Visible Light-Promoted Radical Cyclization of Silicon-Tethered Alkyl Iodide and Phenyl Alkyne. An Efficient Approach to Synthesize Benzosilolines

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Supporting Information

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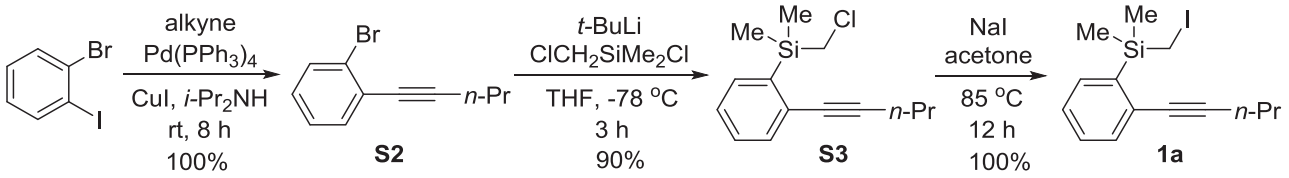
1. General Methods

Commercial reagents were used without any purification. $Ru(bpy)_3Cl_2•6H_2O$ was purchased from J&K Scientific. All reactions were performed using common anhydrous, inert atmosphere techniques. Reactions were monitored by TLC which was performed on glass-backed silica plates and visualized using UV, $KMnO_4$ stains, $H_3PO_4·12MoO_3$/EtOH stains, H_2SO_4(conc.)/anisaldehyde/ EtOH stains. Column chromatography was performed using silica gel (200-300 mesh) eluting with EtOAc/petroleum ether. ^1H NMR spectra were recorded at 400 MHz (Varian) and 600 MHz (Agilent), and ^{13}C NMR spectra were recorded at 100 MHz (Varian) and 150 MHz (Agilent) using $CDCl_3$ (except where noted) with TMS or residual solvent as standard. Infrared spectra were obtained using KCl plates on a VECTOR22. High-resolution mass spectral analyses performed on Waters Q-TOF. CH_3CN, DMSO, DMF, CH_2Cl_2, TMEDA and Et_3N were distilled from CaH_2. Et_2O and THF were distilled from sodium. All spectral data obtained for new compounds are reported here.

2. Experimental Procedures and Spectral Data of Products

2.1. General Procedure to Synthesize 1a-1t



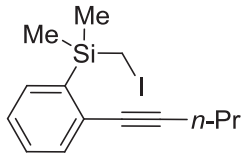
To a solution of 1-bromo-2-iodobenzene (1.0 g, 3.53 mmol) in *i*-Pr_2NH (15 mL) was added CuI (27 mg, 0.14 mmol), $Pd(PPh_3)_4$ (87 mg, 0.07 mmol). The solution was degassed by three freeze-pump-thaw cycles followed by adding 1-pentyne (365 μL, 3.71 mmol) dropwise. The resulting mixture was stirred at room temperature until the starting material was completely consumed (monitored by TLC analysis). The reaction mixture was filtered by Celite and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (eluent: petroleum ether) afforded 1-bromo-2-alkynylbenzene **S2** as a colorless liquid (787 mg, quantitative).

To a solution of **S2** (787 mg, 3.53 mmol) in dry THF (10 mL) in a flame-dried flask under Ar

atmosphere was added *t*-BuLi (5.5 mL of 1.3 M solution in pentane, 7.15 mmol) dropwise at -78 °C. After stirring for 40 min, $ClCH_2SiMe_2Cl$ (0.56 mL, 4.24mmol) was added dropwise. The reaction mixture was then stirred for 3h at –78 °C before quenched with sat. NH_4Cl (8 mL). The mixture was extracted with Et_2O (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: petroleum ether) afforded **S3** as a colorless liquid (798 mg, 90% yield).

To a solution of **S3** (798 mg, 3.18 mmol) in dry acetone (8 mL) was added dry NaI (1.43 g, 9.54 mmol). The reaction mixture was refluxed at 85°C overnight. The reaction allowed to cool to room temperature before quenching with saturated solution of $Na_2S_2O_3$ (10 mL).The aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel flash column chromatography afforded (eluent: petroleum ether) afforded **1a** as a colorless liquid (1.08 g, quantitative).

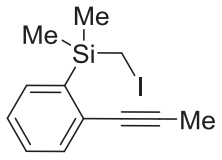
Preparation of 1a



1a

1a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.42 (d, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.31 (dt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.26 (dt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 2.43 (s, 2H), 2.41 (t, J = 7.2 Hz, 2H), 1.65 (tq, J_1 = 7.2 Hz, J_2 = 7.2 Hz, 2H), 1.06 (t, J = 7.2 Hz, 3H), 0.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 134.2, 132.6, 129.3, 129.2, 126.9, 93.7, 81.9, 22.1, 21.6, 13.8, -2.6, -13.2; IR (neat) cm^{-1} 2962s, 2934m, 2901m, 2873m, 2196w, 1462m, 1430m, 1374m, 1251s, 1126m, 1076m, 819s; HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{19}INaSi$ $(M+Na)^+$: 365.0193, found 365.0197.

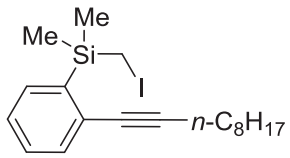
Preparation of 1b



1b

1b: Using the same procedure as that used for **1a** afforded **1b** as a colorless liquid (238 mg, 62% overall yield from **S2-1b**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.41 (d, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.31 (dt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.26 (dt, J_1 = 7.2 Hz, J_2 = 1.6 Hz,1H), 2.41 (s, 2H), 2.07 (s, 3H), 0.50 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5, 134.3, 132.3, 129.3, 129.2, 126.9, 89.3, 81.1, 4.4, -2.6, -13.3; IR (neat) cm^{-1} 3050w, 2958w, 2910w, 1583w, 1431w, 1373w, 1251m, 1127w, 1078w, 819m, 797m, 721m; HRMS (ESI-TOF, m/z) calcd for $C_{12}H_{16}ISi$ $(M+H)^+$: 315.0060, found 315.0054.

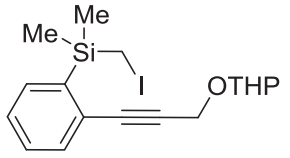
Preparation of 1c



1c

1c: Using the same procedure as that used for **1a** afforded **1c** as a colorless liquid (365 mg, 50% overall yield from 1-bromo-2-iodobenzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.41 (d, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.30 (dt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.25 (dt, J_1 = 7.2 Hz, J_2 = 1.6 Hz,1H), 2.43 (s, 2H), 2.40-2.44 (m, 2H), 1.58-1.63 (m, 2H), 1.43-1.46 (m, 2H), 1.28-1.31 (m, 8H), 0.89 (t, J = 7.2 Hz, 3H), 0.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 134.2, 132.6, 129.4, 129.3, 126.9, 93.9, 81.8, 31.8, 29.2, 29.2, 28.6, 22.6, 19.6, 14.1, -2.6, -13.2; IR (neat) cm^{-1} 2956s, 2928s, 2855s, 1462m, 1430m, 1372m, 1254s, 1093s, 1064s, 838s, 803s, 759m; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{29}INaSi$ $(M+Na)^+$: 435.0975, found 435.0994.

Preparation of 1d

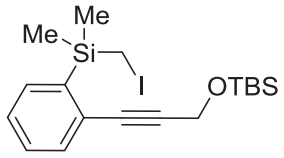


1d

1d: Using the same procedure as that used for **1a** afforded **1d** as a colorless liquid (163 mg, 59% overall yield from **S2-1d**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.50 (m, 2H), 7.29-7.36 (m, *2*H), 4.88 (t, J= 3.2 Hz, 1H), 4.54 (d, J= 16.0 Hz, 1H), 4.47 (d, J= 16.0 Hz, 1H), 3.86-3.92 (m, 1H), 3.56-3,59 (m, 1H), 2.44 (s, 2H), 1.70-1.87 (m, 2H), 1.55-1.69 (m, 4H), 0.52 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1, 134.4, 132.8, 129.4, 127.8, 127.7, 97.0, 96.9, 88.5, 86.9, 62.1, 54.7, 30.3,

25.4, 19.1, 1.0, -2.6, -13.5; IR (neat) cm^{-1} 2958s, 2872s, 2222m, 2184m, 1715m, 1660m, 1460s, 1437s, 1348m, 1257s, 1180m, 1125s, 1026s, 870s, 762s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{23}NaO_2Si$ $(M+Na)^+$: 437.0404, found 437.0405.

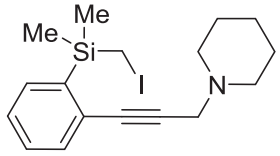
Preparation of 1e



1e

1e: Using the same procedure as that used for **1a** afforded **1e** as a colorless liquid (183 mg, 64% overall yield from **S2-1e**). ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, J = 7.2 Hz, 1H), 7.45 (d, J = 7.2 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 4.55 (s, 2H), 2.43 (s, 2H), 0.94 (s, 9H), 0.52 (s, 6H), 0.17 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.0, 134.4, 132.6, 129.3, 128.0, 127.6, 91.0, 85.8, 52.2, 25.8, 18.3, -2.5, -5.1, -13.4; IR (neat) cm^{-1} 2955s, 2932s, 2892s, 2857s, 2221m, 2185m, 1692m, 1661m, 1466m, 1369m, 1255m, 1084m, 837m, 764m; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{29}INaOSi_2$ $(M+Na)^+$: 467.0694, found 467.0690.

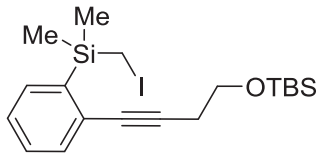
Preparation of 1f



1f

1f: Using the same procedure as that used for **1a** afforded **1f** as a colorless liquid (162 mg, 43% overall yield from **S2-1f**). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.48 (m, 2H), 7.26-7.34 (m, 2H), 3.52 (s, 2H), 2.57 (brs, 2H), 2.42 (s, 2H), 1.62-1.67 (m, 4H), 1.42-1.48 (m, 2H), 0.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 134.3, 133.1, 129.4, 128.4, 127.4, 88.7, 86.1, 53.5, 48.6, 25.9, 23.9, -2.6, -13.3; IR (neat) cm^{-1} 2934s, 2854s, 2753s, 2679m, 1461m, 1431m, 1338m, 1252m, 1110m, 1075m, 999m, 835s, 819s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{25}INSi$ $(M+H)^+$: 398.0795, found 398.0800.

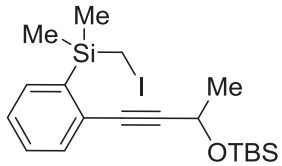
Preparation of 1g



1g

1g: Using the same procedure as that used for **1a** afforded **1g** as a colorless liquid (185 mg, 61% overall yield from **S2-1g**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 3.85 (t, *J* = 7.2 Hz, 2H), 2.66 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 2H), 0.93 (s, 9H), 0.52 (s, 6H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 134.3, 132.5, 129.3, 128.9, 127.0, 90.5, 82.9, 61.7, 25.9, 24.0, 18.3, -2.6, -5.2, -13.3; IR (neat) cm^{-1} 2954s, 2931s, 2895s, 2858s, 1466m, 1432m, 1383m, 1254s, 1106s, 838s, 763s; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{31}INaOSi_2$ $(M+Na)^+$: 481.0850, found 481.0856.

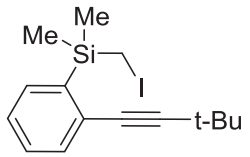
Preparation of 1h



1h

1h: Using the same procedure as that used for **1a** afforded **1h** as a colorless liquid (262 mg, 83% overall yield from **S2-1h**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 4.77 (q, *J* = 6.4 Hz, 1H), 2.45 (s, 2H), 1.53 (d, *J* = 6.4 Hz, 3H), 0.95 (s, 9H), 0.53 (s, 6H), 0.18 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 134.3, 132.6, 129.3, 128.1, 127.5, 94.9, 84.3, 59.4, 25.8, 25.3, 18.2, -2.6, -4.5, -4.9, -13.4; IR (neat) cm^{-1} 2955s, 2931s, 2890s, 2857s, 1465m, 1435m, 1368m, 1253s, 1101s, 1053m, 976s, 833s, 759m; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{31}IKOSi_2$ $(M+K)^+$: 497.0590, found 497.0594.

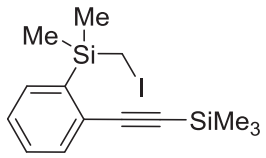
Preparation of 1i



1i

1i: Using the same procedure as that used for **1a** afforded **1i** as a colorless liquid (227 mg, 71% overall yield from **S2-1i**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.41 (d, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.30 (dt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.24 (dt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 2.46 (s, 2H), 1.34 (s, 9H), 0.52 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2, 134.2, 132.7, 129.3, 129.2, 126.9, 101.5, 80.6, 30.8, 28.1, -2.7, -13.1; IR (neat) cm^{-1} 2967s, 2901m, 2867m, 1461m, 1431m, 1367m, 1287m, 1251m, 1126m, 1070m, 817s, 759s; HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{21}INaSi$ $(M+Na)^+$: 379.0349, found 379.0356.

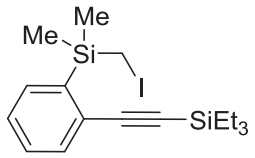
Preparation of 1j



1j

1j: Using the same procedure as that used for **1a** afforded **1j** as a colorless liquid (776 mg, 60% overall yield from 1-bromo-2-iodobenzene). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, J = 7.2 Hz, 1H), 7.47 (d, J = 7.2 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 2.46 (s, 2H), 0.52 (s, 6H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 134.3, 132.9, 129.3, 128.2, 127.8, 106.3, 97.7, -0.2, -2.8, -13.5; IR (neat) cm^{-1} 2959s, 2899m, 2155s, 1461m, 1428m, 1253s, 1125m, 1092m, 1067s, 865s, 803s, 760s; HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{21}INaSi_2$ $(M+Na)^+$: 395.0119, found 395.0117.

Preparation of 1k

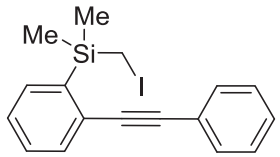


1k

1k: Using the same procedure as that used for **1a** afforded **1k** as a colorless liquid (400 mg, 55% overall yield from 1-bromo-2-iodobenzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.2 Hz, 1H), 7.48 (d, J = 7.2 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 2.02 (s, 2H), 1.06 (t, J = 7.6 Hz, 9H), 0.71 (t, J = 7.6 Hz, 6H), 0.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 134.3, 133.6, 129.3, 128.4, 127.7, 107.3, 95.6, 7.5, 4.3, -2.7, -13.4; IR (neat) cm^{-1} 2956s, 2909m, 2877m,

2151m, 1461m, 1416m, 1373m, 1256s, 1094s, 1065s, 838s, 803s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{28}ISi_2$ $(M+H)^+$: 415.0769, found 415.0764.

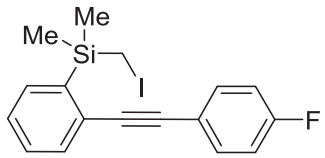
Preparation of 1l



1l

1l: Using the same procedure as that used for **1a** afforded **1l** as a colorless liquid (1.22 g, 92% overall yield from 1-bromo-2-iodobenzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.58 (m, 4H), 7.32-7.40 (m, 5H), 2.50 (s, 2H), 0.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 134.4, 132.6, 131.3, 129.5, 128.5, 128.4, 128.3, 127.6, 122.9, 92.5, 90.6, -2.5, -13.4; IR (neat) cm^{-1} 3053m, 2958m, 1597m, 1492m, 1436m, 1254s, 1124m, 1070m, 816s, 757s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{17}INaSi$ $(M+Na)^+$: 399.0036, found 399.0036.

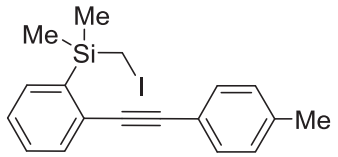
Preparation of 1m



1m

1m: Using the same procedure as that used for **1a** afforded **1m** as a colorless liquid (315 mg, 67% overall yield from 1-bromo-2-iodobenzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.56 (m, 4H), 7.31-7.40 (m, 3H), 7.07 (t, J = 8.4 Hz, 2H), 2.47 (s, 2H), 0.57 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.6 (d, J = 248.8 Hz), 138.8, 134.5, 133.2 (d, J = 8.2 Hz), 132.6, 129.5, 128.2, 127.7, 119.1(d, J = 3.5 Hz), 115.9 (d, J = 21.9 Hz), 91.5, 90.3, -2.5, -13.5; IR (neat) cm^{-1} 3052m, 2959m, 1597s, 1507s, 1465m, 1431m, 1252s, 1130s, 1155m, 1124m, 833s, 759s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{16}FIKSi$ $(M+K)^+$: 432.9682, found 432.9681.

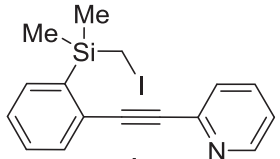
Preparation of 1n



1n

1n: Using the same procedure as that used for **1a** afforded **1n** as a colorless liquid (468 mg, 84% overall yield from 1-bromo-2-iodobenzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.54 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.39 (dt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.33 (dt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.20 (d, J = 7.2 Hz, 1H), 2.51 (s, 2H), 2.38 (s, 3H), 0.59 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.69, 138.68, 134.4, 132.5, 131.2, 129.5, 129.3, 128.6, 127.4, 119.9, 92.7, 90.0, 21.5, -2.6, -13.3; IR (neat) cm^{-1} 3050m, 2958m, 2922m, 1581m, 1510s, 1460m, 1431m, 1253s, 1123s, 817s, 759s; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{19}IKSi$ $(M+K)^+$: 428.9932, found 428.9925.

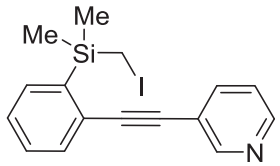
Preparation of 1o



1o

1o: Using the same procedure as that used for **1a** afforded **1o** as a colorless liquid (487 mg, 73% overall yield from 1-bromo-2-iodobenzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 4.8 Hz, 1H), 7.70 (dt, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.67 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.55 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.40 (dt, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.36 (dt, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.26 (t, J = 7.2 Hz, 1H), 2.52 (s, 2H), 0.59 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 143.2, 139.5, 136.2, 134.4, 133.2, 129.4, 128.2, 127.2, 126.8, 122.8, 91.6, 90.2, -2.5, -13.4; IR (neat) cm^{-1} 3000m, 2217m, 1582m, 1562m, 1467m, 1429m, 1253m, 1126m, 760m; HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{16}INNaSi$ $(M+Na)^+$: 399.9989, found 399.9993.

Preparation of 1p

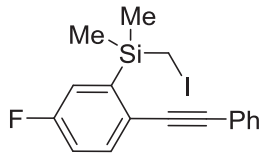


1p

1p: Using the same procedure as that used for **1a** afforded **1d** as a colorless liquid (140 mg, 21% overall yield from 1-bromo-2-iodobenzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.57 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.81 (td, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.55 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.40 (dt, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.36 (dt, J_1 = 1.6 Hz, J_2 =

7.2 Hz, 1H), 7.31 (dd, J_1 = 4.8 Hz, J_2 = 7.2 Hz, 1H), 2.45 (s, 2H), 0.57 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 148.7, 139.1, 138.2, 134.5, 132.8, 129.5, 128.1, 127.5, 123.2, 120.2, 93.9, 88.9, -2.5, -13.8; IR (neat) cm^{-1} 3050s, 2959s, 2215m, 1581m, 1560m, 1479s, 1407m, 1254s, 1125m, 1071m, 804m; HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{16}INNaSi$ $(M+Na)^+$: 399.9989, found 399.9990.

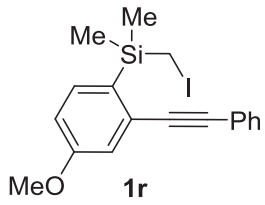
Preparation of 1q



1q

1q: Using the same procedure as that used for **1a** afforded **1q** as a colorless liquid (320 mg, 82% overall yield from 2-bromo-4-fluoro-1-iodobenzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J_1 = 5.6 Hz, J_2 = 8.4 Hz, 1H), 7.50-7.52 (m, 2H), 7.37-7.38 (m, 3H), 7.21 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7. 06 (dt, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 2.47 (s, 2H), 0.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, J = 250.9 Hz), 142.2 (d, J = 4.7 Hz), 134.7 (d, J = 7.1 Hz), 131.5, 131.2, 128.54, 128.53, 128.3, 121.3 (d, J = 19.8 Hz), 116.6 (d, J = 22.1 Hz), 92.1, 89.7, -2.7, -14.3; IR (neat) cm^{-1} 3059m, 2959m, 2215m, 1714m, 1587m, 1566m, 1493s, 1465s, 1256s, 1207s, 906m, 832s, 804s, 756s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{16}FIKSi$ $(M+K)^+$: 432.9682, found 432.9681.

Preparation of 1r

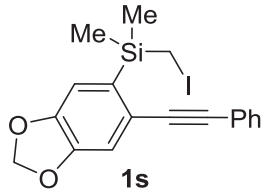


1r

1r: Using the same procedure as that used for **1a** afforded **1r** as a colorless liquid (80 mg, 20% overall yield 4-bromo-3-iodoanisole). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.54 (m, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.37-7.41 (m, 3H), 7.12 (d, J = 2.8 Hz, 1H), 6.90 (dd, J_1 = 2.8 Hz, J_2 = 8.0 Hz, 1H), 3.84 (s, 3H), 2.46 (s, 2H), 0.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 135.9, 131.4, 129.9, 129.7, 128.54, 128.53, 122.9, 117.7, 114.3, 92.2, 90.5, 55.2, 1.0, -2.4, -12.9; IR (neat) cm^{-1} 2958s,

2933s, 1588s, 1553m, 1491m, 1466s, 1404m, 1317m, 1254s, 1223s, 1072s, 1031m, 816s, 756s; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{19}IKOSi$ $(M+K)^+$: 444.9881, found 444.9875.

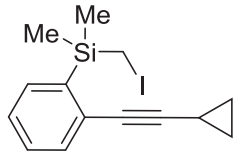
Preparation of 1s



1s

1s: Using the same procedure as that used for **1a** afforded **1d** as a colorless liquid (195 mg, 47% overall yield from 5-bromo-4-iodo-methylenedioxybenzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.50 (m, 2H), 7.32-7.39 (m, 3H), 7.05 (s, 1H), 6.96 (s, 1H), 5.99 (s, 2H), 2.51 (s, 2H), 0.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 147.6, 133.1, 131.1, 128.5, 128.3, 123.1, 122.3, 113.9, 113.0, 91.2, 90.6, -2.4, -13.3; IR (neat) cm^{-1} 2958m, 2897s, 1596s, 1497s, 1474s, 1384m, 1338s, 1232s, 1041s, 935s, 838s, 811s; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{18}IO_2Si$ $(M+H)^+$: 421.0115, found 421.0118.

Preparation of 1t



1t

1t: Using the same procedure as that used for **1a** afforded **1t** as a colorless liquid (288 mg, 71% overall yield from 1-bromo-2-iodobenzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.2 Hz, 1H), 7.40 (d, J = 7.2 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 2.41 (s, 2H), 1.45-1.54 (m, 1H), 0.84-0.92 (m, 2H), 0.80-0.83 (m, 2H), 0.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 134.2, 132.5, 129.4, 129.1, 126.8, 112.5, 96.6, 8.2, 0.3, -2.7, -13.2; IR (neat) cm^{-1} 3008w, 2958w, 2221w, 1462w, 1430w, 1250m, 1127w, 837m, 816m, 758m; HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{17}IKSi$ $(M+K)^+$: 378.9776, found 378.9774.

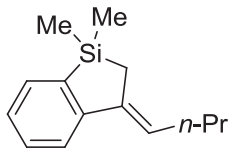
2.2. General Procedure to Synthesize 2 and 3

A flame dried 10 mL borosilicate reaction tube was equipped with a rubber septum and magnetic stir bar and was charged with **1a** (34.2 mg, 0.10 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (1.5 mg, 2.0

μmol), TMEDA (30 μL, 0.20 mmol), DMSO (71 μL, 1.0 mmol) and MeCN (2.0 mL). The mixture was degassed via the freeze-pump-thaw method and $PhSiH_3$ (62 μL, 0.5 mmol) was added via syringe. The reaction mixture was then placed at a distance of ~5 cm from 23 W household compact fluorescent lamp (Philips Tornado 23W CFL) and stirred at room temperature overnight. Upon the reaction was complete (monitored by TLC analysis), the mixture was quenched with water (2.0 mL) and extracted with Et_2O (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated in vacuo. Purification of the crude residue via silica gel flash column chromatography (eluent: petroleum ether) afforded **2a** as a colorless liquid (17.2 mg, *Z:E* ≥ 95:5).

The same procedure as that used for **2a** was employed to synthesize **2b-2k**. The same procedure as that used for **2a** except for without DMSO was employed to synthesize **3a-3h**. Gradient eluent: petroleum ether: EtOAc = 5:1→2:1 for **3d** and **3e**; petroleum ether: EtOAc = 400:1 for **2d**; petroleum ether: EtOAc = 100:1→10:1 for **2f**.

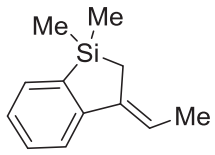
Preparation of 2a



2a

2a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.13 (tt, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 1H), 2.23 (q, *J* = 7.2 Hz, 2H), 1.71 (s, 2H), 1.49 (tq, J_1 = 7.2 Hz, J_2 = 7.2 Hz, 2H), 0.96 (t, *J* =7.2 Hz, 3H), 0.30 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.6, 140.7, 139.7, 132.1, 129.5, 126.6, 124.3, 121.0, 31.7, 22.7, 16.2, 14.0, -1.8; IR (neat) cm^{-1} 3053m, 2960s, 2930s, 2871s, 1678m, 1585m, 1460m, 1440m, 1251s, 1131s, 1030m, 844s, 759s; HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{20}NaSi$ $(M+Na)^+$: 239.1226, found 239.1222.

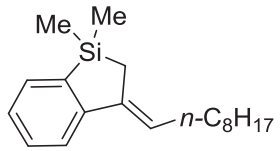
Preparation of 2b



2b

2b: Using the same procedure as that used for **2a** afforded **2b** as a colorless liquid (19 mg, 68% yield, *Z:E* = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.23 (m, 1H, *Z-isomer*), 5.73 (m, 1H, *E-isomer*), 1.98 (s, 2H, *E-isomer*), 1.97 (d, *J* = 6.8 Hz, 2H, *E-isomer*),1.87 (d, *J* = 6.8 Hz, 2H, *Z-isomer*), 1.72 (s, 2H, *Z-isomer*), 0.33 (s, 6H, *Z-isomer*), 0.31 (s, 6H, *E-isomer*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 140.6, 140.5, 132.1, 129.5, 126.5, 120.9, 118.3, 15.8, 15.0, -1.7; IR (neat) cm^{-1} 3054m, 2961s, 2867s, 1679s, 1586w, 1560w, 1442m, 1251s, 1133s, 1065m, 845s, 827s, 760s; HRMS (ESI-TOF, m/z) calcd for $C_{12}H_{16}NaSi$ $(M+Na)^+$: 211.0913, found 211.0914.

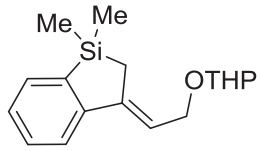
Preparation of 2c



2c

2c: Using the same procedure as that used for **2a** afforded **2c** as a colorless liquid (32 mg, 55% yield, *Z:E* = 86:14). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.12 (t, *J* = 7.2Hz, 1H, *Z-isomer*), 5.58 (t, *J* = 7.2Hz, 1H, *E-isomer*), 2.35-2.40 (m, 2H, *E-isomer*), 2.23-2.27 (m, 2H, *Z-isomer*), 1.87 (s, 2H, *E-isomer*), 1.70 (s, 2H, *Z-isomer*), 1.46-1.47 (m, 2H), 1.28-1.36 (m, 10H), 0.88 (t, *J* =7.2Hz, 3H), 0.30 (s, 6H, *Z-isomer*), 0.28 (s, 6H, *E-isomer*); *Z-isomer* ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 140.6, 139.5, 132.1, 129.5, 126.6, 124.6, 121.0, 31.9, 29.6, 29.5, 29.4, 29.3, 22.7, 16.2, 14.1, -1.8, -2.8; IR (neat) cm^{-1} 3053m, 2955s, 2925s, 2855s, 1680s, 1560m, 1461s, 1441s, 1251s, 1131s, 1062m, 843s, 765s; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{30}KSi$ $(M+K)^+$: 325.1748, found 325.1760.

Preparation of 2d

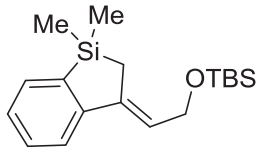


2d

2d: Using the same procedure as that used for **2a** afforded **2d** as a colorless liquid (19 mg, 65% yield, *Z:E* = 83:17) as colorless liquid. ***Z-isomer*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.24-6.28 (m, 1H),

4.70 (dd, J_1 = 4.0 Hz, J_2 = 3.2 Hz, 1H), 4.49 (dd, J_1 = 6.4 Hz, J_2 = 12.4 Hz, 1H), 4.33 (dd, J_1 = 6.4 Hz, J_2 = 3.2 Hz, 1H), 3.92-3.96 (m, 1H), 3.51-3.55 (m, 1H), 1.82-1.89 (m, 1H), 1.78 (s, 2H), 1.72-1.77 (m, 1H), 1.55-1.65 (m, 4H), 0.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 143.2, 141.2, 132.1, 129.6, 127.4, 121.7, 119.7, 97.9, 65.1, 62.4, 30.8, 25.5, 19.6, 16.4, -1.7, -1.8; IR (neat) cm^{-1} 3442brm, 3053m, 2947s, 2871s, 1727m, 1680m, 1441m, 1354m, 1253m, 1133m, 1028m, 828m; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{24}NaO_2Si$ $(M+Na)^+$: 311.1438, found 311.1441.

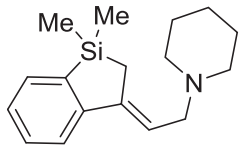
Preparation of 2e



2e

2e: Using the same procedure as that used for **2a** afforded **2e** as a colorless liquid (22 mg, 71% yield, *Z:E* = 80:20). ***Z-isomer*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.20-6.23 (m, 1H), 4.46 (d, *J* = 6.4 Hz, 2H), 1.69 (s, 2H), 0.93 (s, 9H), 0.31 (s, 6H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 140.9, 140.2, 132.1, 129.6, 127.2, 123.6, 121.6, 61.9, 26.0, 18.4, 16.3, -1.8, -5.0; IR (neat) cm^{-1} 2955s, 2927s, 2855s, 1734m, 1650m, 1464m, 1254s, 1086s, 837s; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{30}NaOSi_2$ $(M+Na)^+$: 341.1727, found 341.1728.

Preparation of 2f

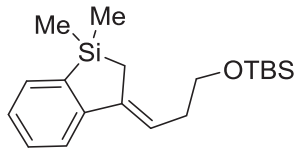


2f

2f: Using the same procedure as that used for **2a** afforded **2f** as a colorless liquid (41mg, 76% yield, *Z:E* = 90:10) as colorless liquid. ***Z-isomer*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.24 (tt, J_1 = 2.0 Hz, J_2 = 6.8 Hz, 1H), 3.22 (d, *J* = 6.8 Hz, 2H), 2.47 (brs, 4H), 1.73 (s, 2H), 1.59-1.64 (m, 4H), 1.45-1.64 (m, 2H), 0.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 142.2, 140.8, 132.0, 129.6, 127.0, 121.5, 120.6, 58.3, 54.6, 25.9, 24.3, 16.7 -1.8; IR (neat) cm^{-1} 2933s, 2854s, 2795s, 1465m, 1250m, 1130m,

963m, 845s, 814s, 757s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{26}NSi$ $(M+H)^+$: 272.1829, found 272.1823.

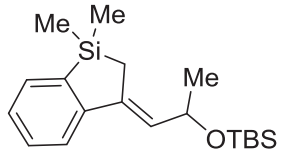
Preparation of 2g



2g

2g: Using the same procedure as that used for **2a** afforded **2g** as a colorless liquid (25 mg, 74% yield, *Z:E* = 94:6). ***Z-isomer*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.11-6.15 (m, 1H), 3.73 (t, *J* = 7.2 Hz, 2H), 2.51 (q, *J* = 7.2 Hz, 2H), 1.73 (s, 2H), 0.92 (s, 9H), 0.31 (s, 6H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 141.4, 140.8, 132.1, 129.5, 126.7, 121.1, 120.1, 62.8, 33.5, 26.0, 18.4, 16.2, -1.8, -5.2; IR (neat) cm^{-1} 2954s, 2897s, 2857s, 1466m, 1444m, 1252s, 1095s, 837s, 773s; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{32}NaOSi_2$ $(M+Na)^+$: 355.1884, found 355.1881.

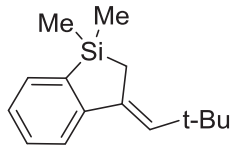
Preparation of 2h



2h

2h: Using the same procedure as that used for **2a** afforded **2h** as a colorless liquid (23 mg, 70% yield, *Z:E* = 88:12) as a colorless liquid. ***Z-isomer*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 4.75 (qd, J_1 = 6.4 Hz, J_2 = 8.0 Hz, 1H), 1.74 (dd, J_1 = 1.6 Hz, J_2 = 16.4 Hz, 1H), 1.66 (dd, J_1 = 1.6 Hz, J_2 = 16.4 Hz, 1H), 1.28 (d, *J* = 6.4 Hz, 3H), 0.89 (s, 9H), 0.31 (s, 3H), 0.30 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 140.8, 137.6, 132.1, 129.7, 129.2, 127.1, 121.6, 67.6, 25.9, 24.3, 18.3, 16.5, -1.8, -2.0, -4.4, -4.7; IR (neat) cm^{-1} 2957s, 2929s, 2892s, 2857s, 1466m, 1443m, 1252s, 1079s, 1003s, 834s, 766s; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{32}NaOSi_2$ $(M+Na)^+$: 355.1884, found 355.1879.

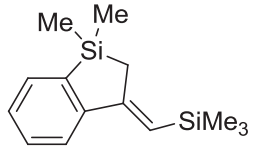
Preparation of 2i



2i

2i: Using the same procedure as that used for **2a** afforded **2i** as a colorless liquid (18.8 mg, 82% yield, *Z:E* ≥ 95:5) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.12 (s, 1H), 1.88 (s, 2H), 1.23 (s, 9H), 0.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ139.6, 138.2, 134.8, 132.0, 129.5, 126.5, 121.3, 111.3, 32.7, 30.7, 18.0, -2.1; IR (neat) cm^{-1} 3056w, 2958s, 2903m, 2867m, 1683m, 1540w, 1458m, 1443m, 1361m, 1252s, 1131s, 1017m, 842s, 810s, 759s; HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{23}Si$ $(M+H)^+$: 231.1564, found 231.1561.

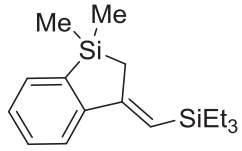
Preparation of 2j



2j

2j: Using the same procedure as that used for 2a afforded 2j as a colorless liquid (33 mg, 67%, *Z:E* = 91:9). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.13 (s, 1H, *Z-isomer*), 5.64 (s, 1H, *E-isomer*), 2.14 (s, 2H, *E-isomer*),1.90 (s, 2H, *Z-isomer*), 0.30 (s, 6H), 0.20 (s, 9H); *Z-isomer* ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.7, 151.1, 140.8, 132.0, 129.6, 127.6, 122.0, 121.5, 21.9, -0.1, -2.2; IR (neat) cm^{-1} 3057m, 2955s, 2923m, 1681m, 1589m, 1558m, 1536m, 1415m, 1250s, 1131m, 1040s, 841brs, 761s; HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{23}Si_2$ $(M+H)^+$: 247.1333, found 247.1338.

Preparation of 2k

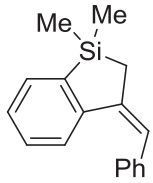


2k

2k: Using the same procedure as that used for **2a** afforded **2k** as a colorless liquid (40 mg, 70% yield, *Z:E* = ≥95:5). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.2 Hz,

1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 6.06 (s, 1H), 1.90 (s, 2H), 0.99 (t, *J* = 7.8 Hz, 9H), 0.71 (q, *J* = 7.8 Hz, 6H), 0.31 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 151.4, 140.7, 132.0, 129.6, 127.5, 122.2, 118.1, 22.6, 7.7, 4.5, -2.2; IR (neat) cm^{-1} 3057m, 2954s, 2909s, 2876s, 1681w, 1594m, 1578m, 1460m, 1443m, 1415m, 1250s, 1130s, 1011s, 837brs, 796s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{28}NaSi_2$ $(M+Na)^+$: 311.1622, found 311.1626.

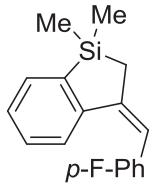
Preparation of 3a



3a

3a: Using the same procedure as that used for **2a** except for without DMSO afforded **3a** as a colorless liquid (106 mg, 85% yield, *E:Z* = 80:20). *E-isomer* ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.54 (d, *J* = 7.2 Hz, 1H), 7.14-7.26 (m, 7H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.63 (s, 1H), 2.02 (s, 1H), 0.36 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.2, 144.0, 141.7, 138.8, 132.0, 128.6, 128.2, 128.1, 127.0, 126.6, 126.2, 123.9, 27.9, -2.7; *Z-isomer* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.37-7.44 (m, 4H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.09 (s, 1H), 2.13 (s, 2H), 0.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 142.3, 140.7, 138.8, 132.2, 129.8, 129.2, 128.2, 127.4, 126.3, 123.5, 121.8, 19.9, -1.9; IR (neat) cm^{-1} 3054s, 2955s, 1593m, 1492m, 1442m, 1249s, 1133s, 843s, 818s, 762s, 695m; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{18}NaSi$ $(M+Na)^+$: 273.1070, found 273.1059.

