Electronic Supplementary Material (ESI) for ChemComm.

Oxime Ester-Enabled Anti-Markovnikov Hydrosilylation of Alkenes

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Supporting Information

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1. General Information

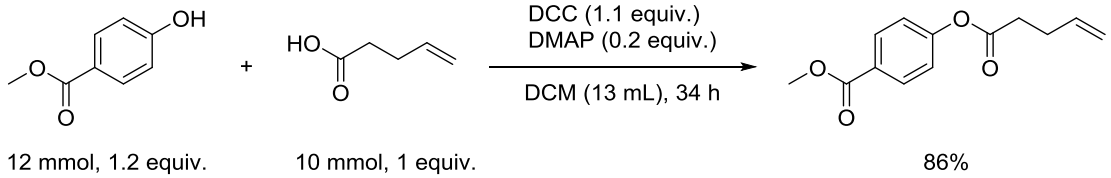
All reactions were performed under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise stated. 1,4-dioxane was distilled from sodium under argon; PhMe and DCM were distilled from calcium hydride under argon; MeOH was distilled from magnesium and iodine under argon; THF was distilled firstly from sodium and then from $LiAlH_4$ under argon. Unless otherwise noted, all the other chemicals were purchased commercially and used without further purification. Column chromatography was performed using silica gel (200-300 mesh). Thin layer chromatography (TLC) was used for monitoring reactions and visualized by a UV lamp (254 nm and 365 nm), I_2 and developing the plates with PMA or CAM. ^1H and ^{13}C NMR were recorded on Bruker DRX-400 NMR spectrometer with TMS as the internal standard and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: ^1H NMR = 7.26 ppm, ^{13}C NMR = 77.16 ppm). Abbreviations in ^1H NMR data are illustrated as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, td = triplet of doublet, tdd = triplet of doublet of doublet, m = multiplet, br = broad. Coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded by using Thermo Scientific Q Exactive hybrid quadrupole-Orbitrap mass spectrometer (Q-exactive orbitrap) and SCIEX QTOF. Gas chromatography mass spectrometry (GC-MS) were recorded by using Shimadzu GCMS-QP2010Plus and Agilent 7890B (GC system) Agilent 5977 MSD. Infrared (IR) spectra were recorded on a BRUKER TENSOR II IR spectrophotometer device and were reported in wavenumbers (cm^{-1}).

2. Syntheses of Initiators and Substrates

The initiators **I-VI** were prepared according to the procedures described before[1].

Synthesis of oxetan-3-yl undec-10-enoate (1e)

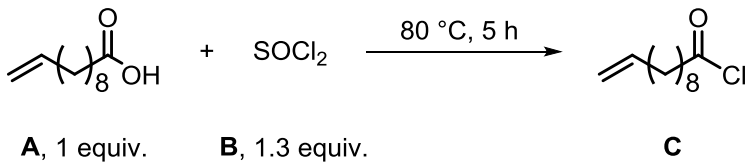
To a refluxing solution of DCC (2.2670 g, 11 mmol, 1.1 equiv.) and DMAP (244.3 mg, 2 mmol, 0.2 equiv.) in CH_2Cl_2 (10 mL) was added allyl acetic acid (983.3 mg, 10 mmol, 1 equiv.) and methylparaben (1.8258 g, 12 mmol, 1.2 equiv.) in DCM (3 mL) dropwise. Then the reaction was stirred at room temperature for 34 h. The mixture was concentrated, and purified by flash chromatography (EA/PE =1/3) to give the desired product (1.9852 g, 86%, pink solid).



Rf = 0.5-0.6 (EA/PE = 1:5; UV & anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.90 (ddt, *J* = 16.8, 10.1, 6.4 Hz, 1H), 5.27 – 5.04 (m, 2H), 3.91 (s, 3H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.51 (q, *J* = 7.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.12, 166.46, 154.48, 136.26, 131.30, 127.82, 121.73, 116.24, 52.33, 33.76, 28.90. **IR** (ATR) 2953, 1761, 1723, 1642, 1436, 1278, 1203, 509 cm^{-1}. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{13}H_{15}O_4$: 235.0965; found: 235.0962. **m.p.**: 28.4-29.4 °C.

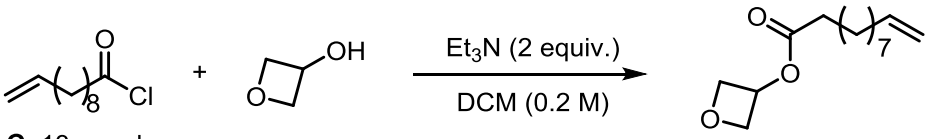
undec-10-enoic acid (C)



To a dried flask equipped with carboxylic acid **A** (20.2 mL, 100 mmol, 1 equiv.) was added thionyl chloride **B** (11.2 mL, 130 mmol, 1.3 equiv.) dropwise in an ice-water bath. The reaction was stirred at 80 °C for 5 h, and concentrated under reduced pressure to obtain the crude acyl chloride **C** which was used in the next step without

further purification.

Synthesis of oxetan-3-yl undec-10-enoate (1q)



C, 13 mmol
1.3 equiv.

D, 10 mmol, 1 equiv.

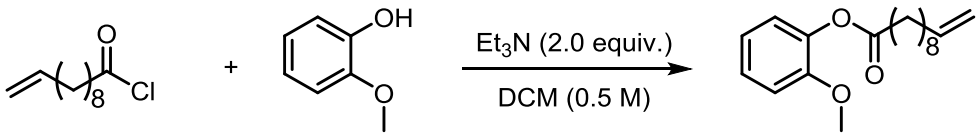
1q, 64%

To a solution of alcohol **D** (695.6 mg, 10 mmol, 1 equiv.) and Et_3N (2.8 mL, 20 mmol, 2 equiv.) in DCM (20 mL) was added acyl chloride **C** (3.6 mL, 13 mmol, 1.3 equiv.) in an ice-water bar. The reaction was stirred at 0 ^oC for 10 min. Then the reaction was warmed to room temperature and stirred overnight. The resulting mixture was quenched by saturated $NaHCO_3$ solution and extracted with DCM (30 mL×5). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by flash column chromatography (EA/PE = 1/5) to afford the alkene (1.4395 g, 64%, colorless oil).

Rf = 0.6-0.7 (EA/PE = 1:5; I_2, anisaldehyde & PMA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.42 (tt, *J* = 6.4, 5.3 Hz, 1H), 5.02 – 4.90 (m, 2H), 4.88 (ddd, *J* = 7.4, 6.4, 1.0 Hz, 2H), 4.62 (ddd, *J* = 7.4, 5.3, 1.0 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 2.07 – 1.99 (m, 2H), 1.63 (q, *J* = 7.6 Hz, 2H), 1.40 – 1.26 (m, 10H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.24, 139.27, 114.30, 77.77, 67.81, 34.08, 33.90, 29.38, 29.28, 29.18, 29.16, 29.00, 24.92. **IR** (ATR) 2926, 2855, 1739, 1640, 1237, 1165, 1121, 1047 cm^{-1}. **HRMS (APCI) m/z:** $[M-H]^-$ calcd for $C_{14}H_{23}O_3$: 239.1653; found: 239.1656.

2-methoxyphenyl undec-10-enoate (1r)



C
13 mmol, 1.3 equiv.

E
10 mmol, 1 equiv.

1r, 71%

To a solution of methyl guaiacol (1.2773 g, 10 mmol, 1 equiv.) and Et_3N (2.8 mL, 20 mmol, 2 equiv.) in DCM (20 mL) was added acyl chloride **C** (3.6 mL, 13 mmol, 1.3 equiv.) in an ice-water bar. The reaction was stirred at 0 ^oC for 10 min. Then the

reaction was warmed to room temperature and stirred overnight. The mixture was quenched by saturated $NaHCO_3$ solution and extracted with DCM (30 mL × 5). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by flash column chromatography (EA/PE= 1/10) to afford the alkene (2.1187 g, 71%, yellow oil).

Rf = 0.6-0.7 (EA/PE = 1:10; UV & anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.02 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.99 – 6.90 (m, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05 – 4.90 (m, 2H), 3.82 (s, 3H), 2.58 (t, *J* = 7.5 Hz, 2H), 2.09 – 2.00 (m, 2H), 1.82 – 1.72 (m, 2H), 1.49 – 1.29 (m, 10H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.03, 151.29, 140.00, 139.30, 126.87, 122.97, 120.87, 114.29, 112.52, 55.93, 34.18, 33.92, 29.47, 29.36, 29.20, 29.17, 29.04, 25.17. **IR** (ATR) 2926, 2854, 1763, 1640, 1280, 1258, 1027, 748 cm^{-1}. **HRMS (APCI) m/z:** $[M+H]^+$ calcd for $C_{18}H_{27}O_3$: 291.1955; found: 291.1952.

Synthesis of methyl 3-methoxy-4-(undec-10-enoyloxy)benzoate (1s)

C 13 mmol, 1.3 equiv

F 10 mmol, 1 equiv.

1s, 82%

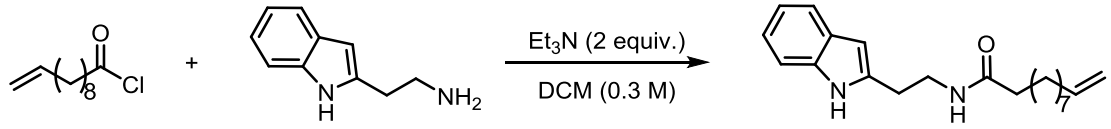
To a solution of methyl vanillate (10 mmol) in DCM (20 mL) and Et_3N (2.8 mL, 20 mmol, 2 equiv.) was added acyl chloride **C** (3.6 mL, 13 mmol, 1.3 equiv.) in an ice-water bar. The reaction was stirred at 0 ^oC for 10 min. Then the reaction was warmed to room temperature and stirred overnight. The mixture was quenched by saturated $NaHCO_3$ solution and extracted with DCM (30 mL×5). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the alkene (2.8693 g, 82%, dark brown oil).

Rf = 0.7-0.8 (EA/PE = 1:5; UV & I_2 & anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03 – 4.88 (m, 2H), 3.91 (s, 3H), 3.87 (s, 3H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.09 – 1.98 (m, 2H), 1.83 – 1.71 (m, 2H), 1.48 – 1.25 (m, 10H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.46, 166.52, 151.20, 143.87, 139.26, 128.80, 122.91, 122.72, 114.29, 113.50, 56.14, 52.37, 34.11, 33.89, 29.43, 29.32, 29.17, 29.11, 29.01, 25.05. **IR** (ATR) 2927, 2854, 1767, 1724, 1640, 1603, 1243, 1198, 1171, 1117, 1034, 761 cm^{-1}. **HRMS (APCI) m/z**: $[M+Na]^+$ calcd for $C_{20}H_{29}O_5$: 371.1829; found: 371.1834.

Synthesis of *N*-(2-(1H-indol-2-yl)ethyl)-*O*-(undec-10-enoyl)hydroxylamine (1t)



C 4.5 mmol, 1.5 equiv. **G** 3 mmol, 1 equiv. **1t**, 35%

To a dried flask quipped with a stir bar, was added tryptamine (480.7 mg, 3 mmol, 1 equiv.). The flask was then evacuated and back-filled with Ar for 3 times. Then DCM (10 mL) and Et_3N (1.4 mL, 10 mmol, 2 equiv.) was added. The reaction was cooled to an ice-water bath and added acyl chloride **C** (1.2 mL, 4.5 mmol, 1.5 equiv.) dropwise. The reaction mixture was stirred overnight. The resulting solution was quenched by saturated $NaHCO_3$ solution (20 mL) and extracted with DCM (30 mL × 5). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by flash column chromatography (EA/PE = 1/1 to EA to MeOH/DCM = 1/10) to afford the desired alkene (347.6 mg, 35%, purple solid).

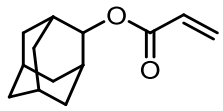
Rf = 0.5-0.6 (EA/PE = 1:1; UV & anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.21 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.16 – 7.10 (m, 1H), 7.04 (d, *J* = 2.3 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.48 (s, 1H), 5.03 – 4.89 (m, 2H), 3.61 (q, *J* = 6.5 Hz, 2H), 2.98 (t, *J* = 6.7 Hz, 2H), 2.13 – 2.07 (m, 2H), 2.03 (qt, *J* = 6.8, 1.4 Hz, 2H), 1.56 (d, *J* = 7.1 Hz, 2H), 1.26 (s, 10H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.41, 139.33, 136.57, 127.50, 122.32, 122.17, 119.60, 118.85, 114.29, 113.13, 111.42, 39.84, 36.97, 33.90, 29.42, 29.40, 29.38, 29.18, 29.01, 25.86, 25.48. **IR** (ATR) 3396, 3271, 3077, 2923, 2852, 1636, 1526, 1456, 1434, 1341, 1226, 1097, 993, 909, 803, 740, 584,

557, 483 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{21}H_{31}N_2O$: 327.2431; found: 327.2433. **m.p.**: 85.6-86.6 °C.

(1*r*,3*r*,5*r*,7*r*)-adamantan-2-yl acrylate (**1ag**)

To a dried flask was equipped with a stir bar and 2-adamantanol (1.5344 g, 10 mmol, 1 equiv.). The flask was then evacuated and back-filled with Ar for 3 times. DCM (14 mL) and Et_3N (2.1 mL, 15 mmol, 1.5 equiv.) was added. The reaction was cooled in an ice-water bath and added acryloyl chloride (809 μL, 10 mmol, 1 equiv.) dropwise. The resulting mixture was stirred overnight, and then concentrated under reduced pressure. The residue was purified by flash column chromatography (EA/PE = 1/10) to afford the alkene (1.2069 g, 79%, white solid).



Rf = 0.8-0.9 (EA/PE = 1:10; I_2 & anisaldehyde).

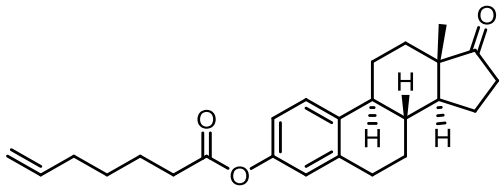
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (dd, *J* = 17.3, 1.6 Hz, 1H), 6.15 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.81 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.04 – 4.95 (m, 1H), 2.04 (dt, *J* = 10.2, 3.0 Hz, 5H), 1.92 – 1.71 (m, 9H), 1.57 (ddt, *J* = 10.9, 3.1, 1.5 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.74, 130.14, 129.49, 77.26, 37.52, 36.47, 32.01, 31.95, 27.39, 27.14. **IR** (ATR) 2908, 2854, 1635, 1449, 1406, 1340, 1296, 1272, 1192, 1098, 1044, 989, 903, 811 cm^{-1}. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{13}H_{19}O_2$: 207.1380; found: 207.1379. **m.p.**: 62.3-63.1 °C.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl hept-6-enoate (**1ak**)

To a dried flask was added the carboxylic acid (1.1mL, 7.5 mmol, 1.5 equiv.), followed by addition of thionyl chloride (0.7 mL, 9 mmol, 1.8 equiv.) dropwise in an ice-water bar. After refluxing the above solution at 80 ℃ for 3 h, extra thionyl chloride was removed under reduced pressure. The crude acyl chloride was used in the next step without further purification.

To a solution of cholesterol (1.3526 g, 5 mmol, 1 equiv.) in DCM (10 mL) was added acyl chloride and Et_3N (1.4 mL, 10 mmol, 2 equiv.) in an ice-water bar. The reaction was stirred at 0 ºC for 10 min. Then the reaction was warmed to room

temperature and stirred for another 11 h. The mixture was poured into saturated $NaHCO_3$ solution (20 mL) and extracted with DCM (30 mL×5). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by flash column chromatography (EA/PE = 1/5) to afford the alkene (1.7500 g, 95%, light yellow oil).



Rf = 0.5-0.6 (EA/PE = 1:5; I_2 & anisaldehyde).

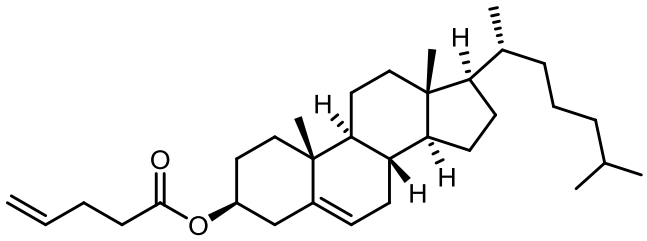
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.5 Hz, 1H), 6.87 – 6.77 (m, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.07 – 4.92 (m, 2H), 2.89 (dd, *J* = 8.2, 3.5 Hz, 2H), 2.56 – 2.51 (m, 2H), 2.51 – 2.44 (m, 1H), 2.42 – 2.35 (m, 1H), 2.30 – 2.22 (m, 1H), 2.16 – 2.07 (m, 3H), 2.05 – 1.92 (m, 3H), 1.76 (p, *J* = 7.5 Hz, 2H), 1.67 – 1.38 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.60, 220.55, 172.33, 172.31, 148.61, 138.27, 137.91, 137.23, 126.32, 121.55, 118.74, 114.82, 50.38, 47.88, 44.11, 37.98, 35.81, 34.17, 33.32, 31.54, 29.37, 28.27, 26.32, 25.73, 24.38, 21.55, 13.80. **IR** (ATR) 2930, 2861, 1740, 1640, 1494, 1208, 1151, 1054, 1007, 912, 820 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{25}H_{33}O_3$: 381.2424; found: 381.2428.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl pent-4-enoate (**1al**)

To a dried flask was added carboxylic acid (1.5018 g, 15 mmol, 1.5 equiv.), followed by addition of thionyl chloride (2.2 mL, 30 mmol, 3 equiv.) dropwise in an ice-water bar. The reaction was stirred at 80 °C for 5 h, then the resulting mixture was concentrated under reduced pressure to remove thionyl chloride. The crude acyl chloride was used in the next step without further purification.

To a solution of cholesterol (3.8666 g, 10 mmol, 1 equiv.) in DCM (10 mL) was added above acyl chloride and Et_3N (5.6 mL, 40 mL, 4 equiv.) in an ice-water bar. The reaction was stirred at this temperature for 10 min. Then the reaction was warmed to room temperature and stirred for another 11 h. The mixture was quenched by

saturated $NaHCO_3$ solution (20 mL) and extracted with DCM (30 mL×5). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by flash column chromatography (EA/PE= 1/50 to 1/30) to afford the alkene (966.0 mg, 21%, white solid).



Rf = 0.5-0.6 (EA/PE = 1:5; I_2 & anisaldehyde).

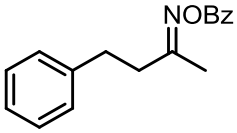
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 – 5.73 (m, 1H), 5.37 (dq, *J* = 5.0, 1.7 Hz, 1H), 5.13 – 4.95 (m, 2H), 4.69 – 4.56 (m, 1H), 2.37 (d, *J* = 2.9 Hz, 3H), 2.34 – 2.28 (m, 2H), 1.99 (ddt, *J* = 20.0, 16.9, 4.3 Hz, 2H), 1.84 (dtd, *J* = 12.8, 6.3, 5.9, 3.4 Hz, 3H), 1.62 – 1.42 (m, 8H), 1.39 – 1.23 (m, 5H), 1.20 – 1.05 (m, 7H), 1.02 (d, *J* = 2.8 Hz, 4H), 0.98 – 0.95 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.68 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.63, 139.82, 136.92, 122.79, 115.56, 74.07, 56.84, 56.29, 50.18, 42.46, 39.88, 39.67, 38.30, 37.14, 36.74, 36.33, 35.94, 34.04, 32.06, 32.01, 29.14, 28.38, 28.17, 27.96, 24.43, 23.98, 22.97, 22.71, 21.18, 19.47, 18.86, 12.01. **IR** (ATR) 2942, 2868, 1734, 1643, 1466, 1378, 1272, 1175, 1000, 914, 752 cm^{-1}. **HRMS (ESI) m/z**: $[M+Na]^+$ calcd for $C_{32}H_{52}NaO_2$: 491.3860; found: 491.3865. **m.p.**: 70.1-71.1 °C.

4-phenylbutan-2-one *O*-benzoyl oxime (VII)

NH_2OH•HCl (6 mmol, 2 equiv.) and acetone (3 mmol, 1 equiv.) in pyridine (3 mL) was stirred 4 hours. the reaction mixture was poured into saturated $NaHCO_3$ solution (60 mL). The resulting mixture was extracted with EA (30 mL × 5). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the crude oxime was obtained.

To a solution of the crude oxime (1.0 equiv.) in CH_2Cl_2 (2.0 mL/mmol) were added triethylamine (6 mmol, 2 equiv.) and benzoyl chloride (4.5 mmol, 1.5 equiv.) in an ice-water bath. After stirring for 14 h, the reaction mixture was quenched by saturated $NaHCO_3$ solution (10 mL). The resulting mixture was extracted with DCM

(10 mL × 5). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by column chromatography (EA/PE = 1/5) to obtain oxime ester **VII** (644.3 mg, 73%, white solid).

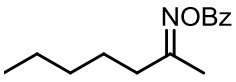


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 7.59 (ddt, *J* = 8.0, 6.9, 1.4 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.34 – 7.29 (m, 2H), 7.26 – 7.19 (m, 3H), 3.01 – 2.93 (m, 2H), 2.80 – 2.71 (m, 2H), 2.14 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.89, 164.08, 140.62, 133.37, 129.74, 129.44, 128.75, 128.67, 128.51, 126.51, 37.95, 32.78, 16.13. **HRMS (ESI) m/z**: $[M+Na]^+$ calcd for $C_{17}H_{17}NNaO_2$: 290.1151; found: 290.1149.

heptan-2-one *O*-benzoyl oxime (VIII)

NH_2OH•HCl (6 mmol, 2 equiv.) and acetone (3 mmol, 1 equiv.) in pyridine (3 mL) was stirred 4 hours. the reaction mixture was poured into saturated $NaHCO_3$ solution (60 mL). The resulting mixture was extracted with EA (30 mL × 5). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the crude oxime was obtained.

To a solution of the crude oxime (1.0 equiv.) in CH_2Cl_2 (2.0 mL/mmol) were added triethylamine (6 mmol, 2 equiv.) and benzoyl chloride (4.5 mmol, 1.5 equiv.) in an ice-water bath. After stirring for 14 h, the reaction mixture was quenched by saturated $NaHCO_3$ solution (10 mL). The resulting mixture was extracted with DCM (10 mL × 5). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by column chromatography (EA/PE = 1/5) to obtain oxime ester **VIII** (155.2 mg, 21%, colorless oil).

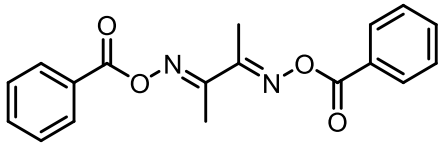


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 2H), 7.62 – 7.55 (m, 1H), 7.47 (td, *J* = 7.7, 3.1 Hz, 2H), 2.57 – 2.49 (m, 1H), 2.46 – 2.38 (m, 0H), 2.11 (d, *J* = 1.8 Hz, 3H), 1.68 – 1.58 (m, 2H), 1.42 – 1.31 (m, *J* = 3.9, 3.3 Hz, 4H), 0.91 (h, *J* = 2.5 Hz, 3H).;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.41, 167.88, 164.14, 133.30, 133.28, 129.71, 129.68, 129.55, 128.68, 128.64, 35.99, 31.88, 31.55, 31.08, 26.20, 25.67, 22.50, 22.47, 20.43, 15.56, 14.07, 14.01. **HRMS (ESI) m/z**: $[M+Na]^+$ calcd for $C_{14}H_{19}NaNO_2$: 256.1308; found: 256.1305.

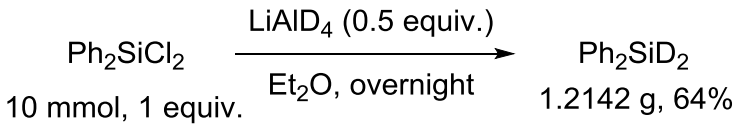
butane-2,3-dione *O*,*O*-dibenzoyl dioxime (IX)

To a solution of oxime (1.0 equiv.) in CH_2Cl_2 (2.0 mL/mmol) were added triethylamine (2.4 mL, 17.5 mmol, 3.5 equiv.) and benzoyl chloride (1.5 mL, 12.5 mmol, 2.5 equiv.) in an ice-water bath. After stirring for 22 h, the reaction mixture was quenched by saturated Na_2CO_3 solution (10 mL). The resulting mixture was extracted with DCM (10 mL × 5). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by column chromatography (EA/PE = 1/1) to obtain oxime ester **IX** (852.8 mg, 53%, white solid).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.11 (m, 4H), 7.65 (ddt, *J* = 8.7, 7.0, 1.4 Hz, 2H), 7.54 – 7.49 (m, 4H), 2.52 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.13, 161.65, 133.82, 129.84, 128.76, 128.46, 12.18. **IR** (ATR) 1748, 1599, 1491, 1451, 1367, 1241, 1180, 1148, 1055, 1023, 974, 927, 706, 653 cm^{-1}. **HRMS (ESI) m/z**: $[M+Na]^+$ calcd for $C_{18}H_{16}N_2NaO_4$: 347.1002; found: 347.0999. **m.p.**: 229.5-230.5 °C.

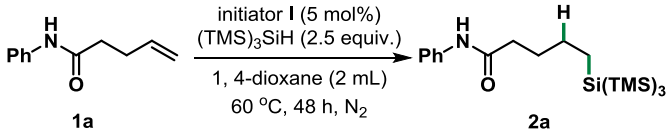
To a solution of $LiAlD_4$ (209.9 mg, 5 mmol, 0.5 equiv.) in anhydrous ethyl ether (20 mL) was added Ph_2SiCl_2 (2.1 mL, 10 mmol, 1 equiv.) in an ice-water bar. The reaction was stirred at this temperature for 10 min. Then the reaction was warmed to room temperature and reflux for overnight. The mixture was quenched by ice-water (2 mL), then added 20 mL water and extracted with ethyl ether (30 mL×5). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE (30-60 °C)) to afford Ph_2SiD_2 (1.2142 g, 64%, D> 99%, colerless oil).



Rf = 0.9-1.0 (PE; UV & I_2).

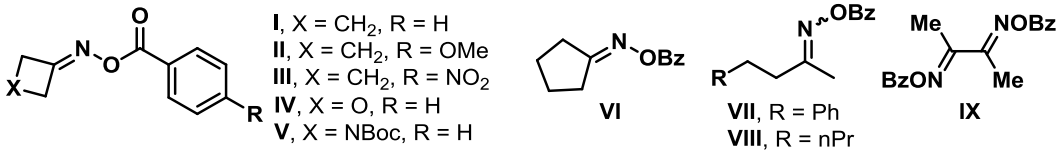
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 4H), 7.41 (ddd, J = 14.2, 7.7, 6.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.84, 131.61, 130.03, 128.28.

3. Optimization of Reaction Conditions.



Entry[a]	variations from the "standard' conditions	Yield[b]
1	none	98% (94%)[c]
2	initiator **II** instead of **I**	98%
3	initiator **III** instead of **I**	nr[d]
4	initiator **IV** instead of **I**	97%
5	initiator **V** instead of **I**	98%
6	initiator **VI** instead of **I**	<5%
7	initiator **VII** instead of **I**	5%[e]
8	initiator **VIII** instead of **I**	10%[f]
9	initiator **IX** instead of **I**	80%
10	1 mol% of initiator I instead of 5 mol%	88%
11	2.0 equiv. of $(TMS)_3SiH$ instead of 2.5 equiv.	92%
12	$PhSiH_3$ instead of $(TMS)_3SiH$	55%
13	Ph_2SiH_2 instead of $(TMS)_3SiH$	20%
14	Et_3SiH instead of $(TMS)_3SiH$	5%
15	$(MeO)_2MeSiH$ instead of $(TMS)_3SiH$	6%
16	PhMe instead of 1, 4-dioxane	93%
17	THF instead of 1, 4-dioxane	80%
18	Et_2O instead of 1, 4-dioxane	60%
19	Ethyl acetate instead of 1, 4-dioxane	88%
20	MeOH instead of 1, 4-dioxane	80%
21	50 °C instead of 60 °C	93%
22	40 °C instead of 60 °C	85%
23	36 h instead of 48 h	89%

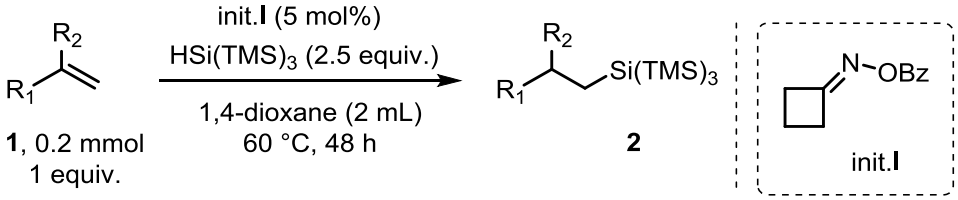
24	without **I**	nr[d]
25	without light	98%



[a] The reaction was performed on a 0.2 mmol scale. [b] Determined by ^{1}H NMR integration against an internal standard (3,4-dimethoxy-acetophenone). [c] Isolated yield. [d] nr = no reaction. [e] 95% of starting material is recovered. [f] 90% of starting material is recovered.

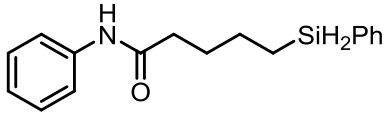
4. General Procedures for Syntheses of Alkyl Silanes

General Procedures for Syntheses of Alkyl Silanes Using Standard Methods



A dried Schlenk tube (10 mL) was charged with a stirring bar, the alkene (**1**, 35.0 mg, 0.2 mmol, 1 equiv.) and oxime ester (0.9 mg, 0.01 mmol, 5 mol%). The Schlenk tube was then evacuated and back-filled with nitrogen (N_2, 99.999%) for 3 times. Then, fresh-distilled anhydrous 1,4-dioxane (2 mL) and $(TMS)_3SiH$ (153 μL, 0.5 mmol, 2.5 equiv.) was added via syringe under N_2. The reaction mixture was stirred at 60 °C for 48 h. After completion, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired alkyl silane products **2**.

N-phenyl-5-(phenylsilyl)pentanamide (3a)

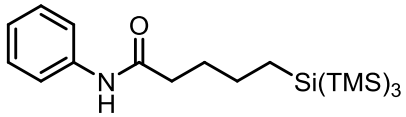


55%; (^{1}H NMR yield, 3,4-dimethoxyacetophenone was an internal standard); R_f = 0.4 – 0.5 (PE/EA = 5:1, UV);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42 –

7.28 (m, 5H), 7.18 (s, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.30 (t, *J* = 3.7 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.80 (p, *J* = 7.5 Hz, 2H), 1.60 – 1.48 (m, 2H), 1.05 – 0.93 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.26, 138.04, 135.34, 132.47, 129.76, 129.12, 128.17, 124.35, 119.94, 37.55, 28.76, 24.95, 10.03. **IR** (ATR) 3297, 2925, 2130, 1599, 1542, 1498, 1116, 879, 840, 754, 697, 560 cm^{-1}. **HRMS (ESI) m/z**: $[M+Na]^+$ Calcd for $C_{17}H_{21}NNaOSi$: 306.1285; found: 306.1282.

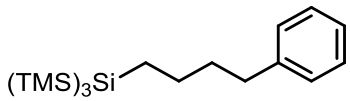
4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-*N*-phenylbutanamide (2a)



79.6 mg, 94%, white solid; Rf = 0.4-0.5 (EA/PE = 1:5; UV);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.40 – 2.28 (m, 2H), 1.76 (p, *J* = 7.5 Hz, 2H), 1.55 – 1.43 (m, 2H), 0.86 – 0.74 (m, 2H), 0.15 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.43, 138.08, 129.09, 124.30, 119.99, 37.58, 30.12, 29.05, 7.52, 1.28. **IR** (ATR) 3288, 2948, 1661 1444, 1302, 830, 690, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+Na]^+$ calcd for $C_{20}H_{41}NNaOSi_4$: 446.2157; found: 446.2158. **m.p.**: 116.6-117.5 °C.

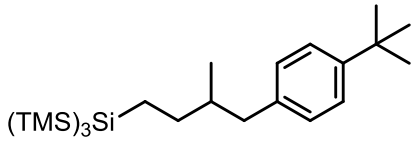
3,3-di-tert-butyl-1,1,1,3,3,3-hexamethyl-2-(4-phenylbutyl)-2-(trimethylsilyl)-trisilane (2b)



83.3 mg, 99%, colorless oil; Rf = 0.9 – 1.0 (PE; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.27 – 7.21 (m, 3H), 2.72 – 2.66 (m, 2H), 1.73 (p, *J* = 7.4 Hz, 2H), 1.54 – 1.45 (m, 2H), 0.90 – 0.84 (m, 2H), 0.22 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.82, 128.56, 128.38, 125.70, 36.08, 35.66, 28.99, 7.61, 1.30. **IR** (ATR) 2948, 1450, 1243, 1029, 831, 744, 691, 622 cm^{-1}. **GC–MS** m/z: 380 M^+, 247 $(TMS)_3Si^+$, 133 $(Ph(CH_2)_4)^+$.

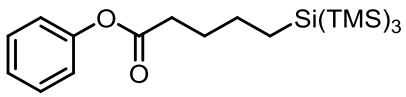
2-(4-(4-(*tert*-butyl)phenyl)-3-methylbutyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2c)



57.6 mg, 64%, colorless oil; Rf = 0.9 – 1.0 (PE; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 2.49 (d, *J* = 7.5 Hz, 2H), 1.66 (ddd, *J* = 14.0, 9.6, 6.1 Hz, 1H), 1.50 – 1.38 (m, 1H), 1.33 (d, *J* = 0.9 Hz, 9H), 1.16 (tdd, *J* = 13.1, 8.1, 4.6 Hz, 1H), 0.96 – 0.84 (m, 4H), 0.69 – 0.60 (m, 1H), 0.15 – 0.12 (m, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.45, 138.59, 128.91, 125.15, 43.01, 38.81, 35.66, 34.46, 31.59, 19.35, 4.68, 1.27. **IR** (ATR) 2952, 1460, 830, 744, 685, 622 cm^{-1}. **GC–MS** m/z: 450 M^+, 247 $(TMS)_3Si^+$, 203 $(M\text{-}Si(TMS)_3)^+$, 146 $(M\text{-}Si(TMS)_3\text{-}^tBu)^+$.

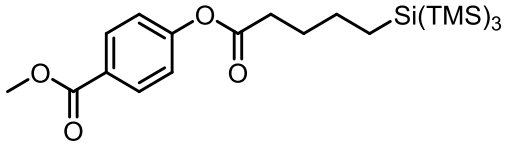
phenyl 5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentanoate (2d)



80.9 mg, 94%, colorless oil; Rf = 0.8 – 0.9 (PE/EA = 20:1; UV, I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.25 – 7.19 (m, 1H), 7.10 – 7.03 (m, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 1.86 – 1.74 (m, 2H), 1.52 (dddd, *J* = 14.9, 9.0, 6.5, 4.2 Hz, 2H), 0.88 – 0.78 (m, 2H), 0.17 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.33, 150.91, 129.52, 125.84, 121.72, 34.16, 29.42, 28.91, 7.52, 1.31. **IR** (ATR) 2949, 1761, 1244, 1195, 1163, 1115, 833, 747, 688, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+Na]^+$ calcd for $C_{20}H_{40}NaO_2Si_4$: 447.1998; found: 447.1997.

methyl 4-((5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentanoyl)-oxy)-benzoate (2e)

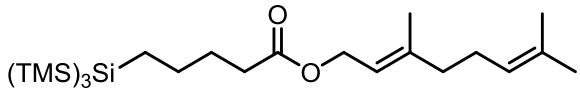


96.9 mg, 98%, colorless oil; Rf = 0.8 – 0.9 (EA/PE = 1:5; UV, I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.18 – 7.12 (m, 2H), 3.91 (s, 3H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.79 (p, *J* = 7.4 Hz, 2H), 1.57 – 1.46 (m, 2H), 0.87 – 0.78 (m, 2H), 0.17 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.72, 166.44, 154.55, 131.27,

127.72, 121.71, 52.28, 34.09, 29.27, 28.82, 7.49, 1.27. **IR** (ATR) 2949, 1764, 1726, 1277, 1243, 1203, 1160, 1101, 1017, 970, 829, 764, 687, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{22}H_{43}O_4Si_4$: 483.2233; found: 483.2238.

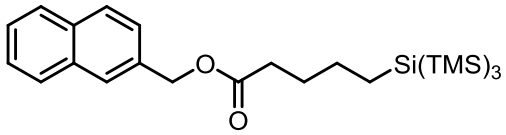
(*E*)-3,7-dimethylocta-2,6-dien-1-yl 5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)pentanoate (2f)



113.1 mg, 100%, colorless oil; Rf = 0.5 – 0.6 (PE/EA = 10:1; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (ddq, *J* = 7.1, 5.7, 1.3 Hz, 1H), 5.08 (tdt, *J* = 5.8, 3.0, 1.5 Hz, 1H), 4.62 – 4.53 (m, 2H), 2.30 (td, *J* = 7.7, 3.0 Hz, 2H), 2.14 – 2.01 (m, 4H), 1.72 – 1.56 (m, 11H), 1.46 – 1.36 (m, 2H), 0.82 – 0.71 (m, 2H), 0.15 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.91, 142.18, 131.91, 123.91, 118.55, 61.37, 39.68, 34.10, 29.47, 28.88, 26.45, 25.82, 17.82, 16.60, 7.39, 1.27. **IR** (ATR) 2948, 1736, 1244, 1180, 982, 831, 748, 687, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{24}H_{53}O_2Si_4$: 485.3117; found: 485.3121.

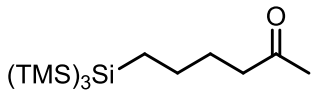
naphthalen-2-ylmethyl 5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentanoate (2g)



101.6 mg, 100%, colorless oil; Rf = 0.4 – 0.5 (PE/EA = 50:1; UV, I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 4H), 7.52 – 7.44 (m, 3H), 5.28 (s, 2H), 2.43 – 2.37 (m, 2H), 1.71 (p, *J* = 7.4 Hz, 2H), 1.48 – 1.40 (m, 2H), 0.81 – 0.75 (m, 2H), 0.15 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.74, 133.63, 133.35, 133.25, 128.52, 128.12, 127.84, 127.50, 126.40, 126.37, 126.06, 66.42, 34.08, 29.42, 28.89, 7.41, 1.27. **IR** (ATR) 2948, 1738, 1244, 1178, 834, 748, 688, 623 cm^{-1}. **HRMS (ESI) m/z**: $[M+Na]^+$ calcd for $C_{25}H_{44}NaO_2Si_4$: 511.2311; found: 511.2306.

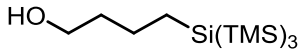
1,1,1,3,3,3-hexamethyl-2-(3-phenoxypropyl)-2-(trimethylsilyl)trisilane (2h)



62.7 mg, 90%, colorless oil; Rf = 0.3 – 0.4 (PE/EA = 20:1; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (t, *J* = 7.5 Hz, 2H), 2.13 (s, 3H), 1.60 (tt, *J* = 8.3, 6.3 Hz, 2H), 1.38 (dddd, *J* = 13.3, 11.3, 6.5, 3.8 Hz, 2H), 0.79 – 0.70 (m, 2H), 0.14 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.30, 43.49, 29.99, 28.94, 28.45, 7.59, 1.27. **IR** (ATR) 2927, 1743, 1452, 1396, 707 cm^{-1}. **GC–MS** m/z: 346 M^+, 247 $(TMS)_3Si^+$, 99 $(M\text{-}Si(TMS)_3)^+$.

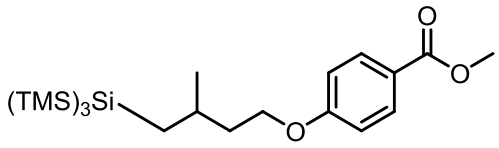
4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)butan-1-ol (2i)



63.9 mg, 100%, colorless oil; Rf = 0.9 – 1.0 (PE/EA = 1/1; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.6 Hz, 2H), 1.64 – 1.52 (m, 3H), 1.49 – 1.39 (m, 2H), 0.81 – 0.75 (m, 2H), 0.15 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 62.58, 37.31, 25.38, 7.62, 1.30; **IR** (ATR) 3325, 2948, 1397, 1244, 622 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{13}H_{37}NaOSi_4$: 321.1916; found: 321.1917.

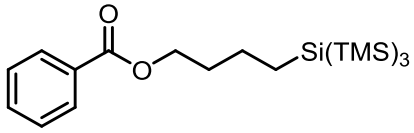
methyl 4-(4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-3-methylbutoxy)benzoate (2j)



43.7 mg, 31%, yellow oil; Rf = 0.6 – 0.7 (PE/EA = 10/1; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 6.93 – 6.86 (m, 2H), 4.04 (qt, *J* = 9.4, 6.3 Hz, 2H), 3.88 (s, 3H), 1.85 (tdd, *J* = 13.4, 9.2, 6.1 Hz, 2H), 1.68 – 1.61 (m, 1H), 1.00 (dd, *J* = 15.1, 5.5 Hz, 4H), 0.77 – 0.69 (m, 1H), 0.17 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.07, 163.08, 131.70, 122.48, 114.18, 66.48, 51.95, 39.65, 29.80, 23.14, 16.72, 1.48. **IR** (ATR) 2952, 1722, 1279, 1251, 1168, 1108, 770, 623 cm^{-1}. **HRMS (ESI) m/z**: $[M+Na]^+$ calcd for $C_{22}H_{44}NaO_3Si_4$: 491.2260; found: 491.2259.

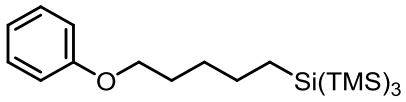
4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)butyl benzoate (2k)



84.6 mg, 100%, colorless oil; Rf = 0.6 – 0.7 (PE/EA = 20:1; UV & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.58 – 7.50 (m, 1H), 7.46 – 7.39 (m, 2H), 4.34 (t, *J* = 6.5 Hz, 2H), 1.81 (p, *J* = 6.8 Hz, 2H), 1.57 (dtd, *J* = 11.6, 9.0, 8.6, 6.2 Hz, 2H), 0.91 – 0.78 (m, 2H), 0.16 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.76, 132.91, 130.62, 129.68, 128.41, 64.60, 33.11, 25.79, 7.49, 1.27. **IR** (ATR) 2945, 2893, 1722, 1272, 1175, 709, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{41}O_2Si_4$: 425.2178; found: 425.2182.

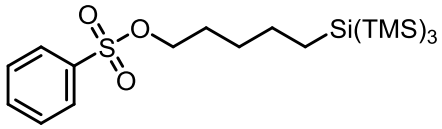
1,1,1,3,3,3-hexamethyl-2-(5-phenoxypentyl)-2-(trimethylsilyl)trisilane (2l)



80.8 mg, 95%, colorless oil; Rf (PE) = 0.5 – 0.6 (PE; UV & I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 6.97 – 6.88 (m, 3H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.80 (dt, *J* = 8.5, 6.2 Hz, 2H), 1.55 – 1.42 (m, 4H), 0.89 – 0.76 (m, 2H), 0.18 (d, *J* = 1.4 Hz, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.27, 129.54, 120.61, 114.63, 68.01, 30.74, 29.23, 29.08, 7.72, 1.34. **IR** (ATR) 2945.71, 1242, 1039, 749, 622 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{43}OSi_4$: 411.2385; found: 411.2390.

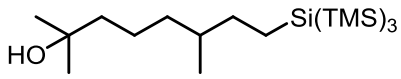
5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentyl benzenesulfonate (2m)



61.3 mg, 65%, colorless oil; Rf = 0.4 – 0.5 (PE/EA = 10:1; UV & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.68 – 7.62 (m, 1H), 7.59 – 7.51 (m, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.69 – 1.58 (m, 2H), 1.38 – 1.29 (m, 4H), 0.76 – 0.63 (m, 2H), 0.13 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.44, 133.78, 129.34, 127.97, 71.05, 29.88, 28.77, 28.57, 7.52, 1.27. **IR** (ATR) 2948, 1364, 1186, 936, 622 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{20}H_{43}O_3SSi_4$: 475.2004; found: 475.2003.

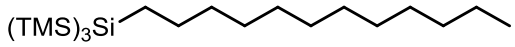
8-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-2,6-dimethyloctan-2-ol (2n)



41.2 mg, 47%, colorless oil; Rf = 0.6 – 0.7 (PE/EA = 5:1; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 – 1.24 (m, 9H), 1.21 (s, 6H), 0.86 (d, *J* = 6.3 Hz, 3H), 0.82 – 0.64 (m, 2H), 0.15 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 71.25, 44.45, 37.04, 36.52, 36.47, 29.40, 29.33, 22.07, 19.32, 4.50, 1.34. **IR** (ATR) 3359, 2948, 1376, 1244, 622 cm^{-1}. **HRMS (APCI) m/z**: $[M+Na]^+$ calcd for $C_{19}H_{48}NaOSi_4$: 427.2674; found: 427.2673.

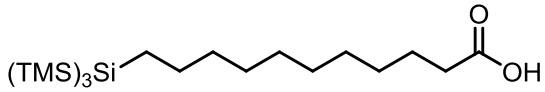
2-dodecyl-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2o)



75.4 mg, 93%, colorless oil; Rf = 0.9 – 1.0 (PE; PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 20H), 0.92 – 0.86 (m, 3H), 0.79 – 0.72 (m, 2H), 0.16 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 34.44, 32.10, 29.86, 29.84, 29.82, 29.77, 29.52, 29.40, 29.37, 22.86, 14.28, 7.72, 1.33. **IR** (ATR) 2922, 2853, 623 cm^{-1}. **GC–MS m/z**: 416 M^+, 247 $(TMS)_3Si^+$, 169 $(M\text{-}Si(TMS)_3)^+$.

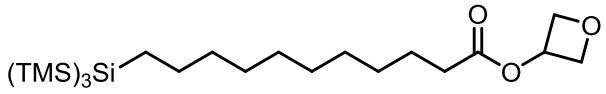
1,1,1,3,3,3-hexamethyl-2-(2-(phenylthio)ethyl)-2-(trimethylsilyl)trisilane (2p)



90.6 mg, 93%, colorless oil; Rf = 0.7 – 0.8 (PE/EA = 1:1; PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (t, *J* = 7.5 Hz, 2H), 1.63 (p, *J* = 7.4 Hz, 2H), 1.38 – 1.23 (m, 14H), 0.80 – 0.70 (m, 2H), 0.15 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.46, 34.39, 34.23, 29.67, 29.57, 29.40, 29.38, 29.30, 29.22, 24.82, 7.70, 1.33. **IR** (ATR) 2923, 2853, 1709, 1243, 622 cm^{-1}. **HRMS (APCI) m/z**: $[M-H]^-$ calcd for $C_{20}H_{47}O_2Si_4$: 431.2659; found: 431.2658.

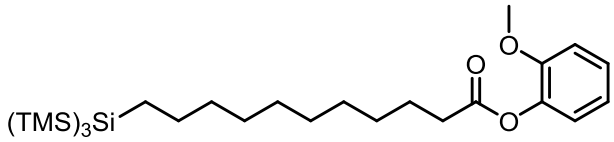
oxetan-3-yl 11-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)undecanoate (2q)



96.9 mg, 100%, colorless oil; Rf = 0.6 – 0.7 (PE/EA = 5:1; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 (tt, *J* = 6.4, 5.3 Hz, 1H), 4.88 (ddd, *J* = 7.5, 6.4, 1.0 Hz, 2H), 4.62 (ddd, *J* = 7.5, 5.3, 1.0 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.38 – 1.19 (m, 14H), 0.80 – 0.64 (m, 2H), 0.15 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.27, 77.78, 67.81, 34.38, 34.11, 29.66, 29.56, 29.37, 29.29, 29.23, 24.94, 7.70, 1.31. **IR** (ATR) 2924, 2854, 1742, 1167, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{23}H_{53}O_3Si_4$: 489.3066; found: 489.3071.

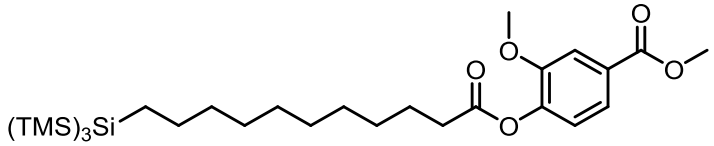
2-methoxyphenyl 2-methoxyphenyl 11-(1,1,1,3,3,3-hexamethyl-2- (trimethylsilyl)-trisilan-2-yl)undecanoate (2r)



93.9 mg, 88%, colorless oil; Rf = 0.4 – 0.5 (PE/EA = 10:1; UV & I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 7.02 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.99 – 6.90 (m, 2H), 3.82 (s, 3H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.77 (p, *J* = 7.4 Hz, 2H), 1.44 – 1.22 (m, 14H), 0.80 – 0.73 (m, 2H), 0.16 (d, *J* = 1.1 Hz, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.06, 151.32, 140.03, 126.88, 122.99, 120.89, 112.54, 55.94, 34.41, 34.21, 29.71, 29.65, 29.45, 29.39, 29.33, 29.23, 25.19, 7.70, 1.32. **IR** (ATR) 2924, 2853, 1765, 1246, 1197, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{27}H_{55}O_3Si_4$: 539.3223; found: 539.3224.

methyl 4-((11-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)undecanoyl)oxy)-3-methoxybenzoate (2s)

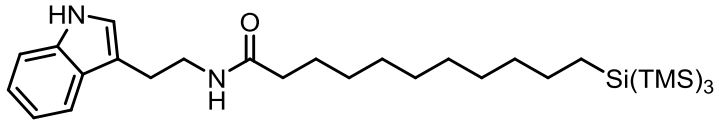


118.5 mg, 97%, colorless oil; Rf = 0.6 – 0.7 (PE/EA = 5:1; UV & I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.45 – 1.25 (m, 14H), 0.80 – 0.72 (m, 2H), 0.15 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.48, 166.53, 151.23, 143.91, 128.81, 122.93, 122.74, 113.52, 56.14, 52.37, 34.38, 34.14,

29.67, 29.62, 29.40, 29.36, 29.30, 29.17, 25.08, 7.68, 1.30. **IR** (ATR) 2924, 2853, 1769, 1725, 1243, 1198, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{29}H_{57}O_5Si_4$: 597.3278; found: 597.3280.

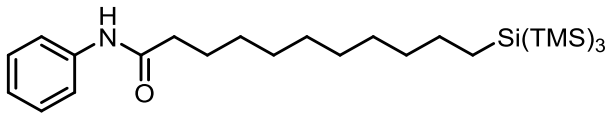
_N_-(2-(1H-indol-3-yl)ethyl)-11-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)undecanamide (2t)



61.5 mg, 53%, colorless oil; Rf = 0.6- 0.7 (PE/EA = 1:1; UV & I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.61 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.21 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 5.58 (d, *J* = 6.8 Hz, 1H), 3.61 (q, *J* = 6.5 Hz, 2H), 2.98 (t, *J* = 6.7 Hz, 2H), 2.10 (t, *J* = 7.7 Hz, 2H), 1.58 (t, *J* = 7.4 Hz, 2H), 1.39 – 1.23 (m, 14H), 0.79 – 0.72 (m, 2H), 0.19 – 0.13 (m, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.42, 136.57, 127.50, 122.28, 122.19, 119.56, 118.82, 113.10, 113.07, 111.43, 39.85, 37.03, 34.41, 29.71, 29.63, 29.51, 29.45, 29.38, 29.32, 25.89, 25.49, 7.69, 1.32. **IR** (ATR) 3287, 2923, 2853, 1646, 1457, 1099, 741, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{30}H_{59}N_2OSi_4$: 575.3699; found: 575.3704.

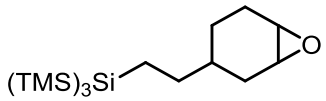
11-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-_N_-phenylundecanamide (2u)



99.4 mg, 98%, colorless oil; Rf = 0.5 – 0.6 (PE/EA = 5:1; UV & I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.71 (q, *J* = 7.3 Hz, 2H), 1.37 – 1.25 (m, 14H), 0.78 – 0.72 (m, 2H), 0.16 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.72, 138.15, 129.07, 124.26, 119.98, 37.95, 34.39, 29.69, 29.62, 29.54, 29.43, 29.37, 29.30, 25.80, 7.69, 1.31. **IR** (ATR) 3299, 2924, 2853, 1661, 751, 623 cm^{-1}. **HRMS (APCI)**: $[M+H]^+$ calcd for $C_{26}H_{54}NOSi_4$: 508.3277; found: 508.3279.

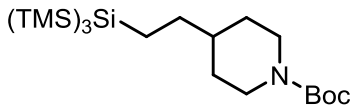
2-(2-(7-oxabicyclo[4.1.0]heptan-3-yl)ethyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2v)



59.1 mg, 78%, colorless oil; Rf = 0.5 – 0.6 (PE/EA = 50:1; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.18 – 3.10 (m, 2H), 2.16 (dddt, *J* = 17.6, 14.7, 2.9, 1.7 Hz, 1H), 2.10 – 1.93 (m, 1H), 1.84 – 1.64 (m, 1H), 1.45 – 1.31 (m, 2H), 1.29 – 1.22 (m, 2H), 1.16 – 1.01 (m, 1H), 0.87 (dtd, *J* = 13.1, 11.1, 6.6 Hz, 1H), 0.75 – 0.67 (m, 2H), 0.14 (d, *J* = 1.1 Hz, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 52.09, 51.59, 50.82, 50.77, 35.09, 34.98, 34.59, 31.99, 30.34, 29.14, 25.65, 24.19, 22.81, 22.47, 3.31, 3.07, -0.00. **IR** (ATR) 3947, 1438, 1244, 831, 623 cm^{-1}. **GC–MS** m/z: 372 M^+, 247 $(TMS)_3Si^+$, 125 $(M\text{-}Si(TMS)_3)^+$.

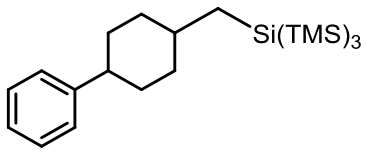
***tert*-butyl 4-(2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)ethyl)-piperidine-1-carboxylate (2w)**



85.8 mg, 94%, colorless oil; Rf = 0.6 – 0.7 (PE/EA = 10:1; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 – 3.94 (m, 2H), 2.65 (t, *J* = 12.8 Hz, 2H), 1.71 – 1.59 (m, 2H), 1.44 (s, 9H), 1.36 – 1.24 (m, 3H), 1.10 – 0.96 (m, 2H), 0.80 – 0.68 (m, 2H), 0.14 (d, *J* = 1.0 Hz, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.99, 79.25, 44.19, 39.75, 36.15, 31.94, 28.61, 4.43, 1.30. **IR** (ATR) 2984, 1696, 1420, 1241, 656, 623 cm^{-1}. **HRMS (ESI)**: $[M+H]^+$ calcd for $C_{21}H_{50}NO_2Si_4$: 460.2913; found: 460.2915.

1,1,1,3,3,3-hexamethyl-2-((4-phenylcyclohexyl)methyl)-2-(trimethylsilyl)trisilane (2x)

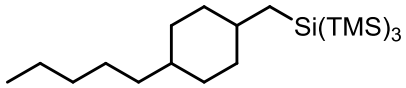


50.3 mg, 60%, colorless oil; Rf = 0.9 – 1.0 (PE; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 2.48 (tt, *J* = 12.2, 3.2 Hz, 1H), 2.00 – 1.86 (m, 4H), 1.47 (qd, *J* = 13.8, 12.9, 3.9 Hz, 2H), 1.41 –

1.32 (m, 1H), 1.19 – 1.04 (m, 2H), 0.84 (d, *J* = 6.8 Hz, 2H), 0.21 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.74, 128.41, 126.98, 125.97, 44.21, 37.52, 37.35, 34.71, 16.41, 1.53. **IR** (ATR) 2920, 1447, 695, 623 cm^{-1}. **GC–MS m/z**: 420 M^+, 247 $(TMS)_3Si^+$, 173 $(M\text{-}Si(TMS)_3)^+$.

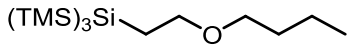
2-benzamido-2-(3-methyl-2-(4,4,4-trifluorobutyl)phenyl)acetic acid (2y)



57.5 mg, 69%, colorless oil; Rf = 0.9 – 1.0 (PE; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 – 1.70 (m, 4H), 1.32 – 1.20 (m, 8H), 1.15 (tt, *J* = 7.3, 3.8 Hz, 3H), 0.90 – 0.85 (m, 6H), 0.75 (d, *J* = 6.8 Hz, 2H), 0.16 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 38.03, 37.53, 37.50, 37.16, 33.80, 32.40, 26.87, 22.88, 16.44, 14.28, 1.52. **IR** (ATR) 2918, 1446, 623 cm^{-1}. **GC–MS m/z**: 414 M^+, 247 $(TMS)_3Si^+$, 153 $(M\text{-}CH_2\text{-}(TMS)_3Si)^+$.

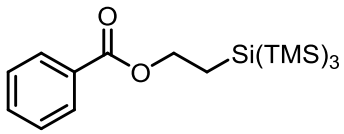
2-(2-butoxyethyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (2z)



69.2 mg, 95%, colorless oil; Rf = 0.5 – 0.6 (PE/EA = 30:1; I_2 & anisaldehyde & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 – 3.43 (m, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 1.56 (ddd, *J* = 7.7, 6.2, 1.3 Hz, 2H), 1.42 – 1.34 (m, 2H), 1.24 – 1.16 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.16 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 70.90, 70.36, 32.09, 19.55, 14.10, 9.47, 1.23. **IR** (ATR) 2951, 1243, 1099, 622 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{15}H_{41}OSi_4$: 349.2229; found: 349.2226.

2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)ethyl benzoate (2aa)

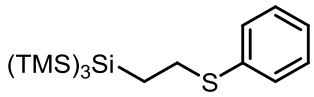


79.9 mg, 95%, colorless oil; Rf = 0.7 – 0.8 (PE/EA = 20:1; UV & I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.57 – 7.51 (m, 1H), 7.46 – 7.40 (m, 2H), 4.43 – 4.35 (m, 2H), 1.40 – 1.33 (m, 2H), 0.22 (s, 27H); **^{13}C NMR** (101

MHz, $CDCl_3$) δ 166.71, 132.88, 130.86, 129.68, 128.44, 65.55, 9.10, 1.21. **IR** (ATR) 2950, 2894, 1717, 1174, 1101, 623 cm^{-1}. **GC–MS m/z**: 396 M^+, 247 $(TMS)_3Si^+$, 149 $(M\text{-}Si(TMS)_3)^+$, 105 $(PhCO)^+$.

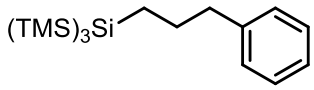
1,1,1,3,3,3-hexamethyl-2-(2-(phenylthio)ethyl)-2-(trimethylsilyl)trisilane (2ab)



74.5 mg, 94%, colorless oil; Rf = 0.9 – 1.0 (PE; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 4H), 7.13 (ddt, *J* = 6.6, 5.7, 2.4 Hz, 1H), 3.00 – 2.92 (m, 2H), 1.19 – 1.11 (m, 2H), 0.13 (d, *J* = 1.0 Hz, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.00, 129.31, 129.01, 125.97, 33.90, 8.63, 1.29. **IR** (ATR) 2953, 2924, 1083, 691, 623 cm^{-1}. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{17}H_{37}SSi_4$: 385.1688; found:385.1684.

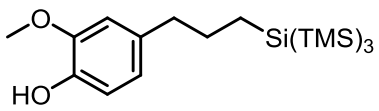
4-(4-(benzamido(carboxy)methyl)-[1,1'-biphenyl]-3-yl)butanoic acid (2ac)



43.3 mg, 62%, colorless oil; Rf = 0.9-1.0 (PE; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.22 – 7.14 (m, 3H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.67 (m, 2H), 0.88 – 0.80 (m, 2H), 0.16 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.53, 128.57, 128.39, 125.78, 40.64, 31.07, 7.59, 1.31. **IR** (ATR) 2951, 1037, 623 cm^{-1}. **GC–MS m/z**: 366 M^+, 247 $(TMS)_3Si^+$, 119 $(M\text{-}Si(TMS)_3)^+$.

5-(3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propyl)-2-methoxyphenol (2ad)

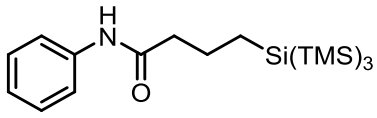


59.4 mg, 72%, colorless oil; Rf = 0.4 – 0.5 (PE/EA = 10:1; UV & I_2 & anisaldehyde & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.81 (m, 1H), 6.66 (d, *J* = 6.8 Hz, 2H), 5.47 (s, 1H), 3.87 (s, 3H), 2.57 (t, *J* = 7.5 Hz, 2H), 1.76 – 1.63 (m, 2H), 0.86 – 0.75 (m, 2H),

0.15 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.41, 143.67, 134.50, 121.14, 114.25, 111.09, 55.96, 40.19, 31.30, 7.41, 1.31. **IR** (ATR) 3556, 2949, 1265, 1123, 1036, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{41}O_2Si_4$: 413.2178; found: 413.2177.

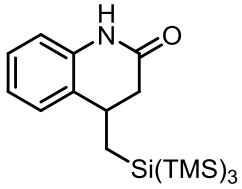
4-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-*N*-phenylbutanamide (2ae)



This reaction was conducted at 110 °C; 64.9 mg, 79%, white solid; Rf = 0.4 – 0.5 (PE/EA = 10:1; UV);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.37 – 7.24 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.82 (dq, *J* = 11.2, 7.4 Hz, 2H), 0.89 – 0.79 (m, 2H), 0.17 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.00, 138.10, 129.10, 124.28, 120.00, 42.11, 25.37, 7.86, 1.51, 1.30, 1.07. **IR** (ATR) 3288, 2950, 2893, 1659, 1442, 1107, 689, 622 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{40}NOSi_4$: 410.2181; found: 410.2181. **m.p.**: 156.9-157.9 °C.

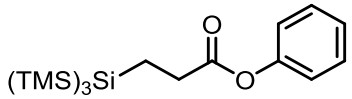
4-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-3,4-dihydroquinolin-2(1H)-one (2ae')



This reaction was conducted at 110 °C; 16.9 mg, 21%, white solid; Rf = 0.2 – 0.3 (PE/EA = 10:1; UV);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 64.1 Hz, 1H), 7.17 (dtd, *J* = 8.2, 4.1, 1.5 Hz, 2H), 7.02 (td, *J* = 7.4, 1.2 Hz, 1H), 6.77 (ddd, *J* = 8.0, 5.2, 1.3 Hz, 1H), 3.05 (dq, *J* = 10.4, 5.2 Hz, 1H), 2.79 – 2.71 (m, 1H), 2.56 (dd, *J* = 16.1, 4.7 Hz, 1H), 1.23 – 1.15 (m, 2H), 0.22 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.98, 135.98, 130.69, 127.56, 126.90, 123.54, 115.89, 37.70, 36.10, 14.37, 1.49. **IR** (ATR) 2951, 168, 1595, 1245, 834, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{38}NOSi_4$: 408.2025; found: 408.2024. **m.p.**: 141.9-142.9 °C.

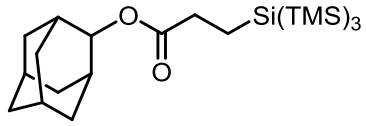
phenyl 3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (2af)



75.1 mg, 91%, colorless oil; Rf = 0.4 – 0.5 (PE/EA = 30:1; UV);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.26 – 7.19 (m, 1H), 7.15 – 7.06 (m, 2H), 2.63 – 2.51 (m, 2H), 1.27 – 1.20 (m, 2H), 0.22 (d, *J* = 1.0 Hz, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.24, 151.03, 129.52, 125.84, 121.70, 33.56, 3.04, 1.23. **IR** (ATR) 2949, 2893, 1761, 1190, 1030, 622 cm^{-1}. **HRMS (APCI)**: $[M+Na]^+$ calcd for $C_{18}H_{36}NaO_2Si_4$: 419.1685; found: 419.1680.

