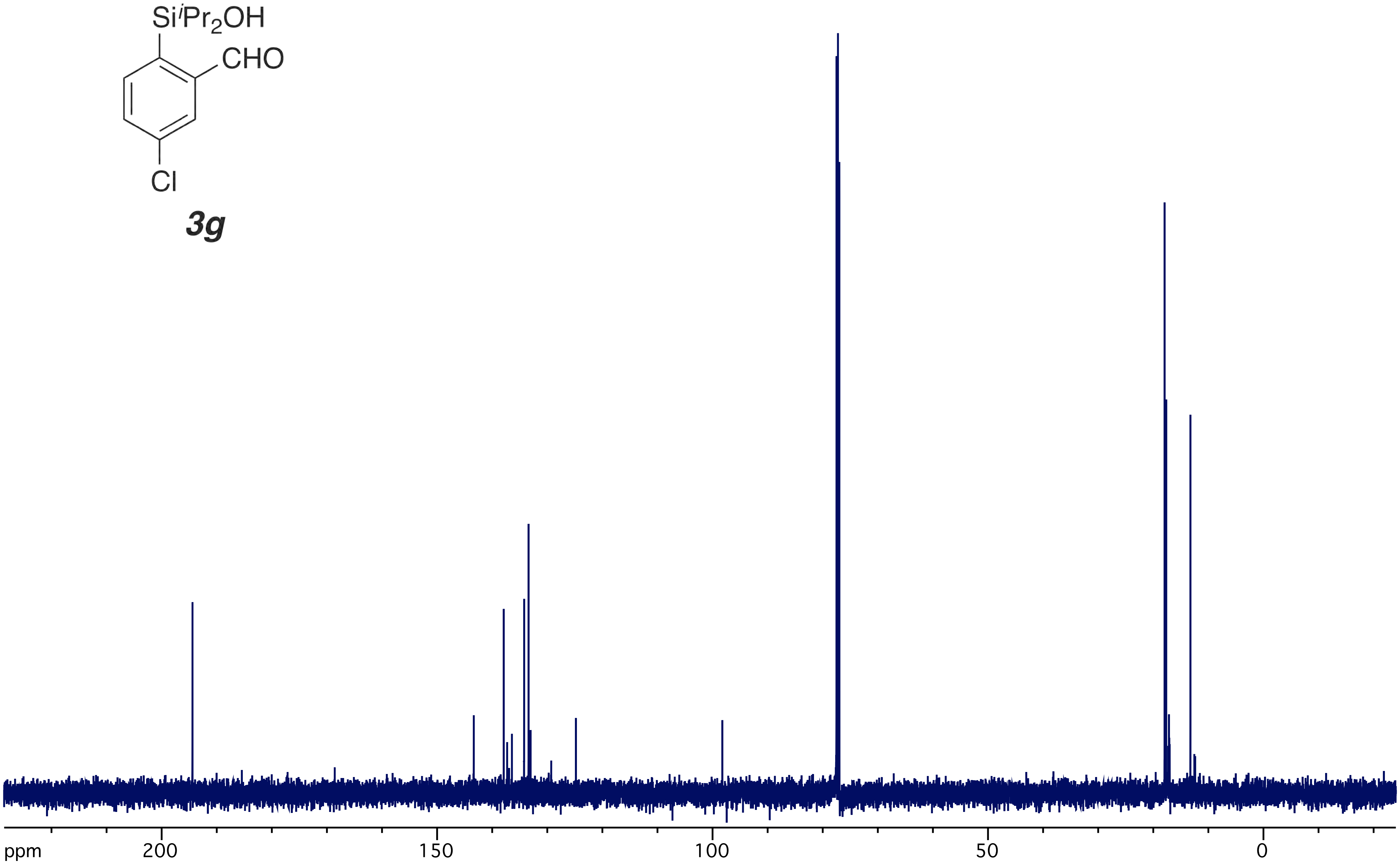

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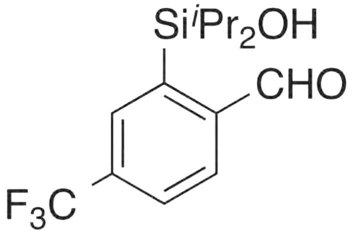

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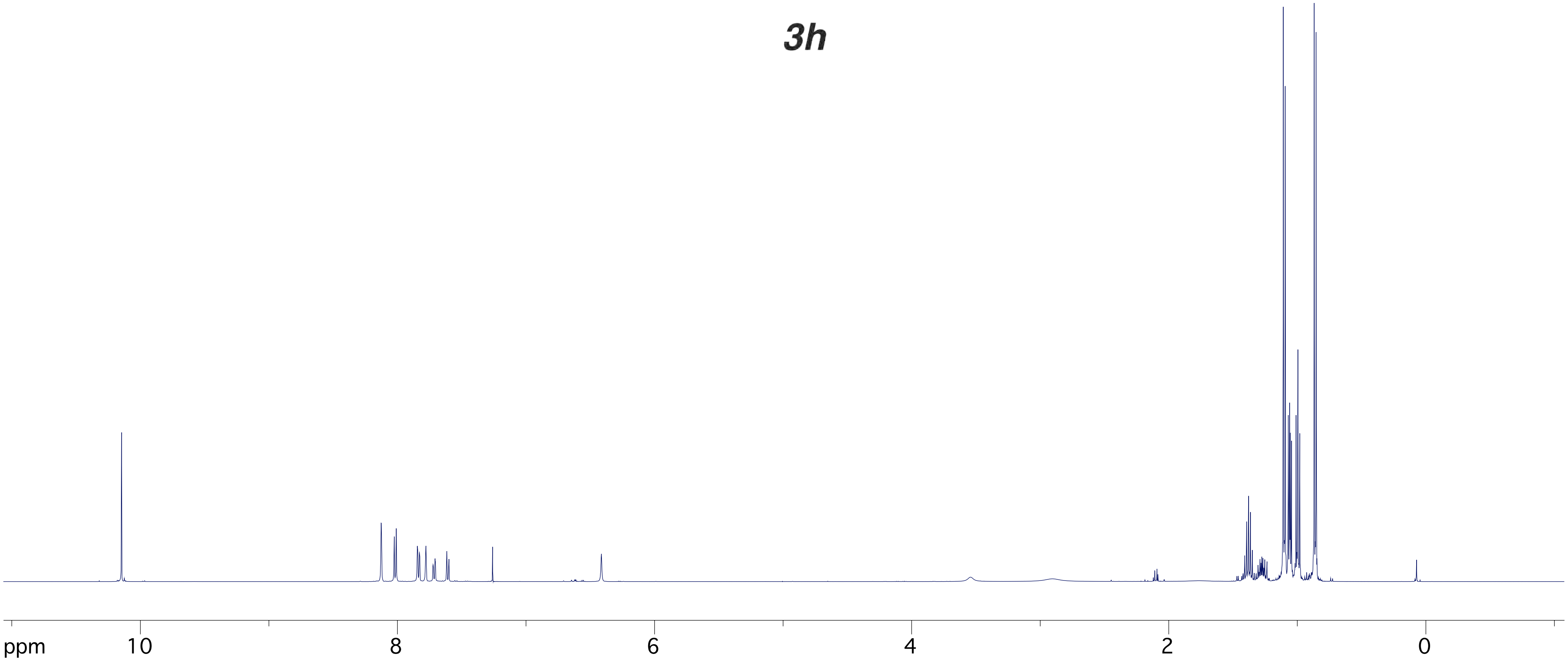

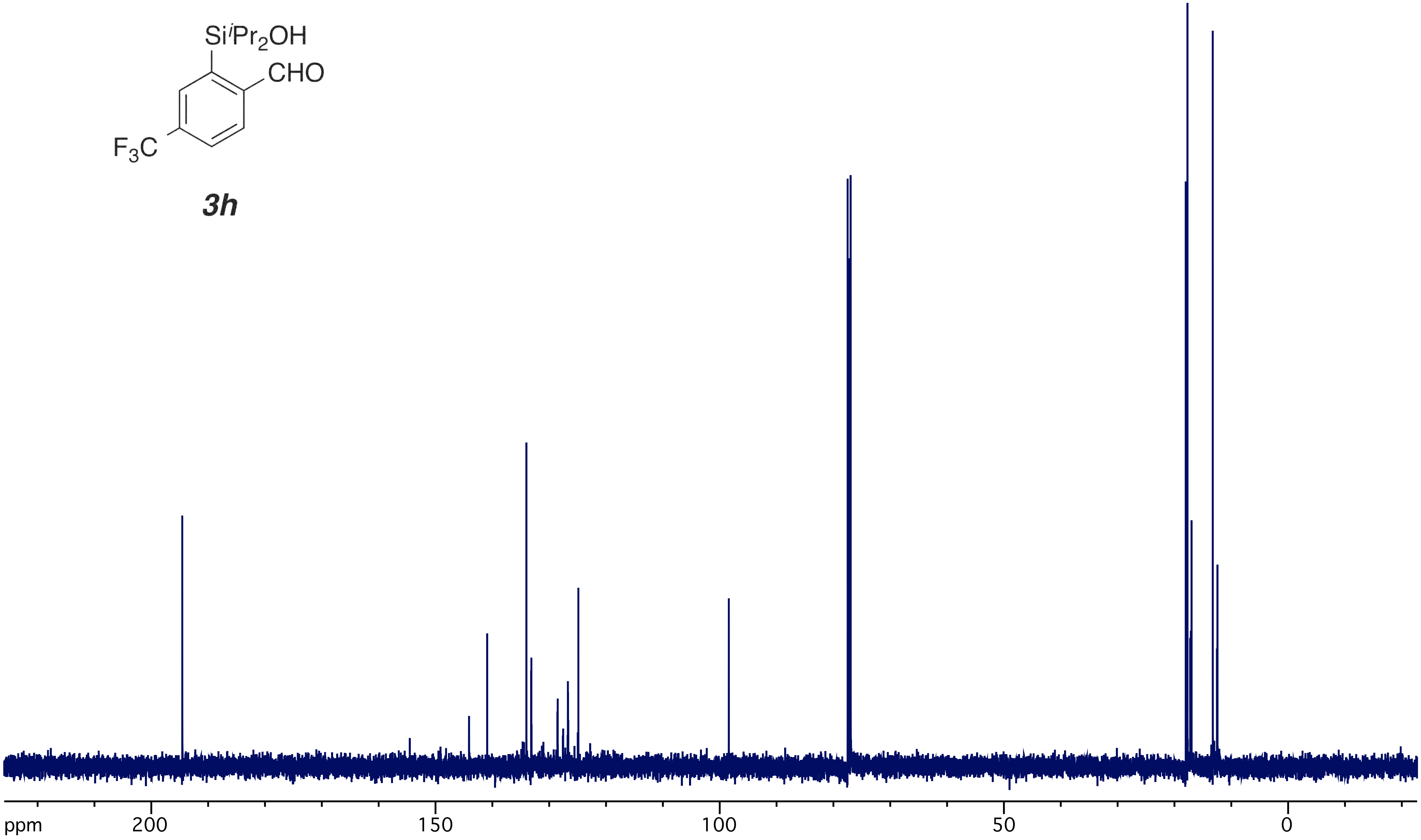

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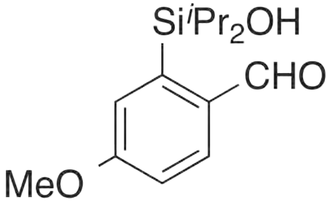

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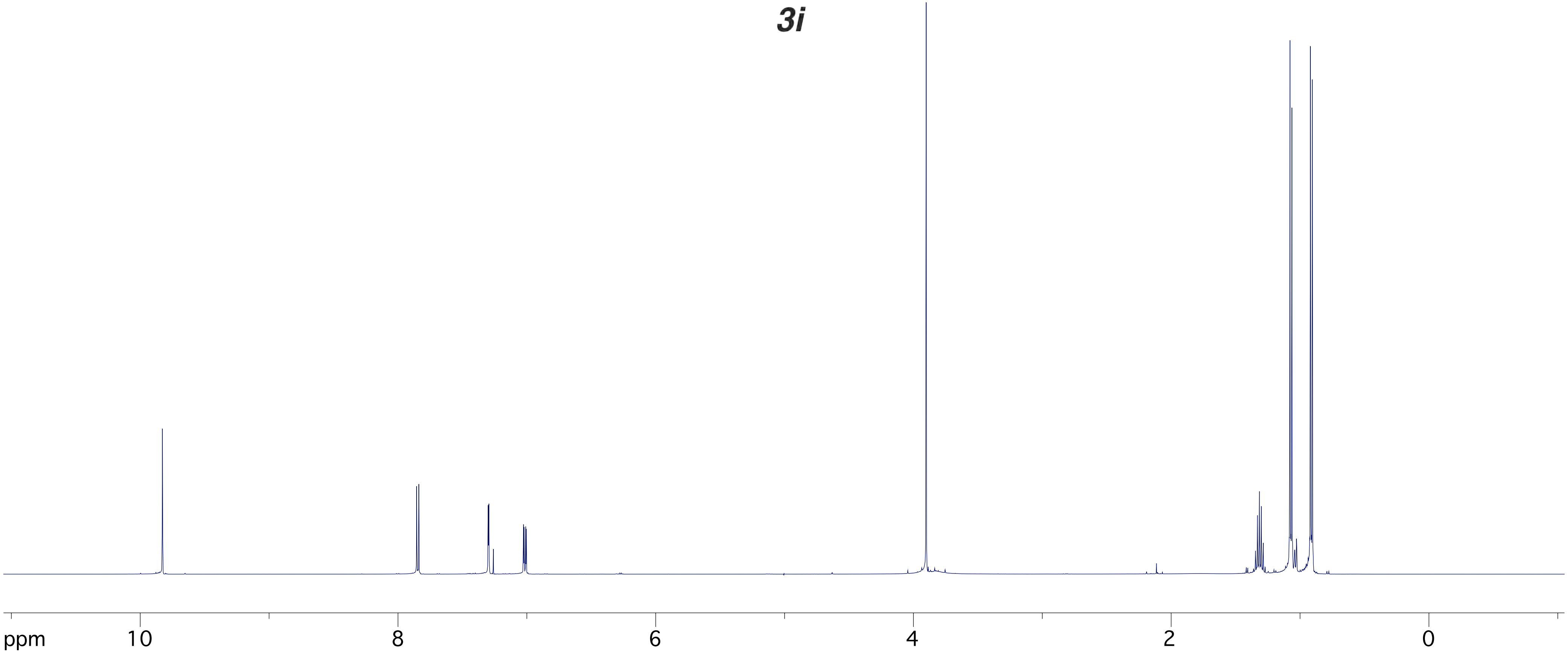

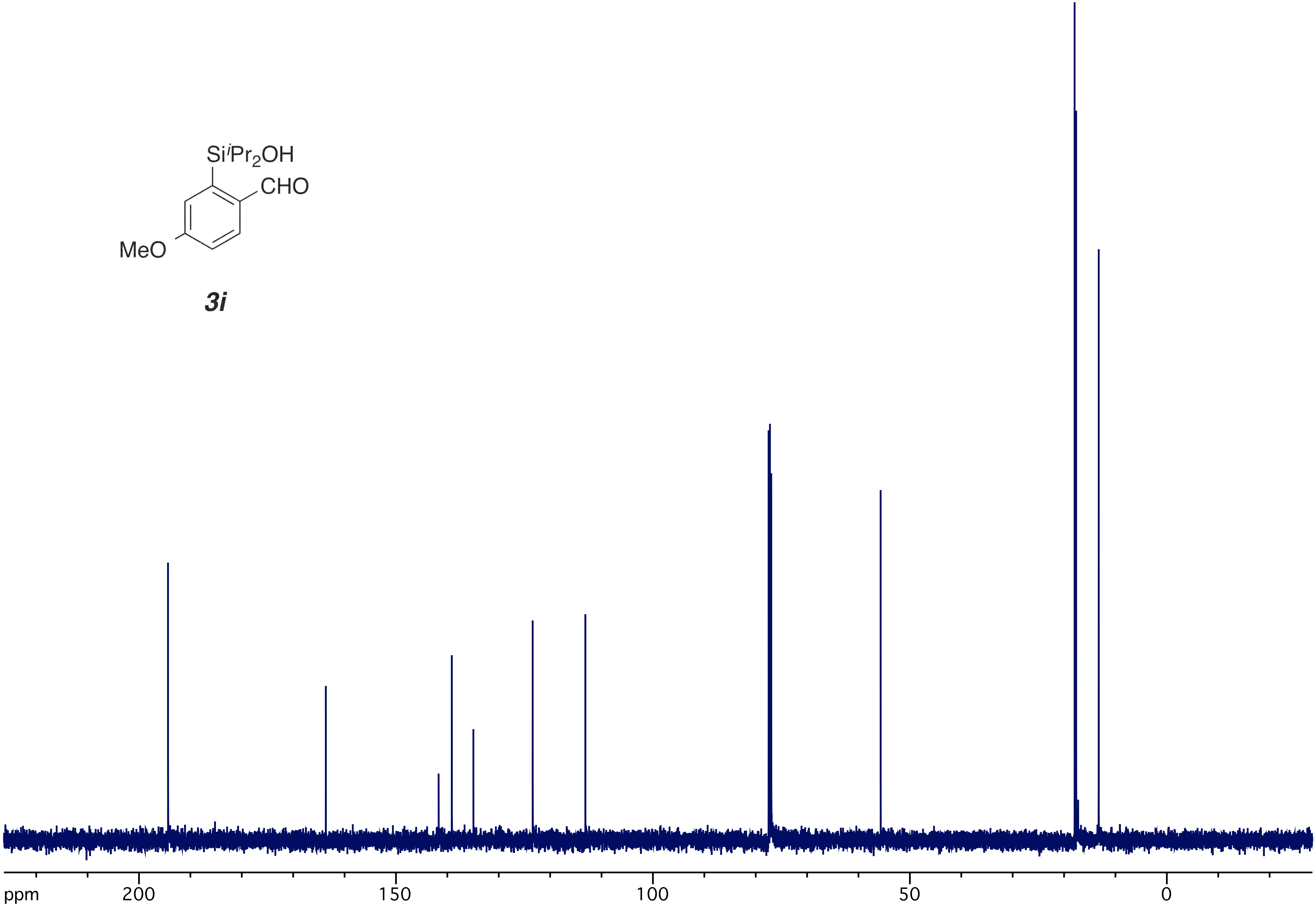

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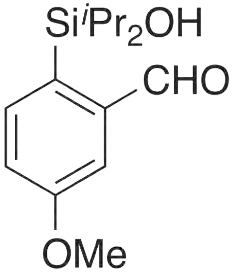

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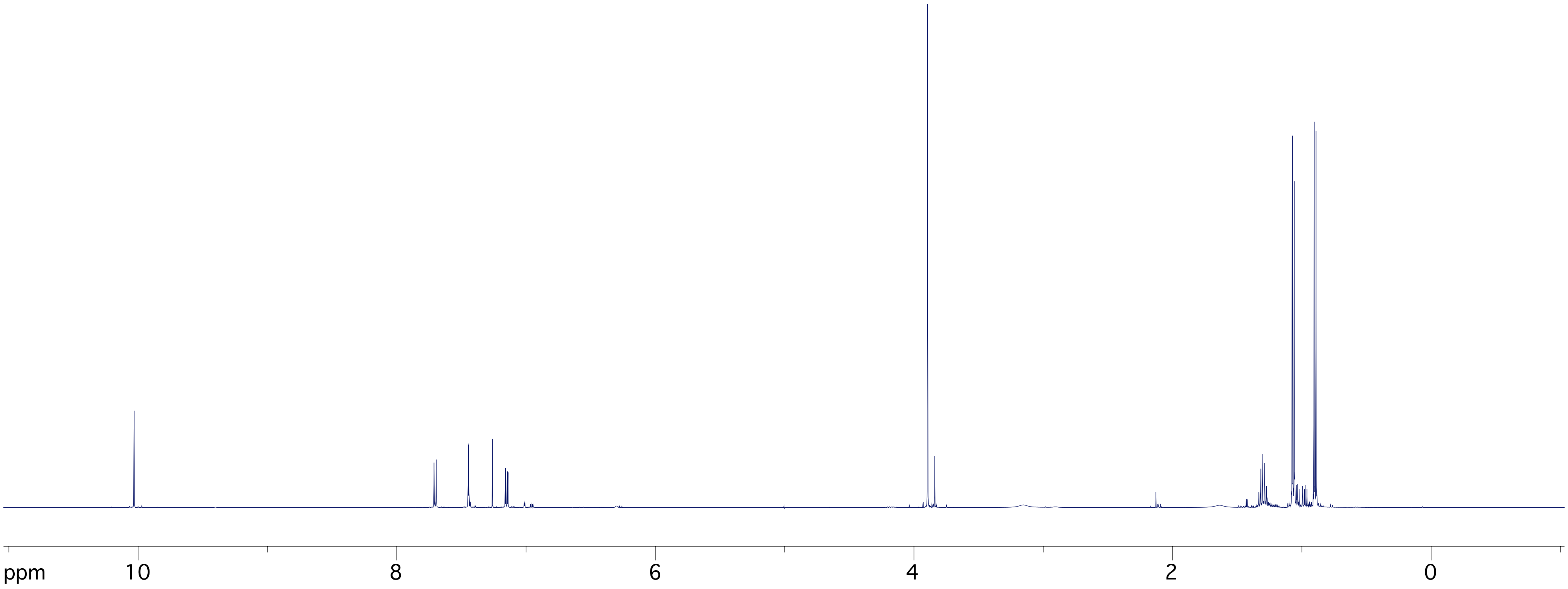

