Nickel-Catalyzed Cascade Hydrosilylation/Cyclization of 1,7-Enynes

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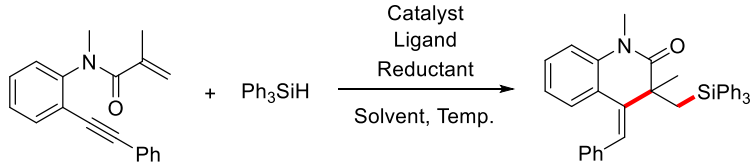
1. General Information

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.

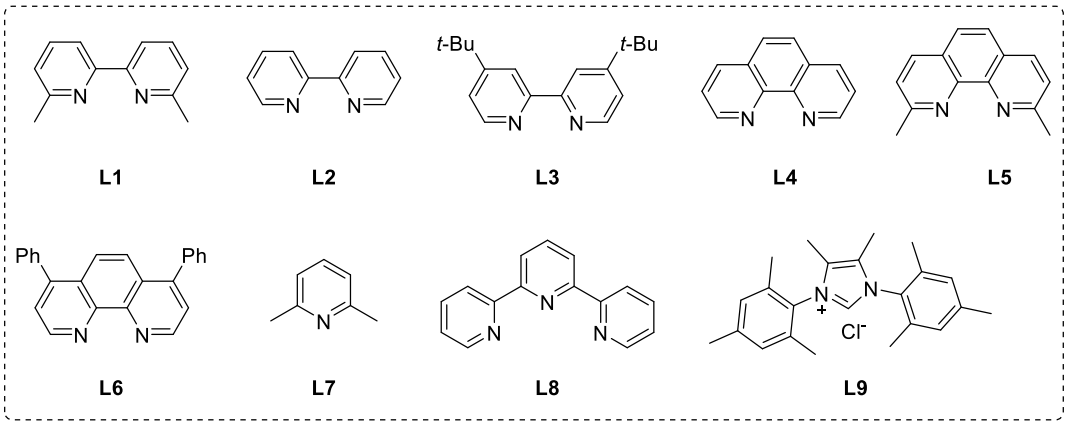
The ^{1}H NMR, ^{13}C NMR and NOESY spectra were recorded on a Bruker 400 or 500 AV spectrometers. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad 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. The 1,7-enynes were prepared according to the known procedure[1-4] and the silanes were commercially available and used as received.

2 Nickel-Catalyzed Hydrosilylation/Cyclization of 1,7-Enynes

2.1 Optimization of reaction conditions[a]



Entry	Catalyst/mol%	Ligand/mol%	Reducant/equiv	Solvent	Temp./ ^{o}C	Yield/**3a**/%
1	$NiBr_2$/10	**L1**/10	-[b]	THF	40	0
2	-[c]	**L1**/10	Zn/2	THF	40	0
3	$NiBr_2$/10	-[d]	Zn/2	THF	40	0
4	$NiBr_2$/10	**L1**/10	Zn/2	THF	40	93
5	$NiCl_2$/10	**L1**/10	Zn/2	THF	40	78
6	$Ni(acac)_2$/10	**L1**/10	Zn/2	THF	40	0
7	$Ni(PPh_3)_2Br_2$/10	**L1**/10	Zn/2	THF	40	0
8	$NiCl_2$ glyme/10	**L1**/10	Zn/2	THF	40	0
9	$Ni(dppe)Cl_2$/(10)	**L1**/10	Zn/2	THF	40	0
10	$Ni(OAc)_2$/10	**L1**/10	Zn/2	THF	40	0
11	$Ni(OTf)_2$/10	**L1**/10	Zn/2	THF	40	6
12	$Ni(cod)_2$/10	**L1**/10	-[b]	THF	40	90
13	$NiBr_2$/10	**L2**/10	Zn/2	THF	40	12
14	$NiBr_2$/10	**L3**/10	Zn/2	THF	40	11
15	$NiBr_2$/10	**L4**/10	Zn/2	THF	40	36
16	$NiBr_2$/10	**L5**/10	Zn/2	THF	40	81
17	$NiBr_2$/10	**L6**/10	Zn/2	THF	40	40
18	$NiBr_2$/10	**L7**/10	Zn/2	THF	40	0
19	$NiBr_2$/10	**L8**/10	Zn/2	THF	40	0
20	$NiBr_2$/10	**L9**/10	Zn/2	THF	40	0
21	$NiBr_2$/10	**L1**/10	Zn/2	Toluene	40	71
22	$NiBr_2$/10	**L1**/10	Zn/2	DMF	40	35
23	$NiBr_2$/10	**L1**/10	Zn/2	Dioxane	40	67
24	$NiBr_2$/10	**L1**/10	Fe/2	THF	40	0
25	$NiBr_2$/10	**L1**/10	Mn/2	THF	40	77
26	$NiBr_2$/10	**L1**/10	$PhSiH_3$/0.2	THF	40	0
27	$NiBr_2$/5	**L1**/10	Zn/2	THF	40	74
28	$NiBr_2$/10	**L1**/10	Zn/1	THF	40	68
29	$NiBr_2$/10	**L1**/5	Zn/2	THF	40	76
30	**$NiBr_2$/10**	**L1/10**	**Zn/2**	**THF**	**40**	**93**
31	$NiBr_2$/10	**L1**/10	Zn/2	THF	25	64
32	$NiBr_2$/10	**L1**/10	Zn/2	THF	40	82[e]

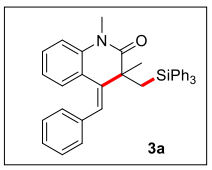


[a]Reaction conditions unless otherwise noted: **1a** (0.1 mmol), **2a** (1.5 equiv), catalyst, ligand, reducant, solvent (1 mL), 40 ^{o}C, 18 h under N_2 atmosphere. [b]No reducant. [c]No catalyst. [d]No ligand. [e]12 h.

2.2 Experimental details and characterization of products

In a 25 mL flame-dried Schlenk tube, **1a** (0.4 mmol, 110.1 mg), Ph_3SiH (0.6 mmol, 156.3 mg), $NiBr_2$ (10 mol%, 0.04 mmol, 8.7 mg), **L1** (10 mol%, 0.04 mmol, 7.4 mg), Zn (2 equiv, 0. 8 mmol, 52.3 mg), THF (4 mL) were added sequentially under nitrogen. The tube was sealed and stirred at 40 ^{o}C for 18 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate (20 mL). The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 20 : 1) to provide the product **3a**.

4-benzylidene-1,3-dimethyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3a)



Yield: 93% (200.3 mg), white solid, mp: 176-178 ^{o}C

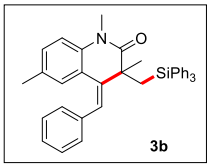
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.48 (m, 6H), 7.35 (t, J = 7.3 Hz, 3H), 7.31-7.27 (m, 6H), 7.23-7.19 (m, 1H), 7.09 (dd, J_1 = 5.1 Hz, J_2 = 1.7 Hz, 3H), 6.94-6.89 (m, 3H), 6.79 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.70 (t, J = 7.3 Hz, 1H), 6.39 (s, 1H), 3.01 (s, 3H), 1.89 (s, 2H), 1.44 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.65, 139.35, 138.69, 137.22, 136.35, 135.26, 130.40, 129.79, 129.44, 128.79, 128.04, 127.81, 126.89, 126.40, 124.17, 122.30, 114.66, 47.94, 30.31, 24.14, 22.75.

HRMS(ESI) Calculated for $C_{37}H_{33}ONNaSi^{+}$ ($[M+Na]^{+}$): 558.22217, found:

558.22236.

4-benzylidene-1,3,6-trimethyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3b)



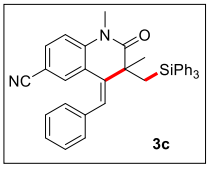
Yield: 89 % (195.5 mg), white solid, mp: 136-139 ^{o}C

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.49 (d, *J* = 6.8 Hz, 6H), 7.35-7.27 (m, 10H), 7.10 (d, *J* = 3.5 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.95-6.91 (m, 2H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.53 (s, 1H), 6.38 (s, 1H), 2.99 (s, 3H), 1.98 (s, 3H), 1.89 (s, 2H), 1.43 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 173.50, 138.80, 137.19, 136.86, 136.34, 135.22, 131.56, 130.85, 129.67, 129.40, 129.29, 127.93, 127.75, 126.87, 126.10, 123.86, 114.47, 47.89, 30.30, 24.06, 22.83, 20.70.

HRMS(ESI) Calculated for $C_{38}H_{35}NONaSi^{+}$ ([M+Na]$^{+}$): 572.23767, found: 572.23801.

4-benzylidene-1,3-dimethyl-2-oxo-3-((triphenylsilyl)methyl)-1,2,3,4-tetrahydroquinoline-6-carbonitrile (3c)



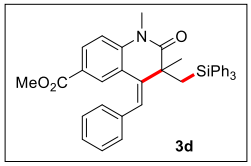
Yield: 68% (152.4 mg), white solid, mp: 194-195 ^{o}C

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.49-7.47 (m, 7H), 7.37 (t, *J* = 7.3 Hz, 3H), 7.31 (t, *J* = 7.3 Hz, 7H), 7.16-7.13 (m, 2H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.87-6.85 (m, 2H), 6.73 (d, *J* = 1.6 Hz, 1H), 6.52 (s, 1H), 3.08 (s, 3H), 1.86 (d, *J* = 15.0 Hz, 1H), 1.81 (d, *J* = 15.0 Hz, 1H), 1.46 (s, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 173.75, 142.86, 136.21, 135.86, 135.82, 134.69, 133.91, 132.56, 129.73, 129.47, 128.77, 128.45, 127.94, 127.86, 124.79, 118.67, 115.00, 105.44, 47.68, 30.40, 23.73, 22.90.

HRMS(ESI) Calculated for $C_{38}H_{32}N_2ONaSi^{+}$ ([M+Na]$^{+}$): 583.21783, found: 583.21761.

Methyl 4-benzylidene-1,3-dimethyl-2-oxo-3-((triphenylsilyl)methyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (3d)



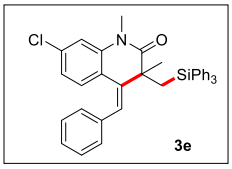
Yield: 76% (182.7 mg), white solid, mp: 173-174 ^{o}C

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.90 (d, *J* = 7.5 Hz, 1H), 7.50-7.47 (m, 7H), 7.35 (t, *J* = 7.1 Hz, 3H), 7.31-7.25 (m, 6H), 7.11 (s, 3H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.89 (s, 2H), 6.49 (s, 1H), 3.73 (s, 3H), 3.01 (s, 3H), 1.87 (s, 2H), 1.44 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.84, 166.46, 143.04, 137.44, 136.56, 136.29, 135.01, 132.05, 130.29, 129.56, 129.54, 128.22, 127.86, 127.62, 127.27, 124.01, 123.83, 114.39, 51.96, 47.89, 30.40, 24.18, 23.01.

HRMS(ESI) Calculated for $C_{39}H_{35}N_2O_3NaSi^+$ ($[M+Na]^+$): 616.22729, found: 616.22784.

4-benzylidene-7-chloro-1,3-dimethyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3e)



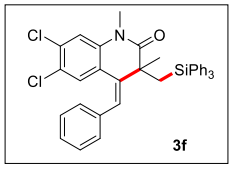
Yield: 55% (125.2 mg), white solid, mp: 158-161 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, J_1 = 7.5 Hz, J_2 = 1 Hz, 6H), 7.37-7.28 (m, 9H), 7.13-7.11 (m, 3H), 6.91-6.88 (m, 3H), 6.65 (d, J =1 Hz, 2H), 6.42 (s, 1H), 2.97 (s, 3H), 1.92-1.85 (m, 2H), 1.43 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.59, 140.52, 137.54, 136.82, 136.33, 135.11, 134.32, 131.38, 129.70, 129.53, 128.21, 127.86, 127.16, 127.09, 122.52, 122.27, 115.03, 47.93, 30.33, 24.30, 22.99.

HRMS(ESI) Calculated for $C_{37}H_{32}ONClNaSi^+$ ($[M+Na]^+$): 592.18372, found: 592.18339.

4-benzylidene-6,7-dichloro-1,3-dimethyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3f)



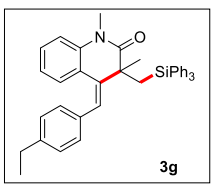
Yield: 72% (173.7 mg), white solid, mp: 161-162 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.47 (m, 6H), 7.38-7.33 (m, 3H), 7.38-7.30 (m, 6H), 7.17-7.14 (m, 3H), 6.99 (s, 1H), 6.91 (dd, J_1 = 6.5, J_2 = 2.6 Hz, 2H), 6.66 (s, 1H), 6.48 (s, 1H), 2.98 (s, 3H), 1.88 (s, 2H), 1.43 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.38, 138.89, 136.29, 136.13, 134.91, 132.23, 131.45, 129.64, 129.52, 128.37, 128.17, 127.91, 127.62, 125.65, 123.92, 116.42, 47.84, 30.44, 24.27, 23.13.

HRMS(ESI) Calculated for $C_{37}H_{31}ONCl_2NaSi^+$ ($[M+Na]^+$): 626.14459, found: 626.14442.

4-(4-ethylbenzylidene)-1,3-dimethyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3g)



Yield: 92% (207.3 mg), white solid, mp: 169-170 °C

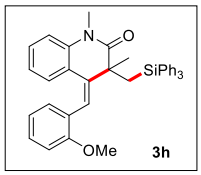
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.47 (m, 6H), 7.38-7.27 (m, 9H), 7.22 (d, J = 5.8 Hz, 1H), 6.92 (dd, J_1 = 7.9, J_2 = 3.8 Hz, 3H), 6.84 (t, J = 8.9 Hz, 3H), 6.71 (t, J = 7.4 Hz, 1H), 6.36 (s, 1H), 3.00

(s, 3H), 2.57 (d, *J* = 7.6 Hz, 1H), 2.54 (d, *J* = 7.6 Hz, 1H), 1.88 (s, 2H), 1.43 (s, 3H), 1.18 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.69, 142.95, 139.25, 137.71, 136.32, 135.24, 134.36, 130.33, 129.70, 129.40, 128.62, 127.77, 127.50, 126.37, 124.37, 122.28, 114.62, 47.83, 30.28, 28.67, 24.05, 22.70, 15.46.

HRMS(ESI) Calculated for $C_{39}H_{37}ONNaSi^+$ ($[M+Na]^+$): 586.25360, found: 586.25366.

4-(2-methoxybenzylidene)-1,3-dimethyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3h)



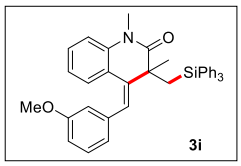
Yield: 66% (149.2 mg), white solid, mp: 218-220 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.2 Hz, 6H), 7.32 (t, *J* = 7.1 Hz, 3H), 7.27 (t, *J* = 7.2 Hz, 6H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.83-6.75 (m, 3H), 6.66 (s, 1H), 6.65-6.60 (m, 2H), 3.71 (s, 3H), 2.88 (s, 3H), 1.93 (s, 2H), 1.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.52, 157.68, 139.08, 139.05, 136.43, 135.41, 131.17, 130.11, 129.24, 128.42, 128.38, 127.65, 126.17, 124.59, 122.16, 121.97, 120.04, 114.43, 110.55, 55.40, 48.11, 30.14, 24.81, 23.83.

HRMS(ESI) Calculated for $C_{38}H_{35}O_2NNaSi^+$($[M+Na]^+$): 558.23230, found: 558.23293.

4-(3-methoxybenzylidene)-1,3-dimethyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3i)



Yield: 63% (142.4 mg), white solid, mp: 176-179 °C

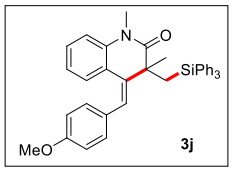
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.48 (m, 6H), 7.36-7.32 (m, 3H), 7.31-7.26 (m, 6H), 7.23-7.21 (m, 1H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.88-6.85 (m, 1H), 6.75-6.70 (m, 1H), 6.67-6.63 (m, 1H), 6.52-6.549 (m, 1H), 6.47-6.45 (m, 1H), 6.37 (s, 1H), 3.61 (s, 3H), 3.00 (s, 3H), 1.91 (s, 1H), 1.90 (s, 1H), 1.44 (s, 3H).

^{13}C NMR (125MHz, $CDCl_3$) δ 173.60, 159.29, 139.28, 139.02, 138.52, 136.35, 135.29, 130.50, 129.42, 128.98, 128.86, 127.79, 126.27, 124.07, 122.43, 122.25, 114.81, 114.58, 113.09, 55.19, 48.04, 30.26, 24.26, 22.79.

HRMS(ESI) Calculated for $C_{38}H_{35}O_2NNaSi^+$($[M+Na]^+$): 558.23230, found:558.23289.

4-(4-methoxybenzylidene)-1,3-dimethyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3j)

Yield: 84% (189.9 mg), white solid, mp: 165-166 °C

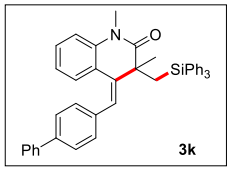


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.0 Hz, 6H), 7.34 (t, *J* = 7.2 Hz, 3H), 7.28 (t, *J* = 7.2 Hz, 6H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 3H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 2H), 6.31 (s, 1H), 3.74 (s, 3H), 3.01 (s, 3H), 1.90 (d, *J* = 15.1 Hz, 1H), 1.86 (d, *J* = 15.1 Hz, 1H), 1.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.79, 158.61, 139.36, 136.77, 136.37, 135.35, 131.02, 130.25, 129.52, 129.40, 128.58, 127.78, 125.99, 124.47, 122.30, 114.66, 113.49, 55.31, 47.89, 30.31, 24.23, 22.68.

HRMS(ESI) Calculated for $C_{38}H_{35}O_2NNaSi^+$([M+Na]$^+$): 558.23230, found: 558.23295.

4-([1,1'-biphenyl]-4-ylmethylene)-1,3-dimethyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3k)



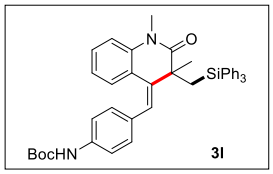
Yield: 96% (237.2 mg), white solid, mp: 155-156 ^{o}C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.54 (m, 2H), 7.53-7.48 (m, 6H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.38-7.33 (m, 5H), 7.33-7.28 (m, 7H), 7.24 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.89 (dd, J_1 = 7.6, J_2 = 1.2 Hz, 1H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.40 (s, 1H), 3.03 (s, 3H), 1.93 (d, *J* = 15.1 Hz, 1H), 1.90 (d, *J* = 15.0 Hz, 1H), 1.46 (s, 3H).

^{13}C NMR (125MHz, $CDCl_3$) δ 173.67, 140.80, 139.49, 139.39, 138.83, 136.39, 136.27, 135.32, 130.45, 130.25, 129.47, 128.96, 128.90, 127.83, 127.47, 127.02, 126.63, 126.03, 124.23, 122.40, 114.72, 48.11, 30.34, 24.27, 22.79.

HRMS(ESI) Calculated for $C_{43}H_{37}ONNaSi^+$ ([M+Na]$^+$): 634.25311, found: 634.25366.

***tert*-butyl (4-((1,3-dimethyl-2-oxo-3-((triphenylsilyl)methyl)-2,3-dihydroquinolin-4(1*H*)-ylidene)methyl)phenyl)carbamate (3l)**



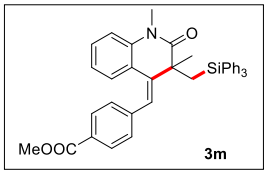
Yield: 71% (184.7 mg), white solid, mp: 189-192 ^{o}C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.1 Hz, 6H), 7.33 (t, *J* = 7.1 Hz, 3H), 7.27 (t, *J* = 7.2 Hz, 6H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.83 (t, *J* = 8.0 Hz, 3H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.52 (s, 1H), 6.30 (s, 1H), 3.01 (s, 3H), 1.91 (d, *J* = 15.0 Hz, 1H), 1.86 (d, *J* = 15.0 Hz, 1H), 1.49 (s, 9H), 1.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.74, 152.80, 139.28, 137.45, 137.20, 136.33, 135.30, 131.73, 130.45, 130.24, 129.40, 128.68, 127.77, 125.92, 124.27, 122.36, 117.94, 114.64, 80.68, 47.96, 30.30, 28.53, 24.27, 22.65.

HRMS(ESI) Calculated for $C_{42}H_{42}N_2O_3NaSi^+$ ($[M+Na]^+$): 673.28528, found: 673.28569.

methyl (*R*,*E*)-4-((1,3-dimethyl-2-oxo-3-((triphenylsilyl)methyl)-2,3-dihydroquinolin-4(1*H*)-ylidene)methyl)benzoate (3m)



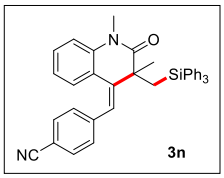
Yield: 77% (182.7 mg), white solid, mp: 152-154 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 6.8 Hz, 6H), 7.39-7.24 (m, 10H), 6.94 (dd, J_1 = 8.2 Hz, J_2 =2.9 Hz, 3H), 6.74-6.67 (m, 2H), 6.38 (s, 1H), 3.86 (s, 3H), 3.03 (s, 3H), 1.95 (d, *J* = 15.0 Hz, 1H), 1.90 (d, *J* = 15.0 Hz, 1H), 1.46 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.33, 167.06, 142.20, 141.12, 139.33, 136.29, 136.20, 135.14, 130.31, 129.68, 129.48, 129.30, 128.34, 127.80, 125.39, 123.52, 122.40, 114.77, 52.15, 48.28, 30.29, 24.35, 22.70.

HRMS(ESI) Calculated for $C_{39}H_{35}N_2O_3NaSi^+$ ($[M+Na]^+$): 616.22729, found: 616.22784.

(*R*,*E*)-4-((1,3-dimethyl-2-oxo-3-((triphenylsilyl)methyl)-2,3-dihydroquinolin-4(1*H*)-ylidene)methyl)benzonitrile (3n)



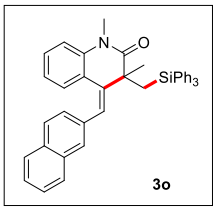
Yield: 68% (152.3 mg), white solid, mp: 146-147 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.47 (m, 6H), 7.38-7.34 (m, 5H), 7.29 (t, *J* = 7.3 Hz, 7H), 6.96 (t, *J* = 7.2 Hz, 3H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.67 (dd, J_1 = 7.6, J_2 = 1.0 Hz, 1H), 6.32 (s, 1H), 3.03 (s, 3H), 1.95 (d, *J* = 15.1 Hz, 1H), 1.89 (d, *J* = 15.0 Hz, 1H), 1.45 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.17, 142.44, 142.29, 139.43, 136.29, 135.08, 131.80, 130.33, 130.18, 129.73, 129.56, 127.86, 124.56, 123.07, 122.51, 119.13, 114.98, 110.23, 48.43, 30.34, 24.38, 22.63.

HRMS(ESI) Calculated for $C_{38}H_{32}N_2ONaSi^+$ ($[M+Na]^+$): 583.21783, found: 583.21767.

(*R*,*E*)-1,3-dimethyl-4-(naphthalen-2-ylmethylene)-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3o)



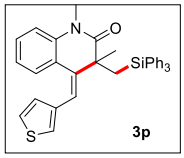
Yield: 86% (201.3 mg), white solid, mp: 171-172 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.74 (m, 1H), 7.72-7.67 (m, 1H), 7.61-7.54 (m, 7H), 7.49-7.44 (m, 2H), 7.43-7.38 (m, 4H), 7.35 (t, *J* = 7.2 Hz, 6H), 7.23-7.20 (m, 1H), 7.09-7.04 (m, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.91-6.85 (m, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.60 (s, 1H), 3.11 (s, 3H), 2.04 (d, *J* = 15.0 Hz, 1H), 1.99 (d, *J* = 15.0 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.41, 139.10, 138.71, 136.13, 135.04 134.47, 133.23, 132.22, 130.20, 129.20, 128.86, 128.73, 127.76, 127.58, 127.49, 126.95, 126.18, 125.87, 123.88, 122.11, 114.45, 47.91, 30.11, 24.19, 22.59.

HRMS(ESI) Calculated for $C_{41}H_{35}NONaSi^+$ ($[M+Na]^+$): 608.23853, found: 608.23801.

(*R*,*E*)-1,3-dimethyl-4-(thiophen-3-ylmethylene)-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3p)



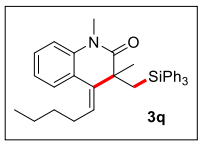
Yield: 69% (149.4 mg), white solid, mp: 158-159 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.0 Hz, 6H), 7.33 (d, *J* = 7.2 Hz, 3H), 7.27 (t, *J* = 7.3 Hz, 7H), 6.99 (m, 2H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.78 (m, 2H), 6.61 (d, *J* = 4.8 Hz, 1H), 6.30 (s, 1H), 2.98 (s, 3H), 1.94 (d, *J* = 15.0 Hz, 1H), 1.87 (d, *J* = 15.0 Hz, 1H), 1.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.66, 139.13, 137.92, 137.59, 136.34, 135.27, 130.15, 129.40, 128.96, 128.27, 127.75, 124.72, 124.58, 124.29, 122.26, 120.78, 114.55, 48.00, 30.25, 24.44, 22.74.

HRMS(ESI) Calculated for $C_{35}H_{31}NOSNaSi^+$ ($[M+Na]^+$): 564.17926, found: 564.17878.

(*R*,*E*)-1,3-dimethyl-4-pentylidene-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3q)



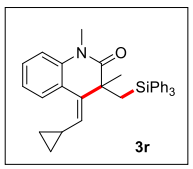
Yield: 76% (156.6 mg), yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.43 (m, 6H), 7.37-7.33 (m, 3H), 7.35-7.29 (m, 7H), 7.00-6.96 (m, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.89 (dd, J_1 = 7.5, J_2 = 1.4 Hz, 1H), 5.41 (dd, J_1 = 8.5 Hz, J_2 =5.5 Hz, 1H), 3.00 (s, 3H), 2.12-2.04 (m, 1H), 1.97-1.93 (m, 1H), 1.80 (d, *J* = 14.9 Hz, 1H), 1.72 (d, *J* = 14.9 Hz, 1H), 1.36 (s, 3H), 1.22-1.16 (m, 2H), 1.15-1.05 (m, 2H), 0.79 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.54, 139.13, 136.34, 135.71, 135.40, 129.42, 129.12, 128.06, 127.78, 125.04, 122.20, 114.28, 47.01, 32.30, 30.23, 29.11, 23.58, 22.68, 22.63, 14.11.

HRMS(ESI) Calculated for $C_{35}H_{37}ONNaSi^+$ ($[M+Na]^+$): 538.25378, found: 538.25366.

4-(cyclopropylmethylene)-1,3-dimethyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3r)



Yield: 78% (155.8 mg), white solid, mp: 145-146 °C

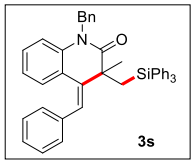
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.46 (m, 6H), 7.37-7.34 (m, 3H), 7.31-7.27 (m, 7H), 7.25 (s, 1H), 7.01-6.96 (m, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 4.85 (d, *J* = 9.9 Hz, 1H), 2.92 (s, 3H), 1.89 (d, *J* = 14.9 Hz, 1H), 1.80 (d, *J* = 14.9 Hz, 1H), 1.68-1.61 (m, 1H), 1.27 (s, 3H), 0.65-0.59 (m, 2H), 0.26-0.19 (m, 1H), -0.04--0.10 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.24, 139.06, 136.42, 135.57, 135.13, 132.45, 129.34, 127.98, 127.76, 125.08, 122.27, 114.37, 47.25, 30.20, 24.90, 22.98, 11.66, 8.52, 7.86.

