Cyclohexa-1,3-diene-based dihydrogen and hydrosilane surrogates in $B(C_6F_5)_3$-catalysed transfer processes

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Electronic Supplementary Information

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1 General Information

Reactions were performed in flame-dried glassware using an *MBraun* glovebox or conventional Schlenk techniques under a static pressure of nitrogen unless otherwise stated. Tris(pentafluorophenyl)borane was purchased from *Boulder Scientific Company* and sublimed before use. 1,3-Cyclohexadiene (**2a**), 1-methoxy-1,3-cyclohexadiene (**2d**), *α*-phellandrene (**2e**), *α*-terpinene (**2f**), and 1,1-diphenylethylene (**5**) were purchased from commercial suppliers and used without further purification. 1-Methyl-1,3-cyclohexadiene (**2b**),[S1,S2] 1,5-dimethyl-1,3-cyclohexadiene (**2c**),[S1,S2] 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (**23**),[S3,S4] as well as various alkenes (**1**; **6**–**13**; **25**–**34**)[S5,S6] were prepared according to reported procedures. Technical grade solvents for extraction or chromatography (*n*-pentane, and dichloromethane) were distilled prior to use. $CDCl_3$ and C_6D_6 were stored over 4Å molecular sieves under an inert atmosphere. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by *Merck* using the indicated solvents. ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded in either $CDCl_3$ or C_6D_6 on a *Bruker* AV500 and *Bruker* AV400 instrument, respectively. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H NMR and $CDCl_3$: δ = 77.16 ppm for ^{13}C NMR; C_6D_5H: δ = 7.16 ppm for ^{1}H NMR and C_6D_6: δ = 128.06 ppm for ^{13}C NMR). ^{19}F and ^{29}Si NMR chemical shifts are referenced in compliance with the unified scale as recommended by the IUPAC stating the chemical shift relative to CCl_3F and Me_4Si.[S7] Dibromomethane was used as an internal standard to calculate NMR yields. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), and integration. High-resolution mass spectrometry (HRMS) was performed at the Analytical Facility of the Institut für Chemie, Technische Universität Berlin.

2 General Procedure for the $B(C_6F_5)_3$-Catalysed Transfer Hydrogenation (GP1)

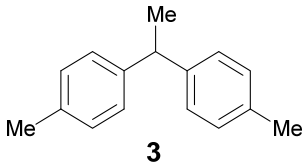
In a glovebox, an oven-dried 2-mL GLC-vial equipped with a magnetic stir bar is charged with *α*-terpinene (39.0 mg, 0.26 mmol, 1.3 equiv, 90% purity) and the alkene substrate (0.20 mmol, 1.0 equiv). A solution of tris(pentafluorophenyl)borane (10.2 mg, 20.0 µmol, 10.0 mol%) in CH_2Cl_2 (0.2 mL, 1.0 M) is added, and the resulting mixture is stirred for 16 hours at room temperature. The reaction mixture is then transferred outside the glovebox and passed through a plug of silica gel using CH_2Cl_2 as eluent. After removal of all volatiles under reduced pressure, the residue is subjected to NMR spectroscopic analysis using dibromomethane as internal standard. The analytically pure transfer hydrogenation product is obtained after flash column chromatography on silica gel using *n*-pentane as eluent.

3 General Procedure for the $B(C_6F_5)_3$-Catalysed Transfer Hydrosilylation (GP2)

In a glovebox, an oven-dried 1-mL sealed tube equipped with a magnetic stir bar is charged with cyclohexa-2,4-dien-1-yltrimethylsilane (20.0 mg, 0.13 mmol, 1.3 equiv) and the alkene substrate (0.1 mmol, 1.0 equiv). A solution of tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) in toluene (0.1 mL, 1.0 M) is added, and the resulting mixture is stirred at 50 °C for 23 hours outside the glovebox. The reaction mixture is then passed through a plug of silica gel using *n*-pentane as eluent. After removal of all volatiles under reduced pressure, the residue is subjected to NMR spectroscopic analysis using dibromomethane as internal standard. Following this procedure, the transfer hydrosilylation products are generally obtained in analytically pure form, not requiring further purification.

4 Characterisation Data of the Transfer Hydrogenation Products

4.1 4,4'-(Ethane-1,1-diyl)bis(methylbenzene) (3)



3

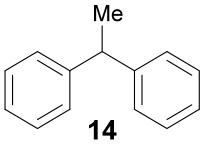
$C_{16}H_{18}$

M = 210.32 g/mol

Prepared from 4,4'-(ethene-1,1-diyl)bis(methylbenzene) **1** (41.7 mg, 0.2 mmol, 1.0 equiv), *α*-terpinene (39 mg, 0.26 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (10.2 mg, 20.0 µmol, 10.0 mol%) according to **GP1**. The title compound **3** (37.0 mg, 88%) was obtained as a colorless oil.

HRMS (APCI) for $C_{16}H_{19}$ [$(M+H)^+$]: calculated 211.1481, found 211.1436. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.63 (d, *J* = 7.2 Hz, 3H), 2.32 (s, 6H), 4.15 (q, *J* = 7.2 Hz, 1H), 7.08–7.16 (m, 8H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 21.1, 22.1, 44.1, 126.1, 127.5, 129.1, 135.5, 143.7 ppm. The spectroscopic data are in accordance with those reported.[S8]

4.2 Ethane-1,1-diyldibenzene (14)



14

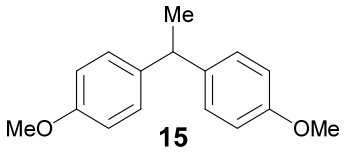
$C_{14}H_{14}$

M = 182.27 g/mol

Prepared from ethene-1,1-diyldibenzene **5** (36.0 mg, 0.2 mmol, 1.0 equiv), *α*-terpinene (39.0 mg, 0.26 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (10.2 mg, 20.0 µmol, 10.0 mol%) according to **GP1**. The title compound **14** (33.5 mg, 92%) was obtained as a colorless oil.

HRMS (APCI) for $C_{14}H_{15}$ [$(M+H)^+$]: calculated 183.1168, found 183.1171. **^{1}H NMR** (400 MHz, $CDCl_3$) : δ = 1.63 (d, *J* = 7.2 Hz, 3H), 4.13 (q, *J* = 7.2 Hz, 1H), 7.13–7.18 (m, 2H), 7.18–7.22 (m, 4H), 7.23–7.28 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 21.9, 44.8, 126.1, 127.7, 128.4, 146.4 ppm. The spectroscopic data are in accordance with those reported.[S8]

4.3 4,4'-(Ethane-1,1-diyl)bis(methoxybenzene) (15)



15

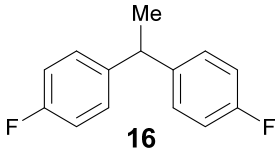
$C_{16}H_{18}O_2$

M = 242.32 g/mol

Prepared from 4,4'-(ethene-1,1-diyl)bis(methoxybenzene) **6** (48.0 mg, 0.2 mmol, 1.0 equiv), *α*-terpinene (39.0 mg, 0.26 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (10.2 mg, 20.0 µmol, 10.0 mol%) according to **GP1**. The title compound **15** (47.5 mg, 98%) was obtained as a yellow oil.

HRMS (APCI) for $C_{16}H_{19}O_2$ [$(M+H)^+$]: calculated 243.1380, found 243.1367. **^{1}H NMR** (500 MHz, $CDCl_3$) : δ = 1.58 (d, *J* = 7.2 Hz, 3H), 3.77 (s, 6H), 4.06 (q, *J* = 7.2 Hz, 1H), 6.80–6.83 (m, 4H), 7.09–7.14 (m, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 22.3, 43.2, 55.3, 113.8, 128.5, 139.1, 157.9 ppm. The spectroscopic data are in accordance with those reported. [S9]

4.4 4,4'-(Ethane-1,1-diyl)bis(fluorobenzene) (16)



16

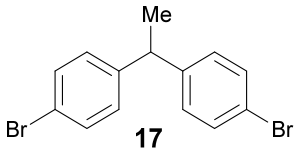
$C_{14}H_{12}F_2$

M = 218.25 g/mol

Prepared from 4,4'-(ethene-1,1-diyl)bis(fluorobenzene) **7** (43.2 mg, 0.2 mmol, 1.0 equiv), *α*-terpinene (39.0 mg, 0.26 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (10.2 mg, 20.0 µmol, 10.0 mol%) according to the **GP1**. The reaction was performed in 1,2–difluorobenzene for 16 h at 50 °C. The title compound **16** (36.7 mg, 84%) was obtained as a colorless oil.

HRMS (APCI) for $C_{14}H_{13}F_2$ [$(M+H)^+$]: calculated 219.0980, found 219.1009. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.60 (d, *J* = 7.2 Hz, 3H), 4.12 (q, *J* = 7.2 Hz, 1H), 6.94–7.00 (m, 4H), 7.10–7.18 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 22.3, 43.4, 115.3 (d, $J_{C,F}$ = 21.4 Hz), 129.1 (d, $J_{C,F}$ = 7.9 Hz), 142.0 (d, $J_{C,F}$ = 3.1 Hz), 161.5 (d, $J_{C,F}$ = 244.4 Hz) ppm.**^{19}F NMR** (471 MHz, $CDCl_3$): δ = –117.2 ppm. The spectroscopic data are in accordance with those reported.[S8]

4.5 4,4'-(Ethane-1,1-diyl)bis(bromobenzene) (17)



17

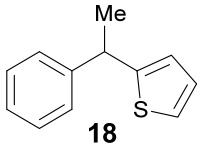
$C_{14}H_{12}Br_2$

M = 340.06 g/mol

Prepared from 4,4'-(ethene-1,1-diyl)bis(bromobenzene) **8** (67.2 mg, 0.2 mmol, 1.0 equiv), *α*-terpinene (39.0 mg, 0.26 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (10.2 mg, 20.0 µmol, 10.0 mol%) according to the **GP1**. The reaction was performed in 1,2–difluorobenzene for 16 h at 50 °C. The title compound **17** (38.8 mg, 57%) was obtained as a colorless oil.

HRMS (APCI) for $C_{14}H_{12}Br_2$ [M^+]: calculated 337.9300, found 337.9293. **^{1}H NMR** (400 MHz, $CDCl_3$) : δ = 1.57 (d, *J* = 7.2 Hz, 3H), 4.08 (q, *J* = 7.2 Hz, 1H), 7.07–7.24 (m, 8H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 22.0, 44.9, 126.1, 127.8, 128.5, 146.5 ppm.

4.6 3-(1-Phenylethyl)thiophene (18)



18

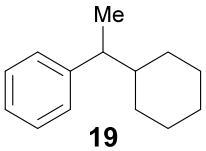
$C_{12}H_{12}S$

M = 188.29 g/mol

Prepared from 3-(1-phenylvinyl)thiophene **9** (37.5 mg, 0.2 mmol, 1.0 equiv), *α*-terpinene (39.0 mg, 0.26 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (10.2 mg, 20.0 µmol, 10.0 mol%) according to the **GP1**. The title compound **18** (15.4 mg, 41%) was obtained as a colorless oil.

HRMS (APCI) for $C_{12}H_{13}S$ [$(M+H)^+$]: calculated 189.0732, found 189.0733. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.75 (d, *J* = 7.2 Hz, 3H), 4.39 (q, *J* = 7.2 Hz, 1H), 6.85 (dt, *J* = 3.4, 1.0 Hz, 1H), 6.97 (dd, *J* = 5.2, 3.5 Hz, 1H), 7.19 (dd, *J* = 5.2, 1.3 Hz, 1H), 7.21–7.38 (m, 5H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 23.4, 40.8, 123.6, 123.7, 126.6 (2C overlapped), 127.4, 128.6, 146.1, 150.8 ppm. The spectroscopic data are in accordance with those reported.[S8]

4.7 (1-Cyclohexylethyl)benzene (19)



19

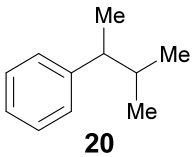
$C_{14}H_{20}$

M = 188.31 g/mol

Prepared from (1-cyclohexylvinyl)benzene **10** (37.2 mg, 0.2 mmol, 1.0 equiv), *α*-terpinene (39.0 mg, 0.26 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (10.2 mg, 20.0 µmol, 10.0 mol%) according to the **GP1**. The title compound **19** (33.9 mg, 90%) was obtained as a colorless oil.

HRMS (APCI) for $C_{14}H_{21}$ [$(M+H)^+$]: calculated 189.1638, found 189.1603. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 0.70–0.91 (m, 3H), 0.97–1.07 (m, 2H), 1.15 (d, *J* = 7.2 Hz, 3H), 1.26–1.39 (m, 2H), 1.49–1.58 (m, 2H), 1.62–1.70 (m, 1H),1.78–1.81 (m, 1H), 2.36 (p, *J* = 7.2 Hz, 1H), 7.04–7.12 (m, 3H), 7.17–7.22 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 19.0, 26.8, 30.7, 31.6, 44.3, 46.1, 125.8, 127.9, 128.1, 147.3 ppm. The spectroscopic data are in accordance with those reported.[S8]

4.8 (3-Methylbutan-2-yl)benzene (20)



20

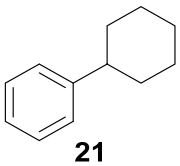
$C_{11}H_{16}$

M = 148.25 g/mol

Prepared from (3-methylbut-1-en-2-yl)benzene **11** (29.0 mg, 0.2 mmol, 1.0 equiv), *α*-terpinene (39.0 mg, 0.26 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (10.2 mg, 20.0 µmol, 10.0 mol%) according to **GP1**. The title compound **20** was obtained as yellow oil (90% NMR yield). Further purification was hampered by the volatility of this compound.

The spectroscopic data are in accordance with those reported.[S10]

4.9 Cyclohexylbenzene (21)



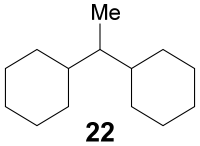
21

$C_{12}H_{16}$

M = 160.26 g/mol

Prepared from 2,3,4,5–tetrahydro–1,1´–biphenyl **12** (32.0 mg, 0.2 mmol, 1.0 equiv), *α*-terpinene (39.0 mg, 0.26 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (10.2 mg, 20.0 µmol, 10.0 mol%) according to the **GP1**. The NMR yield of alkane **21** was (36%). The crude NMR was compared with the reported one.[S11]

4.10 Ethane-1,1-diyldicyclohexane (22)



22

$C_{14}H_{26}$

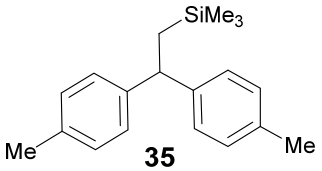
M = 194.36 g/mol

Prepared from ethene-1,1-diyldicyclohexane **13** (38.5 mg, 0.2 mmol, 1.0 equiv), *α*-terpinene (39.0 mg, 0.26 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (10.2 mg, 20.0 µmol, 10.0 mol%) according to the **GP1**. The reaction was performed in 1,2–difluorobenzene for 16 h at 50 °C. The title compound **22** (27.2 mg, 70%) was obtained as a colorless oil.

HRMS (APCI) for $C_{14}H_{26}$ [M^+]: calculated 194.2029, found 194.2027. **^{1}H NMR** (400 MHz, $CDCl_3$) : δ = 0.75 (d, *J* = 7.2 Hz, 3H), 0.81–0.93 (m, 3H), 1.00–1.14 (m, 4H), 1.16–1.19 (m, 1H), 1.20–1.22 (m, 1H), 1.24–1.31 (m, 2H), 1.52–1.58 (m, 3H), 1.59–1.63 (m, 5H), 1.68–1.75 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 12.2, 26.8, 26.9, 28.9, 32.0, 39.6 ppm. The spectroscopic data are in accordance with those reported. [S11]

5 Characterisation Data of the Transfer Hydrosilylation Products

5.1 (2,2-Di-*p*-tolylethyl)trimethylsilane (35)

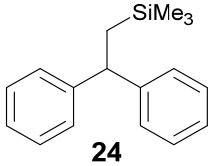


35
$C_{19}H_{26}Si$
M = 282.50 g/mol

Prepared from 4,4'-(ethene-1,1-diyl)bis(methylbenzene) **1** (20.8 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **35** (24.9 mg, 88%) was obtained as a colorless oil.

HRMS (EI) for $C_{19}H_{26}Si$ [M^+]: calculated 282.1798, found 282.1804. **^{1}H NMR** (400 MHz, C_6D_6): δ = –0.10 (s, 9H), 1.36 (d, *J* = 8.0 Hz, 2H), 2.12 (br s, 6H), 4.05 (t, *J* = 7.7 Hz, 1H), 6.96–7.00 (m, 4H), 7.16–7.20 (m, 4H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –1.0, 21.0, 24.4, 47.0, 127.9, 129.3, 135.4, 144.9 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = 0.62 ppm.

5.2 (2,2-Diphenylethyl)trimethylsilane (24)

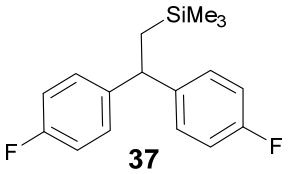


24
$C_{17}H_{22}Si$
M = 254.45 g/mol

Prepared from ethene-1,1-diyldibenzene **5** (18.0 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **24** (21.9 mg, 86%) was obtained as a colorless oil.

HRMS (EI) for $C_{17}H_{22}Si$ [M^+]: calculated 254.1485, found 254.1489. **^{1}H NMR** (400 MHz, C_6D_6): δ = –0.11 (s, 9H), 1.33 (d, *J* = 7.7 Hz, 2H), 4.05 (t, *J* = 7.7 Hz, 1H), 7.03–7.07 (m, 2H), 7.13–7.18 (m, 4H), 7.20–7.24 (m, 4H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –1.1, 24.3, 47.7, 126.3, 128.0, 128.6, 147.4 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = 0.62 ppm. The spectroscopic data are in accordance with those reported.[S12]

5.3 (2,2-Bis(4-fluorophenyl)ethyl)trimethylsilane (37)



37

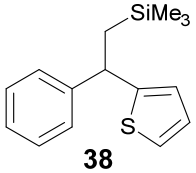
$C_{17}H_{20}F_2Si$

M = 290.43 g/mol

Prepared from 4,4'-(ethene-1,1-diyl)bis(fluorobenzene) **7** (21.6 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **37** (23.2 mg, 80%) was obtained as a colorless oil.

HRMS (APCI) for $C_{16}H_{17}F_2Si$ [$(M–CH_3)^+$]: calculated 275.1068, found 275.1066. **^{1}H NMR** (400 MHz, C_6D_6): δ = –0.20 (s, 9H), 1.07 (d, *J* = 7.7 Hz, 2H), 3.78 (t, *J* = 7.7 Hz, 1H), 6.79–6.80 (m, 4H), 6.81–6.87 (m, 4H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –1.2, 24.4, 46.0, 115.3 (d, $J_{C,F}$ = 21.4 Hz), 129.2 (d, $J_{C,F}$ = 7.5 Hz), 142.9 (d, $J_{C,F}$ = 2.7 Hz), 162.8 (d, $J_{C,F}$ = 244.2 Hz) ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –117.0 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = 0.46 ppm.

5.4 Trimethyl(2-phenyl-2-(thiophen-3-yl)ethyl)silane (38)



38

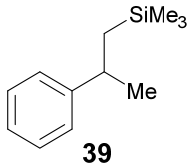
$C_{15}H_{20}SSi$

M = 260.47 g/mol

Prepared from 2-(1-phenylvinyl)thiophene **9** (18.2 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **38** (11.7 mg, 45%) was obtained as a colorless oil.

HRMS (EI) for $C_{15}H_{20}SSi$ [M^+]: calculated 260.1049, found 260.1048. **^{1}H NMR** (500 MHz, C_6D_6): δ = –0.17 (s, 9H), 1.36 (dd, *J* = 14.6, 9.0 Hz, 1H), 1.44 (dd, *J* = 14.6, 7.5 Hz, 1H), 4.24 (t, *J* = 7.1 Hz, 1H), 6.69–6.72 (m, 2H), 6.99–7.03 (m, 1H), 7.08–7.12 (m, 3H), 7.18–7.21 (m, 2H) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ = –1.2, 26.5, 43.4, 123.6, 123.7, 126.6, 126.7, 128.3, 128.8, 146.9, 152.8 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = 0.47 ppm.

5.5 Trimethyl(2-phenylpropyl)silane (39)



39

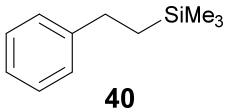
$C_{12}H_{20}Si$

M = 192.38 g/mol

Prepared from prop-1-en-2-ylbenzene **25** (11.8 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **39** (18.8 mg, 98%) was obtained as a colorless oil.

HRMS (APCI) for $C_{11}H_{17}Si$ $[(M–CH_3)^+]$: calculated 177.1100, found 177.1093. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.11 (s, 9H), 0.78 (dd, *J* = 14.8, 6.6 Hz, 1H), 0.92 (dd, *J* = 14.8, 6.6 Hz, 1H), 1.22 (d, *J* = 7.1 Hz, 3H), 2.78 (dp, *J* = 8.3, 6.8 Hz,1H), 7.04–7.12 (m, 3H), 7.15–7.19 (m, 2H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –0.9, 26.9, 27.1, 36.9, 126.2, 127.1, 128.7, 149.7 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = –0.06 ppm. The spectroscopic data are in accordance with those reported.[S12]

5.6 T rimethyl(phenethyl)silane (40)



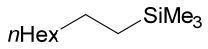
40

$C_{11}H_{18}Si$

M = 178.35 g/mol

Prepared from styrene **26** (10.4 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **40** (15.5 mg, 87%) was obtained as a colorless oil. **HRMS** (APCI) for $C_{10}H_{15}Si$ $[(M–CH_3)^+]$: calculated 163.0943, found 163.0938. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.03 (s, 9H), 0.76–0.81 (m, 2H), 2.52–2.58 (m, 2H), 7.06–7.16 (m, 3H), 7.17–7.22 (m, 2H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –1.7, 18.8, 30.5, 125.9, 128.2, 128.6, 145.3 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = –0.97 ppm. The spectroscopic data are in accordance with those reported.[S12]

5.7 Trimethyl(octyl)silane (41)

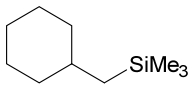


41
$C_{11}H_{26}Si$
M = 186.41 g/mol

Prepared from hept-1-ene **27** (11.2 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5 µmol, 5.0 mol%) according to the **GP2**. The title compound **41** (12.5 mg, 67%) was obtained as a colorless oil.

HRMS (APCI) for $C_{10}H_{23}Si$ [$(M–CH_3)^+$]: calculated 171.1569, found 171.1532. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.30 (s, 9H), 0.47–0.55 (m, 2H), 0.89–0.95 (m, 3H), 1.26–1.37 (m, 12H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –1.5, 14.4, 17.0, 23.1, 24.4, 29.7, 29.8, 32.4, 34.1 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = 0.78 ppm. The spectroscopic data are in accordance with those reported.[S12]

5.8 (Cyclohexylmethyl)trimethylsilane (42)

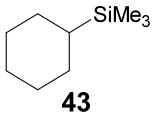


42
$C_{10}H_{22}Si$
M = 170.37 g/mol

Prepared from methylenecyclohexane **28** (10.0 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **42** (16.4 mg, 96%) was obtained as a colorless oil.

HRMS (APCI) for $C_9H_{19}Si$ [$(M–CH_3)^+$]: calculated 155.1256, found 155.1244. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.05 (s, 9H), 0.49 (d, *J* = 7.0 Hz, 2H), 0.88–0.99 (m, 2H), 1.09–1.28 (m, 3H), 1.34–1.41 (m, 1H), 1.59–1.77 (m, 5H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –0.4, 26,0, 26.6, 27.0, 34.8, 37.2 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = –0.23 ppm. The spectroscopic data are in accordance with those reported.[S12]

5.9 Cyclohexyltrimethylsilane (43)



43

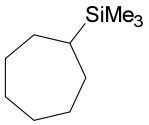
$C_9H_{20}Si$

M = 156.34 g/mol

Prepared from cyclohexene **29** (8.5 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **43** (13.3 mg, 85%) was obtained as a colorless oil.

HRMS (EI) for $C_9H_{20}Si$ [M^+]: calculated 156.1329, found 156.1331. **^{1}H NMR** (400 MHz, C_6D_6): δ = –0.03 (s, 9H), 0.19–0.20 (m, 2H), 0.48 (tt, *J* = 12.8, 3.2 Hz, 1H), 1.18–1.24 (m, 3H), 1.61–1.67 (m, 2H), 1.69–1.76 (m, 3H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –3.5, 26.4, 27.4, 27.7, 28.5 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = 1.79 ppm. The spectroscopic data are in accordance with those reported.[S12]

5.10 Cycloheptyltrimethylsilane (44)



44

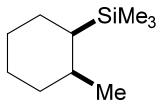
$C_{10}H_{22}Si$

M = 170.37 g/mol

Prepared from cycloheptene **30** (9.7 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **44** (13.6 mg, 80%) was obtained as a colorless oil.

HRMS (EI) for $C_{10}H_{22}Si$ [M^+]: calculated 170.1485, found 170.1483. **^{1}H NMR** (400 MHz, C_6D_6): δ = –0.01 (s, 9H), 0.56 (tt, *J* = 11.0, 3.5 Hz, 1H), 1.14–1.23 (m, 2H), 1.39–1.52 (m, 4H), 1.57–1.65 (m, 2H), 1.67–1.76 (m, 4H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –3.2, 27.0, 28.7 (2C overlapped), 29.2 (2C overlapped), 30.4 (2C overlapped) ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = 3.30 ppm. The spectroscopic data are in accordance with those reported.[S12]

5.11 *cis*-Trimethyl(2-methylcyclohexyl)silane (45)



45

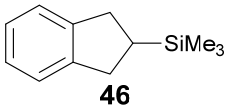
$C_{10}H_{22}Si$

M = 170.37 g/mol

Prepared from 1-methylcyclohex-1-ene **31** (9.6 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **45** (15.2 mg, 89%) was obtained as a colorless oil with a mixture of diastereoisomers (*cis*:*trans* = 90:10), determined by analysis of the ^{1}H NMR spectrum.

HRMS (EI) for $C_{10}H_{22}Si$ [M^+]: calculated 170.1485, found 170.1487. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.01 (s, 9H), 0.19–0.21 (m, 1H), 0.72–0.73 (m, 1H), 0.93 (d, *J* = 7.1 Hz, 3H), 1.19–1.22 (m, 1H), 1.34–1.43 (m, 2H), 1.45–1.49 (m, 3H), 1.66–1.70 (m, 1H), 1.94–1.99 (m, 1H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –1.9, 16.5, 21.7, 22.5, 28.6, 30.0, 30.8, 35.4 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = 1.16 ppm. The spectroscopic data are in accordance with those reported.[S12]

5.12 (2,3-Dihydro-1*H*-inden-2-yl)trimethylsilane (46)



46

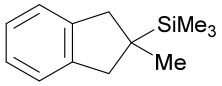
$C_{12}H_{18}Si$

M = 190.36 g/mol

Prepared from 1*H*-indene **32** (11.6 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **46** (17.7 mg, 93%) was obtained as a colorless oil.

HRMS (APCI) for $C_{12}H_{18}Si$ [M^+]: calculated 190.1178, found 190.1171. **^{1}H NMR** (400 MHz, C_6D_6): δ = –0.05 (s, 9H), 1.37 (tt, *J* = 10.0, 8.9 Hz, 1H), 2.64 (dd, *J* = 14.8, 10.3 Hz, 2H), 2.81 (dd, *J* = 15.2, 8.8 Hz, 2H), 7.08–7.13 (m, 2H), 7.14–7.16 (m, 2H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –3.0, 26.3, 34.9, 124.5, 126.4, 145.0 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = 2.67 ppm. The spectroscopic data are in accordance with those reported.[S12]

5.13 Trimethyl(2-methyl-2,3-dihydro-1*H*-inden-2-yl)silane (47)



47

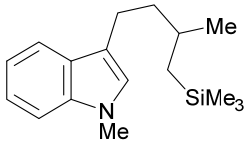
$C_{13}H_{20}Si$

M = 204.39 g/mol

Prepared from 2-methyl-1*H*-indene **33** (13.0 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **47** (14.3 mg, 70%) was obtained as a colorless oil with minor amount of the other regioisomer trimethyl(2-methyl-2,3-dihydro-1H-inden-1-yl)silane (90:10).

HRMS (EI) for $C_{13}H_{20}Si$ [M^+]: calculated 204.1329, found 204.1331. **^{1}H NMR** (400 MHz, C_6D_6): δ = –0.07 (s, 9H), 0.96 (s, 3H), 2.40 (d, *J* = 15.3 Hz, 2H), 2.91 (d, *J* = 15.3 Hz, 2H), 7.10–7.15 (m, 4H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –3.9, 23.5, 28.1, 43.0, 125.1, 126.6, 143.5 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = 6.47 ppm. The spectroscopic data are in accordance with those reported.[S12]

5.14 1-Methyl-3-(3-methyl-4-(trimethylsilyl)butyl)-1H-indole (48)



48

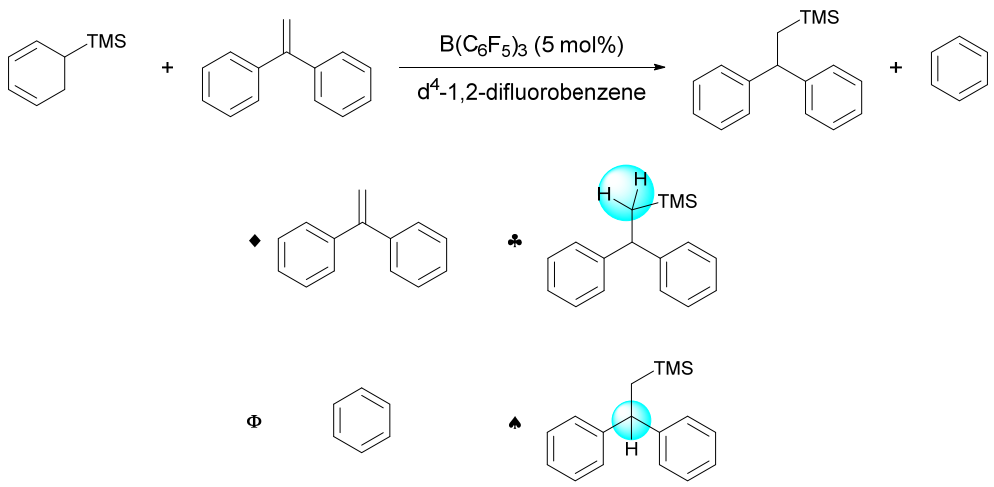
$C_{17}H_{27}NSi$

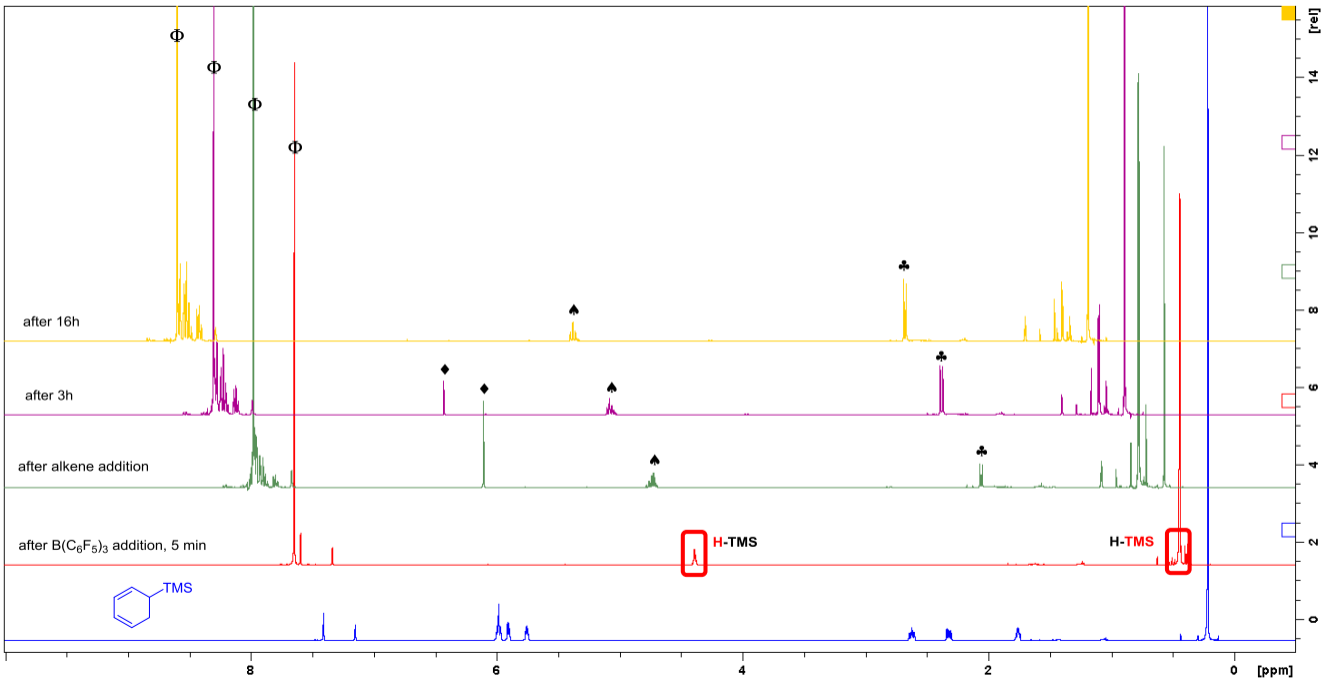
M = 273.50 g/mol

Prepared from 1-methyl-3-(3-methylbut-3-en-1-yl)-1*H*-indole **34** (20.0 mg, 0.10 mmol, 1.0 equiv), 5-trimethylsilyl-subsituted cyclohexa-1,3-diene (20.0 mg, 0.13 mmol, 1.3 equiv), and tris(pentafluorophenyl)borane (2.6 mg, 5.0 µmol, 5.0 mol%) according to the **GP2**. The title compound **48** (24.1 mg, 88%) was obtained as a colorless oil.