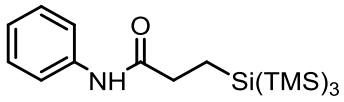
(1*R*,3*R*,5*R*,7*R*)-adamantan-2-yl 3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (2ag)



91.0 mg, 100%, colorless oil; Rf = 0.5 – 0.6 (PE/EA = 10:1; I_2 & anisaldehyde & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 – 4.88 (m, 1H), 2.38 – 2.29 (m, 4H), 2.00 (t, *J* = 7.0 Hz, 4H), 1.87 – 1.81 (m, 4H), 1.79 – 1.71 (m, 4H), 1.61 – 1.50 (m, 2H), 1.17 – 1.08 (m, 2H), 0.18 (d, *J* = 1.2 Hz, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.26, 76.96, 37.56, 36.48, 36.46, 33.96, 31.98, 31.96, 31.93, 27.40, 27.15, 3.33, 1.19. **IR** (ATR) 2909, 2856, 1731, 1199, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{22}H_{47}O_2Si_4$: 455.2648; found: 455.2650.

3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-*N*-phenylpropanamide (2ah)

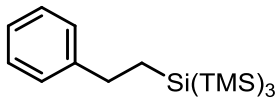


58.5 mg, 68%, white solid; Rf = 0.8 – 0.9 (PE/EA = 5:1; UV);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.17 – 7.05 (m, 2H), 2.46 – 2.33 (m, 2H), 1.26 – 1.15 (m, 2H), 0.20 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.11, 138.11, 129.15, 124.32, 119.83, 36.84, 3.48, 1.27. **IR** (ATR) 3293, 2951, 1660, 1603, 750, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for

$C_{18}H_{38}NOSi_4$: 396.2025; found: 396.2028. **m.p.**: 195.4-196.3 °C.

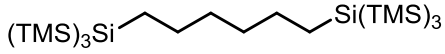
1,1,1,3,3,3-hexamethyl-2-phenethyl-2-(trimethylsilyl)trisilane (2ai)



24.4 mg, 35%, colorless oil; Rf = 0.9 – 1.0 (PE; I_2 & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 3H), 2.74 – 2.66 (m, 2H), 1.18 – 1.10 (m, 2H), 0.23 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.90, 128.58, 127.74, 125.84, 35.65, 10.75, 1.34. **IR** (ATR) 2949, 2892, 1065, 622 cm^{-1}. **GC–MS m/z**: 352 M^+, 247 $(TMS)_3Si^+$, 105 $(M\text{-}Si(TMS)_3)^+$.

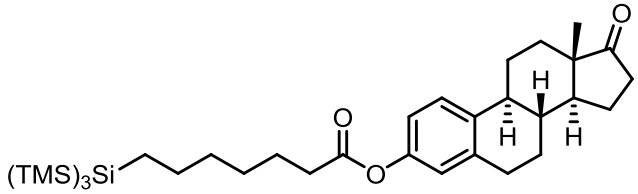
1,6-bis(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)hexane (2aj)



106.0 mg, 91%, white solid; Rf = 0.9 – 1.0 (PE; PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 – 1.30 (m, 8H), 0.81 – 0.74 (m, 4H), 0.16 (s, 54H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 34.23, 29.49, 7.92, 1.40. **IR** (ATR) 2950, 622 cm^{-1}. **GC–MS m/z**: 578 M^+, 247 $(TMS)_3Si^+$. **m.p.**: 175.5-176.5 °C.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 7-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)-trisilan-2-yl)heptanoate (2ak)

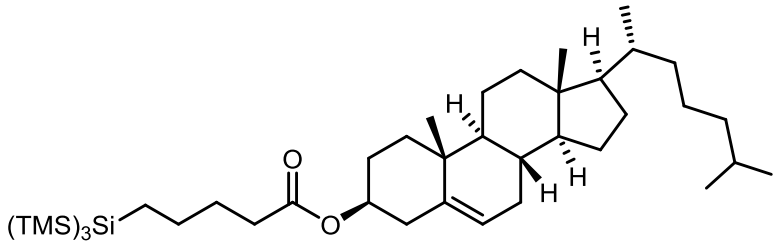


117.0 mg, 95%, colorless oil; Rf = 0.7 – 0.8 (PE/EA = 1:1; UV & I_2 & anisaldehyde & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 1H), 6.87 – 6.80 (m, 2H), 2.91 (dd, *J* = 8.3, 3.6 Hz, 2H), 2.57 – 2.46 (m, 3H), 2.43 – 2.38 (m, 1H), 2.31 – 2.24 (m, 1H), 2.20 – 2.11 (m, 1H), 2.09 – 1.94 (m, 3H), 1.74 (p, *J* = 7.1 Hz, 2H), 1.67 – 1.59 (m, 2H), 1.58 – 1.50 (m, 3H), 1.48 (d, *J* = 4.3 Hz, 1H), 1.45 – 1.38 (m, 6H), 0.91 (s, 3H), 0.82 – 0.74 (m, 2H), 0.16 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.92, 172.72, 148.78,

138.08, 137.38, 126.50, 121.73, 118.91, 50.57, 48.07, 44.28, 38.14, 35.98, 34.53, 34.01, 31.68, 29.53, 29.24, 28.83, 26.48, 25.88, 25.13, 21.71, 13.95, 7.69, 1.31. **IR** (ATR) 2956, 2927, 2858, 1733, 1273, 1073, 623 cm^{-1}. **HRMS (APCI) m/z**: $[M+H]^+$ calcd for $C_{34}H_{61}O_3Si_4$: 629.3692; found: 629.3696.

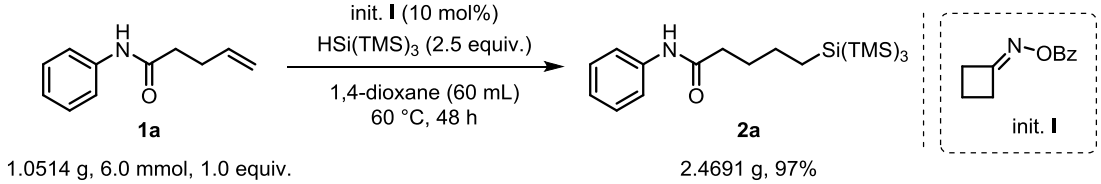
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentanoate (2al)



139.0 mg, 97%, colorless oil; Rf = 0.9 – 1.0 (PE/EA = 10:1; I_2 & anisaldehyde & PMA);

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (tt, *J* = 3.9, 2.5 Hz, 1H), 4.60 (dtd, *J* = 14.3, 7.3, 4.9 Hz, 1H), 2.33 – 2.24 (m, 4H), 1.99 (ddt, *J* = 20.5, 17.6, 4.2 Hz, 2H), 1.84 (dtd, *J* = 12.2, 6.1, 3.5 Hz, 3H), 1.69 – 1.24 (m, 20H), 1.17 – 1.08 (m, 6H), 1.02 (d, *J* = 1.8 Hz, 5H), 0.92 (s, 3H), 0.88 – 0.84 (m, 9H), 0.79 – 0.75 (m, 2H), 0.68 (s, 3H), 0.15 (s, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.26, 139.83, 122.71, 73.85, 56.84, 56.29, 50.18, 42.46, 39.89, 39.68, 38.34, 37.16, 36.74, 36.34, 35.94, 34.47, 32.06, 32.01, 29.58, 28.90, 28.38, 28.16, 27.98, 24.43, 23.98, 22.98, 22.72, 21.18, 19.47, 18.87, 12.00, 7.47, 1.31. **IR** (ATR) 2946, 1734, 1465, 1378, 1186, 834, 623 cm^{-1}. **HRMS (ESI) m/z**: $[M+Na]^+$ calcd for $C_{41}H_{80}NaO_2Si_4$: 739.5128; found: 739.5130.

Gram-Scale Reaction

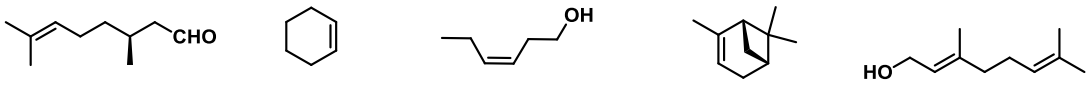


A dried Schlenk bottle (250 mL) was charged with a stirring bar, the alkene (**1a**,

1.0514 g, 6 mmol, 1.0 equiv.) and oxime ester (113.5 mg, 0.6 mmol, 10 mol%). The Schlenk bottle was then evacuated and back-filled with nitrogen (N_2, 99.999%) for 3 times. Then fresh-distilled anhydrous 1,4-dioxane (60 mL) and $(TMS)_3SiH$ (4.6 mL, 15 mmol, 2.5 equiv.) was added via syringe. Then the reaction mixture was stirred at 60 °C for 48 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EA = 6:1) to afford the desired product **2a** (white solid, 2.4691 g, 97% yield).

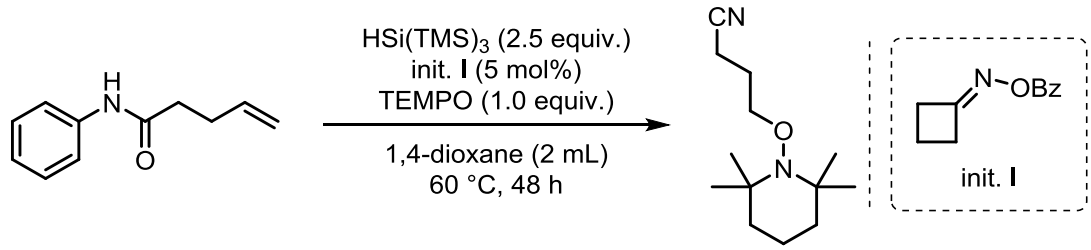
5. Tolerance of Internal Olefins.

We have evaluated several internal olefins. Unfortunately, none of them provides desired products, indicating that the reaction is sensitive to the steric properties of alkenes. Overall, our methodology mainly tolerates mono-substituted and geminal substituted olefins.



no desired product | no desired product | no desired product, partial starting material remained | no desired product, partial starting material remained | n.r., starting material remained

6. Mechanistic Study

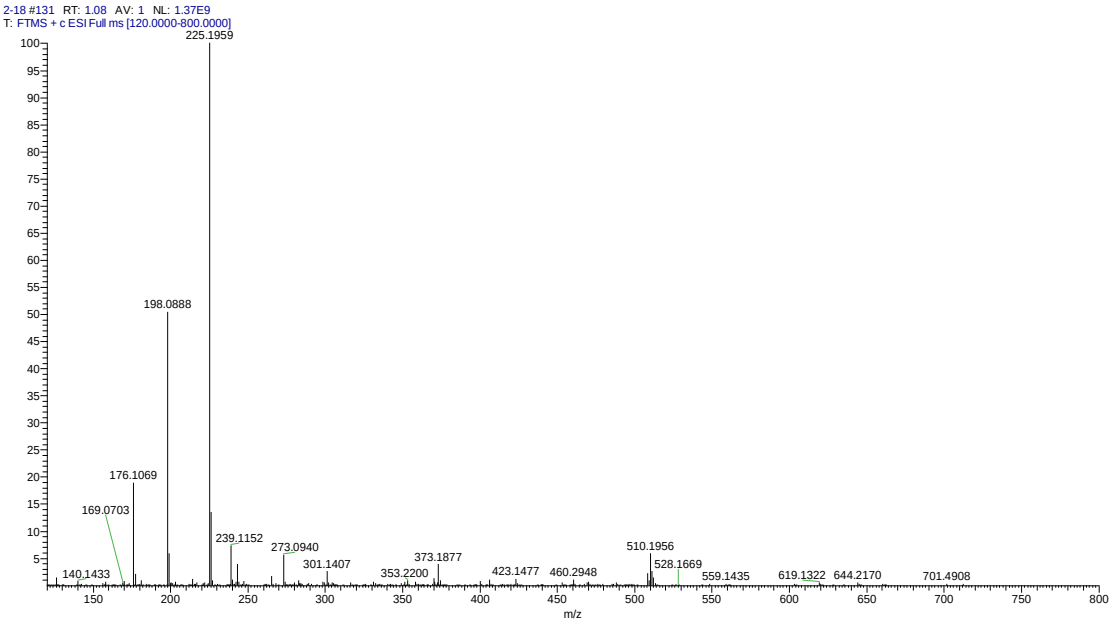


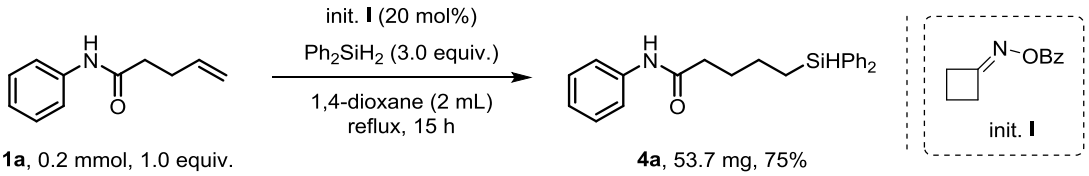
1a, 0.2 mmol, 1.0 equiv.

M/Z $[M+H]^+$: 225.1961
found: 225.1959

A dried Schlenk tube (10 mL) was charged with a stirring bar, alkene **1a**, the initiator **I** (18.9 mg, 0.1 mmol, 1.0 equiv.) and TEMPO (31.3 mg, 0.2 mol, 1.0 equiv.). The Schlenk tube was then evacuated and back-filled with nitrogen (N_2, 99.999%) for 3 times. Then fresh-distilled anhydrous 1,4-dioxane (2 mL) was added via syringe.

The reaction mixture was stirred at 60 °C for 48 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The crude product was dissolved by MeOH and measured via HRMS. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{18}H_{37}O_2Si_4$: 225.1961; found: 225.1959.



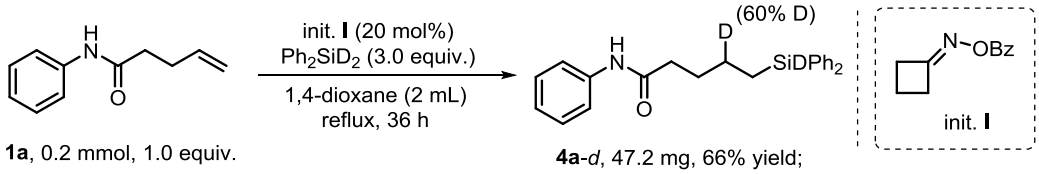


1a, 0.2 mmol, 1.0 equiv. **4a**, 53.7 mg, 75%

A dried Schlenk tube (10 mL) was charged with a stirring bar, alkene **1a** (35.0 mg, 0.2 mmol, 1.0 equiv.) and initiator **I** (7.6 mg, 0.04 mmol, 20 mol%). The Schlenk tube was then evacuated and back-filled with nitrogen (N_2, 99.999%) for 3 times. The fresh-distilled anhydrous 1,4-dioxane (2 mL) (via syringe) and Ph_2SiH_2 (111.8 mg, 0.6 mol, 3.0 equiv.) were added in sequence. The reaction mixture was refluxed for 15 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography (EA/PE = 1/5) to obtain **4a** (53.7 mg, 75%, colorless oil, R_f = 0.4 – 0.5 (PE/EA = 5:1, UV/PMA)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 4H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.30 (m, 8H), 7.13 (q, *J* = 8.0, 7.4 Hz, 2H), 4.89 (t, *J* = 3.7 Hz, 1H), 2.34 (t, *J* = 7.6 Hz,

2H), 1.83 (p, *J* = 7.5 Hz, 2H), 1.64 – 1.52 (m, 2H), 1.27 – 1.15 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.39, 138.02, 135.23, 134.39, 129.73, 129.07, 128.15, 124.33, 120.03, 37.51, 29.07, 24.31, 12.13.



1a, 0.2 mmol, 1.0 equiv.

4a-*d*, 47.2 mg, 66% yield;

A dried Schlenk tube (10 mL) was charged with a stirring bar, alkene **1a** (35.0 mg, 0.2 mmol, 1.0 equiv.) and the initiator **I** (7.6 mg, 0.04 mmol, 20 mol%). The Schlenk tube was then evacuated and back-filled with nitrogen (N_2, 99.999%) for 3 times. The fresh-distilled anhydrous 1,4-dioxane (2 mL) (via syringe) and Ph_2SiD_2 (111.8 mg, 0.6 mol, 3.0 equiv.) were added in sequence. The reaction mixture was refluxed for 36 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography (EA/PE = 1/5) to obtain **4a**-*d* (47.2 mg, 66%, colorless oil, R_f = 0.4 – 0.5 (PE/EA = 5:1, UV/PMA)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.24 (m, 10H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.80 (p, *J* = 7.4 Hz, 2H), 1.55 (p, *J* = 8.0 Hz, 1H), 1.19 (t, *J* = 8.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.56, 139.82, 136.08, 135.56, 135.47, 135.37, 135.32, 131.05, 130.66, 129.75, 129.16, 129.08, 128.98, 128.72, 125.14, 121.34, 37.55, 30.25, 30.15, 25.16, 12.67. 7.

7. The Rational for Both Carbon Radical and Benzoate Radical Interact with Silane via Hydrogen Abstract to Achieve Silyl Radical.

The BDE (Bond Dissociation Energy) of PhCOO-H and H-CH_2CN are 111 and 95 kcal/mol (BDE of H-$CH_2CH_2CH_2CN$ is not found in iBonD data base: http://ibond.nankai.edu.cn/) respectively which are much higher than (TTMS)Si-H(79 kcal/mol). After homolysis of oxime ester, both generated alkyl carbon radical and benzoate radical could feasibly abstract hydrogen radical from (TTMS)SiH to provide

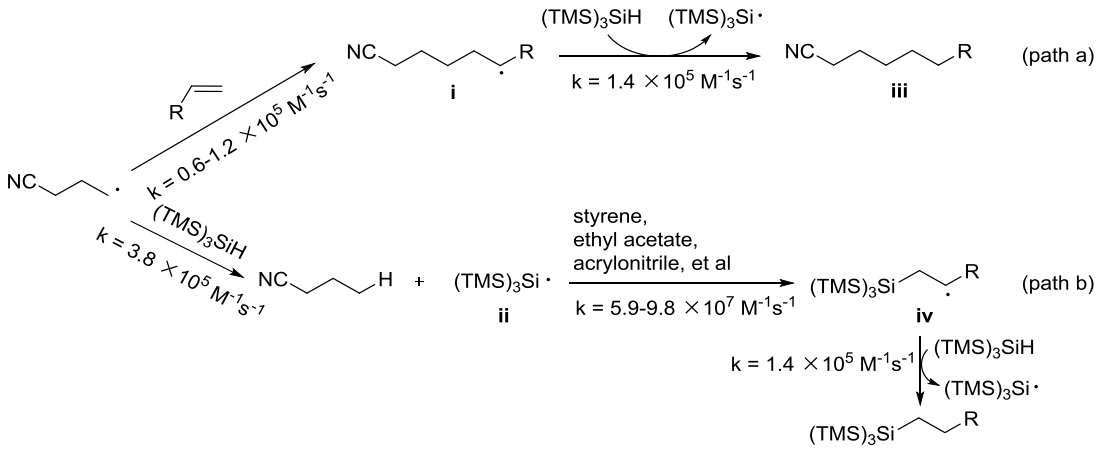
more thermodynamically stable (TTMS)Si·.

8. The Rational for Selecting $(TMS)_3SiH$ as Silane for Condition Optimization.

$(TMS)_3SiH$ has a lower Si-H bond strength of 79 kcal/mol compared with other silanes ($PhSiH_3$, 90 kcal/mol; Ph_2SiH_2, 86 kcal/mol; Et_3SiH, 95 kcal/mol). So, a hydrogen abstract between $(TMS)_3SiH$ and alkyl carbon radical would be proceeded more feasible than other silanes under mild reaction temperature.

9. The Rational for Excellent Chemoselectivity of γ-Cyanoalkyl Radical with Silane and Alkene.

According to the reported references[2-4], the rate constant for the addition of primary carbon radical to olefin is the range 0.6-1.2 $\times 10^5$ $M^{-1}s^{-1}$ (scheme S1, path a). Meanwhile the rate constant for abstraction of (TTMS)Si-H from primary carbon radical is 3.8 $\times 10^5$ $M^{-1}s^{-1}$ (scheme S1, path b). The rate constants of forming silyl radical **ii** is 3-6 times faster than generating carbon radical **i**. More importantly, the rate constant for the addition of an (TTMS)Si· onto olefin is the range 5.8-9.7$\times 10^7$ $M^{-1}s^{-1}$ which is 800-1000 times faster than an alkyl radical onto an olefin. So, it is more reasonable that both carbon radical **i** (path a) and silyl radical **ii** (path b) may exist in this reaction where path b is dominated. Overall, the distinct rate constant that formation of **i**, **ii** and **iv** illustrates the good chemoselectivity in this reaction.



Scheme S1

10. Reference

1. Zhao, B. L. and Shi, Z. Z. Copper-Catalyzed Intermolecular Heck-Like Coupling of Cyclobutanone Oximes Initiated by Selective C-C Bond Cleavage. *Angew Chem Int Ed*, **2017**, *56*, 12727-12731.

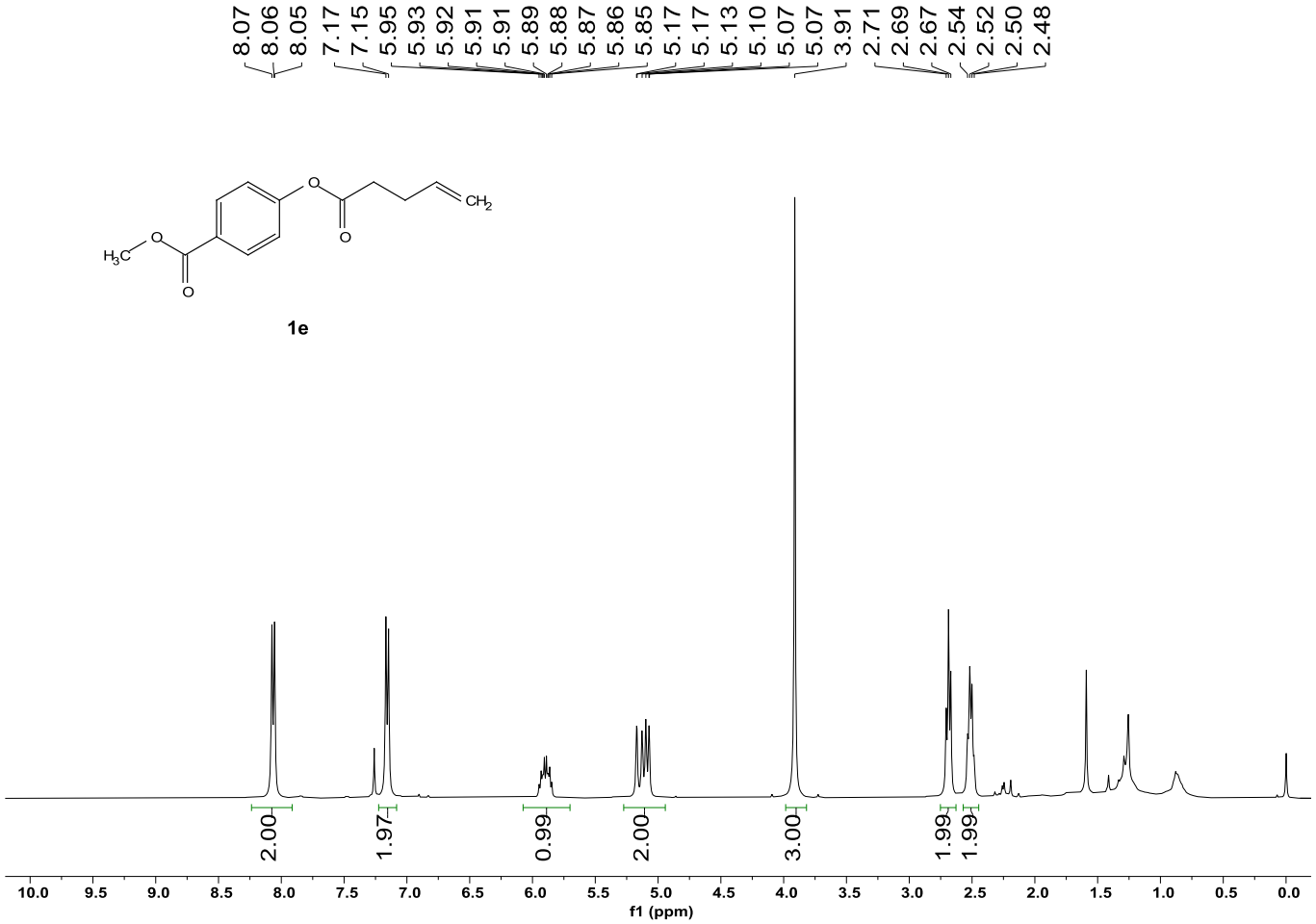
2. C. Chatgilialoglu, Organosilanes as radical-based reducing agents in synthesis. *Acc. Chem. Res*. **1992**, 25, 188-194.

3. L. J. Johnston, J. C. Scaiano and K. U. Ingold,Kinetics of cyclopropyl radical reactions. 1. Absolute rate constants for some addition and abstraction reactions. *J. Am.Chem. Soc*., **1984**, 106, 4877-4881.

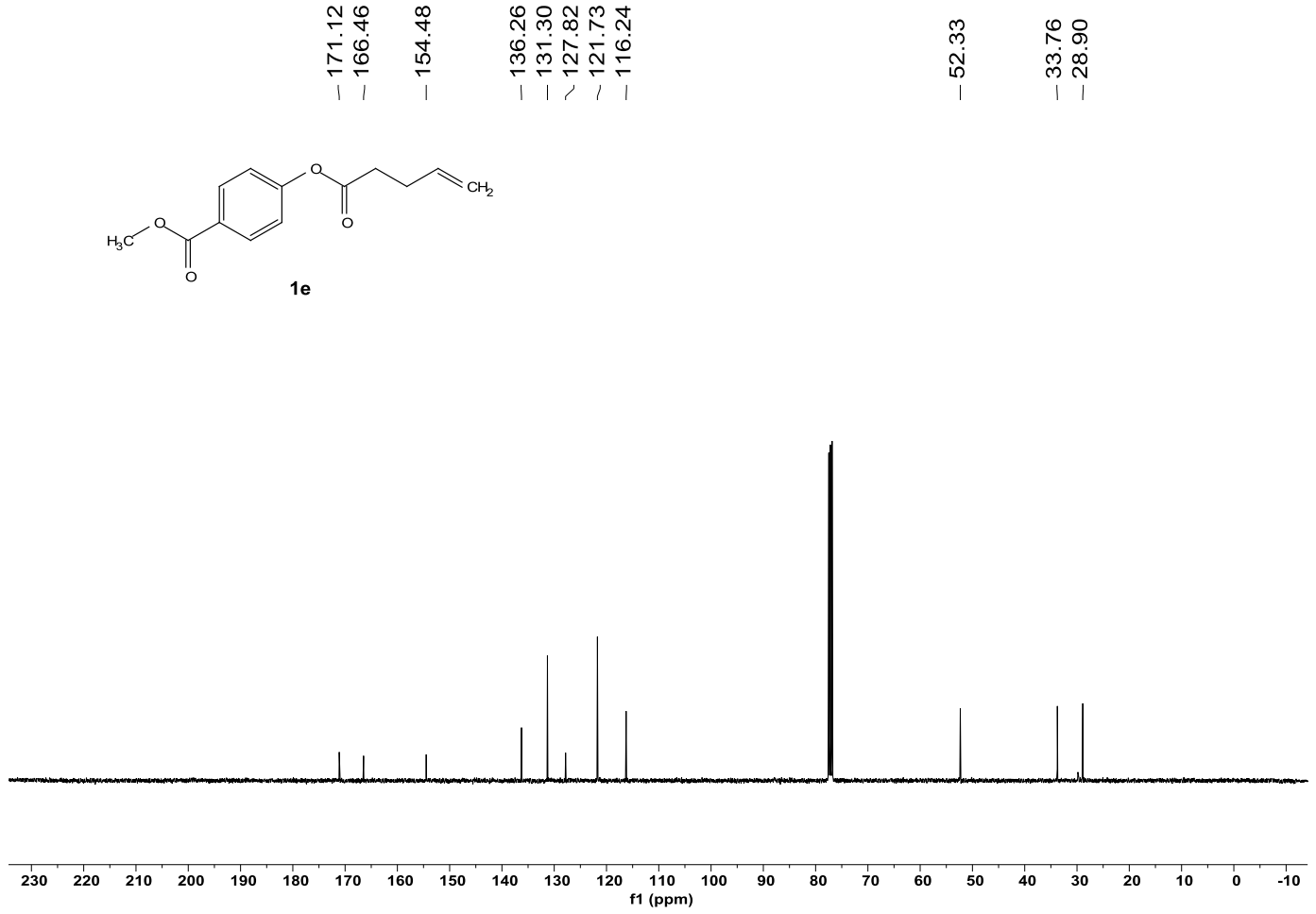
4. D. V. Avila, K. U. Ingold, J. Lusztyk, W. R. Dolbier and H. Q. Pan, Absolute Rate Constants for Radical Additions to Alkenes in Solution. The Synergistic Effect of Perfluorination on the Reactivities of n-Alkyl Radicals.*J. Org. Chem*. **1996**, 61, 2027 - 2030.

11. NMR Spectra

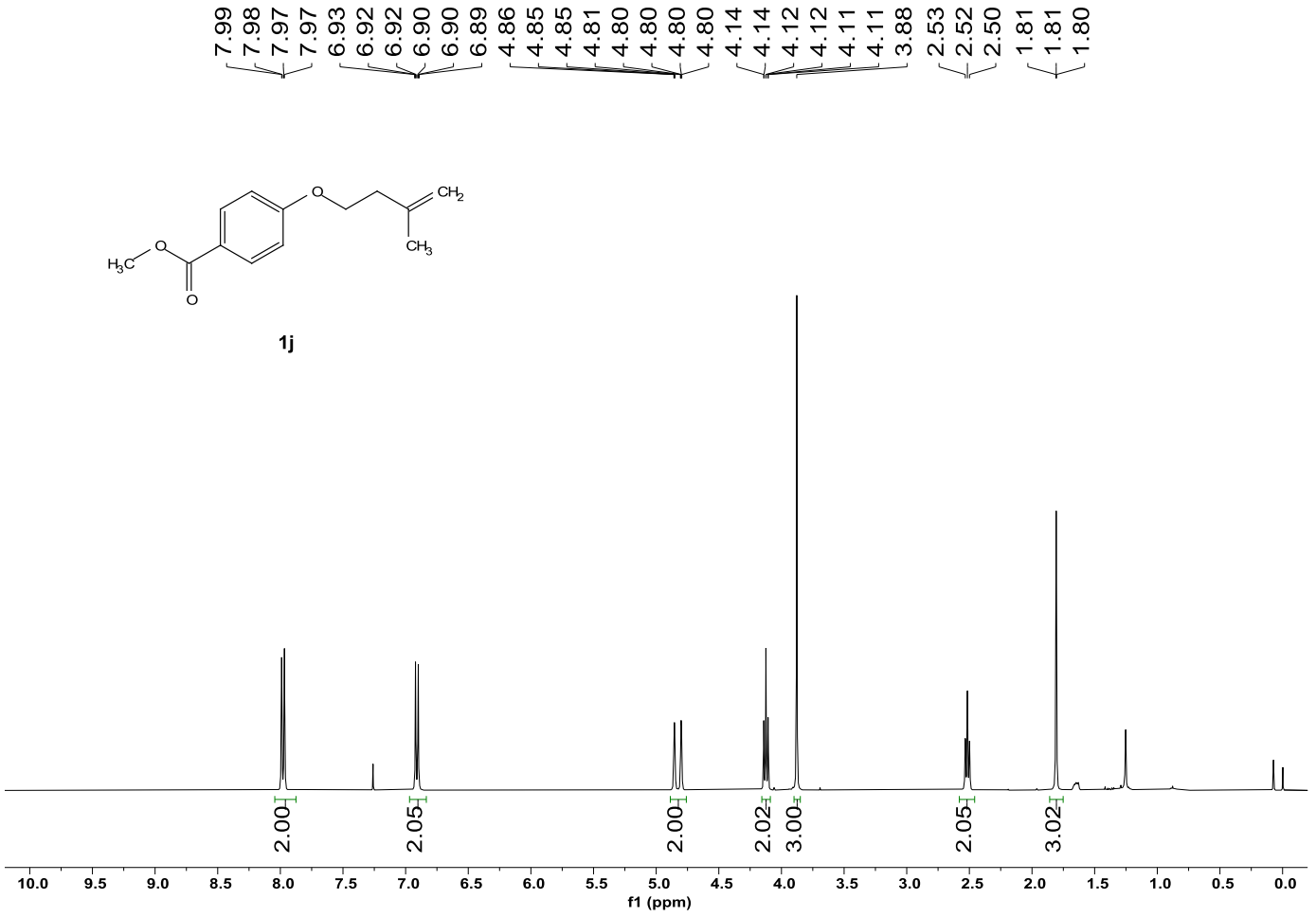
^{1}H NMR spectrum of compound **1e** (400 MHz, $CDCl_3$)



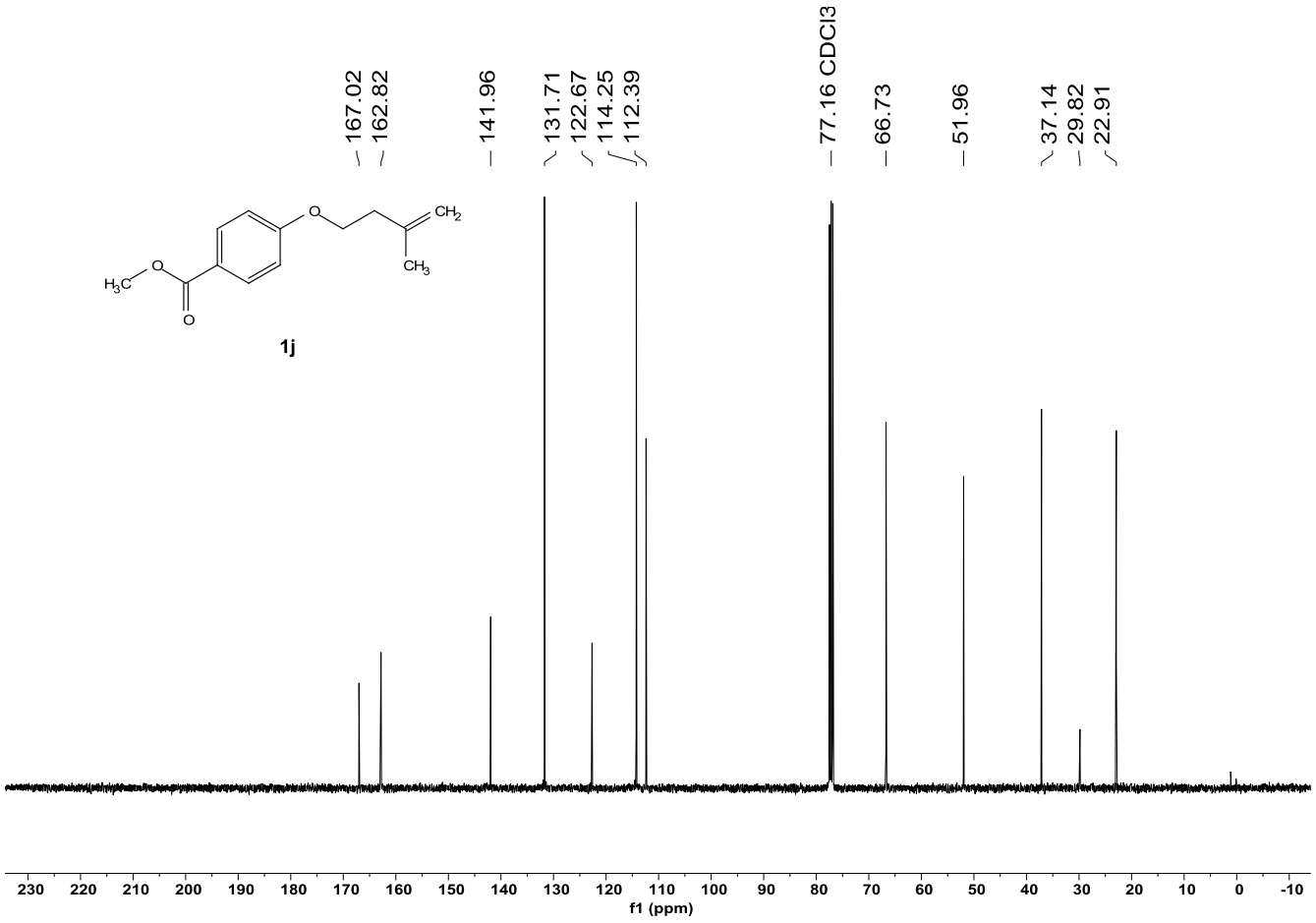
^{13}C NMR spectrum of compound **1e** (101 MHz, $CDCl_3$)



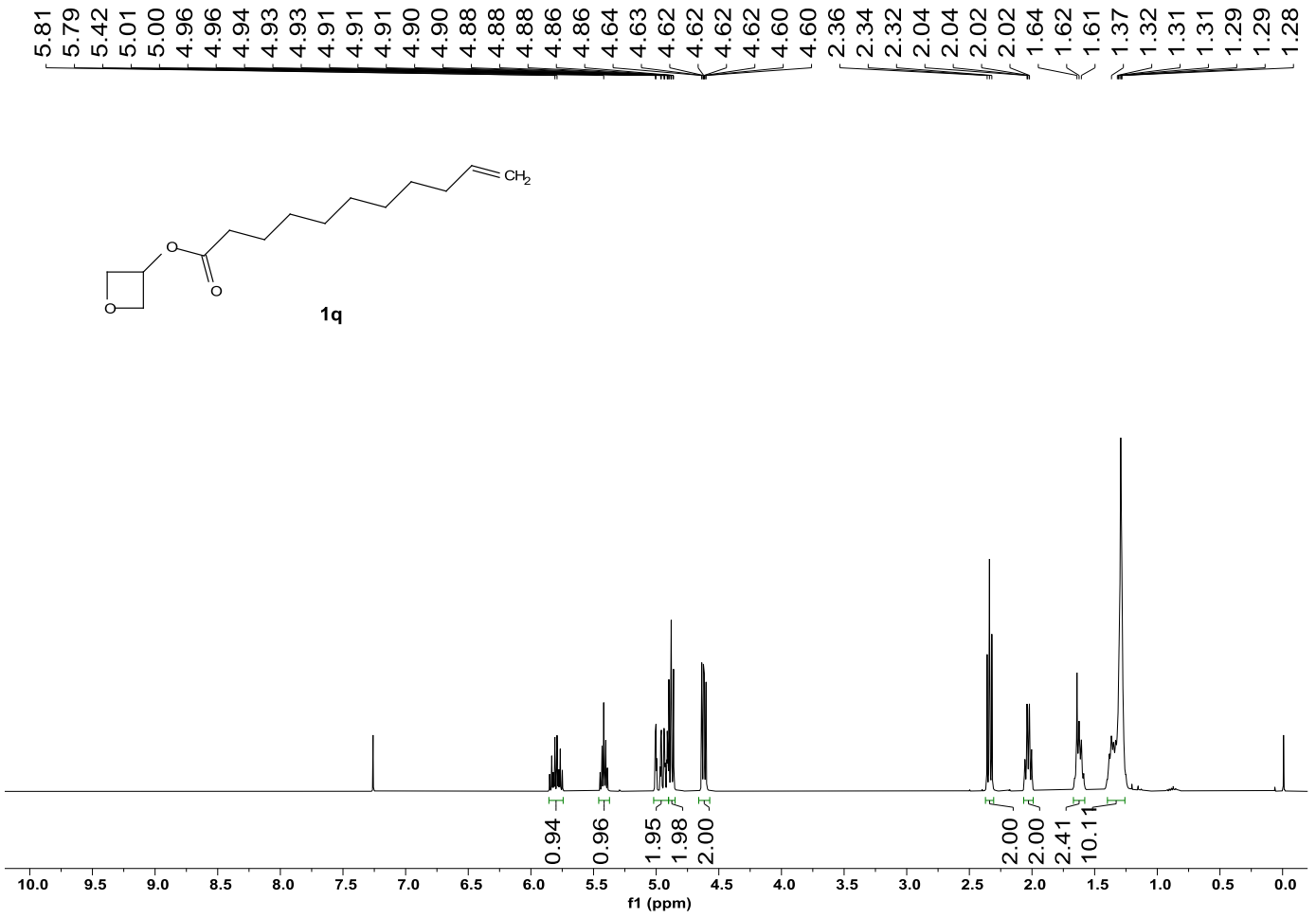
^{1}H NMR spectrum of compound **1j** (400 MHz, $CDCl_3$)



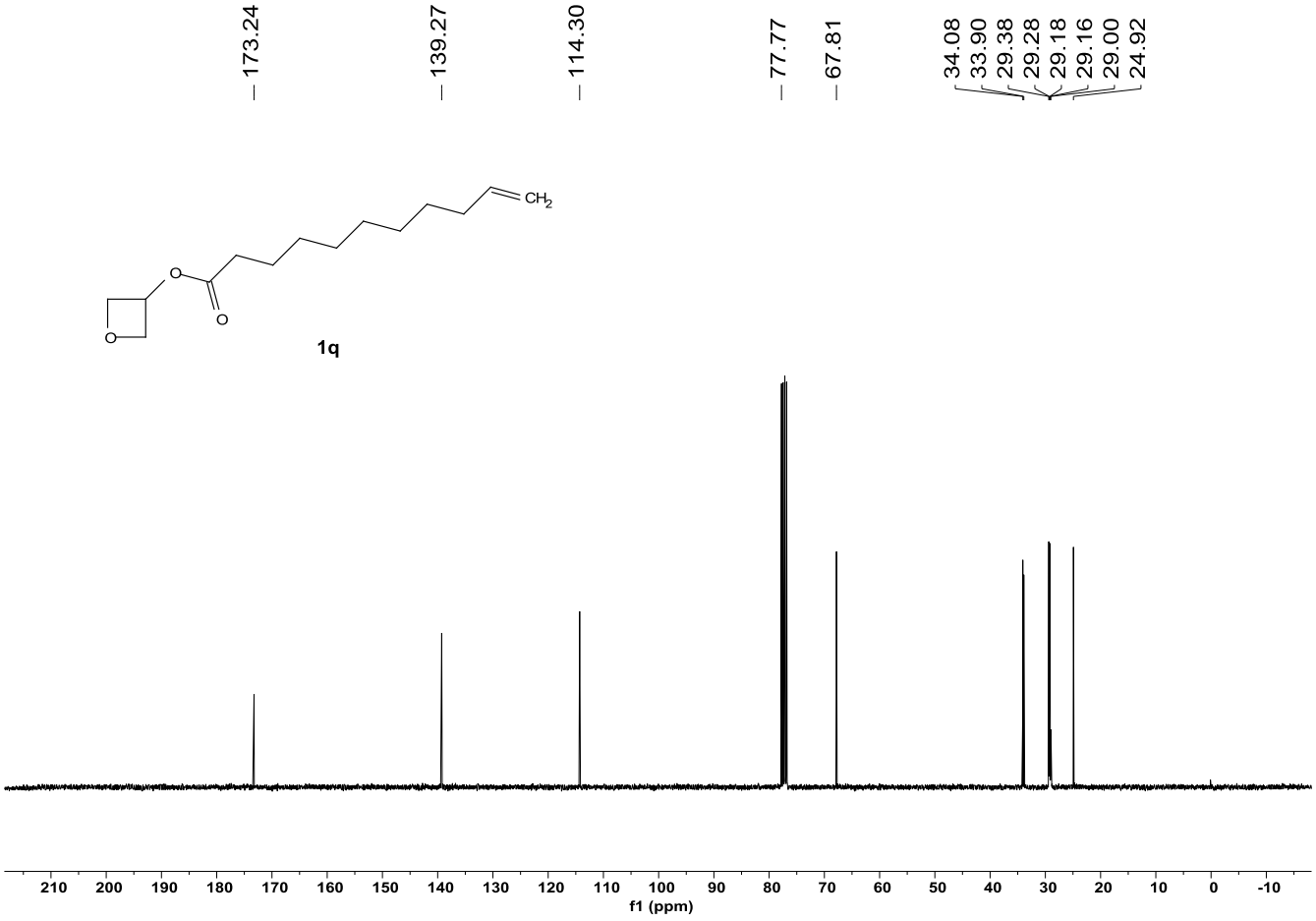
^{13}C NMR spectrum of compound **1j** (101 MHz, $CDCl_3$)



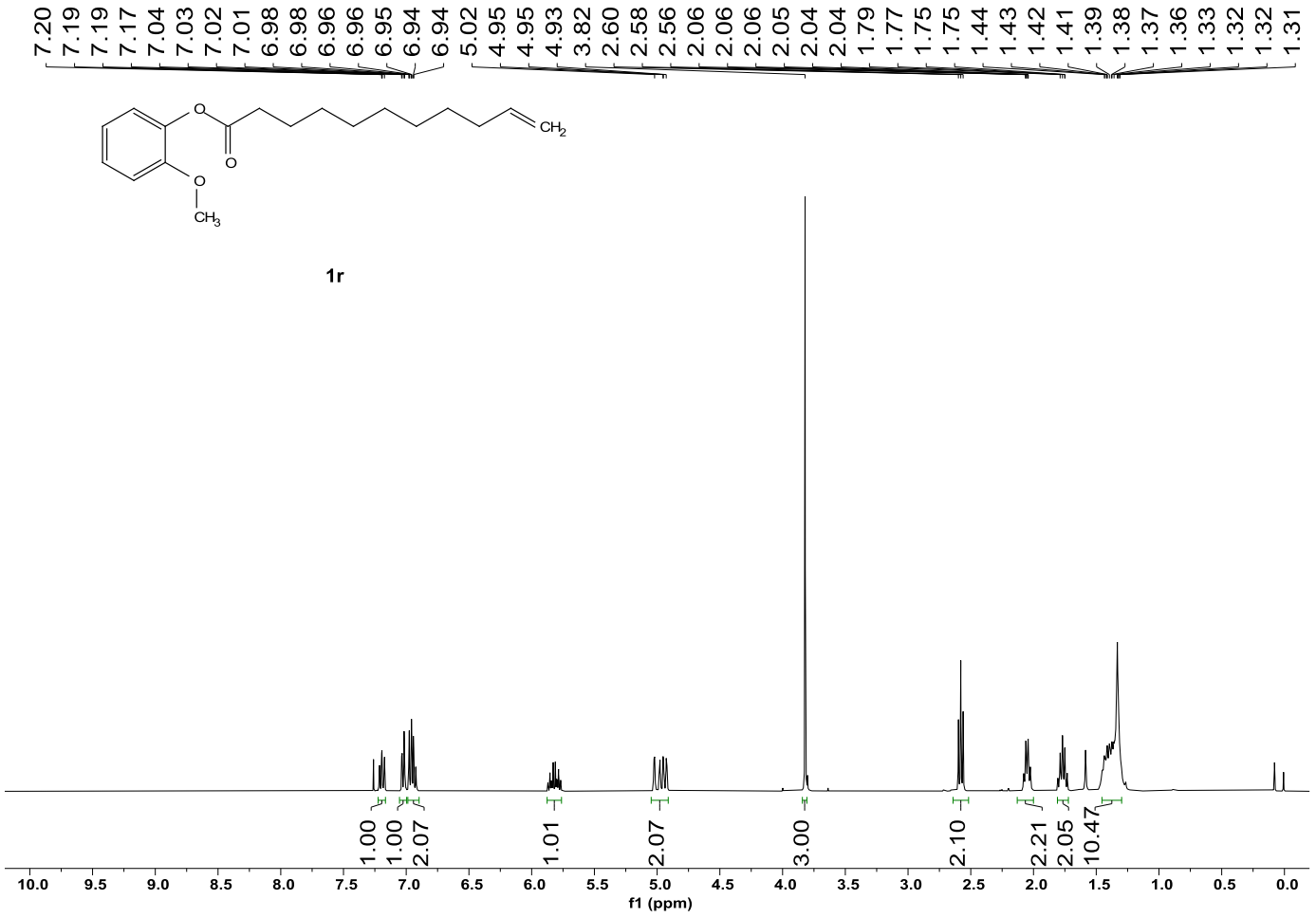
^{1}H NMR spectrum of compound **1q** (400 MHz, $CDCl_3$)



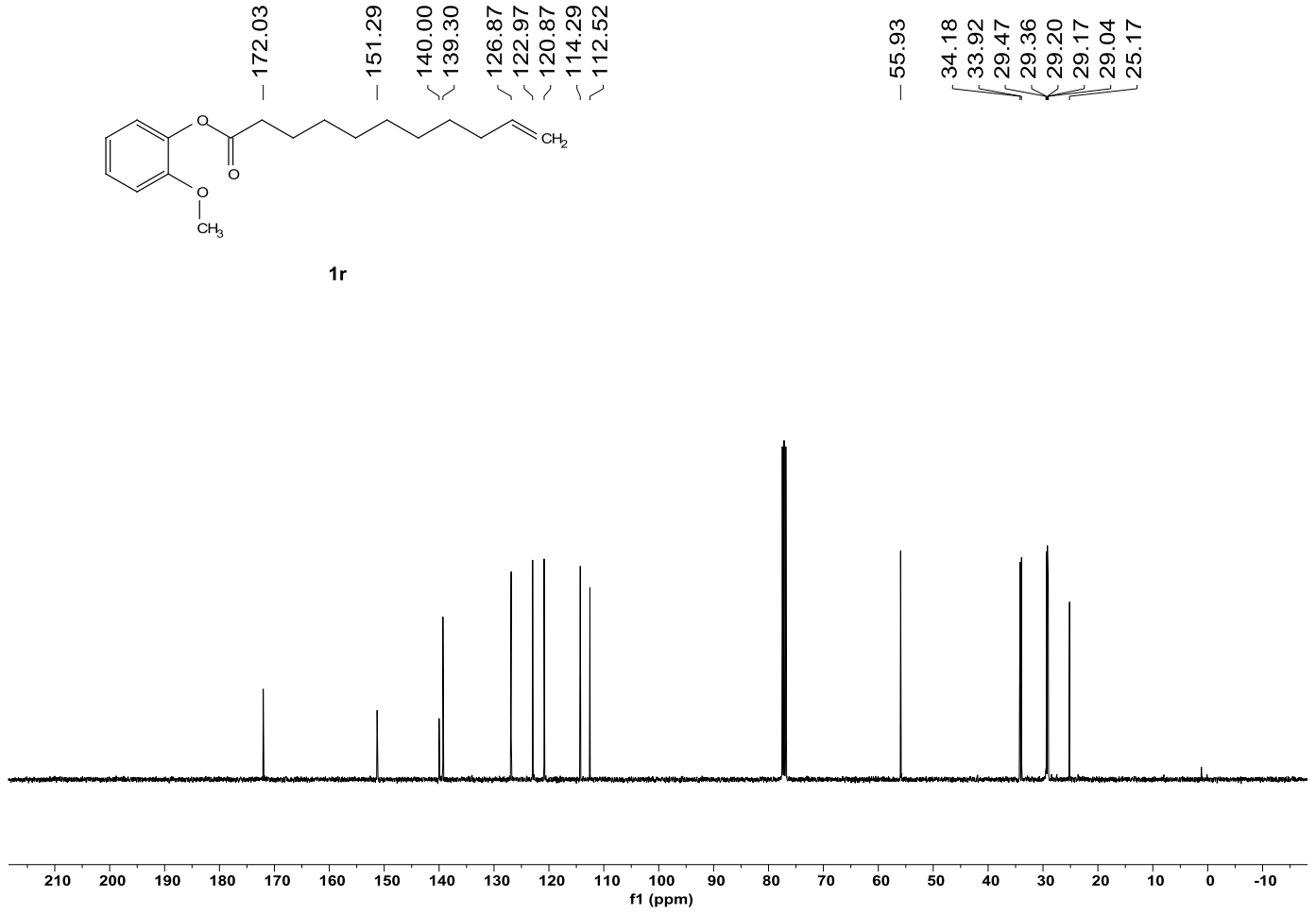
^{13}C NMR spectrum of compound **1q** (101 MHz, $CDCl_3$)



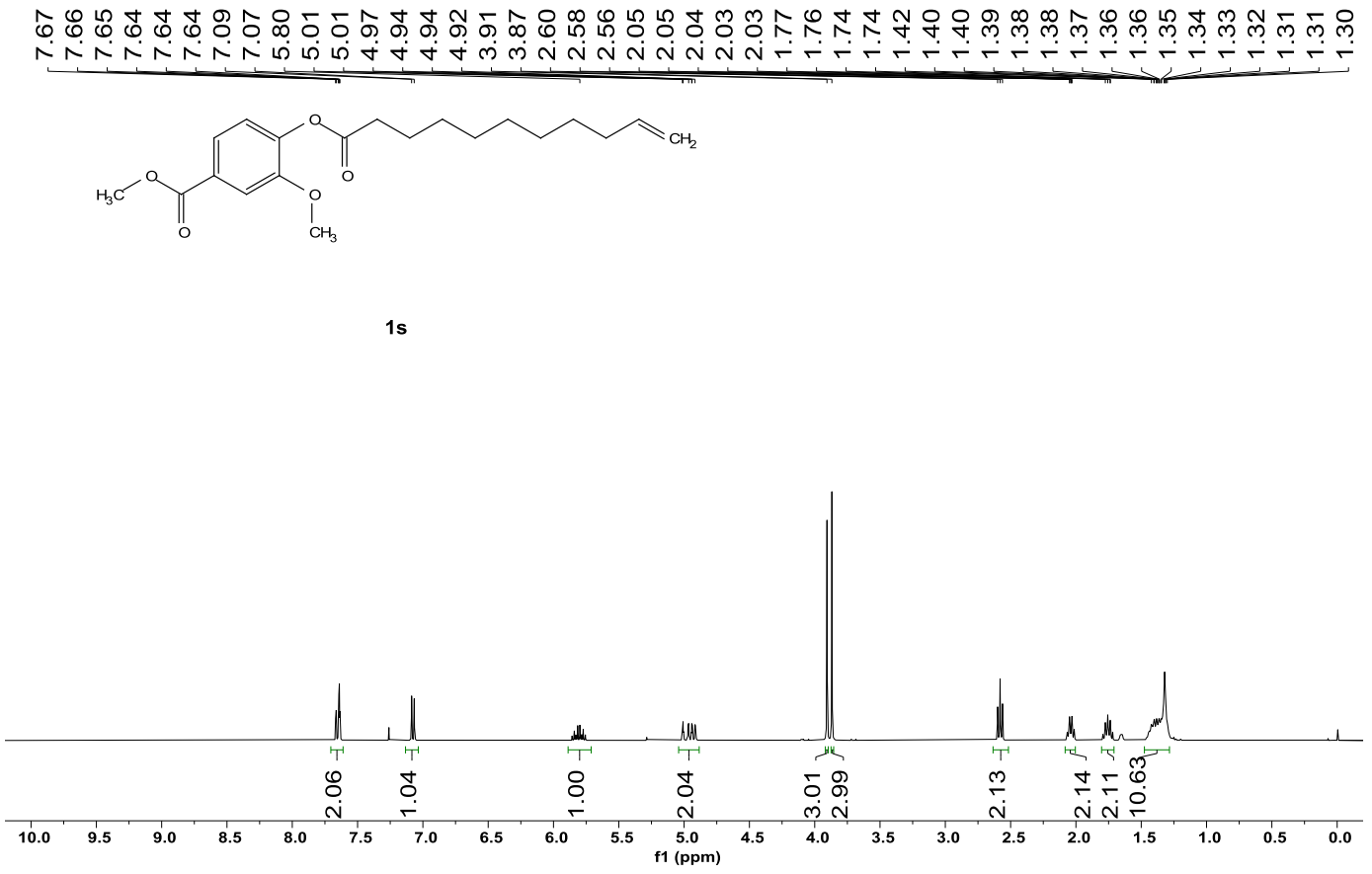
^{1}H NMR spectrum of compound **1r** (400 MHz, $CDCl_3$)



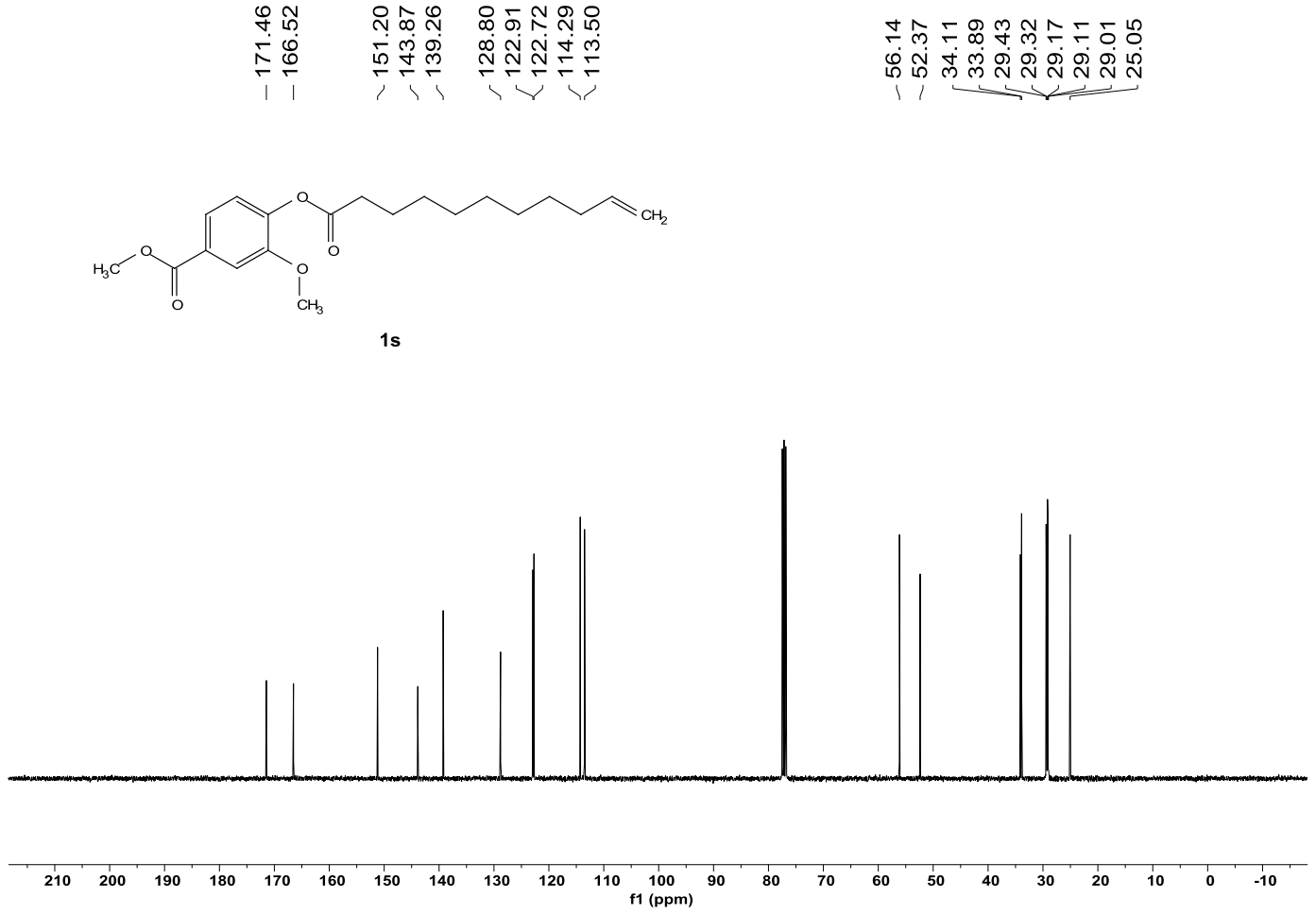
^{13}C NMR spectrum of compound **1r** (101 MHz, $CDCl_3$)



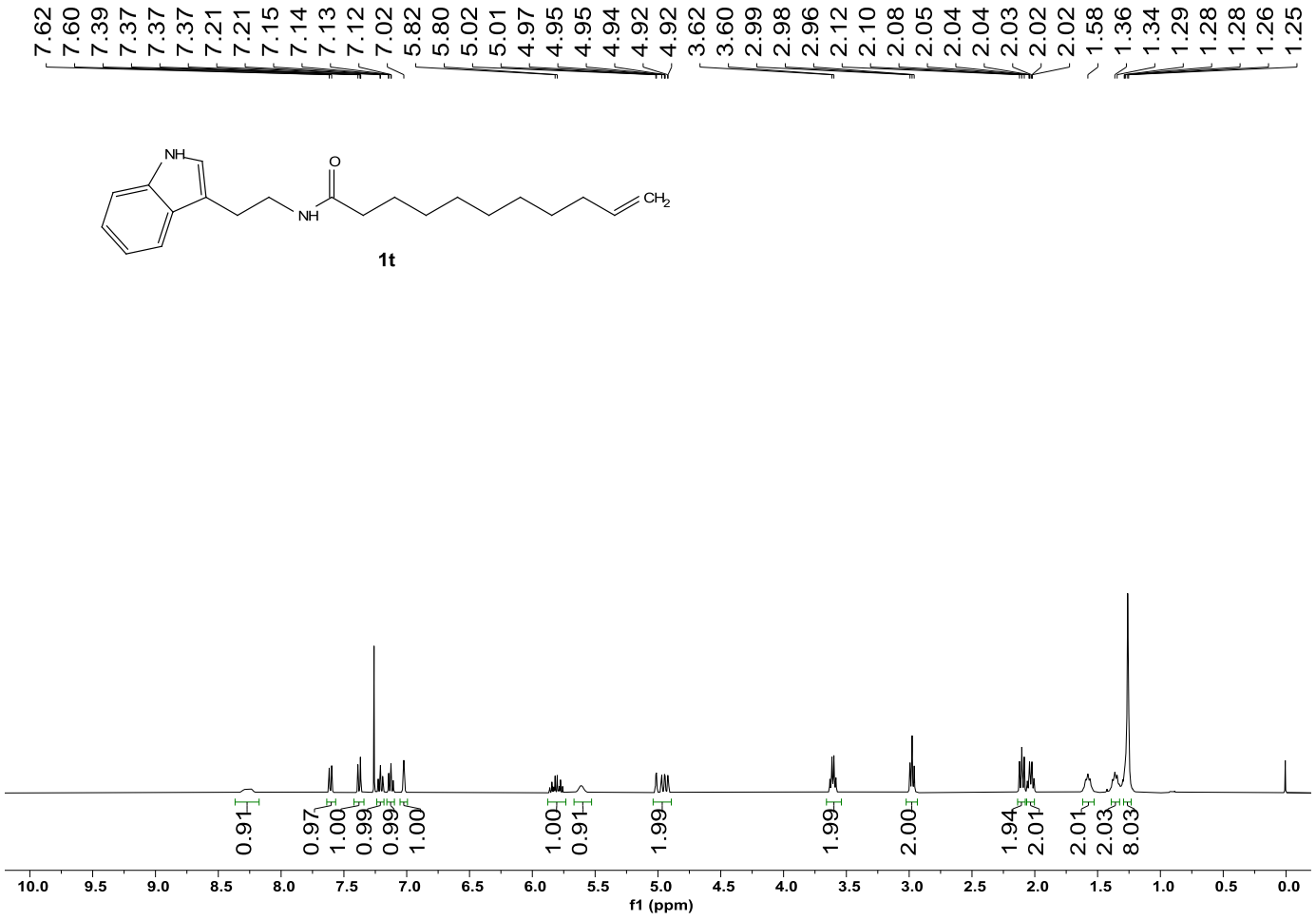
^{1}H NMR spectrum of compound **1s** (400 MHz, $CDCl_3$)



