1,3-γ-Silyl-Elimination in Electron-Deficient Cationic Systems

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Supporting Information: Substrate Synthesis and Solvolytic Studies

Key to Abbreviated Terms:

$CDCl_3$ - Deuterated chloroform
Cy - Cyclohexyl
DCM - Dichloromethane
DME - Dimethoxyethane
Et_2O - Diethyl ether
EtOAc - Ethyl acetate
Hex - Hexanes
HFIP - Hexafluoroisopropanol
HMDS - Hexamethyldisilane
HMPA - Hexamethylphosphoramide
HOAc/NaOAc - Acetic acid/sodium acetate
MeLi – Methyllithium
MsCl - Methanesulfonyl chloride
Ms_2O - Methanesulfonic anhydride
n-Bu - *n*-Butyl
OHFB - 2,2,3,3,4,4,4-heptafluorobutanoate
OPf - 2,3,4,5,6-Pentafluorobenzenesulfonate
OTf - Trifluoromethylsulfonate
OTs - *p*-Toluenesulfonate
Ph - Phenyl
TBAF - Tetrabutylammonium fluoride
^{t}Bu - *tert*-Butyl
Tf_2O – Trifluoromethanesulfonic anhydride
TFE- 2,2,2-Trifluoroethanol
TFE-d_6 - Deuterated 2,2,2-trifluoroethanol
THF - Tetrahydrofuran
TLC - Thin layer chromatography
TCE- 1,1,2 trichloroethane
TMS, Me_3Si - Trimethylsilyl
TMS-CF_3 - Trimethyl(trifluoromethyl)silane
TsCl - *p*-Toluenesulfonyl chloride
TsOH - *p*-Toluenesulfonic acid
Ts_2O - *p*-Toluenesulfonic anhydride
97T - 97% w/w TFE, 3% H_2O

General Considerations:

General:

All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 3,4, or 5-port dual-manifold or in a glove box. Nitrogen or argon was used to provide such an atmosphere. NMR Spectra (^{1}H, ^{13}C, ^{19}F) were collected at 298K on either a Brüker Avance Ultra Shield 300 MHz NMR, Brüker DRX-400 400 MHz NMR, or Brüker Avance 500 MHz NMR. ^{1}H-NMR Spectra obtained in $CDCl_3$ were referenced to residual non-deuterated chloroform (7.26 ppm) or TCE (5.76 ppm) in deuterated TFE or deuterated HFIP. ^{13}C-NMR Spectra obtained in $CDCl_3$ were referenced to chloroform (77.3 ppm). ^{19}F-NMR Spectra were referenced to fluorobenzene (–115.3 ppm) [1] or hexafluorobenzene (-164.9 ppm)[2]. Reactions were monitored by GC-MS using a HP 5890 Series II Gas Chromatograph attached to a 5972 Mass Spectrometer or an Agilent Technologies 7820A Gas Chromatograph attached to a 5975 Mass Spectrometer, by ^{1}H NMR, and/or by TLC on silica gel plates. High-resolution mass spectra were obtained using a JEOL AccuTOF-DART SVP 100 in positive direct analysis in real time (DART) ionization method, using PEG as the internal standard. TLC analysis was performed using hexanes/ethyl acetate as the eluent and visualized using permanganate stain, *p*-anisaldehyde stain, Seebach's Stain, and/or UV light. Flash chromatography was performed on either hand packed glass columns with Dynamic Adsorbants

[1] Furuya, T.; Kaiser, H. M.; Ritter, T. *Angew. Chem., Int. Ed.*, **2008**, *47*, 5993.
[2] Ravikumar, I.; Saha, S.; Ghosh, P. *Chem. Commun*. **2011**, *47*, 4721.

Inc. Flash Silica Gel (60 Å porosity, 32-63 μm). Automated Flash Chromotography was performed using either Biotage SNAP KP-SIL columns or Silicycle SiliaSep Flash Cartridges (60Å porosity, 40-63 μm).

Chemicals:

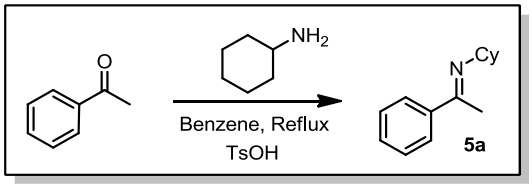
All deuterated solvents ($CDCl_3$, D_2O, pyridine-d_5, HFIP-d_2 TFE-d_3) were purchased from Cambridge Isotope Laboratories. $CDCl_3$ was stored over 4Å molecular sieves or purchased in breakseal ampules. Celite®, zinc dust[3], 2-Cyclohepten-1-one (80% tech. grade), sodium sulfate, $CuSO_4 \cdot 5H_2O$, sodium iodide, lithium diisopropylamide (2 M in THF/Ethyl benzene/heptane), *p*-toluenesulfonic anhydride *p*-toluenesulfonyl chloride[4], trifluoroacetic anhydride, *p*-toluenesulfonic acid monohydrate, anhydrous dimethyoxyethane, THF (anhydrous inhibitor-free and reagent grade), DCM, and diethyl ether (CHROMASOLV®, for HPLC, ≥99.9%, inhibitor-free and reagent grade), 1,2 Dichloroethane (HPLC-Grade), 1,1,2 tichloroethane[5], benzene, cyclohexylamine, acetophenone, *p*-fluoroacetophenone, *p*-iodoacetophenone, *p*-bromoacetophenone, *m*-methoxyacetophenone, *p*-methoxyacetophenone, 2-acetylpyridine, 3-acetylpyridine, and TBAF (1M in THF) were purchased from Sigma-Aldrich. 4-trifluoromethylacetophenone was purchased from Synquest Laboratories. Trifluoromethyltrimethylsilane, heptafluorobutyric anhydride, and Dess-Martin Periodinane were purchased from Synquest Laboratories or Oakwood Products. Vinyltrimethylsilane, (chloromethyl)dimethylphenylsilane, (chloromethyl)trimethylsilane, and hexamethyldisilane was purchased from Gelest. (Iodomethyl)trimethylsilane and (iodomethyl)dimethylphenylsilane were prepared in-house from these chlorides using the procedure[6] of Tilley et al. A procedure for the preparation of the latter compound is given in this SI. Trichloroacetyl chloride was purchased from Fluka or Sigma-Aldrich. 2,2,2-Trifluoroethanol was purchased from Halocarbon® Products Corporation,or Synquest Labroatories. Hexafluoroisopropanol was purchased from Synquest Laboratories. Potassium hydride3 (30% w/w KH in mineral oil) was purchased from ACROS. KH, *p*-toluenesulfonic anhydride and zinc dust were stored under argon in a glove box prior to use. *p*-toluenesulfonic anhydride was purchased from Sigma-Aldrich or Oakwood chemical[7].

[3] Stored under argon in a glove box.
[4] Recrystallized from boiling hexanes prior to use.
[5] Purified to remove 2-propanol stabilizer by washing with deionized water and drying with Na_2SO_4 prior to use.
[6] Tilley, L. J.; Shiner, V. J., Jr. *J. Phys. Org. Chem.* **1999**, *12*, 564.
[7] Alternatively, *p*-toluenesulfonic anhydride can be prepared via the procedure found in *J. Org. Chem.*, **1994**, *59*, 4186. However, noticeable difference was observed between commercially obtained samples or those prepared in-house likely due to residual $SOCl_2$. Recrystallization of the anhydride obtained by this method *must* be performed before use.

Synthesis of Solvolysis Substrates

Route A Sequence to Prepare γ-Silyl Ketones

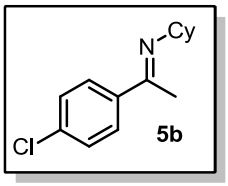
Representative Procedure for Preparation of Cyclohexylimines



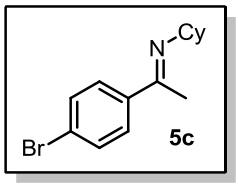
***N*-(1-Phenylethylidene)cyclohexanamine[8], 5a** (16.2 g, 81%). The following is a modification of the procedure outlined by Roberts et al.[9] To a 100 mL one-neck round bottom flask equipped with stirbar, was added benzene (50 mL, 1 M), cyclohexylamine (5.21g, 0.0525 mol, 1.05 equiv), acetophenone (6.01 g, 0.050 mol, 1 equiv) and *p*-toluenesulfonic acid monohydrate (0.0951 g 0.00050 mol, 0.01 equiv) were added. The flask was equipped with a graduated Dean-Stark trap along with a reflux condenser. The reaction mixture was heated to reflux in a 120 ^{o}C[10] oil bath and stirred via a magnetic stir plate. To ensure that the vapor made it to the condenser, the Dean-Stark trap was insulated with a layer of glass wool. The reaction mixture was allowed to reflux until 1 equivalent of water was observed in the trap (≈ 0.9 mL). Upon completion the reaction mixture was cooled to room temperature and the benzene was removed *in vacuo* by rotary evaporation. *p*-Toluenesulfonic acid was precipitated out by diluting the mixture with pentane. The fine precipitate was filtered, followed by removal of the solvent *in vacuo* by rotary evaporation. The crude imine was then purified *via* vacuum distillation (b.p. 96-99 ^{o}C @ 0.1 mmHg) giving the pure **1a** as a clear, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.26 - 1.45 (m, 3 H) 1.56 (qd, *J* = 12.00, 3.00 Hz, 2 H) 1.65 - 1.74 (m, 3 H) 1.80 - 1.88 (m, 2 H) 2.25 (s, 3 H) 3.49 (spt, *J* = 4.80 Hz, 1 H) 7.33 - 7.39 (m, 3 H) 7.75 (dd, *J* = 6.83, 2.73 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 15.31 (CH_3) 25.05 (CH_2) 26.01 (CH_2) 33.77 (CH_2) 60.02 (CH) 126.82 (CH) 128.27 (CH) 129.22 (CH) 142.06 (C) 162.39 (C) **GC-MS** (EI) 201 ($[M]^+$, 20%), 200 ($[M-1]^+$, 51%), 186 (100%), 172 (19%), 158 (47%), 146 (27%), 144 (26%), 130 (29%), 120 (68%), 117 (17%), 104 (94%), 91 (16%), 77 (37%), 55 (24%), 41 (19%).

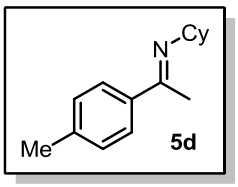
[8] Valdes, C.; Barluenga, J.; Jimenez-Aquino, A.; Aznar, F. *J. Am. Chem. Soc.*, **2009**, *131*, 4031.
[9] Watson, J. M.; Irvine, J. L.; Roberts, R. M. *J. Am. Chem. Soc.*, **1973**, *95*, 3348.
[10] Note that if the oil bath was set higher than this temperature, decomposition occurred in sensitive substrates (e.g. *p*-methoxyacetophenone). This temperature was determined to be ideal to maintain a constant reflux without the risk of diminished yields.



***N*-(1-(4-chlorophenyl)ethylidene)cyclohexanamine, 5b** (22.126 g, 93%) was prepared according to the representative procedure from *p*-chloroacetophenone (15.46 g, 0.10 mol) and obtained as a X solid and used without further purification. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 1.24 - 1.45 (m, 3 H) 1.47 - 1.61 (m, 2 H) 1.63 - 1.72 (m, 3 H) 1.77 - 1.88 (m, 2 H) 2.19 (s, 3 H) 3.42 - 3.52 (m, 1 H) 7.30 (d, *J* = 8.56 Hz, 2 H) 7.69 (d, *J* = 8.56 Hz, 2 H) **^{13}C NMR** ($CDCl_3$ 75 MHz) δ ppm 15.12 (CH_3) 24.97 (CH_2) 25.95 (CH_2) 33.71 (CH_2) 60.06 (CH) 128.19 (CH) 128.37 (CH) 135.27 (C) 140.28 (C) 161.15 (C) **GC-MS** (EI) 237 ($[M]^+$, ^{37}Cl 6%), 235 ($[M]^+$, ^{35}Cl 18%), 222 (33%), 220 (100%), 192 (44%), 180 (32%), 164 (33%), 154 (48%), 138 (85%), 111 (35%), 102 (37%), 75 (29%), 55 (38%), 41 (41%) **HRMS** (DART) calcd for $C_{14}H_{19}ClN$ $[M^+]$: 236.1206, found: 236.1191.

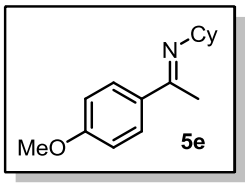


***N*-(1-(4-bromophenyl)ethylidene)cyclohexanamine, 5c** (25.88 g, 92%) was prepared according to the representative procedure from *p*-bromoacetophenone (19.90 g, 0.10 mol) and cyclohexylamine (14.879 g, 0.150 mol, 1.5 equiv[11]) and purified *via* recrystallization from boiling hexanes. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 1.25 - 1.45 (m, 3 H) 1.53 (qd, *J* = 11.20, 3.00 Hz, 2 H) 1.68 (d, *J* = 11.61 Hz, 3 H) 1.83 (d, *J* = 12.63 Hz, 2 H) 2.21 (s, 3 H) 3.47 (spt, *J* = 4.80 Hz, 1 H) 7.48 (d, *J* = 8.53 Hz, 2 H) 7.64 (d, *J* = 8.19 Hz, 2 H) **^{13}C NMR** (125 Mz, $CDCl_3$) δ ppm 15.19 (CH_3) 25.03 (CH_2) 26.00 (CH_2) 33.74 (CH_2) 60.16 (CH_3) 123.73 (C) 128.54 (CH) 131.41 (CH) 140.80 (C) 161.33 (C) **GC-MS** (EI) 280 ($[M]^+$, ^{81}Br 16%), 278 ($[M]^+$, ^{79}Br 16%), 266 (57%), 264 (58%), 252 (29%), 250 (19%), 238 (19%), 236 (18%), 200 (23%), 198 (23%), 183 (97%), 181 (100%), 118 (17%), 102 (37%), 83 (24%), 55 (37%), 41 (21%) **HRMS** (DART) calcd for $C_{14}H_{18}NBr$ $[M^+]$: 280.0701, found: 280.0689.

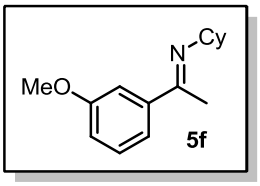


***N*-(1-(p-tolyl)ethylidene)cyclohexanamine, 5d** (17.618 g, 82%) was prepared according to the representative procedure from 4-methylacetophenone (13.42 g, 0.10 mol) and purified *via* vacuum distillation (b.p. 110-113 ^{o}C @ 0.5 mmHg) giving the pure imine as a clear, light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 1.23 - 1.44 (m, 3 H) 1.54 (qd, *J* = 10.50, 3.00 Hz, 2 H) 1.65 - 1.74 (m, 3 H) 1.83 (dt, *J* = 12.77, 3.39 Hz, 2 H) 2.22 (s, 3 H) 2.35 (s, 3 H) 3.43 - 3.51 (m, 1 H) 7.16 (d, *J* = 8.20 Hz, 2 H) 7.65 (d, *J* = 8.20 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 15.36 (CH_3) 21.47 (CH_3) 25.19 (CH_2) 26.11 (CH_2) 33.90 (CH_2) 60.06 (CH) 126.87 (CH) 129.05 (CH) 139.26 (C) 139.46 (C) 162.34 (C) **GC-MS** (EI) 215 ($[M]^+$, 21%), 214 ($[M-1]^+$, 45%), 200 (100%), 186 (16%), 172 (35%), 160 (23%), 158 (23%), 144 (29%), 134 (43%), 131 (16%), 118 (90%), 117 (35%), 115 (19%), 105 (11%), 91 (34%), 65 (11%), 55 (16%), 41 (14%) **HRMS** (DART) calcd for $C_{15}H_{21}N$ $[M]^+$: 216.1752, found: 216.1742.

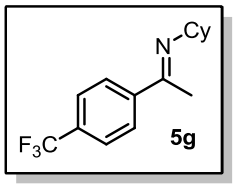
[11] When preparing some substrates, we initially used 1.5 equivalents of cyclohexylamine. We later found that this was unnecessary and comparable yields could be obtained using 1.05 equivalents of the amine.



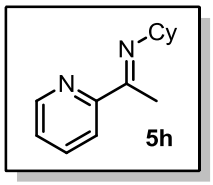
***N*-(1-(4-methoxyphenyl)ethylidene)cyclohexanamine, 5e** (9.93 g, 86%) was prepared according to the representative procedure from 4-methoxyacetophenone (7.015 g, 0.050 mol) and purified *via* vacuum distillation (b.p. 147-151 °C @ 0.7 mmHg) giving the pure imine as a light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 1.26 - 1.43 (m, 3 H) 1.54 (qd, *J* = 10.00, 3.00 Hz, 2 H) 1.65 - 1.73 (m, 3 H) 1.83 (dt, *J* = 13.08, 3.55 Hz, 2 H) 2.21 (s, 3 H) 3.42 - 3.50 (m, 1 H) 3.81 (s, 3 H) 6.87 (d, *J* = 8.80 Hz, 2 H) 7.73 (d, *J* = 8.80 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 15.13 (CH_3) 25.14 (CH_2) 26.05 (CH_2) 33.90 (CH_2) 55.46 (CH_3) 59.90 (CH) 113.57 (CH) 128.28 (CH) 134.80 (C) 160.70 (C) 161.67 (C) **GC-MS** (EI) 231 ($[M]^+$, 24%), 230 ($[M-1]^+$, 37%), 216 (82%), 202 (14%), 188 (32%), 176 (19%), 174 (19%), 160 (19%), 149 (40%), 134 (100%), 119 (14%), 91 (19%), 77 (11%), 55 (14%), 41 (12%) **HRMS** (DART) calcd for $C_{15}H_{21}ON$ $[M]^+$: 232.1701, found: 232.1704.



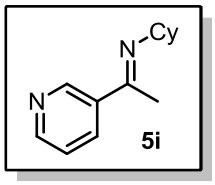
***N*-(1-(3-methoxyphenyl)ethylidene)cyclohexanamine, 5f** (9.27 g, 80%) was prepared according to the representative procedure from 3-methoxyaceophenone (7.015 g, 0.050 mol) and purified *via* vacuum distillation (129-133 °C @ 0.20 mmHg) giving the pure imine as a light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 1.25 - 1.46 (m, 3 H) 1.52 - 1.62 (m, 2 H) 1.67 - 1.76 (m, 3 H) 1.86 (dd, *J* = 12.30, 2.84 Hz, 2 H) 2.26 (s, 3 H) 3.46 - 3.54 (m, 1 H) 3.86 (s, 2 H) 6.93 (dt, *J* = 8.20, 1.26 Hz, 1 H) 7.26 - 7.40 (m, 4 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 15.45 (CH_3) 24.90 (CH_2) 25.83 (CH_2) 33.57 (CH_2) 55.30 (CH_3) 59.90 (CH_3) 112.08 (CH) 114.92 (CH) 119.26 (CH) 129.11 (CH) 143.51 (C) 159.53 (C) 162.27 (C) **GC-MS** (EI) 231 ($[M]^+$, 49%), 230 ($[M-1]^+$, 70%), 216 (100%), 202 (17%), 188 (41%), 176 (23%), 174 (38%), 160 (24%), 150 (35%), 148 (36%), 134 (83%), 119 (16%), 103 (11%), 91 (25%), 77 (20%), 65 (10%), 55 (24%), 41 (18%) **HRMS** (DART), calcd for $C_{15}H_{21}ON$ $[M]^+$: 232.1701, found: 232.1691.



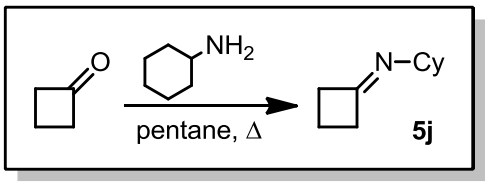
***N*-(1-(4-(trifluoromethyl)phenyl)ethylidene)cyclohexanamine, 5g** (13.132 g, 61%) was prepared according to the representative procedure from 4-trifluoromethylacetophenone (18.02 g, 0.10 mol) and purified *via* vacuum distillation (b.p. 101-104 °C @ 0.25 mmHg) giving the pure imine as a clear, colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 1.26 - 1.44 (m, 3 H) 1.55 (qd, *J* = 11.00, 3.00 Hz, 2 H) 1.67 - 1.73 (m, 3 H) 1.84 (dt, *J* = 13.08, 3.55 Hz, 2 H) 2.26 (s, 3 H) 3.47 - 3.54 (m, 1 H) 7.61 (d, *J* = 8.20 Hz, 2 H) 7.85 (d, *J* = 8.20 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 15.54 (CH_3) 25.05 (CH_2) 26.01 (CH_2) 33.74 (CH_2) 60.40 (CH) 124.43 (q, $J_{C\text{-}F}$ = 272.00 Hz, CF_3) 125.38 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.67 Hz, CH) 127.27 (CH) 131.17 (q, $J_{C\text{-}C\text{-}F}$ = 32.00 Hz, C) 145.28 (C) 161.49 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -65.79 **GC-MS** (EI) 269 ($[M]^+$, 16%), 268 ($[M-1]^+$, 36%), 254 (100%), 250 (11%), 240 (19%), 226 (54%), 214 (26%), 212 (25%), 200 (11%), 198 (24%), 188 (87%), 172 (62%), 159 (11%), 151 (19%), 145 (19%), 103 (13%), 83 (16%), 67 (13%), 55 (34%), 41 (22%) **HRMS** (DART) calcd for $C_{15}H_{19}F_3N$ $[M]^+$: 270.1470, found: 270.1480.



***N*-(1-(pyridin-2-yl)ethylidene)cyclohexanamine[12], 5h** (16.19 g, 80%) was prepared according to the representative imine procedure from 2-acetylpyridine (9.70 g, 0.080 mol) and purified *via* vacuum distillation (b.p. 109-112 °C @ 0.70 mmHg) giving the pure imine as a light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 1.24 - 1.35 (m, 1 H) 1.40 (qt, *J* = 12.00, 3.20 Hz, 2 H) 1.50 - 1.61 (m, 2 H) 1.66 - 1.77 (m, 4 H) 1.84 (dt, *J* = 13.24, 3.47 Hz, 2 H) 2.38 (s, 3 H) 3.50 - 3.65 (m, 1 H) 7.25 (ddd, *J* = 7.57, 5.04, 1.26 Hz, 1 H) 7.68 (td, *J* = 7.80, 1.26 Hz, 1 H) 8.07 (dt, *J* = 8.20, 1.30 Hz, 1 H) 8.58 (dd, *J* = 5.36, 2.21 Hz, 1 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 13.94 (CH_3) 25.03 (CH_2) 26.04 (CH_2) 33.66 (CH_2) 60.44 (CH) 121.31 (CH) 124.03 (CH) 136.47 (CH) 148.36 (CH) 158.69 (C) 163.93 (C) **GC-MS** (EI) 202 ($[M]^+$, 20%), 160 (16%), 159 (100%), 146 (38%), 145 (32%), 104 (23%), 78 (22%), 55 (11%) **HRMS** (DART) calcd for $C_{13}H_{19}N_2$ $[M]^+$: 203.1548, found: 203.1552.



N-(1-(pyridin-3-yl)ethylidene)cyclohexanamine, 5i (16.40 g, 81%) was prepared according to the representative imine procedure from 3-acetylpyridine (12.11 g, 0.10 mol) and purified *via* vacuum distillation (b.p. 107-109 °C @ 0.25 mmHg) giving the pure imine as a light yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 1.12 - 1.36 (m, 3 H) 1.37 - 1.49 (m, 3 H) 1.52 - 1.63 (m, 3 H) 1.68 - 1.77 (m, 2 H) 2.14 (s, 3 H) 3.40 (tt, *J* = 10.00, 4.20 Hz, 1 H) 7.16 (ddd, *J* = 8.01, 4.83, 0.86 Hz, 1 H) 7.97 (dt, *J* = 7.83, 2.08 Hz, 1 H) 8.47 (dd, *J* = 4.77, 1.59 Hz, 1 H) 8.85 (dd, *J* = 2.20, 0.73 Hz, 1 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 15.01 (CH_2) 24.71 (CH_2) 25.75 (CH_2) 33.49 (CH_3) 59.86 (CH) 123.03 (CH) 134.01 (CH) 136.83 (C) 148.26 (CH) 150.10 (CH) 159.96 (C) **GC-MS** (EI) 202 ($[M]^+$, 14%), 201 ($[M-1]^+$, 34%), 187 (100%), 173 (16%), 159 (59%), 147 (24%), 145 (28%), 131 (24%) **HRMS** (DART) calcd for $C_{13}H_{19}N_2$ $[M]^+$: 203.1548, found: 203.1557.



N-cyclobutylidenecyclohexanamine, 5j (6.788 g, 90%). This synthesis was performed according to a modified procedure of Roberts et al.[13] To a 100 mL one-neck round bottom flask equipped with a stir bar, was added pentane (50 mL, 1 M), cyclobutanone (3.505 g, 50 mmol, 1 equiv), cyclohexylamine (5.21 g, 52.5 mmol, 1.05 equiv) were added. The flask was equipped with a graduated Dean-Stark trap along with a reflux condenser. The mixture was heated to reflux and the reaction mixture was allowed to stir at this temperature until 1 equiv of H_2O (≈ 0.9 mL) was observed in the trap (≈18 h). Upon completion, the reaction mixture was cooled to room temperature and the pentane was removed *in vacuo* by rotary evaporation to afford the

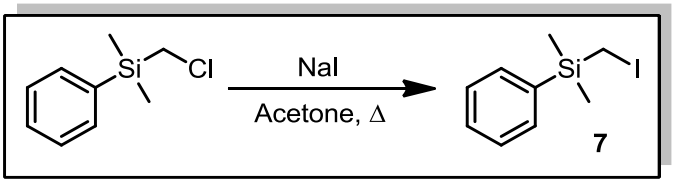
[12] Polm, L. H.; Koten, G. V.; Elsevier, C. J.; Vrieze, K.; Santen, B. F. K. V.; Stam, C. H. *J. Organomet Chem.*, **1986**, *304*, 353.
[13] Watson, J. M.; Irvine, J. L.; Roberts, R. M. *J. Am. Chem. Soc.*, **1973**, *95*, 3348.

crude imine. Further purification was accomplished by vacuum distillation (b.p. 56-58 °C @ 0.1 mmHg) giving the pure imine as a clear colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.99 - 1.34 (m, 6 H) 1.40 - 1.51 (m, 3 H) 1.60 (br. s., 2 H) 1.73 - 1.83 (m, 2 H) 2.69 - 2.80 (m, 3 H) 2.84 - 3.00 (m, 1 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 13.31 (CH_2) 24.77 (CH_2) 25.61 (CH_2) 33.71 (CH_2) 34.33 (CH_2) 37.99 (CH_2) 59.88 (CH) 169.13 (C) **GC-MS** (EI) 151 ([M]$^+$, 3%), 123 (44%), 84 (7%), 83 (100%), 69 (18%), 67 (11%), 55 (75%).

Representative Procedure for Preparation of 3-Trimethylsilyl Ketones

Finkelstein Reaction to Prepare Requisite Iodide

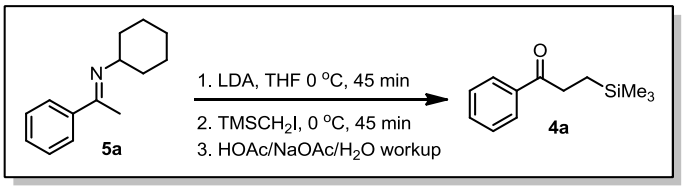


(Iodomethyl)dimethyl(phenyl)silane (7)[14] (30.1 g, 100%). In a 250 mL round bottom flask equipped with a stir bar was added (chloromethyl)dimethyl(phenyl)silane (20.13 g, 0.108 mol, 1 equiv), dry acetone (100 mL, 1.08 M) and sodium iodide (28.4 g, 0.189 mol, 1.75 equiv) and allowed to reflux for 24 hours. After this time, the reaction was cooled to room temperature and the solvent removed *via* rotary evaporation to give a slurry. The resulting slurry was passed through a pad of Celite® which was washed with 100 mL of hexanes. The solvent removed *via* rotary evaporation to give the pure product as a clear, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.49 (s, 6 H) 2.22 (s, 2 H) 7.37 - 7.48 (m, 3 H) 7.54 - 7.63 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -13.25 (CH_2) -2.59 (CH_3) 128.25 (CH) 129.89 (CH) 133.94 (CH) 137.06 (C) **GC-MS** (EI) 276 ([M]$^+$, 8%), 260 (20%), 149 (63%), 135 (100%), 119 (14%) 105 (17%), 92 (14%).

[14] Organ, M. G.; Mallik, D. *Can. J. Chem.* **2006**, *84*, 1259.

Route A Sequence to Prepare γ-Silyl Ketones

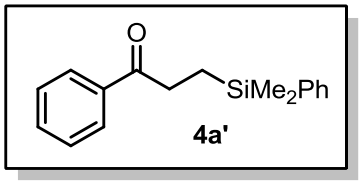


1-Phenyl-3-(trimethylsilyl)propan-1-one[15]**, 4a** (6.47 g, 64%). The following procedure is a modification of the procedure outlined by Fleming and Patel[15]. To a 100 mL round bottom flask equipped with stirbar was added **5a** (5.03 g, 0.025 mol, 1 equiv) and THF (7 mL). The flask was sealed with a rubber septa, placed under a nitrogen atmosphere *via* a nitrogen inlet needle, and stirred *via* a magnetic stir plate. The reaction mixture was cooled to 0 °C in an ice-water bath for approximately 10 minutes. To this chilled mixture was added a 2 M solution of lithium diisopropylamide in THF/ethylbenzene/heptane (13.75 mL, 0.0275 mol, 1.1 equiv) dropwise *via* a 20 mL syringe[16]. The reaction mixture was allowed to stir for 1 hour at 0 °C. After this time, (iodomethyl)trimethylsilane[17] (5.88 g, 0.0275 mol, 1.1 equiv) was added dropwise *via* a 10 mL syringe. The reaction mixture was allowed to stir for 1 hour at 0 °C. After this time, the septa was removed and 25 mL of an acetate buffer (12.5 g NaOAc•3H_2O, 25 mL HOAc, 25 mL H_2O) was added all at once. Initially a precipitate formed but dissolved after stirring for 10 minutes at 0 °C. The reaction mixture was transferred to a large separatory funnel and diluted with ether[18] (≈250 mL) and water (≈100 mL). The layers were separated and the aqueous layer was extracted three times with ether (≈50 mL each). The organic layers were combine and were washed with a saturated sodium bicarbonate solution in a separatory funnel (***CAUTION****: The ether layer contains a large amount of acetic acid. Quenching this with the bicarbonate solution releases CO_2 gas and hence the separatory funnel must be vented often to avoid pressure build-up*). The washes were continued until no more gas was evolved (roughly three washes of 50 mL each). The organic layer was washed with brine (≈ 100 mL) and dried with Na_2SO_4. The solvent was removed *in vacuo* and then purified *via* vacuum distillation (b.p. 78-81 °C @ 0.1 mmHg) giving the pure **2a** as a clear, colorless oil.

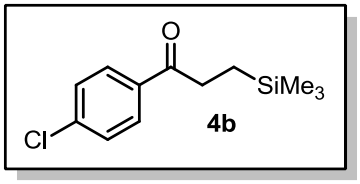
^{1}H NMR (400 MHz, $CDCl_3$) *d* ppm 0.05 (s, 9 H) 0.92 (apparent triplet, *J* = 7.90 Hz, 2 H) 2.94 (apparent triplet, *J* = 8.20 Hz, 2 H) 7.43 - 7.49 (m, 2 H) 7.52 - 7.57 (m, 1 H) 7.95 (d, *J* = 7.17 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) *d* ppm -1.55 (CH_3) 11.16 (CH_2) 33.36 (CH_2) 128.28 (CH) 128.76 (CH) 132.99 (CH) 137.06 (C) 201.49 (C) **GC-MS** (EI) 206 ($[M]^+$, 19%), 205 ($[M-1]^+$, 86%), 191 (68%), 177 (17%), 135 (13%), 117 (79%), 115 (24%), 105 (35%), 91 (10%), 77

[15] Fleming, I.; Patel, S. K.; Urch, C. *J. Chem. Soc. Perk. Trans. I* **1989**, 115.
[16] In some cases the solution became a viscous to semi-solid mixture. In such cases a small amount of THF (approx. 5 mL) was added to increase fluidity. In almost all cases of the substrates examined, an immediate color change was observed, typically to a yellow or orange color.
[17] This reagent is available commercially but is quite costly. However, the chlorinated analog is relatively inexpensive. Therefore this reagent was prepare in-house via a Finkelstein reaction of (chloromethyl)trimethylsilane with sodium iodide in acetone. A convenient procedure for its preparation can be found in Tilley, L. J.; Shiner, V. J., Jr. *J. Phys. Org. Chem.* **1999**, *12*, 564.
[18] Note: By substituting pentane in for ether, a significant decrease in acetic acid taken up into the organic layer. This makes washing with sodium bicarbonate safer and facilitates purification.

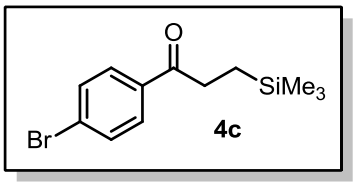
(39%), 65 (33%), 73 (100%), 45 (15%) **HRMS** (DART) calcd for $C_{12}H_{18}OSi$ $[M^+]$: 207.1205, found: 207.1229.



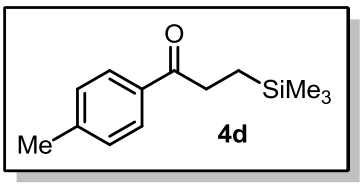
3-(dimethyl(phenyl)silyl)-1-phenylpropan-1-one, 4a′ (15.24 g, 88%) was prepared according to the representative 3-trimethylsilyl ketone procedure from **5a** (13.0 g, 0.064 mol) with *the following modification*: (Iodomethyl)dimethyl(phenyl)silane (19.44 g, 0.0704 mol, 1.1 equiv) was used in place of (iodomethyl)trimethylsilane. Further purification was accomplished by vacuum distillation (b.p. 140-143 °C @ 0.10 mmHg) to give **4a′** as a clear, light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.34 (s, 6 H) 1.17 (apparent triplet, *J* = 8.20 Hz, 2 H) 2.93 (apparent triplet, *J* = 8.20 Hz, 2 H) 7.36 - 7.39 (m, 3 H) 7.43 (apparent triplet, *J* = 7.80 Hz, 2 H) 7.50 - 7.57 (m, 3 H) 7.86 - 7.91 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -2.89 (CH_3) 10.07 (CH_2) 33.23 (CH_2) 128.08 (CH) 128.21 (CH) 128.69 (CH) 129.28 (CH) 132.98 (CH) 133.77 (CH) 136.90 (C) 138.58 (C) 201.07 (C) **GC-MS** (EI) 268 ($[M]^+$, 2%), 267 ($[M-1]^+$, 8%), 253 (100%), 191 (56%), 135 (81%), 117 (33%), 105 (26%), 77 (17%), 43 (6%) **HRMS** (DART) calcd for $C_{17}H_{20}OSi$ $[M-H]^+$: 267.1205, found: 267.1239.



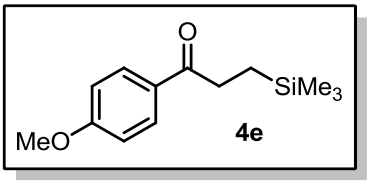
1-(4-chlorophenyl)-3-(trimethylsilyl)propan-1-one, 4b (16.64 g, 78%) was prepared according to the representative 3-trimethylsilyl ketone procedure from **5b** (21.0 g, 0.089 mol) and further purified by vacuum distillation (b.p. 108-110 °C @ 0.25 mmHg) to give **4b** as a clear, yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm -0.03 - 0.08 (m, 9 H) 0.88 (apparent triplet, *J* = 8.20 Hz, 2 H) 2.89 (apparent triplet, *J* = 8.20 Hz, 2 H) 7.40 (d, *J* = 8.56 Hz, 2 H) 7.87 (d, *J* = 8.56 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -1.54 (CH_3) 11.06 (CH_2) 33.36 (CH_2) 129.07 (CH) 129.72 (CH) 135.31 (C) 139.39 (C) 200.14 (C) **GC-MS** (EI) 241 ($[M]^+$, ^{37}Cl 16%), 239 ($[M]^+$, ^{35}Cl 42%), 227 (27%), 225 (72%), 205 (53%), 169 (10%), 153 (18%), 151 (57%), 139 (36%), 115 (36%), 111 (41%), 75 (48%), 73 (100%), 45 (19%) **HRMS** (DART) calcd for $C_{12}H_{18}ClOSi$ $[M]^+$: 241.0815, found: 241.0808.



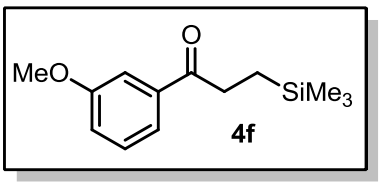
1-(4-bromophenyl)-3-(trimethylsilyl)propan-1-one, **4c** (10.30 g, 60%) was prepared according to the representative 3-trimethylsilyl ketone procedure from **5c** (16.87 g, 0.060 mol) and further purified by vacuum distillation (b.p. 105-108 °C @ 0.25 mmHg) to give **4c** as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 0.03 (s, 9 H) 0.88 (apparent triplet, *J* = 8.20 Hz, 2 H) 2.89 (apparent triplet, *J* = 8.20 Hz, 2 H) 7.59 (d, *J* = 8.83 Hz, 2 H) 7.80 (d, *J* = 8.83 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.50 (CH_3) 11.12 (CH_2) 33.41 (CH_2) 128.16 (C) 129.88 (CH) 132.12 (CH_2) 135.76 (C) 200.46 (C) **GC-MS** (EI) 285 ($[M]^+$, ^{81}Br 24%), 283 ($[M]^+$, ^{79}Br 23%), 271 (43%), 269 (46%), 212 (25%), 210 (26%), 205 (56%), 185 (89%), 182 (91%), 157 (41%), 155 (42%), 116 (64%), 75 (54%), 73 (100%), 50 (15%) **HRMS** (DART) calcd for $C_{12}H_{17}BrOSi$ $[M]^+$: 285.0310, found: 285.0314.



1-(p-tolyl)-3-(trimethylsilyl)propan-1-one, 4d (10.92 g, 83%) was prepared according to the representative 3-trimethylsilyl ketone procedure from **5d** (12.86 g, 0.060 mol) and further purified by vacuum distillation (b.p. 100-105 ^{o}C @ 0.10 mmHg) to give **4d** as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm -0.0474 (s, 9 H) 0.91 (apparent triplet, *J* = 8.20 Hz, 2 H) 2.41 (s, 3 H) 2.91 (apparent triplet, *J* = 7.90 Hz, 2 H) 7.26 (d, *J* = 7.85 Hz, 2 H) 7.85 (d, *J* = 8.19 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.50 (CH_3) 11.31 (CH_2) 21.85 (CH_3) 33.26 (CH_2) 128.45 (CH) 129.47 (CH) 134.57 (C) 143.74 (C) 201.23 (C) **GC-MS** (EI) 219 ($[M-1]^+$, 11%), 205 (100%), 131 (37%), 119 (46%), 91 (25%), 75 (12%), 73 (45%), 65 (10%), 45 (8%) **HRMS** (DART) calcd for $C_{13}H_{20}OSi$ $[M]^+$: 221.1362, found: 221.1336.

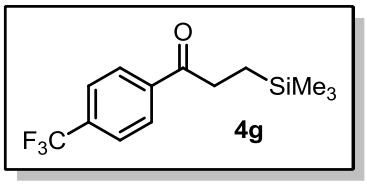


1-(4-methoxyphenyl)-3-(trimethylsilyl)propan-1-one, 4e (9.34 g, 66%) was prepared according to the representative 3-trimethylsilyl ketone procedure from **5e** (13.85 g, 0.060 mol) and further purified by vacuum distillation (b.p. 110-115 ^{o}C @ 0.10 mmHg) to give **4e** as a light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 0.04 (s, 9 H) 0.90 (apparent triplet, *J* = 8.20 Hz, 2 H) 2.87 (apparent triplet, *J* = 8.20 Hz, 2 H) 3.84 (s, 3 H) 6.91 (d, *J* = 8.83 Hz, 2 H) 7.92 (d, *J* = 8.80 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.55 (CH_3) 11.39 (CH_2) 32.96 (CH_2) 55.60 (CH_3) 113.87 (CH) 130.02 (C) 130.50 (CH) 163.45 (C) 200.11 (C) **GC-MS** (EI) 236 ($[M]^+$, 7%), 235 ($[M-1]^+$, 31%), 221 (68%), 205 (17%), 147 (19%), 135 (100%), 92 (13%), 77 (16%), 73 (33%), 45 (7%) **HRMS** (DART) calcd for $C_{13}H_{20}O_2Si$ $[M]^+$: 237.1311, found: 237.1317.

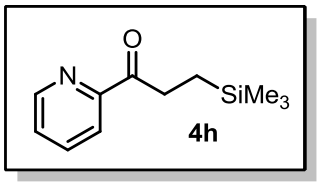


1-(3-methoxyphenyl)-3-(trimethylsilyl)propan-1-one, 4f (10.75 g, 76% [19]) was prepared according to the representative 3-trimethylsilyl ketone procedure from **5f** (13.85 g, 0.060 mol) and further purified by vacuum distillation (b.p. 129-133 ^{o}C @ 0.20 mmHg) to give **4f** as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.07 (s, 9 H) 0.93 (apparent triplet, *J* = 8.20 Hz, 2 H) 2.94 (apparent triplet, *J* = 7.90 Hz, 2 H) 3.88 (s, 3 H) 7.12 (dd, *J* = 8.19, 2.73 Hz, 1 H) 7.38 (t, *J* = 7.85 Hz, 1 H) 7.51 (s, 1 H) 7.55 (apparent doublet, *J* = 7.51 Hz, 1 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -1.55 (CH_3) 11.26 (CH_2) 33.50 (CH_2) 55.64 (CH_3) 112.72 (CH) 119.37 (CH) 120.89 (CH) 129.74 (CH) 138.43 (C) 160.06 (C) 201.35 (C) **GC-MS** (EI) 236 ($[M]^+$, 14%), 235 ($[M-1]^+$, 29%), 221 (100%), 205 (59%), 165 (21%), 147 (38%), 135 (55%), 115 (11%), 107 (18%), 92 (19%), 77 (23%), 75 (26%), 73 (95%), 45 (14%) **HRMS** (DART) calcd for $C_{13}H_{20}O_2Si$ $[M]^+$: 237.13108, found: 237.1299.

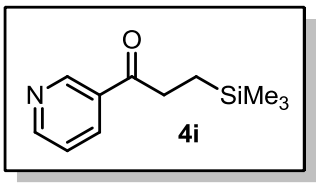
[19] Note that yields improved when freshly ordered LDA was utilized. It is recommended that either the LDA be titrated before performing the alkylation or prepare the LDA solution in-house.



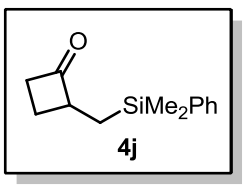
1-(4-(trifluoromethyl)phenyl)-3-(trimethylsilyl)propan-1-one, 4g (12.01 g, 73%) was prepared according to the representative 3-trimethylsilyl ketone procedure from **5g** (16.15 g, 0.060 mol) and further purified by vacuum distillation (b.p. 88-90 ^{o}C @ 0.25 mmHg) to give **4g** as a light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 0.05 (s, 9 H) 0.91 (apparent triplet, *J* = 8.10 Hz, 13 H) 2.96 (apparent triplet, *J* = 8.10 Hz, 14 H) 7.72 (d, *J* = 8.20 Hz, 2 H) 8.05 (d, *J* = 8.83 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.50 (CH_3) 11.05 (CH_2) 33.83 (CH_2) 123.94 (q, $J_{C\text{-}F}$ = 274.00 Hz, CF_3) 125.94 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.80 Hz, CH) 128.68 (CH) 134.46 (q, $J_{C\text{-}C\text{-}F}$ = 32.50 Hz, C) 139.81 (C) 200.50 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -66.24 **GC-MS** (EI) 273 ($[M\text{-}1]^+$, 1%), 254 (9%), 235 (19%), 224 (23%), 185 (13%), 173 (12%), 145 (10%), 101 (23%), 77 (11%), 75 (49%), 73 (100%), 45 (9%) **HRMS** (DART) calcd for $C_{13}H_{18}F_3OSi$ $[M]^+$: 275.1079, found: 275.1090.



1-(pyridin-2-yl)-3-(trimethylsilyl)propan-1-one, 4h (6.0 g, 67%) was prepared according to the representative 3-trimethylsilyl ketone procedure from **5h** (8.00 g, 0.0396 mol) and further purified by vacuum distillation (b.p. 83-86 ^{o}C @ 0.25 mmHg) to give **4h** as a light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 0.01 (s, 9 H) 0.86 (apparent triplet, *J* = 8.20 Hz, 2 H) 3.16 (apparent triplet, *J* = 8.10 Hz, 2 H) 7.41 (ddd, *J* = 7.80, 4.60, 1.20 Hz, 1 H) 7.78 (td, *J* = 7.80, 1.80 Hz, 1 H) 7.99 (d, *J* = 8.20 Hz, 1 H) 8.63 (d, *J* = 5.30 Hz, 1 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.73 (CH_3) 10.27 (CH_2) 32.23 (CH_2) 121.86 (CH) 126.90 (CH) 136.81 (CH) 148.88 (CH) 153.50 (C) 202.91 (C) **GC-MS** (EI) 207 ($[M]^+$, 4%), 206 ($[M\text{-}1]^+$, 10%), 192 (100%), 150 (10%), 118 (25%), 78 (14%), 75 (19%), 73 (35%), 45 (9%) **HRMS** (DART) calcd for $C_{11}H_{17}NOSi$ $[M]^+$: 208.11577, found: 208.1166.



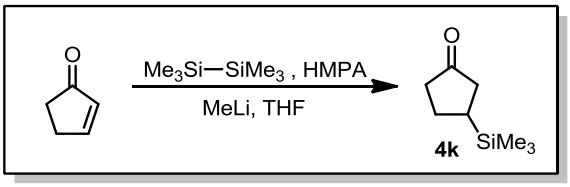
1-(pyridin-3-yl)-3-(trimethylsilyl)propan-1-one, 4i (8.76 g, 70%) was prepared according to the representative 3-trimethylsilyl ketone procedure from **5i** (12.14 g, 0.060 mol) and further purified by vacuum distillation (b.p. 89-90 ^{o}C @ 0.25 mmHg) to give **4i** as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.04 (s, 9 H) 0.91 (apparent triplet, J = 8.30 Hz, 2 H) 2.94 (apparent triplet, *J* = 8.30 Hz, 2 H) 7.40 (ddd, *J* = 8.10, 4.89, 0.73 Hz, 1 H) 8.18 - 8.24 (m, 1 H) 8.21 (dt, *J* = 7.83, 2.20 Hz, 1 H) 8.75 (dd, *J* = 4.89, 1.71 Hz, 1 H) 9.11 - 9.18 (m, 1 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.57 (CH_3) 10.91 (CH_2) 33.78 (CH_2) 123.86 (CH) 132.16 (CH) 135.61 (CH) 149.86 (CH) 153.54 (C) 200.24 (C) **GC-MS** (EI) 207 ($[M]^+$, 16%), 206 (65%), 151 (15%), 136 (27%), 118 (71%), 106 (24%), 78 (56%), 75 (21%), 73 (100%), 58 (17%), 51 (37%), 45 (28%) **HRMS** (DART) calcd for $C_{11}H_{18}NOSi$ $[M]^+$: 208.1158, found: 208.1167.



2-((dimethyl(phenyl)silyl)methyl)cyclobutanone (4j) (9.68 g, 46%) was prepared according to the representative 3-trimethylsilyl ketone procedure from **5j** (14.65 g, 0.0968 mol, 1.09 equiv) *with the following modifications*: a 1 M solution of sodium bis(trimethylsilyl)amide in THF (104.8 mL, 104.8 mmol, 1.18 equiv) was added to the flask via a syringe *slowly* dropwise in

place of a solution of LDA and (iodomethyl)dimethyl(phenyl)silane (24.507 g, 0.0888 mol, 1 equiv) was used in place of (iodomethyl)trimethylsilane. The product was further purified by vacuum distillation (b.p. 82-90 ^{o}C @ 0.10 mmHg) to give a clear, colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.33 (s, 6 H) 0.93 (dd, *J* = 14.79, 11.09 Hz, 1 H) 1.32 (dd, *J* = 14.79, 4.67 Hz, 1 H) 1.48 (s, 1 H) 2.13 (qd, *J* = 10.40, 4.77 Hz, 1 H) 2.81 - 2.92 (m, 1 H) 2.96 - 3.07 (m, 1 H) 3.18 - 3.29 (m, 1 H) 7.34 - 7.39 (m, 3 H) 7.49 - 7.53 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -2.36 (CH_3) -2.34 (CH_3) 16.57 (CH_2) 19.87 (CH_2 44.86 (CH_2) 56.36 (CH) 128.10 (CH) 129.37 (CH) 133.76 (CH) 138.68 (C) 212.91 (C) **GC-MS** (EI) 203 ([M-CH_3]$^{+}$, 1%), 142 (6%), 135 (100%), 105 (8%), 75 (6%), 43 (5%) **HRMS** (DART) calcd for $C_{13}H_{18}OSi$ [M + NH_4]$^{+}$: 236.1470, found: 236.1494.

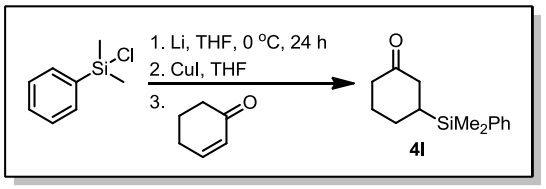
Route B Sequence to Prepare γ-Silyl Ketones



3-(trimethylsilyl)cyclopentanone (4k)[20] (1.463 g, 44%). The following procedure is a modification of the protocol outlined by White.[20] To a 3-neck, 500 mL round bottom flask equipped with two septa and a nitrogen gas inlet adapter was added hexamethyldisilane (7.32 g, 0.050 mol, 1.5 equiv) and HMPA (40 mL). The solution was cooled to -60 ^{o}C using a liquid nitrogen/acetone bath. Methyllithium (1.6 M, 25 mL, 0.040 mol, 1.2 equiv) and dry THF (100 mL, 0.33 M) were then added *via* syringe to the frozen mixture, turning the solution dark red-orange in color. Next, cyclopent-2-enone (2.71 g, 0.033, 1 equiv) in 10 mL of dry THF was added dropwise to the chilled solution. The solution was then stirred for 10 minutes and quenched with deionized water (15 mL), then warmed to -28 ^{o}C where upon it turned a translucent yellow. The solution was allowed to stir for 30 minutes and a sample with the reaction progress monitored by GC/MS. Once complete, the reaction mixture was diluted with pentane (150 mL) and transferred to a separatory funnel. The organic layer was washed with deionized water (2 x 150 mL) and brine (1 x 150 mL). The organic layer was dried with Na_2SO_4 and the solvent was *in vacuo* by rotary evaporation and trace solvent removed by placing the resulting material under a high vacuum (3 mmHg) and placing in a 50 ^{o}C water bath yielding the desired product.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm -0.03 (s, 9 H) 1.20 - 1.34 (m, 1 H) 1.52 - 1.68 (m, 1 H) 1.80 (dd, *J* = 18.25, 13.09 Hz, 1 H) 1.98 - 2.13 (m, 2 H) 2.15 - 2.26 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -3.24 (CH_3) 24.42 (CH) 25.01 (CH_2) 39.63 (CH_2) 40.13 (CH_2) 221.43 (C) **GC-MS** (EI) 155 ([M]$^{+}$:, 24%), 141 (10%), 99 (12%), 75 (41%), 73 (100%), 59 (15%), 45 (17%), 43 (16%) **HRMS** (DART) calcd for $C_8H_{17}OSi$ [M]$^{+}$: 157.1049, found: 157.1043.

[20] Chow, L.; McClure, M.; White, J. *Org.and Biomol. Chem.*, **2004**, *2*, 648.



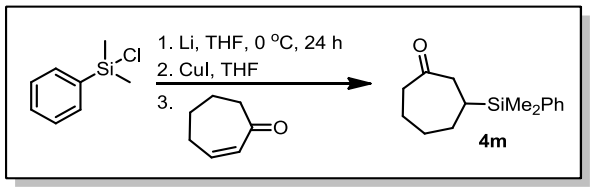
3-(dimethyl(phenyl)silyl)cyclohexanone (4l)[21] (9.52 g, 55%). To a 250 mL three-neck round bottom flask equipped with stirbar, gas inlet, septum, and a glass stopper. The flask was transferred to a glovebox. In the glovebox, lithium ribbon (2.599 g, 0.375 mol, 2.5 equiv.) was cut into small pieces and added piecewise to the flask. The flask was then charged with dry THF (150 mL). The flask was sealed with the septum and removed from the glove box. The gas inlet was connected to argon and the contents of the flask were placed *under an argon atmosphere*[22]. The reaction flask was cooled 0°C in an ice bath and chlorodimethyl(phenyl)silane (25.6 g, 0.15 mol, 1 equiv.) was added dropwise to the flask. Ice was replenished as needed to keep the solution temperature around 0 °C while stirring overnight, generating dimethyl(phenyl)silyl lithium.

To a 500 mL one-neck round bottom flask equipped with a stirbar and septum was added copper iodide (4.202 g, 75 mmol, 0.5 equiv.) and dry THF (150 mL, 0.5 M in copper iodide). The flask was equipped with a septum and cooled in a MeOH/ liquid N_2 bath. The solution of dimethyl(phenyl)silyl lithium was transferred into the copper iodide solution *via* cannulation. Once all of the dimethyl(phenyl)silyl lithium was transferred the solution was allowed to stir at -40 °C for 30 minutes. At this time, 2-cyclohexen-1-one (7.21 g, 75 mmol, 0.5 equiv) was added dropwise to the flask and was stirred for 1 h at -40 °C. After this time, ≈ 40 mL of a saturated NH_4Cl/10% NH_4OH solution was added syringe-wise to the flask. After complete addition, the flask was removed from the methanol bath and an additional 10 mL of the saturated NH_4Cl/10% NH_4OH solution was added. The mixture was allowed to quench at room temperature overnight. The quenched mixture was then transferred to a seperatory funnel and diluted with another 150 mL of the saturated NH_4Cl/10% NH_4OH solution and 300 mL of pentane. The layers were separated and the aqueous phase was extracted with pentane (2 X 200 mL). The combine organic layers were washed with saturated NH_4Cl/10% NH_4OH solution (2 X 150 mL) followed by brine (2 X 250 mL). The organic layer was dried with Na_2SO_4 and the solvent was *in vacuo* by rotary evaporation yielding the crude product. Purification was accomplished by flash column chromatography (4:1 Hex:EtOAc). The solvent was removed *in vacuo via* rotary evaporation and the residue further purified *via* factional distillation (94-96 °C @ 0.2 mmHg) to yield the pure silyl ketone.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.32 (s, 6 H) 1.30 (tt, *J* = 13.40, 3.10 Hz, 1 H) 1.43 (qd, *J* = 12.90, 3.45 Hz, 1 H) 1.69 (qt, *J* = 12.80, 4.20 Hz, 1 H) 1.82 (d, *J* = 13.44 Hz, 1 H) 2.09 - 2.17 (m, 2 H) 2.20 - 2.39 (m, 3 H) 7.34 - 7.38 (m, 3 H) 7.46 - 7.51 (m, 2 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ ppm -5.27 (CH_3) -5.15 (CH_3) 26.17 (CH) 27.72 (CH_2) 29.87 (CH_2) 41.97 (CH_2) 42.49 (CH_2) 128.00 (CH) 129.40 (CH) 134.03 (CH) 136.71 (C) 212.51 (C) **GC-MS** (EI) 232 ($[M]^+$,

[21] Calderone, J. A.; Santos, W. L. *Org. Lett.*, **2012**, *14*, 2090.
[22] Lithium ribbon reacts with N_2 gas therefore an argon atmosphere must be used.

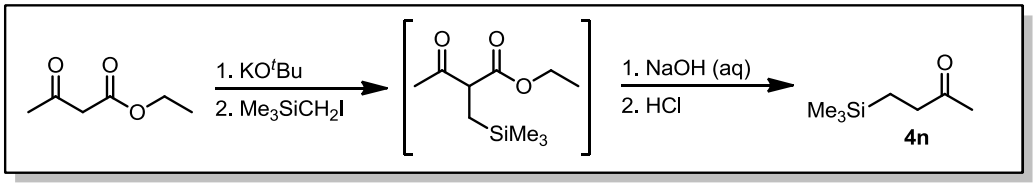
3%), 156 (19%), 137 (28%), 135 (100%), 105 (12%), 75 (17%) **HRMS** (DART) calcd for $C_{14}H_{20}OSi$ $[M + NH_4]^+$: 250.1627, found: 250.1630.



3-(dimethyl(phenyl)silyl)cycloheptanone (4m)[23](1.265 g, 34.3% yield) was prepared using a similar procedure from phenyldimethylsilyl chloride (5.12mL, 0.030mol, 2 equiv), small chunks (1mm x 3mm) of lithium metal (0.833g, 0.120mol, 4 equiv), copper iodide (2.86g, 0.015mol, 1 equiv), and technical grade cycloheptenone (3.36 g, 3.40mL, 0.0244mol, 1.63 equiv) with the following modifications: 1) Generation of phenyldimethylsilyllithium was performed over 24 h at room temperature in the glove box 2) The phenyldimethylsilyllithium was pipetted away from the residual lithium metal into a new 100 mL three-neck flask 3) The cuprate was generated by addition of copper iodide powder *to the phenyl dimethylsilyllithium solution* 4) The cuprate was generated over one hour 5) Further purification was accomplished by flash column chromatography (8:2 Hex:EtOAc) to give the ketone as a clear, colorless oil.[24]

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.30 (d, *J* = 1.75 Hz, 6 H) 1.04 - 1.14 (m, 1 H) 1.14 - 1.23 (m, 1 H) 1.24 - 1.36 (m, 1 H) 1.43 - 1.57 (m, 1 H) 1.83 - 2.05 (m, 3 H) 2.29 - 2.39 (m, 1 H) 2.40 - 2.50 (m, 2 H) 2.51 - 2.62 (m, 1 H) 7.33 - 7.40 (m, 3 H) 7.45 - 7.52 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -4.95 (CH_3) -4.69 (CH_3) 23.55 (CH) 24.62 (CH_2) 31.40 (s, 6 C) 32.12 (CH_2) 43.69 (CH_2) 44.77 (CH_2) 128.12 (CH) 129.47 (CH) 134.17 (CH) 137.29 (C) 215.53 (C) **GC-MS** (EI) 246 ($[M]^+$, 3%), 231 (6%), 170 (8%), 155 (7%), 137 (27%), 135 (100%), 105 (13%), 75 (15%) **HRMS** (DART) calcd for $C_{15}H_{22}OSi$ $[M + NH_4]^+$: 264.1784, found: 264.1766.

Route C Sequence to Prepare γ-Silyl Ketones



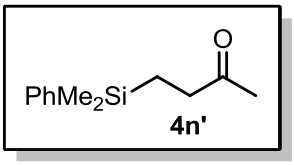
4-(trimethylsilyl)butan-2-one (4n)[25] (9.151 g, 37%). The following is a modification of the procedure outlined by Sommer and Marans.[26] To a 3-neck 250 mL round bottom flask equipped

[23] Lee, K.-s.; Hoveyda, A. H. *J. Am. Chem. Soc.*, **2010** , *132*, 2898.
[24] Note that any impure fractions were subjected to additional purification by flash column chromatography (90:10 Hex:EtOAc) to maximize yield.
[25] Mello, R.; Martínez-Ferrer, J.; Alcalde-Aragonés, A.; Varea, T.; Acerete, R.; Gonzalez-Núñez, M. E.; Asensio, G. *J. Org. Chem*., 2011, 76, 10129.

with stirbar, stopper, septum, and a solid addition funnel with a nitrogen gas inlet, was added *t*-butyl alcohol (95 mL), ethyl acetoacetate (15.195 g, 0.117 mol, 1.0 equiv). Potassium *t*-butoxide (19.90 g, 0.178 mol, 1 equiv) was weighed out in a glovebox and transferred to the solid addition and slowly added to the reaction mixture. After this, iodomethyltrimethylsilane (25.03 g, 0.117 moles 1.0 equiv) was added to the flask. Once added, the addition funnel was replaced with a reflux condenser and the solution heated to reflux for 72 hours. After this time, the reaction mixture was cooled to room temperature diluted with 100 mL of pentane, precipitating out KI that had formed. This slurry was filtered through a pad of Celite® and the solvent removed *via* rotary evaporation to afford the β-keto ester (21.803 g, 77%) as a clear, colorless liquid and was used in the next step without further purification.

To a 250 mL round bottom flask equipped with stirbar was added a 10% (w/w) NaOH solution made from dissolving 10.332 g of NaOH pellets in 93 mL of deionized water. Once completely dissolved, ethyl 3-oxo-2-((trimethylsilyl)methyl)butanoate (21.803 g, 0.1675 mol) was added to the reaction flask. The solution was equipped with a reflux condenser and heated to 90 ^{o}C and left to stir for 72 hours. At this time, the reaction mixture was allowed to cool to room temperature and the solution was acidified using 1 M HCl (340 mL) to a pH of 1. This solution was transferred to a separatory funnel and extracted with Et_2O[27] (4 x 75 mL). The combined organic layers were dried over sodium sulfate and the solvent removed *via* rotary evaporation. The crude product was further purified by vacuum distillation (b.p. 100-104 ^{o}C @ 65 mmHg) to afford the pure ketone as a clear, colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm -0.04 (s, 9 H) 0.71 (apparent triplet, *J* = 8.50 Hz, 2 H) 2.10 (s, 3 H) 2.34 (apparent triplet t, *J* = 8.40 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.69 (CH_3) 10.57 (CH_2) 29.28 (CH_3) 38.46 (CH_2) 210.08 (C) **GC-MS** (EI) 144 ([M]$^{+}$, 14%), 130 (79%), 75 (100%), 73 (80%), 45 (13%), 43 (21%).



4-(dimethyl(phenyl)silyl)butan-2-one (4n′)[28] (15.0 g, 69%), was prepared according to the representative alkylation/decarboxylation procedure from ethyl acetoacetate (18.58 g, 0.143 mol, 1.35 equiv) and potassium *t*-butoxide (15.34 g, 0.137 mol, 1.29 equiv) with the following modification: (iodomethyl)dimethylphenylsilane (29.2 g, 0.106 mol, 1 equiv) was used in place of iodomethyltrimethylsilane. The product was further purified by vacuum distillation (b.p. 75-78 ^{o}C @ 0.1 mmHg) to give # as a clear, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.31 (s, 6 H) 1.03 (t, *J* = 8.40 Hz, 11 H) 2.09 (s, 16 H) 2.39 (t, *J* = 8.60 Hz, 11 H) 7.34 - 7.40 (m, 17 H) 7.48 - 7.55 (m, 11 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -3.05 (CH_3) 9.47 (CH_2) 29.30 (CH_3) 38.26 (CH_2) 128.01 (CH) 129.22 (CH) 133.69 (CH) 138.44 (C) 209.57 (C) **GC-MS** (EI) 191 ([M − CH_3]$^{+}$, 66%), 137 (44%), 135 (100%), 129 (39%), 113 (37%), 105 (43%), 75 (17%), 43 (48%).

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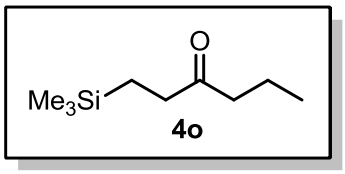
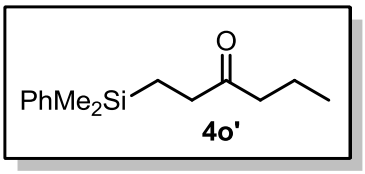
[26] Sommer, L.H.; Marans, N. S. *J. Am. Chem. Soc.* **1950**, *72*, 1935.
[27] Pentane can be used in place of Et_2O.
[28] Fleming, I.; Lee, D. *J. Chem. Soc., Perk. Trans. I* **1998**, 270.



1-(trimethylsilyl)hexan-3-one (4o)[20] (6.998 g, 77%), was prepared according to the representative alkylation/decarboxylation procedure from ethyl acetoacetate (10.70 g, 0.068 mol, 1.0 equiv), iodomethyltrimethylsilane (14.35 g, 0.068 mol, 1 equiv), potassium *t*-butoxide (7.615 g, 0.117 mol, 1.0 equiv). The product was further purified by vacuum distillation (b.p. 75-78 ^{o}C @ 0.1 mmHg) to give **4o** as a clear, colorless liquid.

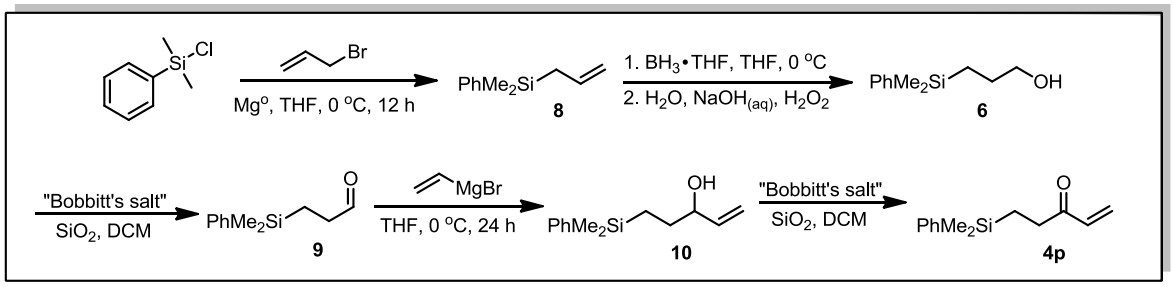
^{1}H NMR (500 MHz, CDCl3) d ppm -0.04 (s, 9 H) 0.71 (t, *J* = 8.50 Hz, 2 H) 0.88 (t, *J* = 7.39 Hz, 3 H) 1.57 (sxt, *J* = 7.50 Hz, 2 H) 2.31 (t, *J* = 8.40 Hz, 2 H) 2.36 (t, *J* = 7.33 Hz, 2 H) **^{13}C NMR** (125 MHz, CDCl3) d ppm -1.65 (CH_3) 10.50 (CH_3) 14.02 (CH_2) 17.68 (CH_2) 37.51 (CH_2) 44.20 (CH_2) 212.33 (C) **GC-MS** (EI) 172 ($[M]^+$, 1%) 157 ($[M\text{-}CH3]^+$, 29%) 144 (15%) 129 (13%) 75 (59%) 74 (9%) 73 (100%) 59 (7%) 43 (19%) 27 (7%) **HRMS** (DART) calcd for $C_9H_{21}OSi$ $[M]^+$:: 173.1362, found: 173.1386. **FTIR** (cm-1, salt plates) 841.08 (vs) 1171.89 (m) 1249.73 (s) 1353.51 (m) 1411.89 (m) 1457.30 (w) 1716.76 (s) 2897 (m) 2949.19 (s).



1-(dimethyl(phenyl)silyl)hexan-3-one (4o′) (15.94 g, 70%), was prepared according to the representative alkylation/decarboxylation procedure from ethyl acetoacetate (18.58 g, 0.143 mol, 1.35 equiv) and potassium *t*-butoxide (15.34 g, 0.137 mol, 1.29 equiv) with the following modification: (iodomethyl)dimethylphenylsilane (29.2 g, 0.106 mol, 1 equiv) was used in place of iodomethyltrimethylsilane. The product was further purified by vacuum distillation (b.p. 97-100 ^{o}C @ 0.1 mmHg) to give **4o′** as a clear, colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.30 (s, 6 H) 0.90 (t, *J* = 7.40 Hz, 3 H) 1.03 (t, *J* = 8.40 Hz, 2 H) 1.58 (sxt, *J* = 7.40 Hz, 2 H) 2.35 (q, *J* = 7.60 Hz, 4 H) 7.34 - 7.40 (m, 3 H) 7.49 - 7.54 (m, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -2.97 (CH_3) 9.43 (CH_3) 13.96 (CH_2) 17.58 (CH_2) 37.35 (CH_2) 44.22 (CH_2) 128.04 (CH) 129.24 (CH) 133.75 (CH) 138.60 (C) 211.79 (C) **GC-MS** (EI) 219 ($[M]^+$, 65%), 157 (36%), 141 (19%), 137 (34%), 135 (100%), 120 (15%), 105 (34%), 75 (15%), 43 (28%) **HRMS** (DART) calcd for $C_{14}H_{22}SiO$ $[M + NH_4]^+$: 252.1784, found: 252.1760.

Route D Sequence to Prepare γ-Silyl Ketones



Allyldimethyl(phenyl)silane (8)[29]

To a 500 mL round bottom flask was added freshly ground magnesium turnings and a stir bar. The flask was equipped with a septum, flame dried, and backfilled with nitrogen. Dry THF (146 mL, 1 M) was added to the flask and cooled in an ice bath to 0 °C. After 10 minutes, chlorodimethyl(phenyl)silane (25.0 g, 0.146 mol, 1 equiv) was added to the flask and allowed to stir for 10 minutes. At this time, allyl bromide was slowly added and the reaction allowed to warm to room temperature for 12 hours. The reaction was then quenched with deionized water (200 mL) and left to stir for 15 minutes. The reaction mixture was transferred to a separatory funnel and extracted with pentane (3 x 100 mL). The combined organic layers were then washed with water (2 x 100 mL) and brine (100mL). The combined organic layers were dried over sodium sulfate and the solvent removed *via* rotary evaporation to give the pure product (24.49 g, 95%) as a clear, colorless liquid which was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.32 (s, 6 H) 1.80 (d, *J* = 8.03 Hz, 2 H) 4.82 - 4.96 (m, 2 H) 5.82 (sxt, *J* = 8.50 Hz, 1 H) 7.34 - 7.43 (m, 3 H) 7.50 - 7.59 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -3.21 (CH_3) 23.96 (CH_2) 113.67 (CH_2) 128.02 (CH) 129.28 (CH) 133.90 (CH) 134.90 (CH) 138.95 (C) **GC-MS** (EI) 176 ($[M]^+$, 1%), 136 (13%), 135 (100%), 121 (6%), 106 (8%).

3-(dimethyl(phenyl)silyl)propan-1-ol (6)[30]

To a 500 mL round bottom flask equipped with a stir bar and septum was added dry THF (66 mL, 1.7 M), and BH_3 (1 M in THF, 50 mL, 0.05 mol, 0.44 equiv) under nitrogen. The solution was then cooled to 0 °C using an ice bath for 10 minutes. At this time, **8** (19.93 g, 0.113 mol, 1 equiv) was added to the flask dropwise. The reaction was allowed to stir at 0 °C for 1.5 hours. After this time, deionized water (16.6 mL), 3 M aqueous NaOH (16.6 mL), and H_2O_2 (16.6 mL) were added dropwise to the reaction flask respectively while cooled to 0 °C. The reaction was allowed to stir for 1 hour at room temperature afterwards. Once complete, the reaction mixture was transferred to a separatory funnel and diluted with ether (100 mL) and washed with brine (2

[29] Ichimaru, N.; Yoshinaga, N.; Nishioka, T.; Miyoshi, H. *Tetrahedron*, **2007**, *63*, 1127.
[30] Soderquist, J. A.; Hassner, A. *J. Org. Chem.*, **1983**, *48*, 1801 .

x 100 mL). The organic layer was dried over sodium sulfate and the solvent removed *via* rotary evaporation to give the pure alcohol (21.65 g, 99%) as a clear, colorless liquid which was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.30 (s, 6 H) 0.71 - 0.81 (m, 2 H) 1.52 - 1.64 (m, 2 H) 3.58 (s, 1 H) 7.33 - 7.40 (m, 3 H) 7.47 - 7.57 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -2.88 (CH_3) 11.66 (CH_2) 27.38 (CH_2) 65.88 (CH_2) 128.04 (CH) 129.17 (CH) 133.79 (CH) 139.31 (C) **GC-MS** (EI) 179 ($[M - CH_3]^+$, 12%), 137 (100%), 135 (62%), 117(11%), 105 (16%), 75 (13%).

3-(dimethyl(phenyl)silyl)propanal (9)[31]

This synthesis was performed according to modified procedure of Bobbitt.[32] To a 2000 mL round bottom flask equipped with a stir bar was added 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium tetrafluoroborate, "Bobbitt's Salt" (31.51 g, 0.105 mol, 1.05 equiv), silica gel (20 g, 1 mass equiv to substrate) and DCM (1000 mL, 0.1 M), and **6** (19.44 g, 0.10 mol, 1 equiv). The flask was sealed with a stopper and the reaction mixture was allowed to react overnight and monitored by GC/MS. Upon complete oxidation, the reaction mixture was filtered through a pad of Celite® and the precipitate washed several times with DCM. The solvent was removed *via* rotary evaporation to give the crude aldehyde. Further purification was accomplished by running the product through a plug of silica. This was done by adding 3-4 weight equivalents of silica (again relative to the theoretical yield) to a 150 mL coarse-porosity fritted glass funnel. An appropriately sized piece of filter paper relative to the size of the funnel was used to the top of the dry silica gel layer and this layer was pre-wet with hexanes. The crude material was added gently on the silica and a piece of filter paper placed on top. The desired aldehyde was eluted off the plug using a 95:5 by volume mixture of Hex:EtOAc. The solvent was removed *in vacuo* by rotary evaporation to afford the product as a clear colorless liquid (16.37 g, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.32 (s, 6 H) 1.03 (t, J = 8.20 Hz, 2 H) 2.39 (t, J = 8.20 Hz, 2 H) 7.35 - 7.42 (m, 3 H) 7.48 - 7.54 (m, 2 H) 9.73 (s, 1 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -3.03 (CH_2) 7.67 (CH_2) 38.62 (CH_2) 128.17 (CH) 129.46 (CH) 133.77 (CH) 138.19 (C) 202.99 (C) **GC-MS** (EI) 177 ($[M - CH_3]^+$, 57%), 159 (14%), 135 (100%), 121 (27%), 115 (37%), 105 (27%), 99 (40%).

5-(dimethyl(phenyl)silyl)pent-1-en-3-ol (10)

To a 250 mL round bottom flask equipped with a stir bar, septum with a thermometer, stopper and gas inlet under nitrogen, was added 0.7 M vinylmagnesium bromide in THF (73.4 mL, 0.0514 mol, 1.1 equiv) *via* syringe. The reaction mixture was cooled to 0 °C with an ice-water bath while stirring. After five minutes, **9** (8.984 g, 0.0467 mol, 1 equiv) was added dropwise *via* syringe. The ice water bath was removed and the reaction mixture was allowed to stir overnight,

[31] Smitrovich, J. H.; Woerpel, K. A. *J. Org. Chem.*, **2000** , 65, 1601.
[32] Bobbitt, J. M. *J. Org. Chem.* **1998**, *63*, 9367.

during which the reaction mixture turned to an orange color. The reaction progression was monitored by GC/MS. The reaction mixture was diluted with pentane (100 mL) and the reaction mixture cooled to 0 °C using an ice-water bath. After approximately five minutes, aqueous saturated K_2CO_3 solution (25 mL) was added dropwise *via* syringe. The reaction mixture was filtered through a pad of Celite® and the filtrate transferred to a separatory funnel. The organic layer was washed with deionized water (3 x 50 mL). The organic layer was dried over Na_2SO_4 and the solvent removed *via* rotary evaporation. The crude product was purified by vacuum distillation (b.p. 85-90 °C @ 0.10 mmHg) giving the pure product as a clear yellow liquid (6.15 g, 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.32 (s, 6 H) 0.71 - 0.81 (m, 1 H) 0.83 - 0.91 (m, 1 H) 1.57 (sxt, *J* = 6.20 Hz, 2 H) 1.91 (br. s., 1 H) 4.03 (q, *J* = 6.30 Hz, 1 H) 5.14 (d, *J* = 10.29 Hz, 1 H) 5.23 (d, *J* = 17.20 Hz, 1 H) 5.85 (ddd, *J* = 16.71, 10.17, 6.18 Hz, 1 H) 7.37 - 7.41 (m, 3 H) 7.52 - 7.57 (m, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -2.93 (CH_3) -2.92 (CH_3) 11.10 (CH_2) 31.41 (CH_2) 75.49 (CH) 115.16 (CH_2) 128.00 (CH) 129.13 (CH) 133.77 (CH) 139.23 (CH) 141.09 (C) **GC-MS** (EI) 205 ($[M - CH_3]^+$, 1%), 137 (39%), 135 (100%), 105 (16%), 75 (10%), 57 (8%), 43 (6%) **HRMS** (DART) calcd for $C_{13}H_{20}OSi$ $[M + NH_4]^+$: 238.1627, found: 238.1644.

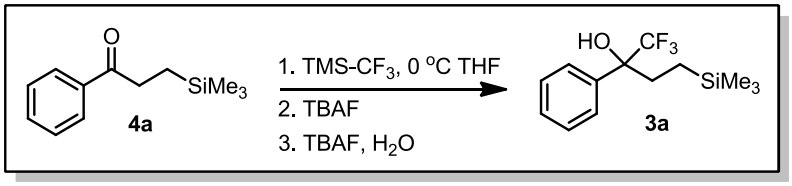
5-(dimethyl(phenyl)silyl)pent-1-en-3-one (4p)[33]

This synthesis was performed according to modified procedure of Bobbitt.[34] To a 250 mL round bottom flask equipped with a stir bar, gas inlet and septum was added 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium tetrafluoroborate, "Bobbitt's Salt" (8.664 g, 0.029 mol, 1.1 equiv), silica gel (8.664 g, 1 mass equiv to "Bobbitt's salt") and DCM (50 mL, 0.5 M). The flask was sealed with a stopper, placed under nitrogen. The **10** (5.807 g, 0.0263 mol, 1 equiv) was added *via* syringe while stirring. The reaction mixture was allowed to react overnight and monitored by GC/MS. Upon complete oxidation, the reaction mixture was filtered with a fritted funnel through DE filter aide and silica gel. The precipitate was washed several times with DCM. The DCM was removed by rotary evaporation. The crude product was purified by vacuum distillation (b.p. 74-80 °C @ 0.10 mmHg) and further purified by flash column chromatography (10:1 Hex:EtOAc). The solvent was removed *in vacuo via* rotary evaporation giving the pure product was a clear colorless liquid (4.138 g, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.32 (s, 6 H) 1.08 (t, *J* = 8.20 Hz, 2 H) 2.55 (t, *J* = 8.60 Hz, 2 H) 5.76 (dd, *J* = 10.51, 1.17 Hz, 1 H) 6.17 (d, *J* = 17.71 Hz, 1 H) 6.35 (dd, *J* = 17.71, 10.51 Hz, 1 H) 7.35 - 7.41 (m, 3 H) 7.50 - 7.56 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -2.92 (CH_3) 9.68 (CH_2) 34.57 (CH_2) 127.97 (CH_2) 128.12 (CH) 129.34 (CH) 133.80 (CH) 136.23 (CH) 138.58 (C) 201.53 (C) **GC-MS** (EI) 218 ($[M]^+$, 1%), 203 (70%), 175 (10%), 141 (51%), 137 (25%), 135 (100%), 125 (35%), 107 (14%), 105 (31%), 75 (13%), 55 (21%), 43 (12%) **HRMS** (DART) calcd for $C_{13}H_{18}OSi$ $[M + NH_4]^+$: 236.1471, found: 236.1468.

[33] Kim, S.; Fuchs, P. L. *J. Am. Chem. Soc.*, **1993**, *115*, 5934
[34] Bobbitt, J. M. *J. Org. Chem.* **1998**, *63*, 9367.

Representative Procedure for Preparation of 1-Trifluoromethyl-3-Trimethylsilyl Carbinols



1,1,1-Trifluoro-2-phenyl-4-(trimethylsilyl)butan-2-ol, 3a (6.88 g (79%). The following is a modification of the procedure outline by Kelly *et al*.[35] To a 100 mL round bottom flask equipped with a stirbar was added **4a** (2.06 g, 0.010 mol, 1 equiv) , THF (18 mL), and (trifluoromethyl)trimethylsilane (1.85g, 0.013 mol, 1.3 equiv). The flask was sealed with a rubber septa and placed under a N_2 atmosphere via an inlet needle. The reaction mixture was cooled to 0 ^oC in an ice-water bath and stirred via a magnetic stir plate. After approximately 10 minutes, TBAF (1 M in THF, 0.1 mL, 0.0001 mol, 0.01 equiv) was added dropwise *via* a syringe.[36] After 10 minutes, the ice-bath was removed and the solution was allowed to stir for approximately 6 hour at room temperature. To cleave the silyl ether formed by the reaction, the reaction mixture was cooled to 0 ^oC in an ice bath. After 10 minutes, H_2O (1 mL, 0.056 mol, 5.6 equiv) was added *via* a syringe. TBAF (1 M in THF, 1 mL, 0.001 mol, 0.1 equiv) was then added. After 10 minutes the ice bath was removed and the reaction mixture was allowed to stir at room temperature. When the cleavage was judged complete[37], the contents of the flask were transferred to a separatory funnel. Brine (≈100 mL) and Et_2O (≈150 mL) were added and the layers were partitioned. The aqueous layer was back-extracted (3X, ≈50 mL each) with Et_2O. The combined ether layers were dried with Na_2SO_4. The solvent was removed *in vacuo* and then purified *via* vacuum distillation (b.p. 85-88 ^oC @ 0.25 mmHg) giving the pure **3a** as a clear, light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.03 (s, 9 H) 0.17 (td, *J* = 13.90, 3.60 Hz, 1 H) 0.57 (td, *J* = 14.00, 4.10 Hz, 1 H) 2.05 (td, *J* = 13.80, 4.30 Hz, 1 H) 2.24 (td, *J* = 14.20, 3.80 Hz, 1 H) 2.62 (s, 1 H) 7.36 - 7.47 (m, 3 H) 7.58 (d, *J* = 7.40 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -1.78 (CH_3) 8.34 (CH_2) 29.73 (CH_2) 78.34 (q, $J_{C\text{-}C\text{-}F}$ = 27.00 Hz, C) 126.16 (q, $J_{C\text{-}F}$ = 287.00 Hz, CF_3) 126.32 (C) 126.82 (CH) 128.58 (CH) 136.79 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.42 **GC-MS** (EI) 156 (60%), 147 (23%), 127 (16%), 117 (24%), 105 (21%), 103 (10%), 101 (25%), 77 (23%), 75 (37%), 73 (100%), 69, (3%), 45 (10%) **HRMS** (DART) calcd for $C_{13}H_{19}F_3OSi$ [M − CF_3]$^+$: 207.1205, found: 207.1198.

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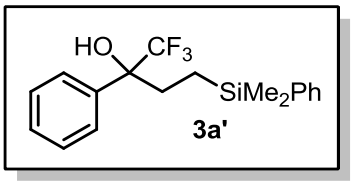
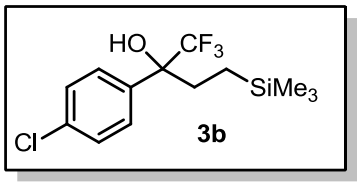
[35] Kelly, C. D.; Colthart, A. M.; Constant, B.D.; Corning, S.R.; Dubois, L. N.E.; Genovese, J. T.; Radziewicz, J. L.; Sletten, E. M.; Whitaker, K. R.; Tilley, L. J. *Org. Lett.* **2011**, *13*, 1646.

[36] Note that on small scales (< 15 mmol) the TBAF could be added relatively fast. However, upon scale-up the addition of TBAF is quite exothermic. Hence, it is recommended that the TBAF be added as slow as possible and/or cooling the reaction mixture to a temperature lower than that of 0 ^oC.

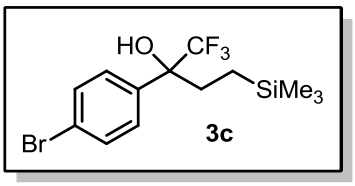
[37] It is recommended that this cleavage step be monitored by some form of spectroscopy (e.g. GC/MS or NMR). Some of the silyl ethers were very slow to cleave and required another addition of TBAF and H_2O.



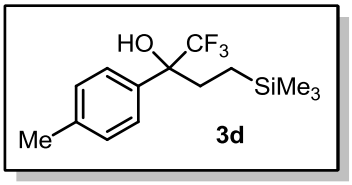
4-(dimethyl(phenyl)silyl)-1,1,1-trifluoro-2-phenylbutan-2-ol, 3a′ (14.47 g, 75%) was prepared according to the representative trifluoromethylation procedure from **4a′** (15.0 g, 0.056 mol) and further purified by vacuum distillation (b.p. 125-127 ^{o}C 0.10 @ mmHg) to give **3a′** as a viscous light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 0.27 (d, *J* = 5.25 Hz, 6 H) 0.37 (td, *J* = 13.87, 3.60 Hz, 1 H) 0.76 (td, *J* = 14.16, 4.38 Hz, 1 H) 1.98 (td, *J* = 13.96, 4.38 Hz, 1 H) 2.18 (td, *J* = 14.16, 3.60 Hz, 1 H) 2.25 (s, 1 H) 7.32 - 7.48 (m, 10 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -3.23 (CH_3) -2.95 (CH_3) 7.65 (CH_2) 29.58 (CH_2) 78.31 (q, $J_{C\text{-}C\text{-}F}$ = 28.00 Hz, C) 126.02 (q, $J_{C\text{-}F}$ = 286.00 Hz, CF_3) 126.80 (CH) 128.18 (CH) 128.59 (CH) 128.63 (CH) 129.47 (CH) 133.79 (CH) 136.49 (C) 138.31 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.65 **GC-MS** (EI) 191 (8%), 167 (51%), 156 (24%), 147 (14%), 137 (53%), 135 (100%), 117 (14%), 105 (25%), 91 (10%), 77 (12%) **HRMS** (DART) calcd for $C_{18}H_{21}F_3OSi$ $[M + NH_4]^+$: 356.1658, found: 356.1684.



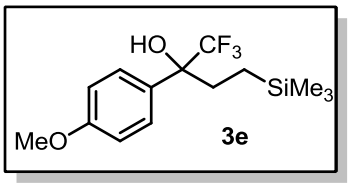
2-(4-chlorophenyl)-1,1,1-trifluoro-4-(trimethylsilyl)butan-2-ol, 3b (17.00 g, 91%) was prepared according to the representative trifluoromethylation procedure from **4b** (14.45 g, 0.06 mol) and further purified by vacuum distillation (b.p. 94-96 ^{o}C 0.25 @ mmHg) to give **3b** as a viscous light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 0.00 (s, 9 H) 0.12 (td, *J* = 13.90, 4.00 Hz, 1 H) 0.52 (td, *J* = 14.20, 4.48 Hz, 1 H) 2.00 (td, *J* = 14.30, 4.36 Hz, 1 H) 2.17 (td, *J* = 14.70, 4.10 Hz, 1 H) 2.47 (s, 1 H) 7.39 (d, *J* = 8.48 Hz, 2 H) 7.48 (d, *J* = 8.72 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.79 (CH_3) 8.34 (CH_2) 29.85 (CH_2) 78.15 (q, $J_{C\text{-}C\text{-}F}$ = 28.00 Hz, C) 125.93 (q, $J_{C\text{-}F}$ = 286.50 Hz, CF_3) 128.37 (CH) 128.81 (CH) 134.74 (C) 135.35 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.73 **GC-MS** (EI) 192 ($[M\text{-}SiMe_3CH_2Cl]^+$, ^{37}Cl 12%), 190 ($[M\text{-}SiMe_3CH_2Cl]^+$, ^{35}Cl 37%), 146 (11%), 141 (13%), 139 (40%), 115 (15%), 111 (18%), 101 (18%), 77 (24%), 75 (24%), 73 (100%), 45 (17%) **HRMS** (DART) calcd for $C_{13}H_{18}ClF_3OSi$ $[M - CF_3]^+$: 241.0815, found: 241.0810.



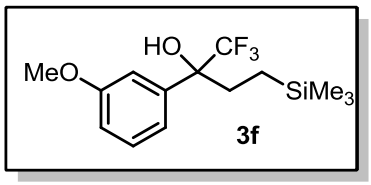
1,1,1-Trifluoro-2-(4-bromophenyl)-4-(trimethylsilyl)butan-2-ol, 3c (10.69 g, 86%) was prepared according to the representative trifluoromethylation procedure from **4c** (10.0 g, 0.035 mol) and further purified by vacuum distillation (b.p. 125-130 ^{o}C @ 0.10 mmHg) to give **3c** as a viscous yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm -0.01 (s, 7 H) 0.09 (td, *J* = 14.00, 3.80 Hz, 2 H) 0.49 (td, *J* = 14.00, 4.30 Hz, 1 H) 1.96 (td, *J* = 14.00, 4.30 Hz, 1 H) 2.13 (td, *J* = 14.20, 3.70 Hz, 1 H) 2.37 (s, 1 H) 7.40 (d, *J* = 8.56 Hz, 2 H) 7.54 (d, *J* = 8.60 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -1.74 (CH_3) 8.33 (CH_2) 29.79 (CH_2) 78.15 (q, $J_{C\text{-}C\text{-}F}$ = 28.00 Hz, C) 122.99 (C) 125.81 (q, $J_{C\text{-}F}$ = 287.00 Hz, CF_3) 128.67 (CH) 131.78 (CH) 135.82 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.71 **GC-MS** (EI) 355 ($[M]^+$, 0.1%), 328 (5%), 236 (17%), 234 (18%), 185 (13%), 183 (11%), 166 (11%), 146 (7%), 116 (10%), 101 (24%), 75 (37%), 73 (100%), 45(8%) **HRMS** (DART) calcd for $C_{13}H_{18}BrF_3OSi$ $[M - CF_3]^+$: 285.0310 found: 285.0315.



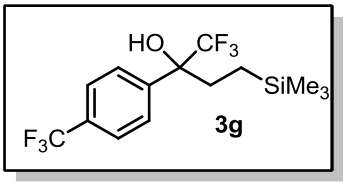
1,1,1-Trifluoro-2-(p-tolyl)-4-(trimethylsilyl)butan-2-ol, 3d (8.745 g, 75%) was prepared according to the representative trifluoromethylation procedure from **4d** (8.85 g, 0.040 mol) and further purified by vacuum distillation (b.p. 80-85 ^{o}C @ 0.10 mmHg) to give **3d** as a viscous light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.00 (s, 9 H) 0.16 (td, *J* = 13.80, 3.90 Hz, 1 H) 0.51 (td, *J* = 14.00, 4.30 Hz, 1 H) 1.99 (td, *J* = 14.00, 4.50 Hz, 1 H) 2.18 (td, *J* = 14.00, 3.70 Hz, 1 H) 2.38 (s, 3 H) 7.23 (d, *J* = 8.17 Hz, 2 H) 7.41 (d, *J* = 7.98 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -1.71 (CH_3) 8.38 (CH_2) 21.32 (CH_3) 29.62 (CH_2) 78.26 (q, $J_{C\text{-}C\text{-}F}$ = 27.00 Hz, C) 126.16 (q, $J_{C\text{-}F}$ = 287.00 Hz, CF_3) 126.70 (CH) 129.35 (CH) 133.73 (C) 138.41 (C) ^{19}F NMR (377 MHz, $CDCl_3$) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.80 **GC-MS** (EI) 290 ($[M]^+$, 0.1%), 275 (1%), 262 (11%). 200 (6%), 181 (8%), 170 (94%), 161 (18%), 146 (10%), 131 (16%), 119 (26%), 101 (20%), 91 (26%), 77 (12%), 75 (29%), 73 (100%), 45(9%) **HRMS** (DART) calcd for $C_{14}H_{21}F_3OSi$ $[M - CF_3]^+$: 221.1362, found: 221.1369.



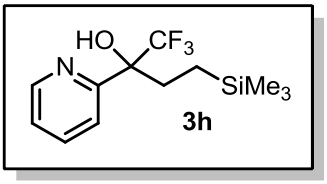
1,1,1-Trifluoro-2-(4-methoxyphenyl)-4-(trimethylsilyl)butan-2-ol, 3e (10.271 g, 84%) was prepared according to the representative trifluoromethylation procedure from **4e** (9.45 g, 0.040 mol) and further purified by vacuum distillation (b.p. 110-115 ^{o}C @ 0.10 mmHg) to give **3e** as a viscous yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.01 (s, 7 H) 0.17 (td, *J* = 13.80, 3.70 Hz, 1 H) 0.52 (td, *J* = 14.00, 4.30 Hz, 1 H) 1.99 (td, *J* = 14.00, 4.30 Hz, 1 H) 2.18 (td, *J* = 14.00, 3.50 Hz, 1 H) 2.53 (br. s., 1 H) 3.83 (s, 3 H) 6.95 (d, *J* = 8.80 Hz, 2 H) 7.46 (d, *J* = 8.76 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -1.76 (CH_3) 8.34 (CH_2) 29.57 (CH_2) 55.45 (CH_3) 78.07 (q, $J_{C\text{-}C\text{-}F}$ = 27.00 Hz, C) 113.95 (CH) 126.21 (d, $J_{C\text{-}F}$ = 287.00 Hz, CF_3) 128.15 (CH) 128.74 (C) 159.73 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.81 **GC-MS** (EI) 306 ($[M]^+$, 6%), 263 (19%), 205 (10%), 186 (65%), 135 (25%), 108 (14%), 101 (14%), 77 (15%), 75 (24%), 73 (100%), 45 (8%) **HRMS** (DART) calcd for $C_{14}H_{21}F_3O_2Si$ $[M - CF_3]^+$: 237.1311, found: 237.1323.



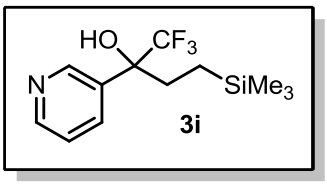
1,1,1-Trifluoro-2-(3-methoxyphenyl)-4-(trimethylsilyl)butan-2-ol, 3f (11.55 g, 84%) was prepared according to the representative trifluoromethylation procedure from **4f** (10.63 g, 0.045 mol) and further purified by vacuum distillation (b.p. 98-100 ^{o}C @ 0.10 mmHg) to give **3f** as a viscous yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm -0.01 (s, 9 H) 0.15 (td, *J* = 14.00, 4.50 Hz, 1 H) 0.52 (br. td, *J* = 13.80, 13.80, 4.40 Hz, 1 H) 1.98 (td, *J* = 14.00, 4.50 Hz, 1 H) 2.16 (td, *J* = 14.00, 3.70 Hz, 1 H) 2.49 (br. s., 1 H) 3.83 (s, 3 H) 6.91 (dd, *J* = 8.08, 2.43 Hz, 1 H) 7.04 - 7.15 (m, 2 H) 7.32 (t, *J* = 7.98 Hz, 1 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -1.74 (CH_3) 8.33 (CH_2) 29.85 (CH_2) 55.50 (CH_3) 78.28 (q, $J_{C\text{-}C\text{-}F}$ = 27.00 Hz, C) 113.03 (CH) 113.81 (CH) 119.03 (CH) 126.06 (q, $J_{C\text{-}F}$ = 287.00 Hz, CF_3) 129.58 (CH) 138.46 (C) 159.87 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.38 **GC-MS** (EI) 306 ($[M]^+$, 10%), 278 (19%), 186 (46%), 177 (10%), 135 (14%), 108 (28%), 101 (13%), 77 (16%), 75 (28%), 73 (100%), 69 (1%), 45(8%) **HRMS** (DART) calcd for $C_{14}H_{22}F_3O_2Si$ $[M]^+$: 307.1341, found: 307.1362.



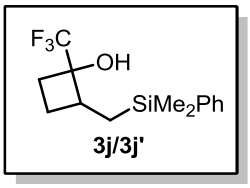
1,1,1-Trifluoro-2-(4-(trifluoromethyl)phenyl)-4-(trimethylsilyl)butan-2-ol, 3g (11.08 g, 80%) was prepared according to the representative trifluoromethylation procedure from **4g** (11.03 g, 0.040 mol) and further purified by vacuum distillation (b.p. 88-90 ^{o}C @ 0.25 mmHg) to give **3g** as a viscous light yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm -0.01 (s, 9 H) 0.06 (td, *J* = 14.20, 3.80 Hz, 1 H) 0.51 (td, *J* = 14.30, 4.40 Hz, 1 H) 2.01 (td, *J* = 14.30, 4.40 Hz, 1 H) 2.19 (td, *J* = 14.20, 4.40 Hz, 1 H) 2.39 (s, 6 H) 7.66 (s, 4 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.75 (CH_3) 8.37 (CH_2) 30.06 (CH_2) 78.27 (q, $J_{C\text{-}C\text{-}F}$ = 27.00 Hz, C) 124.30 (q, $J_{C\text{-}F}$ = 273.00 Hz, CF_3) 125.81 (q, $J_{C\text{-}F}$ = 285.00 Hz, CF_3) 125.58 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.00 Hz, CH) 127.38 (CH) 130.93 (q, $J_{C\text{-}C\text{-}F}$ = 33.00 Hz, C) 140.77 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.50 (s, 3 F) -65.87 (s, 3 F) **GC-MS** (EI) 327 ($[M\text{-}OH]^+$, 1%), 273 (12%), 259 (50%), 205 (47%), 185 (32%), 173 (11%), 165 (22%), 145 (25%), 75 (22%), 73 (100%), 69 (2%), 45 (13%) **HRMS** (DART) calcd for $C_{13}H_{18}F_3OSi$ $[M - CF_3]^+$: 275.1079, found: 275.1096.



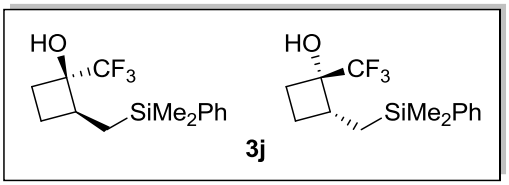
1,1,1-Trifluoro-2-(pyridin-2-yl)-4-(trimethylsilyl)butan-2-ol, 3h (7.90 g, 84%) was prepared according to the representative trifluoromethylation procedure from **4h** (7.01 g, 0.0338 mol) and further purified by vacuum distillation (b.p. 78-81 ^{o}C @ 0.15 mmHg) to give **3h** as a viscous light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm -0.24 (td, *J* = 13.80, 4.40 Hz, 1 H) -0.05 (s, 9 H) 0.60 (td, *J* = 13.80, 4.40 Hz, 1 H) 2.03 (td, *J* = 13.80, 4.40 Hz, 1 H) 2.13 (td, *J* = 13.80, 4.40 Hz, 1 H) 7.35 (dd, *J* = 7.60, 4.80 Hz, 1 H) 7.45 (d, *J* = 7.80 Hz, 1 H) 7.80 (td, *J* = 7.80, 1.90 Hz, 1 H) 8.59 (d, *J* = 4.60 Hz, 1 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.73 (CH_3) 8.27 (CH_2) 28.29 (CH_2) 77.37 (q, $J_{C\text{-}C\text{-}F}$ = 27.50 Hz, C) 121.46 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.83 Hz, CH) 125.92 (q, $J_{C\text{-}F}$ = 287.00 Hz, CF_3) 123.98 (CH) 137.80 (CH) 147.73 (CH) 154.36 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.48 **GC-MS** (EI) 277 ($[M]^+$, 1%), 262 (38%), 249 (38%), 233 (16%), 214 (42%), 177 (100%), 166 (16%), 157 (40%), 148 (28%), 117 (26%), 106 (63%), 79 (49%), 78 (78%), 45 (17%) **HRMS** (DART) calcd for $C_{12}H_{19}F_3NOSi$ $[M]^+$: 278.1188, found: 278.1212.



1,1,1-trifluoro-2-(pyridin-3-yl)-4-(trimethylsilyl)butan-2-ol, 3i (7.04 g, 64%) was prepared according to the representative trifluoromethylation procedure from **4i** (7.03 g, 0.034 mol) and further purified by recrystallization from hexanes/diethyl ether to give **3i** as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm -0.10 (s, 9 H) 0.04 (td, *J* = 13.20, 4.40 Hz, 1 H) 0.61 (td, *J* = 14.00, 4.38 Hz, 1 H) 2.11 (quind, *J* = 13.80, 13.80, 13.80, 13.80, 4.68 Hz, 2 H) 6.06 (s, 1 H) 7.37 (dd, *J* = 7.60, 4.97 Hz, 1 H) 7.96 (d, *J* = 7.89 Hz, 1 H) 8.53 (d, *J* = 4.39 Hz, 1 H) 8.76 (s, 1 H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm -1.84 (CH_3) 8.53 (CH_2) 29.58 (CH_2) 77.28 (q, $J_{C\text{-}C\text{-}F}$ = 27.40 Hz, C) 126.18 (q, $J_{C\text{-}F}$ = 285.40 Hz, CF_3) 123.62 (CH) 133.97 (CH) 135.72 (C) 148.08 (CH) 148.76 (CH) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.76 **GC-MS** (EI) 277 ($[M]^+$, 4%), 249 (29%), 188 (11%), 157 (16%), 148 (11%), 118 (12%), 106 (13%), 75 (40%), 73 (100%), 45 (10%) **HRMS** (DART) calcd for $C_{12}H_{19}F_3NOSi$ $[M]^+$: 278.11880, found: 278.1151.

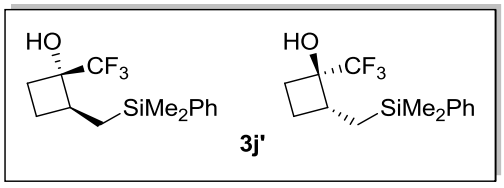


2-((dimethyl(phenyl)silyl)methyl)-1-(trifluoromethyl)cyclobutanol (3j/3j′) (9.943 g, 84%), was prepared according to the representative trifluoromethylation procedure from **4j** (9.00 g, 0.041 mol, 1 equiv) and further purified by vacuum distillation (b.p. 85-90 °C @ 0.1 mmHg) to give a clear, colorless oil containing a 54:46 mixture of diastereomers (**3j**:**3j′**, "*Cis*":"*Trans*"). These diastereomers were then separated by flash column chromatography (9:1 EtOAc: Hex). **3j** eluted before **3j′**.



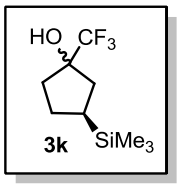
(1*R*,2*S*) & (1*S*,2*R*)-2-((dimethyl(phenyl)silyl)methyl)-1-(trifluoromethyl)cyclobutanol *"Cis"* **(3j)**

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.31 (d, *J* = 2.04 Hz, 6 H) 0.88 (dd, *J* = 14.01, 3.70 Hz, 1 H) 0.95 - 1.05 (m, 1 H) 1.62 (t, *J* = 9.54 Hz, 1 H) 1.84 - 1.94 (m, 2 H) 2.10 (s, 1 H) 2.21 - 2.33 (m, 1 H) 2.63 - 2.73 (m, 1 H) 7.33 - 7.40 (m, 3 H) 7.47 - 7.54 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -2.42 (CH_3) -2.12 (CH_3) 15.30 (CH_2) 23.79 (CH_2) 26.91 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1.65 Hz, CH_2) 35.22 (CH) 76.44 (q, $J_{C\text{-}C\text{-}F}$ = 31.00 Hz, C) 125.41 (q, $J_{C\text{-}F}$ = 282.10 Hz, CF_3) 128.16 (CH) 129.42 (CH) 133.70 (CH) 138.84 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -86.79 **GC-MS** (EI) **HRMS** (DART) calcd for $C_{14}H_{19}F_3OSi$ $[M + NH_4]^+$: 306.1501, found: 306.1518.

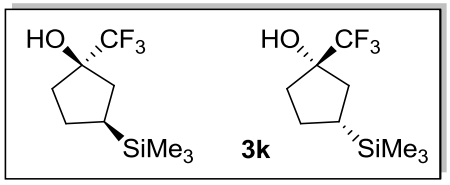


(1*S*,2*S*) & (1*R*,2*R*)-2-((dimethyl(phenyl)silyl)methyl)-1-(trifluoromethyl)cyclobutanol, *"Trans"* **(3j′)**

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.33 (d, *J* = 0.54 Hz, 6 H) 0.99 - 1.09 (m, 1 H) 1.24 (dd, *J* = 14.45, 2.68 Hz, 1 H) 1.39 (quin, *J* = 10.10 Hz, 1 H) 1.85 (q, *J* = 10.10 Hz, 1 H) 1.97 (q, *J* = 10.80 Hz, 1 H) 2.31 - 2.39 (m, 1 H) 2.55 (s, 1 H) 2.58 (q, *J* = 11.20 Hz, 1 H) 7.38 - 7.42 (m, 3 H) 7.52 - 7.56 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -2.45 (CH_3) -2.28 (CH_3) 16.82 (CH_2) 21.44 (CH_2) 29.06 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1.65 Hz, CH_2) 42.85 (CH) 77.91 (q, $J_{C\text{-}C\text{-}F}$ = 28.40 Hz, C) 126.28 (q, $J_{C\text{-}F}$ = 284.10 Hz, CF_3) 128.14 (CH) 129.38 (CH) 133.79 (CH) 138.89 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.10 **GC-MS** (EI) **HRMS** (DART) calcd for $C_{14}H_{19}F_3OSi$ $[M + NH_4]^+$: 306.1501, found: 306.1518.

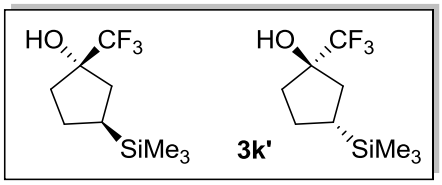


1-(trifluoromethyl)-3-(trimethylsilyl)cyclopentanol (3k) (1.19 g, 57% combined yield of isomers) was prepared according to the representative trifluoromethylation procedure from **4k** (1.44 g, 9.2 mmol) and further purified by flash column chromatography (gradient 50:1 to 20:1 Pentane:EtOAc) to isolate the separate isomers. The solvent was removed *in vacuo* by rotary evaporation for each isomer and then sublimed (40-50 ^{o}C, 10 mmHg) giving the *cis* (0.740 g, 35%) and *trans* (0.450 g, 21%) isomers as white solids.



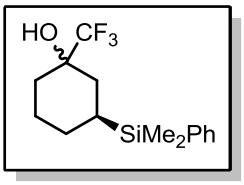
(1*R*,3*S*) & (1*S*, 3*R*)-1-(trifluoromethyl)-3-(trimethylsilyl)cyclopentanol "*Cis*" **(3k)**

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.00 (s, 9 H) 1.07 - 1.20 (m, 1 H) 1.42 - 1.53 (m, 1 H) 1.64 (qd, *J* = 12.60, 6.37 Hz, 1 H) 1.78 - 1.97 (m, 4 H) 2.32 (dd, *J* = 13.96, 9.78 Hz, 1 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -2.91 (CH_3) 27.18 (CH) 27.35 (CH_2) 38.03 (CH_2) 38.07 (CH_2) 83.11 (q, $J_{C\text{-}C\text{-}F}$ = 28.80 Hz, C) 126.97 (q, $J_{C\text{-}F}$ = 281.50 Hz, CF_3) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -84.47 **GC-MS** (EI) 226 ($[M]^+$, 1%), 115 (18%), 97 (41%), 91 (18%), 83 (12%), 77 (24%), 75 (57%), 73 (100%), 67 (32%), 59 (16%) **HRMS** (DART) calcd for $C_9H_{17}F_3OSi$ [$M^+ - CH_3$]: 211.0766, found: 211.0772.



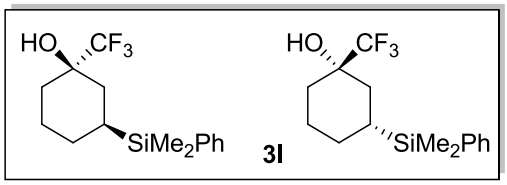
(1*S*,3*S*) & (1*R*, 3*R*)-1-(trifluoromethyl)-3-(trimethylsilyl)cyclopentanol "*Trans*" **(3k)**

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.00 (s, 9 H) 1.36 - 1.56 (m, 2 H) 1.56 - 1.68 (m, 1 H) 1.70 (s, 1 H) 1.75 - 1.80 (m, 1 H) 1.82 (s, 1 H) 1.92 - 2.02 (m, 1 H) 2.07 - 2.16 (m, 1 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -2.93 (CH_3) 24.45 (CH) 26.74 (CH_2) 36.36 (CH_2) 37.68 (CH_2) 83.26 (q, $J_{C\text{-}C\text{-}F}$ = 28.50 Hz, C) 126.76 (q, $J_{C\text{-}F}$ = 282.80 Hz, CF_3) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -83.98. **HRMS** (DART) calcd for $C_9H_{17}F_3OSi$ [$M^+ - CH_3$]: 211.0766, found: 211.0772.



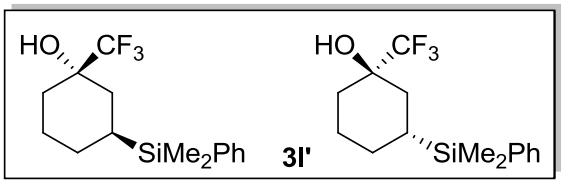
3-(dimethyl(phenyl)silyl)-1-(trifluoromethyl)cyclohexanol (3l) (4.678 g, 57% yield of **3l**) was was prepared according to the representative trifluoromethylation procedure from **4l** (8.959 g, 0.0386 mol) and further purified by flash column chromatography (4:1 Hex:EtOAc). The solvent was removed *in vacuo* via rotary evaporation to give a crude crystalline

material. Recrystallization of this solid (70:30 ratio of isomers) in pentane (50 mL) followed by cooling to -20 ^{o}C overnight in a freezer gave white fluffy crystals with an improved isomer ratio of 97:3 of **3l** (*cis*) to **3l′** (*trans*).



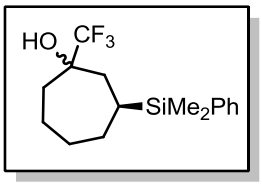
(1*R*,3*S*) & (1*S*,3*R*)-3-(dimethyl(phenyl)silyl)-1-(trifluoromethyl)cyclohexanol "*Cis*" **(3l)**

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.32 (d, *J* = 1.46 Hz, 6 H) 1.16 (q, *J* = 12.94 Hz, 2 H) 1.24 - 1.48 (m, 2 H) 1.48 - 1.62 (m, 1 H) 1.73 (d, *J* = 10.02 Hz, 2 H) 2.09 - 2.22 (m, 3 H) 7.35 - 7.43 (m, 3 H) 7.48 - 7.55 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -4.94 (CH_3) 21.10 (CH) 23.41 (CH_2) 25.62 (CH_2) 33.15 (CH_2) 34.01 (CH_2) 72.31 (q, $J_{C\text{-}C\text{-}F}$ = 27.00 Hz, C) 127.21 (q, $J_{C\text{-}F}$ = 286.10 Hz, CF_3) 128.09 (CH) 129.38 (CH) 134.20 (CH) 137.49 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -80.78 **GC-MS** (EI) 287 ($[M\text{-}CH_3]^+$, 1%), 152 (12%), 137 (82%), 135 (100%), 105 (21%), 91 (13%), 81 (12%), 55 (12%) **HRMS** (DART) calcd for $C_{15}H_{21}F_3OSi$ $[M+NH_4]^+$: 320.1658, found: 320.1660



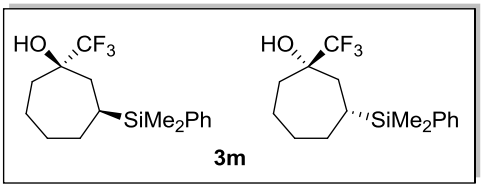
(1*S*,3*S*) & (1*R*,3*R*)-3-(dimethyl(phenyl)silyl)-1-(trifluoromethyl)cyclohexanol "*Trans*" **(3l′)**

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.31 (s, 6 H) 0.99 - 1.13 (m, 1 H) 1.20 - 1.32 (m, 1 H) 1.46 (t, *J* = 13.70 Hz, 1 H) 1.55 (dd, *J* = 11.97, 4.14 Hz, 1 H) 1.59 - 1.65 (m, 1 H) 1.65 - 1.72 (m, 2 H) 1.72 - 1.82 (m, 2 H) 1.83 (s, 1 H) 7.37 - 7.42 (m, 3 H) 7.48 - 7.54 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -5.13 (CH_3) -5.01 (CH_3) 18.65 (CH) 21.47 (CH_2) 26.19 (CH_2) 29.90 (CH_2) 30.86 (CH_2) 72.46 (q, $J_{C\text{-}C\text{-}F}$ = 27.70 Hz, C) 126.77 (q, $J_{C\text{-}F}$ = 284.50 Hz, CF_3) 128.10 (CH) 129.39 (CH) 134.20 (CH) 137.51 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -88.04 **GC-MS** (EI) 302 ($[M]^+$, 1%), 152 (5%), 137 (33%), 135 (100%), 105 (18%), 91 (10%), 84 (10%), 55 (10%) **HRMS** (DART) calcd for $C_{15}H_{21}F_3OSi$ $[M+NH_4]^+$: 320.1658, found: 320.1654



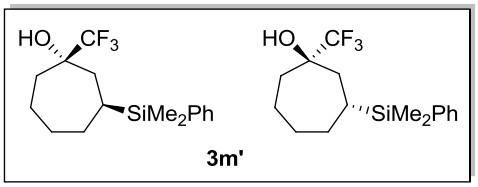
3-(dimethyl(phenyl)silyl)-1-(trifluoromethyl)cycloheptanol (3m) was prepared according to the representative trifluoromethylation procedure from **4m** (1.065 g, 4.32 mmol, 1 equiv), TMS-CF_3 (1.42 g, 9.97 mmol, 2.31 equiv), and TBAF (0.5311mL, 0.001834mol, 0.4246 equiv) with the following modifications: 1) The reaction mixture was refluxed until the

reaction was deemed complete by GC/MS analysis 2) Pentane, rather than Et_2O, was used as the extraction solvent 3) Further purification was accomplished by flash column chromatography (93:7 Hex:EtOAc) to give two isomeric products (in order of elution): **3m′ "***Trans"* (0.497g, 36.9% yield) and **3m** "*Cis"* (0.299g, 22.2% yield). The combined yield of this reaction was (0.796g, 58.2%).



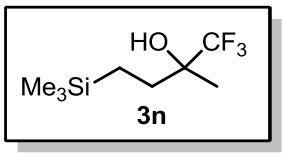
(1*R*,3*S*) & (1*S*,3*R*)-3-(dimethyl(phenyl)silyl)-1-(trifluoromethyl)cycloheptanol "*Cis*" **(3m)**

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.28 (s, 6 H) 0.88 - 0.98 (m, 1 H) 1.08 - 1.31 (m, 2 H) 1.36 - 1.48 (m, 1 H) 1.60 (d, *J*=12.16 Hz, 1 H) 1.69 - 1.84 (m, 2 H) 1.86 - 1.99 (m, 4 H) 2.31 (d, *J*=15.28 Hz, 1 H) 7.34 - 7.39 (m, 3 H) 7.47 - 7.52 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -5.26 (CH_3) -4.68 (CH_3) 22.08 (CH) 22.63 (CH_2) 32.82 (CH_2) 33.16 (CH_2) 34.57 (CH_2) 37.08 (CH_2) 77.96 (q, $J_{C\text{-}C\text{-}F}$ = 25.90 Hz, C) 127.29 (q, $J_{C\text{-}F}$ = 285.60 Hz, CF_3) 128.02 (CH) 129.36 (CH) 134.22 (CH) 137.60 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -85.79 **GC-MS** (EI) 316 ($[M]^+$, 1%), 152 (18%), 137 (97%), 135 (100%), 105 (12%), 95 (10%), 69 (6%) **HRMS** (DART) calcd for $C_{16}H_{23}F_3OSi$ $[M + NH_4]^+$: 334.1814, found: 334.1825.



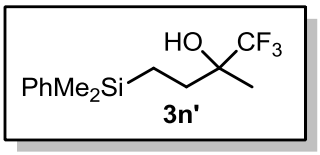
(1*S*,3*S*) & (1*R*,3*R*)-3-(dimethyl(phenyl)silyl)-1-(trifluoromethyl)cycloheptanol "*Trans*" **(3m′)**

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.30 (d, *J* = 1.31 Hz, 6 H) 1.22 - 1.35 (m, 2 H) 1.45 - 1.65 (m, 4 H) 1.67 - 2.01 (m, 6 H) 7.34 - 7.42 (m, 3 H) 7.49 - 7.57 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -5.01 (CH_3) -4.61 (CH_3) 17.80 (CH) 21.75 (CH_2) 29.65 (CH_2) 30.52 (CH_2) 34.45 (CH_2) 34.72 (CH_2) 77.09 (q, $J_{C\text{-}C\text{-}F}$ = 27.60 Hz, C) 127.23 (q, $J_{C\text{-}F}$ = 287.90 Hz, CF_3) 128.15 (CH) 129.41 (CH) 134.17 (CH) 137.98 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -86.42 **GC-MS** (EI) 316 ($[M]^+$, 1%), 152 (9%), 139 (14%), 137 (46%), 135 (100%), 105 (13%), 98 (11%), 69 (6%) **HRMS** (DART) calcd for $C_{16}H_{23}F_3OSi$ $[M + NH_4]^+$: 334.1814, found: 334.1822.

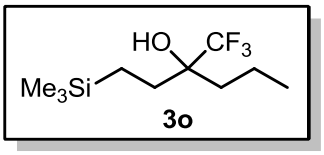


1,1,1-trifluoro-2-methyl-4-(trimethylsilyl)butan-2-ol (3n) (9.222 g, 68%), was prepared according to the representative trifluoromethylation procedure from **4n** (9.151 g, 0.0636 mol) and further purified by vacuum distillation (b.p. 50-55 ^oC @ 5 mmHg) to give # as a clear, colorless

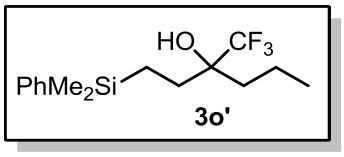
liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 0.01 (s, 9 H) 0.52 (td, *J* = 14.00, 4.50 Hz, 1 H) 0.61 (td, *J* = 13.80, 4.12 Hz, 1 H) 1.31 (s, 3 H) 1.58 (td, *J* = 13.90, 4.60 Hz, 1 H) 1.67 (td, *J* = 13.80, 4.00 Hz, 1 H) 2.10 (br. s., 1 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.77 (CH_3) 8.80 (CH_3) 19.84 (CH_2) 29.78 (CH_2) 74.50 (q, $J_{C\text{-}C\text{-}F}$ = 26.90 Hz, C) 128.19 (t, $J_{C\text{-}F}$ = 286.20 Hz, CF_3) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -85.37 **GC-MS** (EI) 199 ($M - CH_3]^+$, 3%), 103 (15%), 94 (55%), 77 (49%), 75 (66%), 73 (100%), 59 (11%), 55 (18%), 43 (23%).



4-(dimethyl(phenyl)silyl)-1,1,1-trifluoro-2-methylbutan-2-ol (3n′) (12.63 g, 62%), was prepared according to the representative trifluoromethylation procedure from **4n** (15.0 g, 0.073 mol) and further purified by vacuum distillation (b.p. 71-73 °C @ 0.1 mmHg) to give # as a viscous, light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.39 (s, 6 H) 0.87 (td, *J* = 13.60, 4.87 Hz, 1 H) 0.98 (td, *J* = 13.30, 4.38 Hz, 1 H) 1.38 (s, 3 H) 1.70 (td, *J* = 13.60, 4.87 Hz, 1 H) 1.78 (td, *J* = 13.80, 4.48 Hz, 1 H) 2.18 (s, 1 H) 7.42 - 7.47 (m, 3 H) 7.56 - 7.63 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -3.17 (CH_3) -3.15 (CH_3) 8.06 (CH_3) 19.74 (CH_2) 29.69 (CH_2) 74.44 ($J_{C\text{-}C\text{-}F}$ = 27.1 Hz, C) 126.97 ($J_{C\text{-}F}$ = 285.4 Hz, CF_3) 128.18 (CH) 129.40 (CH) 133.78 (CH) 138.58 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -85.21 **GC-MS** (EI) 261 ($[M - CH_3]^+$, 17%), 199 (9%), 139 (19%), 137 (46%), 135 (100%), 105 (29%), 91 (13%), 77 (12%), 43 (26%) **HRMS** (DART) calcd for $C_{13}H_{19}F_3SiO$ $[M + NH_4]^+$: 294.1501, found: 294.1480.

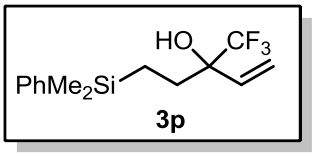


3-(Trifluoromethyl)-1-(trimethylsilyl)hexan-3-ol (3o) (7.737 g, 81%), was prepared according to the representative trifluoromethylation procedure from **4o** (6.79 g, 0.039 mol) and further purified by vacuum distillation (b.p. 51-55 °C @ 1.0 mmHg) to give # as a clear, colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 0.01 (s, 9 H) 0.52 (quind, *J* = 12.60, 12.60, 12.60, 12.60, 6.70 Hz, 2 H) 0.95 (m, *J* = 7.33, 7.33 Hz, 2 H) 1.39 (sxt, *J* = 8.60 Hz, 2 H) 1.57 - 1.73 (m, 4 H) 1.94 - 2.04 (br. s, 1 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ ppm -1.79 (CH_3) 9.19 (CH_2) 14.80 (CH_3) 16.28 (CH_2) 27.97 (CH_2) 35.45 (CH_2) 76.35 (q, $J_{C\text{-}C\text{-}F}$ = 25.90 Hz, C) 128.30 (quin, $J_{C\text{-}F}$ = 287.20 Hz, CF_3) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.16 **GC-MS** (EI) 227 ($[M\text{-}CH_3]^+$, 1%), 122 (14%), 103 (11%), 94 (18%), 91 (16%), 77 (27%), 75 (40%), 73 (100%), 55 (10%), 43 (15%) **HRMS** (DART) calcd for $C_{10}H_{21}F_3OSi$ $[M - CH_3]^+$: 227.1079, found: 227.1051.



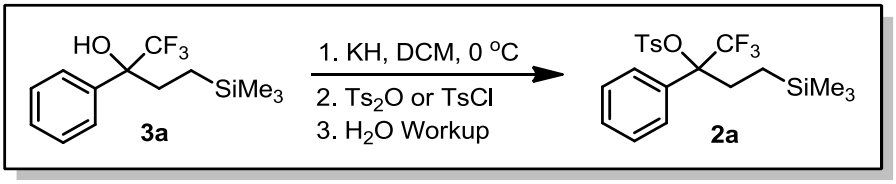
1-(dimethyl(phenyl)silyl)-3-(trifluoromethyl)hexan-3-ol (3o′) (9.75 g, 83%), was prepared according to the representative trifluoromethylation procedure from **4o** (9.01 g, 0.038 mol) and further purified by vacuum distillation (b.p. 88-90 °C @ 0.1 mmHg) to give the pure as a clear, colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.32 (d, *J* = 1.95 Hz, 6 H) 0.77 - 0.85 (m, 2 H) 0.95 (td, *J* = 7.30, 1.56 Hz, 3 H) 1.29 - 1.39 (m, 2 H) 1.58 - 1.75 (m, 4 H) 1.84 (d, *J* = 11.48 Hz, 1 H) 7.36 - 7.42 (m, 3 H) 7.49 - 7.55 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -3.15 (CH_3) -3.13 (CH_3) 8.47 (CH_2) 14.79 (CH_3) 16.21 (CH_2) 27.91 (CH_2) 35.39 (CH_2) 76.31 (q, $J_{C\text{-}C\text{-}F}$ = 26.40 Hz, C) 127.08 (q, $J_{C\text{-}F}$ = 286.80 Hz, CF_3) 128.18 (CH) 129.43 (CH) 133.79 (CH) 138.53 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.17 **GC-MS** (EI) 289 ($[M - CH_3]^+$, 12%), 139 (17%), 137 (50%), 135 (100%), 105 (18%), 91

(14%), 43 (11%).



5-(dimethyl(phenyl)silyl)-3-(trifluoromethyl)pent-1-en-3-ol (3p) (3.055 g, 57%) was prepared according to the representative trifluoromethylation procedure from **4p** (4.038 g, 0.0185 mol) and further purified by vacuum distillation (b.p. 73-80 ^{o}C @ 0.10 mmHg) to give **3p** as a clear, colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.34 (s, 6 H) 0.74 (td, *J* = 13.50, 4.18 Hz, 1 H) 0.86 (td, *J* = 14.00, 4.48 Hz, 1 H) 1.73 (td, *J* = 13.70, 4.38 Hz, 1 H) 1.85 (td, *J* = 13.80, 4.48 Hz, 1 H) 2.15 (br. s., 1 H) 5.46 - 5.59 (m, 2 H) 5.86 (dd, *J* = 17.32, 10.90 Hz, 1 H) 7.39 - 7.44 (m, 3 H) 7.52 - 7.58 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -3.12 (CH_3) -3.01 (CH_3) 7.46 (CH_2) 28.21 (CH_2) 77.29 (q, $J_{C\text{-}C\text{-}F}$ = 27.30 Hz, C) 118.73 (CH_2) 125.87 (q, $J_{C\text{-}F}$ = 286.10 Hz, CF_3) 128.18 (CH) 129.40 (CH) 133.79 (CH) 134.14 (CH) 138.60 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -83.86 **GC-MS** (EI) 273 ($[M\text{-}CH_3]^+$, 4%), 137 (49%), 135 (100%), 125 (10%), 105 (25%), 97 (14%), 91 (14%), 55 (21%) **HRMS** (DART) calcd for $C_{14}H_{19}F_3OSi$ $[M + NH_4]^+$: 306.1501, found: 306.1530.

Representative Procedure for Preparation of 1-Trifluoromethyl-3-Trimethylsilyl Sulfonic Esters



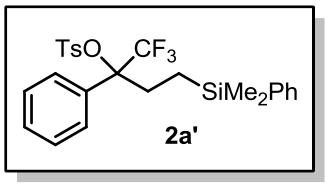
1,1,1-trifluoro-2-phenyl-4-(trimethylsilyl)butan-2-yl 4-methylbenzenesulfonate[38]**, 2a** (10.59 g, 82%). Tosylates were synthesized according to a modified procedure outlined by Kelly et al.35 In a glove box under argon, a suspension of KH in mineral oil was washed multiple times with pentane and allowed to dry. A flame-dried 1000 mL 3-necked, round-bottomed flask equipped with a stir bar, nitrogen inlet adapter, and two septa, was placed in the glove box. The now dry KH (2.41 g, 0.060 mol, 2 equiv) was placed in the flask and sealed with the septa and inlet adapter and removed from the glove box. The flask was then placed under a nitrogen atmosphere *via* the nitrogen inlet adapter. DCM (300 mL, 0.1 M) was added to the flask *via* syring. The reaction mixture was cooled to 0 ^{o}C in an ice-water bath for approximately 10 minutes while stirring. To this chilled mixture was added a solution of **3a** (8.29 g, 0.030 mol, 1 equiv) dissolved in DCM (30 mL, 1 M) and dropwise *via* syringe. Gas evolution and foaming was observed, consistent with deprotonation of the trifluoromethyl alcohol. After five minutes, the ice bath was removed and the reaction mixture allowed to stir at room temperature for 1 hour.

[38] ***IMPORTANT:*** Note that we initially elected to prepare the tosylates as the precursors for the solvolytic studies of our α-aryl systems. However, while successful, the isolation and purification of these reactive species can prove problematic and can be low yielding. We later found that the corresponding mesylates of these α-aryl systems can be used in place of tosylates with no impact on the outcome of solvolysis. Additionally, preparation of mesylates is markedly easier and does not require the use of KH. A representative protocol for mesylate preparation can be found in the Kinetic Supporting Information.

The mixture was then placed back in the ice-water bath and allowed to cool for 10 minutes. Under a stream of nitrogen, the septum was removed and all at once, TsCl[39] (11.44 g, 0.060 mol, 1.5 equiv) was added. The mixture was removed from the ice bath and allowed to stir for 1 hour, at which time it became thicker and an off-white precipitate was observed to form.

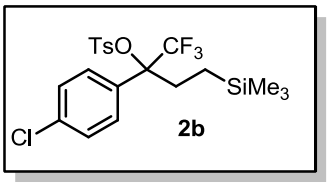
At this point, 300 mL of pentane was syringed into the reaction mixture. Deionized water (50 mL) was then added very slowly to the reaction mixture, to ensure that gas evolution was not too rapid. Caution: it is important that water be added slowly so as not to generate too much heat and avoid the possibility of fire. The reaction mixture was left to stir for 15 minutes. During this time, the solution became clear indicating the quench was complete. The contents of the reaction flask were then transferred into a separatory funnel and the aqueous layer removed. The organic layer containing the tosylated product was transferred to an Erlenmeyer flask and dried with Na_2SO_4. The solvent was then removed *via* rotary evaporation in a 30 ^oC water bath and then placed under a high vacuum to remove residual solvent to give the desired product as a thick, yellow oil and used directly in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.08 (s, 9 H) 0.50 (td, *J* = 14.00, 3.70 Hz, 1 H) 0.82 (td, *J* = 14.20, 3.89 Hz, 1 H) 2.46 (td, *J* = 14.60, 3.70 Hz, 1 H) 2.44 (s, 3 H) 3.04 (td, *J* = 14.40, 3.50 Hz, 1 H) 7.33 (d, *J* = 7.98 Hz, 2 H) 7.36 - 7.39 (m, 3 H) 7.43 - 7.48 (m, 2 H) 7.83 (d, *J* = 8.37 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -1.79 (CH_3) 9.94 (CH_2) 21.75 (CH_3) 27.46 (CH_2) 93.66 (q, $J_{C\text{-}C\text{-}F}$ = 28.50 Hz, C) 123.91 (q, $J_{C\text{-}F}$ = 286.70 Hz, CF_3) 127.32 (CH) 127.52 (CH) 128.53 (CH) 129.47 (CH) 129.86 (CH) 133.82 (C) 136.02 (C) 144.94 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -77.54.

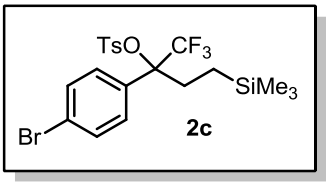


4-(dimethyl(phenyl)silyl)-1,1,1-trifluoro-2-phenylbutan-2-yl 4-methylbenzenesulfonate, 2a′ (20.102 g, 99%) was prepared according to the representative 3-trimethylsilyl tosylation procedure from **3a′** (14.0 g, 0.041 mol) with the following modification: Ts_2O (20.25g, 0.062 mol 1.5 equiv) was used in place of TsCl. The product was obtained as a thick, yellow oil and used directly in the next step. Yield given is with trace amounts of pentane present. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.34 (d, *J* = 11.40 Hz, 6 H) 0.70 (td, *J* = 13.80, 3.40 Hz, 1 H) 1.04 (td, *J* = 13.80, 3.80 Hz, 1 H) 2.37 (td, *J* = 14.60, 4.00 Hz, 1 H) 2.45 (s, 3 H) 2.99 (td, *J* = 14.40, 1 Hz, 2 H) 7.28 - 7.53 (m, 12 H) 7.79 (d, *J* = 8.37 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -3.41 (CH_3) -2.96 (CH_3) 9.22 (CH_2) 21.76 (CH_3) 27.34 (CH_2) 93.55 (q, $J_{C\text{-}C\text{-}F}$ = 29.00 Hz, C) 123.86 (q, $J_{C\text{-}F}$ = 287.00 Hz, CF_3) 127.32 (CH) 127.54 (CH) 128.13 (CH) 128.54 (CH) 129.42 (CH) 129.48 (CH) 129.87 (CH) 131.47 (C) 133.82 (CH) 135.97 (C) 138.24 (C) 144.95 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -77.58.

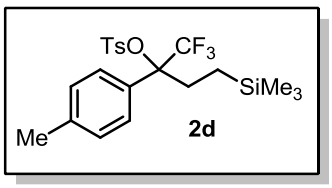
[39] ***IMPORTANT:*** Initially, the authors used recrystallized TsCl but later found that this led to difficulty in isolating pure tosylate products. Byproducts such as olefins were observed as minor products and unable to be removed. To alleviate this issue, Ts_2O was used and upon workup, the tosylates were obtained in near quantitative yield with little to no other impurities present.



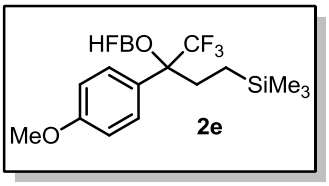
2-(4-chlorophenyl)-1,1,1-trifluoro-4-(trimethylsilyl)butan-2-yl 4-methylbenzenesulfonate, 2b (10.14 g, 87%) was prepared according to the representative 3-trimethylsilyl tosylation procedure from **3b** (7.771 g, 0.025 mol) with the following modification: Ts_2O (9.0 g, 0.0275 mol 1.1 equiv) was used in place of TsCl. The product was obtained as a thick, yellow oil and used directly in the next step. Yield given is with trace amounts of pentane present. Yield given is with trace amounts of pentane present. **^{1}H NMR** (400 MHz, CDCl3) δ ppm 0.07 (s, 9 H) 0.47 (td, *J* = 13.80, 3.51 Hz, 1 H) 0.79 (td, *J* = 14.20, 3.88 Hz, 1 H) 2.44 (s, 3 H) 2.40 (td, *J* = 14.40, 3.63 Hz, 1 H) 2.99 (td, *J* = 14.20, 2.79 Hz, 1 H) 7.30 - 7.40 (m, 6 H) 7.80 (d, *J* = 8.36 Hz, 2 H) **^{13}C NMR** (100 MHz, CDCl3) δ ppm -1.77 (CH_3) 9.99 (CH_2) 21.78 (CH_2) 27.56 (CH_3) 93.01 (q, $J_{C\text{-}C\text{-}F}$ = 28.80 Hz, C) 123.75 (q, $J_{C\text{-}F}$ = 286.50 Hz, CF_3) 127.56 (CH) 128.79 (CH) 128.91 (CH) 129.93 (CH) 132.51 (C) 135.76 (C) 135.88 (C) 145.14 (C) **^{19}F NMR** (377 MHz, CDCl3) δ ppm **GC-MS** (EI) 380 ($[M\text{-}CF_3O]^+$, ^{37}Cl 6%), 378 ($[M\text{-}CF_3O]^+$, ^{35}Cl 15%), 207 (61%), 206 (100%), 187 (18%), 165 (48%), 155 (23%), 143 (23%), 137 (24%), 91 (46%), 73 (35%), 69 (4%), 65 (22%).



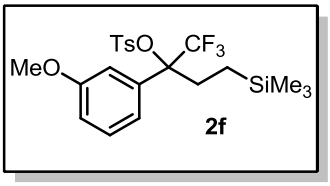
1,1,1-Trifluoro-2-(4-bromophenyl)-4-(trimethylsilyl)butan-2-yl 4-methylbenzenesulfonate, 2c (10.0 g, 68%) was prepared according to the representative 3-trimethylsilyl tosylation procedure from **3c** (10.25 g, 0.030 mol, 1 equiv) and obtained as a powdery, tan solid and used directly in the next step. Yield given is with trace amounts of pentane present. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.06 (s, 9 H) 0.44 (td, *J*=13.90, 3.50 Hz, 1 H) 0.77 (td, *J*=14.20, 3.50 Hz, 1 H) 2.37 (td, *J*=14.60, 3.55 Hz, 1 H) 2.44 (s, 3 H) 2.97 (td, *J*=14.50, 3.26 Hz, 1 H) 7.29 (d, *J*=8.61 Hz, 2 H) 7.33 (d, *J*=8.17 Hz, 3 H) 7.49 (d, *J*=8.81 Hz, 2 H) 7.79 (d, *J*=8.32 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.77 (CH_3) 9.96 (CH_2) 21.84 (CH_3) 27.47 (CH_2) 93.03 (q, $J_{C\text{-}C\text{-}F}$ = 28.60 Hz, C) 123.65 (q, $J_{C\text{-}F}$ = 286.70 Hz, CF_3) 124.05 (C) 127.55 (CH) 129.14 (CH) 129.94 (CH) 131.77 (CH) 132.99 (C) 135.79 (C) 145.15 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -77.65.



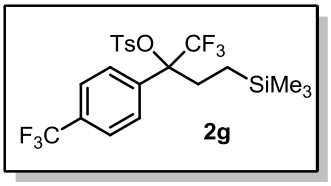
1,1,1-Trifluoro-2-(*p*-tolyl)-4-(trimethylsilyl)butan-2-yl 4-methylbenzenesulfonate, 2d (8.20 g, 98%) was prepared according to the representative 3-trimethylsilyl tosylation procedure from **3d** (5.50 g, 0.019 mol, 1 equiv) and obtained as a thick, orange oil and used directly in the next step. Yield given is with trace amounts of pentane present. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.06 (s, 9 H) 0.48 (td, *J* = 14.00, 3.80 Hz5, 1 H) 0.76 (td, *J* = 14.20, 3.60 Hz, 1 H) 2.39 (td, *J* = 14.00, 3.80 Hz, 1 H) 2.36 (s, 3 H) 2.45 (s, 3 H) 2.96 (td, *J* = 14.20, 4.00 Hz, 1 H) 7.16 (d, *J* = 8.07 Hz, 2 H) 7.31 (t, *J* = 7.58 Hz, 4 H) 7.79 (d, *J* = 8.31 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.71 (CH_3) 10.05 (CH_2) 21.32 (CH_3) 21.88 (CH_3) 27.51 (CH_2) 93.77 (q, $J_{C\text{-}C\text{-}F}$ = 28.20 Hz, C) 123.98 (q, $J_{C\text{-}F}$ = 287.80 Hz, CF_3) 127.40 (CH) 127.60 (CH) 129.27 (CH) 129.84 (CH) 130.78 (C) 136.17 (C) 139.54 (C) 144.84 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -77.64.



1,1,1-trifluoro-2-(4-methoxyphenyl)-4-(trimethylsilyl)butan-2-yl 2,2,3,3,4,4,4-heptafluorobutanoate, 2e (6.50 g, 92%) was prepared according to the representative 3-trimethylsilyl tosylation procedure from **3e** (4.30 g, 0.014 mol) with the following modification: 2,2,3,3,4,4,4-heptafluorobutanoic anhydride[40] (8.63 g, 0.021 mol, 1.5 equiv) was used in place of TsCl. and obtained as a thick, yellow oil and used directly in the next step. Yield given is with trace amounts of pentane present. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.06 (s, 9 H) 0.43 (td, *J* = 13.30, 3.99 Hz, 1 H) 0.67 (td, *J* = 13.90, 4.09 Hz, 1 H) 2.61 (td, *J* = 14.20, 3.26 Hz, 1 H) 2.86 (td, *J* = 14.40, 4.38 Hz, 1 H) 3.83 (s, 3 H) 6.97 (d, *J* = 8.76 Hz, 2 H) 7.38 (d, *J* = 8.86 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -2.00 (CH_3) 9.27 (CH_2) 26.99 (CH_2) 55.48 (CH_3) 89.68 (q, $J_{C\text{-}C\text{-}F}$ = 29.00 Hz, C) 108.52 (tq, $J_{C\text{-}F}$ = 267.20, $J_{C\text{-}C\text{-}F}$ = 38.90 Hz, CF_2) 107.90 (tt, $J_{C\text{-}F}$ = 266.80, $J_{C\text{-}C\text{-}F}$ = 33.20 Hz, CF_2) 114.40 (CH) 117.74 (qt, $J_{C\text{-}F}$ = 288.30, $J_{C\text{-}C\text{-}F}$ = 33.70 Hz, CF_3) 124.04 (q, $J_{C\text{-}F}$ = 285.40 Hz, CF_3) 125.67 (C) 127.99 (CH) 155.33 (t, $J_{C\text{-}C\text{-}F}$ = 30.40 Hz, C) 160.72 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -129.14 (s, 2 F) -121.17 (q, *J* = 9.20 Hz, 2 F) -83.57 (t, *J* = 8.85 Hz, 3 F) -79.35 (s, 3 F).



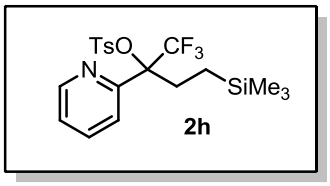
1,1,1-Trifluoro-2-(3-methoxyphenyl)-4-(trimethylsilyl)butan-2-yl 4-methylbenzenesulfonate, 2f (11.55 g, 84%) was prepared according to the representative 3-trimethylsilyl tosylation procedure from **3f** (9.19 g, 0.030 mol, 1 equiv) and obtained as a thick, yellow oil and used directly in the next step. Yield given is with trace amounts of pentane present. **^{1}H NMR** (400 MHz, $CDCl_3$) 0.06 (s, 9 H) 0.48 (td, *J* = 13.90, 3.70 Hz, 1 H) 0.79 (td, *J* = 14.40, 3.75 Hz, 1 H) 2.40 (td, *J* = 15.00, 3.50 Hz, 1 H) 2.44 (s, 3 H) 2.97 (td, *J* = 14.70, 4.04 Hz, 1 H) 3.76 (s, 3 H) 6.91 (dd, *J* = 8.15, 2.17 Hz, 1 H) 6.97 (s, 1 H) 7.00 (d, *J* = 8.08 Hz, 1 H) 7.27 (d, *J* = 8.17 Hz, 1 H) 7.32 (d, *J* = 8.27 Hz, 2 H) 7.80 (d, *J* = 8.32 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -1.73 (CH_3) 10.00 (CH_2) 21.84 (CH_3) 27.67 (CH_2) 55.39 (CH_3) 93.58 (q, $J_{C\text{-}C\text{-}F}$ = 28.70 Hz, C) 113.99 (CH) 114.43 (CH) 119.55 (CH) 123.88 (q, $J_{C\text{-}F}$ = 286.90 Hz, CF_3) 127.57 (CH) 129.55 (CH) 129.87 (CH) 135.36 (C) 136.09 (C) 144.93 (C) 159.66 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -77.51.