Preparation of 3b

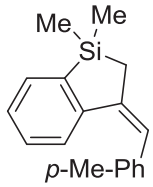


3b

3b: Using the same procedure as that used for **3a** afforded **3b** as a colorless liquid (33 mg, 82%, *E:Z* = 80:20). ***E-isomer*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.2 Hz, 1H), 7.16-7.23 (m, 4H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 8.4 Hz, 2H), 6.58 (s, 1H), 2.02 (s, 2H), 0.37 (s, 6H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 161.4 (d, J = 243.6 Hz), 148.0, 144.1, 142.0, 132.2, 130.2, 130.1, 128.3 (d, J = 3.4 Hz), 127.1, 126.5, 122.7, 115.1 (d, J = 21 Hz), 27.9, -2.7; IR (neat) cm^{-1} 3050m, 2955m, 2926m, 1596m, 1504s, 1250s, 1224s, 1127s, 869s, 843s, 768s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{17}FKSi$ $(M+K)^+$: 307.0715, found 307.0713.

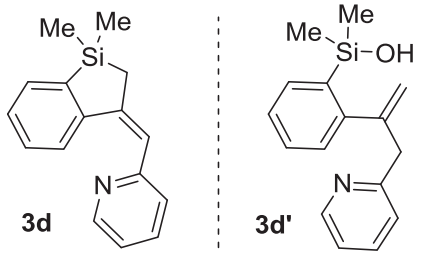
Preparation of 3c



3c

3c: Using the same procedure as that used for **3a** afforded **3c** as a colorless liquid (31 mg, 77%, *E:Z* = 75:25). ***E-isomer*** ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.2 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.16 (d, J = 7.2 Hz, 2H), 7.03-7.06 (m, 3H), 6.06 (s, 1H), 2.33 (s, 3H), 2.02 (s, 2H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 144.0, 141.0, 135.83, 135.81, 132.0, 128.9, 128.5, 128.2, 126.9, 126.6, 123.9, 27.9, 21.2, -2.7; IR (neat) cm^{-1} 2953m, 2923m, 2859m, 1509m, 1442m, 1249s, 1126s, 867s, 841s, 770s, 724s; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{20}KSi$ $(M+K)^+$: 303.0966, found 303.0962.

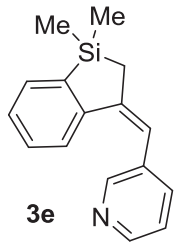
Preparation of 3d and 3d'



3d: Using the same procedure as that used for **3a** afforded **3d** as a pale yellow liquid (26 mg, 34%, *E:Z* ≥ 95:5) and **3d'** as a pale yellow liquid (27.2 mg, 31% yield). **3d:** ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (brs, 1H), 7.70 (t, J = 7.2 Hz, 1H), 7.61(d, J = 7.2 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H), 7.26-7.33 (m, 3H), 7.13-7.16 (m, 1H), 6.53 (s, 1H), 2.28 (s, 1H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 151.4, 149.1, 146.4, 138.2, 136.5, 134.6, 128.9, 128.4, 126.7, 126.4, 123.9, 121.5, 20.9, 1.7; IR (neat) cm^{-1} 2923m, 1636m, 1588m, 1469m, 1431m, 1399m, 1250m, 1129s, 1093s, 906s, 821m, 769s, 737s; HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{18}NSi$ $(M+H)^+$: 252.1203, found 252.1212. **3d':**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 4.0 Hz, 1H), 7.65 (dt, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.52 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.30 (dt, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.23-7.26 (m, 2H), 7.14-7.16 (m, 2H), 5.13 (s, 1H), 4.80 (s, 1H), 3.91 (s, 2H), 0.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 149.9, 149.3, 148.8, 138.7, 137.2, 134.4, 128.6, 127.1, 126.3, 124.5, 121.8, 117.2, 45.3, 2.2; IR (neat) cm^{-1} 2957s, 2854s, 1473m, 1433s, 1252s, 1133brs, 897s, 828s, 780s, 741s; HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{19}NNaOSi$ $(M+Na)^+$: 292.1128, found 292.1132.

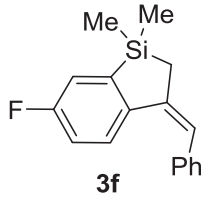
Preparation of 3e



3e

3e: Using the same procedure as that used for **3a** afforded **3e** as a pale yellow liquid (34 mg, 67%, *E:Z* = 77:23). ***E-isomer*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.40 (d, J = 3.6 Hz, 1H), 7.55(t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.13-7.15 (m, 2H), 7.05 (t, J = 7.2 Hz, 1H), 6.53 (s, 1H), 2.05 (s, 2H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 147.5, 147.2, 144.6, 144.2, 135.8, 134.6, 132.4, 128.5, 127.5, 126.3, 123.0, 119.5, 28.4, -2.8; IR (neat) cm^{-1} 3050m, 2926m, 1680m, 1583m, 1475m, 1424m, 1251s, 1128m, 1029m, 892m, 777m, 754m; HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{18}NSi$ $(M+H)^+$: 252.1203, found 252.1208.

Preparation of 3f

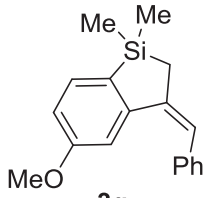


3f

3f: Using the same procedure as that used for **3a** afforded **3f** as a colorless liquid (49 mg, 91%, *E:Z* = 77:23). ***E-isomer*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.28 (m, 4H), 7.15-7.20 (m, 3H), 6.72 (dt, J_1 = 2.8 Hz, J_2 = 8.0 Hz, 1H), 6.60 (s, 1H), 2.05 (s, 2H), 0.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, J = 248.5 Hz), 146.9 (d, J = 4.8 Hz), 143.9 (d, J = 2.7 Hz), s140.5, 138.7, 128.6, 128.3, 128.2 (d, J = 7.2 Hz), 126.3, 123.6, 117.8 (d, J = 19.2 Hz), 115.6 (d, J = 22.5 Hz), 28.0, -2.8; IR

(neat) cm^{-1} 3021m, 2955m, 2926m, 1597m, 1567m, 1455s, 1256, 1207s, 1124m, 903m, 841s, 821s, 798s, 755s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{17}FKSi$ $(M+K)^+$: 307.0715, found 307.0717.

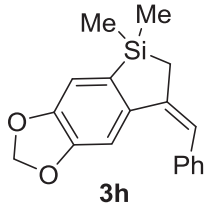
Preparation of 3g



3g

3g: Using the same procedure as that used for **3a** afforded **3g** as a colorless liquid (25 mg, 90%, *E:Z* = 80:20). ***E-isomer*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 1H), 7.24-7.27 (m, 4H), 7.15-7.18 (m, 1H), 6.75 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 1H), 6.69 (s, J = 2.0 Hz, 1H), 6.66 (s, 1H), 3.39 (s, 3H), 2.02 (s, 2H), 0.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 150.0, 141.8, 138.9, 135.0, 132.9, 128.8, 128.2, 126.3, 124.2, 115.4, 110.6, 54.6, 27.7, -2.4; IR (neat) cm^{-1} 2954s, 2924s, 2854s, 1590s, 1555s, 1465s, 1291m, 1232s, 1131m, 845s, 795s, 754s; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{21}OSi$ $(M+H)^+$: 281.1356, found 281.1356.

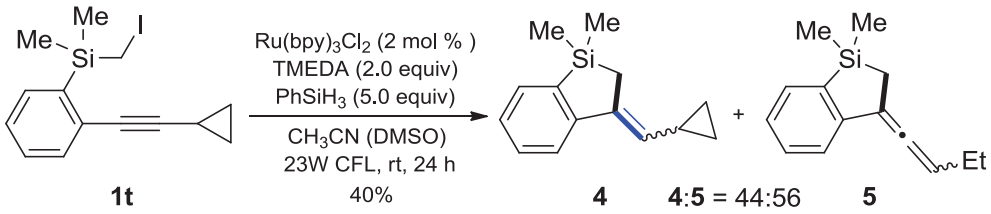
Preparation of 3h



3h

3h: Using the same procedure as that used for **3a** afforded **3h** as a colorless liquid (34 mg, 58%, *E:Z* = 80:20). ***E-isomer*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.25 (m, 4H), 7.16-7.18 (m, 1H), 6.92 (s, 1H), 6.64 (s, 1H), 6.53 (s, 1H), 5.86 (s, 2H), 2.00 (s, 2H), 0.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 147.3, 143.0, 141.0, 138.7, 137.7, 128.6, 128.3, 126.2, 122.6, 110.3, 107.4, 100.8, 28.2, -2.5; IR (neat) cm^{-1} 2954s, 2926s, 2894s, 1596m, 1499s, 1467s, 1346m, 1467s, 1346m, 1313m, 1246s, 1123s, 1040s, 941s, 845s, 756s; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{19}O_2Si$ $(M+H)^+$: 295.1149, found 295.1150.

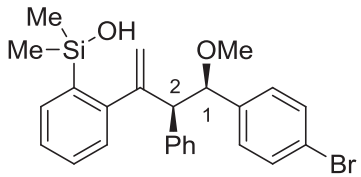
2.3. Mechanistic Studies



Using the same procedure as that used for **2a** afforded **4** (8 mg, 18%, *Z:E* = 3:1) as a colorless liquid and **5** (9 mg, 22%) as a colorless liquid. **4:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 5.52 (td, J_1 = 2.0 Hz, J_2 = 9.6 Hz, 1H), 1.85 (d, *J* = 2.0 Hz, 2H), 1.68-1.73 (m, 1H), 0.85 (dt, J_1 = 4.4 Hz, J_2 = 6.4 Hz, 2H), 0.49 (dt, J_1 = 4.4 Hz, J_2 = 6.4 Hz, 2H), 0.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 140.3, 138.1, 132.2, 129.5, 128.6, 126.3, 120.7, 16.2, 12.0, 7.4, -1.6; **5:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 5.52-5.56 (m, 1H), 2.13 (qd, J_1 = 7.6 Hz, J_2 = 7.2 Hz, 2H), 1.86 (d, *J* = 3.2 Hz, 1H), 1.85 (d, *J* = 3.2 Hz, 1H), 1.06 (t, *J* = 7.6 Hz, 3H), 0.33 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 148.2, 131.9, 130.2, 129.7, 126.3, 123.7, 106.3, 95.7, 22.5, 17.2, 13.6, -1.59, -1.64. IR (neat) cm^{-1} 2961s, 2926s, 2854s, 1681s, 1558m, 1516m, 1252m, 830m, 795m; HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{18}KSi$ $(M+K)^+$: 253.0809, found 253.0818.

2.4. Functionalization of 3a

Preparation of 8

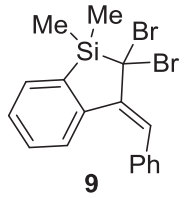


8

To a solution of **3a** (25 mg, 0.1 mmol) and 4-bromobenzaldehyde dimethyl acetal (25 μL, 0.15 mmol) in anhyd. CH_2Cl_2 (2.0 mL) under argon atmosphere, $SnCl_4$ (0.15 mL of 1.0 M solution in CH_2Cl_2, 0.15 mmol) was added dropwise at -78 ^{o}C. The mixture was then stirred overnight before quenching with sat. $NaHCO_3$ (3 mL). The aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 100:1→50:1) afforded **8** (32.7 mg, 70% yield, *syn/anti* = 90 : 10) as colorless

viscous liquid. ***Major isomer***[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J_1 = 1.2 Hz, J_2 = 7.2 Hz, 1H), 7.38 (dd, J_1 = 1.2 Hz, J_2 = 7.2 Hz, 1H), 7.32 (dd, J_1 = 1.2 Hz, J_2 = 7.2 Hz, 1H), 7.16-7.25 (m, 8H), 6.70 (d, J = 8.0 Hz, 1H), 5.26 (s, 1H), 5.18 (s, 1H), 4.55 (d, J = 3.6 Hz, 1H), 4.06 (brs, 1H), 3.94 (s, 1H), 3.03 (s, 3H), 0.46 (s, 3H), 0.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 148.1, 138.5, 138.1, 136.5, 135.1, 131.2, 130.9, 128.9, 128.6, 127.8, 127.4, 126.9, 126.6, 121.1, 119.3, 83.7, 60.0, 57.0, 3.5, 2.2; ***Minor isomer*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 7.6 Hz, 2H), 7.15 (t, J = 7.6 Hz, 1H), 7.09-7.10 (m, 3H), 6.94 (t, J = 7.6 Hz, 1H), 6.84-6.86 (m, 4H), 6.18 (d, J = 7.6 Hz, 2H), 5.64 (s, 1H), 5.56 (s, 1H), 5.35 (s, 1H), 4.64 (d, J = 10.4 Hz, 1H), 3.80 (d, J = 10.4 Hz, 1H), 3.30 (s, 3H), 0.52 (s, 3H), 0.41 (s, 3H); IR (neat) cm^{-1} 3419brm, 2956m, 2920m, 2851m, 1487m, 1254m, 1095m, 826m, 782m; HRMS (ESI-TOF, m/z) calcd for $C_{25}H_{27}BrNaO_2Si$ $(M+Na)^+$: 489.0856, found 489.0859.

Preparation of 9



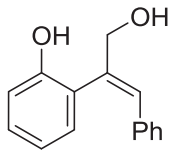
9

To a solution of **3a** (25 mg, 0.1 mmol) in anhyd. CCl_4 (1.0 mL) were added NBS (36 mg, 0.2 mmol) and benzoyl peroxide (1.0 mg, 3 μmol) under argon atmosphere. The mixture was then degassed via the freeze-pump-thaw method and backfilled with argon. After stirring at 80 ^{o}C overnight, the reaction mixture was cooled to 25 °C, filtered through a cotton plug, and concentrated in vacuo. Purification of the crude residue via silica gel flash column chromatography (eluent: petroleum ether) afforded **9** as an off-white solid (35 mg, 85% yield, m.p. 128-130 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.53 (m, 3H), 7.26-7.33 (m, 3H), 7.14-7.21 (m, 3H), 6.95 (s, 1H), 0.45 (s, 3H), 0.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 144.8, 137.3, 136.9, 132.0, 129.5, 128.4, 127.8, 126.6, 125.5, 49.6, -4.8, -5.2; IR (neat) cm^{-1} 2958m, 2924m, 1585m, 1490m, 1440s, 1400s, 1247s,

1. The *syn*-stereochemistry was assigned based on the results from previous studies, which provided structurally similar products to ours. Generally, the *anti*-isomer possesses a larger coupling constant ($J_{H1–H2}$ = 9–10 Hz) than the *syn*-isomer ($J_{H1–H2}$ = 4–8 Hz). Thus, in our case, the major isomer containing a smaller coupling constant ($J_{H1–H2}$ = 3.6 Hz) was assigned as *syn*-stereochemistry, and the minor isomer containing a larger coupling constant ($J_{H1–H2}$ = 10.4 Hz) was assigned as *anti*-stereochemistry. For the related references, see: (a) K. H. Kim, H. S. Lee, S. H. Kim, K. Y. Lee, J.-E. Lee, J. N. Kim, *Bull. Korean Chem. Soc.* 2009, **30**, 1012; (b) H.-J. Gais, L. R. Reddy, G. S. Babu, G. Raabe, *J. Am. Chem. Soc.,*2004, **126**, 4859; (c) M. Bandini, P. G. Cozzi, P. M., A. Umani-Ronchi, *Angew. Chem. Int. Ed.* 2004, **43**, 84; (d) M. Song, J. Montgomery, *Tetrahedron*, 2005, **61**, 11440.

1091s, 937s, 845s, 785s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{16}Br_2NaSi$ $(M+Na)^+$: 428.9280, found 428.9275.

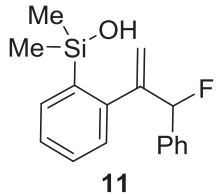
Preparation of 10



10

To a solution of *t*-BuOK (67.3 mg, 0.6 mmol) in anhyd. THF (0.7 mL) was added *tert*-butyl hydroperoxide (0.11 mL of 5.5 M in decane over MS, 0.6 mmol) at 0 °C under argon atmosphere. After stirring for 10 min, a solution of **3a** (25 mg, 0.1 mmol) in anhyd. THF (0.4 mL) and TBAF (0.6 mL of 1.0 M solution in THF, 0.6 mmol) were added sequentially. The mixture was stirred overnight at 70 °C before quenching with sat aq $Na_2S_2O_3$ (3 mL) and sat aq NH_4Cl (5 mL). The aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 20:1→5:1) afforded **10** as a white powder (13 mg, 56% yield, m.p. 108-110 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 7.2 Hz, 1H), 7.13-7.15 (m, 3H), 6.95-7.03 (m, 4H), 6.85-6.88 (m, 2H), 4.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 136.2, 135.5, 132.2, 129.8, 129.5, 128.9, 128.2, 127.7, 125.5, 120.8, 116.7, 69.8; IR (neat) cm^{-1} 3426s, 3084s, 1450s, 1398s, 1365s, 1238s, 1071s, 749s; HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{14}NaO_2$ $(M+Na)^+$: 249.0886, found 249.0889.

Preparation of 11



11

To a solution of **3a** (25 mg, 0.1 mmol) in anhyd. MeCN (2.0 mL) was added Selectfluor (53 mg, 0.15 mmol) under argon atmosphere at -20 °C. The mixture was stirred for 3 h before quenching with water (3 mL). The aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the crude

residue via silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 50:1→20:1) afforded **11** as a colorless viscous liquid (20 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 1H), 7.26-7.36 (m, 6H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 7.2 Hz, 1H), 6.17 (d, *J* = 45.6 Hz, 1H), 5.57 (s, 1H), 5.26 (s, 1H), 2.17 (brs, 1H), 0.43 (s, 3H), 0.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1 (d, *J* = 20.7 Hz), 144.2, 138.2, 137.4, 134.4, 129.2, 128.8, 128.7(d, *J* = 2.4 Hz), 128.4, 126.9, 126.8 (d, *J* = 1.1 Hz), 116.8 (d, *J* = 8.0 Hz), 95.7 (d, *J* = 175.1 Hz), 2.1, 1.8; IR (neat) cm^{-1} 3336brs, 3053s, 2959s, 2926s, 1585m, 1456m, 1255s, 1117s, 1003s, 854s, 831s, 780s, 737s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{19}FNaOSi$ $(M+Na)^+$: 309.1081, found 309.1093.

3. Computational details

All calculations were performed using Gaussian 09 programs package.[1] Geometries were fully optimized at the UB3LYP/6-31+G* level in CH_3CN solvent and characterized by frequency analyses. The wave function stability was tested at the same theoretical level.[2] The self-consistent reaction field (SCRF) method with PCM[3] solvation model was used to evaluate solvent effect on reaction. The intrinsic reaction coordinate (IRC) path was traced in order to check the potential energy profile connecting each transition state to the two associated minima.[4] The Gibbs free energies (G_{298K}) obtained in solvent and corrected by zero-point vibrational effect were used in the discussion.

References:

(1) Guassian 09 (Reversion D. 01), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford CT, 2013.

(2) (a) R. Seeger and J. A. Pople, *J. Chem. Phys.* **1977**, *66*, 3045. (b) R. Bauernschmitt and R. Ahlrichs, *J. Chem. Phys.* **1996**, *104*, 9047.

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(4) (a) K. J. Fukui, *Phys. Chem.* **1970**, *74*, 4161. (b) K. Fukui, *Acc. Chem. Res.***1981**, *14,* 363. (c) C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.***1989**, *90*, 2154.

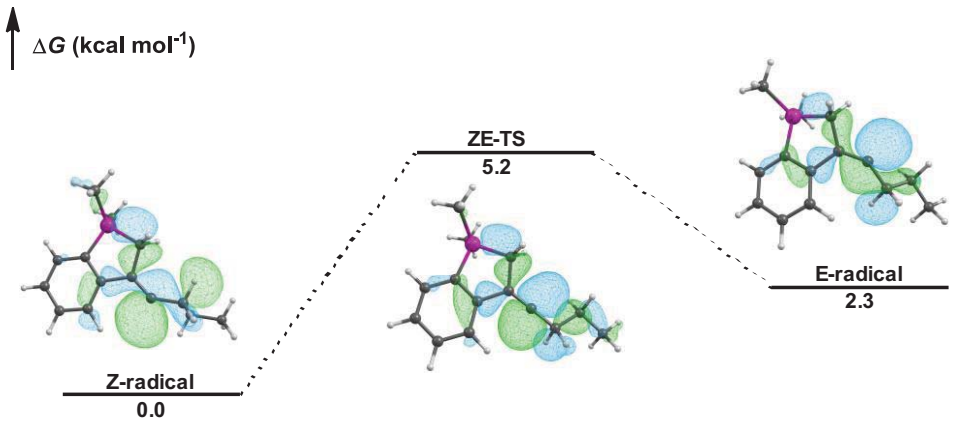


Figure 1. Energy profile for the isomerization between Z-radical and E-radical. Realtive Gibbs free energies (Δ*G*, kcal mol^{-1}) obtained in CH_3CN solvent at the UB3LYP/6-31+G*(PCM, CH_3CN) level are given in parentheses.

XYZ Coordinates and Energies of all the species studied in this work.

Z-radical

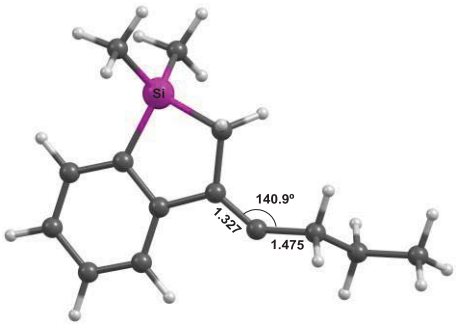
Zero-point correction= 0.28671 (a.u.)

Thermal correction to Gibbs Free Energy= 0.24003 (a.u.)

Sum of electronic and zero-point Energies= -834.12328 (a.u.)

Sum of electronic and thermal Free Energies= -834.16995 (a.u.)

Number of imaginary frequency: 0



34

C	-2.683020	-0.733373	-0.676377
C	-2.789503	0.639256	-0.949233
C	-1.698922	1.479145	-0.706918
C	-0.497143	0.967661	-0.191096
C	-1.498202	-1.261451	-0.165444
C	-0.397837	-0.419121	0.079701
H	-3.717140	1.045499	-1.345274
H	-3.530592	-1.389569	-0.860378
H	-1.790125	2.542505	-0.922323
Si	1.129710	1.828138	0.218932
H	-1.422015	-2.324973	0.049300
C	0.907983	-0.896570	0.617360
C	1.888747	0.246792	0.974333
C	0.949940	3.244487	1.457844
C	2.046810	2.430338	-1.322467
H	1.933198	3.630441	1.756652
H	0.425078	2.916229	2.363194
H	0.384369	4.078420	1.022805
H	2.184044	1.616605	-2.045039
H	1.491502	3.234868	-1.821465
H	3.038052	2.821867	-1.059652
H	2.899462	0.027787	0.611886
H	1.960468	0.345879	2.066506
C	1.223895	-2.175670	0.774784
C	2.335419	-3.032446	1.227620
C	2.879111	-3.985583	0.139847
C	4.024668	-4.864329	0.652966

H	2.011964	-3.631648	2.092959
H	3.160101	-2.392948	1.592522
H	2.058271	-4.617665	-0.223296
H	3.219586	-3.390386	-0.717596
H	4.393462	-5.530323	-0.136084
H	3.698494	-5.489872	1.493854
H	4.869372	-4.254490	0.998278

E-radical

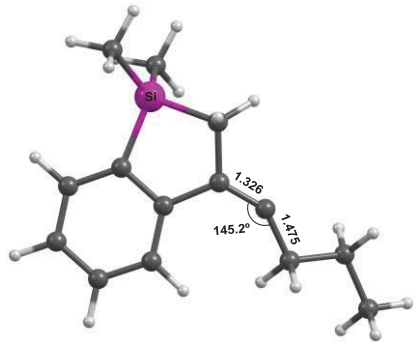
Zero-point correction= 0.28678 (a.u.)

Thermal correction to Gibbs Free Energy= 0.24081 (a.u.)

Sum of electronic and zero-point Energies= -834.12028 (a.u.)

Sum of electronic and thermal Free Energies= -834.16625 (a.u.)

Number of imaginary frequency: 0



34

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C	-1.773469	1.531180	-0.593022
C	-0.599952	0.956222	-0.084404
C	-1.716031	-1.219321	-0.058724
C	-0.569991	-0.438764	0.173852
H	-3.815276	1.205600	-1.223779
H	-3.760547	-1.233212	-0.733266
H	-1.811936	2.599406	-0.799976
Si	1.066264	1.726837	0.360584
H	-1.715131	-2.281164	0.170029
C	0.734242	-0.969837	0.688383
C	1.636922	0.139022	1.253184
C	0.933220	3.236613	1.488389
C	2.105902	2.138167	-1.165513
H	0.458910	4.078176	0.967537
H	1.926970	3.567940	1.816404
H	0.338156	3.014077	2.382335
H	2.219333	1.262235	-1.815961
H	1.640046	2.938001	-1.755285

H	3.108758	2.477104	-0.875428
H	2.696737	-0.112162	1.144501
H	1.440814	0.258509	2.329746
C	1.122789	-2.235041	0.613269
C	0.769246	-3.584824	0.133795
C	1.987643	-4.436213	-0.291021
C	1.580961	-5.827675	-0.786684
H	0.082179	-3.500395	-0.727347
H	0.216543	-4.127718	0.916833
H	2.537167	-3.904313	-1.078709
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Z-E-TS

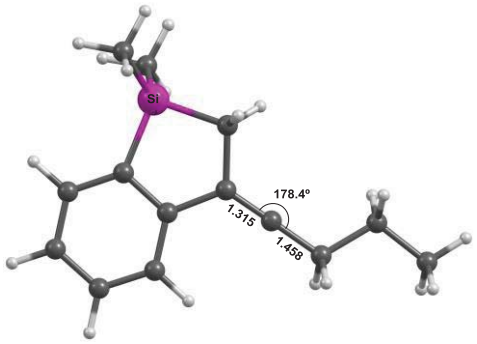
Zero-point correction= 0.28559 (a.u.)

Thermal correction to Gibbs Free Energy= 0.23994 (a.u.)

Sum of electronic and zero-point Energies= -834.11600 (a.u.)

Sum of electronic and thermal Free Energies= -834.16164 (a.u.)

Number of imaginary frequency: 1



34

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C	-0.711226	1.100150	-0.107531
C	-2.050627	-0.912301	-0.462858
C	-0.824470	-0.311092	-0.127428
H	-3.917160	1.891025	-1.005254
H	-4.102308	-0.591847	-1.030160
H	-1.764212	2.965951	-0.422322
Si	1.046383	1.604886	0.356585
H	-2.136972	-1.996840	-0.469993
C	0.415386	-1.086744	0.210842
C	1.548892	-0.187518	0.774915

C	1.131706	2.785667	1.830888
C	2.002146	2.330284	-1.107057
H	0.593838	2.379714	2.696278
H	0.687601	3.758516	1.583604
H	2.172558	2.962993	2.131119
H	1.990533	1.647131	-1.965174
H	1.564755	3.284049	-1.429216
H	3.049482	2.517503	-0.836883
H	2.523040	-0.490653	0.376597
H	1.600090	-0.311207	1.866246
C	0.542146	-2.385129	0.041725
C	0.677574	-3.818751	-0.185481
C	2.120904	-4.377126	-0.044828
C	2.180699	-5.885490	-0.306600
H	0.308091	-4.072146	-1.194158
H	0.024215	-4.362639	0.515661
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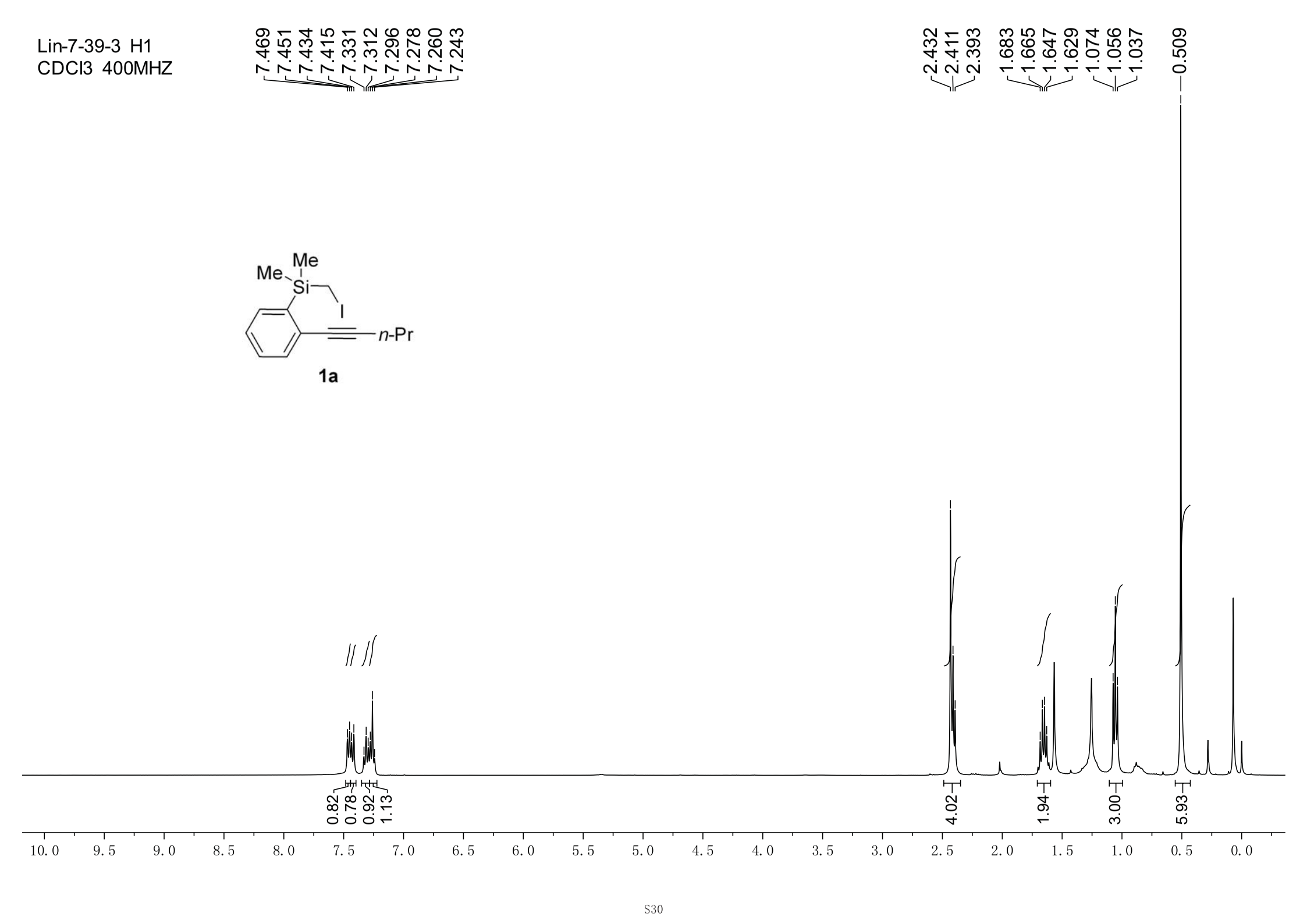
Lin-7-39-3 H1
CDCl3 400MHZ



Lin-7-39-3 C13
CDCl3 100MHZ

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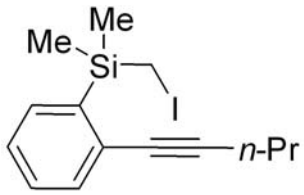

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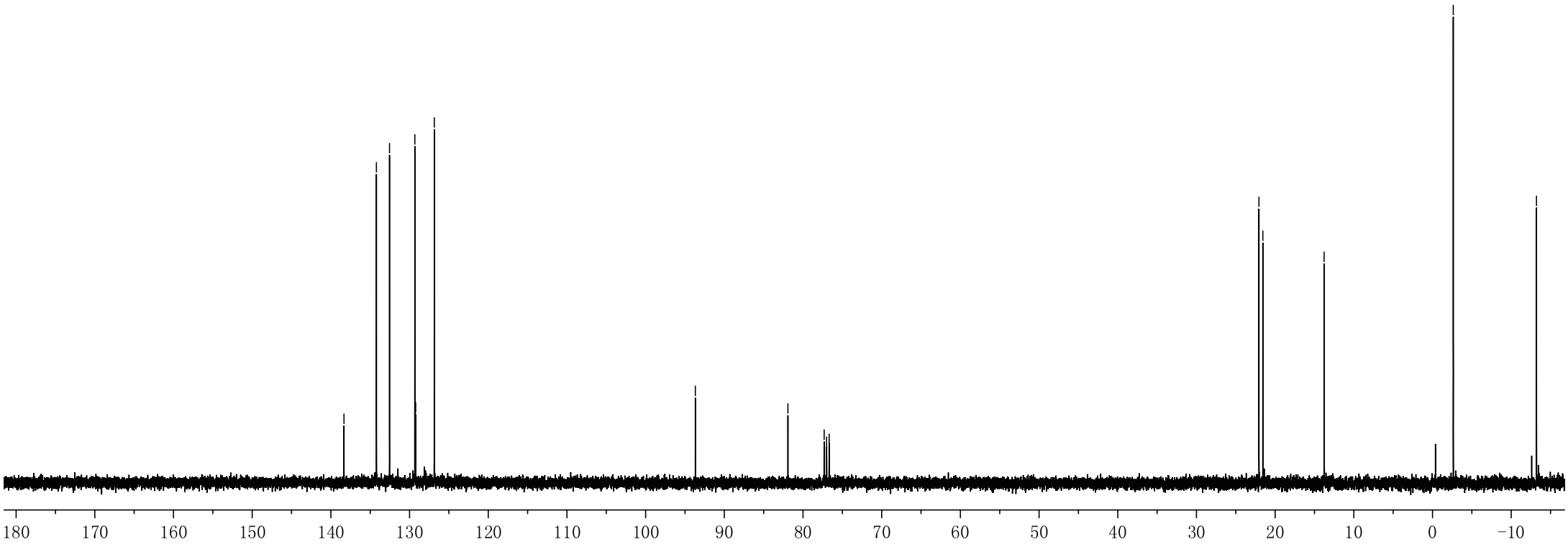
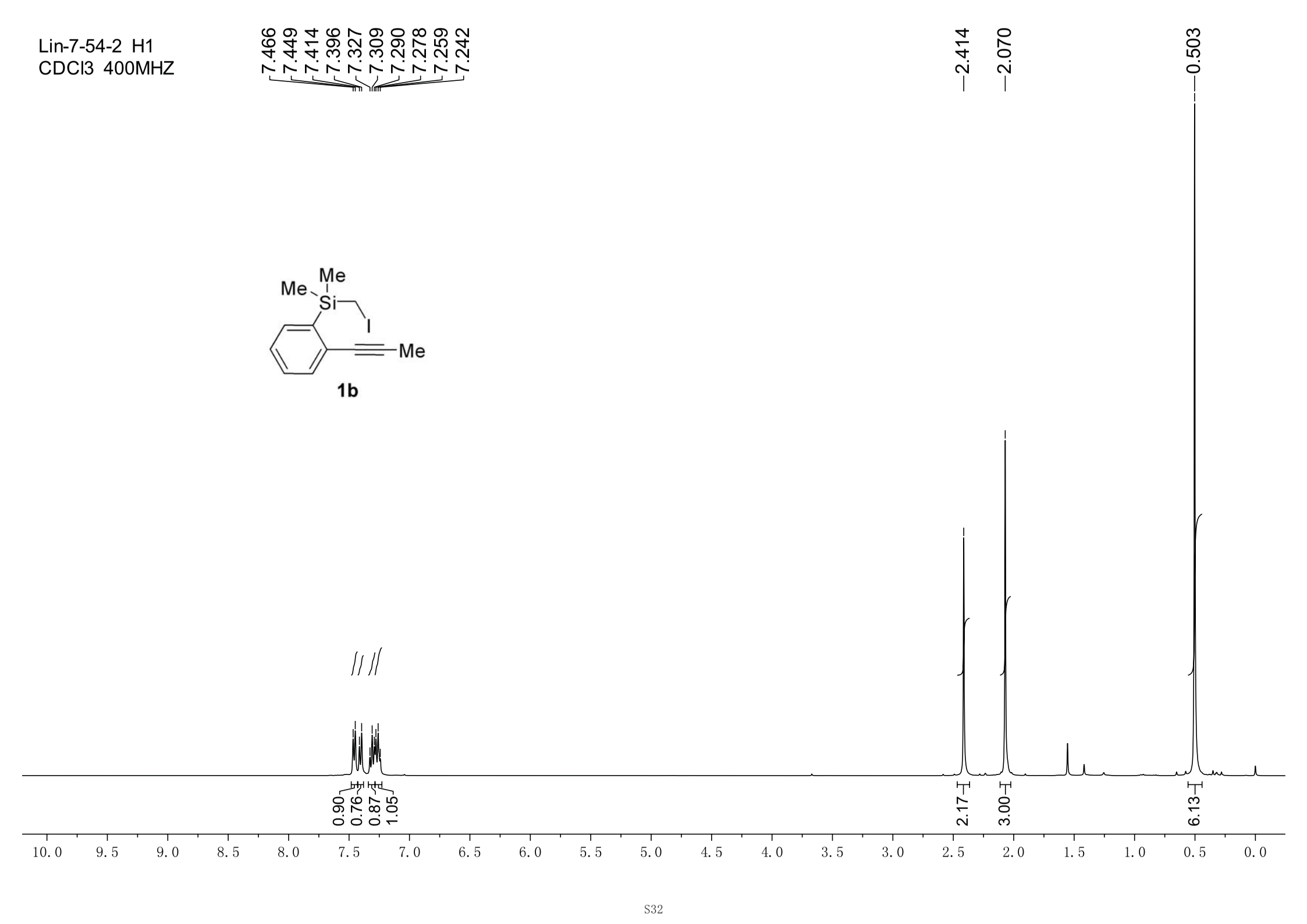