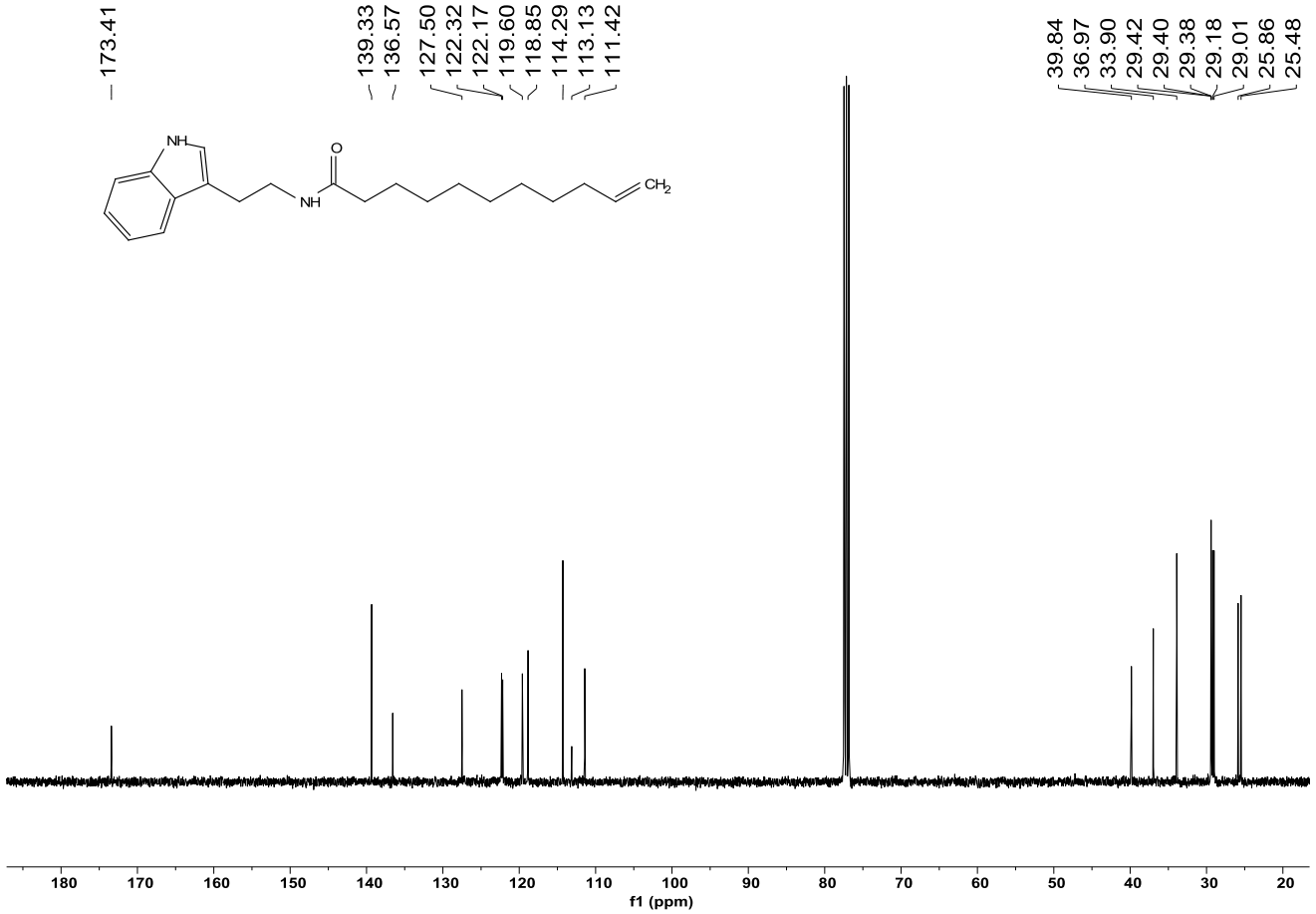
^{13}C NMR spectrum of compound **1s** (101 MHz, $CDCl_3$)



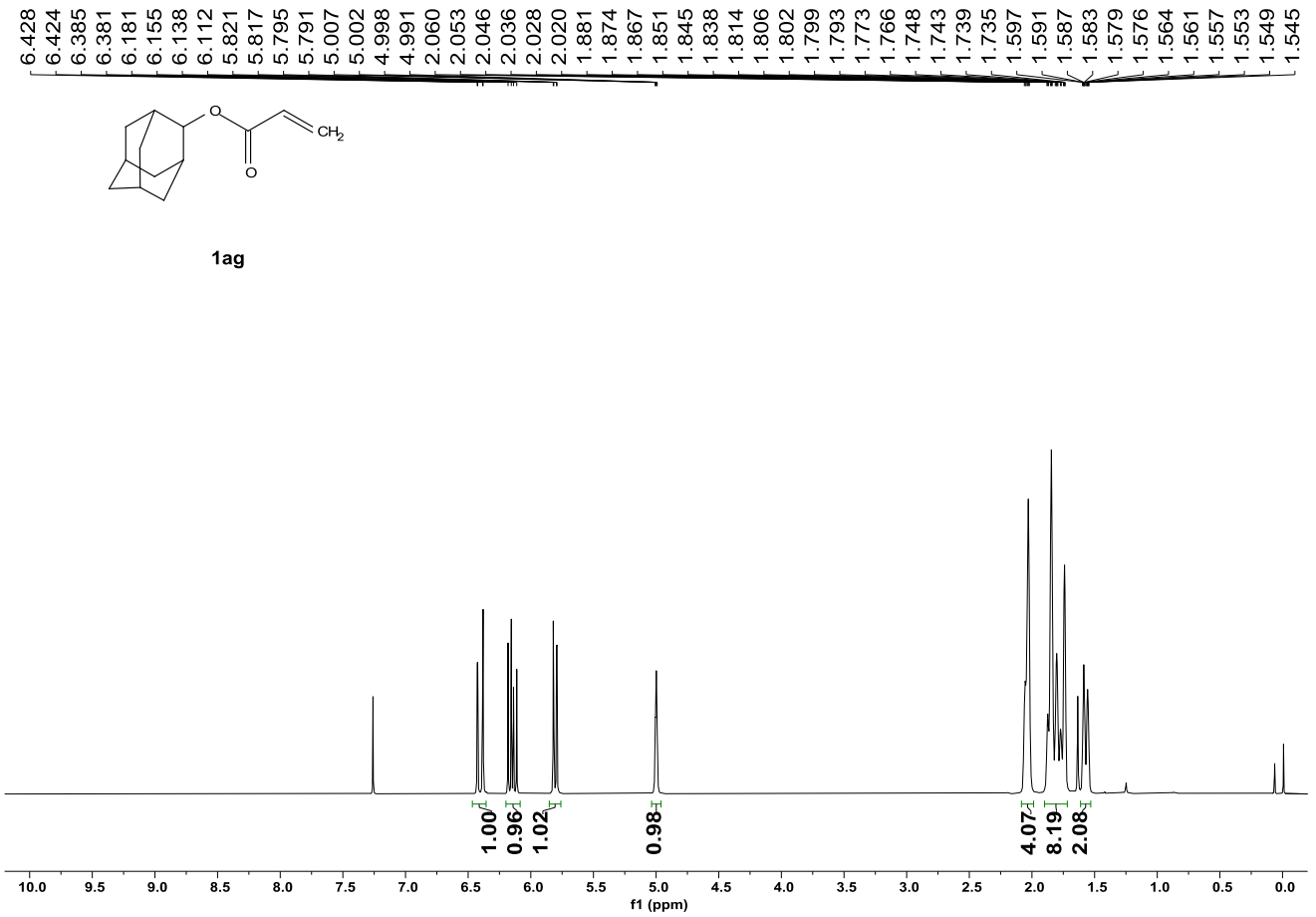
^{1}H NMR spectrum of compound **1t** (400 MHz, $CDCl_3$)



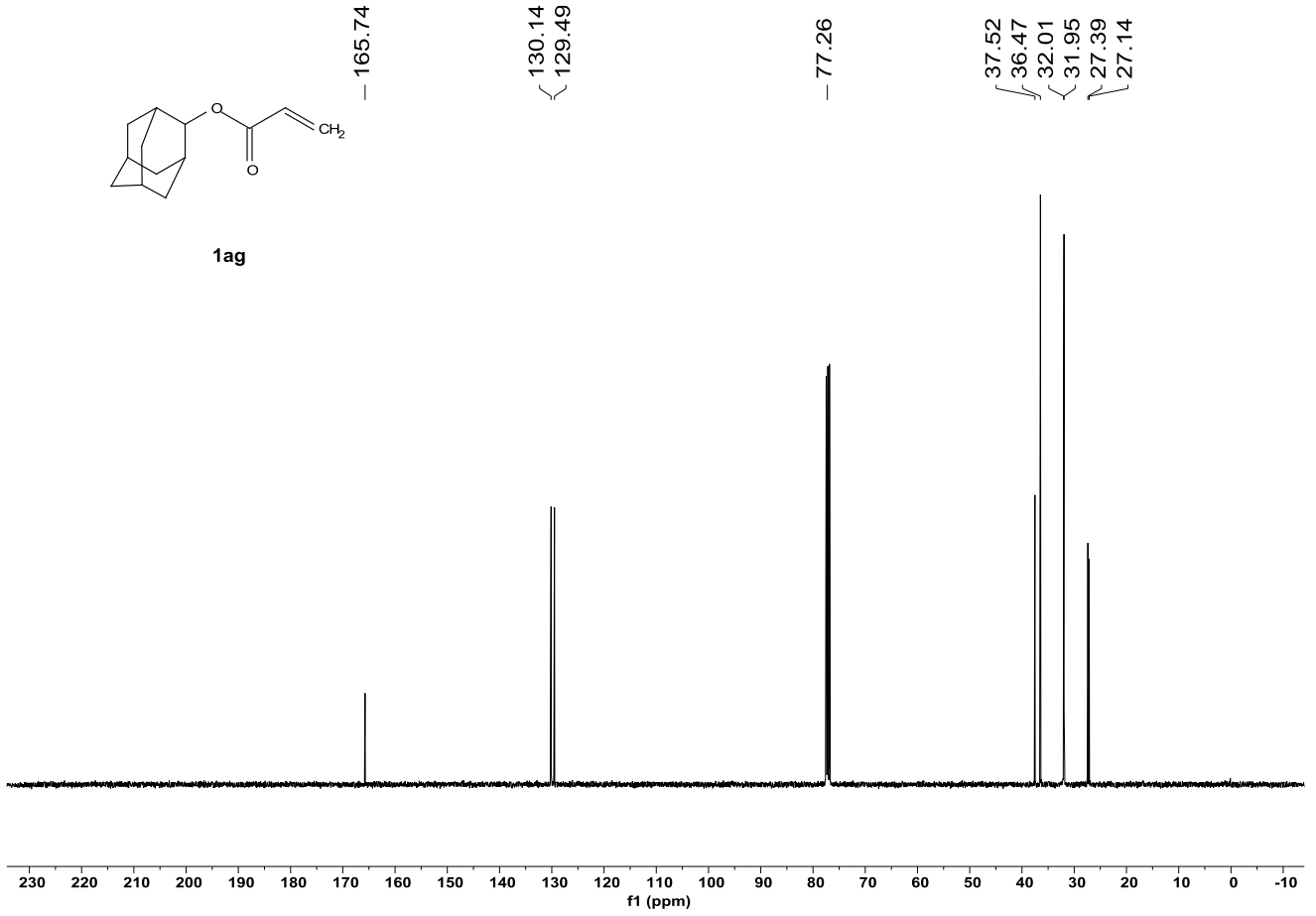
^{13}C NMR spectrum of compound **1t** (101 MHz, $CDCl_3$)



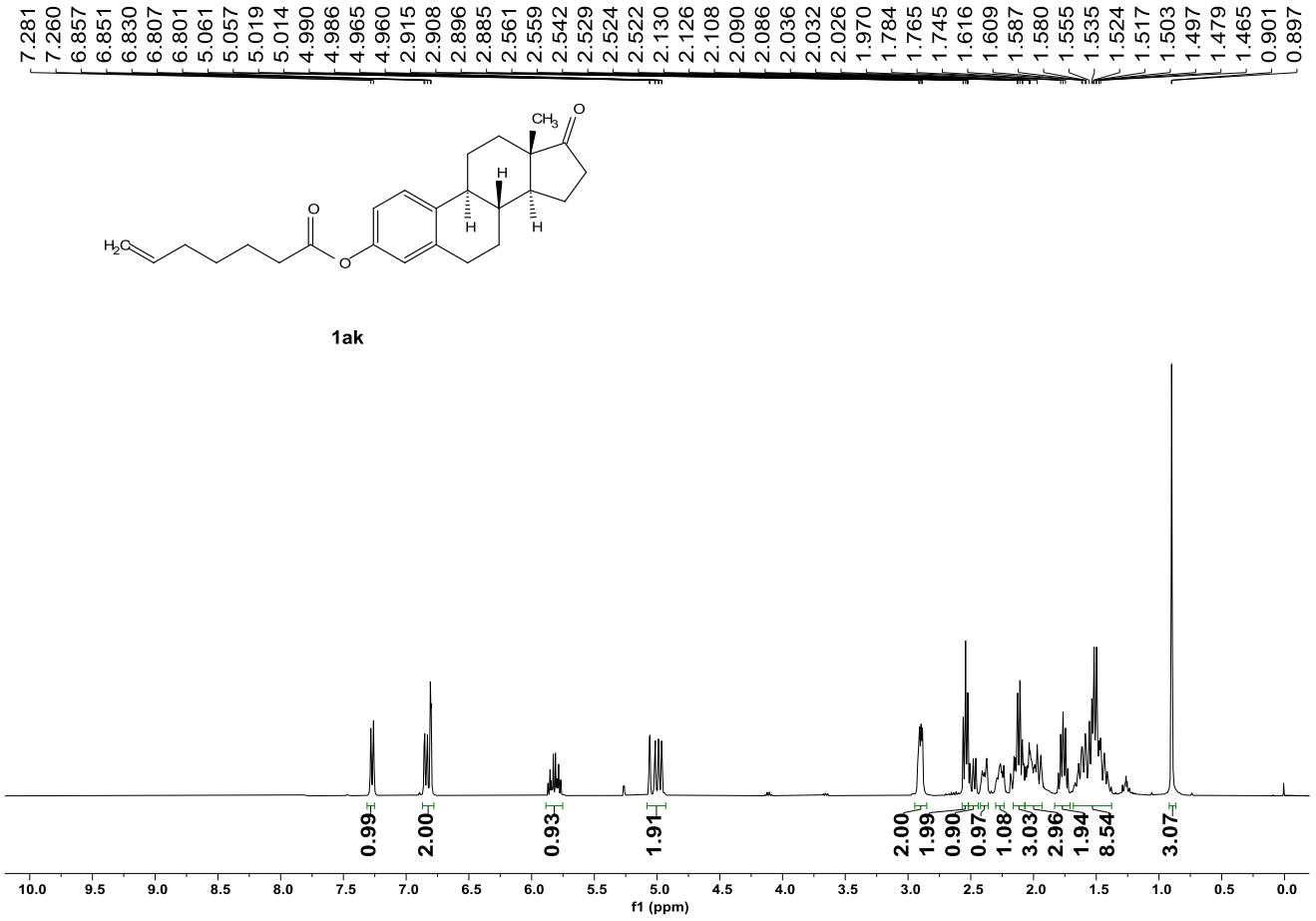
^{1}H NMR spectrum of compound **1ag** (400 MHz, $CDCl_3$)



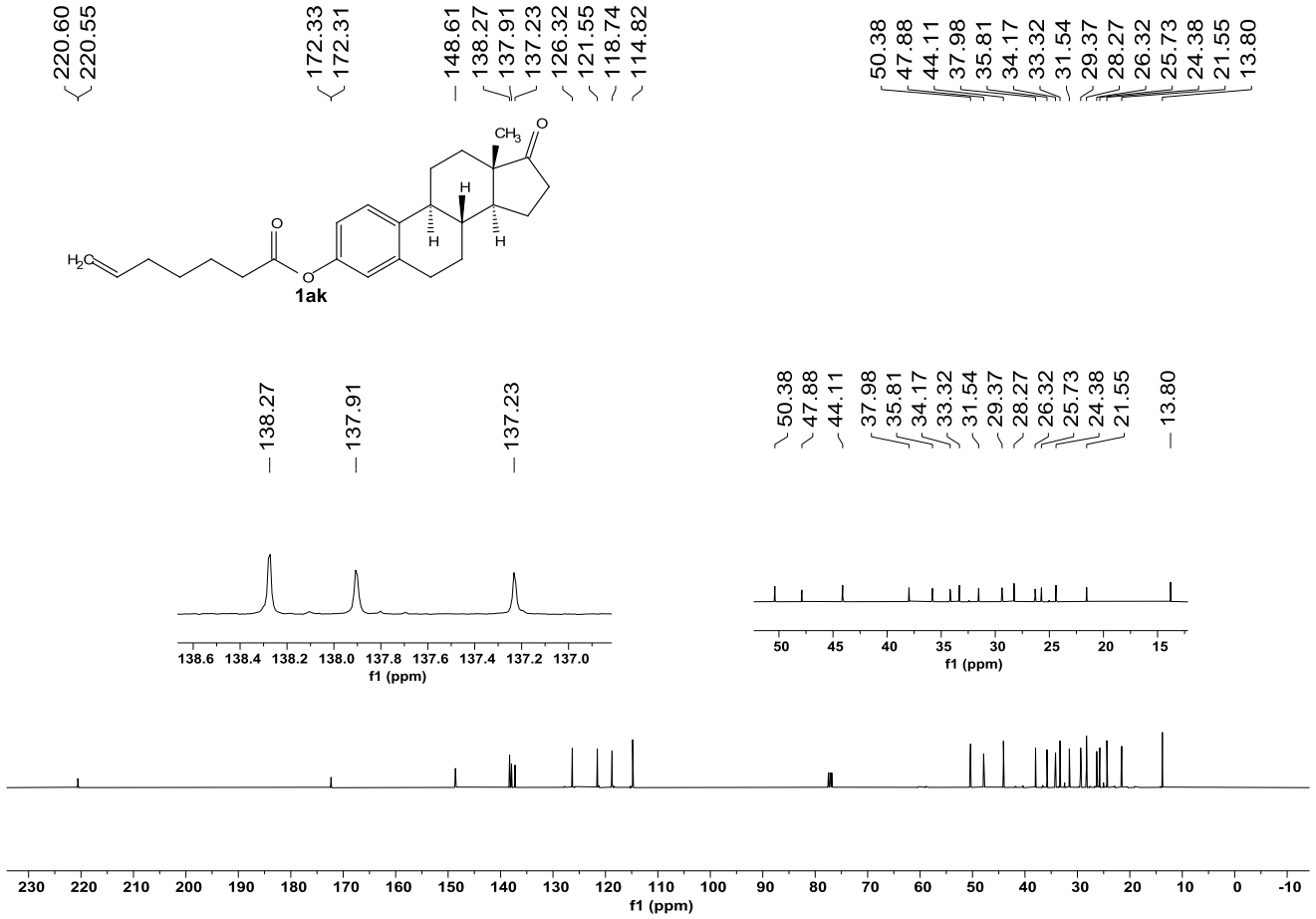
^{13}C NMR spectrum of compound **1ag** (101 MHz, $CDCl_3$)



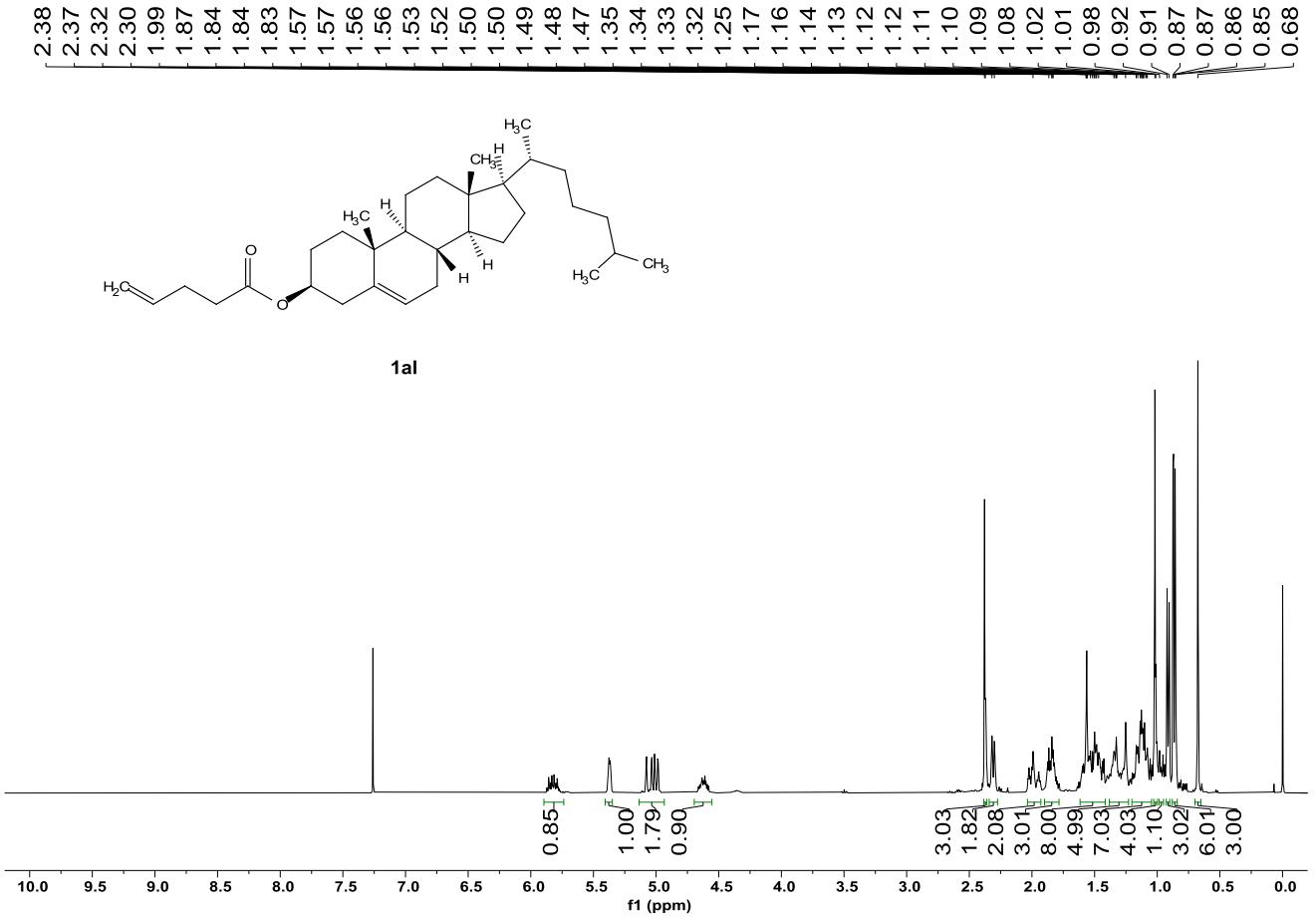
^{1}H NMR spectrum of compound **1ak** (400 MHz, $CDCl_3$)



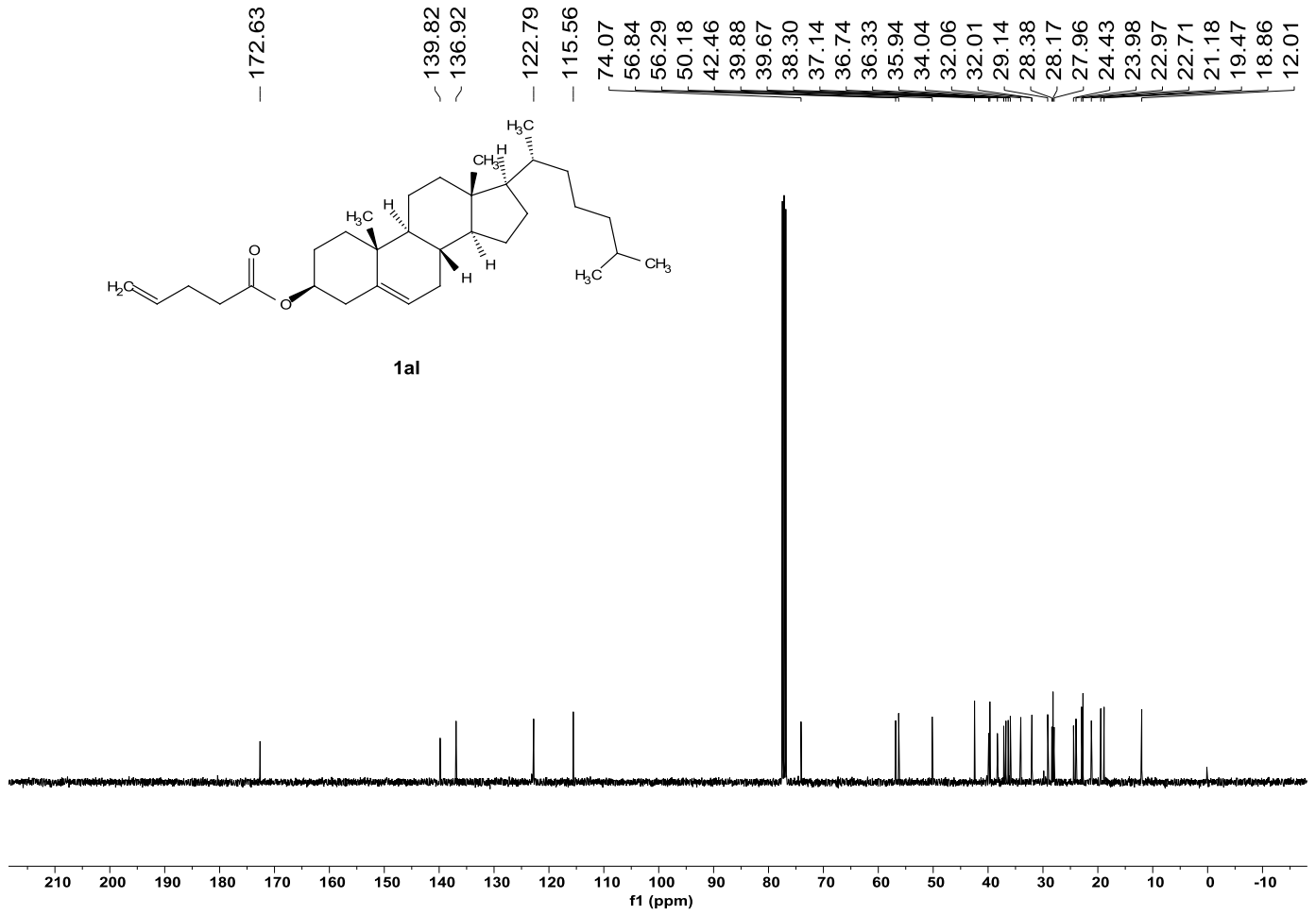
^{13}C NMR spectrum of compound **1ak** (101 MHz, $CDCl_3$)



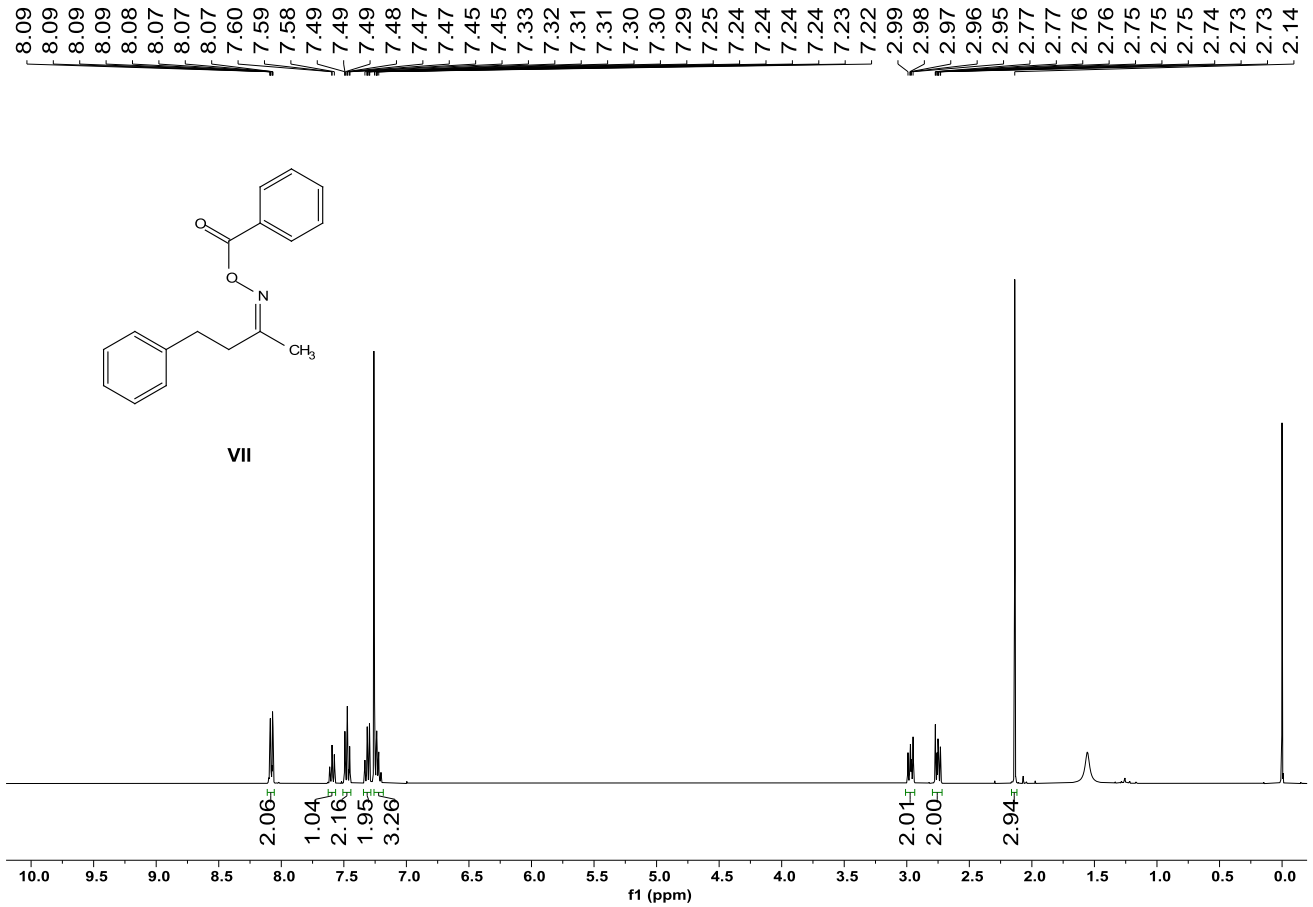
^{1}H NMR spectrum of compound **1al** (400 MHz, $CDCl_3$)



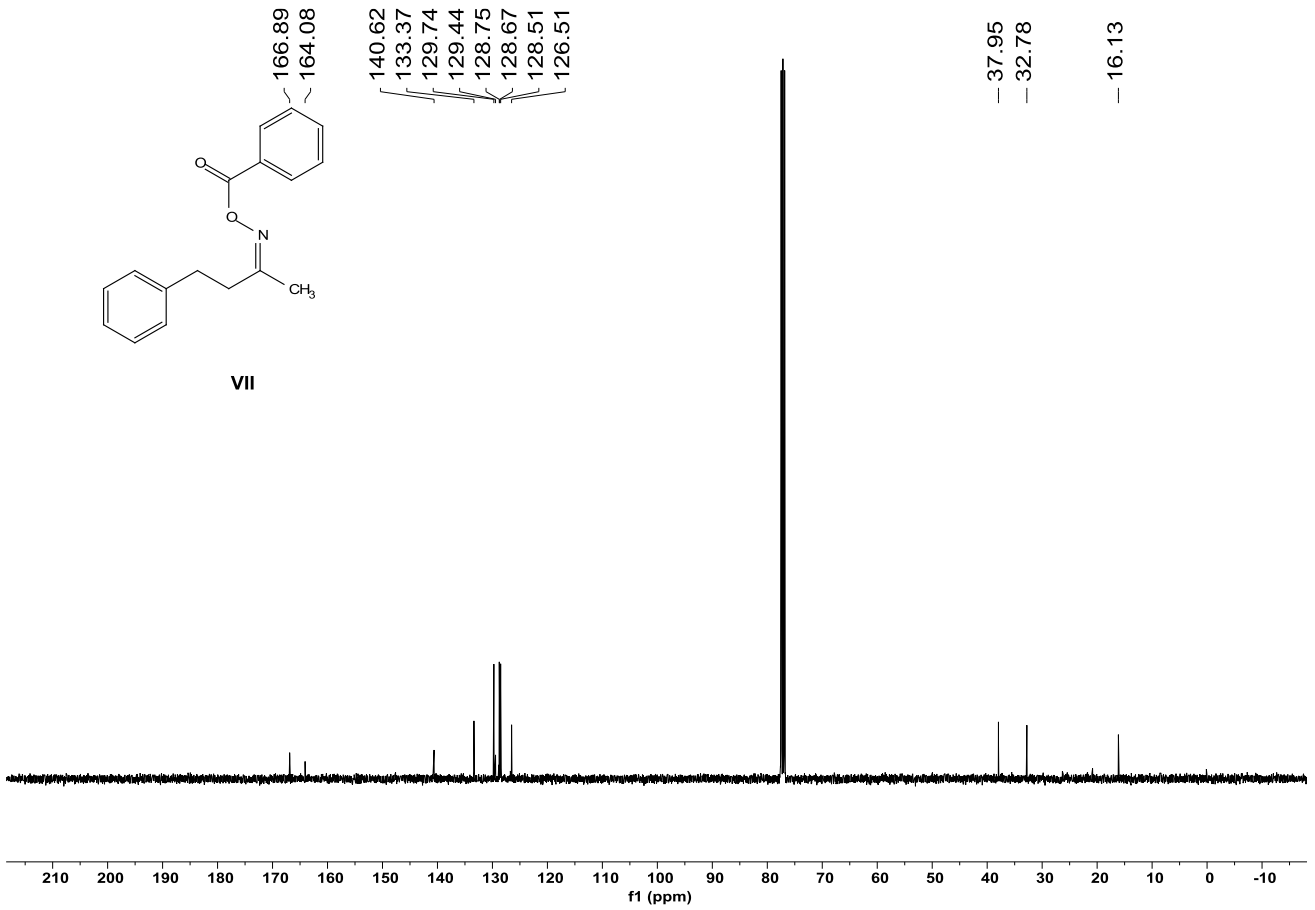
^{13}C NMR spectrum of compound **1al** (101 MHz, $CDCl_3$)



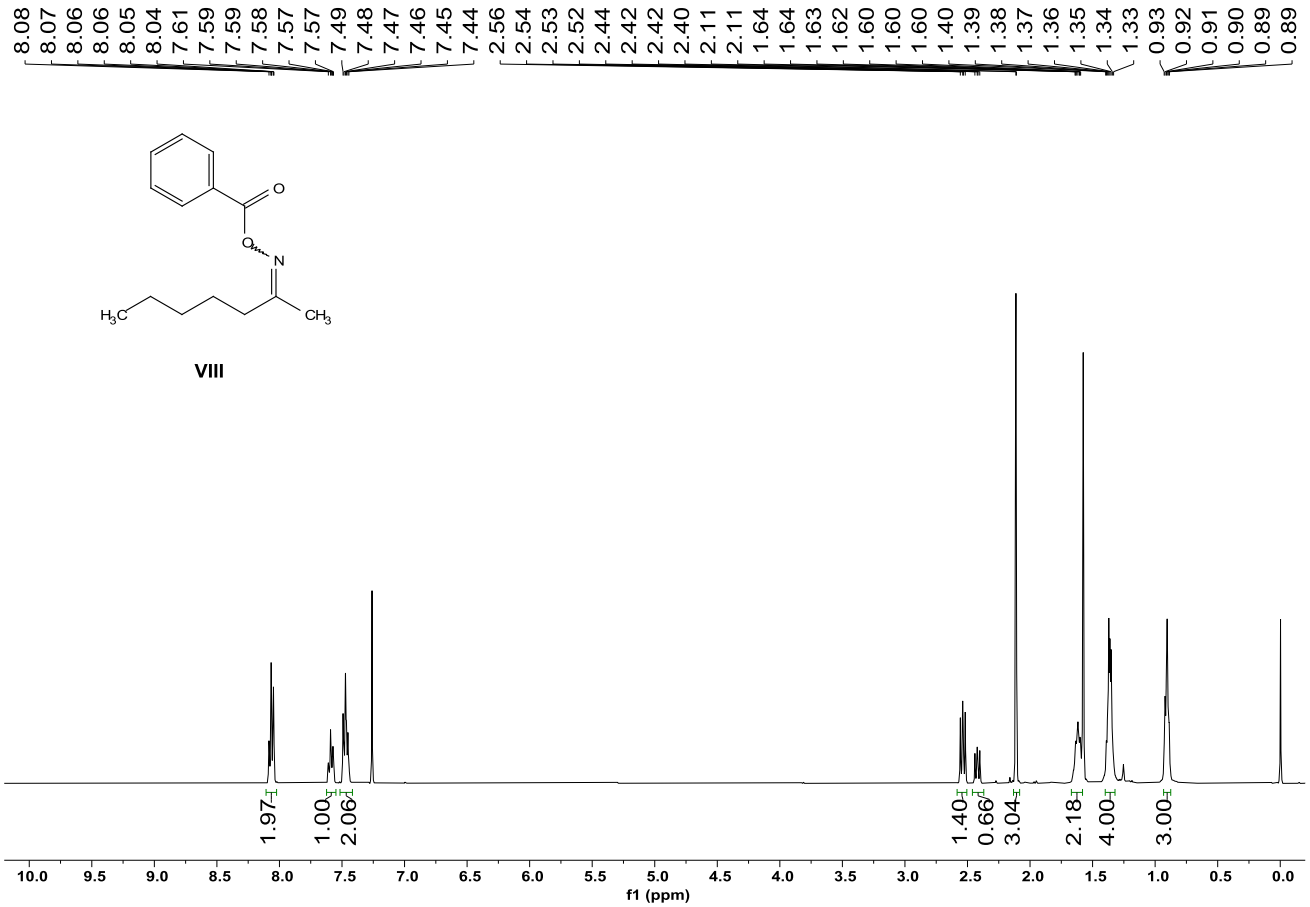
^{1}H NMR spectrum of compound **VII** (400 MHz, $CDCl_3$)



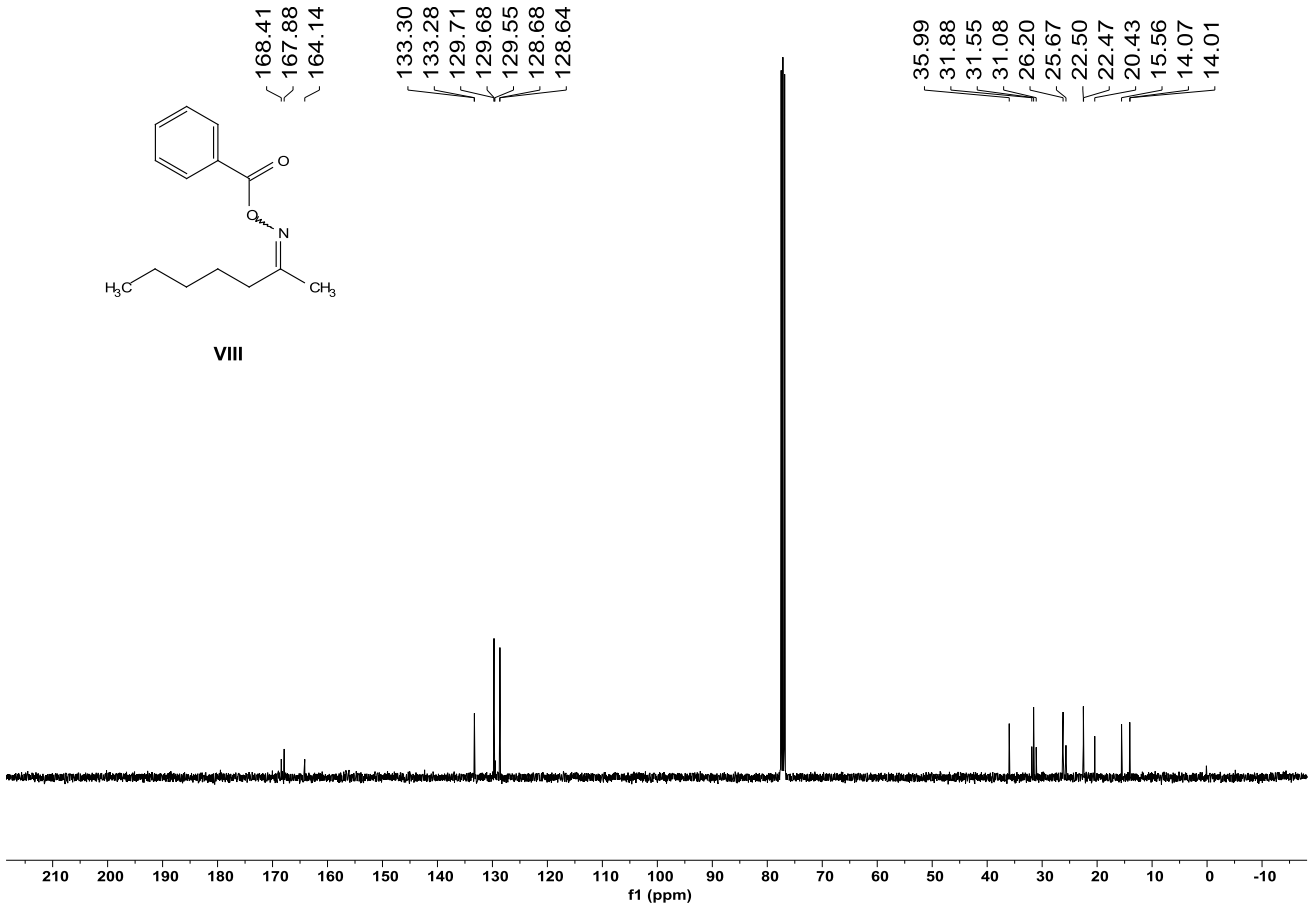
^{13}C NMR spectrum of compound **VII** (400 MHz, $CDCl_3$)



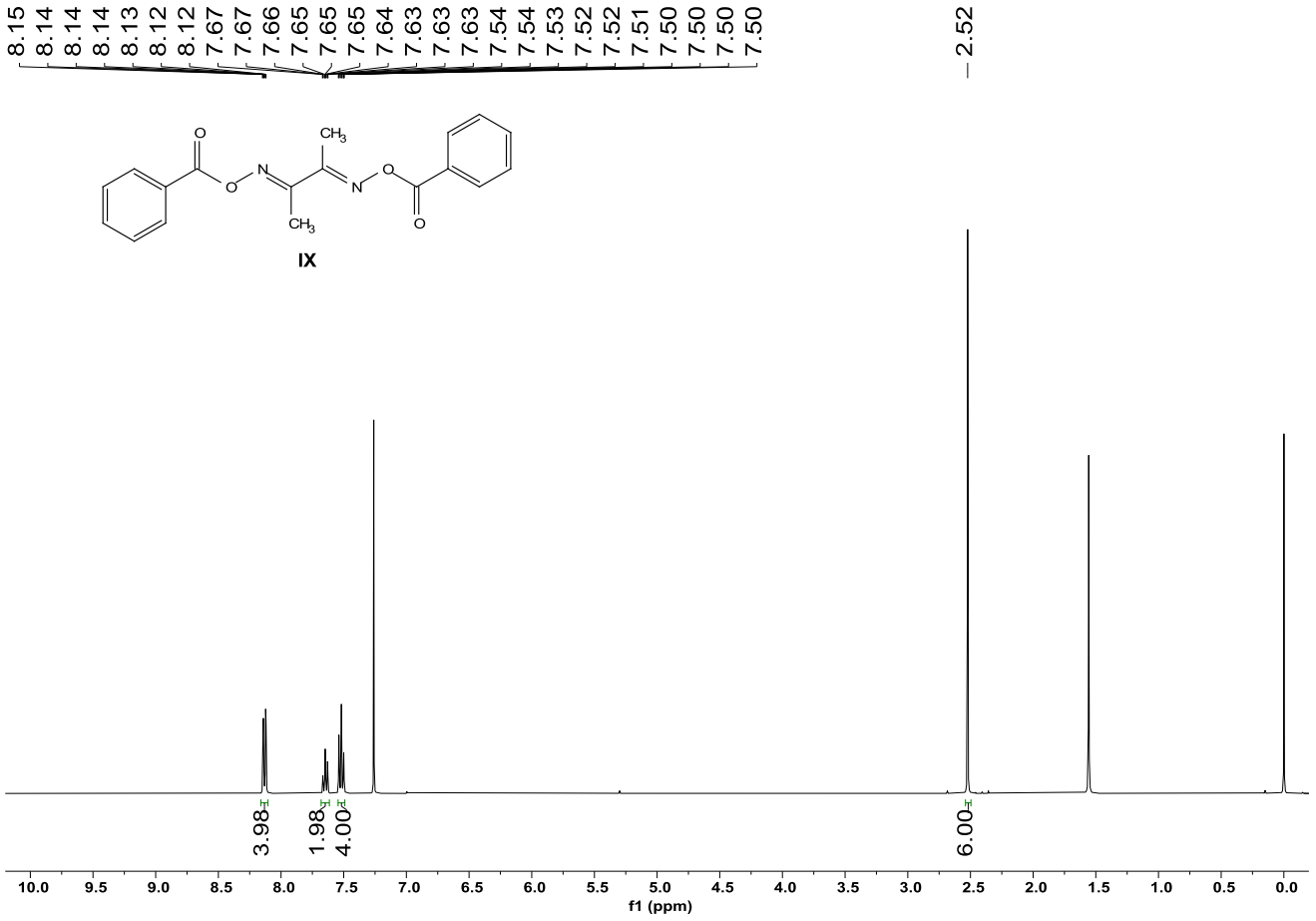
^{1}H NMR spectrum of compound **VIII** (400 MHz, $CDCl_3$)



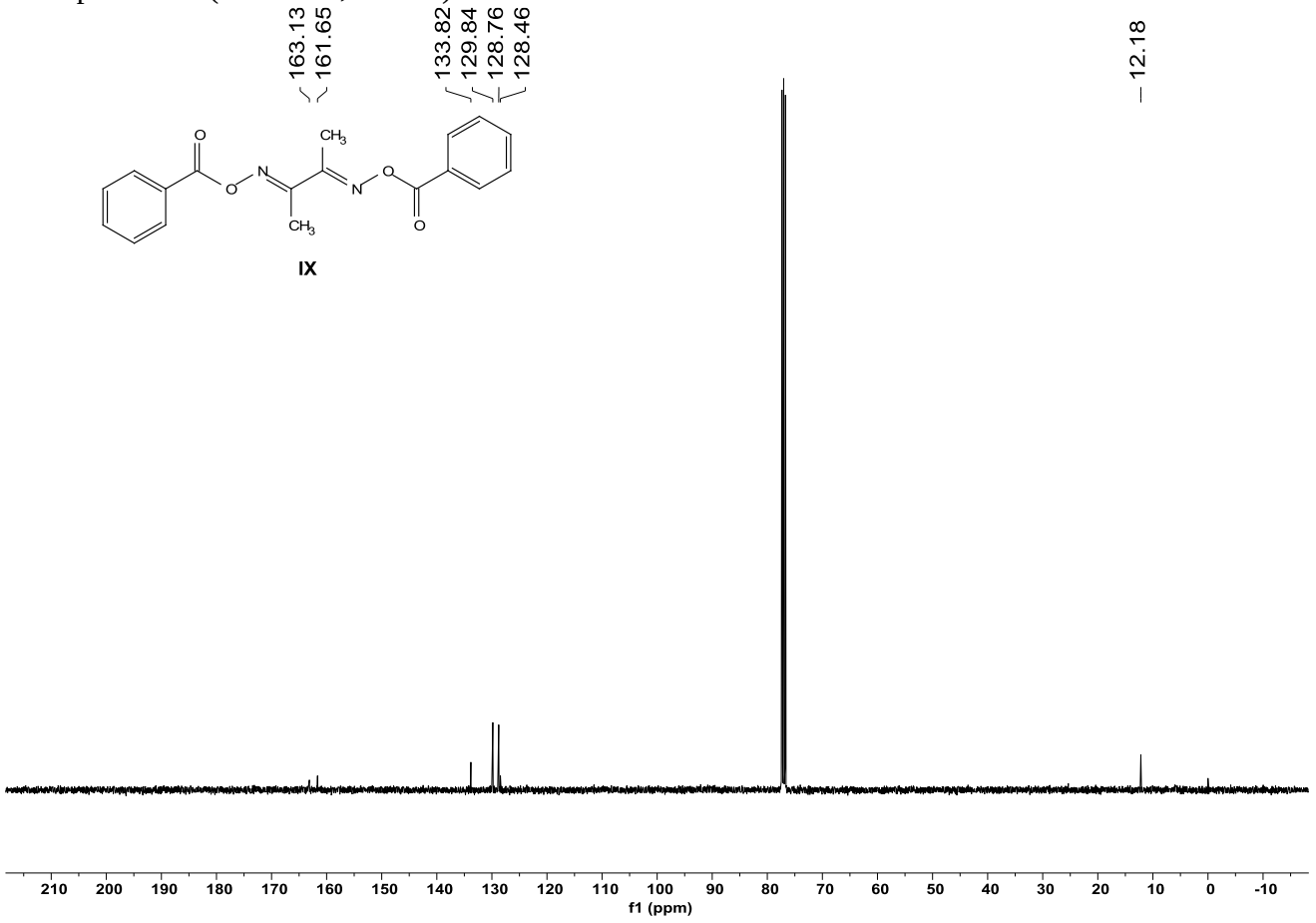
^{13}C NMR spectrum of compound **VIII** (400 MHz, $CDCl_3$)



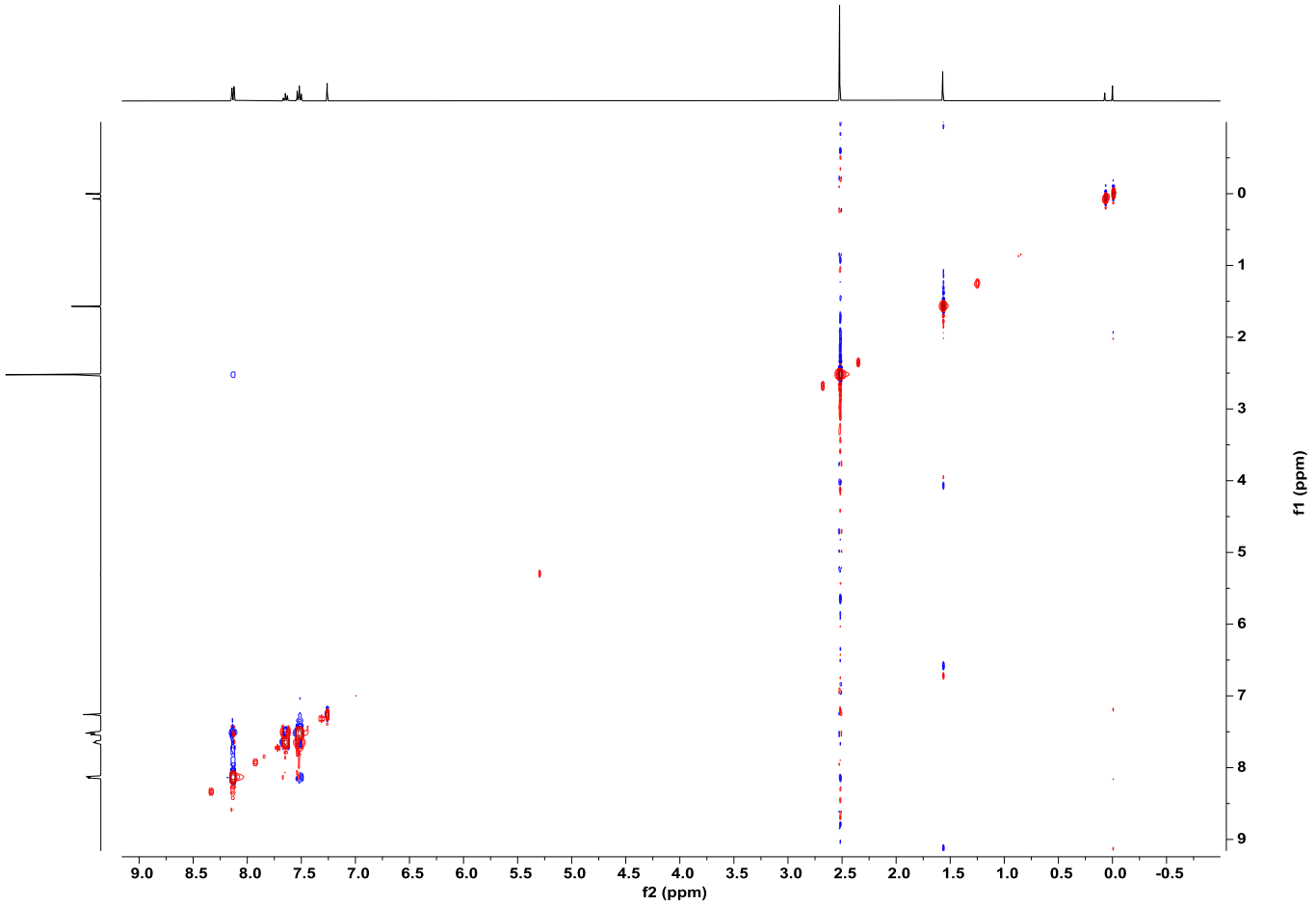
^{1}H NMR spectrum of compound **IX** (400 MHz, $CDCl_3$)



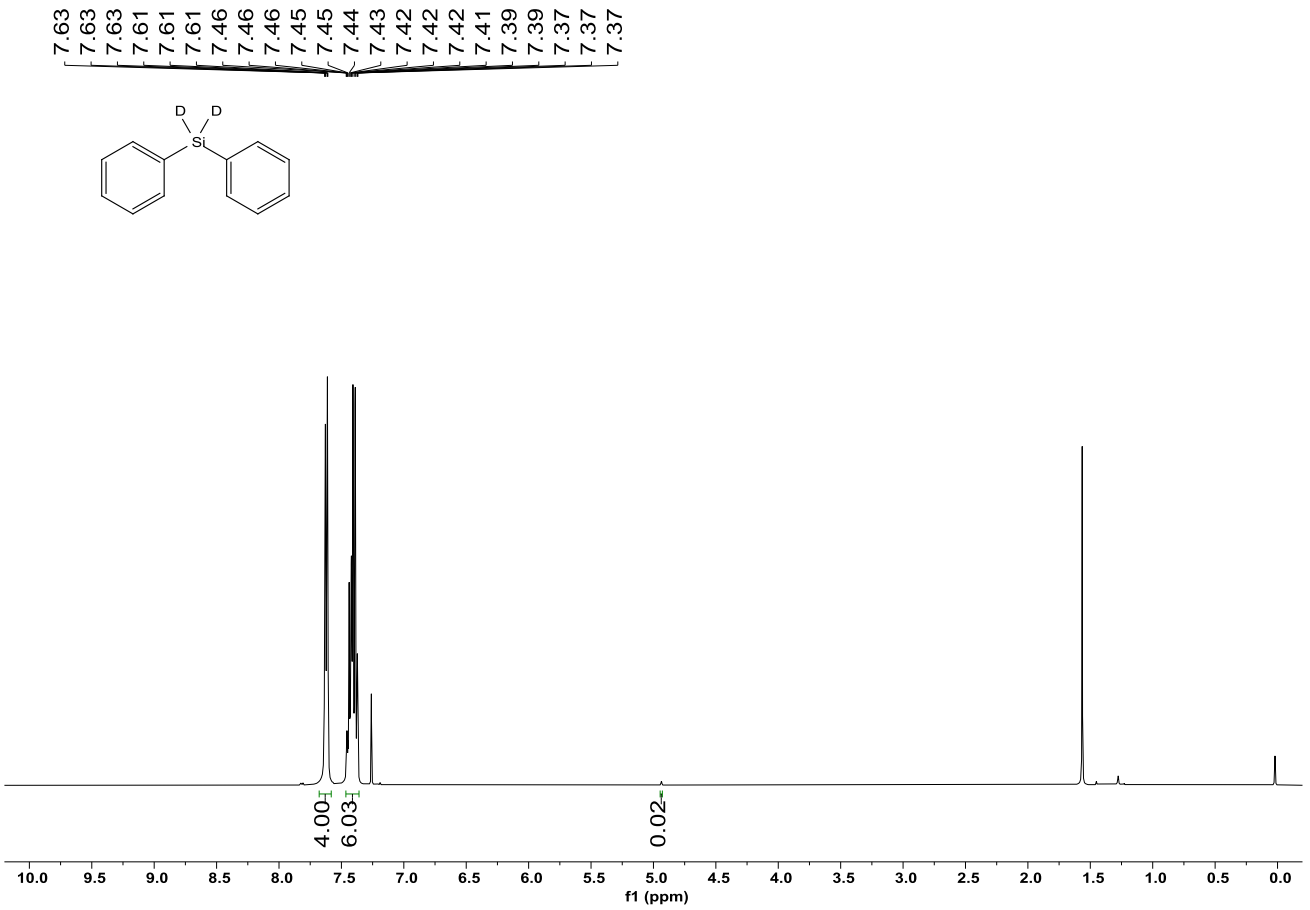
^{13}C NMR spectrum of compound **IX** (101 MHz, $CDCl_3$)



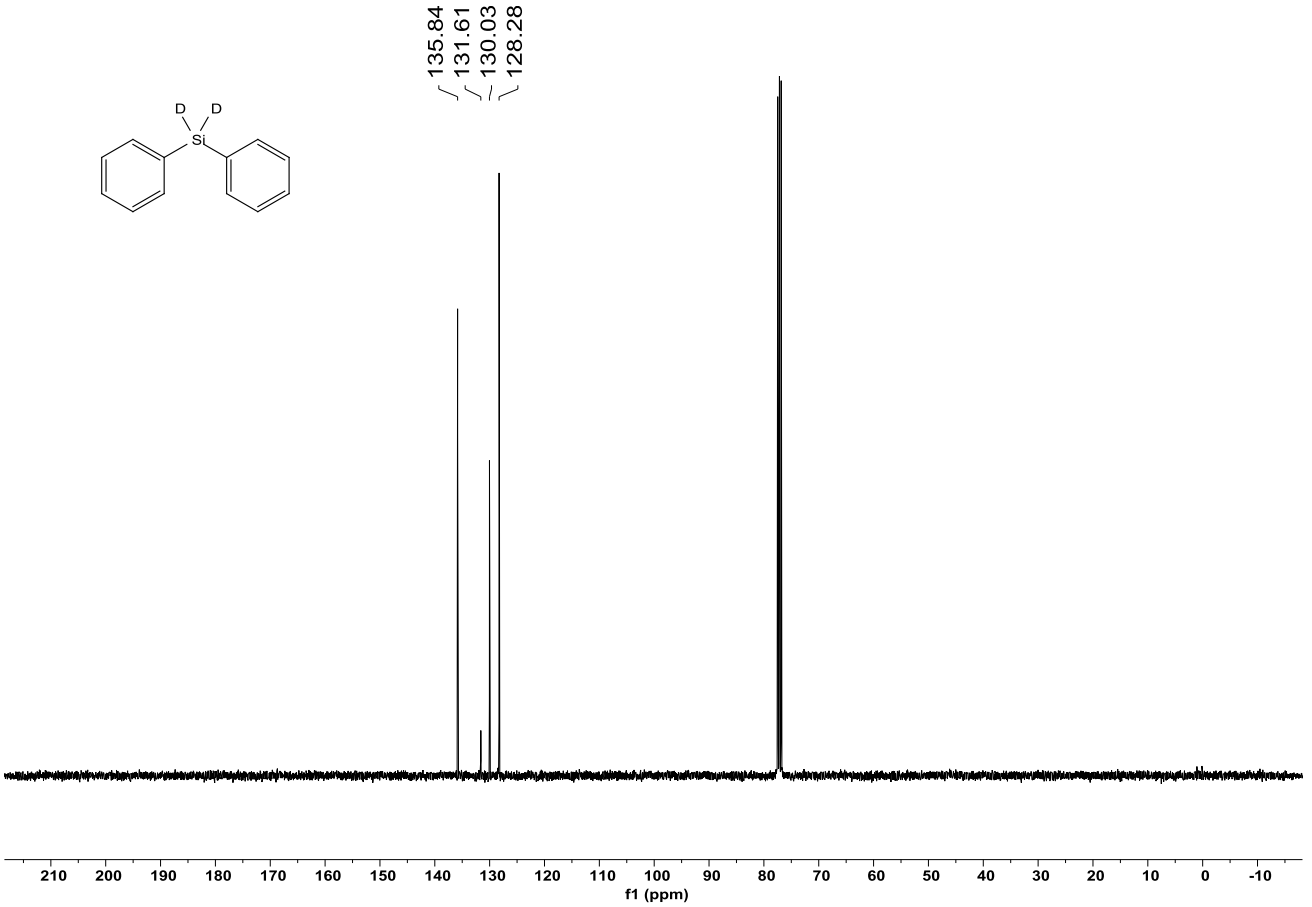
NOESY spectrum of compound **VII** (400 MHz, $CDCl_3$)



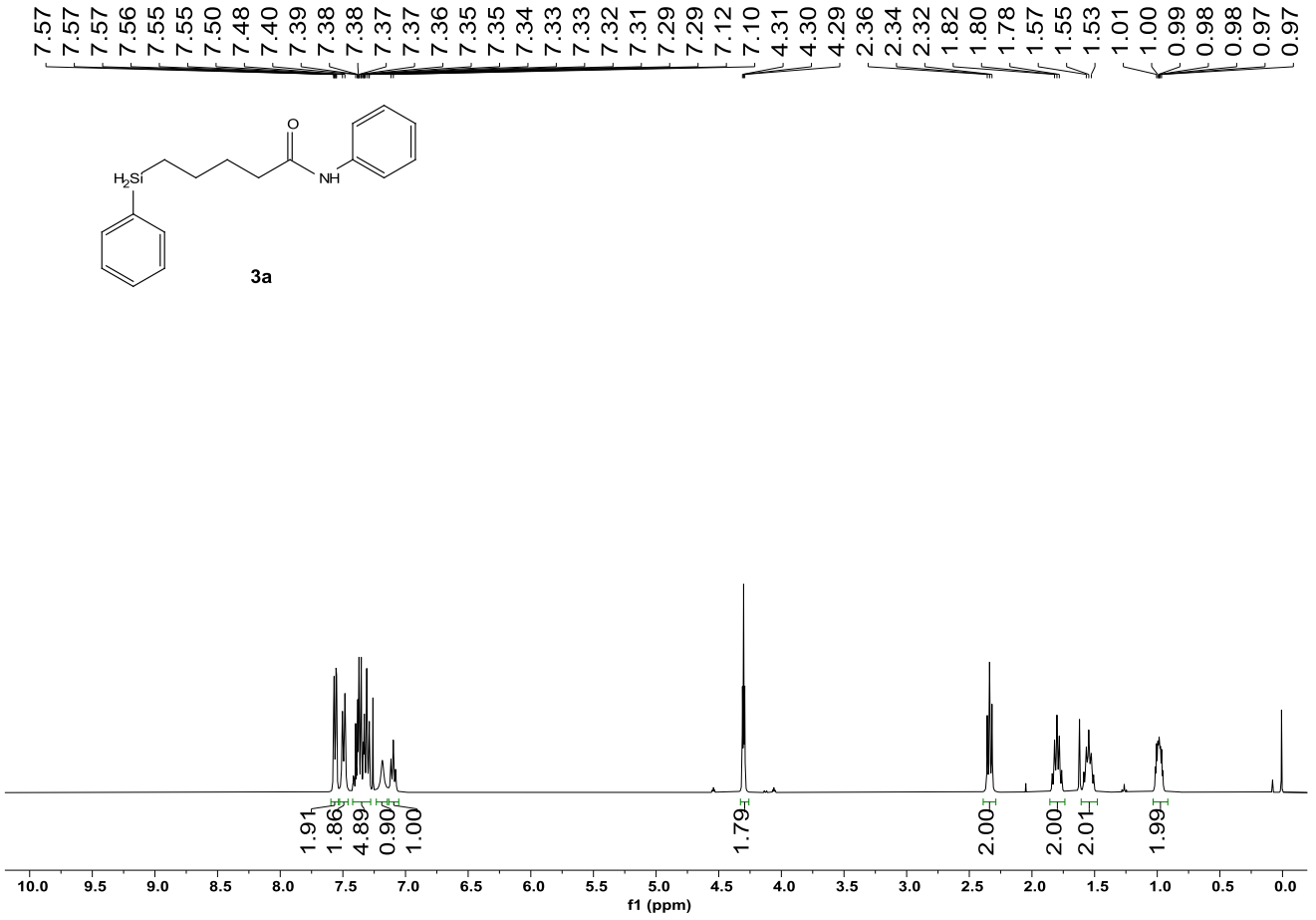
^{1}H NMR spectrum of compound **D_2SiPh_2** (400 MHz, $CDCl_3$)



