www.sciencemag.org/content/361/6400/381/suppl/DC1

Supplementary Materials for

Teaching an old carbocation new tricks: Intermolecular C–H insertion reactions of vinyl cations

Stasik Popov, Brian Shao, Alex L. Bagdasarian, Tyler R. Benton, Luyi Zou, Zhongyue Yang,
K. N. Houk*, Hosea M. Nelson*

*Corresponding author. Email: hosea@chem.ucla.edu (H.M.N.); houk@chem.ucla.edu (K.N.H.)

Published 27 July 2018, *Science* **361**, 381 (2018)
DOI: 10.1126/science.aat5440

This PDF file includes:

- Materials and Methods
- Supplementary Text
- Figs. S1 to S44
- Tables S1 and S2
- Captions for Movies S1 to S5
- References

Other Supporting Online Material for this manuscript includes the following:
(available at www.sciencemag.org/content/361/6400/381/suppl/DC1)

- Movies S1 to S5

Table of Contents

Part I: Experimental Data

Part II: Computational Data

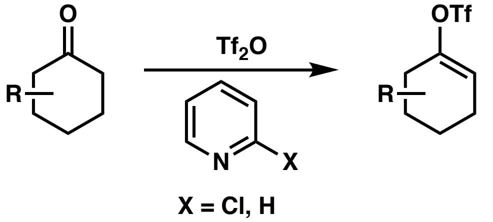
Part I: Experimental Data

1. Materials and methods

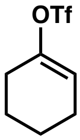
Unless otherwise stated, all reactions were performed in an MBraun glovebox under nitrogen atmosphere with ≤ 0.5 ppm O_2 levels. All glassware and stir-bars were dried in a 160 °C oven for at least 12 hours and dried *in vacuo* before use. All liquid substrates were either dried over CaH_2 or filtered through dry neutral aluminum oxide. Solid substrates were dried over P_2O_5. All solvents were rigorously dried before use. Benzene, *o*-dichlorobenzene, and toluene were degassed and dried in a JC Meyer solvent system and stored inside a glovebox. Cyclohexane, fluorobenzene, and *n*-hexane were distilled over potassium. Chlorobenzene and *o*-difluorobenzene were distilled over sodium. Pentane was distilled over sodium-potassium alloy. Chloroform was dried over CaH_2 and stored in a glovebox. All solvents were stored over 4 Å molecular sieves. Triethylsilane and triisopropylsilane were dried over sodium and stored inside a glovebox. *Closo*-Carborane catalysts were prepared according to literature procedure (*42*). *n*-Butylcyclohexane and *n*-pentylcyclohexane were purchased from Alfa Aesar. Preparatory thin layer chromatography (TLC) was performed using Millipore silica gel 60 F_{254} pre-coated plates (0.25 mm) and visualized by UV fluorescence quenching. SiliaFlash P60 silica gel (230-400 mesh) was used for flash chromatography. $AgNO_3$-Impregnated silica gel was prepared by mixing with a solution of $AgNO_3$ (150% v/w of 10% w/v solution in acetonitrile), removing solvent under reduced pressure, and drying at 120 °C. NMR spectra were recorded on a Bruker AV-300 (^1H, ^{19}F), Bruker AV-400 (^1H, ^{13}C, ^{19}F), Bruker DRX-500 (^1H), and Bruker AV-500 (^1H, ^{13}C). ^1H NMR spectra are reported relative to $CDCl_3$ (7.26 ppm) unless noted otherwise. Data for ^1H NMR spectra are as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), integration. Multiplicities are as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, td = triplet of doublet, m = multiplet. ^{13}C NMR spectra are reported relative to $CDCl_3$ (77.16 ppm) unless noted otherwise. GC spectra were recorded on an Agilent 6850 series GC using an Agilent HP-1 (50 m, 0.32 mm ID, 0.25 μm DF) column. GCMS spectra were recorded on a Shimadzu GCMS-QP2010 using a Restek XTI-5 (50 m, 0.25 mm ID, 0.25 μm DF) column. interface at room temperature. IR Spectra were record on a Perkin Elmer 100 spectrometer and are reported in terms of frequency absorption (cm^{-1}). High resolution mass spectra (HR-MS) were recorded on a Waters (Micromass) GCT Premier spectrometer and are reported as follows: m/z (% relative intensity). Purification by preparative HPLC was done on an Agilent 1200 series instrument with a reverse phase Alltima C_{18} (5μ, 25 cm length, 1 cm internal diameter) column.

2. Synthesis of vinyl triflate substrates

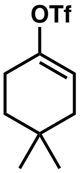
This section outlines the synthesis and purification of the vinyl triflates found in figures 2, 3, 4, 5, and 6 of the manuscript. These procedures have not been optimized.



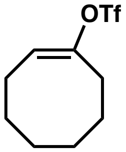
Representative scheme for vinyl triflates synthesized *via* soft enolization



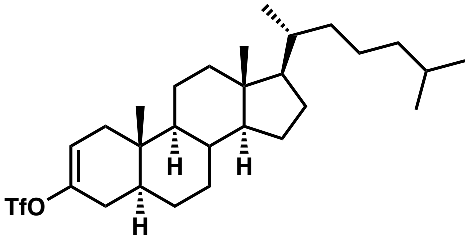
Cyclohex-1-en-1-yl trifluoromethanesulfonate (SI-1). In a flame dried 1 L three-neck flask equipped with a dropping funnel, cyclohexanone (25.0 g, 255 mmol, 1.0 equiv) and freshly distilled anhydrous pyridine (22.2 g, 280 mmol, 1.1 equiv) were dissolved in anhydrous methylene chloride (400 mL). The solution was cooled to 0 °C. The dropping funnel was charged with a solution of triflic anhydride (79.0 g, 280 mmol, 1.1 equiv) in methylene chloride (160 mL). The solution was added dropwise to the reaction (~45 minutes). After addition ceased, the ice bath was removed and the reaction stirred for 16 hours. The volatiles were removed under reduced pressure and the crude material was suspended in petroleum ether and filtered. The supernatant was concentrated and the resulting oil was purified by vacuum distillation at 0.2 mmHg to give cyclohexenyl triflate **(SI-1)** as a colorless oil (25.8 g, 44%). NMR data match those reported in literature (*43*).



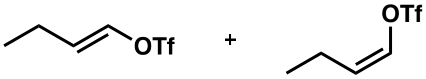
4,4-Dimethylcyclohex-1-en-1-yl trifluoromethanesulfonate (SI-2). In a flame dried 250 mL round bottom flask, 4,4-dimethylcyclohexanone (4.0 g, 31.7 mmol, 1.0 equiv) and freshly distilled 2-chloropyridine (4.0 g, 34.9 mmol, 1.1 equiv) were dissolved in anhydrous methylene chloride (64 mL). The solution was cooled to 0 °C. A solution of triflic anhydride (10.7 g, 38.0 mmol, 1.2 equiv) in methylene chloride (32 mL) was added dropwise. After addition, the ice bath was removed and the reaction stirred for 36 hours. The reaction mixture was poured into saturated aqueous ammonium chloride (100 mL). The phases were separated and the aqueous layer was extracted with diethyl ether (3 x 100 mL). The combined organics were dried over magnesium sulfate, filtered and volatiles removed under reduced pressure to give the crude material as a black oil. The product was purified by flash column chromatography (hexanes) to give triflate **SI-2** as a colorless oil (2.71 g, 33%). NMR data match those reported in literature (*44*).



(*E*)-Cyclooct-1-en-1-yl trifluoromethanesulfonate (SI-3). In a flame dried 250 mL round bottom flask, cyclooctanone (3.0 g, 23.8 mmol, 1.0 equiv) and freshly distilled 2-chloropyridine (3.0 g, 26.1 mmol, 1.1 equiv) were dissolved in anhydrous methylene chloride (90 mL). The solution was cooled to 0 °C. Triflic anhydride (8.1 g, 28.5 mmol, 1.2 equiv) was added dropwise to the solution. After addition, the ice bath was removed and the reaction stirred for 16 hours. The reaction mixture was quenched with 0.5M aqueous HCl (200 mL). The phases were separated and the aqueous layer was extracted with methylene chloride (2 x 100 mL). The combined organics were dried over magnesium sulfate, filtered and volatiles removed under reduced pressure to give the crude material as a purple oil. The product was purified by vacuum distillation (5 mmHg, 100 °C) to give triflate **(SI-3)** as a colorless oil (3.2 g, 51%). NMR data match those reported in literature (*43*).



(5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfonate (SI-4). Synthesized from 5α-cholestan-3-one according to reported literature. NMR data match those reported in literature (*45*).



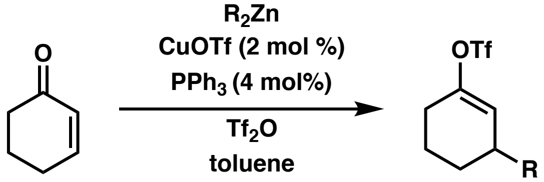
(E/Z)-But-1-en-1-yl trifluoromethanesulfonate (SI-5). In a flame dried 500 mL round bottom flask, butyraldehyde (6.0 g, 83.2 mmol, 1.0 equiv) and freshly distilled 2-chloropyridine (10.4 g, 91.5 mmol, 1.1 equiv) were dissolved in anhydrous methylene chloride (300 mL). The solution was cooled to 0 °C. Triflic anhydride (28.2 g, 99.8 mmol, 1.2 equiv) was added dropwise to this solution. After addition, the ice bath was removed and the reaction was stirred at room temperature overnight. The reaction was quenched with 0.5 M HCl. The phases were separated and the combined organic were dried over magnesium sulfate, filtered and volatiles removed under reduced pressure. The resulting oil was purified by vacuum distillation at 20 mmHg while heating at 60 °C to give triflate **SI-5** as a brown oil (5.7 g, 30%). The distillate was brought into the glovebox and plugged through dry neutral alumina to afford the triflate **SI-5** (1.8:1 Z:E mixture) as an off tan oil.

E isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.53–6.48 (m, 1H), 5.82 (dt, *J* = 11.8, 7.2 Hz, 1H), 2.09 (pd, *J* = 7.2, 1.6 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, C$_6$D$_6$) δ –74.0; ^{13}C NMR (100 MHz, CDCl$_3$) δ 135.8, 124.5, 118.8 (q, $^1J_{\text{C–F}}$ = 319 Hz), 20.3, 13.3.

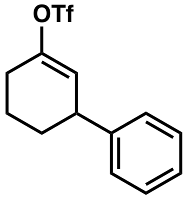
Z isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.53–6.48 (m, 1H), 5.27 (dt, *J* = 7.6, 5.6 Hz, 1H), 2.22 (pd, *J* = 7.6, 1.6 Hz, 2H), 1.04 (t, *J* = 7.6 Hz, 3H); ^{19}F NMR (376 MHz, C$_6$D$_6$) δ –74.4; ^{13}C NMR (100 MHz, CDCl$_3$) δ 134.9, 122.6, 118.8 (q, $^1J_{\text{C–F}}$ = 319 Hz), 17.8, 13.3.

FTIR (Neat film NaCl): 2967, 1719, 1428, 1223, 1177, 1025, 766, 636, 578, 514.

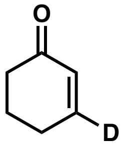
HR-MS (GCT-LIFDI): Calculated for $C_5H_7F_3O_3S$: 204.0068; measured: 204.0075.



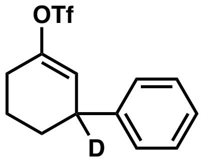
Representative scheme for vinyl triflates synthesized *via 1,4*-addition of diaryl zinc to cyclohexenone followed by triflation.



1,4,5,6-Tetrahydro-[1,1'-biphenyl]-3-yl-1 trifluoromethanesulfonate (SI-6). A flame dried round bottom flask was charged with anhydrous ZnCl$_2$ (3.7 g, 27 mmol, 2.6 equiv) and anhydrous toluene (4 mL). After cooling the mixture to –30 °C, a solution of 1.0 M PhMgBr in Et$_2$O (54 mL, 54 mmol, 5.2 equiv) was added dropwise. The reaction was then left to warm up to room temperature over 2 hours to yield a 0.47 M solution of diphenylzinc. To a separate flame dried schlenk flask was added Cu(OTf)$_2$ (75 mg, 0.21 mmol, 0.02 equiv), PPh$_3$ (109 mg, 0.42 mmol, 0.04 equiv) and anhydrous toluene (50 mL). After stirring for 30 minutes, cyclohex-2-en-1-one (1.00 g, 10.4 mmol, 1.0 equiv) was added and the solution cooled to –30 °C. The solution of 0.47 M diphenylzinc in Et$_2$O (29 mL, 13.5 mmol, 1.3 equiv) was then added dropwise. After 2 hours, the reaction was brought to 0 °C before adding Tf$_2$O (3.5 mL, 20.8 mmol, 2.0 equiv) and allowed to warm to room temperature over 12 hours. The reaction was quenched with saturated aqueous sodium bicarbonate solution (80 mL). The aqueous layer was extracted with Et$_2$O (3 x 60 mL) and the combined organics were dried over MgSO$_4$. After concentrating by rotary evaporation, the crude product was purified by flash chromatography (hexanes) to yield 500 mg (16%) of colorless oil. NMR spectra match those reported in literature (*46*).



Cyclohex-2-en-1-one-3-*d* (SI-7*).* Synthesized from cyclohexane-1,3-dione according to reported literature (*47*).



1,4,5,6-Tetrahydro-[1,1'-biphenyl]-3-yl-1-*d* trifluoromethanesulfonate (SI-8). Synthesized from cyclohex-2-en-1-one-3-*d* according to reported literature with modification (*48*).

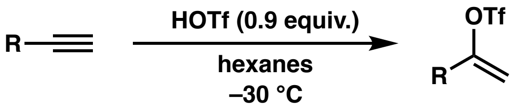
A flame dried round bottom flask was charged with anhydrous $ZnCl_2$ (1.2 g, 9.0 mmol, 2.6 equiv) and anhydrous toluene (15 mL). After cooling the mixture to –30 °C, a solution of 3.0 M PhMgBr in Et_2O (6 mL, 20 mmol, 5.2 equiv) was added dropwise. The reaction was then left to warm up to room temperature over 2 hours to yield a 0.40 M solution of diphenylzinc.

To a separate flame dried schlenk flask was added $Cu(OTf)_2$ (33 mg, 0.09 mmol, 0.02 equiv), PPh_3 (48 mg, 0.18 mmol, 0.04 equiv) and anhydrous toluene (20 mL). After stirring for 30 minutes, cyclohex-2-en-1-one-3-*d* (440 mg, 4.5 mmol, 1.0 equiv) was added and the solution cooled to –30 °C. The solution of 0.4 M diphenylzinc in Et_2O (14 mL, 5.9 mmol, 1.3 equiv) was then added dropwise. After 2 hours, the reaction was brought to 0 °C before adding Tf_2O (1.5 mL, 9.0 mmol, 2 equiv) and allowed to warm to room temperature over 12 hours. The reaction was quenched with saturated aqueous sodium bicarbonate solution (40 mL). The aqueous layer was extracted with Et_2O (3 x 30 mL) and the combined organics were dried over $MgSO_4$. After concentrating by rotary evaporation, the crude product was purified by flash chromatography (hexanes) to yield 260 mg (19%) of colorless oil.

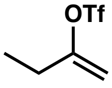
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.21 (m, 2H), 7.26–7.23 (m, 1H), 7.21–7.17 (m, 2H), 5.83 (br s, 1H), 2.50–2.43 (m, 1H), 2.38 (dt, J = 17.5, 5.2 Hz, 1H), 2.01 (ddd, J = 13.2, 7.1, 2.8 Hz, 1H), 1.95–1.87 (m, 1H), 1.82–1.73 (m, 1H), 1.56–1.51 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –74.0; ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 143.7, 127.5, 126.8, 121.5, 118.6 (q, $^1J_{C–F}$ = 318 Hz), 40.9 (t, $^1J_{C–D}$ = 20 Hz), 31.2, 27.6, 21.1.

FTIR (Neat film NaCl): 3062, 3027, 2945, 2864, 1683, 1603, 1414, 1246, 1202, 1139, 1049, 994, 931, 919, 907, 878, 837, 822, 700, 603, 505.

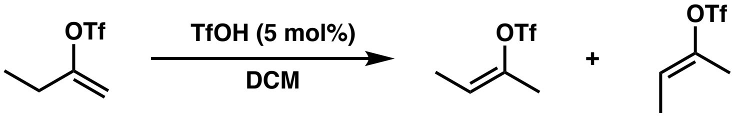
HR-MS (GCT-LIFDI): Calculated for $[C_{13}H_{12}DF_3O_3S + Na]^+$: 330.0498; measured: 330.0509.



Representative Scheme for vinyl triflates synthesized *via* addition of triflic acid to alkynes.

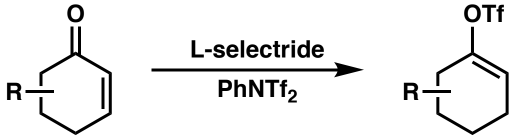


But-1-en-2-yl trifluoromethanesulfonate (SI-9). To a 250 mL flame dried schlenk flask was condensed 1-butyne (5.00 g, 92.0 mmol, 1.1 equiv) at –78 °C. This was dissolved in anhydrous hexanes (92.0 mL) and the solution was warmed to –35 °C. Triflic acid (12.5 g, 83.0 mmol, 1.0 equiv) was added dropwise and the solution was allowed to slowly warm up to room temperature. After 2 hours of stirring, the reaction was quenched with saturated aqueous sodium bicarbonate (100 mL). The layers were separated and the organic layer was washed with saturated aqueous sodium bicarbonate (2 x 100 mL), dried over anhydrous potassium carbonate, filtered and volatiles removed under reduced pressure (being careful of product volatility). The crude product was purified by vacuum distillation (25 mmHg, 50 °C) to give triflate **SI-9** as a colorless oil (6.3 g, 37%).
^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 5.34–5.11 (m, 2H), 2.44 (qt, J = 7.4, 1.0 Hz, 2H), 1.15 (t, J = 7.4 Hz, 3H); ^{19}F NMR (282 MHz, $(CD_3)_2CO$) δ –75.6; ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 158.8, 118.6 (q, $^{1}J_{C–F}$ = 318 Hz), 103.4, 26.8, 10.1.
FTIR (Neat film NaCl): 2986, 2950, 1670, 1415, 1249, 1202, 1138, 929, 848, 610, 506, 469.
HR-MS (GCT-LIFDI): Calculated for $C_5H_7F_3O_3S$: 204.0068; measured: 204.0065.

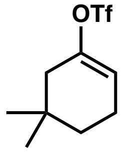


(*E*)-But-2-en-2-yl trifluoromethanesulfonate and **(*Z*)-but-2-en-2-yl trifluoromethanesulfonate (SI-10).** In a 100 mL flame dried round bottom flask, triflate **SI-9** (4.00 g, 19.6 mmol, 1 equiv) was dissolved in anhydrous methylene chloride (35 mL). Triflic acid (0.15 g, 0.98 mmol, 0.05 equiv) was added and the reaction stirred for 1 hour. The reaction was quenched with 5% aqueous sodium bicarbonate (35 mL). The layers were separated and the aqueous layer was extracted with pentane (3 x 20 mL). The volatiles were distilled off at 80 °C and then the product was purified by vacuum distillation (50 mmHg) to give triflate **SI-10** as a 2.5:1 (*E*:*Z*) mixture of isomers (3.1 g, 78%).
Major Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (qd, J = 6.8, 0.8 Hz, 1H), 2.05 (br s, 3H), 1.71 (dq, J = 6.8, 1.6 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –75.0; ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 118.4 (q, $^{1}J_{C–F}$ = 318 Hz), 116.4, 19.6, 11.1.

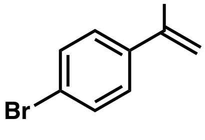
Minor Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (qd, J = 7.2, 0.8 Hz, 1H), 2.03 (br s, 3H), 1.69 (dq, J = 7.2, 1.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –74.2; ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 118.6 (q, $^1J_{C–F}$ = 318 Hz), 116.8, 15.7, 11.9.
FTIR (Neat film NaCl): 2934, 1710, 1412, 1245, 1201, 1135, 936, 876, 728, 632, 468.
HR-MS (GCT-LIFDI): Calculated for $C_5H_7F_3O_3S$: 204.0068; measured: 204.0065.



Representative scheme for vinyl triflates synthesized *via* 1,4-reduction of enones followed by *in situ* triflation of the resulting enolate.



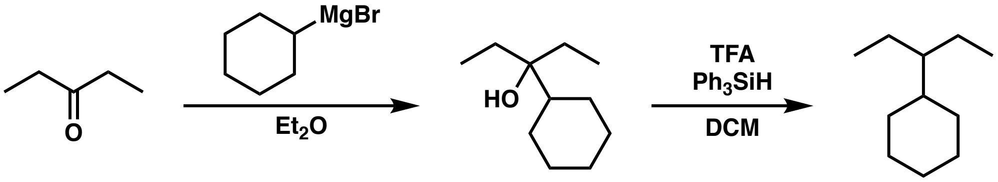
5,5-Dimethylcyclohex-1-en-1-yl trifluoromethanesulfonate (SI-11). 5,5-Dimethylcyclohex-2-en-1-one (1.20 g, 9.66 mmol, 1 equiv) was dissolved in anhydrous tetrahydrofuran (50 mL). This solution was cooled to –78 °C. A 1 M solution of L-selectride (10.2 mL, 10.2 mmol, 1.05 equiv) in tetrahydrofuran was added and the reaction mixture stirred for 1.5 hours. A solution of *N*-phenyl-bis(trifluoromethanesulfonimide) (3.80 g, 10.6 mmol, 1.1 equiv) in tetrahydrofuran (15 mL) was added dropwise to the reaction. The cold bath was removed and the reaction stirred for 36 hours. The reaction was diluted with diethyl ether (100 mL) and quenched with water (50 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (2 x 50 mL). The combined organics were washed with brine (2 x 100 mL), dried over sodium sulfate, filtered and volatiles removed under reduced pressure. The crude material was purified by flash column chromatography to give triflate **SI-10** as a colorless oil (0.50 g, 20%). NMR spectra matched those reported in literature (*44*).



1-(4-bromophenyl)vinyl trifluoromethanesulfonate (SI-12). Synthesized from 1-(4-bromophenyl)ethan-1-one according to reported literature (*44*).

3. Synthesis of authentic products

This section outlines our syntheses of alkane products for reactions where we could only isolate products as a mixture. These compounds were synthesized to confirm the products of our reactions as well as assessing yields *via* GC. These procedures have not been optimized.



3-cyclohexylpentan-3-ol (SI-13). Magnesium turnings (1.13 g, 46.4 mmol, 2 equiv) were flame dried under vacuum in a 250 mL three neck flask fitted with a reflux condenser. The magnesium was suspended in anhydrous diethyl ether (100 mL). Bromocyclohexane (4.54 g, 27.9 mmol, 1.2 equiv) was added slowly and the resulting suspension was refluxed for 1 hour at which point it turned a dark grey. The reaction mixture was cooled to 0 °C and 3-pentanone (2.00 g, 23.2 mmol, 1.0 equiv) was added and the reaction stirred for 1 hour at 0 °C. At this point the ice bath was removed and the reaction was allowed to warm up to room temperature. The reaction was quenched with saturated aqueous ammonium chloride (100 mL). The layers were separated and the aqueous layer was extracted twice with diethyl ether (2 x 50 mL). The combined organics were dried over magnesium sulfate, filtered and volatiles removed under reduced pressure. This material was purified by silica column chromatography (methylene chloride) to give the alcohol **SI-13** as a viscous oil (0.76 g, 19%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.83–1.75 (m, 2H), 1.75–1.63 (m, 3H), 1.58–1.36 (m, 5H), 1.28–0.99 (m, 6H), 0.85 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 75.9, 44.3, 28.1, 27.1, 26.8, 26.7, 7.7.

FTIR (Neat film NaCl): 3483 (br), 2966, 2926, 2853, 1701, 1450, 1379, 1136, 946, 893, 746.

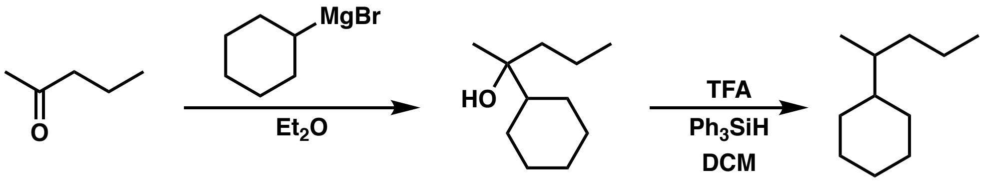
HR-MS (GCT-LIFDI): Calculated for $C_{11}H_{22}O$: 170.1671; measured: 170.1672.

Pentan-3-ylcyclohexane (SI-14). Alcohol **SI-13** (343 mg, 2.01 mmol, 1 equiv) was dissolved in dichloromethane (8 mL). To this solution was added triphenylsilane (629 mg, 2.42 mmol, 1.2 equiv) and trifluoroacetic acid (1.38 g, 12.1 mmol, 6 equiv). The reaction stirred at room temperature for 36 hours at which point it was quenched by addition of solid potassium carbonate. The suspension was filtered and volatiles were removed under reduced pressure. The crude material was purified by silica column chromatography (hexanes) with silver nitrate impregnated silica as the stationary phase to give alkane **SI-14** as a colorless oil (20 mg, 6%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75–1.69 (m, 2H), 1.67–1.61 (m, 1H), 1.60–1.54 (m, 1H), 1.40–1.05 (m, 4H), 1.01 (td, *J* = 12.2, 2.9 Hz, 1H), 0.95–0.88 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 46.9, 39.7, 30.1, 27.2, 27.1, 22.8.

FTIR (Neat film NaCl): 2960, 2922, 2874, 2852, 1462, 1448, 1380, 1118, 891, 712, 699, 511.

HR-MS (GCT-LIFDI): Calculated for $C_{11}H_{22}$: 154.1722; measured: 154.1723.



SI-14 SI-15

2-cyclohexylpentan-2-ol (SI-15). Magnesium turnings (1.13 g, 46.4 mmol, 2.0 equiv) were flame dried under vacuum in a 250 mL three neck flask fitted with a reflux condenser. The magnesium was suspended in anhydrous diethyl ether (100 mL). Bromocyclohexane (4.54 g, 27.9 mmol, 1.2 equiv) was added slowly and the resulting suspension was refluxed for 1 hour at which point it turned dark grey in color. The reaction mixture was cooled to 0 °C and 2-pentanone (2.00 g, 23.2 mmol, 1.0 equiv) was added and the reaction stirred for 1 hour at 0 °C. At this point the ice bath was removed and the reaction was allowed to warm up to room temperature. The reaction was quenched with saturated aqueous ammonium chloride (100 mL). The layers were separated and the aqueous layer was extracted twice with diethyl ether (2 x 50 mL). The combined organics were dried over magnesium sulfate, filtered and volatiles removed under reduced pressure. The crude was purified by silica column chromatography (methylene chloride) to give alcohol **SI-15** as a viscous oil (0.56 g, 14%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82–1.73 (m,3H), 1.70 (d, J = 12.8 Hz, 1H), 1.64 (d, J = 12.4 Hz, 1H), 1.42–1.15 (m, 8H), 1.14–1.07 (m, 1H), 1.06 (s, 3H), 1.04–0.92 (m, 2H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 74.6, 47.4, 42.4, 27.7, 27.0, 26.9, 26.9, 26.7, 24.1, 16.6, 14.9.

FTIR (Neat film NaCl): 3429, 2957, 2926, 2853, 1689, 1450, 1376, 1143, 1116, 930, 893, 734.

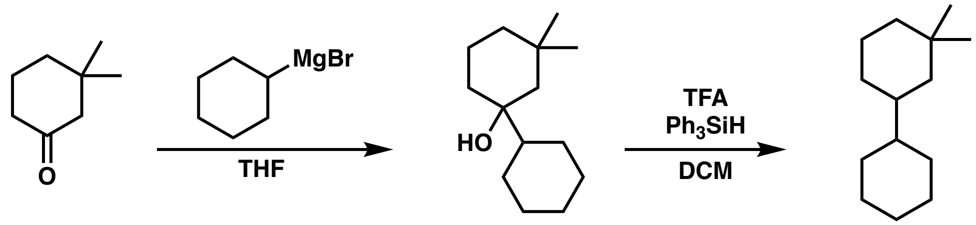
HR-MS (GCT-LIFDI): Calculated for $C_{11}H_{22}O$: 170.1671; measured: 170.1674.

Pentan-2-ylcyclohexane (SI-16). Alcohol **SI-15** (530 mg, 3.11 mmol, 1 equiv) was dissolved in dichloromethane (13 mL). To this solution was added triphenylsilane (973 mg, 3.73 mmol, 1.2 equiv) and trifluoroacetic acid (2.13 g, 18.7 mmol, 6 equiv). The reaction stirred at room temperature for 48 hours at which point it was quenched by addition of solid potassium carbonate. The suspension was filtered and volatiles were removed under reduced pressure. The crude material was purified by silica column chromatography (hexanes) with silver nitrate impregnated silica as the stationary phase to give pure product (**SI-16**) as a colorless oil (33 mg, 7%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76–1.68 (m, 2H), 1.68–1.62 (m, 1H), 1.62–1.55 (m, 2H), 1.40–0.93 (m, 11H), 0.87 (t, J = 6.8 Hz, 3H), 0.80 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.9, 37.9, 36.6, 30.9, 28.8, 27.2, 27.1, 27.0, 20.8, 16.2, 14.6.

FTIR (Neat film NaCl): 2956, 2922, 2852, 1449, 1379, 1263, 1118, 890, 737, 689, 510.

HR-MS (GCT-LIFDI): Calculated for $C_{11}H_{22}$: 154.1722; measured: 154.1716.



3,3-dimethyl-[1,1'-bi(cyclohexan)]-1-ol (SI-17). Magnesium turnings (0.76 g, 31.4 mmol) were flame dried under vacuum in a 250 mL three neck flask fitted with a reflux condenser. The magnesium was suspended in anhydrous tetrahydrofuran (31 mL). Bromocyclohexane (3.88 g, 23.8 mmol) was added slowly and the resulting suspension was refluxed for 5 hours at which point it turned a dark grey. The reaction mixture was cooled to 0 °C and 3,3-dimethylcyclohexan-1-one (3.00 g, 23.8 mmol) was added over 1 hour and the reaction stirred for 1 hour at 0 °C and then 12 hours at room temperature. The reaction was quenched with saturated aqueous ammonium chloride (50 mL). The layers were separated and the aqueous layer was extracted twice with diethyl ether (3 x 25 mL). The combined organics were dried over magnesium sulfate, filtered and volatiles removed under reduced pressure. This material was purified by silica column chromatography (5% diethyl ether in pentane) to give the alcohol **SI-17** as a viscous oil (305 mg, 6%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.85 – 1.71 (m, 5H), 1.67 – 1.62 (m, 2H), 1.60 – 1.55 (m, 1H), 1.48 – 1.33 (m, 3H), 1.25 – 1.09 (m, 6H), 1.08 (s, 3H), 1.07 – 0.94 (m, 3H), 0.90 (s, 1H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 74.4, 50.3, 46.5, 39.5, 34.8, 34.7, 30.7, 27.4, 27.0, 26.8, 26.7, 18.6.

FTIR (Neat film NaCl): 3490 (br), 2925, 2853, 1451, 1363, 1020, 982, 959, 836.

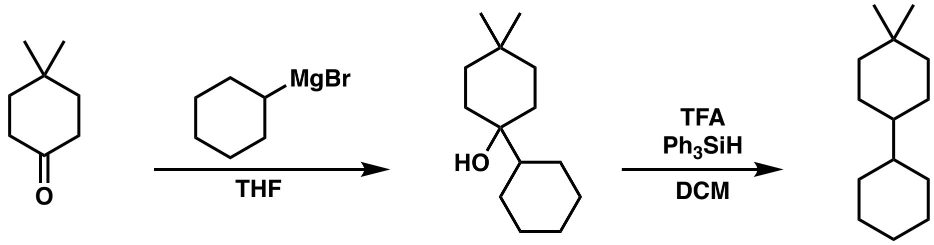
HR-MS (GC-CI): Calculated for $C_{14}H_{26}O$: 210.1984; measured: 210.1988.

3,3-dimethyl-1,1'-bi(cyclohexane) (SI-18). Alcohol **SI-17** (250 mg, 1.19 mmol) was dissolved in dichloromethane (5 mL). To this solution was added triphenylsilane (371 mg, 1.43 mmol) and trifluoroacetic acid (813 mg, 7.13 mmol). The reaction stirred at room temperature for 18 hours at which point it was quenched by addition of solid potassium carbonate. The suspension was filtered and volatiles were removed under reduced pressure. The crude material was purified by silica column chromatography (pentane) with silver nitrate impregnated silica as the stationary phase to give alkane **SI-18** as a colorless oil (44 mg, 19%).

^{1}H NMR (500 MHz, $CDCl_3$) d 1.74 – 1.60 (m, 6H), 1.57 – 1.50 (m, 1H), 1.43 – 1.28 (m, 3H), 1.27 – 1.07 (m, 4H), 1.07 – 0.92 (m, 4H), 0.88 (s, 3H), 0.86 (s, 3H), 0.83 – 0.72 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) d 43.7, 43.6, 39.7, 38.8, 33.9, 31.0, 30.4, 30.2, 30.1, 27.1, 27.0, 25.0, 22.9.

FTIR (Neat film NaCl): 2919, 2851, 1449, 1384, 1363, 1178, 891, 849.

HR-MS (GCT-LIFDI): Calculated for $C_{14}H_{26}$: 194.2034; measured: 194.2035.



4,4-dimethyl-[1,1'-bi(cyclohexan)]-1-ol (SI-19). Magnesium turnings (0.25 g, 10.3 mmol) were flame dried under vacuum in a 250 mL three neck flask fitted with a reflux condenser. The magnesium was suspended in anhydrous diethyl ether (31 mL). Bromocyclohexane (1.01 g, 6.18 mmol) was added slowly and the resulting suspension was refluxed for 2 hours at which point it turned a dark grey. The reaction mixture was cooled to 0 °C and 4,4-dimethylcyclohexan-1-one (0.65 g, 5.15 mmol) was added over 1 hour as a solution in 3 mL of ether and the reaction stirred for 1 hour at 0 °C and then 12 hours at room temperature. The reaction was quenched with saturated aqueous ammonium chloride (10 mL). The layers were separated and the aqueous layer was extracted twice with diethyl ether (3 x 10 mL). The combined organics were dried over magnesium sulfate, filtered and volatiles removed under reduced pressure. This material was purified by silica column chromatography (5% diethyl ether in pentane) to give the alcohol **SI-19** as a viscous oil (140 mg, 15%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.85 – 1.77 (m, 4H), 1.69 – 1.63 (m, 1H), 1.59 – 1.46 (m, 4H), 1.41 – 1.37 (m, 2H), 1.27 – 1.00 (m, 9H), 1.08 (s, 3H), 1.07 – 0.94 (m, 3H), 0.92 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.9, 34.8, 32.3, 30.5, 29.9, 27.0, 26.8, 24.2.

FTIR (Neat film NaCl): 3490 (br), 2927, 2852, 1449, 1363, 1037, 956, 893.

HR-MS (GC-CI): Calculated for [$C_{14}H_{26}O$ + NH_4]: 228.2327; measured: 228.2323.

4,4-dimethyl-1,1'-bi(cyclohexane) (SI-20). Alcohol **SI-19** (140 mg, 0.67 mmol) was dissolved in dichloromethane (3 mL). To this solution was added triphenylsilane (208 mg, 0.80 mmol) and trifluoroacetic acid (455 mg, 3.99 mmol). The reaction stirred at room temperature for 36 hours at which point it was quenched by addition of solid potassium carbonate. The suspension was filtered and volatiles were removed under reduced pressure. The crude material was purified by silica column chromatography (pentane) with silver nitrate impregnated silica as the stationary phase to give alkane **SI-20** as a colorless oil (70 mg, 54%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.75 – 1.66 (m, 4H), 1.65 – 1.61 (m, 1H), 1.51 – 1.46 (m, 2H), 1.41 – 1.33 (m, 2H), 1.27 – 1.03 (m, 8H), 1.01 – 0.90 (m, 3H), 0.87 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 43.5, 43.3, 39.8, 33.2, 30.5, 30.3, 27.1, 27.0, 26.0, 24.4.

FTIR (Neat film NaCl): 2920, 2851, 1449, 1384, 1363, 1178, 891, 848, 754.

HR-MS (GCT-LIFDI): Calculated for $C_{14}H_{26}$: 194.2034; measured: 194.2035.

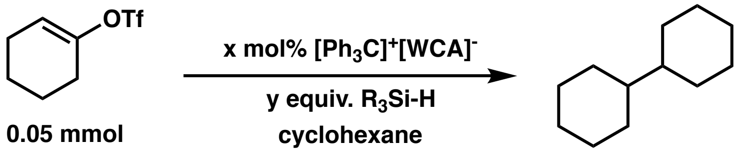
3. General procedure for yield calculations by GC

Calibration curves were made by first preparing 5:1, 3:1, 1:1, 1:3, and 1:5 molar ratio solutions of nonane to product. GC analysis of the chromatogram integrations was plotted on Microsoft Excel to form a linear calibration curve line. All curves were tested to be within ≤ 5% error. For analysis of reactions, nonane (1.12 equiv) was added to the reaction mixture after completion and aliquots were prepared by diluting in hexanes, quenched with a saturated aqueous sodium bicarbonate solution, and the organic layer filtered through a kim-wipe. Yields are then calculated by comparing the integration ratios of nonane to the product against their respective calibration curve.

4. Alkane Alkylation Reactions

4.1 Optimization table for alkylation reaction

This section outlines the optimization of the reaction shown below. All yields of bicyclohexyl (**SI-21)** are GC yields.

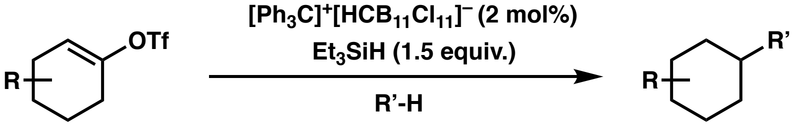


Anion	% Cat. Loading	Conc.	Temp.	Silane	Yield
$[HCB_{11}Cl_{11}]$	2 mol%	0.1 M	30 °C	Et_3SiH (150 mol%)	87%
$[HCB_{11}Cl_{11}]$	2 mol%	0.1 M	30 °C	iPr_3SiH (150 mol%)	68%
$[HCB_{11}Cl_{11}]$	0 mol%	0.1 M	30 °C	Et_3SiH (120 mol%)	0%
$[HCB_{11}Cl_{11}]$	2 mol%	0.1 M	30 °C	none	0%
$[HCB_{11}H_5Cl_6]$	2 mol%	0.1 M	30 °C	Et_3SiH (150 mol%)	50%
$[HCB_{11}Br_{11}]$	2 mol%	0.1 M	30 °C	Et_3SiH (150 mol%)	69%
$[B(C_6F_5)_4]$	2 mol%	0.1 M	30 °C	Et_3SiH (150 mol%)	6%

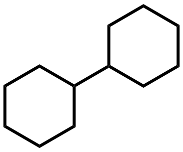
Table S1. Optimization of intermolecular alkylation reaction.

4.2 General Procedure for Intermolecular Alkane Insertion Reactions.

In this section, we outline the procedure used for the intermolecular reductive cross-coupling of cyclic vinyl triflates with alkanes.



In a well-kept glovebox, H_2O, $O_2 \leq 0.5$ ppm, a dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.02 equiv) and this was suspended in alkane (0.1 M). Triethylsilane (1.5 equiv) along with a magnetic stirring bar were added to the mixture, and the resulting suspension stirred for 10 minutes. At this point, vinyl triflate (1.0 equiv) was added to the reaction and stirred for 0.16–12 hours at 30 °C (see substrates for specific details). Upon completion, the reaction mixture was passed through a short plug of silica gel inside the glovebox and washed with hexanes. The solution was brought out and volatiles removed under reduced pressure. Some substrates needed further purification by silica column chromatography (see below).



Bicyclohexyl (SI-21). Synthesized according to general procedure 4.2. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol, 0.02 equiv) and this was suspended in cyclohexane (0.5 mL, 4.63 mmol). Triethylsilane (12 µL, 0.075 mmol, 1.5 equiv) along with a magnetic stirring bar were added to the mixture and the resulting suspension stirred for 10 minutes. Cyclohexenyl triflate (**SI-1**) (11.5 mg, 0.05 mmol, 1.0 equiv) was added to the reaction and stirred for 1.5 hours at 30 °C. Upon completion the reaction was plugged through silica and bicyclohexyl was obtained in 87% GC yield. The crude could be further purified by flash column chromatography (hexanes) to give bicyclohexyl as a colorless oil. NMR spectra match those reported in literature (*49*).

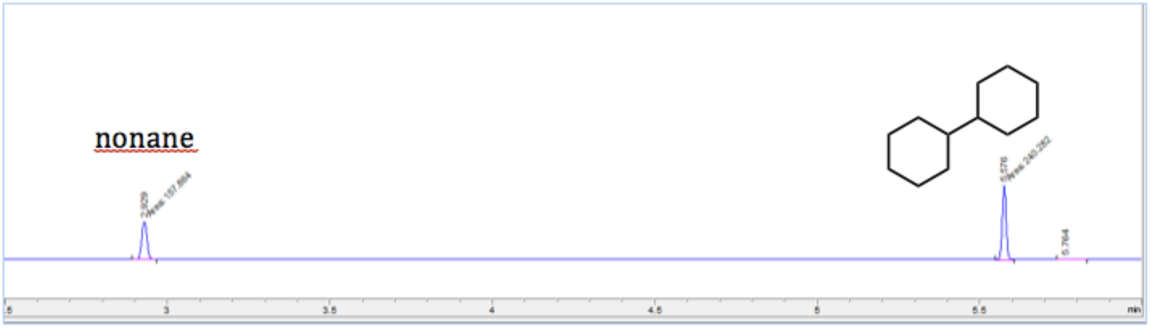


Fig. S1. GC trace showing one to one mixture of nonane to bicyclohexyl.

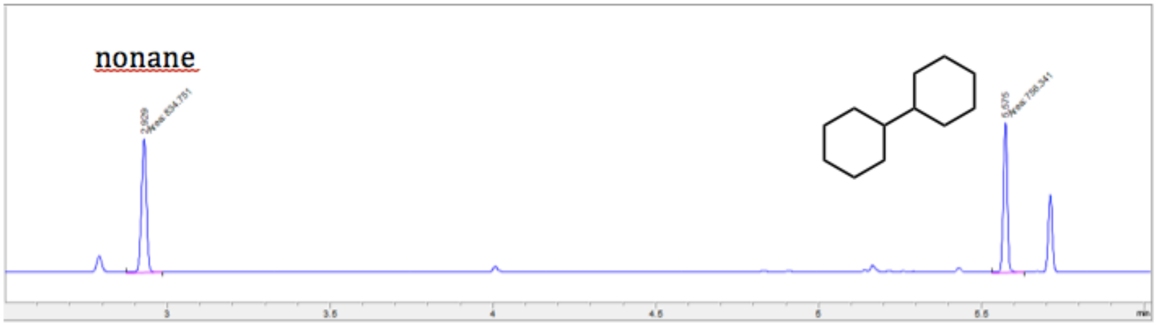
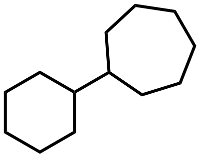


Fig. S2. GC trace showing 87% yield of bicyclohexyl.



Cyclohexylcycloheptane (SI-22). Synthesized according to general procedure 4.2. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol, 0.02 equiv) and this was suspended in cycloheptane (0.5 mL). Triethylsilane (12 µL, 0.075 mmol, 1.5 equiv) along with a magnetic stirring bar were added to the mixture and the resulting suspension stirred for 10 minutes. Cyclohexenyl triflate (**SI-1**) (11.5 mg, 0.05 mmol, 1 equiv) was added to the reaction and stirred for 2 hours at 30 °C. Upon completion the reaction was plugged through silica and cyclohexylcycloheptane was obtained in 88% GC yield. The crude could be further purified by flash column chromatography (hexanes) to give cyclohexylcycloheptane as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.74–1.68 (m, 2H), 1.68–1.52 (m, 9H), 1.50–1.43 (m ,2H), 1.42–1.34 (m, 2H), 1.32–1.07 (m, 7H), 1.06–0.96 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.0, 44.9, 31.5, 30.0, 28.6, 27.6, 27.2, 27.1.

FTIR (Neat film NaCl): 2918, 2850, 2670, 1448, 1349, 1263, 972, 893, 844.

HR-MS (GCT-LIFDI): Calculated for $C_{13}H_{24}$: 180.1878; measured: 180.1881.

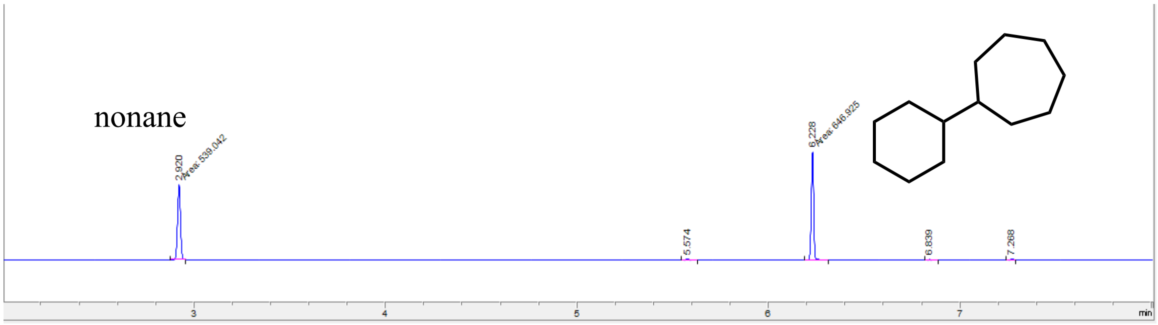


Fig. S3. GC trace showing one to one mixture of nonane to cyclohexylcycloheptane.

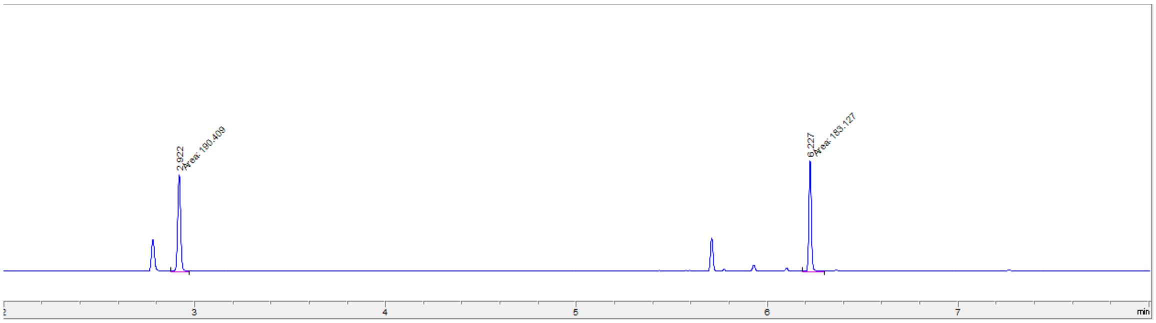
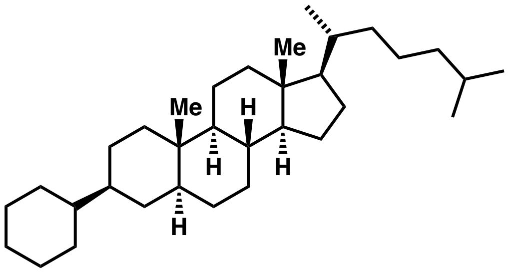


Fig. S4. GC trace showing 88% yield of cyclohexylcycloheptane.



(3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-Cyclohexyl-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene (SI-23). Synthesized according to general procedure 4.2. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol, 0.02 equiv) and this was suspended in cyclohexane (0.5 mL, 4.63 mmol). Triethylsilane (12 μL, 0.075 mmol, 1.5 equiv) along with a magnetic stirring bar were added to the mixture and the resulting suspension stirred for 10 minutes. Triflate **SI-4** (26.0 mg, 0.05 mmol, 1.0 equiv) was added to the reaction and it stirred for 3 hours at 30 °C. Upon completion the reaction was passed through silica and volatiles removed under reduced pressure to give product **SI-23** as a white solid (19.5 mg, 88%). GC-FID analysis showed ~15:1 d.r. In order to assign the stereochemistry of the newly formed C–C bond, the material was crystallized by vapor diffusion in the following manner: ~3 mg of the material was dissolved in a minimal amount of cyclohexane in a small crystallization tube. This was placed into a 20 mL vial of acetone and the vial was capped. After 3 days, a crystal suitable for single crystal X-ray diffraction was grown.

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.79–0.66 (m, 4H), 0.83 (s, 3H), 0.96 (dd, *J* = 6.7, 2.3 Hz, 8H), 1.00 (d, *J* = 6.5 Hz, 3H), 1.37–1.04 (m, 22H), 1.49–1.37 (m, 4H), 1.69–1.56 (m, 3H), 1.85–1.70 (m, 7H), 1.95–1.86 (m, 1H), 2.05 (dt, *J* = 12.5, 3.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.8, 56.5, 54.9, 47.0, 43.8, 43.6, 42.8, 40.3, 39.7, 39.1, 36.4, 36.2, 36.0, 35.7, 32.6, 32.4, 30.5, 30.4, 29.4, 28.4, 28.2, 27.1, 27.0, 25.8, 24.4, 24.0, 23.0, 22.7, 21.2, 18.8, 12.5, 12.3.

FTIR (Neat film NaCl): 2917, 2848, 1446, 1383, 1172, 930, 890.

HR-MS (GCT-LIFDI): Calculated for $C_{33}H_{58}$: 454.4539; measured: 454.4536.

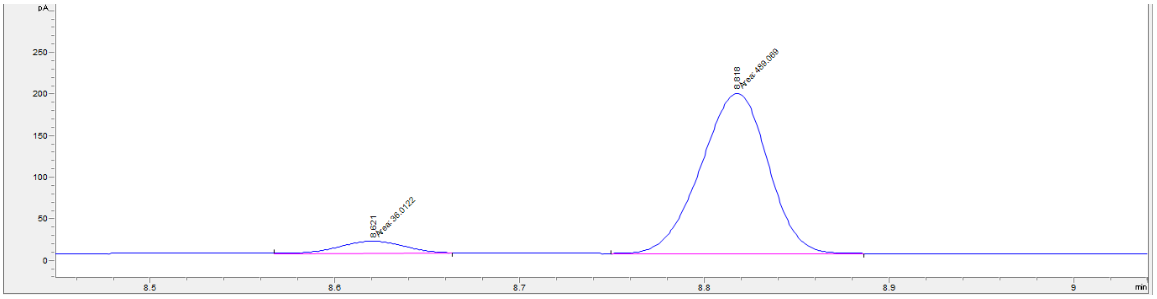
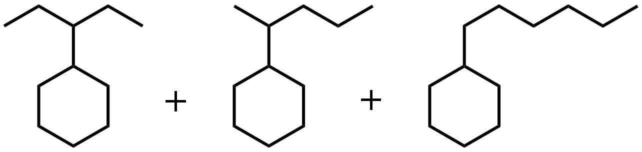


Fig. S5. GC trace showing ~15:1 d.r. **SI-23**.



Pentylcyclohexane (mixture of isomers, SI-14, SI-16, SI-24). Synthesized according to general procedure 4.2. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol, 0.02 equiv) and this was suspended in pentane (0.5 mL). Triethylsilane (12 μL, 0.075 mmol, 1.5 equiv) along with a magnetic stirring bar were added to the mixture and the resulting suspension stirred for 10 minutes. Cyclohexenyl triflate (**SI-1**) (11.5 mg, 0.05 mmol, 1.0 equiv) was added to the reaction and it stirred for 1.5 hours at 30 °C to give 11% of 3-cyclohexylpentane **SI-14**, 36% of 2-cyclohexylpentane **SI-16** and 21% of 1-cyclohexylpentane **SI-24** (GC). Upon completion the reaction was passed through silica and an inseparable mixture of the three isomers were obtained as a colorless oil (4.3 mg, 56%). The NMR data of this mixture matched those of the three authentic samples.

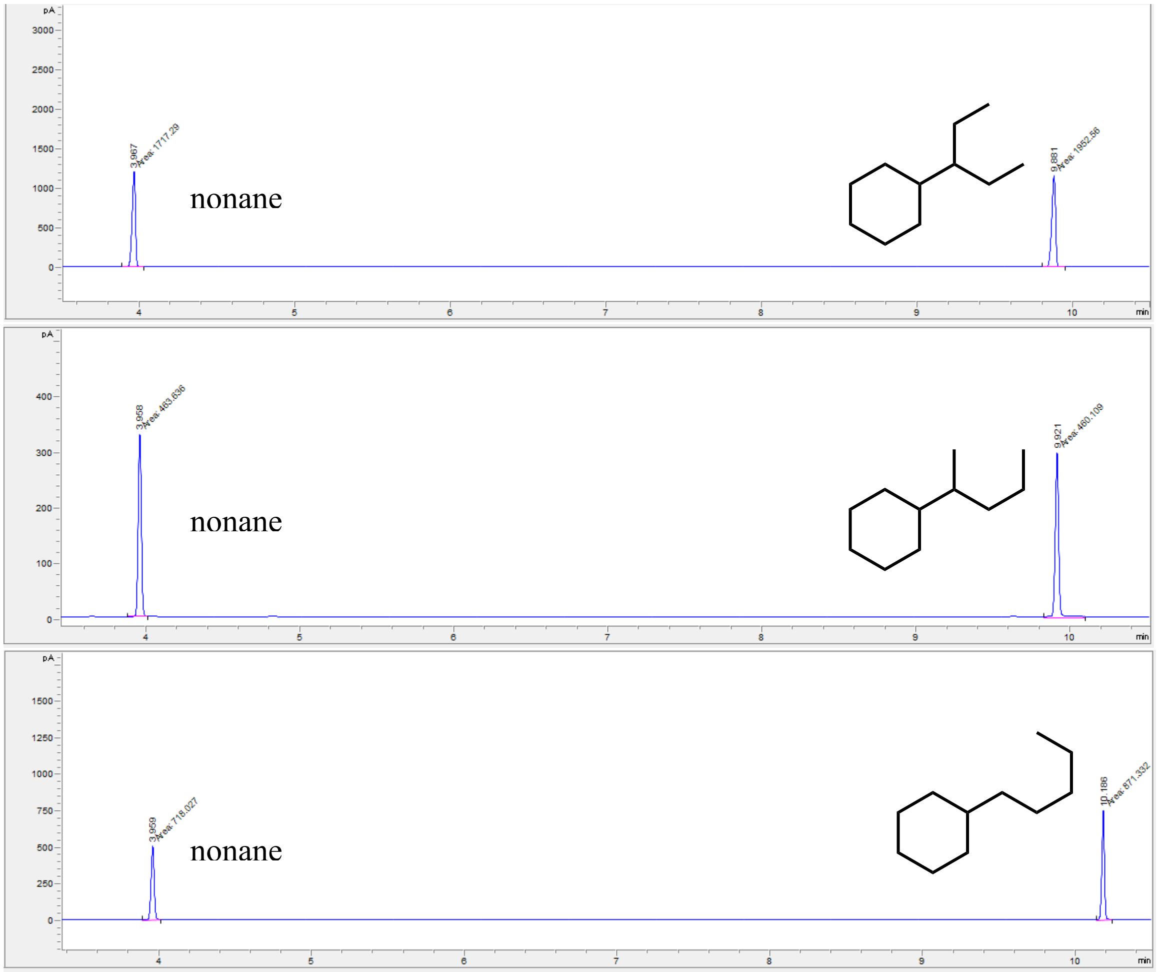


Fig. S6. GC traces showing one to one mixture of nonane to 3-cyclohexylpentane (top), nonane to 2-cyclohexylpentane (middle), and nonane to 1-cyclohexylpentane (bottom).

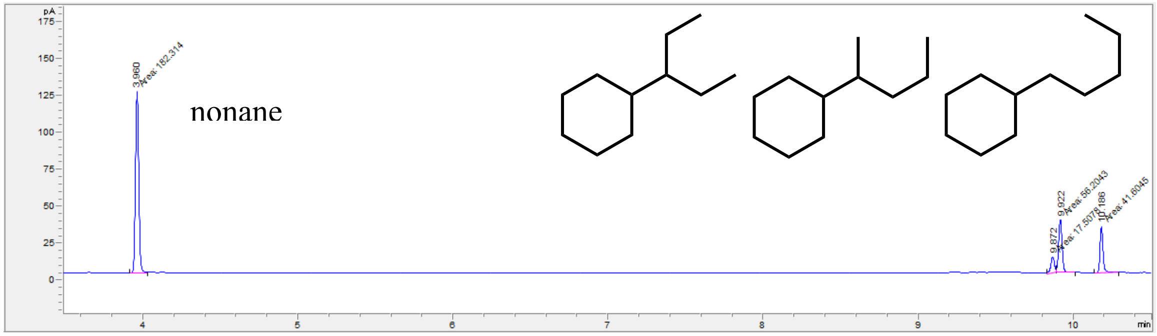
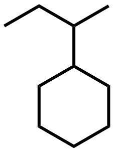


Fig. S7. GC trace showing 11% of 3-cyclohexylpentane, 36% of 2-cyclohexylpentane and 21% of 1-cyclohexylpentane.



***sec*-Butylcyclohexane (SI-25).** Synthesized according to a modified version of general procedure 4.2. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol, 0.02 equiv) and this was suspended in cyclohexane (0.5 mL, 5.63 mmol). Triisopropylsilane (15 µL, 0.075 mmol, 1.2 equiv) along with a magnetic stirring bar were added to the mixture and the resulting suspension stirred for 10 minutes. Triflate **SI-10** (10.2 mg, 0.05 mmol, 1.0 equiv) was added to the reaction and it stirred for 6 hours at 30 °C. Upon completion the reaction was passed through silica inside the glovebox and volatiles removed under reduced pressure. The crude product was further purified by silica column chromatography (hexanes) to give product **SI-25** as a colorless oil. (85% GC yield). NMR spectra match those reported in literature (*50*).

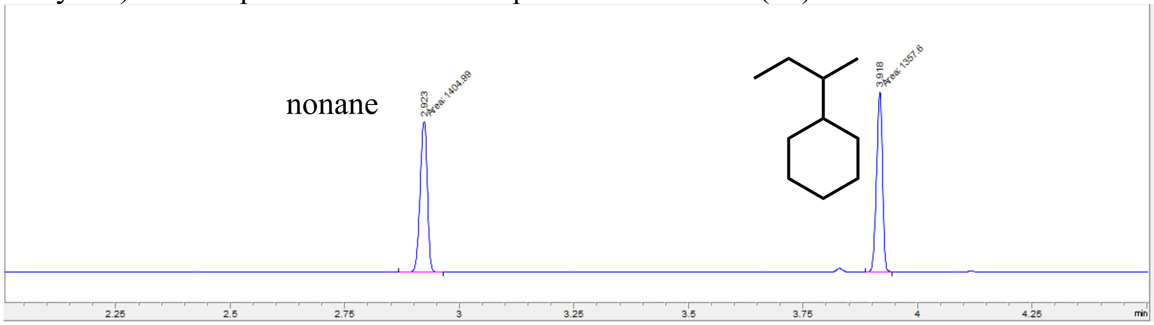


Fig. S8. GC trace showing one to one mixture of nonane to *s*-butylcyclohexane.

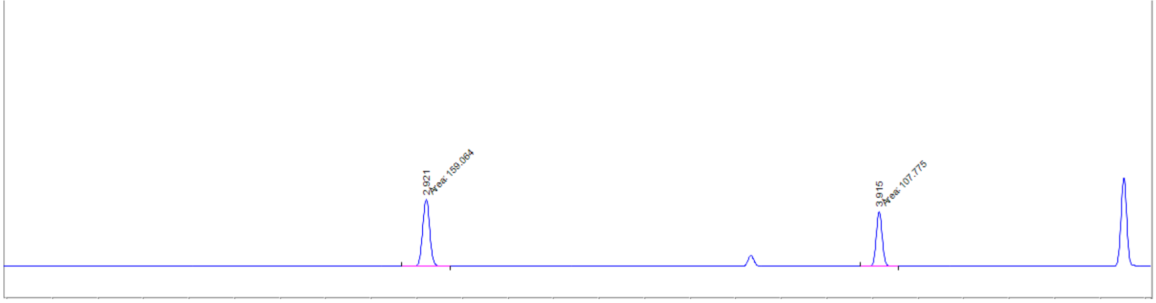
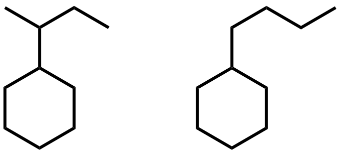


Fig. S9. GC trace showing 85% yield of *s*-butylcyclohexane.



Butylcyclohexane (~1:1 mixture of isomers, SI-25 and SI-26). Synthesized according to a modified version of general procedure 4.2. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol, 0.02 equiv) and this was suspended in cyclohexane (9 mL). Triflate **SI-9** (10.2 mg, 0.05 mmol, 1.0 equiv) was added to the reaction along with a magnetic stir bar. A solution of triethylsilane (12 µl, 0.075 mmol, 1.5 equiv) in cyclohexane (1 mL) was added portionwise to the reaction mixture over 10 minutes (100 µL every minute). 1 hour after the last addition of silane, the reaction was passed through silica in the glovebox and volatiles removed under reduced pressure to give the ~1:1 mixture of products *s*-butylcyclohexane **SI-25** and *n*-butylcyclohexane **SI-26** in 40% and 39% GC yields respectively. The NMR spectra of the mixture matched the isolated NMR of the *s*-butylcyclohexane and the NMR of the commercial *n*-butylcyclohexane (*50*).

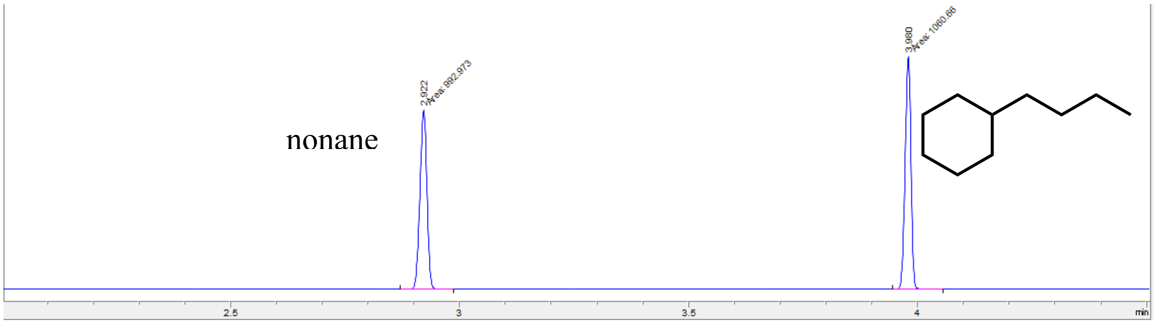


Fig. S10. GC trace showing one to one mixture of nonane to *n*-butylcyclohexane.

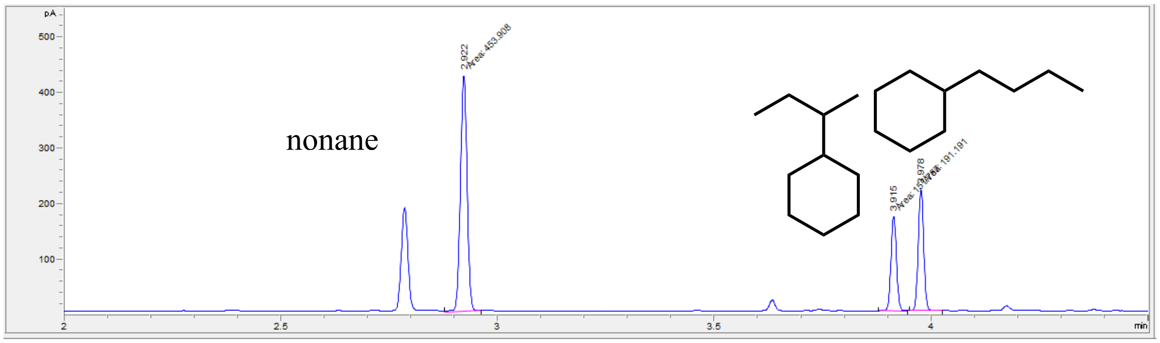
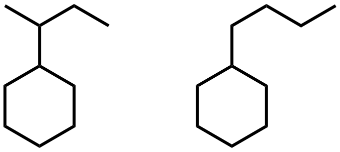


Fig. S11. GC trace showing 40% yield of *s*-butylcyclohexane and 39% yield of *n*-butylcyclohexane.

A similar product distribution was achieved albeit with a lower yield by starting with butyraldehyde derived triflate SI-5.



Butylcyclohexane (~1:1 mixture of isomers, SI-25, SI-26). A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol, 0.02 equiv) and this was suspended in cyclohexane (0.5 mL). Triisopropylsilane (11.9 mg, 0.075 mmol, 1.5 equiv) was added the reaction along with a magnetic stir bar. After stirring the reaction for 5 minutes, triflate **SI-5** (10.2 mg, 0.05 mmol, 1.0 equiv) was added and the reaction was heated to 70 °C. After 10 days, the reaction was cooled to room temperature and was passed through silica in the glovebox and volatiles removed under reduced pressure to give the ~1:1 mixture of product (16% *s*-butylcyclohexane, 19% *n*-butylcyclohexane GC yield).

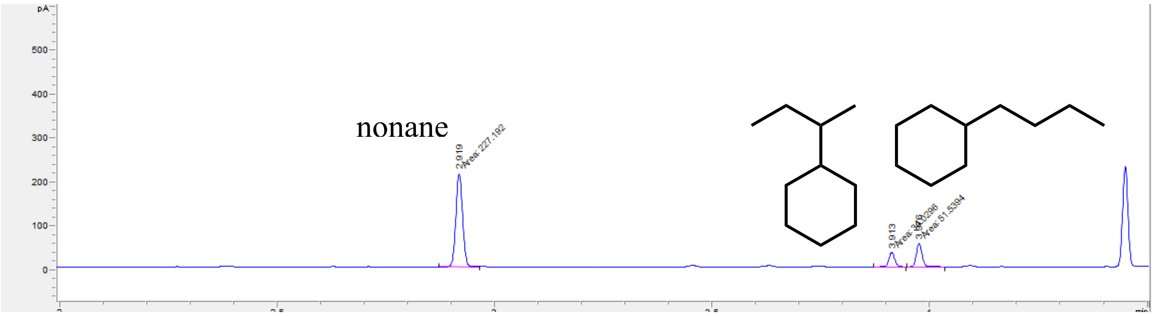
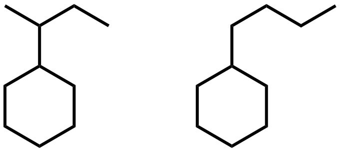


Fig. S12. GC trace showing 16% yield of *sec*-butylcyclohexane and 19% yield of *n*-butylcyclohexane.

Selective formation of 1-cyclohexylbutane could be achieved by performing the reaction at lower temperature with a lower concentration of cyclohexane.



Butylcyclohexane (1:2 mixture of isomers, SI-25, and SI-26). A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (1.9 mg, 0.0025 mmol, 0.05 equiv) and this was dissolved in chloroform (3 mL) and hexanes (3 mL). Triflate **SI-9** (10.2 mg, 0.05 mmol, 1.0 equiv) was added to the solution and it was cooled to –40 °C. Triethylsilane (12 μL, 0.075 mmol, 1.5 equiv) was quickly added and the reaction was stirred at –40 °C for 12 hours to give *n*-butylcyclohexane (**SI-26,** 34% GC yield) and *s*-butylcyclohexane (**SI-25**, 17% GC yield).

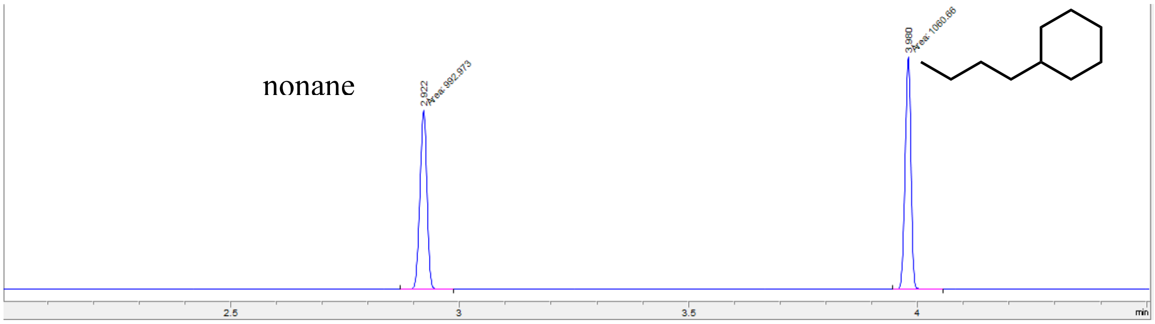


Fig. S13. GC trace showing one to one mixture of nonane to *n*-butylcyclohexane.

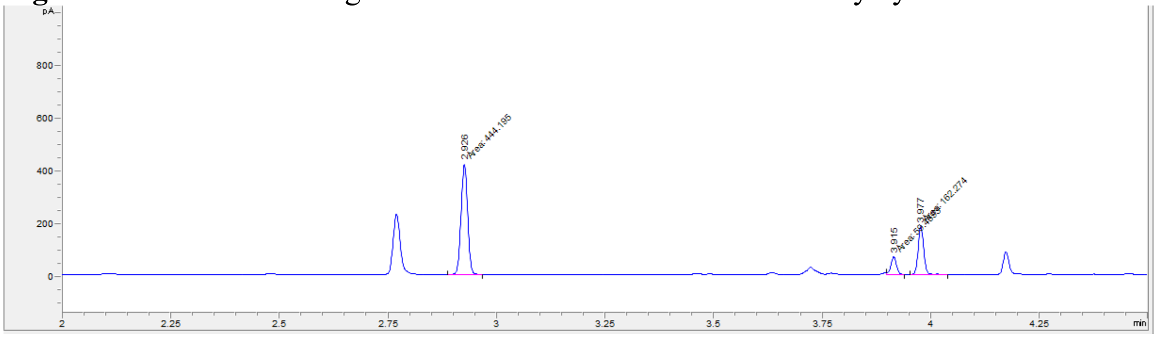
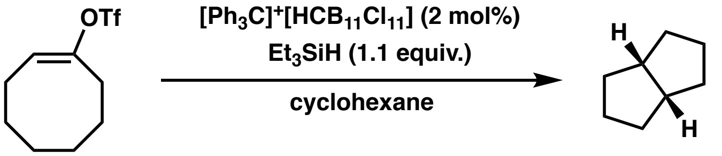


Fig. S14. GC trace showing 17% yield of *s*-butylcyclohexane and 34% yield of *n*-butylcyclohexane.

4.3 Intramolecular C–H insertion reaction of SI-3



(3a,6a)-Octahydropentalene (SI-27). Synthesized according to general procedure 4.2. A dram vial was charged with [Ph$_3$C]$^+$[HCB$_{11}$Cl$_{11}$]$^-$ (0.8 mg, 0.001 mmol) and this was suspended in cyclohexane (0.5 mL, 4.63 mmol). Triethylsilane (12 µL, 0.075 mmol) along with a magnetic stirring bar were added to the mixture and the resulting suspension stirred for 10 minutes. Cyclooctenyl triflate (**SI-3)** (18.0 mg, 0.07 mmol, 1.0 equiv) was added to the reaction and it stirred for 1 hours at 30 °C. The reaction was passed through silica in the glovebox and volatiles removed under reduced pressure to give product **SI-27** as a colorless oil (91% GC yield). NMR spectra match those reported in literature (*51*).

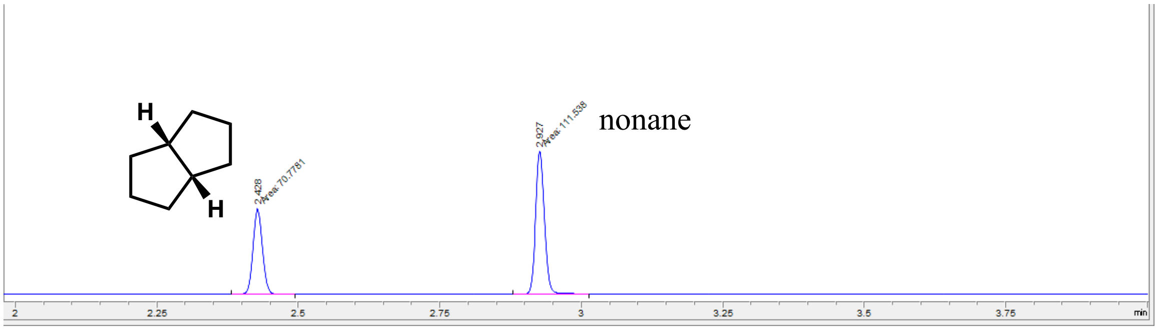


Fig. S15. GC trace showing one to one mixture of nonane to octahydropentalene.

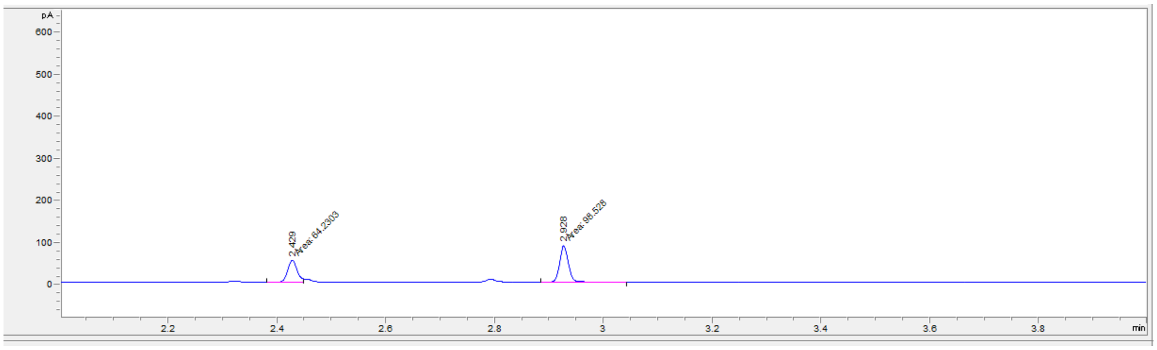
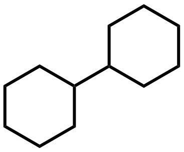


Fig. S16. GC trace showing 91% yield of **SI-27**

4.4 Procedure for benchtop preparatory-scale alkane insertion reaction

This section outlines the alkylation reaction of cyclohexenyl triflate on preparative scale on the benchtop.



Bicyclohexyl (SI-21). Synthesized according to general procedure 4.2. Inside a glovebox, $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (8.3 mg, 0.011 mmol, 0.01 equiv) was weighed into a dry 50 mL schlenk flask with a magnetic stir bar. The flask was brought out of the glovebox and put on a schlenk line under nitrogen. The catalyst was suspended in cyclohexane (10 mL, 92.6 mmol). Triethylsilane (260 μL, 1.63 mmol, 1.5 equiv) was added to the mixture and the resulting suspension stirred for 10 minutes. Cyclohexenyl triflate (**SI-1**) (250 mg, 1.09 mmol, 1.0 equiv) was added to the reaction and it stirred for 1.5 hours at 30 °C. Upon completion the volatiles were removed under reduced pressure and bicyclohexyl was obtained in 93% GC yield. The crude product was purified via flash column chromatography (hexanes) to give bicyclohexyl as a colorless oil (151 mg, 84%). NMR spectra match those reported in literature (*49*).

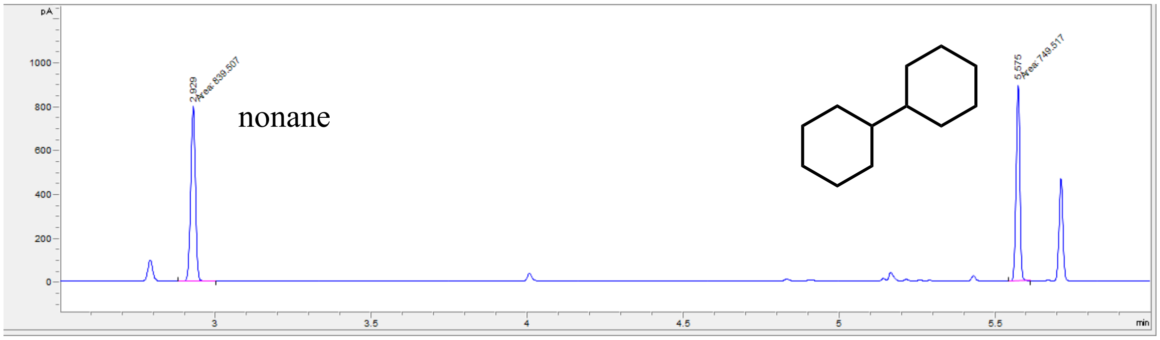
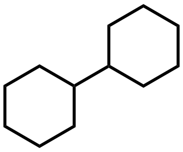


Fig. S17. GC trace showing 93% yield of bicyclohexyl.

4.5 Solvent Free "neat" Alkylation

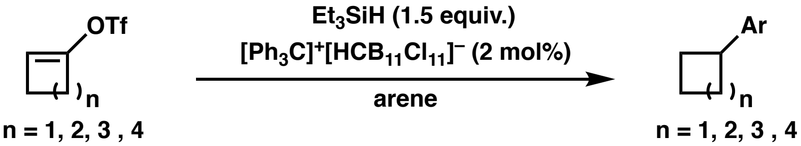


Bicyclohexyl (SI-21). Synthesized according to general procedure 4.2. Inside a glovebox, $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (7.7 mg, 0.01 mmol, 0.02 equiv) was weighed into a dram vial.. The catalyst was suspended in cyclohexane (.108 mL, 1 mmol, 2 equiv). Triethylsilane (120 µL, 0.75 mmol, 1.5 equiv) was added to the mixture and the resulting suspension stirred for 10 minutes. Cyclohexenyl triflate (**SI-1**) (115 mg, 0.5 mmol, 1.0 equiv) was added to the reaction and it stirred for 2 hours at 30 °C. The reaction mixture was passed through silica inside the glovebox with hexanes to give bicyclohexyl as a colorless oil (66 mg, 79%).

5. Arene Alkylation Reactions

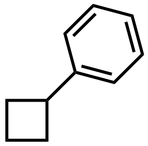
This section outlines the procedures used to obtain the arylated products found in figure 5 of the manuscript.

5.1. General Procedures for Intermolecular Arene Insertion Reactions.

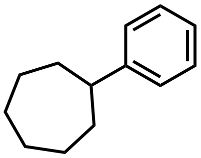


General Procedure A. In a well kept glovebox, (H_2O, O_2 < 0.5 ppm), a dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.02 equiv.) and this was dissolved in arene (enough to make a 0.1 M solution of vinyl triflate). Triethylsilane (1.5 equiv.) along with a magnetic stirring bar were added to the mixture and was shaken until it turned colorless. At this point, vinyl triflate (1.0 equiv.) was added to the reaction and it stirred for 0.1–48 hours at 30–75 °C (see substrates for specific details). Upon completion, the reaction mixture was pushed through a short plug of silica gel inside the glovebox and washed with hexanes. The solution was brought out and volatiles removed under reduced pressure. Some substrates needed further purification by silica column chromatography (see below) or preparative high pressure liquid chromatography (HPLC).

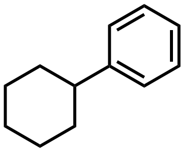
General Procedure B. In a well kept glovebox, (H_2O, $O_2 < 0.5$ ppm), a dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.02 equiv.) and this was dissolved in chloroform (enough to make a 0.1 M solution of vinyl triflate). Arene (10-50 equiv.) and vinyl triflate (1 equiv.) were added along with a magnetic stirring bar to the solution. The solution was cooled to –40 °C. At this point, silane (1.5 equiv.) was added to the reaction and it stirred at this temperature until completion (see substrates for specific details). Upon completion, the reaction mixture was pushed through a short plug of silica gel inside the glovebox and washed with hexanes. The solution was brought out and volatiles removed under reduced pressure. Some substrates needed further purification by silica column chromatography (see below) or preparative high pressure liquid chromatography (HPLC).



Phenylcyclobutane (SI-28). Synthesized according to a modified general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol) and this was dissolved in benzene (10 mL, 112 mmol). Triisopropylsilane (15 µL, 0.075 mmol) along with a magnetic stirring bar were added to the mixture and stirred until colorless. Cyclobutenyl triflate (**SI-10**) (10.0 mg, 0.05 mmol) was added to the reaction and stirred for 0.5 hours at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give product **SI-24** in 57% yield (NMR). The crude product was purified *via* silica column chromatography (hexanes) to give phenylcyclobutane as a colorless oil. NMR data match those reported in literature (*52*).



Phenylcycloheptane (SI-29). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (1.6 mg, 0.002 mmol) and this was suspended in benzene (1 mL, 11.2 mmol). Triethylsilane (24 µL, 0.15 mmol) along with a magnetic stirring bar were added to the mixture and stirred until colorless. Cycloheptenyl triflate (**SI-3**) (24.0 mg, 0.10 mmol) was added to the reaction and stirred for 1.5 hours at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give product **SI-29** in 71% yield (NMR) with ~10% yield of (cyclohexylmethyl)benzene as a small inseparable side product. NMR data match those reported in literature (*20, 53*).



Phenylcyclohexane (SI-30). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.002 mmol) and this was suspended in pentane (0.5 mL, 11.1 mmol). Triethylsilane (9.6 µL, 0.060 mmol), benzene (18 µL, 0.2 mmol, 4 equiv), and a magnetic stirring bar were added respectively to the mixture and stirred for 10 minutes. Cyclohexenyl triflate (**SI-1**) (12.0 mg, 0.050 mmol) was added to the reaction and stirred for 2 hour at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give product **SI-30** in 74% yield (GC). NMR spectra match those reported in literature (*20*).

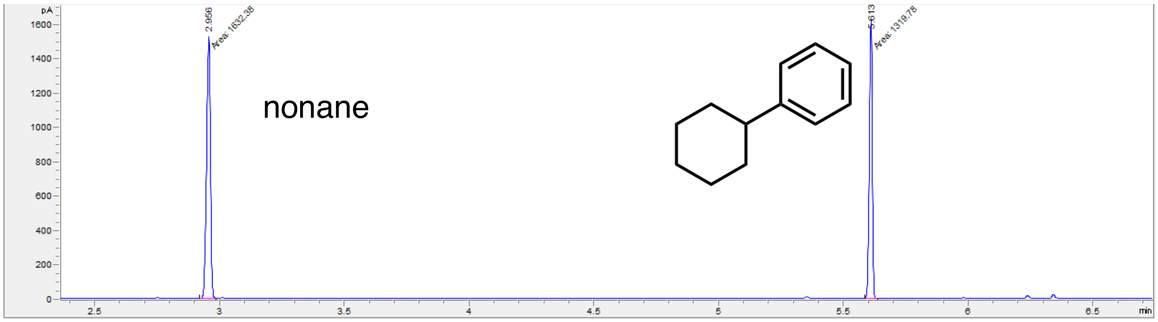


Fig. S18. GC trace showing one to one mixture of nonane to phenylcyclohexane.

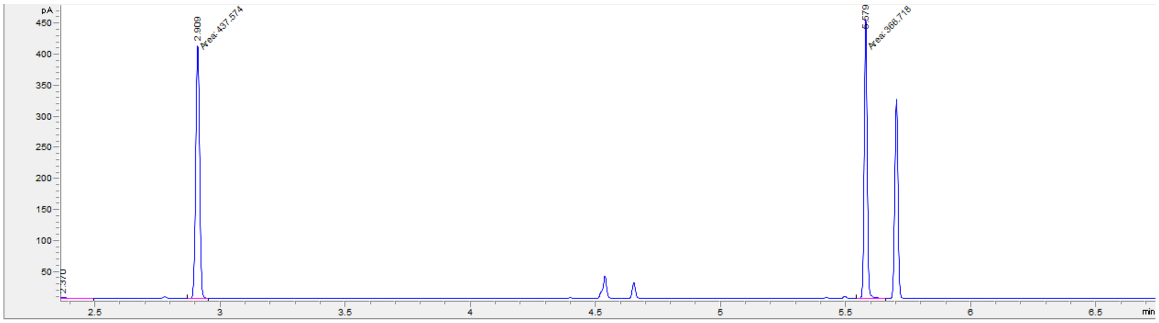
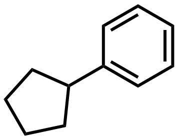
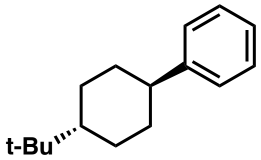


Fig. S19. GC trace showing 74% yield of phenylcyclohexane.

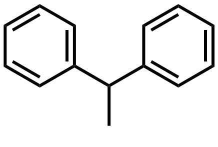


Phenylcyclopentane (SI-31). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (1.6 mg, 0.002 mmol) and this was suspended in benzene (1 mL, 11.2 mmol). Triethylsilane (24 µL, 0.15 mmol) along with a magnetic stirring bar were added to the mixture and stirred until colorless. Cyclopentenyl triflate

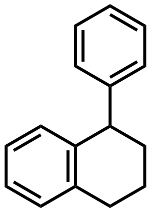
(**SI-4**) (22.0 mg, 0.10 mmol) was added to the reaction and stirred for 6 days at 70 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give phenylcyclopentane (**SI-31**) in 64% yield (NMR). The crude product was further purified by flash column chromatography (hexanes) to give phenylcyclopentane as a colorless oil (7.6 mg, 52%). NMR spectra match those reported in literature (*20*).



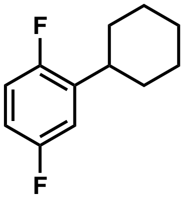
***anti*-4-(*tert*-Butyl)cyclohexyl)benzene (SI-32).** Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (1.6 mg, 0.002 mmol) and this was suspended in benzene (1 mL, 11.2 mmol). Triethylsilane (24 µL, 0.15 mmol) along with a magnetic stirring bar were added to the mixture and stirred until colorless. Triflate **SI-9** (29.0 mg, 0.10 mmol) was added to the reaction and stirred for 10 minutes at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give **SI-32** as a mixture of diastereomers (44% NMR yield of *trans*, 5% NMR yield of *cis*) (*54*). The crude product was further purified by reverse phase prep HPLC (95:5 acetonitrile/water) to give the *trans* product **SI-32** as a colorless oil (7.5 mg, 35%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.23 – 7.20 (m, 2H), 7.20 – 7.16 (m, 1H), 2.45 (tt, *J* = 12.2, 3.5 Hz, 1H), 1.99 – 1.87 (m, 4H), 1.45 (qd, *J* = 12.5, 2.6 Hz, 2H), 1.21 – 1.05 (m, 3H), 0.89 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 128.4, 127.0, 125.9, 47.92, 44.7, 34.9, 32.6, 27.9, 27.8.
FTIR (Neat film NaCl): 3061, 3027, 2937, 2921, 2855, 1602, 1493, 1479, 1448, 1364, 1232, 895, 755, 697, 532.
HR-MS (GCT-LIFDI): Calculated for $C_{16}H_{24}$: 216.1878; measured: 216.1889.



1,1-Diphenylethane (SI-33). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (1.6 mg, 0.002 mmol) and this was suspended in benzene (1 mL, 11.2 mmol). Triethylsilane (24 ,µL, 0.15 mmol) along with a magnetic stirring bar were added to the mixture and stirred until colorless. Triflate **SI-14** (29.0 mg, 0.10 mmol) was added to the reaction and stirred for 1 hour at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give triflate **SI-33** in 77% yield (NMR). Crude material was further purified via flash column chromatography (hexanes) to give product **SI-34** as a colorless oil (12.2 mg, 67%). NMR spectra match those reported in literature (*55*).



1-phenyl-1,2,3,4-tetrahydronaphthalene (SI-34). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (1.6 mg, 0.002 mmol) and this was suspended in benzene (1 mL, 11.2 mmol). Triethylsilane (24 μL, 0.15 mmol) along with a magnetic stirring bar were added to the mixture and stirred until colorless. Triflate **SI-7** (28.0 mg, 0.10 mmol) was added to the reaction and stirred for 2 days at 60 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give triflate **SI-34** in 43% yield (NMR). Crude material was purified by flash column chromatography (hexanes) to give product **SI-34** as a colorless oil (8.6 mg, 41.3%). NMR spectra match those reported in literature (*55*).

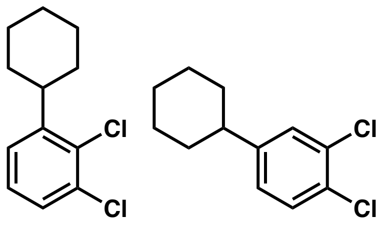


2-cyclohexyl-1,4-difluorobenzene (SI-35). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (3.2 mg, 0.004 mmol) and this was suspended in pentane (0.5 mL) and 1,4-difluorobenzene (51 μL, 0.50 mmol). Triethylsilane (9.6 μL, 0.06 mmol) along with a magnetic stirring bar were added to the mixture and stirred for 10 minutes. Cyclohexenyltriflate **(SI-1**) (12.0 mg, 0.05 mmol) was added to the reaction and stirred for 3 hours at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to yield **SI-35** in 49% yield (NMR). **SI-35** was also synthesized as described above in 1,4-difluorobenzene solvent (0.5 mL). Crude material was purified by flash column chromatography (hexanes) to yield a colorless oil (22 mg, 56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 – 6.88 (m, 2H), 6.83 – 6.78 (m, 1H), 2.84 (t, J = 10.8 Hz, 1H), 1.85 (br d, J = 10.5 Hz, 4H), 1.76 (br d, J = 12.9 Hz, 1H), 1.47 – 1.32 (m, 4H), 1.29 – 1.20 (m, 1H); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -119.4 (J = 17.7 Hz), -125.7 (J = 17.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9 (dd, $^1J_{C-F}$ = 240.8 Hz, $^4J_{C-F}$ = 2.3 Hz), 156.4 (dd, $^1J_{C-F}$ = 239.9 Hz, $^4J_{C-F}$ = 2.4 Hz), 136.3 (dd, $^2J_{C-F}$ = 17.4 Hz, $^3J_{C-F}$ = 7.0 Hz), 115.9 (dd, $^2J_{C-F}$ = 26.2 Hz, $^3J_{C-F}$ = 8.7 Hz), 114.1 (dd, $^2J_{C-F}$ = 24.0 Hz, $^3J_{C-F}$ = 5.5 Hz), 113.1 (dd, $^2J_{C-F}$ = 24.1 Hz, $^3J_{C-F}$ = 8.8 Hz), 37.1, 32.9, 26.7, 26.0.

FTIR (Neat film NaCl): 2928, 2854, 1625, 1596, 1493, 1450, 1425, 1232, 1178, 866, 810, 780, 731.