Lin-7-54-2 H1
CDCl3 400MHZ



Lin-7-54-2 C13
CDCl3 150MHZ

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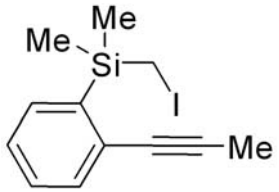

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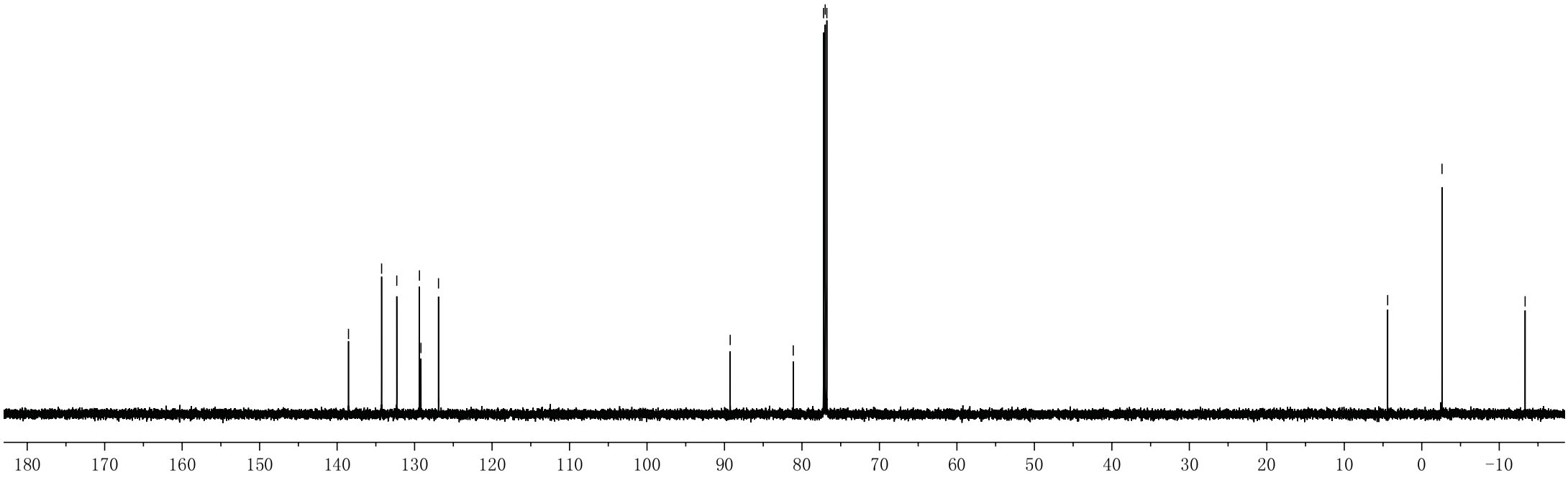
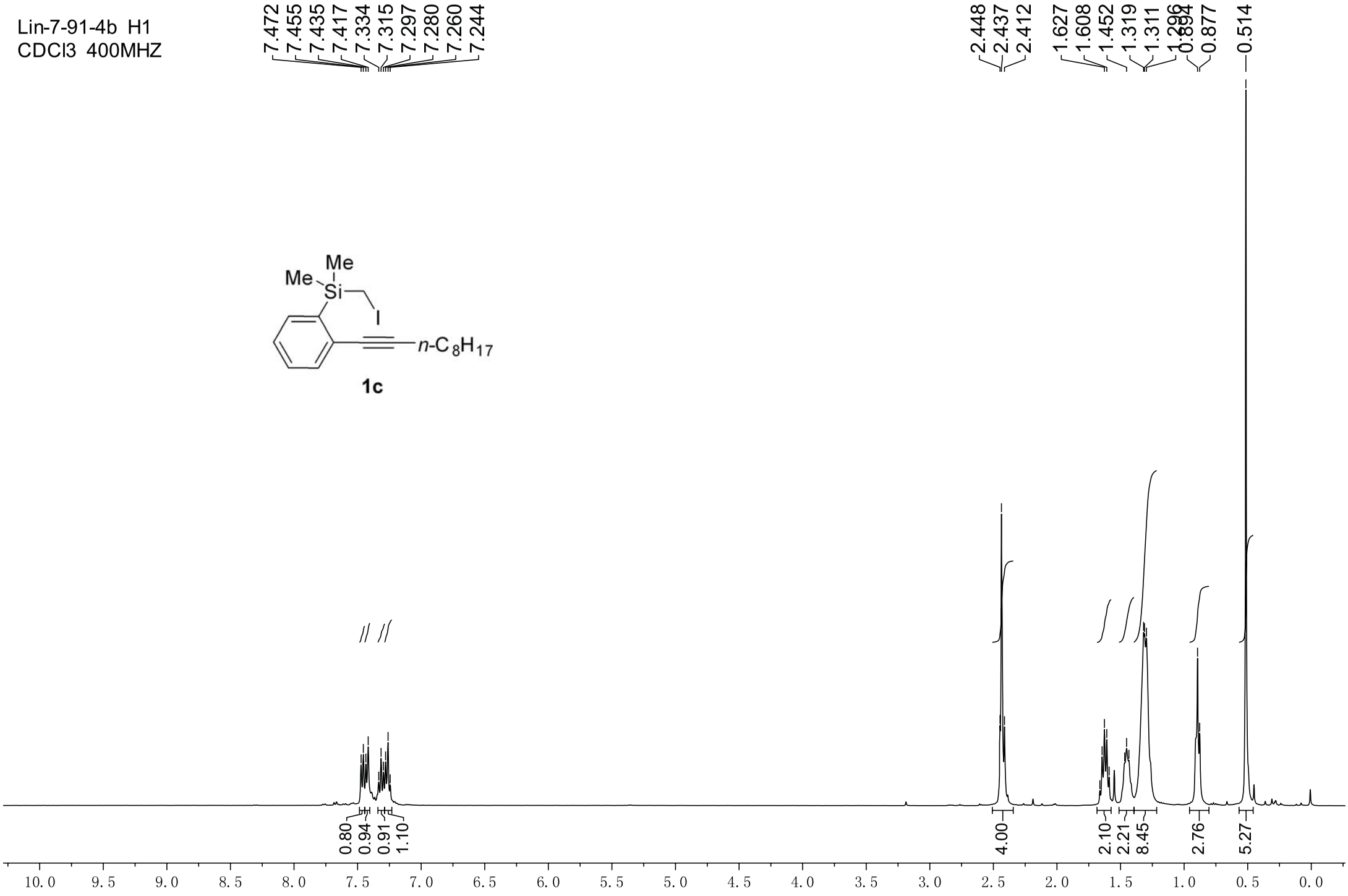
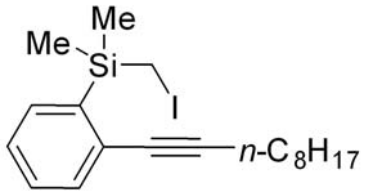


Lin-7-91-4b H1
CDCl3 400MHZ

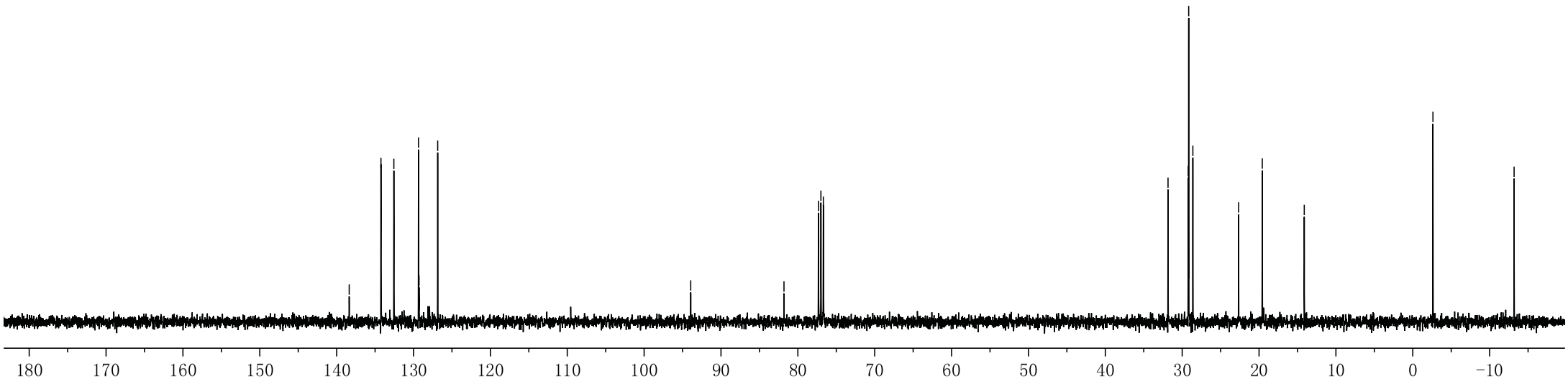


Lin-7-91-4b C13
CDCl3 100MHZ

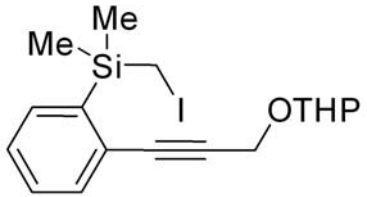
138.368
134.239
132.558
129.352
129.282
126.855
93.937
81.804
77.316
77.000
76.682
31.841
29.211
29.153
28.611
22.661
19.580
14.117
-2.624
-13.182



1c

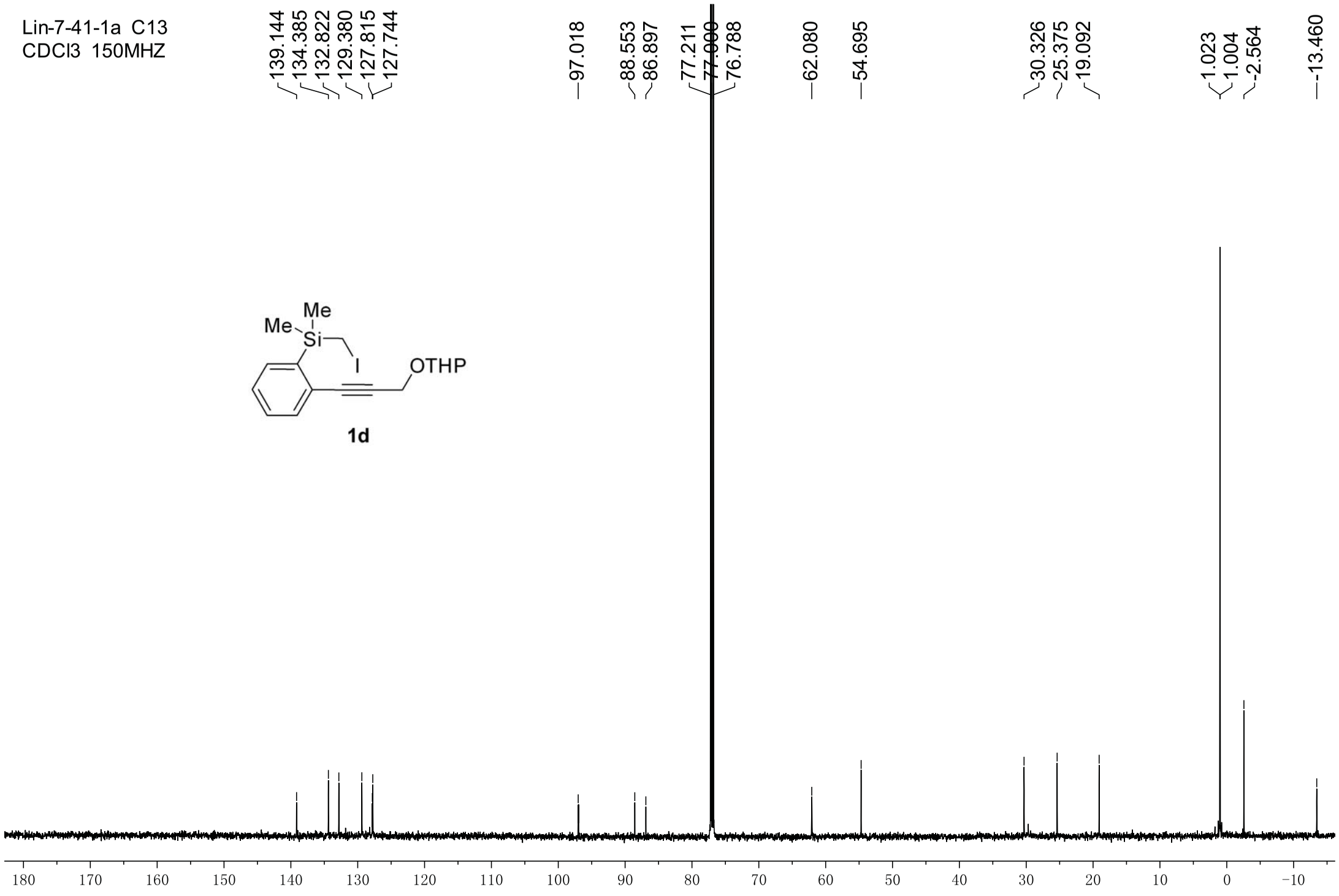


Lin-7-93-3 H1
CDCl3 400MHZ

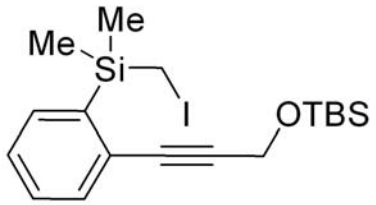


1d

Lin-7-41-1a C13
CDCl3 150MHZ



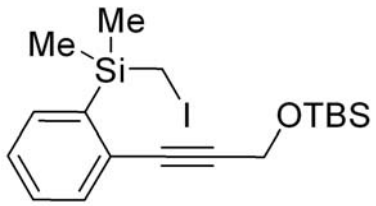
Lin-7-53-5a H1
CDCl3 600MHZ



1e

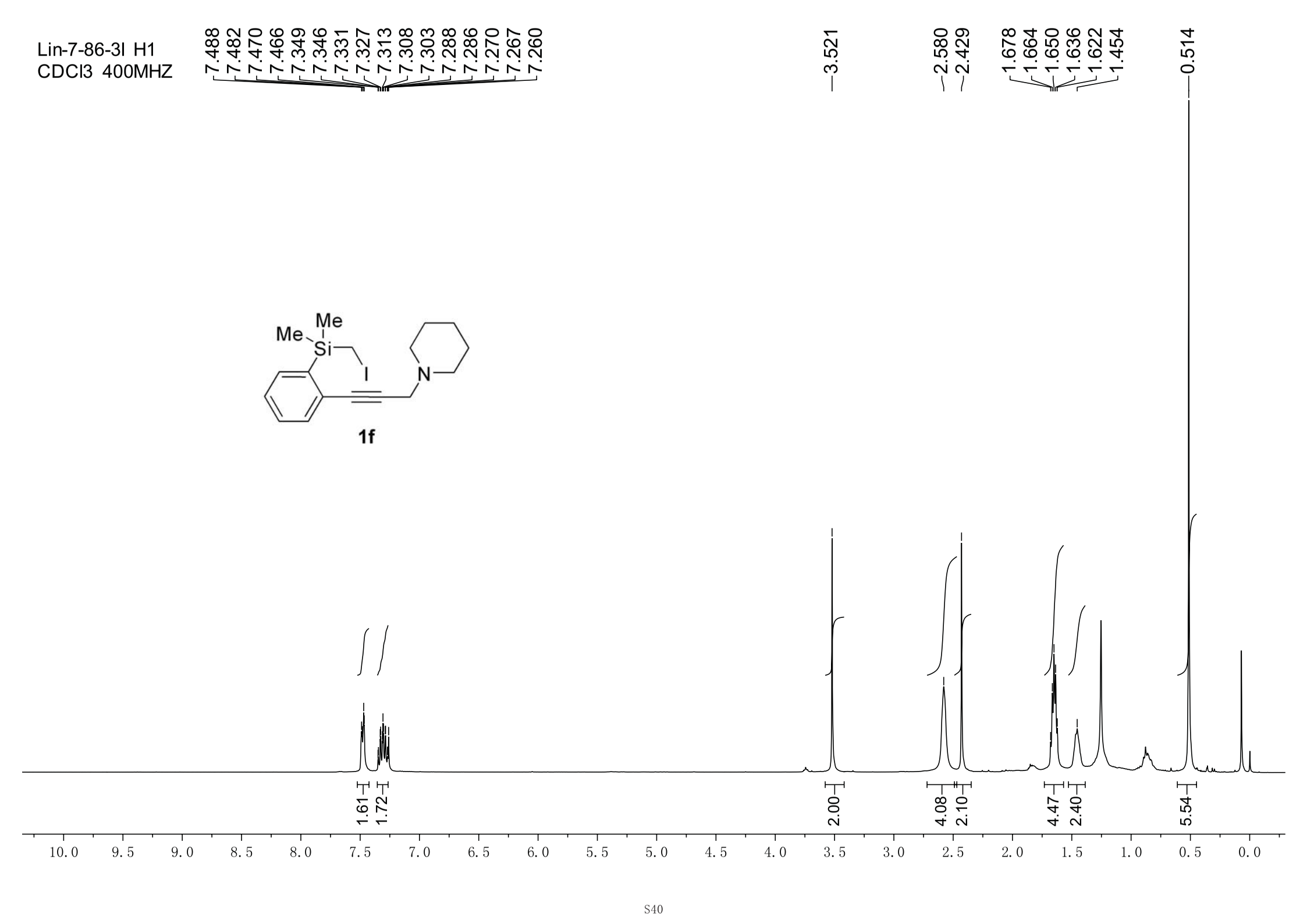
Lin-7-53-5a C13
CDCl3 150MHZ

138.978
134.369
132.637
129.359
128.041
127.587
90.982
85.783
77.212
77.000
76.788
52.214
25.855
18.338
-2.485
-5.136
-13.413



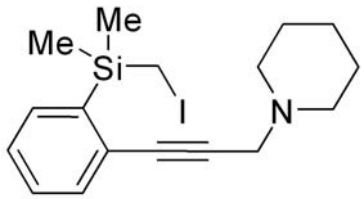
1e

Lin-7-86-3I H1
CDCl3 400MHZ

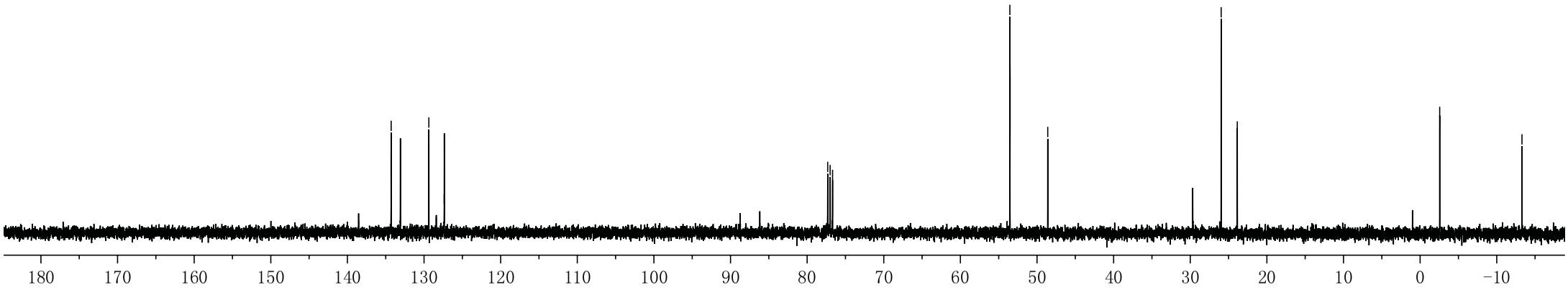


Lin-7-86-3I C13
CDCl3 100MHZ

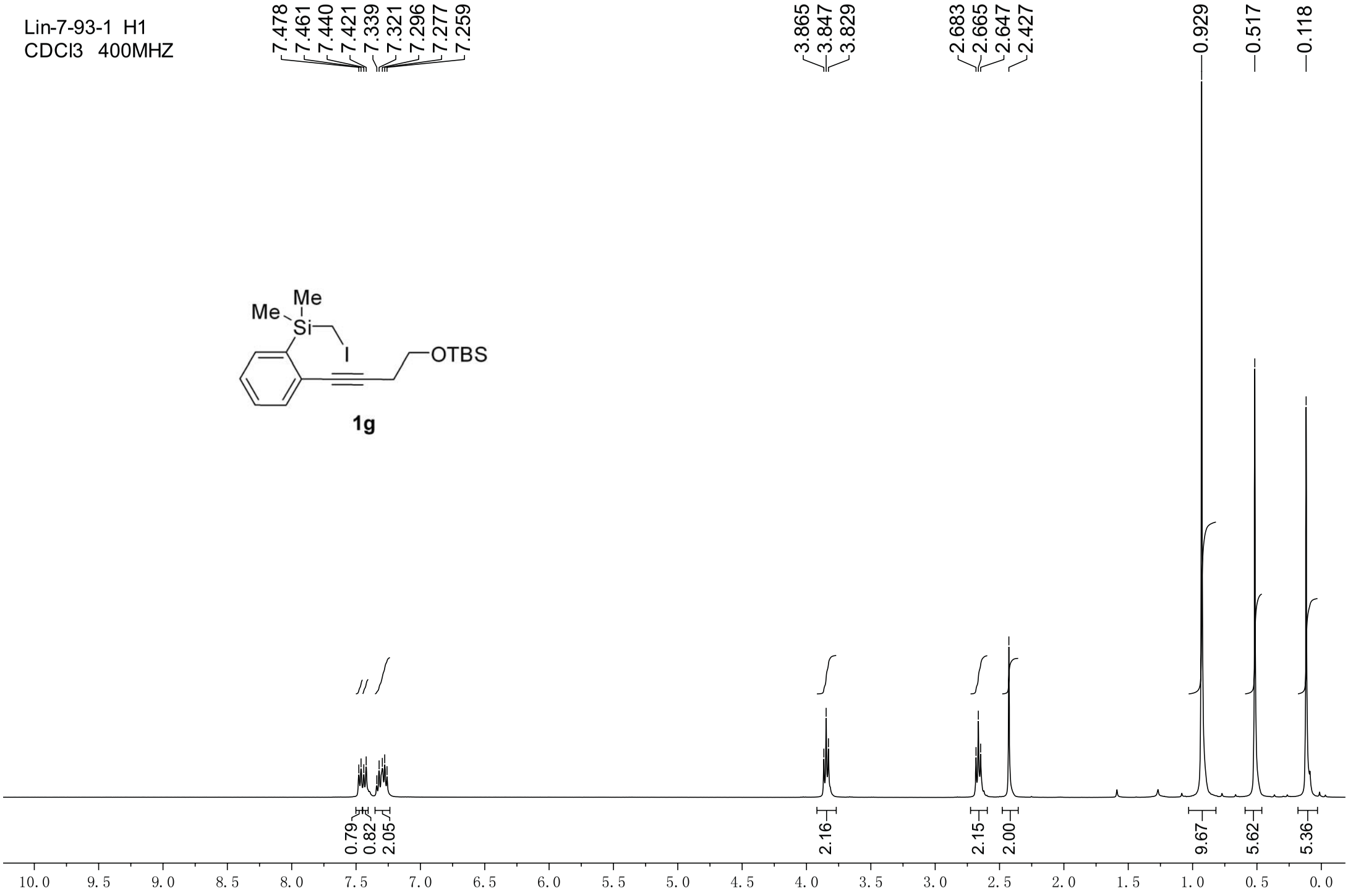
138.527
134.290
133.066
129.371
128.415
127.369
88.706
86.157
77.317
77.000
76.683
53.542
48.600
25.966
23.864
-2.555
-13.292



1f



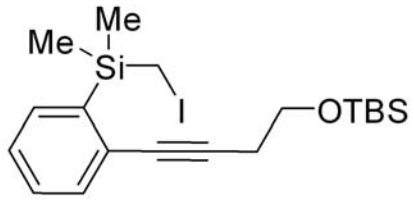
Lin-7-93-1 H1
CDCl3 400MHZ



1g

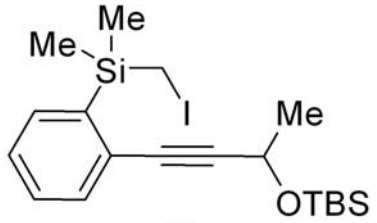
Lin-7-93-1 C13
CDCl3 100MHZ

138.610
134.252
132.521
129.354
128.868
127.075
90.481
82.882
77.319
77.000
76.685
61.747
25.922
23.966
18.337
-2.597
-5.225
-13.304



1g

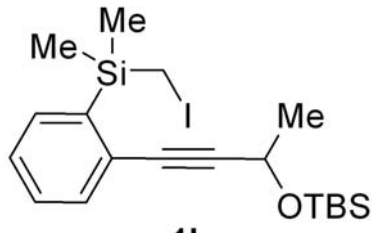
Lin-7-93-2 H1
CDCl3 400MHZ



1h

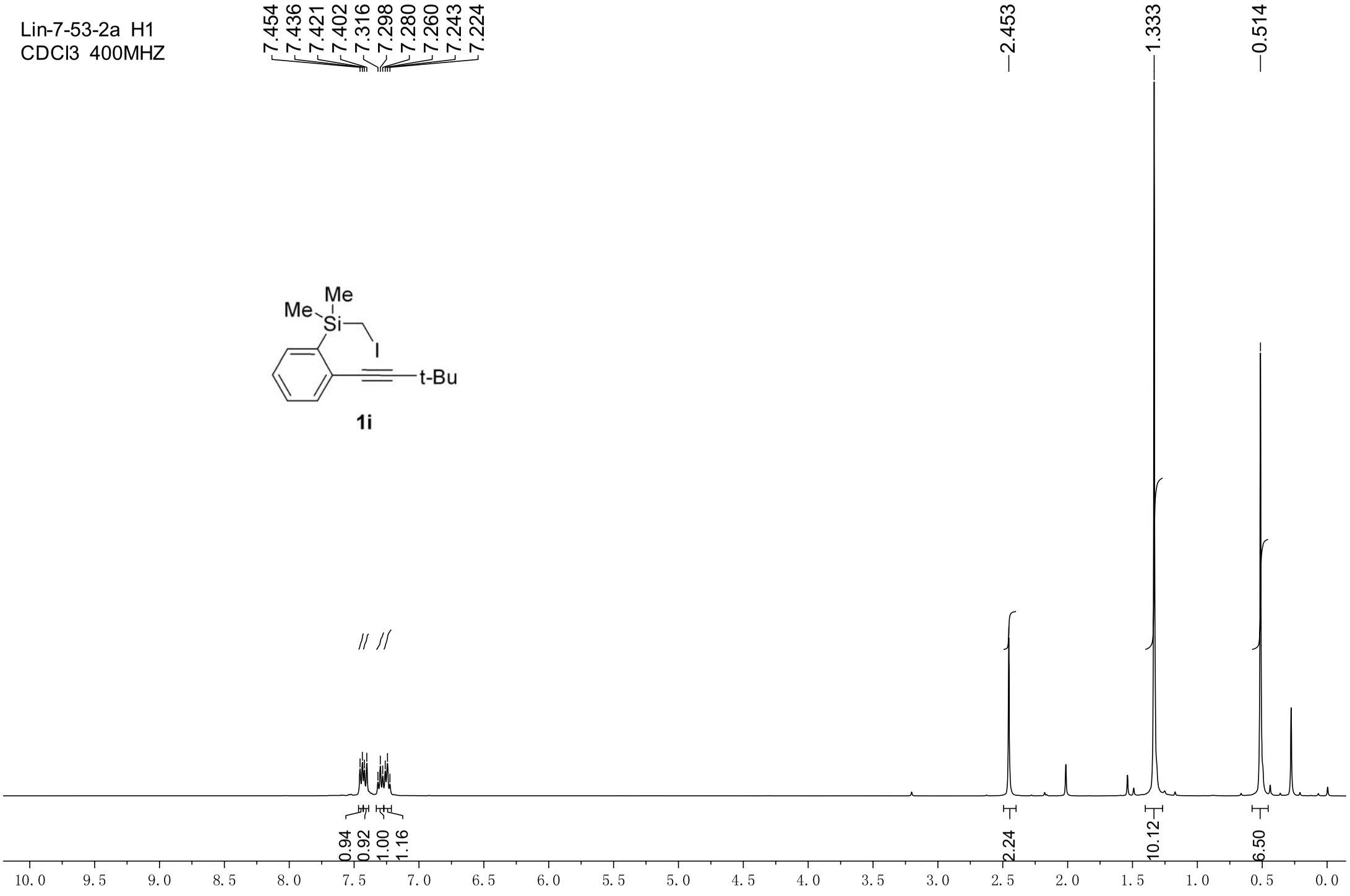
Lin-7-93-2 C13
CDCl3 100MHZ

138.681
134.311
132.653
129.351
128.174
127.464
94.894
84.281
77.317
77.000
76.684
59.412
25.828
25.292
18.223
-2.532
-2.557
-4.483
-4.893
-13.371



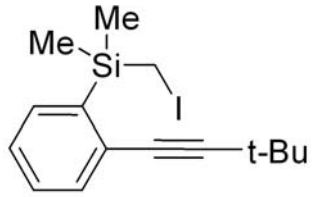
1h

Lin-7-53-2a H1
CDCl3 400MHZ

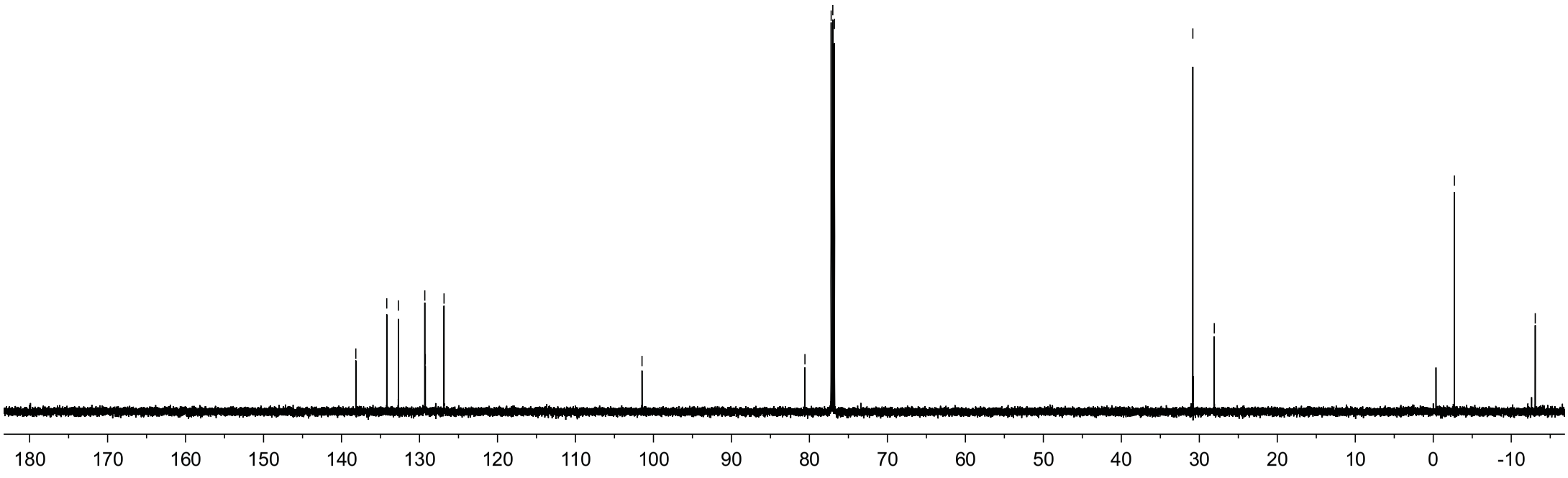


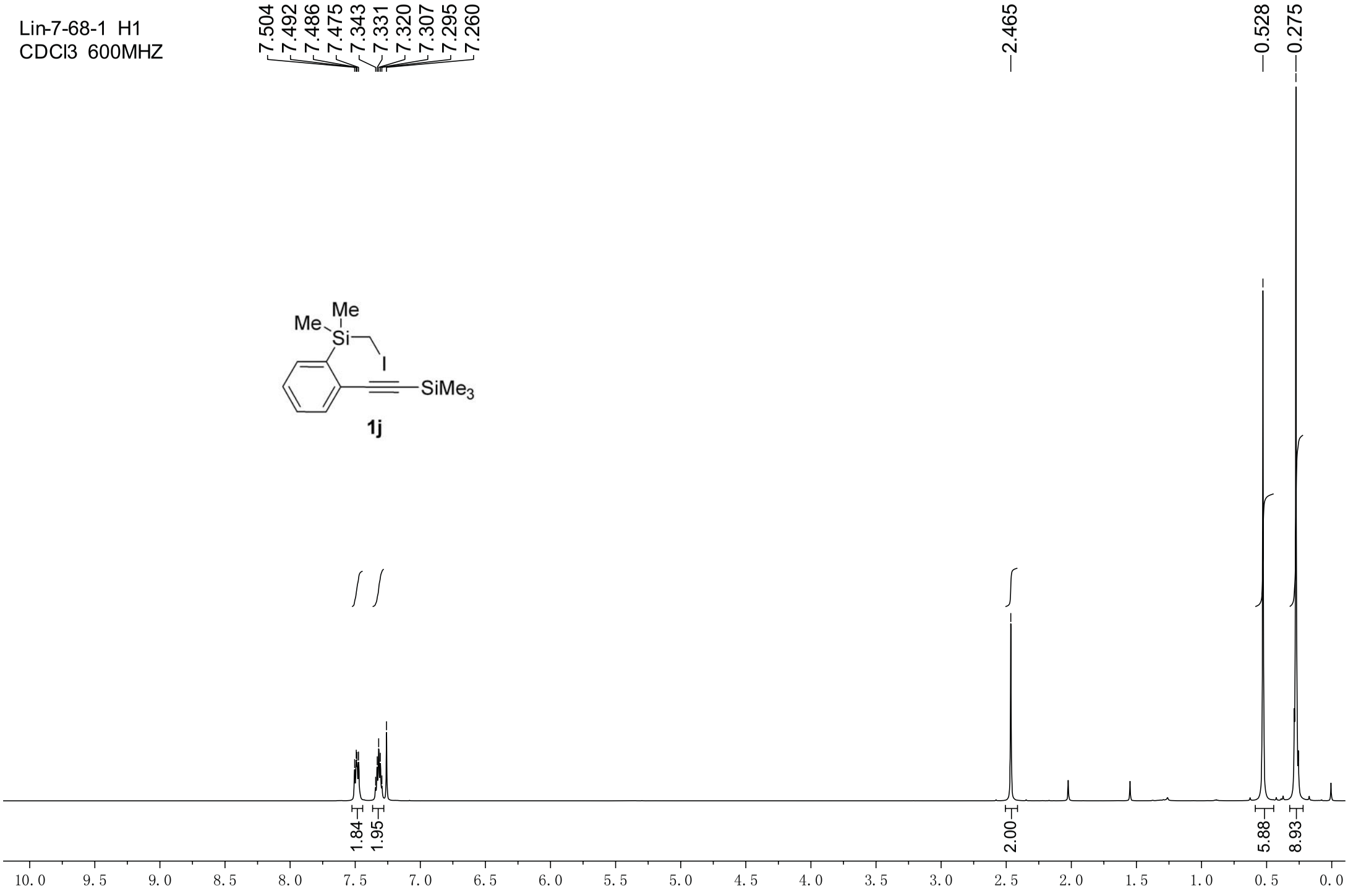
Lin-7-53-2a C13
CDCl3 150MHZ

138.166
134.198
132.714
129.322
129.254
126.856
101.466
80.575
77.212
77.000
76.789
30.829
28.082
-2.711
-13.080