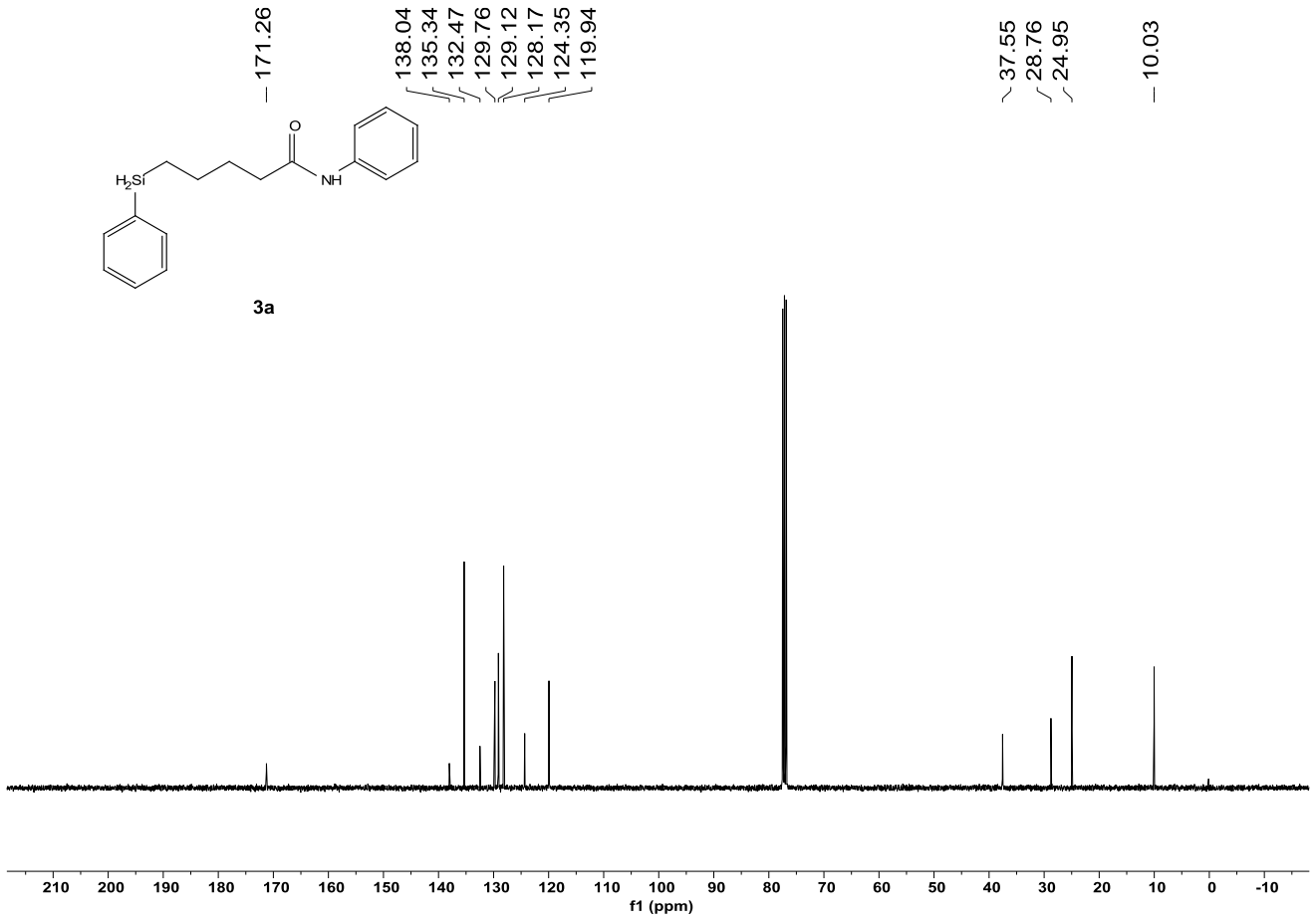
^{13}C NMR spectrum of compound **D_2SiPh_2** (101 MHz, $CDCl_3$)



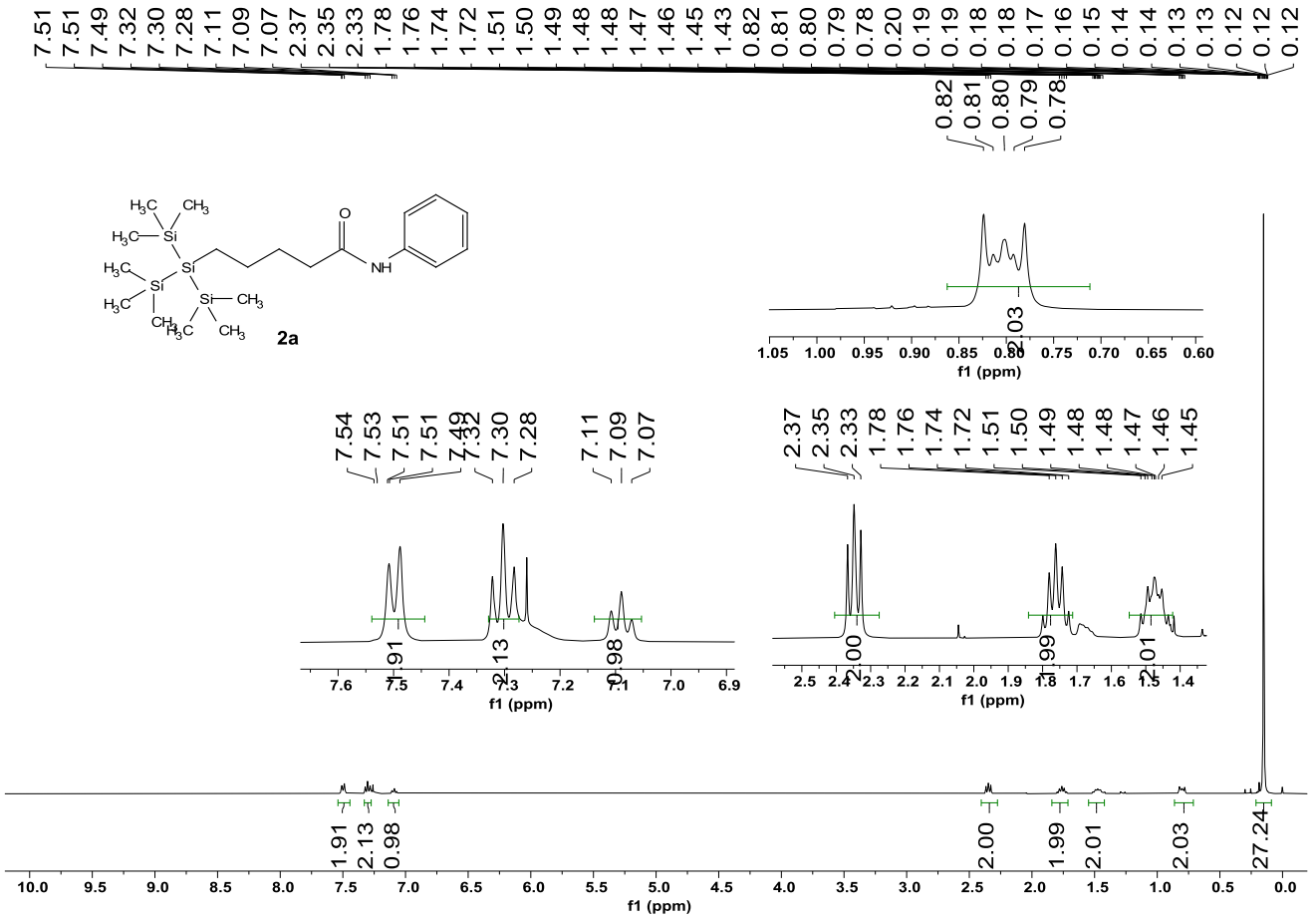
^{1}H NMR spectrum of compound **3a** (400 MHz, $CDCl_3$)



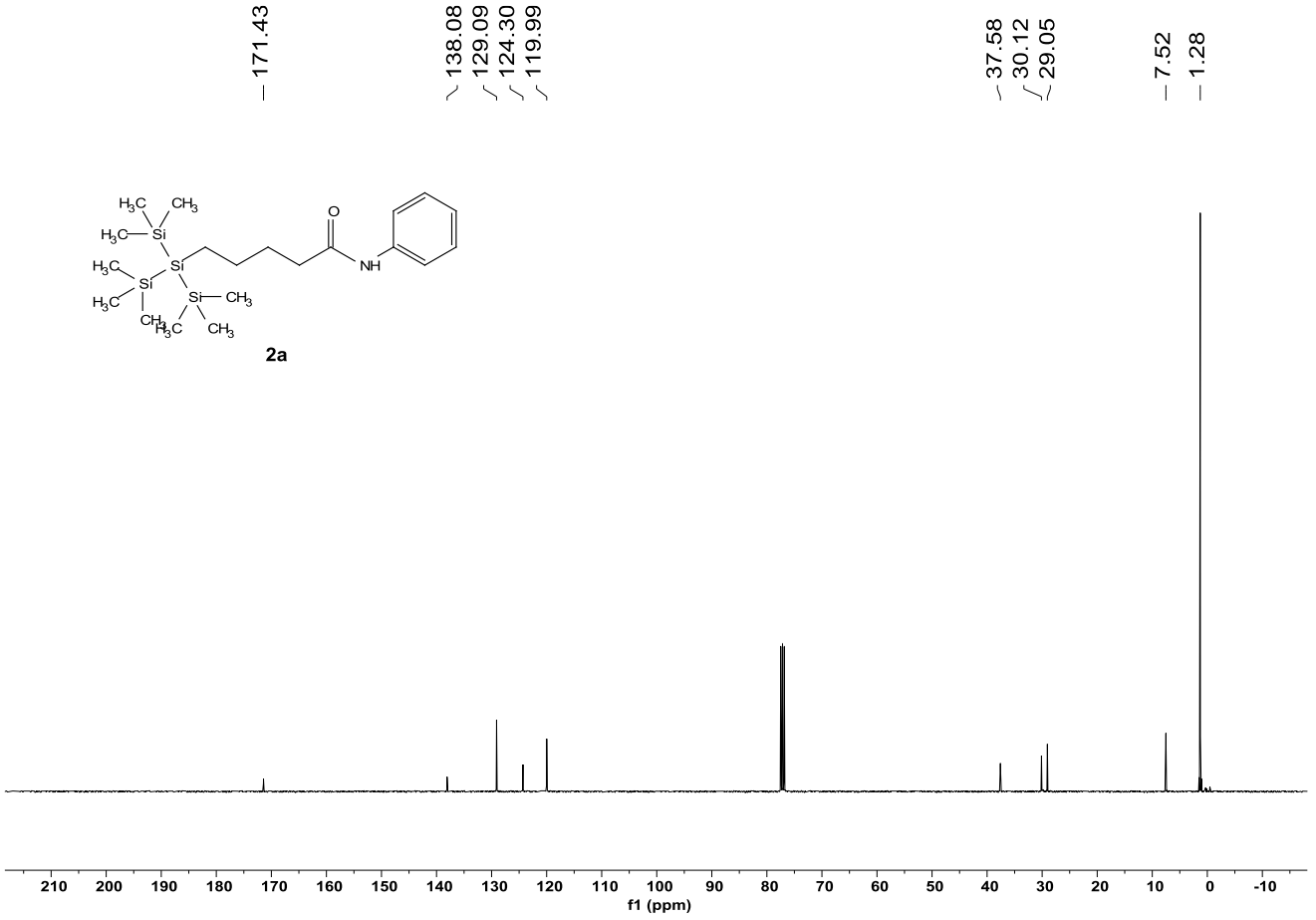
^{13}C NMR spectrum of compound **3a** (101 MHz, $CDCl_3$)



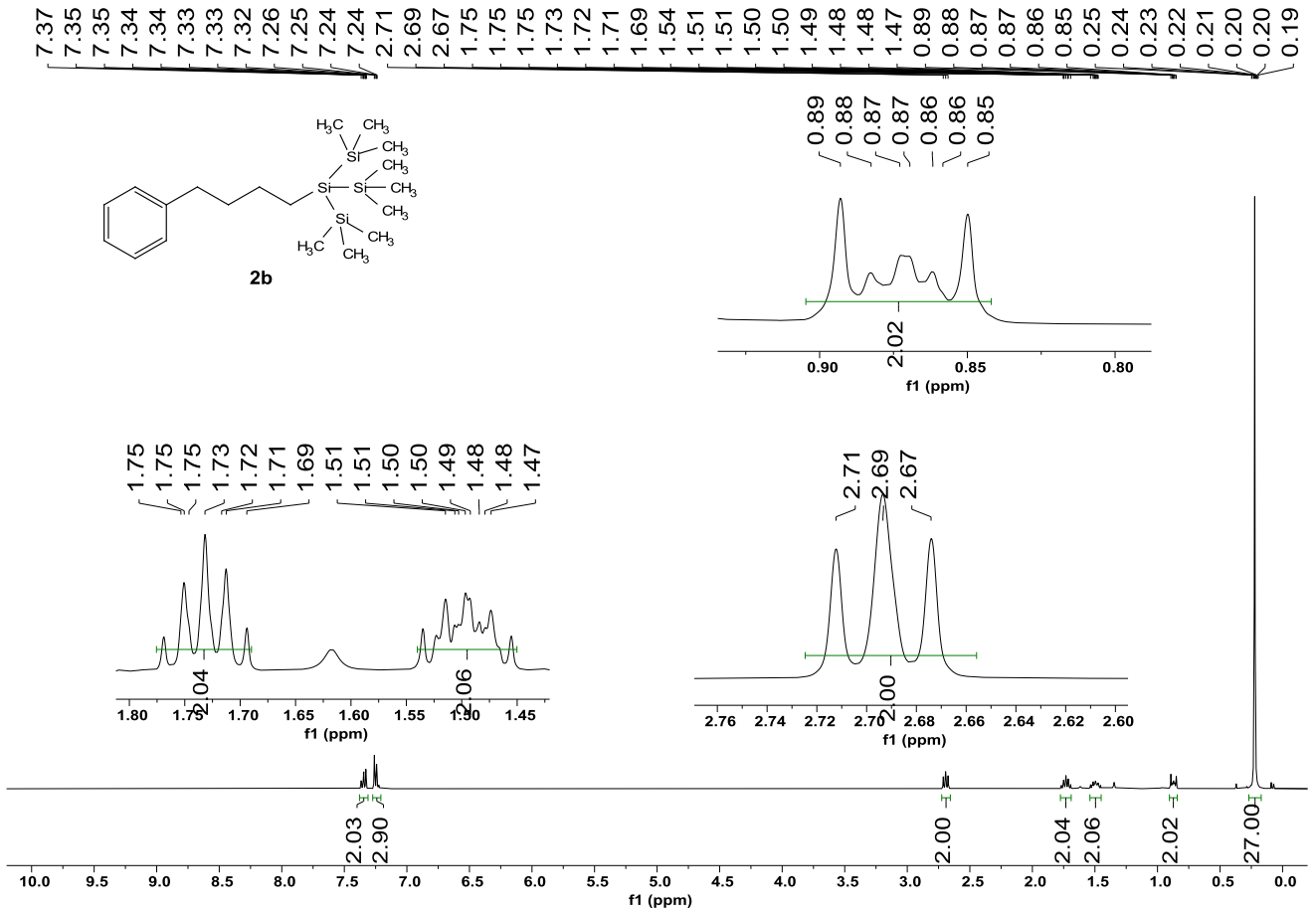
^{1}H NMR spectrum of compound **2a** (400 MHz, $CDCl_3$)



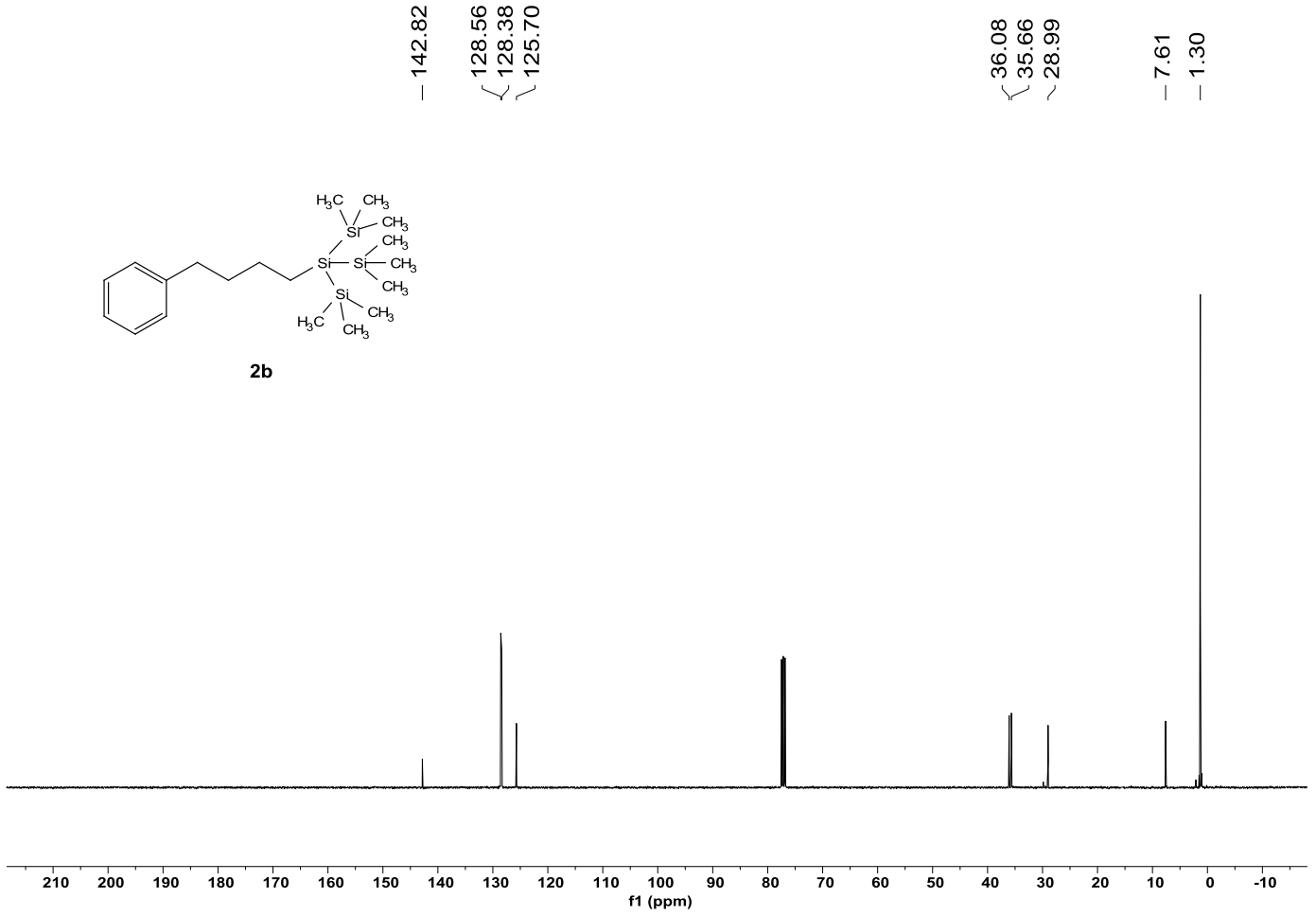
^{13}C NMR spectrum of compound **2a** (101 MHz, $CDCl_3$)



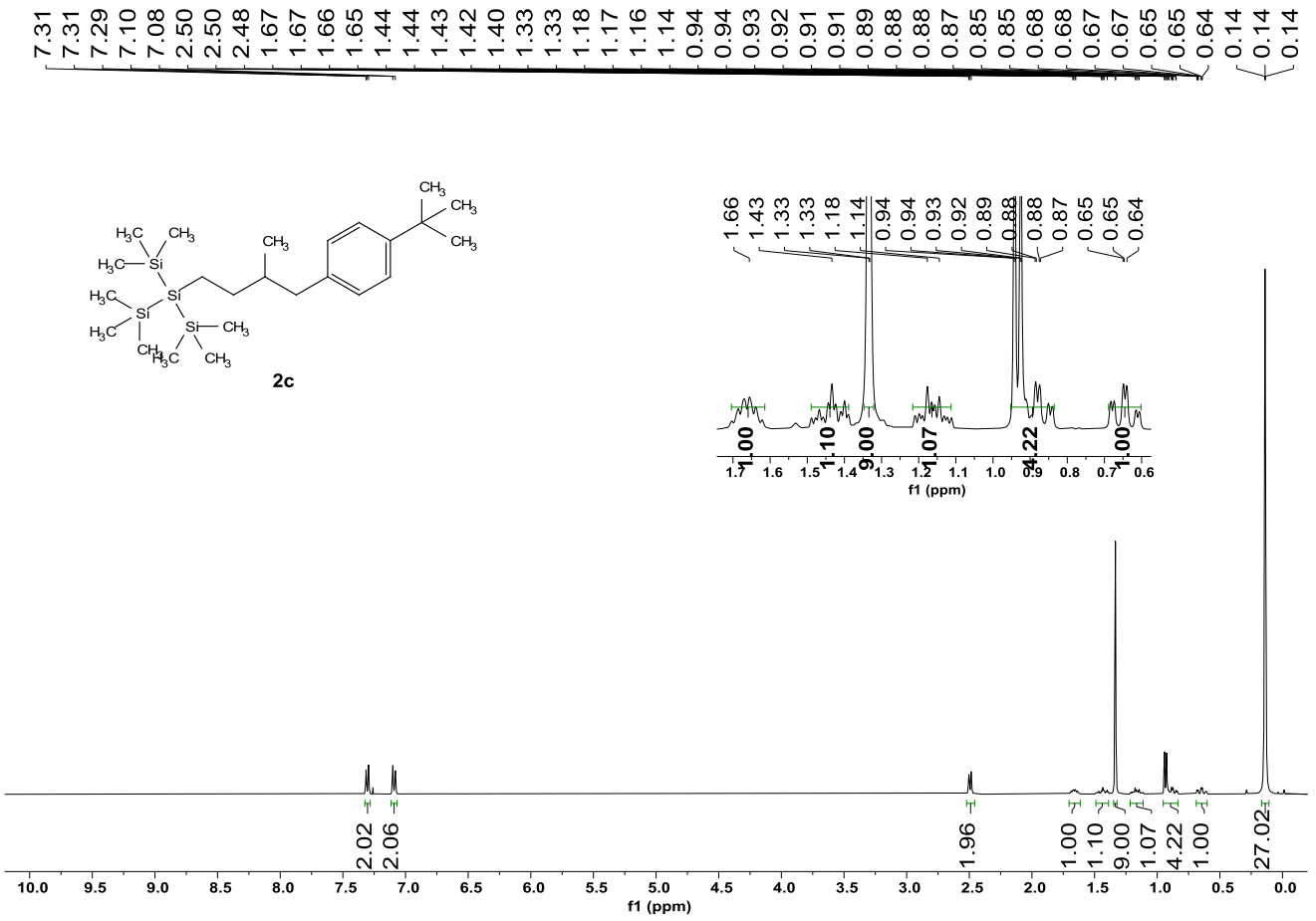
^{1}H NMR spectrum of compound **2b** (400 MHz, $CDCl_3$)



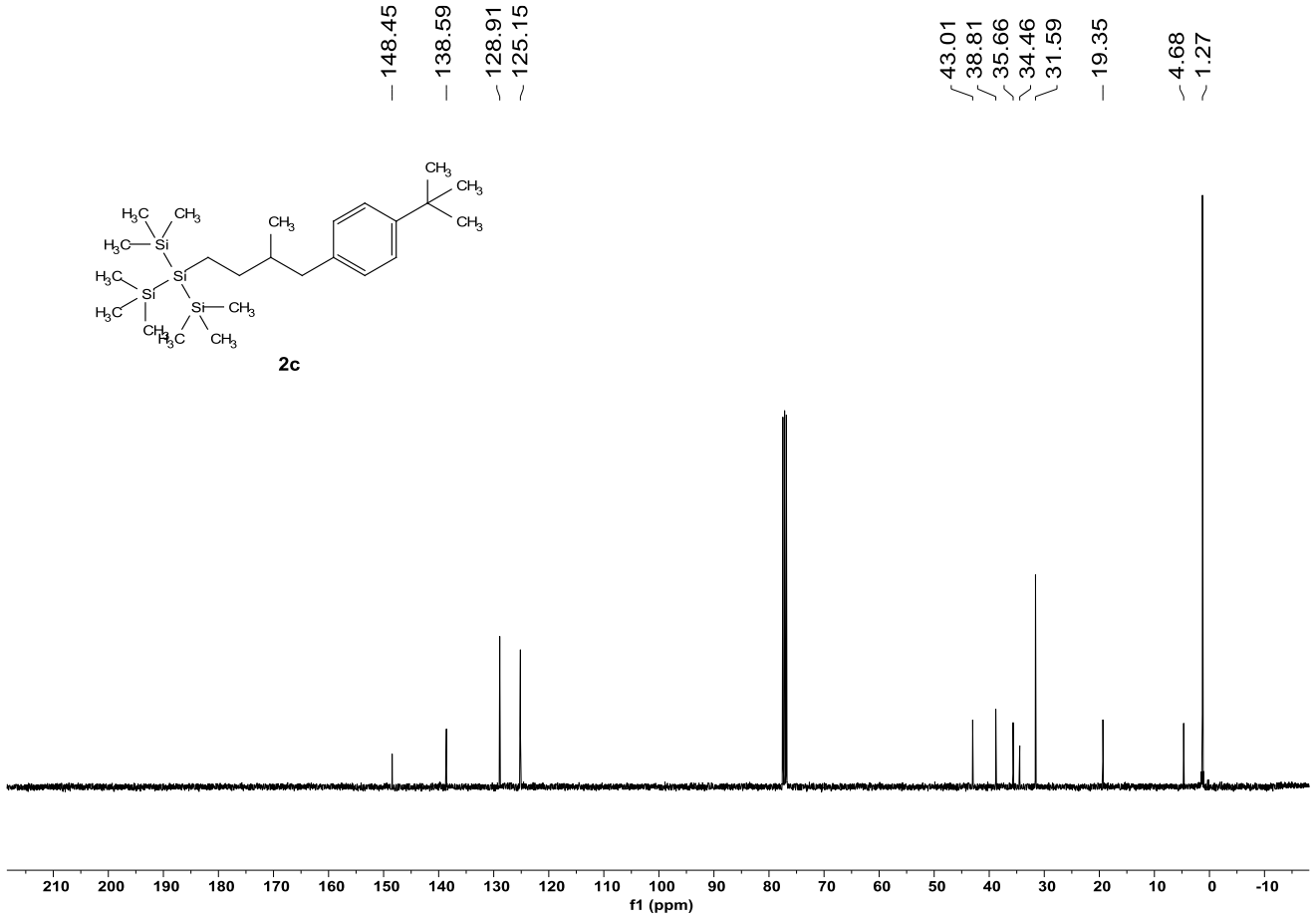
^{13}C NMR spectrum of compound **2b** (101 MHz, $CDCl_3$)



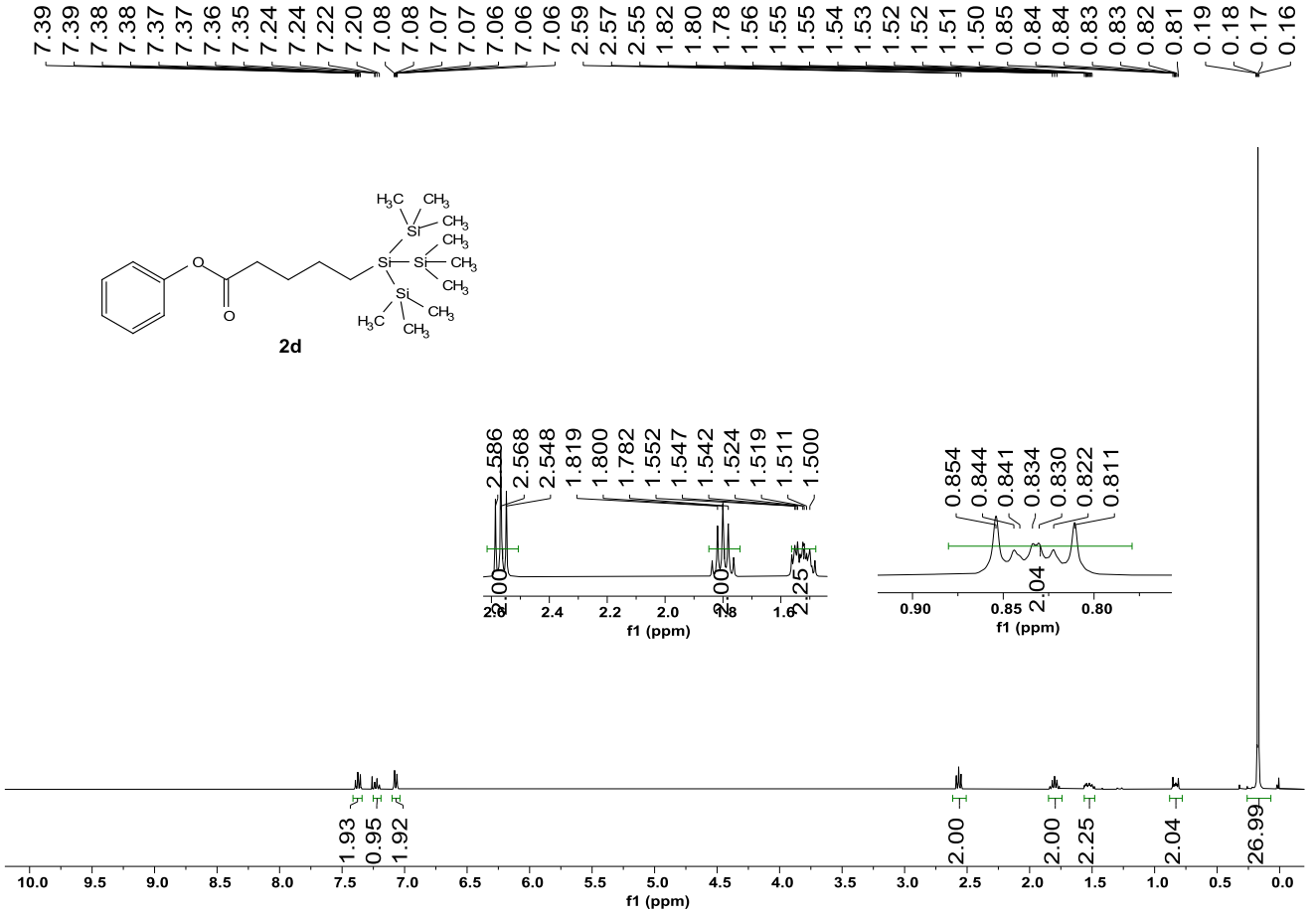
^{1}H NMR spectrum of compound **2c** (400 MHz, $CDCl_3$)



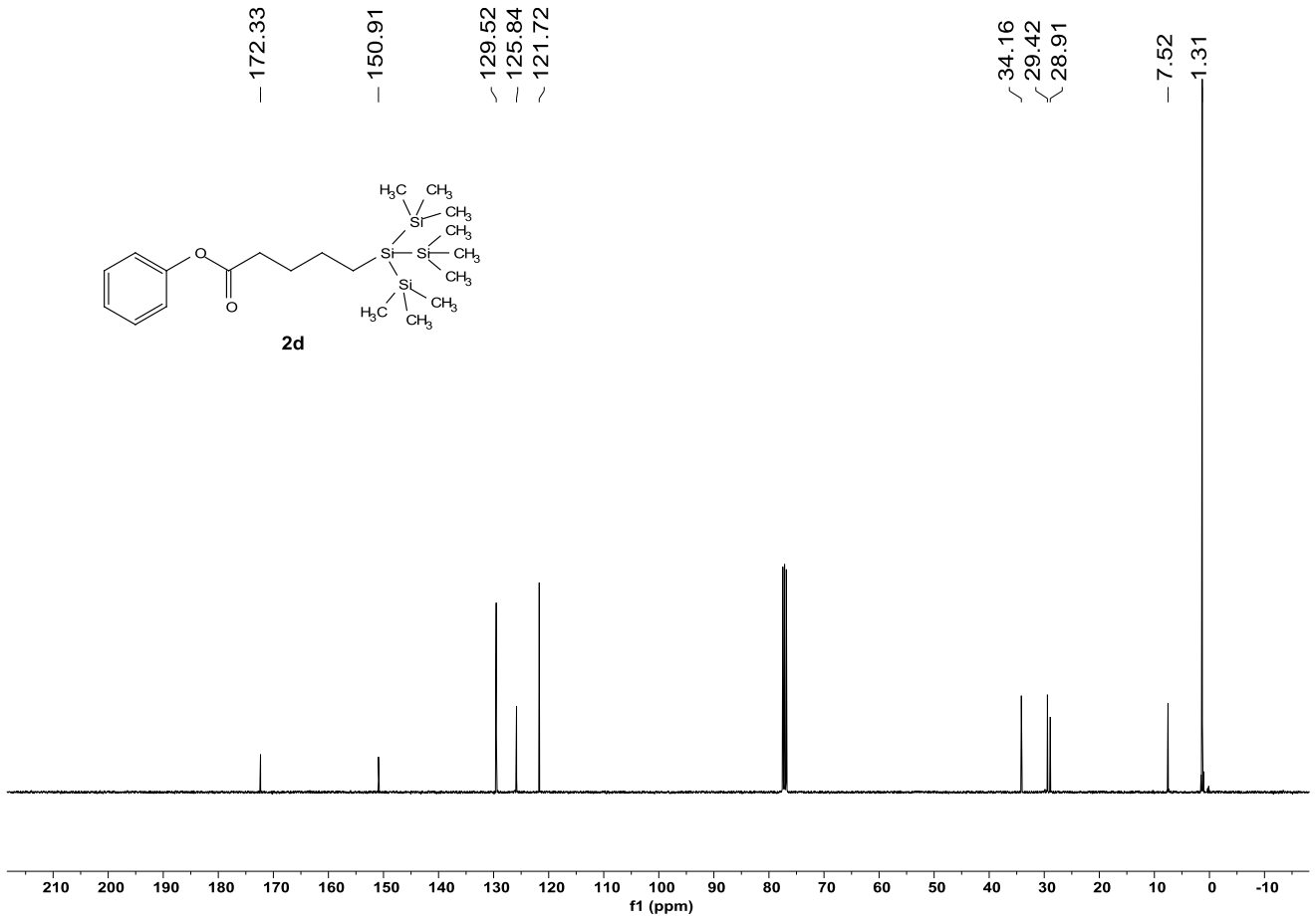
^{13}C NMR spectrum of compound **2c** (101 MHz, $CDCl_3$)



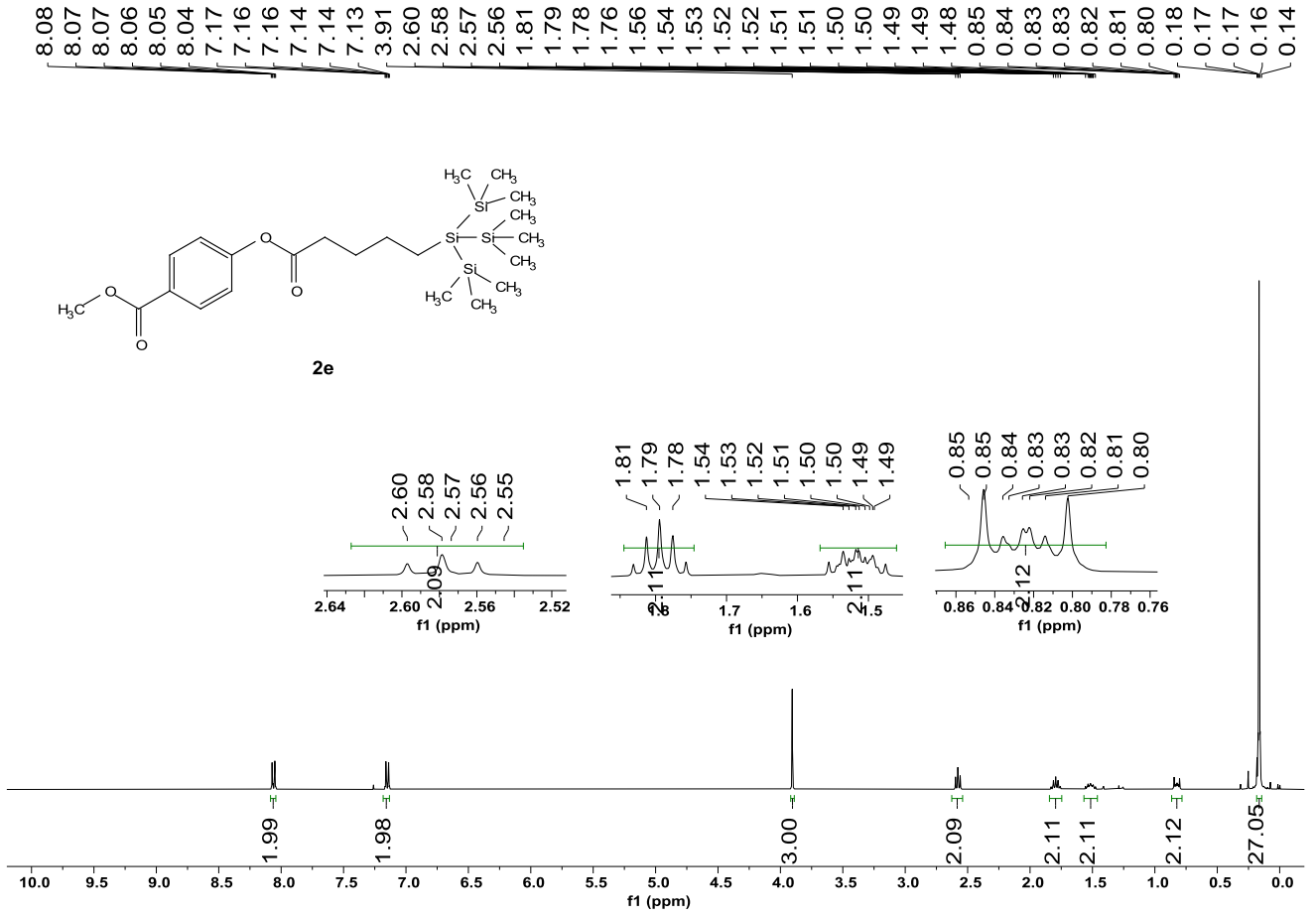
^{1}H NMR spectrum of compound **2d** (400 MHz, $CDCl_3$)



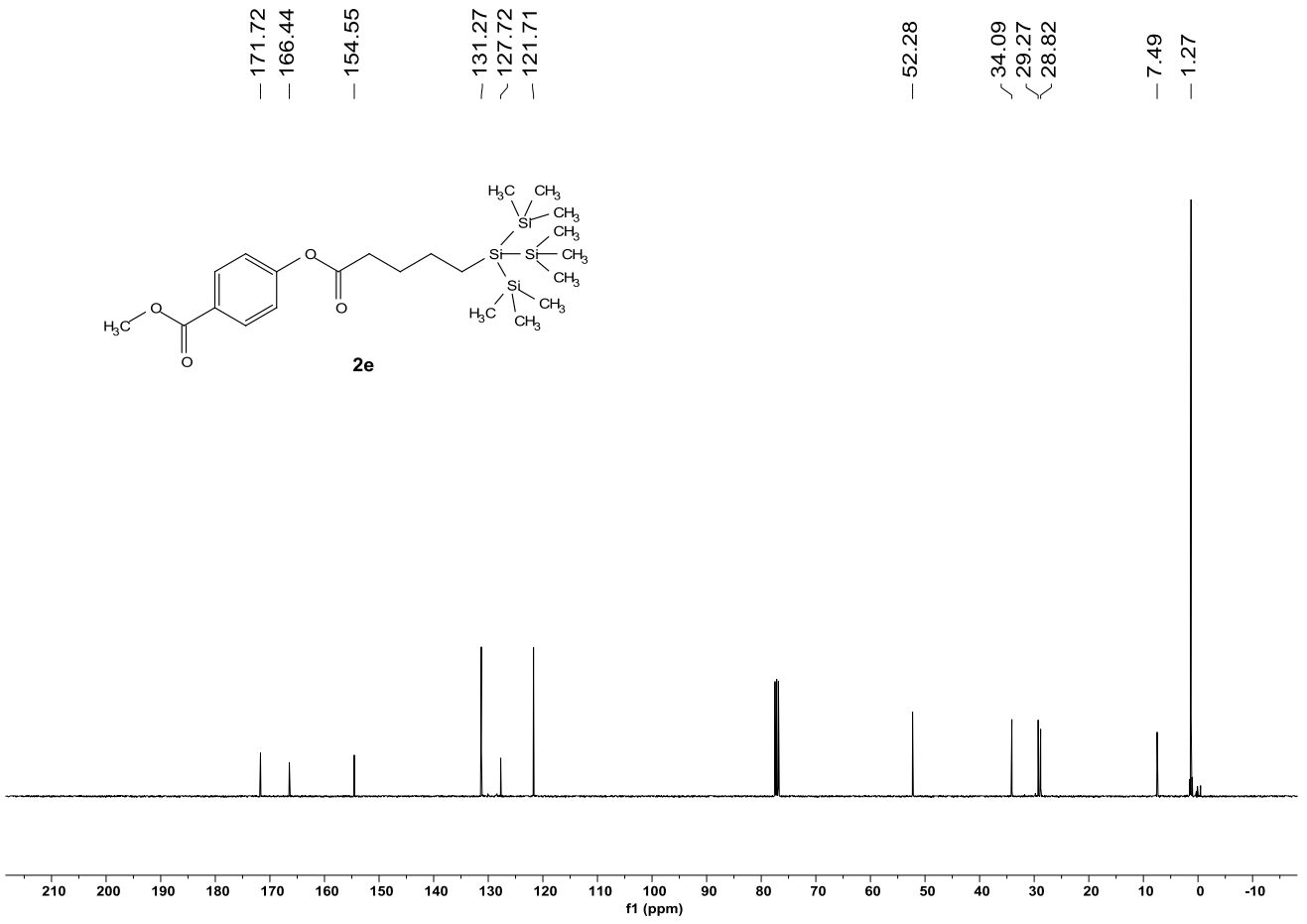
^{13}C NMR spectrum of compound **2d** (101 MHz, $CDCl_3$)



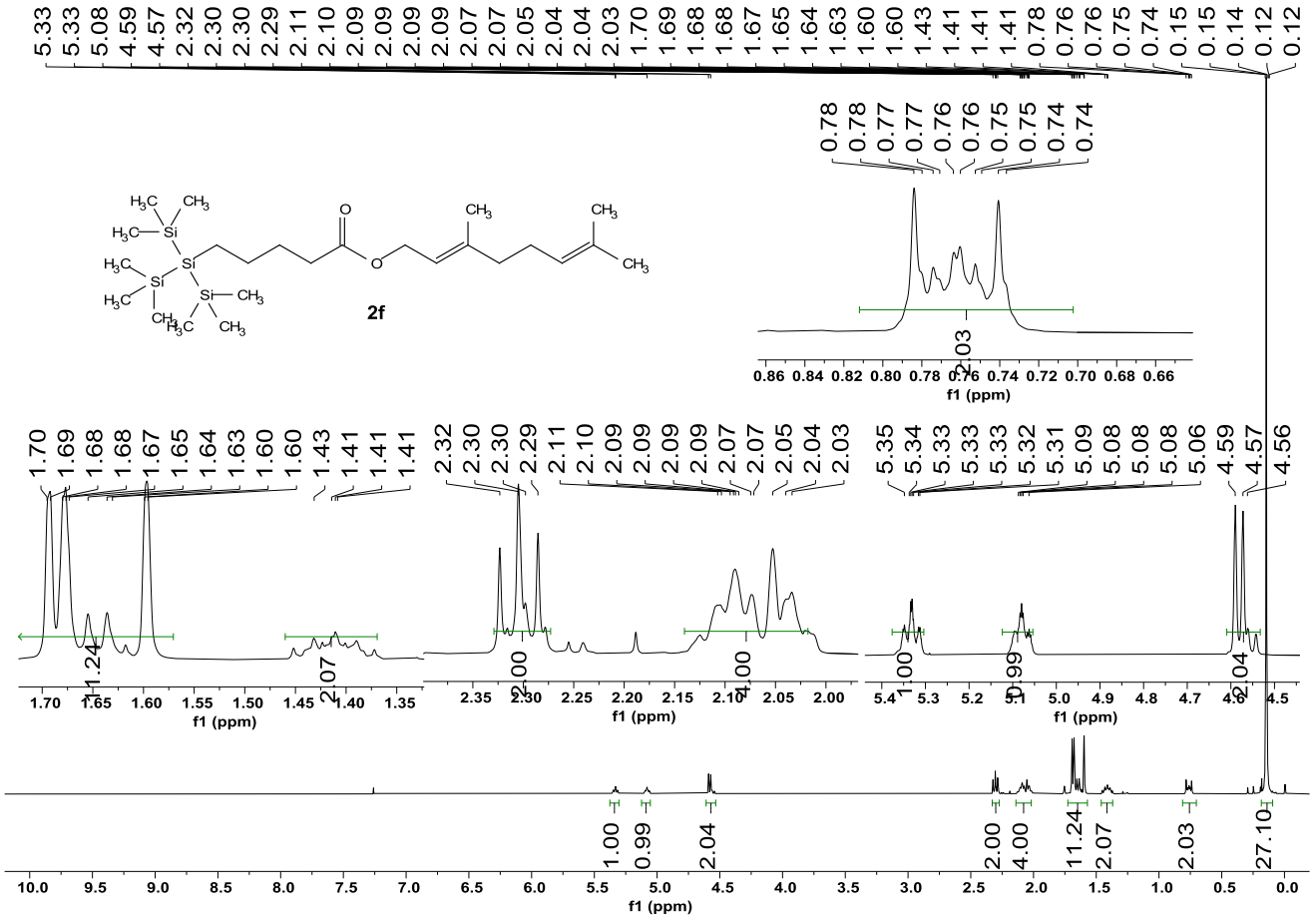
^{1}H NMR spectrum of compound **2e** (400 MHz, $CDCl_3$)



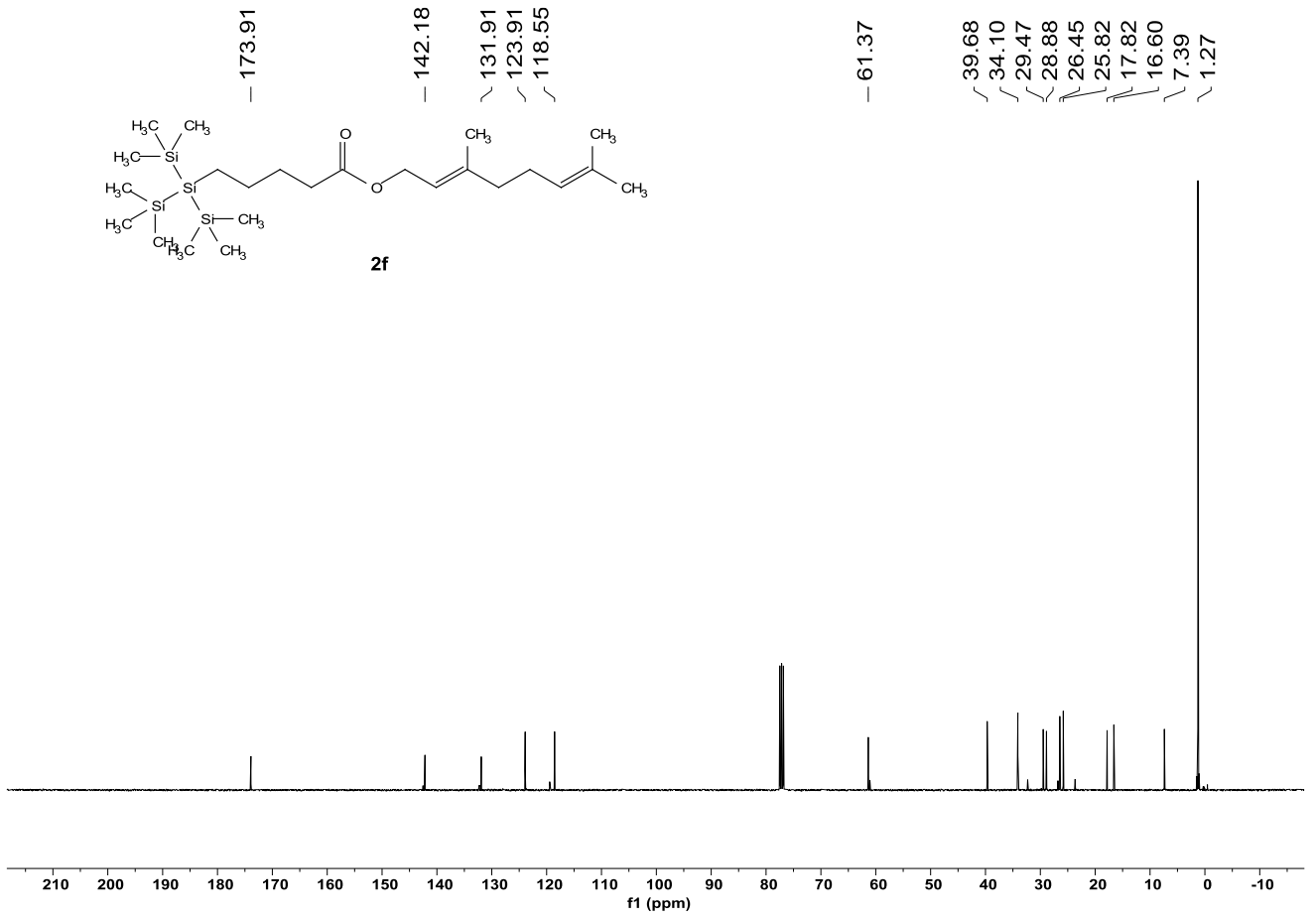
^{13}C NMR spectrum of compound **2e** (101 MHz, $CDCl_3$)



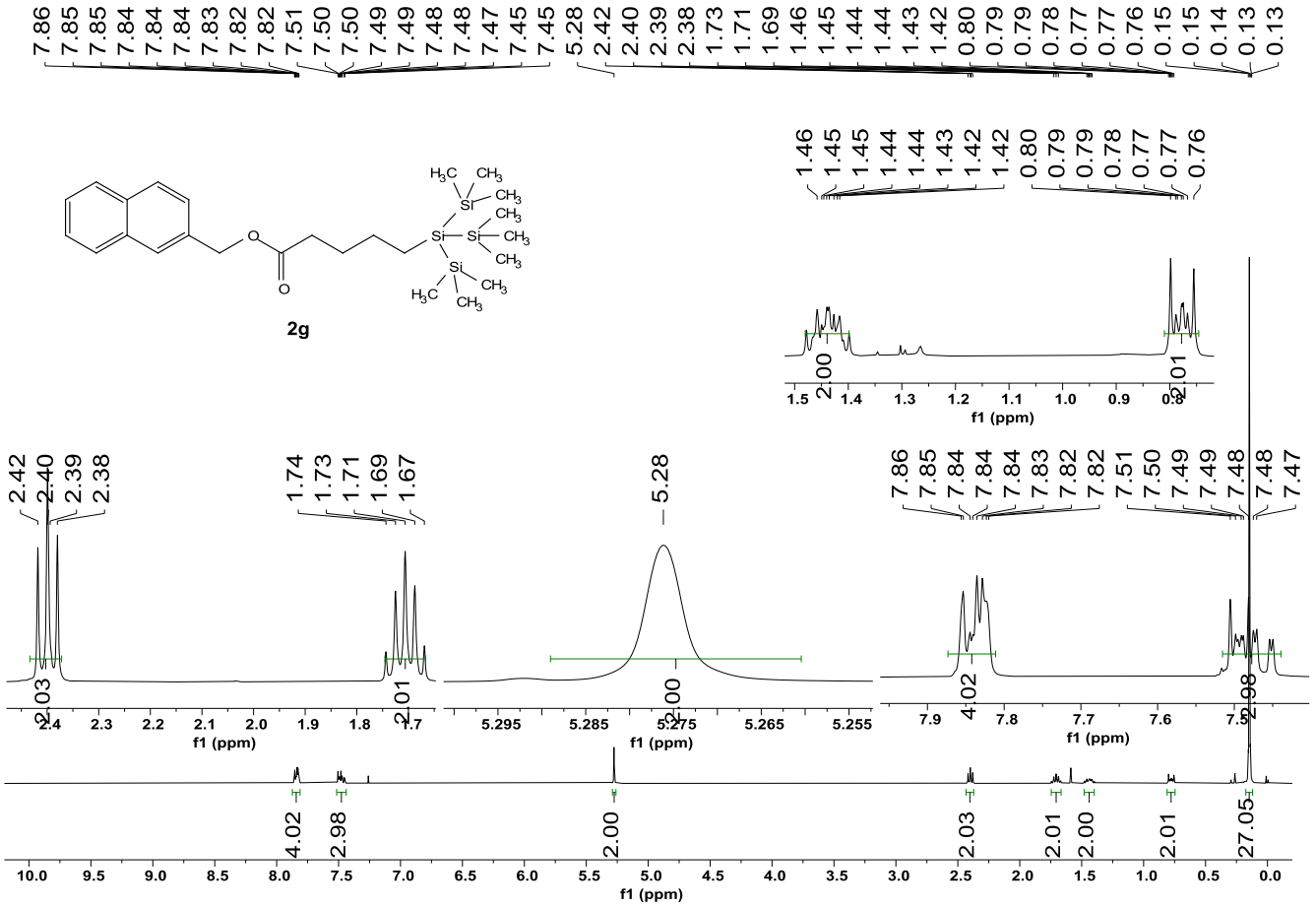
^{1}H NMR spectrum of compound **2f** (400 MHz, $CDCl_3$)



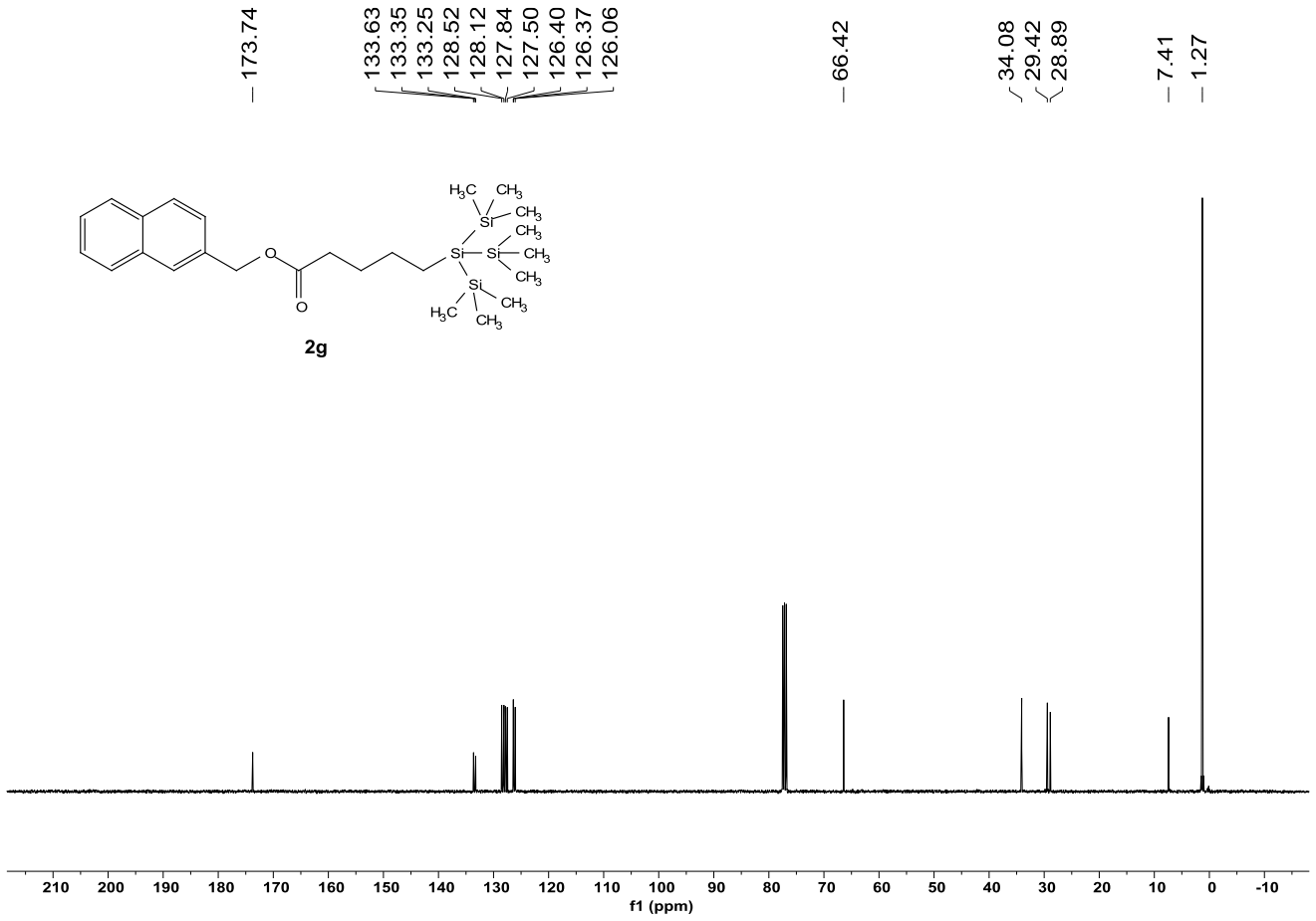
^{13}C NMR spectrum of compound **2f** (101 MHz, $CDCl_3$)



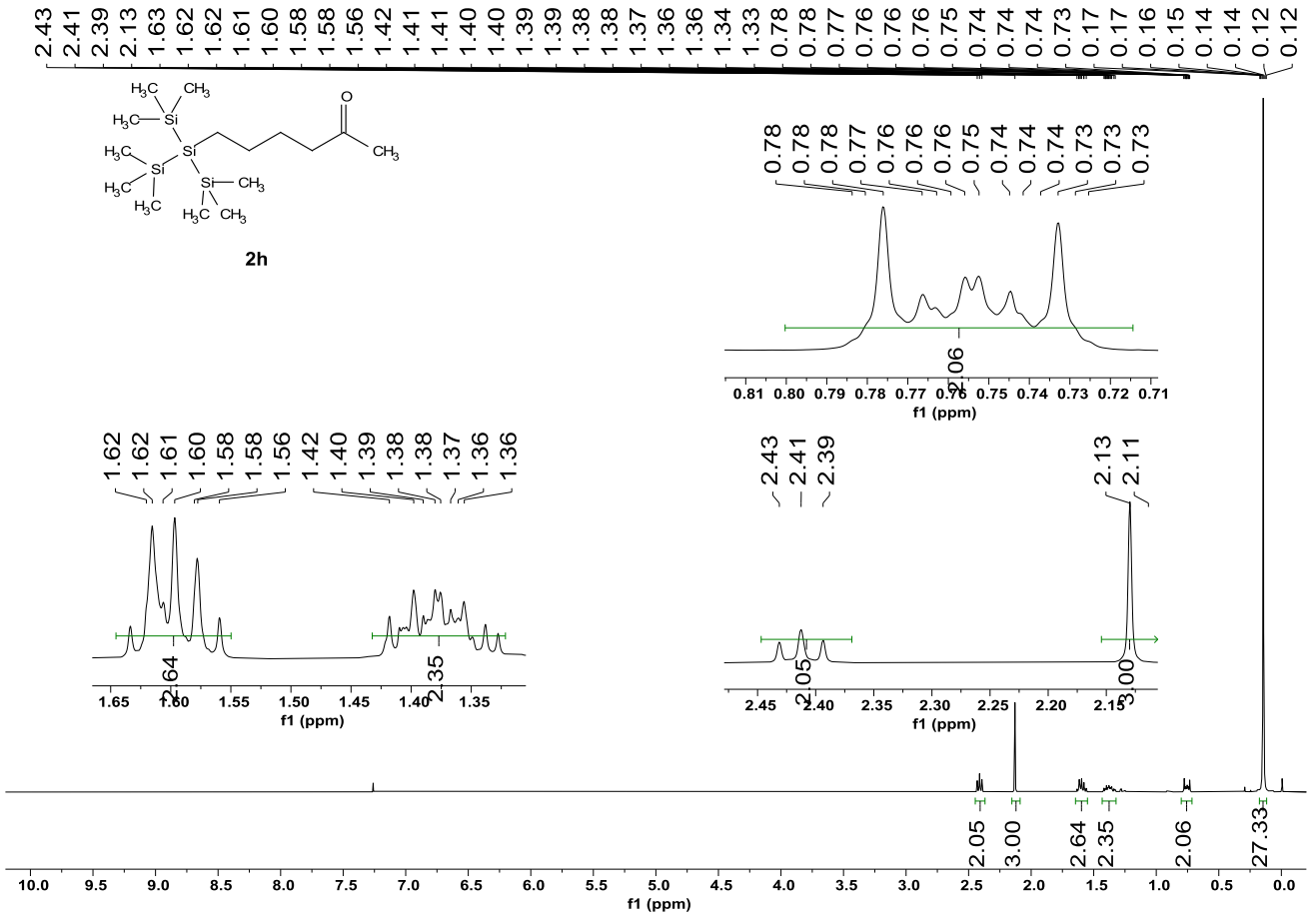
^{1}H NMR spectrum of compound **2g** (400 MHz, $CDCl_3$)



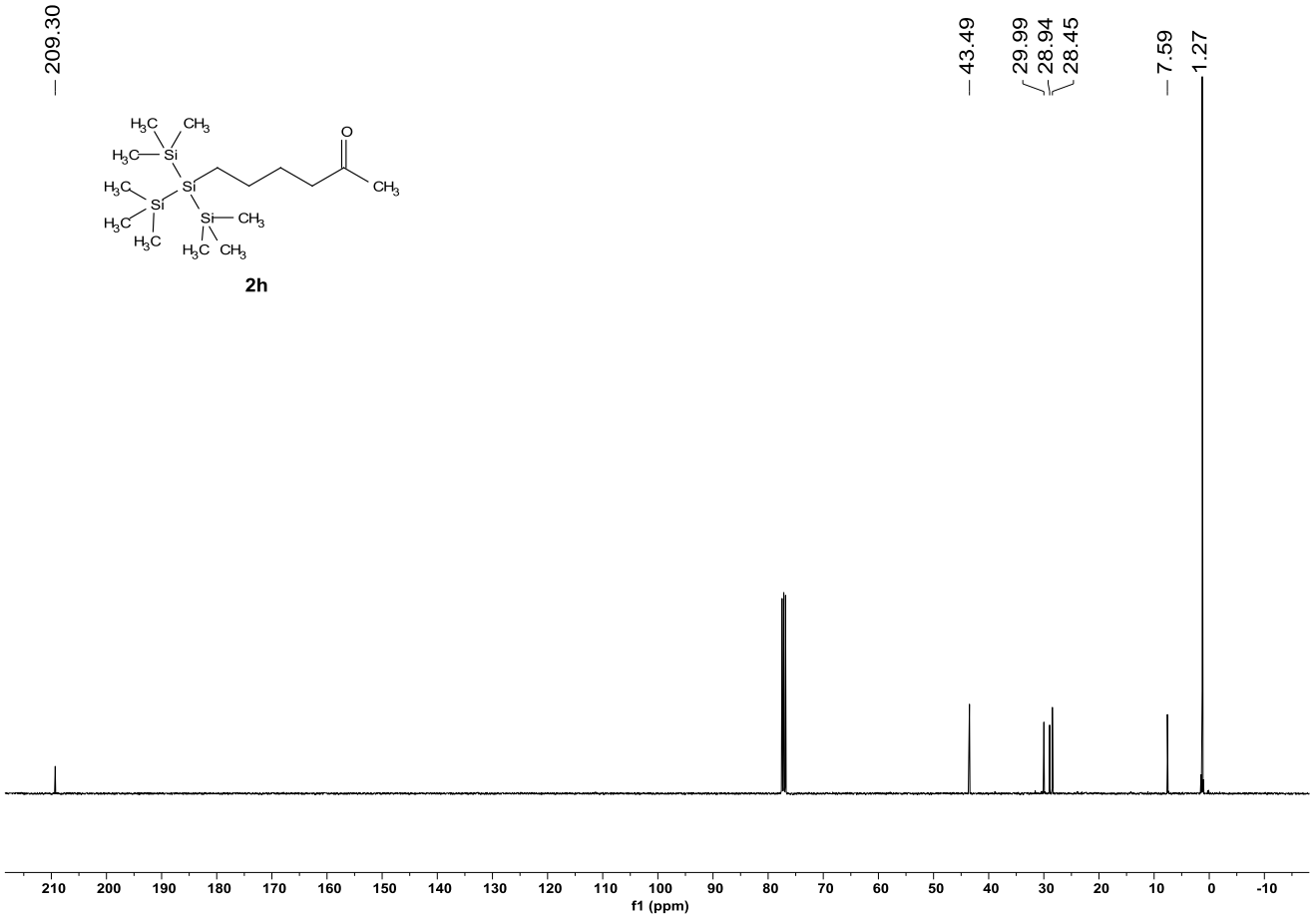
^{13}C NMR spectrum of compound **2g** (101 MHz, $CDCl_3$)