HRMS(ESI) Calculated for $C_{34}H_{33}NONaSi^+$ ($[M+Na]^+$): 522.22229, found: 522.22236.

1-benzyl-4-benzylidene-3-methyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3s)

Yield: 84% (205.4 mg), white solid, mp: 170-172 °C

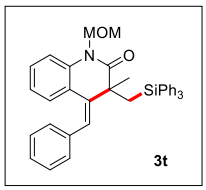


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 6.8 Hz, 6H), 7.34-7.25 (m, 12H), 7.19 (d, *J* = 7.0 Hz, 3H), 7.06 (s, 3H), 6.85 (d, *J* = 4.5 Hz, 3H), 6.67 (d, *J* = 7.1 Hz, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.40 (s, 1H), 5.04 (d, *J* = 16.4 Hz, 1H), 4.72 (d, *J* = 16.4 Hz, 1H), 2.13 (d, *J* = 14.8 Hz, 1H), 1.98 (d, *J* = 14.8 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.11, 138.38, 137.66, 137.29, 136.99, 136.31, 135.16, 130.27, 129.77, 129.47, 128.85, 128.74, 127.96, 127.79, 127.11, 126.91, 126.87, 126.32, 124.38, 122.39, 115.49, 48.15, 46.53, 24.30, 22.01.

HRMS(ESI) Calculated for $C_{43}H_{37}NONaSi^+$ ($[M+Na]^+$): 634.25311, found: 634.25366.

4-benzylidene-1-(methoxymethyl)-3-methyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3t)



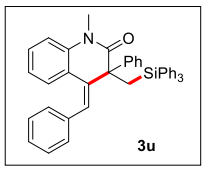
Yield: 76% (171.8 mg), white solid, mp: 167-170 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 6.8 Hz, 6H), 7.34 (t, *J* = 7.3 Hz, 3H), 7.28 (t, *J* = 7.3 Hz, 7H), 7.22-7.19 (m, 1H), 7.08-7.05 (m, 3H), 6.85 (dd, J_1 = 6.4 Hz, J_2 = 2.6 Hz, 2H), 6.69 (t, *J* = 4.6 Hz, 2H), 6.33 (s, 1H), 5.15 (d, *J* = 10.6 Hz, 1H), 5.01 (d, *J* = 10.6 Hz, 1H), 3.34 (s, 3H), 2.08 (d, *J* = 15.0 Hz, 1H), 1.89 (d, *J* = 15.0 Hz, 1H), 1.549 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 175.05, 138.19, 137.29, 136.96, 136.32, 135.17, 130.21, 129.78, 129.50, 129.00, 127.98, 127.82, 127.09, 126.96, 124.14, 122.91, 115.89, 74.57, 56.28, 48.20, 24.00, 21.96.

HRMS(ESI) Calculated for $C_{43}H_{35}N_2ONaSi^+$ ($[M+Na]^+$): 588.23348, found: 588.24361.

4-benzylidene-1-methyl-3-phenyl-3-((triphenylsilyl)methyl)-3,4-dihydroquinolin-2(1*H*)-one (3u)



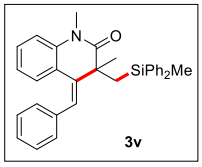
Yield: 68% (162.5 mg), white solid, mp: 255-256 ^{o}C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.9 Hz, 6H), 7.30 (d, *J* = 7.2 Hz, 3H), 7.25 (t, *J* = 7.1 Hz, 8H), 7.12-7.01 (m, 6H), 7.04-6.96 (m, 2H), 6.91 (d, *J* = 3.9 Hz, 2H), 6.85 (s, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 6.58 (t, *J* = 7.5 Hz, 1H), 2.87 (s, 3H), 2.77 (d, *J* = 15.0 Hz, 1H), 2.14 (d, *J* = 15.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.51, 144.36, 138.97, 136.67, 136.61, 136.52, 136.24, 130.11, 129.99, 129.79, 129.06, 128.82, 128.55, 128.15, 127.57, 127.28, 126.75, 126.24, 124.34, 122.19, 114.88, 59.46, 30.50, 27.65.

HRMS(ESI) Calculated for $C_{42}H_{35}NONaSi^{+}$ ($[M+Na]^{+}$): 620.23724, found: 620.23709.

(R,E)-4-benzylidene-1,3-dimethyl-3-((methyldiphenylsilyl)methyl)-3,4-dihydroquinolin-2(1H)-one



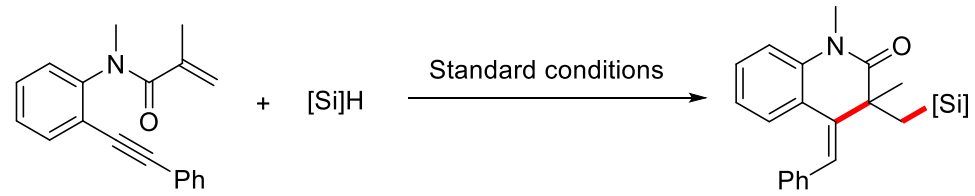
Yield: 68% (128.8 mg), sticky oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.35-7.29 (m, 5H), 7.27-7.18 (m, 4H), 7.15 (q, *J* = 7.2 Hz, 3H), 7.04-7.02 (m, 2H), 6.93-6.87 (m, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.54 (s, 1H), 3.06 (s, 3H), 1.56 (d, *J* = 14.8 Hz, 1H), 1.51 (s, 3H), 1.42 (d, *J* = 14.8 Hz, 1H), 0.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.61, 139.30, 137.50, 134.78, 134.53, 130.40, 129.64, 129.29, 129.17, 128.71, 128.25, 127.89, 127.83, 126.96, 125.90, 122.20, 114.76, 47.38, 30.18, 23.88, 22.84, -2.68.

HRMS(ESI) Calculated for $C_{32}H_{31}NONaSi^{+}$ ($[M+Na]^{+}$): 496.20719, found: 496.20701.

2.3 Evaluation of different silanes



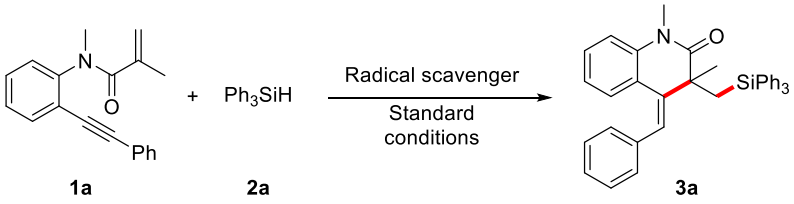
1a **2** **3**

Ph_2MeSiH	$PhSiH_3$	Ph_2SiH_2	Et_3SiH	$(EtO)_3SiH$	$^iPr_3SiH$
68% (**3v**)	trace	trace	NR	NR	NR

In a 25 mL flame-dried Schlenk tube, 1, 7-enynes (0.4 mmol, 110.1mg), silane (1.5 equiv), $NiBr_2$ (10 mol%, 0.04 mmol, 8.7 mg), **L1** (10 mol%, 0.02 mmol, 7.4 mg), Zn (2 equiv, 0.8 mmol, 52.3 mg), and THF (4 mL) were added sequentially under nitrogen. The tube was sealed and stirred at 40 ^oC for 18 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate (20 mL). The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 20 : 1) to provide the product.

3 Mechanistic Studies

3.1 Radical trapping experiments



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

Radical scavenger	yield of **3a**
TEMPO	NR
BHT	89%
1,1-diphenylethene	87%

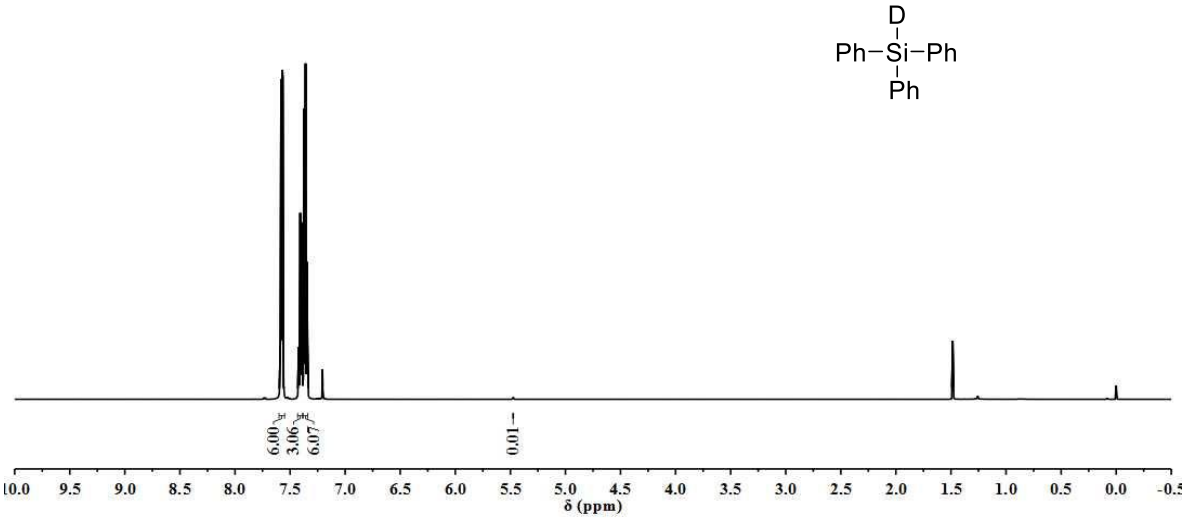
Experimental procedure:

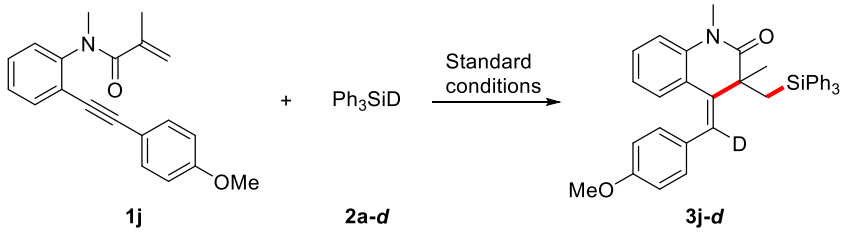
In a 25 mL flame-dried Schlenk tube, 1, 7-Enynes (0.4 mmol, 110.1mg), Ph_3SiH

(1.5 equiv, 156.3 mg), $NiBr_2$ (10 mol%, 0.04 mmol, 8.7 mg), **L1** (10 mol%, 0.02 mmol, 7.4 mg), Zn (2 equiv, 0.8 mmol, 52.3 mg), THF (4 mL) and radical scavenger (1 equiv) were added sequentially under nitrogen. The tube was sealed and stirred at 40 ^{o}C for 18 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate (20 mL). The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 20 : 1) to provide the product **3a**.

3.2 Deuterium-labelling experiment

Ph_3SiD (99% D) was synthesized according to the known literature[5]. **^{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).



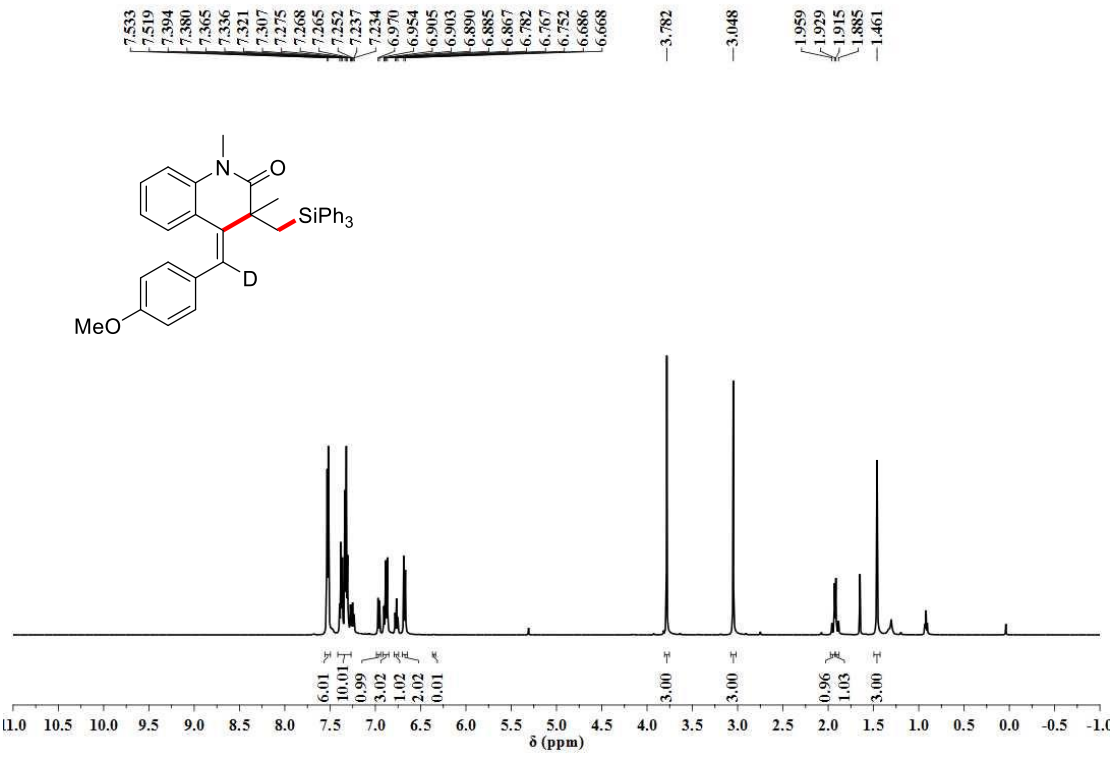


1j **2a-*d*** **3j-*d***

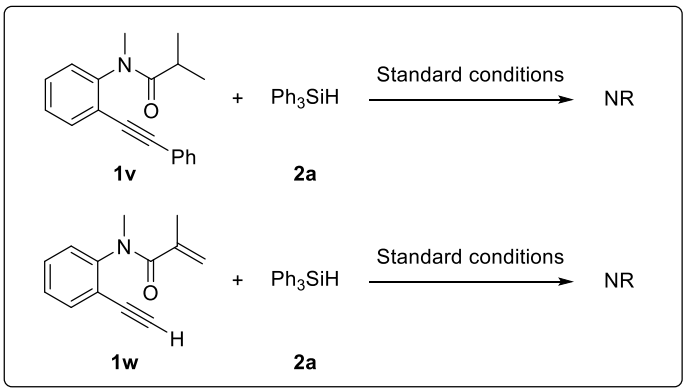
Experimental procedure:

In a 25 mL flame-dried Schlenk tube, 1, 7-Enynes (0.4 mmol, 110.1 mg), Ph_3SiD

(1.5 equiv, 99% D, 157.9 mg), $NiBr_2$ (10 mol%, 0.04 mmol, 8.7 mg), **L1** (10 mol%, 0.02 mmol, 7.4 mg), Zn (2 equiv, 0.8 mmol, 52.3 mg), THF (4 mL) were added sequentially under nitrogen. The tube was sealed and stirred at 40 ^{o}C for 18 h. After completion, the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate (20 mL). The combined organic phase was concentrated and purified by silica gel column chromatography (Petroleum ether : Ethyl acetate = 20 : 1) to provide the product **3j-*d*** in 81% yield.



3.3 The reaction of 1v or 1w with 2a



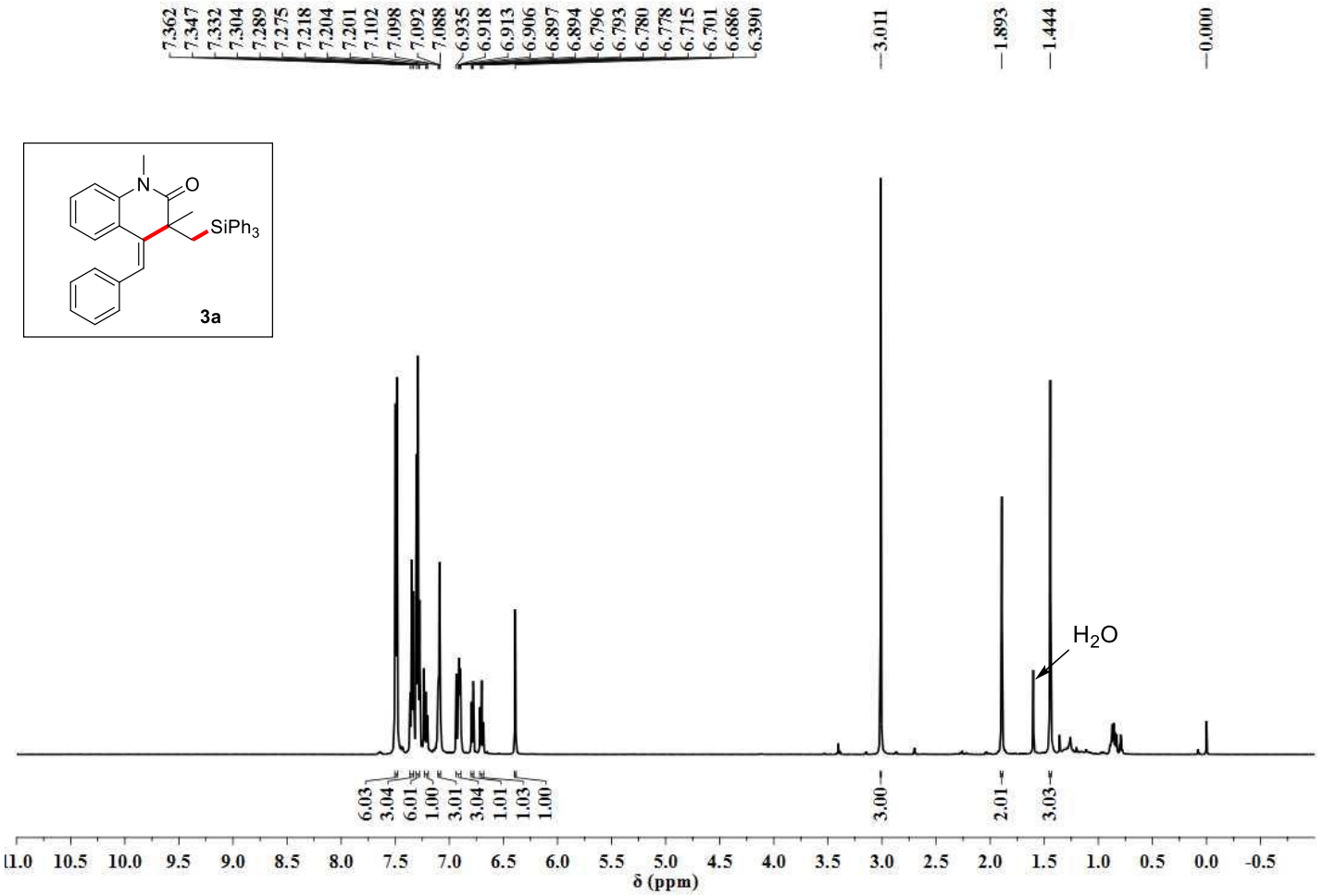
Experimental procedure:

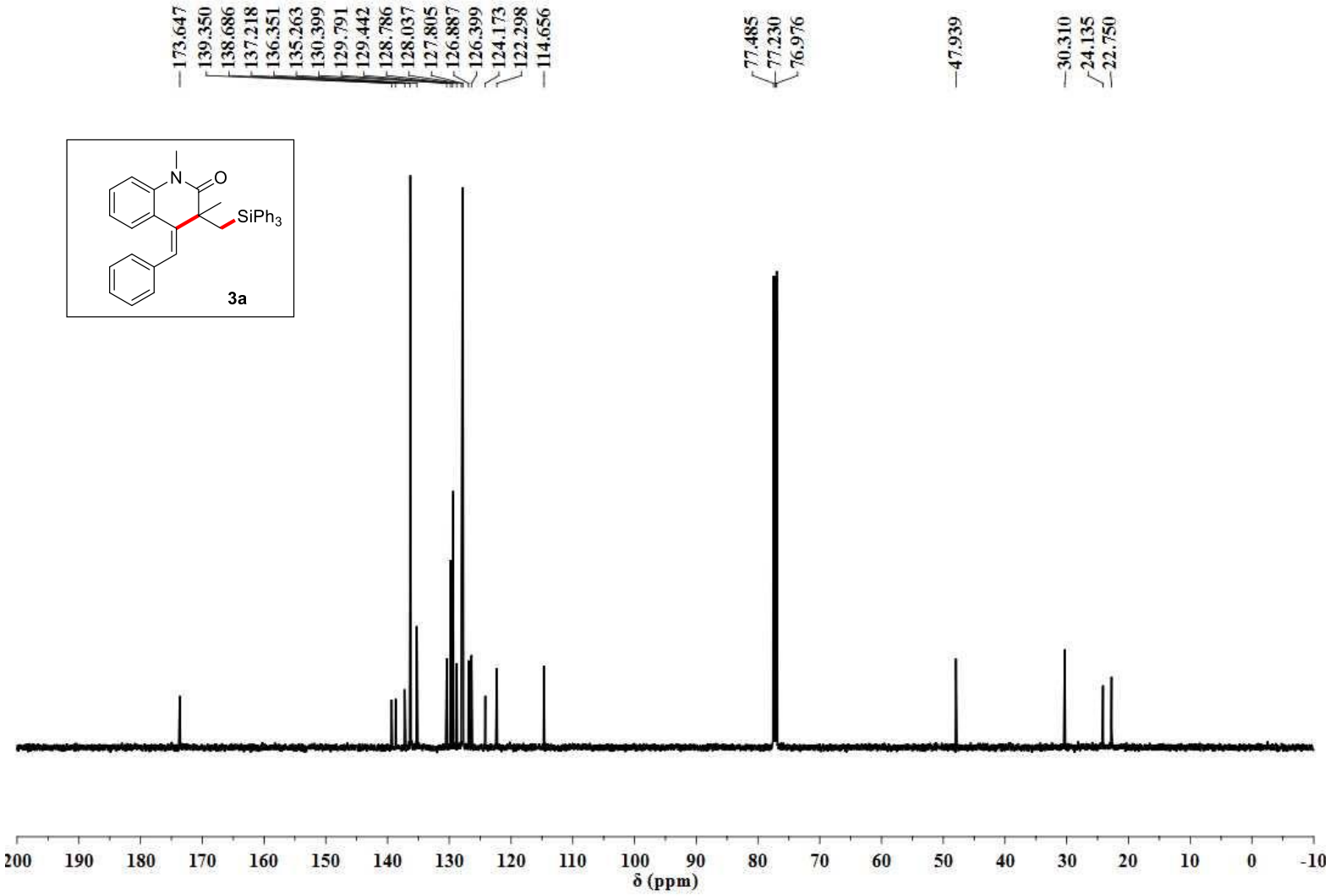
In a 25 mL flame-dried Schlenk tube, **1v** (0.4 mmol, 110.8 mg) or **1w** (0.2 mmol, 79.6 mg), Ph_3SiH (1.5 equiv, 156.3 mg), $NiBr_2$ (10 mol%, 0.04 mmol, 8.7 mg), **L1** (10 mol%, 0.02 mmol, 7.4 mg), Zn (2 equiv, 0.8 mmol, 52.3 mg) and THF (4 mL) were added sequentially under nitrogen. The tube was sealed and stirred at 40 ^{o}C for 18 h. After completion, the reaction mixture was monitored by TLC analysis and no any product was detected.

4. References

1. J. T. M. Correia, G. P. da Silva, E. Andr é and M. W. Paix ão, *Adv. Synth. Catal.* 2019, **361**, 5558.
2. C. Wu, J. Liao and S. Ge, *Angew. Chem. Int. Ed.* 2019, **58**, 8882.
3. H.-Y. Liu, Y. Lu, Y. Li and J.-H. Li, *Organ. Lett.* 2020, **22**, 8819.
4. Y. Qu, W. Xu, J. Zhang, Y. Liu, Y. Li, H. Song and Q. Wang, *J. Org. Chem.* 2020, **85**, 5379.
5. V. Leich, T. P. Spaniol and J. Okuda, *Organometallics* 2016, **35**, 1179.