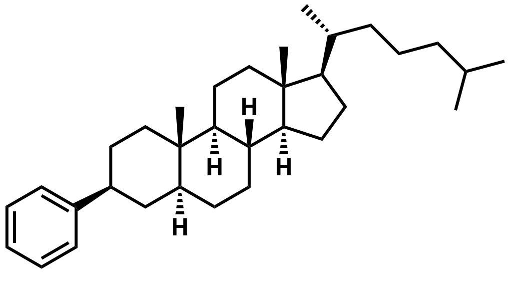
HR-MS (GCT-LIFDI): Calculated for $C_{12}H_{14}F_2$: 196.1064; measured: 196.1067.



~1:5 ratio

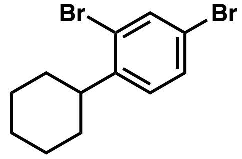
1,2-dichloro-4-cyclohexylbenzene (SI-36). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (3.2 mg, 0.004 mmol) and this was suspended in 1,4-difluorobenzene (2 mL, 19.5 mmol). Triethylsilane (48 μL, 0.3 mmol) along with a magnetic stirring bar were added to the mixture and stirred until colorless. Cyclohexenyltriflate (**SI-1**) (46.0 mg, 0.20 mmol) was added the reaction and it stirred for 1 hour at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give product **SI-36** as a mixture of isomers in 47% yield (NMR) and 9% yield (NMR). Crude material was further purified via flash column chromatography (hexanes) to give product **SI-36** (mixture of isomers) as a colorless oil. Major isomer was assigned based on the coupling constants in the ^{1}H NMR. These coupling constants are consistent with a 1,2,4-substituted benzene ring, but not with a 1,2,3-substituted benzene ring. HSQC and HMBC were used to determine which carbon peaks in ^{13}C NMR belonged to the major isomer.

^{1}H NMR major isomer (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.3 Hz, 1H), 7.28 (d, J = 1.9 Hz, 1H), 7.03 (dd, J = 8.3, 1.9 Hz, 1H), 2.46 (dd, J = 10.2, 7.5 Hz, 1H), 1.84 (br d, J = 12.9 Hz, 4H), 1.75 (br d, J = 12.9 Hz, 1H), 1.41 – 1.33 (m, 4H), 1.28 – 1.19 (m, 2H); ^{13}C NMR major isomer (125 MHz, $CDCl_3$) δ 148.4, 132.2, 130.3, 129.6, 129.0, 126.5, 44.0, 34.4, 26.8, 26.1.
FTIR (Neat film NaCl): 2924, 2852, 1584, 1560, 1475, 1461, 1449, 1131, 1028, 671, 592.
HR-MS (GCT-LIFDI): Calculated for $C_{12}H_{14}Cl_2$: 228.0473; measured: 228.0473.

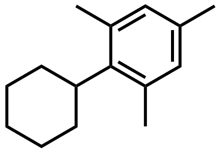


(3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-phenylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene (SI-37). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol) and this was suspended in benzene (0.5 mL, 5.6 mmol). Triethylsilane (12 μL, 0.075 mmol) along with a magnetic stirring bar were added to the mixture and the resulting suspension stirred for 10 minutes. Triflate **SI-6** (26.0 mg, 0.05 mmol) was added to the reaction and stirred for 2 hours at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give product **SI-37** as a diastereomeric mixture in 79% and 11% yield (NMR) of the major and minor diastereomers, respectively. The crude mixture was purified via silica column chromatography (hexanes) to give an inseparable mixture of diastereomers as a white solid (18.5 mg, 85% of mixture). Assignment of major isomer was based on key cross-peaks in ^{1}H COSY and ^{1}H NOESY spectroscopy experiments. From the major benzylic proton, adjacent protons were identified at 1.47 ppm and 1.72 ppm through COSY. The same peaks were observed in NOESY in addition to two peaks at 1.08 ppm and 1.26 ppm corresponding to 1,3-diaxial interactions of the benzylic proton. Through 2D HSQC and HMBC experiments, the cross-peak at 1.26 ppm was determined to be the *trans*-decalin proton.

Major Isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.27 – 7.24 (m, 2H), 7.22 – 7.18 (m, 1H), 2.58 (tt, J = 11.5, 5.0 Hz, 1H), 2.02 (dt, J = 12.5, 3.4 Hz, 1H), 1.90 – 1.80 (m, 2H), 1.77 – 1.66 (m, 3H), 1.65 – 1.58 (m, 2H), 1.56 – 1.46 (m, 3H), 1.43 – 1.25 (m, 9H), 1.23 – 1.00 (m, 11H), 0.94 (d, J = 6.6 Hz, 3H), 0.91 (d, J = 2.3 Hz, 3H), 0.90 (s, 3H), 0.89 (d, J = 2.3 Hz, 3H), 0.77 – 0.71 (m, 1H), 0.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 128.4, 127.0, 125.9, 56.8, 56.5, 54.8, 47.2, 45.0, 42.8, 39.7, 39.1, 36.8, 36.4, 36.0, 35.9, 35.7, 30.0, 28.2, 24.0, 23.0, 22.7, 18.9, 12.7, 12.3.
FTIR (Neat film NaCl): 3070, 3023, 2926, 2846, 1466, 1381, 757, 696, 513.
HR-MS (GCT-LIFDI): Calculated for $C_{33}H_{52}$: 448.4069; measured: 448.4058.



2,4-dibromo-1-cyclohexylbenzene (SI-38). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol) and this was dissolved in 1,3-dibromobenzene (0.5 mL, 3.4 mmol). Triethylsilane (12 μL, 0.075 mmol) along with a magnetic stirring bar were added to the mixture and the resulting solution stirred for 10 minutes. Triflate **SI-1** (12.0 mg, 0.05 mmol) was added to the reaction and stirred for 2 hours at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give product **SI-38** in 51% yield (NMR). The crude product was further purified by reverse phase HPLC (9:1 acetonitrile_water) to give pure product as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 2.0 Hz, 2H), 7.38 (dd, J = 8.3, 2.0 Hz, 2H), 7.11 (d, J = 8.3 Hz, 1H), 2.90 (tt, J = 11.6, 3.0 Hz, 1H), 1.90 – 1.81 (m, 4H), 1.49 – 1.18 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 135.1, 130.8, 128.6, 125.1, 119.7, 43.0, 33.3, 26.9, 26.2.
FTIR (Neat film NaCl): 2924, 2851, 1730, 1577, 1551, 1465, 1448, 1379, 1083, 1033, 998, 812, 779, 720, 700, 553.
HR-MS (GCT-LIFDI): Calculated for $C_{12}H_{14}Br_2$: 317.9442; measured: 317.9455.

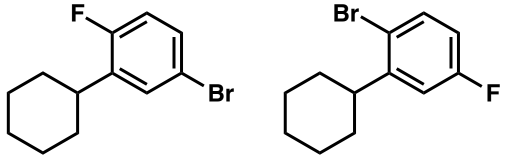


2-cyclohexyl-1,3,5-trimethylbenzene (SI-39). Synthesized according to a modified procedure. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (1.6 mg, 0.002 mmol) and this was suspended in perfluorohexanes (1.0 mL). Triethylsilane (24 μL, 0.15 mmol) and mesitylene (120 mg, 0.1 mmol) along with a magnetic stirring bar were added to the mixture and the resulting suspension stirred for 10 minutes. Triflate **SI-1** (24.0 mg, 0.1 mmol) was added to the reaction and stirred for 3 minutes at 30 °C. The reaction mixture was quenched with anhydrous ether inside the glovebox and then plugged through silica inside the glovebox to give the crude material as a colorless oil in 61% NMR yield. The crude was further purified by reverse phase HPLC (85:15 acetonitrile:water) to give product **SI-39** as a colorless oil.

^{1}H NMR (500 MHz, 57 °C, $CDCl_3$) δ 6.79 (s, 2H), 3.02 – 2.94 (m, 1H), 2.37 (s, 6H), 2.23 (s, 3H), 1.96 – 1.85 (m, 3H), 1.77 (br d, J = 12.3 Hz, 1H), 1.68 (br d, J = 13.1 Hz, 1H), 1.44 – 1.26 (m, 4H); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (s, 2H), 2.97 (tt, J = 12.4, 3.3 Hz, 1H), 2.51 – 2.29 (m, 6H), 2.24 (s, 3H), 1.96 – 1.83 (m, 4H), 1.80–1.74 (m, 1H), 1.71 – 1.65 (m, 2H), 1.45 – 1.23 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 136.3, 134.9, 131.3, 129.4, 41.4, 30.7, 27.9, 26.6, 21.8, 20.7.

FTIR (Neat film NaCl): 2924, 2851, 1612, 1483, 1448, 1369, 1261, 1025, 849, 572.

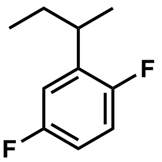
HR-MS (GCT-LIFDI): Calculated for $C_{15}H_{22}$: 202.1721; measured: 202.1727.



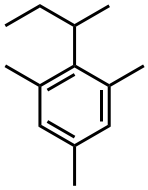
5.4:1

4-bromo-2-cyclohexyl-1-fluorobenzene (SI-40) . Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol) and this was dissolved in 1,4-bromofluorobenzene (0.5 mL, 4.6 mmol). Triethylsilane (12 μL, 0.075 mmol) along with a magnetic stirring bar were added to the mixture and the resulting solution stirred for 10 minutes. Triflate **SI-1** (12.0 mg, 0.05 mmol) was added to the reaction and stirred for 2 hours at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give product **SI-40** as a mixture of isomers in 43% and 8% yield (NMR), respectively. The reaction mixture was purified by reverse phase HPLC (85:15 acetonitrile:water) to give the product **SI-40** and a regioisomer as a mixture (~5:1 ratio) as a colorless oil. Major isomer was assigned by looking at the ^{13}C NMR and the HSQC. By ^{13}C NMR, the carbon on the fluorine and the carbons *ortho* to the fluorine could be assigned by their large $^1J_{C\text{-}F}$ and $^2J_{C\text{-}F}$ values respectively. Of the two carbons *ortho* to the fluorine, only one of them was attached to a hydrogen, meaning that the other position was cyclohexylated.

^{1}H NMR major isomer (500 MHz, CDCl$_3$) δ 7.33 (dd, J = 6.5, 2.5 Hz, 1H), 7.25 – 7.22 (m, 1H), 6.87 (dd, J = 9.9, 8.7 Hz, 1H), 2.85 – 2.77 (m, 1H), 1.87 – 1.80 (m, 4H), 1.79 – 1.72 (m, 1H), 1.44 – 1.36 (m, 4H), 1.30 – 1.21 (m, 1H); ^{19}F {^{1}H} NMR (376 MHz, CDCl$_3$) δ –119.4; ^{13}C NMR major isomer (125 MHz, CDCl$_3$) δ 159.8 (d, $^1J_{C–F}$ = 244.9 Hz), 137.0 (d, $^2J_{C–F}$ = 16.3 Hz), 130.9 (d, $^3J_{C–F}$ = 5.4 Hz), 130.0 (d, $^3J_{C–F}$ = 5.7 Hz), 117.1 (d, $^2J_{C–F}$ = 24.8 Hz), 116.7 (d, $^4J_{C–F}$ = 3.3 Hz), 37.2 (d, $^3J_{C–F}$ = 1.7 Hz, 33.0, 26.8, 26.2.
FTIR (Neat film NaCl): 2929, 2853, 1605, 1579, 1480, 1449, 1232, 1181, 1168, 1099, 1005, 869, 810, 612.
HR-MS (GCT-LIFDI): Calculated for $C_{12}H_{14}BrF$: 256.0263; measured: 256.0260.



2-(*sec*-butyl)-1,4-difluorobenzene (SI-41). Synthesized according to general procedure B. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (1.6 mg, 0.002 mmol) and this was dissolved in chloroform (1 mL). 1,4-Difluorobenzene (114 mg, 1 mmol) and but-1-en-2-yl trifluoromethanesulfonate (**SI-15**) (20.4 mg, 0.1 mmol) were added along with a magnetic stirring bar to the solution. The solution was cooled to –40 °C. At this point, triisopropylsilane (23.8 mg, 0.15 mmol) was added to the reaction and it stirred at –40 °C for 3 hours. The reaction mixture was warmed to room temparature and pushed through a short plug of silica gel inside the glovebox and washed with hexanes. The solution was brought out and volatiles removed under reduced pressure. The crude material was further purified by flash column chromatography (petroleum ether) with silver nitrate impregnated silica gel as a stationary phase to give product **SI-41** as a colorless oil. (46% NMR yield)
^{1}H NMR (500 MHz, CDCl$_3$) δ 6.94 (td, J = 9.2, 4.6 Hz, 1H), 6.88 (ddd, J = 12.8, 6.2, 3.4 Hz, 1H), 6.85 – 6.79 (m, 1H), 3.00 – 2.93 (sex, J = 7.0, 2H), 1.60 (sex, J = 7.0 Hz, 2H), 1.22 (d, J = 7.0 Hz, 3H), 0.84 (t, J = 7.0, 3H); ^{19}F {^{1}H} NMR (282 MHz, CDCl$_3$) δ –119.5 (d, J = 17.8 Hz), –125.2 (d, J = 17.8 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 158.9 (d, $^1J_{C–F}$ = 241.0 Hz), 156.7 (d, $^1J_{C–F}$ = 239.8 Hz), 136.0 (dd, $^2J_{C–F}$ = 17.5 Hz, $^3J_{C–F}$ = 6.9 Hz), 116.1 (dd, $^2J_{C–F}$ = 26.3 Hz, $^3J_{C–F}$ = 8.7 Hz), 114.2 (dd, $^2J_{C–F}$ = 13.8 Hz, $^3J_{C–F}$ = 5.6 Hz), 113.3 (dd, $^2J_{C–F}$ = 24.1 Hz, $^3J_{C–F}$ = 8.8 Hz), 34.1, 29.8, 20.4, 12.0.
FTIR (Neat film NaCl): 2963, 2931, 2875, 1596, 1496, 1464, 1415, 1380, 1180, 1165, 870, 810, 758, 731.
HR-MS (GCT-LIFDI): Calculated for $C_{10}H_{12}F_2$: 170.0907; measured: 170.0905.

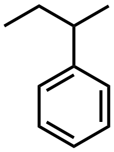


2-(*sec*-butyl)-1,3,5-trimethylbenzene (SI-42). Synthesized according to general procedure B. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (1.6 mg, 0.002 mmol) and this was dissolved in chloroform (1 mL). Mesitylene (120 mg, 1 mmol) and but-1-en-2-yl trifluoromethanesulfonate (**SI-15**) (20.4 mg, 0.1 mmol) were added along with a magnetic stirring bar to the solution. The solution was cooled to –40 °C. At this point, triethylsilane (17.4 mg, 0.15 mmol) was added to the reaction and it stirred at –-40 °C for 1 hour. The reaction mixture was warmed to room temperature and pushed through a short plug of silica gel inside the glovebox and washed with hexanes. The solution was brought out and volatiles removed under reduced pressure. The crude material was purified by flash column chromatography (hexanes) to give **SI-42** as a colorless oil (80% NMR yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (s, 2H), 3.14 (sex, *J* = 7.5 Hz, 1H), 2.32 (br s, 6H), 2.26 (s, 3H), 1.83 – 1.67 (m, 2H), 1.30 (d, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 136.4, 134.8, 131.2, 129.6, 36.7, 28.4, 21.7, 20.8, 19.0, 13.3.

FTIR (Neat film NaCl): 2962, 2926, 2872, 1612, 1455, 1377, 850, 578.

HR-MS (GCT-LIFDI): Calculated for $C_{13}H_{20}$: 176.1565; measured: 176.1572.



***sec*-butylbenzene (SI-43).** Synthesized according to a modified general procedure B. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol, 0.02 equiv.) and this was dissolved in chloroform (0.4 mL). Benzene (195 mg, 2.5 mmol, 50 equiv.) and but-1-en-2-yl trifluoromethanesulfonate (**SI-15**) (10.2 mg, 0.05 mmol) were added along with a magnetic stirring bar to the solution. Triisopropylsilane (11.9 mg, 0.075 mmol, 1.5 equiv.) was added dropwise to the reaction and stirred for 1 hour. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure. The solution was brought out and volatiles removed under reduced pressure) to give product **SI-43** in 95% yield (GC) as a colorless oil. NMR spectra match those reported in literature (*56*).

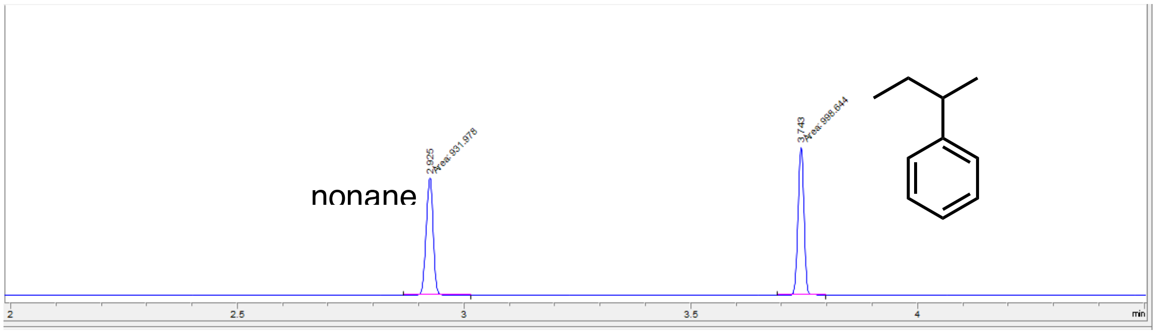


Fig. S20. GC Trace of a 1:1 mixture of nonane to *s*-butylbenzene.

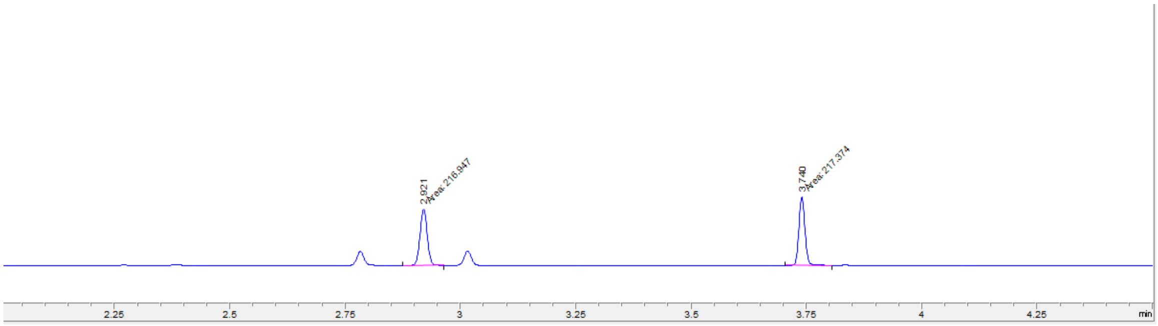
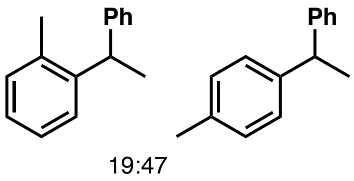
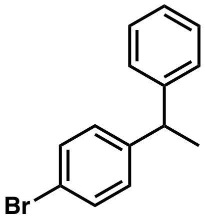


Fig. S21. GC Trace showing a 95% yield of *s*-butylbenzene.



1-methyl-4-(1-phenylethyl)benzene (SI-44). Synthesized according to general procedure B. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (1.6 mg, 0.002 mmol) and this was dissolved in chloroform (1 mL). Toluene (92 mg, 1 mmol) and 1-phenylvinyl trifluoromethanesulfonate (**SI-14**) (25.2 mg, 0.1 mmol) were added along with a magnetic stirring bar to the solution. The solution was cooled to –40 °C. At this point, triethylsilane (17.4 mg, 0.15 mmol) was added to the reaction and stirred at –40 °C for 1 hour. The reaction mixture was warmed to room temperature and was plugged through silica in the glovebox and volatiles removed under reduced pressure. The crude material was purified by flash column chromatography (hexanes) to give an inseparable mixture of products **SI-44** in 47% and 19% yield, para and ortho isomers, respectively, as a colorless oil. NMR spectra match those reported in literature (*57*, *58*).



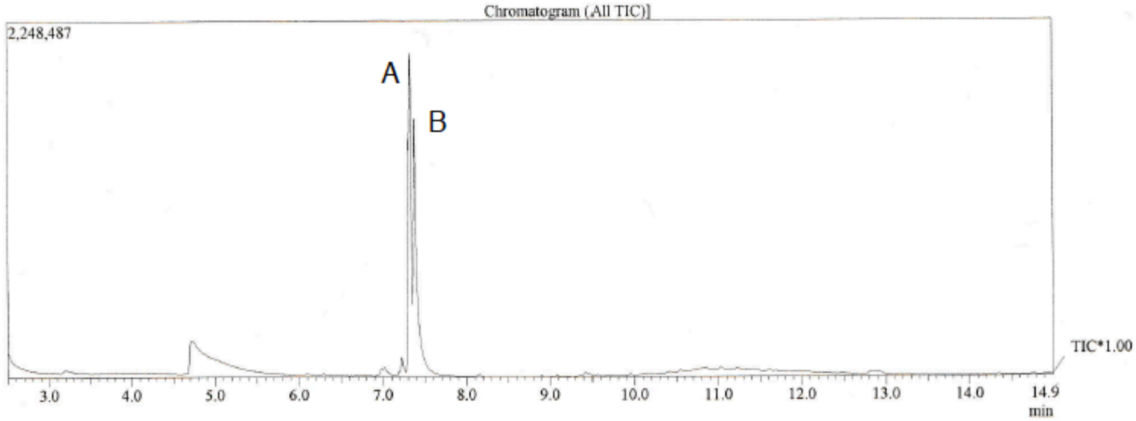
1-bromo-4-(1-phenylethyl)benzene (SI-45). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol, 0.02 equiv.) and this was dissolved in benzene (0.5 mL). Triethylsilane (7.0 mg, 0.060 mmol, 1.2 equiv.) and 1-(4-bromophenyl)vinyl trifluoromethanesulfonate (**SI-12**) (10.2 mg, 0.05 mmol) were added along with a magnetic stirring bar to the solution and stirred for 2 hours. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give product **SI-45** in 51% yield (NMR) as a colorless oil. NMR spectra match those reported in literature (*59*).

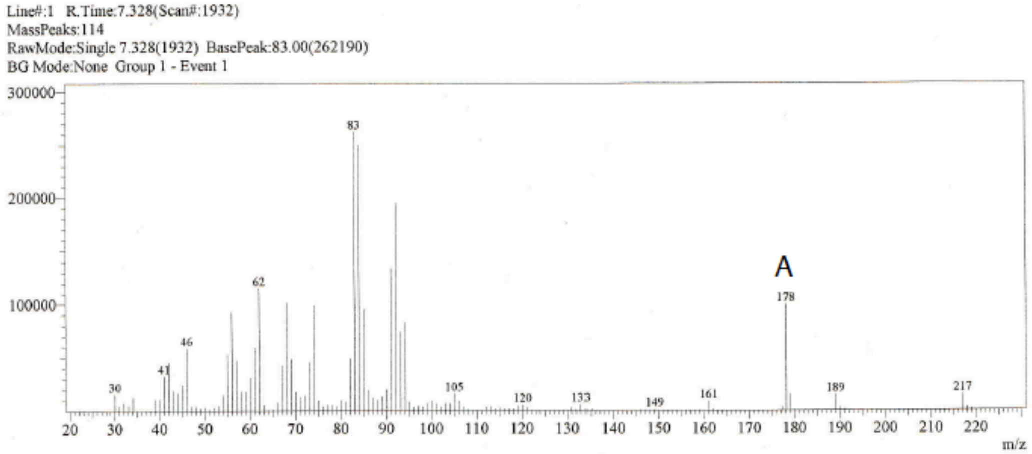
6. Mechanism Experiments

Deuterium labeling experiments were conducted in order to elucidate the nature of the key C–H insertion step, as well as to understand the kinetics of our reaction.

6.1 Procedure for Deuterium Competition Experiments

In order to probe the kinetics of our reaction, we subjected **SI-1** to a competition experiment with 1:1 C_6H_{12}:C_6D_{12}. Lack of deuterium crossover (**Fig. S22**) and a kinetic isotope effect (KIE) of 0.96 suggest that the C–H insertion step is not rate-determining. Outlined below is the procedure for conducting our alkane competition experiment.





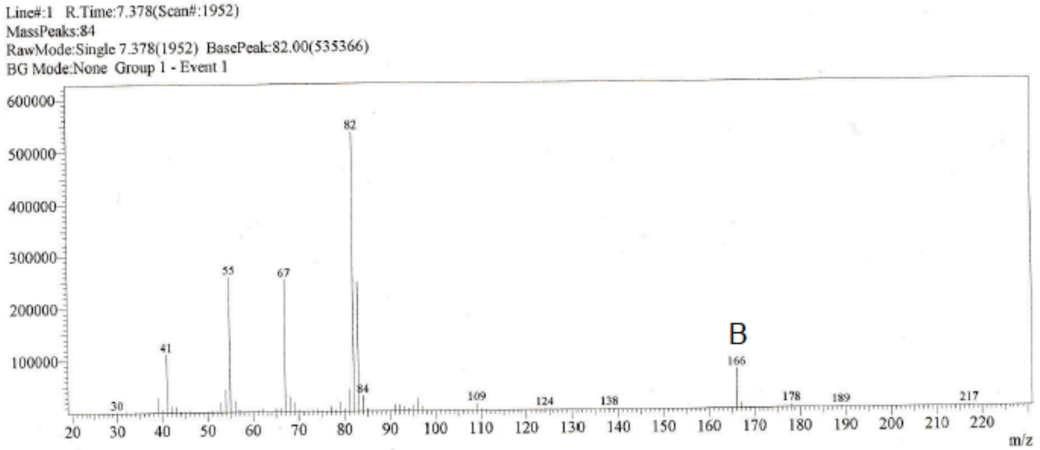


Fig. S22. GCMS spectrum of C_6H_{12}/C_6D_{12} crossover experiment. A = cyclohexylcyclohexane-d_{12} (m/z = 178); B = cyclohexylcyclohexane (m/z = 166).

Similarly, we also subjected **SI-1** to a competition experiment with 1:1 Et_3SiH:Et_3SiD. An equal distribution of D_1:D_0 products by qualitative GCMS analysis (**Fig. S23**) suggests that the silane quench is also not rate-determining. Outlined below is the procedure for conducting our alkane competition experiment.

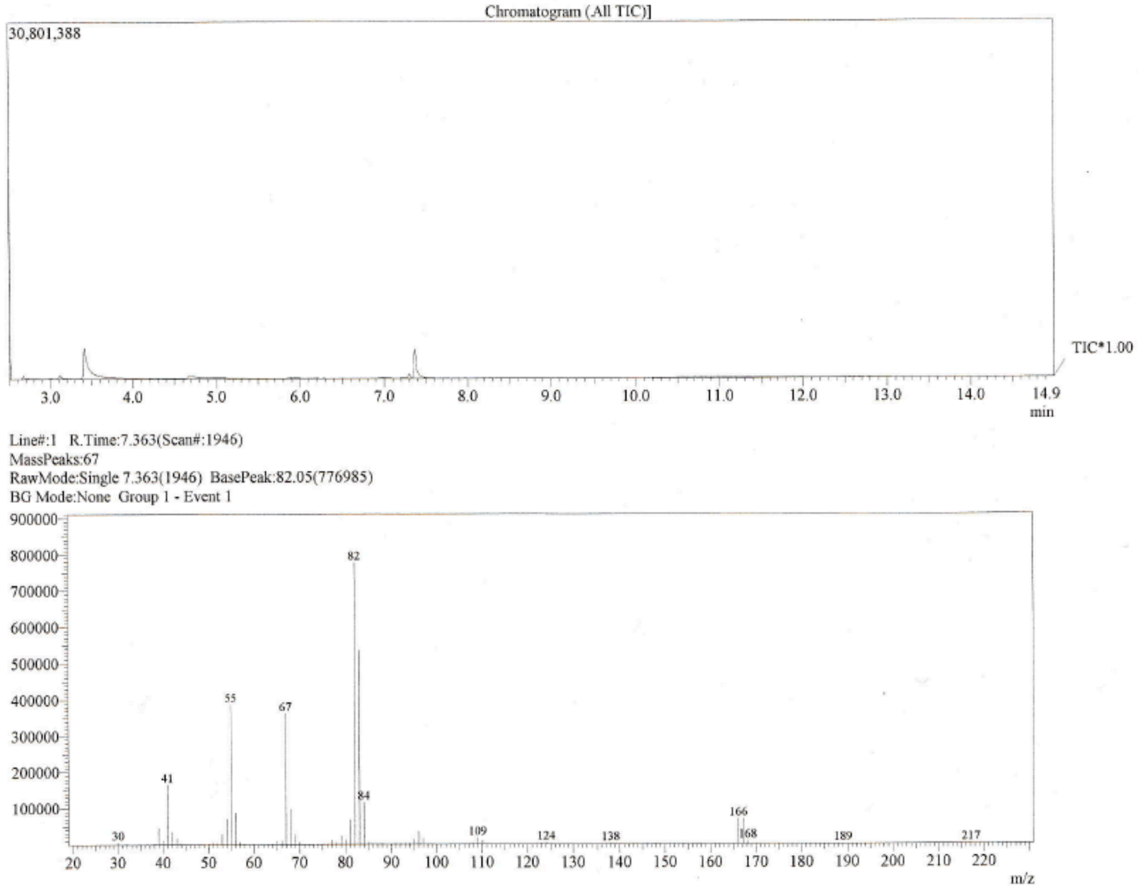


Fig. S23. GCMS spectrum of Et_3SiH/Et_3SiD competition experiment.

only D_0 (m/z = 140) and D_{12} (m/z = 152) products observed

Lastly, the butenyl triflate **SI-9** was also subjected to a competition/crossover experiment with a 1:1 ratio of C_6D_{12}:C_6H_{12}. Only D_0 and D_{12} butylcyclohexane isomers were observed suggesting a concerted C–H insertion in the C–C bond-forming event instead of the hydride transfer/rebound mechanism alluded to by previous work. If a hydride transfer from the cyclohexane to the vinyl cation was prominent, D_{11} as well as D_1 product would likely be observed. As a comparison, this reaction was also carried out in purely C_6H_{12} as well as purely C_6D_{12}.

A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol, 0.02 equiv) and this was suspended in a 1:1 mixture of C_6D_{12}:C_6H_{12} (2 mL). Triflate **SI-9** (10.2 mg, 0.05 mmol, 1.0 equiv) was added along with a magnetic stirring bar to the solution. Triethylsilane (8.75 mg, 0.075 mmol, 1.5 equiv) was added portionwise to the reaction over 10 minutes. The reaction stirred for 1 hour at room temperature and was then analyzed by GCMS. The C_6H_{12} only reaction and the C_6D_{12} only reactions were setup with the same procedure using 2 mL of C_6H_{12} and 2 mL of C_6D_{12} respectively.

1:1 C_6D_{12}:C_6H_{12} experiment

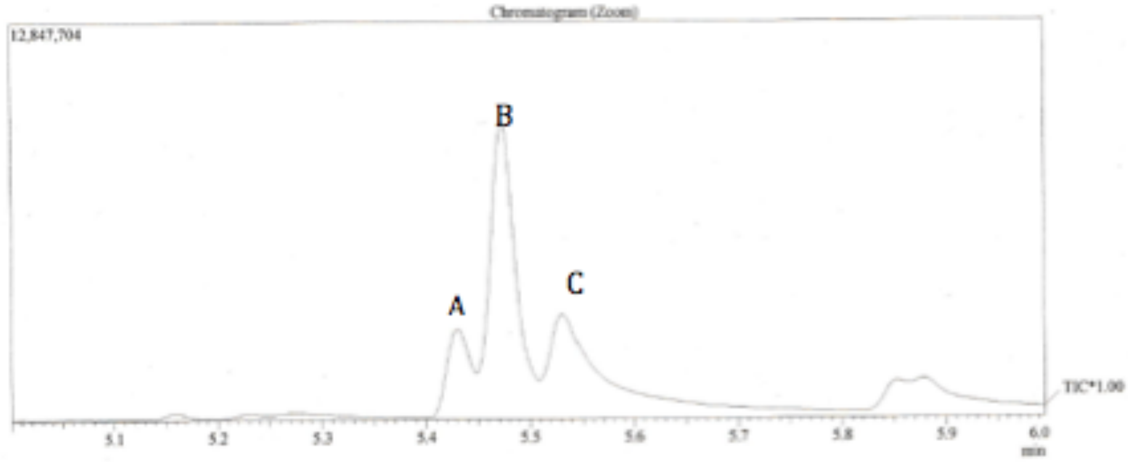
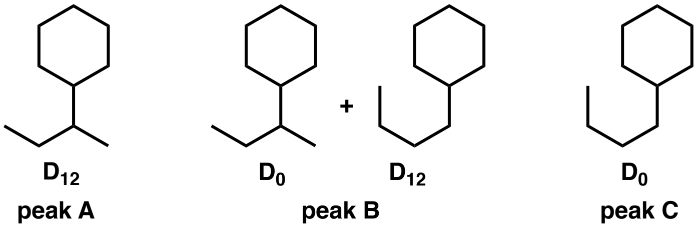


Fig. S24. Chromatogram of competition experiment.



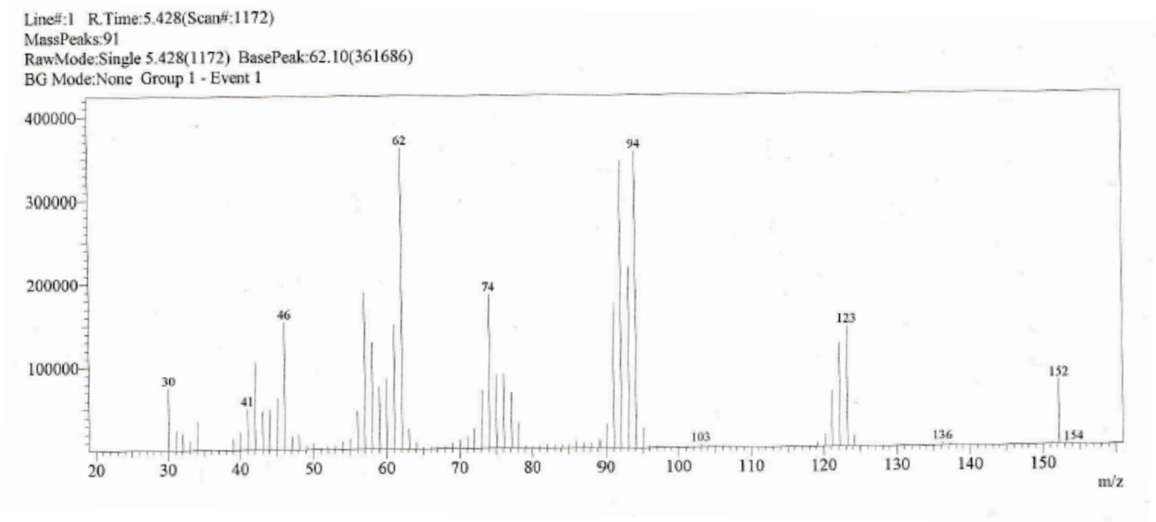


Fig. S25. Mass spectrum of peak A showing only a D_{12} isomer.

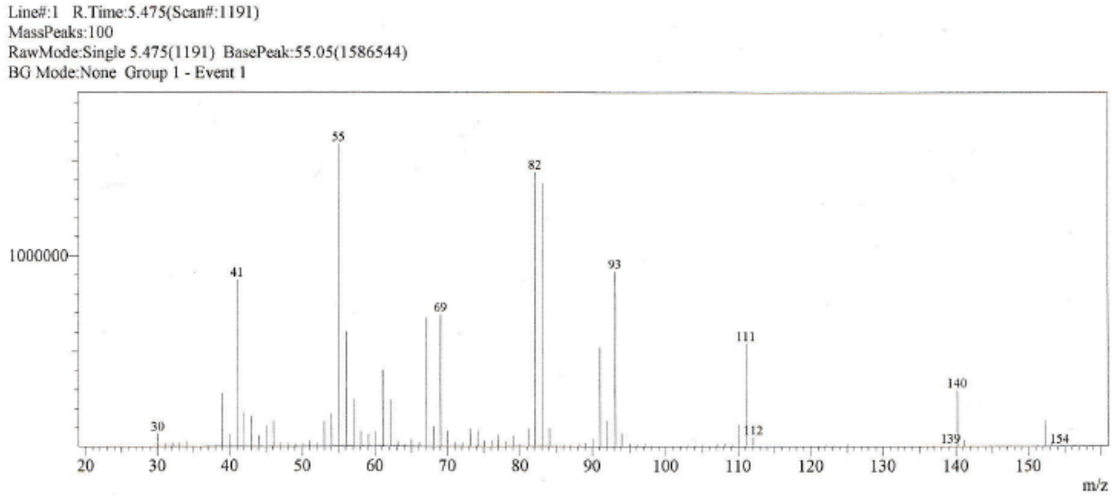


Fig. S26. Mass Spectrum of Peak B showing only D_0 and D_{12} isomers (these two compounds do not separate by GCMS)

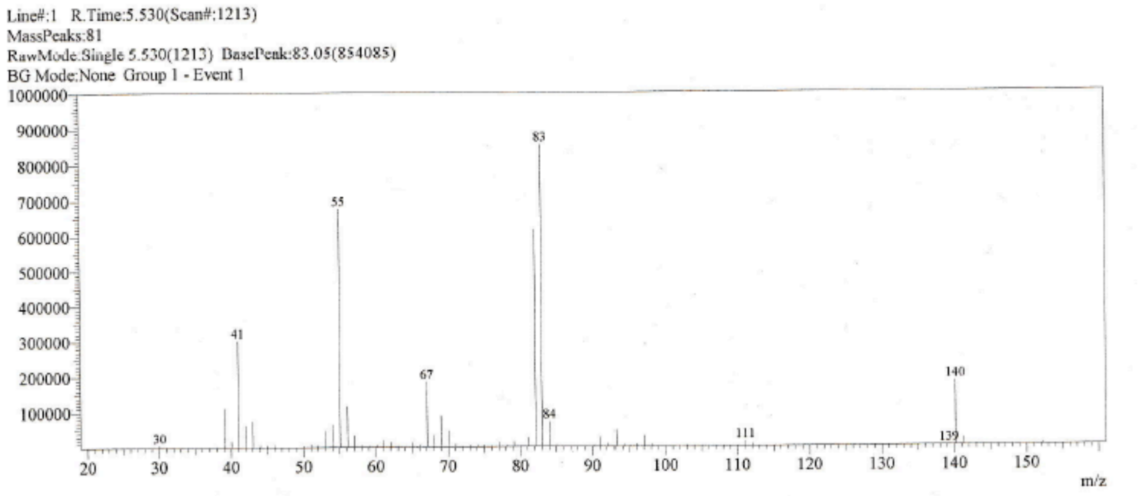
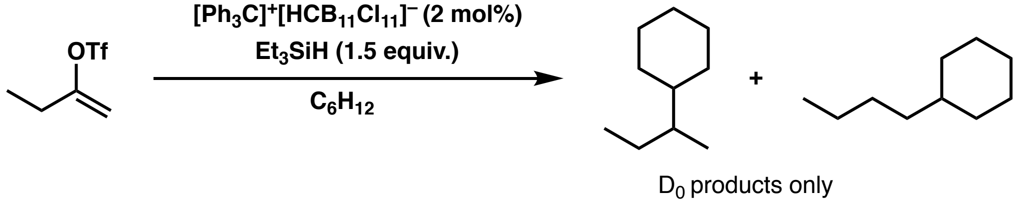


Fig. S27. Mass Spectrum of Peak C showing only the D_0 isomer.

C_6H_{12} experiment



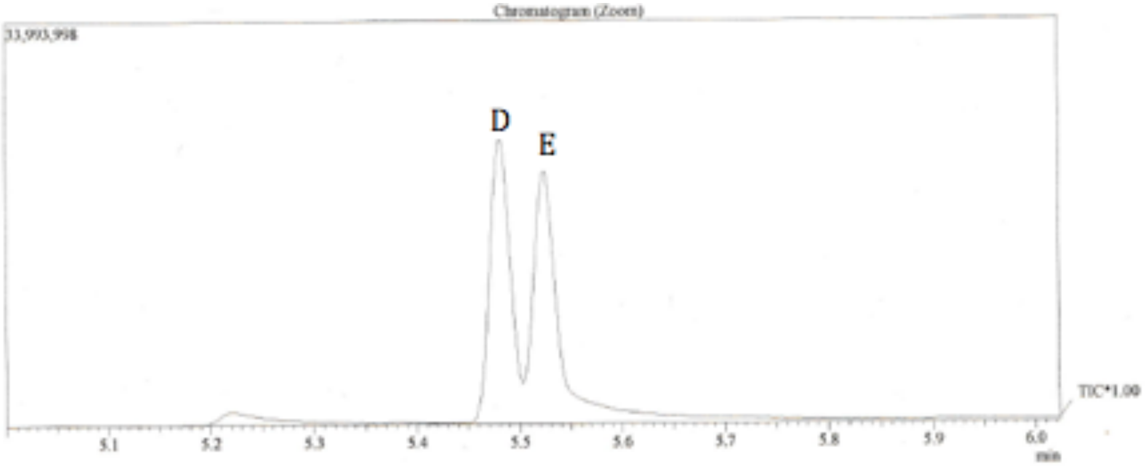
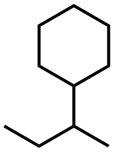
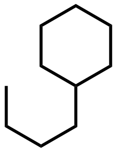


Fig. S28. Chromatogram of the C_6H_{12} control experiment.



D_0

peak D



D_0

peak E

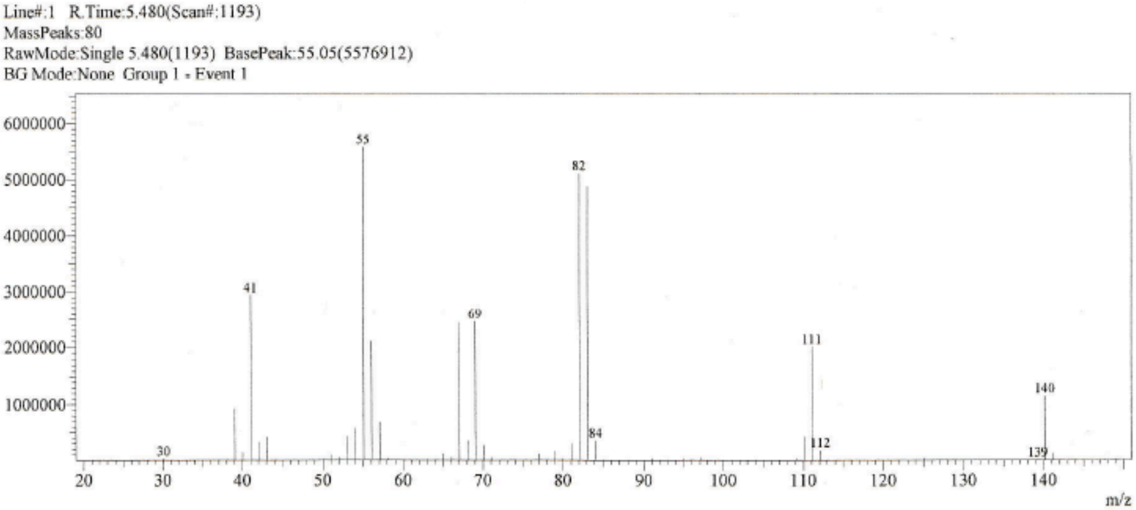


Fig. S29. Mass spectrum of peak D showing only the D_0 isomer.

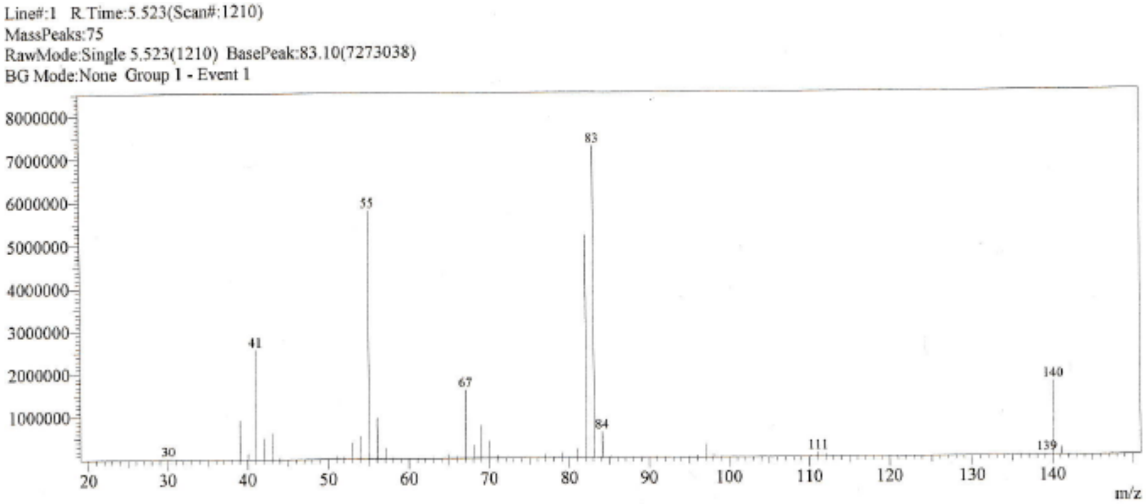
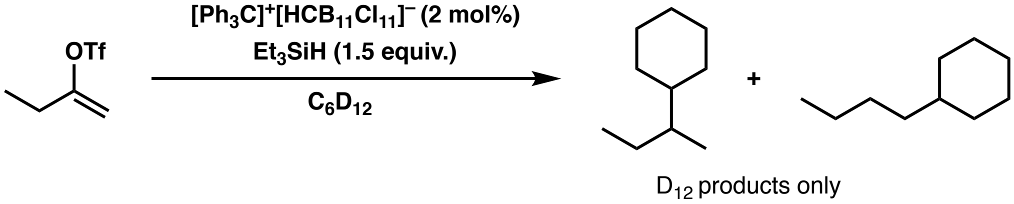


Fig. S30. Mass Spectrum of peak E showing only the D_0 isomer. Peaks D and E overlap with peaks B and C of the competition experiment.

C_6D_{12} experiment



D_{12} products only

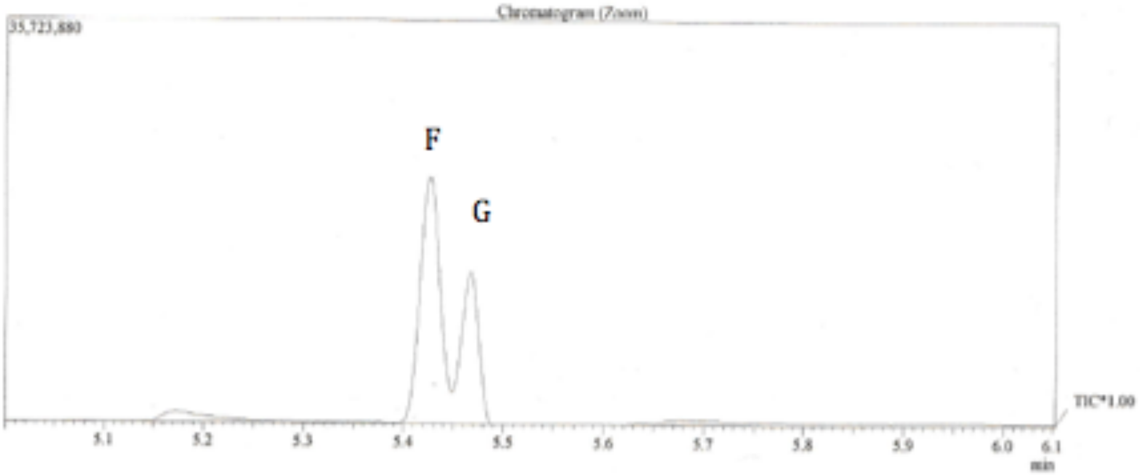
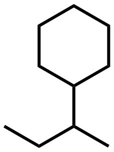
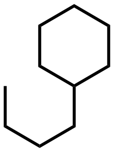


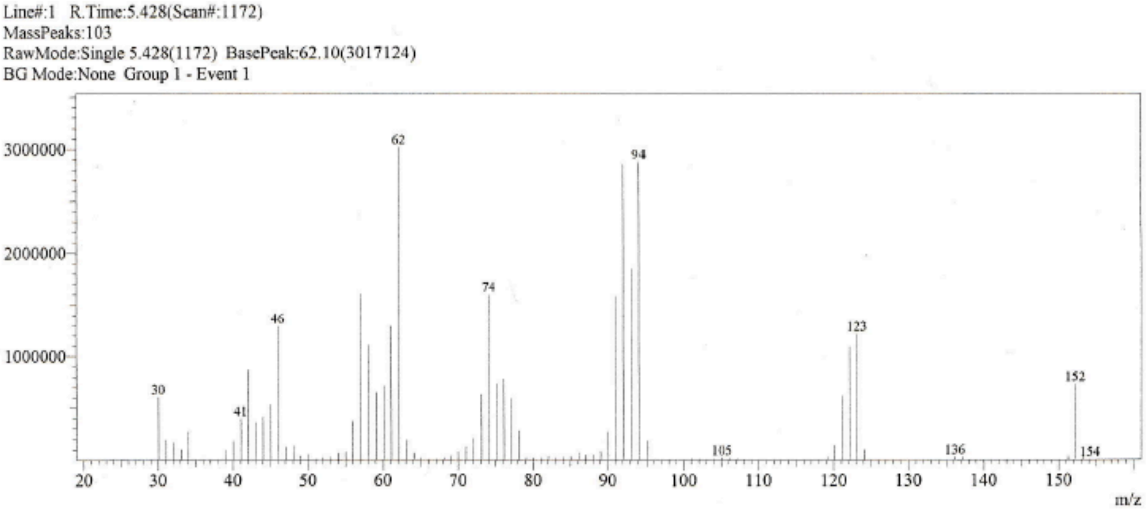
Fig. S31. Chromatogram of the C_6D_{12} control experiment.



D_{12}
peak F



D_{12}
peak G



Line#:1 R.Time:5.428(Scan#:1172)
MassPeaks:103
RawMode:Single 5.428(1172) BasePeak:62.10(3017124)
BG Mode:None Group 1 - Event 1

Fig. S32. Mass spectrum of peak F showing only the D_{12} isomer.

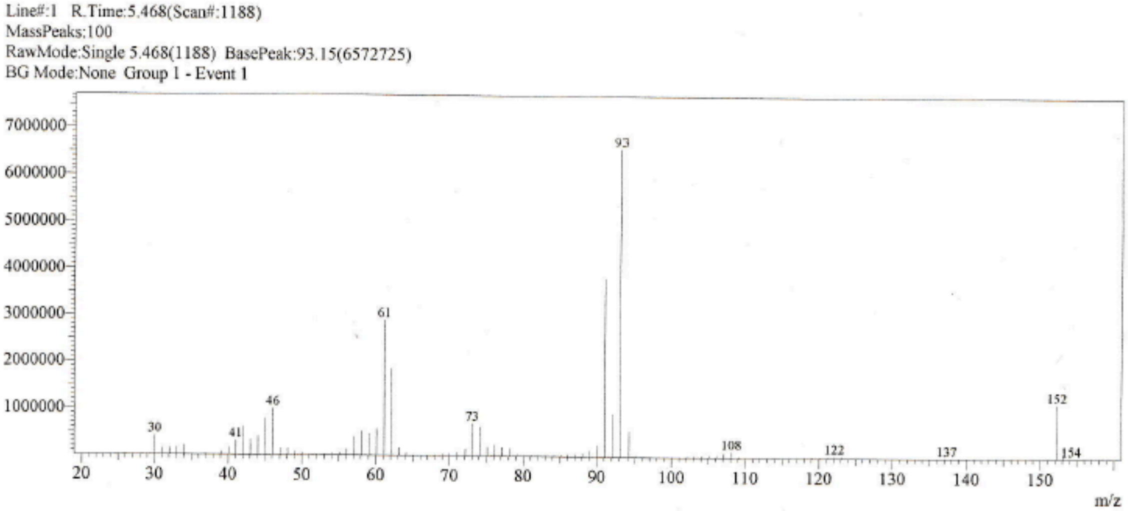
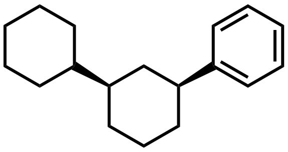


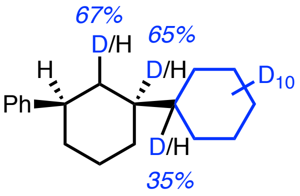
Fig. S33. Mass spectrum of peak G showing only the D_{12} isomer. Peaks F and G overlap with peaks A and B respectively of the competition experiment.

6.2 Procedure for D-labeling experiments

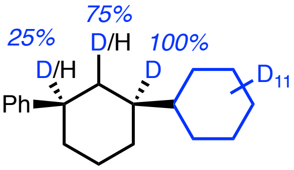
In order to distinguish between a *1*,*1*- and *1*,*2*-insertion event, we used a modified procedure from general procedure 4.2 using C_6D_{12} in place of cyclohexane. NMR data reveals both *1*,*2*-hydride and deuterium shifts in our substrate, suggestive of an incipient secondary carbocation intermediate resulting from a *1*,*1*-insertion.



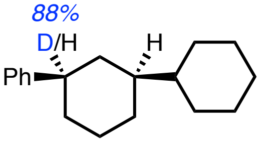
(*cis*)-3-Phenyl-1,1'-bi(cyclohexane) (SI-46). Compound was purchased from Sigma Aldrich as a mixture of isomers. Major *cis* isomer was isolated by reverse phase prepatory HPLC (95:5 acetonitrile:water).



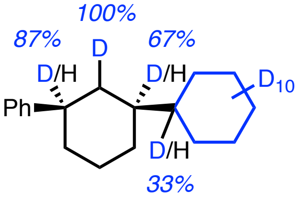
D_{12}-(*cis*)-3-Phenyl-1,1'-bi(cyclohexane) (SI-47). $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (2.4 mg, 3.0 μmol, 0.02 equiv) was suspended in cyclohexane-d_{12} (1.5 mL) before addition of triethylsilane (29 μL, 0.18 mmol, 1.2 equiv). After stirring for 10 minutes, vinyl triflate **SI-6** (46 mg, 0.15 mmol, 1.0 equiv) was added and the reaction was stirred at room temperature for 17 hours. The reaction was passed through a small layer of silica gel to remove excess silylium reagent inside a well-kept glovebox, ≤ 0.5 ppm O_2. Crude material was purified by flash chromatography (hexanes) to yield a mixture of diastereomers. Major *cis* product was isolated by reverse phase preparatory HPLC (95:5 acetonitrile:water) to yield 7.3 mg (19%) of colorless oil.



D_{13}-(*cis*)-3-Phenyl-1,1'-bi(cyclohexane) (SI-48). $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (2.4 mg, 3.0 μmol, 0.02 equiv) was suspended in cyclohexane-d_{12} (1.5 mL) before addition of triethylsilane-d_1 (29 μL, 0.18 mmol, 1.2 equiv). After stirring for 10 minutes, vinyl triflate **SI-6** (46 mg, 0.15 mmol, 1.0 equiv) was added and the reaction was stirred at room temperature for 17 hours. The reaction was passed through a small layer of silica gel to remove excess silylium reagent inside a well-kept glovebox, ≤ 0.5 ppm O_2. Crude material was purified by flash chromatography (hexanes) to yield a mixture of diastereomers. Major *cis* product was isolated by reverse phase preparatory HPLC (95:5 acetonitrile:water) to yield 6.0 mg (16%) of colorless oil.



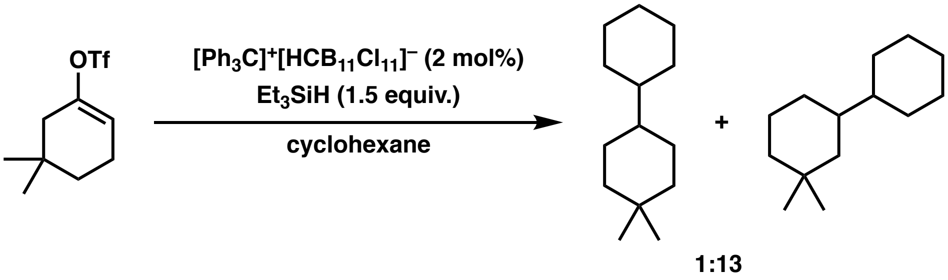
D_1-(*cis*)-3-Phenyl-1,1'-bi(cyclohexane) (SI-49). $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (2.4 mg, 3.0 μmol, 0.02 equiv) was suspended in cyclohexane (1.5 mL) before addition of triethylsilane (36 μL, 0.18 mmol, 1.5 equiv). After stirring for 10 minutes, vinyl triflate **SI-8** (46 mg, 0.15 mmol, 1.0 equiv) was added and the reaction was stirred at room temperature for 1 hour. The reaction was passed through a small layer of silica gel to remove excess silylium reagent inside a well-kept glovebox, ≤ 0.5 ppm O_2. Crude material was purified by flash chromatography (hexanes) to yield a mixture of diastereomers. Major *cis* product was isolated by reverse phase preparatory HPLC (95:5 acetonitrile:water) to yield 6.2 mg (17%) of colorless oil.



D_{13}-(*cis*)-3-Phenyl-1,1'-bi(cyclohexane) (SI-50). $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (2.4 mg, 3.0 μmol, 0.02 equiv) was suspended in D_{12}-cyclohexane (1.5 mL) before addition of triethylsilane (36 µL, 0.18 mmol, 1.5 equiv). After stirring for 10 minutes, vinyl triflate **SI-8** (46 mg, 0.15 mmol, 1.0 equiv) was added and the reaction was stirred at room temperature for 17 hours. The reaction was passed through a small layer of silica gel to remove excess silylium reagent inside a well-kept glovebox, ≤ 0.5 ppm O_2. Crude material was purified by flash chromatography (hexanes) to yield a mixture of diastereomers. Major *cis* product was isolated by reverse phase preparatory HPLC (95:5 acetonitrile:water) to yield 8.8 mg (23%) of colorless oil.

6.3 Chemoselectivity Experiments.

The following sections outlines the reactions of cyclic triflates (**SI-2** and **SI-11**) with benzene and cyclohexane in order to determine the nature of the reactive intermediate. The conclusion of these experiments show that in arylation, only the C-OTf carbon is functionalized. In contrast, some minor amounts of alkylation are observed on the adjacent carbon in the alkylation case.



3,3-Dimethyl-1,1'-bi(cyclohexane) (SI-18). Synthesized according to general procedure 4.2. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (3.2 mg, 0.004 mmol, 0.02 equiv.) and this was suspended in cyclohexane (2 mL, 18.5 mmol). Triethylsilane (48 µL, 0.3 mmol, 1.5 equiv.) along with a magnetic stirring bar were added to the mixture and the resulting suspension stirred for 10 minutes. Triflate **SI-11** (52.0 mg, 0.2 mmol) was added the reaction and it stirred for 1.5 hours at 30 °C. Upon completion the reaction was plugged through silica and a 13:1 mixture of products **SI-18** to **SI-20** was obtained as a colorless oil (78% and 6% GC yields respectively). Spectral data matched those of the authentic samples of these compounds.

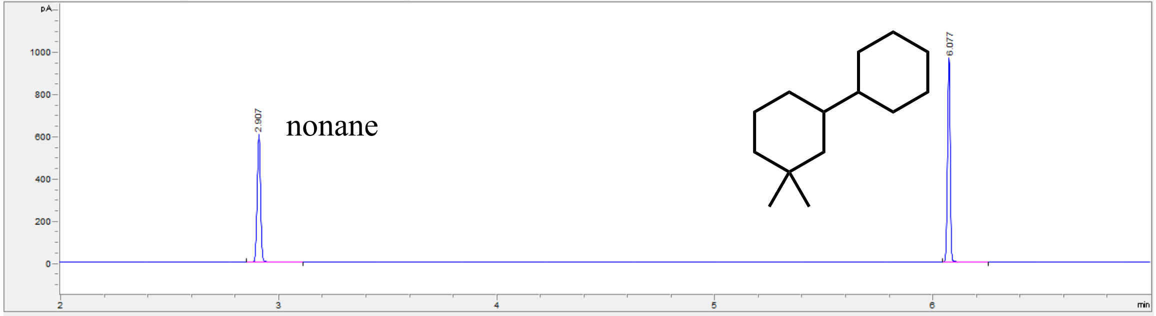


Fig. S34. GC trace showing one to one mixture of nonane to 3,3-Dimethyl-1,1'-bi(cyclohexane).

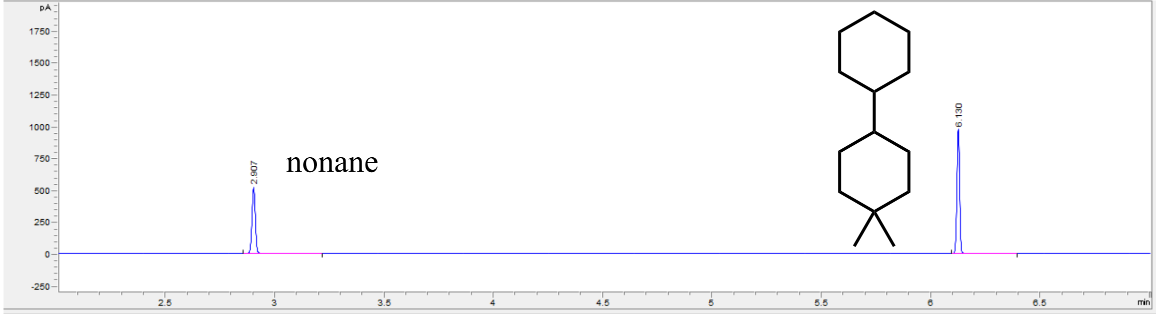


Fig. S35. GC trace showing one to one mixture of nonane to 4,4-Dimethyl-1,1'-bi(cyclohexane).

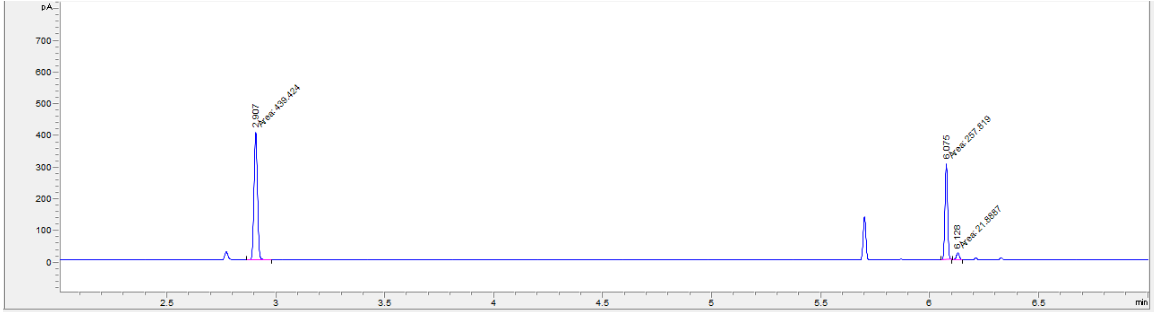
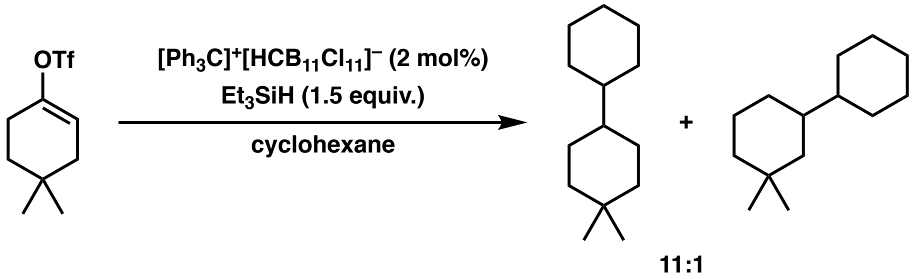


Fig. S36. GC trace showing 78% yield of **SI-18** and 6% yield of **SI-20**.



4,4-Dimethyl-1,1'-bi(cyclohexane) (SI-20). Synthesized according to general procedure 4.2. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (3.2 mg, 0.004 mmol, 0.02 equiv.) and this was suspended in cyclohexane (2 mL, 18.5 mmol). Triethylsilane (48 µL, 0.3 mmol, 1.5 equiv.) along with a magnetic stirring bar were added to the mixture and the resulting suspension stirred for 10 minutes. Triflate **SI-2** (52.0 mg, 0.2 mmol) was added the reaction and it stirred for 1 hours at 30 °C. Upon completion the reaction was plugged through silica and a 11:1 mixture of products **SI-20** to **SI-18** was obtained as a colorless oil (68% and 6% GC yields respectively). Spectral data matched those of the authentic samples of these compounds.

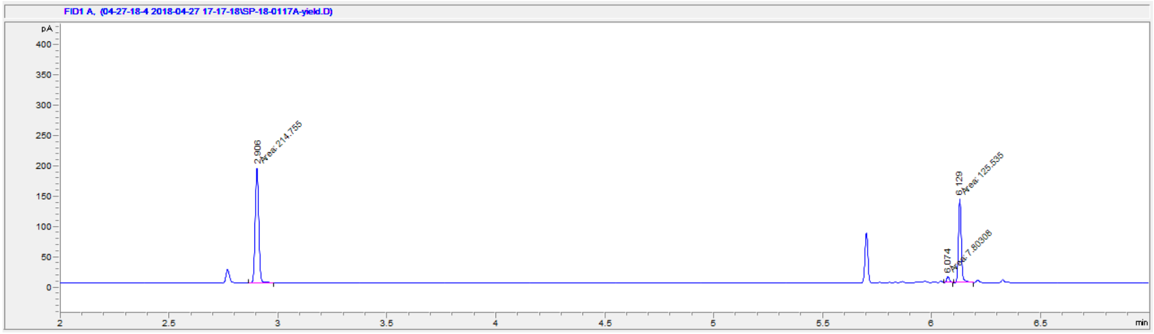
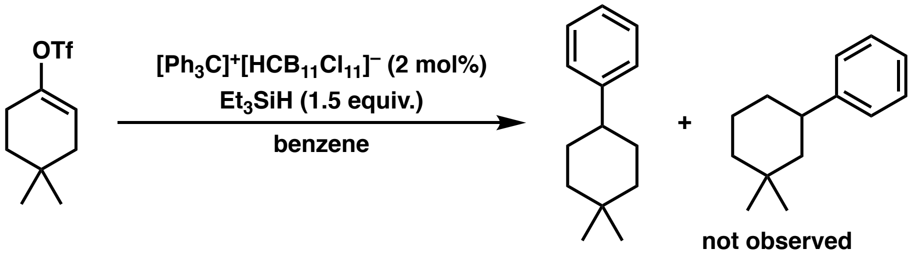
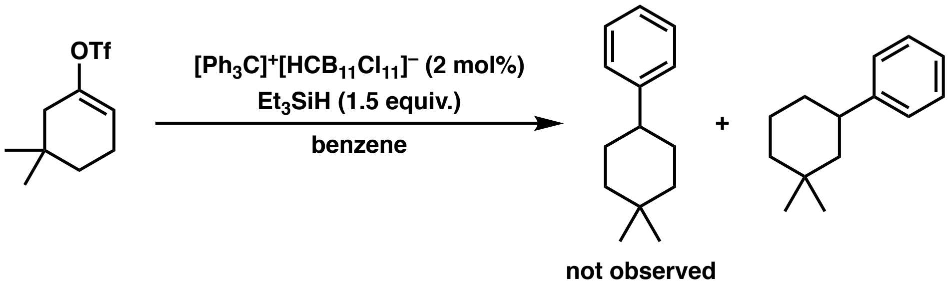


Fig. S37. GC trace showing 68% yield of **SI-20** and 6% yield of **SI-18**

.



(4,4-Dimethylcyclohexyl)benzene (SI-51). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (1.6 mg, 0.002 mmol) and this was suspended in benzene (1 mL, 11.2 mmol). Triethylsilane (24 µL, 0.15 mmol) along with a magnetic stirring bar were added to the mixture and stirred until colorless. Triflate **SI-2** (25.8 mg, 0.10 mmol) was added to the reaction and stirred for 1.5 hours at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give **SI-51** in 78% yield (NMR). The crude product was further purified by flash column chromatography (hexanes) to give **SI-51** as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.25 – 7.22 (m, 2H), 7.20 – 7.16 (m, 1H), 2.42 (tt, *J* = 11.9, 4.0 Hz, 1H), 1.73 – 1.59 (m, 4H), 1.53 – 1.47 (m, 2H), 1.34 (td, *J* = 13.1, 4.1 Hz, 2H), 0.98 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 128.3, 126.9, 125.8, 44.5, 39.7, 33.2, 30.2, 29.8, 24.2.
FTIR (Neat film NaCl): 3062, 3027, 2923, 2861, 2843, 1740, 1602, 1471, 1451, 1385, 1364, 753, 697, 532.
HR-MS (GCT-LIFDI): Calculated for $C_{14}H_{20}$: 188.1565; measured: 188.1572.



(3,3-Dimethylcyclohexyl)benzene (SI-52). Synthesized according to general procedure A. A dram vial was charged with $[Ph_3C]^+[HCB_{11}Cl_{11}]^-$ (0.8 mg, 0.001 mmol) and this was suspended in benzene (0.5 mL, 5.6 mmol). Triethylsilane (12 µL, 0.075 mmol) along with a magnetic stirring bar were added to the mixture and stirred until colorless. Triflate **SI-11** (12.9 mg, 0.05 mmol) was added to the reaction and stirred for 1.5 hours at 30 °C. The reaction was plugged through silica in the glovebox and volatiles removed under reduced pressure to give **SI-52** in 88% yield (NMR). The crude product was further purified by flash column chromatography (hexanes) to give **SI-52** as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.20 (m, 2H), 7.20 – 7.15 (m, 1H), 2.70 (tt, *J* = 12.5, 3.4 Hz, 1H), 1.91 – 1.84 (m, 1H), 1.71 – 1.52 (m, 3H), 1.46 – 1.41 (m, 1H), 1.36 – 1.26 (m, 2H), 1.19 (td, *J* = 13.2, 4.4 Hz, 1H), 1.01 (s, 3H), 0.95 (s, 3H);

^{13}C NMR (125 MHz, CDCl$_3$) δ 148.0, 128.4, 127.1, 125.9, 47.7, 40.1, 39.0, 34.2, 33.6, 31.4, 24.8, 22.9.

FTIR (Neat film NaCl): 3062, 3027, 2922, 2862, 2844, 1602, 1493, 1471, 1451, 1385, 1363, 756, 697, 538, 525.

HR-MS (GCT-LIFDI): Calculated for $C_{14}H_{20}$: 188.1565; measured: 188.1571.

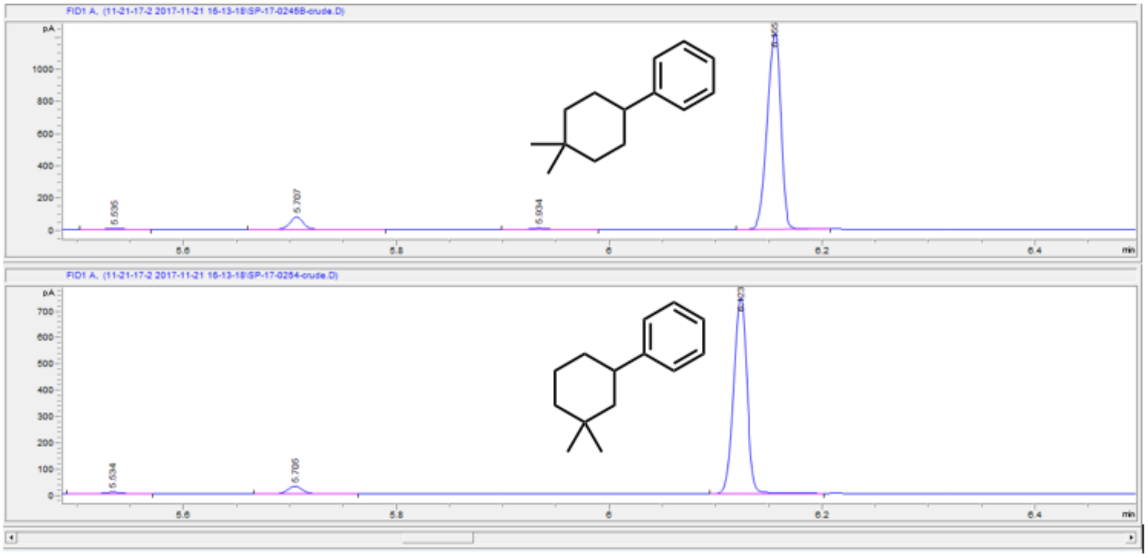
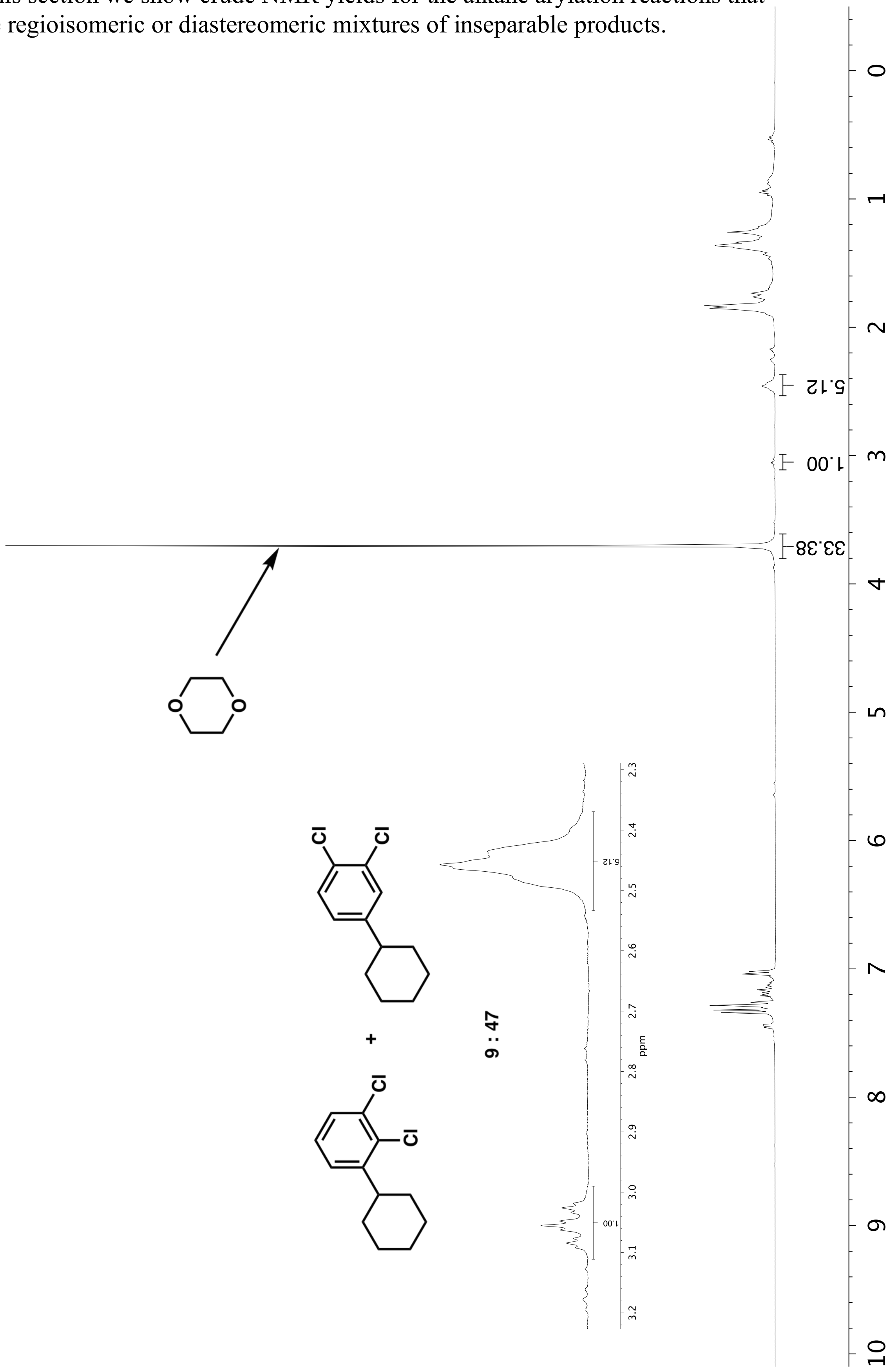


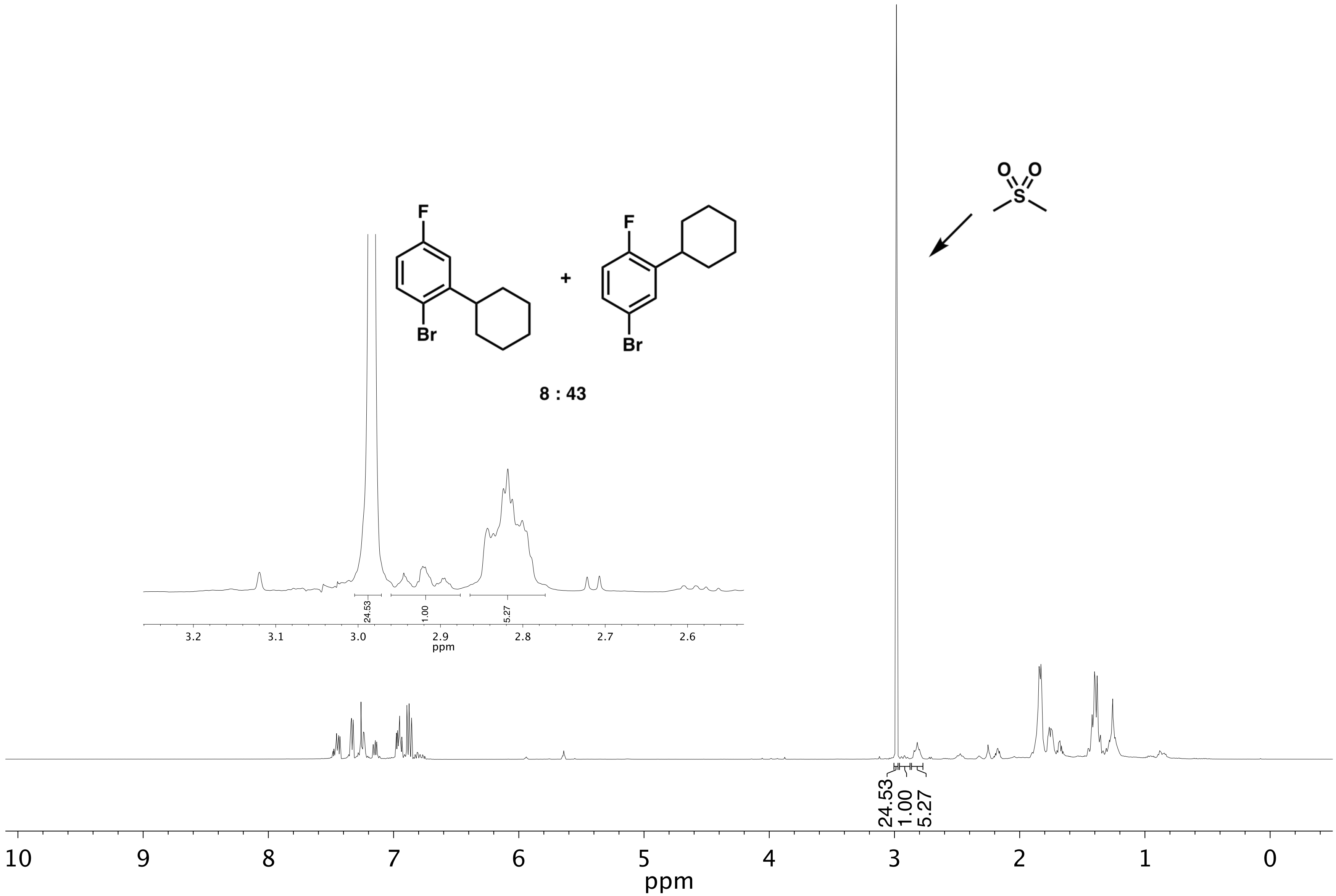
Fig. S38. Overlay of GC traces of the crude reactions above showing a single regioisomer observed in each reaction. (Top trace corresponds to reaction of **SI-2**; bottom trace corresponds to reaction of **SI-17**)

7. Crude ^{1}H NMR Spectral Data

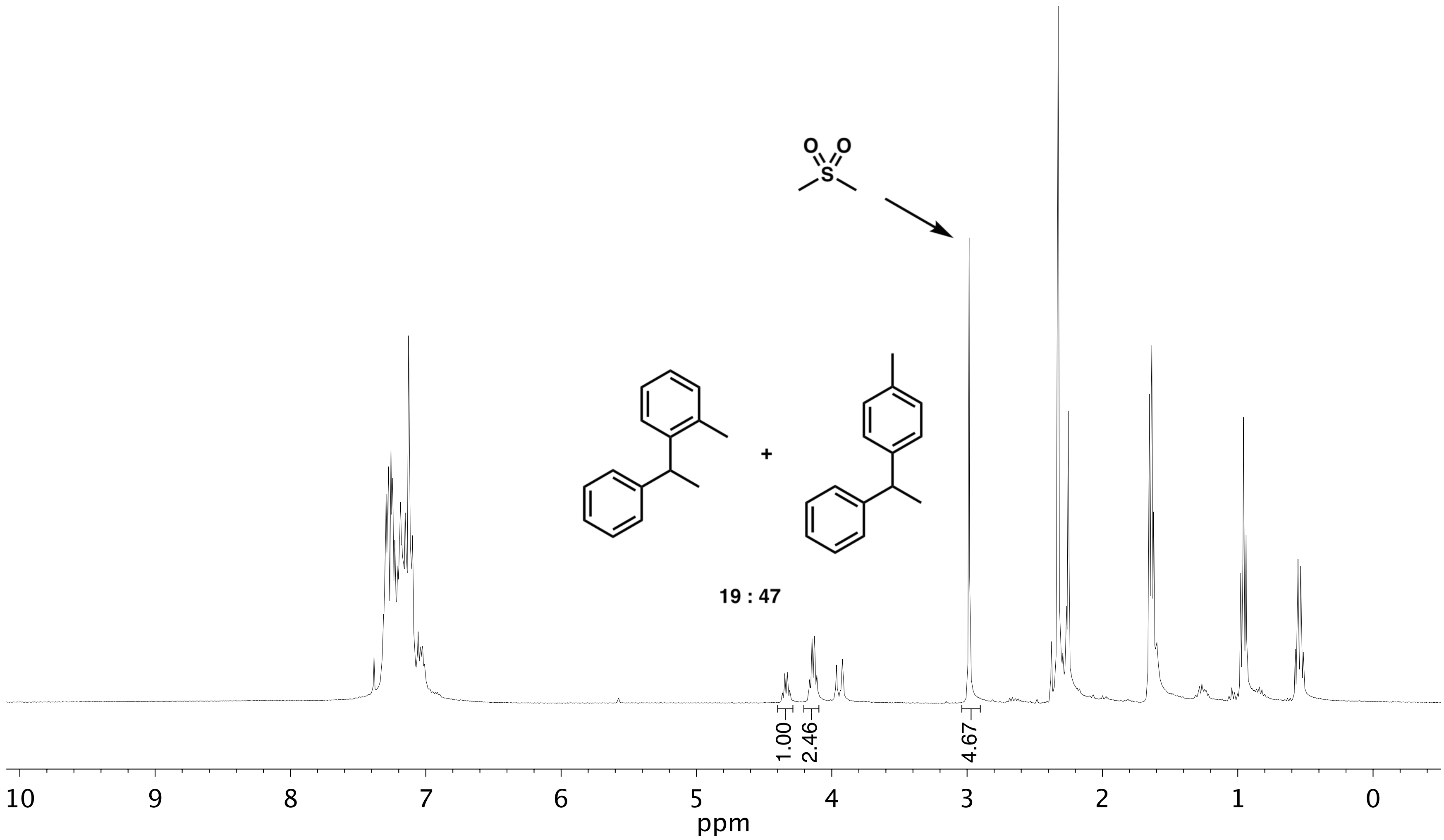
In this section we show crude NMR yields for the alkane arylation reactions that give regioisomeric or diastereomeric mixtures of inseparable products.



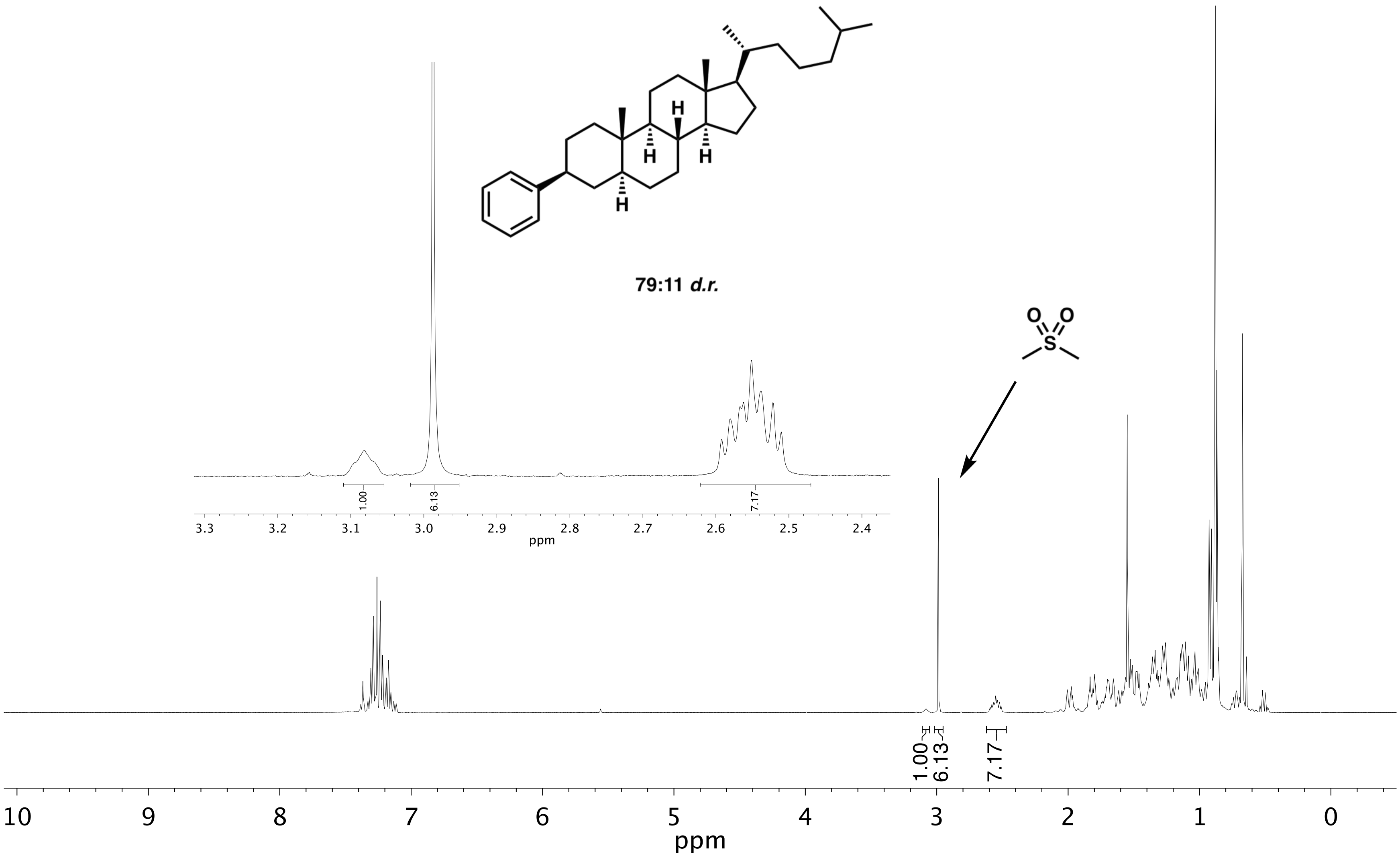
^{1}H NMR (400 MHz, $CDCl_3$) of crude **SI-32** with 5μL of 1,4-dioxane.



^{1}H NMR (400 MHz, $CDCl_3$) of crude **SI-36** with 4.7 mg of dimethylsulfone.

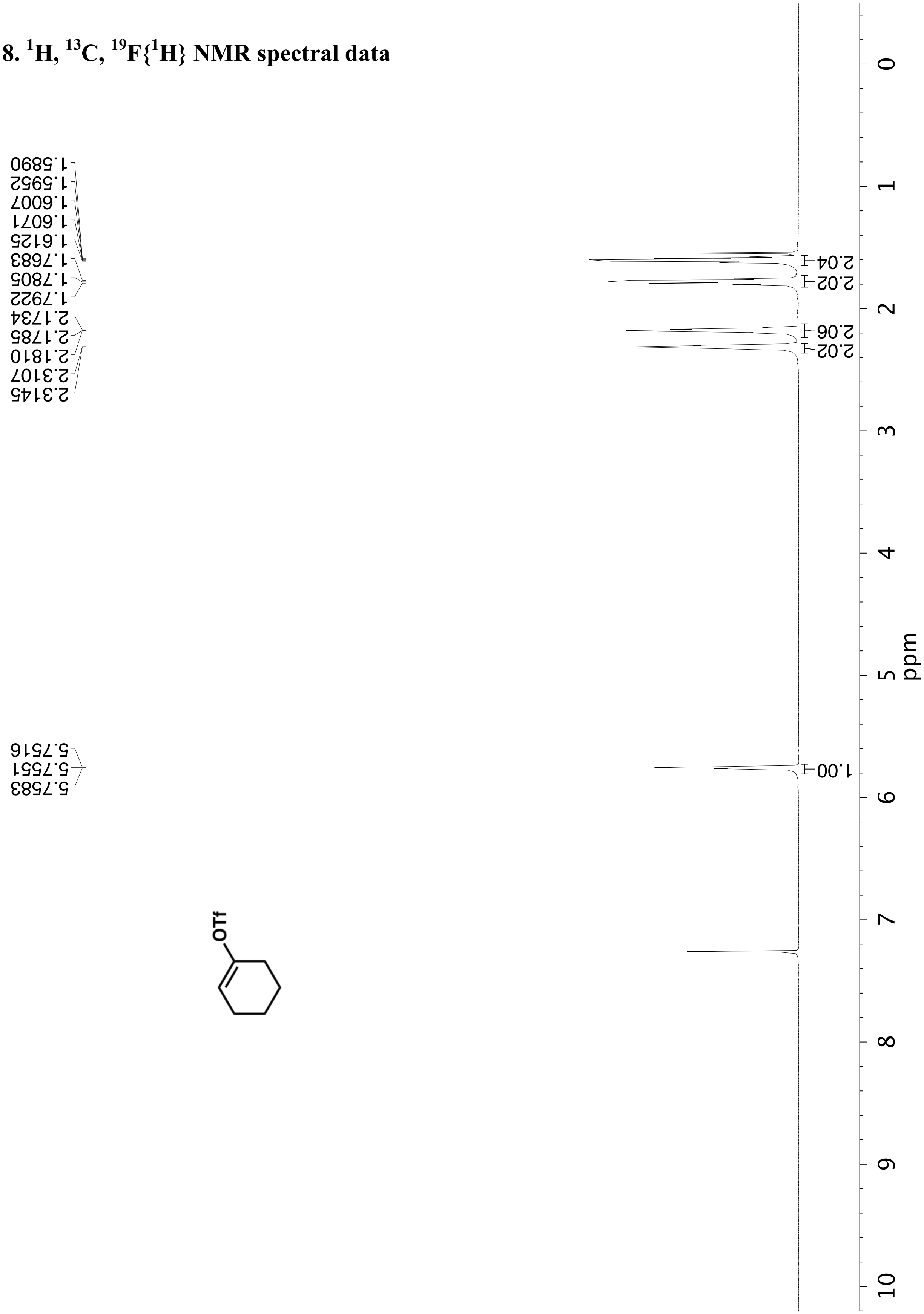


^{1}H NMR (400 MHz, CDCl$_3$) of crude **SI-40** with 0.67 mg of dimethylsulfone.