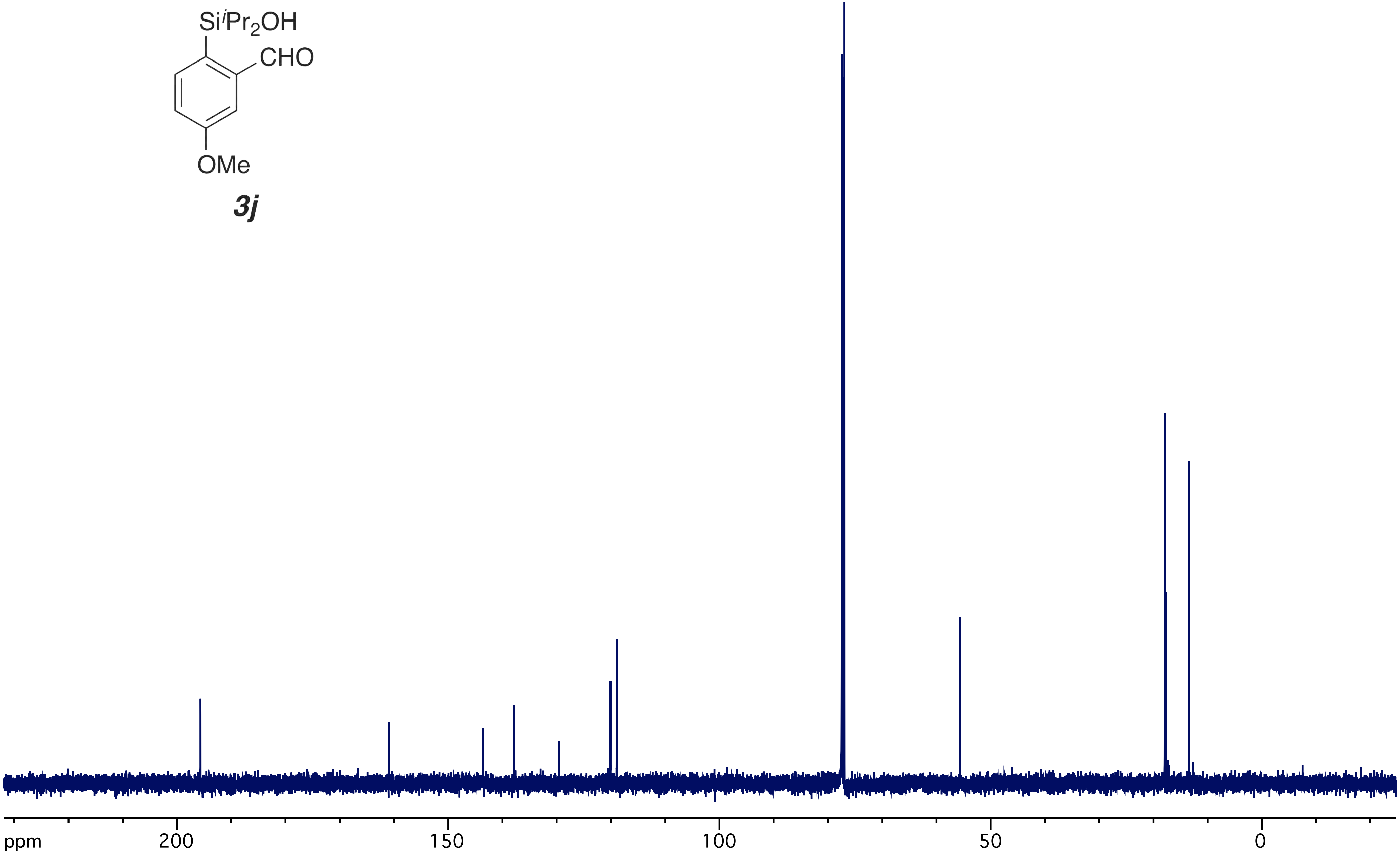

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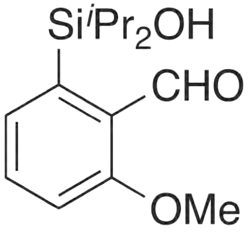

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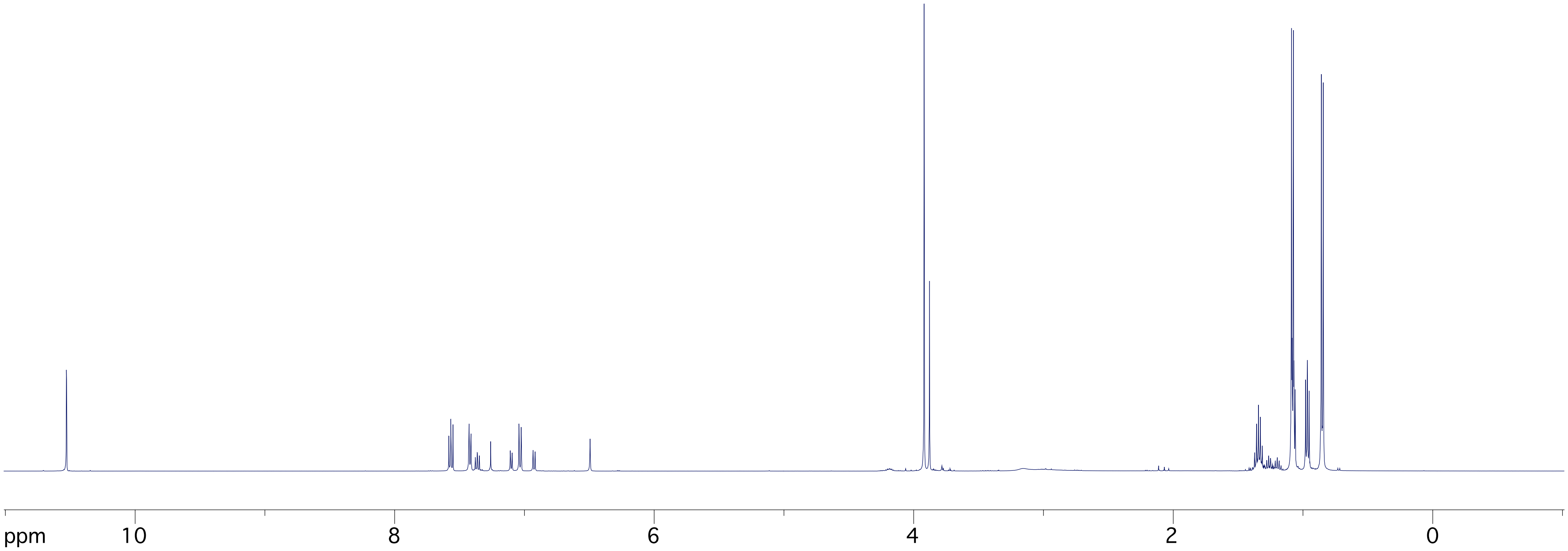

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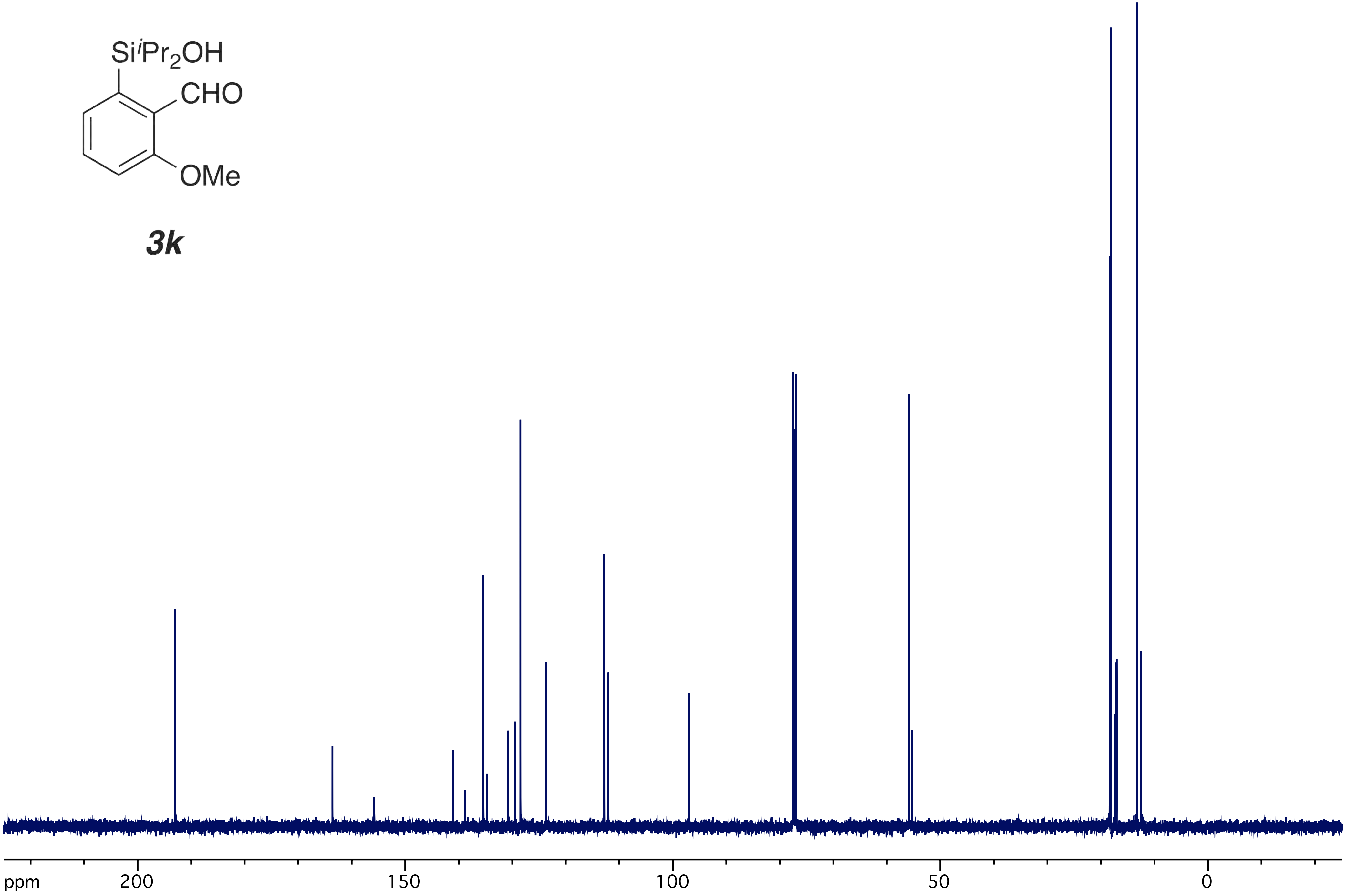

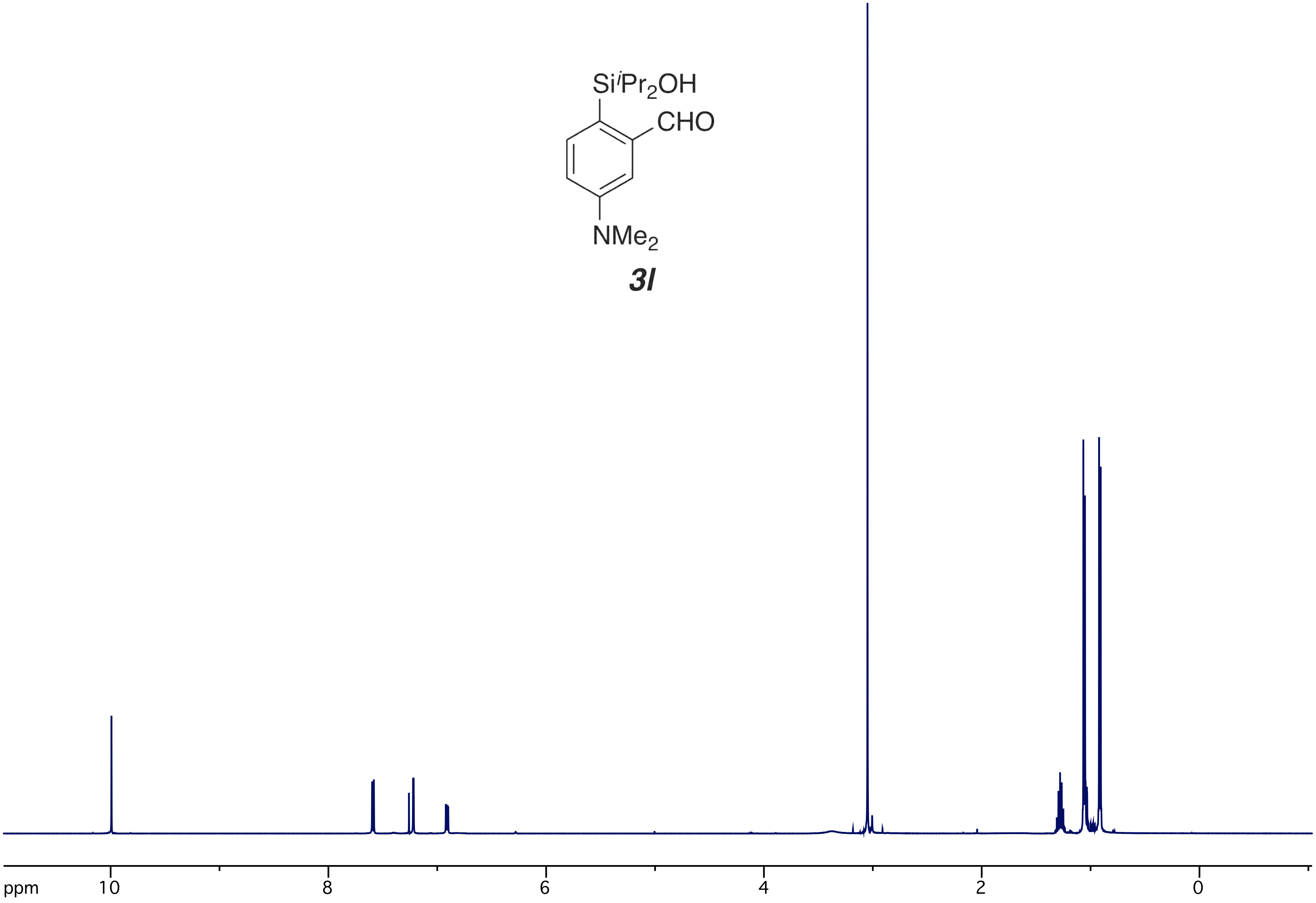

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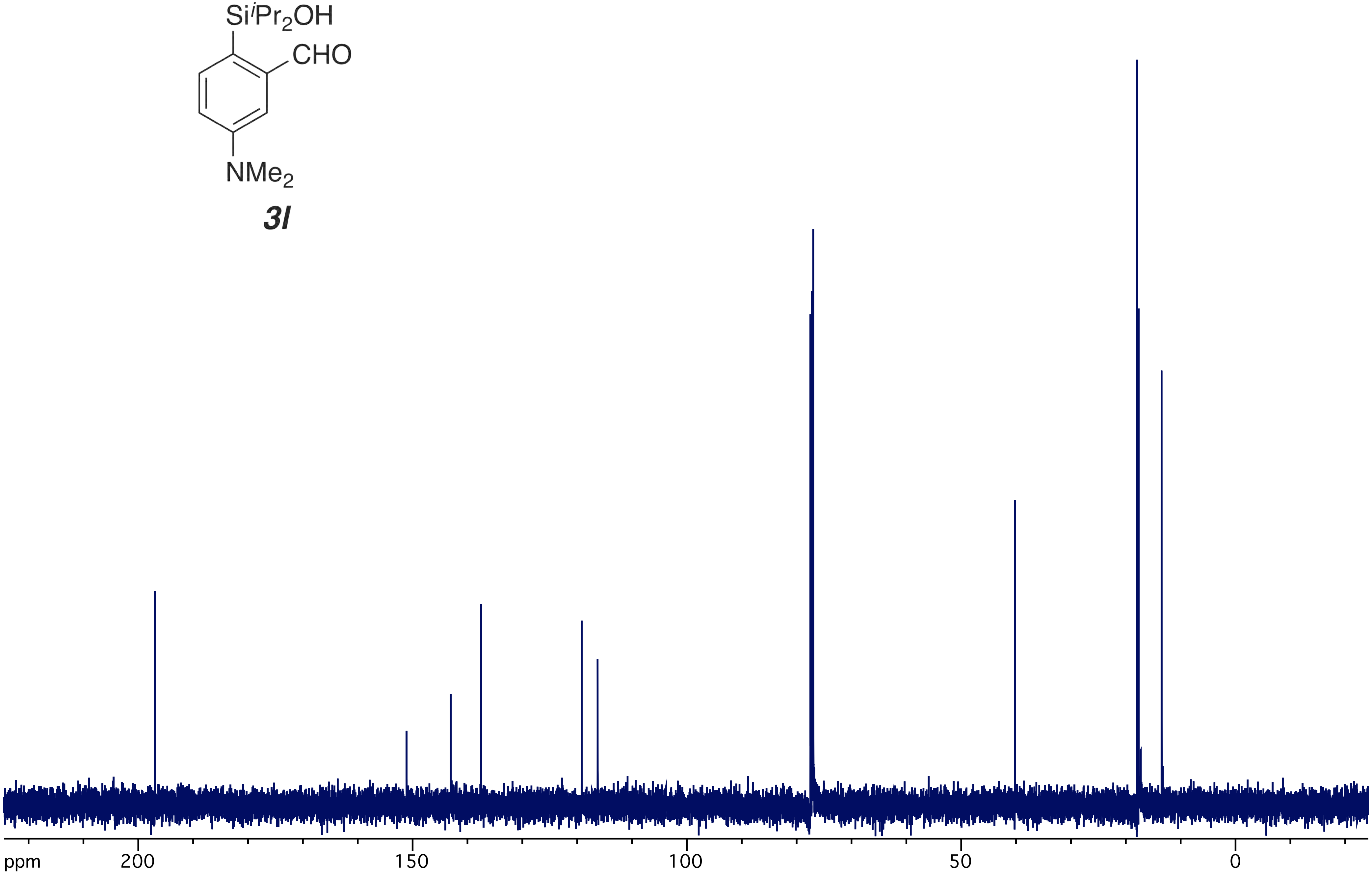

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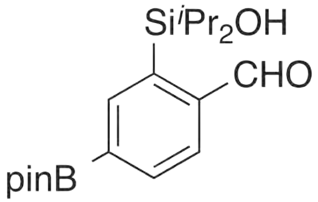

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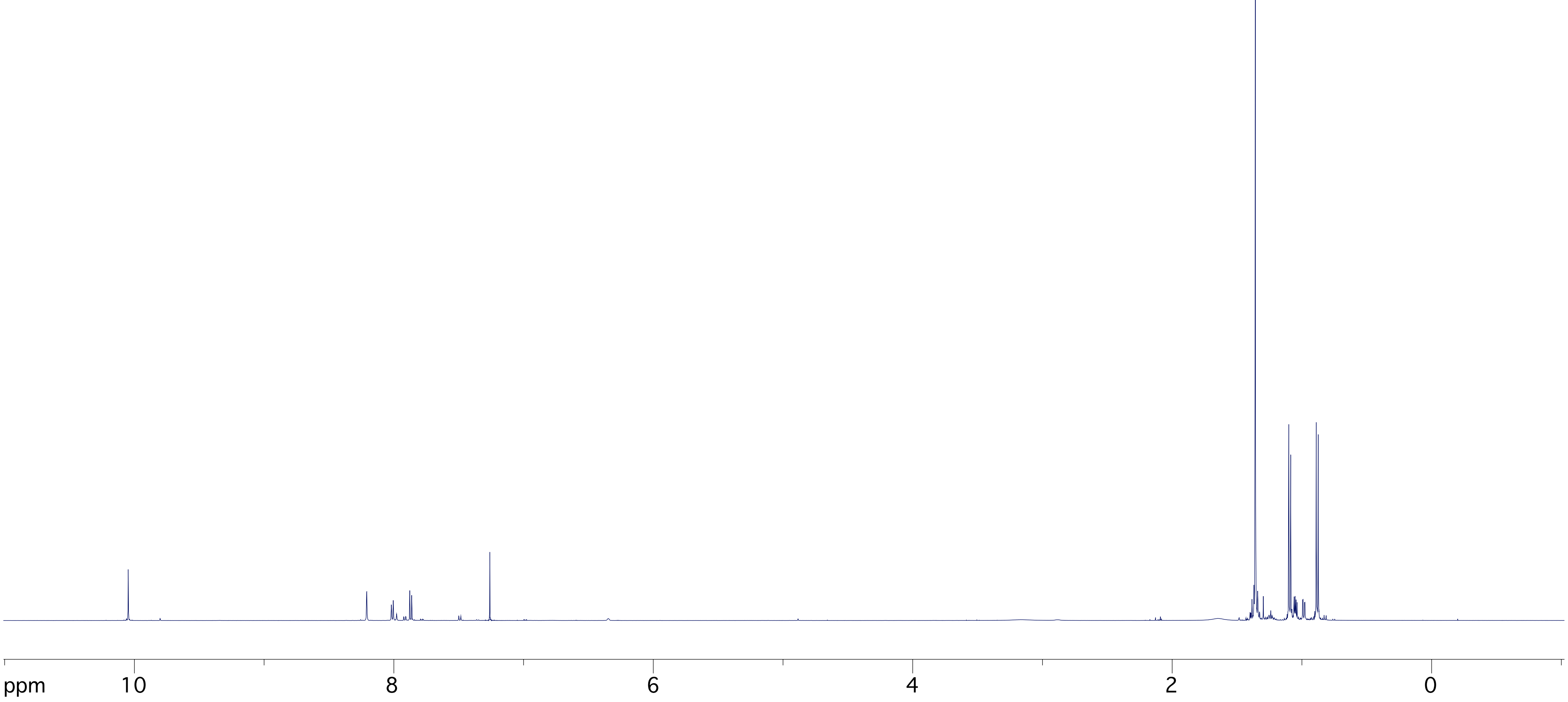