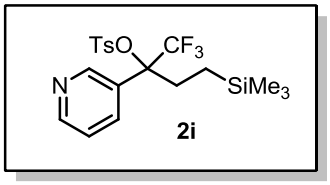
1,1,1-Trifluoro-2-(4-(trifluoromethyl)phenyl)-4-(trimethylsilyl)butan-2-yl 4-methylbenzenesulfonate, 2g (10.19 g, 68%) was prepared according to the representative 3-trimethylsilyl tosylation procedure from **3g** (10.33 g, 0.030 mol, 1 equiv) and obtained as a light tan, crystalline solid and used directly in the next step. Yield given is with trace amounts of pentane present. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 0.06 (s, 9 H) 0.40 (td, *J* = 13.70, 3.67 Hz, 1 H) 0.78 (td, *J* = 14.40, 3.42 Hz, 1 H) 2.41 (td, *J* = 14.90, 3.20 Hz, 1 H) 2.45 (s, 3 H) 3.02 (td, *J* = 14.90, 4.16 Hz, 1 H) 7.34 (d, *J* = 7.83 Hz, 2 H) 7.56 (d, *J* = 8.31 Hz, 2 H) 7.63 (d, *J* = 8.31 Hz, 2 H) 7.81 (d, *J* = 8.31 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.85 (CH_3) 9.90 (s, 5 C) 21.79 (CH_3) 27.56 (CH_2) 92.88 (q, $J_{C\text{-}C\text{-}F}$ = 29.00 Hz, C) 123.61 (q, $J_{C\text{-}F}$ = 287.00 Hz, CF_3) 123.90 (q, $J_{C\text{-}F}$ = 272.90 Hz, CF_3) 125.52 (d, $J_{C\text{-}C\text{-}F}$ = 3.30 Hz, CH) 127.56 (CH) 127.89 (CH) 129.97 (CH) 131.61 (q, $J_{C\text{-}C\text{-}F}$ =

[40] As the tosylate readily decomposed upon workup, we elected to prepare the OHFB analog instead of the OTs. This compound was able to be isolated with ease.

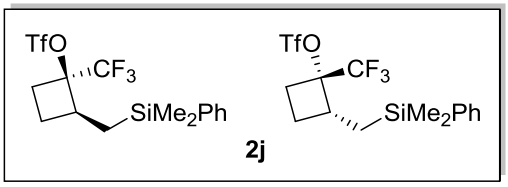
32.80 Hz, C) 135.68 (C) 137.93 (C) 145.26 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -77.47 (s, 3 F) -66.01 (s, 3 F).



1,1,1-Trifluoro-2-(pyridin-2-yl)-4-(trimethylsilyl)butan-2-yl 4-methylbenzenesulfonate, 2h (4.45 g, 38%) was prepared according to the representative 3-trimethylsilyl tosylation procedure from **3h** (2.774 g, 0.01 mol) and purified by silica flash column chromatography (gradient 95:5 to 9:1 to 8:2 Hex:EtOAc) to give **2h** as a thick, orange oil and used directly in the next step. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 0.05 (s, 9 H) 0.38 (td, *J* = 13.90, 3.15 Hz, 1 H) 0.79 (td, *J* = 13.90, 3.80 Hz, 1 H) 2.47 (s, 3 H) 2.73 (td, *J* = 14.34, 3.47 Hz, 1 H) 2.95 (td, *J* = 13.90, 3.78 Hz, 1 H) 7.24 - 7.33 (m, 1 H) 7.37 (d, *J* = 8.20 Hz, 2 H) 7.63 (d, *J* = 8.20 Hz, 1 H) 7.73 (td, *J* = 7.90, 1.58 Hz, 1 H) 7.86 (d, *J* = 8.20 Hz, 2 H) 8.63 (d, *J* = 3.78 Hz, 1 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm -1.94 (CH_3), 9.65 (CH_2), 21.63 (CH_3) , 26.88 (CH_2), 94.06 (C, q, $J_{C\text{-}C\text{-}F}$ = 27.5 Hz) 123.84 (q, $J_{C\text{-}F}$ = 105.39 Hz, CF_3) 124.54 (CH) 127.62 (CH) 129.91 (CH) 135.84 (C) 136.49 (CH) 144.79 (C) 148.75 (CH) 153.37 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -76.84 **GC-MS** (EI): 416 ($[M - CH_3]^+$, 0.25%), 358 (5.8%), 309(17%), 276(31.9%), 260 (10.8%), 244 (25.6%), 229 (26.8%),186 (24%), 176 (100%), 166 (37.8%), 149 (11.4%), 117 (18%), 91 (24.5%), 73 (26.2%) **HRMS** (DART): calcd for $C_{19}H_{24}F_3NO_3SSi$ $[M]^+$: 432.1276, found: 432.1304.



1,1,1-trifluoro-2-(pyridin-3-yl)-4-(trimethylsilyl)butan-2-yl 4-methylbenzenesulfonate, 2i (6.01 g, 48%)[41] was prepared according to the representative 3-trimethylsilyl tosylation procedure from **3i** (2.774 g, 0.01 mol) and purified by silica flash column chromatography (gradient 95:5 to 9:1 to 8:2 Hex:EtOAc) to give **2i** as a tan powdery solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.05 (s, 9 H) 0.42 (td, *J* = 14.20, 3.67 Hz, 1 H) 0.77 (td, *J* = 14.20, 3.67 Hz, 1 H) 2.39 (td, *J* = 14.50, 3.18 Hz, 1 H) 2.46 (s, 3 H) 2.98 (td, *J* = 13.90, 3.79 Hz, 1 H) 7.29 - 7.37 (m, 3 H) 7.73 (d, *J* = 8.07 Hz, 1 H) 7.80 (d, *J* = 8.31 Hz, 2 H) 8.58 - 8.66 (m, 2 H).

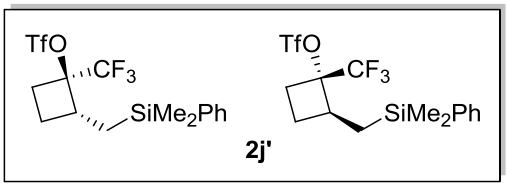


(1*R*,2*S*) & (1*S*,2*R*)-2-((dimethyl(phenyl)silyl)methyl)-1-(trifluoromethyl)cyclobutyl trifluoromethanesulfonate "*Cis*" **(2j)** (0.421 g, 50.8%), was prepared according to the representative tosylation procedure from **3j** (0.430 g, 2.96 mmol) with the following

[41] This compound was stable to column chromatography, it could not be separated from its alcohol precursor. Therefore, when it was later used in the cyclopropanation reaction, it was used as an impure, 85% w/w mixture. Separation of the cyclopropane solvolysis product from the alcohol proved unproblematic. Only ^{1}H NMR data is given for this compound because it is an impure mixture.

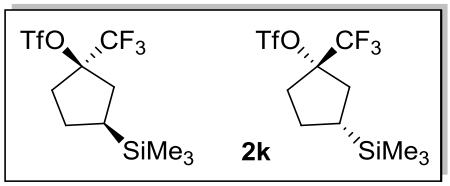
modifications: Tf_2O (7.67 g, 0.027 mol, 1.2 equiv) was used in place of TsCl. The resulting triflate was obtained as a clear, colorless liquid and used directly in the next step.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.33 (s, 6 H) 1.01 - 1.18 (m, 2 H) 1.64 (spt, *J*=5.90 Hz, 1 H) 1.93 - 2.05 (m, 1 H) 2.63 (s, 1 H) 2.90 (br. s., 2 H) 7.35 - 7.41 (m, 3 H) 7.46 - 7.52 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -2.42 (CH_3) -2.32 (CH_3) 16.38 (s, 5 C) 23.34 (s, 4 C) 26.08 (CH_2) 37.92 (CH) 92.17 (q, $J_{C\text{-}C\text{-}F}$ = 33.70 Hz, C) 118.46 (q, $J_{C\text{-}F}$ = 319.50 Hz, CF_3) 123.23 (q, $J_{C\text{-}F}$ = 282.60 Hz, CF_3) 128.33 (CH) 129.69 (CH) 133.68 (CH) 137.99 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -84.49 (s, 3 F) -78.22 (s, 3 F) **HRMS** (DART) calcd for $C_{15}H_{18}F_6O_3SSi$ [M^++NH_4]: 438.0994, found: 438.0997.



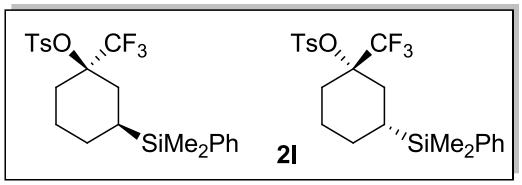
(1*R*,2*R*) & (1*S*,2*S*)-2-((dimethyl(phenyl)silyl)methyl)-1-(trifluoromethyl)cyclobutyl trifluoromethanesulfonate "*Trans*" **(2j')** (0.566 g, 68.6%) was prepared according to the representative tosylation procedure from **3j'** (0.428 g, 1.97 mmol) with the following modifications: Tf_2O (0.888 g, 2.46 mmol, equiv) was used in place of Ts_2O. The resulting triflate was obtained as a clear, colorless liquid and used directly in the next step.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.31 - 0.36 (m, 6 H) 1.01 - 1.12 (m, 1 H) 1.37 - 1.51 (m, 2 H) 1.97 (q, *J* = 11.00 Hz, 1 H) 2.52 - 2.67 (m, 2 H) 3.15 (q, *J* = 11.60 Hz, 1 H) 7.36 - 7.42 (m, 3 H) 7.49 - 7.55 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -2.68 (CH_3) -2.59 (CH_3) 16.69 (CH_2) 22.26 (CH_2) 28.21 (CH_2) 42.68 (CH) 92.67 (q, $J_{C\text{-}C\text{-}F}$ = 31.20 Hz, C) 118.37 (q, $J_{C\text{-}F}$ = 319.30 Hz, CF_3) 123.51 (q, $J_{C\text{-}F}$ = 282.40 Hz, CF_3) 128.25 (CH) 129.64 (CH) 133.74 (CH) 137.91 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -79.98 (s, 3 F) -78.75 (s, 3 F).



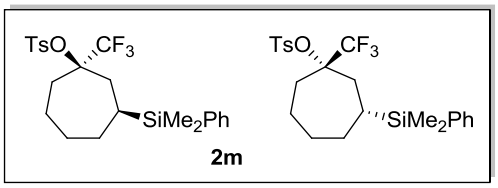
1-(trifluoromethyl)-3-(trimethylsilyl)cyclopentyl trifluoromethanesulfonate "*Cis*" **(2k)** (0.082 g, 50%), was prepared according to the representative tosylation procedure from **3k** (0.10 g, 4.42 mmol) with the following modifications: Tf_2O (0.235 g, 8.33 mmol, 1.9 equiv) was used in place of Ts_2O. The resulting triflate was obtained as a yellow oil and used directly in the next step.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.04 (s, 9 H) 1.15 (spt, *J* = 6.80 Hz, 1 H) 1.81 (qd, *J* = 12.50, 7.10 Hz, 1 H) 1.89 - 1.99 (m, 1 H) 2.12 - 2.26 (m, 2 H) 2.50 - 2.62 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -3.22 (CH_3) 27.18 (CH) 27.80 (CH_2) 36.18 (CH_2) 37.36 (CH_2) 102.85 (q, $J_{C\text{-}C\text{-}F}$ = 31.70 Hz, C) 118.40 (q, $J_{C\text{-}F}$ = 319.50 Hz, CF_3) 124.16 (q, $J_{C\text{-}F}$ = 282.40 Hz, CF_3) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.51 (s, 3 F) -78.81 (s, 3 F).



(1R,3S) & (1S,3R)- 3-(dimethyl(phenyl)silyl)-1-(trifluoromethyl)cyclohexyl 4-methylbenzenesulfonate "*Cis*" **(2l)** (4.31 g, 63%) was prepared according to the representative tosylation procedure from 3-(dimethyl(phenyl)silyl)-1-(trifluoromethyl)cyclohexanol (4.503 g, 15 mmol) with the following modifications: Ts_2O (5.361 g, 16.42 mmol, 1.1 equiv) was used in place of TsCl. **2l** was obtained as a light yellow crystals and used directly in the next step.

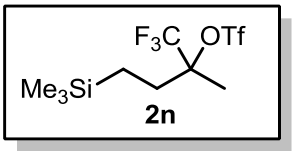
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.28 (s, 6 H) 1.08 - 1.19 (m, 2 H) 1.24 - 1.31 (m, 1 H) 1.46 - 1.61 (m, 1 H) 1.62 - 1.71 (m, 1 H) 1.74 - 1.85 (m, 1 H) 2.04 - 2.15 (m, 1 H) 2.21 - 2.35 (m, 2 H) 2.45 (s, 3 H) 7.31 (d, *J*=8.13 Hz, 2 H) 7.34 - 7.41 (m, 3 H) 7.42 - 7.48 (m, 2 H) 7.75 (d, *J*=8.27 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -5.24 (CH_3) -5.18 (CH_3) 21.87 (CH_3) 21.96 (CH) 24.43 (CH_2) 25.08 (CH_2) 30.64 (CH_2) 31.89 (CH_2) 90.30 (q, $J_{C\text{-}C\text{-}F}$ = 28.40 Hz, C) 124.91 (q, $J_{C\text{-}F}$ = 286.30 Hz, CF_3) 127.54 (CH) 128.14 (CH) 129.53 (CH) 129.91 (CH) 134.10 (CH) 136.49 (C) 136.84 (C) 144.84 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -77.41.



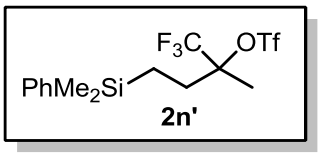
(1R,3S) & (1S,3R)- 3-(dimethyl(phenyl)silyl)-1-(trifluoromethyl)cycloheptyl 4-methylbenzenesulfonate "*Cis*" **(2m)** (0.217 g, 48.5%) was prepared according to the representative tosylation procedure from **3m** (0.299 g, 0.945 mmol) with the following modifications: Ts_2O (0.342 g, 1.0395 mmol, 1.1 equiv) was used in place of TsCl. **2m** was obtained. Further purification was accomplished by tituration of residual tosic anhydride from pentane to give the desired sulfonic ester as a thick light brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.27 (d, *J* = 3.89 Hz, 6 H) 0.89 (t, *J* = 11.10 Hz, 1 H) 1.09 - 1.26 (m, 2 H) 1.72 - 1.83 (m, 2 H) 1.84 - 1.98 (m, 3 H) 2.10 - 2.22 (m, 1 H) 2.44 (s, 3 H) 2.47 - 2.61 (m, 2 H) 7.30 (d, *J* = 8.13 Hz, 2 H) 7.34 - 7.41 (m, 3 H) 7.42 - 7.51 (m, 2 H) 7.74 (d, *J* = 8.27 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -5.33 (CH_3) -4.84 (CH_3) 21.92 (CH_3) 22.34

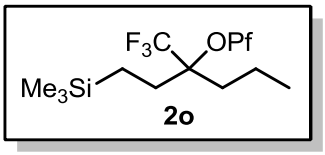
(CH) 22.62 (CH_2) 32.71 (CH_2) 32.90 (CH_2) 33.47 (CH_2) 34.84 (CH_2) 95.54 (q, $J_{C\text{-}C\text{-}F}$ = 26.80 Hz, C) 124.96 (q, $J_{C\text{-}F}$ = 286.10 Hz, CF_3) 127.69 (CH) 128.05 (CH) 129.47 (CH) 129.88 (CH) 134.20 (CH) 136.13 (C) 137.15 (C) 144.85 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.22.



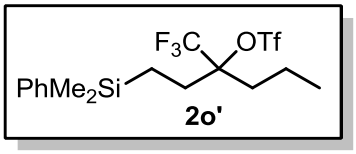
1,1,1-Trifluoro-2-methyl-4-(trimethylsilyl)butan-2-yl Trifluoromethanesulfonate (2n) (4.892 g, 75%), was prepared according similarly to the representative 3-trimethylsilyl tosylation procedure from **3n** (3.956 g, 0.0185 mol) with the following modifications: Tf_2O (6.292 g, 0.022 mol, 1.2 equiv) was used in place of Ts_2O and the reaction left to stir for 1 hour at 0 °C before quenching with deionized water. The resulting triflate was obtained as a clear, colorless liquid and used directly in the next step. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.05 (s, 9 H) 0.65 - 0.70 (m, 1 H) 1.28 - 1.36 (m, 1 H) 1.85 (s, 3 H) 1.89 - 2.01 (m, 1 H) 2.05 - 2.17 (m, 1 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -1.96 (CH_3) 9.55 (CH_3) 18.33 (CH_2) 30.47 (CH_2) 97.16 (q, $J_{C\text{-}C\text{-}F}$ = 30.10 Hz, C) 118.38 (q, $J_{C\text{-}F}$ = 320.00 Hz, CF_3) 123.71 (q, $J_{C\text{-}F}$ = 284.50 Hz, CF_3) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.49 (s, 3 F) -78.65 (s, 3 F).



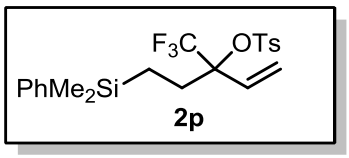
4-(dimethyl(phenyl)silyl)-1,1,1-trifluoro-2-methylbutan-2-yl trifluoromethanesulfonate (2n′) (8.075 g, 91%), was prepared according to the representative tosylation procedure from **3n′** (6.0 g, 0.0217 mol) with the following modifications: Tf_2O (9.19 g, 0.0326 mol, 1.5 equiv) was used in place of Ts_2O. The resulting triflate was obtained as a dark yellow oil and used directly in the next step. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.37 (s, 6 H) 0.93 (t, *J* = 7.02 Hz, 1 H) 0.98 (quin, *J* = 6.40 Hz, 1 H) 1.87 (s, 3 H) 1.98 (m, 1 H) 2.15 (m, 1 H) 7.39 - 7.44 (m, 3 H) 7.50 - 7.56 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -3.31 (CH_3) -3.28 (CH_3) 8.86 (CH_3) 18.37 (CH_2) 30.47 (CH_2) 96.94 (q, $J_{C\text{-}C\text{-}F}$ = 30.50 Hz, C) 118.38 (q, $J_{C\text{-}F}$ = 318.70 Hz, CF_3) 123.65 (q, $J_{C\text{-}F}$ = 285.70 Hz, CF_3) 128.35 (CH) 129.72 (CH) 133.75 (CH) 137.54 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -82.45 (s, 3 F) -78.61 (s, 3 F).



3-(trifluoromethyl)-1-(trimethylsilyl)-3-hexanyl-2,3,4,5,6-pentafluorobenzenesulfonate (2o) (1.317 g, 68%) was prepared according to the representative tosylation procedure from **3o** (1.0 g, 4.13 mmol) with the following modifications: Pentafluorobenzene sulfonyl chloride (1.20 g, 4.5 mmol, 1.1 equiv) was used in place of Ts_2O. The resulting perflate was obtained as a clear, colorless liquid and used directly in the next step. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.04 (s, 9 H) 0.64 (apparent triplet, *J* = 8.70 Hz, 2 H) 0.99 (t, *J* = 7.32 Hz, 3 H) 1.42 - 1.54 (m, 2 H) 2.01 - 2.24 (m, 4 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm-1.92 (CH_3) 9.87 (CH_2) 14.45 (CH_3) 16.77 (CH_2) 27.68 (CH_2) 34.48 (CH_2) 98.12 (q, $J_{C\text{-}C\text{-}F}$ = 28.20 Hz, C) 114.93 (t, $J_{C\text{-}C\text{-}F}$ = 12.30 Hz, C) 124.23 (q, $J_{C\text{-}F}$ = 286.80 Hz, CF_3) 138.20 (d, $J_{C\text{-}F}$ = 261.53 Hz, CF) 145.05 (d, $J_{C\text{-}F}$ = 264.09 Hz, CF) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -161.50 - -161.15 (m, 2 F) -146.76 - -146.45 (m, 1 F) -137.66 - -137.39 (m, 2 F) -77.33 (d, *J* = 4.09 Hz, 3 F)



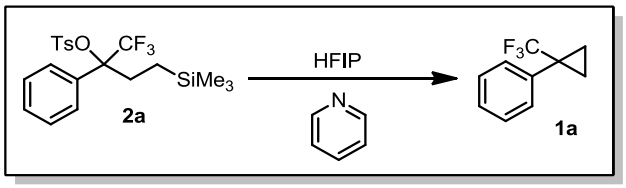
1-(dimethyl(phenyl)silyl)-3-(trifluoromethyl)hexan-3-yl trifluoromethanesulfonate (2o′) (6.11 g, 69%), was prepared according to the representative tosylation procedure from **3o′** (6.0 g, 0.0197 mol) with the following modifications: Tf_2O (8.34 g, 0.0296 mol, 1.5 equiv) was used in place of Ts_2O. The resulting triflate was obtained as a clear, colorless liquid and used directly in the next step. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.24 (s, 6 H) 0.87 (t, *J* = 7.30 Hz, 3 H) 1.16 - 1.41 (m, 4 H) 1.98 - 2.11 (m, 4 H) 7.27 - 7.30 (m, 3 H) 7.39 - 7.43 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -3.44 (CH_3) -3.40 (CH_3) 9.17 (CH_3) 14.32 (CH_2) 16.70 (CH_2) 27.79 (CH_2) 34.53 (CH_2) 100.74 (q, $J_{C\text{-}C\text{-}F}$ = 29.00 Hz, C) 118.44 (q, $J_{C\text{-}F}$ = 319.00 Hz, CF_3) 123.79 (q, $J_{C\text{-}F}$ = 285.90 Hz, CF_3) 128.34 (CH) 129.73 (CH) 133.75 (CH) 137.56 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -78.60 (s, 3 F) -77.83 (s, 3 F).



5-(dimethyl(phenyl)silyl)-3-(trifluoromethyl)pent-1-en-3-yl trifluoromethanesulfonate (2p) (0.537 g, 76%), was prepared according to the representative tosylation procedure from **3p** (0.50 g, 1.73 mmol) with the following modifications: (0.630 g, 1.92 mmol, 1.11 equiv) was used in place of TsCl. **2p** was obtained as a yellow-orange oil and used directly in the next step. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.36 (s, 6 H) 1.00 (t, *J* = 9.10 Hz, 2 H) 2.13 - 2.23 (m, 1 H) 2.30 - 2.41 (m, 1 H) 2.44 - 2.49 (m, 3 H) 5.49 - 5.57 (m, 2 H) 6.02 (dd, *J* = 17.42, 11.29 Hz, 1 H) 7.30 - 7.37 (m, 2 H) 7.39 - 7.43 (m, 3 H) 7.55 (m, *J* = 3.70 Hz, 2 H) 7.80 (d, *J* = 8.22 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm -3.17 (CH_3) -3.13 (CH_3) 8.96 (CH_2) 21.84 (CH_3) 27.33 (CH_2) 90.45 (q, $J_{C\text{-}C\text{-}F}$ = 28.80 Hz, 2 C) 123.67 (q, $J_{C\text{-}F}$ = 286.10 Hz, CF_3) 122.48 (CH_2) 127.74 (CH) 128.17 (CH) 129.44 (C) 129.91 (CH) 130.22 (C) 133.79 (CH) 135.85 (C) 138.24 (C) 45.04 (CH) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -78.98 **HRMS** (DART) calcd for $C_{21}H_{25}F_3SiONH_4$ [M^++NH_4]: 460.1590, found: 460.1579.

Solvolysis Studies

General Procedure A: Representative Procedure for Synthesis and Isolations of α-Aryl CF_3 Cyclopropanes



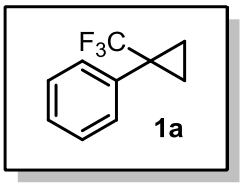
(1-(Trifluoromethyl)cyclopropyl)benzene, 1a (0.8292 g, 58%). To a 25 mL screw top vial equipped with stirbar was added HFIP (7.8 mL, 1 M in substrate) and pyridine (1.22 g, 0.0155 mol, 2 equiv) (***CAUTION***: mildly exothermic). The mixture was allowed to stir at room temperature for approximately five minutes. At this time **2a**[42] (3.33 g, 7.73 mmol, 1 equiv) was added all at once (***CAUTION***: mildly exothermic) and the vial was sealed. The initially heterogeneous reaction mixture was stirred at room temperature. The mixture gradually turned homogenous and clear brown. Once the reaction was judged complete[43], the reaction mixture was transferred to a separatory funnel and diluted with pentane (≈ 100 mL) and deionized water (≈ 100 mL). The layers were separated and the aqueous layer was extracted twice with pentane (≈ 100 mL). The combined organic layers were washed with deionized water twice (≈ 100 mL) and one with brine (≈ 100 mL). The organic layer was dried with Na_2SO_4 and the solvent was removed *in vacuo* via rotary evaporation (50 mmHg, 30 ^oC water bath).[44] Further purification was accomplished by flash column chromatography (hexanes) to give the pure CF_3 cyclopropane, **1a** as a clear, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.10 (br. s., 2 H) 1.43 (*apparent triplet*, *J* = 5.80 Hz, 2 H) 7.35 - 7.46 (m, 3 H) 7.55 (dd, *J* = 6.85, 1.22 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 9.94 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.20 Hz, CH_2) 28.50 (q, $J_{C\text{-}C\text{-}F}$ = 33.50 Hz, C) 126.74 (q, $J_{C\text{-}F}$ = 274.00 Hz, CF_3) 128.59 (CH) 128.64 (CH) 131.59 (CH) 136.48 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -73.28 **GC-MS** (EI) 186 ([M]$^+$, 40%), 165 (9%), 118 (10%), 117 (100%), 116 (12%), 115 (54%), 91 (19%), 69 (4%), 51 (7%) **HRMS** (DART) calcd for $C_{10}H_9F_3$ [M]$^+$: 186.0656, found: 186.0661.

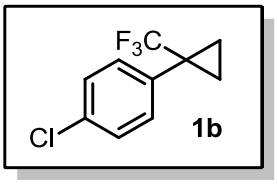
[42] Mesylates can be used in place of tosylates for the α-aryl systems with no effect on the outcome of solvolysis, see Kinetic SI for a representative protocol for mesylate preparation.

[43] Note that, it is likely that these reaction are completed after the solid material dissolves (<1 hr) due to the rapidity of ring closure and the strong solvolytic power of HFIP. However, it is recommended that the reaction is monitored by NMR to determine reaction progress. Other forms of reactions monitoring (TLC or GC/MS) proved ineffective for determining progress due to decomposition of the OTs starting material.

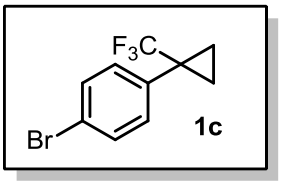
[44] Note it is ***imperative*** that higher pressures are used during rotary evaporation to ensure good yields. Many of the CF_3 cyclopropanes synthesized are highly volatile and can easily be lost during solvent removal at lower pressures.



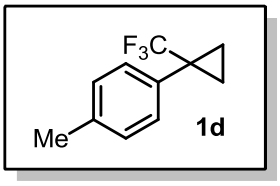
(1-(trifluoromethyl)cyclopropyl)benzene (1a) (1.07 g, 58%) was prepared according to the representative solvolysis procedure A from **2a′** (4.93 g, 10.0 mmol) and further purified by flash column chromatography (Hexanes) to give **1a′** as a clear, colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 1.10 (br. s., 2 H) 1.43 (*apparent triplet*, *J* = 5.80 Hz, 2 H) 7.35 - 7.46 (m, 3 H) 7.55 (dd, *J* = 6.85, 1.22 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 9.94 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.20 Hz, CH_2) 28.50 (q, $J_{C\text{-}C\text{-}F}$ = 33.50 Hz, C) 126.74 (q, $J_{C\text{-}F}$ = 274.00 Hz, CF_3) 128.59 (CH) 128.64 (CH) 131.59 (CH) 136.48 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -73.28 **GC-MS** (EI) 186 ([M]$^+$, 40%), 165 (9%), 118 (10%), 117 (100%), 116 (12%), 115 (54%), 91 (19%), 69 (4%), 51 (7%) **HRMS** (DART) calcd for $C_{10}H_9F_3$ [M]$^+$: 186.0656, found: 186.0661.



1-chloro-4-(1-(trifluoromethyl)cyclopropyl)benzene (1b) (1.69 g, 76%) was prepared according to the representative solvolysis procedure A from **2b** (4.65 g, 0.010 mol) and further purified by flash column chromatography (Hexanes) to give **1b** as a clear colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 1.01 - 1.06 (m, 2 H) 1.40 (apparent quartet, *J* = 3.80 Hz, 2 H) 7.35 (d, *J* = 8.42 Hz, 2 H) 7.43 (d, *J* = 8.54 Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 10.02 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.54 Hz, CH_2) 27.98 (q, $J_{C\text{-}C\text{-}F}$ = 33.90 Hz, C) 126.50 (qd, $J_{C\text{-}F}$ = 273.00, 4.24 Hz, CF_3) 128.89 (CH) 132.91 (CH) 134.68 (C) 134.99 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -70.27 **GC-MS** (EI) 222 ([M]$^+$, ^{37}Cl 15%), 220 ([M]$^+$, ^{35}Cl 43%), 185 (65%), 165 (64%), 151 (35%), 145 (20%), 116 (58%), 115 (100%), 75 (14%), 69 (12%) **HRMS** (DART) calcd for C_9H_8Cl [M]$^+$: 151.0315, found: 151.0321.



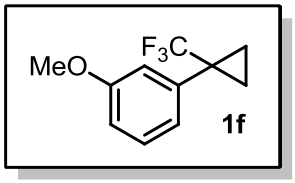
1-bromo-4-(1-(trifluoromethyl)cyclopropyl)benzene (1c)[45] (0.793 g, 74%) was prepared according to the representative solvolysis procedure A from **2c** (1.95 g, 3.83 mmol) and further purified by flash column chromatography (Hexanes) to give **1c** as a clear, pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 1.03 (tt, *J* = 6.80, 1.60 Hz, 2 H) 1.40 (*apparent* dd, *J* = 6.70, 5.09 Hz, 2 H) 7.33 - 7.37 (m, 2 H) 7.43 (d, *J* = 8.60 Hz, 2 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 10.02 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.45 Hz, CH_2) 28.04 (d, $J_{C\text{-}C\text{-}F}$ = 34.00 Hz, C) 126.37 (q, $J_{C\text{-}F}$ = 274.00 Hz, CF_3) 122.83 (C) 131.84 (CH) 133.22 (CH) 135.44 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -73.58 **GC-MS** (EI) 266 ([M]$^+$, ^{81}Br 46%), 264 ([M]$^+$, ^{79}Br 47%), 185 (61%), 165 (78%), 145 (20%), 116 (100%), 115 (75%), **HRMS** (DART) calcd for $C_{10}H_8BrF_2$ [M − F]$^+$: 244.9777, found: 244.9789.



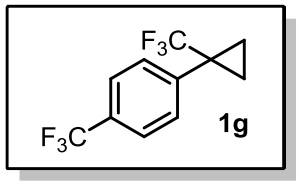
1-methyl-4-(1-(trifluoromethyl)cyclopropyl)benzene (1d) (0.7102 g, 72%) was prepared according to the representative solvolysis procedure A from **2d** (2.20 g, 0.0495 mol) and further purified by flash column chromatography (Hexanes) to give **1d** as a clear, colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 1.05 (br. s, 2 H) 1.38 (*apparent triplet*, *J* = 5.80 Hz, 2 H) 2.40 (s, 3 H) 7.20 (d, *J* = 7.98 Hz, 2 H) 7.41 (d, *J* = 7.98

[45] Barnes-Seeman, D.; Jain, M.; Bell, L.; Ferreira, S.; Cohen, S.; Chen, X.-H.; Amin, J.; Snodgrass, B.; Hatsis, P. *ACS Med. Chem. Lett.*, **2013**, *4*, 514.

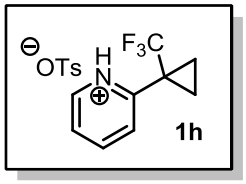
Hz, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 9.94 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.20 Hz, CH_2) 21.39 (CH_3) 28.07 (q, $J_{C\text{-}C\text{-}F}$ = 34.00 Hz, C) 126.81 (q, $J_{C\text{-}F}$ = 273.00 Hz, CF_3) 129.34 (CH) 131.44 (CH) 133.52 (C) 138.44 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -73.28 **GC-MS** (EI) 200 ($[M]^+$, 65%), 185 (62%), 165 (45%), 164 (18%), 145 (10%), 132 (12%), 131 (100%), 129 (21%), 128 (15%), 116 (34%), 115 (44%), 91 (36%), 77 (10%), 69 (6%), 51 (9%) **HRMS** (DART) calcd for $C_{11}H_{11}F_3$ $[M]^+$: 200.0813, found: 200.0819.



1-methoxy-3-(1-(trifluoromethyl)cyclopropyl)benzene (1f) (1.28 g, 74%) was prepared according to the representative solvolysis procedure A from **2f** (3.685 g, 8.0 mmol) and further purified by flash column chromatography (Gradient Hexanes to 95:5 Hex:EtOAc) to give **1f** as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 1.08 (br. s, 2 H) 1.38 (*apparent triplet*, *J* = 5.80 Hz, 2 H) 3.84 (s, 3 H) 6.91 (ddd, *J* = 8.30, 2.40, 1.00 Hz, 1 H) 7.03 - 7.13 (m, 2 H) 7.25 - 7.33 (m, 1 H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 10.00 (CH_2) 28.49 (q, $J_{C\text{-}C\text{-}F}$ = 33.50 Hz, C) 55.43 (CH_3) 113.94 (CH) 117.34 (CH) 123.76 (CH) 126.67 (q, $J_{C\text{-}F}$ = 273.20 Hz, CF_3) 129.56 (CH) 137.88 (C) 159.73 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -73.07 **GC-MS** (EI) 217 ($[M+1]^+$, 12%), 216 ($[M]^+$, 100%), 215 ($[M-1]^+$, 29%), 201 (11%), 185 (30%), 173 (10%), 165 (23%), 151 (10%), 147 (66%), 145 (13%), 133 (34%), 132 (12%), 131 (11%), 127 (12%), 117 (13%), 115 (37%), 103 (19%), 91 (24%), 77 (15%), 69 (6%), 63 (11%) **HRMS** (DART) calcd for $C_{11}H_{12}F_3O$ $[M^+]$: 217.0840, found: 217.0857.

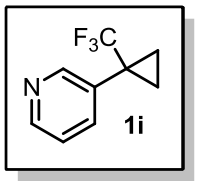


1-(trifluoromethyl)-4-(1-(trifluoromethyl)cyclopropyl)benzene (1g) (4.59 g, 95%) was prepared according to the representative solvolysis procedure A from **2g** (9.5 g, 0.191 mol) with the following modifications: The solvolysis was carried out in TFE (100 mL, 0.1 M) and heated to 50 °C for 12 hours. The same isolation and purification procedure was followed thereafter. Further purification was accomplished by flash column chromatography (Hexanes) to give **1g** as a clear, colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 1.06 (br. s, 2 H) 1.43 (*apparent triplet*, *J* = 6.00 Hz, 2 H) 7.58 - 7.66 (m, 4 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 10.10 (CH_2) 28.44 (q, $J_{C\text{-}C\text{-}F}$ = 34.50 Hz, C) 124.31 (q, $J_{C\text{-}F}$ = 271.50 Hz, CF_3) 126.38 (q, $J_{C\text{-}F}$ = 273.00 Hz, CF_3) 125.67 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.18 Hz, CH) 130.97 (q, $J_{C\text{-}C\text{-}F}$ = 32.60 Hz, C) 131.98 (CH) 140.44 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -72.93 (s, 3 F) -65.70 (s, 3 F) **GC-MS** (EI) 254 ($[M]^+$, 54%), 235 (26%), 185 (100%), 165 (73%), 164 (28%), 151 (11%), 145 (20%), 133 (10%), 116 (24%), 115 (32%), 69 (8%) **HRMS** (DART) calcd for $C_{11}H_8F_6$ $[M]^+$: 254.0530, found: 254.0508.



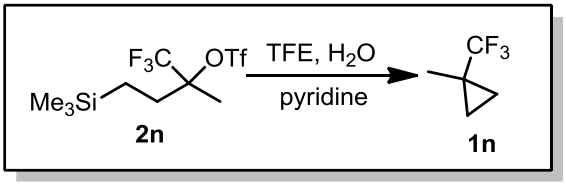
2-(1-(trifluoromethyl)cyclopropyl)pyridin-1-ium tosylate (1h) (3.34 g, 100%) was prepared according to the representative solvolysis procedure A from **2h** (4.01 g, 9.29 mmol) with the following modifications: The solvolysis was carried out in TFE (100 mL, 0.1 M) and heated to 50 °C for 72 hours. Once complete, the solvent was removed to give **1h** as a pale green solid which was recrystallized from hexanes to give a powdery off-white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 1.50 (br. s., 2 H) 1.54 - 1.60 (m, 2 H) 2.31 (s, 3 H) 7.14 (d, *J* = 7.93 Hz, 2 H) 7.74 (d, *J* = 8.03 Hz, 2 H) 7.91 - 8.02 (m, 2 H) 8.45 (t, *J* = 7.79 Hz,

1 H) 9.10 (d, *J* = 5.16 Hz, 1 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 11.23 (CH_2) 21.48 (CH_3) 27.25 (q, $J_{C\text{-}C\text{-}F}$ = 35.20 Hz, C) 124.63 (q, $J_{C\text{-}F}$ = 274.00 Hz, CF_3) 126.16 (CH) 127.42 (CH) 129.04 (CH) 130.10 (CH) 140.60 (C) 141.94 (C) 144.07 (CH) 146.65 (CH) 149.48 (C) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -73.22 **GC-MS** (EI) **HRMS** (ESI+) calcd for $C_{16}H_{16}F_3NO_3S$ [M - OTs]$^+$: 188.0687, found: 188.0710.



3-(1-(trifluoromethyl)cyclopropyl)pyridine (1i) (1.454 g, 65%) was prepared according to the representative solvolysis procedure A from **2i** (5.13 g, 0.012 mol) and further purified by flash column chromatography (Gradient Hexanes to 9:1 to 8:2 to 7:3 to 6:4 Hex:EtOAc) to give **1i** as a clear red-brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.98 (br. s., 2 H) 1.35 (apparent triplet, *J* = 6.00 Hz, 2 H) 7.21 (dd, *J* = 7.88, 4.77 Hz, 1 H) 7.71 (d, *J* = 7.78 Hz, 1 H) 8.50 (dd, *J* = 4.77, 1.46 Hz, 1 H) 8.64 (d, *J* = 1.56 Hz, 1 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 9.48 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.20 Hz, CH_2) 26.33 (q, $J_{C\text{-}C\text{-}F}$ = 34.00 Hz, C) 126.14 (q, $J_{C\text{-}F}$ = 274.00 Hz, CF_3) 123.40 (CH) 132.12 (C) 139.03 (CH) 149.69 (CH) 152.51 (CH) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -73.55 **GC-MS** (EI) 187 ([M]$^+$, 86%), 186 ([M-1]$^+$, 62%), 166 (13%), 148 (12%), 118 (100%), 117 (83%), 91 (42%), 89 (10%), 69 (7%), 63 (21%), 51 (15%), 39 (12%) **HRMS** (DART) calcd for $C_9H_9F_3N$ [M + H]$^+$: 188.0687, found: 188.0708.

General Procedure B: Representative Procedure for Synthesis and Isolations of Straight Chain CF_3 Cyclopropanes

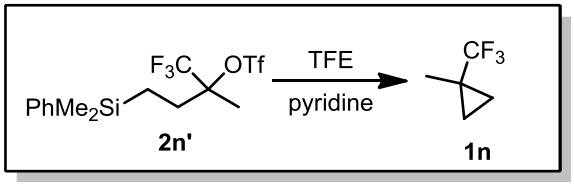


1-(trifluoromethyl)-1-methylcyclopropane, 1n (1.075 g, 29%). The following procedure is a modification of the procedure outlined by Kelly *et al*.[46] To a 200 mL round bottom flask equipped with stirbar was added deionized water (74 mL), TFE (37 mL), and pyridine (2.73 g, 34.5 mmol, 2.06 eq.). The solution was cooled to 0 ^{o}C in an ice bath and stirred for several minutes. At this time, **1n** (5.435 g, 0.01729 mol, 1 equiv) was added to the flask *slowly* (**Caution**: *Mildly Exothermic*). Upon complete addition, the mixture was stoppered with a glass stopper, then the neck of the flask was sealed with Parafilm, and clamped with a Keck clamp. The mixture was stirred overnight at room temperature. Upon completion of reaction (confirmed by ^{1}H NMR analysis), the flask was equipped with a Vigreux column (140 mm) and distillation head. The product was then distilled directly from the crude reaction mixture. **Note:** Due to the low boiling nature of the product, the distillation head and receiving flask were cooled with a -5 ^{o}C NaCl/ice water coolant. This distillation afforded 1.496 g of crude material product were obtained. To remove the trimethylsilylfluoride byproduct which co-distillated, crude material was dissolved in TCE (7 mL) and washed 2 M potassium hydroxide (3 x 5 mL). The combine

[46] Kelly, C. D.; Colthart, A. M.; Constant, B.D.; Corning, S.R.; Dubois, L. N.E.; Genovese, J. T.; Radziewicz, J. L.; Sletten, E. M.; Whitaker, K. R.; Tilley, L. J. *Org. Lett.* **2011**, *13*, 1646

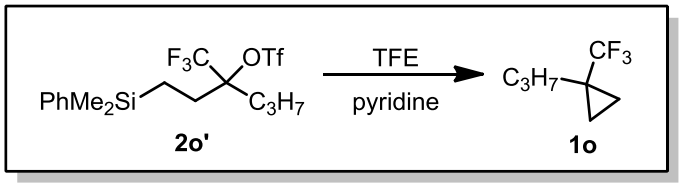
KOH wash was extracted with 3 mL of TCE. The combined TCE layers were dried with Na_2SO_4 and distilled in the same manner as before affording the CF_3 cyclopropane.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.48 - 0.54 (m, 2 H) 0.94 (t, *J* = 6.00 Hz, 2 H) 1.27 (s, 3 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 10.01 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.90 Hz, CH_3) 17.41 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1.47 Hz, CH_2) 18.45 (q, $J_{C\text{-}C\text{-}F}$ = 33.70 Hz, C) 127.86 (q, $J_{C\text{-}F}$ = 272.90 Hz, CF_3) **GC-MS** (EI) 124 ($[M]^+$, 20%), 104 (12%), 89 (16%), 77 (32%), 69 (27%), 55 (100%), 51 (16%), 39 (30%) **FTIR** (cm-1, salt plates) 3104.86 (w), 3027.03 (w), 2988.11 (m), 1476.76 (m), 1392.43 (s), 1165.41 (vs).



1-(trifluoromethyl)-1-methylcyclopropane, 1n′ (1.571 g, 64%) was prepared in a similar manner to the above procedure B from **2n′** (8.08 g, 0.0198 mol) with the following modification: The reaction was performed in TFE (40 mL) rather than a mixture of TFE and water. **1n** was isolated by fractional distillation (b.p. 23-24 ^oC) and obtained as a clear, colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.48 - 0.54 (m, 2 H) 0.94 (t, *J* = 6.00 Hz, 2 H) 1.27 (s, 3 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 10.01 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.90 Hz, CH_3) 17.41 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1.47 Hz, CH_2) 18.45 (q, $J_{C\text{-}C\text{-}F}$ = 33.70 Hz, C) 127.86 (q, $J_{C\text{-}F}$ = 272.90 Hz, CF_3) **GC-MS** (EI) 124 ($[M]^+$, 20%), 104 (12%), 89 (16%), 77 (32%), 69 (27%), 55 (100%), 51 (16%), 39 (30%) **FTIR** (cm-1, salt plates) 3104.86 (w), 3027.03 (w), 2988.11 (m), 1476.76 (m), 1392.43 (s), 1165.41 (vs)

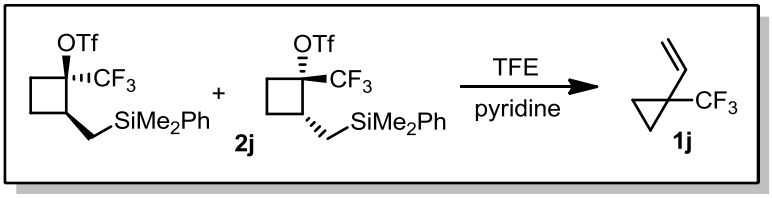


1-propyl-1-(trifluoromethyl)cyclopropane, 1o (0.723 g, 35%) was prepared according to the representative solvolysis procedure B from **2o′** (6.112 g, 0.0135 mol) with the following modification: The reaction was performed in TFE (50 mL) rather than a mixture of TFE and water. **1o** was isolated by fractional distillation (b.p. 53-55 ^oC)[47] and obtained as a clear, colorless oil.

[47] If any TFE co-distills, it can be removed by washing with cold deionized water followed by drying and removal of the drying salt. Interestingly, a trace amount of benzene was observed in the ^{1}H NMR spectra which may be a decomposition product of the silyl cation after γ-silyl elimination.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.52 - 0.58 (m, 2 H) 0.87 - 0.95 (m, 5 H) 1.39 - 1.49 (m, 2 H) 1.50 - 1.57 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 8.91 (q, $J_{C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.80 Hz, CH_3) 14.54 (CH_2) 20.10 (CH_2) 22.50 (q, $J_{C\text{-}C\text{-}F}$ = 31.50 Hz, C) 34.39 (CH_2) 128.02 (q, $J_{C\text{-}F}$ = 274.40 Hz, CF_3) **^{19}F NMR** (377 MHz, $CDCl_3$) δ ppm -72.87 **GC-MS** (EI) 152 ($[M]^+$, 3%), 123 (14%), 104 (30%), 103 (100%), 97 (22%), 89 (21%), 83 (97%), 77 (75%), 75 (32%), 69 (84%), 59 (31%), 55 (84%), 51 (40%), 41 (65%), 39 (98%).

^{1}H NMR Solvolysis Studies



1-(trifluoromethyl)-1-vinylcyclopropane 1j via 2j ("*cis*")

This procedure is a modification of the procedure outlined by Kelly *et al*.[48] An NMR tube was charged with 10 µL 1,1,2-trichloroethane, 0.5 mL TFE-d_6, and pyridine-d_5 (19.1 µL, 0.238 mmol, 2 equiv). The tube was then placed into the NMR and the sample was locked and shimmed on the TFE deuterium signal and a baseline ^{1}H spectrum was obtained. Because the solvent signal was obscured by the CH_2 signal of the TCE, the spectrum was calibrated using one of the pyridine peaks determined earlier. Using this method, the CH signal of the 1,1,2-trichlorethane was determined to be 5.76 ppm. The tube was ejected and **2j** (0.050 g, 0.119 mmol) was added to the tube. The NMR tube was injected back into the spectrometer and was monitored by ^{1}H NMR. After 12 hours the reaction was complete. Yield was determined by our established protocol for NMR solvolysis studies. A representative example is given below:

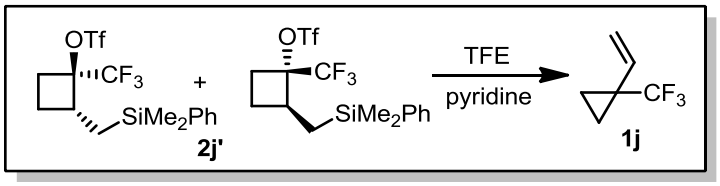
Upon the addition **2j** to the NMR tube, an initial (T_0) ^{1}H NMR spectrum was collected .The area of the CH peak of the 1,1,2-trichloroethane was calibrated to 1.000, and the area of all peaks in the methyl region of the $SiMe_2Ph$ group (≈ 0.28 ppm) was determined relative to this and this value was divided by 6. These peaks represented SiMe2Ph peaks for the starting triflate as well as a small amount of $PhMe_2SiOCD_2CF_3$ that was beginning to form as a result of the reaction taking place. Once the reaction was judge complete a second spectrum was collected. The area of the CH for the 1,1,2-trichloroethane was calibrated to 1.000, but, this time, the area for each of the product peaks of vinylcyclopropane the was determined and an average value was found). Using the areas from the spectra at the initial and final times, the percent yield of the reaction was calculated as follows:

$$\%\ \text{yield} = \frac{(\text{Average Area of Peaks of } \mathbf{1j})}{(\text{Area of } SiMe_2Ph \text{ Peak}) / 6} \times 100$$

Using this method, the yield was determined to be 84%

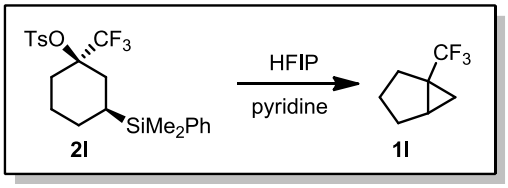
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.82 - 0.90 (m, 2 H) 1.13 - 1.20 (m, 2 H) 5.14 (d, *J* = 7.79 Hz, 1 H) 5.17 - 5.19 (m, 1 H) 6.00 (dd, *J* = 17.32, 10.90 Hz, 2 H)

[48] Kelly, C. D.; Colthart, A. M.; Constant, B.D.; Corning, S.R.; Dubois, L. N.E.; Genovese, J. T.; Radziewicz, J. L.; Sletten, E. M.; Whitaker, K. R.; Tilley, L. J. *Org. Lett.* **2011**, *13*, 1646



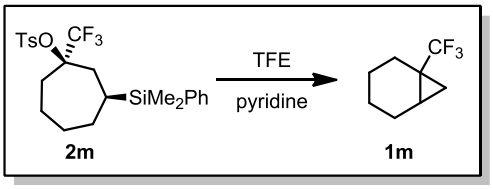
1-(trifluoromethyl)-1-vinylcyclopropane, 1j via 2j' ("*trans*") was solvolyzed according to the representative NMR-scale solvolysis procedure from the triflate **2j'** (0.48g, 0.119 mmol, 1 equiv), 10 µL 1,1,2-trichloroethane, 0.5 mL TFE-d_6, and pyridine-d_5(19 µL, 0.237 mmol, 2 equiv). The reaction was complete in about 3 hours. ^{1}H NMR yield was determined to be 87% using the representative protocol for determining yield by NMR.

^{1}H NMR (400 MHz, CF_3CD_2OD) δ ppm 0.82 - 0.90 (m, 2 H) 1.13 - 1.20 (m, 2 H) 5.14 (d, *J* = 7.79 Hz, 1 H) 5.17 - 5.19 (m, 1 H) 6.00 (dd, *J* = 17.32, 10.90 Hz, 2 H)



1-(trifluoromethyl)bicyclo[3.1.0]hexane (1l) was solvolyzed according to the representative NMR-scale solvolysis procedure from **2l** (0.1046 g, 0.219 mmol, 1 equiv) with the following mofications: 1) The reaction was performed in HFIP (2 mL) 2) The reaction was heated to 40 ^{o} C for 24 h before yield determination. Yield was determined by weight percent assay using dimethyl fumarate as a standard. Using this method, the yield (0.0314 g, 95%) was determined. A protocol for weight percent assay is given below for the NMR solvolysis study of **1n**.

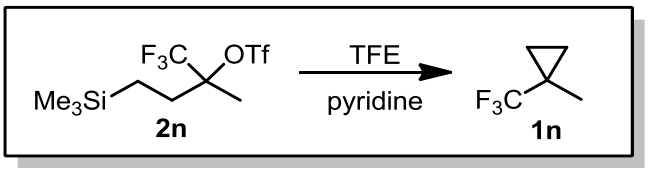
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.67 (t, *J*=4.40 Hz, 1 H) 0.96 (dd, *J*=9.44, 8.71 Hz, 1 H) 1.24 - 1.35 (m, 1 H) 1.64 (dt, *J*=8.42, 4.20 Hz, 1 H) 1.69 - 1.92 (m, 2 H) 1.93 - 2.04 (m, 1 H)



1-(trifluoromethyl)bicyclo[4.1.0]heptane (1m) was solvolyzed according to the representative NMR-scale solvolysis procedure from the tosylate **2m** (0.050 g, 0.106mmol, 1 equiv) with the following modifications: 1) The solvolysis was conducted at 50 ^{o}C over seven days in a screw-

top vial and was then transferred to an NMR tube upon reaction completion. ^{1}H NMR yield was determined to be 92% using the representative protocol for determining yield by NMR.[49]

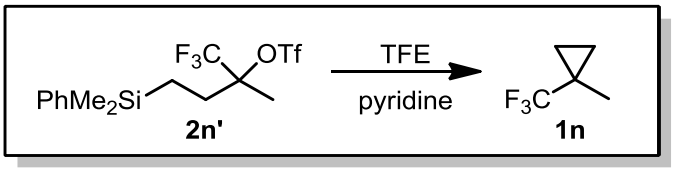
^{1}H NMR (300 MHz, CF_3CD_2OD) δ ppm 0.44 (quint, *J* = 4.90, 1.70 Hz, 1 H), 1.03 (ddq, *J* = 9.80, 5.30, 0.40 Hz, 1 H), 1.11 - 1.24 (m, 1 H), 1.24 - 1.38 (m, 4 H), 1.61 - 1.76 (m, 2 H), 1.80 - 1.94 (m, 1 H), 2.06 (dt, *J* = 14.13, 6.80 Hz, 1 H)



1-(trifluoromethyl)-1-methylcyclopropane (1n) was solvolyzed according to the representative NMR-scale solvolysis procedure from **2n** (0.2912 g, 0.639 mmol, 1 equiv, 76 wt%). Yield was determined by weight percent assay using 1.2,4,5 tetramethylbenzene as a standard. A representative protocol for this determination is given below:

After the reaction was judged to be complete by ^{1}H NMR, a sample of the reaction mixture (461.4 mg) was removed and placed in a screw-top vial. The vial was charged with 19.8 mg of 1.2,4,5 tetramethylbenzene and diluted with ≈ 2 mL of $CDCl_3$. The contents of the vial were thoroughly mixed by shaking the sealed vessel. A quantitative ^{1}H NMR spectrum was obtained. Weight percent of the product in solution was determined by integration of the CH_3 of the product relative to the CH of the standard. Using this value (1.23 wt%) and the total mass of solution (5.89 g) the yield (0.07245 g, 91%) could be determined.

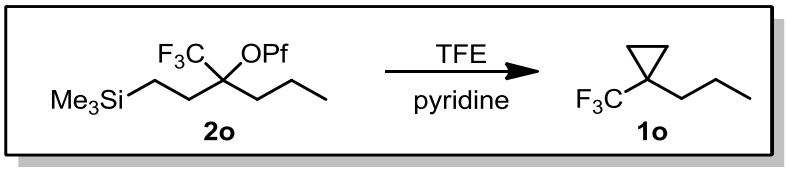
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.48 - 0.54 (m, 2 H) 0.94 (t, *J* = 6.00 Hz, 2 H) 1.27 (s, 3 H)



[49] Note that due to being observed as a reaction mixture, the bridgehead peaks for this particular cyclopropane was obscured. To assist in visualization, the mixture was transferred to a vial equipped with a stir bar. To this vial was added 0.50mL of D_2O, three drops of a 30% w.w. NaOD solution in D_2O, and 1mL of $CDCl_3$. The solution was stirred for fifteen minutes. After this time, the phases were separated by careful pipetting and the organic layer was washed three times with D_2O, and dried with Na_2SO_4. This was then transferred to a micro-distillation apparatus and liquid was collected from 75°C-92°C. The collected material was then poured into a screw-top vial, 1 mL of D_2O was added, and the vial shaken. The top layer was disposed and the bottom layer dried with Na_2SO_4. An NMR was taken, but residual impurities remained and this entire process was repeated an additional time. A new NMR spectrum was acquired showing acceptable visualization of the desired peaks.

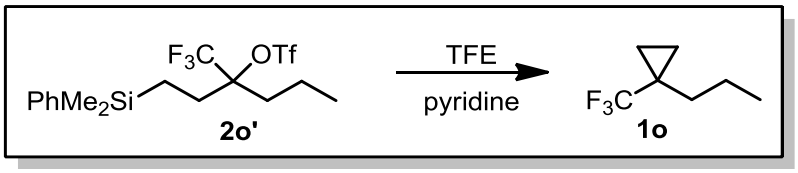
1-(trifluoromethyl)-1-methylcyclopropane (1n′) was solvolyzed according to the representative NMR-scale solvolysis procedure from **2n′** (0.570 g, 0.883 mmol, 1 equiv, 79.5 wt%). Yield was determined by weight percent assay using 1.2,4,5 tetramethylbenzene as a standard. Using this method, the yield (0.104 g, 95%) was determined.

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.48 - 0.54 (m, 2 H) 0.94 (t, *J* = 6.00 Hz, 2 H) 1.27 (s, 3 H)



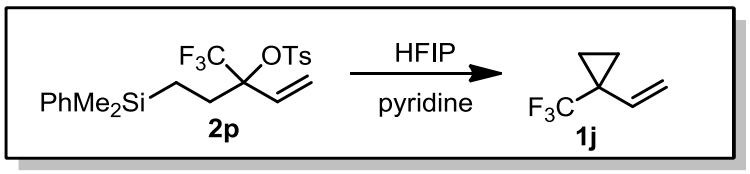
1-propyl-1-(trifluoromethyl)cyclopropane (1o) was solvolyzed according to the representative NMR-scale solvolysis procedure from **2o** (0.050 g, 0.106 mmol, 1 equiv. ^{1}H NMR yield was determined to be 91% using the representative protocol for determining yield by NMR.

^{1}H NMR (300 MHz, CF_3CD_2OD) δ ppm 0.52 - 0.58 (m, 2 H) 0.87 - 0.95 (m, 5 H) 1.39 - 1.49 (m, 2 H) 1.50 - 1.57 (m, 2 H)



1-propyl-1-(trifluoromethyl)cyclopropane (1o) was solvolyzed according to the representative NMR-scale solvolysis procedure from **2o′** (0.240 g, 0.165 mmol, 1 equiv, 30 wt%). Yield was determined by weight percent assay using dimethyl fumarate as a standard. Using this method, the yield (0.0246 g, 98%) was determined.

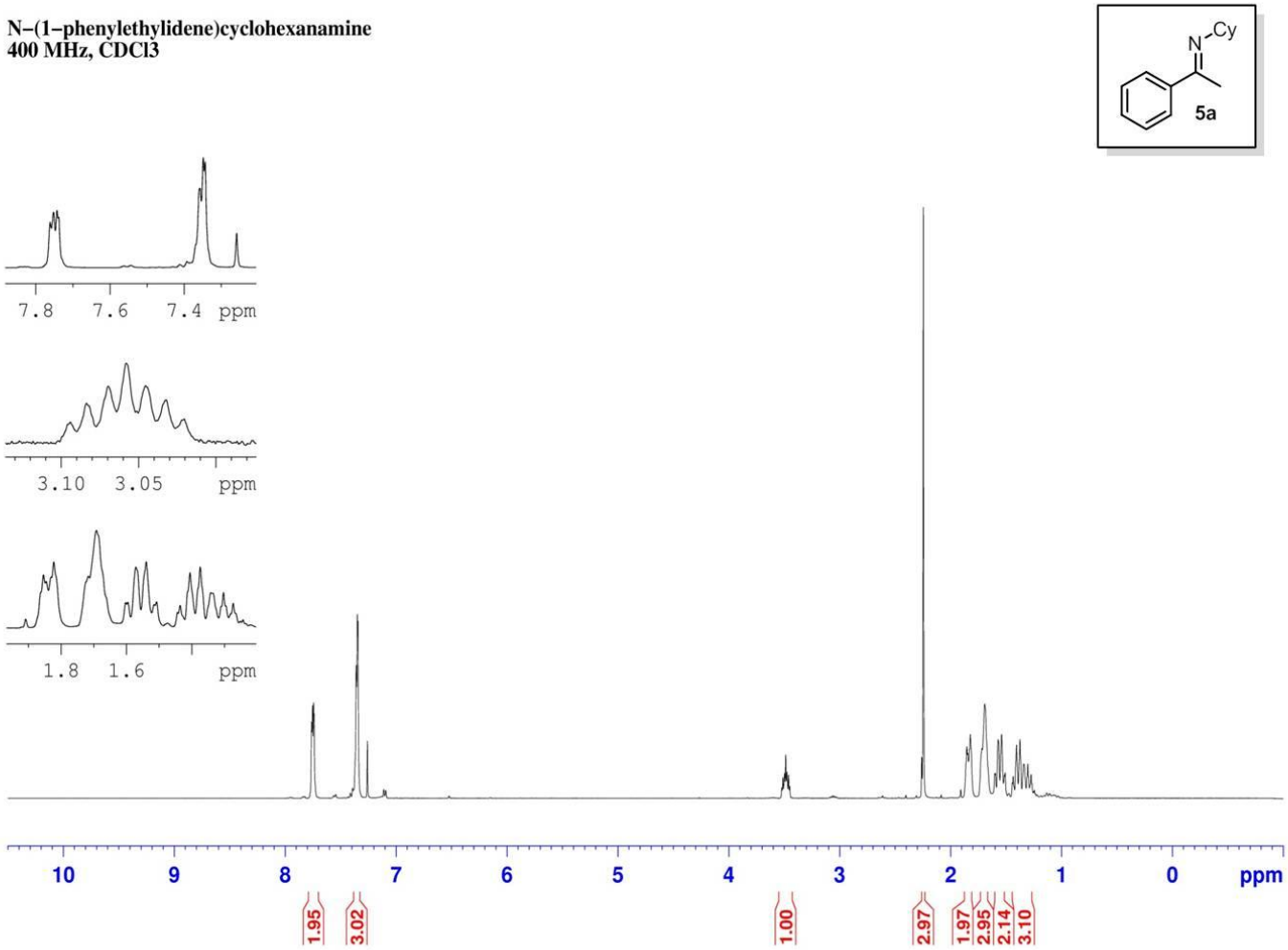
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.52 - 0.58 (m, 2 H) 0.87 - 0.95 (m, 5 H) 1.39 - 1.49 (m, 2 H) 1.50 - 1.57 (m, 2 H)



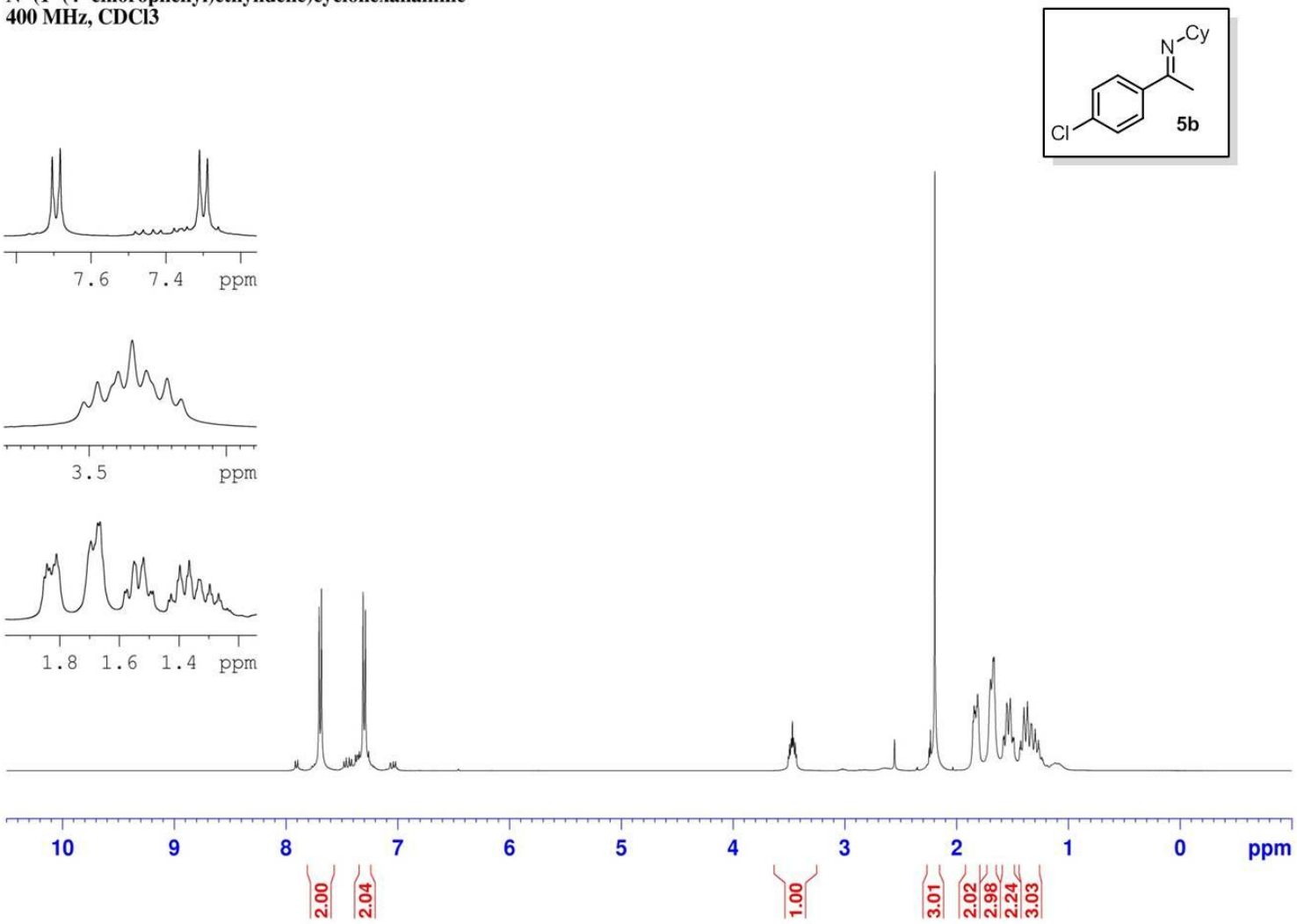
1-(trifluoromethyl)-1-vinylcyclopropane (1j) was solvolyzed according to the representative NMR-scale solvolysis procedure in HFIP from **2p** (0.066 g, 0.149 mmol, 1 equiv). ^{1}H NMR yield was determined to be 68% using the representative protocol for determining yield by NMR.

^{1}H NMR (400 MHz, CF_3CD_2OD) δ ppm 0.82 - 0.90 (m, 2 H) 1.13 - 1.20 (m, 2 H) 5.14 (d, *J* = 7.79 Hz, 1 H) 5.17 - 5.19 (m, 1 H) 6.00 (dd, *J* = 17.32, 10.90 Hz, 2 H)

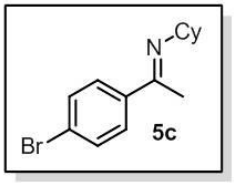
^{1}H-NMR Spectra of Synthesized Compounds

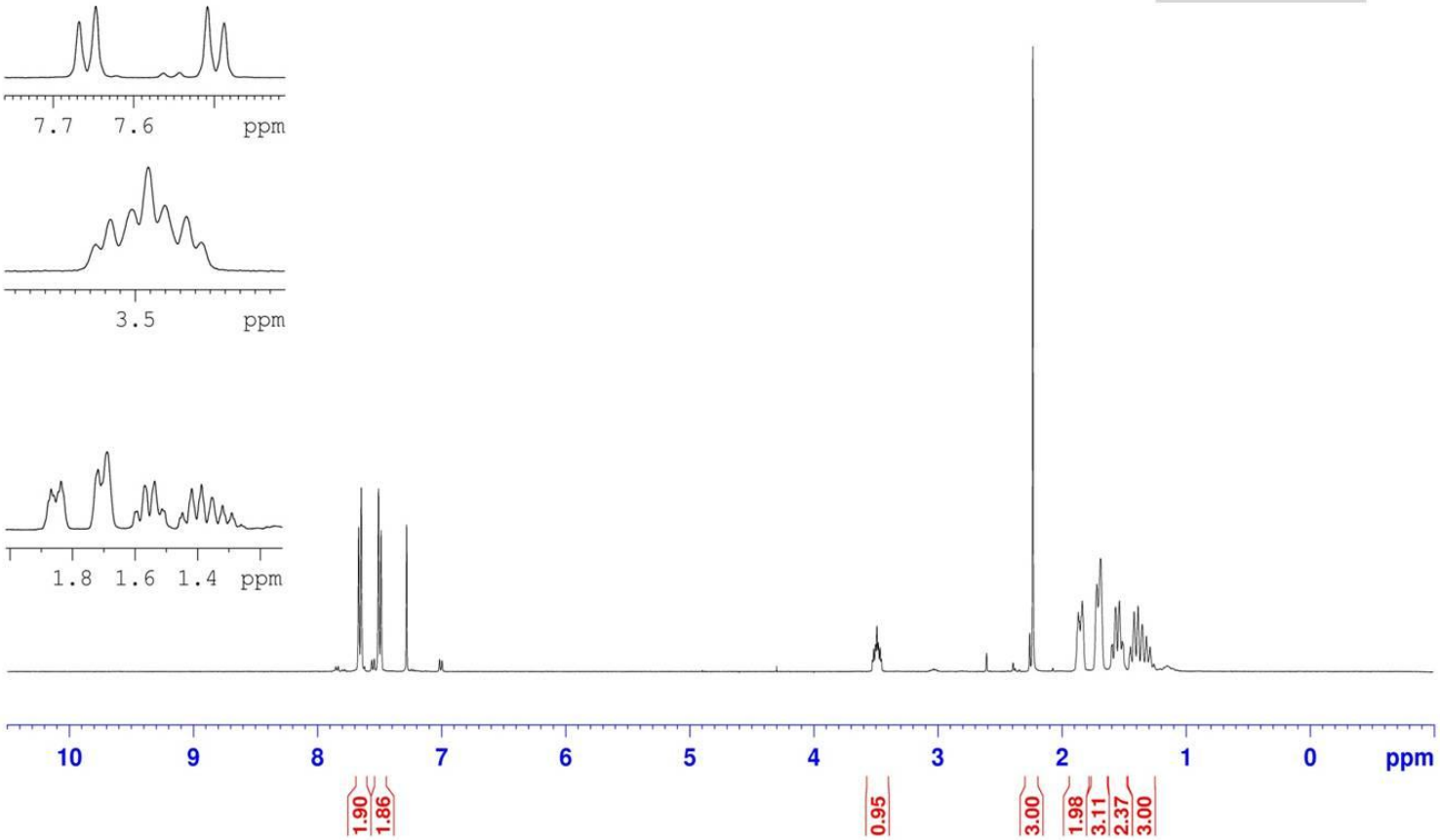


N–(1–(4–chlorophenyl)ethylidene)cyclohexanamine
400 MHz, CDCl3

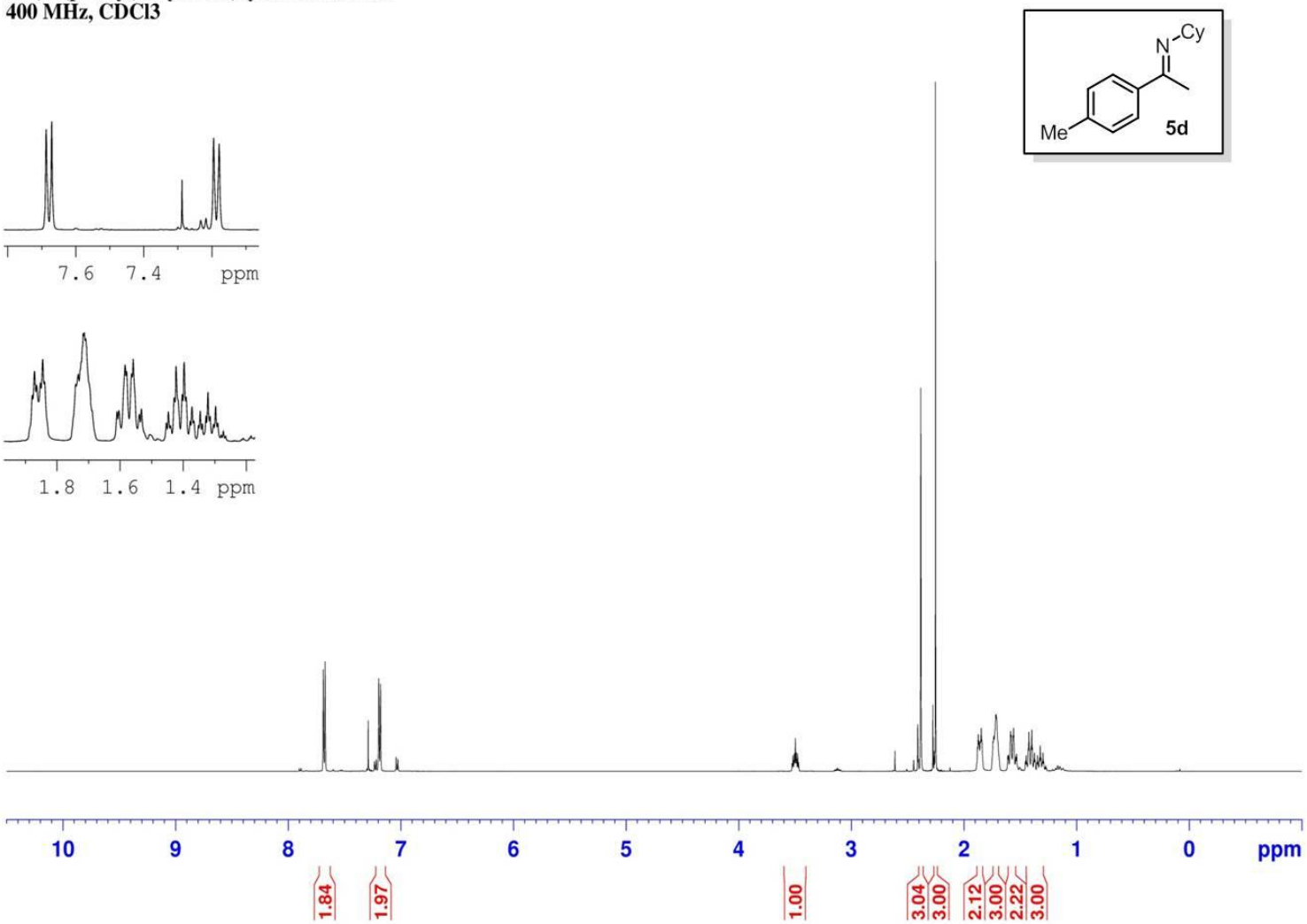


N–(1–(4–bromophenyl)ethylidene)cyclohexanamine
400 MHz, CDCl3

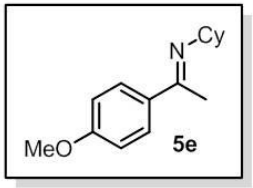


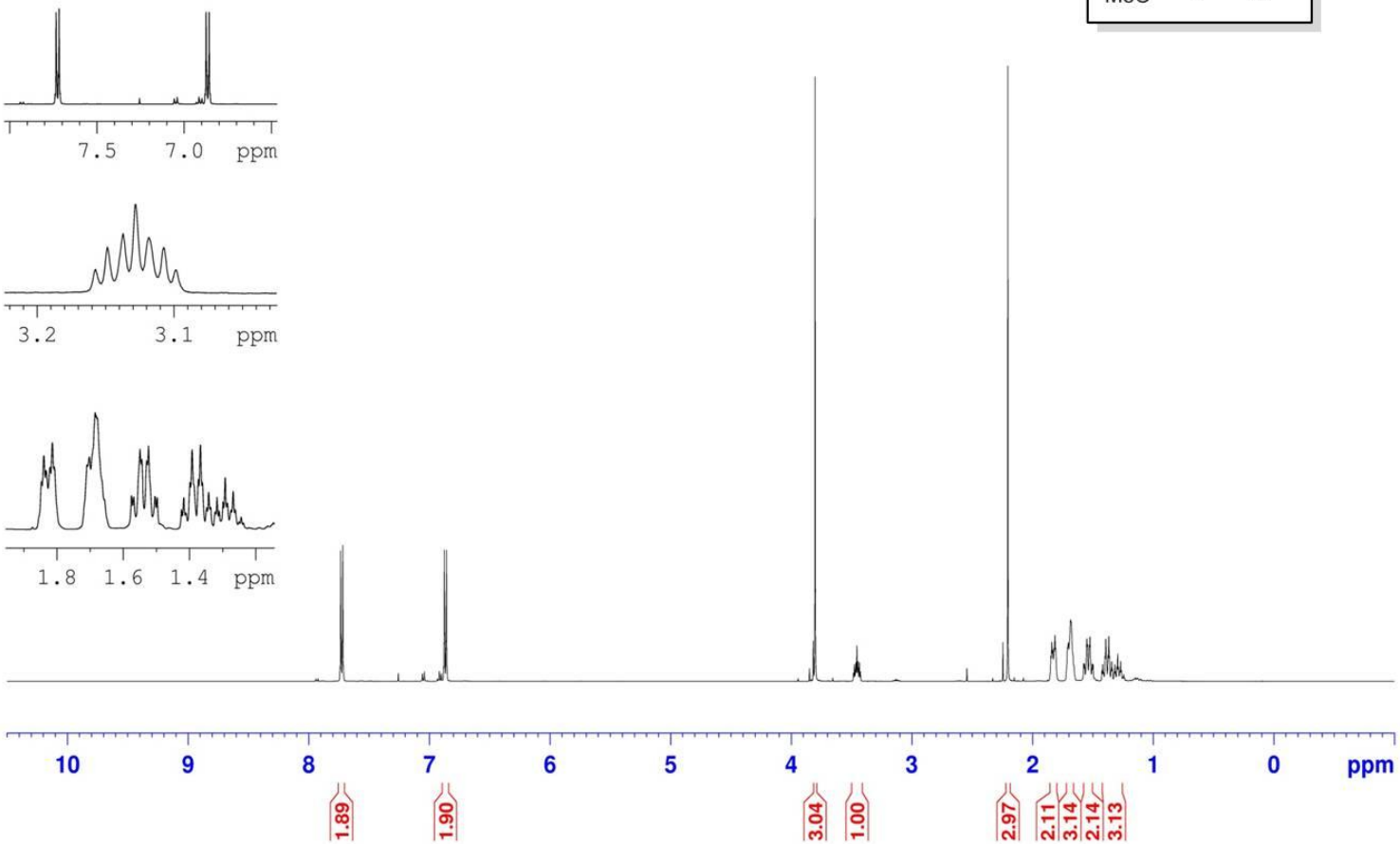


N–(1–(p–tolyl)ethylidene)cyclohexanamine
400 MHz, CDCl3

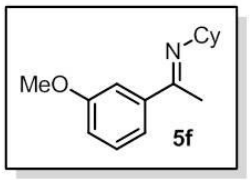


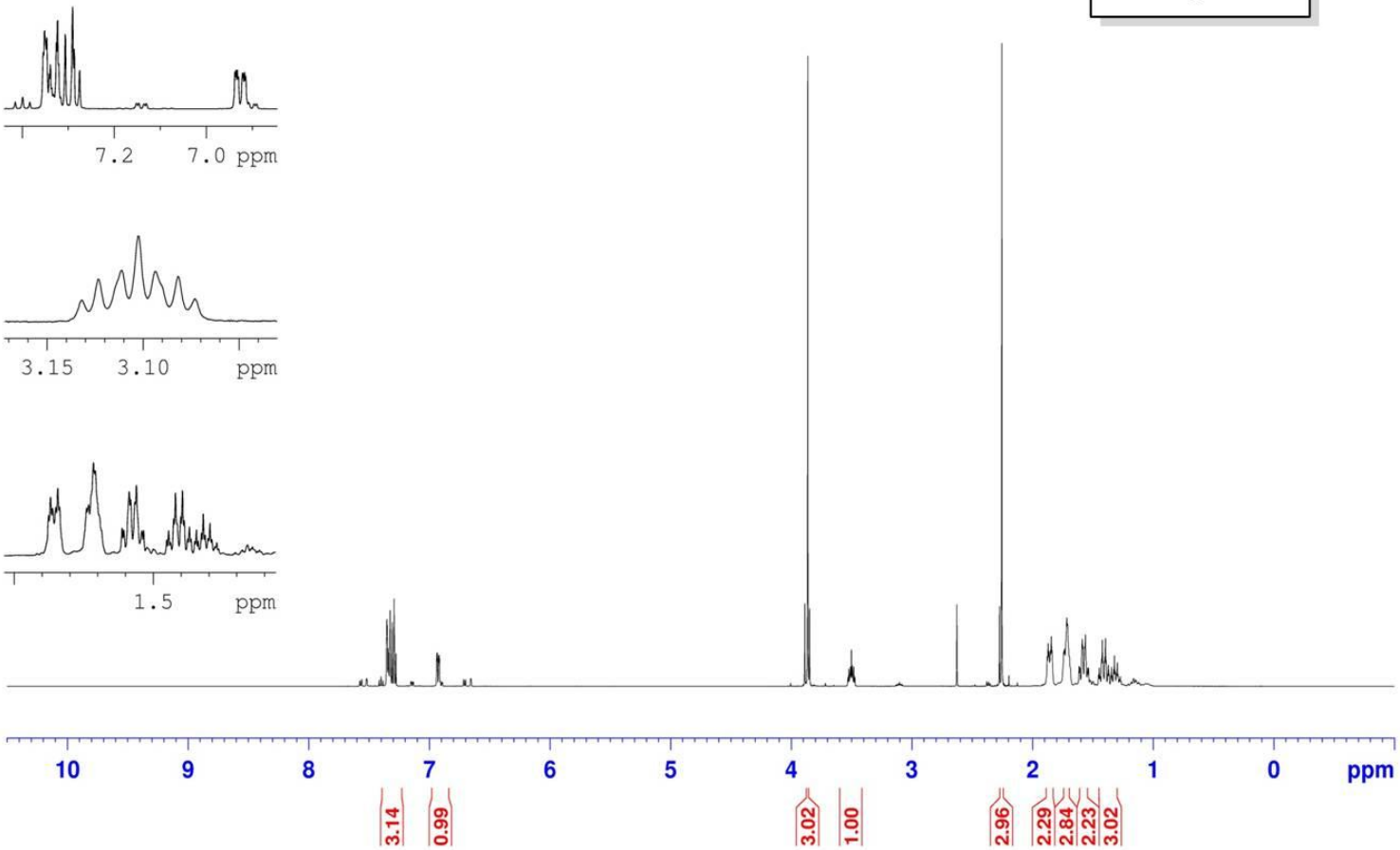
N–(1–(4–methoxyphenyl)ethylidene)cyclohexanamine
400 MHz, CDCl3



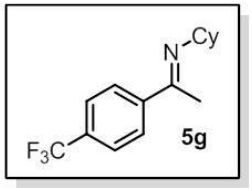


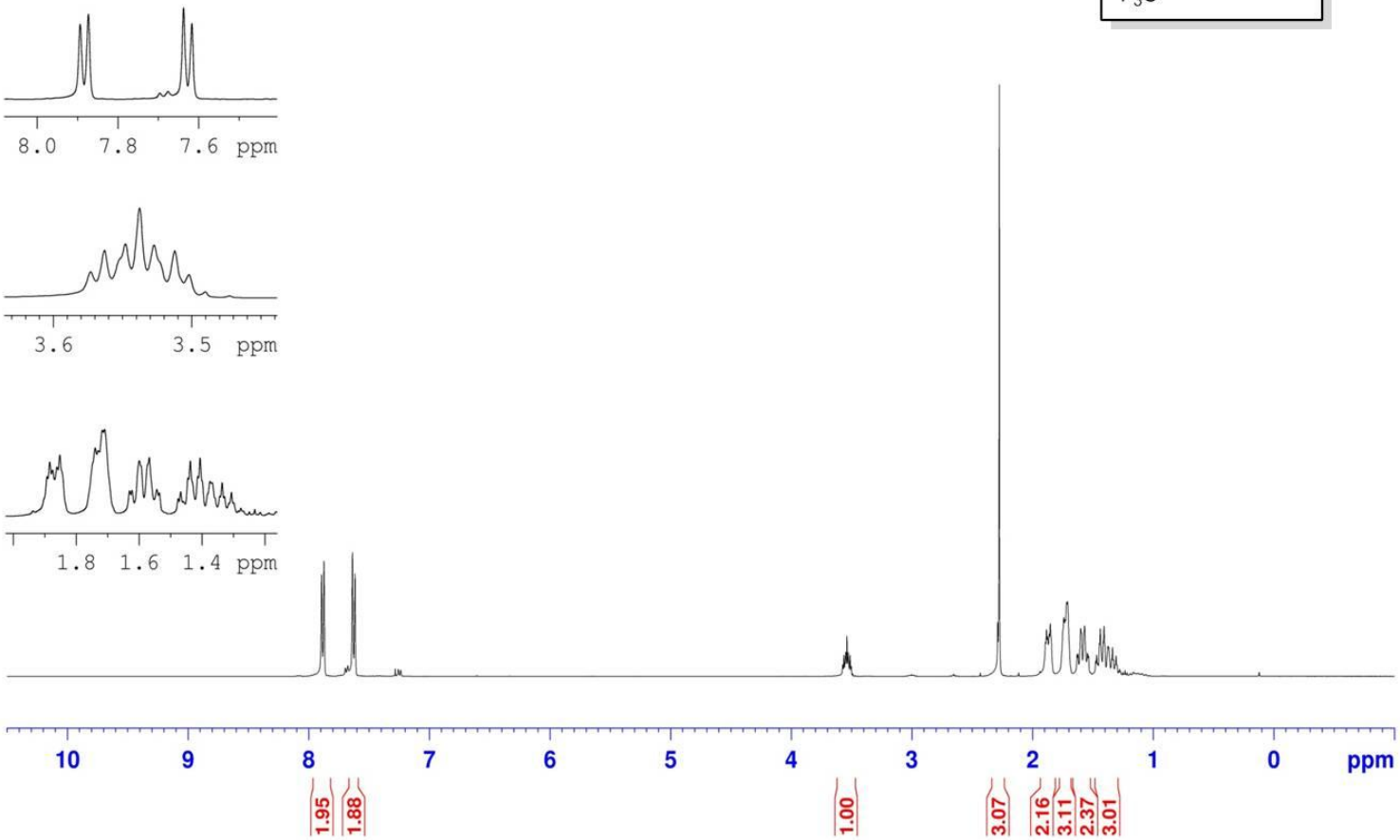
N–(1–(3–methoxyphenyl)ethylidene)cyclohexanamine
400 MHz, CDCl3



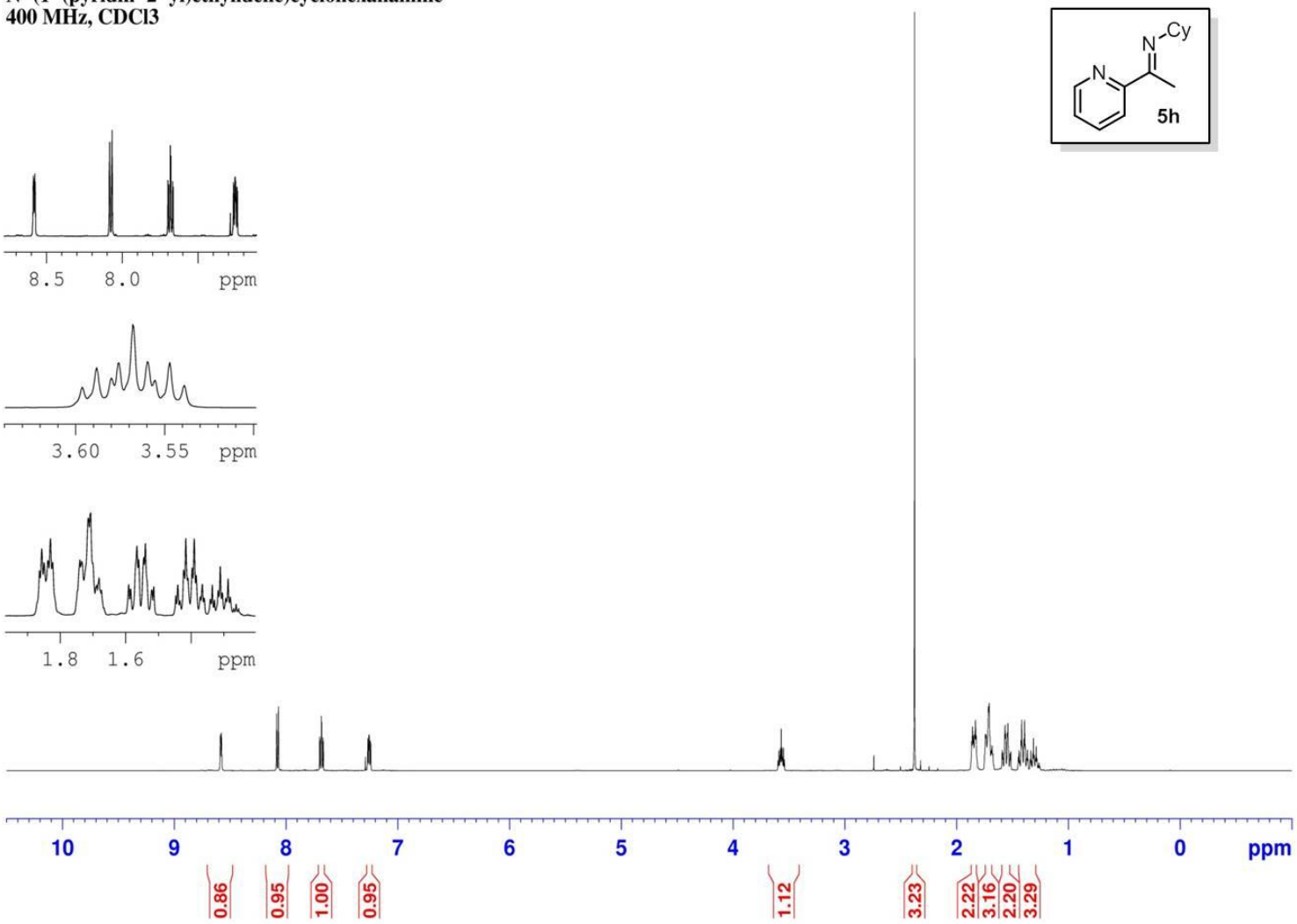


N–(1–(4–(trifluoromethyl)phenyl)ethylidene)cyclohexanamine
400 MHz, CDCl3

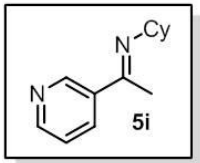


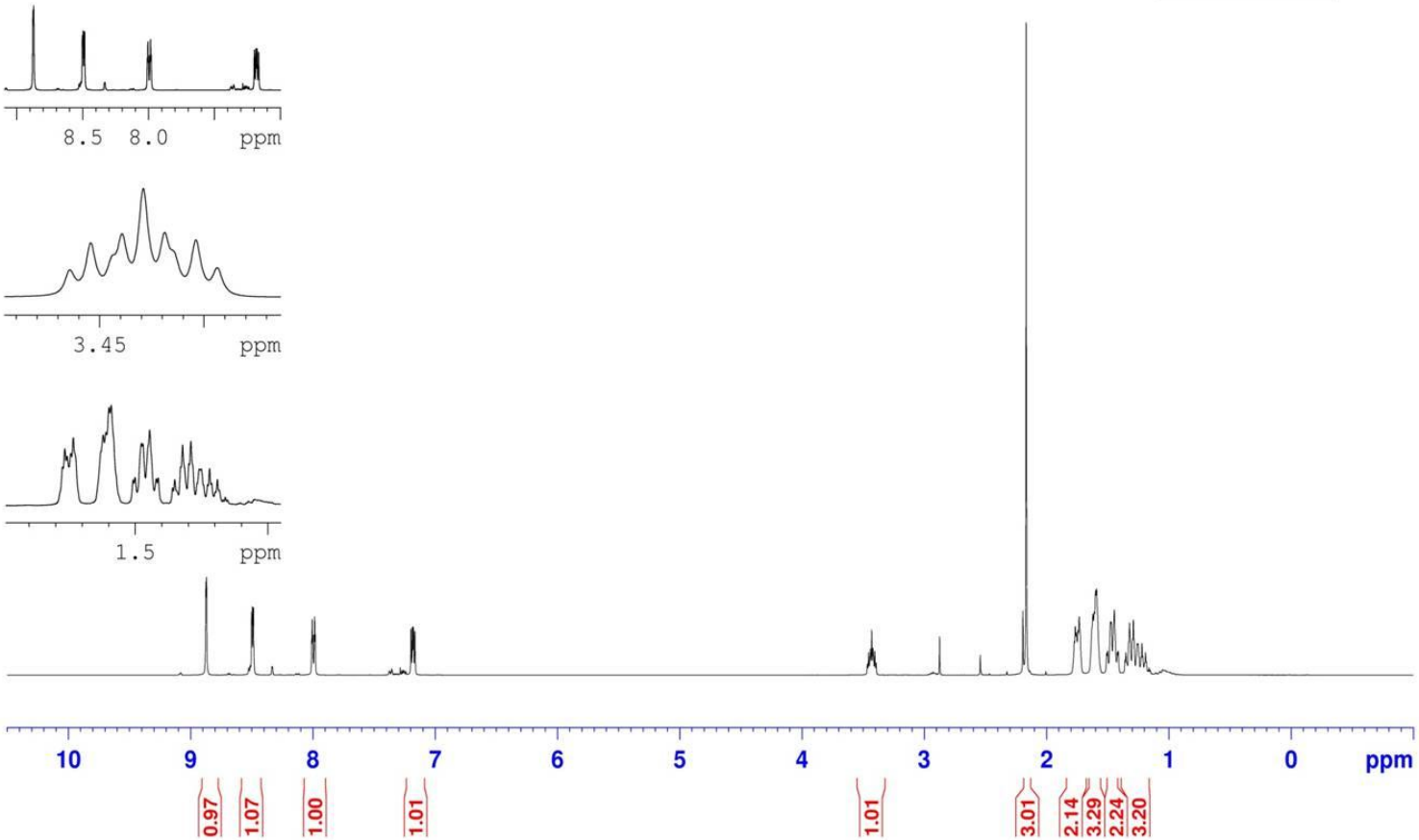


N–(1–(pyridin–2–yl)ethylidene)cyclohexanamine
400 MHz, CDCl3

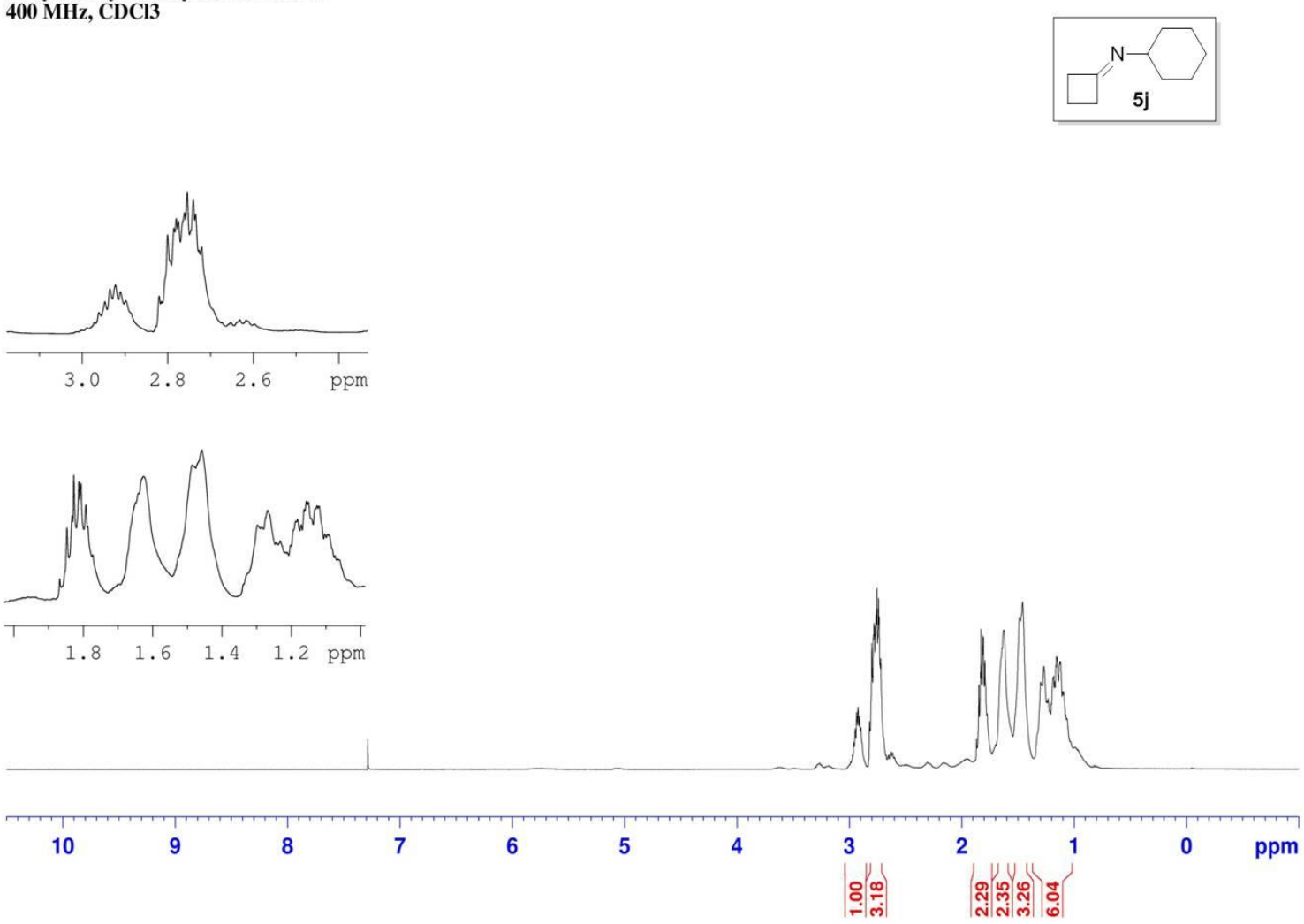


N–(1–(pyridin–3–yl)ethylidene)cyclohexanamine
400 MHz, CDCl3

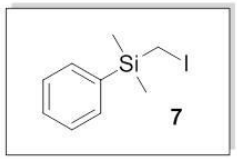


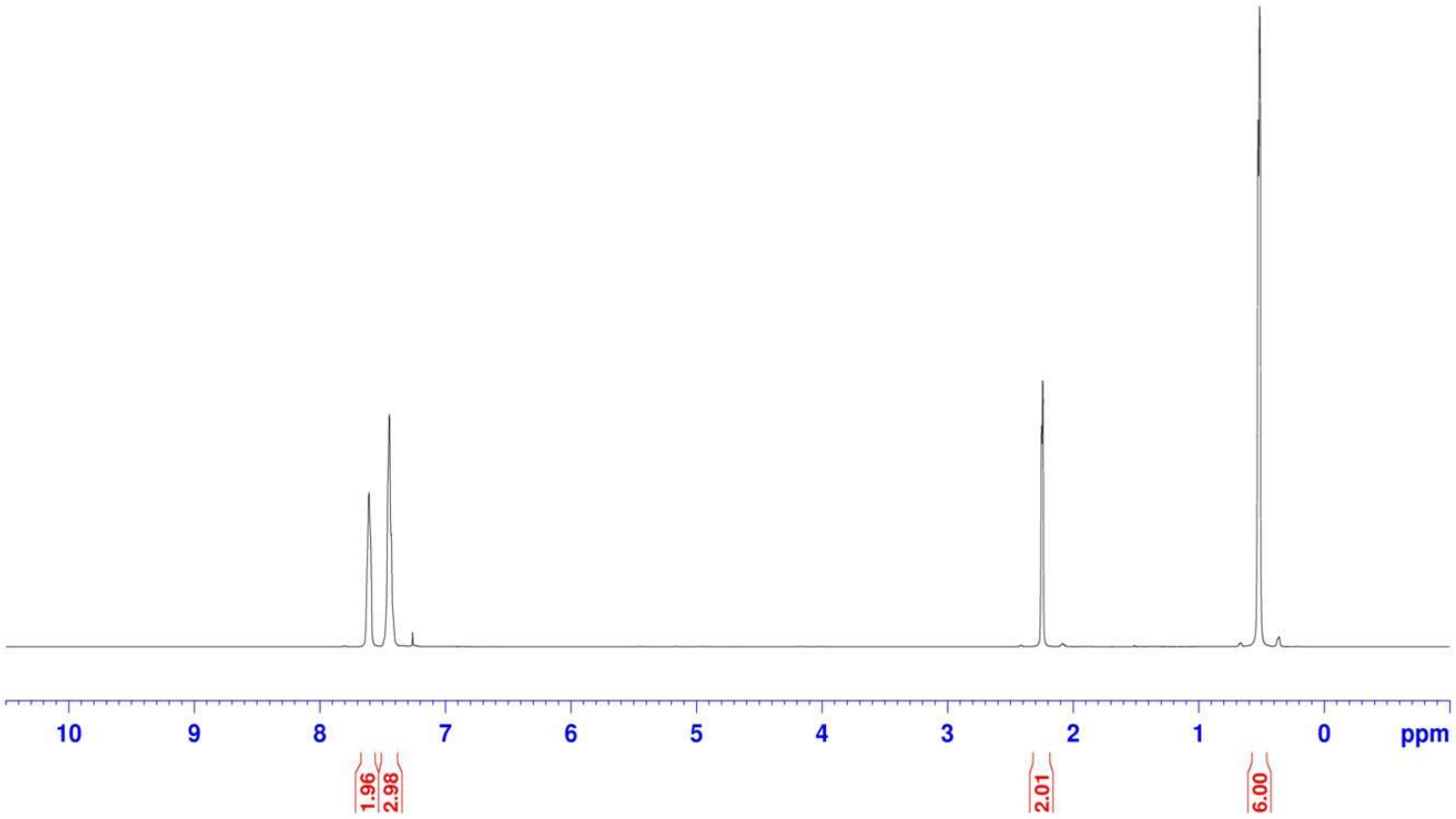


N–cyclobutylidenecyclohexanamine
400 MHz, CDCl3

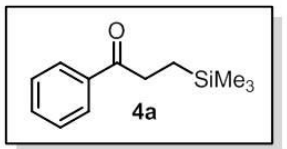


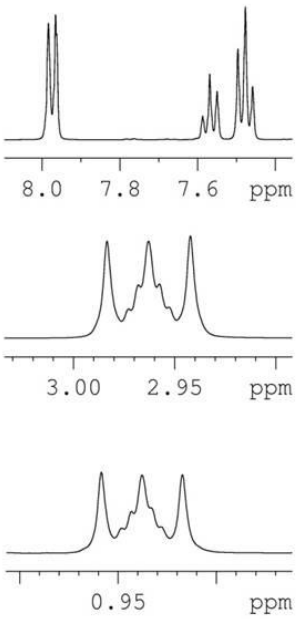
(iodomethyl)dimethyl(phenyl)silane
400 MHz, CDCl3



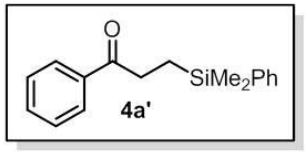


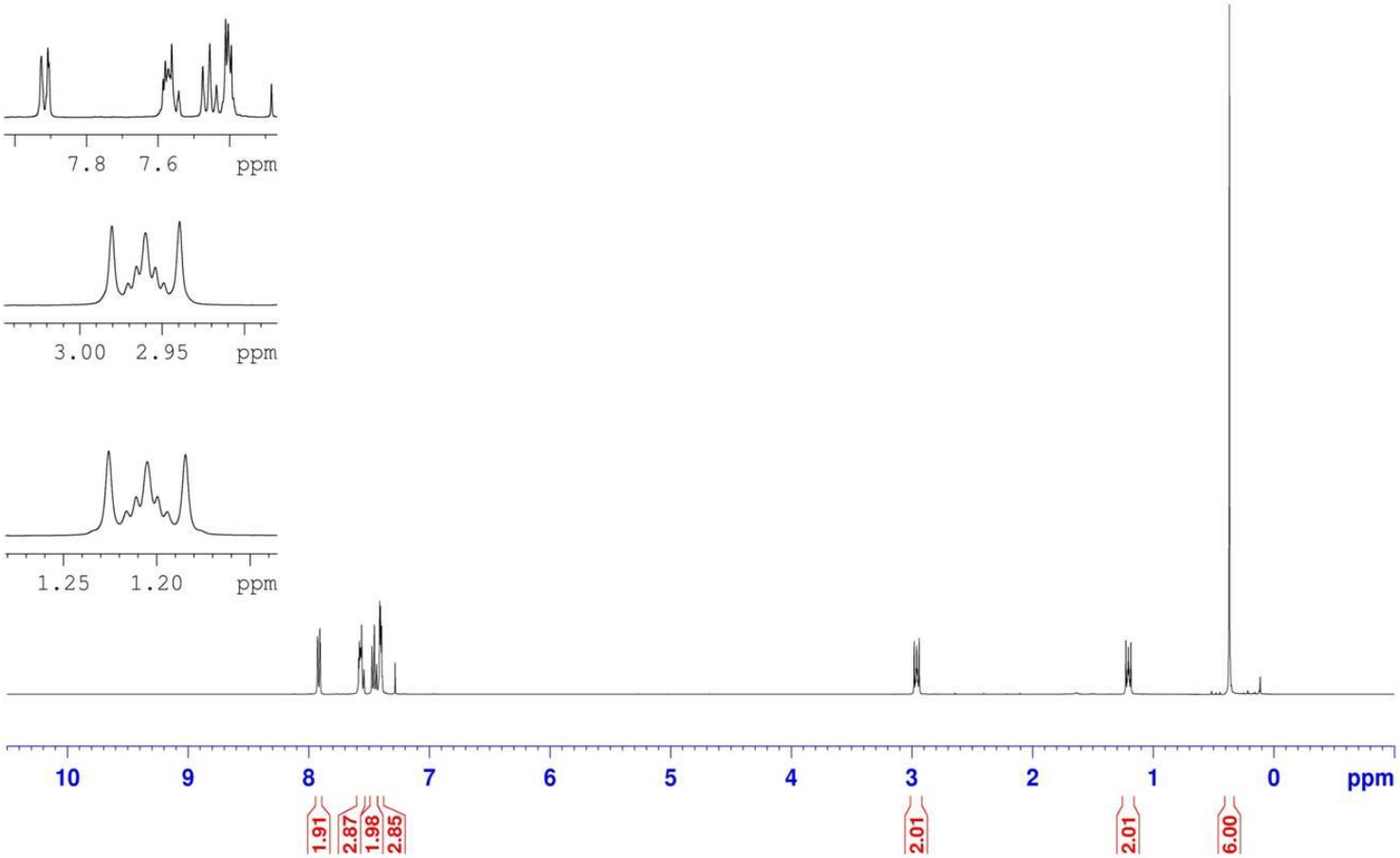
1–phenyl–3–(trimethylsilyl)propan–1–one
400 MHz, CDCl3



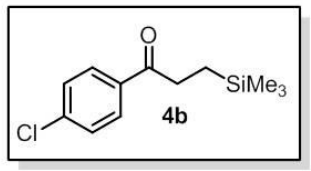


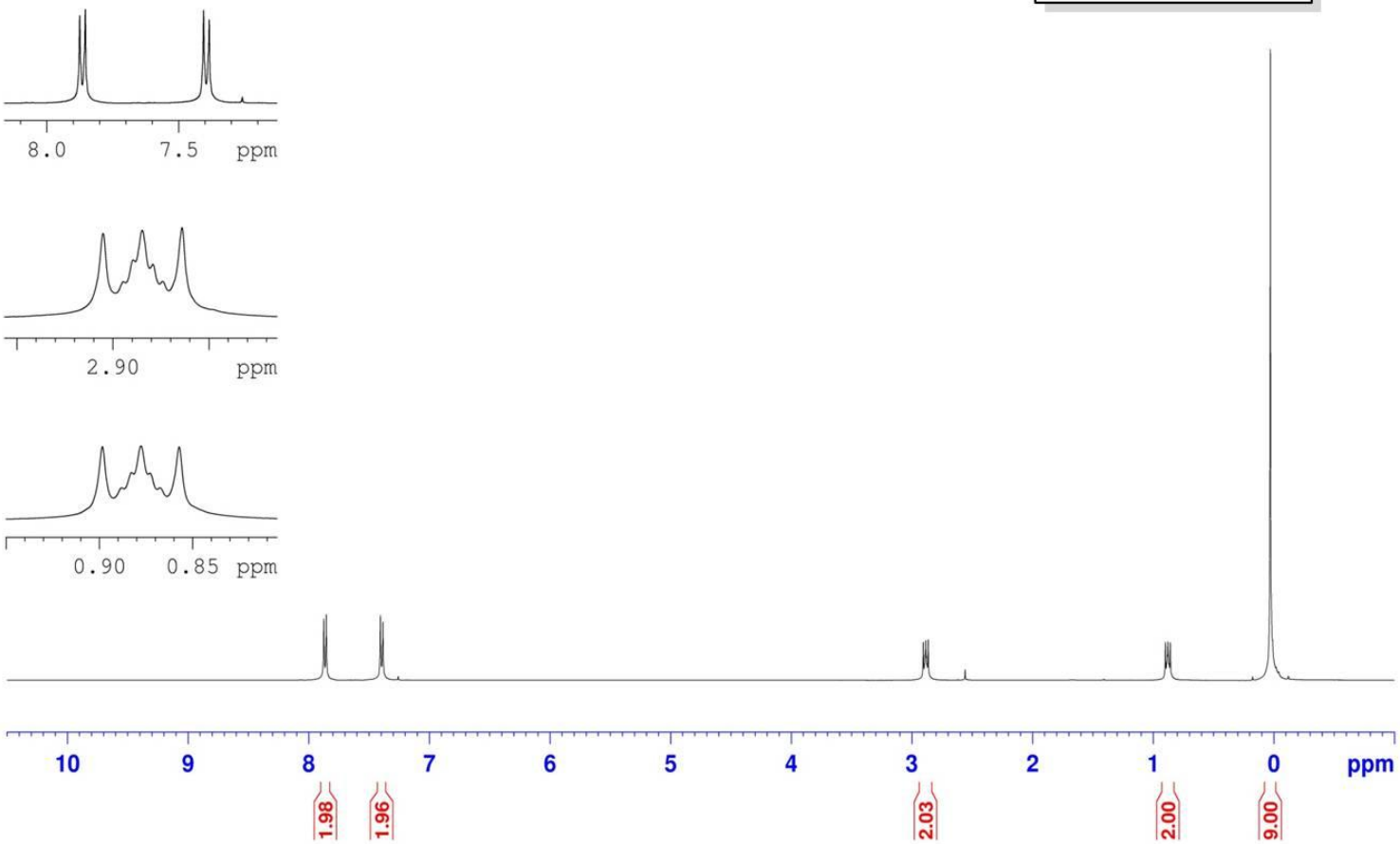
3–(dimethyl(phenyl)silyl)–1–phenylpropan–1–one
400 MHz, CDCl3



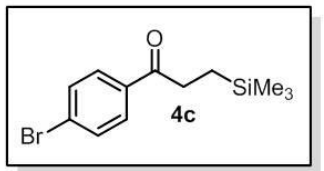


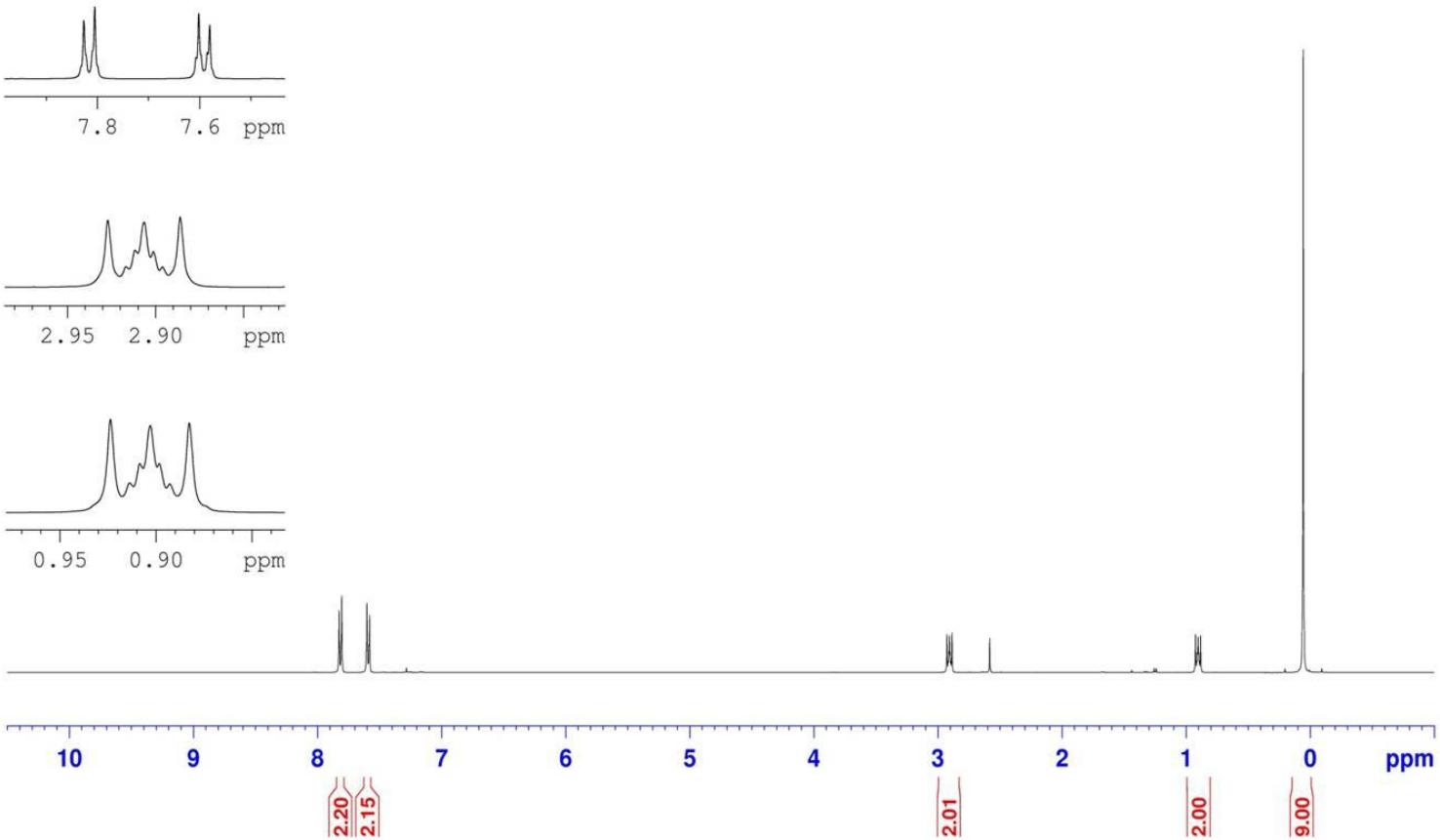
1–(4–chlorophenyl)–3–(trimethylsilyl)propan–1–one
400 MHz, CDCl3



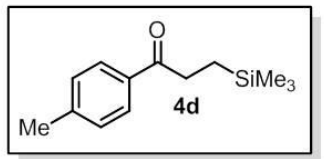


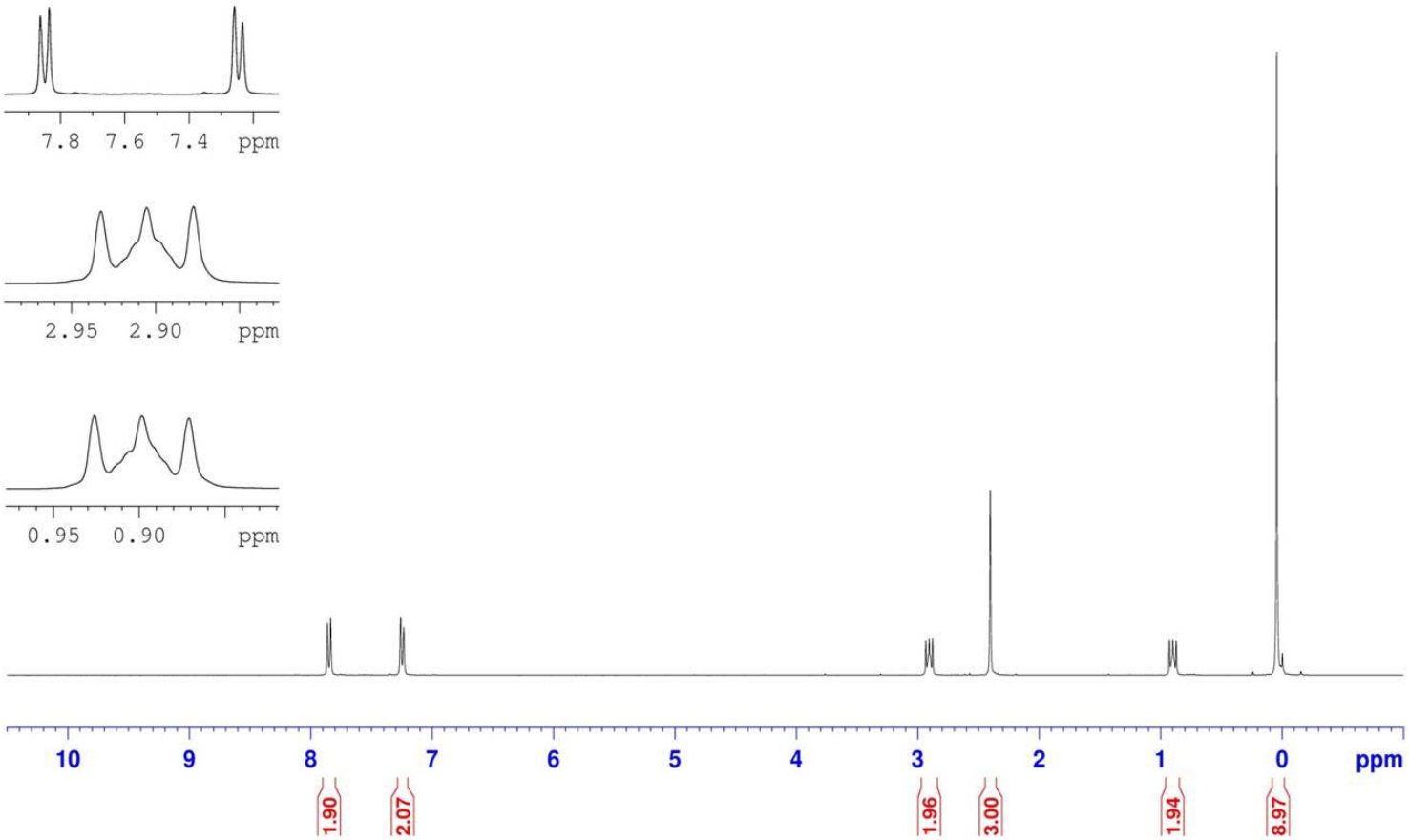
1–(4–bromophenyl)–3–(trimethylsilyl)propan–1–one
400 MHz, CDCl3



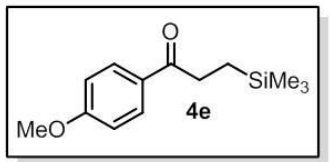


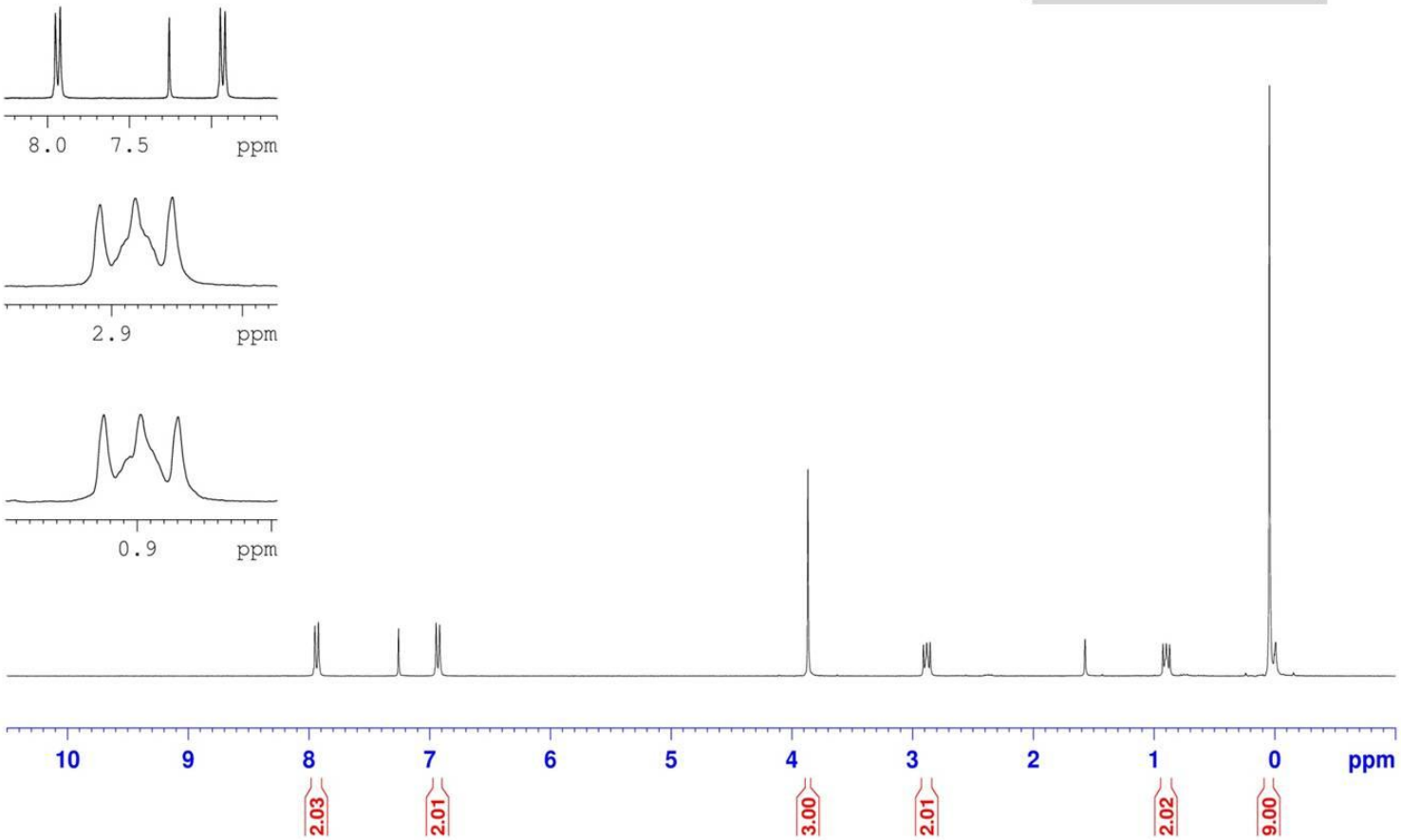
1–(p–tolyl)–3–(trimethylsilyl)propan–1–one
400 MHz, CDCl3



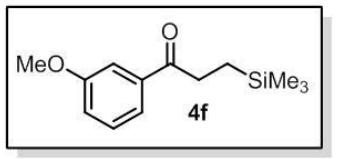


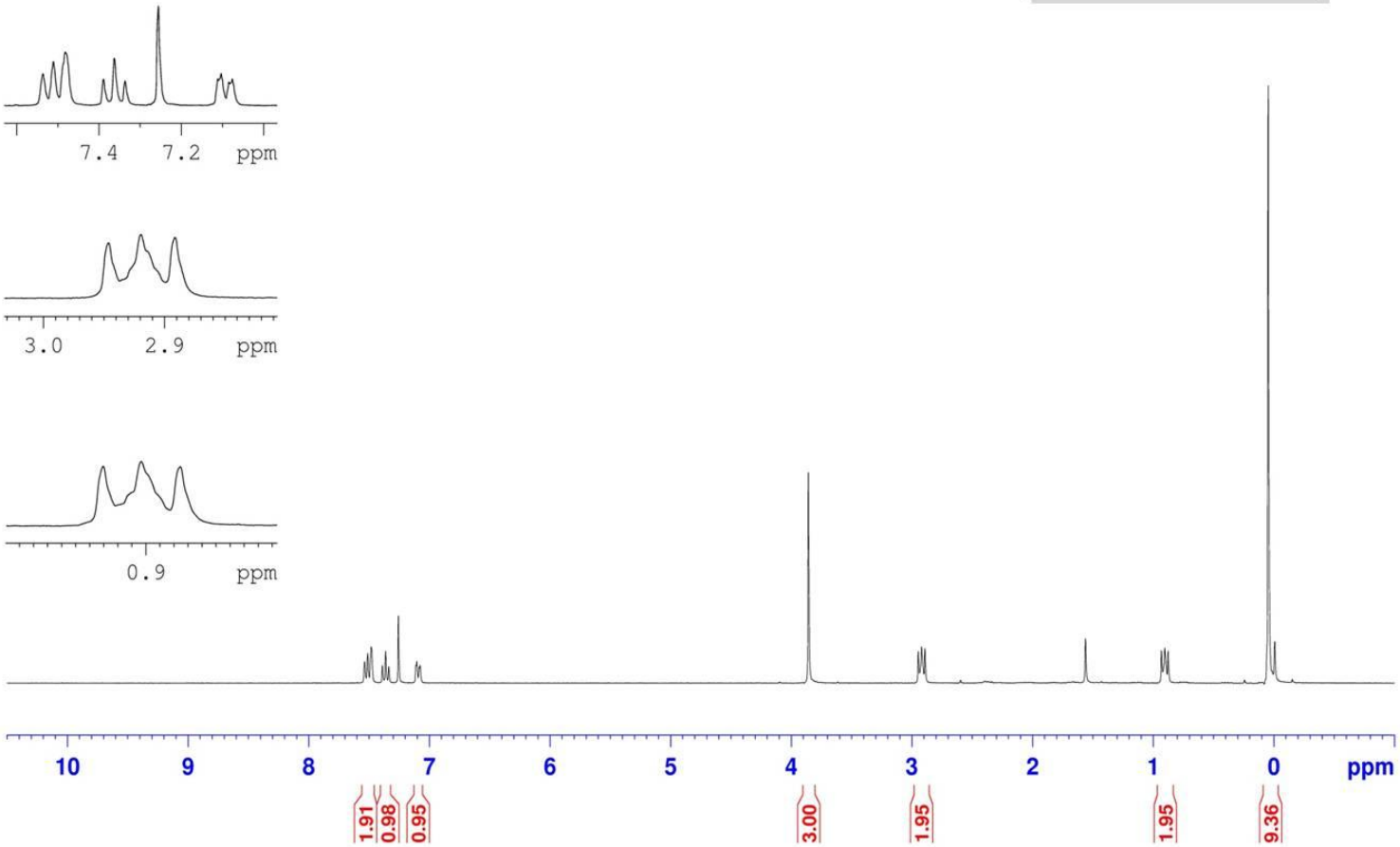
1–(4–methoxyphenyl)–3–(trimethylsilyl)propan–1–one
400 MHz, CDCl3



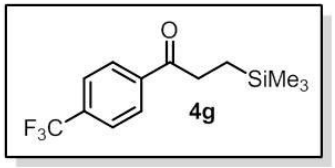


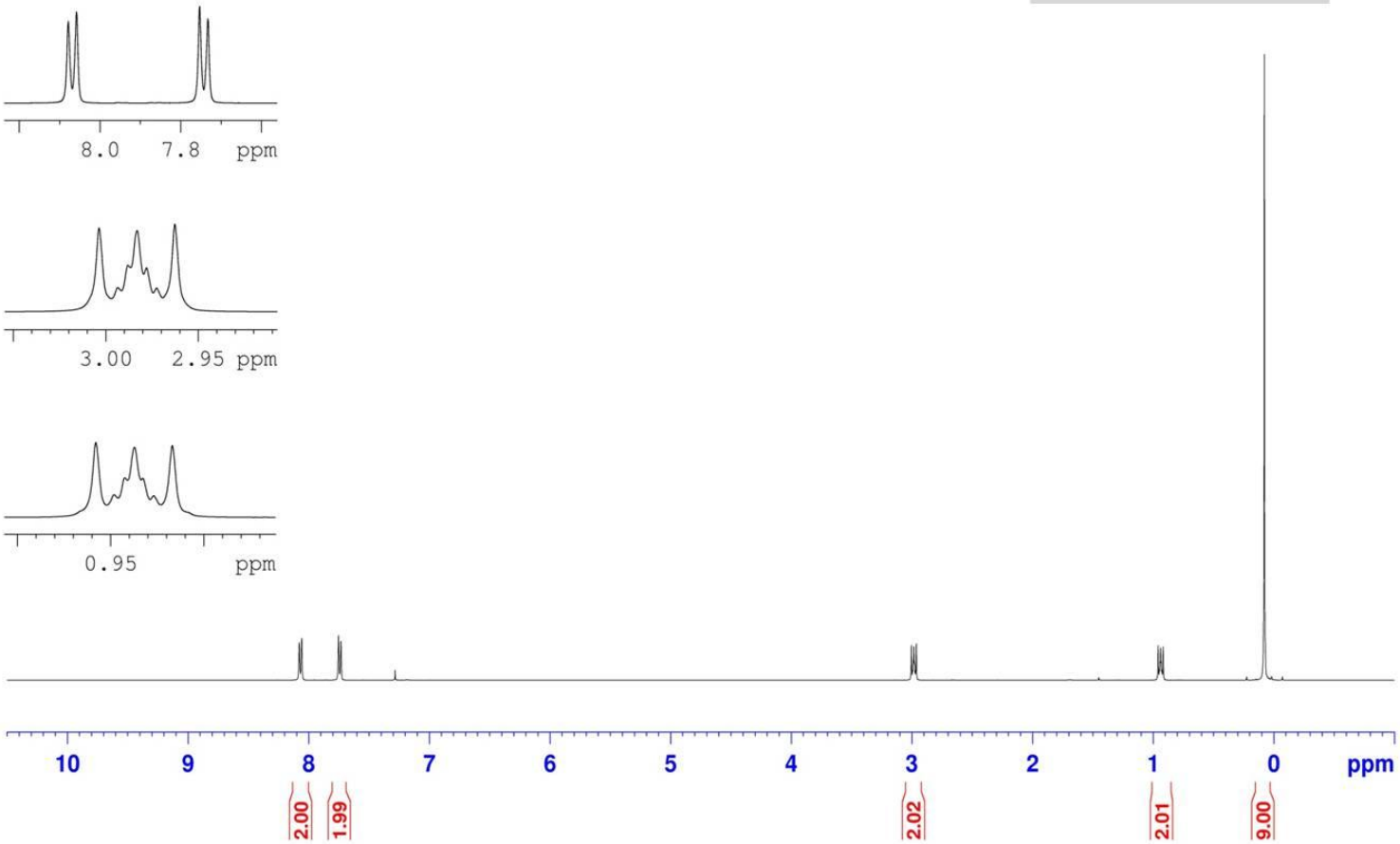
1–(3–methoxyphenyl)–3–(trimethylsilyl)propan–1–one
400 MHz, CDCl3



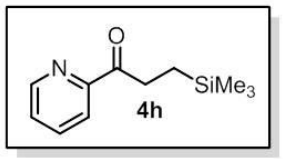


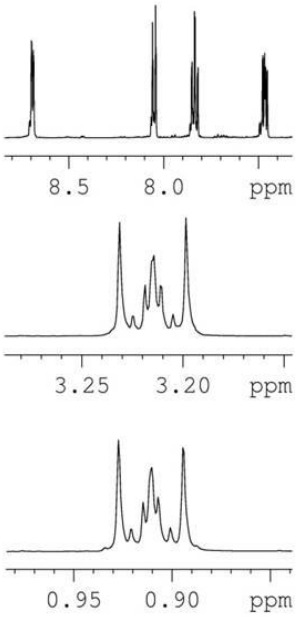
1–(4–(trifluoromethyl)phenyl)–3–(trimethylsilyl)propan–1–one
400 MHz, CDCl3





1–(pyridin–2–yl)–3–(trimethylsilyl)propan–1–one
400 MHz, CDCl3





1–(pyridin–3–yl)–3–(trimethylsilyl)propan–1–one
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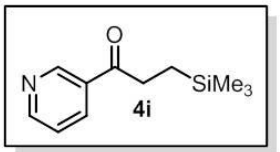
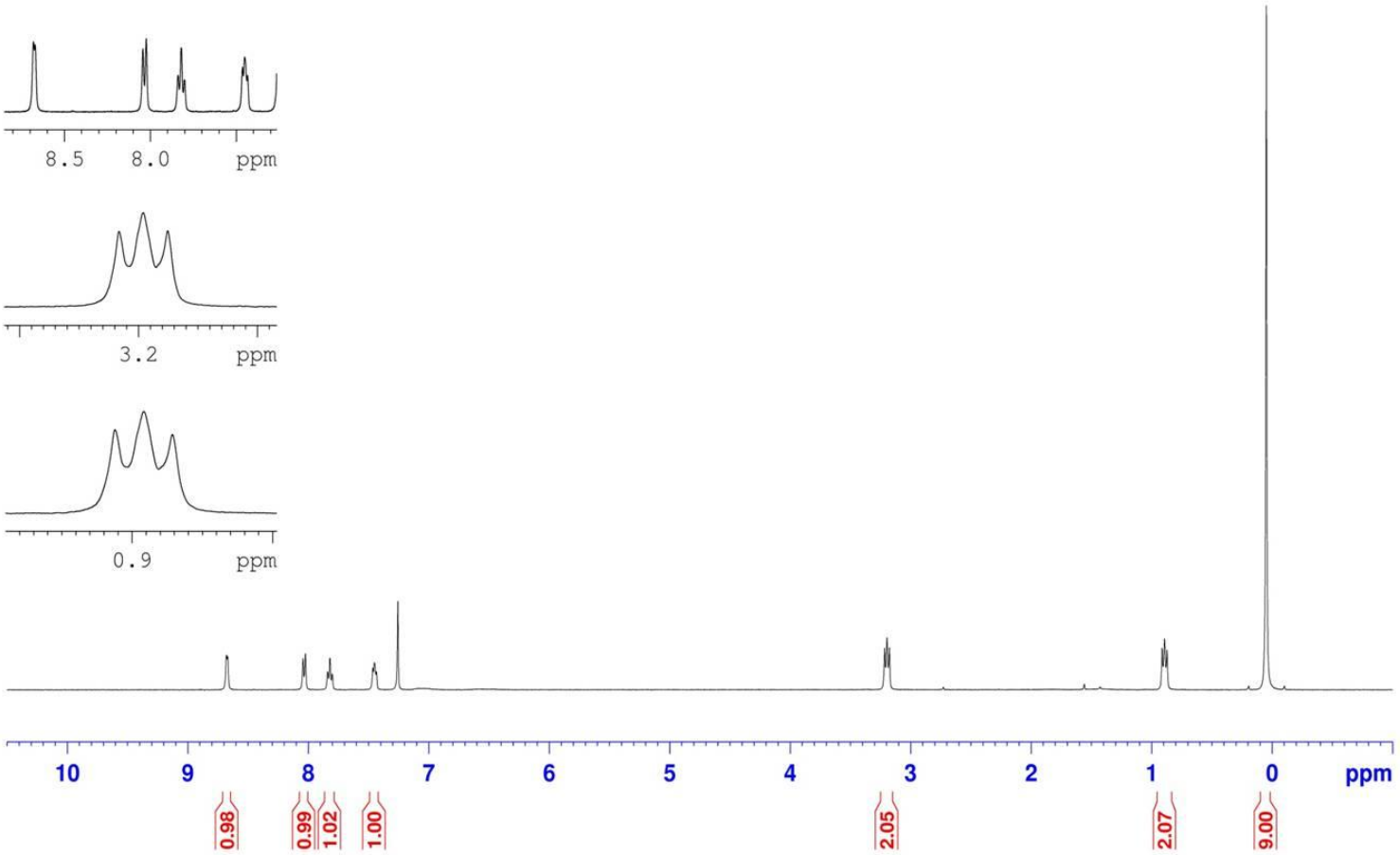
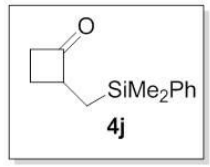
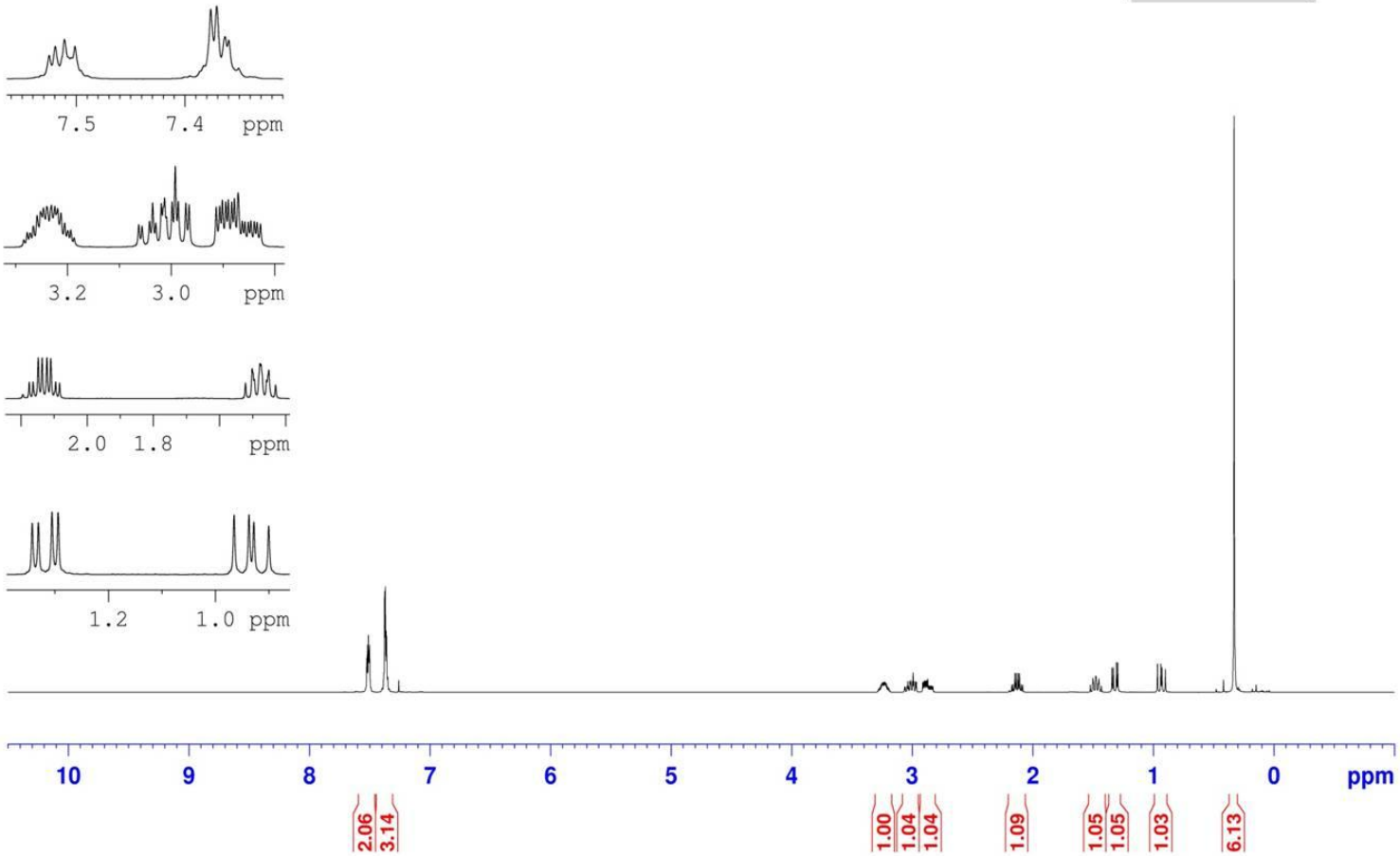


4i

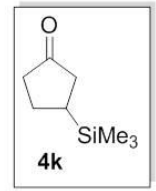


2–((dimethyl(phenyl)silyl)methyl)cyclobutanone
400 MHz, CDCl3

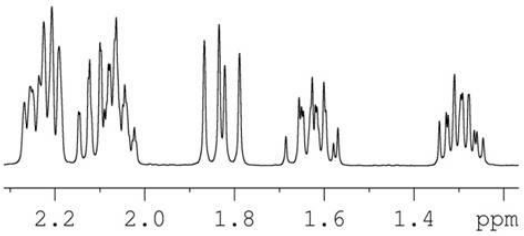




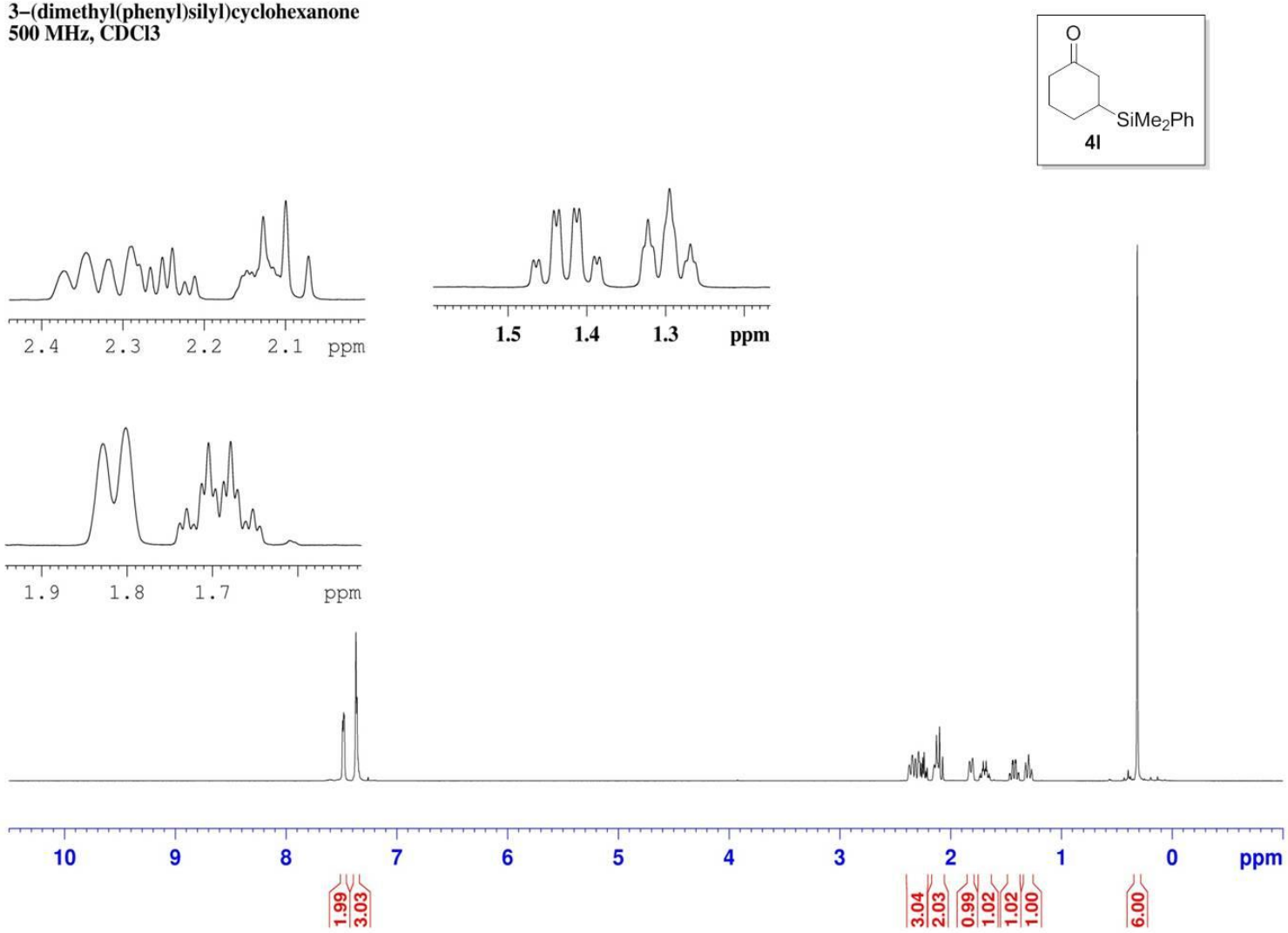
3–(trimethylsilyl)cyclopentanone
400 MHz, CDCl3