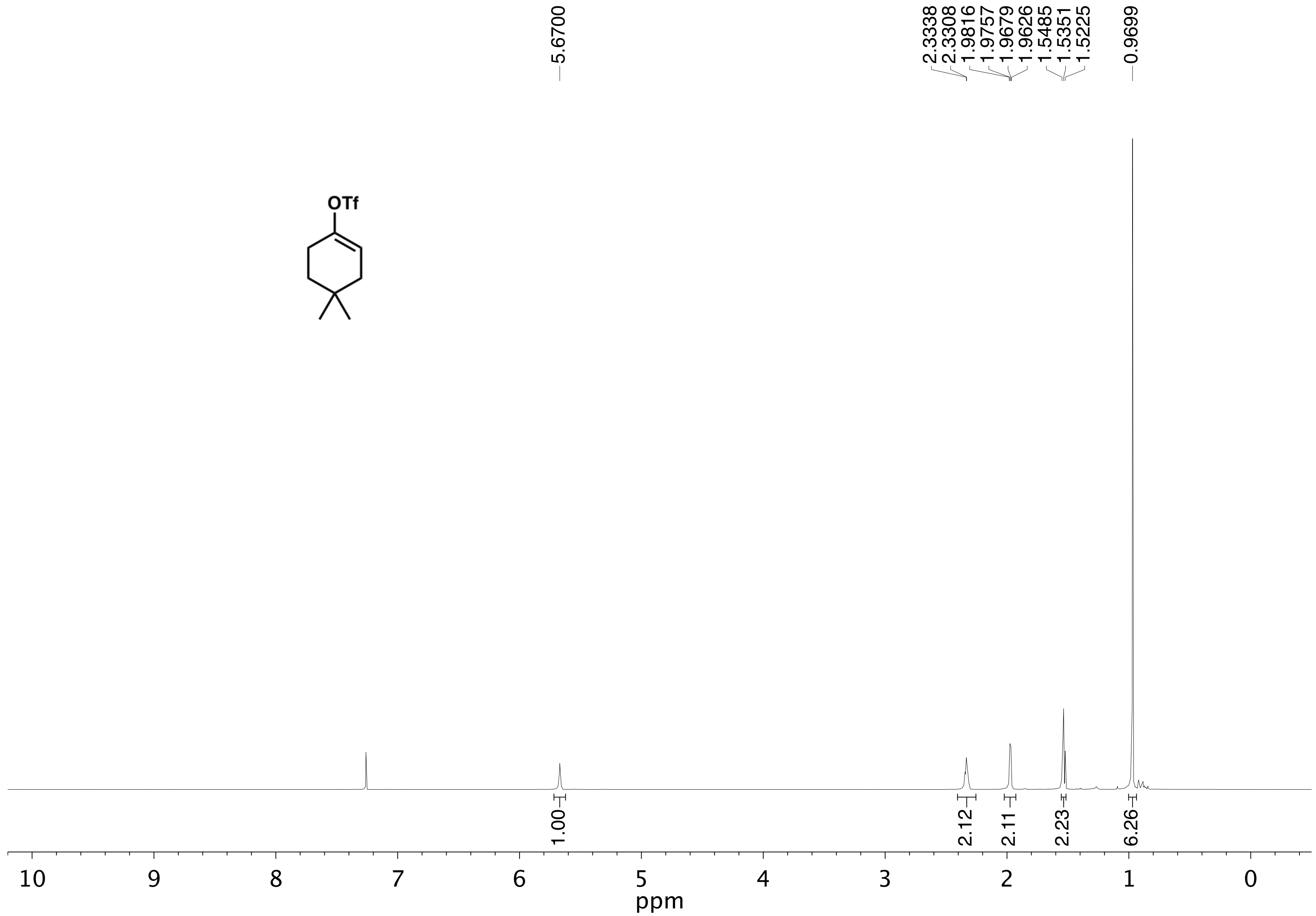


^{1}H NMR (400 MHz, $CDCl_3$) of crude **SI-33** with 0.53 mg of dimethylsulfone.

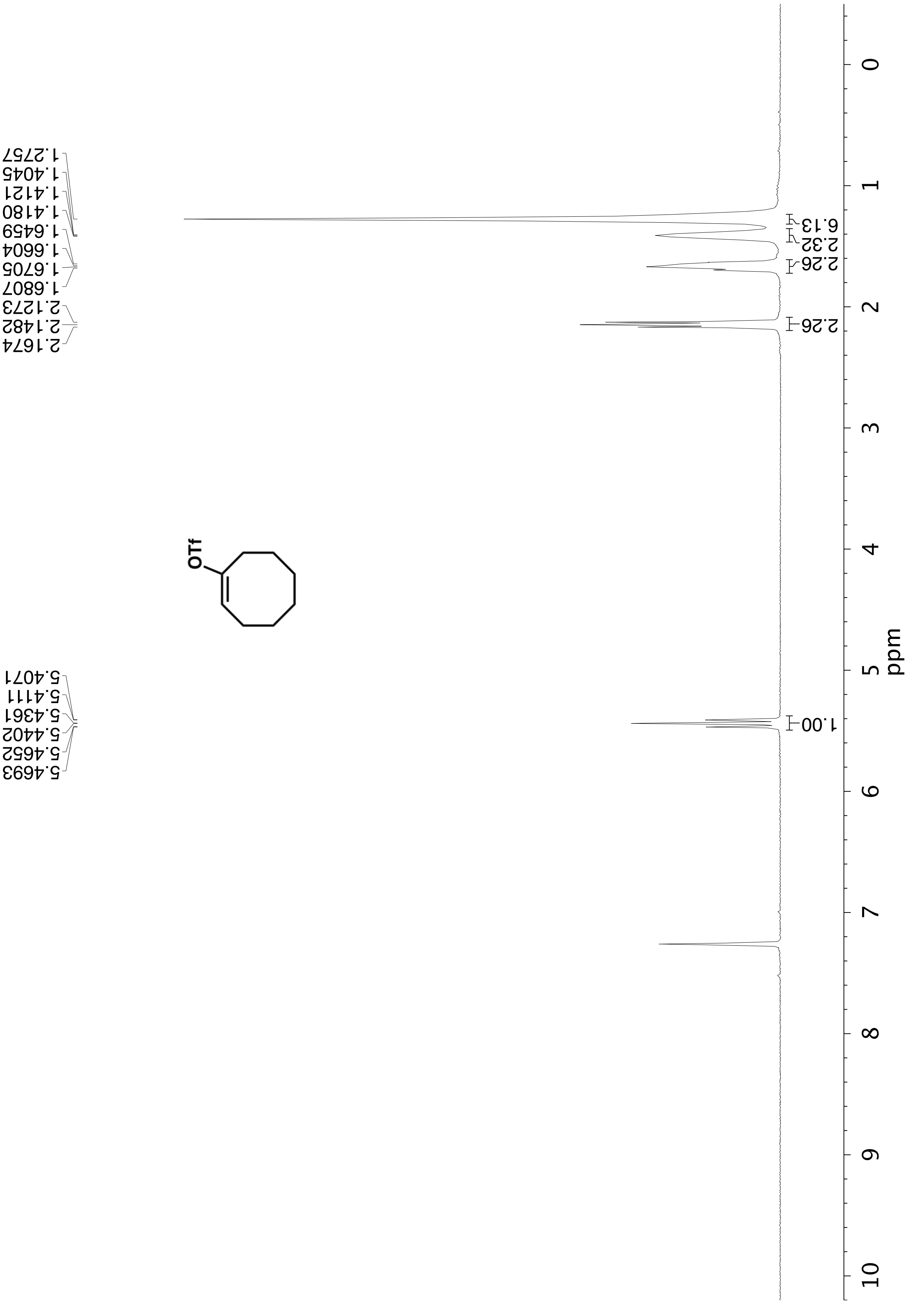
8. ^{1}H, ^{13}C, $^{19}F\{^{1}H\}$ NMR spectral data



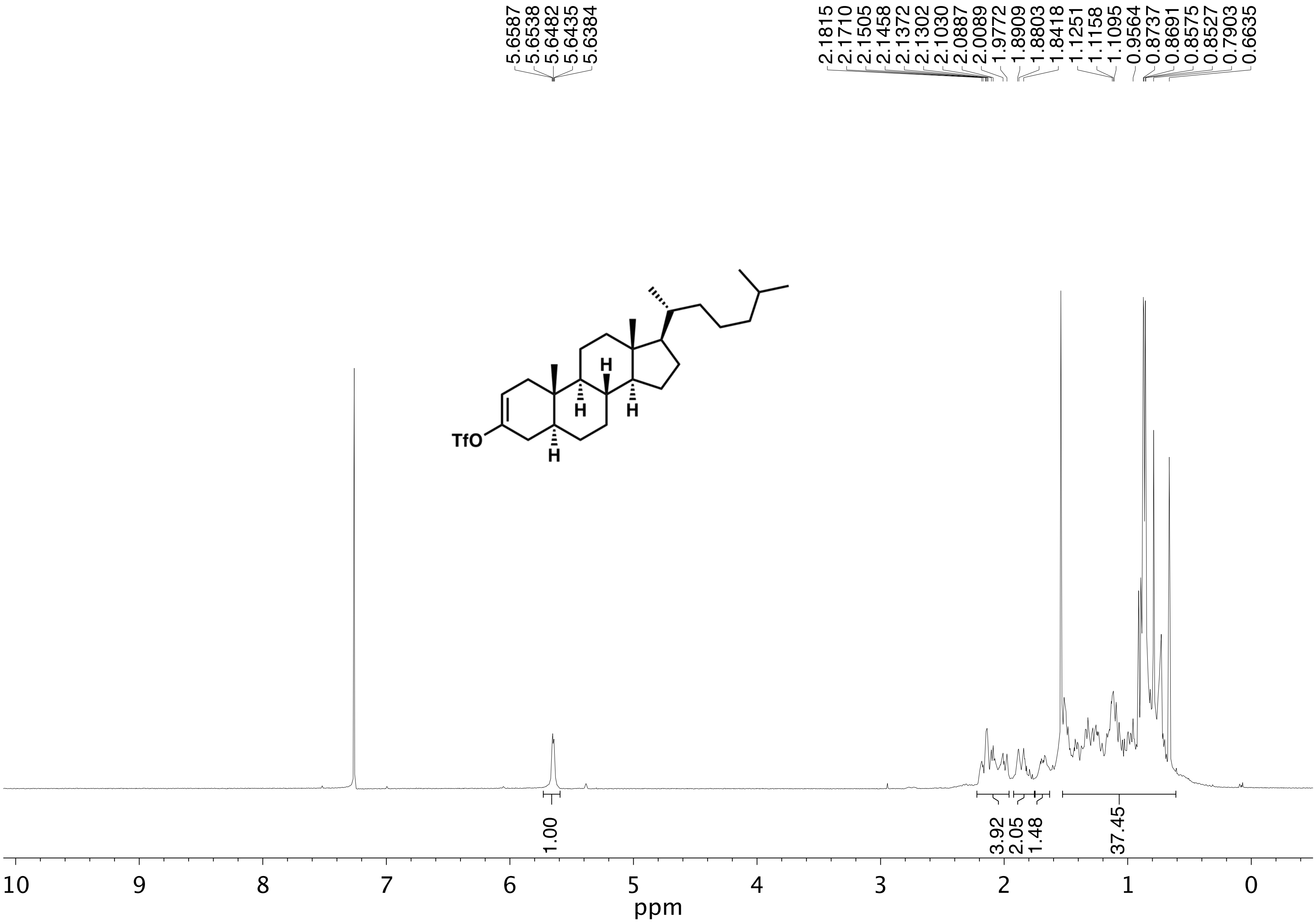
^{1}H NMR (400 MHz, $CDCl_3$) of **SI-1**.



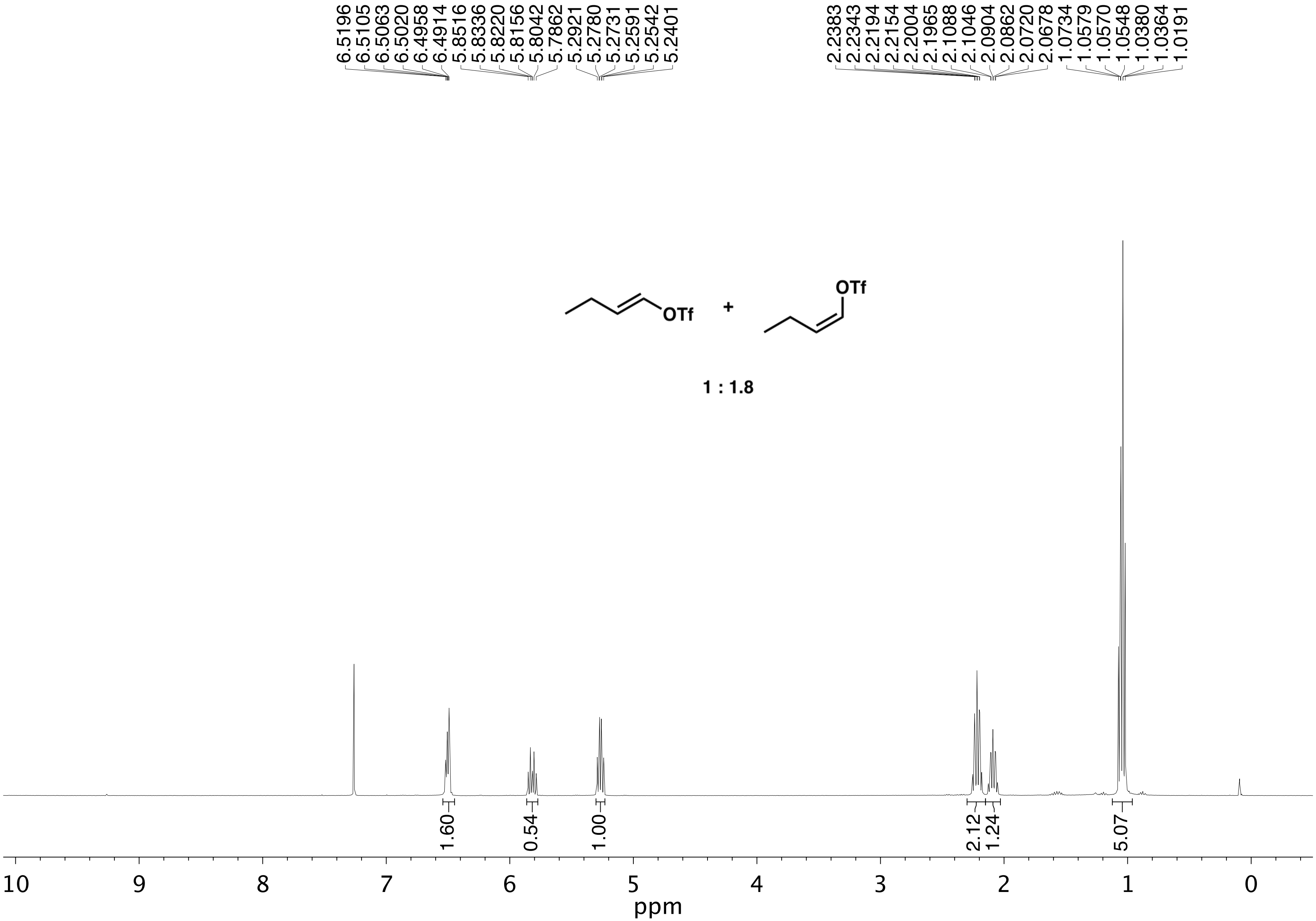
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-2**.



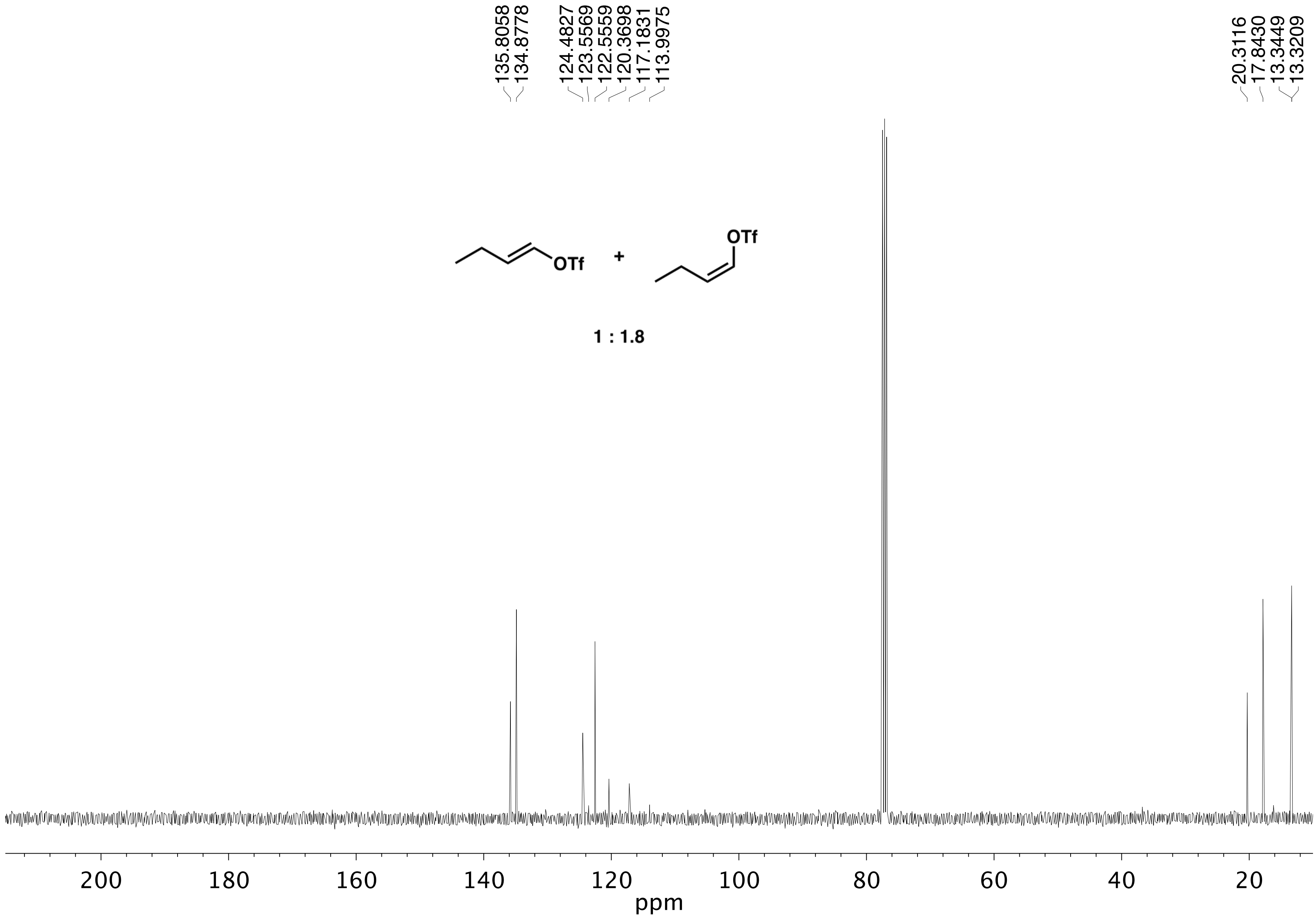
^{1}H NMR (400 MHz, $CDCl_3$) of **SI-3**.



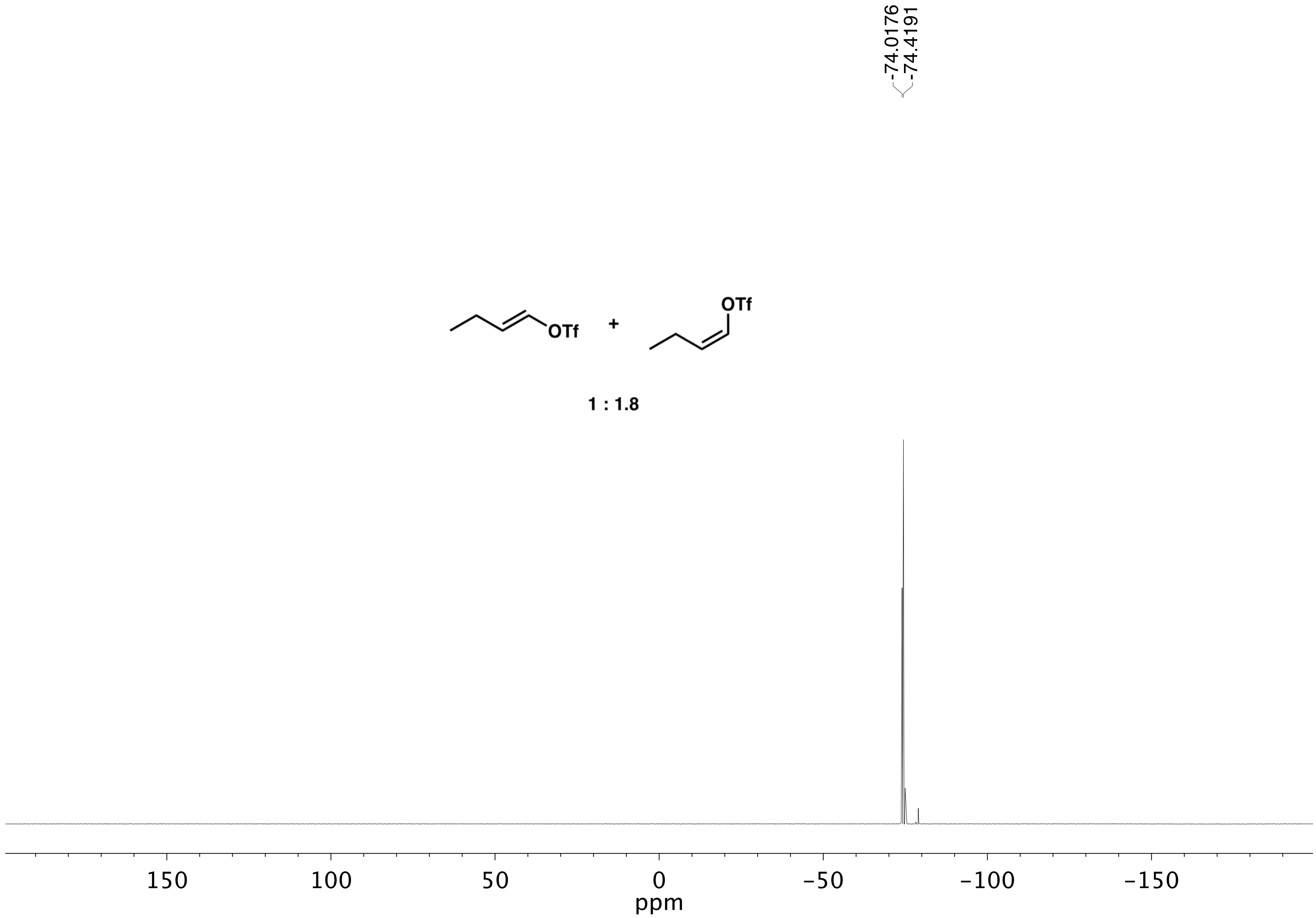
^{1}H NMR (500 MHz, $CDCl_3$) of **SI-4**.



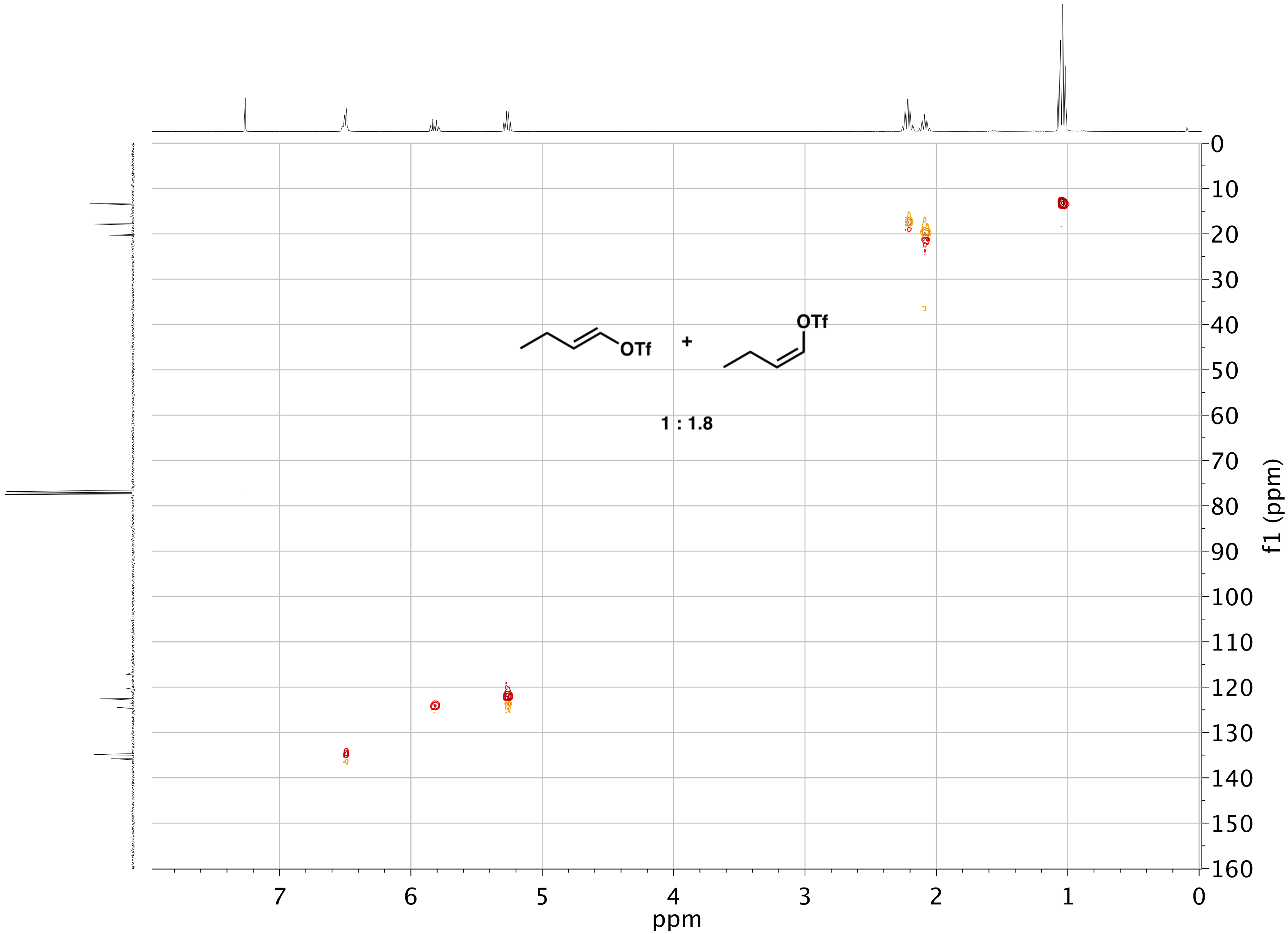
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-5**.



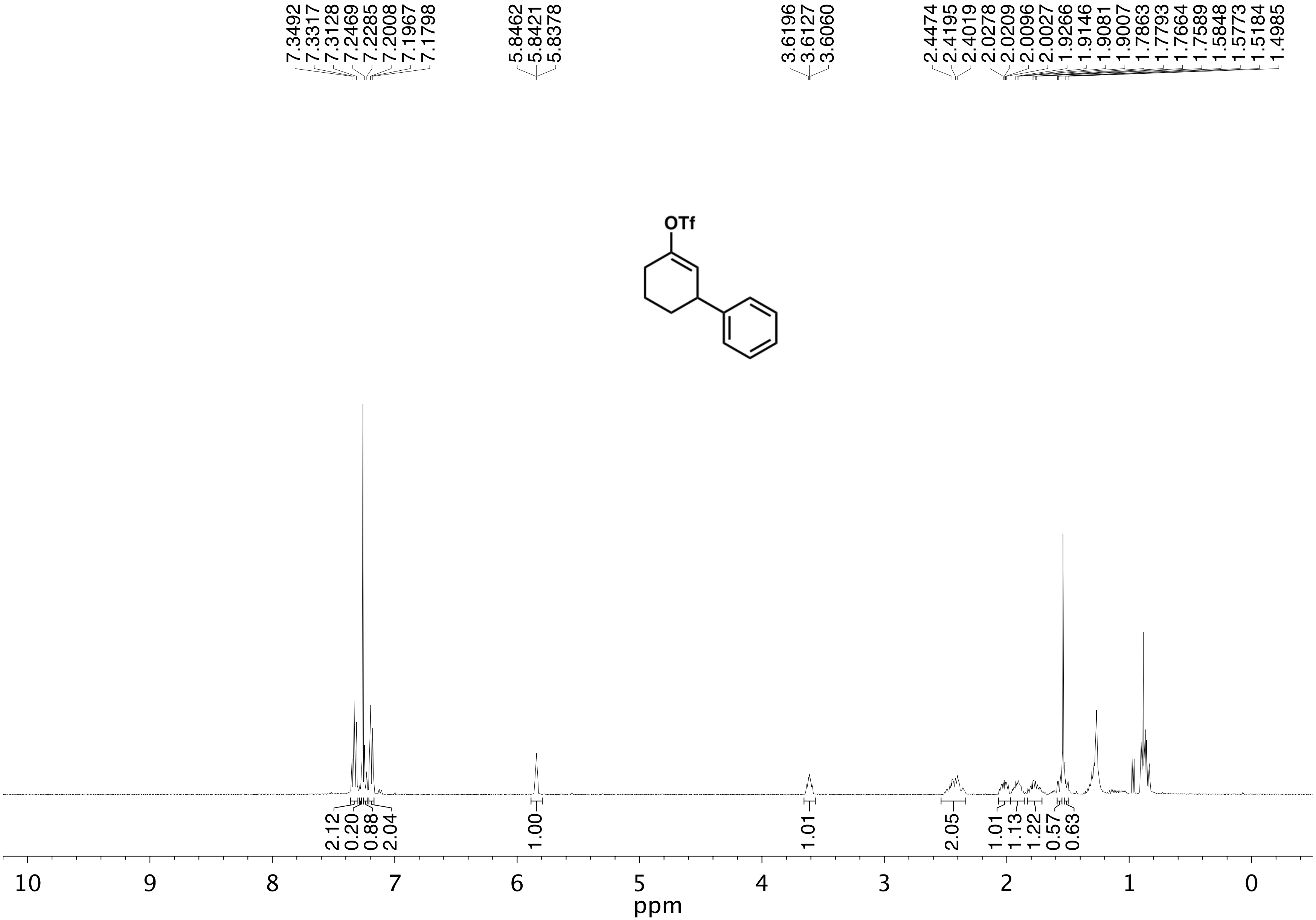
^{13}C NMR (100 MHz, CDCl$_3$) of **SI-5**.



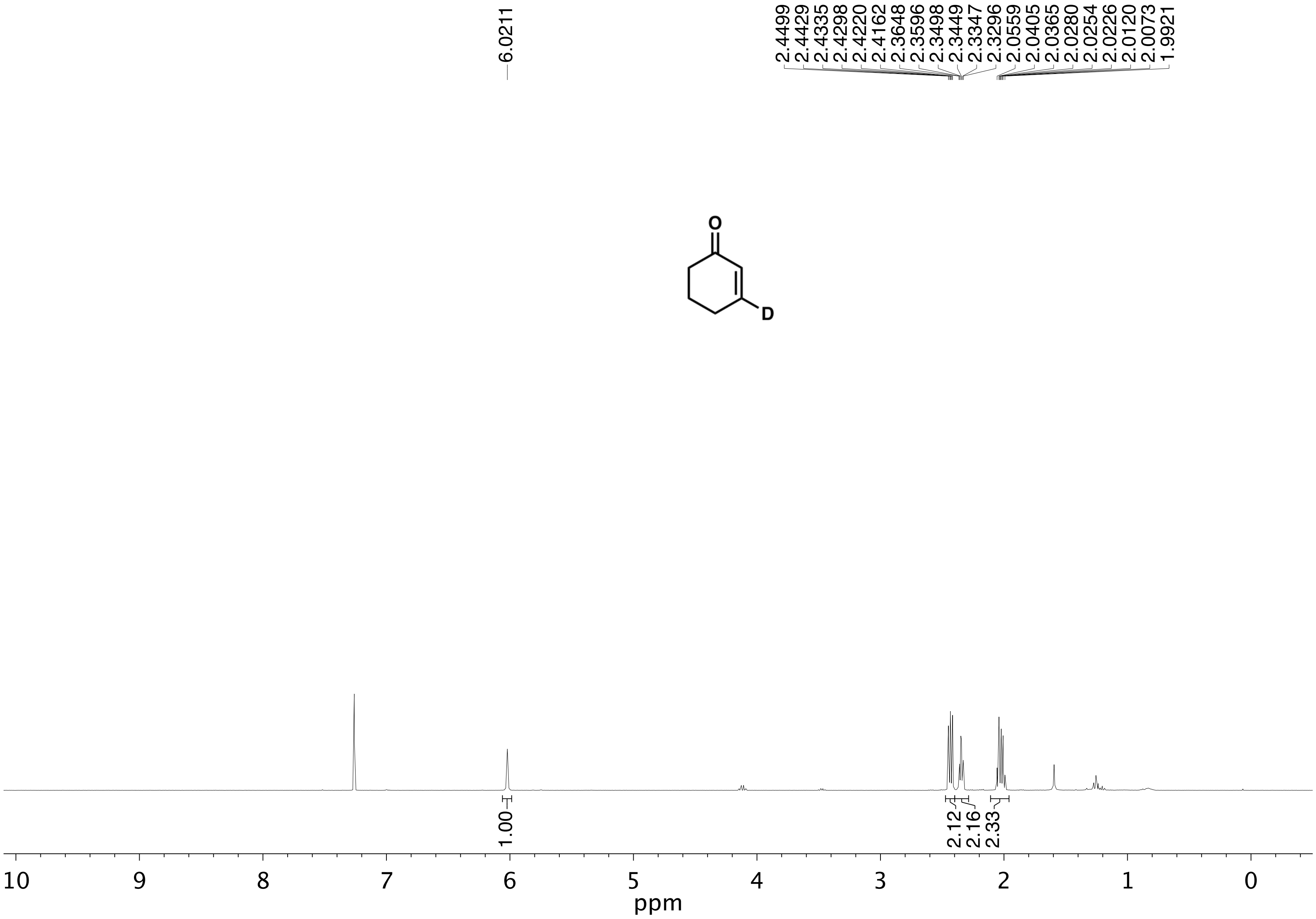
^{19}F NMR (376 MHz, CDCl$_3$) of **SI-5**.



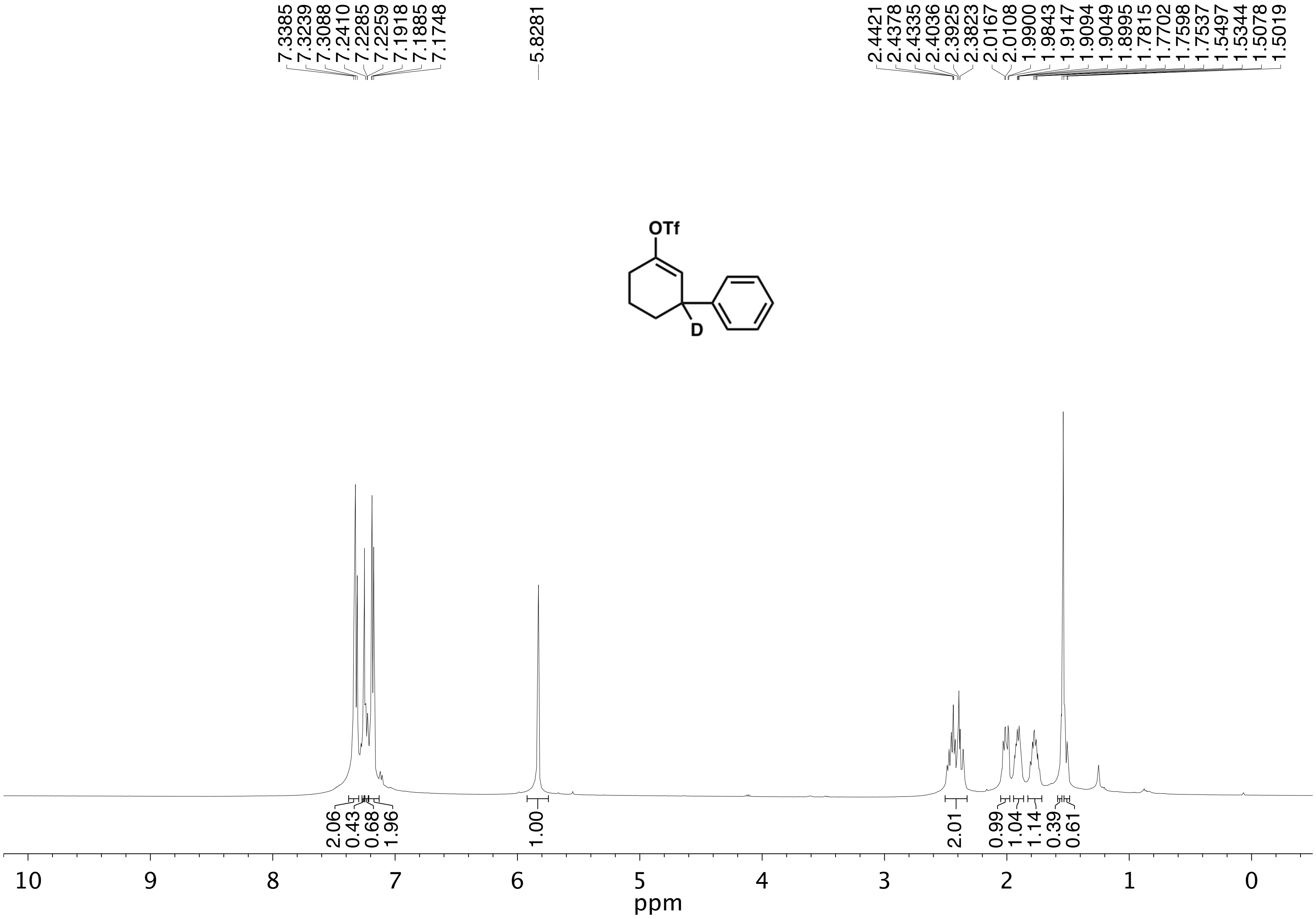
2D HSQC NMR (500 MHz, $CDCl_3$) of **SI-5**.



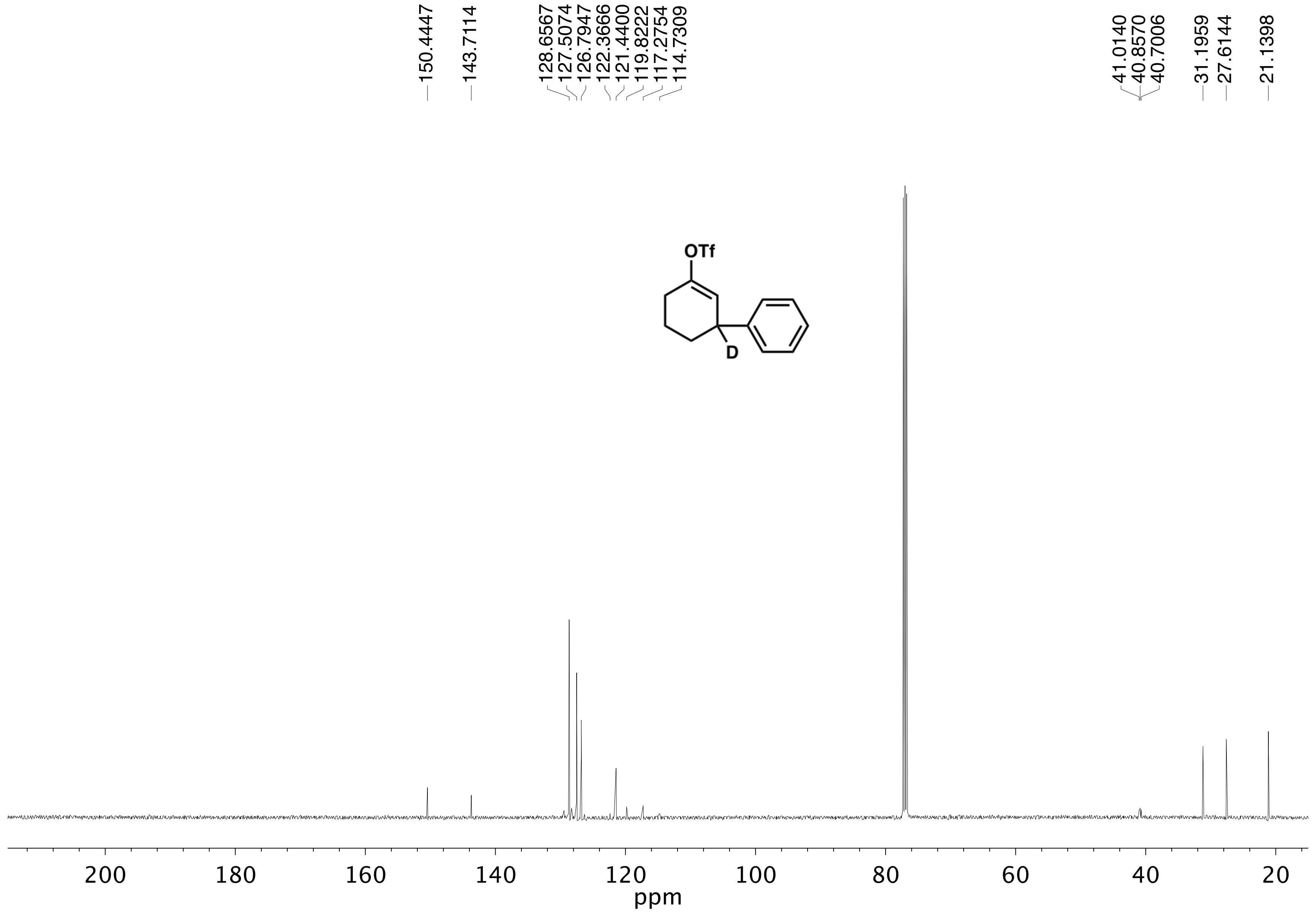
^{1}H NMR (400 MHz, $CDCl_3$) of **SI-6**.



^{1}H NMR (300 MHz, CDCl$_3$) of **SI-7**.

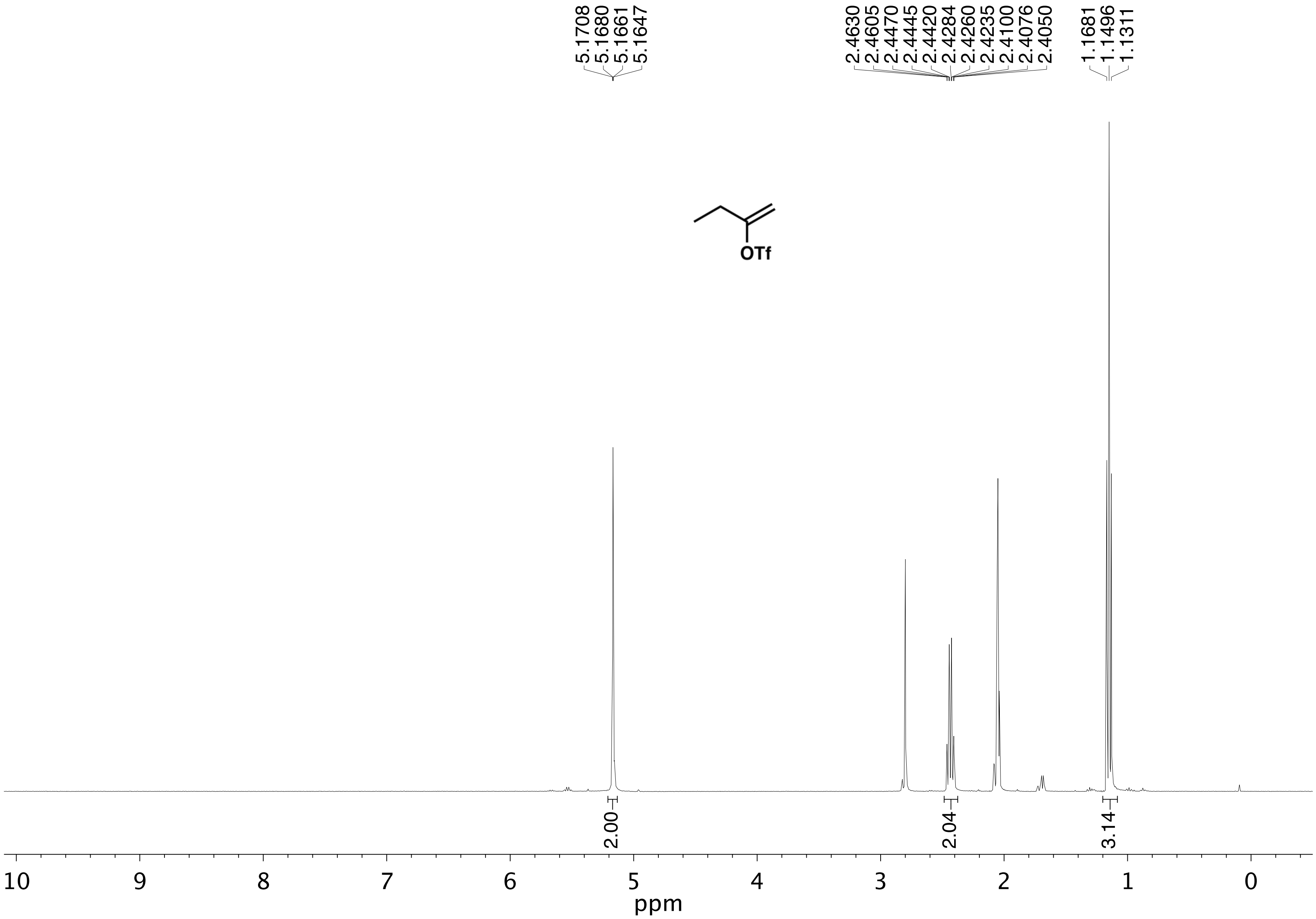


^{1}H NMR (400 MHz, $CDCl_3$) of **SI-8**.

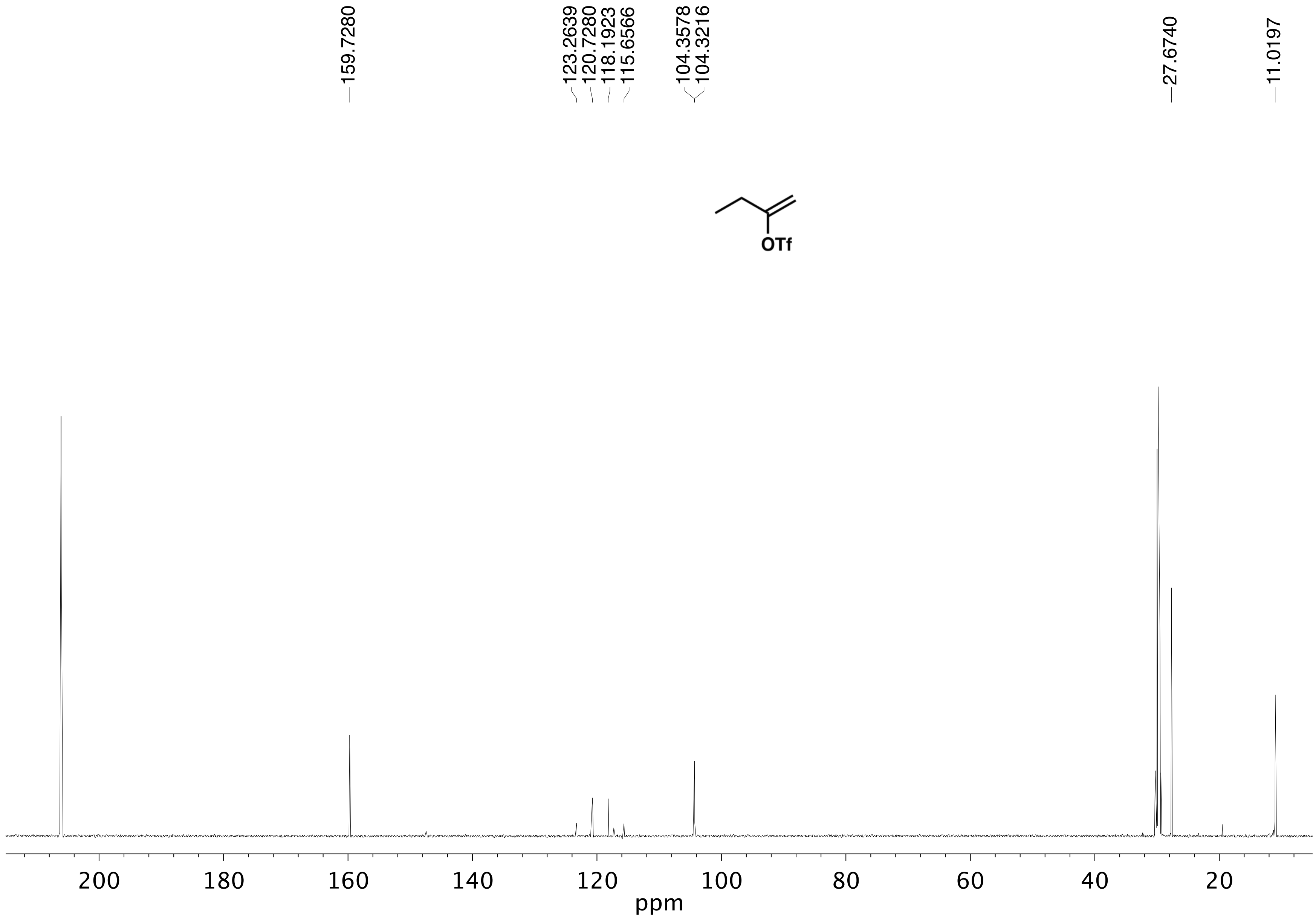


^{13}C NMR (125 MHz, CDCl$_3$) of **SI-8**.

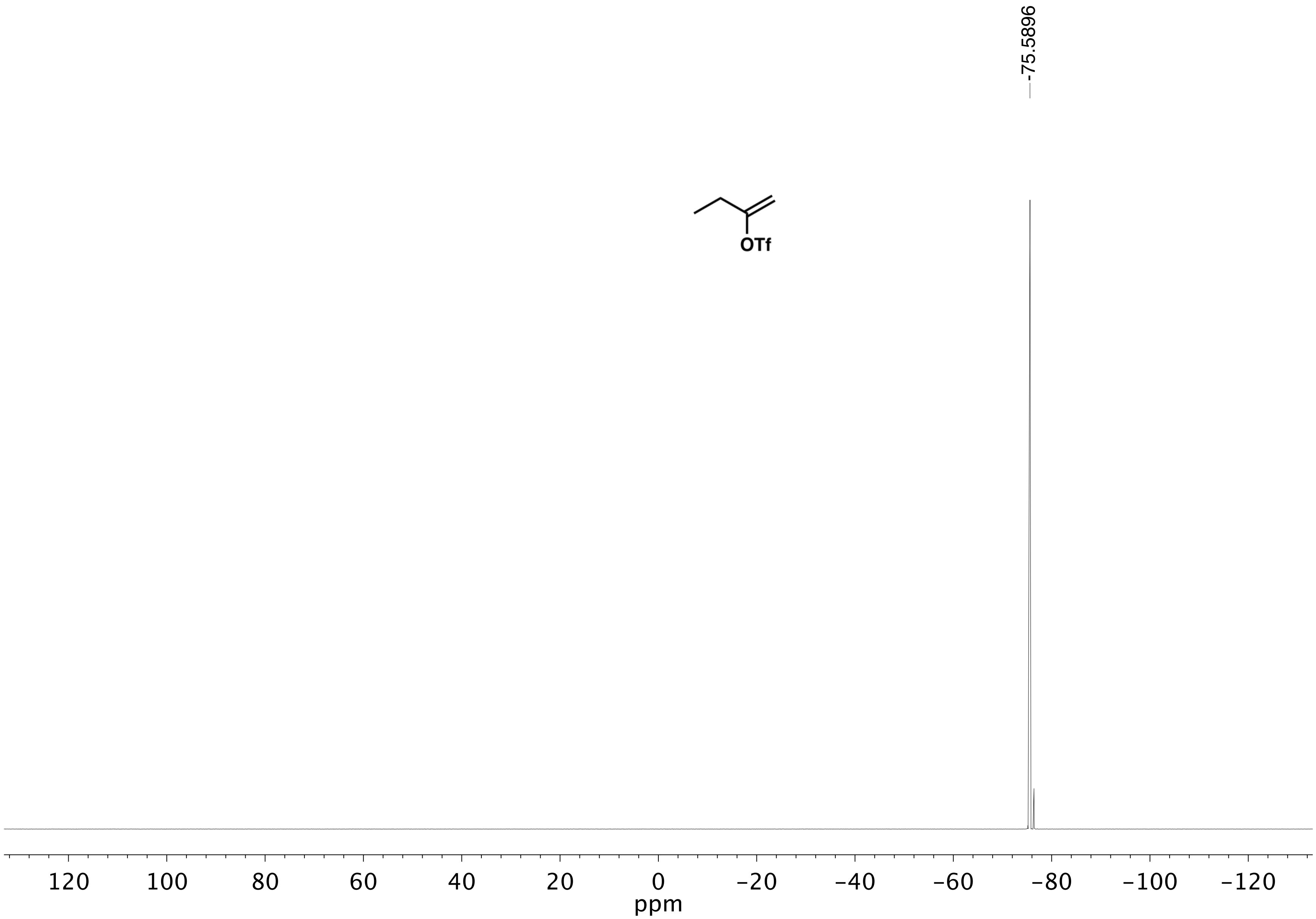
^{19}F NMR (376 MHz, CDCl$_3$) of **SI-8**.



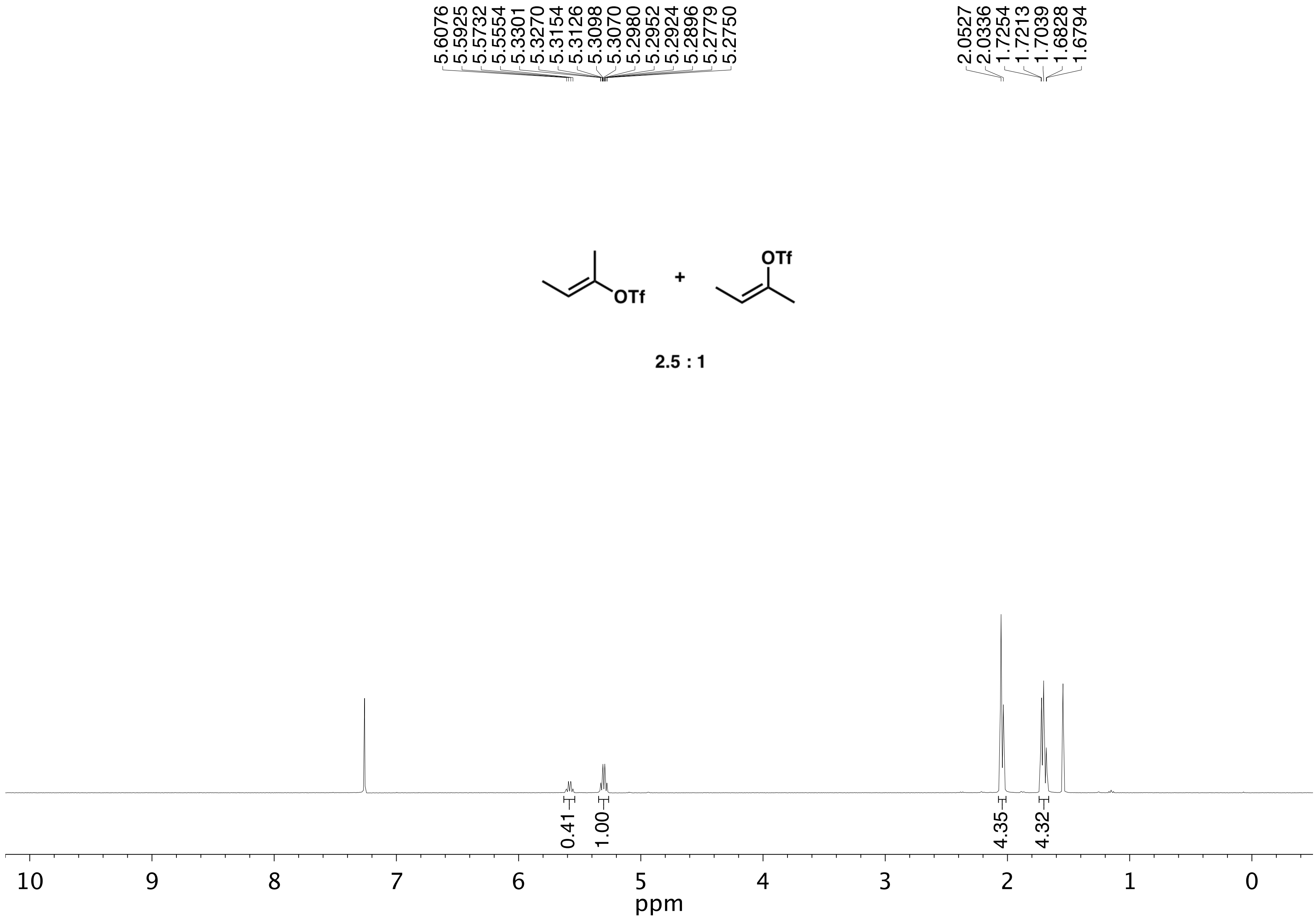
^{1}H NMR (400 MHz, $(CD_3)_2CO$) of **SI-9**.



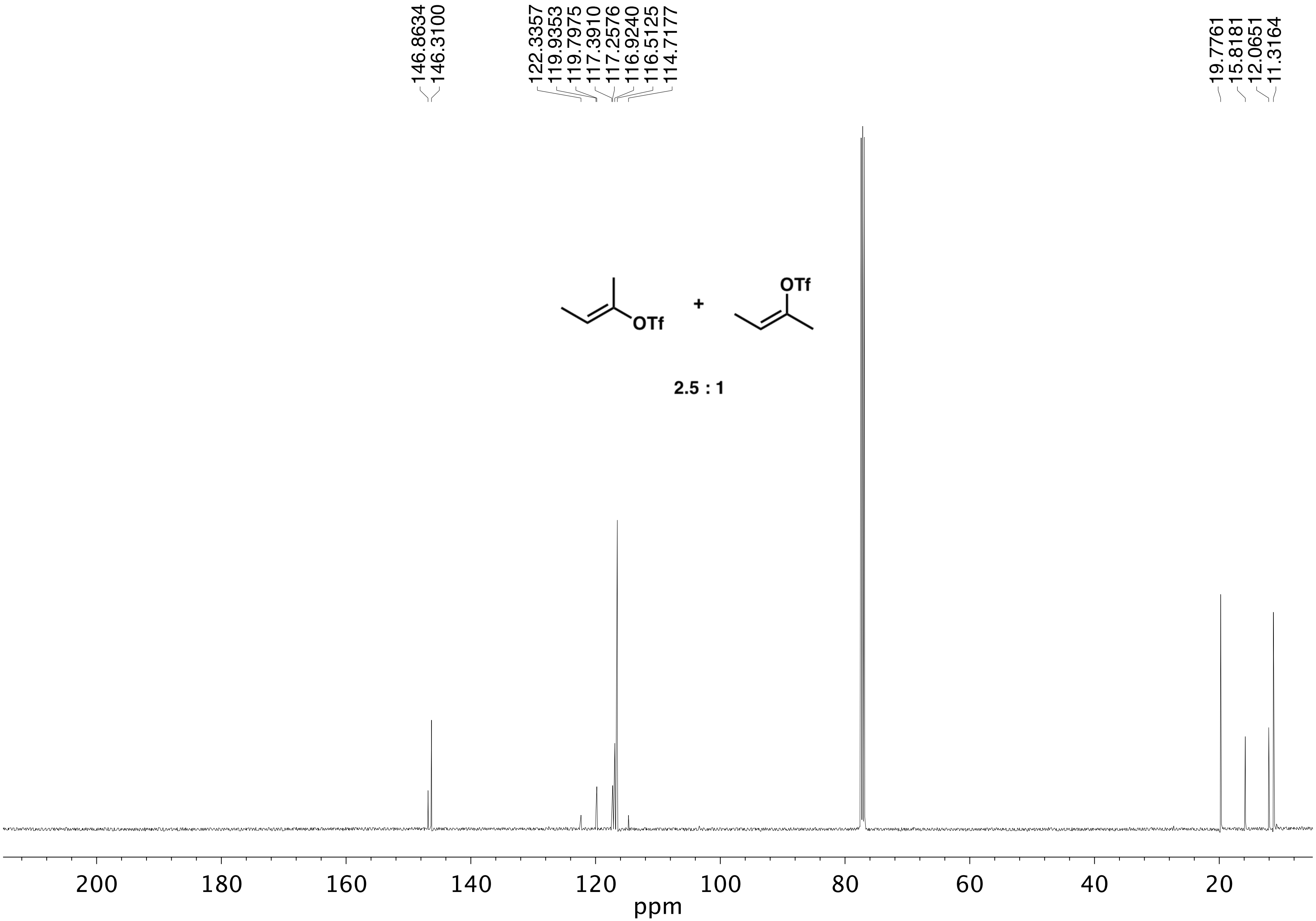
^{13}C NMR (125 MHz, $(CD_3)_2CO$) of **SI-9**.



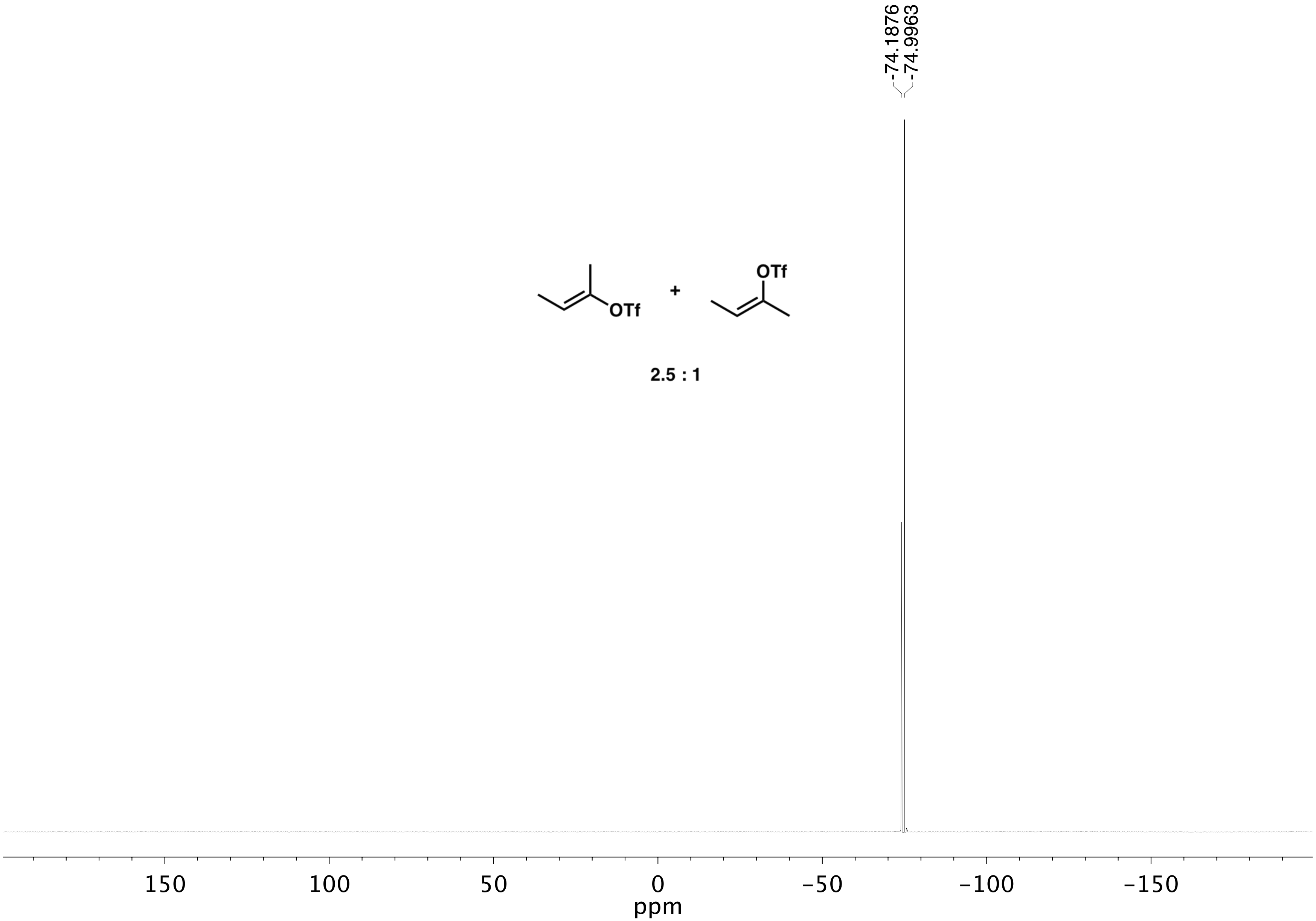
^{19}F NMR (282 MHz, $(CD_3)_2CO$) of **SI-9**.



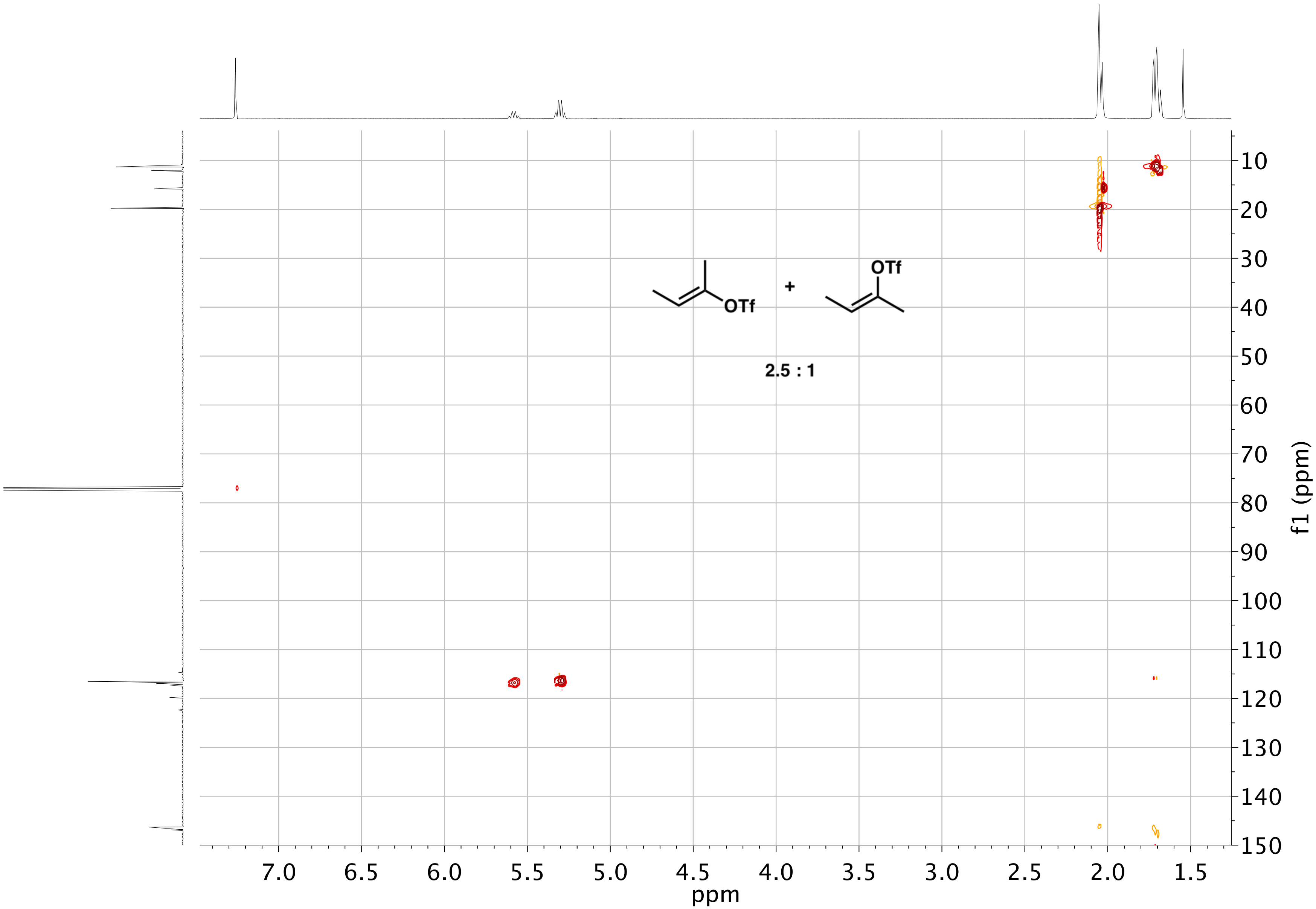
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-10**.



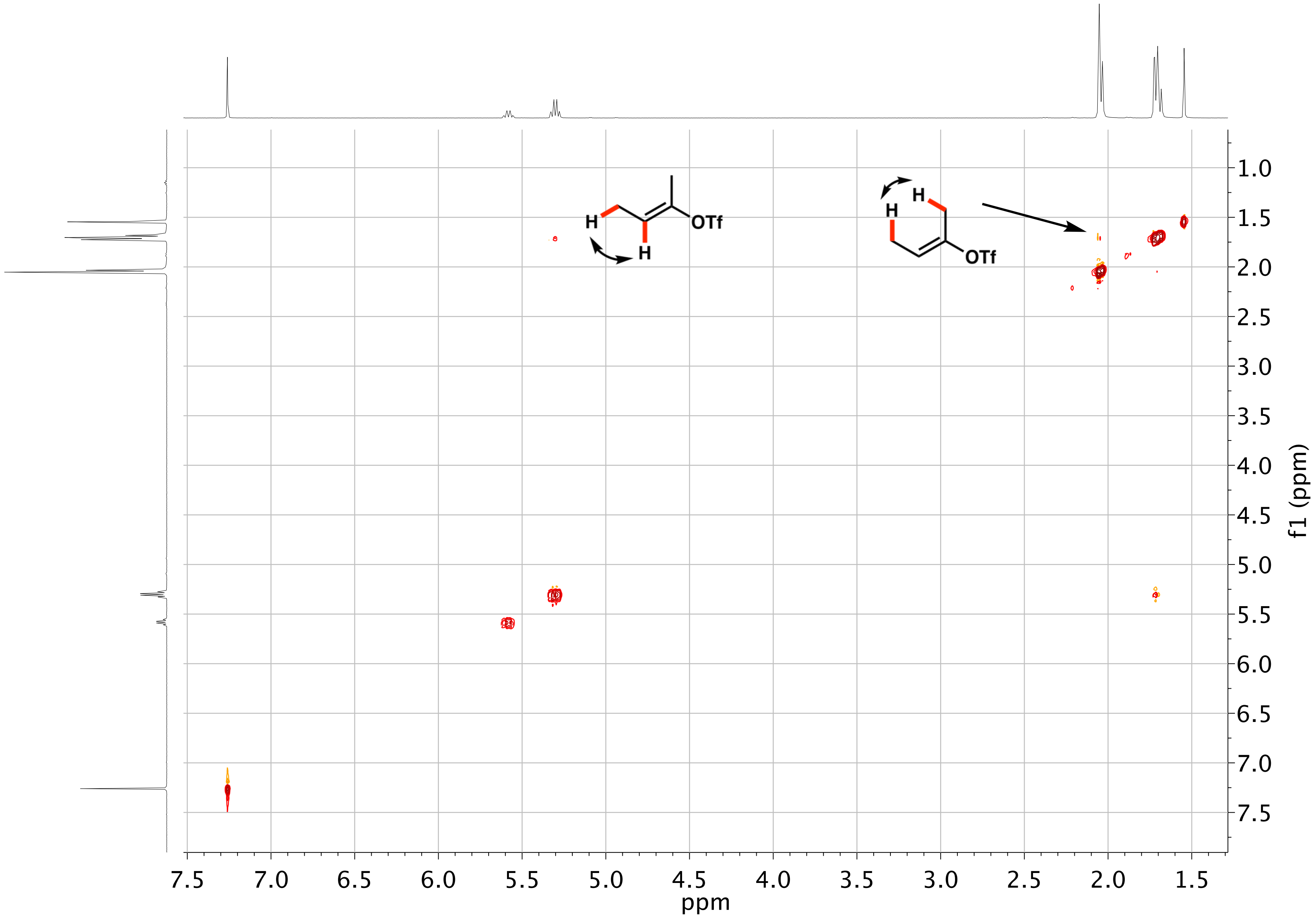
^{13}C NMR (125 MHz, $CDCl_3$) of **SI-10**.



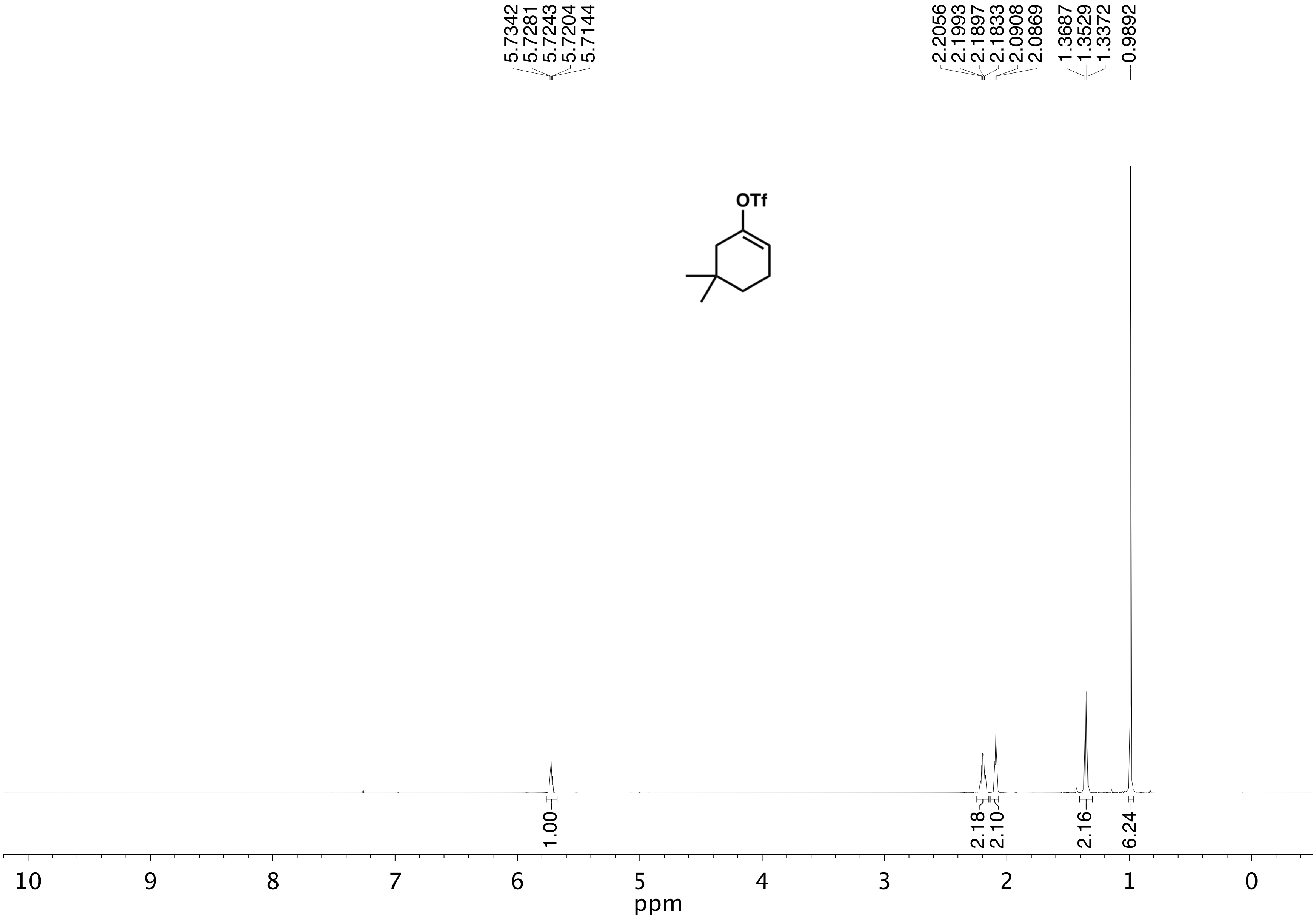
^{19}F NMR (376 MHz, CDCl$_3$) of **SI-10**.



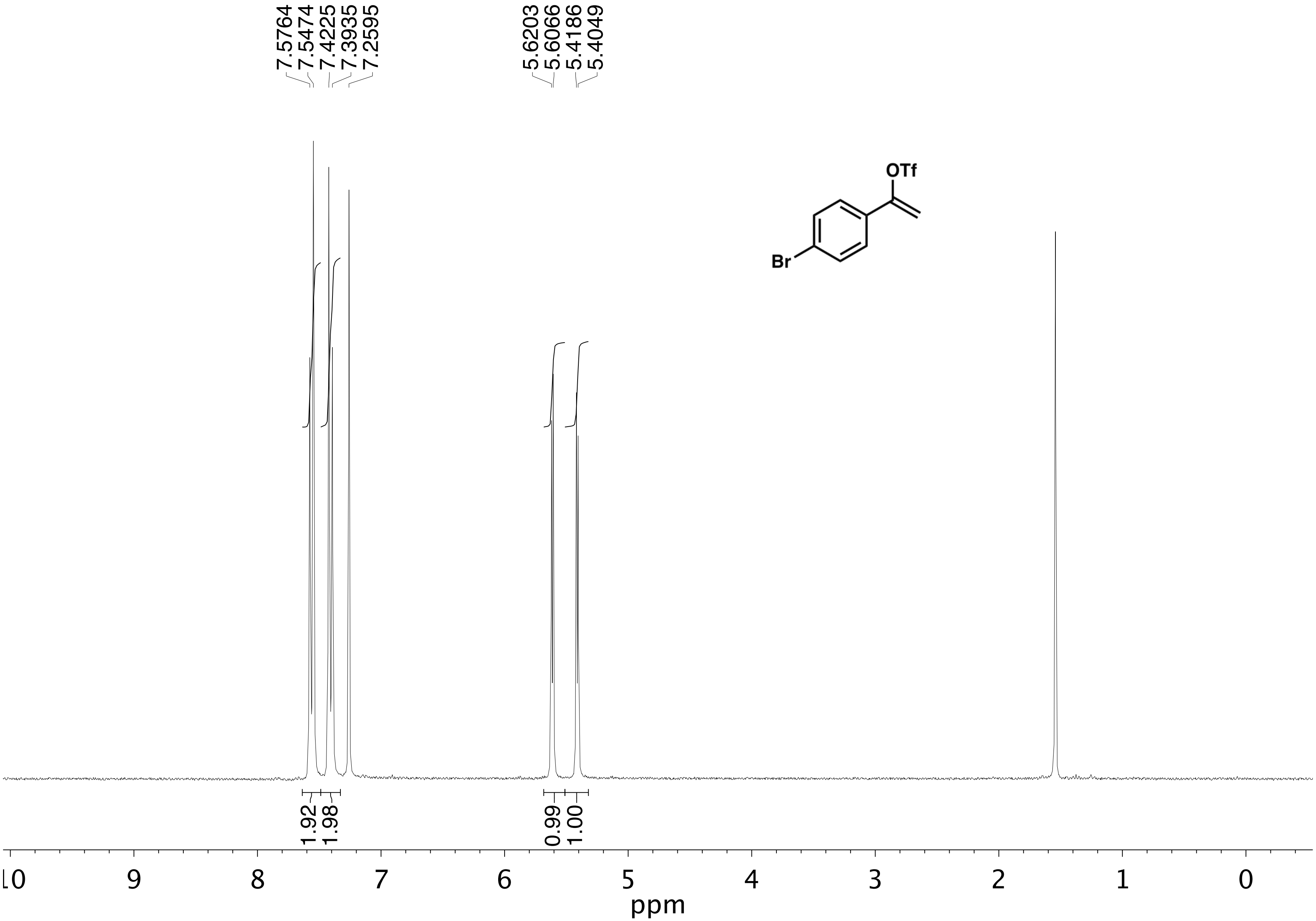
2D HSQC NMR (400 MHz, $CDCl_3$) of **SI-10**.



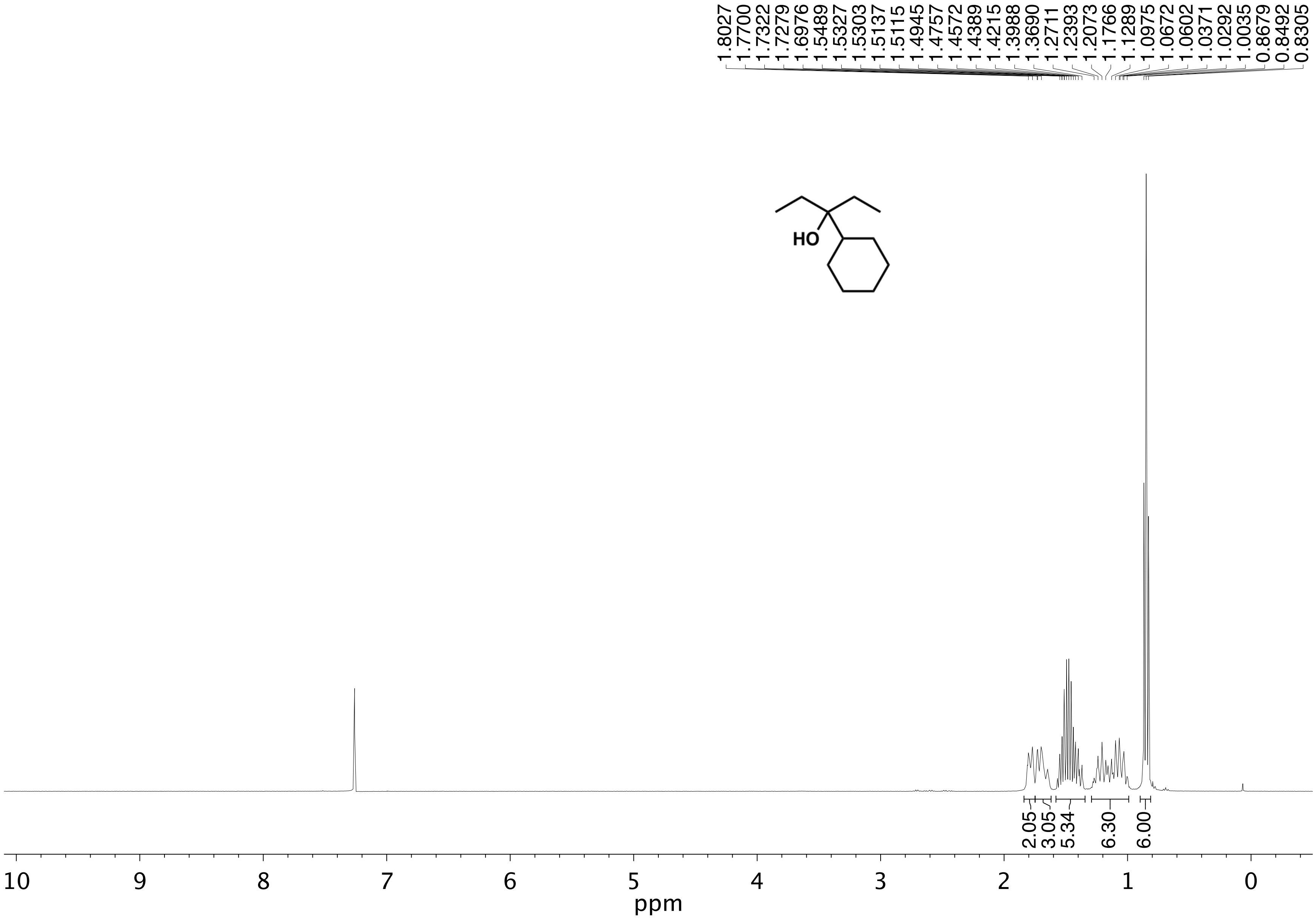
^{1}H NOESY NMR (500 MHz, CDCl$_3$) of **SI-10**.



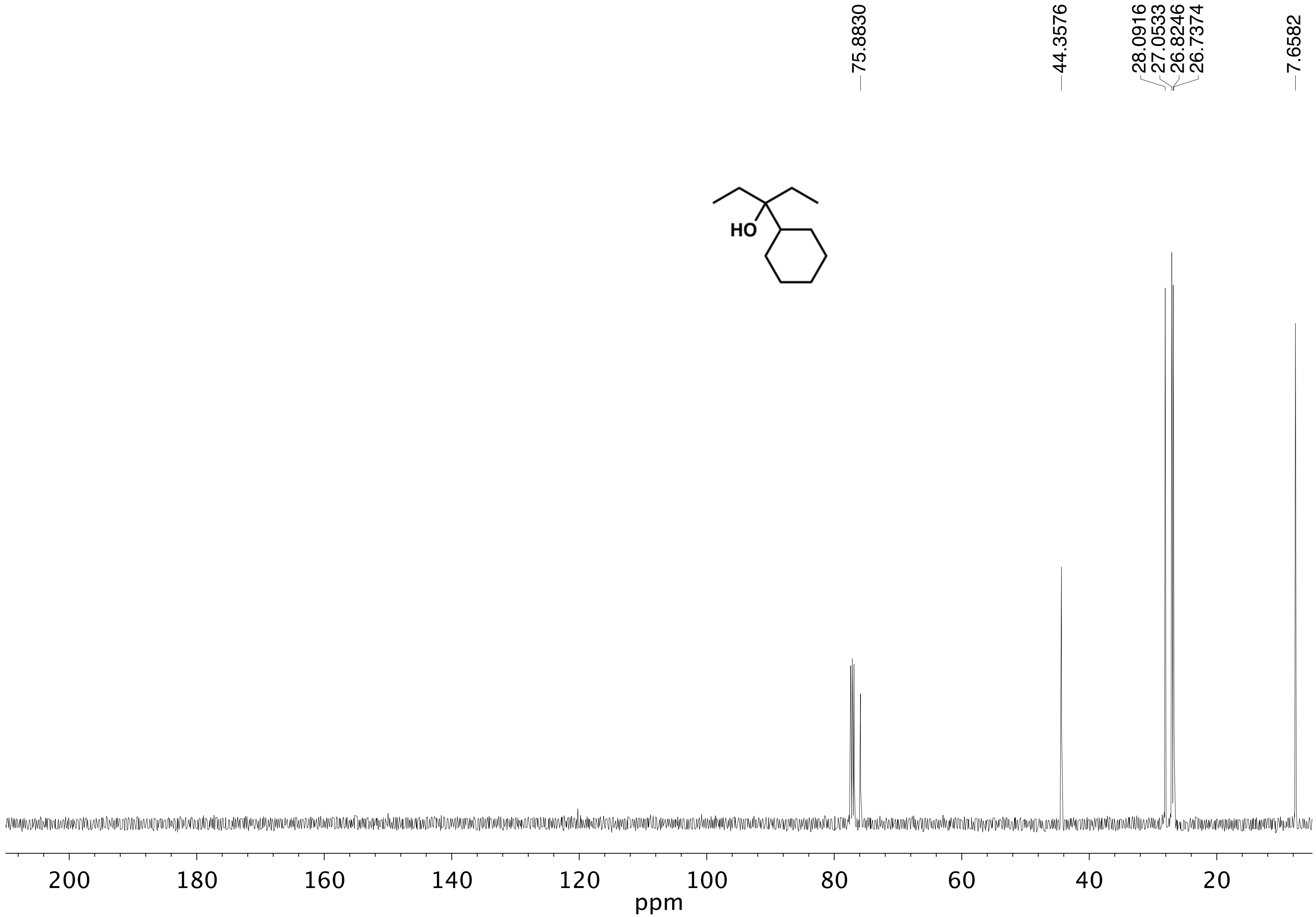
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-11**.



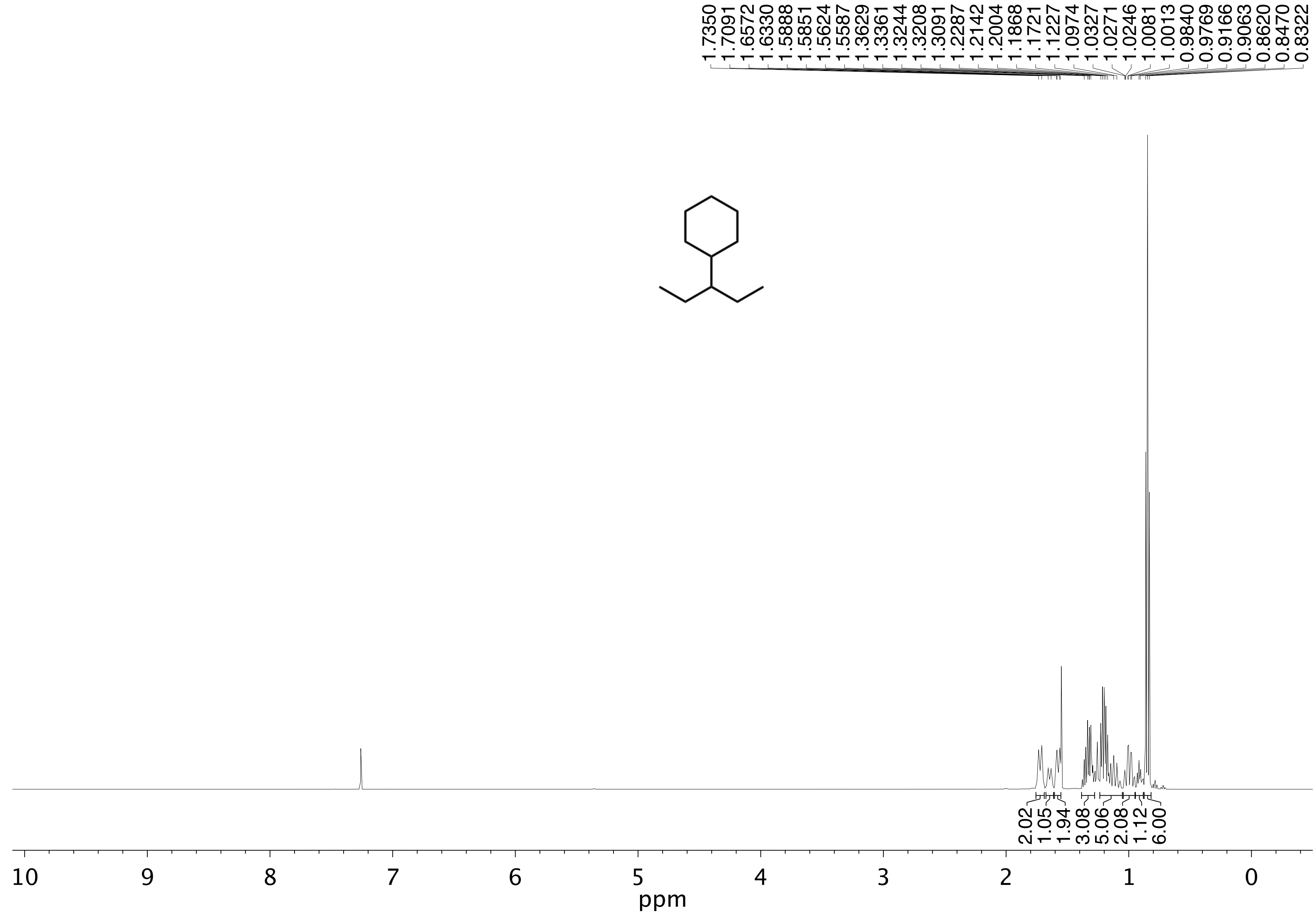
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI-12**.