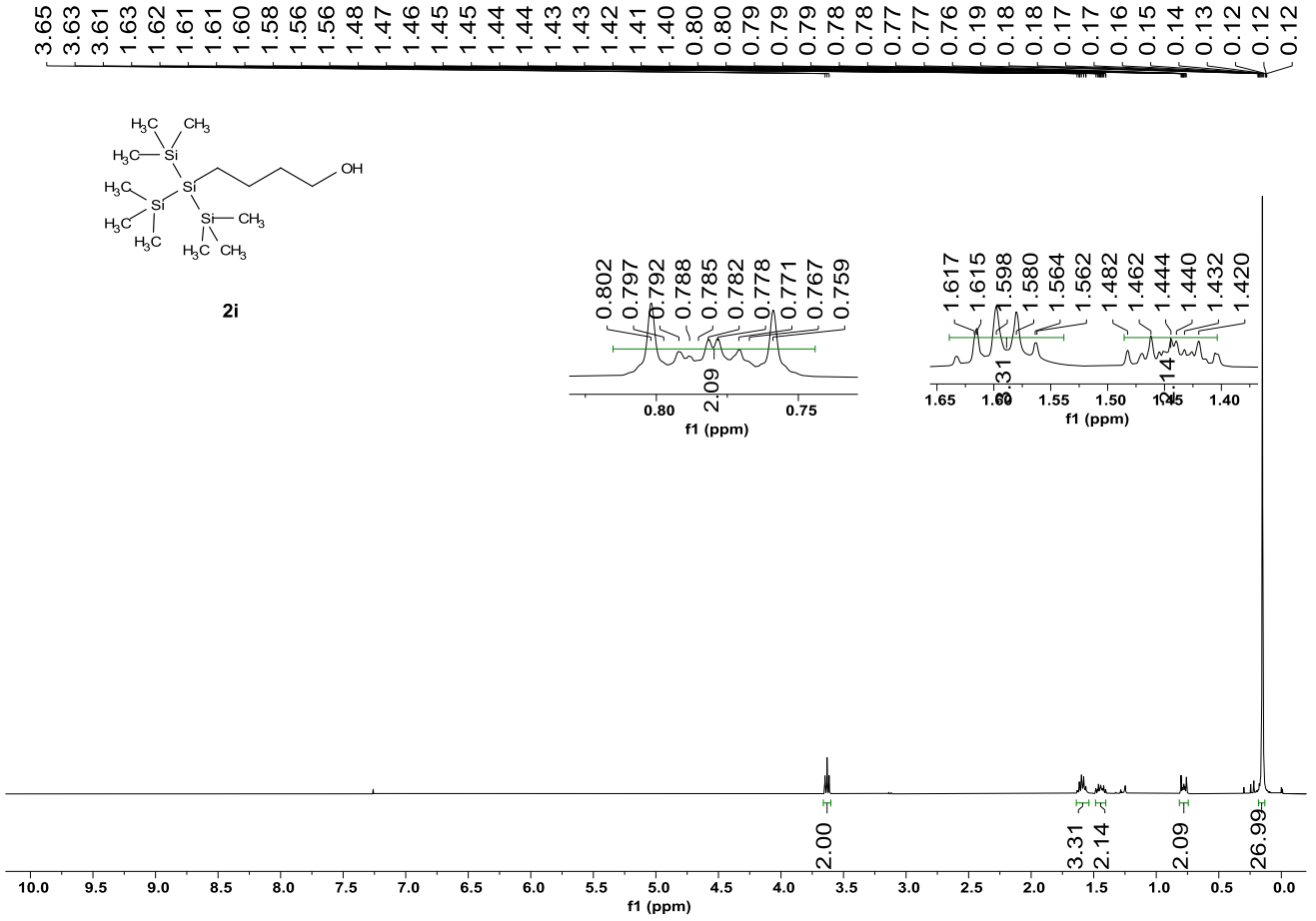
^{1}H NMR spectrum of compound **2h** (400 MHz, $CDCl_3$)



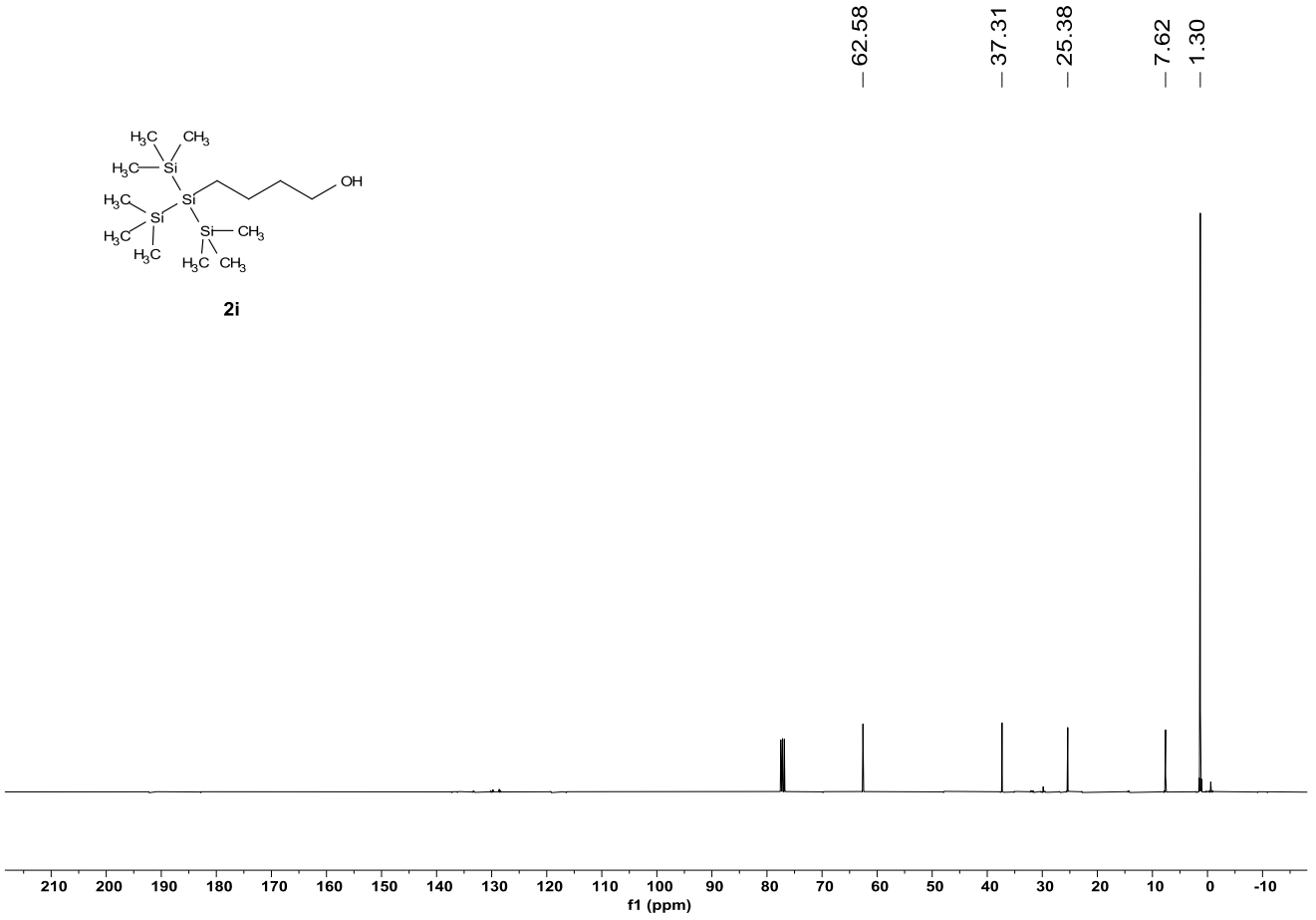
^{13}C NMR spectrum of compound **2h** (101 MHz, $CDCl_3$)



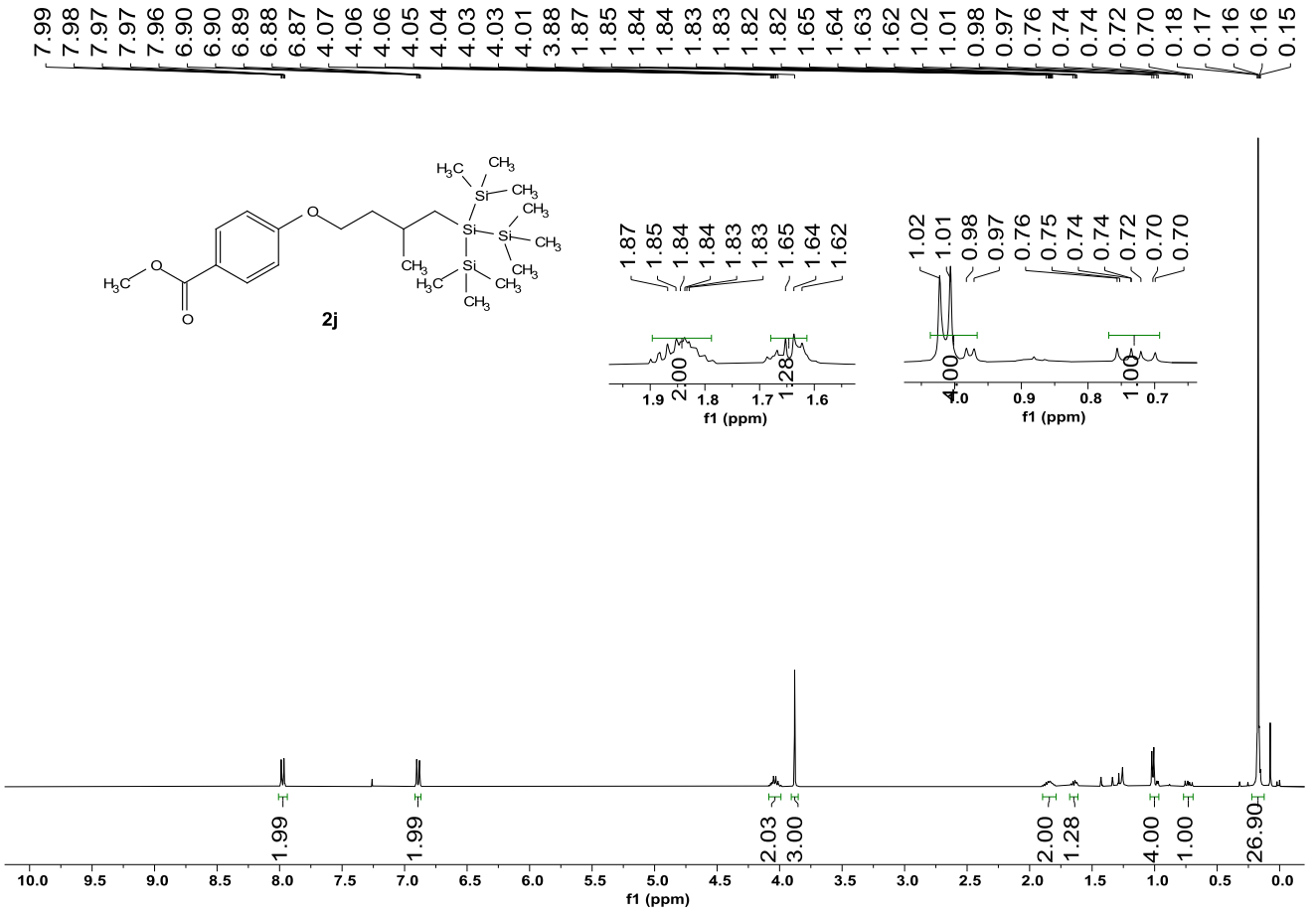
^{1}H NMR spectrum of compound **2i** (400 MHz, $CDCl_3$)



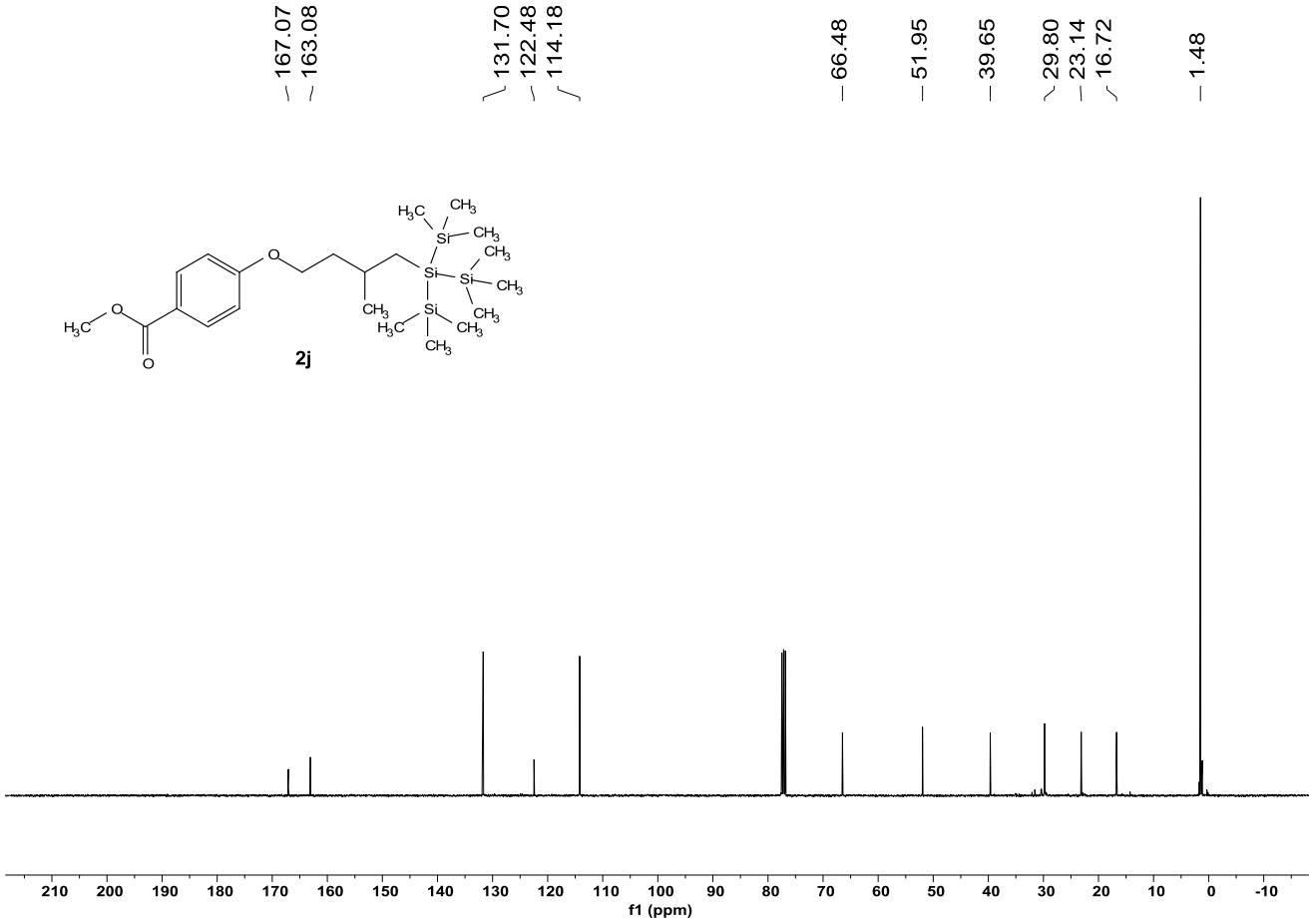
^{13}C NMR spectrum of compound **2i** (101 MHz, $CDCl_3$)



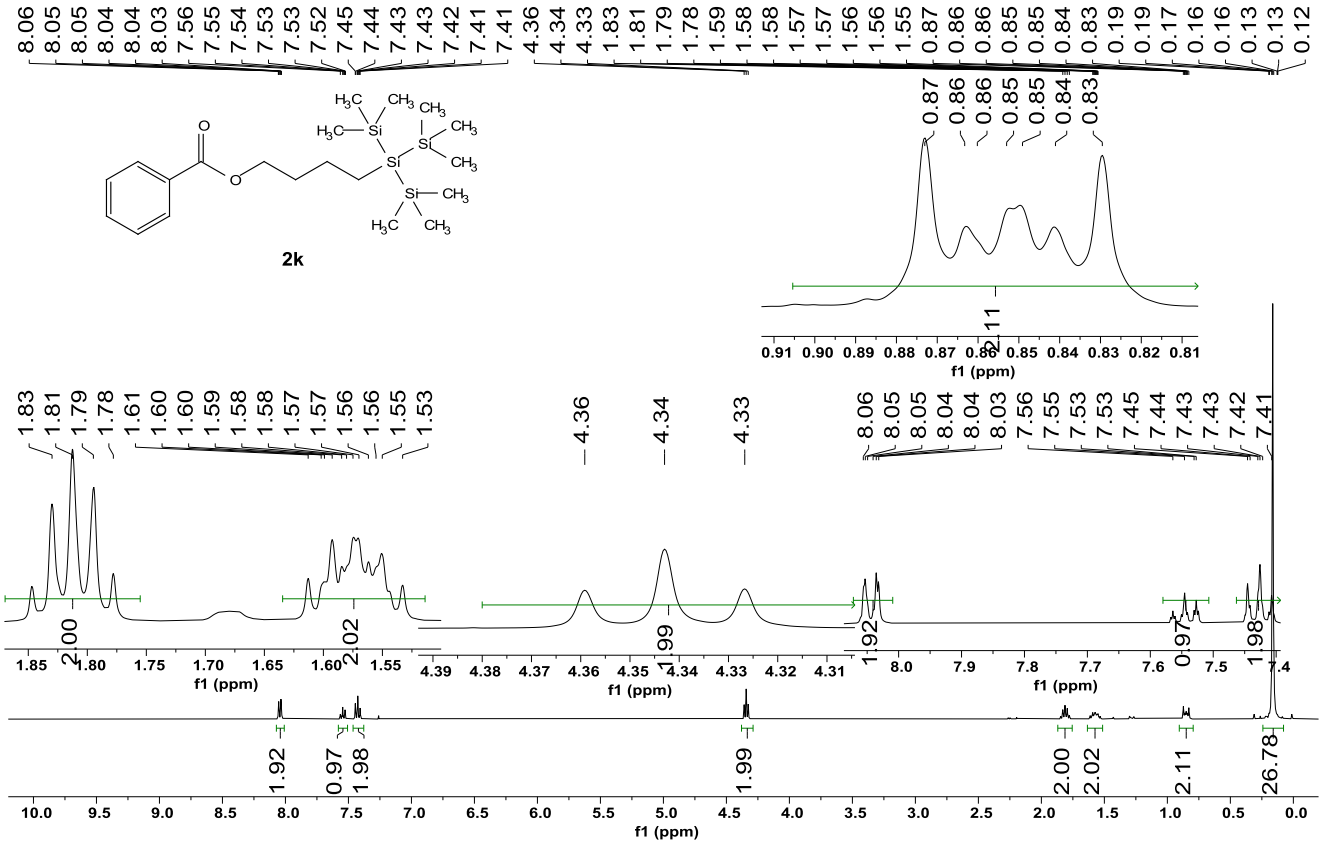
^{1}H NMR spectrum of compound **2j** (400 MHz, $CDCl_3$)



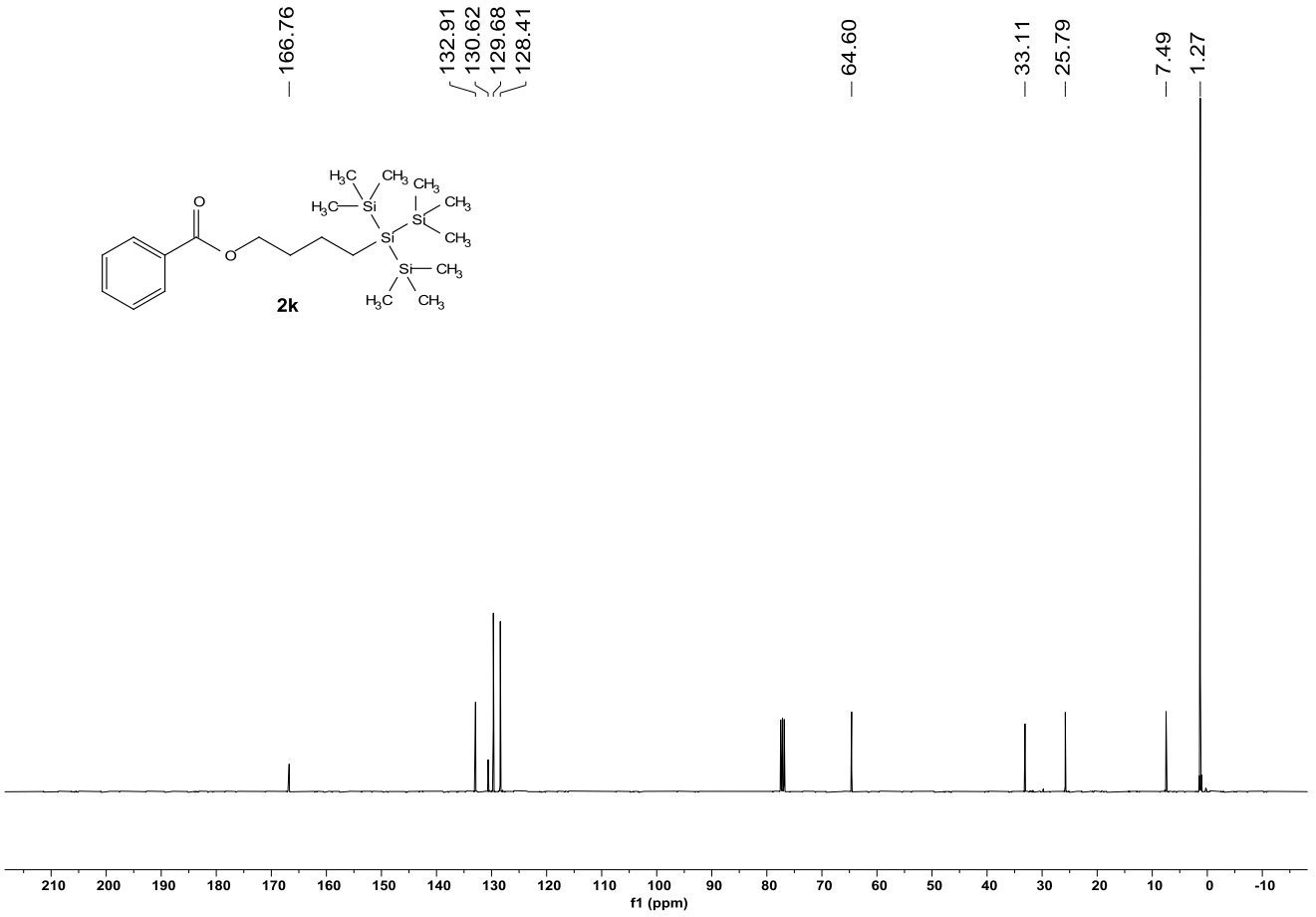
^{13}C NMR spectrum of compound **2j** (101 MHz, $CDCl_3$)



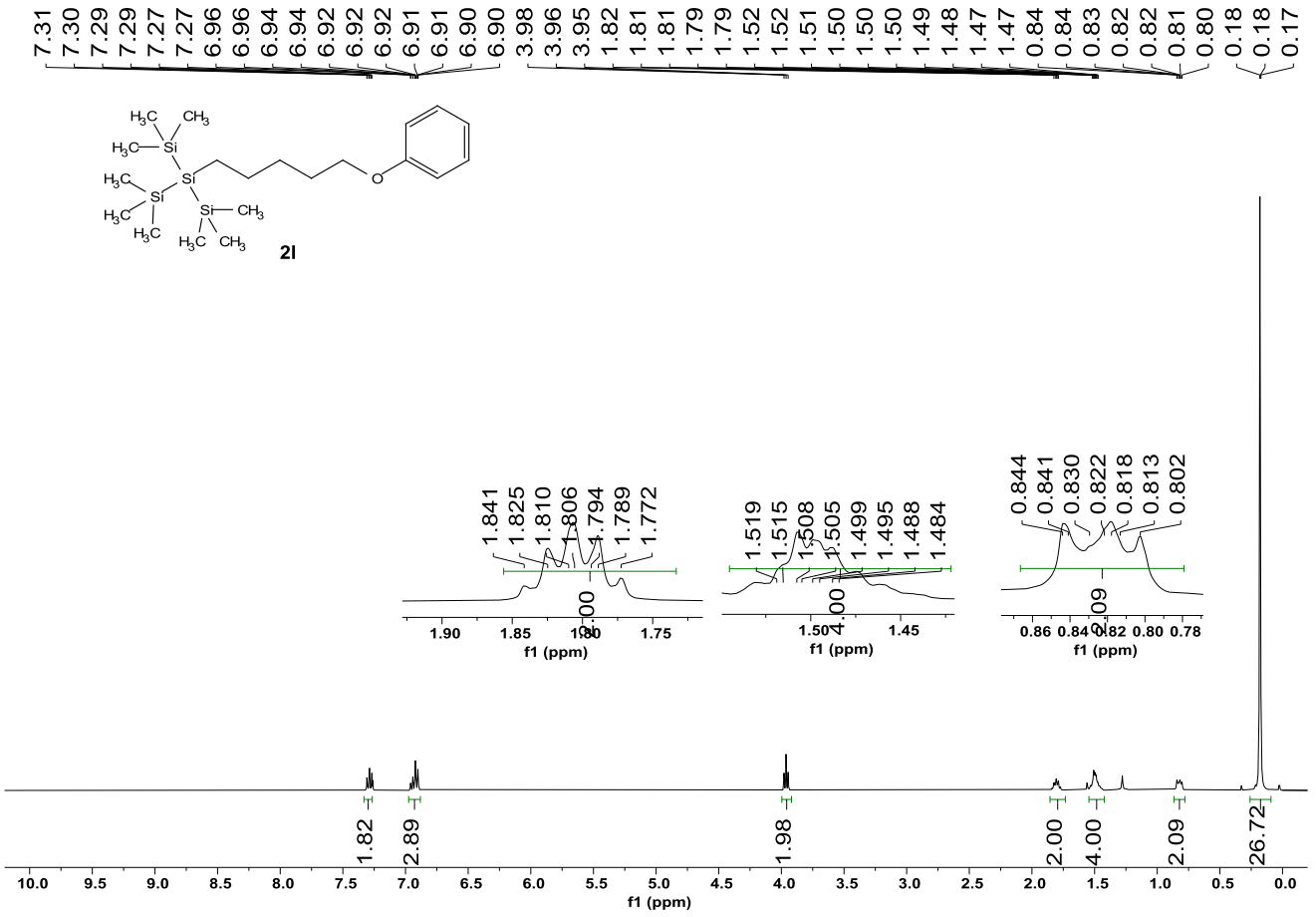
^{1}H NMR spectrum of compound **2k** (400 MHz, $CDCl_3$)



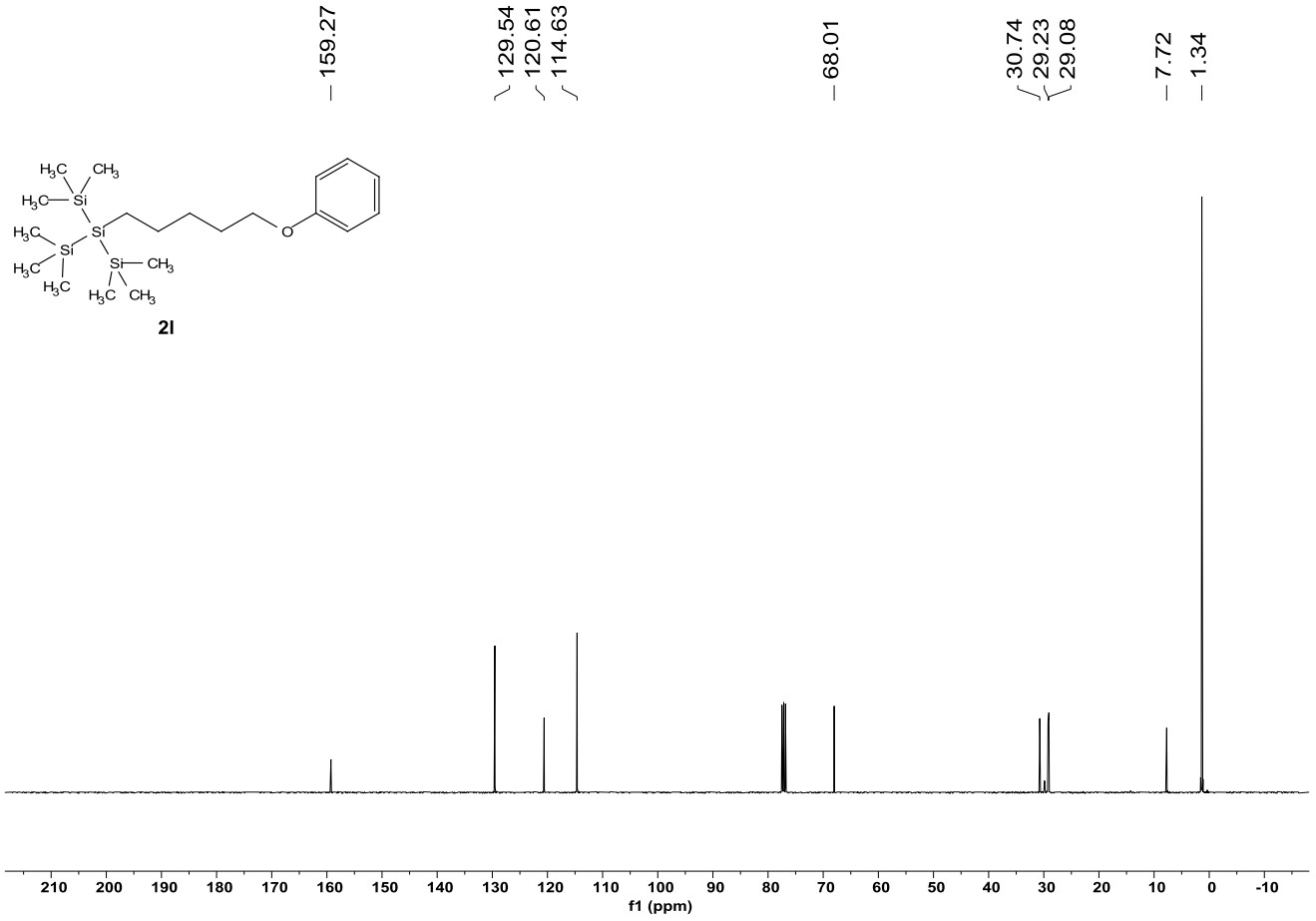
^{13}C NMR spectrum of compound **2k** (101 MHz, $CDCl_3$)



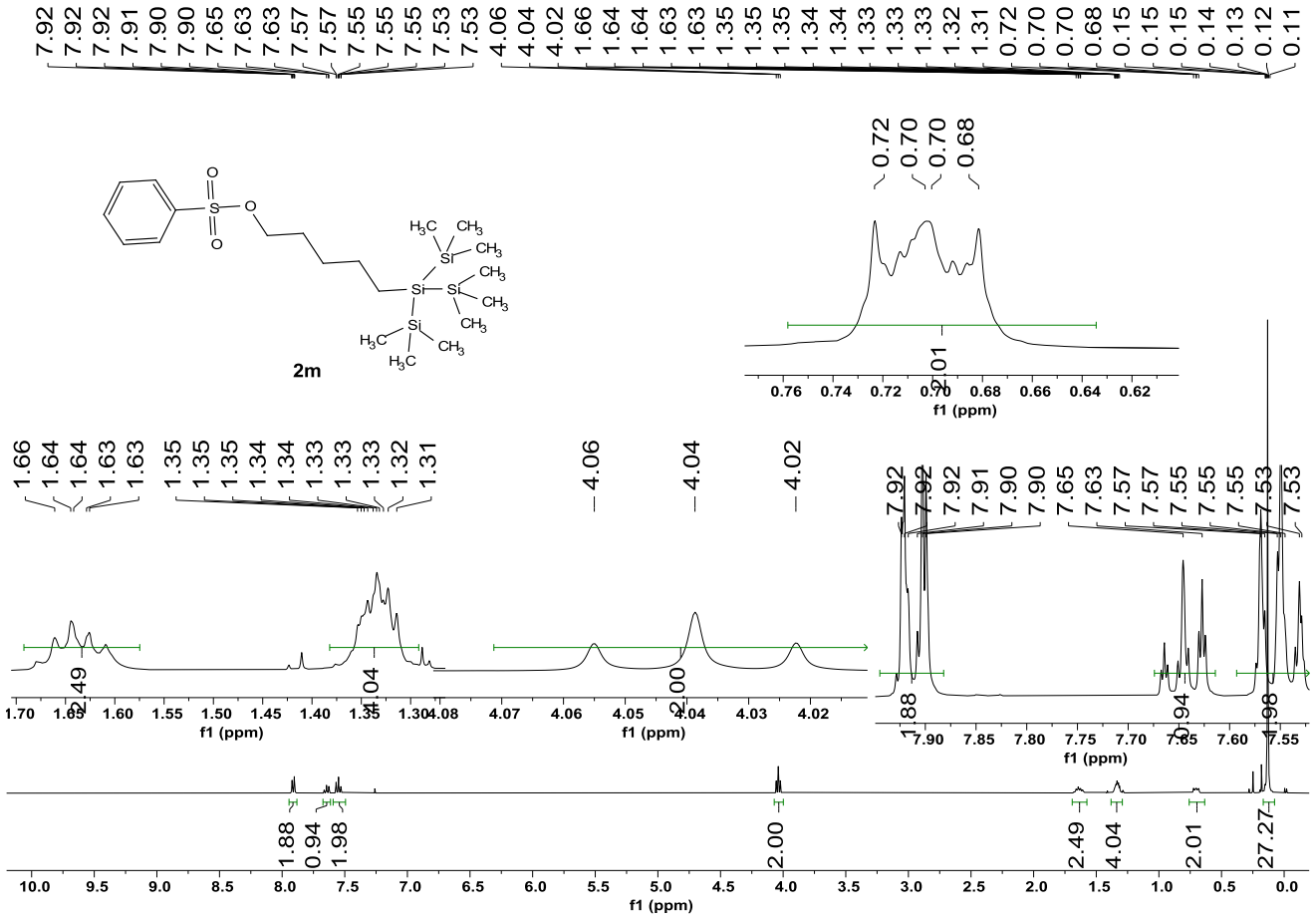
^{1}H NMR spectrum of compound **2l** (400 MHz, $CDCl_3$)



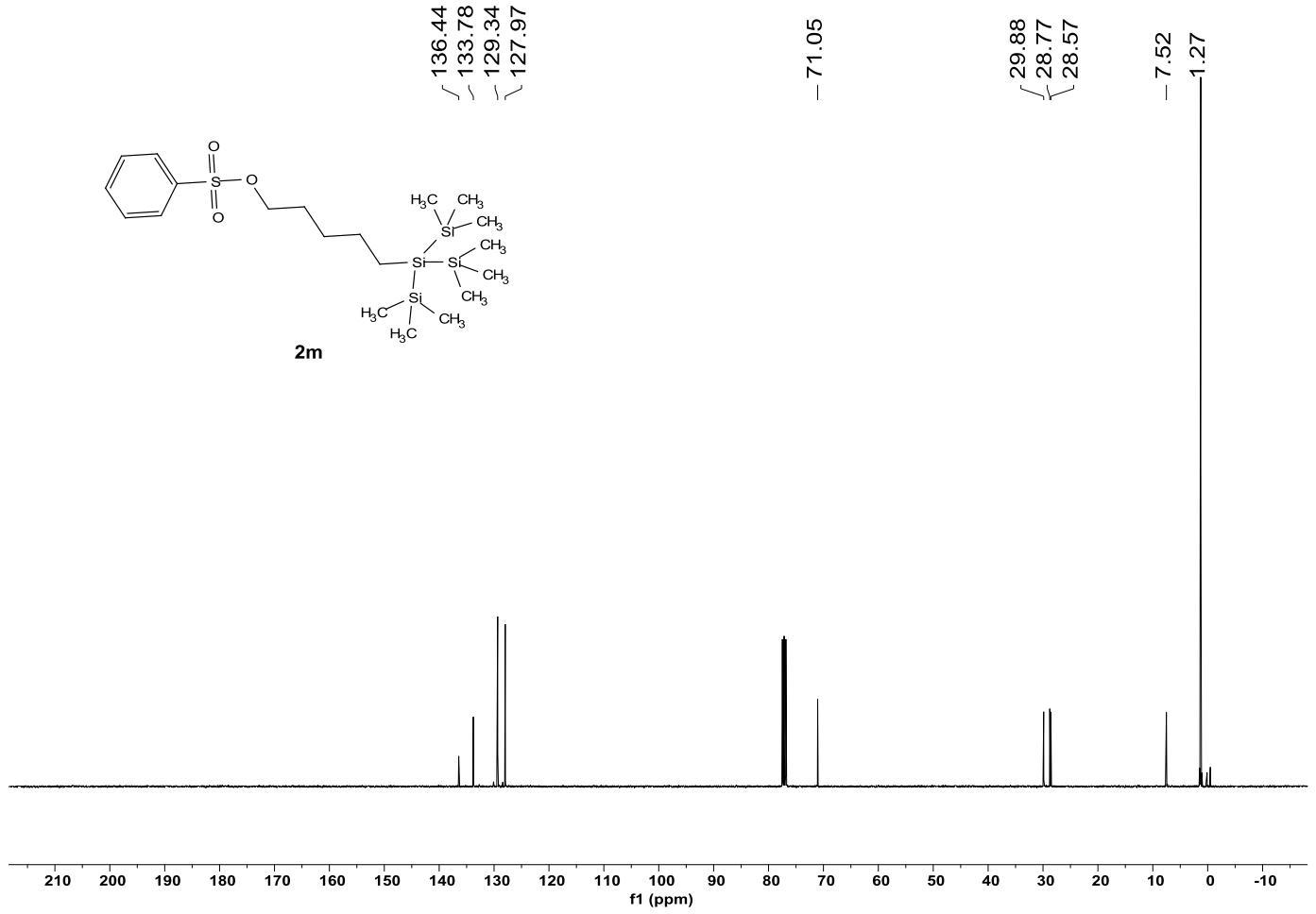
^{13}C NMR spectrum of compound **2l** (101 MHz, $CDCl_3$)



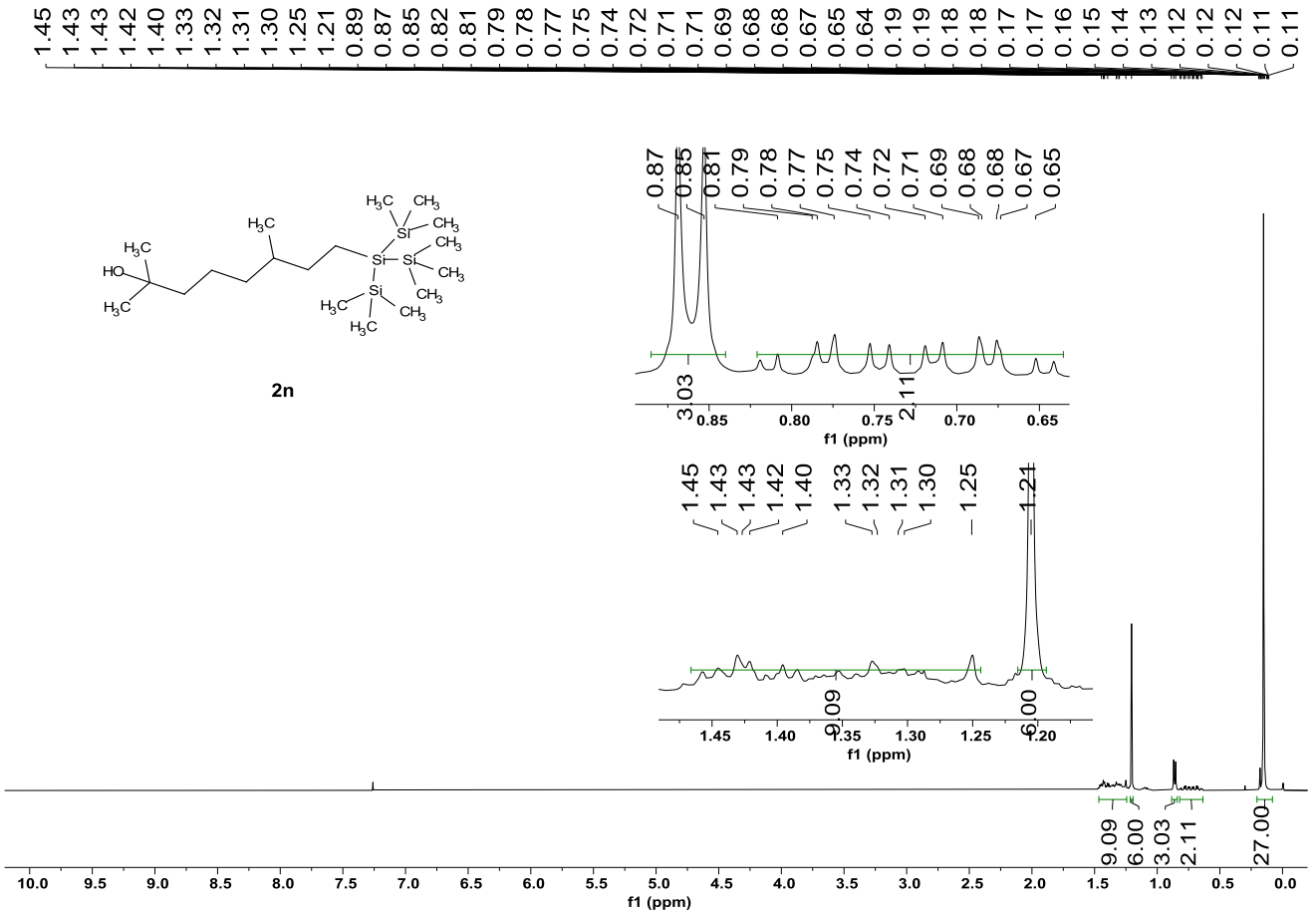
^{1}H NMR spectrum of compound **2m** (400 MHz, $CDCl_3$)



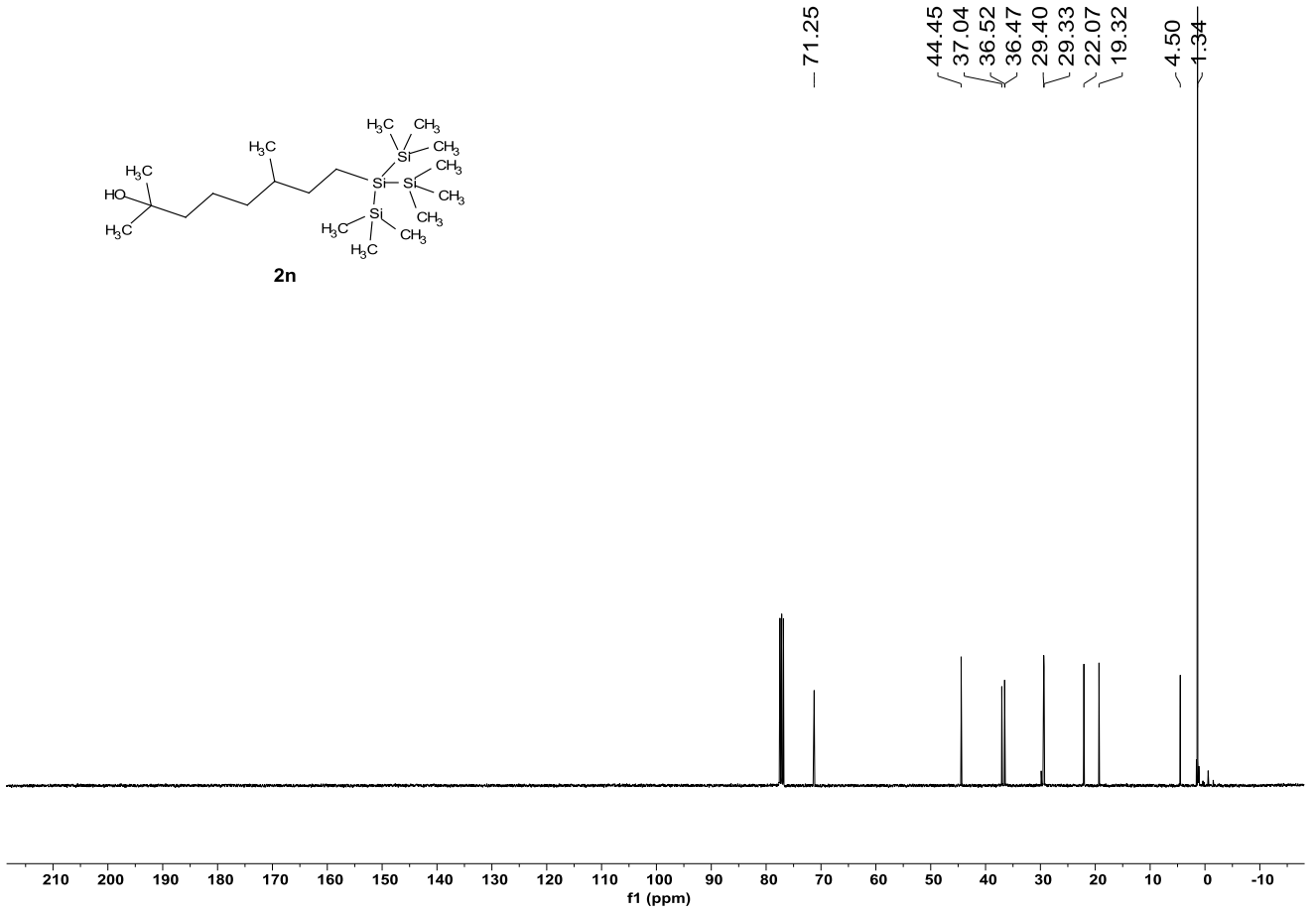
^{13}C NMR spectrum of compound **2m** (101 MHz, $CDCl_3$)



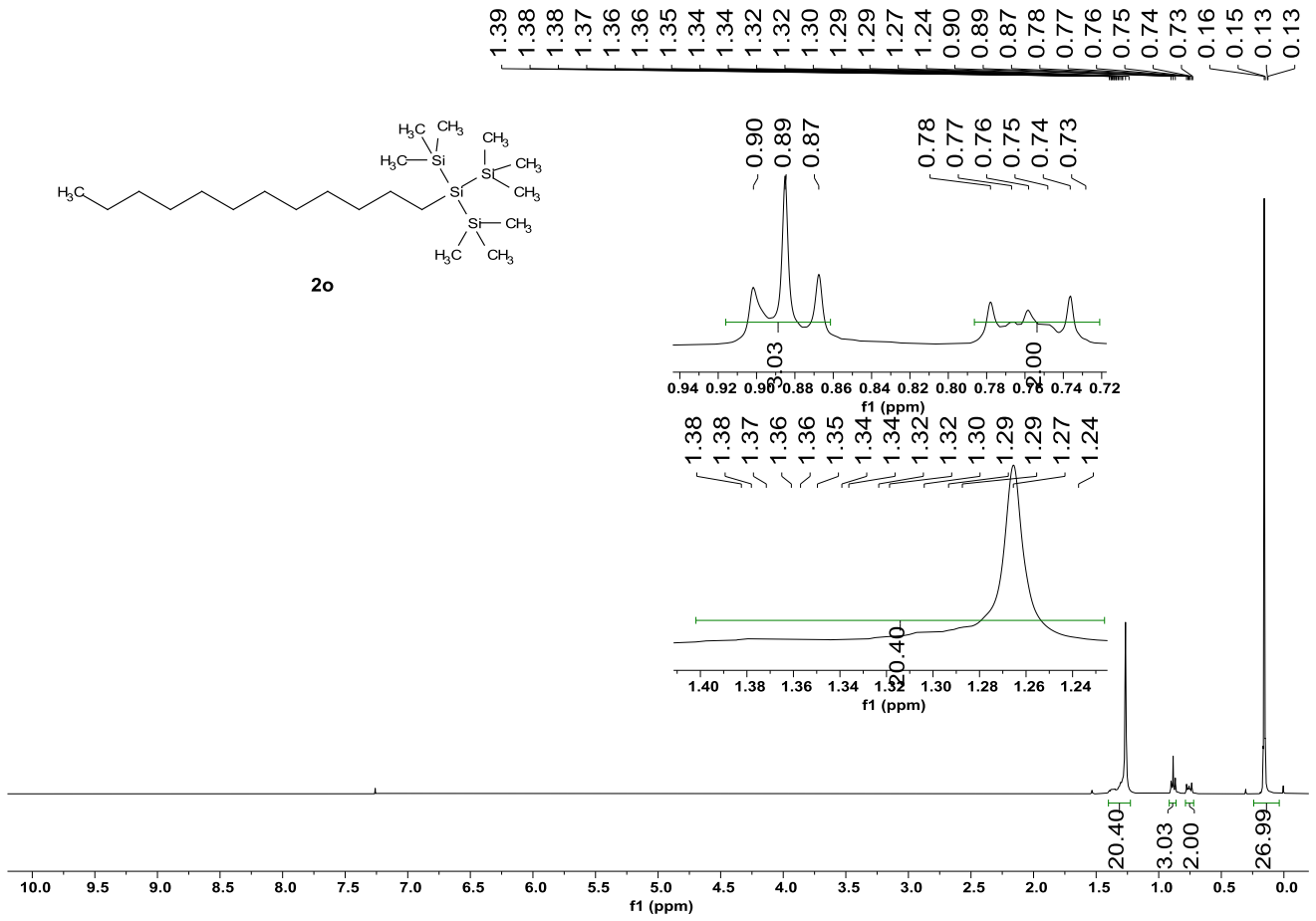
^{1}H NMR spectrum of compound **2n** (400 MHz, $CDCl_3$)



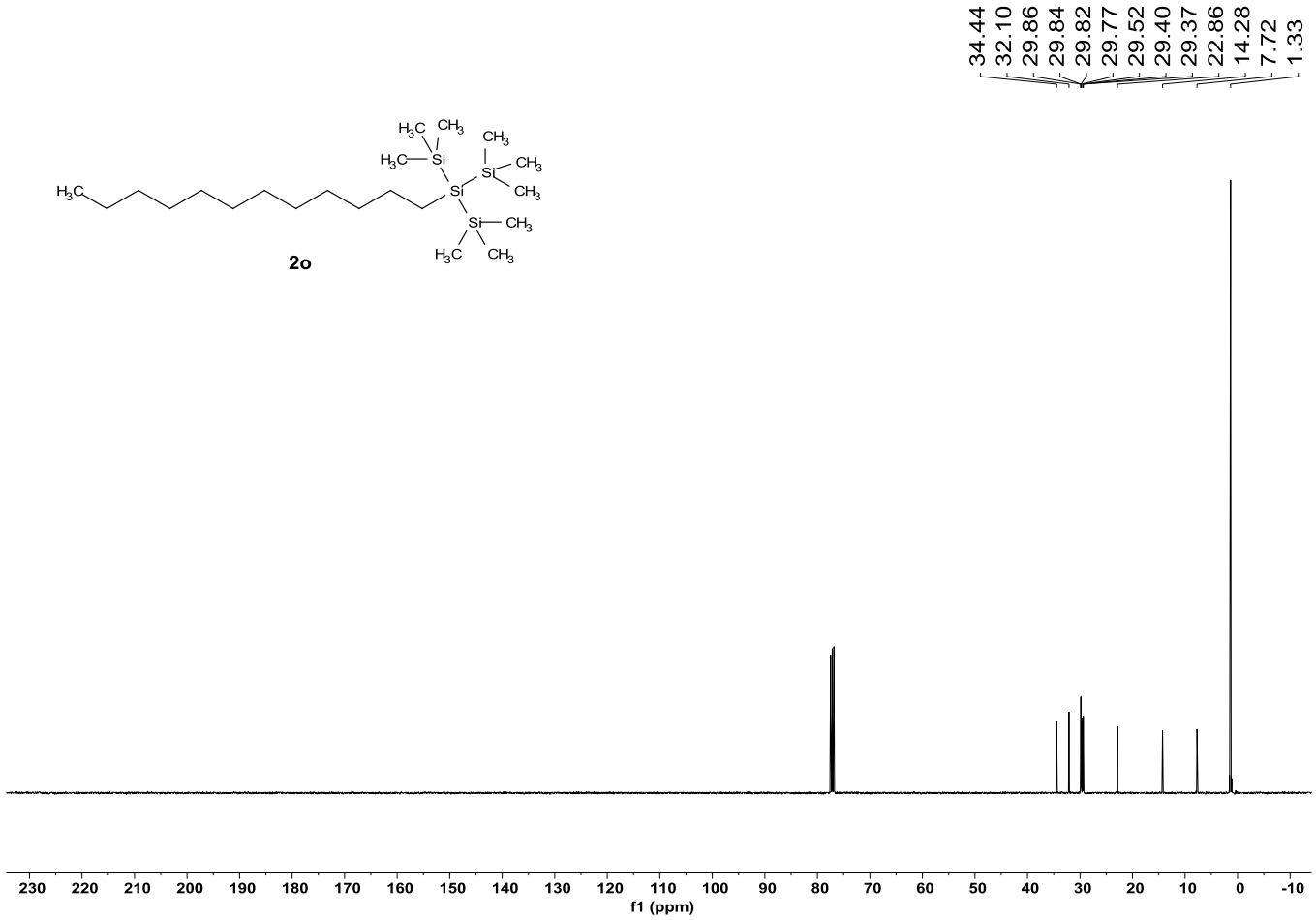
^{13}C NMR spectrum of compound **2n** (101 MHz, $CDCl_3$)



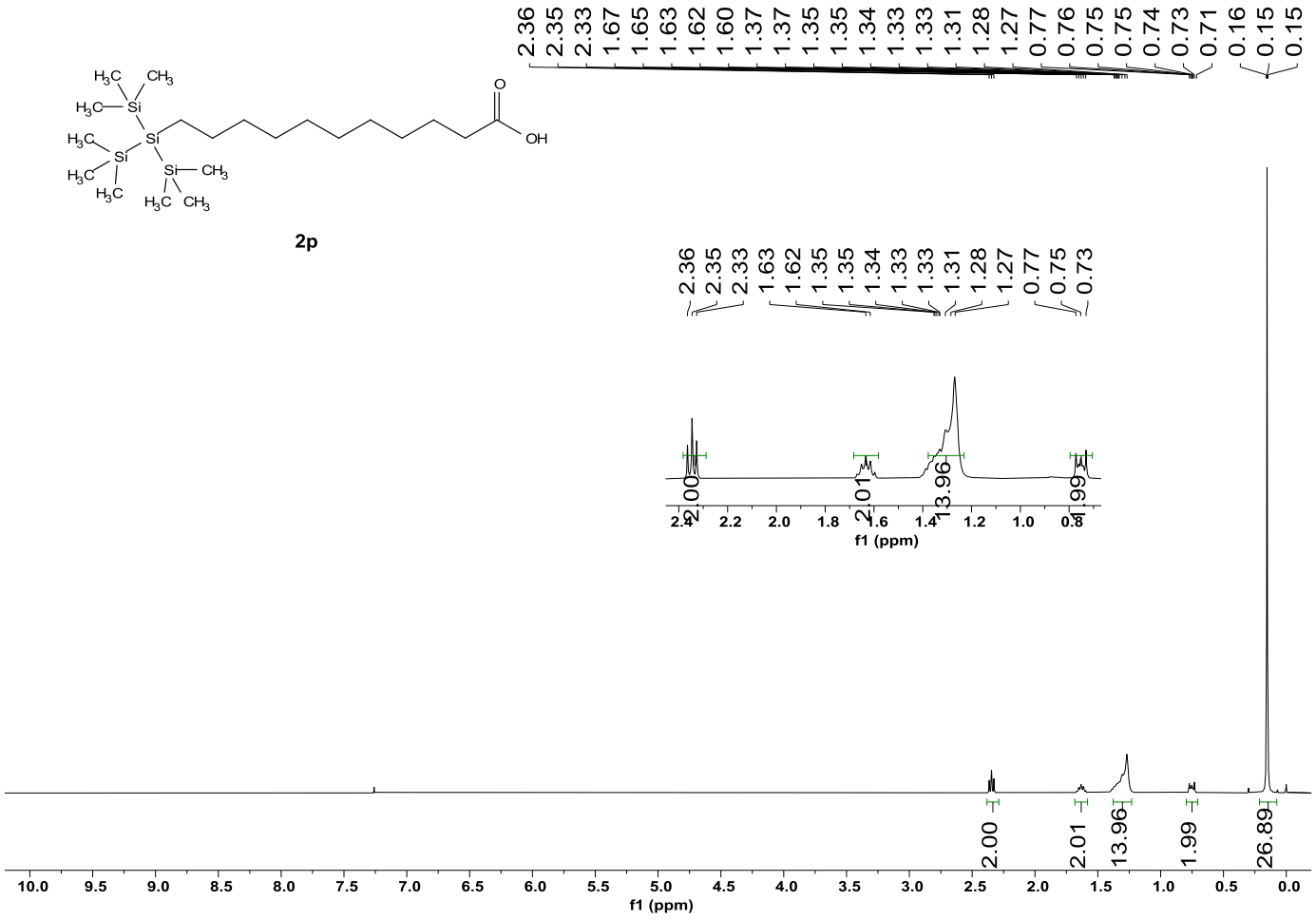
^{1}H NMR spectrum of compound **2o** (400 MHz, $CDCl_3$)



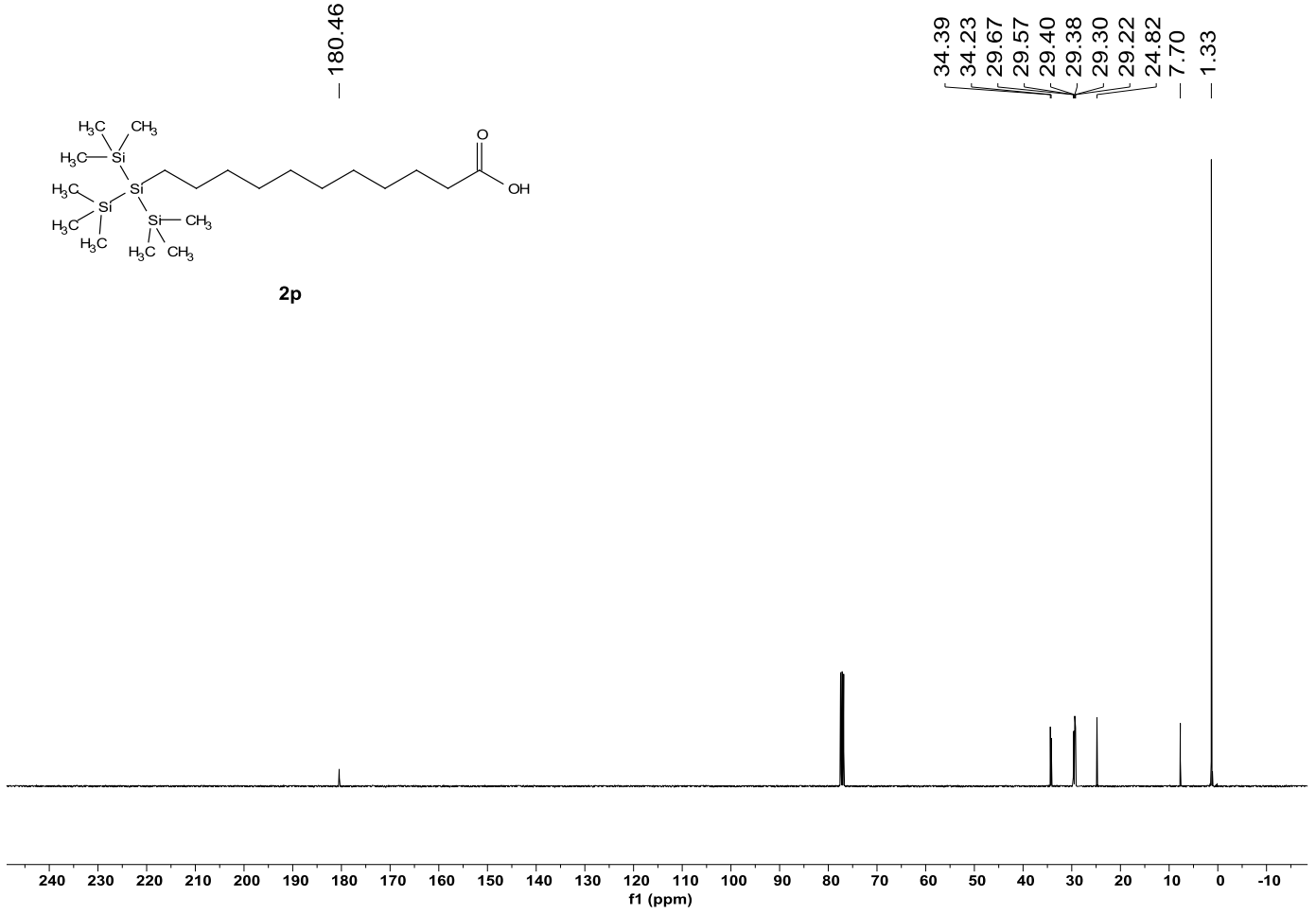
^{13}C NMR spectrum of compound **2o** (101 MHz, $CDCl_3$)



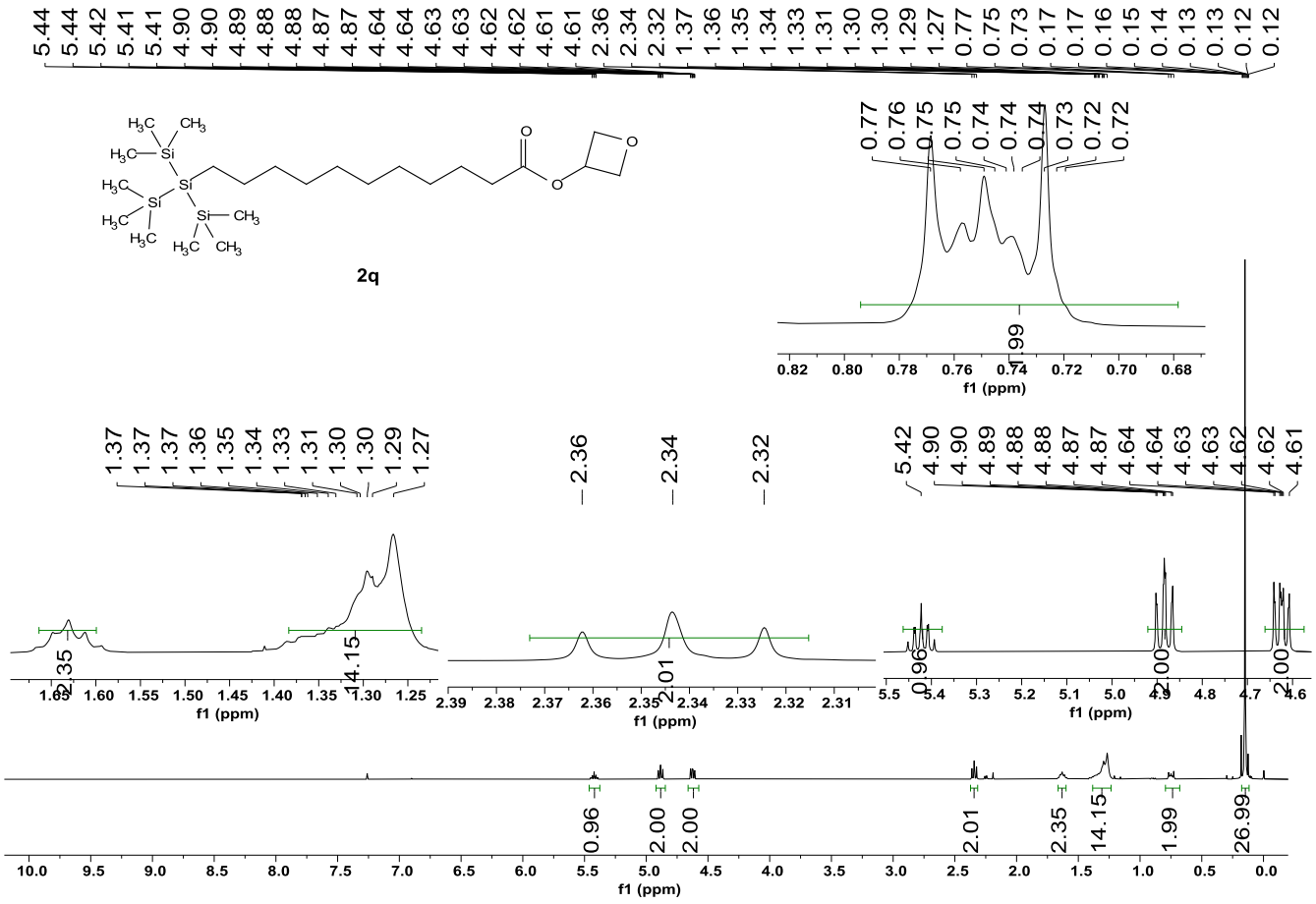
^{1}H NMR spectrum of compound **2p** (400 MHz, $CDCl_3$)