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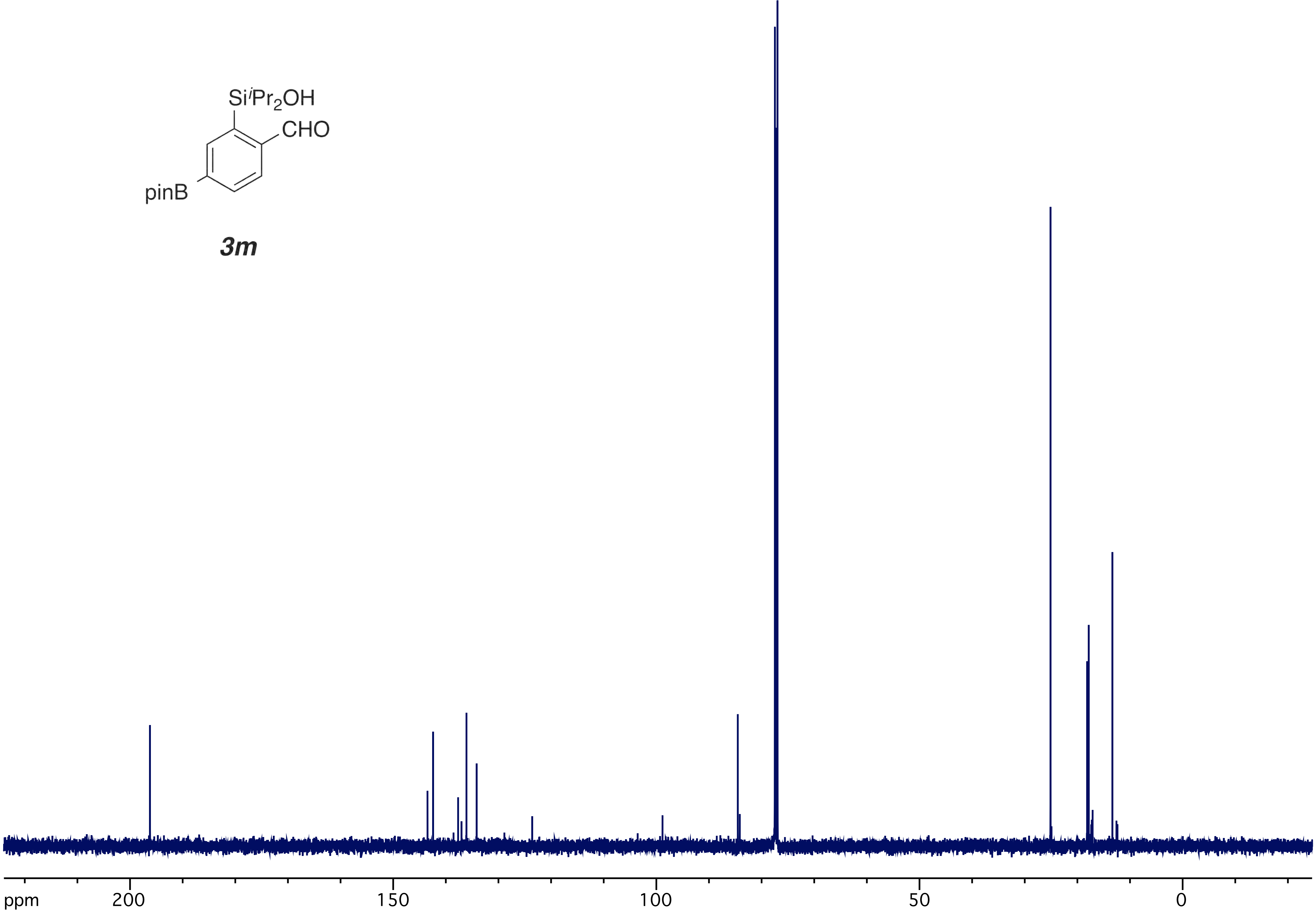

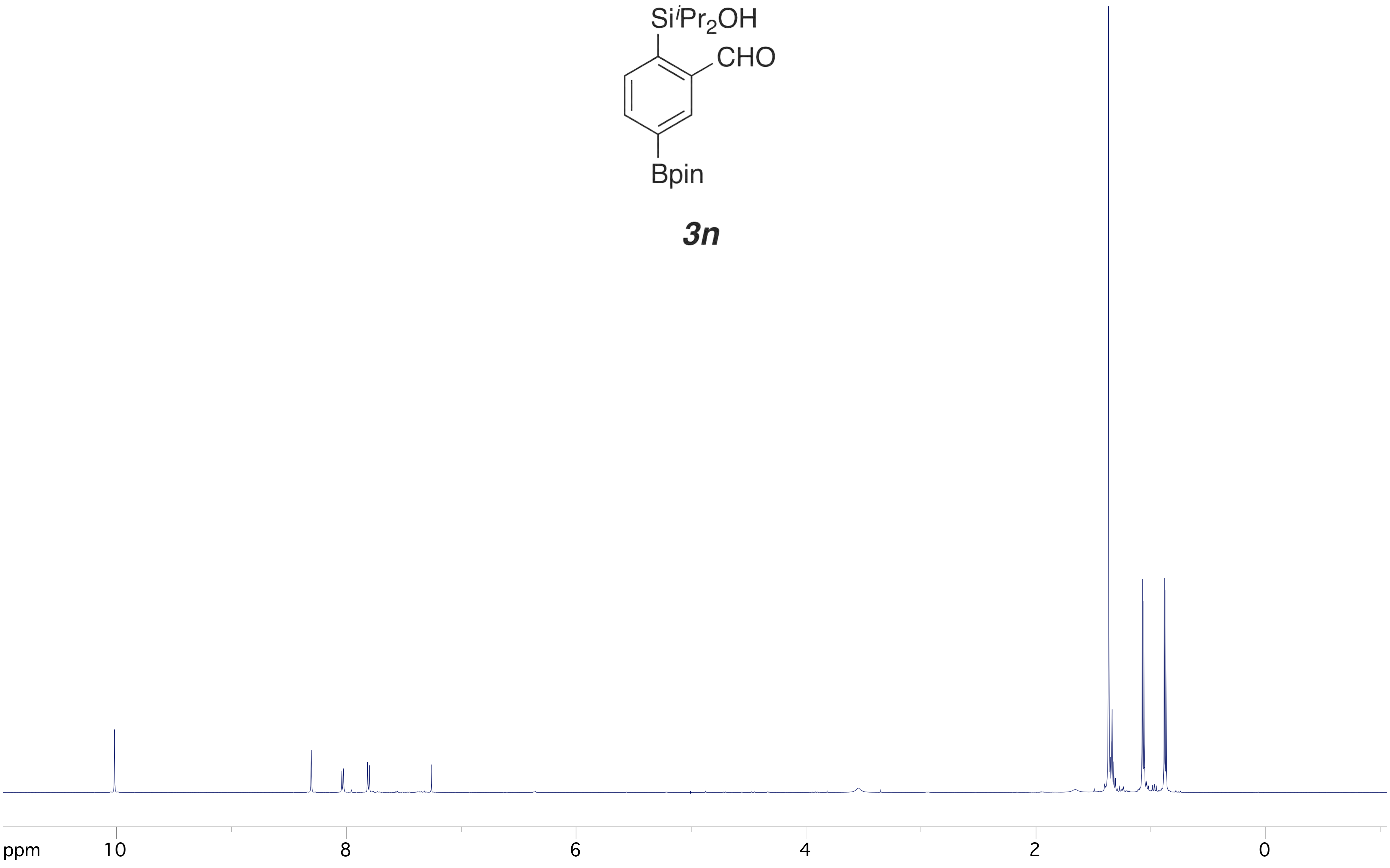

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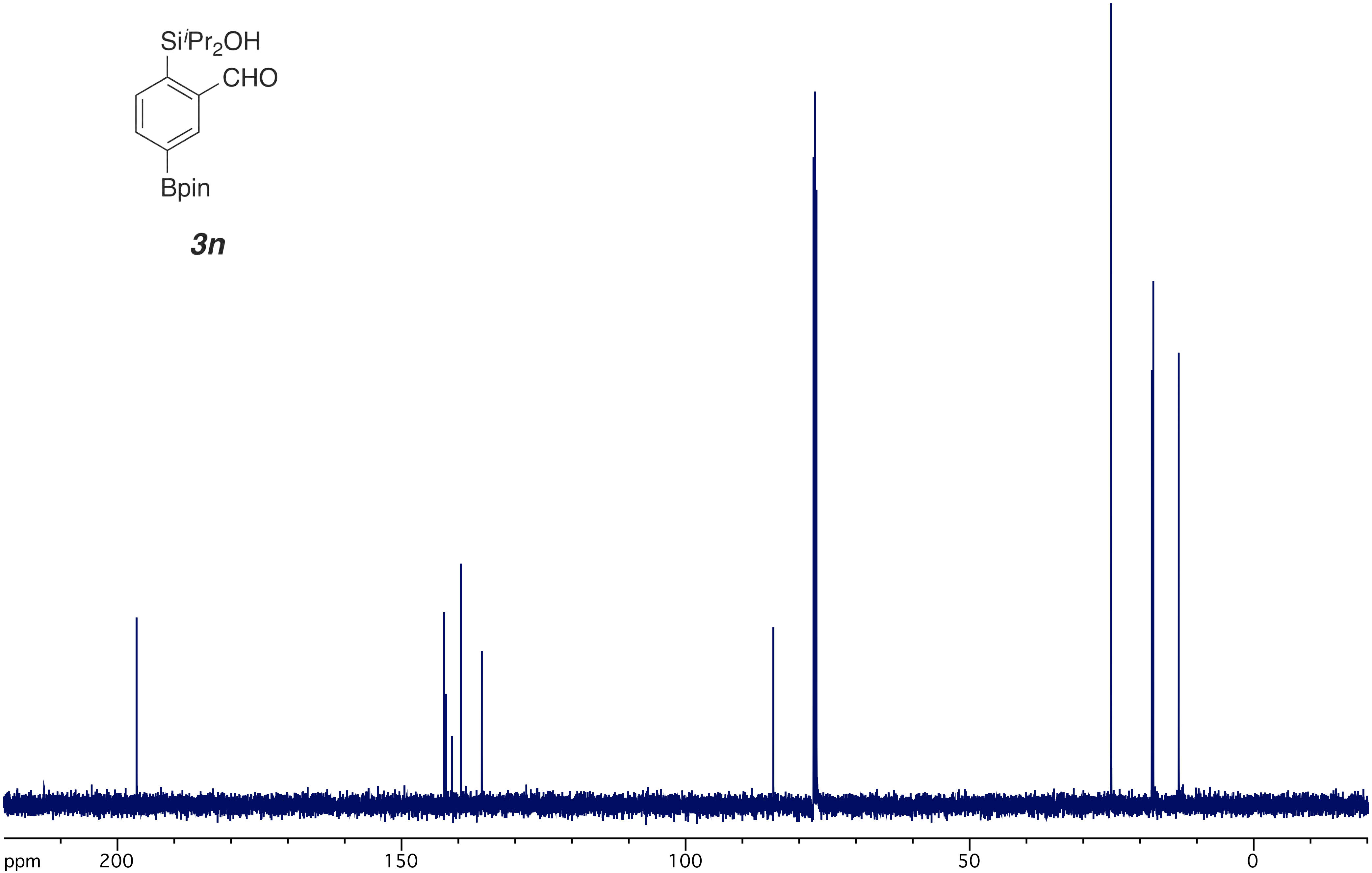

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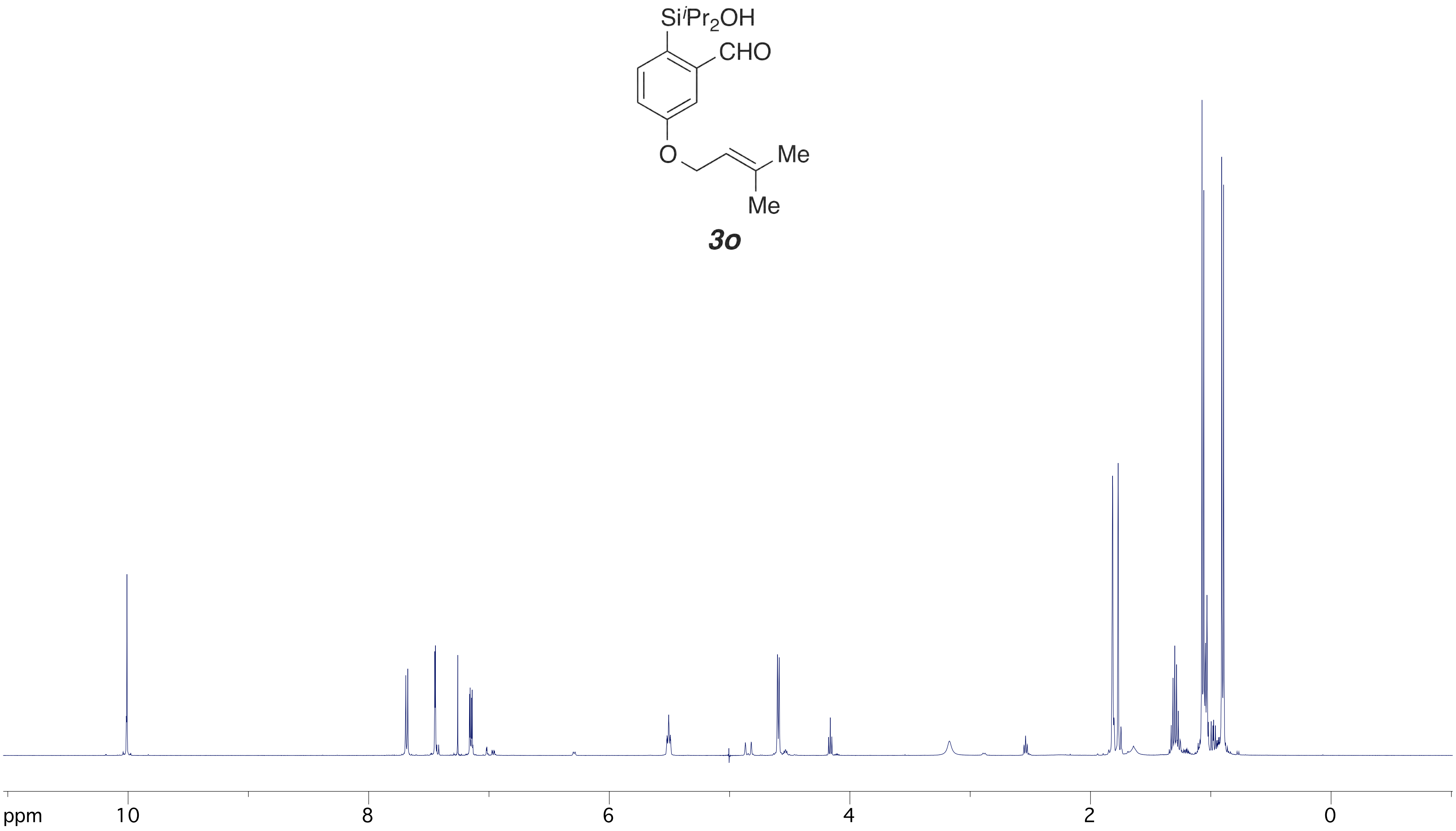

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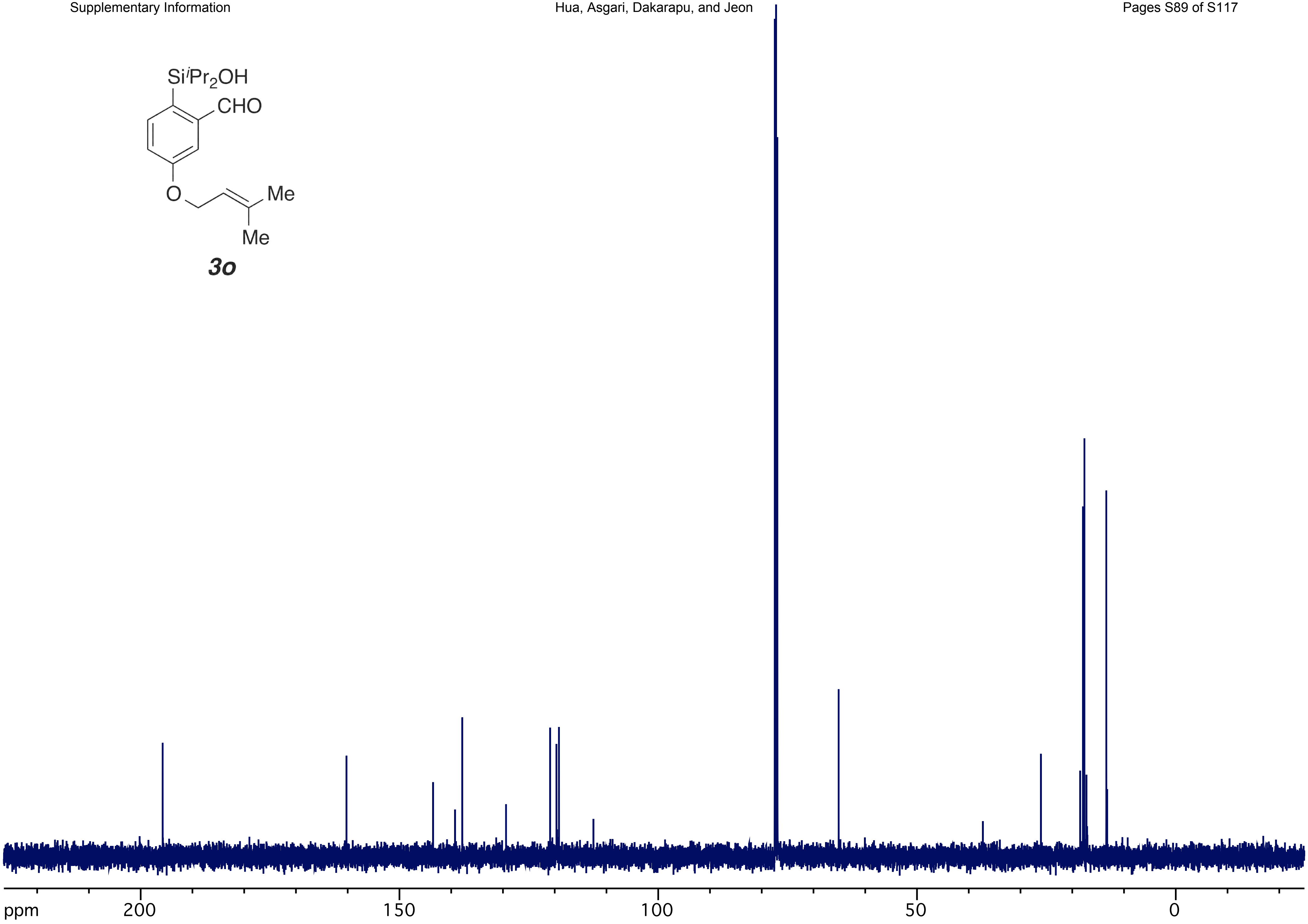
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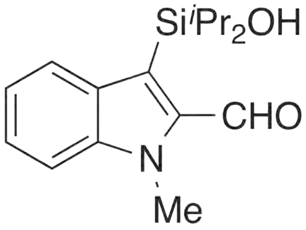