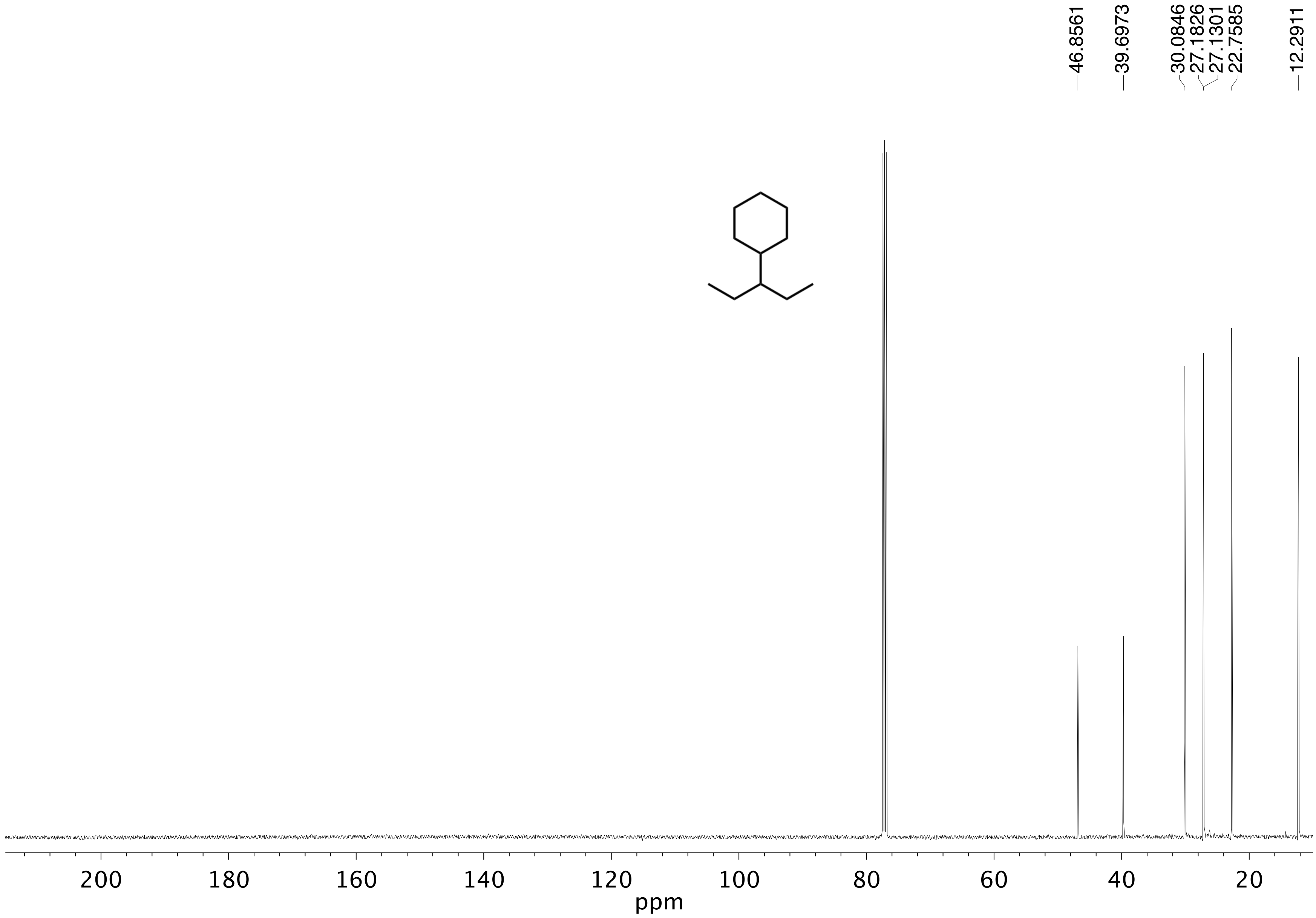
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-13**.



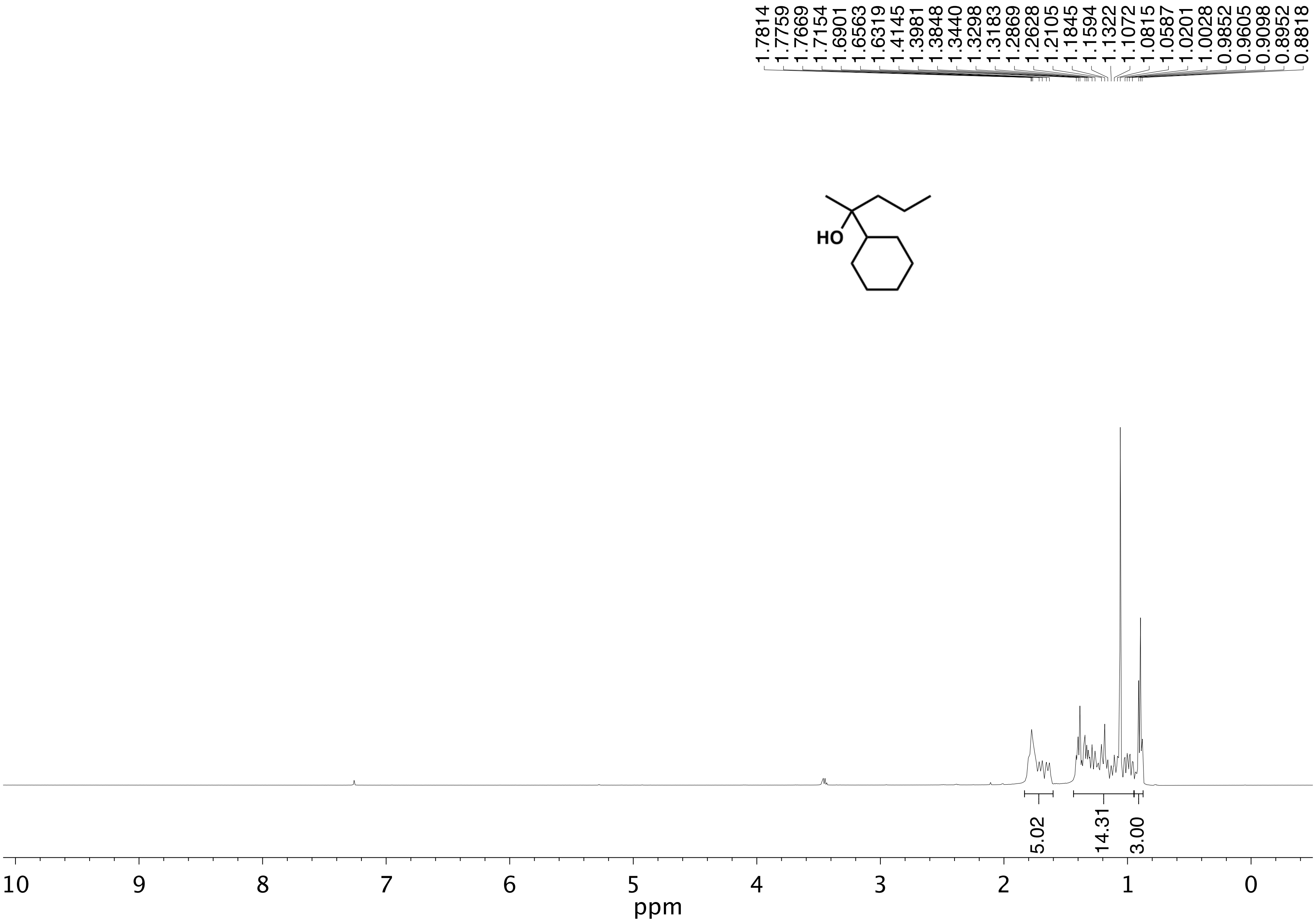
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-13**.



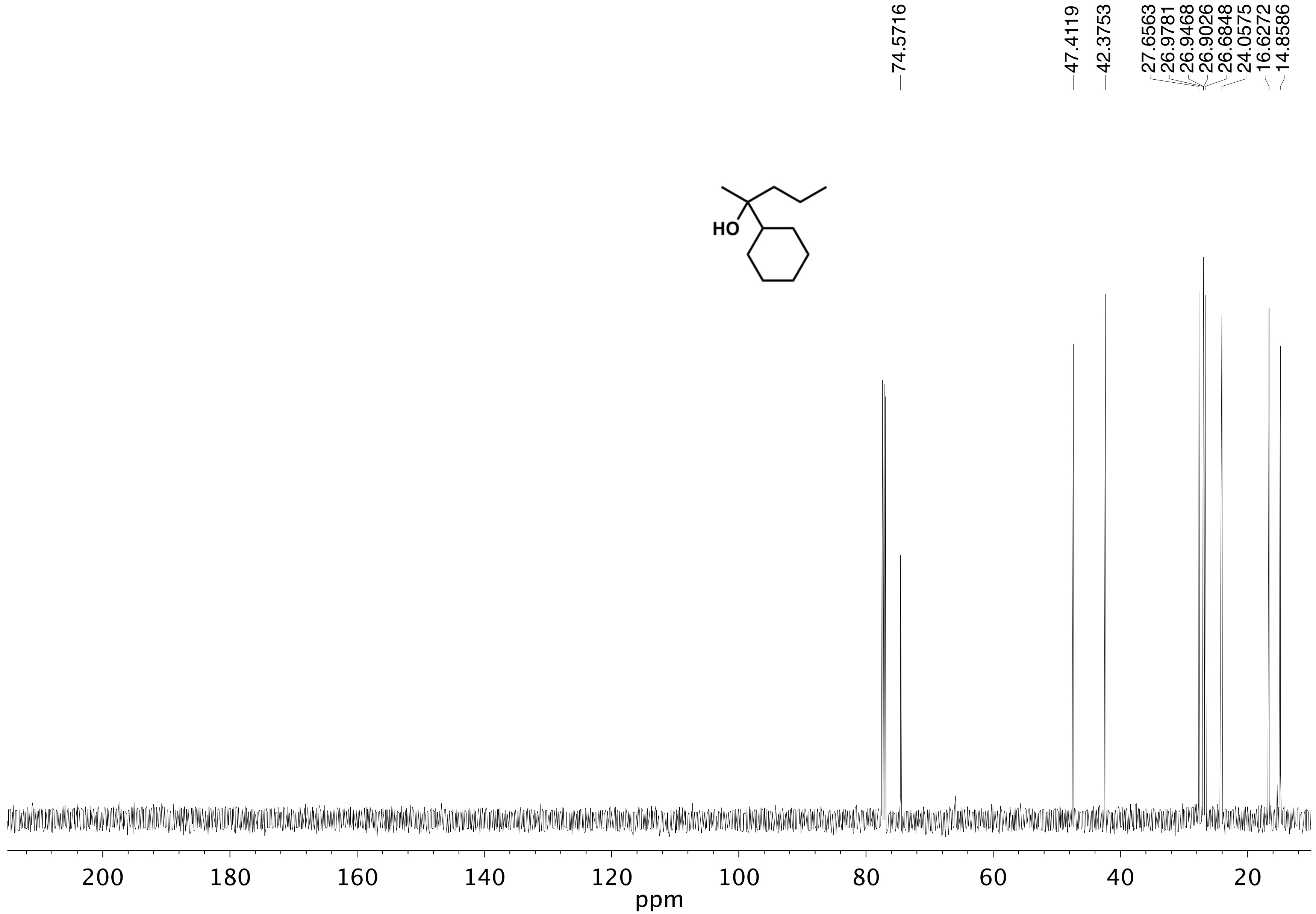
^{1}H NMR (500 MHz, CDCl$_3$) of **SI-14**.



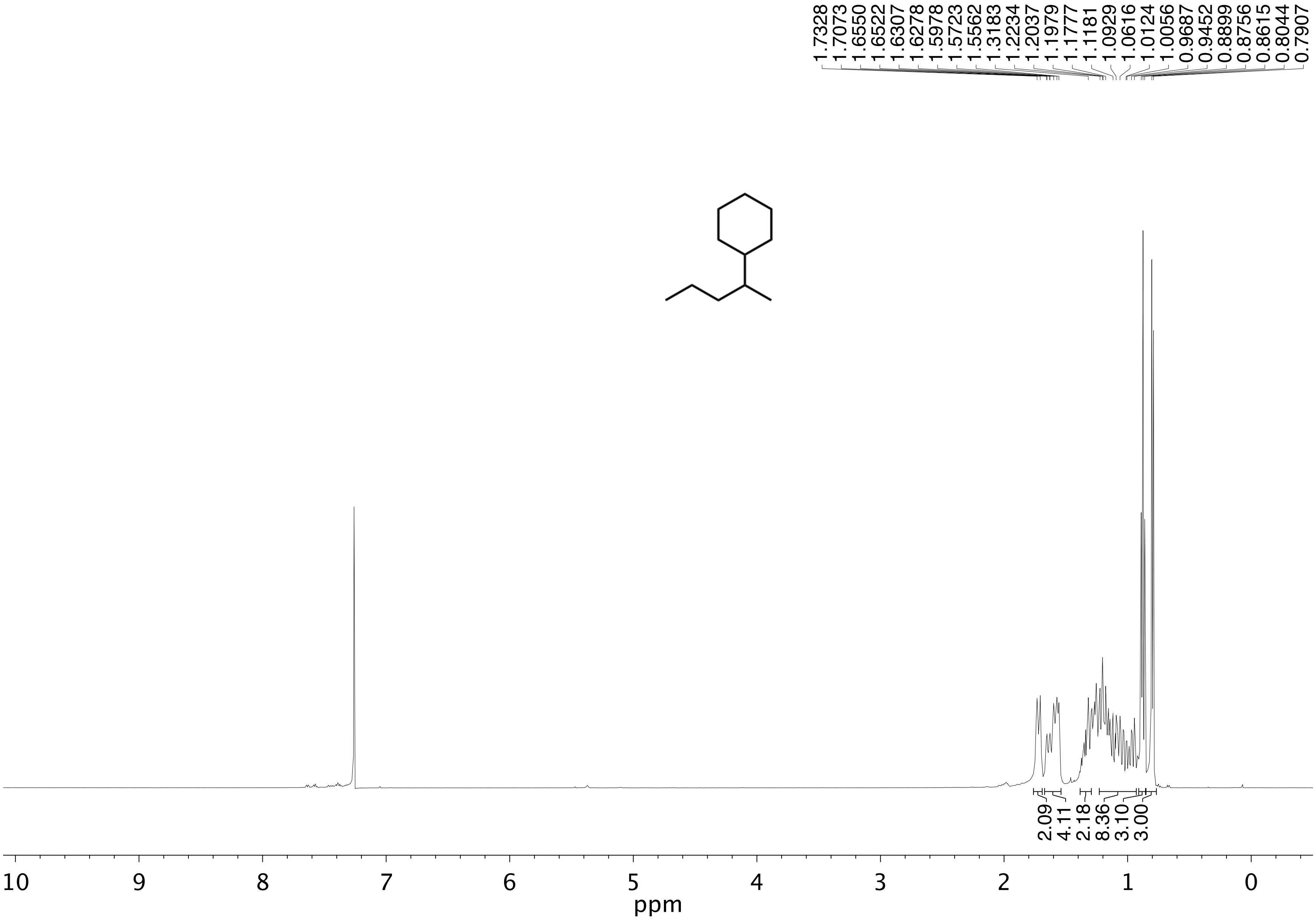
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-14**.



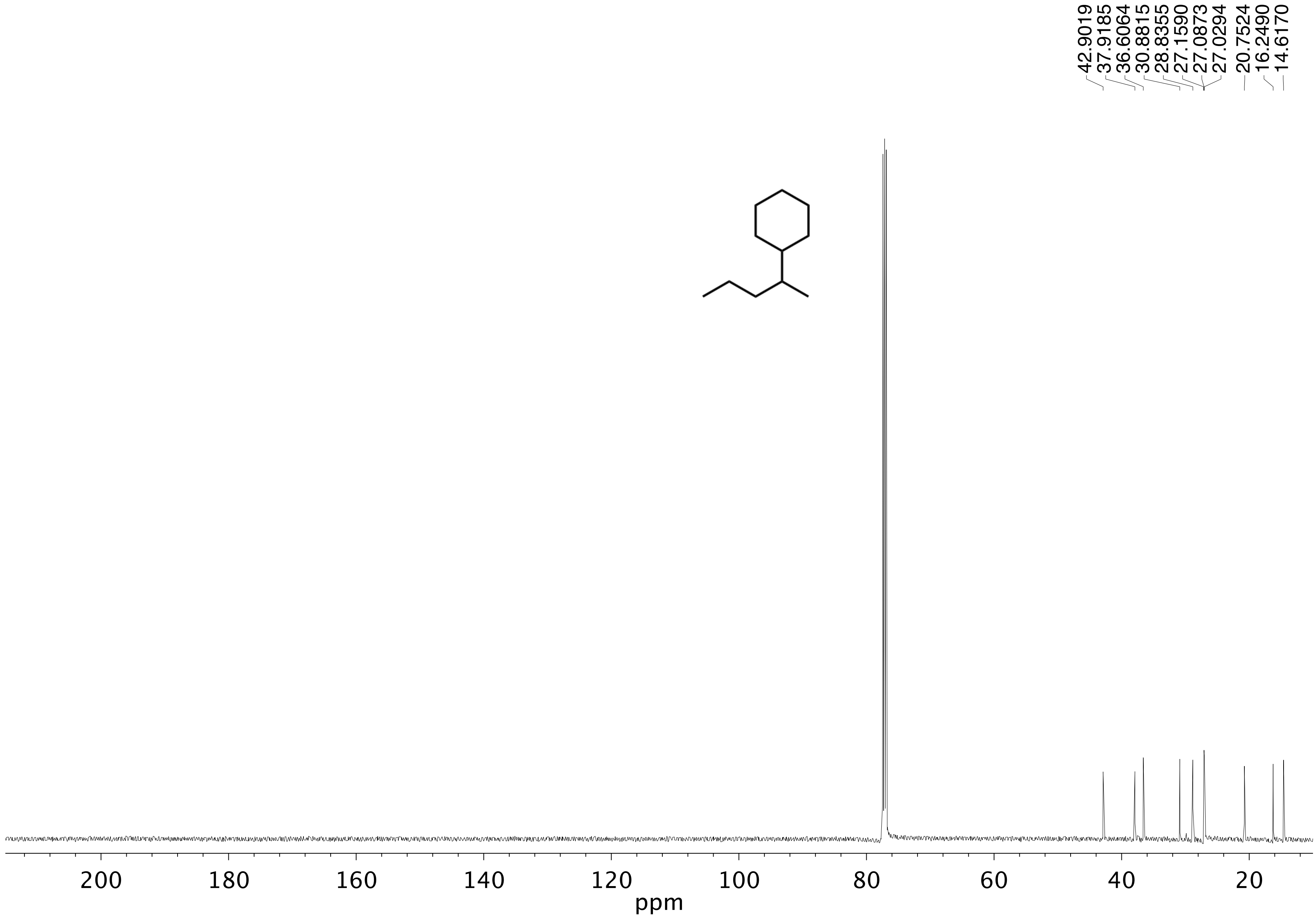
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-15**.



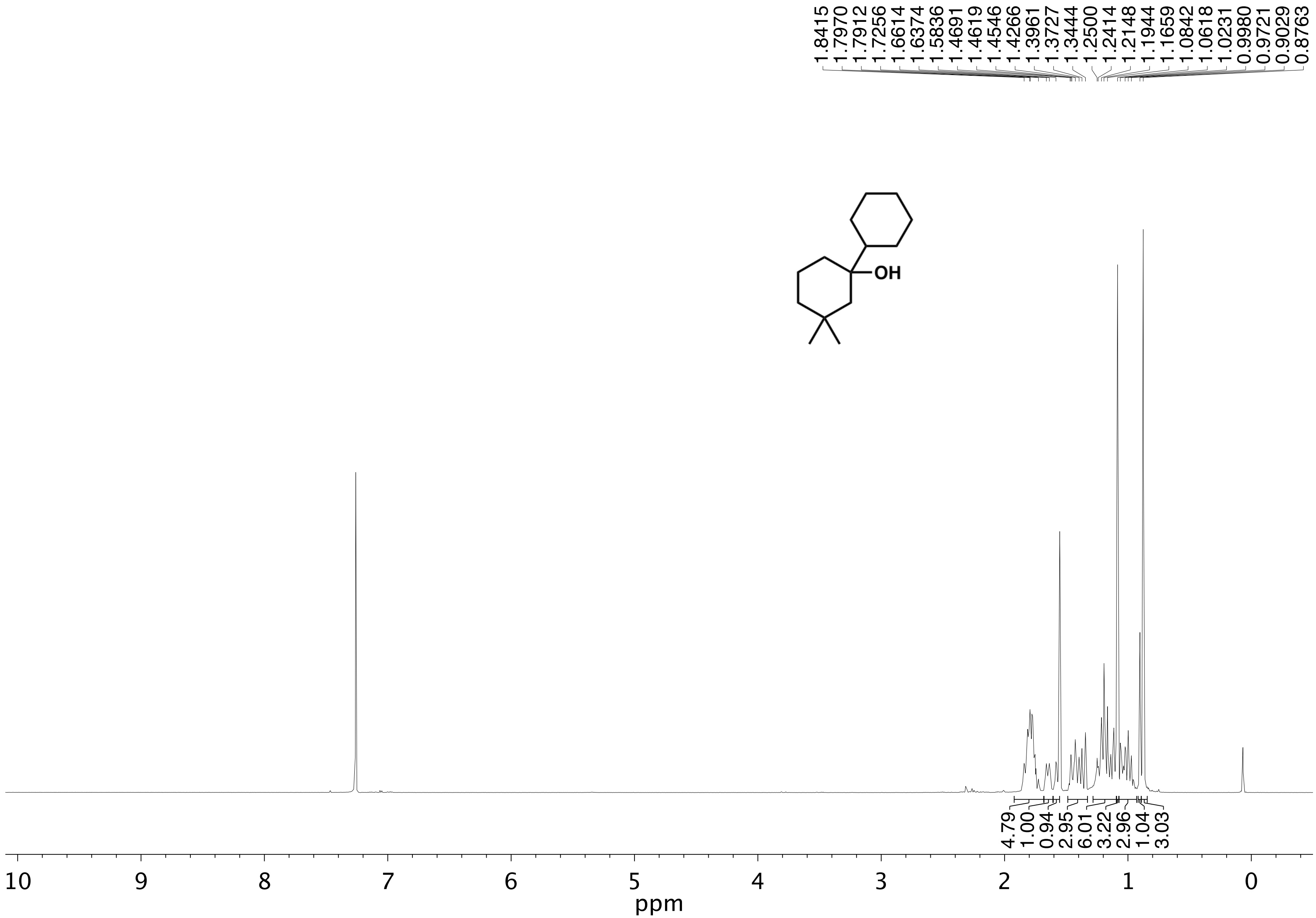
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-15**.



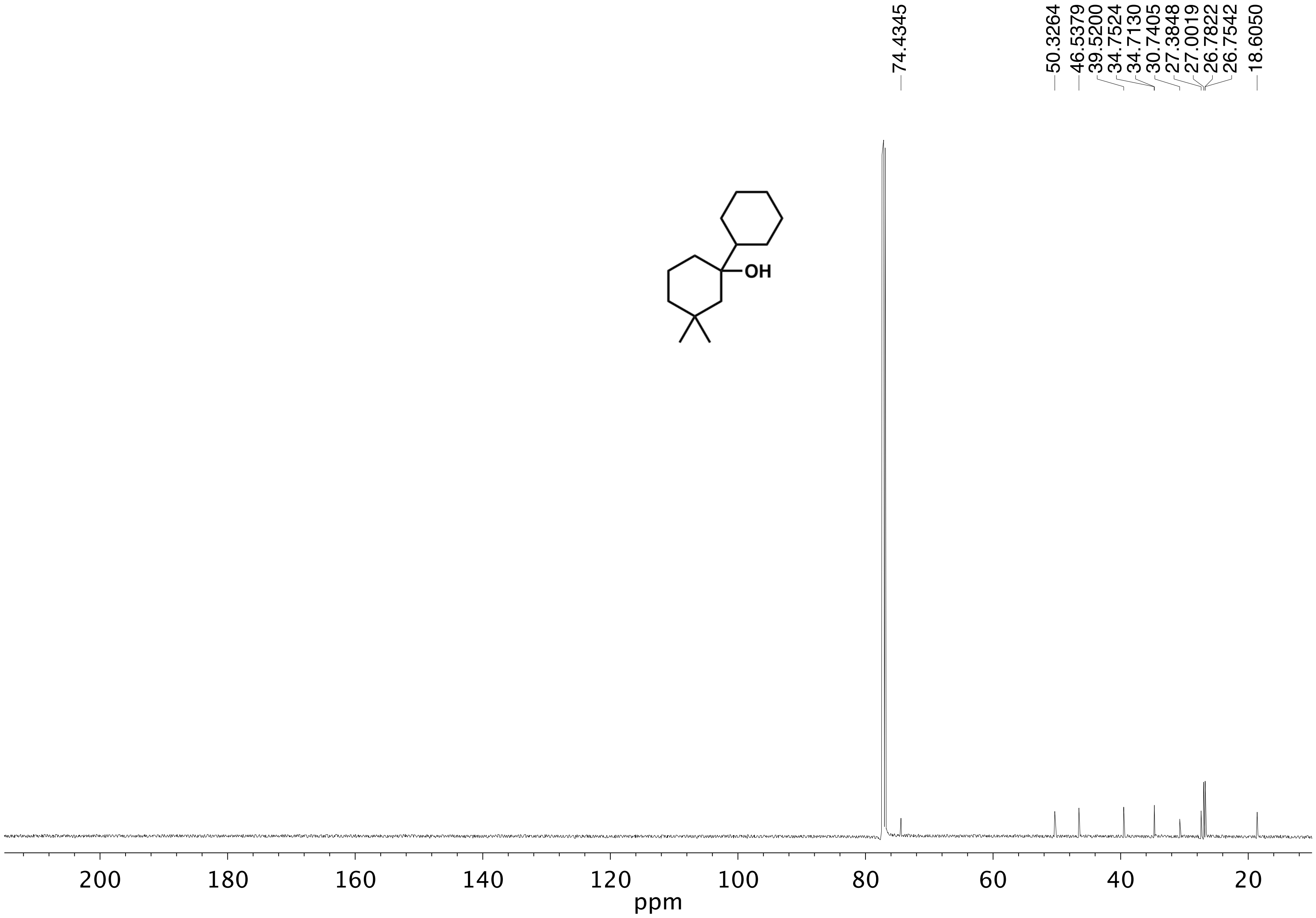
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-16**.



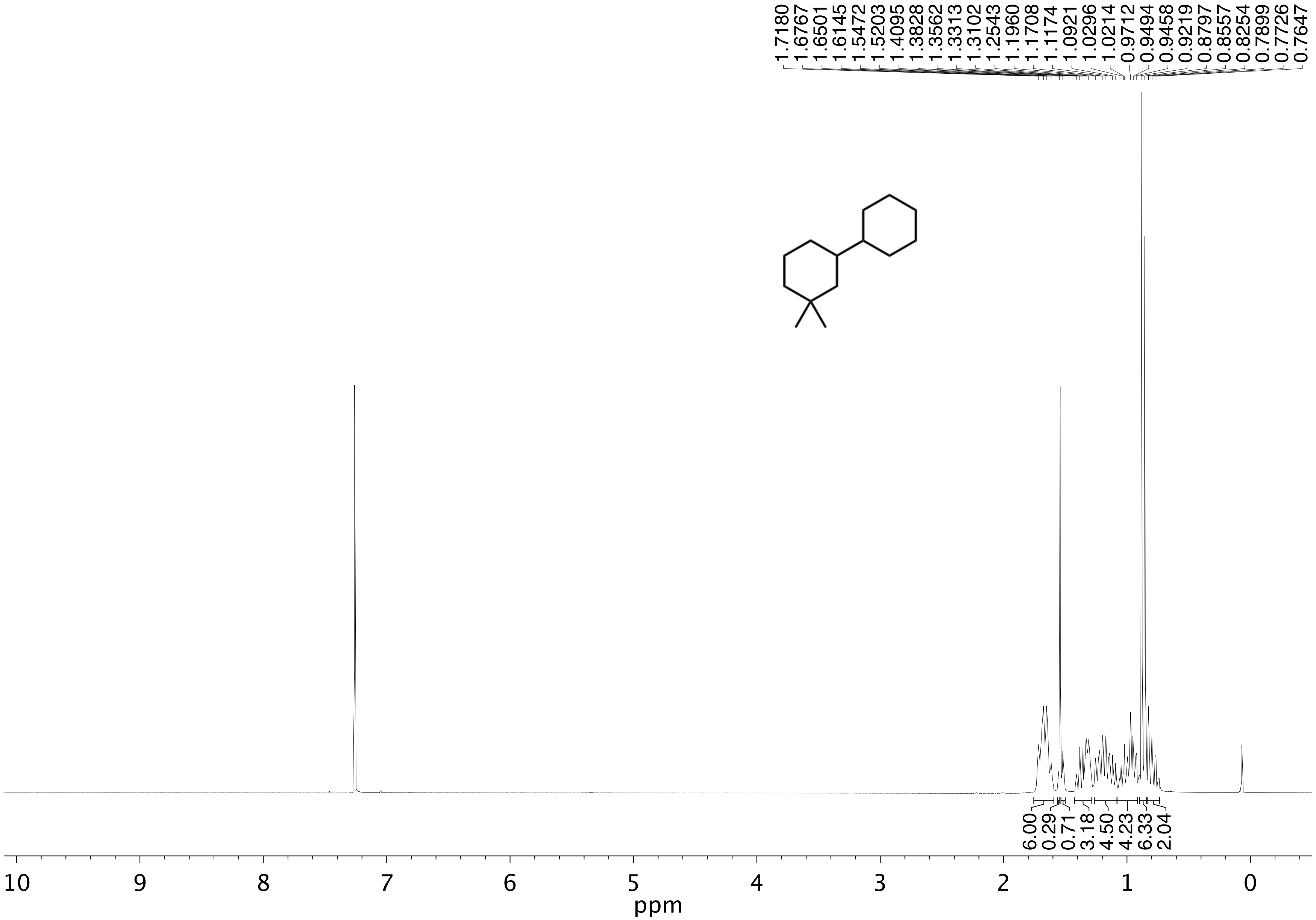
^{13}C NMR (100 MHz, CDCl$_3$) of **SI-16**.



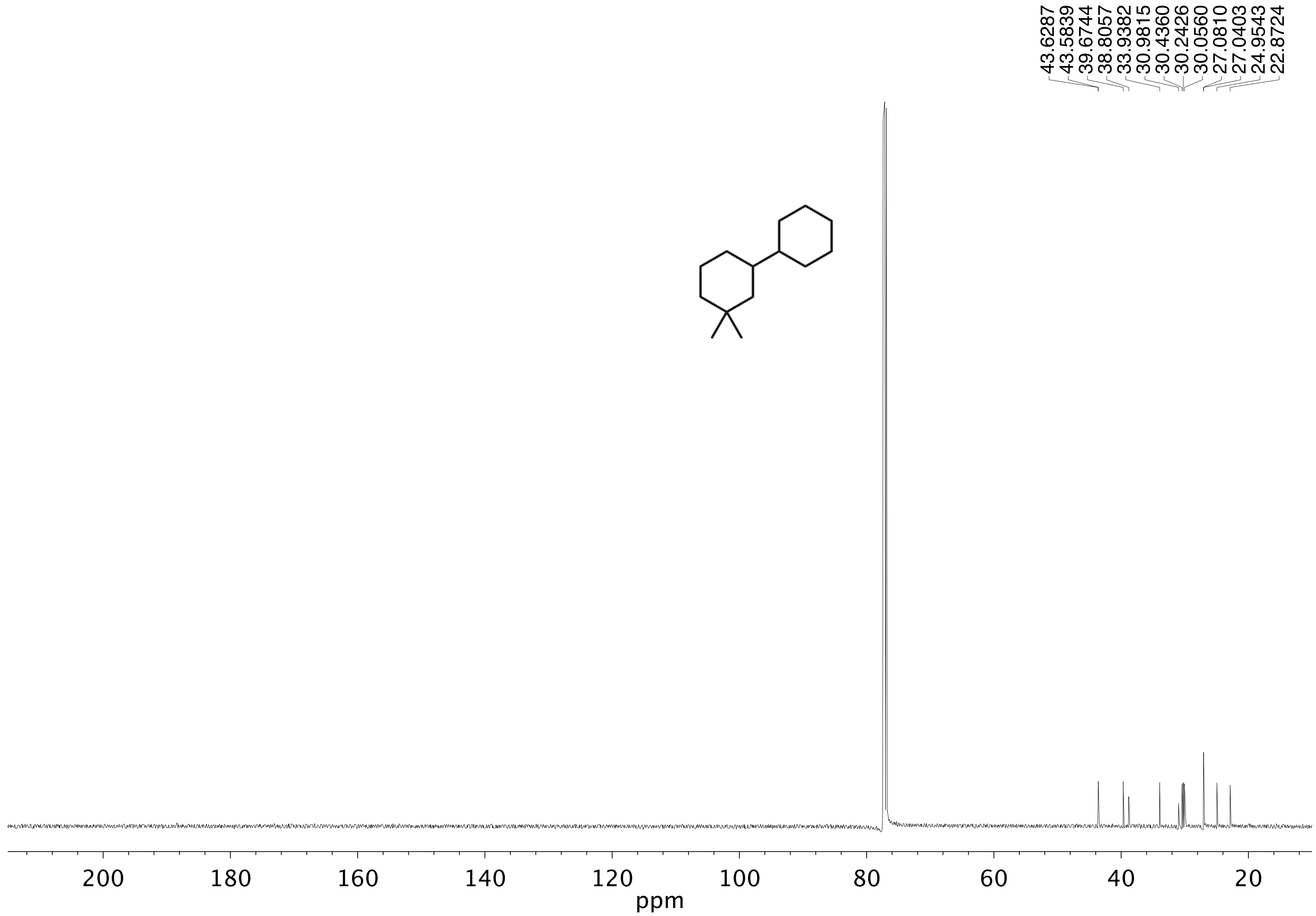
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-17**.



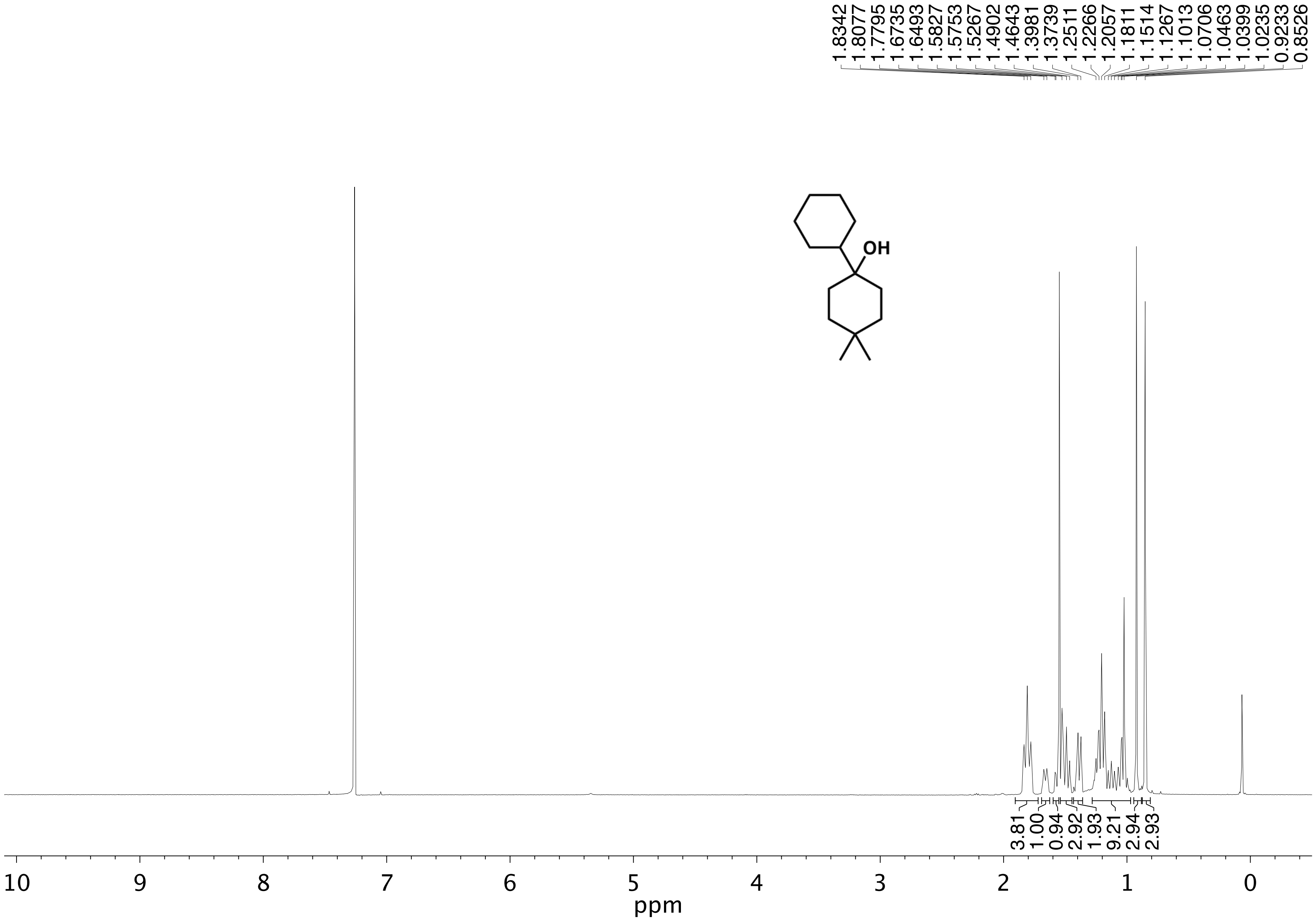
^{13}C NMR (125 MHz, $CDCl_3$) of **SI-17**.



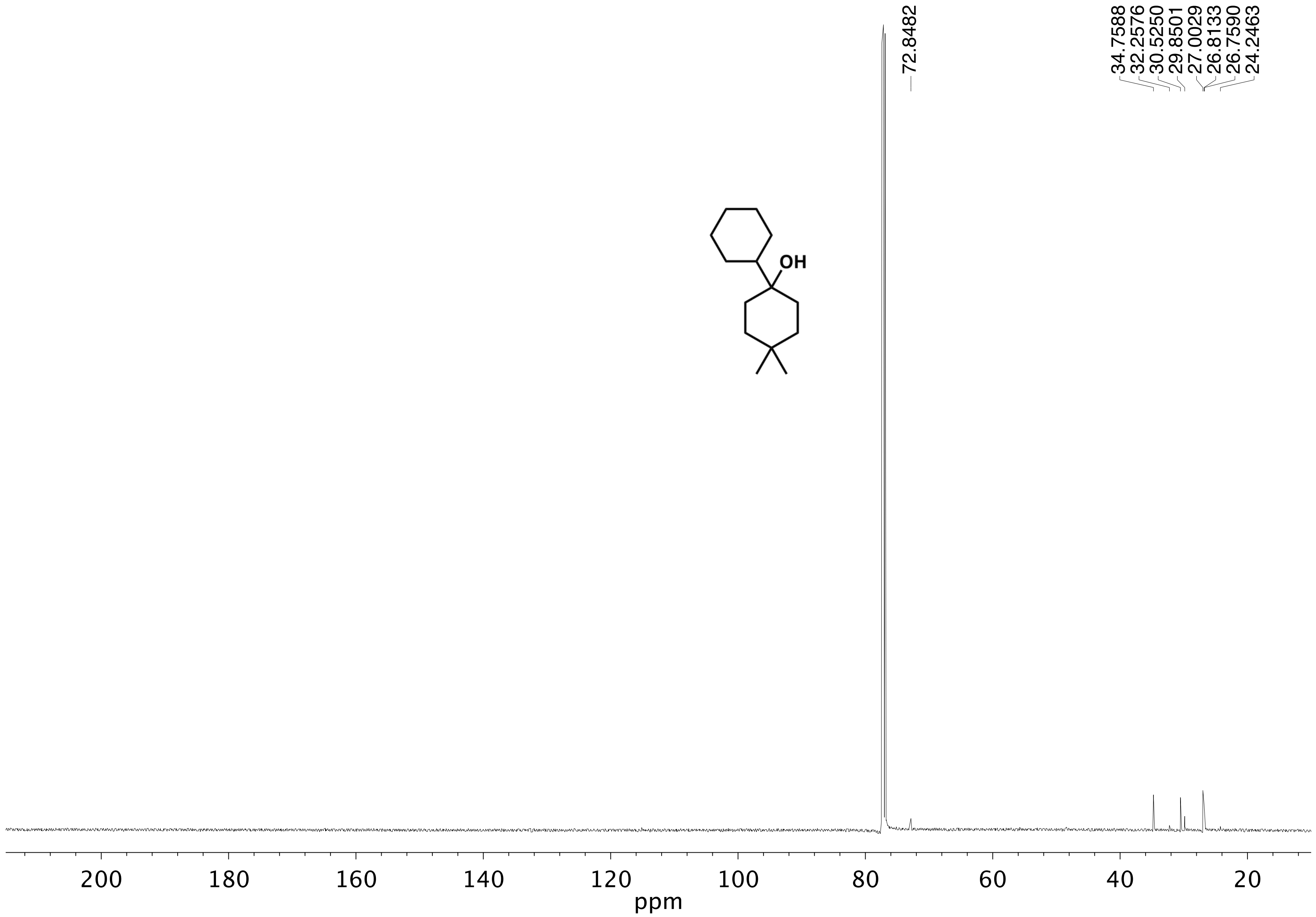
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-18**.



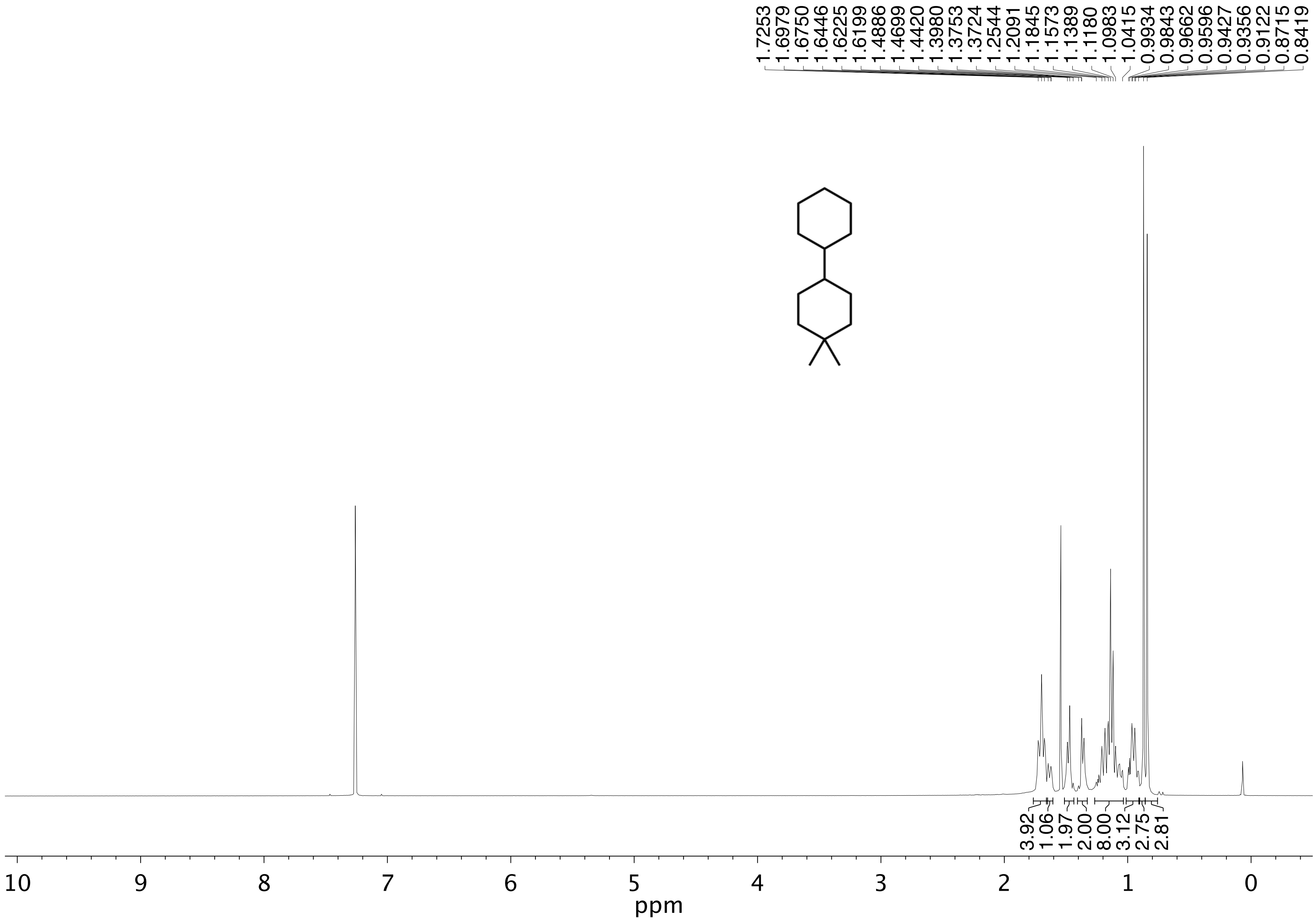
^{13}C NMR (125 MHz, $CDCl_3$) of **SI-18**.



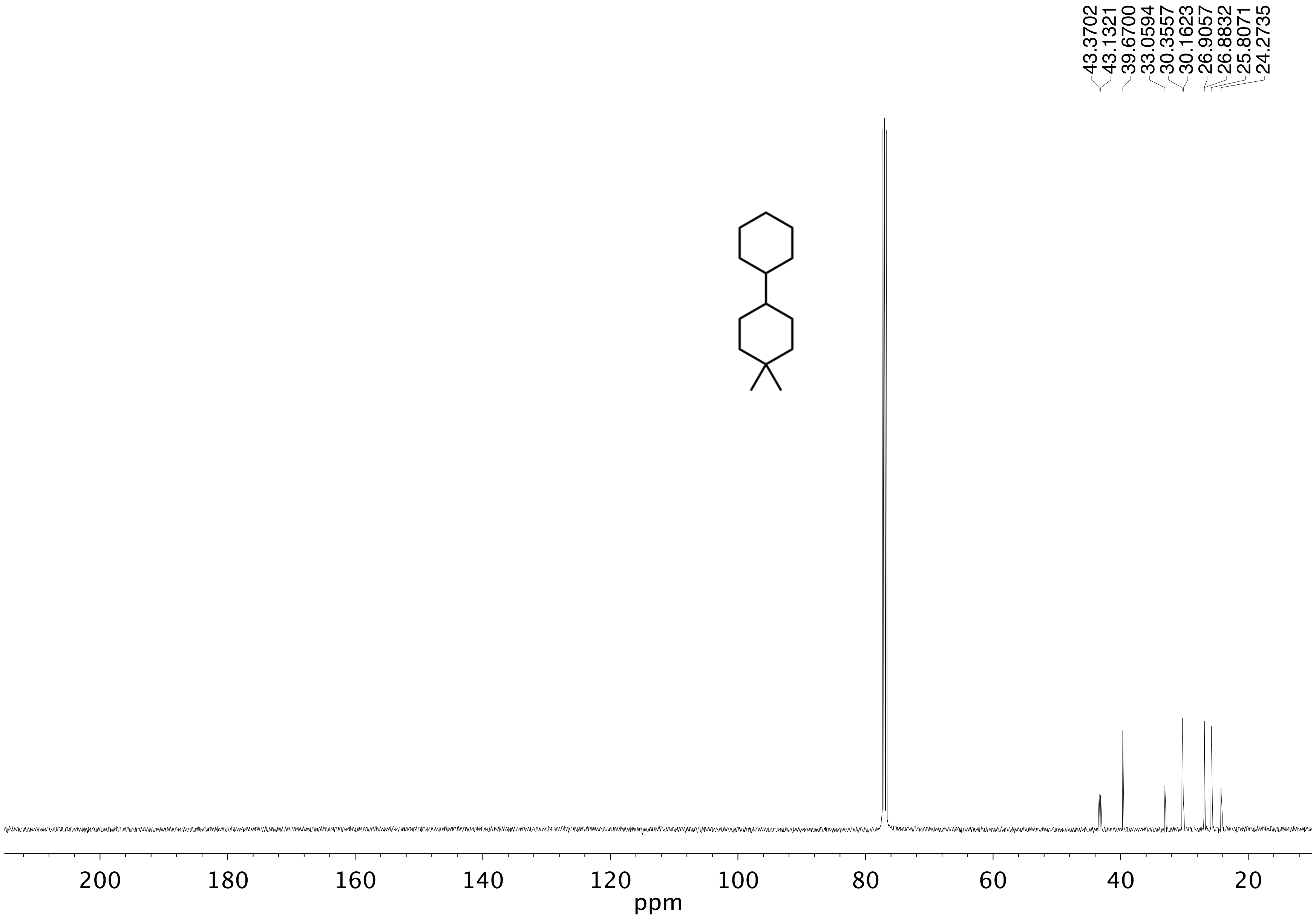
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-19**.



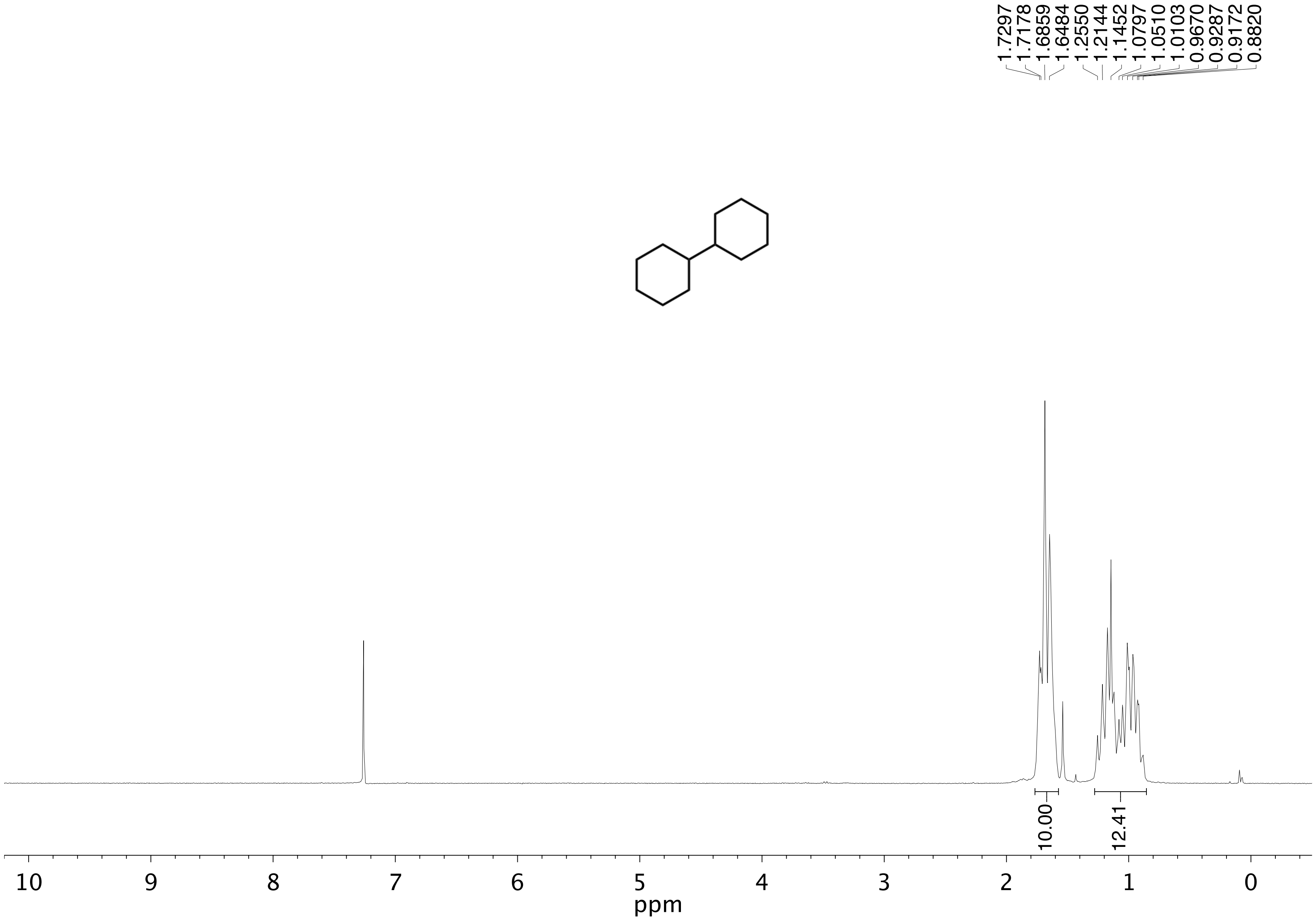
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-19**.



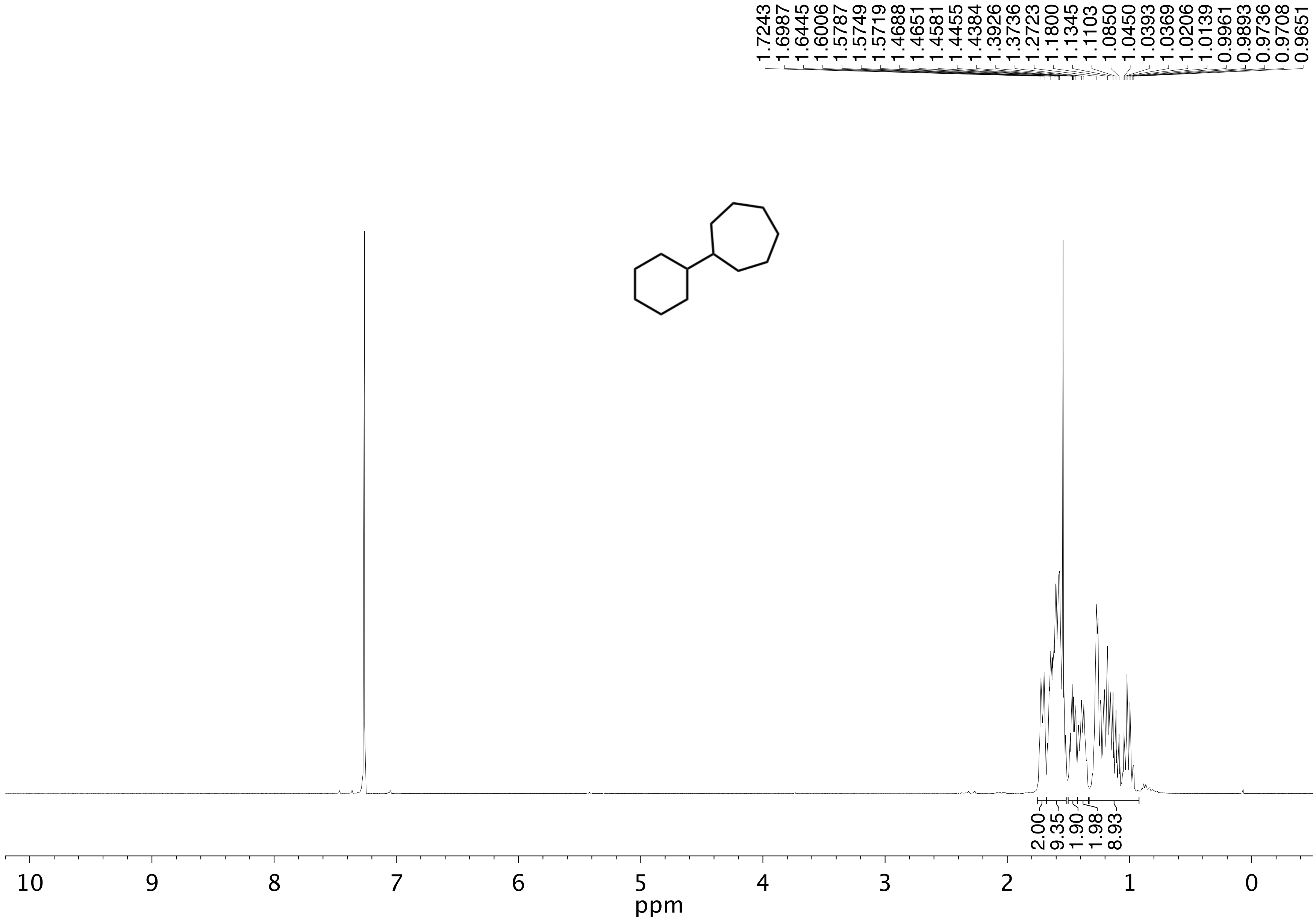
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-20**.



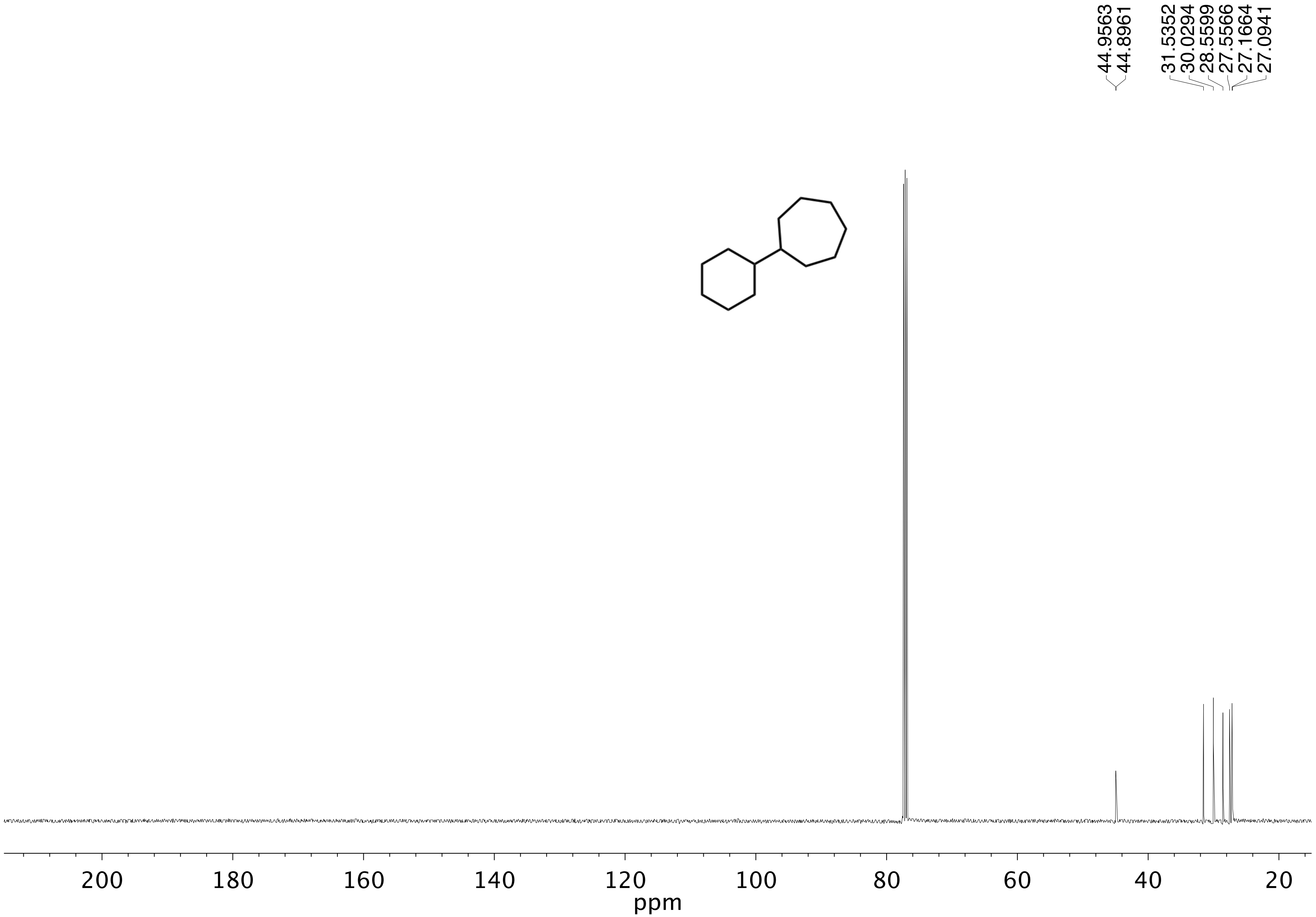
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-20**.



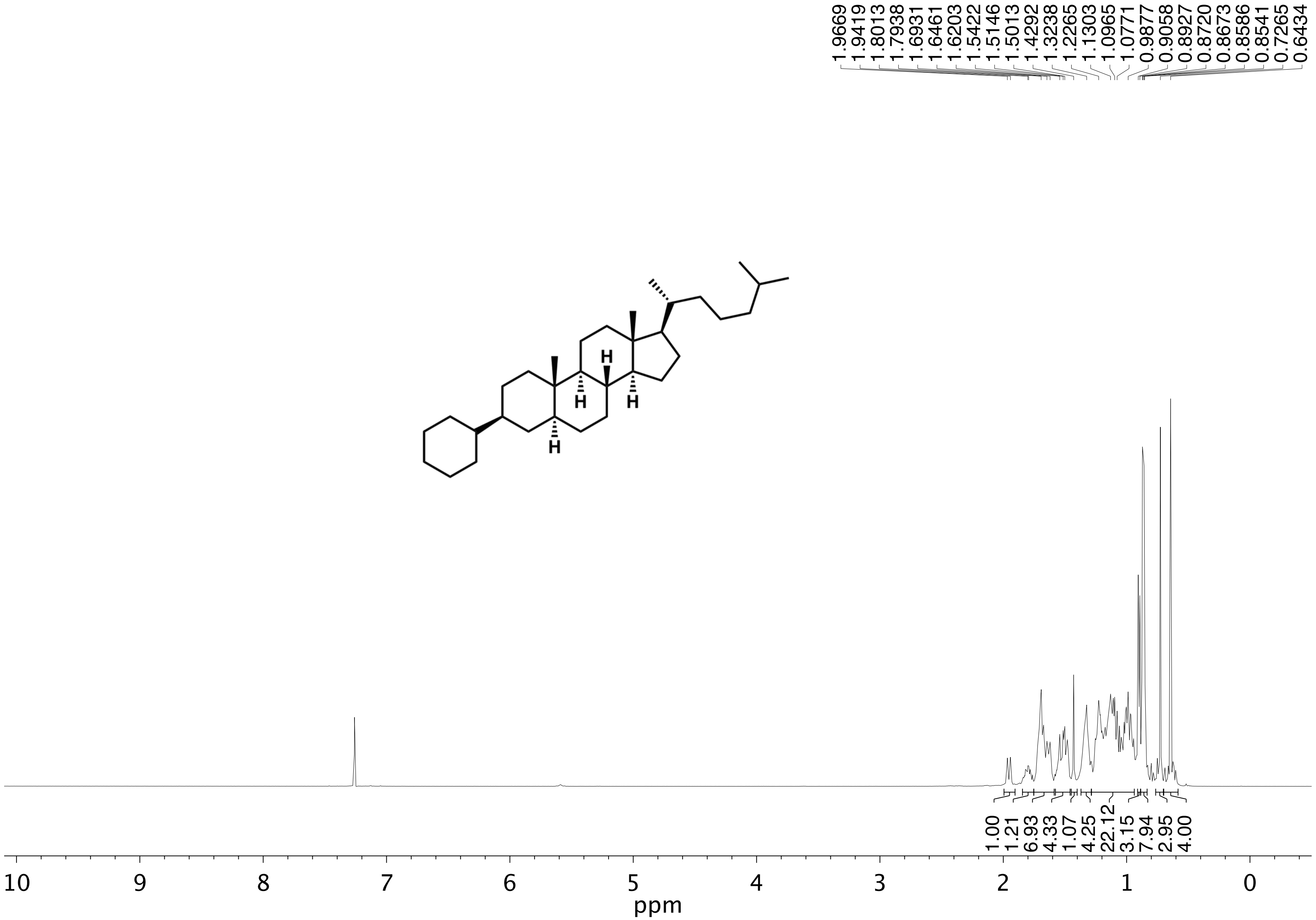
^{1}H NMR (400 MHz, $CDCl_3$) of **SI-21**.



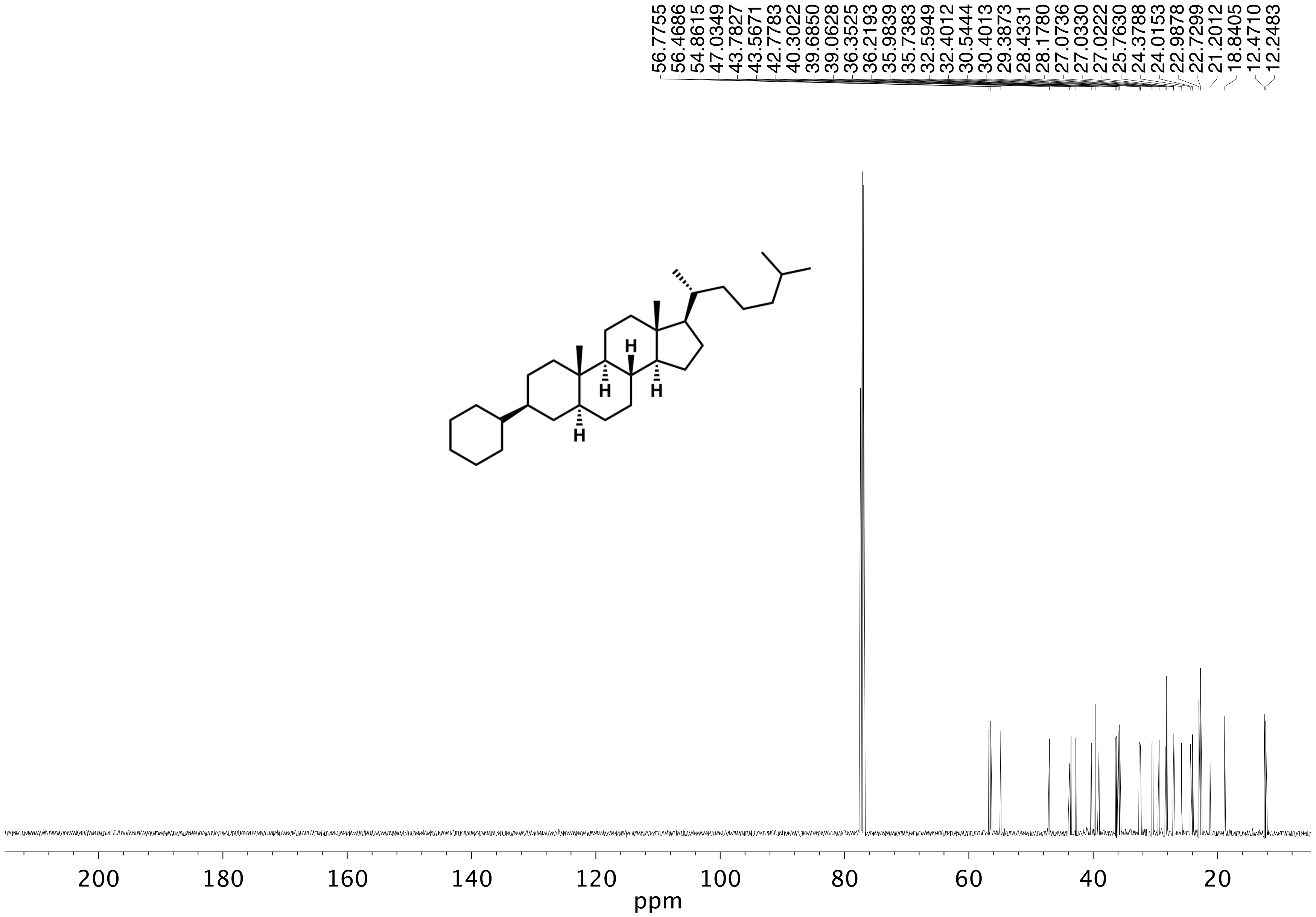
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-22**.



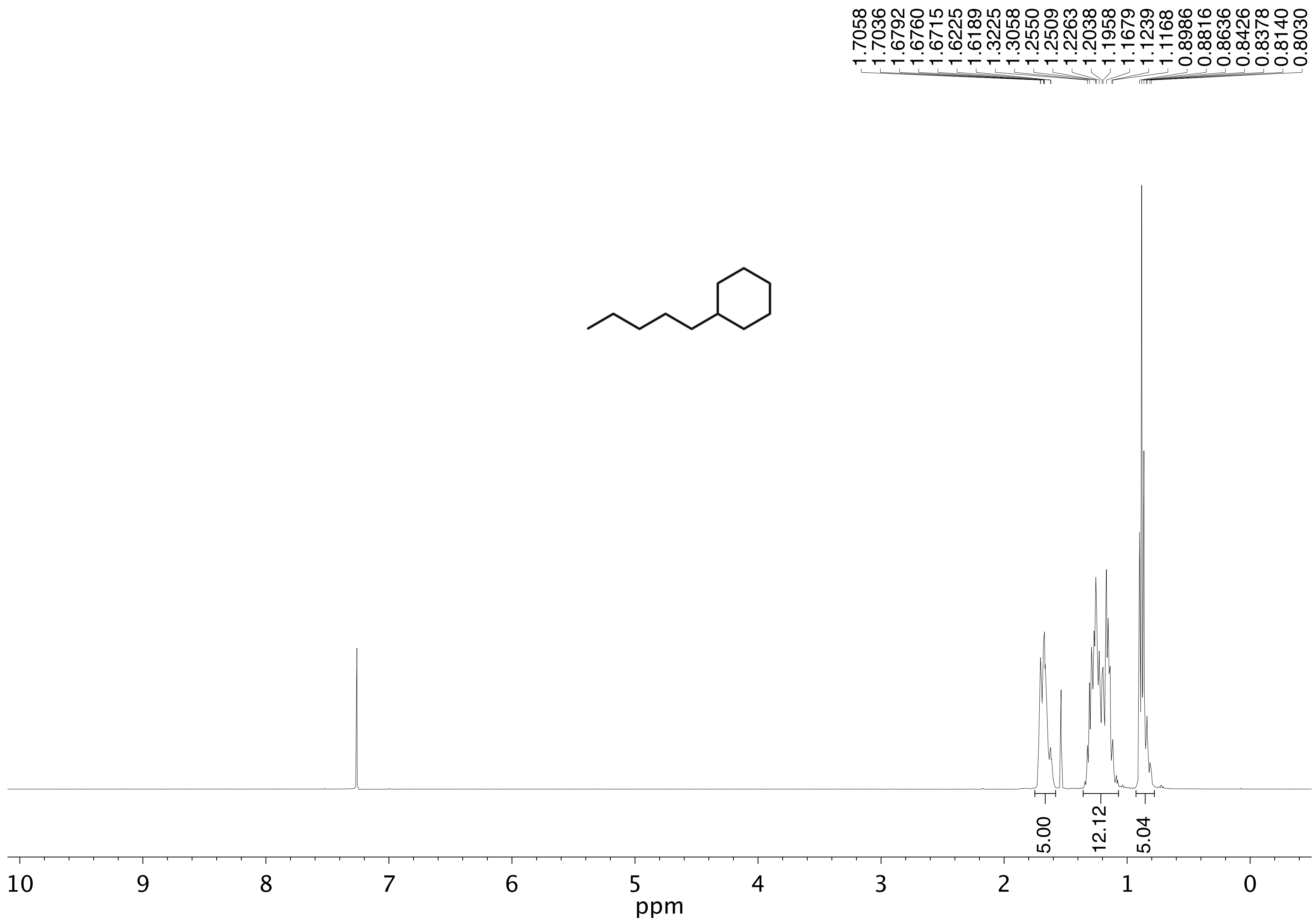
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-22**.



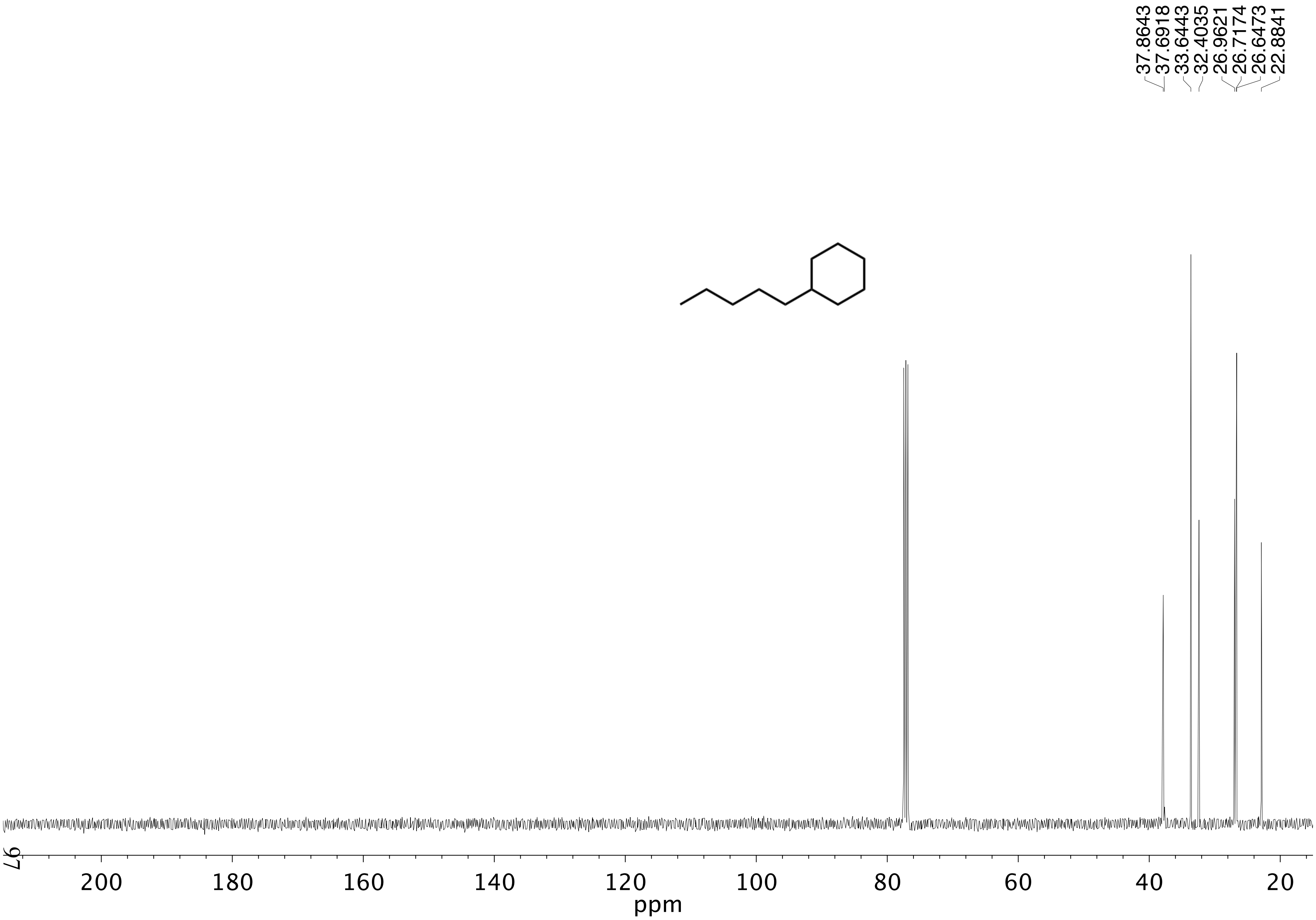
^{1}H NMR (500 MHz, CDCl$_3$) of **SI-23**.



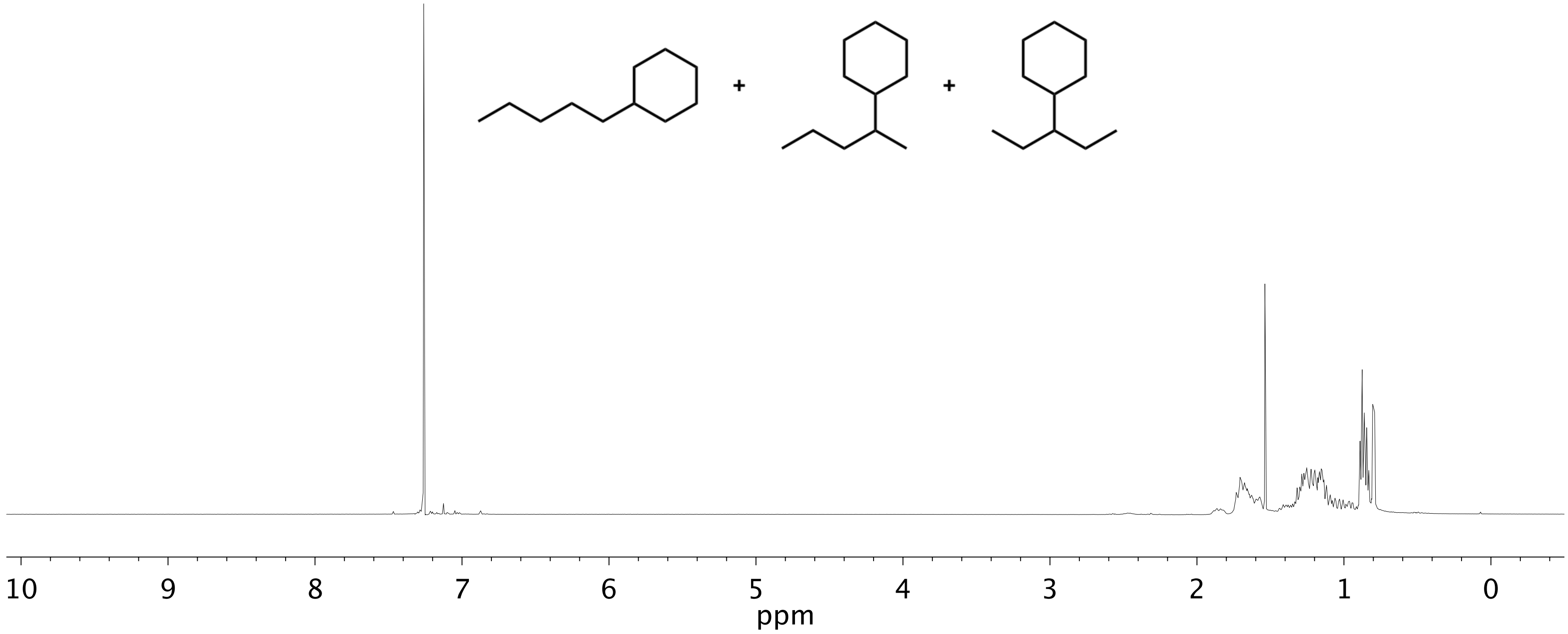
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-23**.



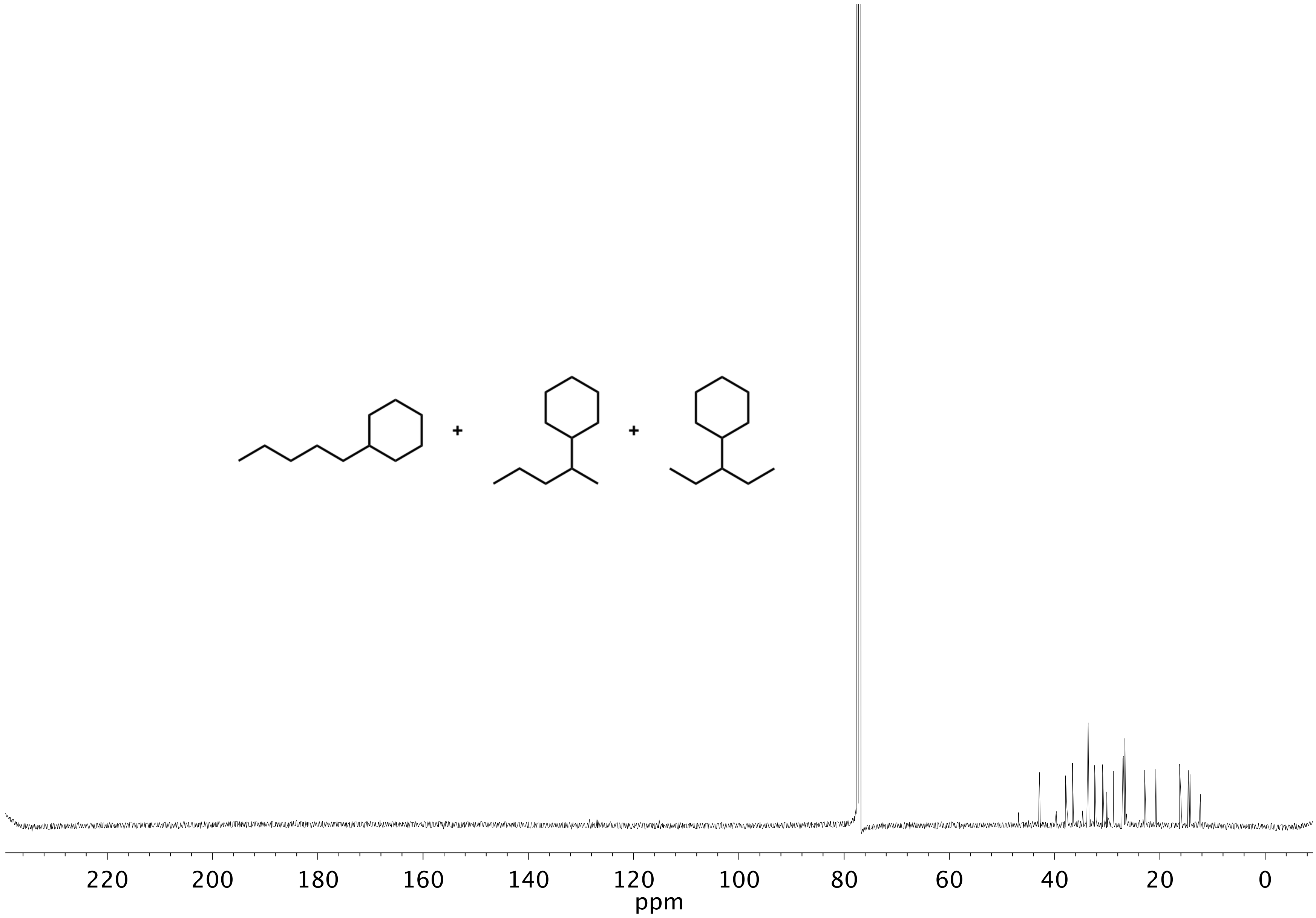
^{1}H NMR (400 MHz, CDCl$_3$) of compound **SI-24**.



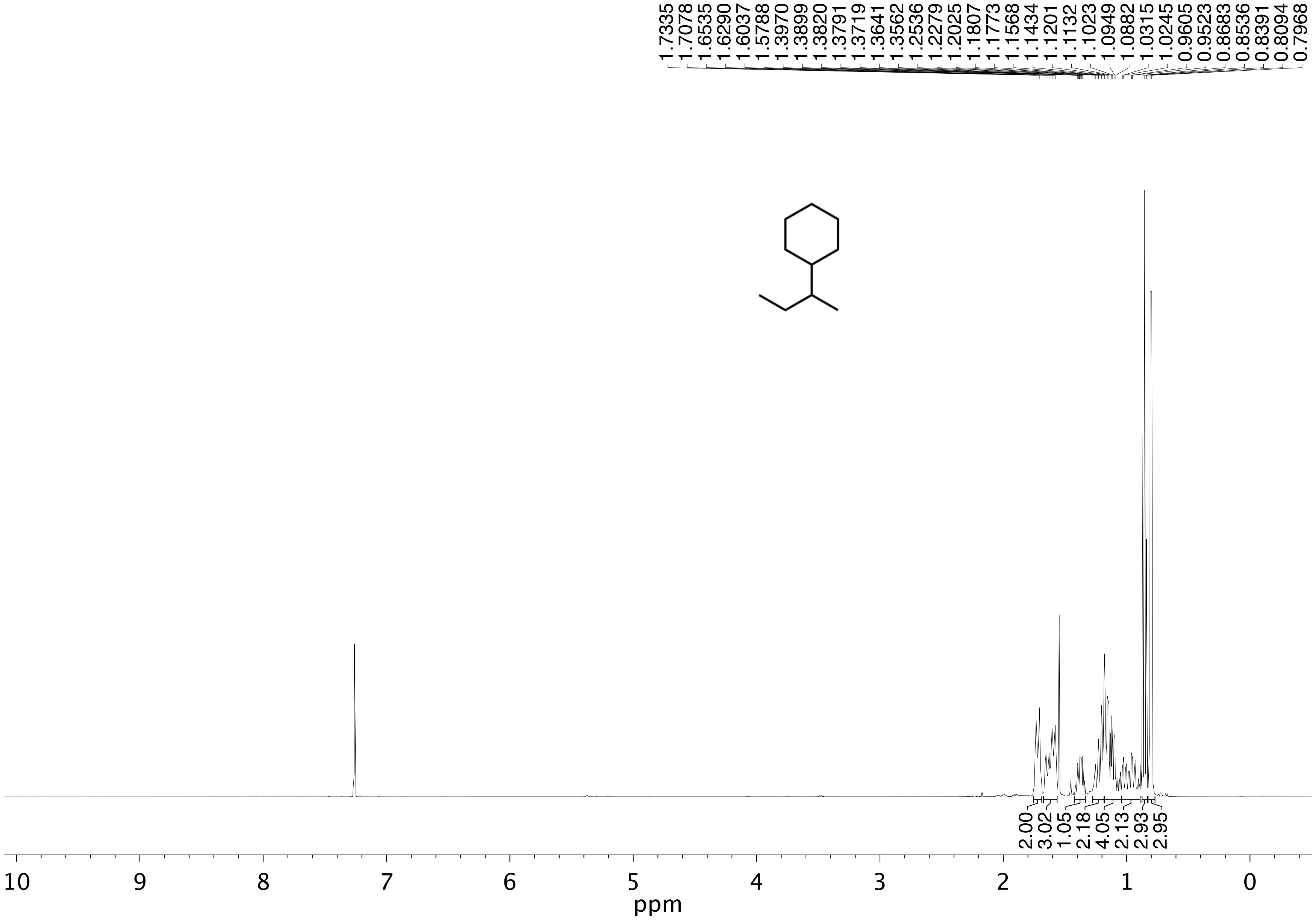
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-24**



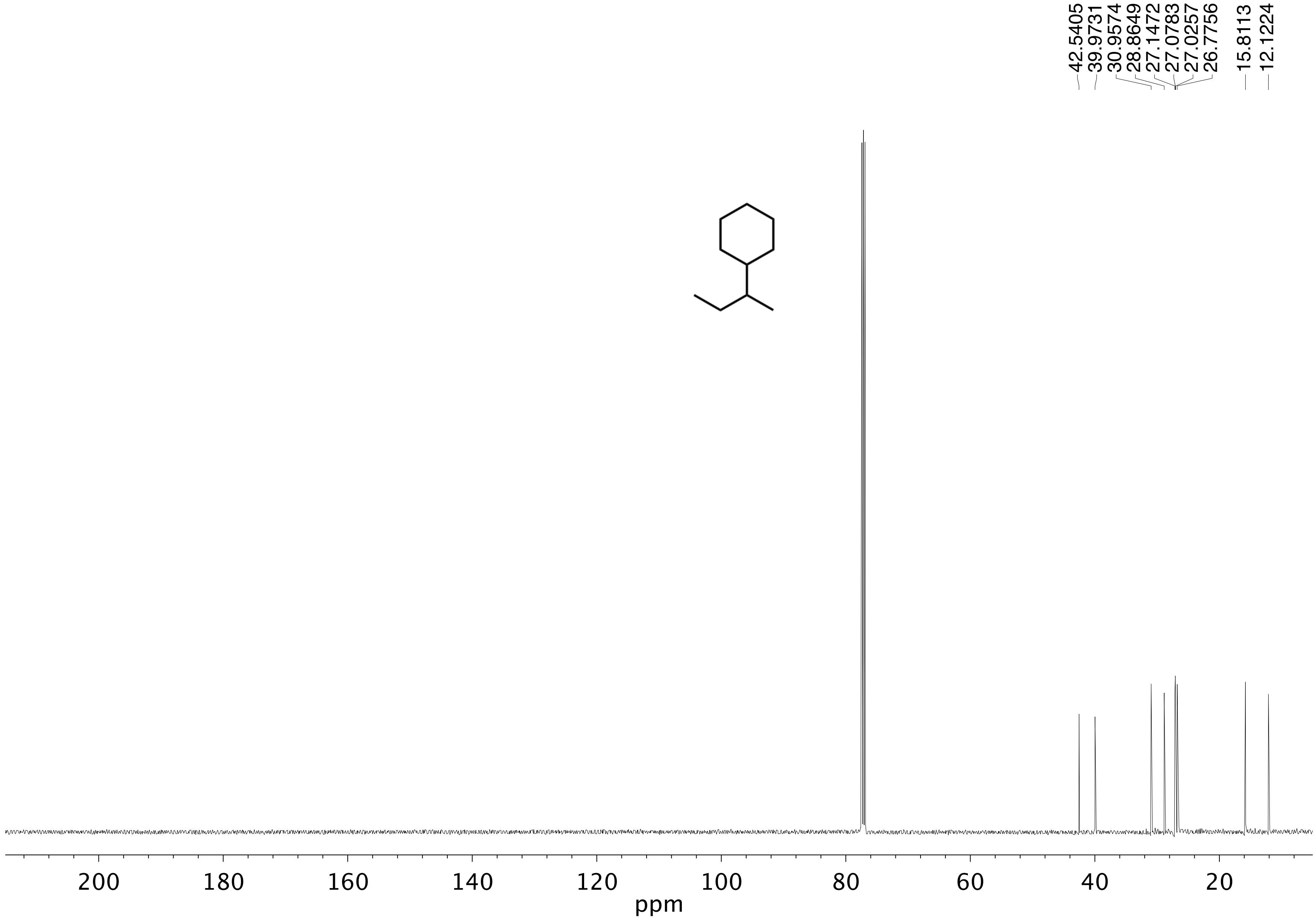
^{1}H NMR (400 MHz, $CDCl_3$) of **SI-14, SI-16, SI-24**



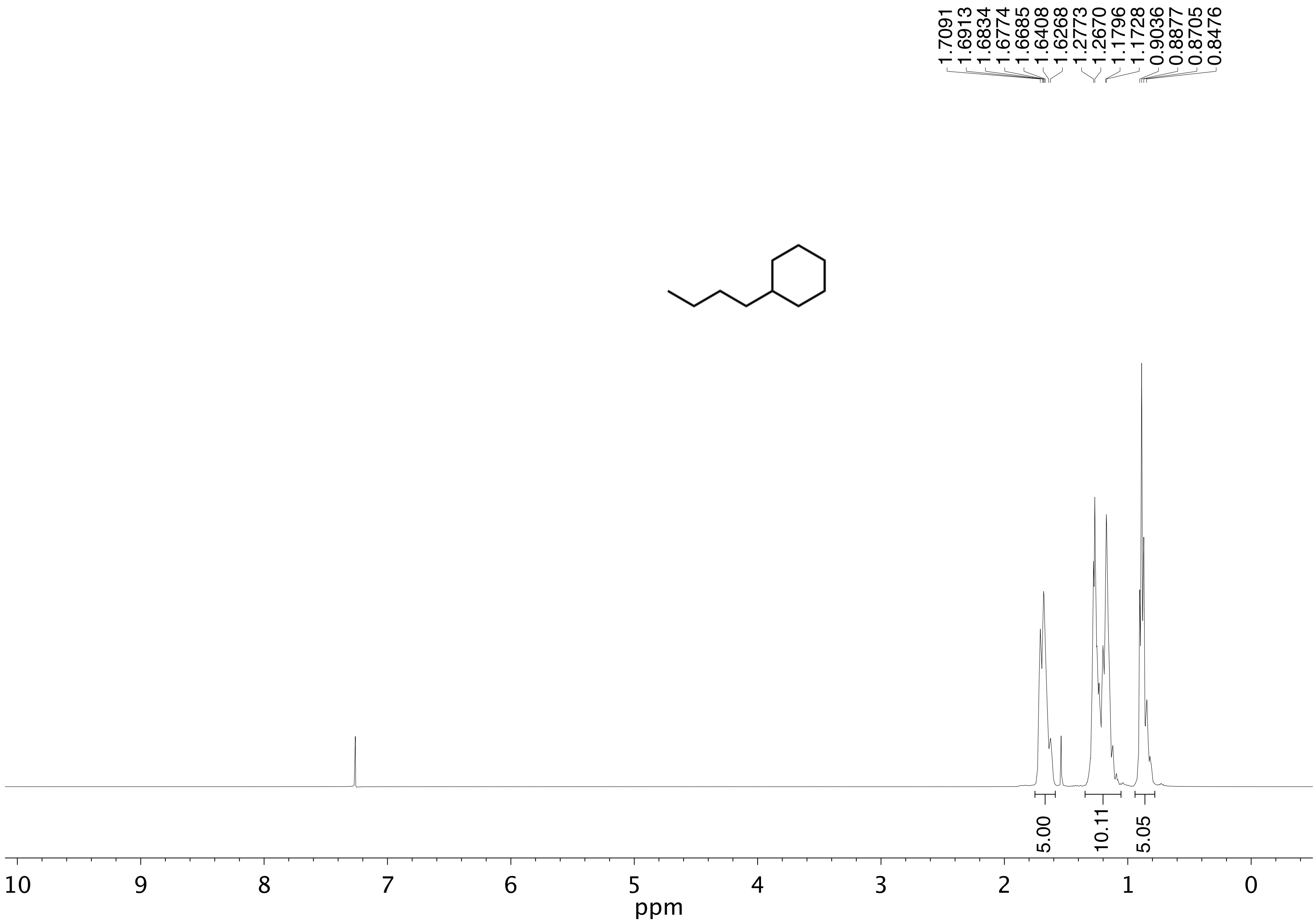
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-14, SI-16, SI-24**.