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

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126.399
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114.656
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77.230
76.976
47.939
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O
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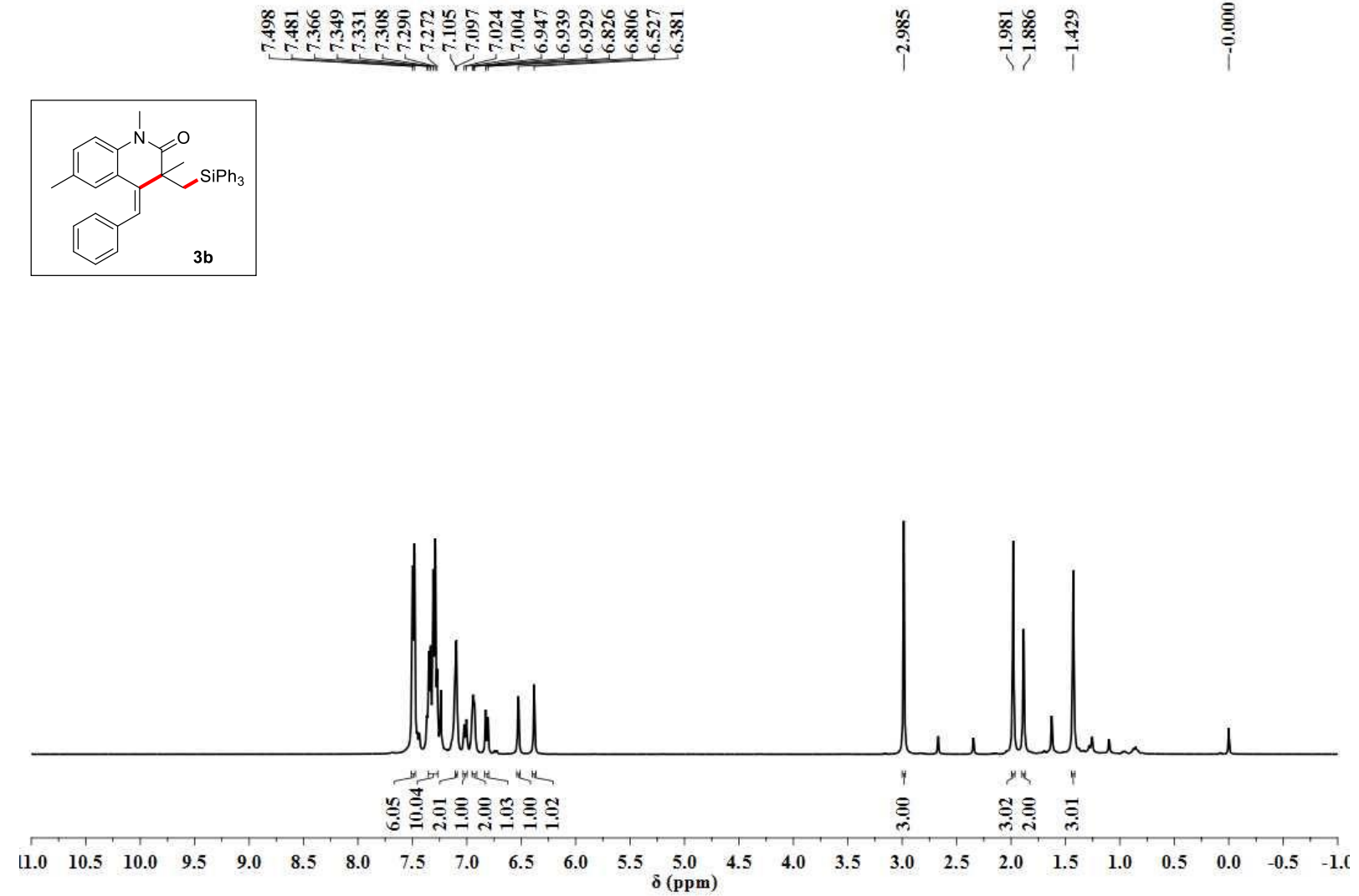
δ (ppm)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6.947
6.939
6.929
6.826
6.806
6.527
6.381
2.985
1.981
1.886
1.429
0.000
N
O
SiPh3
3b
6.05
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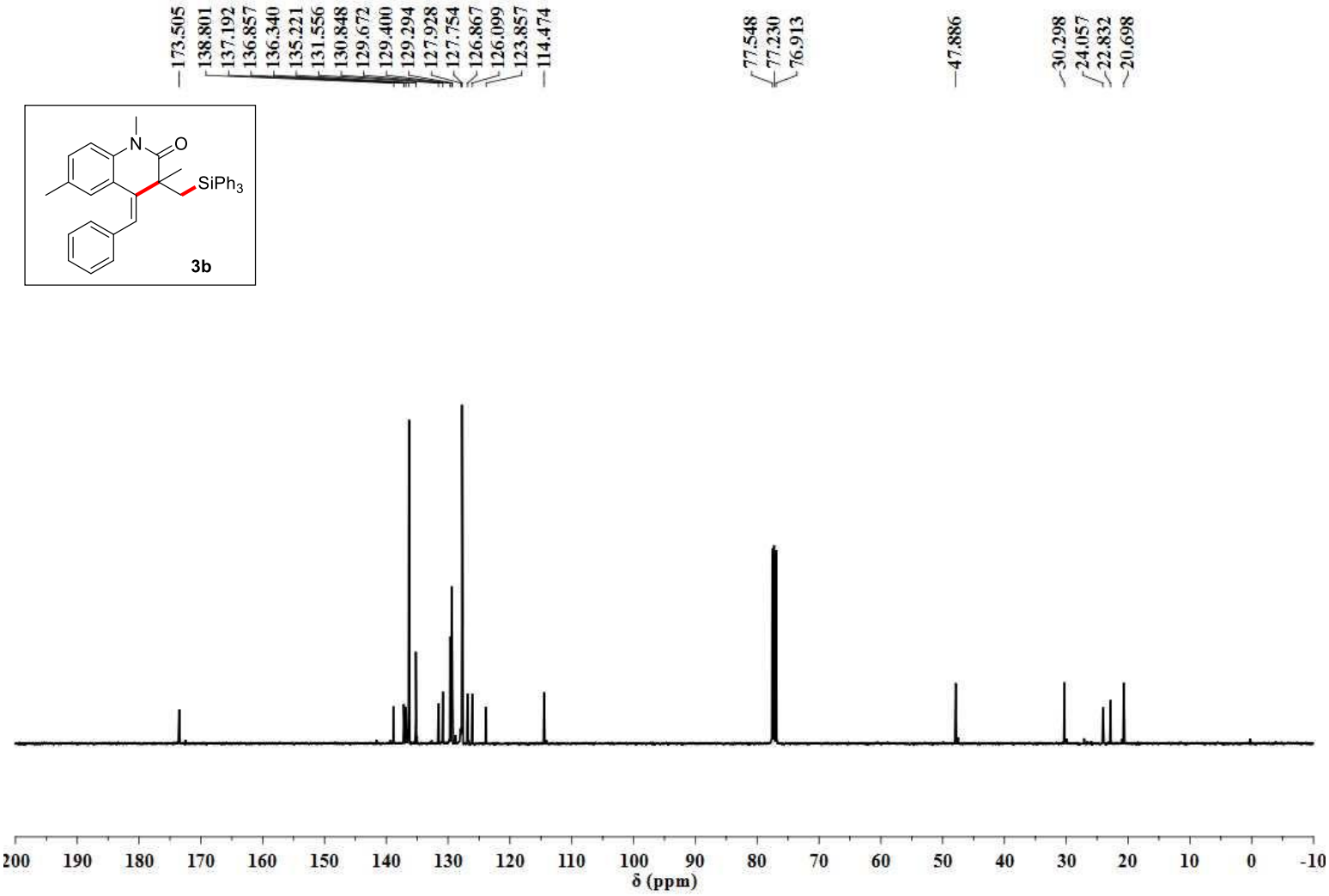
3.02
2.00
3.01
δ (ppm)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77.548
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76.913
47.886
30.298
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O
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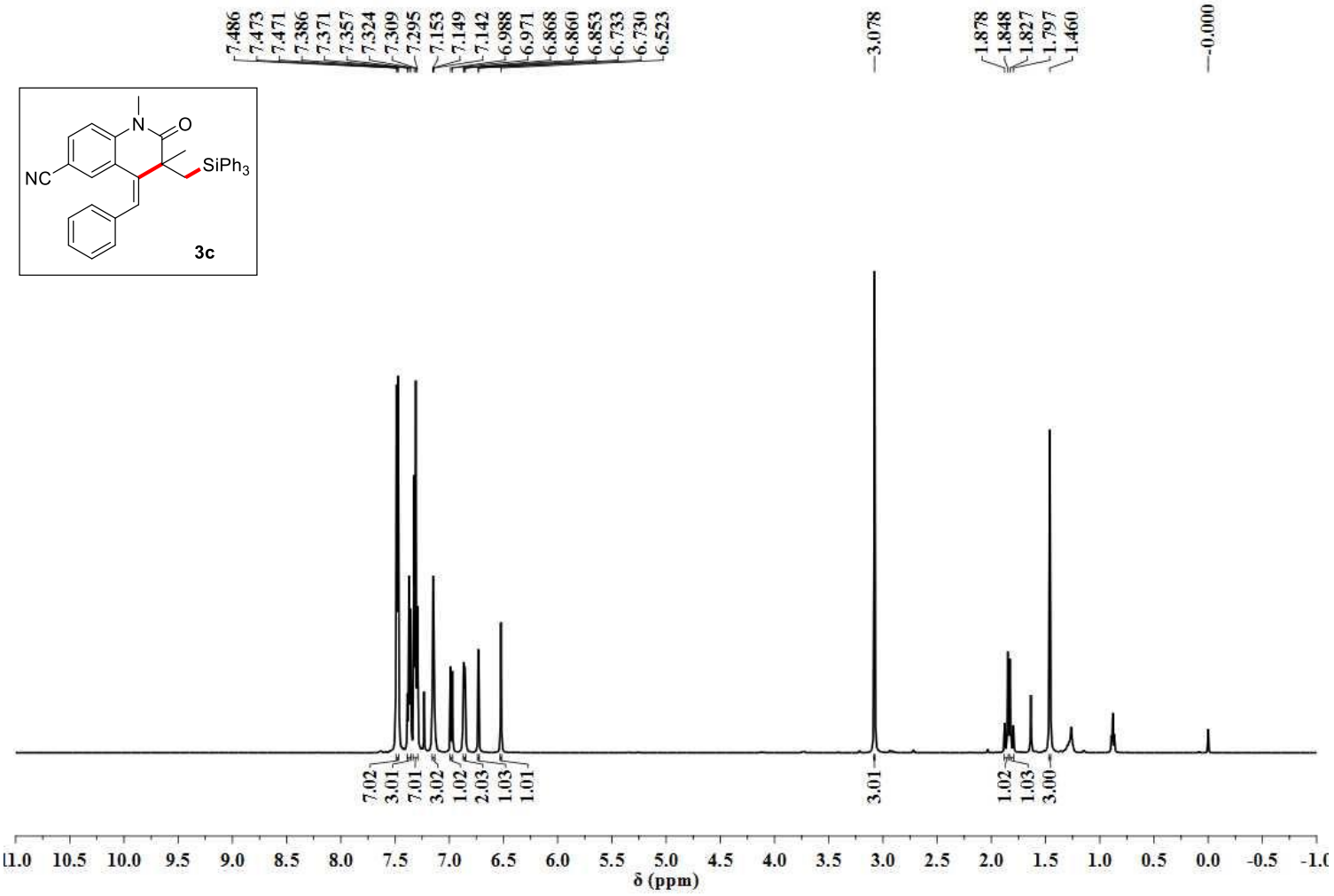
δ (ppm)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1.878
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1.797
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SiPh3
3c
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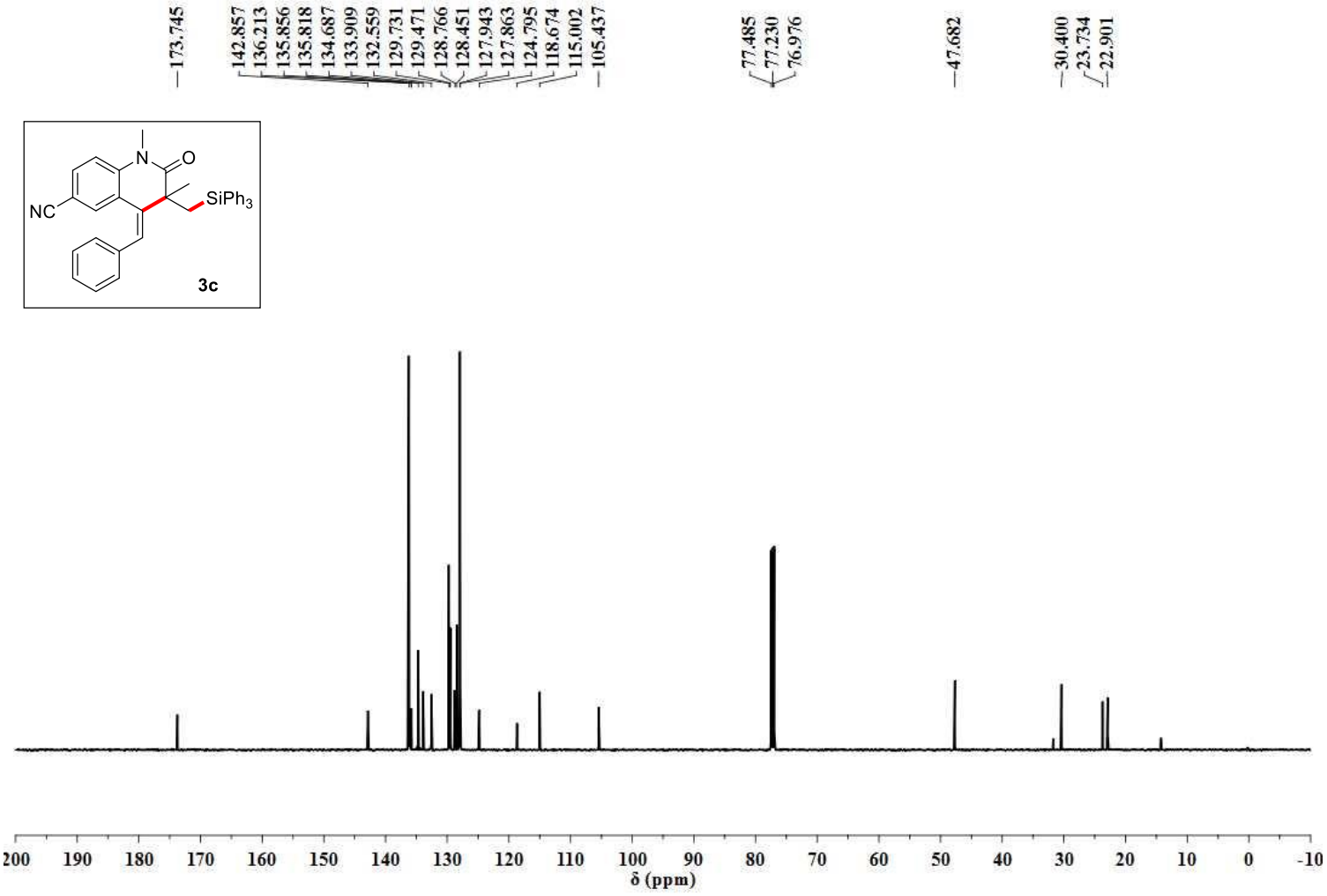
δ (ppm)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124.795
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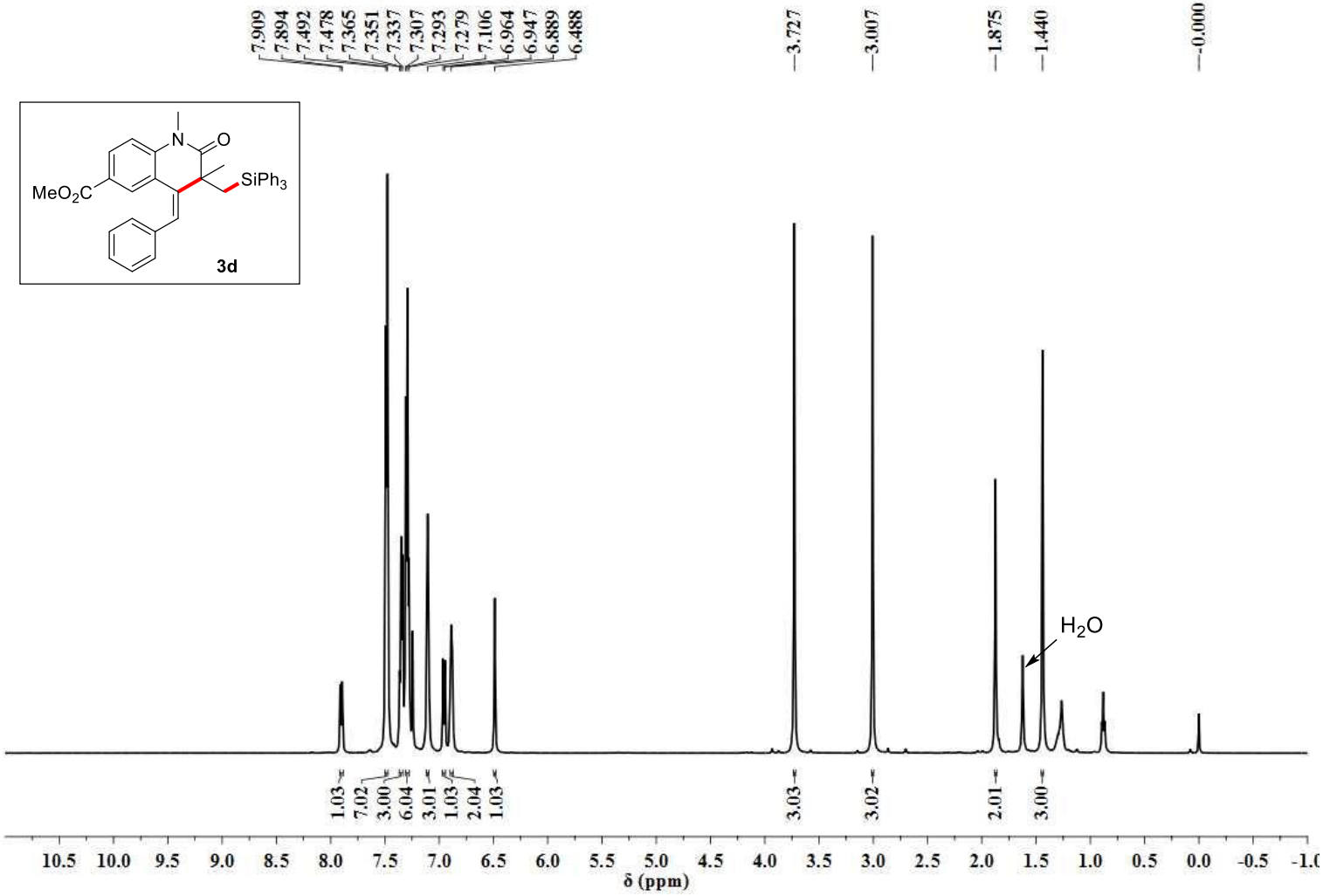
3c