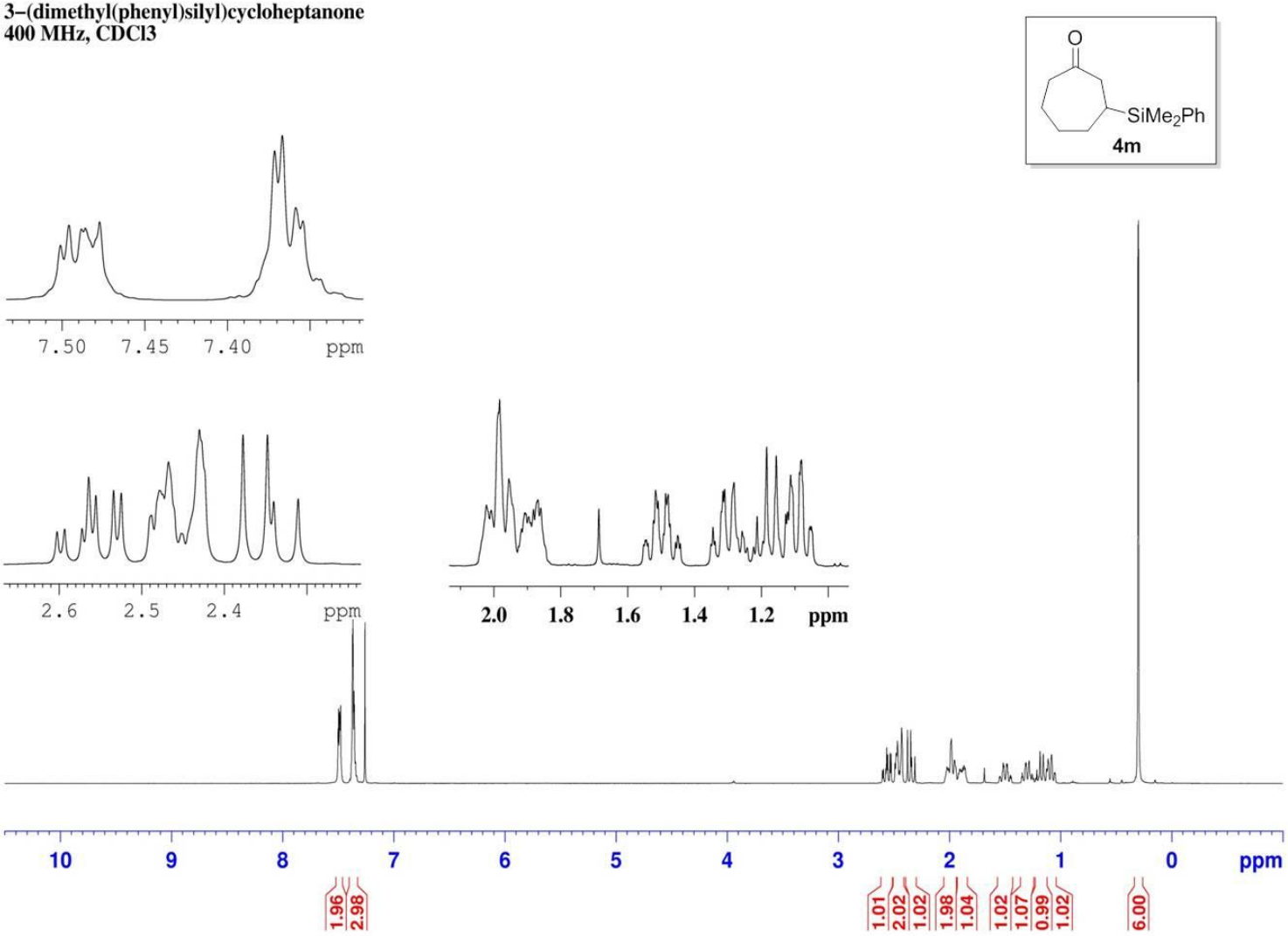
4k



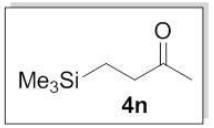
3–(dimethyl(phenyl)silyl)cyclohexanone
500 MHz, CDCl3

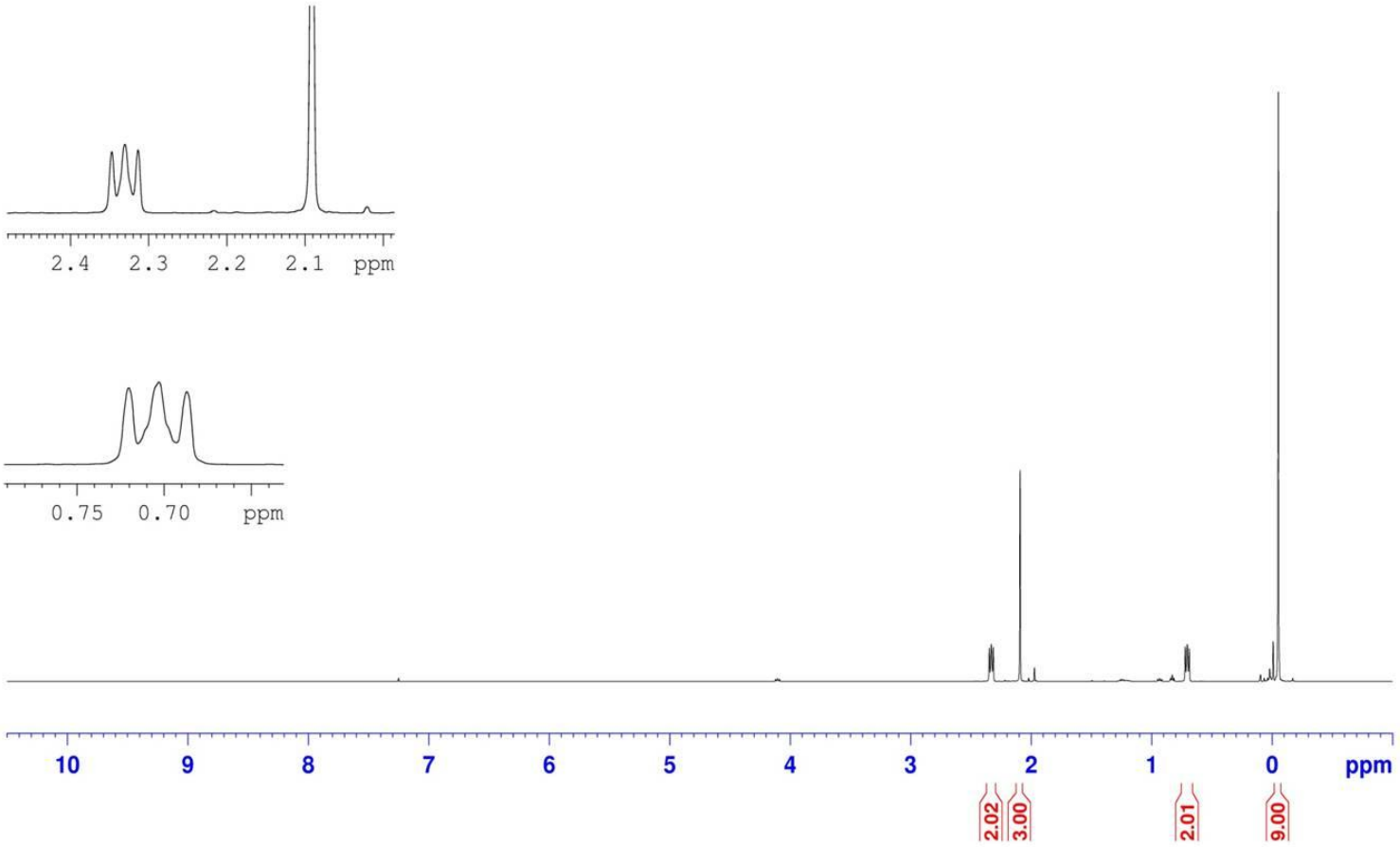


3–(dimethyl(phenyl)silyl)cycloheptanone
400 MHz, CDCl3

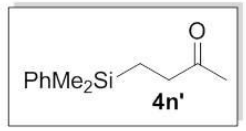


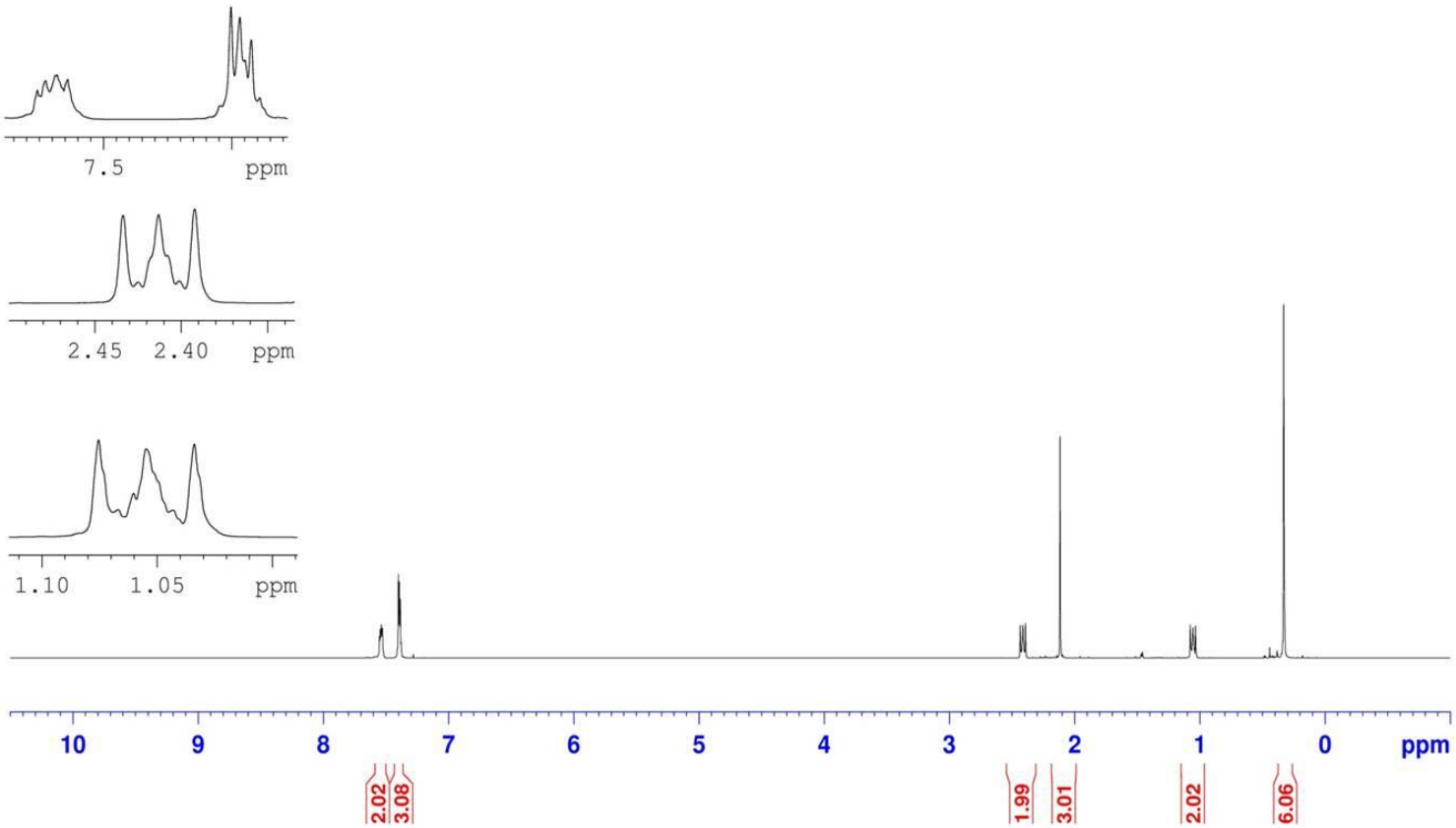
4–(trimethylsilyl)butan–2–one
500 MHz, CDCl3



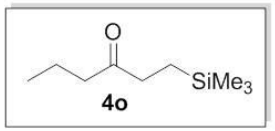


4–(dimethyl(phenyl)silyl)butan–2–one
400 MHz, CDCl3

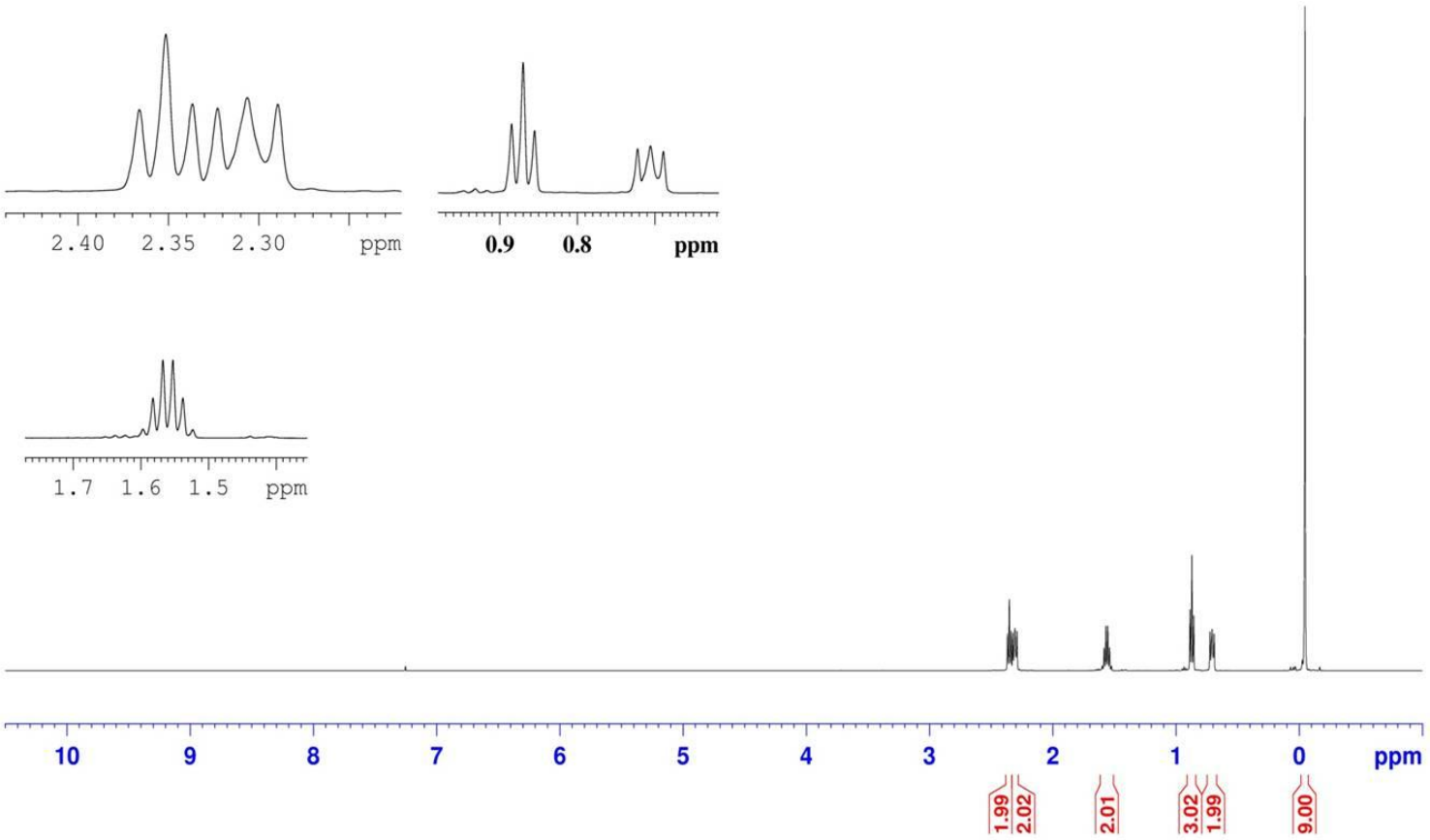




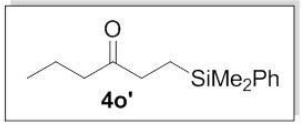
1–(trimethylsilyl)hexan–3–one
500 MHz, CDCl3

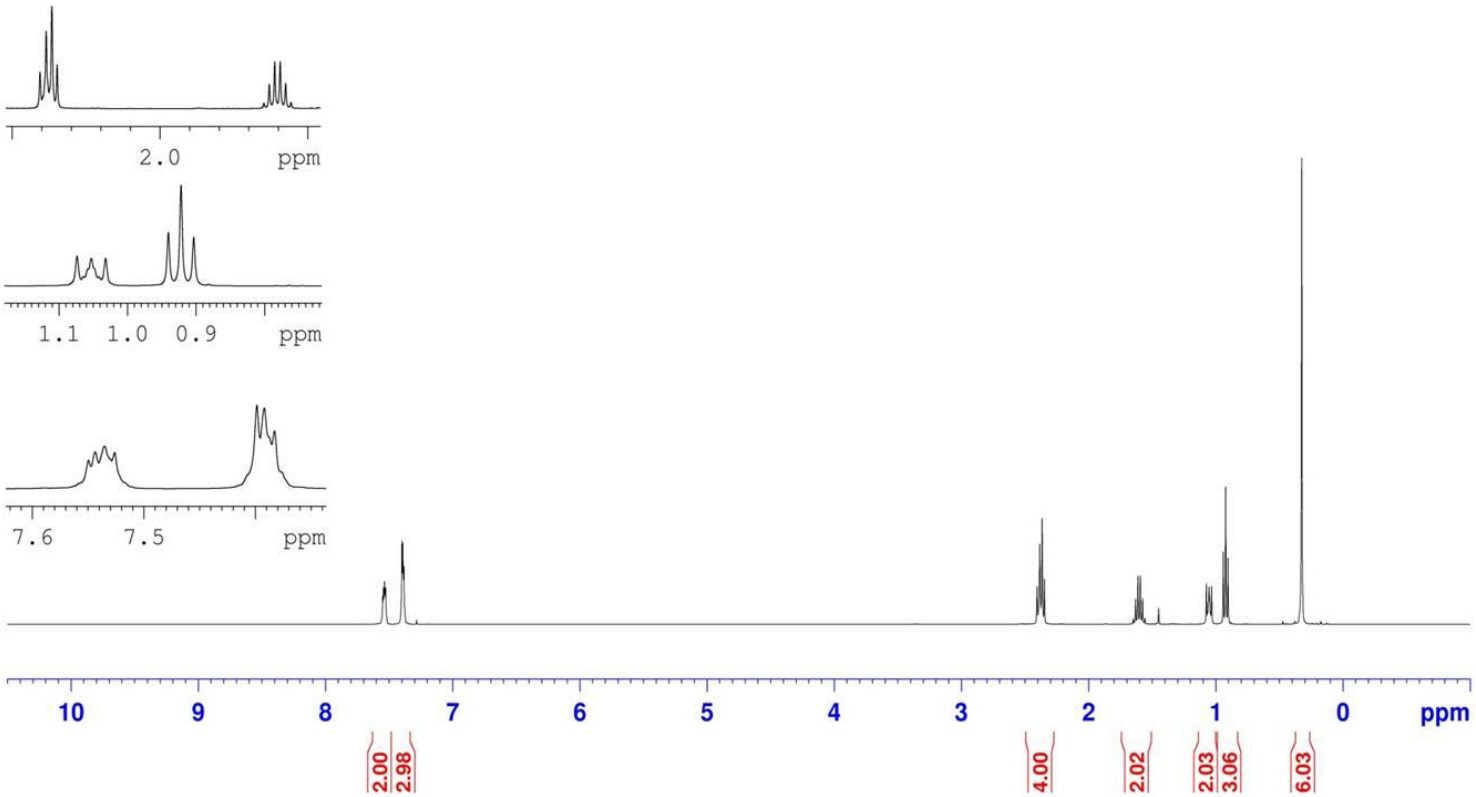


4o

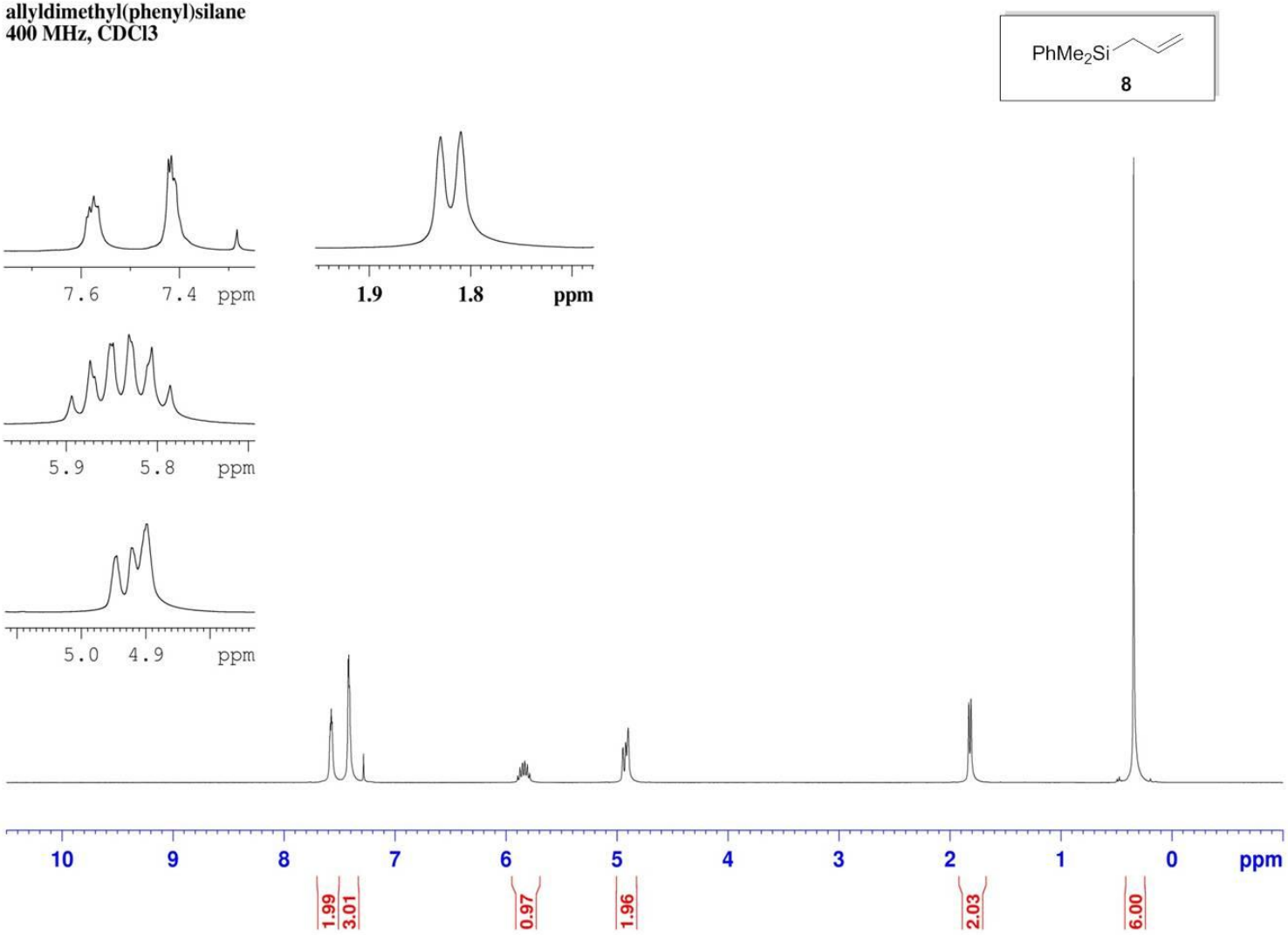


1–(dimethyl(phenyl)silyl)hexan–3–one
400 MHz, CDCl3

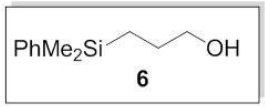


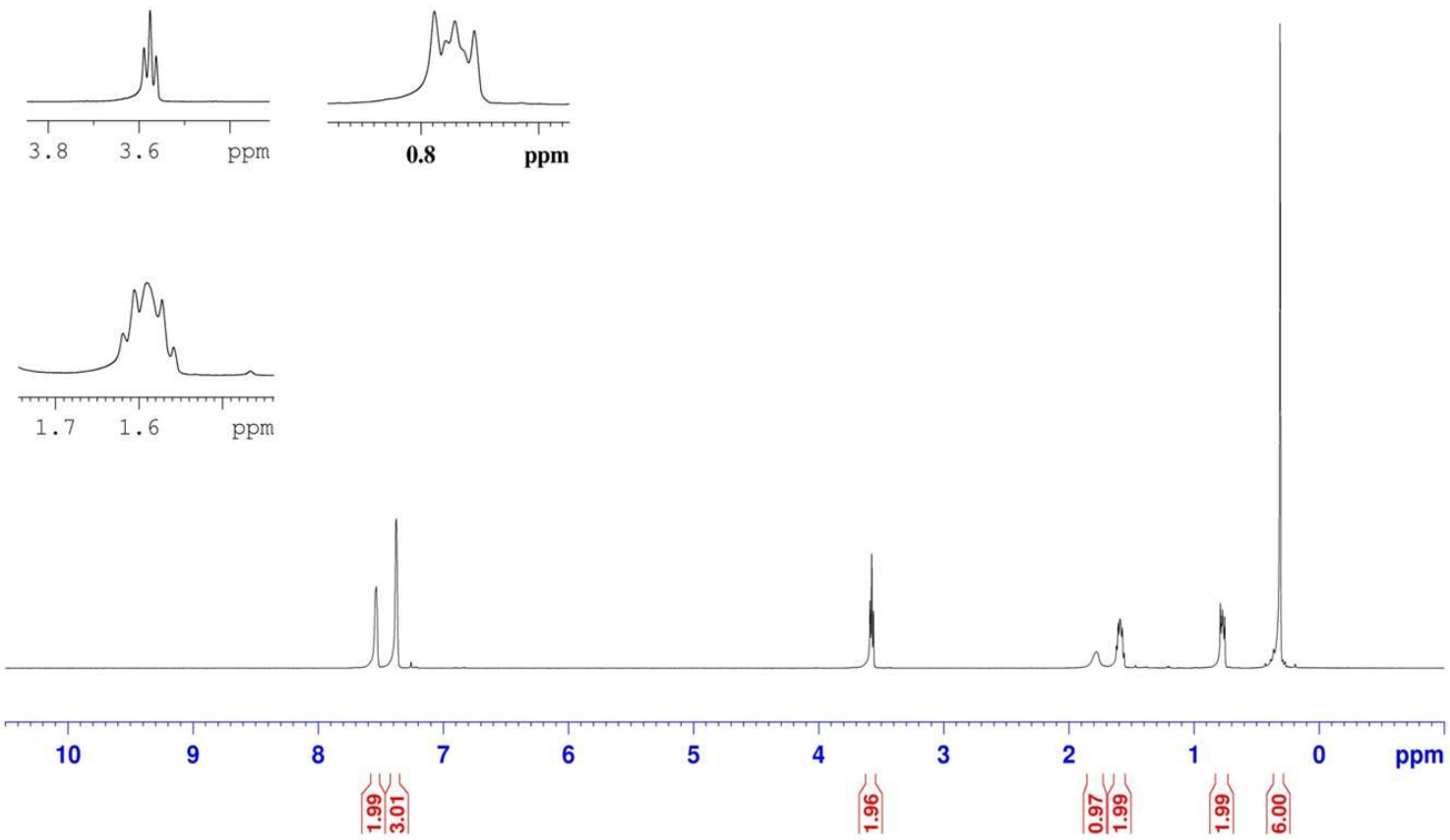


allyldimethyl(phenyl)silane
400 MHz, CDCl3

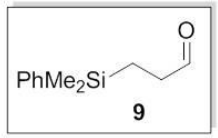


3–(dimethyl(phenyl)silyl)propan–1–ol
500 MHz, CDCl3





3–(dimethyl(phenyl)silyl)propanal
400 MHz, CDCl3



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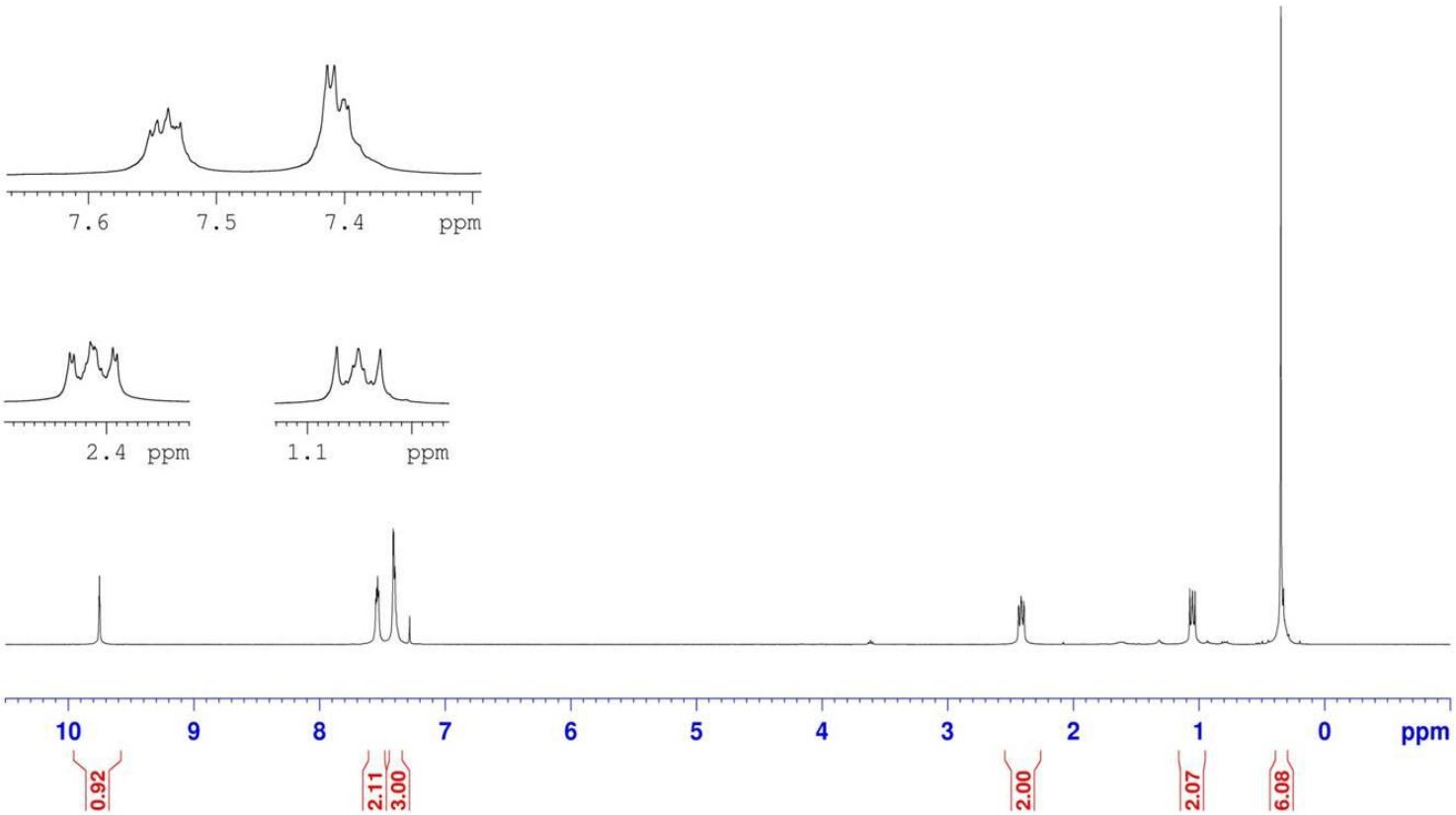
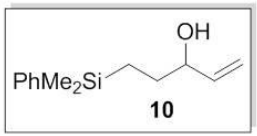
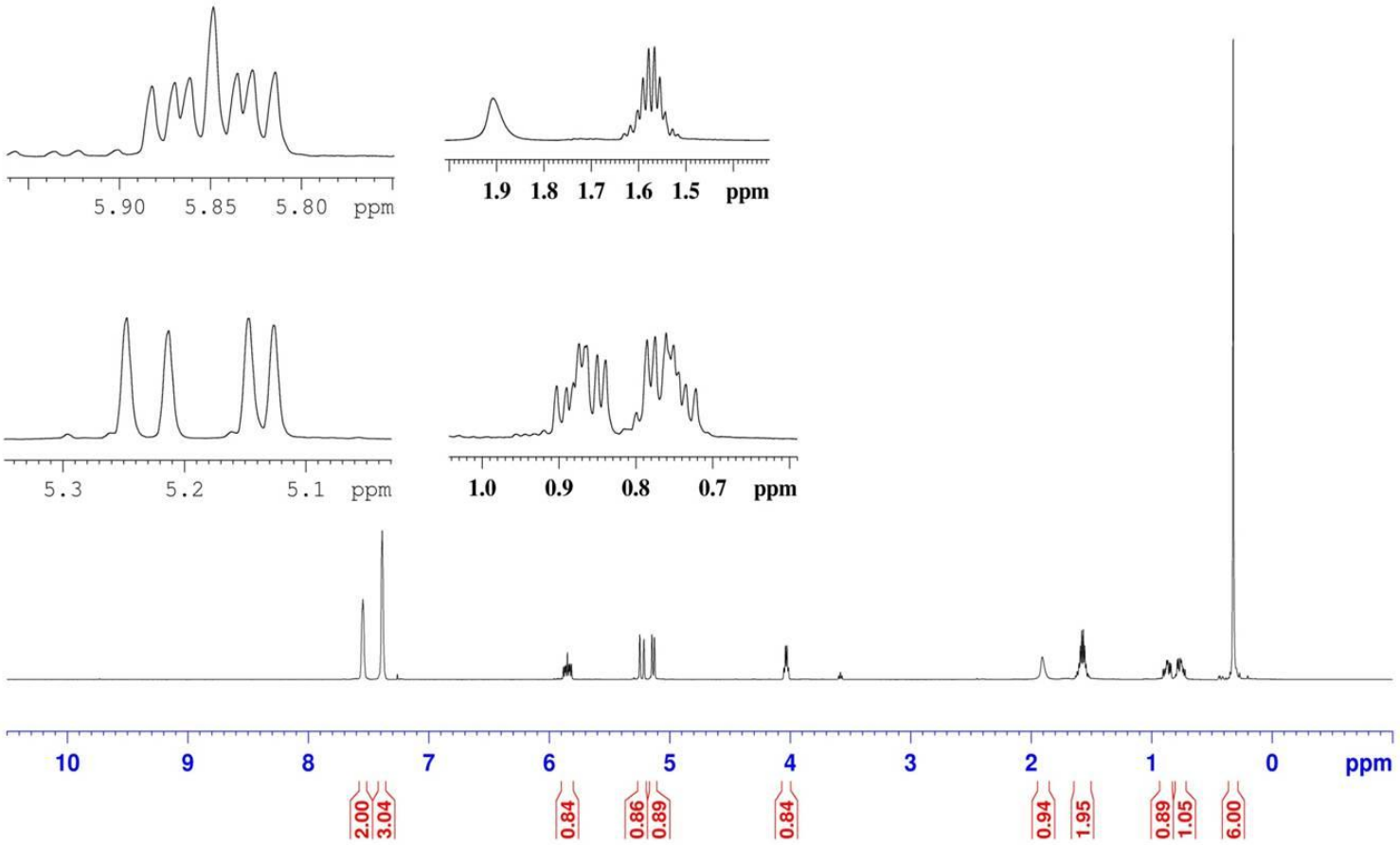
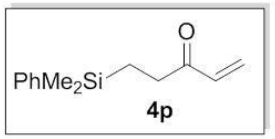


5–(dimethyl(phenyl)silyl)pent–1–en–3–ol
500 MHz, CDCl3

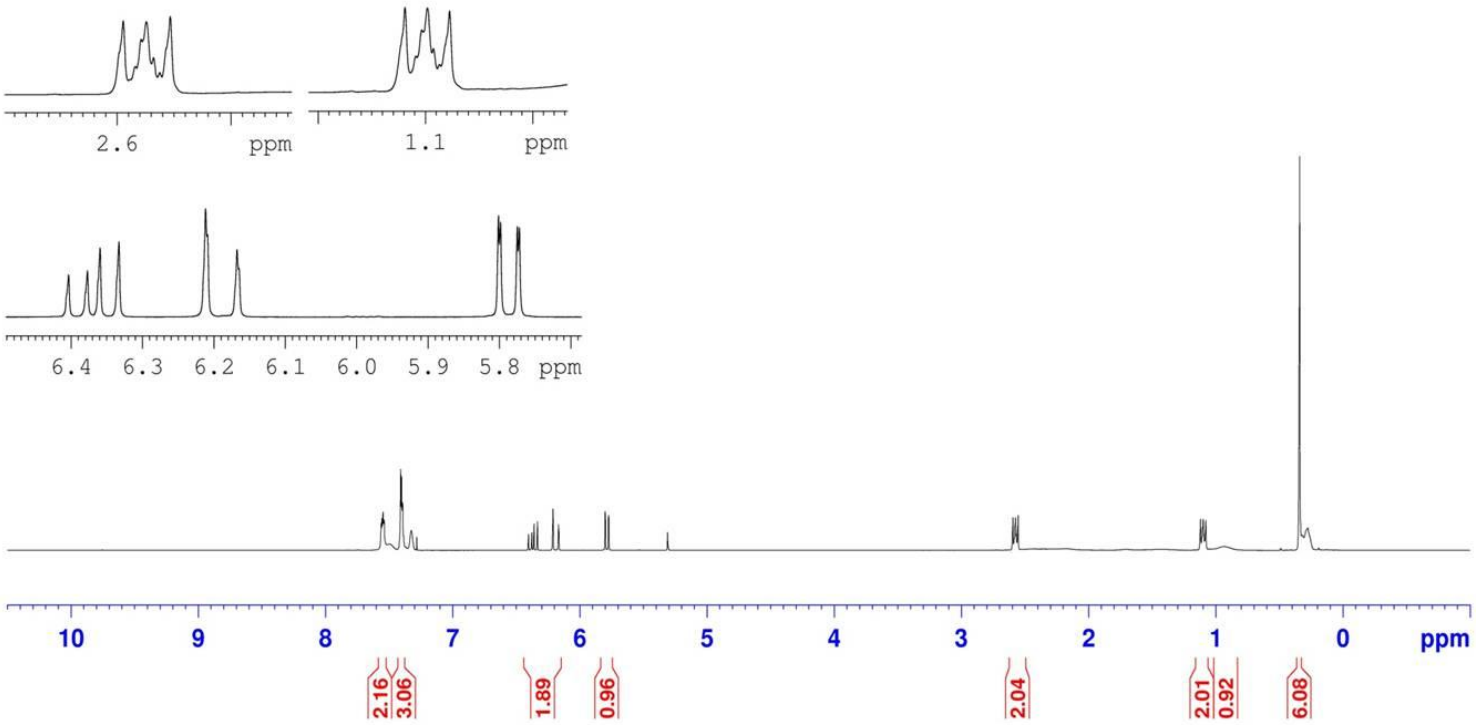




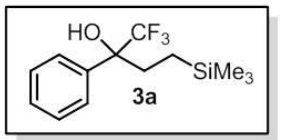
5–(dimethyl(phenyl)silyl)pent–1–en–3–one
400 MHz, CDCl3

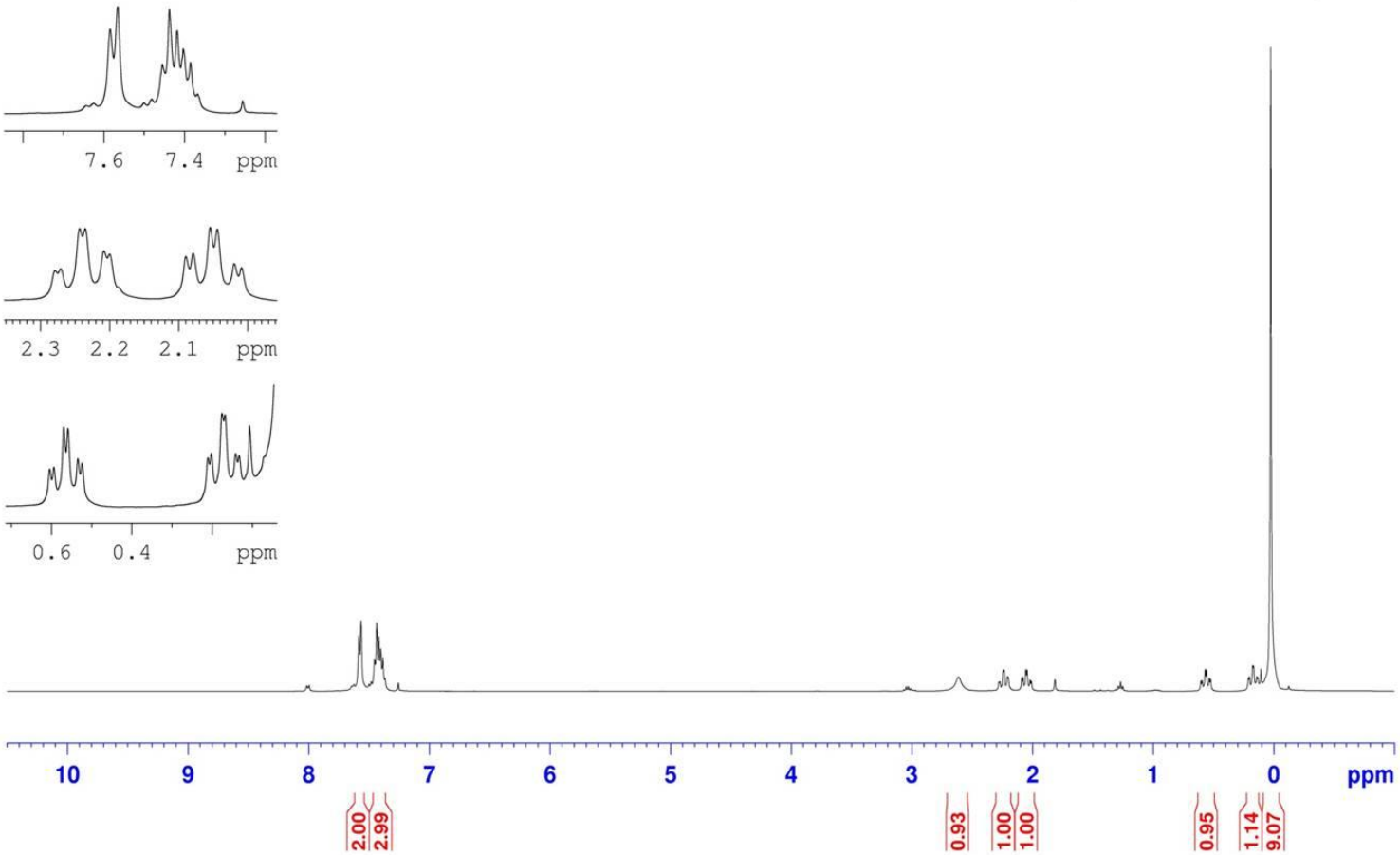


4p

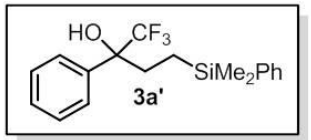


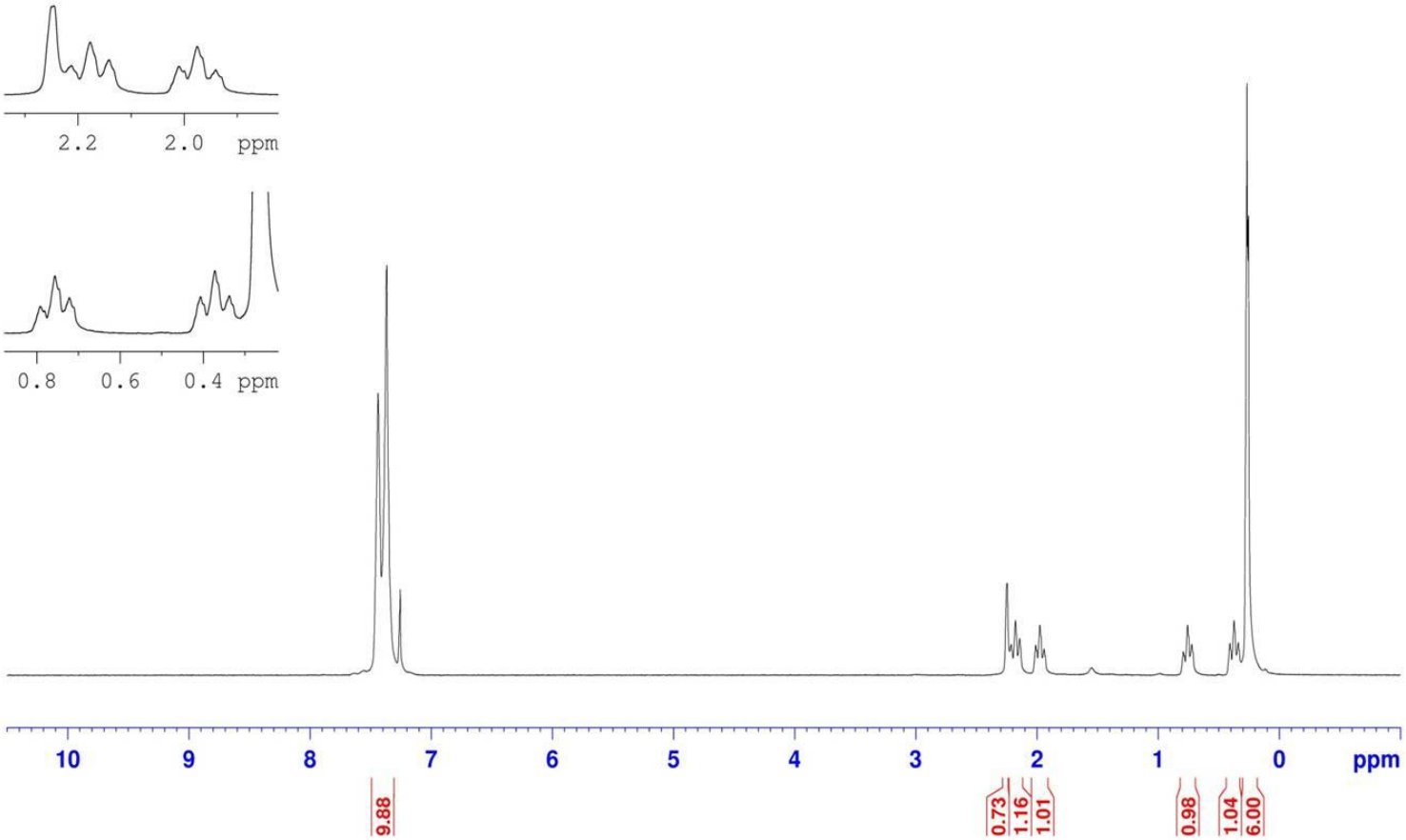
1,1,1−trifluoro−2−phenyl−4−(trimethylsilyl)butan−2−ol
400 MHz, CDCl3



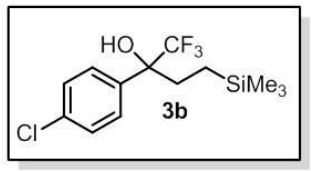


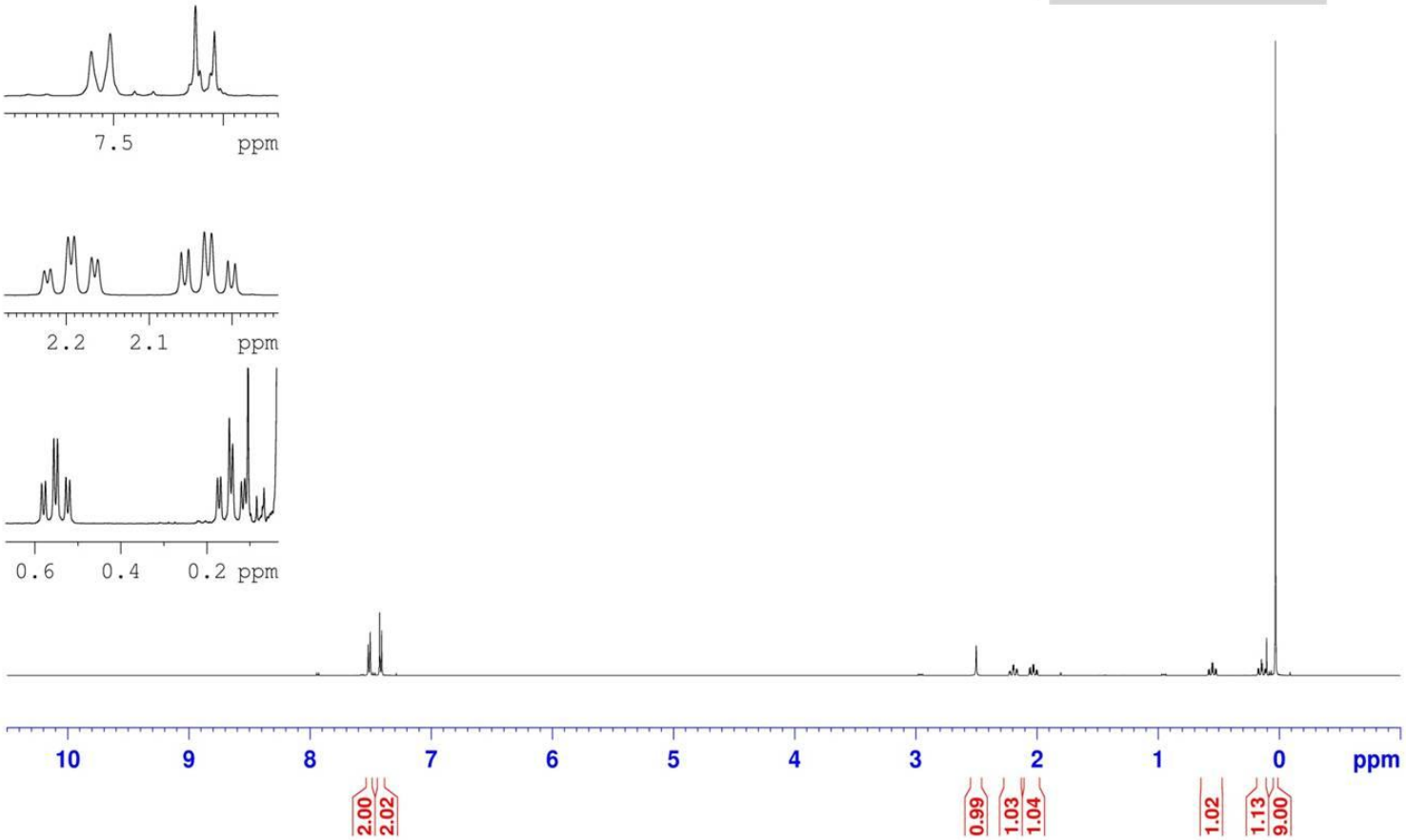
4–(dimethyl(phenyl)silyl)–1,1,1–trifluoro–2–phenylbutan–2–ol
400 MHz, CDCl3



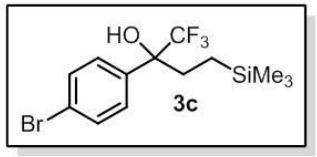


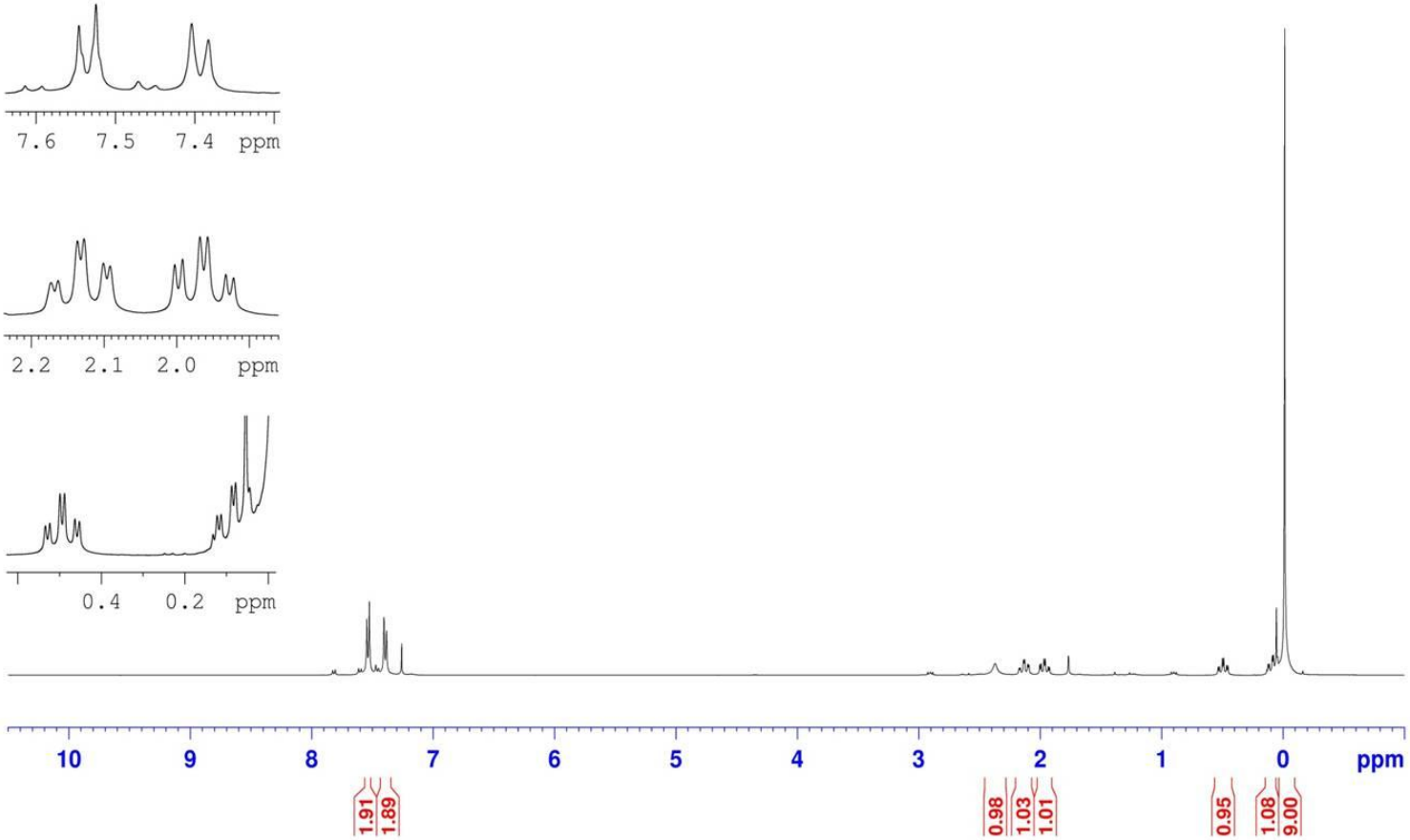
2–(4–chlorophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–ol
400 MHz, CDCl3



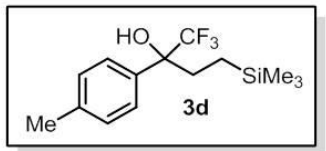


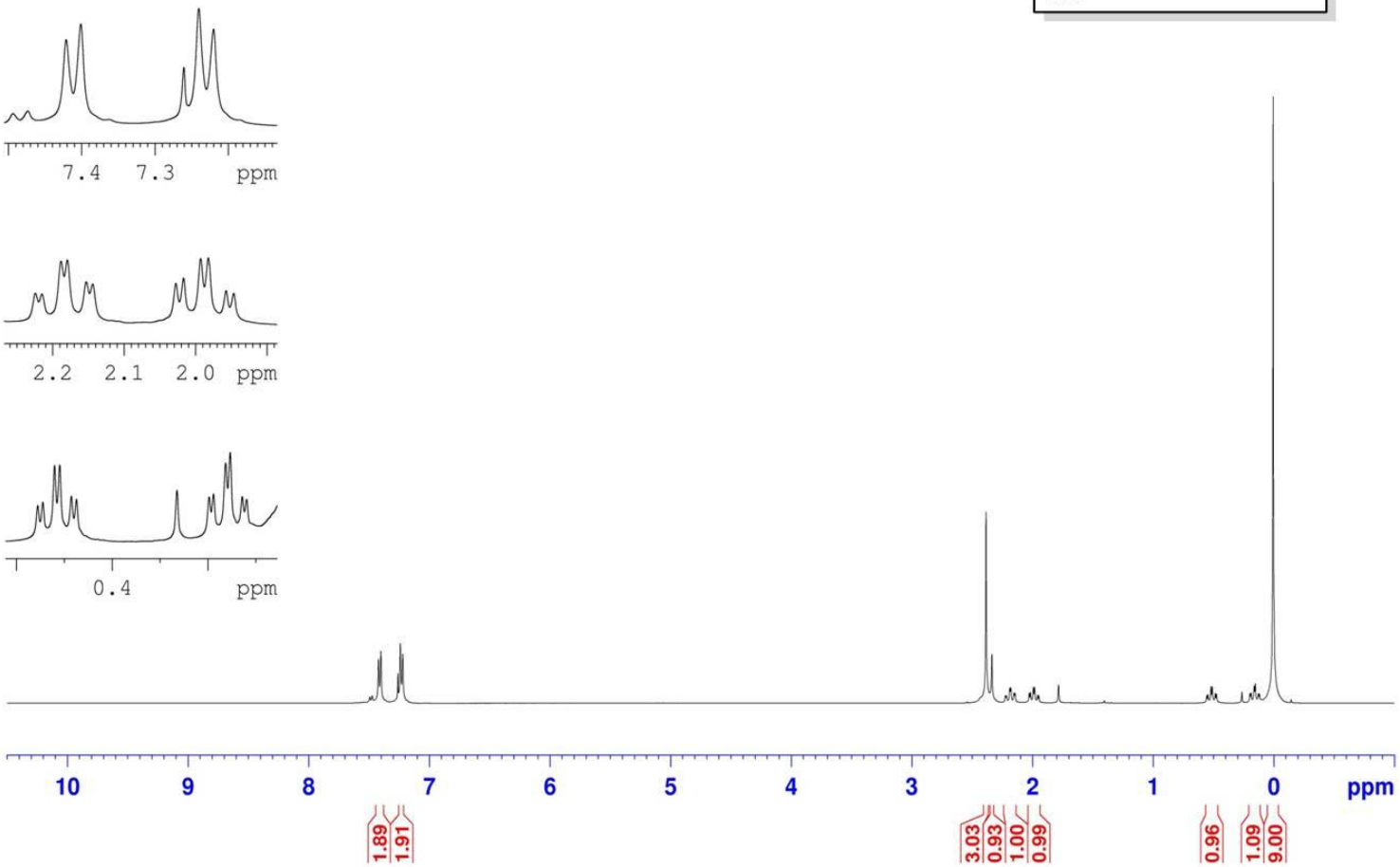
2–(4–bromophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–ol
400 MHz, CDCl3



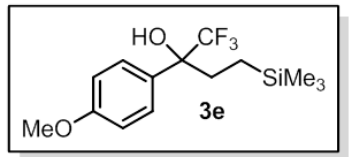


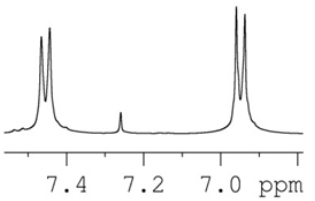
1,1,1–trifluoro–2–(p–tolyl)–4–(trimethylsilyl)butan–2–ol
400 MHz, CDCl3

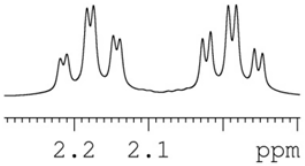


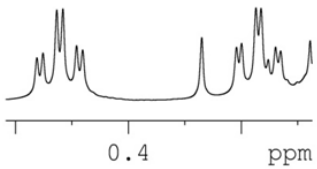


1,1,1–trifluoro–2–(4–methoxyphenyl)–4–(trimethylsilyl)butan–2–ol
400 MHz, CDCl3

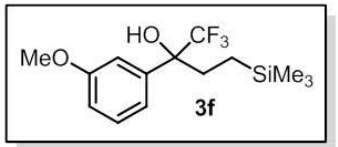


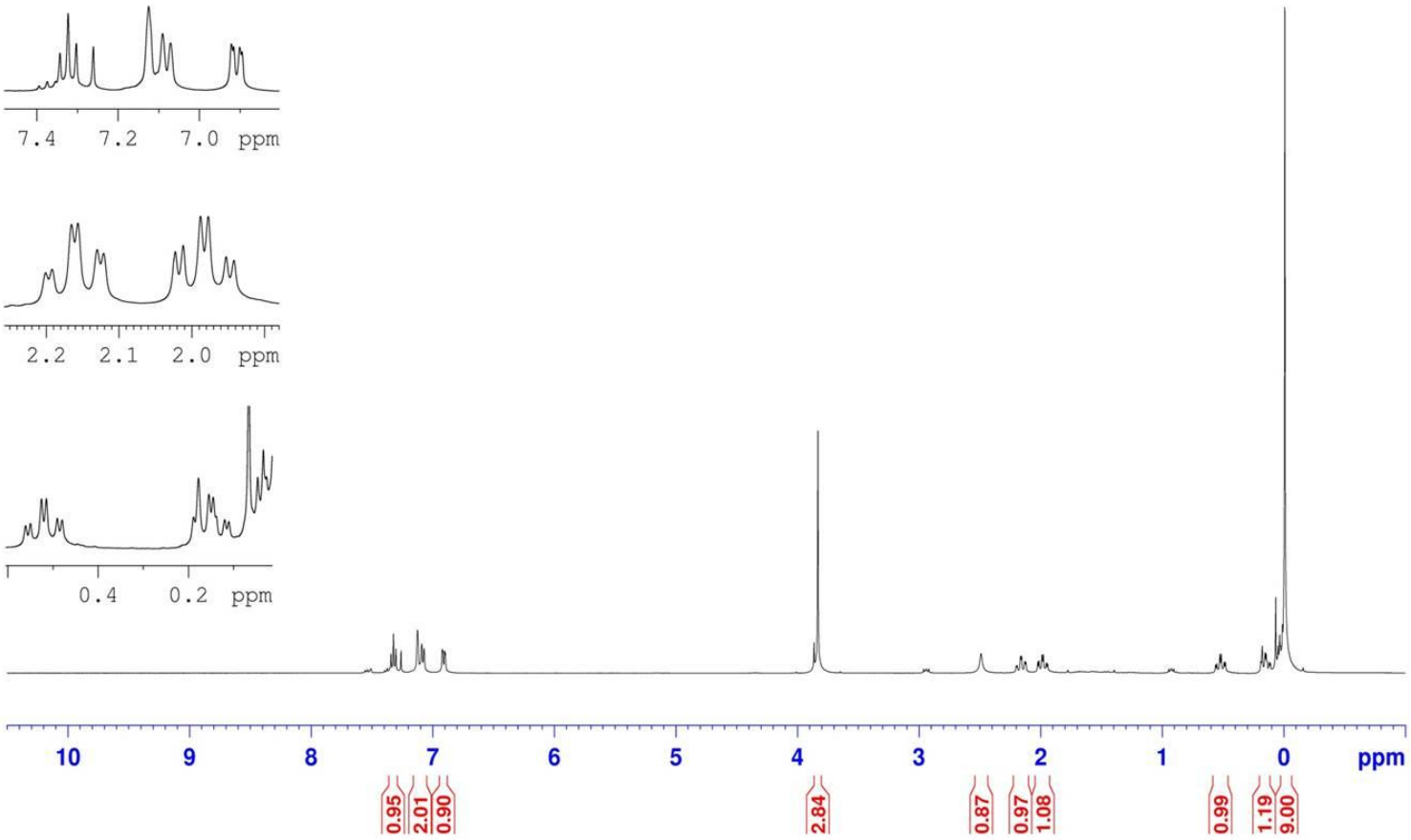




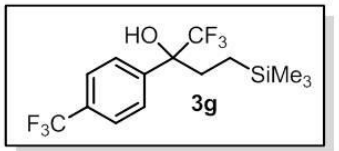


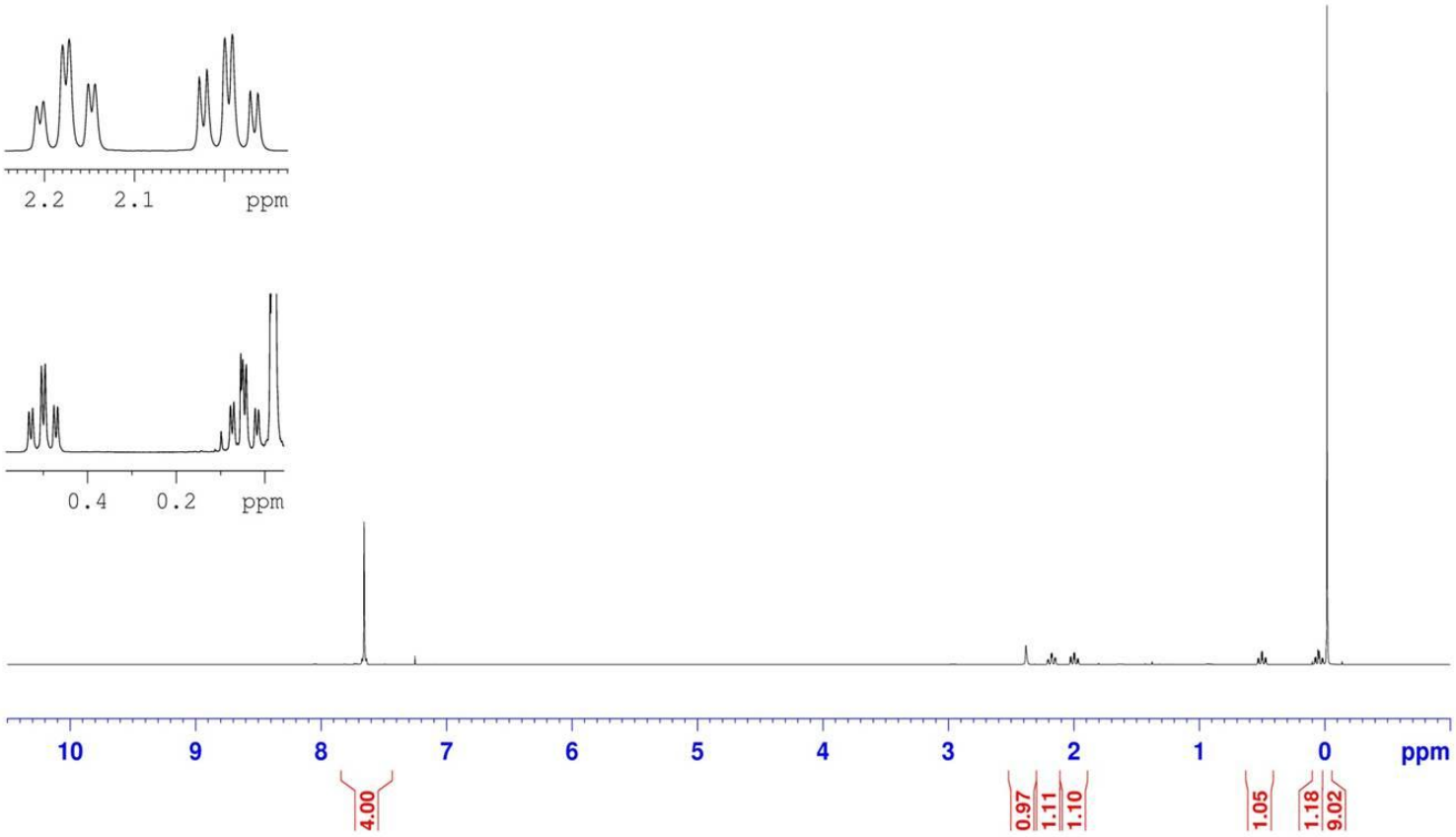
1,1,1−trifluoro−2−(3−methoxyphenyl)−4−(trimethylsilyl)butan−2−ol
400 MHz, CDCl3



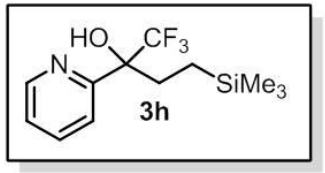


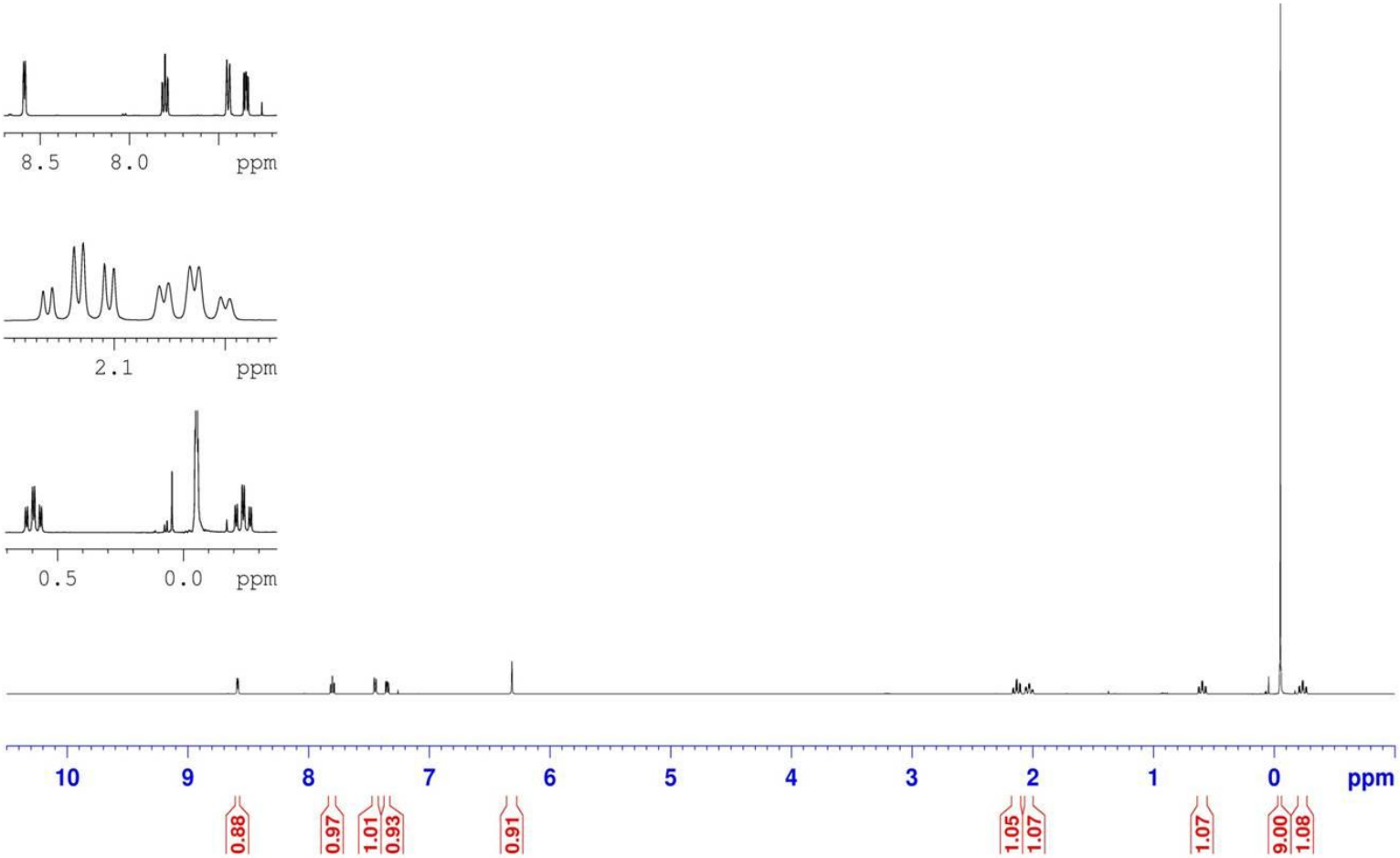
1,1,1–trifluoro–2–(4–(trifluoromethyl)phenyl)–4–(trimethylsilyl)butan–2–ol
400 MHz, CDCl3



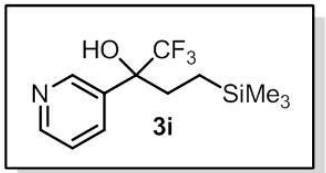


1,1,1–trifluoro–2–(pyridin–2–yl)–4–(trimethylsilyl)butan–2–ol
400 MHz, CDCl3

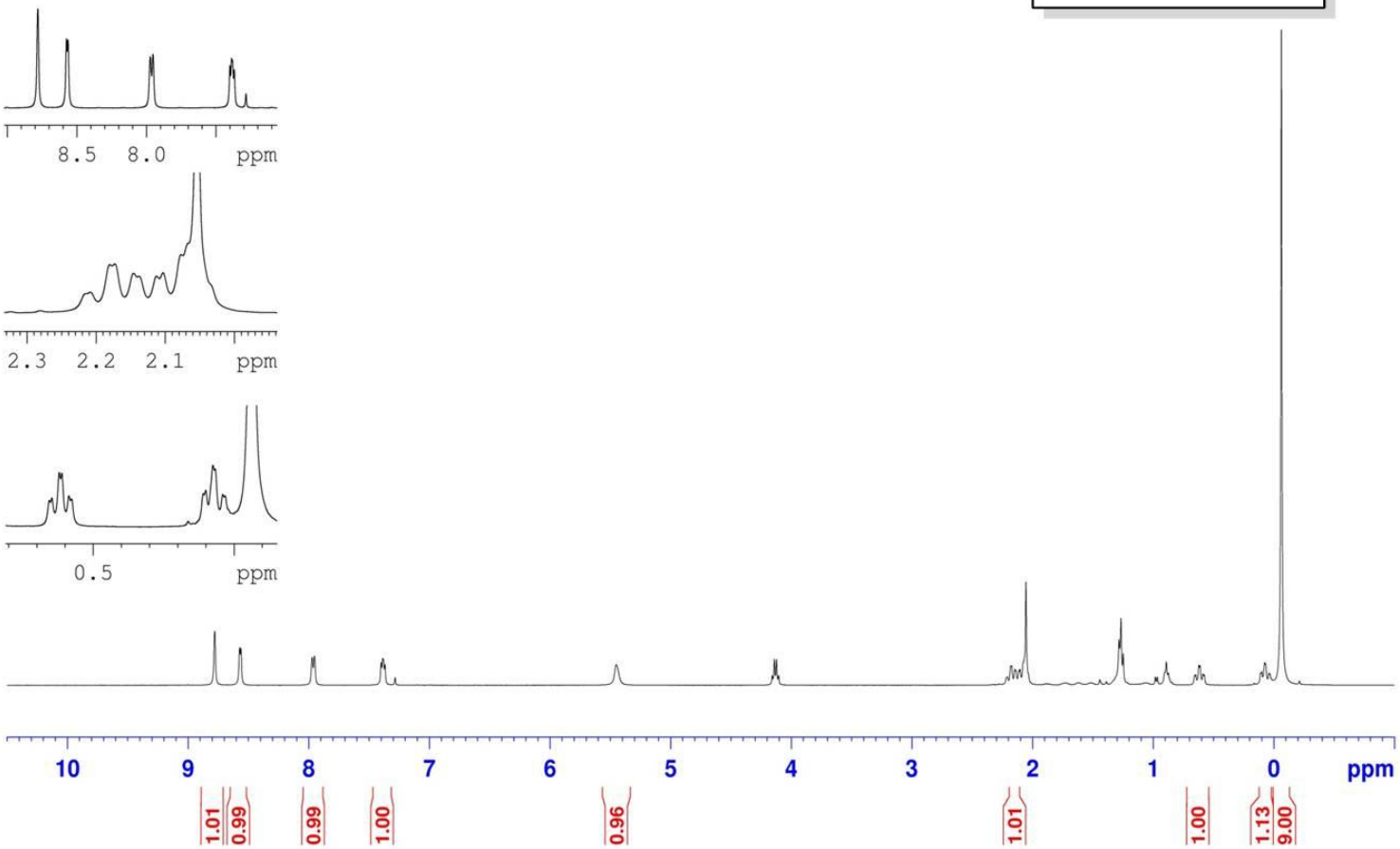




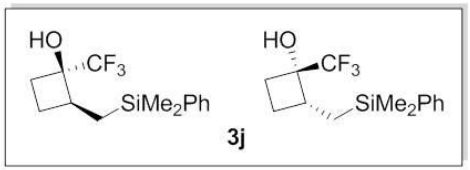
1,1,1−trifluoro−2−(pyridin−3−yl)−4−(trimethylsilyl)butan−2−ol
400 MHz, CDCl3



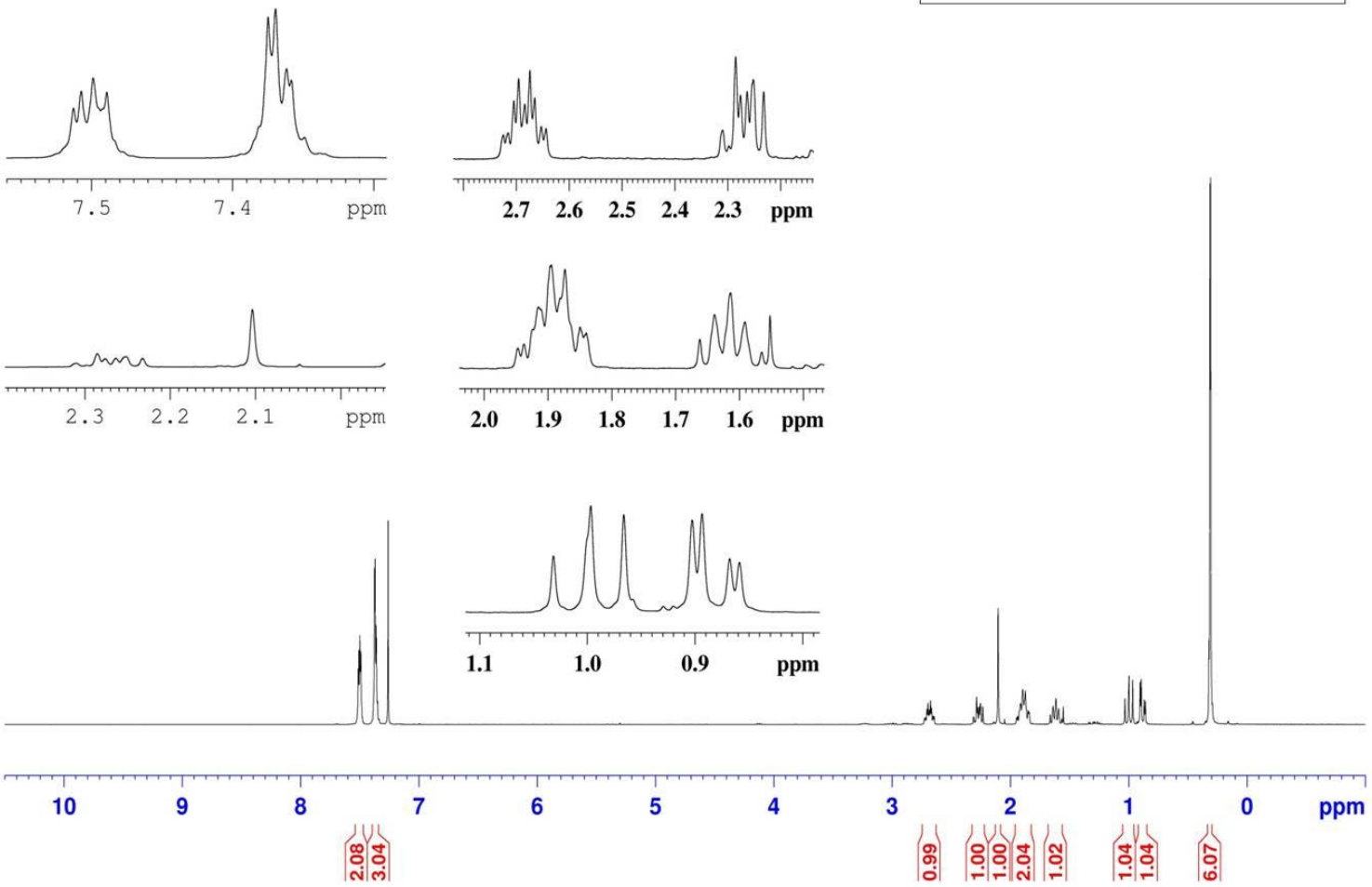
3i



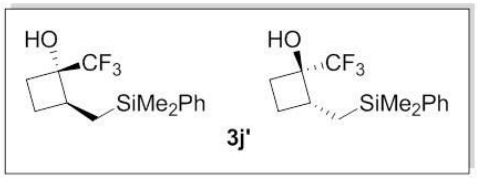
(1R,2S) & (1S,2R)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutanol (3j)
400 MHz, CDCl3



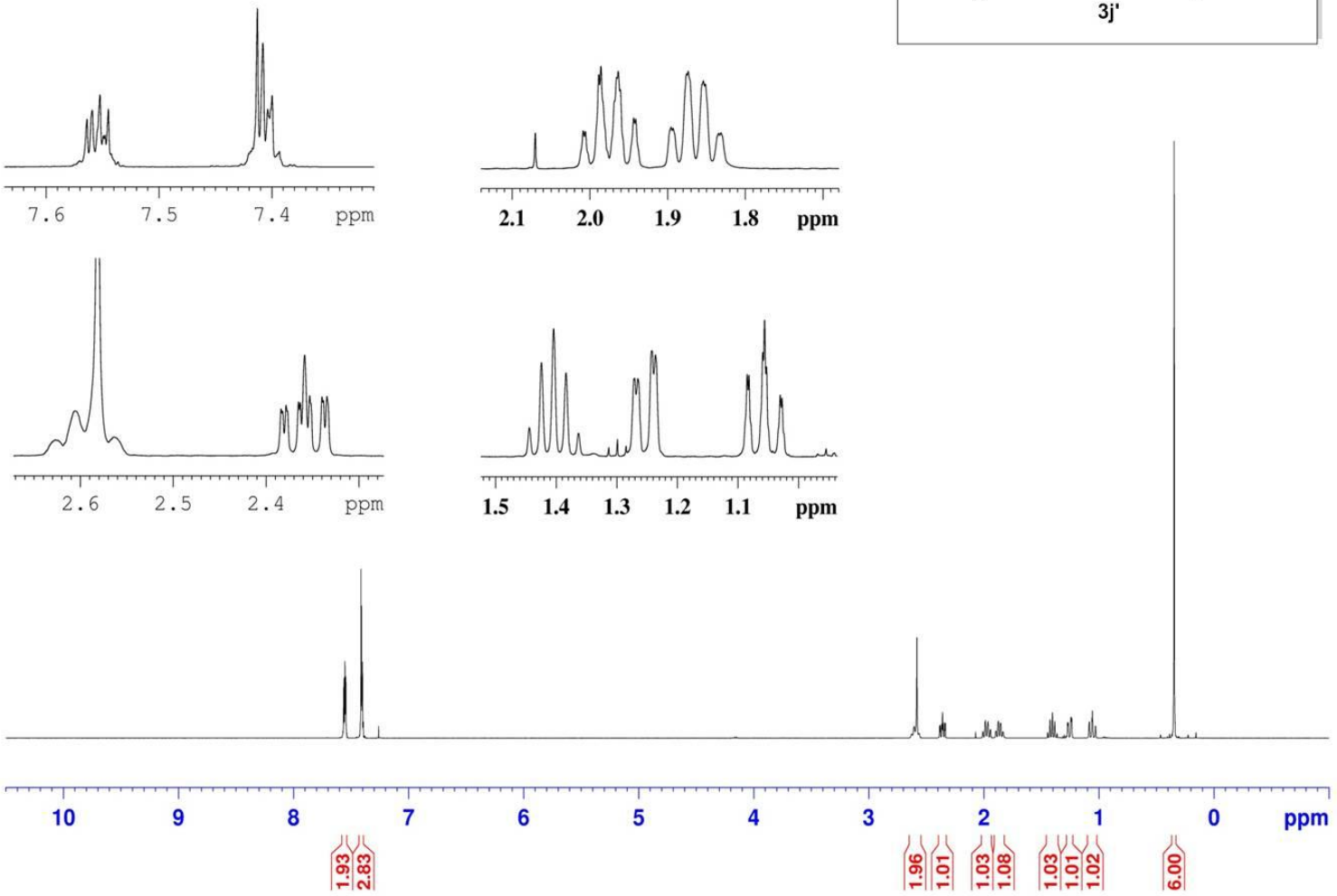
3j



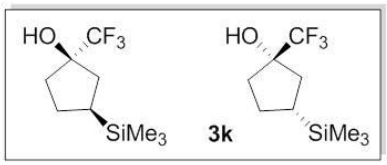
(1S,2S) & (1R,2R)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutanol
400 MHz, CDCl3

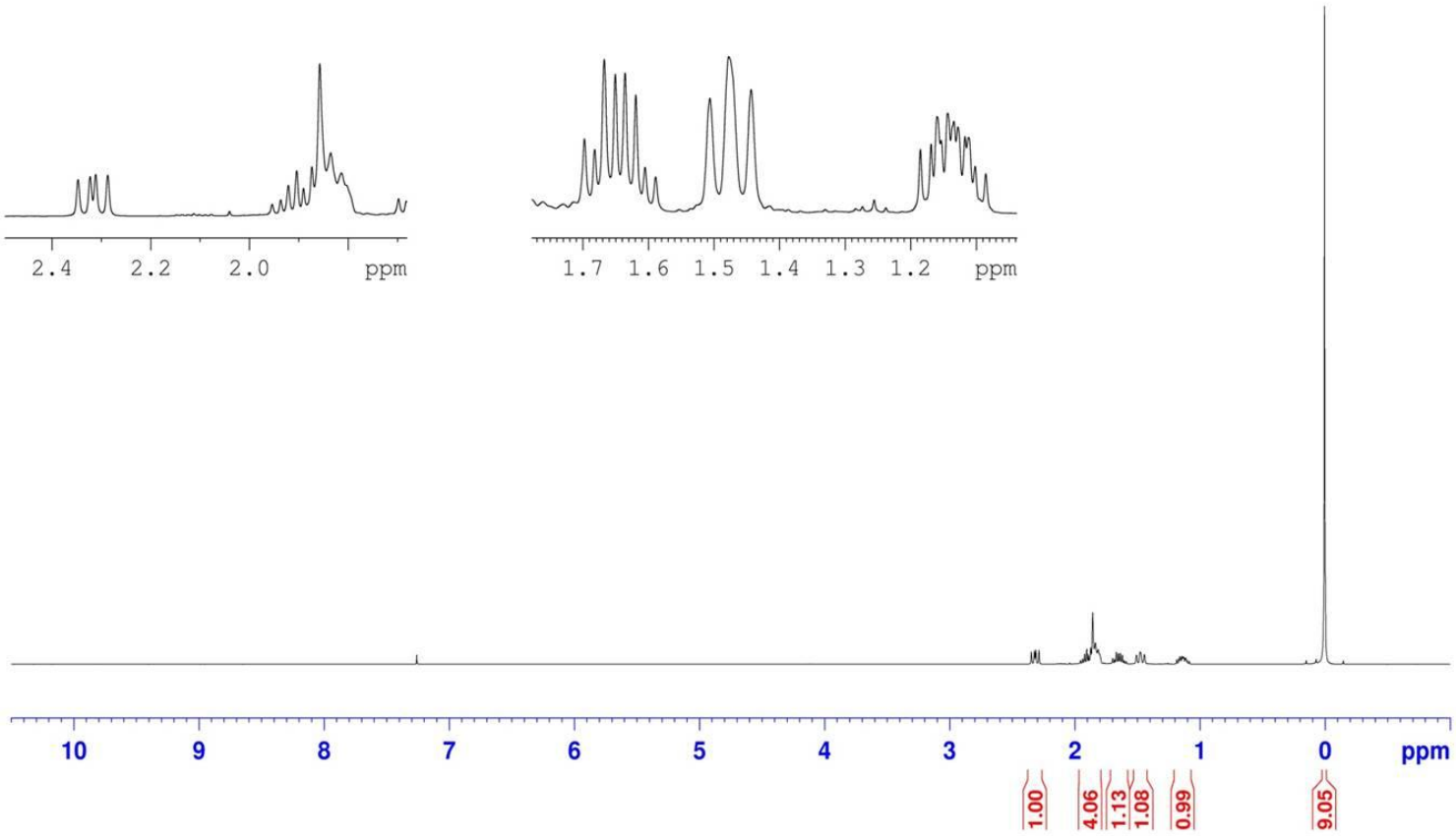


3j'

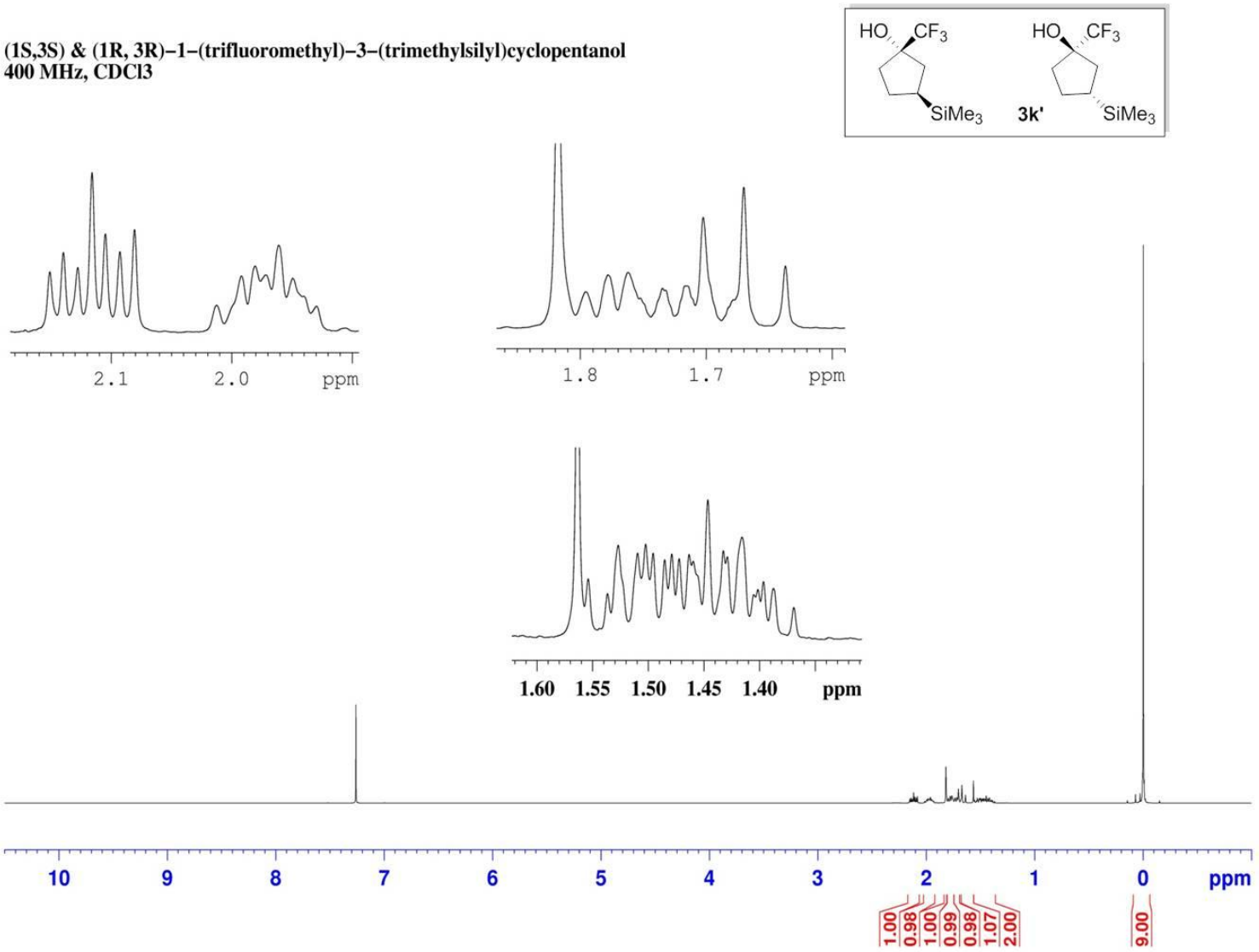


(1R,3S) & (1S, 3R)−1−(trifluoromethyl)−3−(trimethylsilyl)cyclopentanol
400 MHz, CDCl3

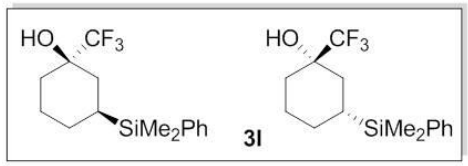




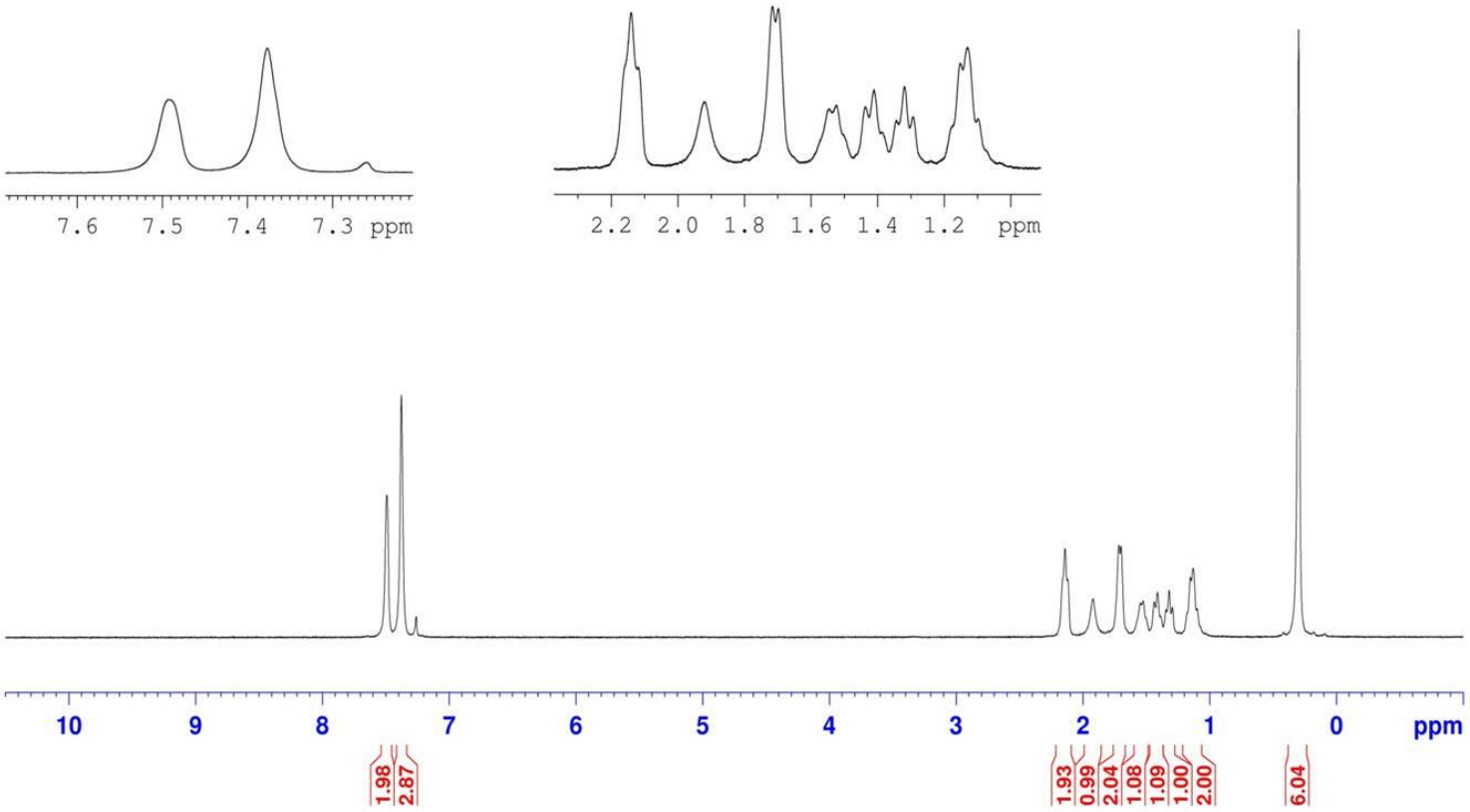
(1S,3S) & (1R, 3R)−1−(trifluoromethyl)−3−(trimethylsilyl)cyclopentanol
400 MHz, CDCl3



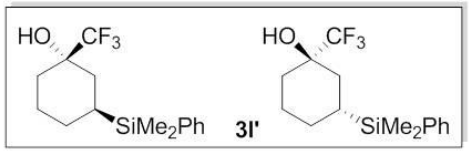
(1R,3S) & (1S,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cyclohexanol
400 MHz, CDCl3

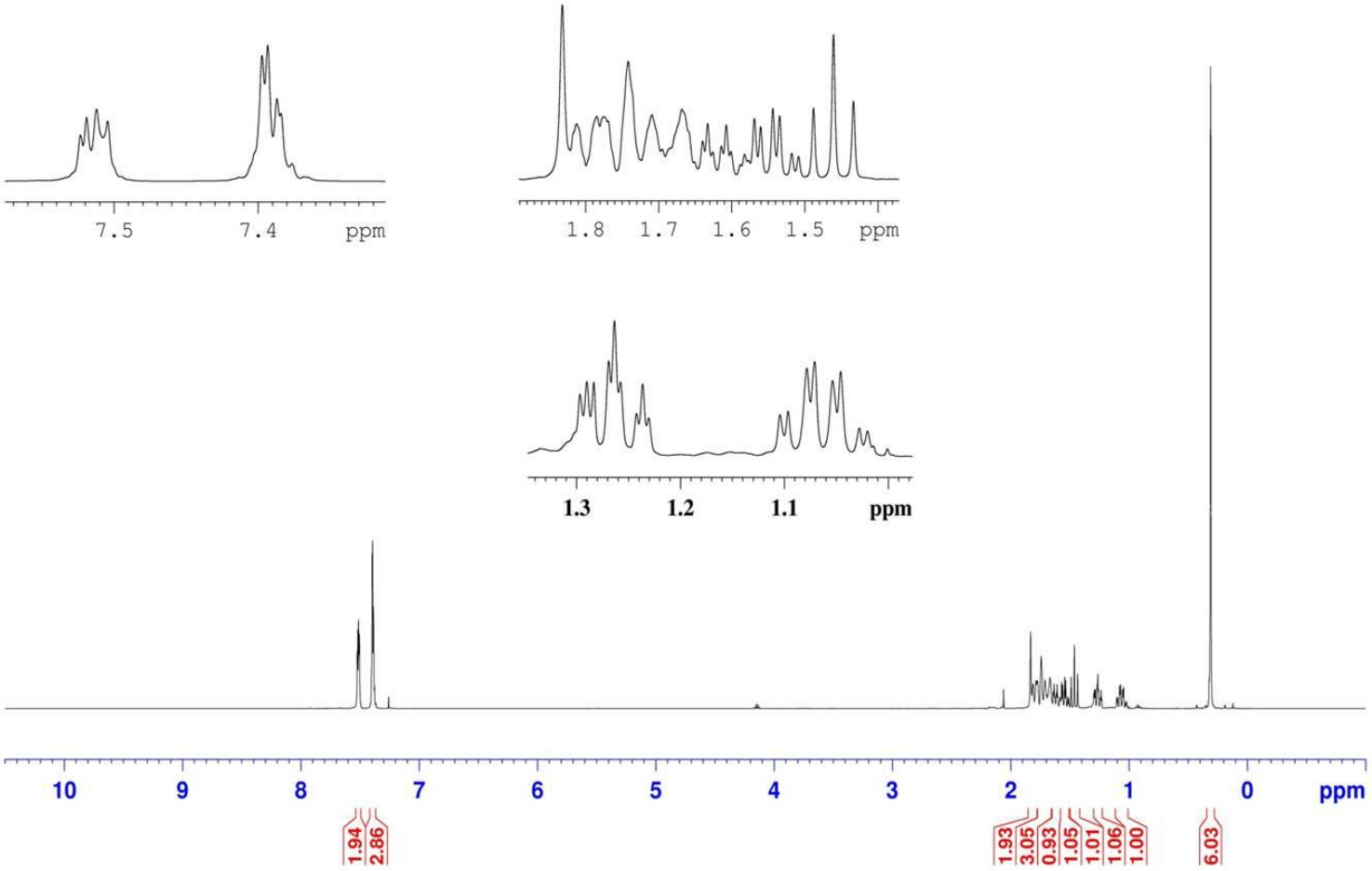


3l

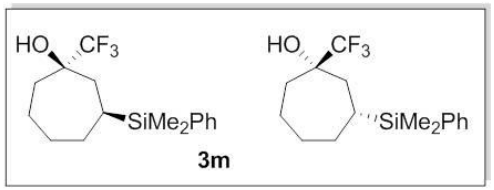


(1S,3S) & (1R,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cyclohexanol
400 MHz, CDCl3

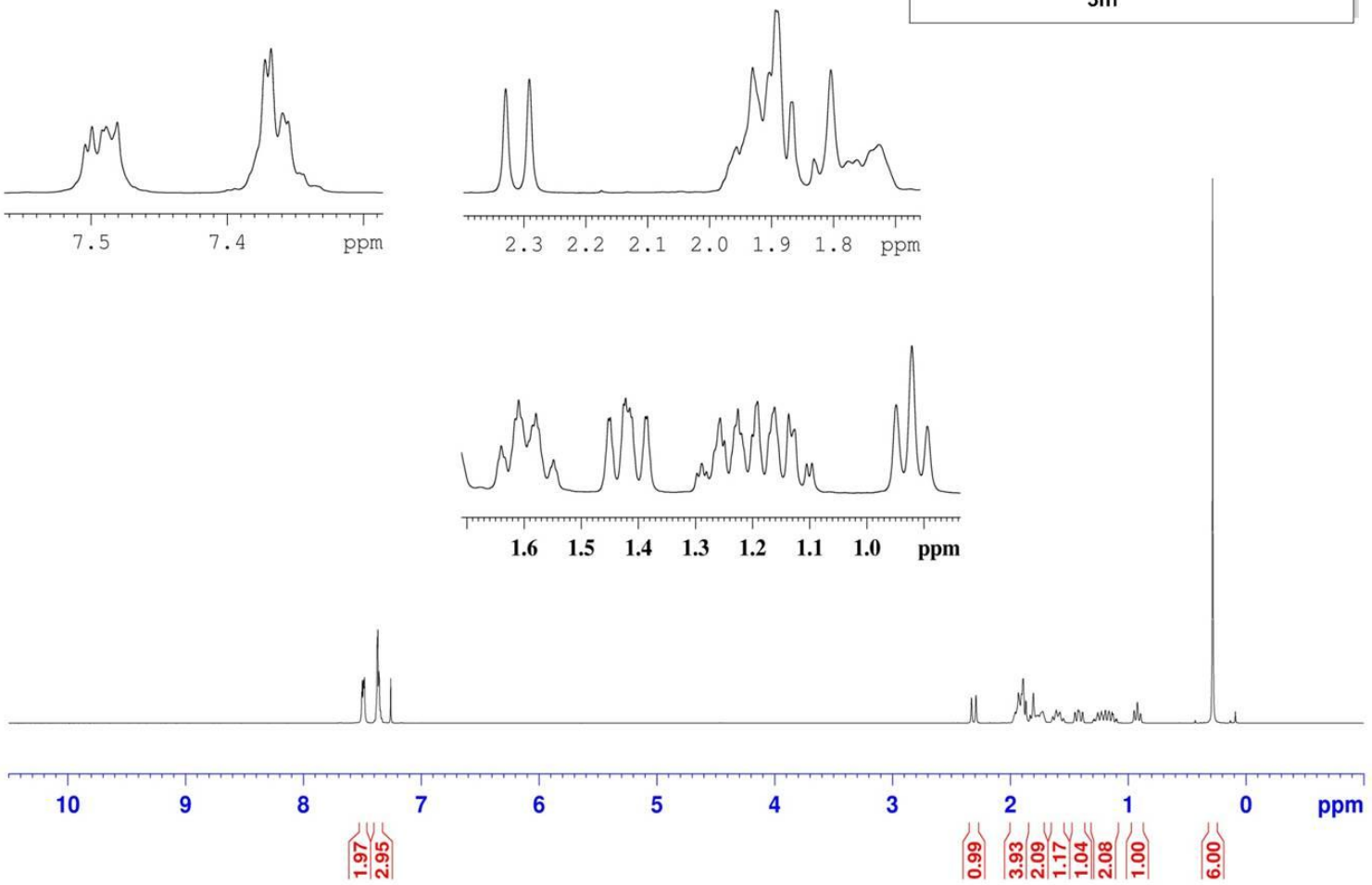




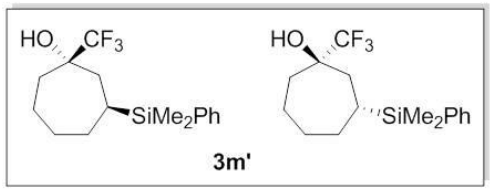
(1R,3S) & (1S,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cycloheptanol
400 MHz, CDCl3



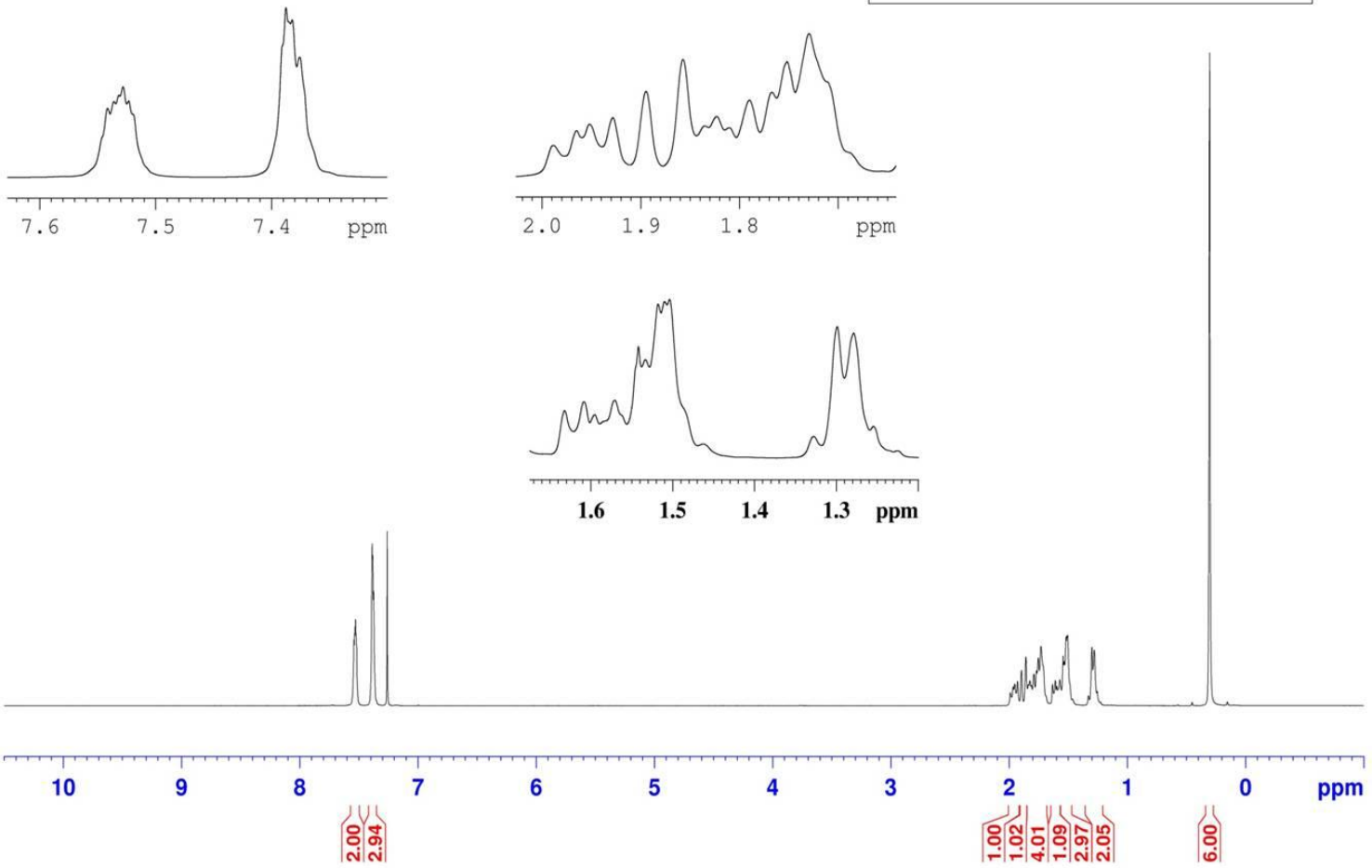
3m



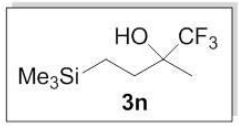
(1S,3S) & (1R,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cycloheptanol
400 MHz, CDCl3

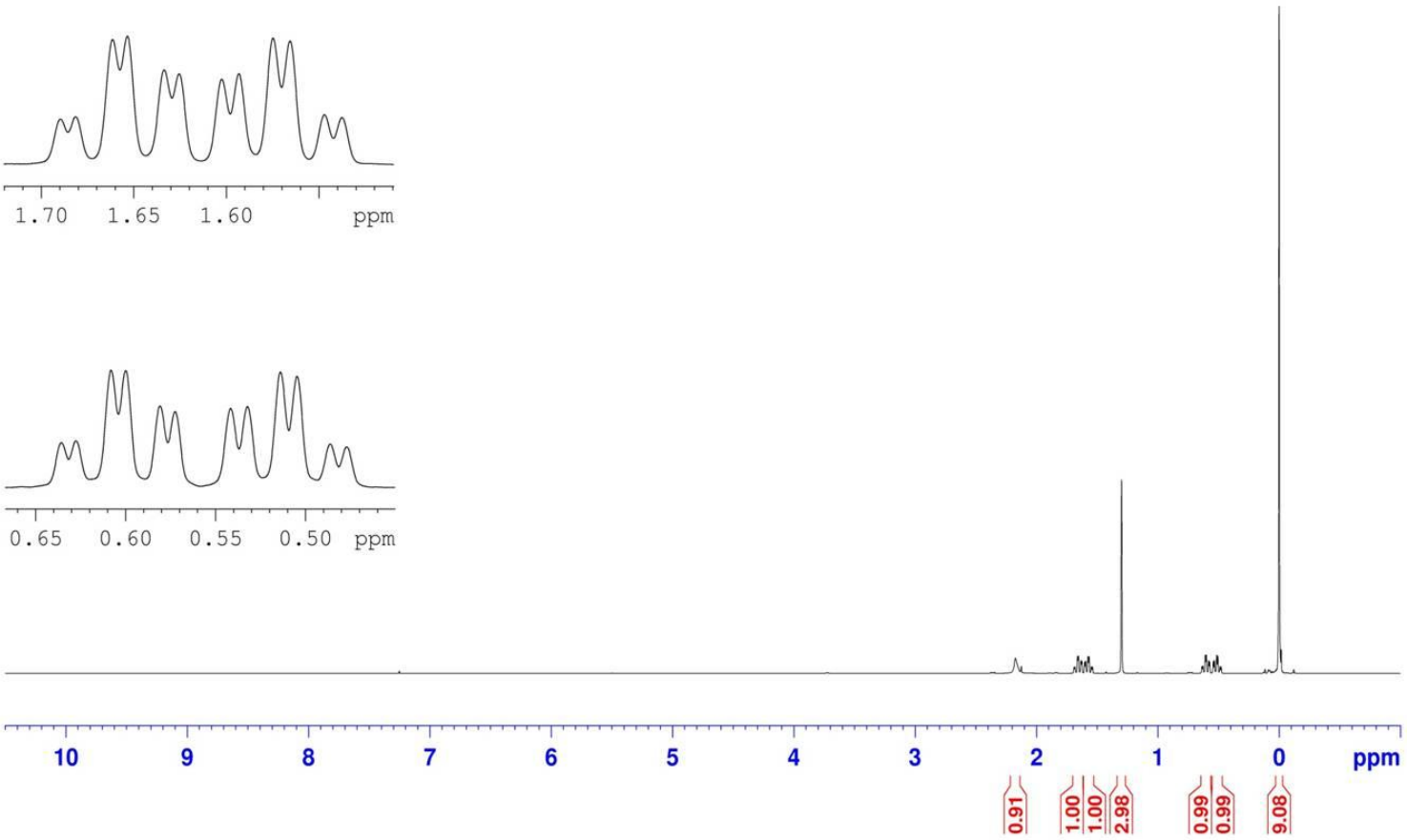


3m'

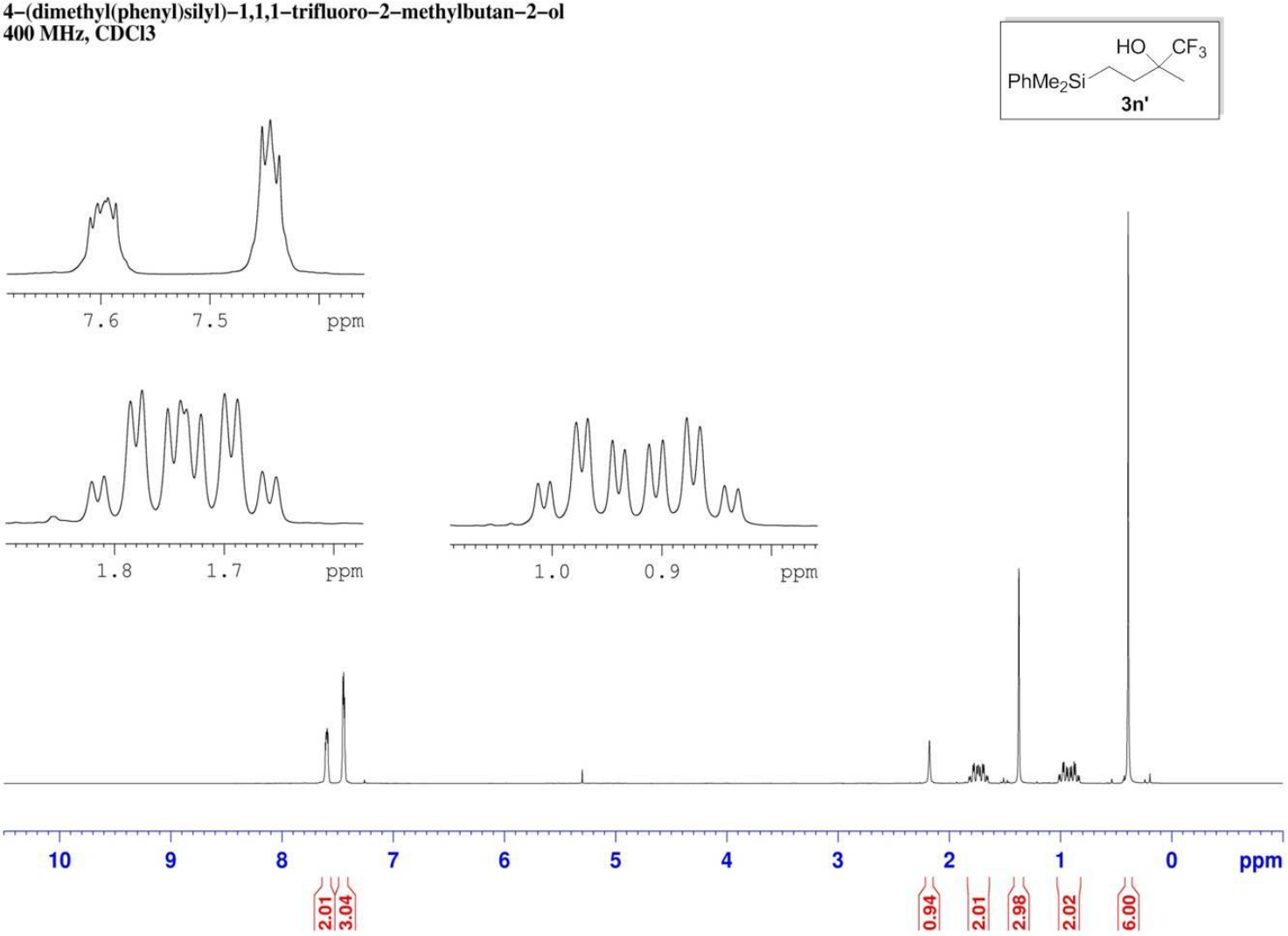


1,1,1−trifluoro−2−methyl−4−(trimethylsilyl)butan−2−ol
500 MHz, CDCl3

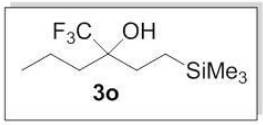




4–(dimethyl(phenyl)silyl)–1,1,1–trifluoro–2–methylbutan–2–ol
400 MHz, CDCl3



3–(trifluoromethyl)–1–(trimethylsilyl)hexan–3–ol
500 MHz, CDCl3



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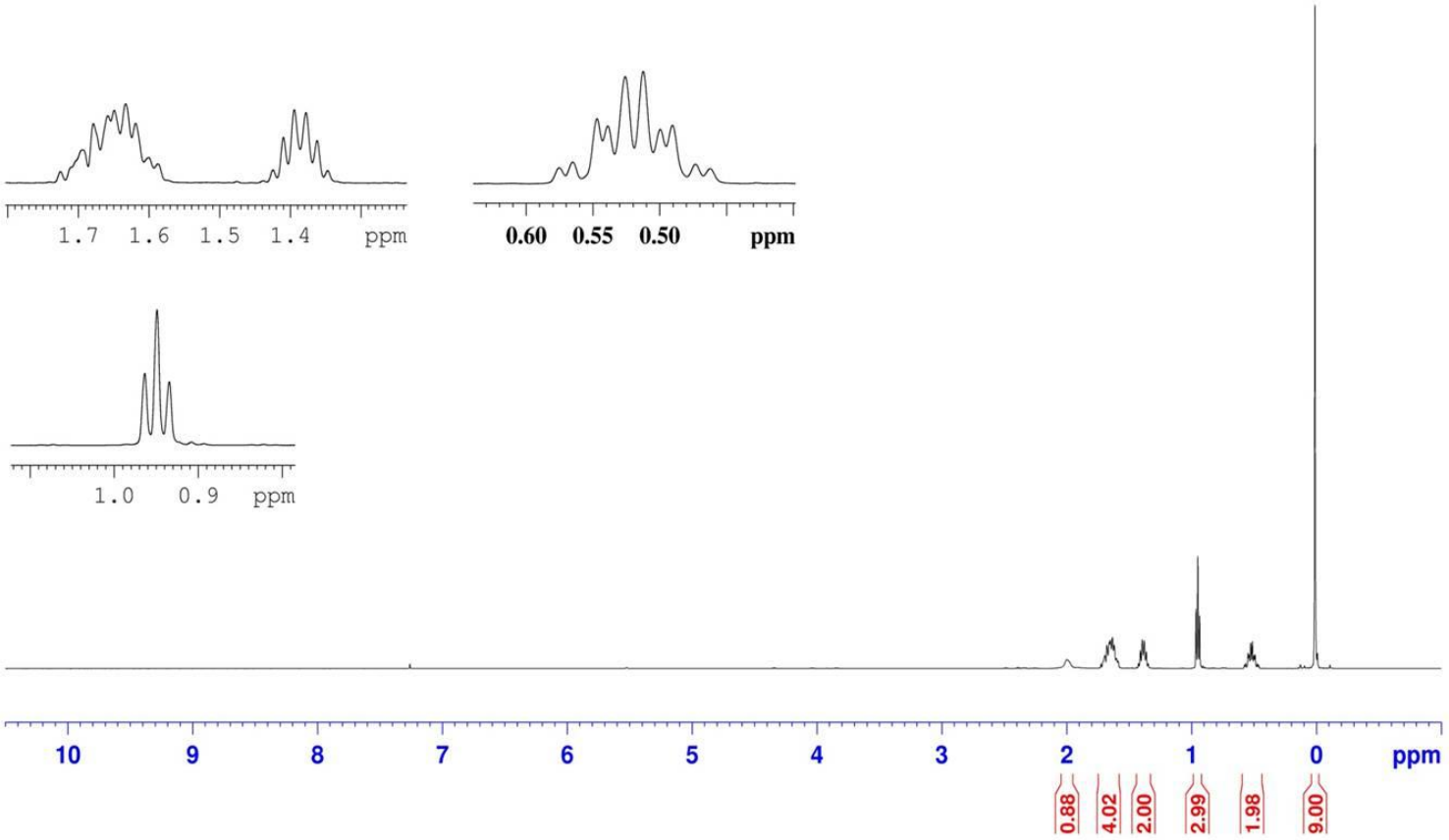
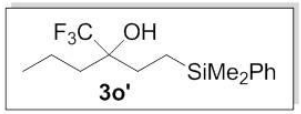
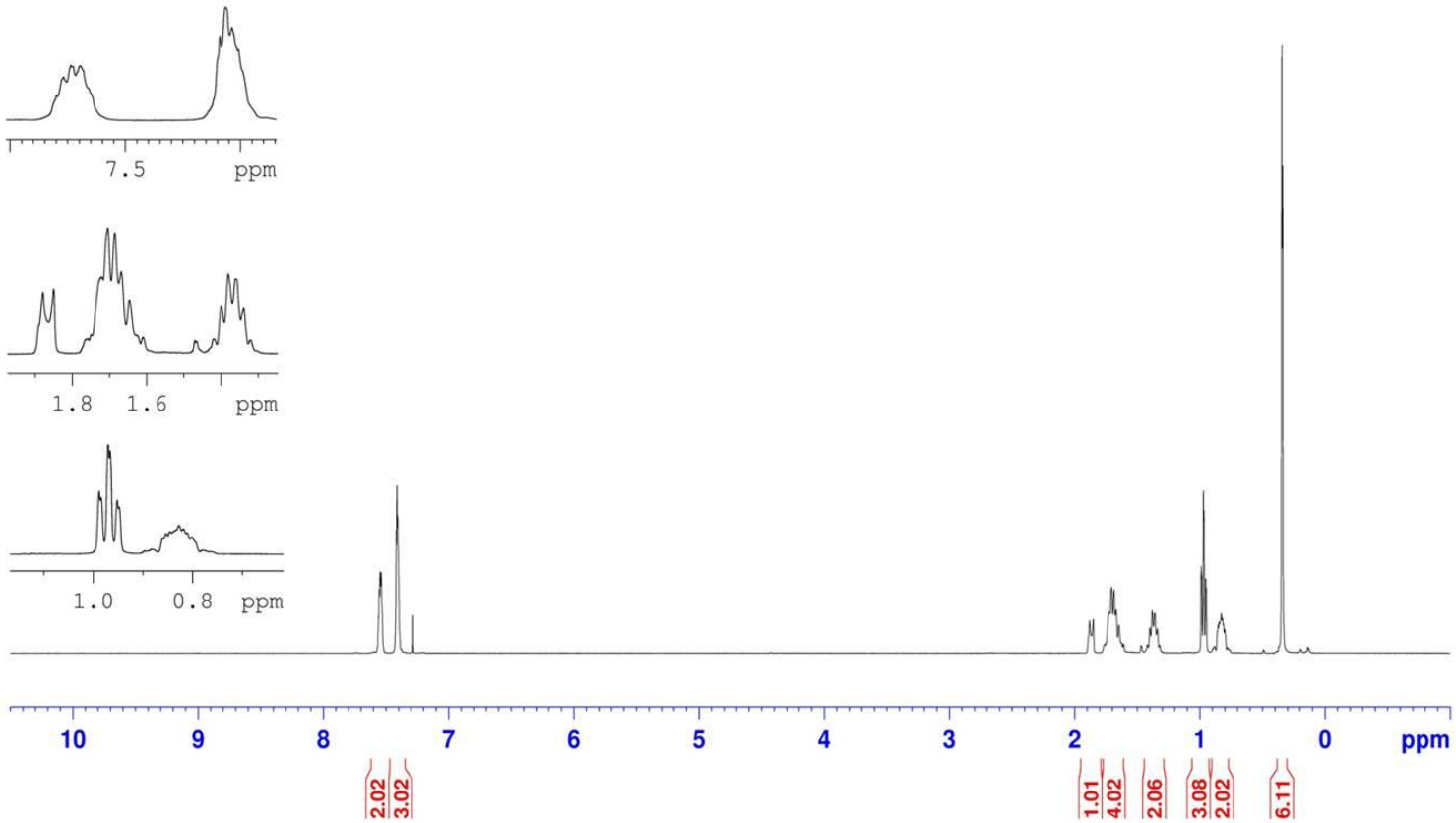


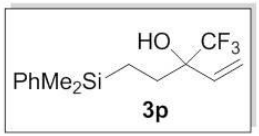
1–(dimethyl(phenyl)silyl)–3–(trifluoromethyl)hexan–3–ol
400 MHz, CDCl3

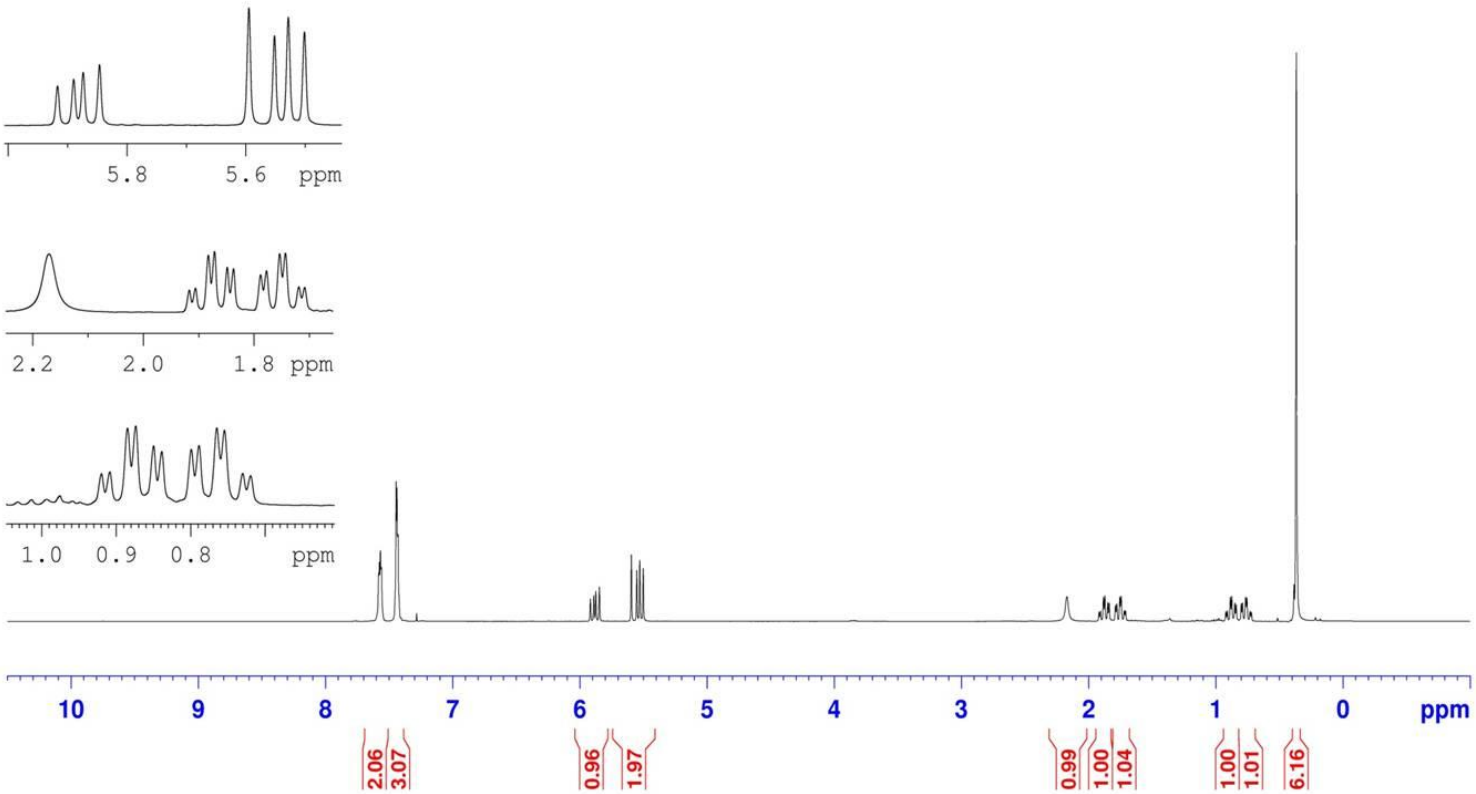


3o'

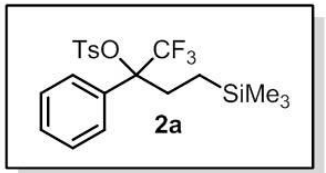


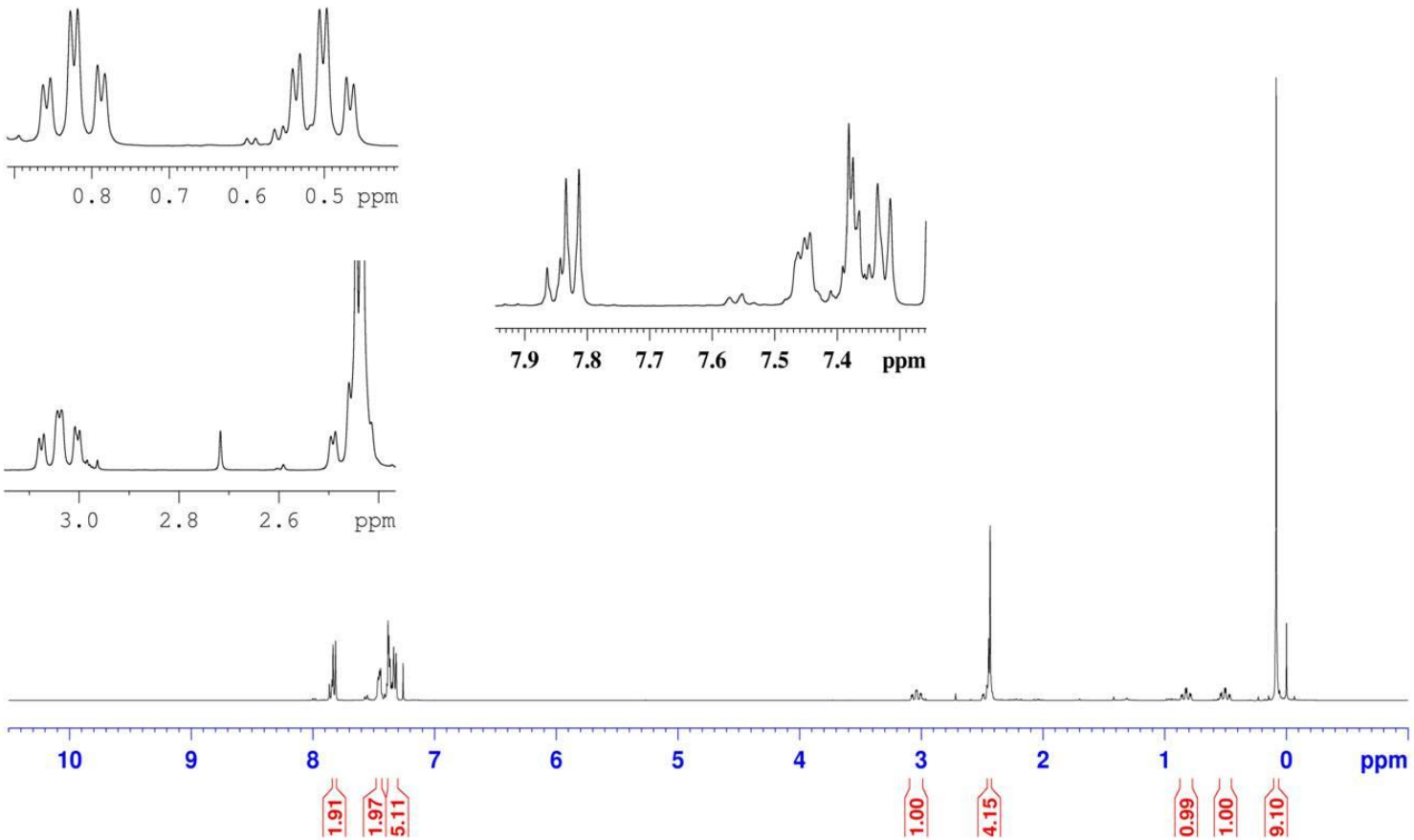
5–(dimethyl(phenyl)silyl)–3–(trifluoromethyl)pent–1–en–3–ol
400 MHz, CDCl3



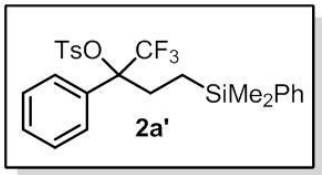


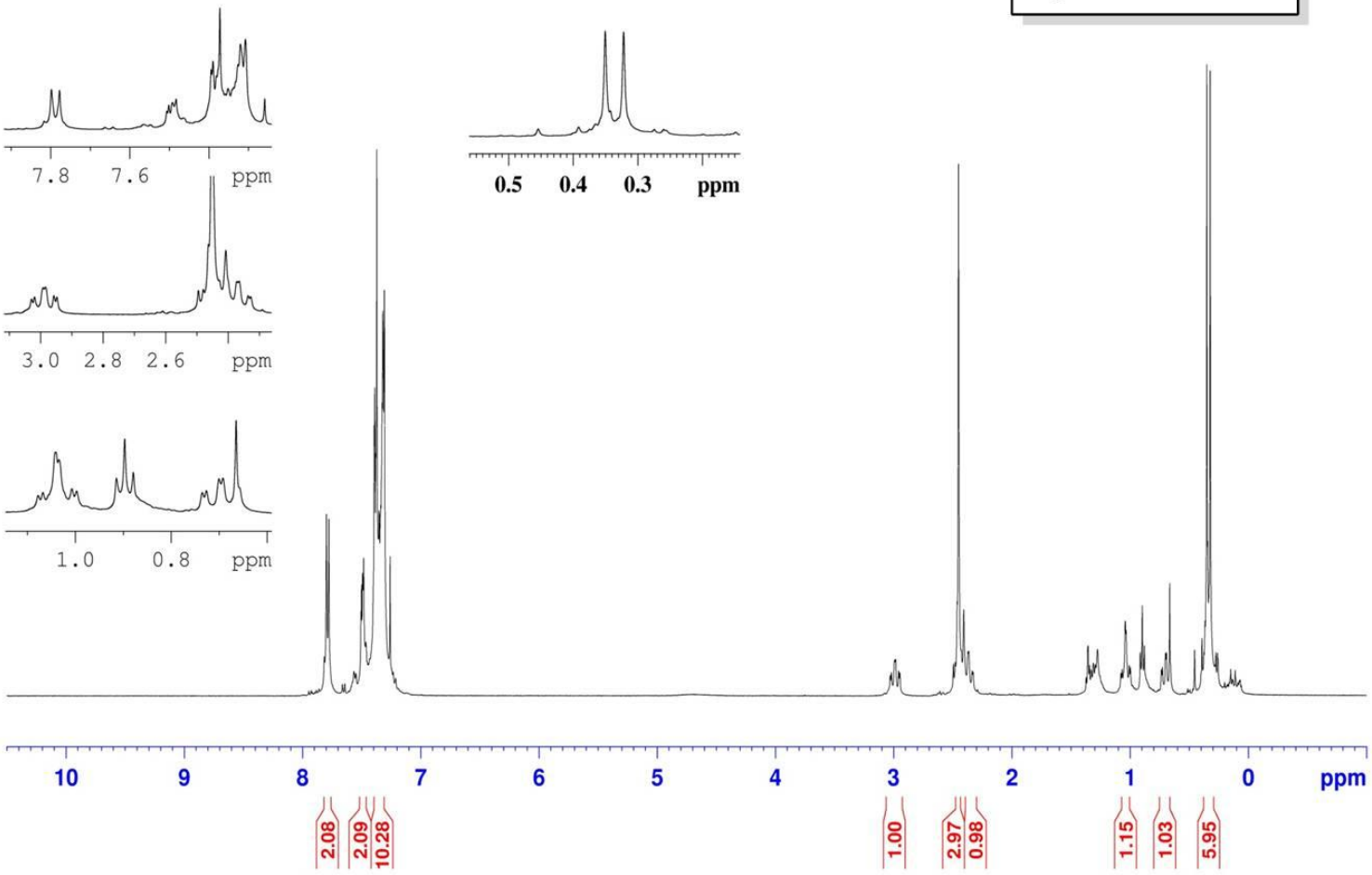
1,1,1−trifluoro−2−phenyl−4−(trimethylsilyl)butan−2−yl 4−methylbenzenesulfonate
400 MHz, CDCl3



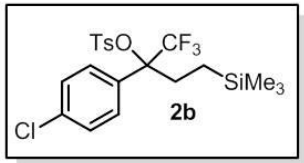


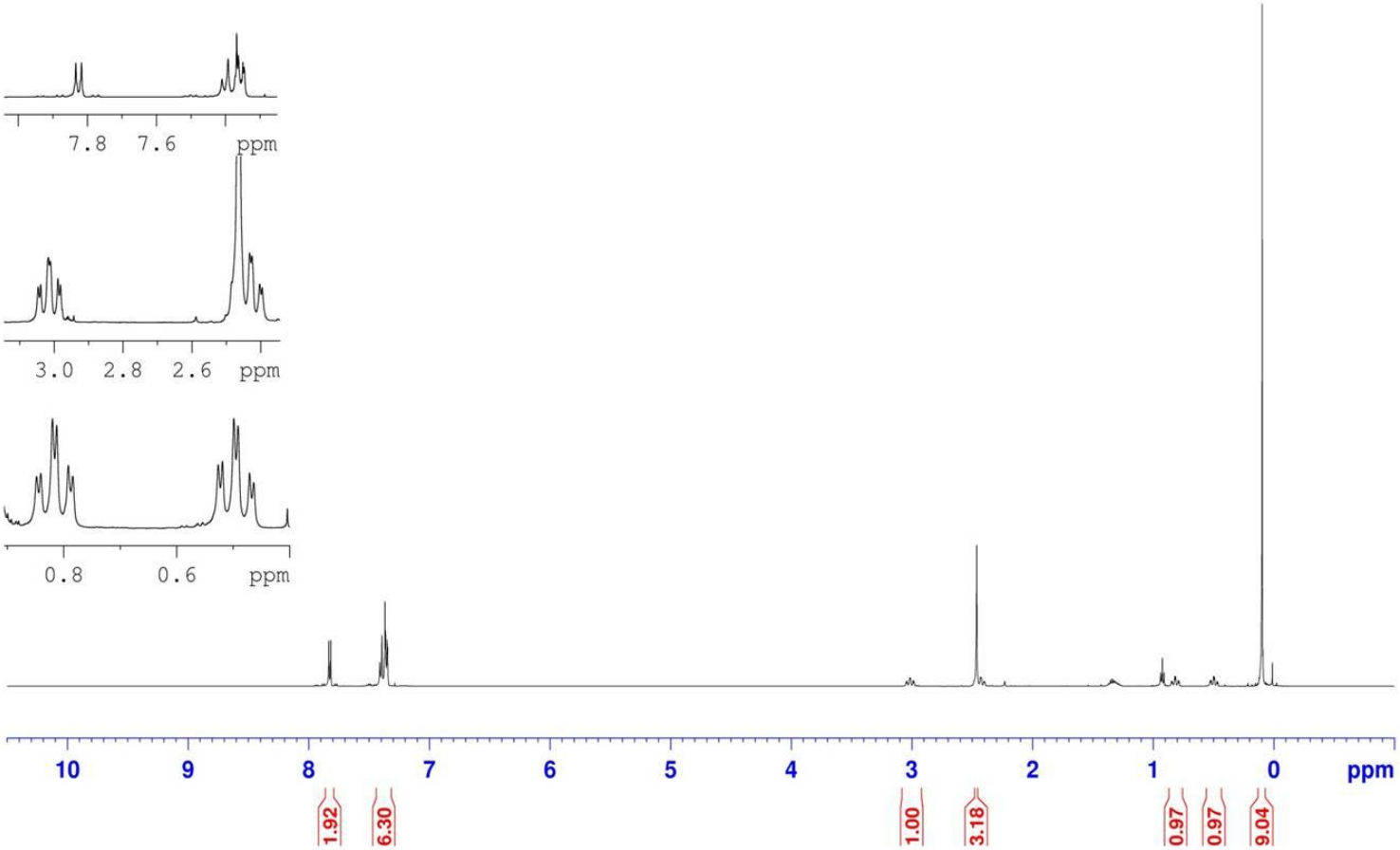
4–(dimethyl(phenyl)silyl)–1,1,1–trifluoro–2–phenylbutan–2–yl 4–methylbenzenesulfonate
400 MHz, CDCl3