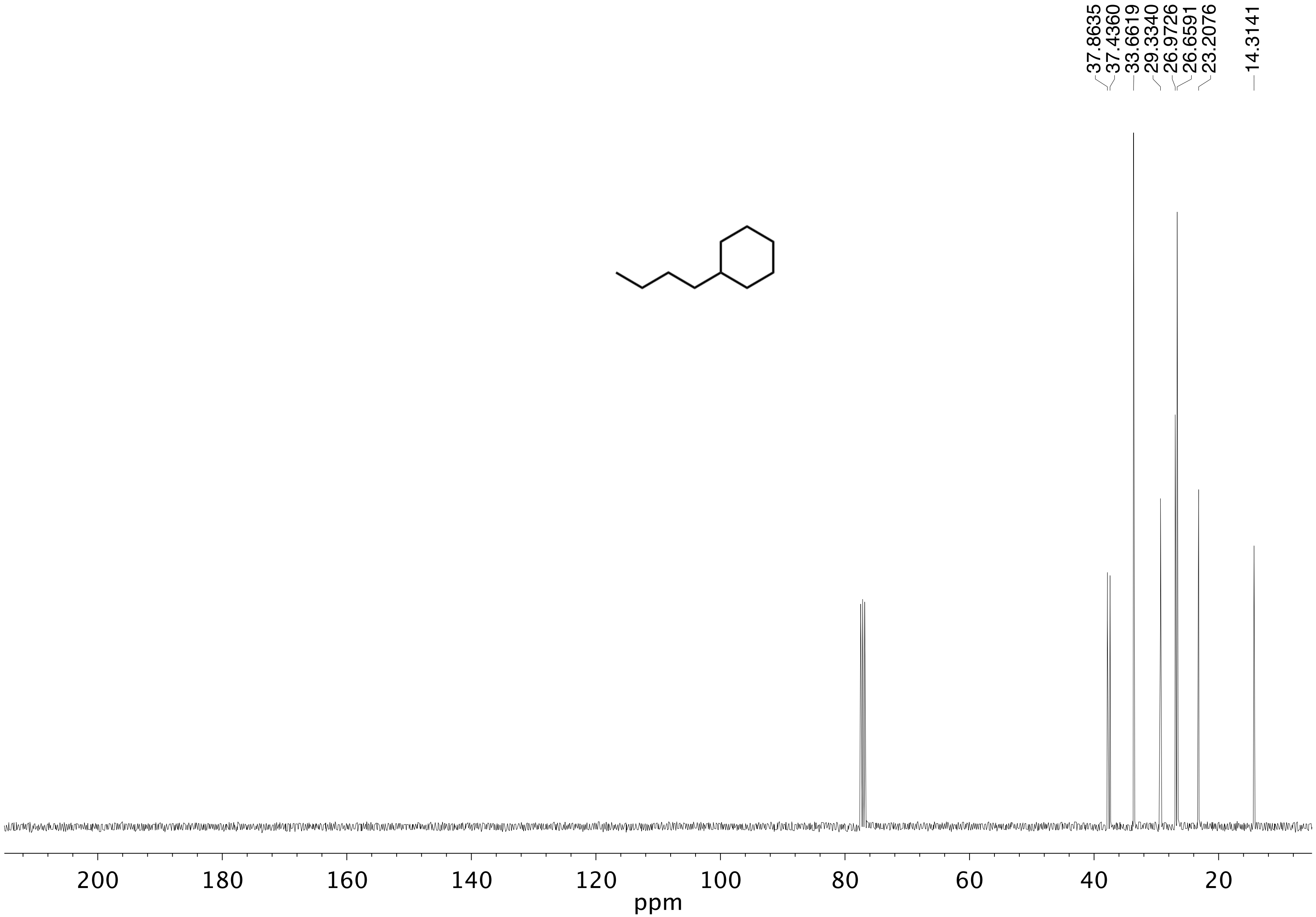
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-25**.



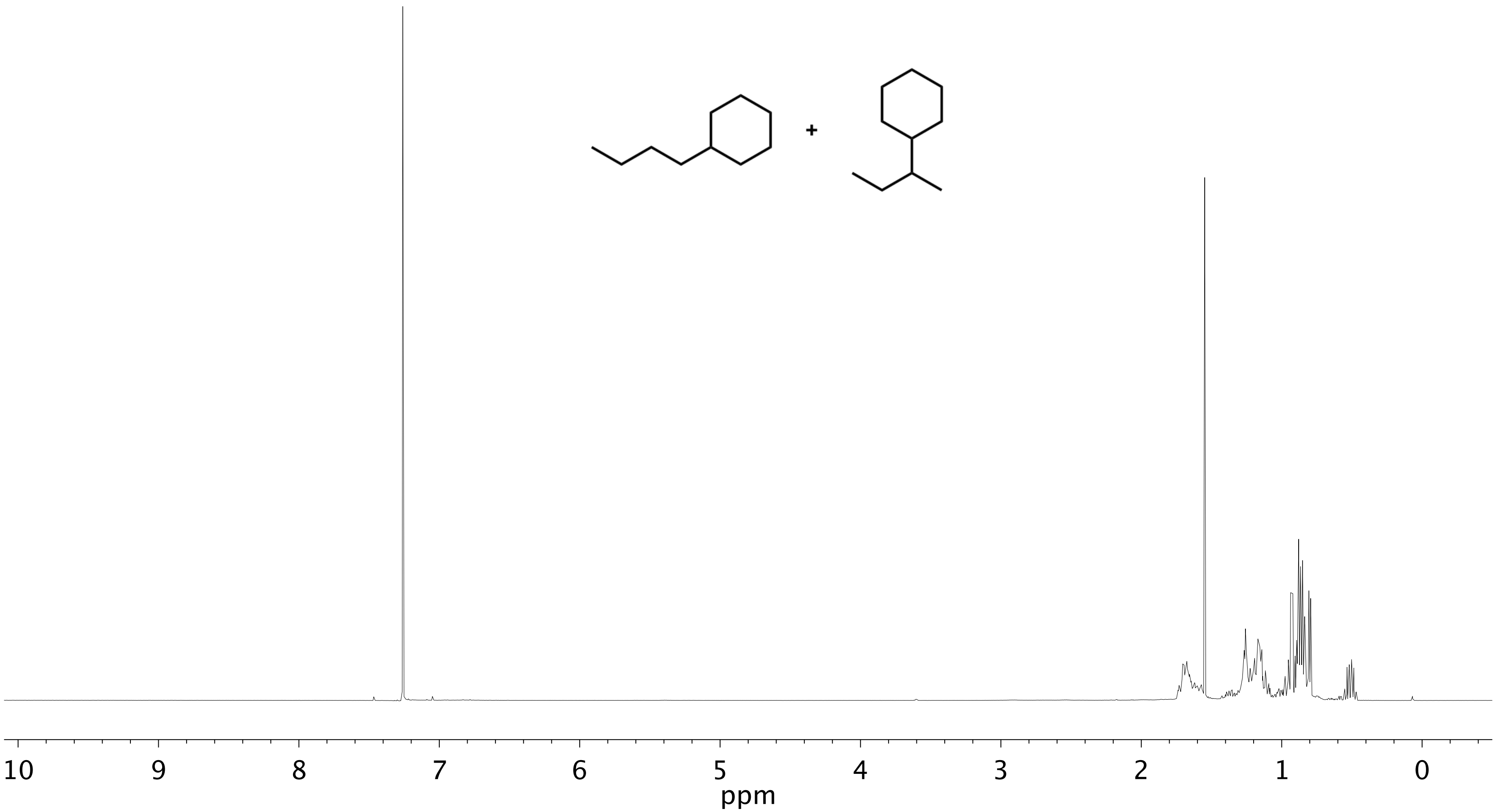
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-25**.



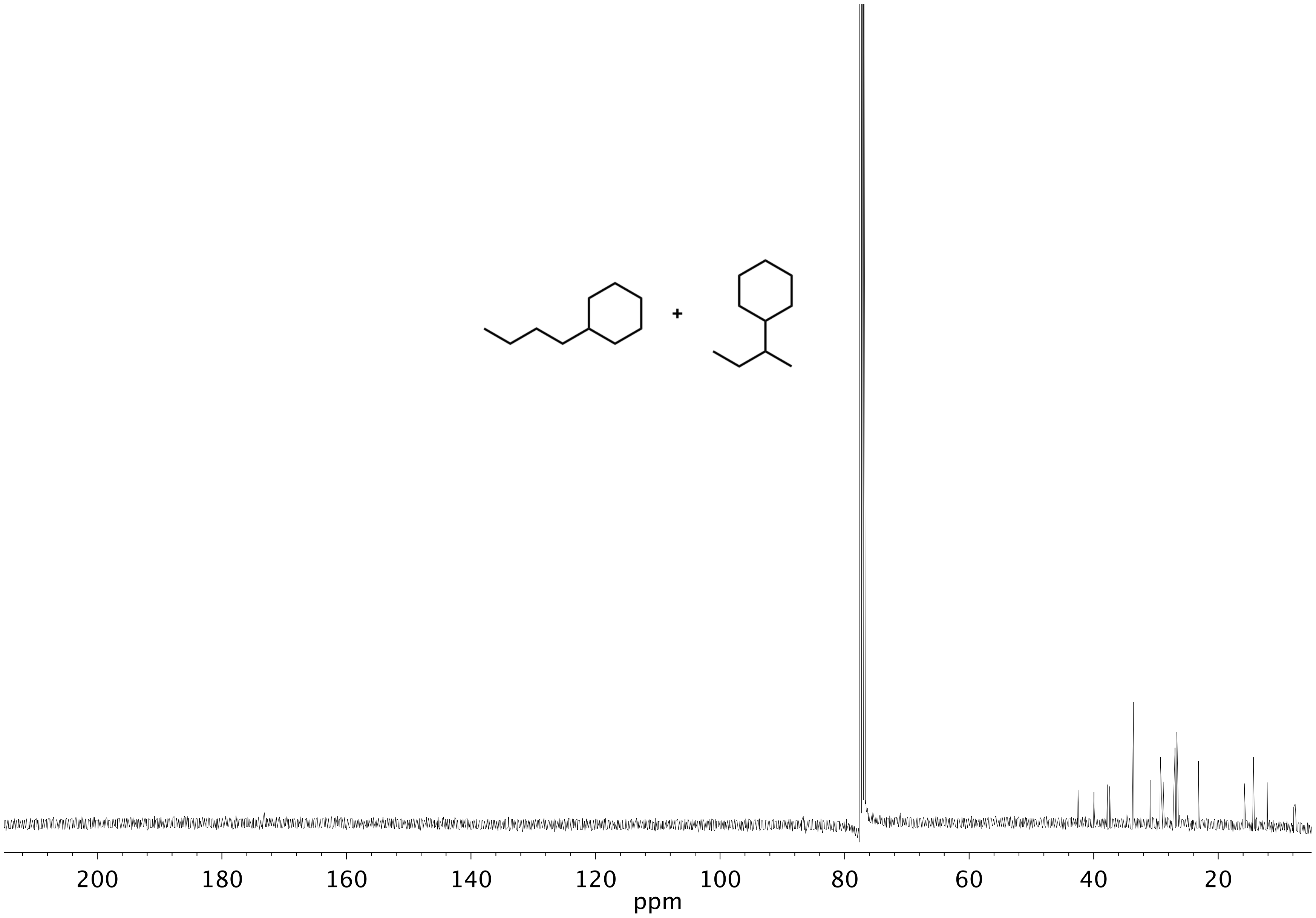
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI-26**.



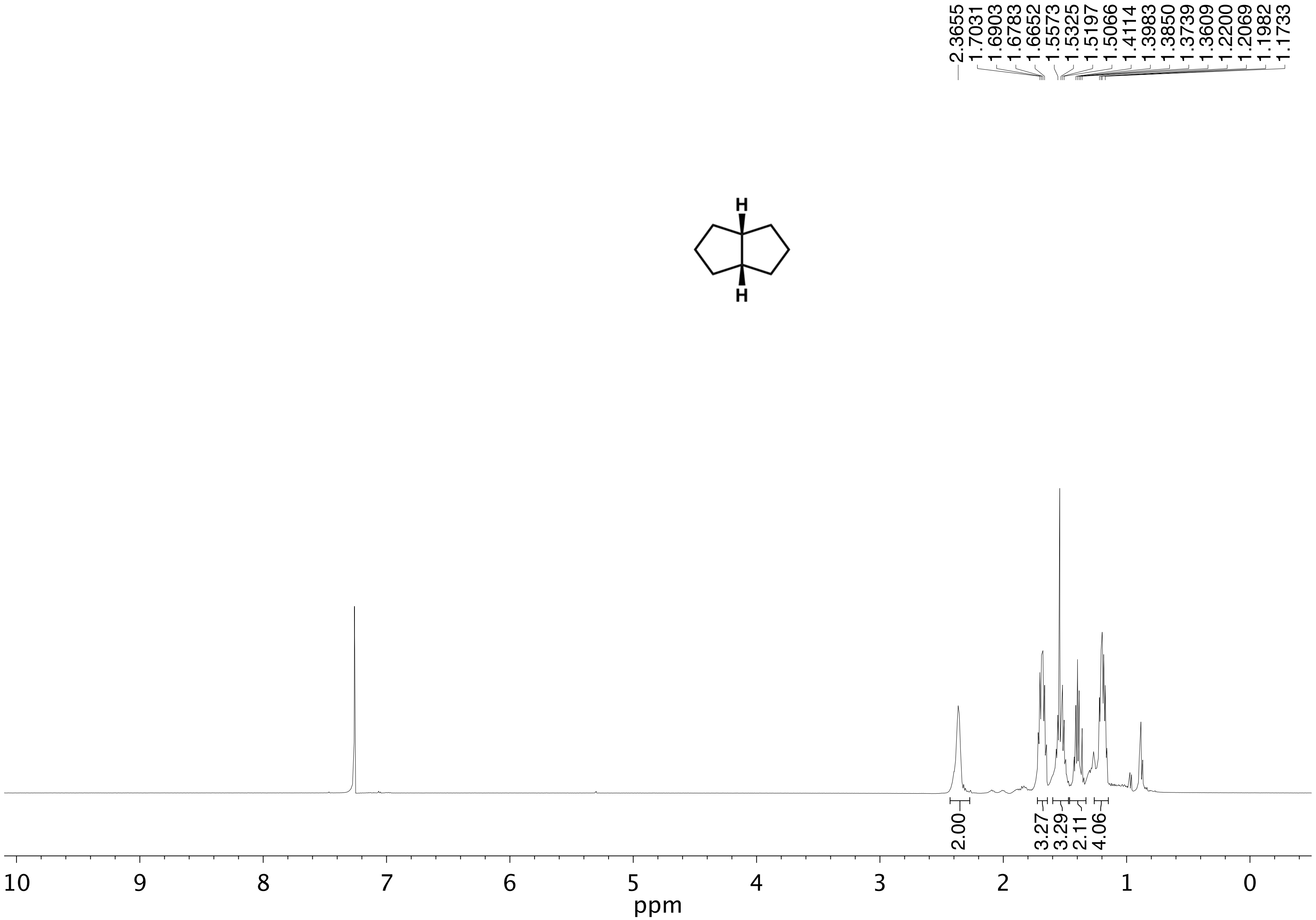
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-26**.



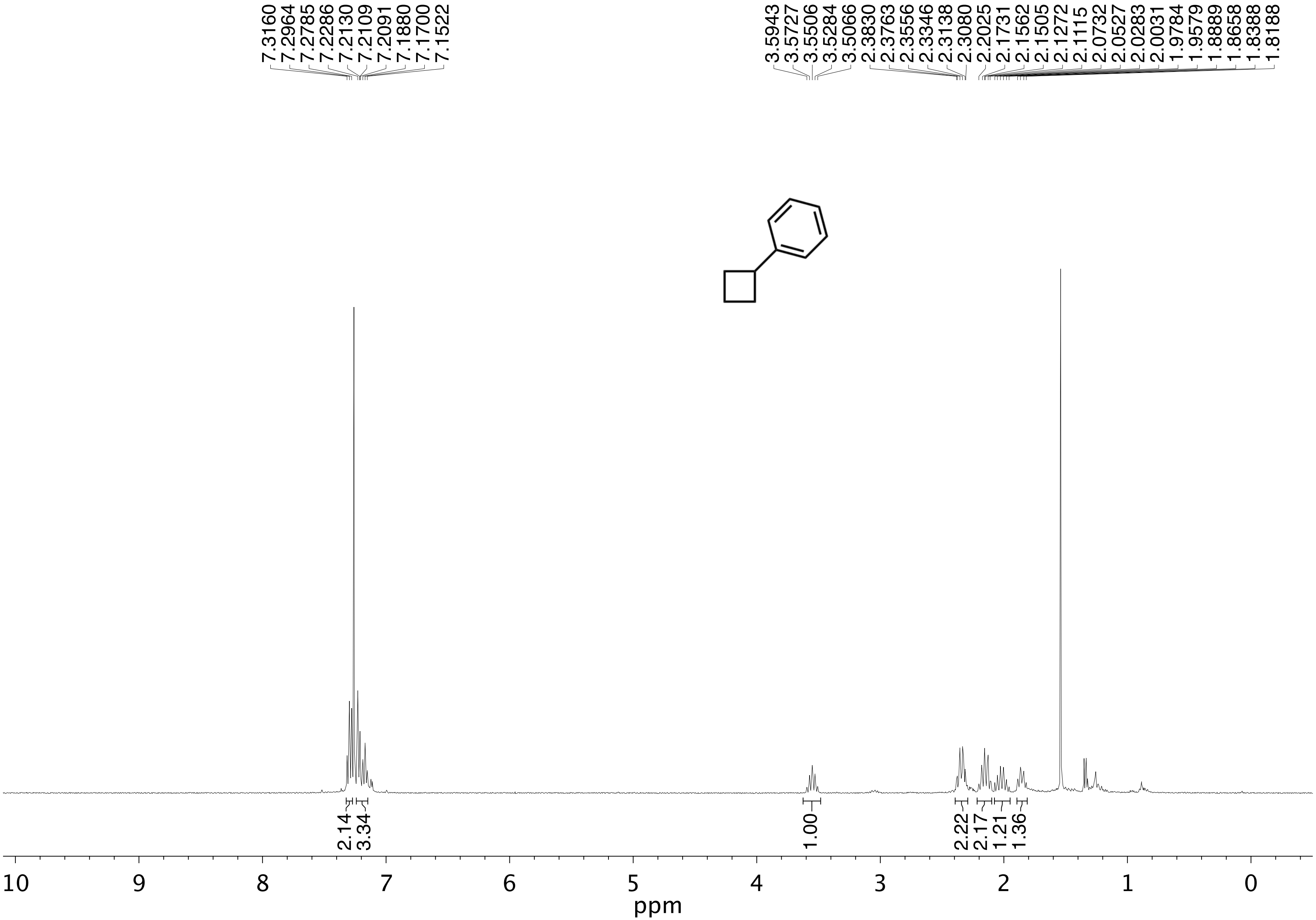
^{1}H NMR (400 MHz, $CDCl_3$) of **SI-25, SI-26**.



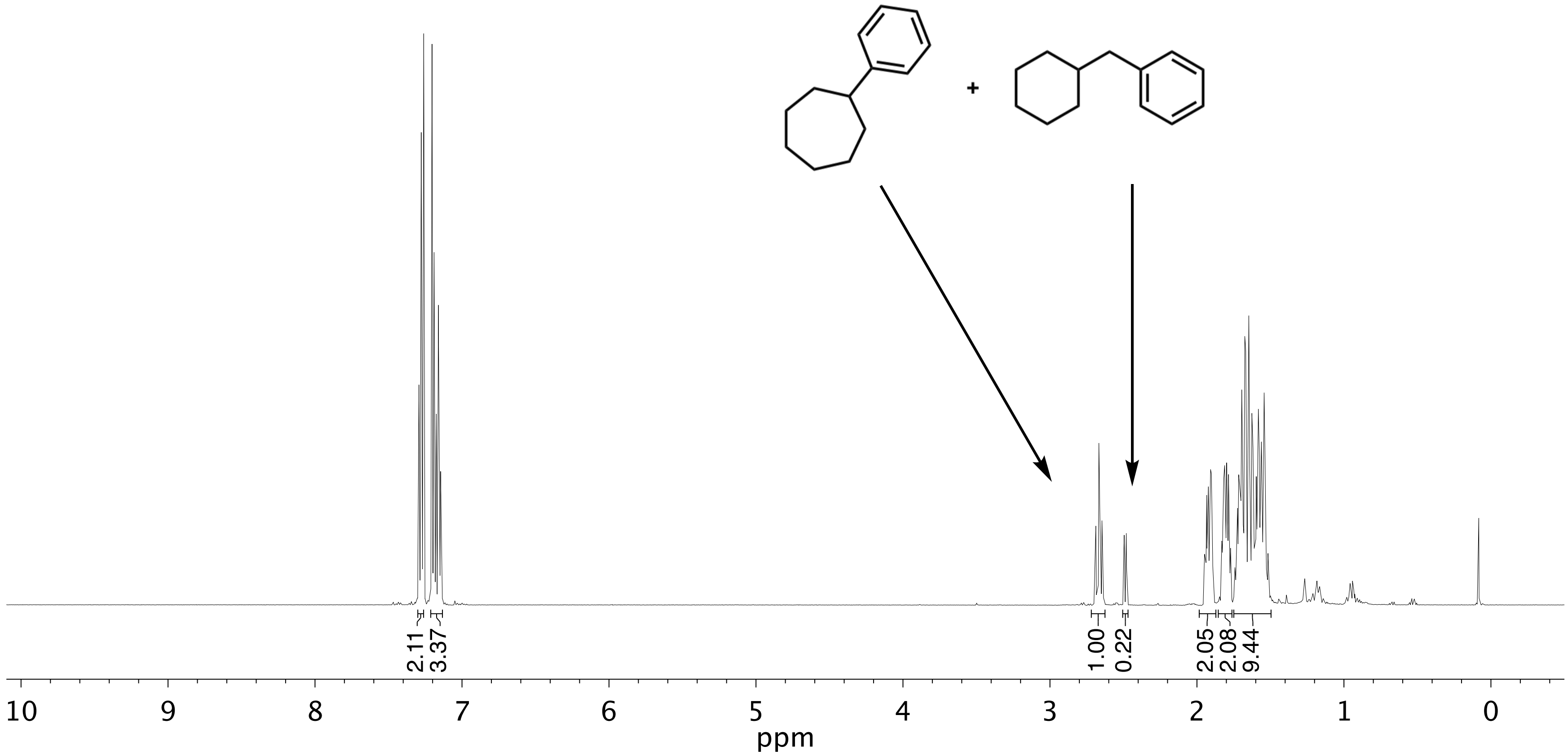
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-25, SI-26**.



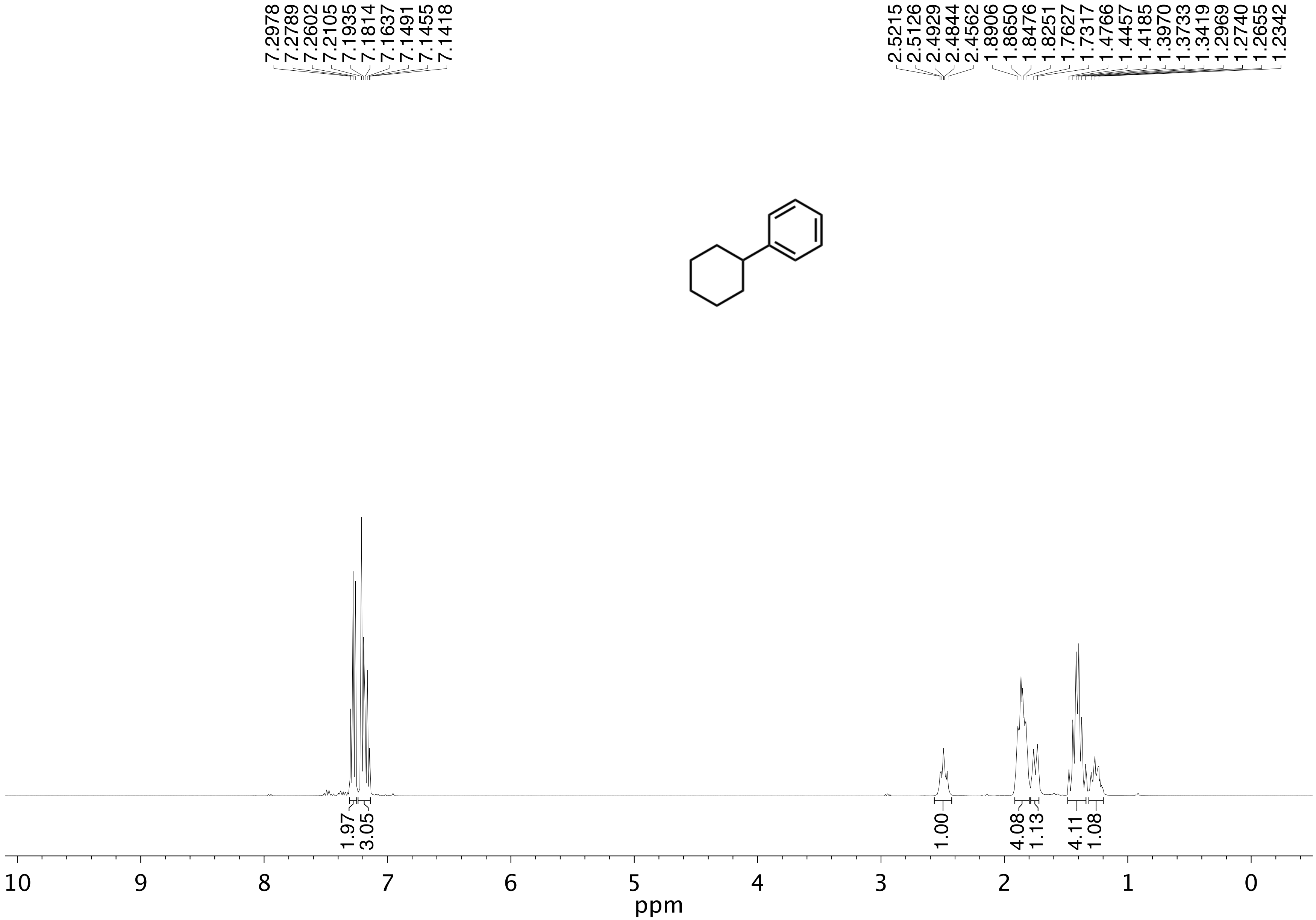
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-27**.



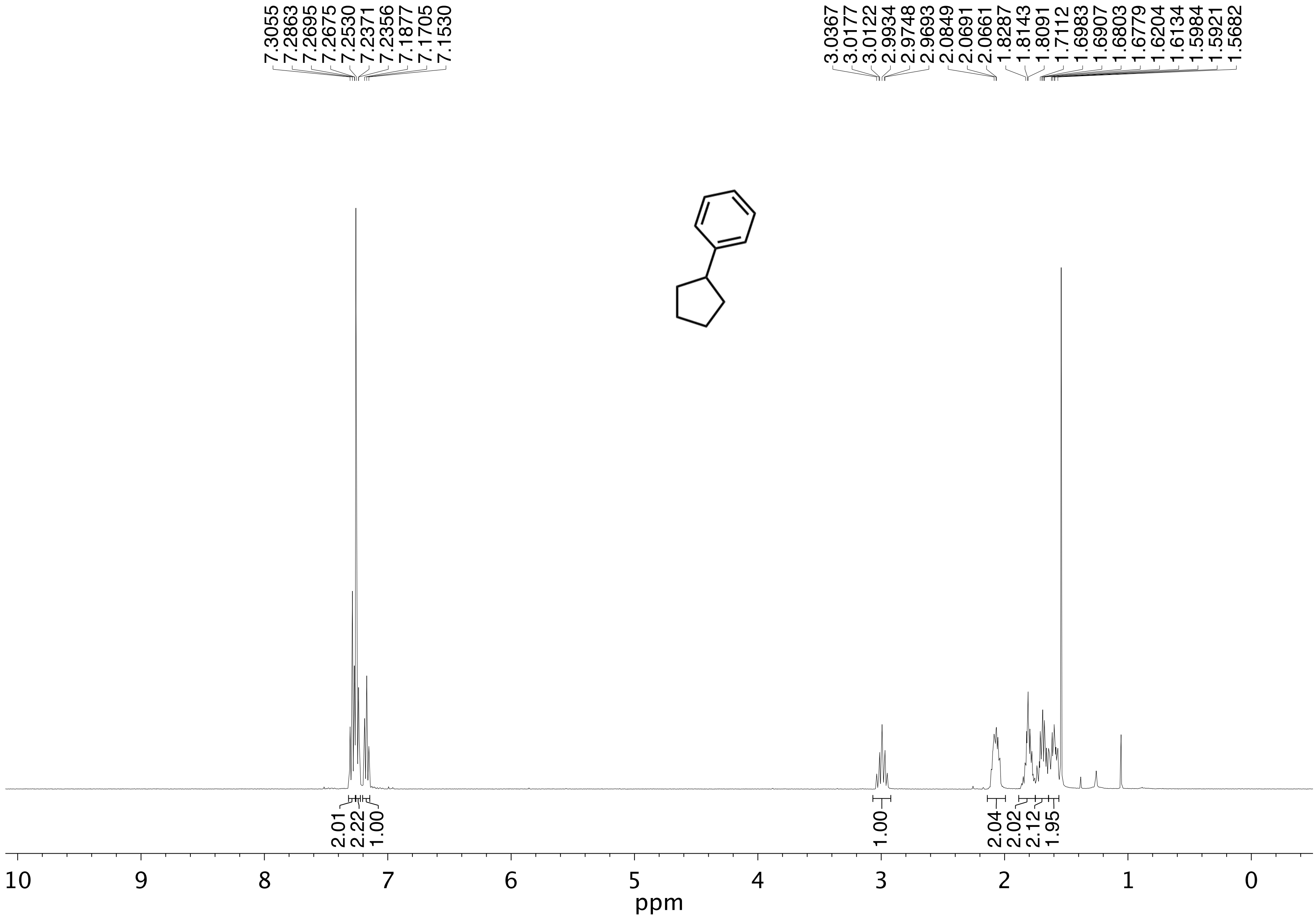
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-28**.



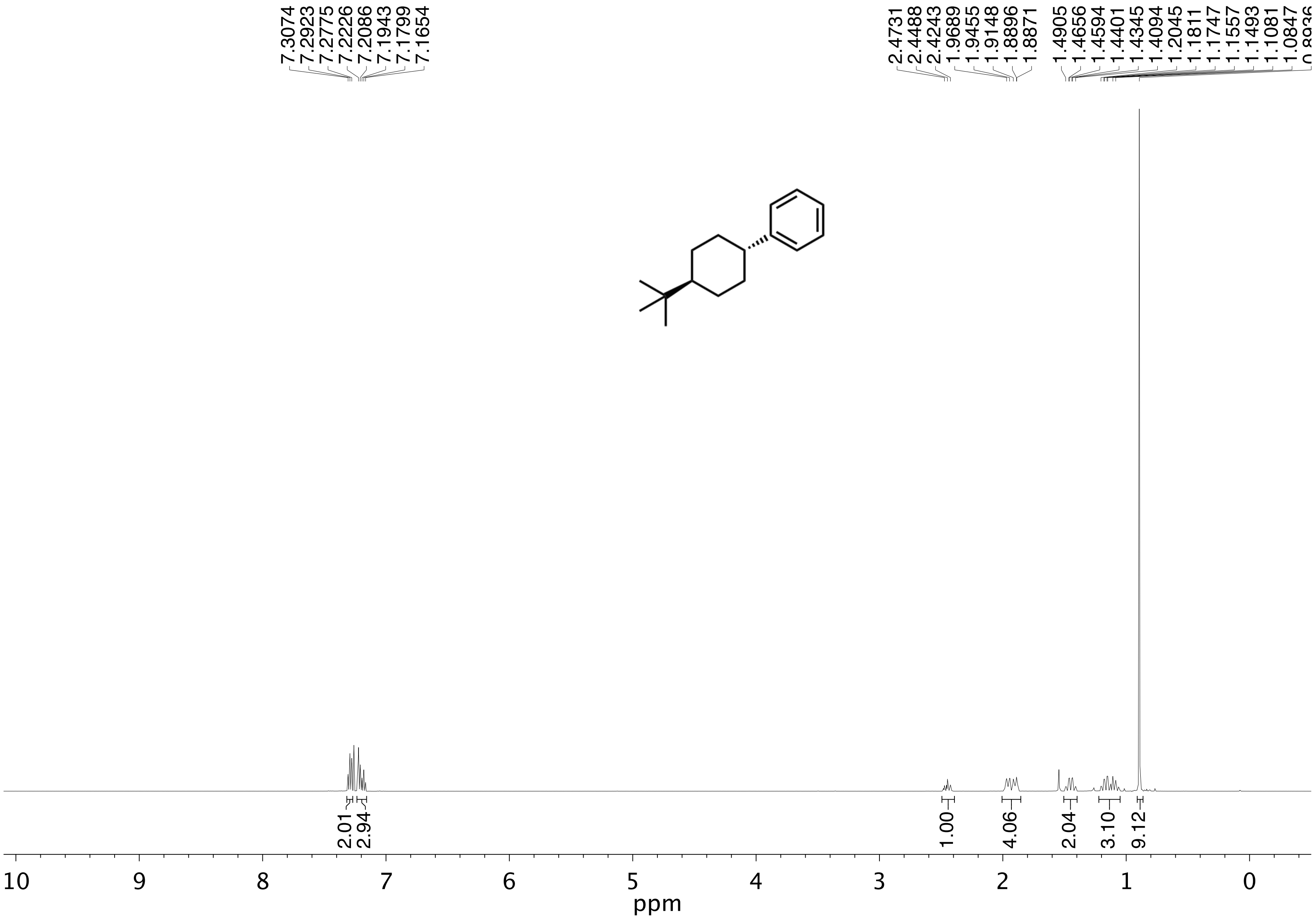
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-29**.



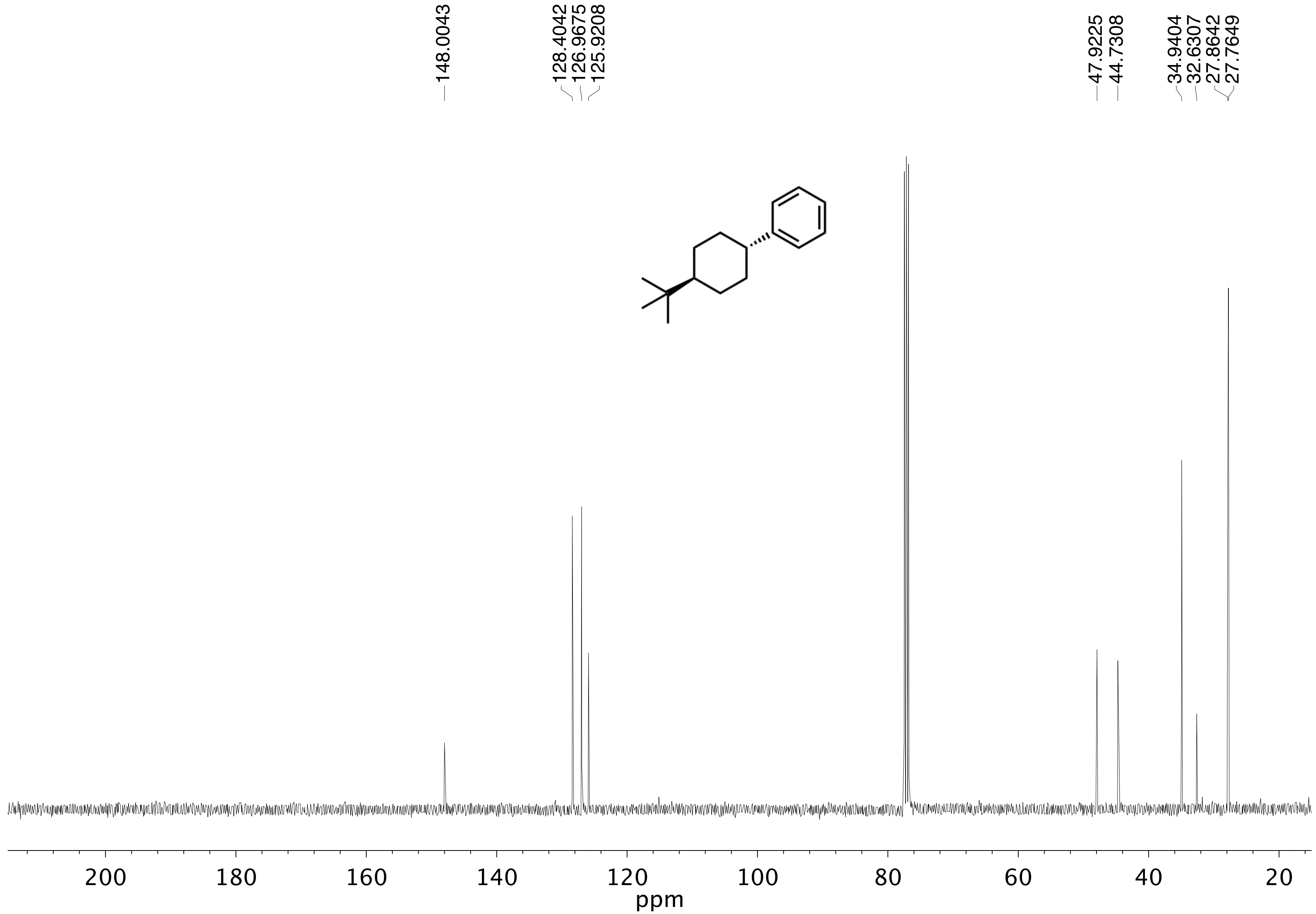
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-30**.



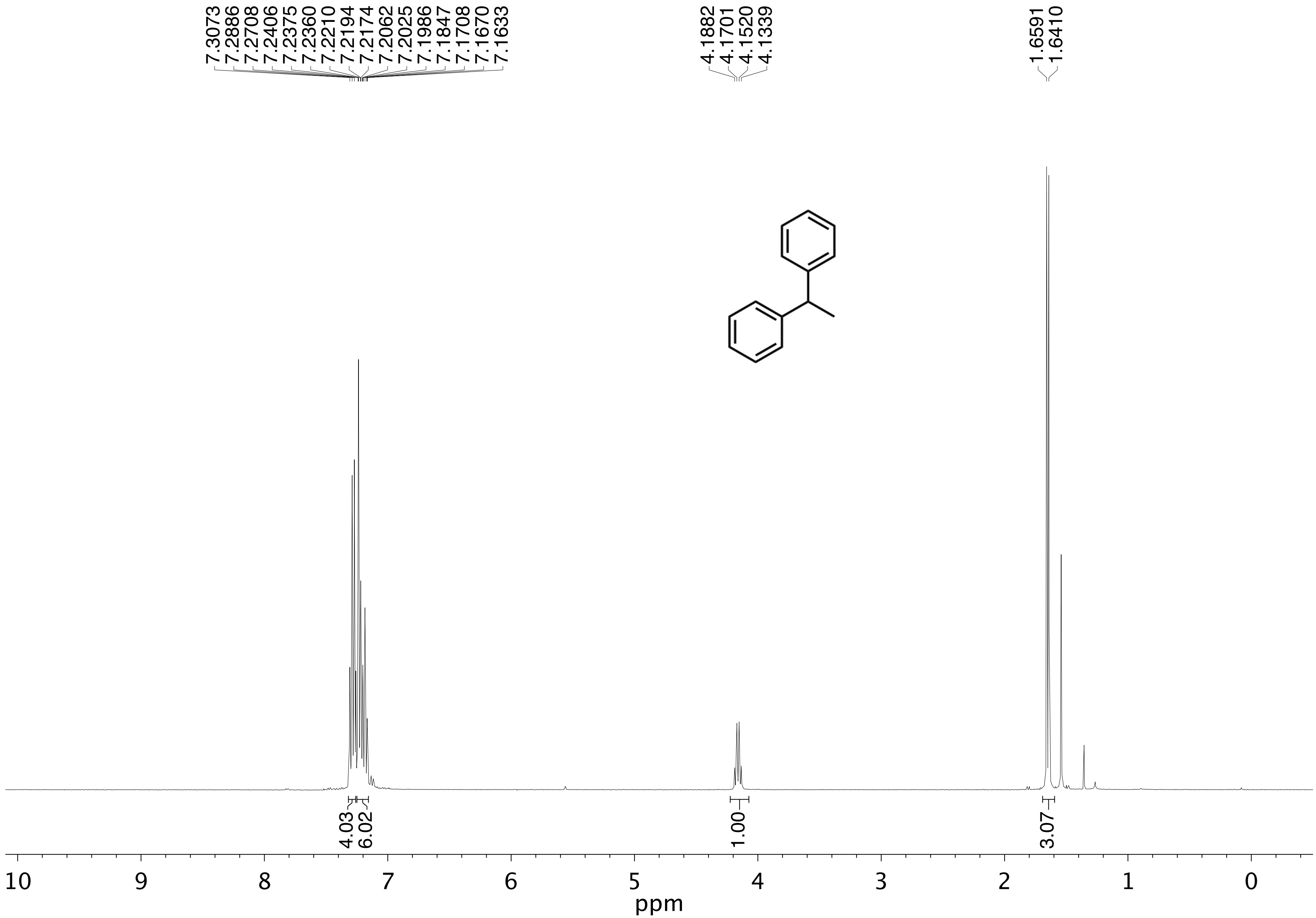
^{1}H NMR (400 MHz, CDCl$_3$) of compound **SI-31**.



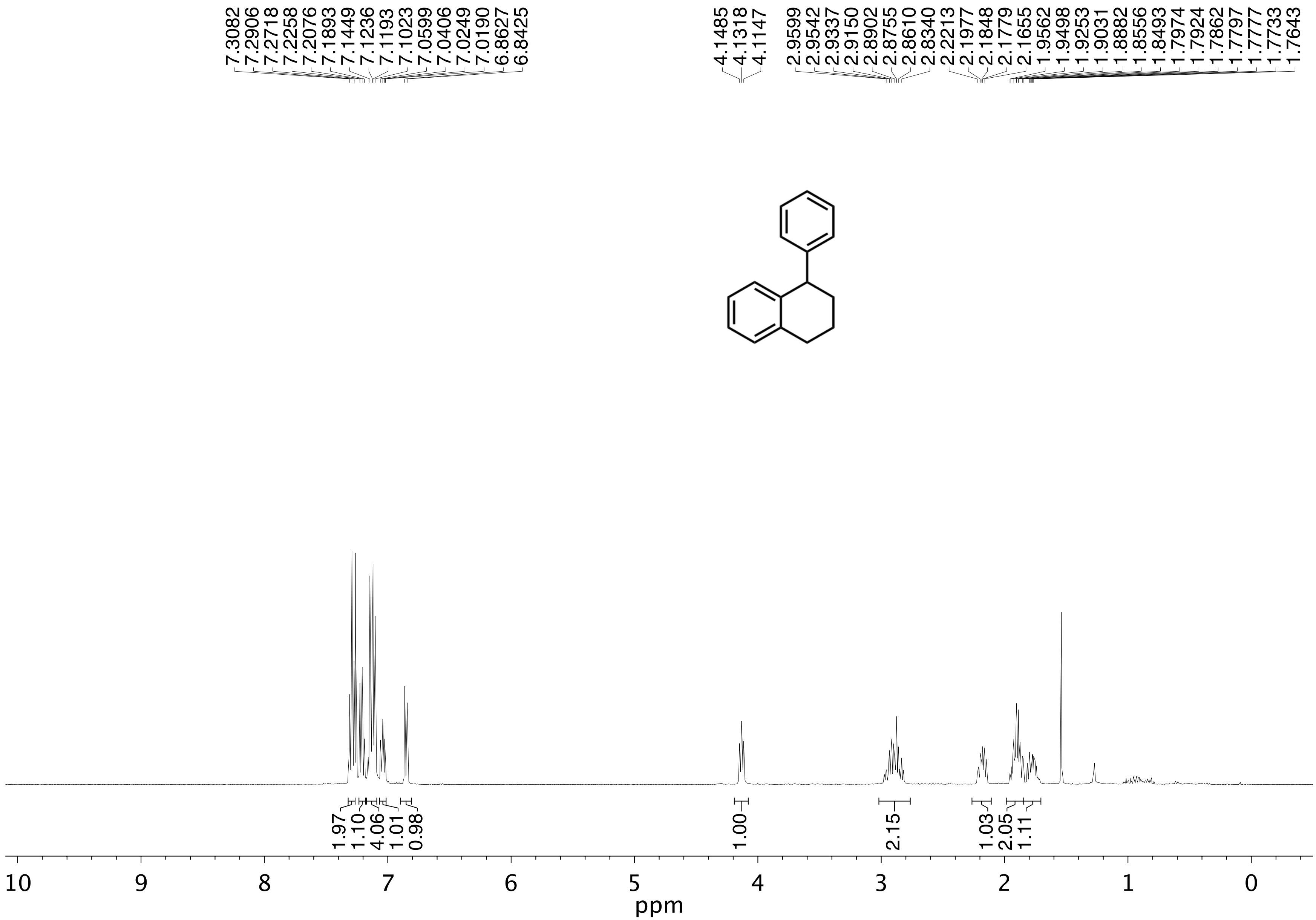
^{1}H NMR (400 MHz, CDCl$_3$) of compound **SI-32**.



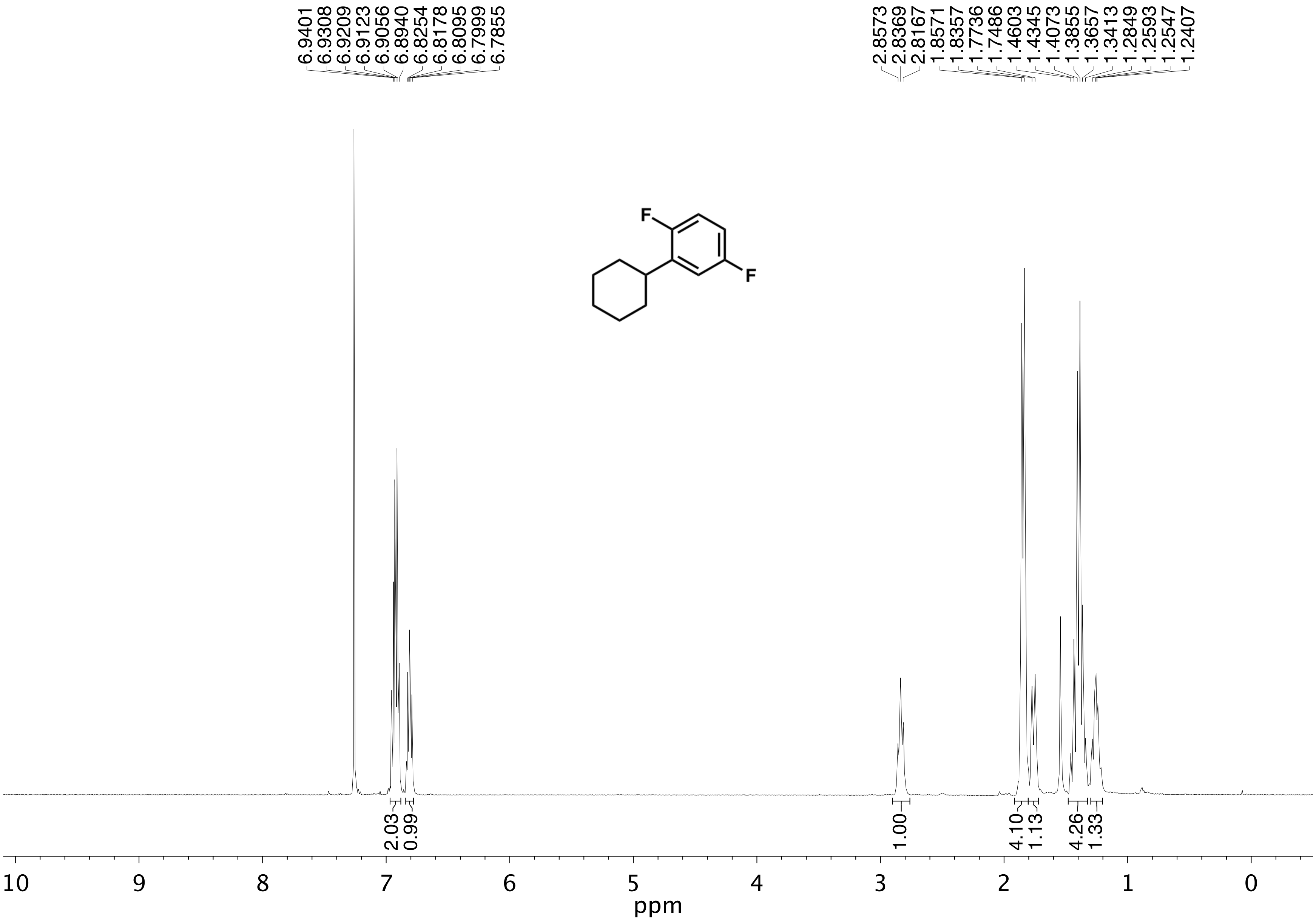
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-32**.



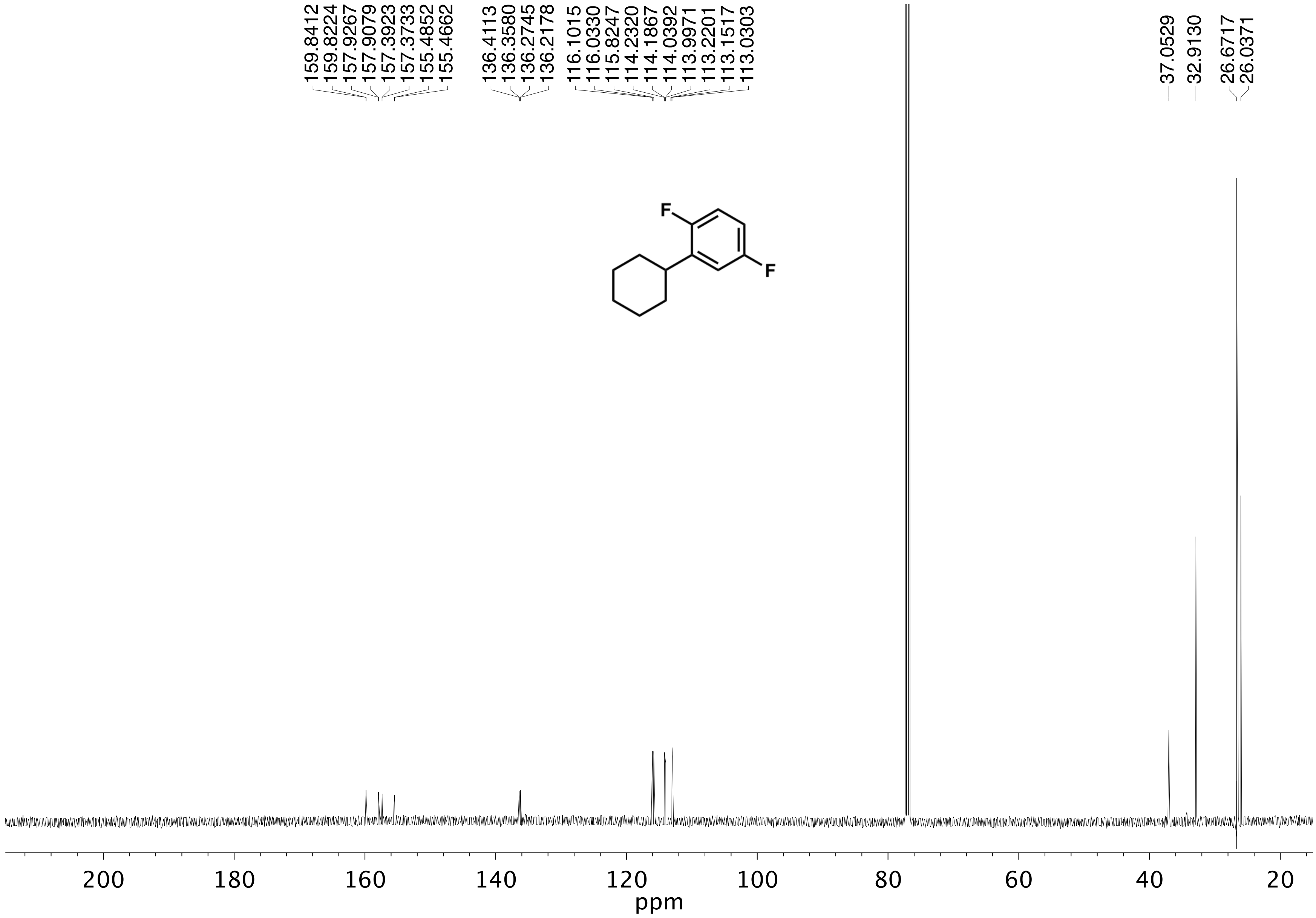
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI-33**.



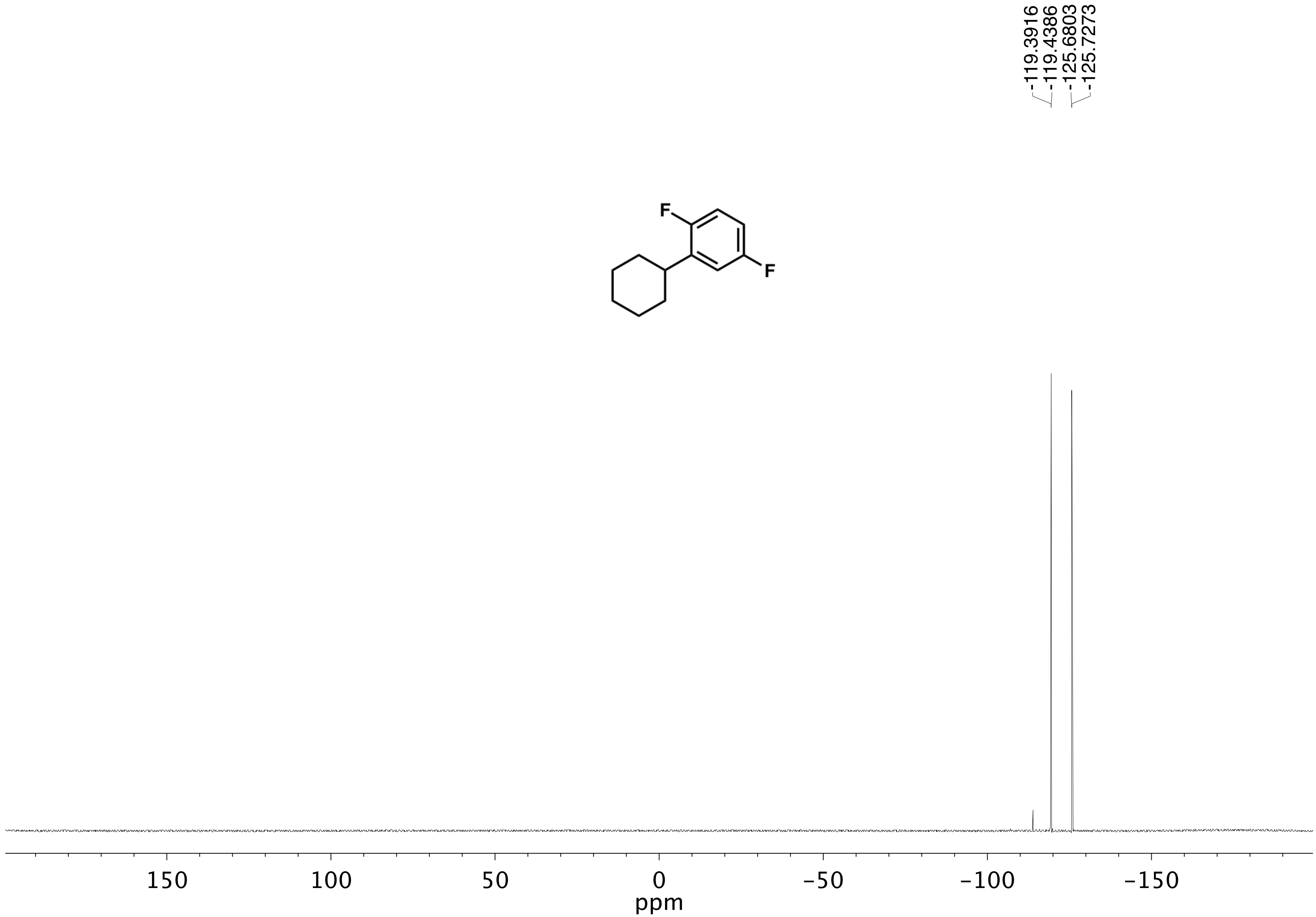
^{1}H NMR (400 MHz, CDCl$_3$) of compound **SI-34**.



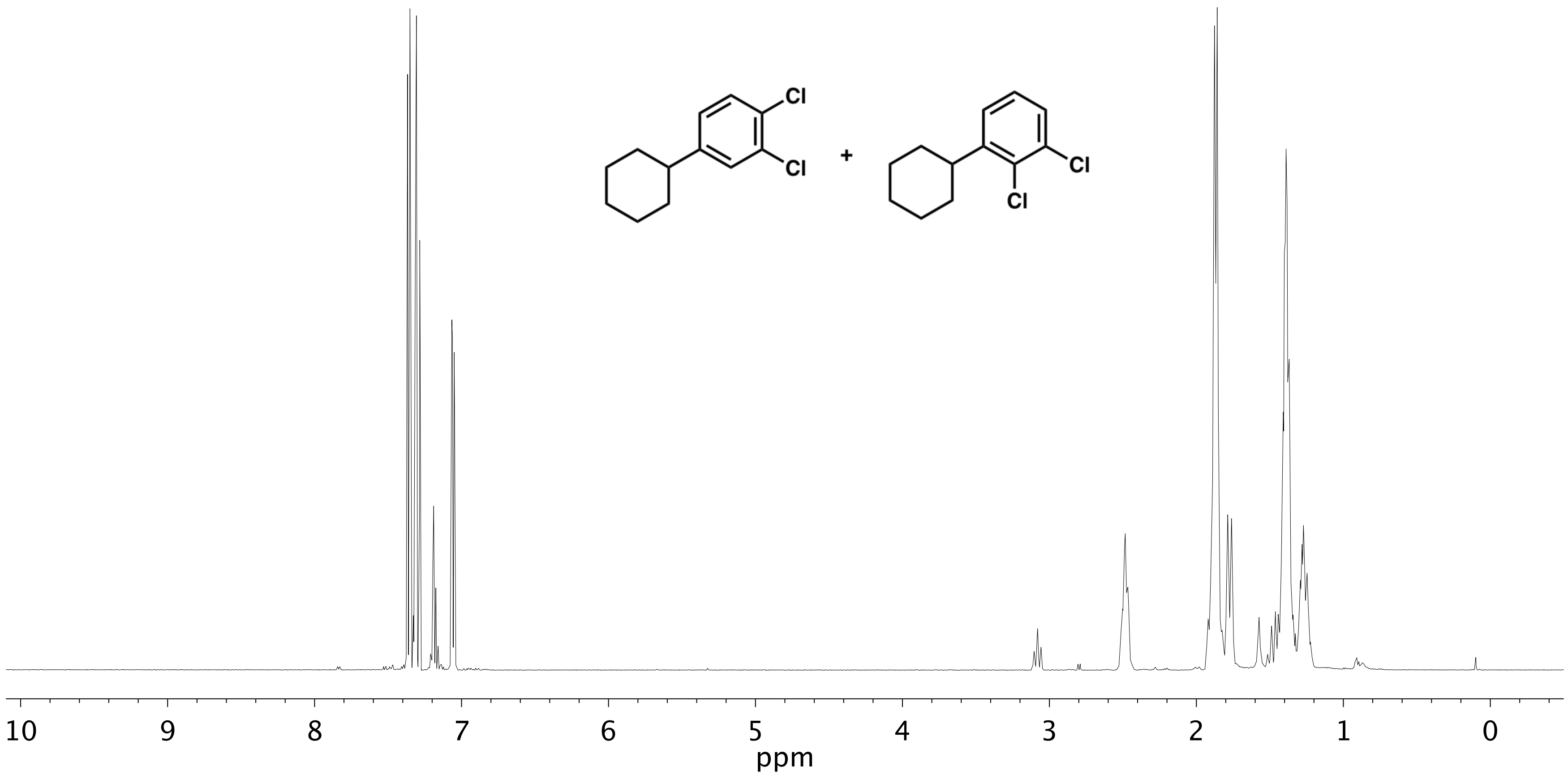
^{1}H NMR (500 MHz, CDCl$_3$) of compound **SI-35**.



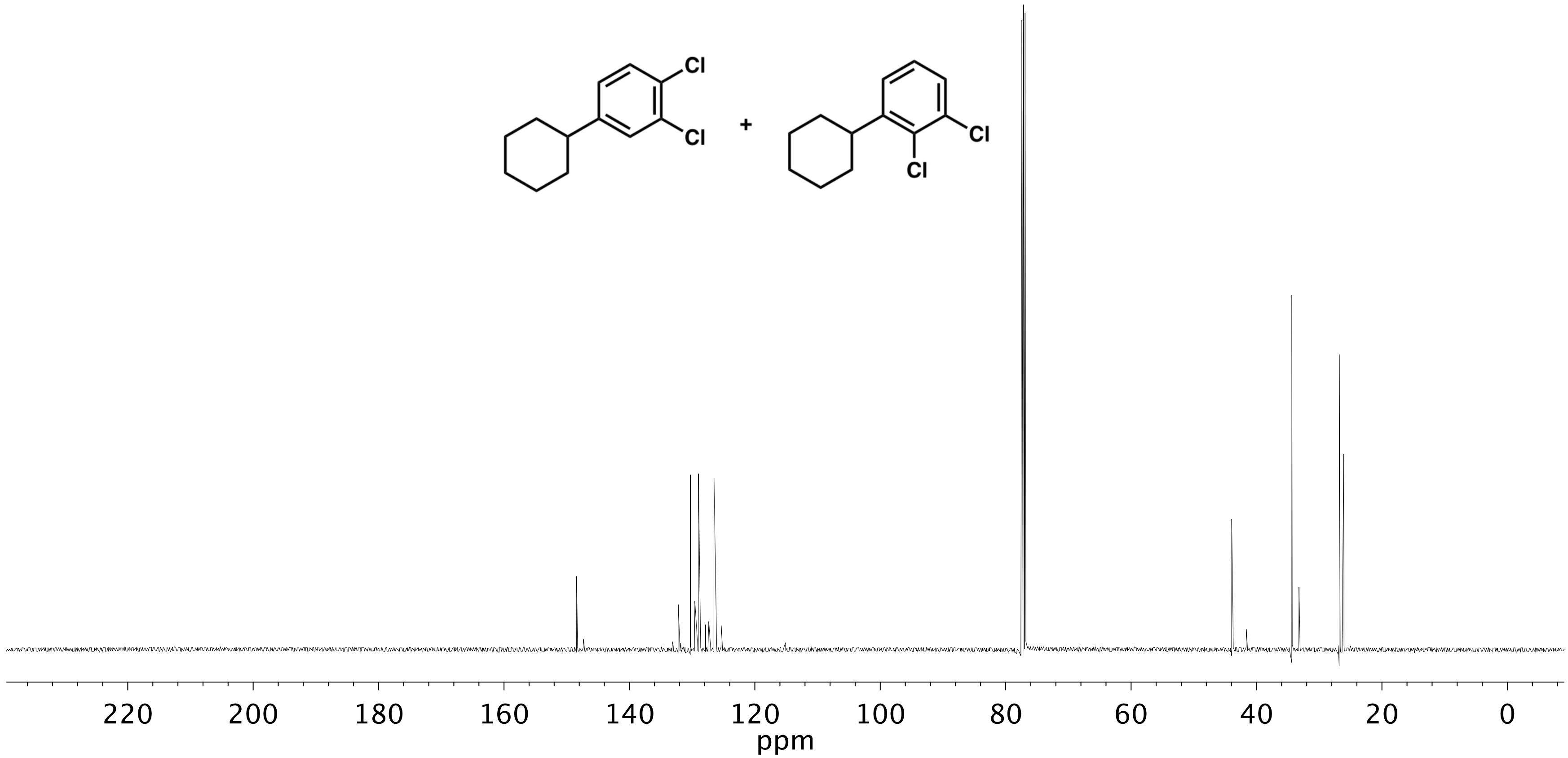
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-35**.



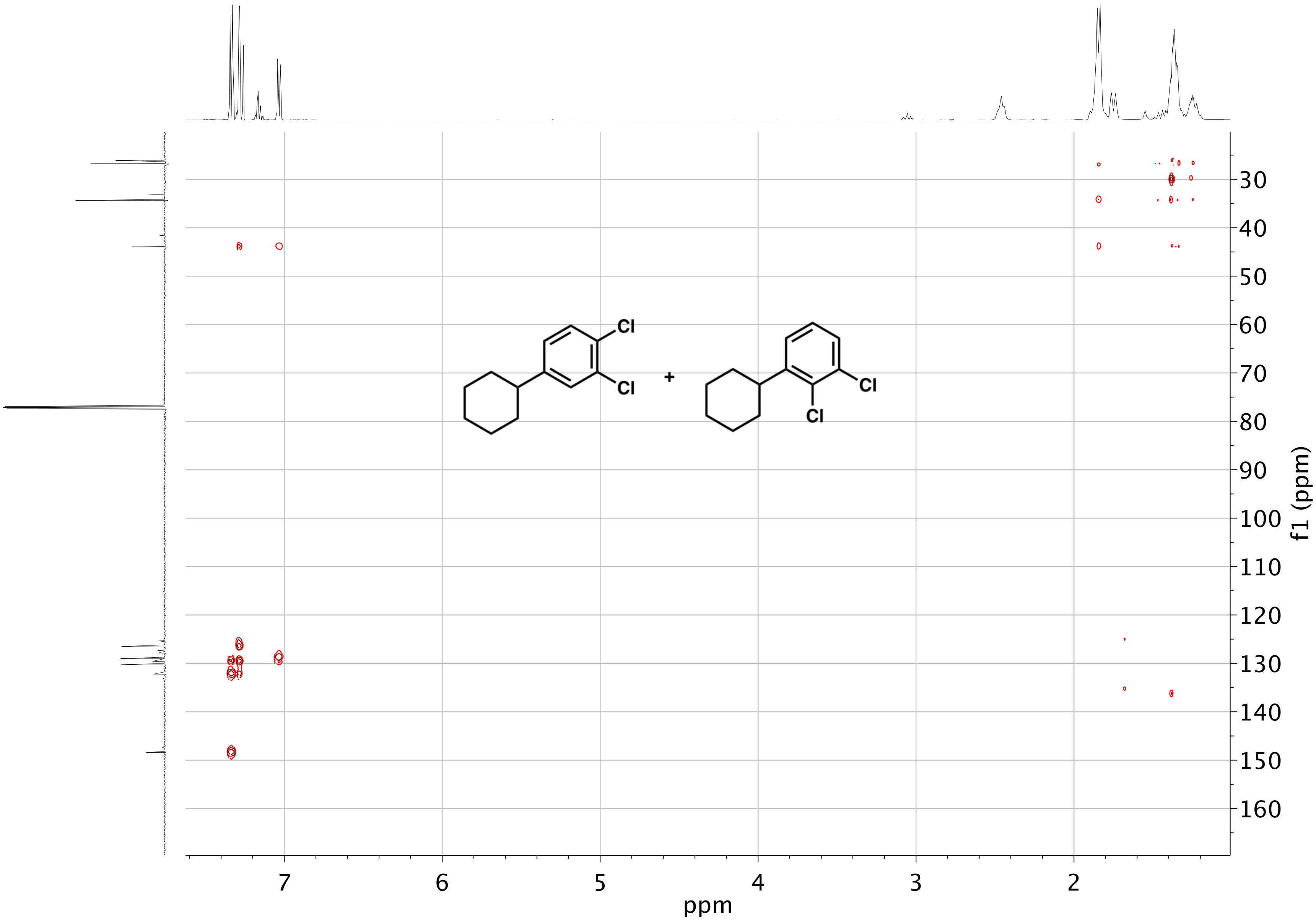
^{19}F NMR (376 MHz, $CDCl_3$) of compound **SI-35**.



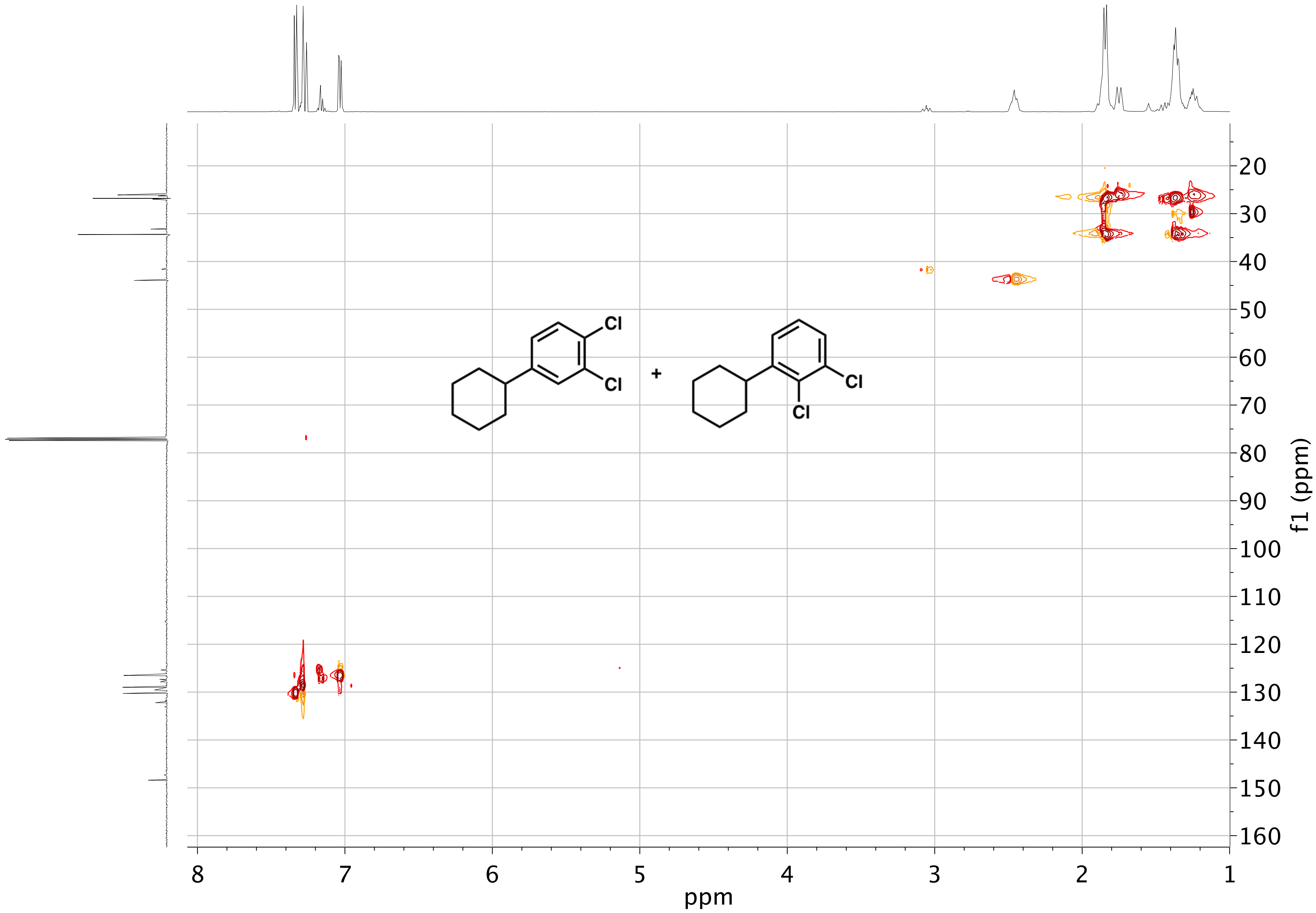
^{1}H NMR (500 MHz, $CDCl_3$) of **SI-36**.



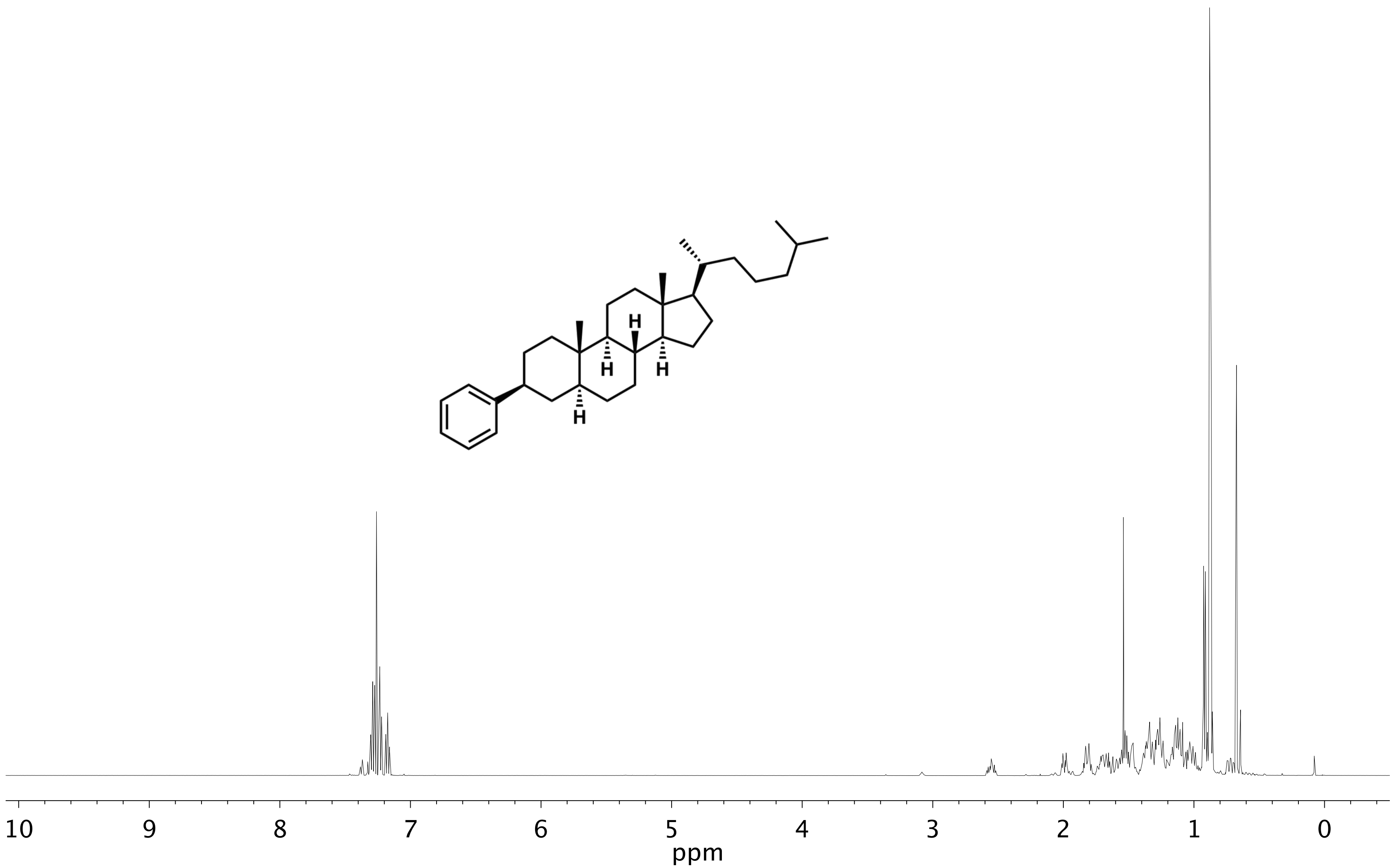
^{13}C NMR (125 MHz, CDCl$_3$) of compound **SI-36**.



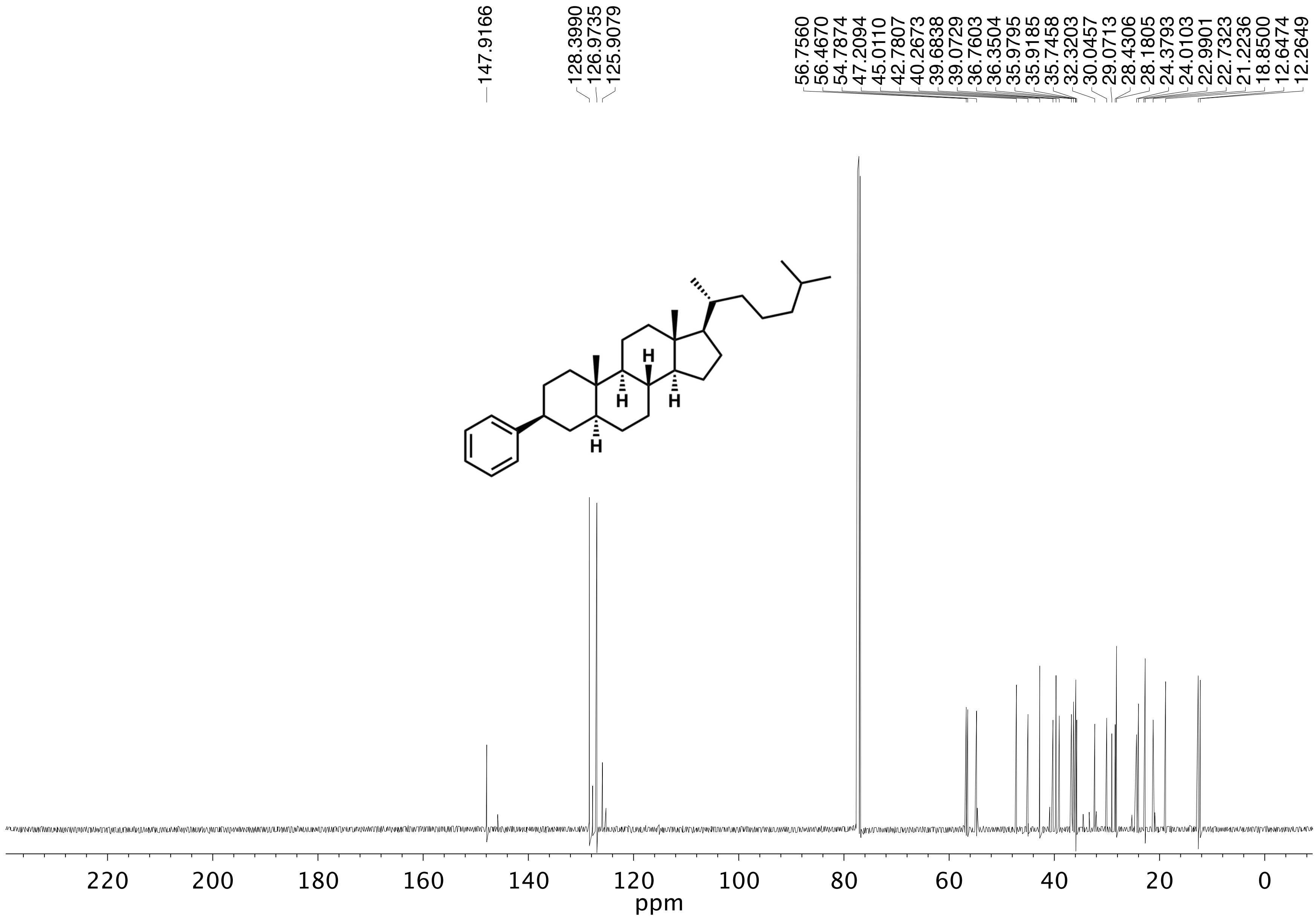
2D HMBC NMR (500 MHz, CDCl$_3$) of compound **SI-36**.



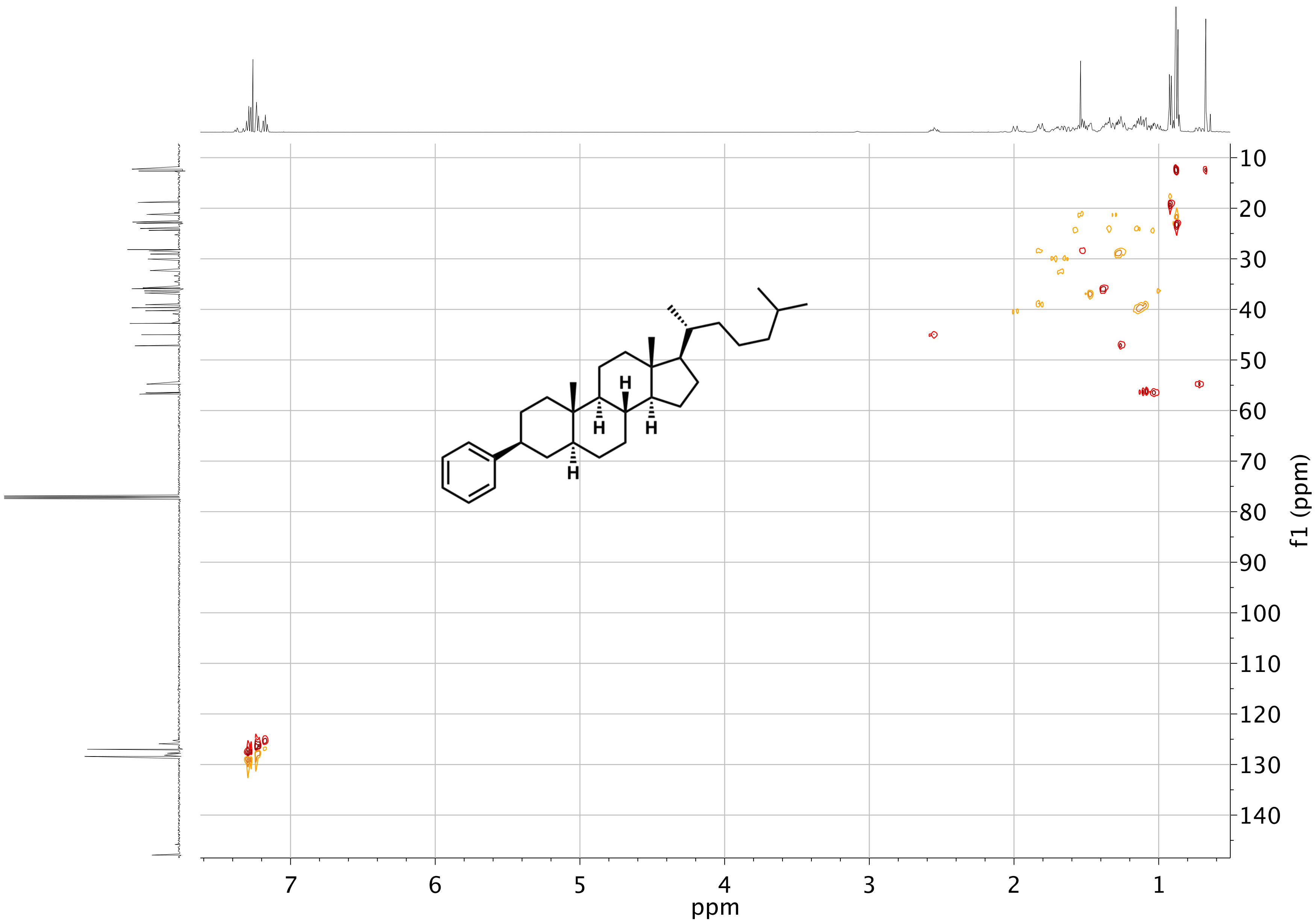
2D HSQC NMR (500 MHz, $CDCl_3$) of compound **SI-36**.



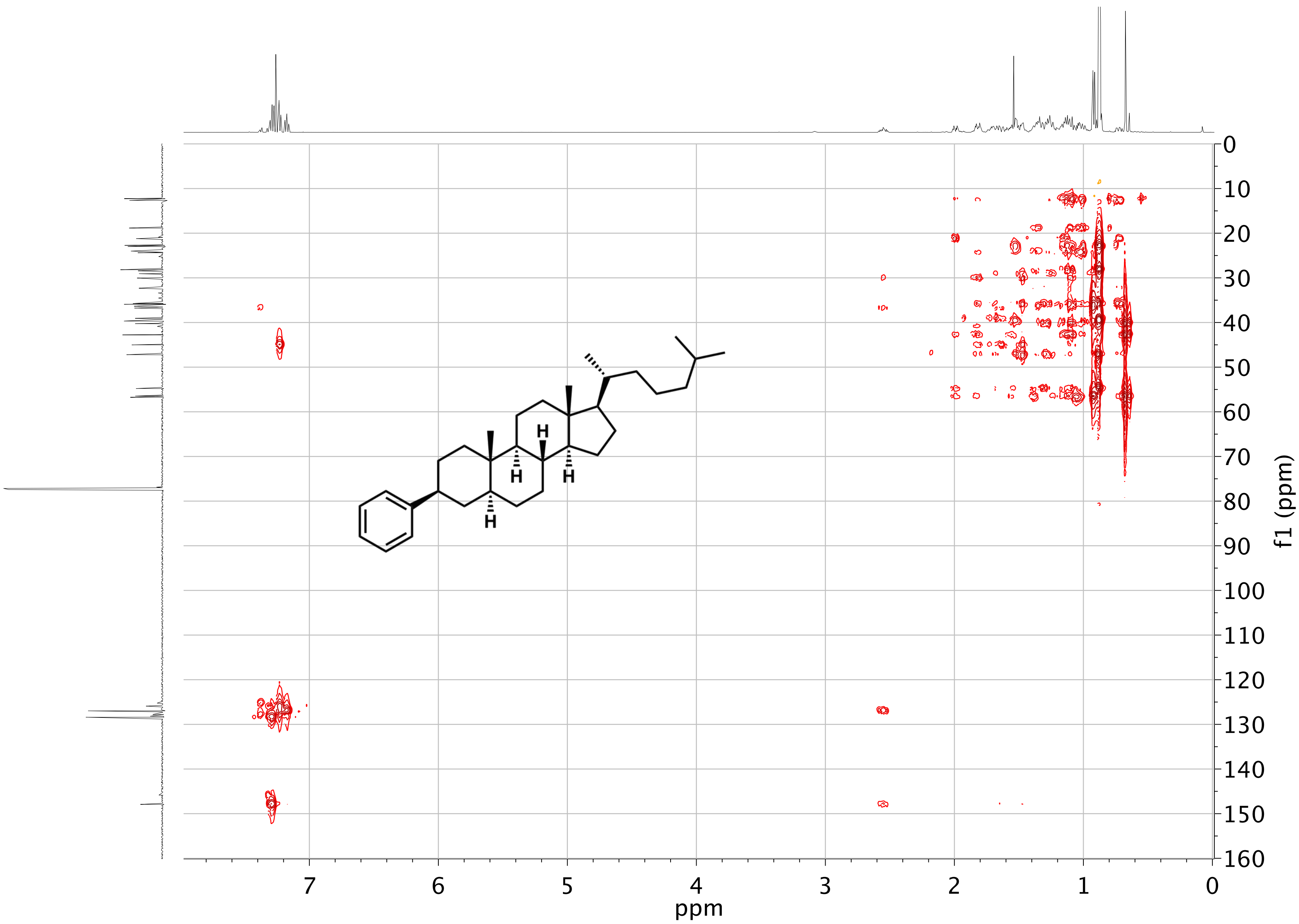
^{1}H NMR (500 MHz, CDCl$_3$) of **SI-37**.