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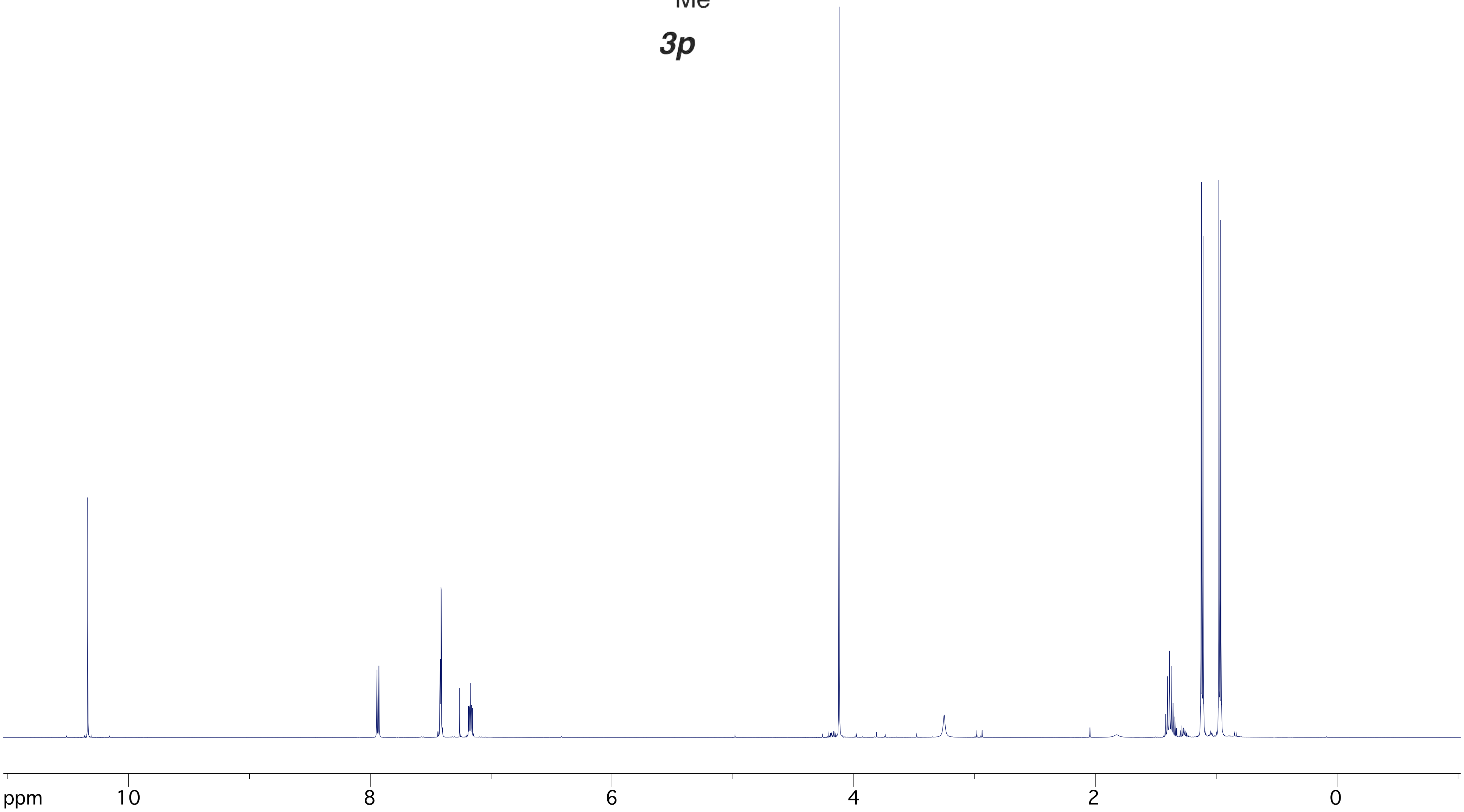

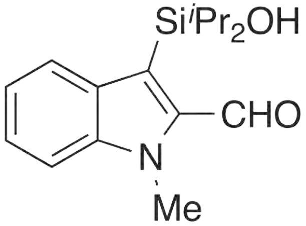

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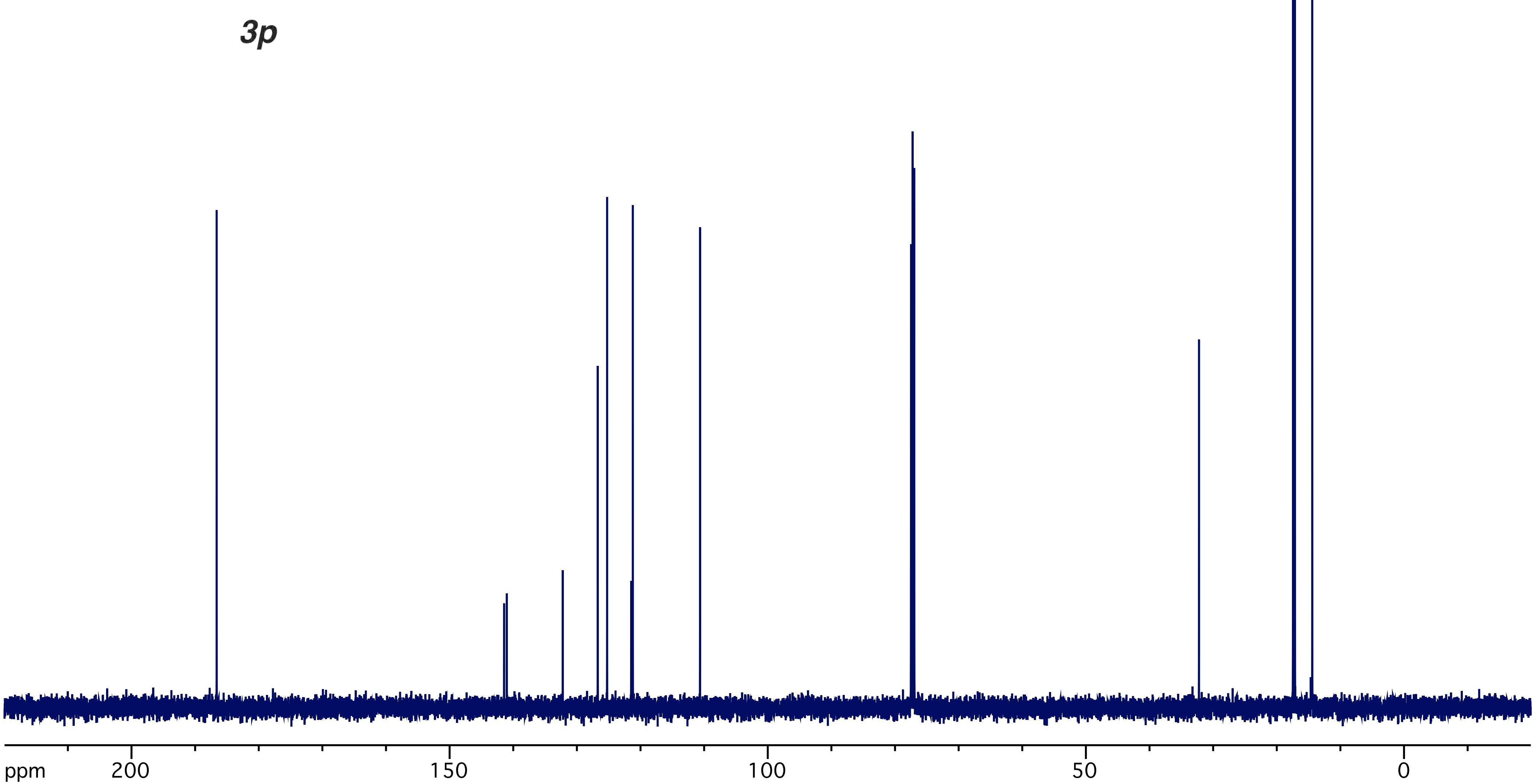

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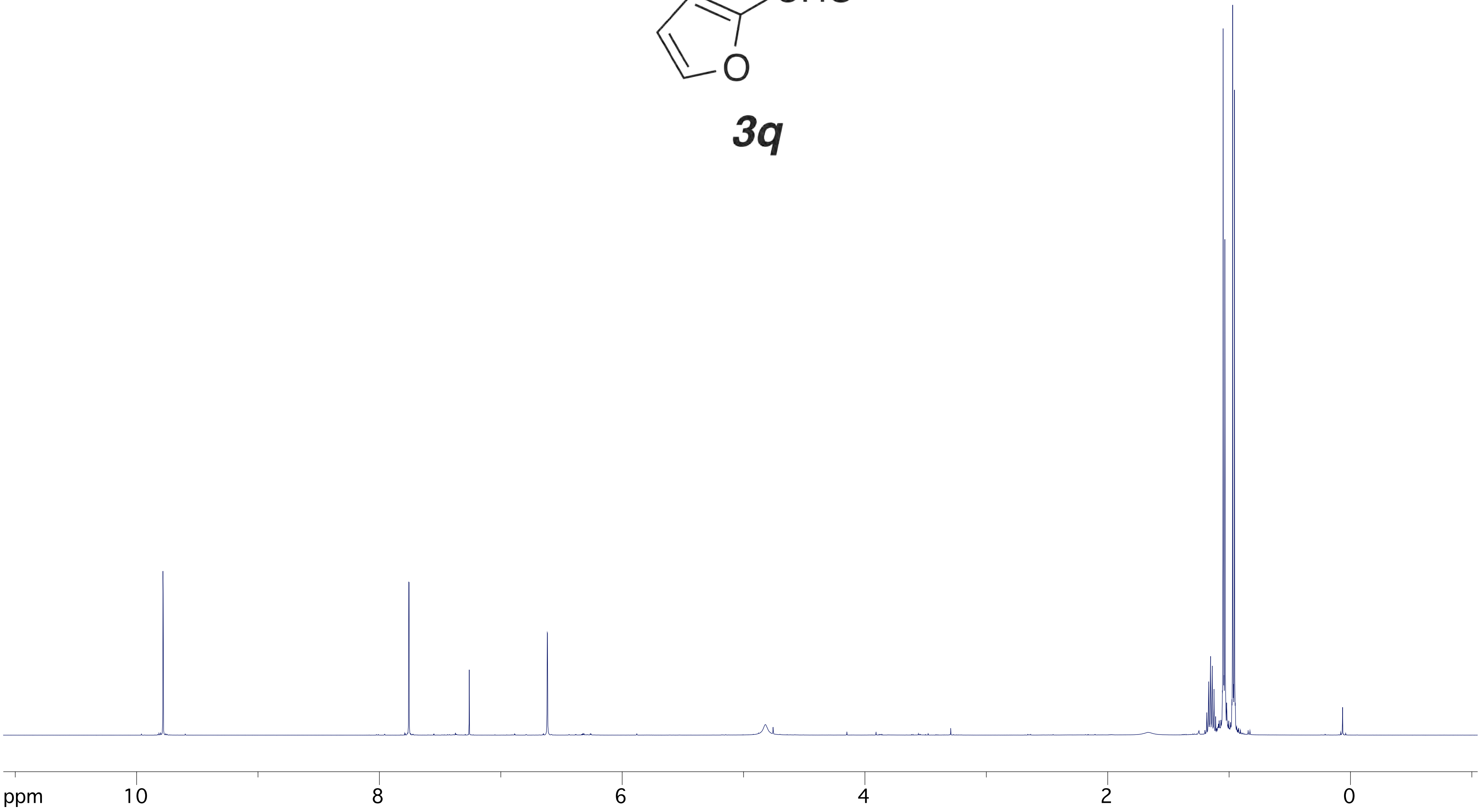

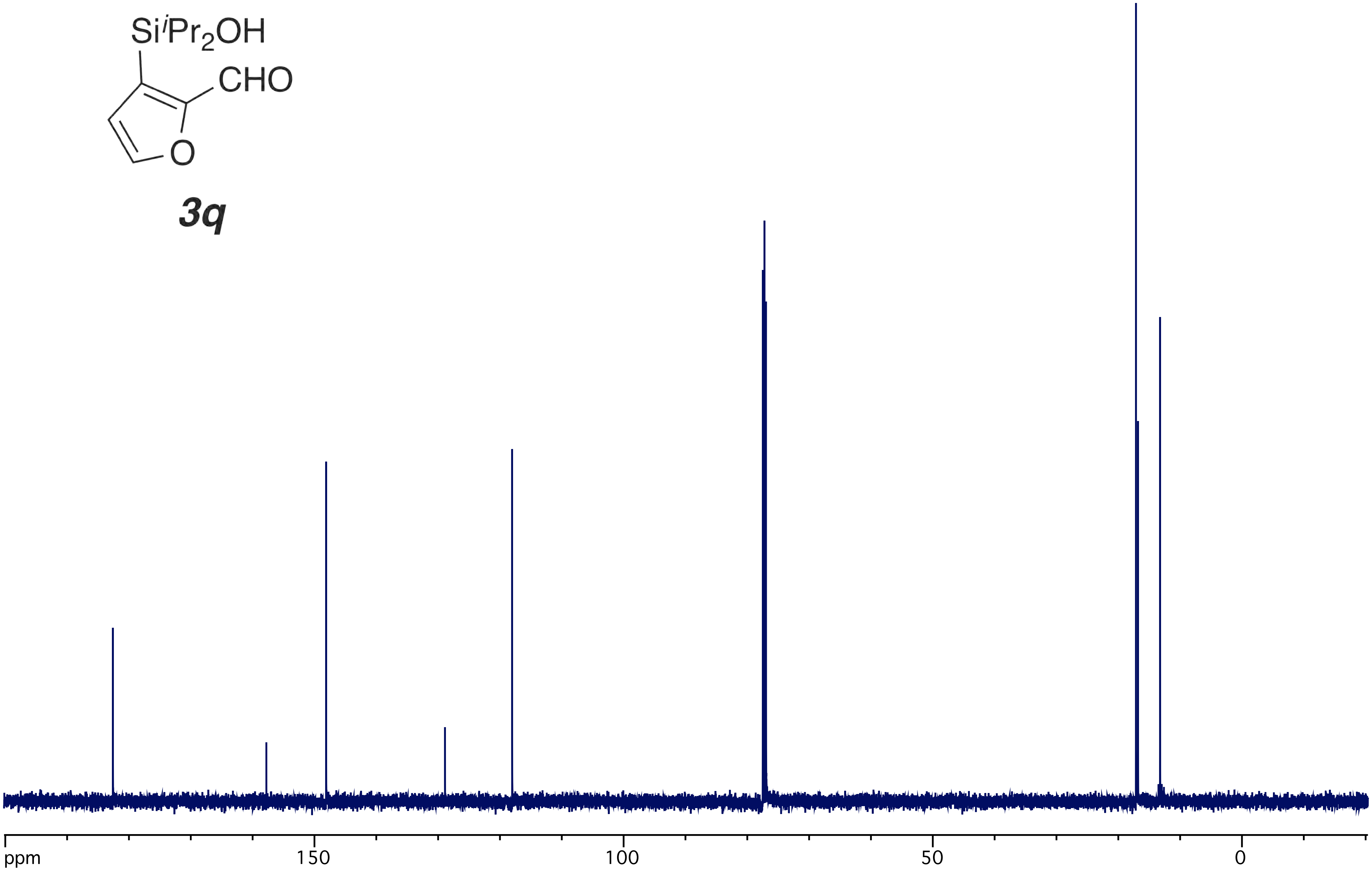
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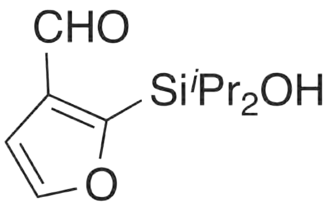

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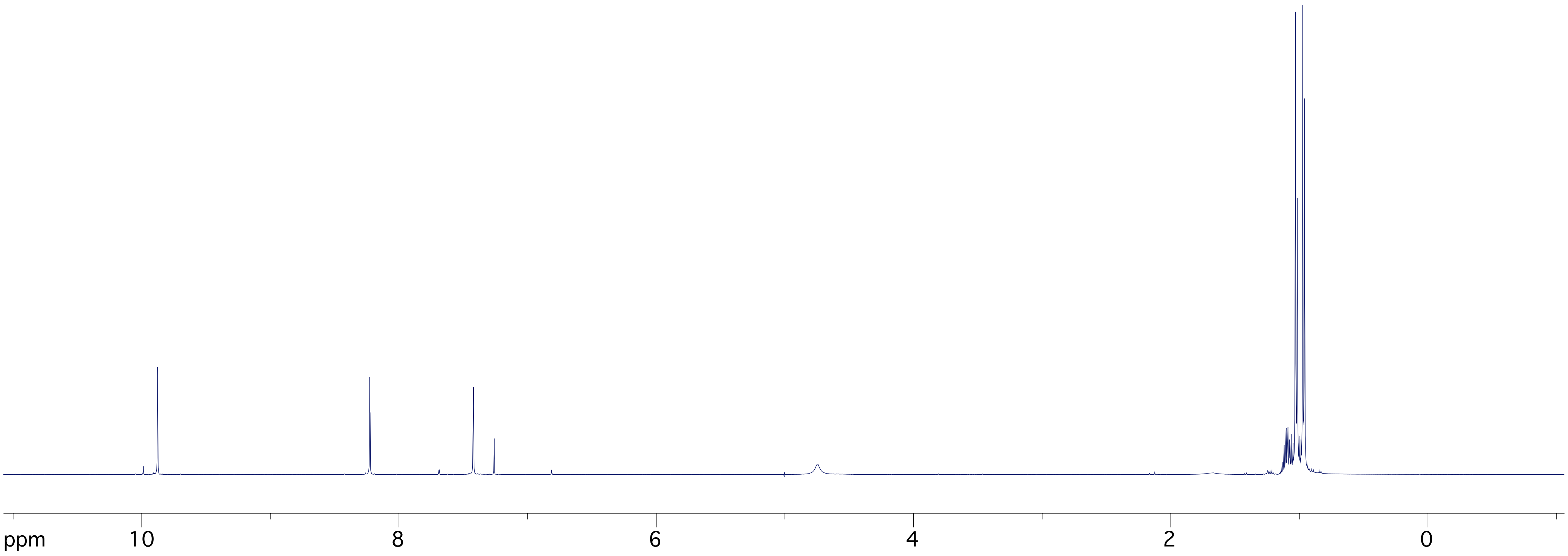

