Nickel-Catalyzed Remote Hydrosilylation of Unconjugated Enones with Bulky Triphenylsilane

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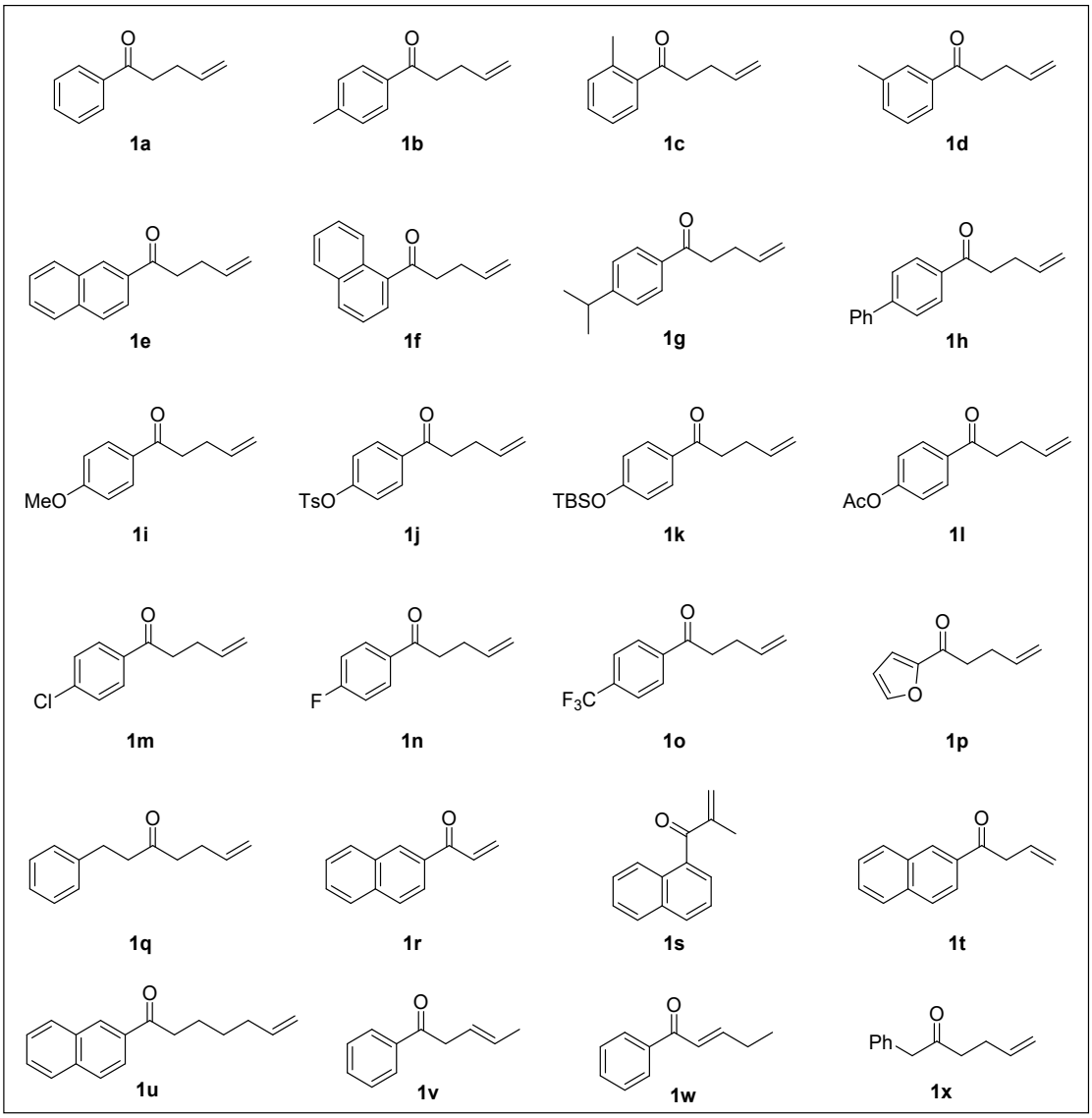
1. General Information

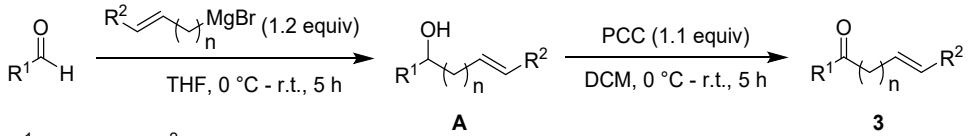
Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. All commercially available reagents were obtained from chemical suppliers and used after proper purification if necessary. Flash column chromatography was performed on silica gel (200-300 mesh) with the indicated solvent mixtures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 AV or 500 AV spectrometers. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad, h = sixtet and all combinations thereof can be explained by their integral parts. Coupling constant (*J*) was reported in hertz unit (Hz). The high resolution mass spectra (HRMS) were recorded on an Agilent 6210 LC/TOF spectrometer.

2. Preparation of Unconjugated Enones



General procedure:

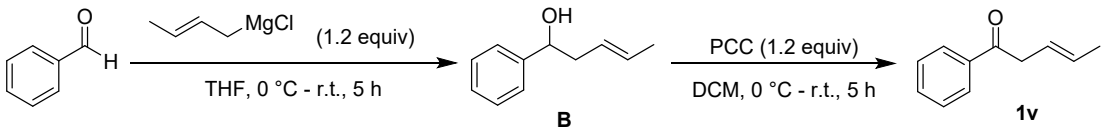


According to the known literature[1], aldehyde (5 mmol) was dissolved in 10 mL of dried THF in 50 mL Schlenk tube under N_2. The mixture was cooled to 0 °C and Grignard reagent (1.2 equiv) was added dropwise with stirring under ice bath. Then it was allowed to warm to room temperature and stirred for 5 h. After completion, the mixture was quenched with NH_4Cl (aq.). The aqueous layer was extracted with ethyl acetate (3×25 mL). The combined organic layers were

dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel to give the desired products **A**.

Products **A** (3 mmol) was dissolved in 10 mL DCM in round bottom flask, PCC (1.2 equiv) was added into solution in batches with stirring under ice bath. Then it was allowed to warm to room temperature and stirred for 5 h. After completion, the aqueous layer was extracted with DCM (3×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel to give the desired products. Substrates **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1o**, **1p**, **1q**, **1r**, **1s**, **1t**, **1u**, and **1x** were prepared according to the general procedure.

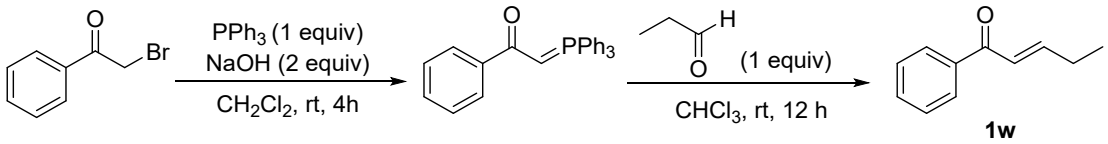
Procedure for the preparation of 1v.



According to the known literature[2], aldehyde (5 mmol) was dissolved in 10 mL of dried THF in 50 mL Schlenk tube under N_2. The mixture was cooled to 0 °C and Grignard reagent (1.2 equiv) was added dropwise with stirring under ice bath. Then it was allowed to warm to room temperature and stirred for 5 h. After completion, the mixture was quenched with NH_4Cl (aq.). The aqueous layer was extracted with ethyl acetate (3×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel to give the desired product **B**.

Product **B** (3 mmol) was dissolved in 10 mL DCM in round bottom flask, PCC (1.2 equiv) was added into solution in batches with stirring under ice bath. Then it was allowed to warm to room temperature and stirred for 5 h. After completion, the aqueous layer was extracted with DCM (3×25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel to give the product **1v**.

Procedure for the preparation of 1w.

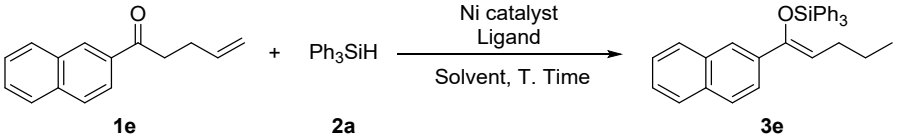


1w

According to the known literature[3]，To a solution of α-bromoacetophenone (990 mg, 5 mmol) in CH_2Cl_2 (10 ml) was added triphenylphosphine (1.31 g, 5 mmol) slowly at room temperature. The solution was allowed to stir for 4 h, and the resulting mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 : H_2O (12 mL, 4:6) and NaOH (400 mg, 10 mmol) was added. Then the mixture was stirred at room temperature for 1 h before being extracted with CH_2Cl_2 (3 x 15 mL). The combine organic extracts were washed with brine (3 x 25 mL), dried, filtered and concentrated under vacuum to give the crude mixture, which was used without further purification. To a solution of propionaldehyde (290 mg, 5 mmol) in $CHCl_3$ (10 mL) at room temperature was added the above mixture and the solution was allowed to stir for 12 h. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to provide the product **1w.**

3. Nickel-Catalyzed Remote Hydrosilylation of Unconjugated Enones with Bulky Triphenylsilane

3.1 Optimization of reaction conditions[a]



1e **2a** **3e**

Entry	Catalyst/mol%	Ligand/equiv	Solvent/mL	T/°C	Time/h	**1e**:**2a**	Yield[b]/%
1	$NiCl_2$/10	*t*-BuNC/0.5	Xylene/2	120	12	1:2	73
2	$NiCl_2$·dme/10	*t*-BuNC/0.5	Xylene/2	120	12	1:2	70
3	$Ni(acac)_2$/10	*t*-BuNC/0.5	Xylene/2	120	12	1:2	64
4	$NiBr_2$/10	*t*-BuNC/0.5	Xylene/2	120	12	1:2	18
5	$Ni(OTf)_2$/10	*t*-BuNC/0.5	Xylene/2	120	12	1:2	NR
6	NiI_2/10	*t*-BuNC/0.5	Xylene/2	120	12	1:2	NR
7	-[c]	*t*-BuNC/0.5	Xylene/2	120	12	1:2	NR
8	$Ni(PCy_3)Cl_2$/10	-[d]	Xylene/2	120	12	1:2	NR
9	$Ni(dppp)Cl_2$/10	-[d]	Xylene/2	120	12	1:2	NR
10	$NiCl_2$/10	AdNC/0.5	Xylene/2	120	12	1:2	70
11	$NiCl_2$/10	Dmbpy	Xylene/2	120	12	1:2	NR
12	$NiCl_2$/10	Tpy	Xylene/2	120	12	1:2	NR
13	$NiCl_2$/10	PhNC	Xylene/2	120	12	1:2	NR
14	$NiCl_2$/10	2,6-Lutidine	Xylene/2	120	12	1:2	NR
15	$NiCl_2$/10	*t*-BuNC/0.5	Toluene/2	120	12	1:2	51
16	$NiCl_2$/10	*t*-BuNC/0.5	THF/2	120	12	1:2	26
17	$NiCl_2$/10	*t*-BuNC/0.5	MeCN/2	120	12	1:2	NR
18	$NiCl_2$/10	*t*-BuNC/0.5	1,4-Dioxane/2	120	12	1:2	Trace
19	$NiCl_2$/10	*t*-BuNC/0.5	DMF/2	120	12	1:2	NR
20	$NiCl_2$/5	*t*-BuNC/0.5	Xylene/2	120	12	1:2	31
21	$NiCl_2$/10	*t*-BuNC/1	Xylene/2	120	12	1:2	65
22	$NiCl_2$/10	*t*-BuNC/1.5	Xylene/2	120	12	1:2	67

23	$NiCl_2$/10	*t*-BuNC/0.3	Xylene/2	120	12	1:2	35
24	$NiCl_2$/10	*t*-BuNC/0.1	Xylene/2	120	12	1:2	5
25	$NiCl_2$/10	*t*-BuNC/0.5	Xylene/1	120	12	1:2	73
26	***$NiCl_2$/10***	***t-BuNC/0.5***	***Xylene/1***	***120***	***12***	***1：1.5***	***79***
27	$NiCl_2$/10	*t*-BuNC/0.5	Xylene/1	120	12	1:1.2	75
28	$NiCl_2$/10	*t*-BuNC/0.5	Xylene/1	120	12	1:1:	62
29	$NiCl_2$/10	*t*-BuNC/0.5	Xylene/1	120	12	1.5:1	32
30	$NiCl_2$/10	*t*-BuNC/0.5	Xylene/1	120	12	2:1	10
31	$NiCl_2$/10	*t*-BuNC/0.5	Xylene/1	150	12	1：1.5	57
32	$NiCl_2$/10	*t*-BuNC/0.5	Xylene/1	90	12	1：1.5	31
33	$NiCl_2$/10	*t*-BuNC/0.5	Xylene/1	r.t.	12	1：1.5	0
34	$NiCl_2$/10	*t*-BuNC/0.5	Xylene/1	120	8	1：1.5	63
35	$NiCl_2$/10	*t*-BuNC/0.5	Xylene/1	120	4	1：1.5	42

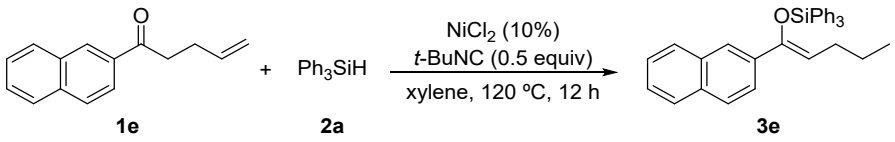
[a]Reaction was conducted on a 0.4 mmol scale. [b]Isolated yield. [c]No catalyst. [d]No ligand. Ad = Admantyl. Dmbpy = 4,4'-Dimethyl-2,2'-bipyridine. Tpy =2,2':6',2''-Terpyridine.

In addition to triphenylsilane **2a**, other hydrosilanes were examined under the optimized reaction conditions. However, they cannot proceed this reaction at all and the starting material was recovered.

Inviable hydrosilanes:

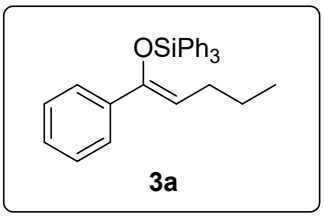
Et_3SiH $PhMe_2SiH$ $(EtO)_2MeSiH$ $(EtO)_3SiH$ Ph_2SiH_2 $PhSiH_3$

3.2 Experimental details and characterization of products



To a 25 ml flame-dried Schlenk tube containing a stirring bar was added $NiCl_2$ (10 mol%, 0.04 mmol, 5.2 mg), Ph_3SiH (0.6 mmol, 156 mg), xylene (1 mL), *t*-BuNC (0.2 mmol, 16.6 mg), and 1-(naphthalen-2-yl)pent-4-en-1-one (0.4 mmol, 84 mg) sequentially under nitrogen. The tube was sealed and stirred at 120 °C for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the product **3e** in 79% yield.

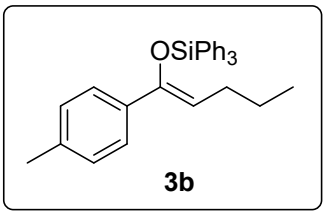
(Z)-triphenyl((1-phenylpent-1-en-1-yl)oxy)silane (3a)



Purified by silica gel column chromatography as colorless oil (121 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 6H), 7.42 – 7.35 (m, 3H), 7.34 – 7.28 (m, 8H), 7.11 – 7.03 (m, 3H), 5.12 (t, *J* = 7.3 Hz, 1H), 1.99 (q, *J* = 7.2 Hz, 2H), 1.23 -1.13 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.2, 138.8, 135.7, 134.1, 130.1, 127.8, 127.7, 127.3, 126.2, 112.3, 28.7, 22.8, 13.9. **HRMS(ESI)** Calculated for $C_{29}H_{29}OSi^+$ ($[M+H]^+$): 421.1988, found: 421.1975.

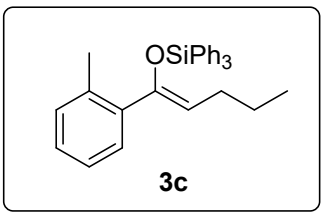
(Z)-triphenyl((1-(p-tolyl)pent-1-en-1-yl)oxy)silane (3b)



Purified by silica gel column chromatography as colorless oil (132 mg, 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 6H), 7.42 – 7.37 (m, 3H), 7.35 – 7.29 (m, 6H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 5.07 (t, *J* = 7.3 Hz, 1H), 2.24 (s, 3H), 2.01 – 1.93 (m, 2H), 1.23 – 1.11 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 149.2, 136.8, 136.0, 135.6, 134.2, 129.9, 128.4, 127.6, 126.1, 111.3, 28.5, 22.7, 21.0, 13.8. HRMS(ESI) Calculated for C30H31OSi ([M+H]+): 435.2144, found: 435.2131.

(Z)-triphenyl((1-(o-tolyl)pent-1-en-1-yl)oxy)silane (3c)

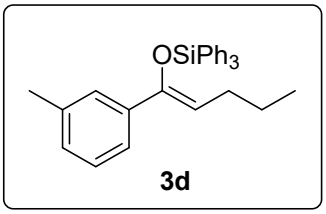


3c

Purified by silica gel column chromatography as white solid (78 mg, 45% yield). mp: 74-76 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 6H), 7.39 – 7.33 (m, 3H), 7.29 – 7.24 (m, 6H), 7.05 – 6.99 (m, 1H), 6.88 – 6.82 (m, 3H), 4.70 (t, *J* = 7.2 Hz, 1H), 2.21 (q, *J* = 7.3 Hz, 2H), 2.08 (s, 3H), 1.41 – 1.34 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.2, 139.1, 136.9, 135.5, 134.1, 129.9, 129.8, 129.4, 127.7, 127.6, 125.0, 113.6, 28.0, 22.9, 19.9, 14.0. **HRMS(ESI)** Calculated for $C_{30}H_{31}OSi$ ($[M+H]^+$): 435.2144, found: 435.2130.

(Z)-triphenyl((1-(m-tolyl)pent-1-en-1-yl)oxy)silane (3d)

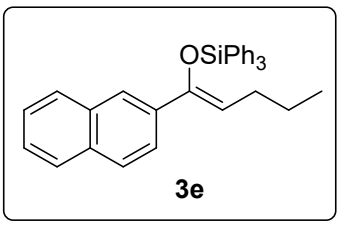


3d

Purified by silica gel column chromatography as white solid (108 mg, 62% yield, Z/E = 97:3).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 6H), 7.41 – 7.36 (m, 3H), 7.34 – 7.29 (m, 6H), 7.14 – 7.08 (m, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.89 (d, J = 7.5 Hz, 1H), 5.11 (t, *J* = 7.3 Hz, 1H), 2.08 (s, 3H), 2.01 (q, *J* = 7.5 Hz, 2H), 1.23 – 1.15 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 149.3, 138.6, 137.1, 135.6, 134.1, 129.9, 127.9, 127.6, 127.2, 123.2, 111.9, 28.5, 22.7, 21.2, 13.8. **HRMS(ESI)** Calculated for $C_{30}H_{31}OSi$ ($[M+H]^+$): 435.2144, found: 435.2133.

(Z)-((1-(naphthalen-2-yl)pent-1-en-1-yl)oxy)triphenylsilane (3e)

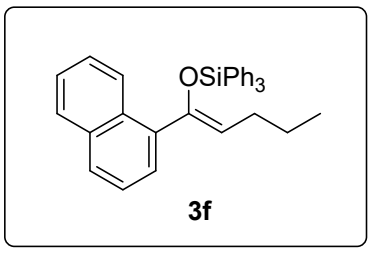


3e

Purified by silica gel column chromatography as white solid (147 mg, 79% yield). mp: 84-86 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.67 – 7.59 (m, 6H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.42 – 7.37 (m, 4H), 7.36 – 7.27 (m, 8H), 5.32 (t, *J* = 7.3 Hz, 1H), 2.06 (q, *J* = 7 Hz, 2H), 1.21 (h, *J* = 7.5 Hz, 2H), 0.76 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 149.1, 135.8, 135.6, 134.0, 133.0, 132.7, 130.0, 128.2, 127.7, 127.3, 127.2, 125.8, 125.6, 125.0, 124.1, 112.7, 28.7, 22.7, 13.8. **HRMS(ESI)** Calculated for $C_{33}H_{31}OSi$ ($[M+H]^+$): 471.2144, found: 471.2133.

(Z)-((1-(naphthalen-1-yl)pent-1-en-1-yl)oxy)triphenylsilane (3f)

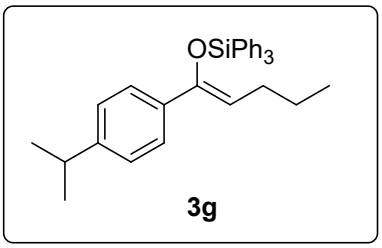


3f

Purified by silica gel column chromatography as colorless oil (85 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 1H), 7.66 – 7.60 (m, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.35 (m, 6H), 7.33 – 7.24 (m, 5H), 7.20 – 7.13 (m, 6H), 7.11 – 7.03 (m, 2H), 4.95 (t, *J* = 7.2 Hz, 1H), 2.31 (q, *J* = 7.3 Hz, 2H), 1.47 – 1.36 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.6, 137.3, 135.4, 133.9, 133.4, 131.9, 129.8, 128.3, 127.8, 127.5, 126.7, 126.7, 125.8, 125.5, 124.8, 115.1, 28.2, 22.9, 14.1. **HRMS(ESI)** Calculated for $C_{33}H_{31}OSi$ ($[M+H]^+$): 471.2144, found: 471.2132.

(Z)-((1-(4-isopropylphenyl)pent-1-en-1-yl)oxy)triphenylsilane (3g)

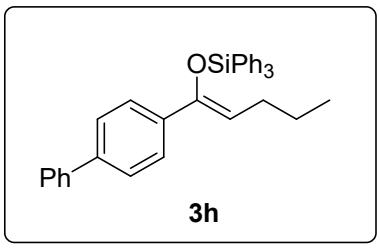


3g

Purified by silica gel column chromatography as colorless oil (133 mg, 72% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 6H), 7.39 – 7.34 (m, 3H), 7.31 – 7.27 (m, 6H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 5.07 (t, *J* = 7.3 Hz, 1H), 2.82 – 2.72 (m, 1H), 2.00 (q, *J* = 7.5 Hz, 2H), 1.21 – 1.14 (m, 8H), 0.74 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 149.3, 147.8, 136.4, 135.6, 134.2, 129.9, 127.6, 126.2 125.7, 111.3, 33.7, 28.5, 23.9, 22.7, 13.8. **HRMS(ESI)** Calculated for $C_{32}H_{35}OSi$ ($[M+H]^+$): 473.2457, found: 473.2445.

(Z)-((1-([1,1'-biphenyl]-4-yl)pent-1-en-1-yl)oxy)triphenylsilane (3h)

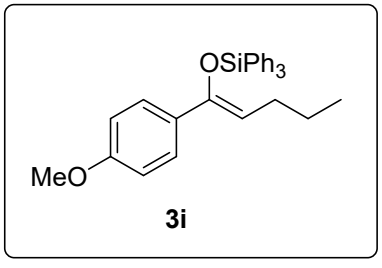


3h

Purified by silica gel column chromatography as white solid (139 mg, 70% yield). mp: 88-90 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 6H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.41 – 7.35 (m, 7H), 7.34 – 7.28 (m, 9H), 5.18 (t, *J* = 7.3 Hz, 1H), 2.03 (q, *J* = 7.4 Hz, 2H), 1.25 – 1.17 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 149.0, 140.9, 139.9, 137.8, 135.7, 134.1, 130.1, 128.8, 127.8, 127.2, 127.0, 126.6, 126.5, 112.3, 28.7, 22.7, 13.9. **HRMS(ESI)** Calculated for $C_{35}H_{33}OSi$ ($[M+H]^+$): 497.2301, found: 497.2291.

(Z)-((1-(4-methoxyphenyl)pent-1-en-1-yl)oxy)triphenylsilane (3i)

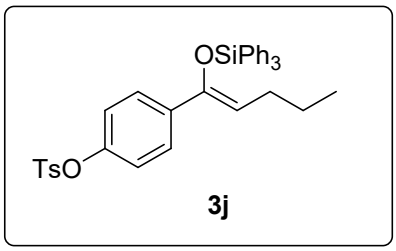


3i

Purified by silica gel column chromatography as colorless oil (130 mg, 73% yield, Z/E = 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 1H), 7.62 – 7.57 (m, 5H), 7.43 – 7.35 (m, 3H), 7.31 (t, *J* = 7.3 Hz, 6H), 7.26 – 7.20 (m, 2H), 6.64 – 6.58 (m, 2H), 5.04 – 4.95 (m, 1H), 3.69 (s, 3H), 2.02 – 1.91 (m, 2H), 1.22 – 1.10 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.9, 148.9, 135.6, 135.0, 134.1, 129.9, 127.9, 127.6, 113.1, 110.7, 55.2, 28.5, 22.7, 13.8. **HRMS(ESI)** Calculated for $C_{30}H_{31}O_2Si$ ($[M+H]^+$): 451.2093, found: 451.2081.

(Z)-4-(1-((triphenylsilyl)oxy)pent-1-en-1-yl)phenyl 4-methylbenzenesulfonate (3j)

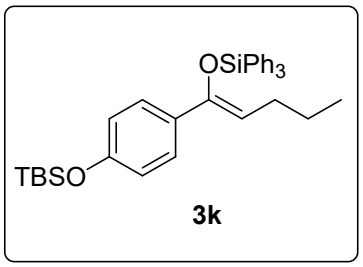


3j

Purified by silica gel column chromatography as colorless oil (130 mg, 55% yield, Z/E = 93:7).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.60 (m, 2H), 7.60 – 7.49 (m, 6H), 7.44 – 7.37 (m, 3H), 7.35 – 7.27 (m, 6H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.17 (m, 2H), 6.73 – 6.63 (m, 2H), 5.11 – 5.03 (m, 1H), 2.41 (s, 3H), 2.00 – 1.93 (m, 2H), 1.20 – 1.12 (m, 2H), 0.76 – 0.69 (m, 3H).**^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.6, 148.0, 145.1, 137.8, 135.5, 133.6, 132.4, 130.1, 129.6, 128.4, 127.7, 127.2, 121.5, 113.1, 28.5, 22.5, 21.6, 13.7. **HRMS(ESI)** Calculated for $C_{36}H_{33}O_4SSi$ ($[M-H]^-$): 589.1869, found: 589.1871.

(Z)-tert-butyldimethyl(4-(1-((triphenylsilyl)oxy)pent-1-en-1-yl)phenoxy)silane (3k)

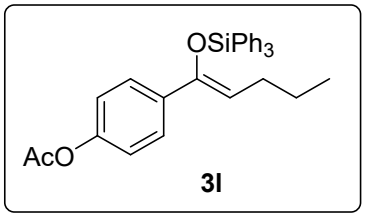


3k

Purified by silica gel column chromatography as colorless oil (152 mg, 69% yield, Z/E = 91:9).

^{1}H NMR (500 MHz, $CDCl_3$) 7.59 (d, *J* = 6.8 Hz, 5H), 7.47 (d, *J* = 6.8 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 3H), 7.33 – 7.29 (m, 5H), 7.24 (s, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.54 (d, *J* = 8.6 Hz, 2H), 5.04 – 4.94 (m, 1H), 2.03 – 1.90 (m, 2H), 1.22 – 1.13 (m, 2H), 0.97 (s, 9H), 0.73 (t, *J* = 7.3 Hz, 3H), 0.13 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 159.4, 153.5, 140.1, 139.6, 138.6, 134.4, 132.1, 131.9, 123.7, 115.3, 32.9, 30.1, 27.2, 22.6, 18.2, 0.00. **HRMS(ESI)** Calculated for $C_{35}H_{43}O_2Si_2$ ($[M+H]^+$): 551.2802, found: 551.2788.