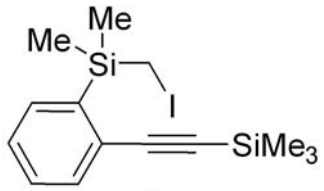
1i



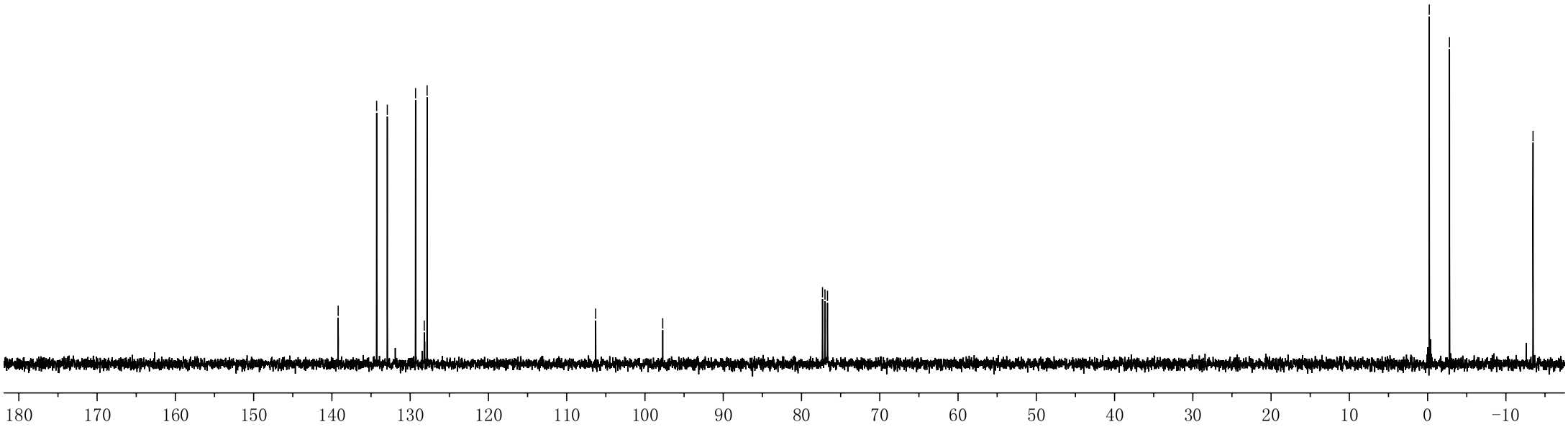

Lin-7-68-1 H1
CDCl3 600MHZ
7.504
7.492
7.486
7.475
7.343
7.331
7.320
7.307
7.295
7.260
2.465
0.528
0.275
Me
Me
Si
I
SiMe3
1j
1.84
1.95
2.00
5.88
8.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

Lin-7-68-1 C13
CDCl3 100MHZ

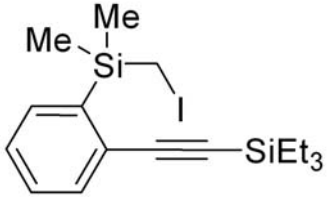
139.199
134.285
132.922
129.312
128.201
127.836
106.297
97.730
77.317
77.000
76.681
-0.208
-2.790
-13.468



1j



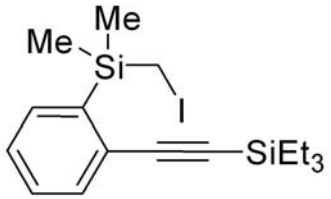
Lin-7-68-2 H1
CDCl3 400HMZ



1k

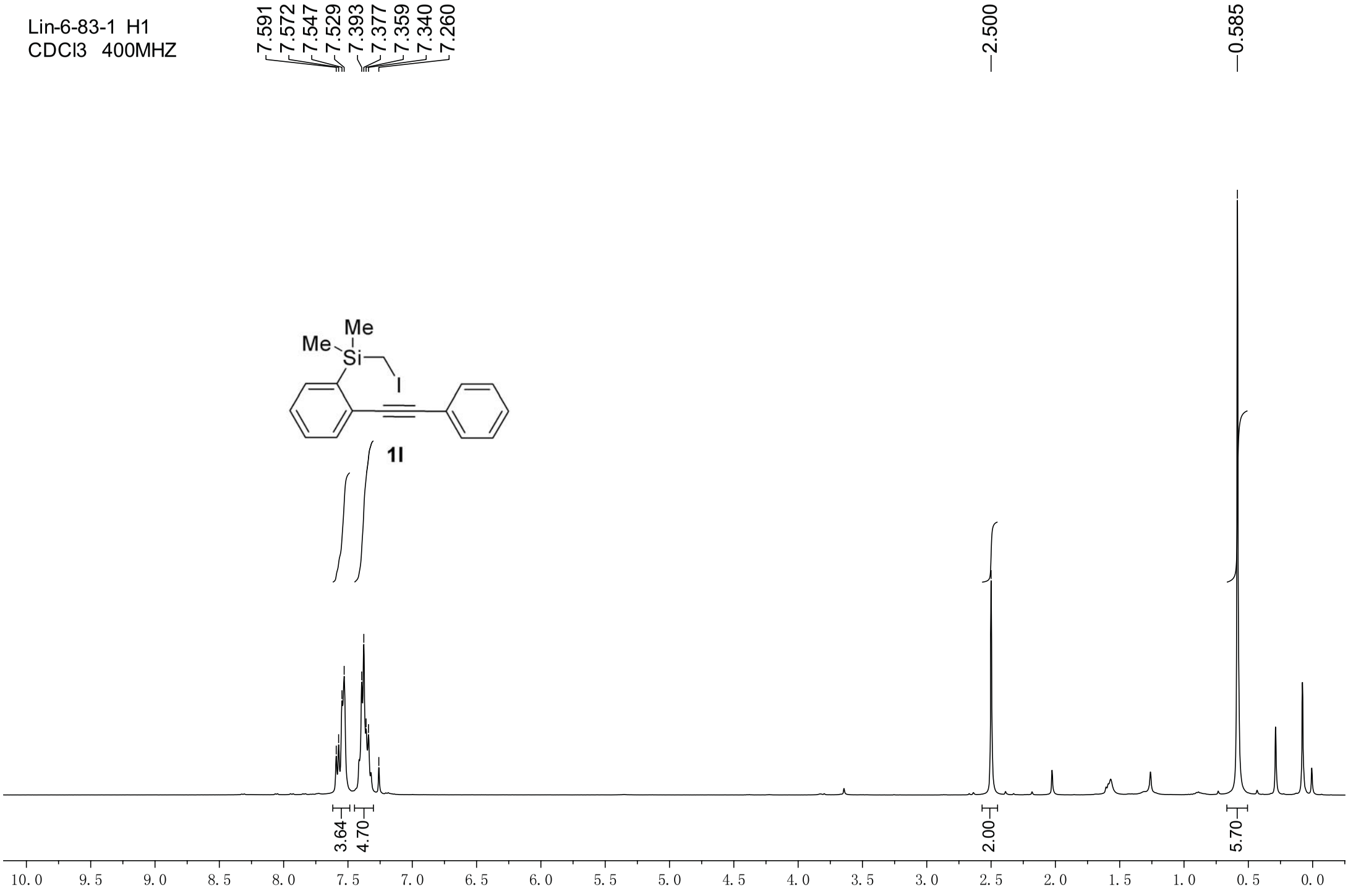
Lin-7-68-2 C13
CDCl3 100HMZ

138.882
134.273
133.561
129.291
128.397
127.738
107.271
95.612
77.317
77.000
76.684
7.508
4.300
-2.738
-13.365



1k

Lin-6-83-1 H1
CDCl3 400MHZ



Lin-6-83-1 C13
CDCl3 100MHZ

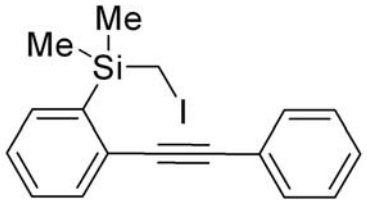
138.772
134.417
132.618
131.278
129.468
128.502
128.458
128.295
127.593
122.972

92.505
90.641

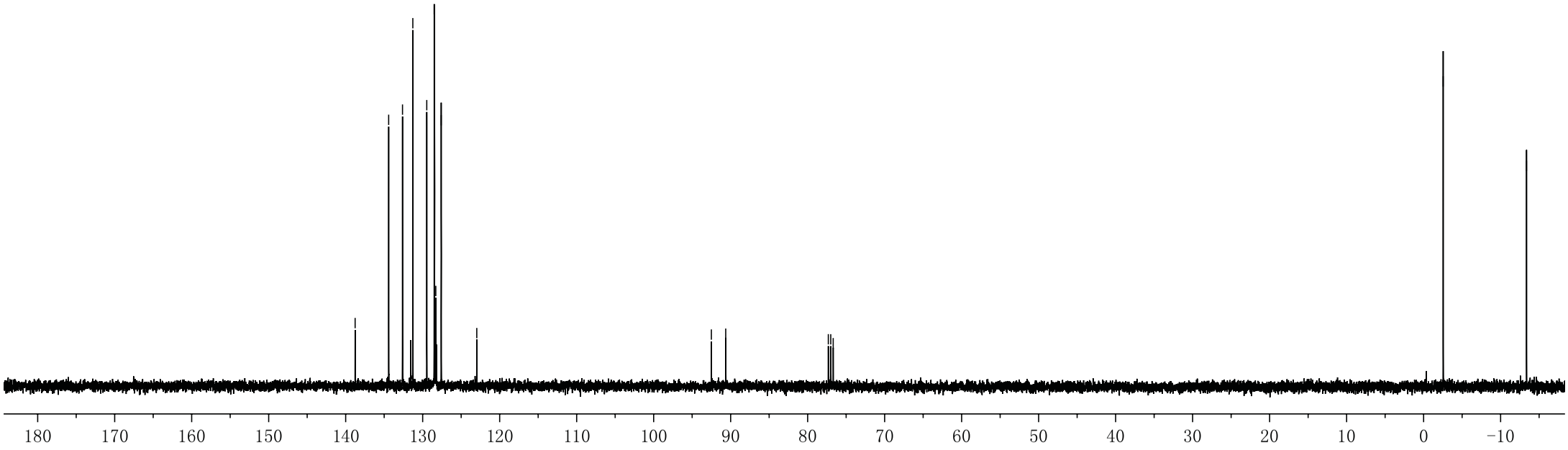
77.316
77.000
76.682

-2.538

-13.365



1l

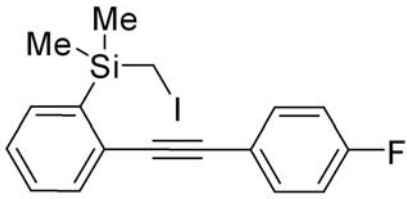


Lin-7-53-4a H1
CDCl3 400MHZ

7.577
7.556
7.531
7.517
7.510
7.496
7.413
7.395
7.376
7.361
7.343
7.325
7.260
7.108
7.086
7.065

2.479

0.578



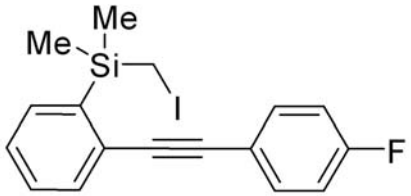
1m

4.02
2.24
1.84
2.00
5.59

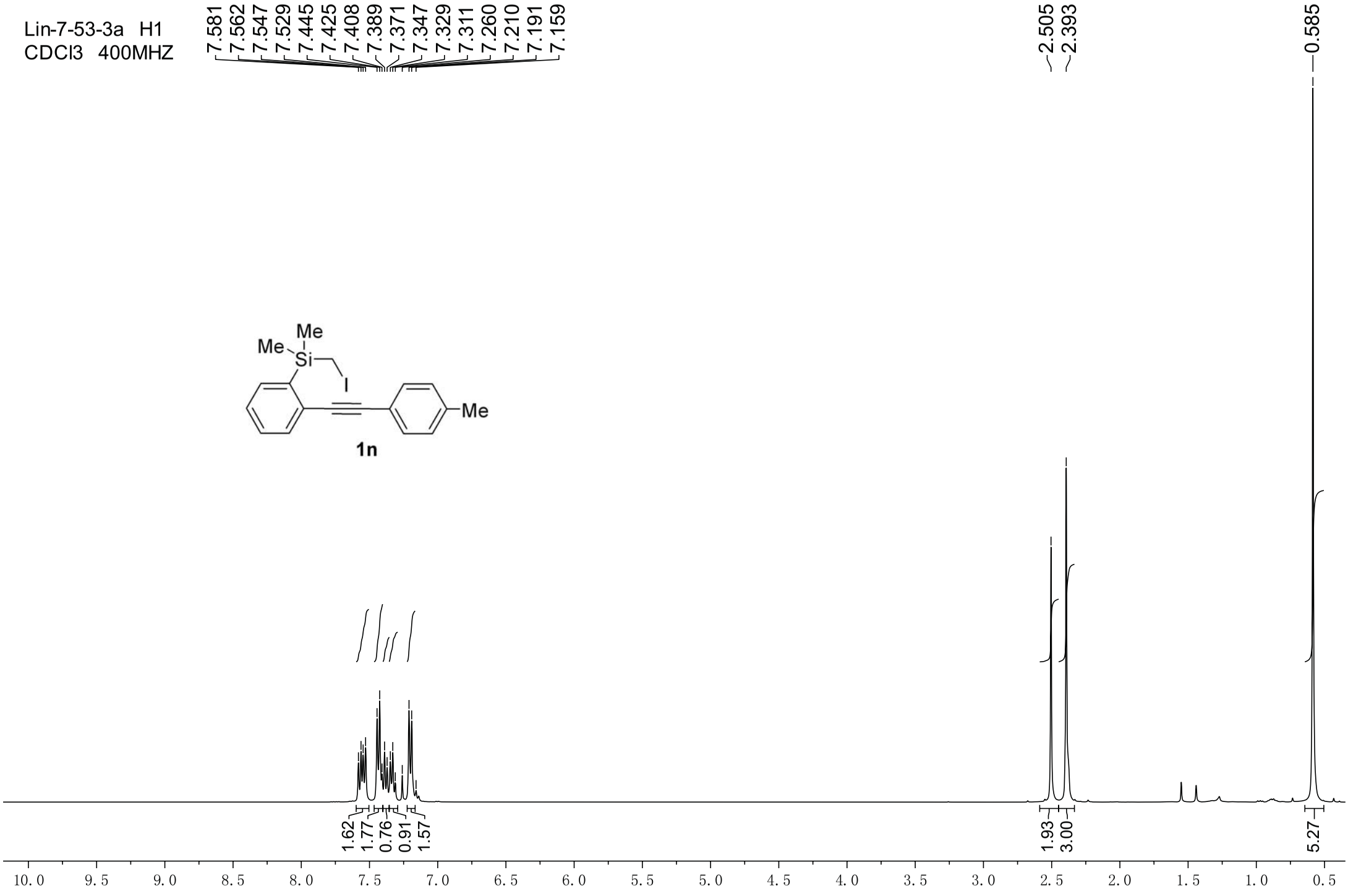
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

Lin-7-53-4a C13
CDCl3 150MHZ

163.436
161.779
138.774
134.461
133.228
133.173
132.603
129.516
128.162
127.691
119.125
119.102
115.948
115.802
91.450
90.343
77.212
77.000
76.789
-2.531
-13.509

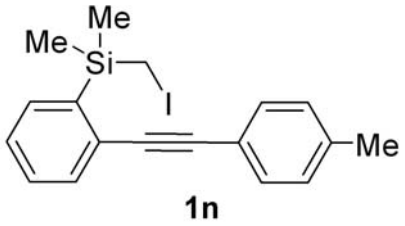


1m


Lin-7-53-3a H1
CDCl3 400MHZ
7.581
7.562
7.547
7.529
7.445
7.425
7.408
7.389
7.371
7.347
7.329
7.311
7.260
7.210
7.191
7.159
2.505
2.393
0.585
Me
Me
Si
I
Me
1n
1.62
1.77
0.76
0.91
1.57
1.93
3.00
5.27
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

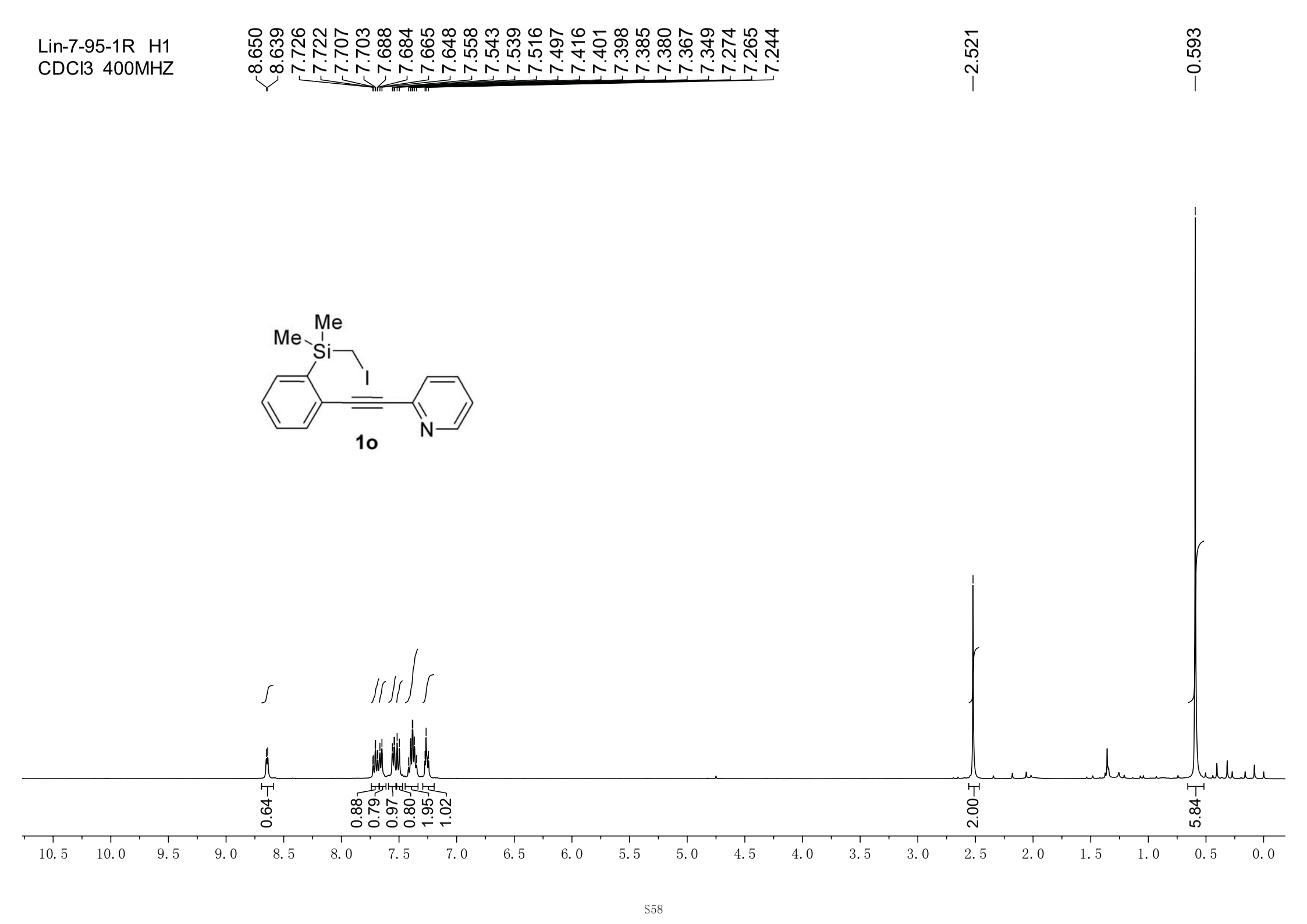
Lin-7-53-3a C13
CDCl3 100MHZ

138.683
134.411
132.520
131.205
129.468
129.289
128.575
127.430
119.951
92.754
90.046
77.212
77.000
76.788
21.532
-2.544
-13.287



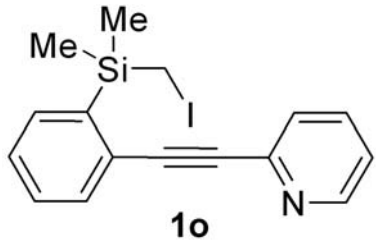
1n

Lin-7-95-1R H1
CDCl3 400MHZ

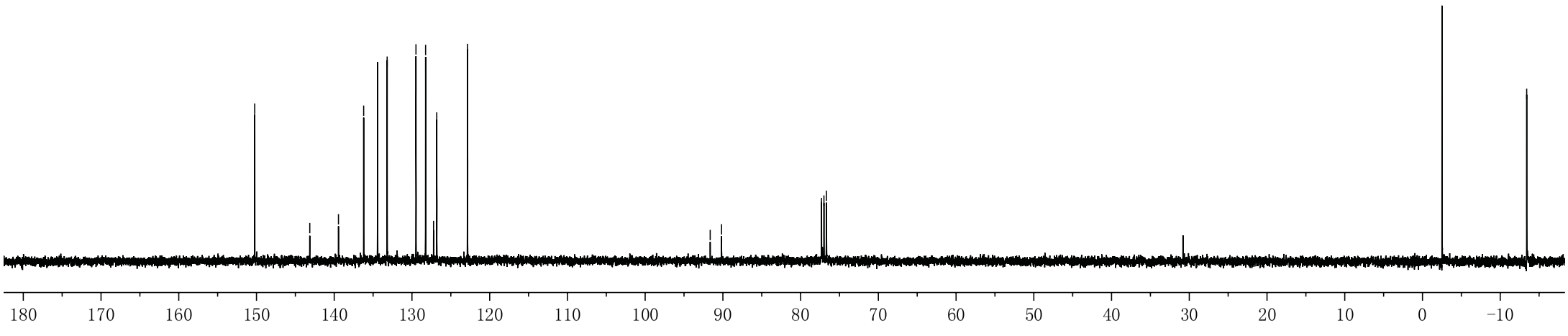


Lin-7-95-1R C13
CDCl3 100MHZ

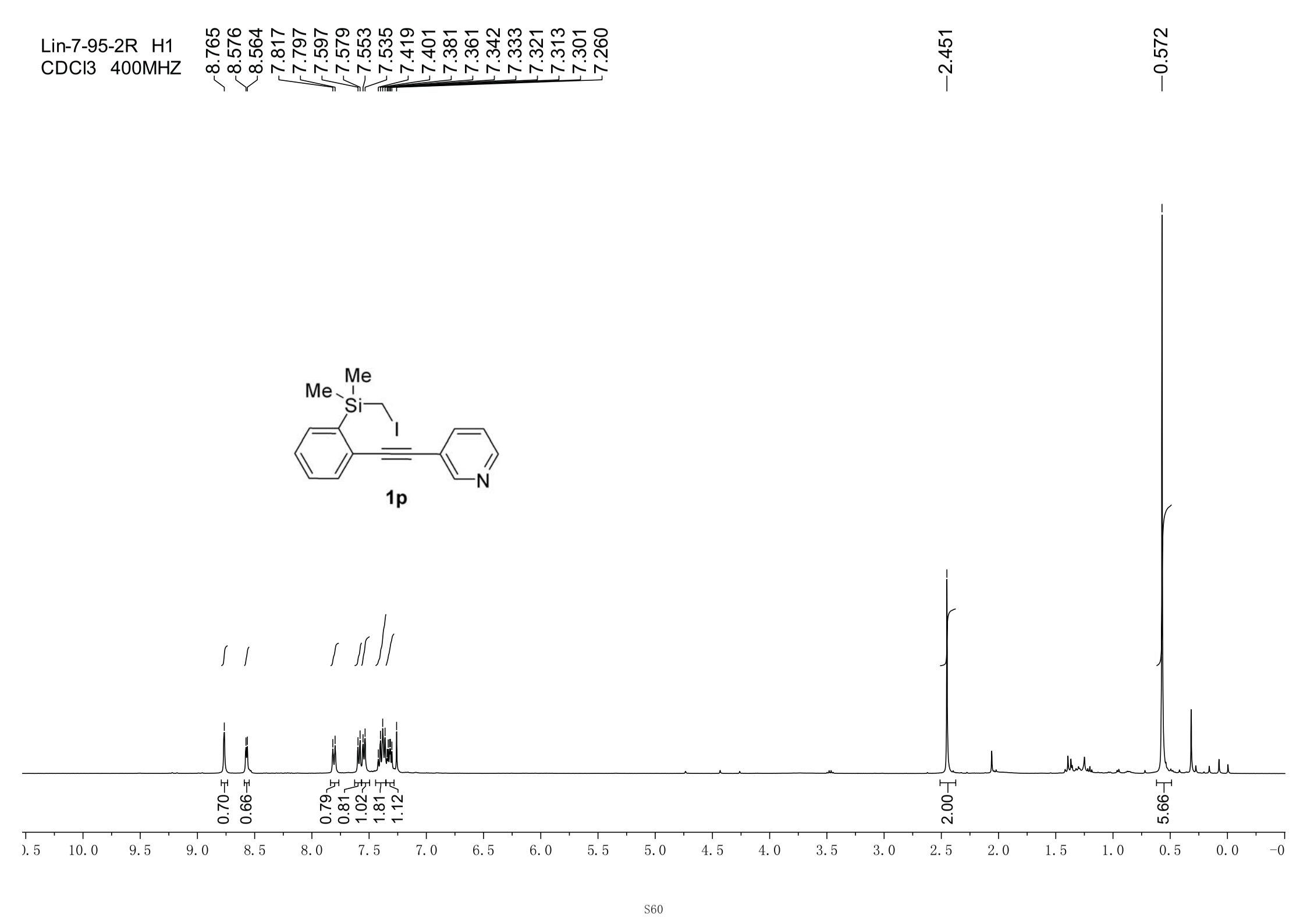
150.228
143.144
139.454
136.211
134.424
133.190
129.485
128.245
127.221
126.808
122.858
91.632
90.173
77.320
77.000
76.681
-2.511
-13.406



1o

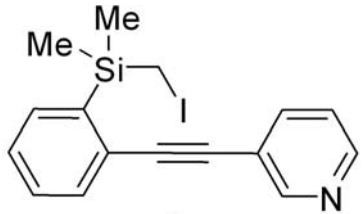


Lin-7-95-2R H1
CDCl3 400MHZ

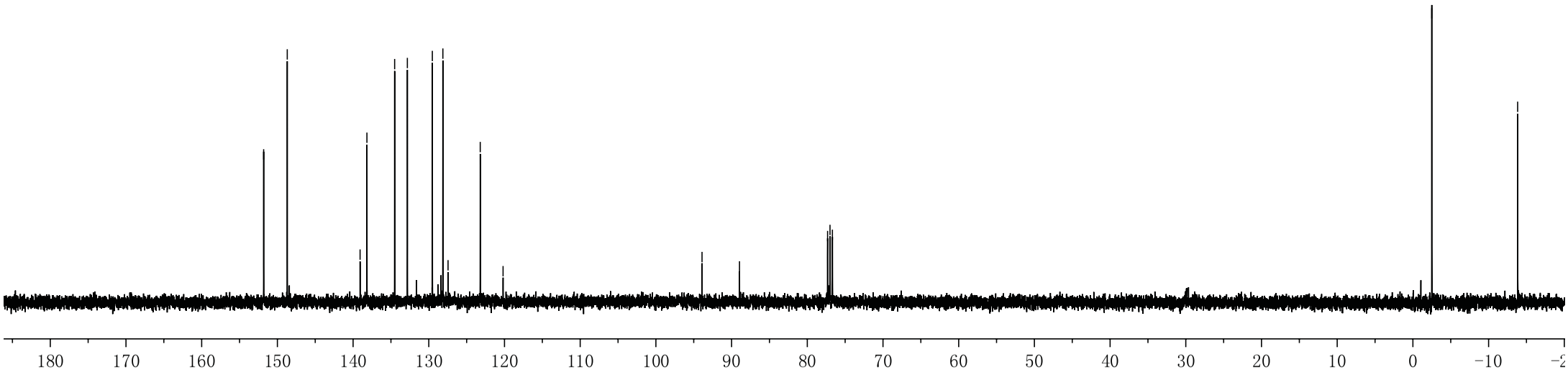


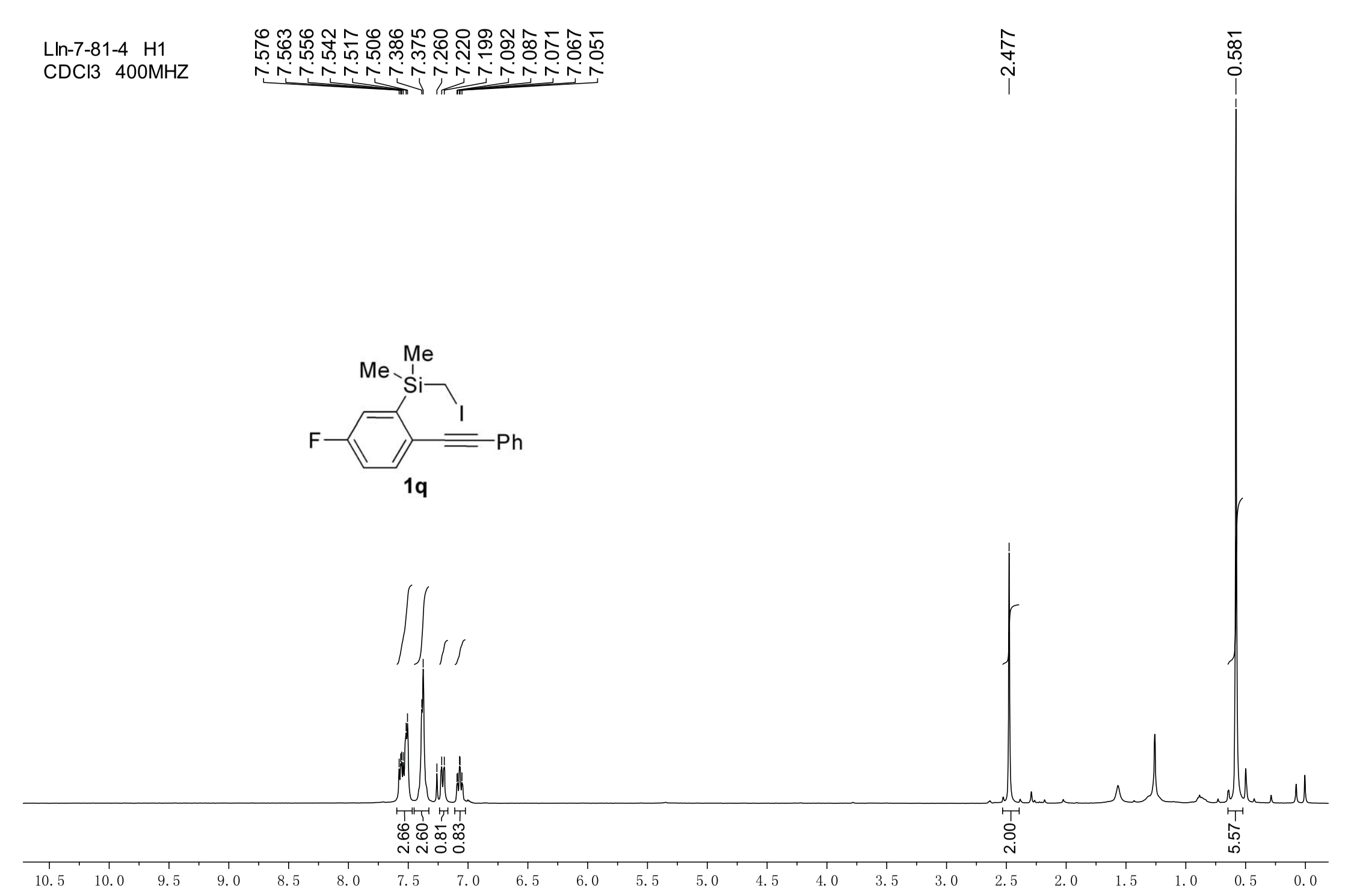
Lin-7-95-2R C13
CDCl3 100MHZ

151.813
148.697
139.076
138.172
134.510
132.832
129.532
128.140
127.456
123.204
120.188
93.906
88.956
77.319
77.000
76.684
-2.491
-13.837



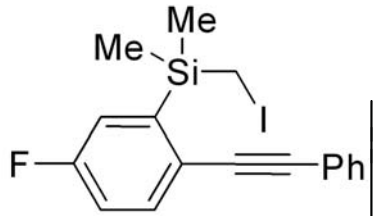
1p




LIn-7-81-4 H1
CDCl3 400MHZ
7.576
7.563
7.556
7.542
7.517
7.506
7.386
7.375
7.260
7.220
7.199
7.092
7.087
7.071
7.067
7.051
2.477
0.581
Me
Me
Si
I
F
Ph
1q
2.66
2.60
0.81
0.83
2.00
5.57
10.5
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

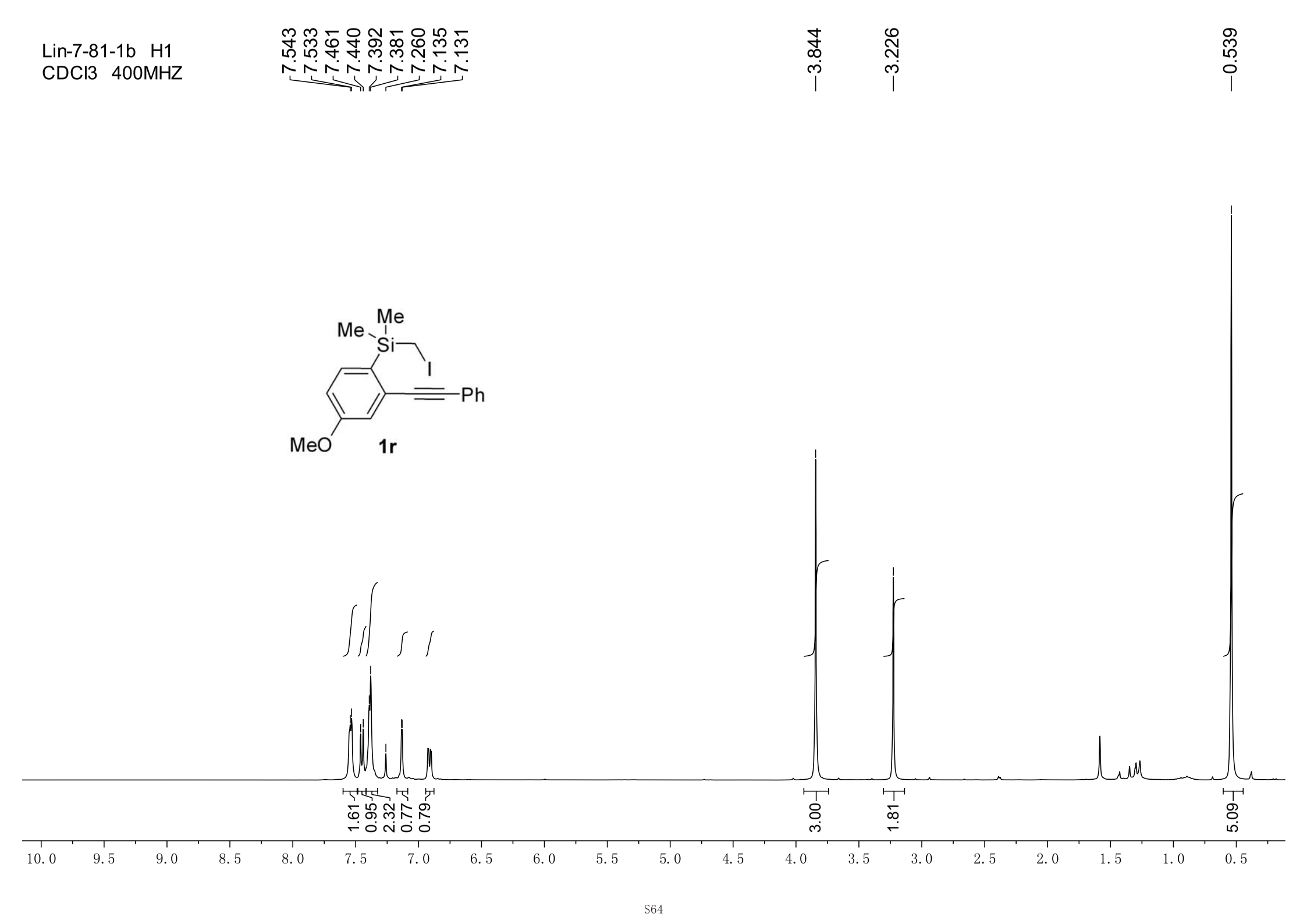
LIn-7-81-4 C13
CDCl3 100MHZ

163.248
160.602
142.210
142.163
134.753
134.678
131.523
131.224
128.540
128.530
128.344
128.322
121.374
121.175
116.727
116.509
92.074
89.660
77.316
77.000
76.671
-2.721
-14.335