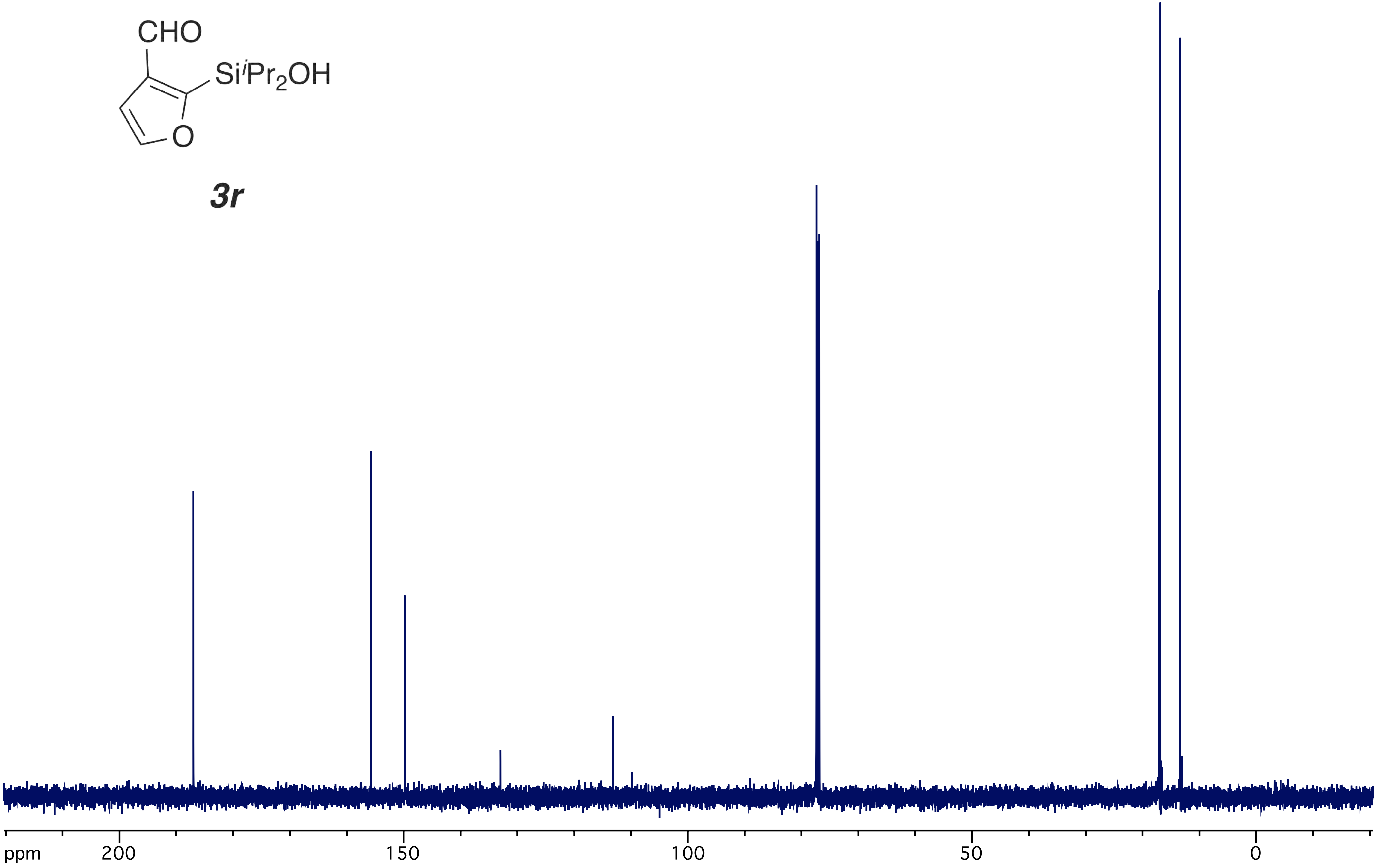

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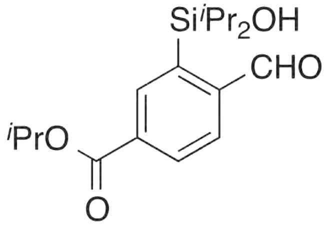
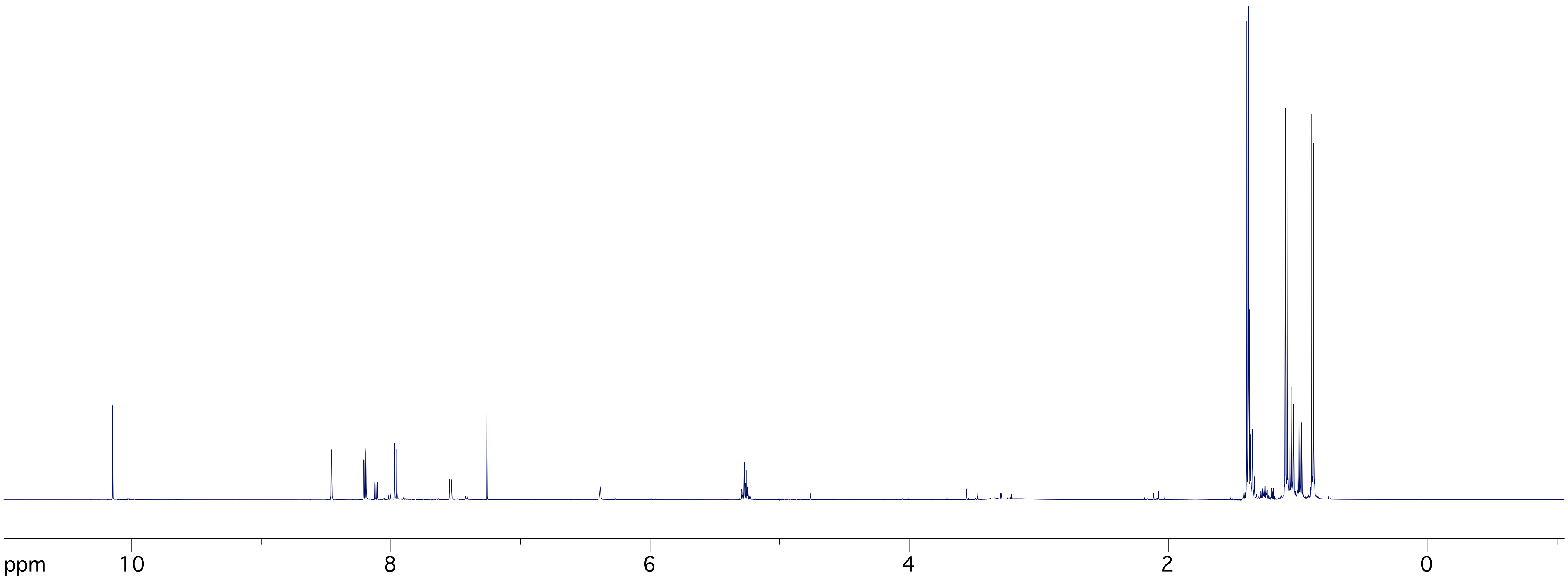
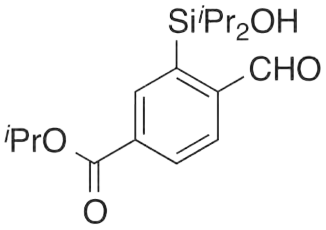
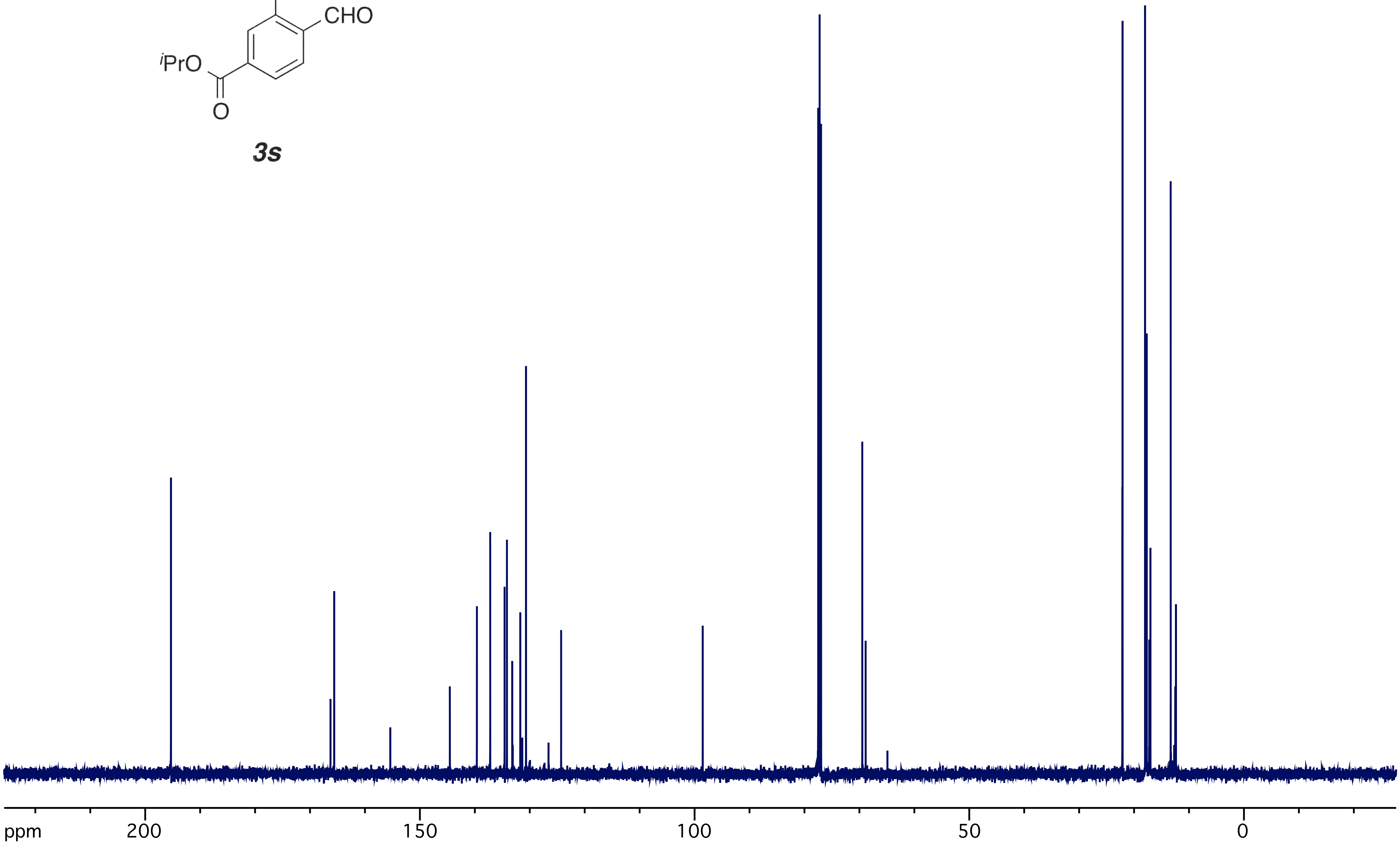


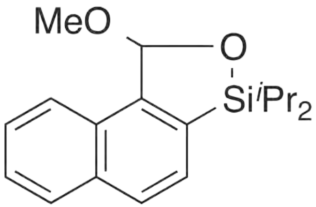
3s



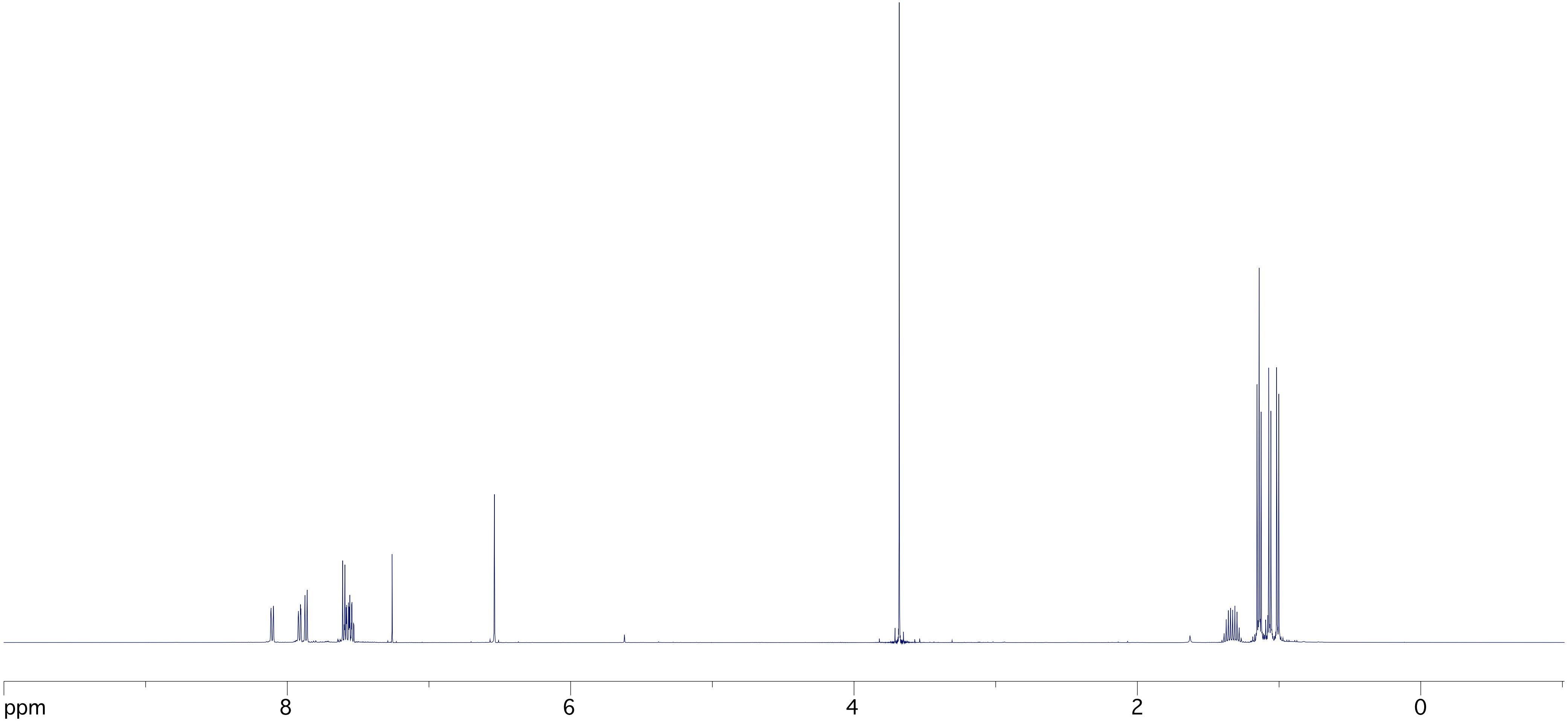


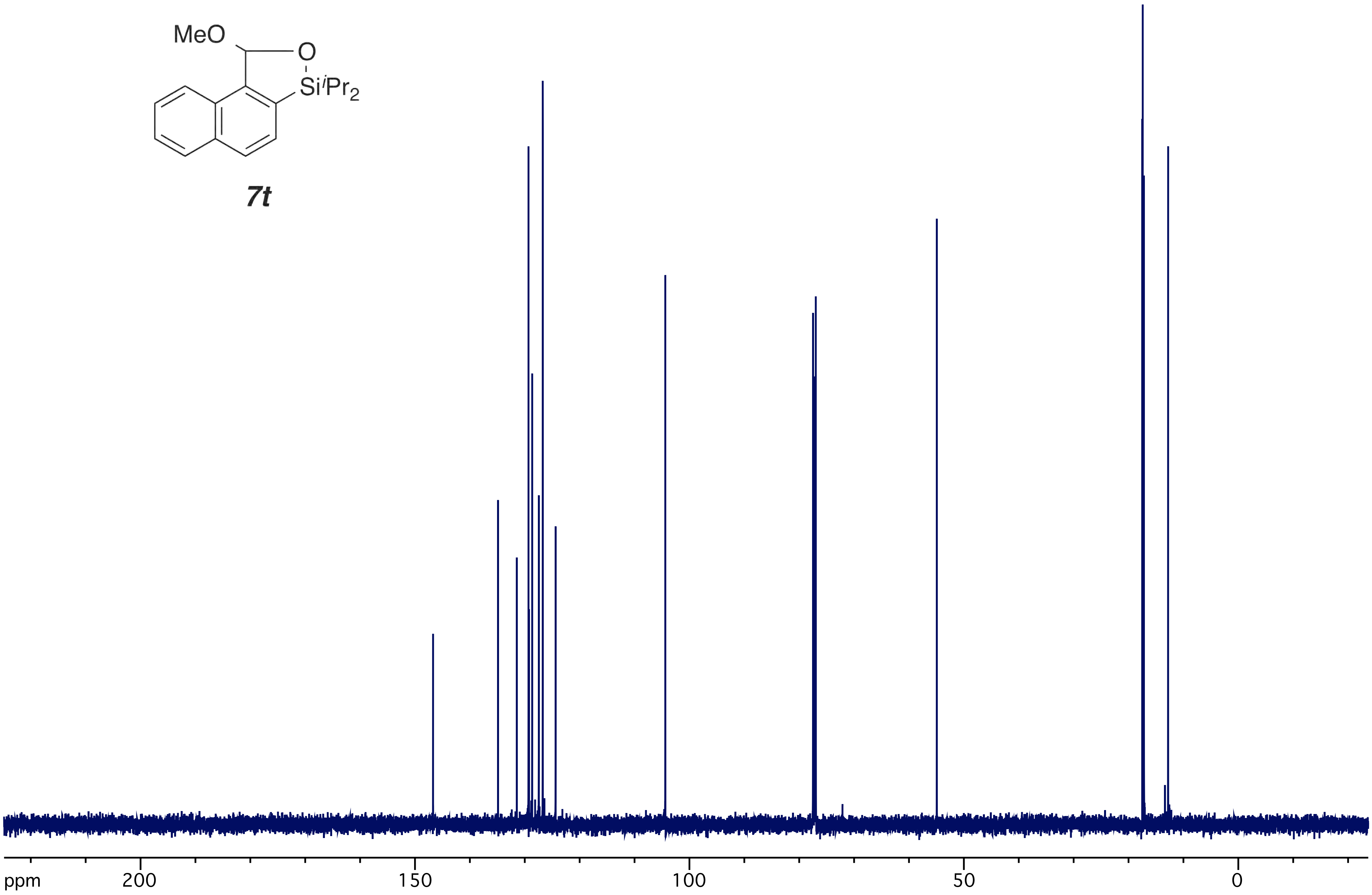
3s





7t





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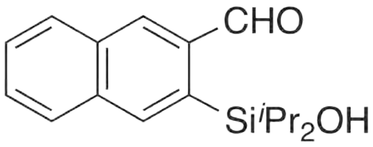
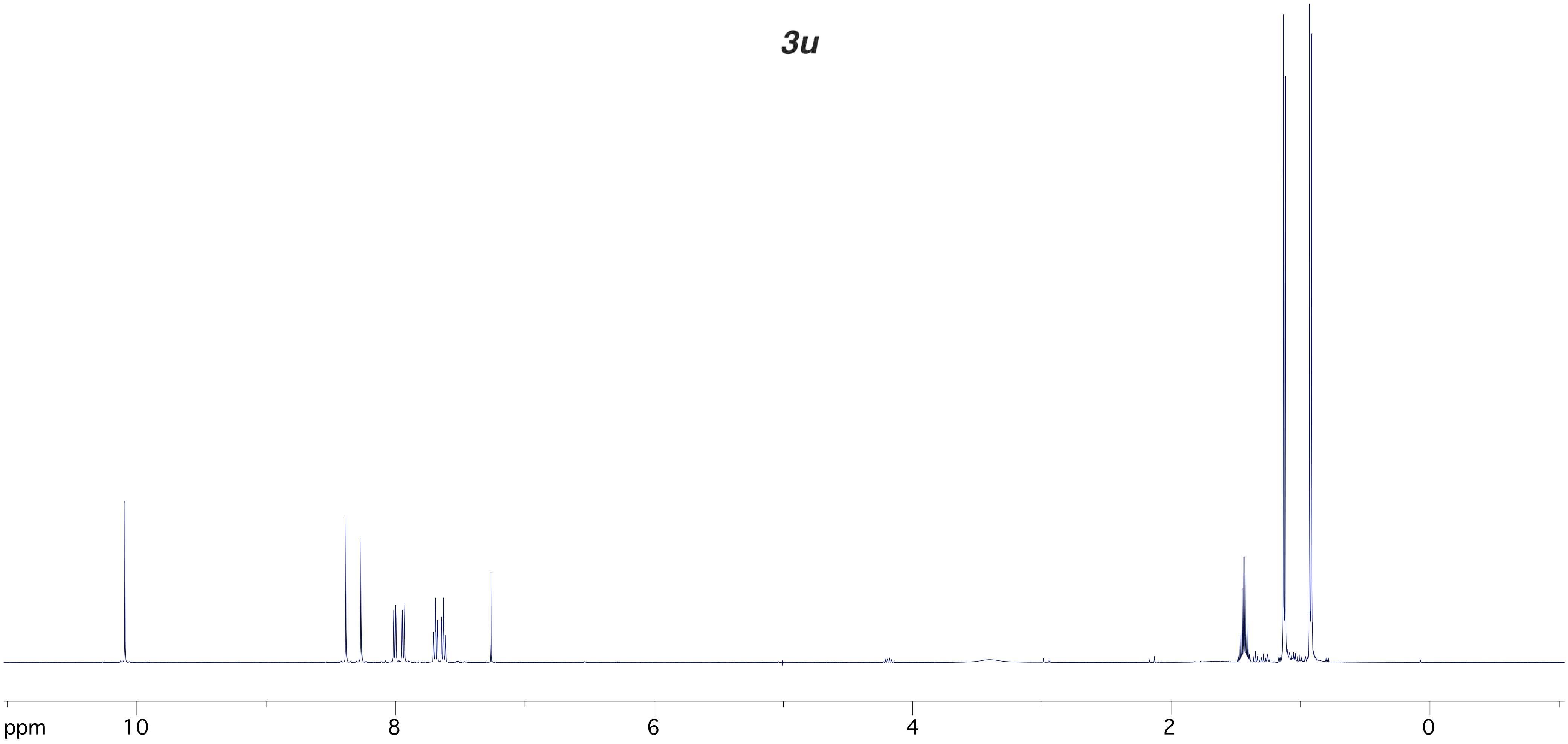