δ (ppm)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6.889
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SiPh3
3d
H2O
1.03
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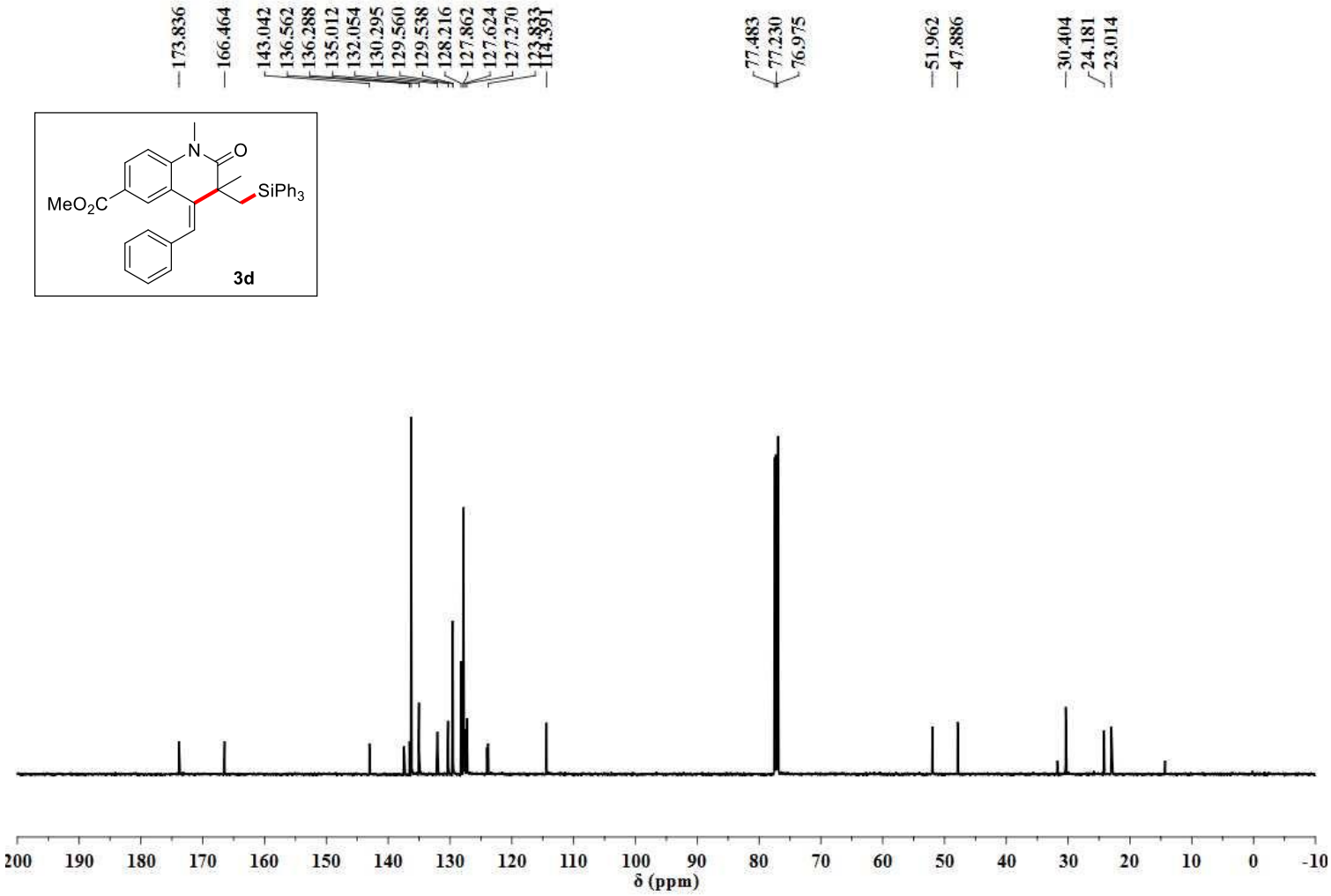
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77.230
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30.404
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MeO2C
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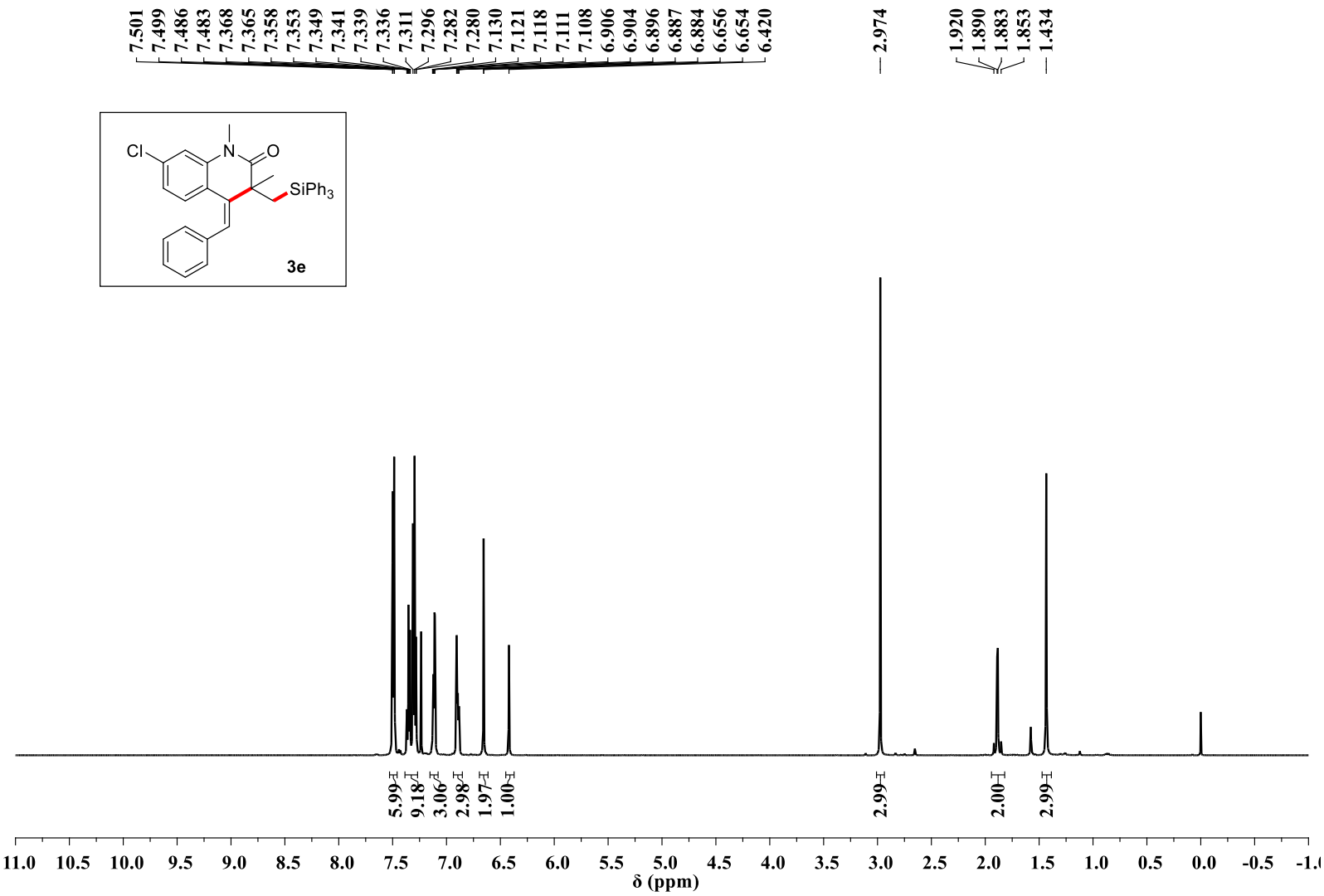
δ (ppm)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1.883
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O
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9.18
3.06
2.98
1.97
1.00
2.99
2.00
2.99
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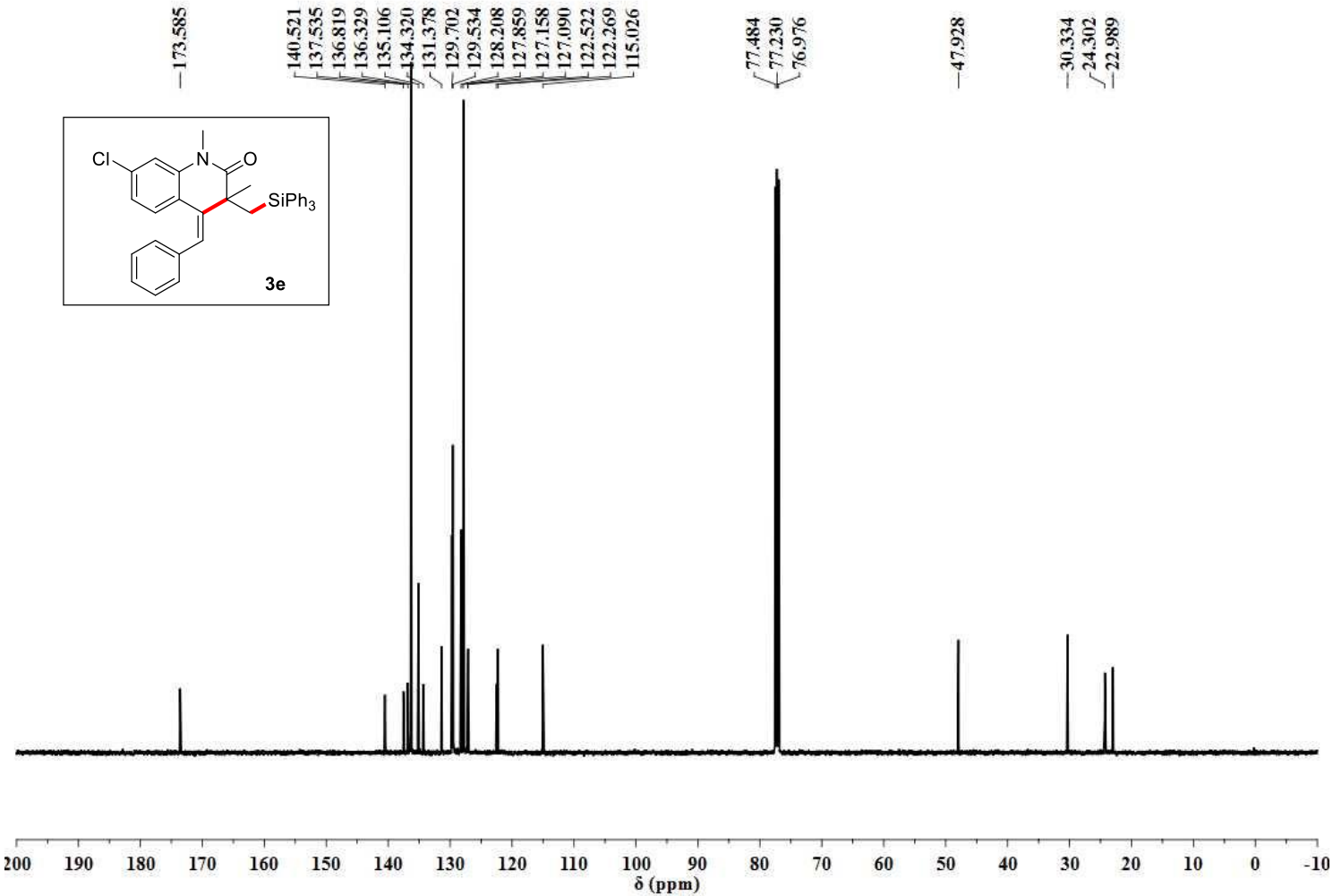
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O
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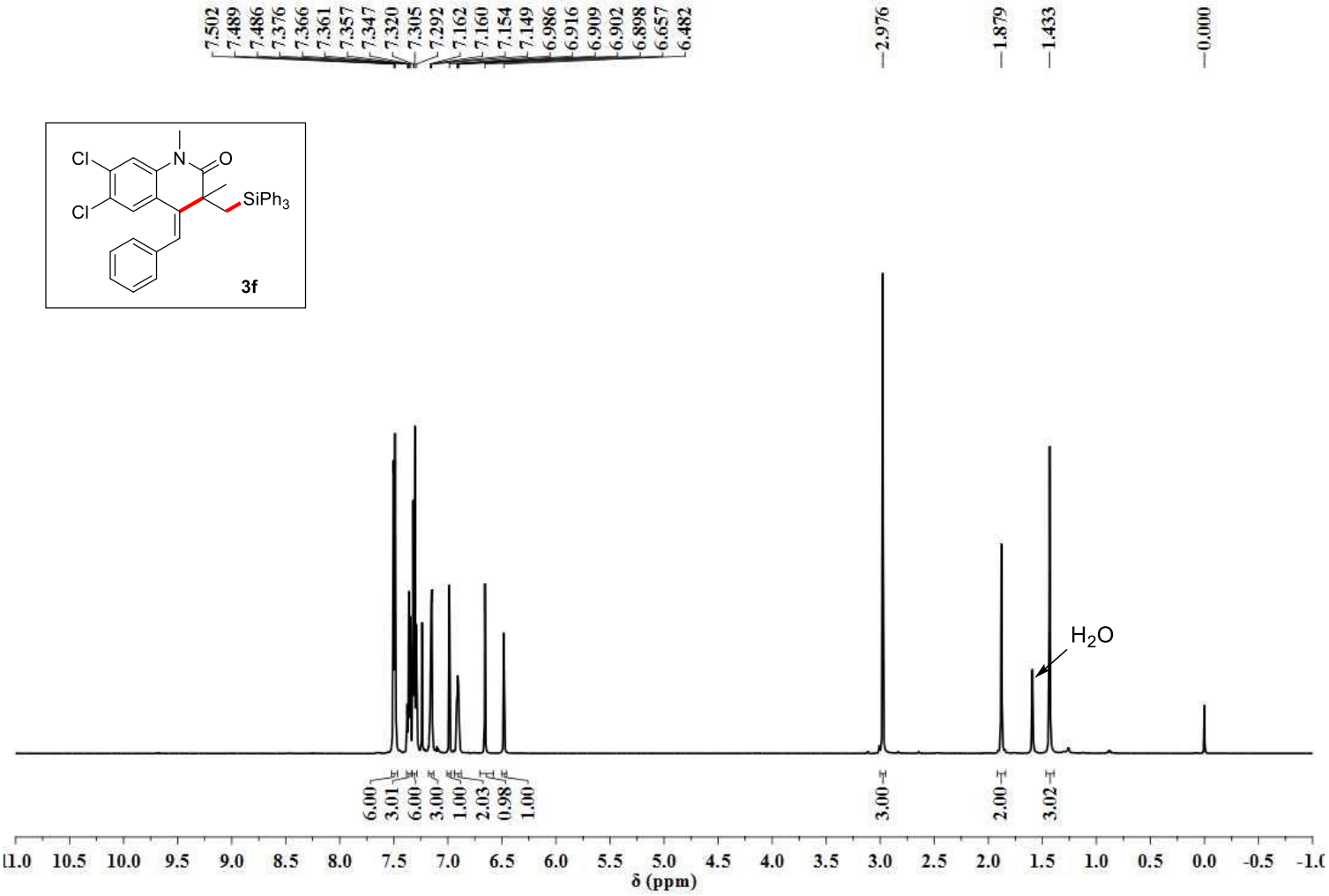
δ (ppm)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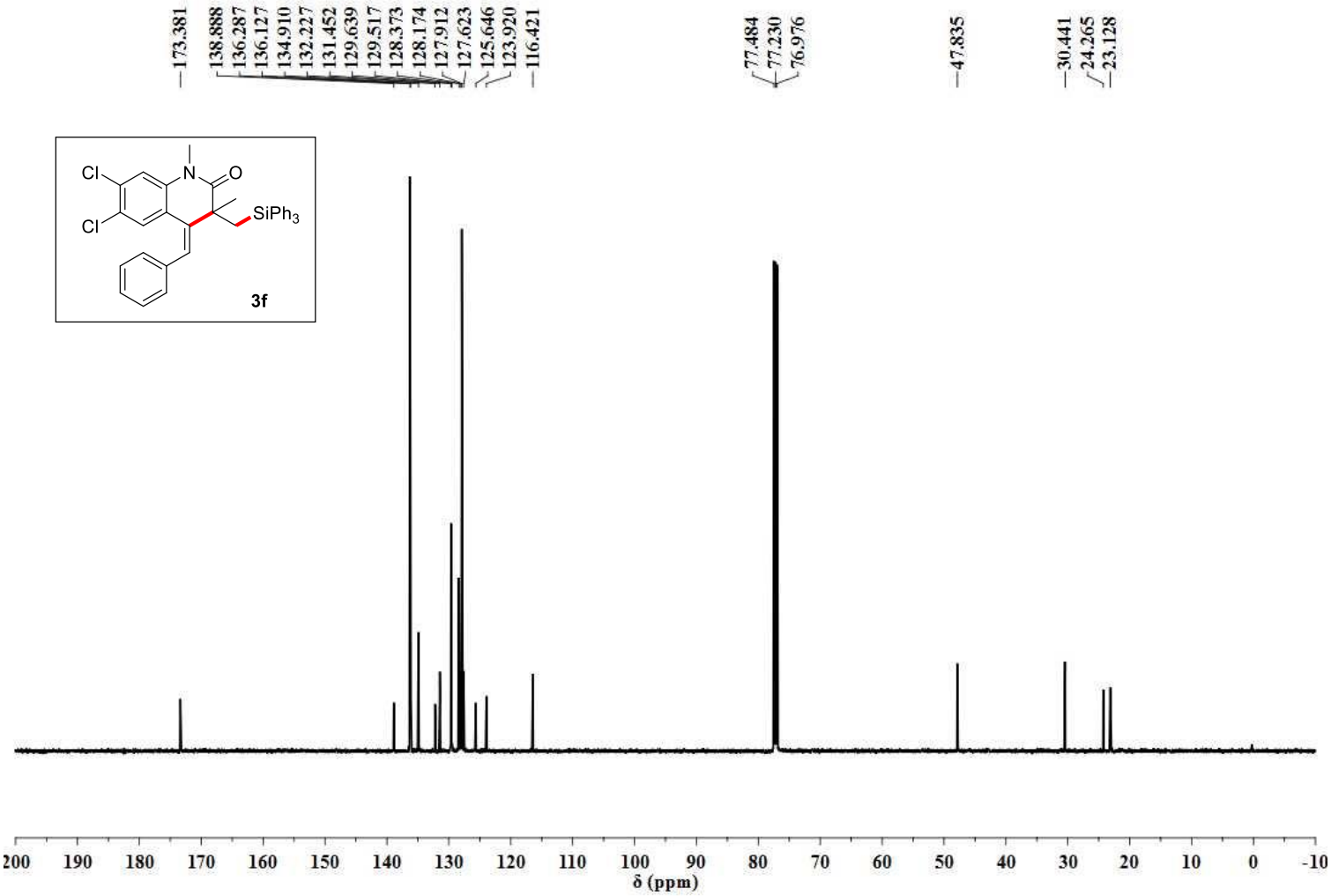
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Cl
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O
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3f
200
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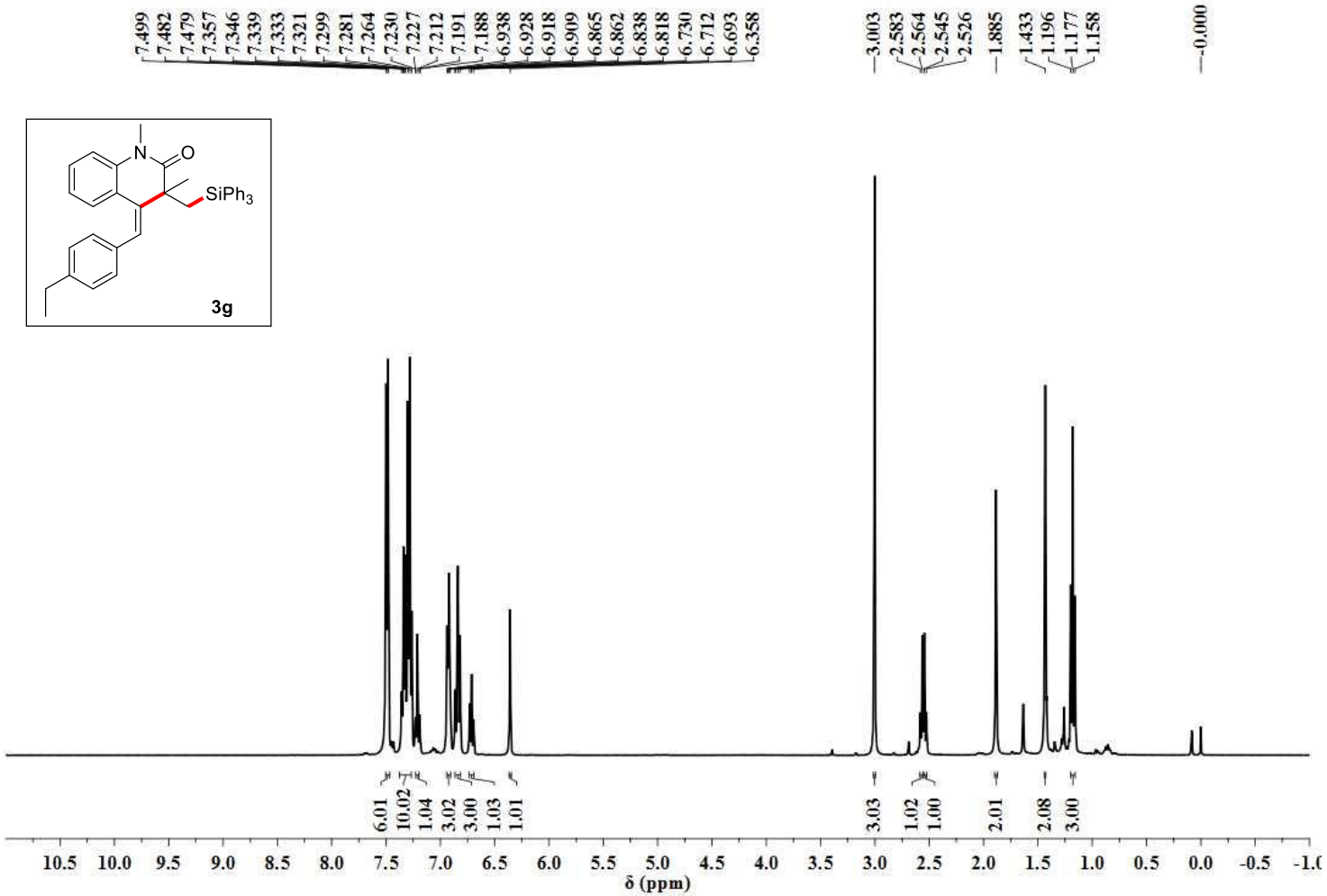
δ (ppm)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3.02
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1.01