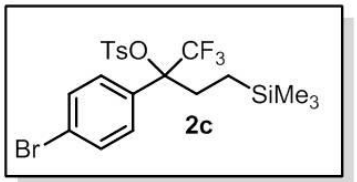


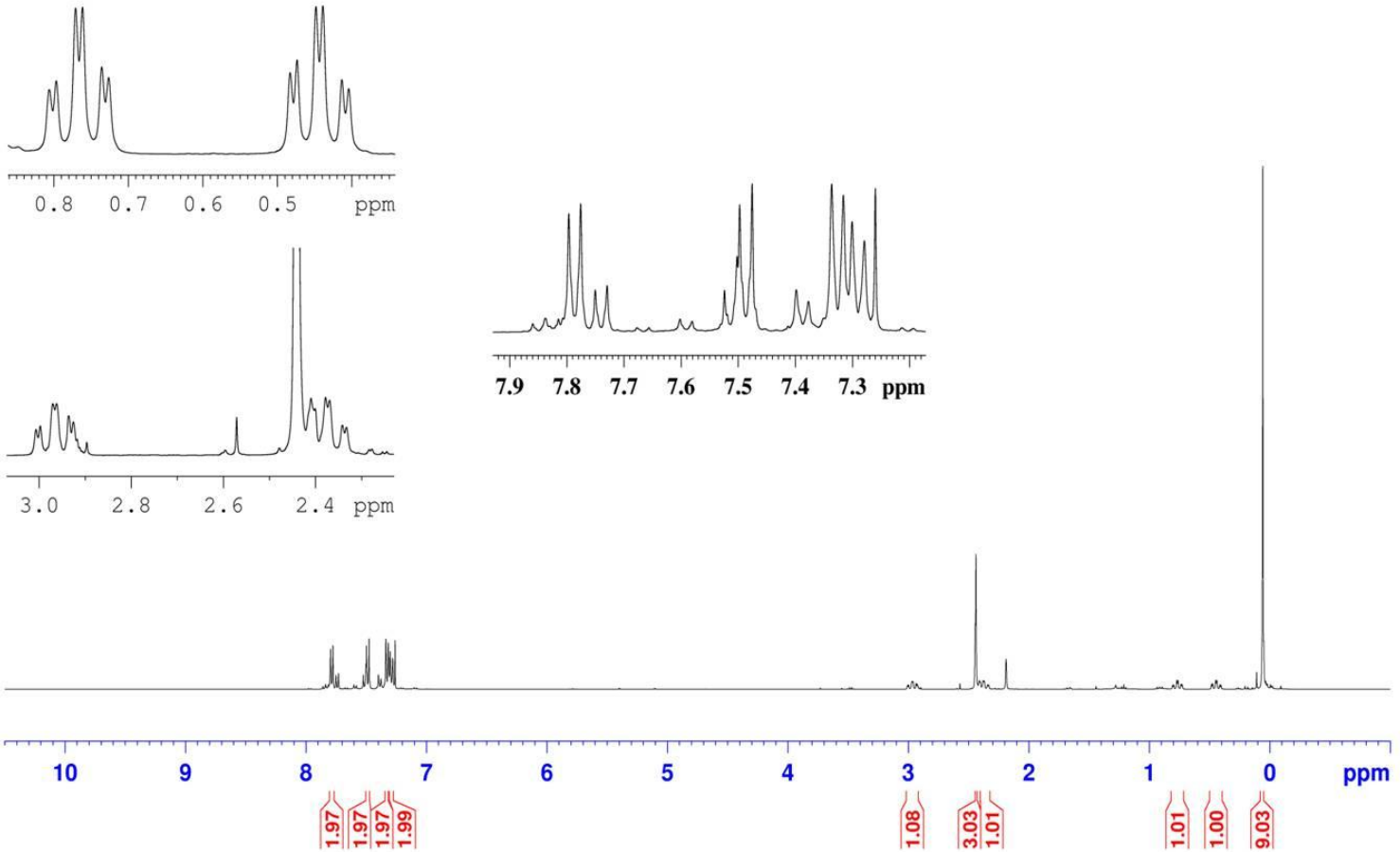
2–(4–chlorophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
400 MHz, CDCl3



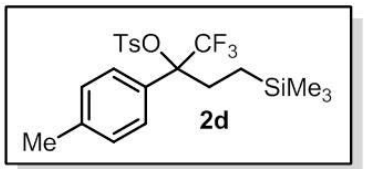


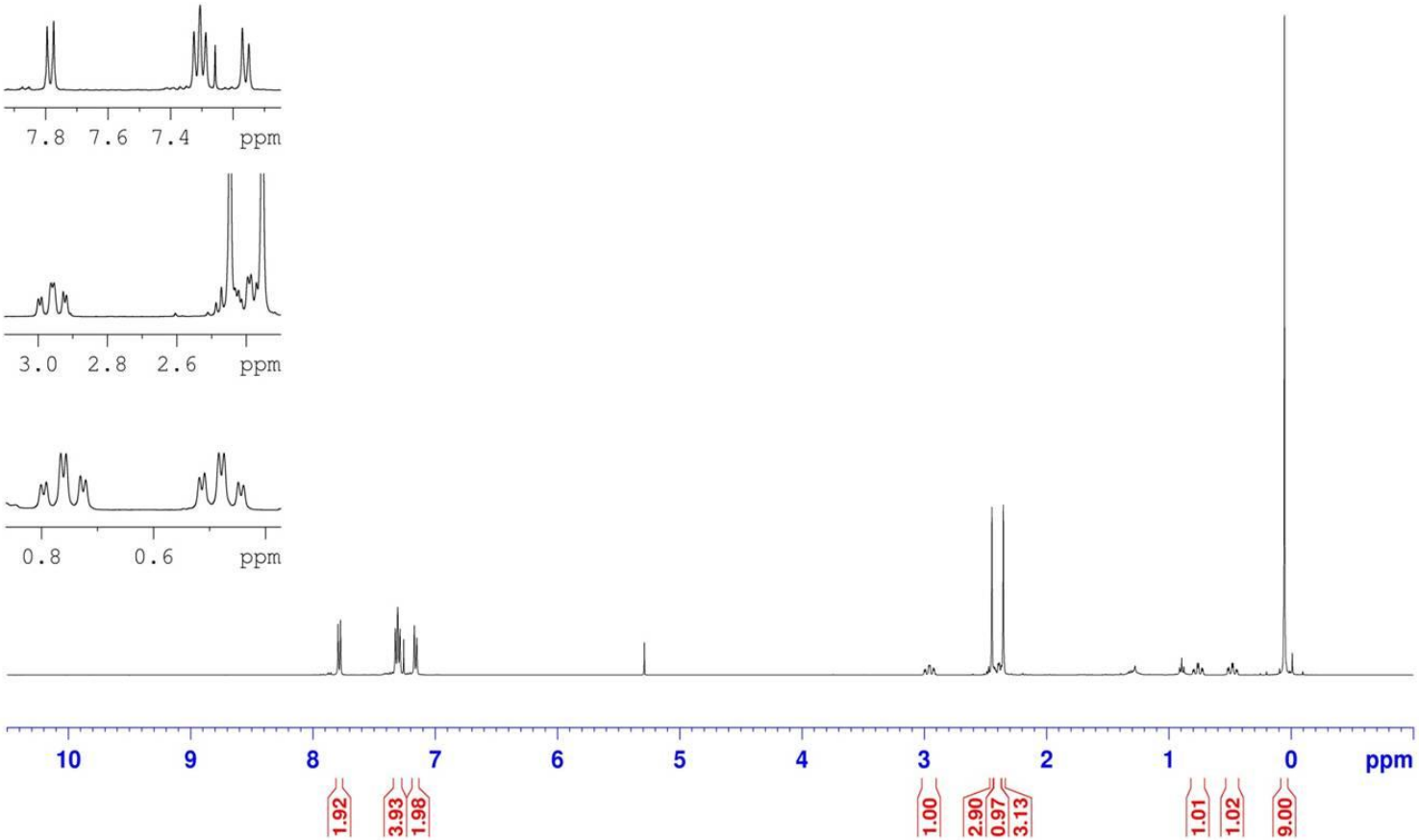
2–(4–bromophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
400 MHz, CDCl3



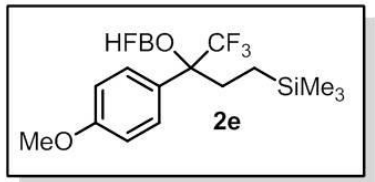


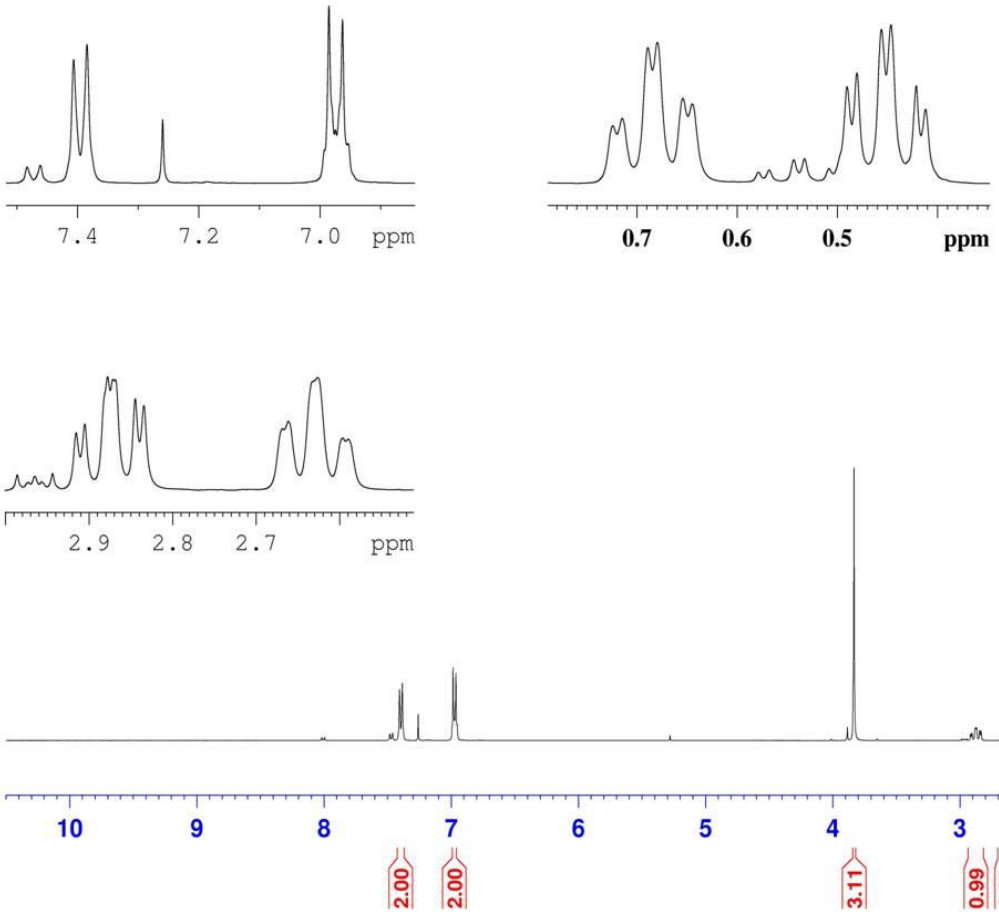
1,1,1–trifluoro–2–(p–tolyl)–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
400 MHz, CDCl3



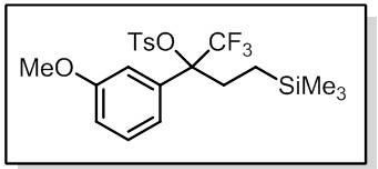


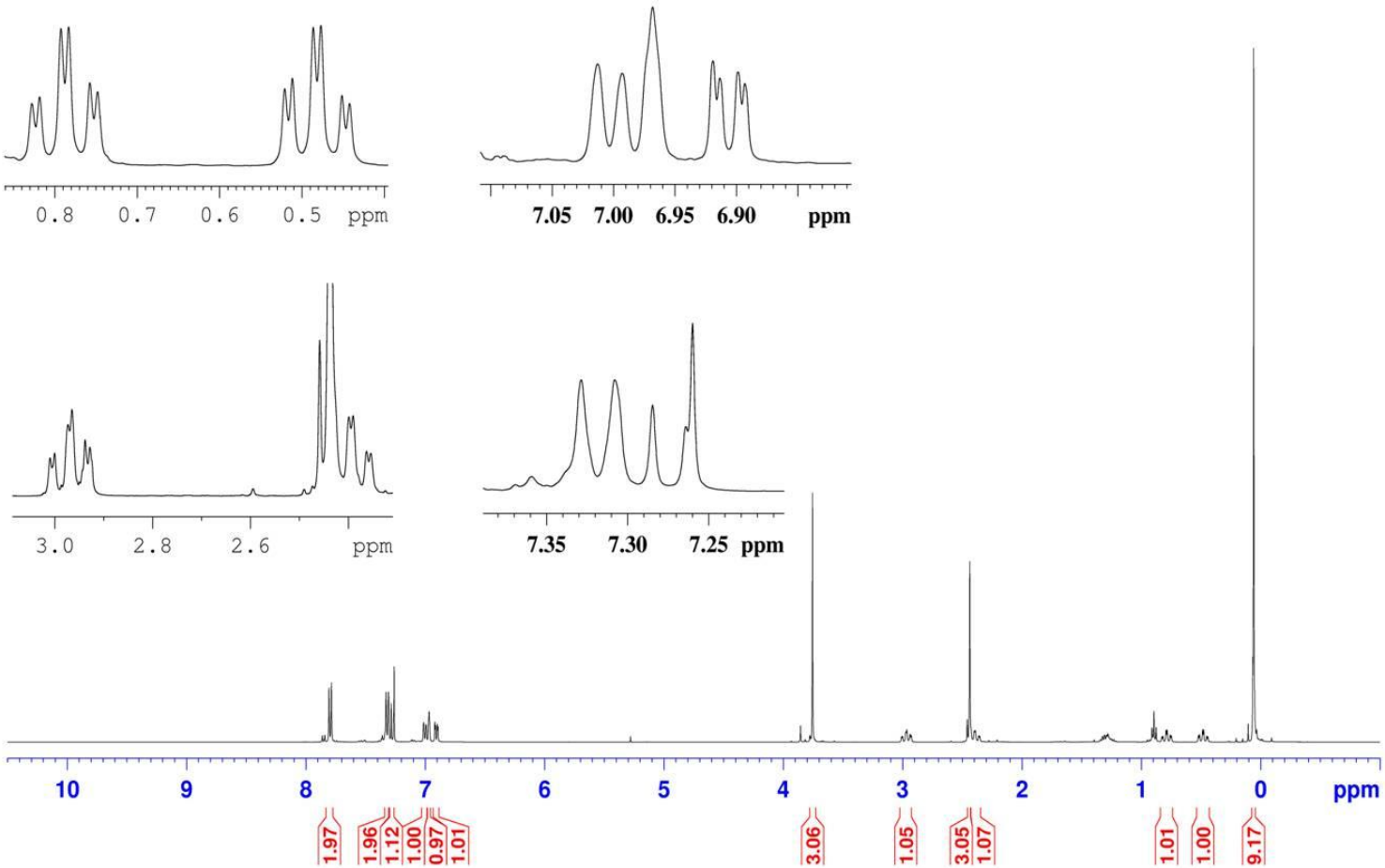
1,1,1–trifluoro–2–(4–methoxyphenyl)–4–(trimethylsilyl)butan–2–yl 2,2,3,3,4,4,4–heptafluorobutanoate
400 MHz, CDCl3



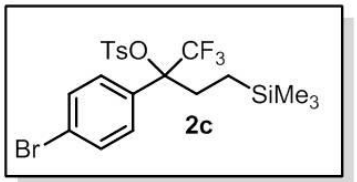


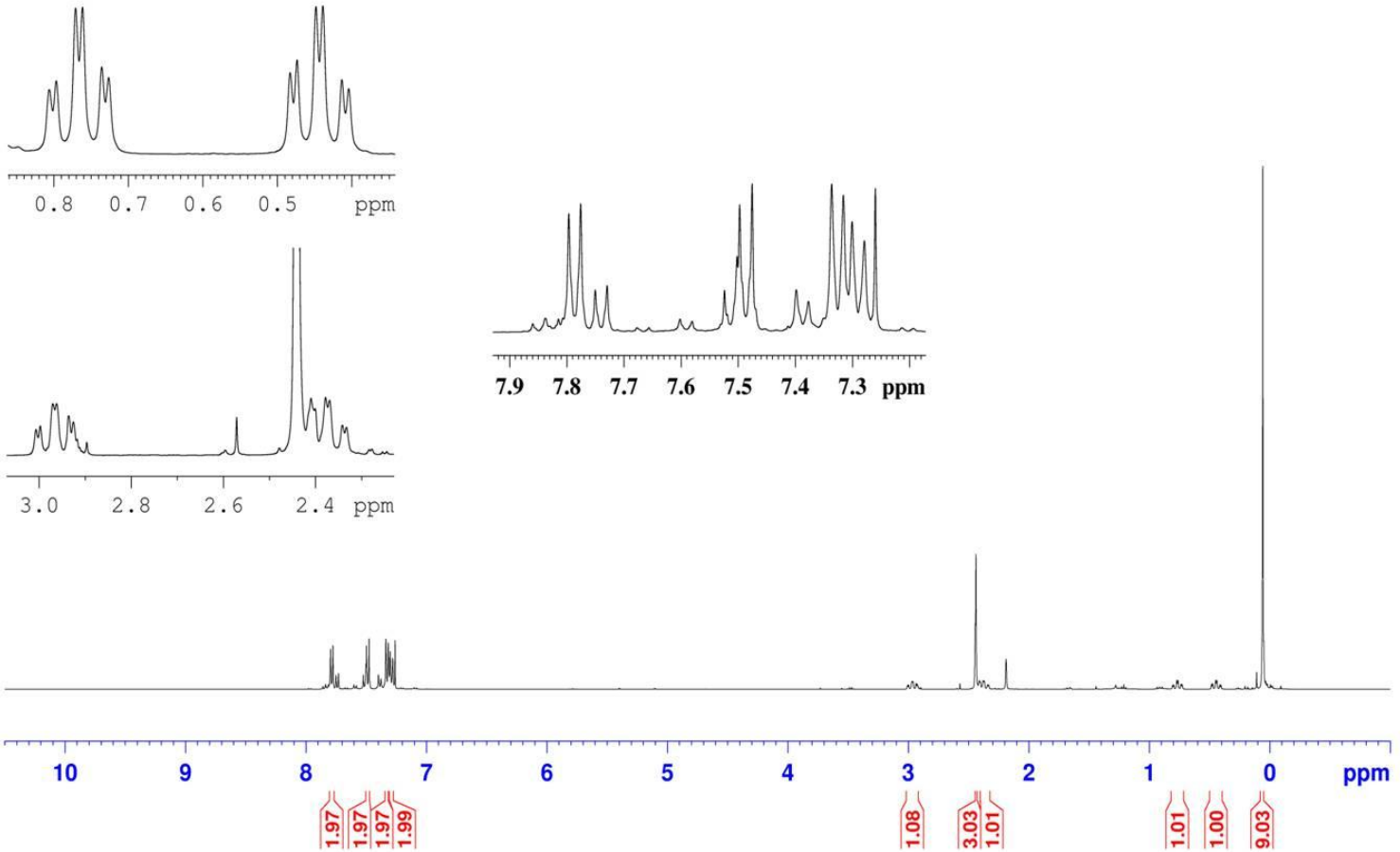
1,1,1−trifluoro−2−(3−methoxyphenyl)−4−(trimethylsilyl)butan−2−yl 4−methylbenzenesulfonate
400 MHz, CDCl3



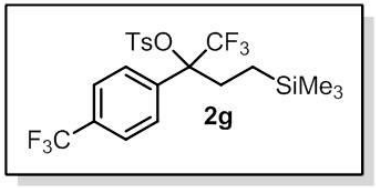


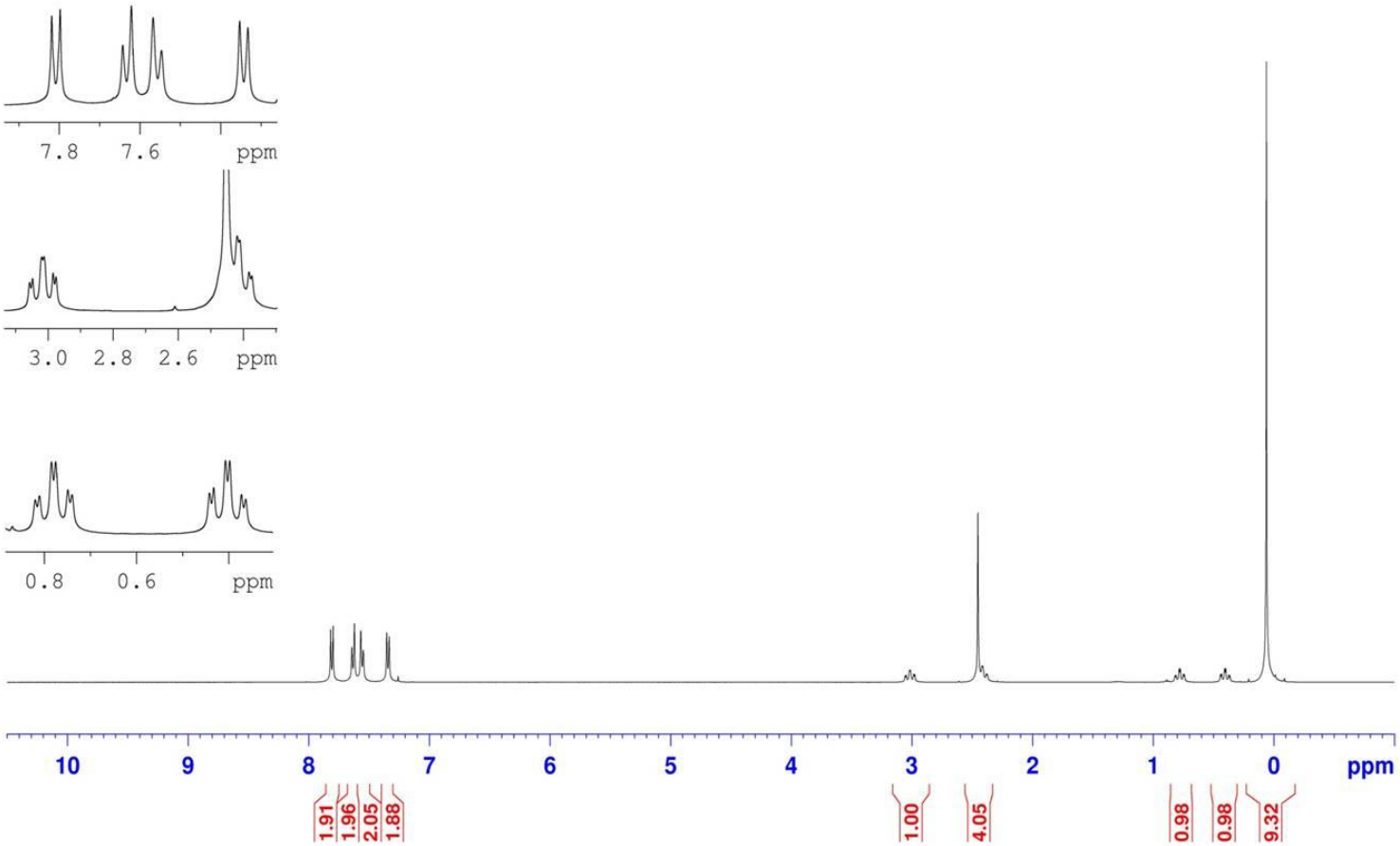
2–(4–bromophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
400 MHz, CDCl3



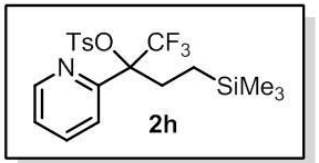


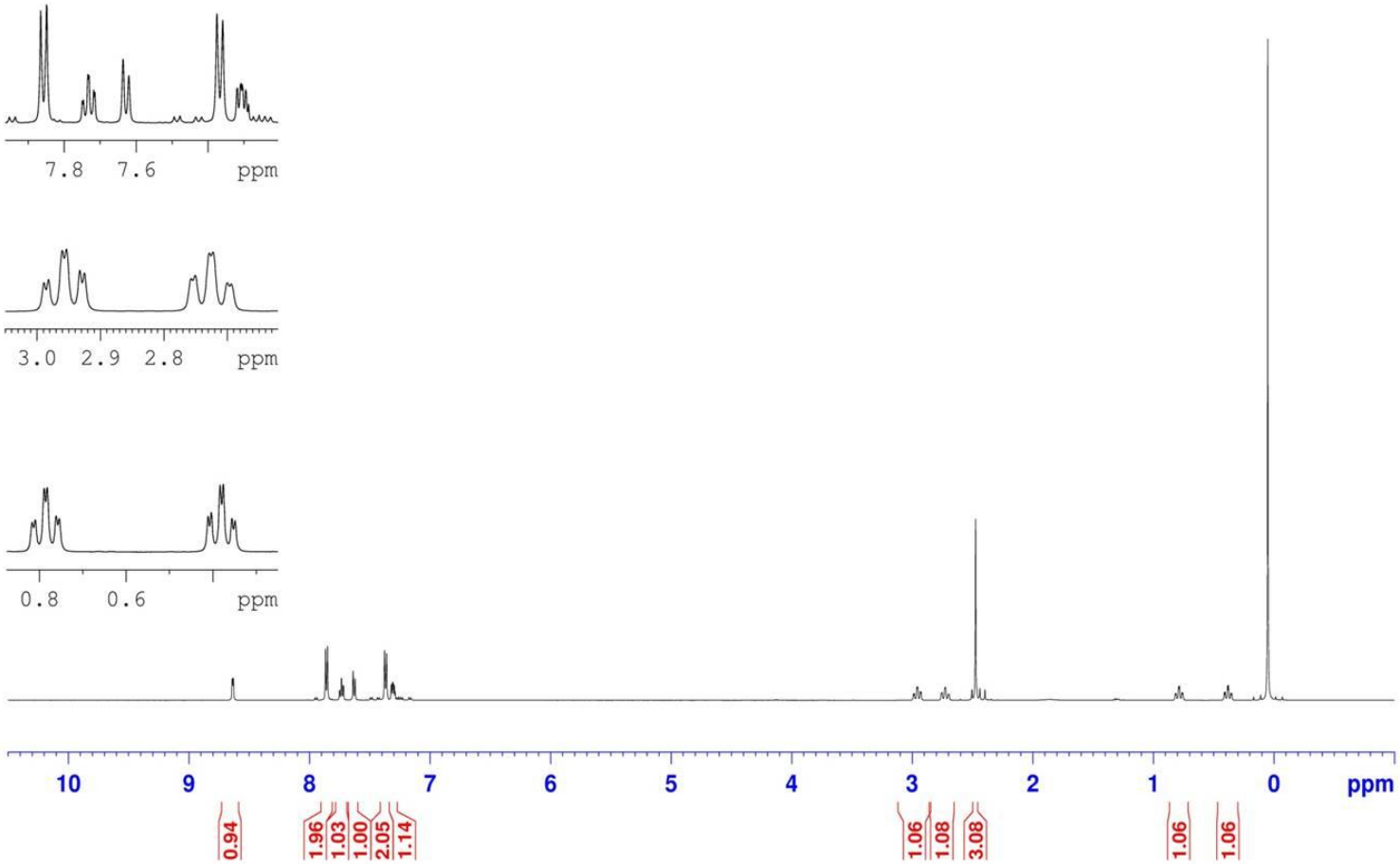
1,1,1–trifluoro–2–(4–(trifluoromethyl)phenyl)–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
400 MHz, CDCl3



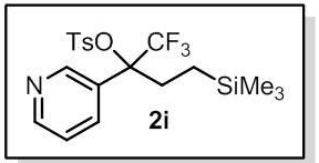


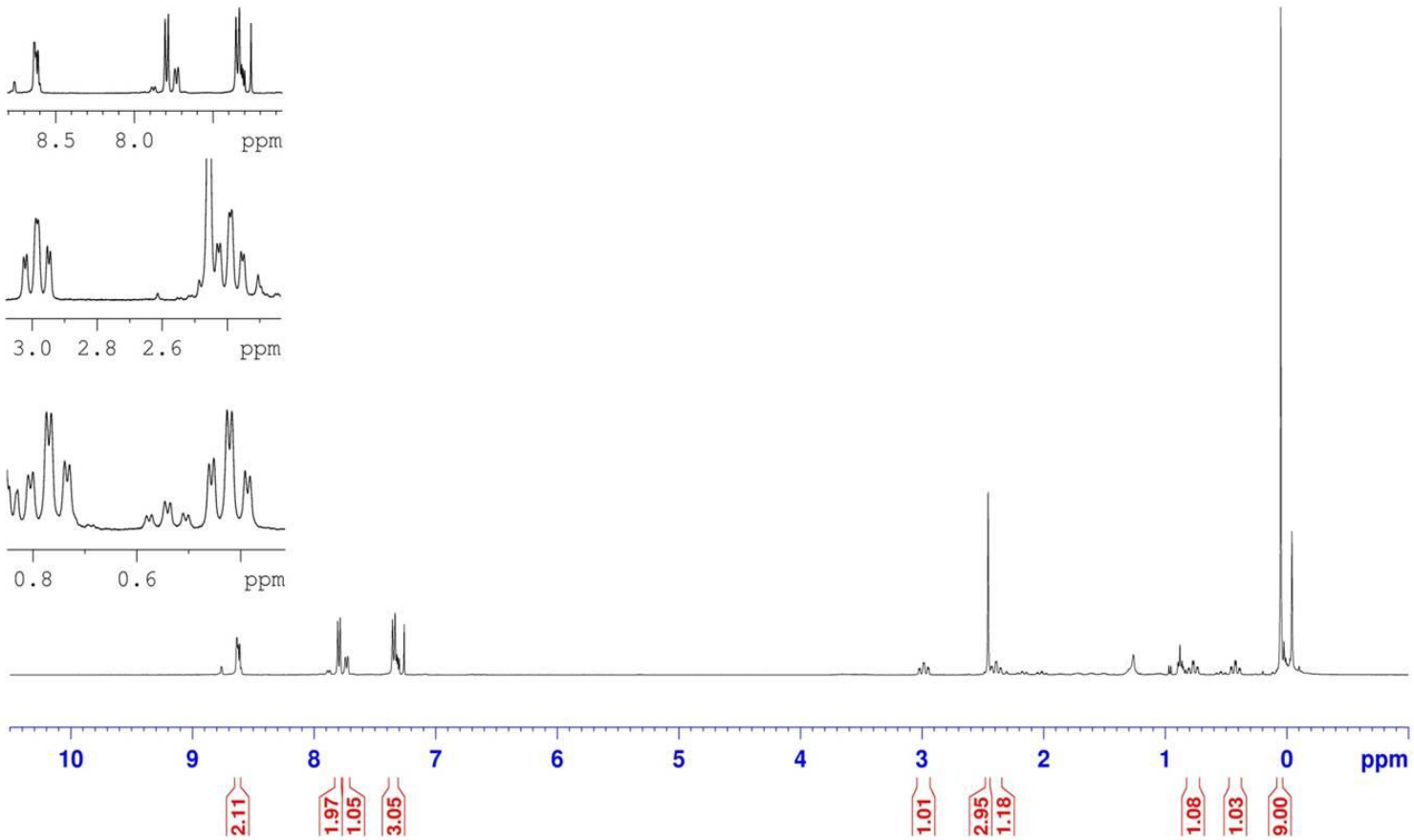
1,1,1–trifluoro–2–(pyridin–2–yl)–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
400 MHz, CDCl3



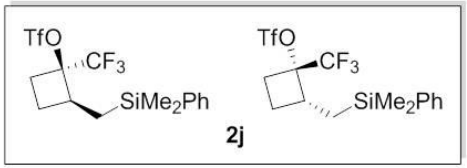


1,1,1–trifluoro–2–(pyridin–3–yl)–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
400 MHz, CDCl3





(1R,2S) & (1S,2R)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutyl trifluoromethanesulfonate
400 MHz, CDCl3



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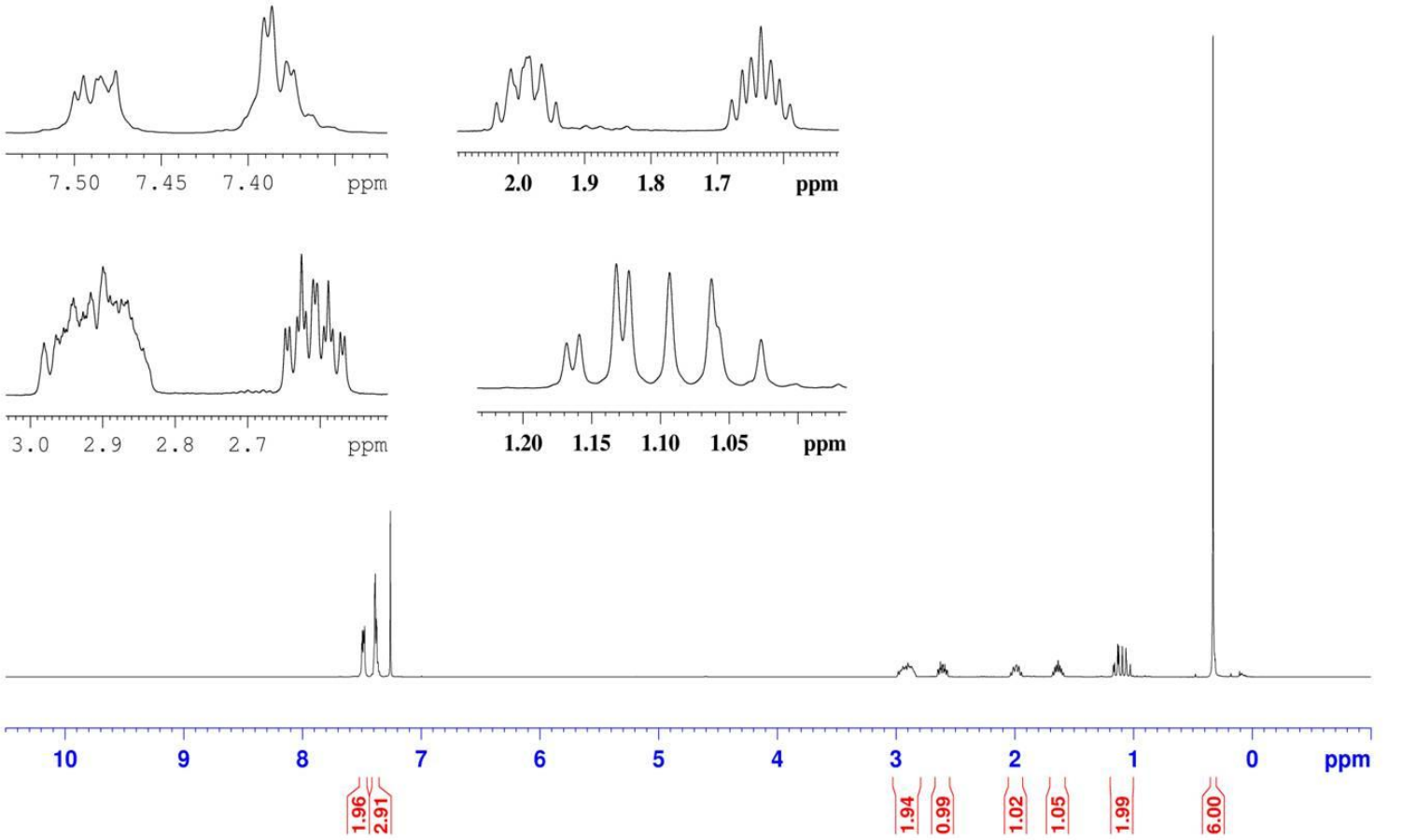
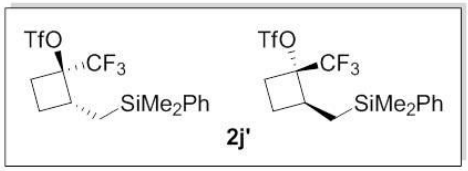


(1R,2R) & (1S,2S)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutyl trifluoromethanesulfonate
400 MHz, CDCl3



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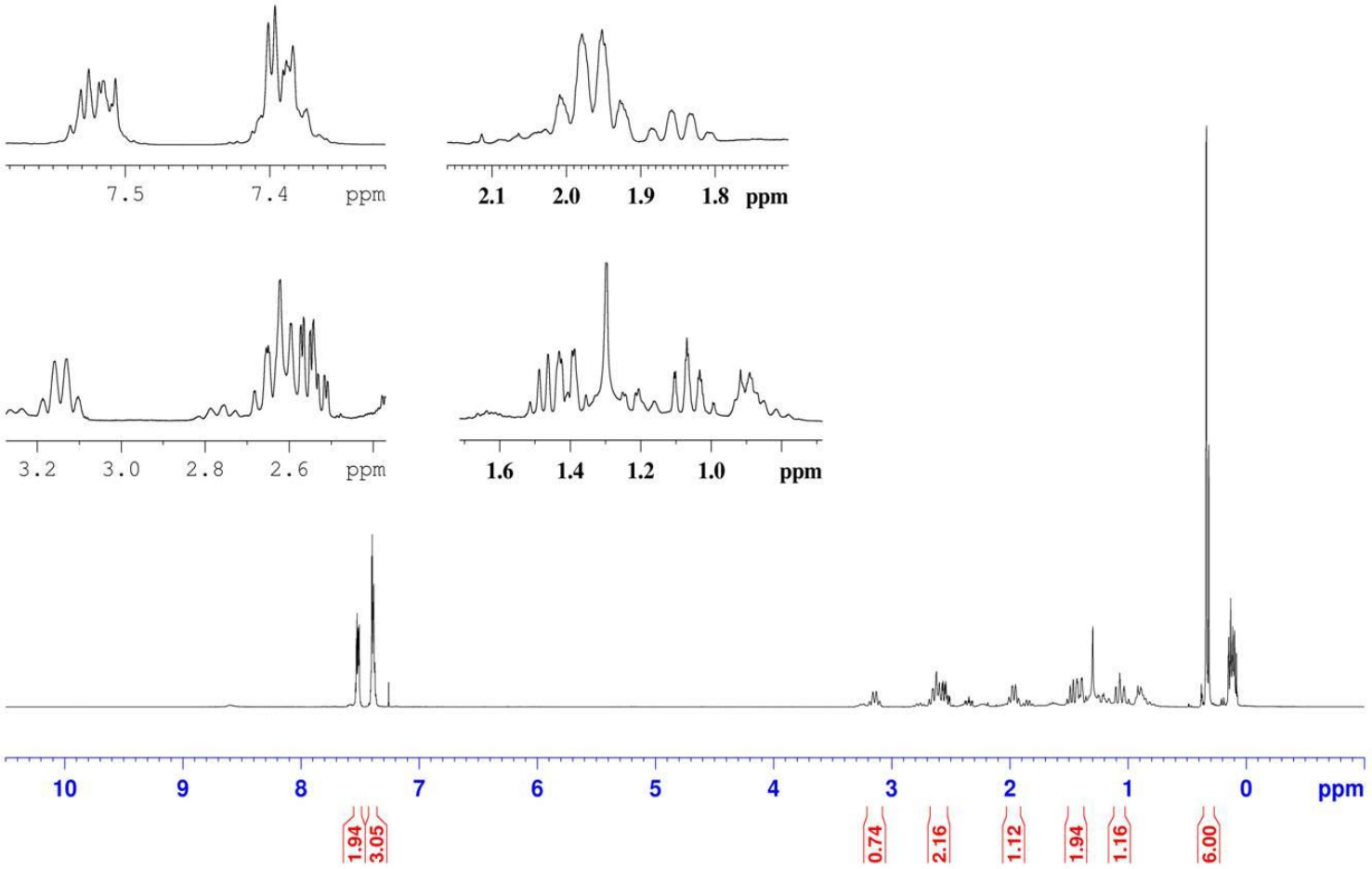
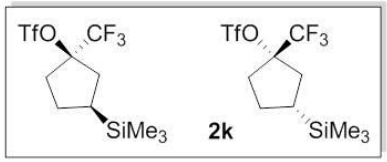
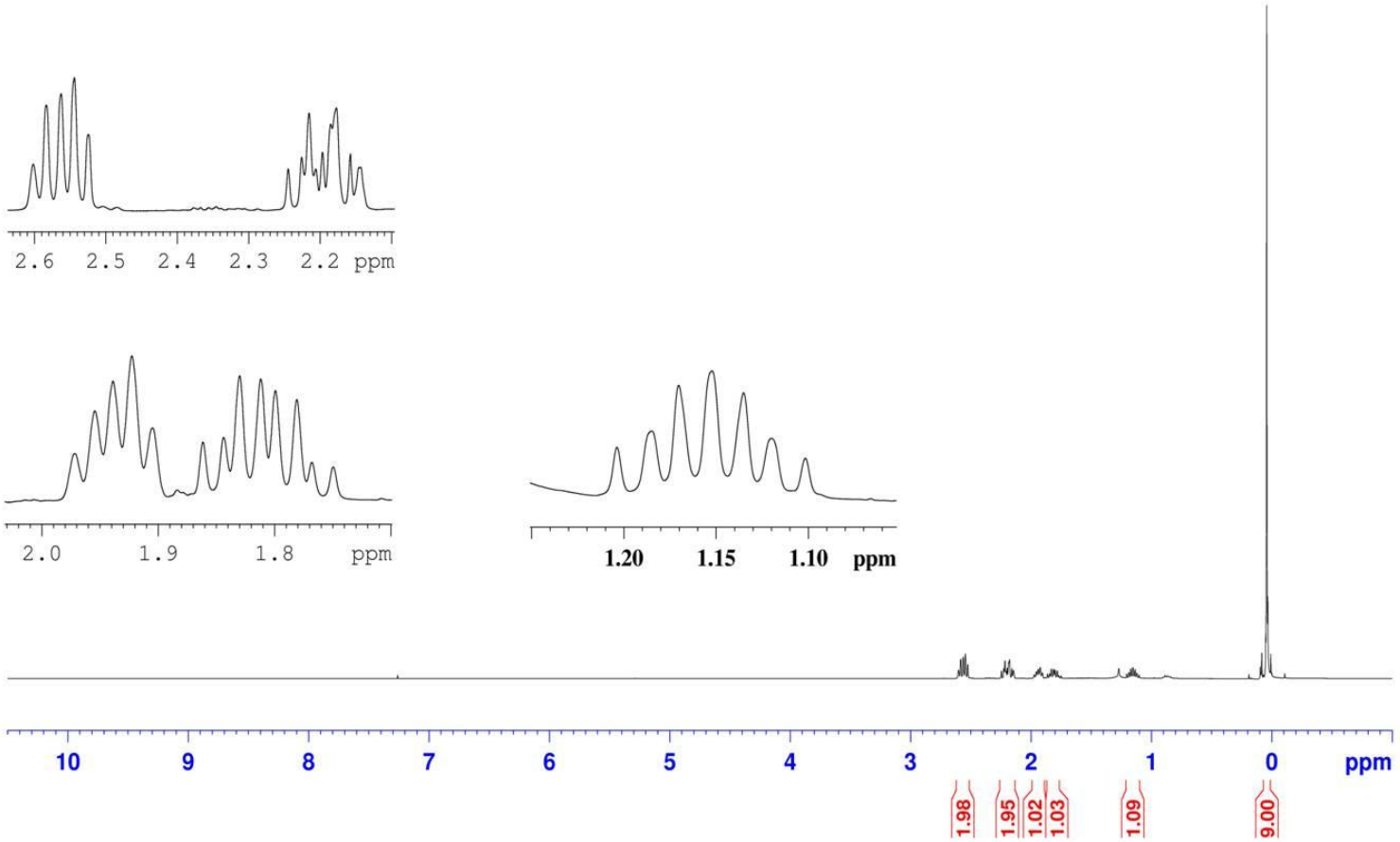
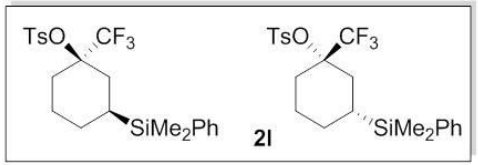


(1R,3S) & (1S,3R)−1−(trifluoromethyl)−3−(trimethylsilyl)cyclopentyl trifluoromethanesulfonate
400 MHz, CDCl3





(1R,3S) & (1S,3R)– 3–(dimethyl(phenyl)silyl)–1–(trifluoromethyl)cyclohexyl 4–methylbenzenesulfonate
400 MHz, CDCl3



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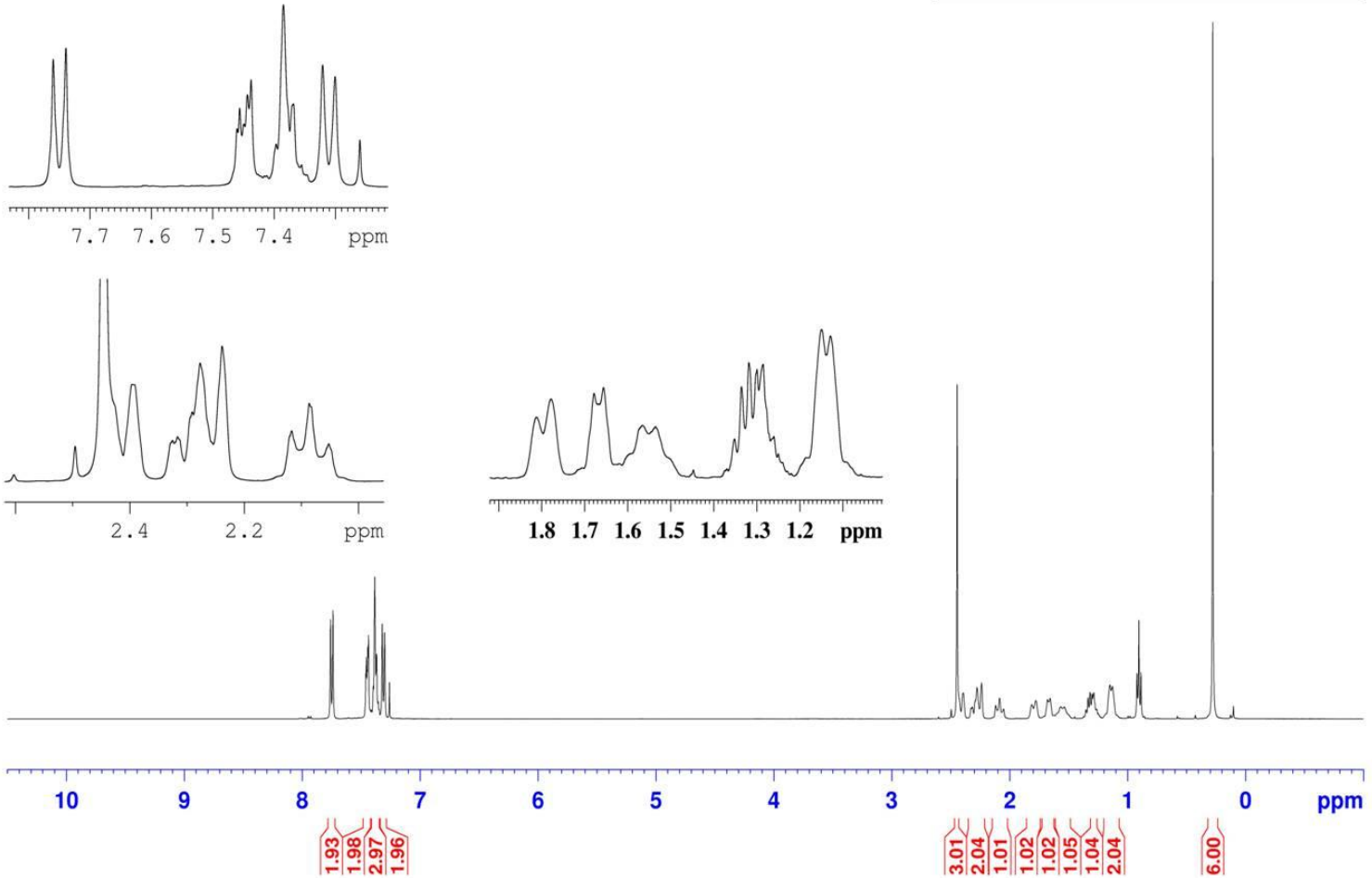
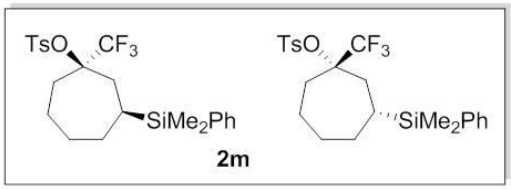
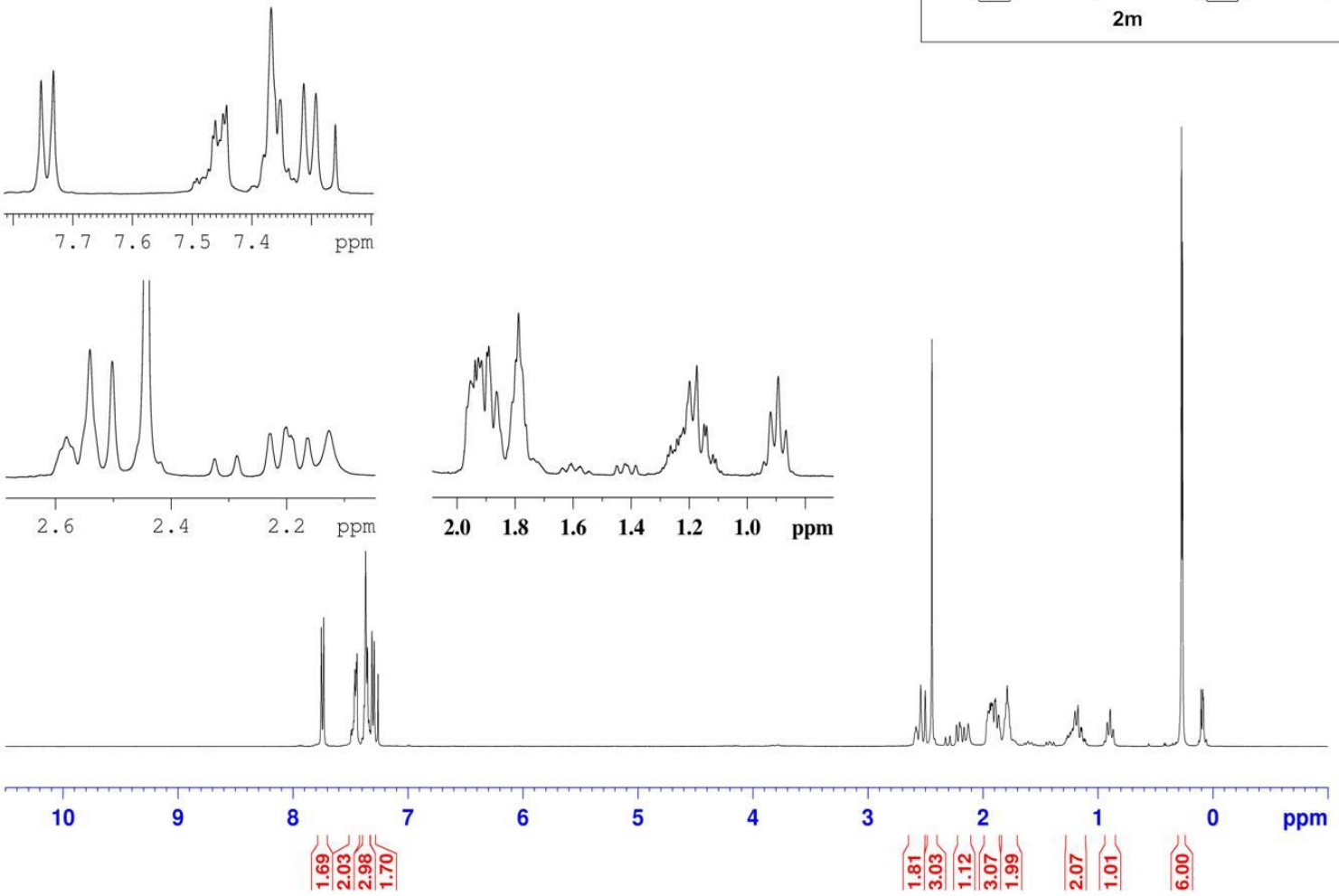
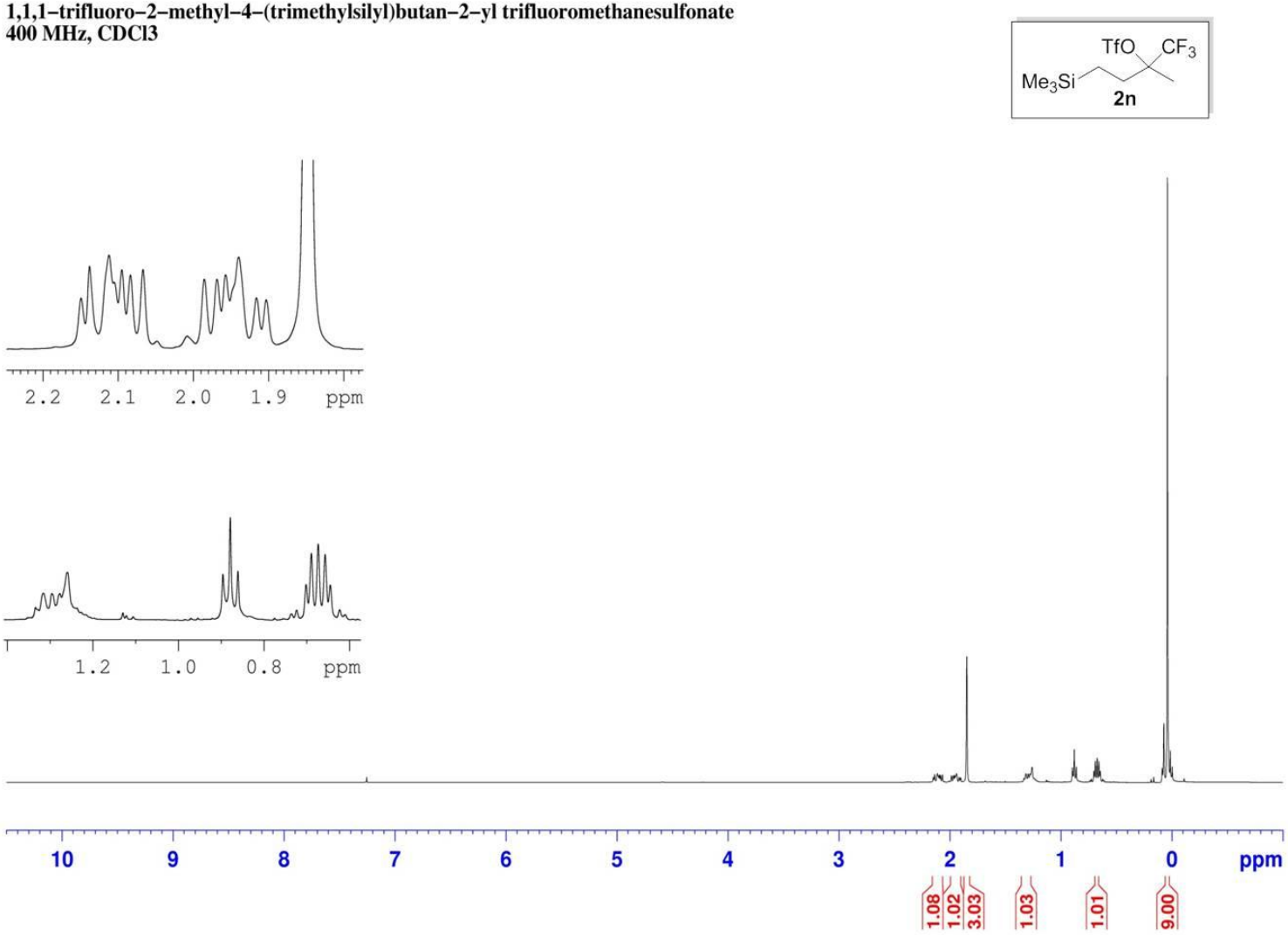


(1R,3S) & (1S,3R)– 3–(dimethyl(phenyl)silyl)–1–(trifluoromethyl)cycloheptyl 4–methylbenzenesulfonate
400 MHz, CDCl3

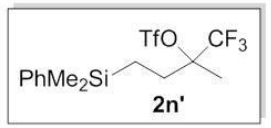


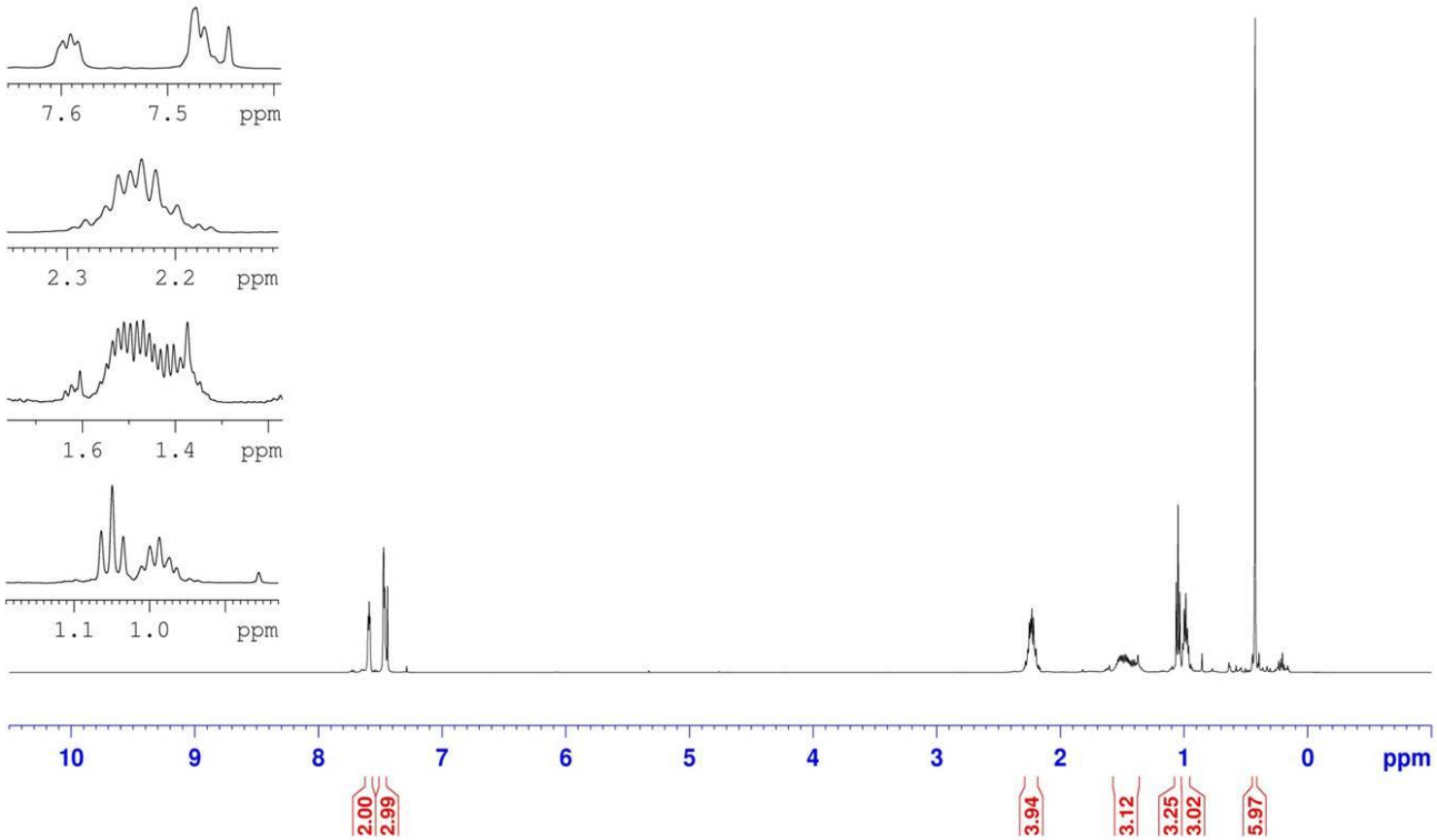


1,1,1−trifluoro−2−methyl−4−(trimethylsilyl)butan−2−yl trifluoromethanesulfonate
400 MHz, CDCl3

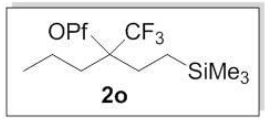


1−(dimethyl(phenyl)silyl)−3−(trifluoromethyl)hexan−3−yl trifluoromethanesulfonate
500 MHz, CDCl3





3–(trifluoromethyl)–1–(trimethylsilyl)hexan–3–yl 2,3,4,5,6–pentafluorobenzenesulfonate
500 MHz, CDCl3



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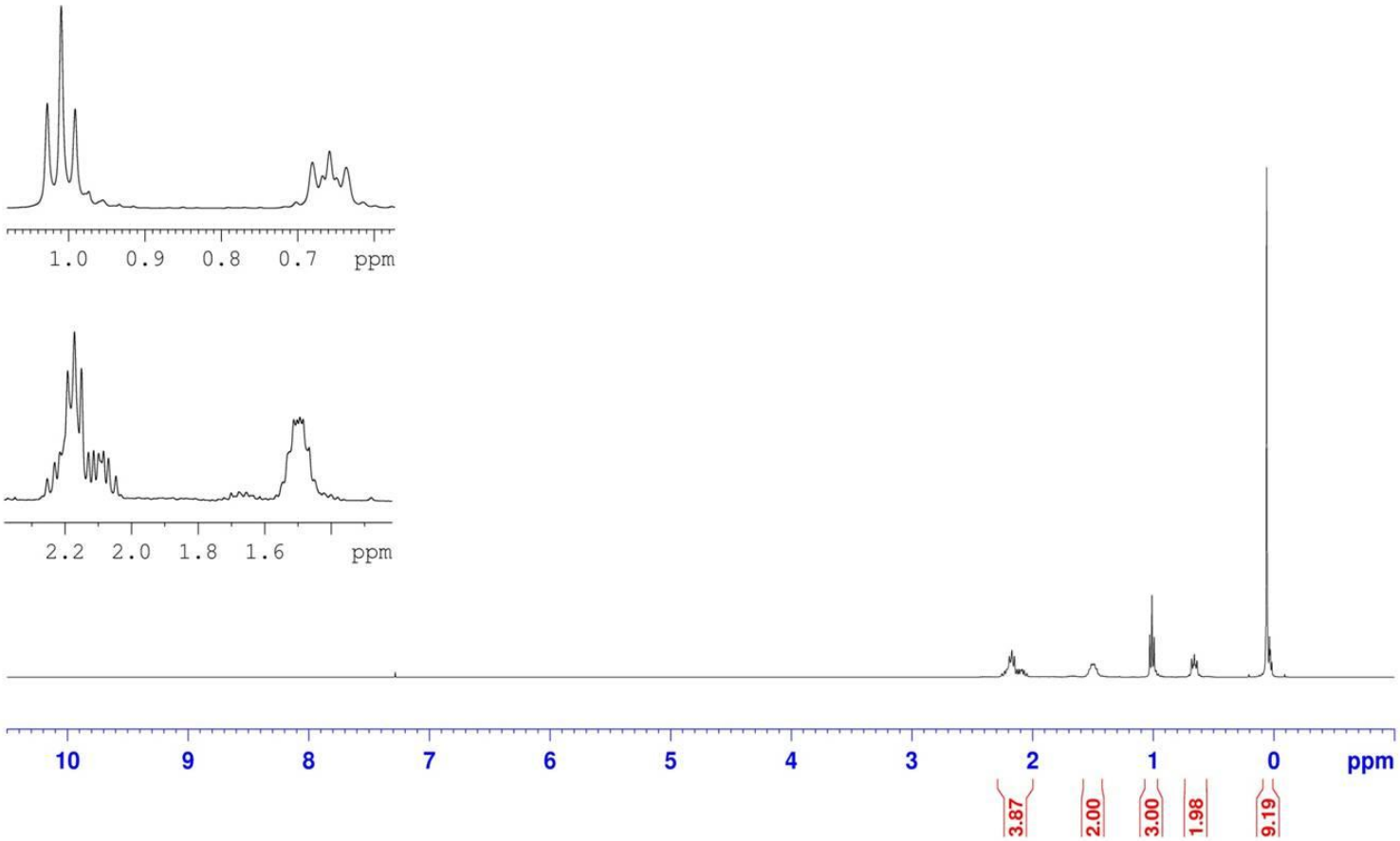
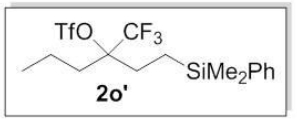


1–(dimethyl(phenyl)silyl)–3–(trifluoromethyl)hexan–3–yl trifluoromethanesulfonate
500 MHz, CDCl3



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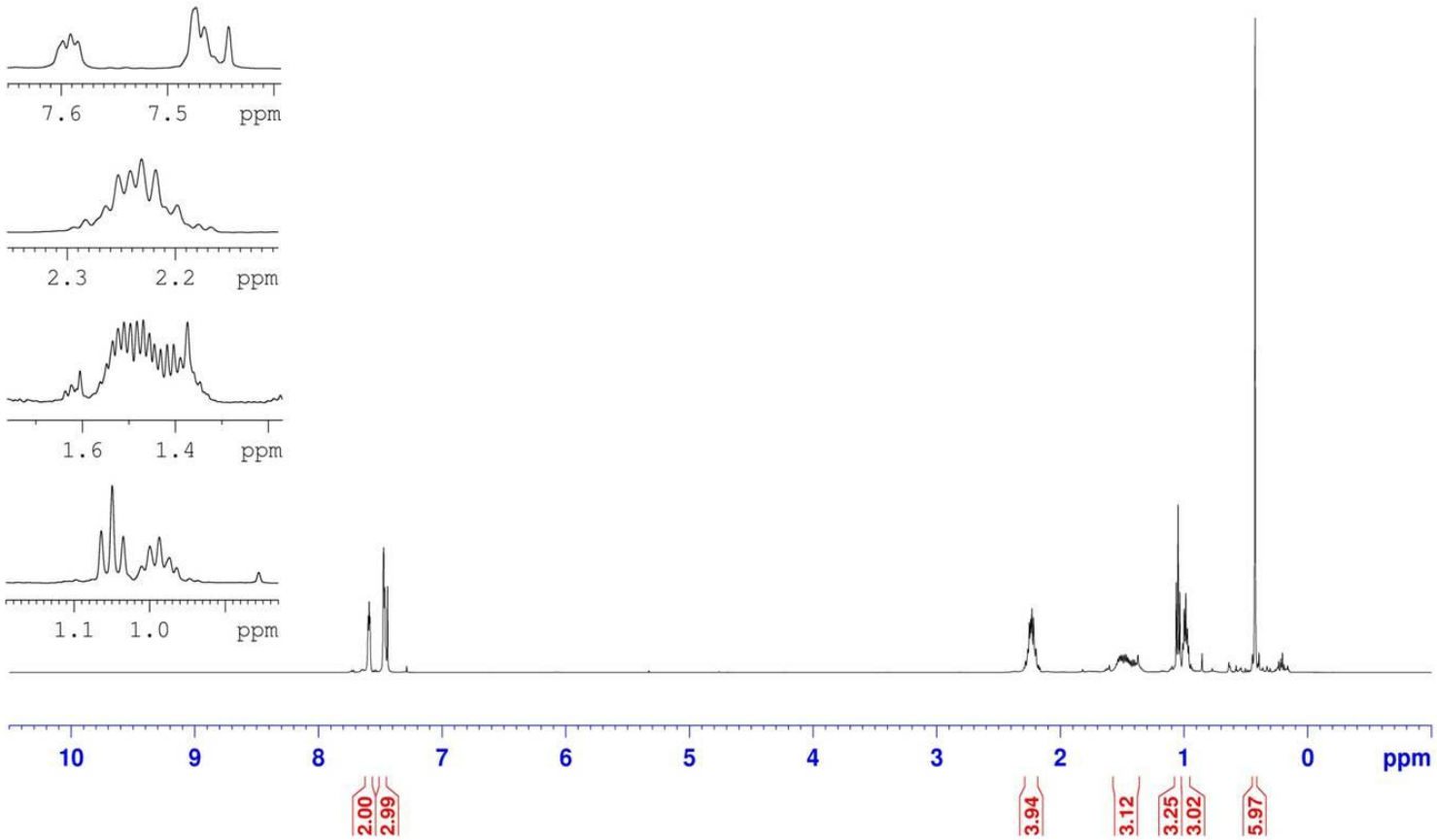
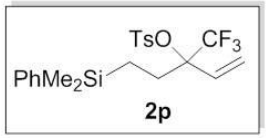


5–(dimethyl(phenyl)silyl)–3–(trifluoromethyl)pent–1–en–3–yl 4–methylbenzenesulfonate
400 MHz, CDCl3



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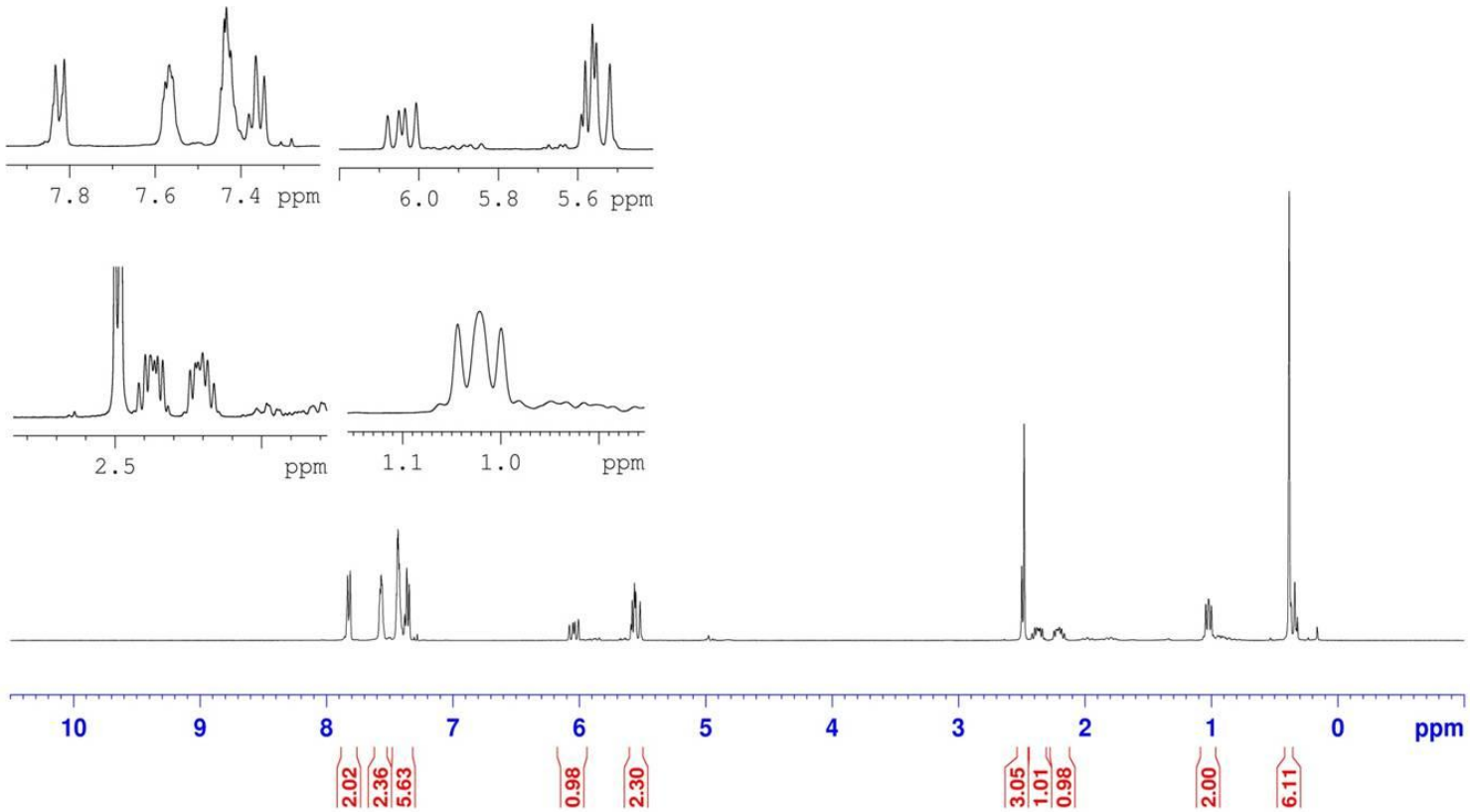
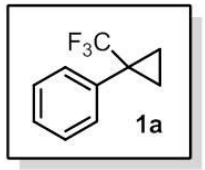
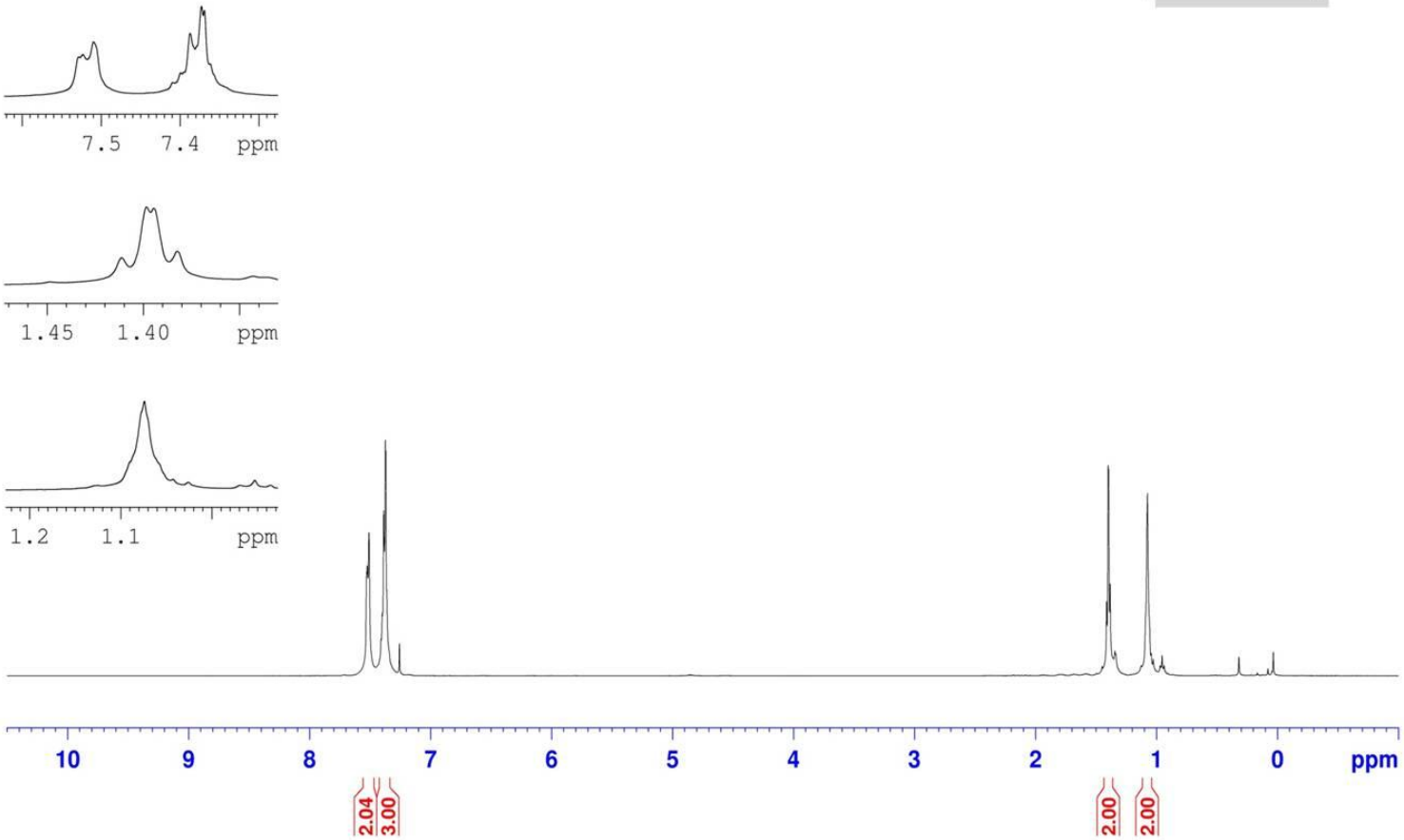
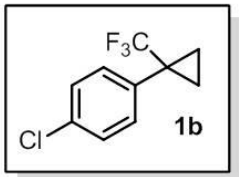


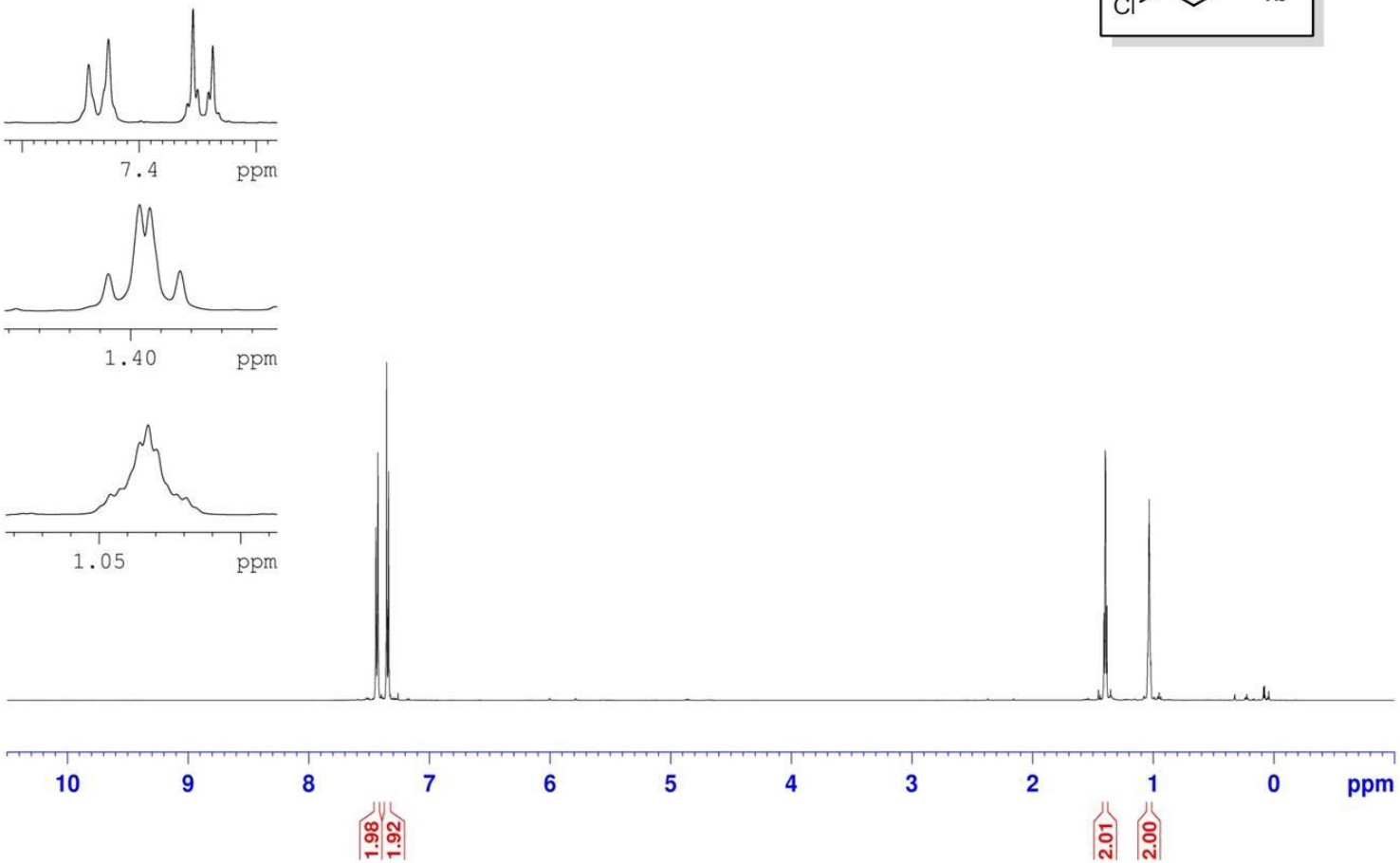
(1–(trifluoromethyl)cyclopropyl)benzene
400 MHz, CDCl3



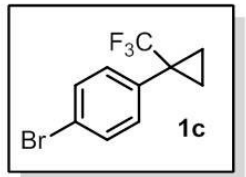


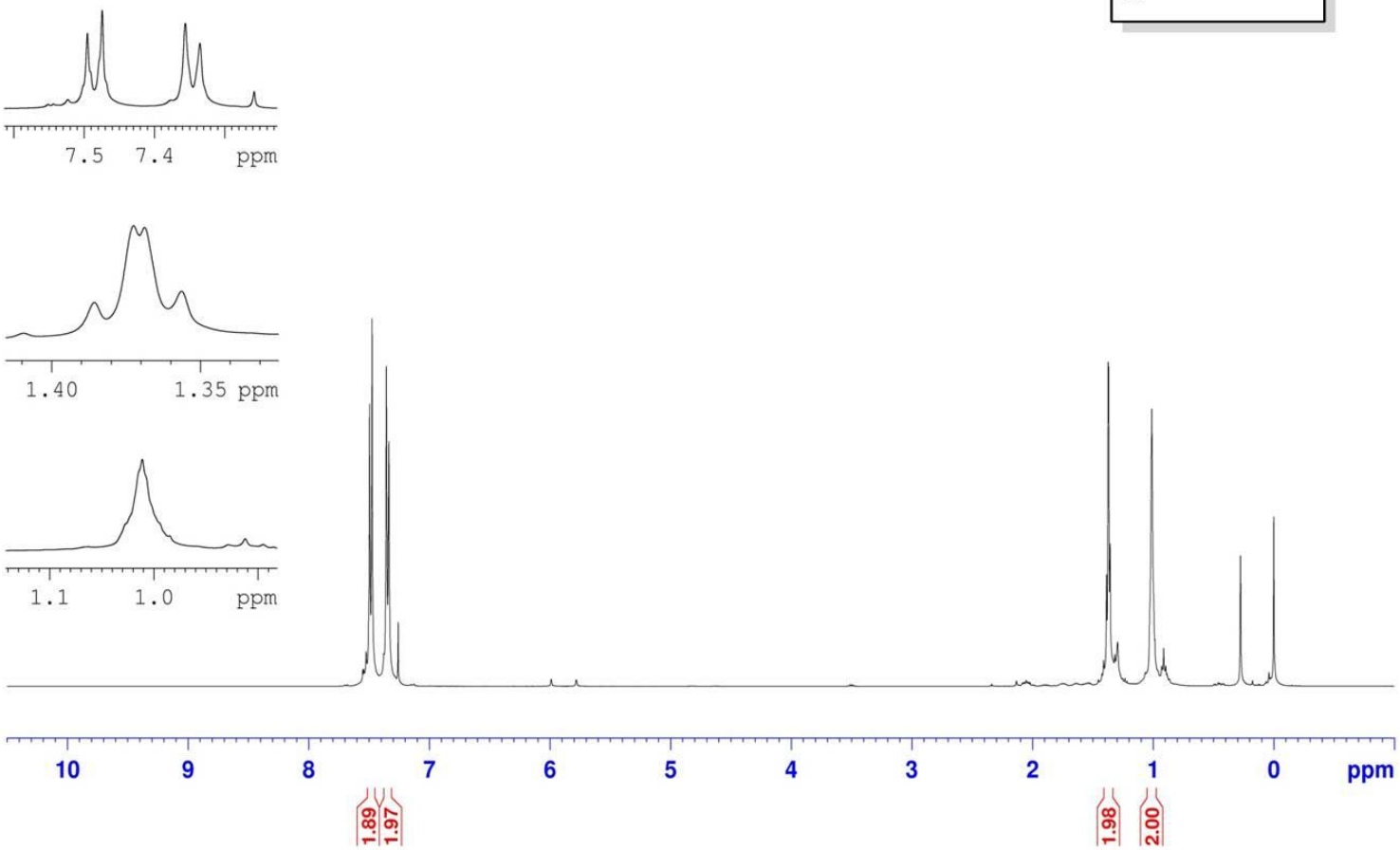
1−chloro−4−(1−(trifluoromethyl)cyclopropyl)benzene
400 MHz, CDCl3



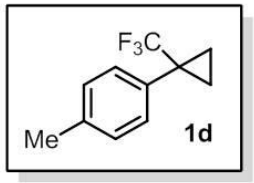


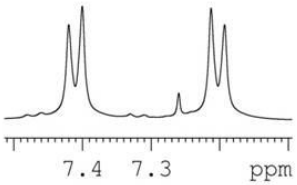
1−bromo−4−(1−(trifluoromethyl)cyclopropyl)benzene
400 MHz, CDCl3

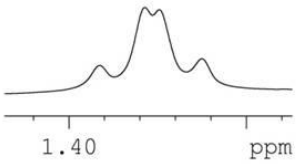


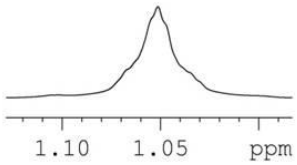


1−methyl−4−(1−(trifluoromethyl)cyclopropyl)benzene
400 MHz, CDCl3

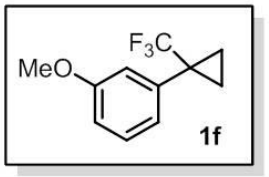


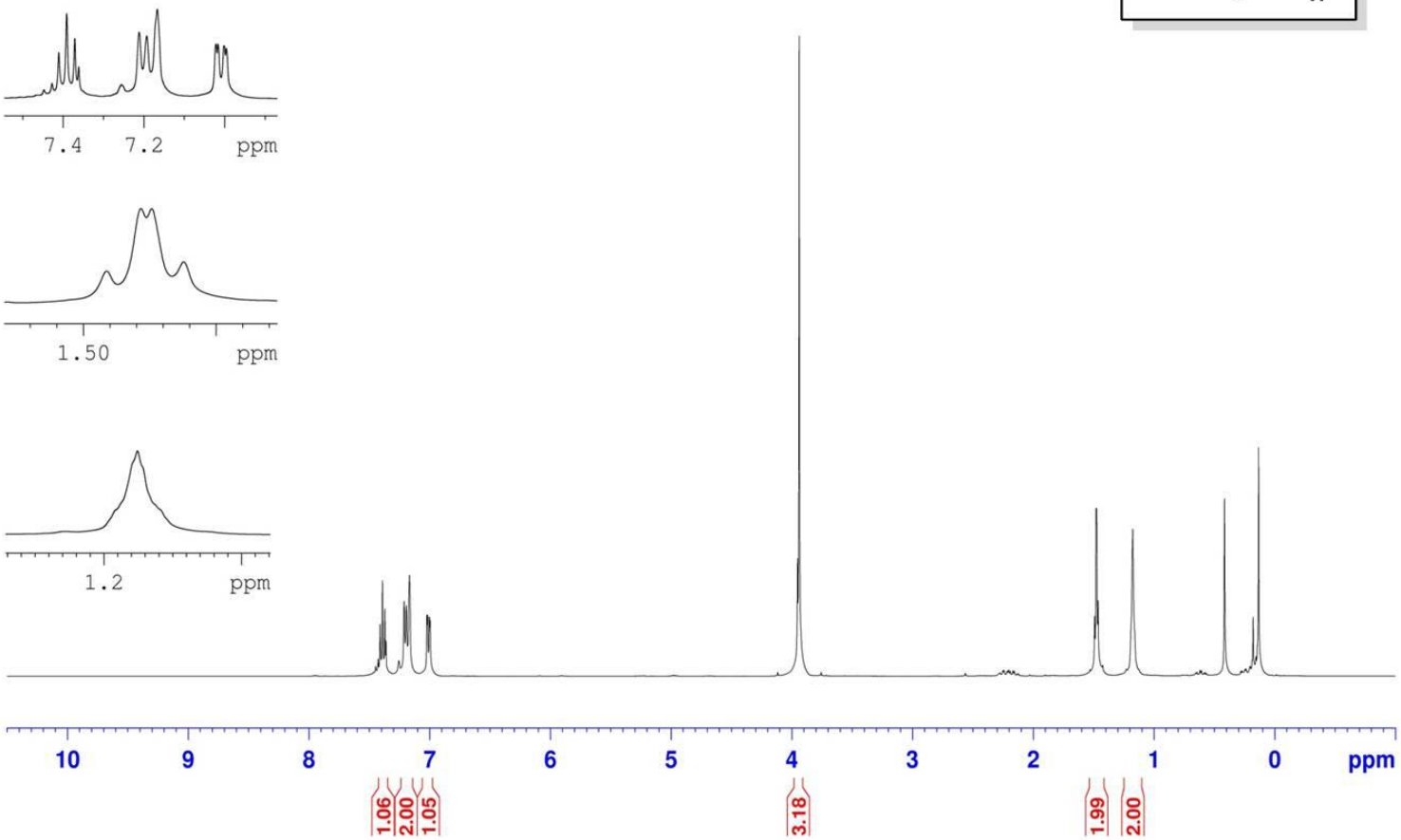




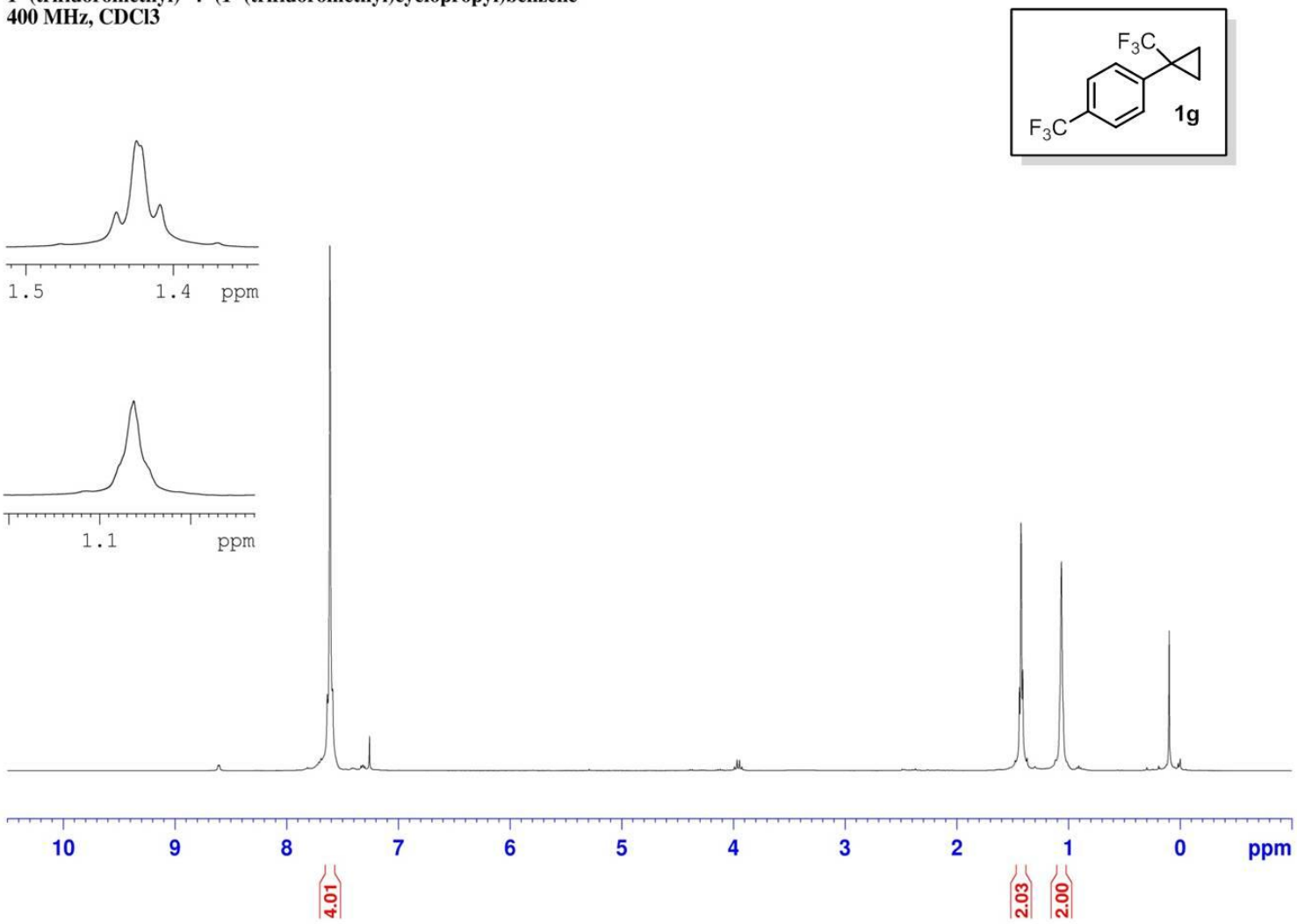


1–methoxy–3–(1–(trifluoromethyl)cyclopropyl)benzene
400 MHz, CDCl3

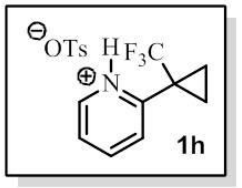


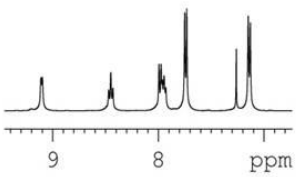


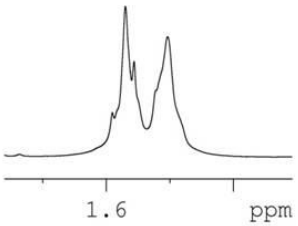
1−(trifluoromethyl)−4−(1−(trifluoromethyl)cyclopropyl)benzene
400 MHz, CDCl3



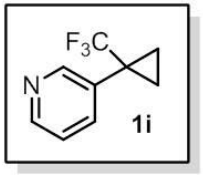
2–(1–(trifluoromethyl)cyclopropyl)pyridin–1–ium tosylate
400 MHz, CDCl3

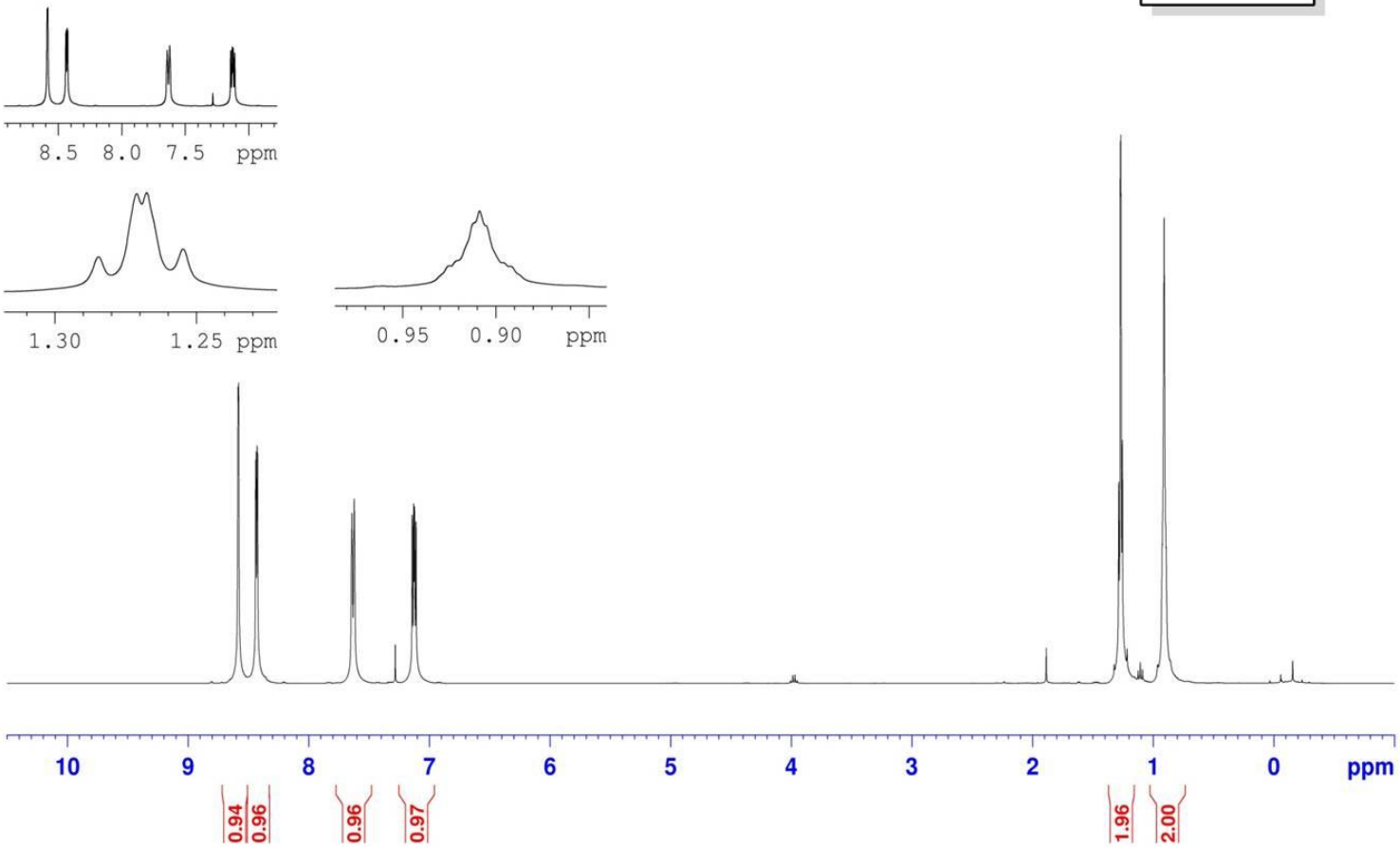




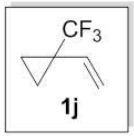


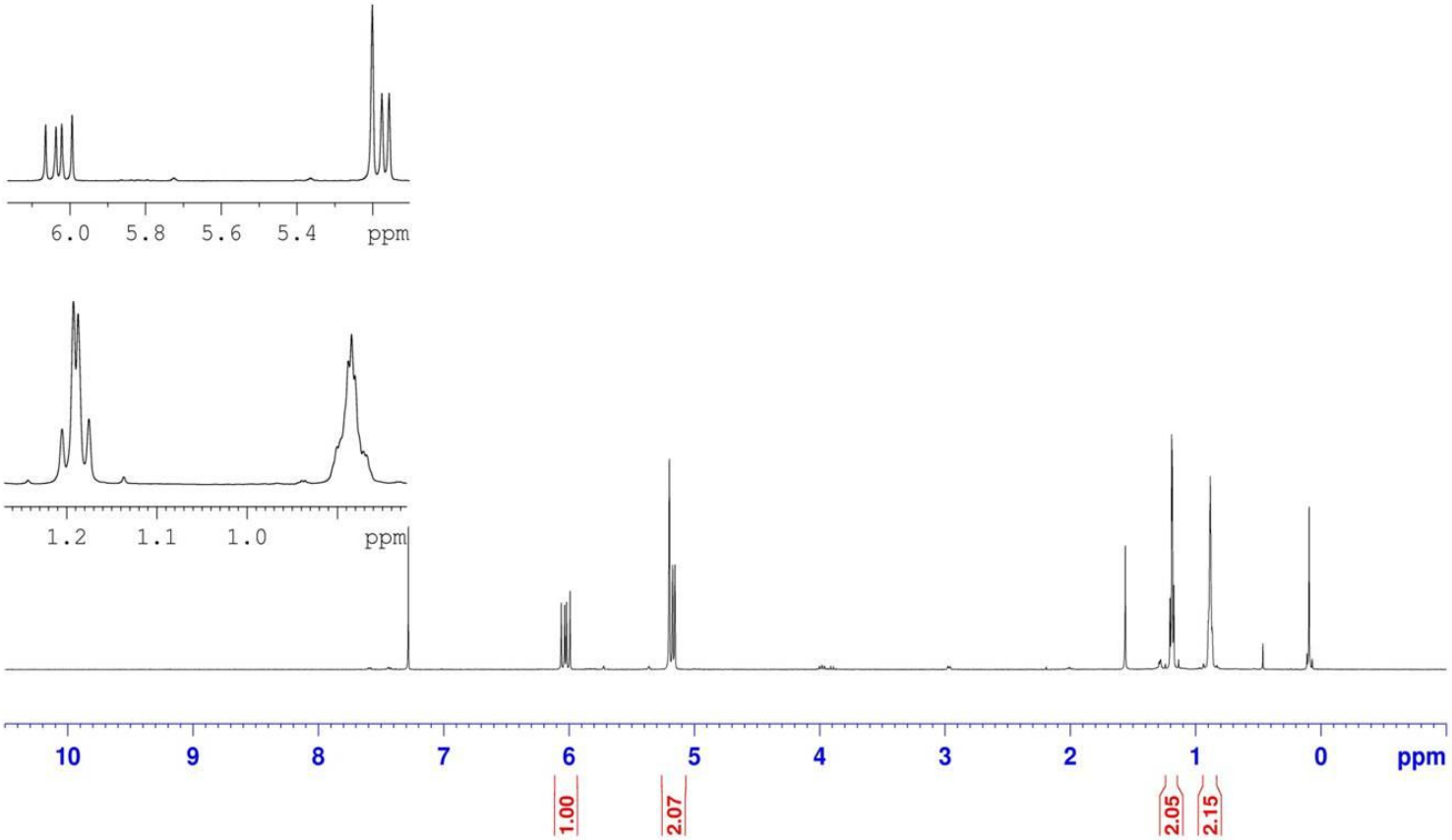
3–(1–(trifluoromethyl)cyclopropyl)pyridine
400 MHz, CDCl3



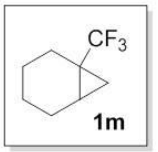


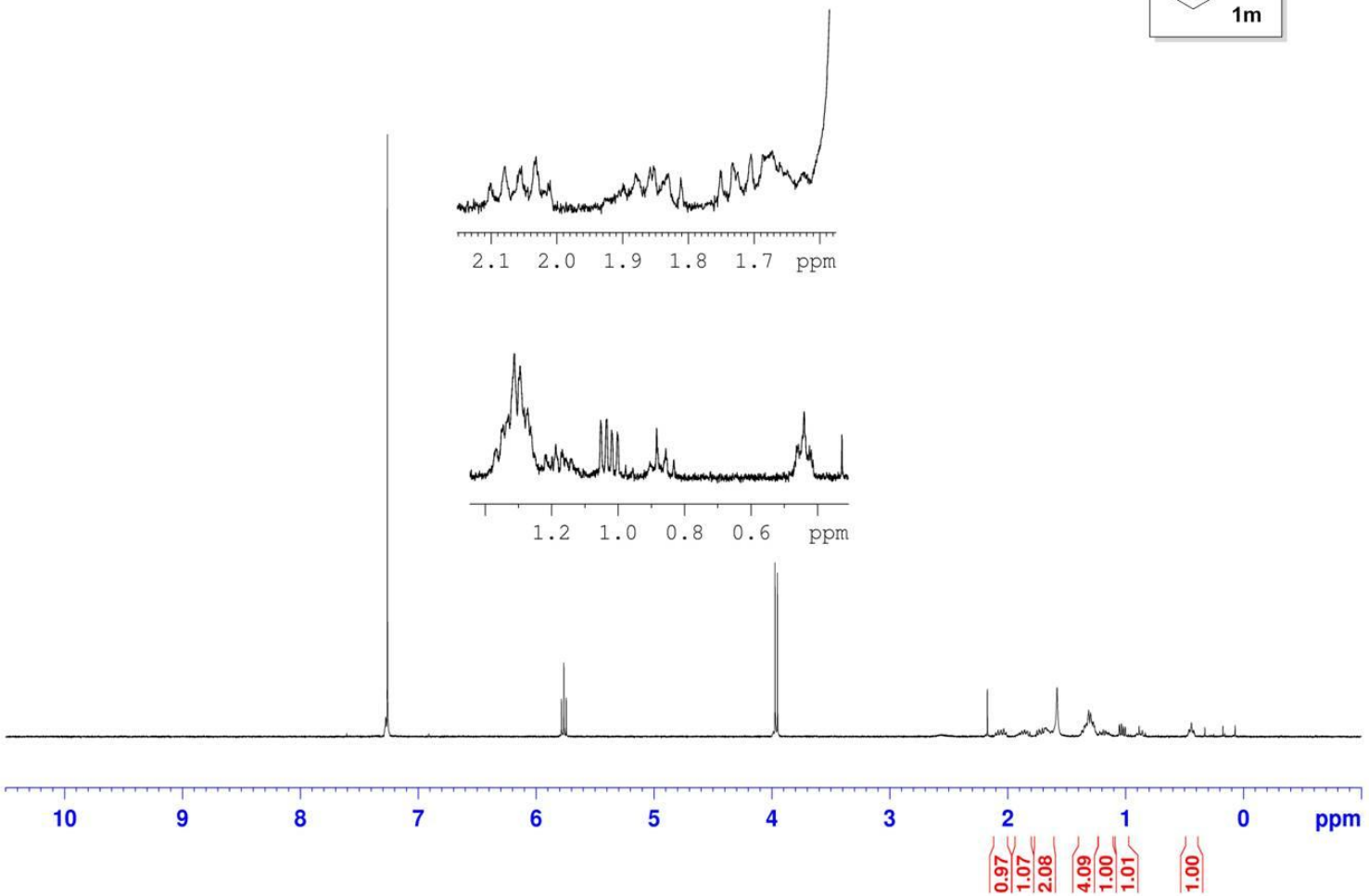
1–(trifluoromethyl)–1–vinylcyclopropane
400 MHz, CDCl3



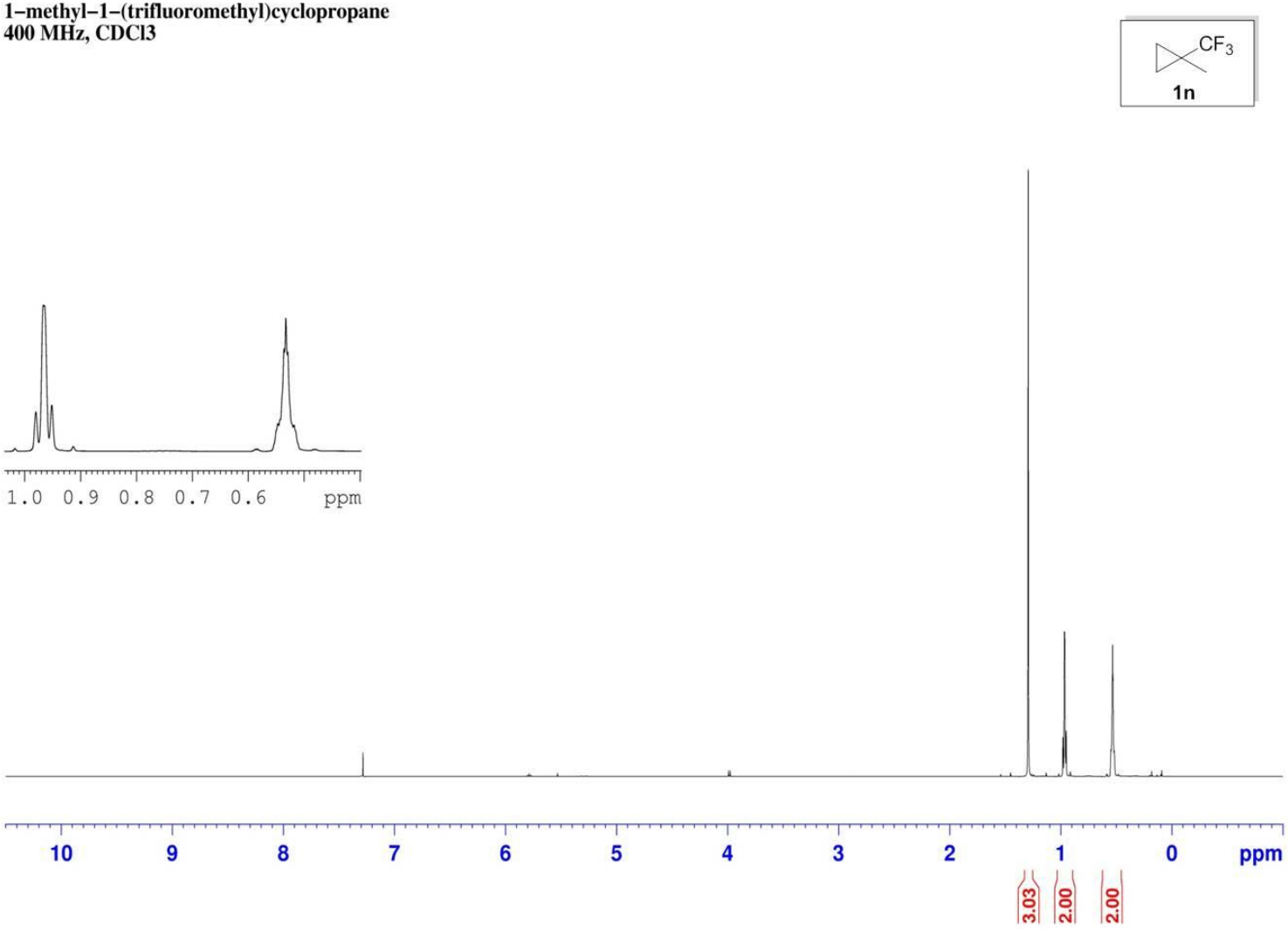


1−(trifluoromethyl)bicyclo[4.1.0]heptane
400 MHz, CDCl3

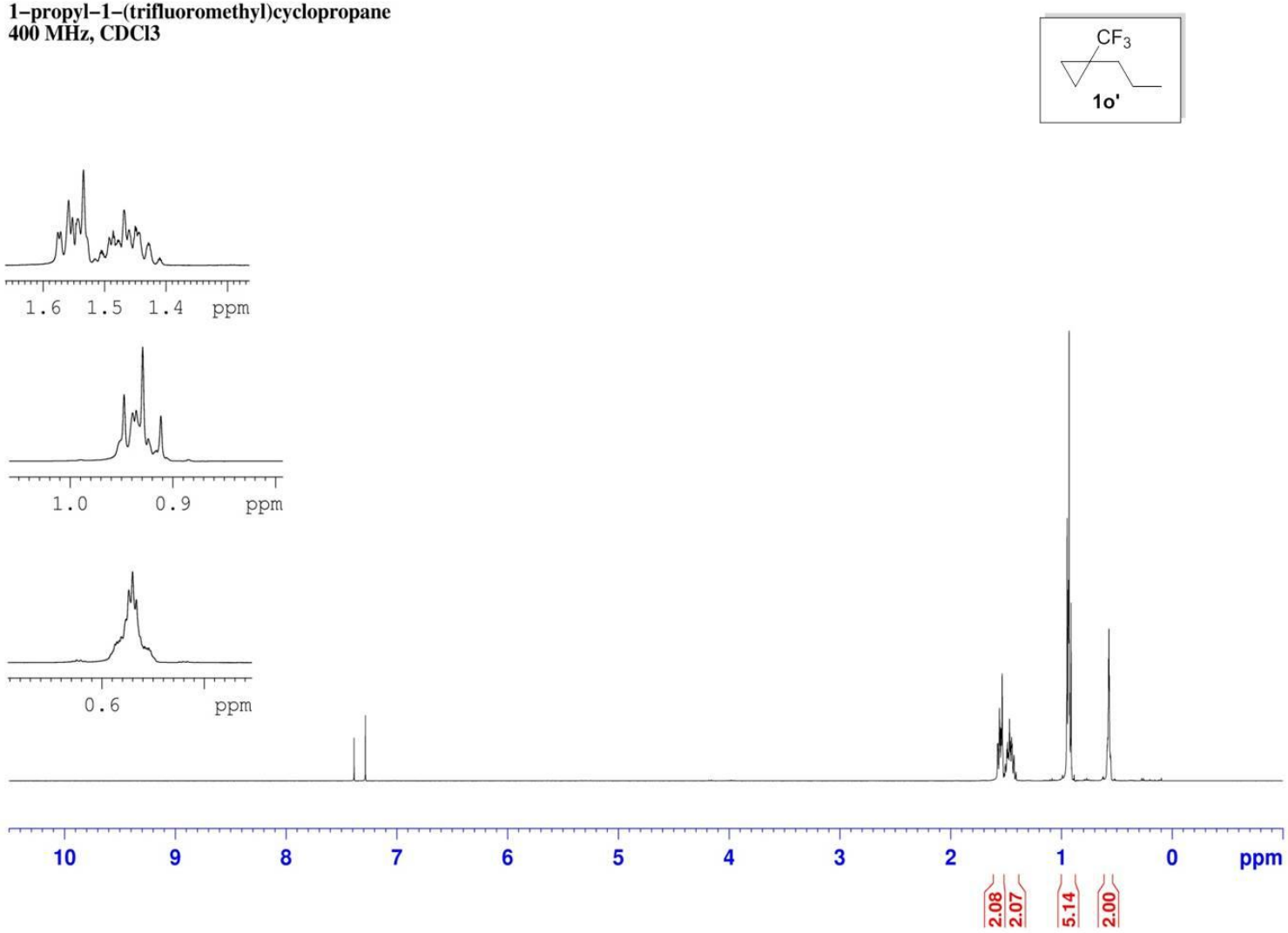




1–methyl–1–(trifluoromethyl)cyclopropane
400 MHz, CDCl3

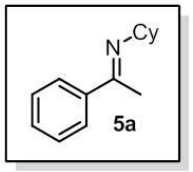


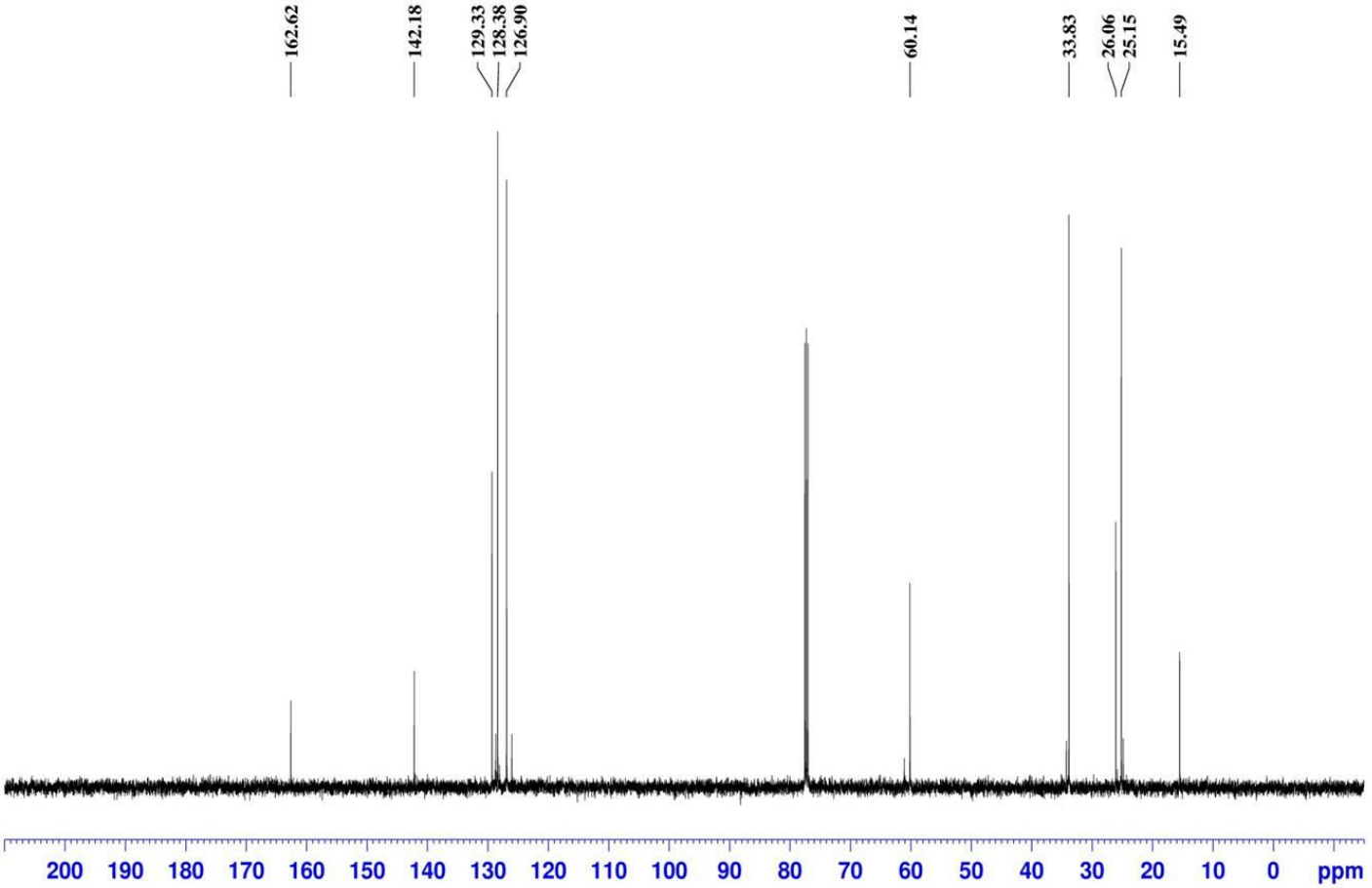
1–propyl–1–(trifluoromethyl)cyclopropane
400 MHz, CDCl3



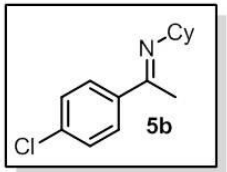
^{13}C-NMR Spectra of Synthesized Compounds

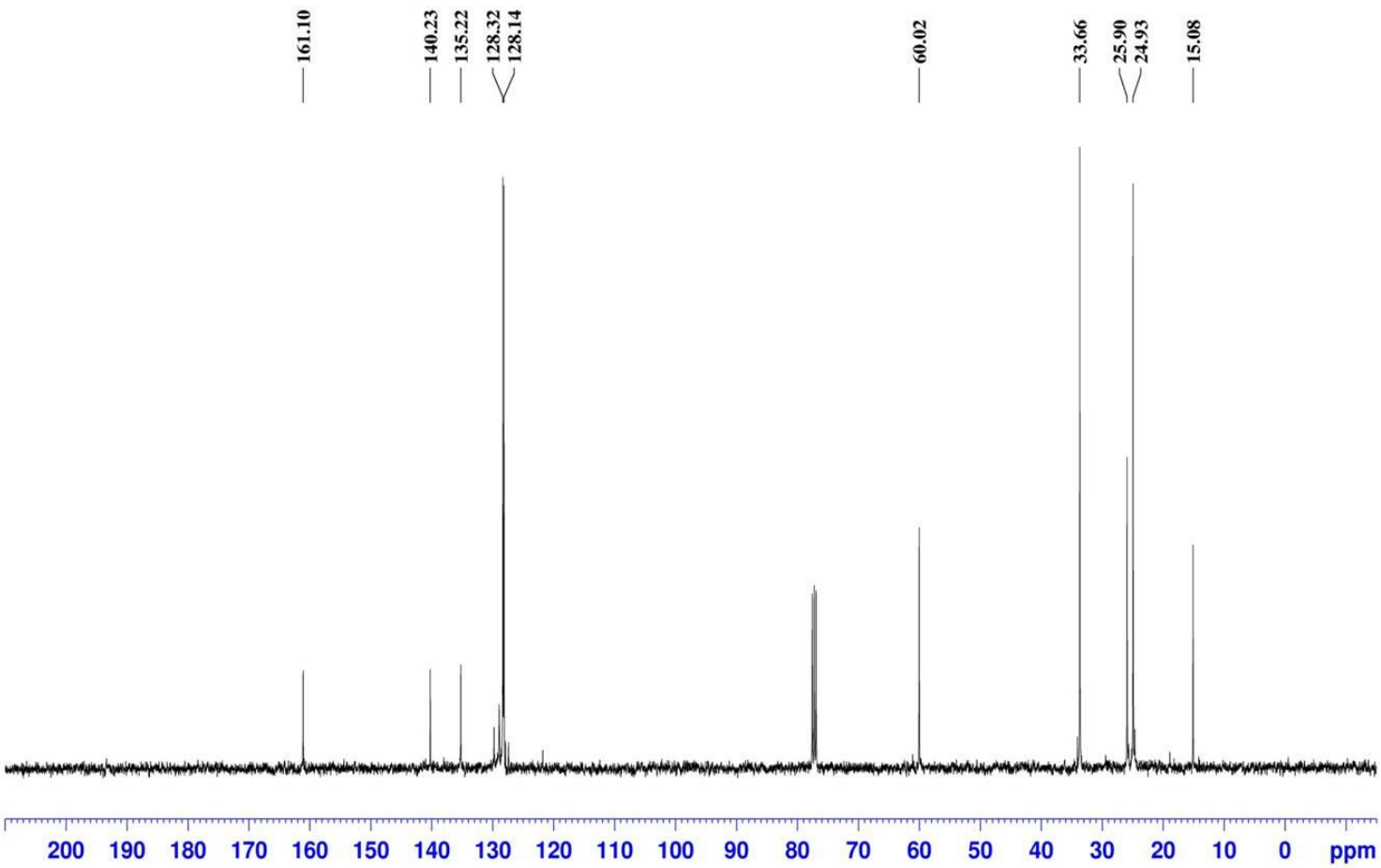
N–(1–phenylethylidene)cyclohexanamine
100 MHz, CDCl3



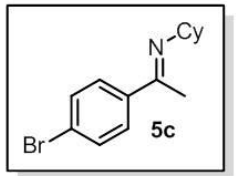


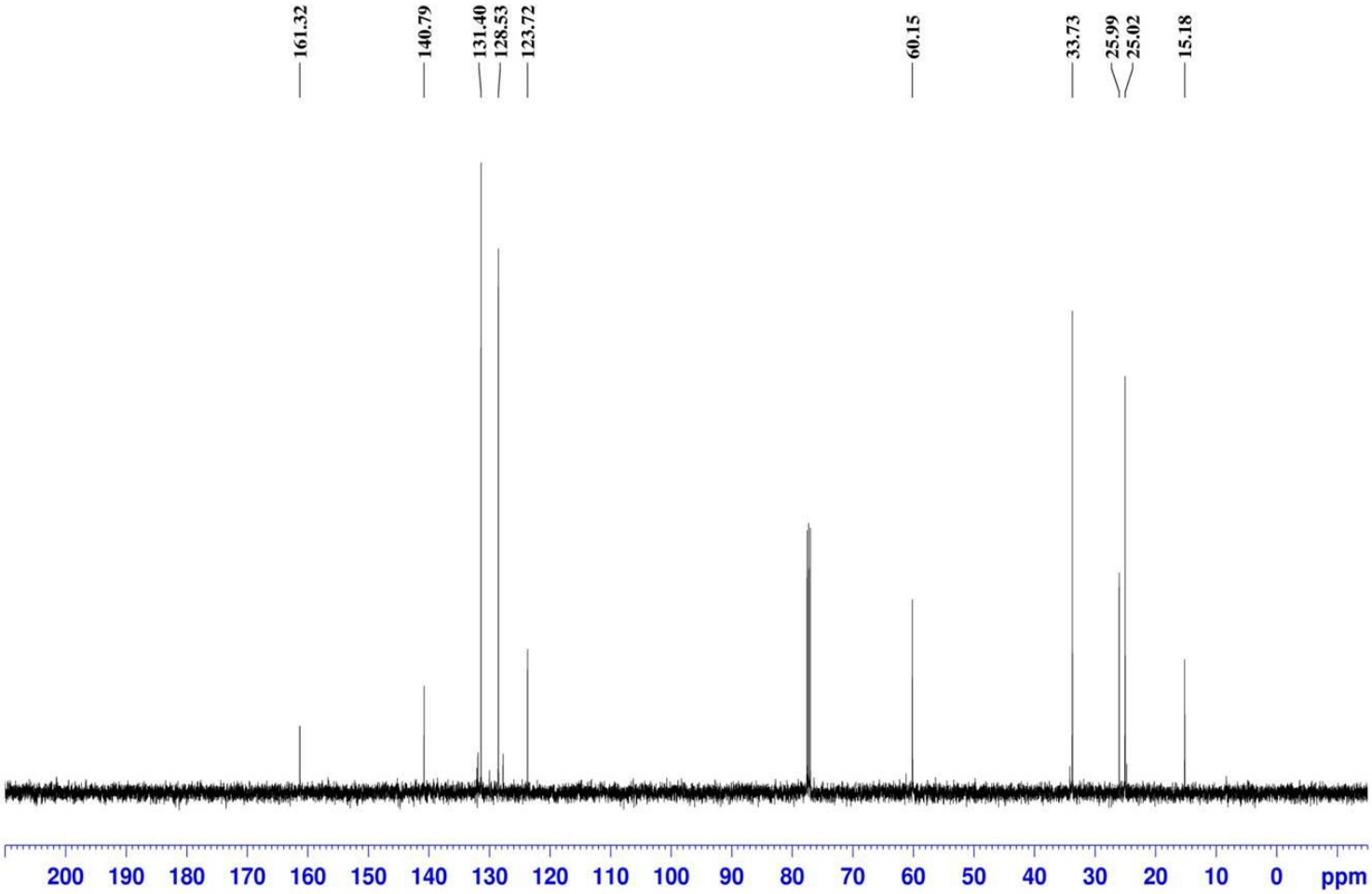
N–(1–(4–chlorophenyl)ethylidene)cyclohexanamine
100 MHz, CDCl3



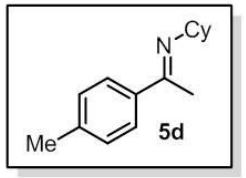


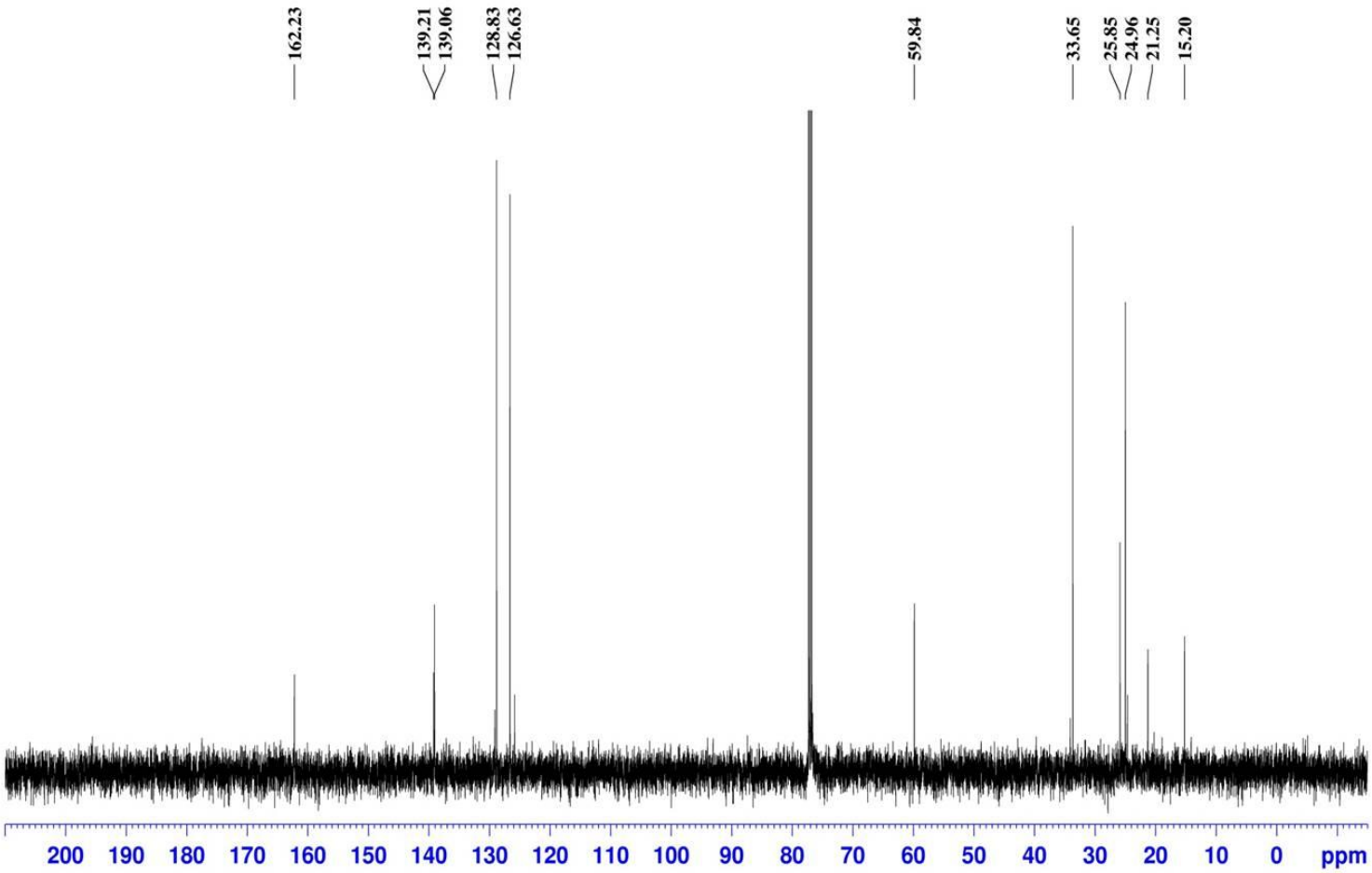
N–(1–(4–bromophenyl)ethylidene)cyclohexanamine
100 MHz, CDCl3



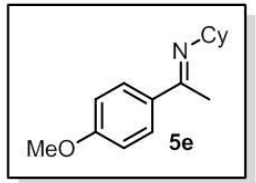


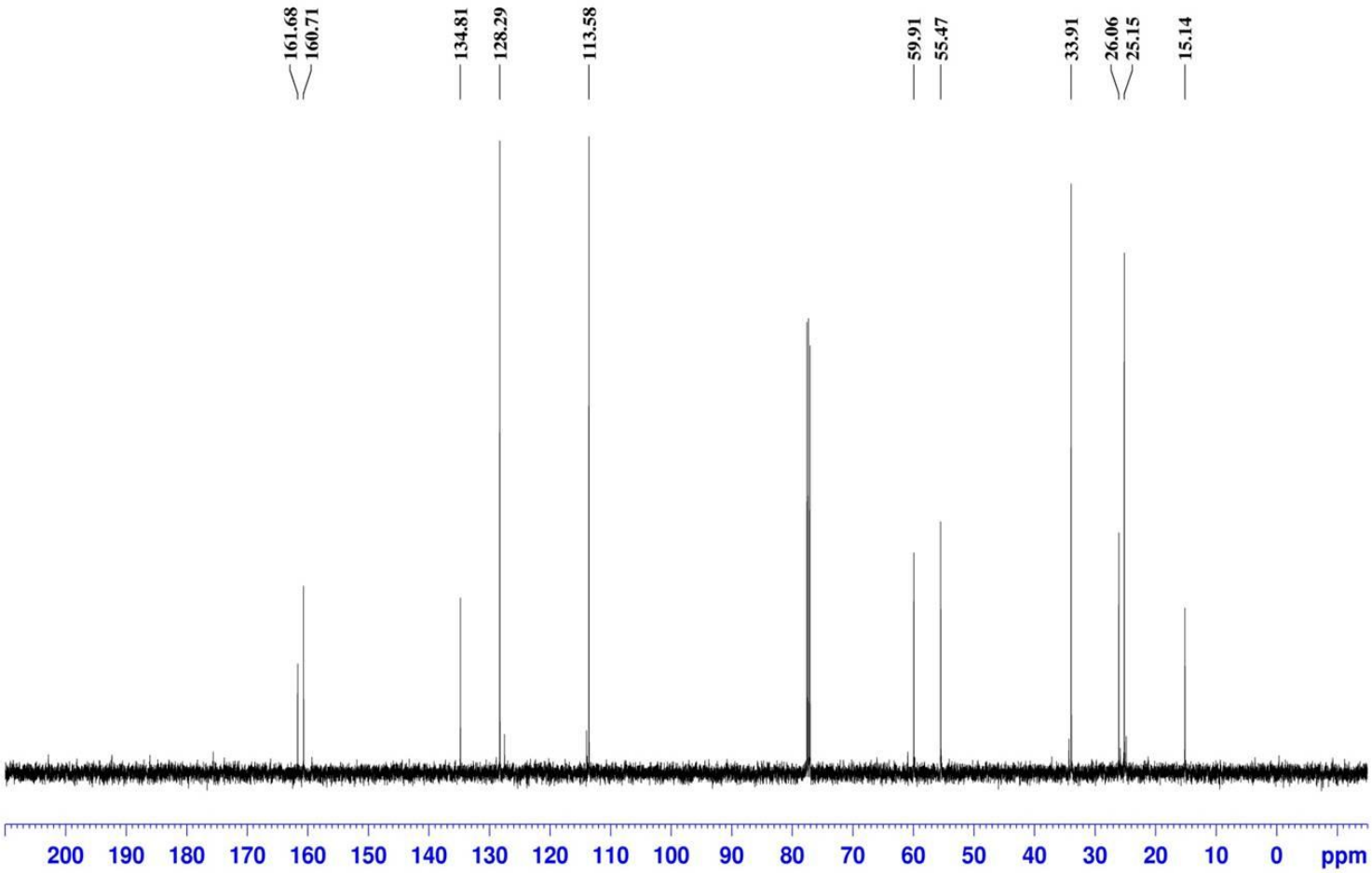
N–(1–(p–tolyl)ethylidene)cyclohexanamine
100 MHz, CDCl3



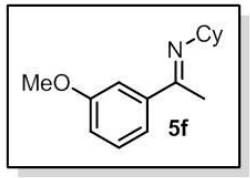


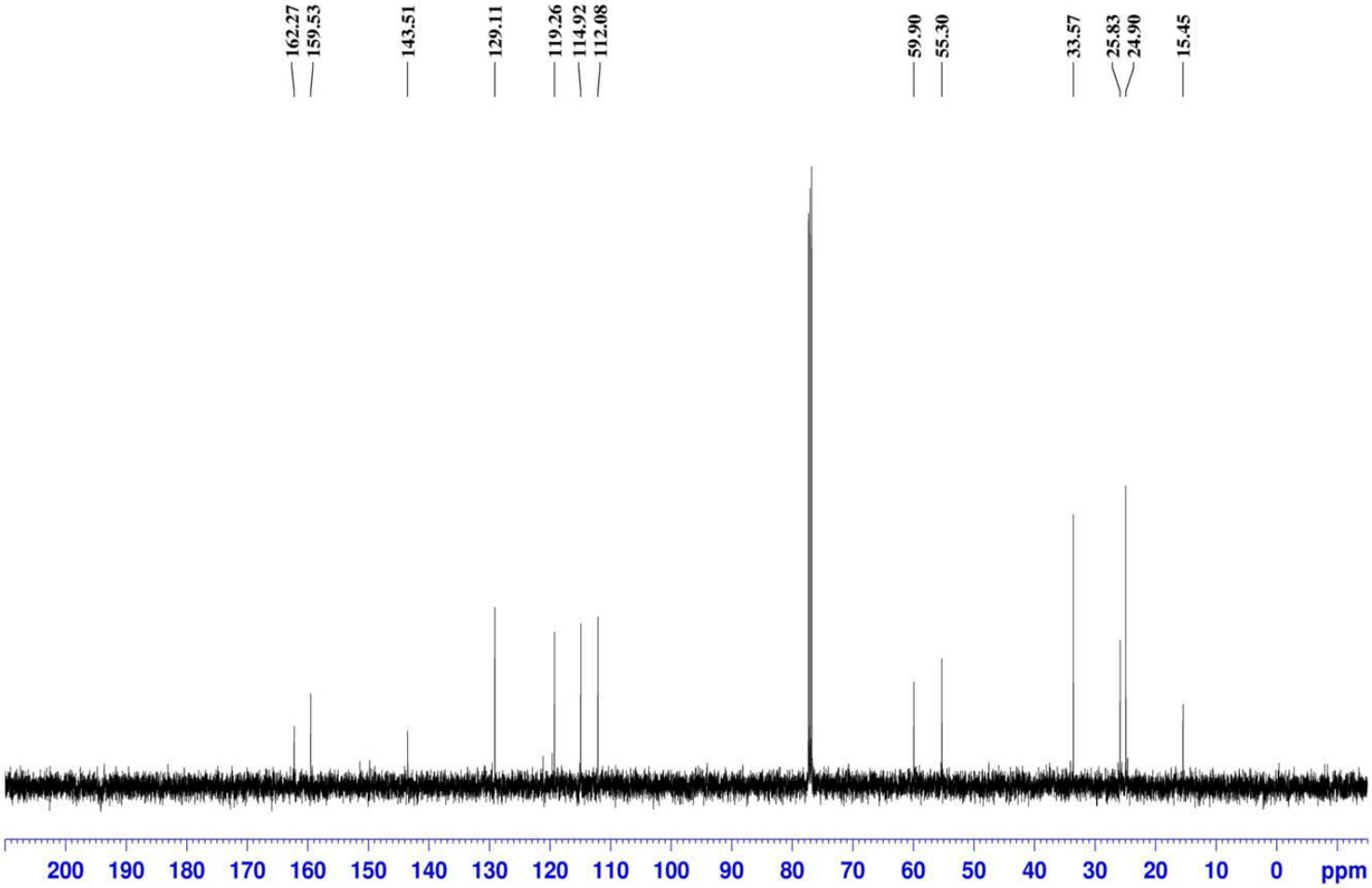
N–(1–(4–methoxyphenyl)ethylidene)cyclohexanamine
100 MHz, CDCl3



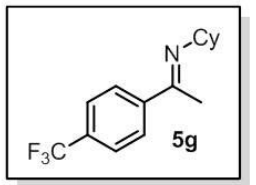


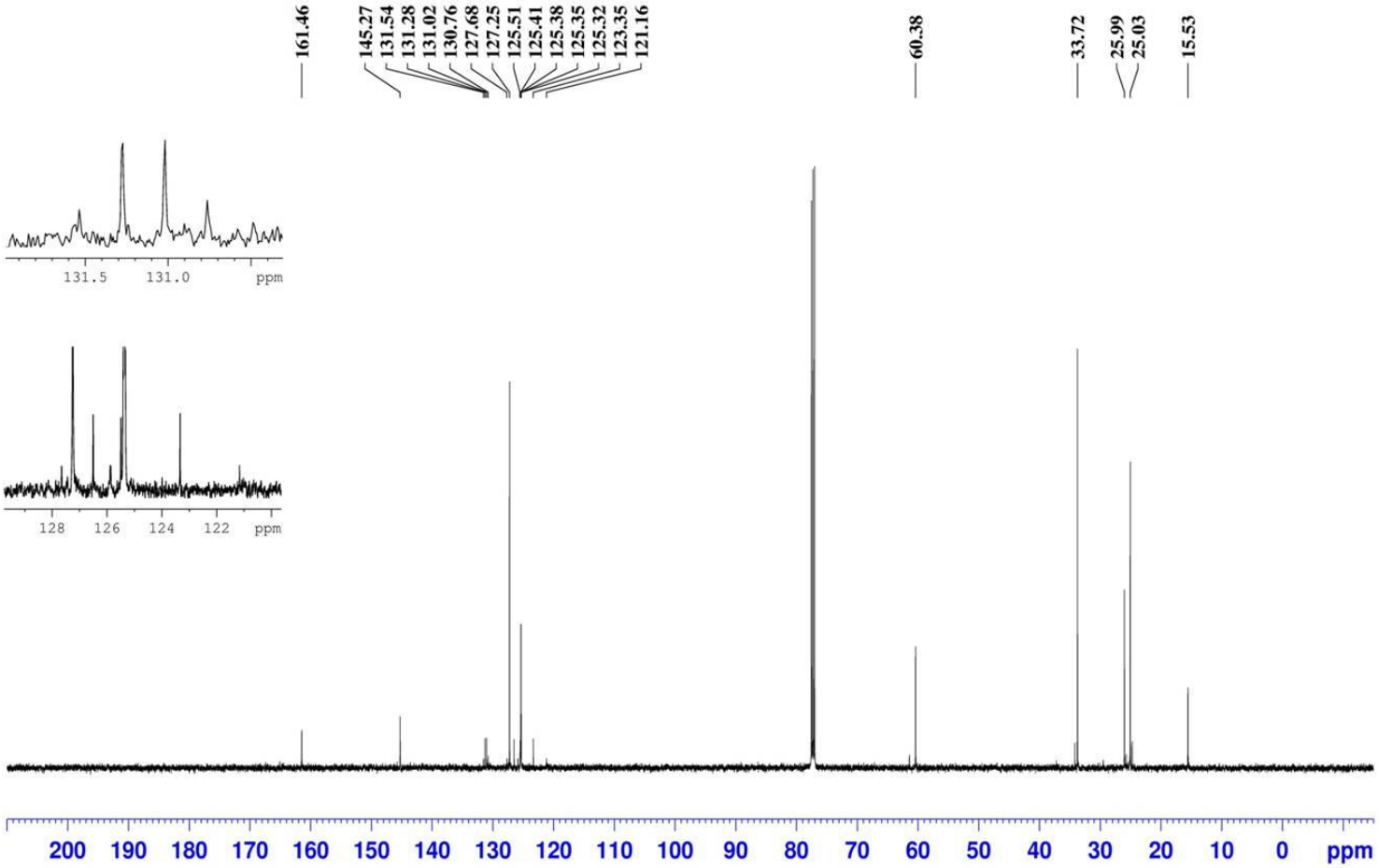
N–(1–(3–methoxyphenyl)ethylidene)cyclohexanamine
100 MHz, CDCl3



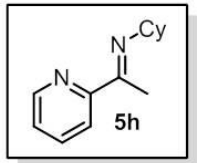


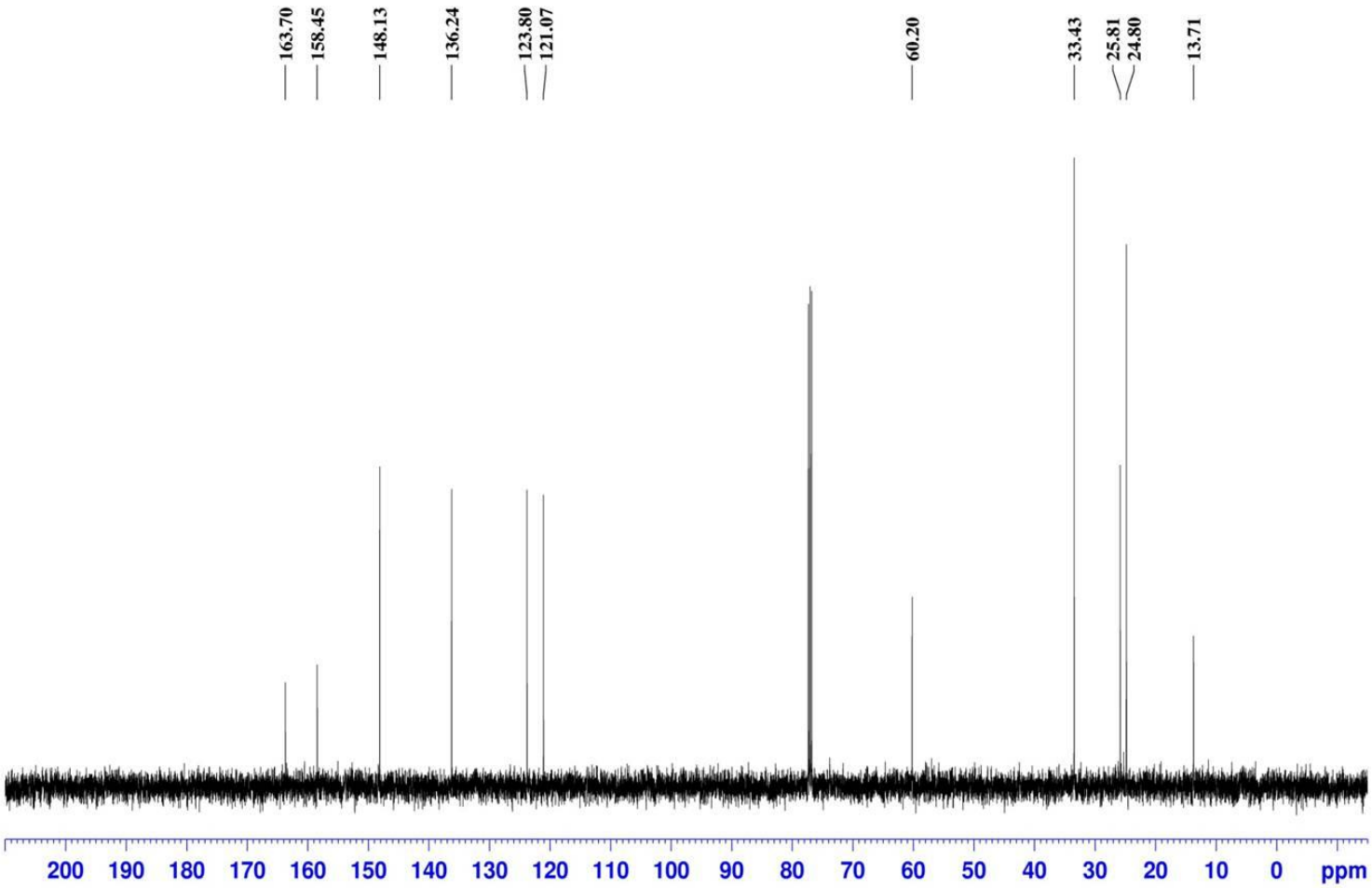
N–(1–(4–(trifluoromethyl)phenyl)ethylidene)cyclohexanamine
100 MHz, CDCl3