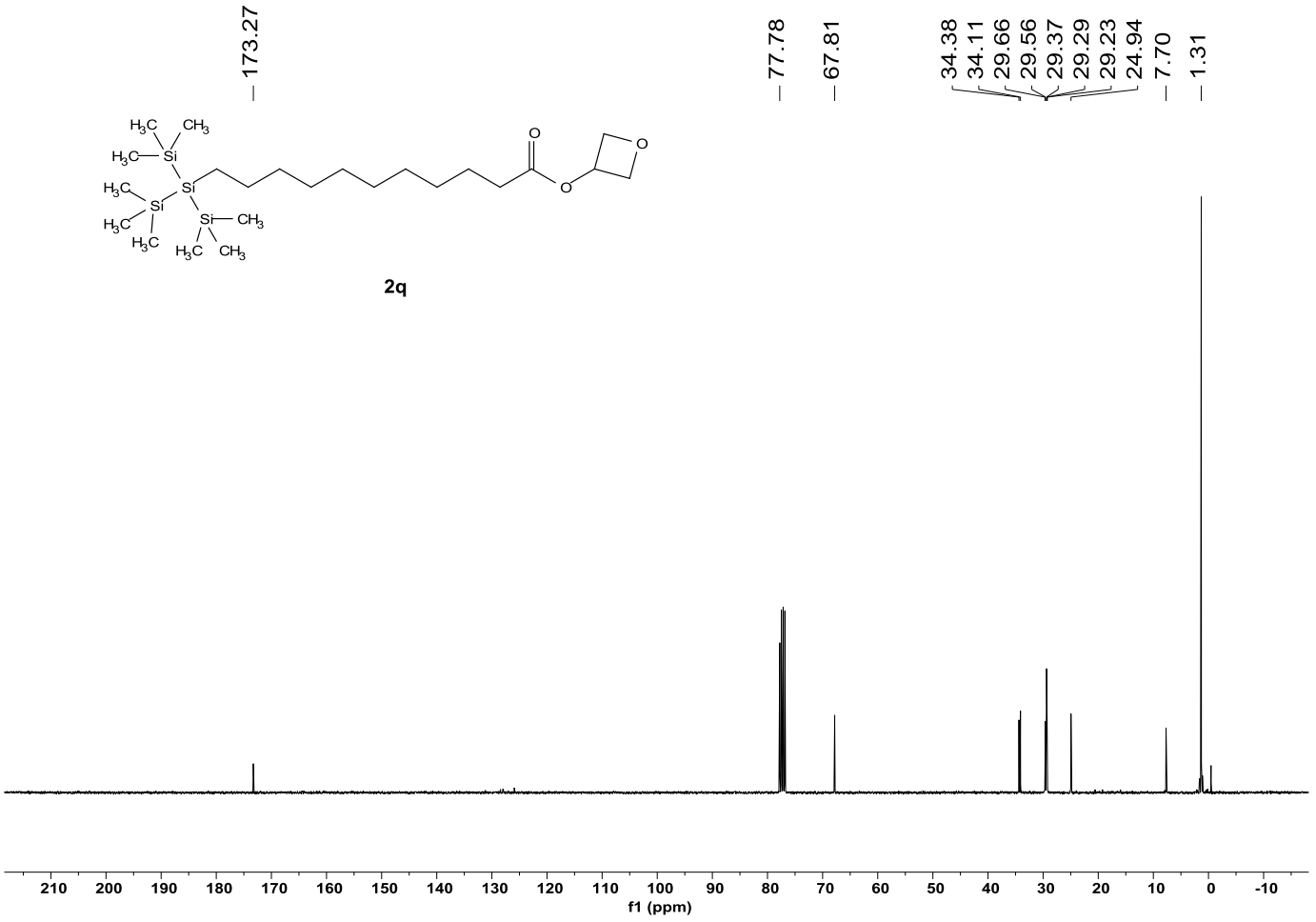
^{13}C NMR spectrum of compound **2p** (101 MHz, $CDCl_3$)



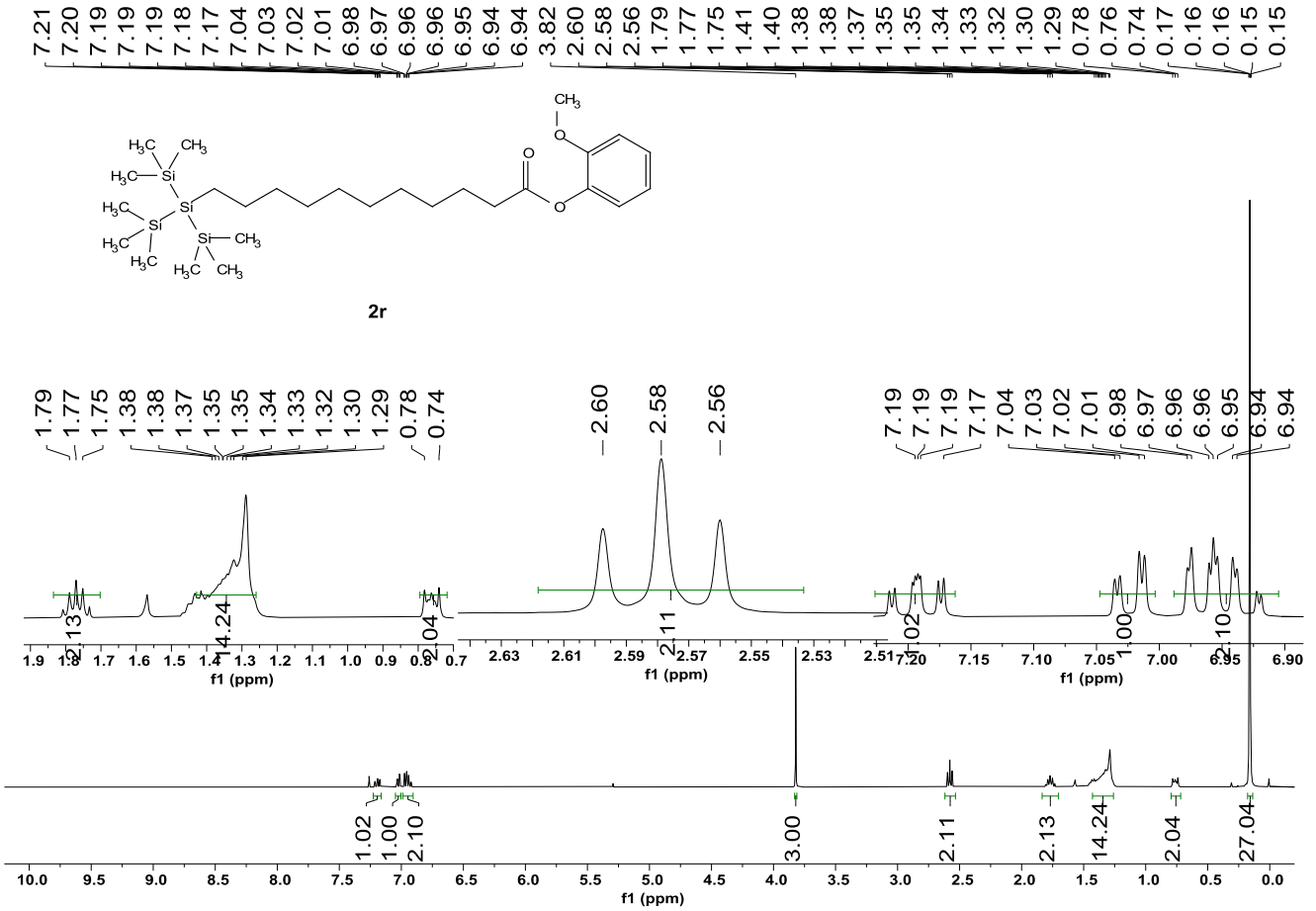
^{1}H NMR spectrum of compound **2q** (400 MHz, $CDCl_3$)



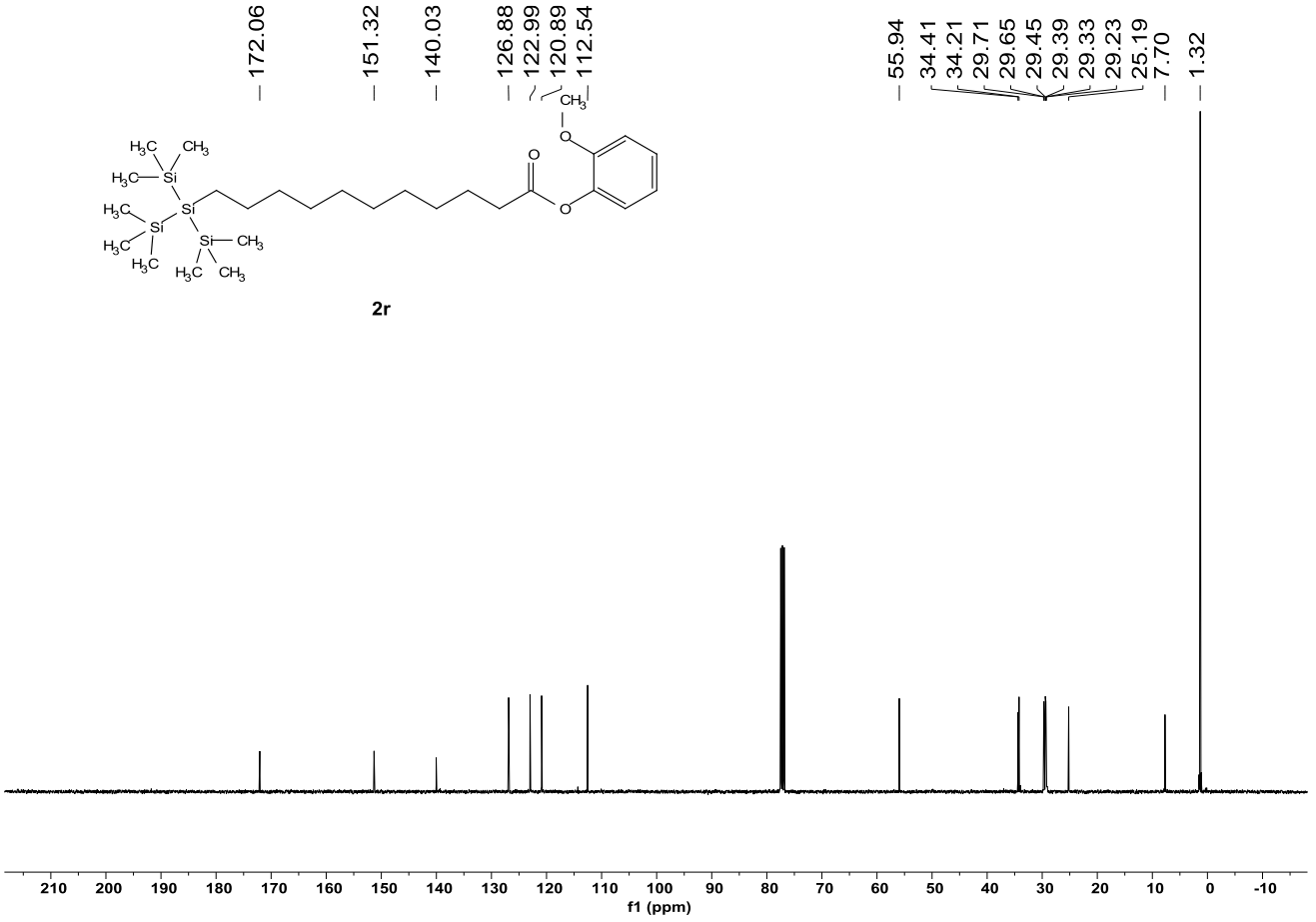
^{13}C NMR spectrum of compound **2q** (101 MHz, $CDCl_3$)



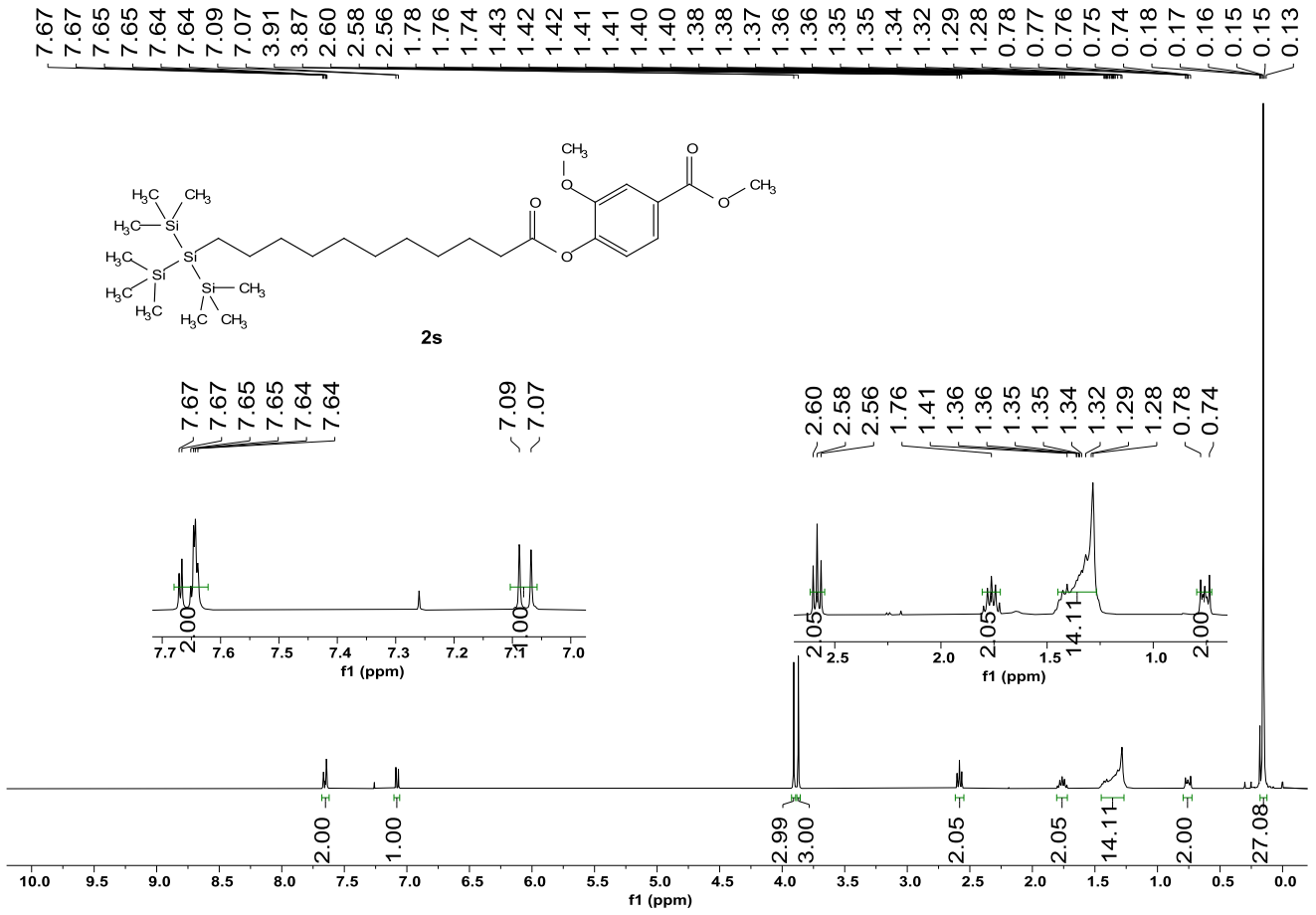
^{1}H NMR spectrum of compound **2r** (400 MHz, $CDCl_3$)



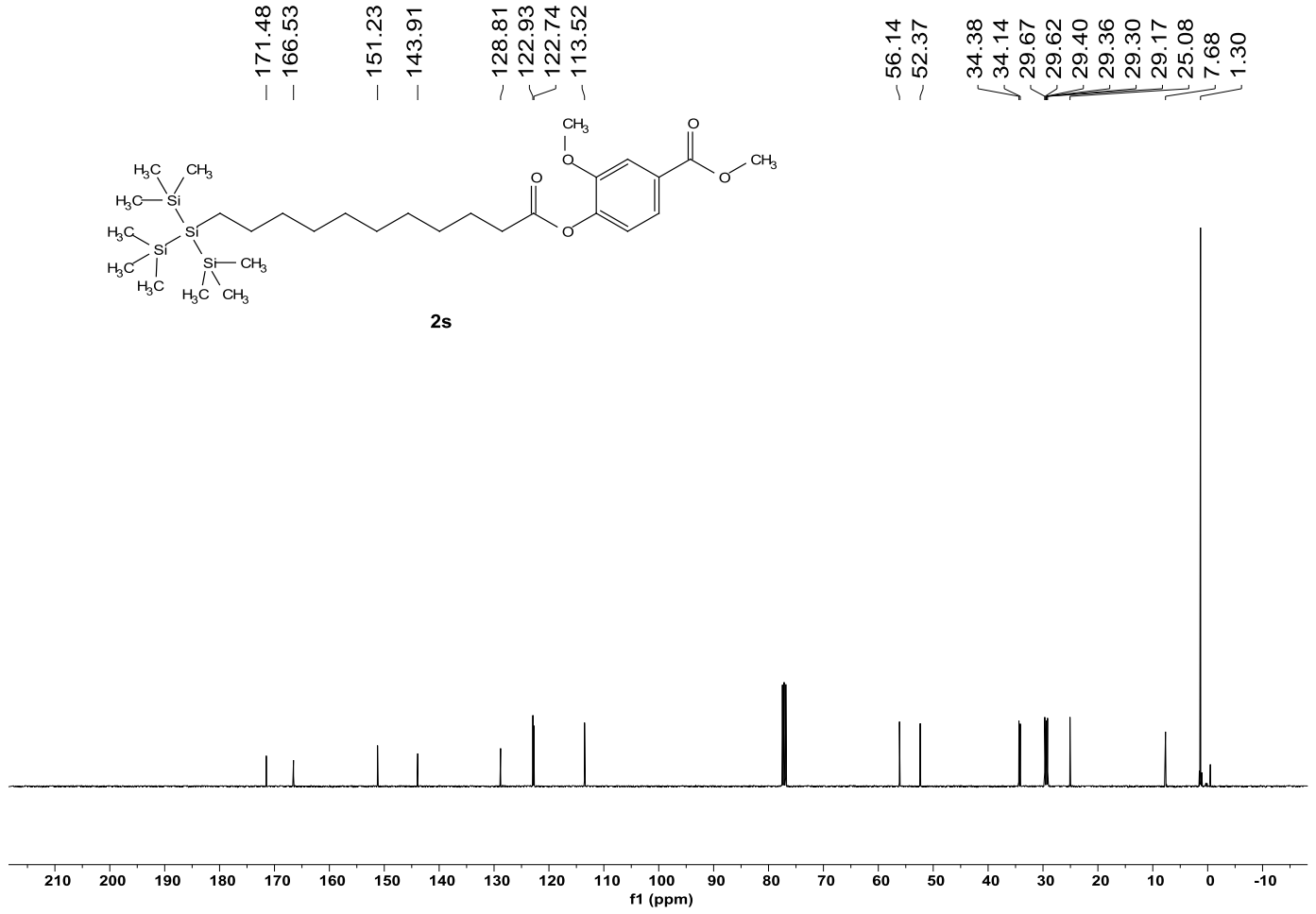
^{13}C NMR spectrum of compound **2r** (101 MHz, $CDCl_3$)



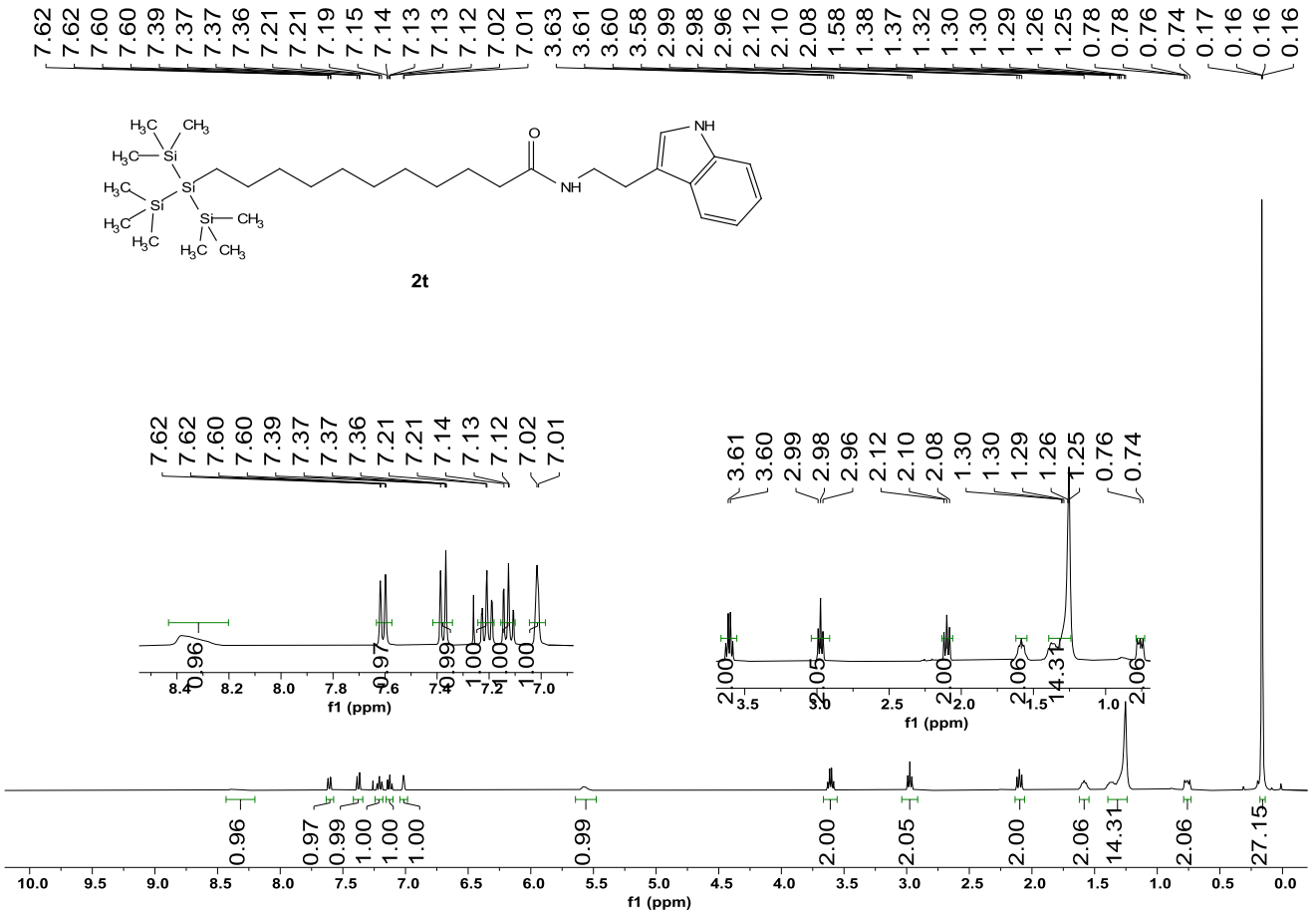
^{1}H NMR spectrum of compound **2s** (400 MHz, $CDCl_3$)



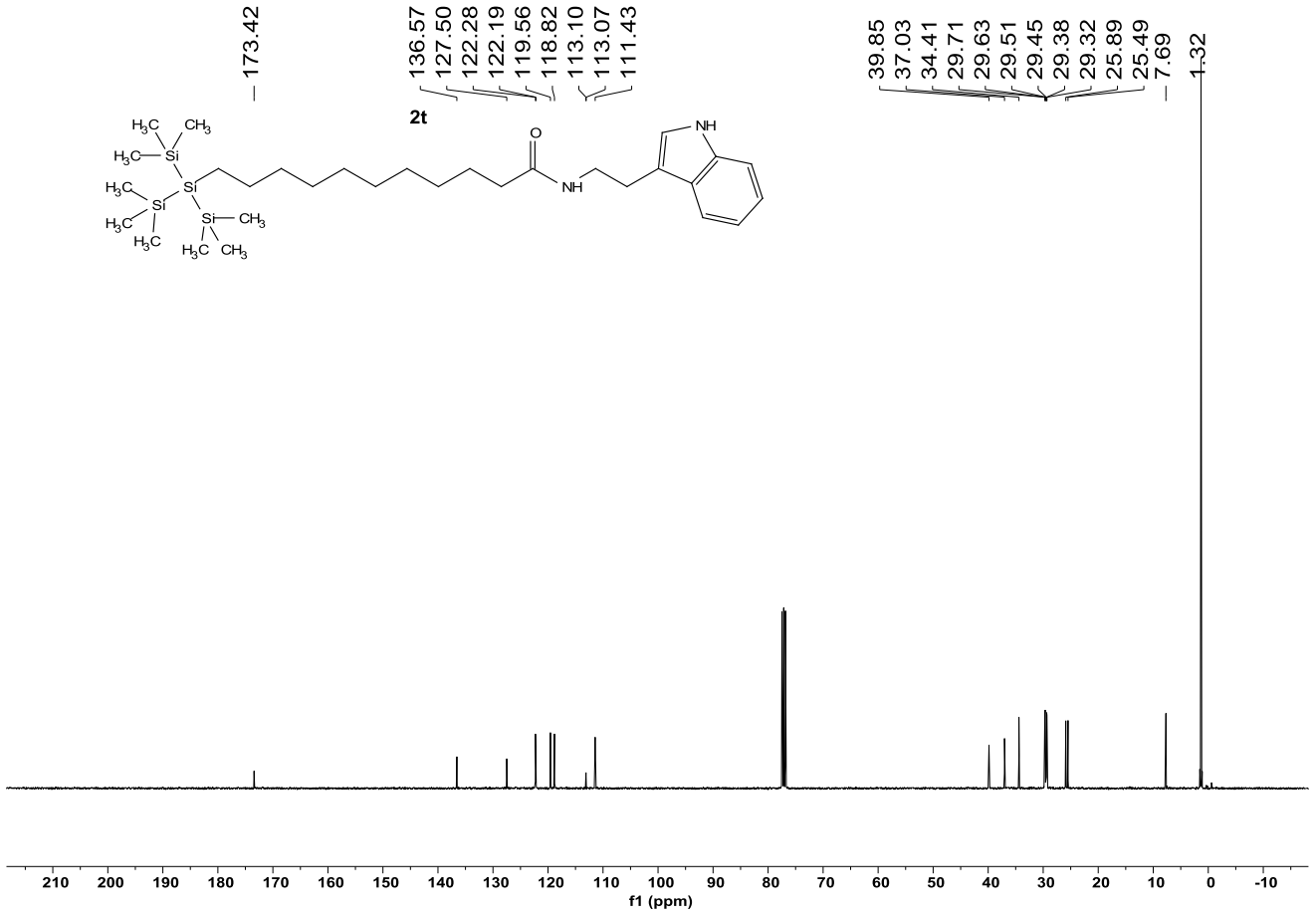
^{13}C NMR spectrum of compound **2s** (101 MHz, $CDCl_3$)



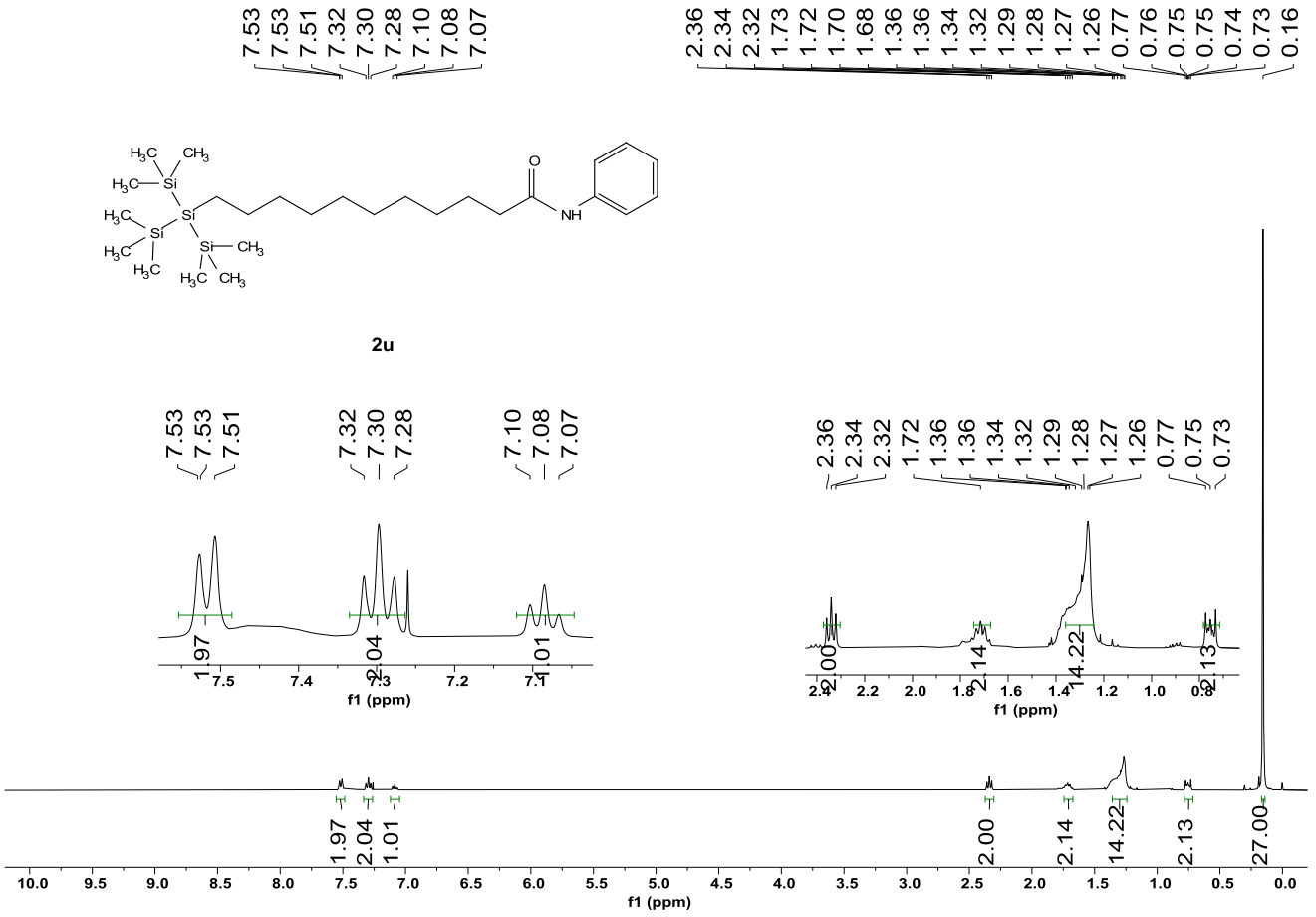
^{1}H NMR spectrum of compound **2t** (400 MHz, $CDCl_3$)



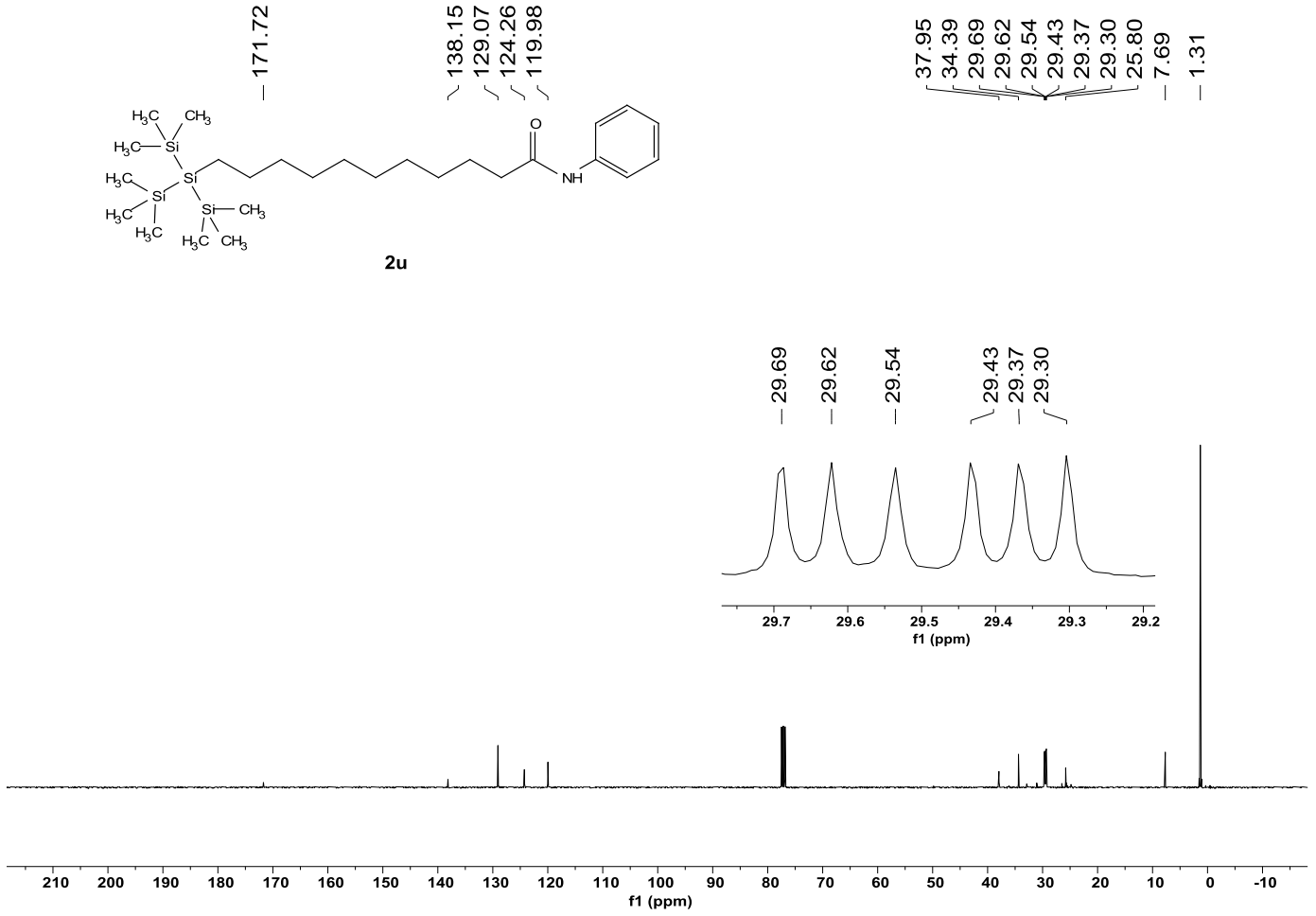
^{13}C NMR spectrum of compound **2t** (101 MHz, $CDCl_3$)



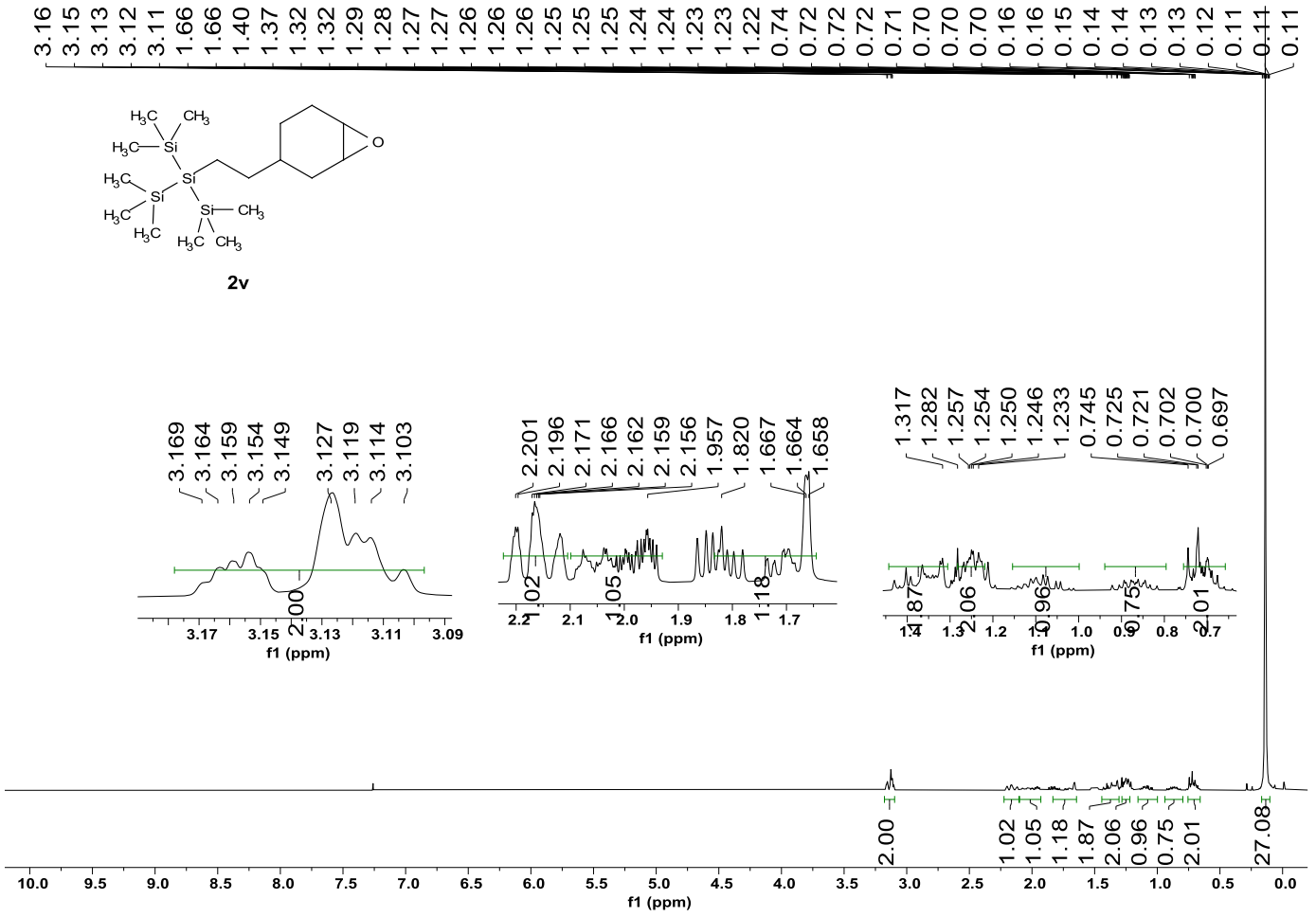
^{1}H NMR spectrum of compound **2u** (400 MHz, $CDCl_3$)



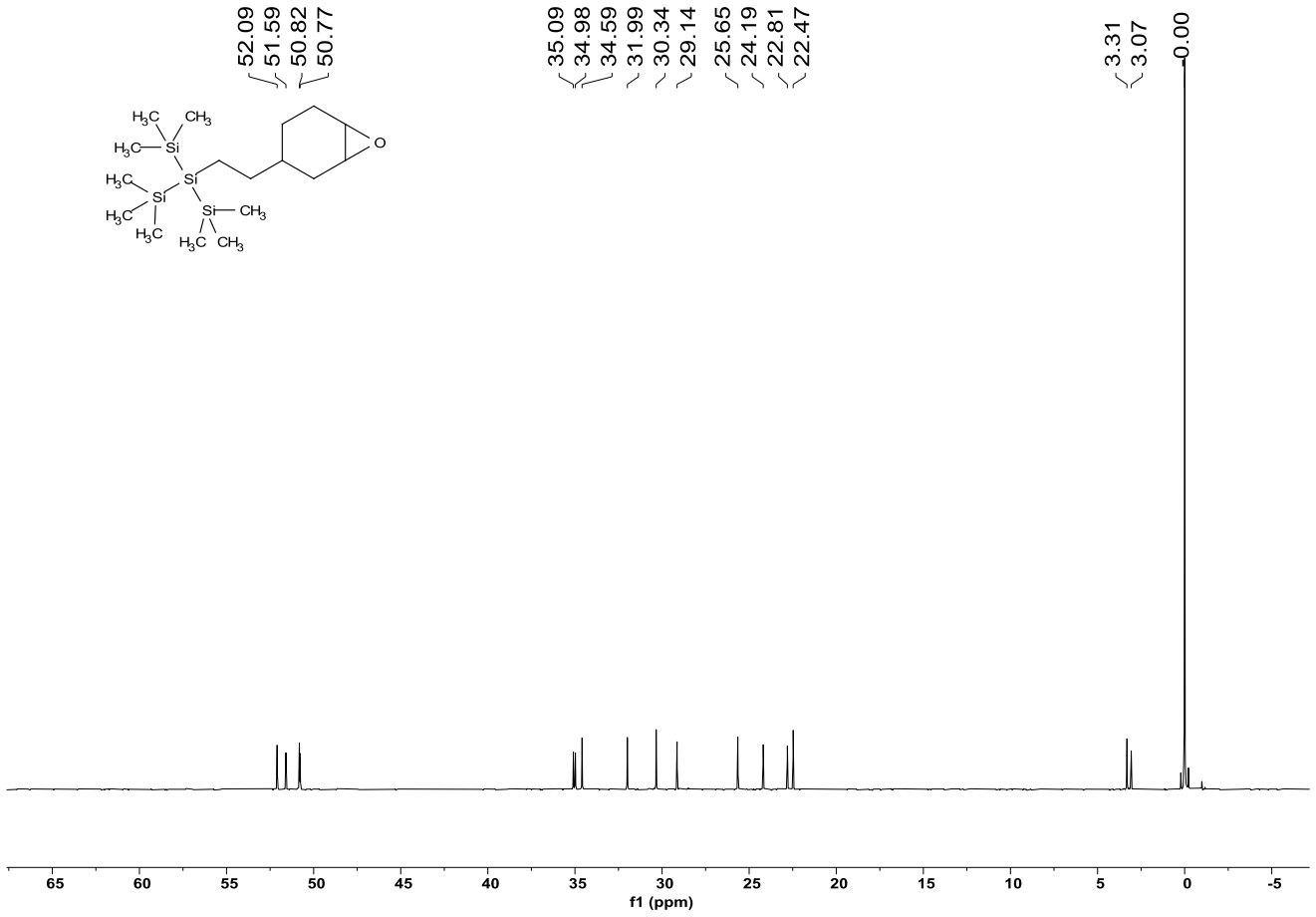
^{13}C NMR spectrum of compound **2u** (101 MHz, $CDCl_3$)



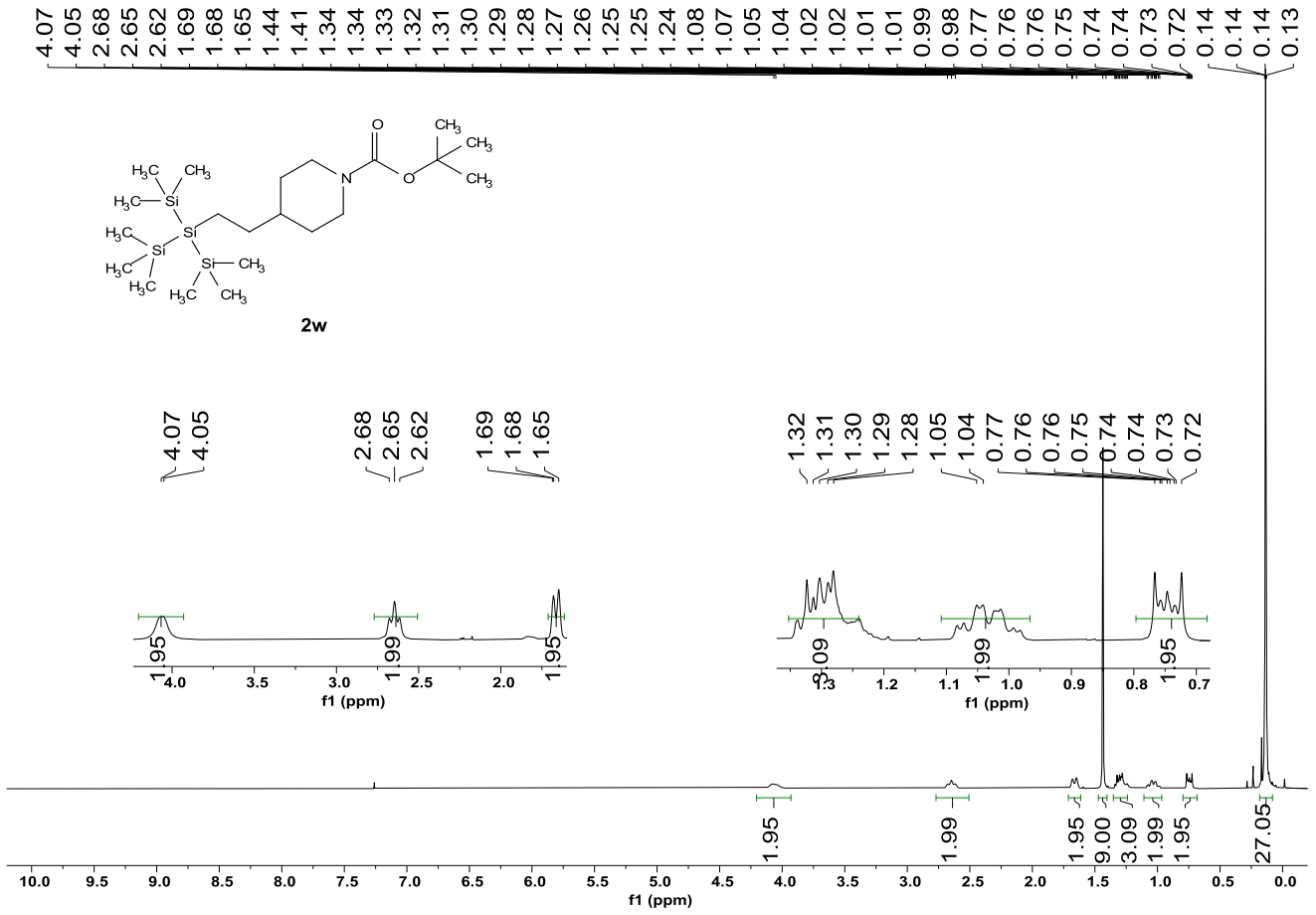
^{1}H NMR spectrum of compound **2v** (400 MHz, $CDCl_3$)



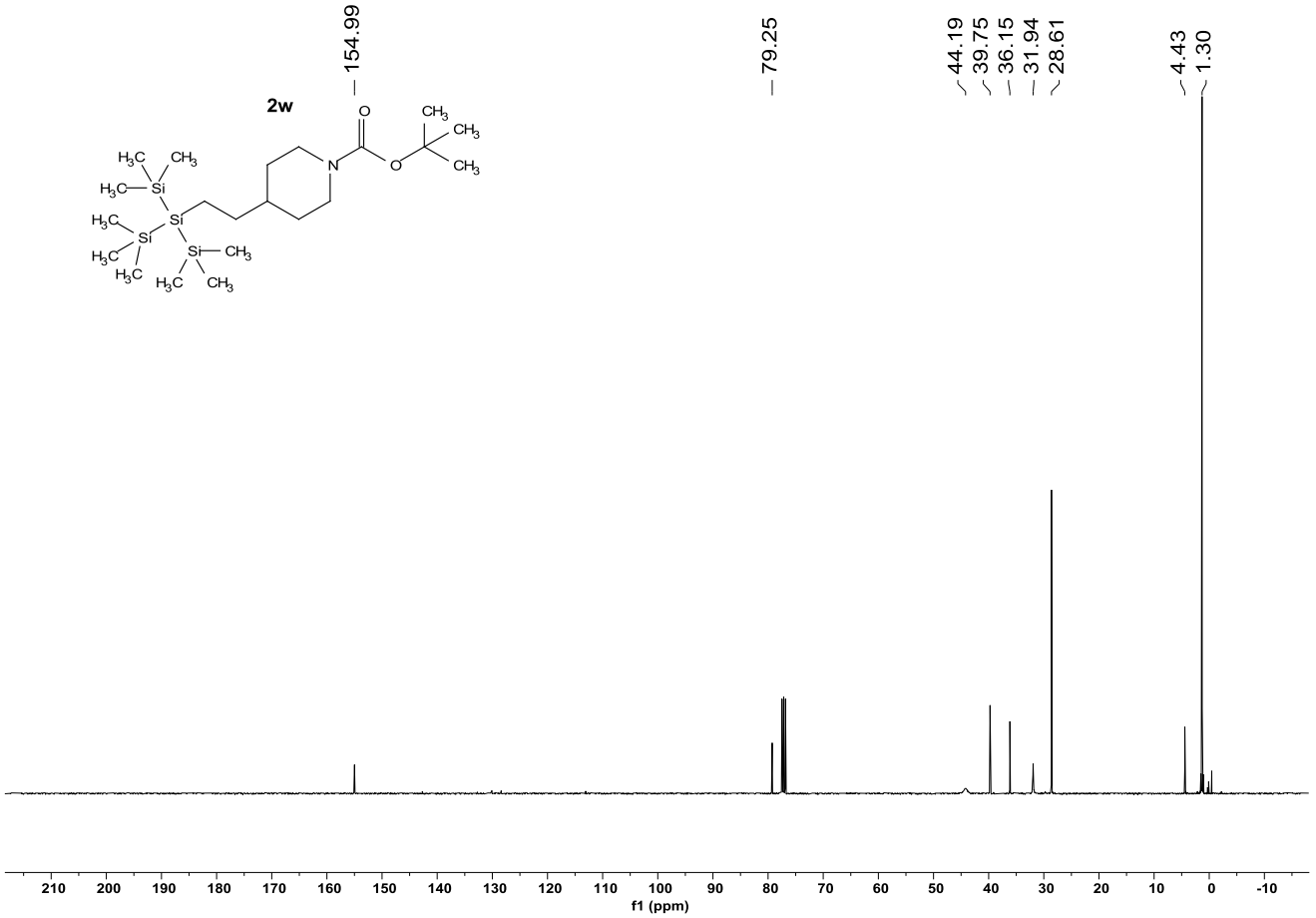
^{13}C NMR spectrum of compound **2v** (101 MHz, $CDCl_3$)



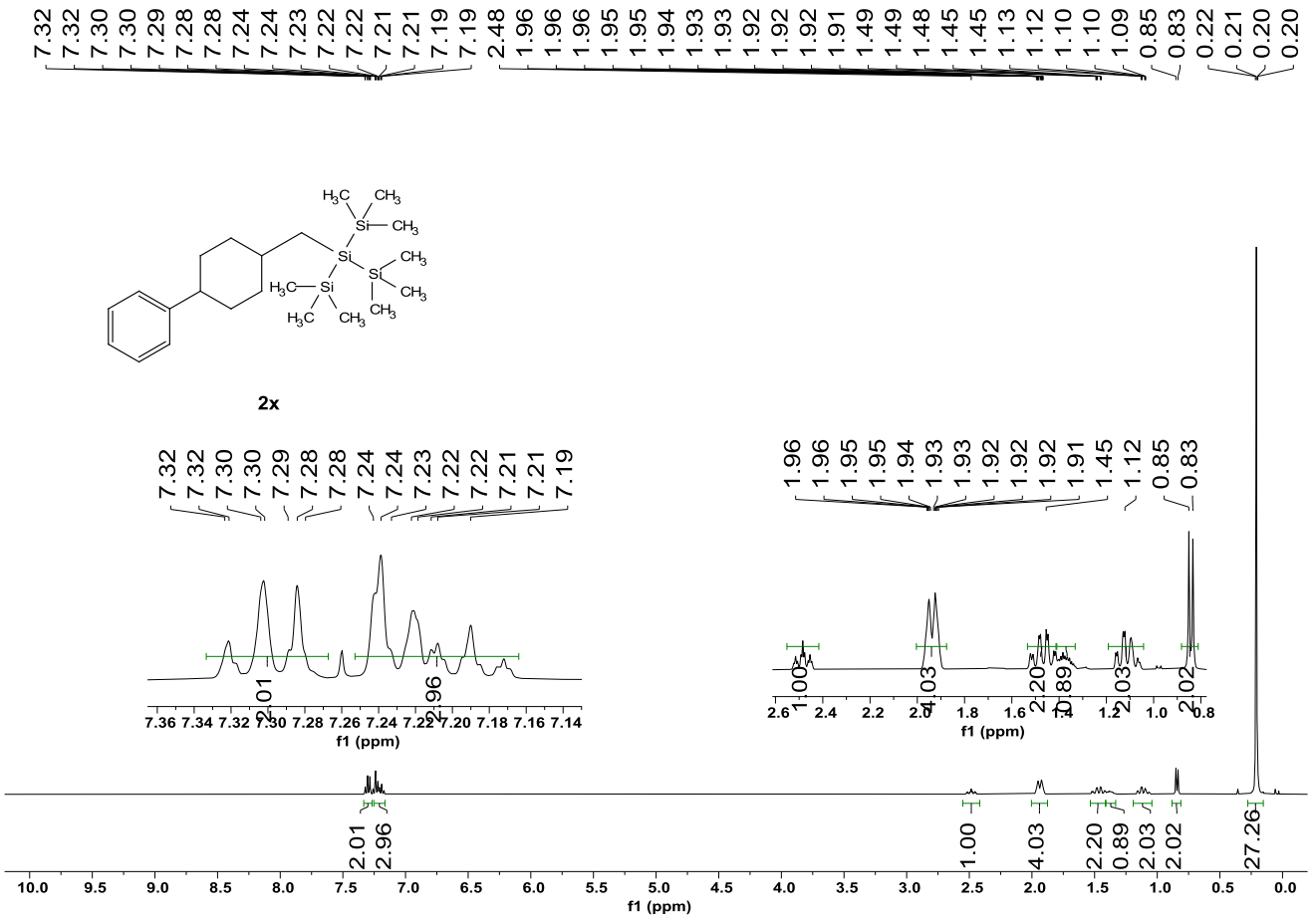
^{1}H NMR spectrum of compound **2w** (400 MHz, $CDCl_3$)



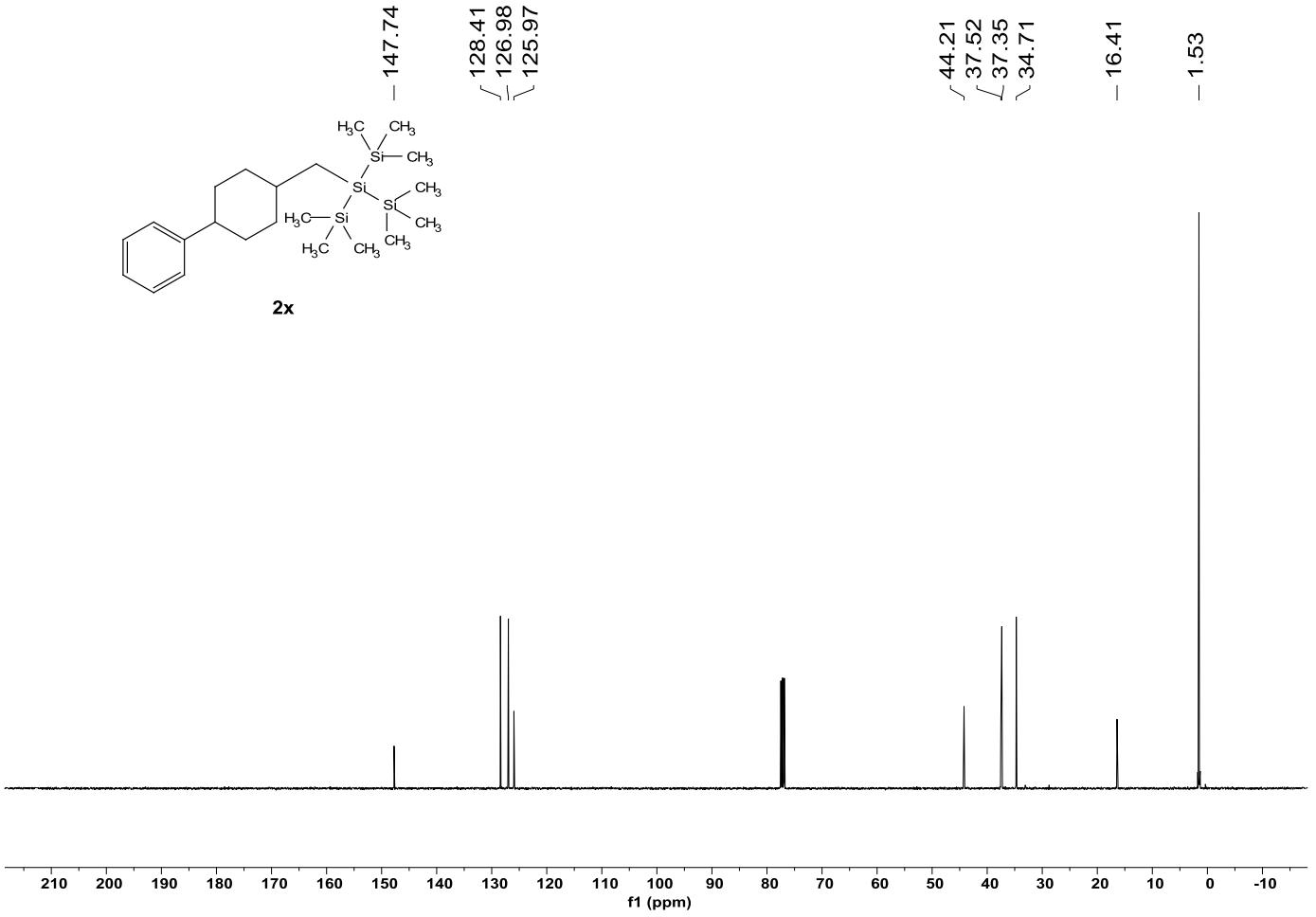
^{13}C NMR spectrum of compound **2w** ($CDCl_3$)



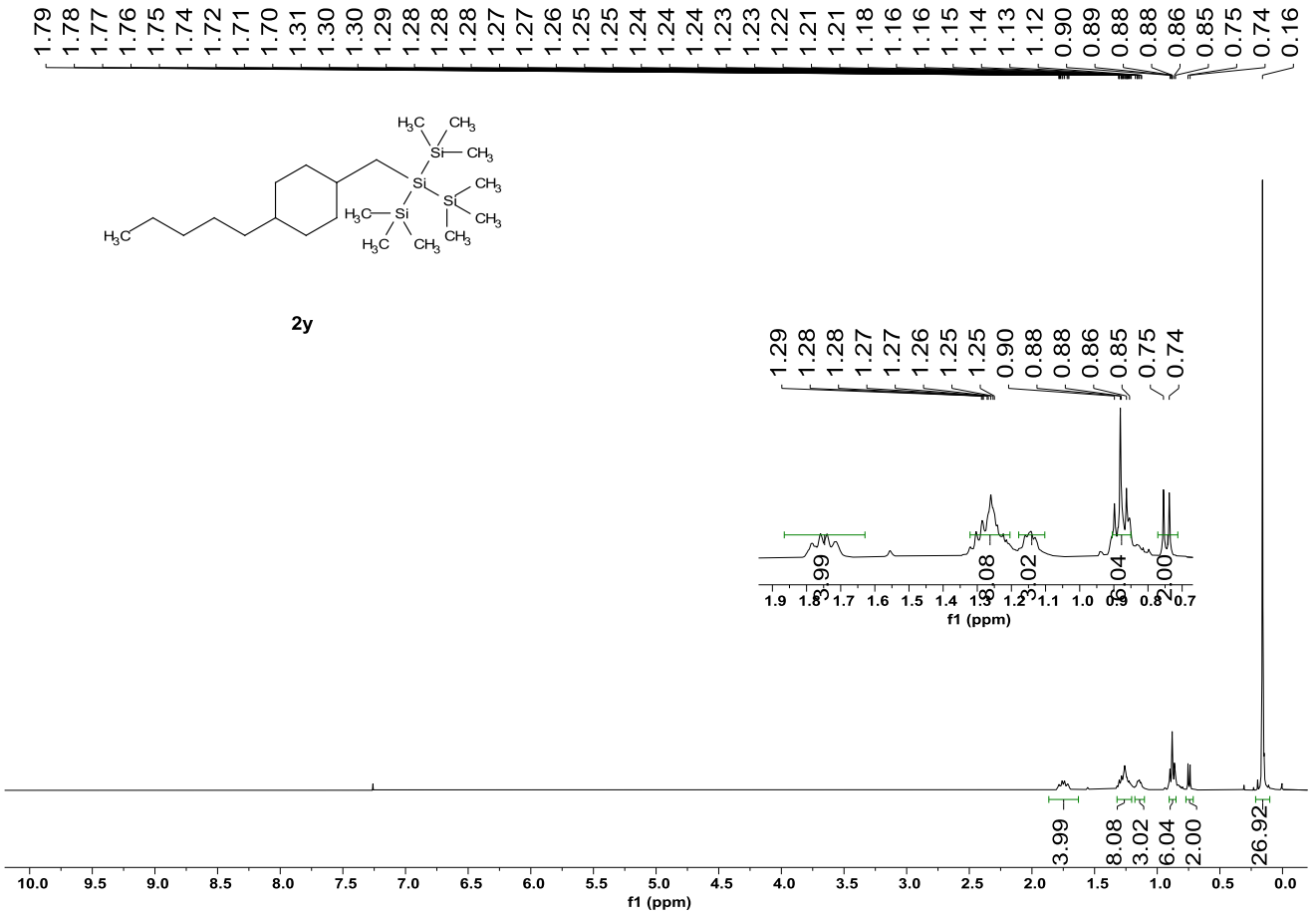
^{1}H NMR spectrum of compound **2x** (400 MHz, $CDCl_3$)