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1.00
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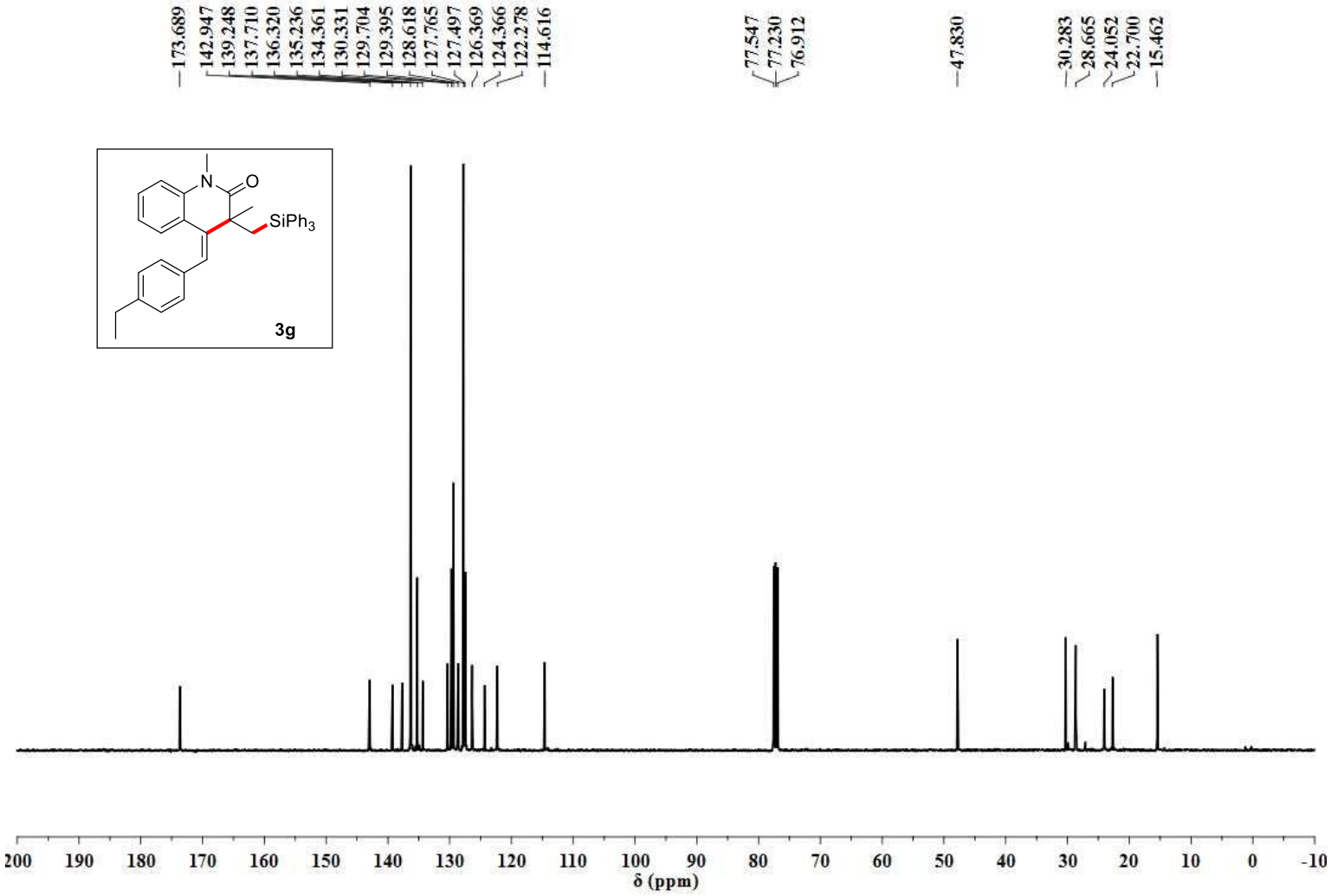
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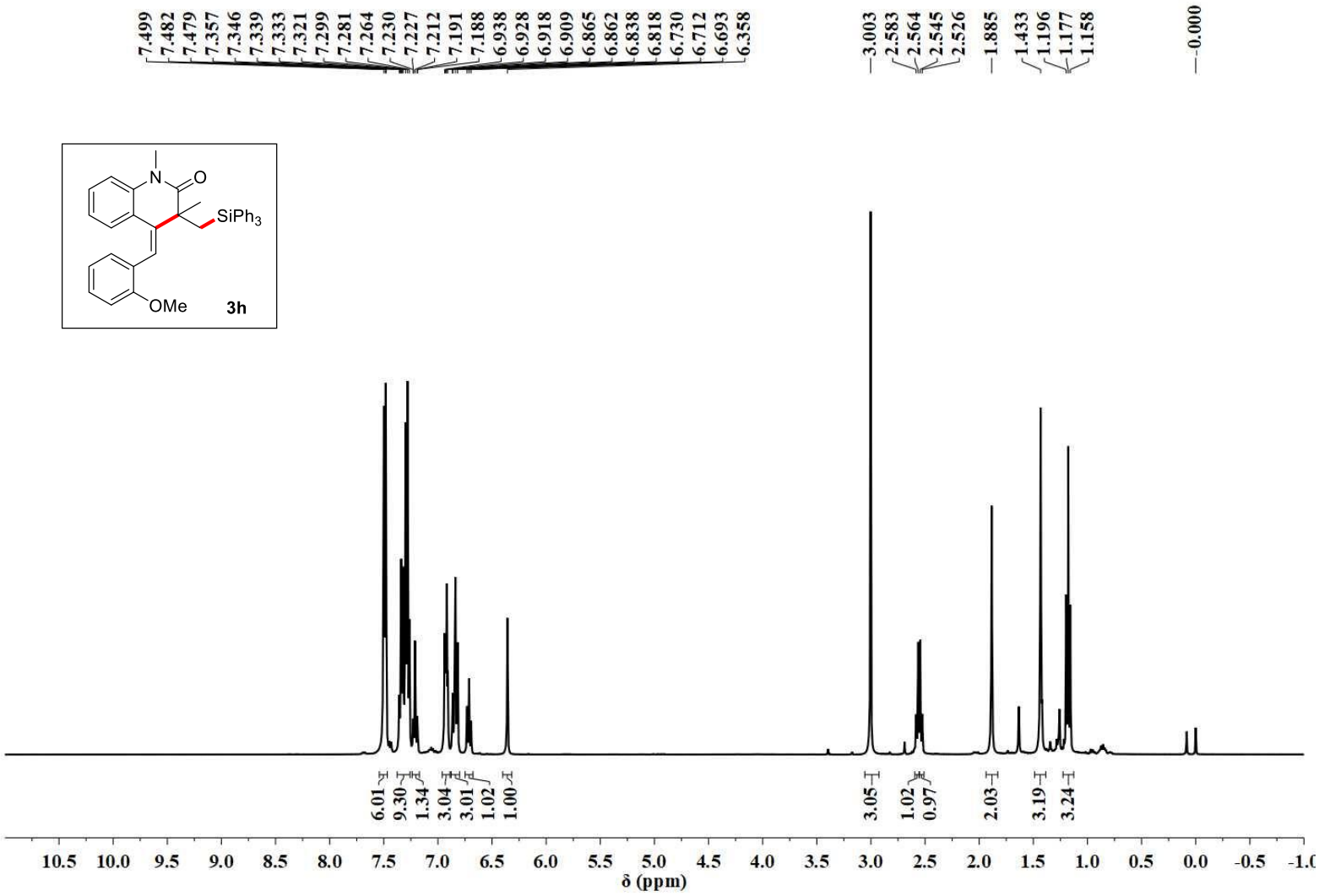
δ (ppm)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OMe
3h
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1.02
1.00
3.05
1.02
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3.19
3.24
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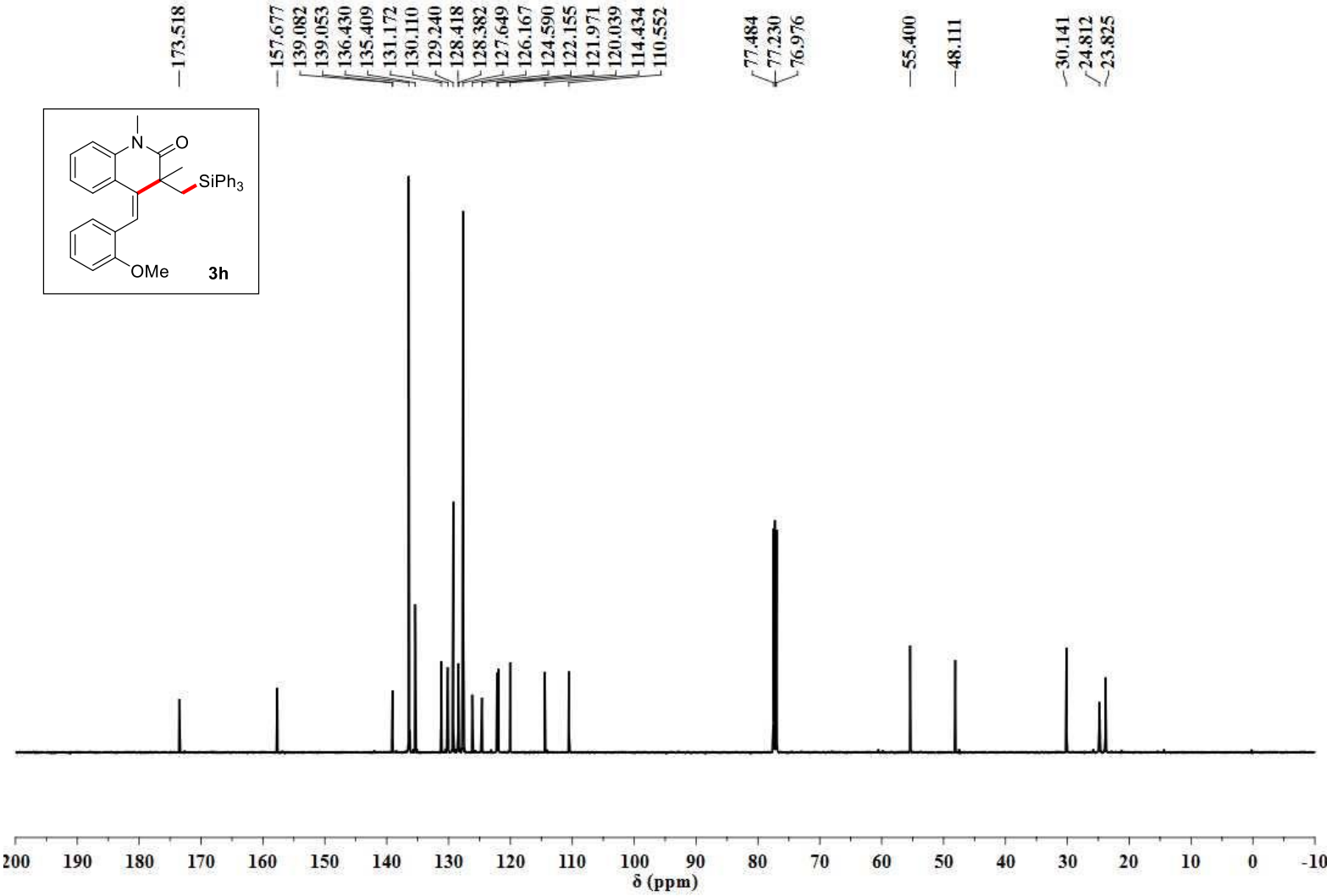
δ (ppm)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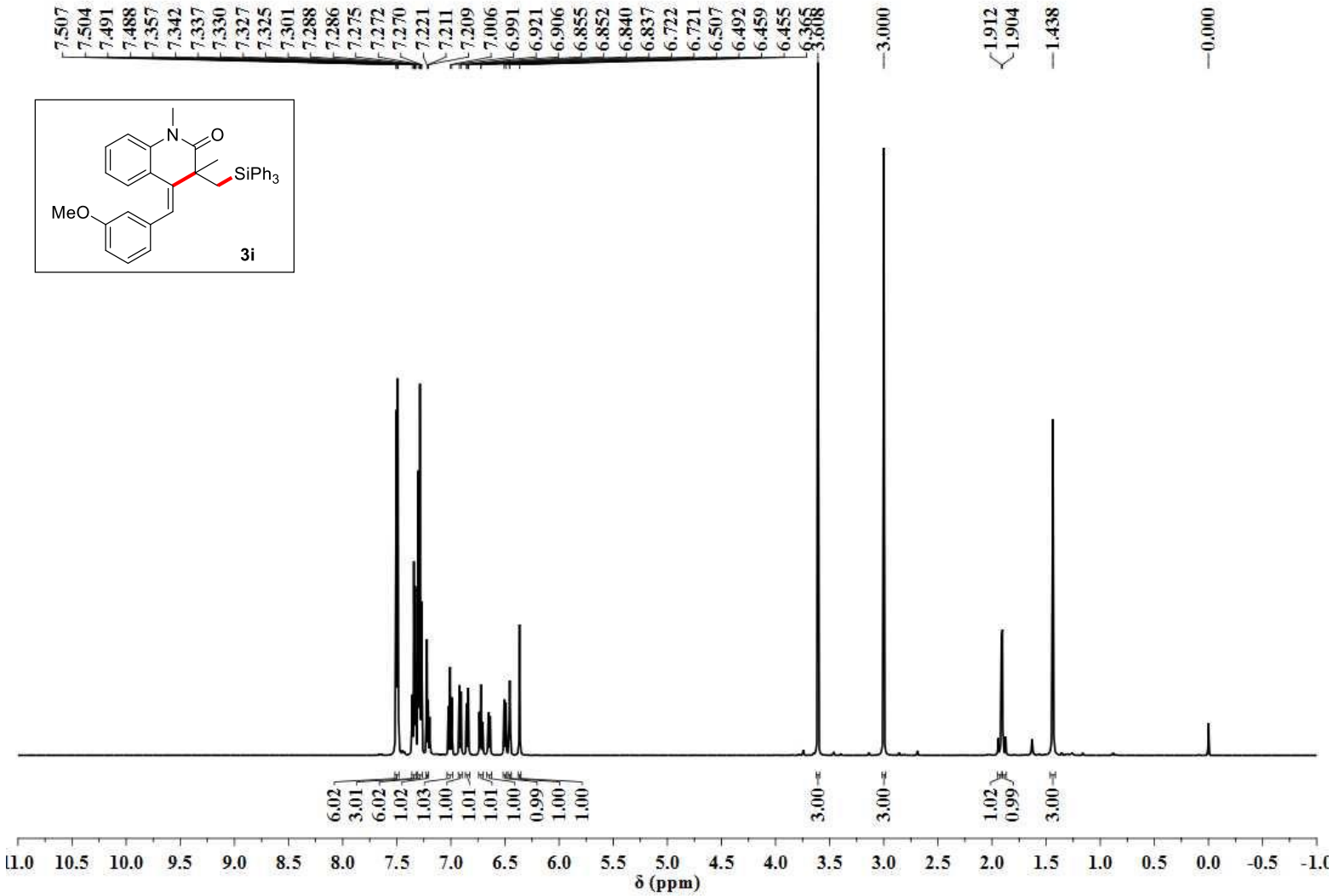
δ (ppm)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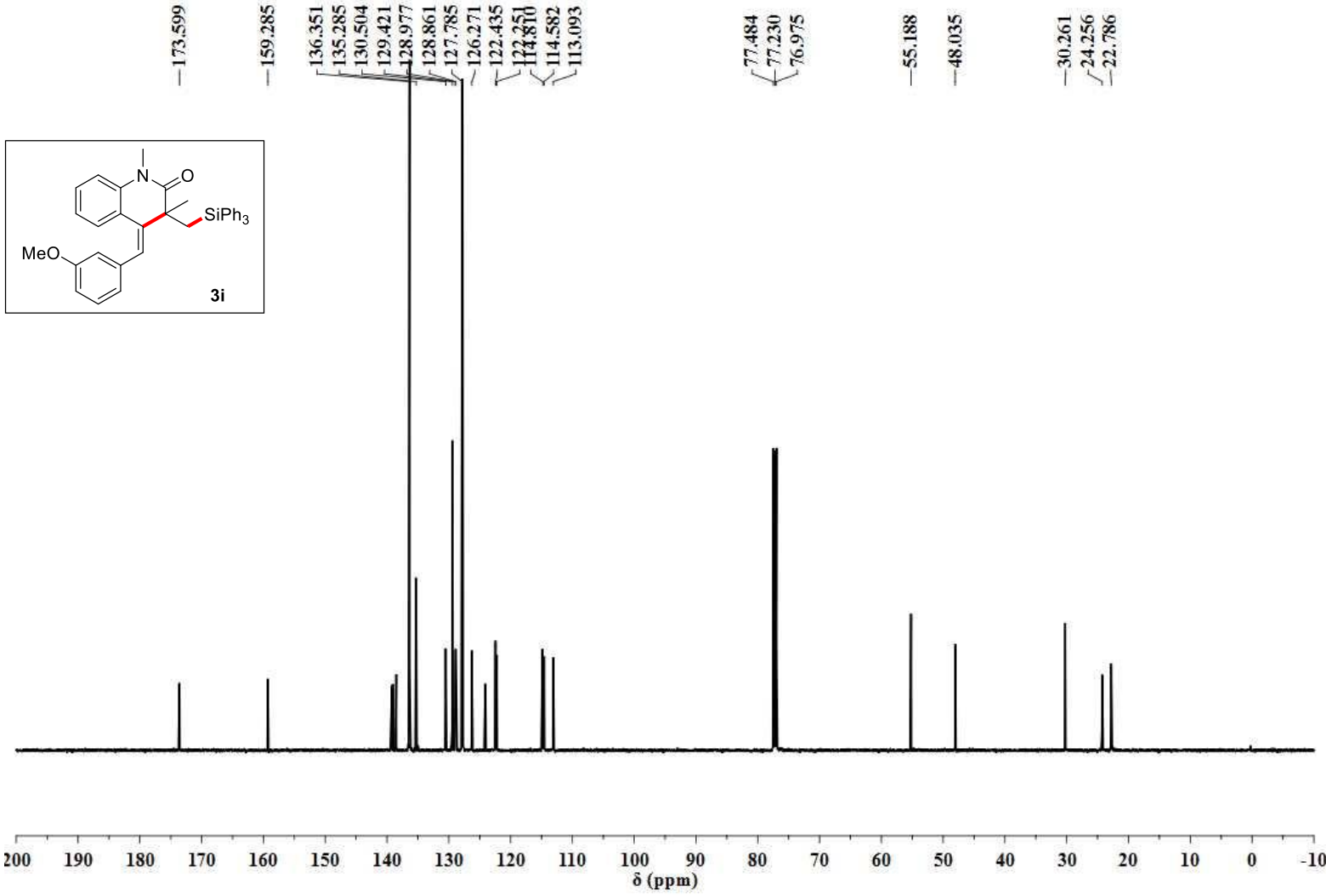
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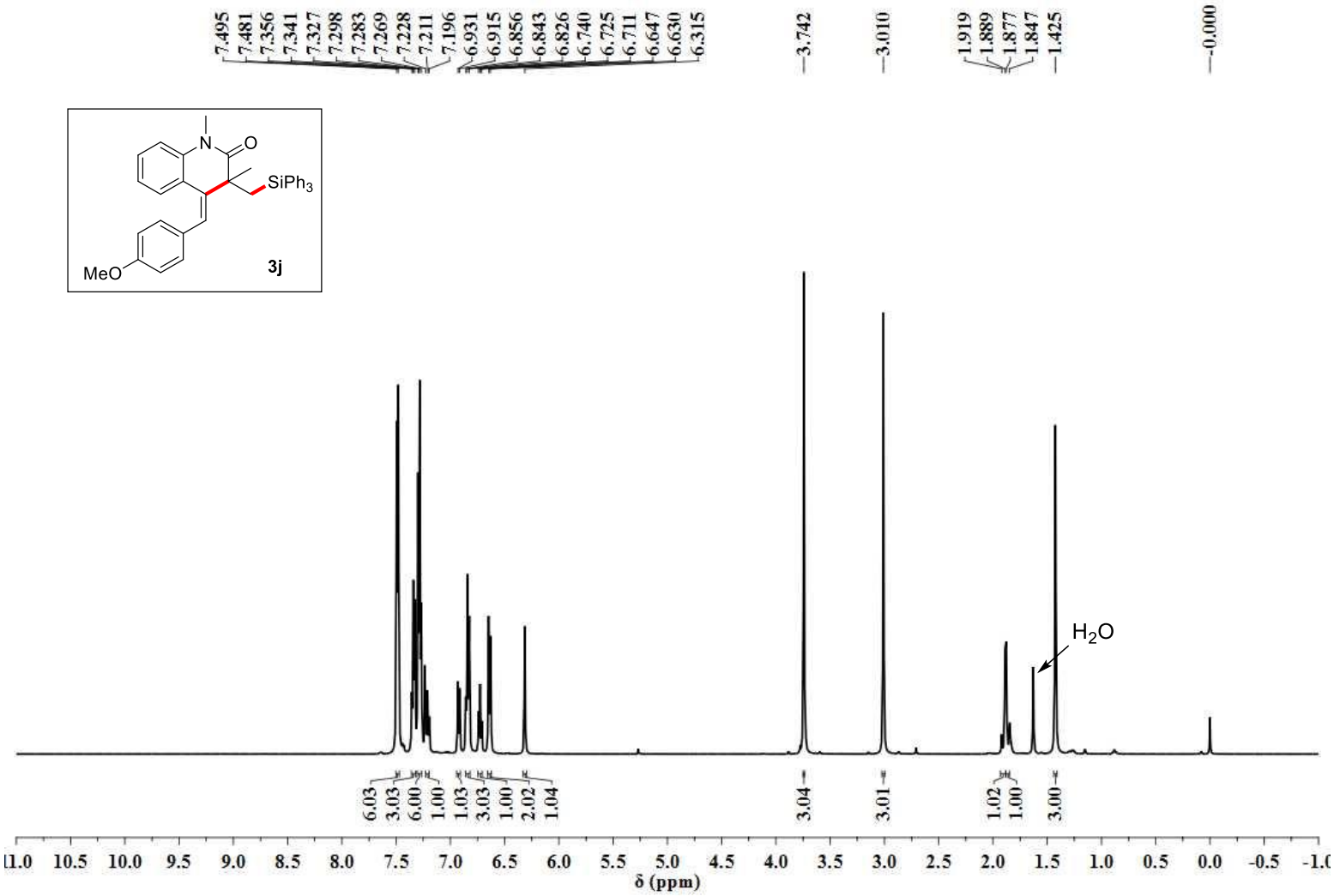
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MeO
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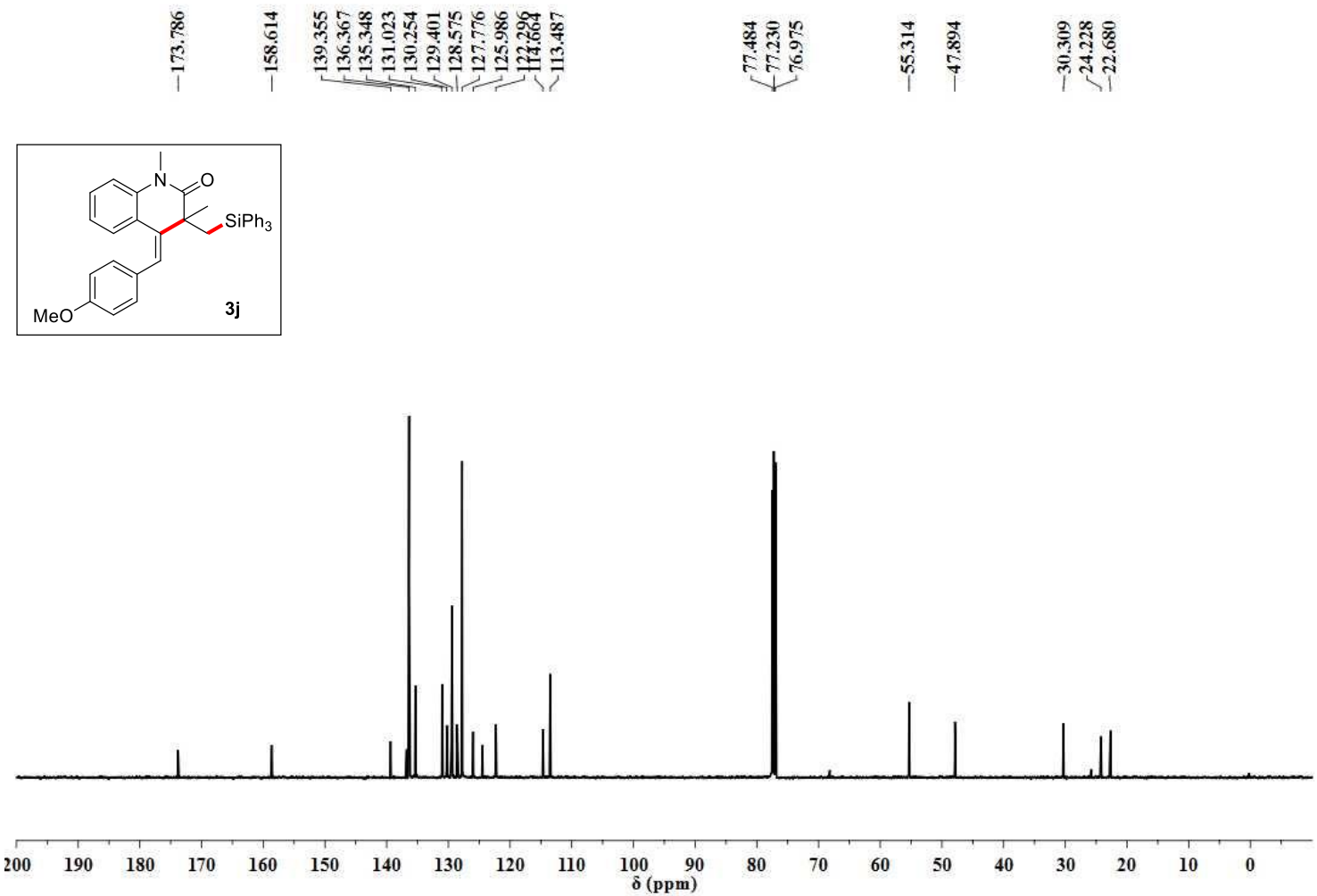
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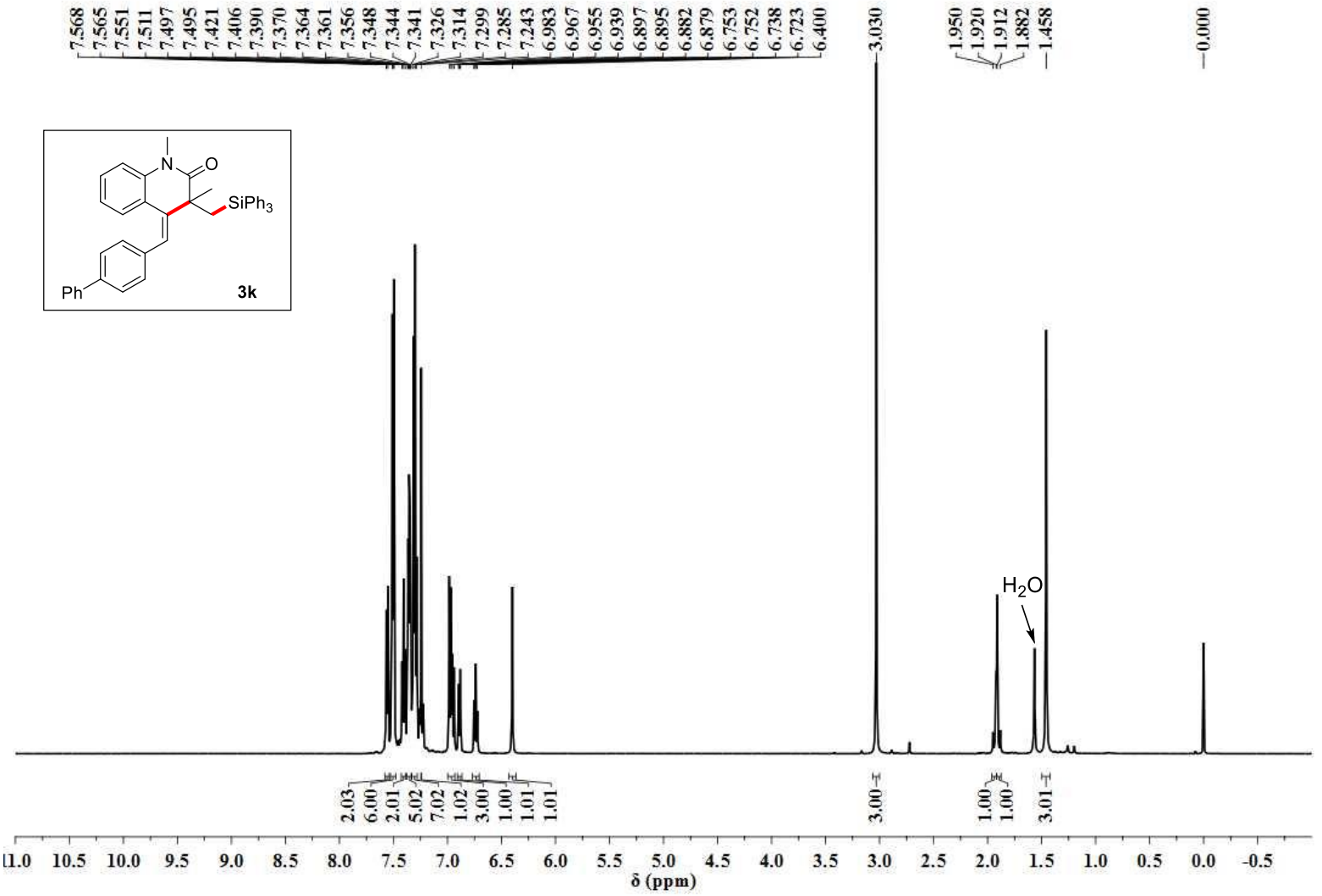
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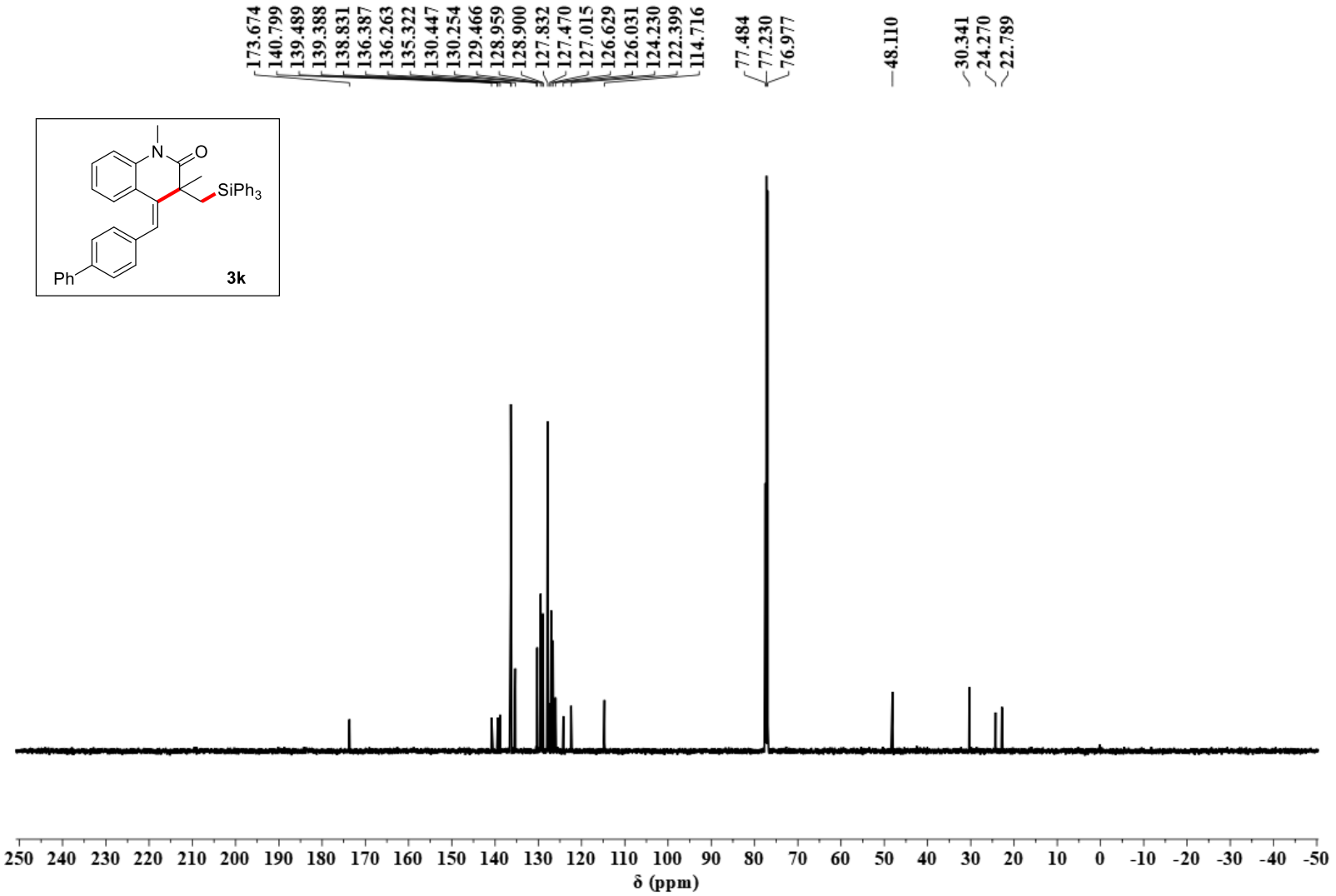
δ (ppm)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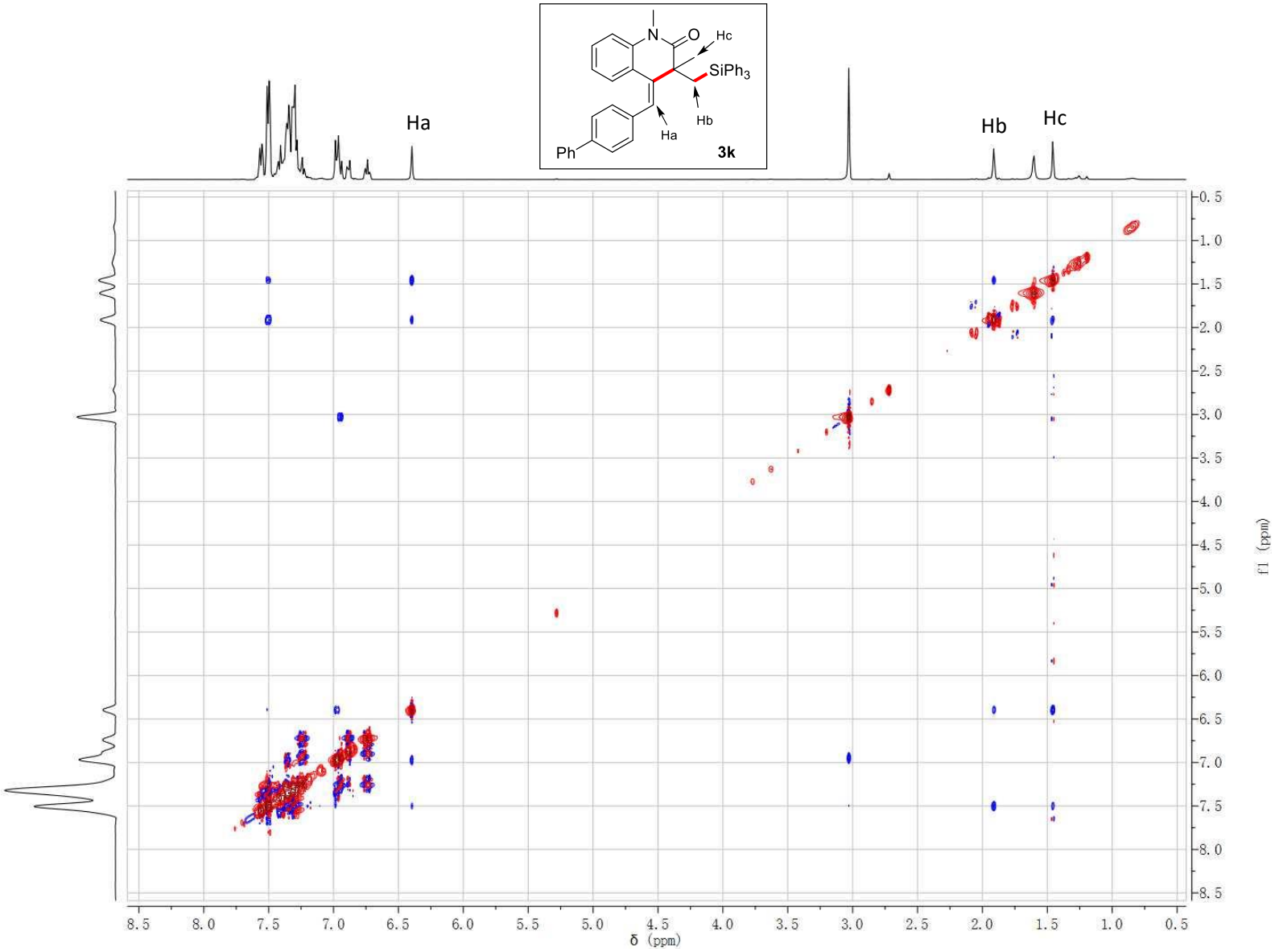
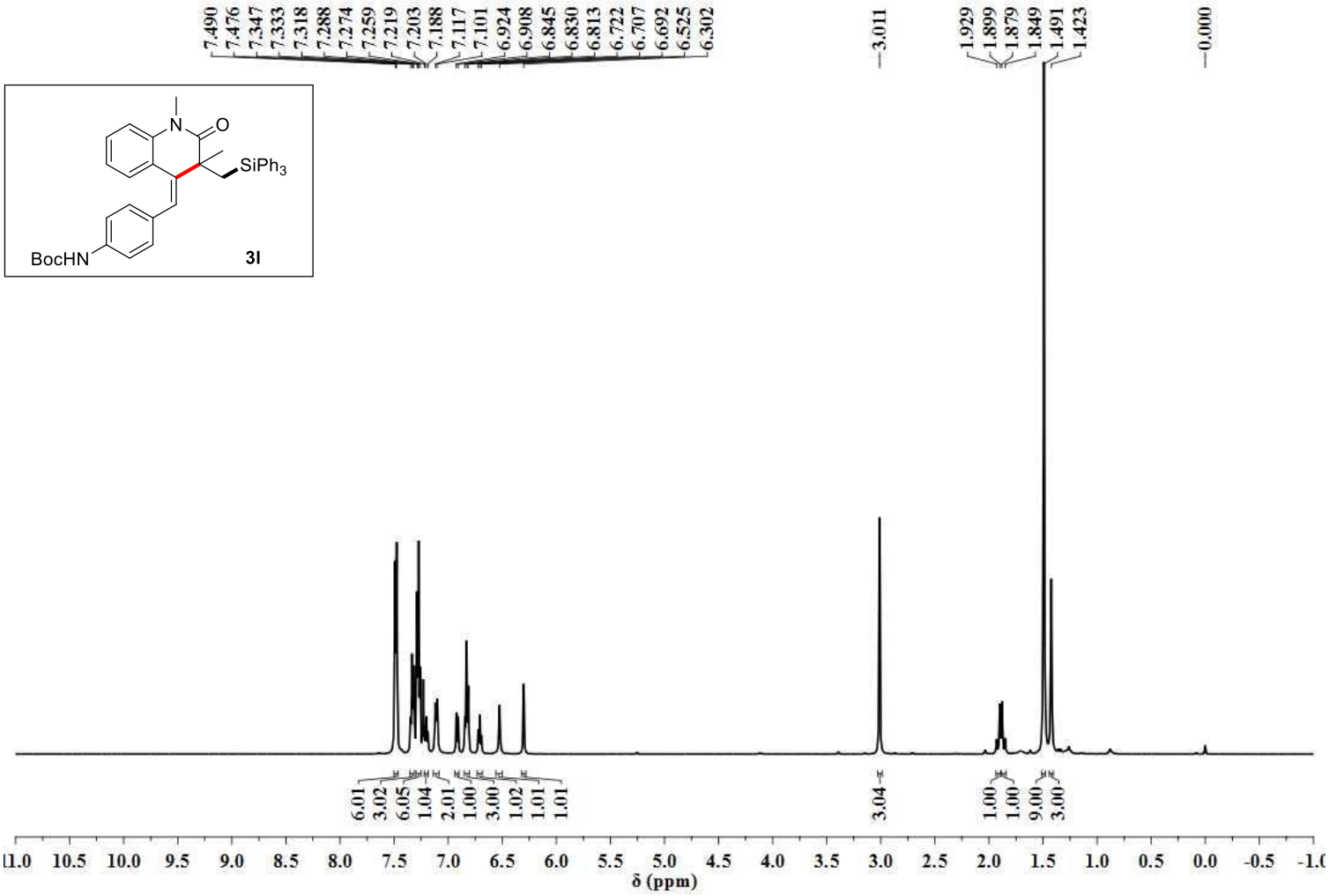
SiPh3
Ph
3k
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
δ (ppm)