(Z)-4-(1-((triphenylsilyl)oxy)pent-1-en-1-yl)phenyl acetate (3l)

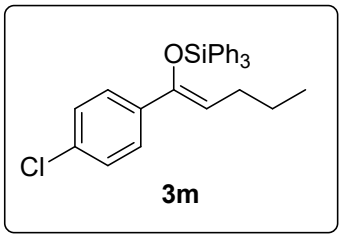


3l

Purified by silica gel column chromatography as colorless oil (86 mg, 45% yield, Z/E = 90:10).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 6H), 7.40 (t, *J* = 7.4 Hz, 3H), 7.34 – 7.27 (m, 8H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.08 (t, *J* = 7.3 Hz, 1H), 2.24 (s, 3H), 2.02 – 1.96 (m, 2H), 1.21 – 1.14 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.3, 149.8, 148.4, 136.6, 135.5, 133.9, 130.0, 127.7, 127.2, 120.7, 112.3, 28.5, 22.6, 21.1, 13.7. **HRMS(ESI)** Calculated for $C_{31}H_{31}O_3Si$ ($[M+H]^+$): 479.2042, found: 479.2031.

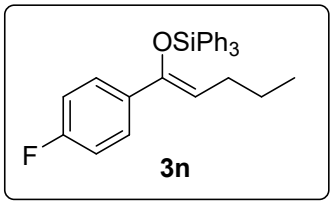
(Z)-((1-(4-chlorophenyl)pent-1-en-1-yl)oxy)triphenylsilane (3m)



Purified by silica gel column chromatography as colorless oil (44 mg, 24% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 6H), 7.42 – 7.38 (m, 3H), 7.34 – 7.30 (m, 6H), 7.22 – 7.19 (m, 2H), 7.04 – 7.00 (m, 2H), 5.09 (t, *J* = 7.3 Hz, 1H), 1.99 (q, *J* =7.5 Hz, 2H), 1.22 – 1.14 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.2, 137.3, 135.5, 133.8, 132.8, 130.1, 127.8, 127.7, 127.4, 112.7, 28.5, 22.6, 13.8. **HRMS(ESI)** Calculated for $C_{29}H_{28}ClOSi$ ($[M+H]^+$): 479.2042, found: 479.2031.

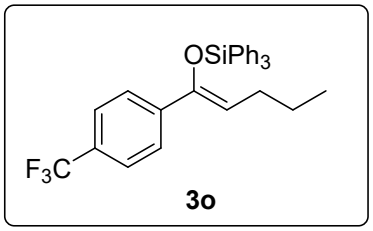
(Z)-((1-(4-fluorophenyl)pent-1-en-1-yl)oxy)triphenylsilane (3n)



Purified by silica gel column chromatography as colorless oil (124 mg, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 6H), 7.42 – 7.38 (m, 3H), 7.34 – 7.30 (m, 6H), 7.25 – 7.21 (m, 2H), 6.76 – 6.69 (m, 2H), 5.03 (t, *J* = 7.3 Hz, 1H), 2.02 – 1.97 (m, 2H), 1.22 – 1.15 (m, 2H), 0.74 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.0 (d, $^1J_{C\text{-}F}$ = 246.1 Hz), 148.3, 135.5, 135.0 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 133.8, 130.0, 127.8 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 127.7, 114.4 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 112.1, 28.5, 22.6, 13.8. **HRMS(ESI)** Calculated for $C_{29}H_{28}FOSi$ ($[M+H]^+$): 439.1893, found: 439.1881.

(Z)-triphenyl((1-(4-(trifluoromethyl)phenyl)pent-1-en-1-yl)oxy)silane (3o)

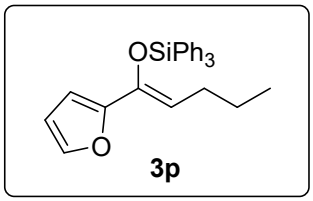


Purified by silica gel column chromatography as colorless oil (110 mg, 57% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 6H), 7.43 –

7.36 (m, 5H), 7.34 – 7.27 (m, 8H), 5.20 (t, J = 7.3 Hz, 1H), 2.06 – 1.99 (m, 2H), 1.24 – 1.16 (m, 2H), 0.75 (t, J = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.1, 142.3, 135.6, 133.6, 130.5, 129.0 (q, $^{2}J_{C\text{-}F}$ = 32.3 Hz), 127.8, 126.2, 124.71 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz),124.2 (q, $^{1}J_{C\text{-}F}$ = 270.2 Hz), 114.3, 28.6, 22.6, 13.8. **HRMS(ESI)** Calculated for $C_{30}H_{28}F_3OSi$ ($[M+H]^+$): 489.1862, found: 489.1848.

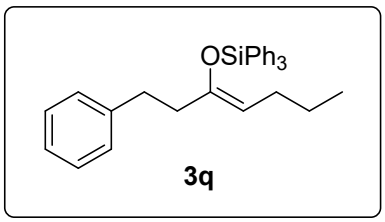
(Z)-((1-(furan-2-yl)pent-1-en-1-yl)oxy)triphenylsilane (3p)



Purified by silica gel column chromatography as colorless oil (93 mg, 57% yield, Z/E = 88:12).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 6H), 7.43 – 7.39 (m, 3H), 7.38 – 7.34 (m, 6H), 7.14 (d, J = 1.0 Hz, 1H), 6.14 – 6.10 (m, 1H), 5.98 (d, J = 3.3 Hz, 1H), 5.31 (t, J = 7.5 Hz, 1H), 1.94 (q, J = 7.6 Hz, 2H), 1.18 – 1.10 (m, 2H), 0.74 – 0.68 (m, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 152.2, 141.2, 140.7, 135.6, 133.9, 130.2, 127.8, 110.9, 110.8, 106.3, 27.8, 22.6, 13.8. **HRMS(ESI)** Calculated for $C_{27}H_{27}O_2Si$ ($[M+H]^+$): 411.1780, found: 411.1767.

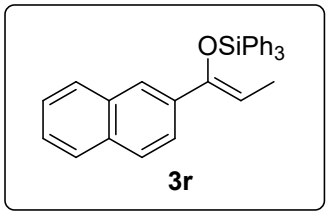
(Z)-triphenyl((1-phenylhept-3-en-3-yl)oxy)silane (3q)



Purified by silica gel column chromatography as colorless oil (127 mg, 69% yield, Z/E = 71:29).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 6H), 7.46 – 7.39 (m, 3H), 7.39 – 7.33 (m, 6H), 7.24 – 7.13 (m, 2.79H), 7.13 – 7.07 (m, 1.77H), 6.93 – 6.84 (m, 0.56H), 4.65 (t, J = 7.7 Hz, 0.69H), 4.48 (t, J = 7.1 Hz, 0.28H), 2.85 – 2.80 (m, 1.42H), 2.70 – 2.62 (m, 0.58H), 2.44 – 2.36 (m, 1.43H), 2.27 – 2.20 (m, 0.58H), 1.92 (q, J = 7.5 Hz, 0.57H), 1.69 (q, J = 7.5 Hz, 1.43H), 1.19 – 1.09 (m, 0.59H), 1.01 (h, J = 7.5 Hz, 1.44H), 0.73 (t, J = 7.4 Hz, 0.87H), 0.62 (t, J = 7.4 Hz, 2.14H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 150.0, 149.6, 142.0, 141.7, 135.5, 135.5, 134.5, 134.3, 130.0, 130.0, 128.5, 128.3, 128.2, 128.1, 127.8, 127.8, 125.7, 125.6, 109.6, 109.5, 38.5, 34.0, 33.5, 33.4, 28.8, 27.6, 23.3, 22.7, 13.8, 13.4. **HRMS(ESI)** Calculated for $C_{31}H_{33}OSi$ ($[M+H]^+$): 449.2301, found: 449.2290.

(Z)-((1-(naphthalen-2-yl)prop-1-en-1-yl)oxy)triphenylsilane (3r)

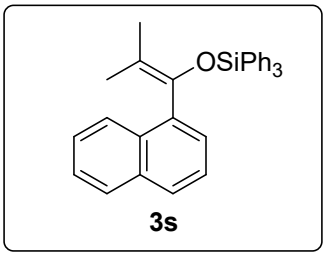


3r

Purified by silica gel column chromatography as white solid (134 mg, 76% yield, Z/E = 98:2). mp: 80-82 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.67 – 7.61 (m, 6H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.36 – 7.28 (m, 8H), 5.43 – 5.33 (m, 1H), 1.59 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 150.2, 135.7, 135.3, 134.1, 133.1, 132.7, 130.1, 128.2, 127.8, 127.4, 127.3, 125.9, 125.7, 125.0, 124.1, 106.8, 12.3. **HRMS(ESI)** Calculated for $C_{31}H_{27}OSi$ ($[M+H]^+$): 443.1831, found: 443.1818.

(Z)-(2-methyl-1-(naphthalen-1-yl)prop-1-en-1-yl)oxy)triphenylsilane (3s)

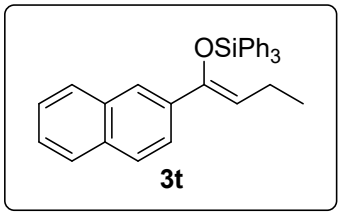


3s

Purified by silica gel column chromatography as white solid (84 mg, 46% yield). mp: 73-75 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.39 (m, 7H), 7.38 – 7.31 (m, 4H), 7.26 – 7.20 (m, 6H), 7.17 (dd, J_1 = 8.1, J_2 = 7.2 Hz, 1H), 7.02 – 6.97 (m, 1H), 2.08 (s, 3H), 1.51 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 141.8, 135.6, 135.1, 134.2, 133.4, 132.1, 129.5, 128.0, 127.8, 127.7, 127.3, 126.5, 125.7, 125.3, 124.7, 114.5, 19.6, 17.9. **HRMS(ESI)** Calculated for $C_{32}H_{28}OSi$ ($[M]^+$): 456.1909, found: 456.1893.

(Z)-((1-(naphthalen-2-yl)but-1-en-1-yl)oxy)triphenylsilane (3t)

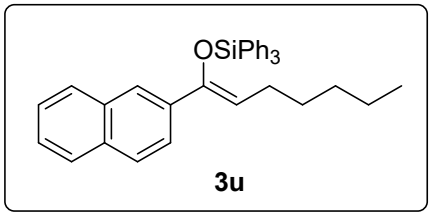


3t

Purified by silica gel column chromatography as white solid (127 mg, 70% yield, Z/E = 98:2). mp: 97-99 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.66 – 7.60 (m, 6H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.38 (m, 4H), 7.36 – 7.27 (m, 8H), 5.29 (t, *J* = 7.2 Hz, 1H), 2.11 (m, 2H), 0.78 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.5, 135.6, 134.0, 133.0, 132.7, 130.0, 128.2, 127.7, 127.3, 127.3, 125.8, 125.6, 125.0, 124.1, 114.5, 20.0, 13.9. **HRMS(ESI)** Calculated for $C_{32}H_{28}OSi$ ($[M]^+$): 457.1988, found: 457.1973.

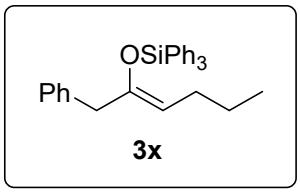
(Z)-((1-(naphthalen-2-yl)hept-1-en-1-yl)oxy)triphenylsilane (3u)



Purified by silica gel column chromatography as colorless oil (106 mg, 53% yield, Z/E = 98:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.80 – 7.76 (m, 1H), 7.75 – 7.70 (m, 6H), 7.67 (d, J = 8.7 Hz, 1H), 7.57 (dd, J_1 = 8.6, J_2 = 1.8 Hz, 1H), 7.51 – 7.46 (m, 4H), 7.45 – 7.38 (m, 8H), 5.41 (t, J = 7.2 Hz, 1H), 2.17 (q, J = 7.5 Hz, 2H), 1.33 – 1.18 (m, 6H), 0.92 (t, J = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, CDCl3)** δ 148.9, 136.5, 135.6, 134.0, 133.1, 132.7, 130.0, 128.2, 127.7, 127.3, 127.2, 125.8, 125.6, 125.0, 124.1, 113.0, 31.6, 29.2, 26.7, 22.5, 14.1. **HRMS(ESI)** Calculated for $C_{35}H_{35}OSi$ ($[M+H]^+$): 499.2452, found: 499.2448.

(Z)-triphenyl((1-phenylhex-2-en-2-yl)oxy)silane (3x)

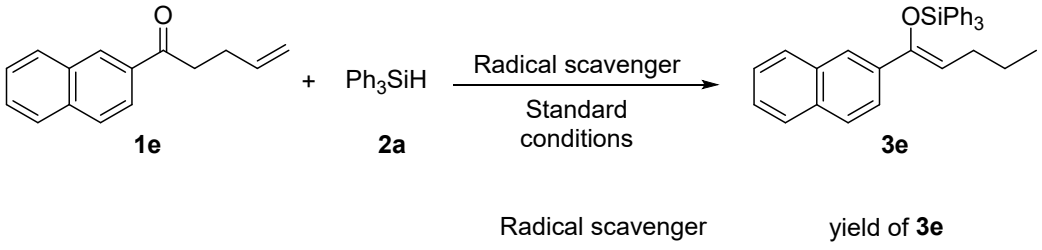


Purified by silica gel column chromatography as colorless oil (124 mg, 72% yield, Z/E = 92:8).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 6H), 7.42 – 7.34 (m, 4H), 7.33 – 7.29 (m, 5H), 7.24 – 7.19 (m, 3H), 7.18 – 7.15 (m, 2H), 4.75 (t, J = 7.6 Hz, 1H), 3.43 (s, 2H), 1.93 (q, J = 7.4 Hz, 2H), 1.21 – 1.13 (m, 2H), 0.71 (t, J = 7.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 149.3, 138.8, 135.5, 134.1, 129.9, 129.0, 128.2, 127.6, 126.0, 110.1, 37.6, 29.2, 23.5, 13.5. **HRMS(ESI)** Calculated for $C_{30}H_{31}OSi$ ($[M+H]^+$): 435.2139, found: 435.2136.

3.3 Mechanistic experiments

3.3.1 Radical trapping experiments



Radical scavenger	yield of **3e**
TEMPO	NR
BHT	56%
1,1'-diphenylethene	78%

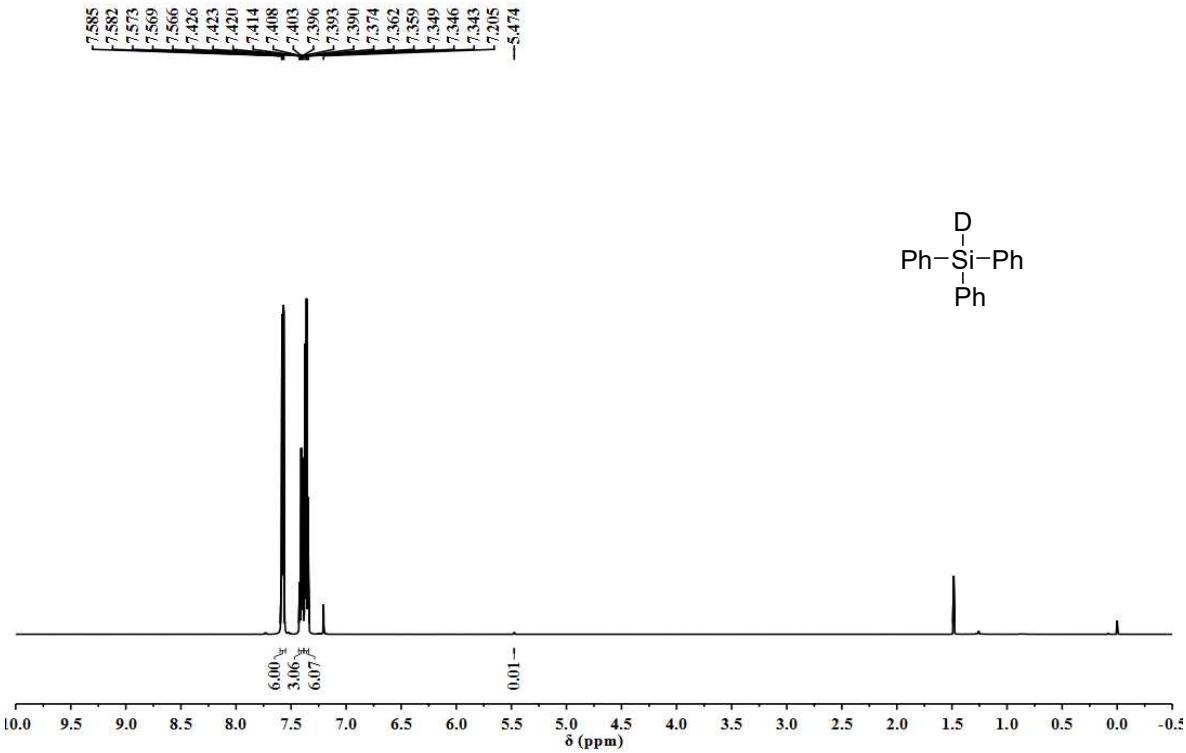
Experimental procedure:

To a 25 ml flame-dried Schlenk tube containing a stirring bar was added $NiCl_2$ (10 mol%, 0.04 mmol, 5.2 mg), Ph_3SiH (0.6 mmol, 156 mg), xylene (1 mL), *t*-BuNC (0.2 mmol, 16.6 mg), 1-(naphthalen-2-yl)pent-4-en-1-one (0.4 mmol, 84 mg) and radical scavenger (1 equiv.), sequentially under nitrogen. The tube was sealed and stirred at 120 °C for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the product **3e**.

3.3.2 Deuterium-labelling experiment

Ph_3SiD (>99% D) was synthesized according to the known literature[4].

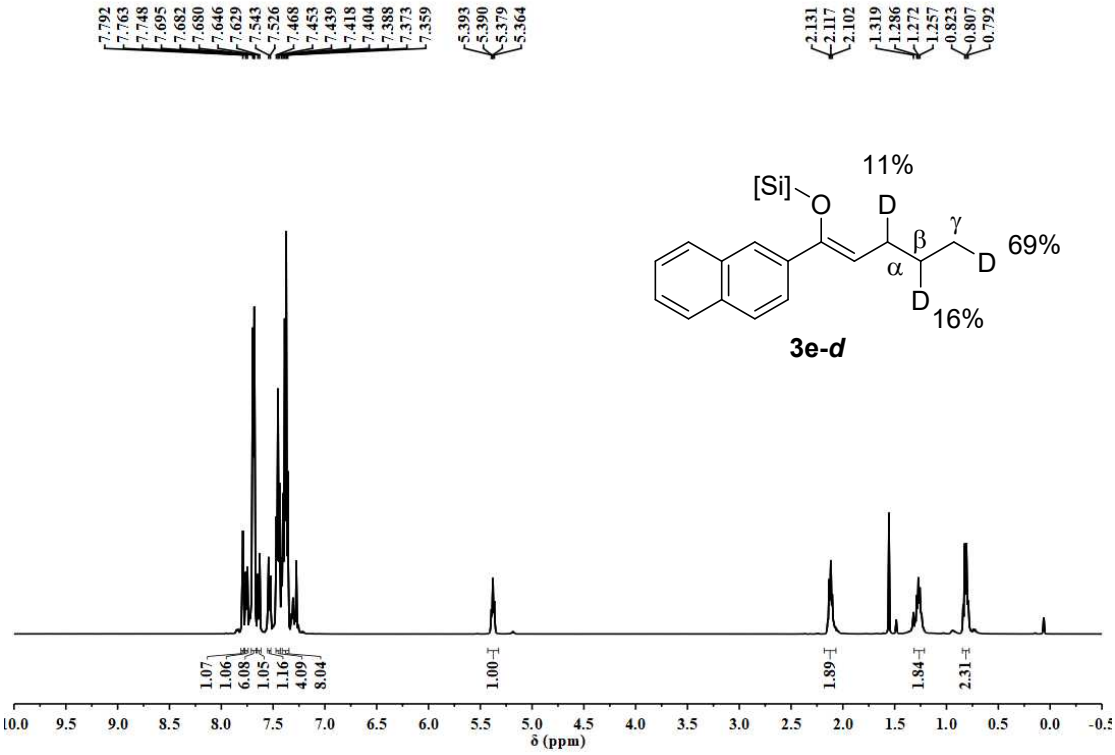
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 6H), 7.43 – 7.39 (m, 3H), 7.38 – 7.34 (m, 6H).



Experimental procedure:

To a 25 ml flame-dried Schlenk tube containing a stirring bar was added $NiCl_2$ (10 mol%, 0.04 mmol, 5.2 mg), Ph_3SiD (0.6 mmol, 156.6 mg), xylene (1 mL), *t*-BuNC (0.2 mmol, 16.6 mg), and

1-(naphthalen-2-yl)pent-4-en-1-one (0.4 mmol, 84 mg) sequentially under nitrogen. The tube was sealed and stirred at 120 °C for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the deuterated product **3e-*d*** in 76% yield.

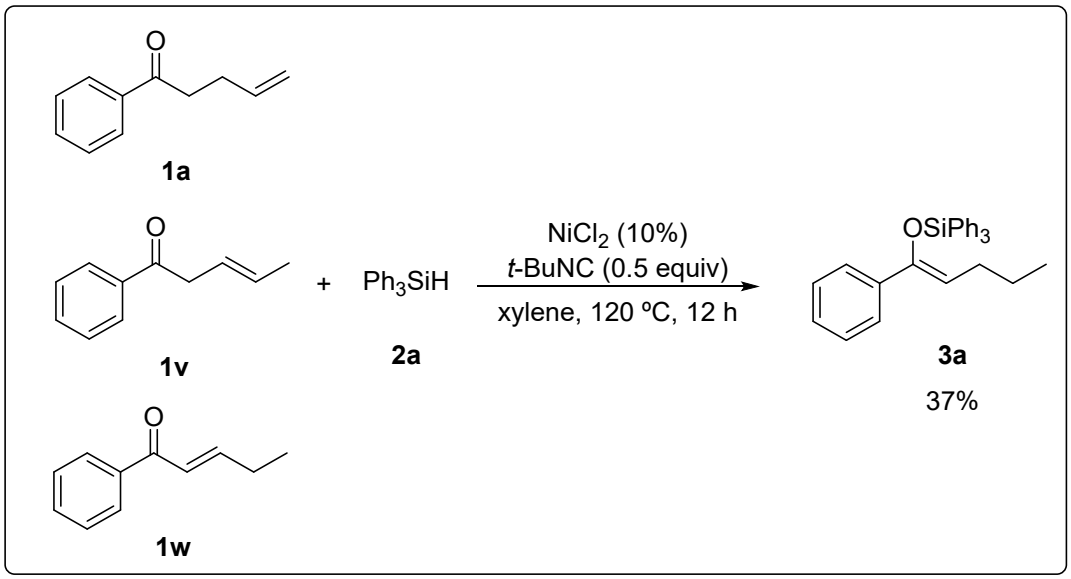


3.4 Synthetic applications

3.4.1 Preparation of silyl enol ether 3x

Following the general procedure, see Section 3.2.

3.4.2 Reaction of mixed isomers 1a, 1v, and 1w with 2a



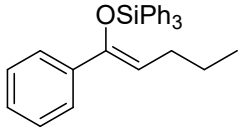
Experimental procedure:

To a 25 ml flame-dried Schlenk tube containing a stirring bar was added $NiCl_2$ (10 mol%, 0.03 mmol, 3.9 mg), Ph_3SiH (0.45 mmol, 117 mg), xylene (1 mL), *t*-BuNC (0.15 mmol, 12.5 mg), **1a** (0.1 mmol, 16 mg), **1v** (0.1 mmol, 16 mg) and **1w** (0.1 mmol, 16 mg) sequentially under nitrogen. The tube was sealed and stirred at 120 ^oC for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the same product **3a** in 37% yield.

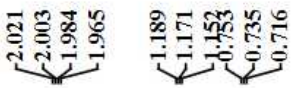
4. References

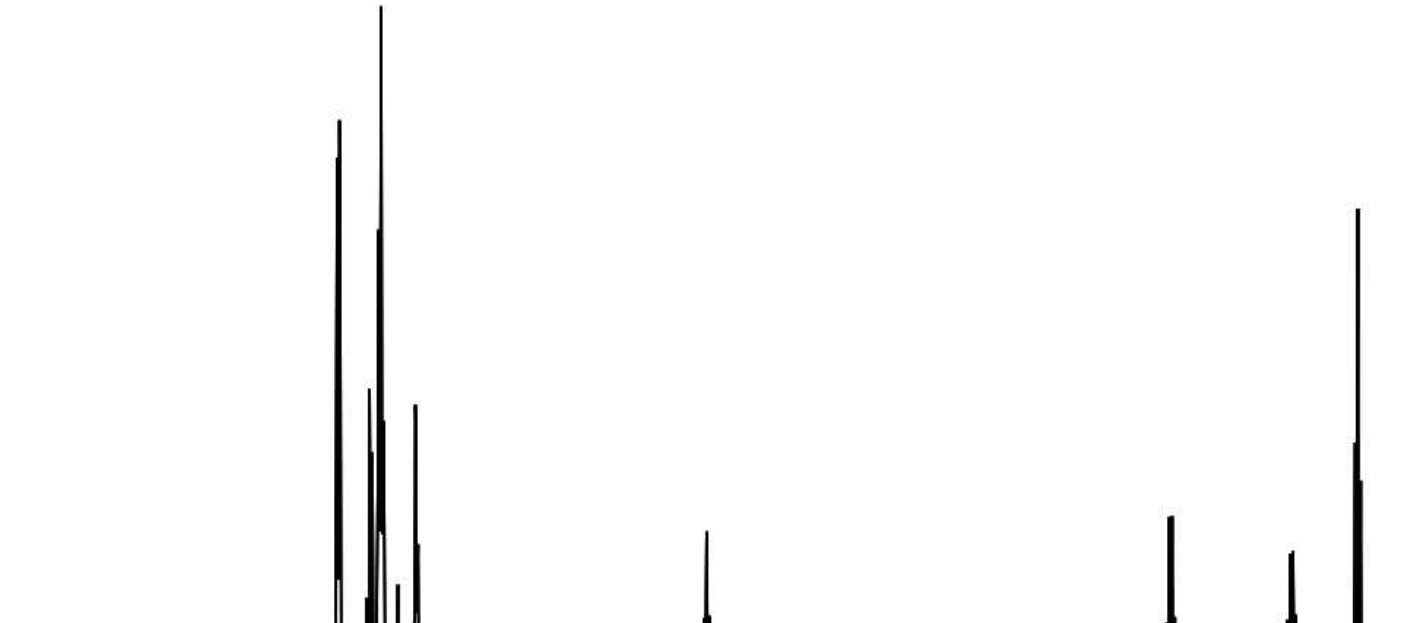
1. (a) S. Guven, G. Kundu, A. Weßels, J. S. Ward, K. Rissanen, F. Schoenebeck, *J. Am. Chem. Soc.* 2021**, 143**, 8375-8380. (b) W. Kong, H. An, Q. Song, *Chem. Commun*. 2017, **53**, 8968-8971.
2. R.Thapar, Reshma, S. S. Bari, *J. Chem. Sci.* 2016, **128**, 1745-1753.
3. L. Zhang, J. Duan, G. Xu, X. Ding, Y. Mao, B. Rong, N. Zhu, Z. Fang, Z. Li, K. Guo, *J. Org. Chem.* 2020, **85**, 2532-2542.
4. V. Leich, T. P. Spaniol, J. Okuda, *Organometallics.* 2016**, 35**, 1179-1182.