3u



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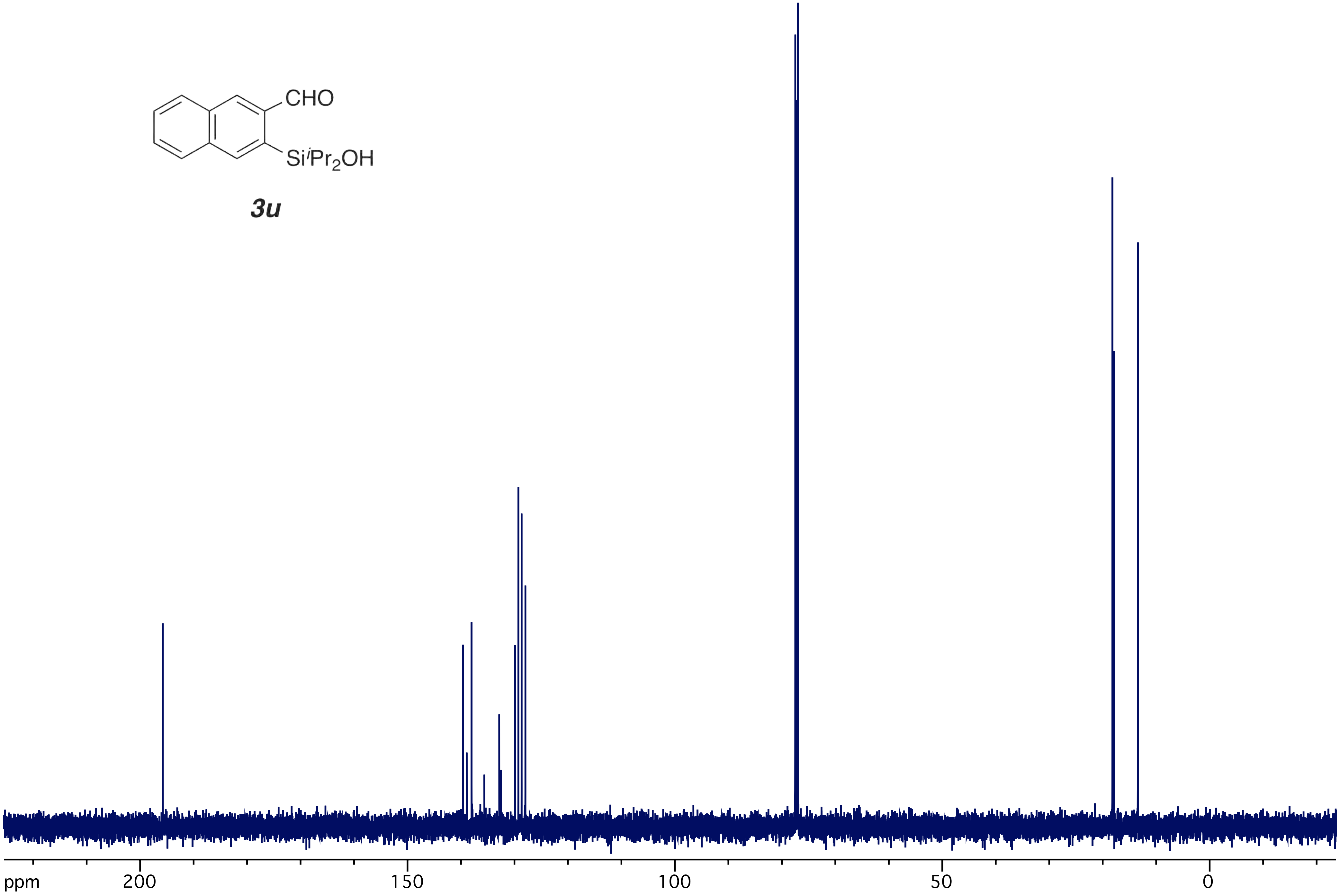
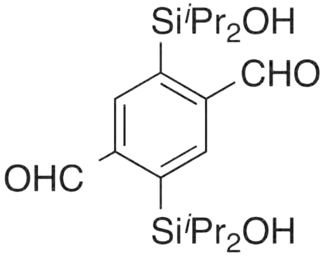
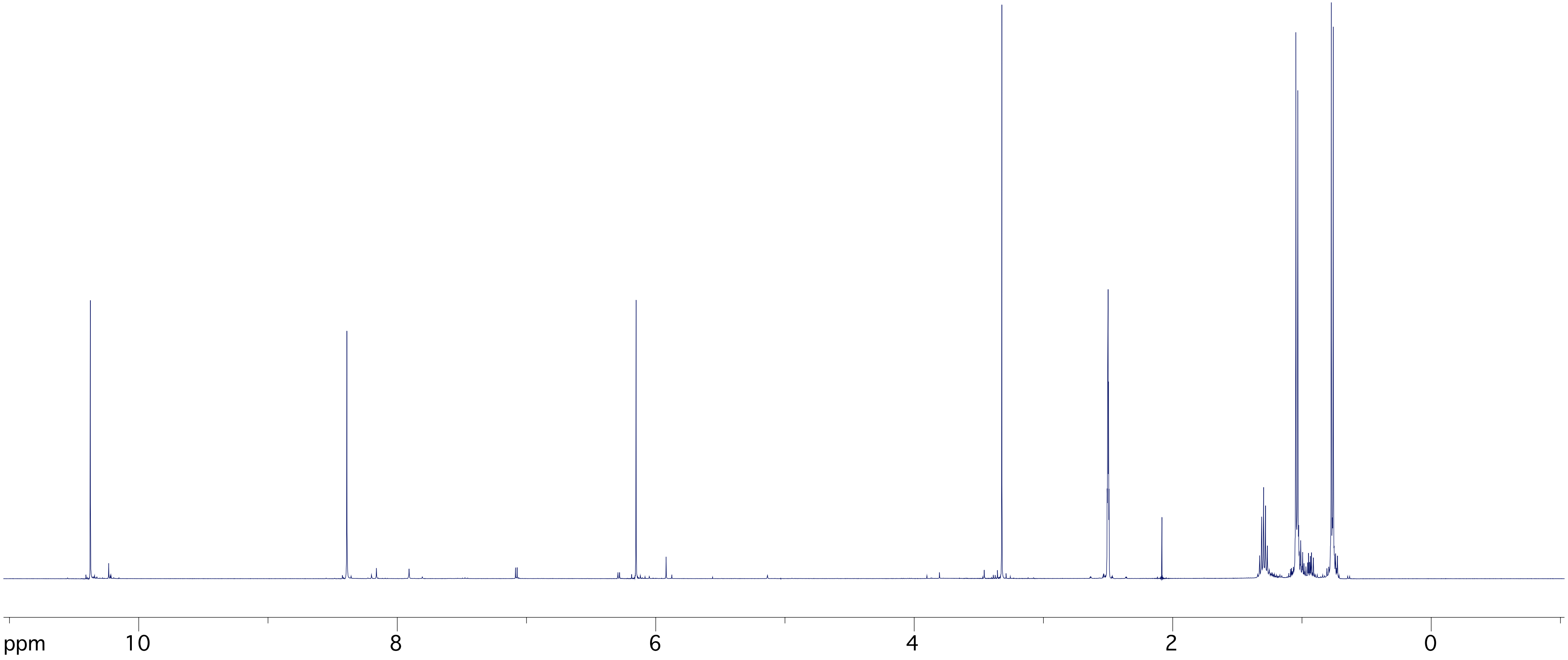
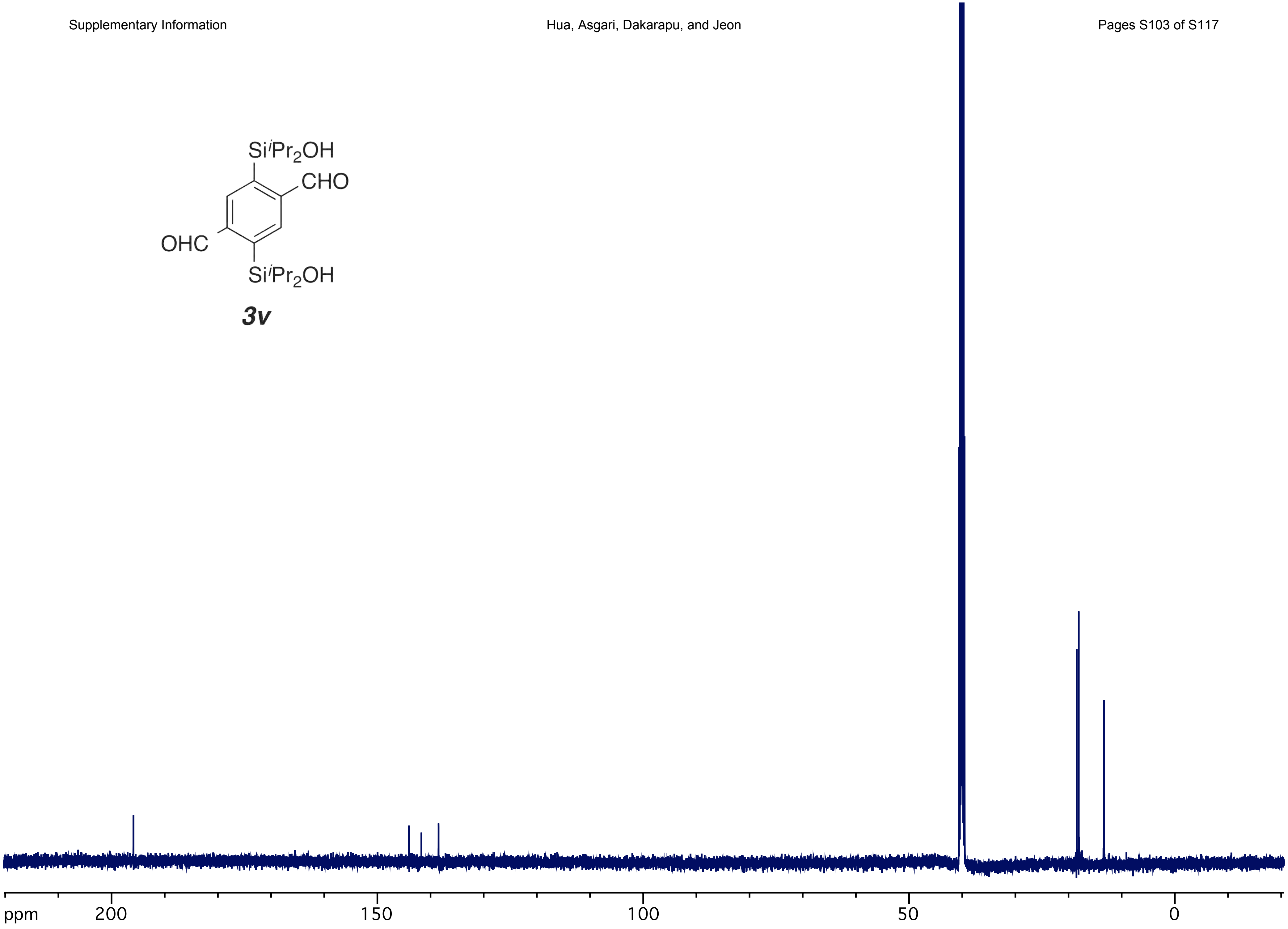




3v





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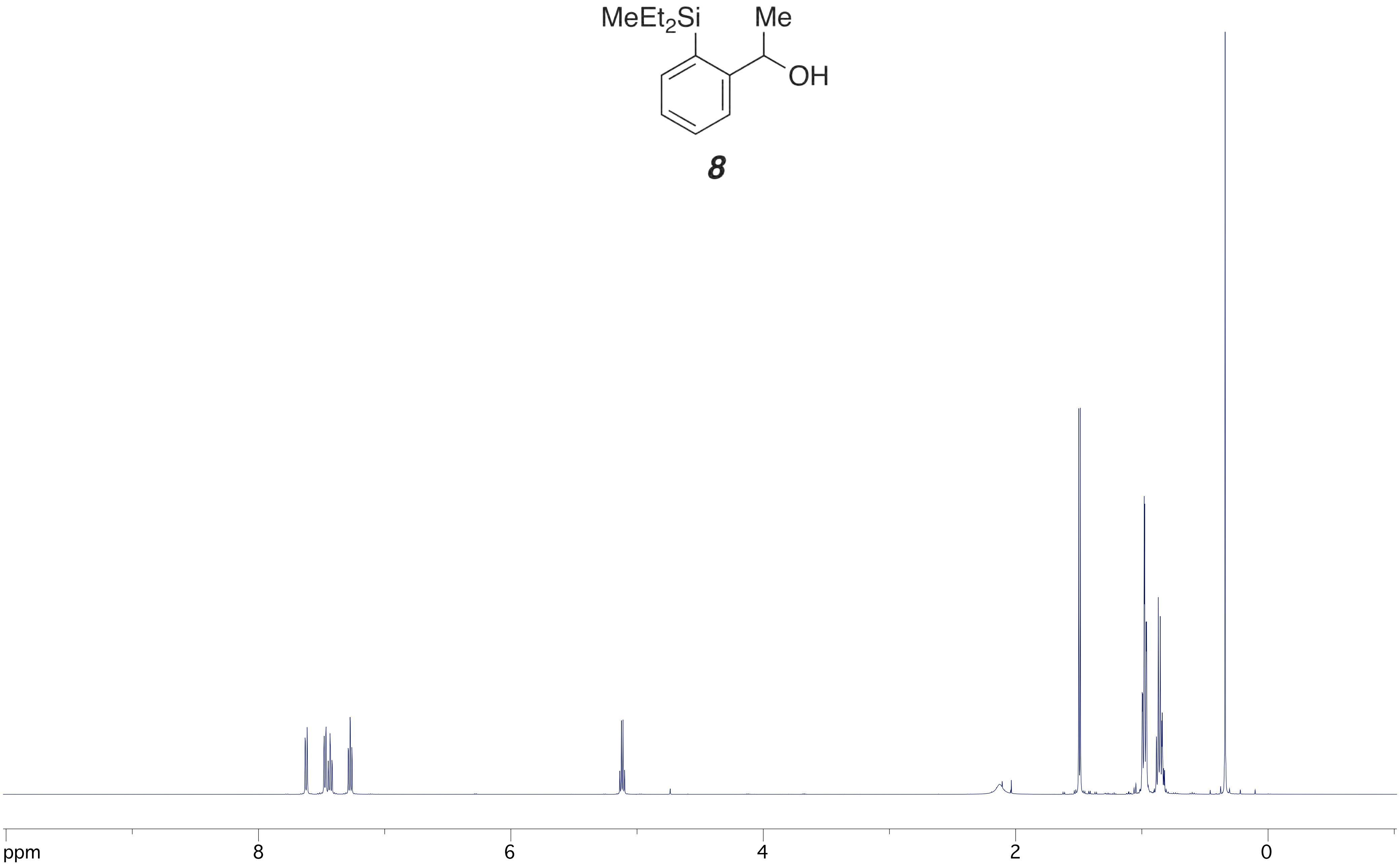
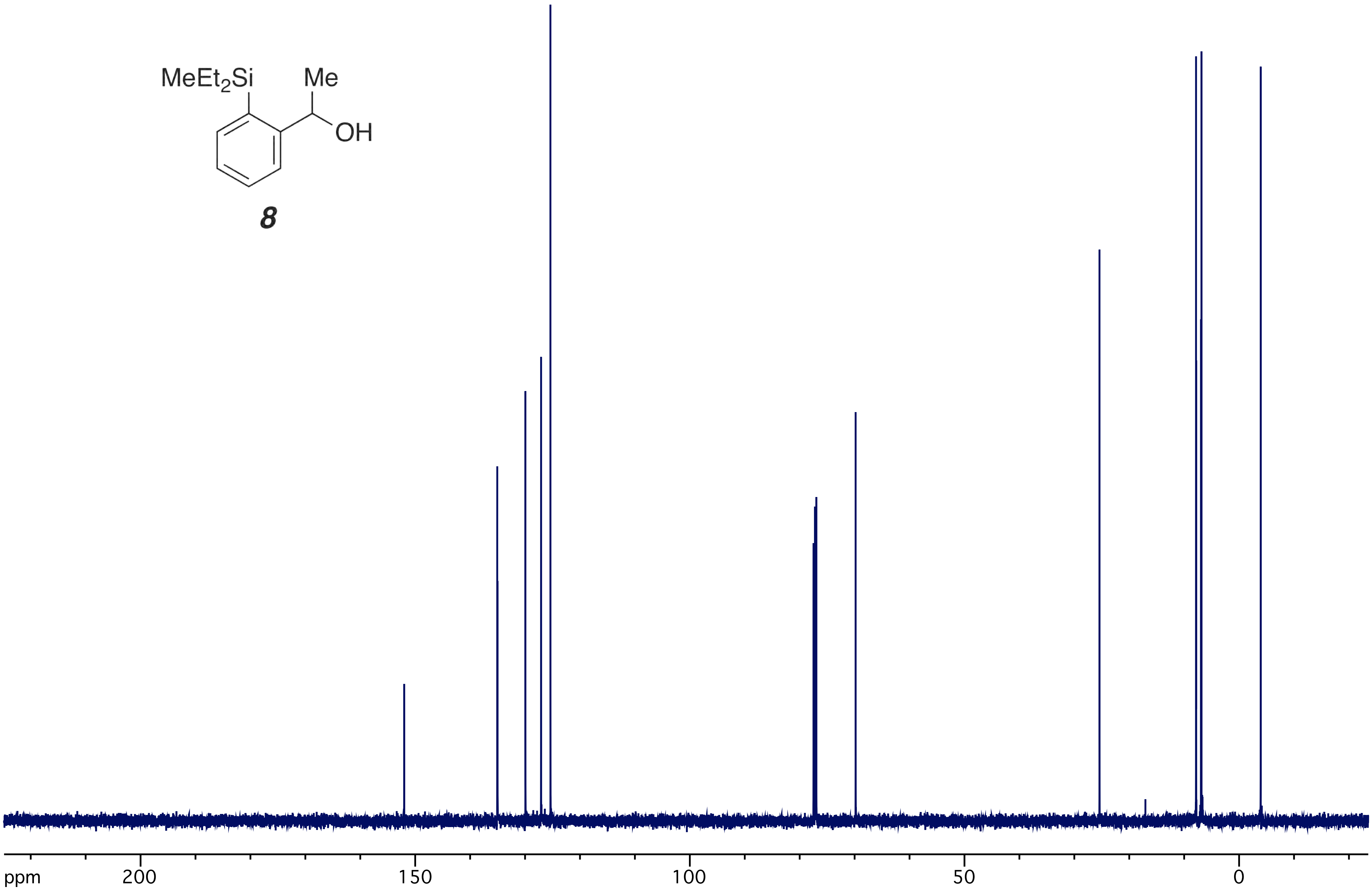
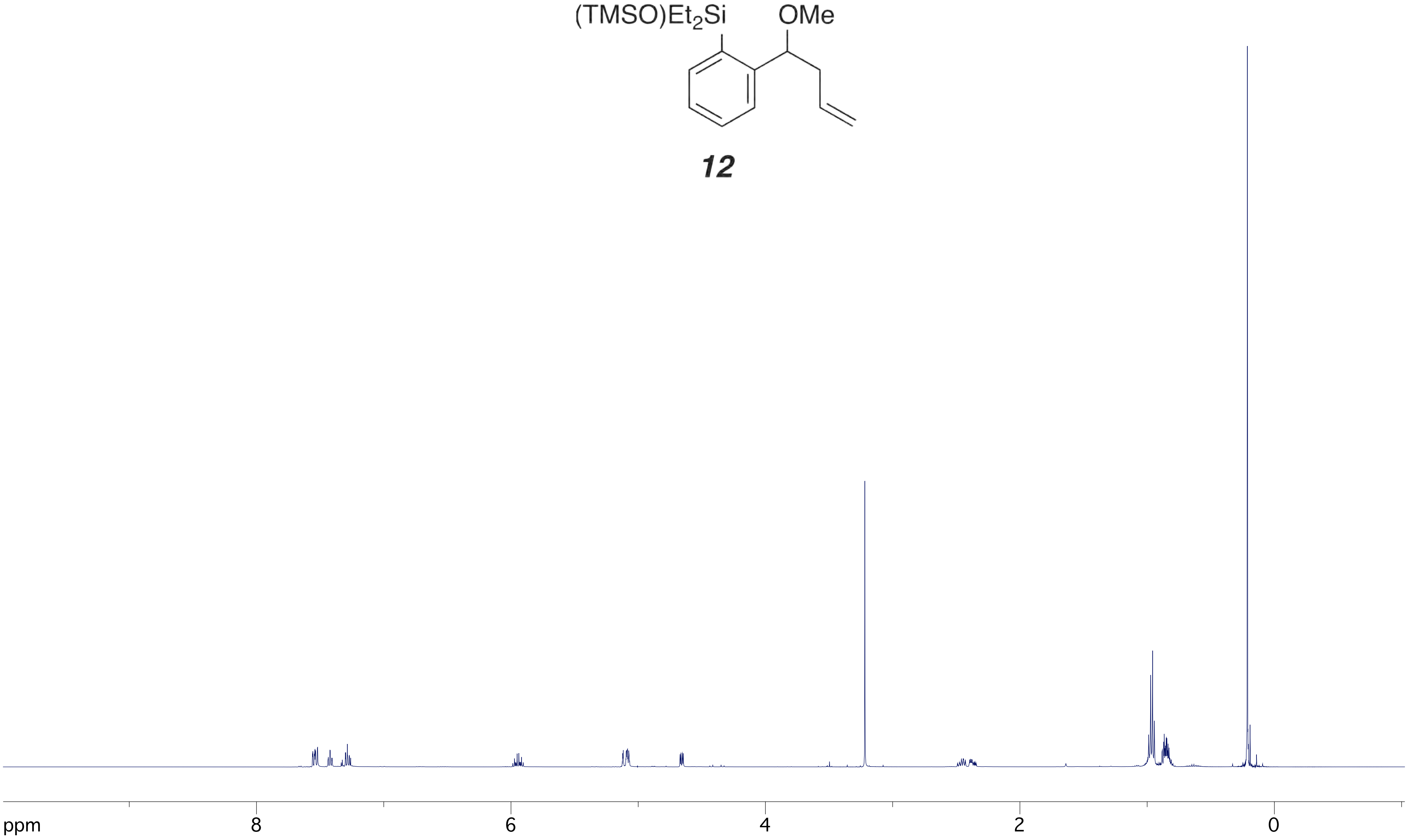
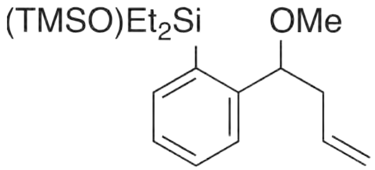