Ha
Hb
Hc
N
O
Hc
SiPh3
Hb
Ha
Ph
3k
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
f1 (ppm)
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
δ (ppm)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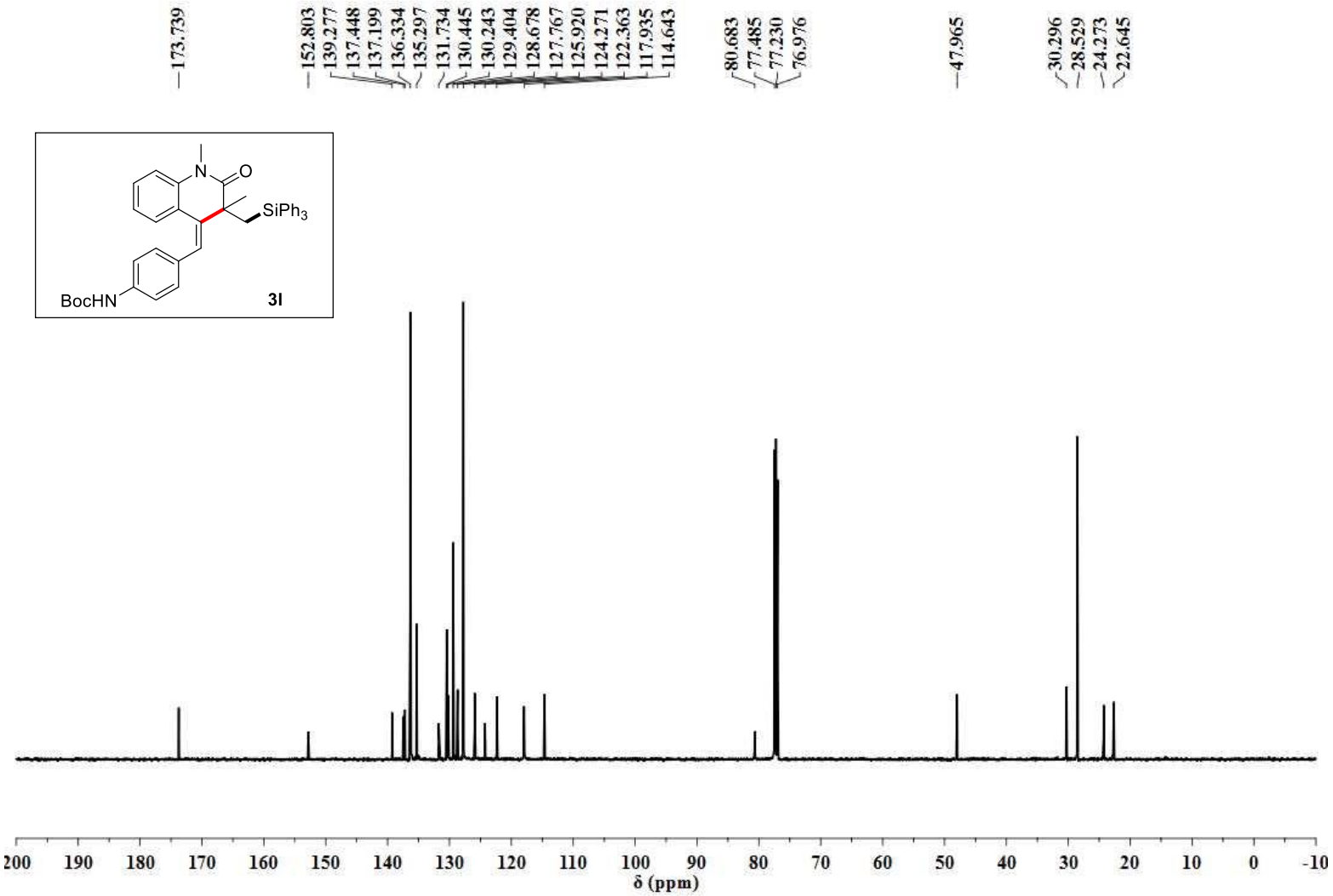
7.288
7.274
7.259
7.219
7.203
7.188
7.117
7.101
6.924
6.908
6.845
6.830
6.813
6.722
6.707
6.692
6.525
6.302
3.011
1.929
1.899
1.879
1.849
1.491
1.423
0.000
N
O
SiPh3
BocHN
3l
6.01
3.02
6.05
1.04
2.01
1.00
3.00
1.02
1.01
1.01
3.04
1.00
1.00
9.00
3.00
δ (ppm)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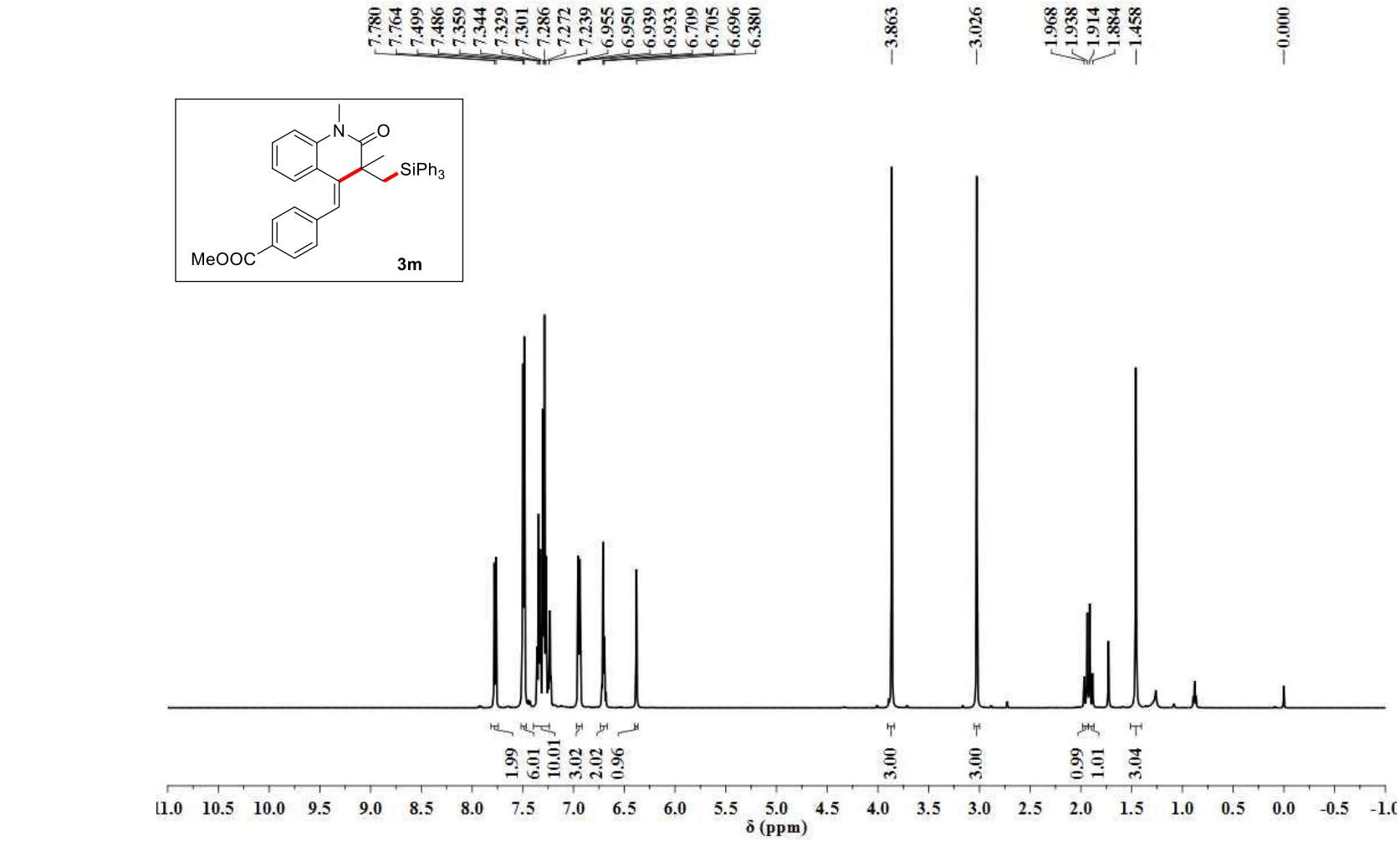
139.277
137.448
137.199
136.334
135.297
131.734
130.445
130.243
129.404
128.678
127.767
125.920
124.271
122.363
117.935
114.643
80.683
77.485
77.230
76.976
47.965
30.296
28.529
24.273
22.645
N
O
SiPh3
BocHN
3l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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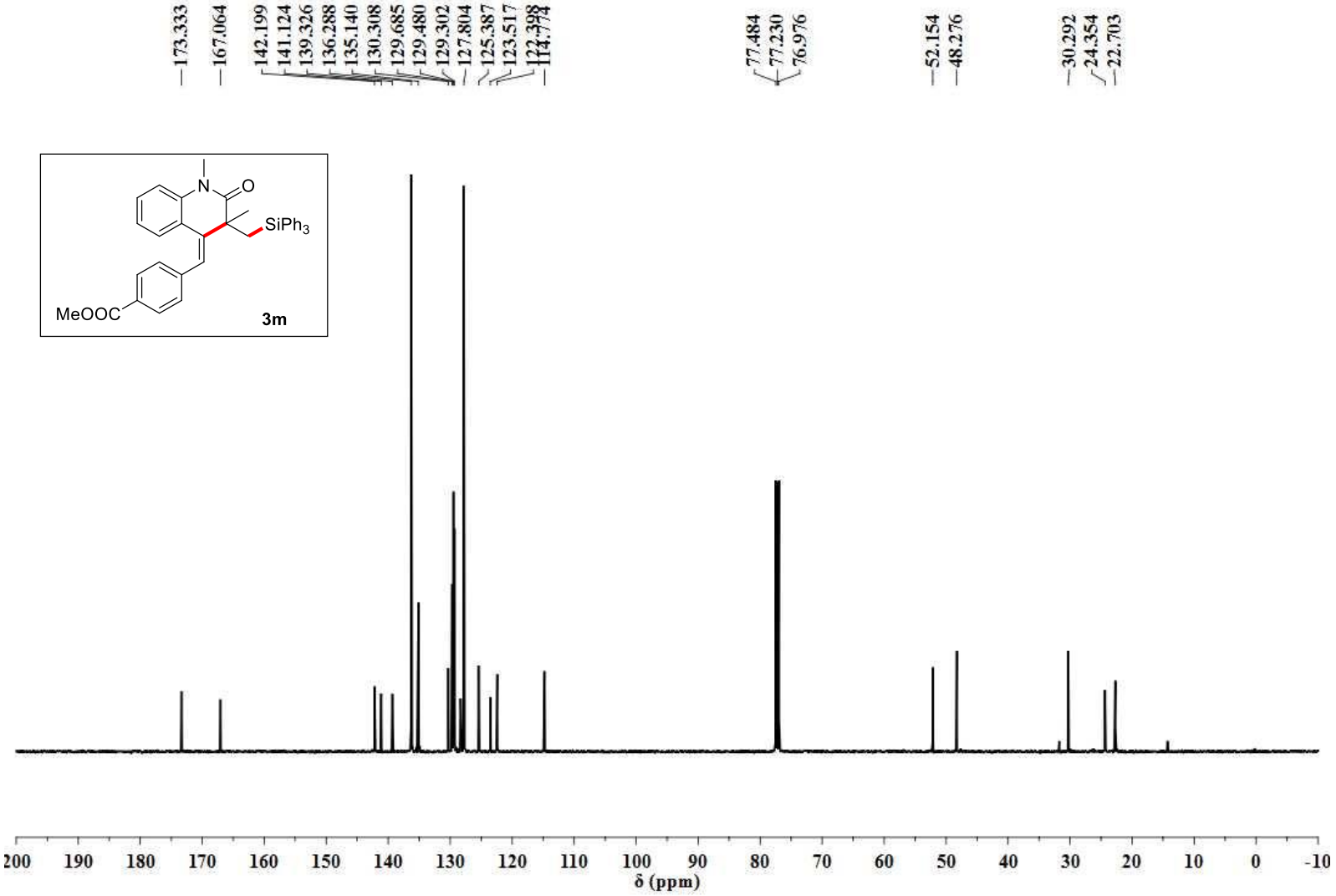
7.764
7.499
7.486
7.359
7.344
7.329
7.301
7.286
7.272
7.239
6.955
6.950
6.939
6.933
6.709
6.705
6.696
6.380
3.863
3.026
1.968
1.938
1.914
1.884
1.458
0.000
N
O
SiPh3
MeOOC
3m
1.99
6.01
10.01
3.02
2.02
0.96
3.00
3.00
0.99
1.01
3.04
δ (ppm)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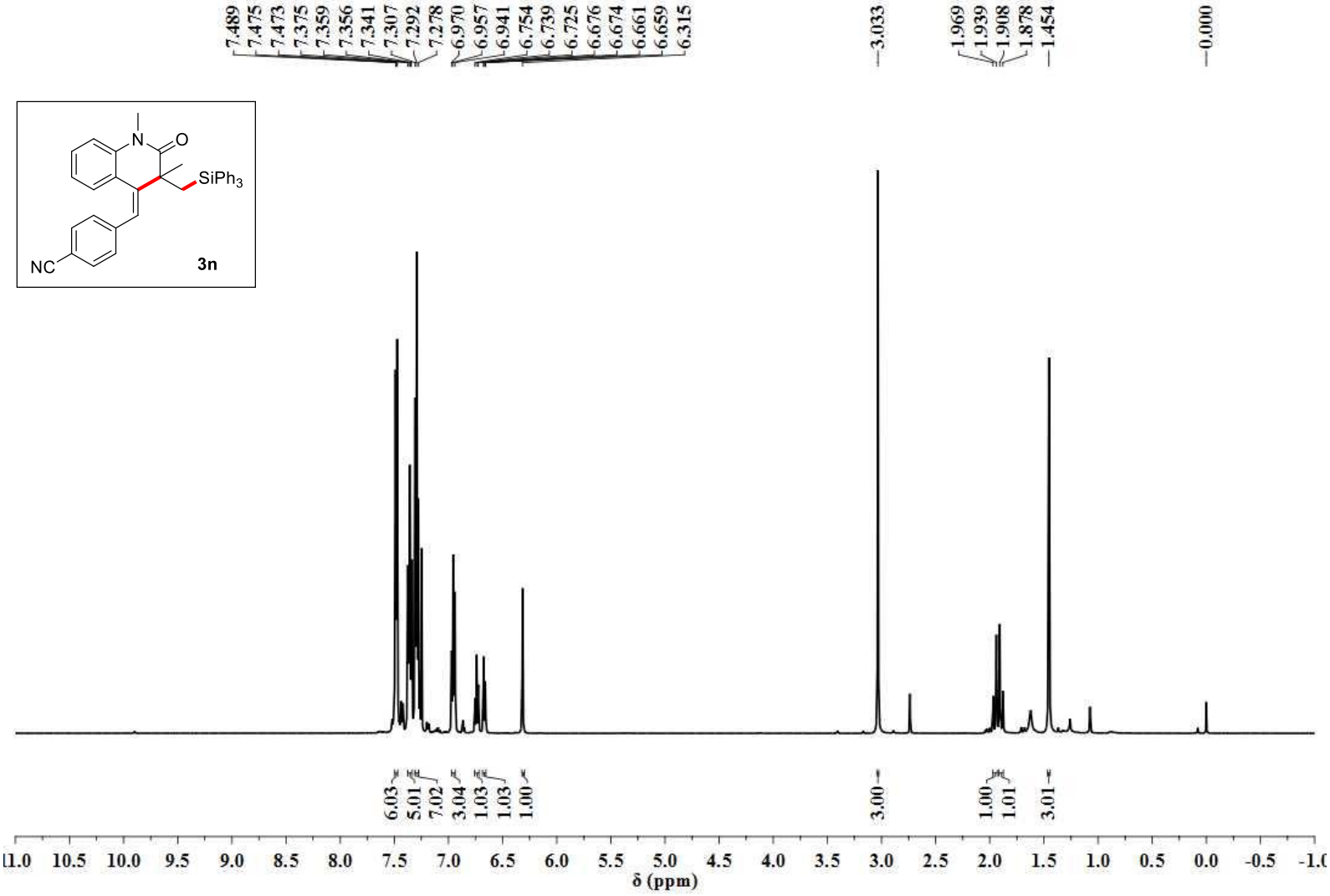
167.064
142.199
141.124
139.326
136.288
135.140
130.308
129.685
129.480
129.302
127.804
125.387
123.517
77.484
77.230
76.976
52.154
48.276
30.292
24.354
22.703
N
O
SiPh3
MeOOC
3m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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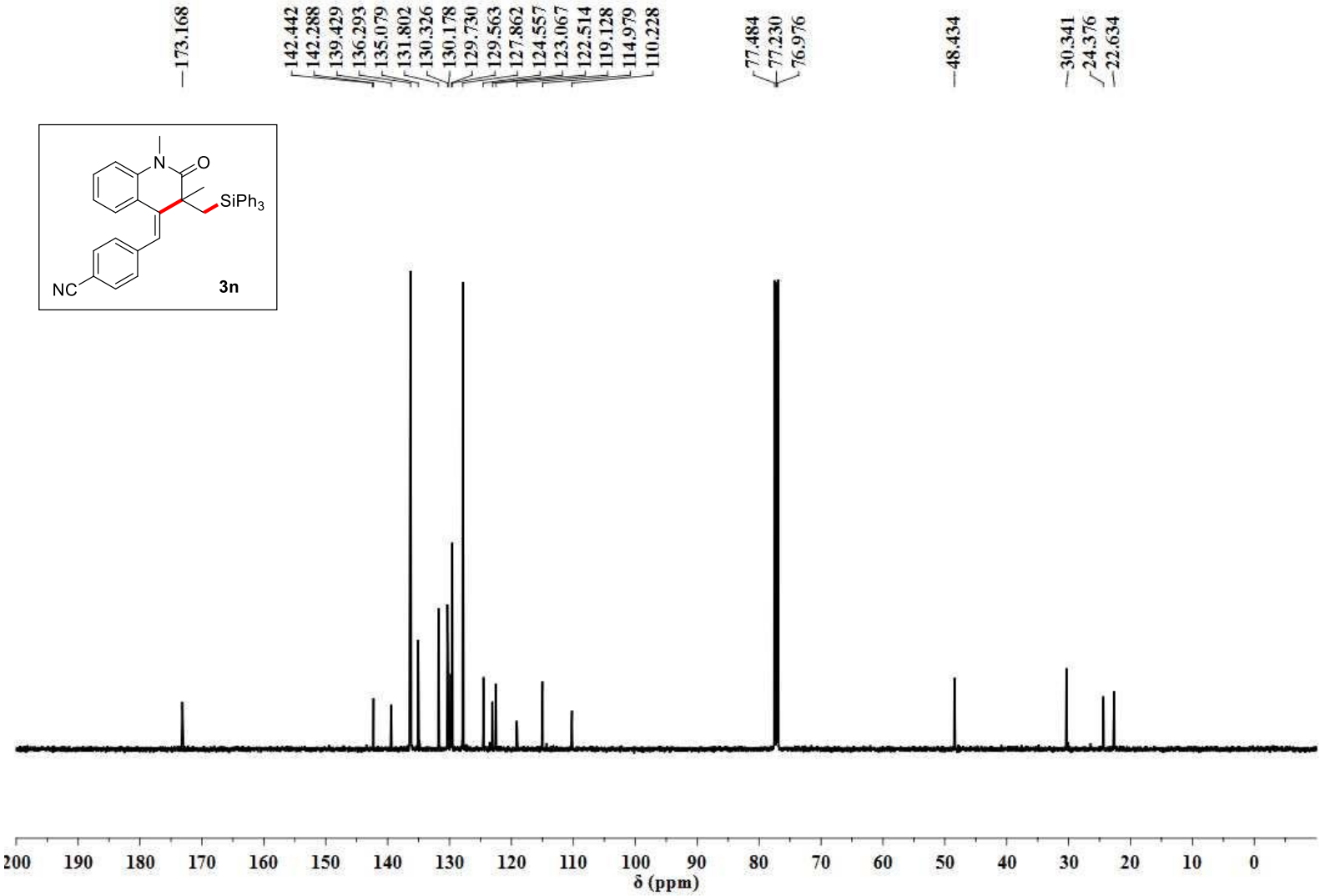
7.475
7.473
7.375
7.359
7.356
7.341
7.307
7.292
7.278
6.970
6.957
6.941
6.754
6.739
6.725
6.676
6.674
6.661
6.659
6.315
3.033
1.969
1.939
1.908
1.878
1.454
0.000
N
O
SiPh3
NC
3n
6.03
5.01
7.02
3.04
1.03
1.03
1.00
3.00
1.00
1.01
3.01
δ (ppm)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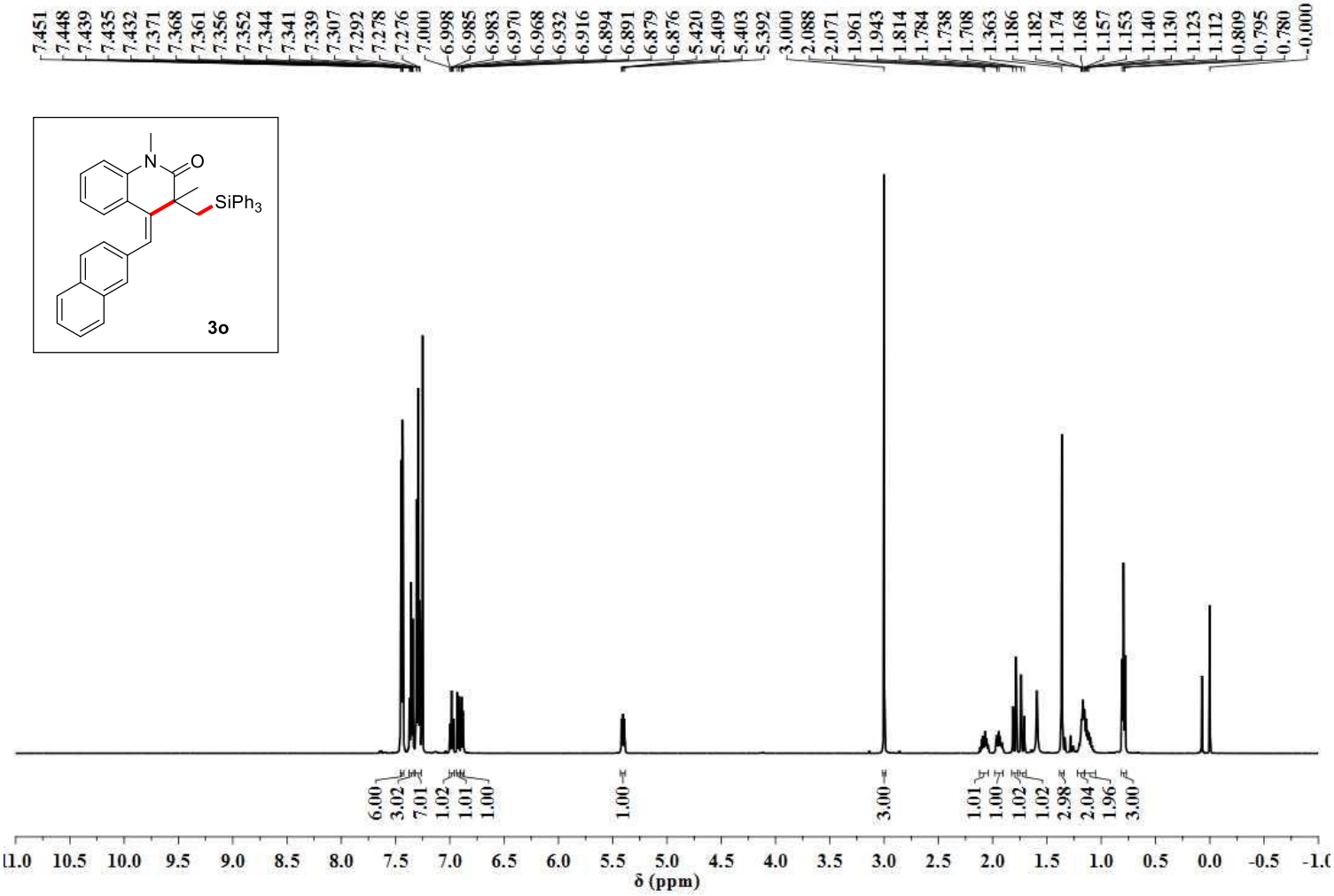
142.442
142.288
139.429
136.293
135.079
131.802
130.326
130.178
129.730
129.563
127.862
124.557
123.067
122.514
119.128
114.979
110.228
77.484
77.230
76.976
48.434
30.341
24.376
22.634
N
O
SiPh3
NC
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)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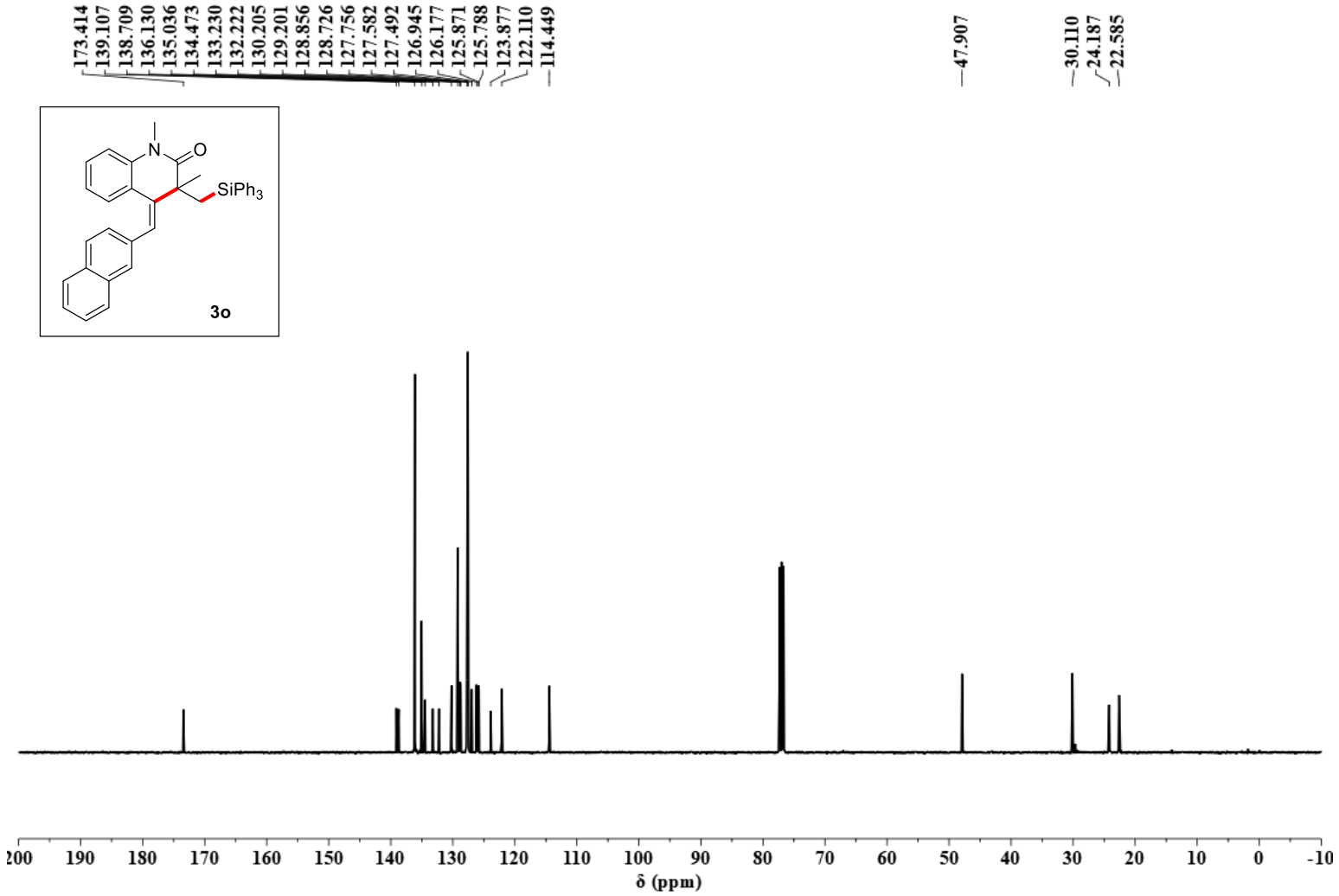
7.448
7.439
7.435
7.432
7.371
7.368
7.361
7.356
7.352
7.344
7.341
7.339
7.307
7.292
7.278
7.276
7.000
6.998
6.985
6.983
6.970
6.968
6.932
6.916
6.894
6.891
6.879
6.876
5.420
5.409
5.403
5.392
3.000
2.088
2.071
1.961
1.943
1.814
1.784
1.738
1.708
1.363
1.186
1.182
1.174
1.168
1.157
1.153
1.140
1.130
1.123
1.112
0.809
0.795
0.780
0.000
N
O
SiPh3
3o
6.00
3.02
7.01
1.02
1.01
1.00
1.00
3.00
1.01
1.00
1.02
1.02
2.98
2.04
1.96
3.00