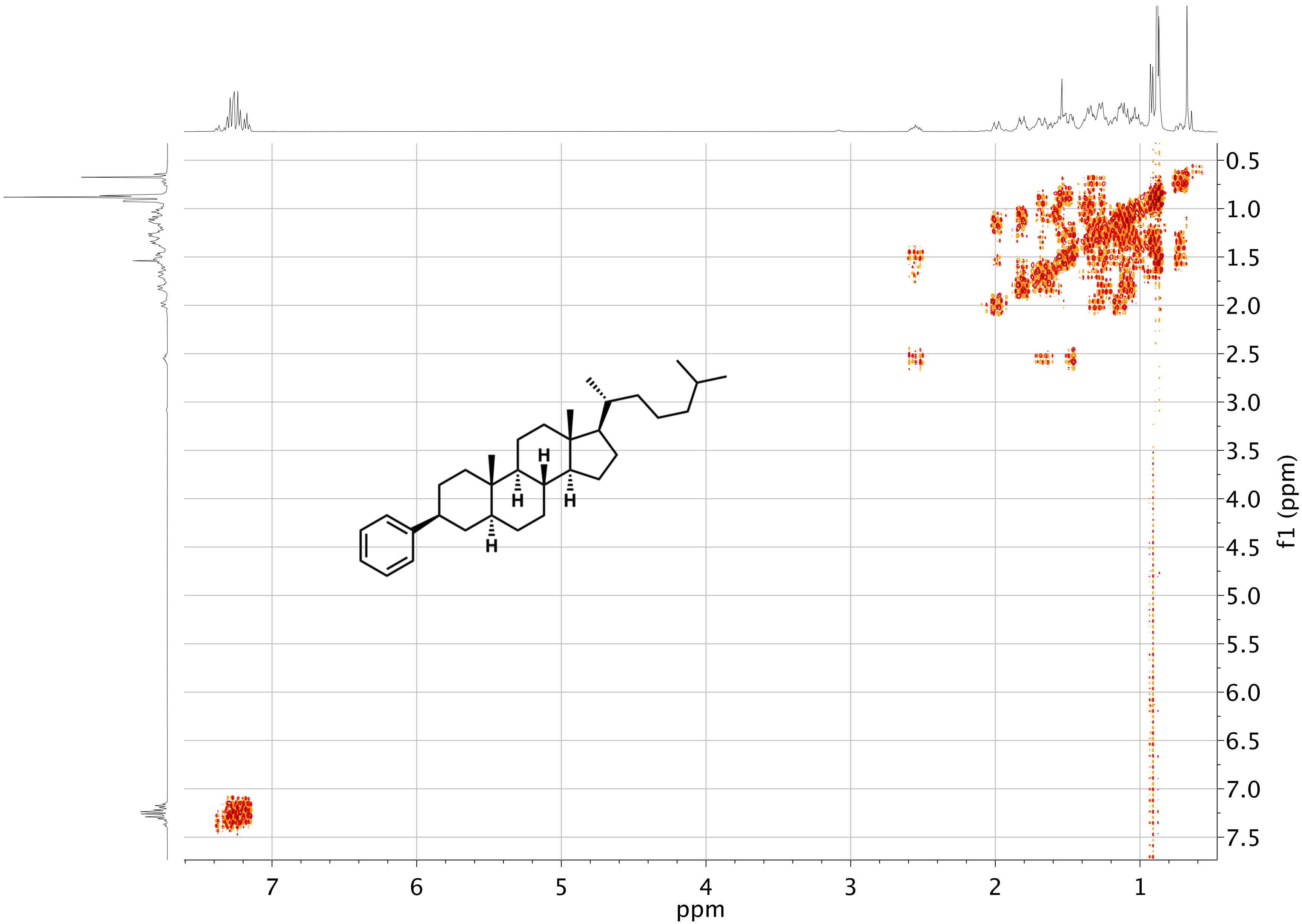
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-37**.



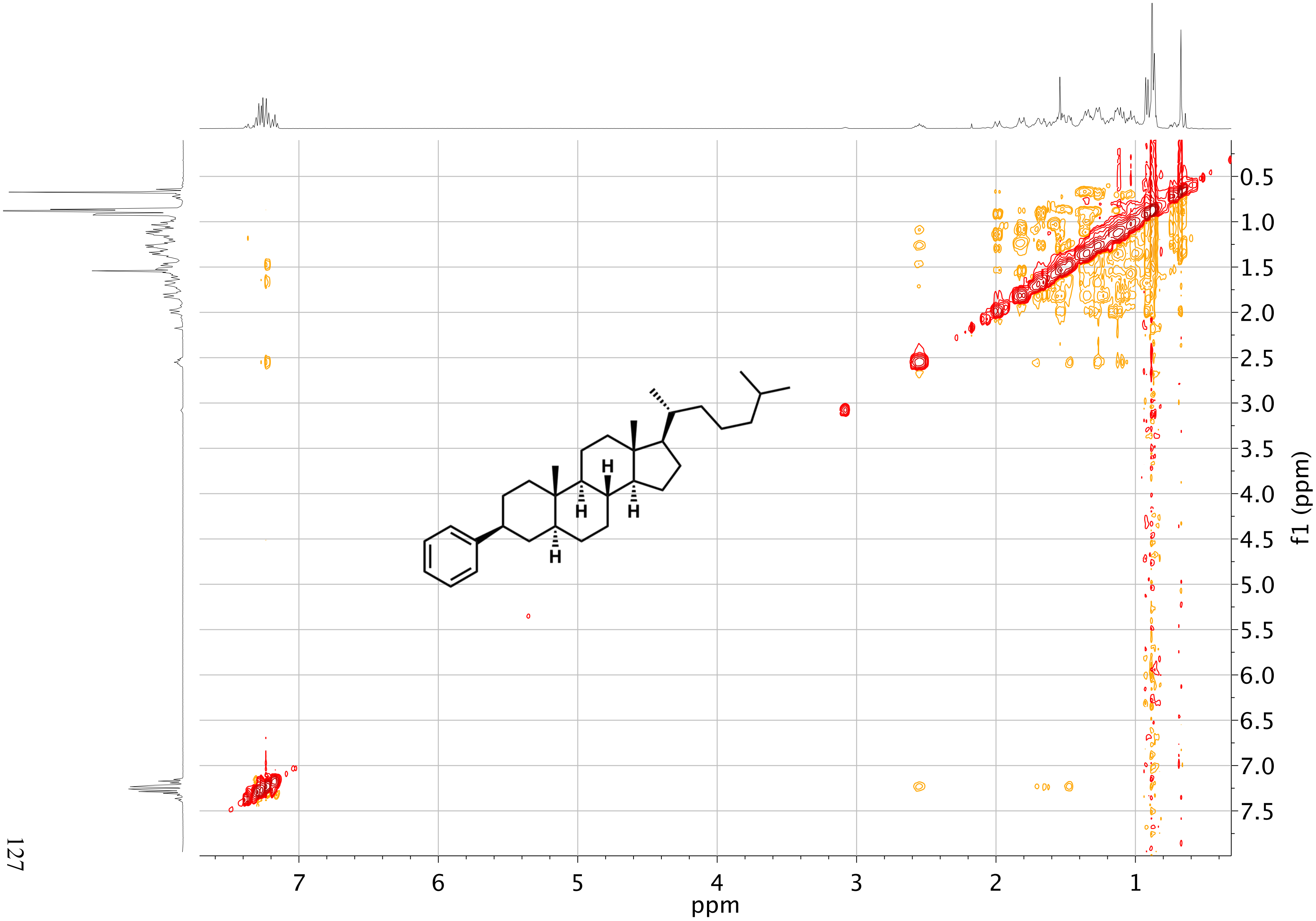
2D HSQC NMR (500 MHz, $CDCl_3$) of **SI-37**.



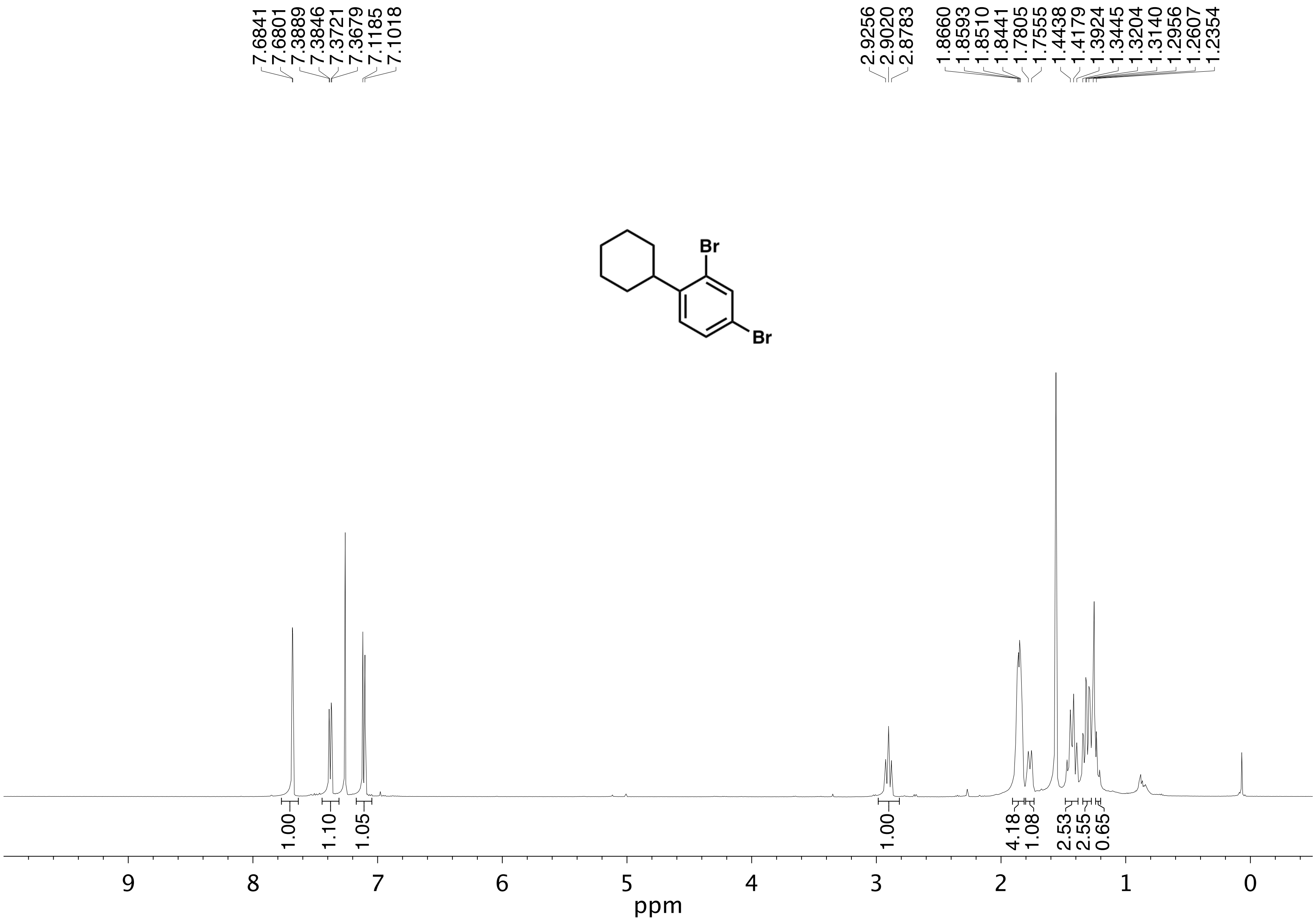
HMBC NMR (500 MHz, CDCl$_3$) of **SI-37**.



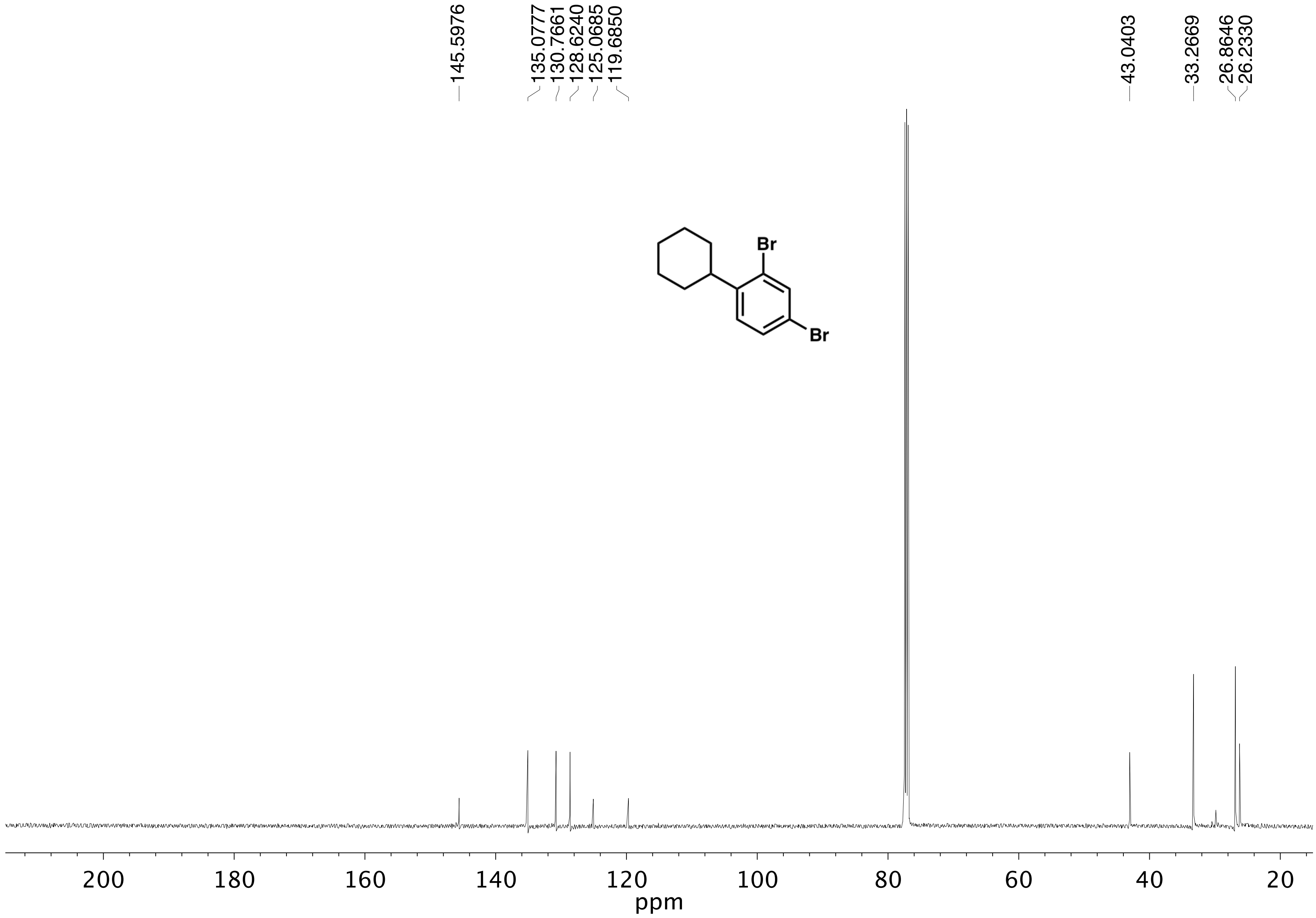
^{1}H COSY NMR (400 MHz, CDCl$_3$) of **SI-37**.



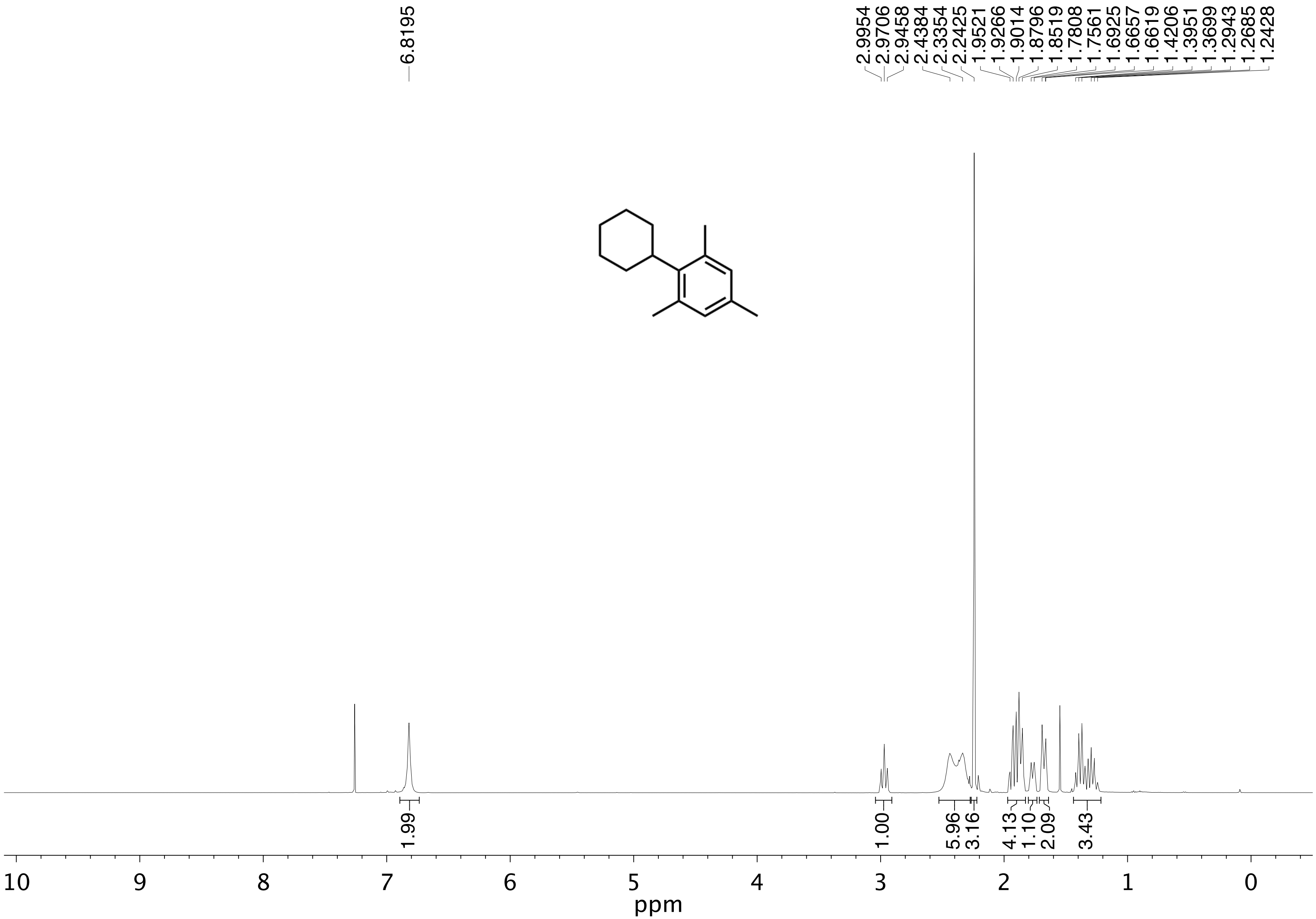
^{1}H NOESY NMR (500 MHz, $CDCl_3$) of **SI-37**.



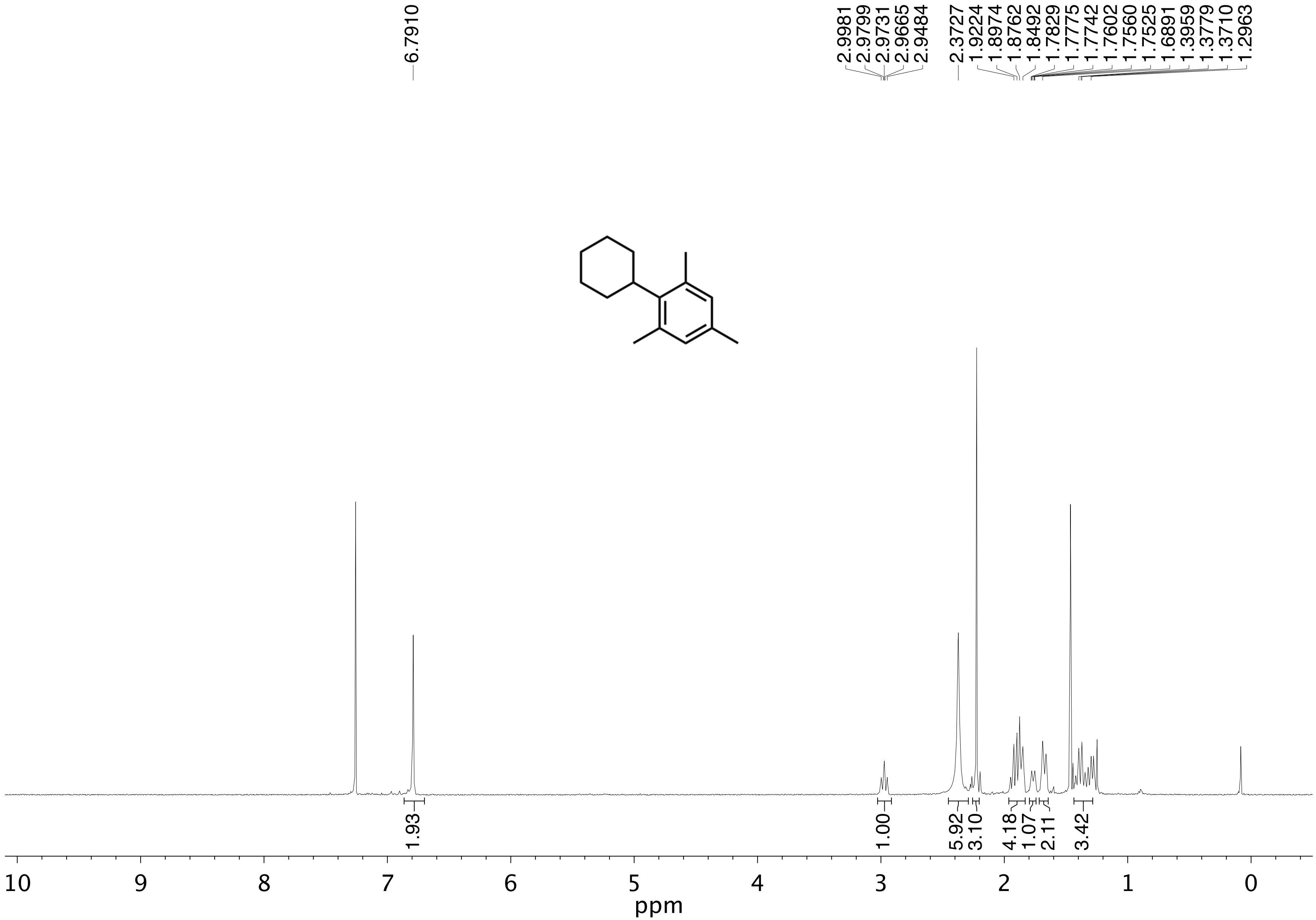
^{1}H NMR (500 MHz, $CDCl_3$) of **SI-38**.



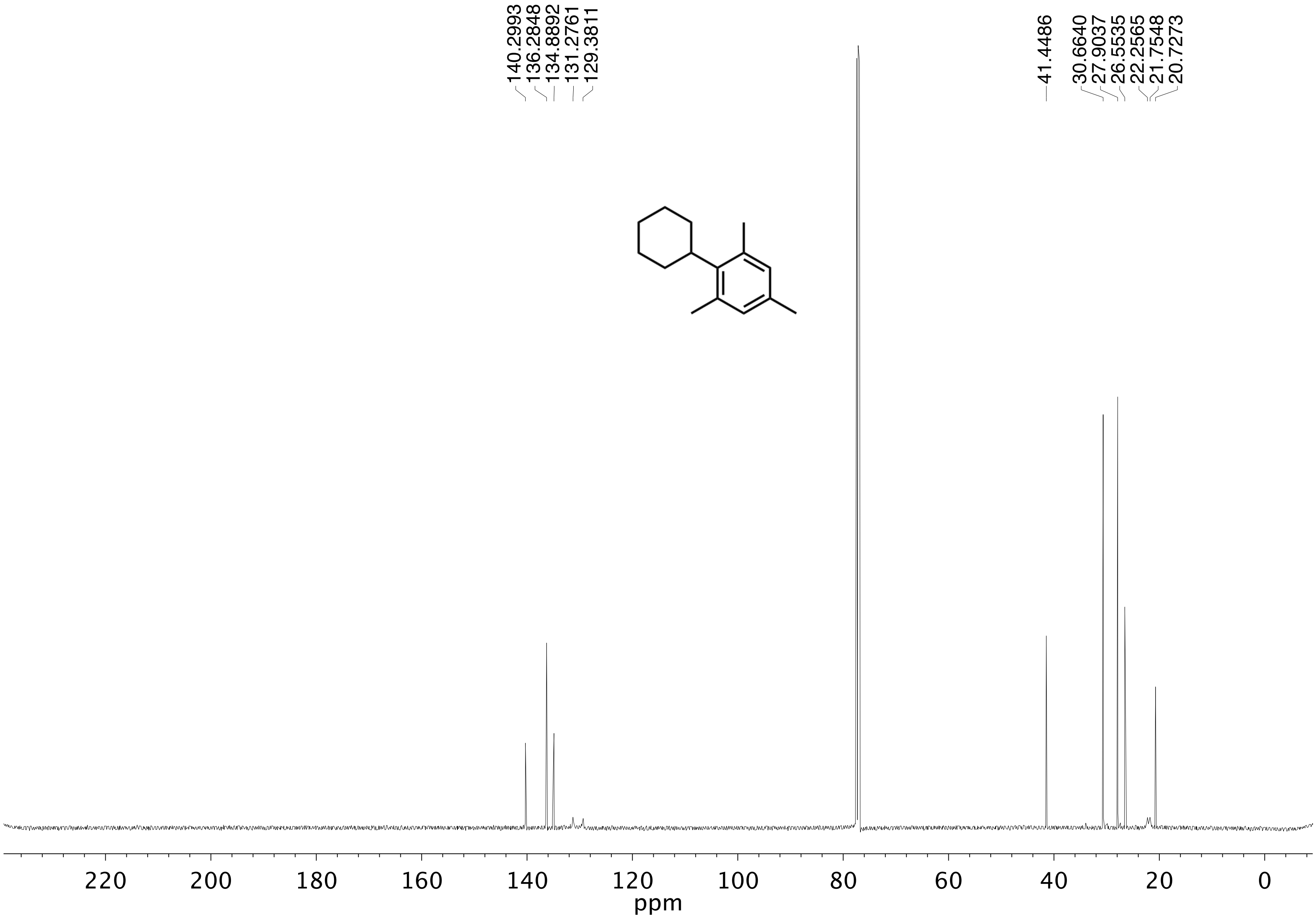
^{13}C NMR (125 MHz, $CDCl_3$) of **SI-38**.



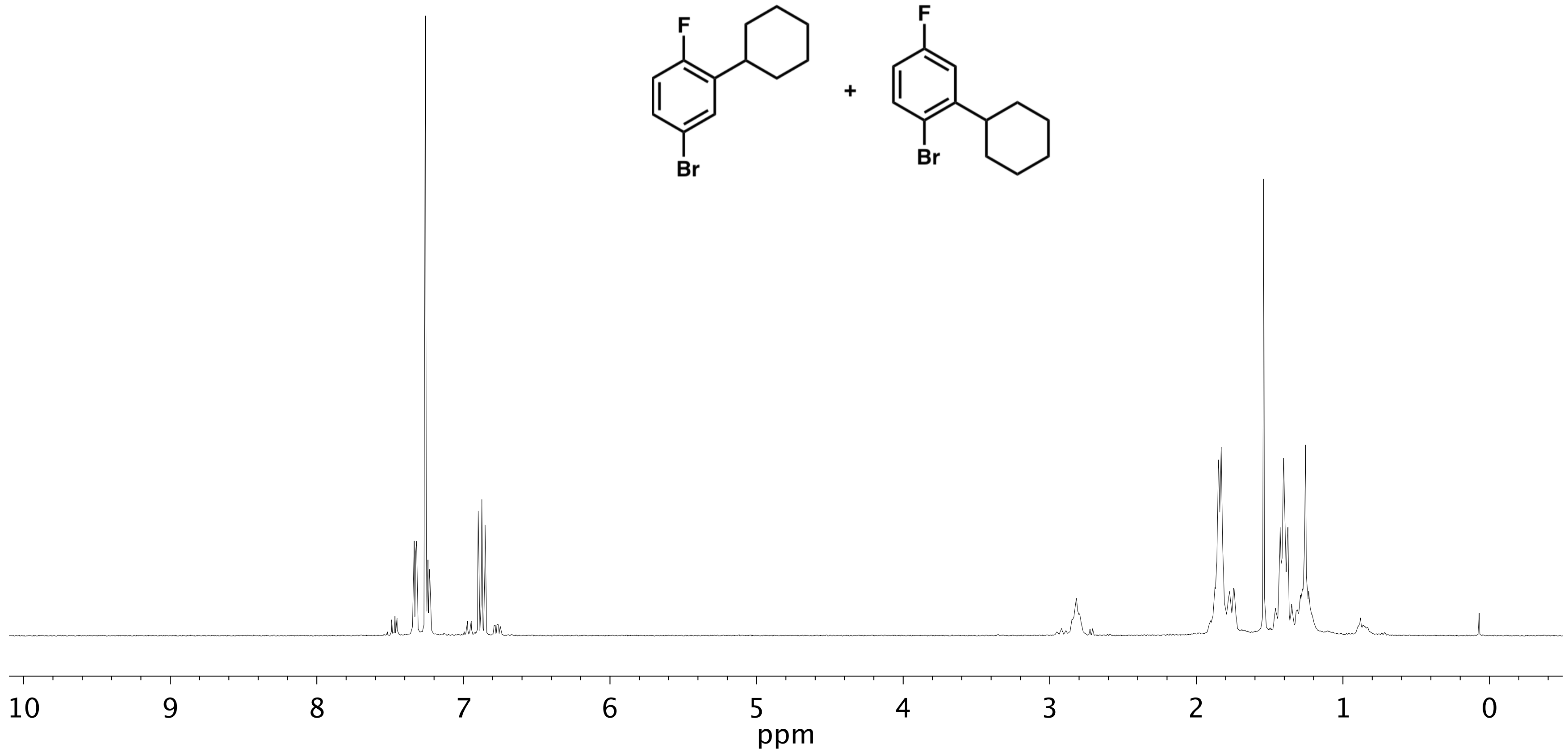
^{1}H NMR (500 MHz, CDCl$_3$) of **SI-39**.



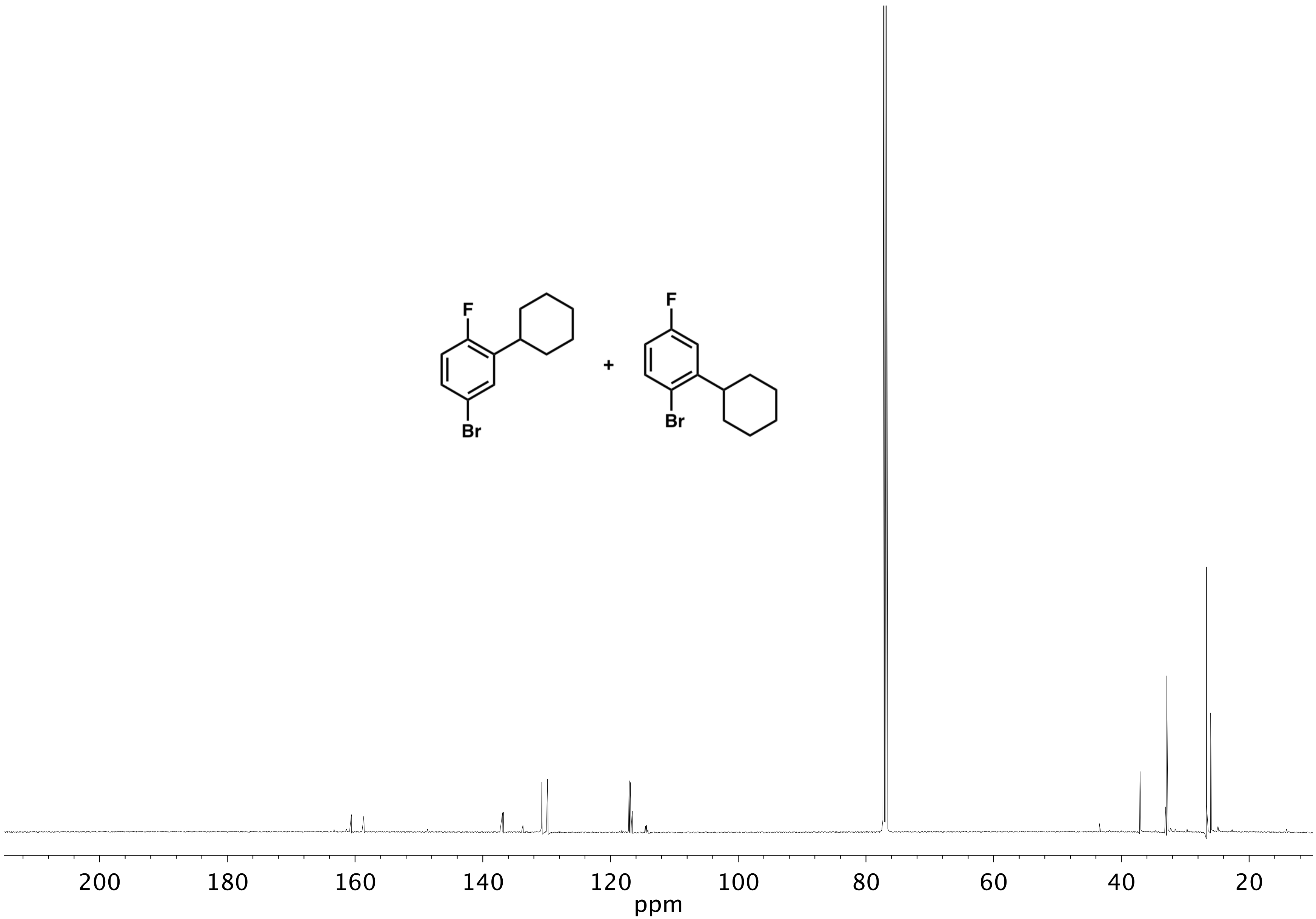
^{1}H NMR (500 MHz, 57 °C, CDCl$_3$) of **SI-39**.



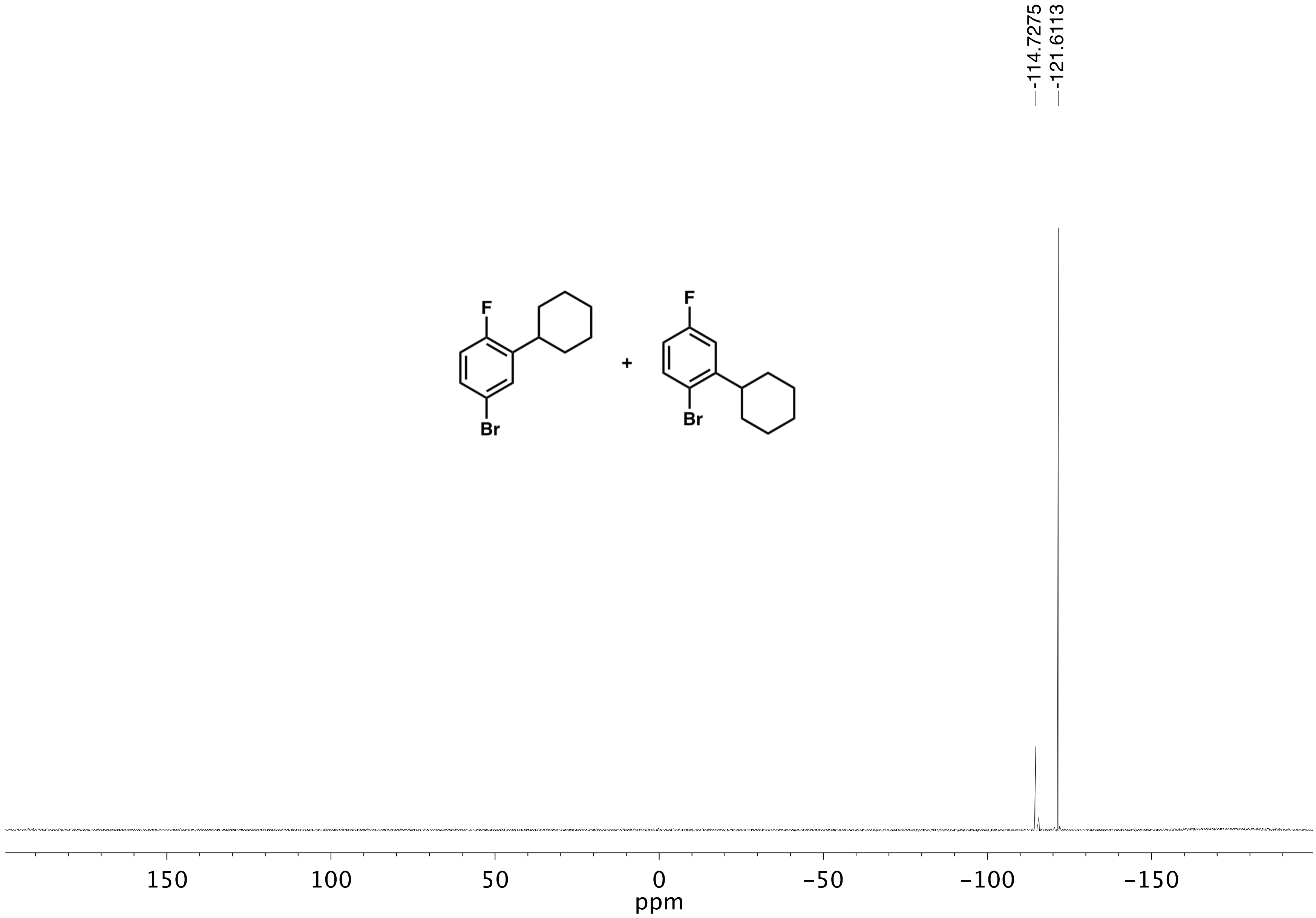
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-39**.



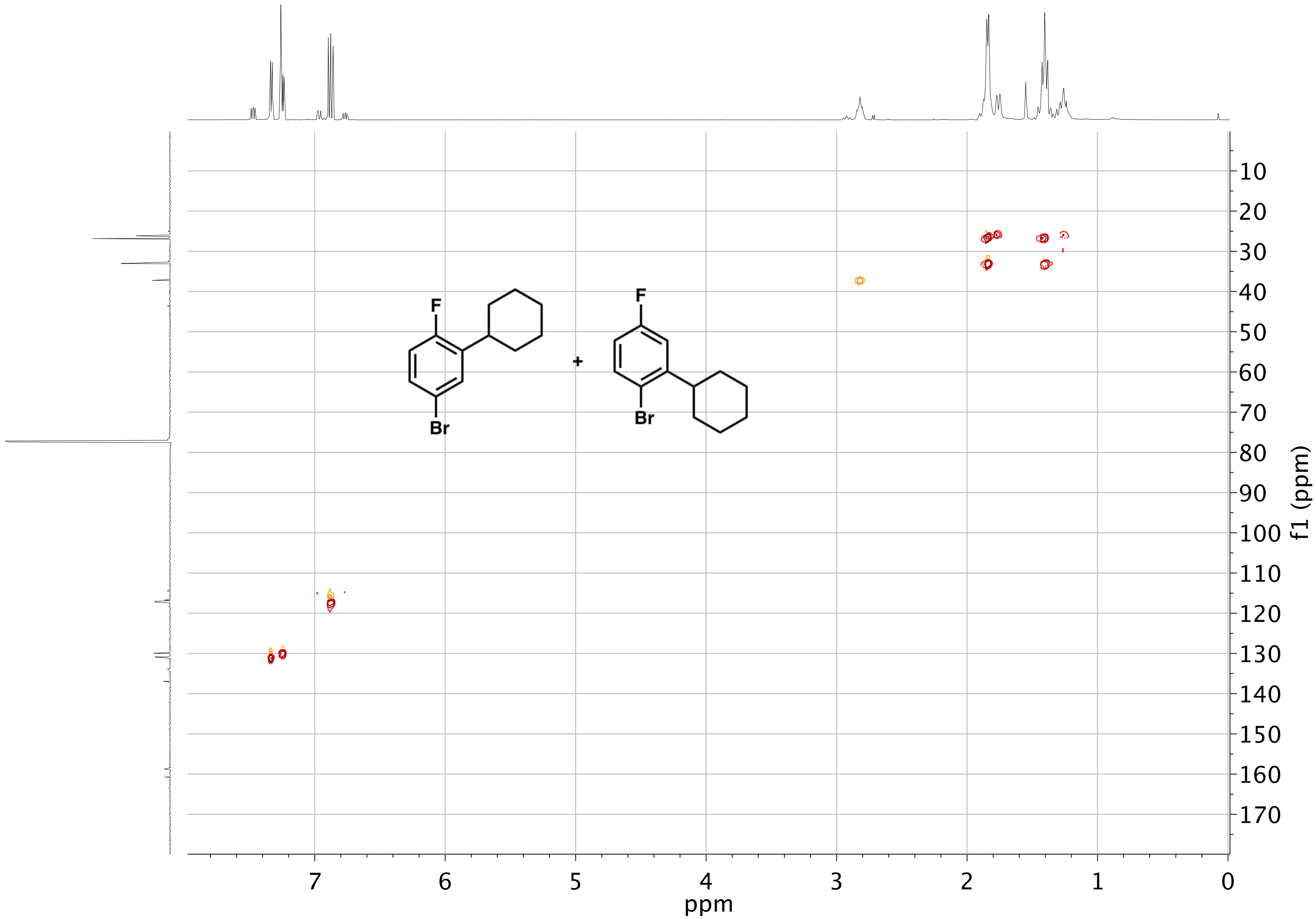
^{1}H NMR (500 MHz, CDCl$_3$) of **SI-40**.



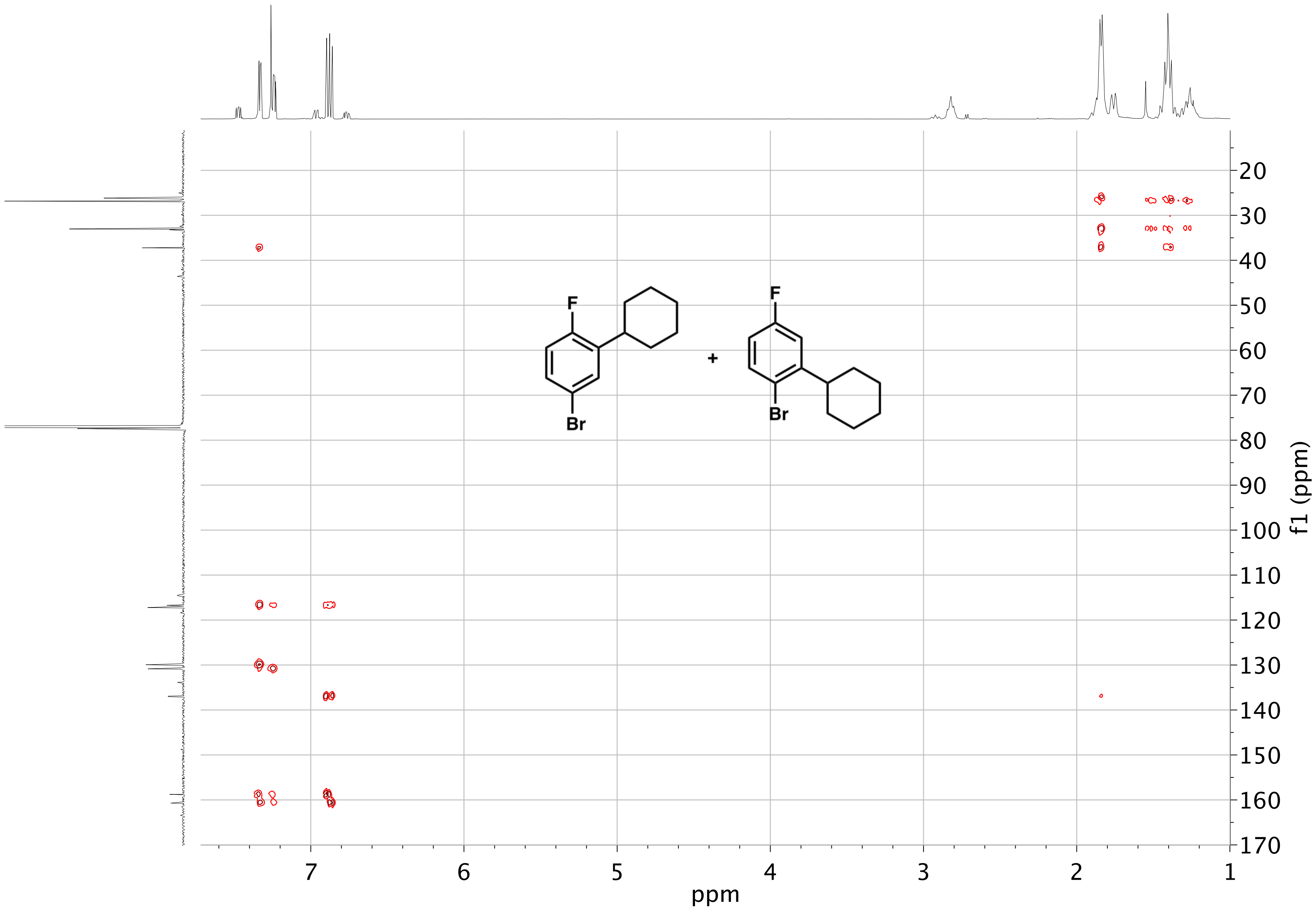
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-40**.



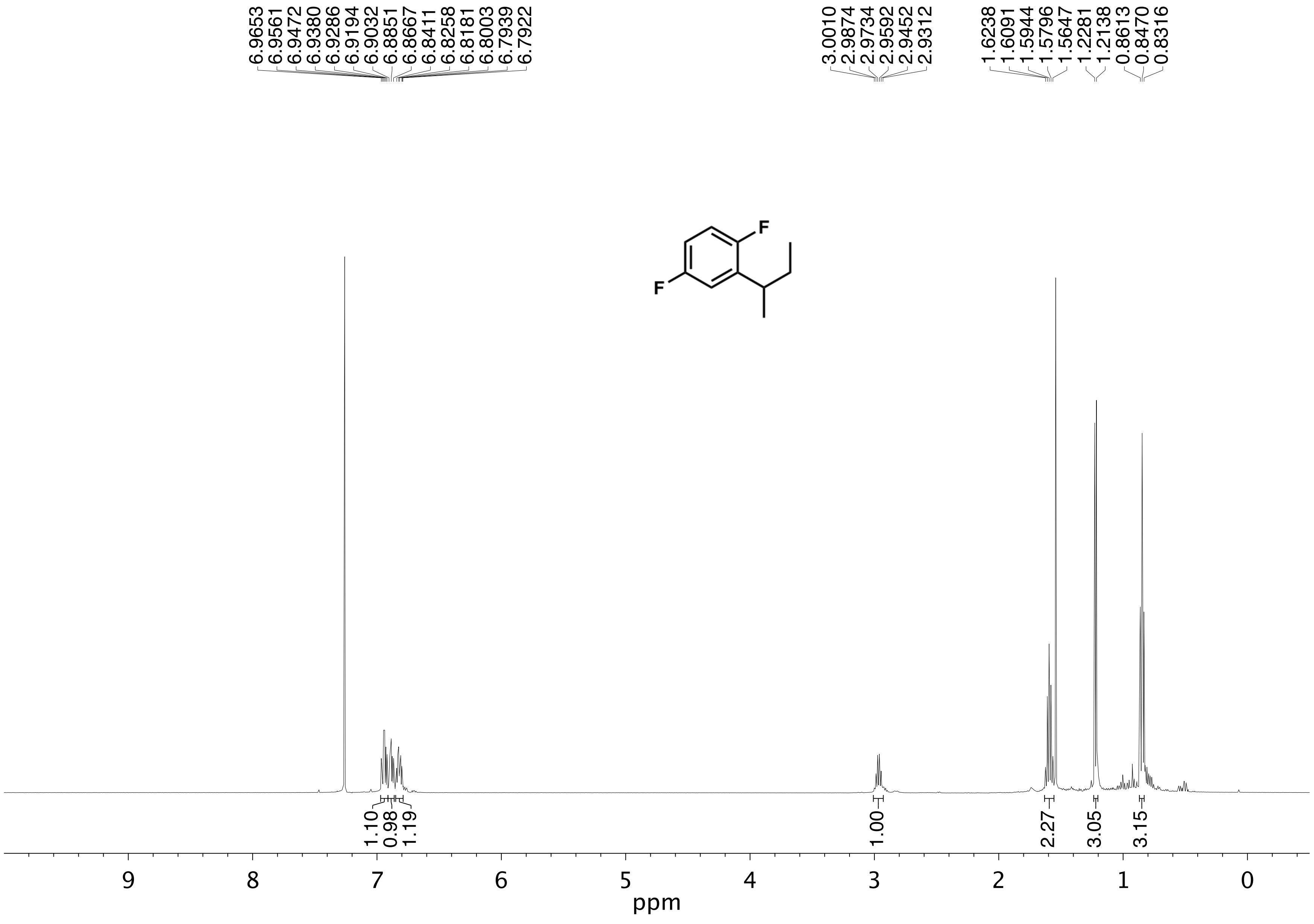
^{19}F NMR (300 MHz, CDCl$_3$) of **SI-40**.



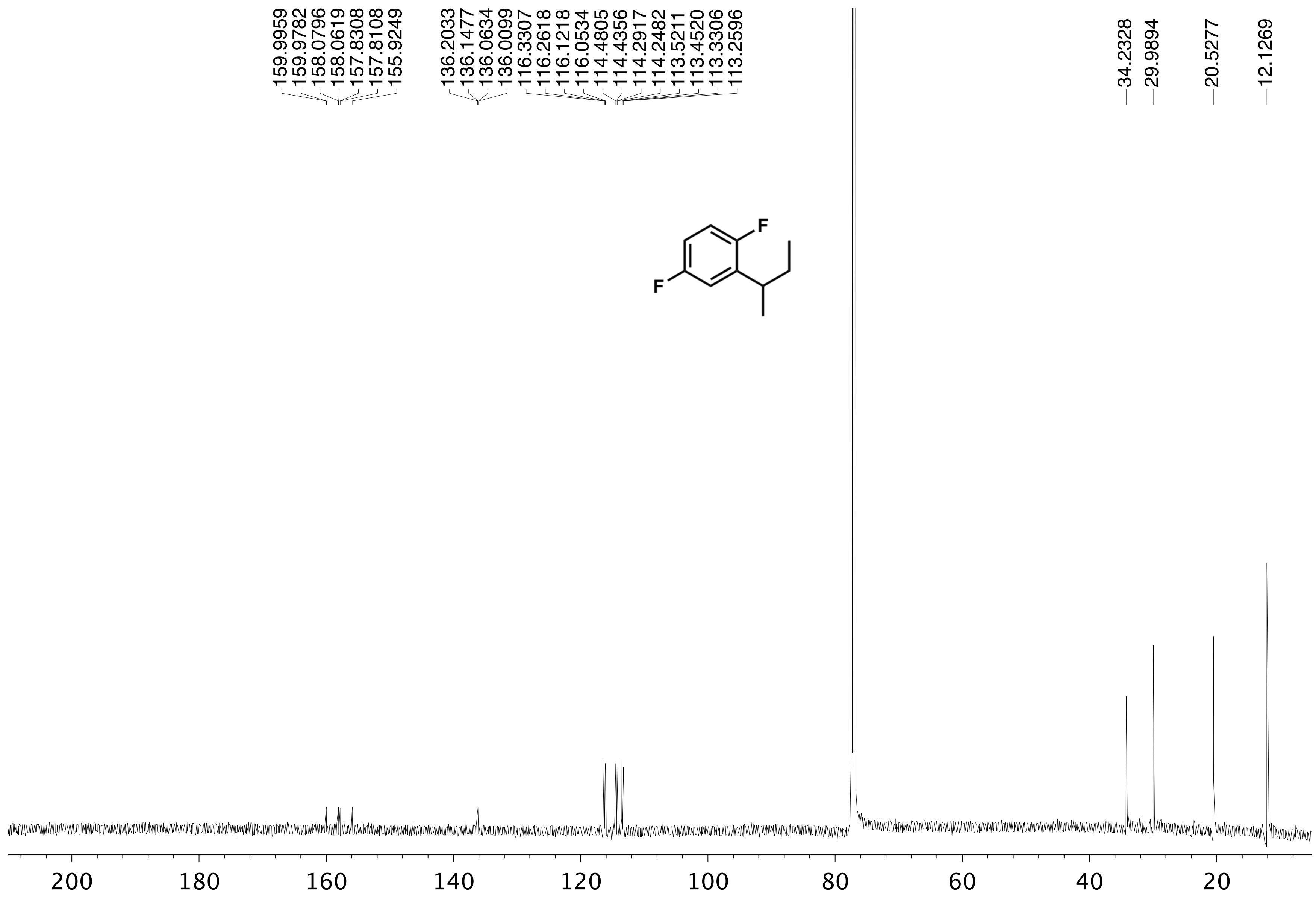
2D HSQC NMR (500 MHz, $CDCl_3$) of **SI-40**.



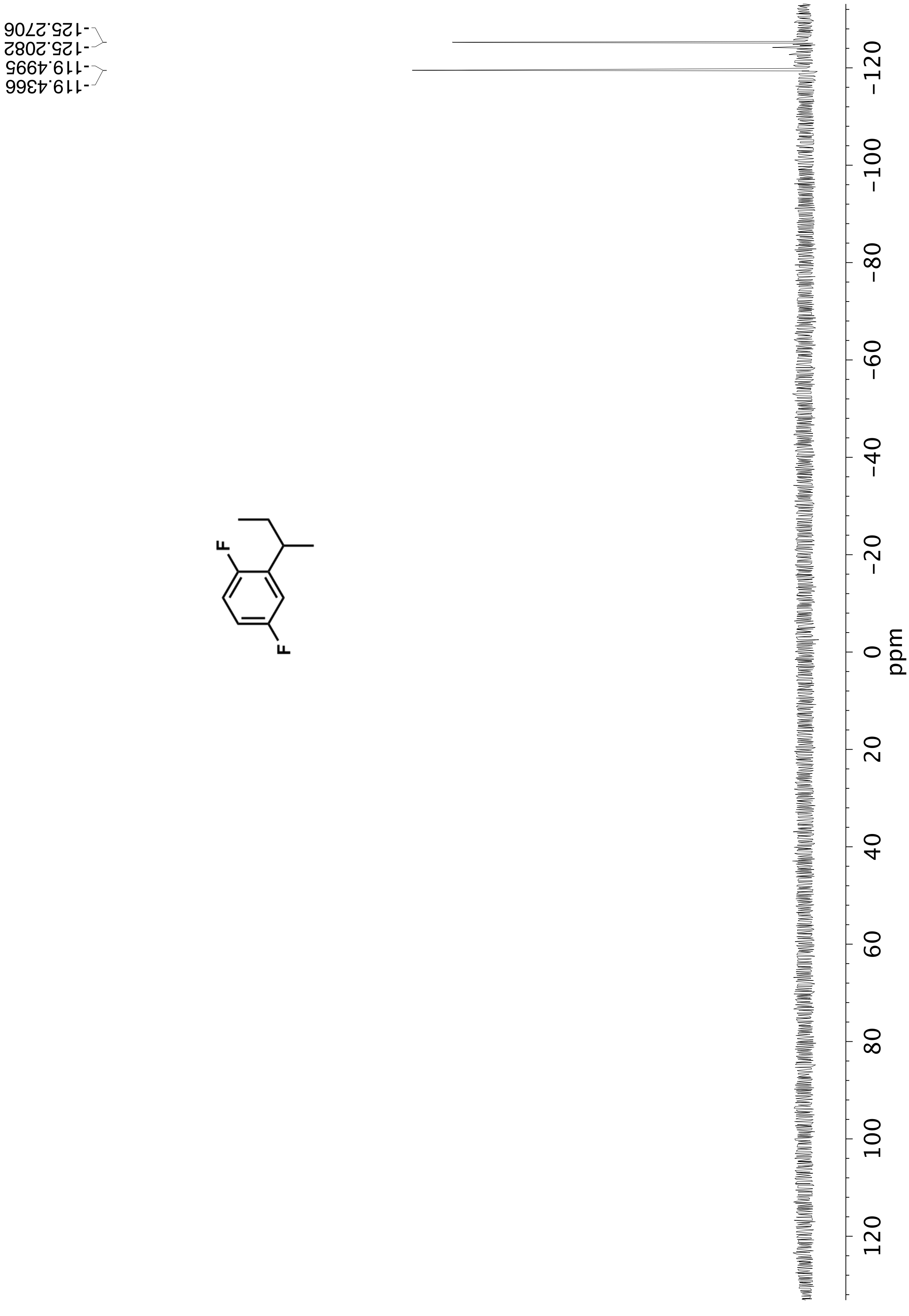
2D HMBC NMR (500 MHz, $CDCl_3$) of **SI-40**.



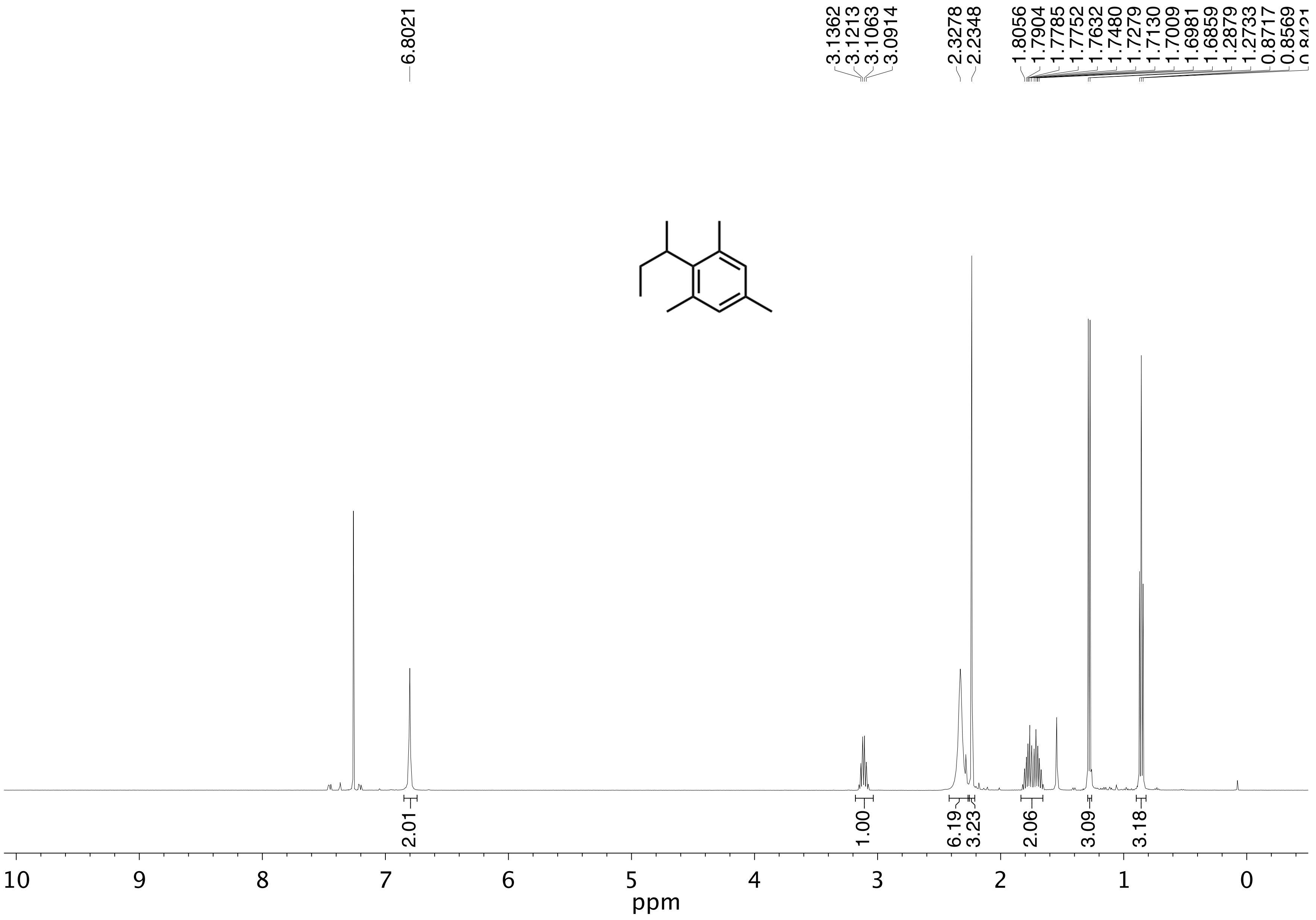
^{1}H NMR (500 MHz, CDCl$_3$) of **SI-41**.



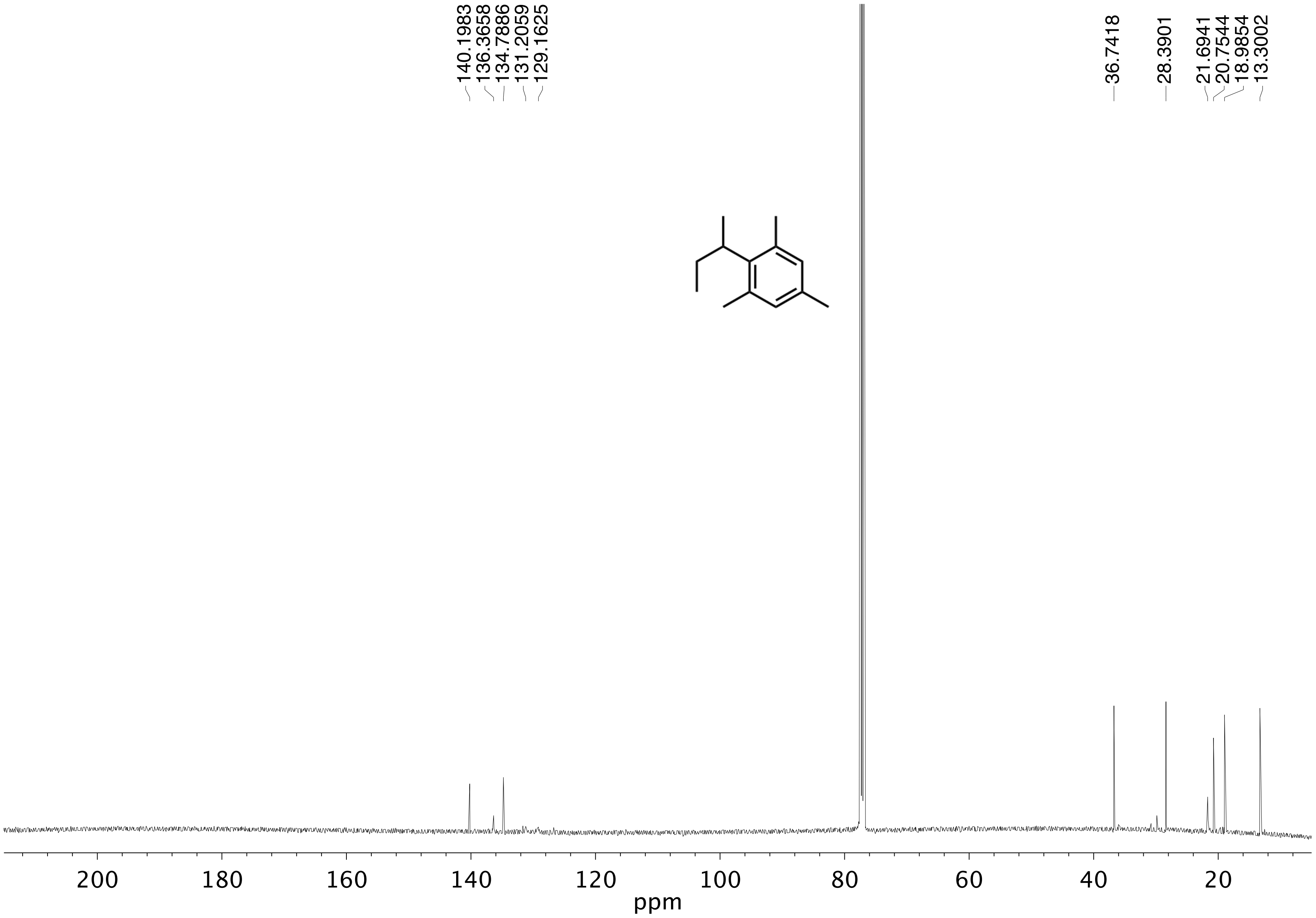
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-41**.



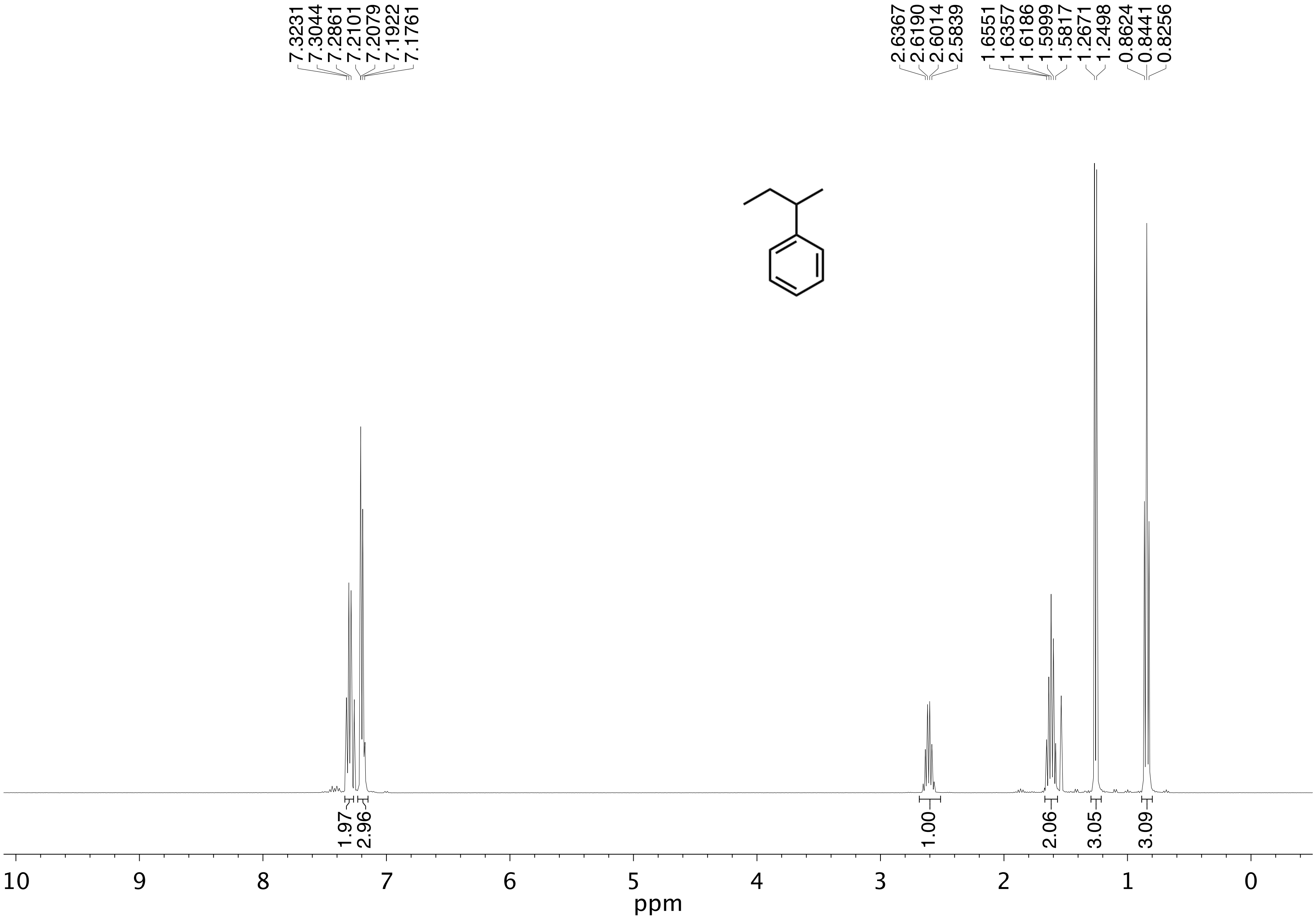
^{19}F NMR (376 MHz, $CDCl_3$) of **SI-41**.



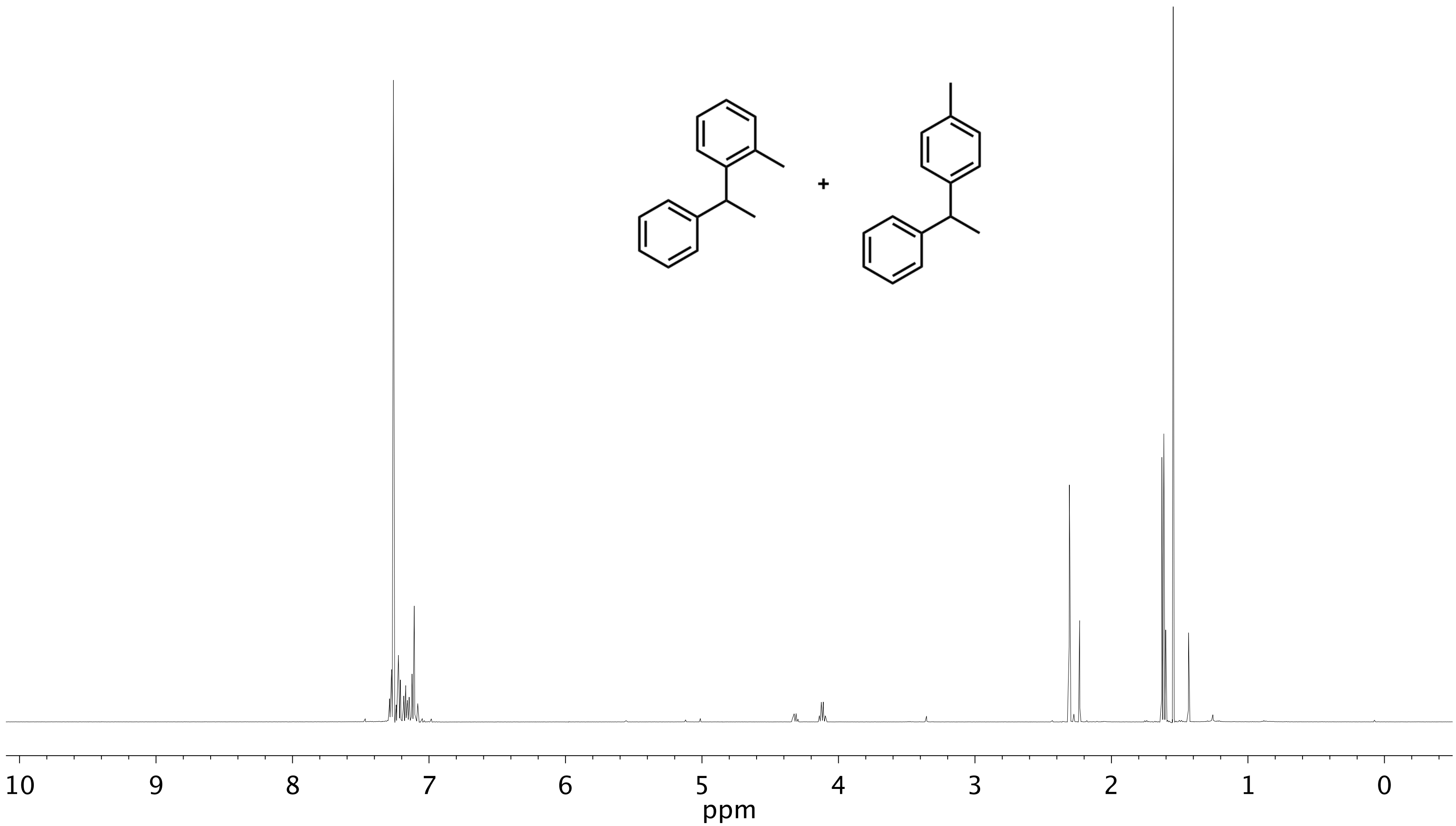
^{1}H NMR (500 MHz, $CDCl_3$) of **SI-42**.



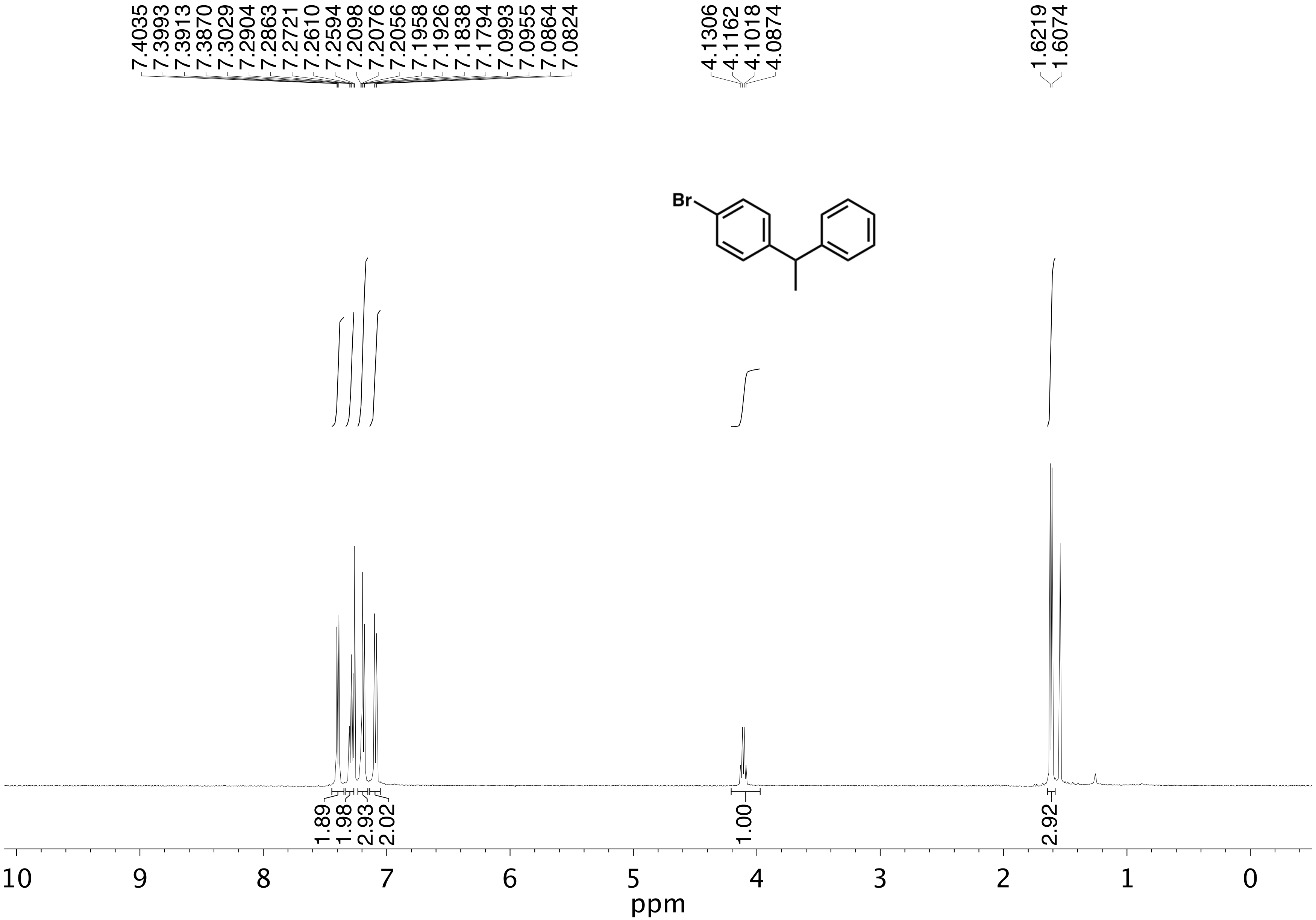
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-42**.



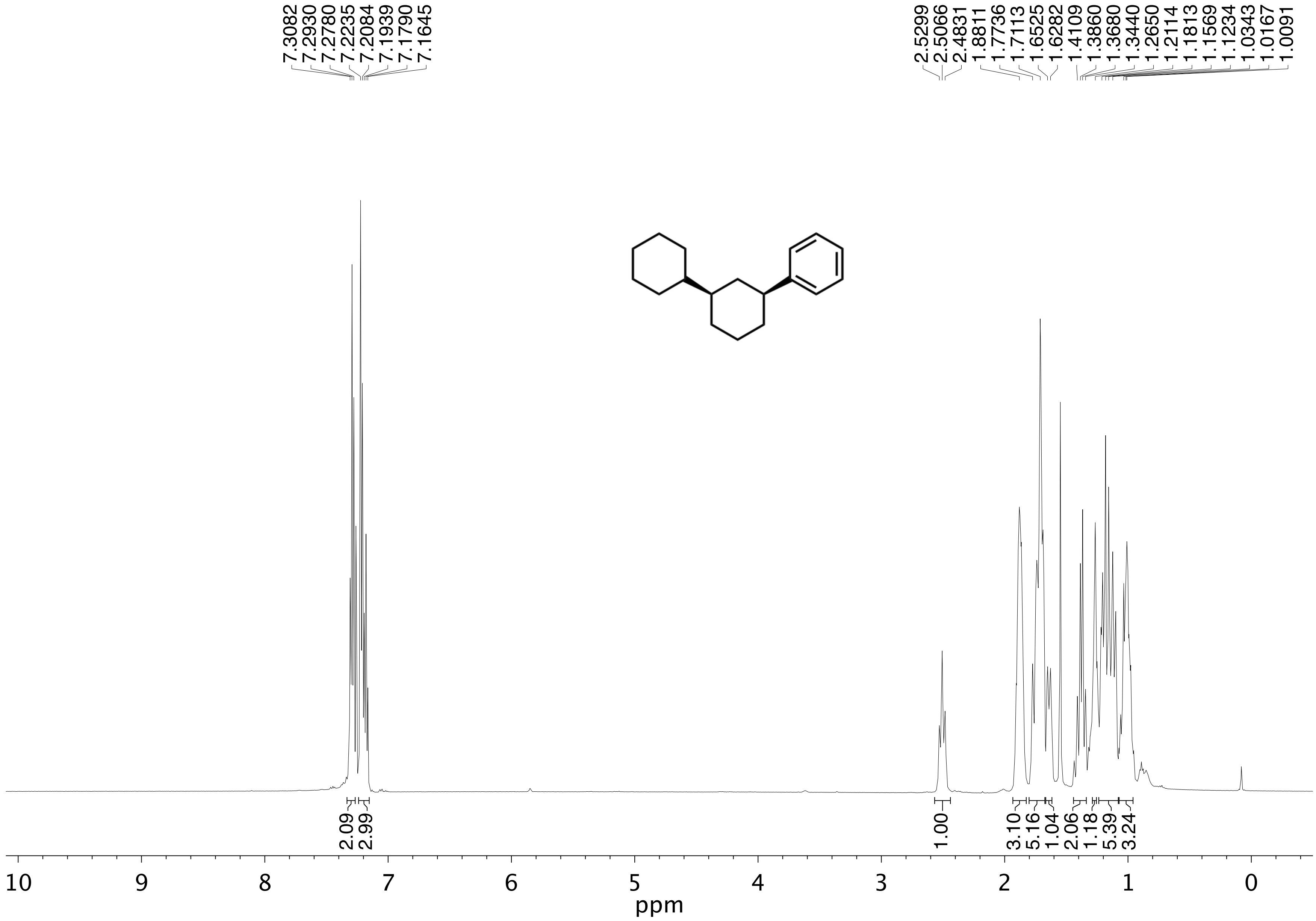
^{1}H NMR (400 MHz, $CDCl_3$) of **SI-43**.



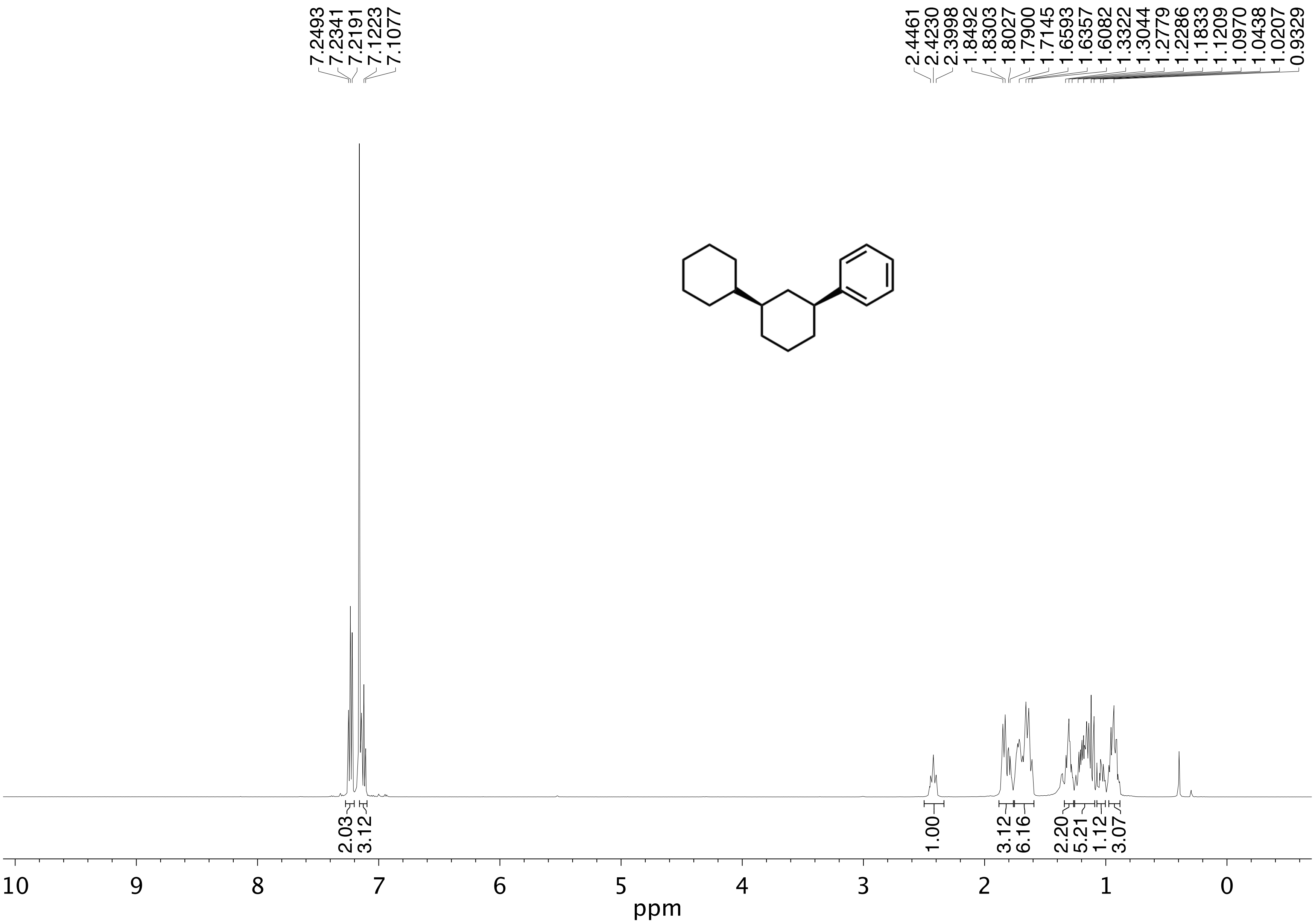
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-44**



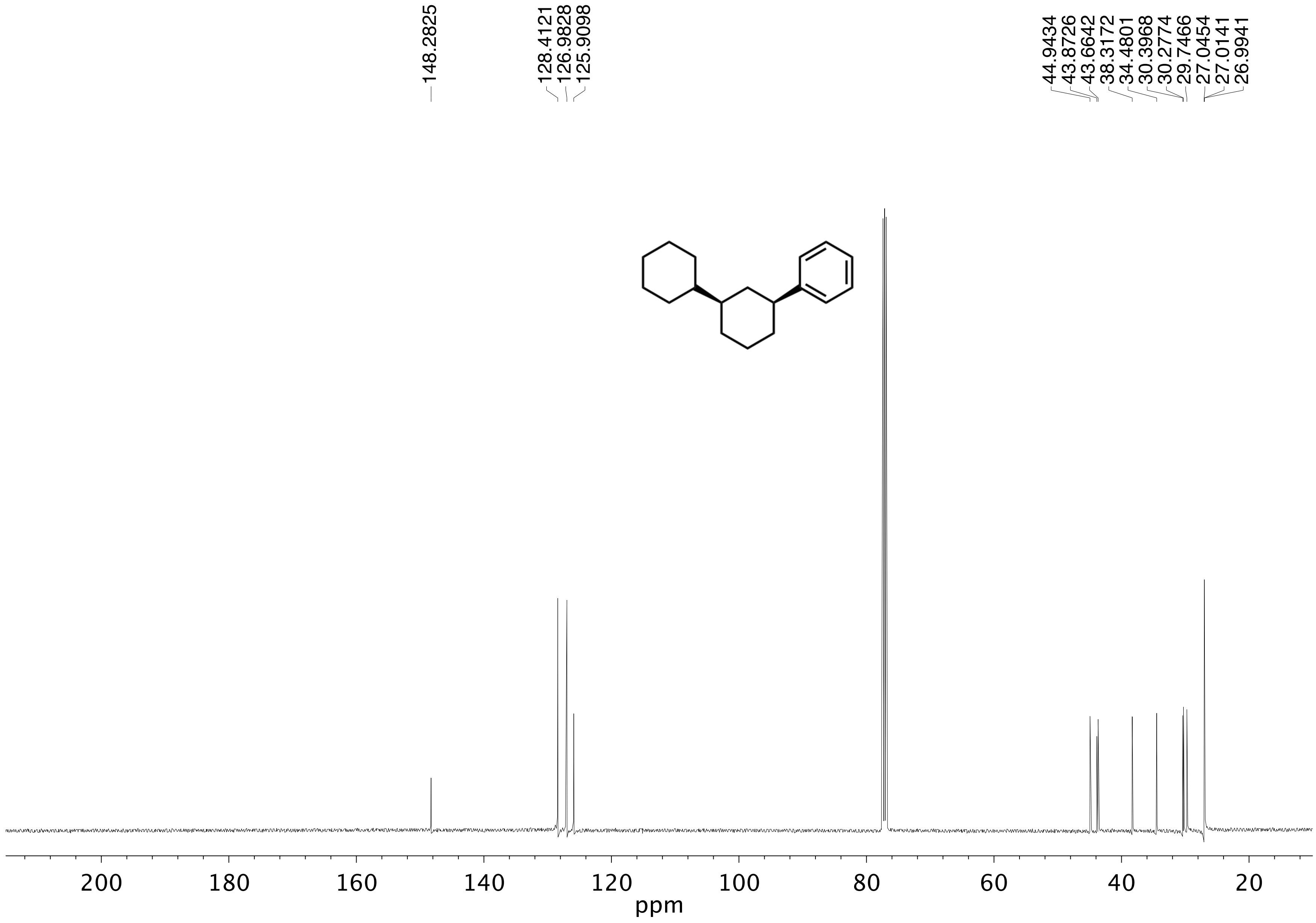
^{1}H NMR (500 MHz, CDCl$_3$) of compound **SI-45**.



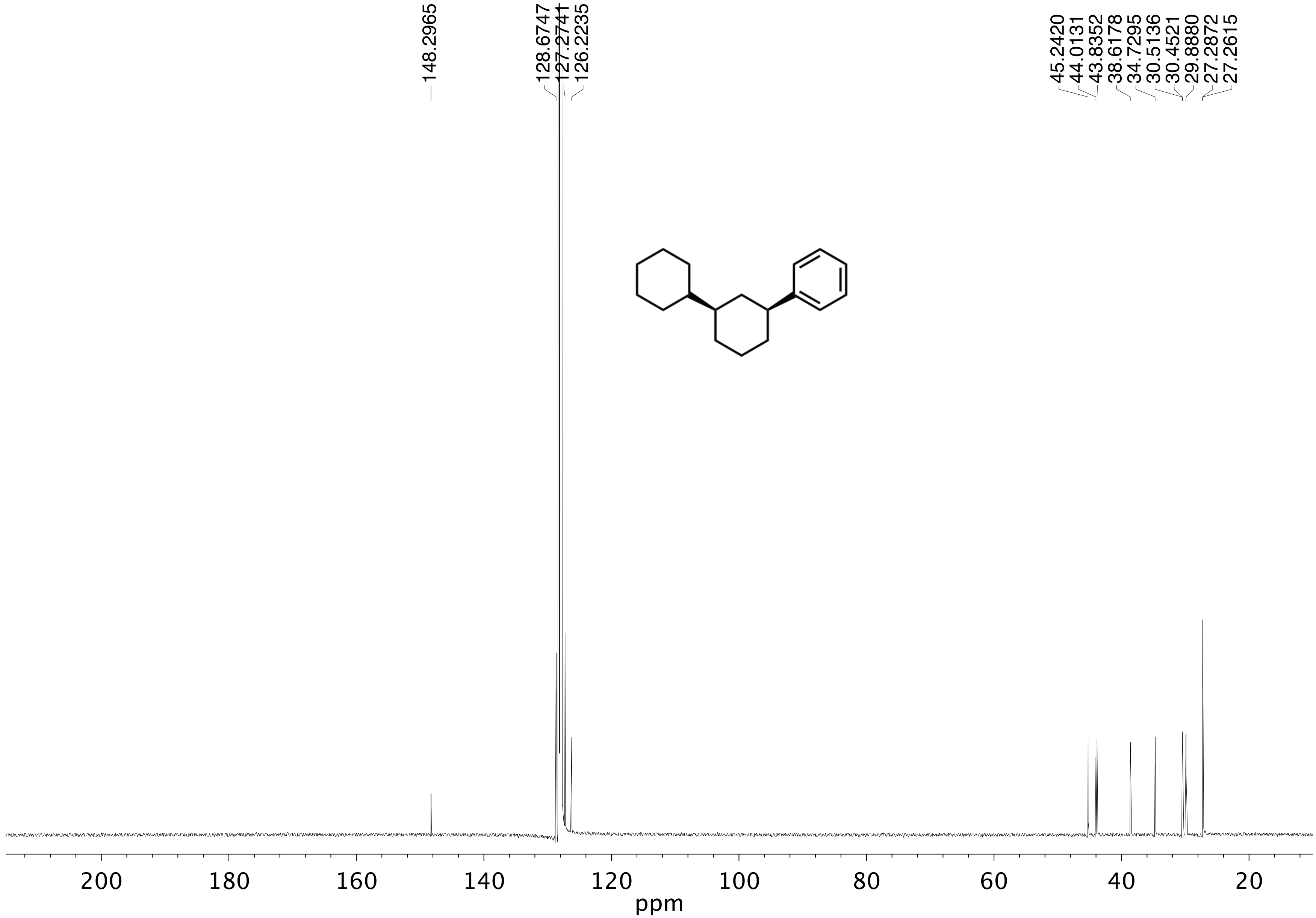
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-46**.