.**HRMS** (EI) for $C_{17}H_{27}NSi$ [M^+]: calculated 273.1907, found 273.1906. **^{1}H NMR** (400 MHz, C_6D_6): δ = 0.47 (s, 9H), 0.48 (dd, *J* = 14.7, 8.1 Hz, 1H), 0.77 (dd, *J* = 14.7, 4.7 Hz, 1H), 1.05 (d, *J* = 5.5 Hz, 3H), 1.66–1.84 (m, 3H), 2.78–2.87 (m, 2H), 3.00 (s, 3H), 6.46 (s, 1H), 7.05–7.09 (m, 1H), 7.21–7.30 (m, 2H), 7.75–7.78 (m, 1H) ppm. **^{13}C NMR** (101 MHz, C_6D_6): δ = –0.4, 23.2, 23.3, 25.4, 29.9, 31.8, 41.8, 109.4, 115.9, 119.0, 119.6, 121.8, 125.8, 128.8, 137.8 ppm. **^{29}Si DEPT NMR** (99 MHz, C_6D_6): δ = 0.07 ppm.

6 Time-Dependent ^{1}H HMR Experiment for Transfer Hydrosilylation

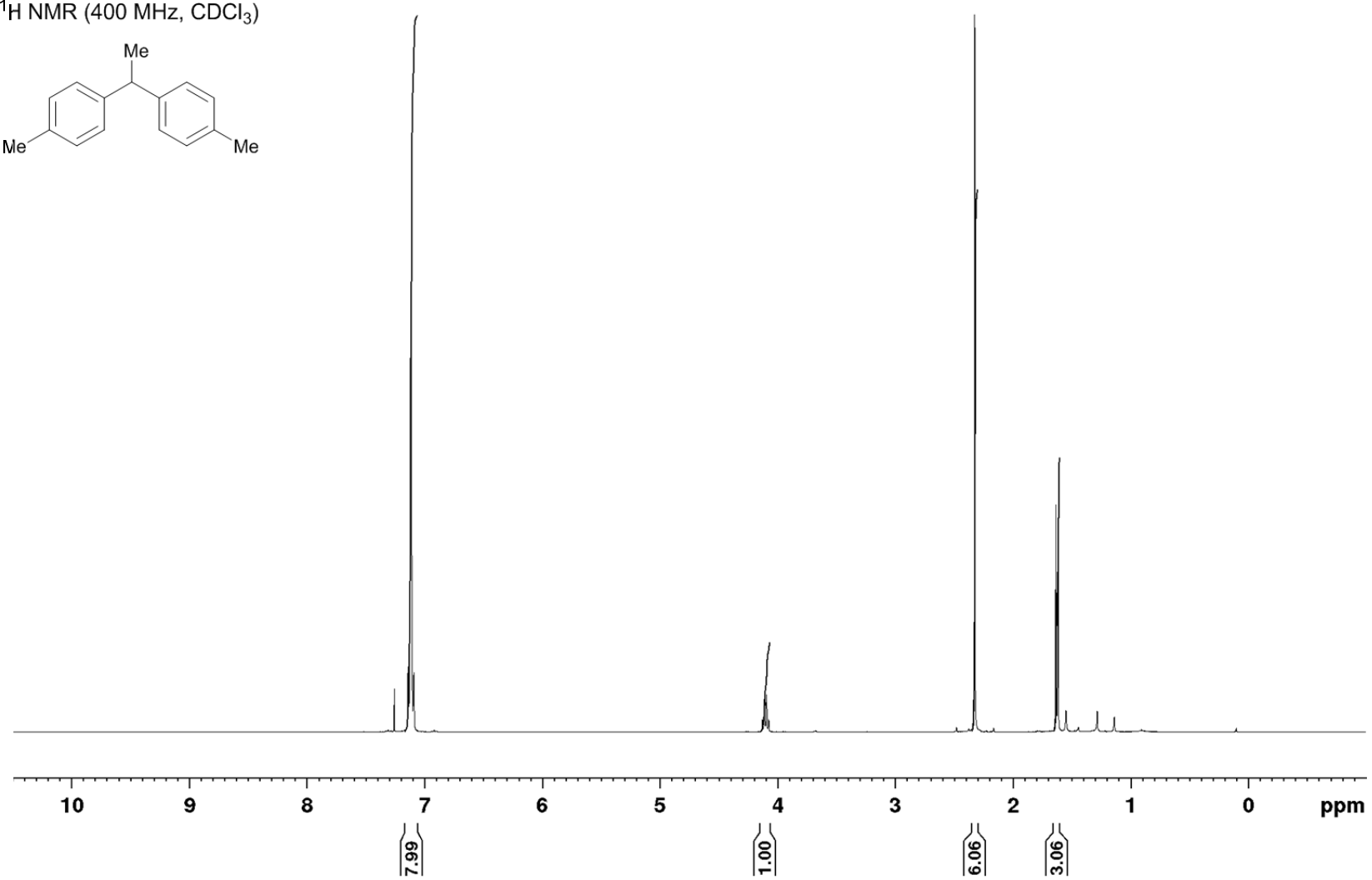




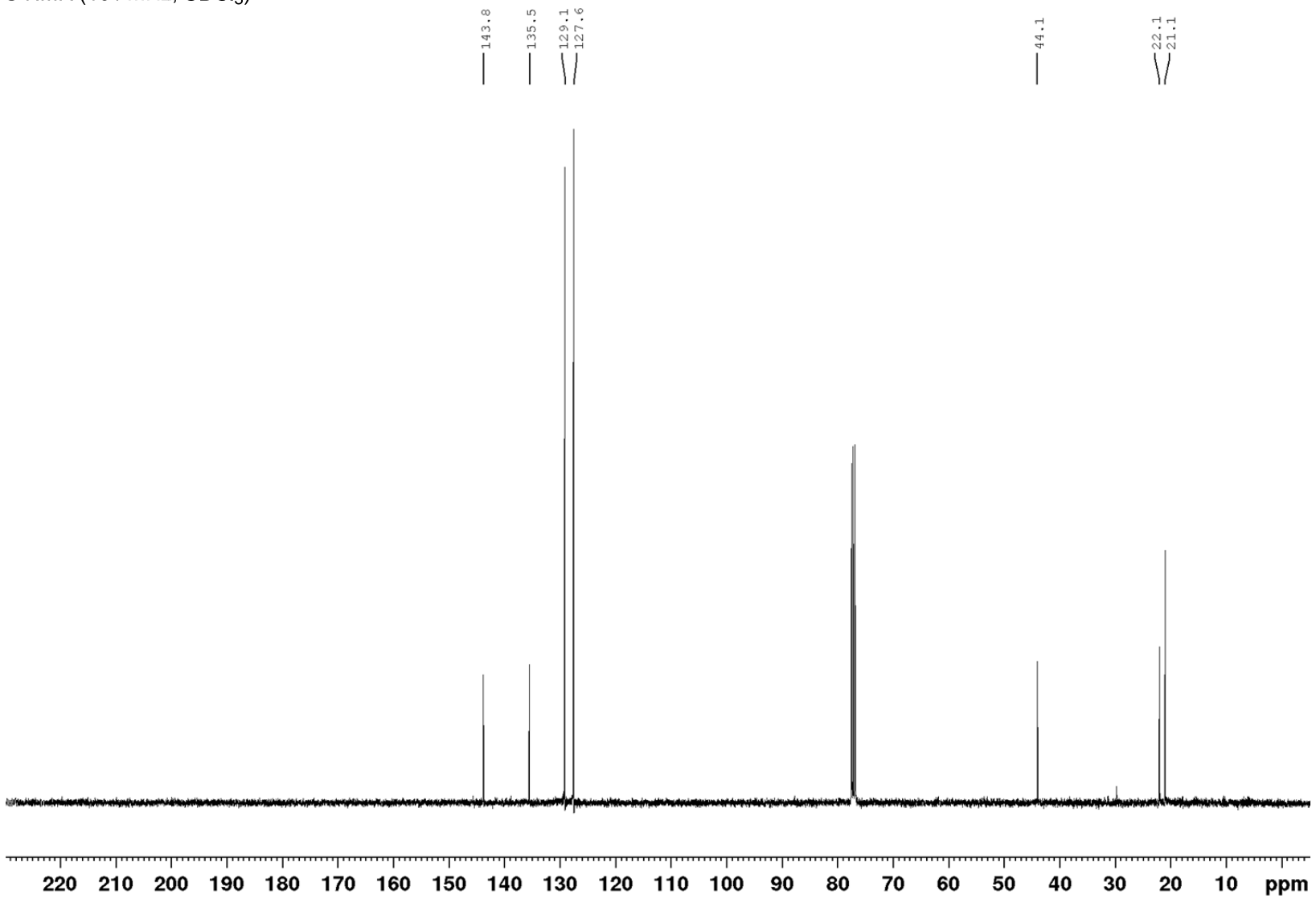
7 NMR Spectra

4,4'-(Ethane-1,1-diyl)bis(methylbenzene) (3)

^{1}H NMR (400 MHz, $CDCl_3$)

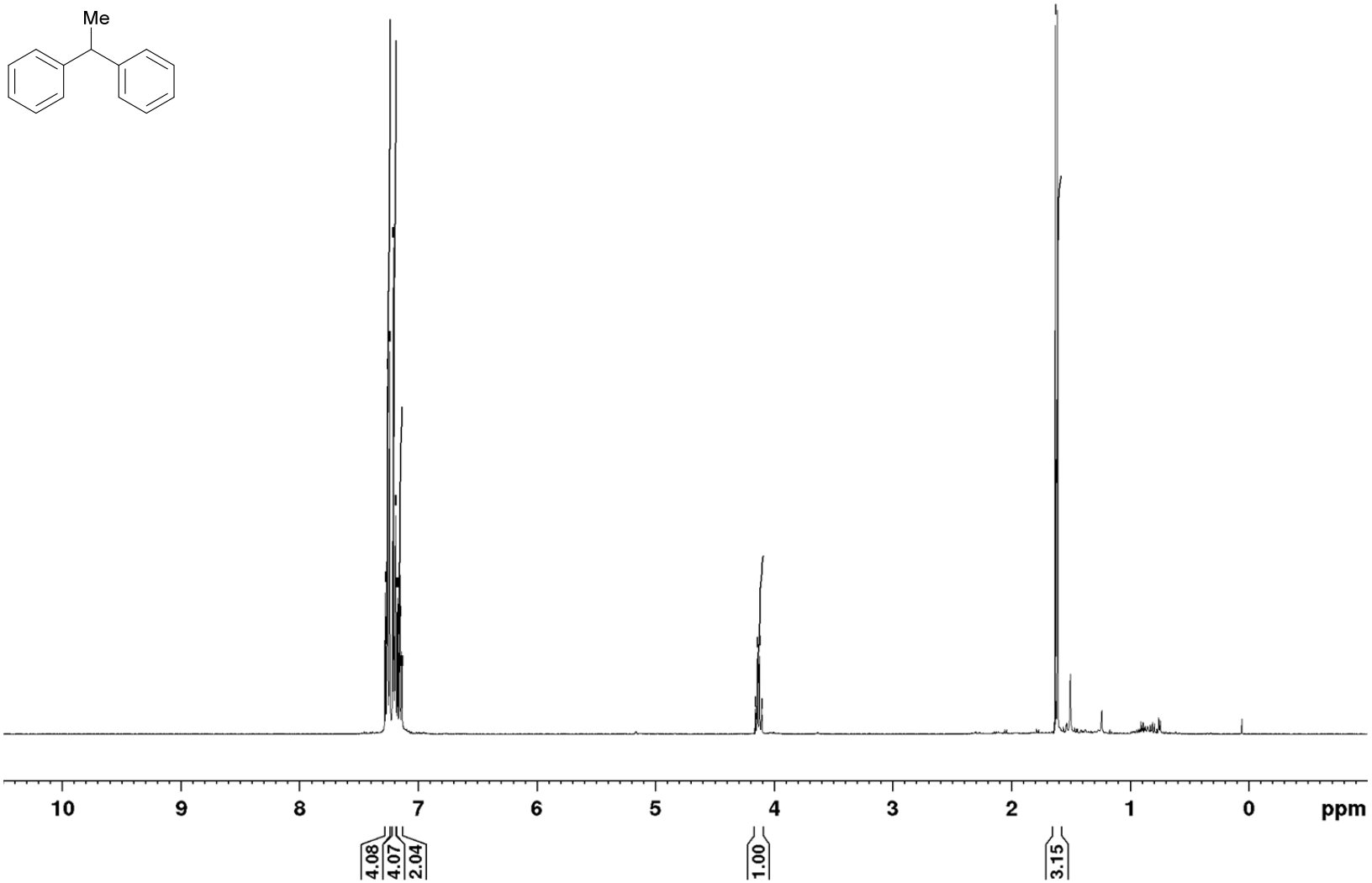


^{13}C NMR (101 MHz, $CDCl_3$)

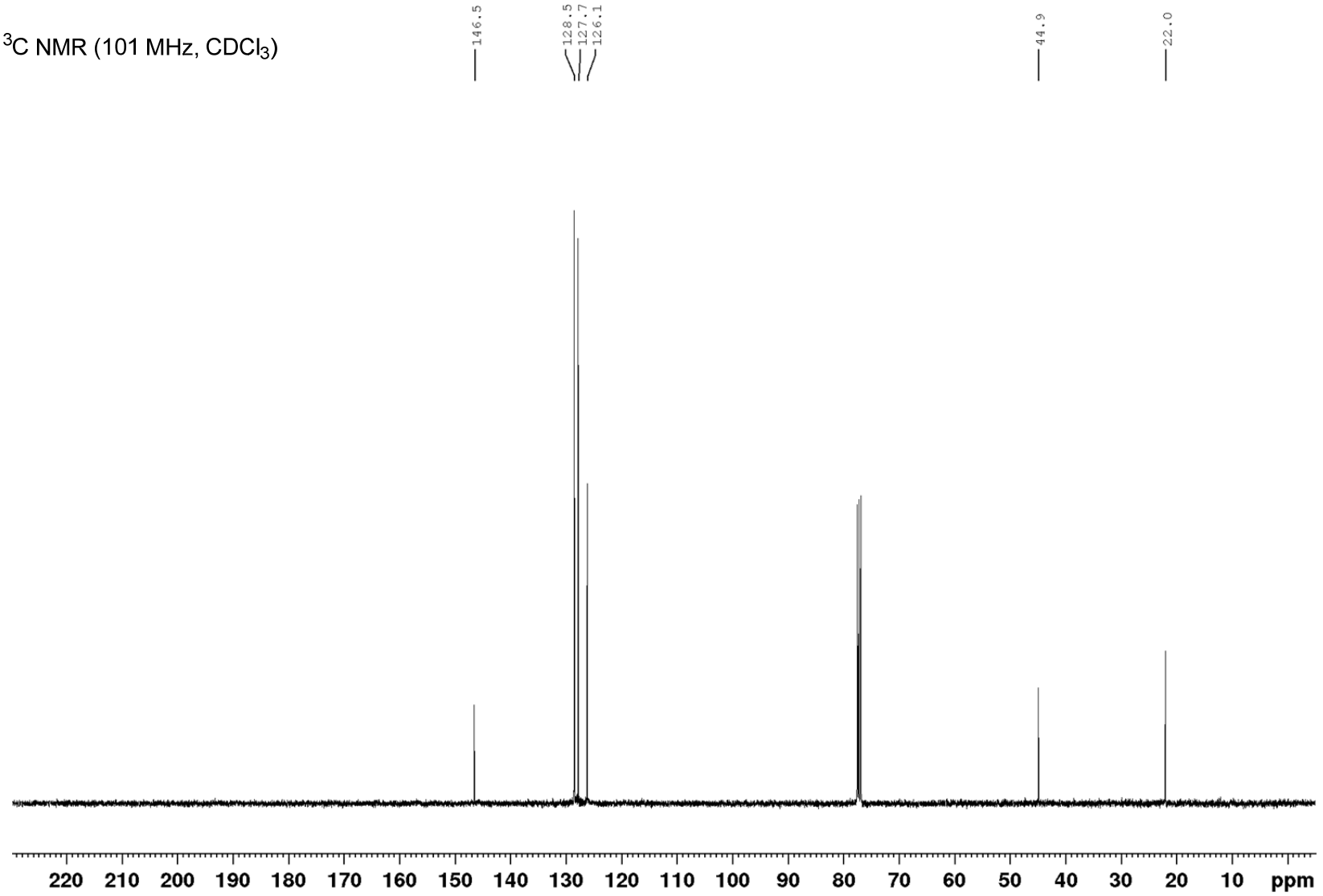


4,4'-(Ethane-1,1-diyl)bis(methylbenzene) (14)

^{1}H NMR (400 MHz, $CDCl_3$)

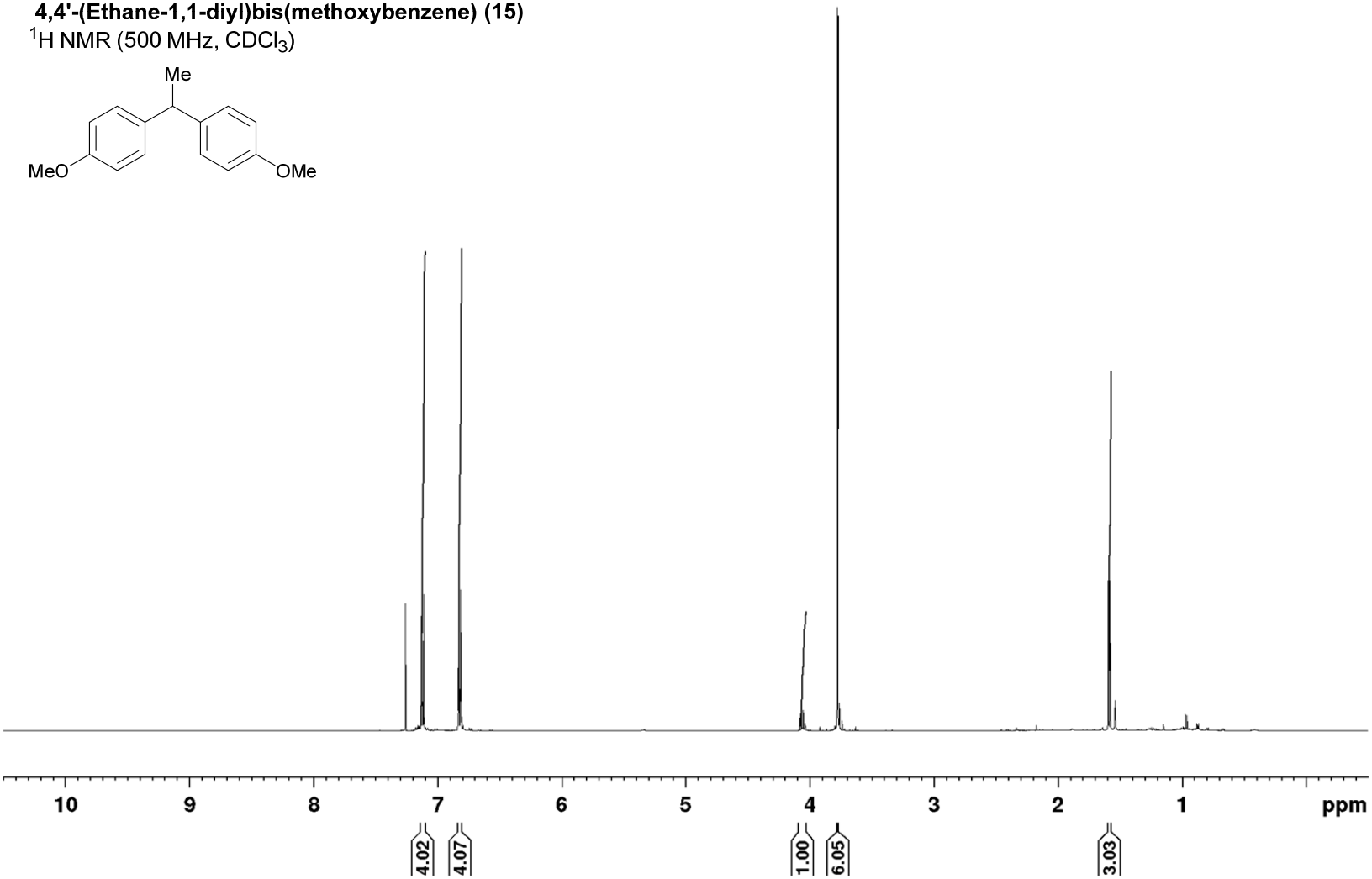


^{13}C NMR (101 MHz, $CDCl_3$)

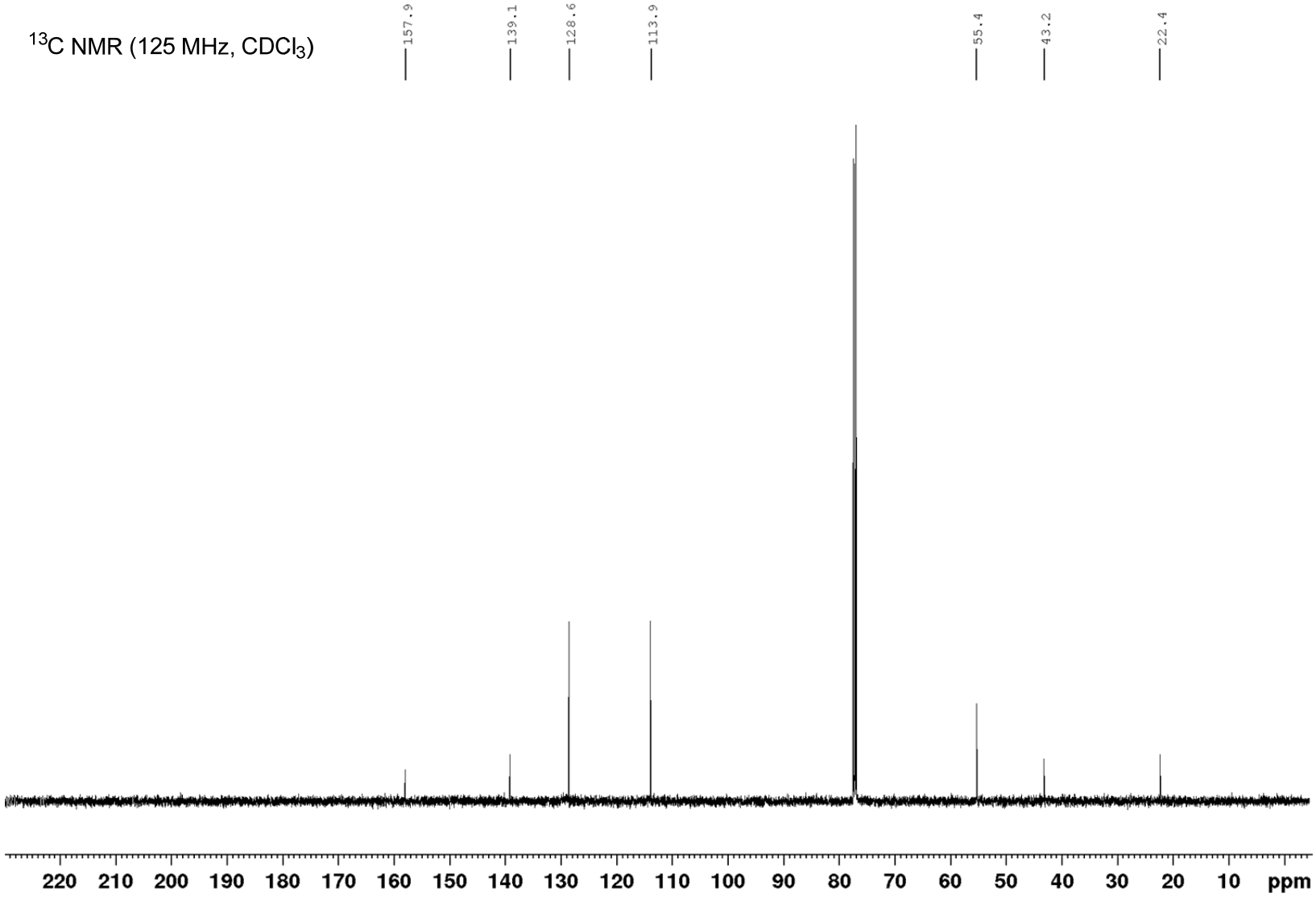


4,4'-(Ethane-1,1-diyl)bis(methoxybenzene) (15)

^{1}H NMR (500 MHz, $CDCl_3$)

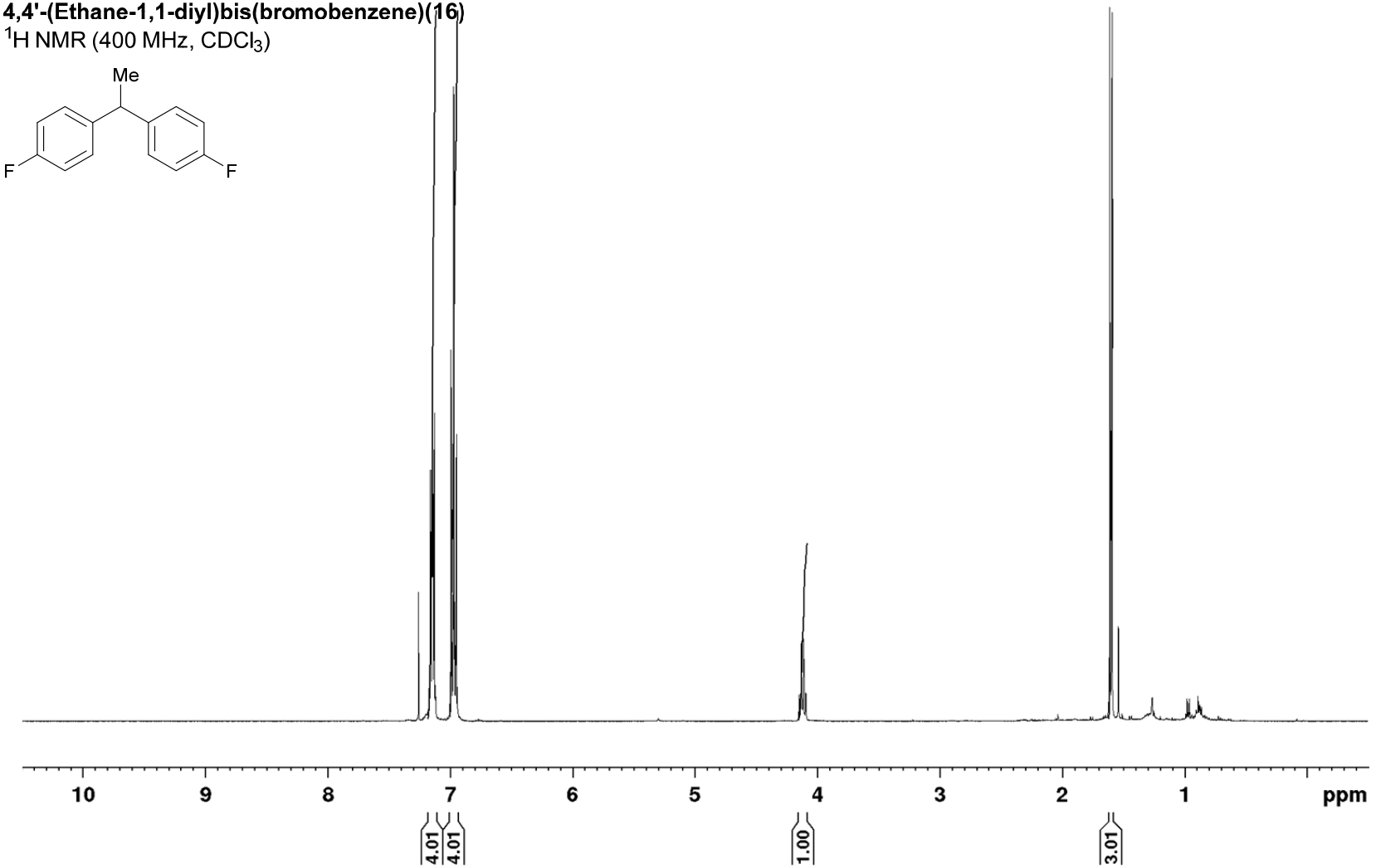


^{13}C NMR (125 MHz, $CDCl_3$)

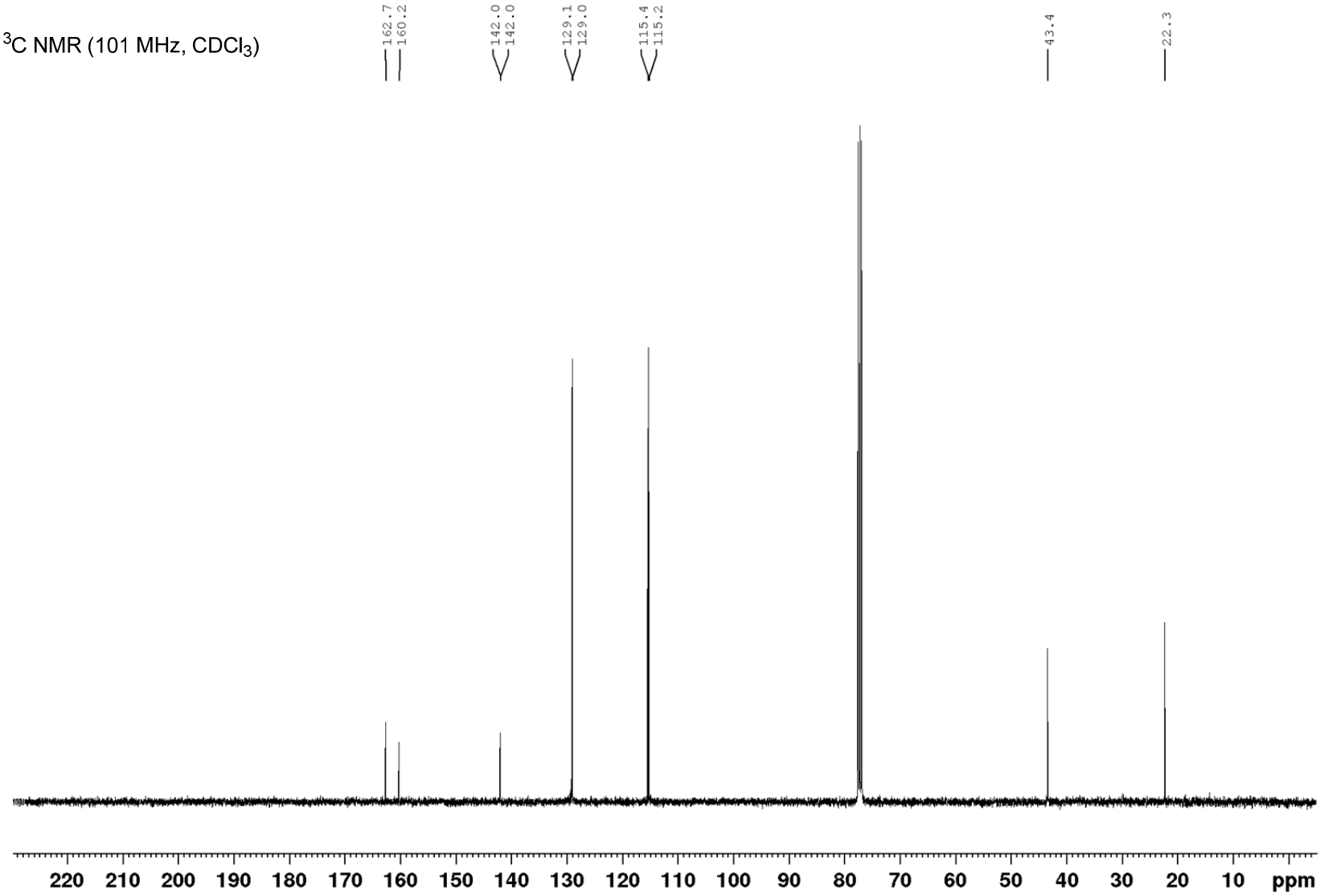


4,4'-(Ethane-1,1-diyl)bis(bromobenzene)(16)