δ (ppm)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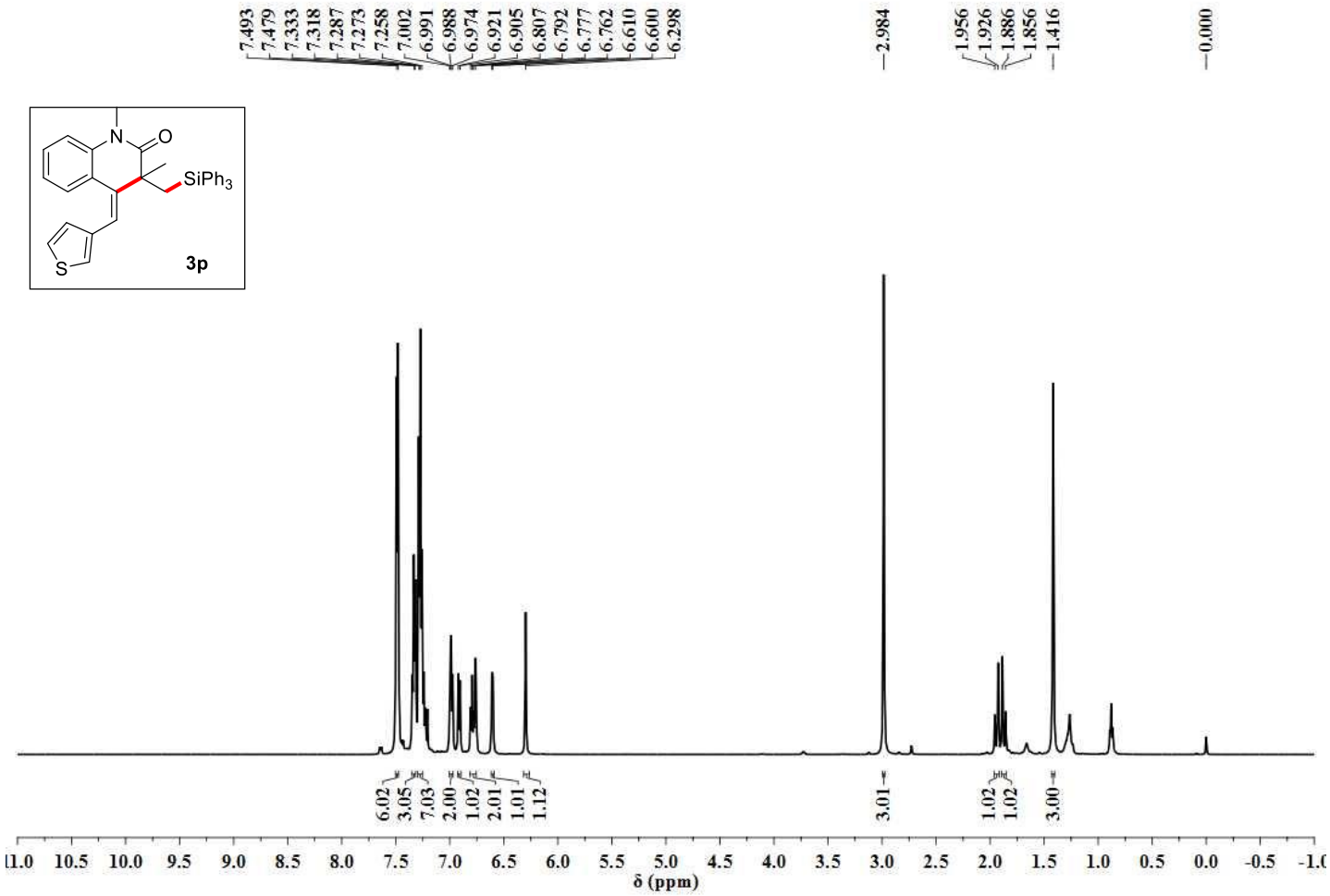
138.709
136.130
135.036
134.473
133.230
132.222
130.205
129.201
128.856
128.726
127.756
127.582
127.492
126.945
126.177
125.871
125.788
123.877
122.110
114.449
47.907
30.110
24.187
22.585
N
O
SiPh3
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.273
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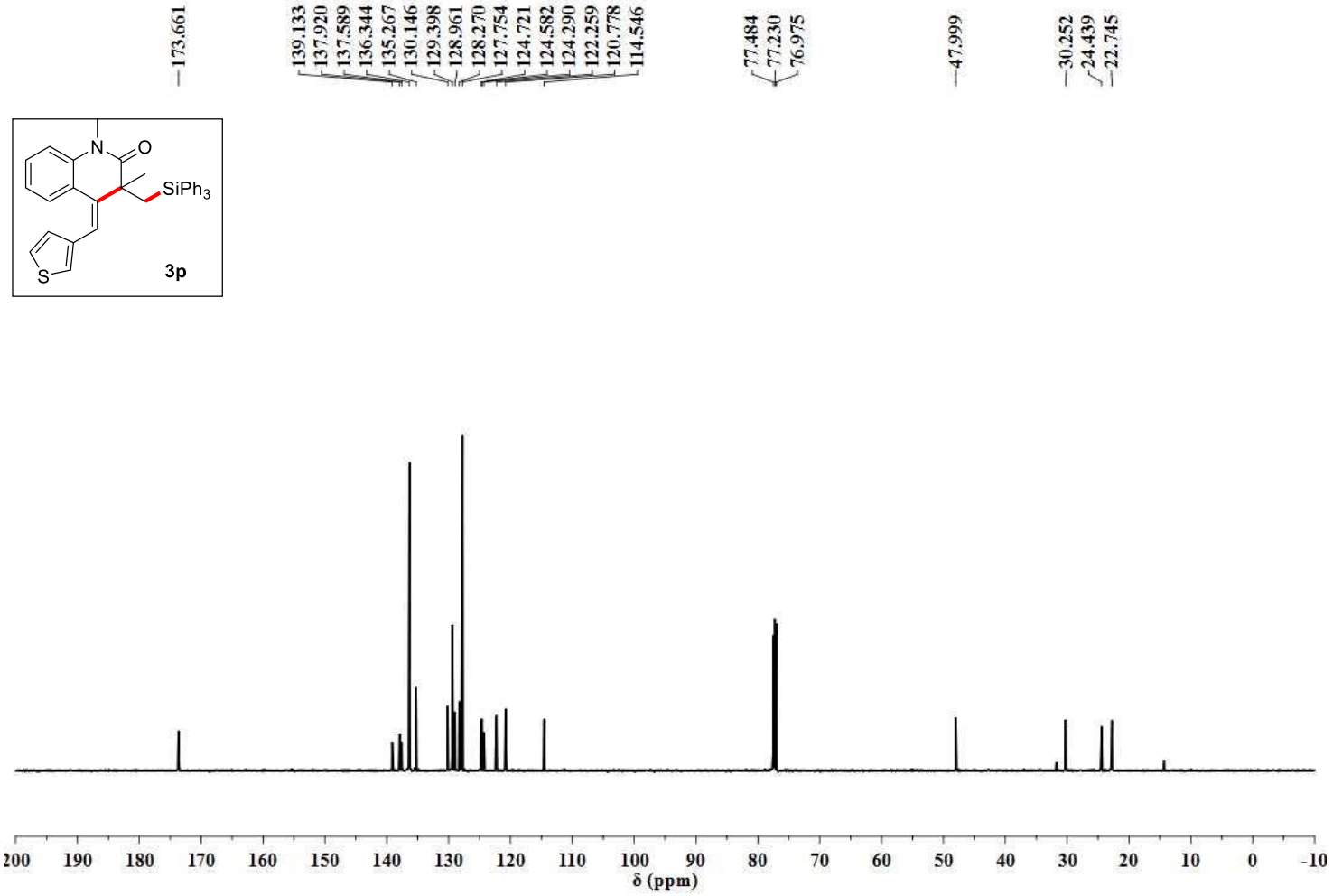
7.002
6.991
6.988
6.974
6.921
6.905
6.807
6.792
6.777
6.762
6.610
6.600
6.298
2.984
1.956
1.926
1.886
1.856
1.416
0.000
N
O
SiPh3
S
3p
6.02
3.05
7.03
2.00
1.02
2.01
1.01
1.12
3.01
1.02
1.02
3.00
δ (ppm)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137.920
137.589
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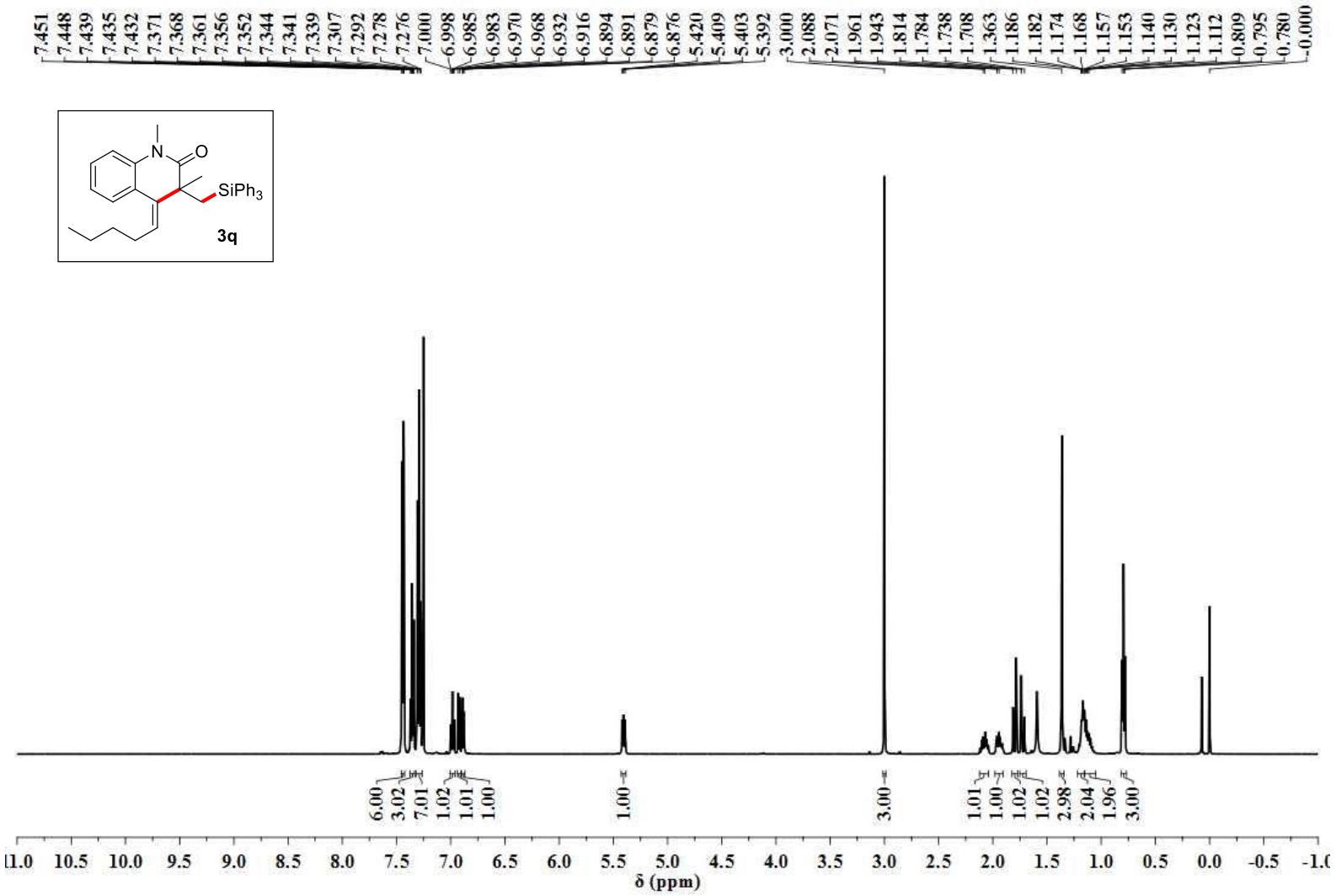
135.267
130.146
129.398
128.961
128.270
127.754
124.721
124.582
124.290
122.259
120.778
114.546
77.484
77.230
76.975
47.999
30.252
24.439
22.745
N
O
SiPh3
S
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.448
7.439
7.435
7.432
7.371
7.368
7.361
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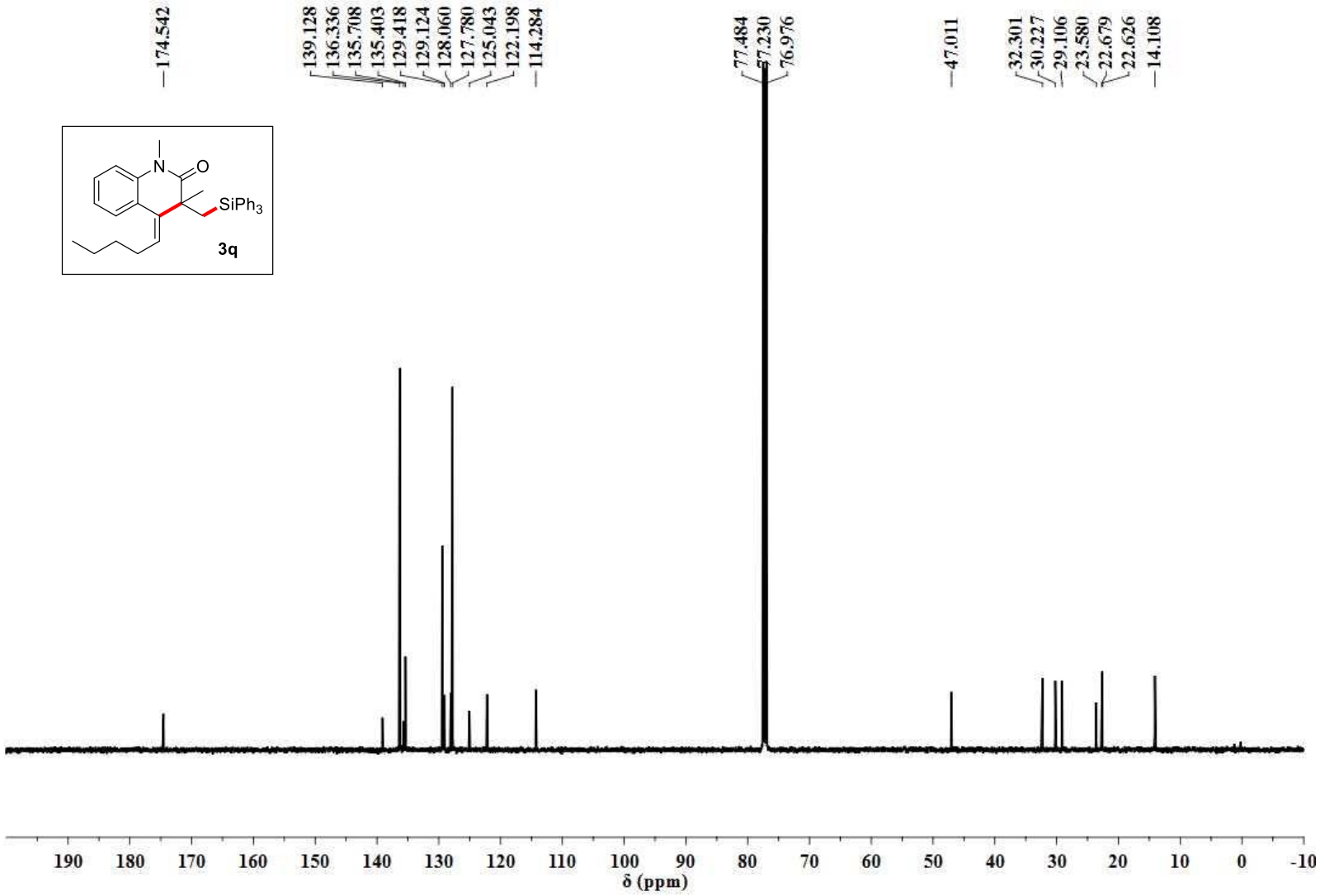
7.352
7.344
7.341
7.339
7.307
7.292
7.278
7.276
7.000
6.998
6.985
6.983
6.970
6.968
6.932
6.916
6.894
6.891
6.879
6.876
5.420
5.409
5.403
5.392
3.000
2.088
2.071
1.961
1.943
1.814
1.784
1.738
1.708
1.363
1.186
1.182
1.174
1.168
1.157
1.153
1.140
1.130
1.123
1.112
0.809
0.795
0.780
-0.000
N
O
SiPh3
3q
6.00
3.02
7.01
1.02
1.01
1.00
1.00
3.00
1.01
1.00
1.02
1.02
2.98
2.04
1.96
3.00
δ (ppm)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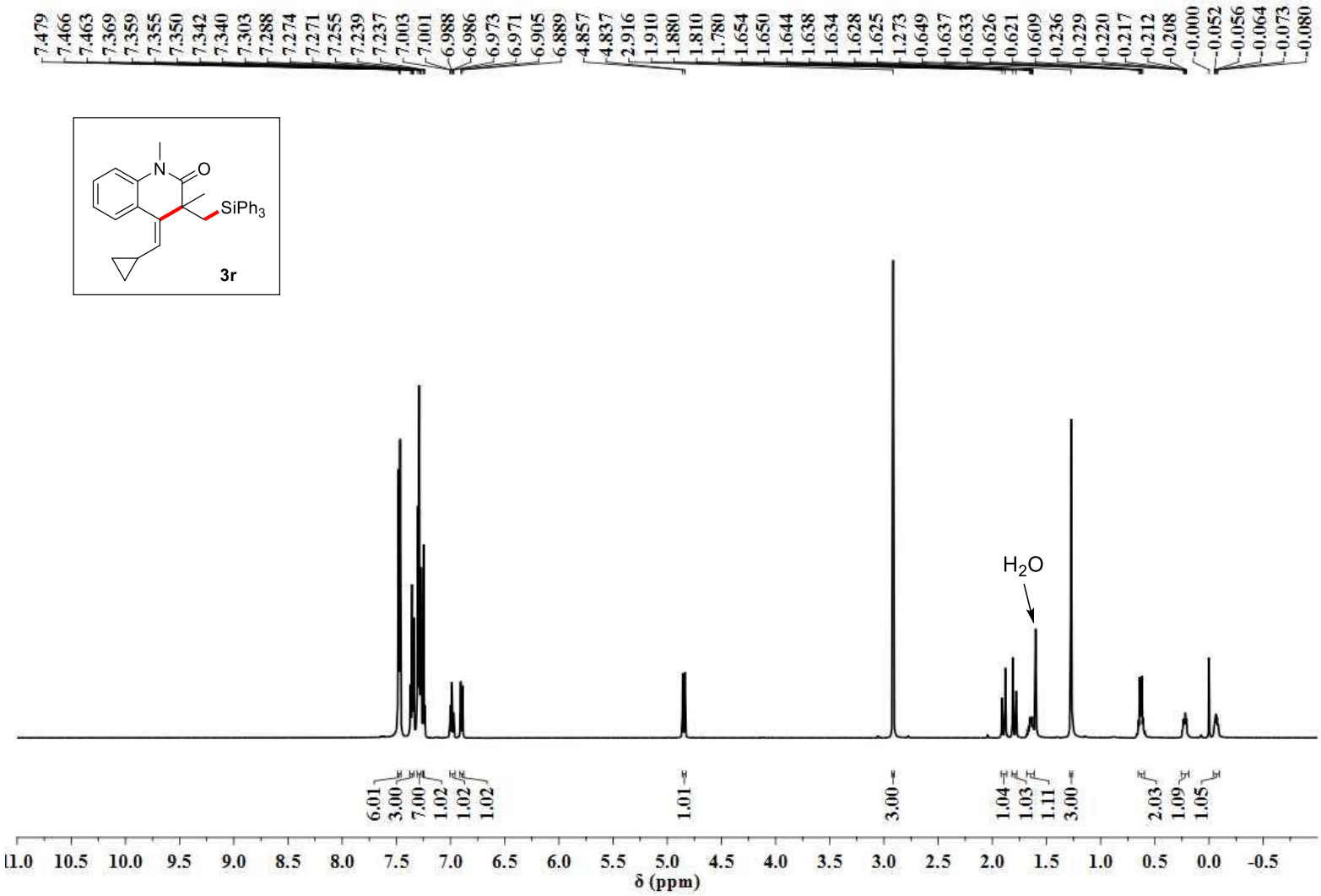
128.060
127.780
125.043
122.198
114.284
77.484
77.230
76.976
47.011
32.301
30.227
29.106
23.580
22.679
22.626
14.108
N
O
SiPh3
3q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.350
7.342
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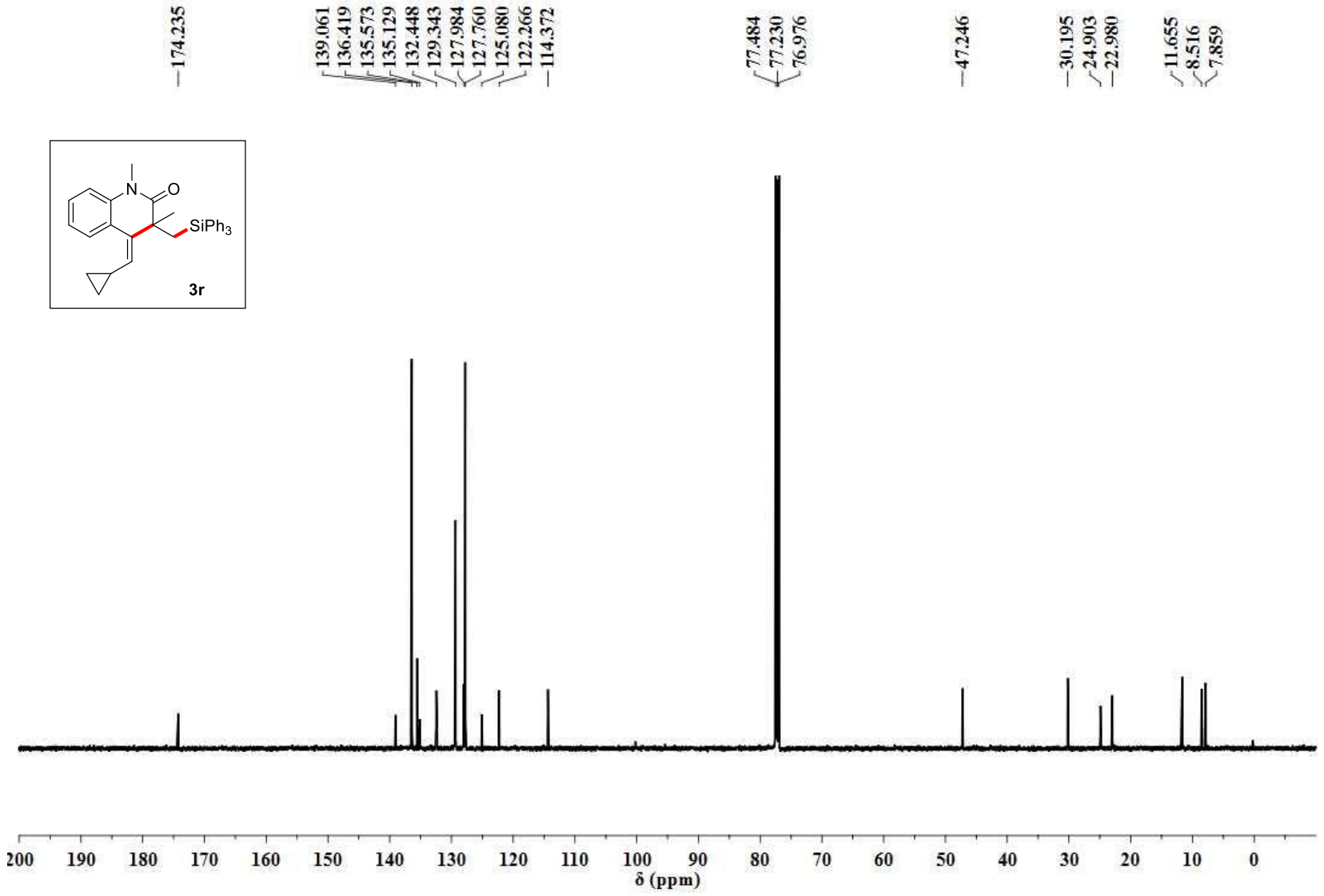
7.288
7.274
7.271
7.255
7.239
7.237
7.003
7.001
6.988
6.986
6.973
6.971
6.905
6.889
4.857
4.837
2.916
1.910
1.880
1.810
1.780
1.654
1.650
1.644
1.638
1.634
1.628
1.625
1.273
0.649
0.637
0.633
0.626
0.621
0.609
0.236
0.229
0.220
0.217
0.212
0.208
-0.000
-0.052
-0.056
-0.064
-0.073
-0.080
SiPh3
3r
H2O
6.01
3.00
7.00
1.02
1.02
1.02
1.01
3.00
1.04
1.03
1.11
3.00
2.03
1.09
1.05
δ (ppm)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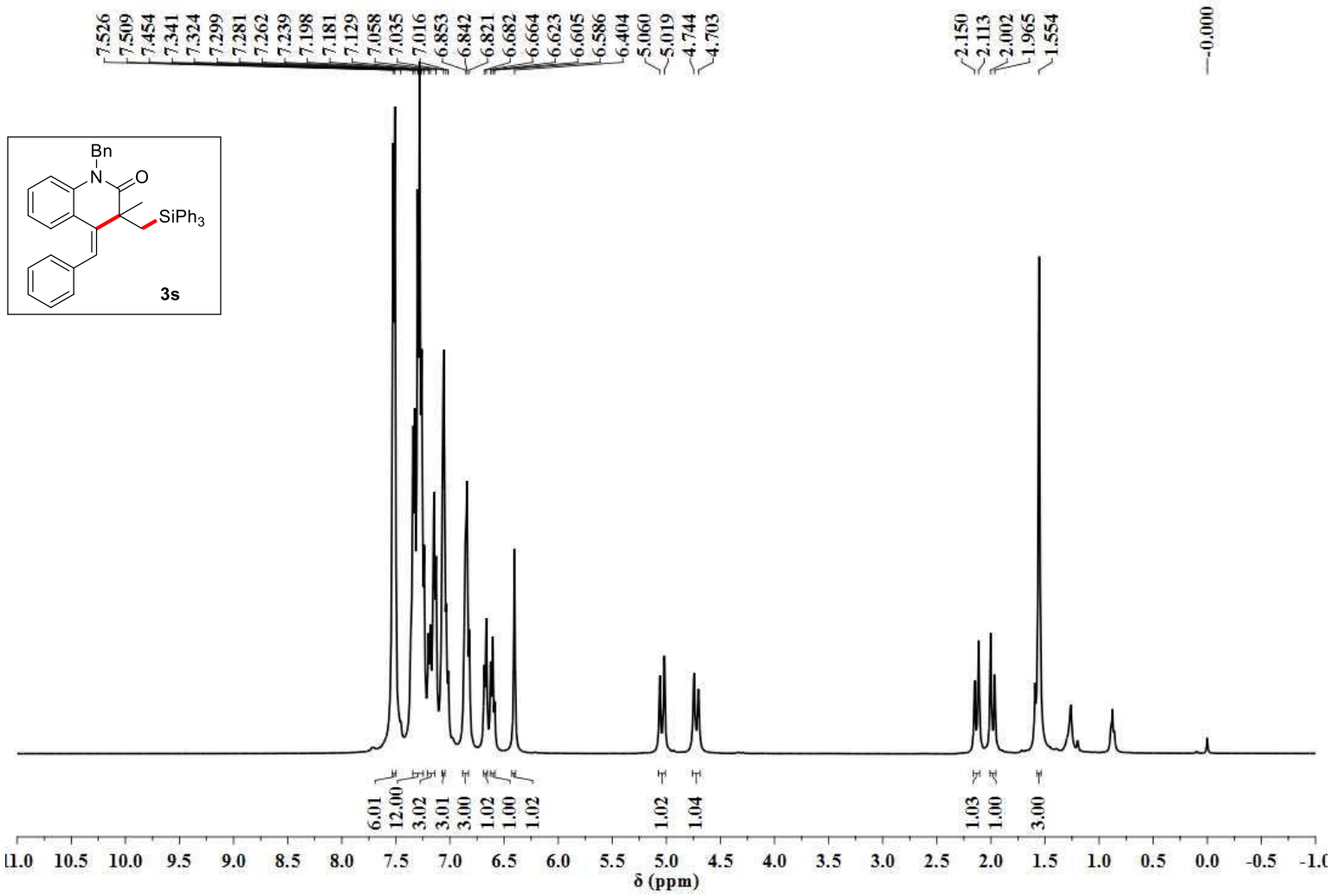
127.984
127.760
125.080
122.266
114.372
77.484
77.230
76.976
47.246
30.195
24.903
22.980
11.655
8.516
7.859
N
O
SiPh3
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)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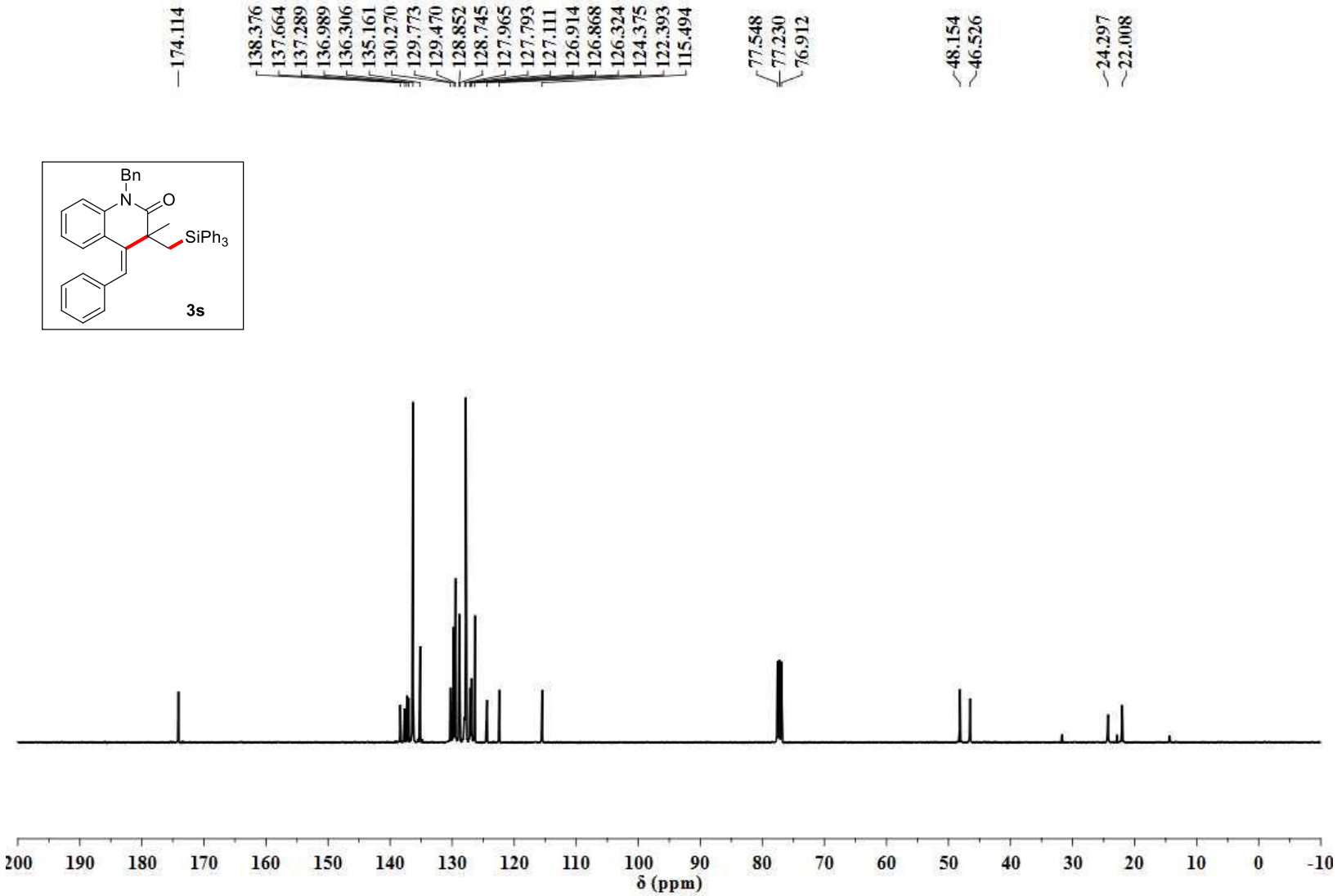
7.262
7.239
7.198
7.181
7.129
7.058
7.035
7.016
6.853
6.842
6.821
6.682