5. ^{1}H and ^{13}C NMR Spectra



3a





OSiPh3

3a

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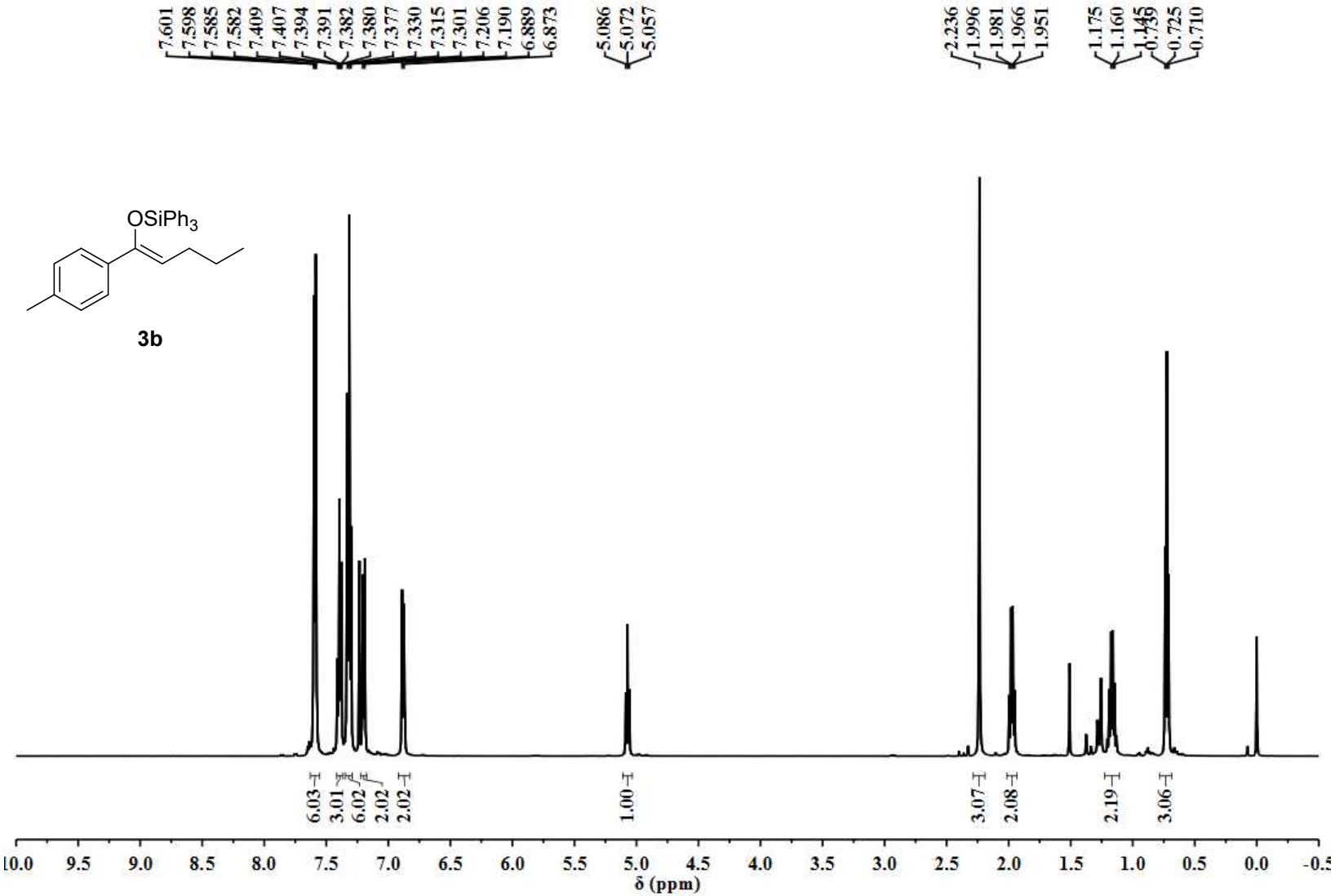
134.083
130.058
127.760
127.728
127.251
126.208
112.275
28.646
22.752
13.893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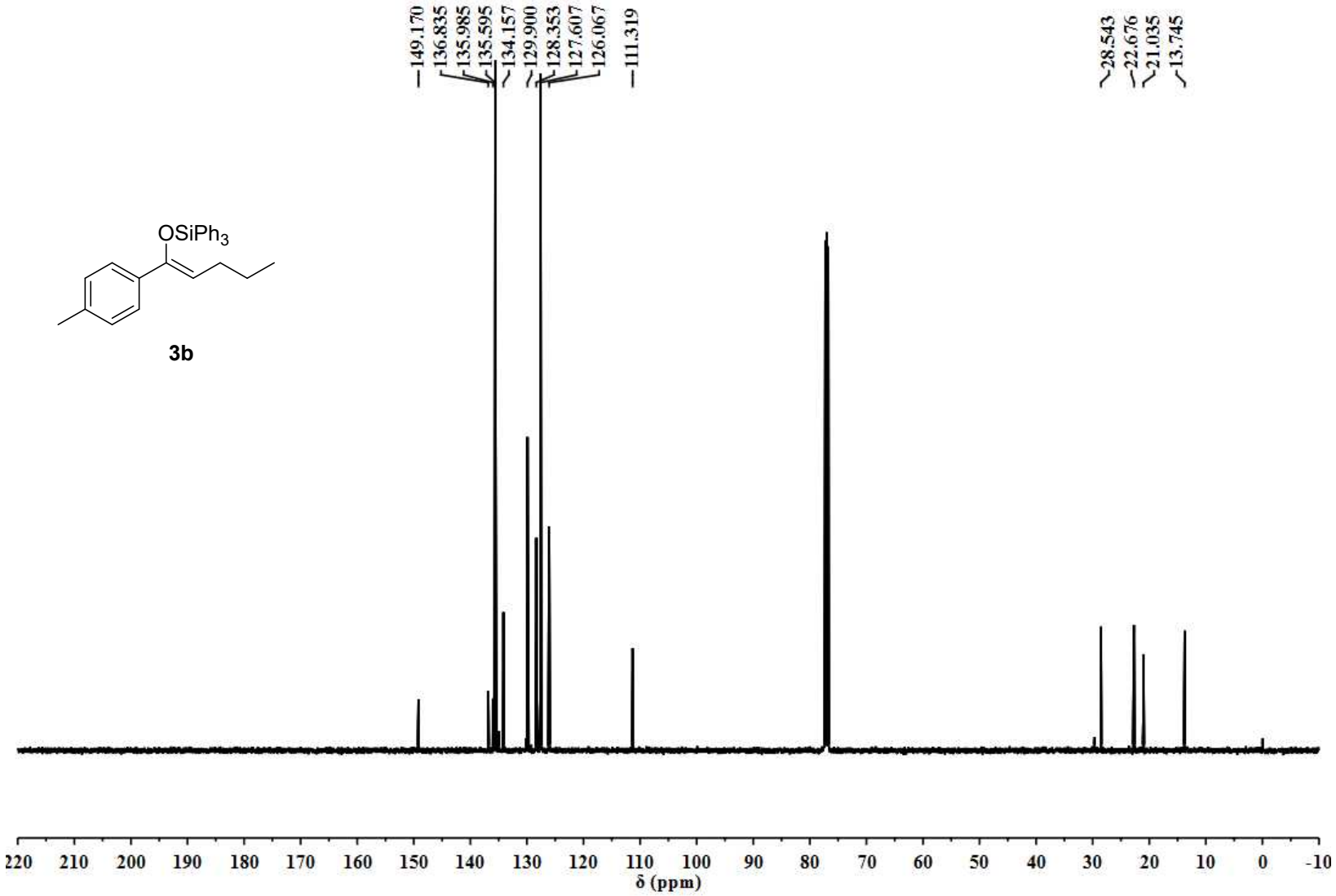
7.301
7.206
7.190
6.889
6.873
5.086
5.072
5.057
2.236
1.996
1.981
1.966
1.951
1.175
1.160
0.739
0.725
0.710
OSiPh3
3b
6.03
3.01
6.02
2.02
2.02
1.00
3.07
2.08
2.19
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)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13.745
OSiPh3
3b
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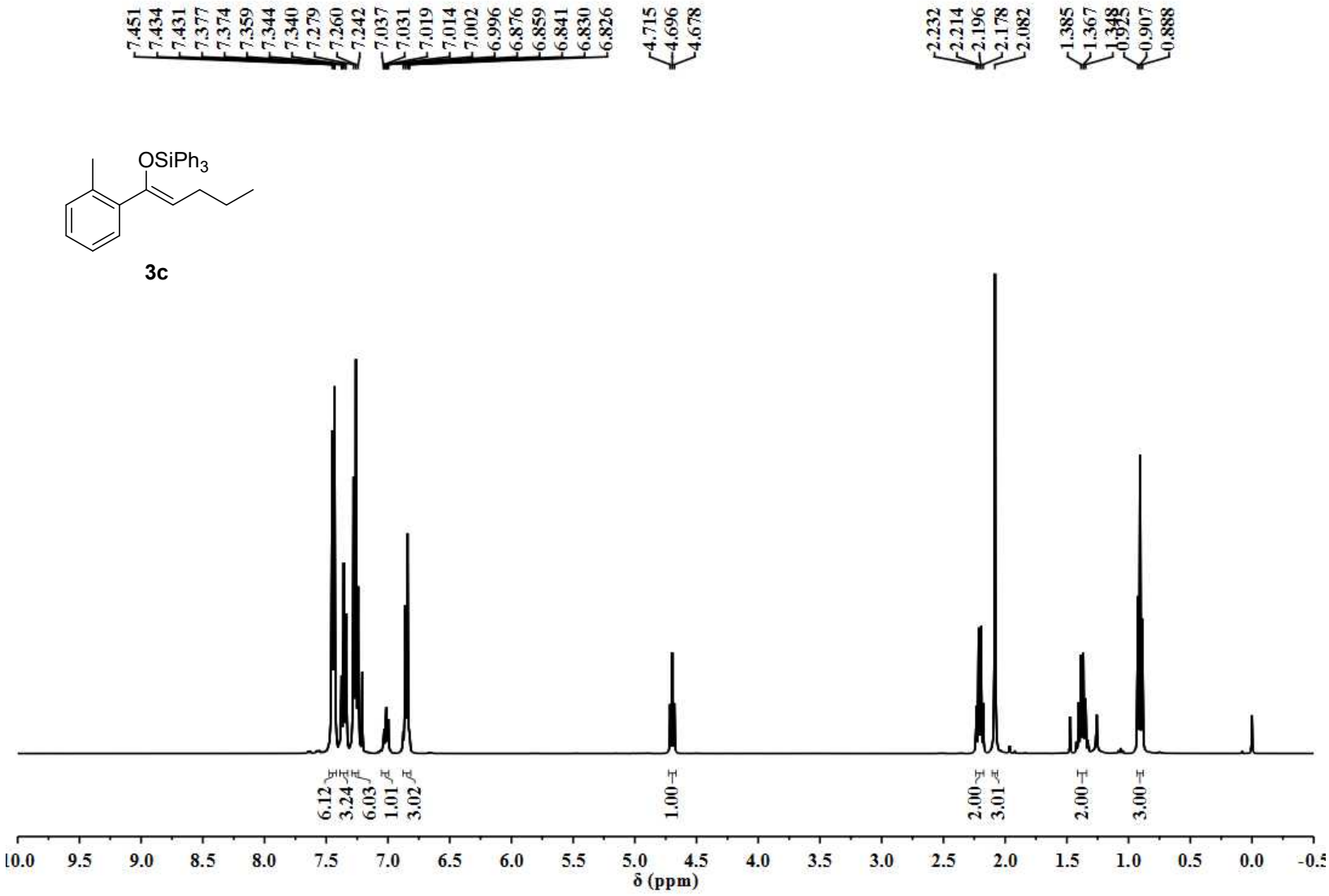
δ (ppm)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7.431
7.377
7.374
7.359
7.344
7.340
7.279
7.260
7.242
7.037
7.031
7.019
7.014
7.002
6.996
6.876
6.859
6.841
6.830
6.826
4.715
4.696
4.678
2.232
2.214
2.196
2.178
2.082
1.385
1.367
0.907
0.888
OSiPh3
3c
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6.03
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3.01
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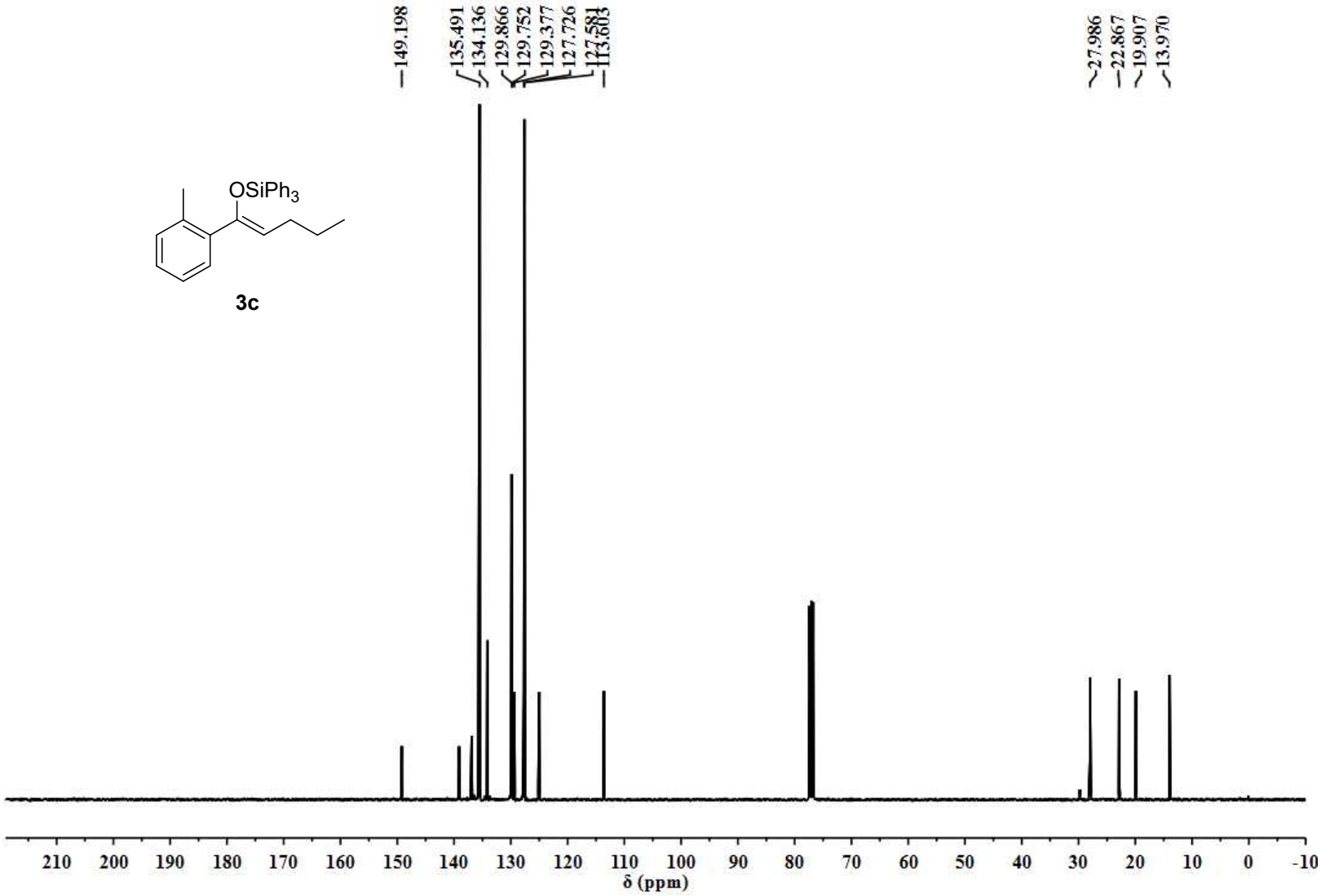
3.00
δ (ppm)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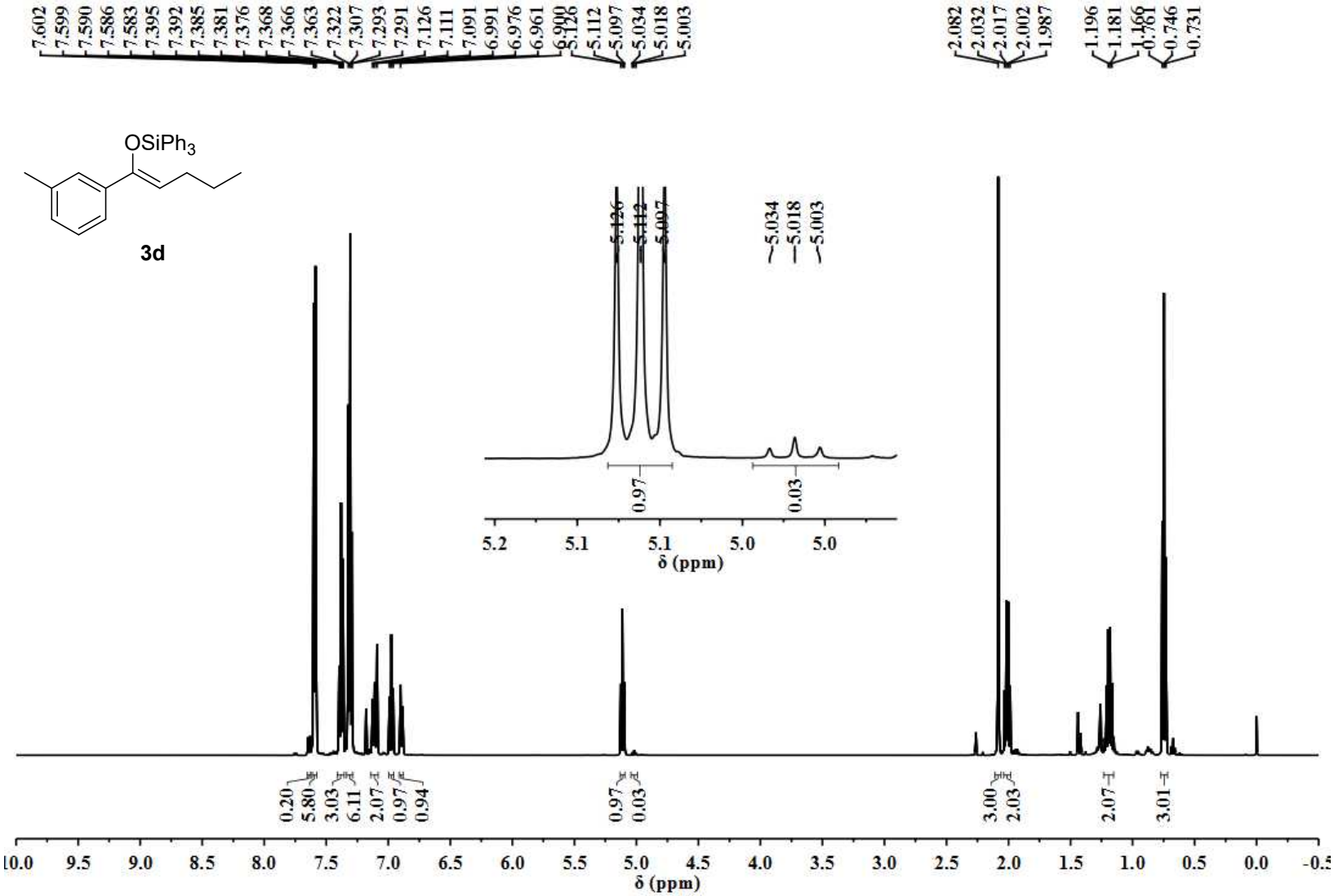
13.970
OSiPh3
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.363
7.322
7.307
7.293
7.291
7.126
7.111
7.091
6.991
6.976
6.961
6.900
5.126
5.112
5.097
5.034
5.018
5.003
2.082
2.032
2.017
2.002
1.987
1.196
1.181
1.166
0.761
0.746
0.731
OSiPh3
3d
0.20
5.80
3.03
6.11
2.07
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0.03
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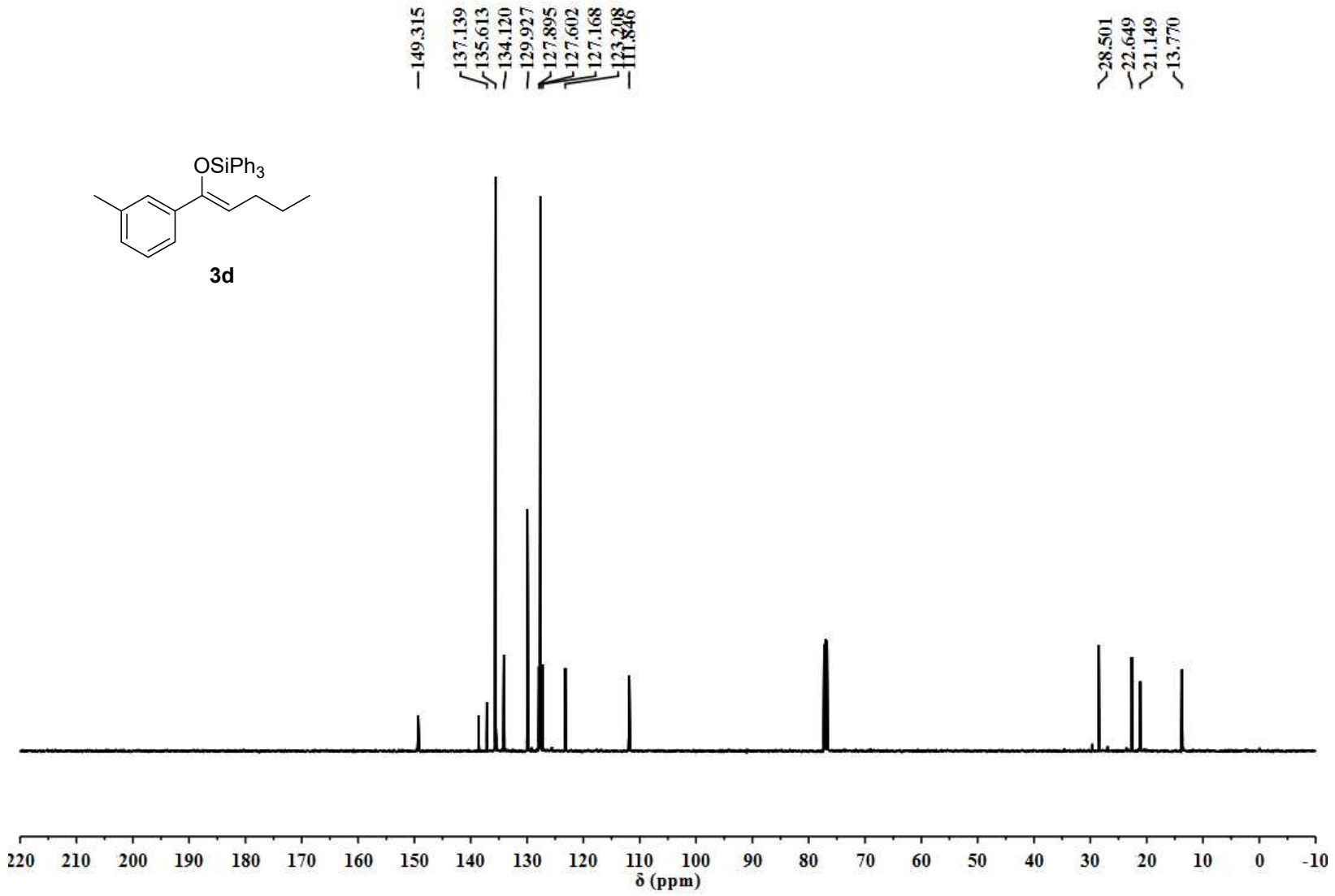
2.03
2.07
3.01
δ (ppm)
0.97
0.03
δ (ppm)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123.208
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13.770
OSiPh3
3d
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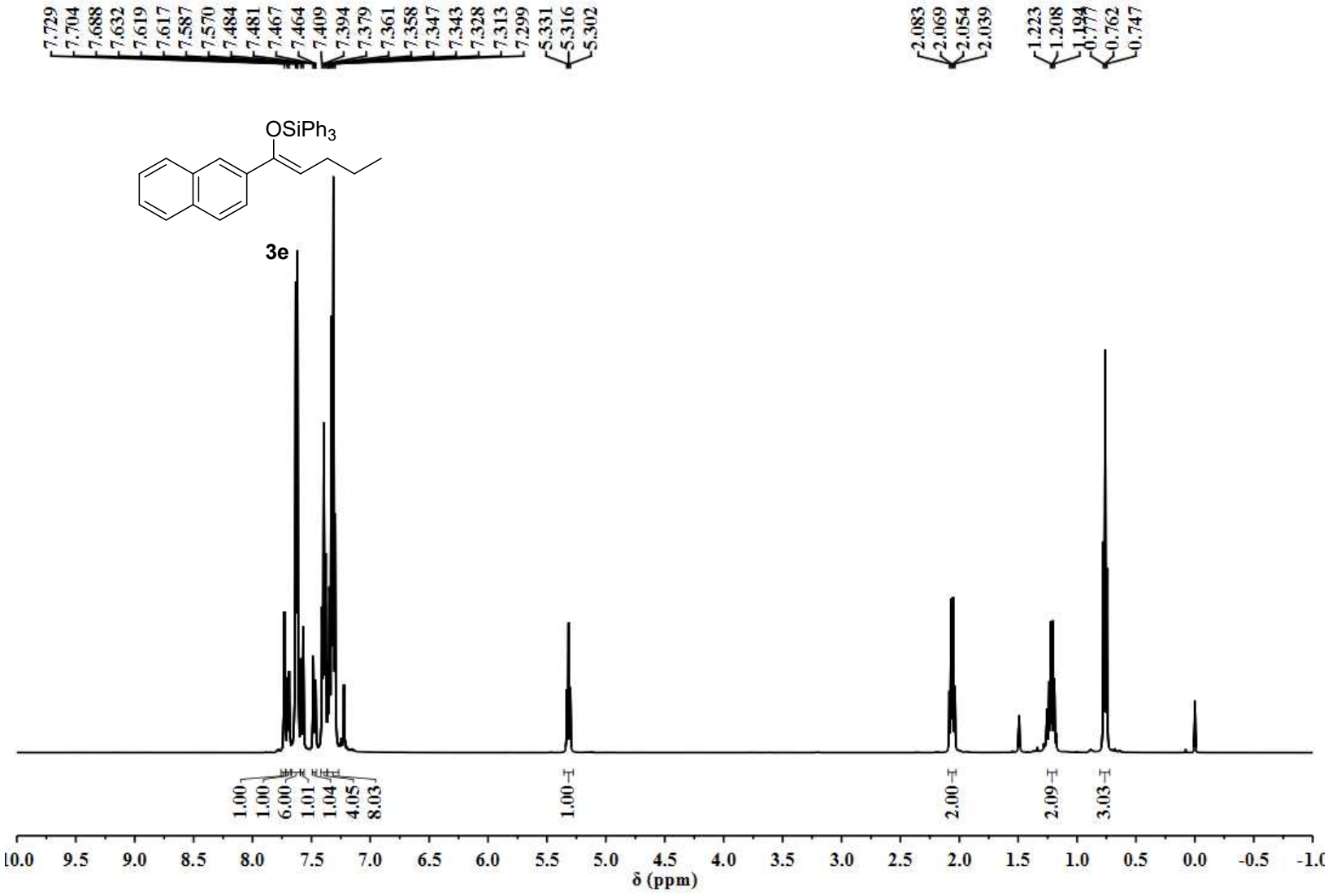
δ (ppm)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7.299
5.331
5.316
5.302
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2.039
1.223
1.208
0.762
0.747