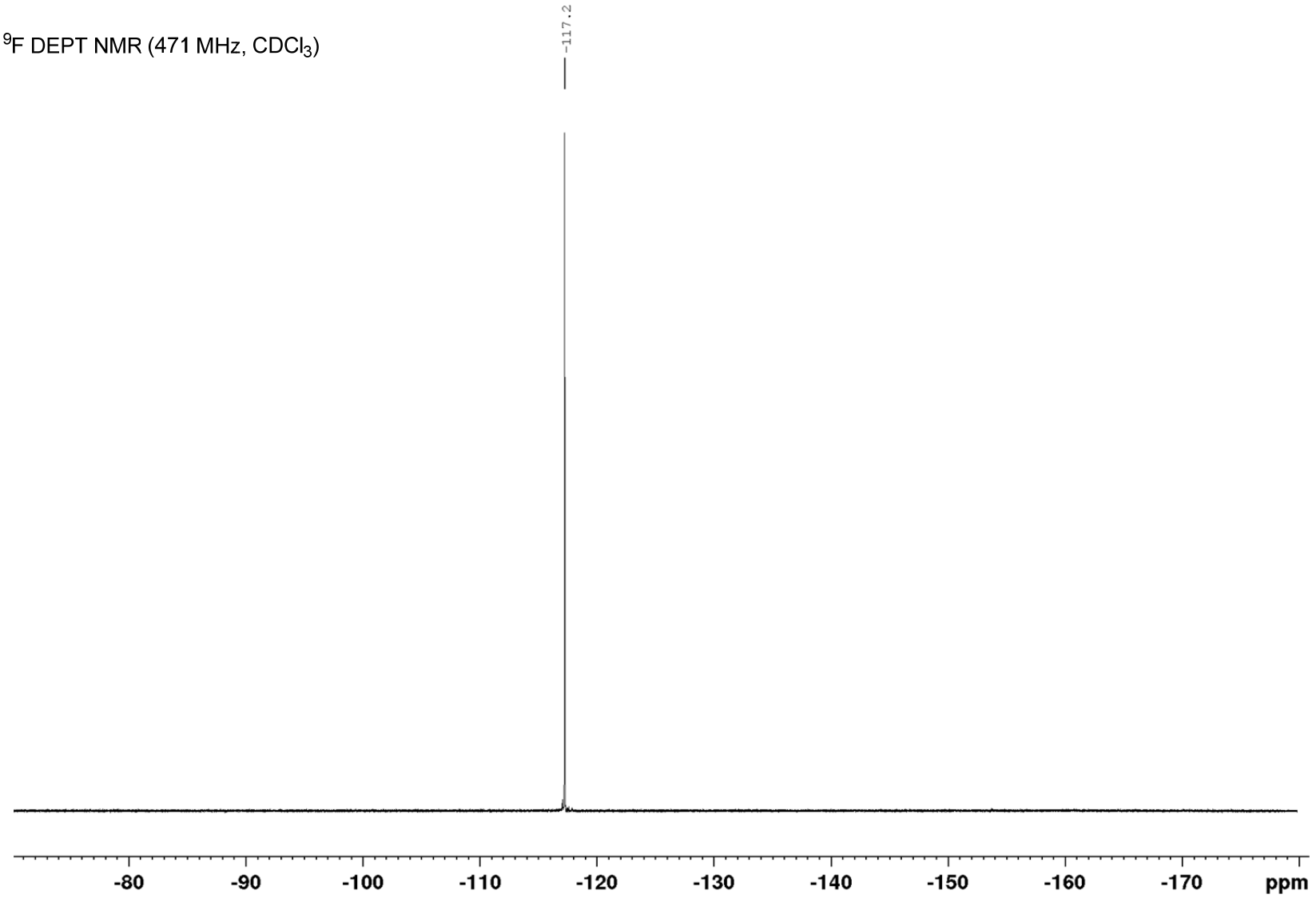
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

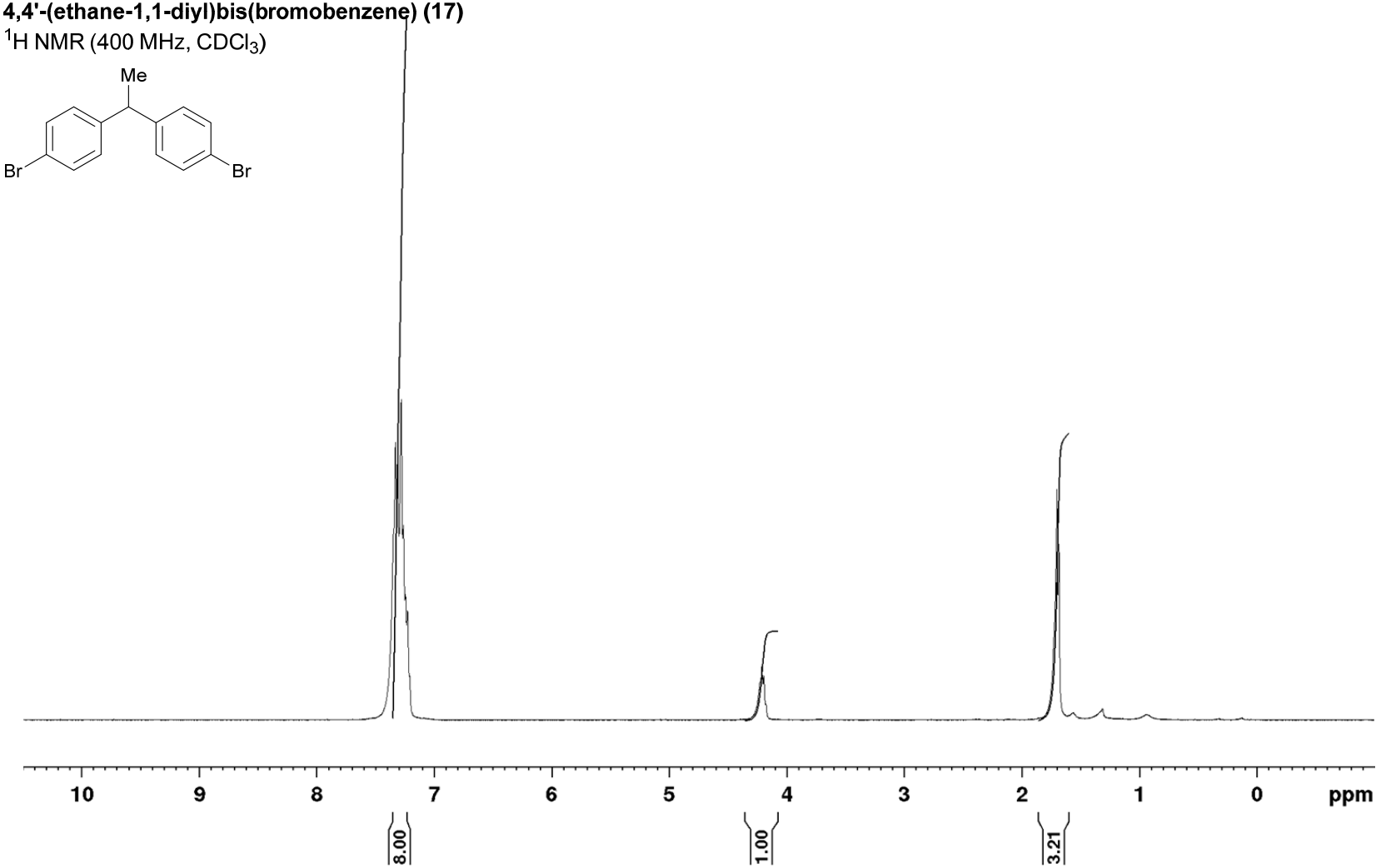


^{19}F DEPT NMR (471 MHz, $CDCl_3$)

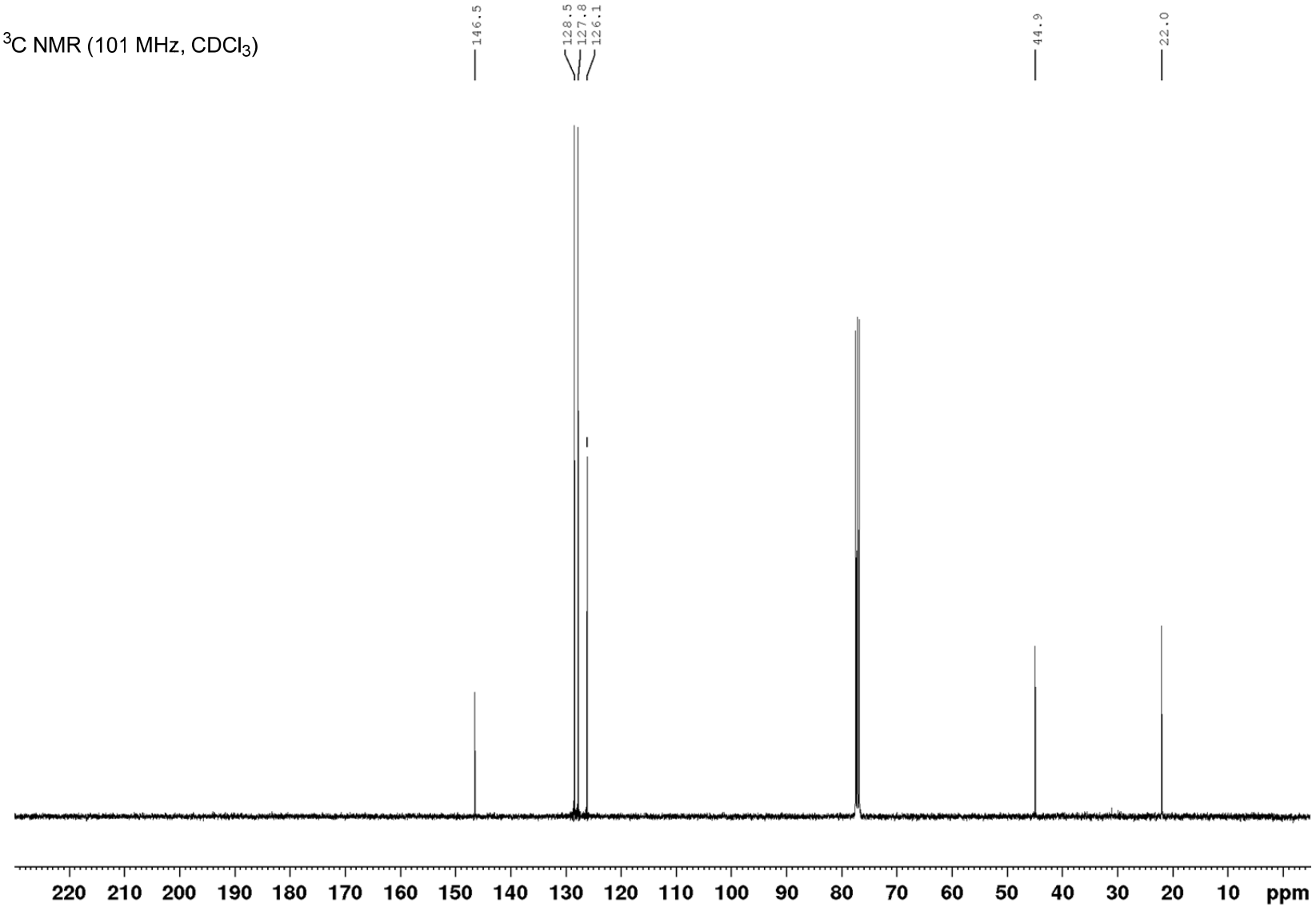


4,4'-(ethane-1,1-diyl)bis(bromobenzene) (17)

^{1}H NMR (400 MHz, $CDCl_3$)

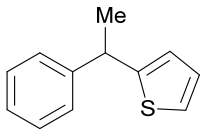


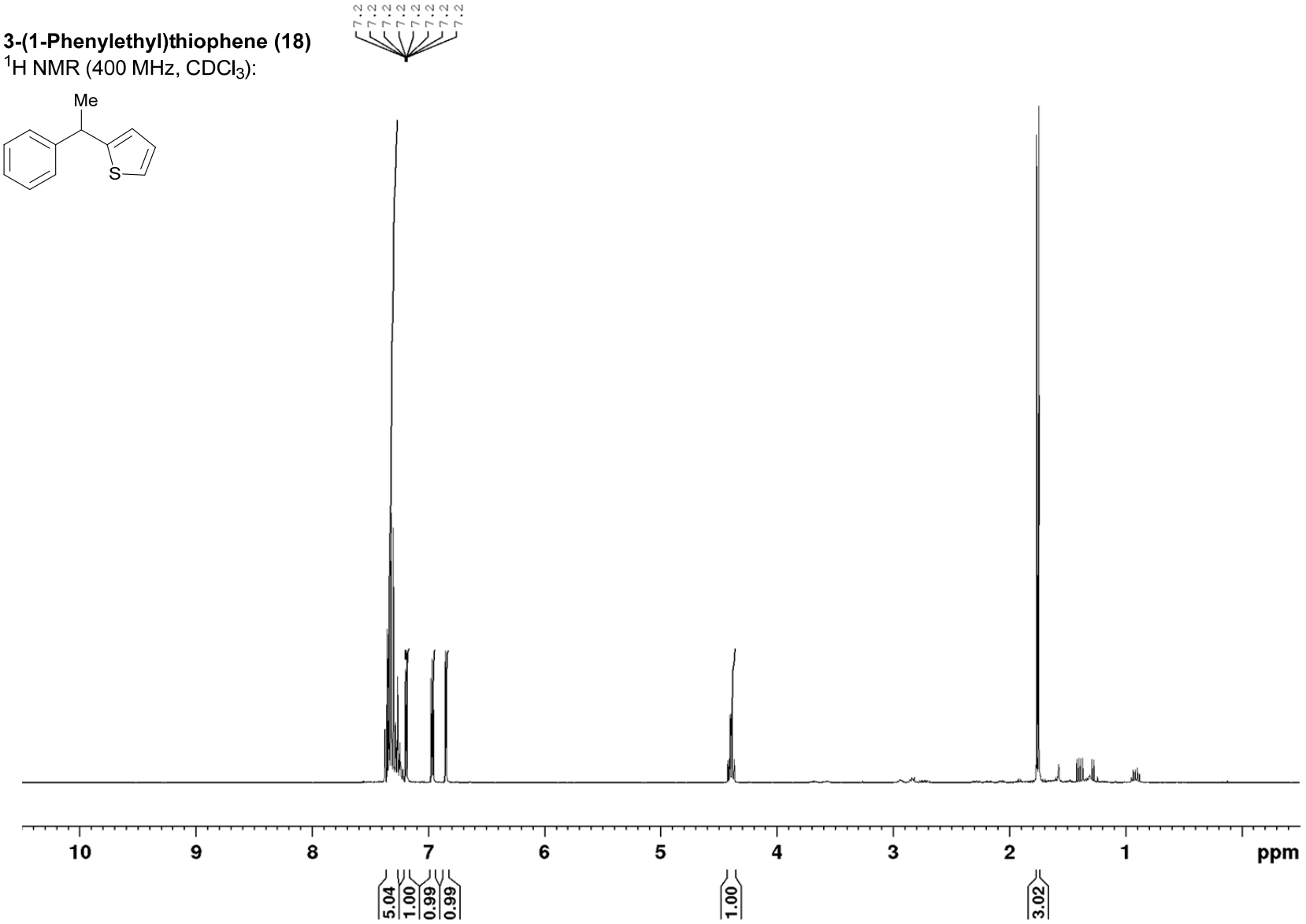
^{13}C NMR (101 MHz, $CDCl_3$)



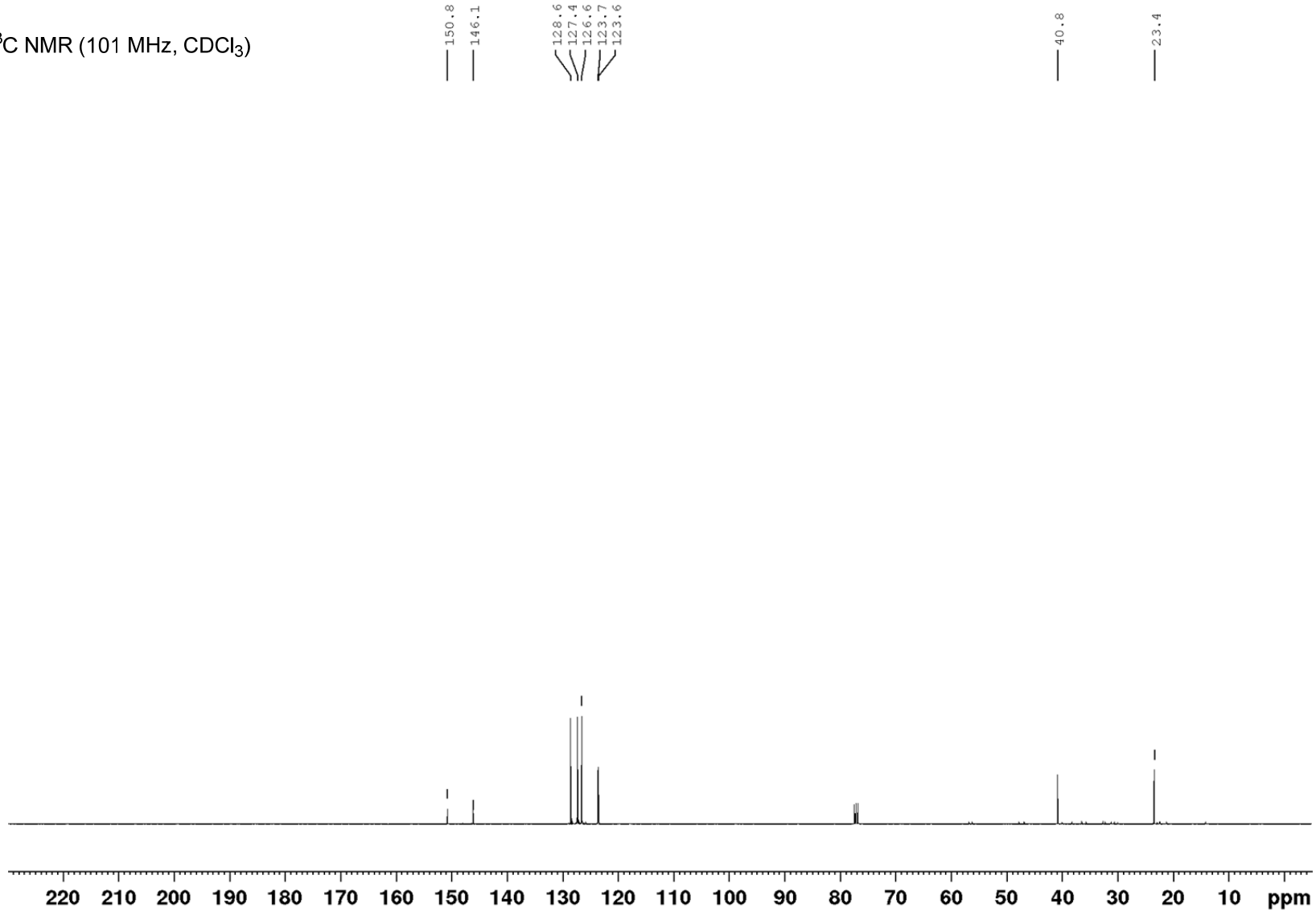
3-(1-Phenylethyl)thiophene (18)

^{1}H NMR (400 MHz, $CDCl_3$):



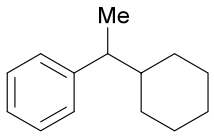


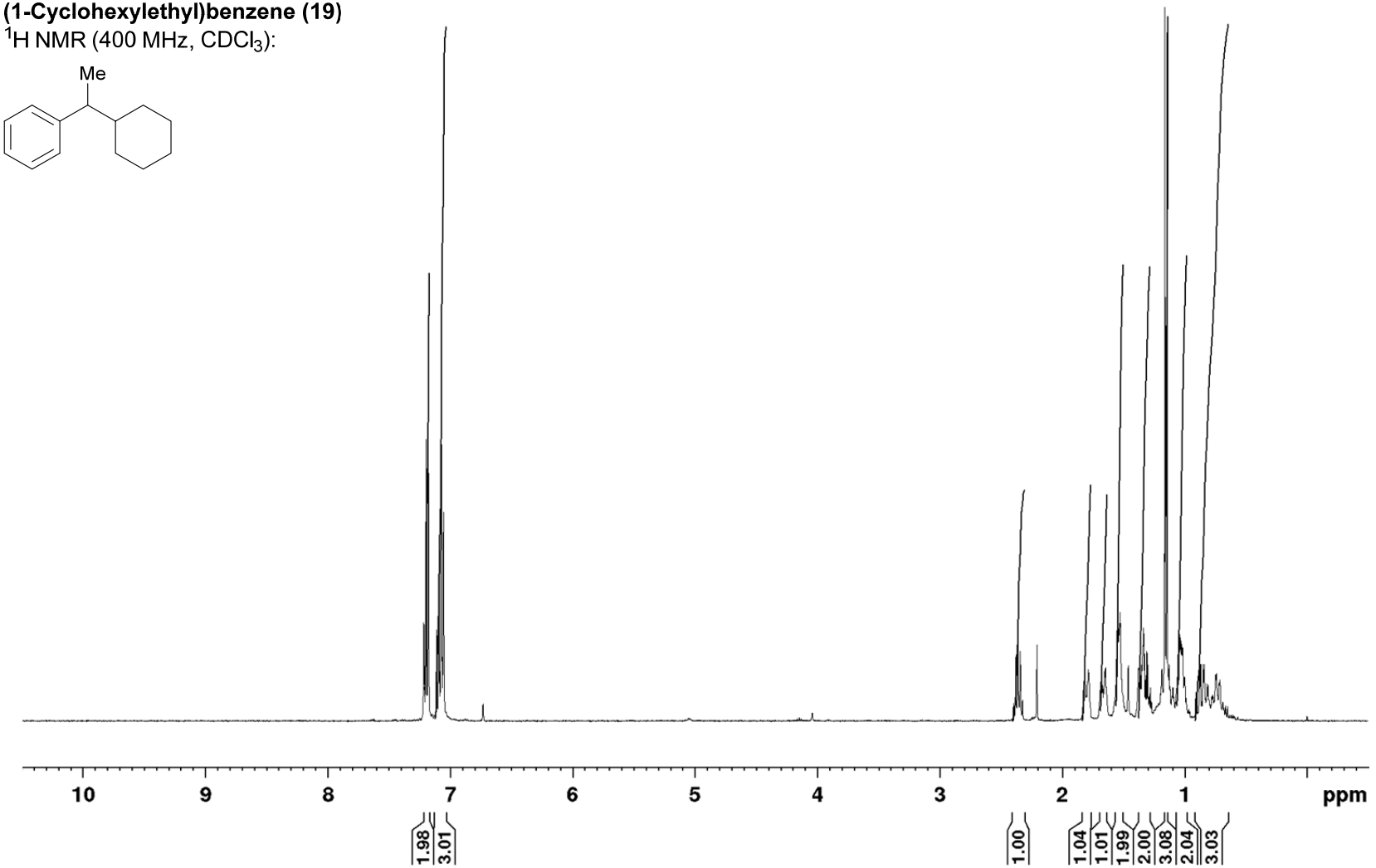
^{13}C NMR (101 MHz, $CDCl_3$)



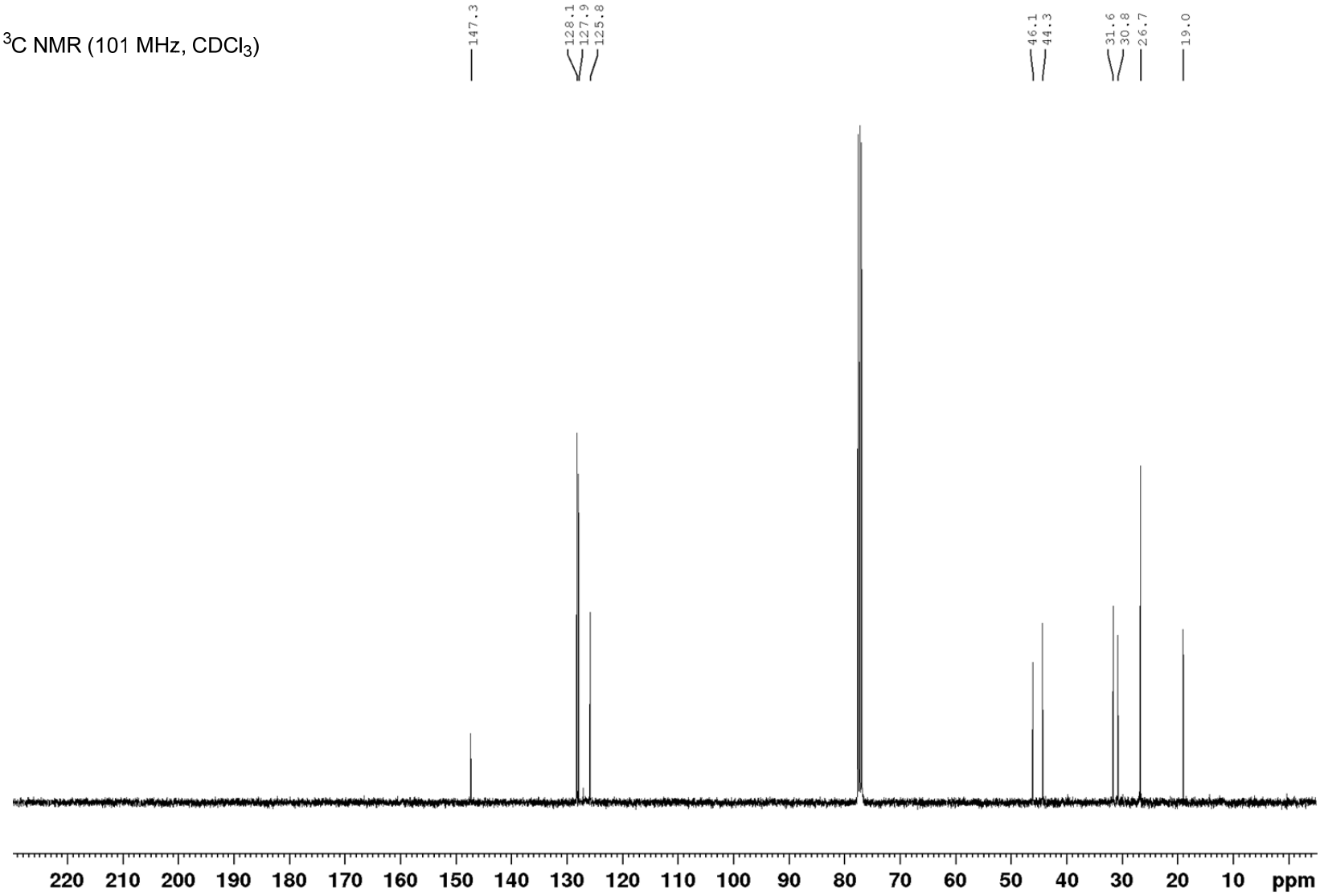
(1-Cyclohexylethyl)benzene (19)

^{1}H NMR (400 MHz, $CDCl_3$):



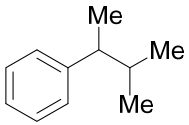


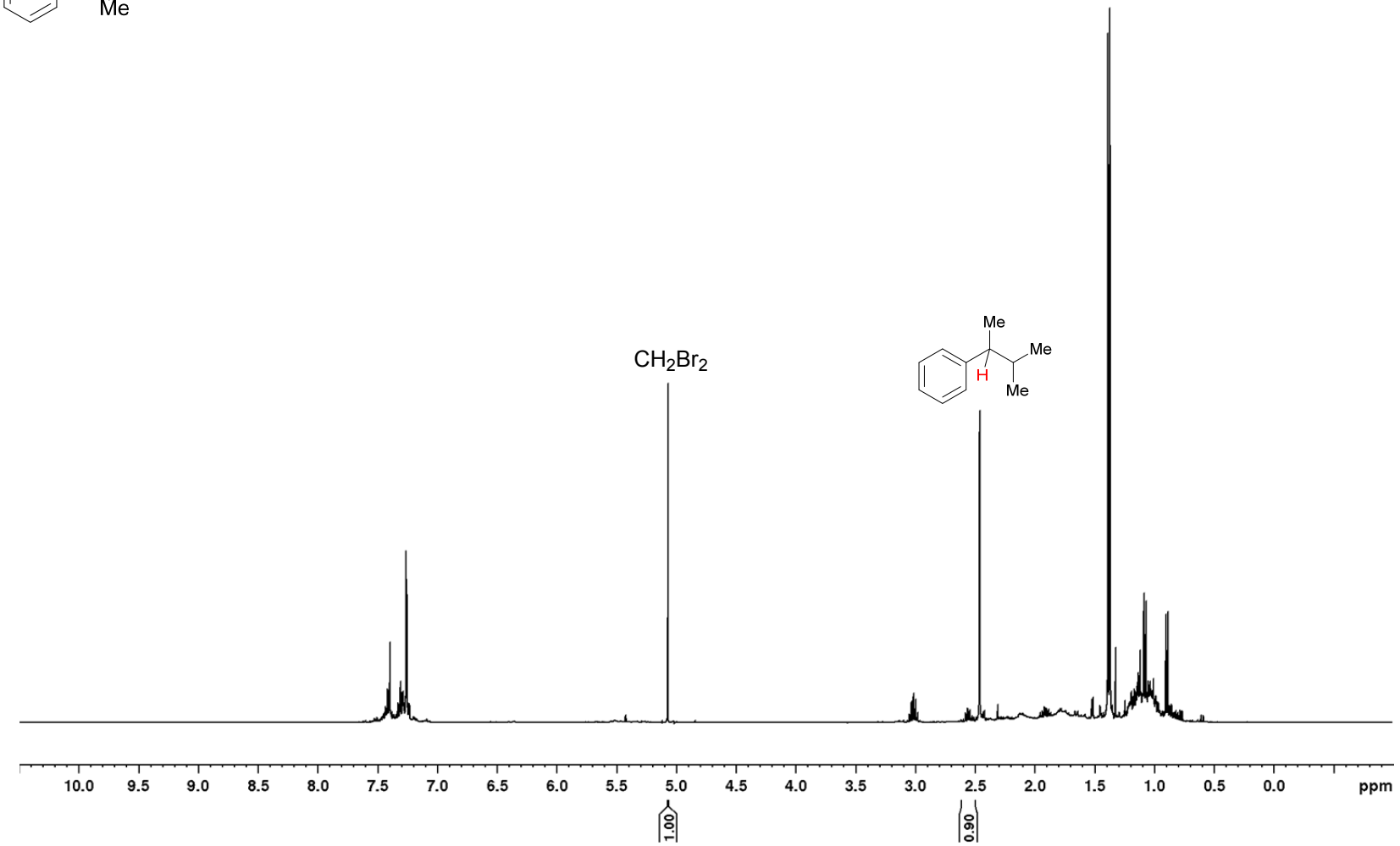
^{13}C NMR (101 MHz, $CDCl_3$)



(3-Methylbutan-2-yl)benzene (20)

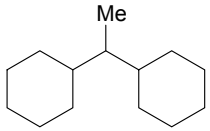
^{1}H NMR (400 MHz, $CDCl_3$)

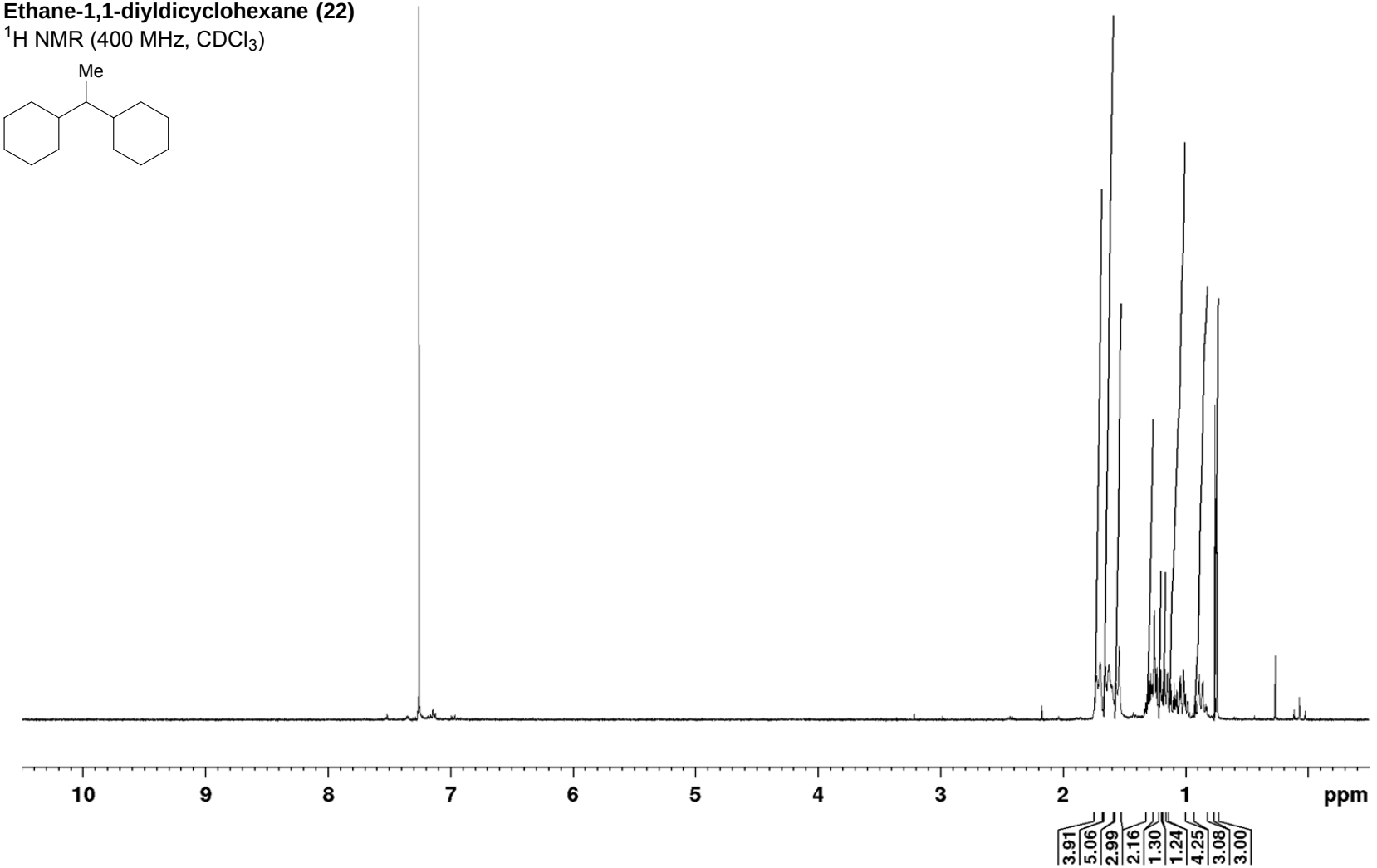




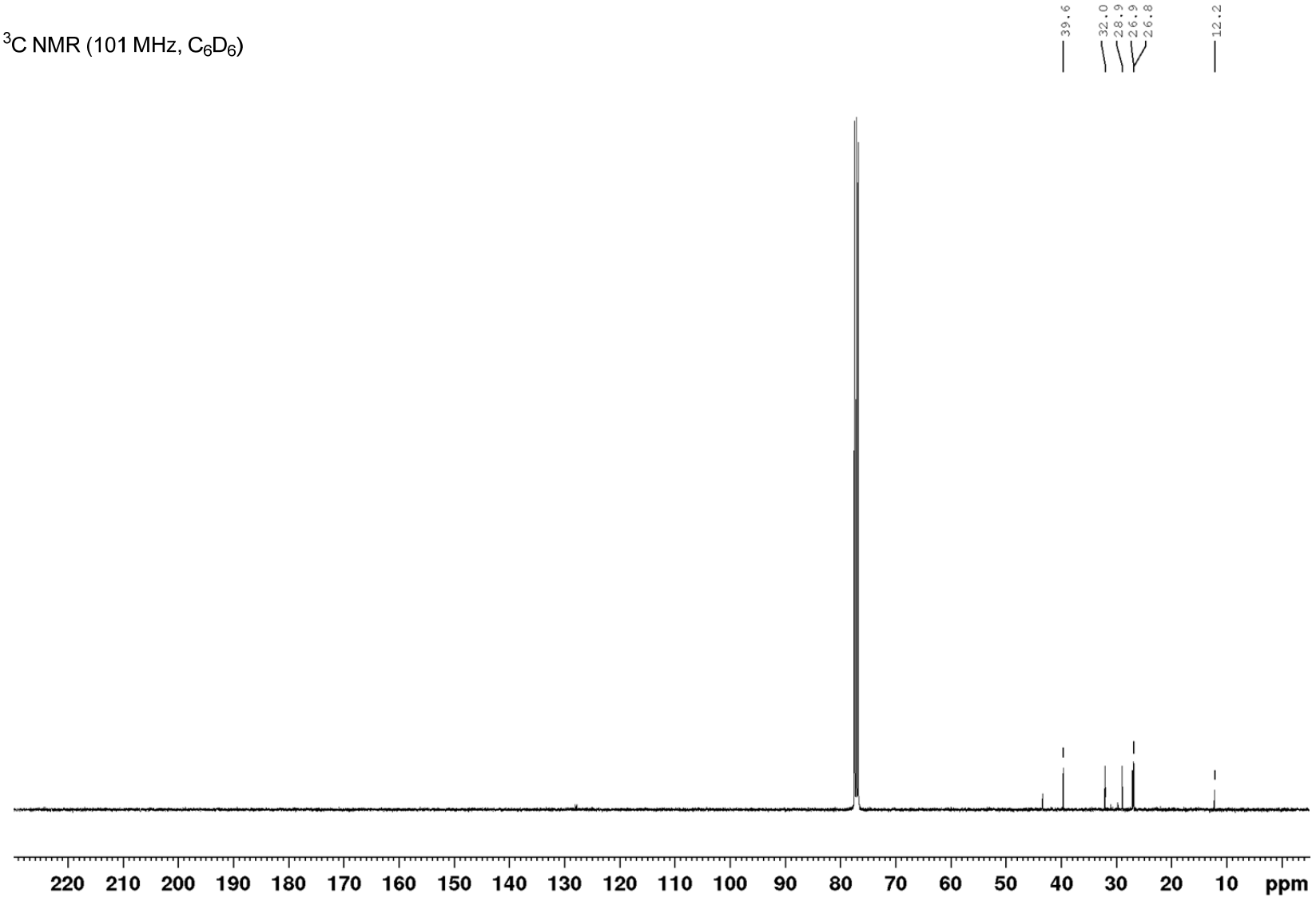
Ethane-1,1-diyldicyclohexane (22)