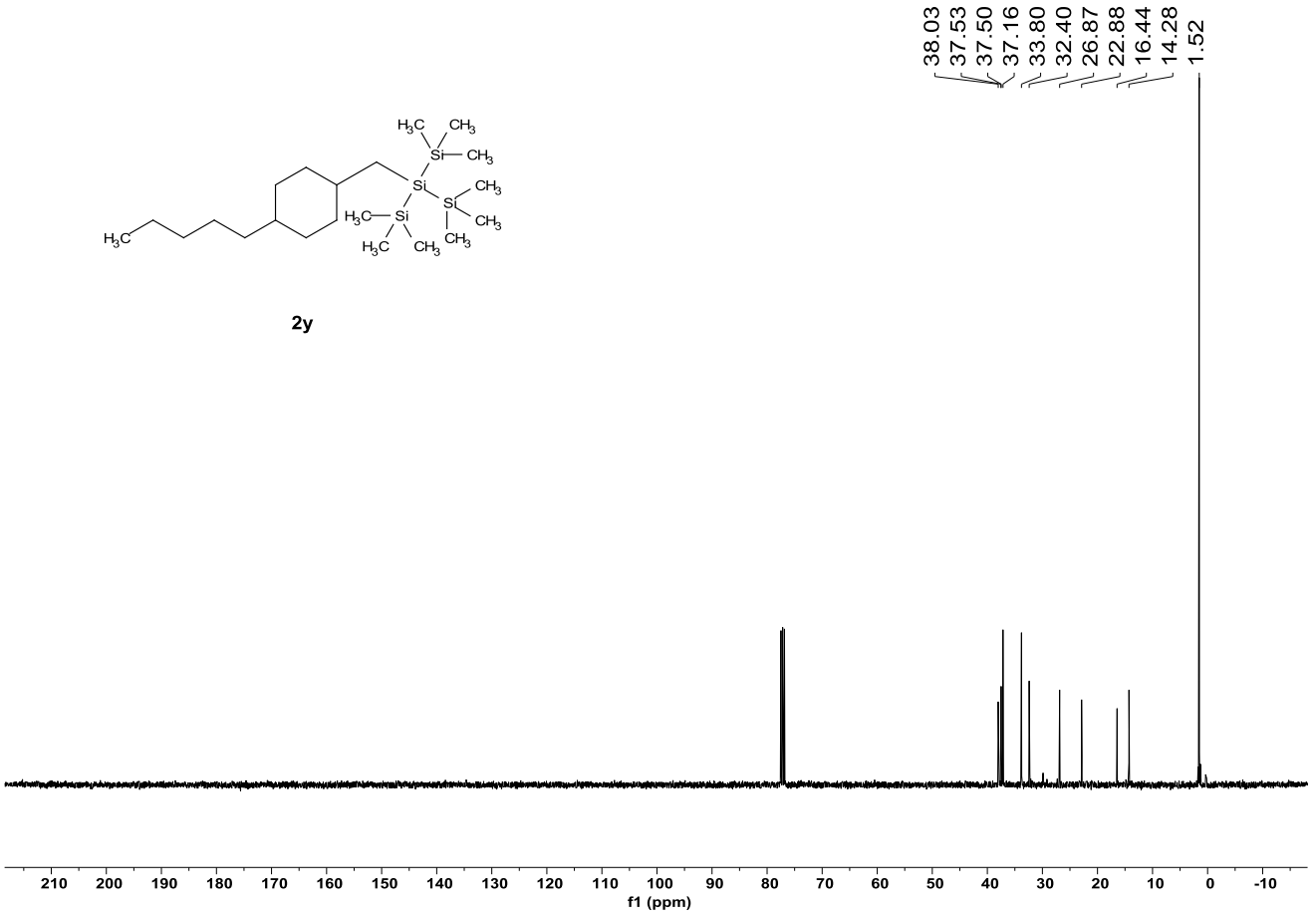
^{13}C NMR spectrum of compound **2x** (101 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **2y** (400 MHz, $CDCl_3$)

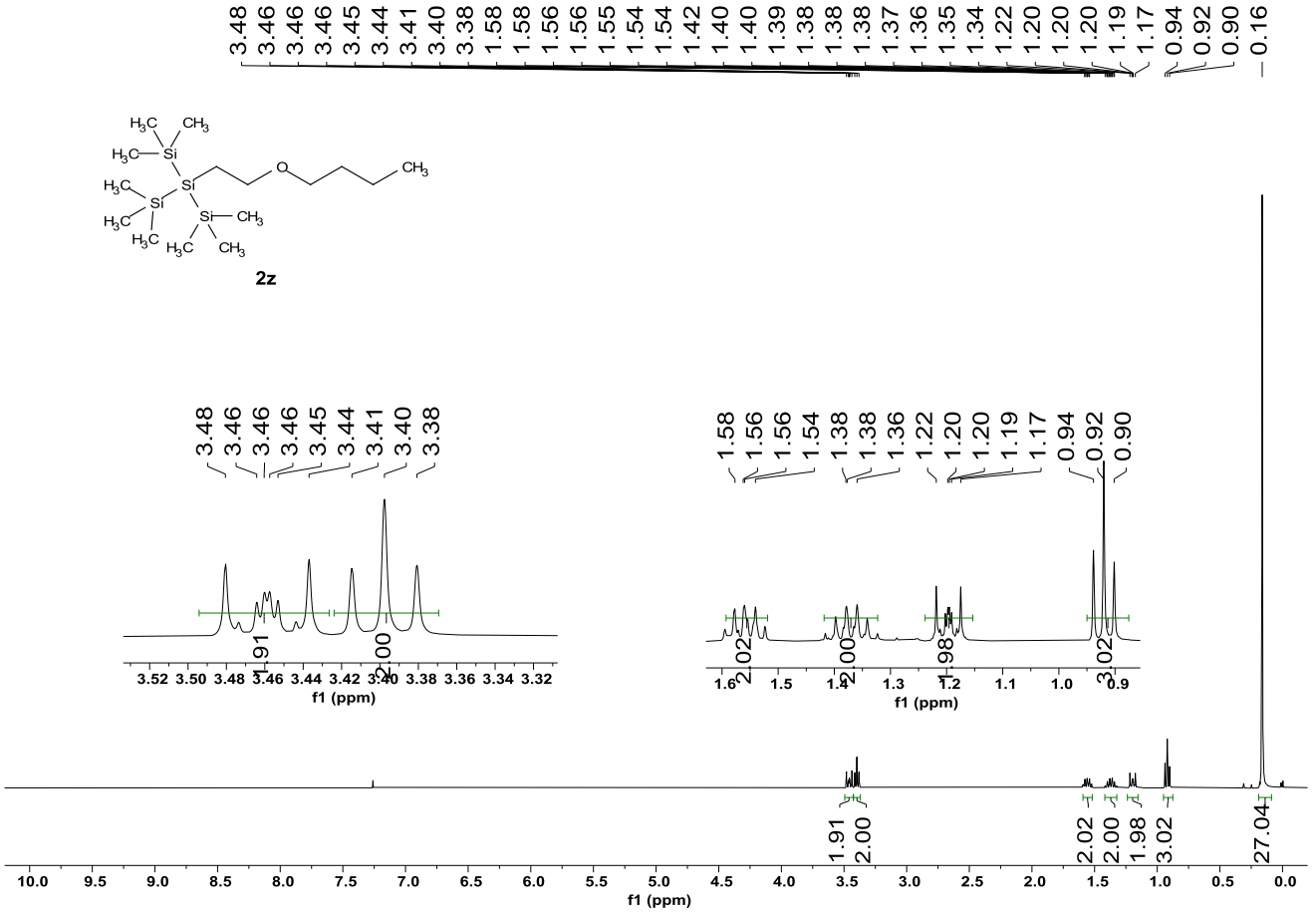


^{13}C NMR spectrum of compound **2y** (101 MHz, $CDCl_3$)

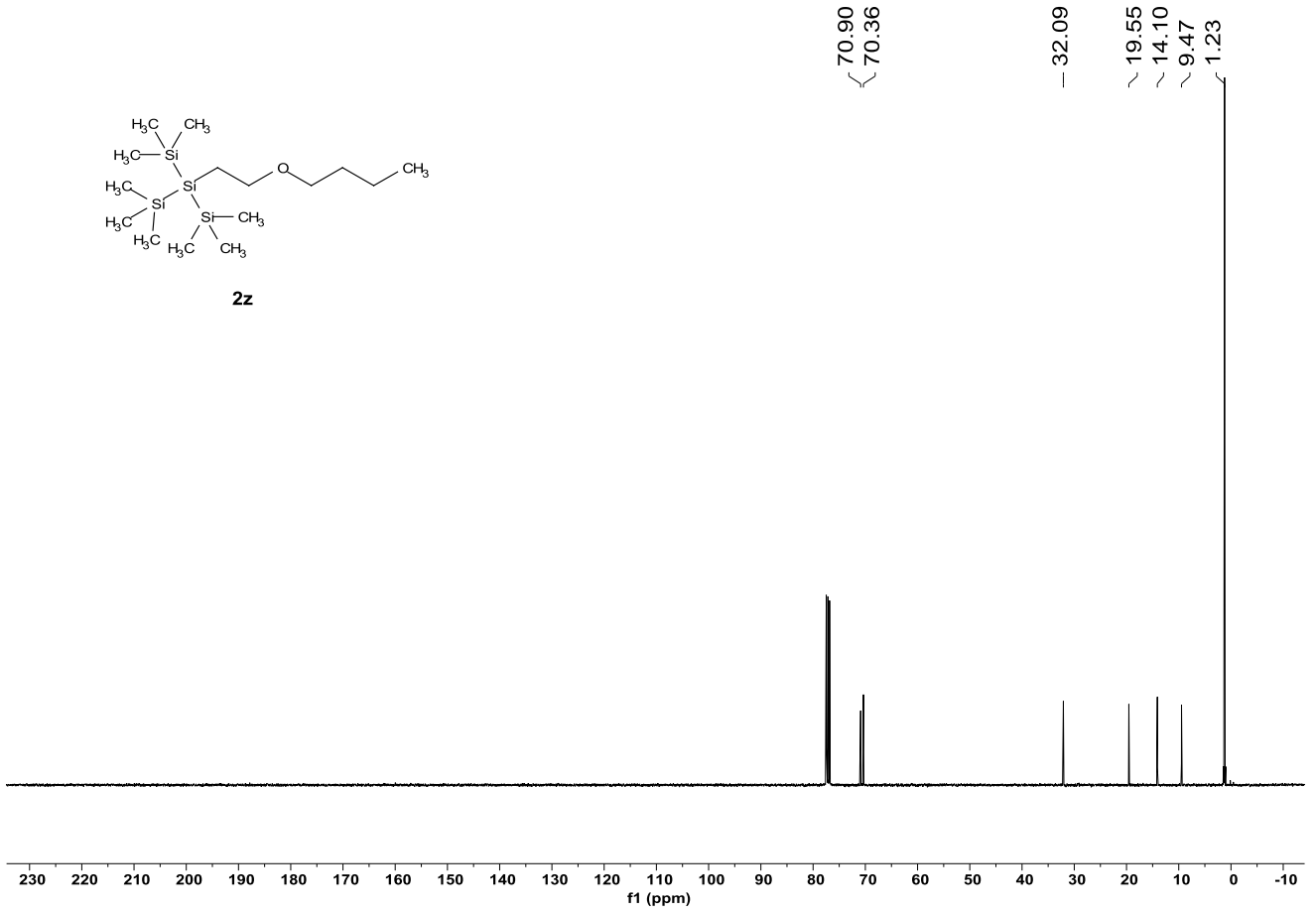


2y

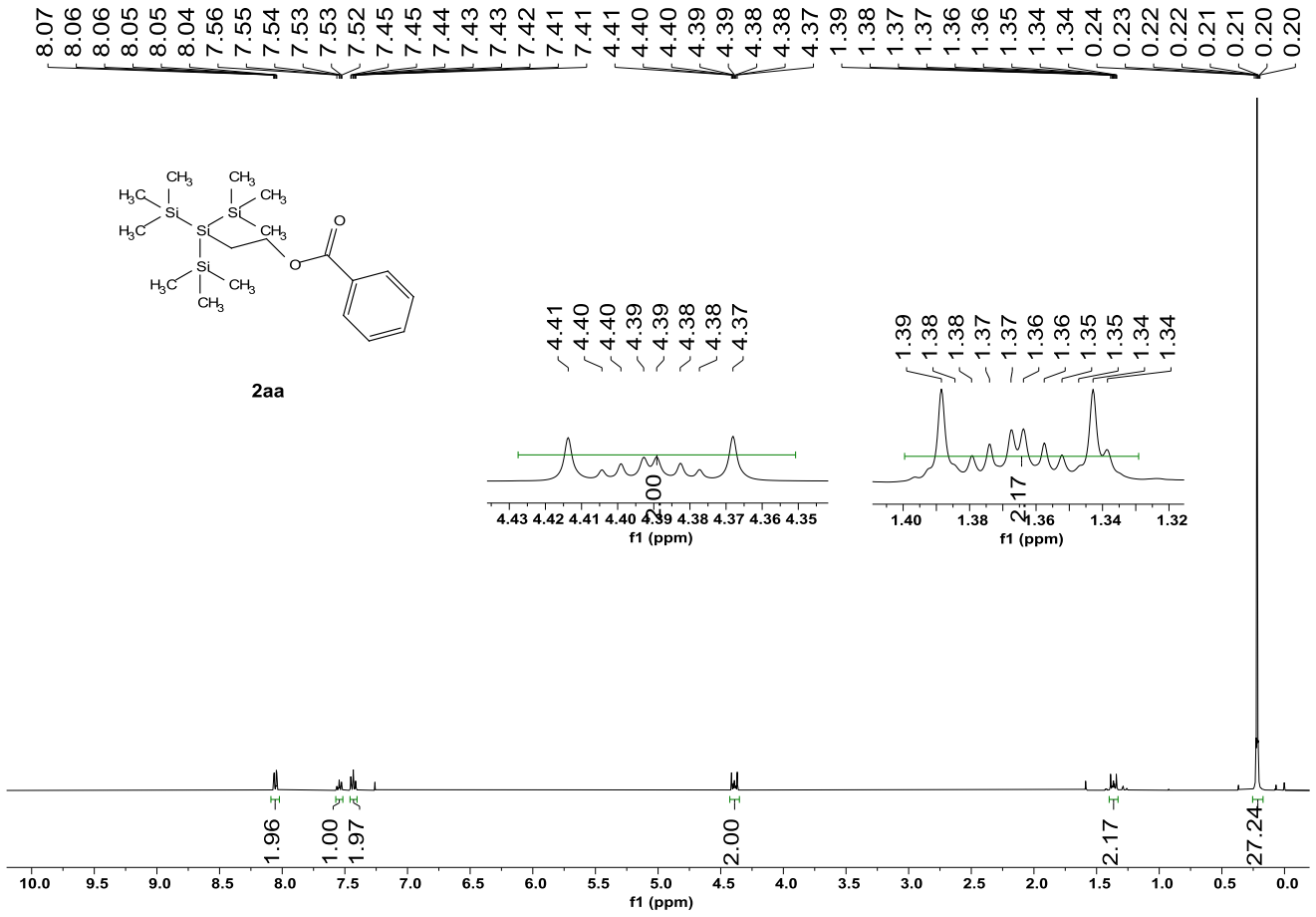
^{1}H NMR spectrum of compound **2z** (400 MHz, $CDCl_3$)



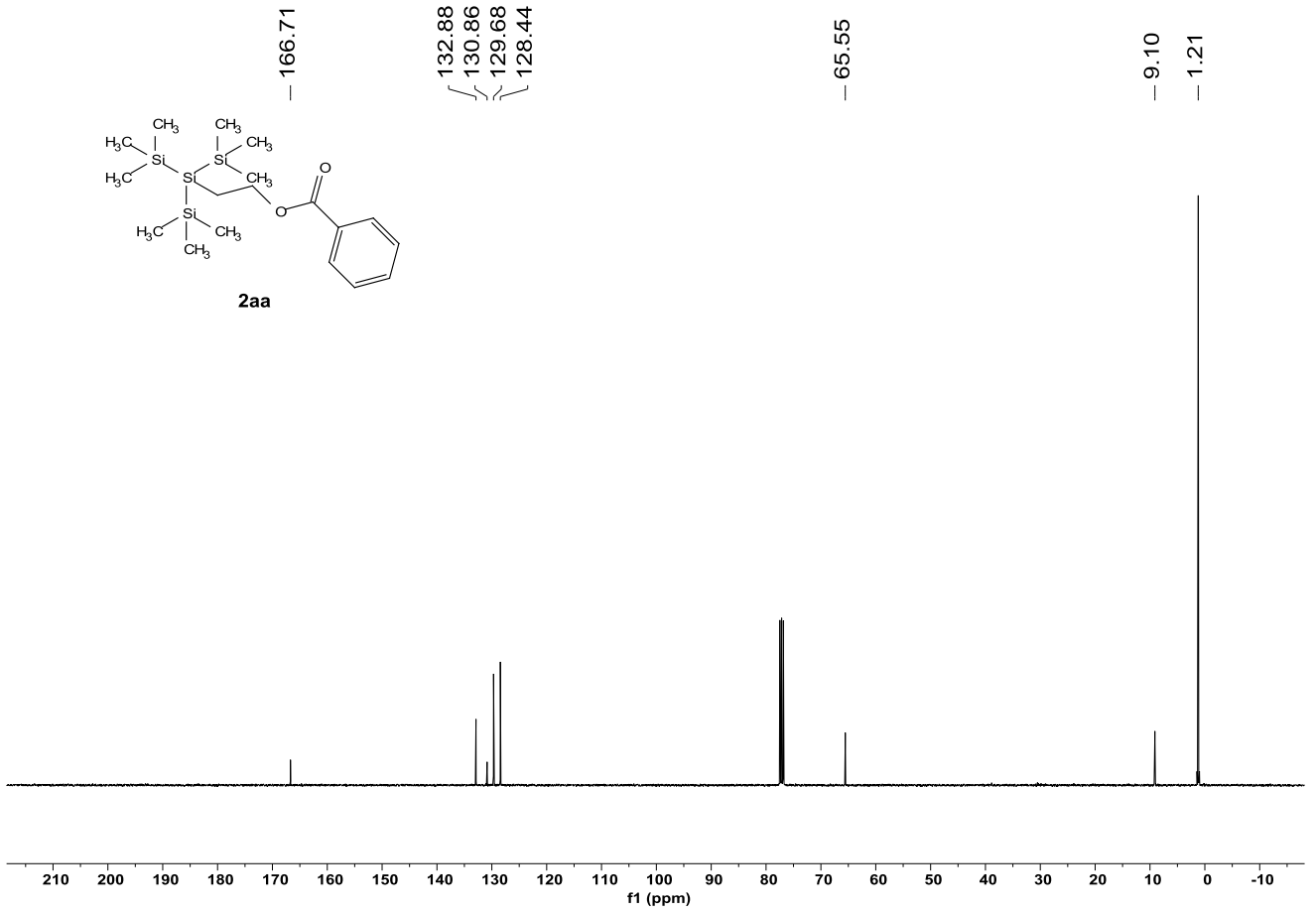
^{13}C NMR spectrum of compound **2z** (101 MHz, $CDCl_3$)



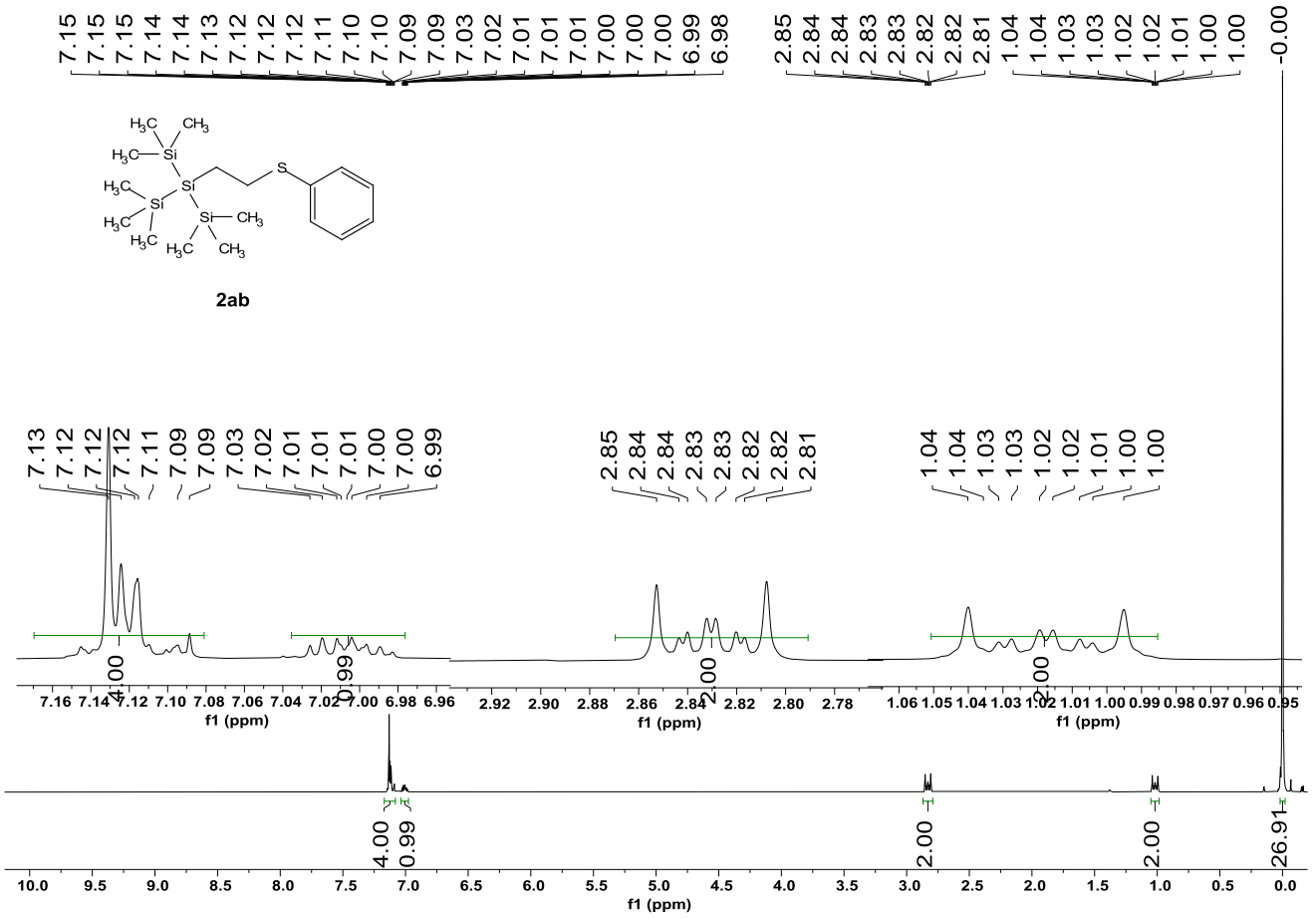
^{1}H NMR spectrum of compound **2aa** (400 MHz, $CDCl_3$)



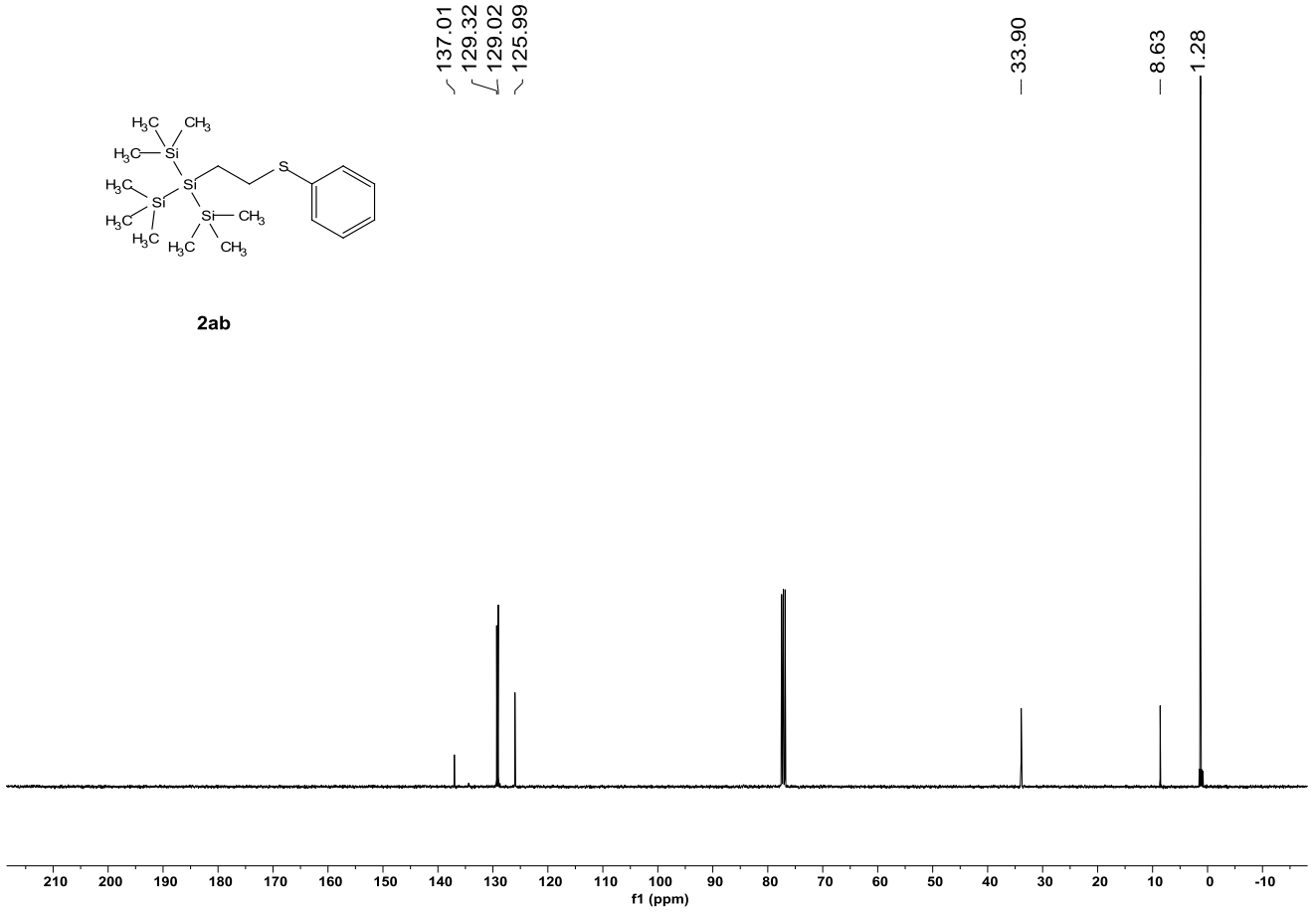
^{13}C NMR spectrum of compound **2aa** (101 MHz, $CDCl_3$)



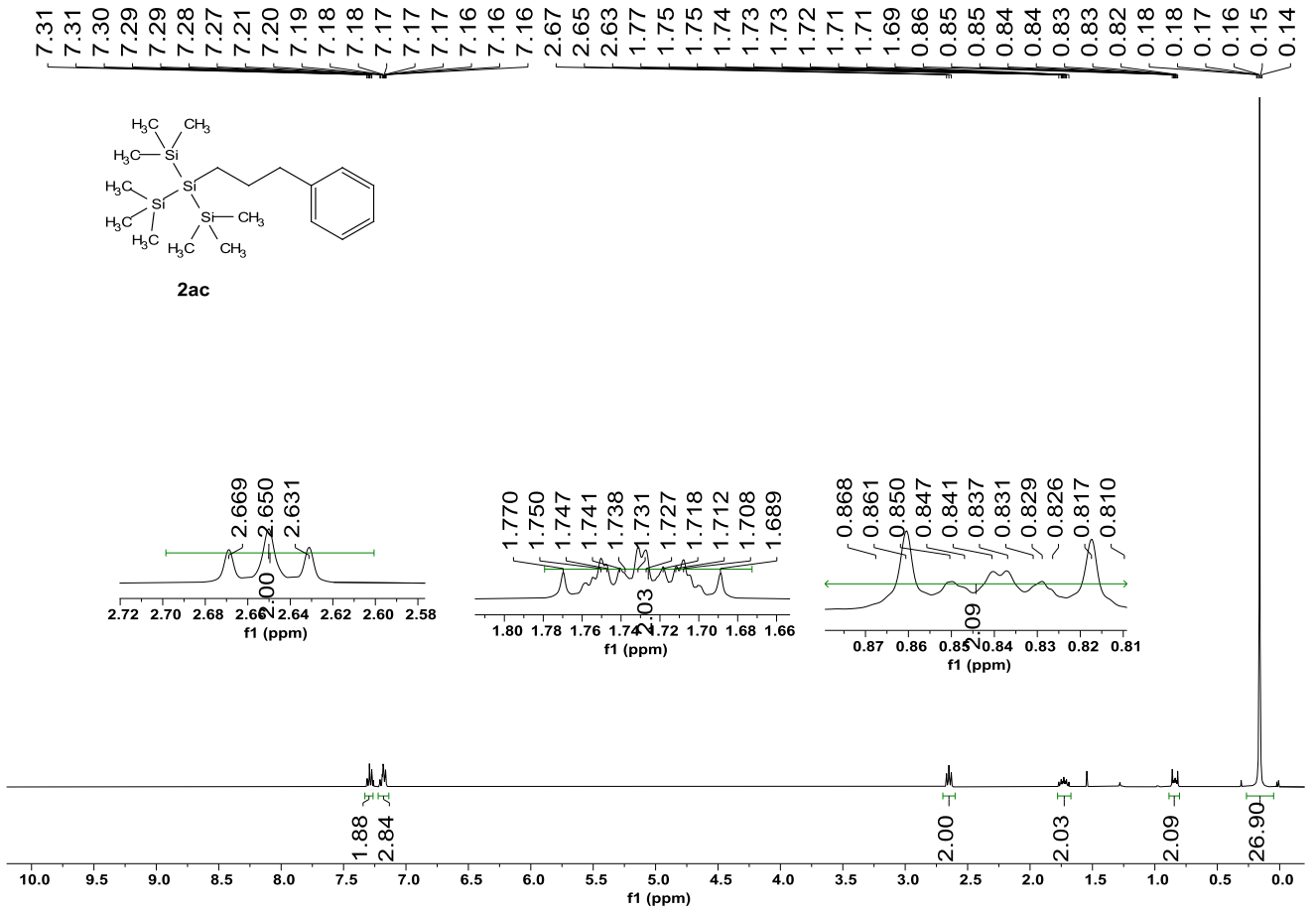
^{1}H NMR spectrum of compound **2ab** (400 MHz, $CDCl_3$)



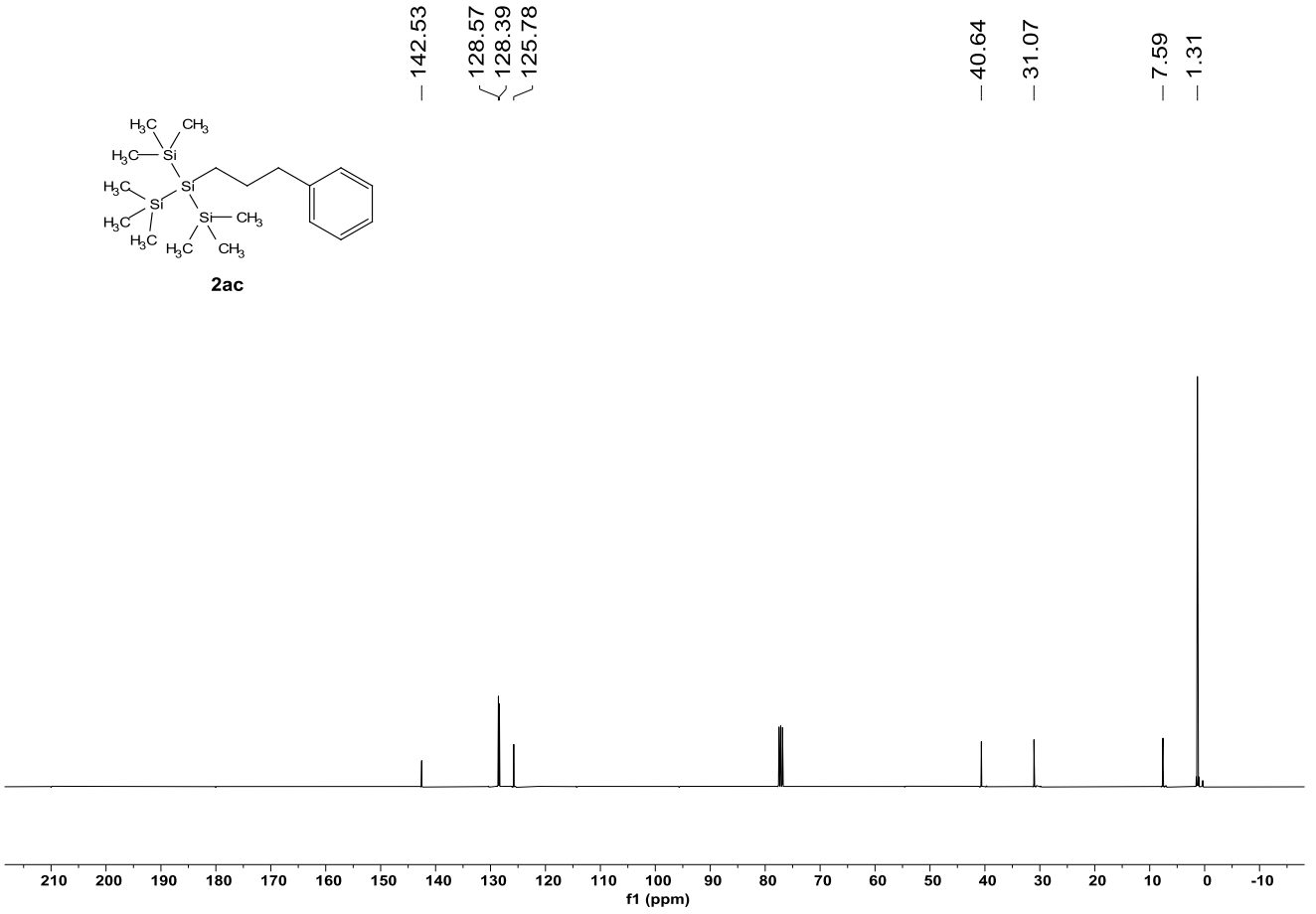
^{13}C NMR spectrum of compound **2ab** ($CDCl_3$)



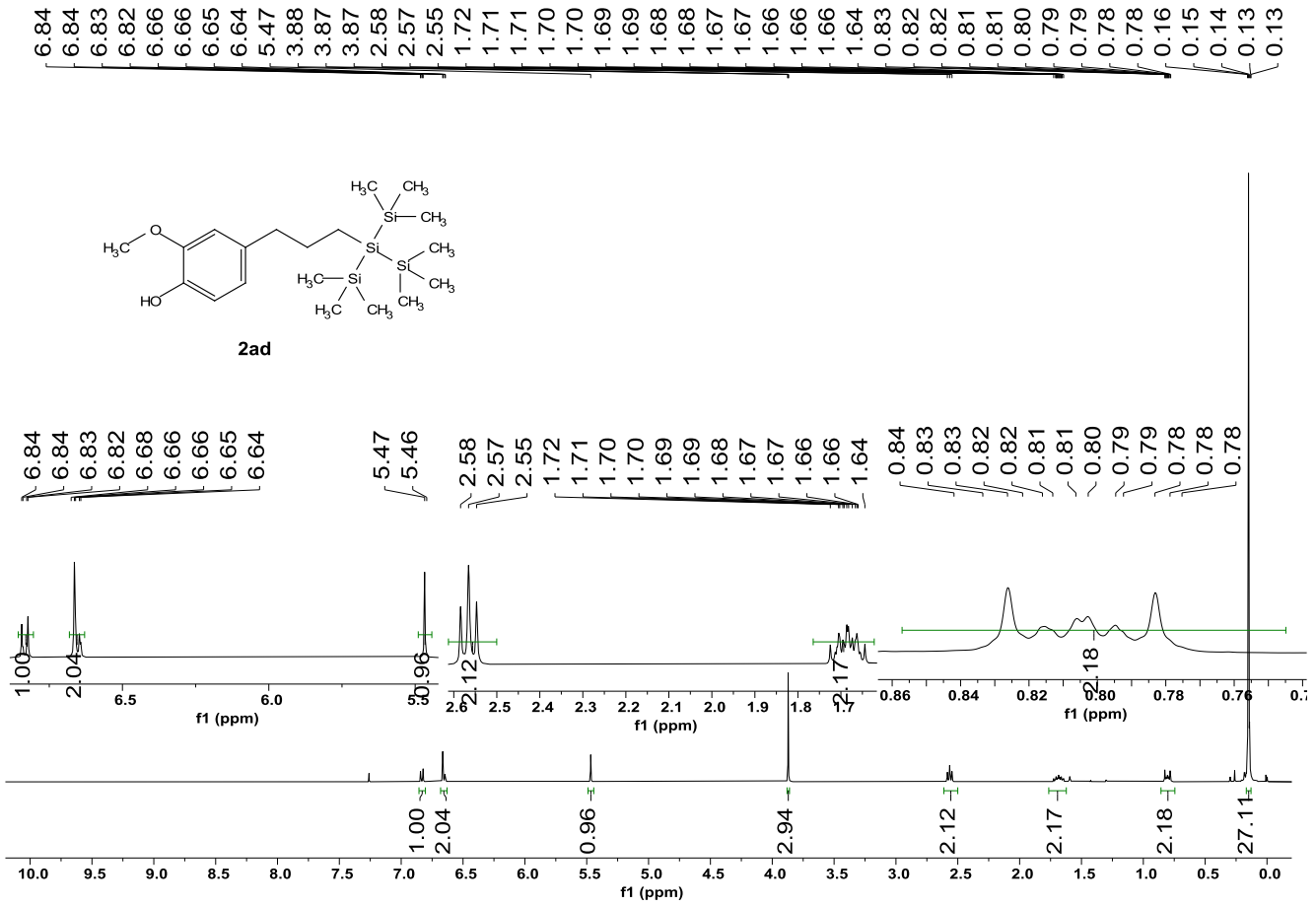
^{1}H NMR spectrum of compound **2ac** (400 MHz, $CDCl_3$)



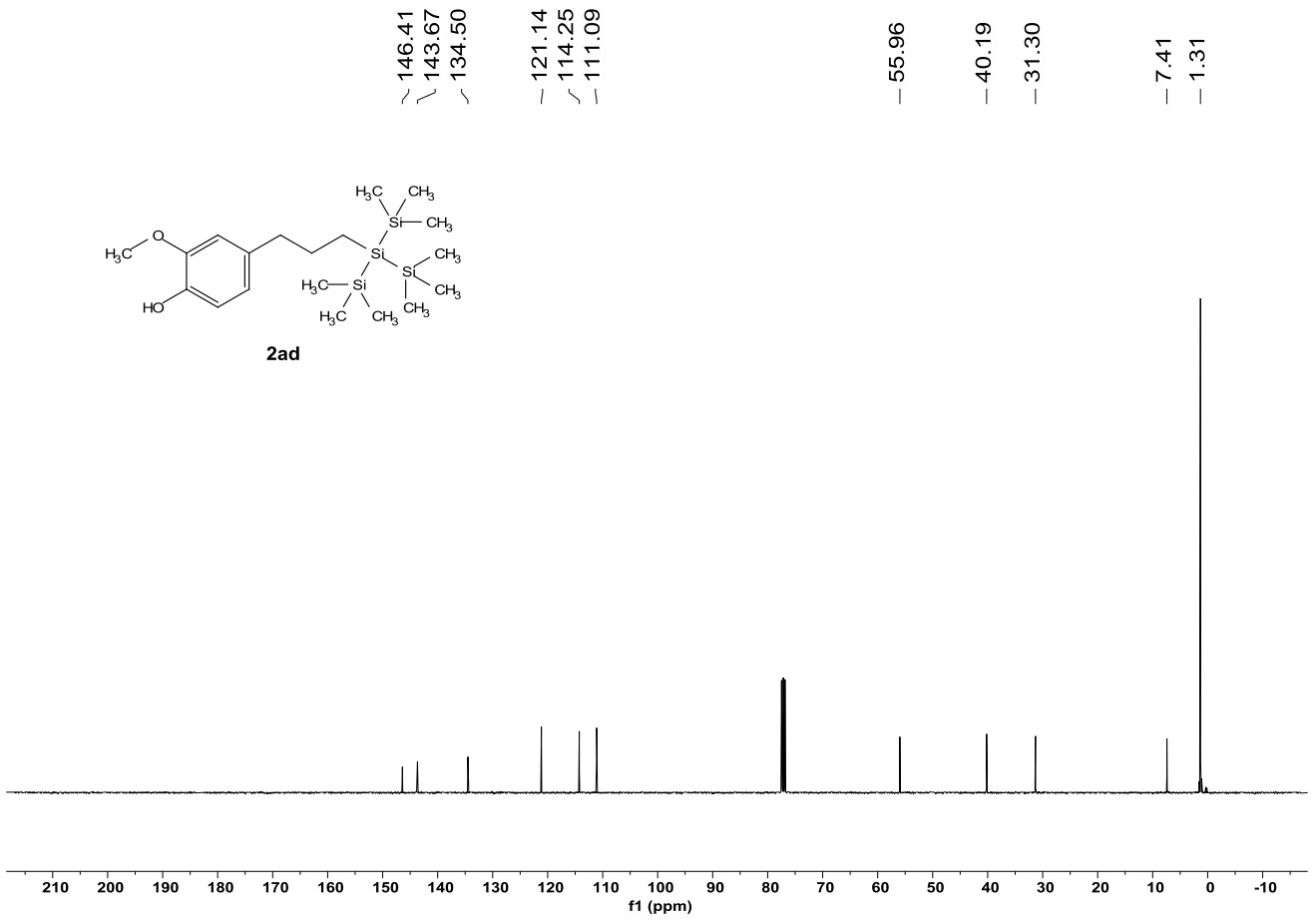
^{13}C NMR spectrum of compound **2ac** (101 MHz, $CDCl_3$)



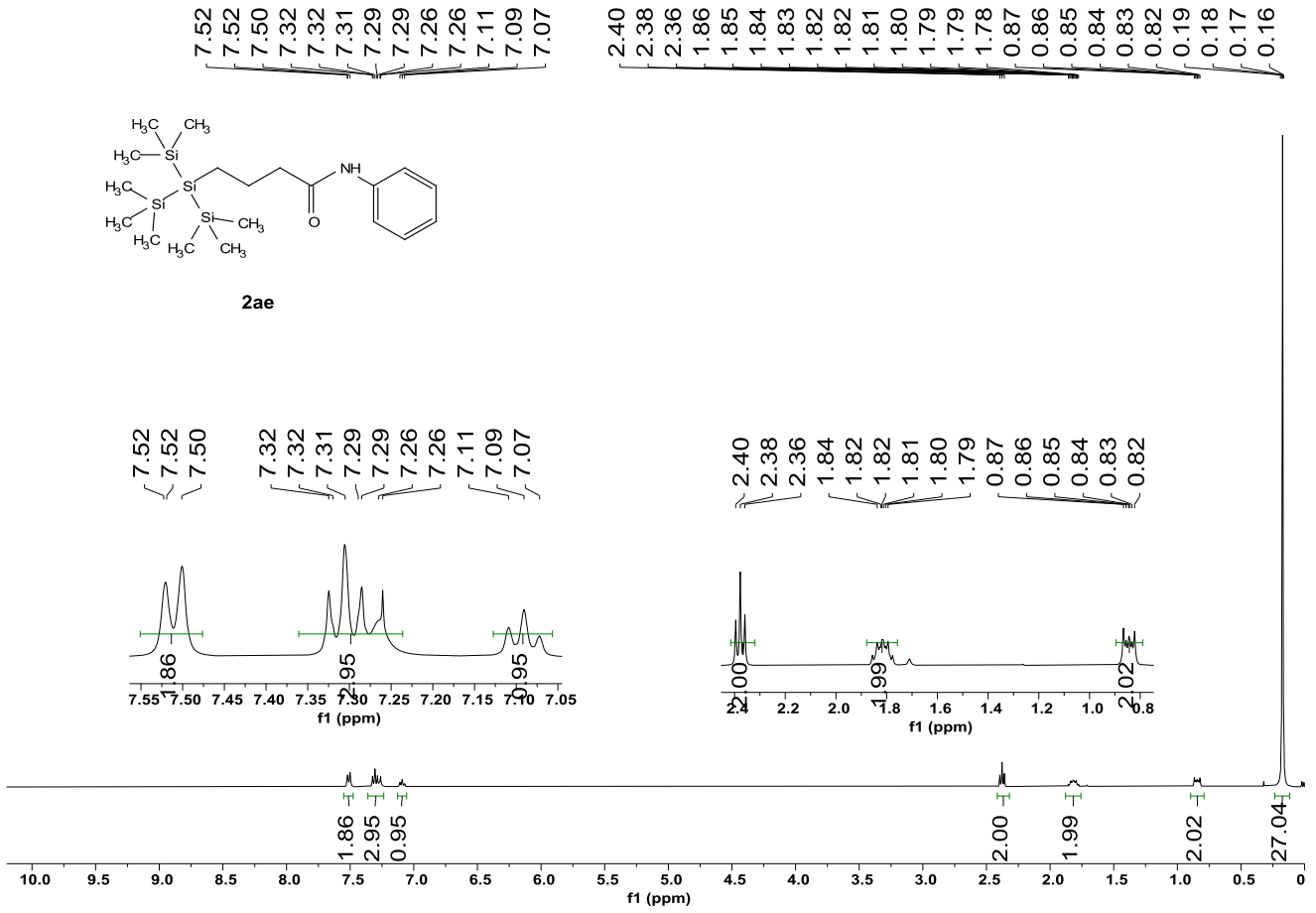
^{1}H NMR spectrum of compound **2ad** (400 MHz, $CDCl_3$)



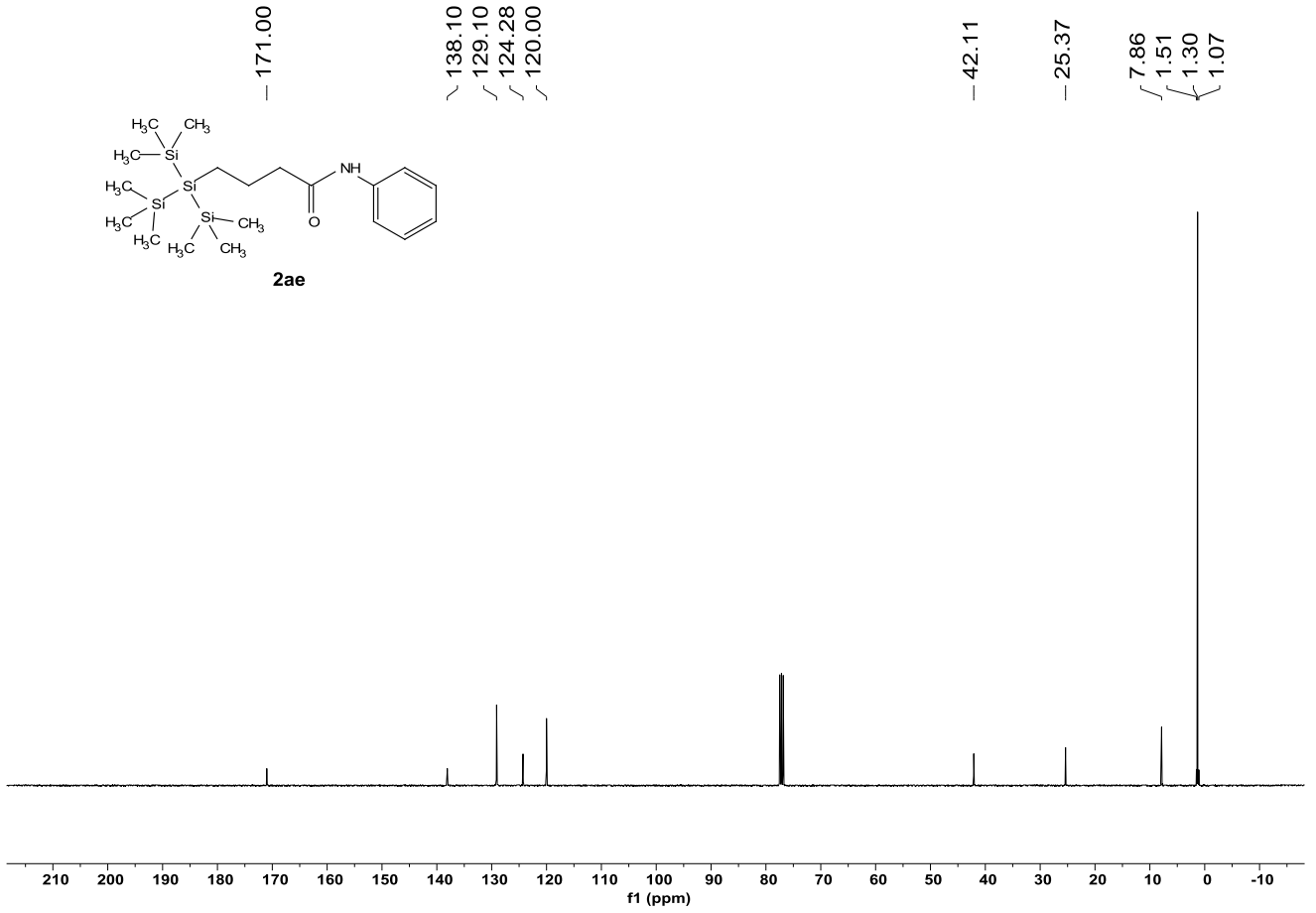
^{13}C NMR spectrum of compound **2ad** ($CDCl_3$)



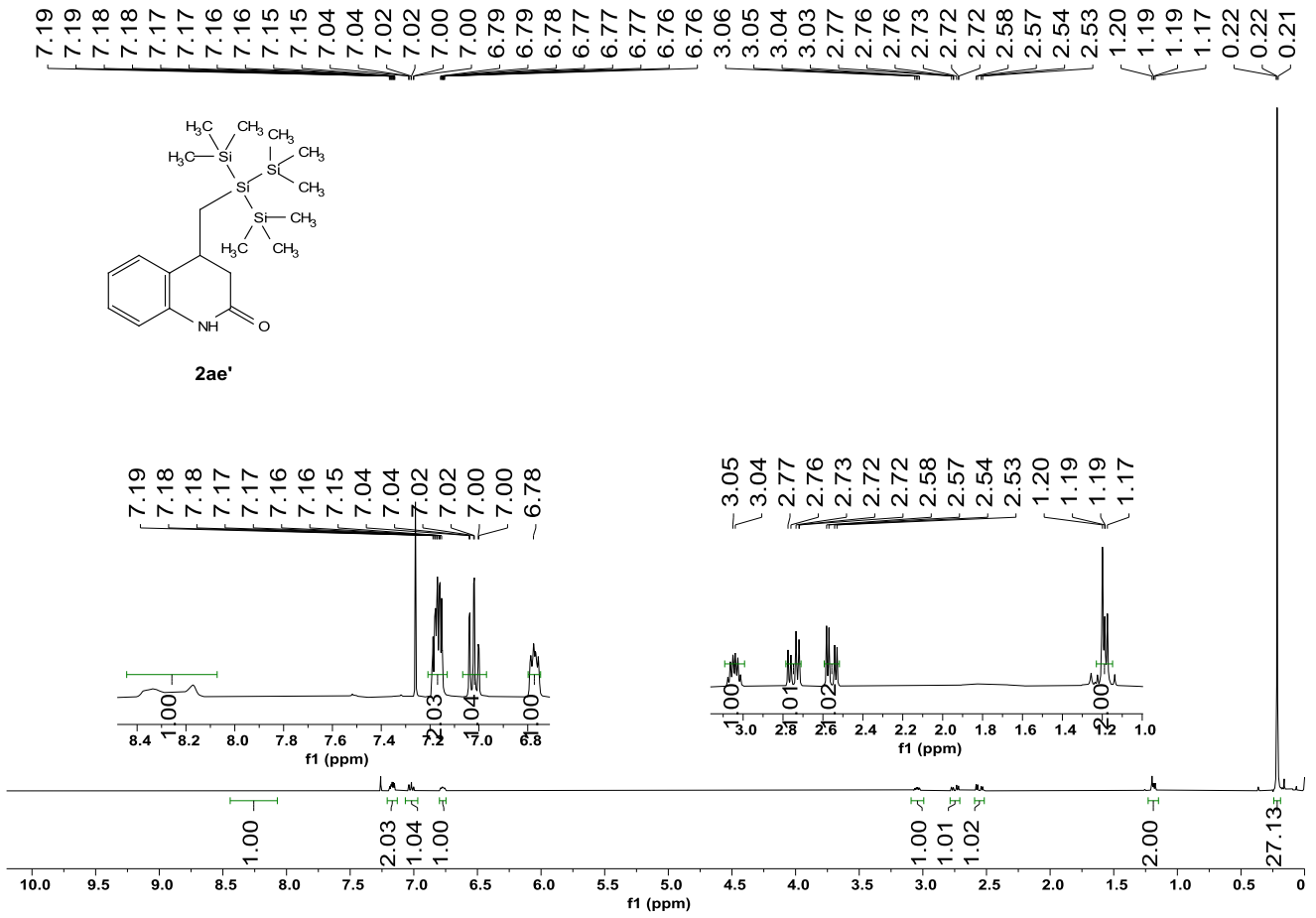
^{1}H NMR spectrum of compound **2ae** (400 MHz, $CDCl_3$)



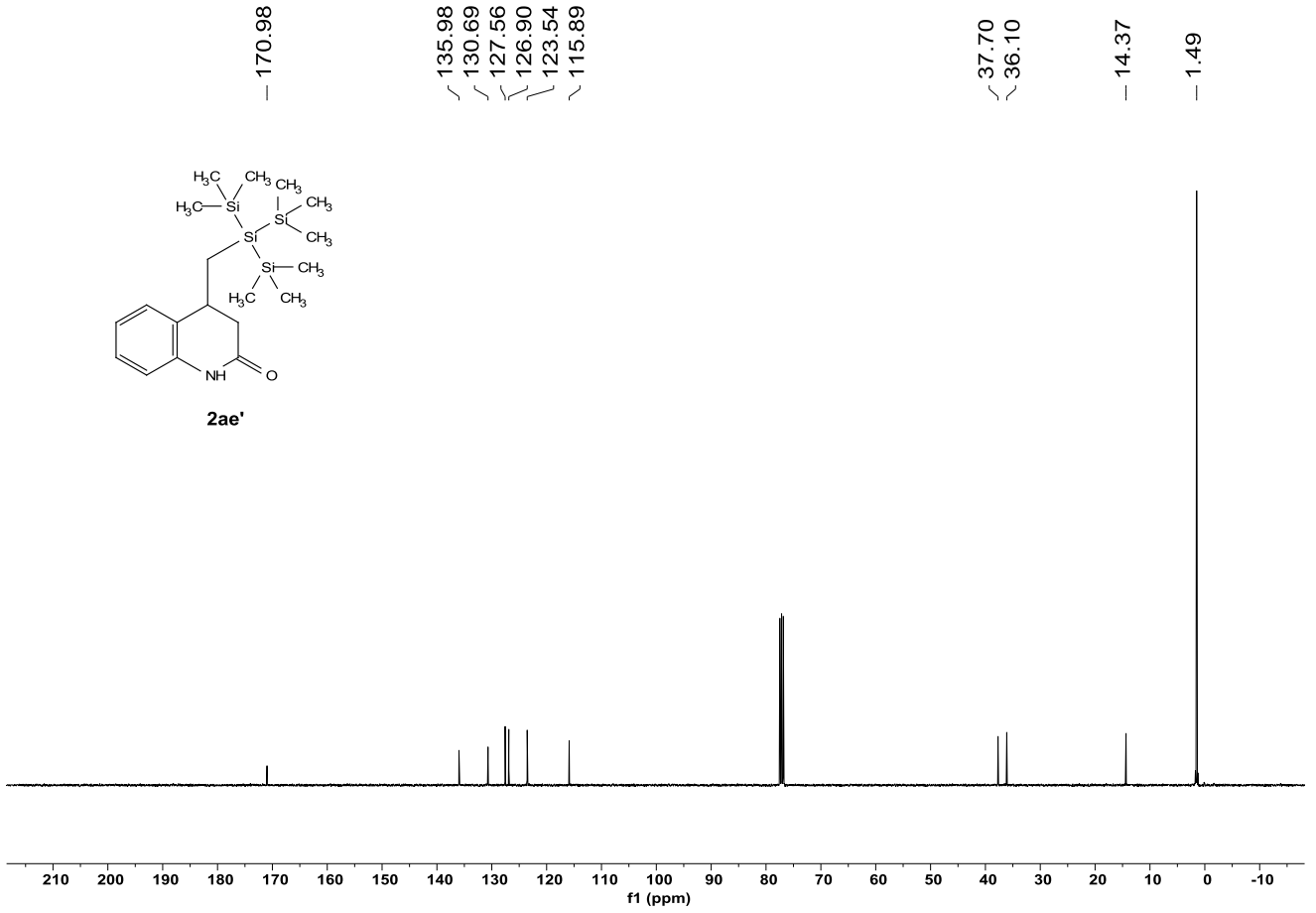
^{13}C NMR spectrum of compound **2ae** (101 MHz, $CDCl_3$)



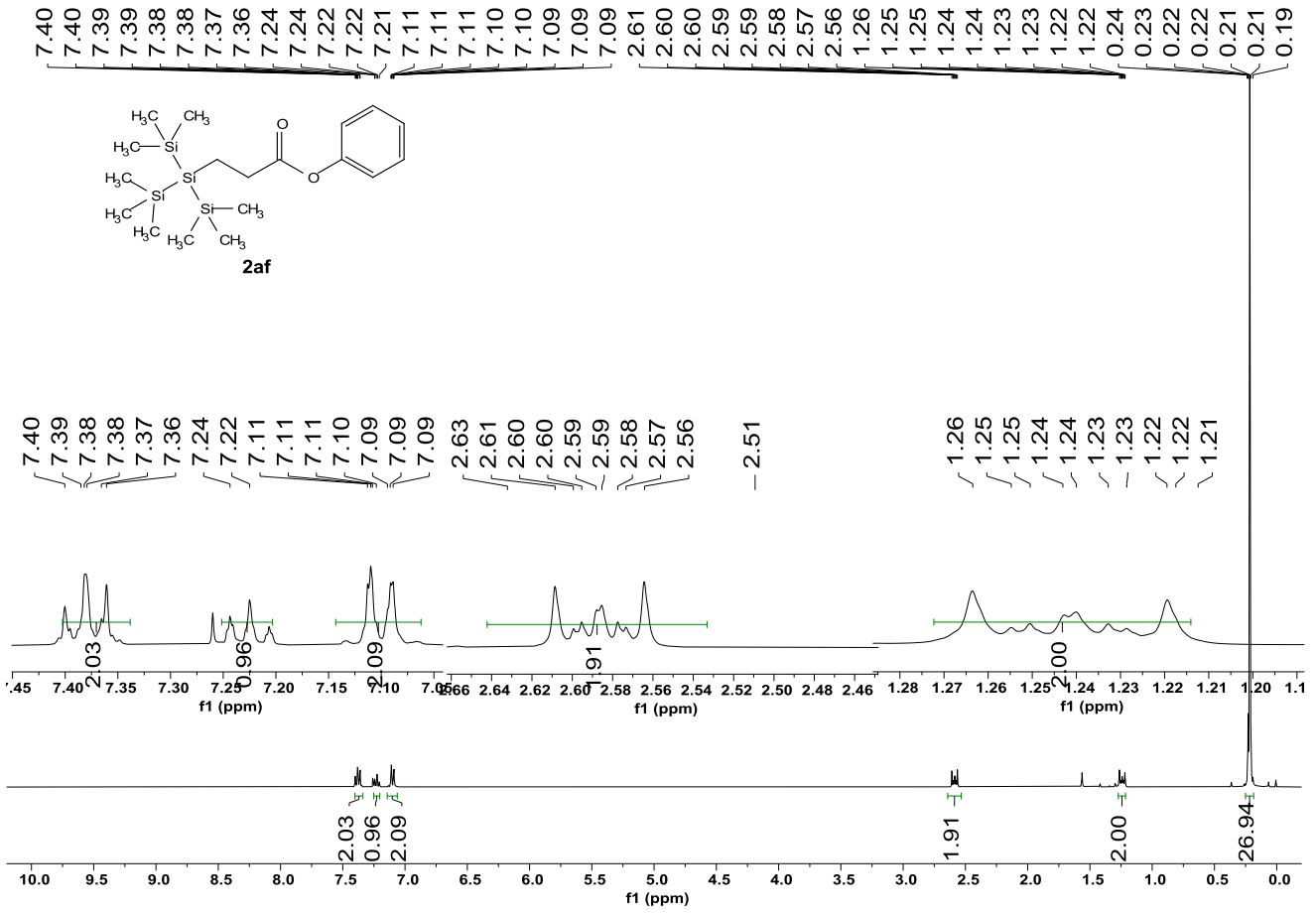
^{1}H NMR spectrum of compound **2ae'** (400 MHz, $CDCl_3$)



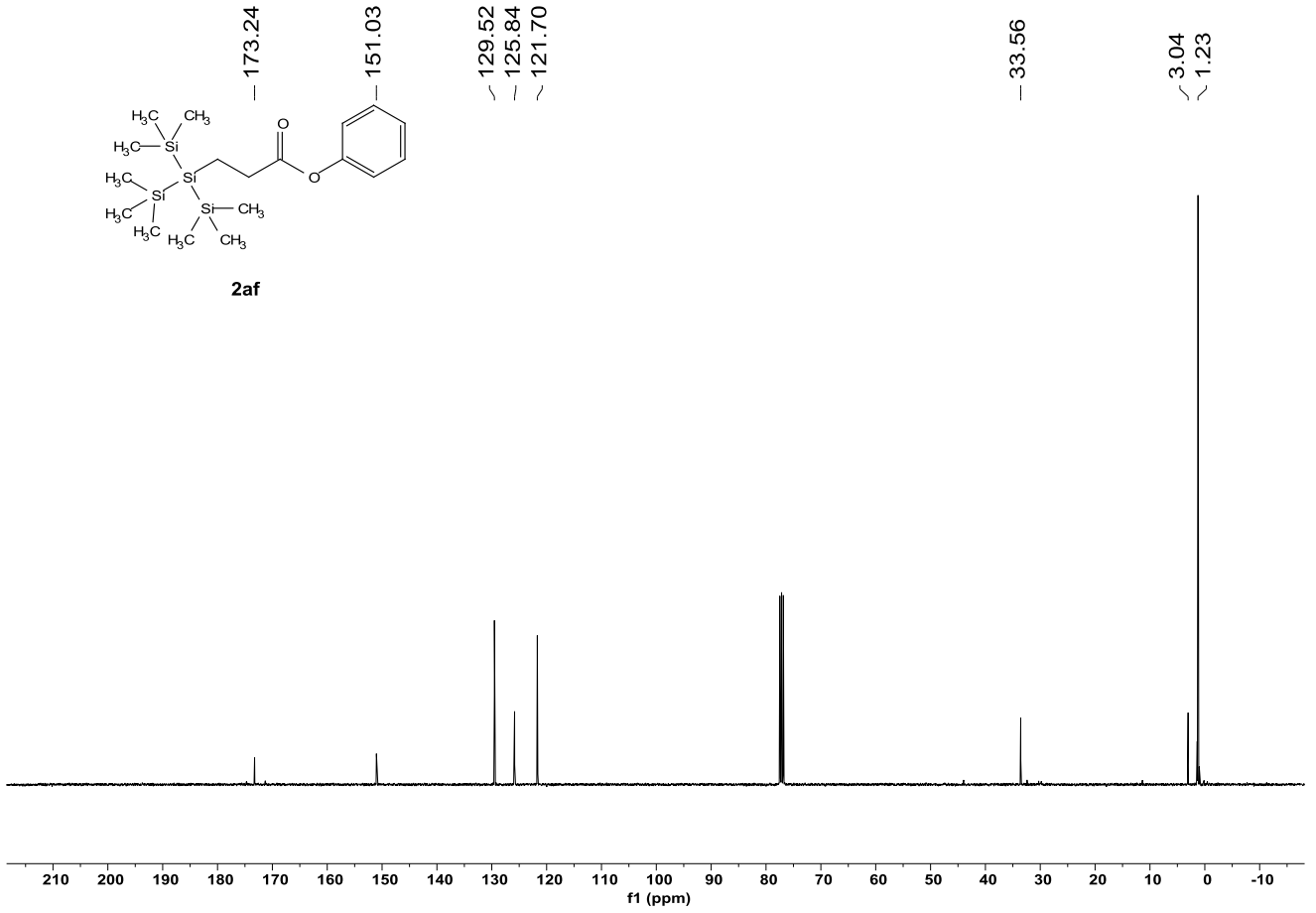
^{13}C NMR spectrum of compound **2ae'** (101 MHz, $CDCl_3$)