OSiPh3
3e
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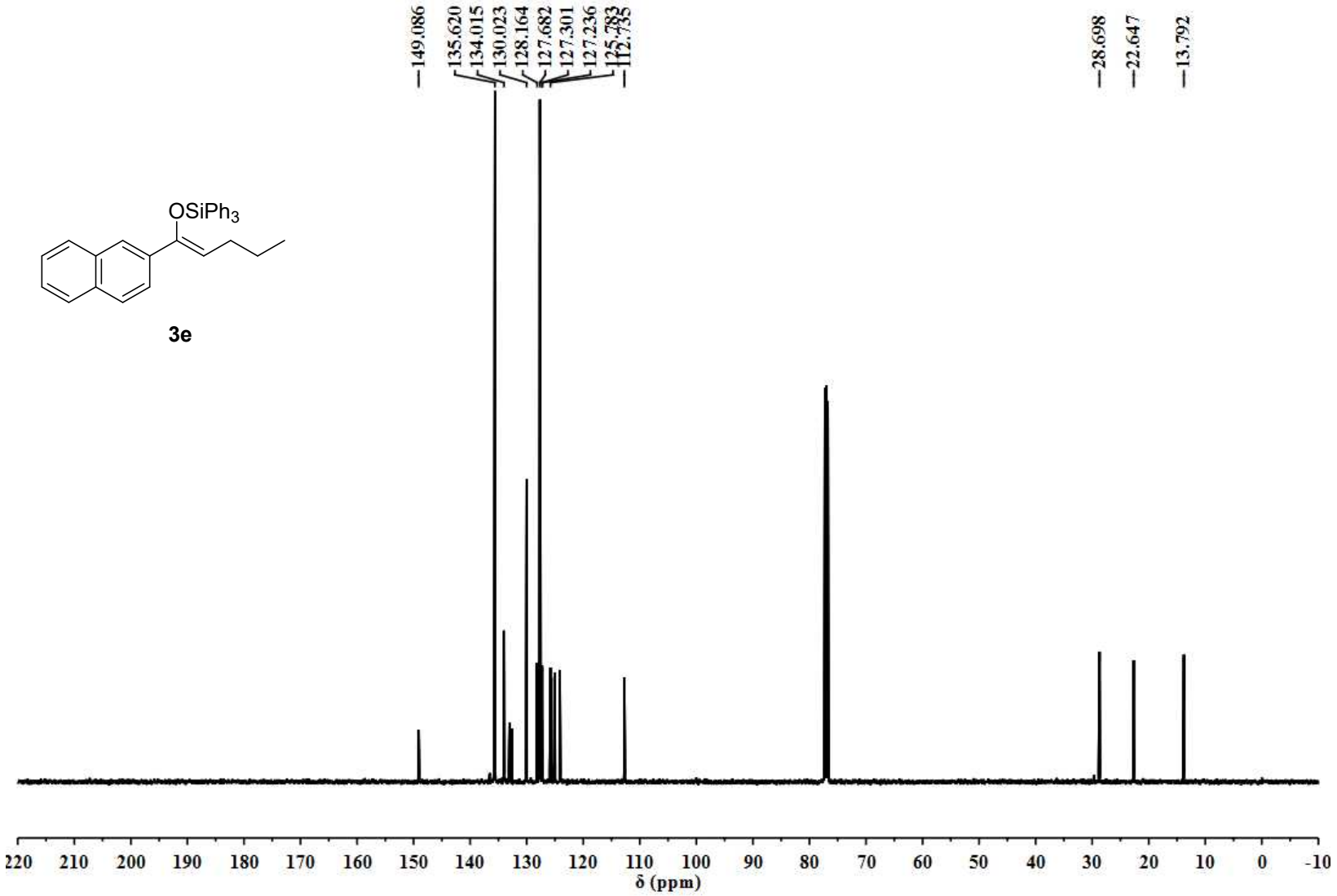
δ (ppm)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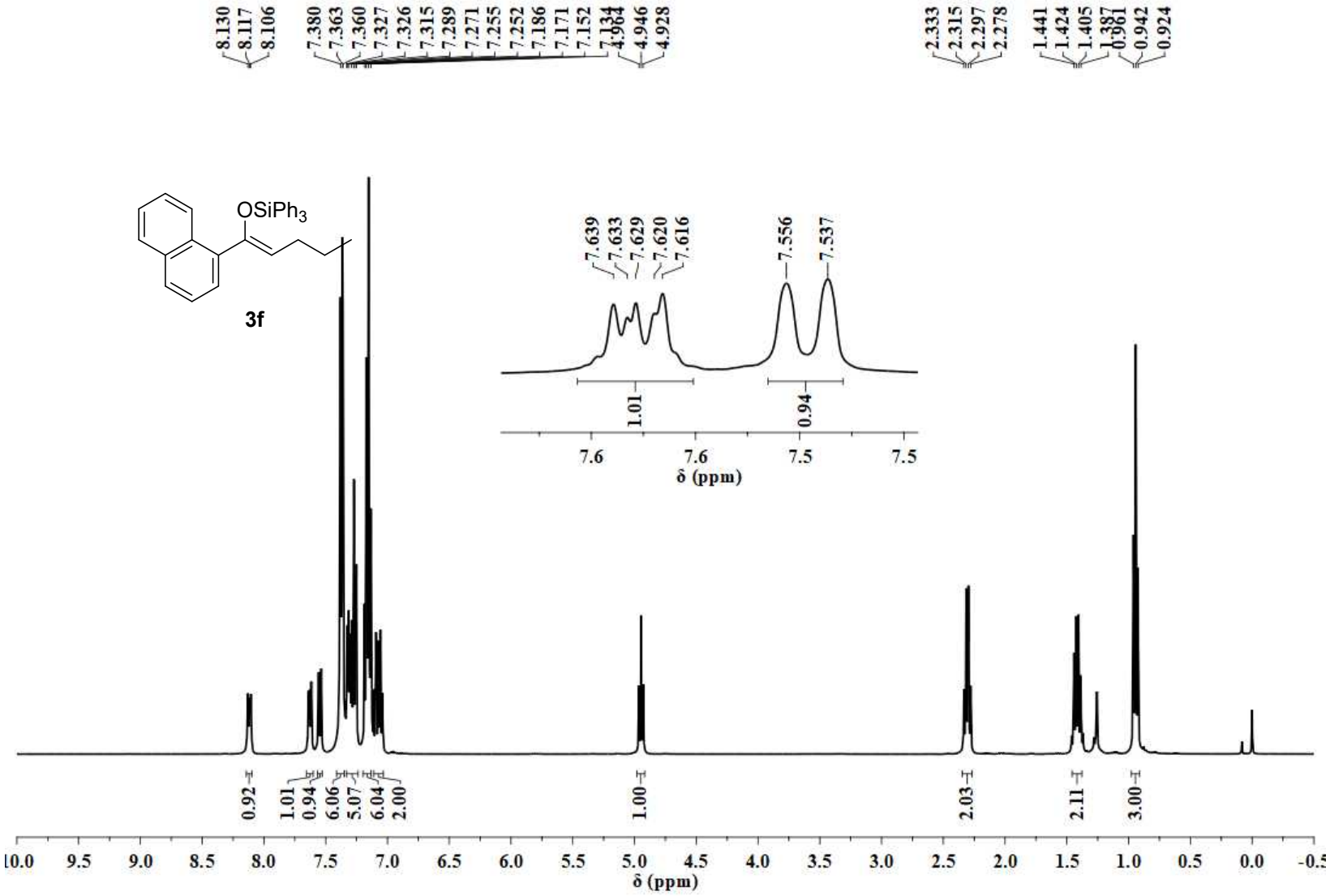
δ (ppm)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7.252
7.186
7.171
7.152
4.946
4.928
2.333
2.315
2.297
2.278
1.441
1.424
1.405
0.942
0.924
OSiPh3
3f
7.639
7.633
7.629
7.620
7.616
7.556
7.537
1.01
0.94
δ (ppm)
0.92
1.01
0.94
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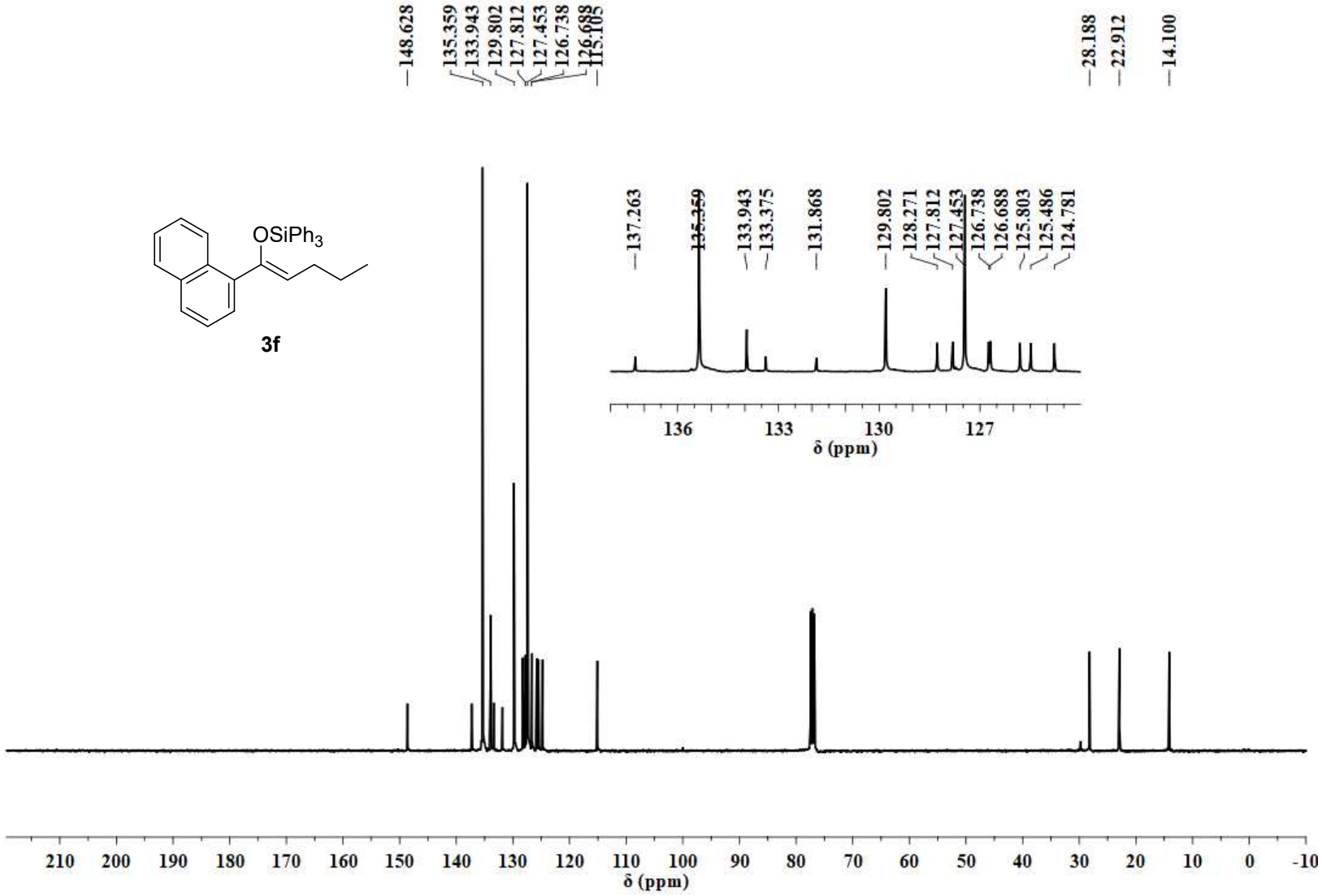
1.00
2.03
2.11
3.00
δ (ppm)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14.100
OSiPh3
3f
137.263
135.359
133.943
133.375
131.868
129.802
128.271
127.812
127.453
126.738
126.688
125.803
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133
130
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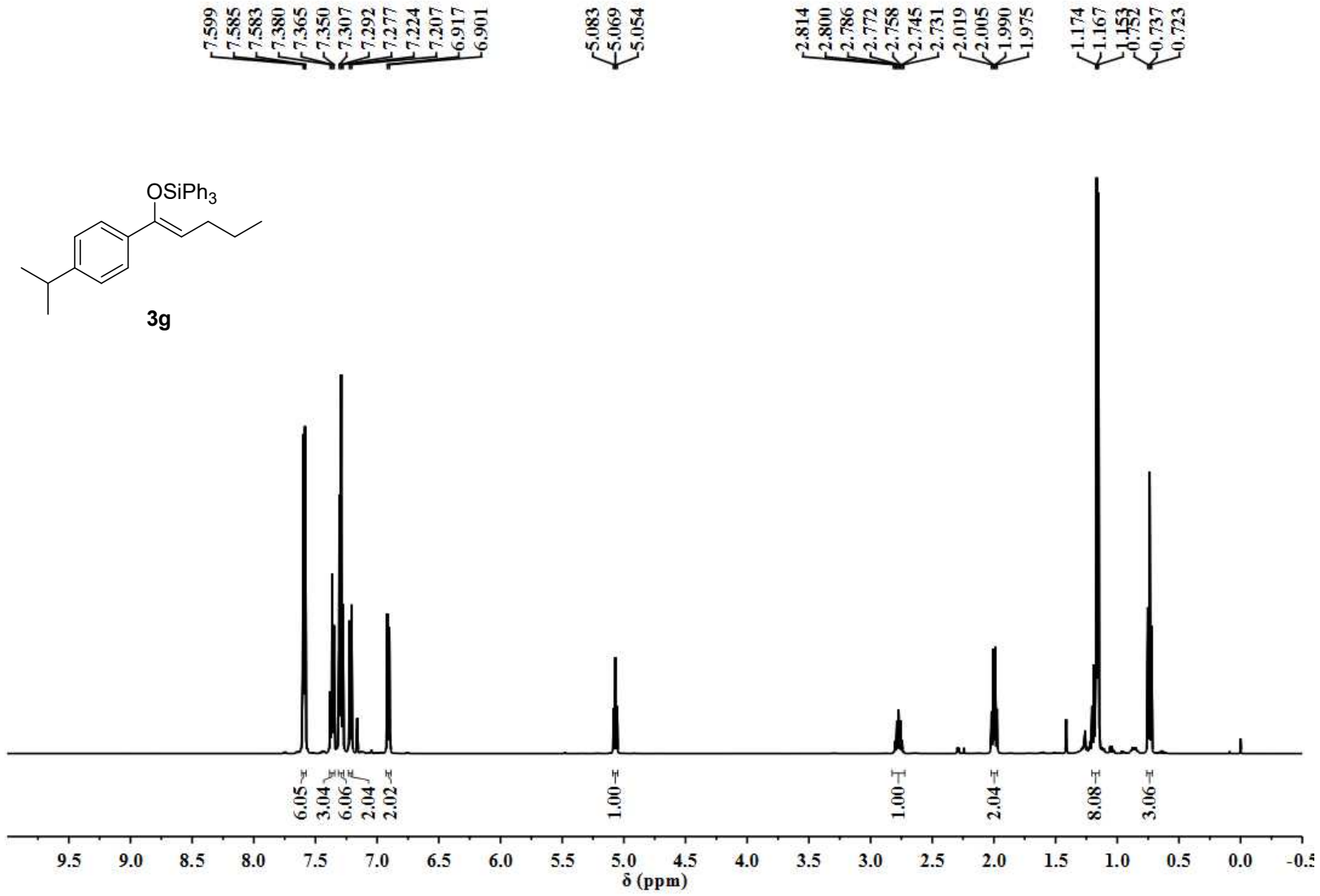
δ (ppm)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2.758
2.745
2.731
2.019
2.005
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1.975
1.174
1.167
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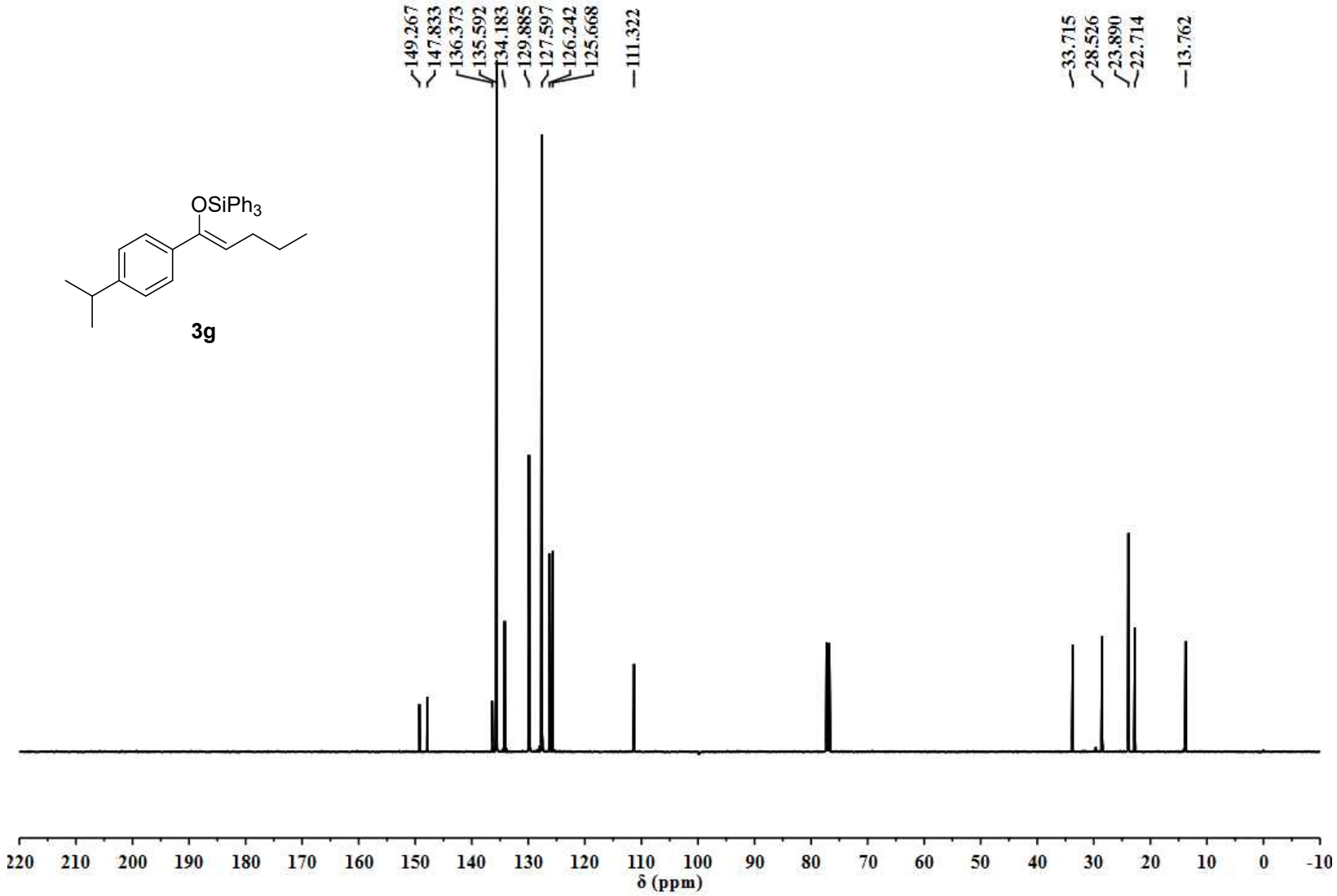
0.737
0.723
OSiPh3
3g
6.05
3.04
6.06
2.04
2.02
1.00
1.00
2.04
8.08
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)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3g
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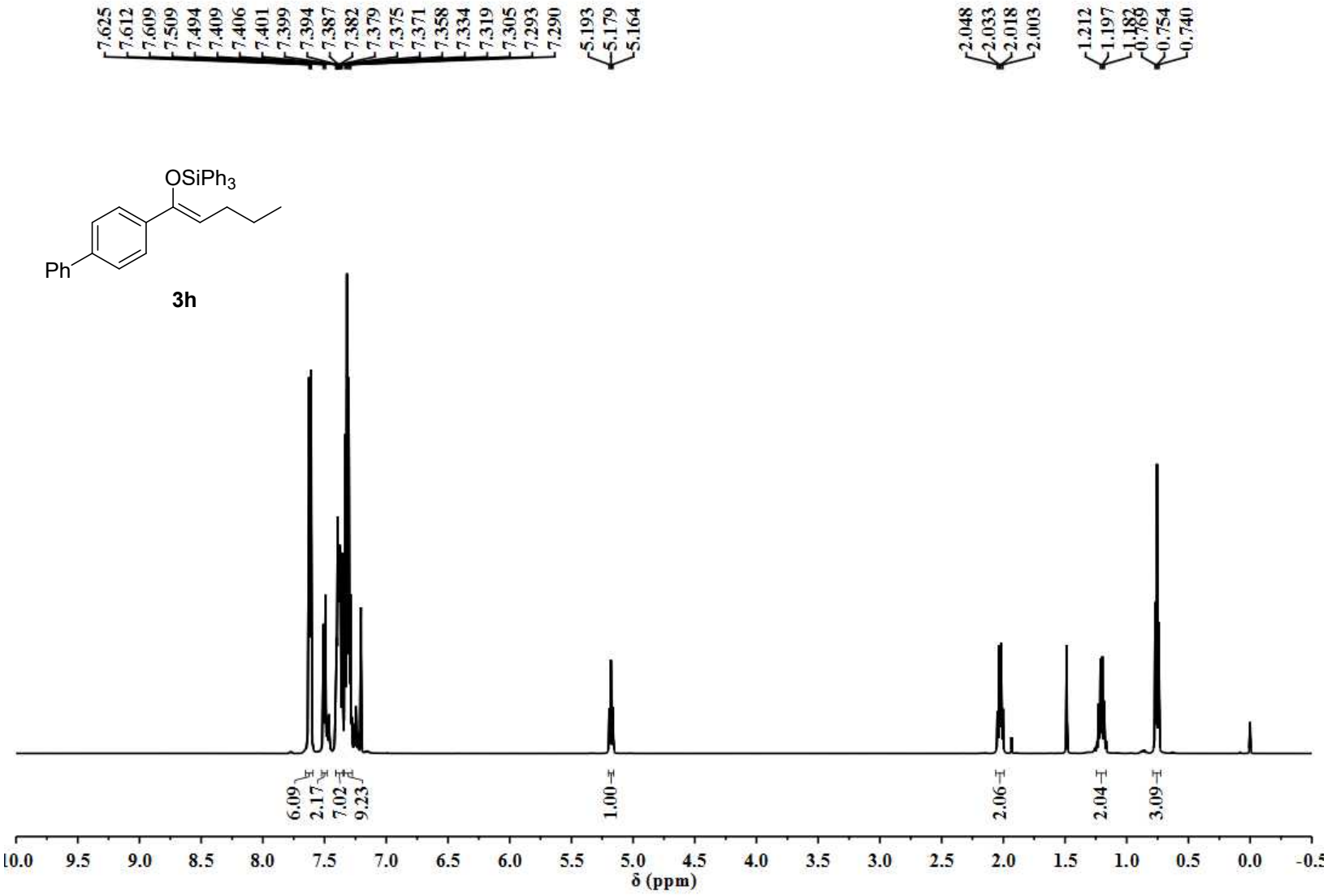
δ (ppm)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7.293
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5.164
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2.018
2.003
1.212
1.197
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0.740
OSiPh3
Ph
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2.04
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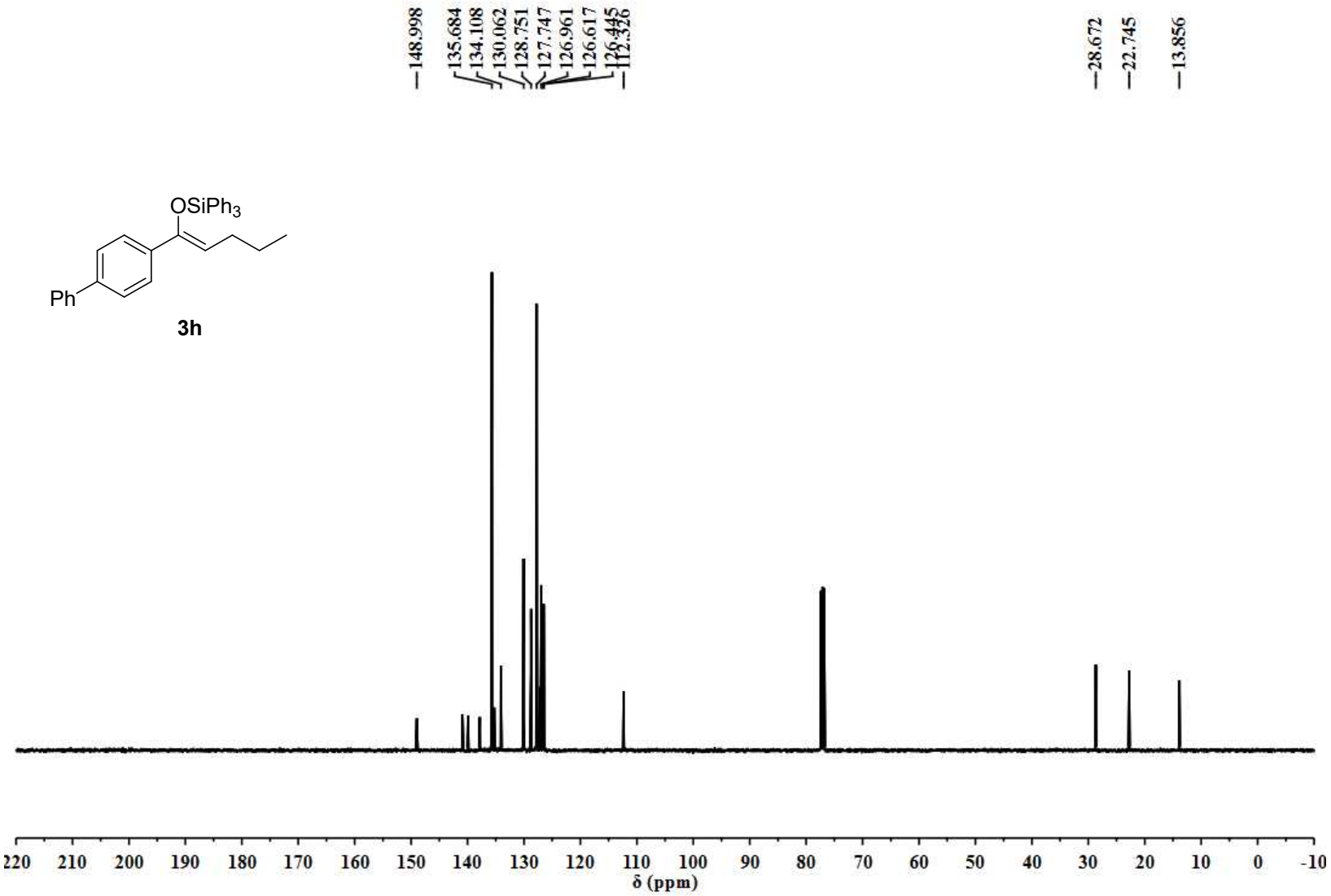
δ (ppm)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3h
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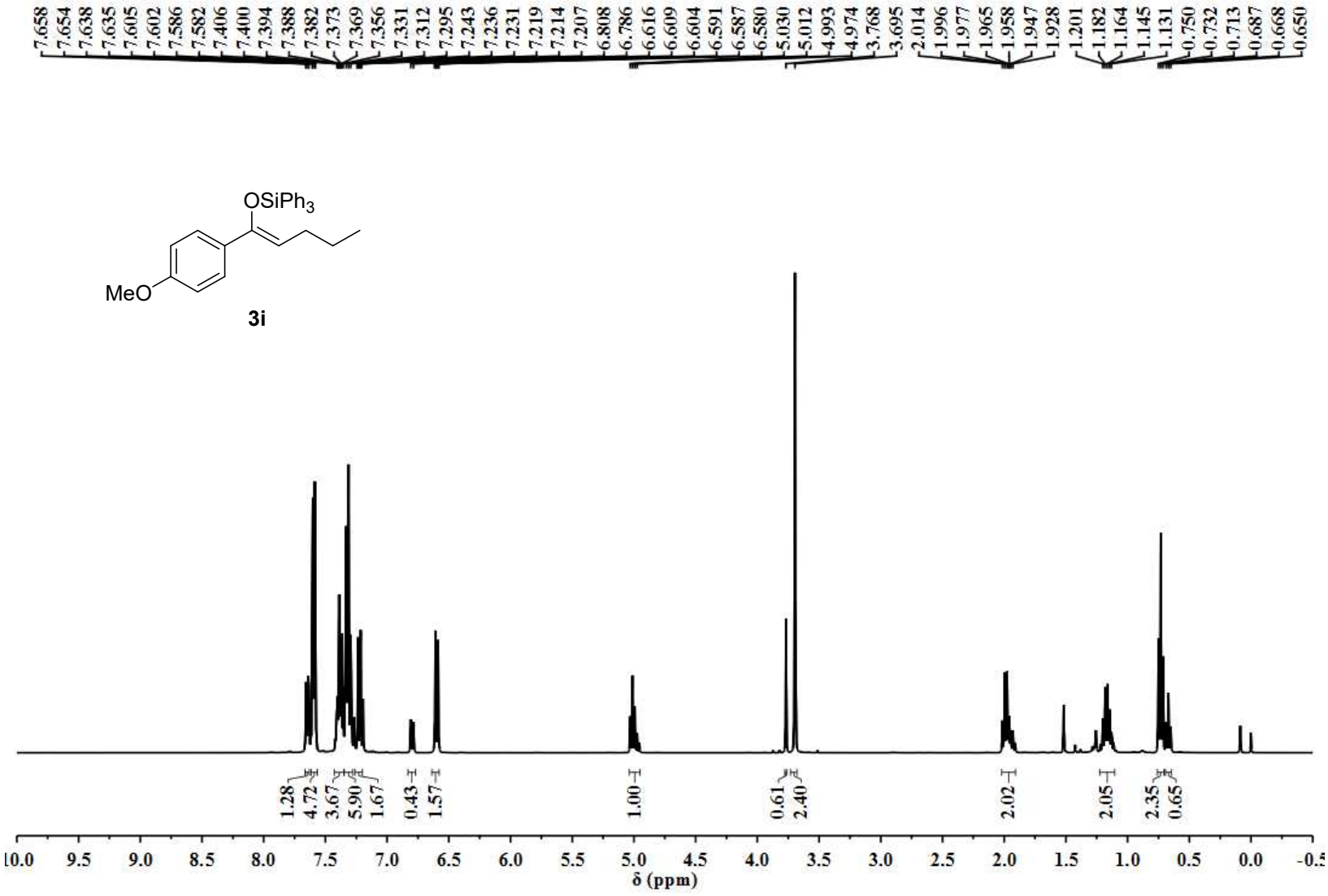
δ (ppm)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0.713
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0.668
0.650
OSiPh3
MeO
3i