^{1}H NMR (400 MHz, $CDCl_3$)



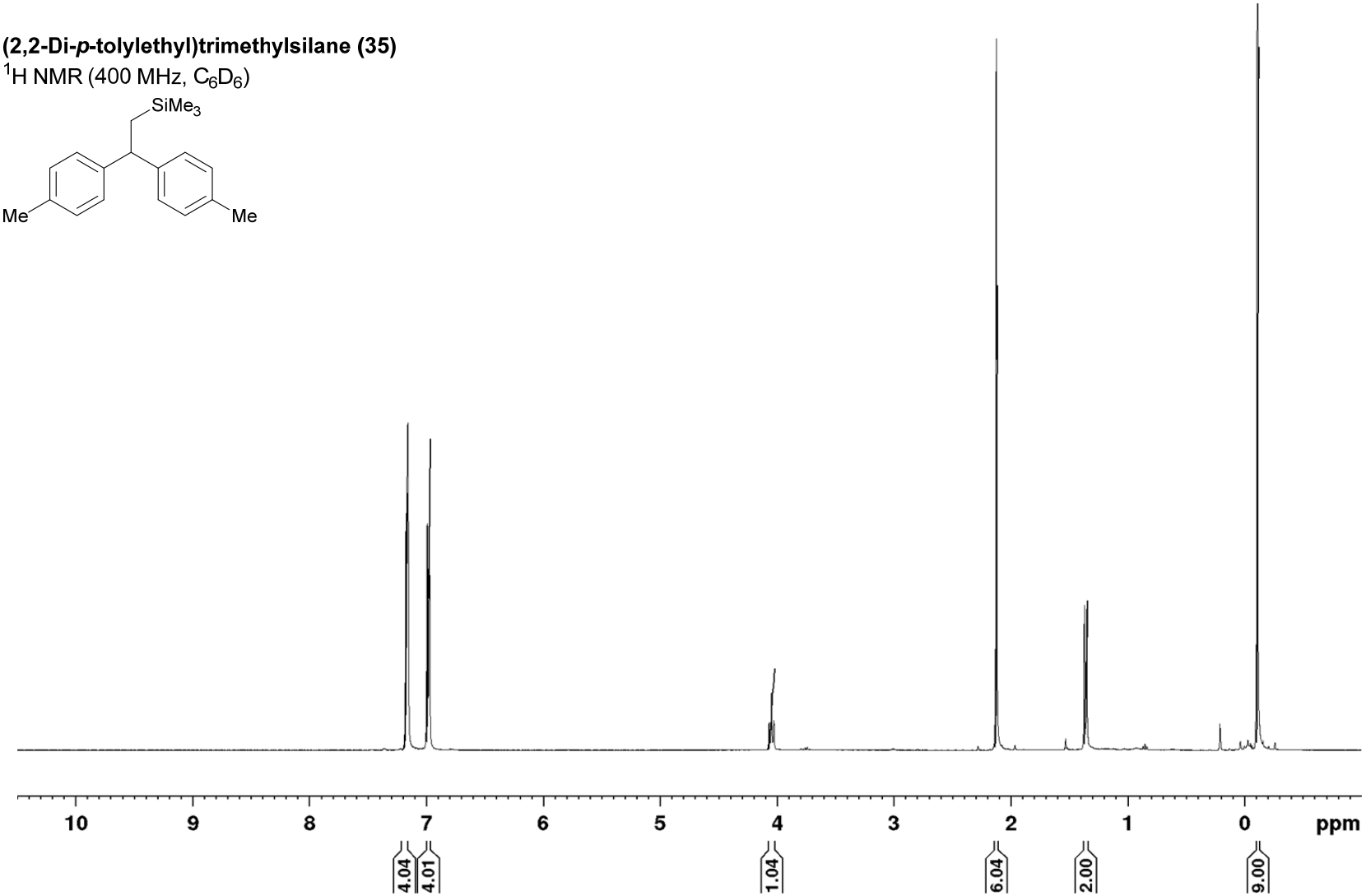


^{13}C NMR (101 MHz, C_6D_6)

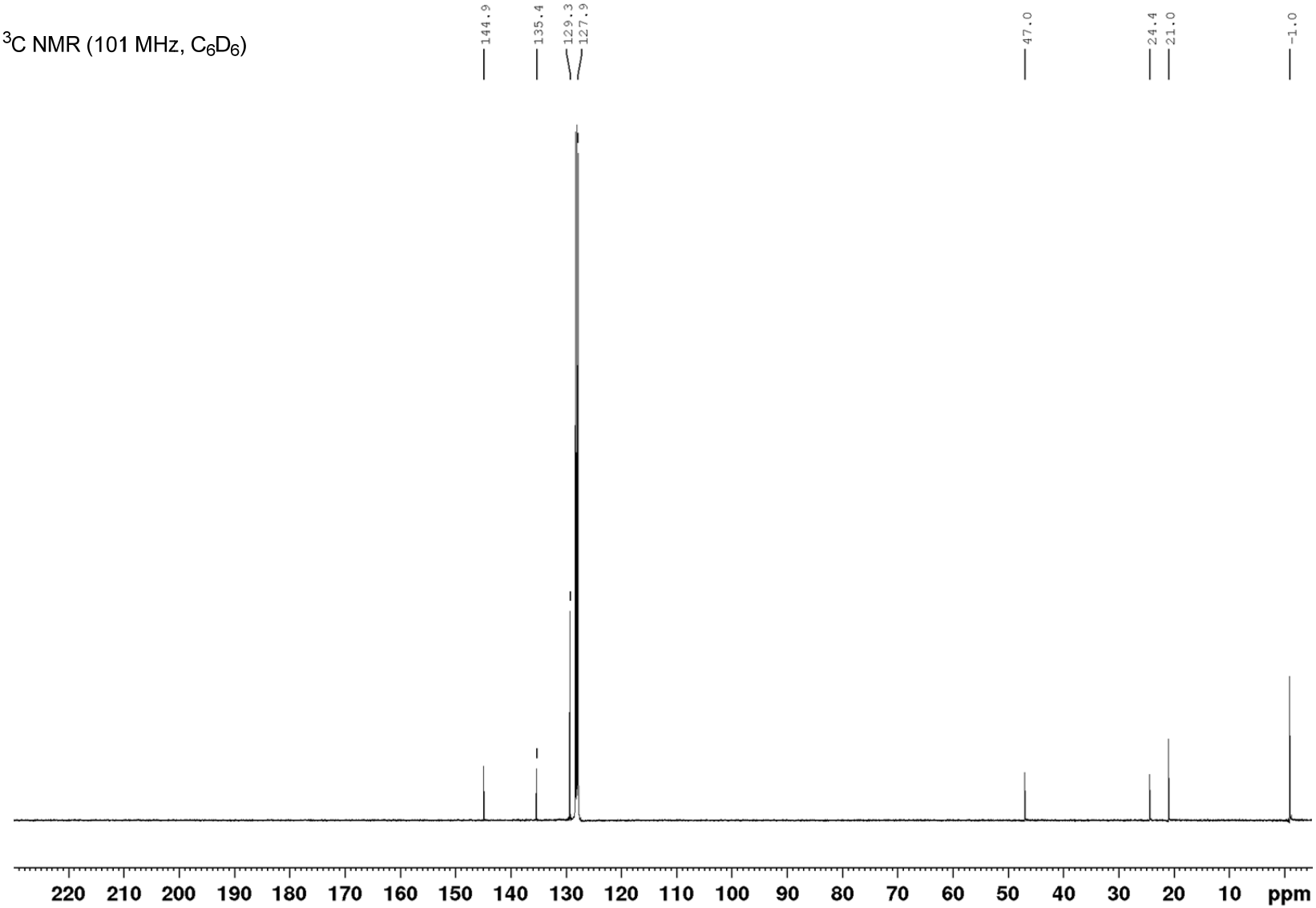


(2,2-Di-*p*-tolylethyl)trimethylsilane (35)

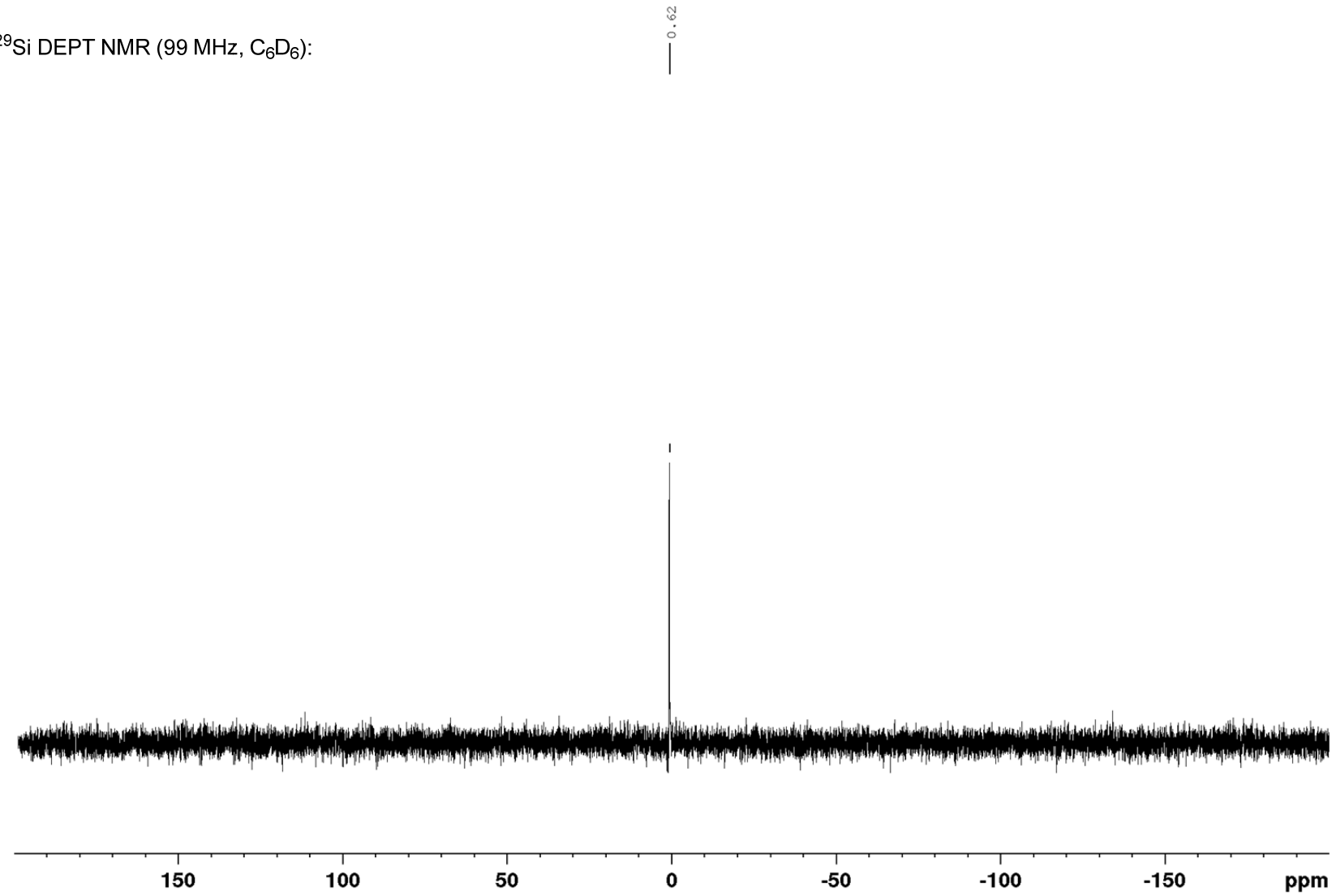
^{1}H NMR (400 MHz, C_6D_6)



^{13}C NMR (101 MHz, C_6D_6)

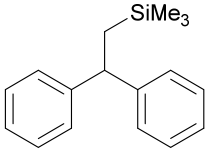


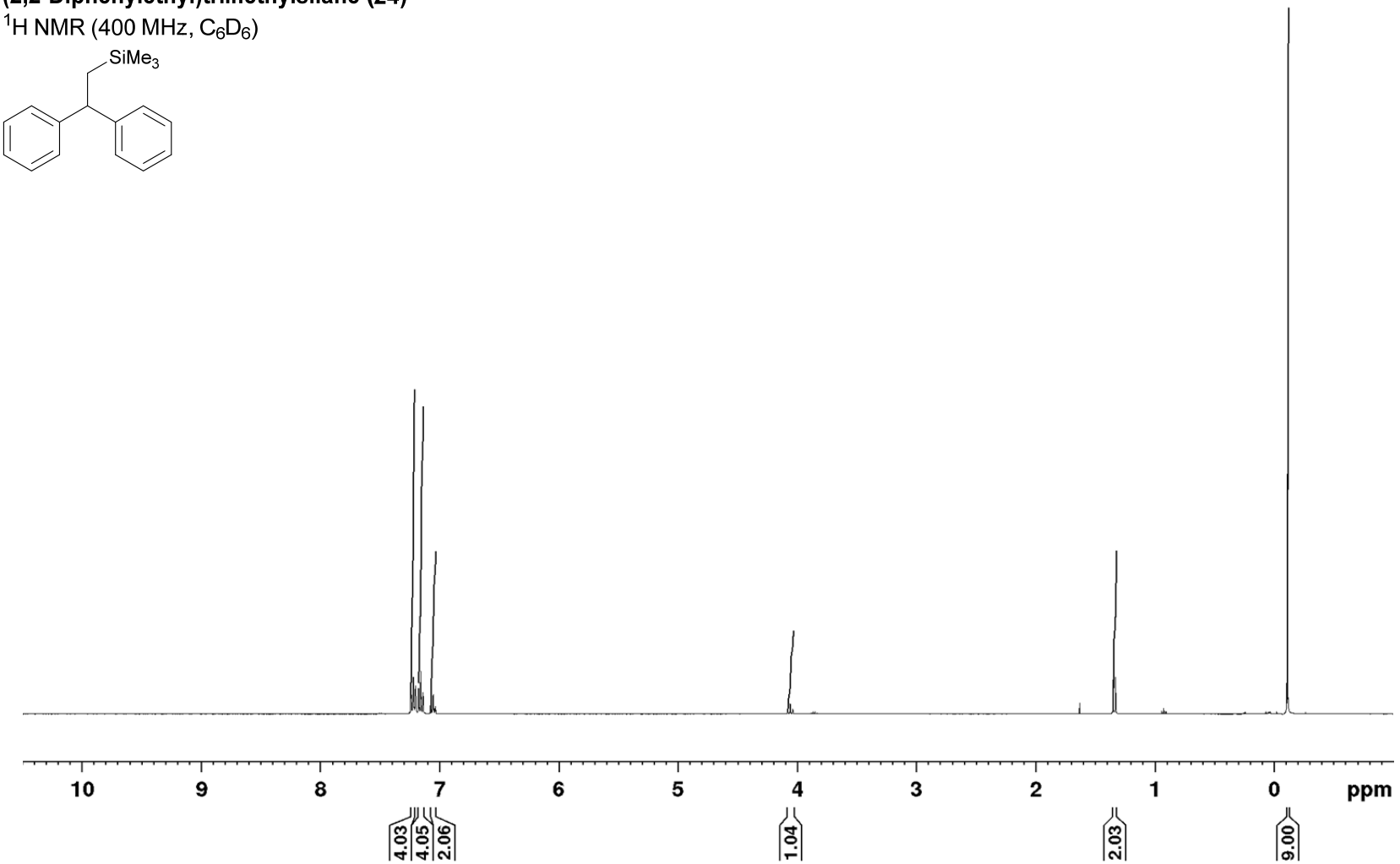
^{29}Si DEPT NMR (99 MHz, C_6D_6):



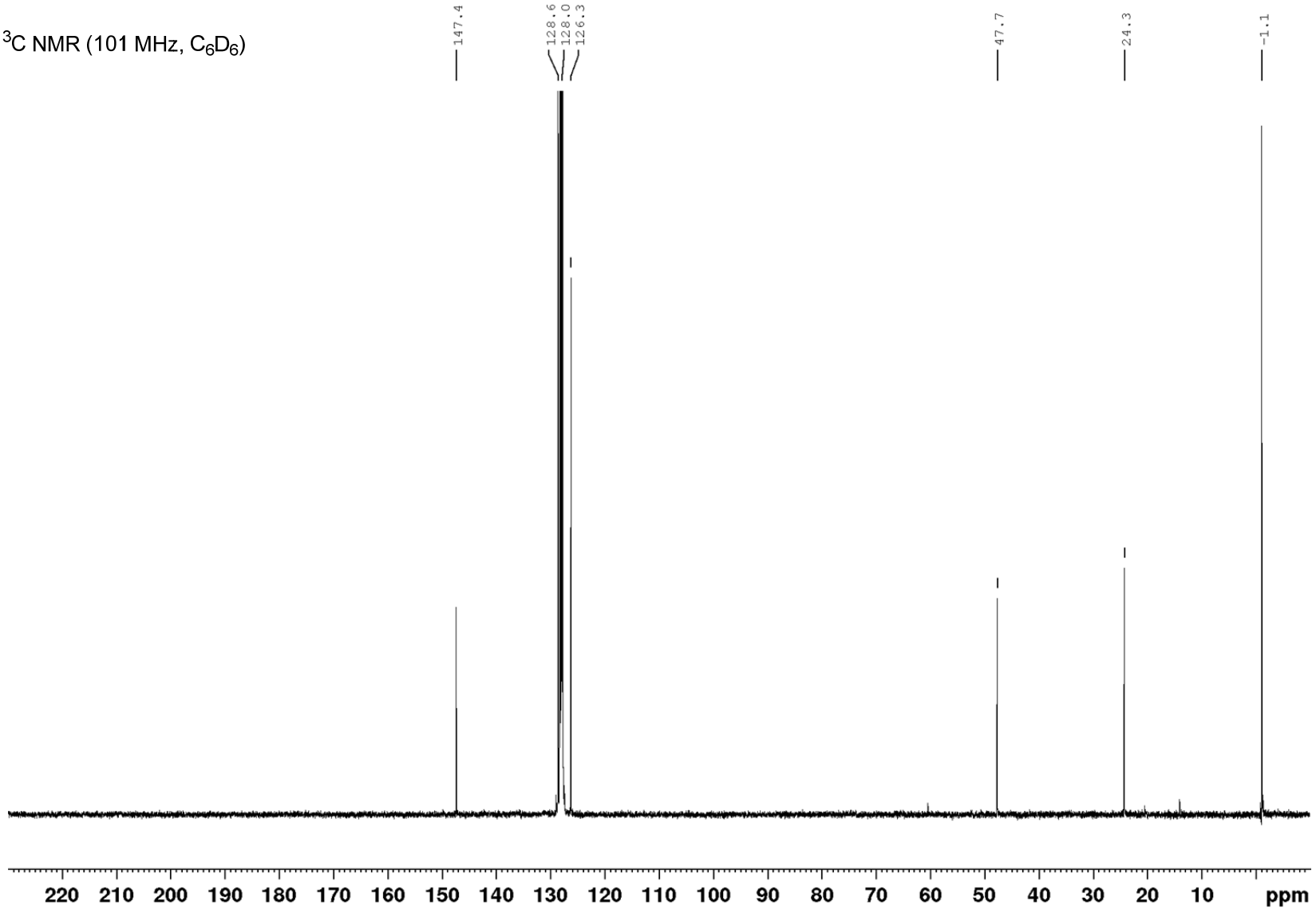
(2,2-Diphenylethyl)trimethylsilane (24)

^{1}H NMR (400 MHz, C_6D_6)

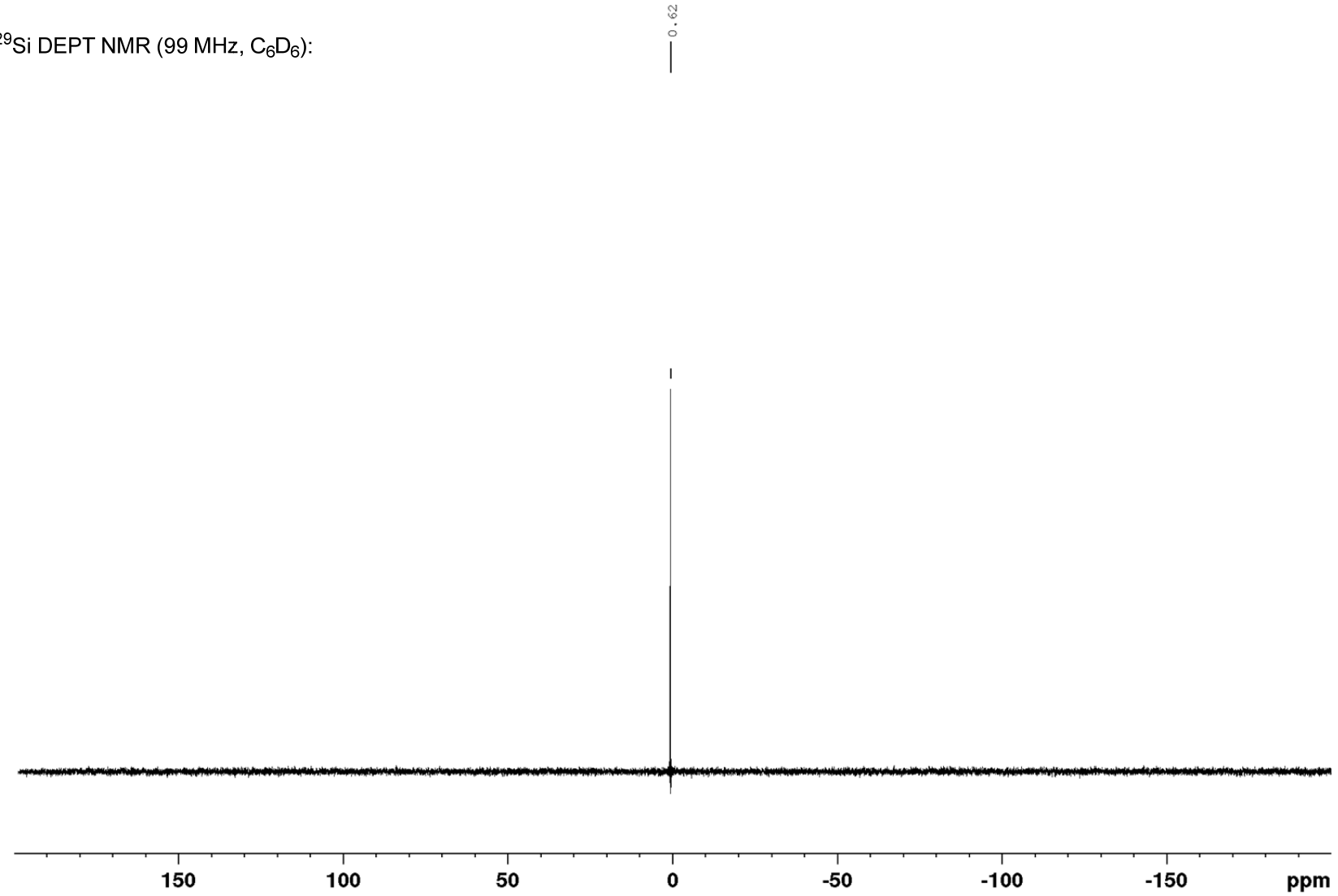




^{13}C NMR (101 MHz, C_6D_6)

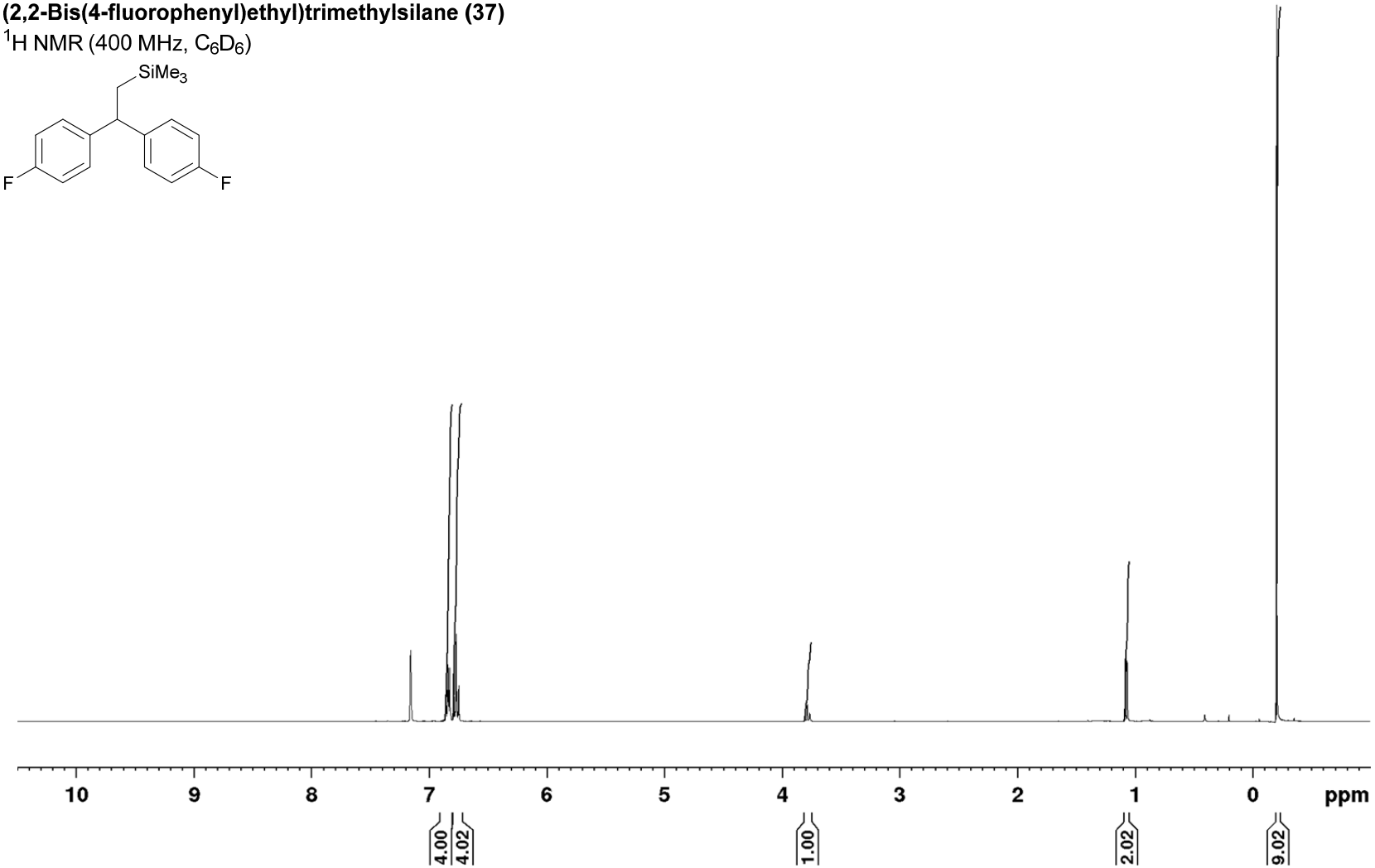


^{29}Si DEPT NMR (99 MHz, C_6D_6):

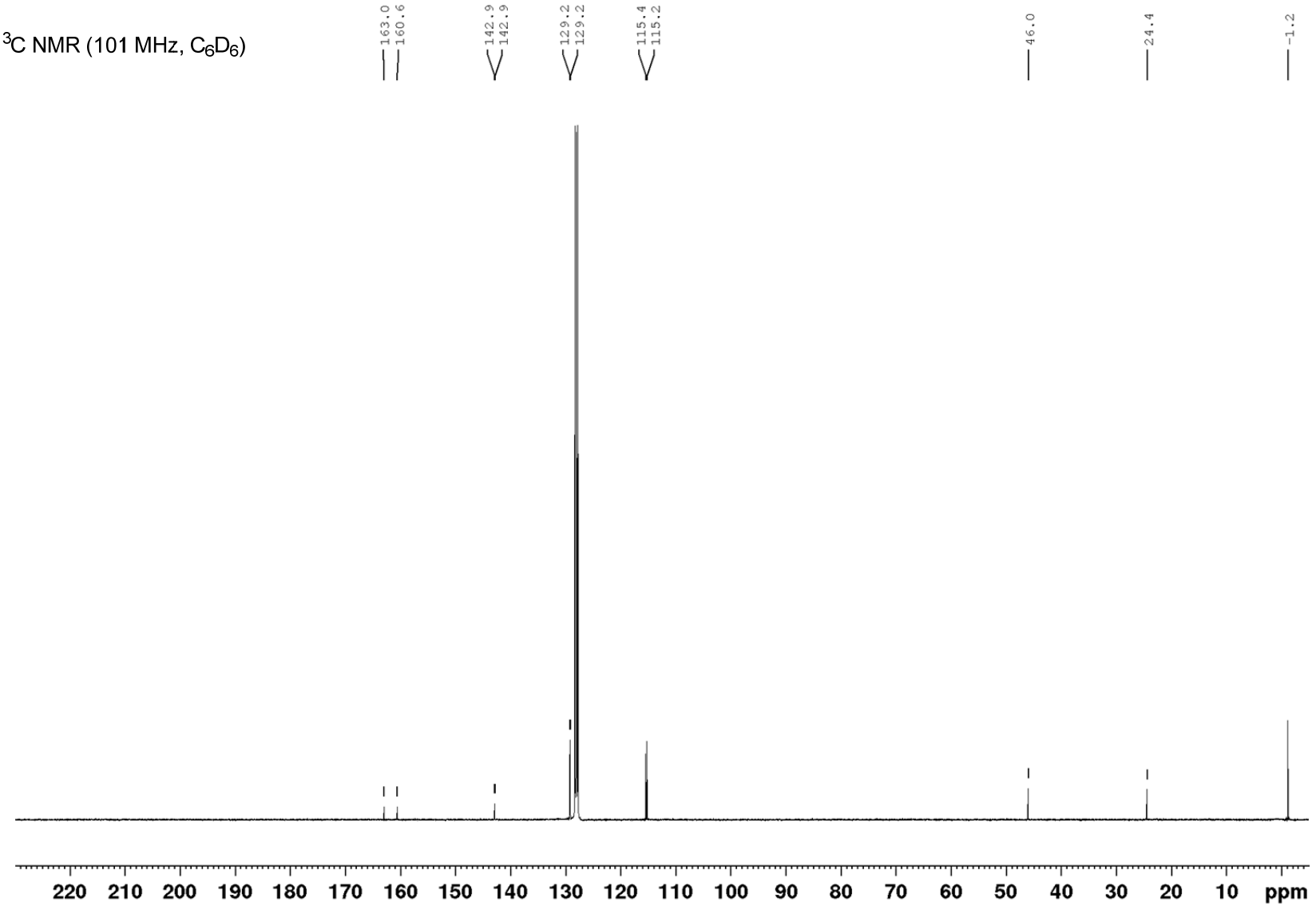


(2,2-Bis(4-fluorophenyl)ethyl)trimethylsilane (37)