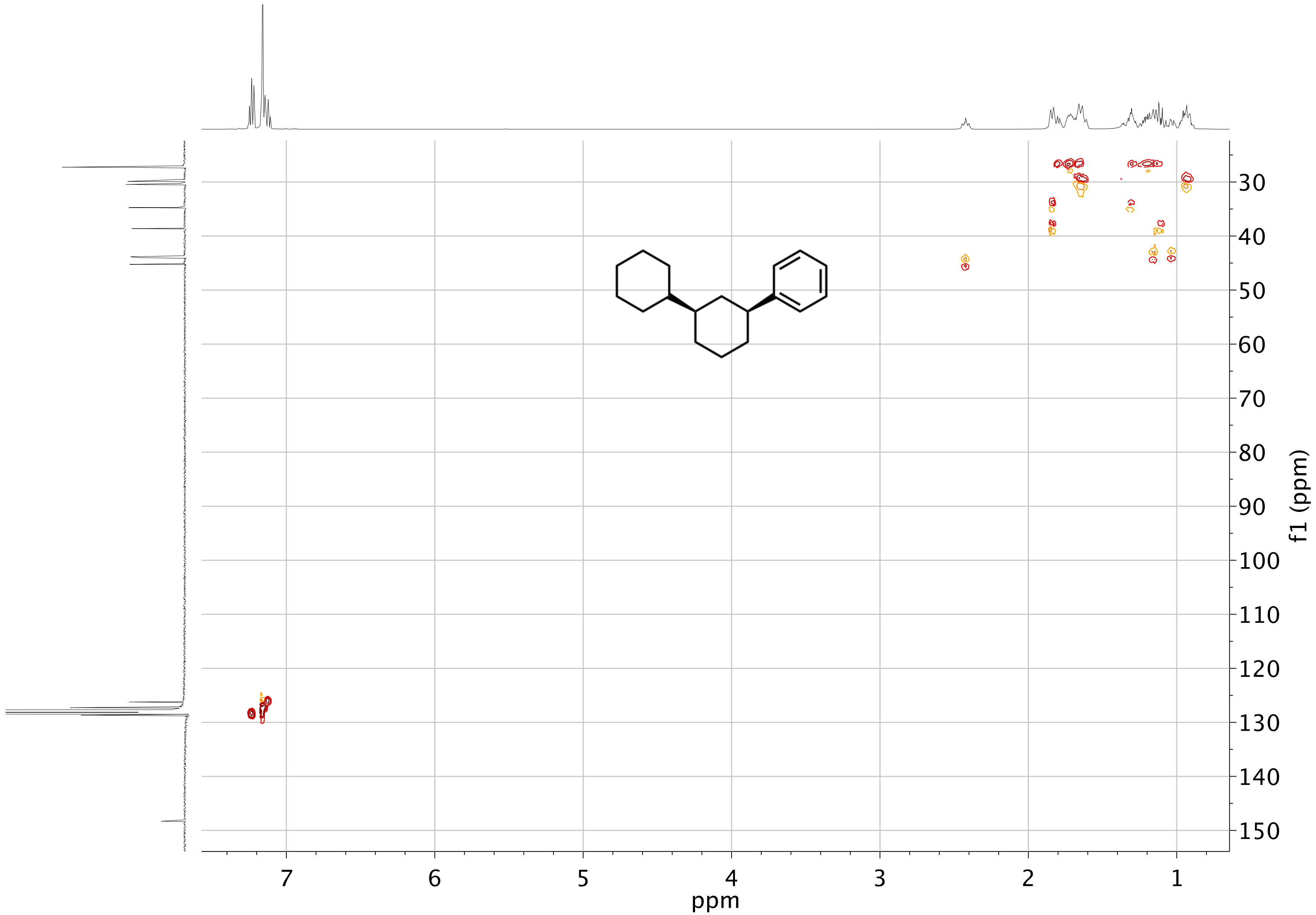
^{1}H NMR (400 MHz, C_6D_6) of **SI-46**.



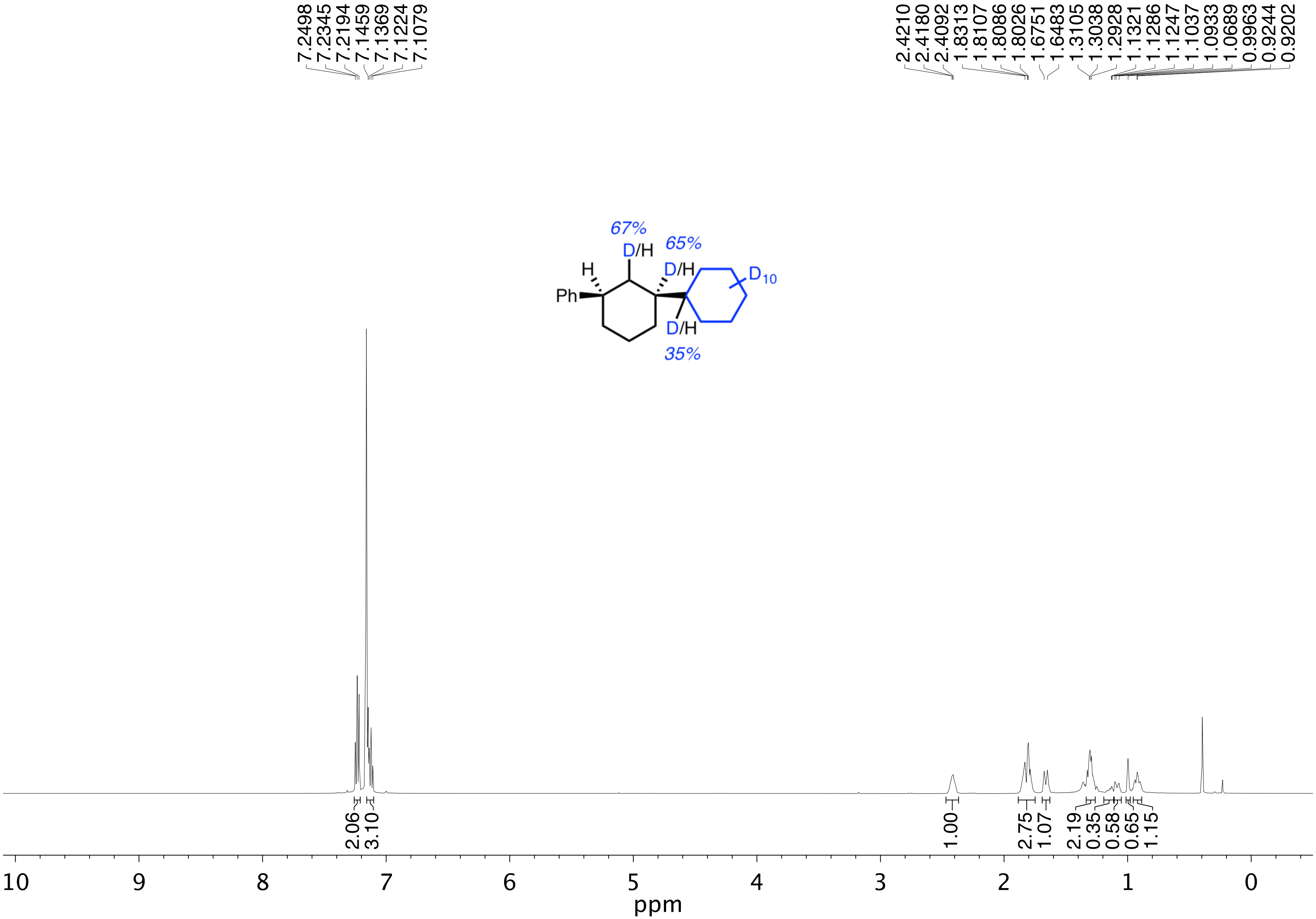
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-46**.



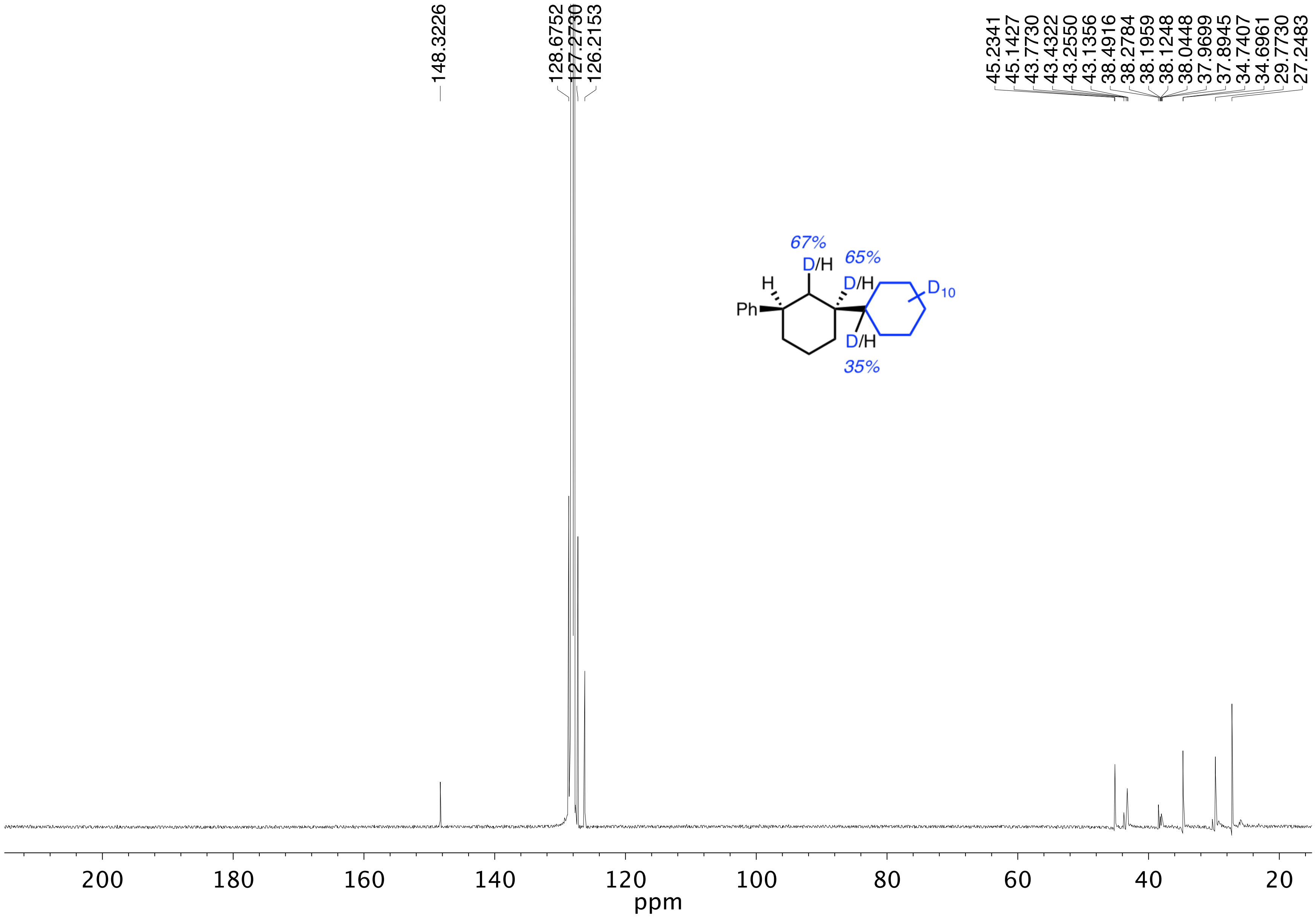
^{13}C NMR (125 MHz, C_6D_6) of **SI-46**.



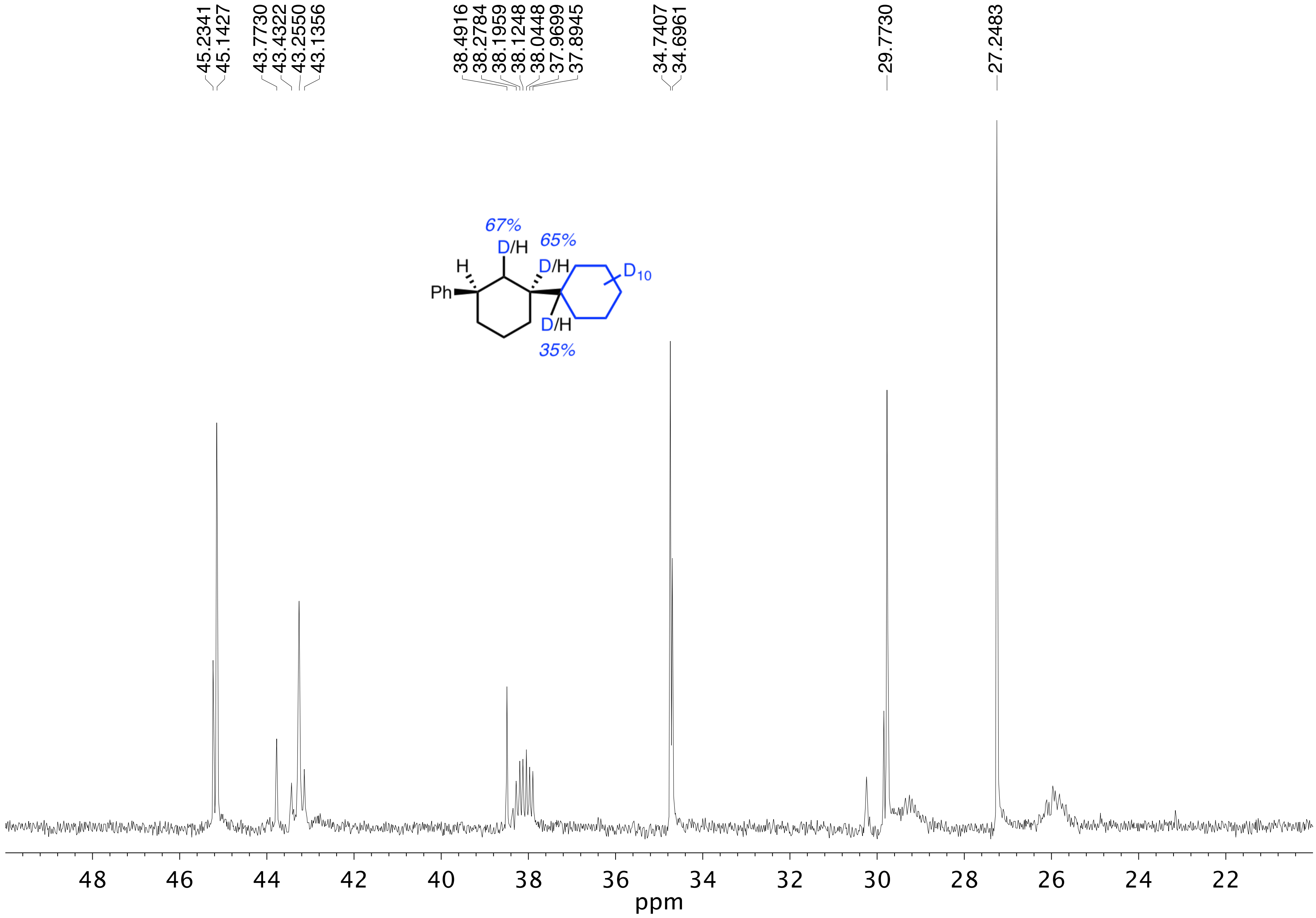
2D HSQC NMR (500 MHz, C_6D_6) of **SI-46**.



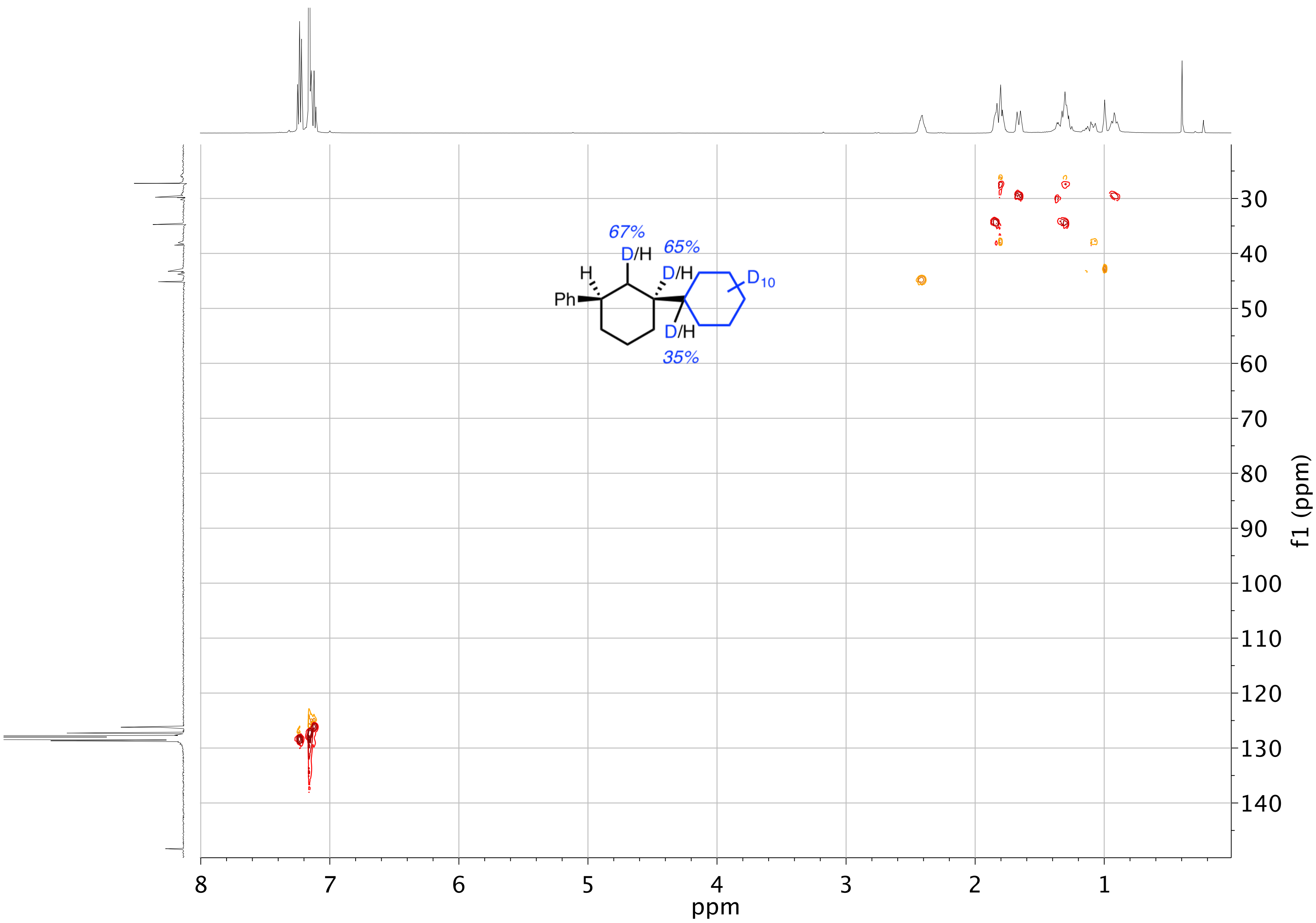
^{1}H NMR (500 MHz, C_6D_6) of **SI-47**.



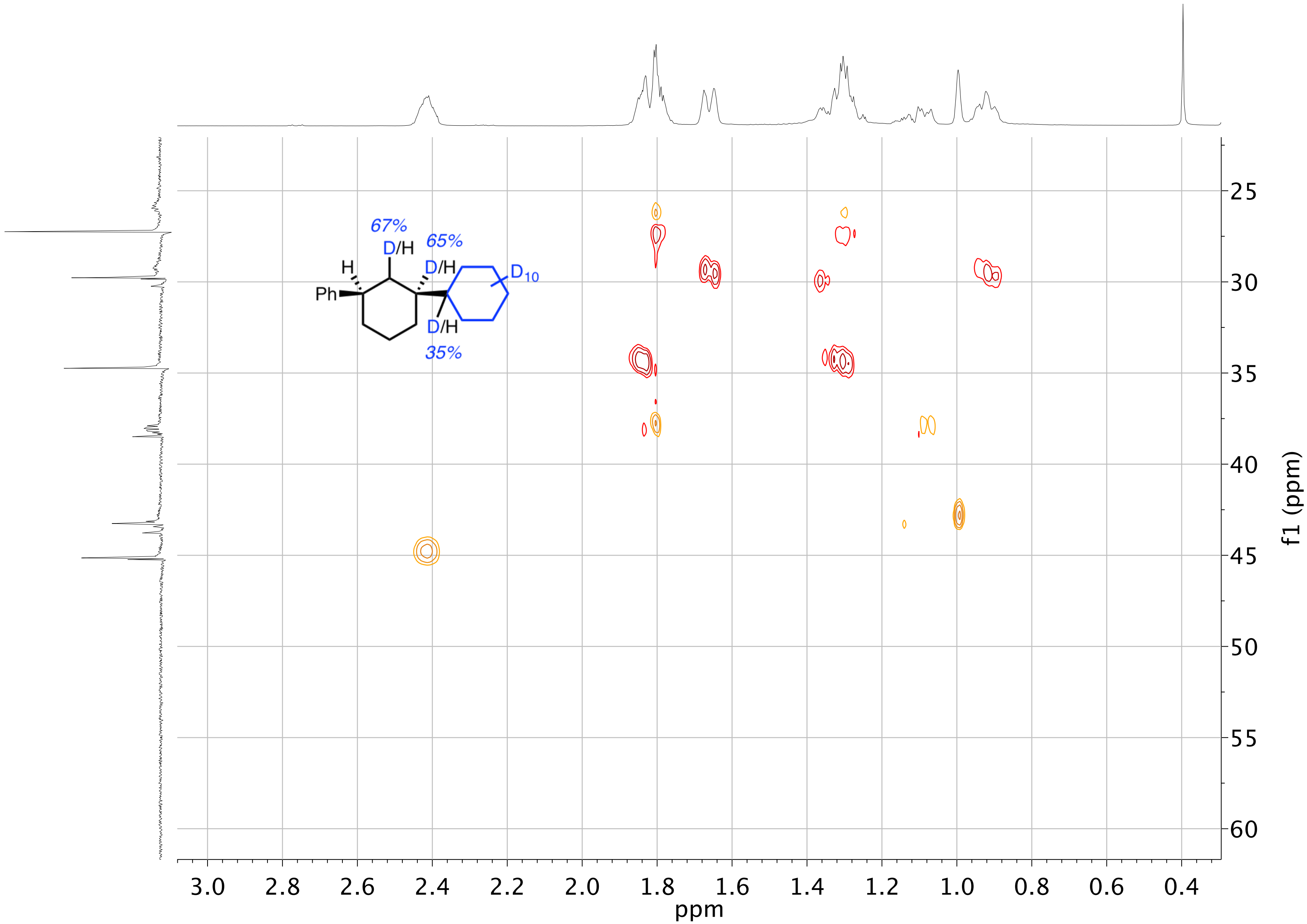
^{13}C NMR (125 MHz, C_6D_6) of **SI-47**.



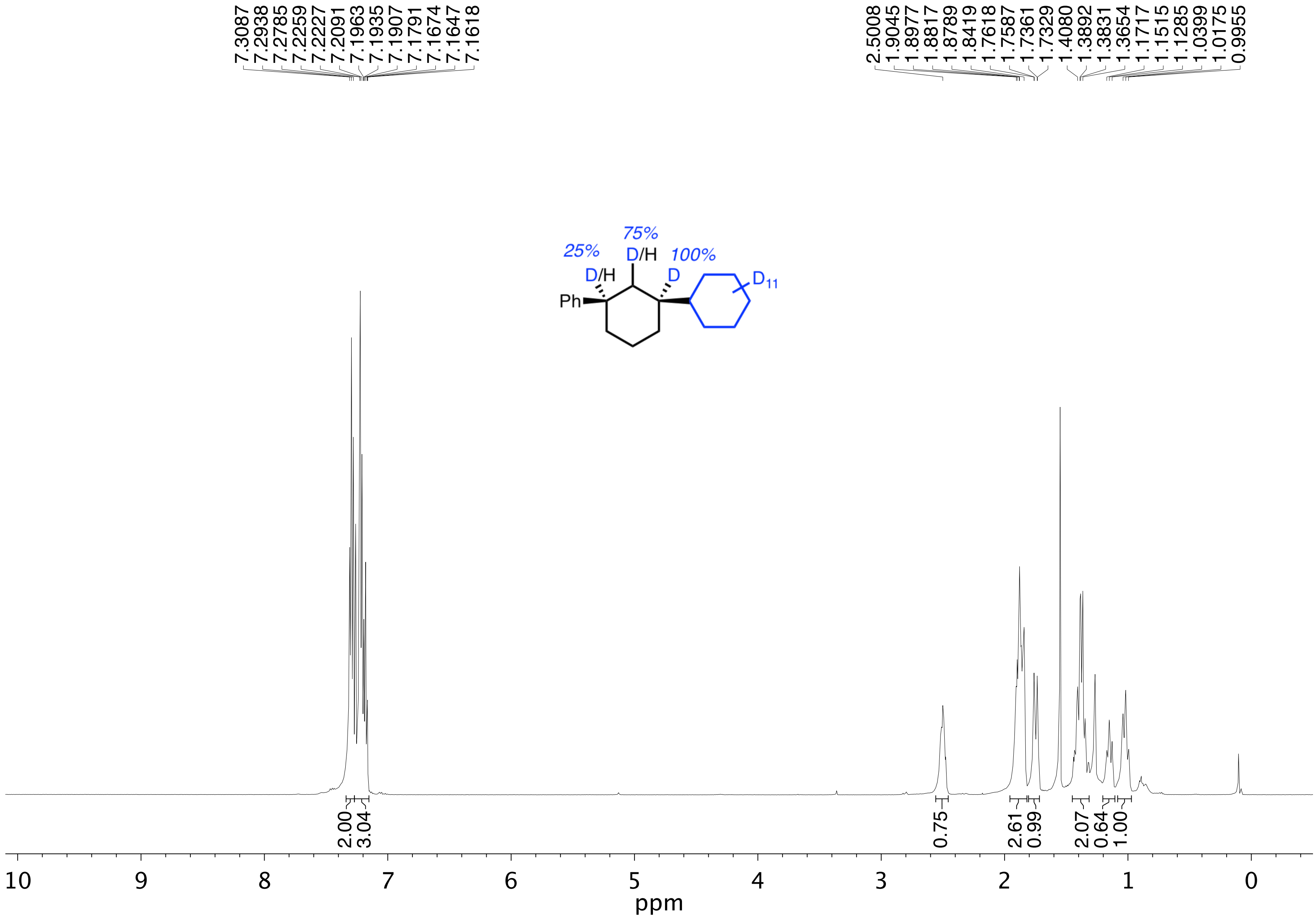
^{13}C NMR (125 MHz, C_6D_6) of **SI-47**.



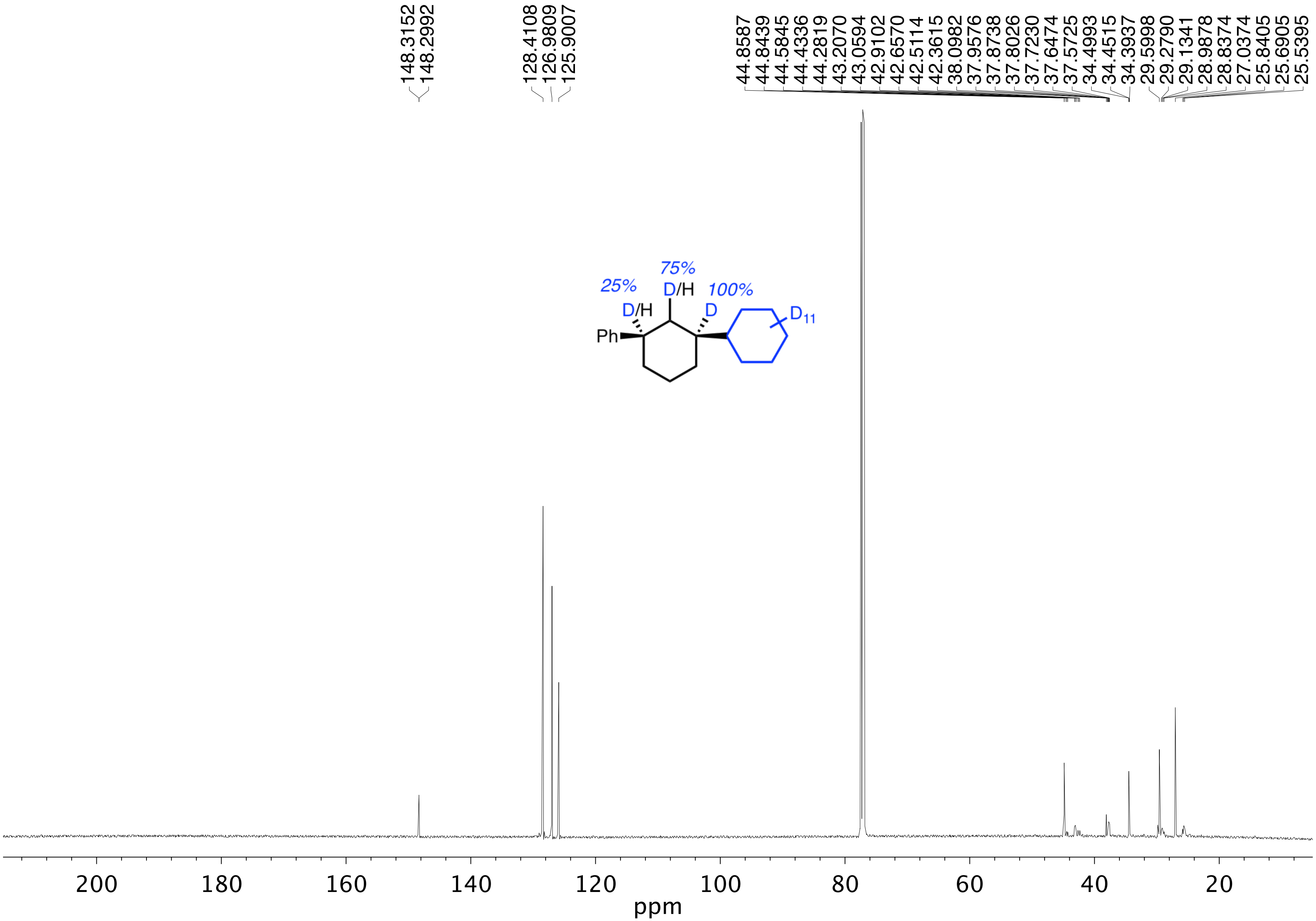
2D HSQC NMR (125 MHz, C_6D_6) of **SI-47**.



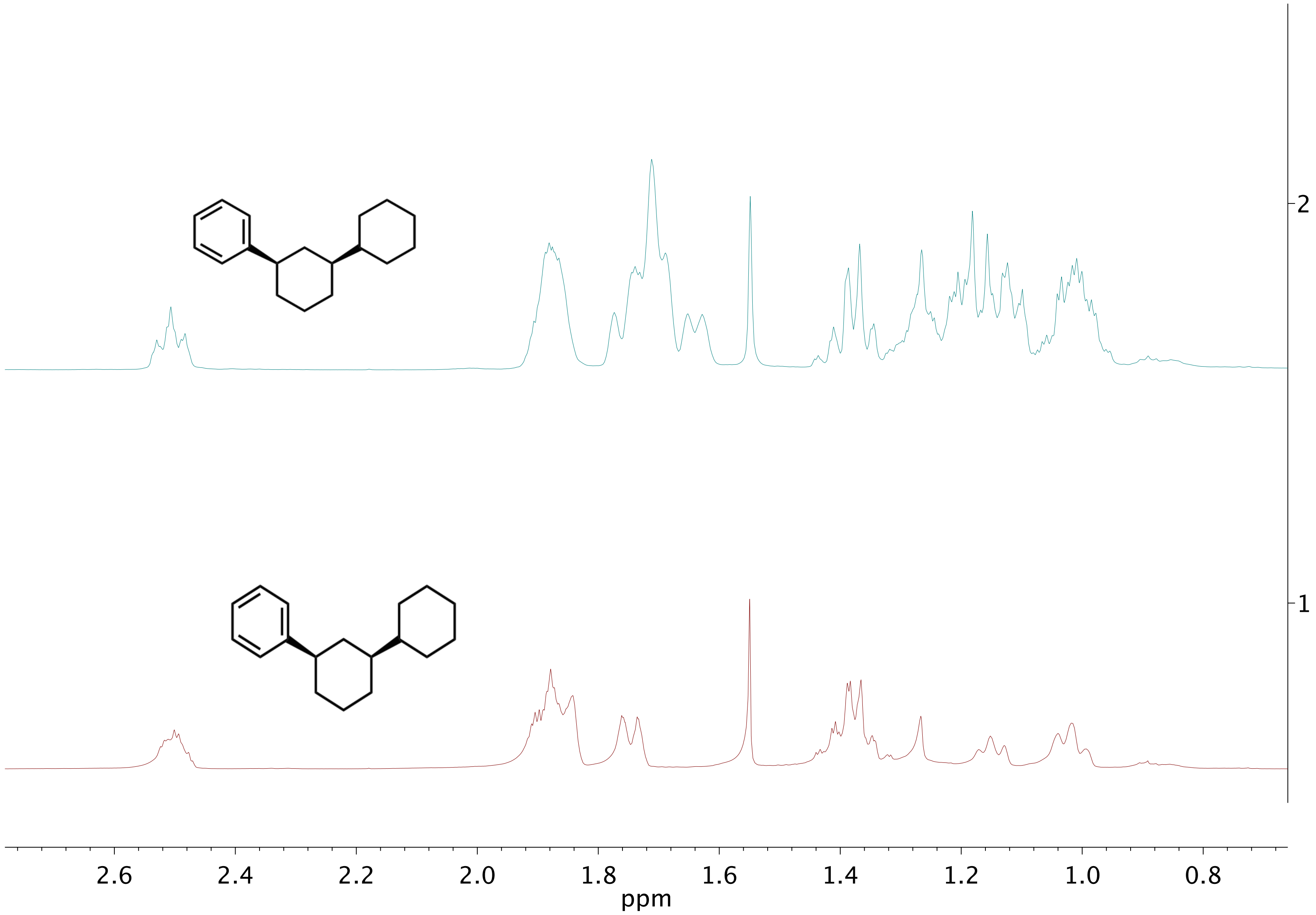
2D HSQCNMR (400 MHz, C_6D_6) of **SI-47**.



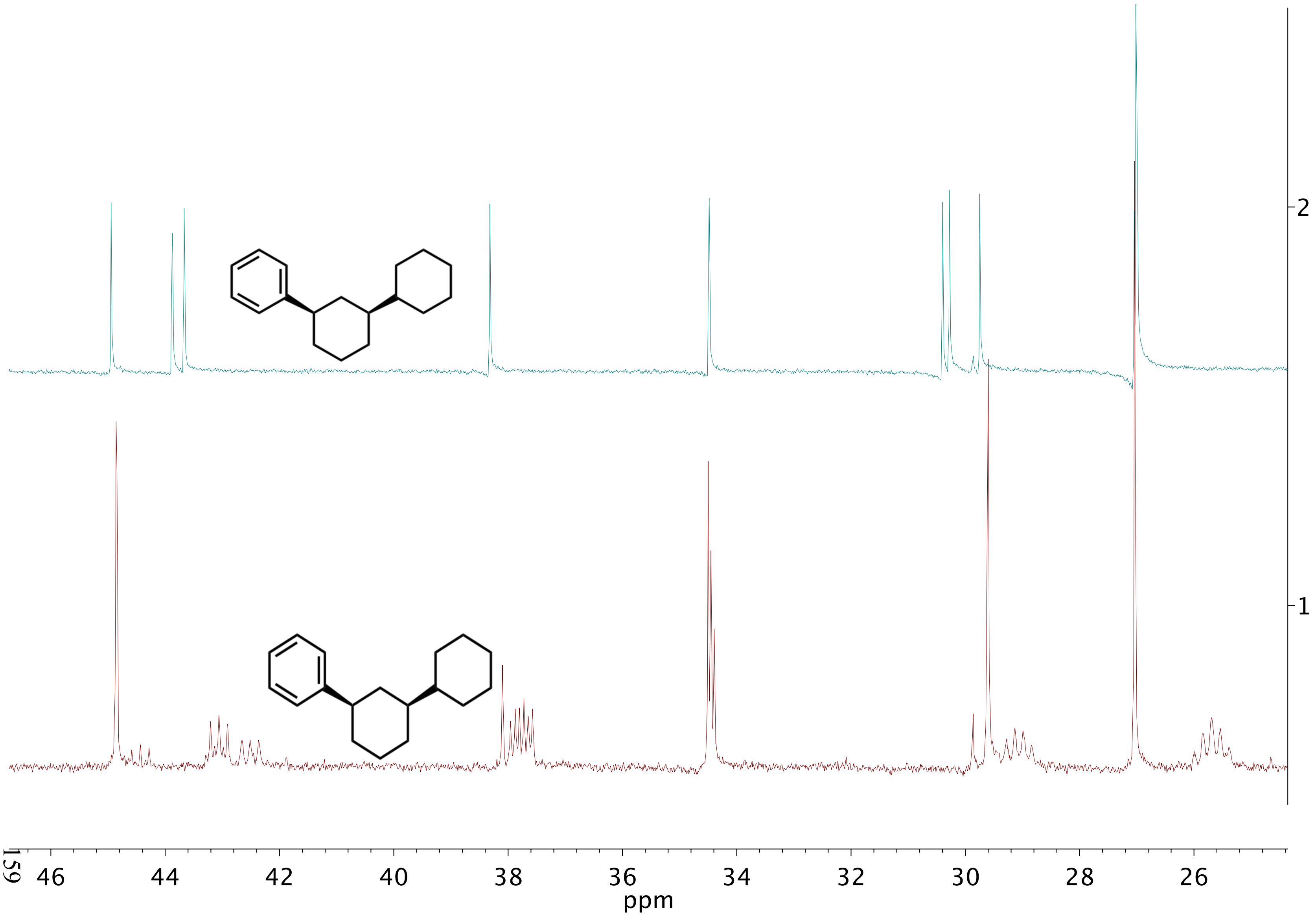
^{1}H NMR (500 MHz, CDCl$_3$) of **SI-48**.



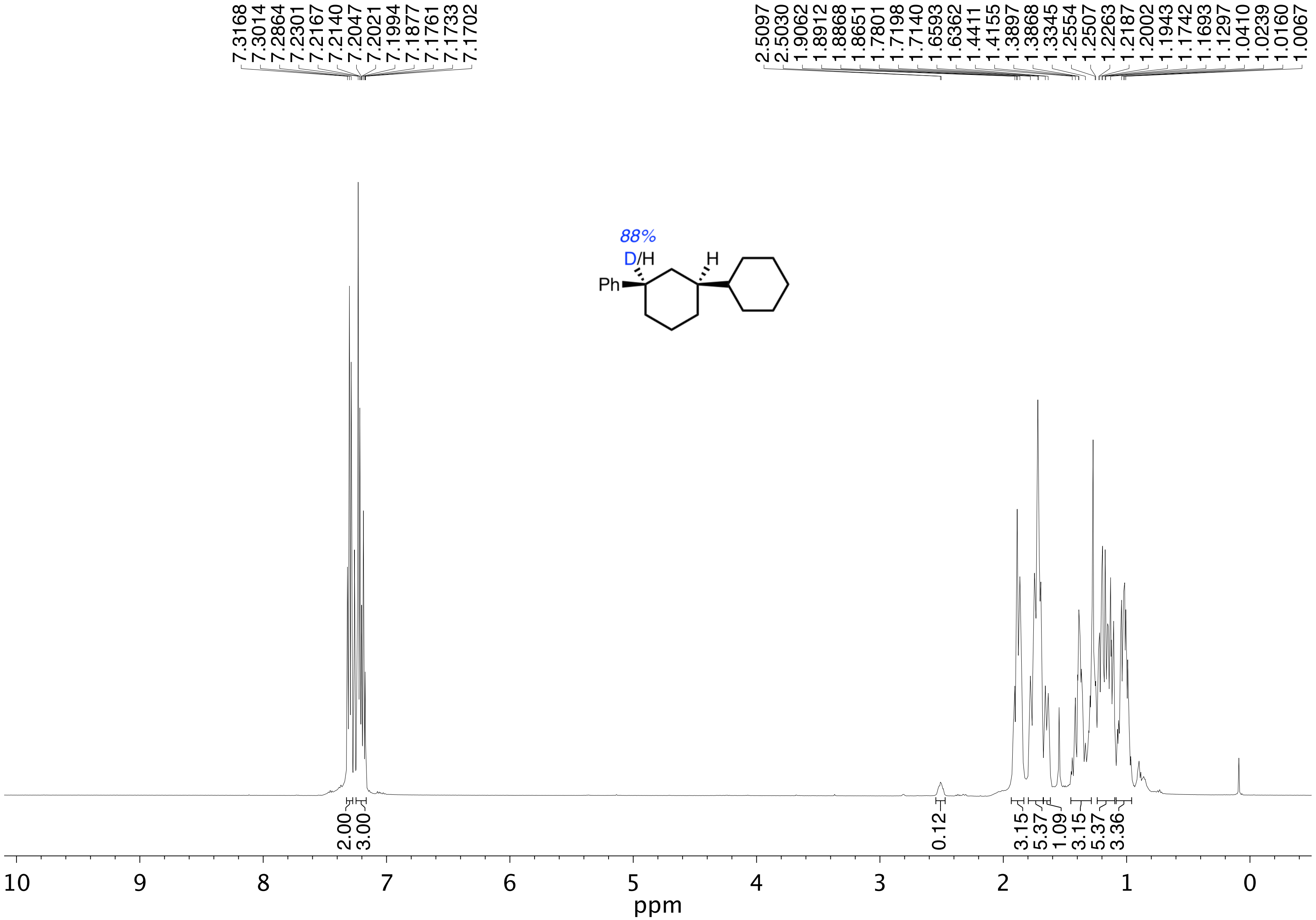
^{13}C NMR (125 MHz, $CDCl_3$) of **SI-48**.



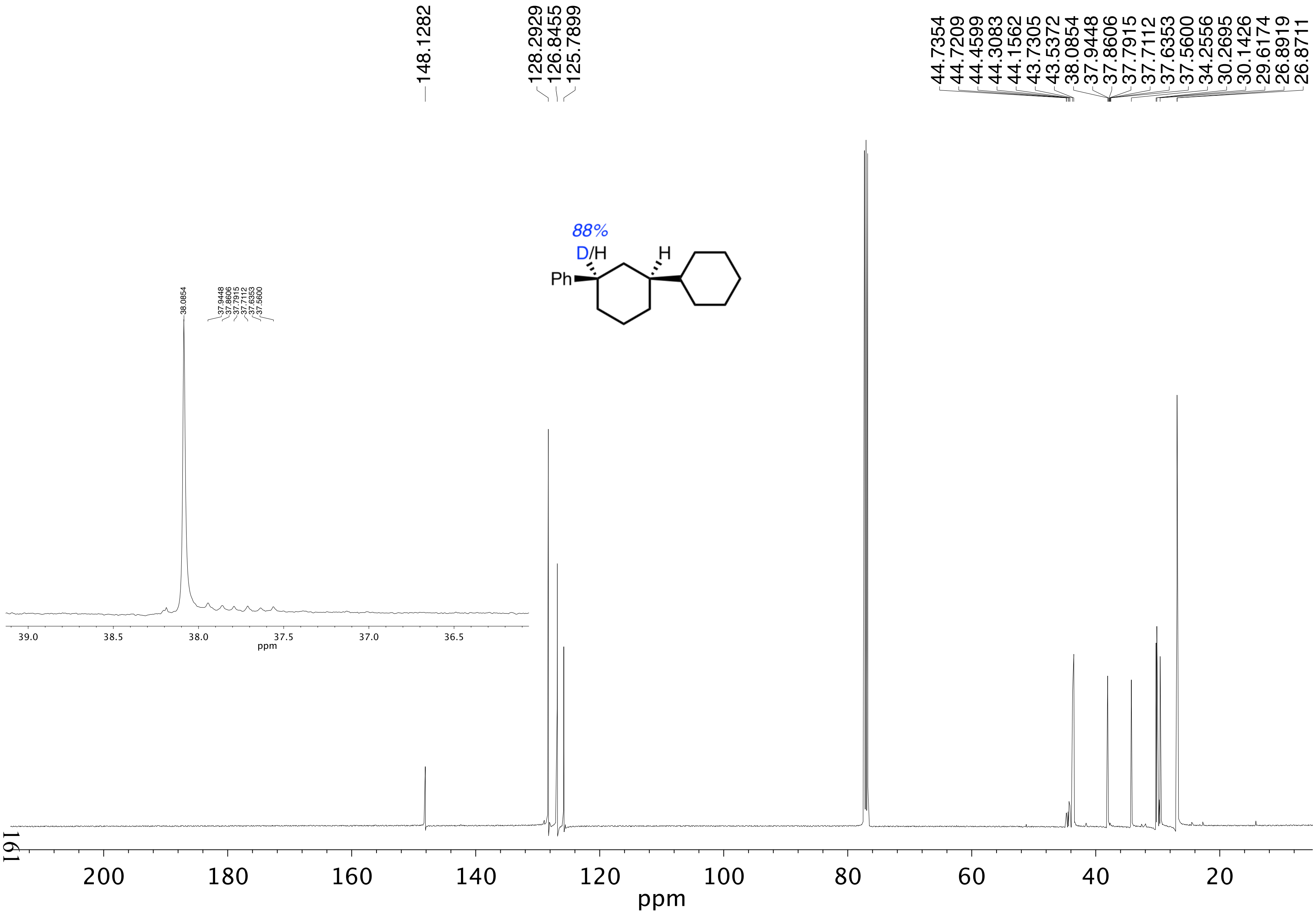
^{1}H NMR (500 MHz, $CDCl_3$) comparison of **SI-48** (below) with authentic **SI-46** (top).



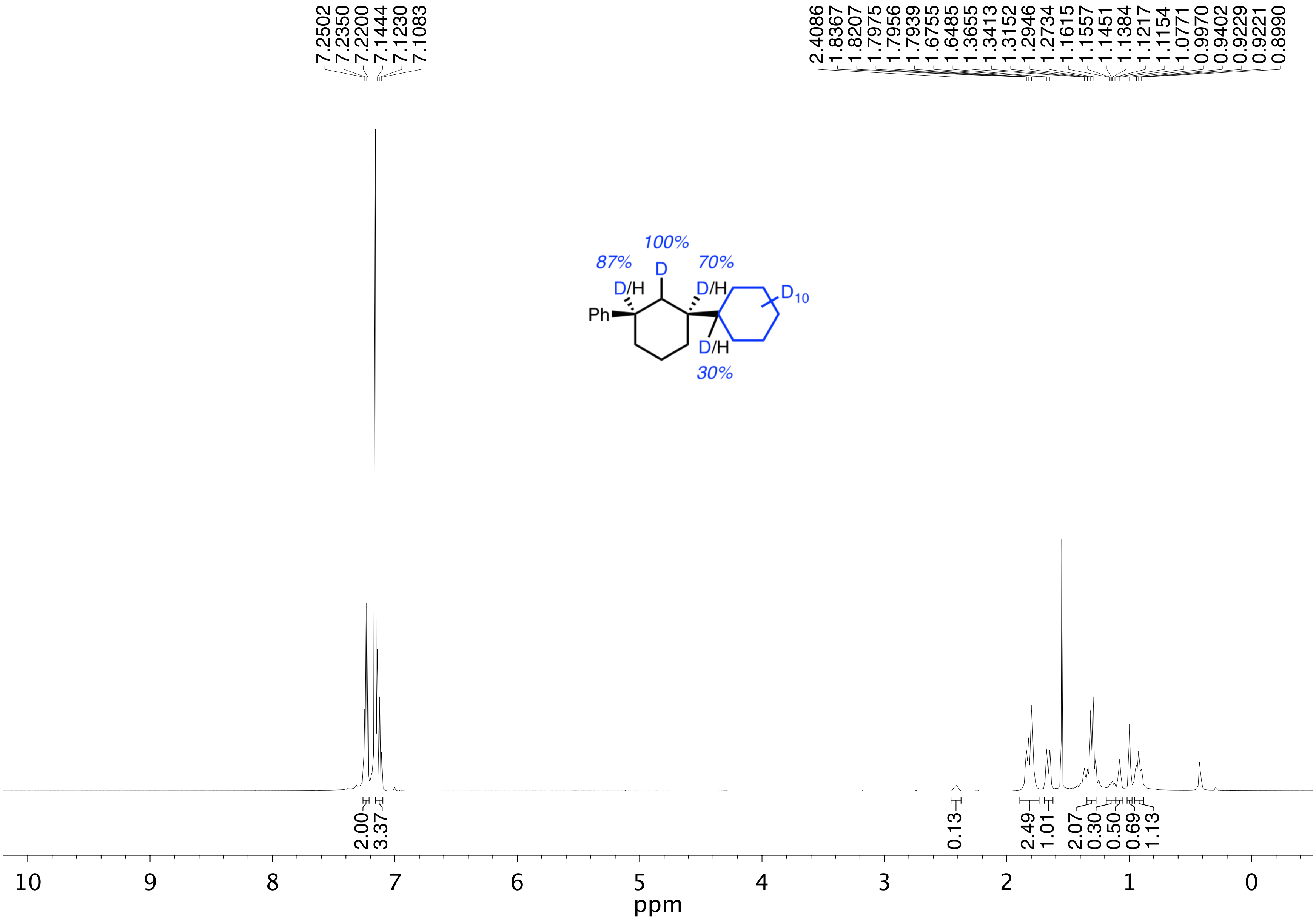
^{13}C NMR (125 MHz, CDCl$_3$) comparison of **SI-48** (below) with authentic **SI-46** (top).



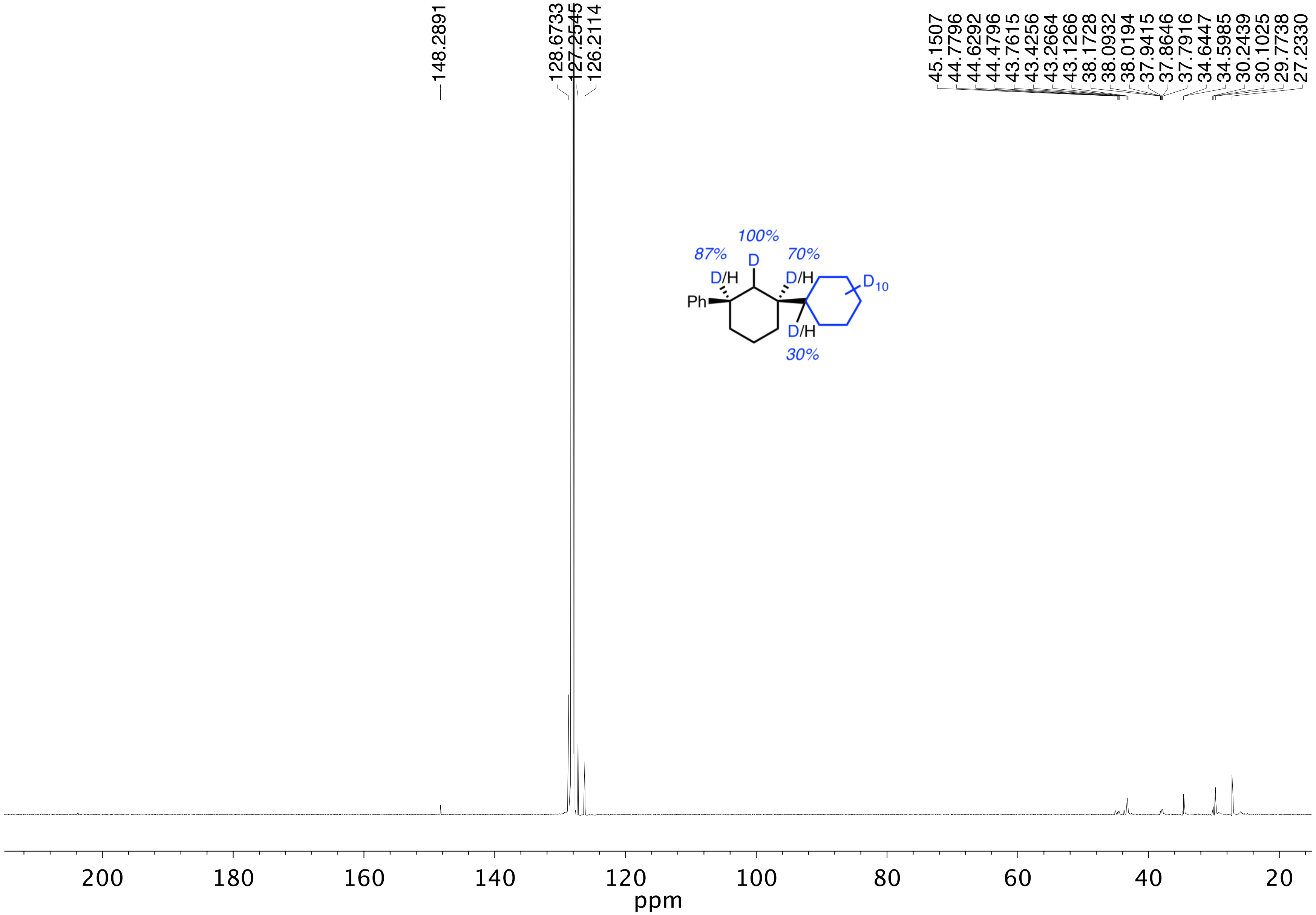
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-49**.



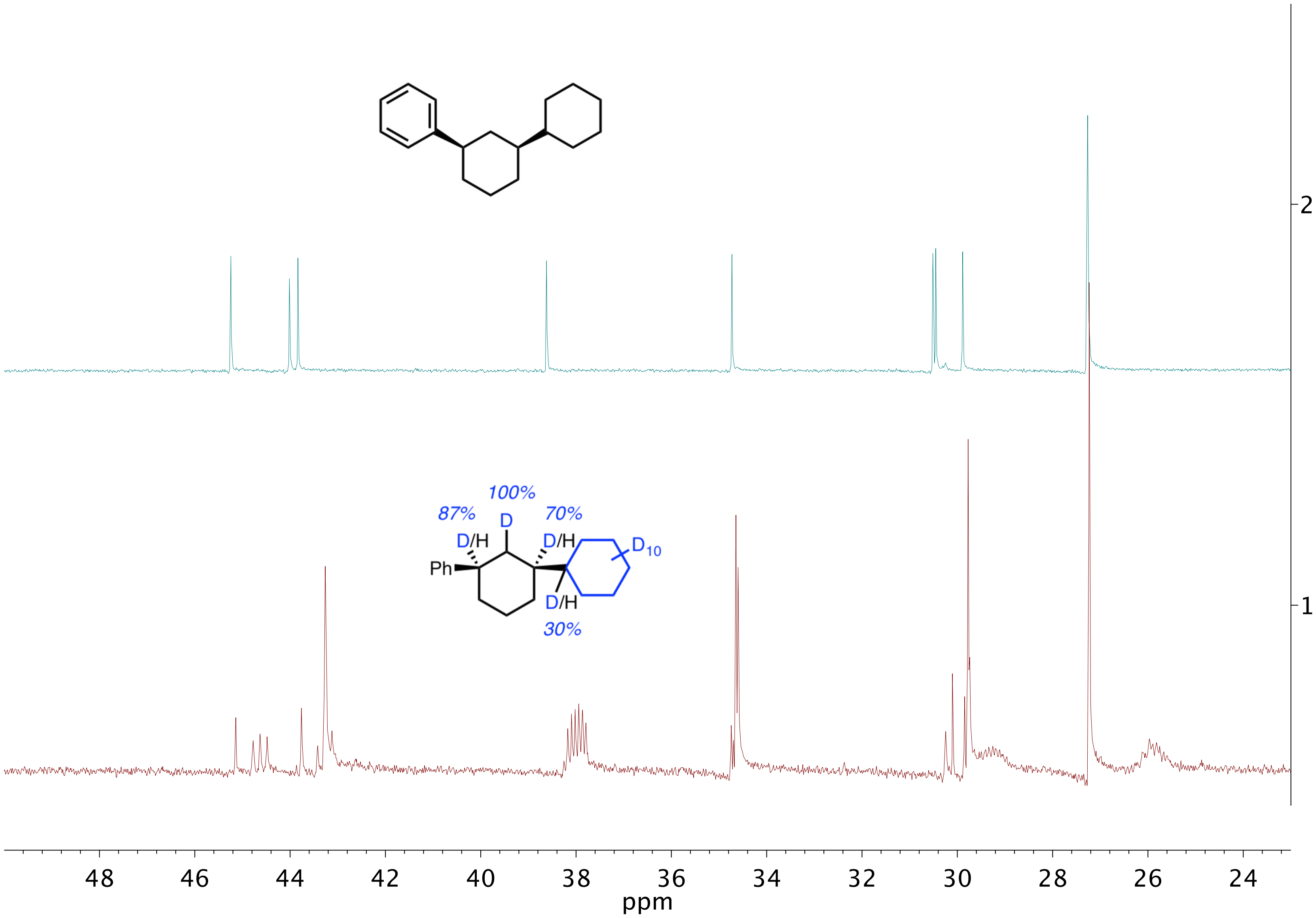
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-49**.



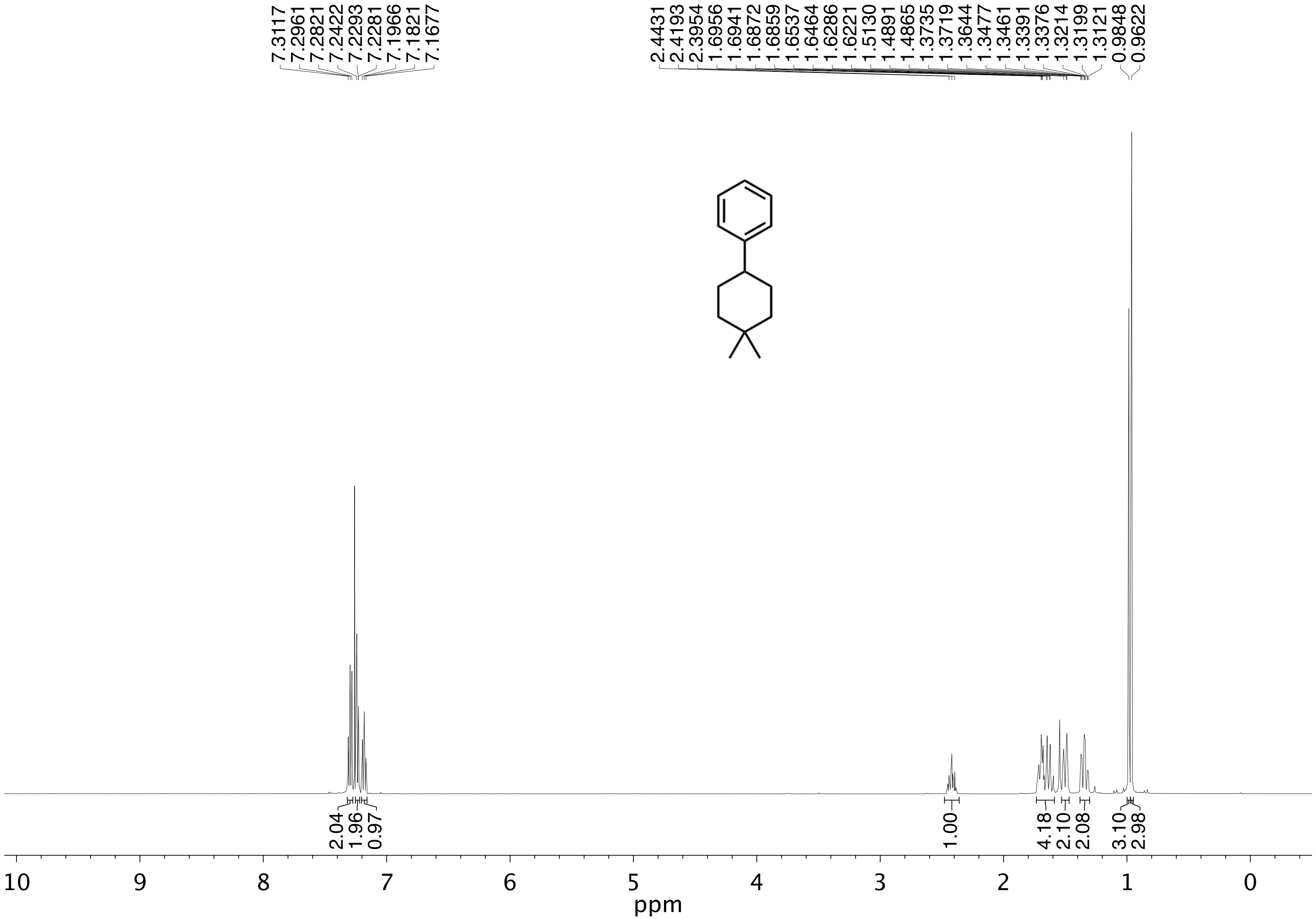
^{1}H NMR (500 MHz, C_6D_6) of **SI-50**.



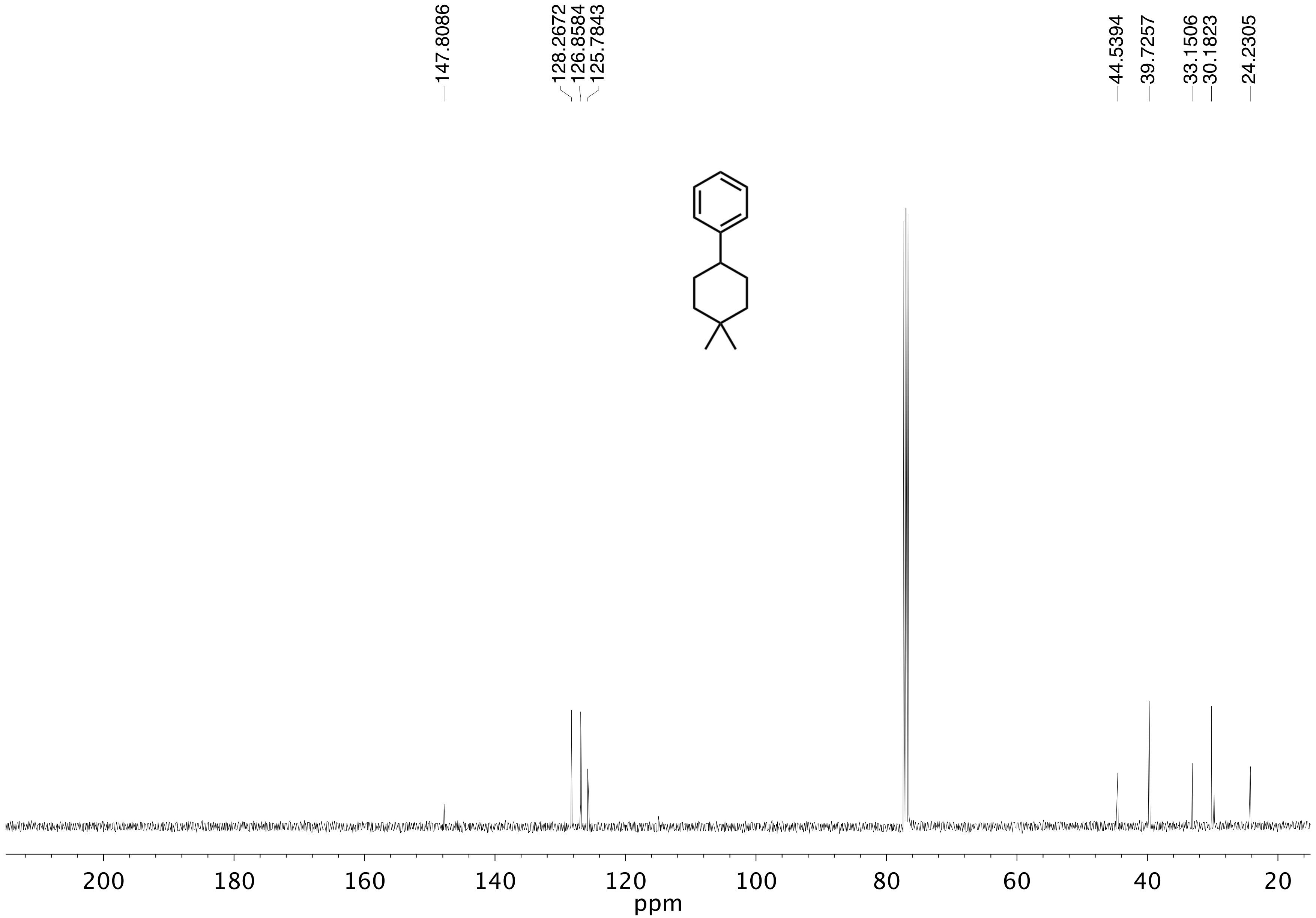
^{13}C NMR (125 MHz, C_6D_6) of **SI-50**.



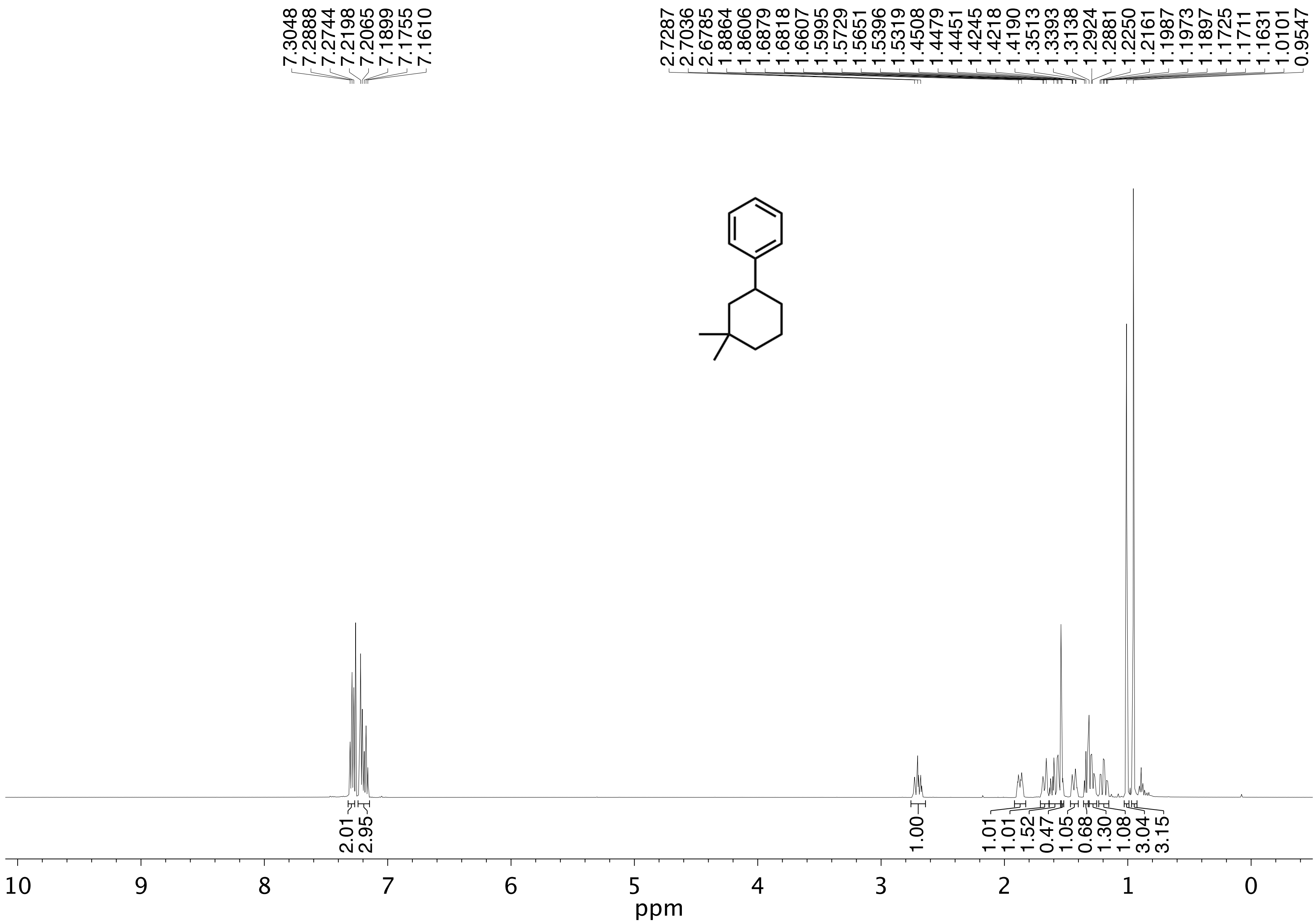
^{13}C NMR (125 MHz, C_6D_6) comparison of **SI-50** (below) with authentic **SI-46** (top).



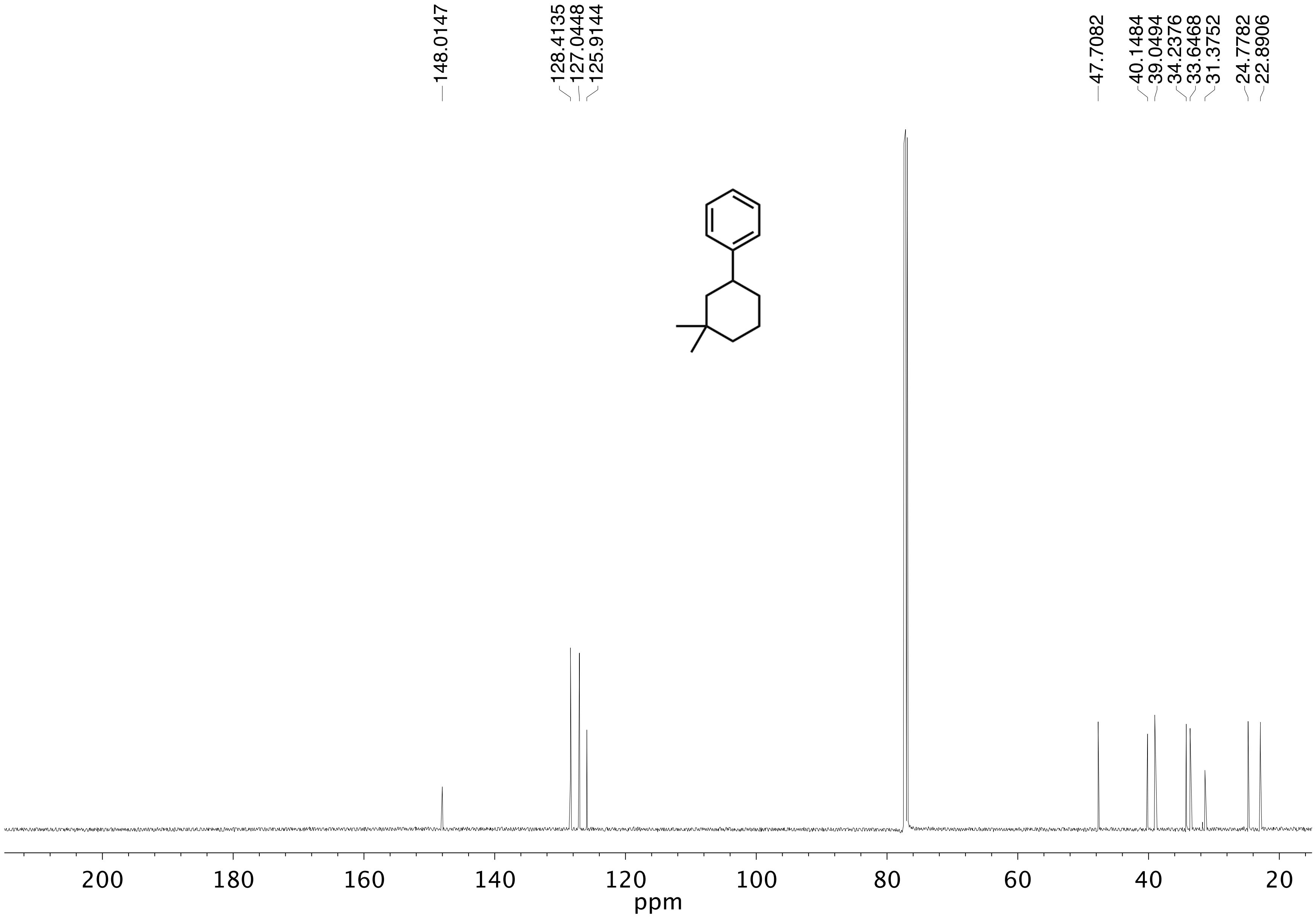
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-51**.



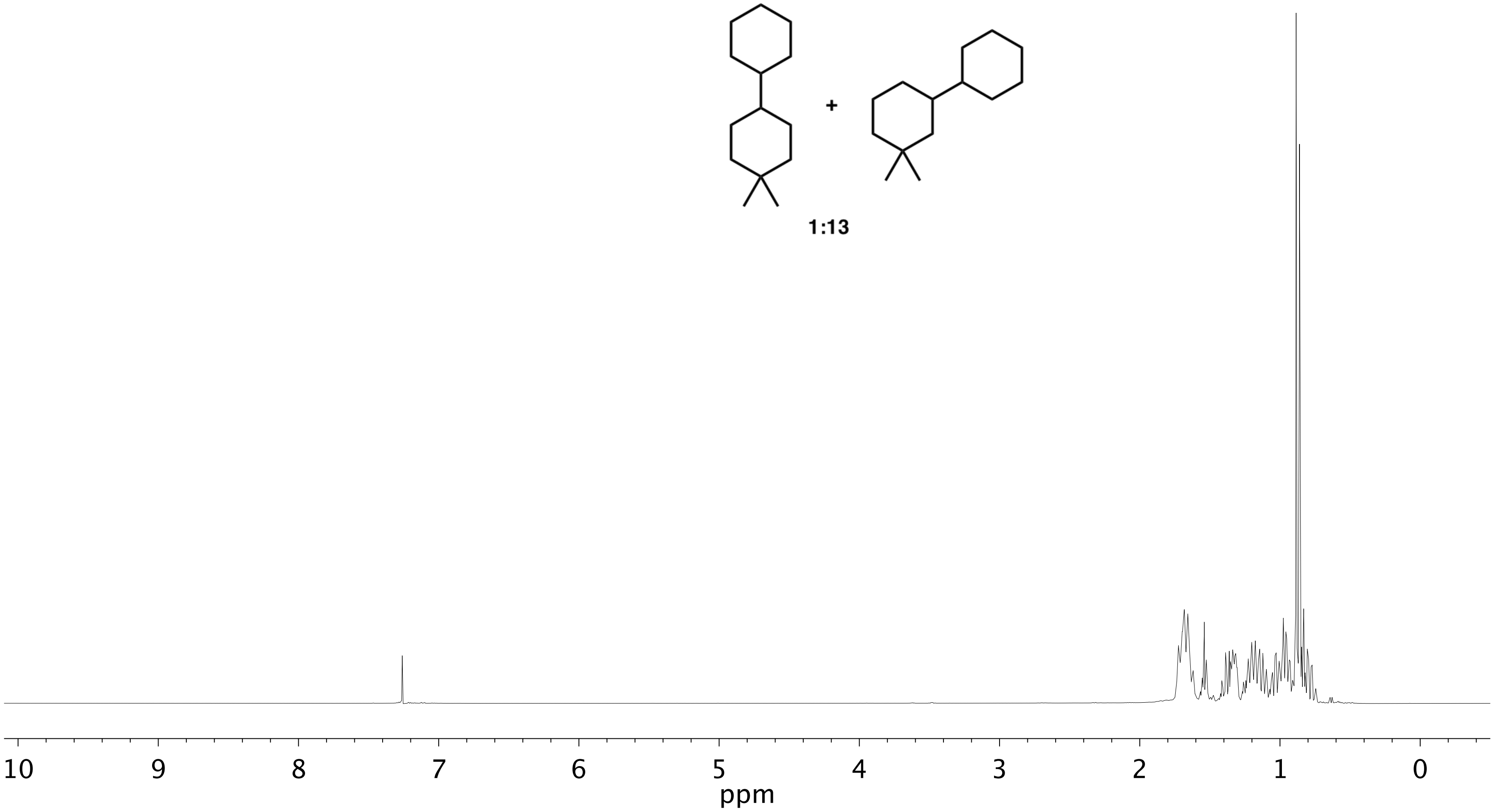
^{13}C NMR (125 MHz, $CDCl_3$) of **SI-51**.



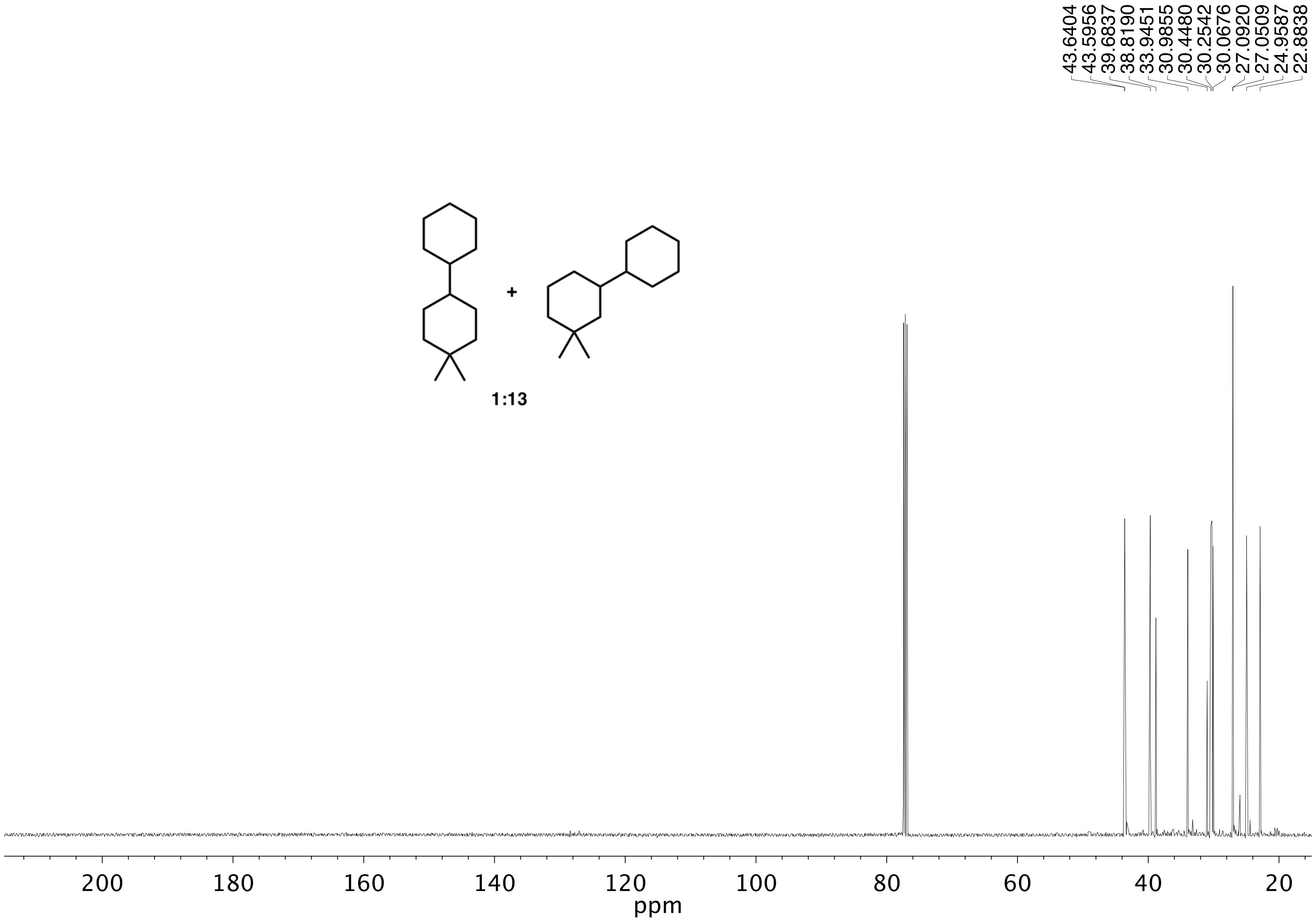
^{1}H NMR (400 MHz, CDCl$_3$) of **SI-52**.



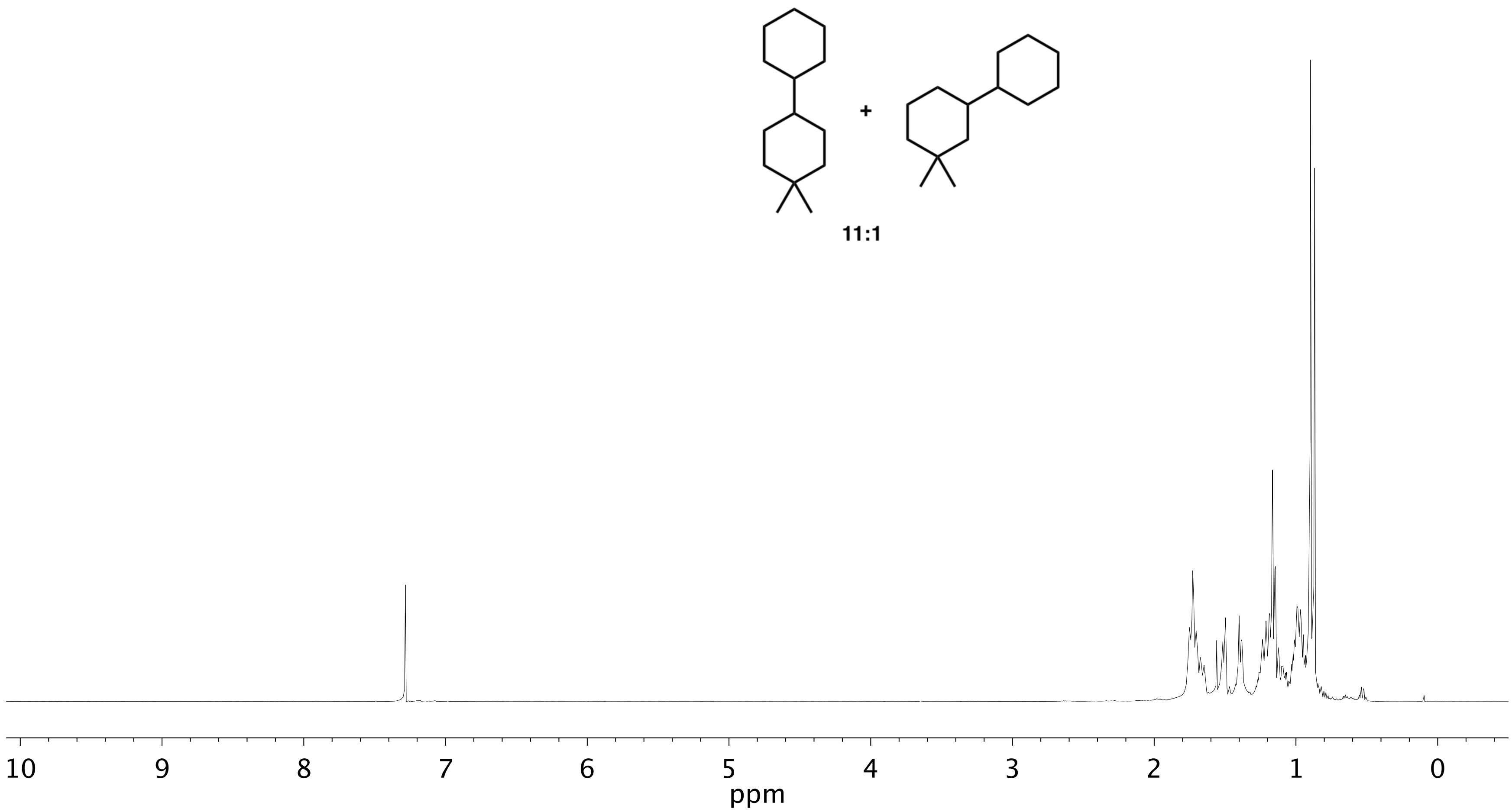
^{13}C NMR (125 MHz, CDCl$_3$) of **SI-52**.



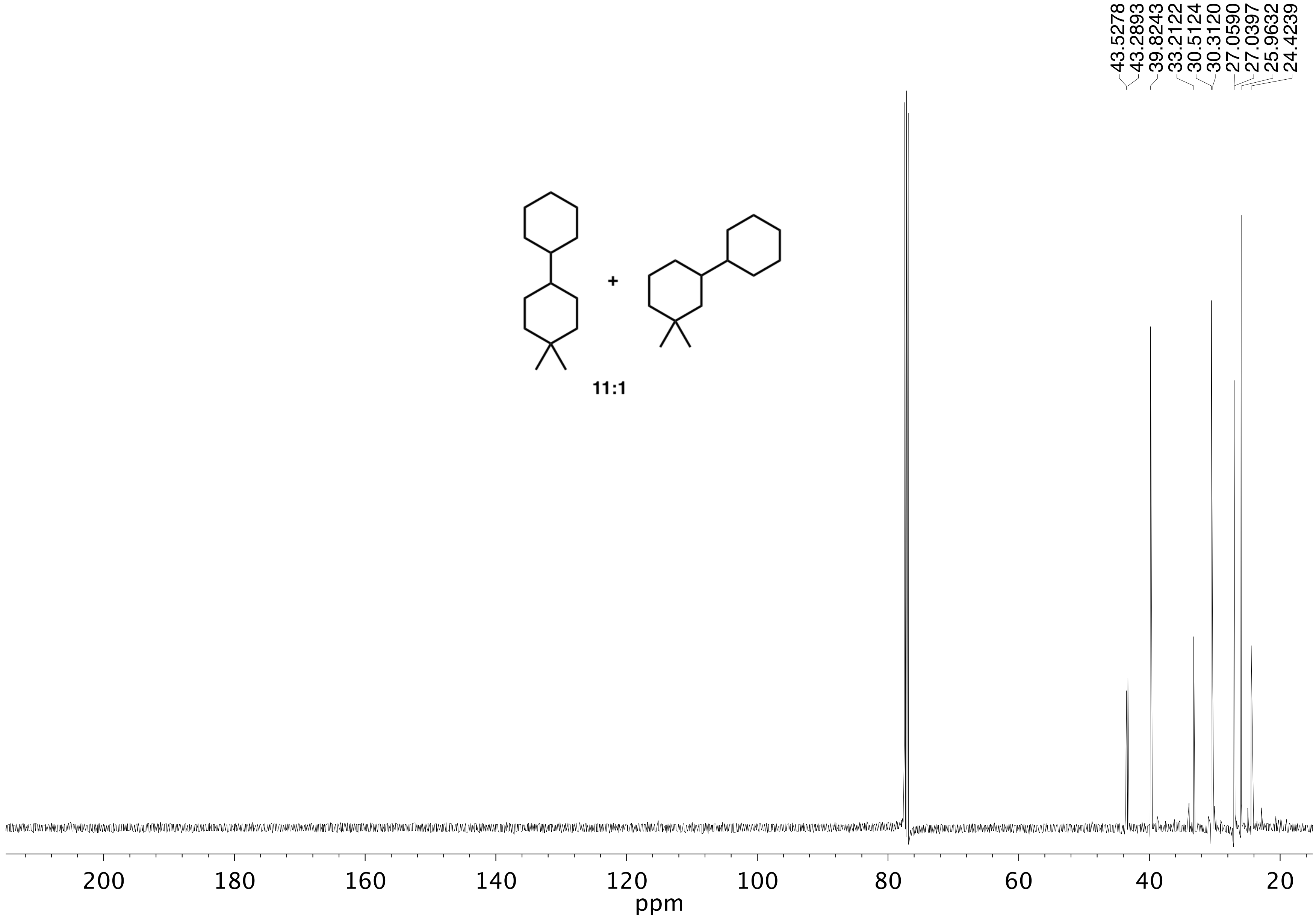
^{1}H NMR (400 MHz, $CDCl_3$) of a 13:1 mixture of **SI-18** to **SI-20**.



^{13}C NMR (125 MHz, $CDCl_3$)) of a 13:1 mixture of **SI-18** to **SI-20**.



^{1}H NMR (400 MHz, $CDCl_3$) of) of a 11:1 mixture of **SI-20** to **SI-18**.



^{13}C NMR (125 MHz, CDCl$_3$) of a 11:1 mixture of **SI-20** to **SI-18**.

9. X-ray crystallographic data

X-ray structure of **SI-23**

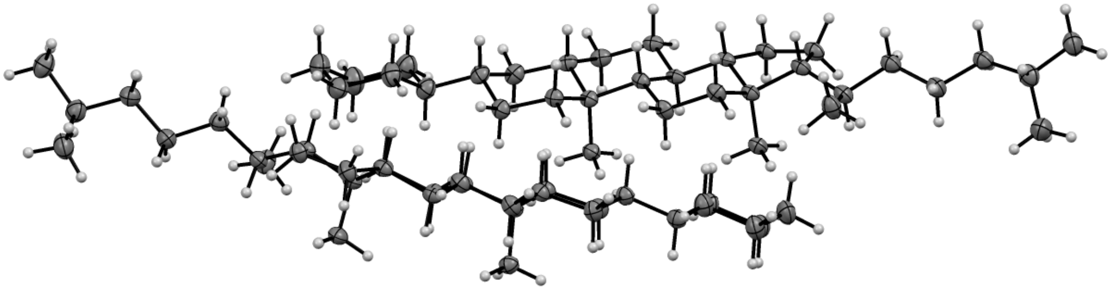


Table S2. Crystal data and structure refinement for **SI-23**

Identifcation code	cu_hosea1702s_a
Empirical formula	$C_{33}H_{58}$
Formula weight	454.79
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	15.2991(3)
b/Å	9.6363(2)
c/Å	19.3364(4)
α/°	90

β/°	93.9340(10)
γ/°	90
Volume/ Å^3	2843.98(10)
Z	4
ρ_{calc}g/cm^3	1.062
μ/mm^{-1}	0.423
F(000)	1024
Crystal size/mm^3	0.160 x 0.080 x 0.020
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	2.290 to 69.491
Index ranges	$-18 \leq h \leq 18, -11 \leq k \leq 11, -22 \leq l \leq 22$
Reflections collected	42182
Independent reflections	10489 [R_{int} = 0.0408, R_{sigma} = 0.0351]
Data/restraints/parameters	10489/1/605
Goodness-of-fit on F^2	1.048
Final R indexes [I >=2σ(I)]	R_1 = 0.0417, wR_2 = 0.1040
Final R indexes [all data]	R_1 = 0.0508, wR_2 = 0.1096
Largest diff. peak/hole / e Å^{-3}	0.0367/–0.163
Flack parameter	–0.1(3)

Part II: Computational Section

10. Full computational details

All density functional theory (DFT) calculations were performed using Gaussian 09 (*60*). Geometry optimizations and frequency calculations were performed, unless noted otherwise at the M06-2X/6-311+G-(d,p) (gas phase) level of theory (*61–64*). ZPE, enthalpy and free energy corrections were obtained using a standard state of 1 atmosphere of pressure and 298 K and energies were obtained from these M06-2X/6-311+G-(d,p) (gas phase) level calculations, unless noted otherwise. Normal vibrational mode analysis confirmed that optimized structures are minima (no imaginary frequency) or transition structures (one imaginary frequency). Transition structures have also been verified by intrinsic reaction coordinate (IRC) calculations. All 3D rendering of stationary points was generated using CYLview (*65*).

Molecular dynamics (MD) simulations were performed at the M06-2X/6-31G(d) or M06-2X/6-311+G(d,p) level of theory in the gas phase, using a standard state of 1 atmosphere of pressure and 298 K. Quasiclassical trajectories (QCTs) were initiated in the region of the potential energy surface near the found optimized TS. The trajectories were then propagated in the forward and backward directions for 300 fs or 500 fs. The classical equations of motion were integrated with a velocity-Verlet algorithm using Singleton's program Progdyn (*66*), with the energies and derivatives computed on the fly with M06-2X using Gaussian 09 to recalculate forces constants at each step. The step length for integration was 1 fs. The simulations were visualized and rendered into animated movies using CYLview (*65*).