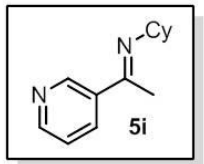


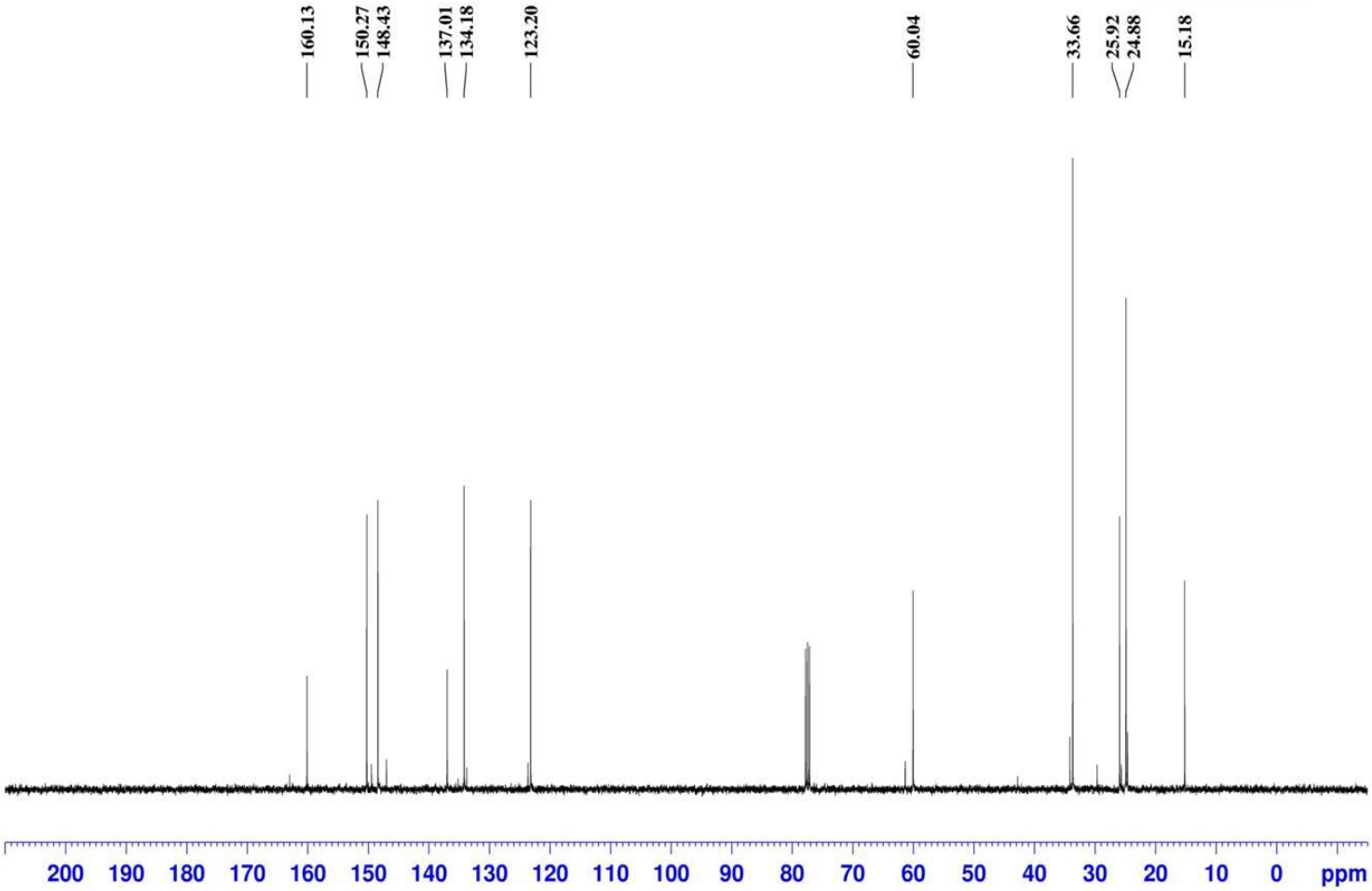
N–(1–(pyridin–2–yl)ethylidene)cyclohexanamine
100 MHz, CDCl3

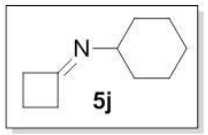


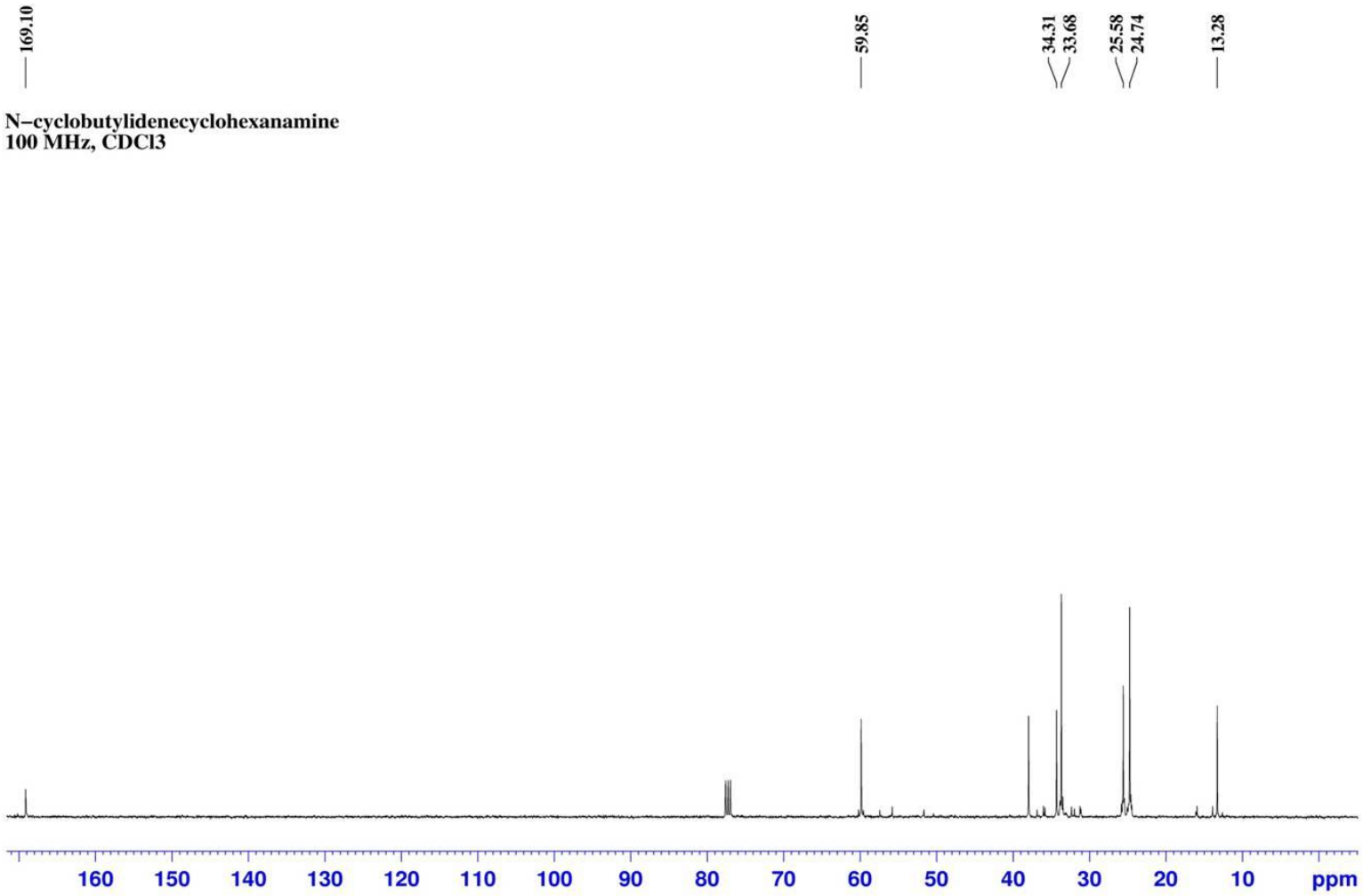


N–(1–(pyridin–3–yl)ethylidene)cyclohexanamine
100 MHz, CDCl3



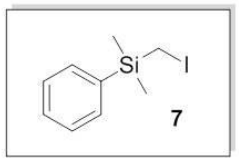


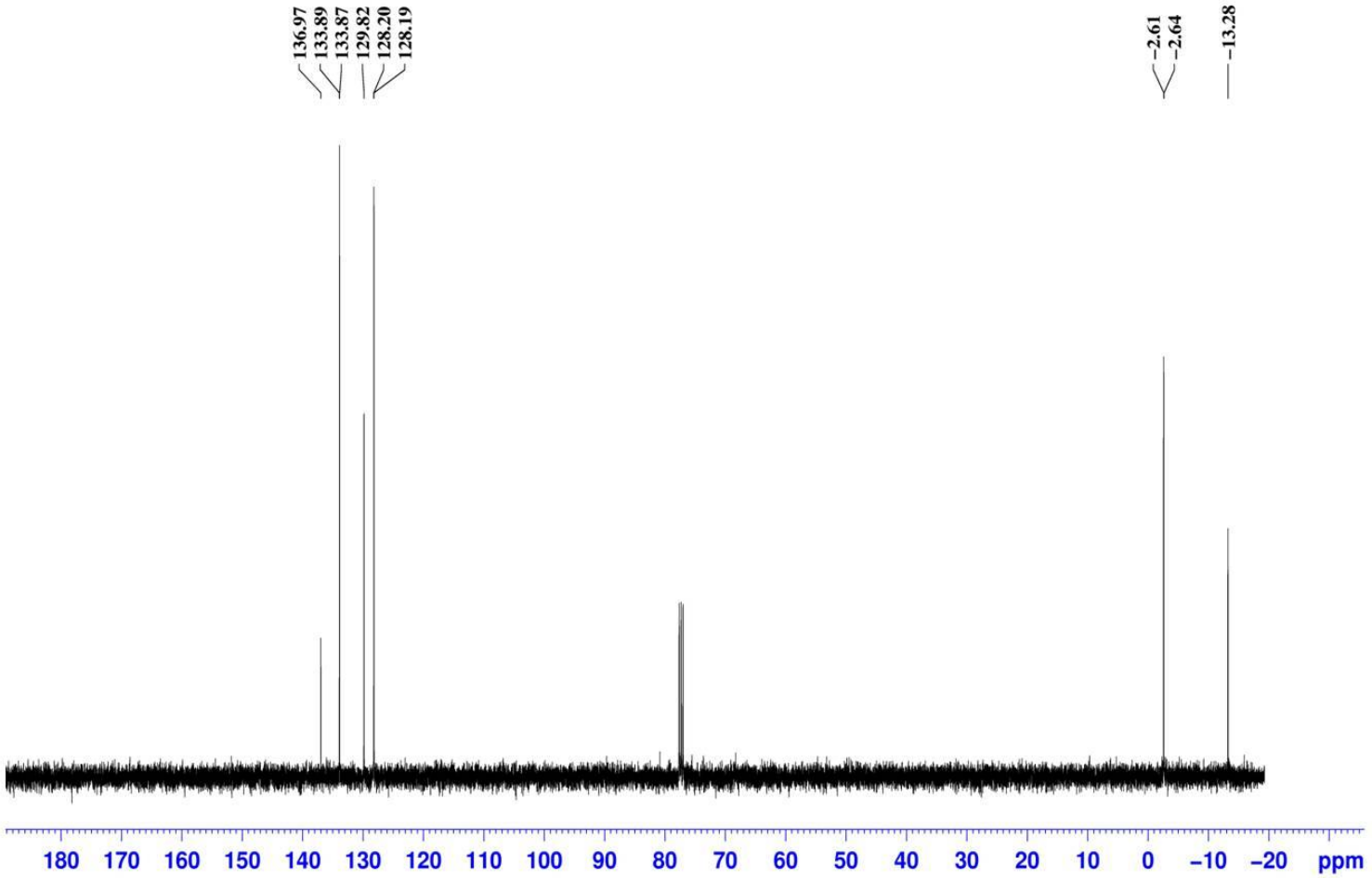




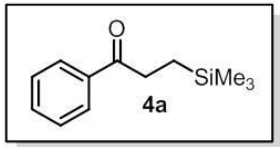
N–cyclobutylidenecyclohexanamine
100 MHz, CDCl3

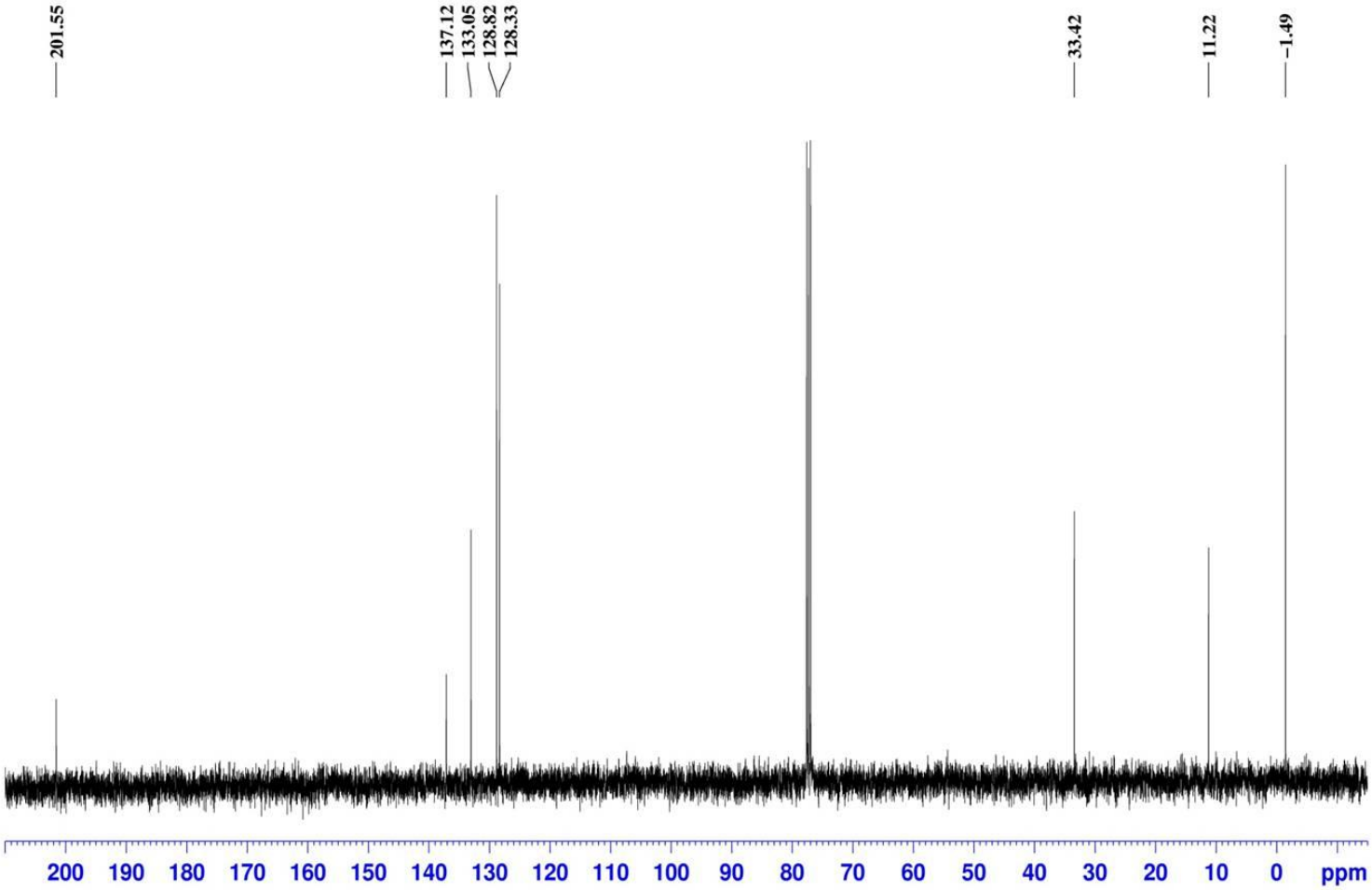
(iodomethyl)dimethyl(phenyl)silane
100 MHz, CDCl3



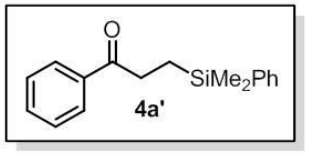


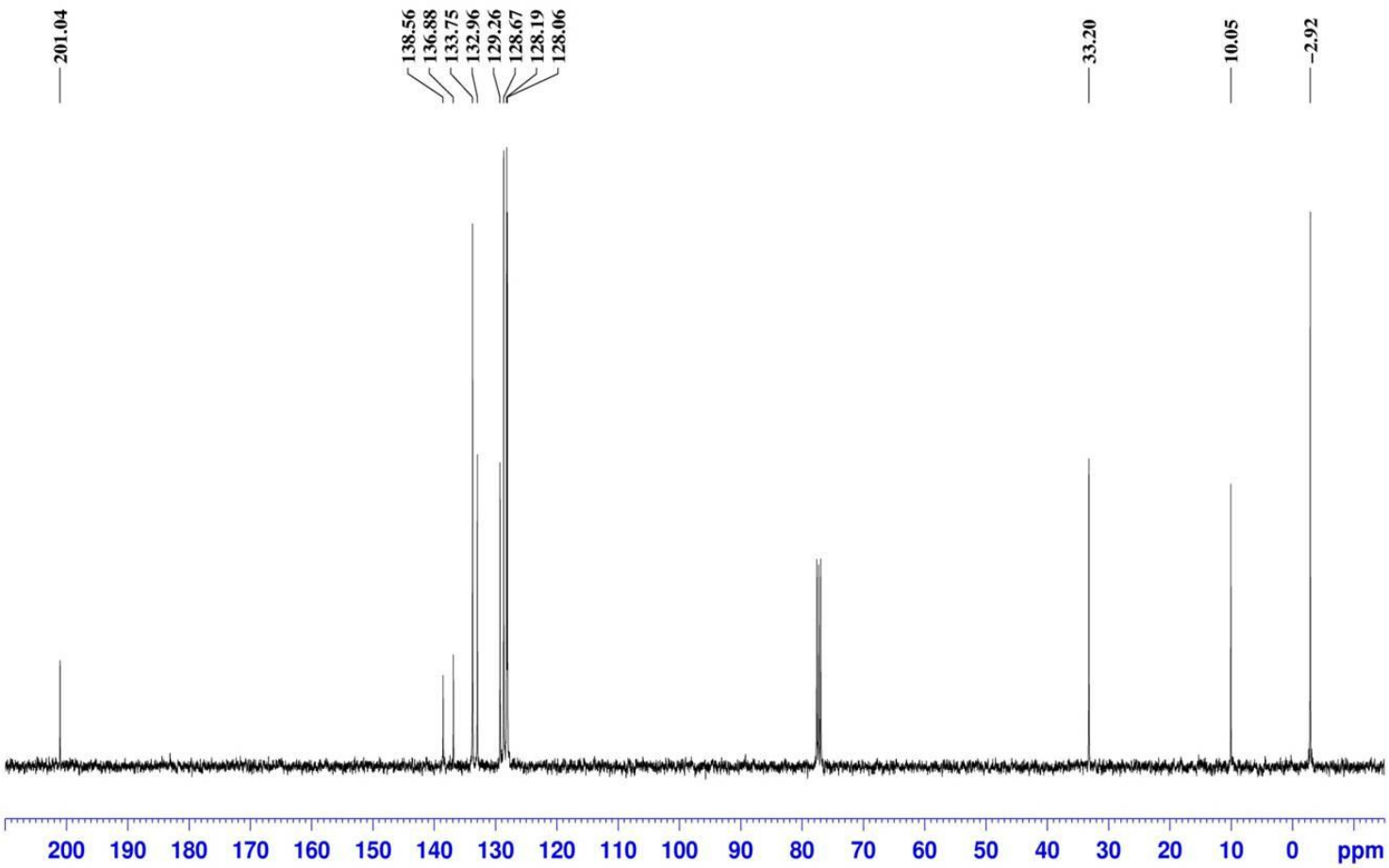
1–phenyl–3–(trimethylsilyl)propan–1–one
100 MHz, CDCl3



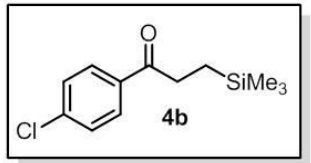


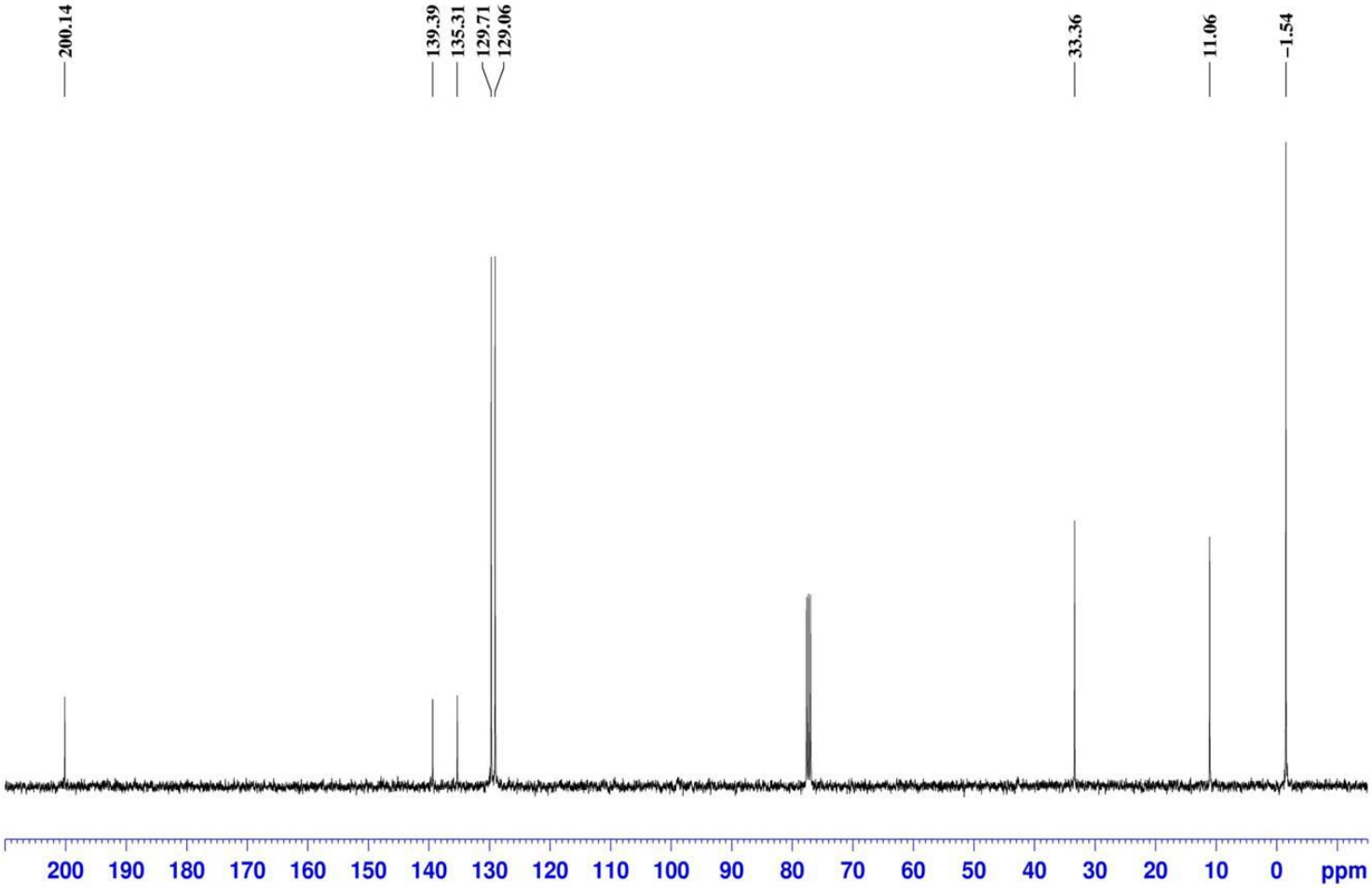
3–(dimethyl(phenyl)silyl)–1–phenylpropan–1–one
100 MHz, CDCl3



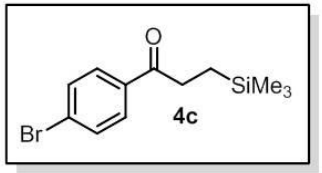


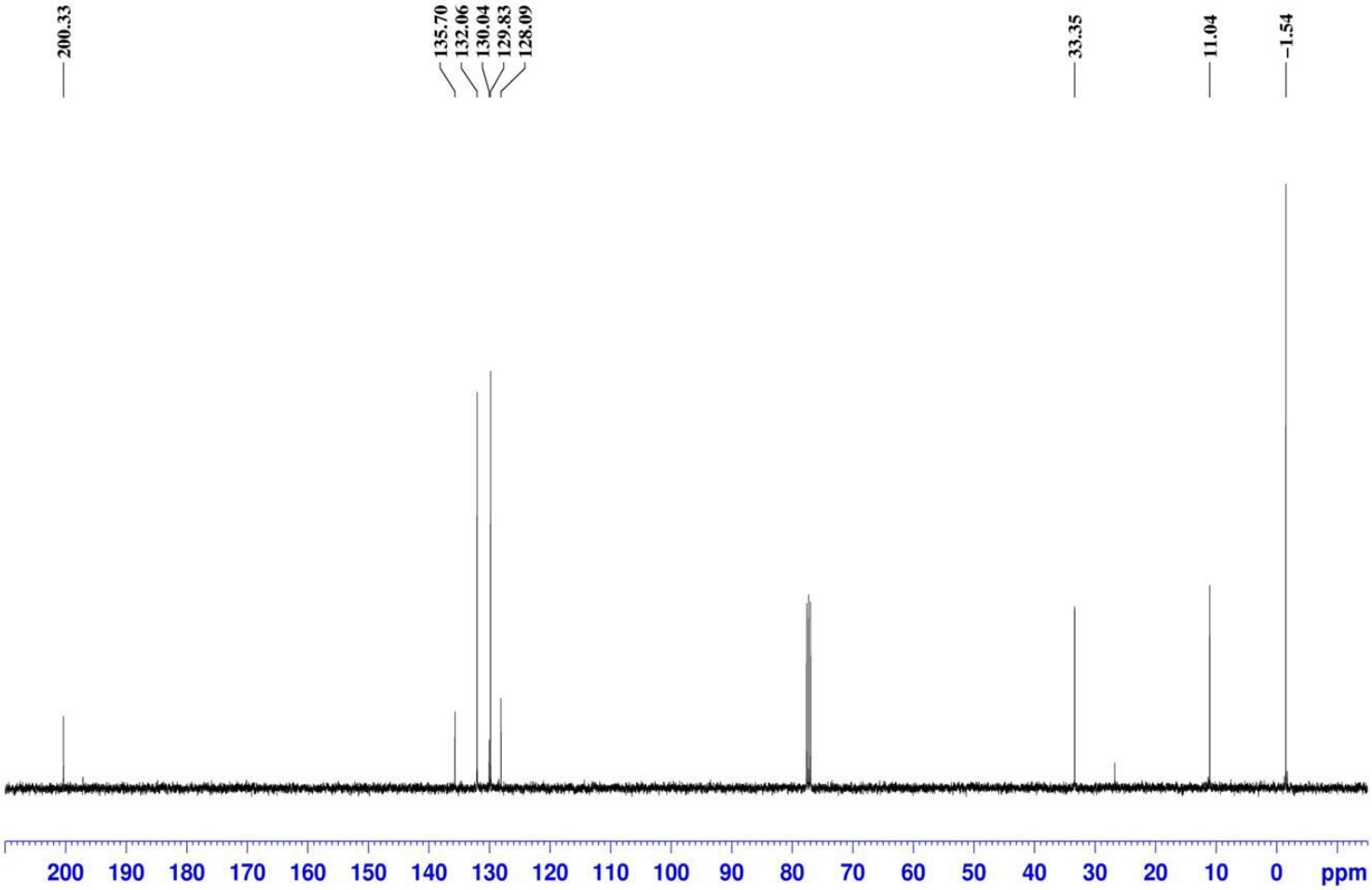
1–(4–chlorophenyl)–3–(trimethylsilyl)propan–1–one
100 MHz, CDCl3



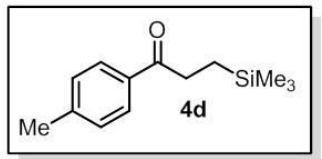


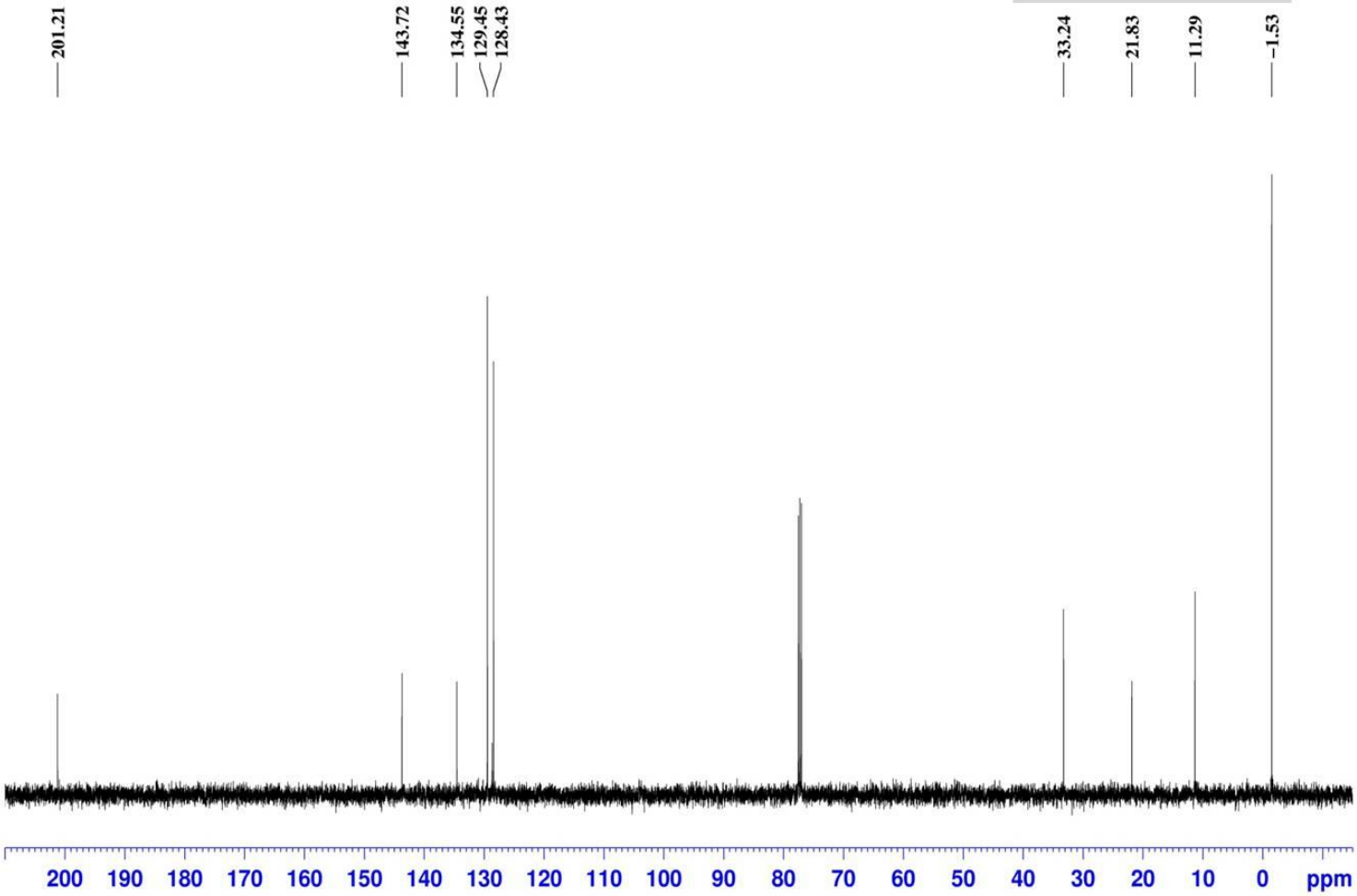
1–(4–bromophenyl)–3–(trimethylsilyl)propan–1–one
100 MHz, CDCl3



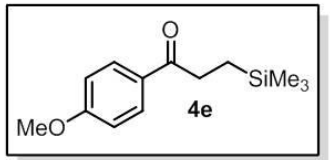


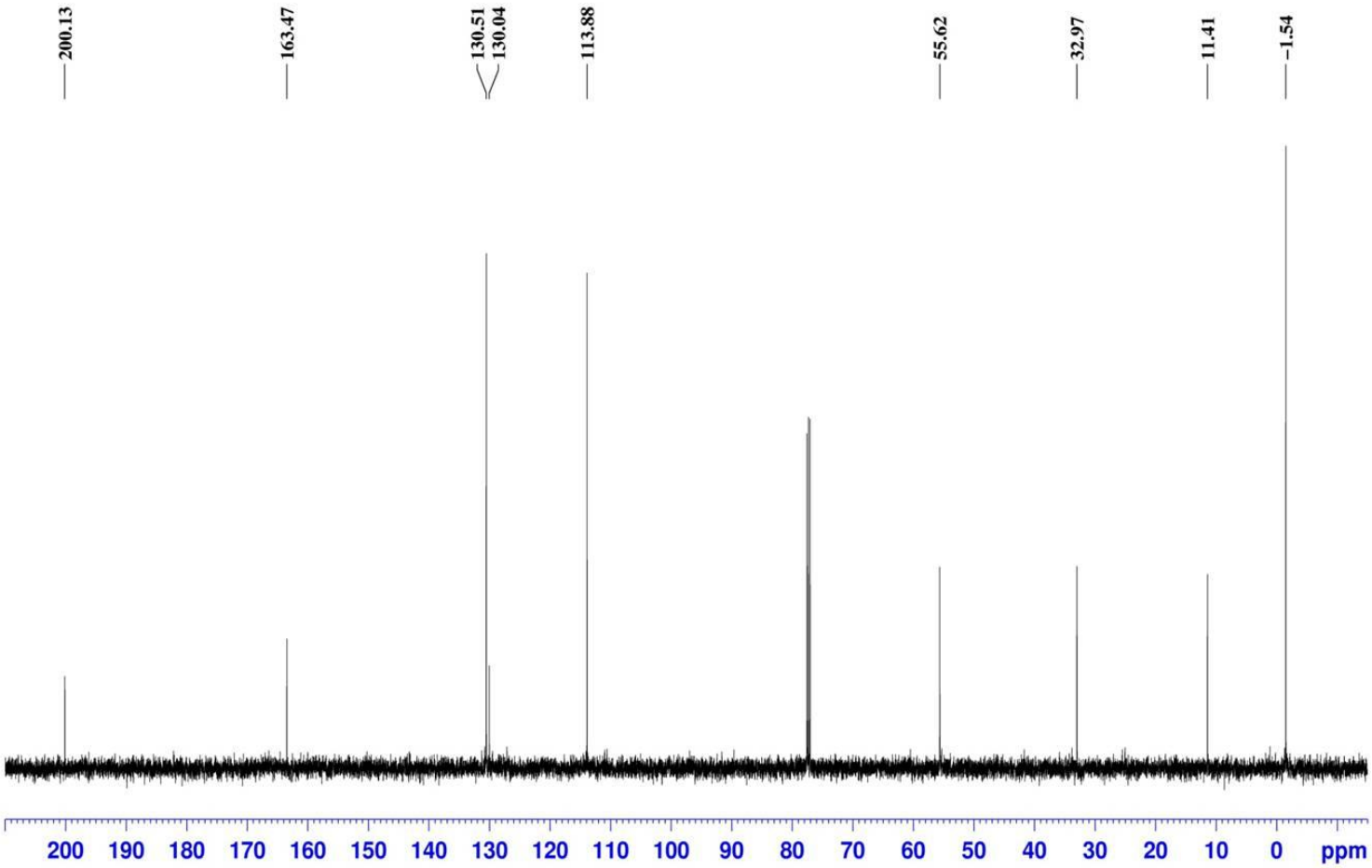
1–(p–tolyl)–3–(trimethylsilyl)propan–1–one
100 MHz, CDCl3



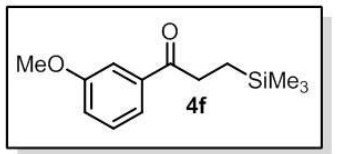


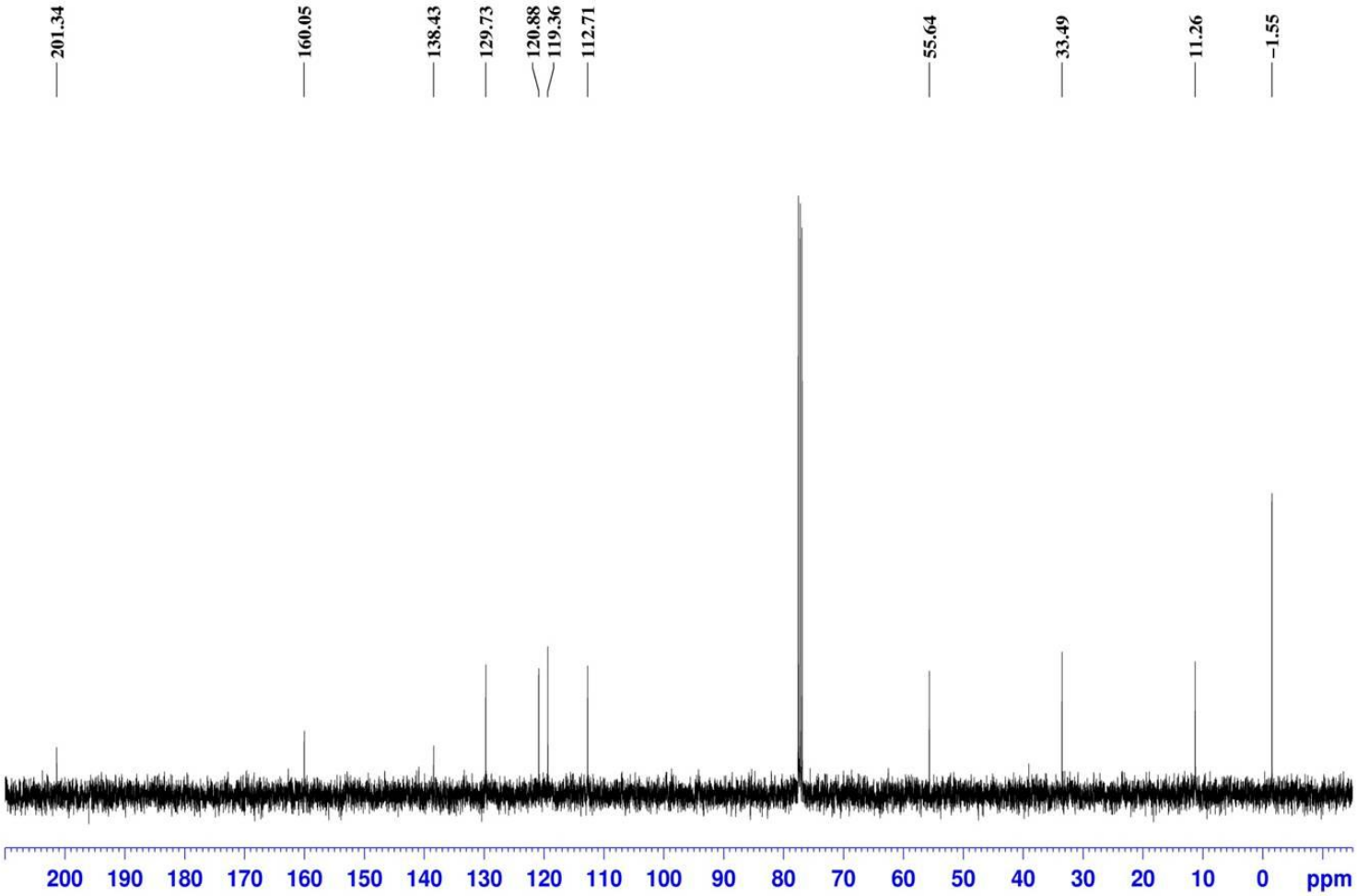
1–(4–methoxyphenyl)–3–(trimethylsilyl)propan–1–one
100 MHz, CDCl3



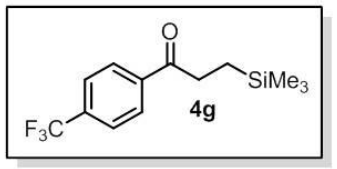


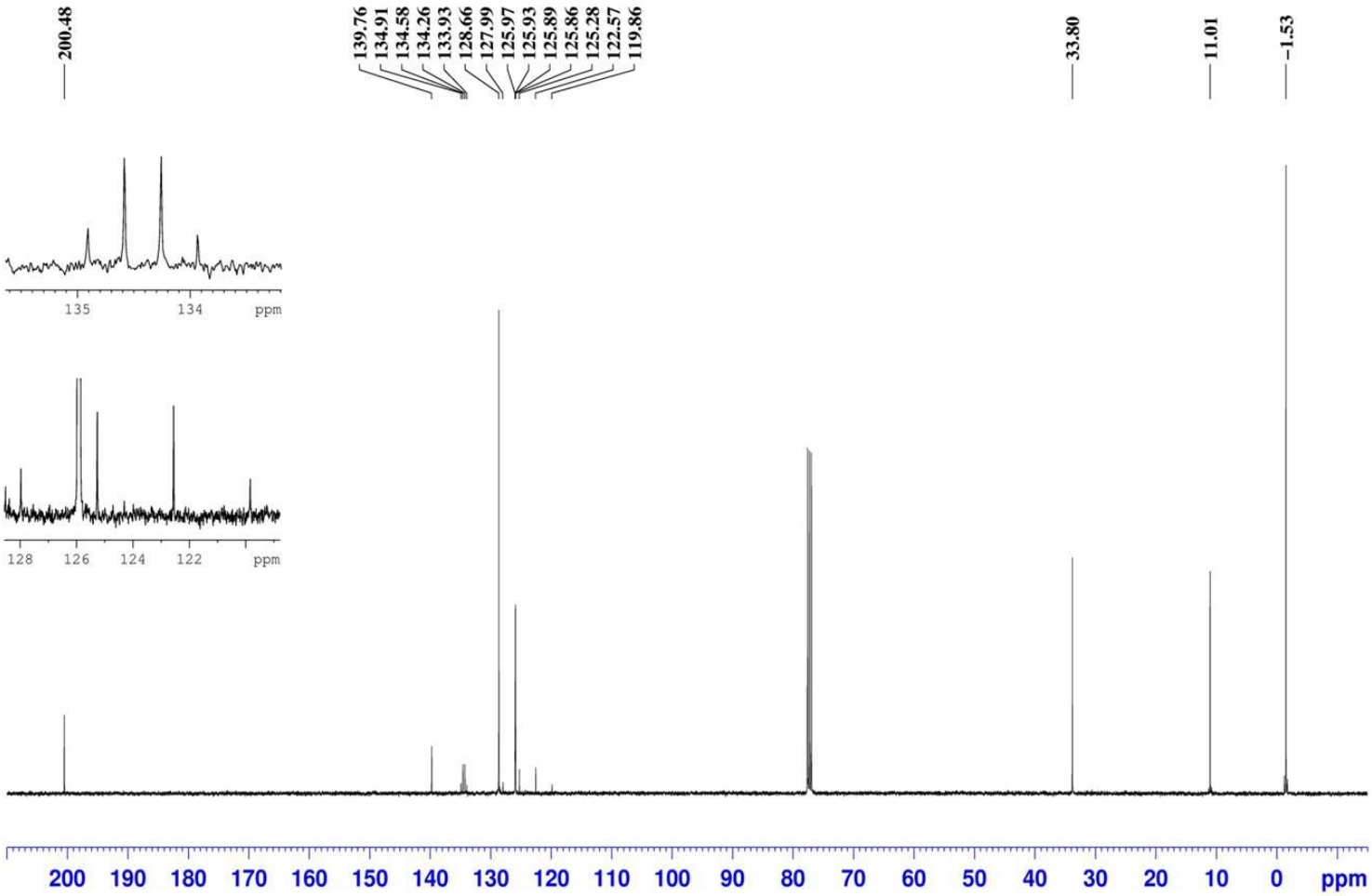
1–(3–methoxyphenyl)–3–(trimethylsilyl)propan–1–one
100 MHz, CDCl3



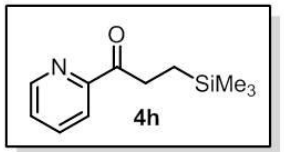


1–(4–(trifluoromethyl)phenyl)–3–(trimethylsilyl)propan–1–one
100 MHz, CDCl3

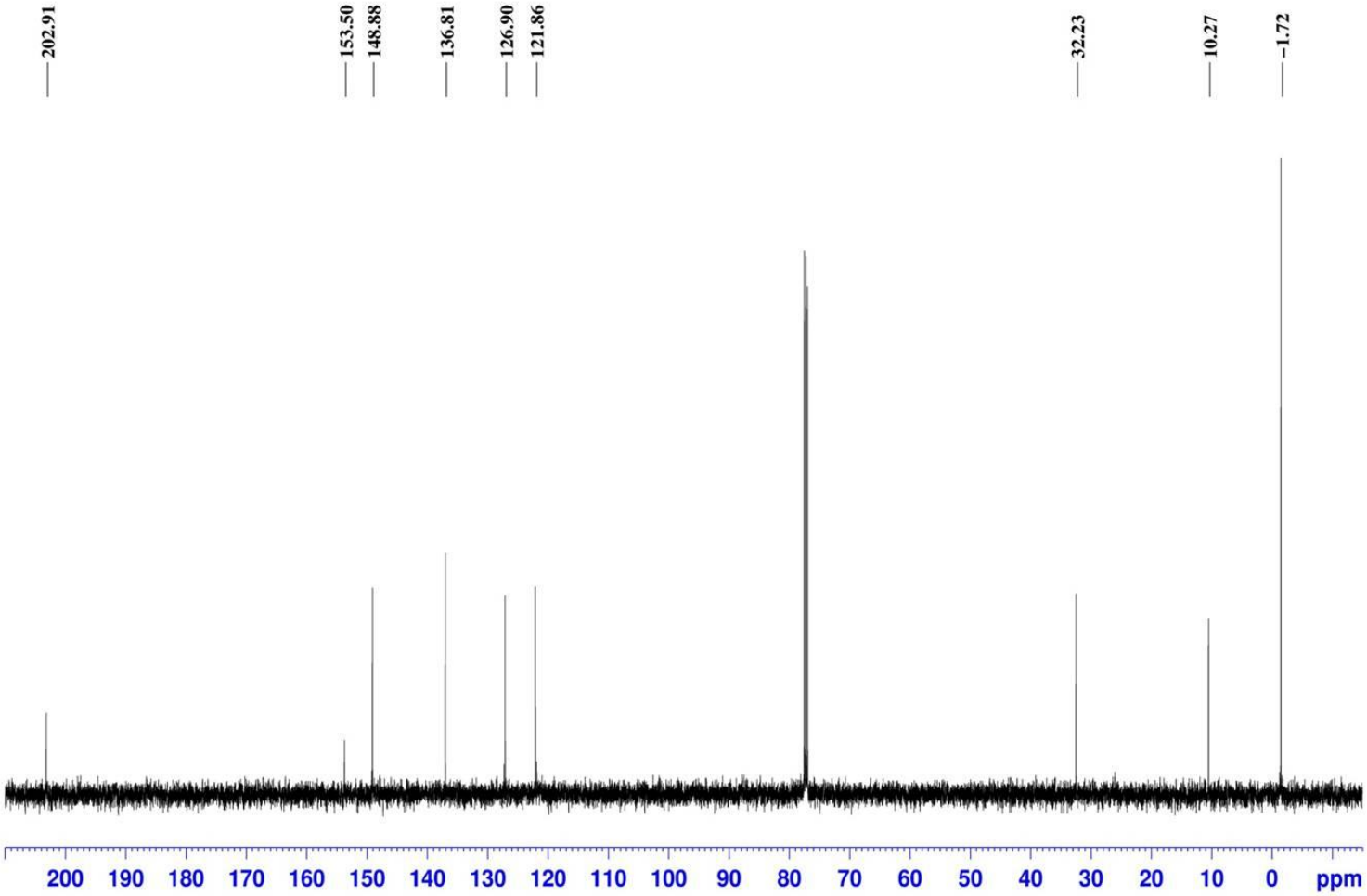




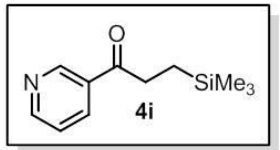
1–(pyridin–2–yl)–3–(trimethylsilyl)propan–1–one
100 MHz, CDCl3



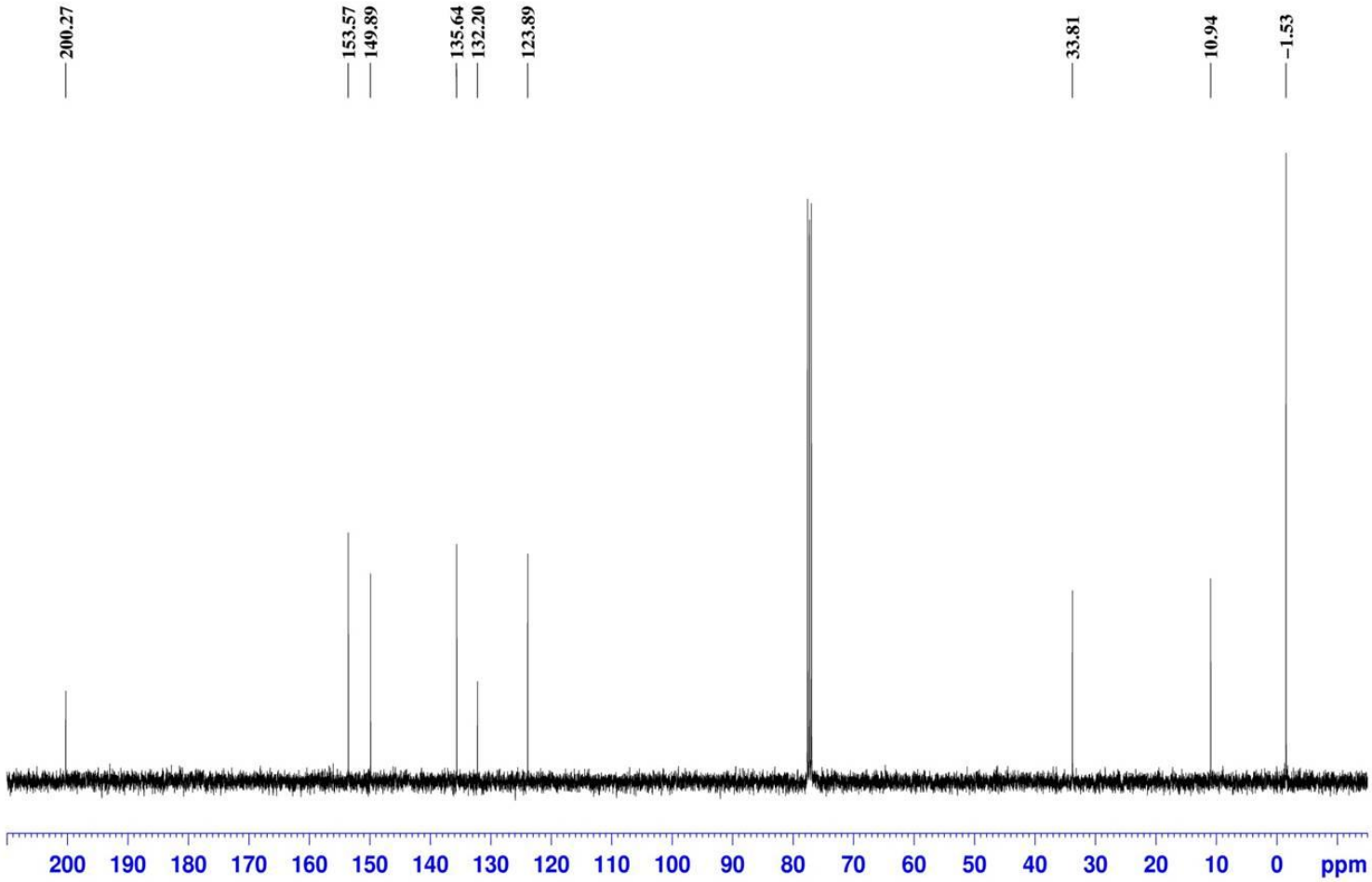
4h



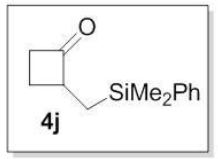
1–(pyridin–3–yl)–3–(trimethylsilyl)propan–1–one
100 MHz, CDCl3

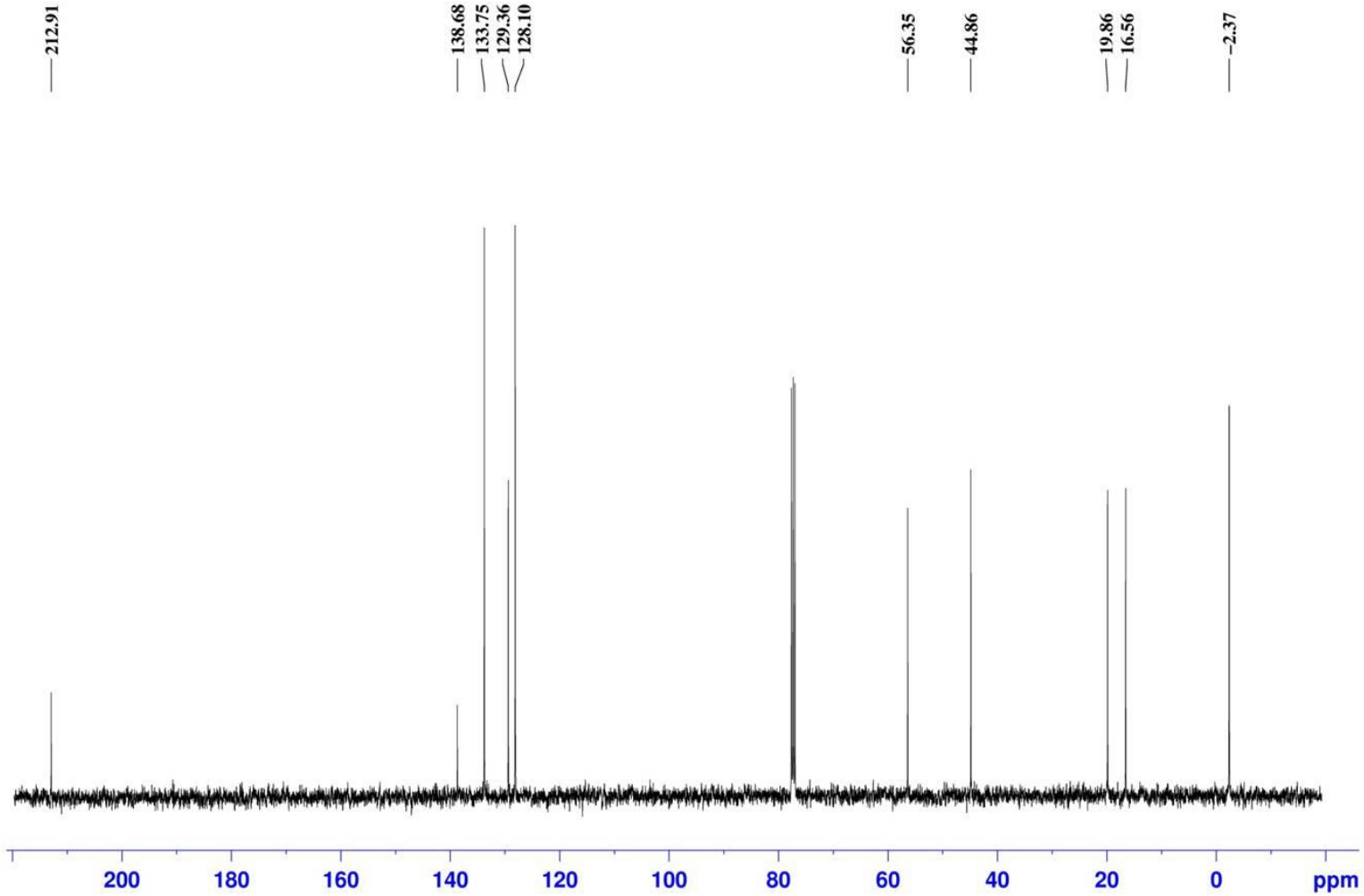


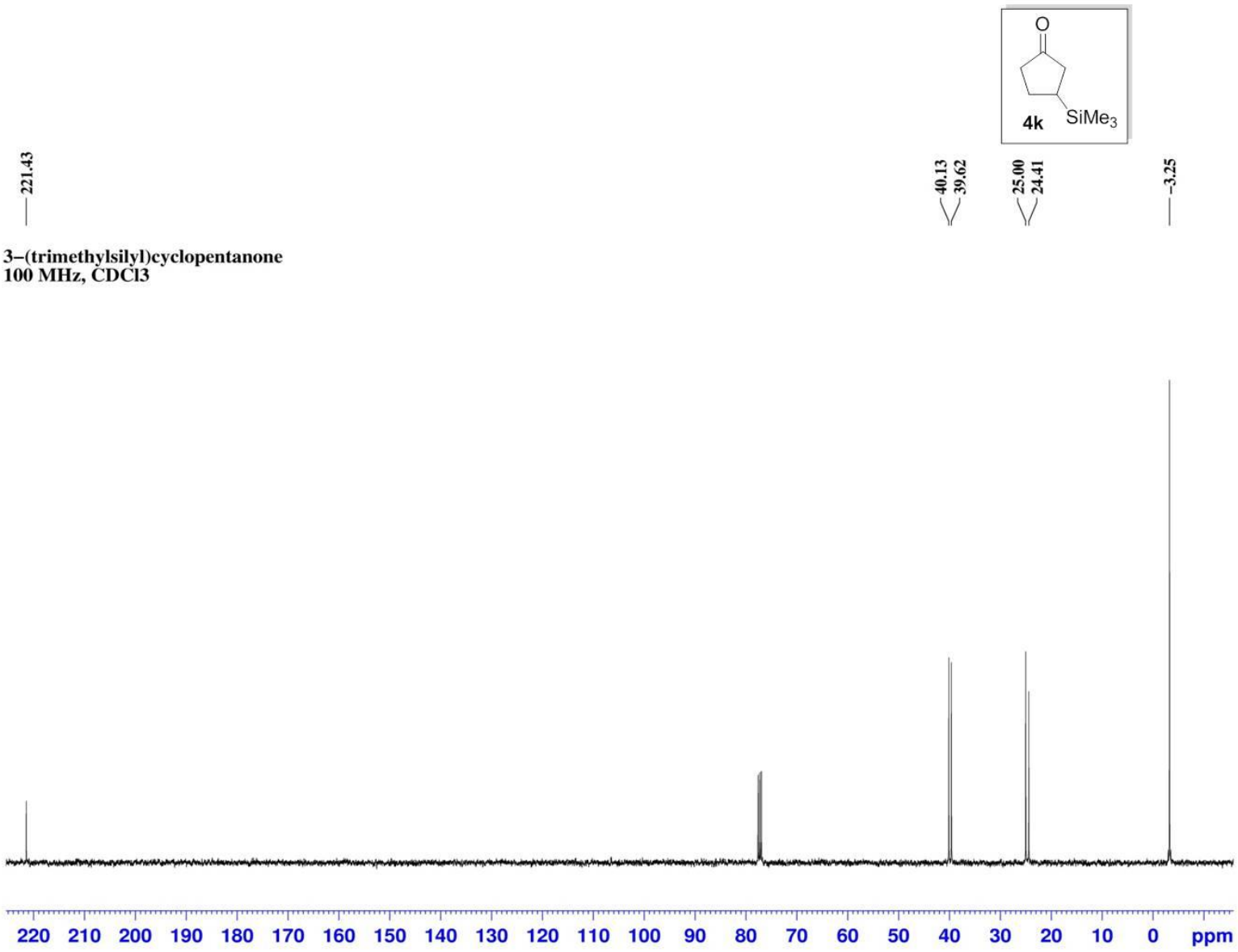
4i

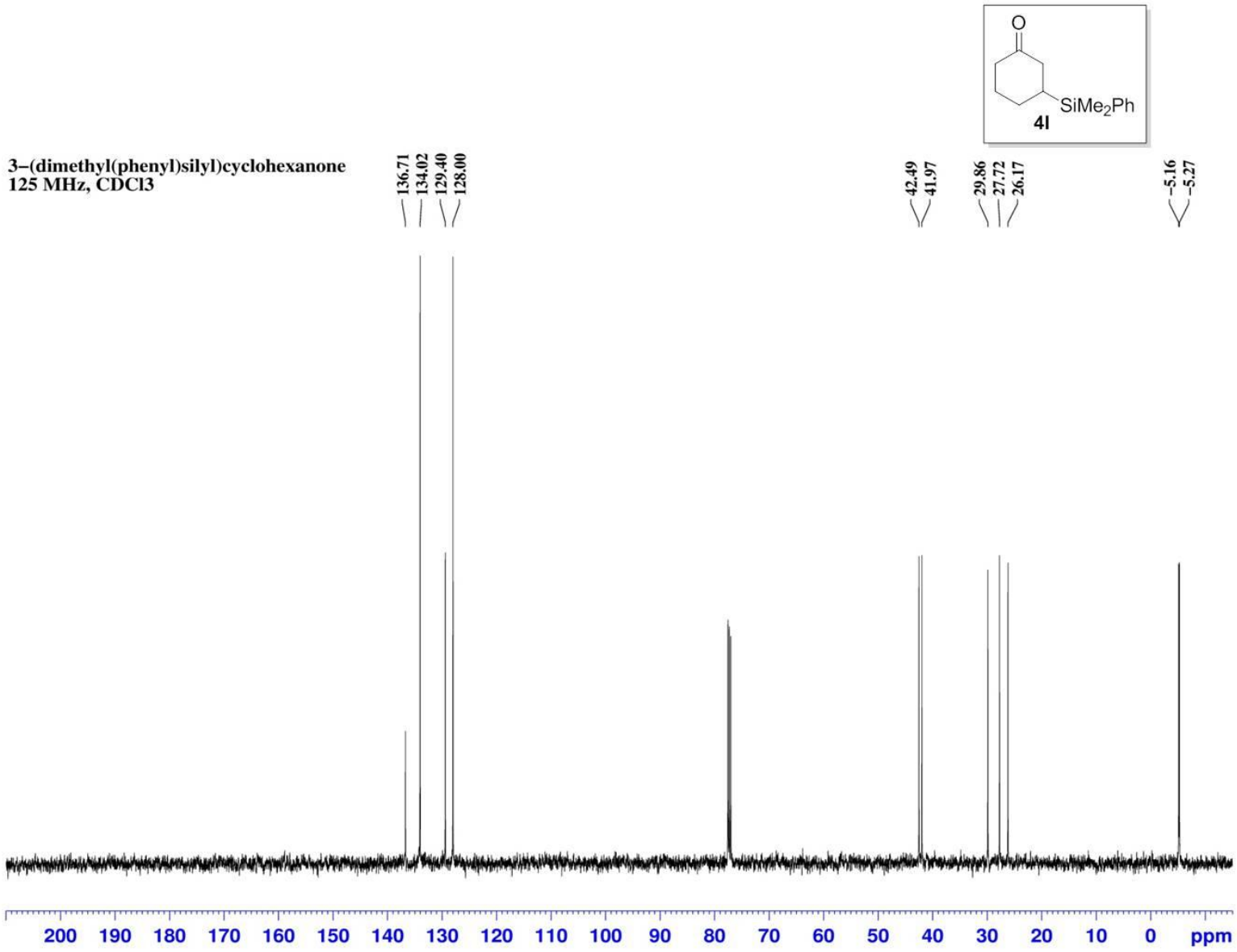


2–((dimethyl(phenyl)silyl)methyl)cyclobutanone
100 MHz, CDCl3

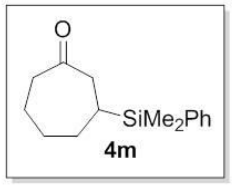




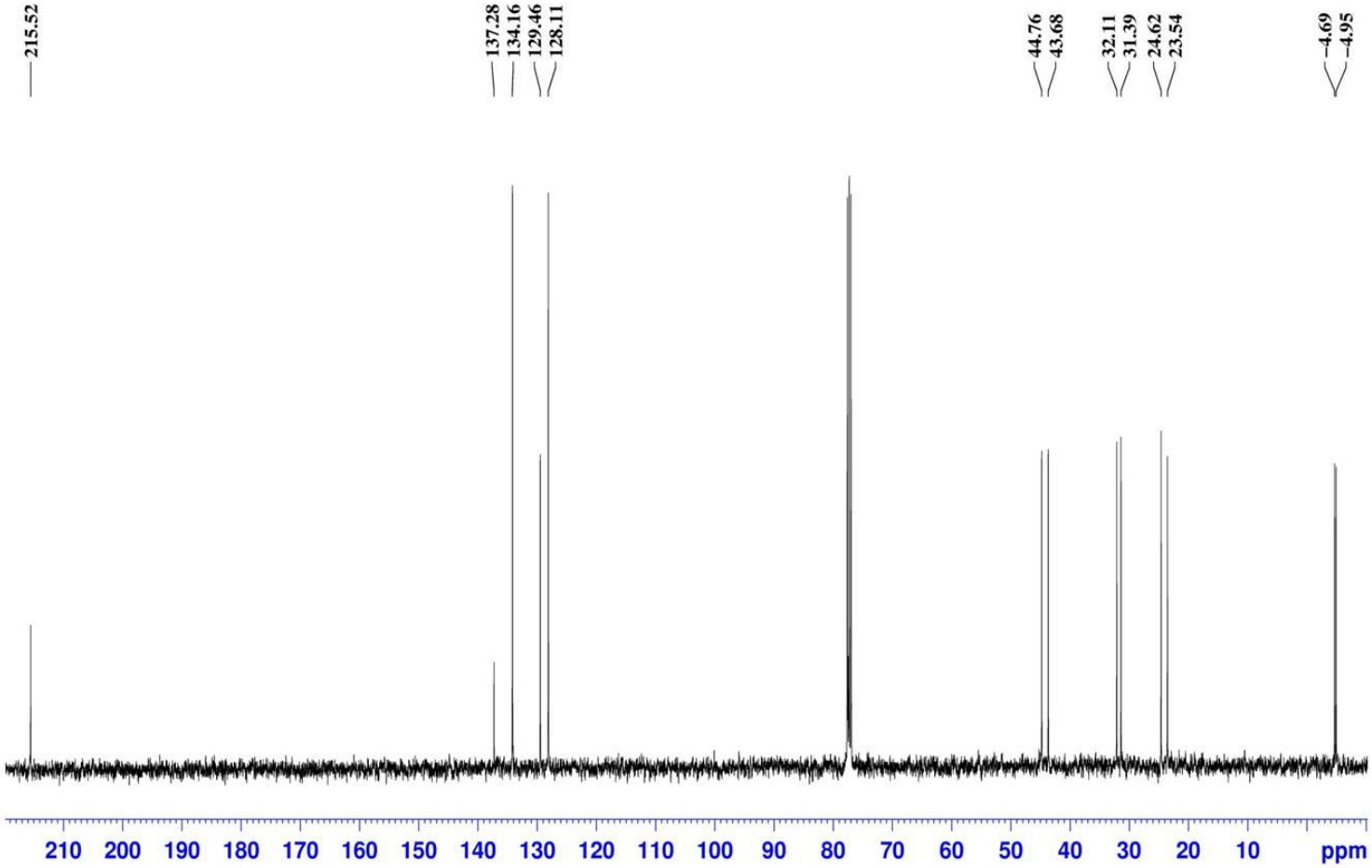

O
SiMe3
4k
221.43
40.13
39.62
25.00
24.41
-3.25
3–(trimethylsilyl)cyclopentanone
100 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
SiMe2Ph
4l
3–(dimethyl(phenyl)silyl)cyclohexanone
125 MHz, CDCl3
136.71
134.02
129.40
128.00
42.49
41.97
29.86
27.72
26.17
-5.16
-5.27
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

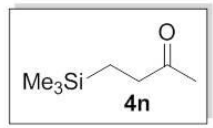
3–(dimethyl(phenyl)silyl)cycloheptanone
100 MHz, CDCl3

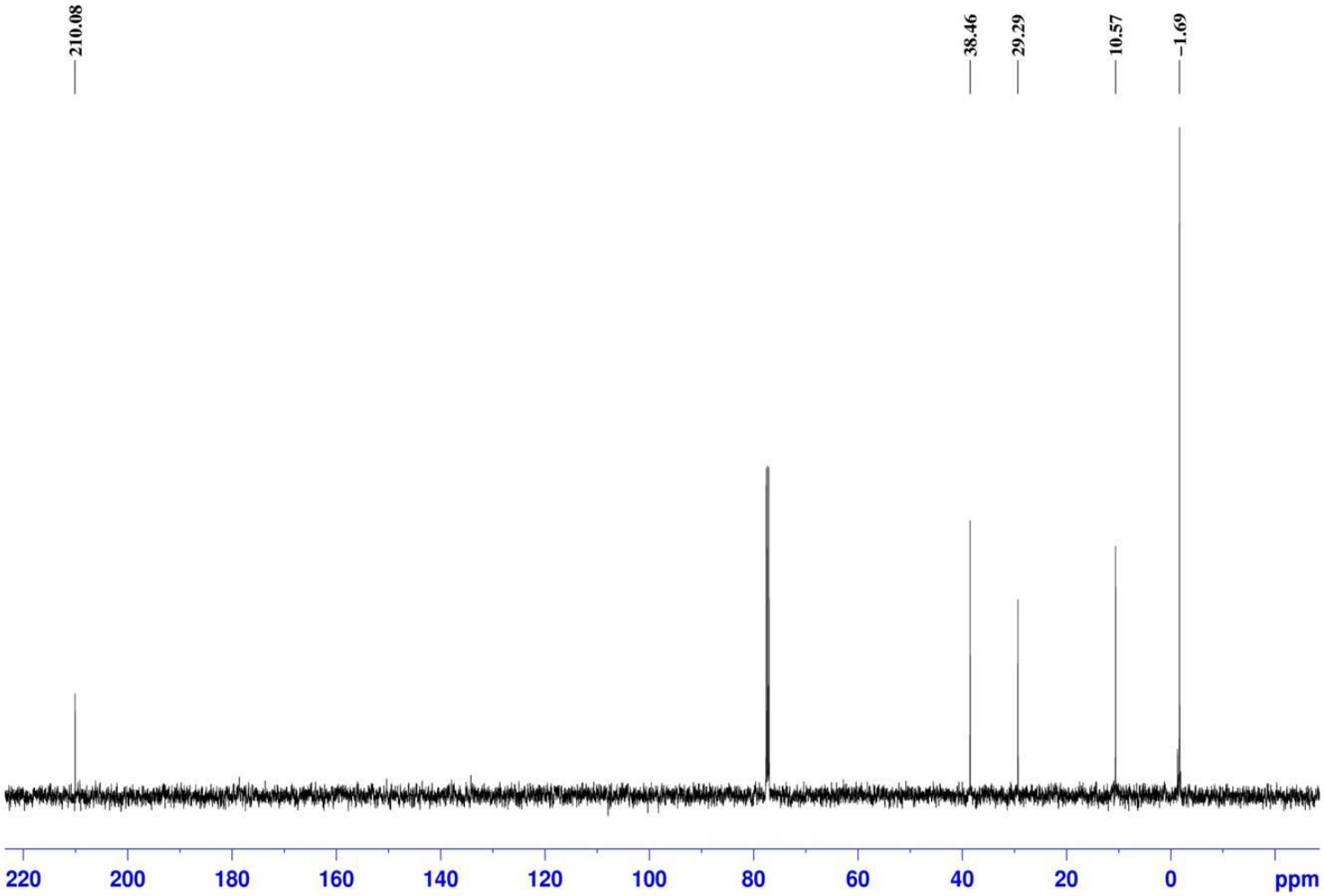


4m

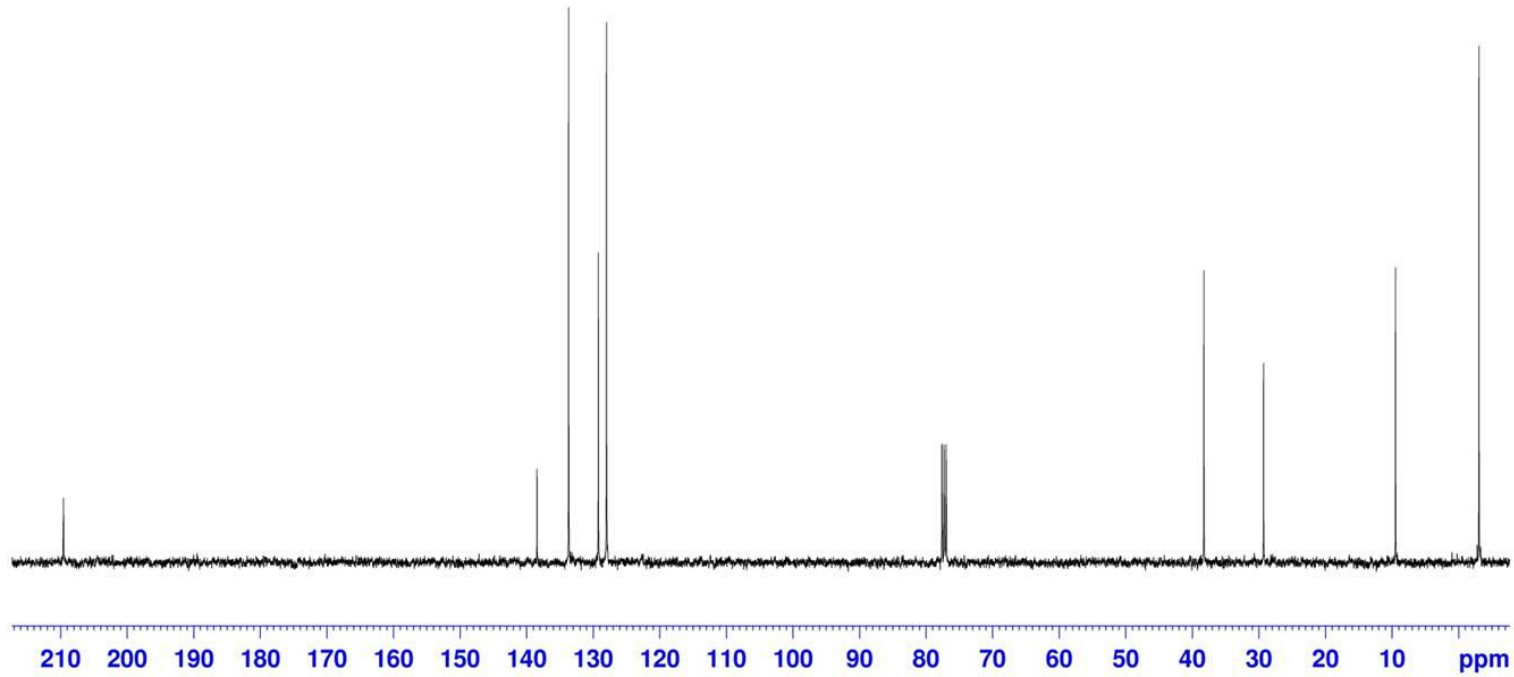


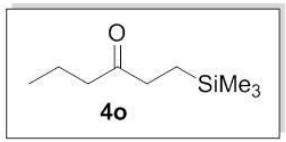
4–(trimethylsilyl)butan–2–one
125 MHz, CDCl3





4–(dimethyl(phenyl)silyl)butan–2–one
100 MHz, CDCl3



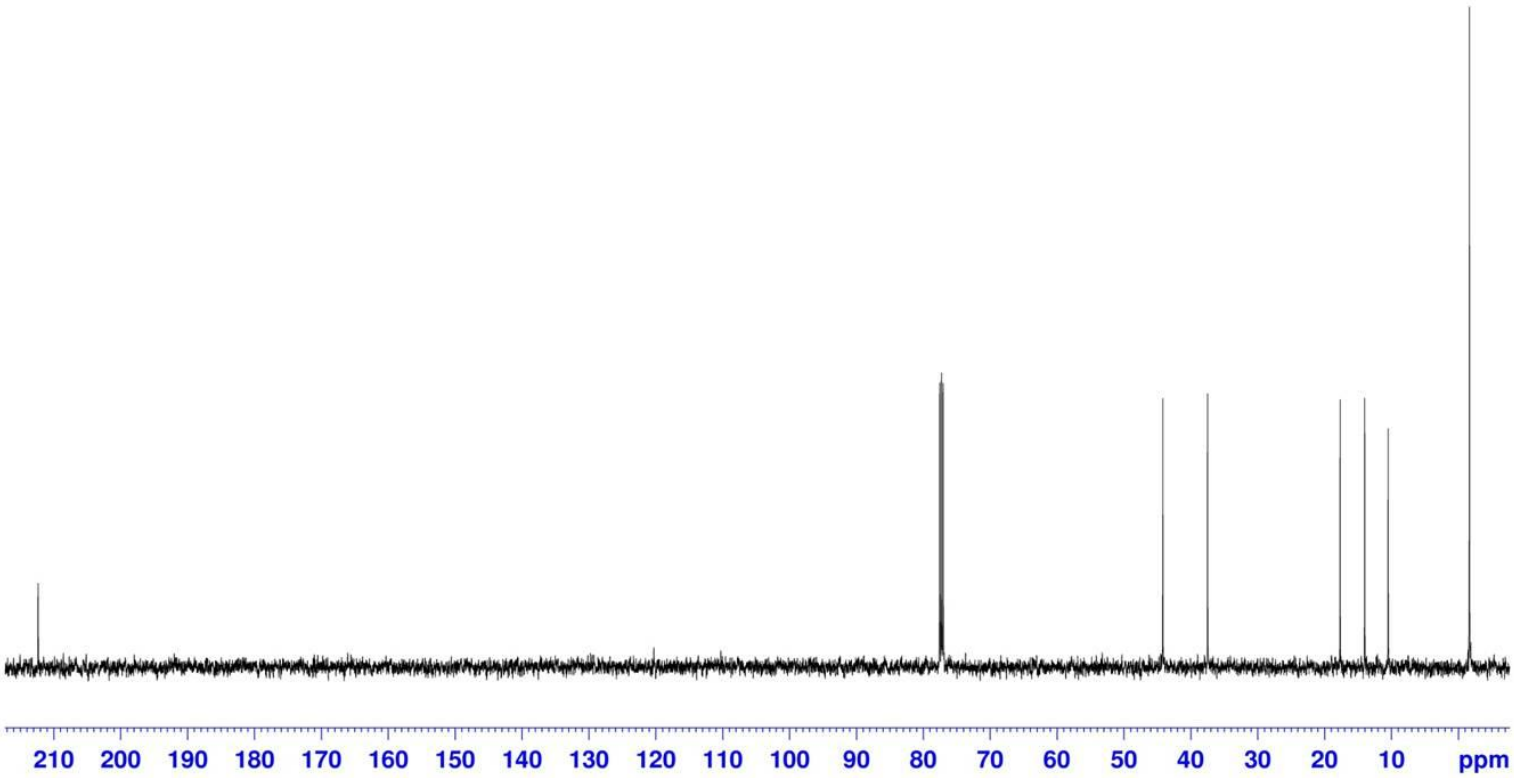


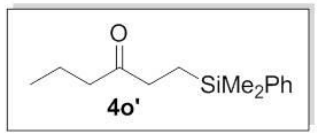
4o

212.31

44.17
37.48
17.66
14.00
10.48
-1.67

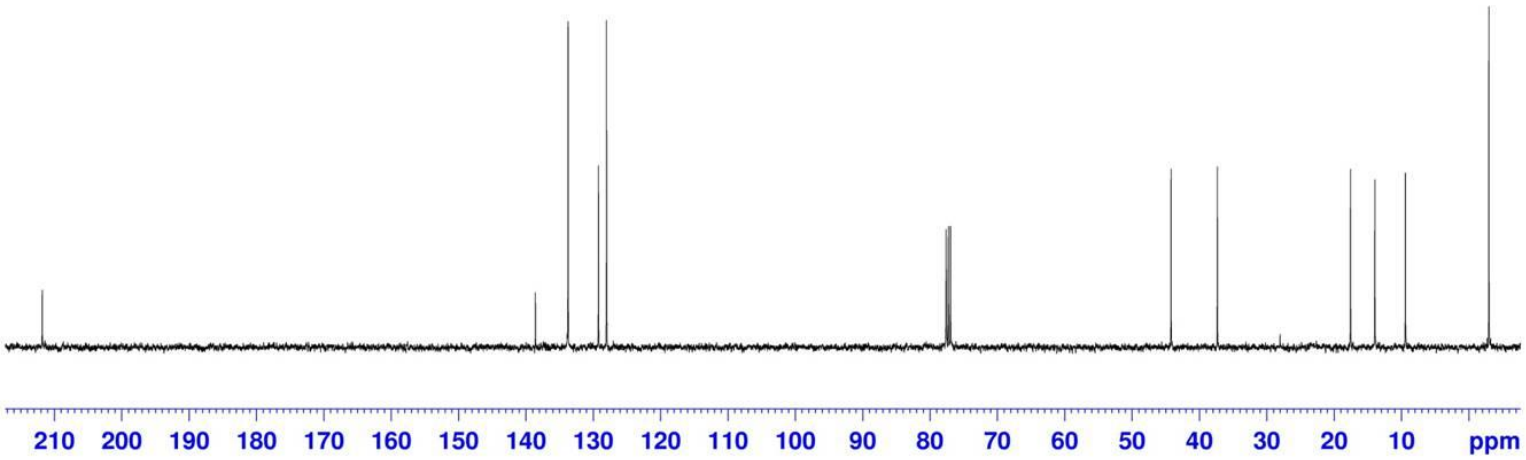
1–(trimethylsilyl)hexan–3–one
100 MHz, CDCl3



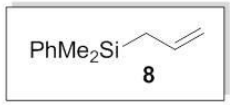


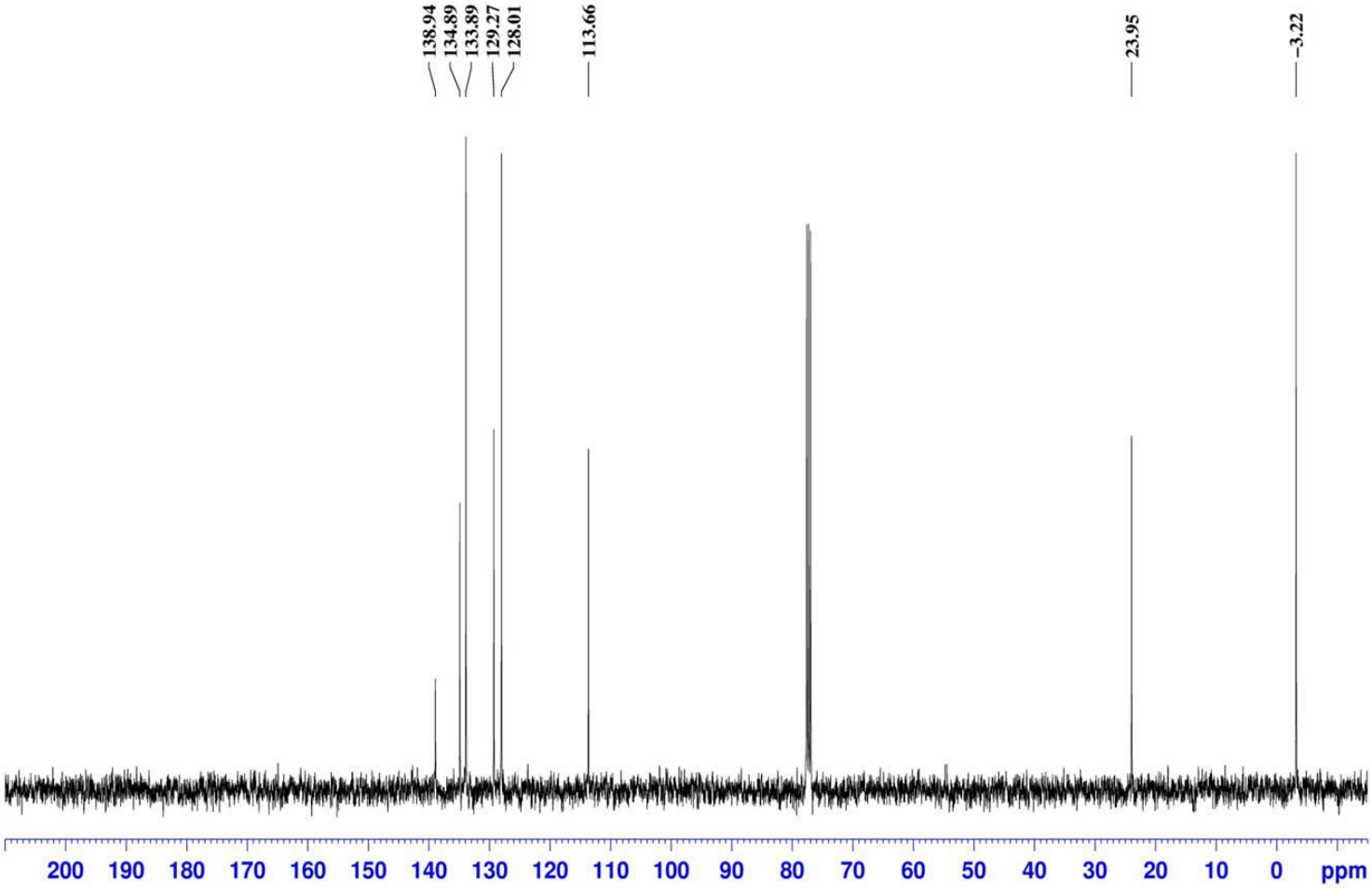
211.77
138.58
133.73
129.21
128.01
44.19
37.32
17.55
13.94
9.40
-3.00

1-(dimethyl(phenyl)silyl)hexan-3-one
100 MHz, CDCl3

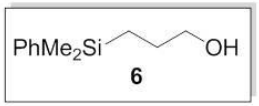


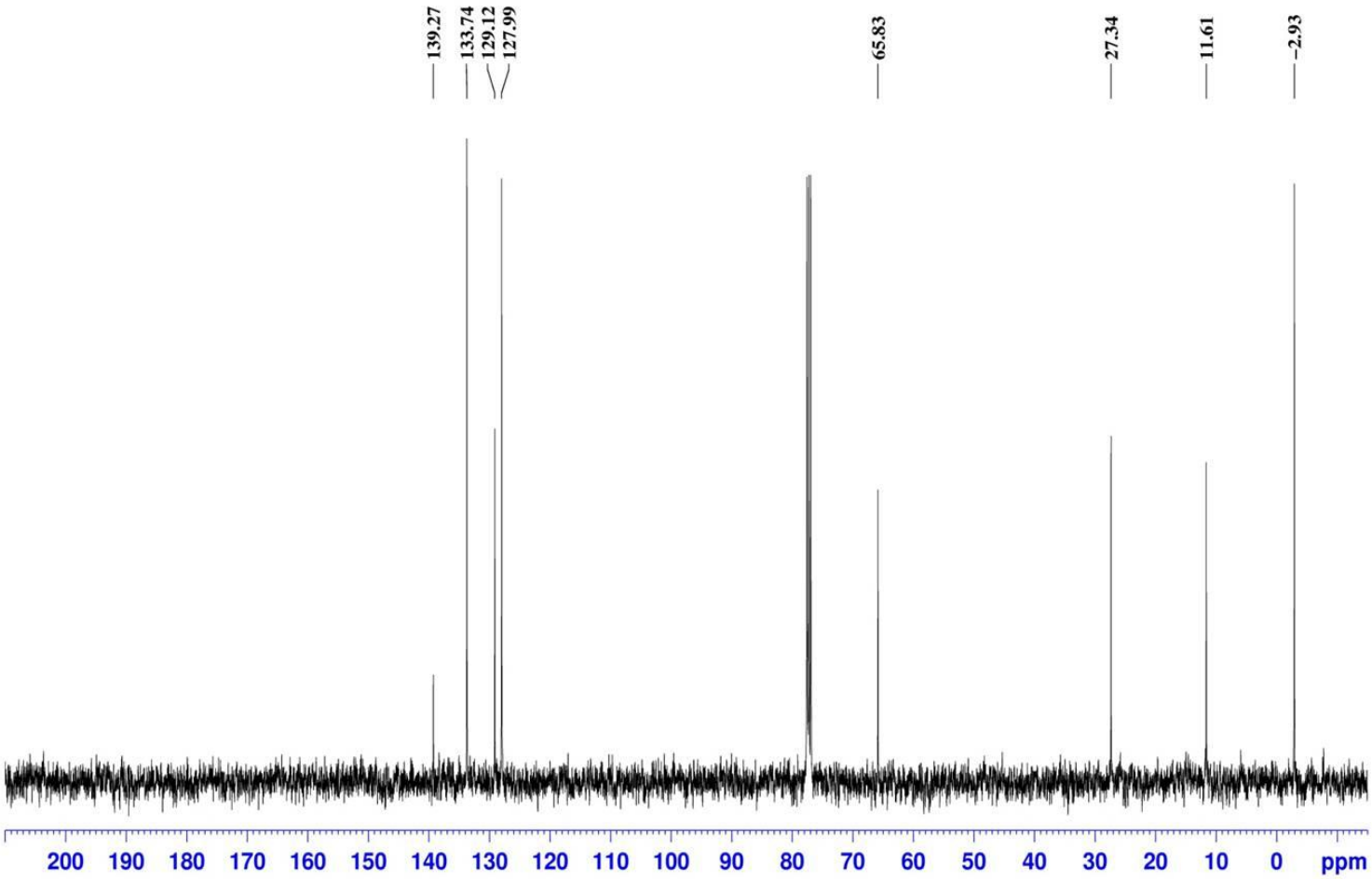
allyldimethyl(phenyl)silane
100 MHz, CDCl3

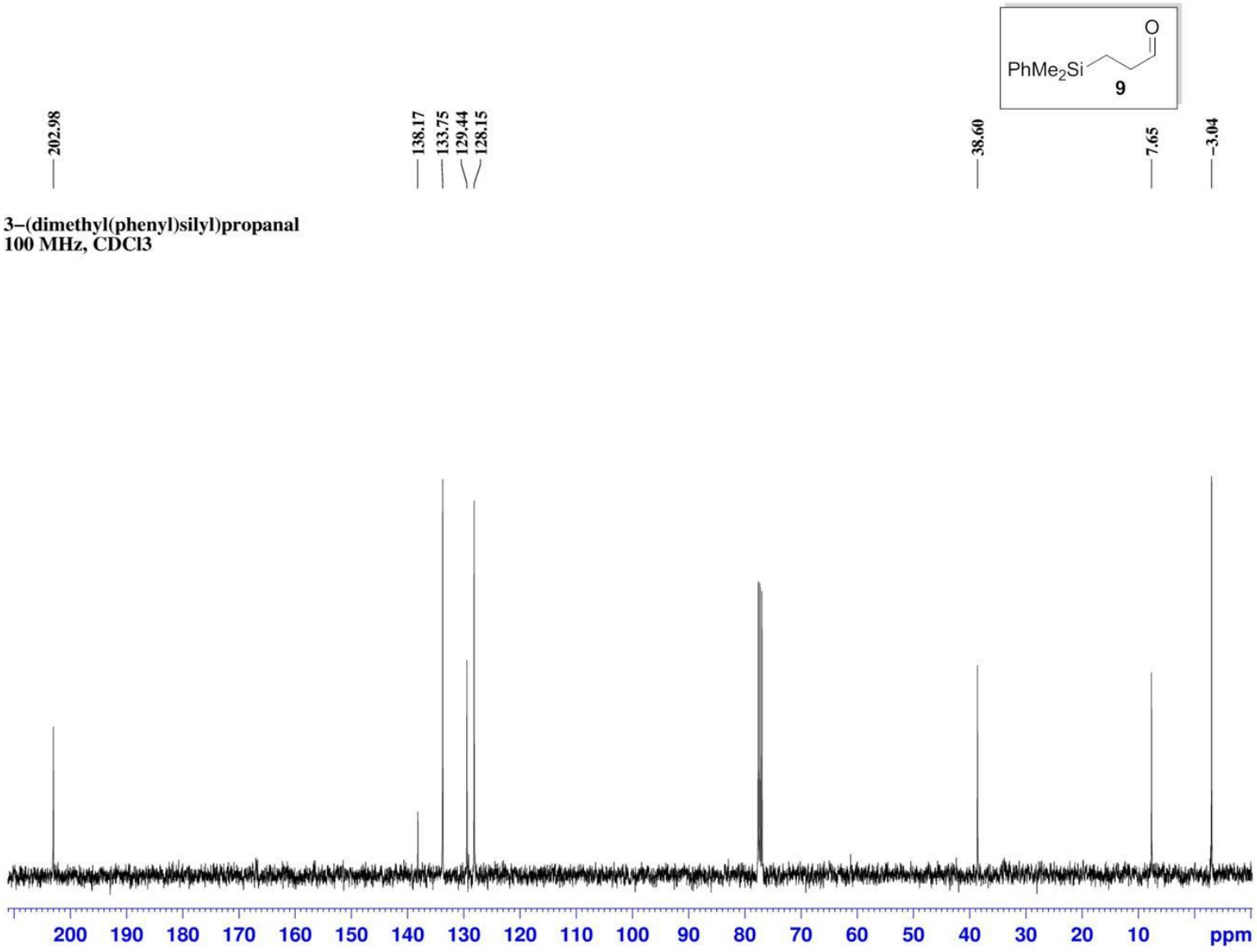


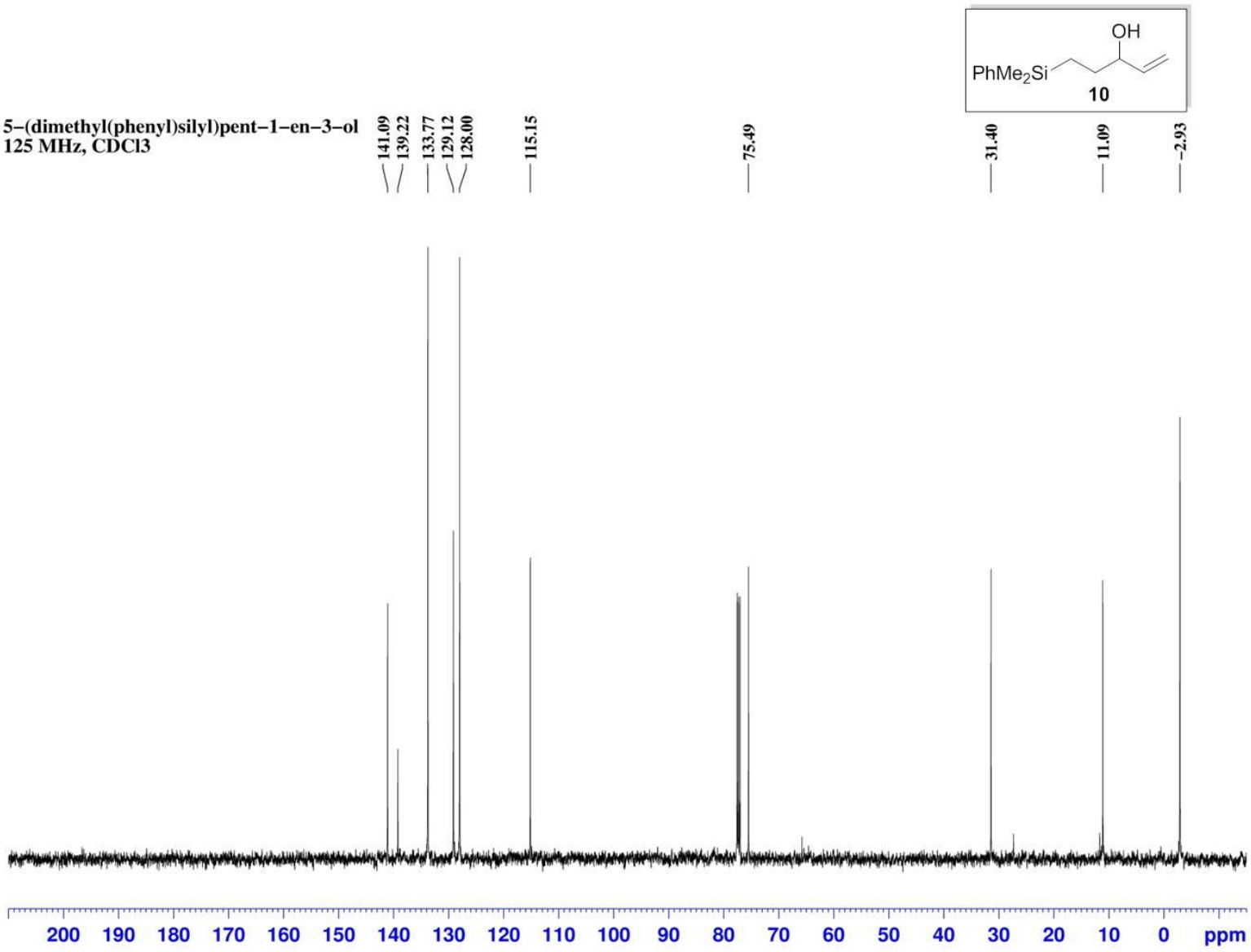


3–(dimethyl(phenyl)silyl)propan–1–ol
100 MHz, CDCl3

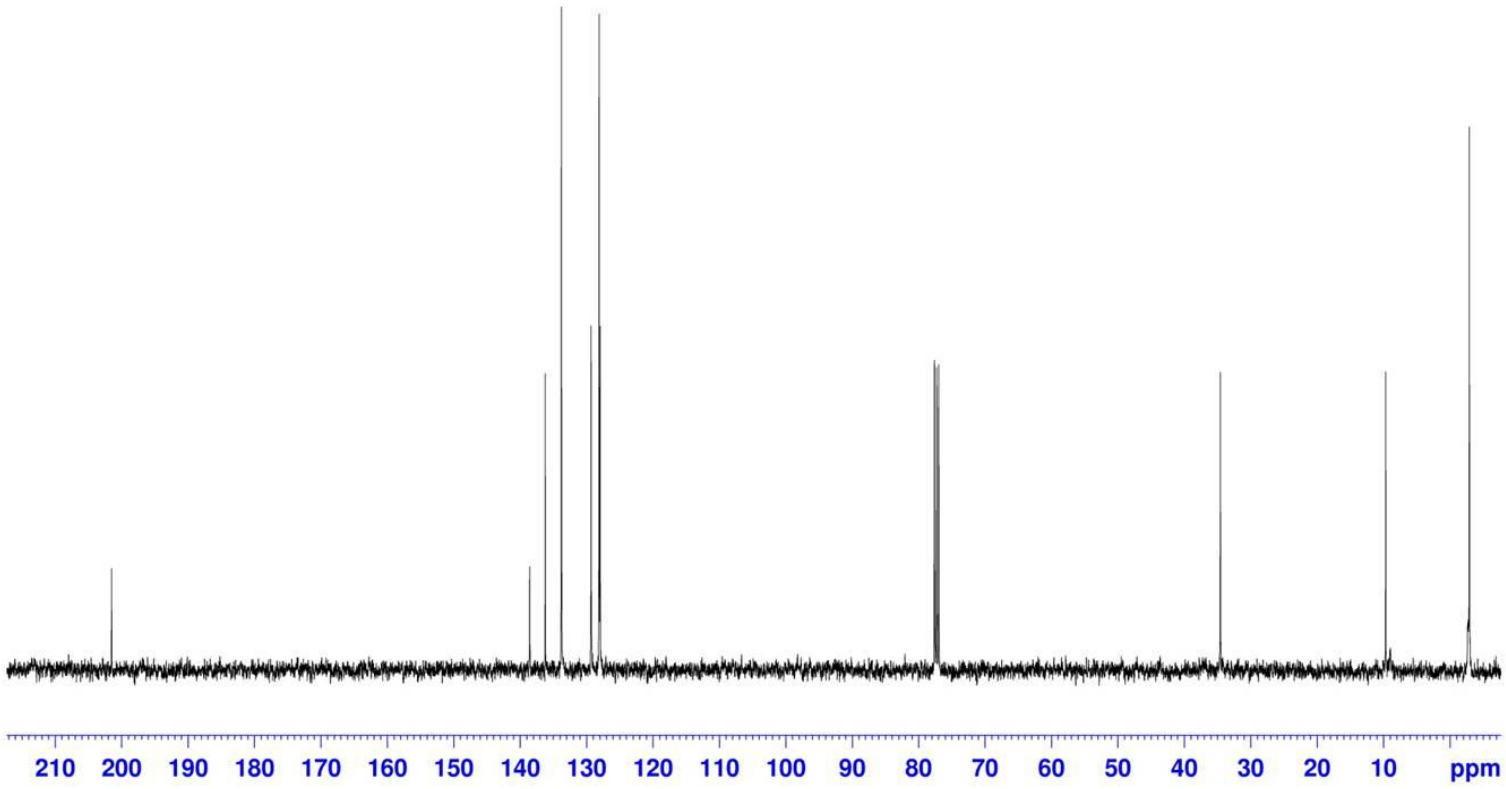




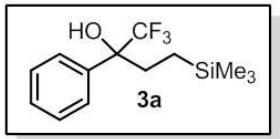

PhMe2Si
O
9
202.98
138.17
133.75
129.44
128.15
38.60
7.65
-3.04
3-(dimethyl(phenyl)silyl)propanal
100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

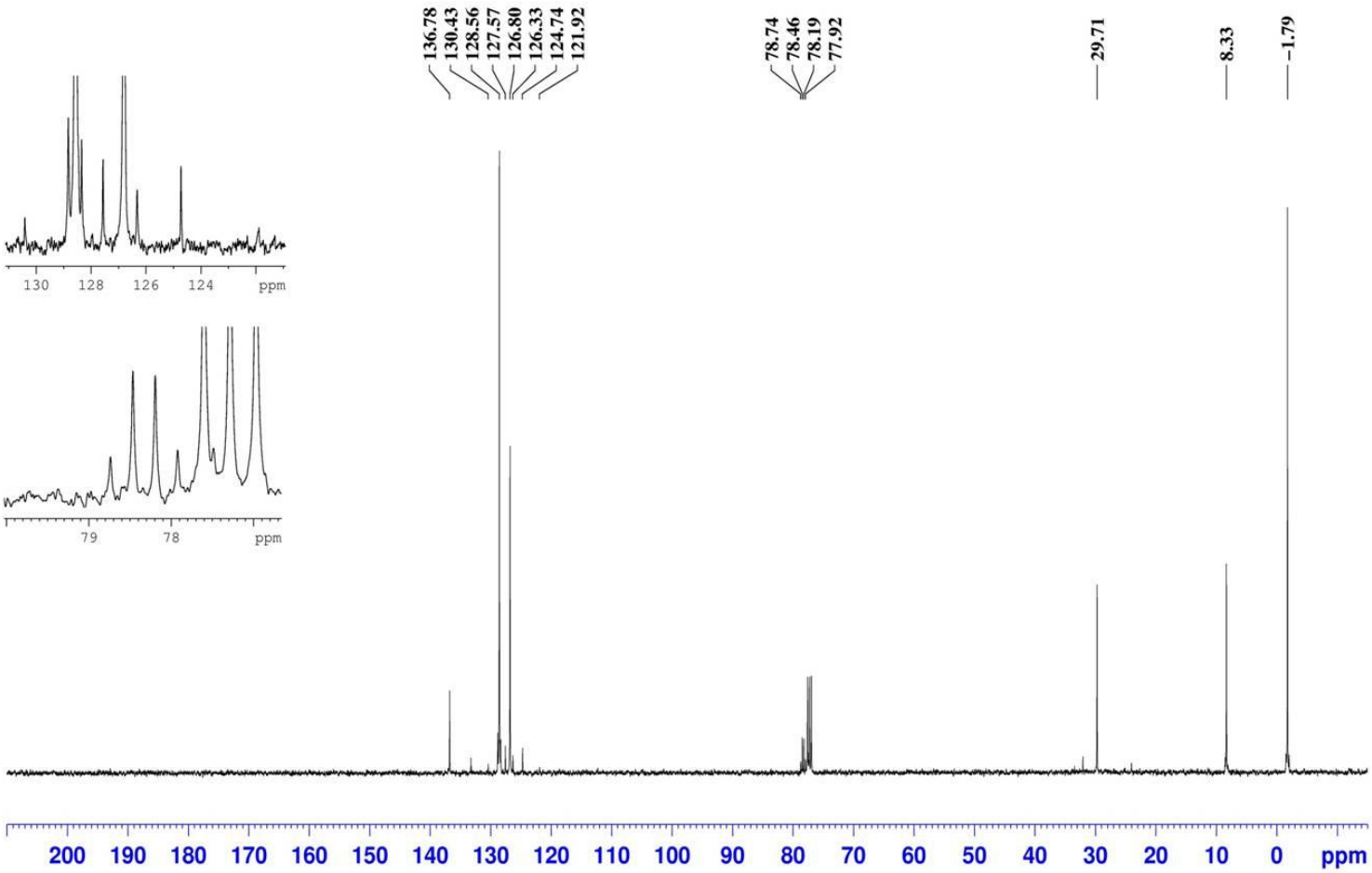

5–(dimethyl(phenyl)silyl)pent–1–en–3–ol
125 MHz, CDCl3
141.09
139.22
133.77
129.12
128.00
115.15
75.49
31.40
11.09
–2.93
OH
PhMe2Si
10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

5–(dimethyl(phenyl)silyl)pent–1–en–3–one
100 MHz, CDCl3

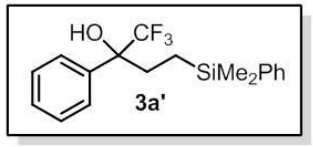


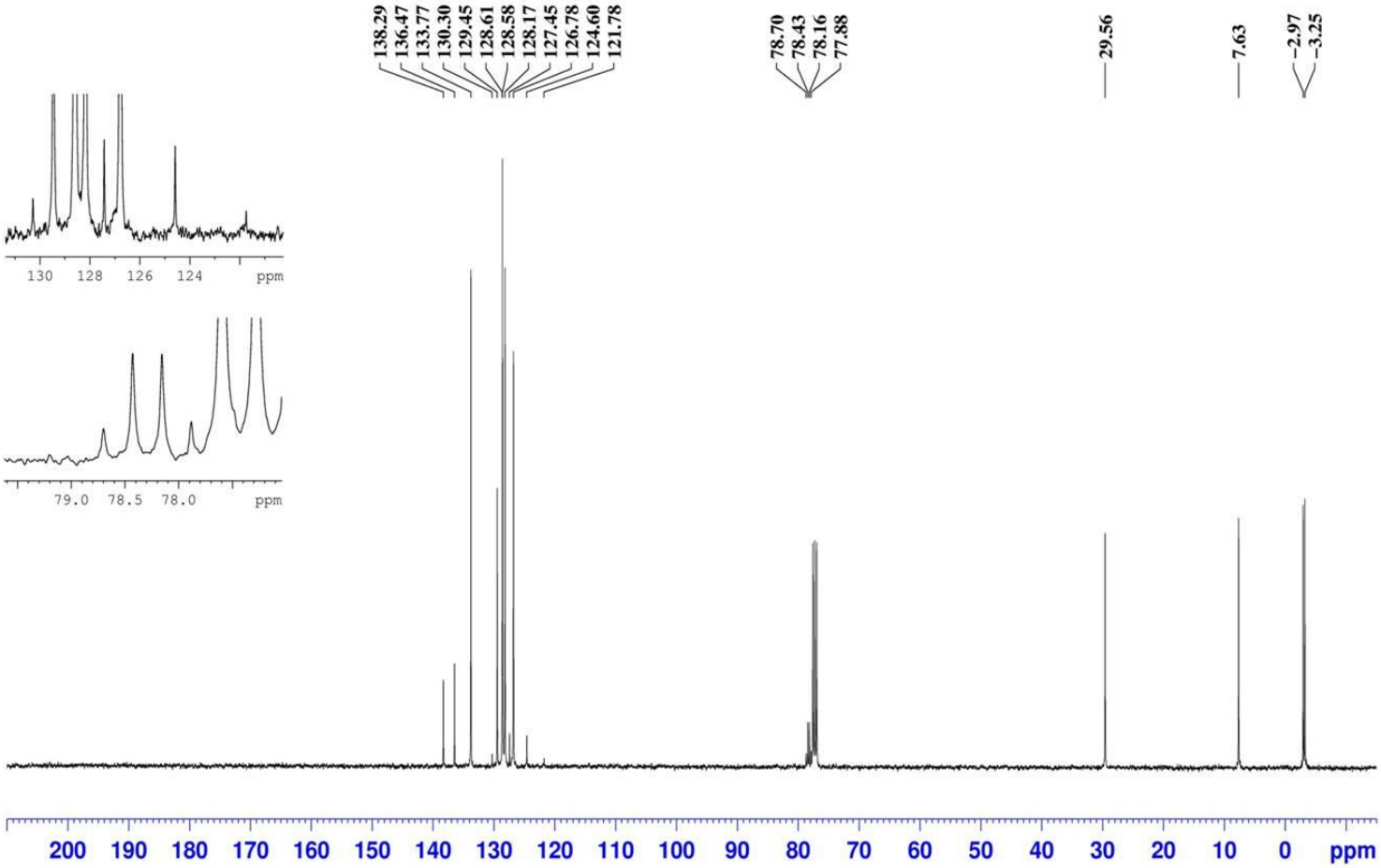
1,1,1–trifluoro–2–phenyl–4–(trimethylsilyl)butan–2–ol
100 MHz, CDCl3



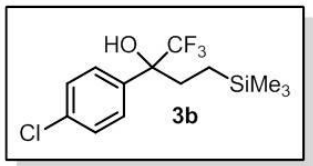


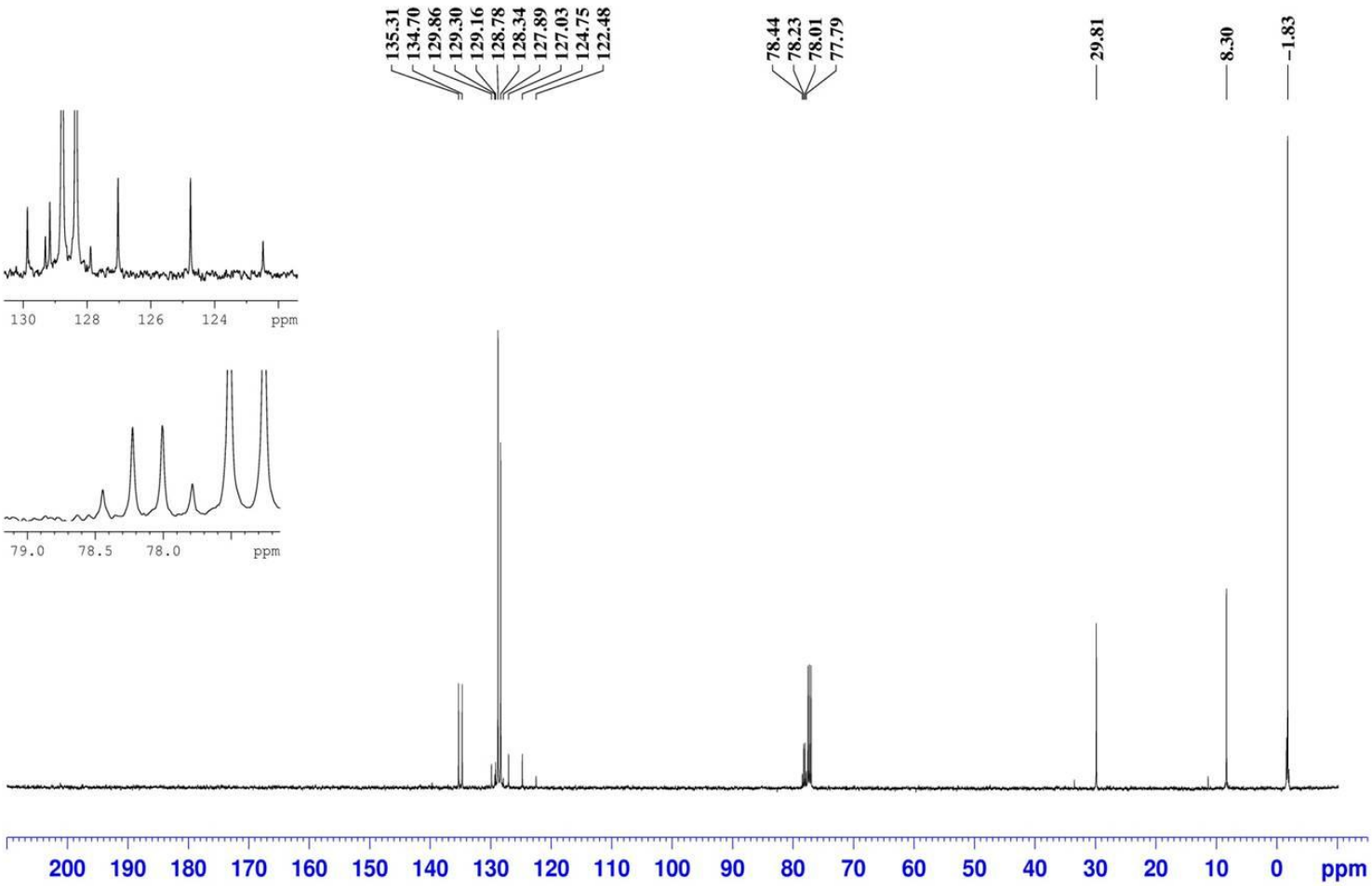
4–(dimethyl(phenyl)silyl)–1,1,1–trifluoro–2–phenylbutan–2–ol
100 MHz, CDCl3



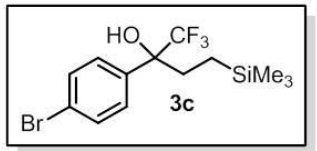


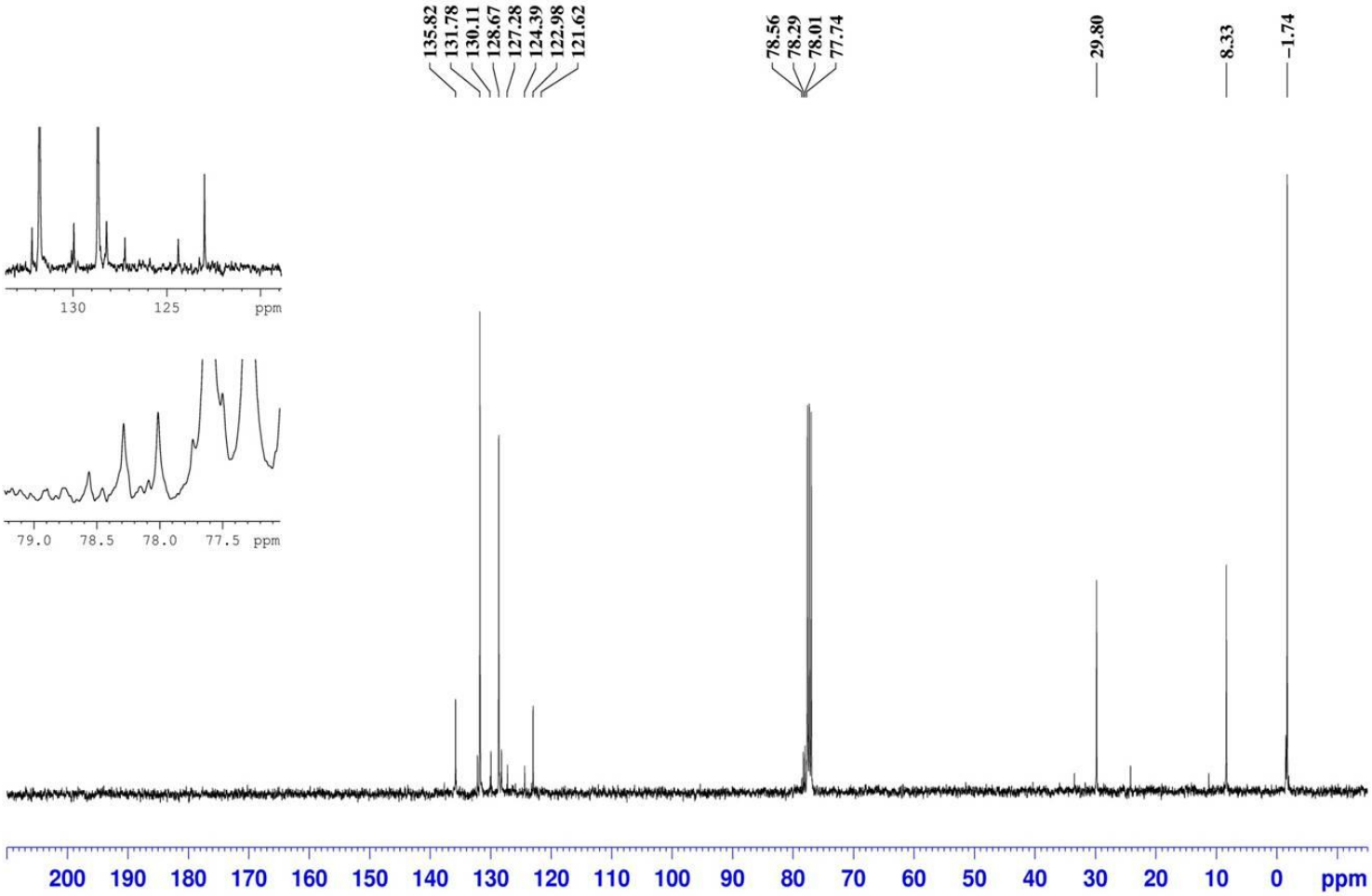
2–(4–chlorophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–ol
100 MHz, CDCl3



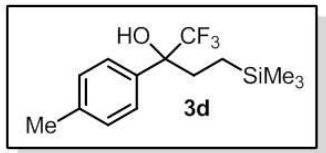


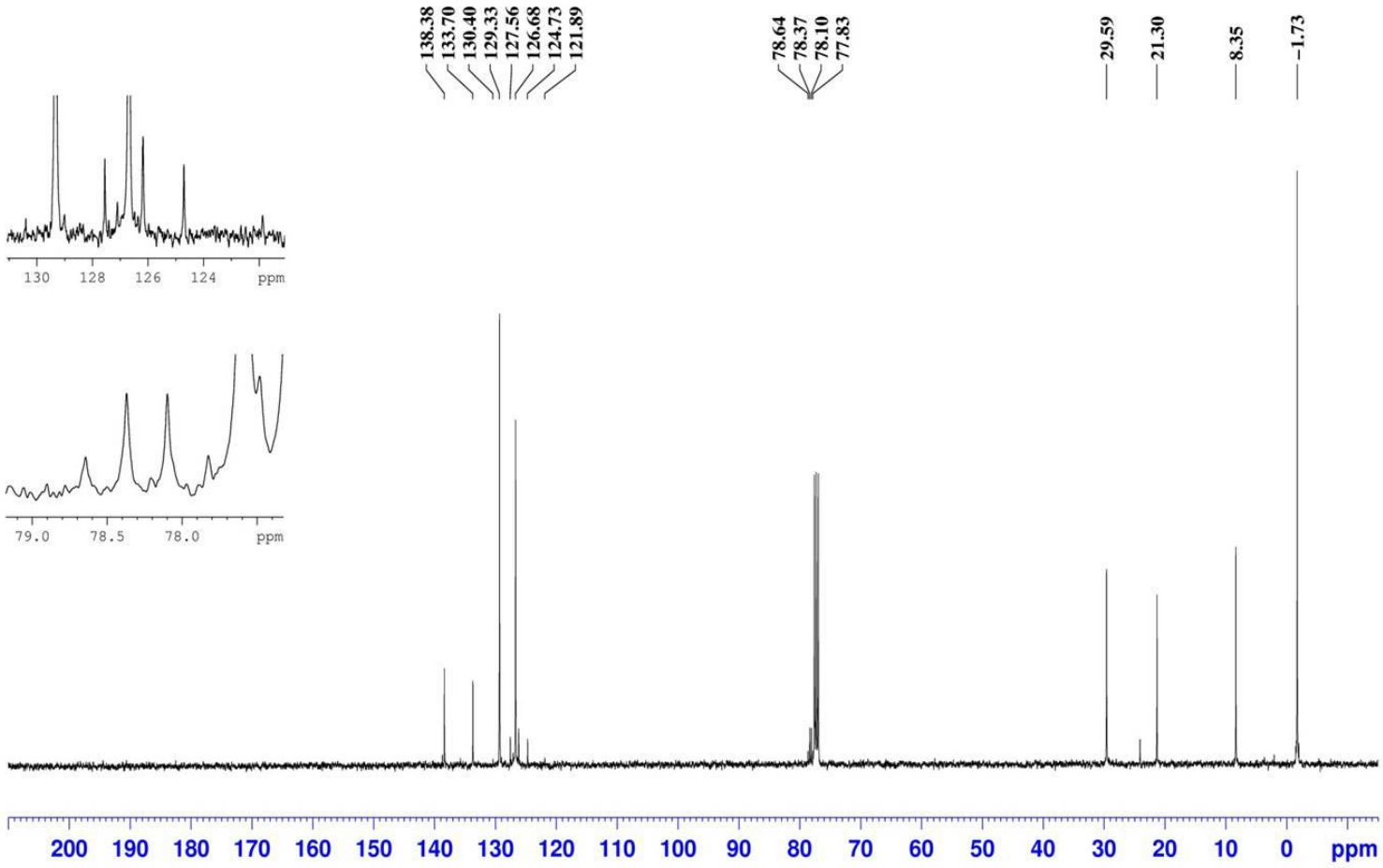
2–(4–bromophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–ol
100 MHz, CDCl3



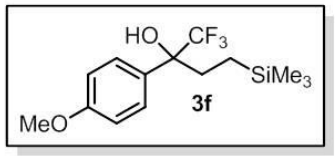


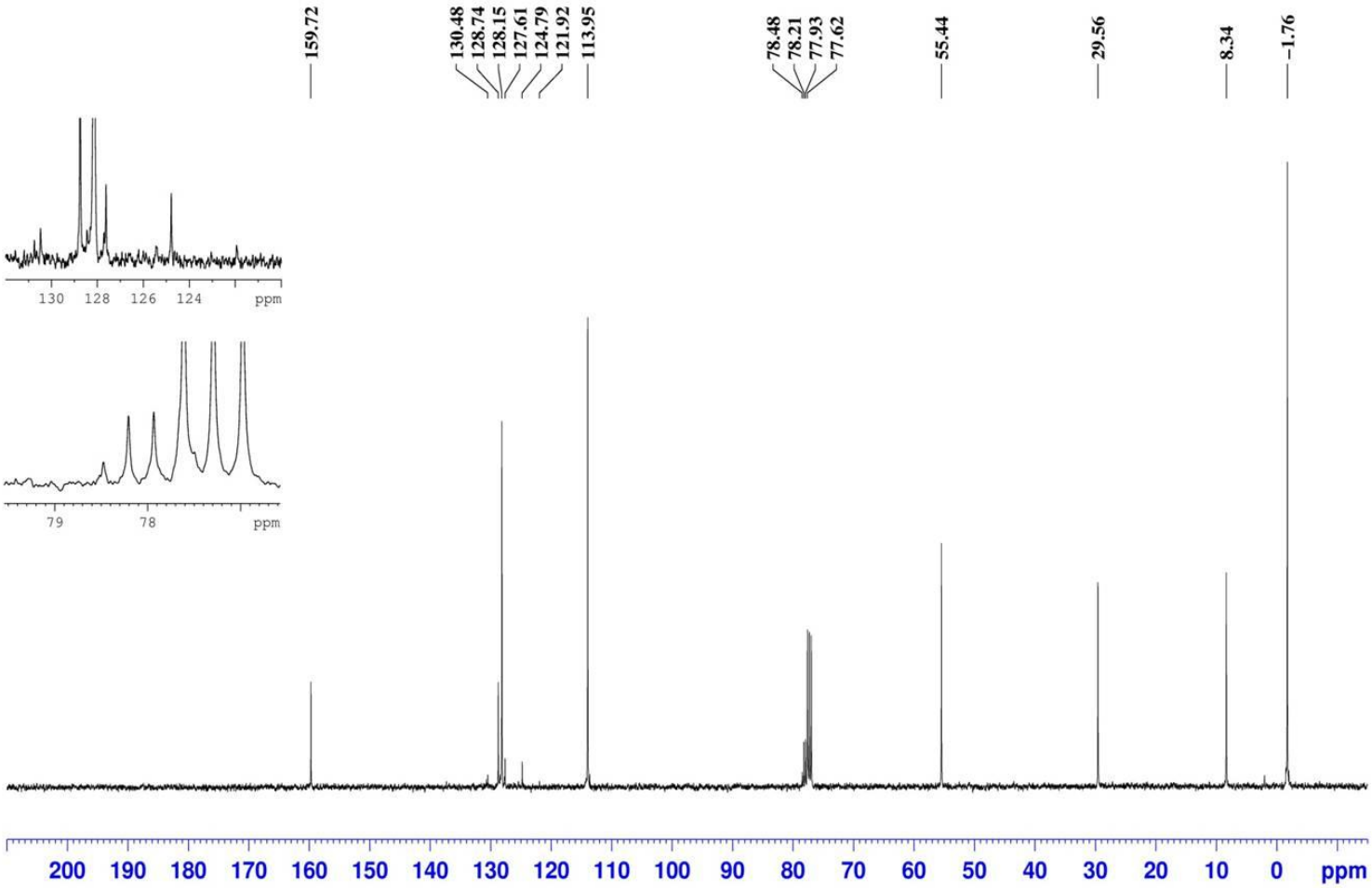
1,1,1–trifluoro–2–(p–tolyl)–4–(trimethylsilyl)butan–2–ol
100 MHz, CDCl3



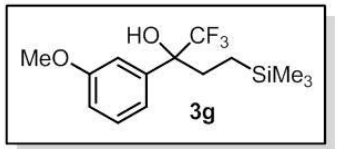


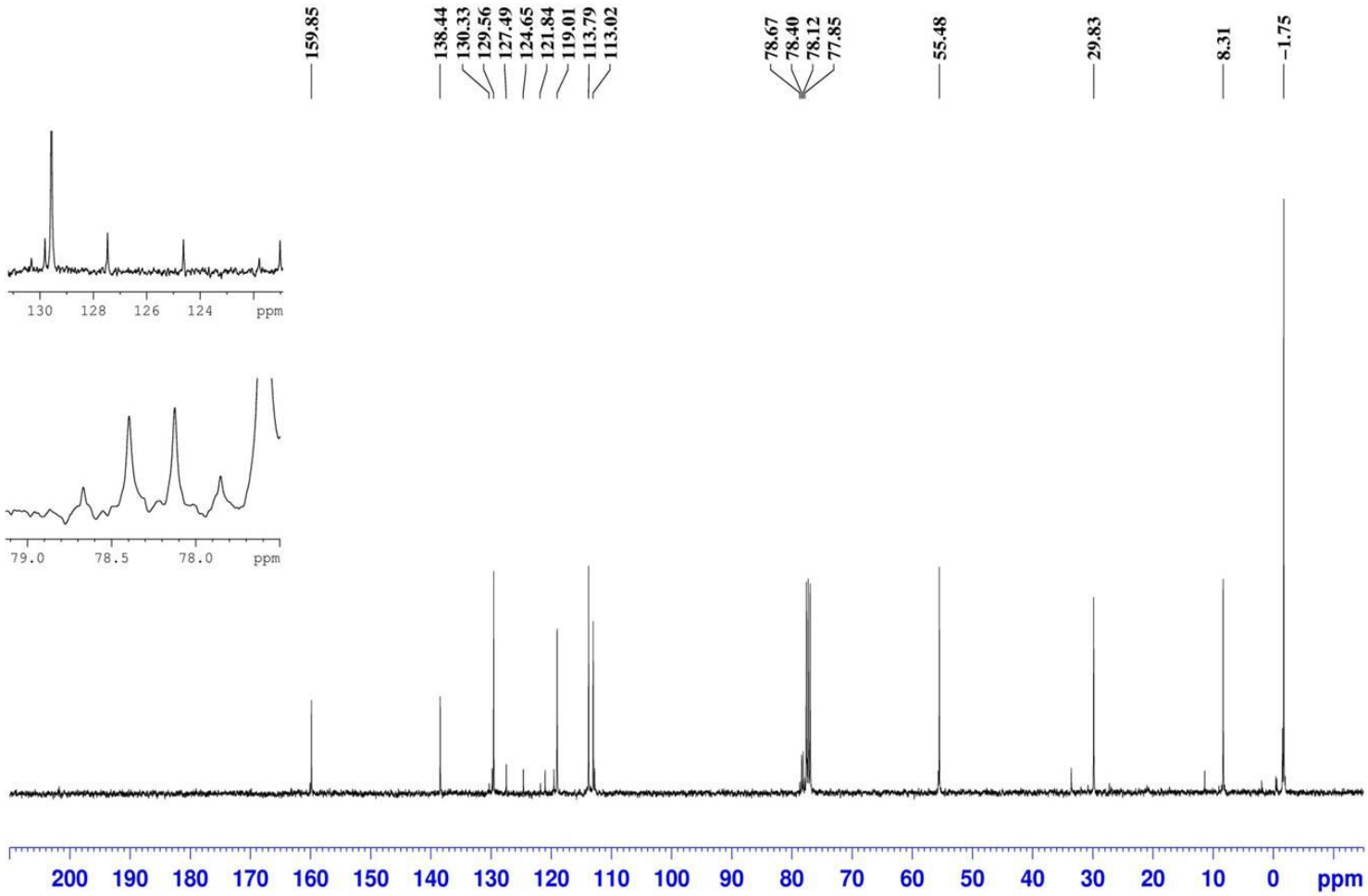
1,1,1–trifluoro–2–(4–methoxyphenyl)–4–(trimethylsilyl)butan–2–ol
100 MHz, CDCl3



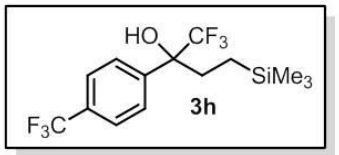


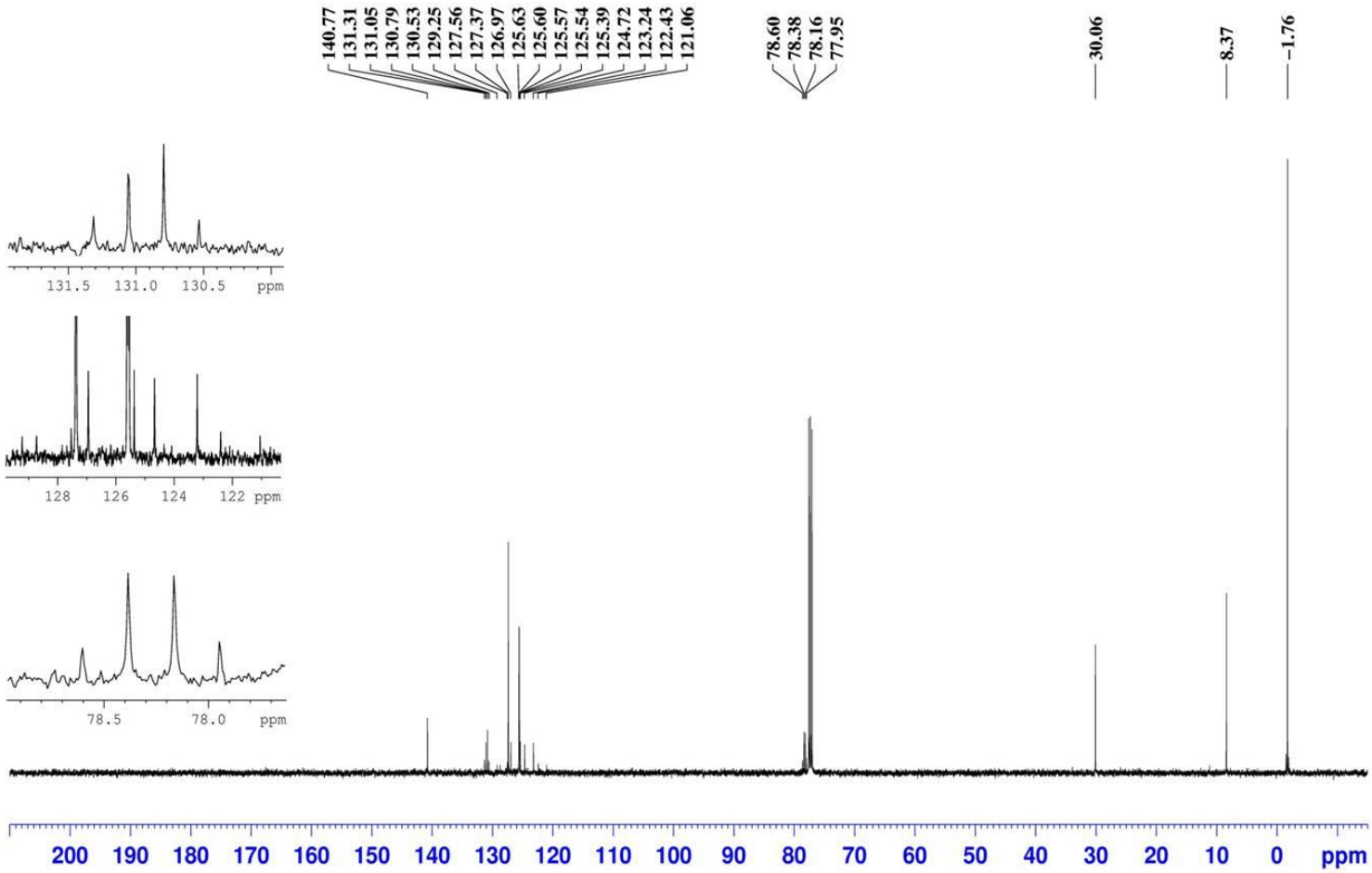
1,1,1−trifluoro−2−(3−methoxyphenyl)−4−(trimethylsilyl)butan−2−ol
100 MHz, CDCl3



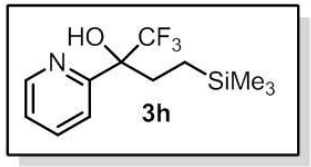


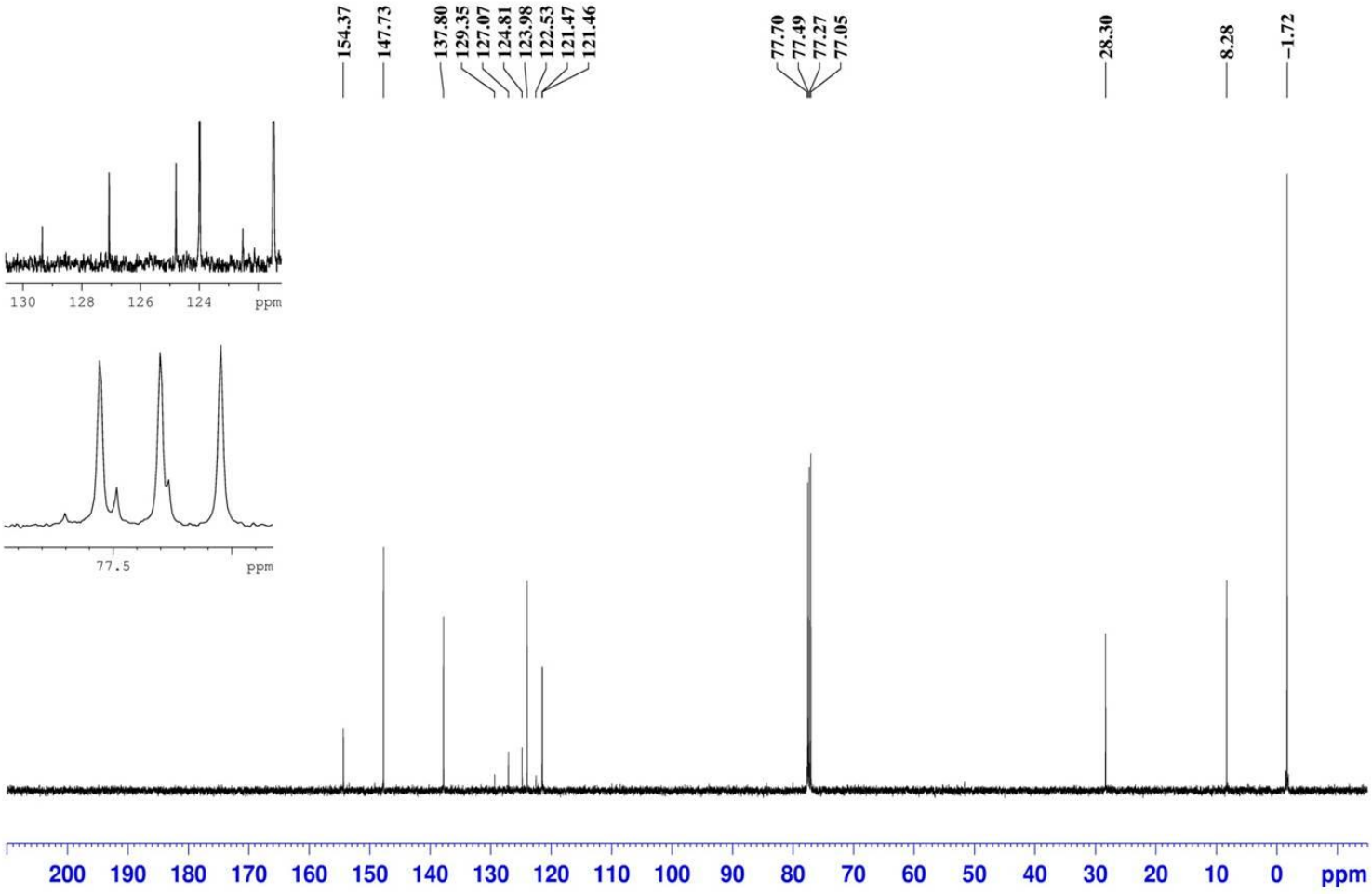
1,1,1−trifluoro−2−(4−(trifluoromethyl)phenyl)−4−(trimethylsilyl)butan−2−ol
100 MHz, CDCl3



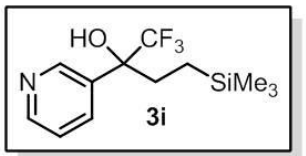


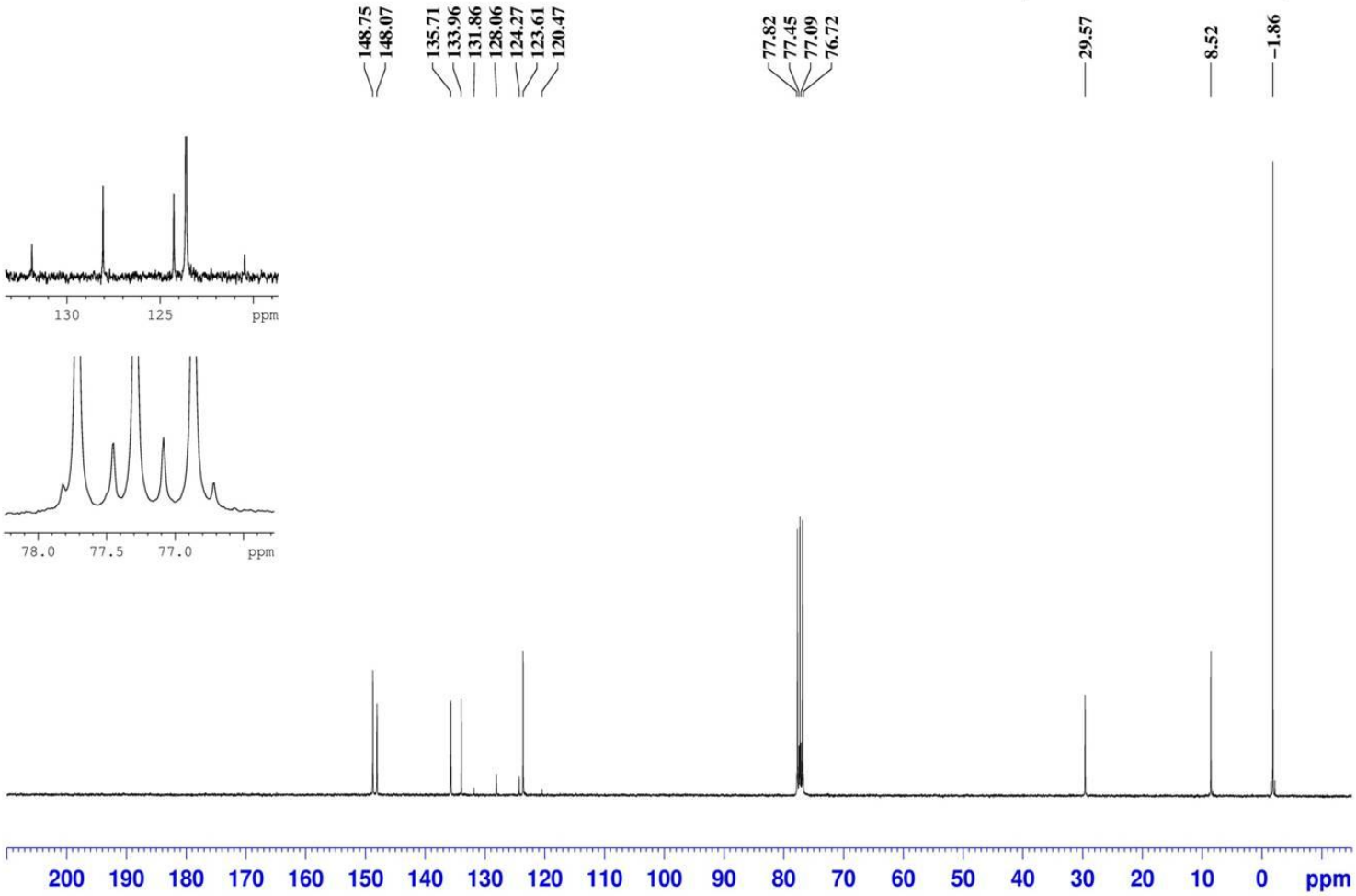
1,1,1−trifluoro−2−(pyridin−2−yl)−4−(trimethylsilyl)butan−2−ol
100 MHz, CDCl3