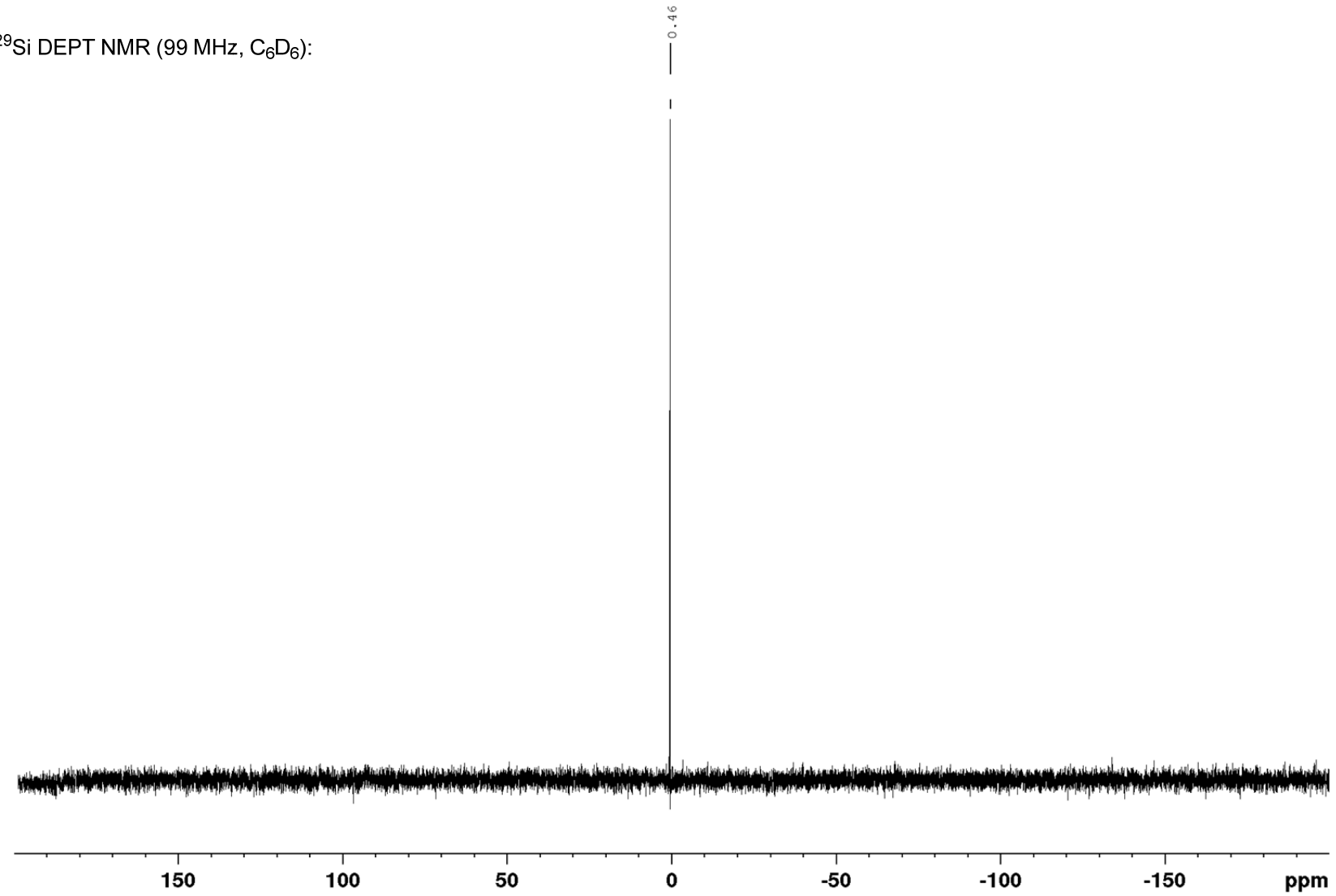
^{1}H NMR (400 MHz, C_6D_6)



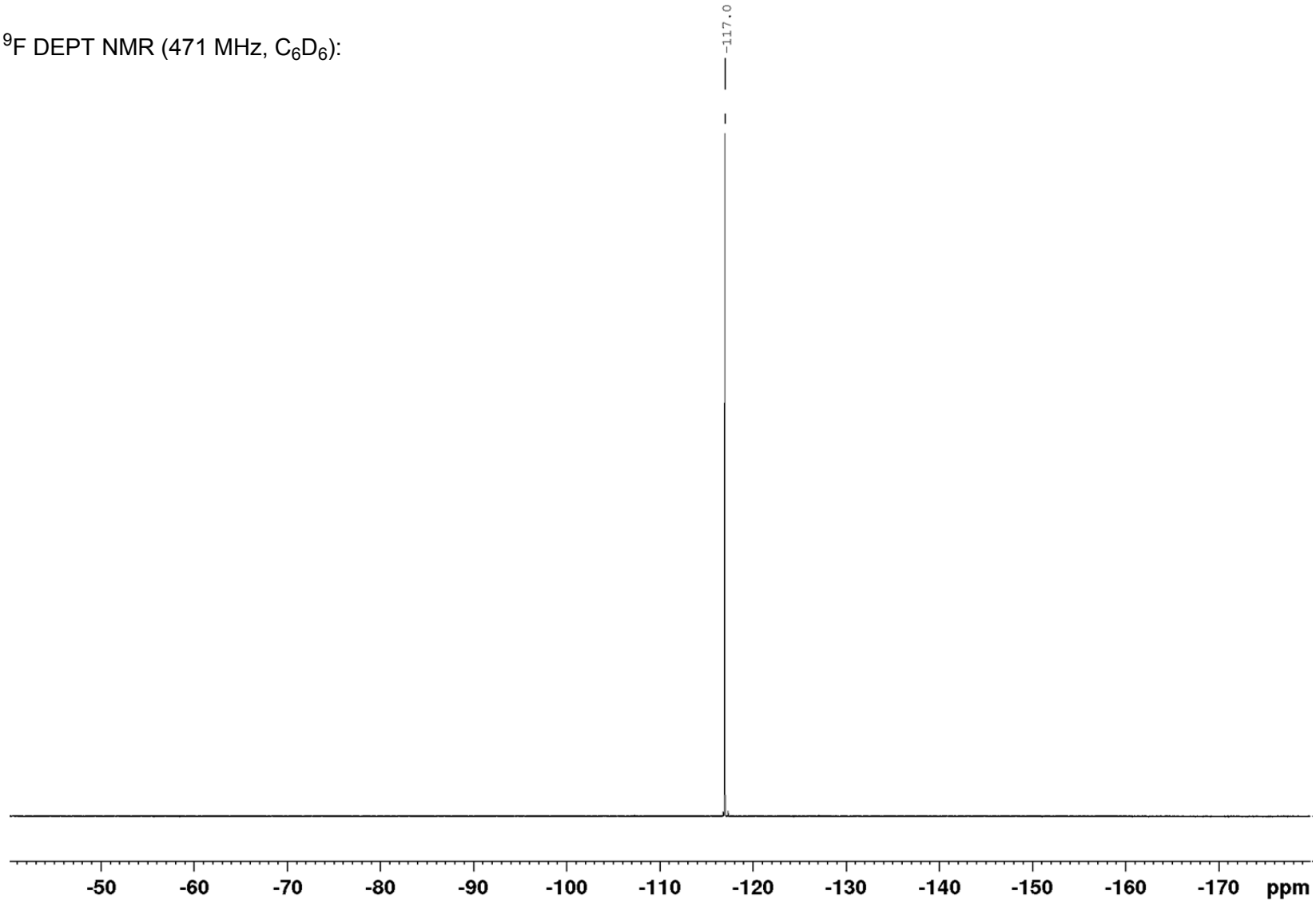
^{13}C NMR (101 MHz, C_6D_6)



^{29}Si DEPT NMR (99 MHz, C_6D_6):

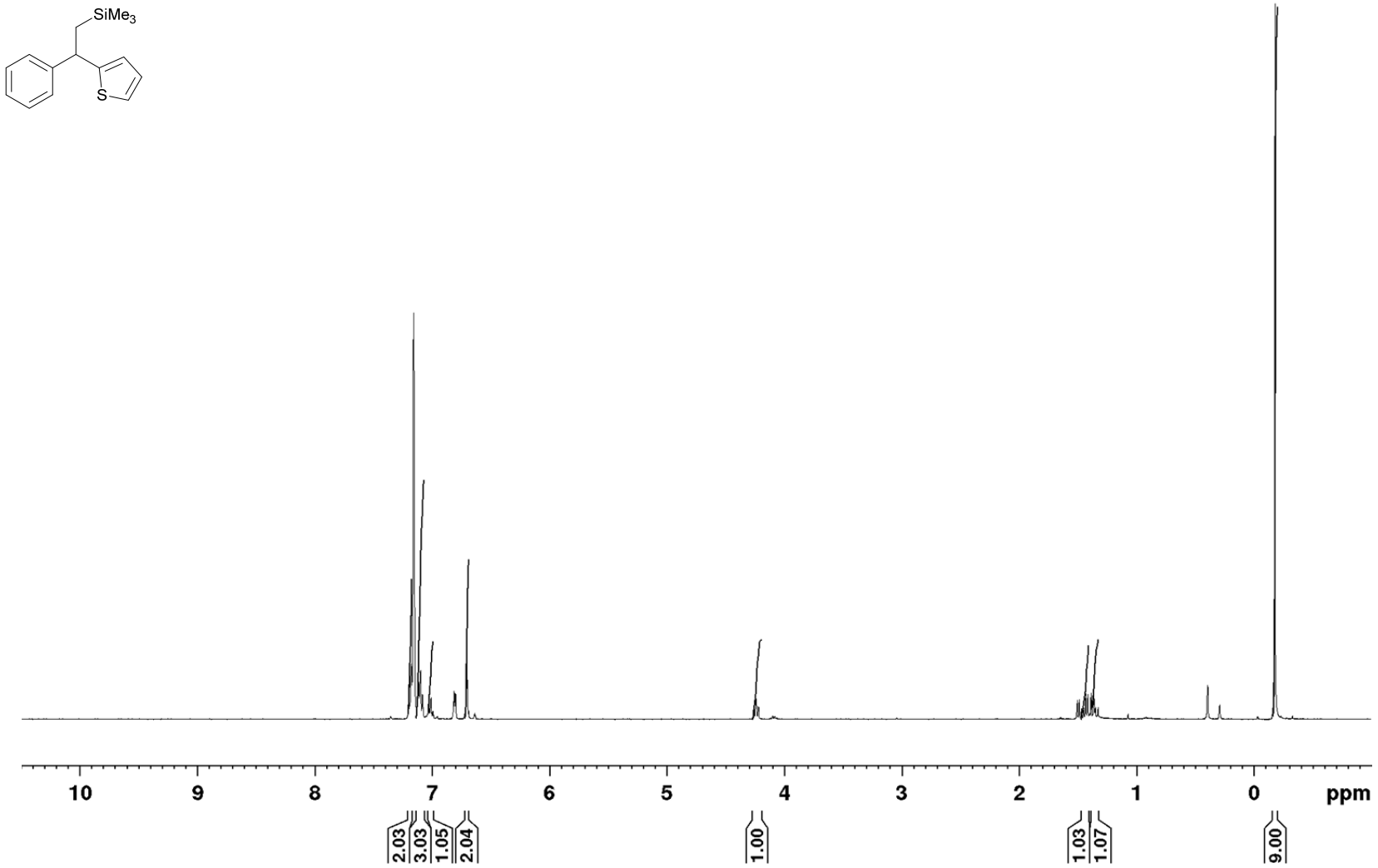


^{19}F DEPT NMR (471 MHz, C_6D_6):

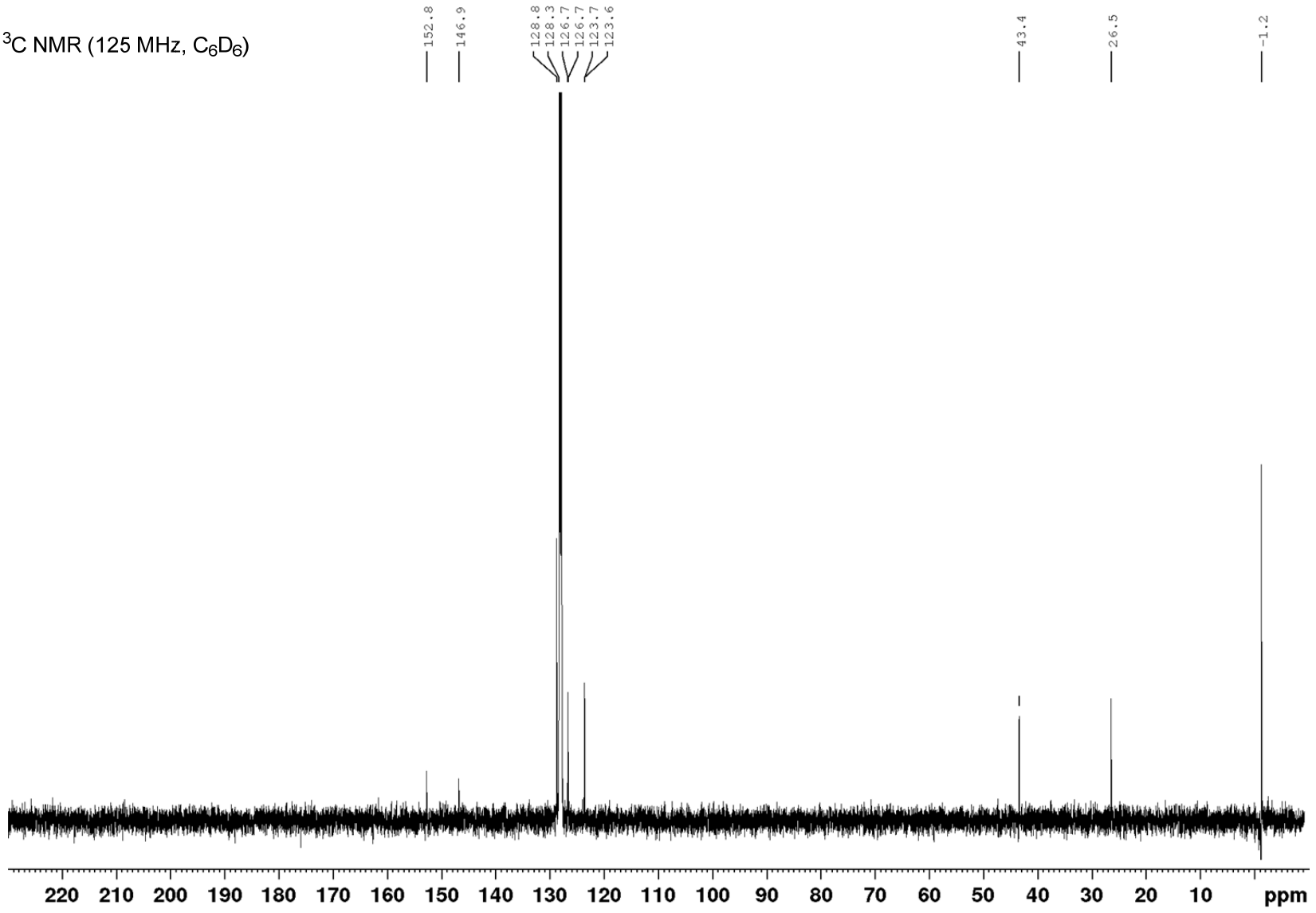


Trimethyl(2-phenyl-2-(thiophen-2-yl)ethyl)silane (38)

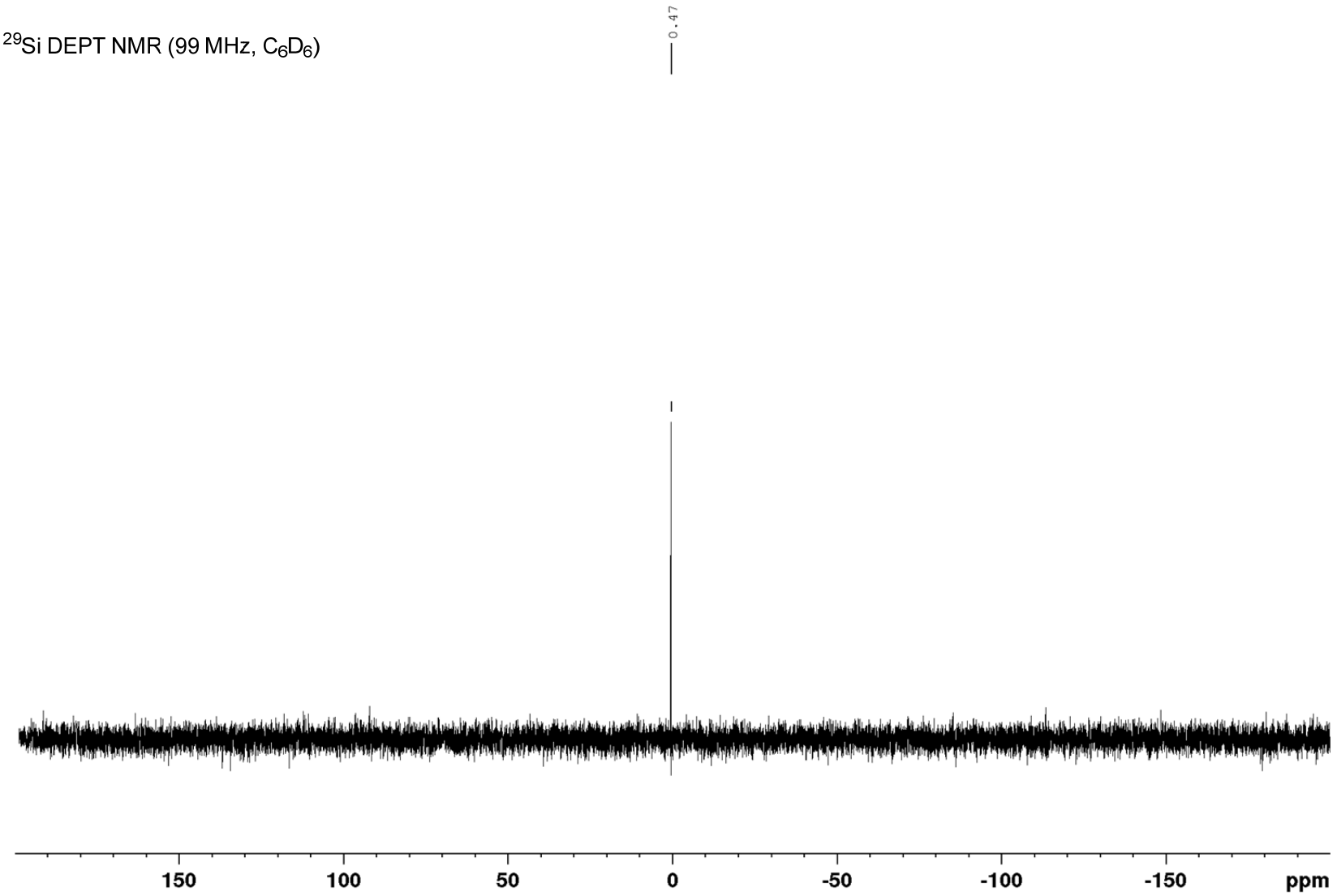
^{1}H NMR (500 MHz, C_6D_6)



^{13}C NMR (125 MHz, C_6D_6)

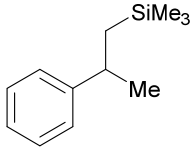


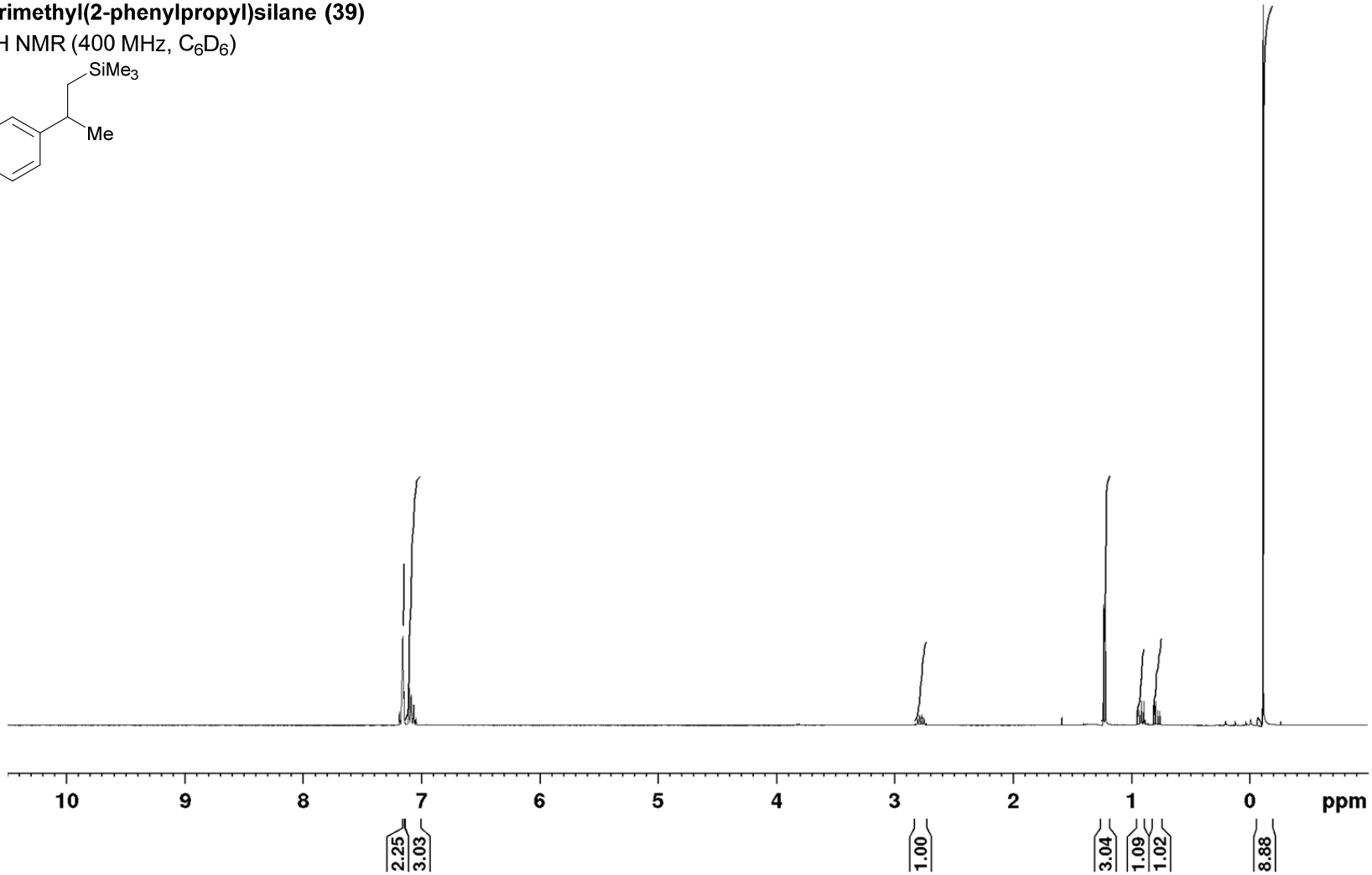
^{29}Si DEPT NMR (99 MHz, C_6D_6)



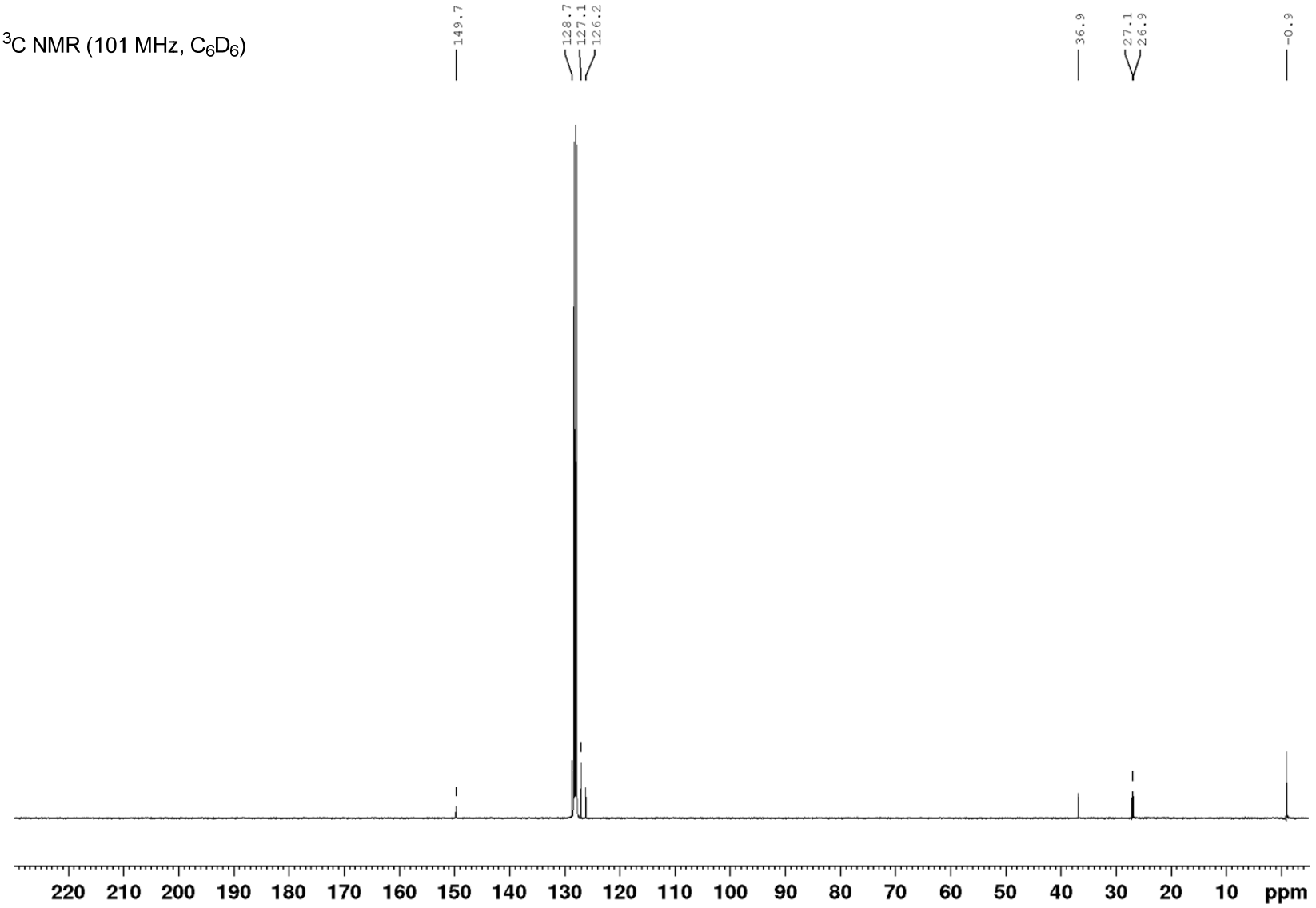
Trimethyl(2-phenylpropyl)silane (39)

^{1}H NMR (400 MHz, C_6D_6)

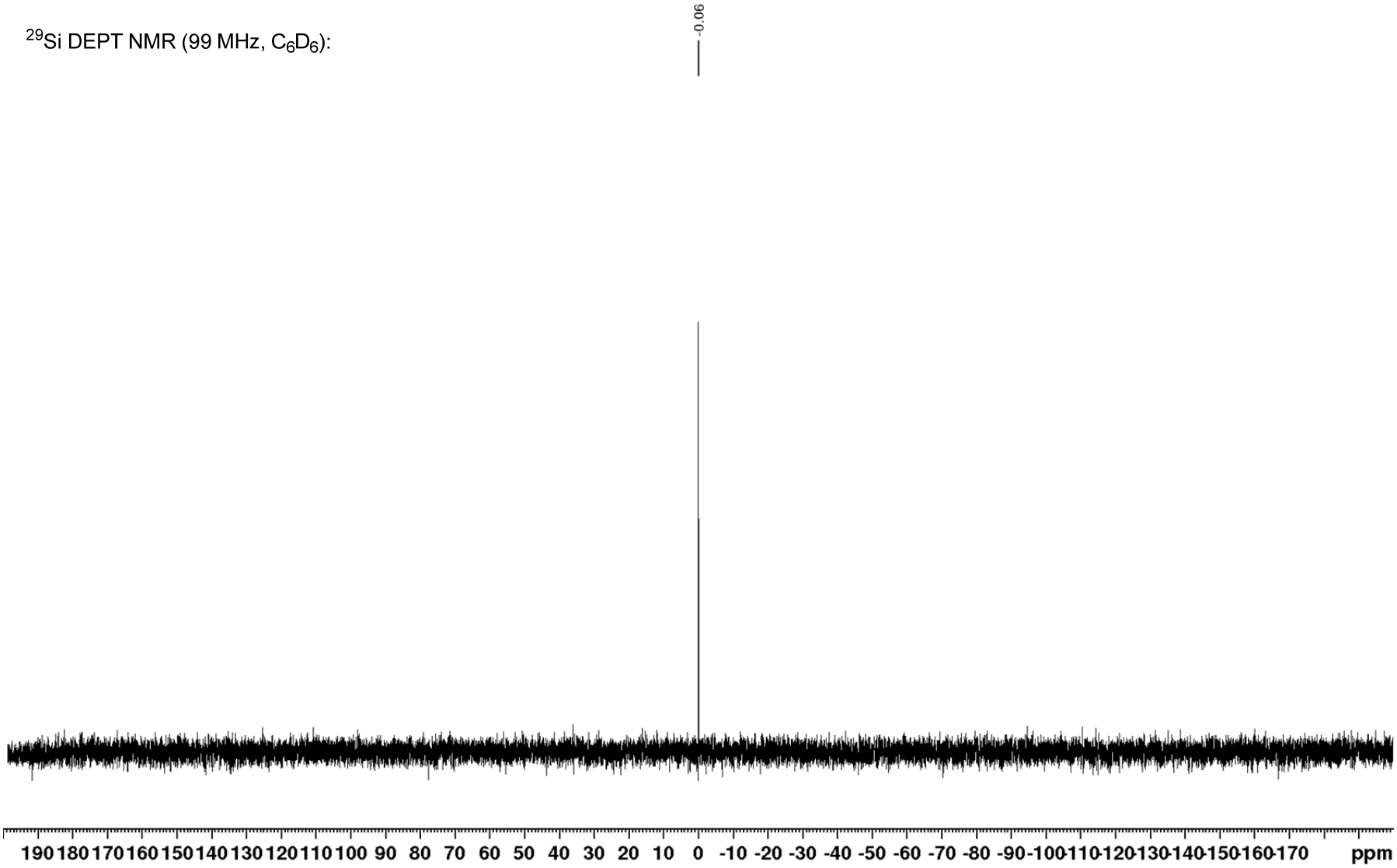




^{13}C NMR (101 MHz, C_6D_6)

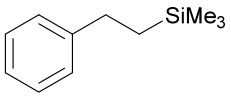


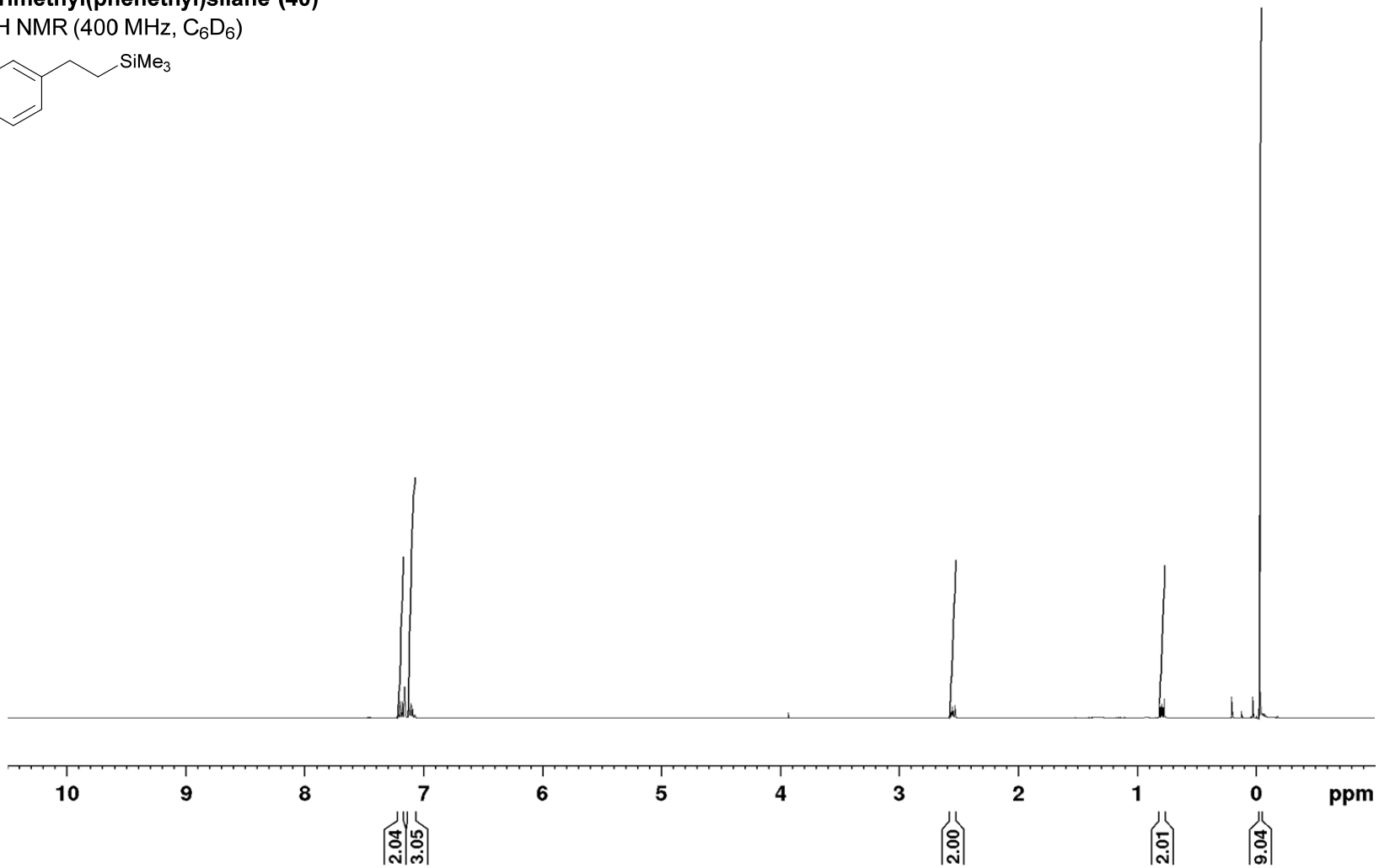
^{29}Si DEPT NMR (99 MHz, C_6D_6):