8

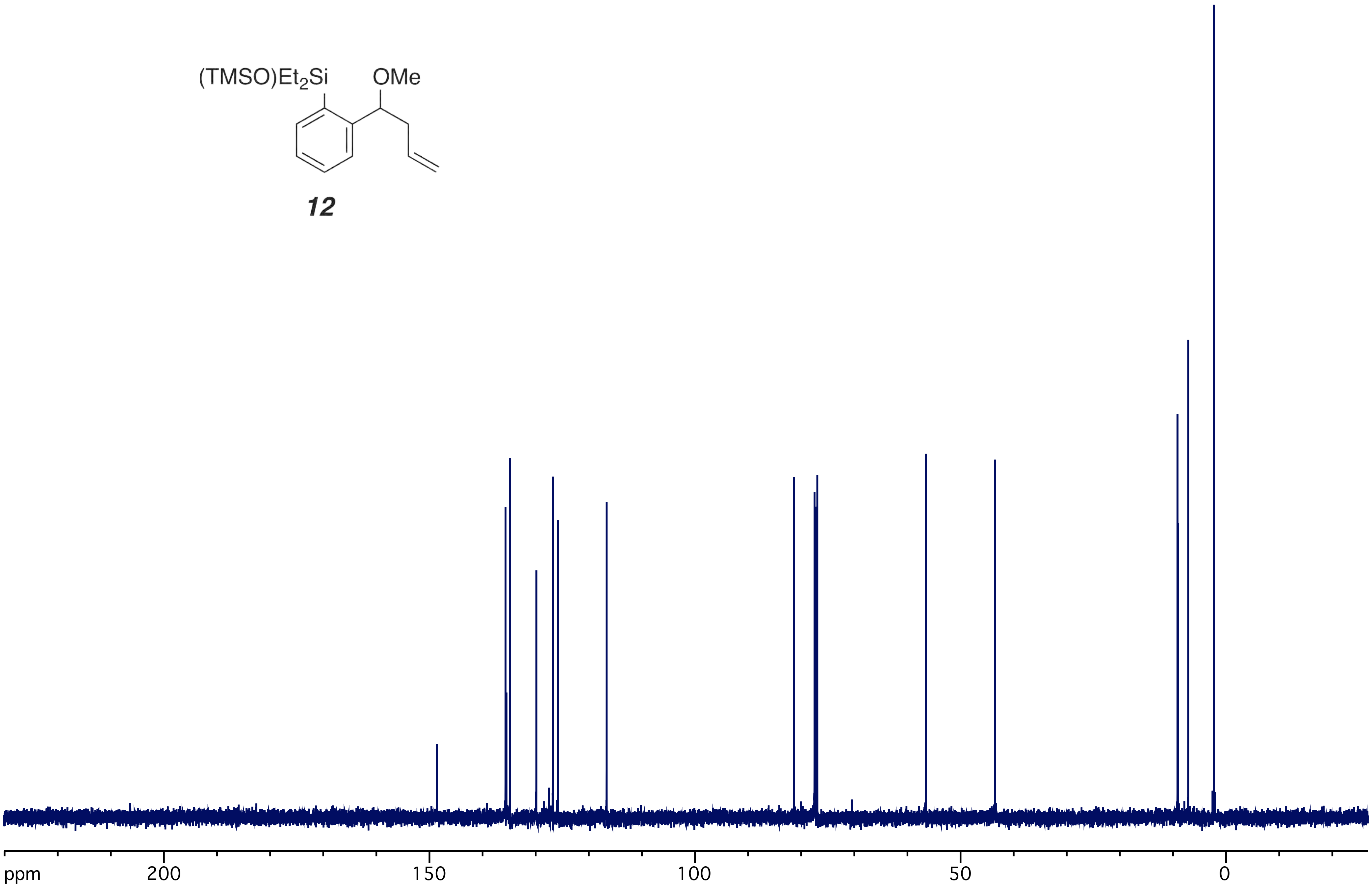


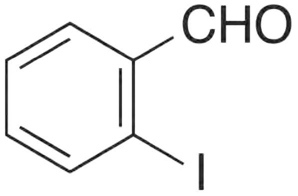
8


(TMSO)Et$_2$Si
OMe
12
ppm
8
6
4
2
0

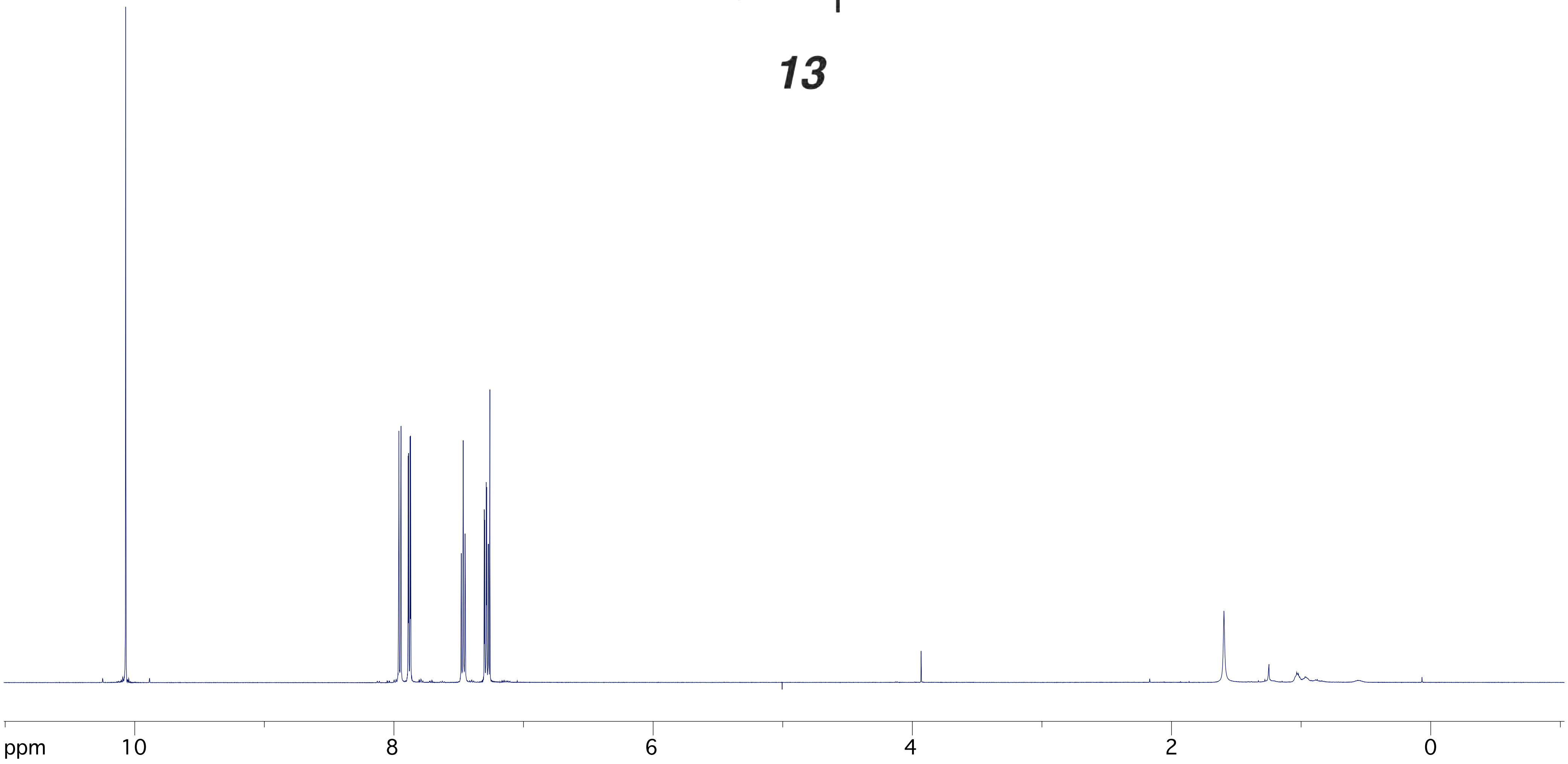


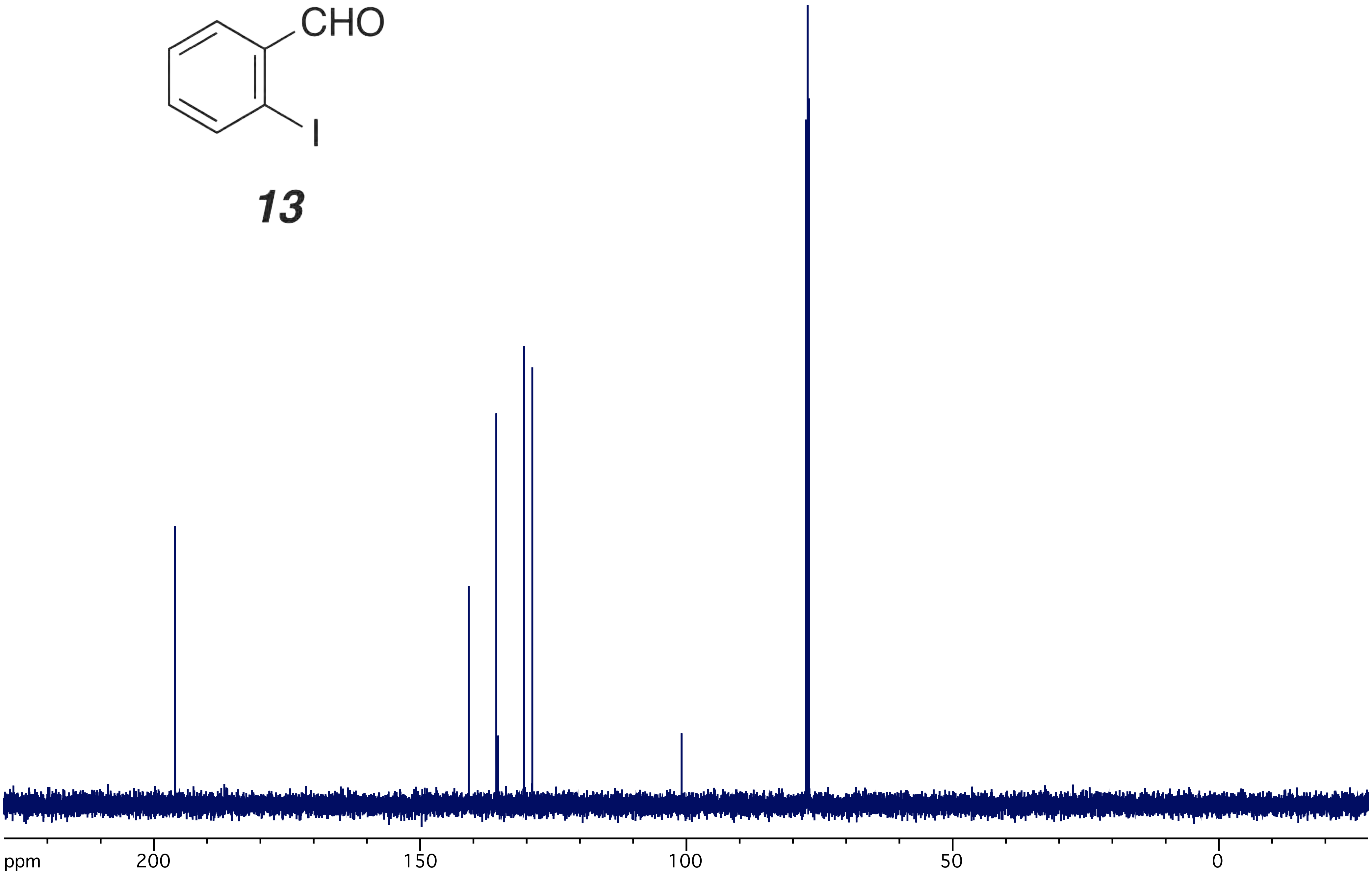
12



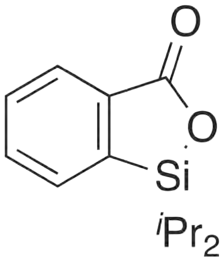


13

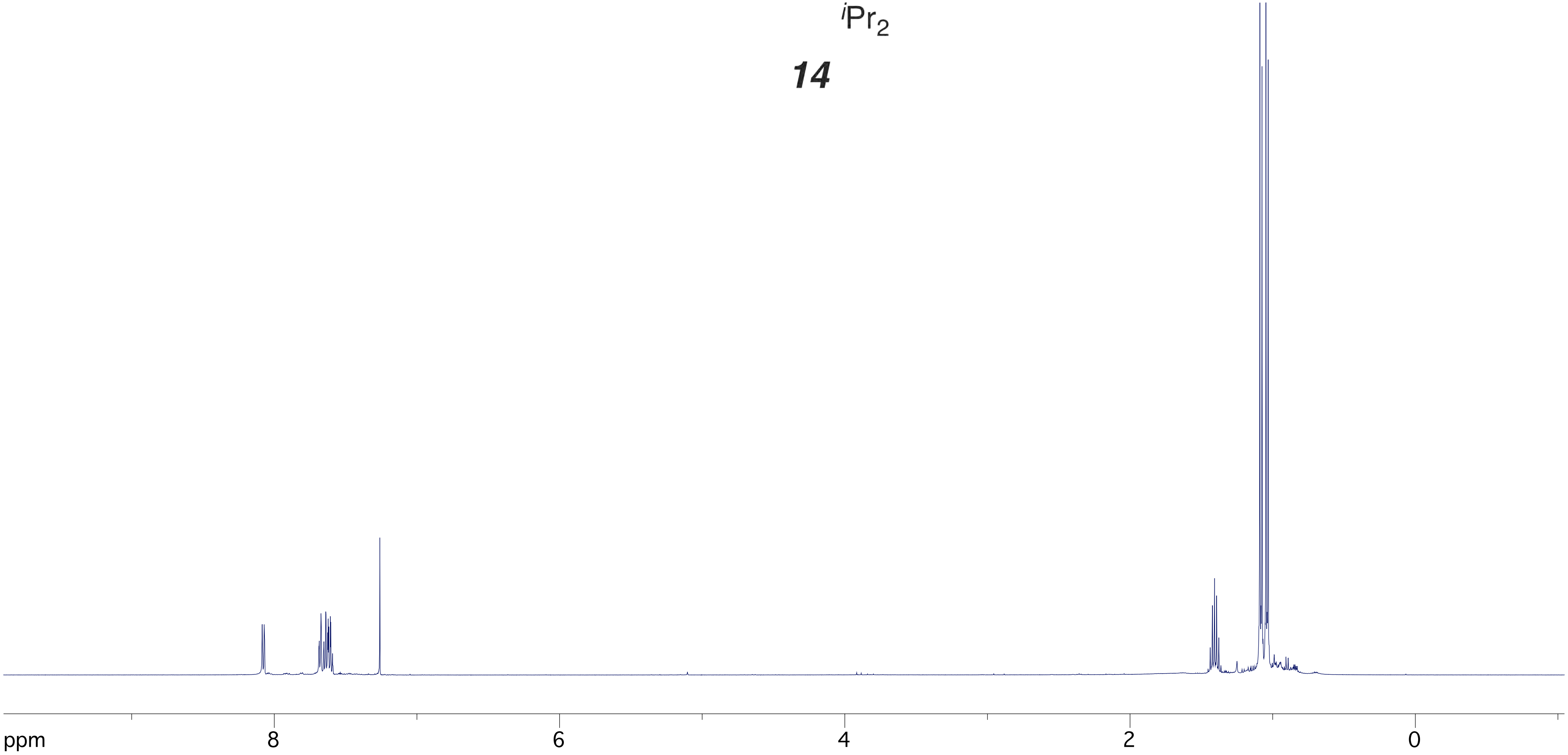


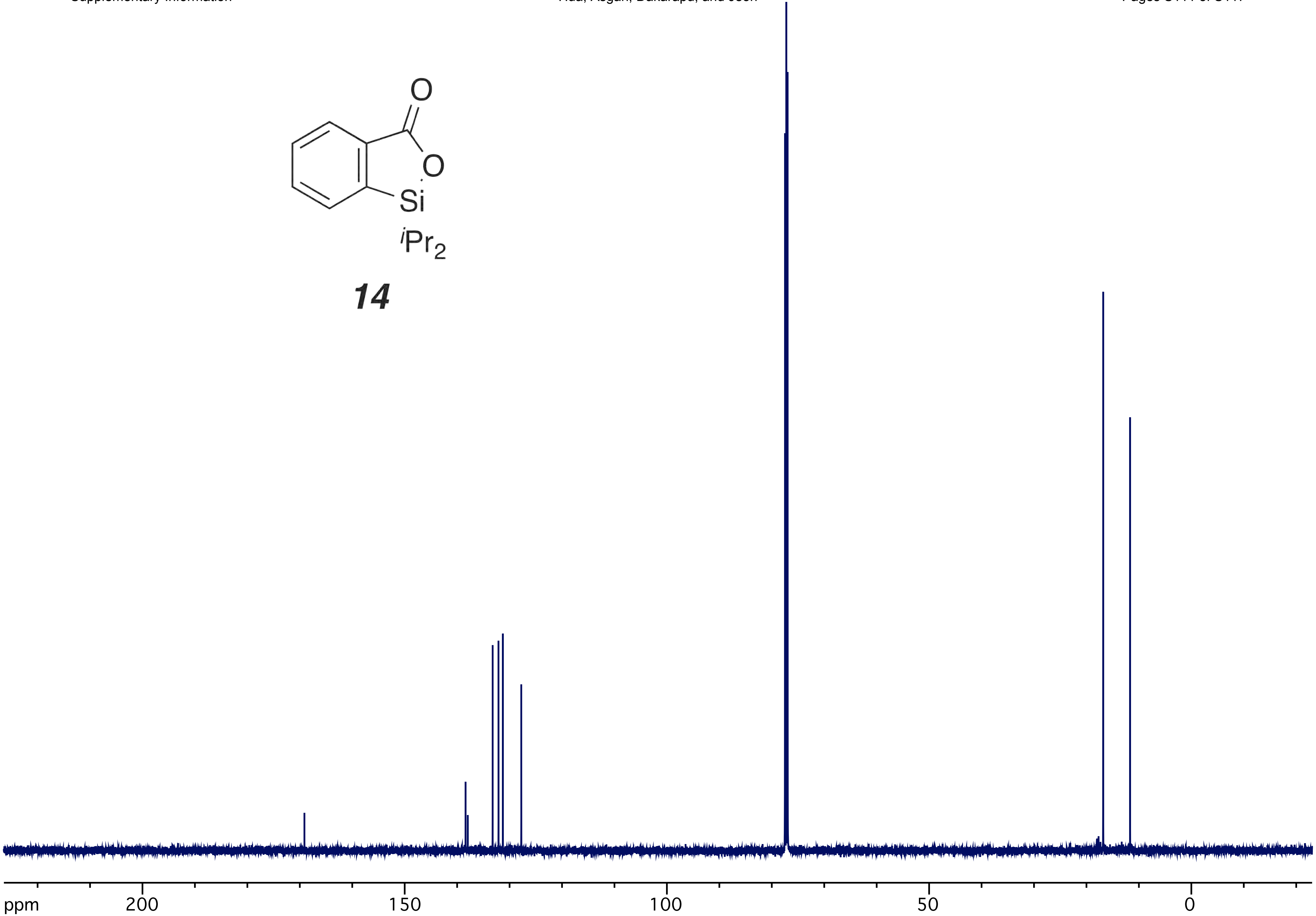


13

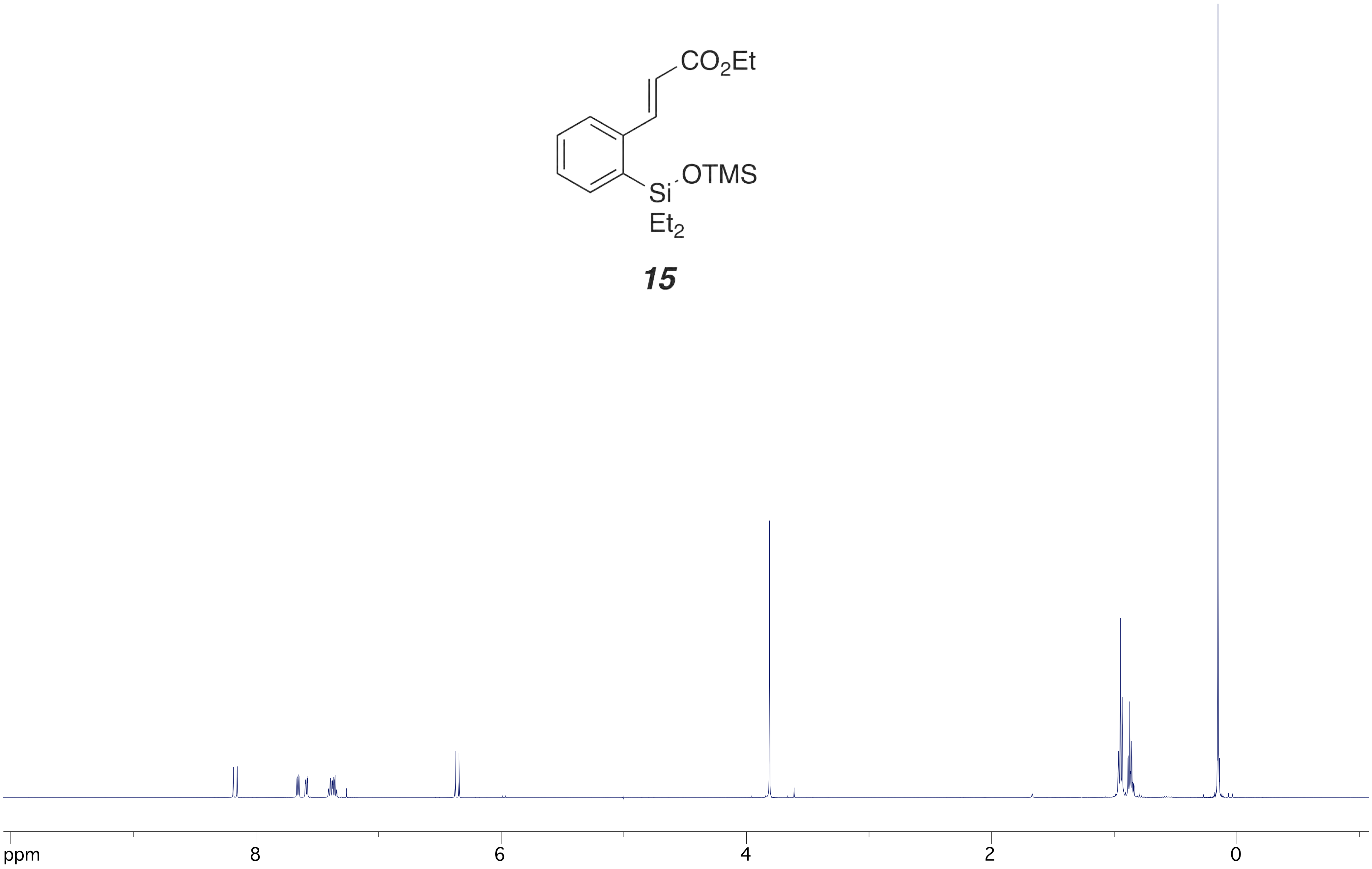


14

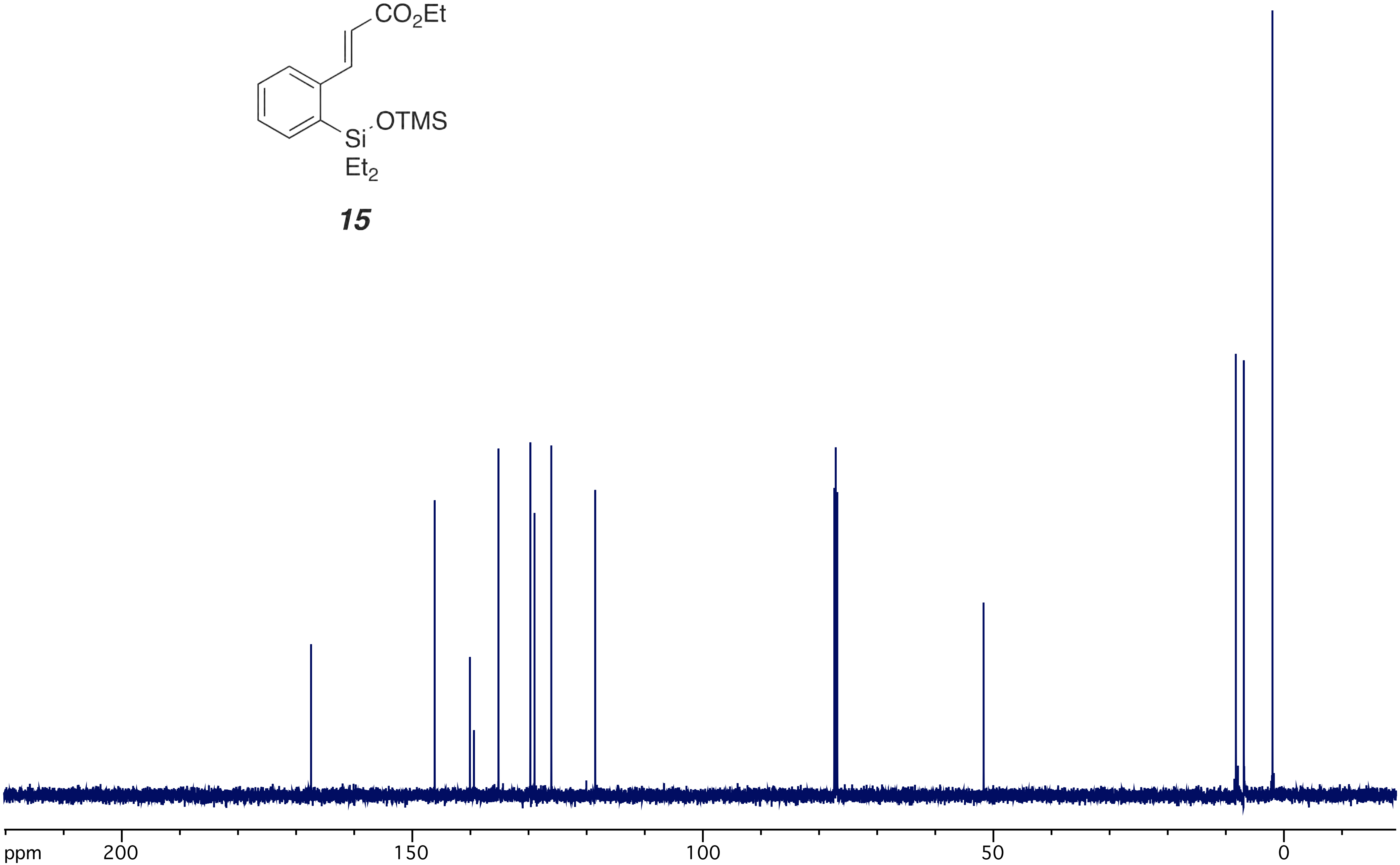