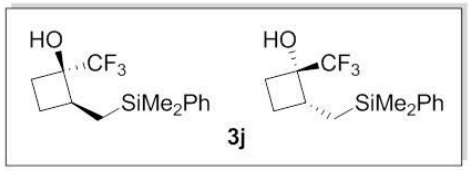


1,1,1–trifluoro–2–(pyridin–3–yl)–4–(trimethylsilyl)butan–2–ol
100 MHz, CDCl3

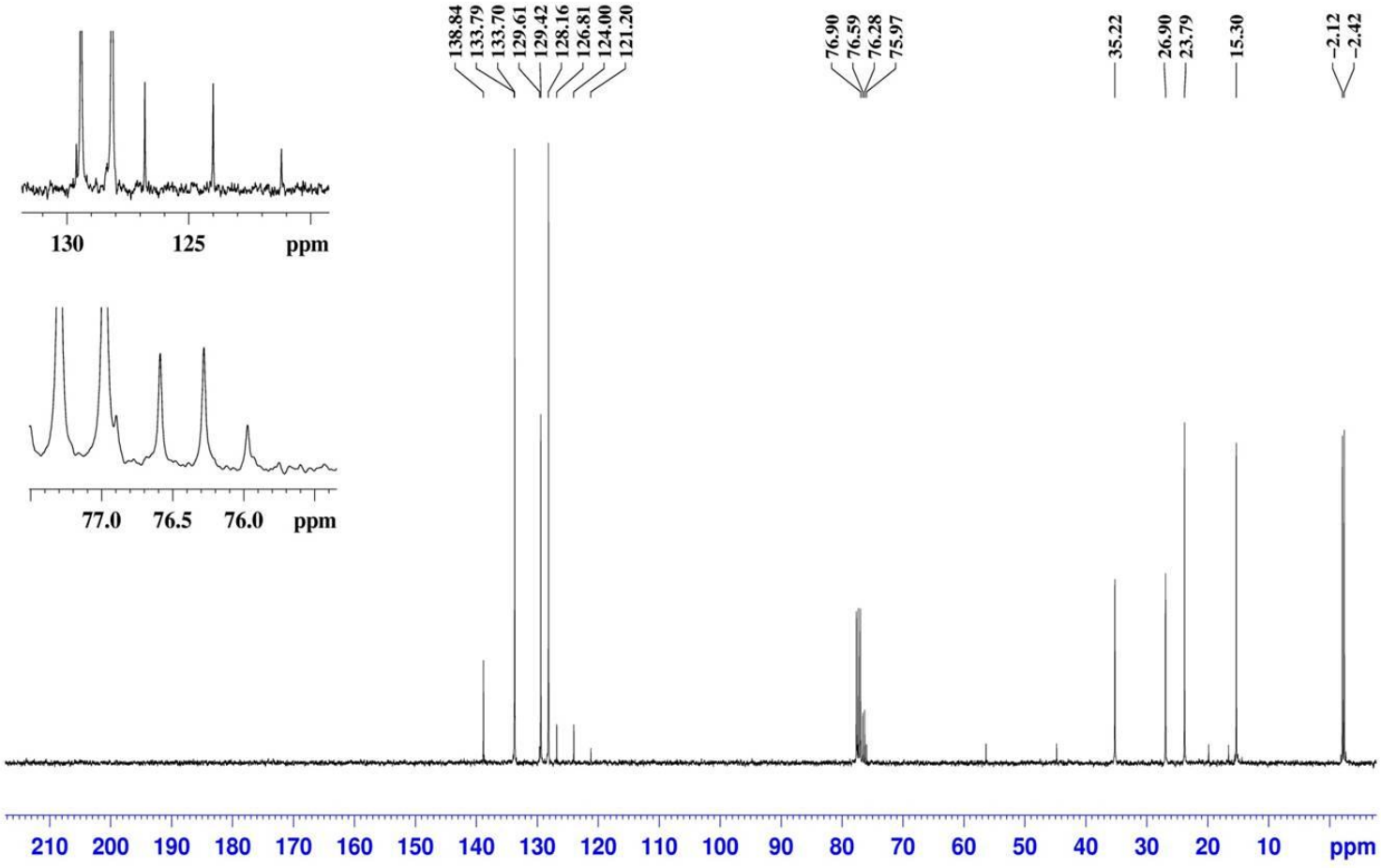




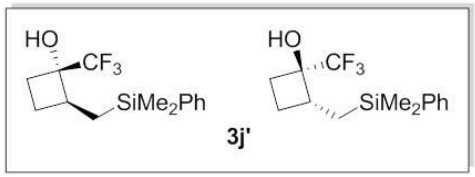
(1R,2S) & (1S,2R)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutanol
100 MHz, CDCl3



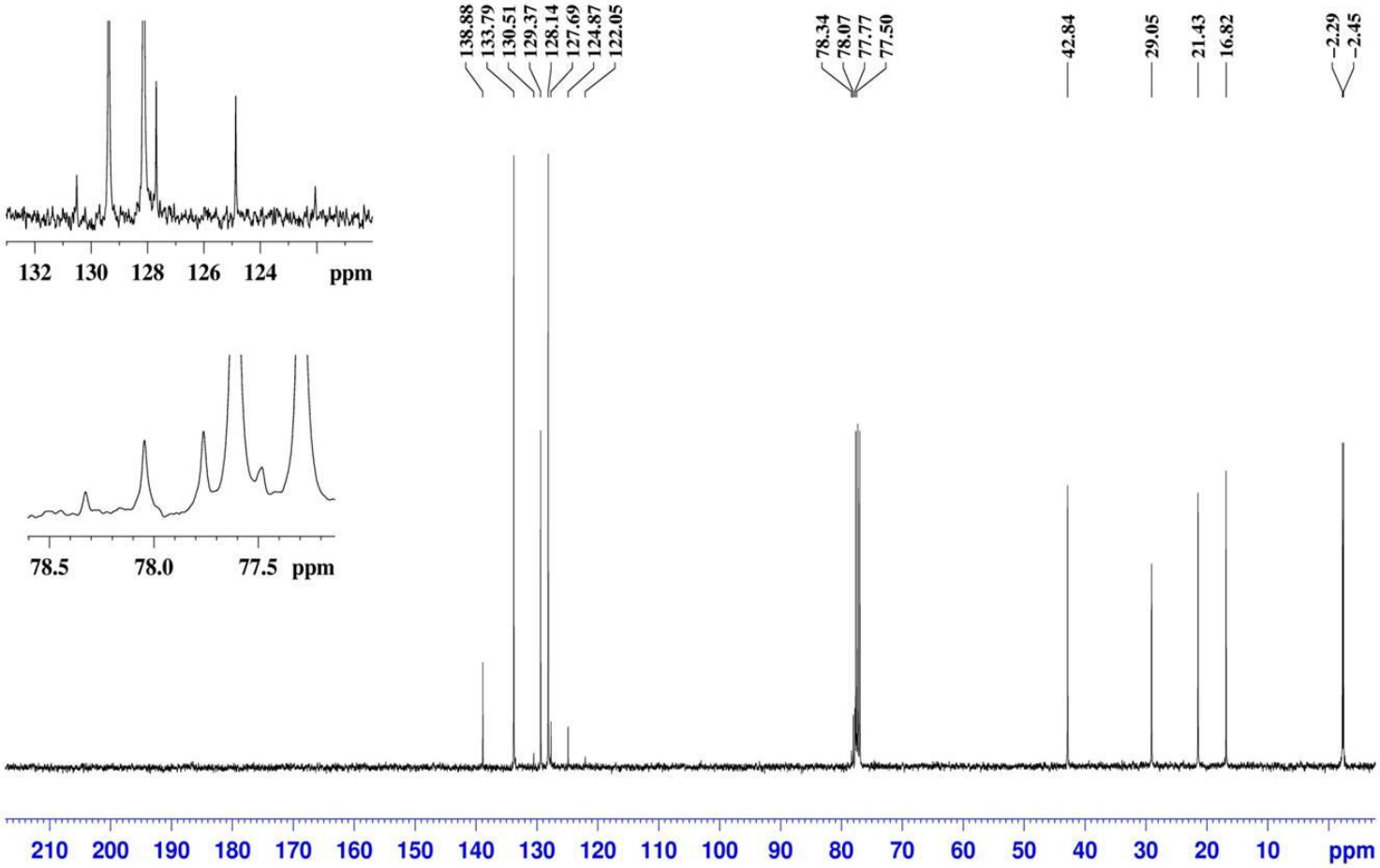
3j



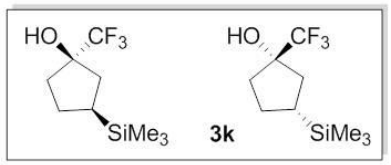
(1S,2S) & (1R,2R)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutanol
100 MHz, CDCl3

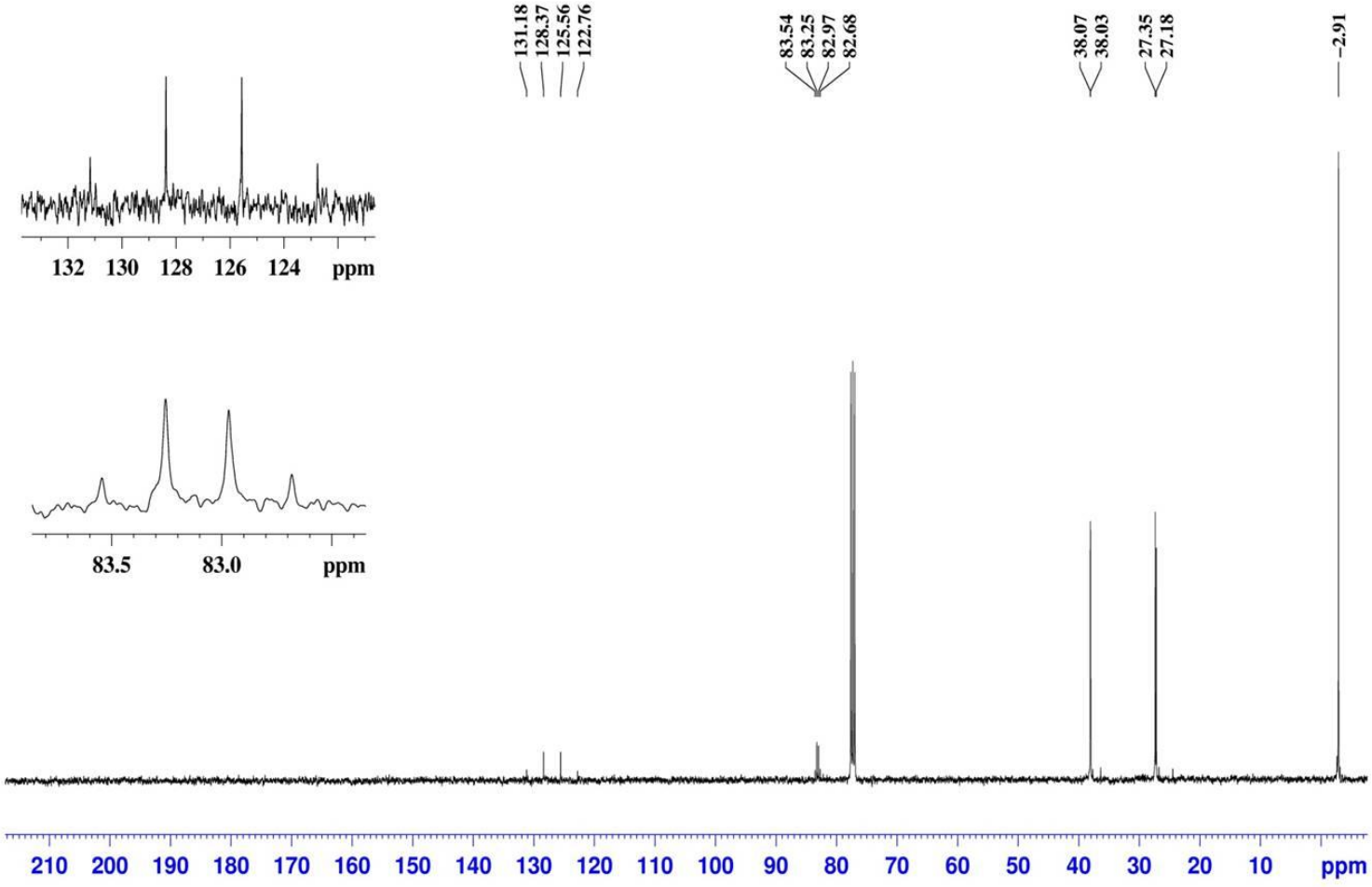


3j'

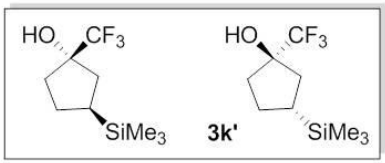


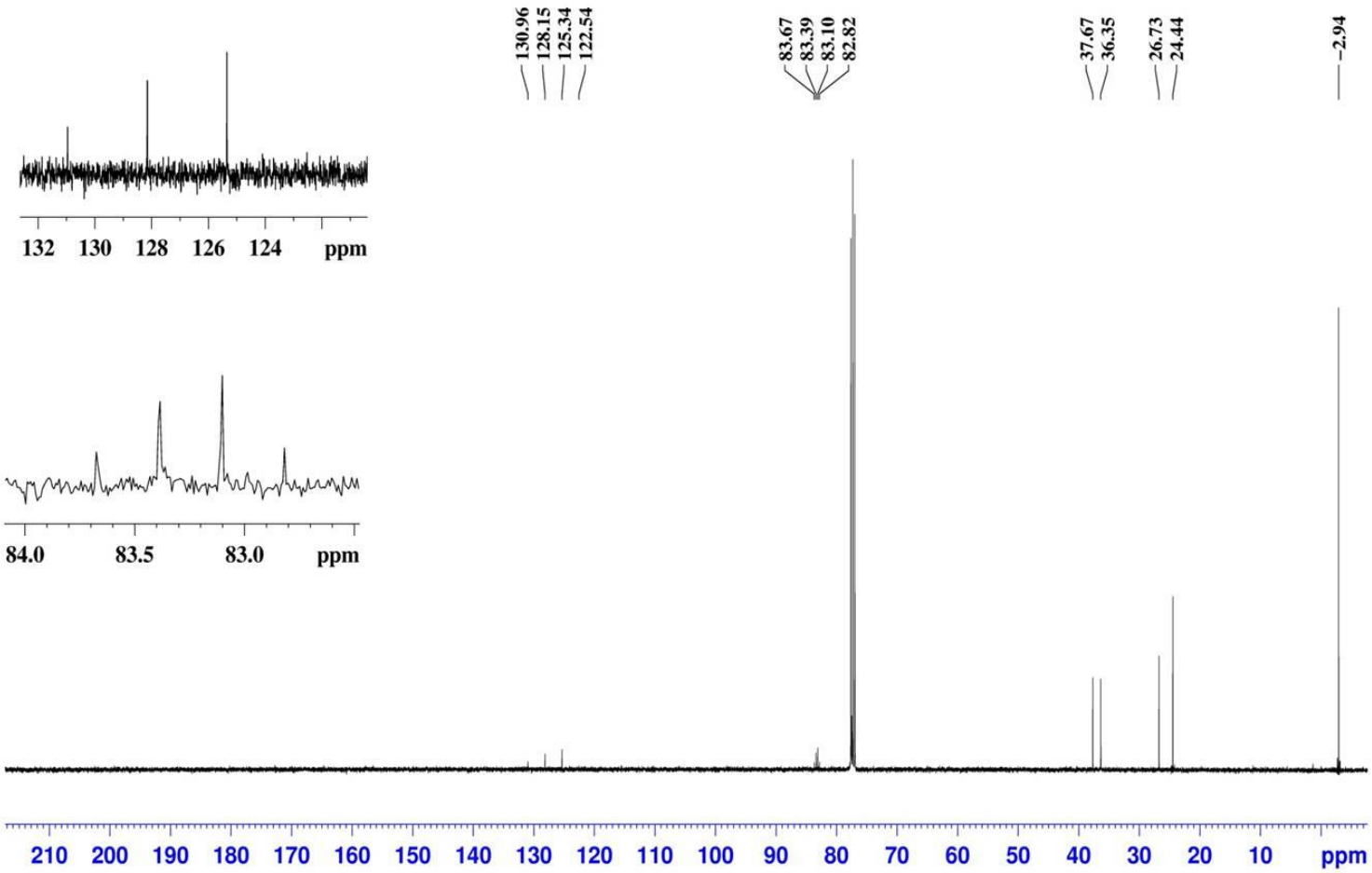
(1R,3S) & (1S, 3R)−1−(trifluoromethyl)−3−(trimethylsilyl)cyclopentanol
100 MHz, CDCl3



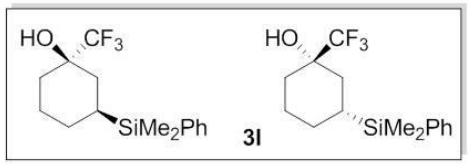


(1S,3S) & (1R, 3R)−1−(trifluoromethyl)−3−(trimethylsilyl)cyclopentanol
100 MHz, CDCl3

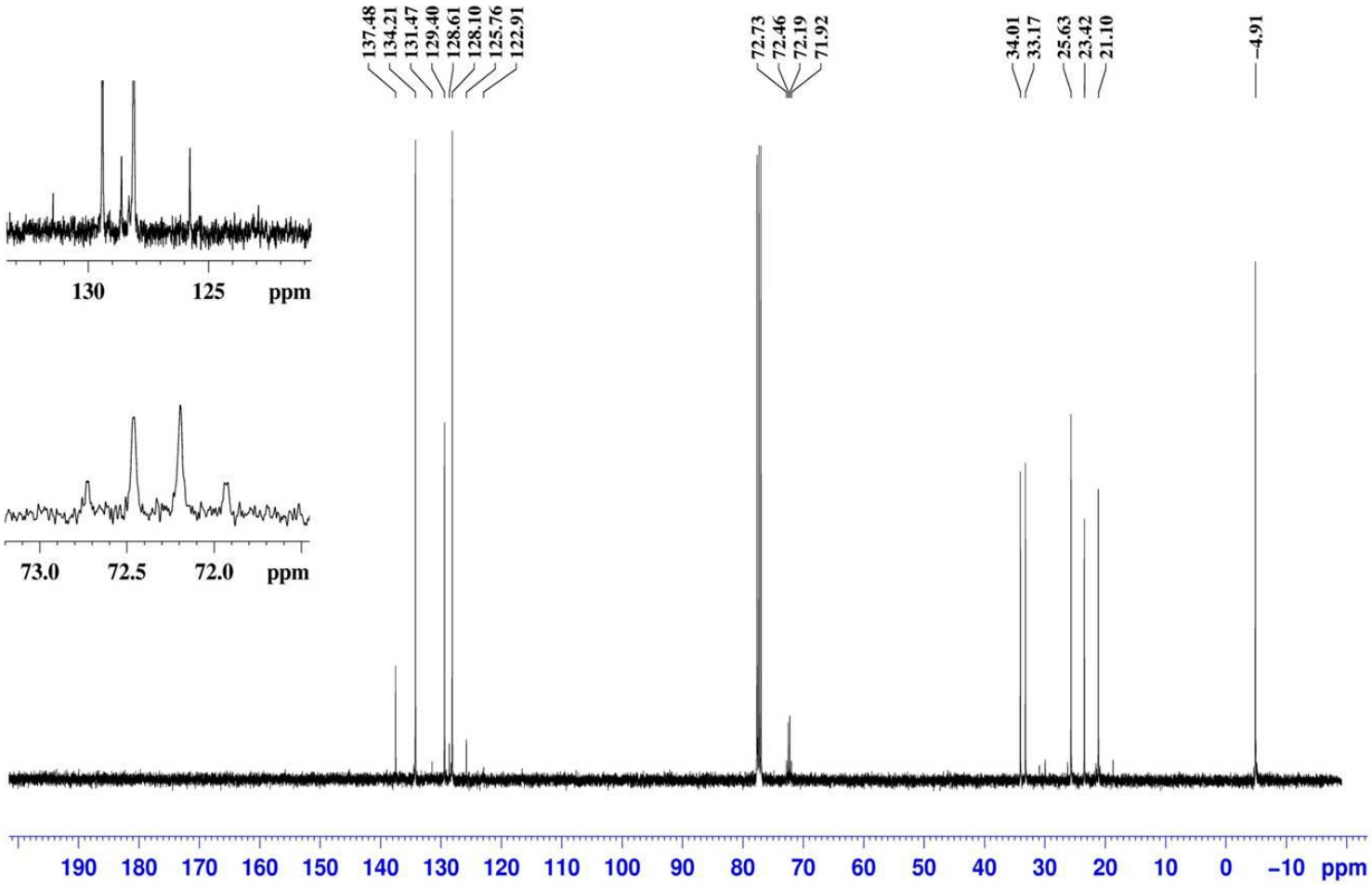


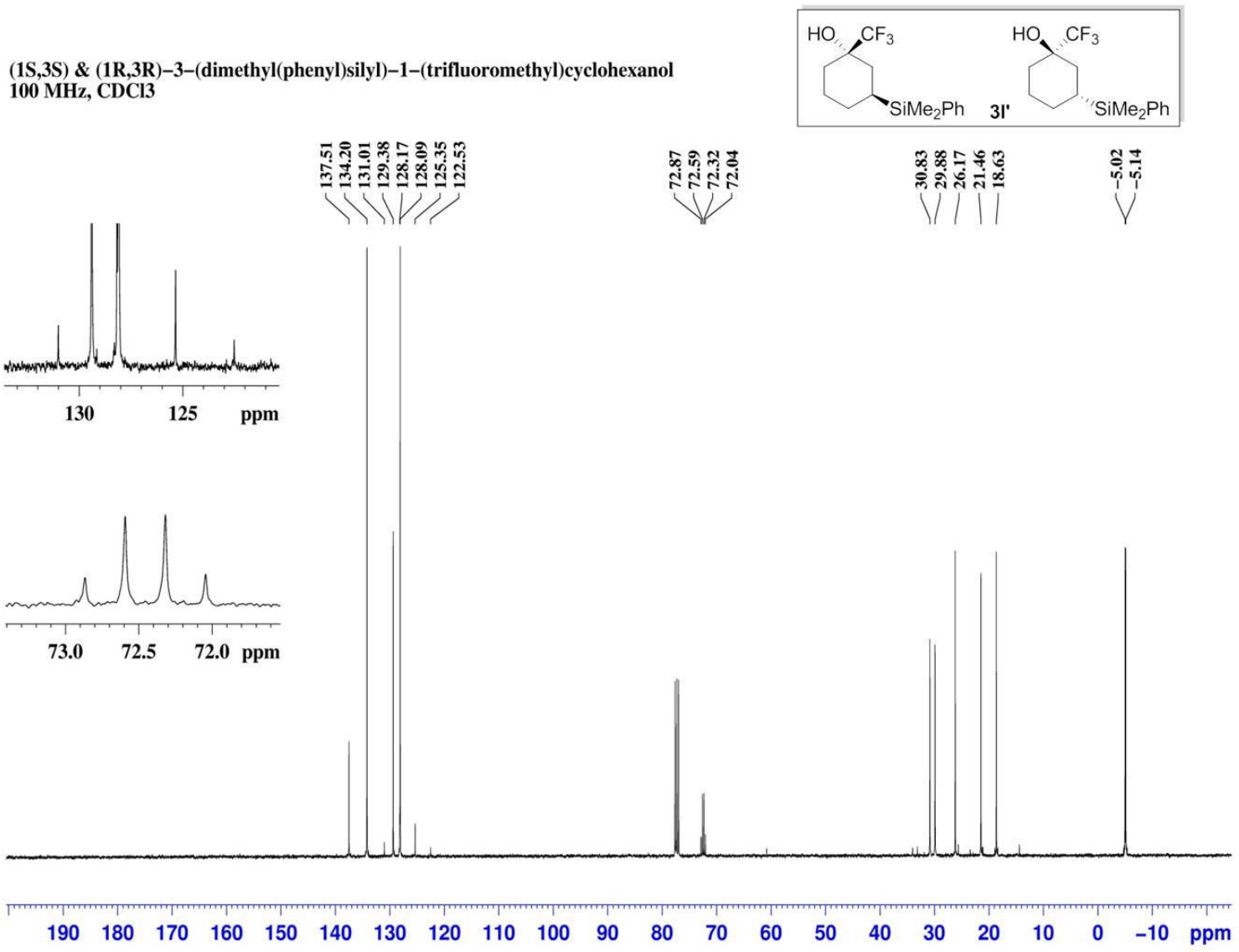


(1R,3S) & (1S,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cyclohexanol
100 MHz, CDCl3

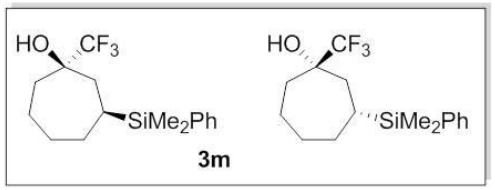


3l

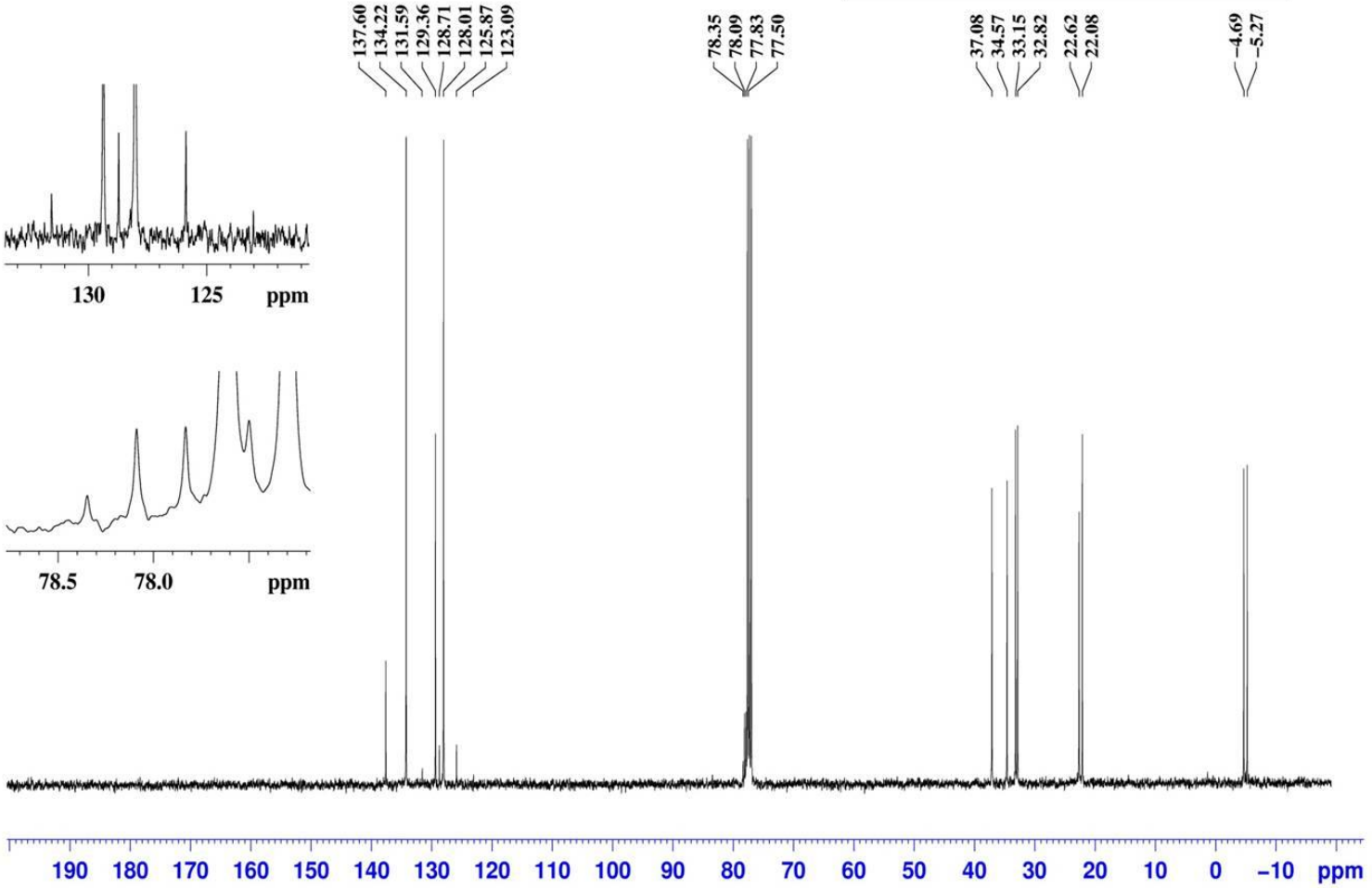



(1S,3S) & (1R,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cyclohexanol
100 MHz, CDCl3
HO
CF3
SiMe2Ph
3l'
137.51
134.20
131.01
129.38
128.17
128.09
125.35
122.53
72.87
72.59
72.32
72.04
30.83
29.88
26.17
21.46
18.63
−5.02
−5.14
130
125
ppm
73.0
72.5
72.0
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

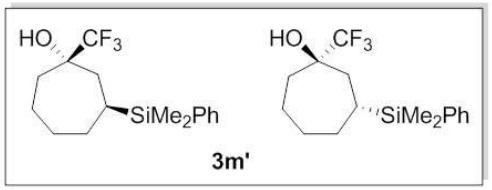
(1R,3S) & (1S,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cycloheptanol
100 MHz, CDCl3



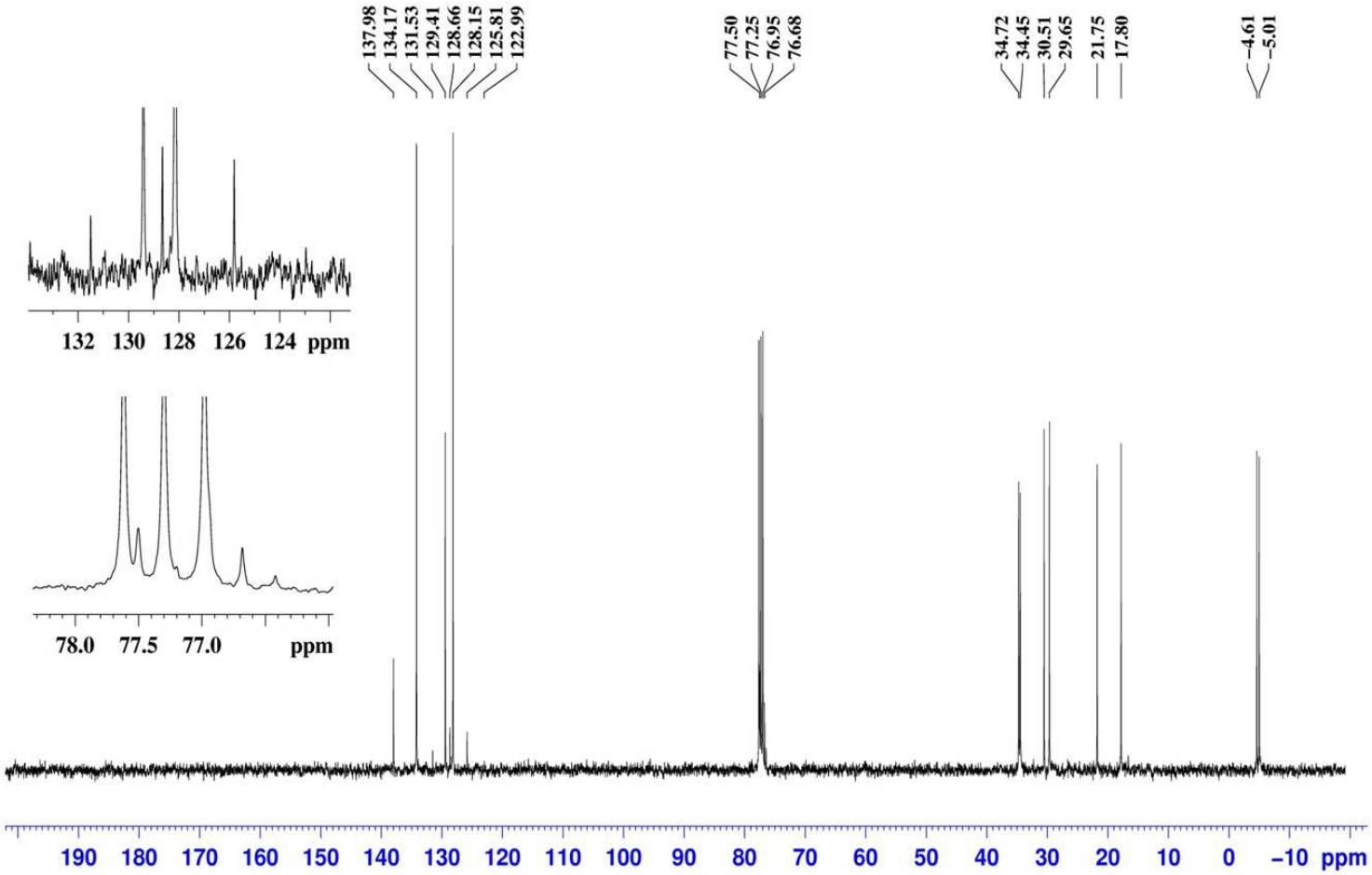
3m

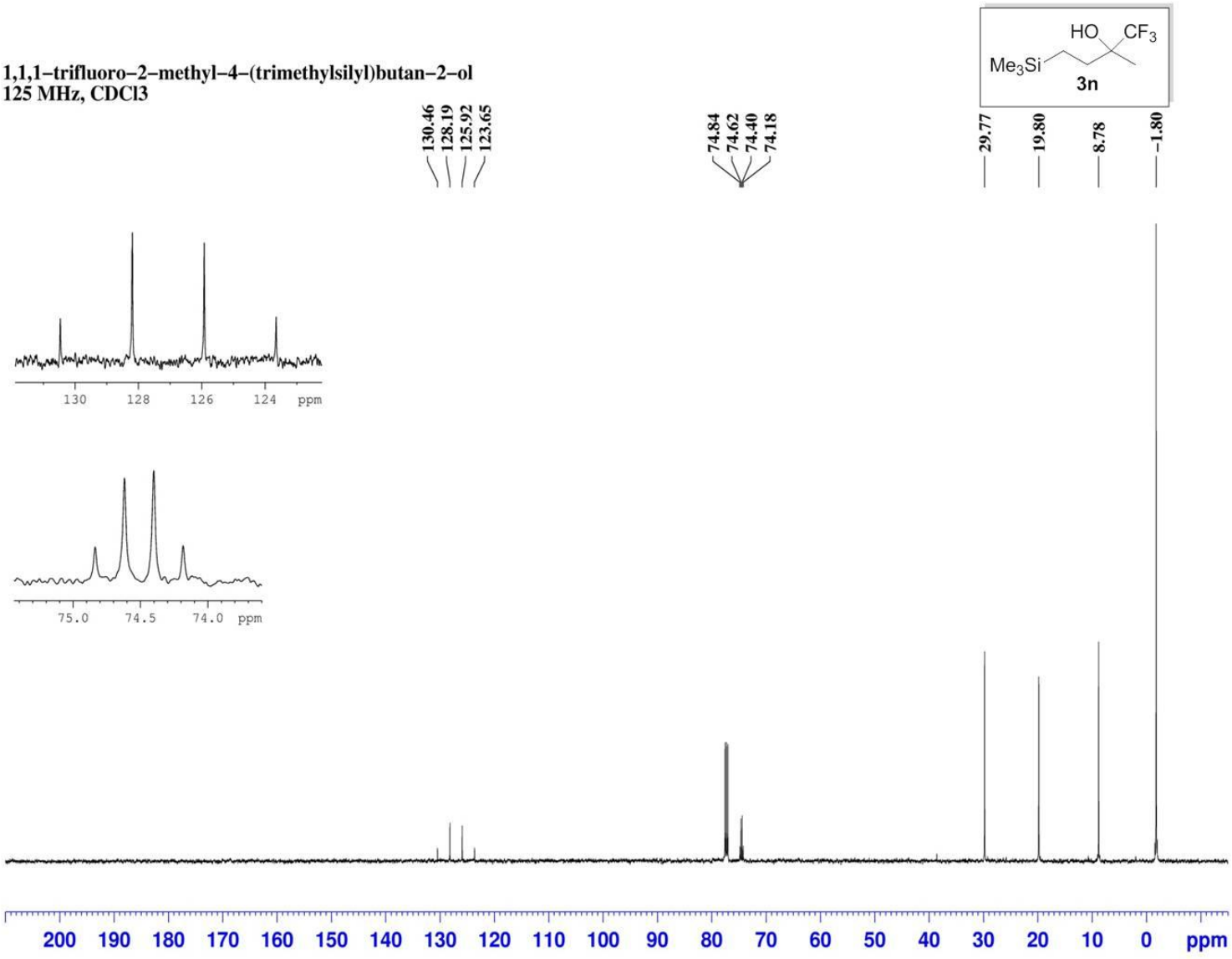


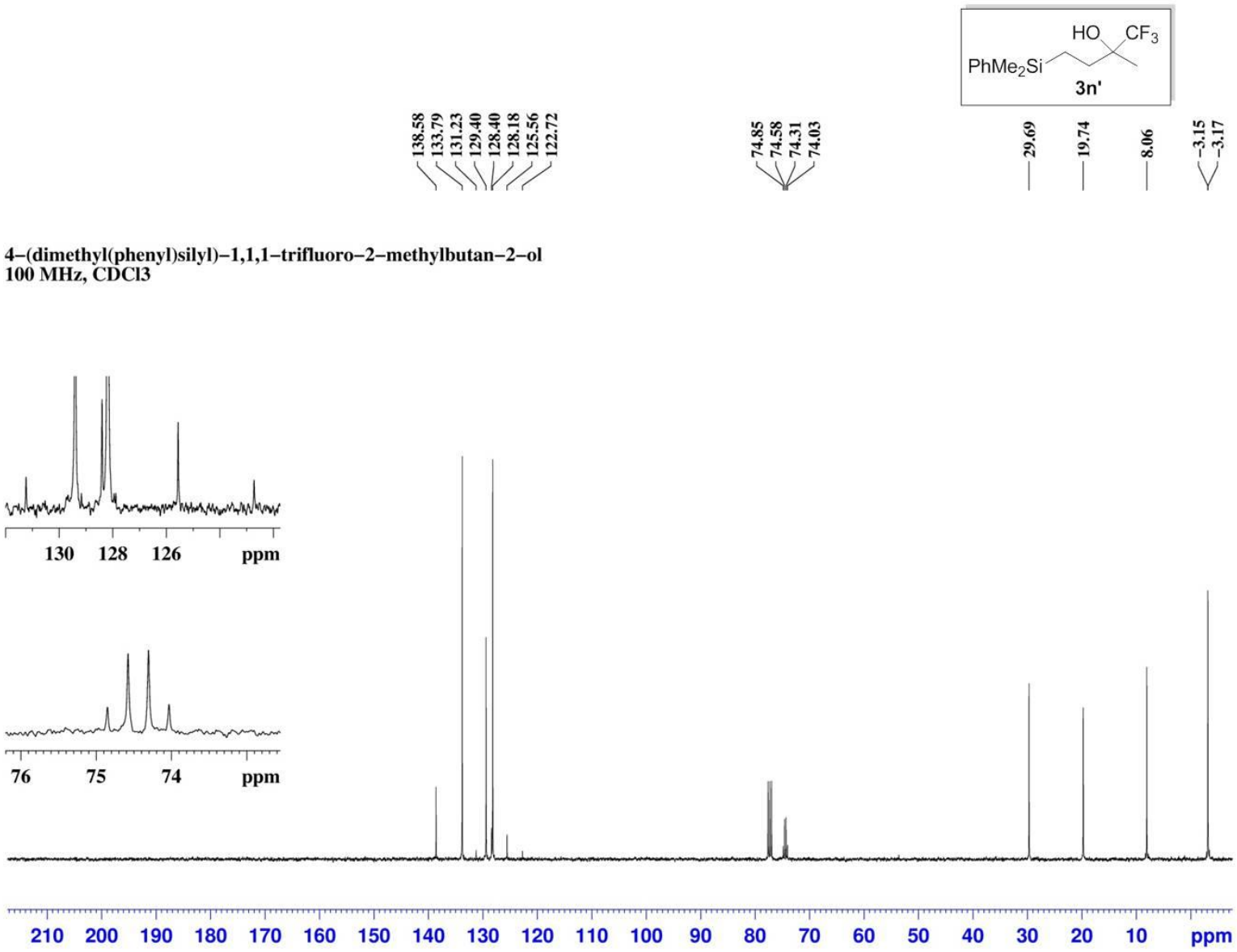
(1S,3S) & (1R,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cycloheptanol
100 MHz, CDCl3



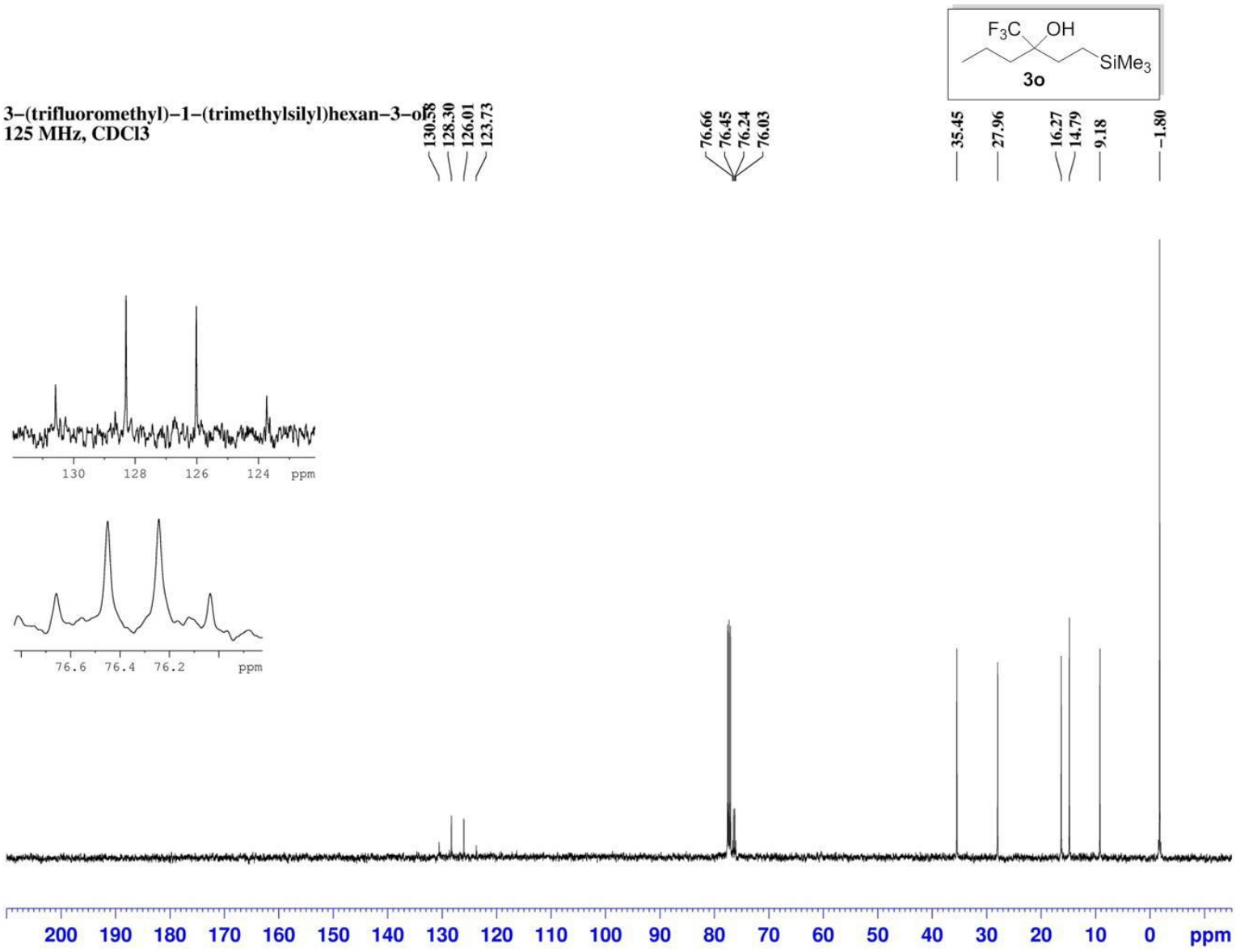
3m'

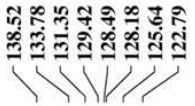


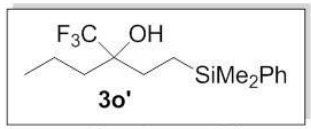

1,1,1−trifluoro−2−methyl−4−(trimethylsilyl)butan−2−ol
125 MHz, CDCl3
HO
CF3
Me3Si
3n
130.46
128.19
125.92
123.65
74.84
74.62
74.40
74.18
29.77
19.80
8.78
−1.80
130
128
126
124
ppm
75.0
74.5
74.0
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

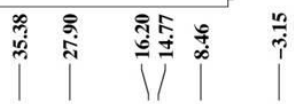


4–(dimethyl(phenyl)silyl)–1,1,1–trifluoro–2–methylbutan–2–ol
100 MHz, CDCl3

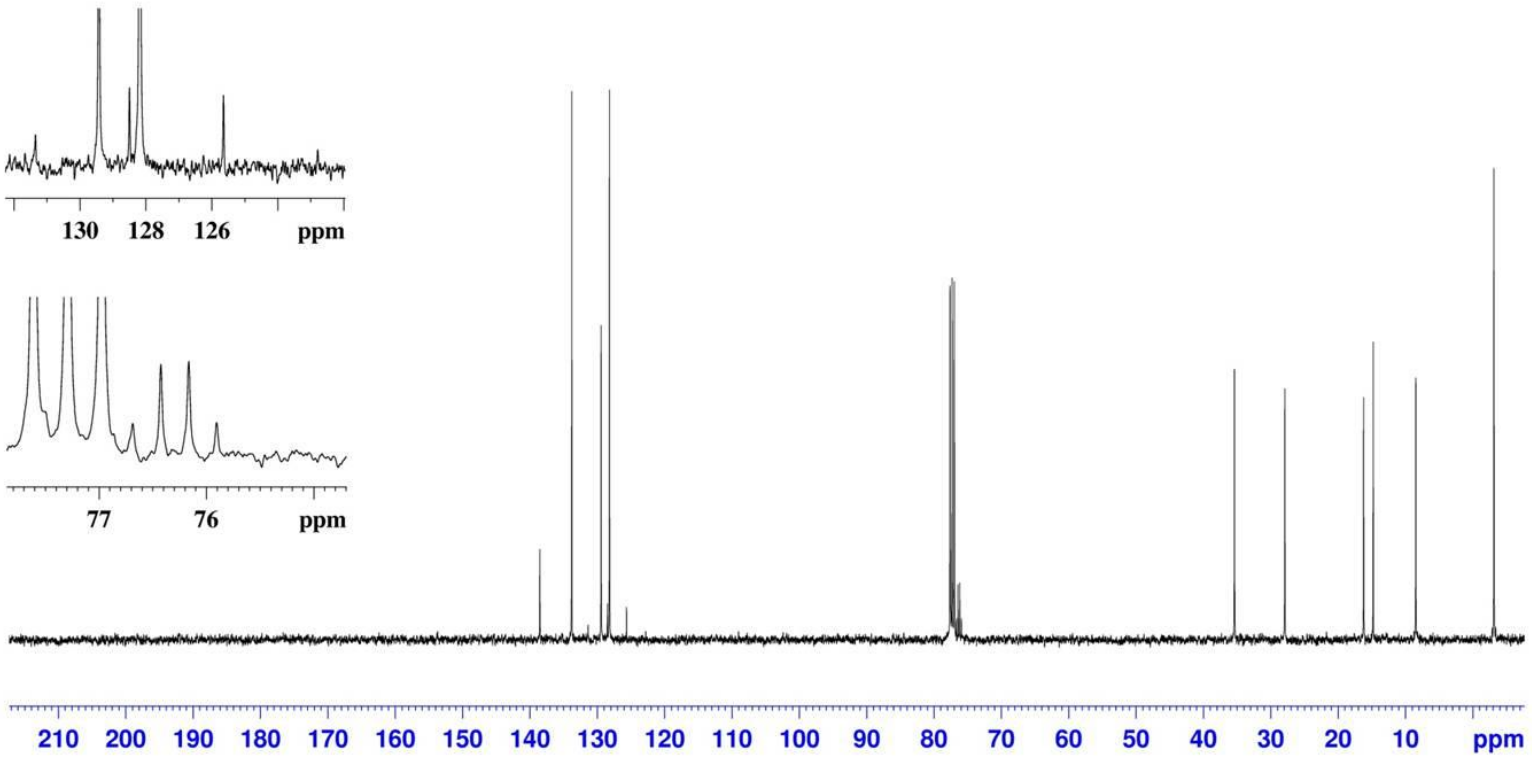

3–(trifluoromethyl)–1–(trimethylsilyl)hexan–3–ol
125 MHz, CDCl3
F3C
OH
SiMe3
3o
130.58
128.30
126.01
123.73
76.66
76.45
76.24
76.03
35.45
27.96
16.27
14.79
9.18
–1.80
130
128
126
124
ppm
76.6
76.4
76.2
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

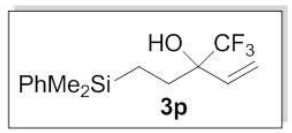






1–(dimethyl(phenyl)silyl)–3–(trifluoromethyl)hexan–3–ol
100 MHz, CDCl3





138.59
134.13
133.77
130.11
129.38
128.16
127.27
124.43
121.59
118.72

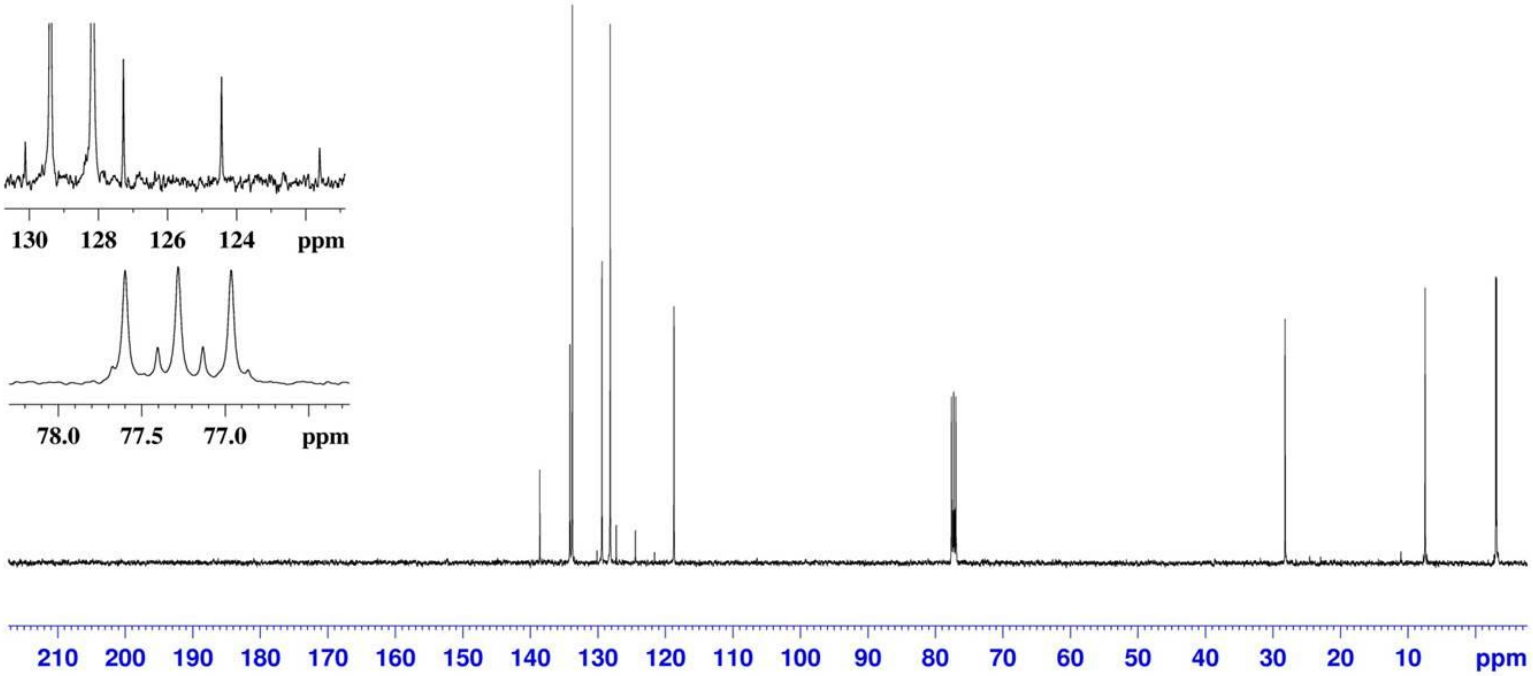
77.68
77.42
77.14
76.87

28.19

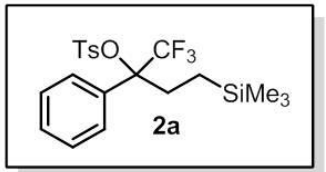
7.45

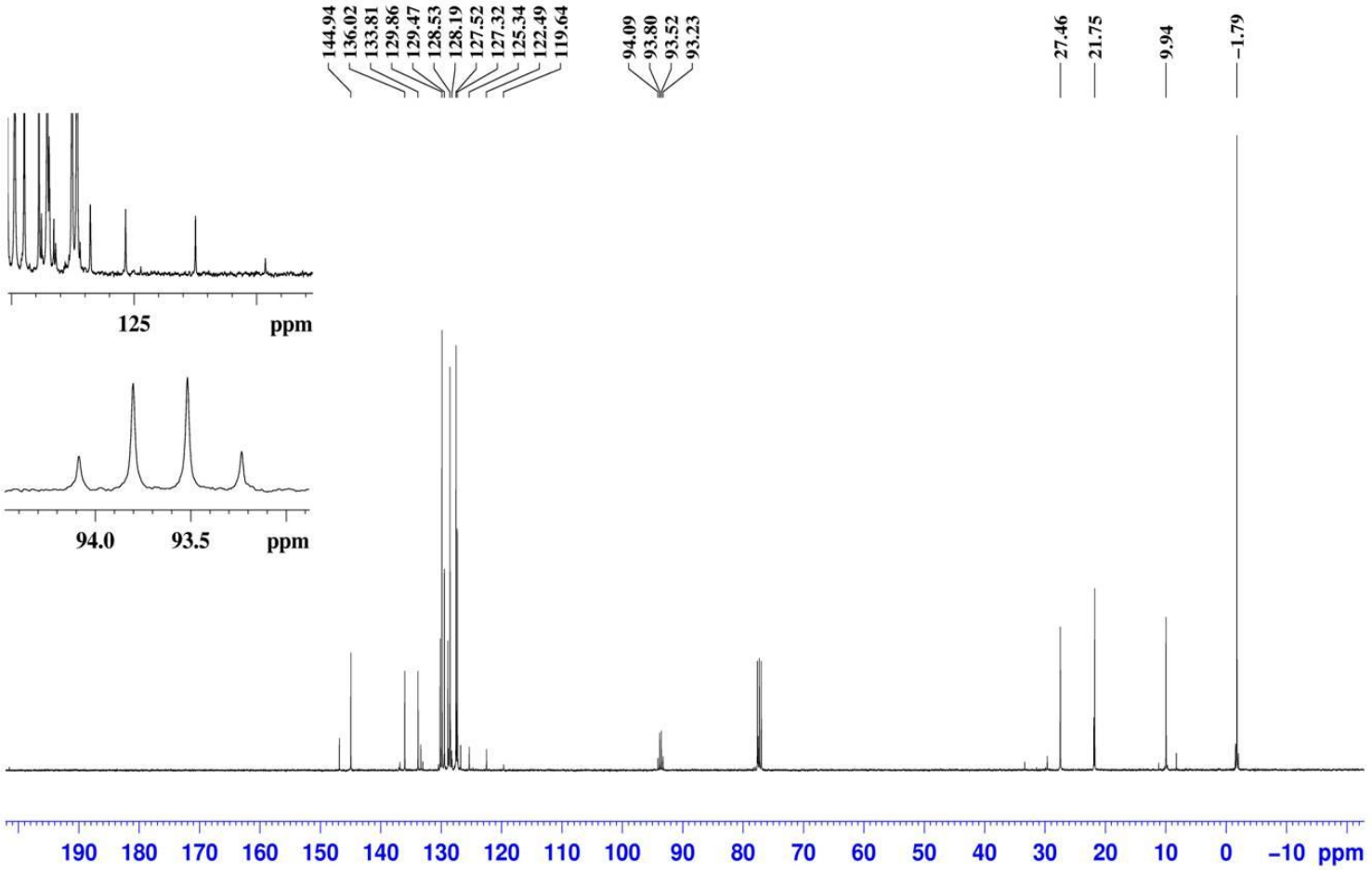
-3.02
-3.13

5–(dimethyl(phenyl)silyl)–3–(trifluoromethyl)pent–1–en–3–ol
100 MHz, CDCl3

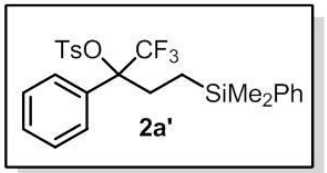


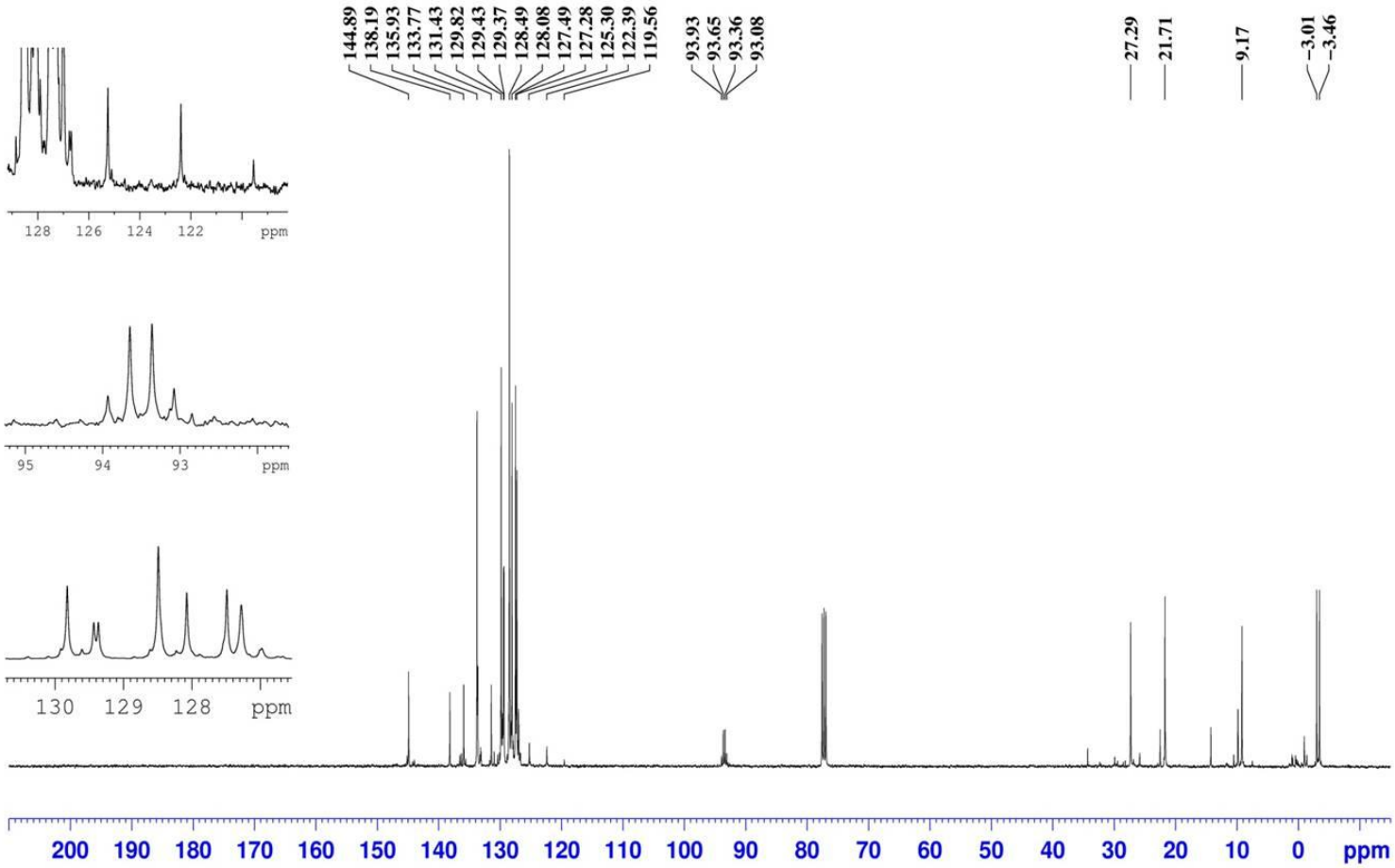
1,1,1−trifluoro−2−phenyl−4−(trimethylsilyl)butan−2−yl 4−methylbenzenesulfonate
100 MHz, CDCl3



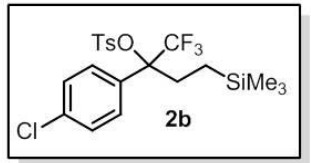


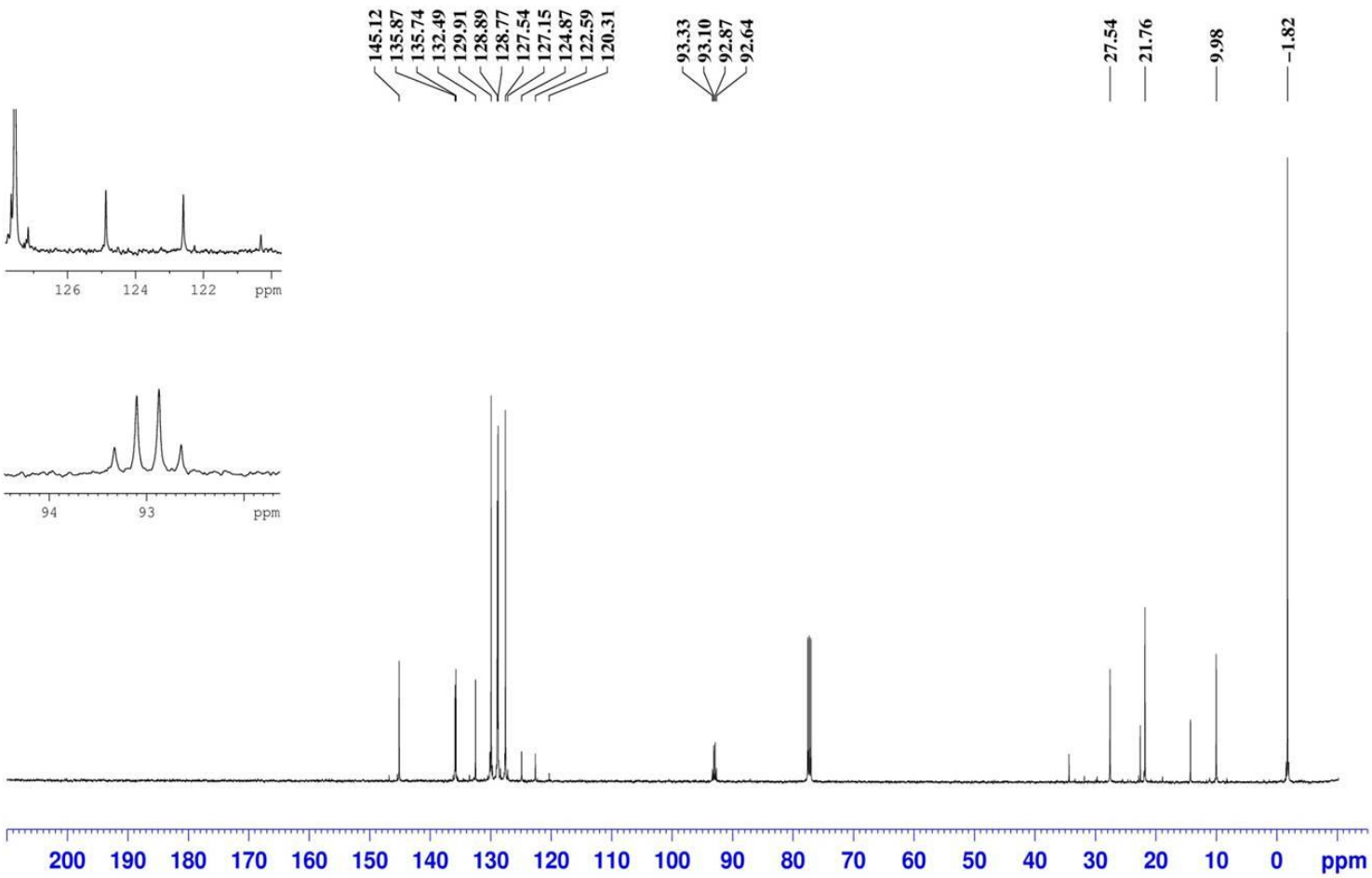
4–(dimethyl(phenyl)silyl)–1,1,1–trifluoro–2–phenylbutan–2–yl 4–methylbenzenesulfonate
100 MHz, CDCl3



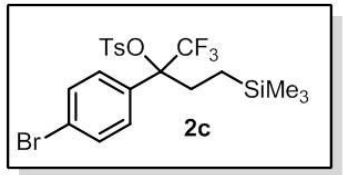


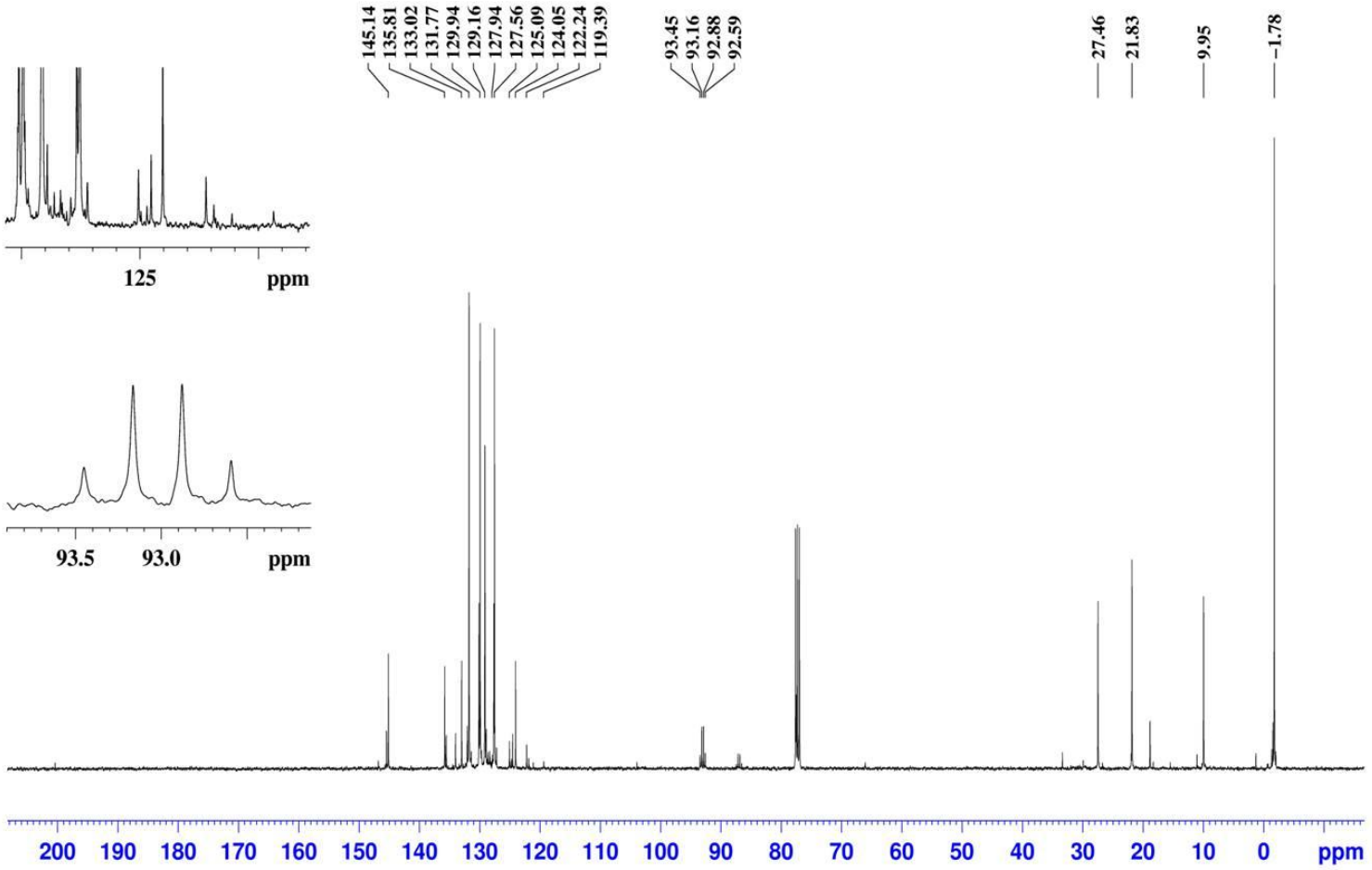
2–(4–chlorophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
100 MHz, CDCl3



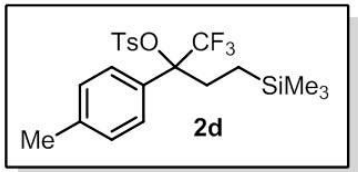


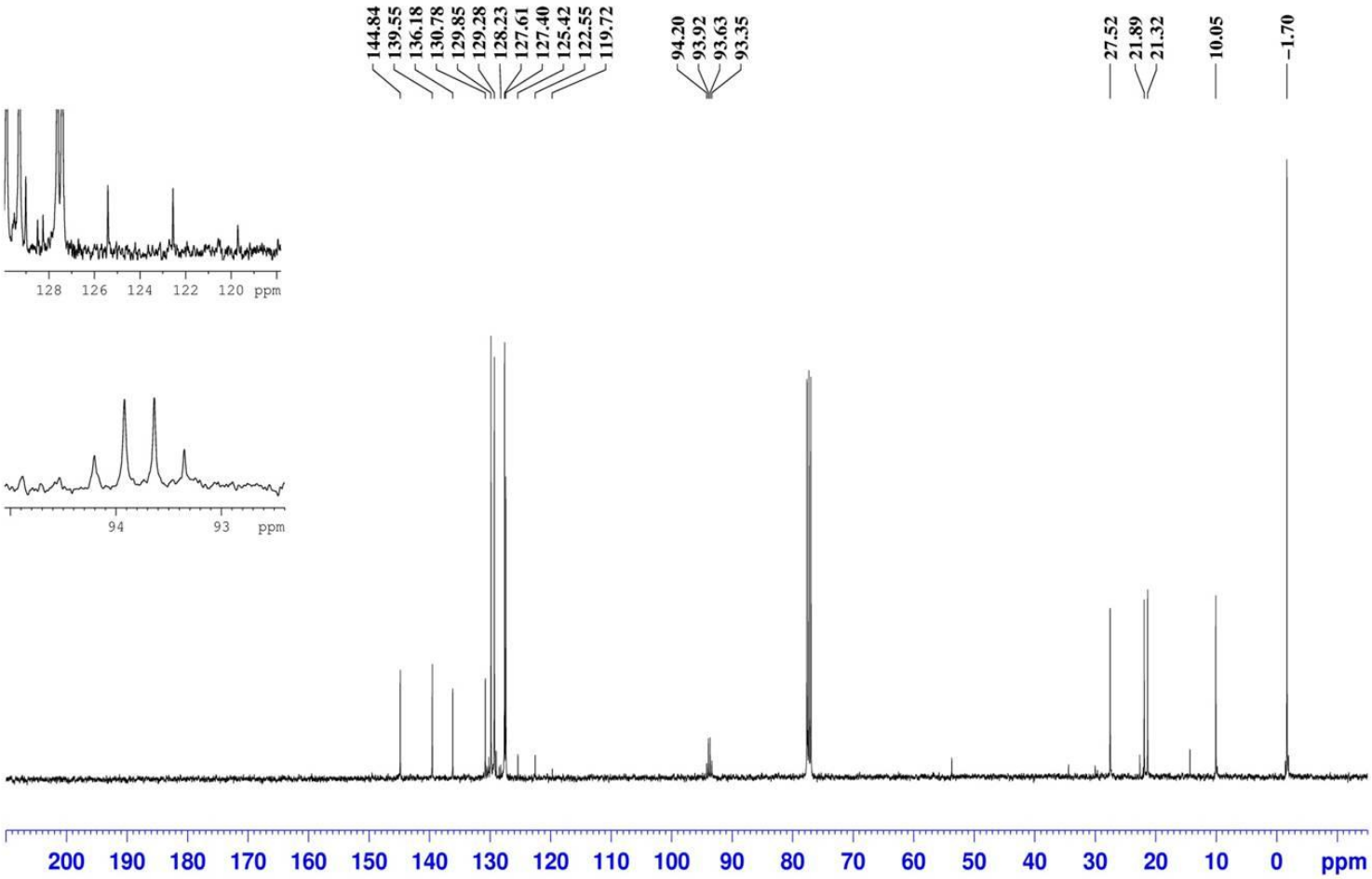
2–(4–bromophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
100 MHz, CDCl3



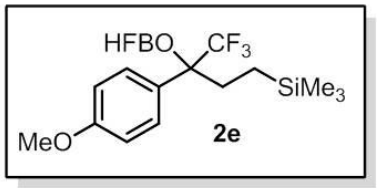


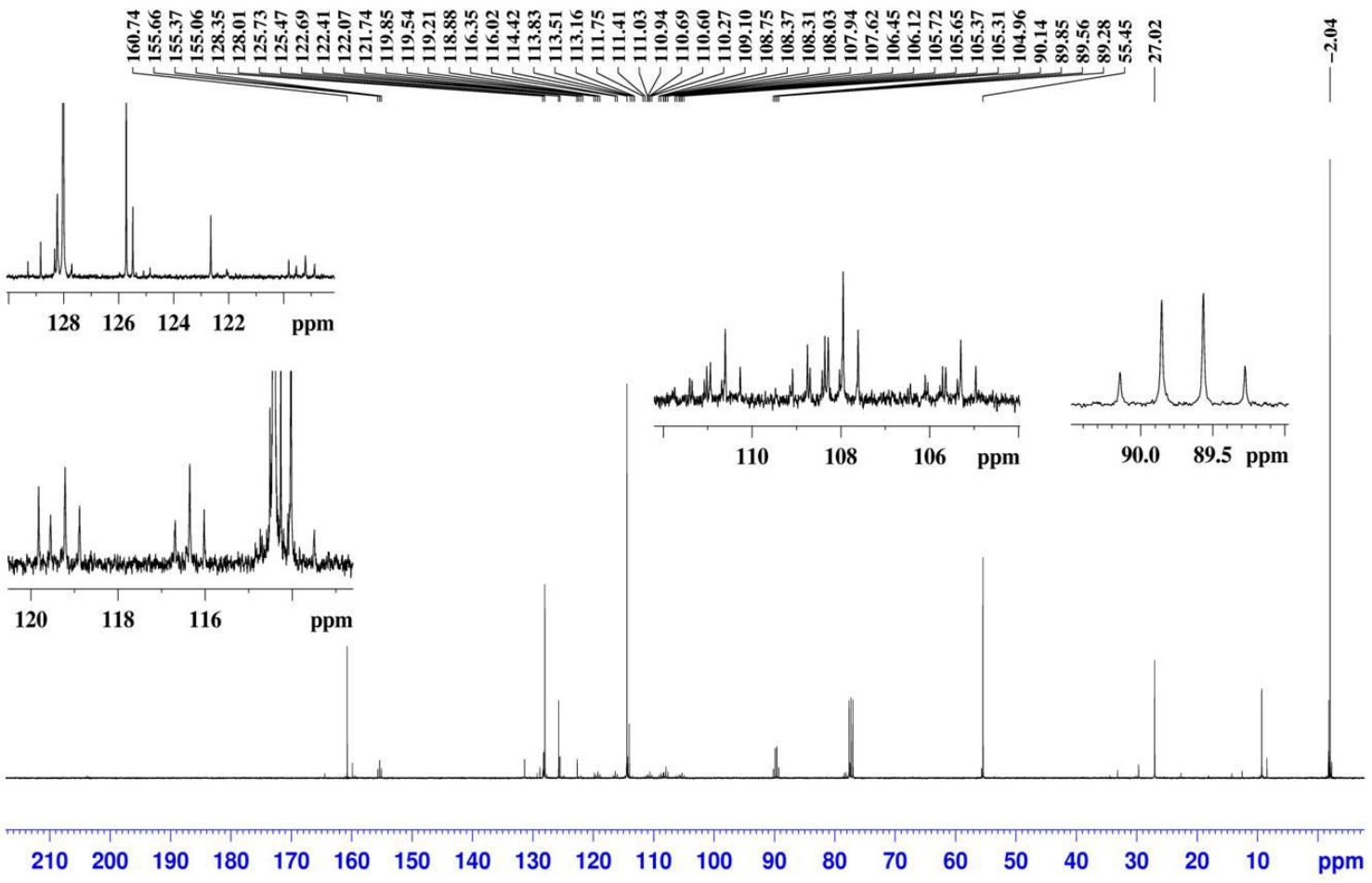
1,1,1−trifluoro−2−(p−tolyl)−4−(trimethylsilyl)butan−2−yl 4−methylbenzenesulfonate
100 MHz, CDCl3



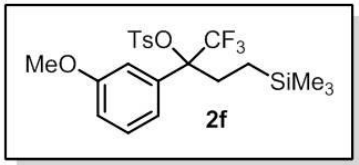


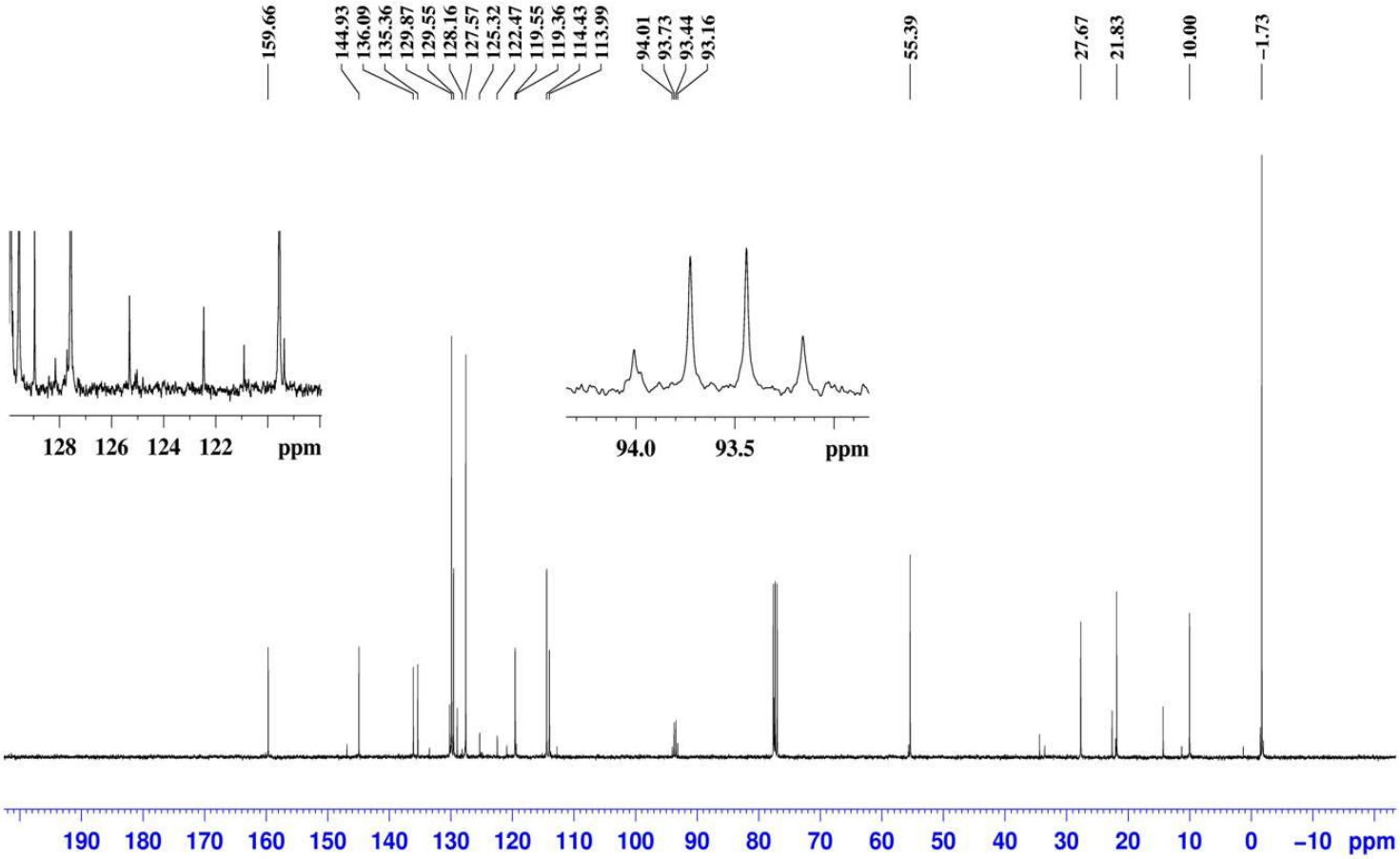
1,1,1–trifluoro–2–(4–methoxyphenyl)–4–(trimethylsilyl)butan–2–yl 2,2,3,3,4,4,4–heptafluorobutanoate
100 MHz, CDCl3



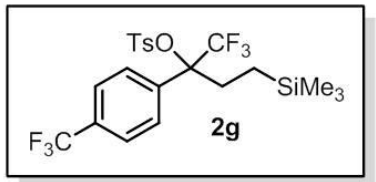


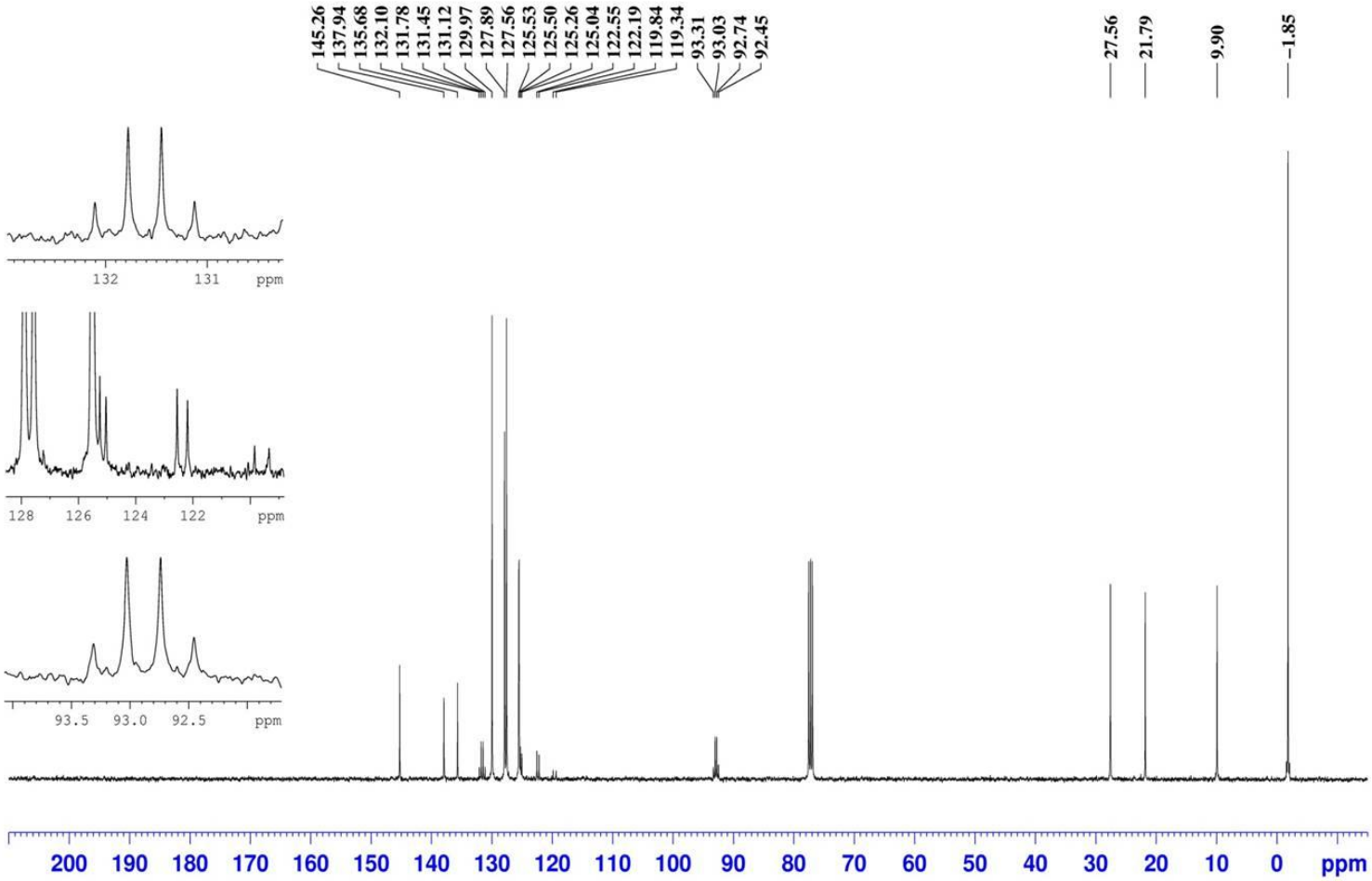
1,1,1–trifluoro–2–(3–methoxyphenyl)–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
100 MHz, CDCl3



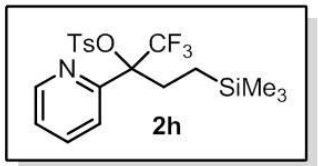


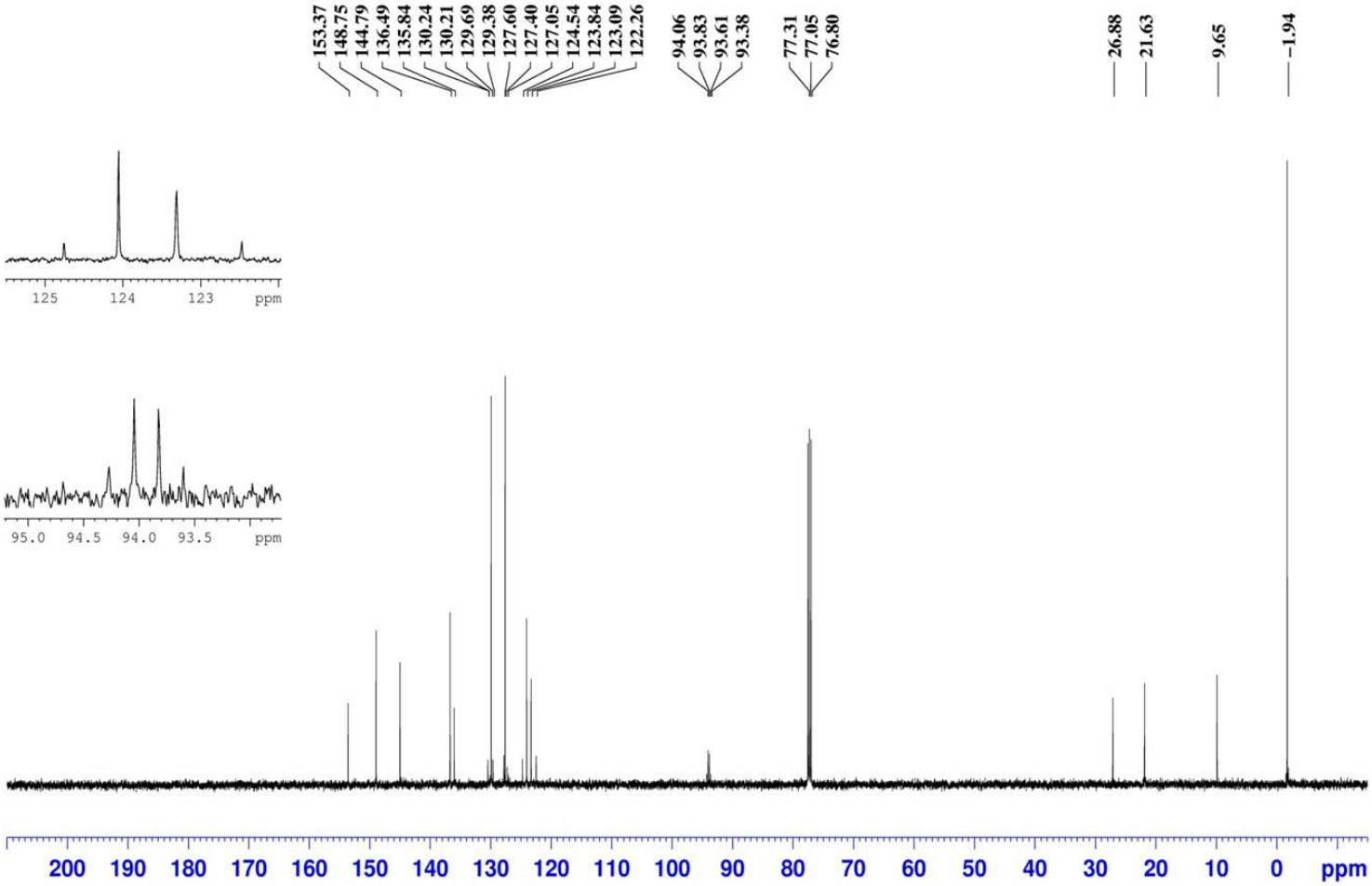
1,1,1−trifluoro−2−(4−(trifluoromethyl)phenyl)−4−(trimethylsilyl)butan−2−yl 4−methylbenzenesulfonate
100 MHz, CDCl3



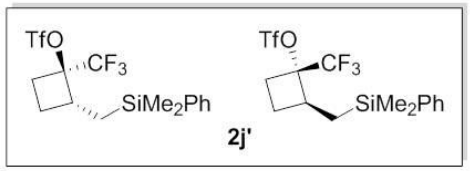


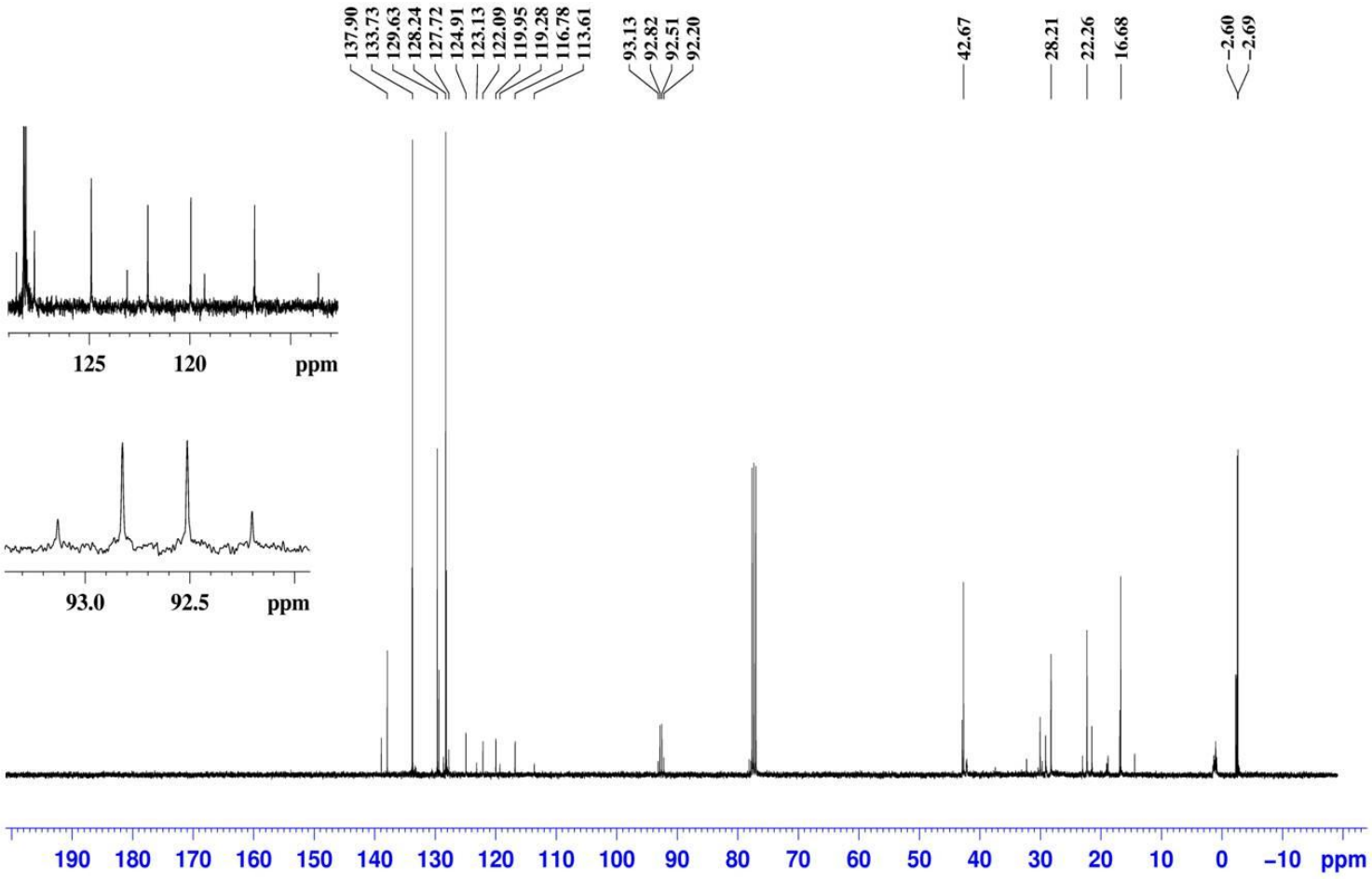
1,1,1–trifluoro–2–(pyridin–2–yl)–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
100 MHz, CDCl3



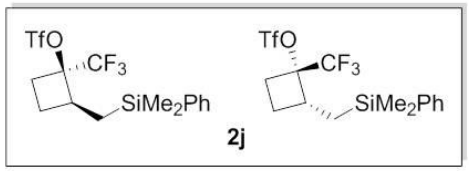


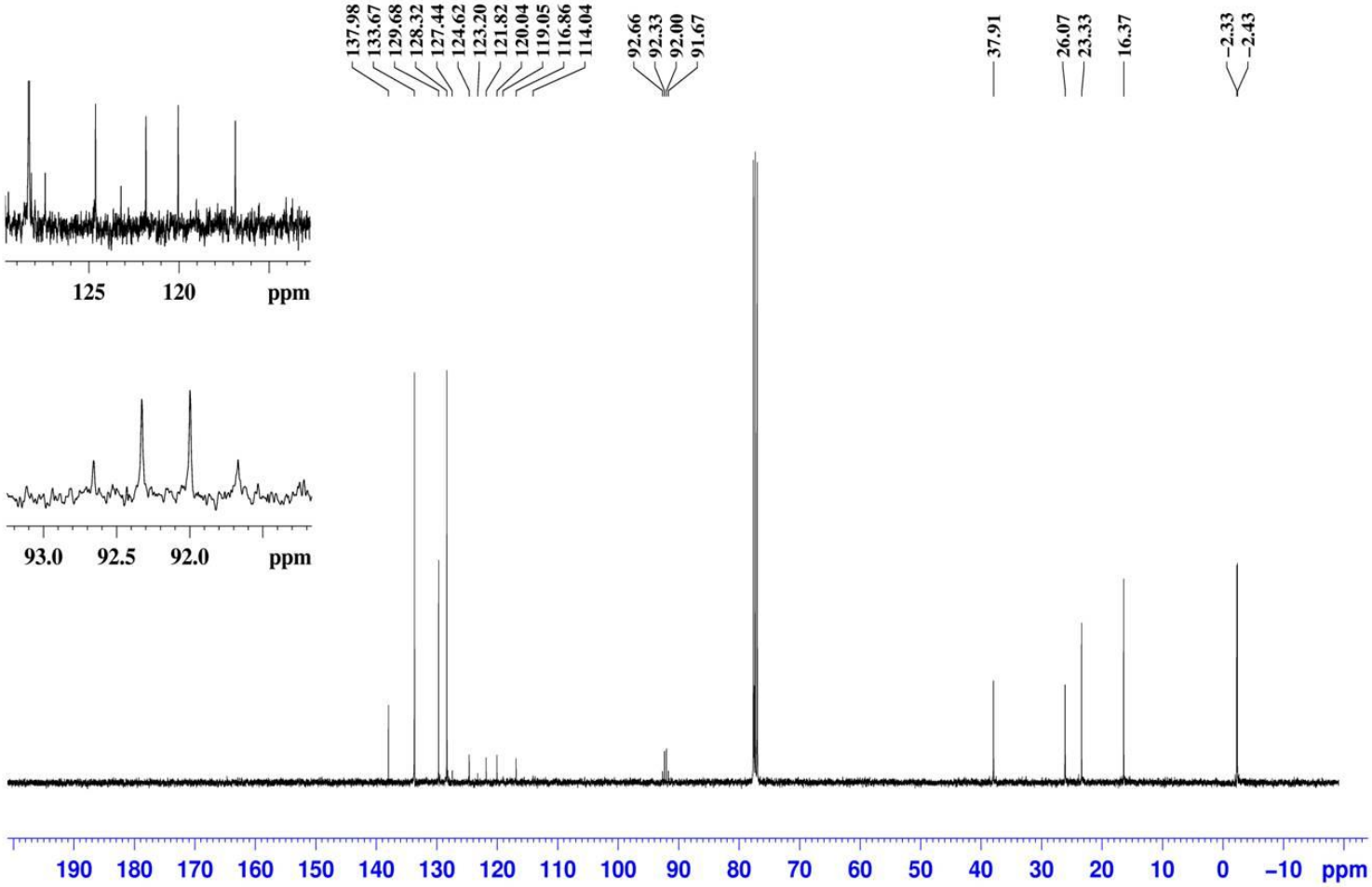
(1R,2R) & (1S,2S)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutyl trifluoromethanesulfonate
400 MHz, CDCl3



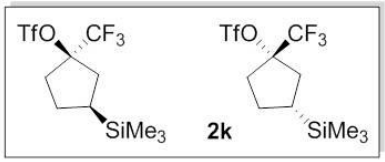


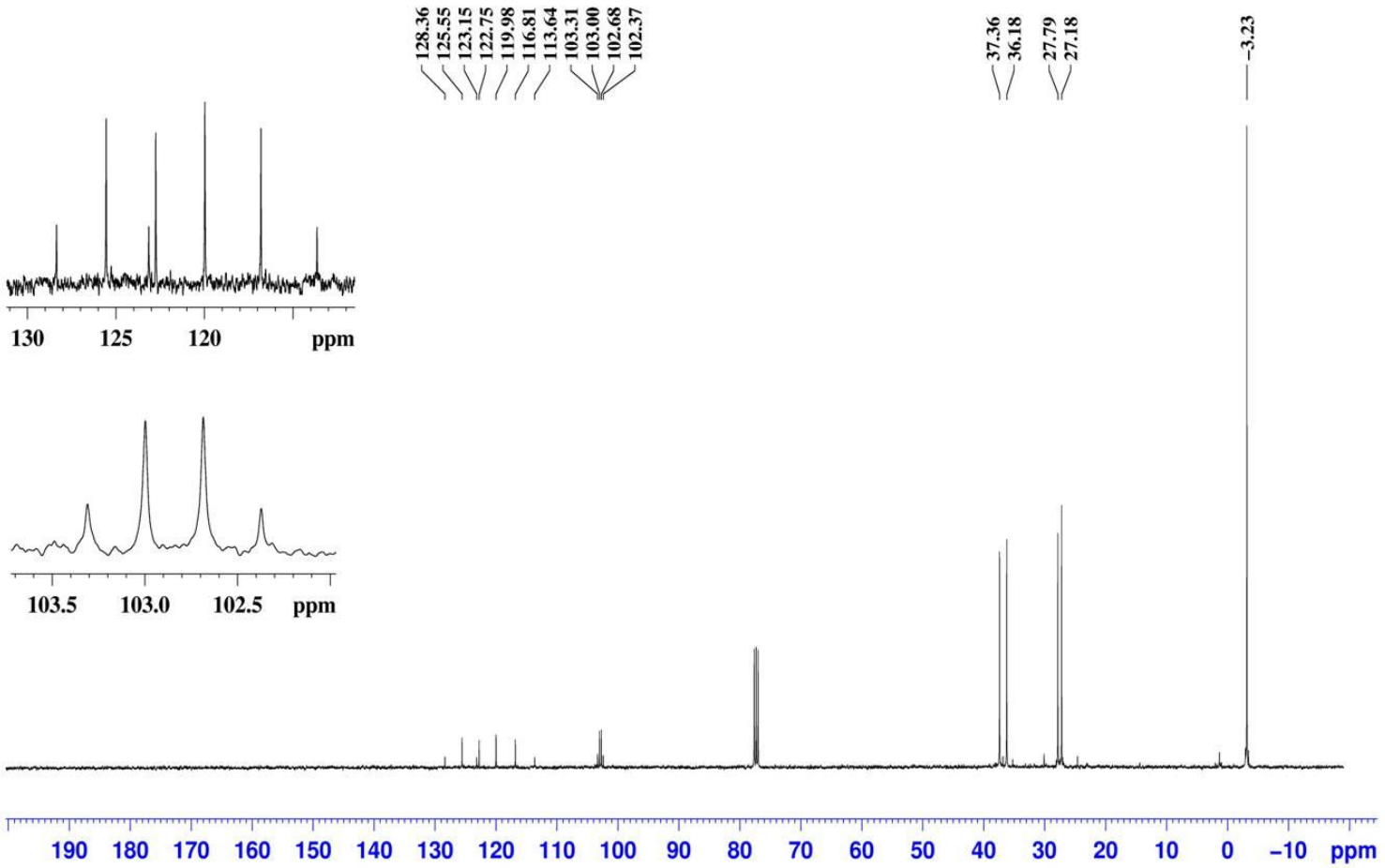
(1R,2S) & (1S,2R)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutyl trifluoromethanesulfonate
100 MHz, CDCl3



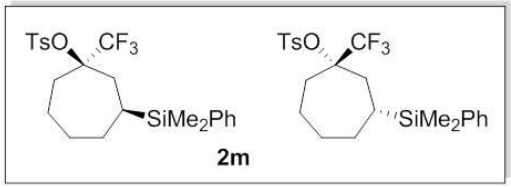


(1R,3S) & (1S,3R)−1−(trifluoromethyl)−3−(trimethylsilyl)cyclopentyl trifluoromethanesulfonate
100 MHz, CDCl3

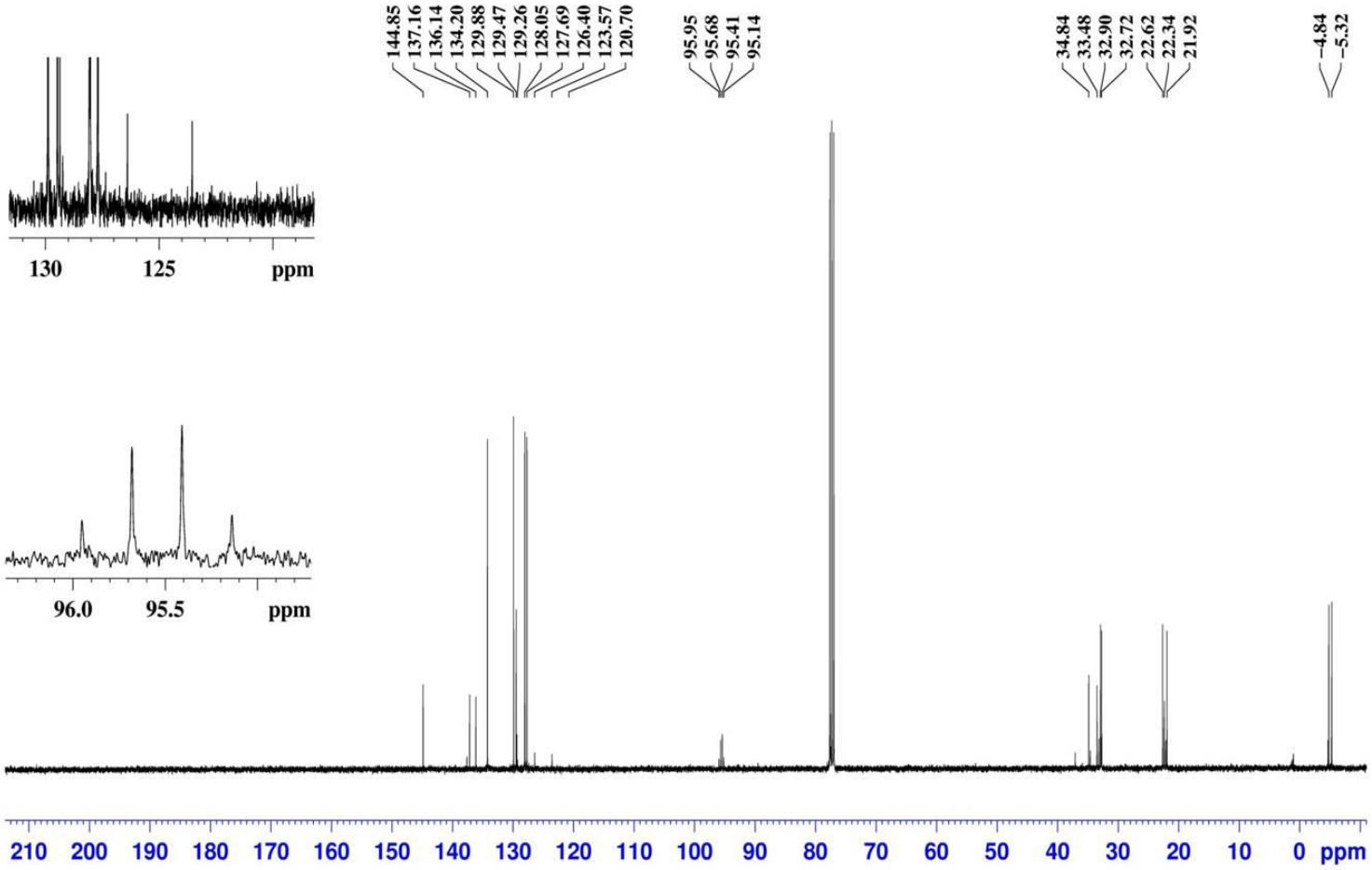




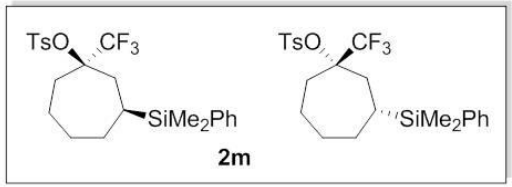
(1R,3S) & (1S,3R)– 3–(dimethyl(phenyl)silyl)–1–(trifluoromethyl)cycloheptyl 4–methylbenzenesulfonate
400 MHz, CDCl3



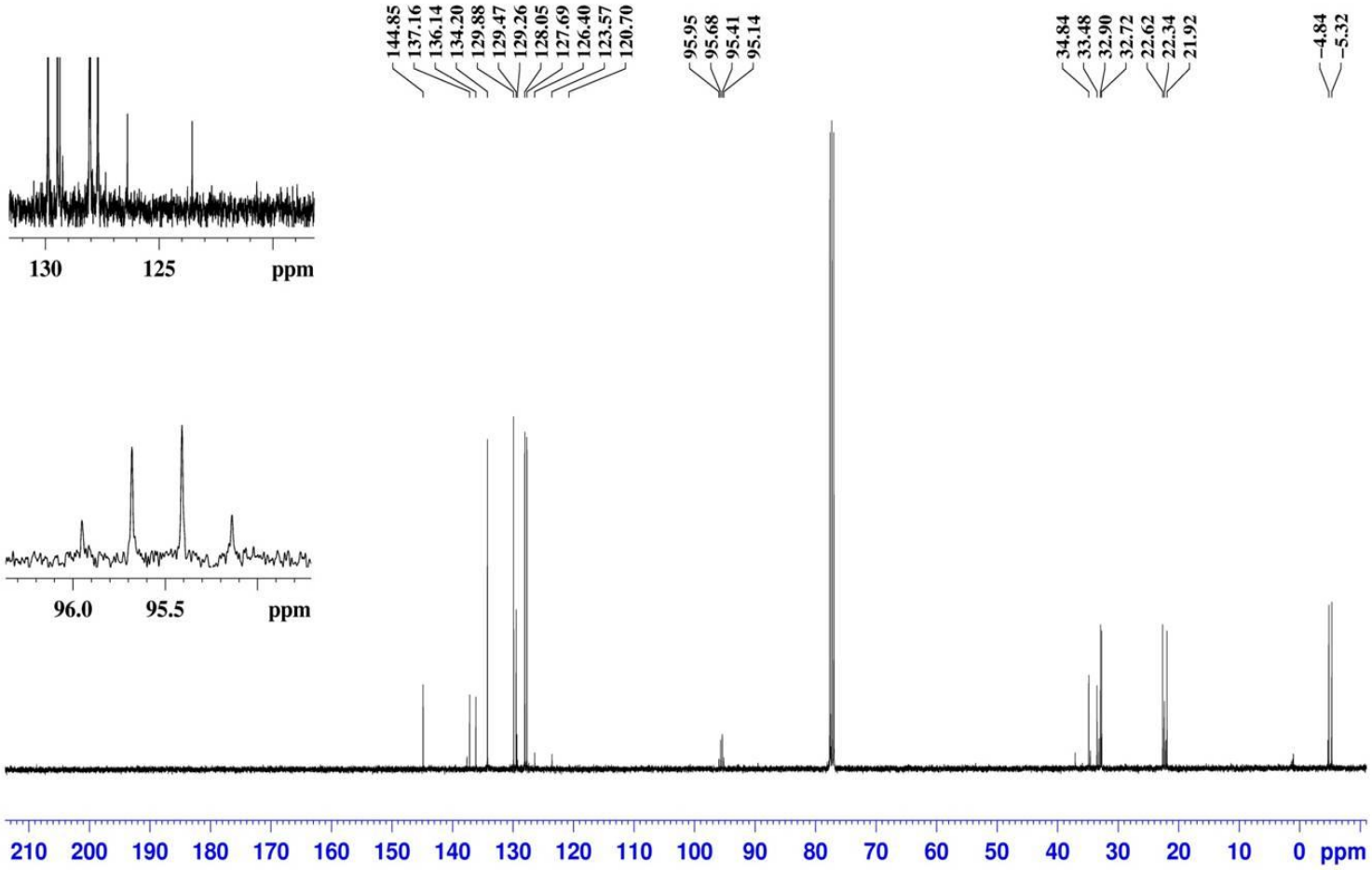
2m



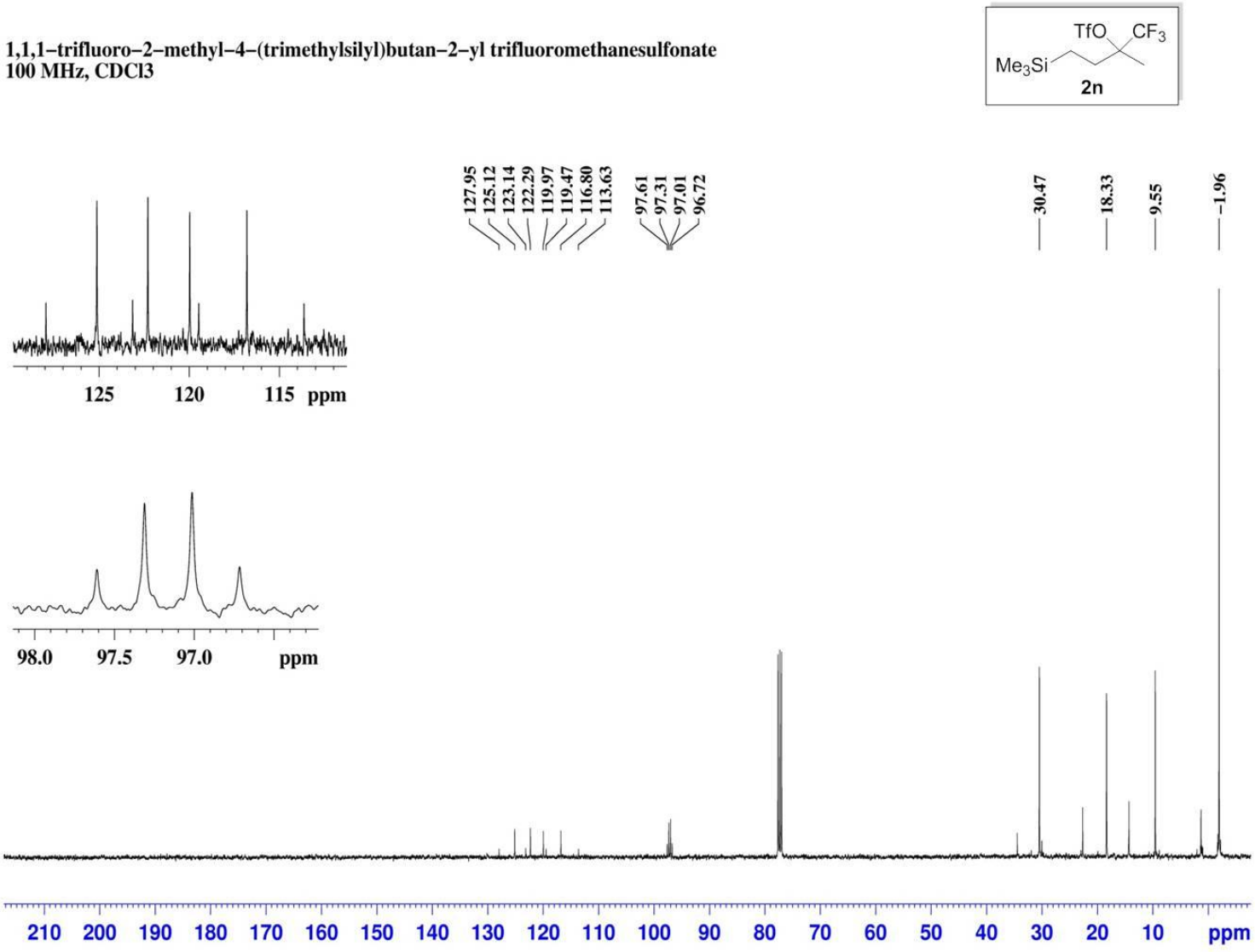
(1R,3S) & (1S,3R)– 3–(dimethyl(phenyl)silyl)–1–(trifluoromethyl)cycloheptyl 4–methylbenzenesulfonate
400 MHz, CDCl3

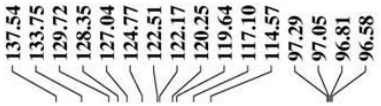


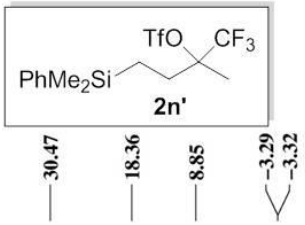
2m



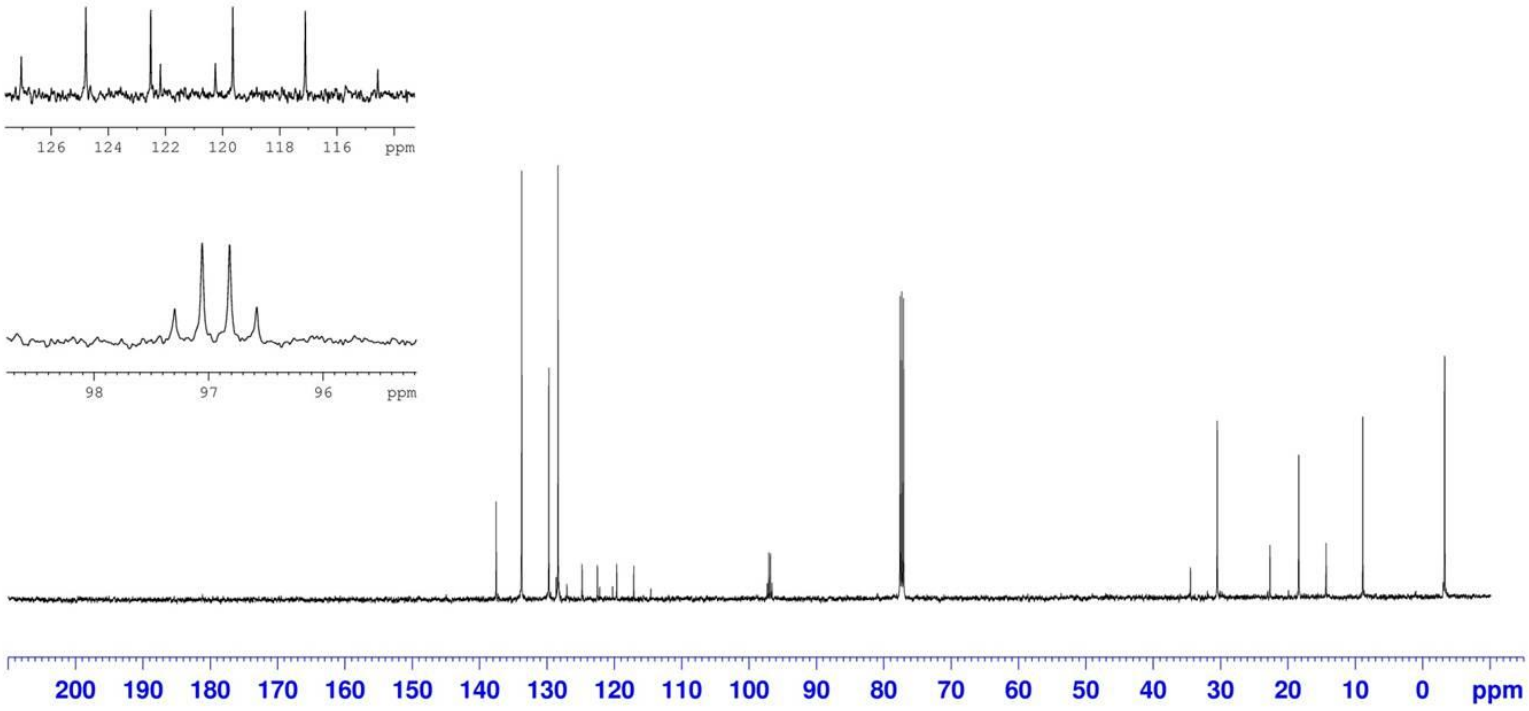
1,1,1–trifluoro–2–methyl–4–(trimethylsilyl)butan–2–yl trifluoromethanesulfonate
100 MHz, CDCl3

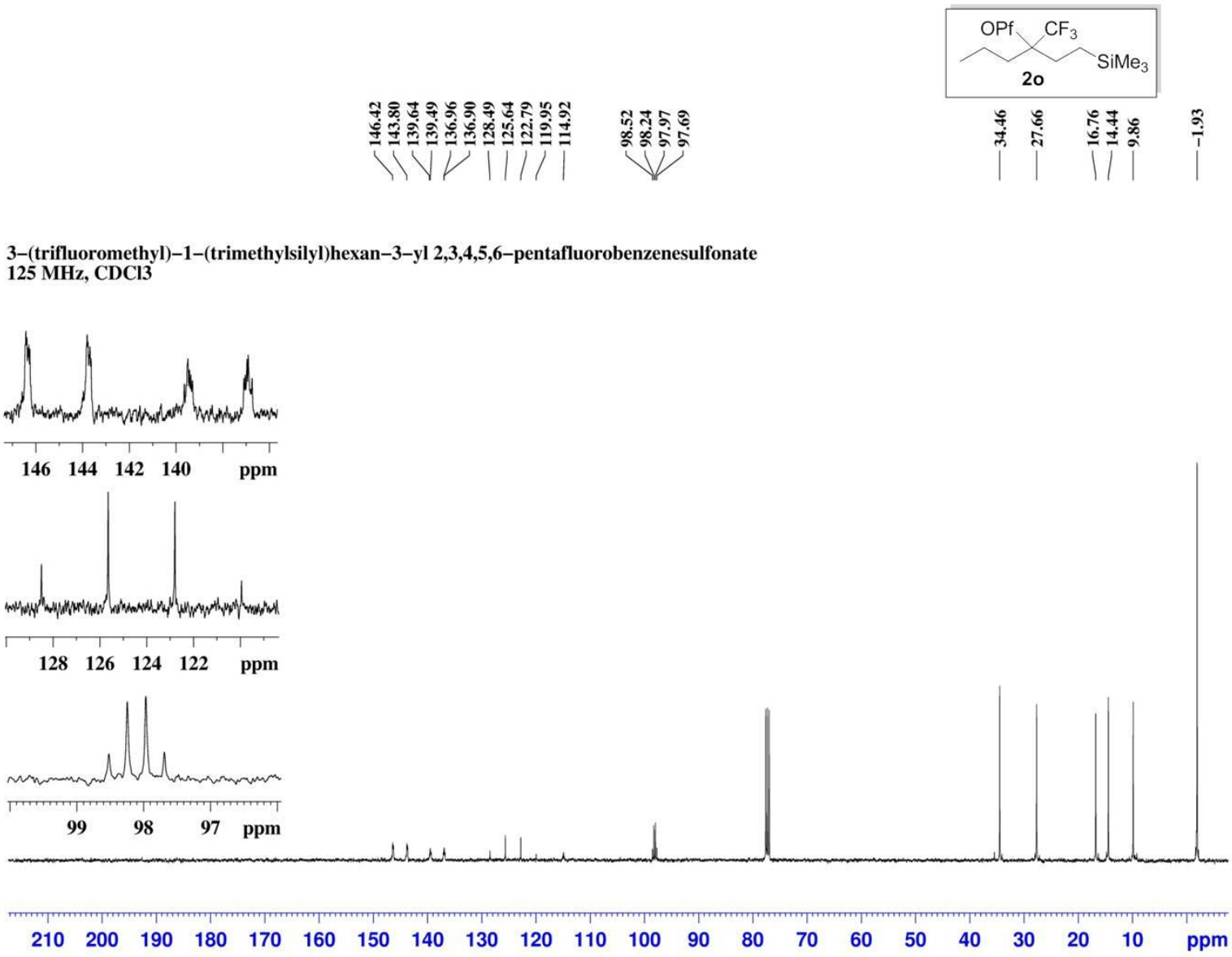


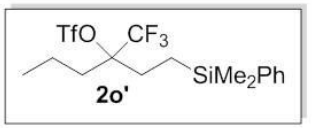




4–(dimethyl(phenyl)silyl)–1,1,1–trifluoro–2–methylbutan–2–yl trifluoromethanesulfonate
125 MHz, CDCl3



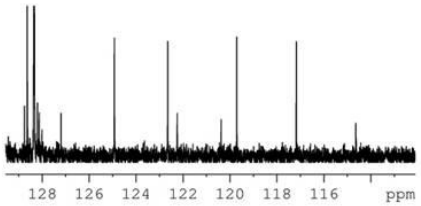

OPf
CF3
SiMe3
2o
146.42
143.80
139.64
139.49
136.96
136.90
128.49
125.64
122.79
119.95
114.92
98.52
98.24
97.97
97.69
34.46
27.66
16.76
14.44
9.86
-1.93
3-(trifluoromethyl)-1-(trimethylsilyl)hexan-3-yl 2,3,4,5,6-pentafluorobenzenesulfonate
125 MHz, CDCl3
146 144 142 140 ppm
128 126 124 122 ppm
99 98 97 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

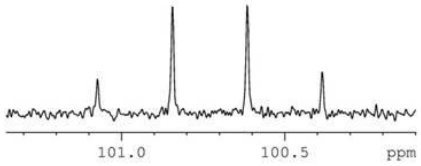


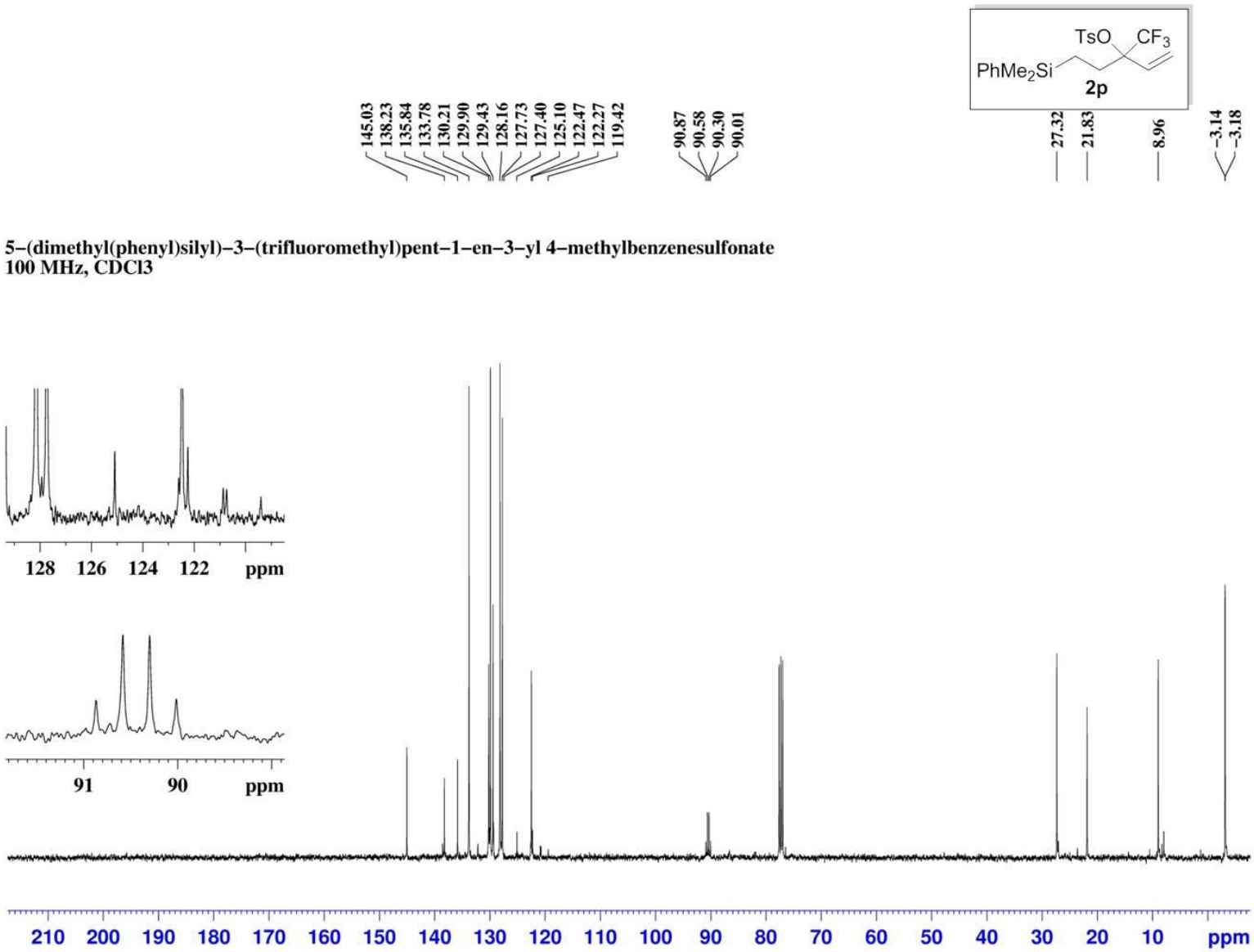
137.55
133.74
129.72
128.62
128.33
127.20
124.92
122.64
122.24
120.37
119.71
117.17
114.63
101.07
100.84
100.61
100.39

34.52
27.78
16.70
14.32
9.16
-3.41
-3.44

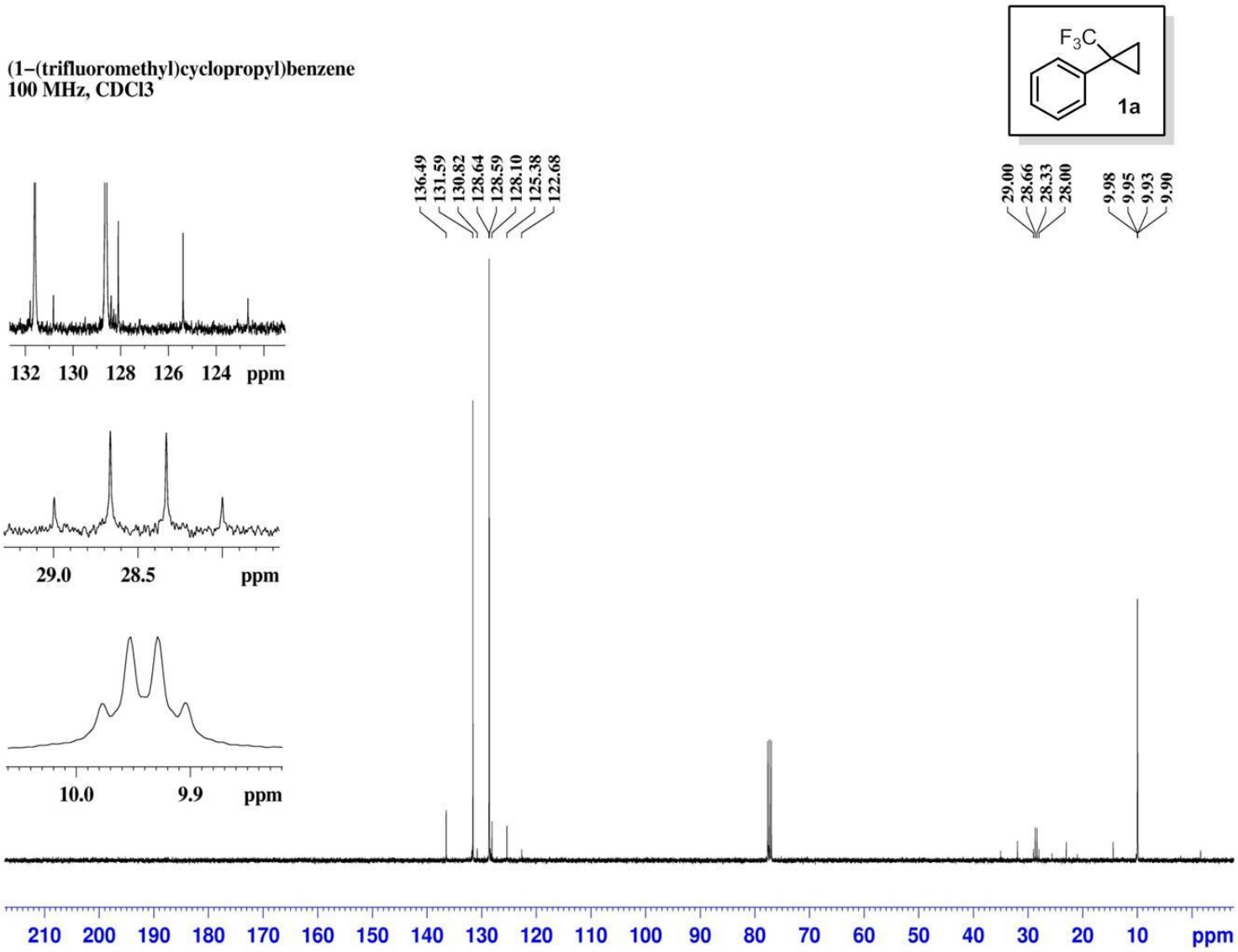
1–(dimethyl(phenyl)silyl)–3–(trifluoromethyl)hexan–3–yl trifluoromethanesulfonate
100 MHz, CDCl3



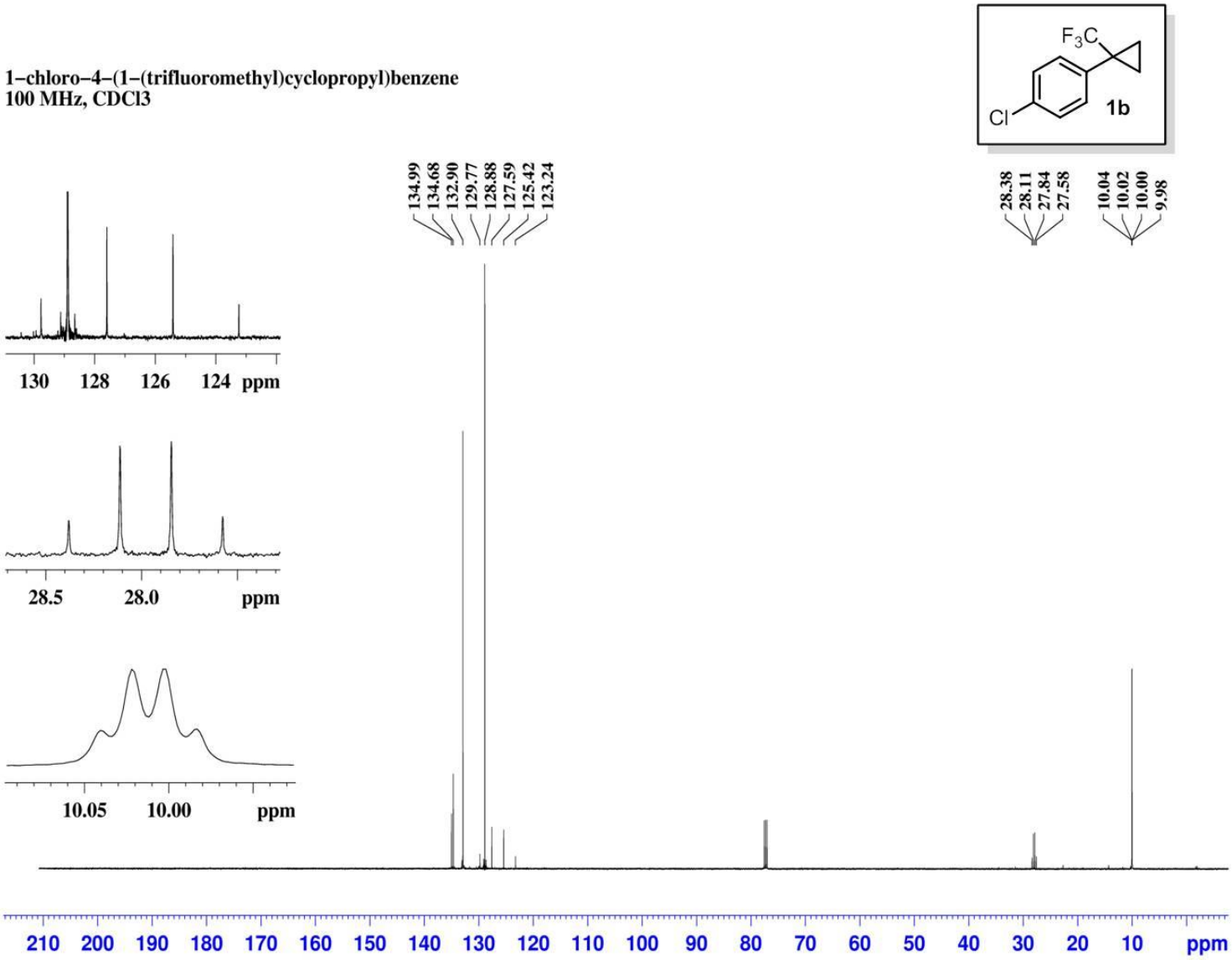


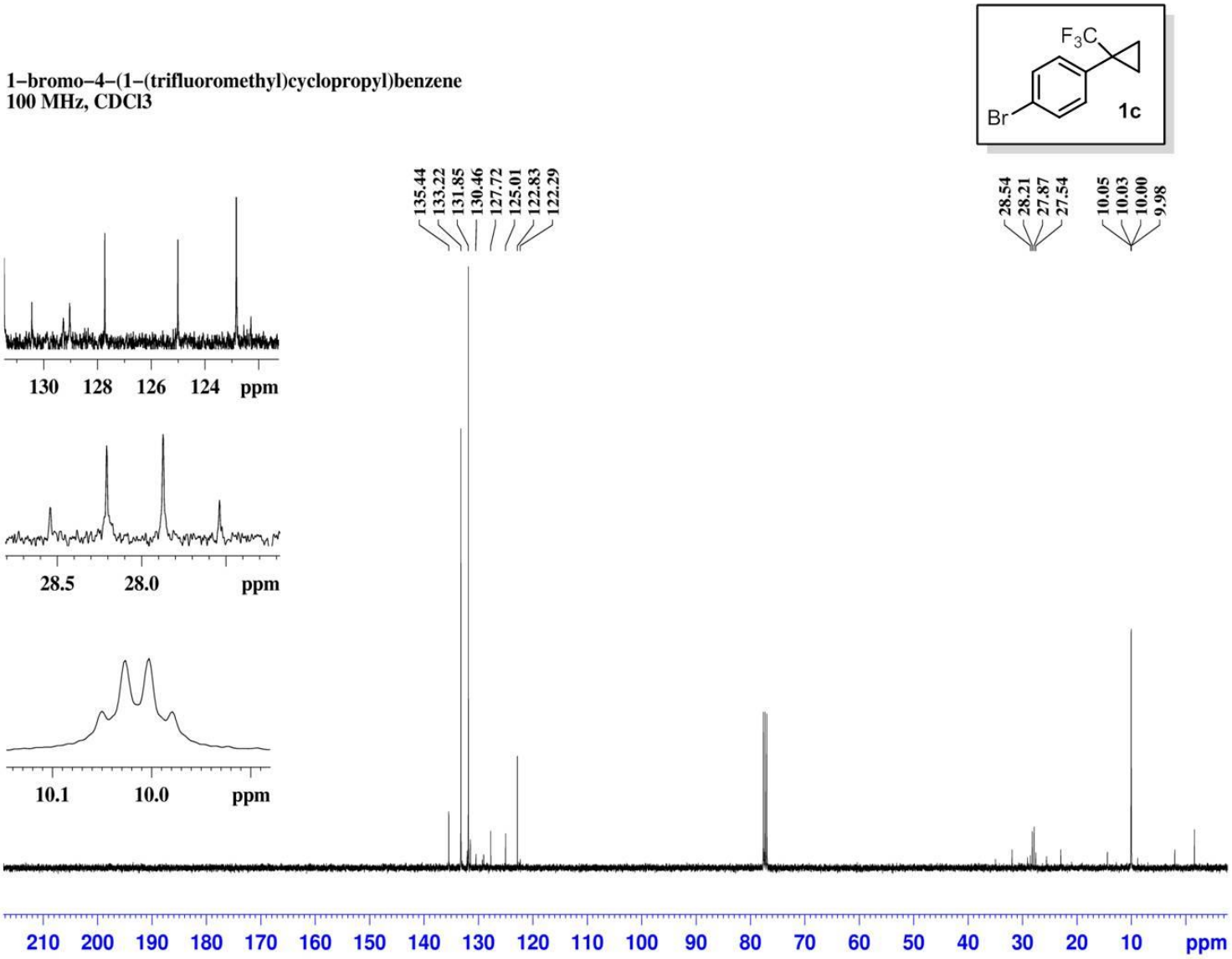


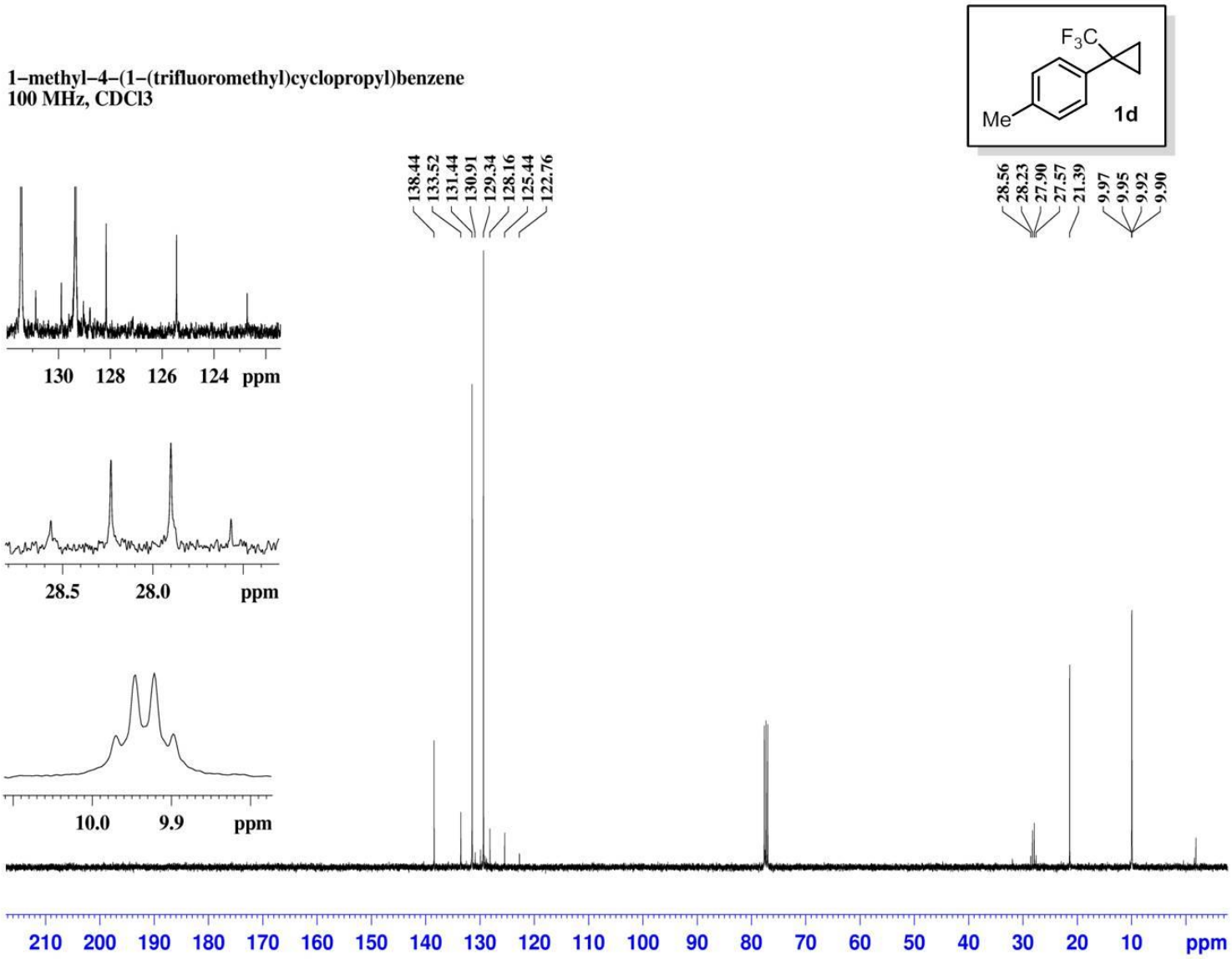
5–(dimethyl(phenyl)silyl)–3–(trifluoromethyl)pent–1–en–3–yl 4–methylbenzenesulfonate
100 MHz, CDCl3