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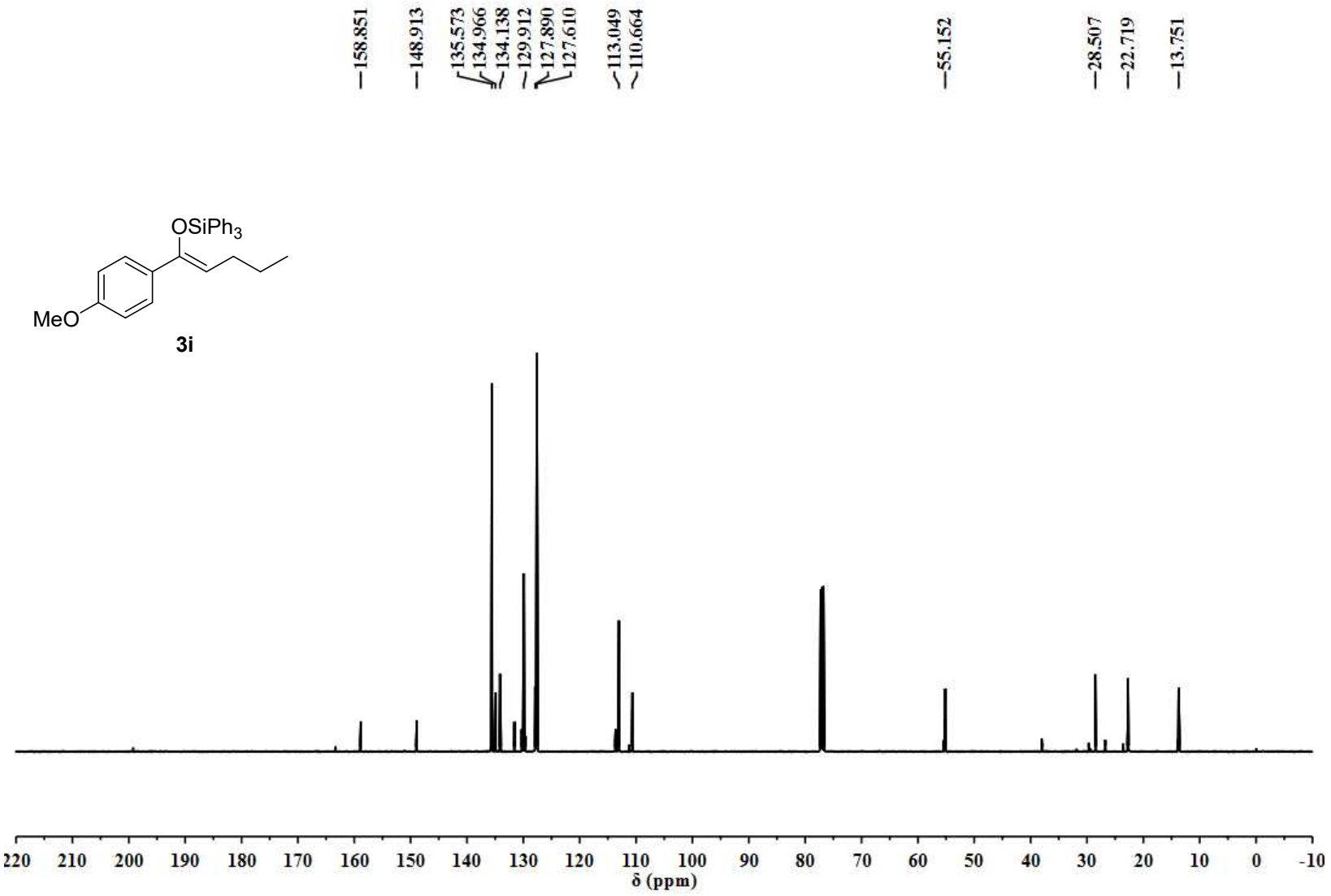
δ (ppm)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22.719
13.751
OSiPh3
MeO
3i
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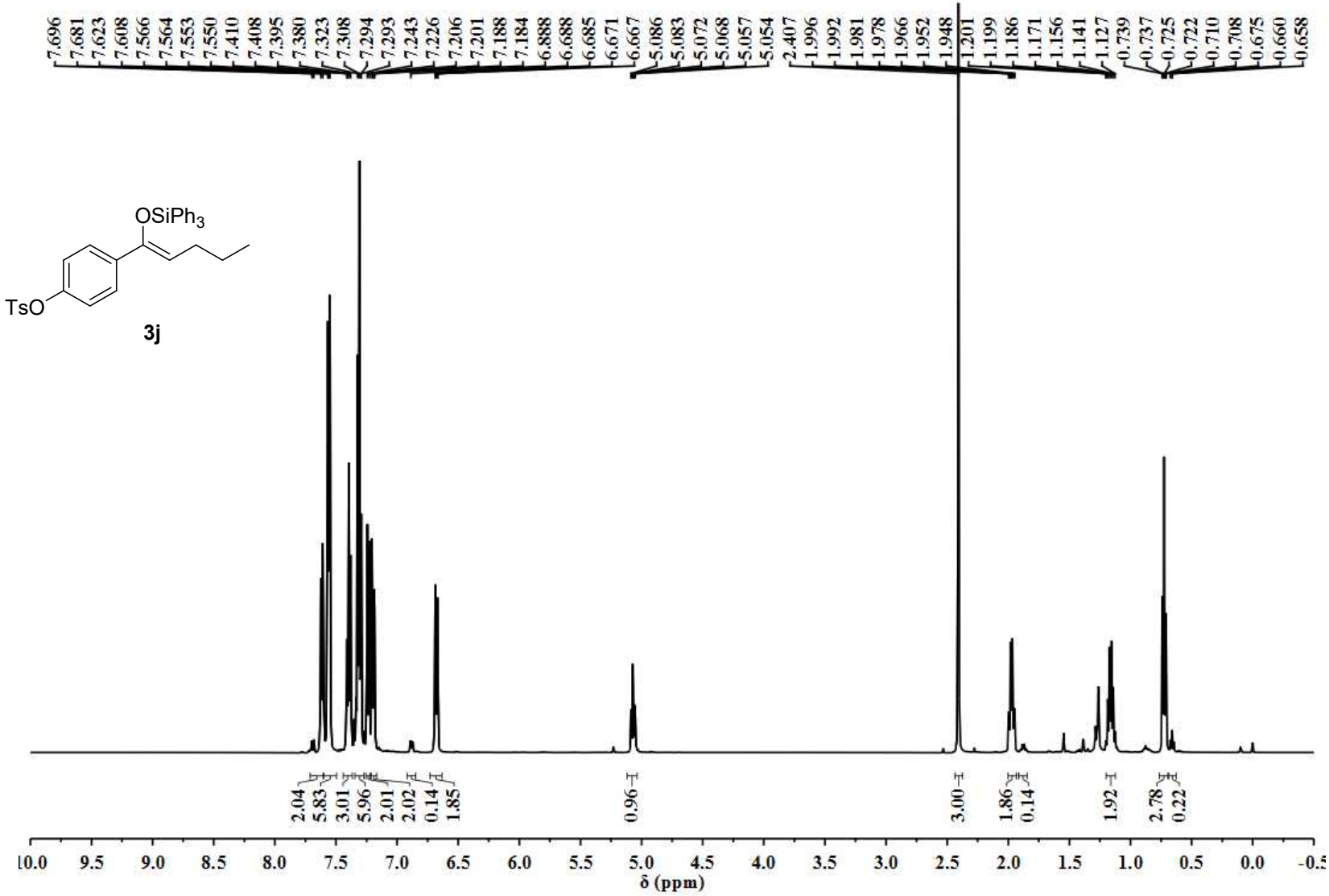
δ (ppm)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7.408
7.395
7.380
7.323
7.308
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7.206
7.201
7.188
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6.688
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1.156
1.141
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0.722
0.710
0.708
0.675
0.660
0.658
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5.83
3.01
5.96
2.01
2.02
0.14
1.85
0.96
3.00
1.86
0.14
1.92
2.78
0.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.0
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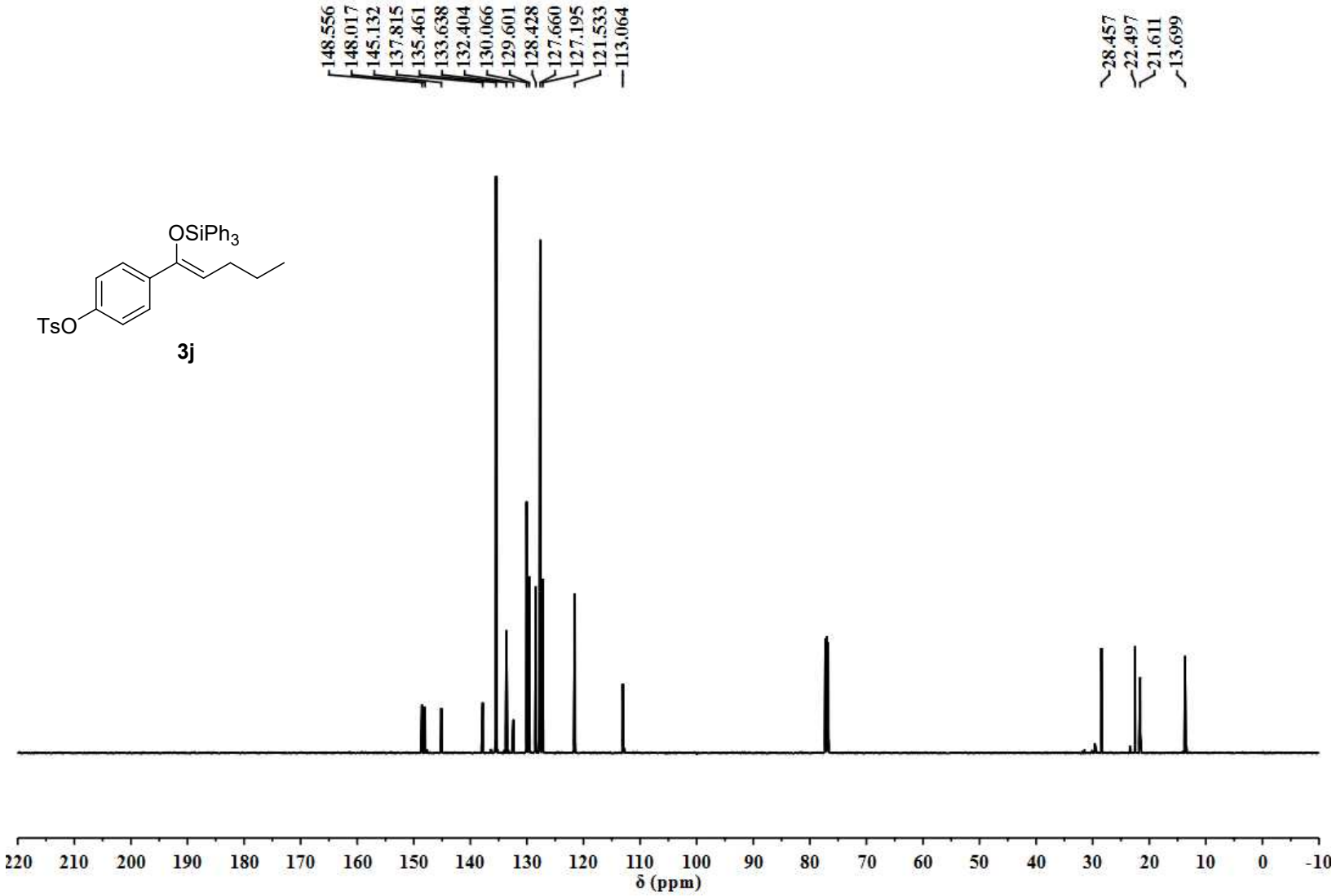
1.0
0.5
0.0
δ (ppm)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113.064
28.457
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OSiPh3
TsO
3j
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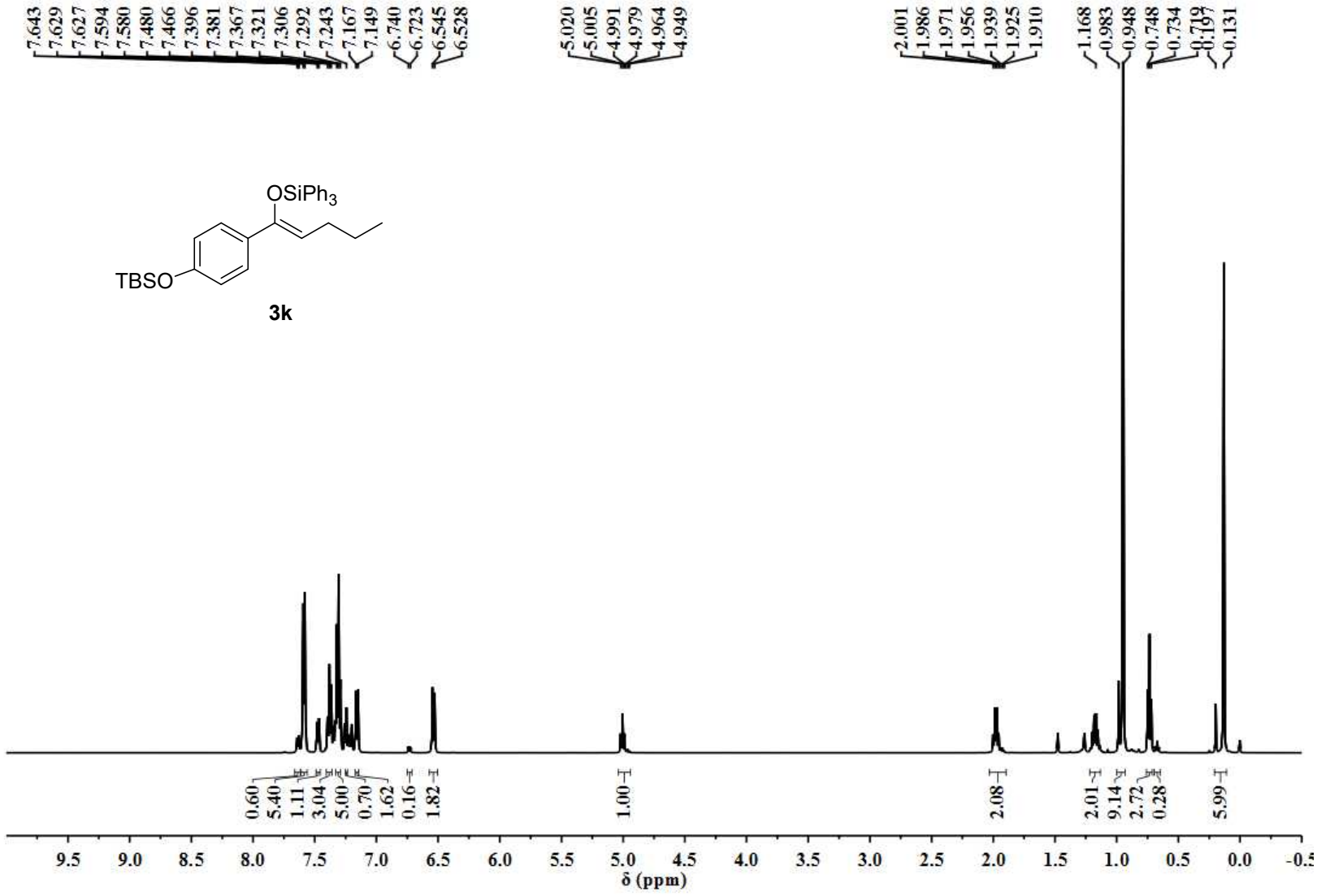
δ (ppm)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7.243
7.167
7.149
6.740
6.723
6.545
6.528
5.020
5.005
4.991
4.979
4.964
4.949
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1.986
1.971
1.956
1.939
1.925
1.910
1.168
0.983
0.948
0.748
0.734
0.719
0.197
0.131
OSiPh3
TBSO
3k
0.60
5.40
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5.00
0.70
1.62
0.16
1.82
1.00
2.08
2.01
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2.72
0.28
5.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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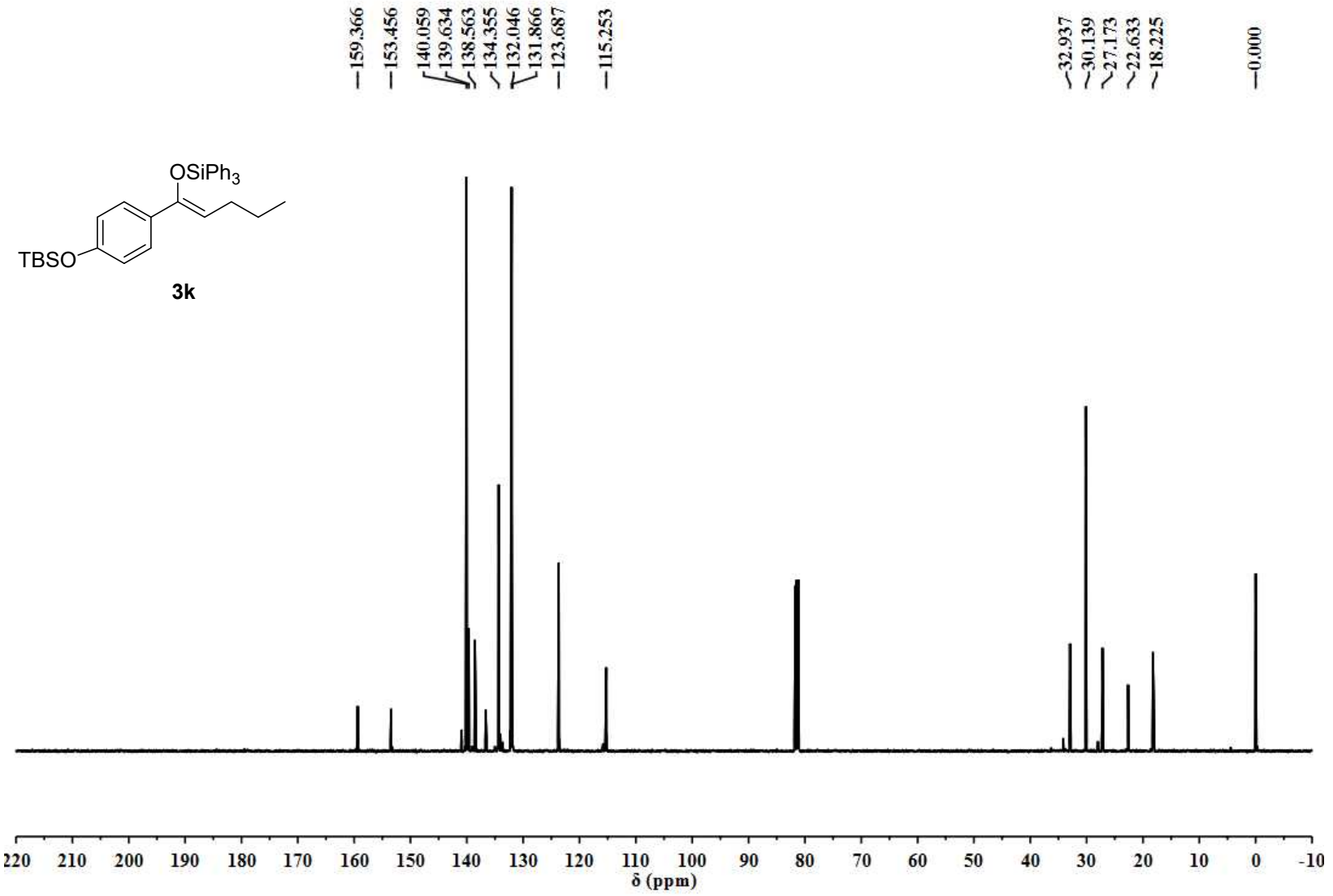
δ (ppm)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131.866
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27.173
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TBSO
3k
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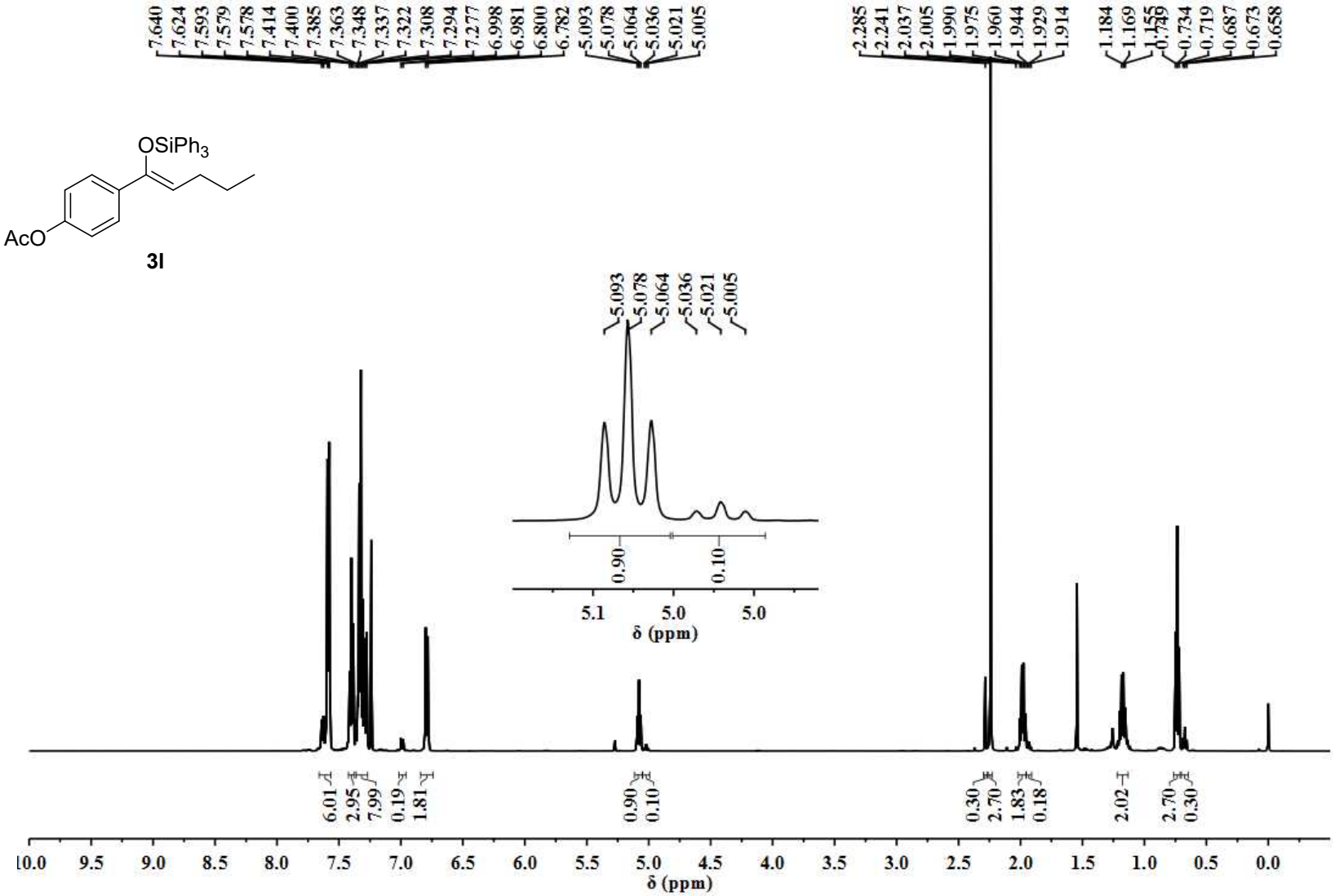
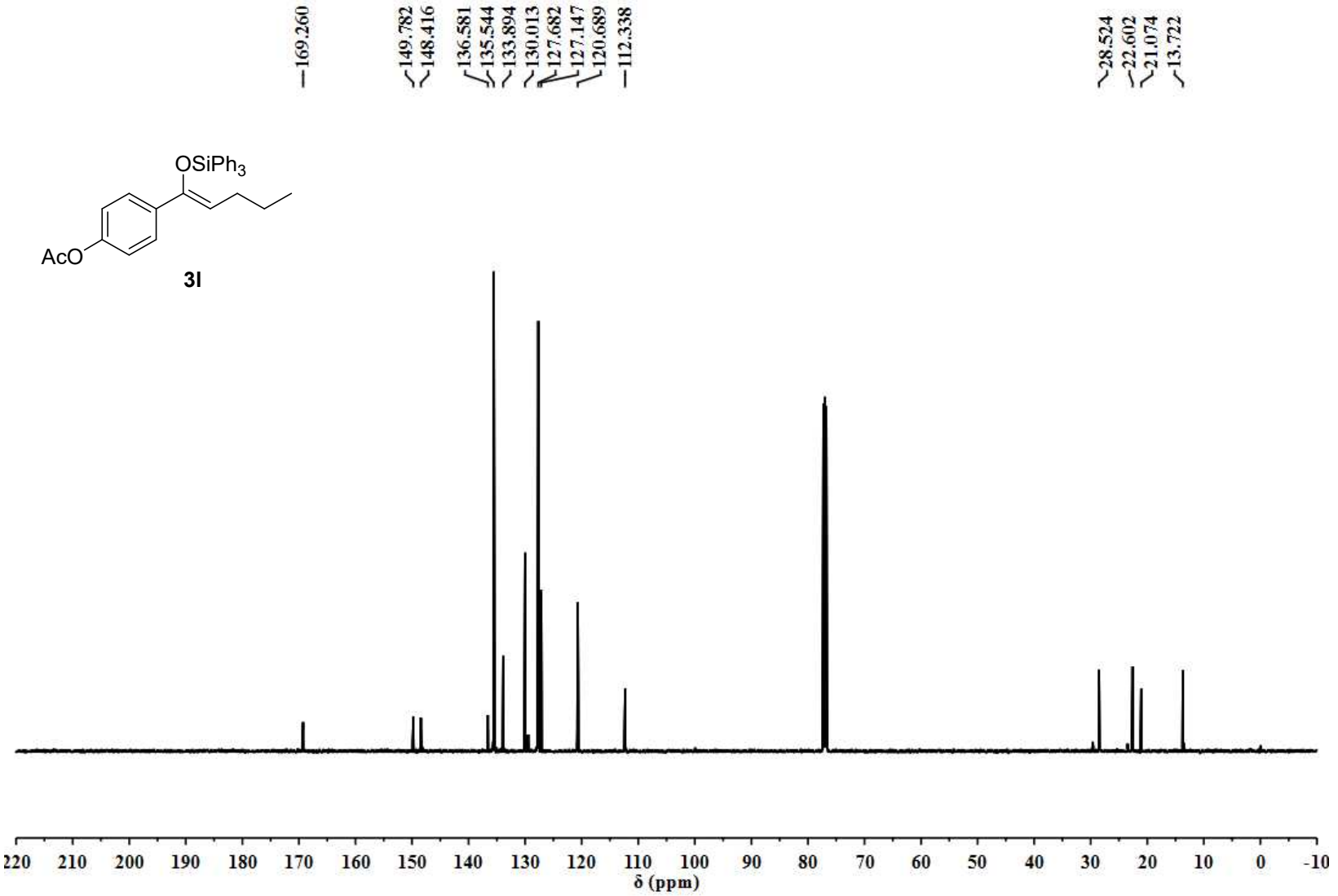
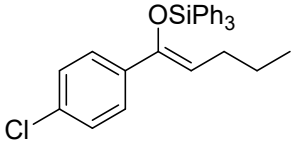
δ (ppm)