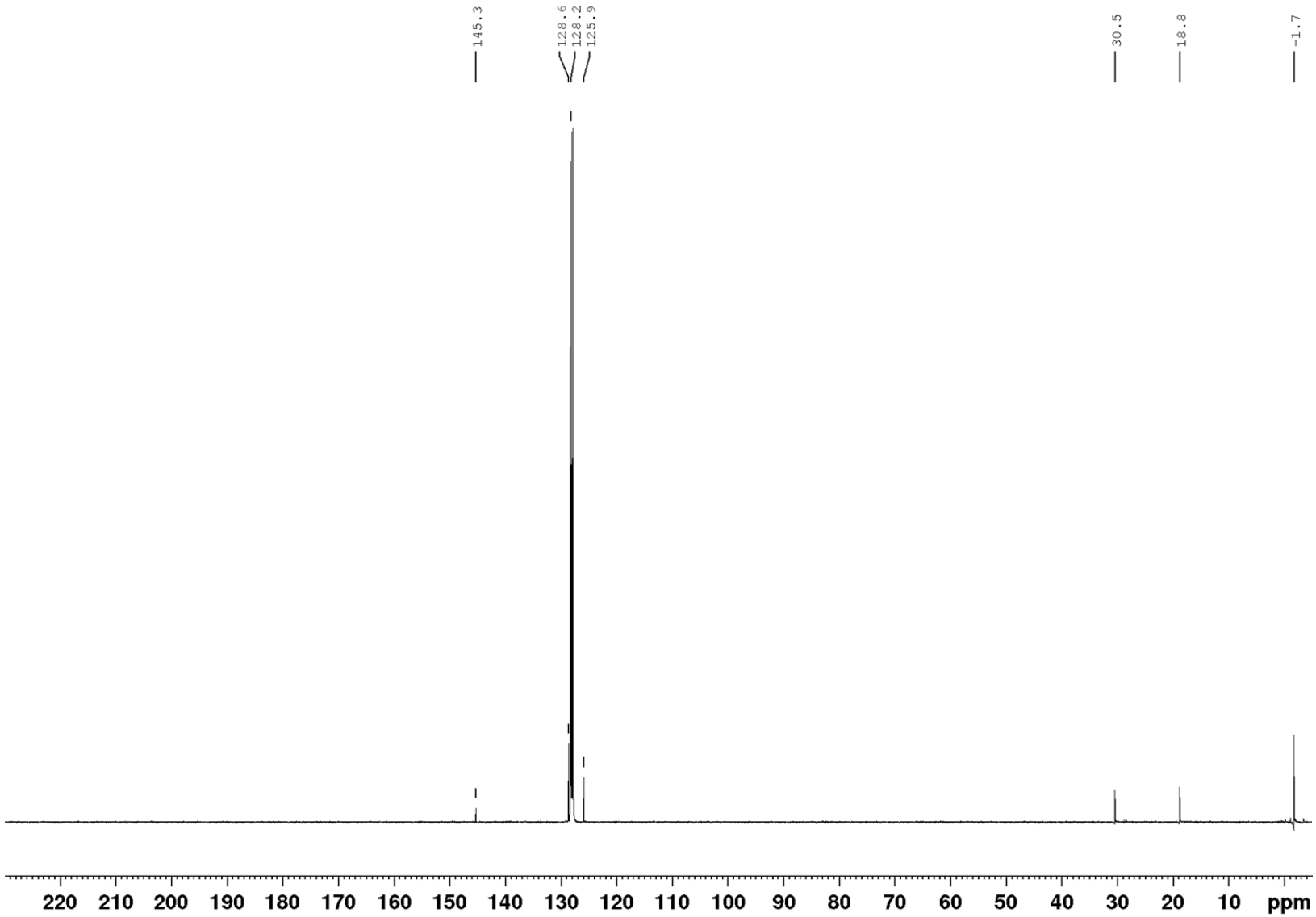
Trimethyl(phenethyl)silane (40)

^{1}H NMR (400 MHz, C_6D_6)

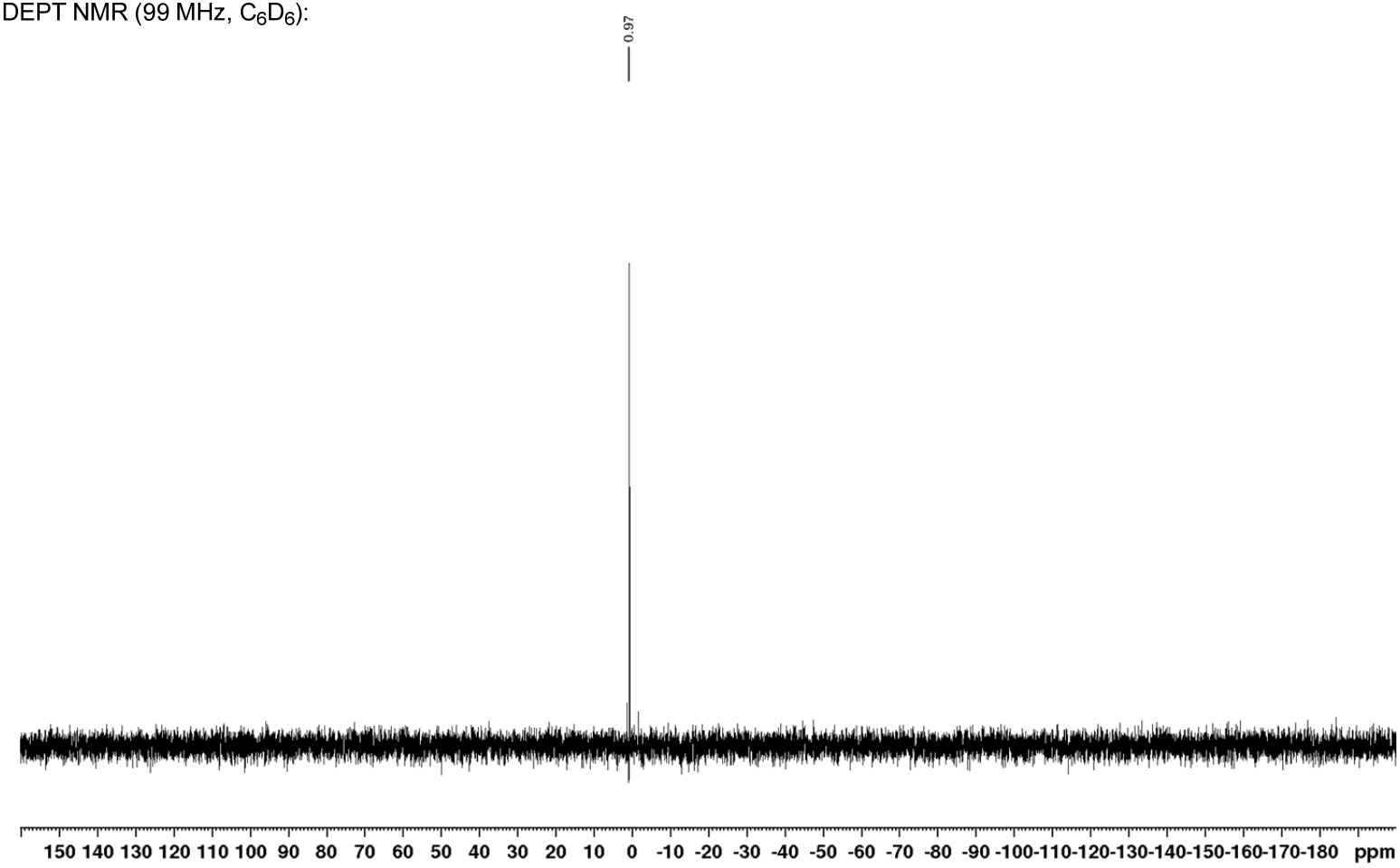




^{13}C NMR (101 MHz, C_6D_6)

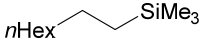


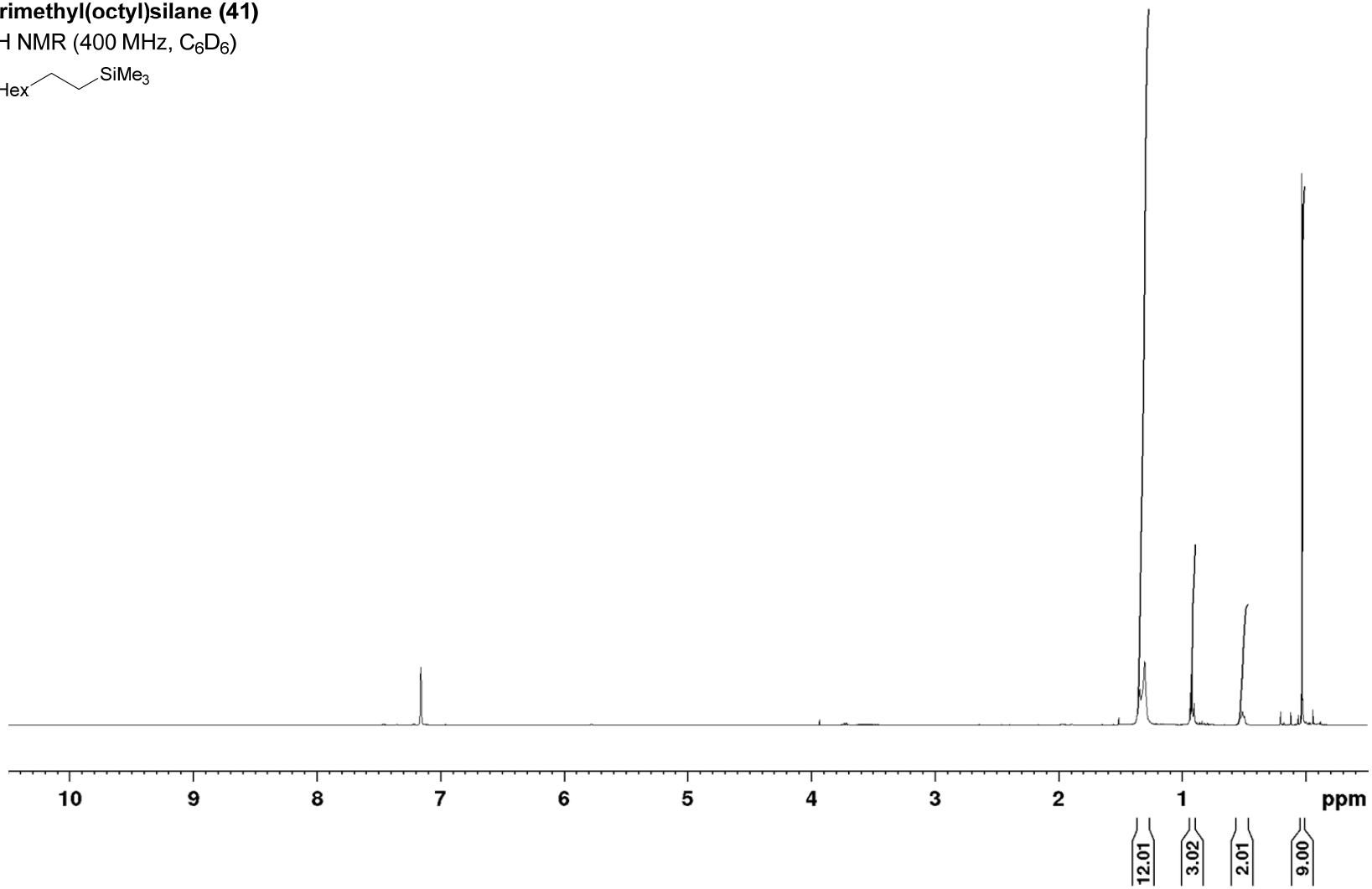
^{29}Si DEPT NMR (99 MHz, C_6D_6):



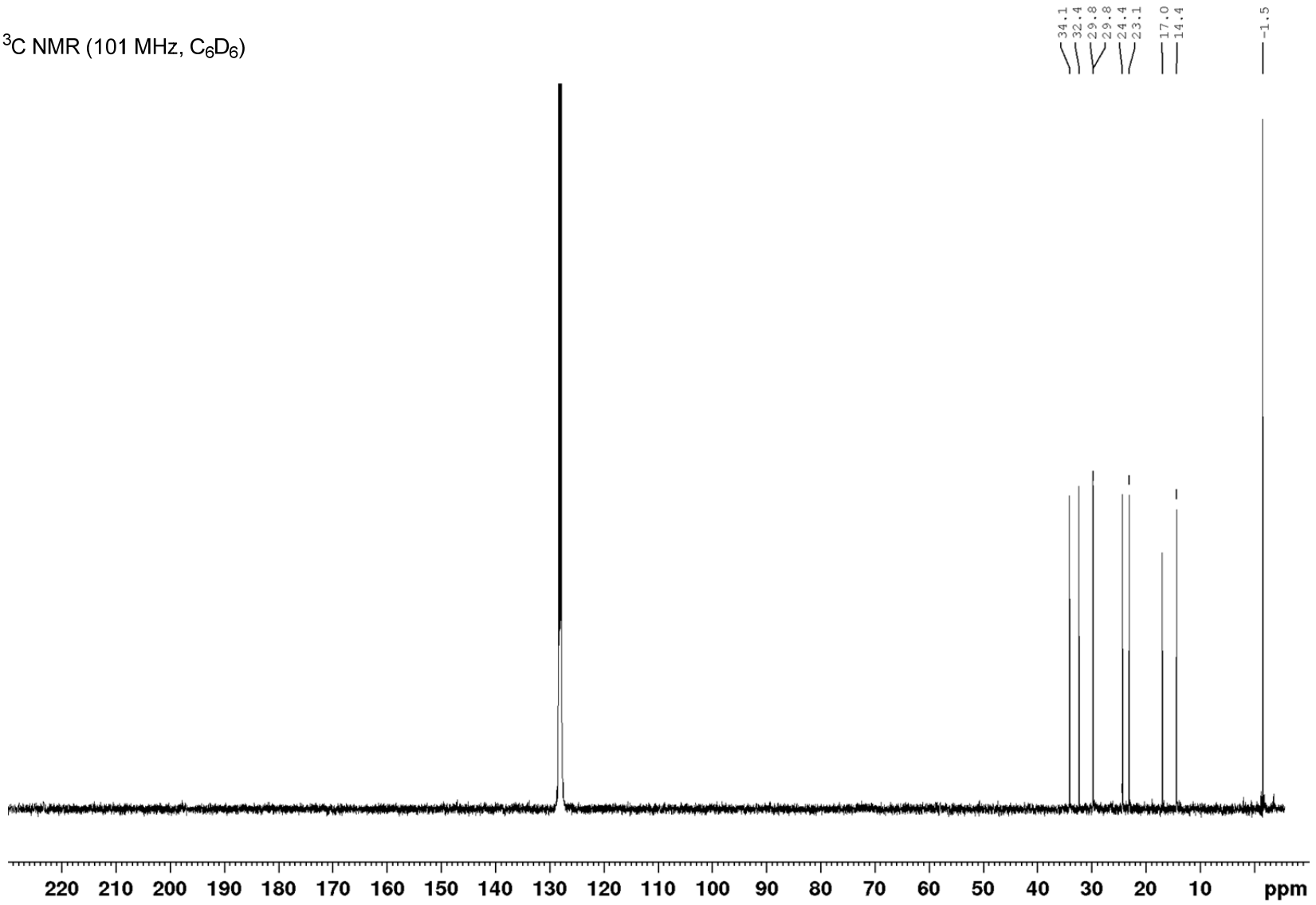
Trimethyl(octyl)silane (41)

^{1}H NMR (400 MHz, C_6D_6)

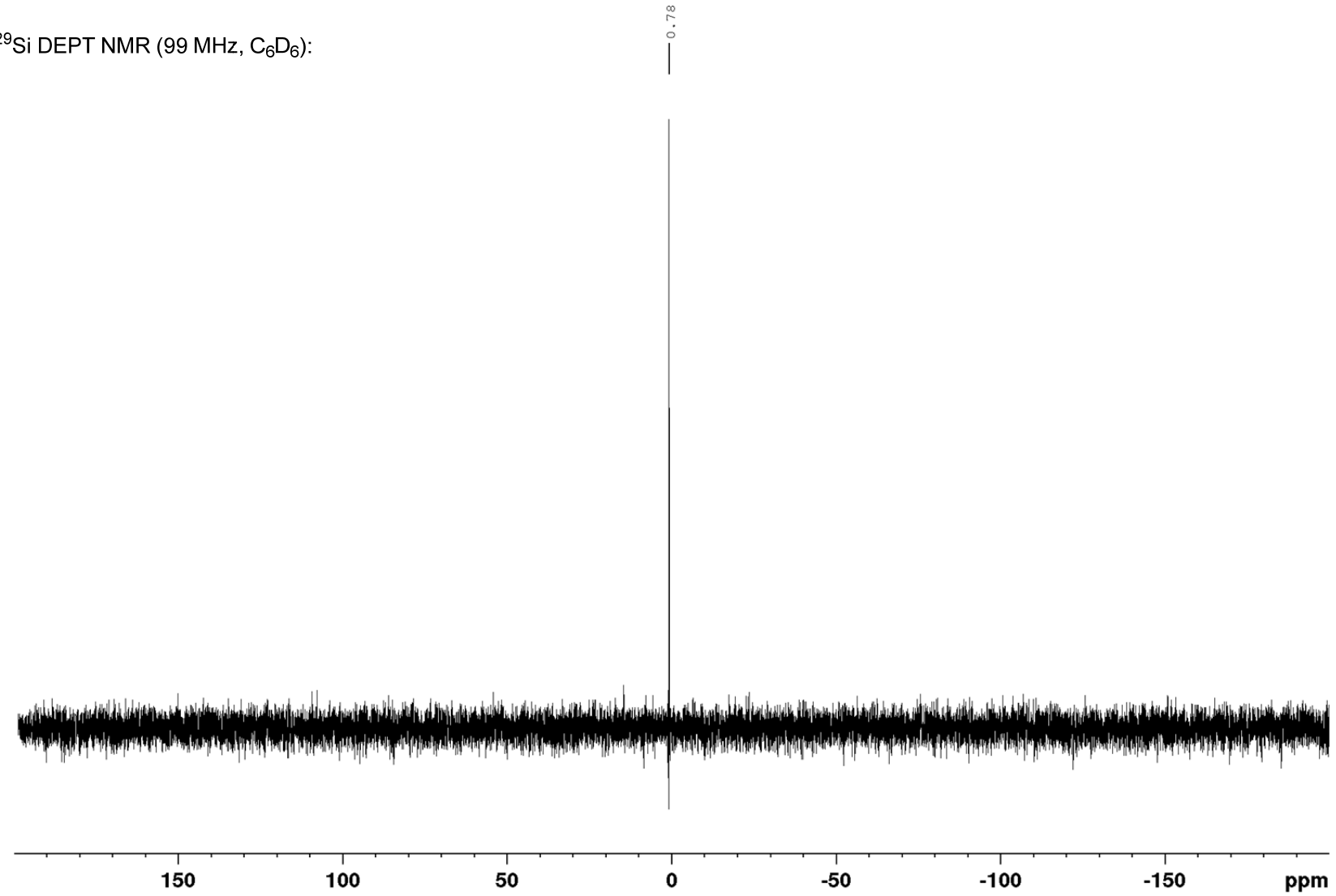




^{13}C NMR (101 MHz, C_6D_6)

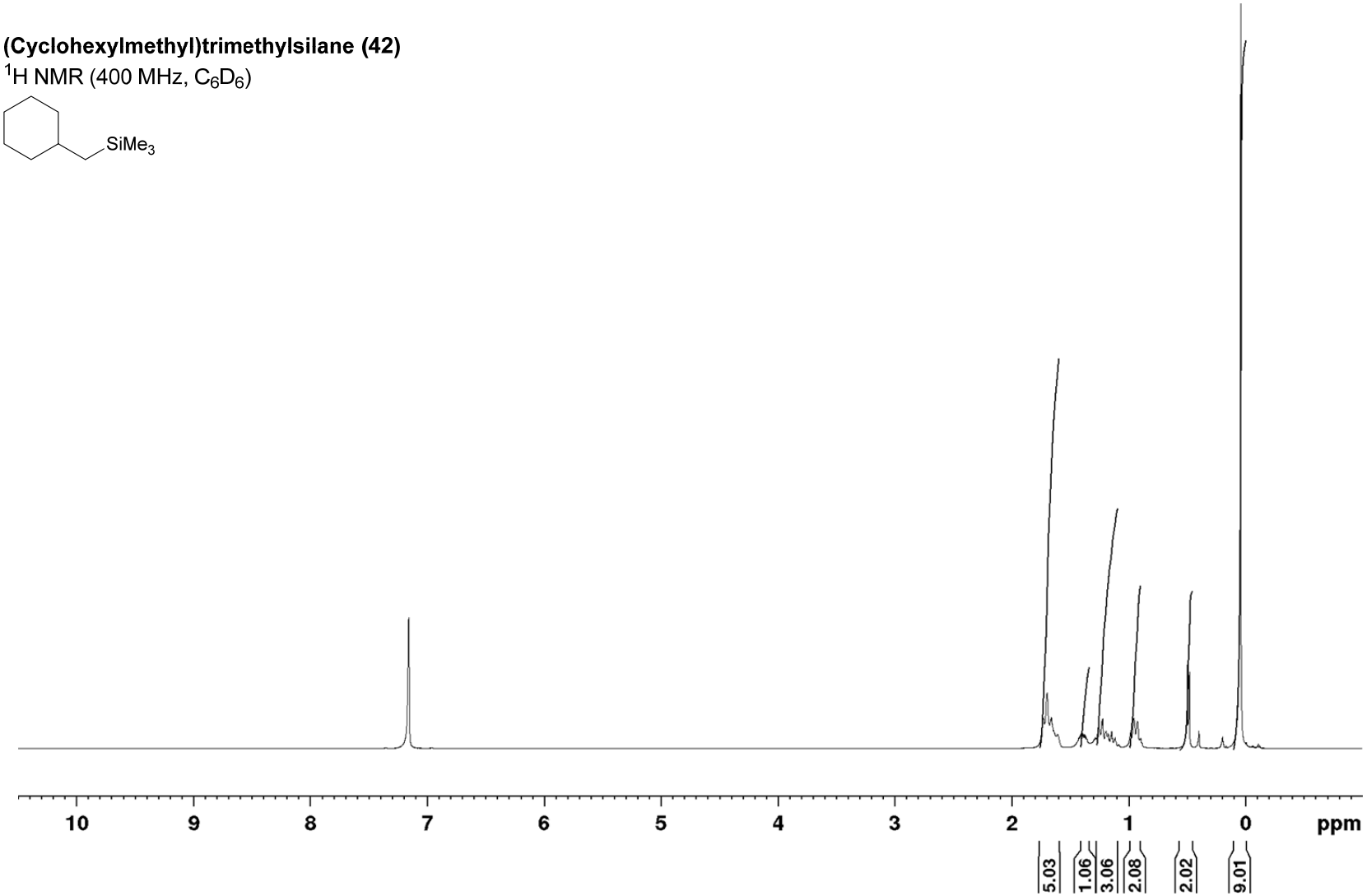


^{29}Si DEPT NMR (99 MHz, C_6D_6):

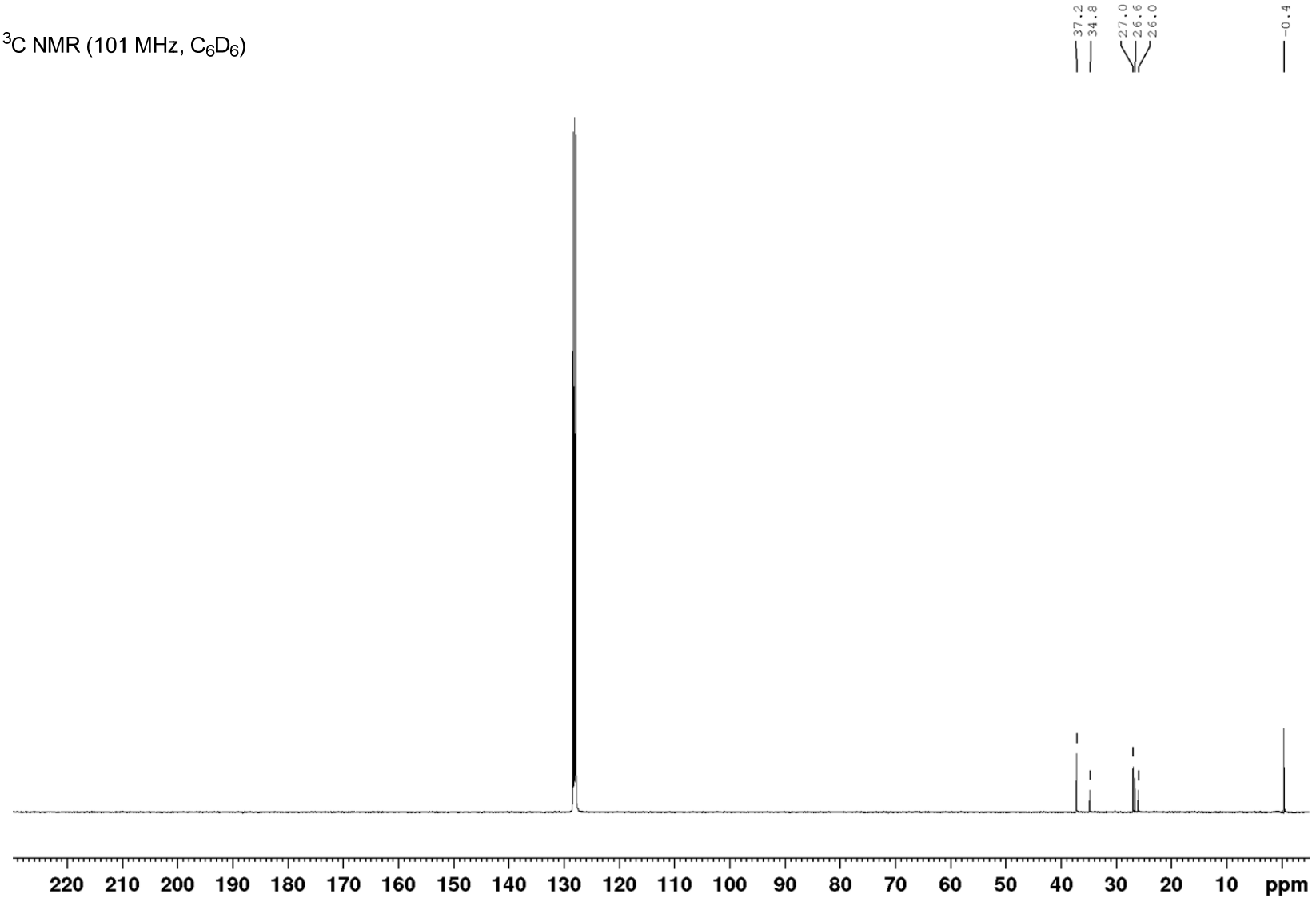


(Cyclohexylmethyl)trimethylsilane (42)

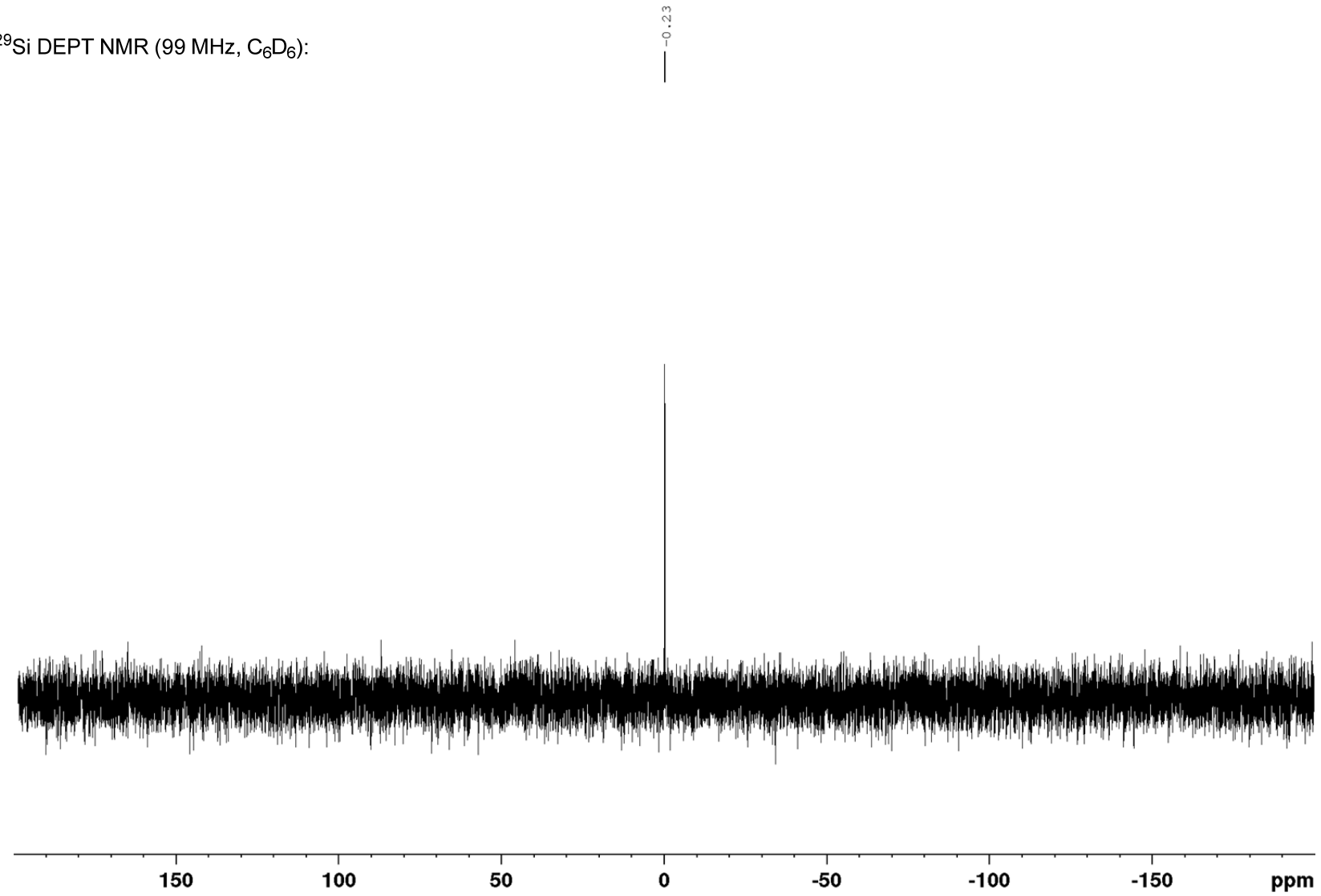
^{1}H NMR (400 MHz, C_6D_6)



^{13}C NMR (101 MHz, C_6D_6)