(1–(trifluoromethyl)cyclopropyl)benzene
100 MHz, CDCl3
F3C
1a
136.49
131.59
130.82
128.64
128.59
128.10
125.38
122.68
29.00
28.66
28.33
28.00
9.98
9.95
9.93
9.90
132 130 128 126 124 ppm
29.0 28.5 ppm
10.0 9.9 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

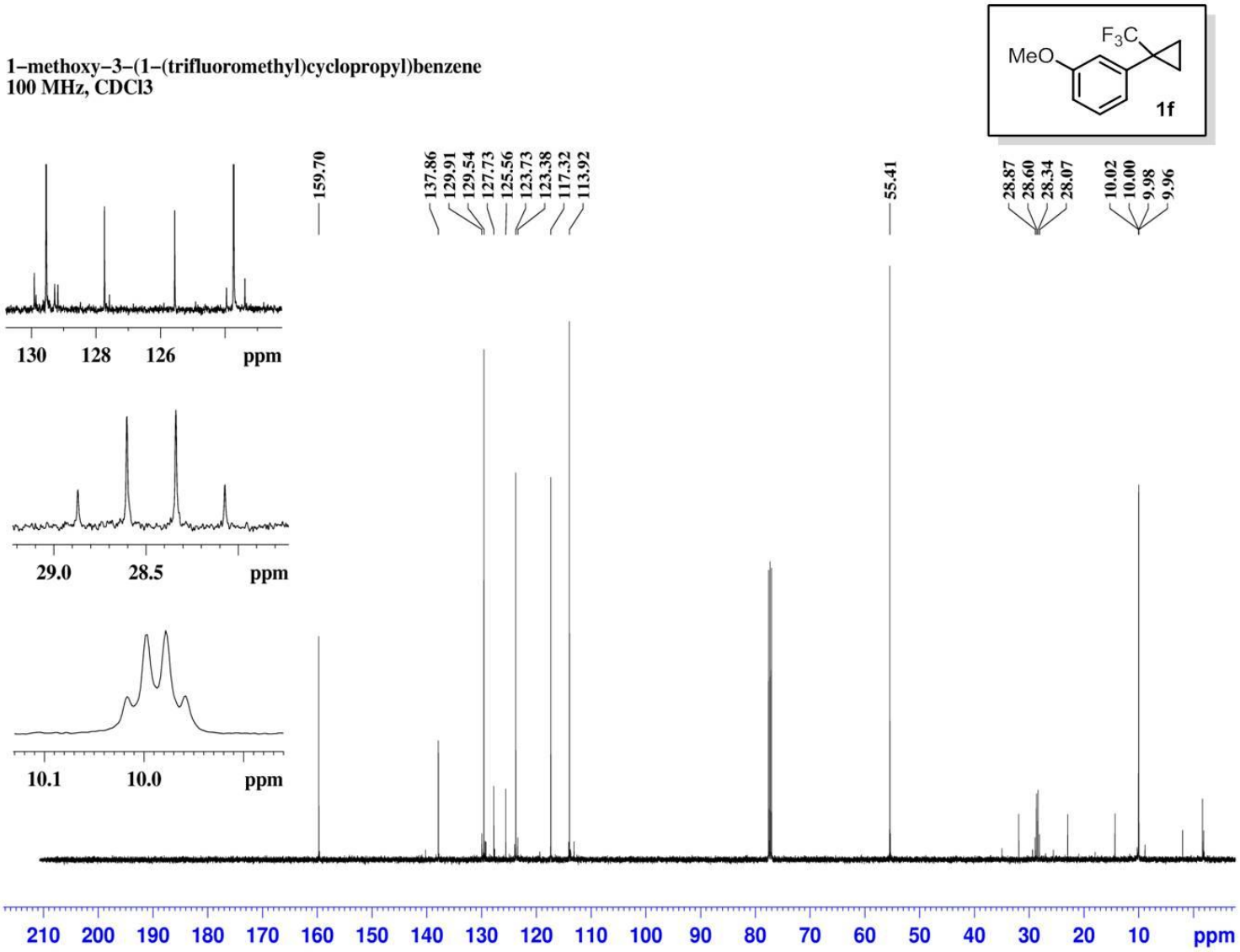
1−chloro−4−(1−(trifluoromethyl)cyclopropyl)benzene
100 MHz, CDCl3

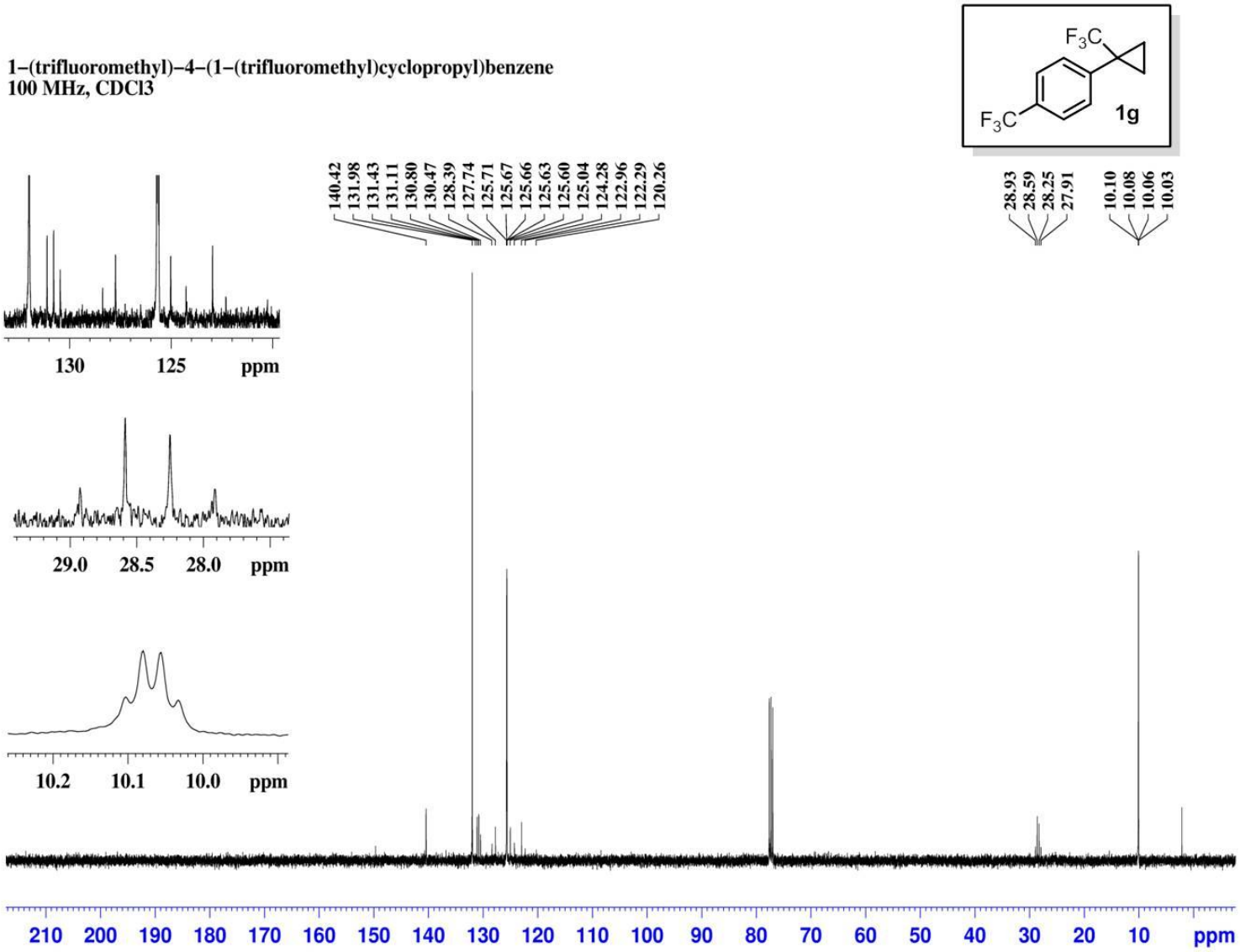



1-bromo-4-(1-(trifluoromethyl)cyclopropyl)benzene
100 MHz, CDCl3
F3C
Br
1c
135.44
133.22
131.85
130.46
127.72
125.01
122.83
122.29
28.54
28.21
27.87
27.54
10.05
10.03
10.00
9.98
130 128 126 124 ppm
28.5 28.0 ppm
10.1 10.0 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

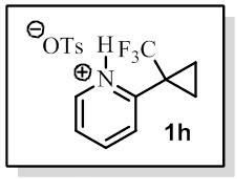

1–methyl–4–(1–(trifluoromethyl)cyclopropyl)benzene
100 MHz, CDCl3
F3C
Me
1d
138.44
133.52
131.44
130.91
129.34
128.16
125.44
122.76
28.56
28.23
27.90
27.57
21.39
9.97
9.95
9.92
9.90
130 128 126 124 ppm
28.5 28.0 ppm
10.0 9.9 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

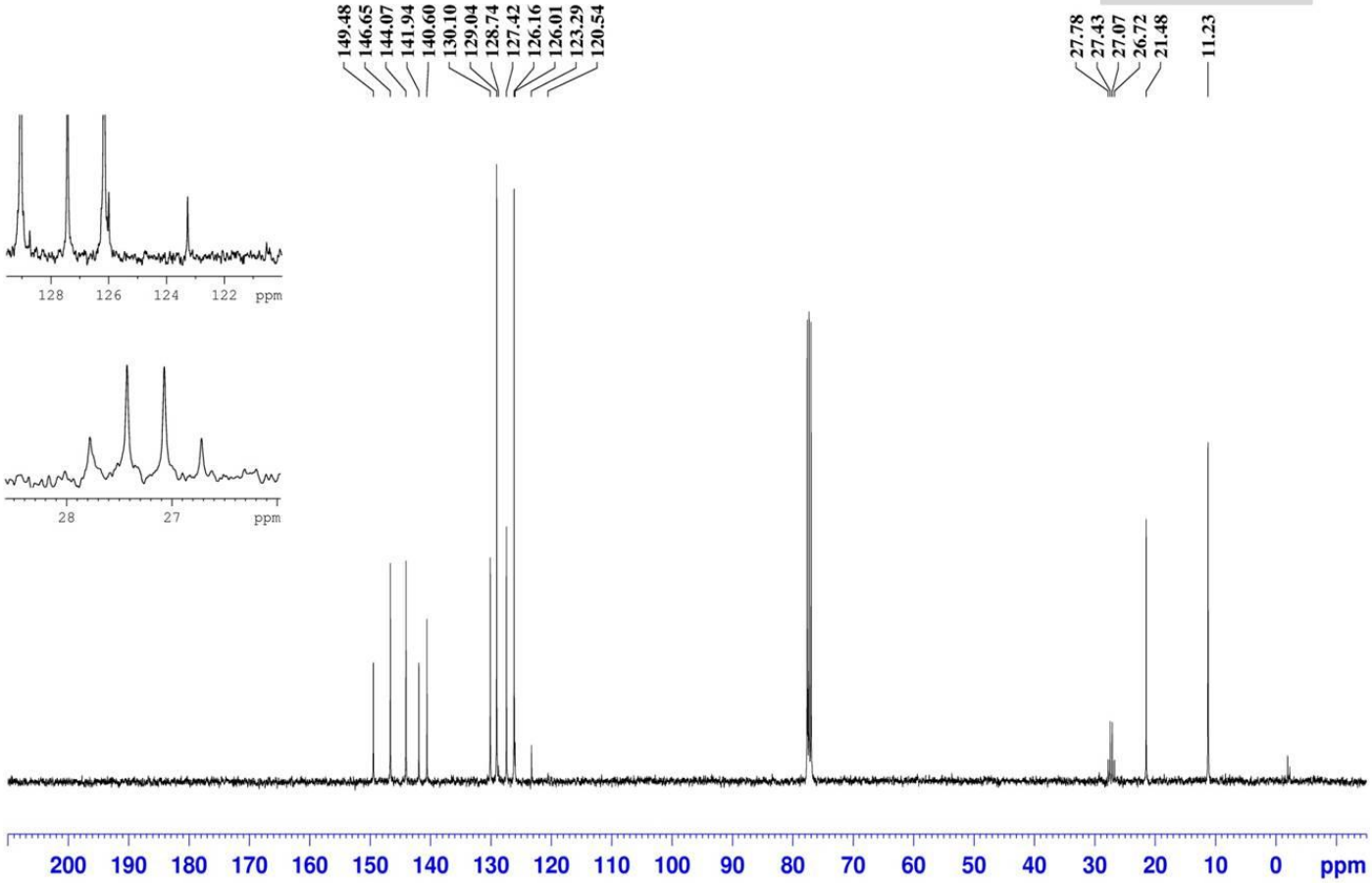
1–methoxy–3–(1–(trifluoromethyl)cyclopropyl)benzene
100 MHz, CDCl3

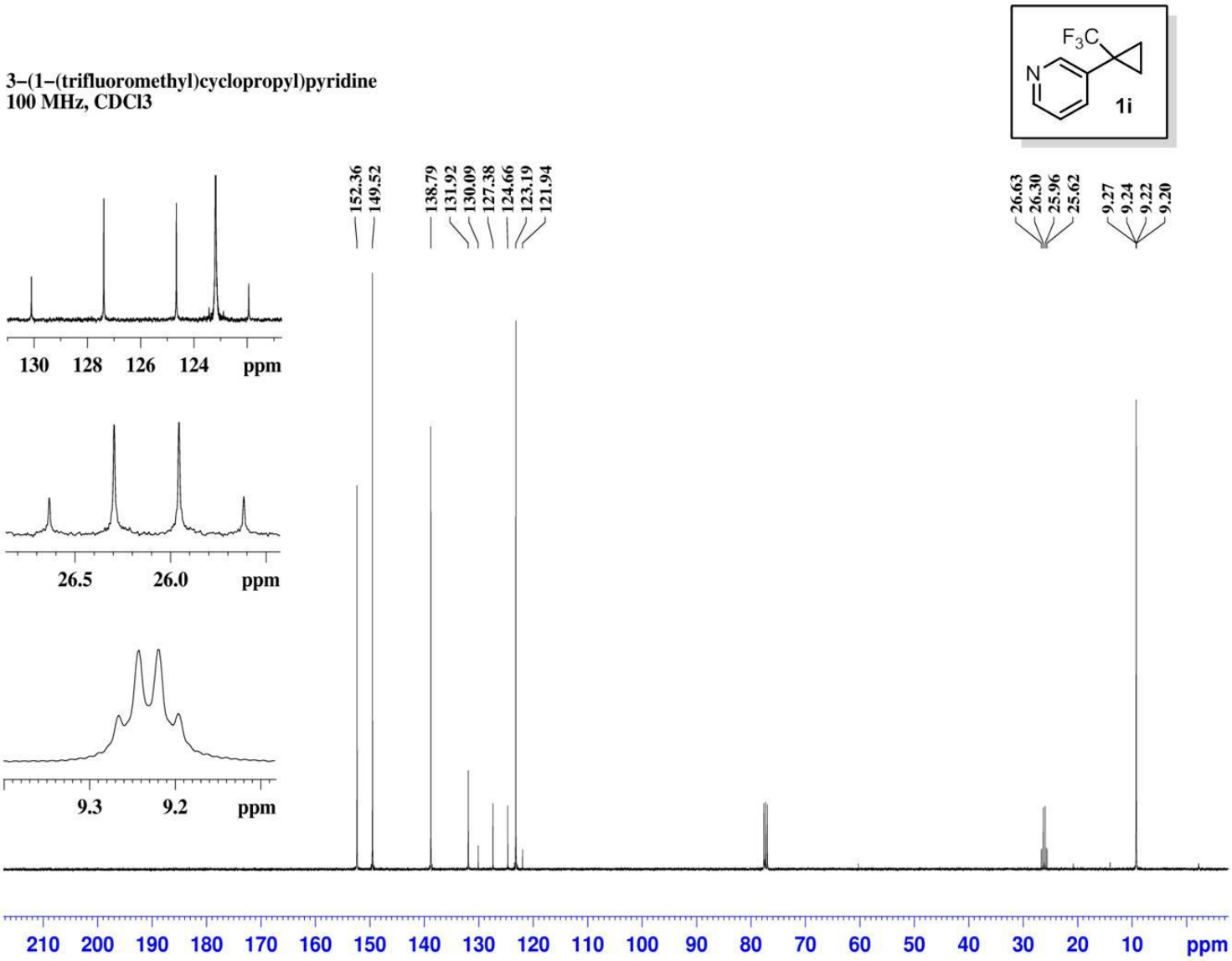


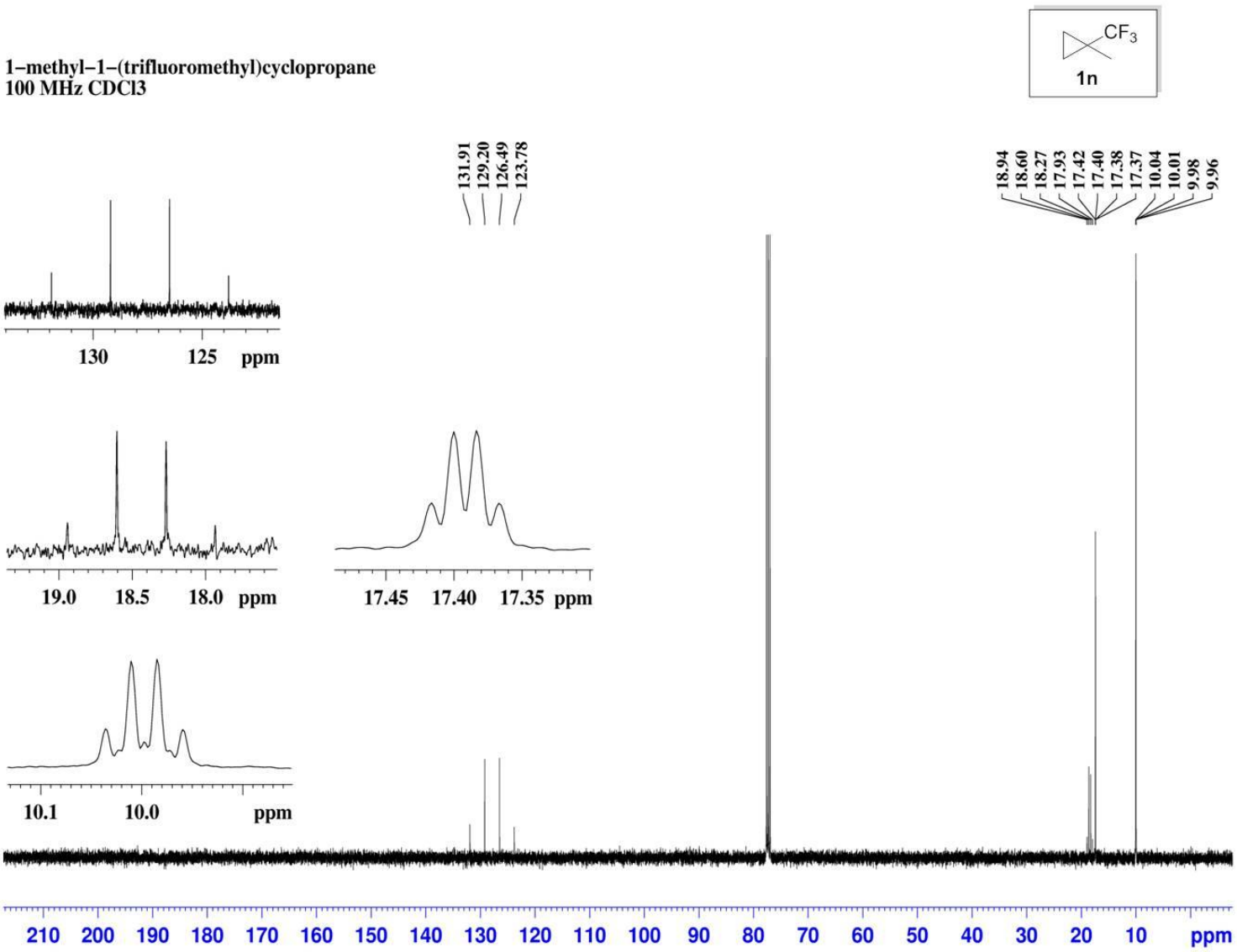

1–(trifluoromethyl)–4–(1–(trifluoromethyl)cyclopropyl)benzene
100 MHz, CDCl3
F3C
F3C
1g
140.42
131.98
131.43
131.11
130.80
130.47
128.39
127.74
125.71
125.67
125.66
125.63
125.60
125.04
124.28
122.96
122.29
120.26
28.93
28.59
28.25
27.91
10.10
10.08
10.06
10.03
130
125
ppm
29.0
28.5
28.0
ppm
10.2
10.1
10.0
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

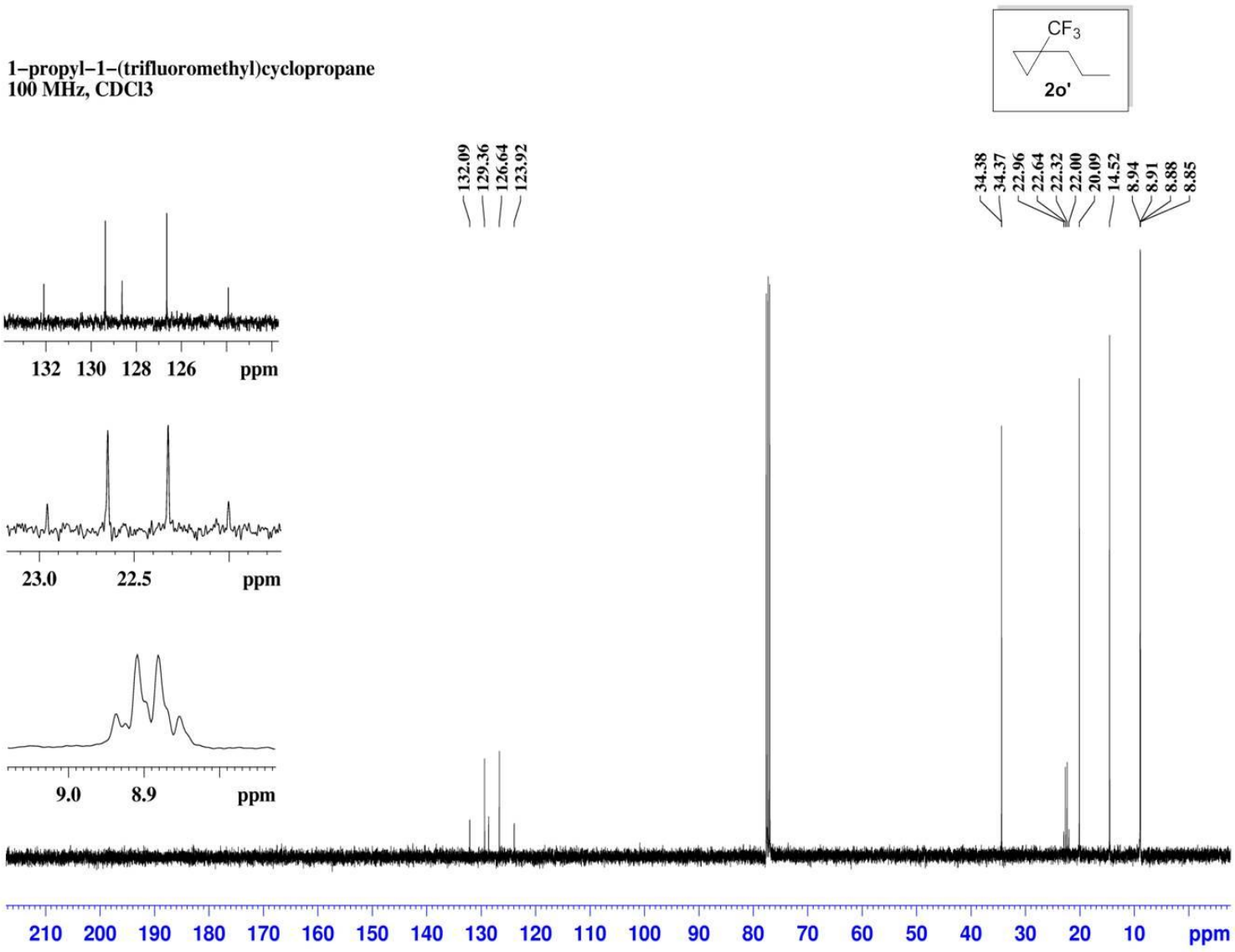
2–(1–(trifluoromethyl)cyclopropyl)pyridin–1–ium tosylate
100 MHz, CDCl3





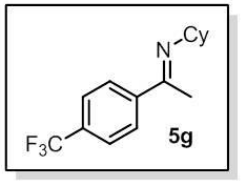

3–(1–(trifluoromethyl)cyclopropyl)pyridine
100 MHz, CDCl3
F3C
N
1i
152.36
149.52
138.79
131.92
130.09
127.38
124.66
123.19
121.94
26.63
26.30
25.96
25.62
9.27
9.24
9.22
9.20
130 128 126 124 ppm
26.5 26.0 ppm
9.3 9.2 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


1−methyl−1−(trifluoromethyl)cyclopropane
100 MHz CDCl3
CF3
1n
131.91
129.20
126.49
123.78
18.94
18.60
18.27
17.93
17.42
17.40
17.38
17.37
10.04
10.01
9.98
9.96
130
125
ppm
19.0
18.5
18.0
ppm
17.45
17.40
17.35
ppm
10.1
10.0
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

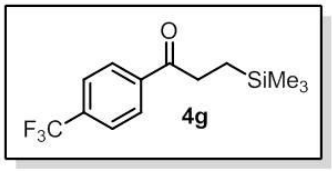

1−propyl−1−(trifluoromethyl)cyclopropane
100 MHz, CDCl3
CF3
2o'
132.09
129.36
126.64
123.92
34.38
34.37
22.96
22.64
22.32
22.00
20.09
14.52
8.94
8.91
8.88
8.85
132 130 128 126 ppm
23.0 22.5 ppm
9.0 8.9 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{19}F-NMR Spectra of Synthesized Compounds

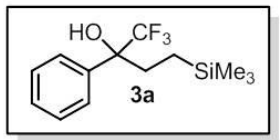
N–(1–(4–(trifluoromethyl)phenyl)ethylidene)cyclohexanamine
377 MHz, CDCl3

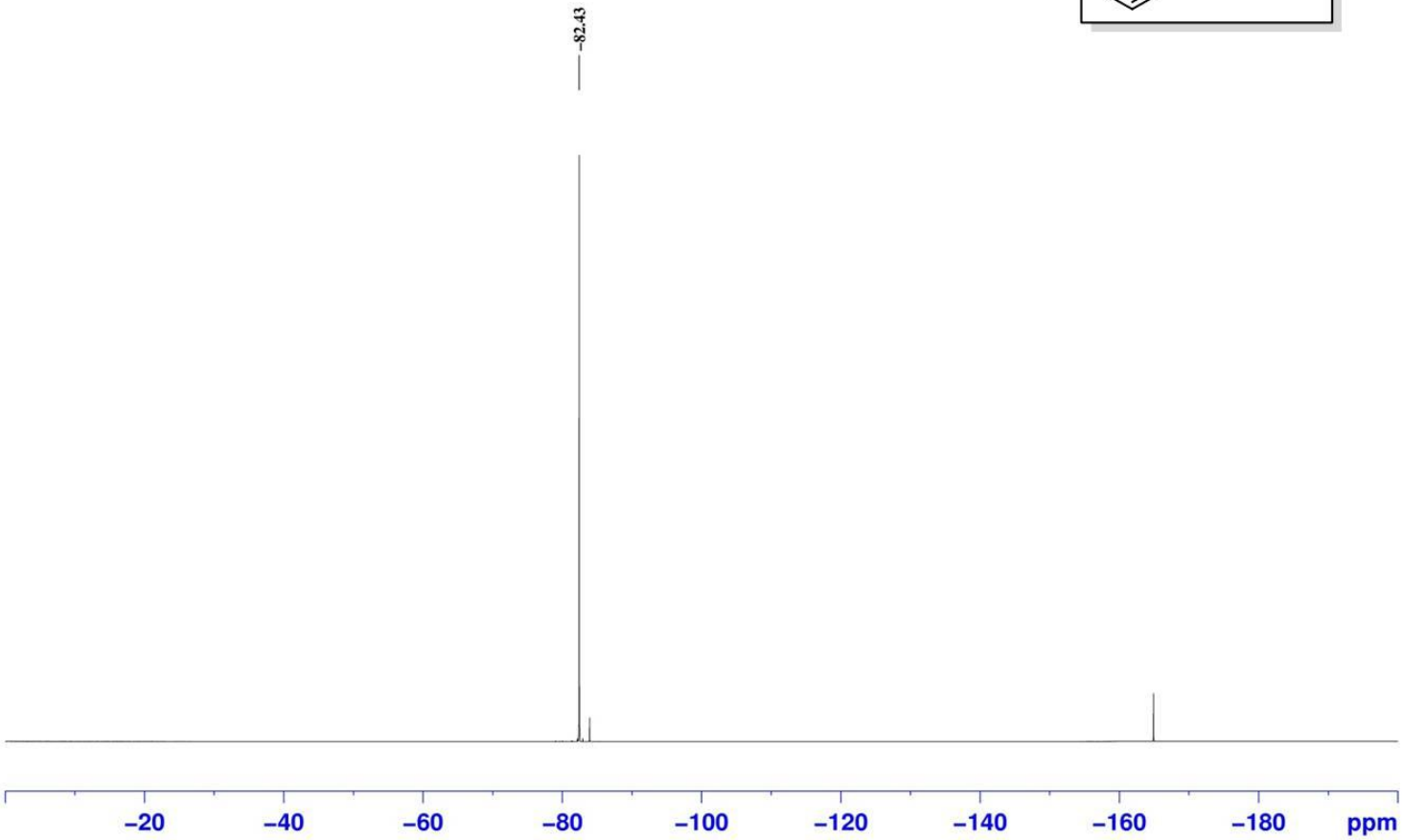


1–(4–(trifluoromethyl)phenyl)–3–(trimethylsilyl)propan–1–one
377 MHz, CDCl3

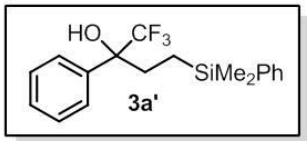


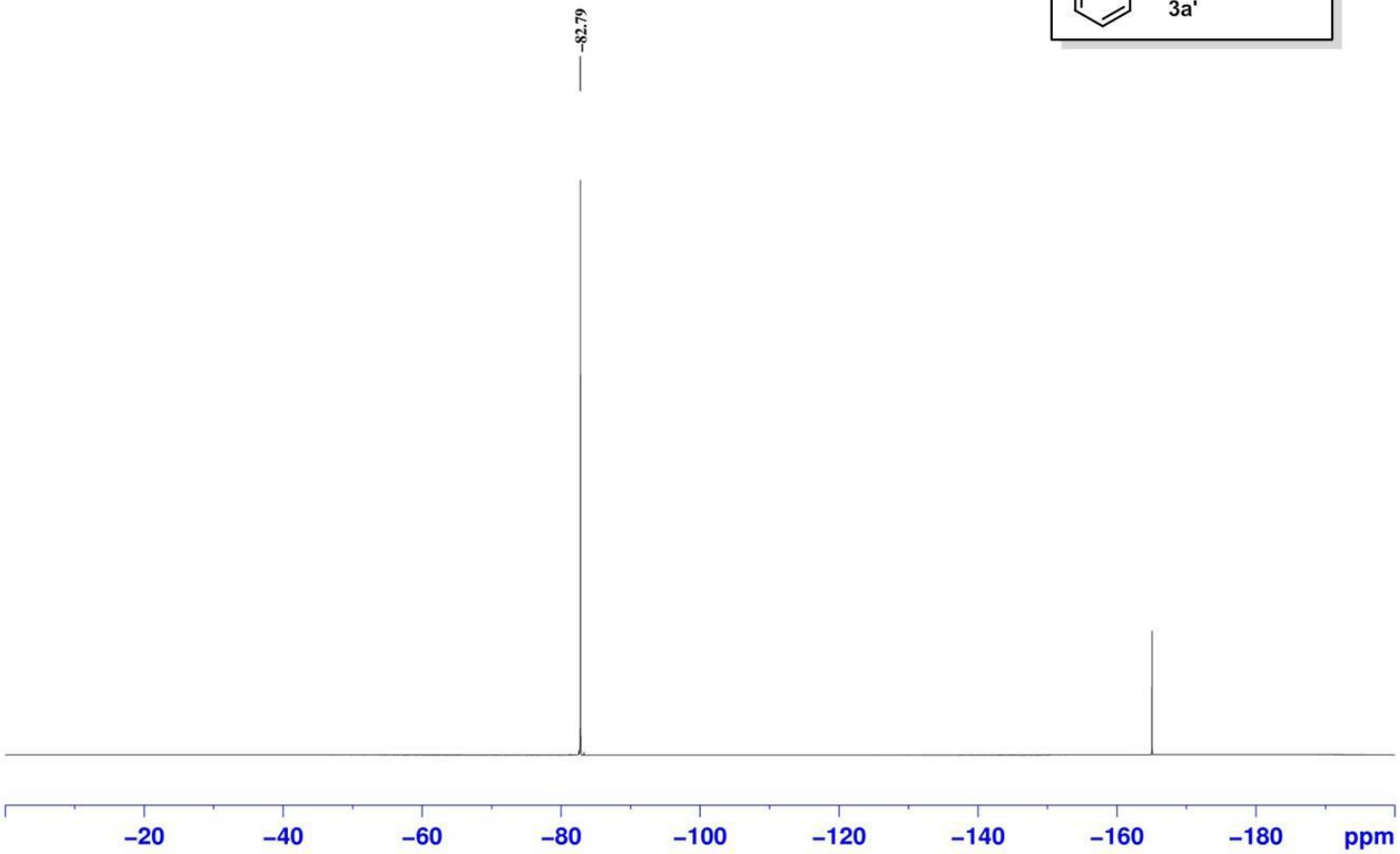
1,1,1−trifluoro−2−phenyl−4−(trimethylsilyl)butan−2−ol
377 MHz, CDCl3



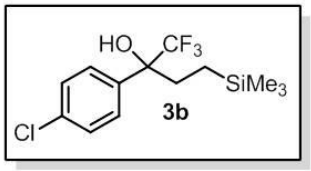


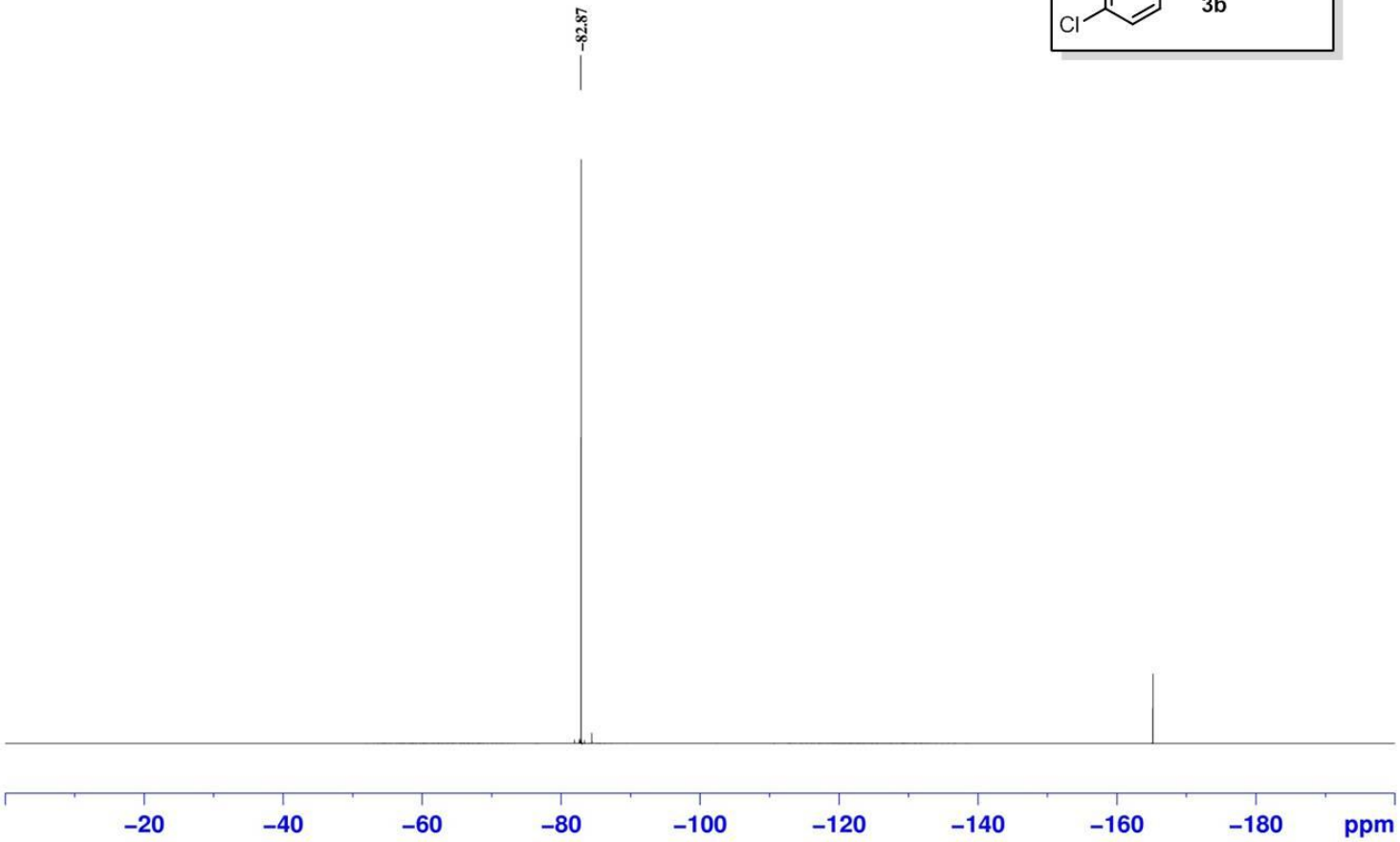
4–(dimethyl(phenyl)silyl)–1,1,1–trifluoro–2–phenylbutan–2–ol
377 MHz, CDCl3



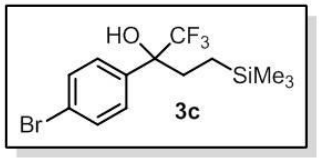


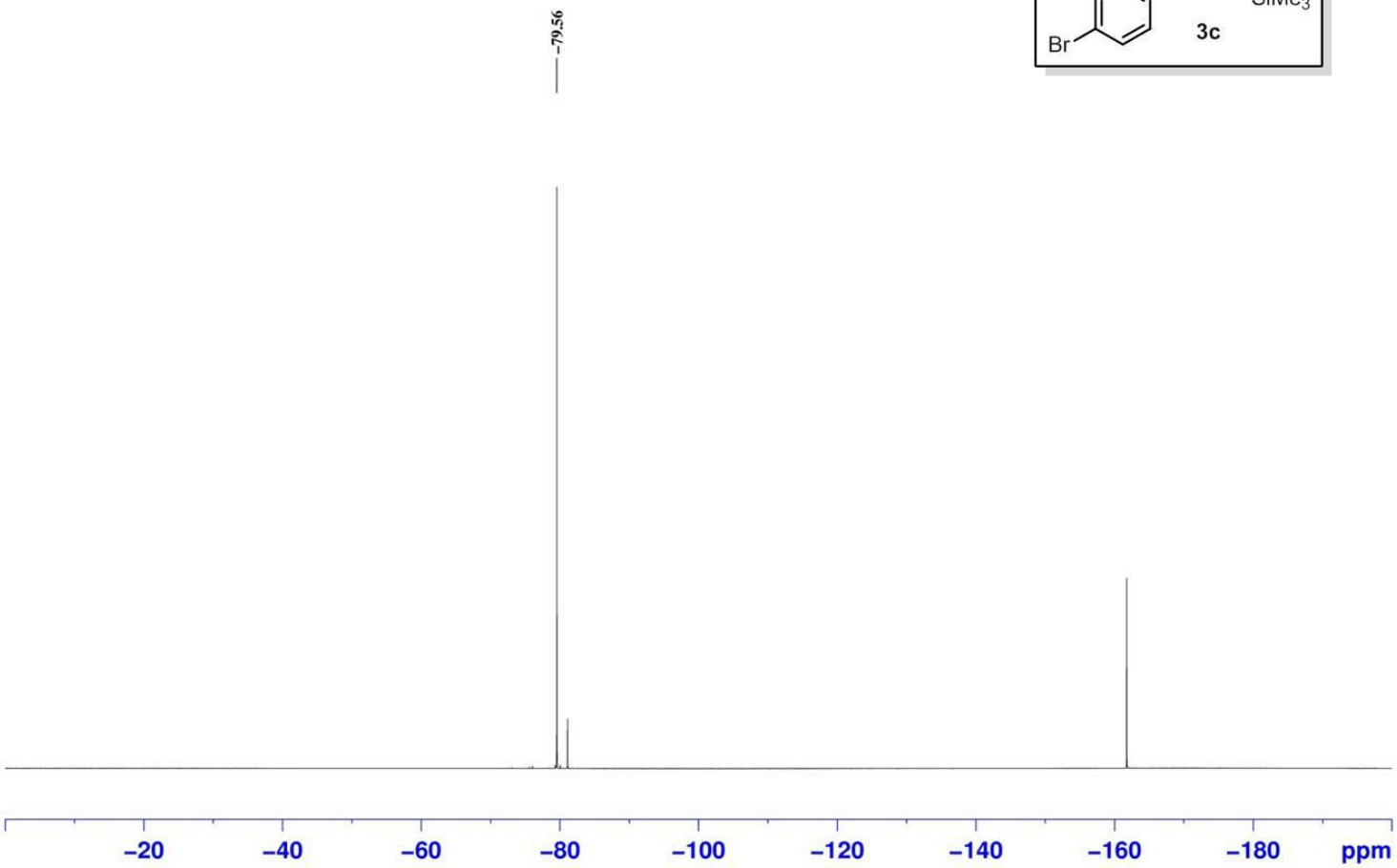
2–(4–chlorophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–ol
377 MHz, CDCl3



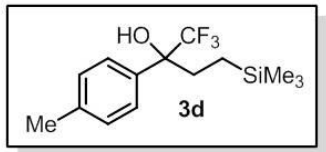


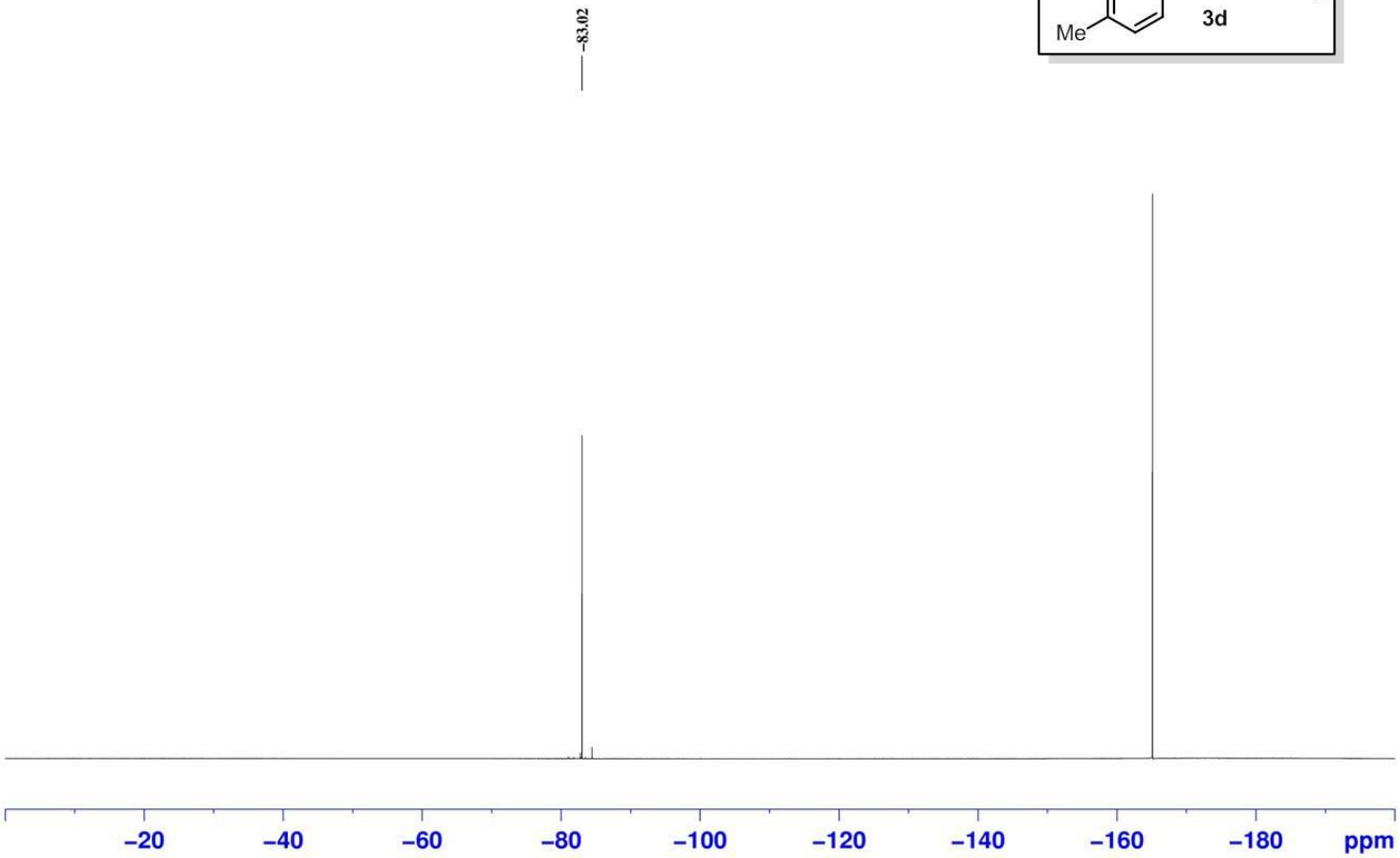
2–(4–bromophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–ol
377 MHz, CDCl3



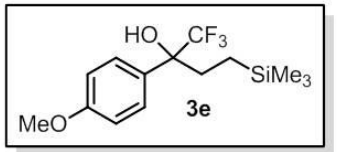


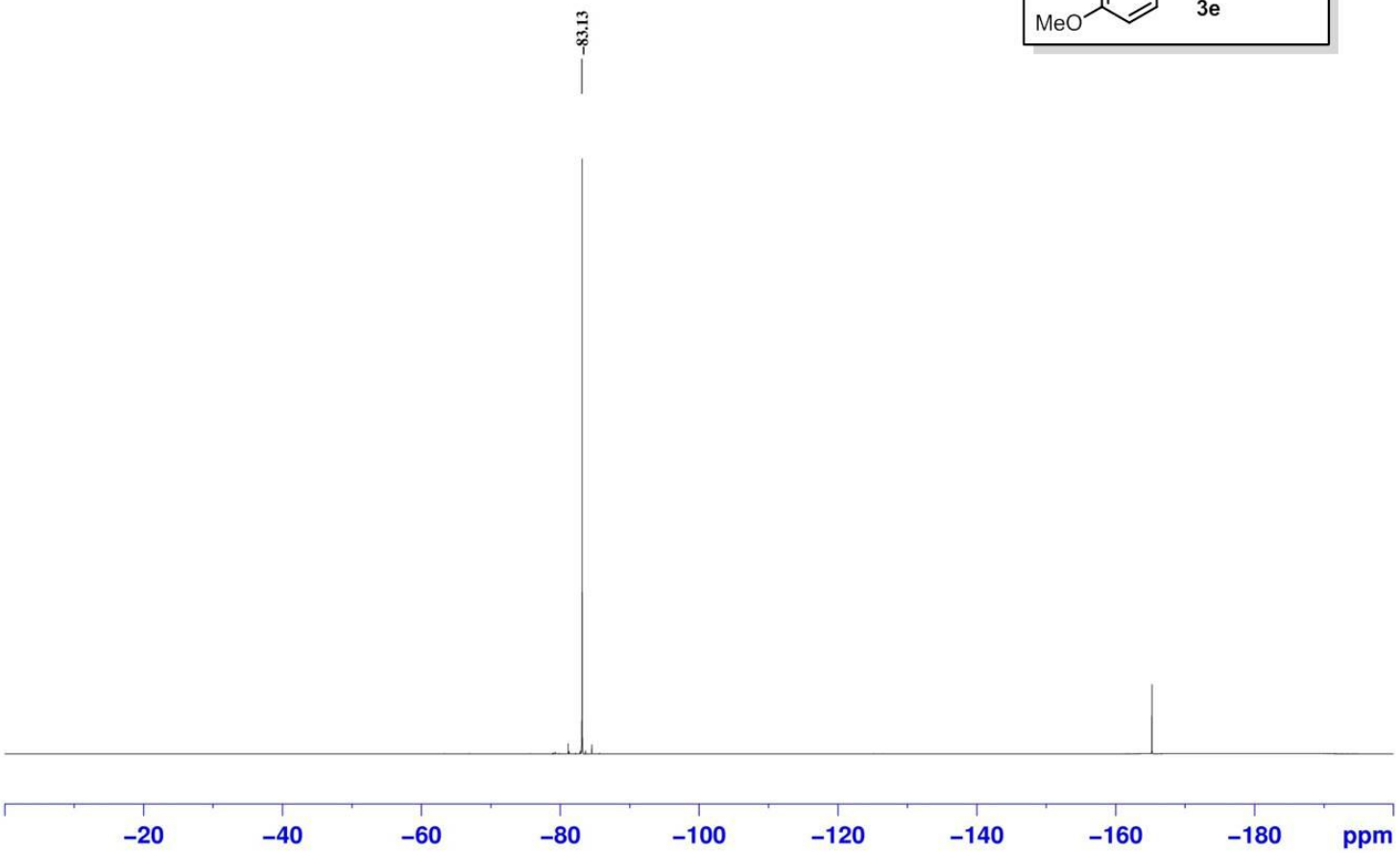
1,1,1−trifluoro−2−(p−tolyl)−4−(trimethylsilyl)butan−2−ol
377 MHz, CDCl3



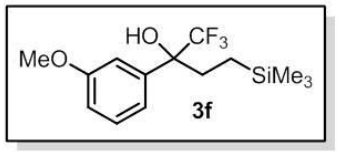


1,1,1–trifluoro–2–(4–methoxyphenyl)–4–(trimethylsilyl)butan–2–ol
377 MHz, CDCl3

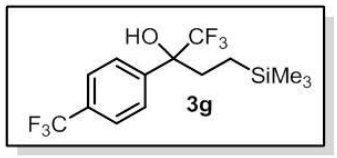




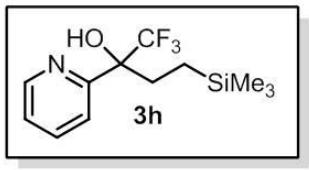
1,1,1−trifluoro−2−(3−methoxyphenyl)−4−(trimethylsilyl)butan−2−ol
377 MHz, CDCl3



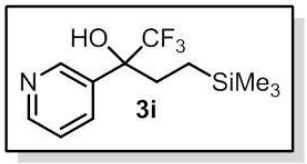
1,1,1−trifluoro−2−(4−(trifluoromethyl)phenyl)−4−(trimethylsilyl)butan−2−ol
377 MHz, CDCl3

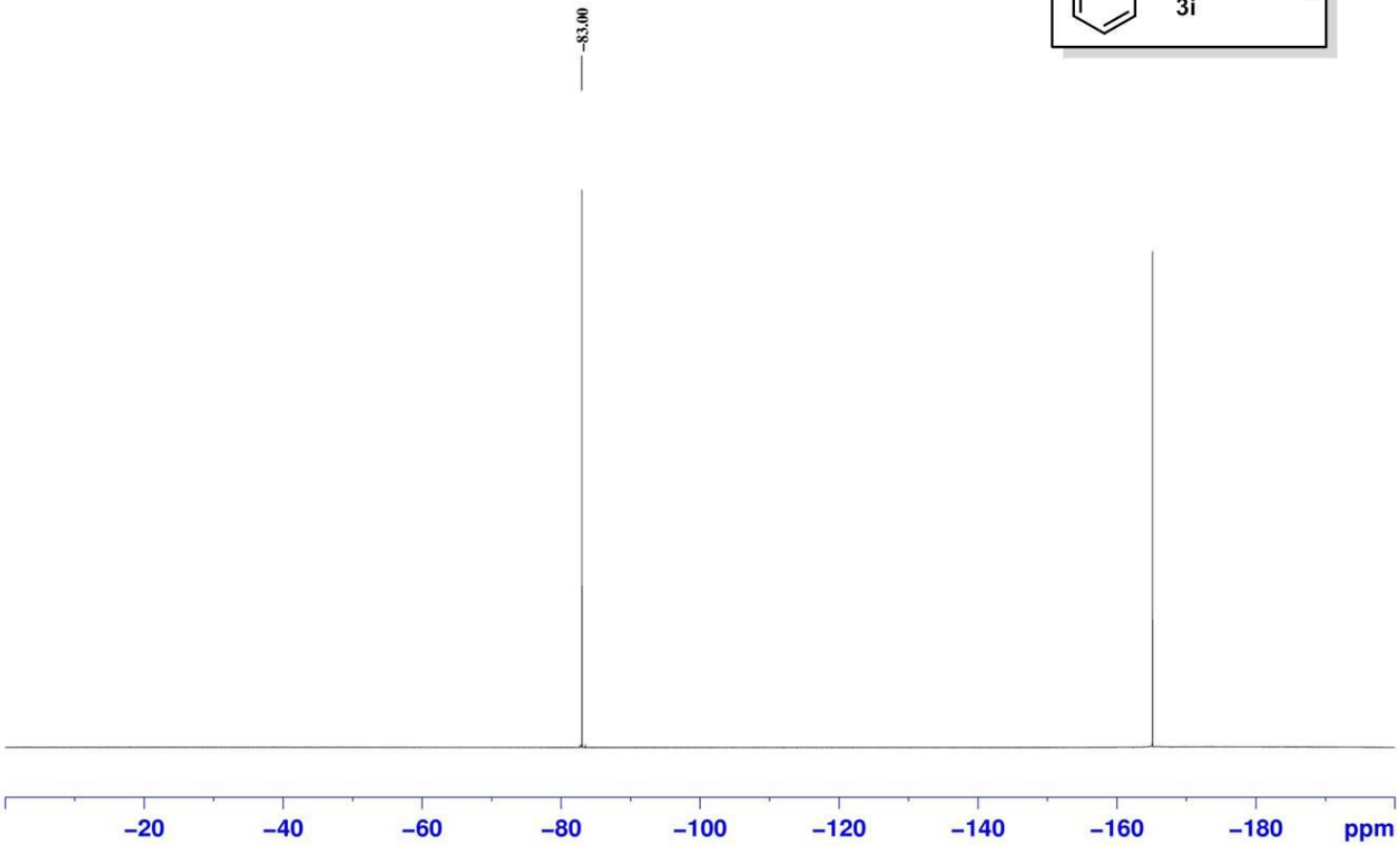


1,1,1−trifluoro−2−(pyridin−2−yl)−4−(trimethylsilyl)butan−2−ol
377 MHz, CDCl3

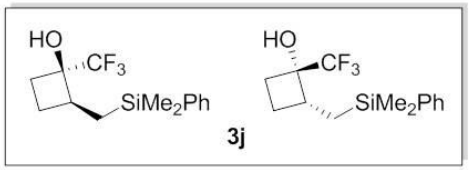


1,1,1−trifluoro−2−(pyridin−3−yl)−4−(trimethylsilyl)butan−2−ol
377 MHz, CDCl3

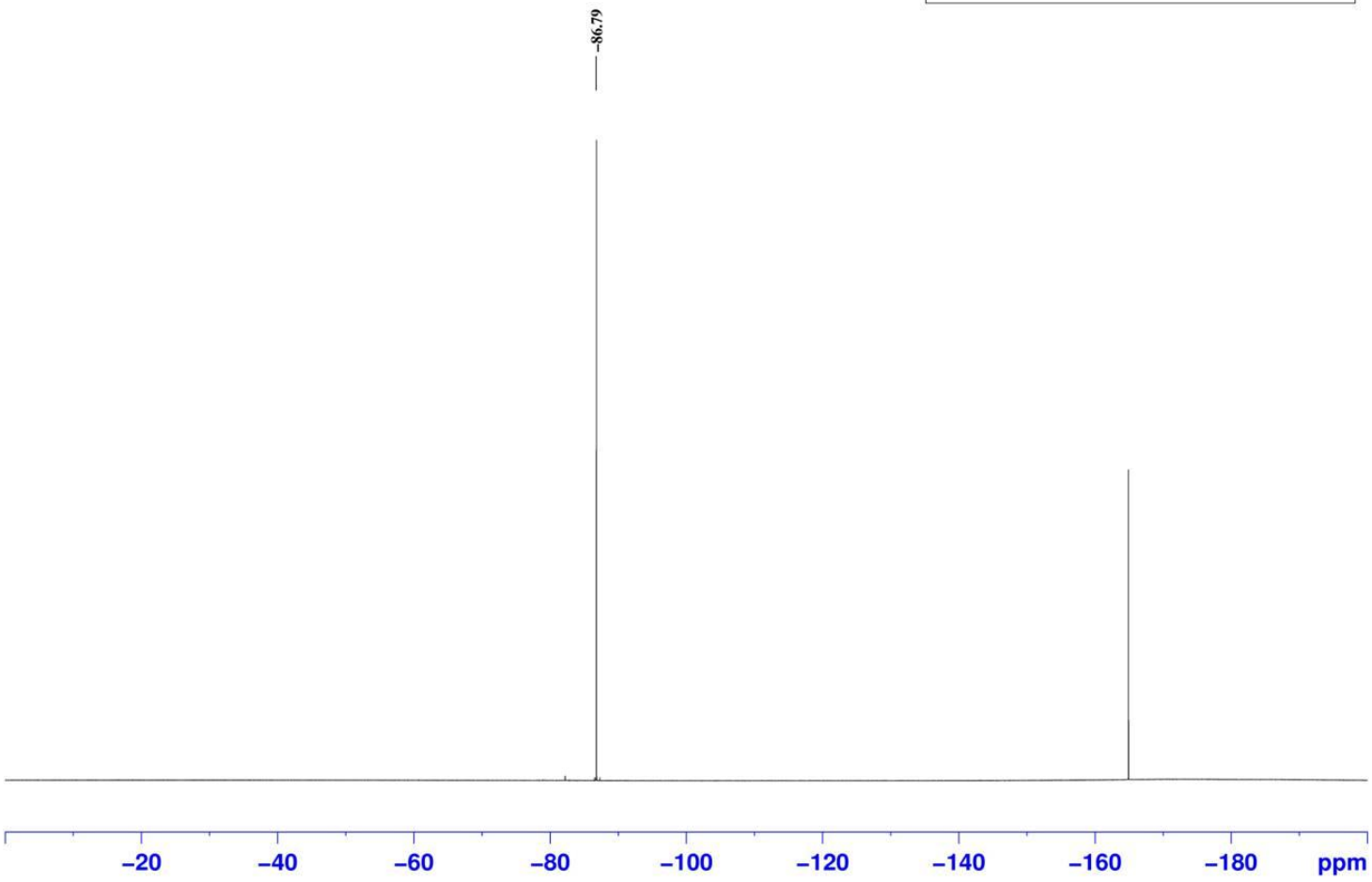




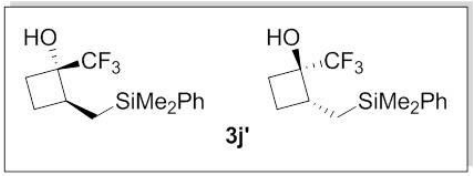
(1R,2S) & (1S,2R)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutanol
377 MHz, CDCl3



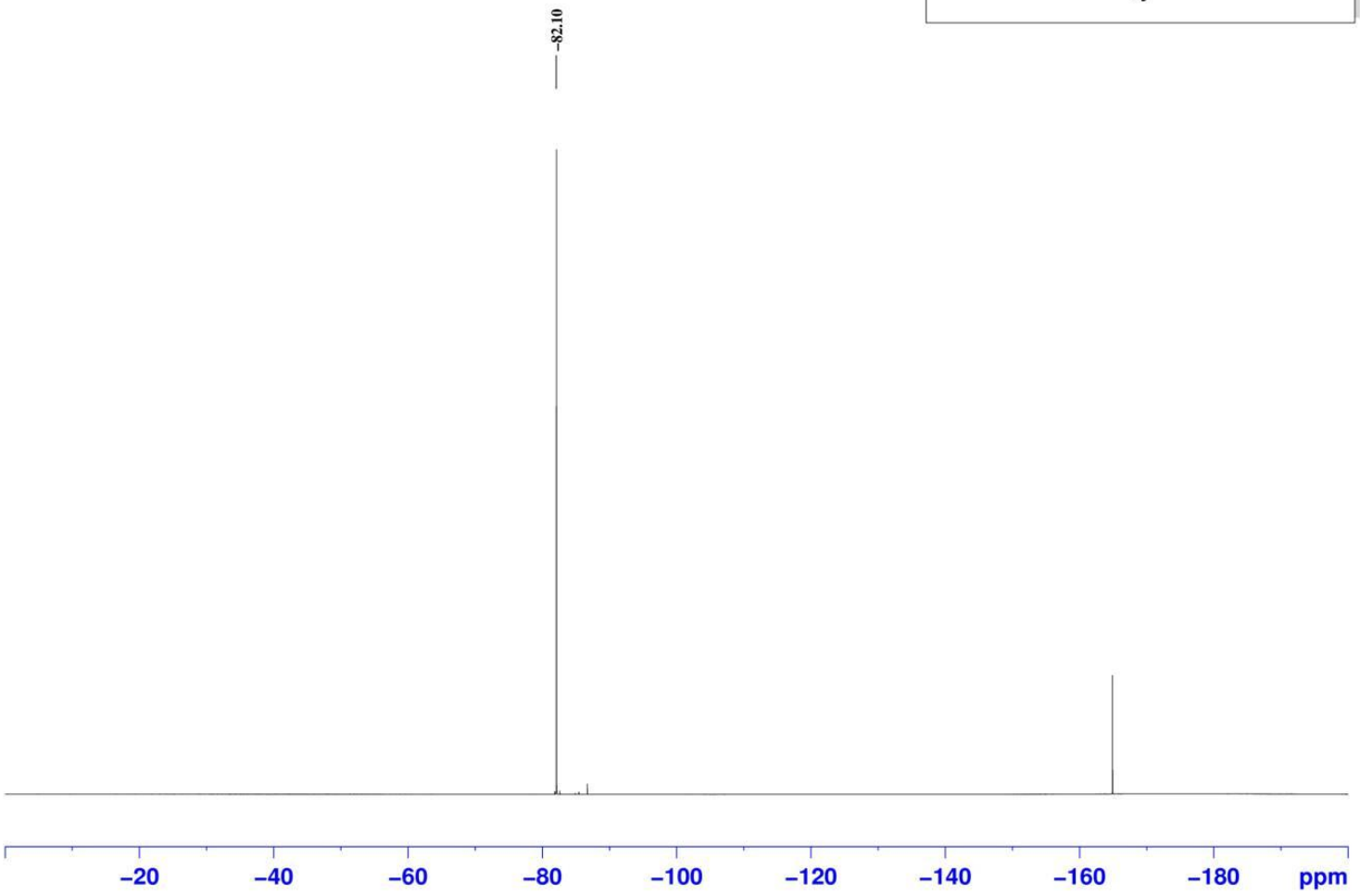
3j



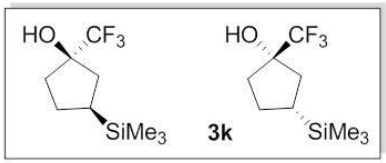
(1S,2S) & (1R,2R)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutanol
377 MHz, CDCl3

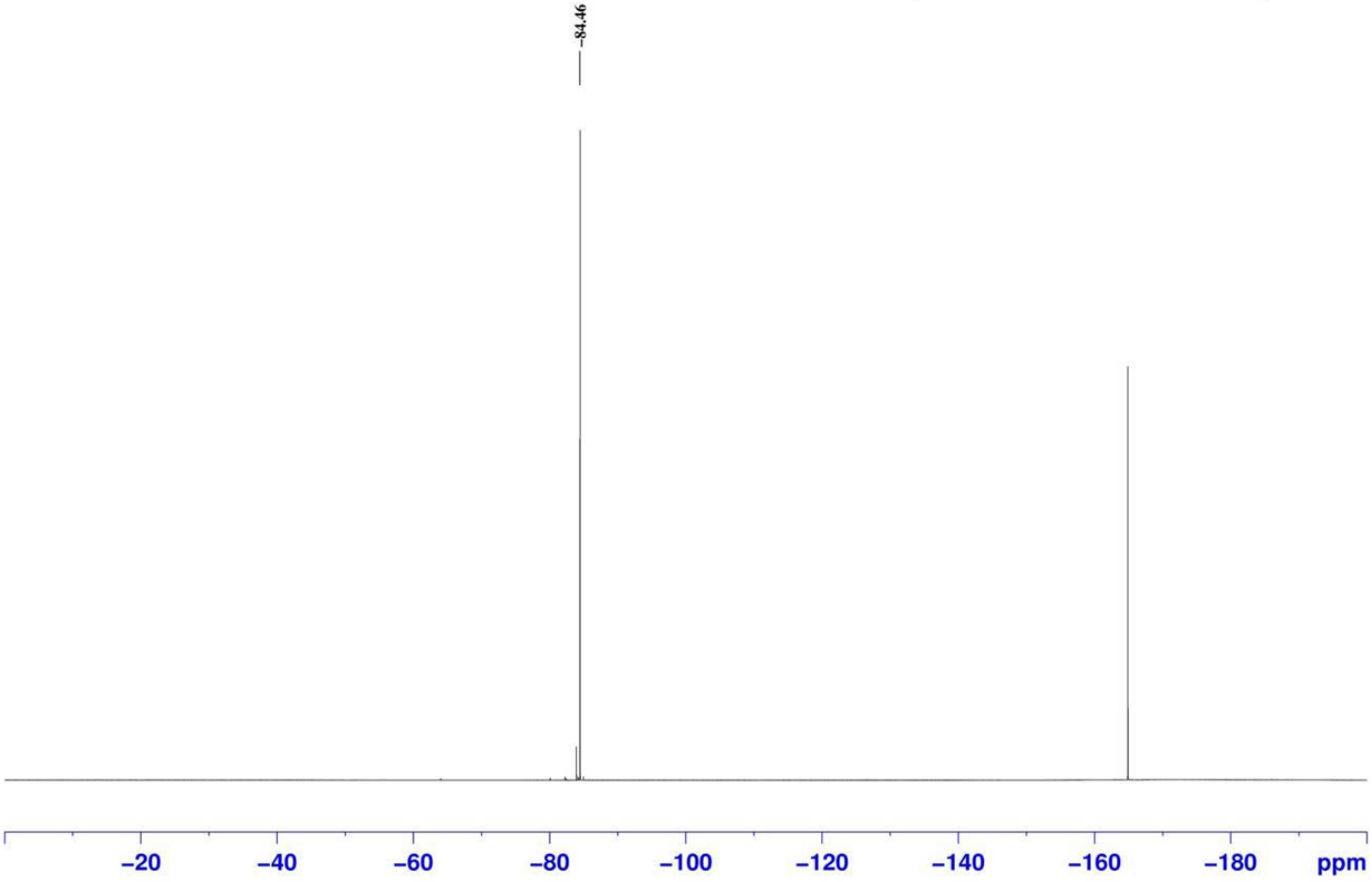


3j'

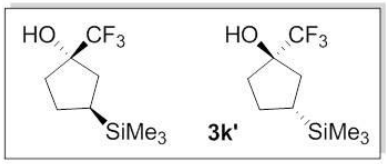


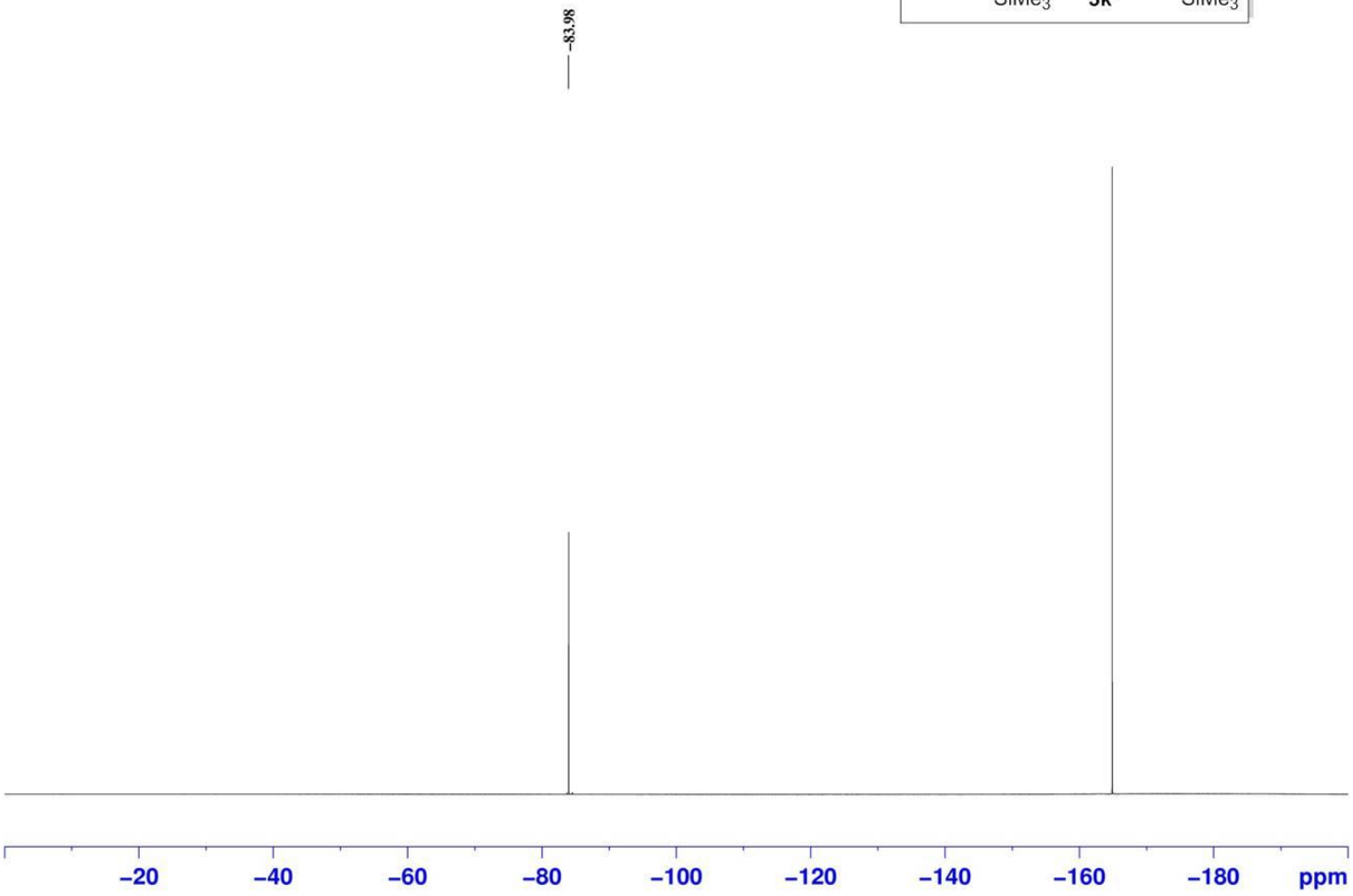
(1R,3S) & (1S, 3R)−1−(trifluoromethyl)−3−(trimethylsilyl)cyclopentanol
377 MHz, CDCl3



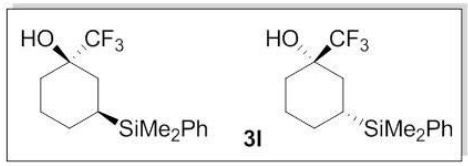


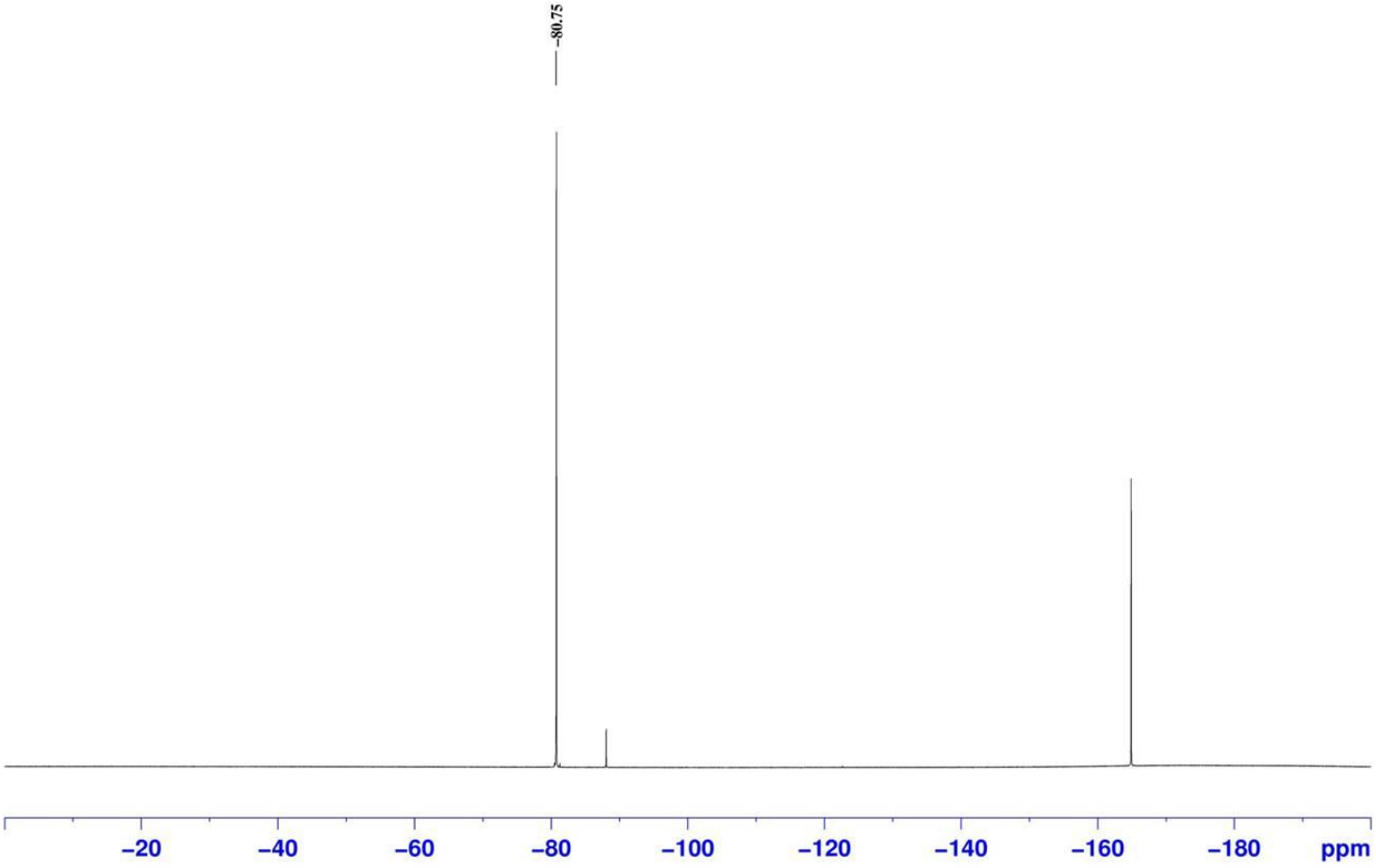
(1S,3S) & (1R, 3R)−1−(trifluoromethyl)−3−(trimethylsilyl)cyclopentanol
377 MHz, CDCl3



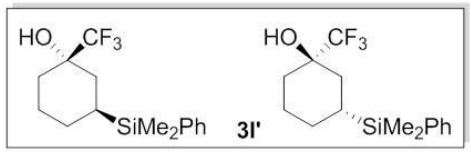


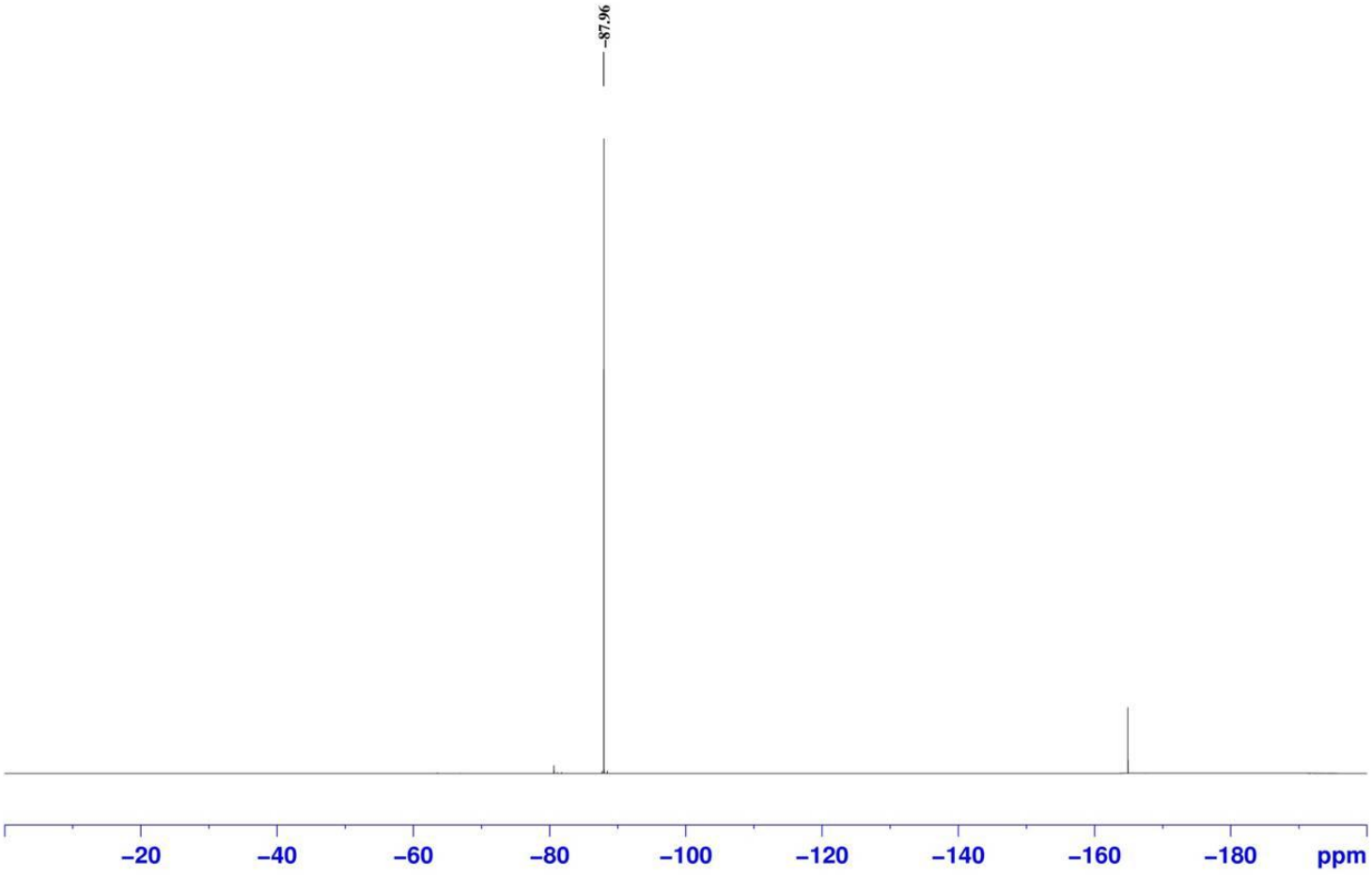
(1R,3S) & (1S,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cyclohexanol
377 MHz, CDCl3



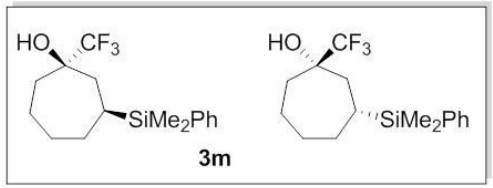


(1S,3S) & (1R,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cyclohexanol
377 MHz, CDCl3

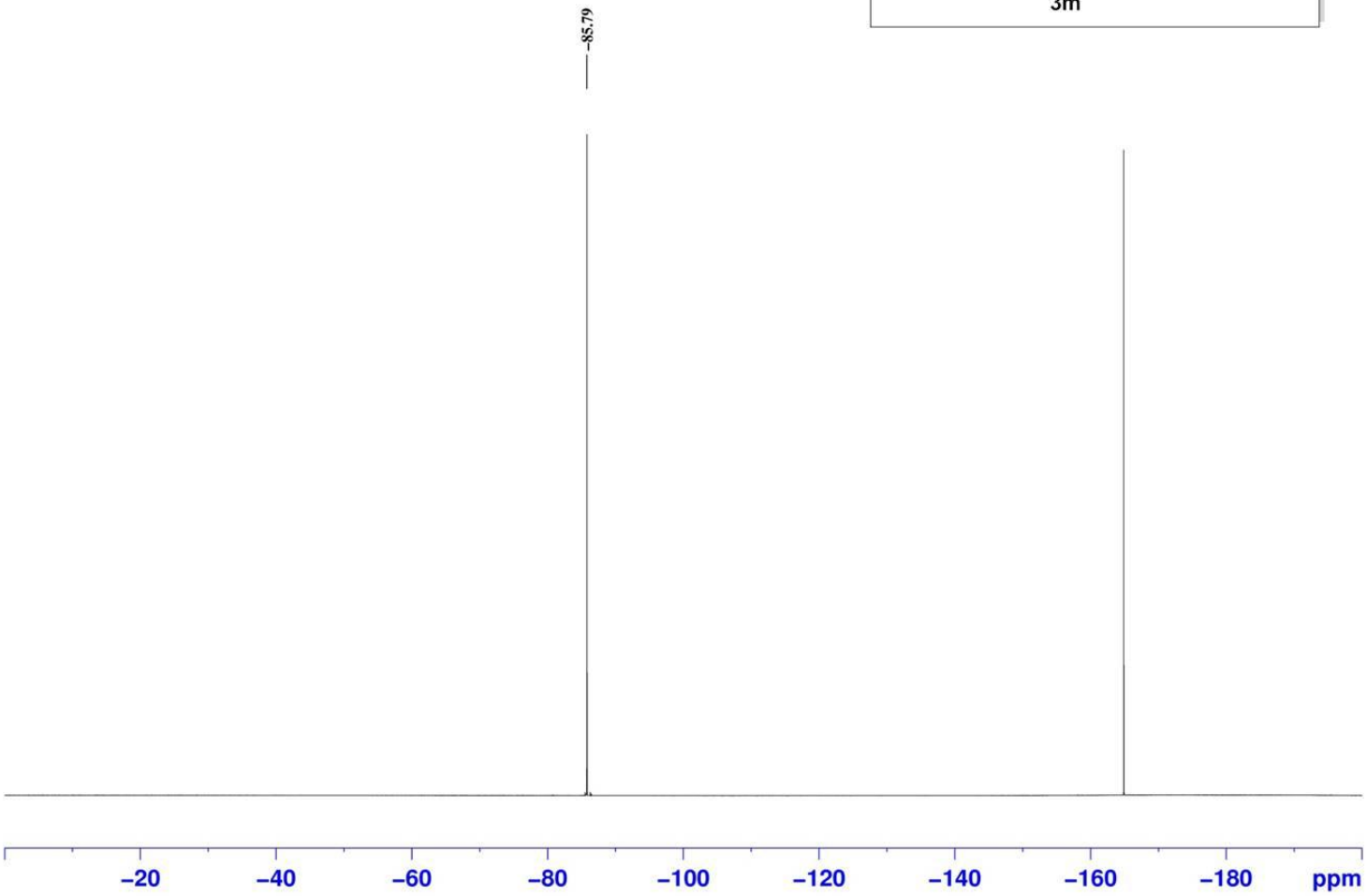




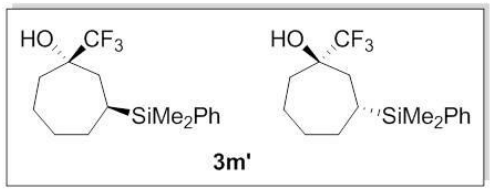
(1R,3S) & (1S,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cycloheptanol
377 MHz, CDCl3

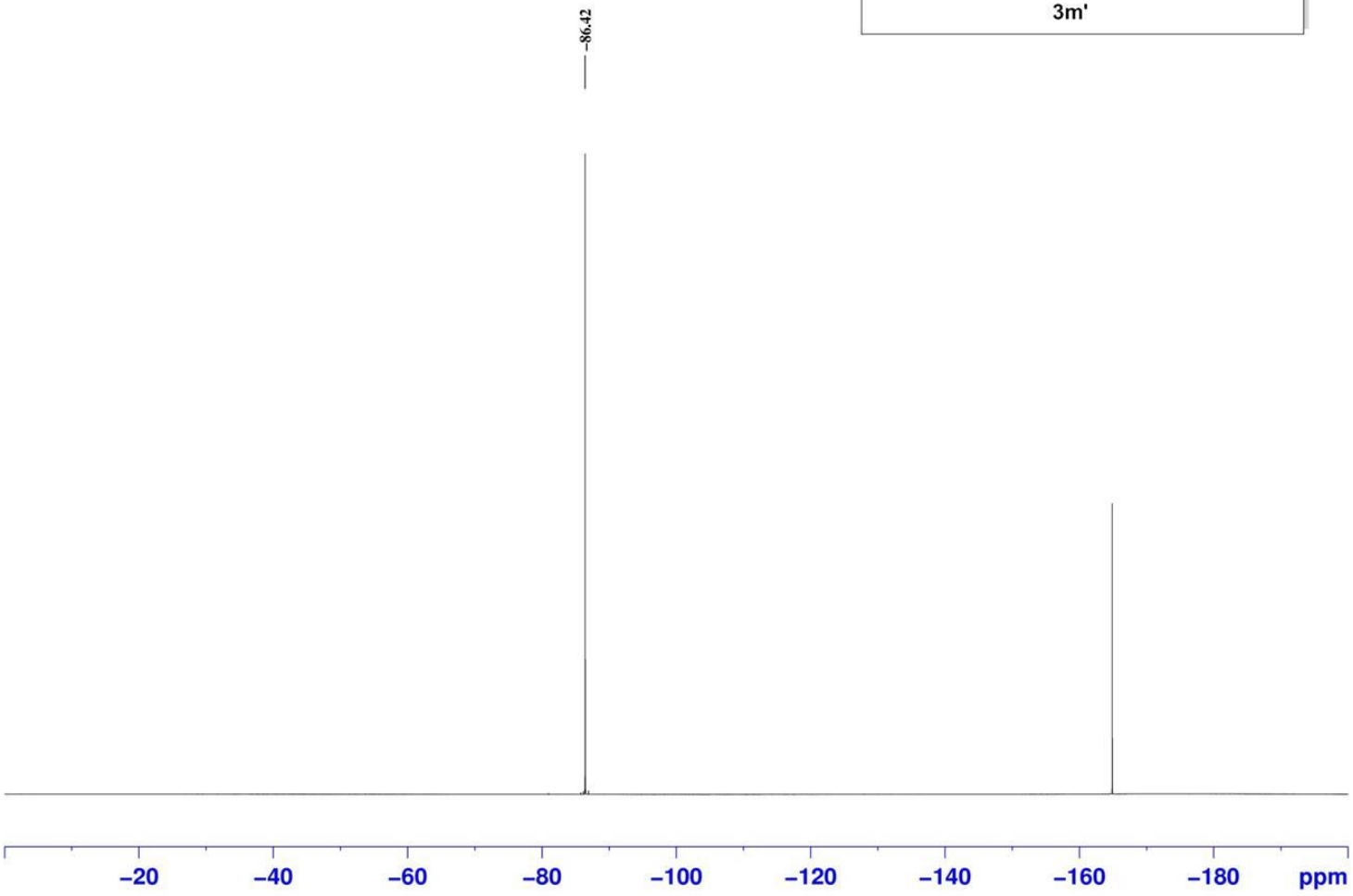


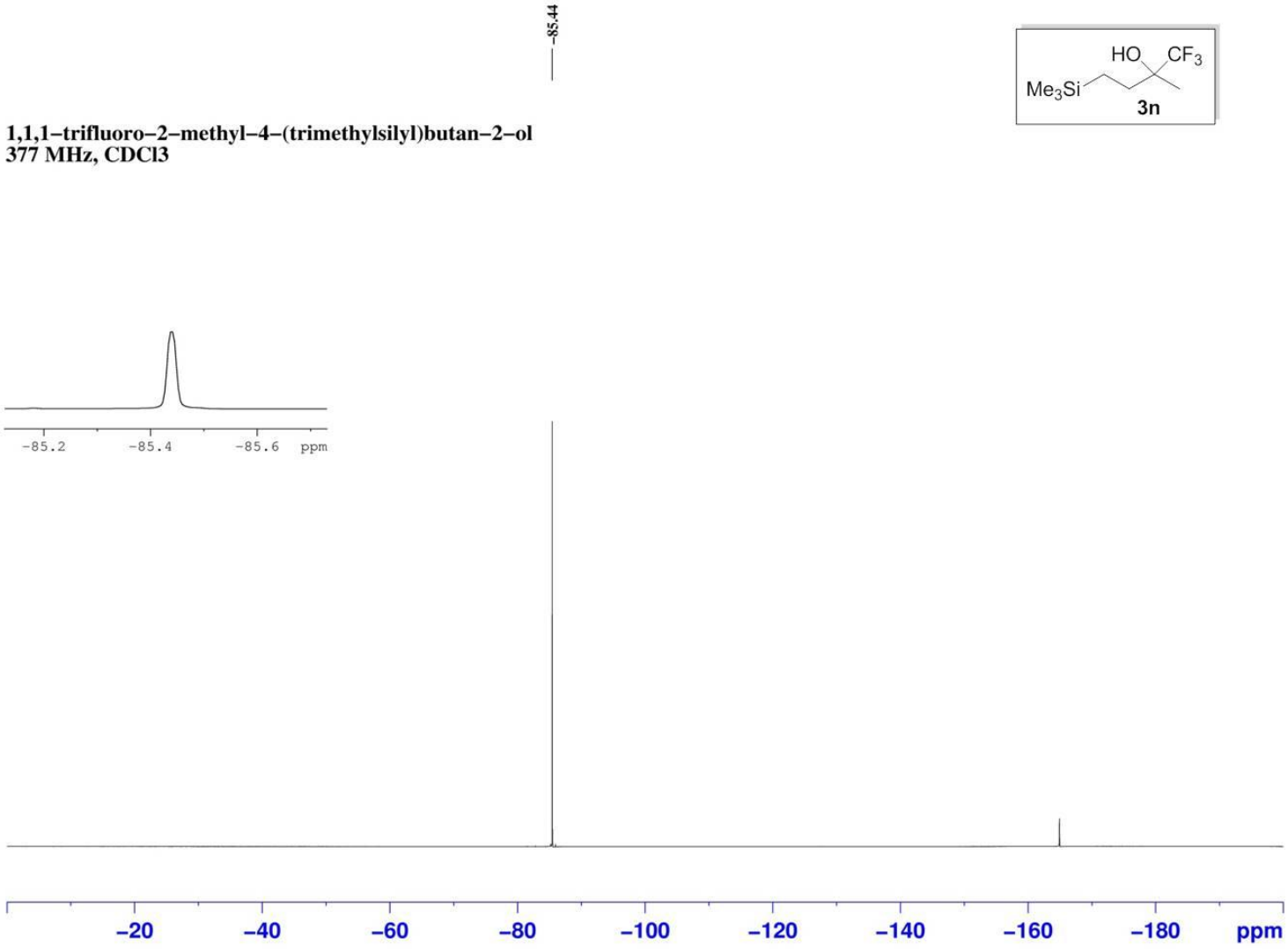
3m



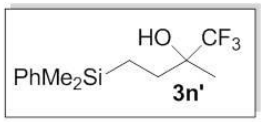
(1S,3S) & (1R,3R)−3−(dimethyl(phenyl)silyl)−1−(trifluoromethyl)cycloheptanol
377 MHz, CDCl3



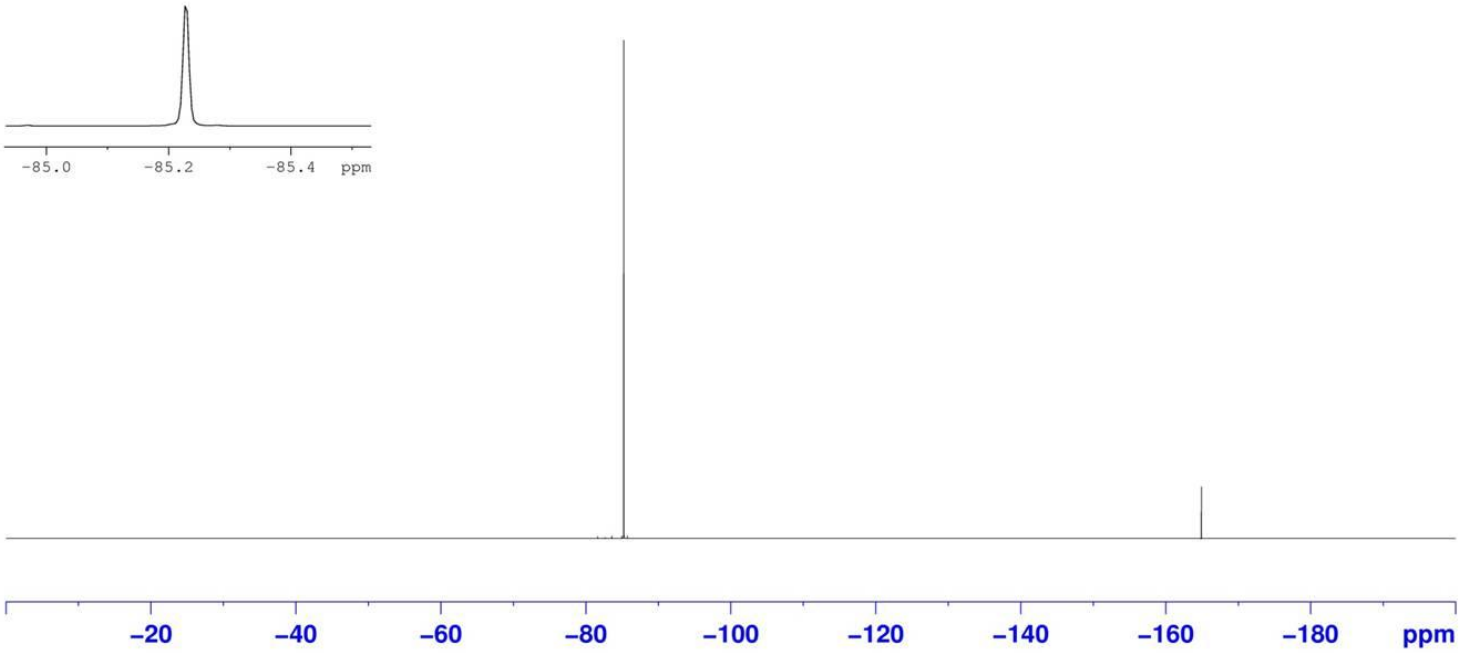


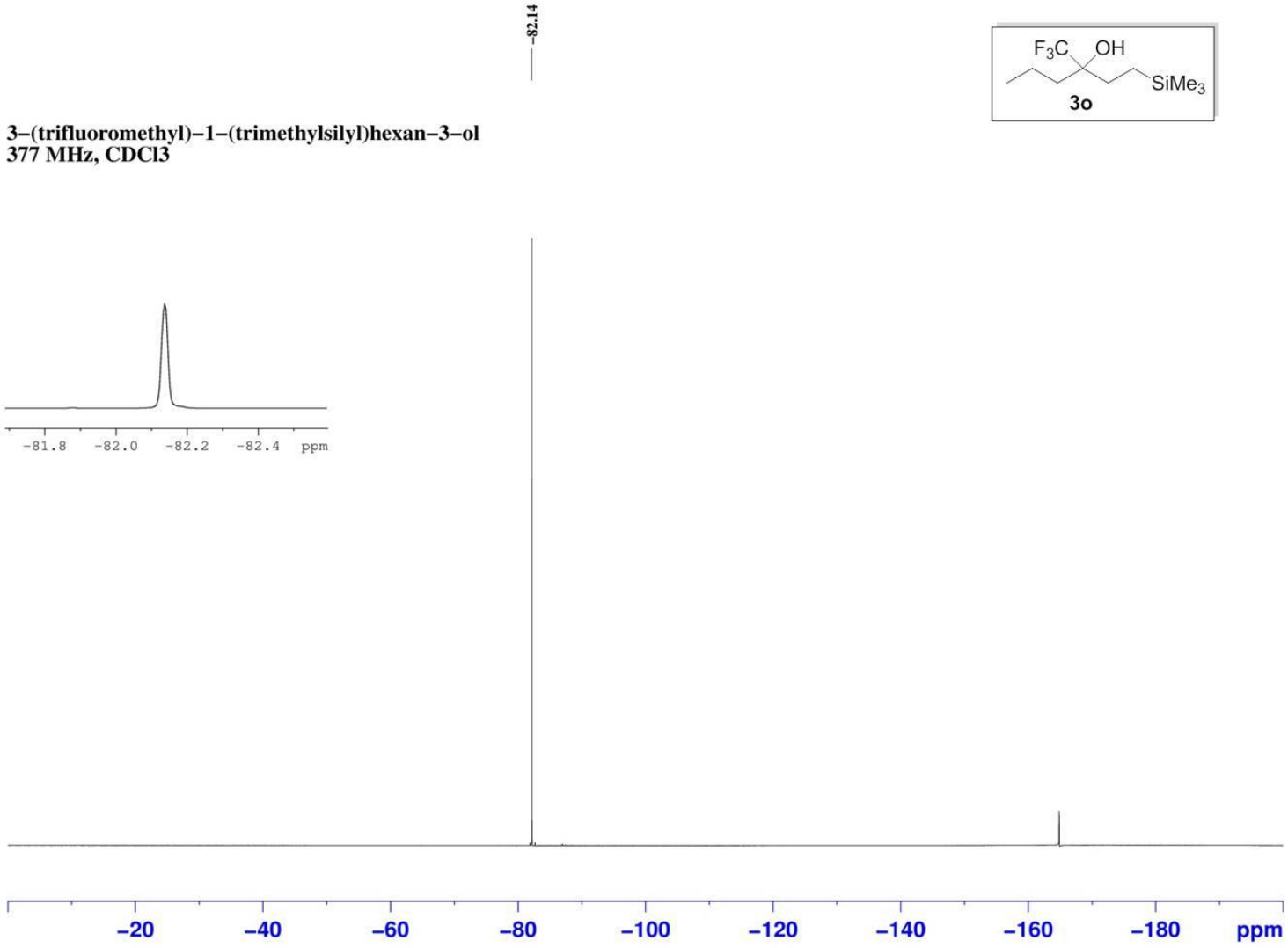

-85.44
HO
CF3
Me3Si
3n
1,1,1–trifluoro–2–methyl–4–(trimethylsilyl)butan–2–ol
377 MHz, CDCl3
-85.2
-85.4
-85.6
ppm
–20
–40
–60
–80
–100
–120
–140
–160
–180
ppm

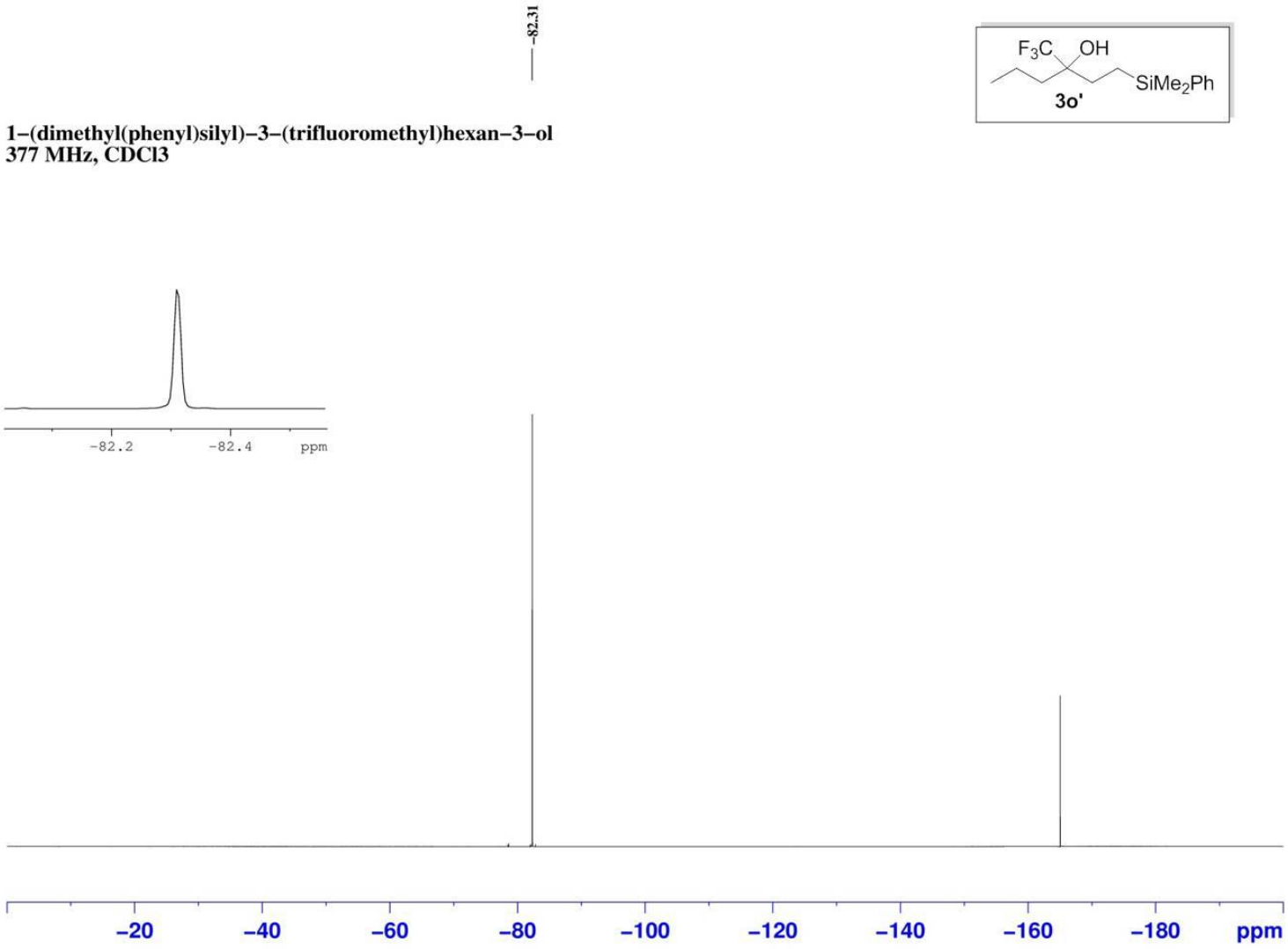
-85.23

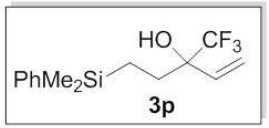


4–(dimethyl(phenyl)silyl)–1,1,1–trifluoro–2–methylbutan–2–ol
377 MHz, CDCl3



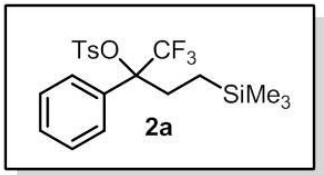

-82.14
F3C
OH
SiMe3
3o
3–(trifluoromethyl)–1–(trimethylsilyl)hexan–3–ol
377 MHz, CDCl3
-81.8
-82.0
-82.2
-82.4
ppm
–20
–40
–60
–80
–100
–120
–140
–160
–180
ppm

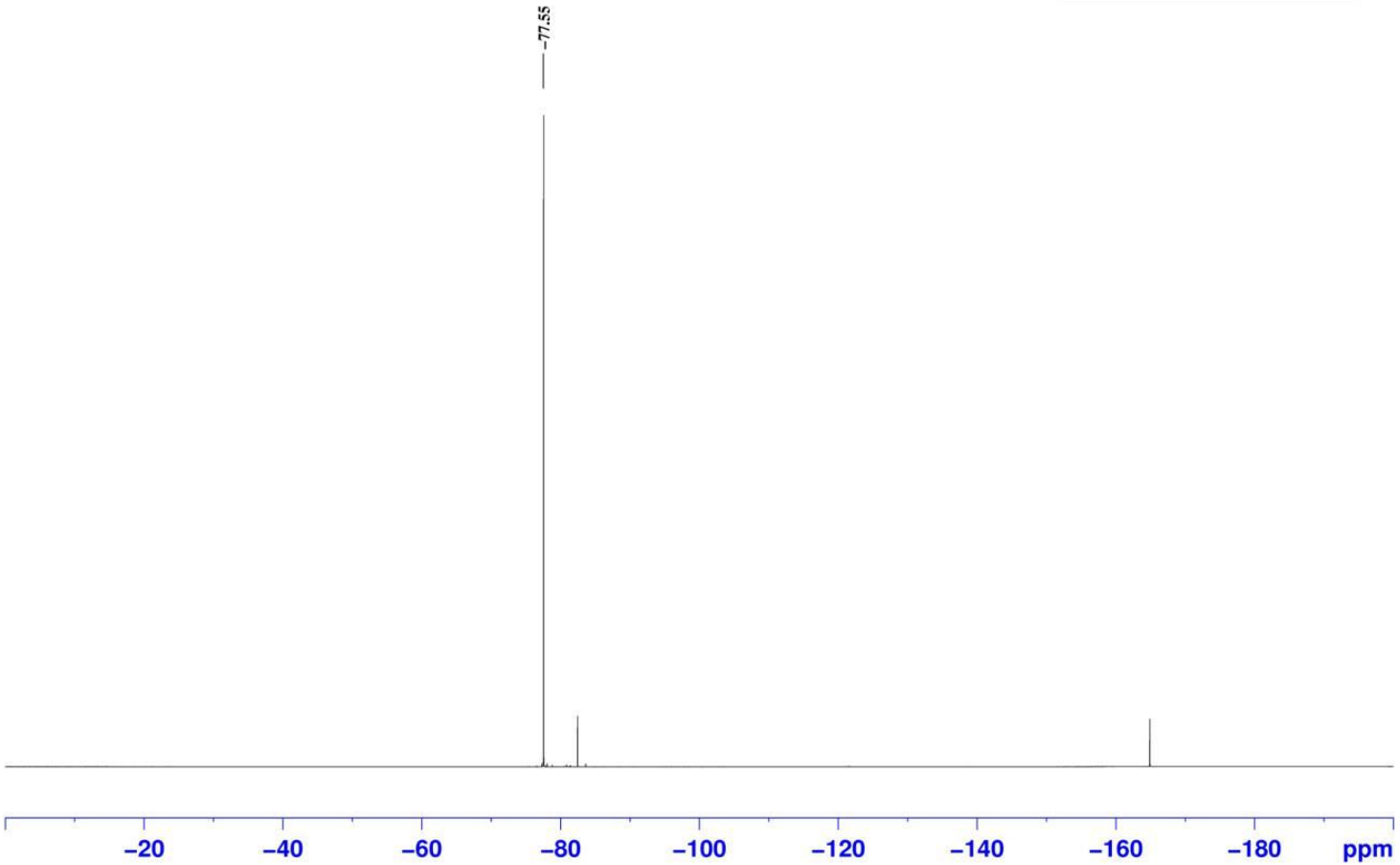

-82.31
F3C
OH
SiMe2Ph
3o'
1-(dimethyl(phenyl)silyl)-3-(trifluoromethyl)hexan-3-ol
377 MHz, CDCl3
-82.2
-82.4
ppm
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm



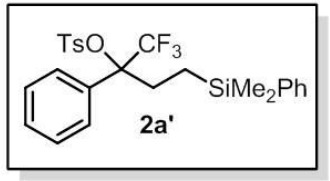
5–(dimethyl(phenyl)silyl)–3–(trifluoromethyl)pent–1–en–3–ol
377 MHz, CDCl3

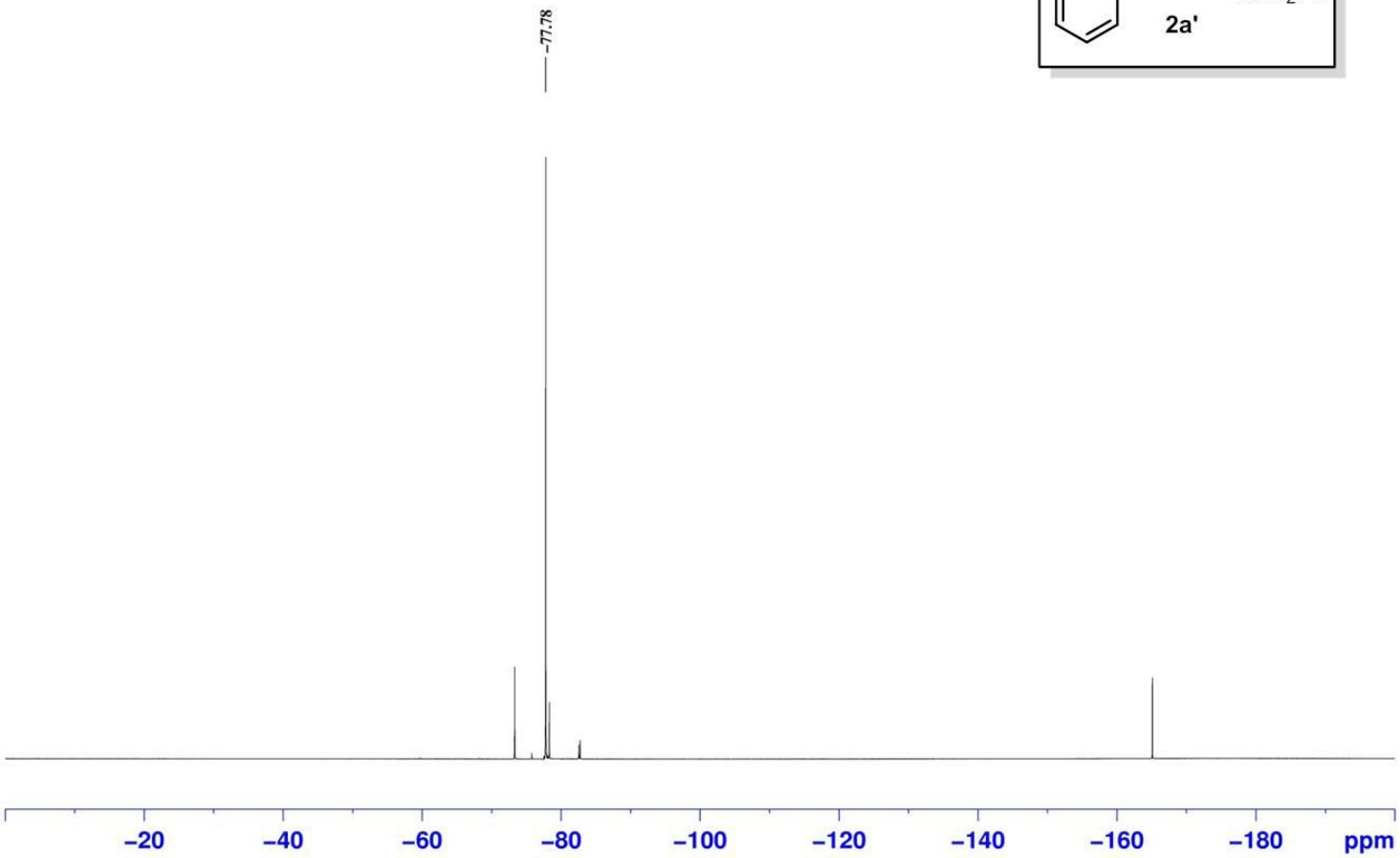
1,1,1−trifluoro−2−phenyl−4−(trimethylsilyl)butan−2−yl 4−methylbenzenesulfonate
377 MHz, CDCl3



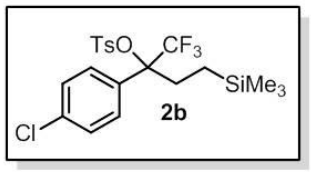


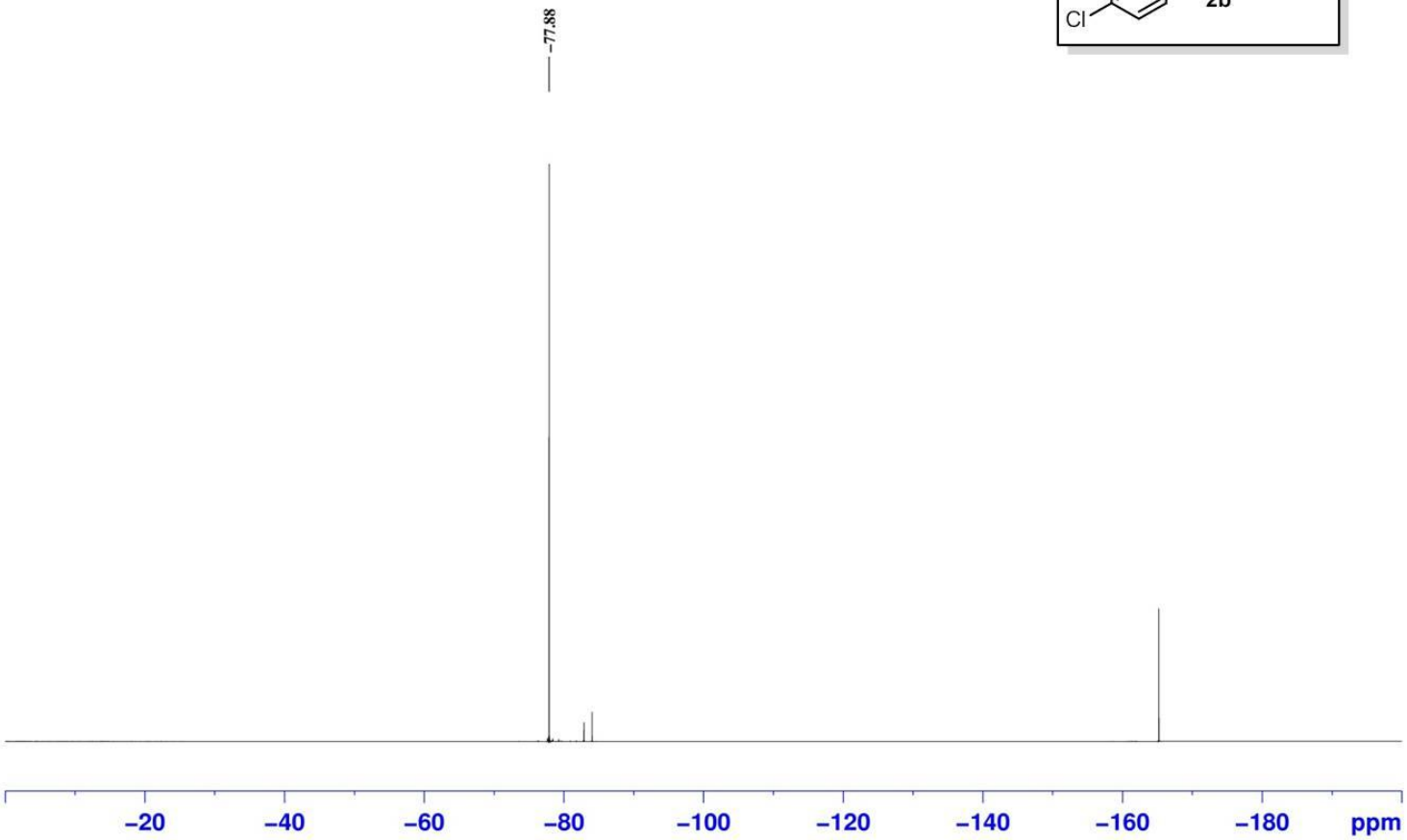
4–(dimethyl(phenyl)silyl)–1,1,1–trifluoro–2–phenylbutan–2–yl 4–methylbenzenesulfonate
377 MHz, CDCl3



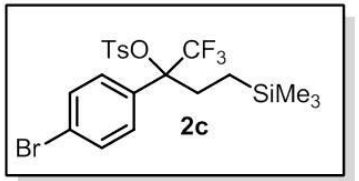


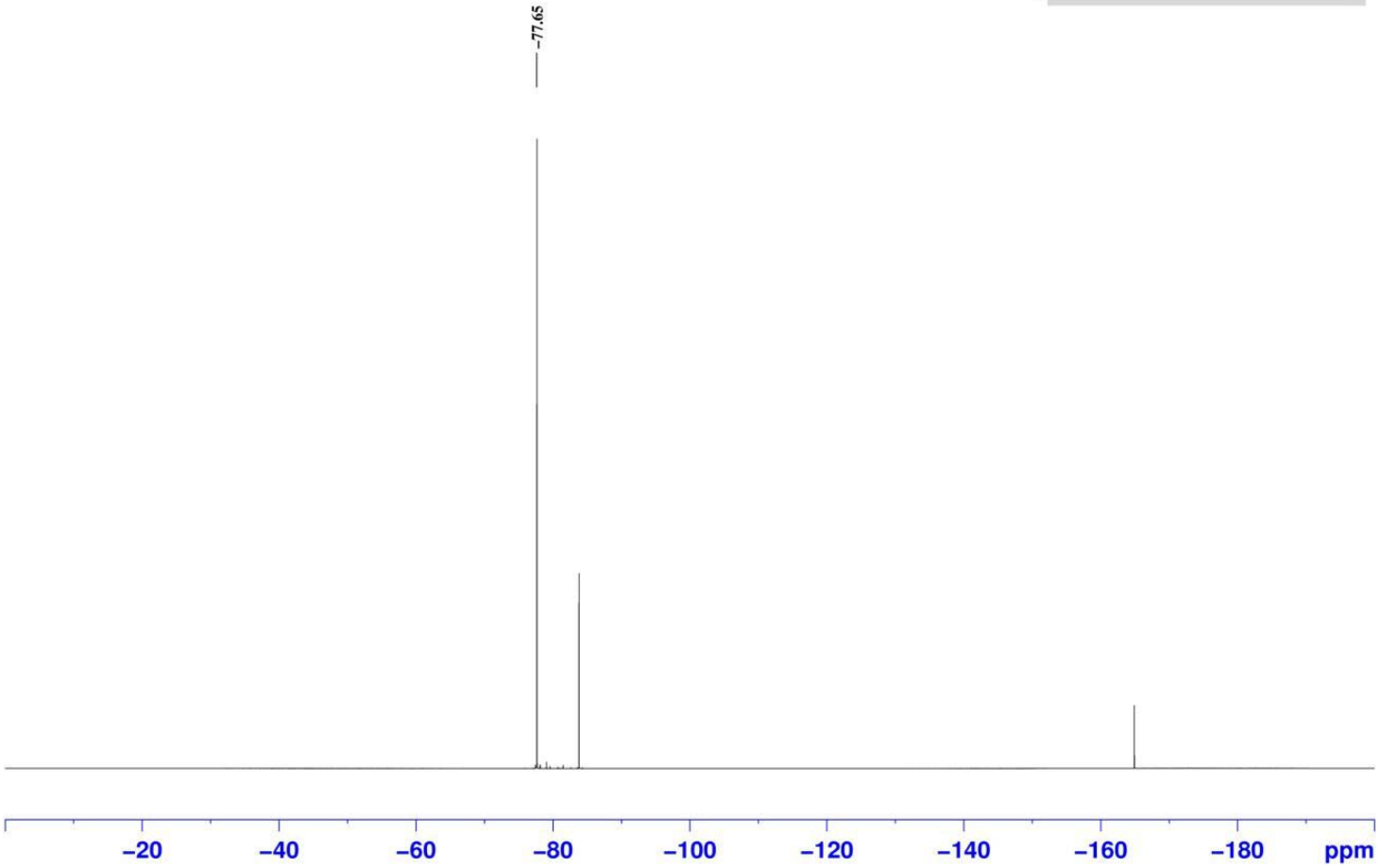
2–(4–chlorophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
377 MHz, CDCl3



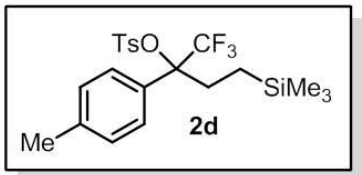


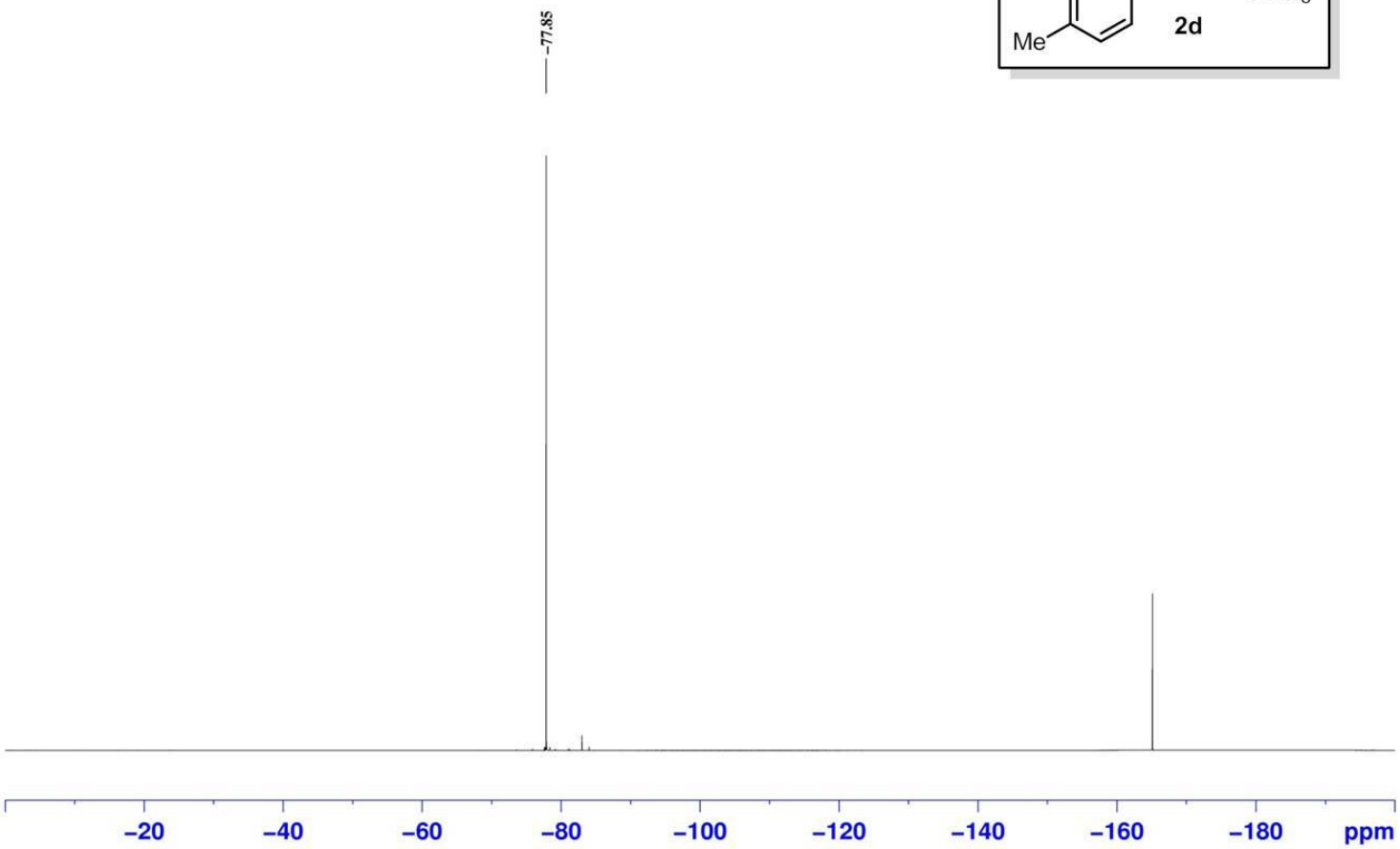
2–(4–bromophenyl)–1,1,1–trifluoro–4–(trimethylsilyl)butan–2–yl 4–methylbenzenesulfonate
377 MHz, CDCl3



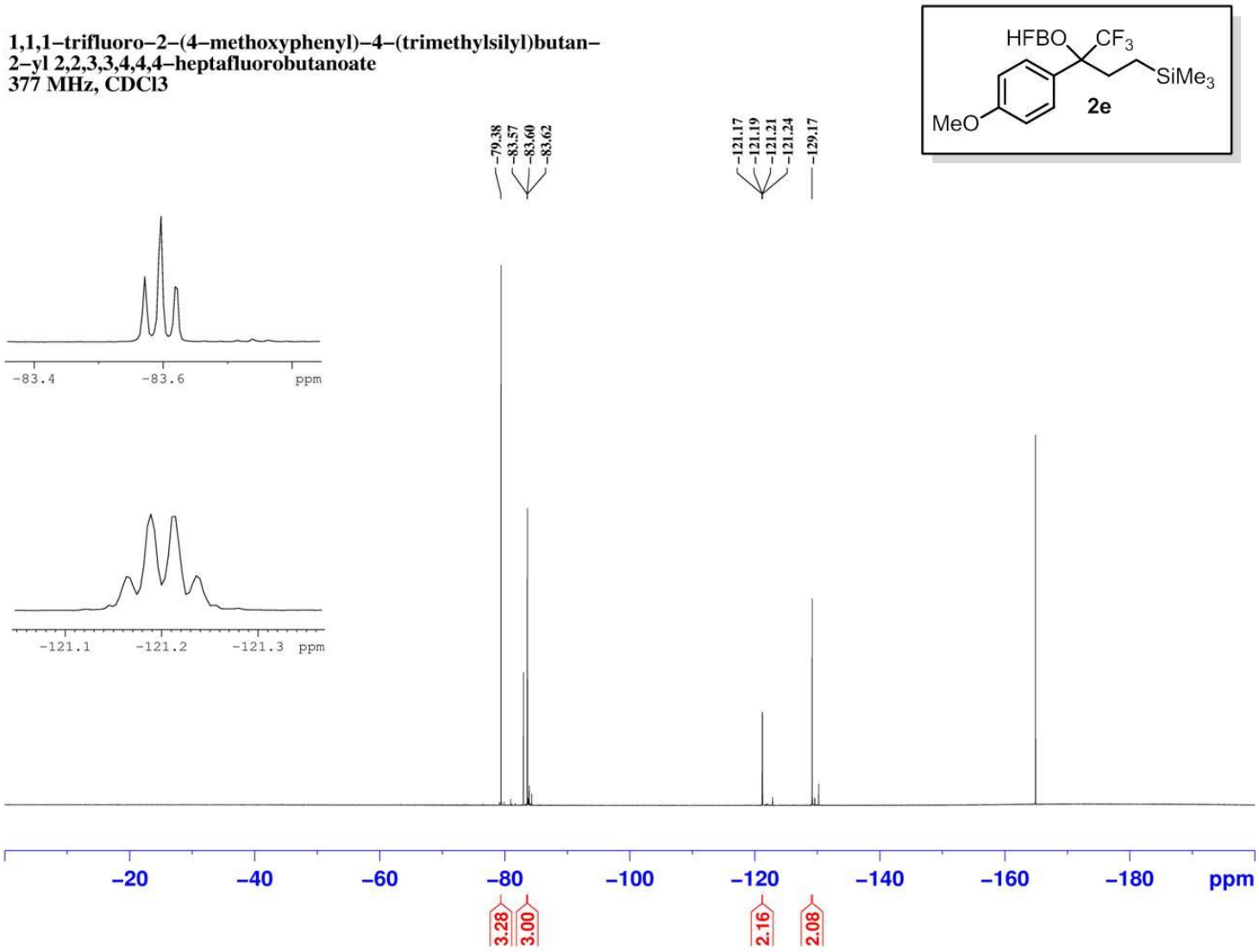


1,1,1−trifluoro−2−(p−tolyl)−4−(trimethylsilyl)butan−2−yl 4−methylbenzenesulfonate
377 MHz, CDCl3

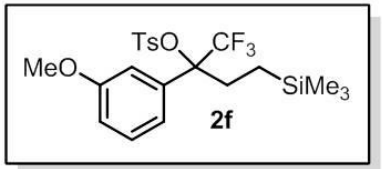




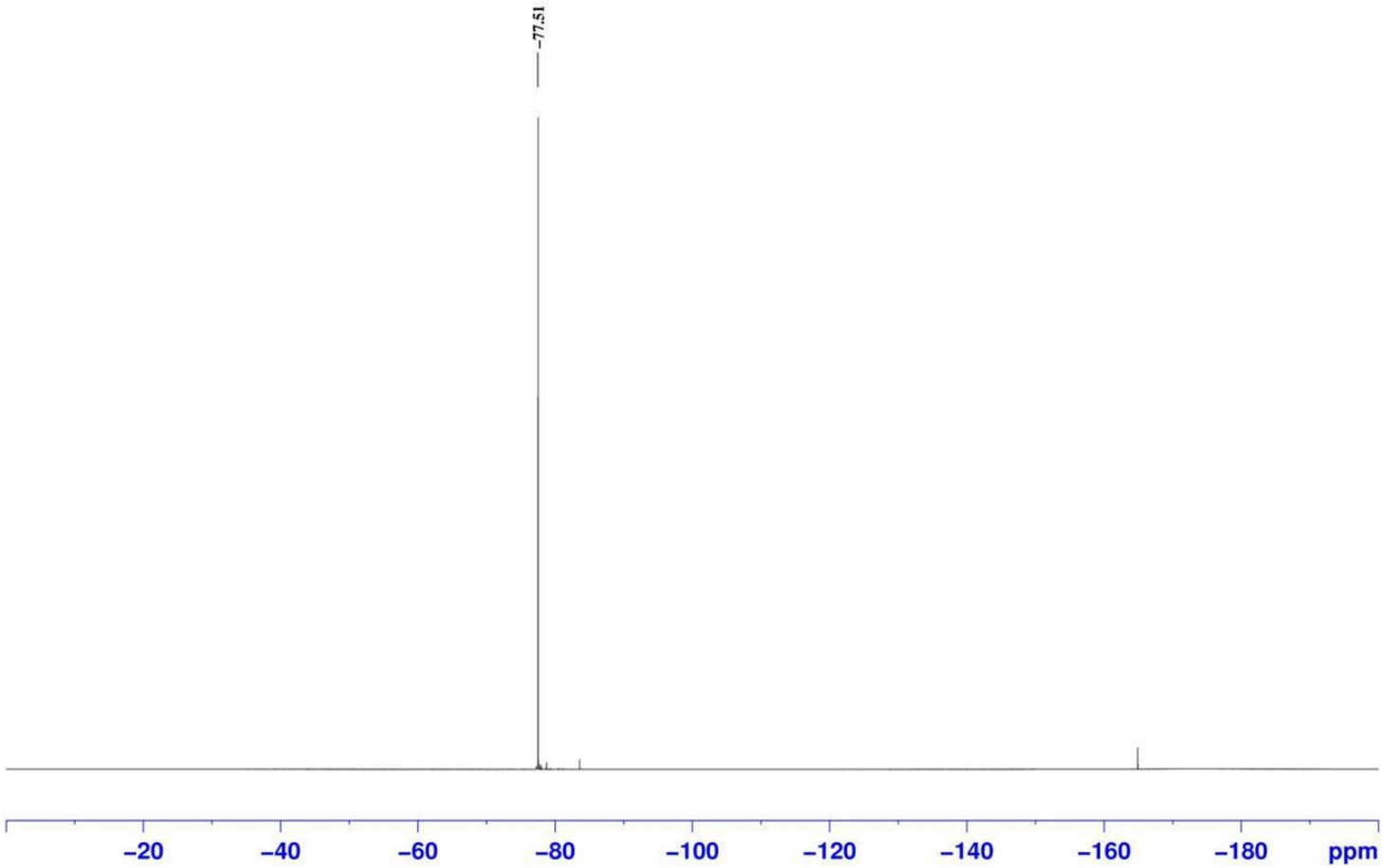
1,1,1−trifluoro−2−(4−methoxyphenyl)−4−(trimethylsilyl)butan−2−yl 2,2,3,3,4,4,4−heptafluorobutanoate
377 MHz, CDCl3



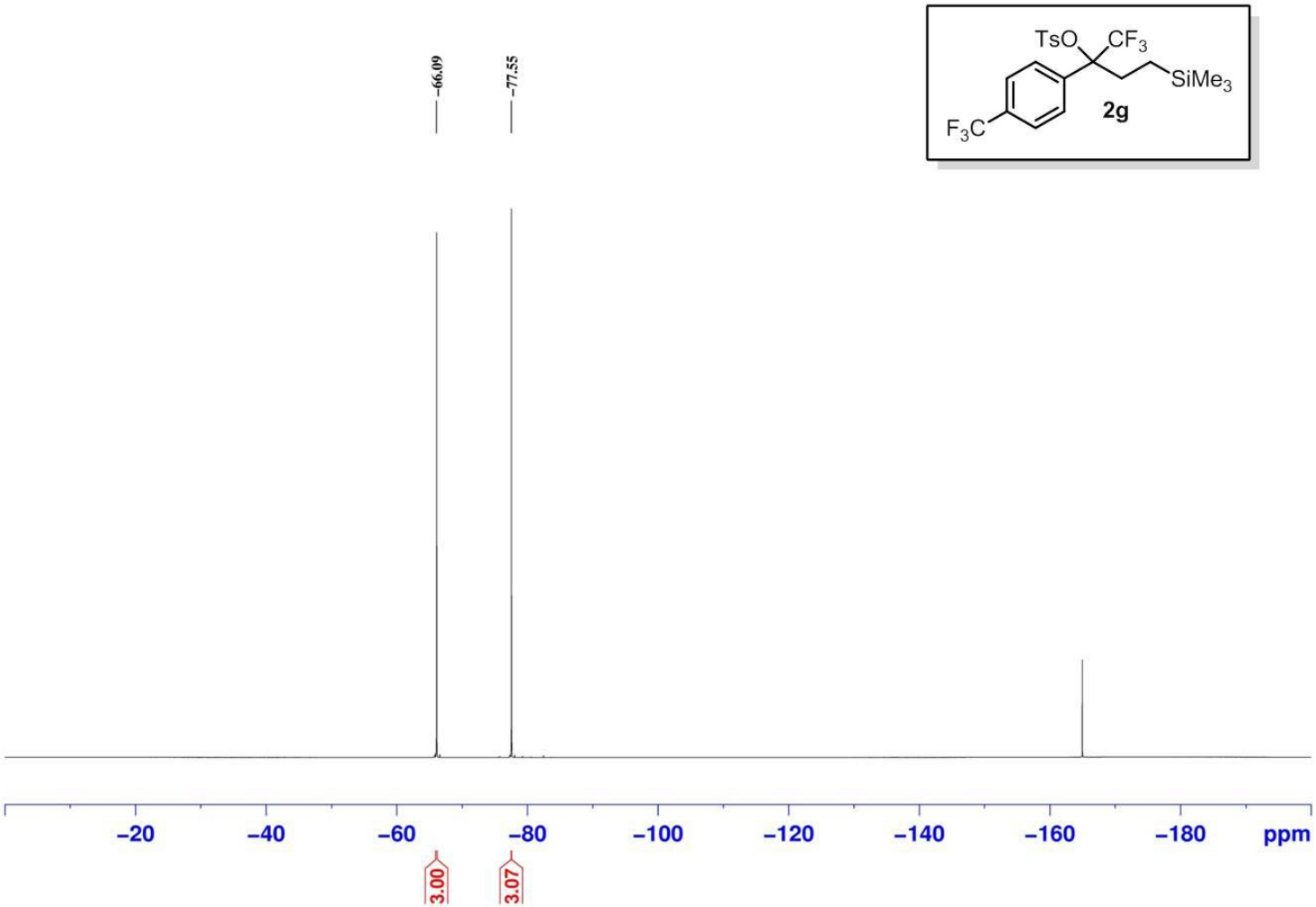
1,1,1−trifluoro−2−(3−methoxyphenyl)−4−(trimethylsilyl)butan−2−yl 4−methylbenzenesulfonate
377 MHz, CDCl3



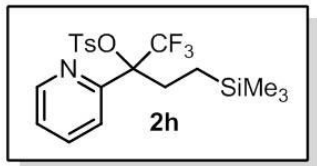
2f



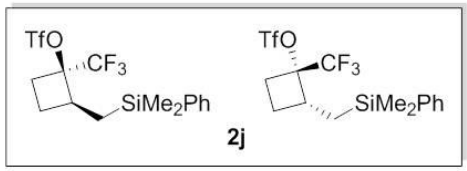
1,1,1−trifluoro−2−(4−(trifluoromethyl)phenyl)−4−(trimethylsilyl)butan−2−yl 4−methylbenzenesulfonate
377 MHz, CDCl3



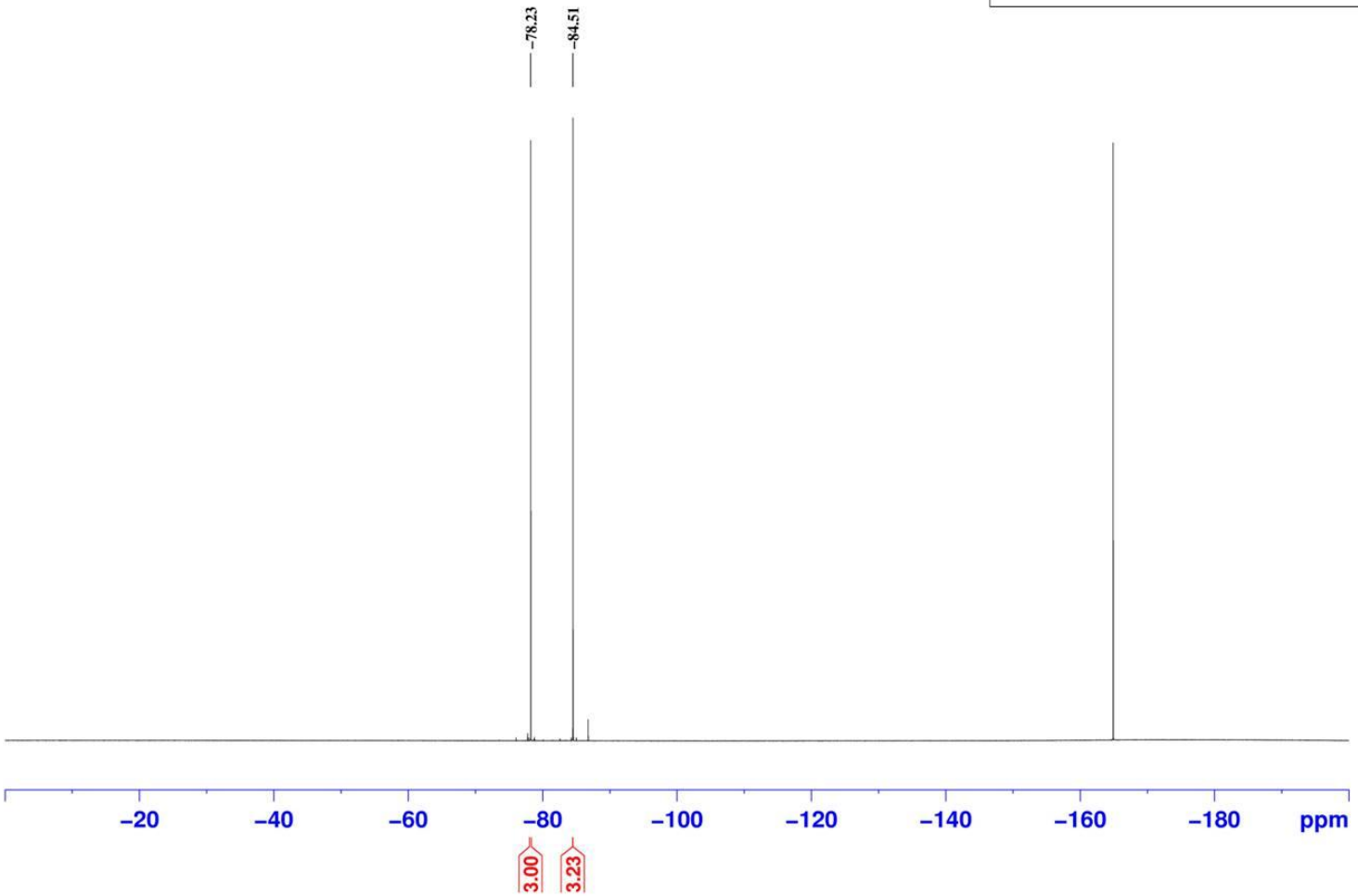
1,1,1−trifluoro−2−(pyridin−2−yl)−4−(trimethylsilyl)butan−2−yl 4−methylbenzenesulfonate
377 MHz, CDCl3



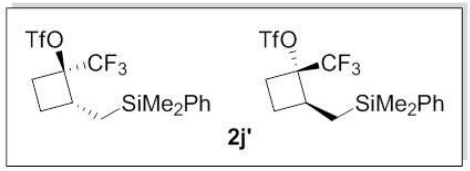
(1R,2S) & (1S,2R)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutyl trifluoromethanesulfonate
400 MHz, CDCl3