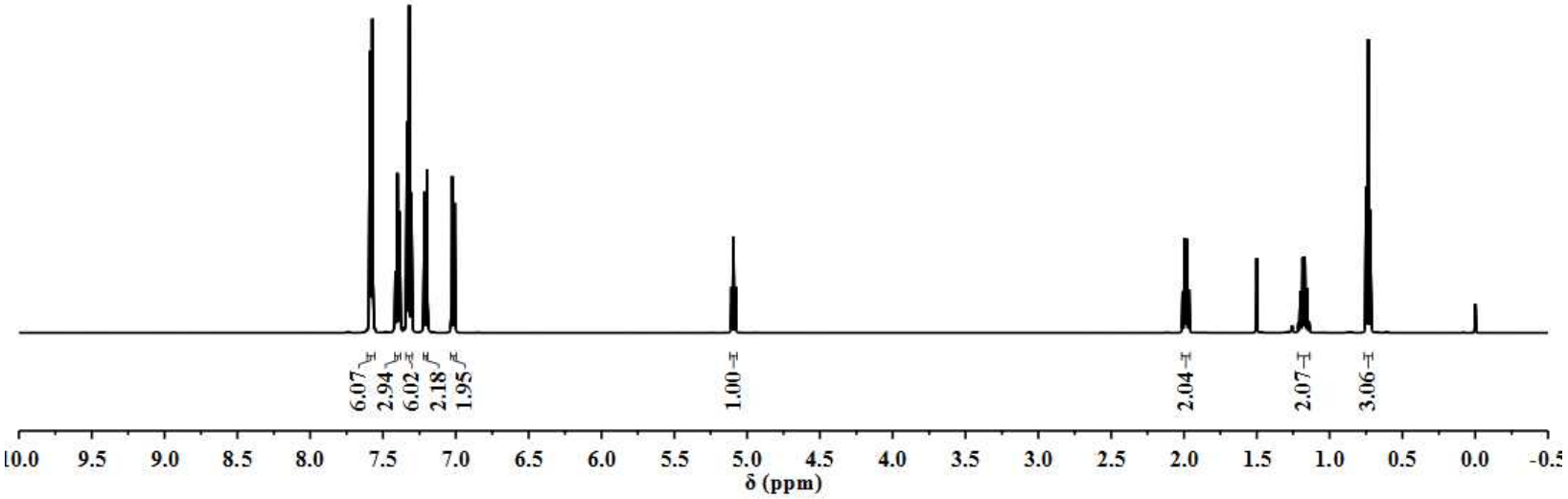

OSiPh3
AcO
3l
δ (ppm)

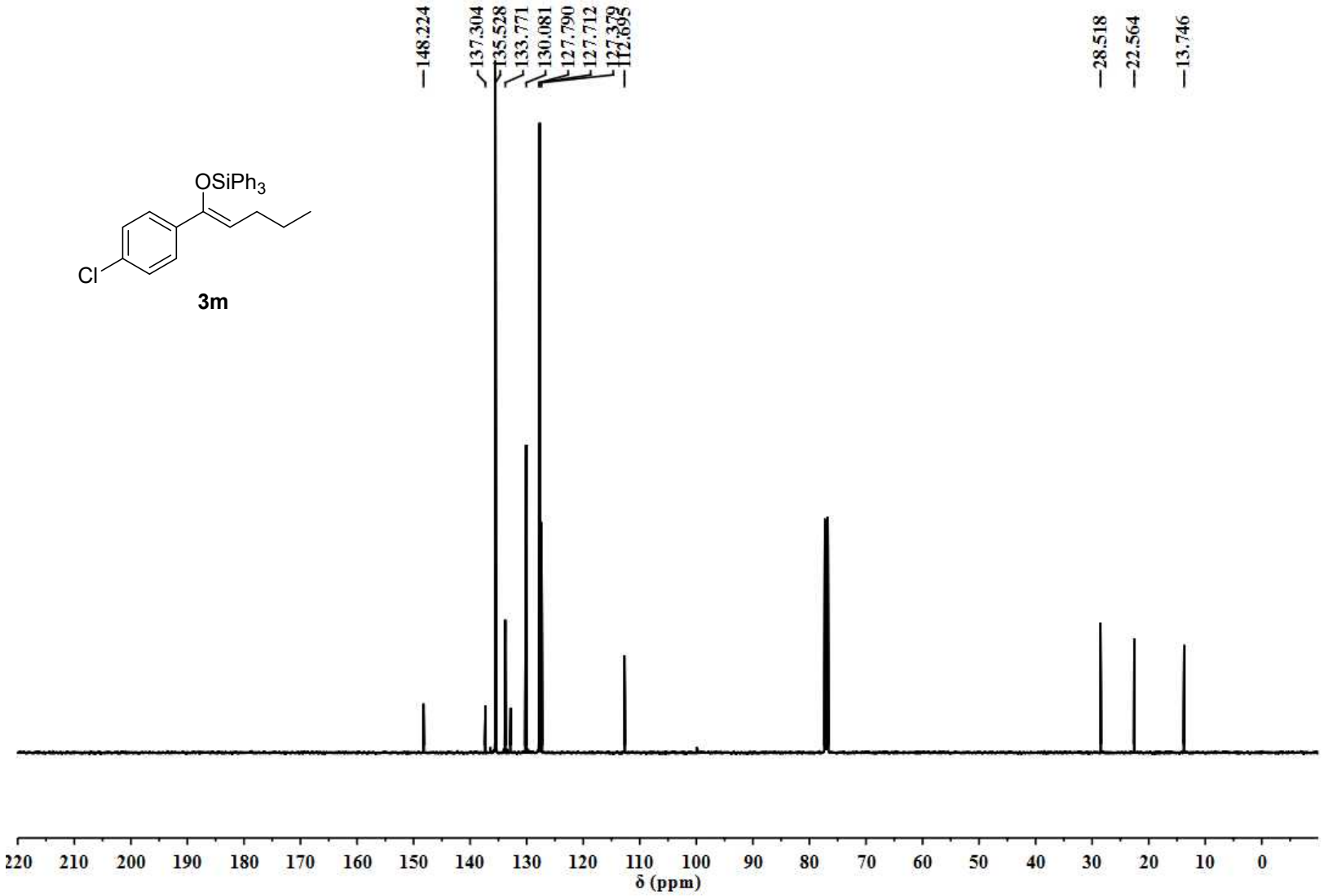

169.260
149.782
148.416
136.581
135.544
133.894
130.013
127.682
127.147
120.689
112.338
28.524
22.602
21.074
13.722
OSiPh3
AcO
3l
δ (ppm)

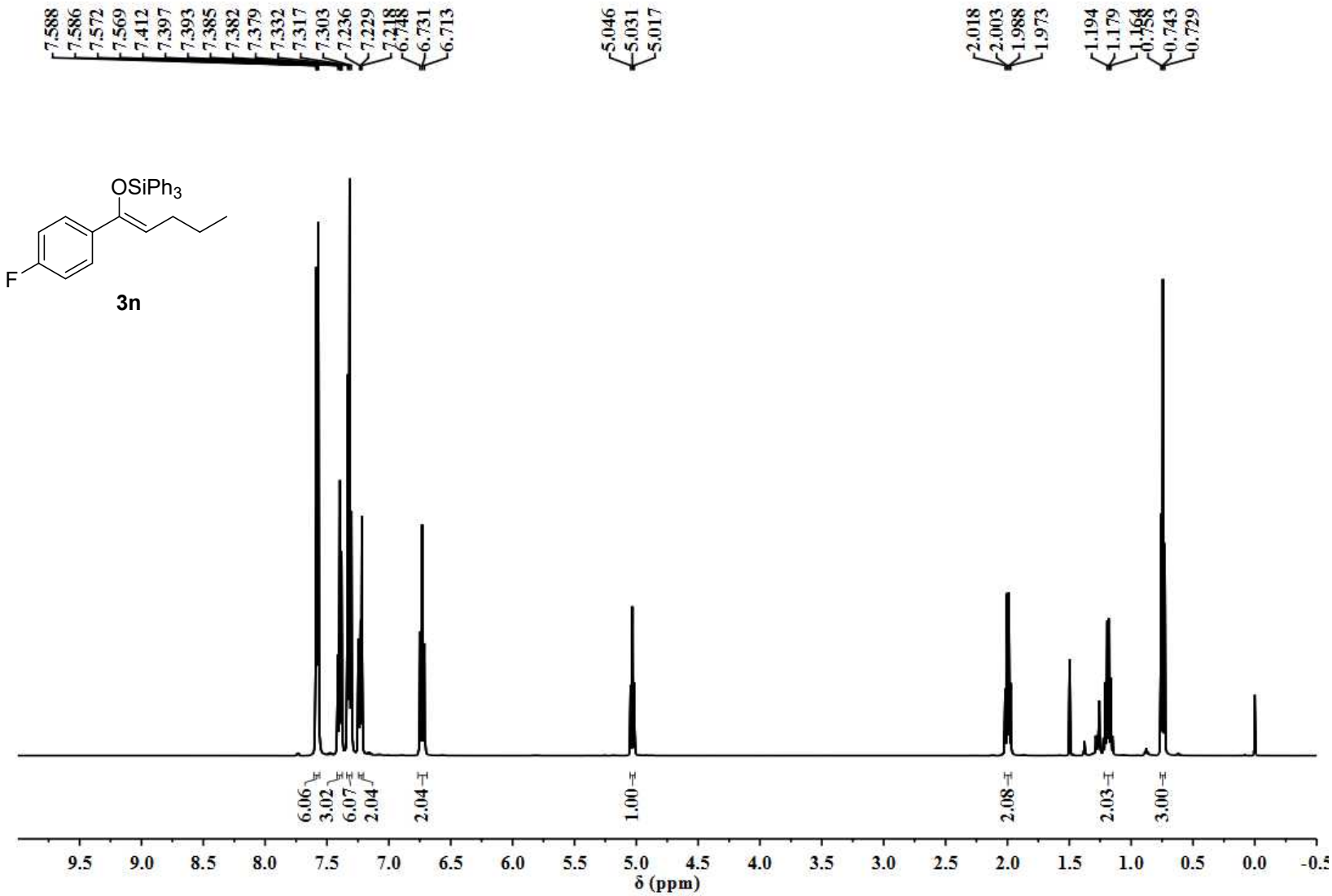

7.590
7.588
7.578
7.574
7.572
7.415
7.405
7.400
7.396
7.388
7.386
7.383
7.334
7.332
7.319
7.308
7.305
7.303
7.216
7.215
7.201
7.197
7.025
7.021
5.093
5.078
2.009
1.995
1.980
1.965
1.185
1.170
0.734
0.719

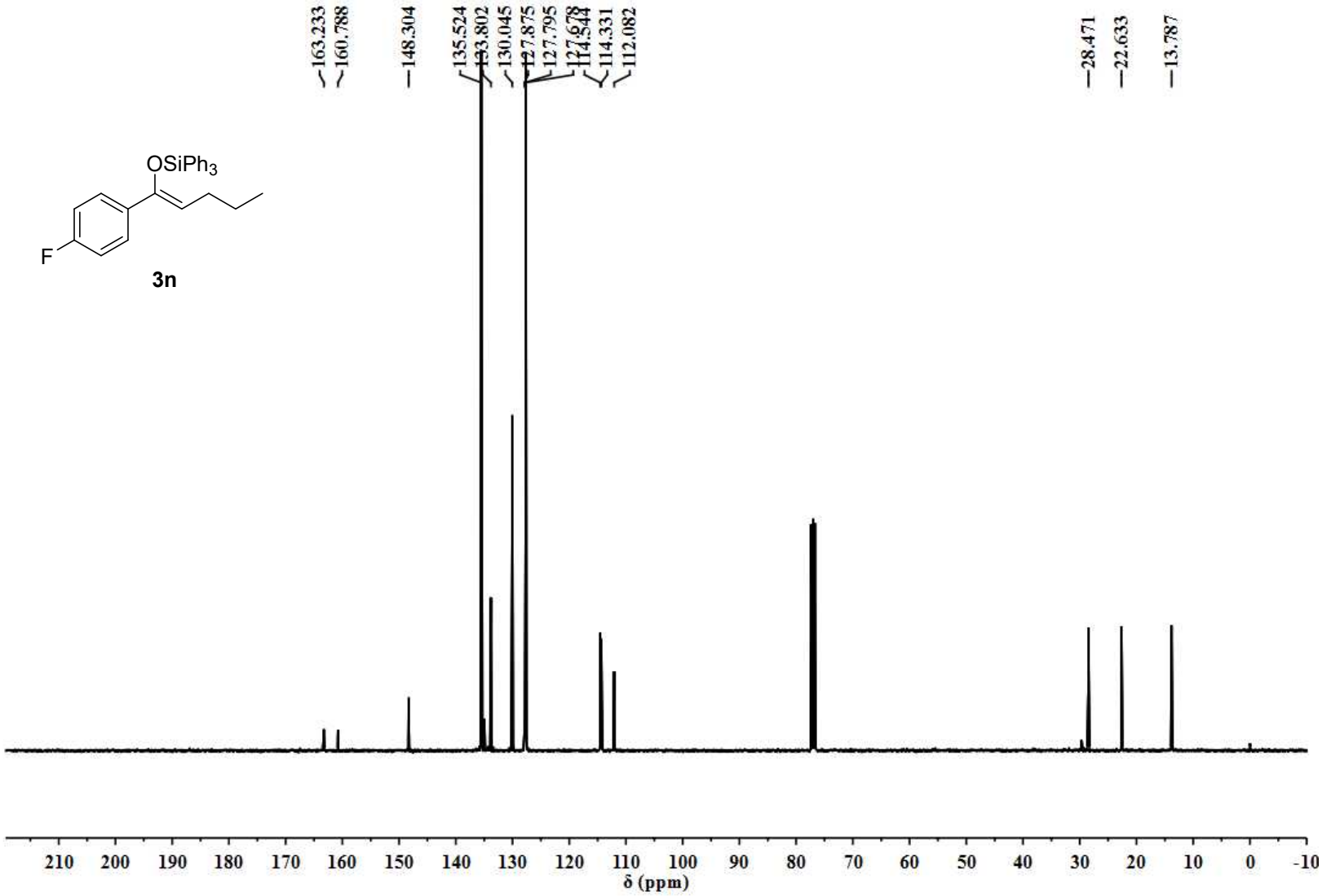

OSiPh3
Cl

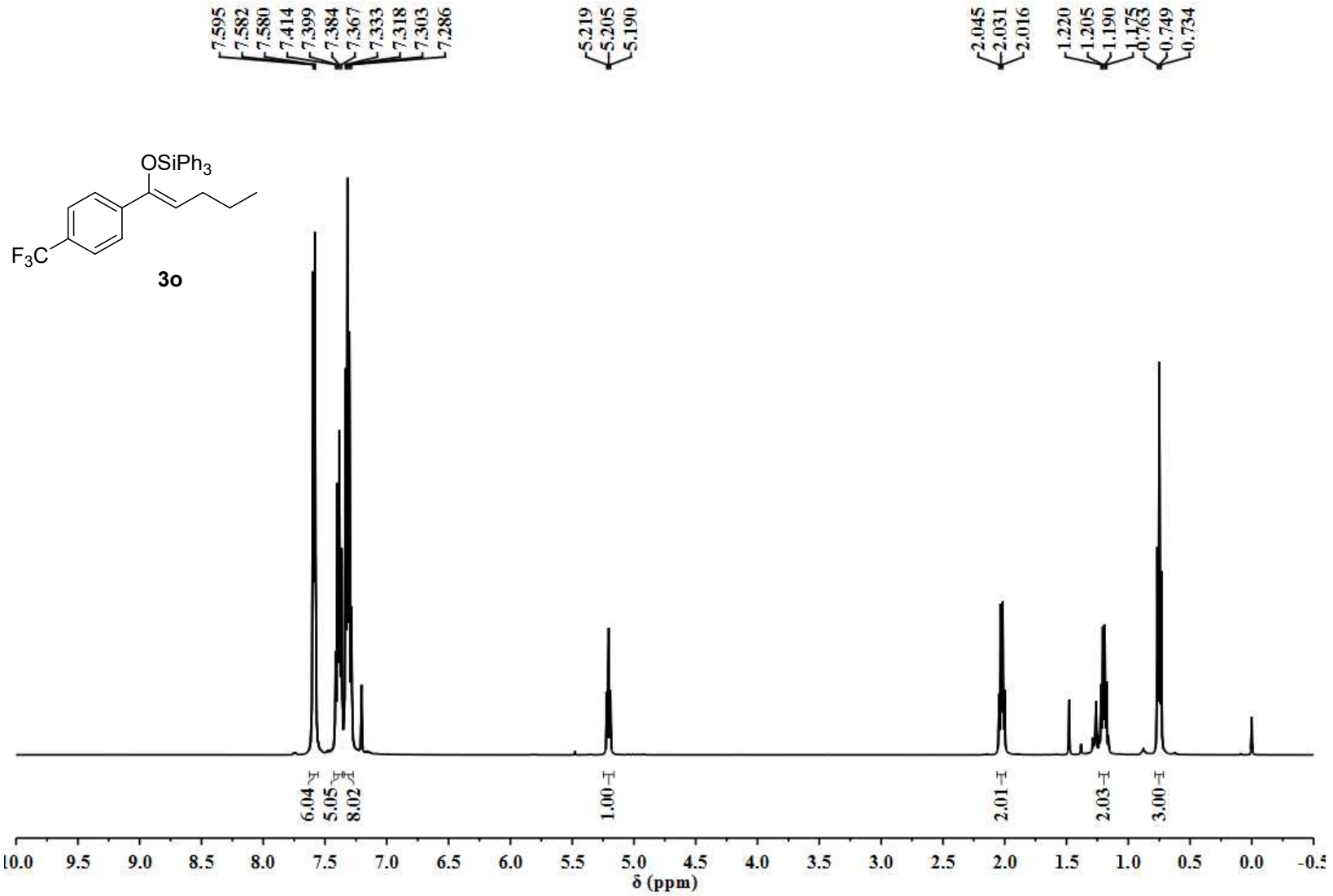
3m

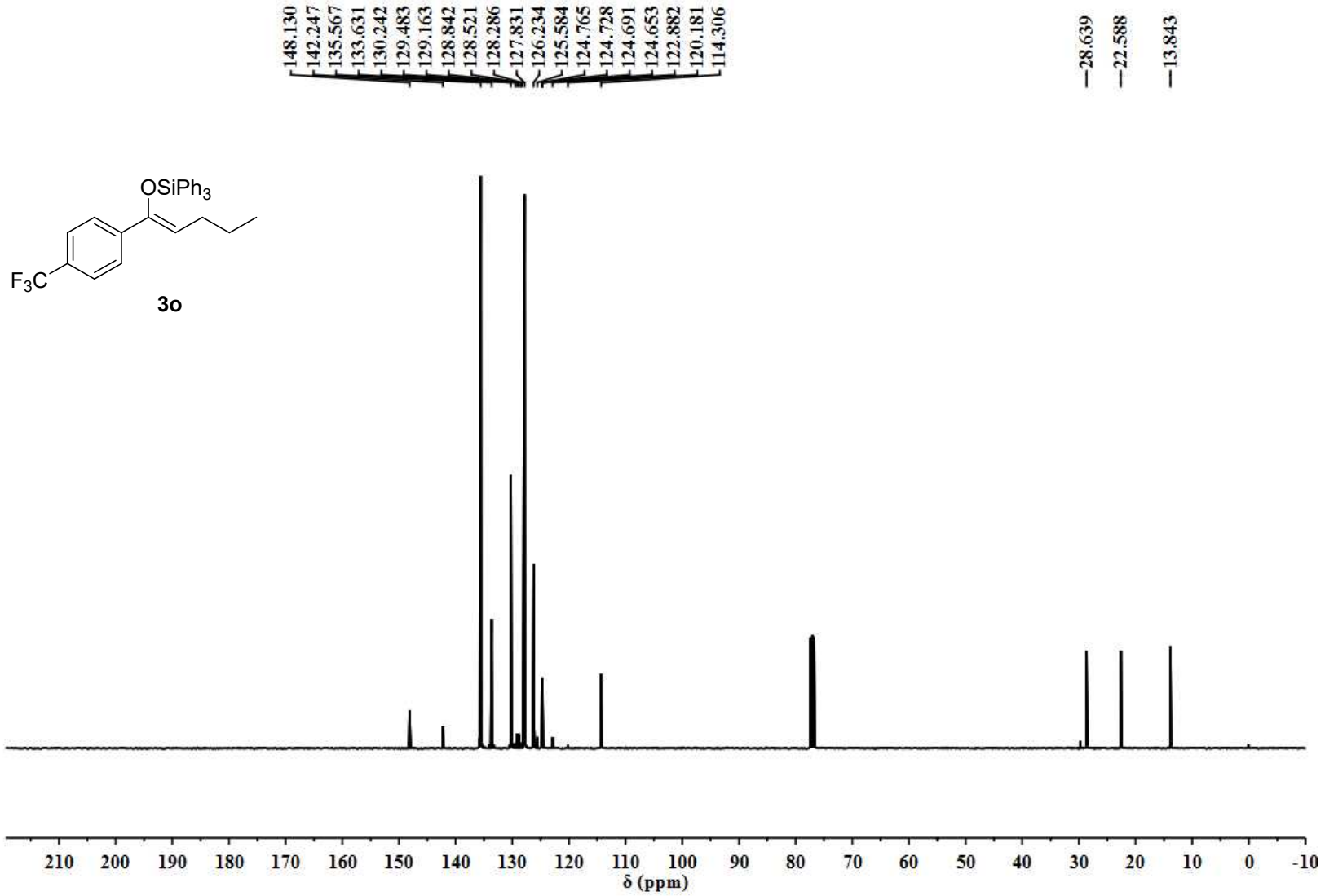

6.07
2.94
6.02
2.18
1.95
1.00
2.04
2.07
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

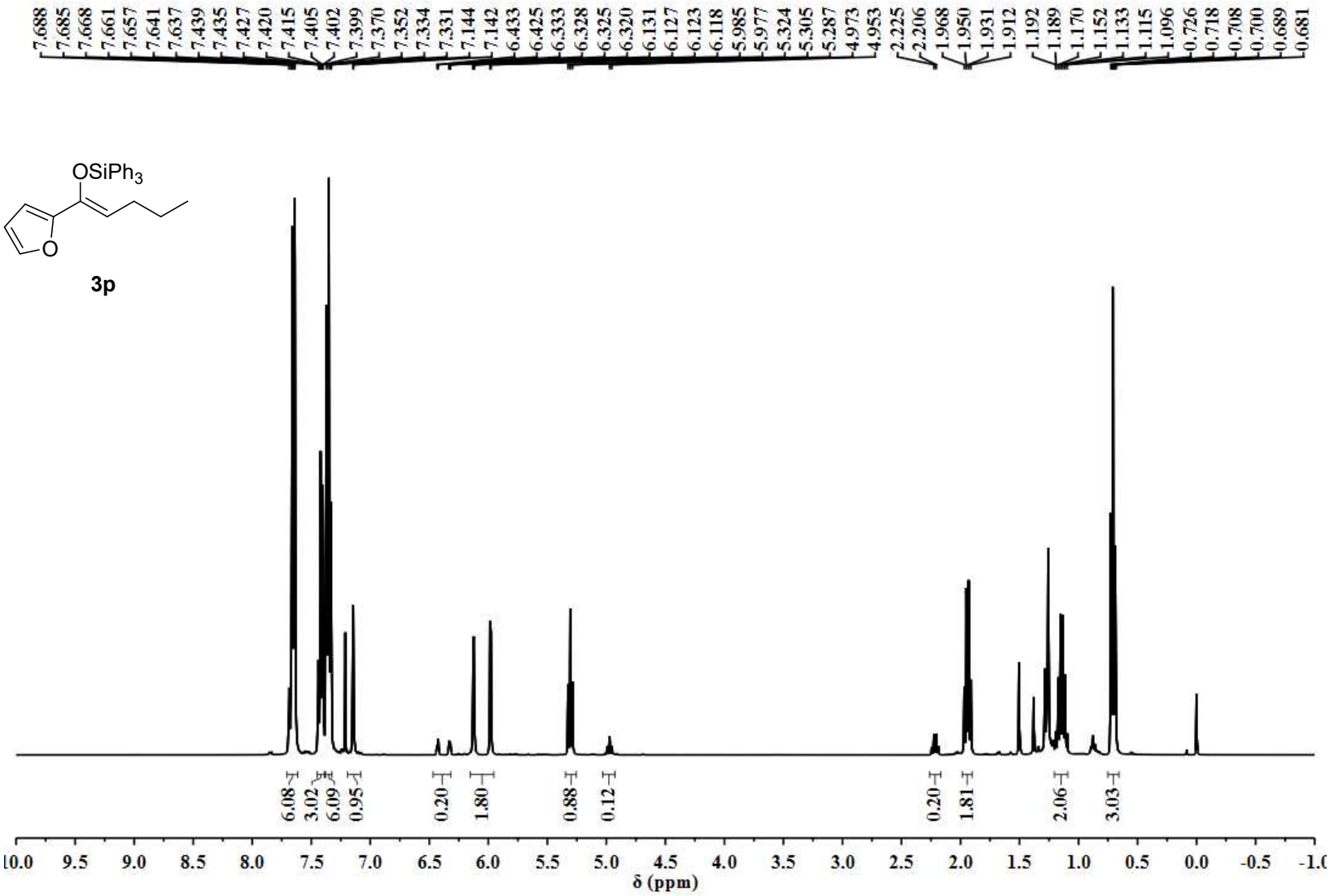

148.224
137.304
135.528
133.771
130.081
127.790
127.712
127.379
112.695
28.518
22.564
13.746
OSiPh3
Cl
3m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