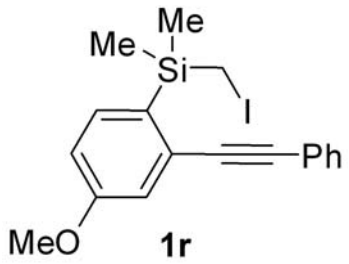
1q

Lin-7-81-1b H1
CDCl3 400MHZ

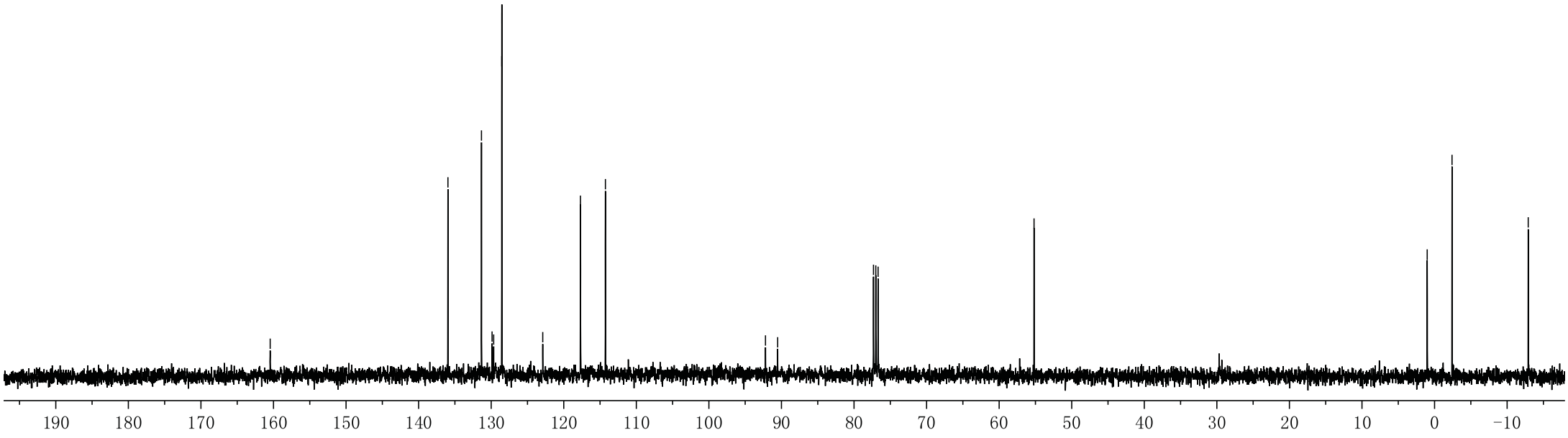


Lin-7-81-1b C13
CDCl3 100MHZ

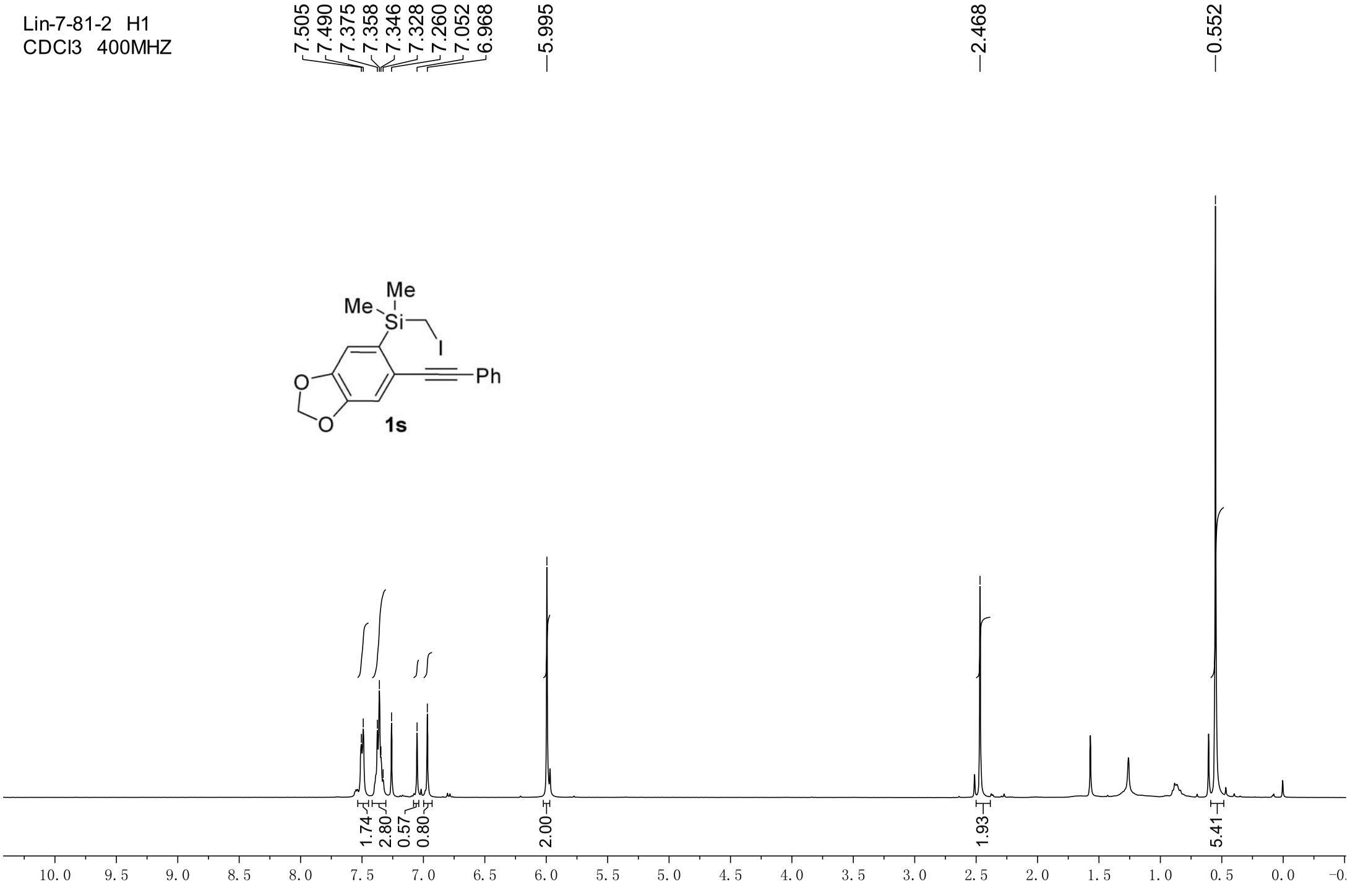
160.456
135.961
131.341
129.879
129.658
128.542
128.528
122.896
117.700
114.259
92.201
90.522
77.318
77.000
76.682
55.191
1.013
-2.408
-12.908



1r

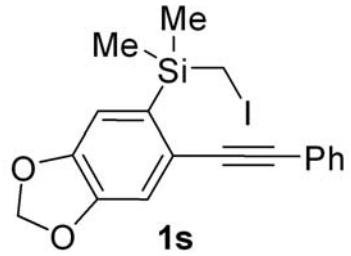


Lin-7-81-2 H1
CDCl3 400MHZ

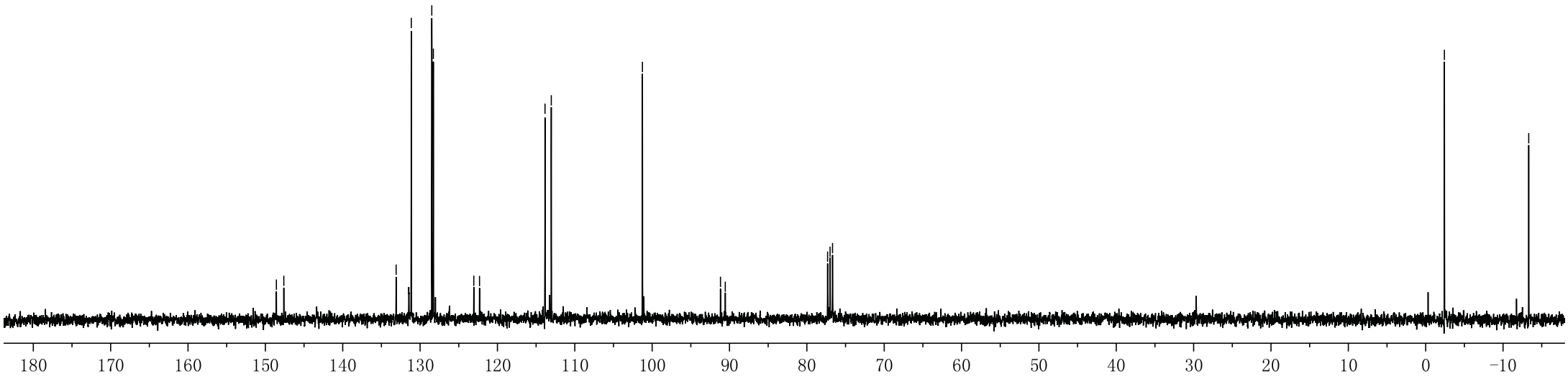


Lin-7-81-2 C13
CDCl3 100MHZ

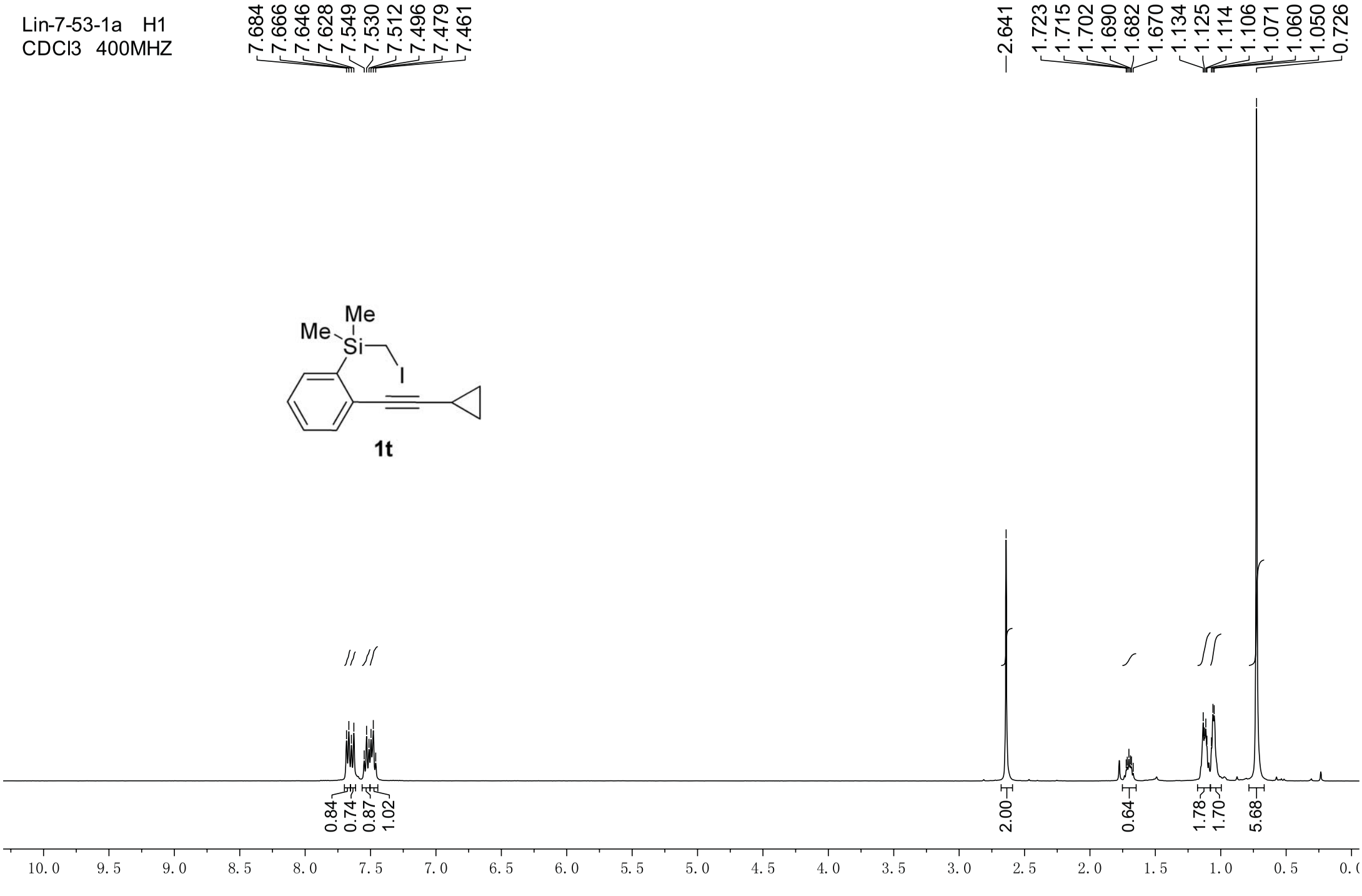
148.577
147.615
133.096
131.139
128.486
128.283
123.055
122.315
113.850
113.040
101.256
91.168
90.547
77.317
77.000
76.681
-2.416
-13.320



1s



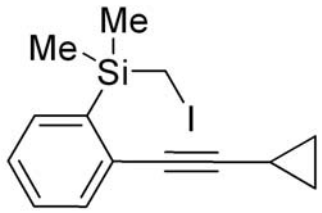
Lin-7-53-1a H1
CDCl3 400MHZ



1t

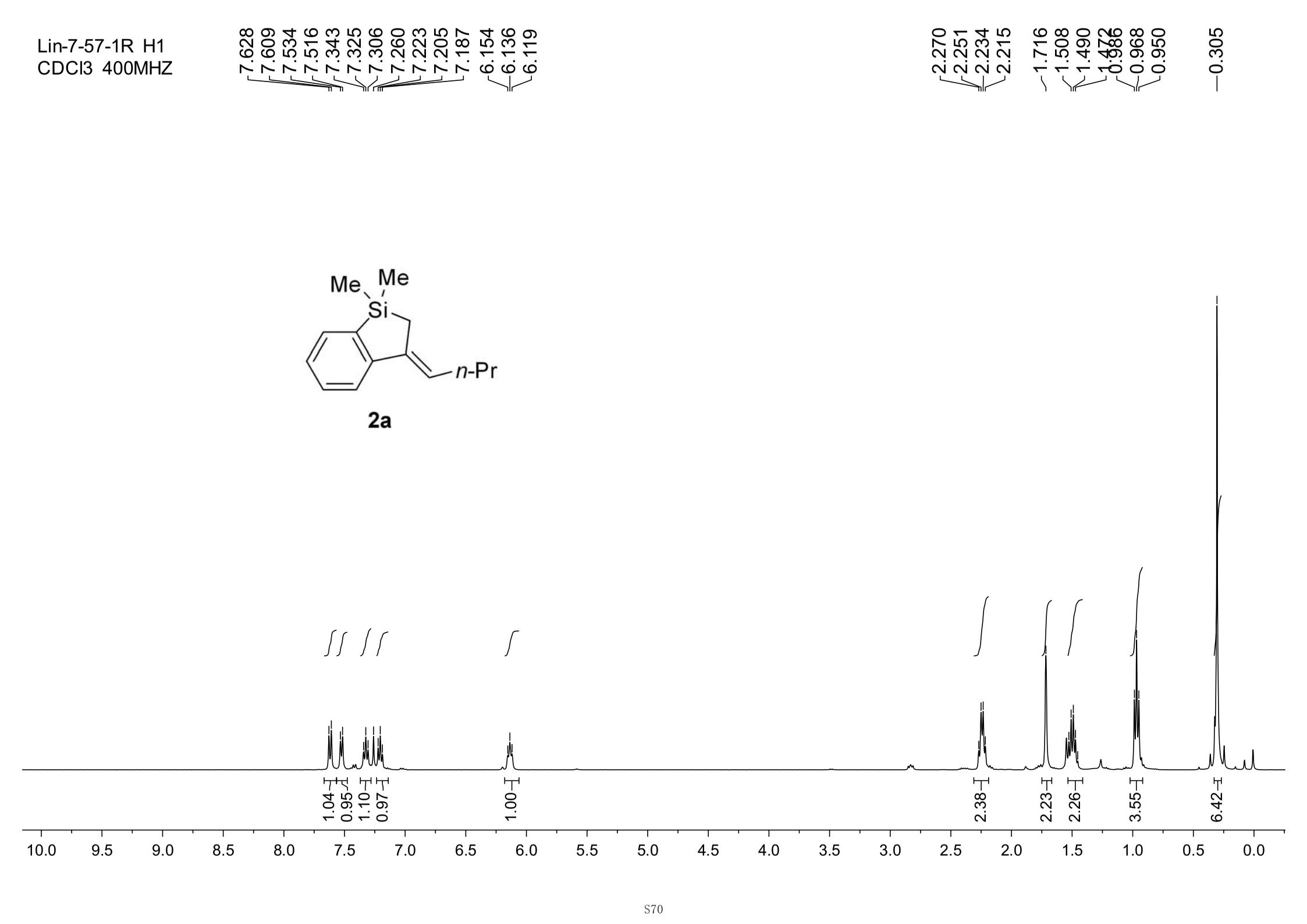
Lin-7-53-1a C13
CDCl3 100MHZ

138.496
134.218
132.506
129.353
129.132
126.844
112.471
96.636
77.212
77.000
76.788
8.252
0.267
-2.669
-13.217

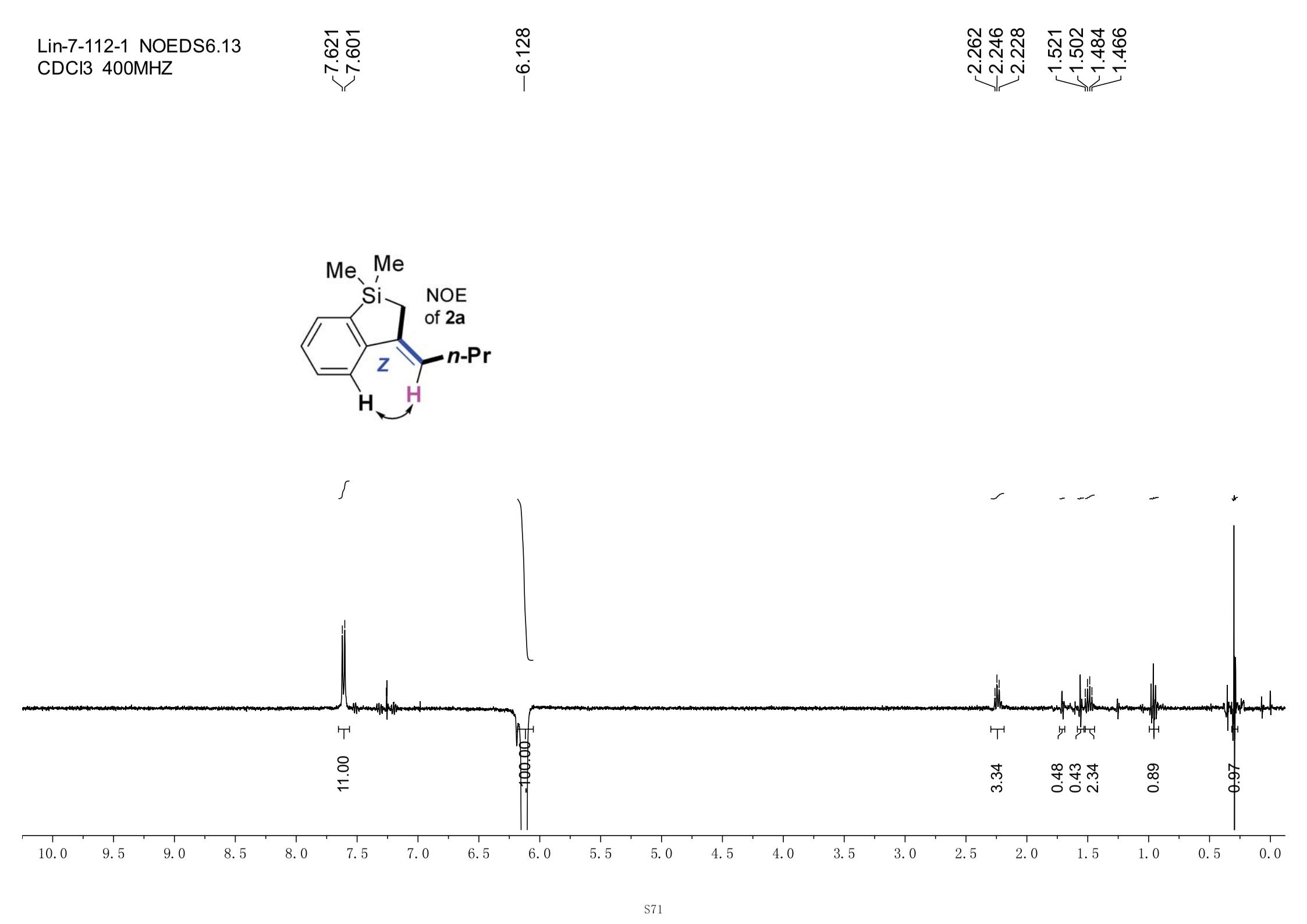


1t

Lin-7-57-1R H1
CDCl3 400MHZ

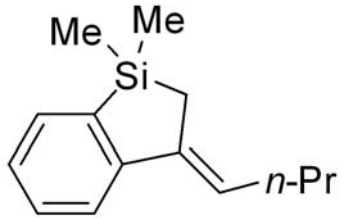


Lin-7-112-1 NOEDS6.13
CDCl3 400MHZ

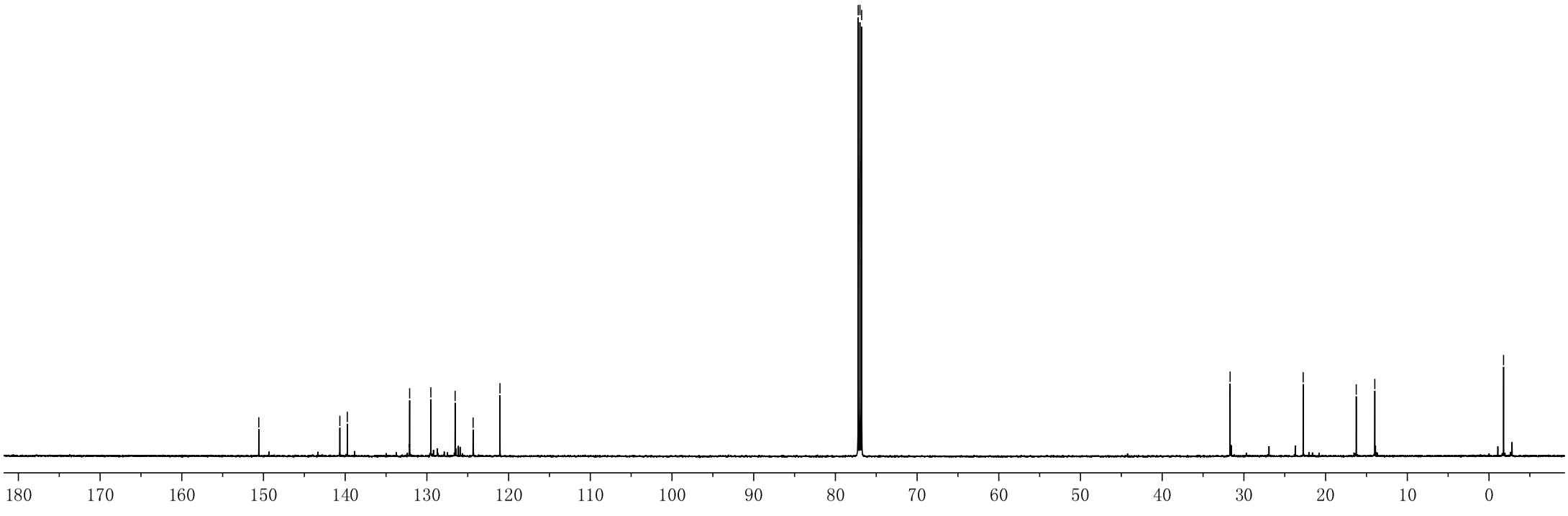


Lin-7-44-1a C13
CDCl3 150MHZ

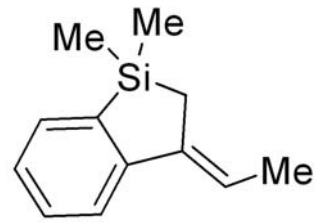
150.573
140.654
139.742
132.113
129.517
126.547
124.345
121.057
77.212
77.000
76.789
31.688
22.747
16.250
13.977
-1.783



2a



Lin-7-104-3 H1
CDCl3 400MHZ

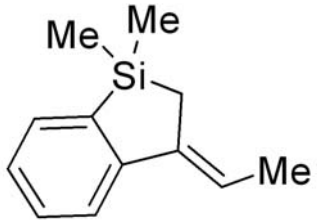


2b

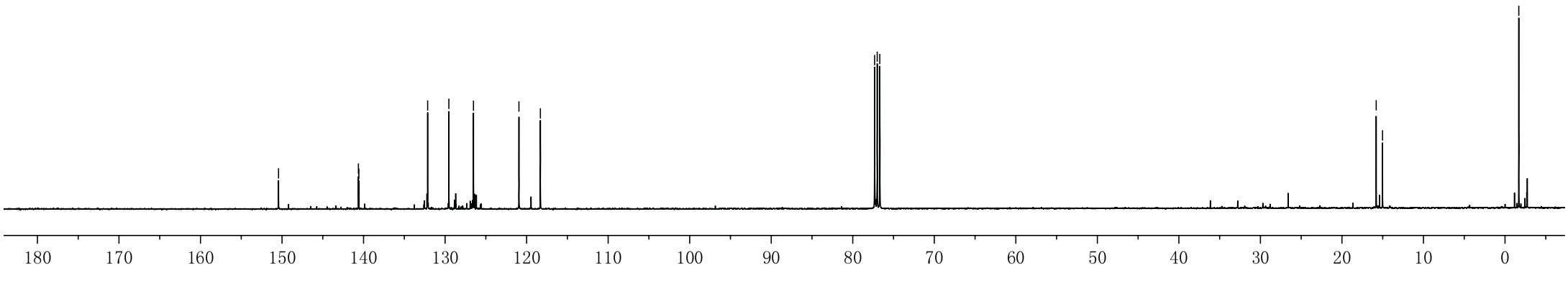
***Z*- isomer** **E- isomer**

Lin-7-104-3 C13
CDCl3 100MHZ

150.427
140.630
140.577
132.137
129.537
126.520
120.943
118.313
77.318
77.000
76.683
15.799
15.024
1.691



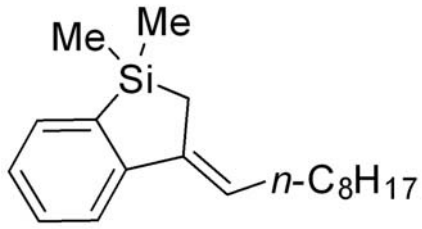
2b



Lin-7-91-4 H1
CDCl3 400MHZ

7.615 7.595 7.523 7.506 7.423 7.404 7.314 7.296 7.273 7.251 7.238 7.212 7.194 7.176 6.140 6.122 6.104 5.589 5.571 5.553

2.860 2.841 2.821 2.254 2.232 1.869 1.703 1.475 1.457 1.277 0.896 0.881 0.864 0.314 0.297 0.284 0.000

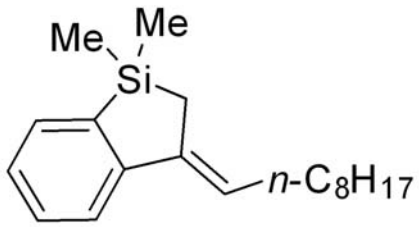


2c

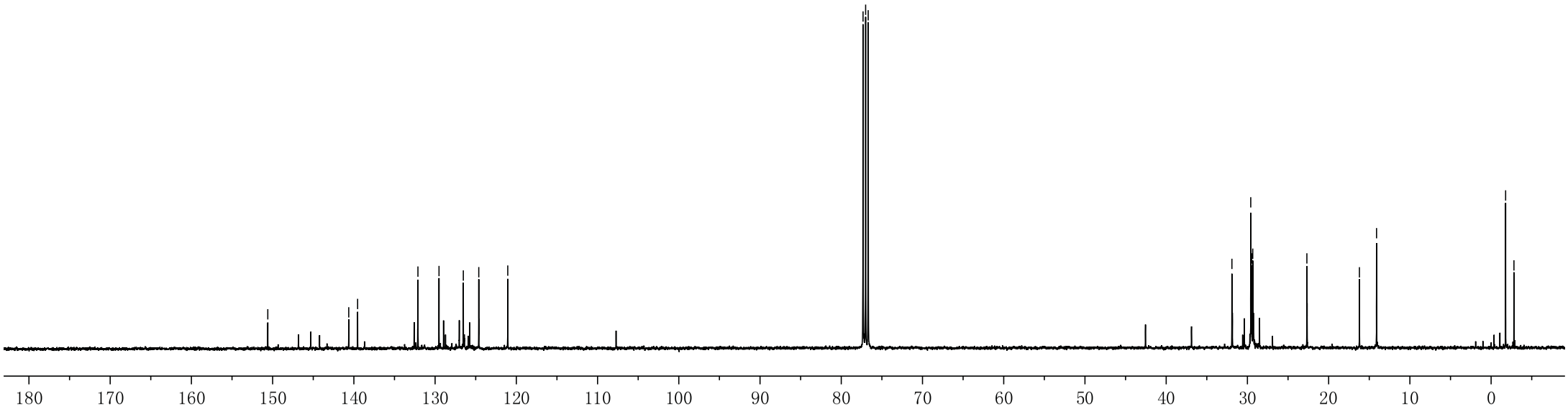
***Z*- isomer** **E- isomer**

Lin-7-91-4 C13
CDCl3 100MHZ

150.596
140.631
139.538
132.113
129.518
126.526
124.623
121.055
77.318
77.000
76.683
31.909
29.590
29.557
29.472
29.344
22.680
16.212
14.103
-1.786
-2.811

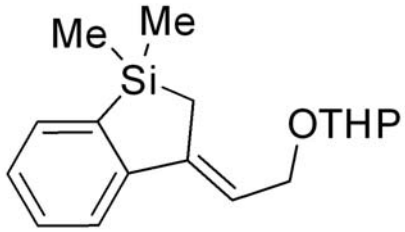


2c



Lin-7-66-3R H1
CDCl3 400MHZ

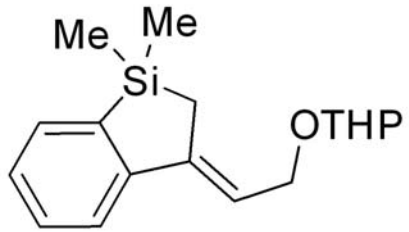
7.676 7.656 7.546 7.528 7.364 7.362 7.345 7.327 7.268 7.260 7.251 7.233 6.276 6.260 6.243 4.709 4.701 4.691 4.515 4.500 4.484 4.469 4.361 4.342 4.329 4.311 3.964 3.943 3.916 3.553 3.540 3.526 1.881 1.858 1.775 1.753 1.745 1.631 1.594 1.580 1.563 0.309



2d

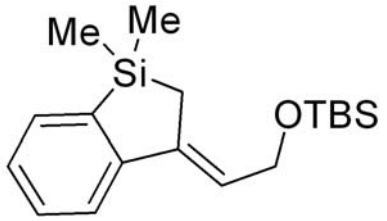
Lin-7-66-3R C13
CDCl3 100MHZ

149.607
143.239
141.226
132.089
129.619
127.407
121.726
119.673
97.897
77.318
77.000
76.683
65.132
62.398
30.754
25.497
19.640
16.351
-1.799
-1.838



2d

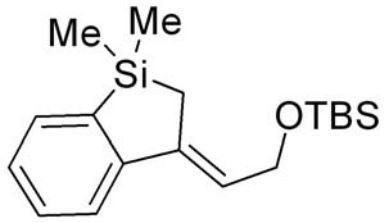
Lin-7-66-1R H1
CDCl3 400MHZ



2e

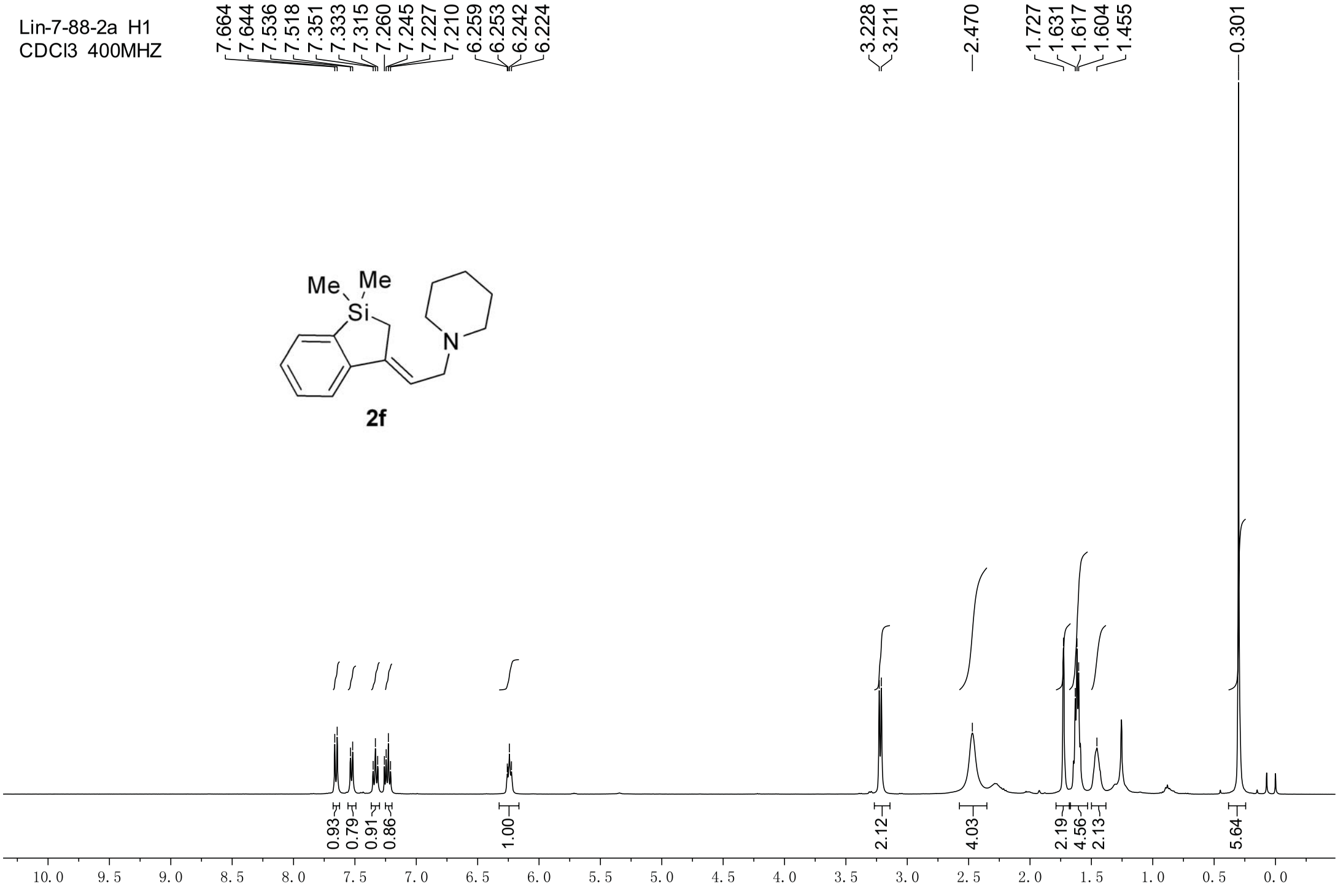
Lin-7-104-2 C13
CDCl3 100MHZ

149.809
140.941
140.205
132.070
129.633
127.206
123.565
121.613
77.317
77.000
76.682
61.922
26.023
18.444
16.298
-1.800
-5.008



2e

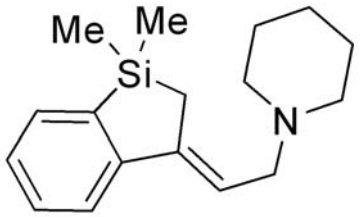
Lin-7-88-2a H1
CDCl3 400MHZ



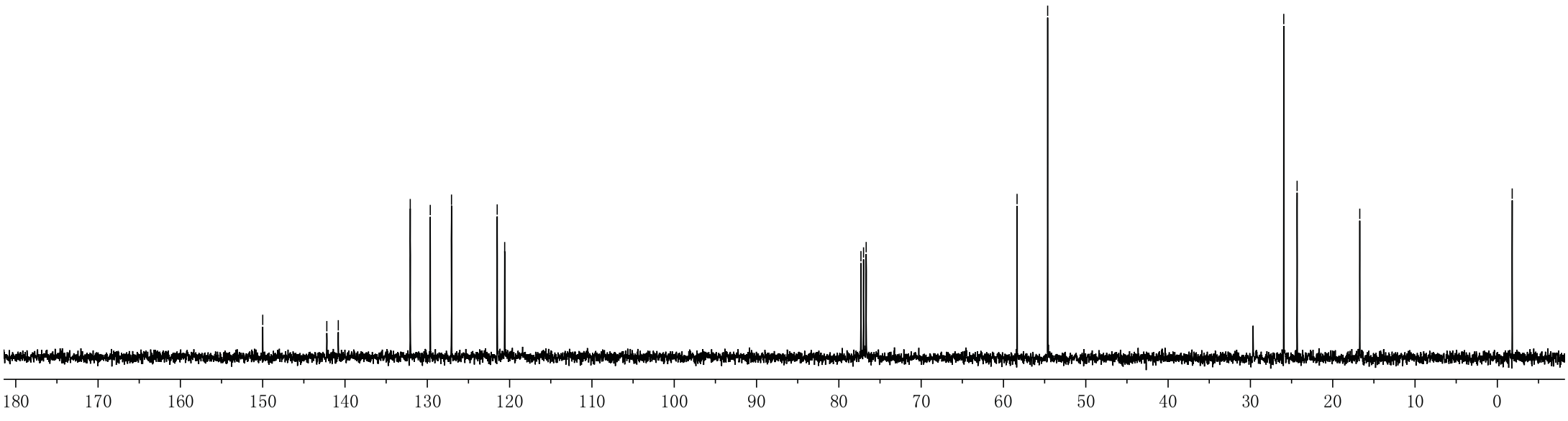
2f

Lin-7-88-2a C13
CDCl3 100MHZ

149.995
142.209
140.816
132.074
129.641
127.061
121.509
120.599
77.318
77.000
76.681
58.350
54.633
25.949
24.328
16.715
-1.805

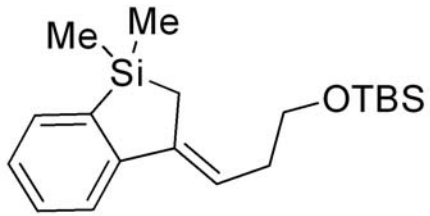


2f



Lin-7-66-2R H1
CDCl3 400MHZ

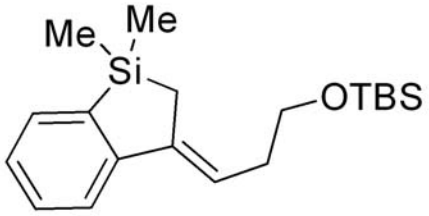
7.617
7.597
7.535
7.518
7.347
7.328
7.309
7.260
7.233
7.216
7.198
6.152
6.146
6.134
6.116
3.749
3.731
3.714
2.537
2.519
2.502
2.484
1.733
0.918
0.306
0.084