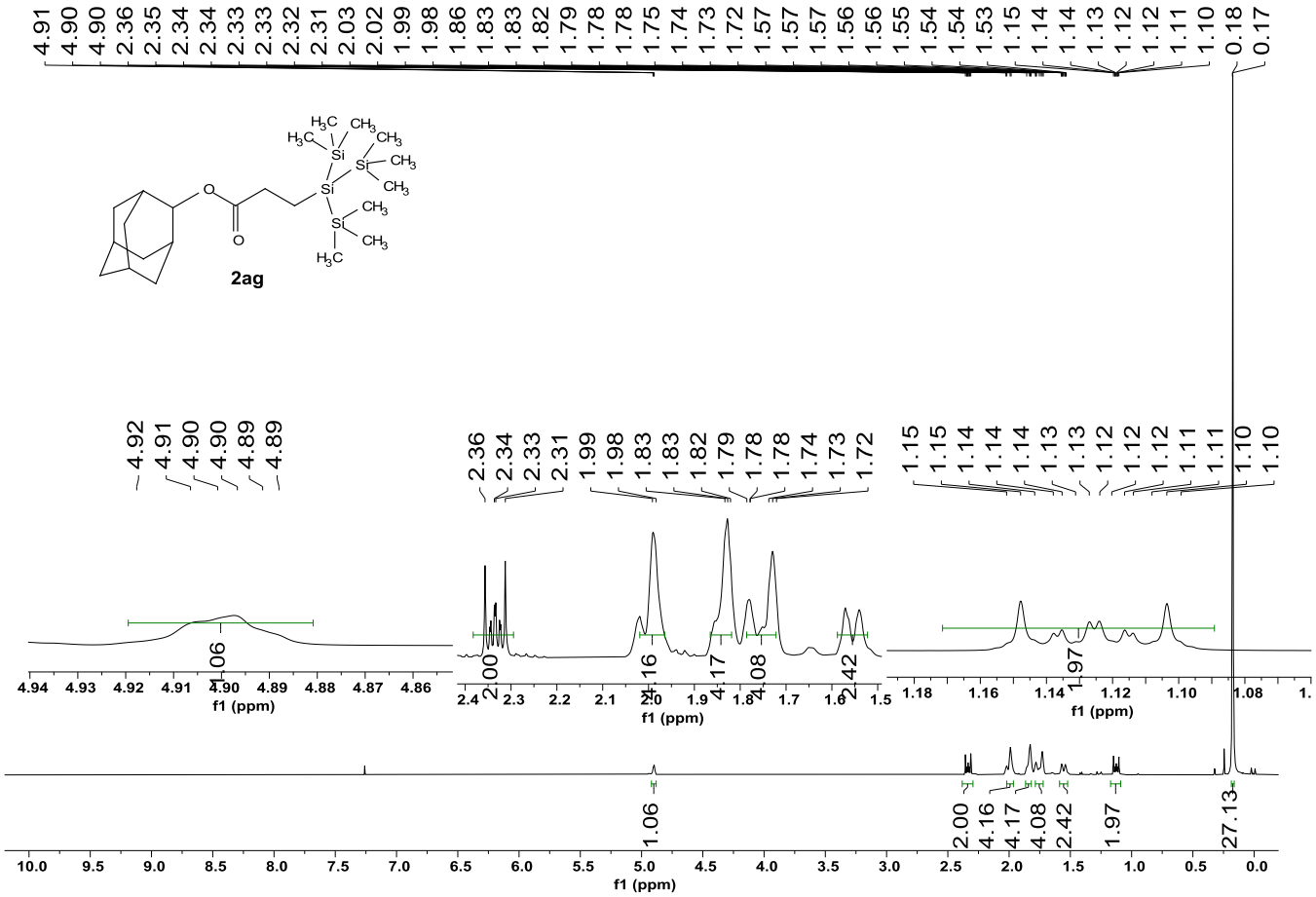
^{1}H NMR spectrum of compound **2af** (400 MHz, $CDCl_3$)



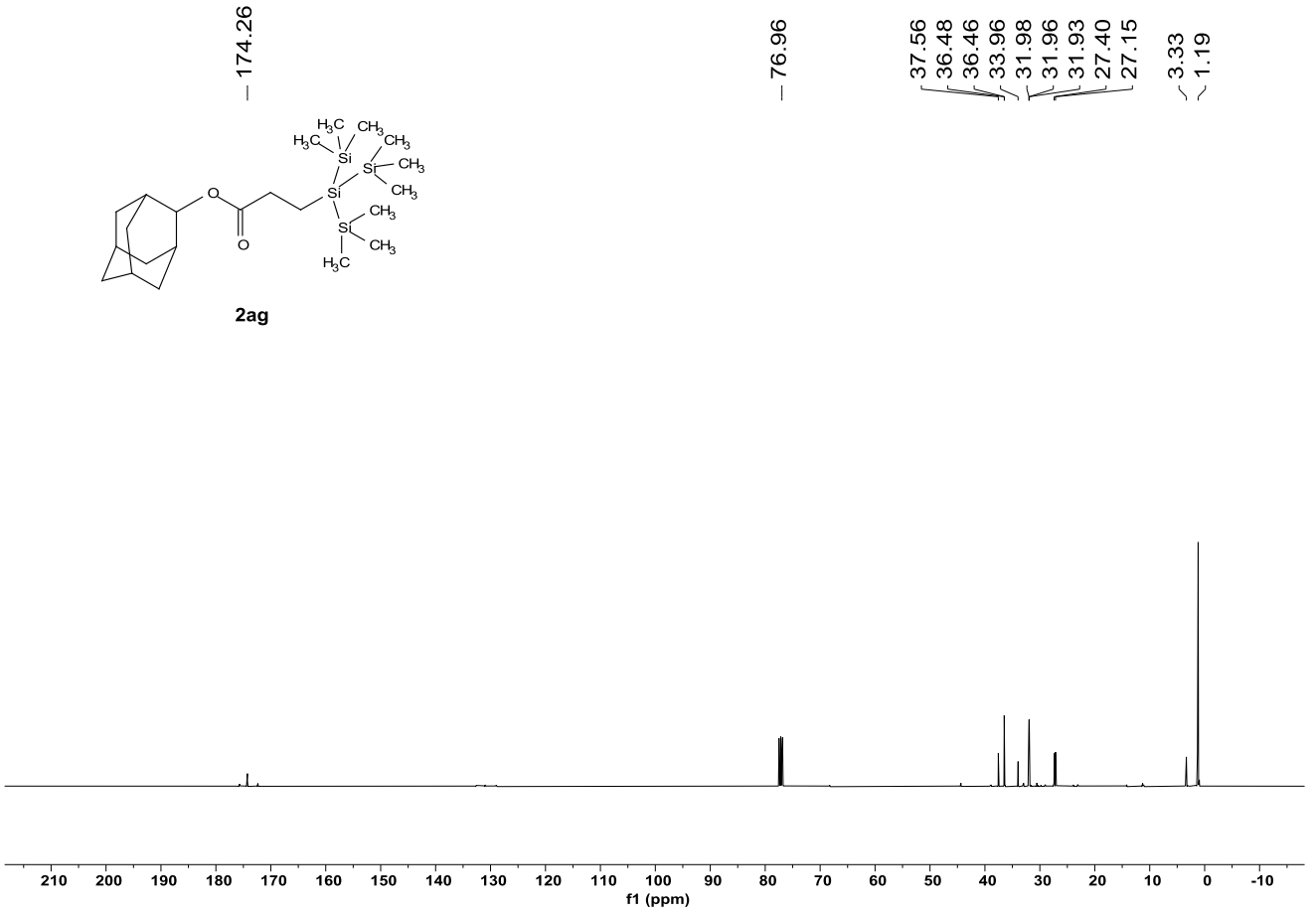
^{13}C NMR spectrum of compound **2af** (101 MHz, $CDCl_3$)



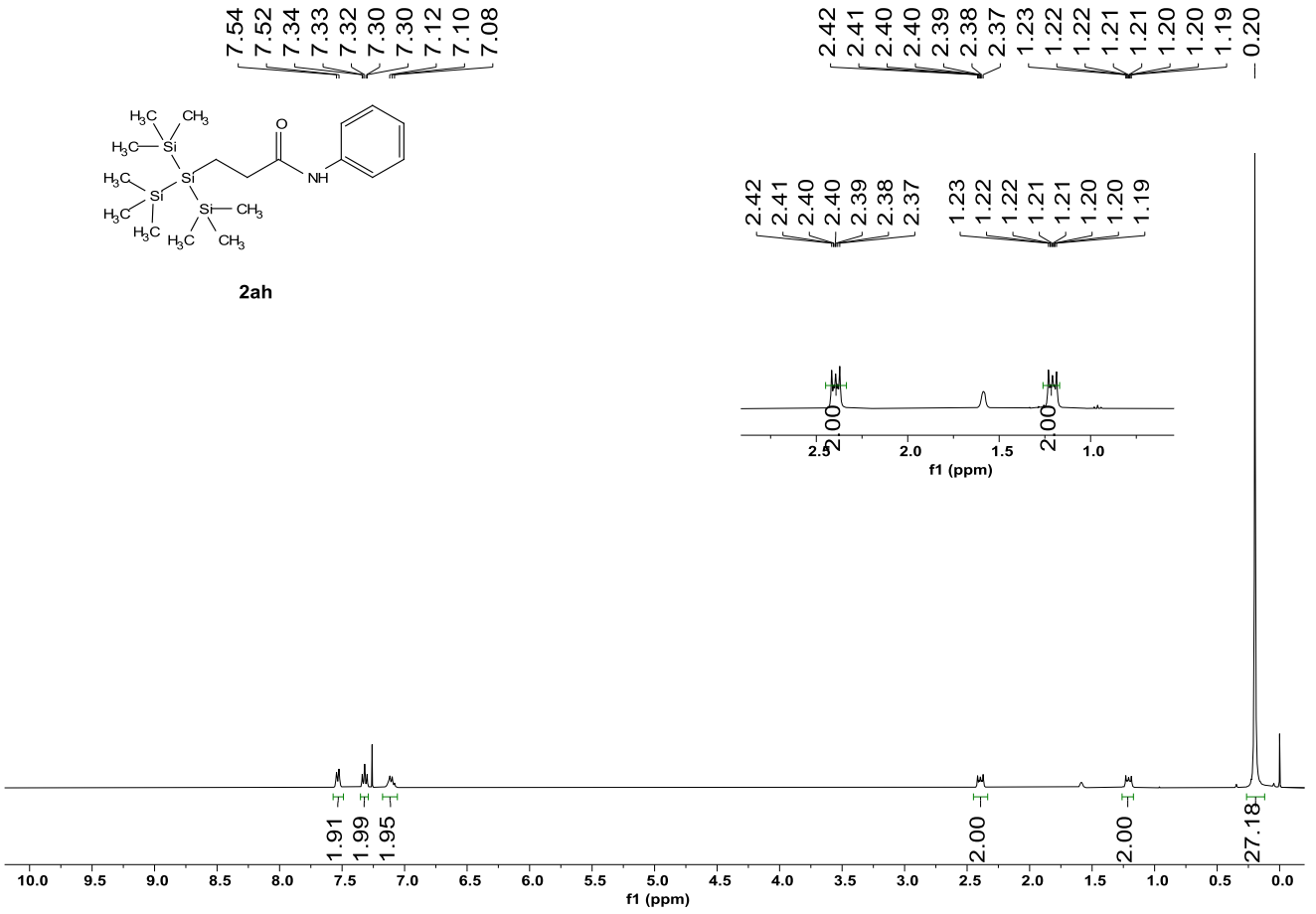
^{1}H NMR spectrum of compound **2ag** (400 MHz, $CDCl_3$)



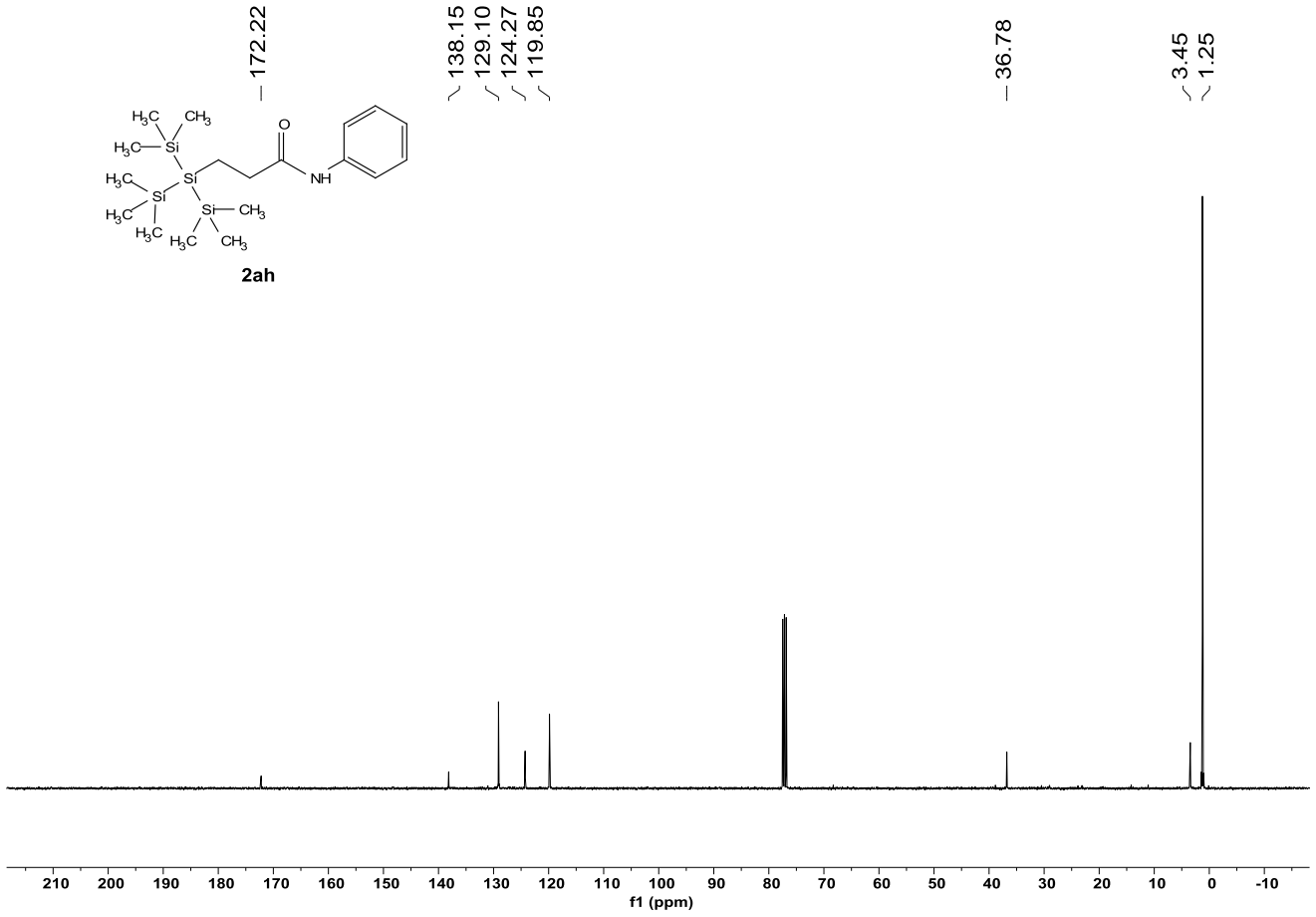
^{13}C NMR spectrum of compound **2ag** (101 MHz, $CDCl_3$)



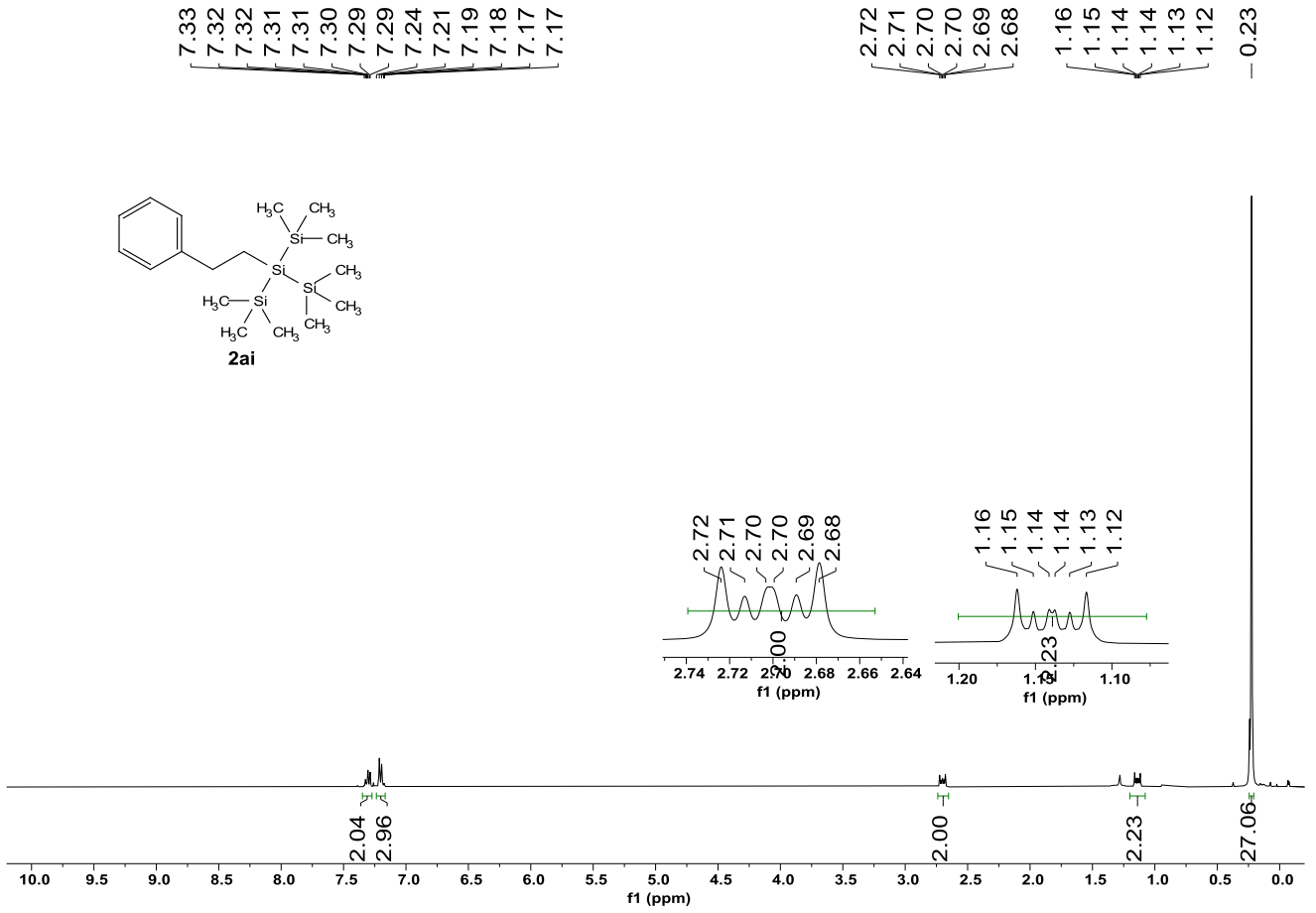
^{1}H NMR spectrum of compound **2ah** (400 MHz, $CDCl_3$)



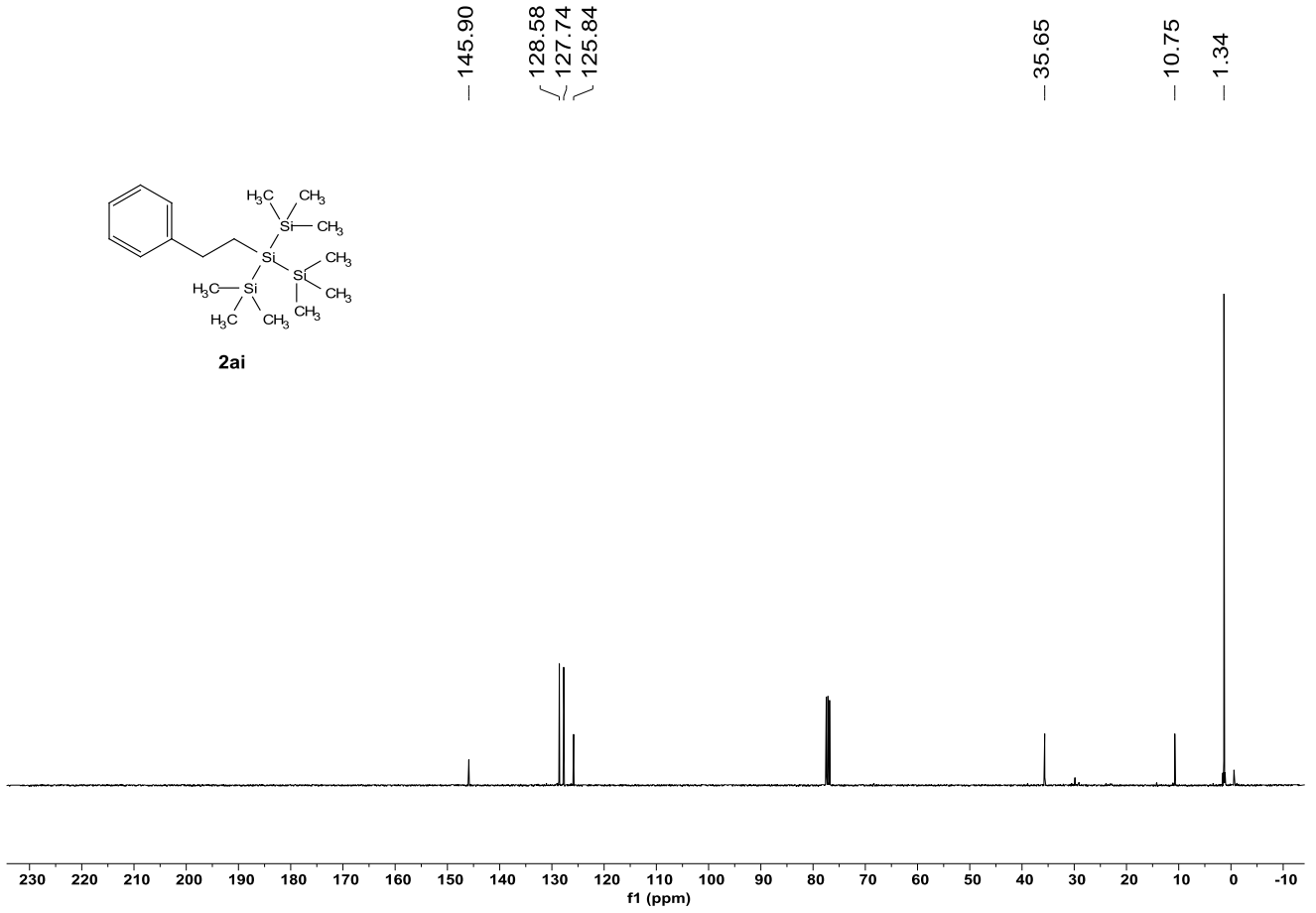
^{13}C NMR spectrum of compound **2ah** (101 MHz, $CDCl_3$)



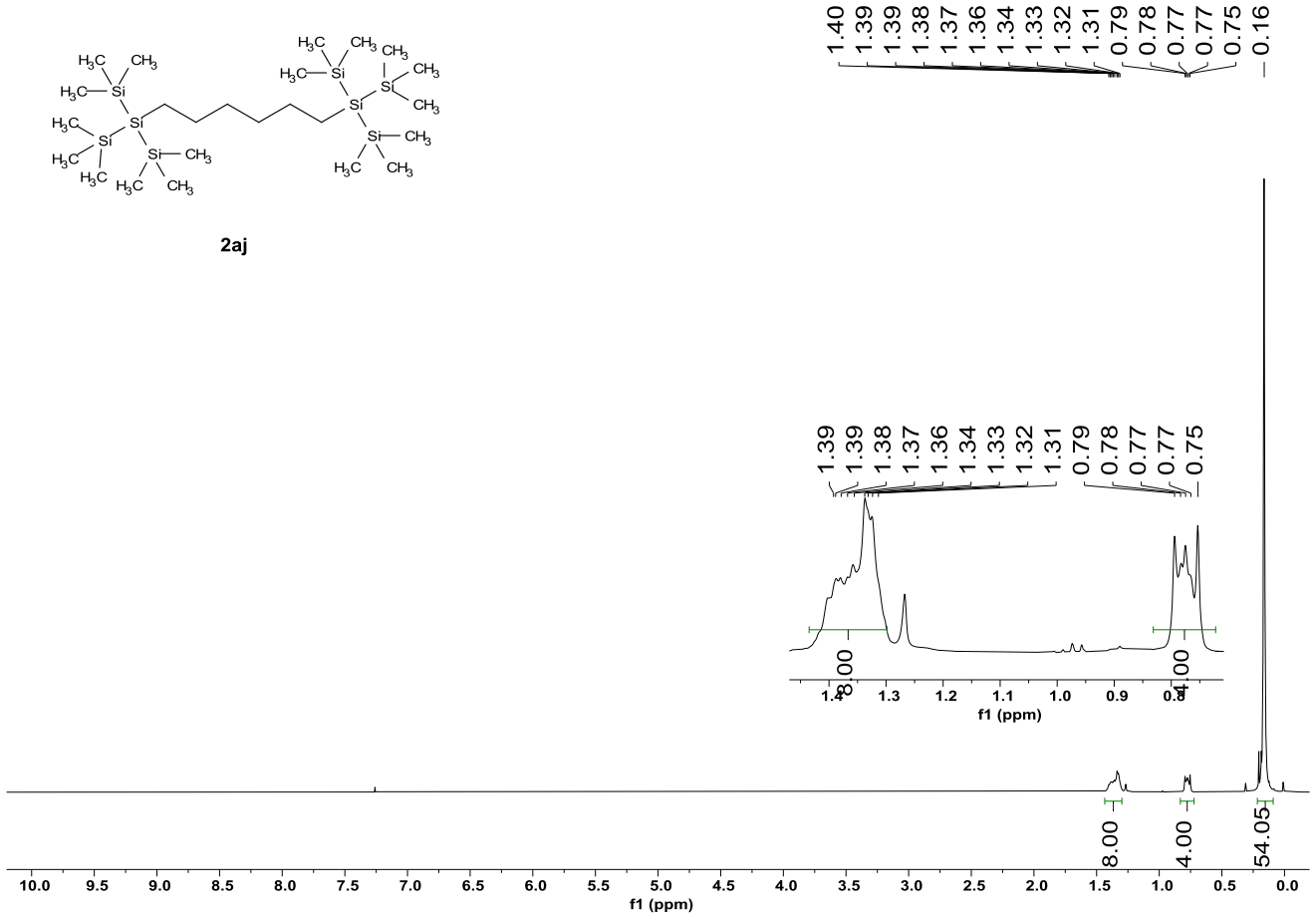
^{1}H NMR spectrum of compound **2ai** (400 MHz, $CDCl_3$)



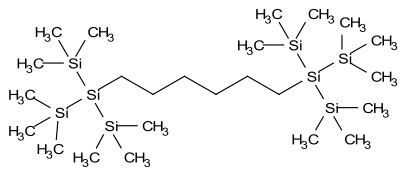
^{13}C NMR spectrum of compound **2ai** (101 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **2aj** (400 MHz, $CDCl_3$)

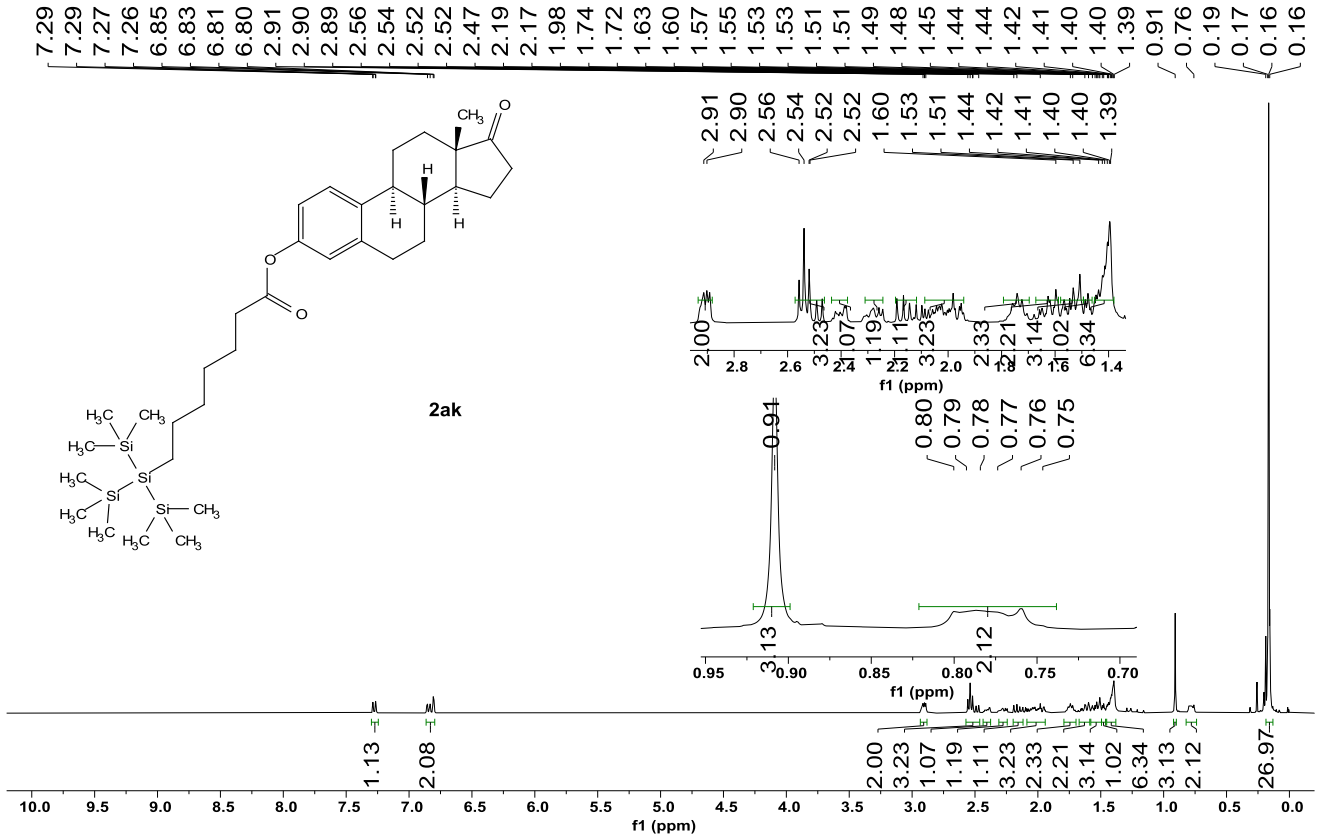


^{13}C NMR spectrum of compound **2aj** (101 MHz, $CDCl_3$)

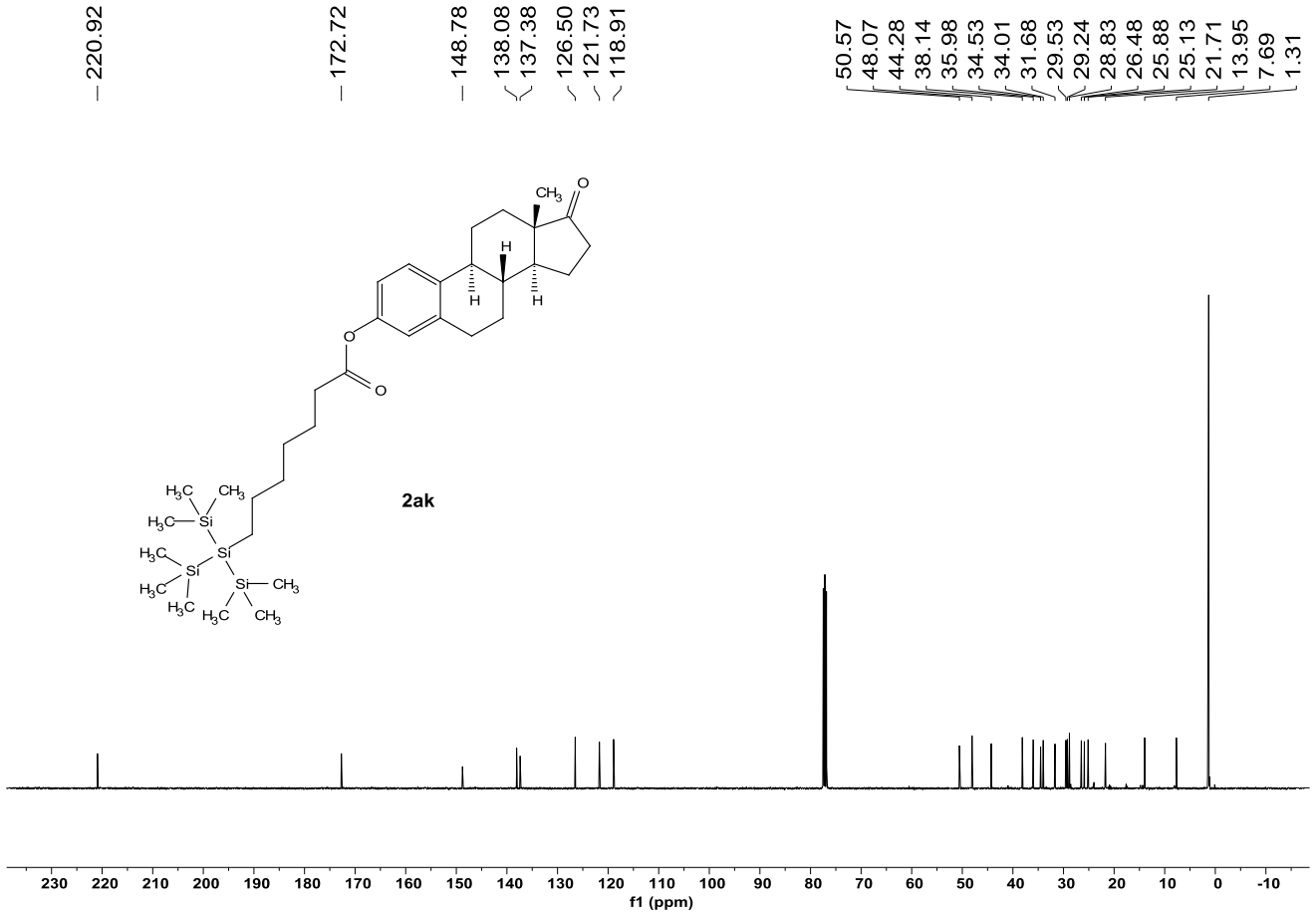


2aj

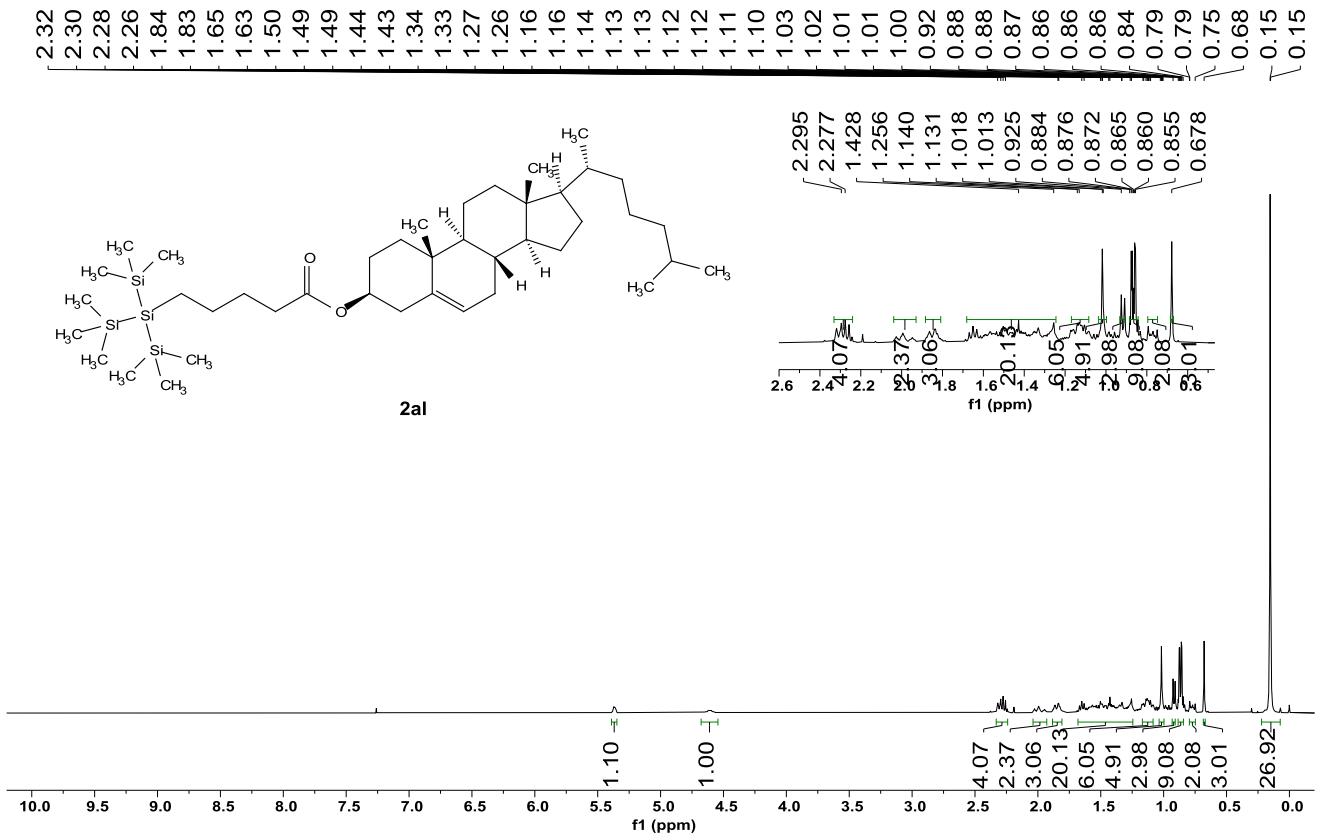
^{1}H NMR spectrum of compound **2ak** (400 MHz, $CDCl_3$)



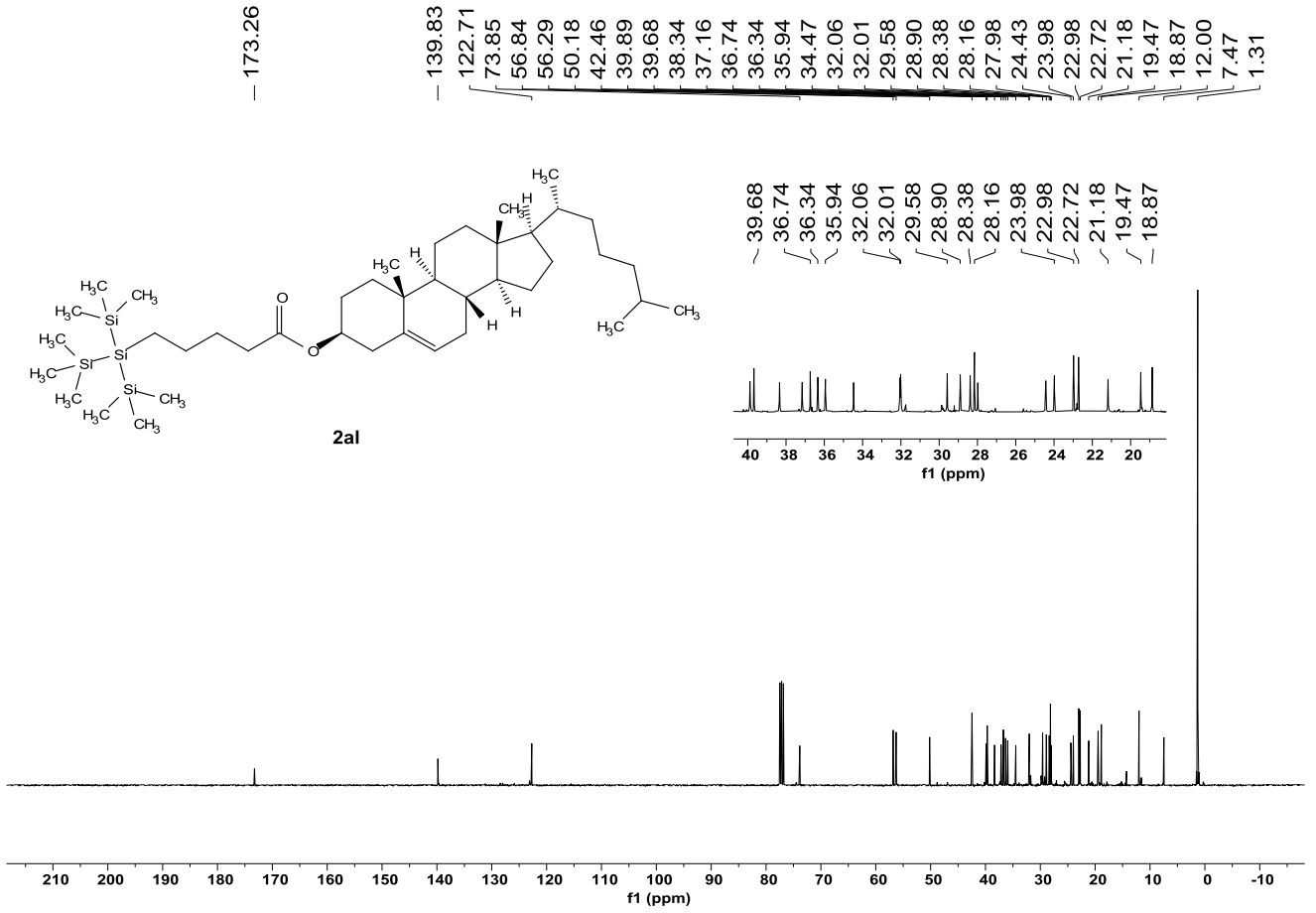
^{13}C NMR spectrum of compound **2ak** (101 MHz, $CDCl_3$)



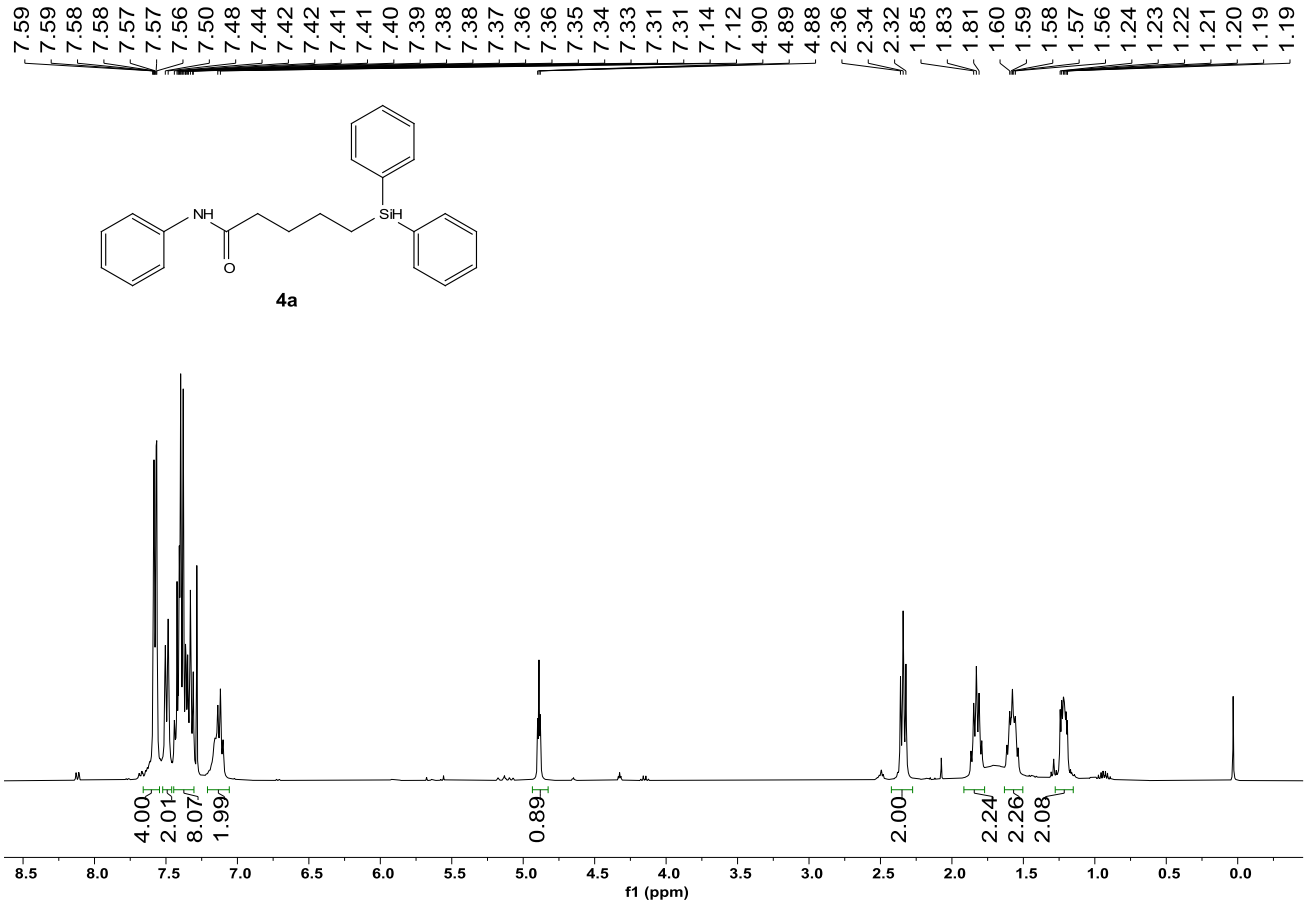
^{1}H NMR spectrum of compound **2al** (400 MHz, $CDCl_3$)



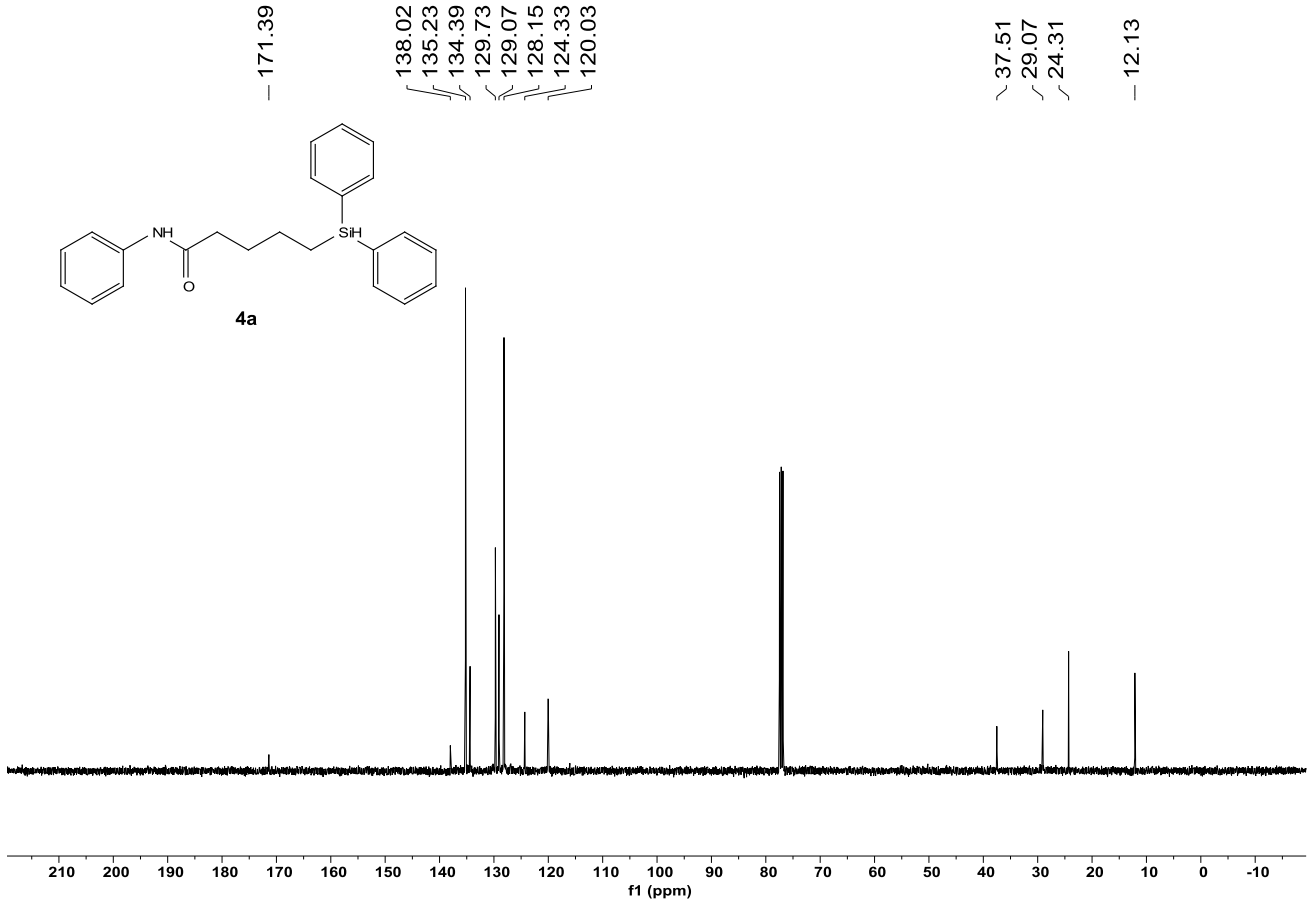
^{13}C NMR spectrum of compound **2al** (101 MHz, $CDCl_3$)



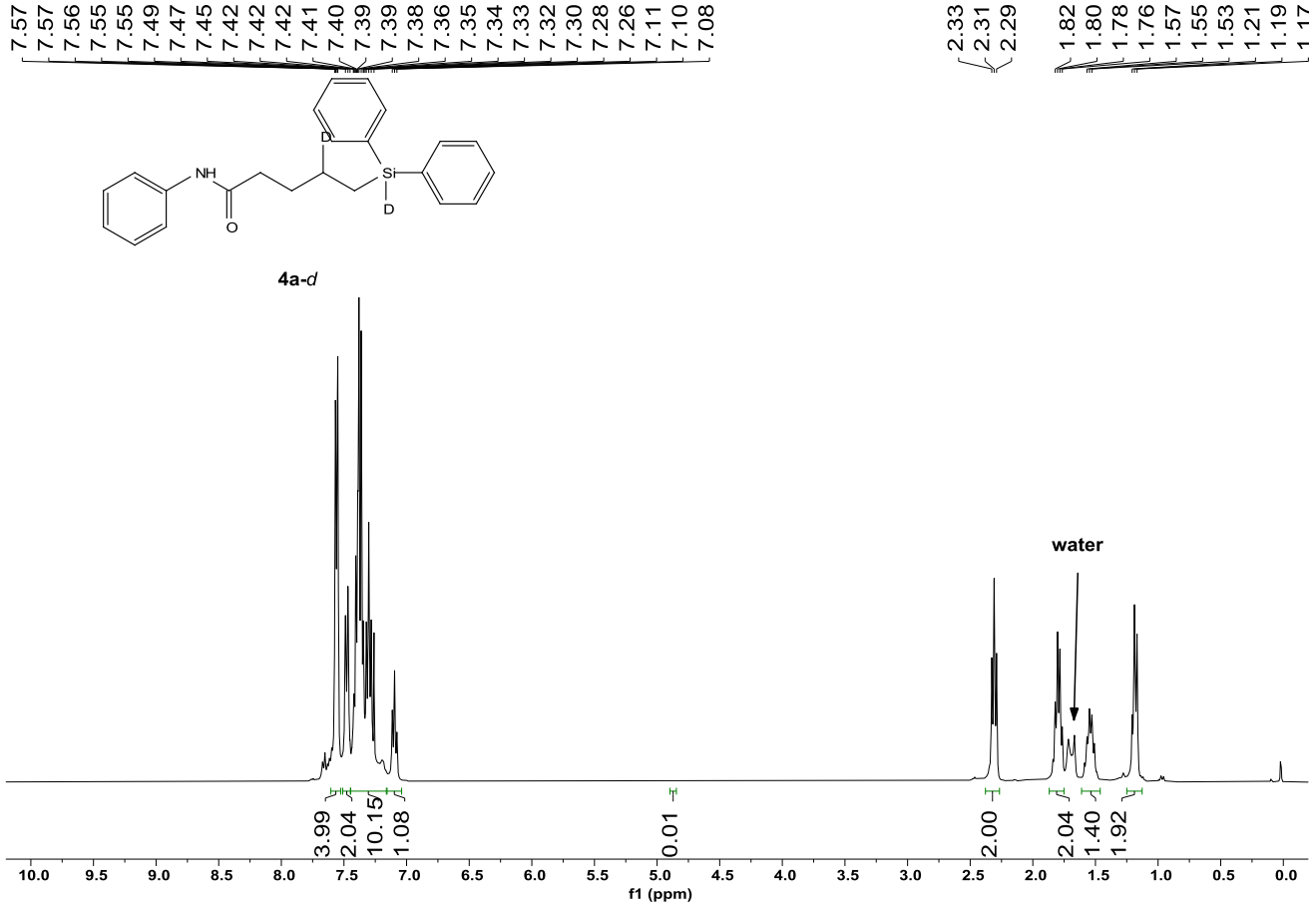
^{1}H NMR spectrum of compound **4a** (400 MHz, $CDCl_3$)



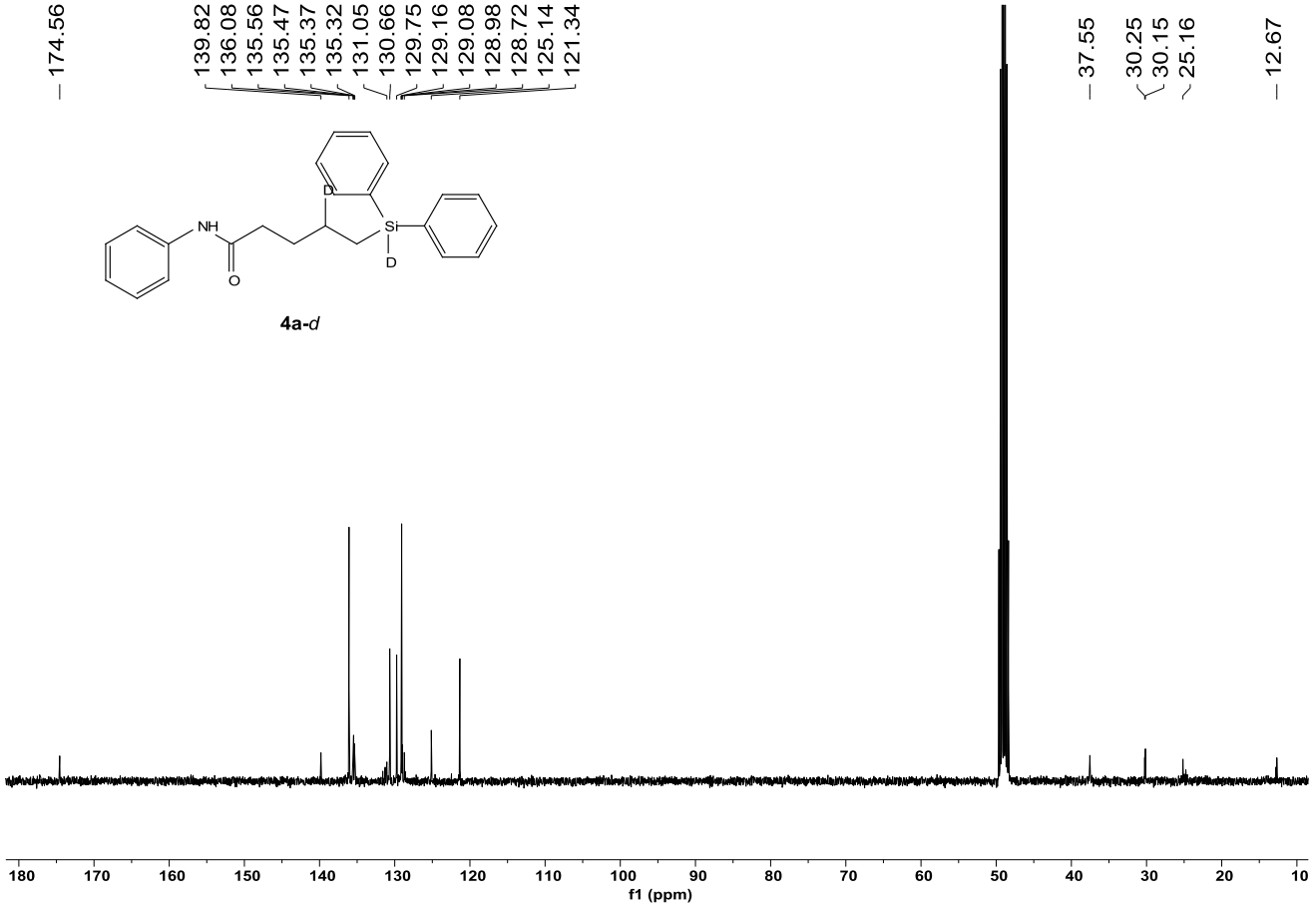
^{13}C NMR spectrum of compound **4a** (101 MHz, $CDCl_3$)



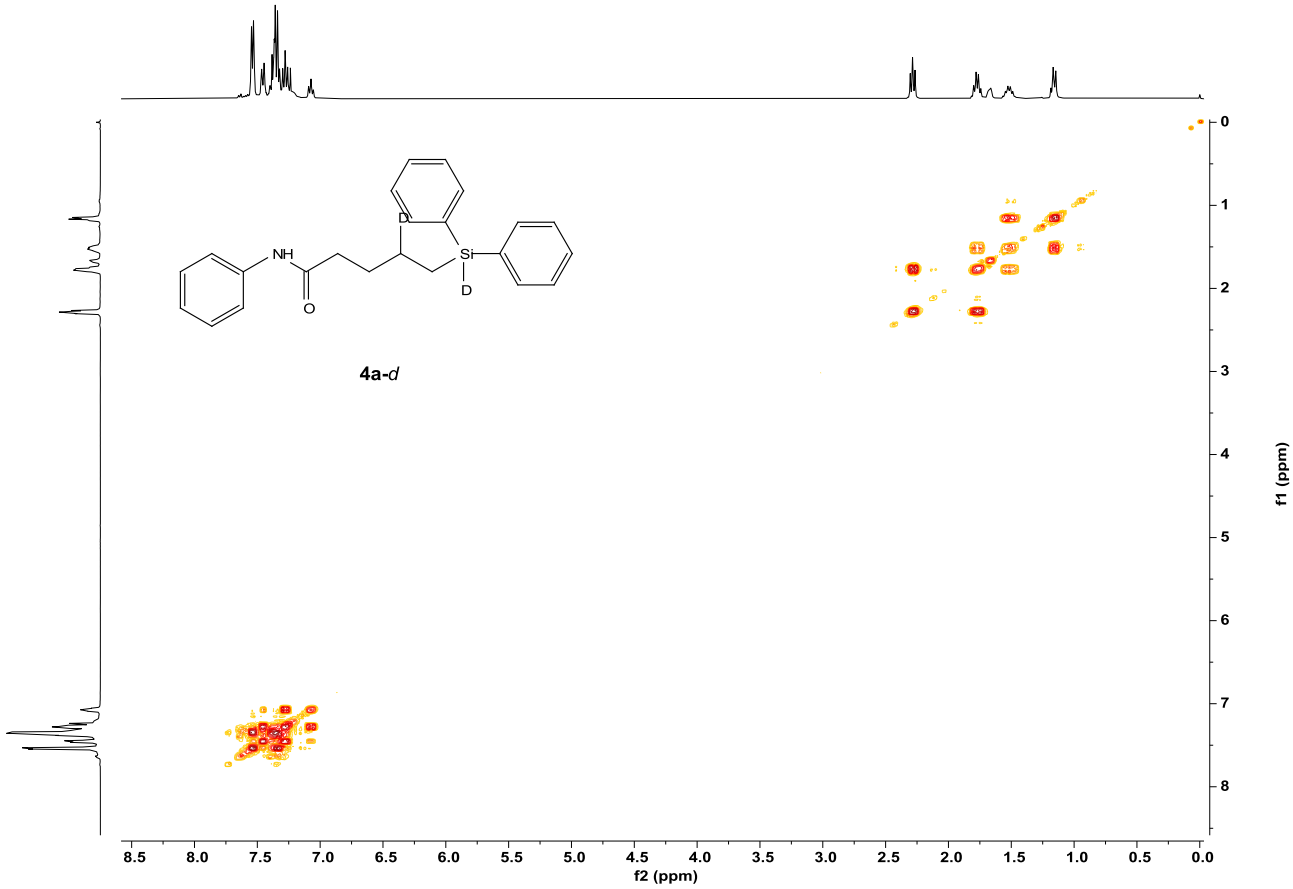
^{1}H NMR spectrum of compound **4a**-*d* (400 MHz, $CDCl_3$)



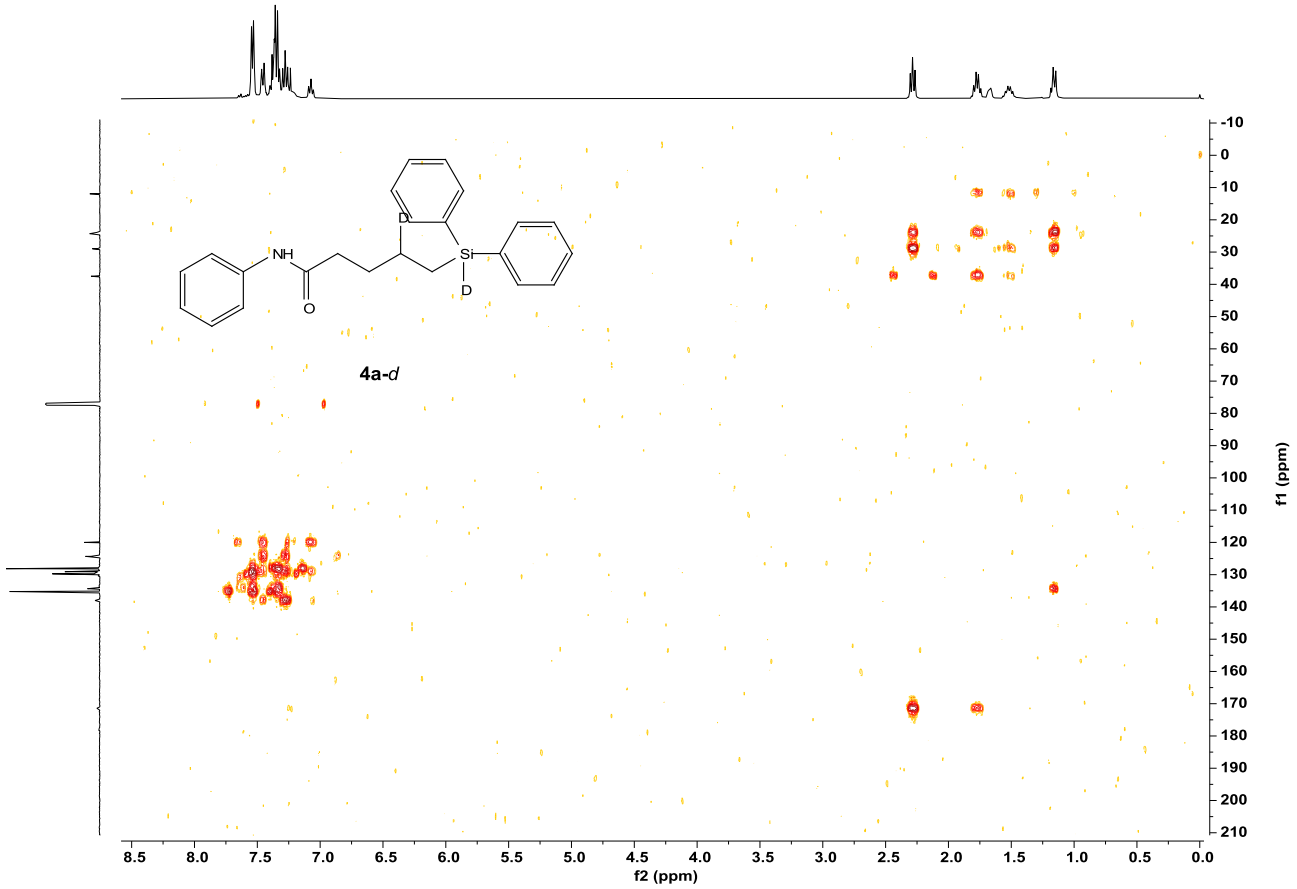
^{13}C NMR spectrum of compound **4a**-*d* ($CDCl_3$)



COSY spectrum of compound **4a**-*d* (101 MHz, $CDCl_3$)



HMBC spectrum of compound **4a**-*d* (101 MHz, $CDCl_3$)



HSQC spectrum of compound **4a**-*d* (101 MHz, $CDCl_3$)