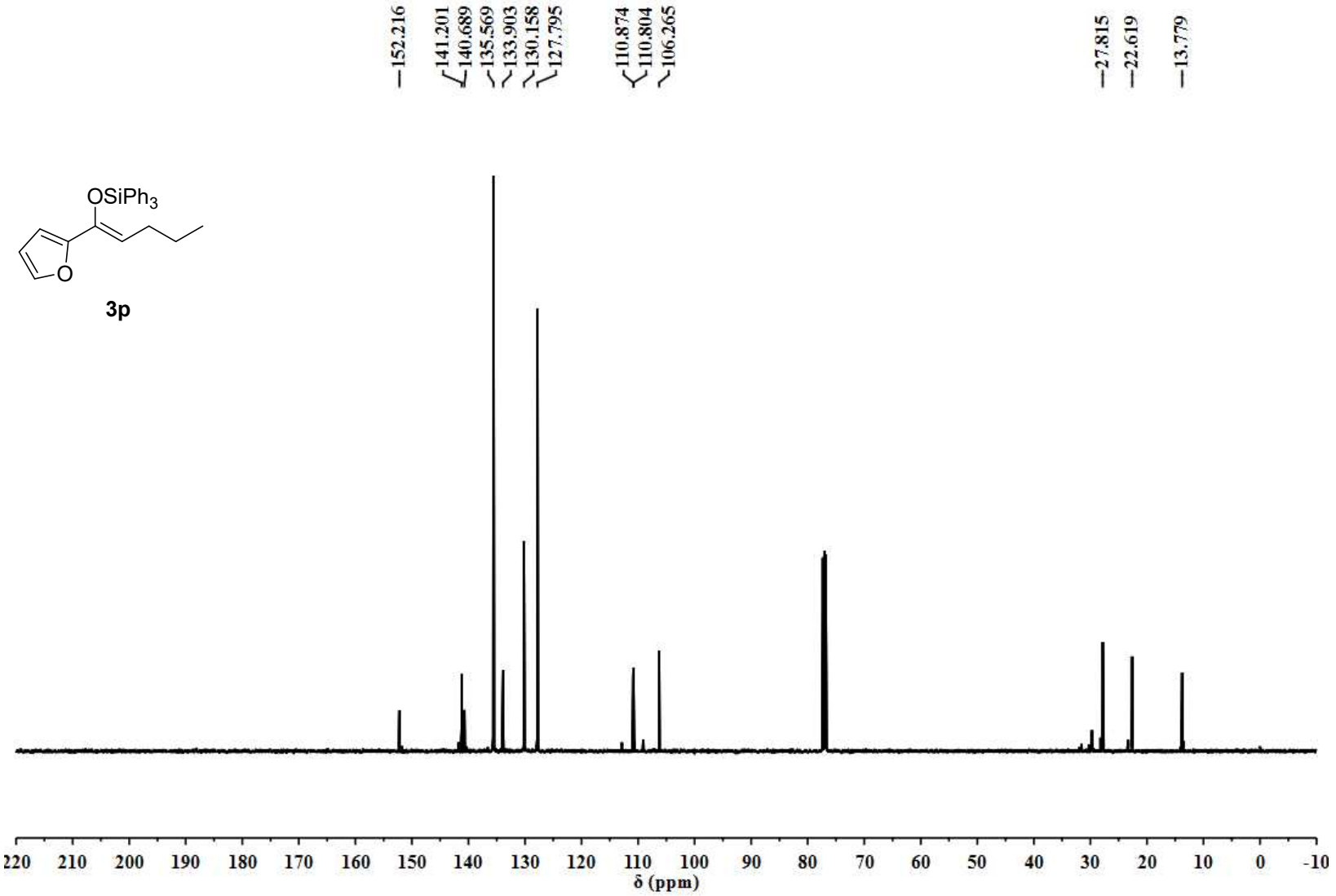

7.588
7.586
7.572
7.569
7.412
7.397
7.393
7.385
7.382
7.379
7.332
7.317
7.303
7.236
7.229
7.218
6.748
6.731
6.713
5.046
5.031
5.017
2.018
2.003
1.988
1.973
1.194
1.179
1.164
0.758
0.743
0.729
OSiPh3
F
3n
6.06
3.02
6.07
2.04
2.04
1.00
2.08
2.03
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

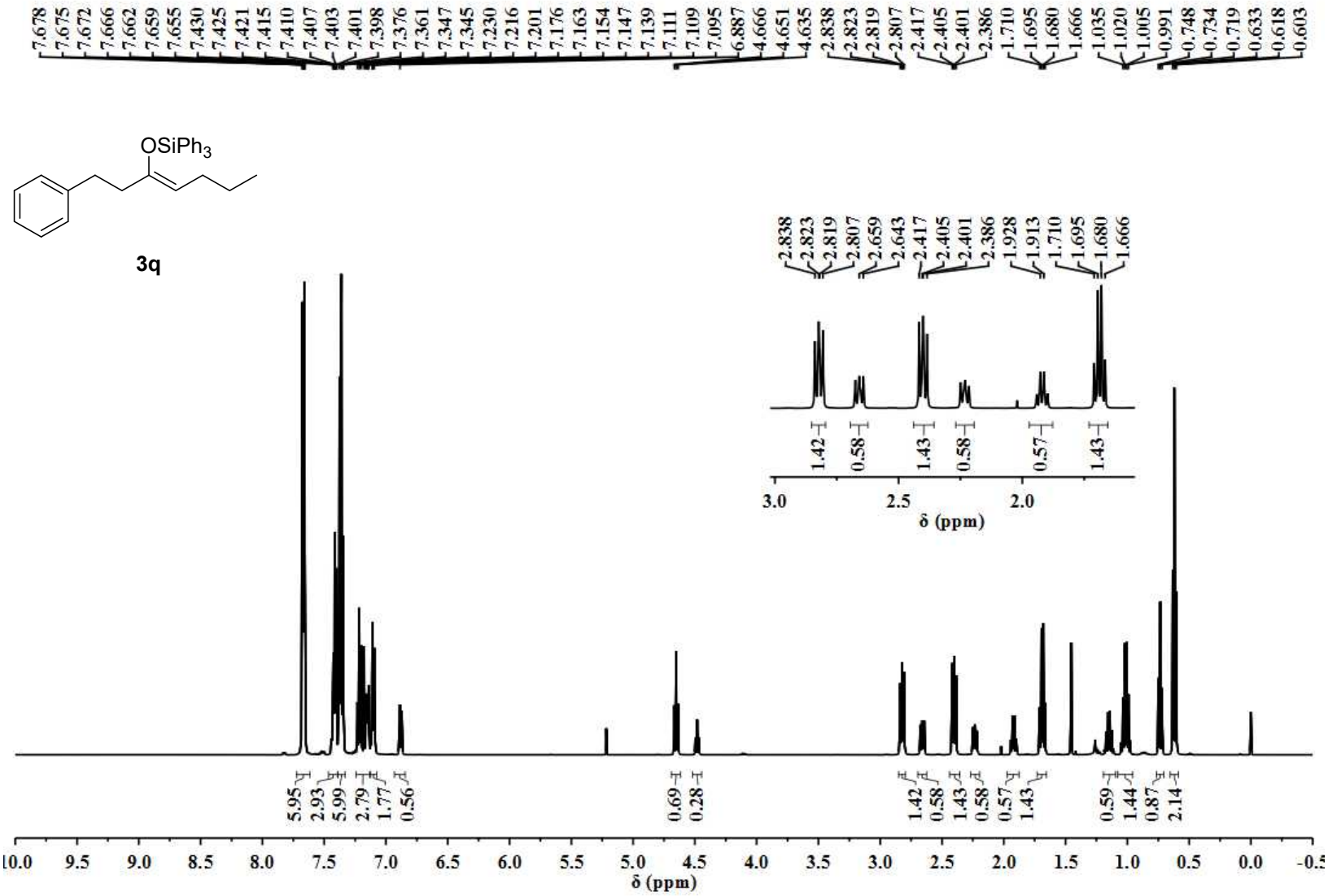

163.233
160.788
148.304
135.524
133.802
130.045
127.875
127.795
127.678
114.544
114.331
112.082
28.471
22.633
13.787
OSiPh3
F
3n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

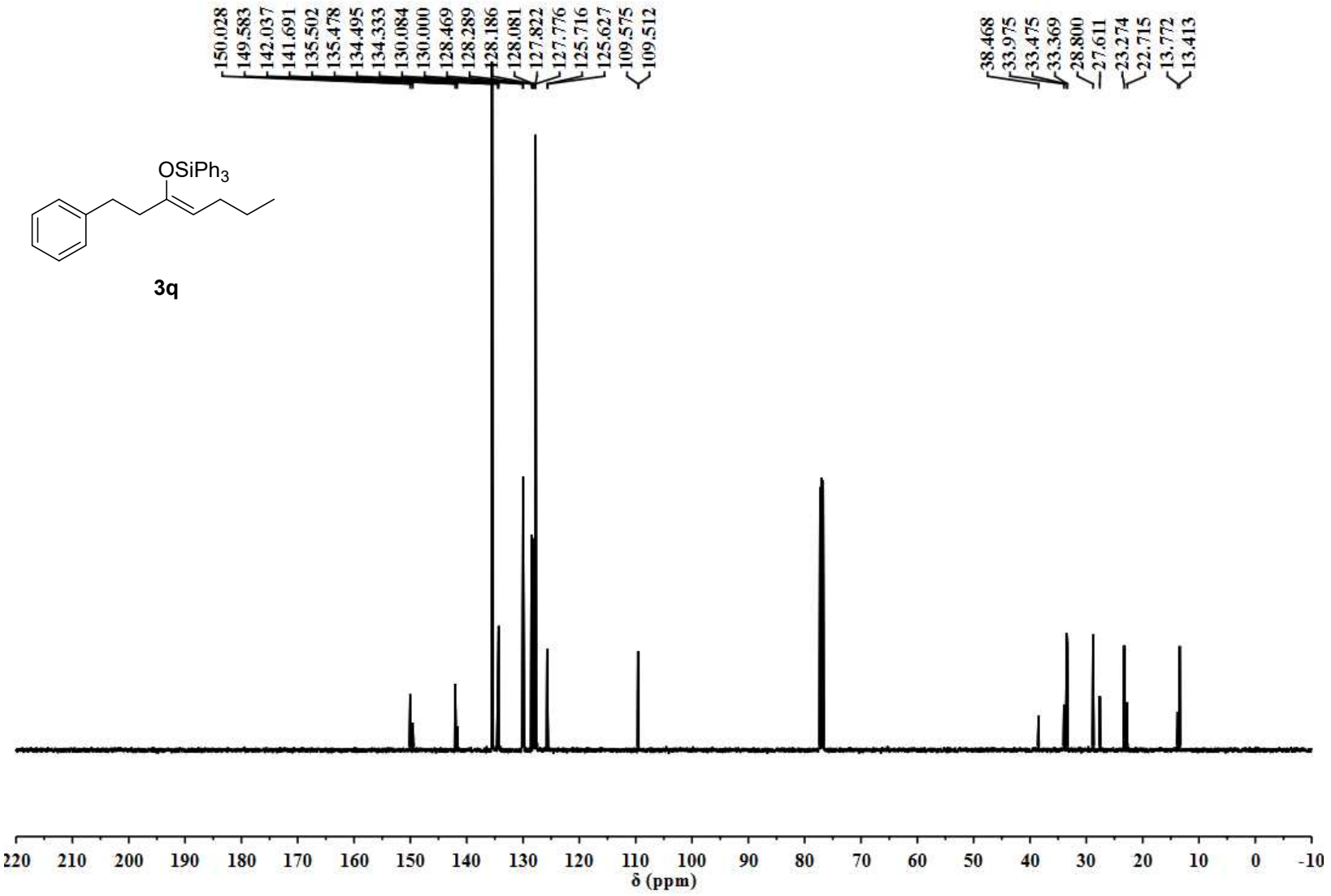

7.595
7.582
7.580
7.414
7.399
7.384
7.367
7.333
7.318
7.303
7.286
5.219
5.205
5.190
2.045
2.031
2.016
1.220
1.205
1.190
1.175
0.763
0.749
0.734
OSiPh3
F3C
3o
6.04
5.05
8.02
1.00
2.01
2.03
3.00
δ (ppm)

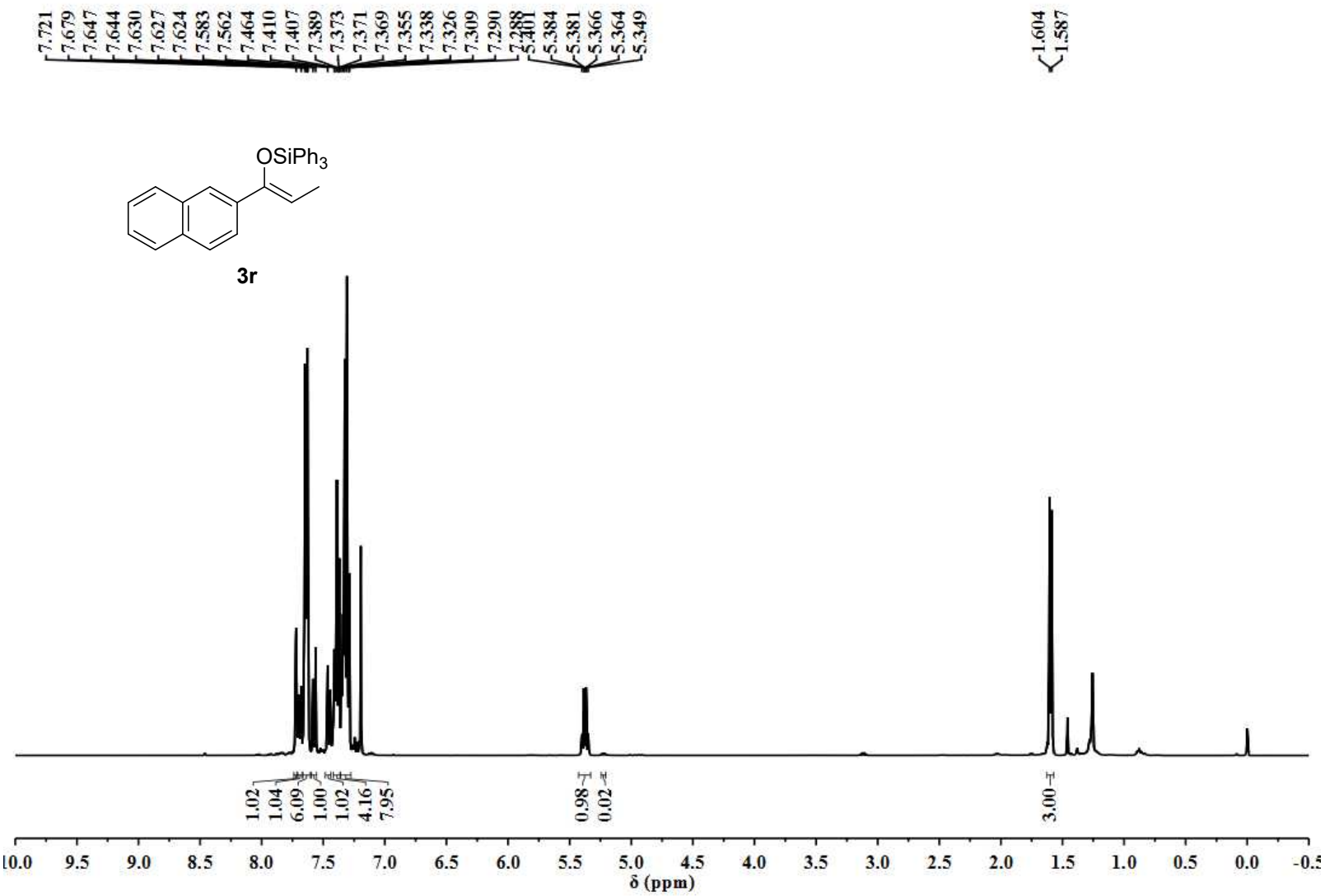

148.130
142.247
135.567
133.631
130.242
129.483
129.163
128.842
128.521
128.286
127.831
126.234
125.584
124.765
124.728
124.691
124.653
122.882
120.181
114.306
28.639
22.588
13.843
OSiPh3
F3C
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

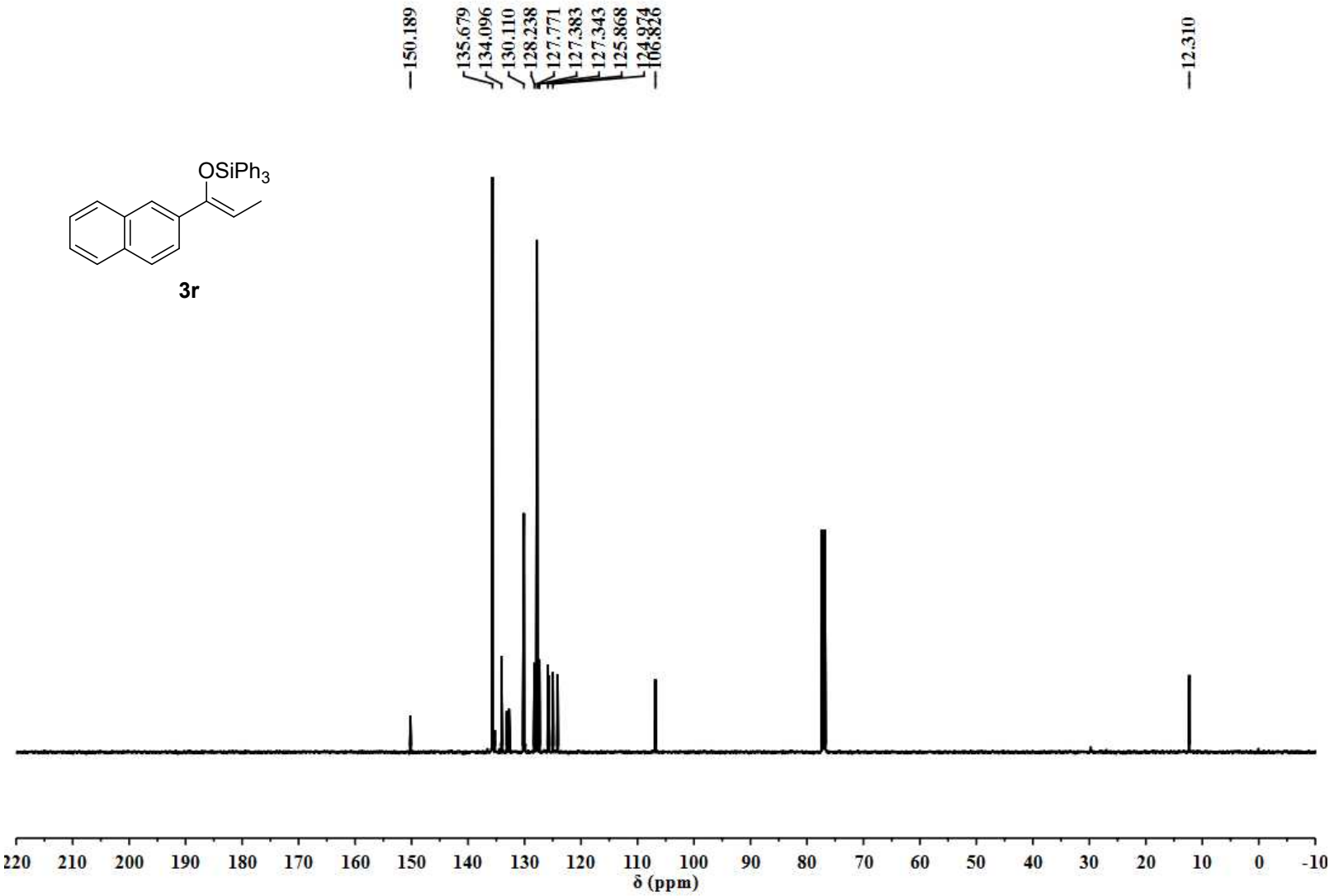

7.688
7.685
7.668
7.661
7.657
7.641
7.637
7.439
7.435
7.427
7.420
7.415
7.405
7.402
7.399
7.370
7.352
7.334
7.331
7.144
7.142
6.433
6.425
6.333
6.328
6.325
6.320
6.131
6.127
6.123
6.118
5.985
5.977
5.324
5.305
5.287
4.973
4.953
2.225
2.206
1.968
1.950
1.931
1.912
1.192
1.189
1.170
1.152
1.133
1.115
1.096
0.726
0.718
0.708
0.700
0.689
0.681
OSiPh3
O
3p
6.08
3.02
6.09
0.95
0.20
1.80
0.88
0.12
0.20
1.81
2.06
3.03
δ (ppm)

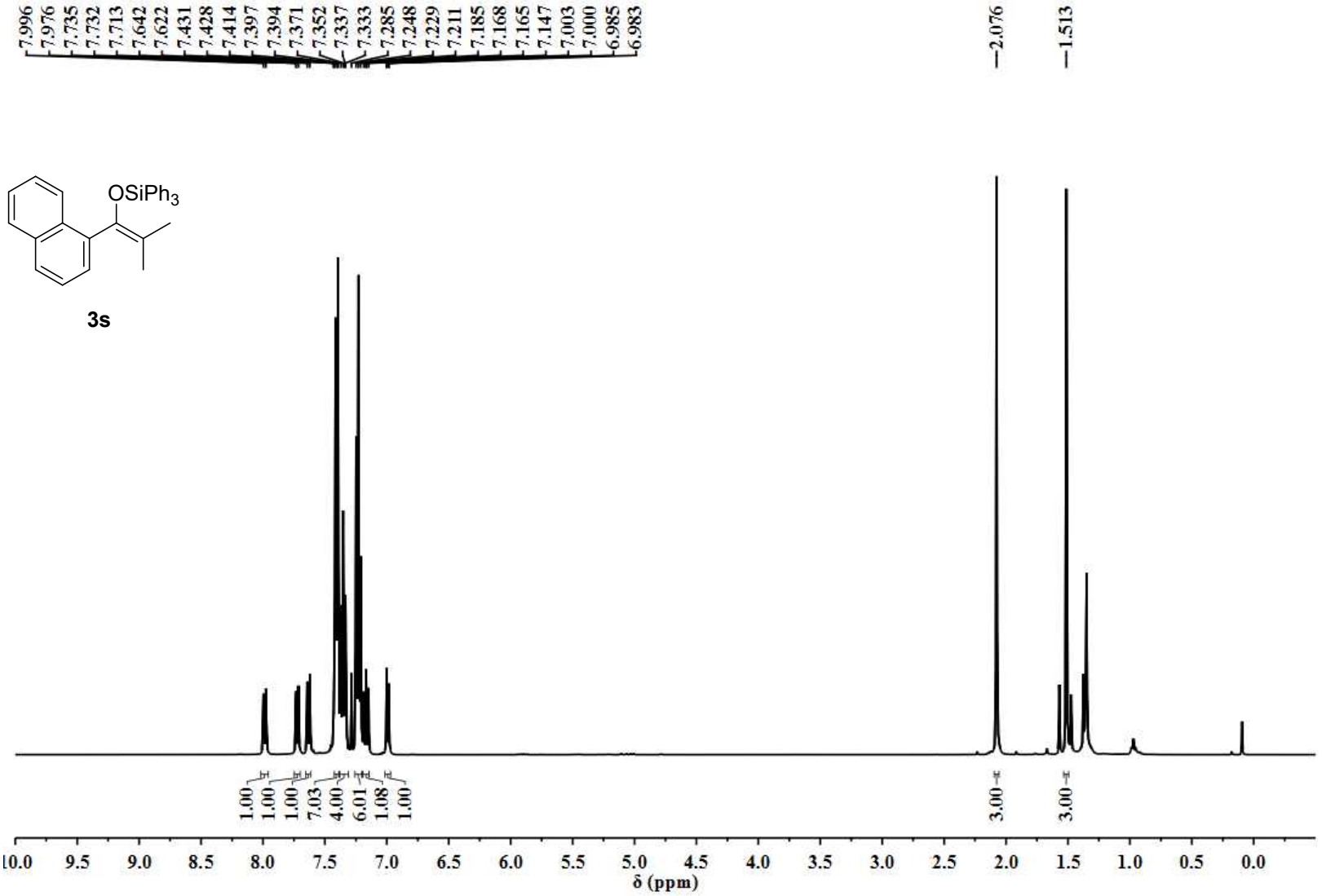

152.216
141.201
140.689
135.569
133.903
130.158
127.795
110.874
110.804
106.265
27.815
22.619
13.779
OSiPh3
O
3p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