6.664
6.623
6.605
6.586
6.404
5.060
5.019
4.744
4.703
2.150
2.113
2.002
1.965
1.554
-0.000
Bn
N
O
SiPh3
3s
6.01
12.00
3.02
3.01
3.00
1.02
1.00
1.02
1.02
1.04
1.03
1.00
3.00
δ (ppm)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128.745
127.965
127.793
127.111
126.914
126.868
126.324
124.375
122.393
115.494
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77.230
76.912
48.154
46.526
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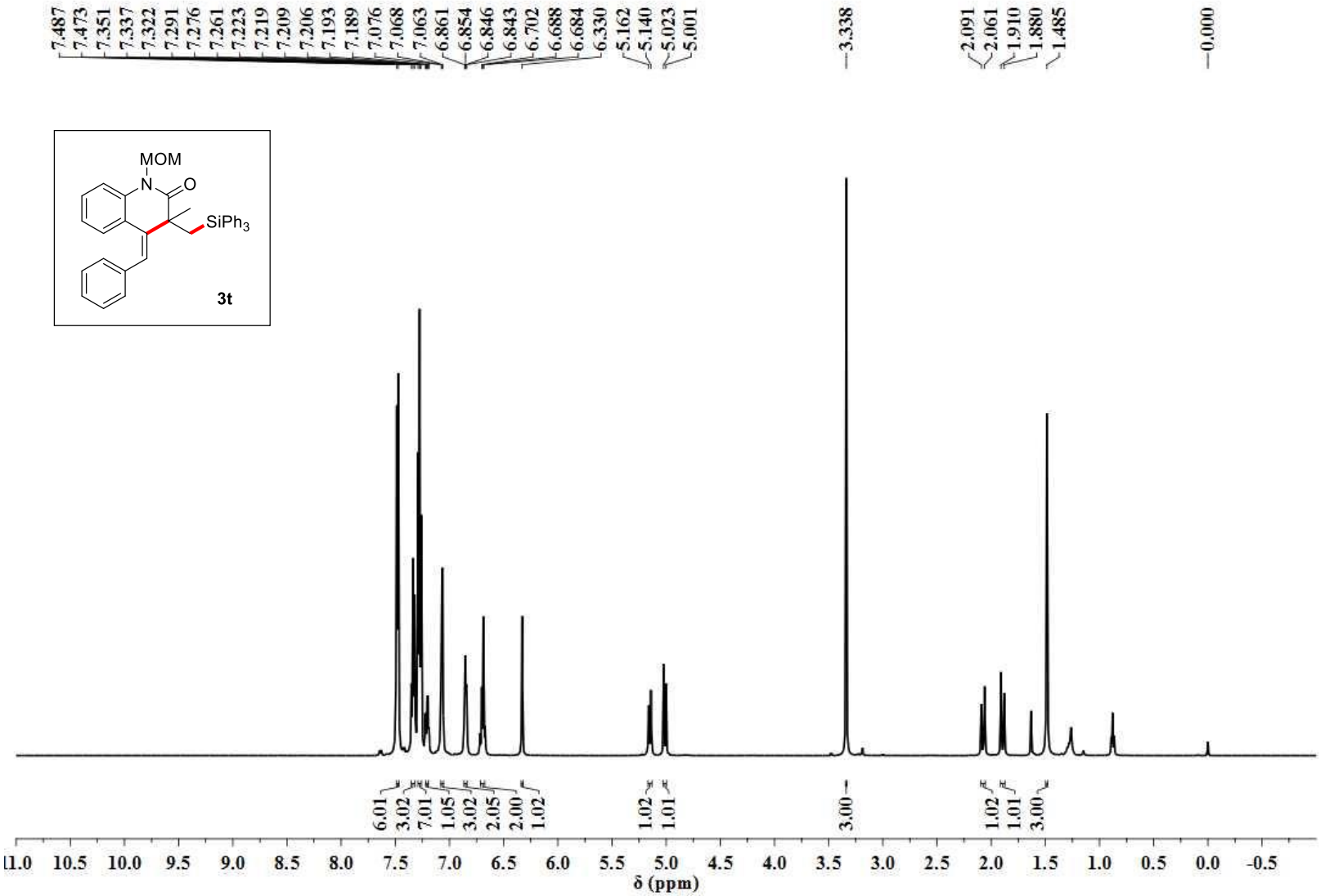
22.008
Bn
N
O
SiPh3
3s
δ (ppm)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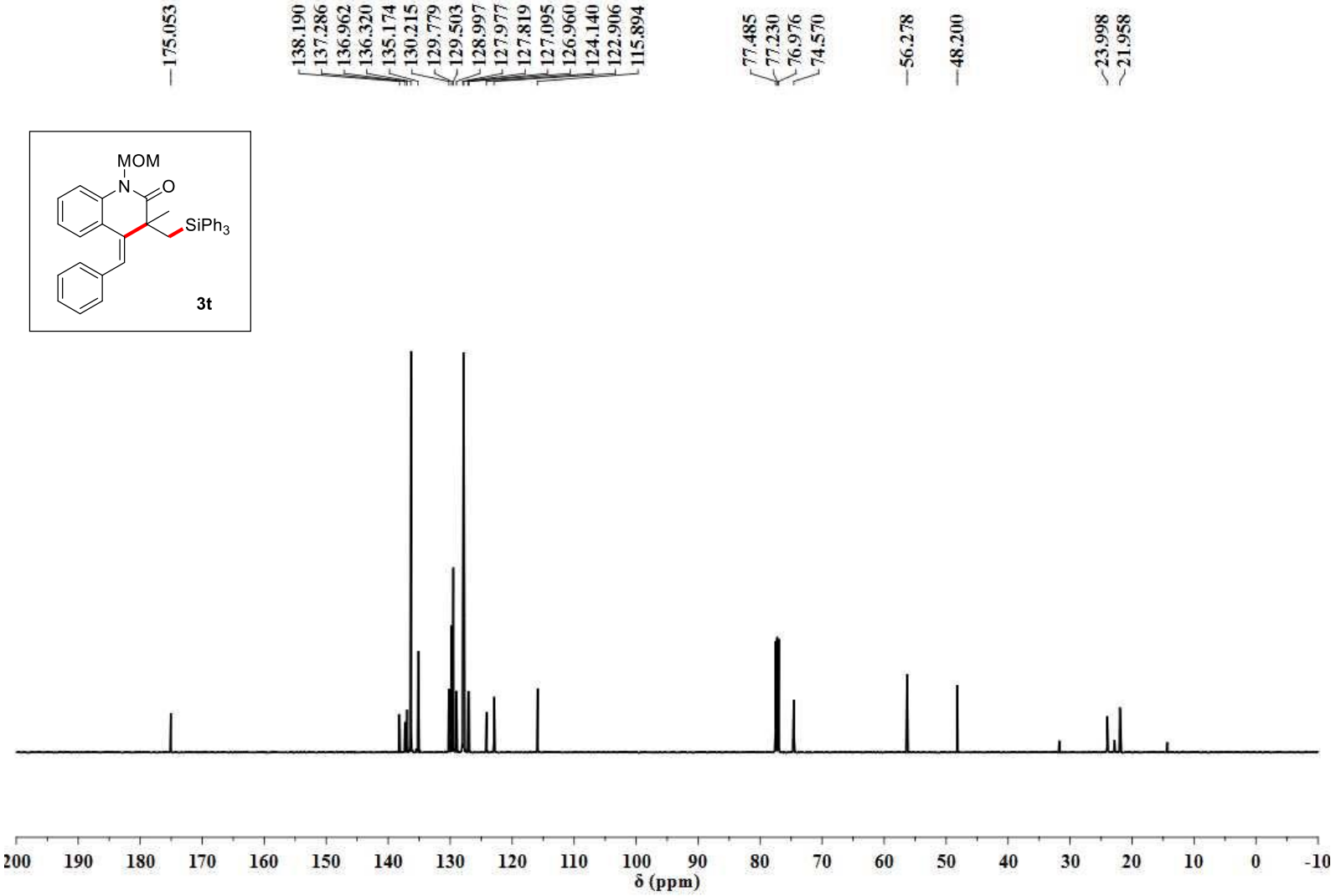
7.276
7.261
7.223
7.219
7.209
7.206
7.193
7.189
7.076
7.068
7.063
6.861
6.854
6.846
6.843
6.702
6.688
6.684
6.330
5.162
5.140
5.023
5.001
3.338
2.091
2.061
1.910
1.880
1.485
0.000
MOM
N
O
SiPh3
3t
6.01
3.02
7.01
1.05
3.02
2.05
2.00
1.02
1.02
1.01
3.00
1.02
1.01
3.00
δ (ppm)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137.286
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130.215
129.779
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128.997
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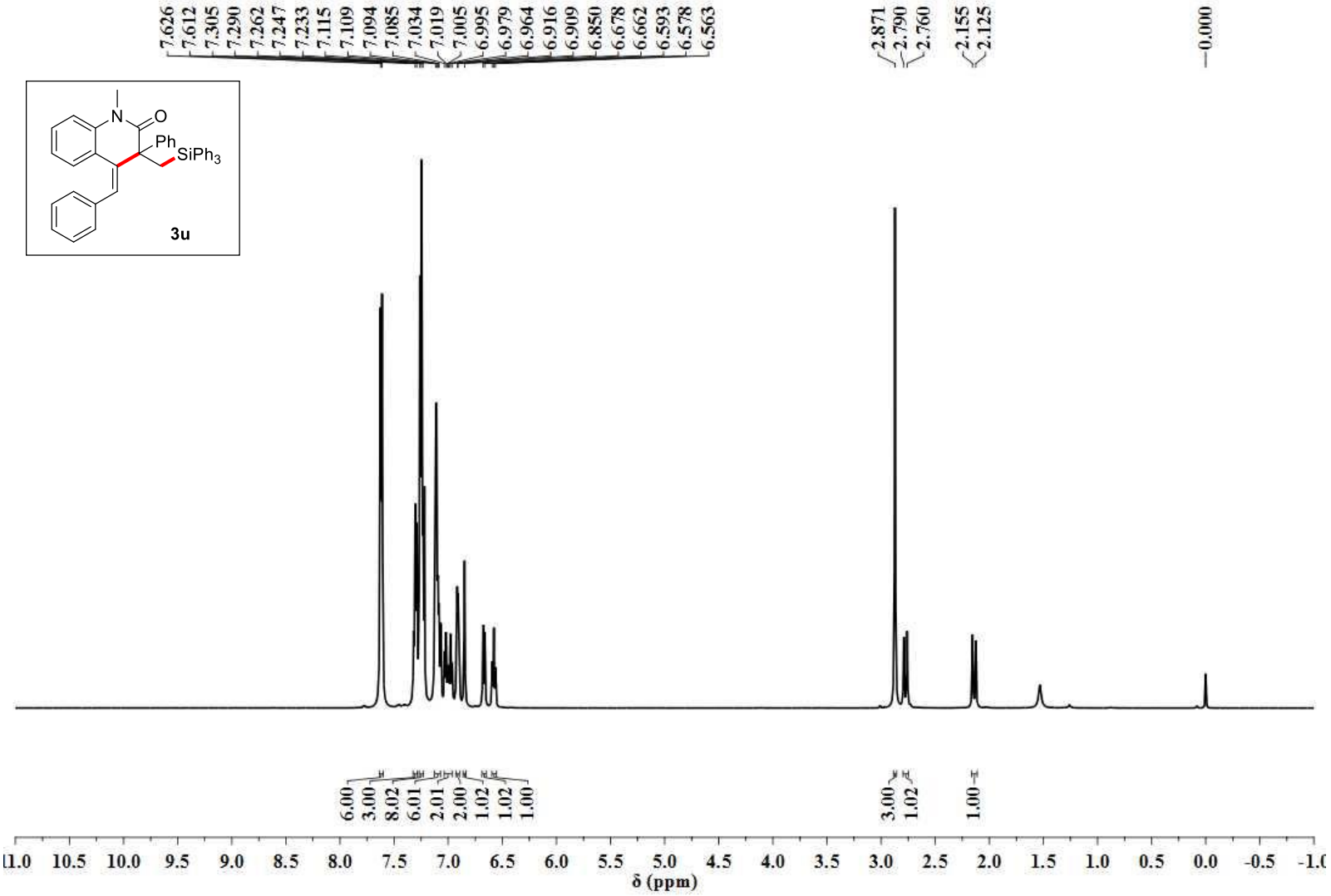
127.819
127.095
126.960
124.140
122.906
115.894
77.485
77.230
76.976
74.570
56.278
48.200
23.998
21.958
MOM
N
O
SiPh3
3t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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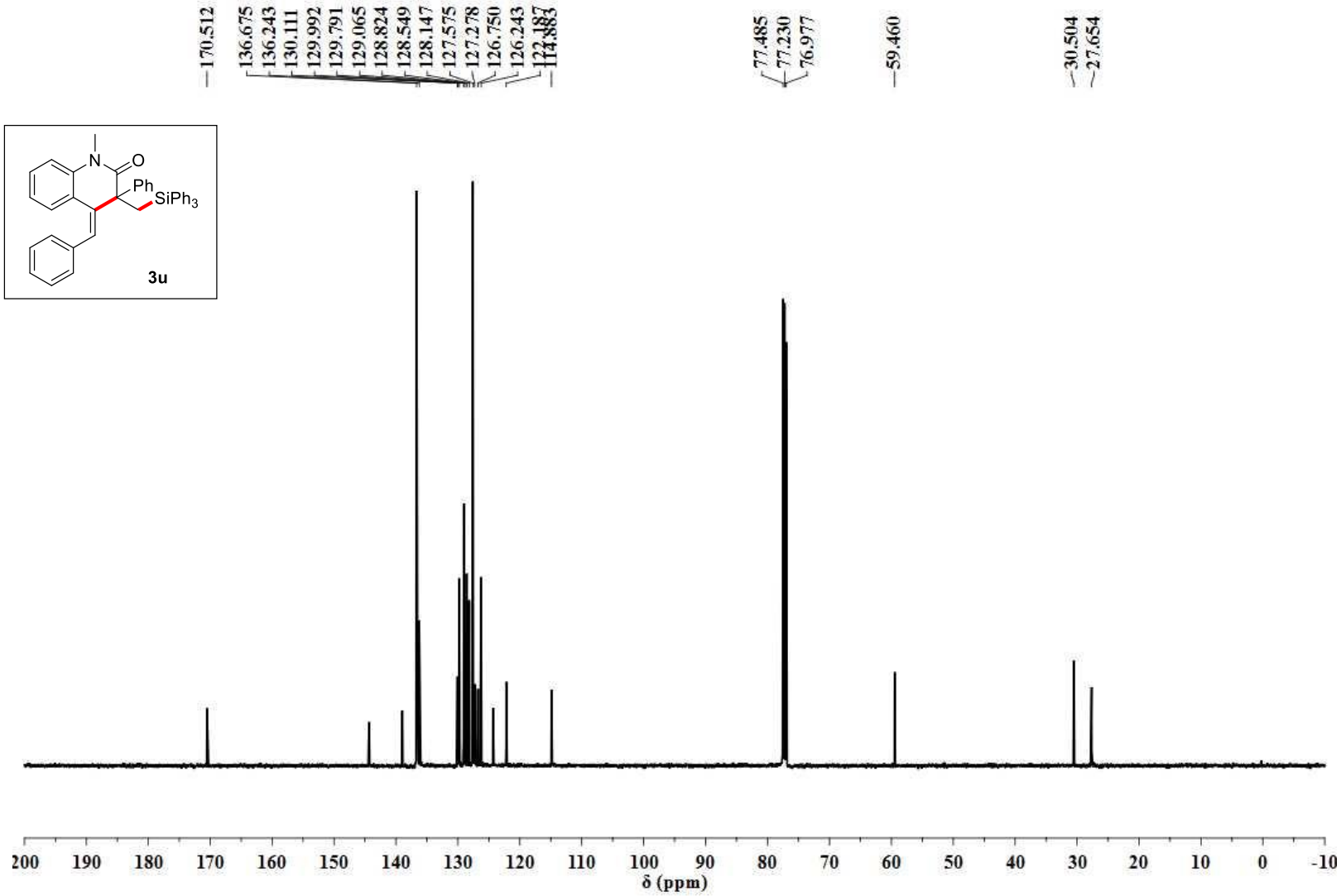
7.290
7.262
7.247
7.233
7.115
7.109
7.094
7.085
7.034
7.019
7.005
6.995
6.979
6.964
6.916
6.909
6.850
6.678
6.662
6.593
6.578
6.563
2.871
2.790
2.760
2.155
2.125
0.000
N
O
Ph
SiPh3
3u
6.00
3.00
8.02
6.01
2.01
2.00
1.02
1.02
1.00
3.00
1.02
1.00
δ (ppm)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136.675
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129.992
129.791
129.065
128.824
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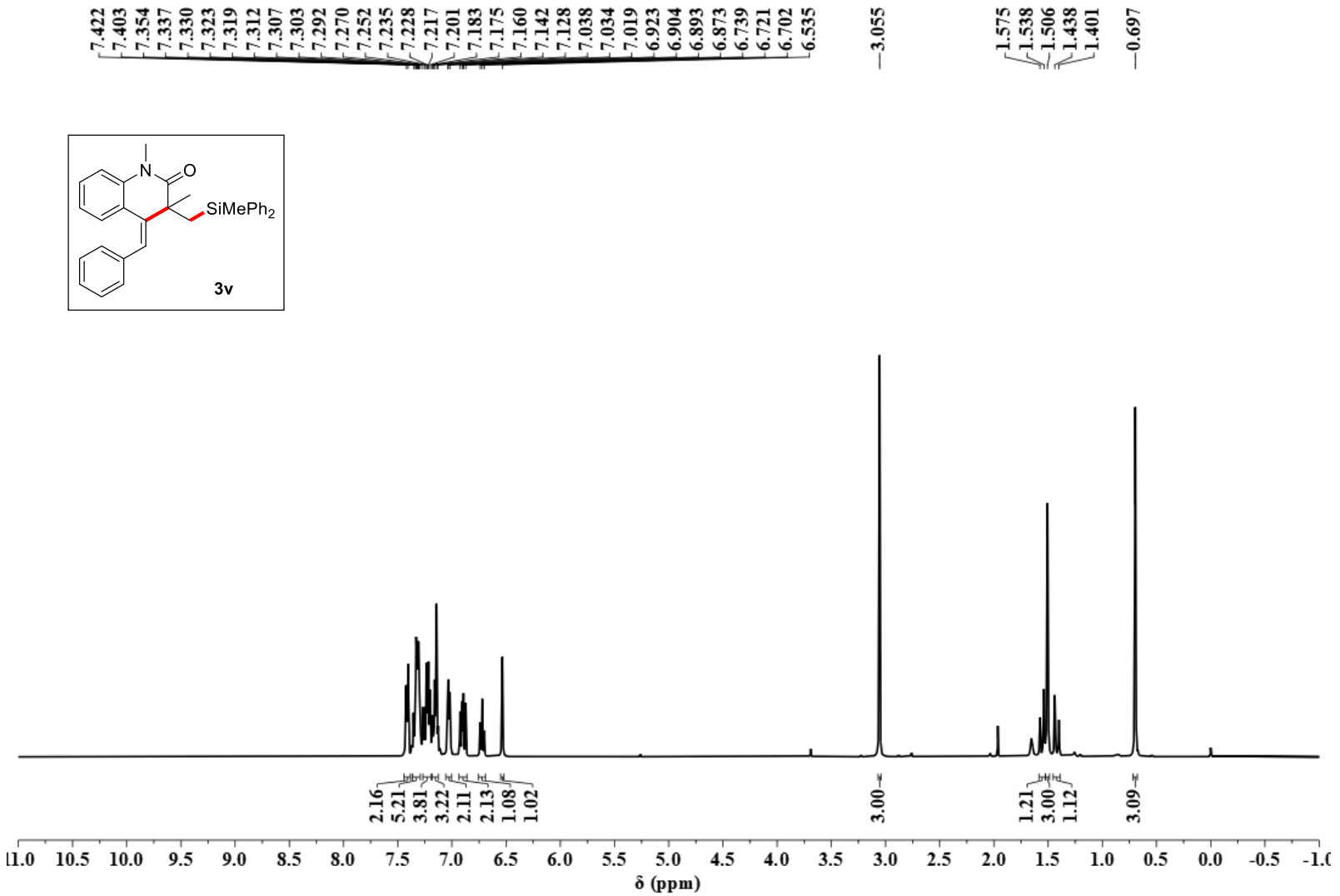
128.147
127.575
127.278
126.750
126.243
77.485
77.230
76.977
59.460
30.504
27.654
Ph
SiPh3
3u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.323
7.319
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7.303
7.292
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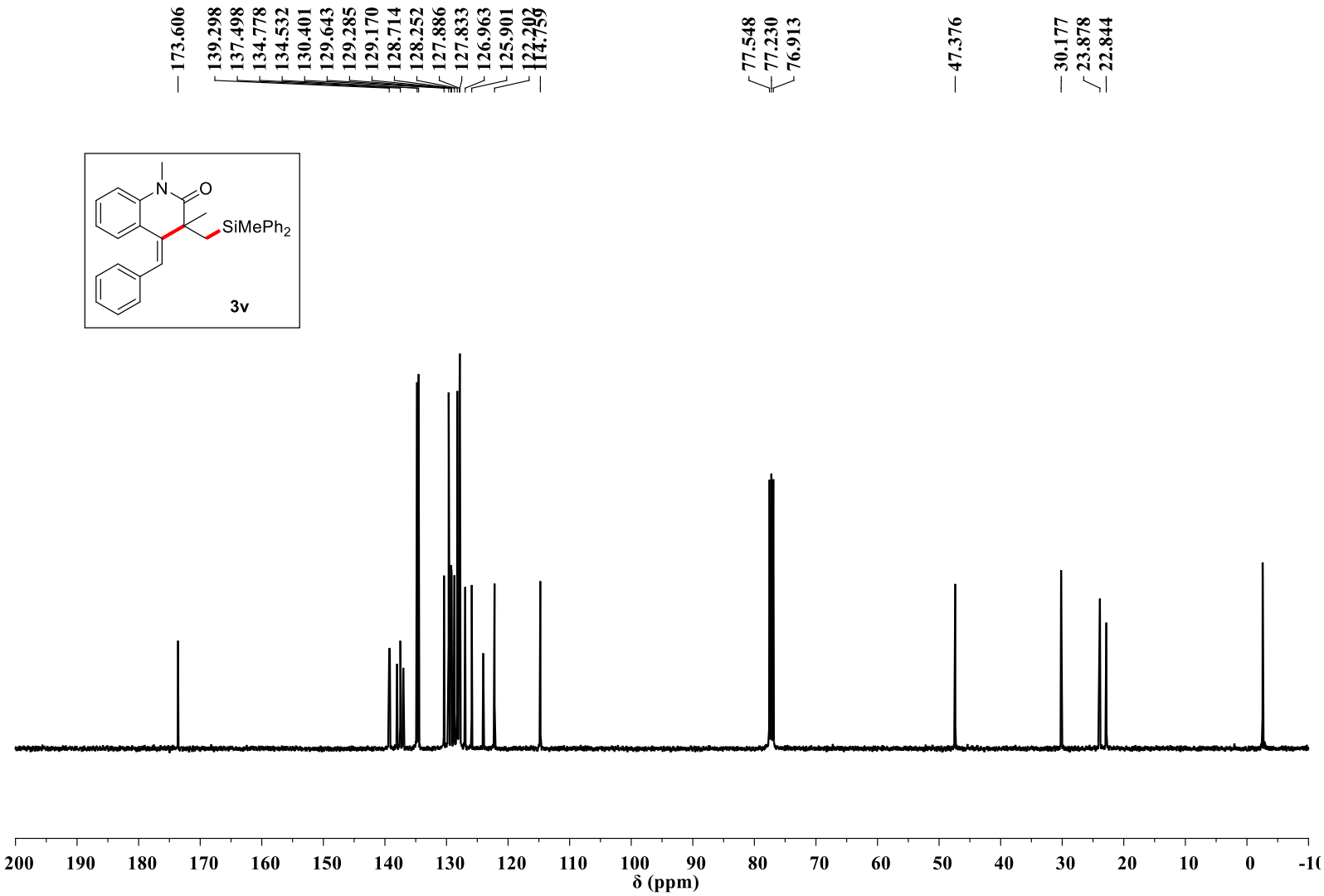
7.252
7.235
7.228
7.217
7.201
7.183
7.175
7.160
7.142
7.128
7.038
7.034
7.019
6.923
6.904
6.893
6.873
6.739
6.721
6.702
6.535
3.055
1.575
1.538
1.506
1.438
1.401
0.697
N
O
SiMePh2
3v
2.16
5.21
3.81
3.22
2.11
2.13
1.08
1.02
3.00
1.21
3.00
1.12
3.09
δ (ppm)


173.606
139.298
137.498
134.778
134.532
130.401
129.643
129.285
129.170
128.714
128.252
127.886
127.833
126.963
125.901
77.548
77.230
76.913
47.376
30.177
23.878
22.844
SiMePh2
3v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)