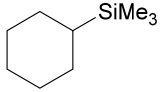


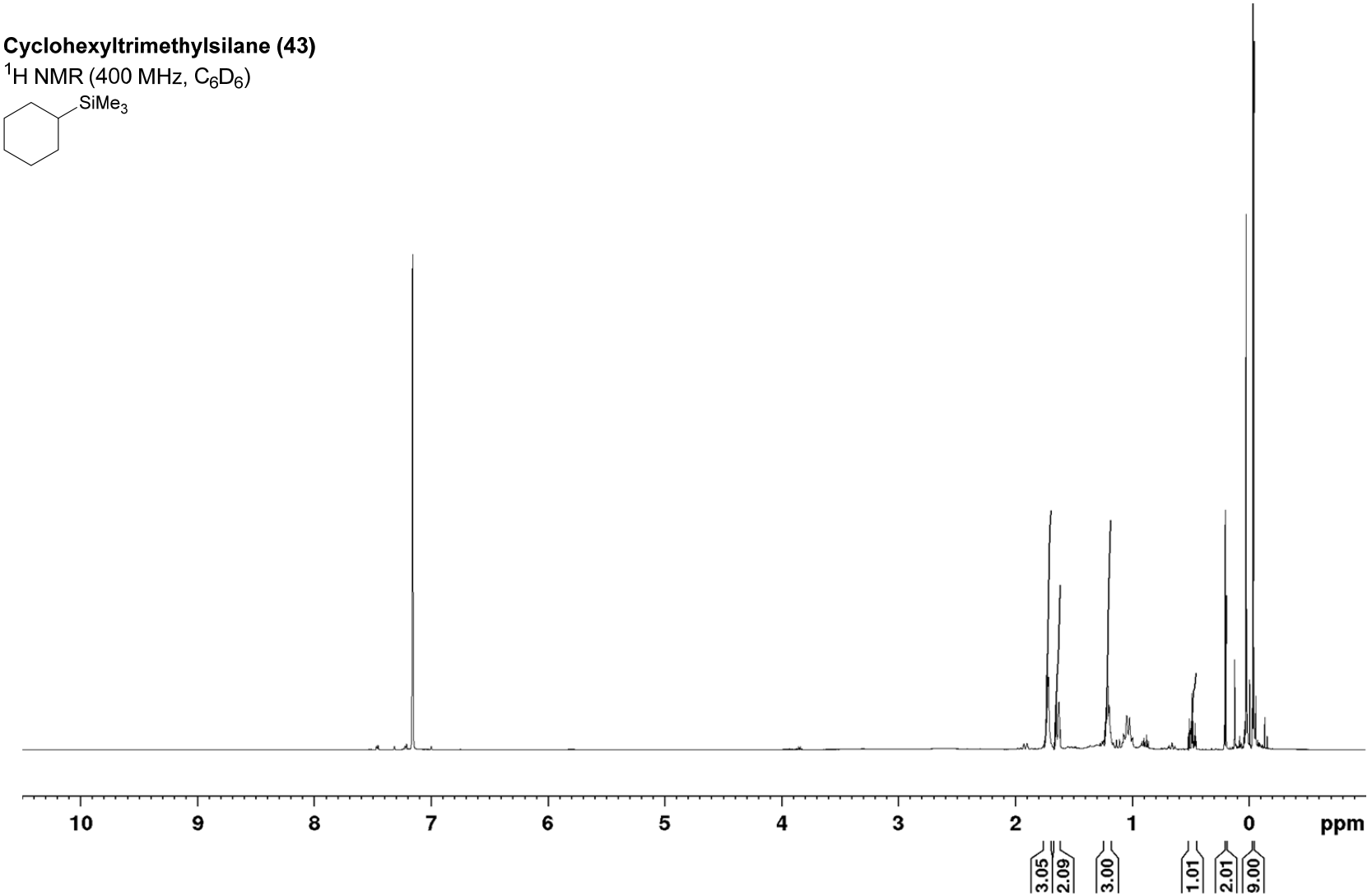
^{29}Si DEPT NMR (99 MHz, C_6D_6):



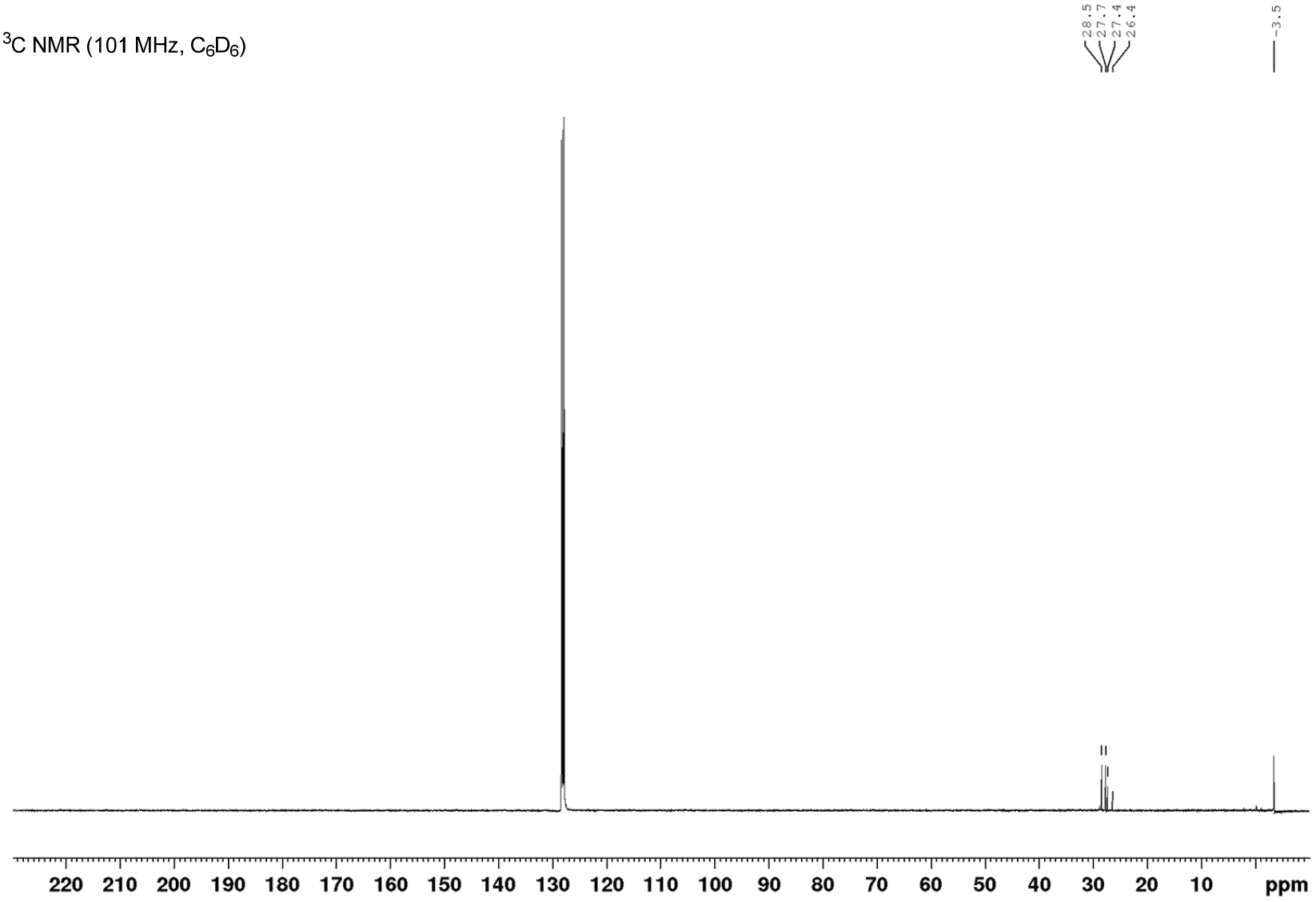
Cyclohexyltrimethylsilane (43)

^{1}H NMR (400 MHz, C_6D_6)

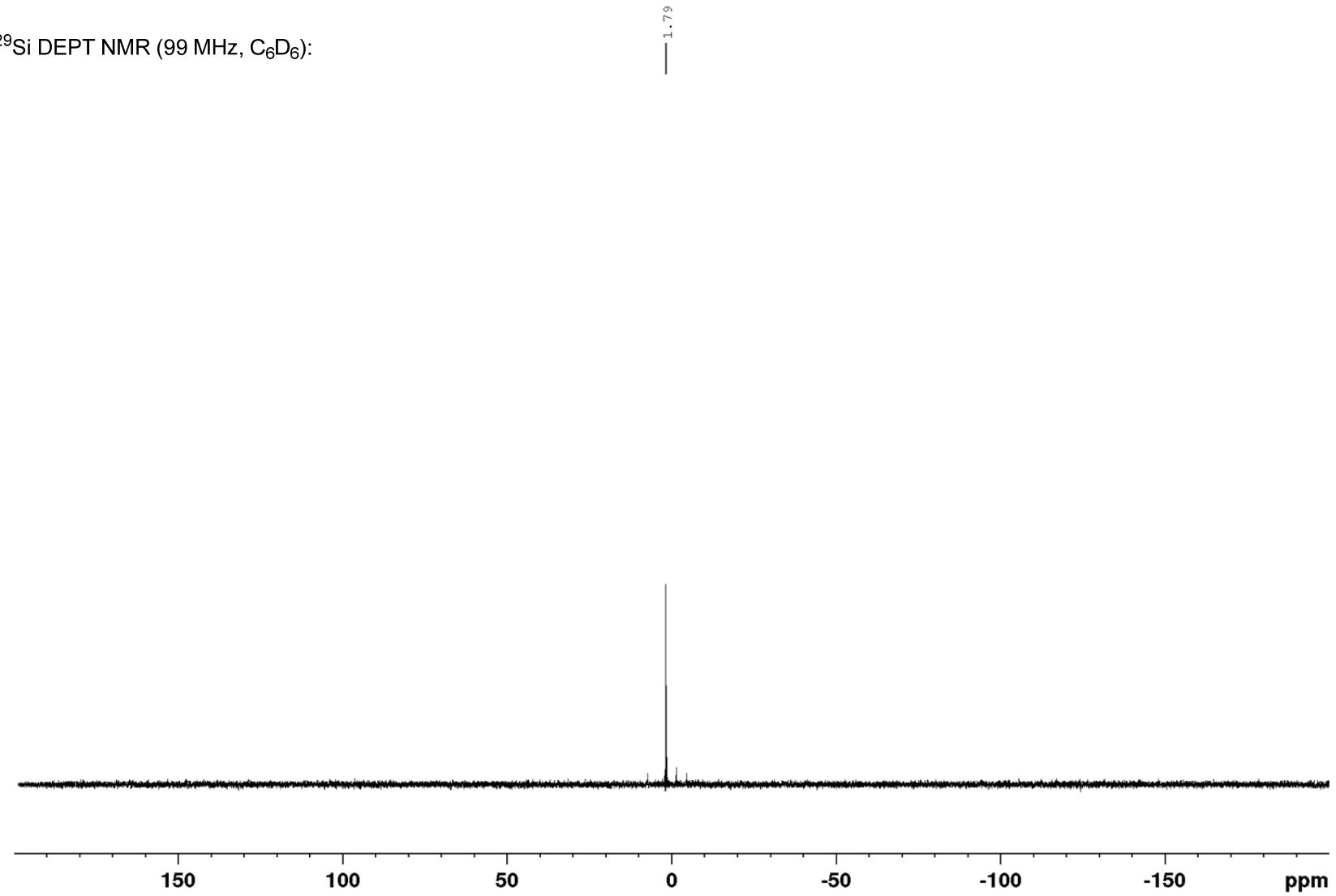




^{13}C NMR (101 MHz, C_6D_6)

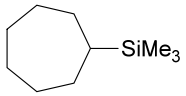


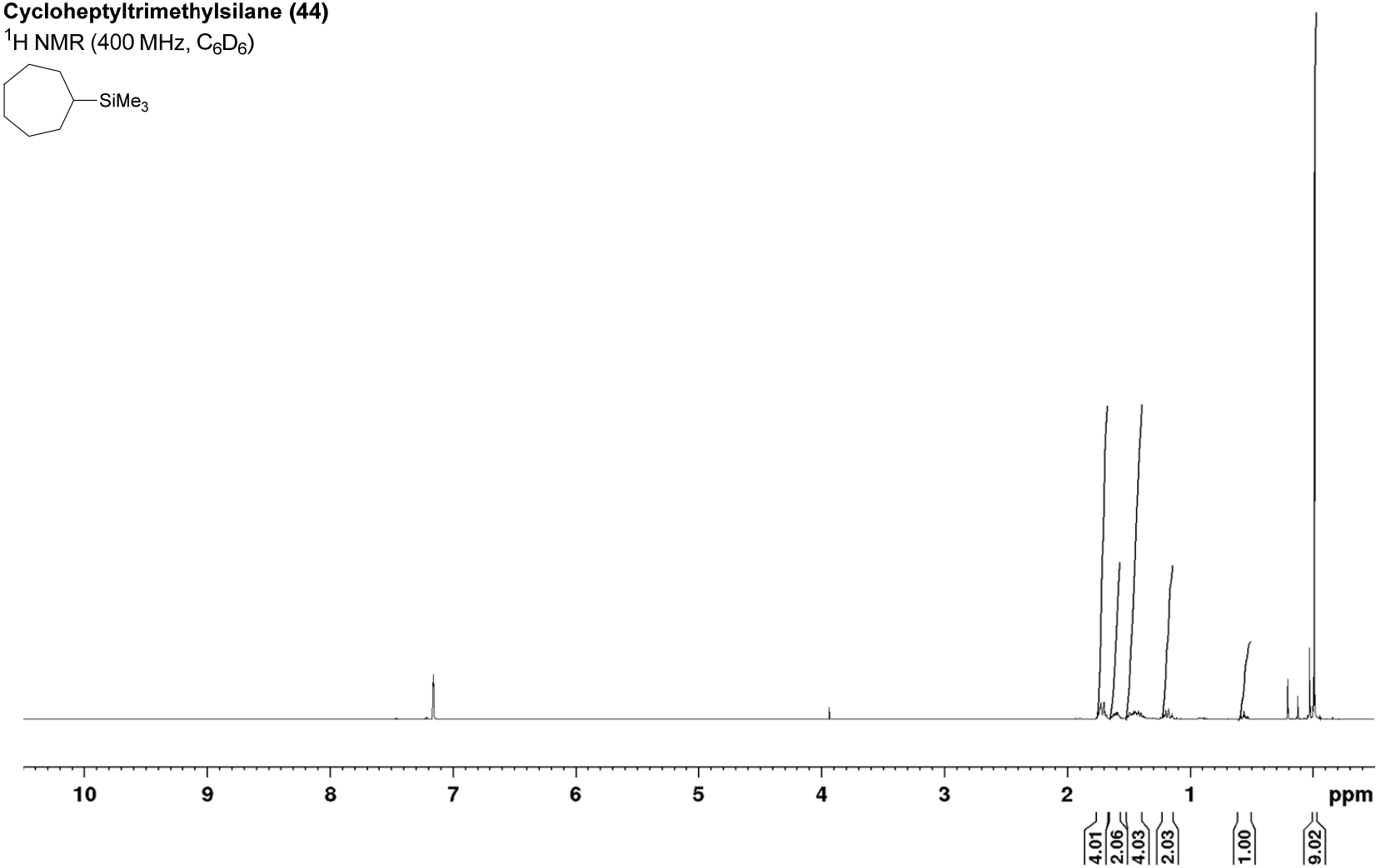
^{29}Si DEPT NMR (99 MHz, C_6D_6):



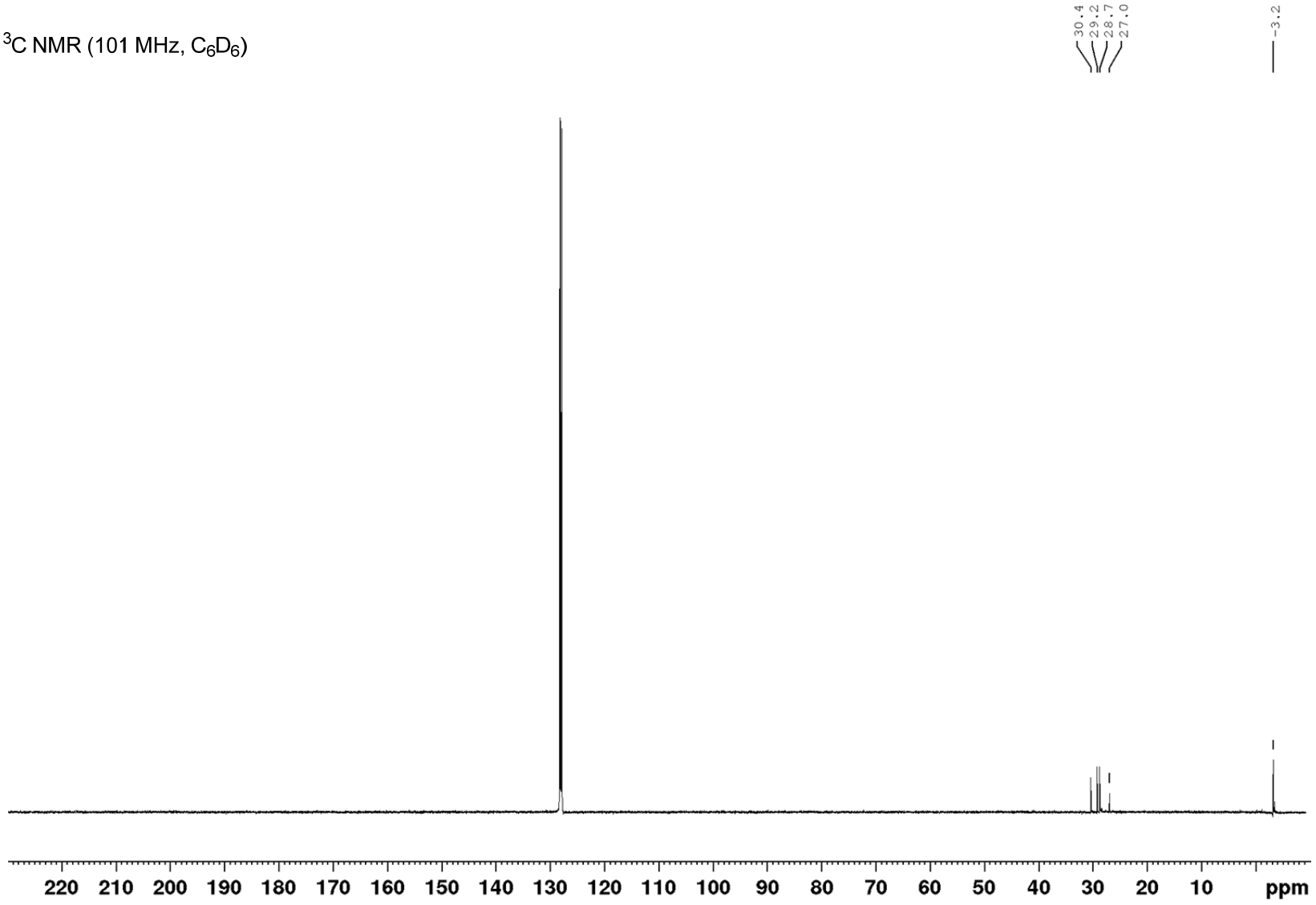
Cycloheptyltrimethylsilane (44)

^{1}H NMR (400 MHz, C_6D_6)

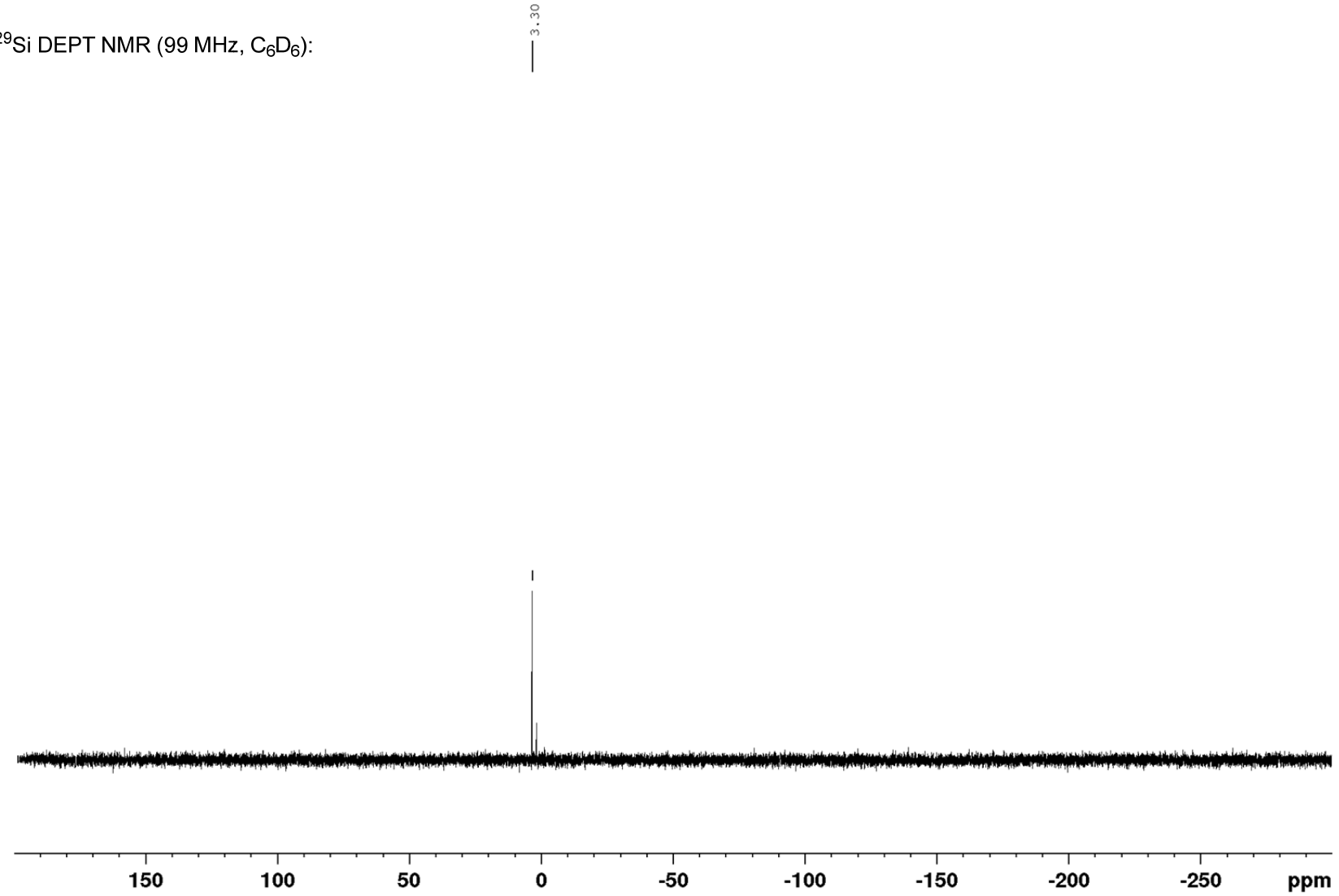




^{13}C NMR (101 MHz, C_6D_6)

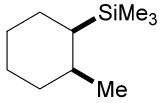


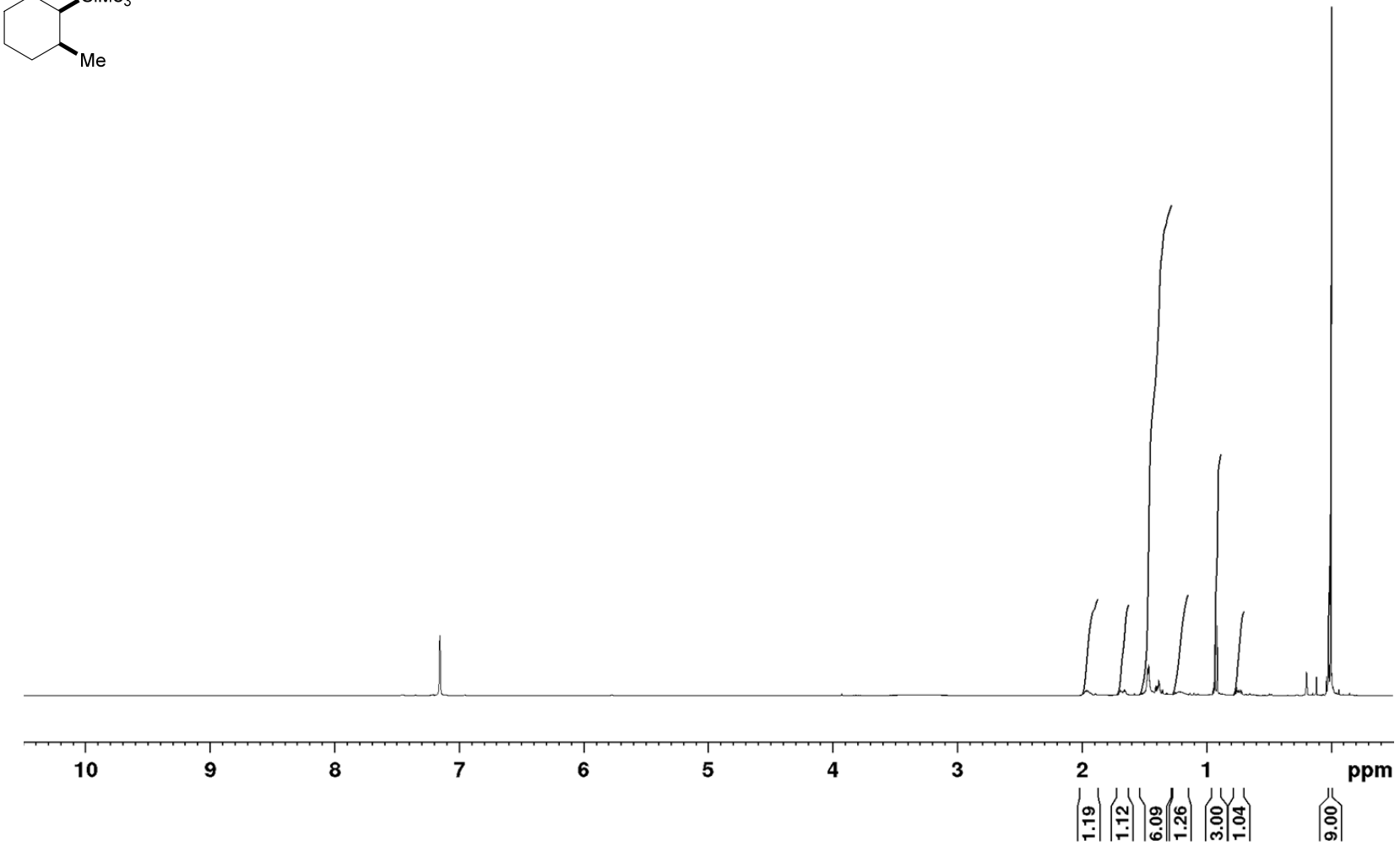
^{29}Si DEPT NMR (99 MHz, C_6D_6):



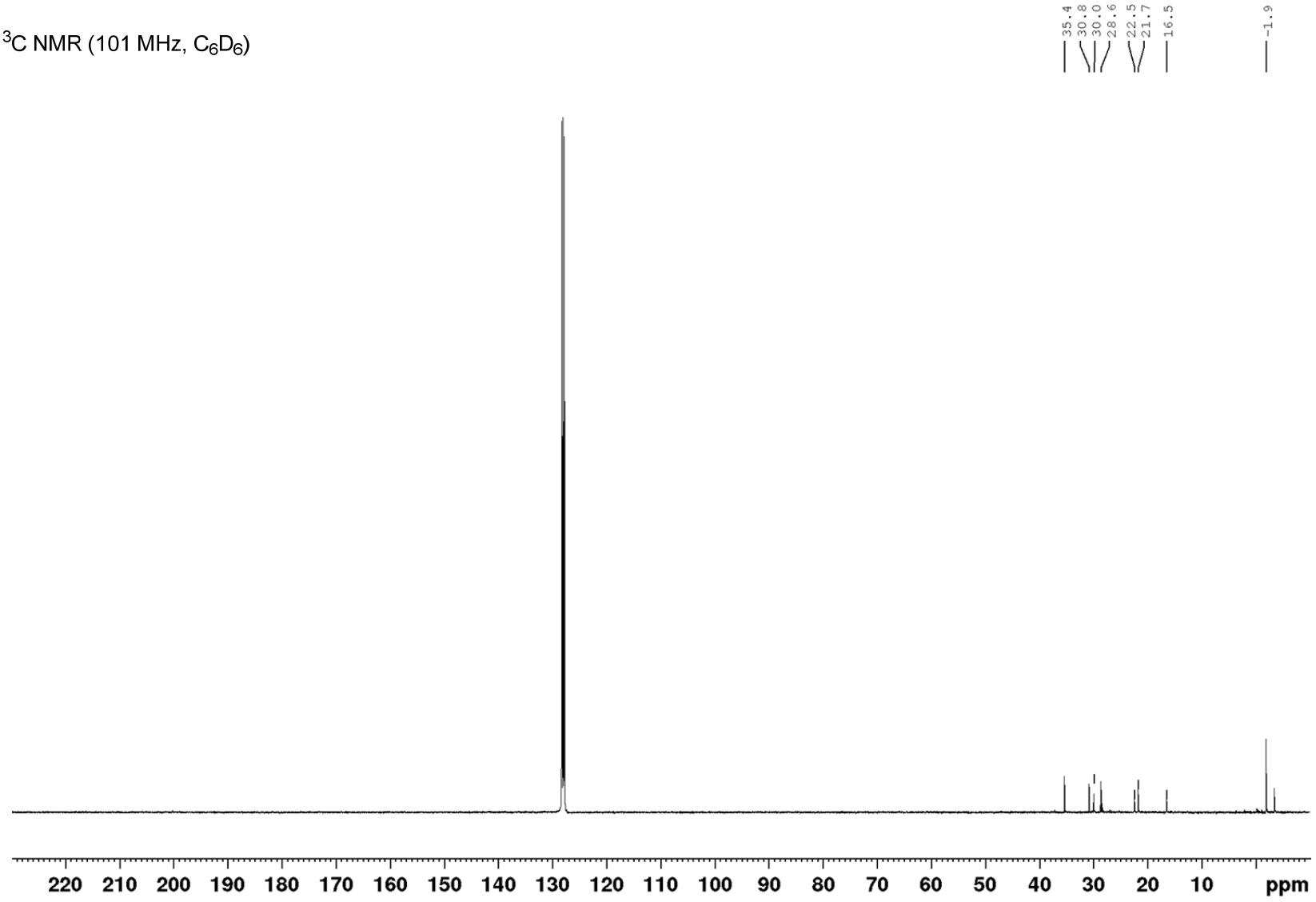
Trimethyl((1*R*,2*S*)-2-methylcyclohexyl)silane (45)

^{1}H NMR (400 MHz, C_6D_6)

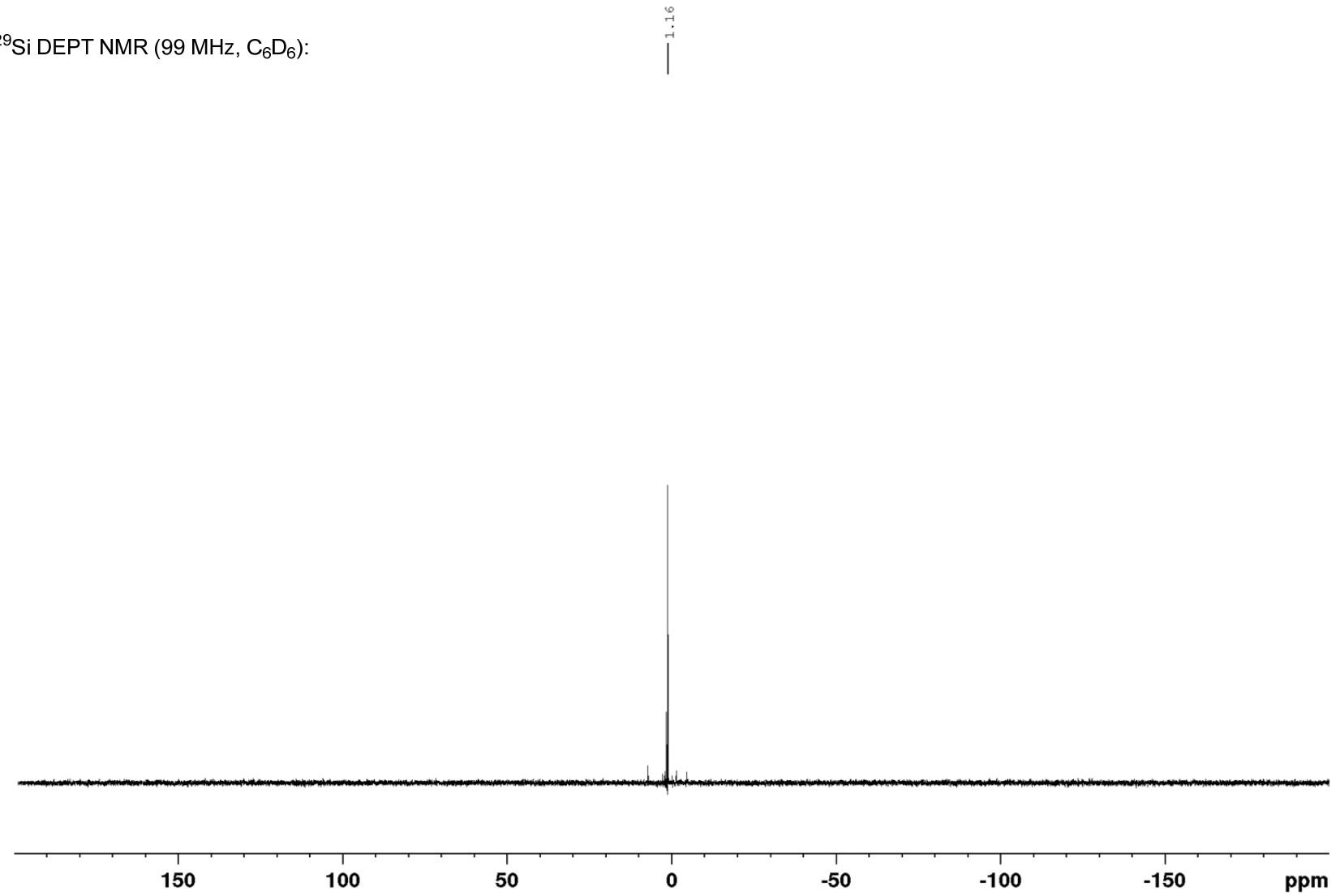




^{13}C NMR (101 MHz, C_6D_6)