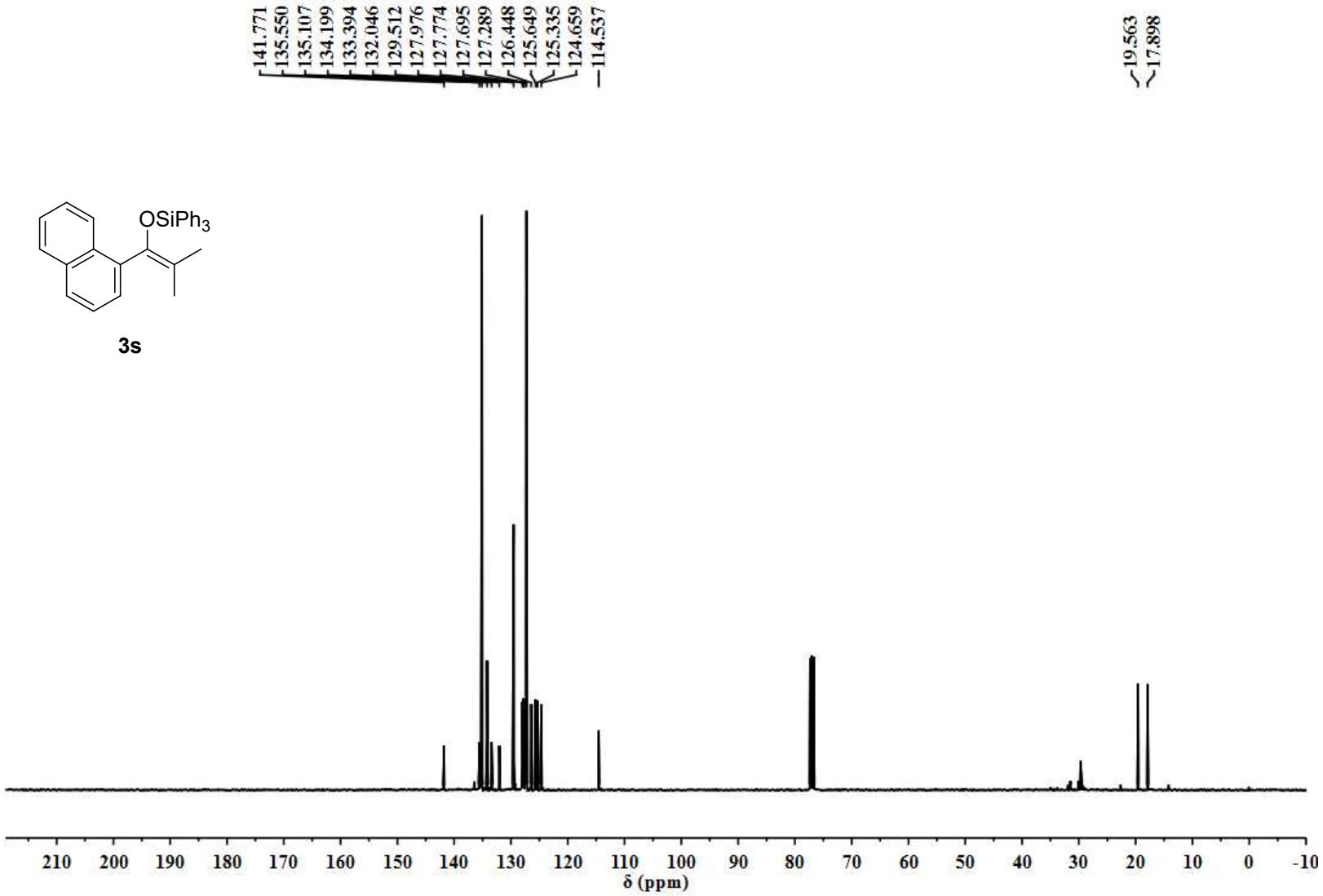

7.678
7.675
7.672
7.666
7.662
7.659
7.655
7.430
7.425
7.421
7.415
7.410
7.407
7.403
7.401
7.398
7.376
7.361
7.347
7.345
7.230
7.216
7.201
7.176
7.163
7.154
7.147
7.139
7.111
7.109
7.095
6.887
4.666
4.651
4.635
2.838
2.823
2.819
2.807
2.417
2.405
2.401
2.386
1.710
1.695
1.680
1.666
1.035
1.020
1.005
0.991
0.748
0.734
0.719
0.633
0.618
0.603
OSiPh3
3q
2.838
2.823
2.819
2.807
2.659
2.643
2.417
2.405
2.401
2.386
1.928
1.913
1.710
1.695
1.680
1.666
1.42
0.58
1.43
0.58
0.57
1.43
3.0
2.5
2.0
δ (ppm)
5.95
2.93
5.99
2.79
1.77
0.56
0.69
0.28
1.42
0.58
1.43
0.58
0.57
1.43
0.59
1.44
0.87
2.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

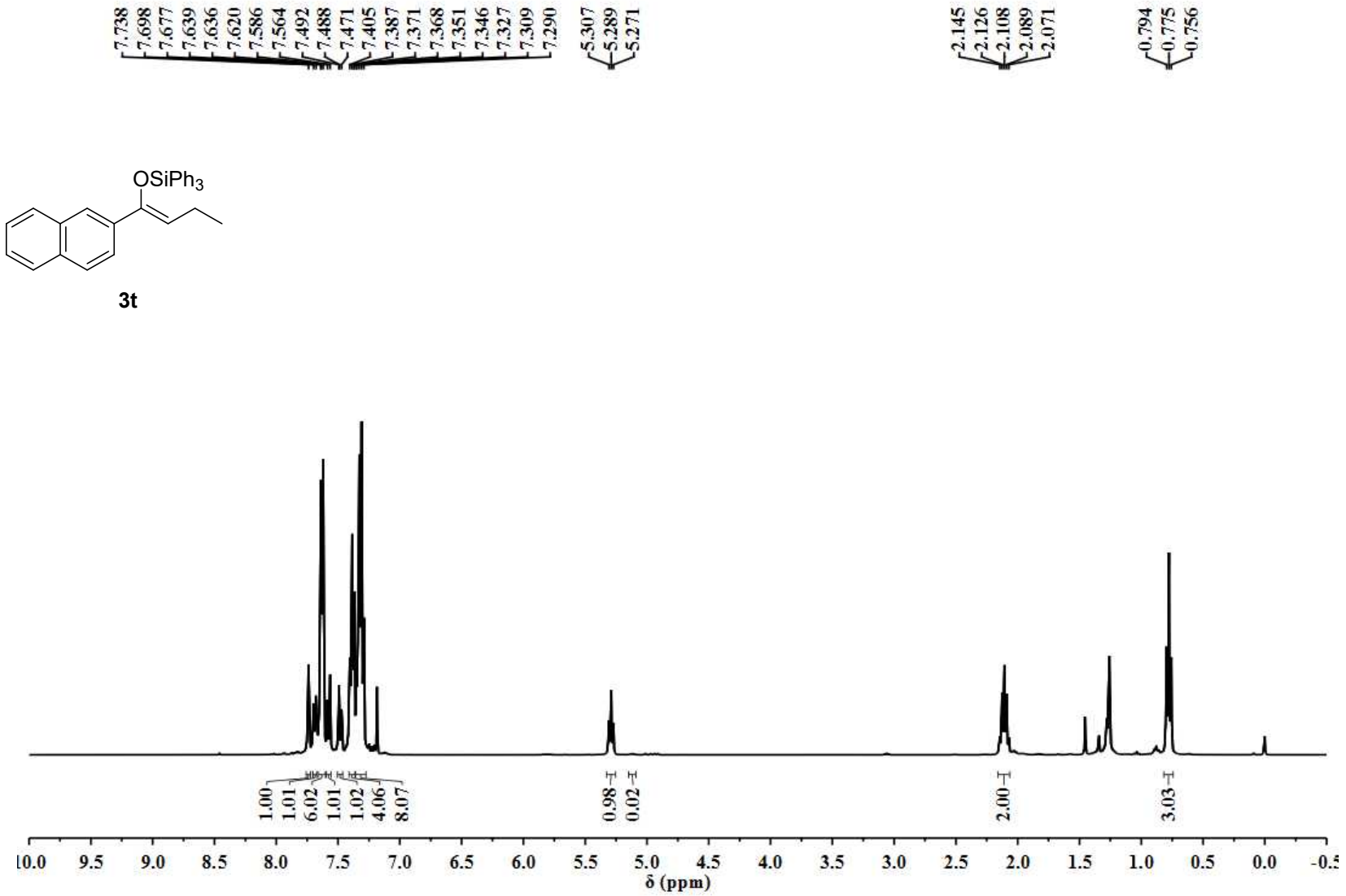

150.028
149.583
142.037
141.691
135.502
135.478
134.495
134.333
130.084
130.000
128.469
128.289
128.186
128.081
127.822
127.776
125.716
125.627
109.575
109.512
38.468
33.975
33.475
33.369
28.800
27.611
23.274
22.715
13.772
13.413
OSiPh3
3q
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


7.721
7.679
7.647
7.644
7.630
7.627
7.624
7.583
7.562
7.464
7.410
7.407
7.389
7.373
7.371
7.369
7.355
7.338
7.326
7.309
7.290
7.288
5.401
5.384
5.381
5.366
5.364
5.349
1.604
1.587
OSiPh3
3r
1.02
1.04
6.09
1.00
1.02
4.16
7.95
0.98
0.02
3.00
δ (ppm)

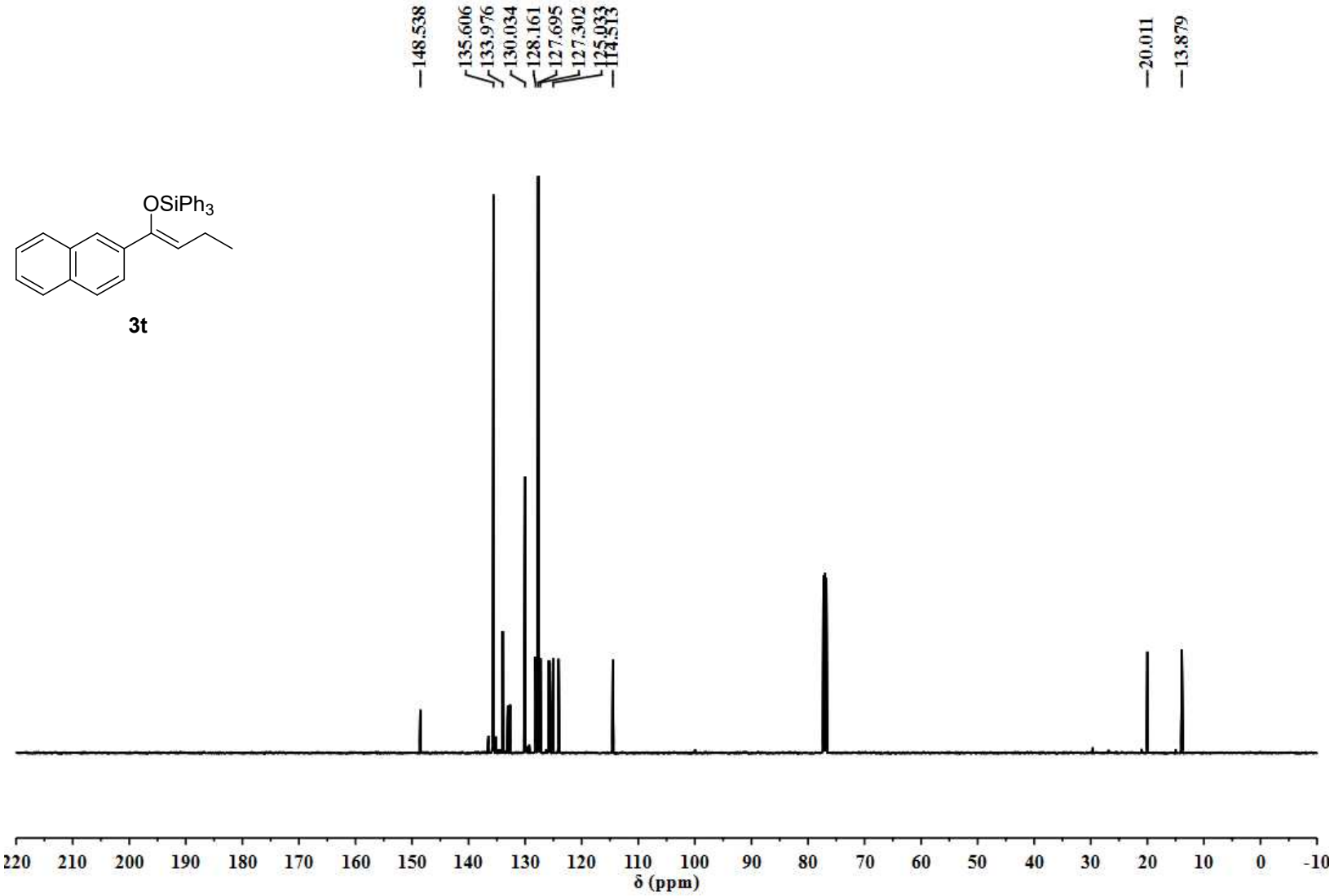

150.189
135.679
134.096
130.110
128.238
127.771
127.383
127.343
125.868
124.974
106.826
12.310
OSiPh3
3r
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

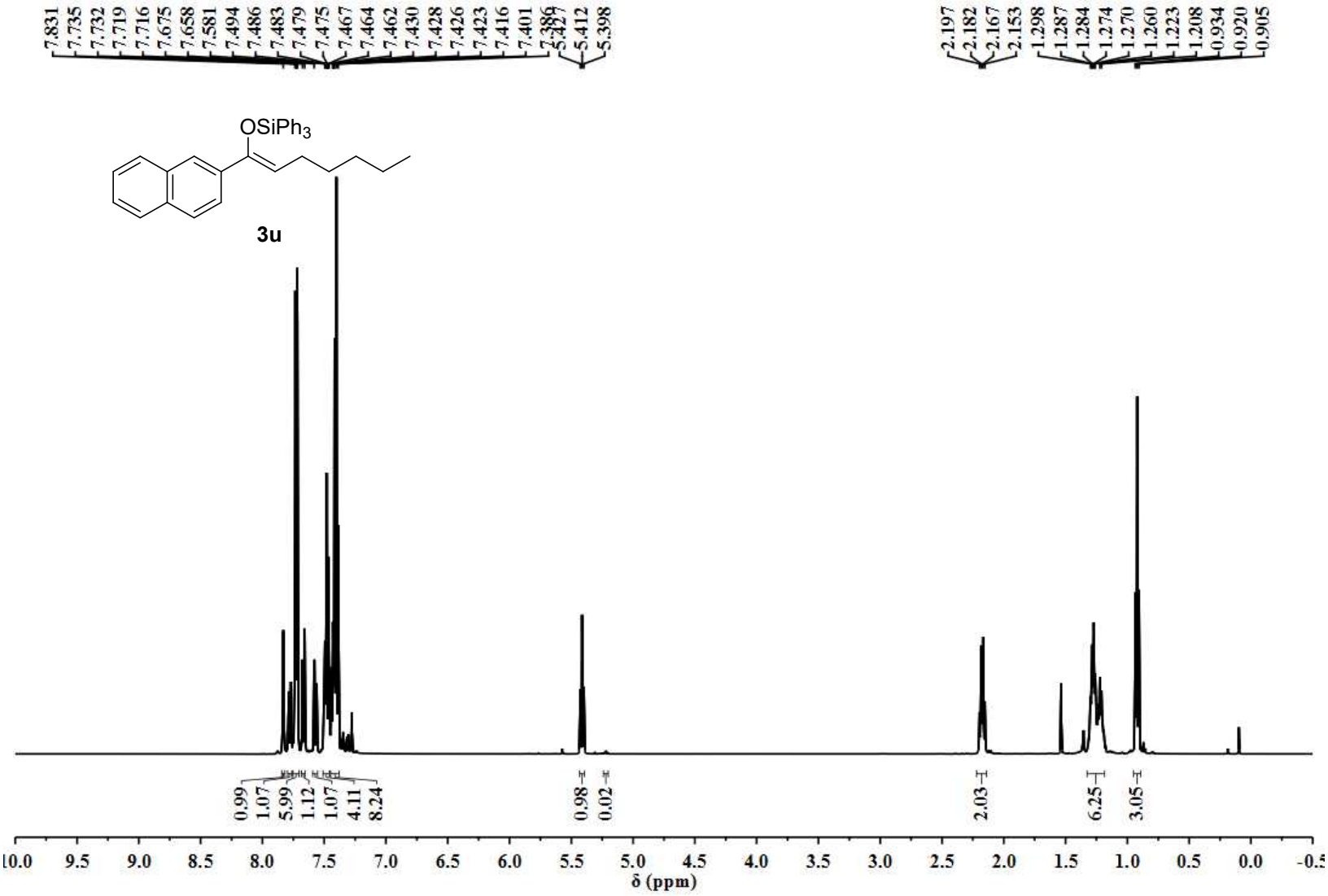

7.996
7.976
7.735
7.732
7.713
7.642
7.622
7.431
7.428
7.414
7.397
7.394
7.371
7.352
7.337
7.333
7.285
7.248
7.229
7.211
7.185
7.168
7.165
7.147
7.003
7.000
6.985
6.983
2.076
1.513
OSiPh3
3s
1.00
1.00
1.00
7.03
4.00
6.01
1.08
1.00
3.00
3.00
δ (ppm)

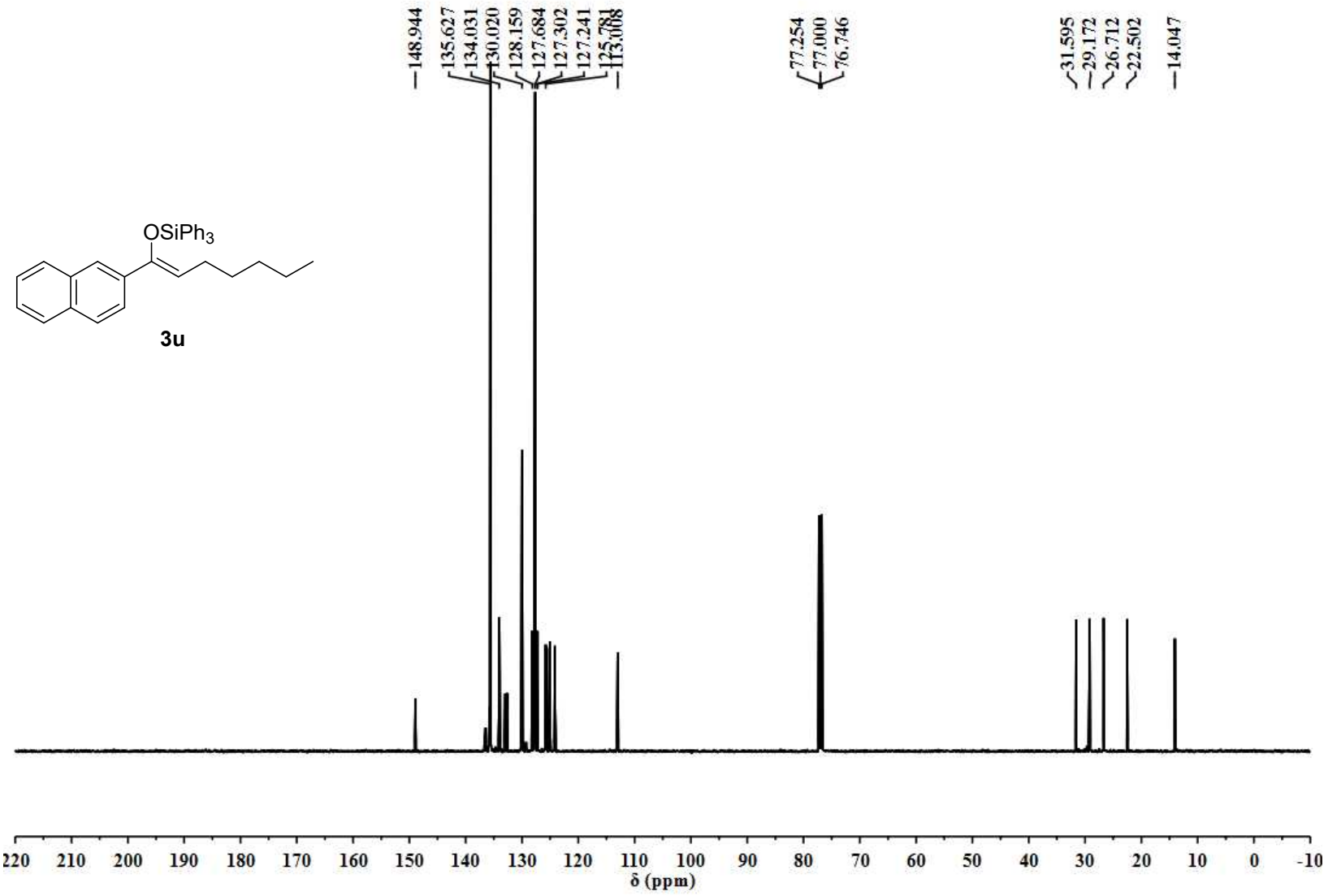

141.771
135.550
135.107
134.199
133.394
132.046
129.512
127.976
127.774
127.695
127.289
126.448
125.649
125.335
124.659
114.537
19.563
17.898
OSiPh3
3s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


7.738
7.698
7.677
7.639
7.636
7.620
7.586
7.564
7.492
7.488
7.471
7.405
7.387
7.371
7.368
7.351
7.346
7.327
7.309
7.290
5.307
5.289
5.271
2.145
2.126
2.108
2.089
2.071
0.794
0.775
0.756
OSiPh3
1.00
1.01
6.02
1.01
1.02
4.06
8.07
0.98
0.02
2.00
3.03
δ (ppm)

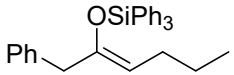
3t


148.538
135.606
133.976
130.034
128.161
127.695
127.302
125.033
114.513
20.011
13.879
OSiPh3
3t
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

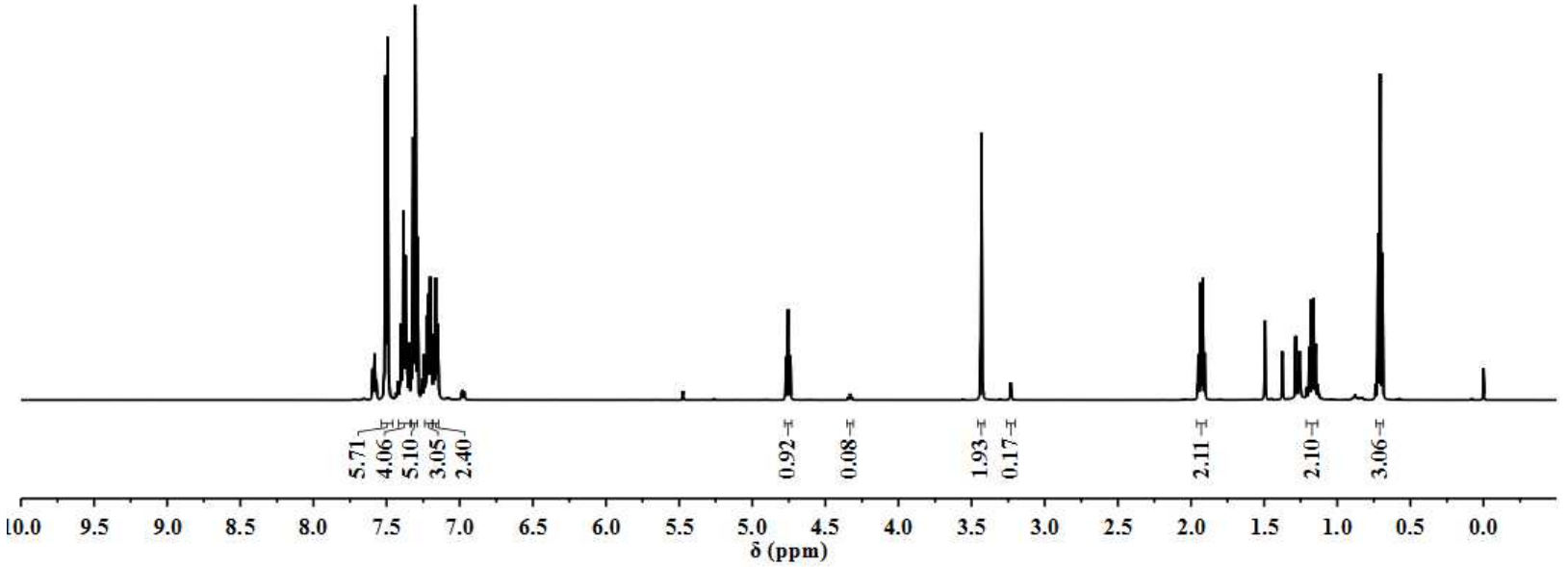

7.831
7.735
7.732
7.719
7.716
7.675
7.658
7.581
7.494
7.486
7.483
7.479
7.475
7.467
7.464
7.462
7.430
7.428
7.426
7.423
7.416
7.401
5.412
5.398
2.197
2.182
2.167
2.153
1.298
1.287
1.284
1.274
1.270
1.260
1.223
1.208
0.934
0.920
0.905
OSiPh3
3u
0.99
1.07
5.99
1.12
1.07
4.11
8.24
0.98
0.02
2.03
6.25
3.05
δ (ppm)

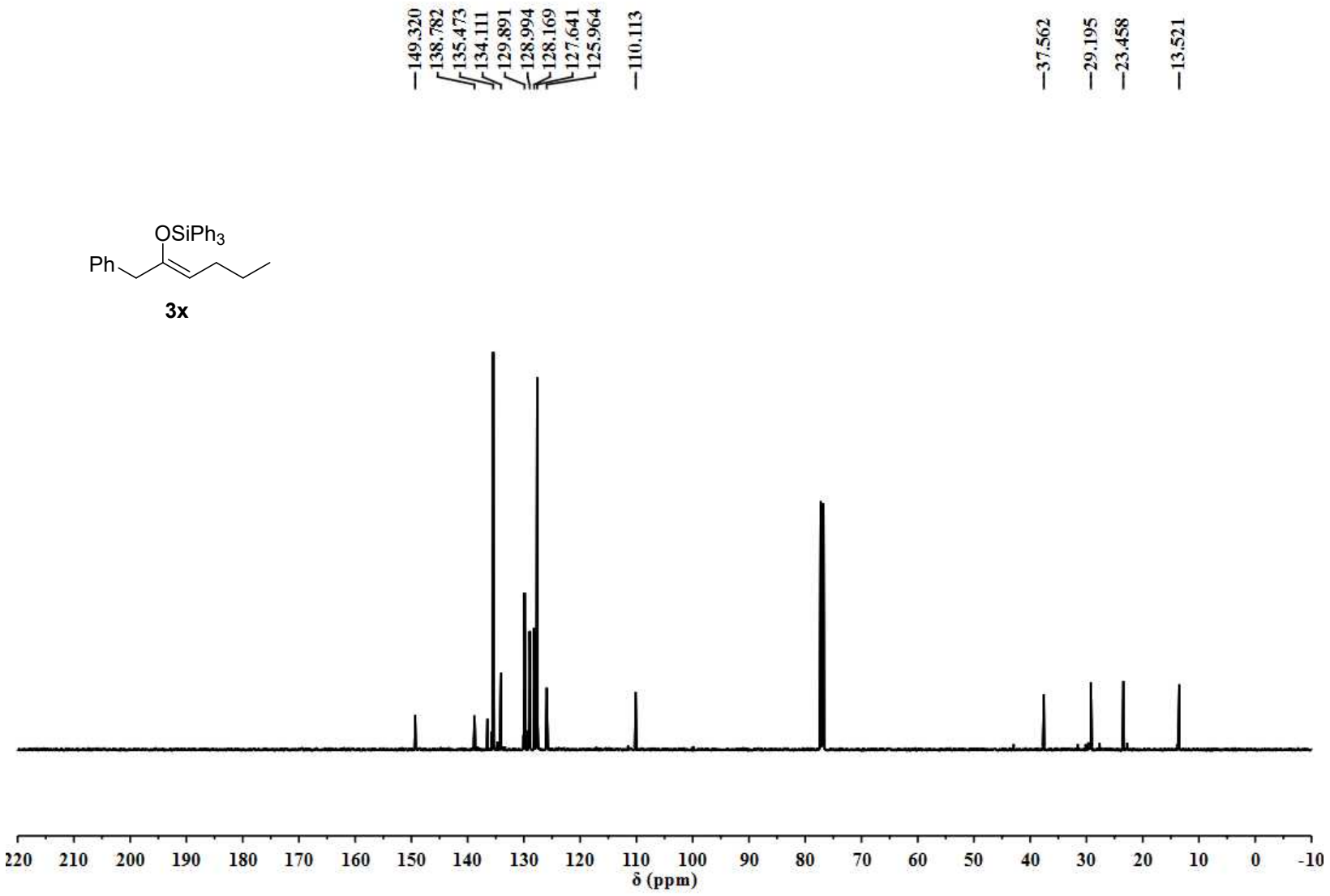

148.944
135.627
134.031
130.020
128.159
127.684
127.302
127.241
125.781
113.008
77.254
77.000
76.746
31.595
29.172
26.712
22.502
14.047
OSiPh3
3u
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


7.510
7.507
7.498
7.494
7.491
7.400
7.390
7.385
7.381
7.373
7.371
7.368
7.318
7.303
7.289
7.288
7.221
7.216
7.213
7.204
7.202
7.190
7.176
7.167
7.163
7.150
4.760
4.754
4.739
4.345
4.331
4.317
3.433
3.233
1.950
1.935
1.921
1.906
1.177
1.162
0.721
0.706
0.691


OSiPh3
Ph

3x


5.71
4.06
5.10
3.05
2.40
0.92
0.08
1.93
0.17
2.11
2.10
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


149.320
138.782
135.473
134.111
129.891
128.994
128.169
127.641
125.964
110.113
37.562
29.195
23.458
13.521
OSiPh3
Ph
3x
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)