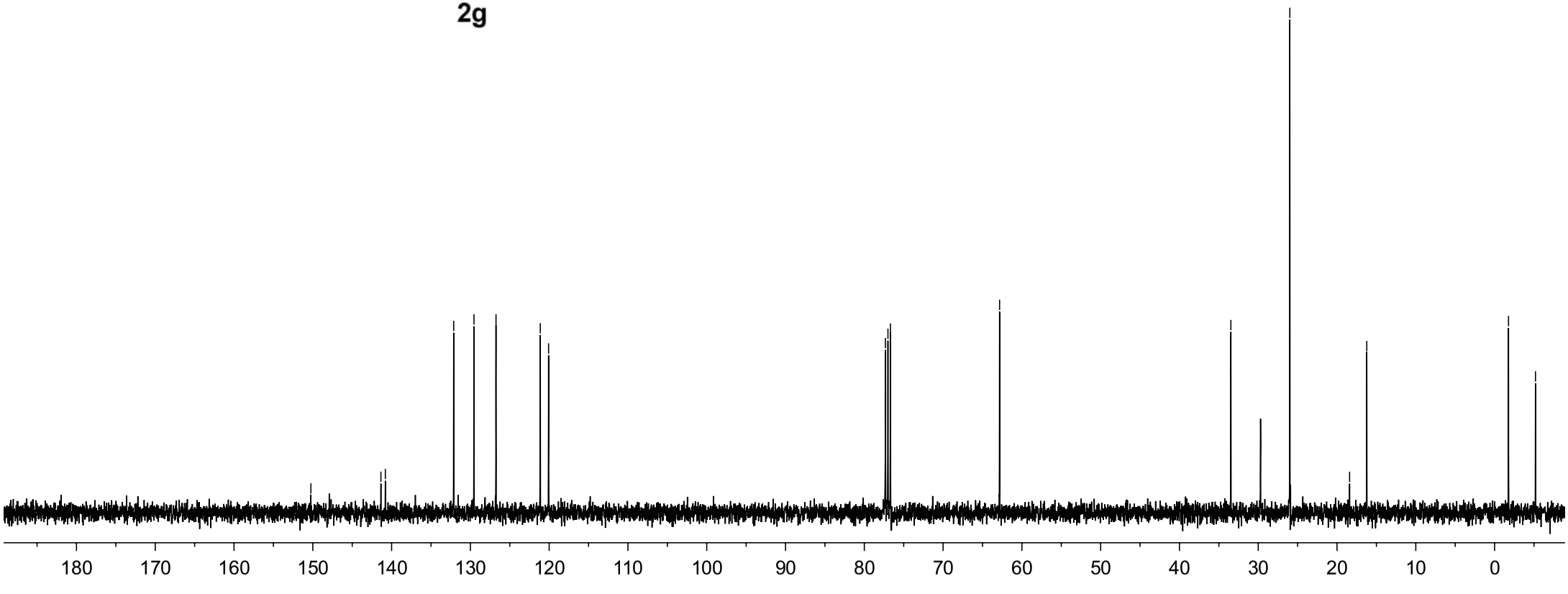
2g

Lin-7-66-2R C13
CDCl3 100MHZ

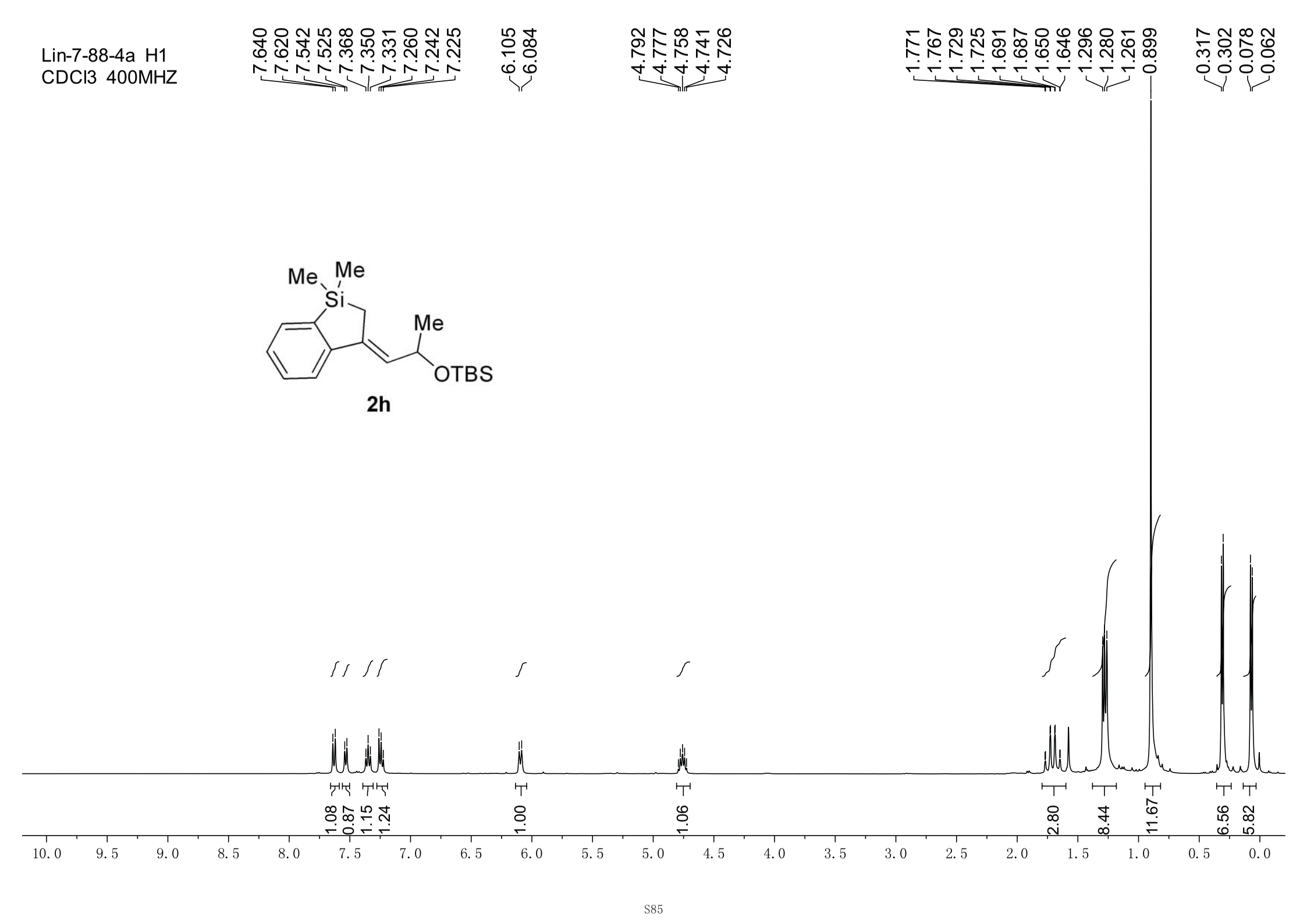
150.244
141.355
140.795
132.118
129.548
126.748
121.129
120.075
77.319
77.000
76.682
62.829
33.472
25.989
18.403
16.222
-1.767
-5.193



2g

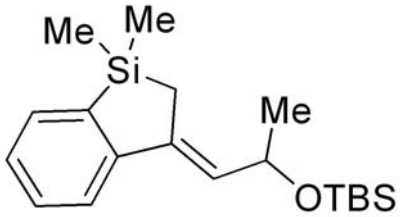


Lin-7-88-4a H1
CDCl3 400MHZ



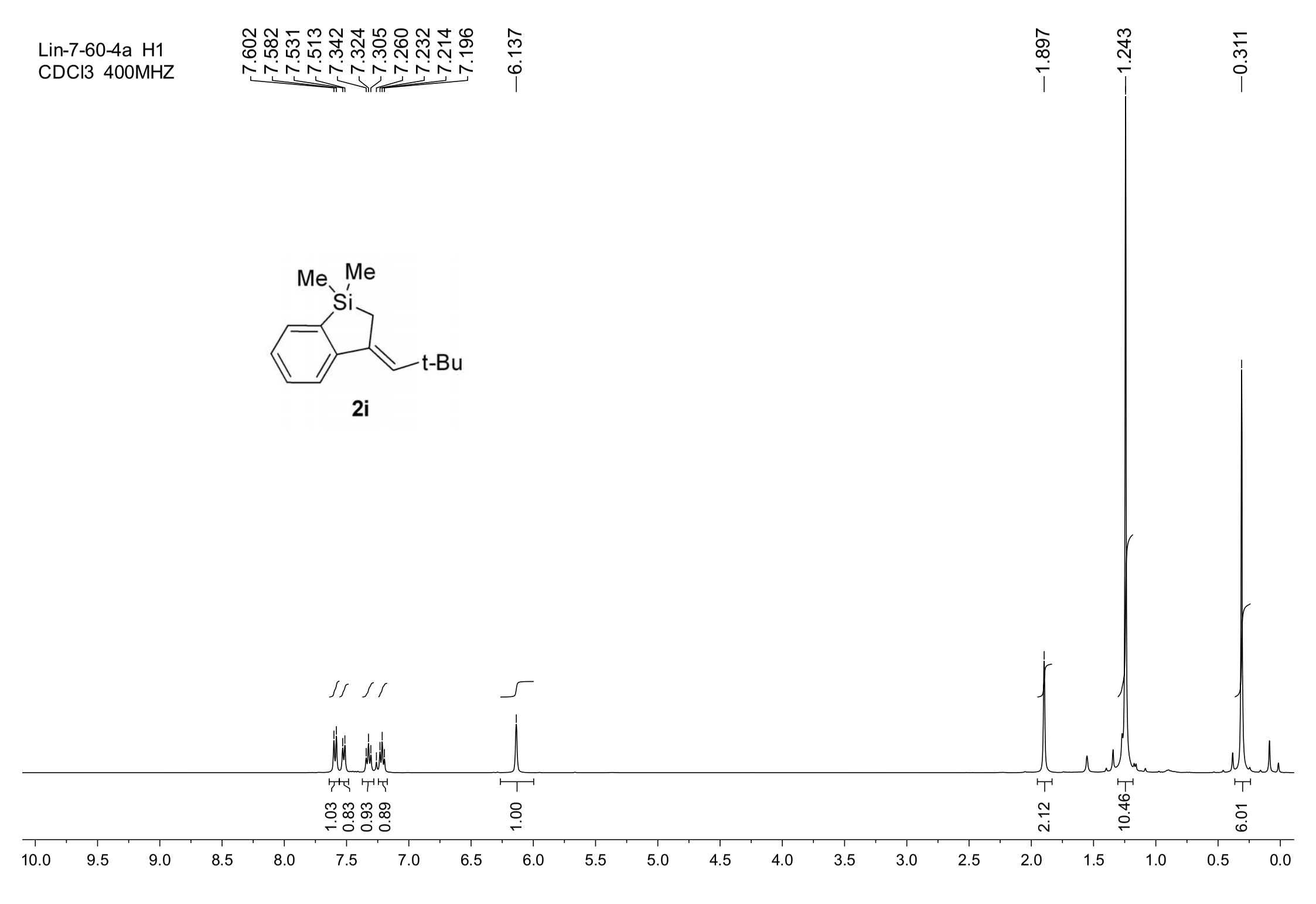
Lin-7-88-4a 13
CDCl3 100MHZ

150.126
140.801
137.655
132.052
129.674
129.198
127.132
121.619
77.320
77.000
76.685
67.577
25.936
24.313
18.309
16.514
-1.817
-1.983
-4.392
-4.659



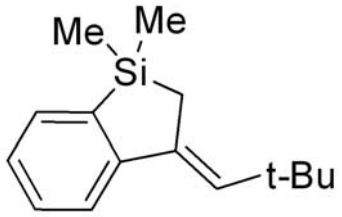
2h

Lin-7-60-4a H1
CDCl3 400MHZ

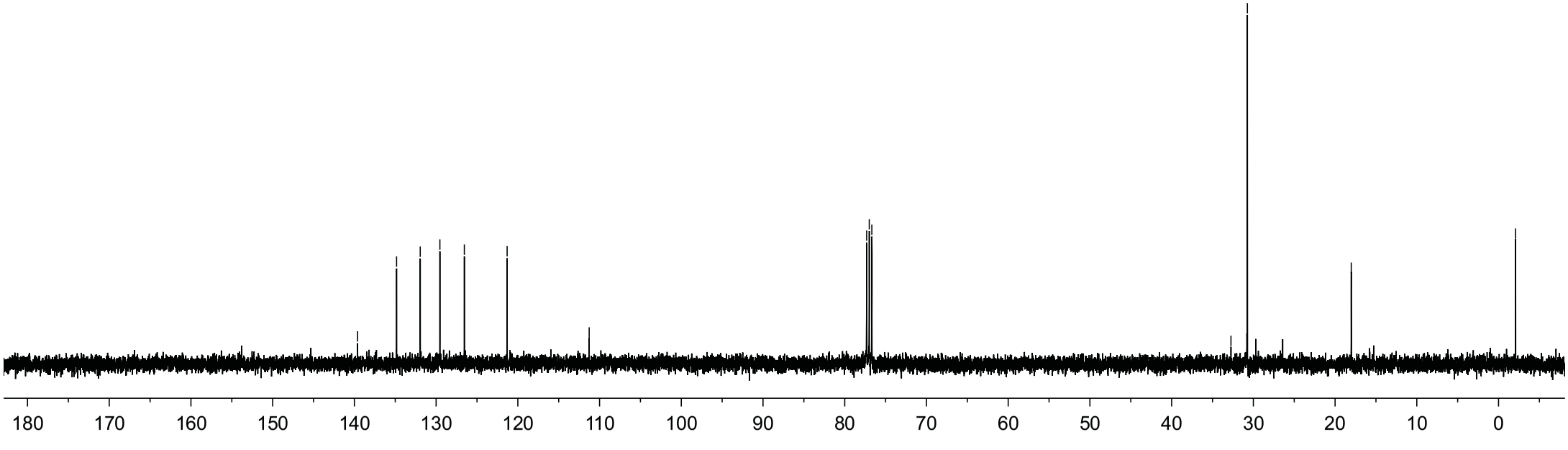


Lin-7-60-4a C13
CDCl3 100MHZ

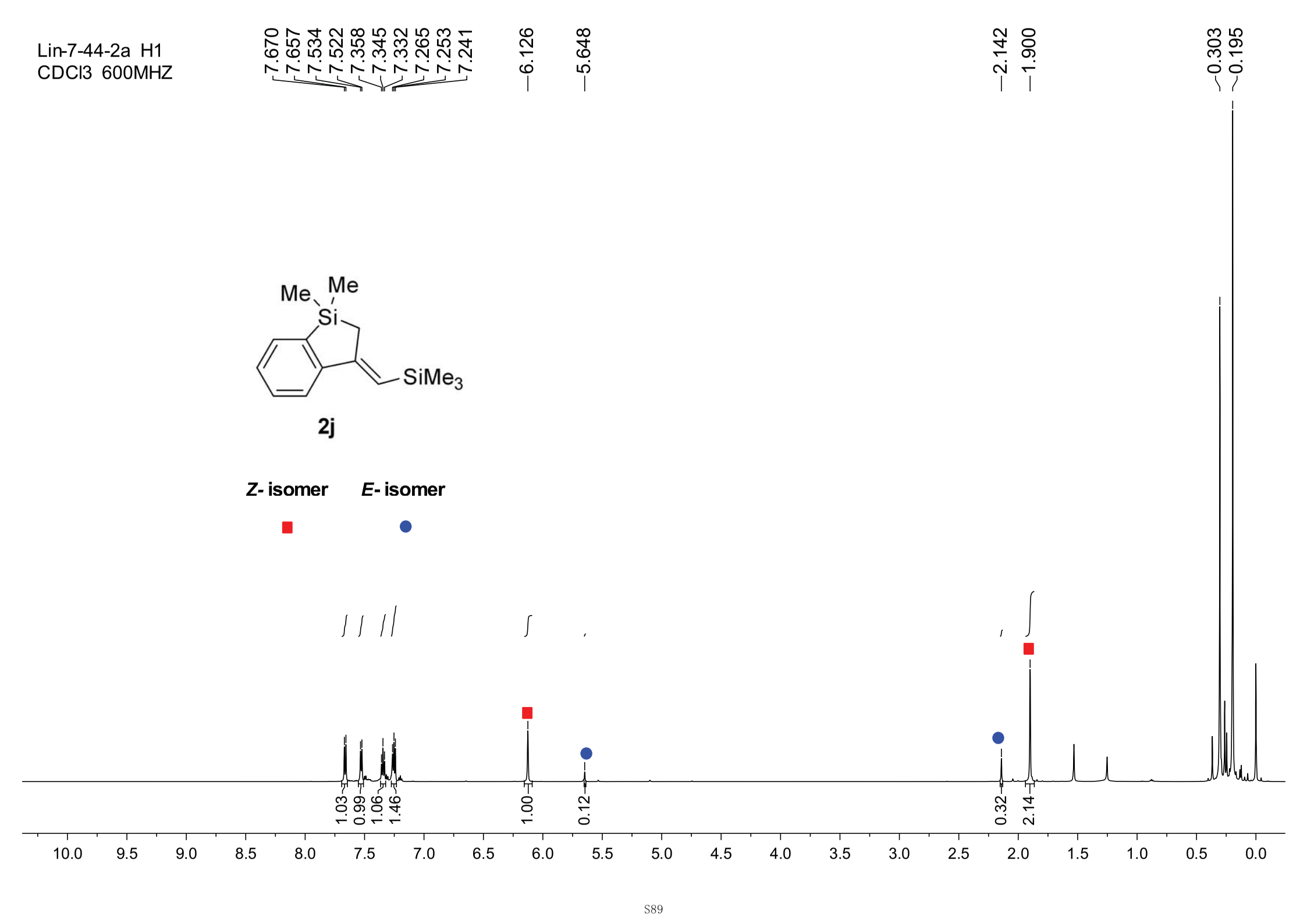
139.611
138.199
134.839
131.944
129.539
126.546
121.311
111.271
77.319
77.000
76.685
32.741
30.733
18.022
-2.084



2i

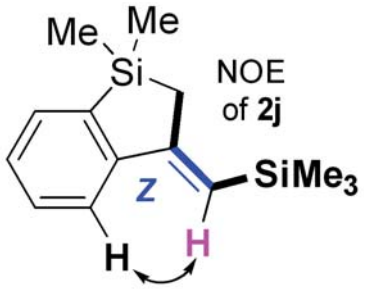


Lin-7-44-2a H1
CDCl3 600MHZ



Lin-6-77-1a NOEDS 6.119
CDCl3 600MHZ

7.677
7.664
6.130
0.198

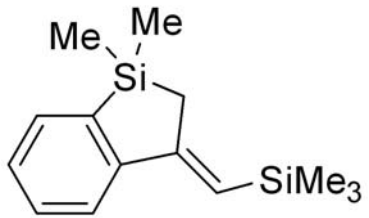


3.40
100.00
0.68

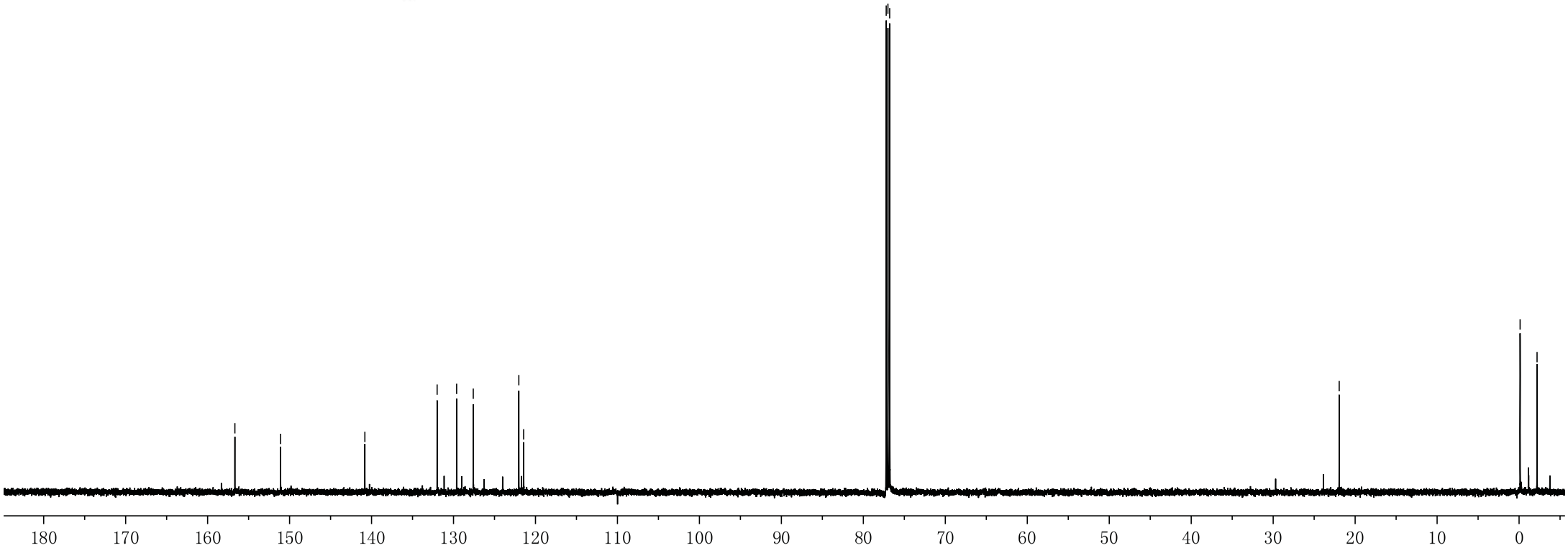
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

Lin-7-44-2a C13
CDCl3 150MHZ

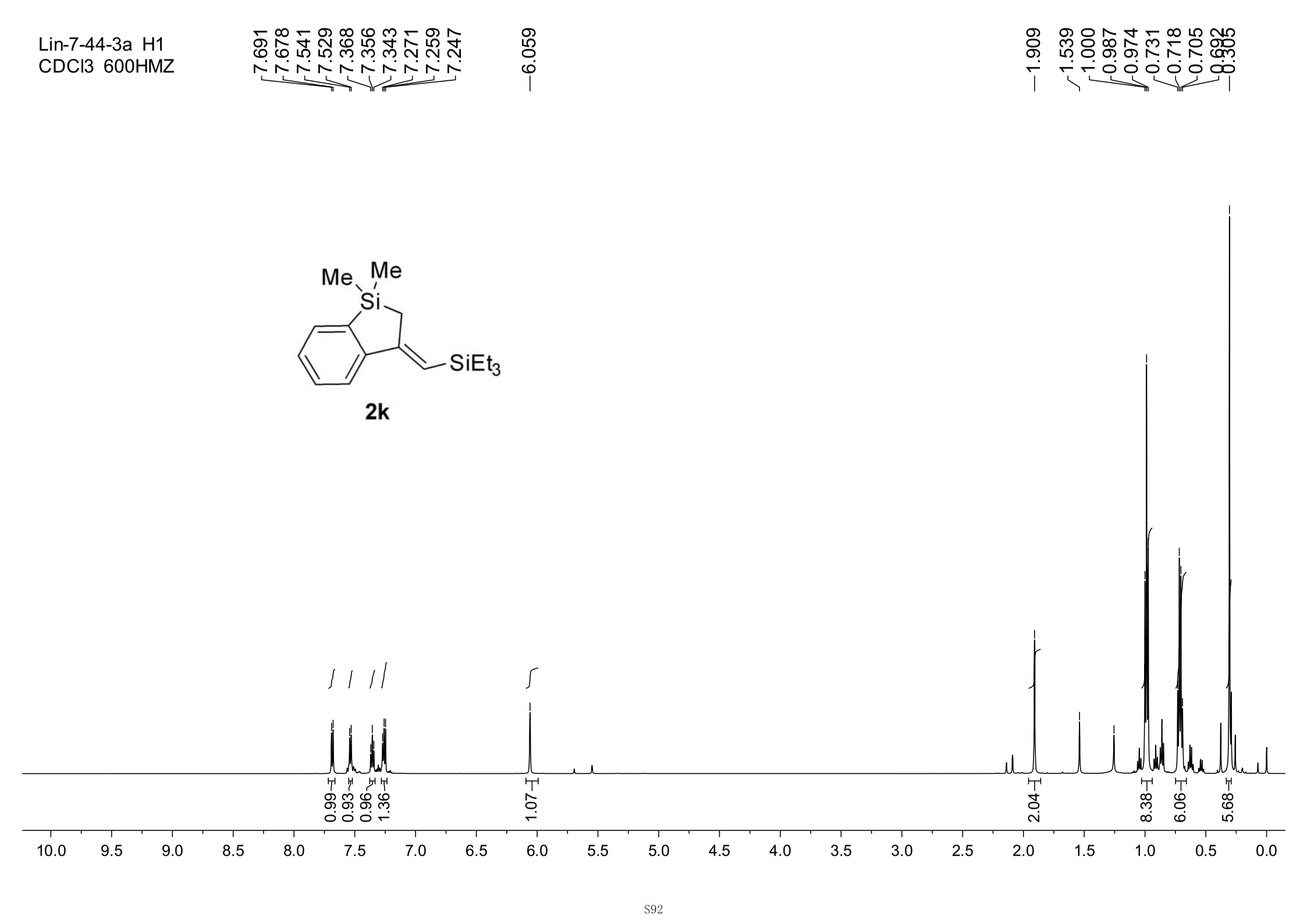
156.673
151.099
140.815
131.999
129.618
127.592
122.032
121.444
77.212
77.000
76.788
21.944
-0.125
-2.193



2j

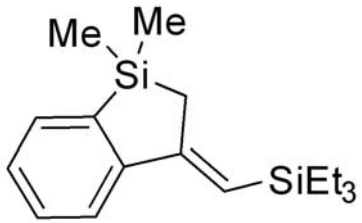


Lin-7-44-3a H1
CDCl3 600HMZ

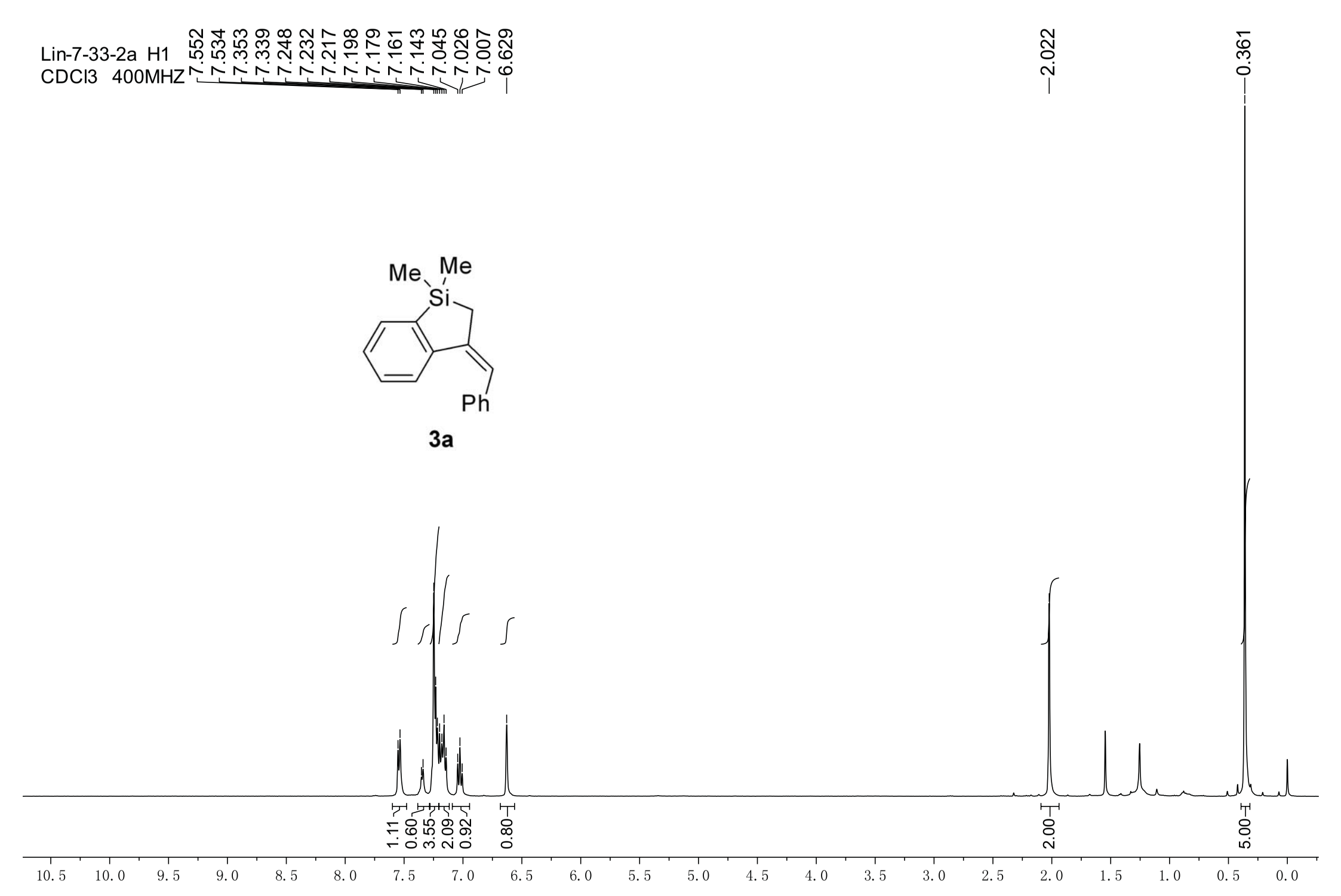


Lin-7-44-3a C13
CDCl3 150HMZ

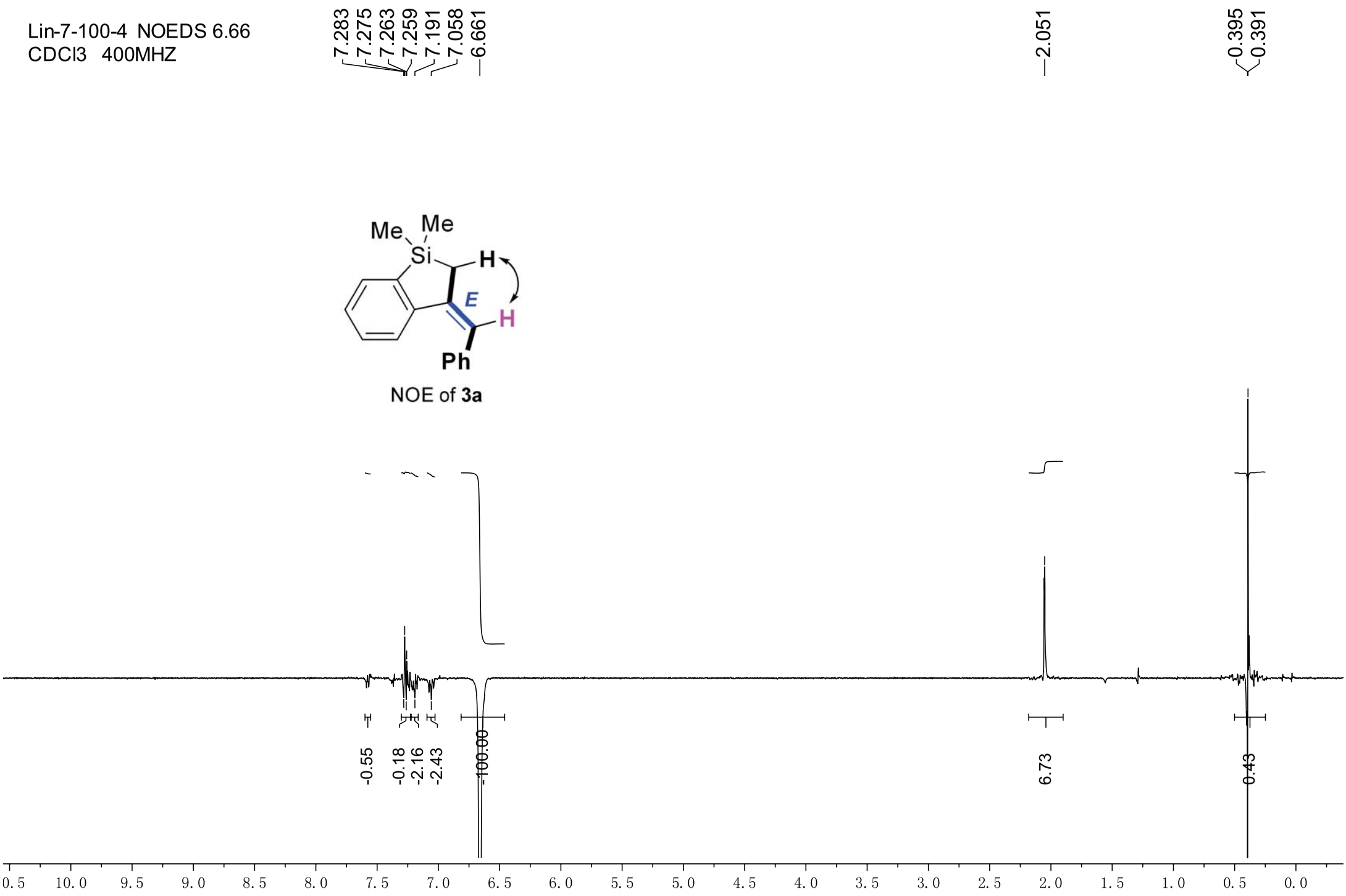
157.457
151.347
140.740
131.979
129.593
127.529
122.185
118.096
77.212
77.000
76.789
22.609
7.683
4.550
-2.223



2k


Lin-7-33-2a H1
CDCl3 400MHZ
7.552
7.534
7.353
7.339
7.248
7.232
7.217
7.198
7.179
7.161
7.143
7.045
7.026
7.007
6.629
2.022
0.361
Me
Me
Si
Ph
3a
1.11
0.60
3.55
2.09
0.92
0.80
2.00
5.00
10.5
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

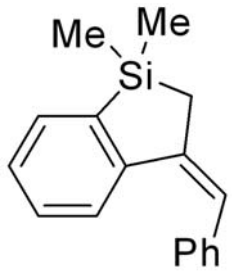
Lin-7-100-4 NOEDS 6.66
CDCl3 400MHZ



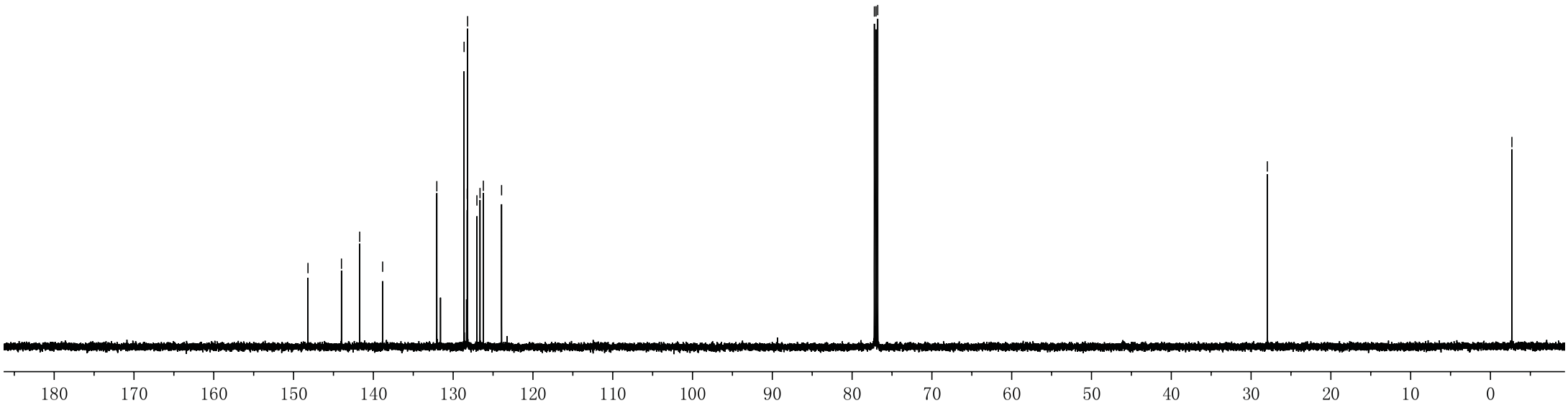
NOE of **3a**

Lin-7-33-2a C13
CDCl3 150MHZ

148.194
143.997
141.712
138.835
132.046
128.630
128.238
128.189
127.023
126.634
126.216
123.930
77.212
77.000
76.788
27.961
-2.688

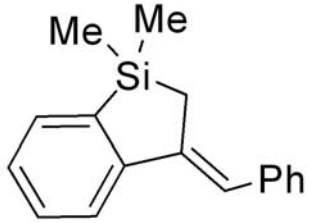


3a



Lin-7-120-2R H1
CDCl3 400MHZ

7.782
7.762
7.604
7.588
7.569
7.420
7.412
7.393
7.374
7.321
7.303
7.263
7.244
7.085
2.131
0.332