11. Input parameters for Progdyn

For MD simulations of the cyclohexenyl (**9**), 4,4-dimethylcyclohexenyl (**16**), and 5,5-dimethylcyclohexenyl (**17**) vinyl cations reacting with cyclohexane, the parameters were used as shown below with a duration of 300 fs. For the reaction between but-1-en-2-yl (**25**) vinyl cation and cyclohexane the parameters were the same with the exception of the use of M06-2X/6-31G(d) and a duration of 500 fs.

```
method m062x/6-311+g(d,p)
method2 unrestricted
charge 1
multiplicity 1
processors 8
memory 200mw
killcheck 1
diagnostics 0
title cf2 Cy_Cy_TS MD 298 dis2
initialdis 2
timestep 1E-15
scaling 1.0
temperature 298.15
#*** method3, method4, method5, and method6 -- These keywords let you add extra lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line.  Here are some examples to uncomment if
needed
#method3 IOp(3/76=0572004280)
#method3 scrf=(pcm,solvent=dichloromethane)
#add the line below with big structures to get it to put out the distance matrix and the input orientation
#method3 iop(2/9=2000)
#method4 scrf=(pcm,solvent=dmso,read)
#method5 radii=bondi
#method6
#*** methodfile -- This keyword lets you add more complicated endings to gaussian input files
#such as a gen basis set.  Put after the keyword the number of lines in a file you create called
#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
#*** numimag --This tells the program the number of imaginary frequencies in the starting structure.
#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the direction defined by searchdir
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in random direction
numimag 1
#*** searchdir -- This keyword says what direction to follow the mode associated with the imaginary frequency.
#The choices are "negative" and "positive".  Positive moves in the direction defined in the gaussian frequency
calculation
#for the imaginary frequency, while negative moves in the opposite direction.  The correct choice can be made
either
#by a careful inspection of the normal modes and standard orientation geometry, or by trial and error.
searchdir negative
#*** classical --  for quassiclassical dynamics, the default, use 0.  for classical dynamics, use 1
#if there are no normal modes and the velocities are to be generated from scratch, use classical 2
```

```
classical 0
#*** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line below, otherwise leave it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
#*** cannonball -- The program can "fire" a trajectory from a starting position toward a particular target, such as toward
#a ts.  To use this, make a file cannontraj with numAtom lines and three numbers per line that defines the vector
#for firing the trajectory, relative to the starting geometry's standard orientation.  The number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
#*** keepevery --This tells the program how often to write the gaussian output file to file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or molden loading time.
keepevery 1
#*** highlevel --For ONIOM jobs, the following line states the number of highlevel atoms,
#which must come before the medium level atoms.  Use some high value such as 999 if not using ONIOM
highlevel 999
#*** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is, initialdis=0
#fixedatom1 2
#fixedatom2 3
#fixedatom3 19
#*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the edge
#are reflected back toward the middle.  Useful for dynamics with solvent molecules.  This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15 x 15 angstroms
boxon 0
boxsize 7.5
#*** displacements -- This keyword lets you set the initialdis of particular modes by using a series of lines of the format
# displacements NumberOfMode InitialDisForThatMode, as in the example below. You should be able to do as many of these as you like
# you might consider this for rotations where a straight-line displacement goes wrong at large displacements
# The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same thing as 0 but is maintained for now because
# a previous version of the program had a bug that made 0 not work.
#displacements 1 0
#*** etolerance --This sets the allowable difference between the desired energy in a trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial velocities.
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems.  For very large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 1
#*** controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.
#controlphase 2 positive
```

```
#*** damping -- The damping keyword lets you add or subtract energy from the system at each point, by
multiplying the velocities
#by the damping factor.  A damping of 1 has no effect, and since you mostly want to change the energy slowly,
normal values range
#from 0.95 to 1.05.  The use of damping lets one do simulated annealing - you add energy until the structure is
moving enough
#to sample the kinds of possibilities you are interested in, then you take away the energy slowly.
damping 1
#*** reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.
reversetraj true


#updated Aug 9, 2007 to include the possibility of classical dynamics by the keyword classical
#updated Jan 2008 to include fixed atoms, ONIOM jobs, keepevery, and box size
#update Feb 2008 to include methodfile parameter
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# update Aug 2010 to include etolerance, damping controlphase and reversetraj
```

12. Additional Figures and Discussion

The flatness of the potential energy surface made finding sufficient stationary points difficult, thus MD simulations were indispensable to understand and explain the mechanism of selectivity. Various geometries taken from the MD simulations were used as starting points for the geometry optimization calculations. The resulting optimized structures and their relative energies are depicted in the following figures. The MD simulations of the cyclohexenyl (**9**), 4,4-dimethylcyclohexenyl (**16**), and 5,5-dimethylcyclohexenyl (**17**) vinyl cations reacting with cyclohexane each had similar trajectory outcomes. In all examples, a nonclassical bridging structure was seen as the dominate species with lifetimes of approximately 100 to 300 fs (or till the end of the simulation). Only about 9% of all trajectories showed the *1*,*2*-hydride shift to form the tertiary cyclohexylcyclohexyl cation, although this likely would increase to 100% if the simulations were to be run for longer durations. These results suggest that the inferred stability of the nonclassical bridging carbocation delays the energetically favored *1*,*2*-hydride shift, allowing for the experimentally observed distribution of products. The final distribution of products observed in the MD simulations for 4,4-dimethylcyclohexenyl (**16**) was 50:7 (**19:20**) and 9:46 (**19:20**) for 5,5-dimethylcyclohexenyl (**17**) vinyl cation. These results were obtained by analyzing each trajectory and recording the resulting products at the end of the 300 fs simulation. In the case where a bridging product existed at the end of the simulation the product was decided by analyzing the C–C bond lengths of the bridging bonds (from C1 and C2, to the cyclohexane C), and the shorter bond length (at least 0.1 Å shorter, if less the trajectory was omitted) was determined to be the resulting C1 or C2 alkylation product.

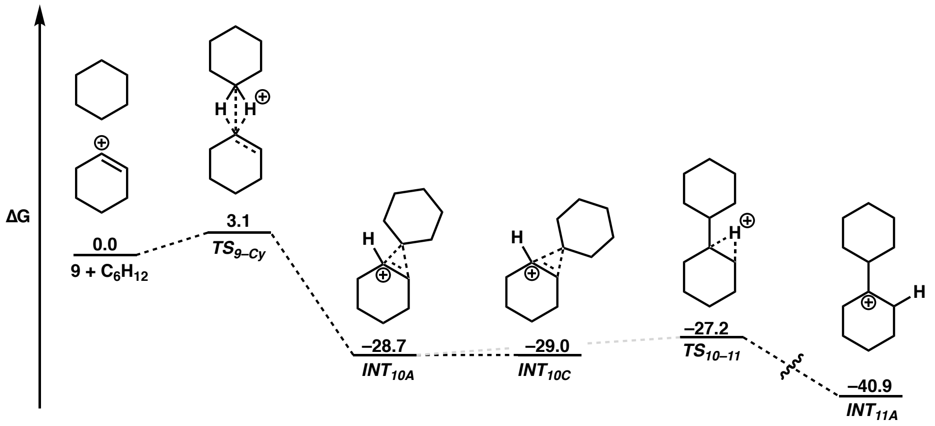
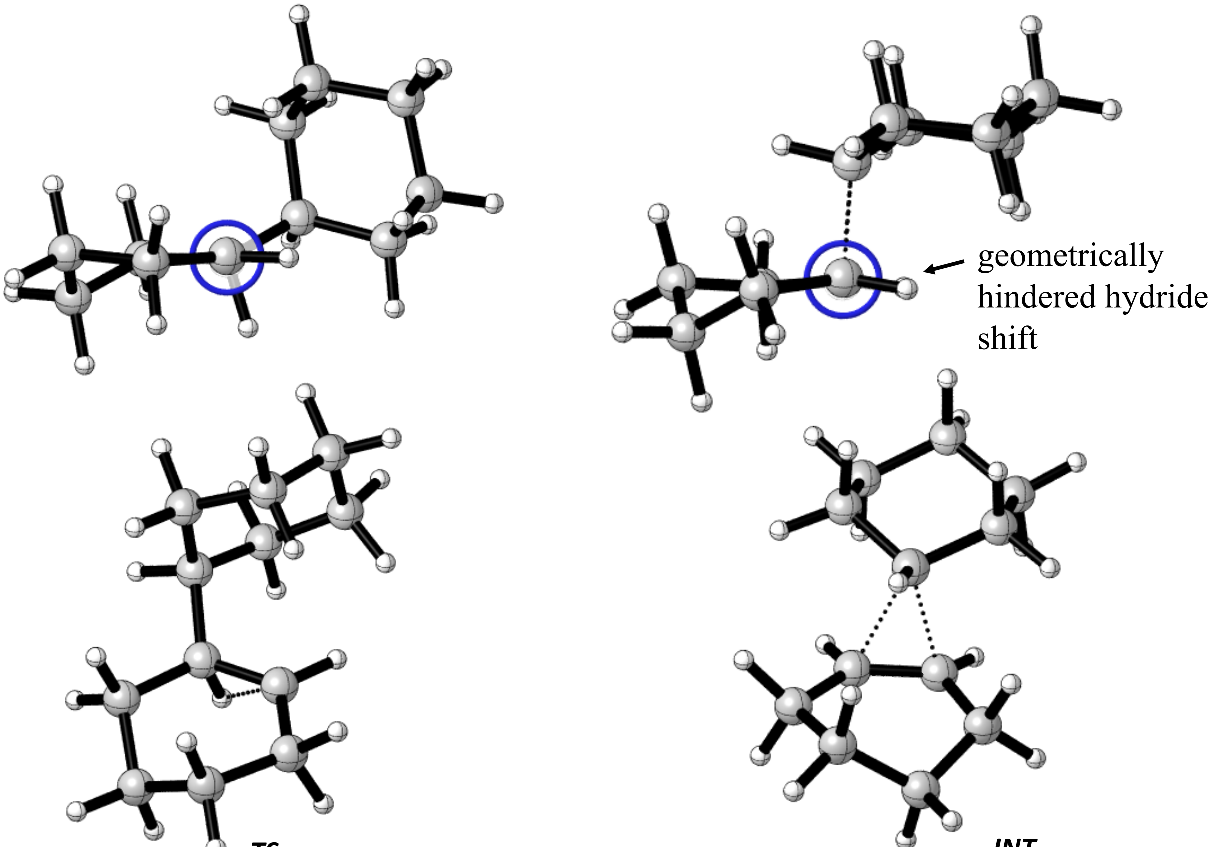


Fig. S39. Represented is the reaction coordinate diagram for vinyl cation (***9***) and the corresponding free energies of intermediates and transition structures. The flat potential energy surface illustrates that the ambimodal TS (**$TS_{9\text{-}Cy}$**) leads directly to multiple products without any intervening minima or barriers, arriving at either **INT_{11A}** or **INT_{11B}**. **INT_{11B}** and its corresponding H-shift TS is not depicted here but is equivalent to **INT_{11A}** with the cyclohexyl–cyclohexyl bond at C2 instead of C1, as is the case of **INT_{11A}**. *Geometries optimized and energies, including thermodynamic contributions, calculated with M06-2X/6-311+G(d,p). Relative energies are Gibbs free energies and given in kcal/mol, using a standard state of 1 atmosphere of pressure and 298 K in the gas phase.



$TS_{10\text{-}11}$

1,*2*-hydride shift TS

INT_{10A}

unsymmetrical nonclassical carbocation

Fig. S40. On the left is the TS (***$TS_{10\text{-}11}$***) for the *1*,*2*-hydride shift to form the tertiary cyclohexylcyclohexyl cation (***INT_{11A}***). The top view illustrates via Newman projection that the favorable hydride shift is allowed without interference from the vicinal hydrogen. On the right is the unsymmetrical nonclassical carbocation intermediate (***INT_{10A}***). The alternate view in the top right illustrates the vicinal hydrogens overlapping, preventing the hydride shift in this geometrical conformation. *Geometries optimized with M06-2X/6-311+G(d,p).

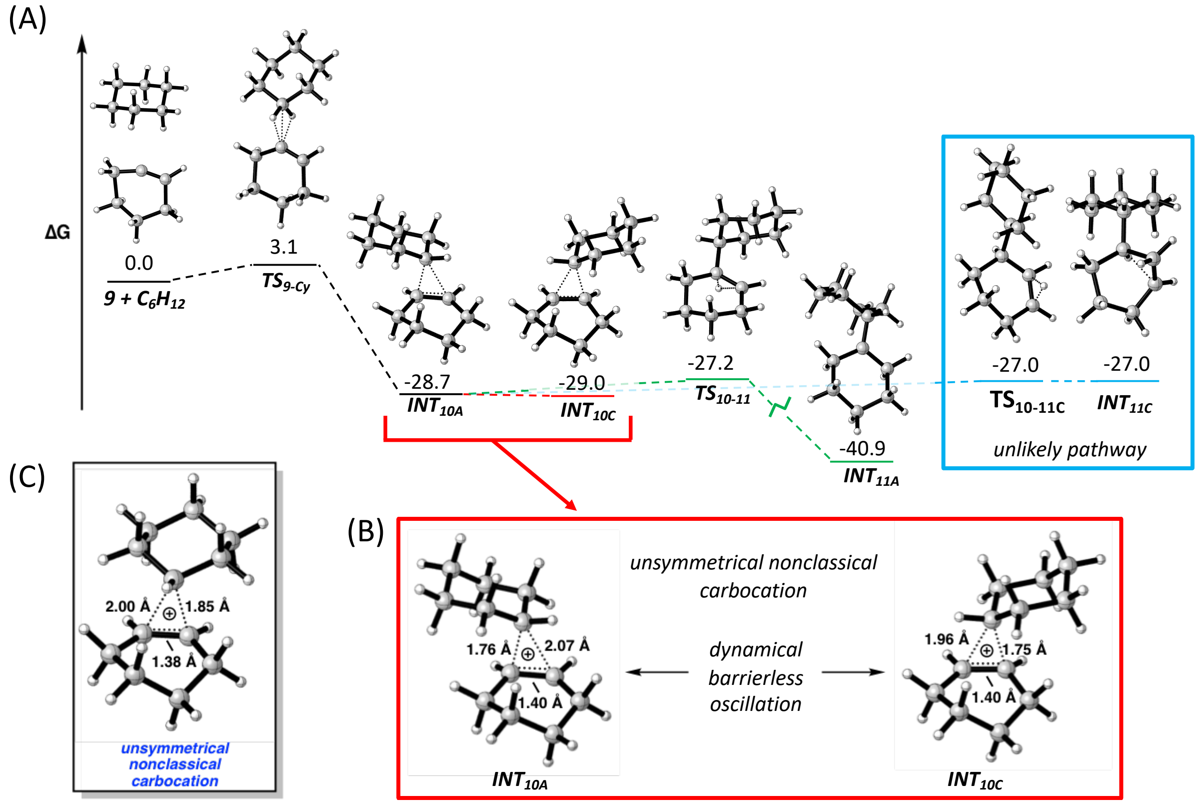


Fig. S41. (A) Reaction coordinate diagram for vinyl cation (***9***) showing the general reaction coordinate diagram and corresponding intermediates and transition structures. **(B)** More advanced look into the non-symmetric nonclassical carbocation structural variations. Minor differences in geometry and energy are due to the asymmetric half chair conformer of the lower cyclohexenyl ring. The MD simulations show a vibrational oscillation between these nonclassical species with a significant lifetime. **(C)** In search for a symmetric minimum, an additional bridged stationary point was found which is 0.6 kcal/mol higher in energy compared to ***INT$_{10A}$***. *Geometries optimized and energies, including thermodynamic contributions, calculated with M06-2X/6-311+G(d,p). Relative energies are Gibbs free energies and given in kcal/mol, using a standard state of 1 atmosphere of pressure and 298 K in the gas phase.

For the but-1-en-2-yl vinyl cation **(*23*)** the flat potential energy surface again lead to difficulty obtaining stationary points that could describe the experimentally observed product distribution. MD simulations were essential to understand and explain the mechanism of selectivity, as well as identifying structures that could be used as starting points for the geometry optimization calculations. 70 MD simulations (500 fs) were run, only 27 of which proceeded to form C–C bonds (the rest separated into cyclohexane cation and butene, compared to over 90% successful C–C bonds formed for the cyclohexenyl vinyl cation substrates). All 27 of these successful trajectories went only to the terminal addition with each simulation ending up in a bridging structure such as ***INT$_{23B}$***.

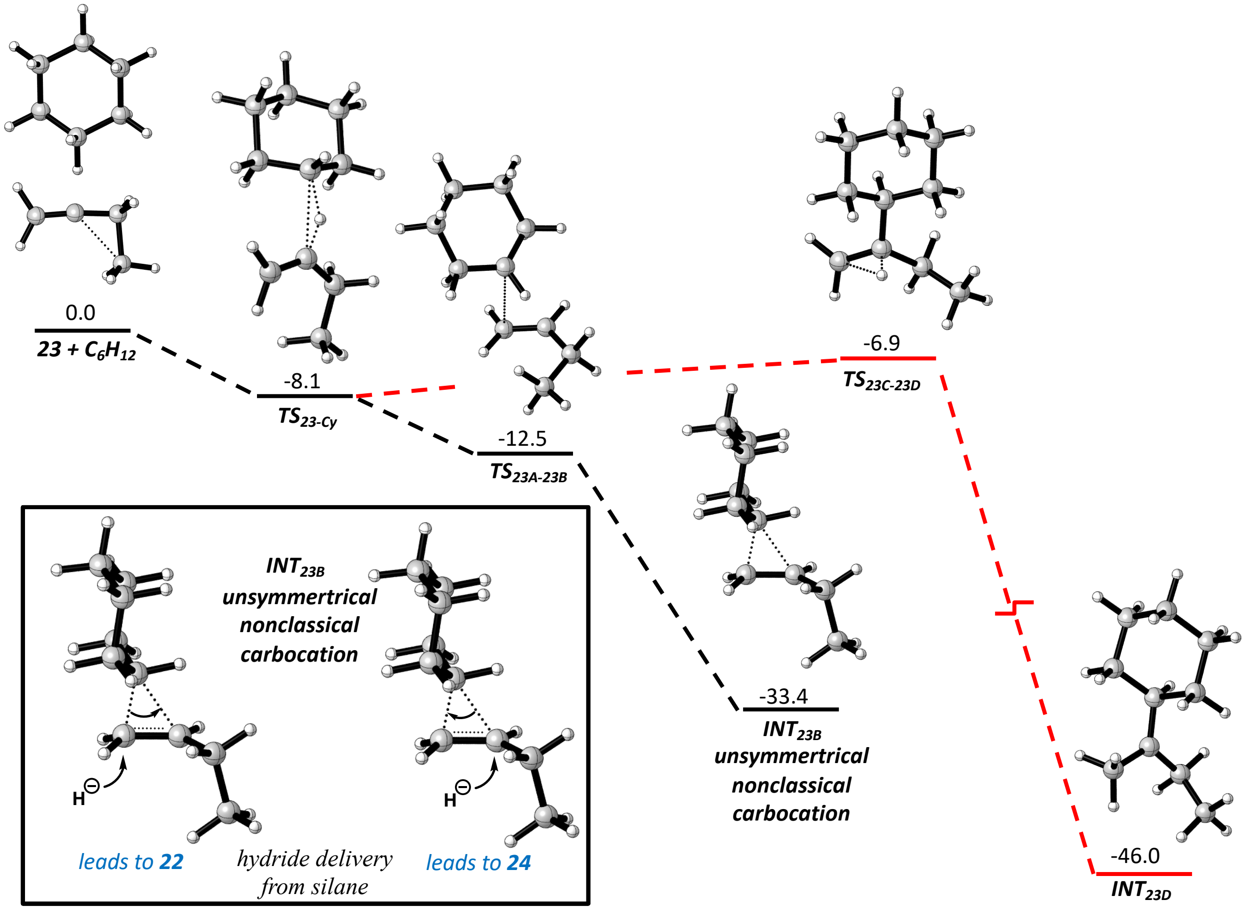


Fig. S42. The reaction coordinate diagram showing the generic reaction path and corresponding intermediates and transition structures. Also depicted is the representative illustration of the hydride delivery to the two carbons resulting in products **22** and **24** (attempts to optimize these transition structures were unfruitful, so no energetic comparison is available). The thermodynamically favored product ***INT$_{23D}$*** is avoided due to the generation of a higher energy primary carbocation. As shown in the figure, as well as seen in the MD simulations, the reaction pathway is overall barrierless and leads downhill directly to ***INT$_{23B}$***. We can deduce that it is only through ***INT$_{23B}$*** that the resulting products are formed. *Geometries optimized and energies, including thermodynamic contributions, calculated with M06-2X/6-311+G(d,p). Relative energies are Gibbs free energies and given in kcal/mol, using a standard state of 1 atmosphere of pressure and 298 K in the gas phase.

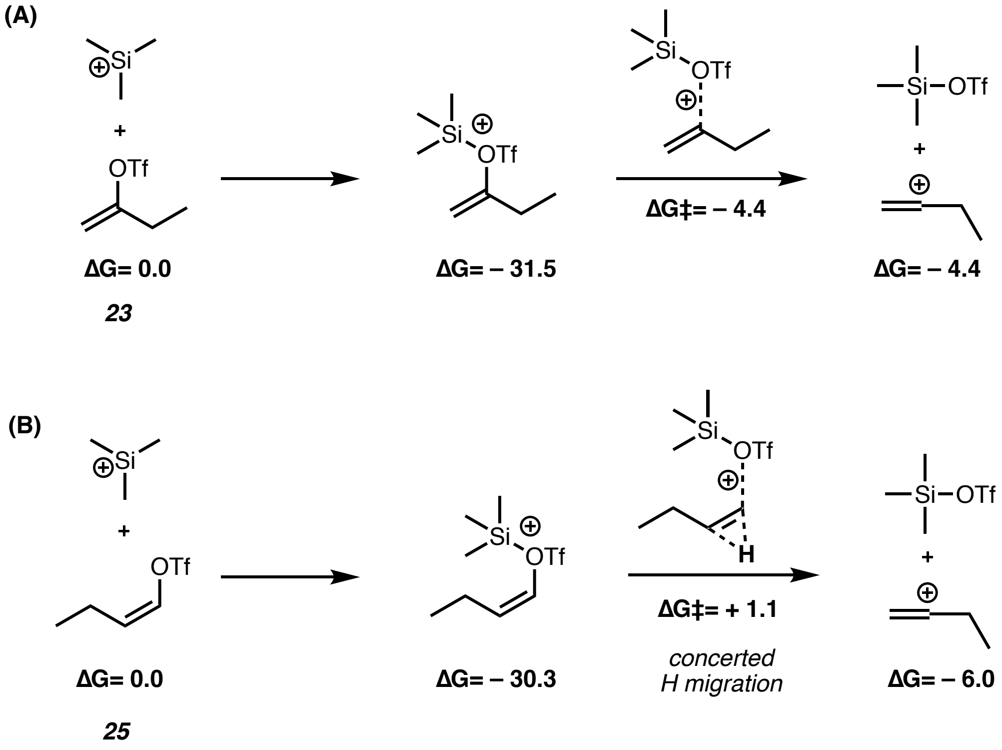


Fig. S43. (A) The calculations illustrate vinyl triflate ***23*** undergoes abstraction of the triflate via silylium to the vinyl cation with a barrier of 27.1 kcal/mol. **(B)** Terminal triflate ***25*** undergoes a similar triflate abstraction mechanism albeit with a concerted *H* migration and a higher barrier of 31.4 kcal/mol. The difference in free energy of activation of 4.3 kcal/mol is supported by the lower reactivity and increase in reaction time required for triflate ***25***. Additionally, the identical product distribution from ***23*** and ***25*** reacting with cyclohexane provides evidence that they both proceed through a common vinyl cation intermediate. *Geometries optimized and energies, including thermodynamic contributions, calculated with M06-2X/6-311+G(d,p). Relative energies are Gibbs free energies and given in kcal/mol, using a standard state of 1 atmosphere of pressure and 298 K in the gas phase.

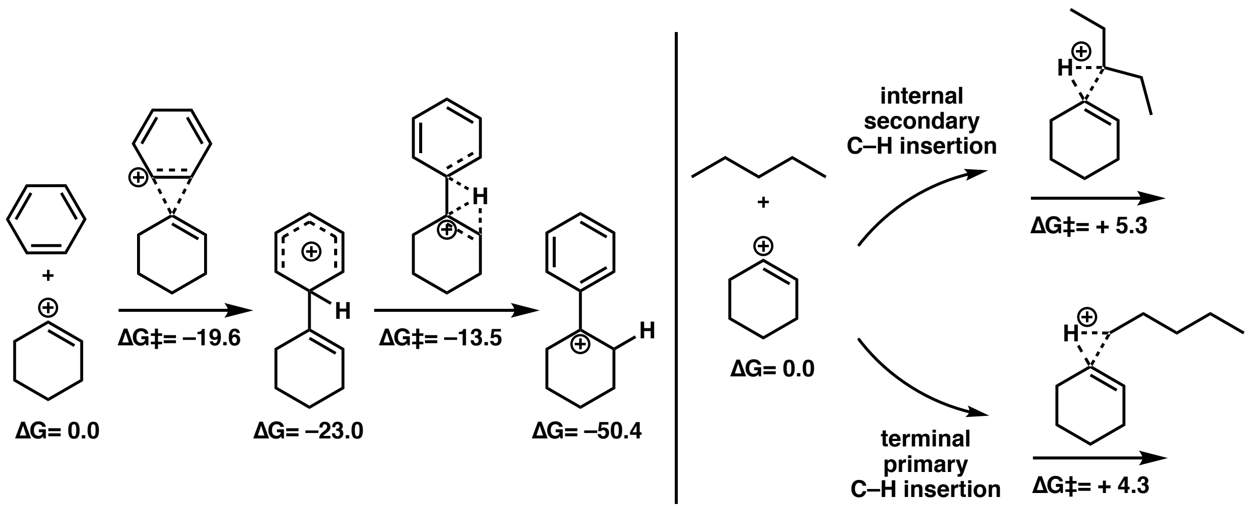


Fig. S44. The reaction of vinyl cation ***9*** with benzene is spontaneous, without a barrier and highly exothermic. Comparatively the reaction of vinyl cation ***9*** with the pentane solvent, while still thermodynamically favorable has an energy of activation barrier of 4.3 to 5.3 kcal/mol for the primary and secondary C–H insertions respectively. *Geometries optimized and energies, including thermodynamic contributions, calculated with M06-2X/6-311+G(d,p). Relative energies are Gibbs free energies and given in kcal/mol, using a standard state of 1 atmosphere of pressure and 298 K in the gas phase.

Movies S1 – S5

Movie S1 4,4-dimethylcyclohexene vinyl cation C2 addition. MD Simulation of 4,4-dimethylcyclohexene vinyl cation reacting with cyclohexane. This video follows the reaction progress from a 1,1 insertion to the C2 alkylated product. The second half of the video visualizes the reaction while highlighting the key points throughout. Time scale of 300 fs is illustrated in the video. See supporting computational details for methods, video was animated using CYLView.

Movie S2 4,4-dimethylcyclohexene vinyl cation C1 addition. MD Simulation of 4,4-dimethylcyclohexene vinyl cation reacting with cyclohexane. This video follows the reaction progress from a 1,1 insertion to the C1 alkylated product followed by the 1,2-hydride shift. This was the most common pathway for this substrate. The second half of the video visualizes the reaction while highlighting the key points throughout. Time scale of 300 fs is illustrated in the video. See supporting computational details for methods, video was animated using CYLView.

Movie S3 5,5-dimethylcyclohexene vinyl cation C2 addition. MD Simulation of 5,5-dimethylcyclohexene vinyl cation reacting with cyclohexane. This video follows the reaction progress from a 1,1 insertion to the C2 alkylated product. Time scale of 300 fs is illustrated in the video. See supporting computational details for methods, video was animated using CYLView.

Movie S4 5,5-dimethylcyclohexene vinyl cation C1 addition. MD Simulation of 5,5-dimethylcyclohexene vinyl cation reacting with cyclohexane. This video follows the reaction progress from a 1,1 insertion to the C1 alkylated product followed by the 1,2-hydride shift. This was the most common pathway for this substrate. Time scale of 300 fs is illustrated in the video. See supporting computational details for methods, video was animated using CYLView.

Movie S5 Butenyl vinyl cation reaction with cyclohexane. MD Simulation of but-1-en-2-yl vinyl cation reacting with cyclohexane. This video follows the reaction progress from a 1,1 insertion to the bridging nonclassical carbocation. This was the most common pathway for this substrate. Time scale of 500 fs is illustrated in the video. See supporting computational details for methods, video was animated using CYLView.

13. Cartesian Coordinates, Energies and Vibrational Frequencies

These geometries and thermal corrections were obtained at the M062X/6-311+G(d,p) level of theory (gas phase), unless otherwise specified. ZPE, enthalpy and free energy corrections were obtained using a standard state of 1 atmosphere of pressure and 298 K. Energies and energy corrections are reported in hartree below, along with the Cartesian coordinates.

Cyclohexene vinylcation (9)

Charge: +1

ZPE	0.133275
DE	0.139068
DH	0.140013
DG	0.104552
E	-233.642679
H	-233.502666
G	-233.538126

Cartesian coordinates

C	1.602842	-0.511545	0.119591
C	0.370034	-1.140080	0.048497
C	-0.896584	-1.239556	-0.014877
C	-1.506914	0.191566	-0.133033
C	-0.466606	1.215913	0.311753
C	0.898360	0.945298	-0.303435
H	2.043439	-0.456642	1.113992
H	2.315941	-0.735528	-0.672421
H	-1.807895	0.317757	-1.176113
H	-2.400926	0.214642	0.491381
H	-0.782499	2.217699	0.009804
H	-0.391293	1.216658	1.402061
H	0.864625	0.943976	-1.392476
H	1.657122	1.647538	0.044855
H	-1.505308	-2.135682	0.007939

There are no imaginary frequencies.

Cyclohexene allyl cation (13)

Charge: +1

ZPE	0.134081
DE	0.139639
DH	0.140583
DG	0.105467
E	-233.690673
H	-233.550090
G	-233.585206

Cartesian coordinates

C	-0.663242	1.255195	0.179235
H	-1.037819	2.171057	-0.288320
H	-0.819925	1.423998	1.262346
C	-1.379679	0.002256	-0.315508
H	-1.379347	0.002449	-1.408830
H	-2.419532	0.003902	0.007957
C	-0.667352	-1.253202	0.178868
H	-1.044506	-2.167619	-0.289450
H	-0.825212	-1.422162	1.261777
C	0.797407	1.183136	0.015104
H	1.365067	2.109012	0.093948
C	0.793687	-1.185550	0.015984
H	1.358304	-2.113437	0.093063
C	1.491630	-0.002352	-0.152016
H	2.568268	-0.004101	-0.262495

There are no imaginary frequencies.

Cyclohexene vinyl cation H-shift TS (*$TS_{9\text{-}13}$*)

Charge: +1

ZPE	0.129823
DE	0.135213
DH	0.136157
DG	0.101326
E	-233.581763
H	-233.445606
G	-233.480437

Cartesian coordinates

C	1.400831	-0.005434	0.468050
H	2.466705	0.148143	0.321861
H	1.165451	-0.076457	1.529679
C	0.571670	1.195482	-0.189444
H	0.873474	1.299796	-1.232446
H	0.909302	2.096161	0.328492
C	-0.957011	1.053669	-0.077769
H	-1.450030	1.465421	-0.965555
H	-1.352534	1.611315	0.776091
C	0.799198	-1.060691	-0.362822
H	1.231310	-1.309043	-1.330349
C	-1.431430	-0.381898	0.088577

H	-2.422592	-0.581741	0.490448
C	-0.491765	-1.374029	-0.090486
H	-0.770043	-1.216188	1.065146

1 imaginary frequency: –877.9 cm^{-1}.

5,5-DimethylCyclohexene-Cy TS (*TS*$_{17\text{-}20/19}$)

Charge: +1

ZPE	0.361507
DE	0.376157
DH	0.377101
DG	0.320556
E	-548.090684
H	-547.713583
G	-547.770128

Cartesian coordinates

C	0.519135	0.414014	0.047309
C	-1.493183	0.093058	0.432177
H	-1.086904	0.195620	-0.605441
H	-0.747458	0.215064	1.251720
C	2.294609	1.964187	-0.329304
C	3.012659	0.723080	-0.859816
H	4.089388	0.908599	-0.876806
H	2.703894	0.545451	-1.895637
C	2.738412	-0.542328	-0.032145
C	1.197959	-0.871503	-0.088568
H	0.956530	-1.552241	0.732092
H	0.934812	-1.354644	-1.034704
C	0.832616	1.675943	-0.013299
H	0.133738	2.487425	0.147921
C	-2.069432	-1.325119	0.524562
H	-1.300126	-2.077866	0.336667
H	-2.426398	-1.475906	1.548027
C	-2.519429	1.223983	0.583029
H	-2.057303	2.203492	0.436923
H	-2.895512	1.197858	1.610485
C	-3.230293	-1.475426	-0.464696
H	-3.677756	-2.463762	-0.343979
H	-2.841600	-1.425402	-1.489142
C	-3.670223	1.013277	-0.406863
H	-3.296941	1.146043	-1.429476
H	-4.427431	1.782554	-0.244443
C	-4.280389	-0.381879	-0.262194
H	-4.723974	-0.484374	0.734839
H	-5.091251	-0.508397	-0.981702
H	2.324785	2.773746	-1.061705
H	2.760362	2.346173	0.584823
C	3.157787	-0.348571	1.427649
H	3.059104	-1.283525	1.983736
H	4.205861	-0.043148	1.474874
H	2.563352	0.412897	1.939081
C	3.479122	-1.735985	-0.635594
H	4.557436	-1.581452	-0.552505
H	3.232129	-2.659579	-0.106362
H	3.235159	-1.865015	-1.692770

1 imaginary frequency: –512.14 cm^{-1}.

4,4-DimethylCyclohexene-Cy TS (*TS*$_{16\text{-}19/20}$)

Charge: +1

ZPE	0.361108
DE	0.375761
DH	0.376705
DG	0.320160
E	-548.089441
H	-547.712736
G	-547.769281

Cartesian coordinates

C	-0.414947	0.076012	-0.416485
C	1.615430	0.048803	-0.543859
H	1.076233	0.062996	0.438677
H	0.970349	0.084958	-1.453460
C	-2.445490	1.346652	-0.243672
C	-3.083158	0.016213	0.195488
C	-2.462898	-1.131110	-0.617697
C	-0.932542	-1.294200	-0.385223
H	-0.505975	-1.909410	-1.180127
H	-0.719306	-1.772180	0.575615
C	-0.930029	1.272805	-0.372291
H	-0.345268	2.183458	-0.423092
C	2.397239	-1.271018	-0.573578
H	1.726628	-2.128609	-0.483257
H	2.890233	-1.346541	-1.547600
C	2.473053	1.320743	-0.554761
H	1.857182	2.217952	-0.457959
H	2.970282	1.378238	-1.527979
C	3.442305	-1.275602	0.547721
H	4.041124	-2.185205	0.473448
H	2.931739	-1.310927	1.517971
C	3.513589	1.251201	0.567969
H	3.003655	1.299750	1.537819
H	4.163026	2.126479	0.508566
C	4.335888	-0.035915	0.484924
H	4.905312	-0.044250	-0.451495
H	5.065133	-0.063557	1.296432
H	-2.682892	2.138283	0.473219
H	-2.837964	1.668841	-1.214870
H	-2.631343	-0.956946	-1.684283
H	-2.938377	-2.079845	-0.358106
C	-4.586339	0.070844	-0.089095

H	-5.077288	-0.837039	0.268183
H	-5.044824	0.921123	0.421431
H	-4.786020	0.168663	-1.159284
C	-2.856452	-0.202952	1.696627
H	-3.392210	0.553258	2.274568
H	-3.232546	-1.182502	2.002293
H	-1.800781	-0.141862	1.976887

1 imaginary frequency: –548.19 cm^{-1}.

Cyclohexene cation-Cy TS (***$TS_{9\text{-}Cy}$***)

Charge: +1

ZPE	0.305379
DE	0.317264
DH	0.318208
DG	0.267546
E	-469.475320
H	-469.157112
G	-469.207774

Cartesian coordinates

C	-1.090110	0.056634	-0.183865
C	0.920068	0.030574	-0.472657
H	0.461749	0.080424	0.548947
H	0.205041	0.037337	-1.329755
C	-3.107525	1.327921	0.110356
H	-3.593793	1.613281	-0.828256
H	-3.280563	2.140742	0.818860
C	-3.657007	0.004344	0.644196
H	-4.747151	0.026185	0.613208
H	-3.368967	-0.111854	1.693701
C	-3.137829	-1.183387	-0.163543
H	-3.402350	-1.064838	-1.217482
H	-3.574219	-2.120322	0.184461
C	-1.591263	-1.317046	-0.055838
H	-1.220711	-1.959321	-0.857436
H	-1.293182	-1.751676	0.902889
C	-1.609744	1.252492	-0.156038
H	-1.040393	2.161739	-0.307106
C	1.699848	-1.289755	-0.519080
H	1.040637	-2.144427	-0.351446
H	2.119640	-1.395828	-1.523910
C	1.773703	1.300514	-0.593622
H	1.166964	2.201767	-0.478081
H	2.192043	1.323996	-1.604508
C	2.824231	-1.258667	0.521321
H	3.415140	-2.172326	0.435033
H	2.387184	-1.257851	1.527476
C	2.899151	1.267283	0.445641
H	2.467691	1.355662	1.449926
H	3.542681	2.136987	0.300758
C	3.711990	-0.025022	0.347885
H	4.208845	-0.069598	-0.628110
H	4.500631	-0.025387	1.102295

1 imaginary frequency: –555.64 cm^{-1}.

Cyclohexane

Charge: 0

ZPE	0.170924
DE	0.176603
DH	0.177547
DG	0.142192
E	-235.816790
H	-235.639242
G	-235.674597

Cartesian coordinates

C	-0.815295	1.208712	0.233683
C	0.639197	1.310092	-0.233567
C	1.454390	0.101640	0.233276
C	0.815295	-1.208711	-0.233684
C	-0.639197	-1.310092	0.233567
C	-1.454390	-0.101640	-0.233276
H	2.483289	0.174204	-0.129834
H	0.660935	1.355371	-1.329560
H	1.091786	2.236509	0.130640
H	-0.843677	1.250514	1.329649
H	-1.391738	2.063452	-0.130769
H	0.843677	-1.250514	-1.329650
H	1.391738	-2.063451	0.130769
H	-1.091786	-2.236509	-0.130640
H	-0.660935	-1.355371	1.329560
H	-1.503732	-0.105051	-1.329345
H	-2.483289	-0.174204	0.129834
H	1.503733	0.105051	1.329345

There are no imaginary frequencies.

Cyclohexane-Cy H-shift TS (***$TS_{10\text{-}11}$***)

Charge: +1

ZPE	0.307409
DE	0.318415
DH	0.319360
DG	0.270966
E	-469.527109
H	-469.207749

G	-469.256142

Cartesian coordinates

C	0.602069	-0.577581	-0.478427
C	-0.812161	-1.179307	-0.251808
H	-0.665718	-2.253039	-0.396436
C	1.956274	1.591941	-0.307861
H	1.632849	2.524988	0.178860
H	2.313151	1.956327	-1.289275
C	3.031848	0.823781	0.457569
H	2.792551	0.834466	1.524779
H	3.988906	1.332154	0.340927
C	3.105784	-0.620027	-0.038766
H	3.891672	-1.160021	0.489801
H	3.374819	-0.636590	-1.101652
C	1.765775	-1.322856	0.177151
H	1.566595	-1.406711	1.248629
H	1.785861	-2.340813	-0.217471
C	0.742721	0.834794	-0.609549
C	-1.913847	-0.724146	-1.229137
H	-1.551911	-0.767182	-2.262003
H	-2.698680	-1.483740	-1.160545
C	-1.243110	-0.929858	1.205246
H	-0.457159	-1.218770	1.905088
H	-2.093029	-1.589874	1.408092
C	-2.567016	0.640143	-0.944211
H	-3.483650	0.707198	-1.533776
H	-1.949572	1.472259	-1.298854
C	-1.683329	0.512742	1.422624
H	-0.849480	1.207739	1.207402
H	-1.920089	0.676363	2.475938
C	-2.886238	0.842758	0.538749
H	-3.712213	0.183424	0.826456
H	-3.228203	1.865023	0.710944
H	-0.072003	1.370797	-1.091369
H	0.742679	-0.628298	-1.615017

1 imaginary frequency: –111.57 cm^{-1}.

Cyclohexane-Cy intermediate (10A)

Charge: +1

ZPE	0.310629
DE	0.322064
DH	0.323009
DG	0.273763
E	-469.532257
H	-469.209248
G	-469.258493

Cartesian coordinates

C	0.519665	0.191716	-0.808114
C	-0.463051	0.510189	0.620913
H	-0.215230	0.398245	-1.582230
H	0.118633	0.905431	1.458616
C	2.559763	1.190717	0.355565
H	2.421987	1.344610	1.435024
H	3.120582	2.075270	0.031451
C	3.303808	-0.112283	0.057301
H	4.129469	-0.225853	0.759748
H	3.741848	-0.055136	-0.943250
C	2.352089	-1.302491	0.131227
H	1.948825	-1.385214	1.146464
H	2.889536	-2.230806	-0.065608
C	1.222473	-1.151688	-0.890030
H	0.503386	-1.966240	-0.815271
H	1.638487	-1.209971	-1.902066
C	1.229924	1.282292	-0.301095
H	0.803022	2.275195	-0.409695
C	-0.986234	-0.876212	1.049652
H	-0.174897	-1.579887	1.226846
H	-1.446057	-0.691128	2.028257
C	-1.604507	1.472675	0.271458
H	-1.231346	2.412097	-0.143004
H	-2.066468	1.733483	1.230905
C	-2.045598	-1.440395	0.103442
H	-2.410969	-2.382766	0.517044
H	-1.609821	-1.678071	-0.873338
C	-2.679807	0.873262	-0.638520
H	-2.294618	0.724899	-1.653788
H	-3.493062	1.595598	-0.730378
C	-3.197307	-0.454548	-0.088942
H	-3.696605	-0.284060	0.871427
H	-3.943997	-0.875107	-0.764306

There are no imaginary frequencies.

Cyclohexane-Cy intermediate (10C)

Charge: +1

ZPE	0.310621
DE	0.322035
DH	0.322979
DG	0.273928
E	-469.532856
H	-469.209877
G	-469.258929

Cartesian coordinates

C	-1.207380	1.314753	-0.307146
C	0.451522	0.641515	0.494544
H	-0.864095	2.328044	-0.501071
H	-0.077093	1.215340	1.271291
C	-1.190441	-1.119778	-1.005895

H	-0.621022	-1.872142	-0.462624
H	-1.137170	-1.410861	-2.057352
C	-2.650768	-1.117451	-0.535033
H	-2.982205	-2.144893	-0.383477
H	-3.288019	-0.694526	-1.318500
C	-2.832094	-0.297109	0.741252
H	-2.207080	-0.692371	1.548113
H	-3.862865	-0.347717	1.092659
C	-2.466410	1.158793	0.466279
H	-2.448307	1.785889	1.361662
H	-3.219862	1.622484	-0.191652
C	-0.524025	0.246937	-0.903238
H	0.160618	0.498906	-1.706334
C	1.653374	1.466094	0.015781
H	1.327268	2.318376	-0.587094
H	2.117254	1.885857	0.915045
C	0.852893	-0.681749	1.178520
H	-0.020546	-1.285082	1.423262
H	1.290545	-0.377051	2.136157
C	2.697273	0.637738	-0.737125
H	3.557562	1.274779	-0.950269
H	2.308164	0.314695	-1.709776
C	1.903373	-1.461981	0.385730
H	1.484231	-1.840121	-0.552760
H	2.197830	-2.334733	0.972332
C	3.117653	-0.589079	0.069927
H	3.595871	-0.270200	1.002968
H	3.859099	-1.166773	-0.484156

There are no imaginary frequencies.

<u>Cyclohexane-Cy intermediate</u> (11A)

Charge: +1

ZPE	0.308942
DE	0.320296
DH	0.321240
DG	0.271848
E	-469.549729
H	-469.228489
G	-469.277882

<u>Cartesian coordinates</u>

C	0.547557	0.149090	0.279053
C	-0.742541	0.349035	0.955449
H	-0.416126	0.784944	1.921588
C	2.944694	0.996567	0.236702
H	3.166208	0.830267	1.296833
H	3.506011	1.881422	-0.071484
C	3.335163	-0.229530	-0.580933
H	4.396848	-0.448391	-0.437517
H	3.192707	-0.029287	-1.650570
C	2.501107	-1.432513	-0.156521
H	2.729214	-1.701892	0.880549
H	2.720649	-2.310275	-0.768389
C	0.986142	-1.147244	-0.259843
H	0.374484	-1.969750	0.113613
H	0.722676	-1.040309	-1.334751
C	1.440409	1.311627	0.087405
H	1.253047	1.604807	-0.965052
C	-1.634287	-0.874940	1.197088
H	-1.065977	-1.687543	1.662052
H	-2.384421	-0.571550	1.936645
C	-1.571143	1.493042	0.262124
H	-0.954239	2.376008	0.077960
H	-2.339806	1.783616	0.985895
C	-2.358514	-1.349464	-0.069889
H	-3.029826	-2.172012	0.192384
H	-1.641146	-1.758994	-0.793630
C	-2.232025	0.984443	-1.018681
H	-1.461949	0.702941	-1.754217
H	-2.804233	1.801972	-1.467637
C	-3.138700	-0.212942	-0.731944
H	-3.953041	0.107706	-0.069401
H	-3.603640	-0.565272	-1.656848
H	1.125377	2.158571	0.701919

There are no imaginary frequencies.

<u>Cyclohexane-Cy intermediate</u> (Fig. S41(C))

Charge: +1

ZPE	0.310849
DE	0.322335
DH	0.323279
DG	0.273935
E	-469.531383
H	-469.208104
G	-469.257448

Cartesian coordinates

C	-0.822801	0.774028	-0.795451
C	0.373262	0.038899	0.628760
H	-0.141478	1.358509	-1.405464
H	-0.366494	0.083559	1.425226
C	-1.759962	-1.497941	-0.222245
H	-1.468562	-1.897468	0.753867
H	-1.842271	-2.357607	-0.890167
C	-3.097702	-0.758904	-0.111489
H	-3.815641	-1.387416	0.415866
H	-3.502391	-0.585599	-1.113934
C	-2.926041	0.578381	0.607538
H	-2.552921	0.412248	1.622822
H	-3.886287	1.083688	0.715364
C	-1.971783	1.487065	-0.171629
H	-1.612016	2.333843	0.421884

H	-2.490465	1.944452	-1.027252
C	-0.668220	-0.597192	-0.765686
H	0.065982	-1.029100	-1.436701
C	1.278918	1.286740	0.625499
H	0.711712	2.214795	0.548212
H	1.719357	1.287510	1.630391
C	1.266505	-1.217532	0.776060
H	0.677579	-2.134609	0.757268
H	1.659867	-1.121385	1.796368
C	2.411348	1.219673	-0.400585
H	3.006753	2.131328	-0.326717
H	2.011576	1.196237	-1.422611
C	2.440128	-1.286457	-0.200888
H	2.085624	-1.465182	-1.222349
H	3.047657	-2.155126	0.060657
C	3.283482	-0.013167	-0.168211
H	3.776294	0.073640	0.806178
H	4.073329	-0.067880	-0.918945

There are no imaginary frequencies.

1Butene carbocation (23)

Charge: +1

ZPE	0.094200
DE	0.099721
DH	0.100665
DG	0.066751
E	-156.237285
H	-156.136620
G	-156.170534

Cartesian coordinates

C	-1.763925	-0.271981	0.000011
H	-2.670175	0.334001	-0.000128
H	-1.851321	-1.356956	0.000078
C	-0.633876	0.303899	0.000003
C	0.663780	0.800787	0.000022
H	0.935667	1.329509	0.911095
H	0.935611	1.329424	-0.911137
C	1.385962	-0.641317	-0.000003
H	1.148315	-1.202957	-0.897554
H	2.441677	-0.378463	-0.000205
H	1.148583	-1.202886	0.897655

There are no imaginary frequencies.

1Butene cation-Cy TS ($TS_{23\text{-}Cy}$)

Charge: +1

ZPE	0.267299
DE	0.278646
DH	0.279590
DG	0.230321
E	-392.075401
H	-391.795812
G	-391.845080

Cartesian coordinates

C	2.229953	1.640764	-0.356530
H	1.626092	2.458577	-0.731042
H	3.208231	1.887740	0.043964
C	1.832693	0.384403	-0.396343
C	2.449469	-0.896929	0.053379
H	2.487921	-1.589925	-0.793052
H	1.808211	-1.360753	0.810285
C	3.852323	-0.683830	0.627143
H	3.825486	-0.024169	1.495987
H	4.266387	-1.641389	0.941653
H	4.520591	-0.254008	-0.120393
C	-2.579334	1.122588	0.317642
C	-3.027483	-0.294836	0.657506
C	-2.450706	-1.299936	-0.333278
C	-0.883921	-1.216496	-0.353454
C	-0.614978	0.195554	-0.687769
C	-1.014136	1.223965	0.291670
H	-2.706318	-2.327841	-0.071371
H	-2.712619	-0.552219	1.673905
H	-4.118182	-0.348048	0.639677
H	-2.980756	1.428045	-0.653283
H	-2.928340	1.849013	1.053174
H	-0.516321	-1.463806	0.644421
H	-0.480995	-1.911519	-1.090048
H	0.840988	0.222675	-0.962461
H	-0.724710	0.469109	-1.741849
H	-0.624586	0.994154	1.285425
H	-0.715274	2.228048	-0.005683
H	-2.839086	-1.115168	-1.339109

1 imaginary frequency: –40.9 cm^{-1}.

1Butene cation-Cy intermediate (23B)

Charge: +1

ZPE	0.272387
DE	0.283451
DH	0.284395
DG	0.235888
E	-392.121347
H	-391.836952
G	-391.885458

Cartesian coordinates

C	-2.434552	-0.925436	-0.716596
C	-1.217815	-1.387181	0.092336
C	-0.190956	-0.252135	0.169170
C	-0.742775	1.072351	0.710358
C	-1.968683	1.485411	-0.111261
C	-3.016062	0.371038	-0.149985
H	-1.520391	-1.637217	1.114550
H	-0.767873	-2.283016	-0.345755
H	-2.141250	-0.773592	-1.762105
H	-3.184582	-1.718371	-0.711457
H	-1.024738	0.915939	1.756521
H	0.022876	1.852141	0.688296
H	-2.391649	2.395360	0.318249
H	-1.655333	1.733637	-1.132276
H	-3.391533	0.189218	0.863474
H	-3.871628	0.686482	-0.749404
H	0.090457	-0.038265	-0.890041
C	1.072489	-0.725663	1.095081
C	1.703252	-0.577363	-0.156764
H	1.697032	-1.434366	-0.829903
C	2.515934	0.596789	-0.549613
H	2.385055	0.827680	-1.607973
H	2.254194	1.469194	0.051375
H	0.885200	-1.725770	1.468870
C	3.989579	0.201911	-0.284290
H	4.281609	-0.672111	-0.867828
H	4.625534	1.035404	-0.580674
H	4.161031	-0.003285	0.772794
H	1.283523	0.022600	1.852667

There are no imaginary frequencies.

2Butane cation-Cy H-shift TS ($TS_{23C-23D}$)

Charge: +1

ZPE	0.270371
DE	0.280869
DH	0.281813
DG	0.234869
E	-392.078105
H	-391.796292
G	-391.843236

Cartesian coordinates

C	2.504884	0.938864	0.071203
C	1.048061	1.226990	0.438699
C	0.080230	0.326793	-0.344618
C	0.422381	-1.148014	-0.099857
C	1.878797	-1.437894	-0.472890
C	2.840857	-0.535264	0.297384
H	0.902156	1.046142	1.512600
H	0.830150	2.288564	0.265454
H	2.669498	1.195716	-0.981391
H	3.162941	1.578980	0.661792
H	0.271414	-1.375659	0.963850
H	-0.240197	-1.802208	-0.672556
H	2.099536	-2.488952	-0.277478
H	2.012100	-1.282318	-1.549830
H	2.776047	-0.762259	1.367835
H	3.870276	-0.734979	-0.005560
H	0.198385	0.529847	-1.418800
C	-1.373213	0.665165	0.014234
C	-1.774844	1.996486	-0.190134
H	-2.783719	2.312491	0.074266
H	-1.114914	2.761021	-0.603406
C	-2.533973	-0.340759	-0.445622
H	-3.433463	0.218974	-0.708647
H	-2.141373	-0.762875	-1.374104
C	-2.868092	-1.411144	0.582209
H	-3.599151	-2.099595	0.155257
H	-1.990327	-1.986462	0.873645
H	-3.312429	-0.972563	1.478166
H	-1.527453	0.648797	1.135255

1 imaginary frequency: –439.34 cm^{-1}.

2Butane cation-Cy intermediate (23D)

Charge: +1

ZPE	0.271064
DE	0.282543
DH	0.283487
DG	0.233998
E	-392.139513
H	-391.856026
G	-391.905515

Cartesian coordinates

C	2.564030	0.773609	-0.475304
C	1.160917	1.312690	-0.194950
C	0.111802	0.240998	-0.491034
C	0.373057	-1.048903	0.425190
C	1.795254	-1.546635	0.138212
C	2.847799	-0.465932	0.371517
H	1.097614	1.617380	0.855374
H	0.957966	2.197630	-0.805338
H	2.654489	0.527176	-1.539203
H	3.298738	1.553560	-0.269498
H	0.278259	-0.759542	1.476090
H	-0.356498	-1.831503	0.209668
H	1.973852	-2.406183	0.789565
H	1.846217	-1.907847	-0.893775
H	2.858926	-0.189931	1.432191
H	3.837190	-0.863768	0.139652

H	0.185863	-0.133496	-1.518273
C	-1.269777	0.512665	-0.163167
C	-1.607316	1.515563	0.856253
H	-2.671206	1.600618	1.057214
H	-1.061629	1.302000	1.783887
H	-1.204301	2.479906	0.515522
C	-2.345830	-0.240449	-0.828476
H	-2.907365	0.533384	-1.380844
H	-1.935967	-0.934728	-1.563001
C	-3.321167	-0.949683	0.133989
H	-4.083455	-1.454853	-0.457189
H	-2.799461	-1.699670	0.729358
H	-3.821847	-0.253680	0.805214

There are no imaginary frequencies.

1Butene cation-Cy TS ($TS_{23A-23B}$)

Charge: +1

ZPE	0.266638
DE	0.278719
DH	0.279664
DG	0.227490
E	-392.079652
H	-391.799988
G	-391.852162

Cartesian coordinates

C	1.734571	0.075049	1.577821
H	1.945132	1.133330	1.455249
H	1.168605	-0.216079	2.456972
C	2.231854	-0.840954	0.742604
H	2.035047	-1.892870	0.946646
C	3.077960	-0.562498	-0.465612
H	2.602155	-1.024536	-1.342834
C	3.380425	0.908146	-0.729146
H	3.996359	1.015859	-1.621655
H	2.471750	1.500217	-0.884958
H	3.921706	1.353855	0.107374
H	4.014681	-1.118072	-0.347883
C	-3.094860	-0.062556	0.446669
C	-2.576978	1.285918	-0.046120
C	-1.036650	1.320677	-0.063349
C	-0.393322	0.099904	-0.526565
C	-1.020668	-1.209933	-0.434541
C	-2.561143	-1.196022	-0.424968
H	-0.601107	2.195615	-0.553115
H	-2.940666	1.479357	-1.058889
H	-2.932777	2.103161	0.580911
H	-2.800440	-0.220532	1.490524
H	-4.185537	-0.065513	0.424844
H	0.590023	0.175921	-0.984458
H	-0.569260	-1.908744	-1.143449
H	-0.664710	-1.553118	0.558578
H	-2.916747	-1.079537	-1.452173
H	-2.911914	-2.166587	-0.074798
H	-0.669440	1.381884	0.982356

1 imaginary frequency: –123.38 cm^{-1}.

Trimethylsilyl cation

Charge: +1

ZPE	0.109090
DE	0.115296
DH	0.116240
DG	0.079434
E	-408.924102
H	-408.807862
G	-408.844668

Cartesian coordinates

Si	-0.000012	-0.000079	-0.045105
C	0.046331	1.825462	0.007787
H	-0.835665	2.273076	-0.453830
H	0.049580	2.131498	1.063840
H	0.954186	2.226818	-0.446181
C	-1.604497	-0.872519	0.007858
H	-2.405977	-0.287762	-0.447060
H	-1.549944	-1.860361	-0.453233
H	-1.871959	-1.022538	1.063702
C	1.557933	-0.953027	0.007924
H	1.452065	-1.940990	-0.443845
H	2.384829	-0.412851	-0.456978
H	1.824458	-1.105287	1.063636

There are no imaginary frequencies.

1ButeneOTf (*23*) & TMS+_TS

Charge: +1

ZPE	0.237444
DE	0.258436
DH	0.259380
DG	0.187789
E	-1526.925463
H	-1526.666083
G	-1526.737674

Cartesian coordinates

C	-0.245571	3.122626	-1.145802

H	0.513041	2.363573	-1.323599
H	0.039923	3.708704	-0.274397
H	-0.309639	3.767883	-2.020506
C	-1.603987	2.443707	-0.937687
H	-2.412604	3.215167	-0.890579
H	-1.901577	1.764886	-1.741539
C	-1.868640	1.866184	0.326708
C	-2.308564	1.604107	1.496384
H	-3.086890	2.269776	1.877645
H	-1.944327	0.796128	2.122725
O	-0.455036	-0.033259	0.016299
S	0.843075	0.169477	0.915926
C	2.219263	-0.083846	-0.335958
F	3.231700	0.666315	0.025018
F	2.568604	-1.349277	-0.363774
F	1.783428	0.285993	-1.533067
O	0.863088	1.562754	1.269618
O	0.916347	-0.880457	1.891492
Si	-1.298318	-1.579049	-0.345441
C	-2.460865	-1.023183	-1.682798
H	-3.195386	-0.299361	-1.319206
H	-1.924486	-0.602097	-2.536729
H	-3.024597	-1.885587	-2.050540
C	-2.148930	-2.069863	1.227964
H	-2.974647	-1.402120	1.485321
H	-2.576708	-3.069865	1.109834
H	-1.443061	-2.115266	2.061054
C	-0.018800	-2.786062	-0.912818
H	-0.529219	-3.703192	-1.223133
H	0.550564	-2.422996	-1.771222
H	0.674638	-3.052195	-0.112610

1 imaginary frequency: –45.11 cm^{-1}.

TMSOTf

Charge: 0

ZPE	0.141538
DE	0.156953
DH	0.157897
DG	0.098059
E	-1370.678152
H	-1370.520255
G	-1370.580094

Cartesian coordinates

O	0.443589	-0.163455	-0.712436
S	-0.783630	-0.873197	-0.061252
C	-1.938567	0.574345	-0.021171
F	-2.173991	1.005962	-1.247140
F	-3.074585	0.204238	0.543159
F	-1.394461	1.554242	0.689721
O	-1.345110	-1.828665	-0.967798
O	-0.492177	-1.207330	1.311095
Si	2.011358	0.198060	-0.017246
C	2.884470	0.968205	-1.462070
H	2.962177	0.262436	-2.291403
H	2.347715	1.851615	-1.814108
H	3.895025	1.275116	-1.180434
C	2.738875	-1.421820	0.524616
H	2.782814	-2.131544	-0.304700
H	3.755931	-1.277699	0.898869
H	2.139684	-1.861333	1.324944
C	1.720999	1.371841	1.392456
H	2.670832	1.631702	1.867745
H	1.248616	2.295628	1.051875
H	1.078514	0.912568	2.147160

There are no imaginary frequencies.

1ButeneOTf (*23*) & TMS+ minima

Charge: +1

ZPE	0.242486
DE	0.263390
DH	0.264335
DG	0.191624
E	-1526.972467
H	-1526.708133
G	-1526.780844

Cartesian coordinates

C	-3.549046	-0.928720	1.254727
H	-3.307337	0.136211	1.253416
H	-2.887944	-1.433595	1.960585
H	-4.573871	-1.028888	1.610879
C	-3.432955	-1.532868	-0.147716
H	-3.770416	-2.571198	-0.153530
H	-4.070046	-0.983504	-0.848609
C	-2.048862	-1.531746	-0.689065
C	-1.264713	-2.500641	-1.118737
H	-1.624525	-3.520038	-1.072530
H	-0.291931	-2.311332	-1.553450
O	-1.535179	-0.157977	-0.800232
S	-0.367095	0.306201	0.098813
C	-0.473944	2.146157	-0.247588
F	0.559456	2.684654	0.358543
F	-0.415945	2.339029	-1.537381
F	-1.598836	2.579380	0.255962
O	-0.479317	0.016043	1.491807
O	0.911866	-0.129399	-0.564263
Si	2.519869	-0.726553	0.149407
C	3.504193	-0.853394	-1.403459
H	3.058074	-1.558453	-2.107721
H	3.599831	0.117200	-1.894127

H	4.512093	-1.209440	-1.171467
C	2.043436	-2.319688	0.955831
H	1.649945	-3.039062	0.234514
H	2.924990	-2.771709	1.419986
H	1.301397	-2.164261	1.742747
C	2.996932	0.627939	1.312241
H	3.935006	0.362387	1.808778
H	3.159613	1.573966	0.791854
H	2.249199	0.775114	2.095943

There are no imaginary frequencies.

1ButeneOTf (*23*)

Charge: 0

ZPE	0.129842
DE	0.142294
DH	0.143238
DG	0.089901
E	-1117.975920
H	-1117.832682
G	-1117.886019

Cartesian coordinates

C	2.407564	-1.787265	0.600430
H	1.364686	-2.093861	0.505704
H	2.528779	-1.315145	1.576553
H	3.029296	-2.682786	0.563516
C	2.801546	-0.825405	-0.524200
H	3.856918	-0.554869	-0.454740
H	2.650900	-1.307578	-1.495787
C	2.005999	0.436324	-0.503399
C	2.419765	1.681801	-0.338803
H	3.472635	1.870197	-0.179974
H	1.735842	2.520387	-0.358843
O	0.623579	0.174054	-0.719333
S	-0.416742	0.606231	0.421668
C	-1.796749	-0.436072	-0.252768
F	-2.080450	-0.072075	-1.487598
F	-1.448744	-1.709947	-0.229082
F	-2.852848	-0.251779	0.519975
O	-0.027746	0.061286	1.691737
O	-0.791026	1.983643	0.275054

There are no imaginary frequencies.

Terminal-ButeneOTf (*25*) & TMS+_minima

Charge: +1

ZPE	0.242351
DE	0.263678
DH	0.264622
DG	0.189162
E	-1526.965632
H	-1526.701010
G	-1526.776470

Cartesian coordinates

C	-4.513177	0.549154	0.011326
H	-4.921045	-0.352824	0.477568
H	-4.760422	0.502368	-1.051524
C	-3.027009	0.533866	0.191635
H	-2.632539	0.559951	1.205752
C	-2.179372	0.532133	-0.817727
O	-0.764426	0.621156	-0.518524
S	0.157466	-0.574610	-0.921175
C	-0.018066	-1.774563	0.509609
F	0.151971	-1.082533	1.620060
F	-1.210779	-2.307145	0.470116
F	0.918143	-2.680195	0.384877
O	-0.165113	-1.201860	-2.152618
O	1.532646	-0.033595	-0.764661
Si	2.611714	1.095614	0.233892
C	1.412331	2.180356	1.129482
H	0.803762	2.772736	0.443792
H	0.750651	1.610678	1.785512
H	1.975663	2.875780	1.759558
C	3.585105	1.896082	-1.109238
H	2.944498	2.476964	-1.775708
H	4.320798	2.579238	-0.674917
H	4.126855	1.155651	-1.701066
C	3.520336	-0.124690	1.279741
H	4.309473	0.386438	1.839053
H	2.866957	-0.611224	2.007096
H	3.997719	-0.891347	0.665360
C	-5.137857	1.790332	0.657549
H	-4.757365	2.703545	0.197294
H	-6.220834	1.772562	0.536160
H	-4.919628	1.828607	1.726763
H	-2.380607	0.533265	-1.879703

There are no imaginary frequencies.

Terminal-ButeneOTf (*25*)

Charge: 0

ZPE	0.129742
DE	0.142488
DH	0.143432
DG	0.088396
E	-1117.971864
H	-1117.828431
G	-1117.883468

Cartesian coordinates

C	-3.650560	0.590507	0.411615
H	-3.781080	1.677082	0.423927
H	-3.548693	0.270986	1.451996
C	-2.396176	0.263699	-0.341705
H	-2.324509	0.563331	-1.384049
C	-1.390077	-0.402299	0.193104
O	-0.287251	-0.734061	-0.618906
S	1.161100	-0.901030	0.036892
C	1.718175	0.870785	-0.012594
F	1.746248	1.297791	-1.260494
F	0.874561	1.612825	0.688075
F	2.925750	0.951601	0.515326
O	1.037987	-1.261614	1.421129
O	1.957803	-1.625165	-0.900739
C	-4.882322	-0.062113	-0.222905
H	-4.787798	-1.149566	-0.218488
H	-5.788093	0.207037	0.322867
H	-5.004069	0.261000	-1.259297
H	-1.324950	-0.770098	1.209643

There are no imaginary frequencies.

Terminal-ButeneOTf (*25*) & TMS+_TS

Charge: +1

ZPE	0.237062
DE	0.258780
DH	0.259725
DG	0.184035
E	-1526.910448
H	-1526.650723
G	-1526.726412

Cartesian coordinates

C	5.467151	-0.427981	-0.138642
H	5.831776	0.512599	0.279255
H	5.867827	-0.533609	-1.145960
C	3.974197	-0.293963	-0.258505
H	3.333408	-0.141052	0.665508
C	2.970401	-0.295307	-1.001687
O	1.142692	0.046421	0.647152
S	-0.107851	0.276494	-0.062866
C	-0.519520	2.068592	0.177555
F	-0.592069	2.336711	1.461979
F	0.441553	2.780235	-0.382667
F	-1.673166	2.321616	-0.406636
O	-0.076716	0.018699	-1.489270
O	-1.276179	-0.392589	0.644423
Si	-2.723798	-1.291789	0.048585
C	-3.579510	-1.640324	1.647507
H	-3.813763	-0.715414	2.178227
H	-4.519075	-2.168280	1.463984
H	-2.963693	-2.265459	2.297044
C	-2.019263	-2.773597	-0.811347
H	-1.379438	-3.355077	-0.143814
H	-2.827732	-3.429317	-1.146307
H	-1.443091	-2.481877	-1.692300
C	-3.591596	-0.107700	-1.078815
H	-4.461378	-0.598120	-1.524934
H	-3.946442	0.776471	-0.545453
H	-2.939855	0.212829	-1.895436
C	5.845399	-1.611310	0.754684
H	5.469611	-2.549605	0.346772
H	6.931904	-1.673538	0.811305
H	5.457903	-1.485414	1.766275
H	2.072021	-0.281754	-1.605515

1 imaginary frequency: –298.39 cm^{-1}.

Phenylcyclohexane benzyl cation

Charge: +1

ZPE	0.241009
DE	0.251162
DH	0.252107
DG	0.204582
E	-465.947996
H	-465.695890
G	-465.743415

Cartesian coordinates

C	-0.606771	0.101676	0.650172
C	-2.290033	1.185851	-0.713116
H	-1.637398	1.134294	-1.589755
H	-2.885428	2.095705	-0.801124
C	-3.167958	-0.055932	-0.620081
H	-3.726461	-0.177210	-1.551279
H	-3.904500	0.071186	0.179581
C	-2.334352	-1.304027	-0.357189
H	-1.696682	-1.530562	-1.217332
H	-2.961602	-2.177368	-0.173510
C	-1.431189	-1.099640	0.905561
H	-0.856967	-1.994229	1.126457
H	-2.092253	-0.896099	1.752991
C	-1.400327	1.344280	0.572755
H	-0.812474	2.253508	0.496314
C	1.397125	-1.210186	0.053074
C	2.724649	-1.268582	-0.311362
C	3.472854	-0.091173	-0.392767
C	2.890929	1.149044	-0.122371
C	1.556090	1.219850	0.215483
C	0.771177	0.039083	0.314486
H	0.829148	-2.129137	0.103825

H	3.188197	-2.222610	-0.527082
H	4.521160	-0.141345	-0.665350
H	3.486194	2.051580	-0.174825
H	1.125997	2.185956	0.439702
H	-2.070086	1.414859	1.433520

There are no imaginary frequencies.

Benzene

Charge: 0

ZPE	0.100928
DE	0.105312
DH	0.106257
DG	0.073471
E	-232.198367
H	-232.092111
G	-232.124896

Cartesian coordinates

C	-1.028777	-0.937015	-0.000001
C	0.297076	-1.359300	0.000026
C	1.326130	-0.422394	-0.000013
C	1.028779	0.937012	0.000006
C	-0.297078	1.359299	0.000012
C	-1.326130	0.422397	-0.000018
H	-1.830167	-1.666634	0.000004
H	0.528082	-2.418186	-0.000023
H	2.358461	-0.751887	-0.000036
H	1.830162	1.666639	-0.000027
H	-0.528072	2.418188	0.000035
H	-2.358464	0.751883	-0.000030

There are no imaginary frequencies.

Phenylcyclohexane arenium int.

Charge: +1

ZPE	0.238921
DE	0.249564
DH	0.250508
DG	0.201730
E	-465.901405
H	-465.650897
G	-465.699674

Cartesian coordinates

C	-0.564728	-0.204592	0.258082
C	-2.173460	1.418286	-0.722895
H	-2.289234	1.345336	-1.811281
H	-2.262982	2.480721	-0.481802
C	-3.254331	0.604216	-0.012284
H	-4.230346	0.821866	-0.448034
H	-3.299260	0.901403	1.040871
C	-2.946627	-0.889265	-0.105366
H	-2.870375	-1.179065	-1.158437
H	-3.750006	-1.482140	0.334610
C	-1.628966	-1.211438	0.603390
H	-1.287620	-2.217575	0.332559
H	-1.767629	-1.220032	1.692348
C	-0.789551	0.951996	-0.362112
H	0.041601	1.605156	-0.619972
C	1.647262	0.481149	1.256602
C	2.782892	0.980553	0.690770
C	3.258980	0.396931	-0.502370
C	2.631470	-0.692560	-1.126590
C	1.501894	-1.214248	-0.554183
C	0.905226	-0.623779	0.645207
H	1.241770	0.908518	2.168247
H	3.317407	1.809277	1.136653
H	4.155528	0.808753	-0.957201
H	3.039317	-1.103517	-2.040774
H	0.987967	-2.057222	-1.006568
H	0.753480	-1.404978	1.409279

There are no imaginary frequencies.

Cyclohexenyl cation arylation TS

Charge: +1

ZPE	0.238831
DE	0.248609
DH	0.249553
DG	0.203950
E	-465.898140
H	-465.648587
G	-465.694191

Cartesian coordinates

C	-0.418266	-0.394303	-0.037467
C	-1.888669	1.603865	-0.305197
H	-2.071405	1.880036	-1.353968
H	-1.804795	2.556463	0.227669
C	-3.025813	0.739735	0.238486
H	-3.983870	1.159370	-0.069773
H	-3.006576	0.757397	1.332618
C	-2.884220	-0.698947	-0.250378
H	-2.890462	-0.722403	-1.344862
H	-3.722694	-1.308929	0.088363
C	-1.579260	-1.316377	0.266741
H	-1.418340	-2.294801	-0.191056
H	-1.656601	-1.476796	1.347274
C	-0.563203	0.922360	-0.269118

H	0.317120	1.531924	-0.461705
C	2.001383	0.255871	1.415738
C	2.828807	0.819647	0.496110
C	2.799955	0.420532	-0.888227
C	1.945174	-0.536016	-1.309837
C	1.010225	-1.155870	-0.376840
C	1.087859	-0.764211	1.006388
H	2.050575	0.527530	2.462106
H	3.552121	1.564019	0.809553
H	3.506450	0.866298	-1.577688
H	1.951524	-0.884969	-2.335203
H	0.700383	-2.168309	-0.612245
H	0.592739	-1.364544	1.760524

1 imaginary frequency: –74.391 cm^{-1}.

Phenylcyclohexane arenium H-shift TS

Charge: +1

ZPE	0.235434
DE	0.245598
DH	0.246542
DG	0.199520
E	-465.884092
H	-465.637550
G	-465.684573

Cartesian coordinates

C	0.664683	-0.016797	-0.175146
C	2.821877	-1.270912	-0.204611
H	3.305290	-1.367076	-1.186351
H	3.011722	-2.220642	0.305262
C	3.390272	-0.086773	0.574044
H	4.479231	-0.101414	0.524904
H	3.114421	-0.176030	1.629714
C	2.841397	1.220518	0.008271
H	3.092278	1.290515	-1.055099
H	3.294358	2.081037	0.501737
C	1.320375	1.296581	0.175024
H	0.930247	2.094137	-0.460533
H	1.041729	1.548608	1.204630
C	1.351670	-1.148929	-0.433801
H	0.831688	-2.024646	-0.815805
C	-1.645987	1.172991	-0.288072
C	-3.013048	1.181992	-0.077378
C	-3.678406	-0.005559	0.215464
C	-2.981075	-1.214692	0.303807
C	-1.617439	-1.242715	0.109112
C	-0.924747	-0.040756	-0.191383
H	-1.136583	2.093743	-0.539599
H	-3.561476	2.112537	-0.147079
H	-4.749145	0.006476	0.382110
H	-3.507762	-2.128190	0.548862
H	-1.074552	-2.171456	0.225756
H	-0.248878	-0.107286	-1.210491

1 imaginary frequency: –545.498 cm^{-1}.

---

14. References

1. G. A. Olah, 100 years of carbocations and their significance in chemistry. *J. Org. Chem.* **66**, 5943–5957 (2001). doi:10.1021/jo010438x Medline
2. T. L. Jacobs, S. Searles Jr., Acetylenic ethers. IV. hydration. *J. Am. Chem. Soc.* **66**, 686–689 (1944). doi:10.1021/ja01233a007
3. C. A. Grob, J. Csapilla, G. Cseh, Die solvoltische Decarboxylierung von α, β-ungesättigeten β-Halogensäuren Fragmentierungsreaktionen, 9. Miteilung. *Helv. Chim. Acta* **47**, 1590–1602 (1964). doi:10.1002/hlca.19640470621
4. M. Hanack, Mechanistic and preparative aspects of vinyl cation chemistry. *Angew. Chem. Int. Ed. Engl.* **17**, 333–341 (1978). doi:10.1002/anie.197803331
5. Z. Rappoport, A. Gal, Vinylic cations from solvolysis. I. Trianisylvinyl halide system. *J. Am. Chem. Soc.* **91**, 5246–5254 (1969). doi:10.1021/ja01047a012
6. L. Radom, P. C. Hariharan, J. A. Pople, P. R. Schleyer, Molecular orbital theory of the electronic structure of organic compounds. XIX. Geometries and energies of $C_3H_5^+$ cations. Energy relations among allyl, vinyl, and cyclopropyl cations. *J. Am. Chem. Soc.* **95**, 6531–6544 (1973). doi:10.1021/ja00801a003
7. P. J. Stang, Z. Rappoport, *Dicoordinated Carbocations* (Wiley, 1997).
8. S. A. Sherrod, R. G. Bergman, Synthesis and solvolysis of 1-cyclopropyl-1-iodoethylene. generation of an unusually stable vinyl cation. *J. Am. Chem. Soc.* **91**, 2115–2117 (1969). doi:10.1021/ja01036a045
9. T. Müller, M. Juhasz, C. A. Reed, The x-ray structure of a vinyl cation. *Angew. Chem. Int. Ed.* **43**, 1543–1546 (2004). doi:10.1002/anie.200352986 Medline
10. W. M. Jones, F. W. Miller, The generation of vinyl cations from vinyltriazenes. *J. Am. Chem. Soc.* **89**, 1960–1962 (1967). doi:10.1021/ja00984a041
11. R. J. Hinkle, A. J. McNeil, Q. A. Thomas, M. N. Andrews, Primary vinyl cations in solution: Kinetics and products of β,β-disubstituted alkenyl(aryl)iodonium triflate fragmentations. *J. Am. Chem. Soc.* **121**, 7437–7438 (1999). doi:10.1021/ja9916310
12. Y. Apeloig, W. Franke, Z. Rappoport, H. Schwarz, D. Stahl, Dissociative ionization of aryl-substituted vinyl bromides in the gas phase: Experimental and computational evidence for the formation of stable α-arylvinyl cations both by direct means and by spontaneous exothermic isomerization of unstable isomeric ions. *J. Am. Chem. Soc.* **103**, 2770–2780 (1981). doi:10.1021/ja00400a047
13. J. A. Pople, W. A. Lathan, W. J. Hehre, Molecular orbital theory of the electronic structure of organic compounds. VI. Geometries and energies of small hydrocarbons. *J. Am. Chem. Soc.* **93**, 808–815 (1971). doi:10.1021/ja00733a002
14. R. Pellicciari, B. Natalini, B. M. Sadeghpour, M. Marinozzi, J. P. Snyder, B. L. Williamson, J. T. Kuethe, A. Padwa, The reaction of α-diazo-β-hydroxy esters with boron trifluoride etherate: Generation and rearrangement of destabilized vinyl cations. A detailed experimental and theoretical study. *J. Am. Chem. Soc.* **118**, 1–12 (1996). doi:10.1021/ja950971s

15. P. A. Byrne, S. Kobayashi, E. U. Würthwein, J. Ammer, H. Mayr, Why are vinyl cations sluggish electrophiles? *J. Am. Chem. Soc.* **139**, 1499–1511 (2017). doi:10.1021/jacs.6b10889 Medline

16. A. J. Walkinshaw, W. Xu, M. G. Suero, M. J. Gaunt, Copper-catalyzed carboarylation of alkynes via vinyl cations. *J. Am. Chem. Soc.* **135**, 12532–12535 (2013). doi:10.1021/ja405972h Medline

17. W. S. Johnson, C. E. Ward, S. G. Boots, M. B. Gravestock, R. L. Markezich, B. E. McCarry, D. A. Okorie, R. J. Parry, Formation of vinyl halides from vinyl cations generated by acetylenic participation in biomimetic polyene cyclizations. *J. Am. Chem. Soc.* **103**, 88–98 (1981). doi:10.1021/ja00391a017

18. M. Hanack, Vinyl cations in solvolysis reactions. *Acc. Chem. Res.* **3**, 209–216 (1970). doi:10.1021/ar50031a001

19. P. J. Stang, Z. Rappaport, M. Hanack, L. R. Subramanian, *Vinyl Cations* (Academic Press, 1979).

20. B. Shao, A. L. Bagdasarian, S. Popov, H. M. Nelson, Arylation of hydrocarbons enabled by organosilicon reagents and weakly coordinating anions. *Science* **355**, 1403–1407 (2017). doi:10.1126/science.aam7975 Medline

21. E. Lamparter, M. Hanack, Vinyl-kationen, VI solvolyse von 1-cyclononenyl- und 1-cyclodedecenyl-trifluormethansulfonat. *Eur. J. Inorg. Chem.* **105**, 3789–3793 (1972).

22. R. J. Hargrove, P. J. Stang, Solvolysis of medium ring size cycloalkenyl triflates: A comparison of relative rates vs ring size. *Tetrahedron* **32**, 37–41 (1976). doi:10.1016/0040-4020(76)80018-X

23. G. A. Olah, H. Mayr, Stable carbocations. 198. Formation of allyl cations via protonation of alkynes in magic acid solution. evidence for 1,2-hydrogen and alkyl shifts in the intermediate vinyl cations. *J. Am. Chem. Soc.* **98**, 7333–7340 (1976). doi:10.1021/ja00439a600

24. M. I. Kanishchev, A. A. Shegolev, W. A. Smit, R. Caple, M. J. Kelner, 1,5-Hydride shifts in vinyl cation intermediates produced upon the acylation of acetylenes. *J. Am. Chem. Soc.* **101**, 5660–5671 (1979). doi:10.1021/ja00513a034

25. S. Fornarini, M. Speranza, Gas-phase addition of the vinyl cation to hydrogen and methane. A nuclear decay study. *J. Phys. Chem.* **91**, 2154–2160 (1987). doi:10.1021/j100292a035

26. U. Biermann, R. Koch, J. O. Metzger, Intramolecular concerted insertion of vinyl cations into C–H bonds: Hydroalkylating cyclization of alkynes with alkyl chloroformates to give cyclopentanes. *Angew. Chem. Int. Ed.* **45**, 3076–3079 (2006). doi:10.1002/anie.200504288 Medline

27. S. E. Cleary, M. J. Hensinger, M. Brewer, Remote C–H insertion of vinyl cations leading to cyclopentenones. *Chem. Sci.* **8**, 6810–6814 (2017). doi:10.1039/C7SC02768K Medline

28. S. Körbe, P. J. Schreiber, J. Michl, Chemistry of the carba-*closo*-dodecaborate(–) anion, $CB_{11}H_{12}^{-}$. *Chem. Rev.* **106**, 5208–5249 (2006). doi:10.1021/cr050548u Medline

29. F. A. Carey, H. S. Tremper, Carbonium ion-silane hydride transfer reactions. V. Tert-alkyl cations. *J. Org. Chem.* **36**, 758–761 (1971). doi:10.1021/jo00805a005

30. D. H. Ess, S. E. Wheeler, R. G. Iafe, L. Xu, N. Celebi-Olçüm, K. N. Houk, Bifurcations on potential energy surfaces of organic reactions. *Angew. Chem. Int. Ed.* **47**, 7592–7601 (2008). doi:10.1002/anie.200800918 Medline

31. P. Yu, A. Patel, K. N. Houk, Transannular [6 + 4] and ambimodal cycloaddition in the biosynthesis of heronamide A. *J. Am. Chem. Soc.* **137**, 13518–13523 (2015). doi:10.1021/jacs.5b06656 Medline

32. Y. J. Hong, D. J. Tantillo, A potential energy surface bifurcation in terpene biosynthesis. *Nat. Chem.* **1**, 384–389 (2009). doi:10.1038/nchem.287 Medline

33. P. R. Schleyer, W. D. Pfeifer, C. A. Bahn, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, P. J. Stang, Behavior of bent vinyl cations generated by solvolysis of cyclic trifluoromethanesulfonates. *J. Am. Chem. Soc.* **93**, 1513–1516 (1971). doi:10.1021/ja00735a045

34. See supplementary materials.

35. T. Okuyama, T. Takino, T. Sueda, M. Ochiai, Solvolysis of cyclohexenyliodonium salt, a new precursor for the vinyl cation: Remarkable nucleofugality of the phenyliodonio group and evidence for internal return from an intimate ion-molecule pair. *J. Am. Chem. Soc.* **117**, 3360–3367 (1995). doi:10.1021/ja00117a006

36. L. A. Curtiss, J. A. Pople, Theoretical study of structures and energies of acetylene, ethylene, and vinyl radical and cation. *J. Chem. Phys.* **88**, 7405–7409 (1988). doi:10.1063/1.454303

37. J. Weber, M. Yoshimine, A. D. McLean, A CI study of the classical and nonclassical structures of the vinyl cation and their optimum path for rearrangement. *J. Chem. Phys.* **64**, 4159–4164 (1976). doi:10.1063/1.431986

38. B. T. Psciuk, V. A. Benderskii, H. B. Schlegel, Protonated acetylene revisited. *Theor. Chem. Acc.* **118**, 75–80 (2007). doi:10.1007/s00214-006-0242-x

39. G. A. Olah, N. Hartz, G. Rasul, G. K. S. Prakash, M. Burkhart, K. Lammertsma, Protio-2-propyl dication (propane dication, $C_3H_8^{2+}$): Hydrogen/deuterium exchange and theoretical study. Differentiation of reactive gitonic (proximal) from stable distonic (distant) dications and their protosolvolytic activation of carbocations. *J. Am. Chem. Soc.* **116**, 3187–3191 (1994). doi:10.1021/ja00087a003

40. J. M. Coxon, A. J. Thorpe, Density functional theory study of the mechanism of the BF_3-catalyzed rearrangement of 2,3,3-trimethyl-1,2-epoxybutane to 2,3,3-trimethylbutanal. *J. Org. Chem.* **65**, 8421–8429 (2000). doi:10.1021/jo000591b Medline

41. P. J. Stang, A. Anderson, Preparation and chemistry of vinyl triflates. 16. Mechanism of alkylation of aromatic substrates. *J. Am. Chem. Soc.* **100**, 1520–1525 (1978). doi:10.1021/ja00473a033

42. C. A. Reed, H^+, CH_3^+, and R_3Si^+ carborane reagents: When triflates fail. *Acc. Chem. Res.* **43**, 121–128 (2010). doi:10.1021/ar900159e Medline

43. X. Su, H. Huang, Y. Yuan, Y. Li, Radical desulfur-fragmentation and reconstruction of enol triflates: Facile access to α-trifluoromethyl ketones. *Angew. Chem. Int. Ed.* **56**, 1338–1341 (2017). doi:10.1002/anie.201608507 Medline

44. T. G. Crisp, W. J. Scott, A convenient synthesis of vinyl triflates from enones. *Synthesis* **1985**, 335–337 (1985). doi:10.1055/s-1985-31204

45. Y. Hioki, K. Okano, A. Mori, Generation of cycloalkynes through deprotonation of cyclic enol triflates with magnesium bisamides. *Chem. Commun. (Camb.)* **53**, 2614–2617 (2017). doi:10.1039/C6CC09920C Medline

46. P. Alonso, P. Pardo, A. Galván, F. J. Fañanás, F. Rodríguez, Synthesis of cyclic alkenyl triflates by a cationic cyclization reaction and its application in biomimetic polycyclizations and synthesis of terpenes. *Angew. Chem. Int. Ed.* **54**, 15506–15510 (2015). doi:10.1002/anie.201508077 Medline

47. G. Dauphin, J. C. Gramain, A. Kergomard, M. F. Renard, H. Vesch'ambre, Microbiological synthesis of optically active 3-deuterio-cycloalkanones. *J. Chem. Soc. Chem. Commun.* **0**, 318–319 (1980). doi:10.1039/c39800000318

48. B. Y. Lim, B. E. Jung, C. G. Cho, Ene-hydrazide from enol triflate for the regioselective Fischer indole synthesis. *Org. Lett.* **16**, 4492–4495 (2014). doi:10.1021/ol502031q Medline

49. X. Xu, D. Cheng, W. Pei, Iron-catalyzed homocoupling of bromide compounds. *J. Org. Chem.* **71**, 6637–6639 (2006). doi:10.1021/jo060673l Medline

50. W.-H. Lin, R. J. Lagow, The synthesis of highly fluorinated alkylcyclohexanes for use as oxygen carriers and the ^{19}F and ^{13}C NMR spectra of alkylcyclohexanes. *J. Fluor. Chem.* **50**, 345–358 (1990). doi:10.1016/S0022-1139(00)85000-9

51. D. D. Günbaş, F. Algı, T. Hökelek, W. H. Watson, M. Balci, Functionalization of saturated hydrocarbons. high temperature bromination of octahydropentalene. Part 19. *Tetrahedron* **61**, 11177–11183 (2005). doi:10.1016/j.tet.2005.09.019

52. A. Maercker, K. S. Oeffner, U. Girreser, Polylithiumorganic compounds. Part 29: C–C bond cleavage of phenyl substituted and strained carbocycles using lithium metal. *Tetrahedron* **60**, 8245–8256 (2004). doi:10.1016/j.tet.2004.06.105

53. N. Kalutharage, C. S. Yi, Scope and mechanistic analysis for chemoselective hydrogenolysis of carbonyl compounds catalyzed by a cationic ruthenium hydride complex with a tunable phenol ligand. *J. Am. Chem. Soc.* **137**, 11105–11114 (2015). doi:10.1021/jacs.5b06097 Medline

54. M. Kato, Y. Okamoto, T. Chikamoto, T. Miwa, The relative rates of ene reaction of benzyne with cyclic olefins: The stereochemical course. *Bull. Chem. Soc. Jpn.* **51**, 1163–1167 (1978). doi:10.1246/bcsj.51.1163

55. A. Vasilopoulos, S. L. Zultanski, S. S. Stahl, Feedstocks to pharmacophores: Cu-catalyzed oxidative arylation of inexpensive alkylarenes enabling direct access to diarylalkanes. *J. Am. Chem. Soc.* **139**, 7705–7708 (2017). doi:10.1021/jacs.7b03387 Medline

56. Z. Duan, W. Li, A. Lei, Nickel-catalyzed reductive cross-coupling of aryl bromides with alkyl bromides: Et_3N as the terminal reductant. *Org. Lett.* **18**, 4012–4015 (2016). doi:10.1021/acs.orglett.6b01837 Medline

57. S. Podder, J. Choudhury, S. Roy, Secondary benzylation with benzyl alcohols catalyzed by a high-valent heterobimetallic Ir-Sn complex. *J. Org. Chem.* **72**, 3129–3132 (2007). doi:10.1021/jo0625094 Medline

58. T. vom Stein, M. Peréz, R. Dobrovetsky, D. Winkelhaus, C. B. Caputo, D. W. Stephan, Electrophilic fluorophosphonium cations in the frustrated Lewis pair hydrogen activation and catalytic hydrogenation of olefins. *Angew. Chem. Int. Ed.* **54**, 10178–10182 (2015). doi:10.1002/anie.201504109 Medline

59. I. Chatterjee, Z. W. Qu, S. Grimme, M. Oestreich, $B(C_6F_5)_3$-catalyzed transfer of dihydrogen from one unsaturated hydrocarbon to another. *Angew. Chem. Int. Ed.* **54**, 12158–12162 (2015). doi:10.1002/anie.201504941 Medline

60. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, rev. D.01 (Gaussian, Inc., 2010).

61. Y. Zhao, D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, 215–241 (2008). doi:10.1007/s00214-007-0310-x

62. R. Ditchfield, W. J. Hehre, J. A. Pople, Self-consistent molecular-orbital methods. IX. An extended Gaussian-type basis for molecular-orbital studies of organic molecules. *J. Chem. Phys.* **54**, 724–728 (1971). doi:10.1063/1.1674902

63. W. J. Hehre, R. Ditchfield, J. A. Pople, Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.* **54**, 2257–2261 (1971).

64. P. C. Hariharan, J. A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta* **28**, 213–222 (1973). doi:10.1007/BF00533485

65. C. Y. Legault, CYLview, 1.0b (Université de Sherbrooke, 2009); www.cylview.org.

66. B. R. Ussing, C. Hang, D. A. Singleton, Dynamic effects on the periselectivity, rate, isotope effects, and mechanism of cycloadditions of ketenes with cyclopentadiene. *J. Am. Chem. Soc.* **128**, 7594–7607 (2006). doi:10.1021/ja0606024 Medline