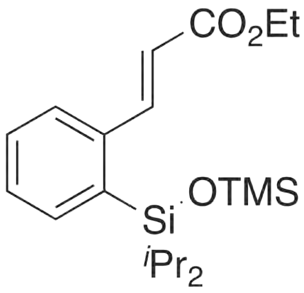
14



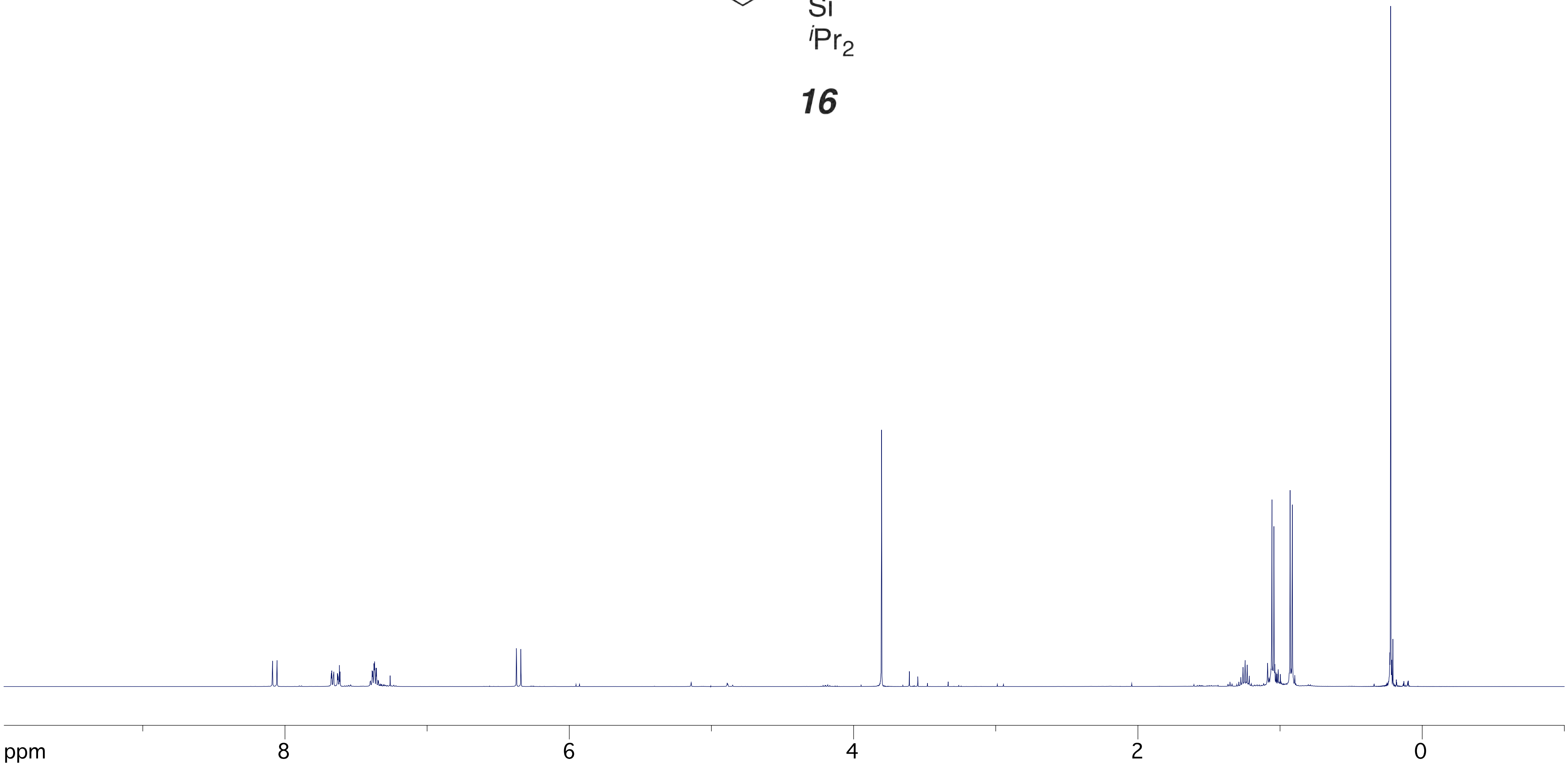
15

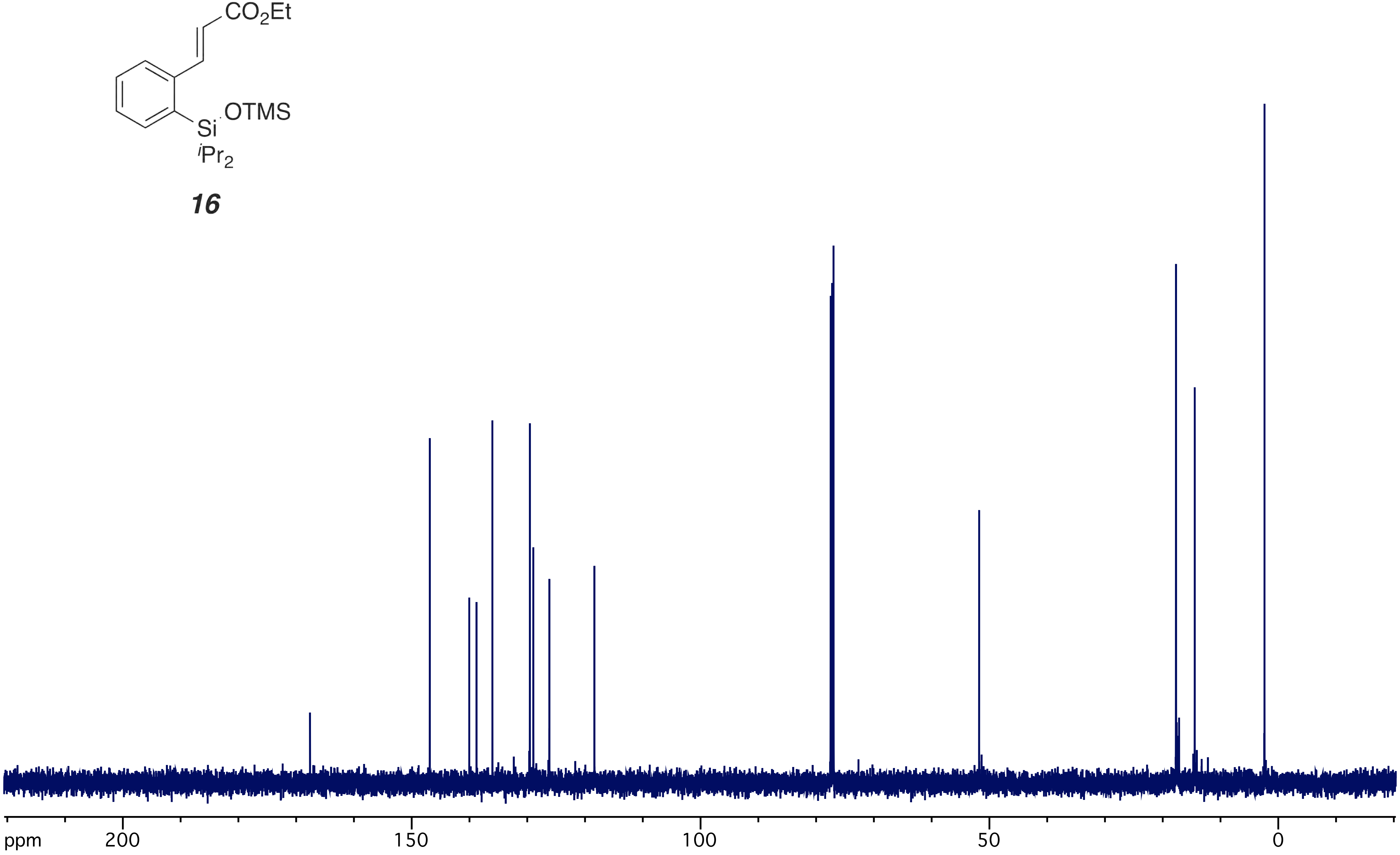


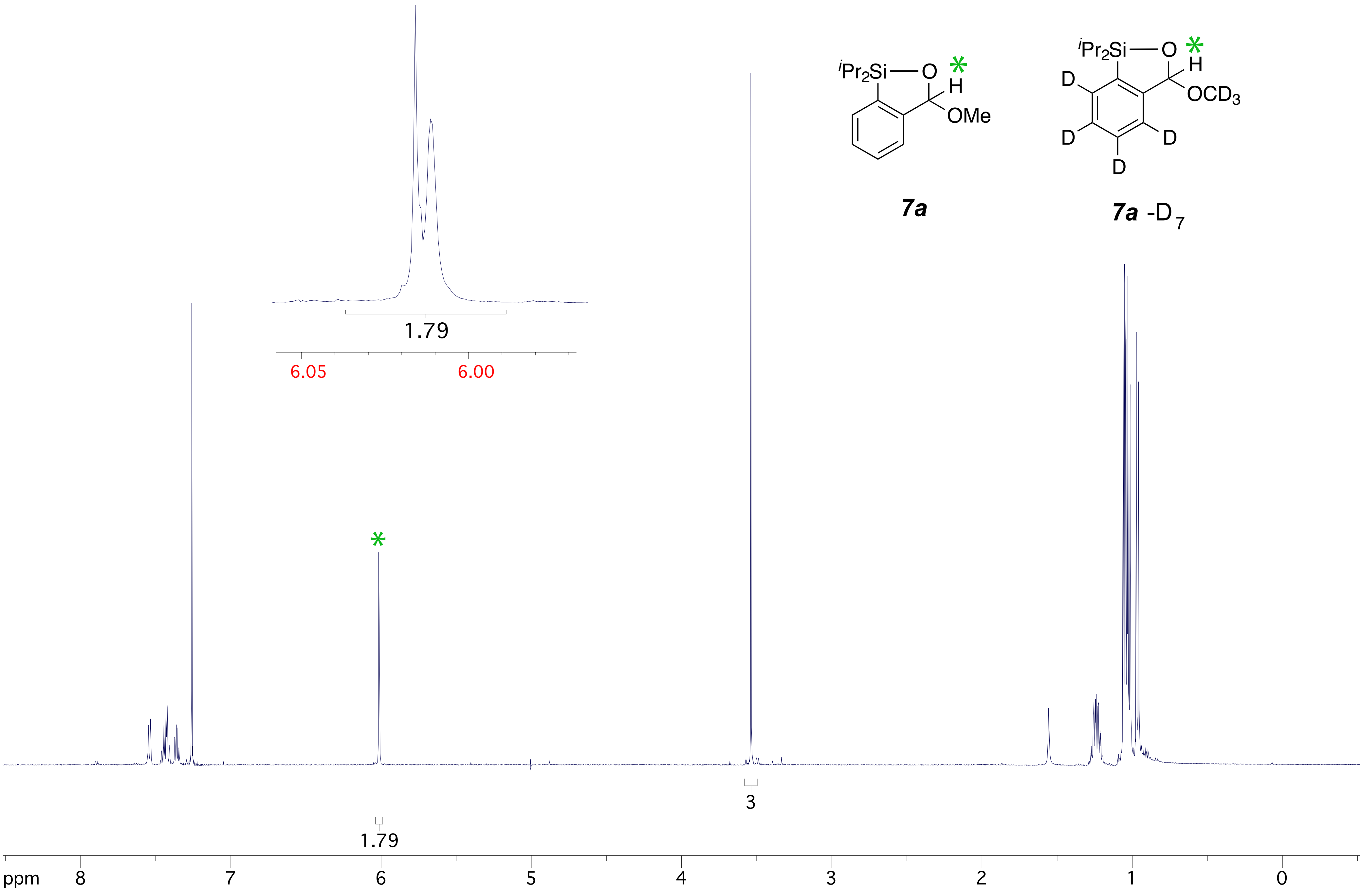
15

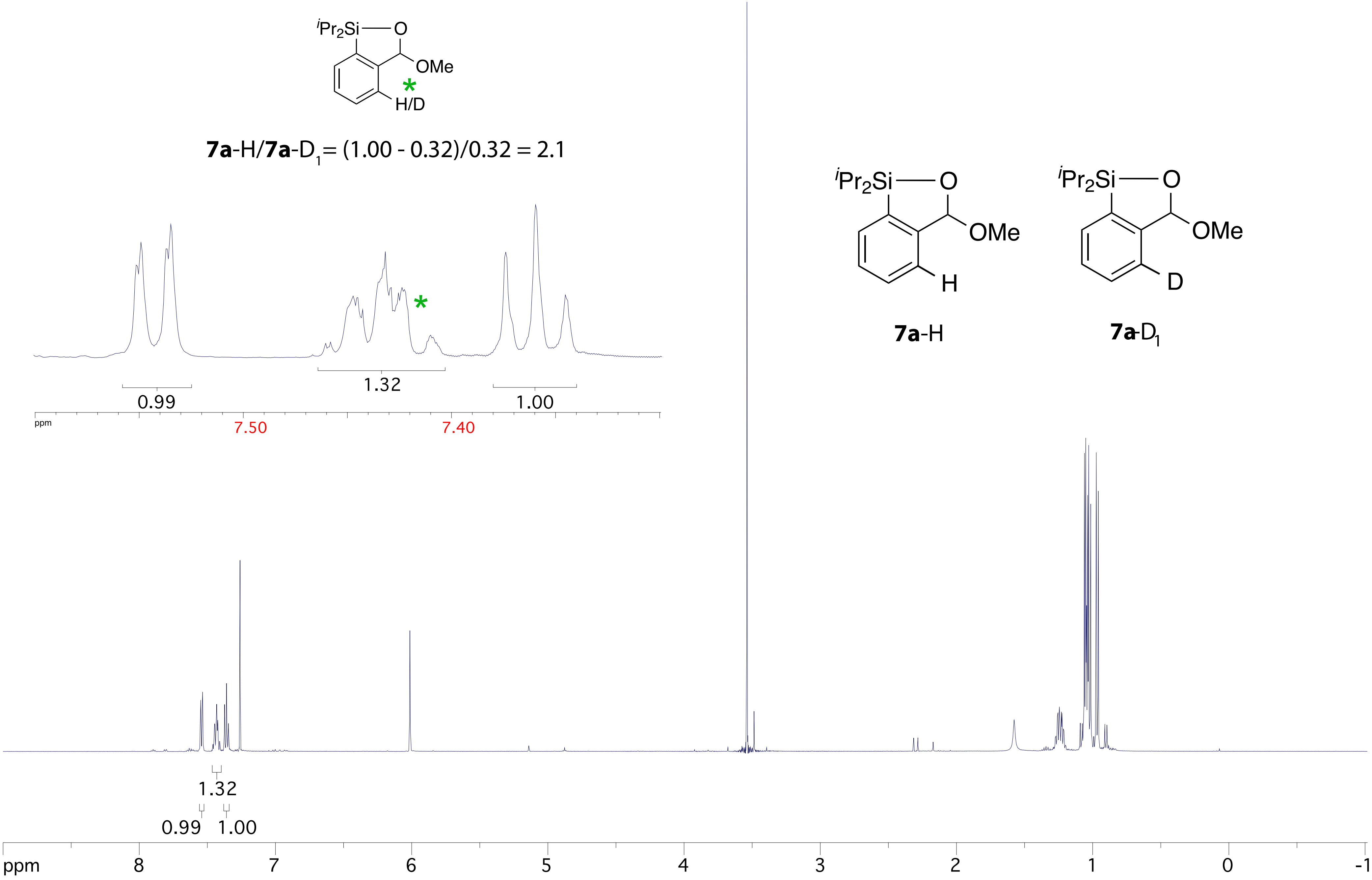


16




CO2Et
OTMS
Si
iPr2
16
ppm
200
150
100
50
0


*
1.79
6.05
6.00
^{i}Pr$_2$Si
O
*
H
OMe
7a
^{i}Pr$_2$Si
O
*
H
OCD$_3$
D
D
D
D
7a -D$_7$
*
3
1.79
ppm
8
7
6
5
4
3
2
1
0



7a-H/**7a**-D_1 = (1.00 - 0.32)/0.32 = 2.1