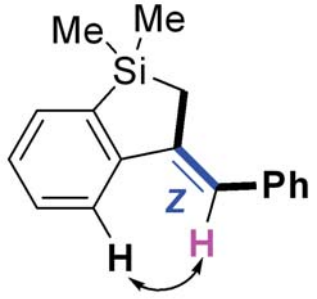


3a-Z

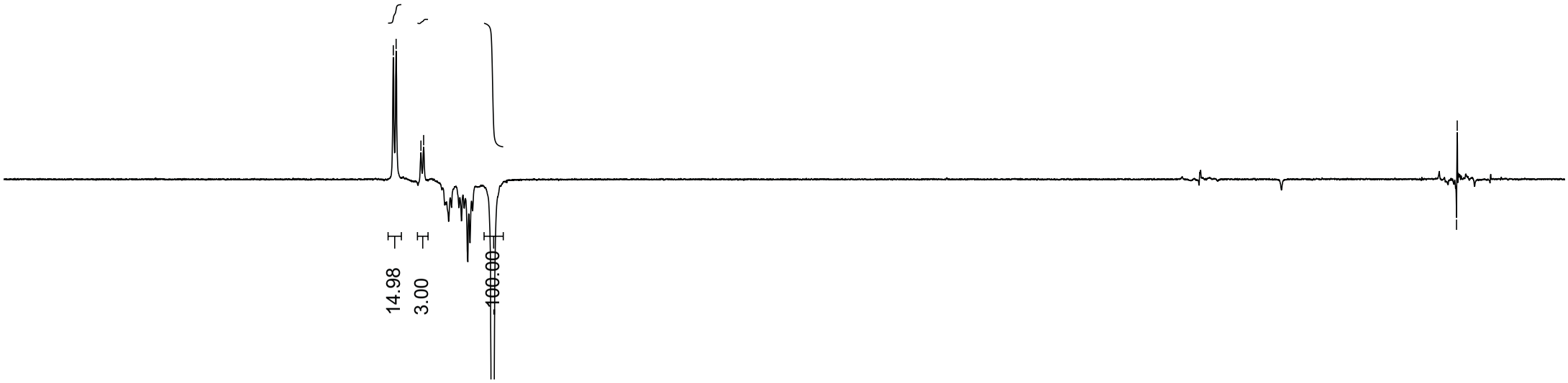
Lin-7-120-2R NOEDS 7.09
CDCl3 400MHZ

7.782
7.762
7.588
7.569
7.086

0.335
0.330



NOE of **3a-Z**



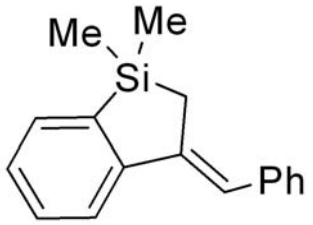
Lin-7-120-2R C13
CDCl3 100MHZ

151.290
142.246
140.712
138.788
132.143
129.829
129.165
128.170
127.432
126.285
123.450
121.842

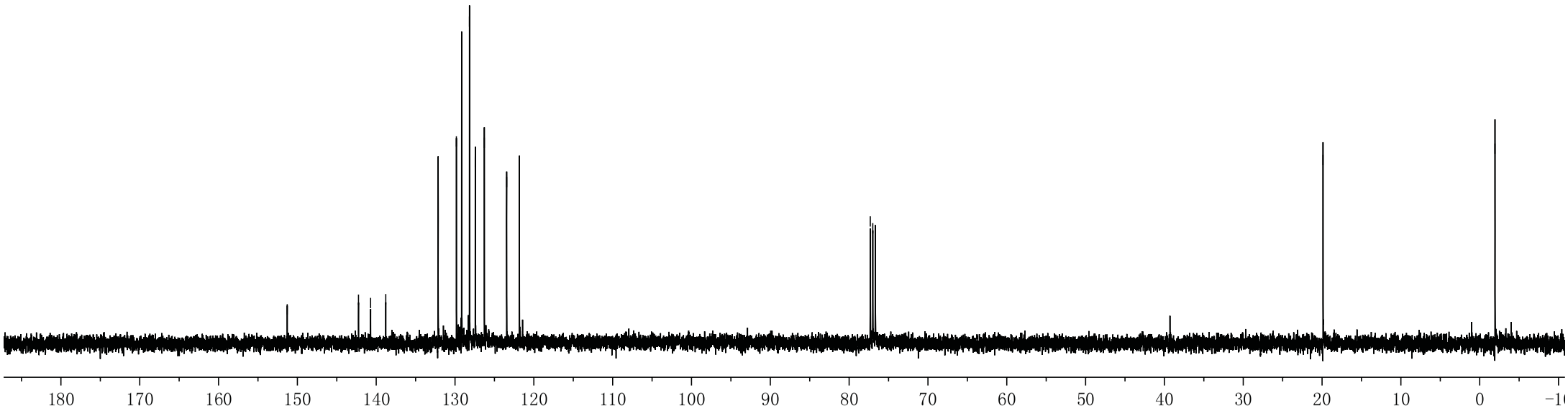
77.317
77.000
76.684

19.880

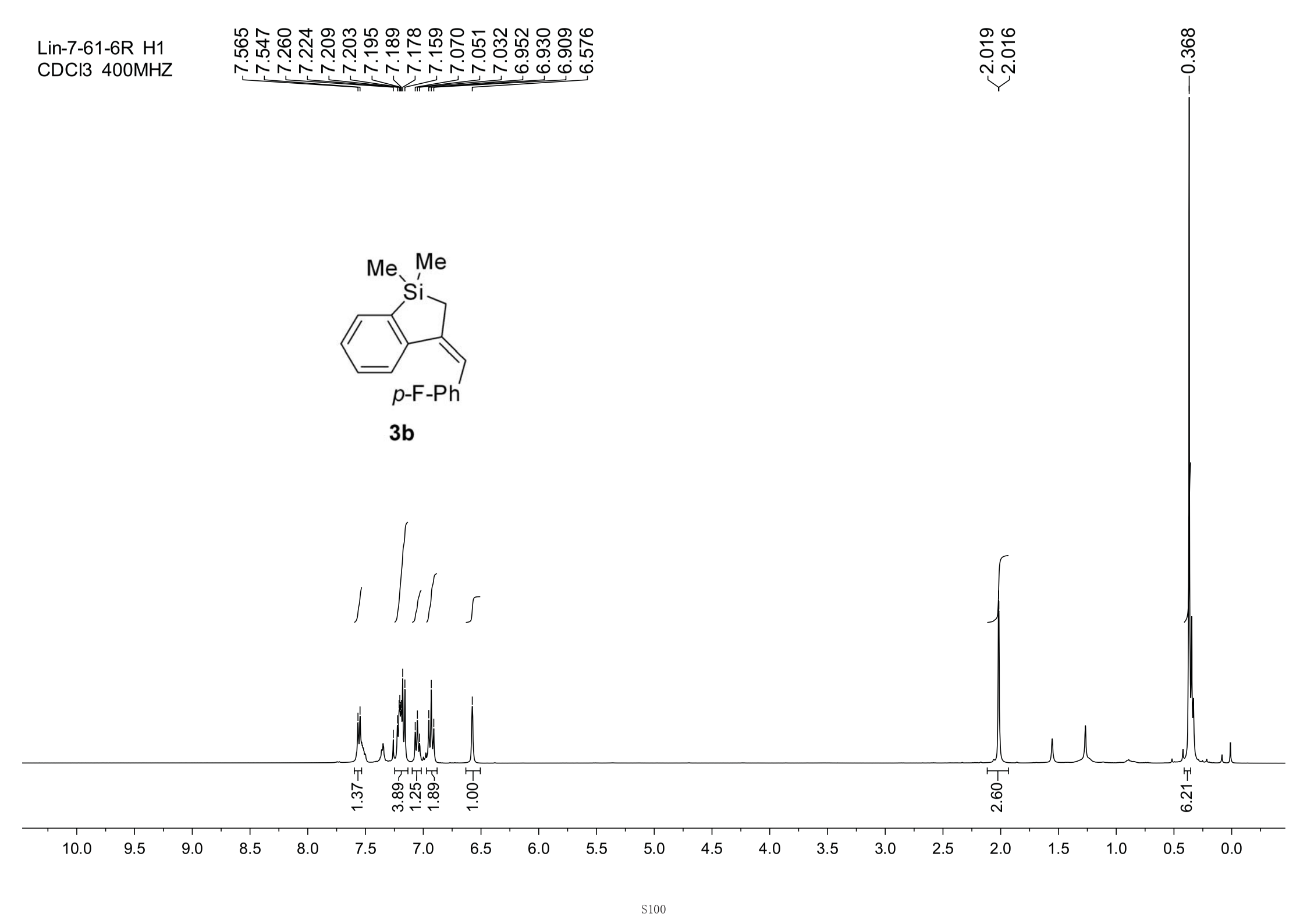
-1.936



3a-Z



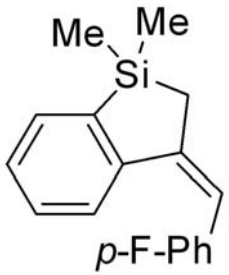
Lin-7-61-6R H1
CDCl3 400MHZ



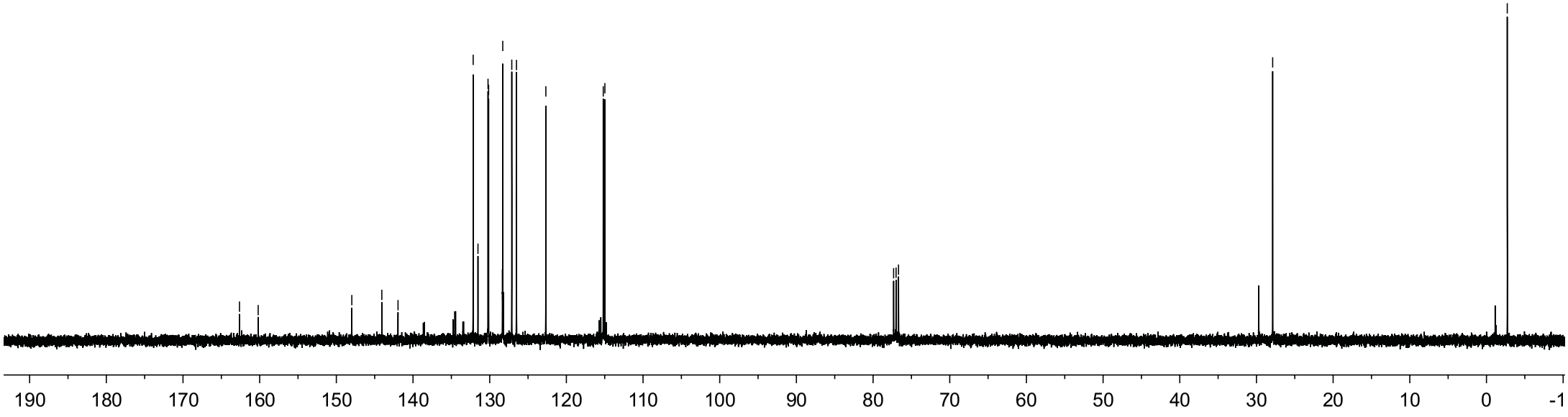
3b

Lin-7-87-2 C13
CDCl3 100MHZ

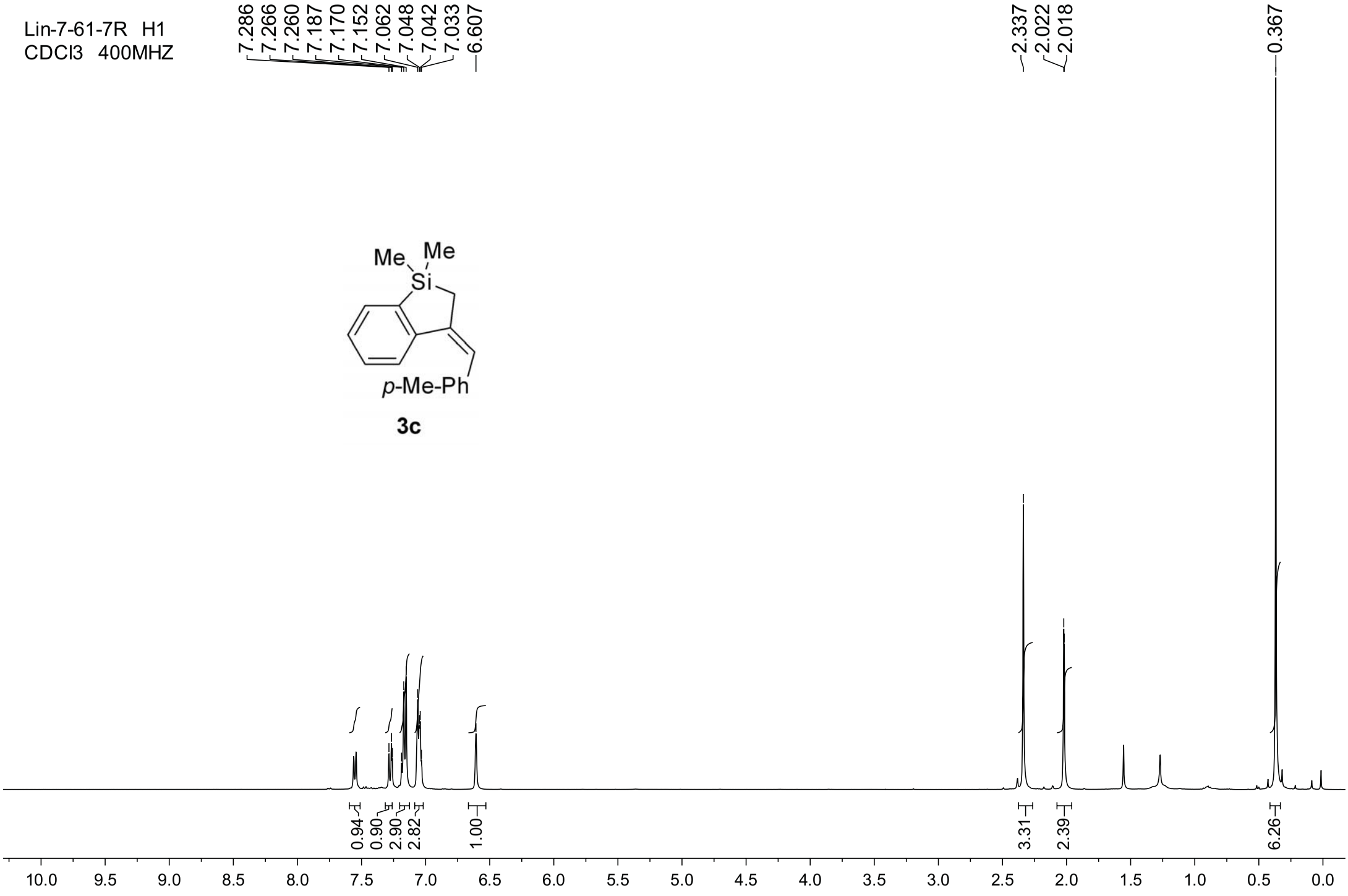
162.631
160.194
147.982
144.068
141.955
132.154
130.217
130.141
128.297
127.119
126.507
115.188
114.977
77.317
77.000
76.682
27.883
-2.711



3b



Lin-7-61-7R H1
CDCl3 400MHZ

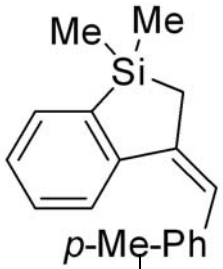


Lin-7-87-1 C13
CDCl3 100MHZ

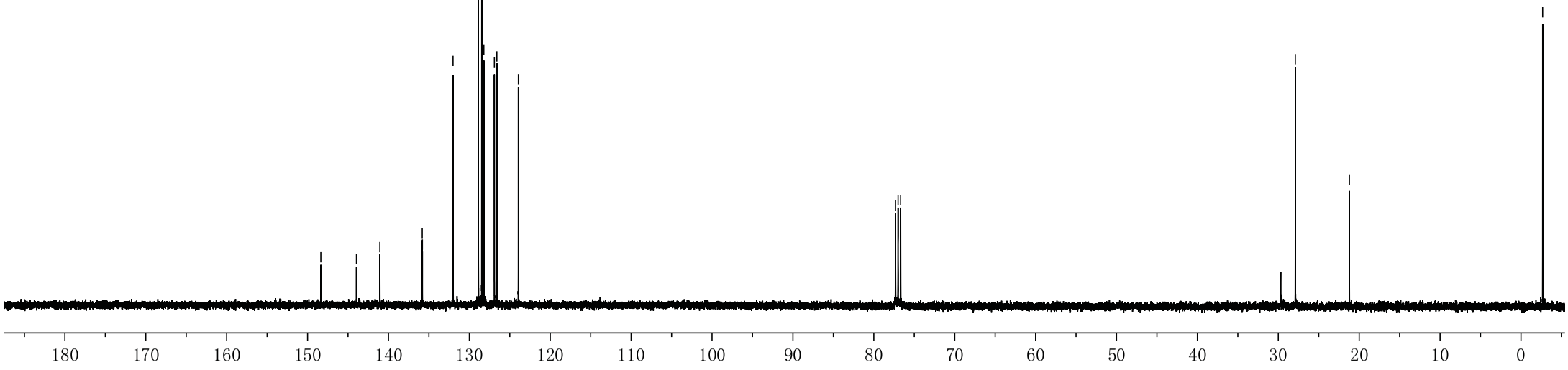
148.360
143.958
141.063
135.823
135.803
132.017
128.887
128.466
128.207
126.906
126.599
123.939

77.319
77.000
76.684

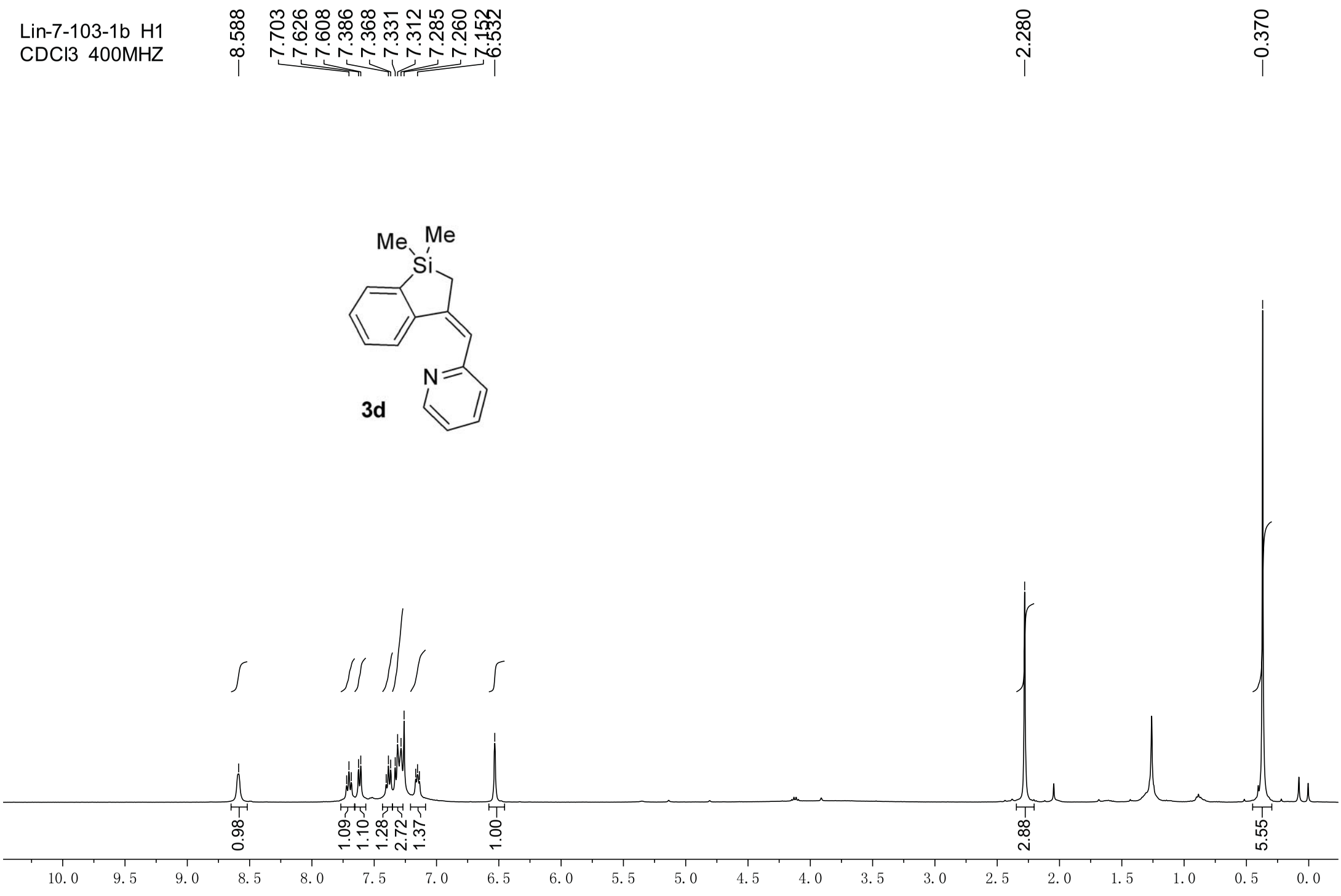
27.896
21.211
-2.680



3c

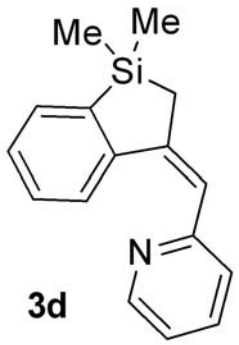


Lin-7-103-1b H1
CDCl3 400MHZ



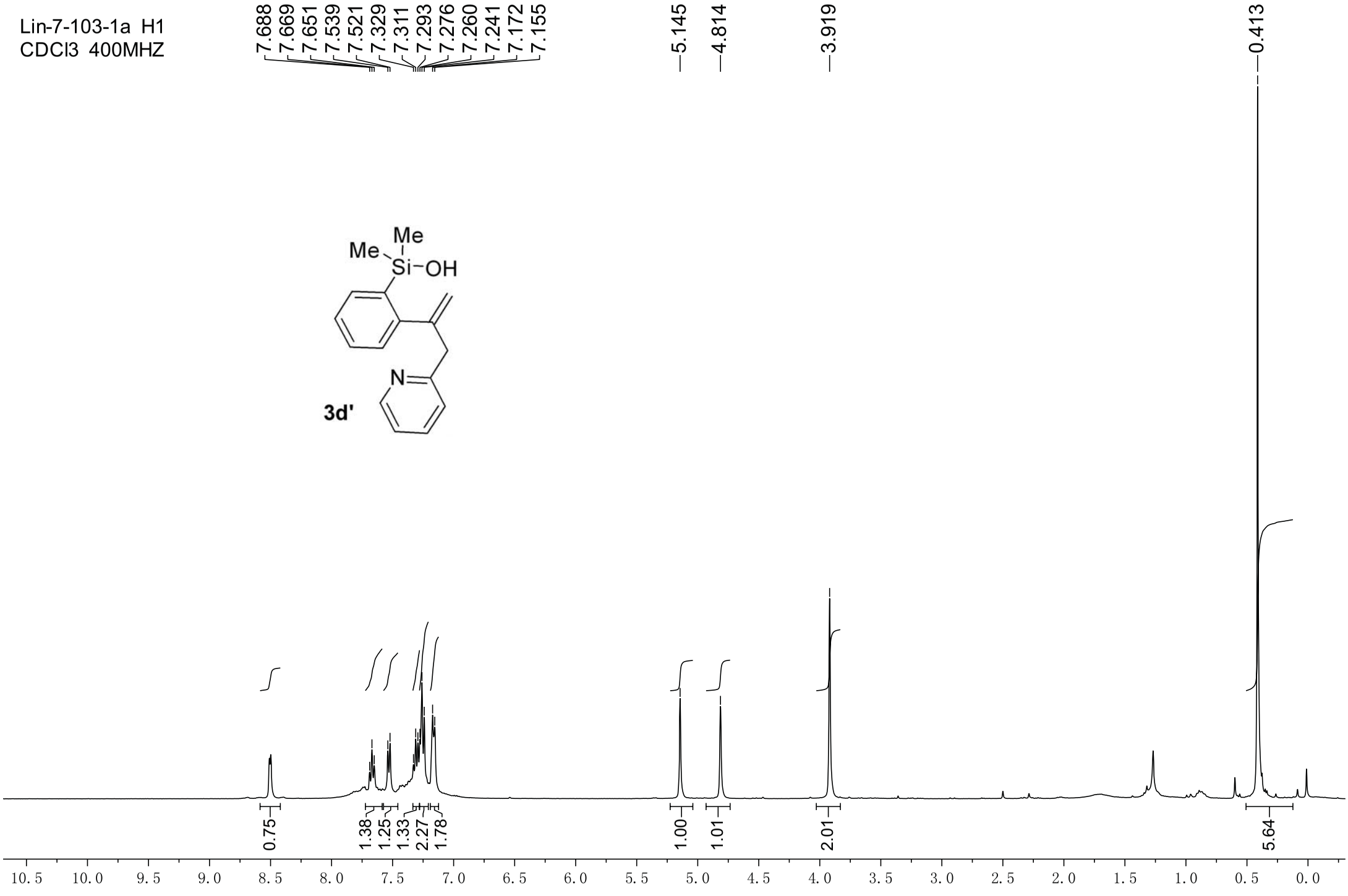
Lin-7-103-1b C13
CDCl3 100MHZ

156.619
151.421
149.118
146.361
138.213
136.484
134.552
128.897
128.422
126.746
126.440
123.899
121.462
77.318
77.000
76.683
20.970
1.735



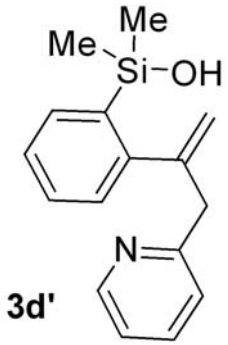
3d

Lin-7-103-1a H1
CDCl3 400MHZ

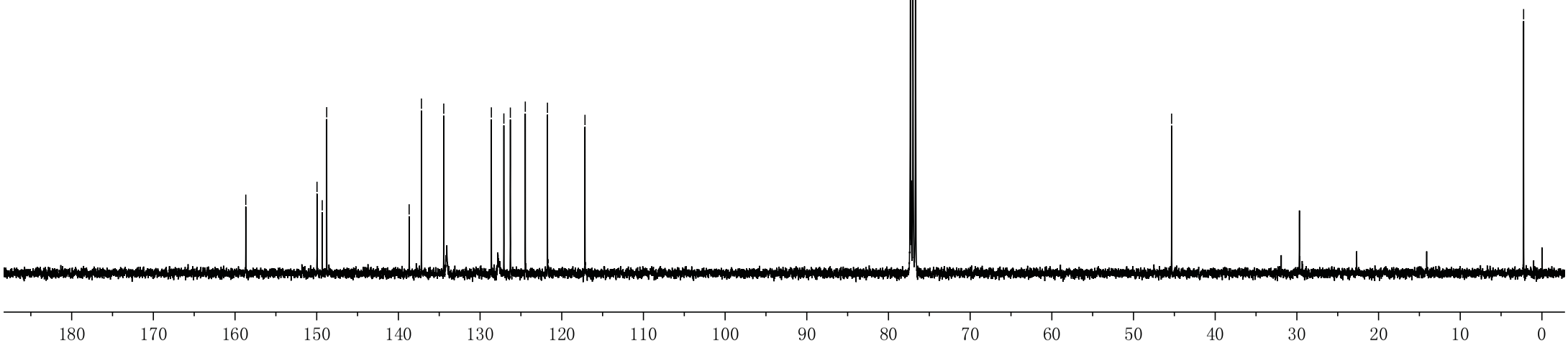


Lin-7-103-1a C13
CDCl3 100MHZ

158.682
149.964
149.323
148.776
138.682
137.178
134.448
128.617
127.087
126.292
124.465
121.751
117.156
77.317
77.000
76.682
45.336
2.240

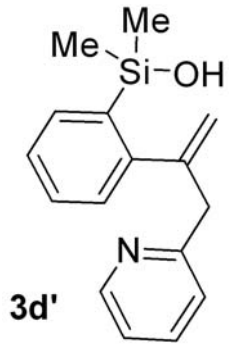


3d'

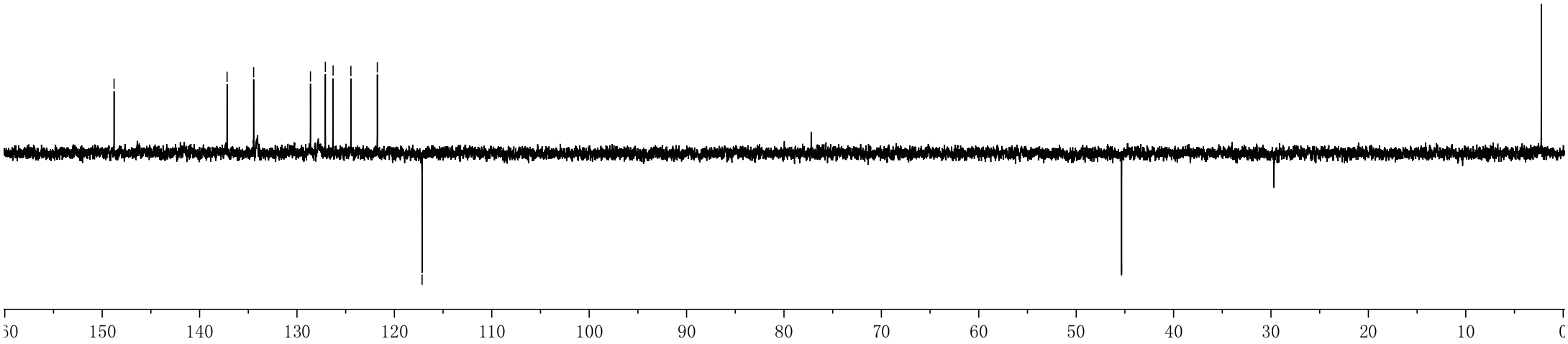


Lin-7-103-1a DEPT135
CDCl3 100MHZ

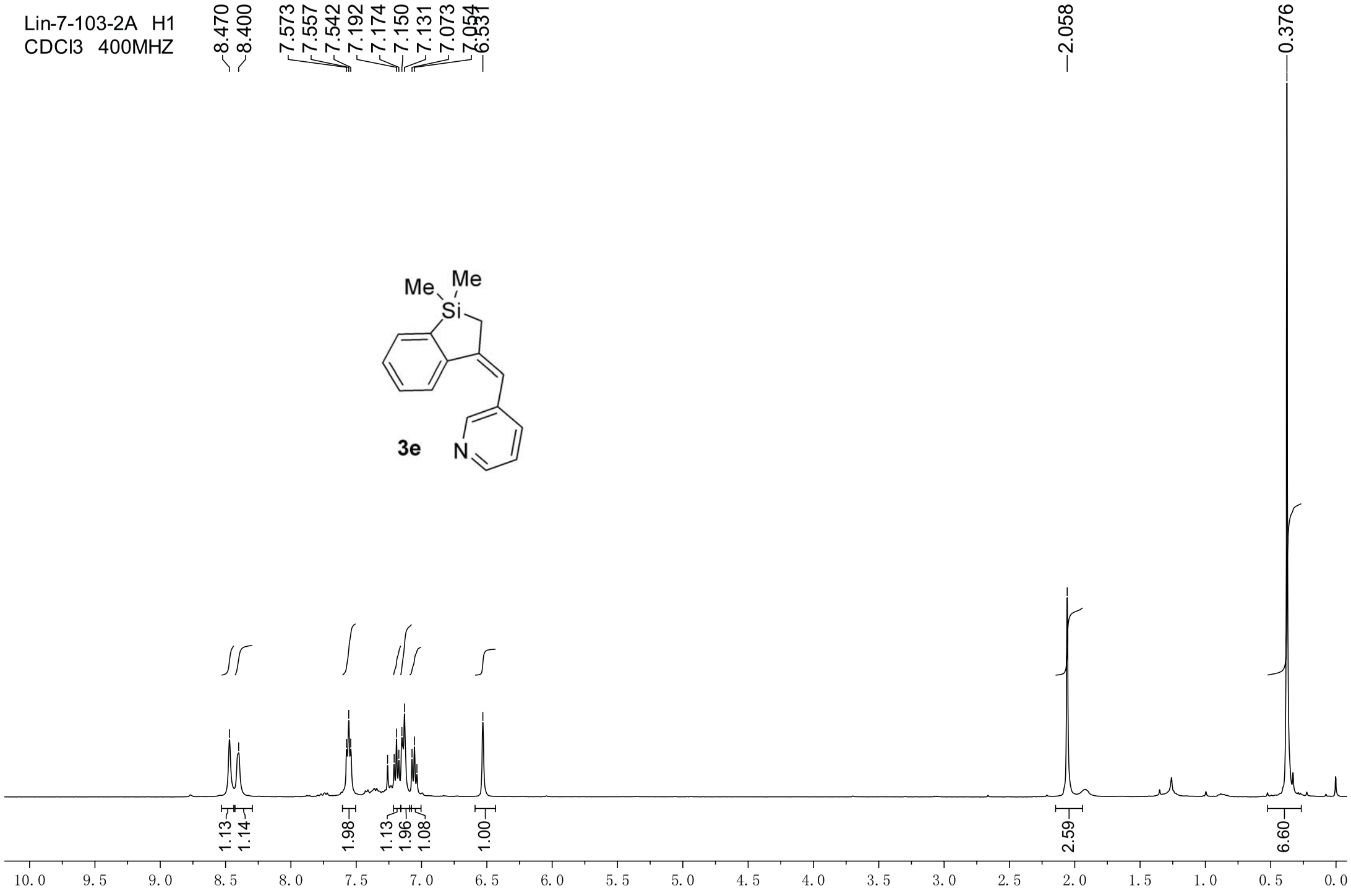
148.780
137.178
134.450
128.618
127.088
126.293
124.466
121.752
117.156
45.339
2.241



3d'

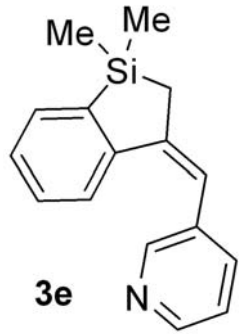


Lin-7-103-2A H1
CDCl3 400MHZ



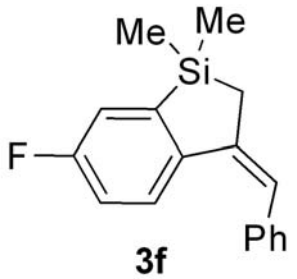
Lin-7-103-2A C13
CDCl3 100MHZ

149.928
147.516
147.245
144.556
144.204
135.776
134.587
132.351
128.546
127.536
126.268
122.991
119.542
77.318
77.000
76.683
28.435
-2.764



3e

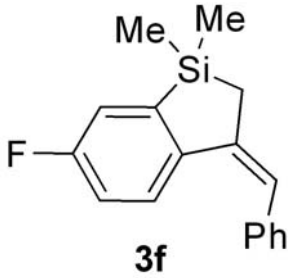
LIn-7-84-2 H1
CDCl3 400MHZ



3f

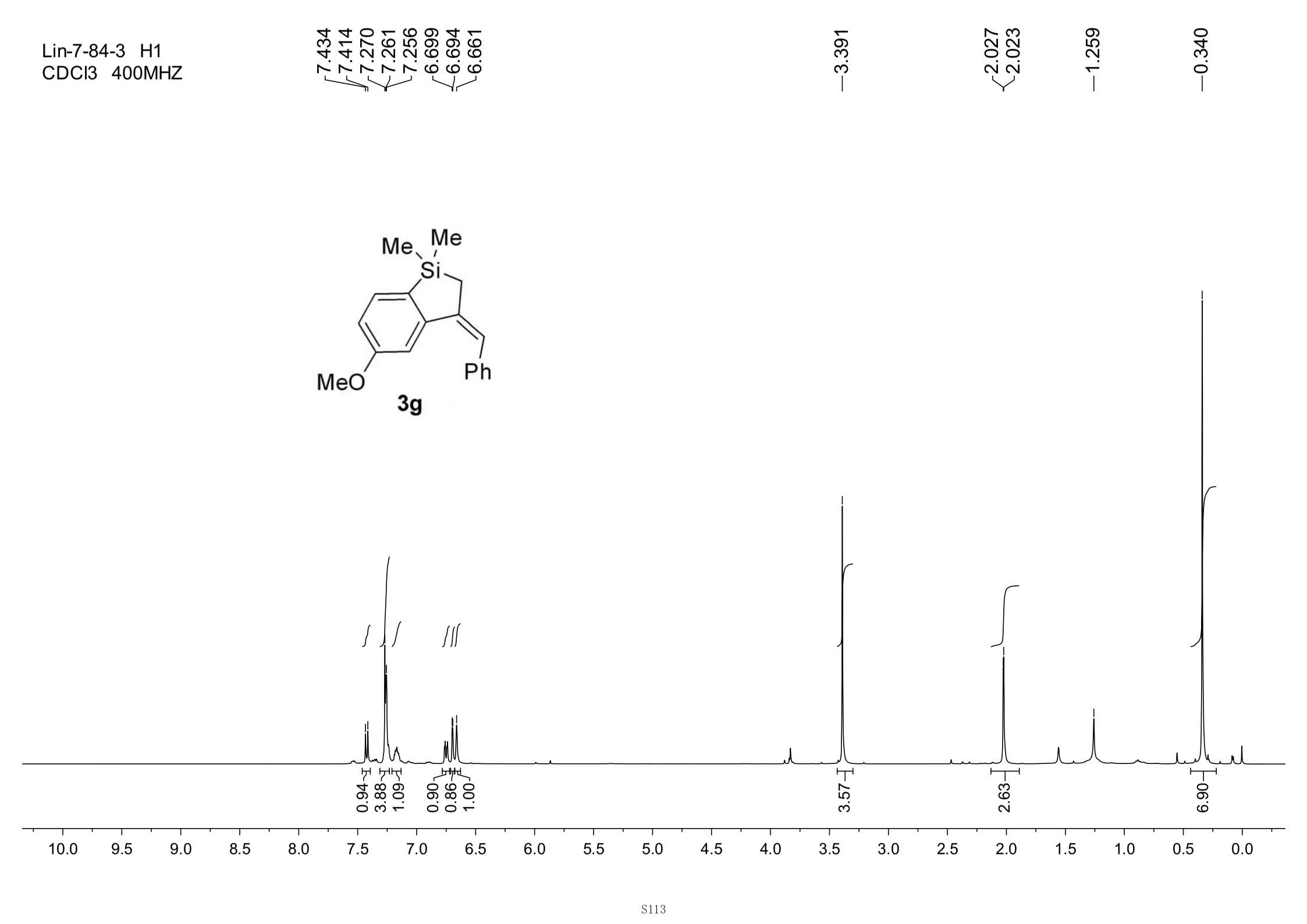
LIn-7-84-2 C13
CDCl3 100MHZ

163.130
160.646
146.969
146.921
143.943
143.916
140.471
138.685
128.588
128.318
128.296
128.246
126.319
123.607
123.594
117.846
117.660
115.707
115.485
77.316
77.000
76.682
28.028
-2.833