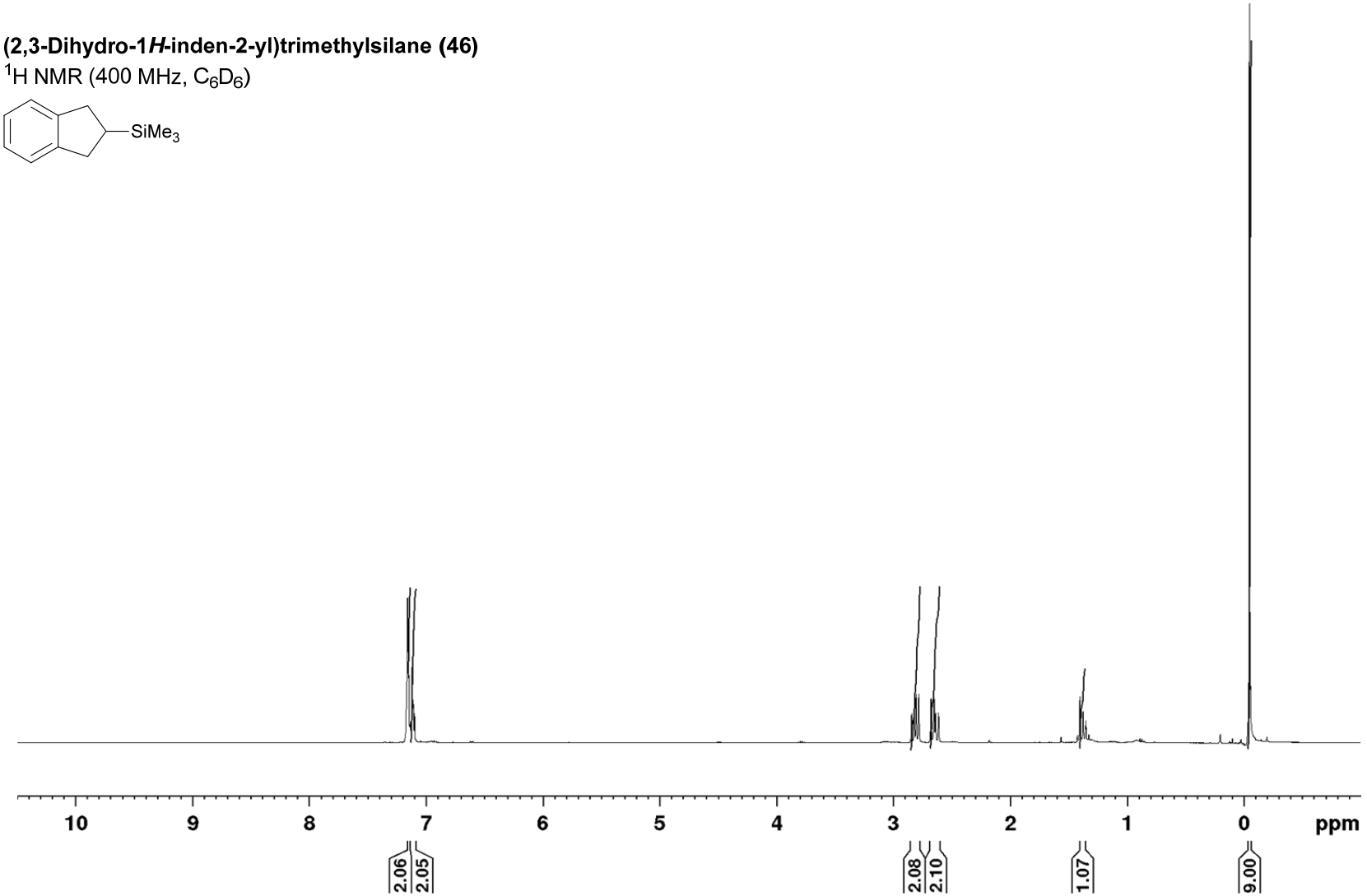


^{29}Si DEPT NMR (99 MHz, C_6D_6):

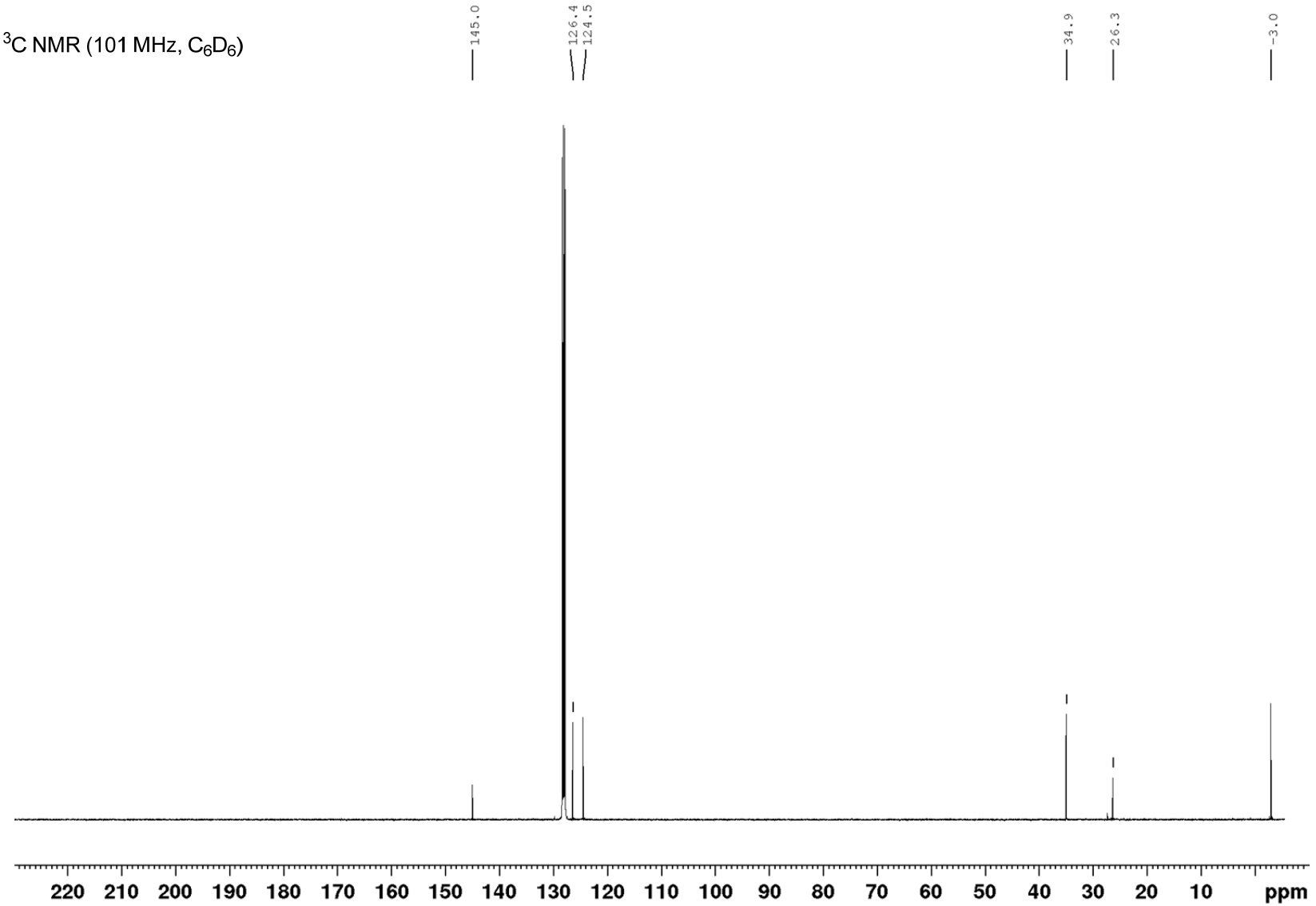


(2,3-Dihydro-1*H*-inden-2-yl)trimethylsilane (46)

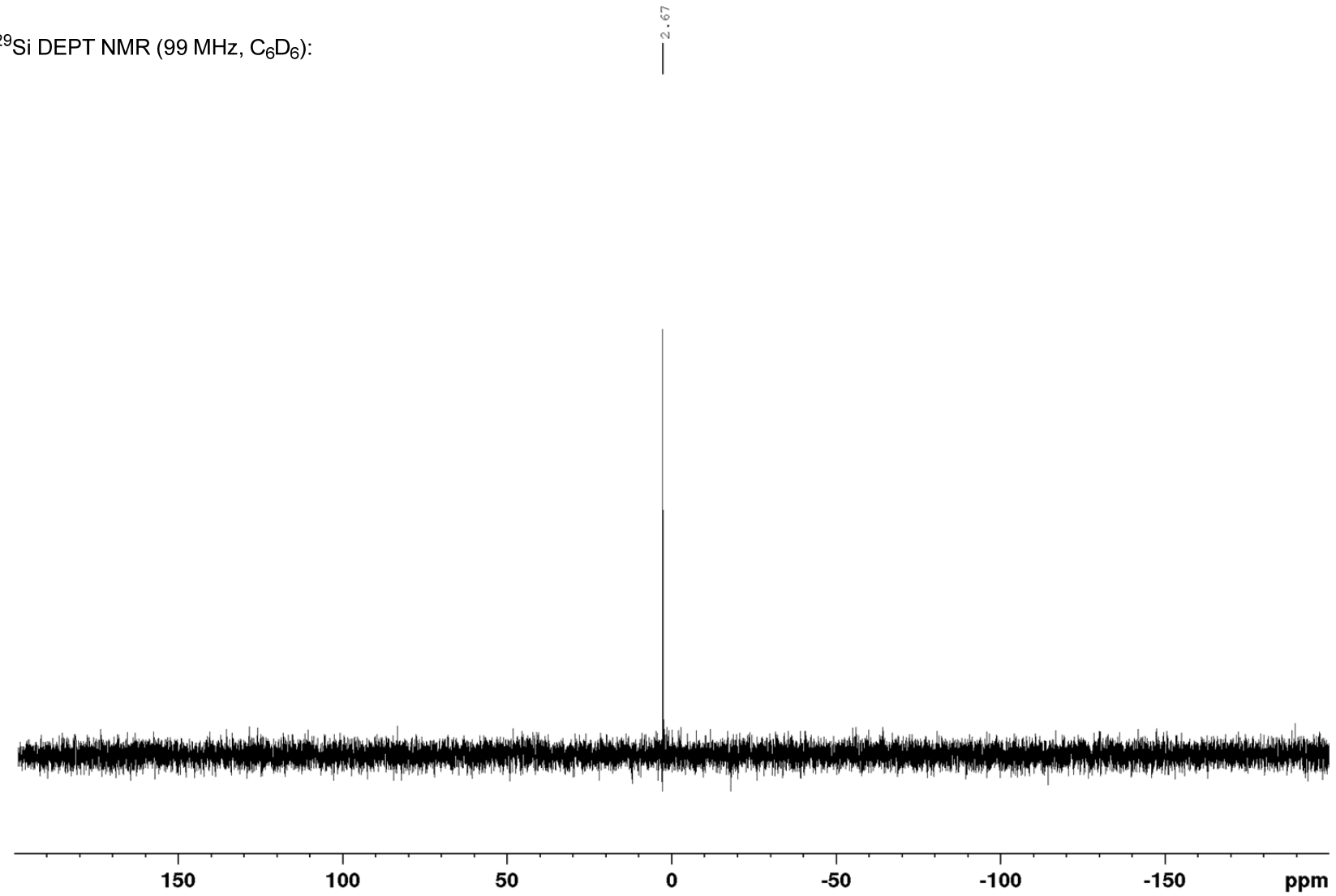
^{1}H NMR (400 MHz, C_6D_6)



^{13}C NMR (101 MHz, C_6D_6)

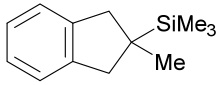


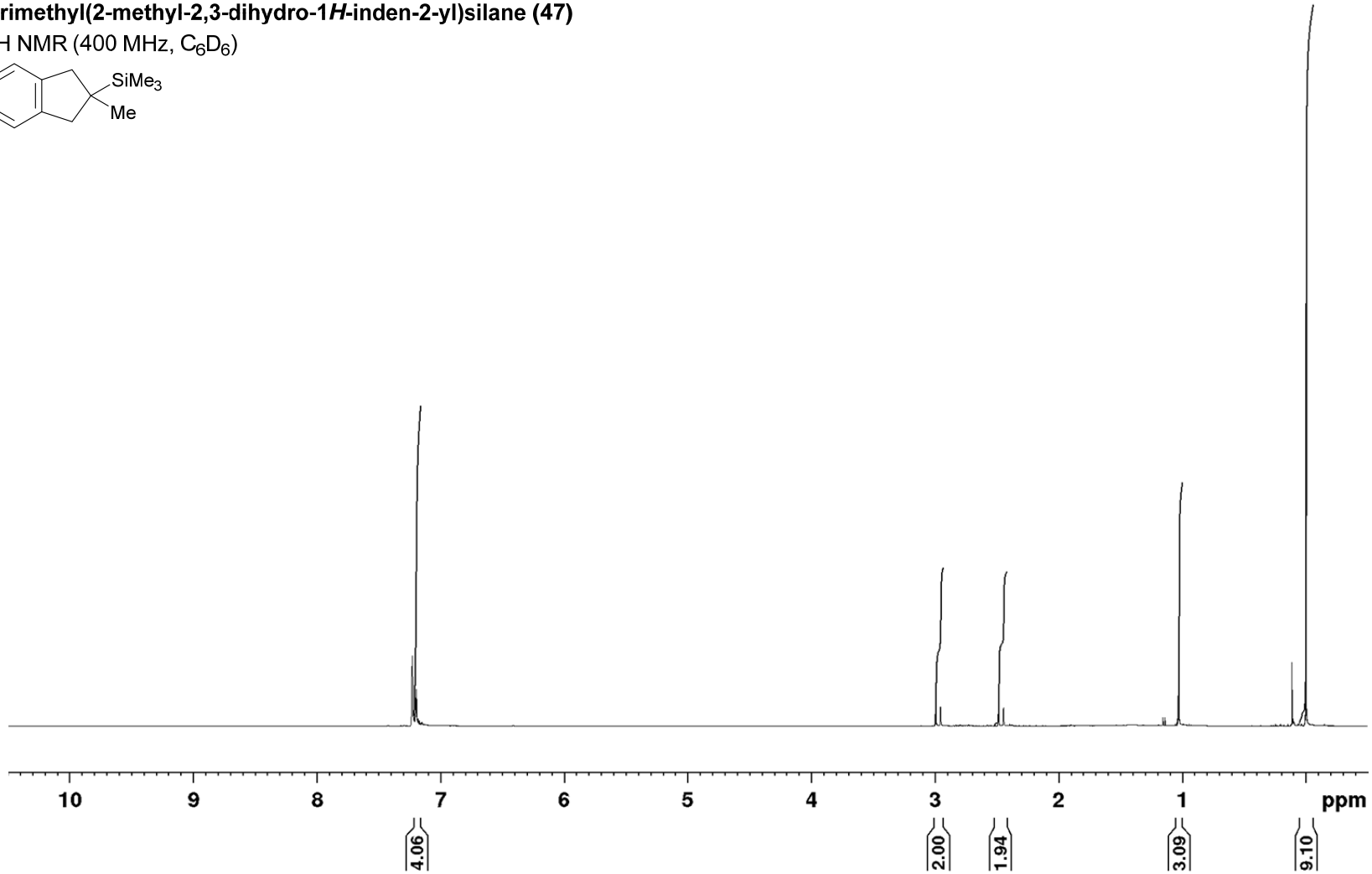
^{29}Si DEPT NMR (99 MHz, C_6D_6):



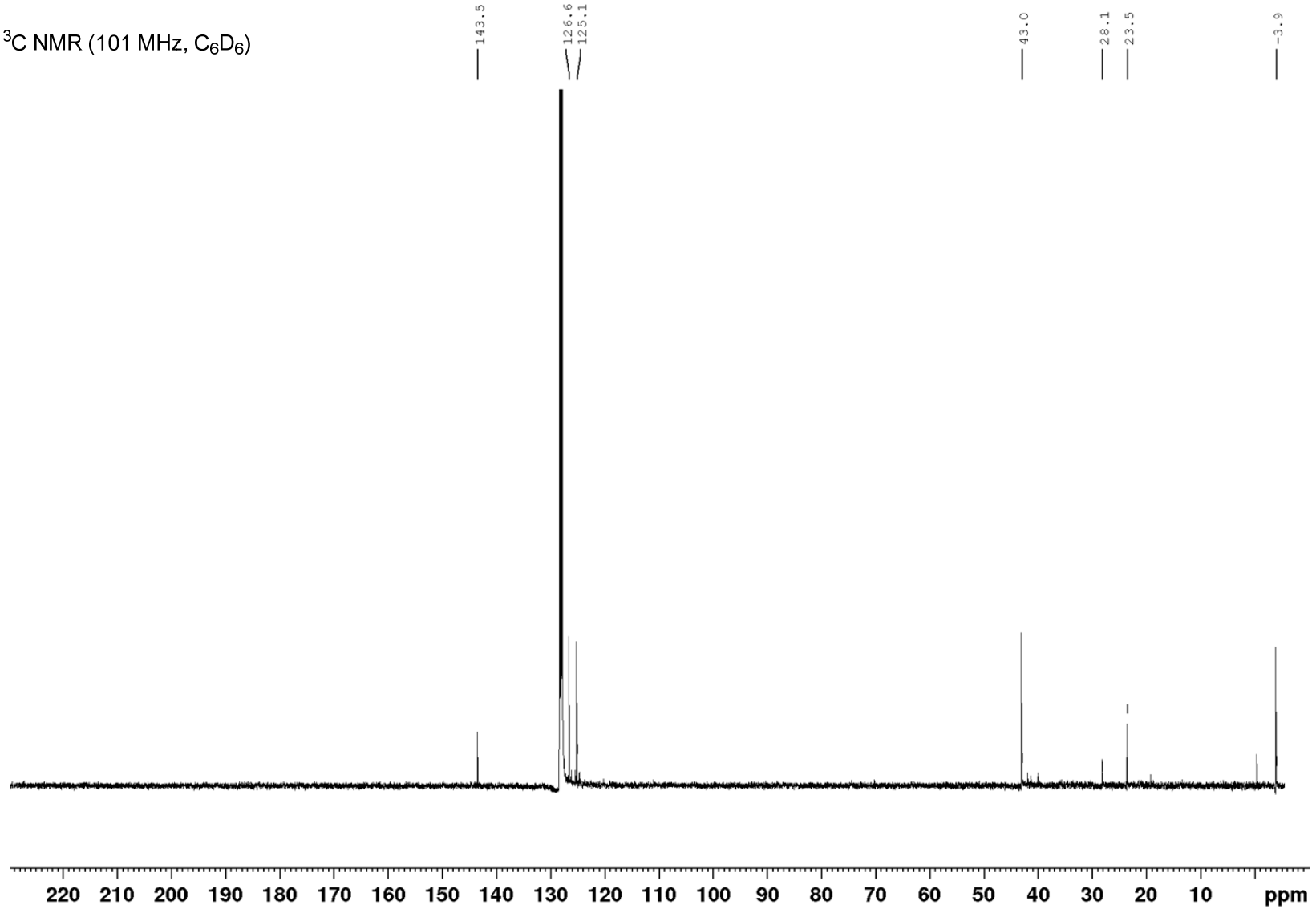
Trimethyl(2-methyl-2,3-dihydro-1*H*-inden-2-yl)silane (47)

^{1}H NMR (400 MHz, C_6D_6)

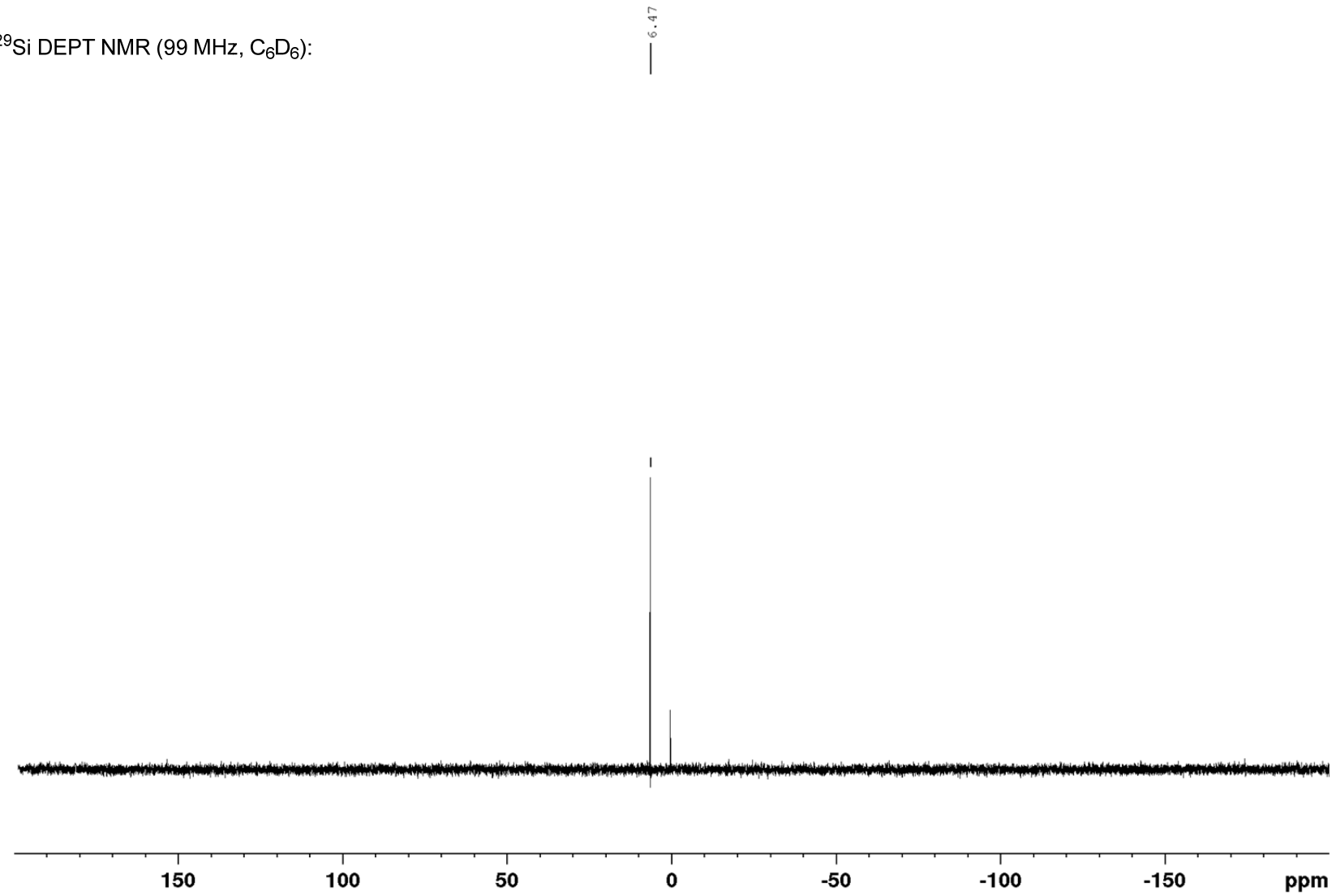




^{13}C NMR (101 MHz, C_6D_6)

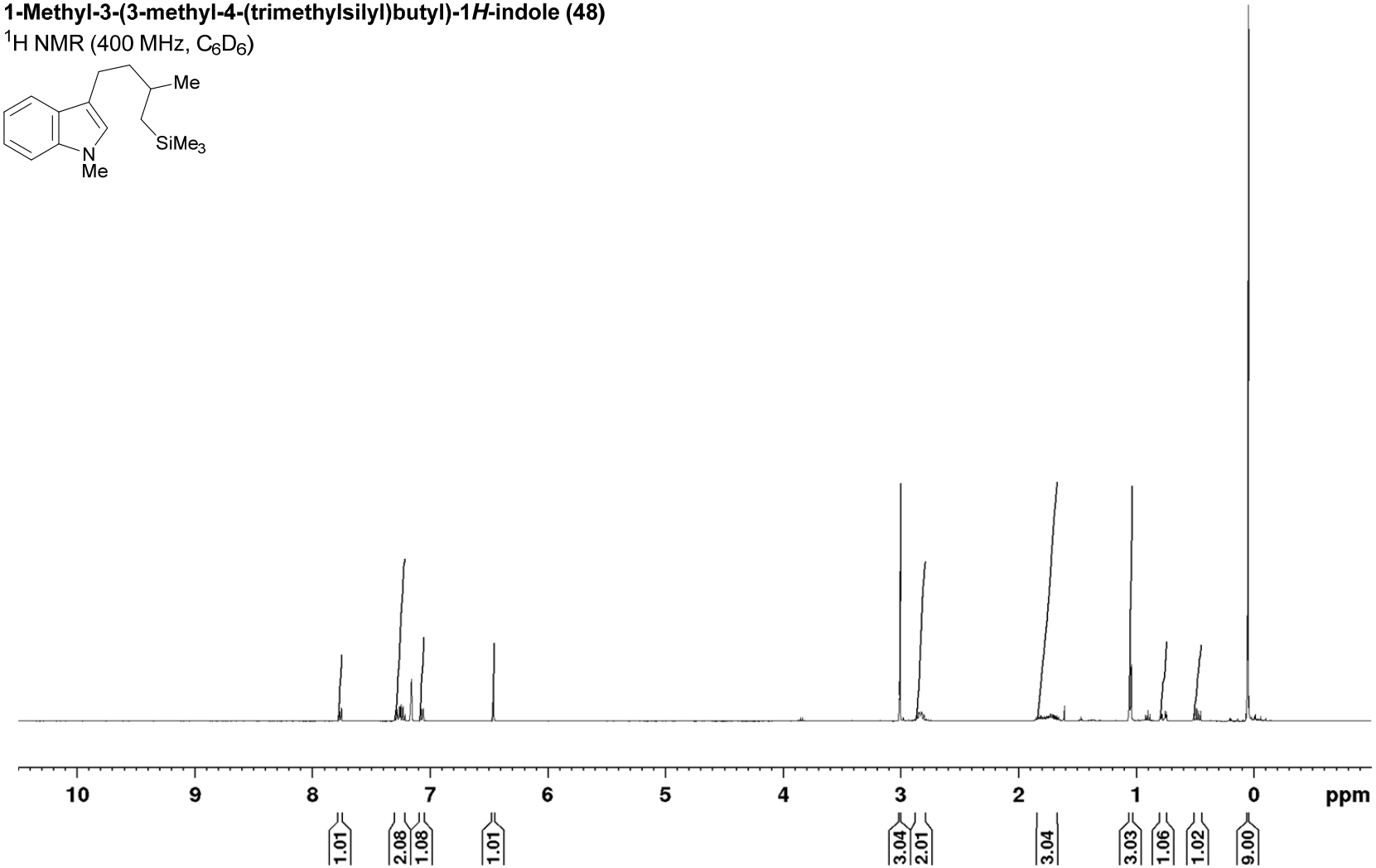


^{29}Si DEPT NMR (99 MHz, C_6D_6):

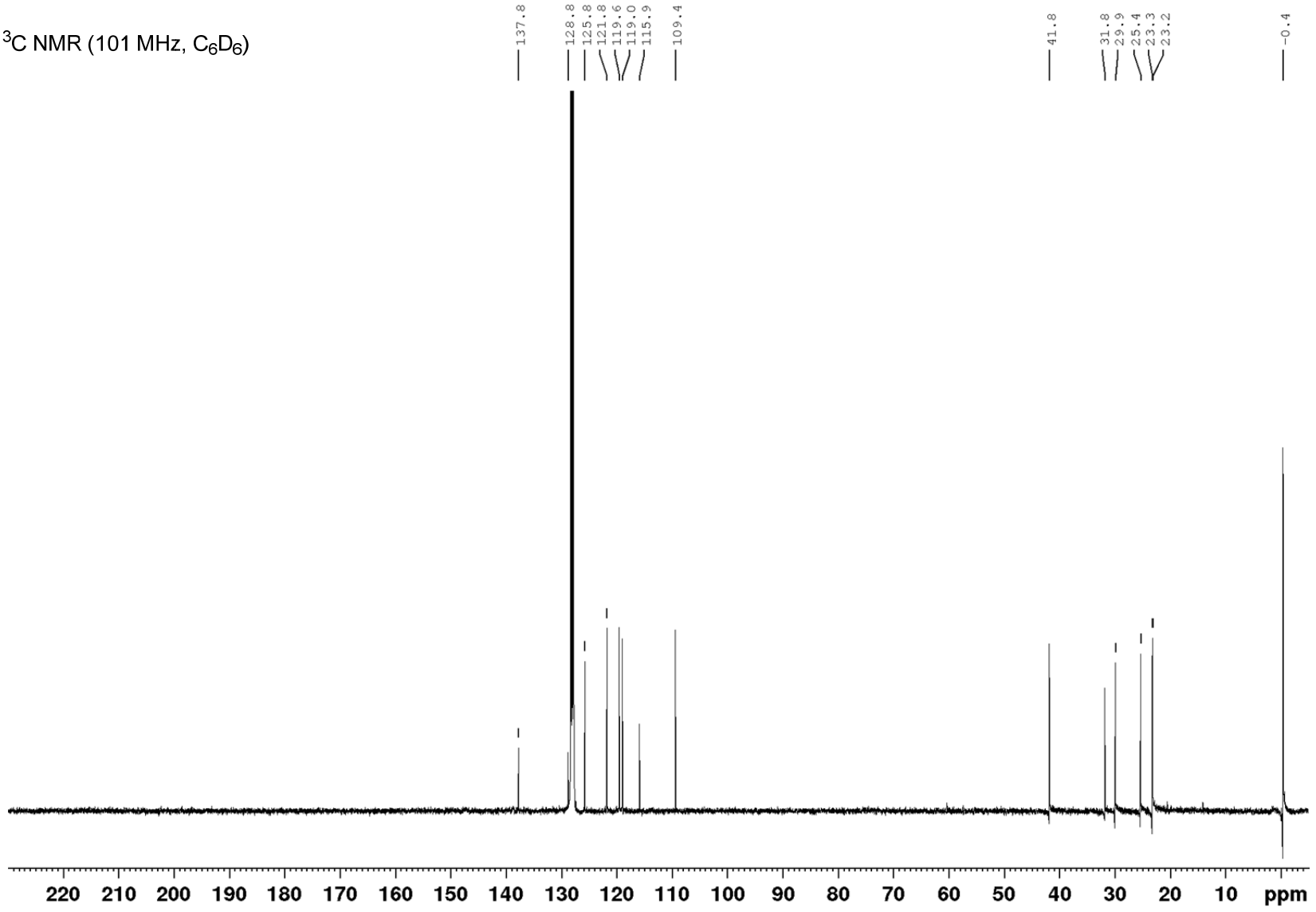


1-Methyl-3-(3-methyl-4-(trimethylsilyl)butyl)-1*H*-indole (48)

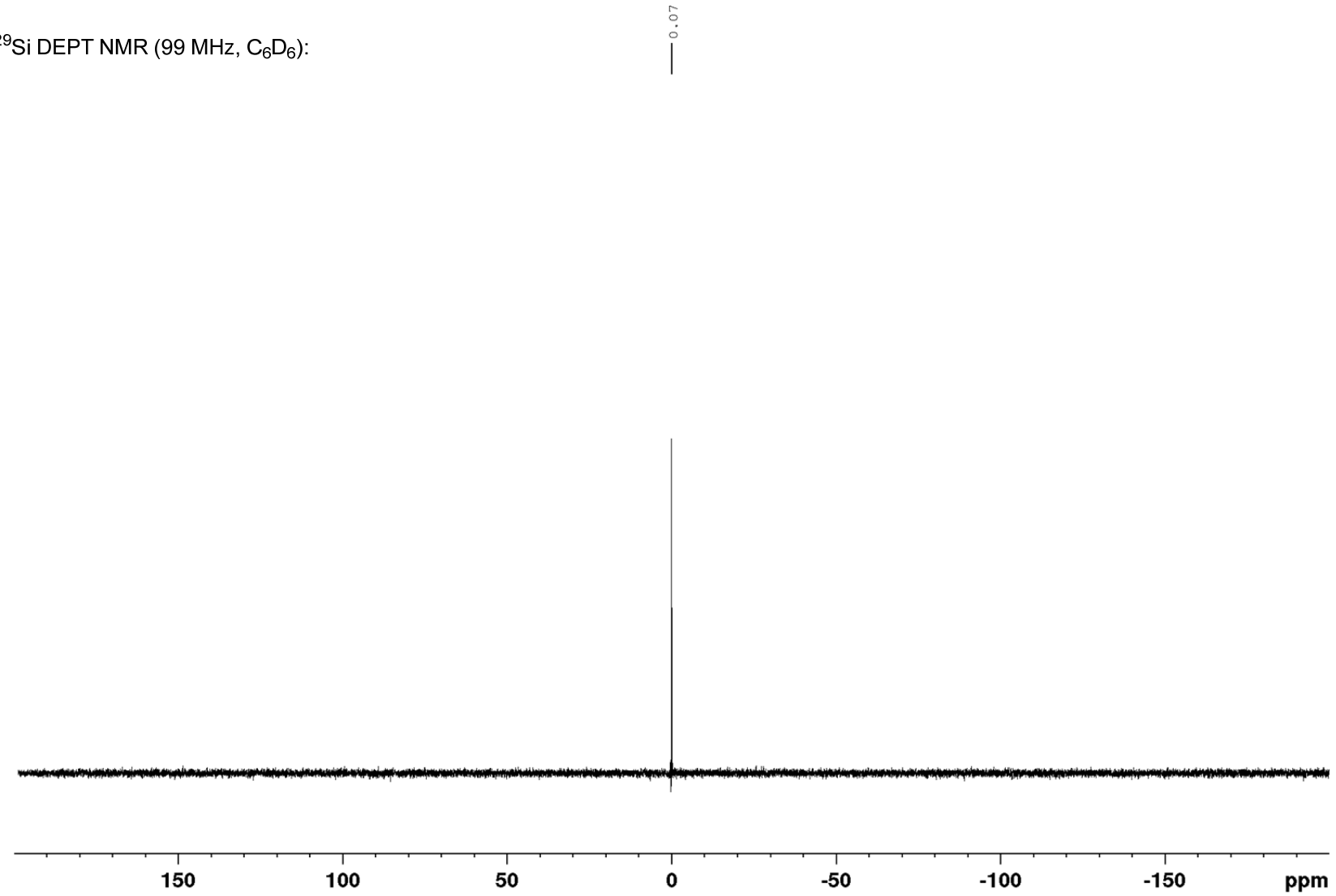
^{1}H NMR (400 MHz, C_6D_6)



^{13}C NMR (101 MHz, C_6D_6)



^{29}Si DEPT NMR (99 MHz, C_6D_6):



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