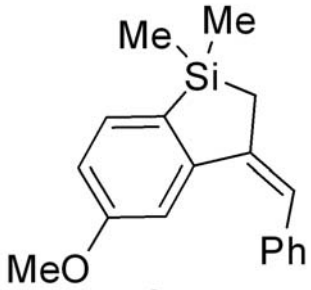
3f

Lin-7-84-3 H1
CDCl3 400MHZ



Lin-7-84-3 C13
CDCl3 100MHZ

159.818
150.031
141.783
138.919
135.022
132.921
128.820
128.214
126.308
124.224
115.419
110.615
77.317
77.000
76.682
54.591
27.743
-0.015
-0.454
-2.358



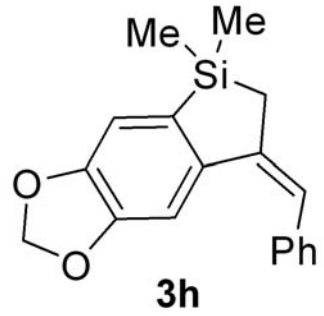
3g

Lin-7-84-1a H1
CDCl3 400MHZ

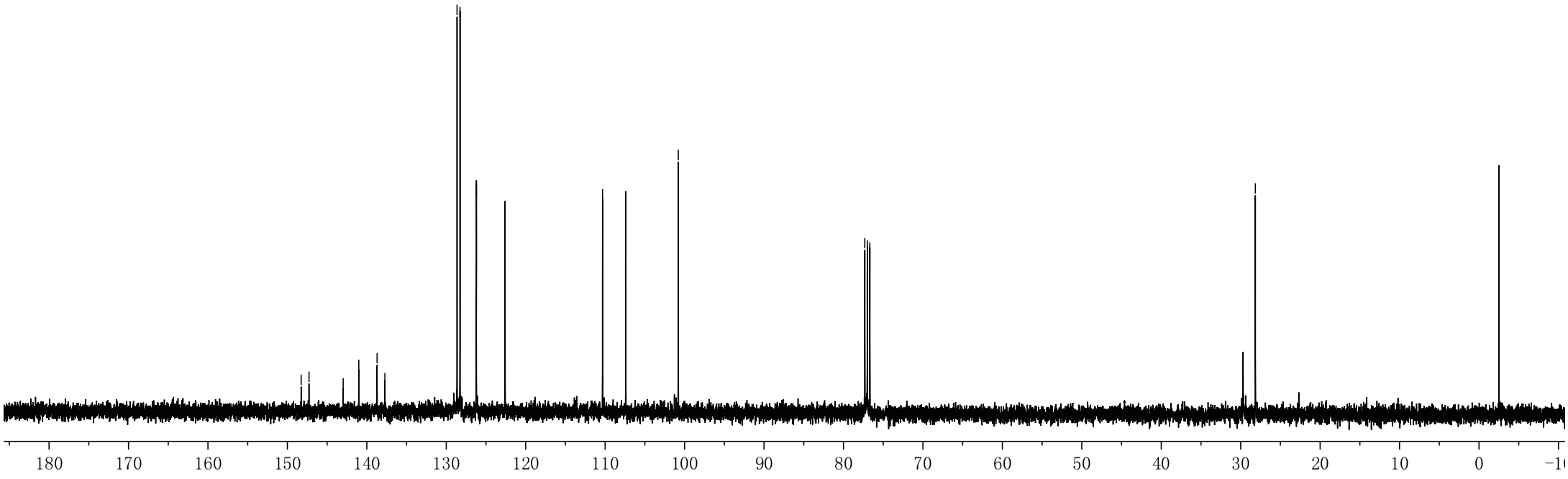
3h

Lin-7-84-1a C13
CDCl3 100MHZ

148.266
147.281
142.977
141.010
138.710
137.724
128.643
128.271
126.210
122.600
110.329
107.410
100.797
77.317
77.000
76.683
28.156
-2.501

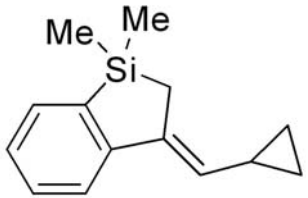


3h

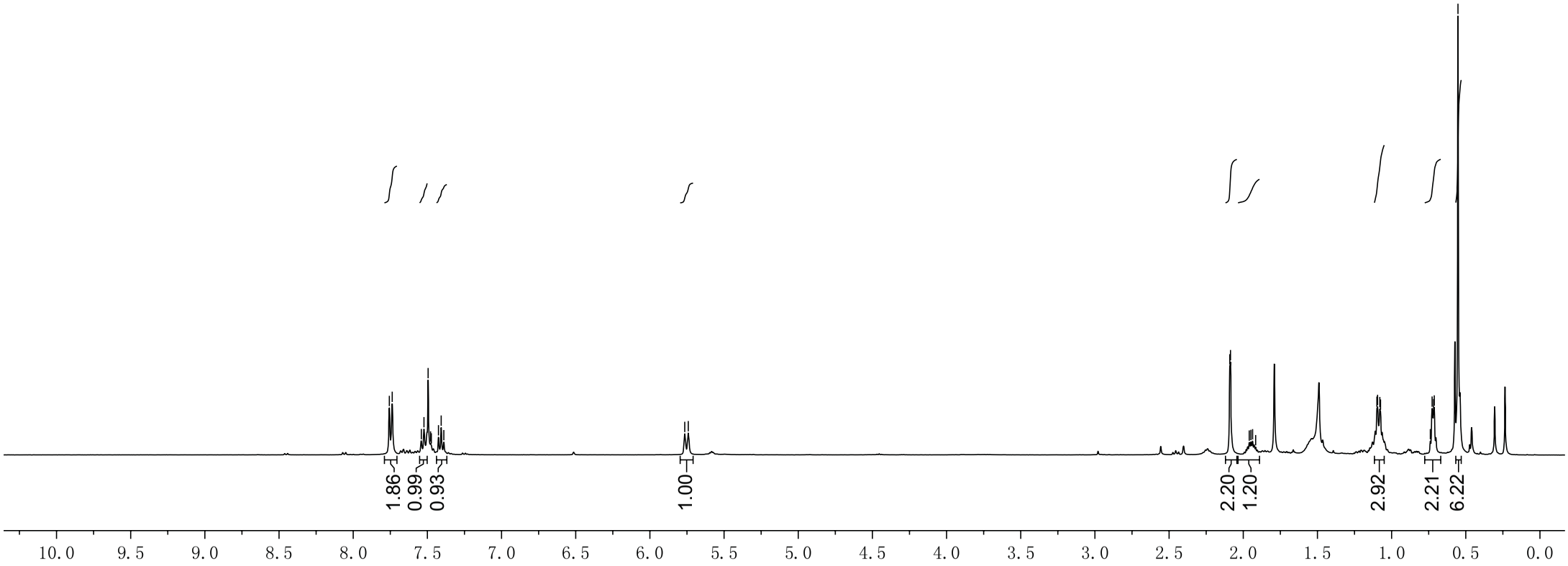


Lin-7-104-4b H1
CDCl3 400MHZ

7.756
7.737
7.541
7.523
7.495
7.479
7.473
7.425
7.407
7.389
5.765
5.741
2.091
2.086
1.960
1.948
1.937
1.916
1.099
1.095
1.079
1.075
0.739
0.727
0.717
0.712
0.553

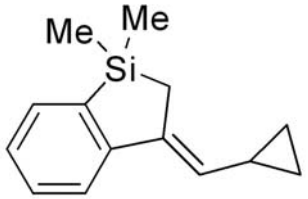


4



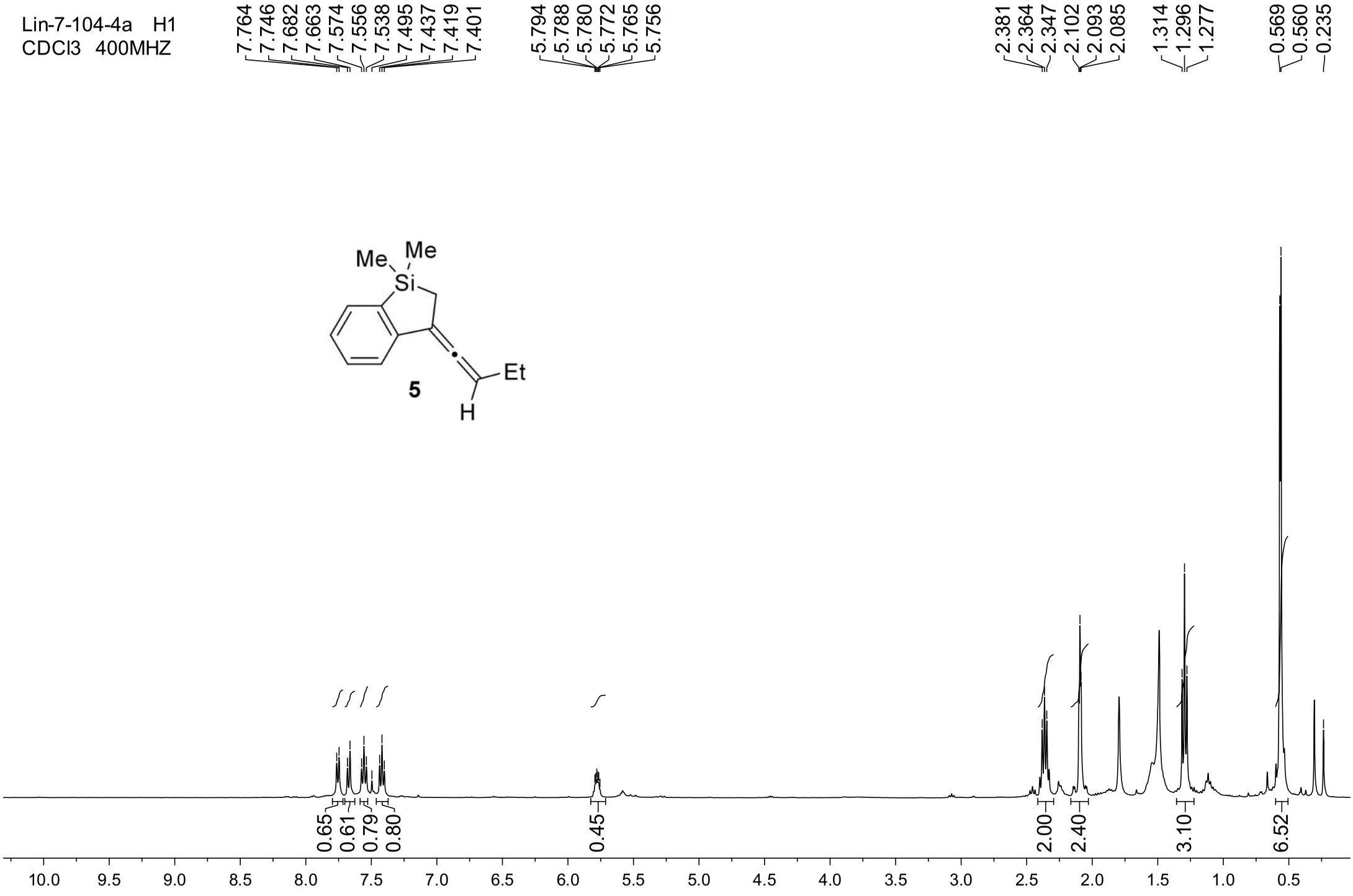
Lin-7-104-4b C13
CDCl3 100MHZ

150.315
140.275
138.131
132.160
129.505
128.610
126.294
120.668
77.317
77.000
76.682
16.236
11.984
7.351
-1.641



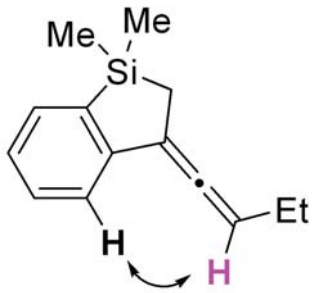
4

Lin-7-104-4a H1
CDCl3 400MHZ



Lin-7-104-4a NOEDS 5.54
CDCl3 400MHZ

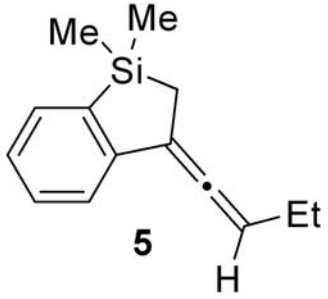
7.744 7.743 7.680 7.660 7.573 7.554 7.495 7.423 7.416 5.781 2.381 2.363 2.346 2.105 2.101 2.097 2.093 2.085 1.318 1.314 1.299 1.295 1.277 0.601 0.597 0.572 0.568 0.563 0.559 0.538



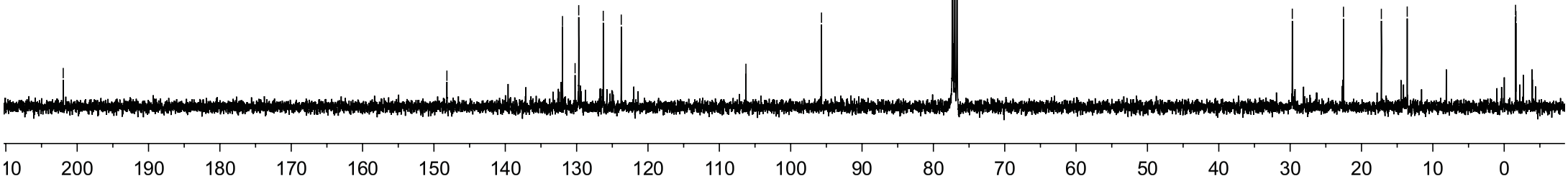
NOE of **5**

Lin-7-104-4a C13
CDCl3 100MHZ

201.956
148.182
131.980
130.218
129.706
126.269
123.746
106.274
95.682
77.318
77.000
76.683
29.696
22.524
17.216
13.592
-1.591
-1.643



5

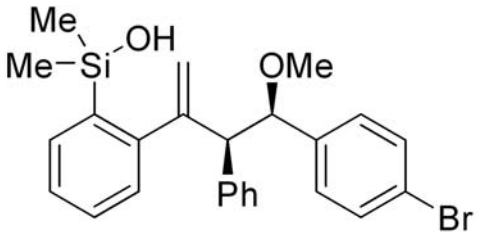


10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

Lin-7-114-1a H1
CDCl3 400MHZ

7.595 7.577 7.400 7.382 7.364 7.341 7.324 7.241 7.221 7.205 7.182 6.716 6.696

5.261 5.176 4.554 4.546 4.063 3.936 3.034 0.454 0.411 -0.000



8

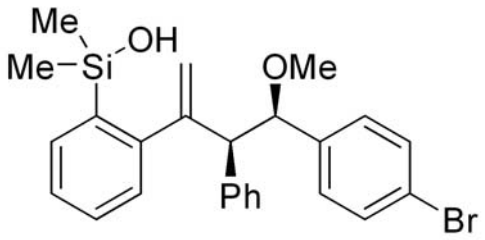
Lin-7-114-1a C13
CDCl3 100MHZ

150.864
148.134
138.537
138.052
135.058
131.194
130.867
128.889
128.617
127.818
127.400
126.931
126.554
121.069
119.275

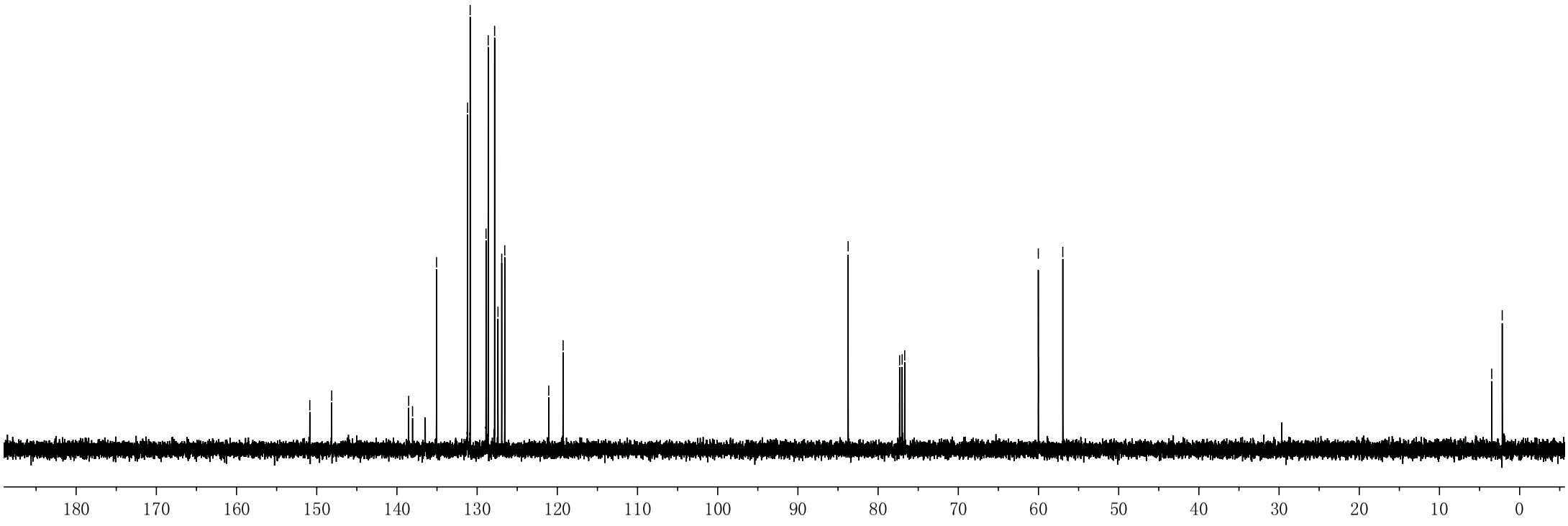
83.738
77.317
77.000
76.682

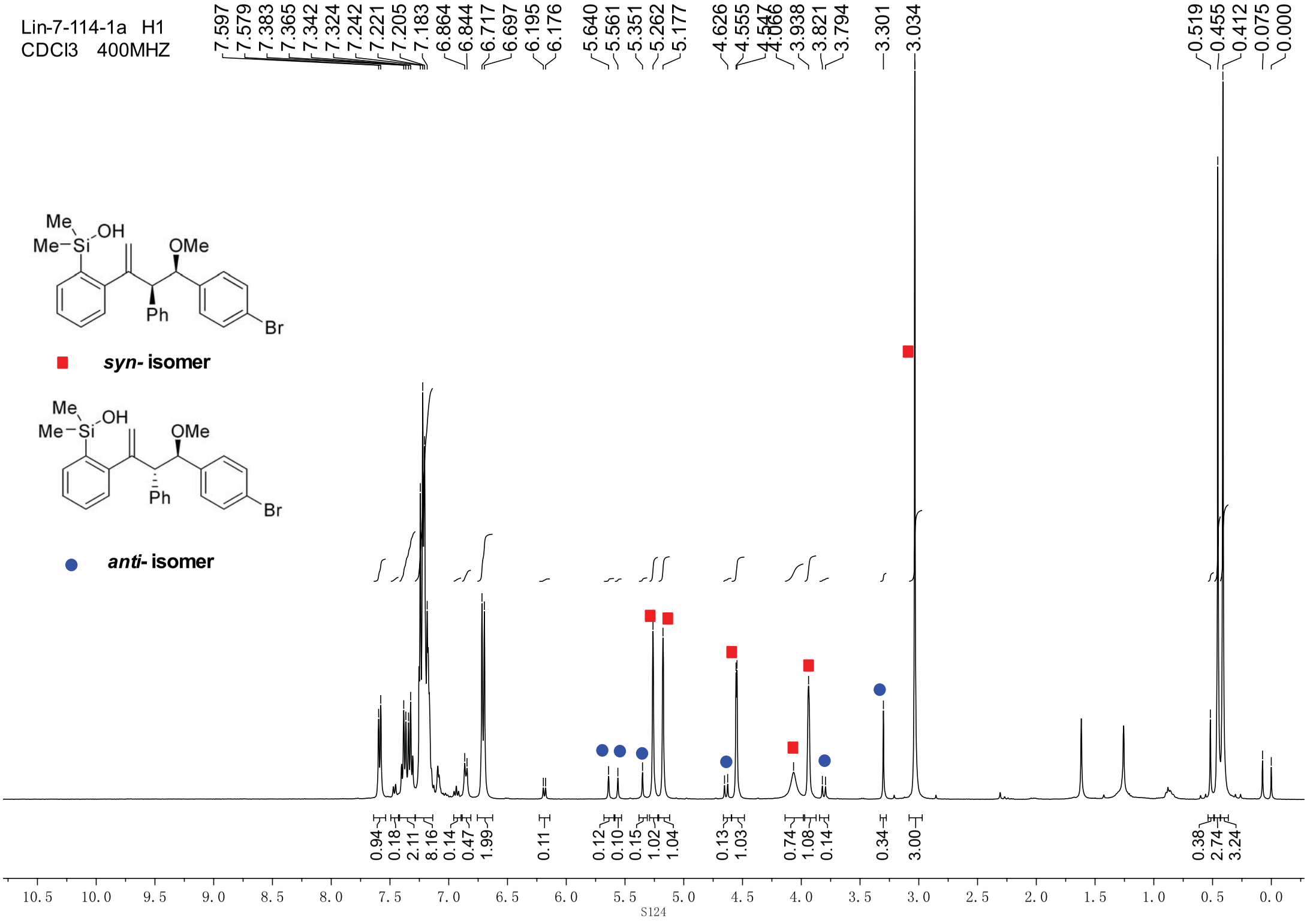
60.023
56.970

3.482
2.171

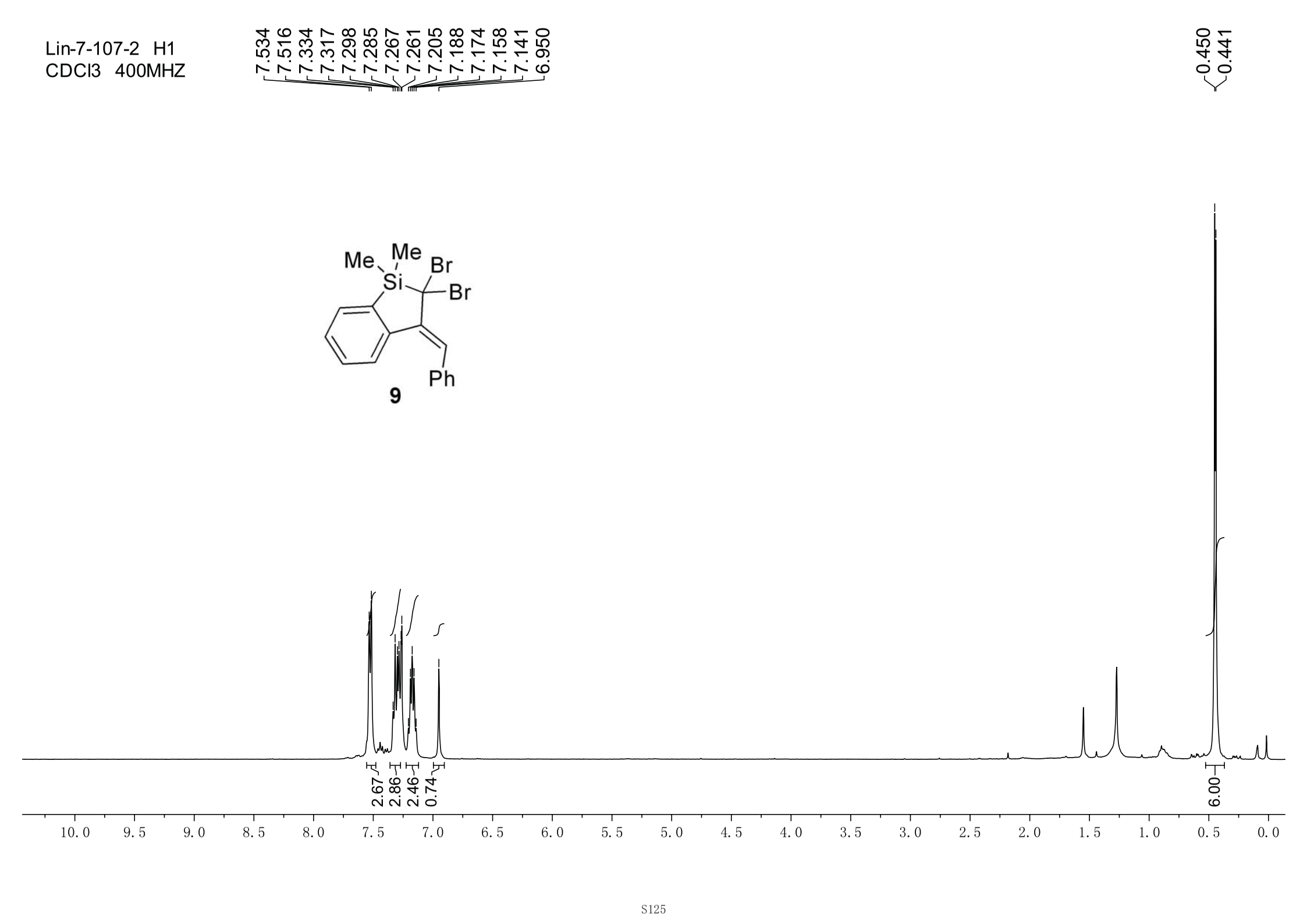


8



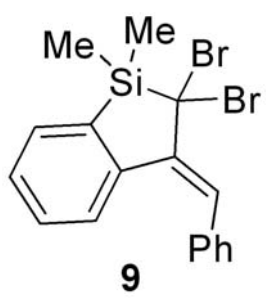

Lin-7-114-1a H1
CDCl3 400MHZ
7.597
7.579
7.383
7.365
7.342
7.324
7.242
7.221
7.205
7.183
6.864
6.844
6.717
6.697
6.195
6.176
5.640
5.561
5.351
5.262
5.177
4.626
4.555
4.547
4.066
3.938
3.821
3.794
3.301
3.034
0.519
0.455
0.412
0.075
0.000
Me
Me
Si
OH
OMe
Ph
Br
syn- isomer
anti- isomer
0.94
0.18
2.11
8.16
0.14
0.47
1.99
0.11
0.12
0.10
0.15
1.02
1.04
0.13
1.03
0.74
1.08
0.14
0.34
3.00
0.38
2.74
3.24
10.5
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

Lin-7-107-2 H1
CDCl3 400MHZ



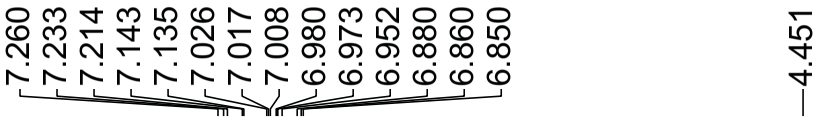
Lin-7-114-2 C13
CDCl3 100MHZ

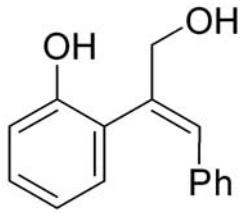
151.426
144.816
137.253
136.926
132.018
129.448
128.425
127.758
126.632
125.458
77.318
77.000
76.683
49.574
-4.770
-5.244



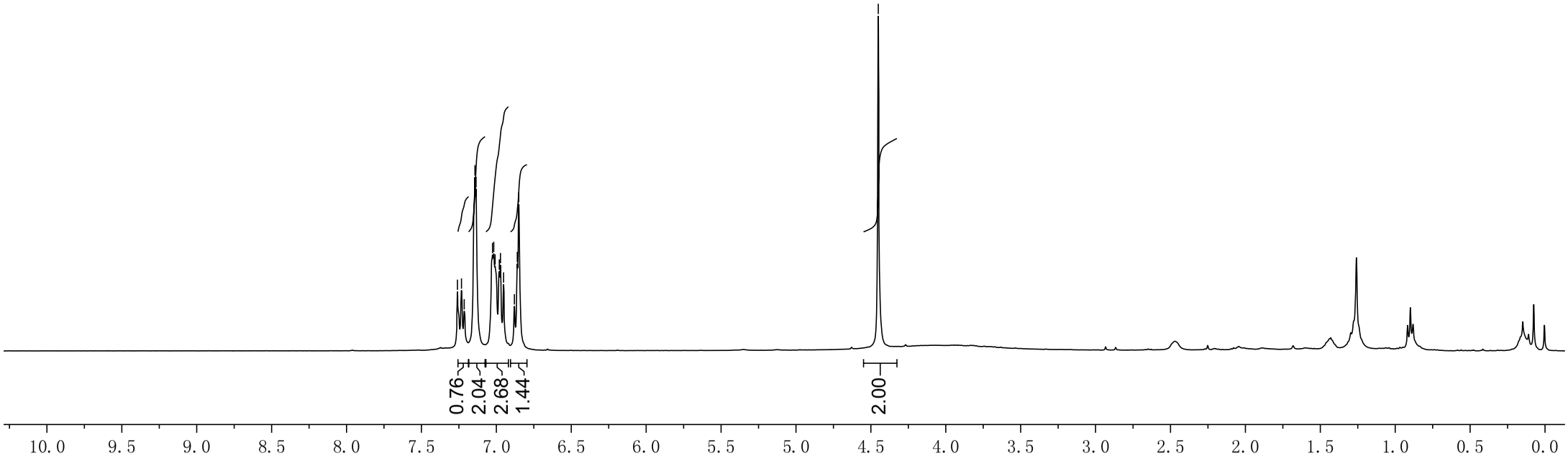
9

Lln-8-1-2a H1
CDCl3 400MHZ



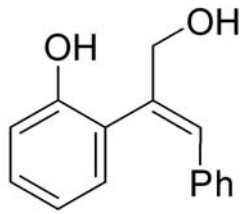


10

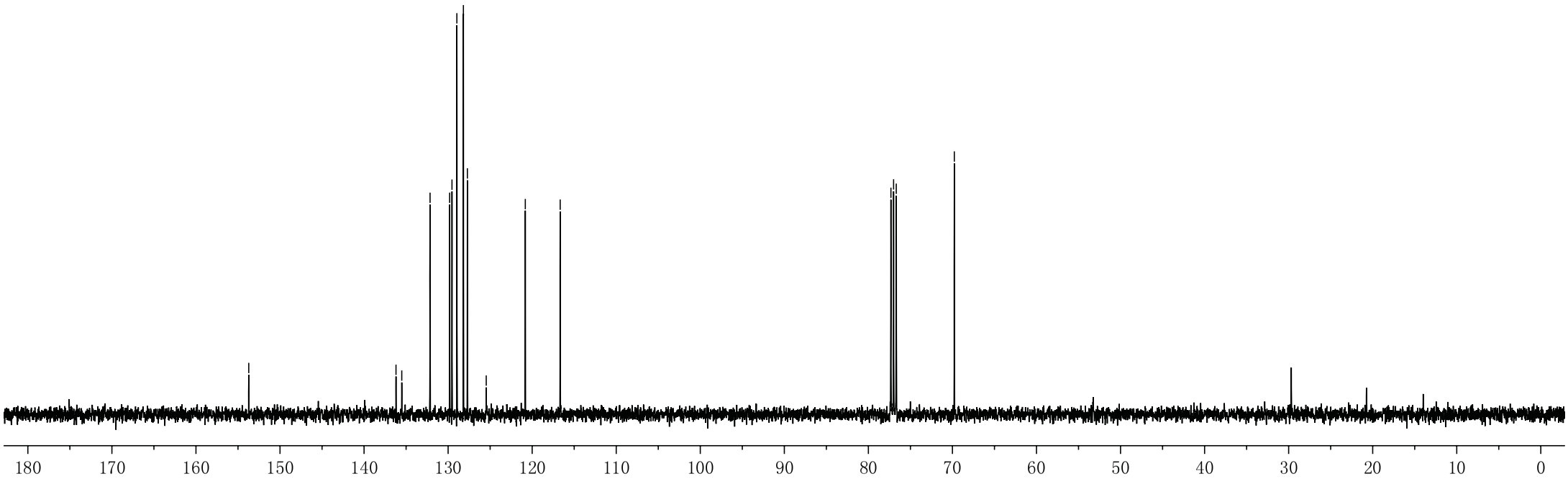


Lln-8-1-2a C13
CDCl3 100MHZ

153.718
136.201
135.514
132.148
129.821
129.540
128.959
128.183
127.709
125.465
120.818
116.666
77.318
77.000
76.683
69.776

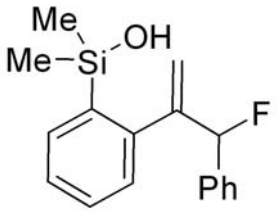


10



Lin-7-116-2 H1
CDCl3 400MHZ

7.609 7.591 7.356 7.330 7.312 7.292 7.272 7.261 7.227 7.208 7.190 6.751 6.733 6.229 6.114 5.574 5.256 2.161 0.425 0.412



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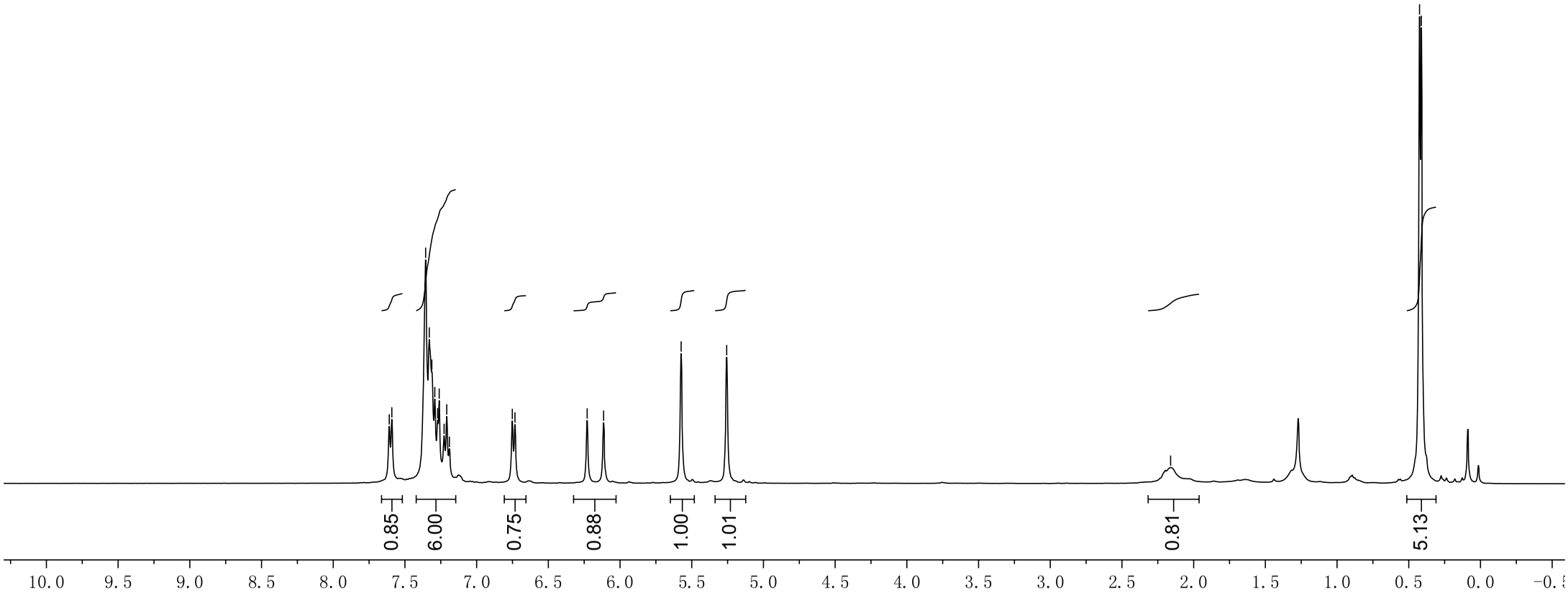
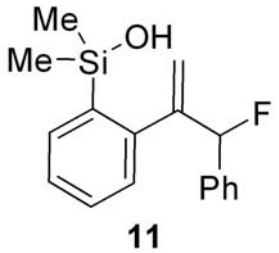


Lin-7-116-2 C13
CDCl3 100MHZ

150.207
149.999
144.154
138.183
137.421
134.347
129.176
128.750
128.723
128.702
128.349
126.930
126.879
126.868
116.846
116.764
96.594
94.847
77.319
77.000
76.682
2.144
1.858



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