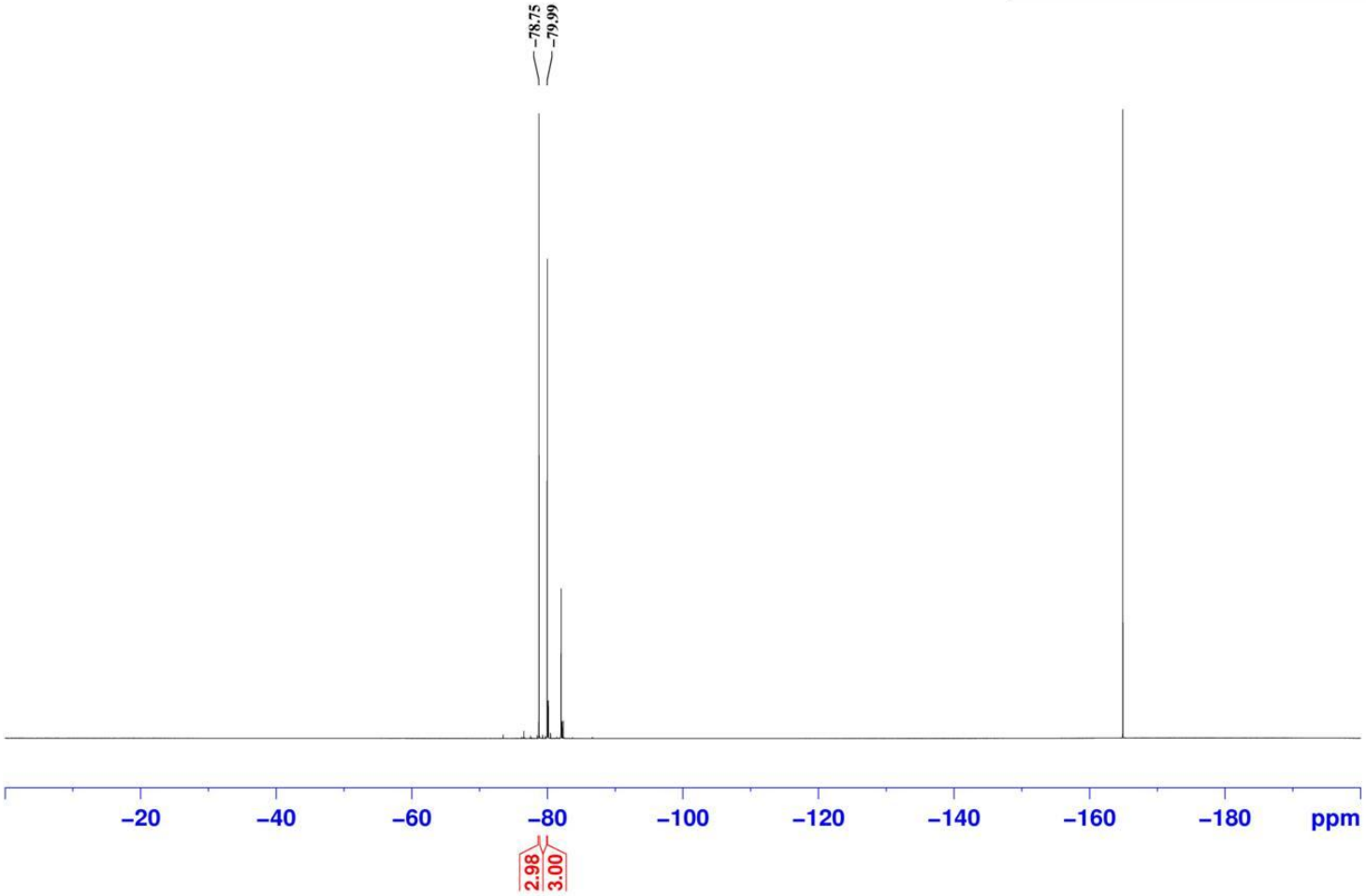


2j

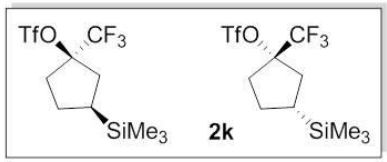


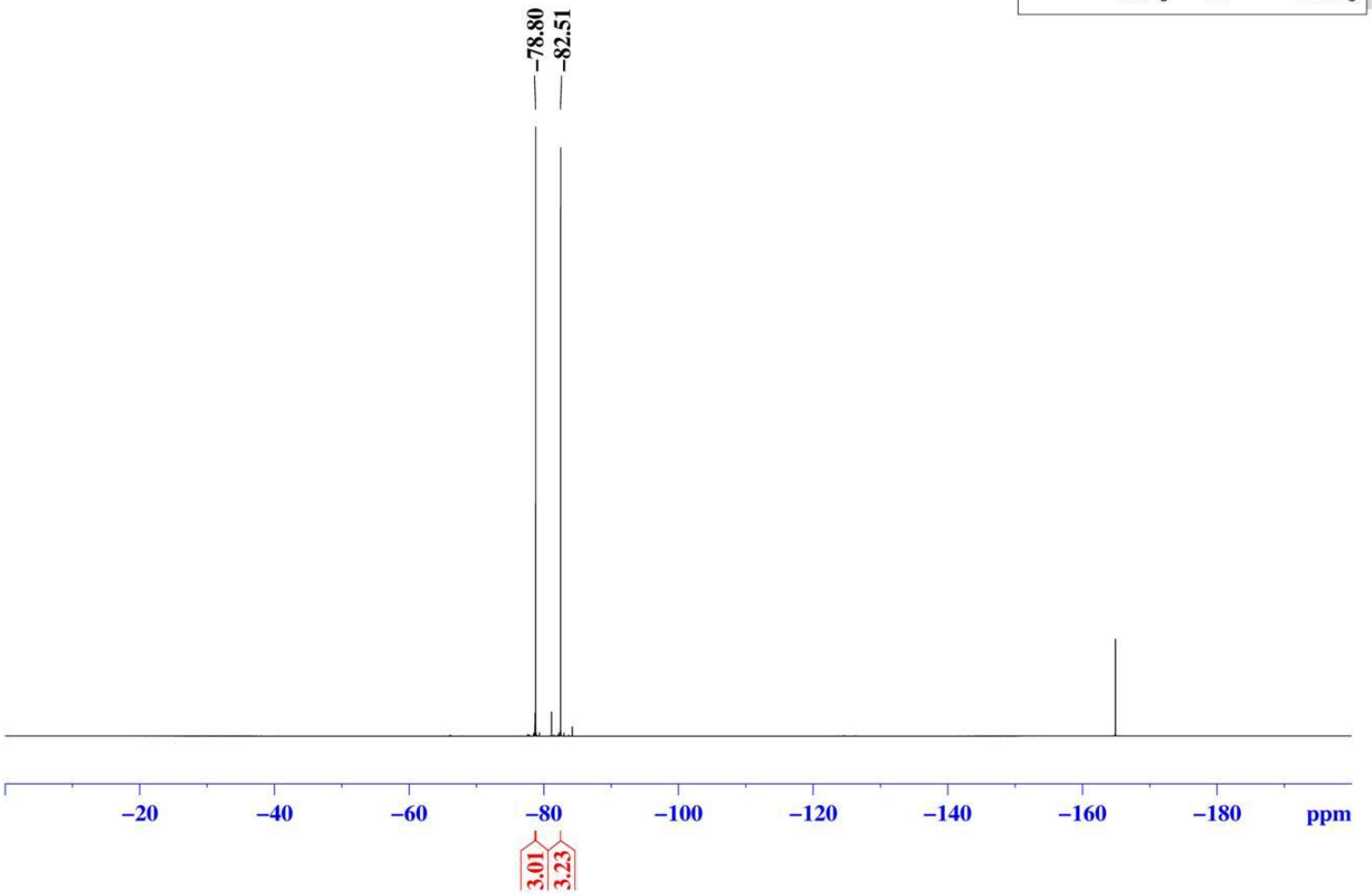
(1R,2R) & (1S,2S)−2−((dimethyl(phenyl)silyl)methyl)−1−(trifluoromethyl)cyclobutyl trifluoromethanesulfonate
400 MHz, CDCl3



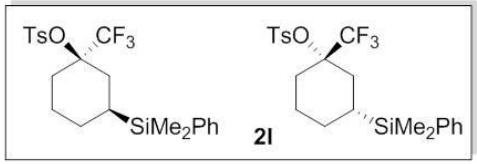


(1R,3S) & (1S,3R)−1−(trifluoromethyl)−3−(trimethylsilyl)cyclopentyl trifluoromethanesulfonate
377 MHz, CDCl3

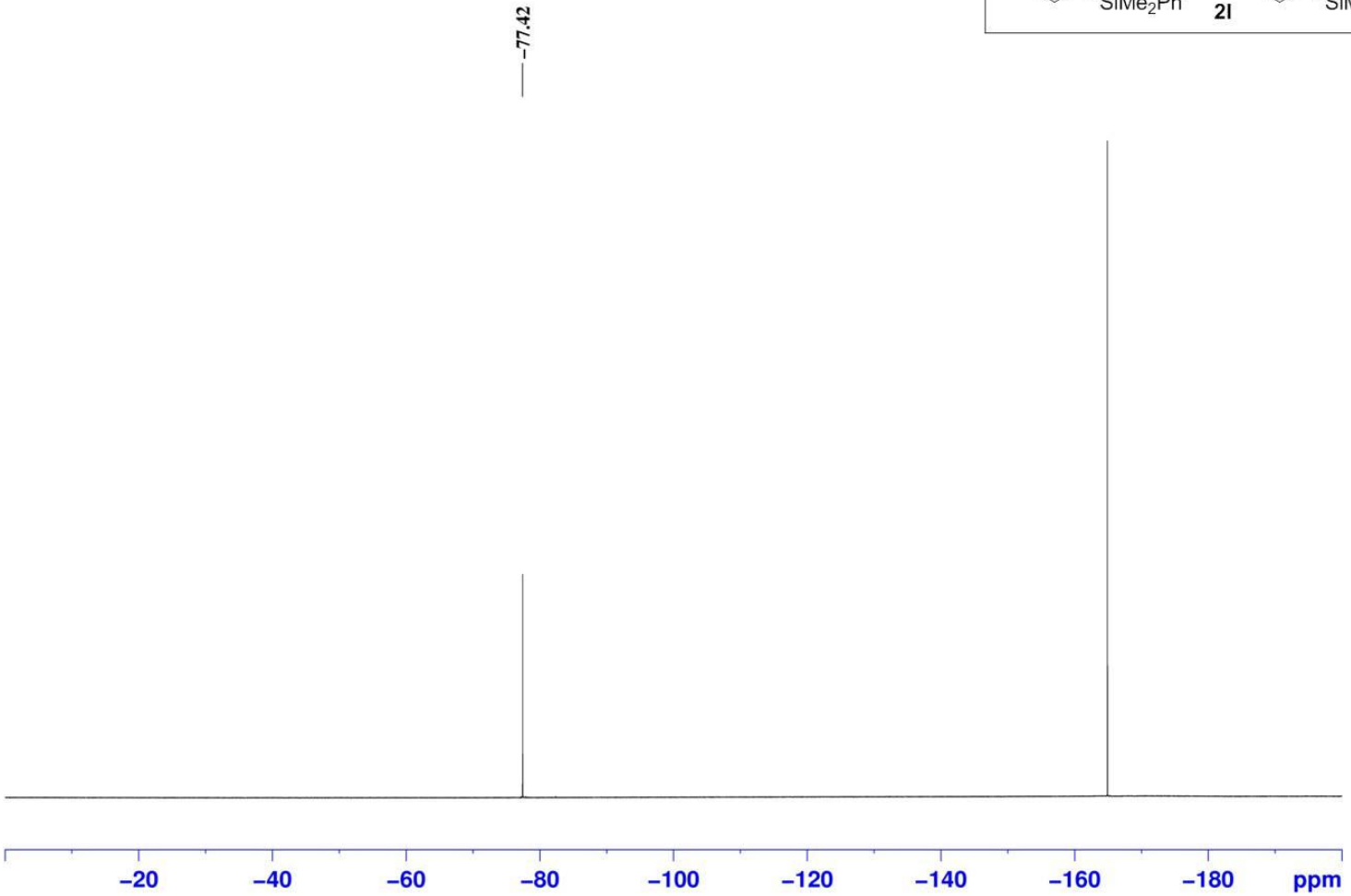




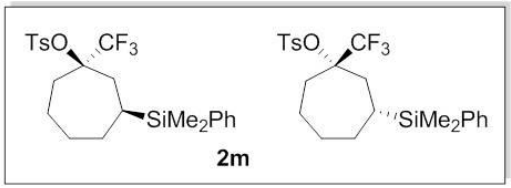
(1R,3S) & (1S,3R)– 3–(dimethyl(phenyl)silyl)–1–(trifluoromethyl)cyclohexyl 4–methylbenzenesulfonate
377 MHz, CDCl3



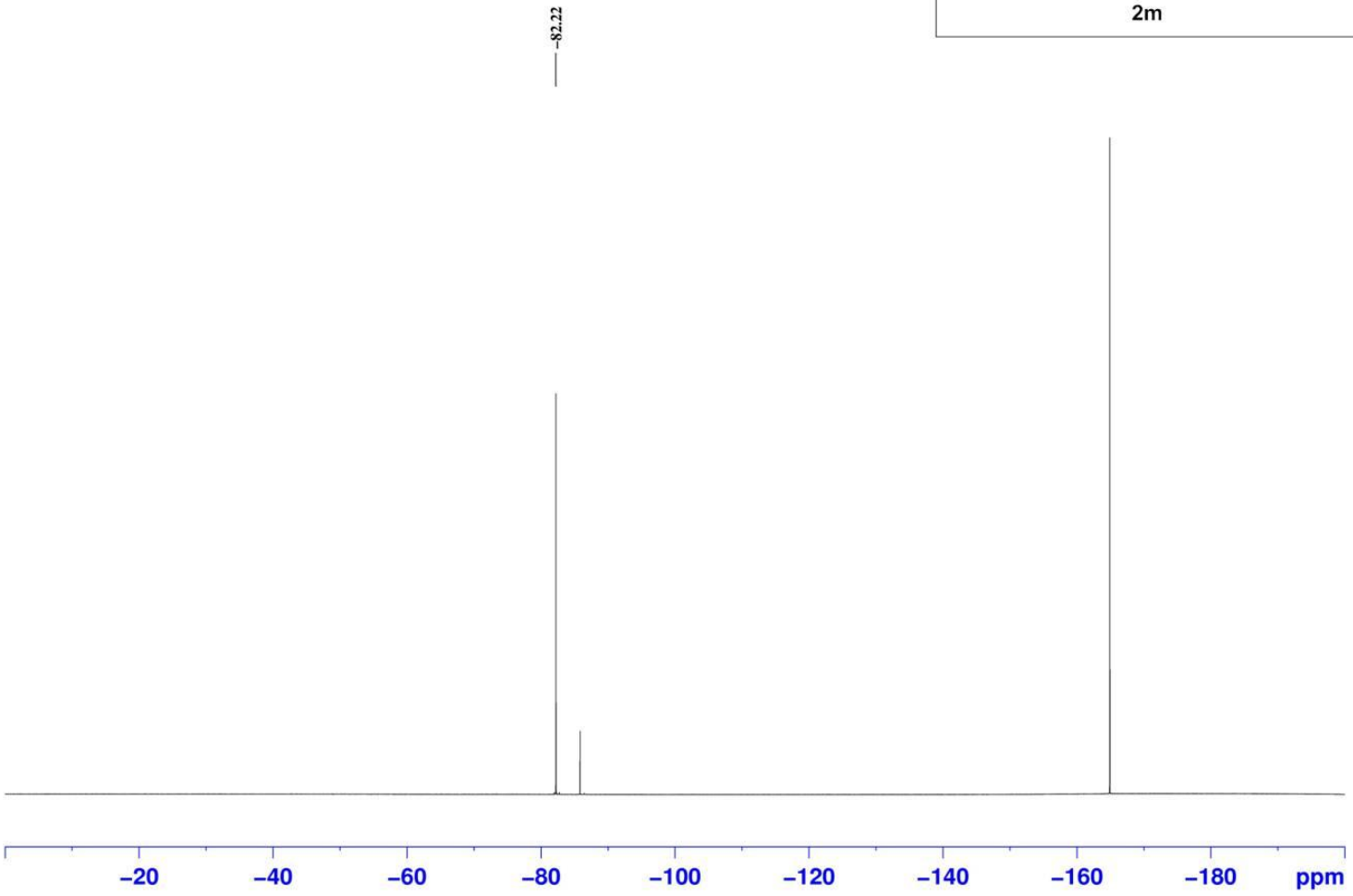
2l

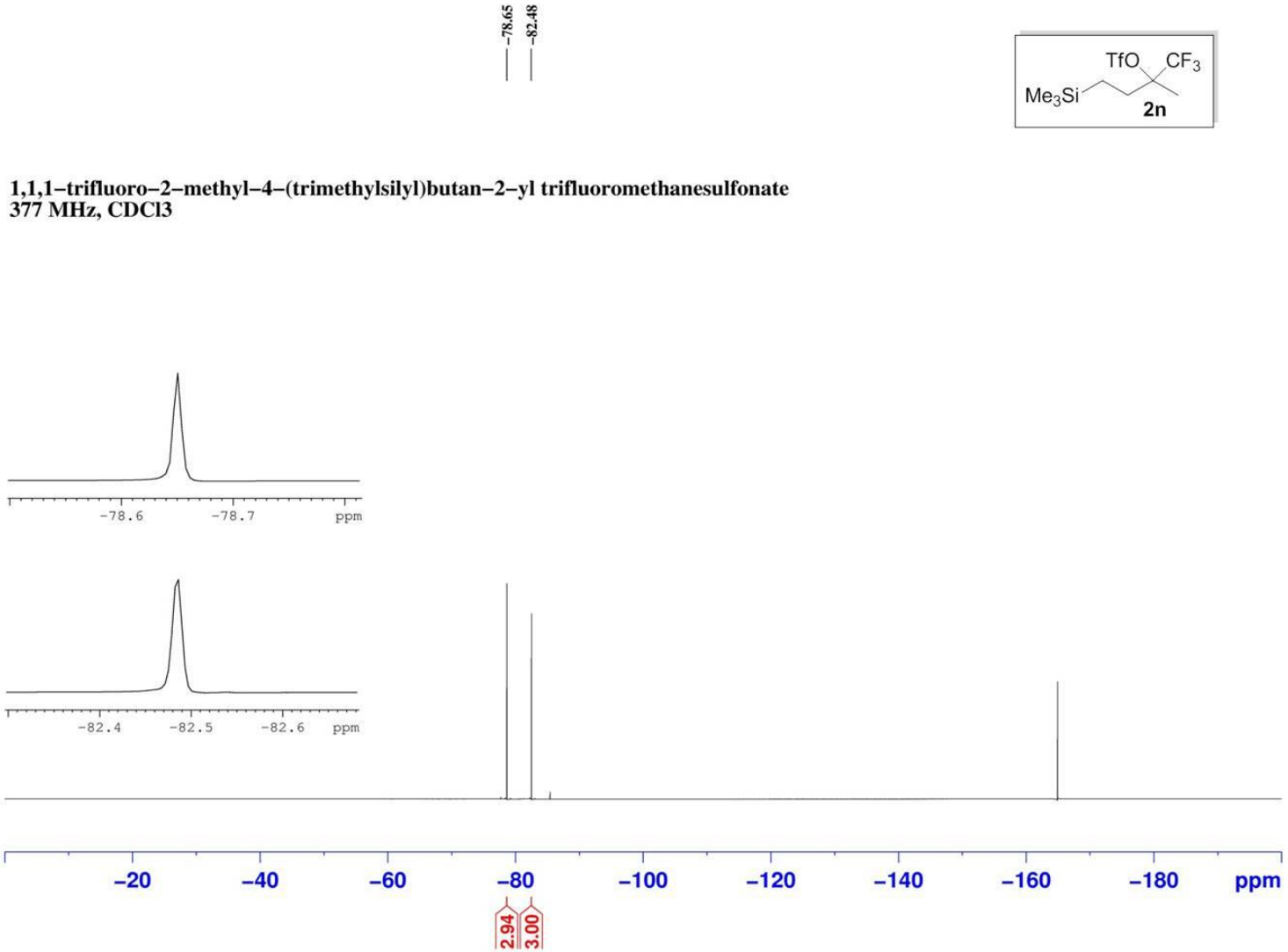


(1R,3S) & (1S,3R)– 3–(dimethyl(phenyl)silyl)–1–(trifluoromethyl)cycloheptyl 4–methylbenzenesulfonate
400 MHz, CDCl3

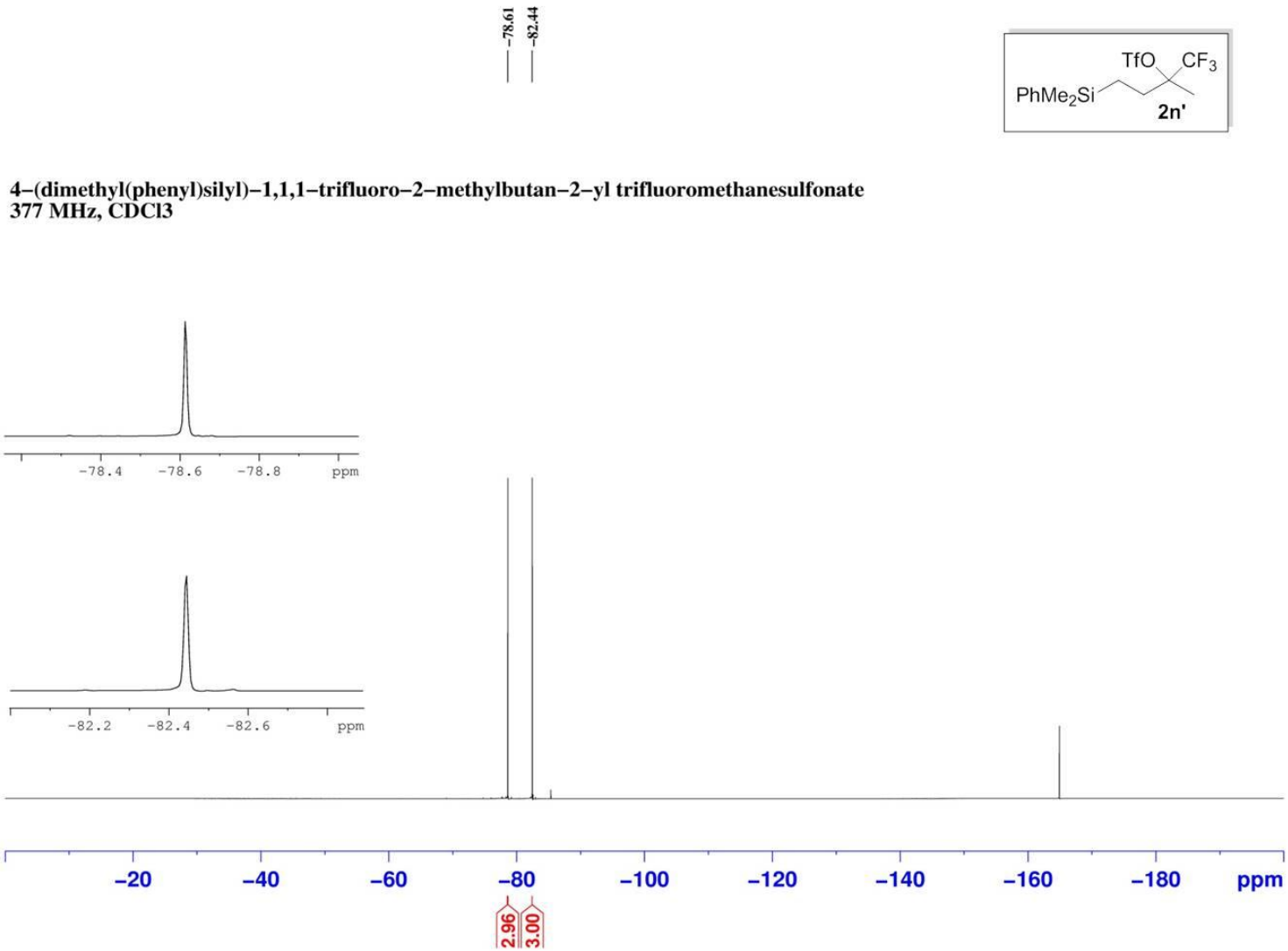


2m

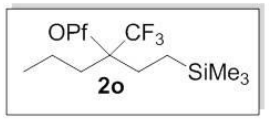


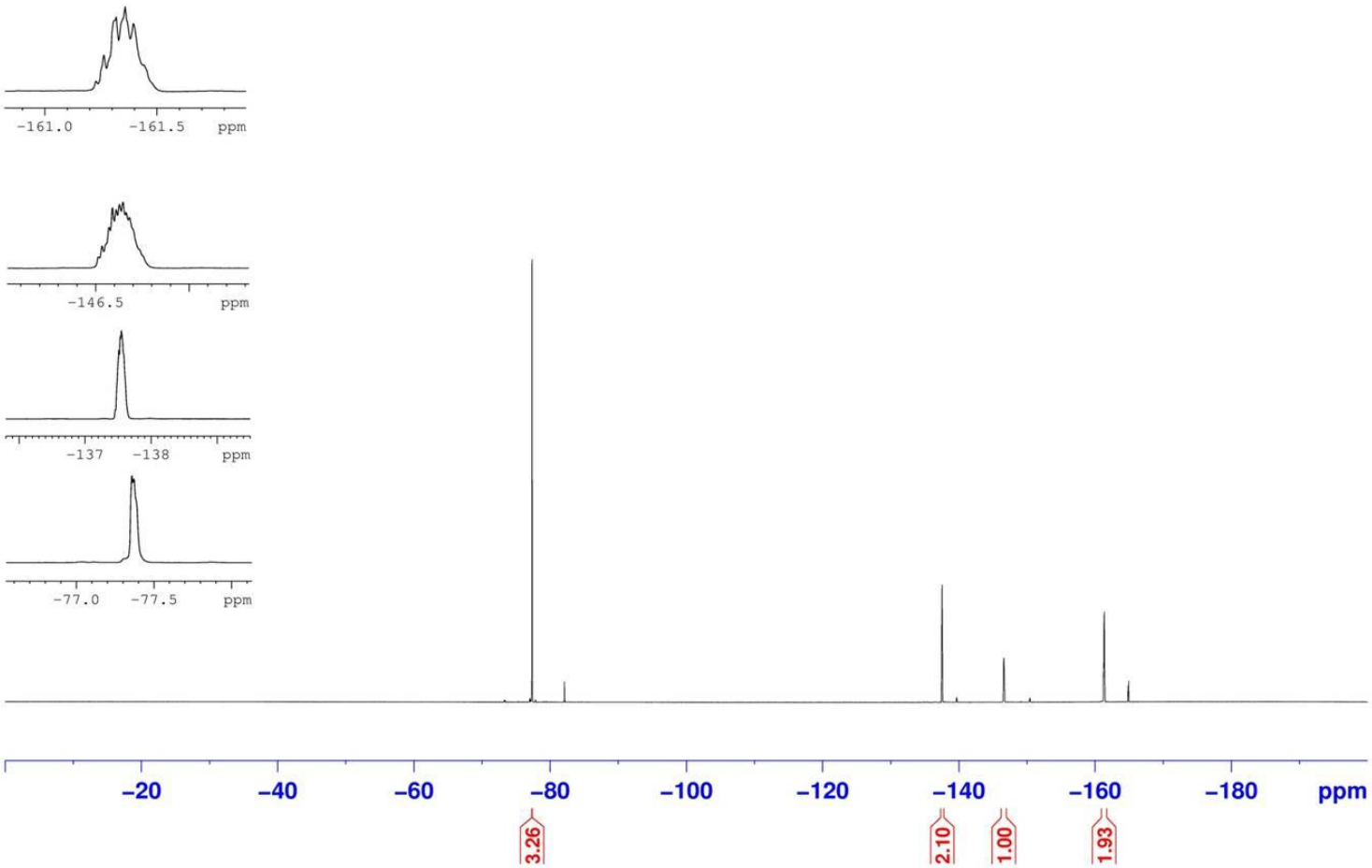


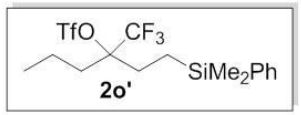
1,1,1–trifluoro–2–methyl–4–(trimethylsilyl)butan–2–yl trifluoromethanesulfonate
377 MHz, CDCl3


-78.61
-82.44
TfO
CF3
PhMe2Si
2n'
4–(dimethyl(phenyl)silyl)–1,1,1–trifluoro–2–methylbutan–2–yl trifluoromethanesulfonate
377 MHz, CDCl3
-78.4
-78.6
-78.8
ppm
-82.2
-82.4
-82.6
ppm
–20
–40
–60
–80
–100
–120
–140
–160
–180
ppm
2.96
3.00

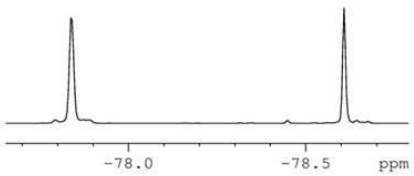
3–(trifluoromethyl)–1–(trimethylsilyl)hexan–3–yl 2,3,4,5,6–pentafluorobenzenesulfonate
377 MHz, CDCl3

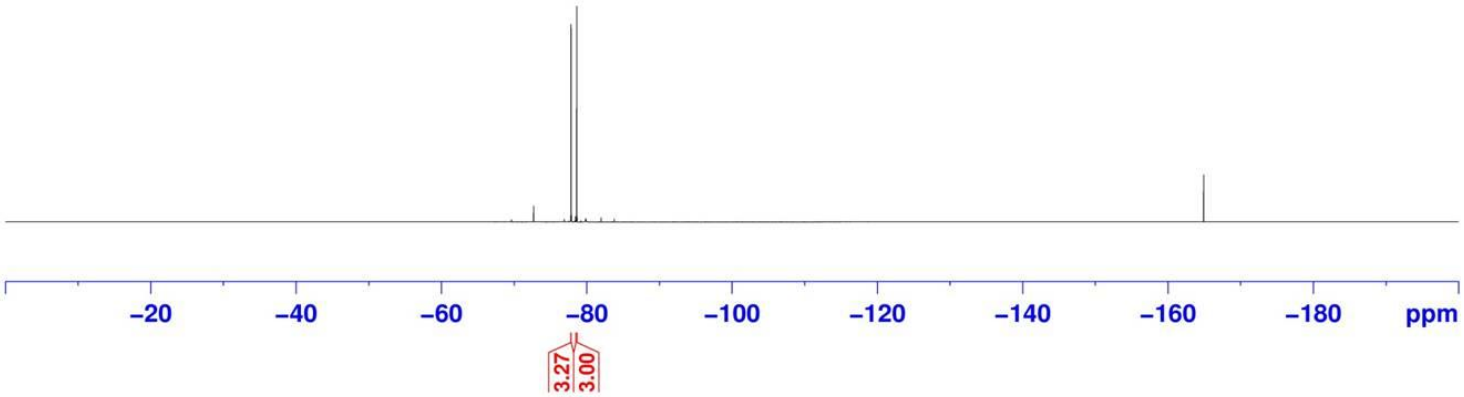




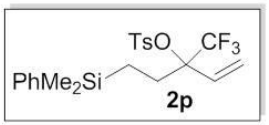


1–(dimethyl(phenyl)silyl)–3–(trifluoromethyl)hexan–3–yl trifluoromethanesulfonate
377 MHz, CDCl3

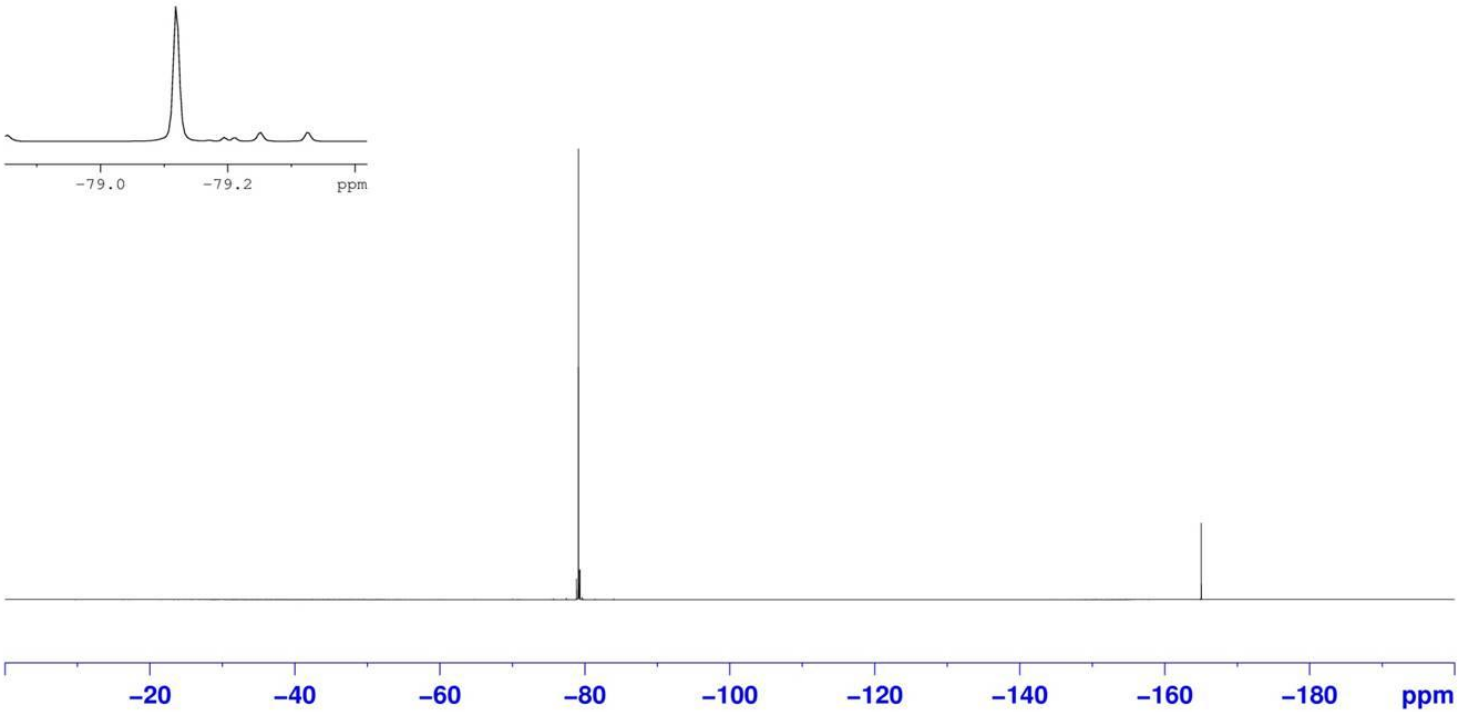




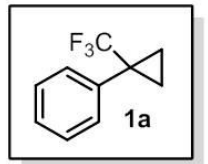
-79.12

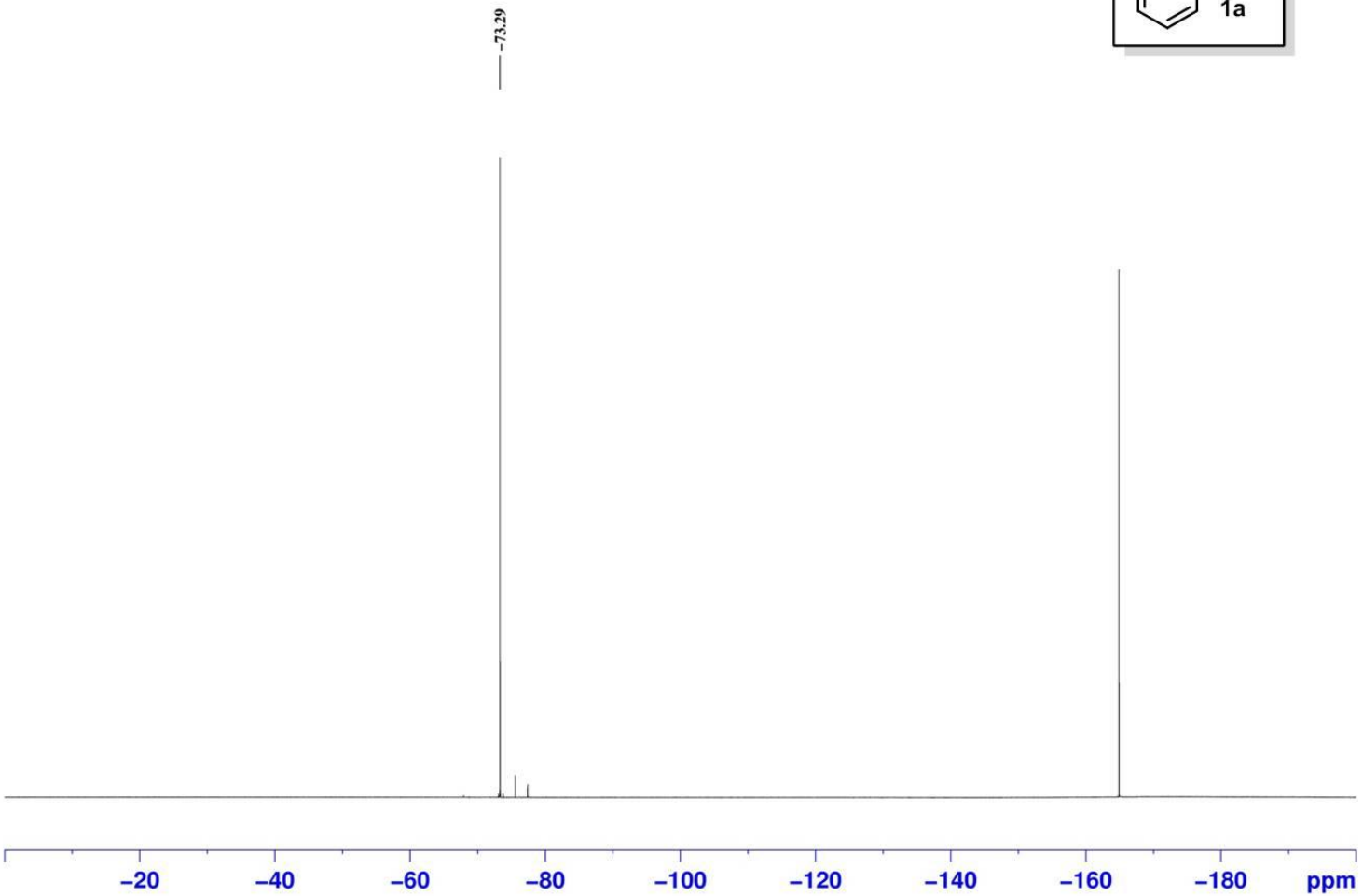


5–(dimethyl(phenyl)silyl)–3–(trifluoromethyl)pent–1–en–3–yl 4–methylbenzenesulfonate
377 MHz, CDCl3

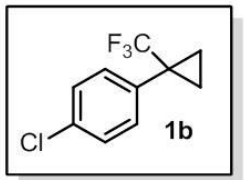


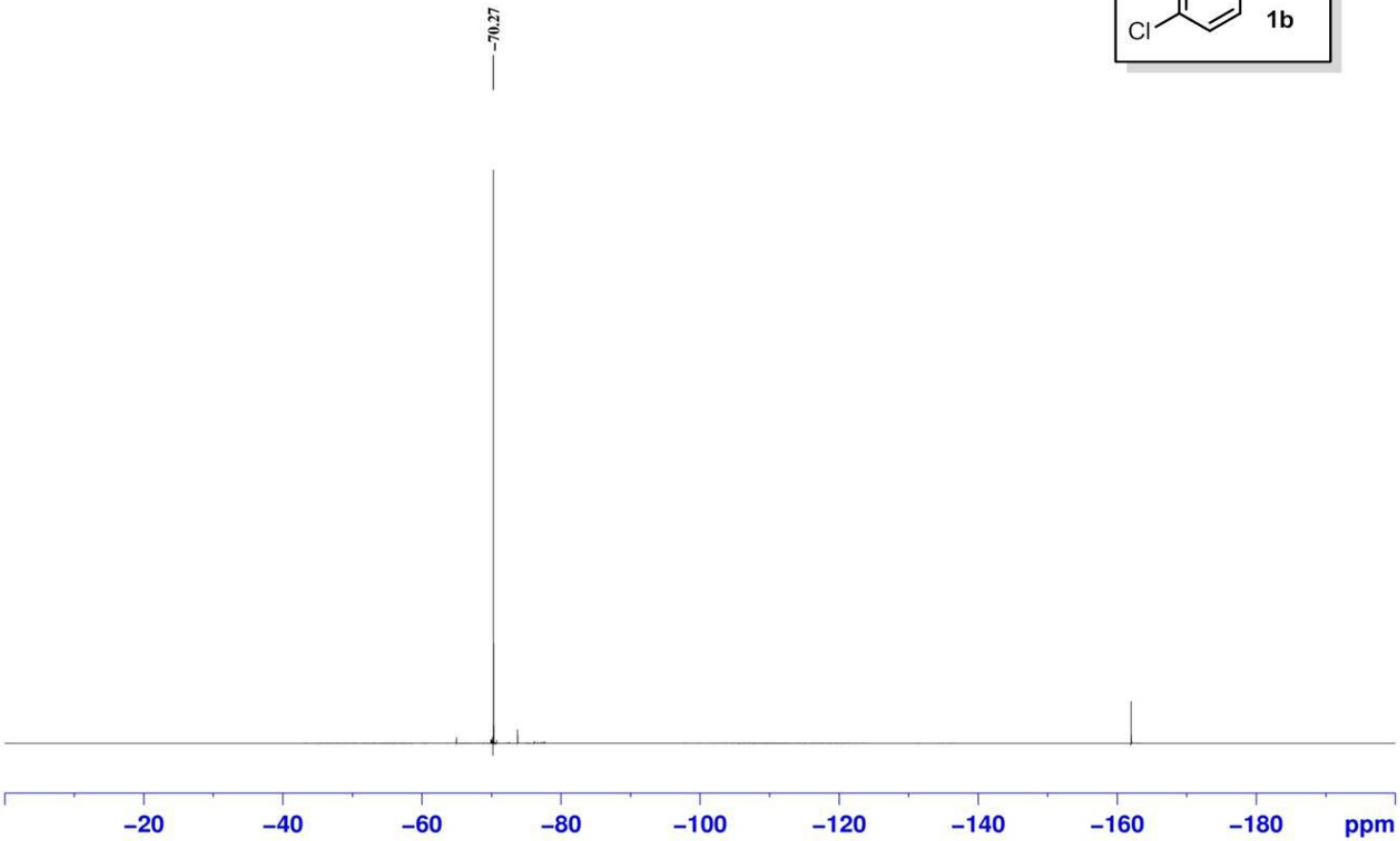
(1−(trifluoromethyl)cyclopropyl)benzene
377 MHz, CDCl3



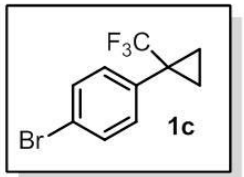


1−chloro−4−(1−(trifluoromethyl)cyclopropyl)benzene
377 MHz, CDCl3

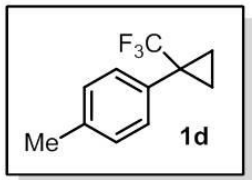


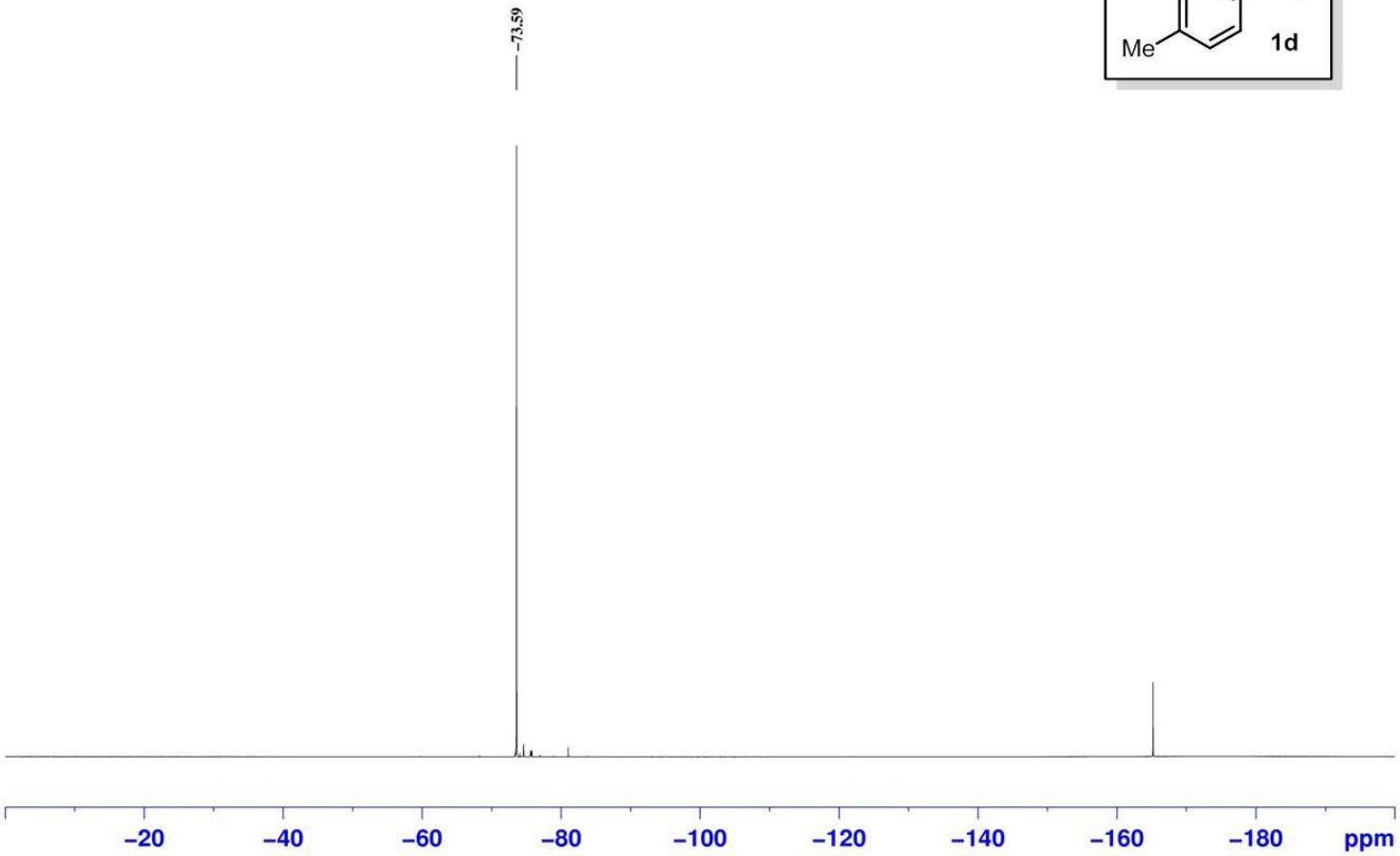


1−bromo−4−(1−(trifluoromethyl)cyclopropyl)benzene
377 MHz, CDCl3

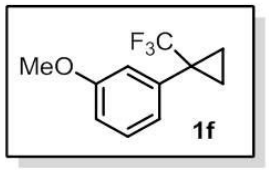


1−methyl−4−(1−(trifluoromethyl)cyclopropyl)benzene
377 MHz, CDCl3

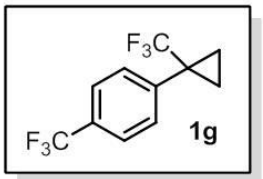




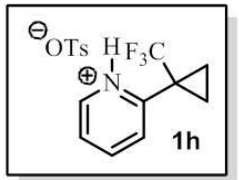
1−methoxy−3−(1−(trifluoromethyl)cyclopropyl)benzene
377 MHz, CDCl3



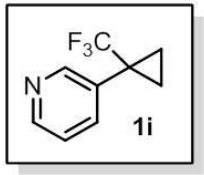
1–(trifluoromethyl)–4–(1–(trifluoromethyl)cyclopropyl)benzene
377 MHz, CDCl3



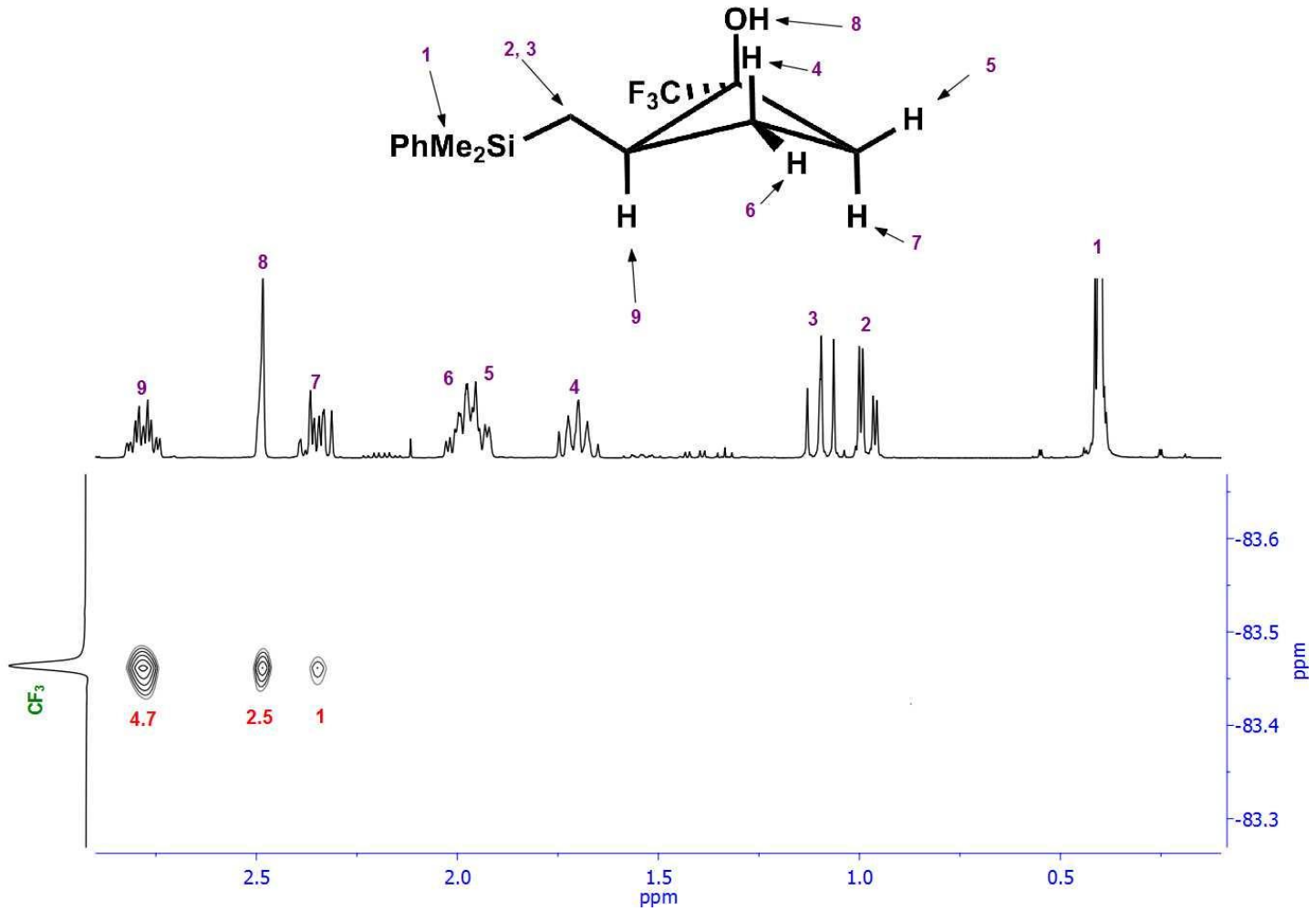
2–(1–(trifluoromethyl)cyclopropyl)pyridin–1–ium tosylate
377 MHz, CDCl3



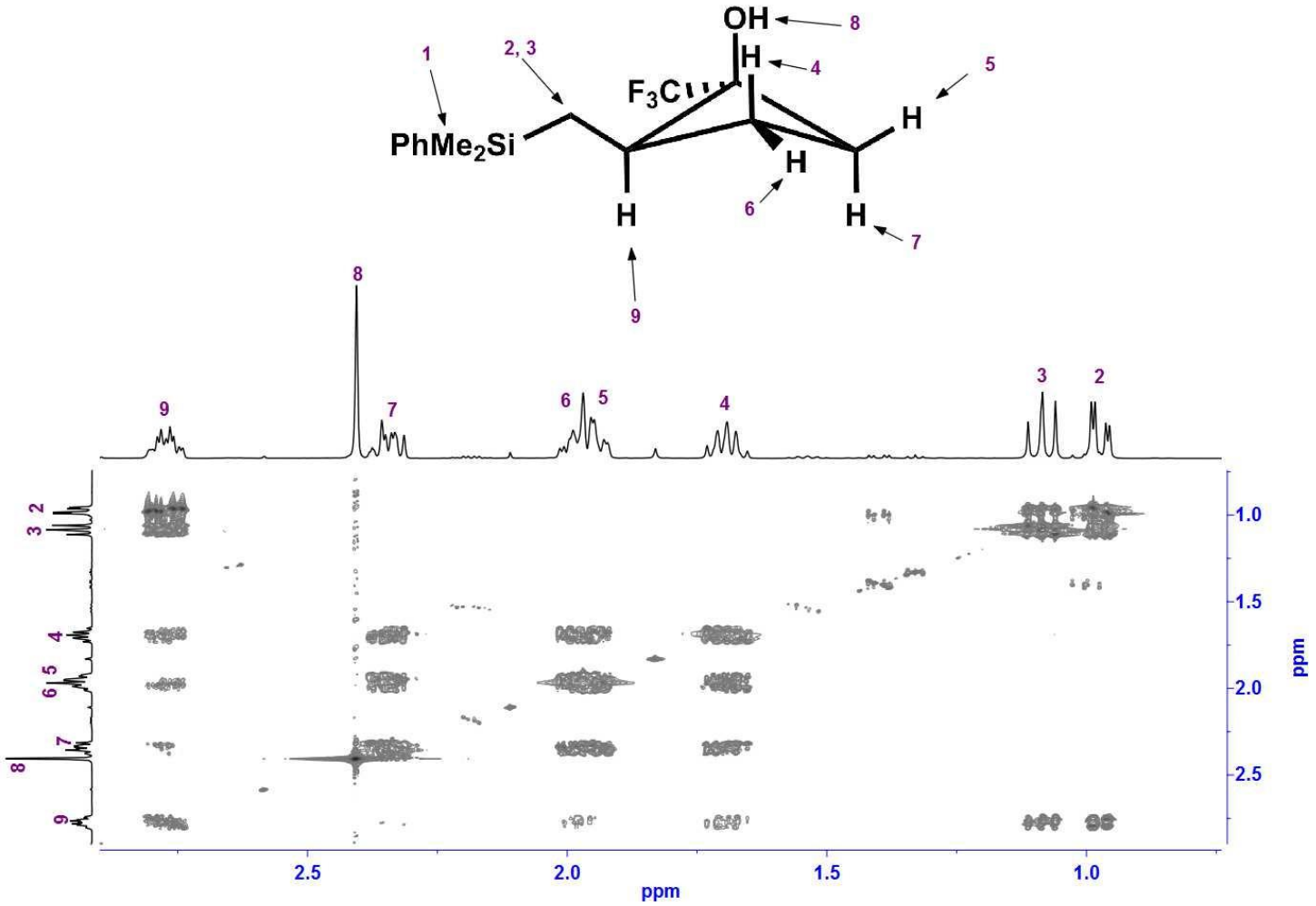
3–(1–(trifluoromethyl)cyclopropyl)pyridine
377 MHz, CDCl3



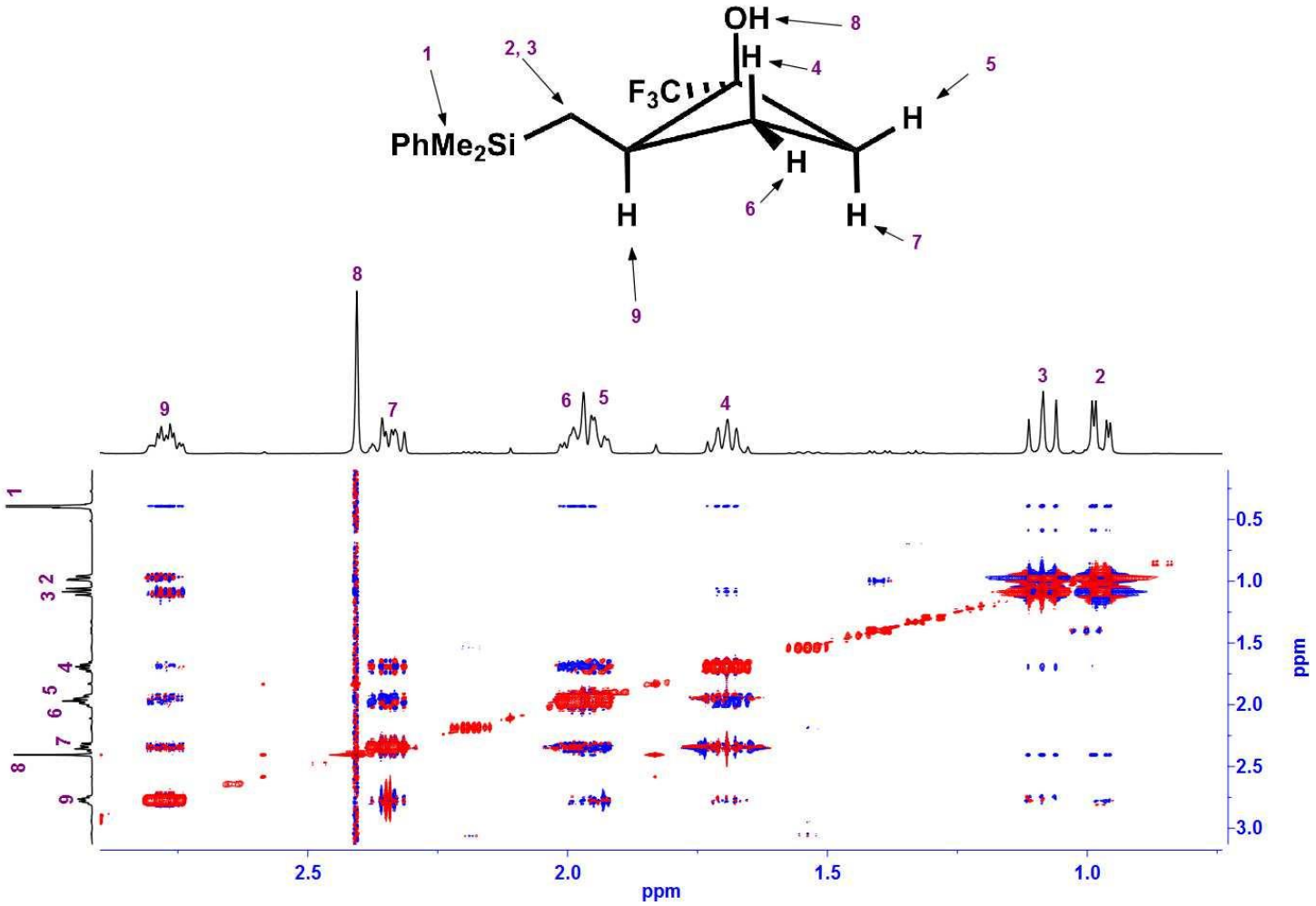
2D-NMR Spectra of Select Compounds



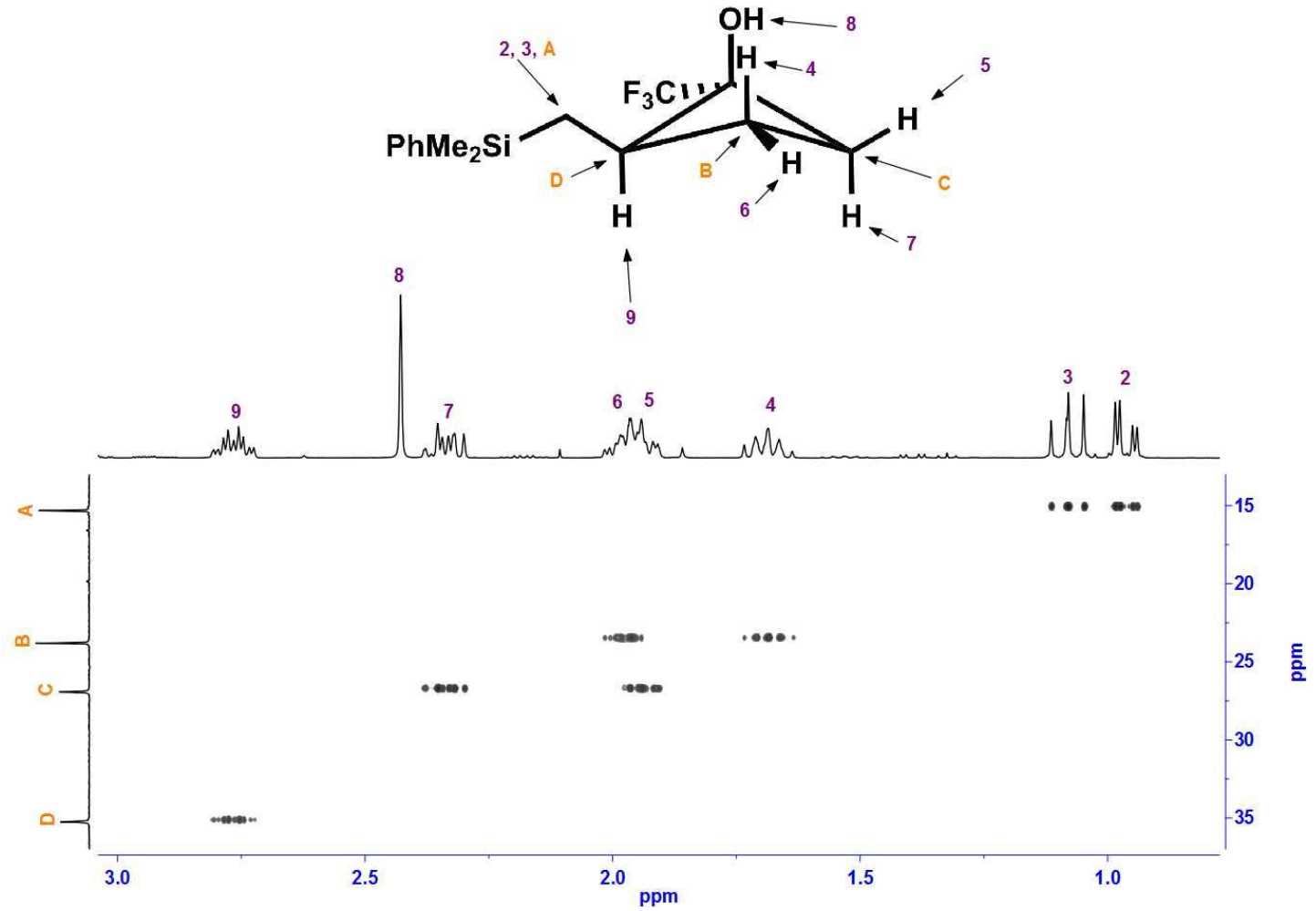
^{1}H-^{19}F HOESY of cyclobutanol **3j**. The red numbers correspond to the intensity of the cross peak normalized to the weakest signal followed by normalization to the number of protons corresponding to that signal. The HOESY spectrum was collected on a Brüker DRX-400 400 MHz NMR spectrometer. A hoseyph pulse sequence was used with 96 scans of a 2k X 128 matrix collected. The spectrum was obtained using a relaxation delay of 2.2 s, mixing time of 2.4 s, and a phase-sensitive TPPI method. Processing was performed using MestReNova.



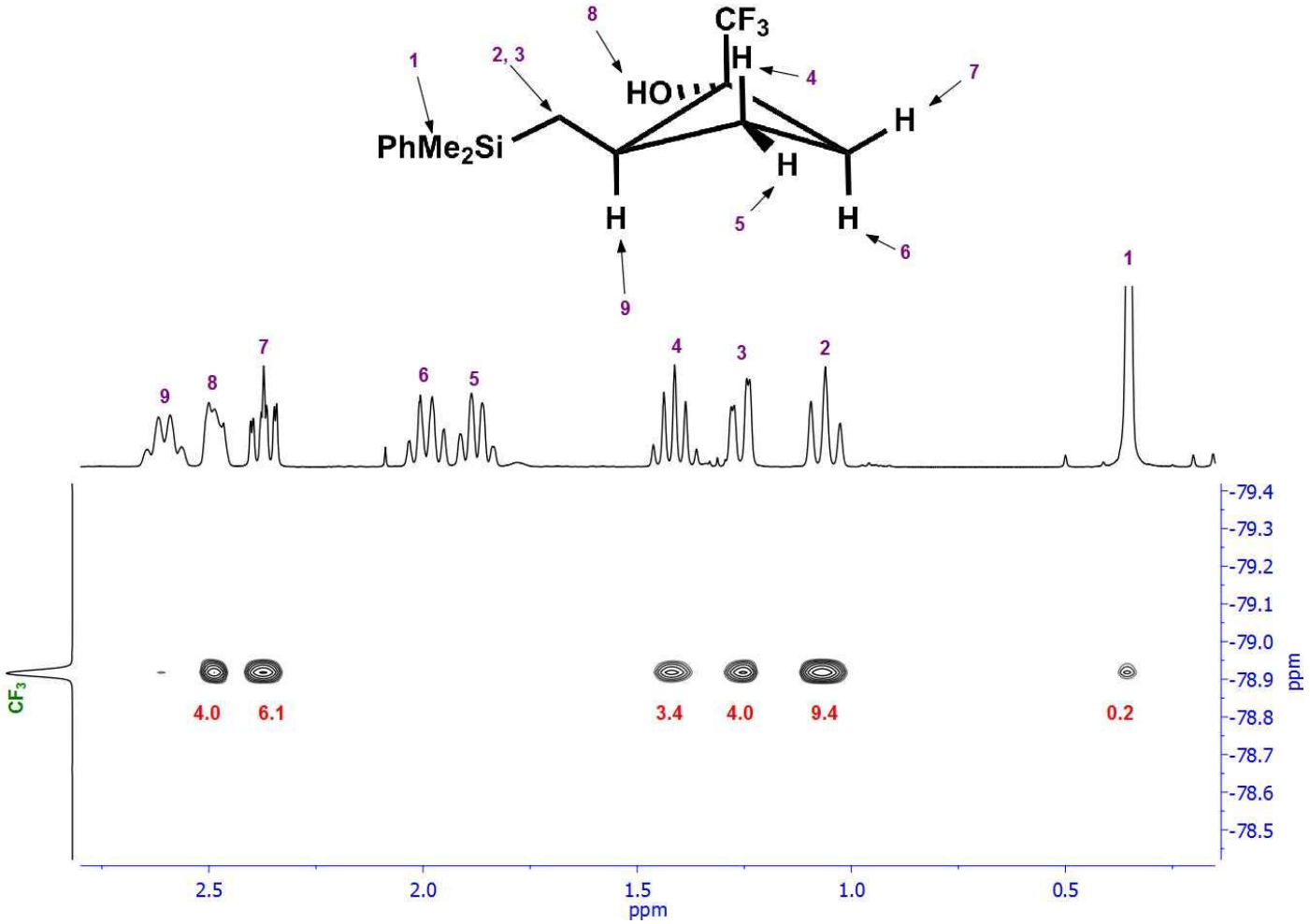
^{1}H COSY of cyclobutanol **3j**. Processing was performed using MestReNova.



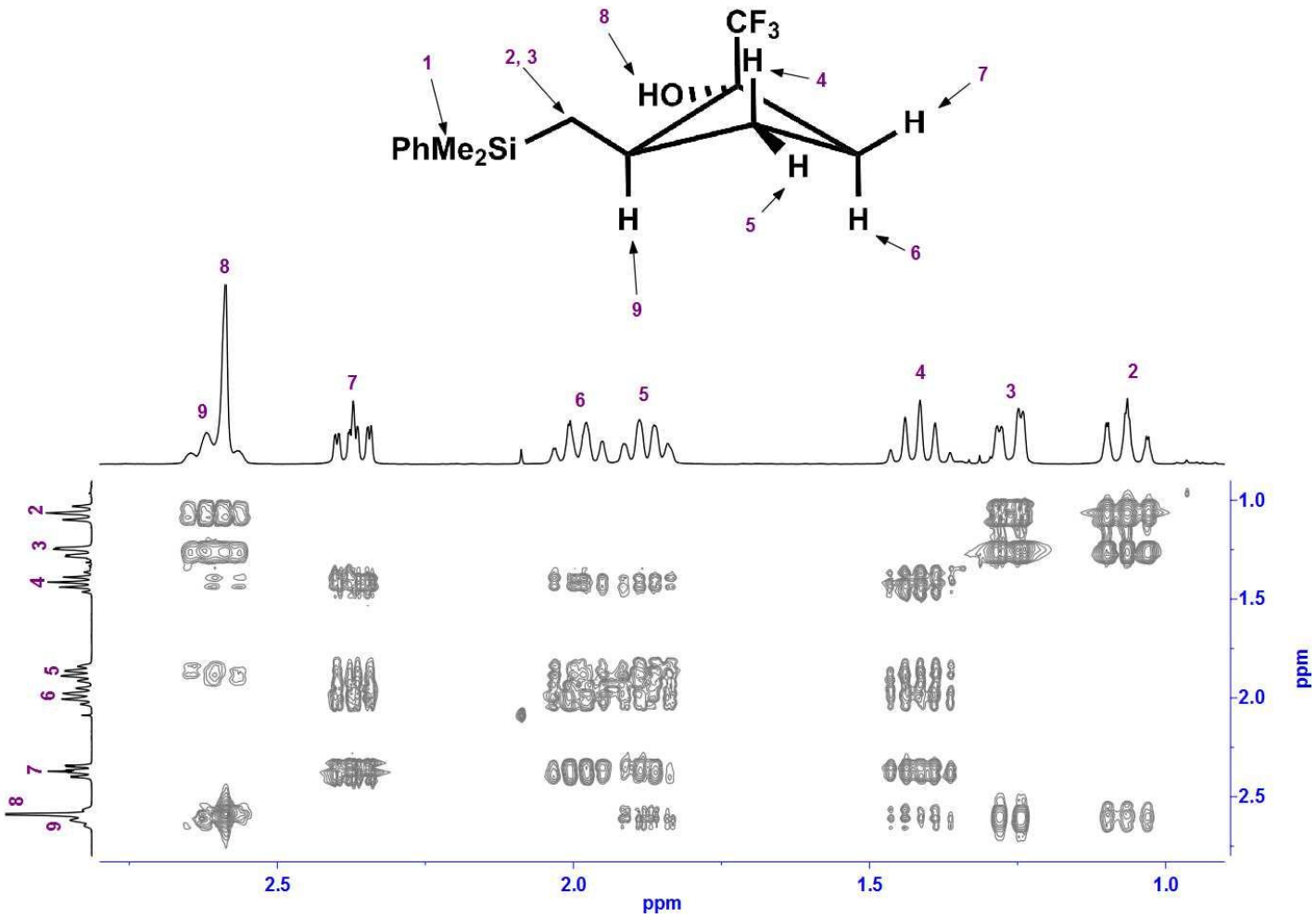
^{1}H NOESY of cyclobutanol **3j**. Red indicates positive intensities while blue indicates negative intensities. Processing was performed using MestReNova.



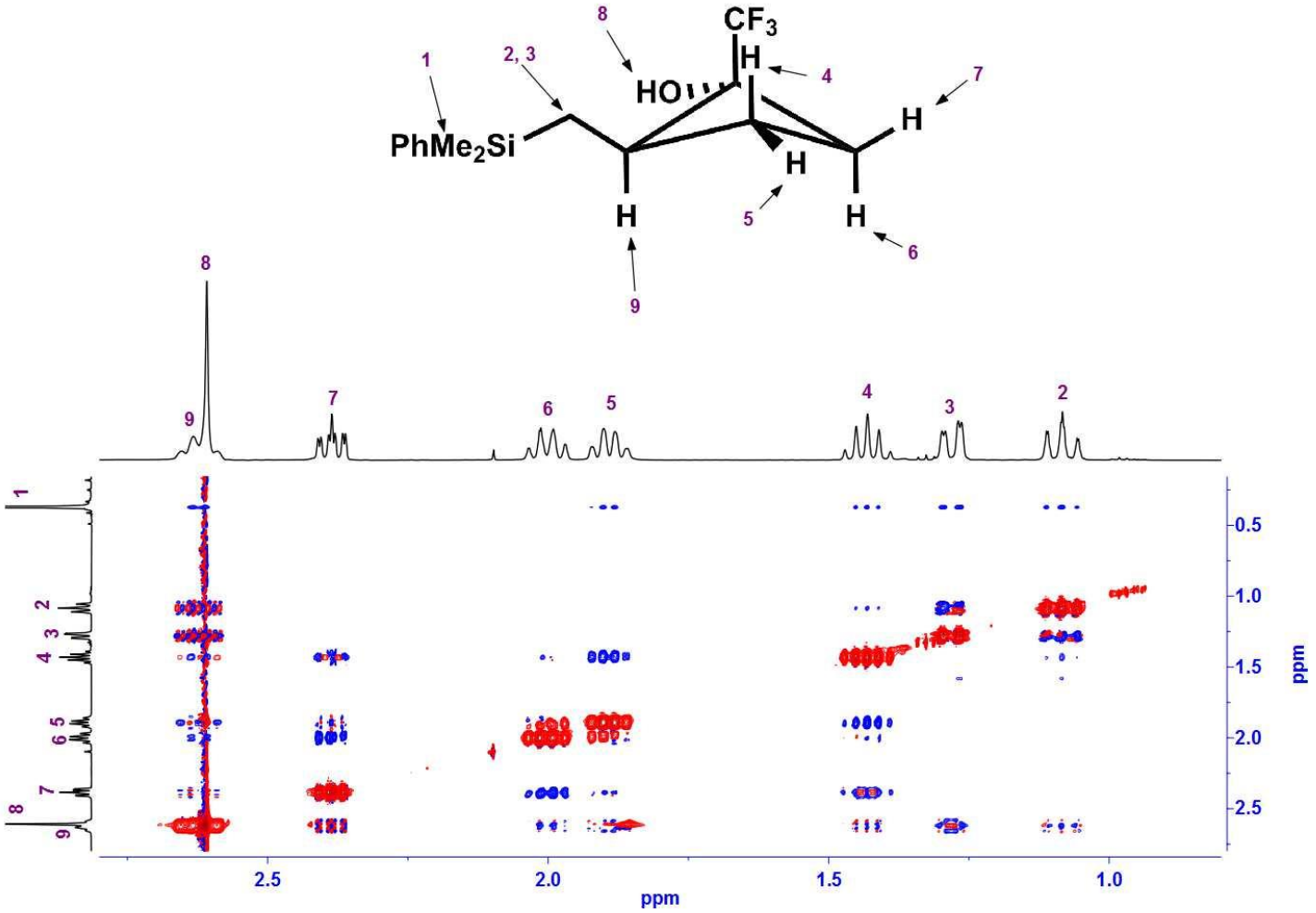
^{1}H-^{13}C HSQC of cyclobutanol **3j**. Processing was performed using MestReNova.



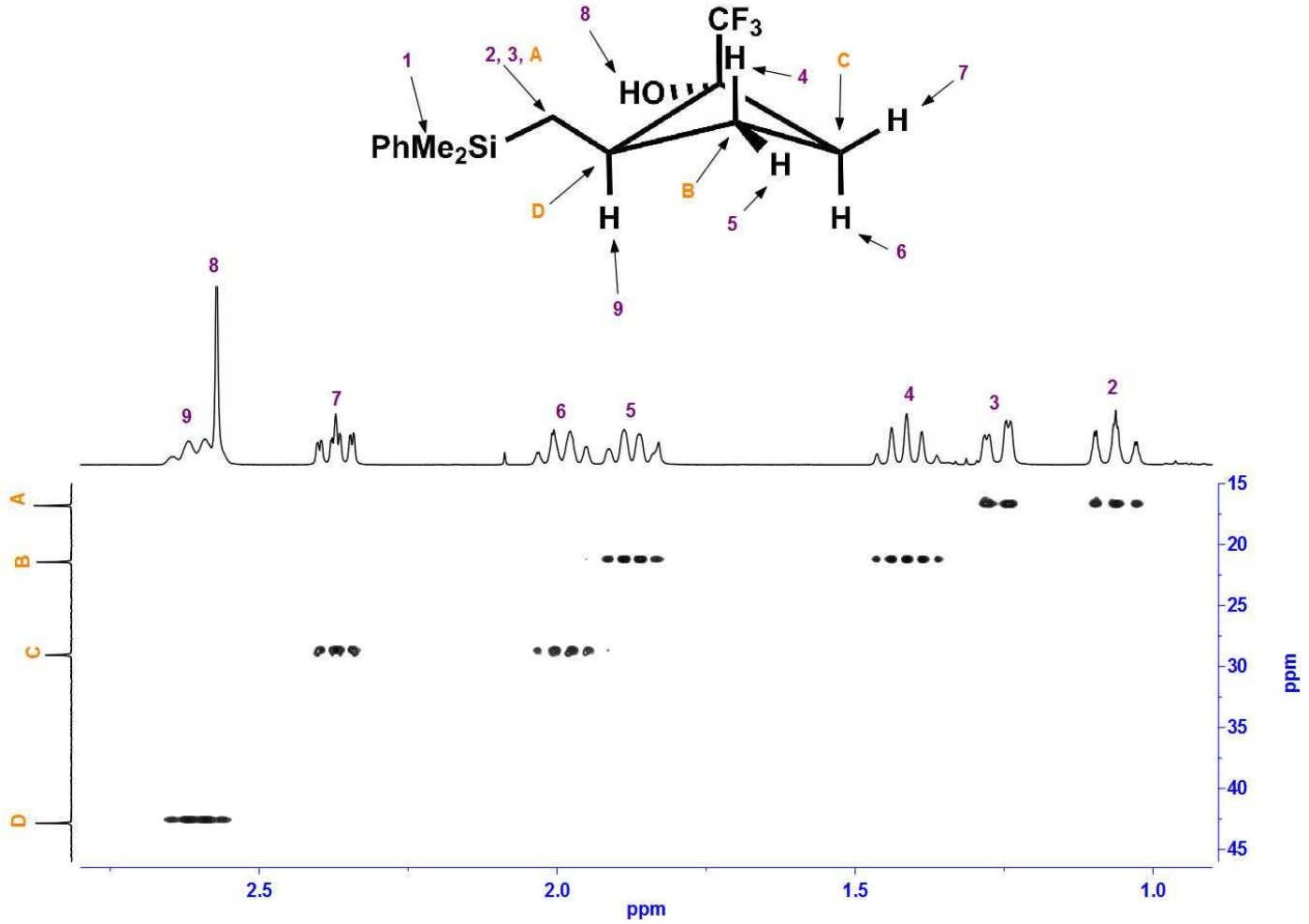
^{1}H-^{19}F HOESY of cyclobutanol **3j′**. The red numbers correspond to the intensity of the cross peak normalized to the weakest signal followed by normalization to the number of protons corresponding to that signal. The HOESY spectrum was collected on a Brüker DRX-400 400 MHz NMR spectrometer. A hoseyph pulse sequence was used with 96 scans of a 2k X 128 matrix collected. The spectrum was obtained using a relaxation delay of 2.2 s, mixing time of 2.4 s, and a phase-sensitive TPPI method. Processing was performed using MestReNova.



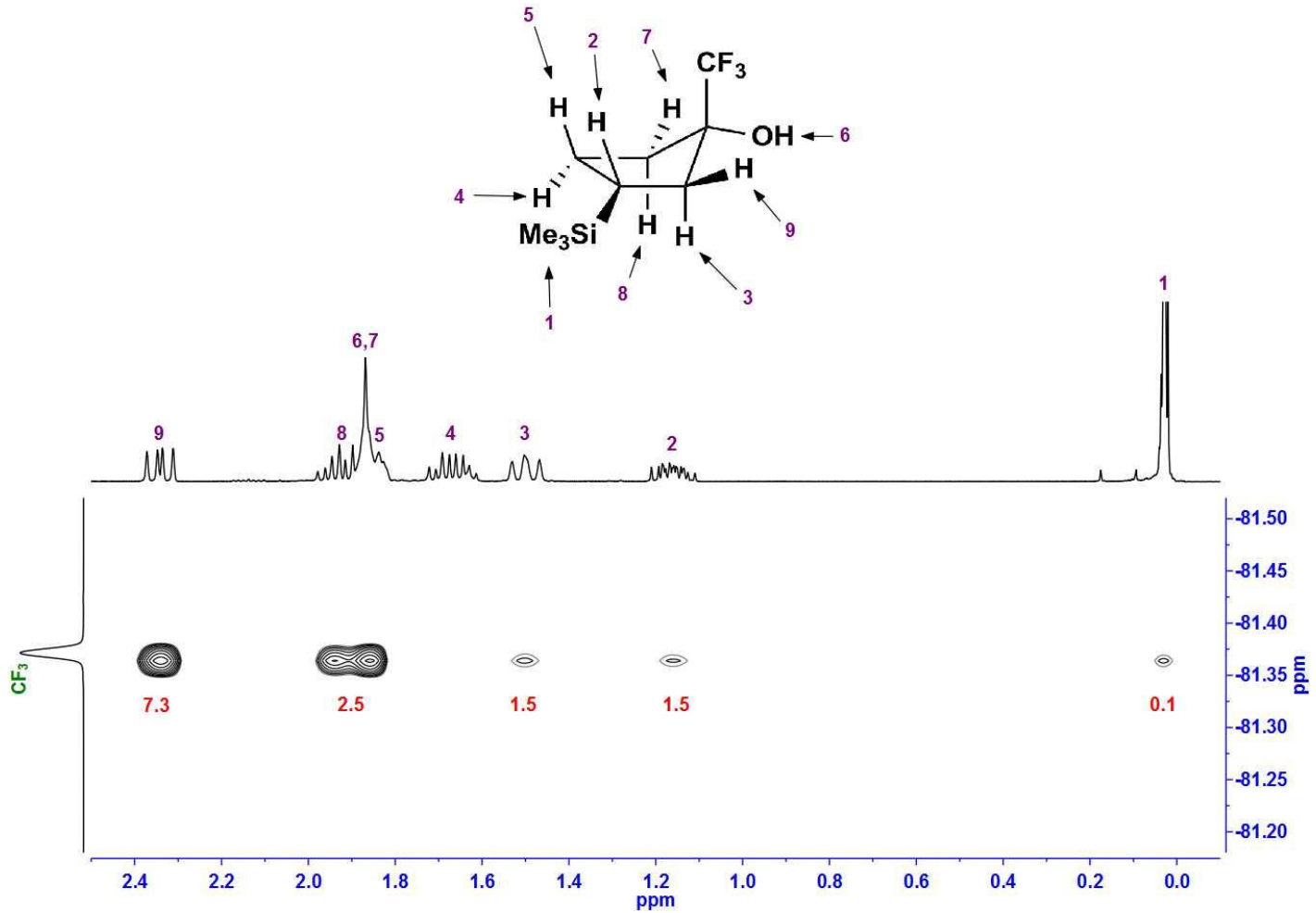
^{1}H COSY of cyclobutanol **3j′**. Processing was performed using MestReNova.



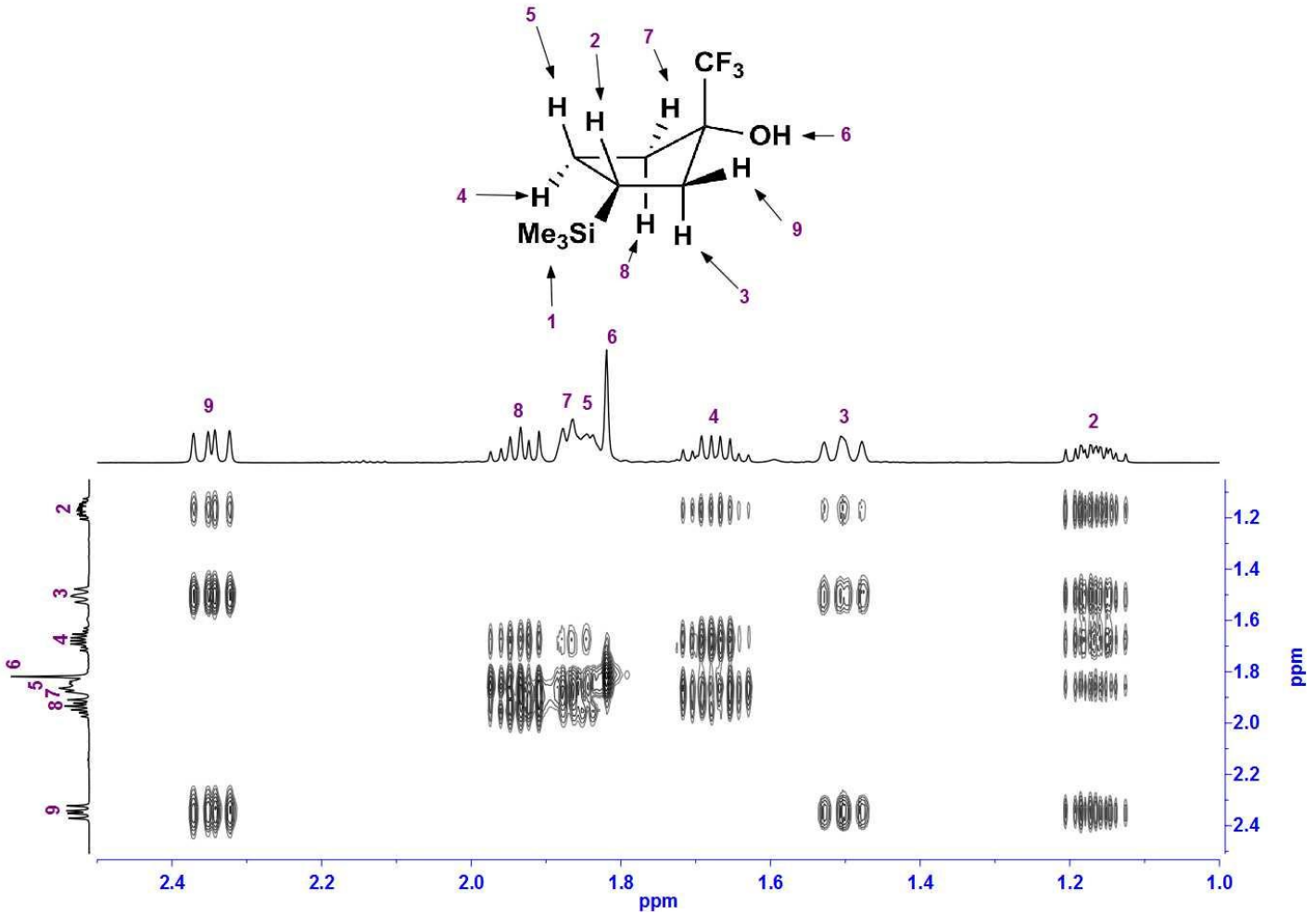
^{1}H NOESY of cyclobutanol **3j'**. Red indicates positive intensities while blue indicates negative intensities. Processing was performed using MestReNova.



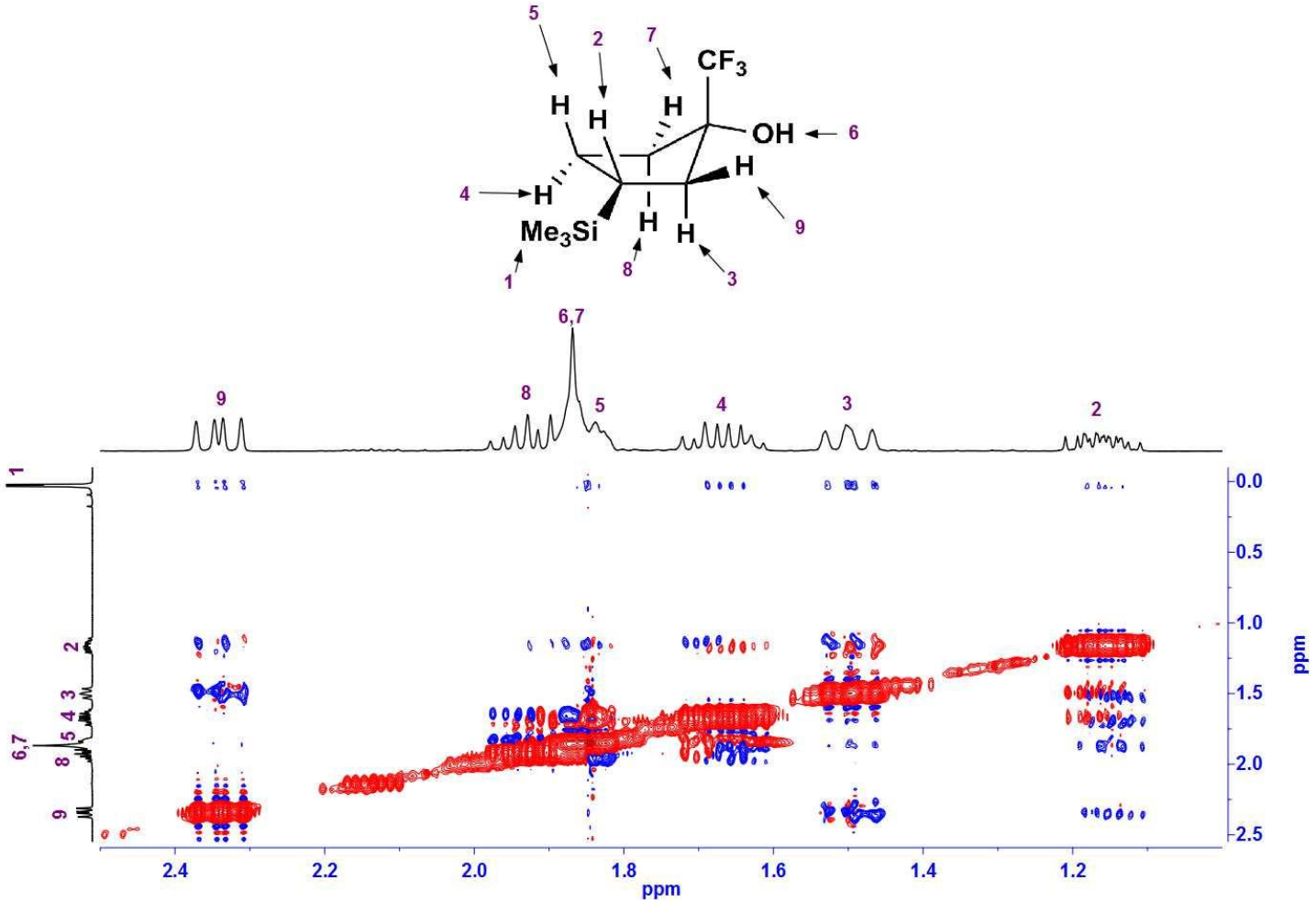
^{1}H-^{13}C HSQC of cyclobutanol **3j'**. Processing was performed using MestReNova.



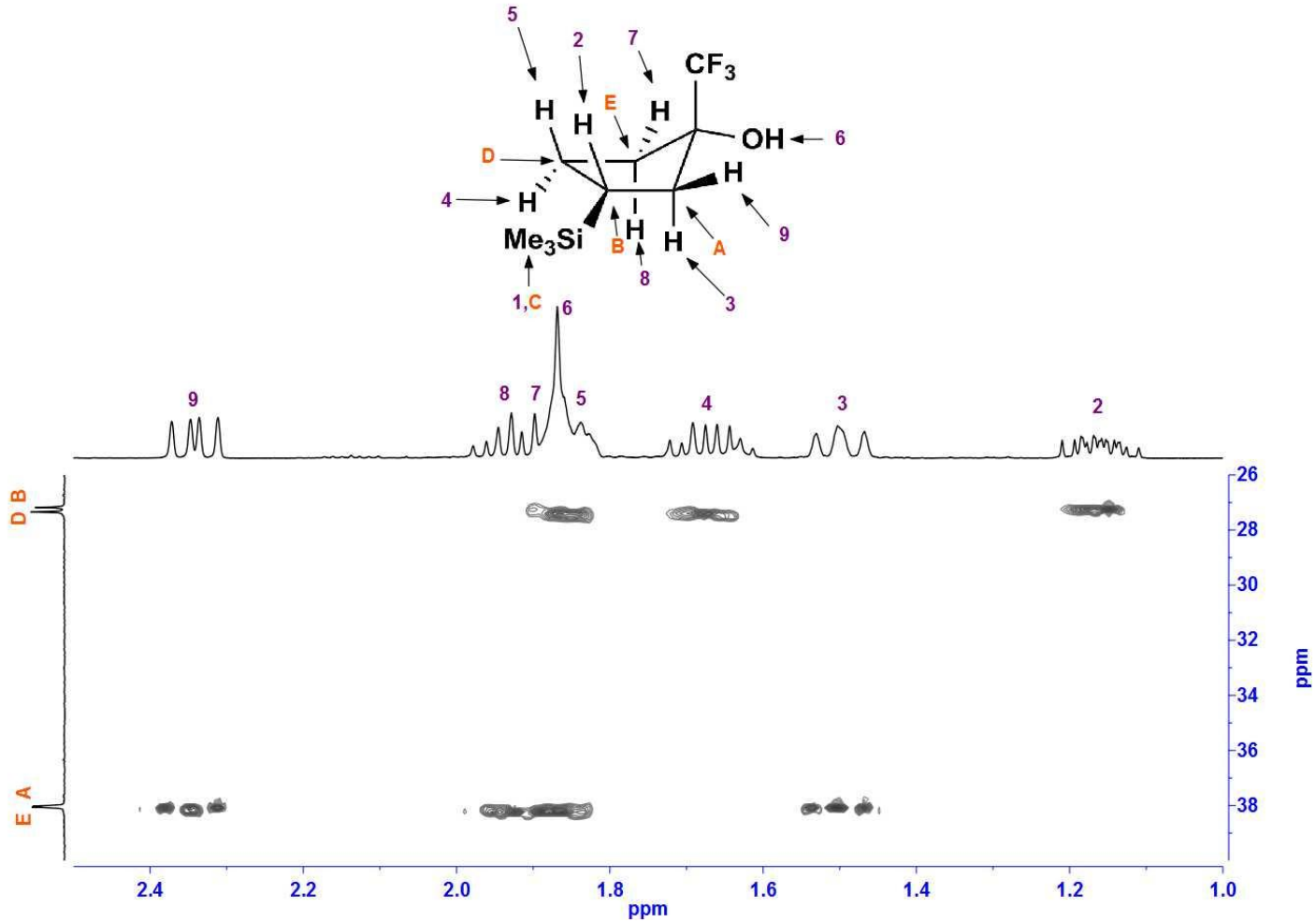
^{1}H-^{19}F HOESY of cyclopentanol **3k**. The red numbers correspond to the intensity of the cross peak normalized to the weakest signal followed by normalization to the number of proton corresponding to that signal. The HOESY spectrum was collected on a Brüker DRX-400 400 MHz NMR spectrometer. A hoseyph pulse sequence was used with 96 scans of a 2k X 128 matrix collected. The spectrum was obtained using a relaxation delay of 2.2 s, mixing time of 2.4 s, and a phase-sensitive TPPI method. Processing was performed using MestReNova.



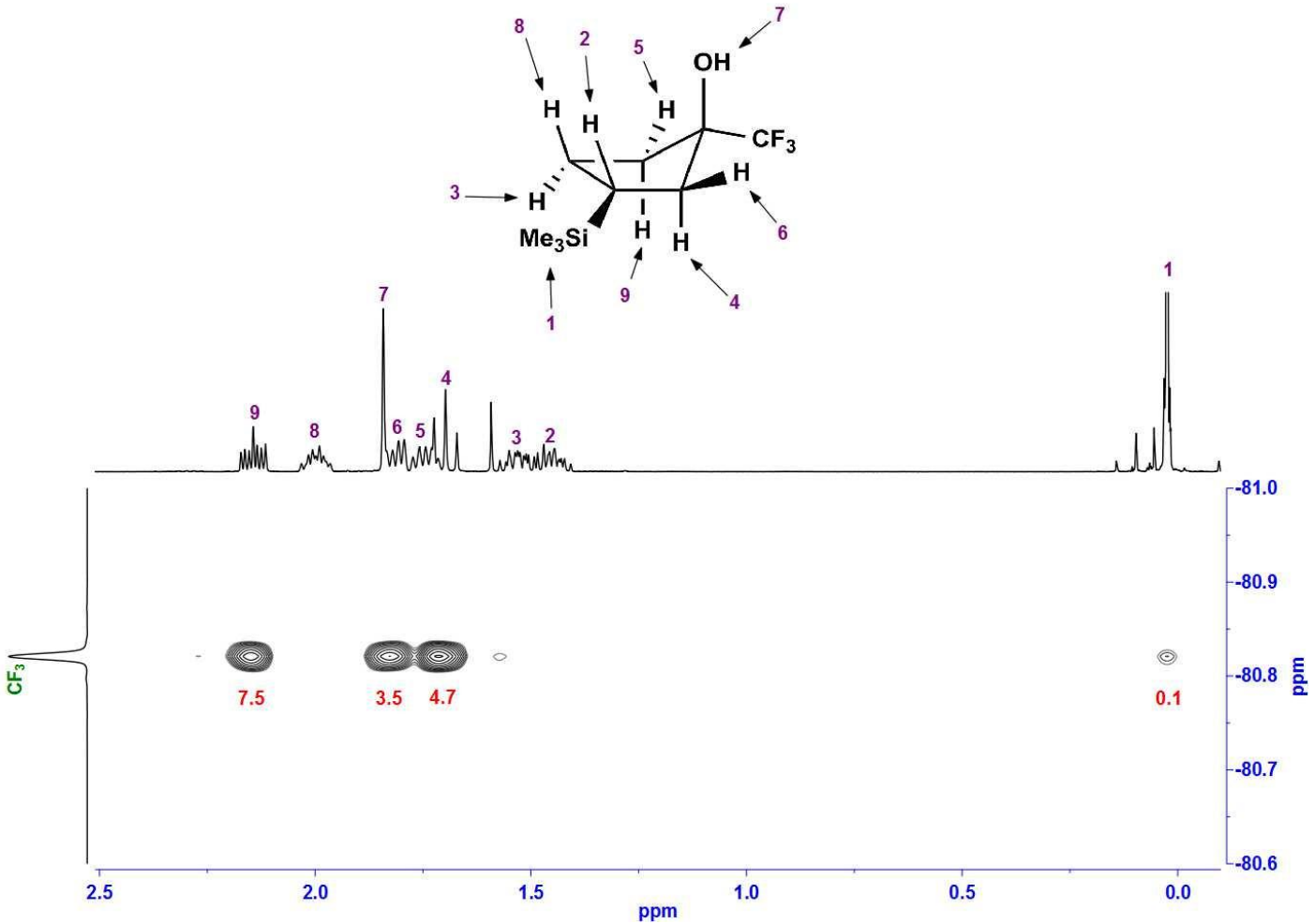
^{1}H COSY of cyclopentanol **3k**. Processing was performed using MestReNova.



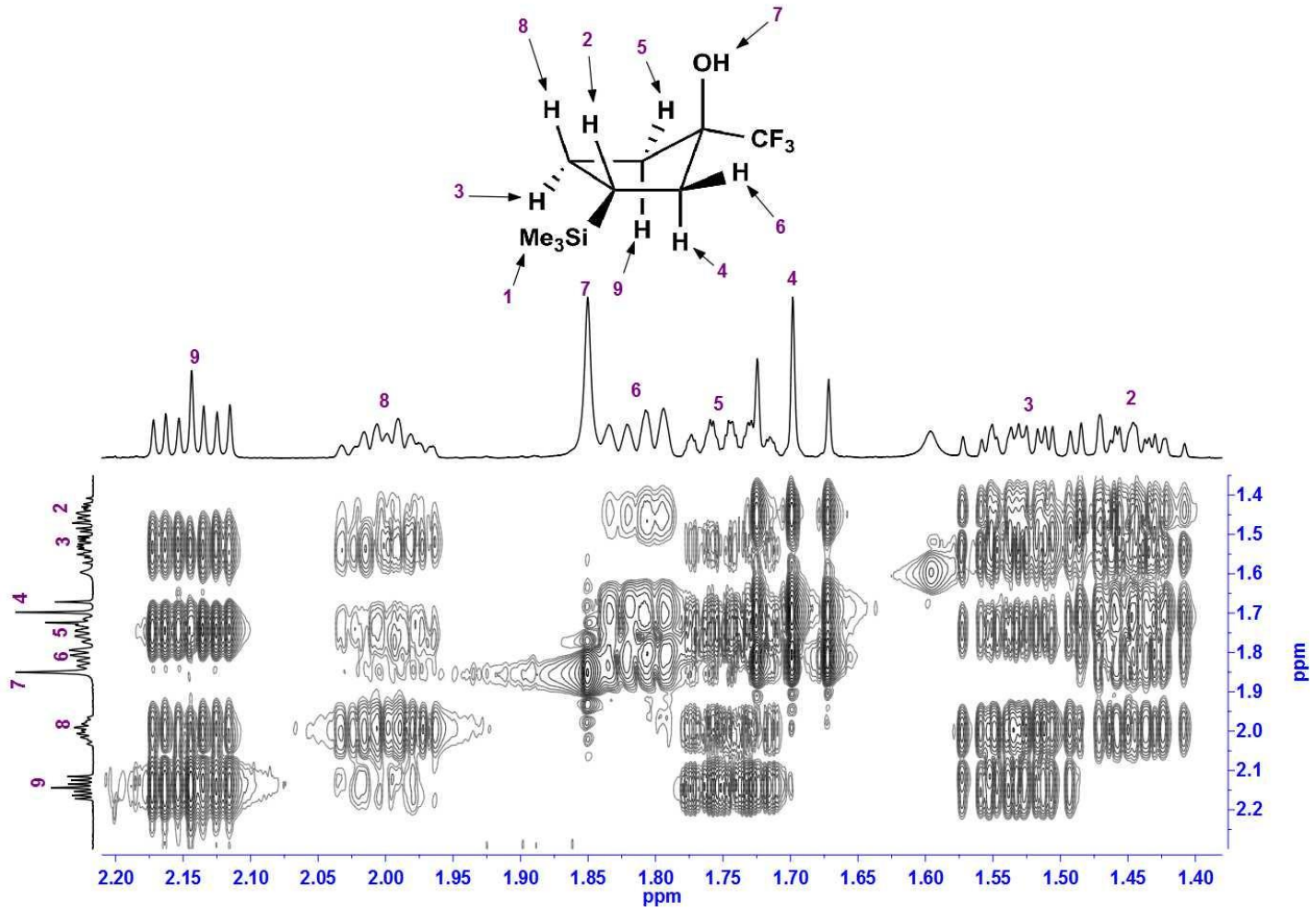
^{1}H NOESY of cyclopentanol **3k**. Red indicates positive intensities while blue indicates negative intensities. Processing was performed using MestReNova.



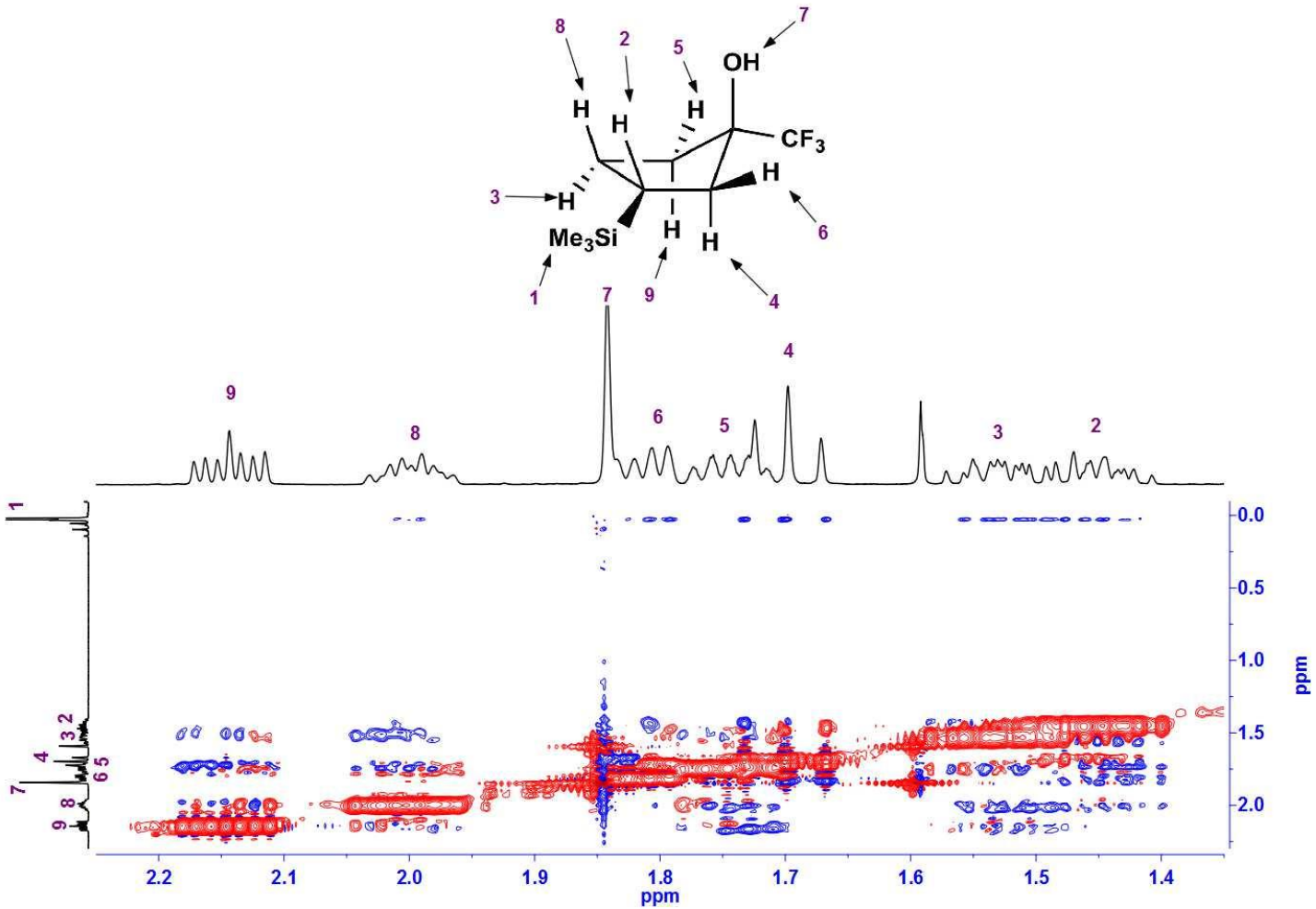
^{1}H-^{13}C HSQC of cyclopentanol **3k**. Processing was performed using MestReNova.



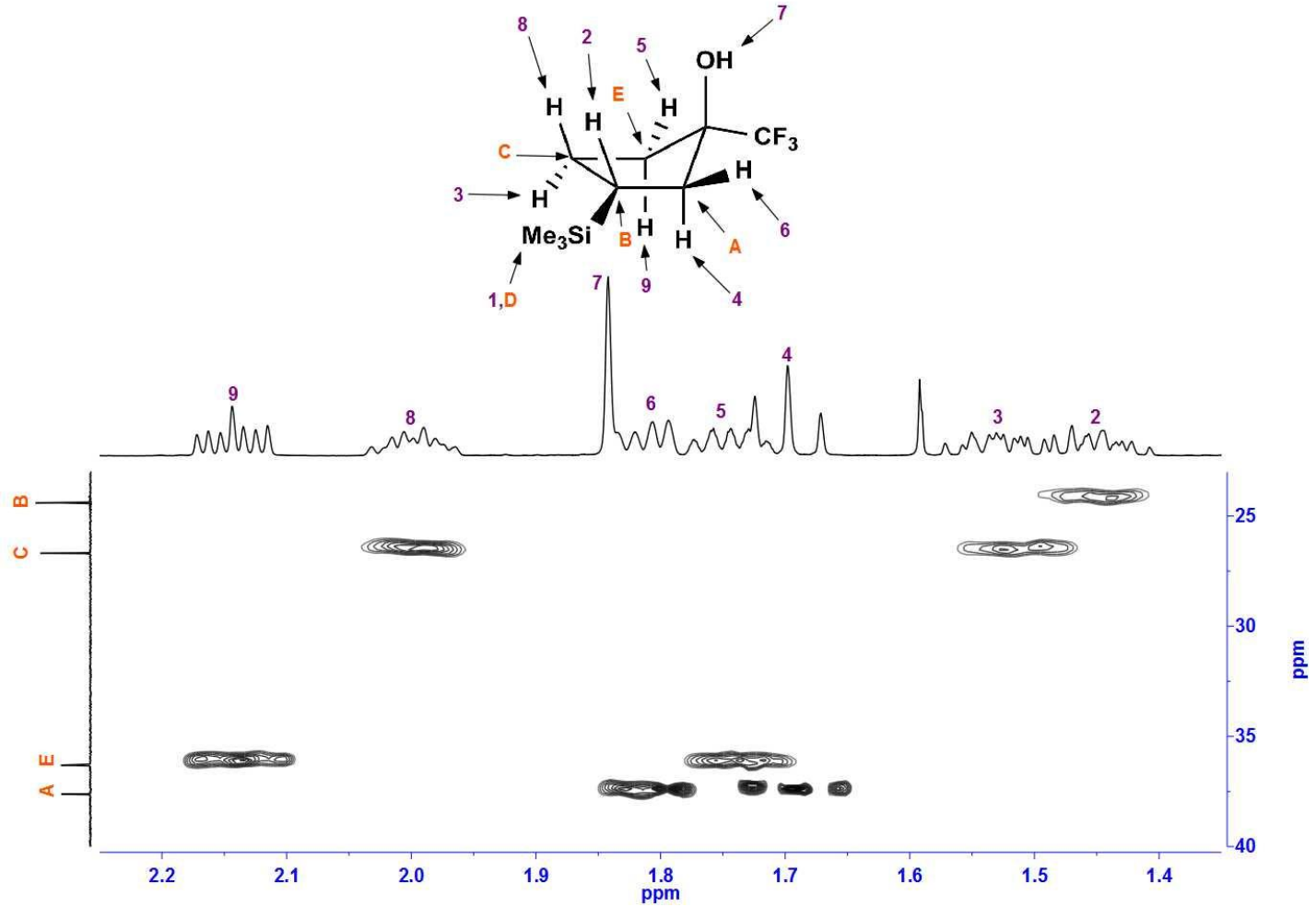
^{1}H-^{19}F HOESY of cyclopentanol **3k′**. The red numbers correspond to the intensity of the cross peak normalized to the weakest signal followed by normalization to the number of proton corresponding to that signal. The HOESY spectrum was collected on a Brüker DRX-400 400 MHz NMR spectrometer. A hoseyph pulse sequence was used with 96 scans of a 2k X 128 matrix collected. The spectrum was obtained using a relaxation delay of 2.2 s, mixing time of 2.4 s, and a phase-sensitive TPPI method. Processing was performed using MestReNova.



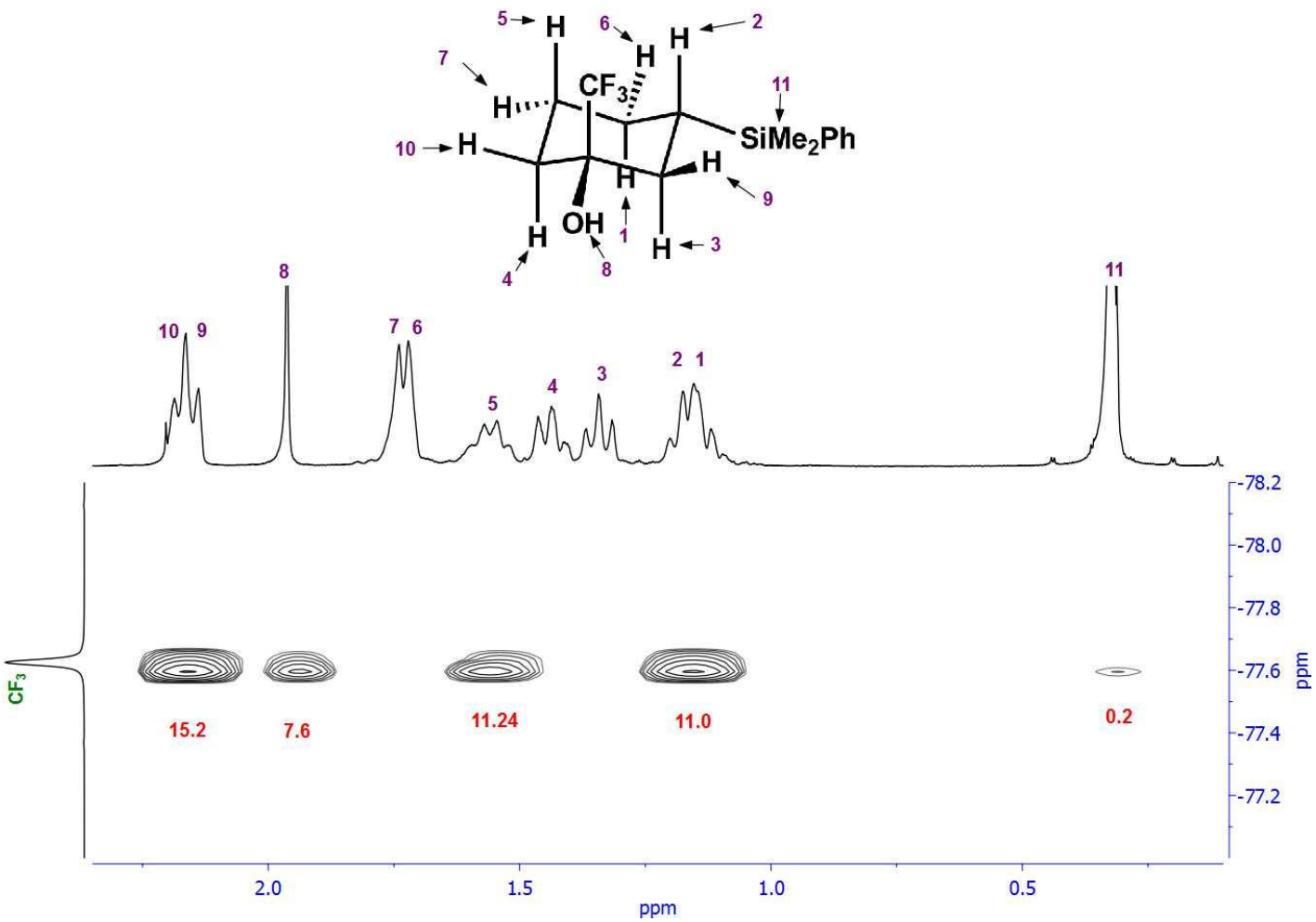
^{1}H COSY of cyclopentanol **3k′**



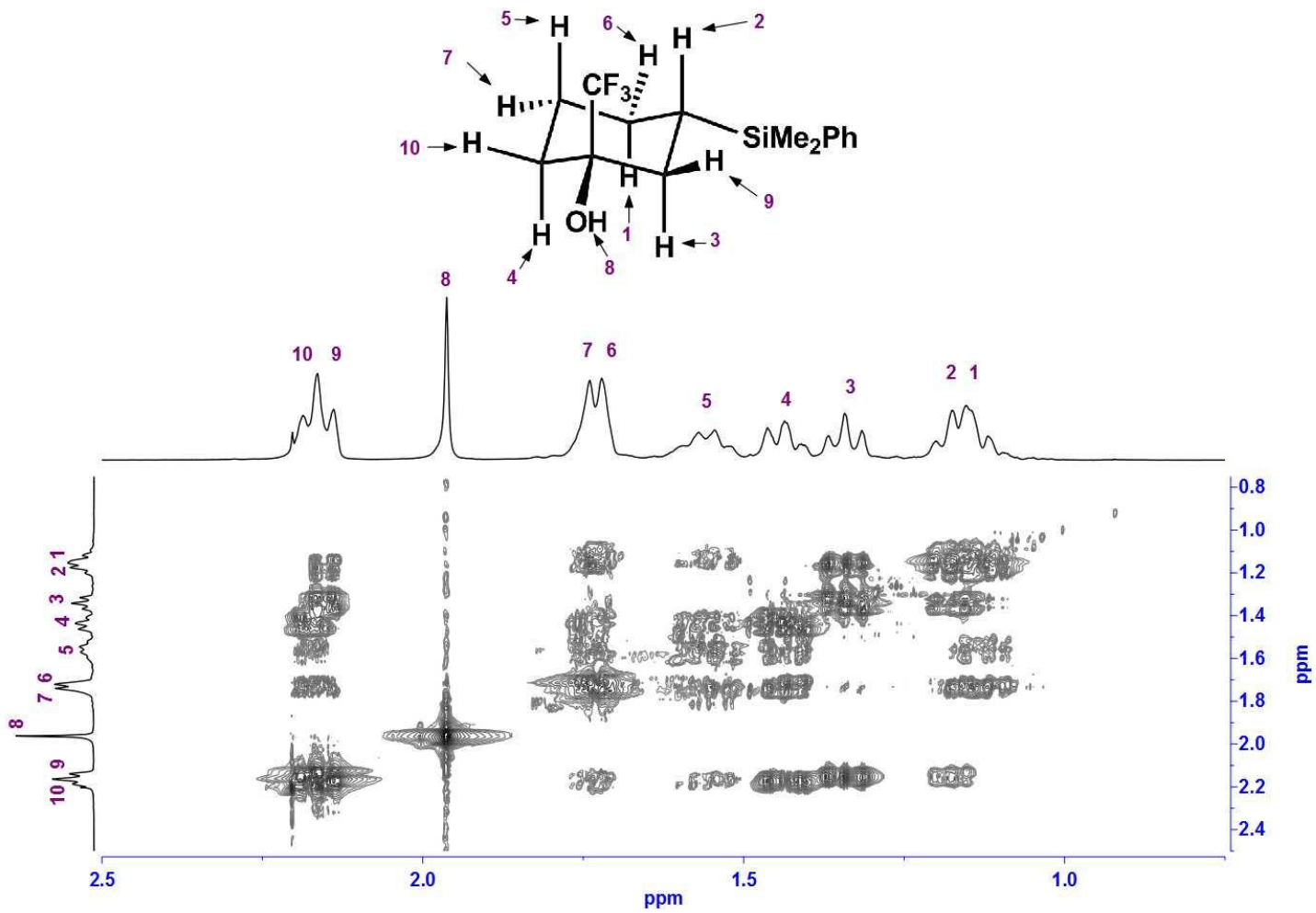
^{1}H NOESY of cyclopentanol **3k′**. Red indicates positive intensities while blue indicates negative intensities



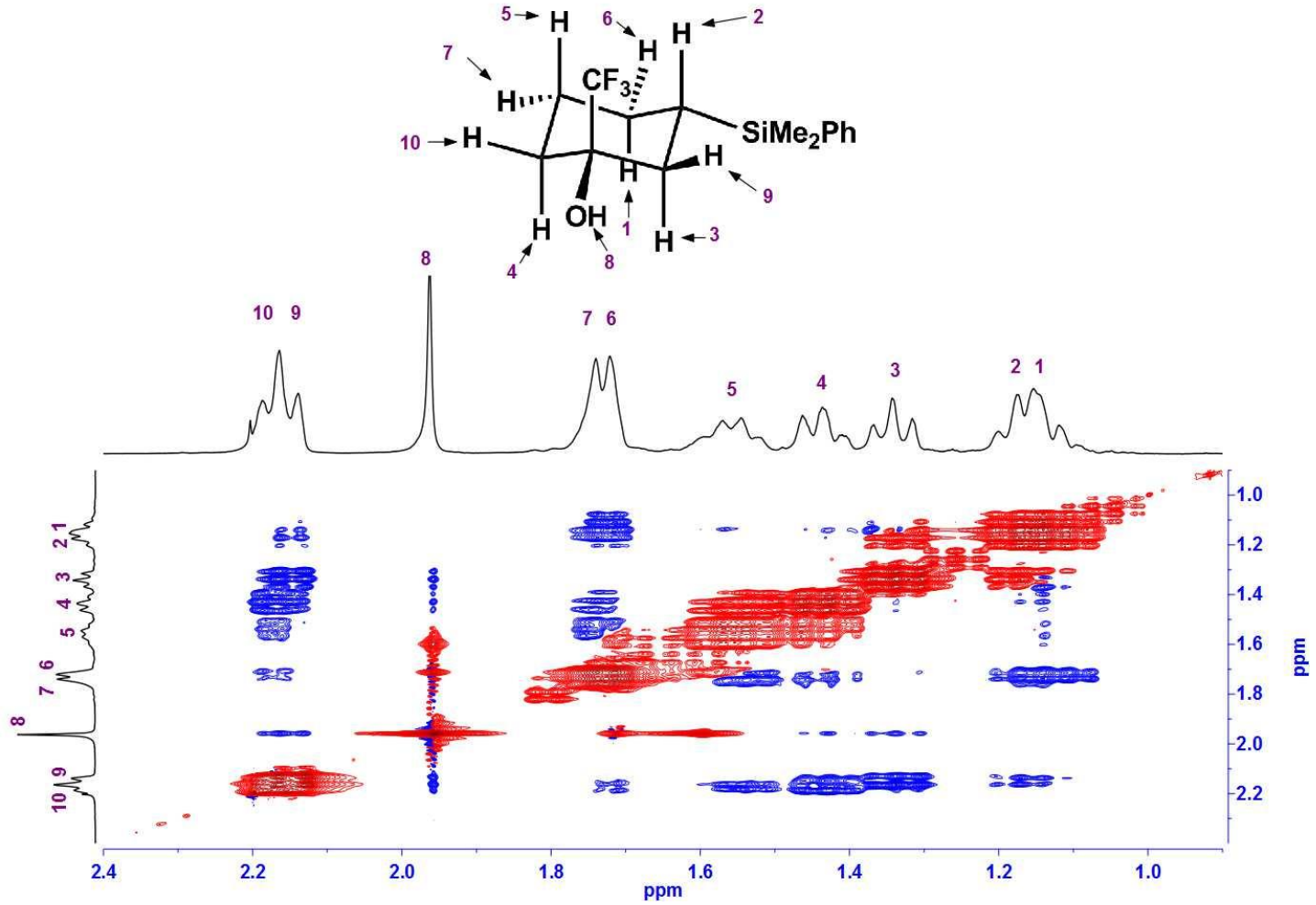
^{1}H-^{13}C HSQC of cyclopentanol **3k′**.



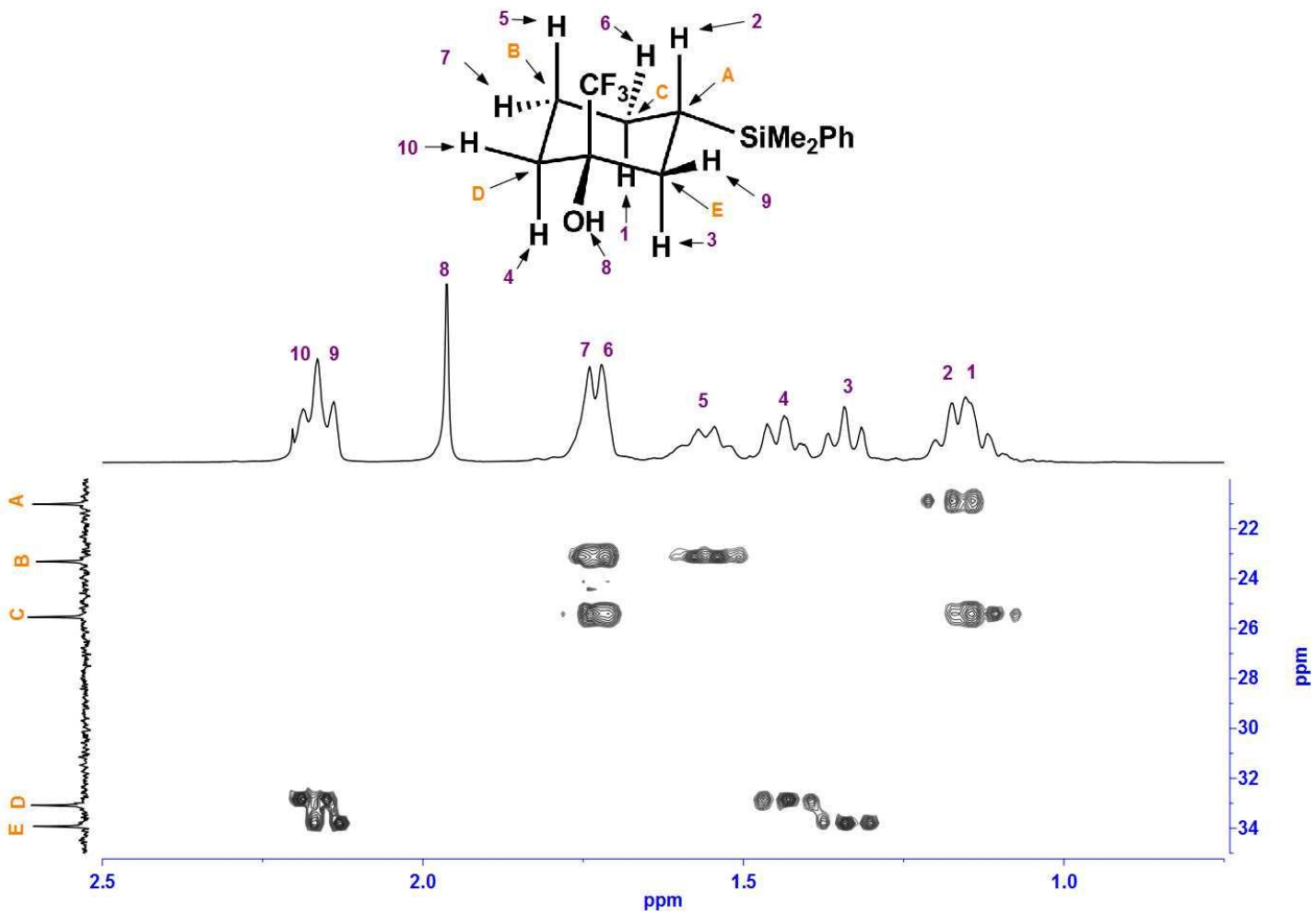
^{1}H-^{19}F HOESY of cyclohexanol **3l**. The red numbers correspond to the intensity of the cross peak normalized to the weakest signal followed by normalization to the number of proton corresponding to that signal. The HOESY spectrum was collected on a Brüker DRX-400 400 MHz NMR spectrometer. A hoseyph pulse sequence was used with 96 scans of a 2k X 128 matrix collected. The spectrum was obtained using a relaxation delay of 2.2 s, mixing time of 2.4 s, and a phase-sensitive TPPI method. Processing was performed using MestReNova.



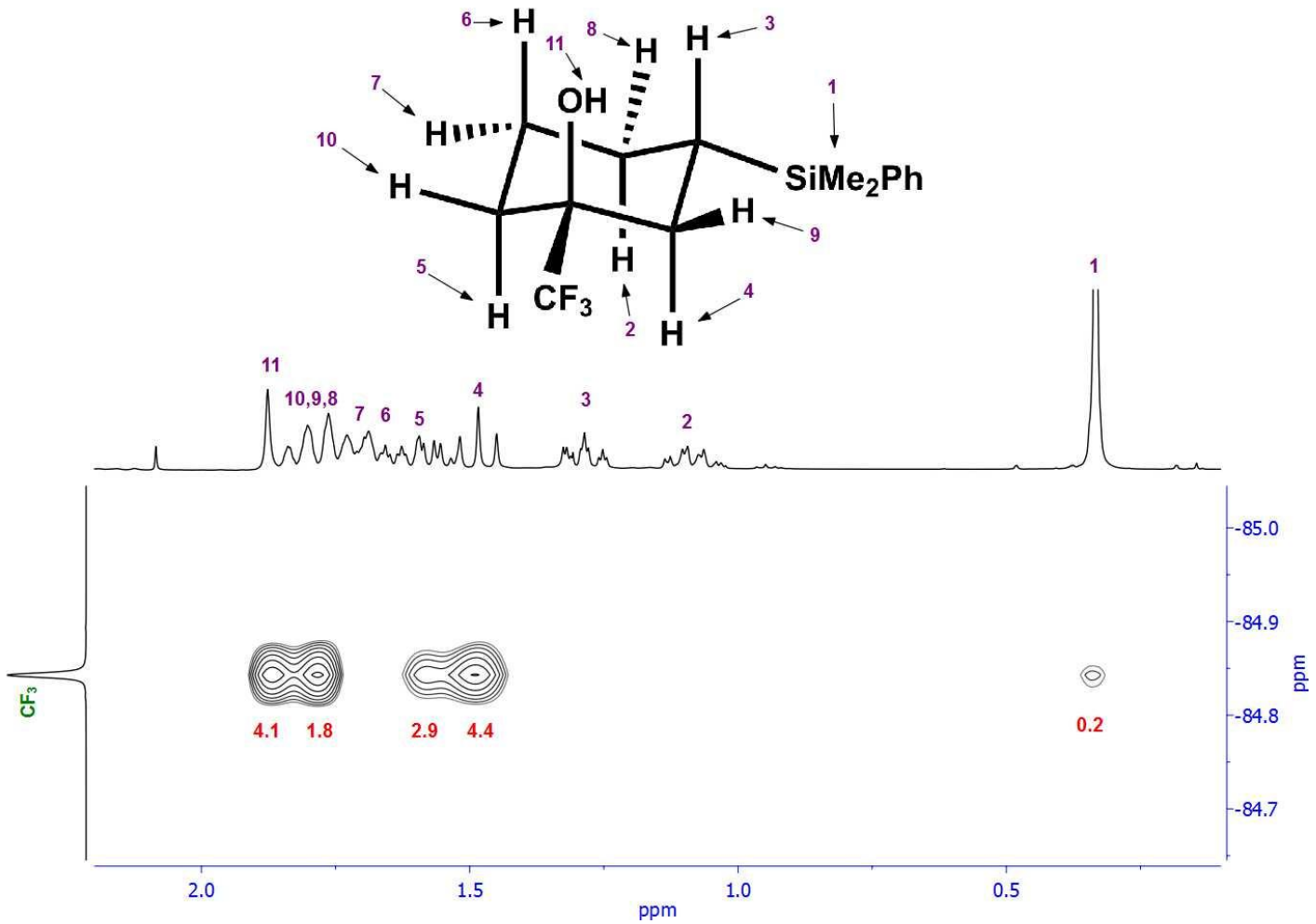
^{1}H COSY of cyclohexanol **3l**. Processing was performed using MestReNova.



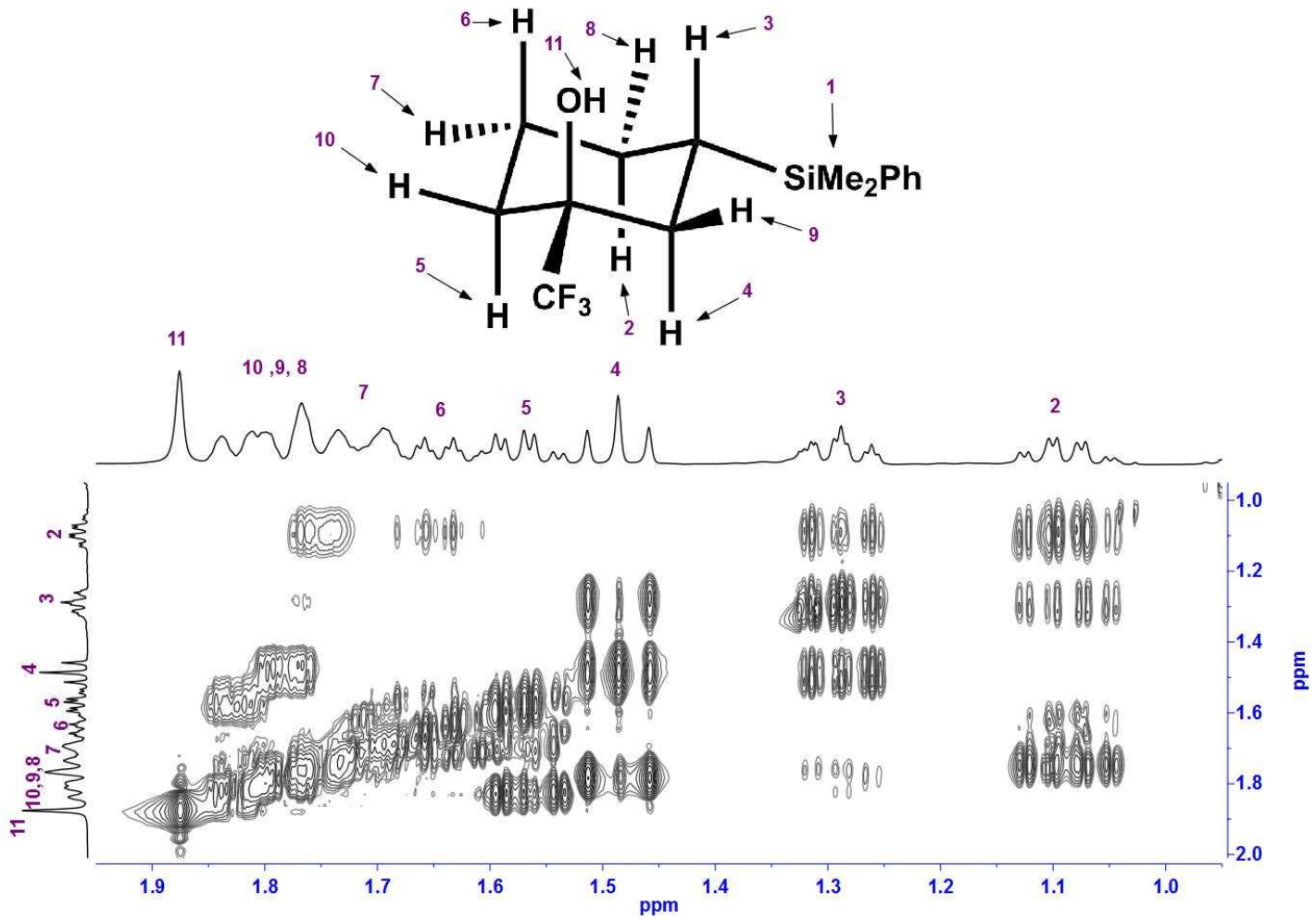
^{1}H NOESY of cyclohexanol **3l**. Red indicates positive intensities while blue indicates negative intensities. Processing was performed using MestReNova.



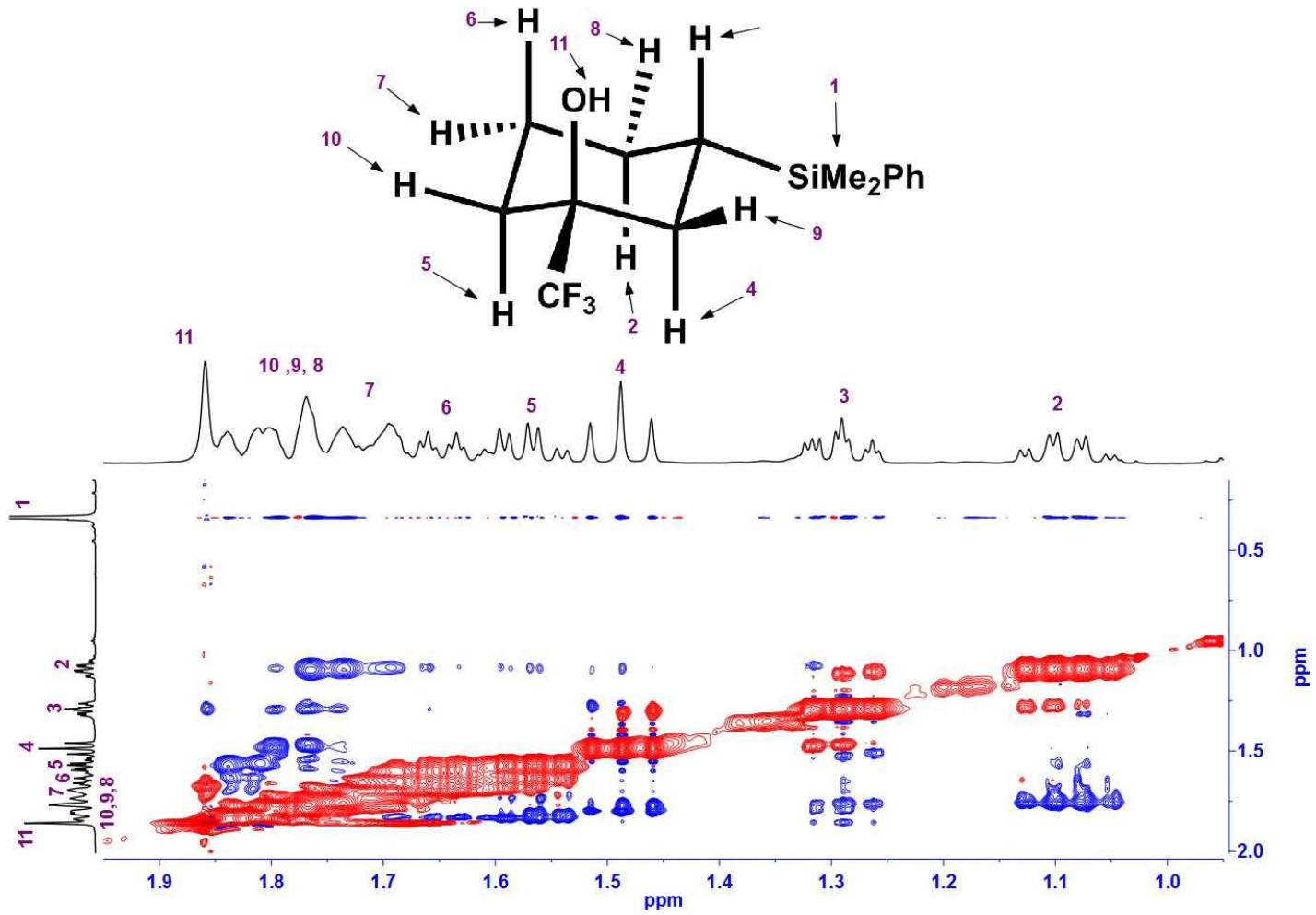
^{1}H-^{13}C HSQC of cyclohexanol **3l**. Processing was performed using MestReNova.



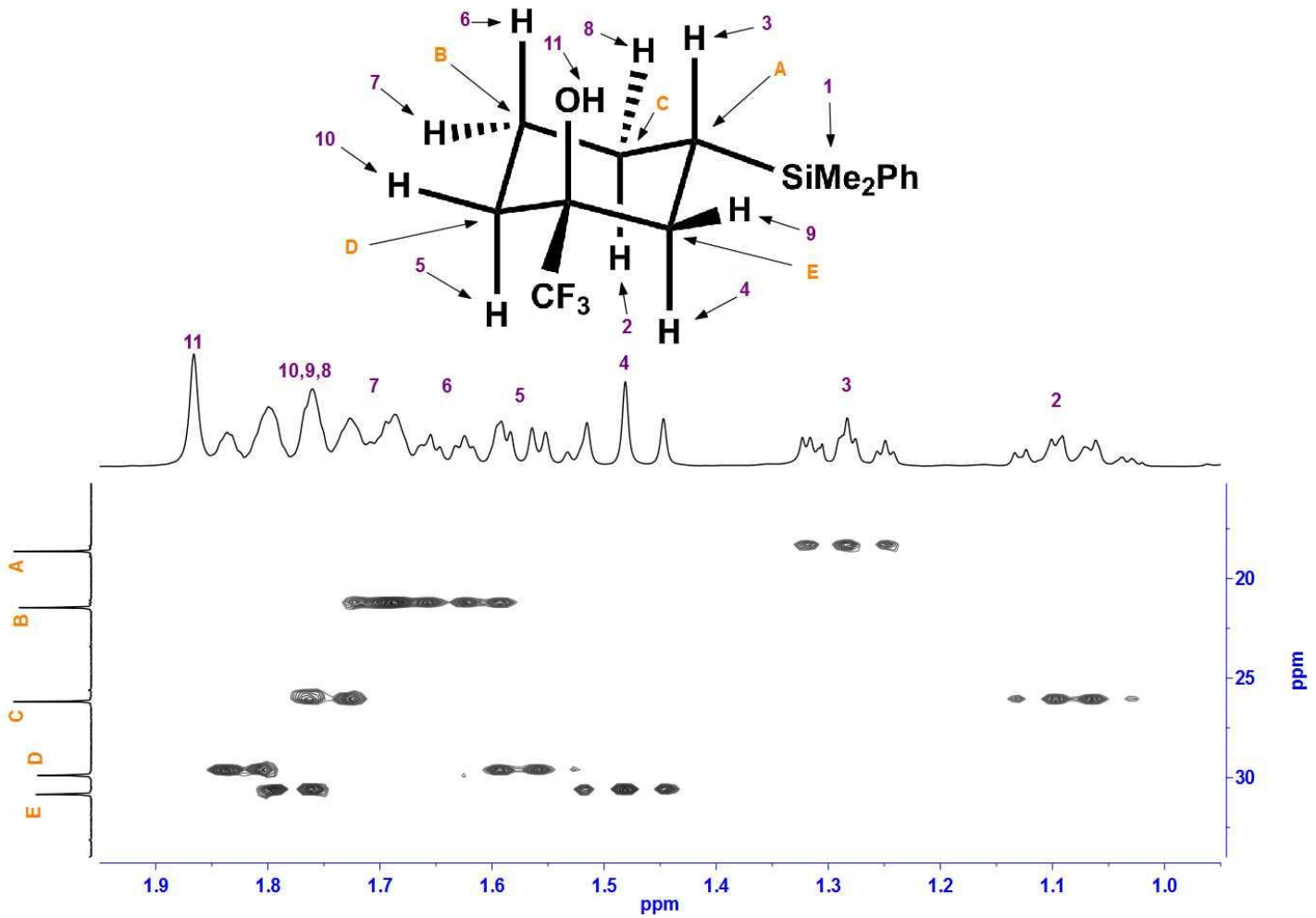
^{1}H-^{19}F HOESY of cyclohexanol **3l′**. The red numbers correspond to the intensity of the cross peak normalized to the weakest signal followed by normalization to the number of proton corresponding to that signal. The HOESY spectrum was collected on a Brüker DRX-400 400 MHz NMR spectrometer. A hoseyph pulse sequence was used with 96 scans of a 2k X 128 matrix collected. The spectrum was obtained using a relaxation delay of 2.2 s, mixing time of 2.4 s, and a phase-sensitive TPPI method. Processing was performed using MestReNova.



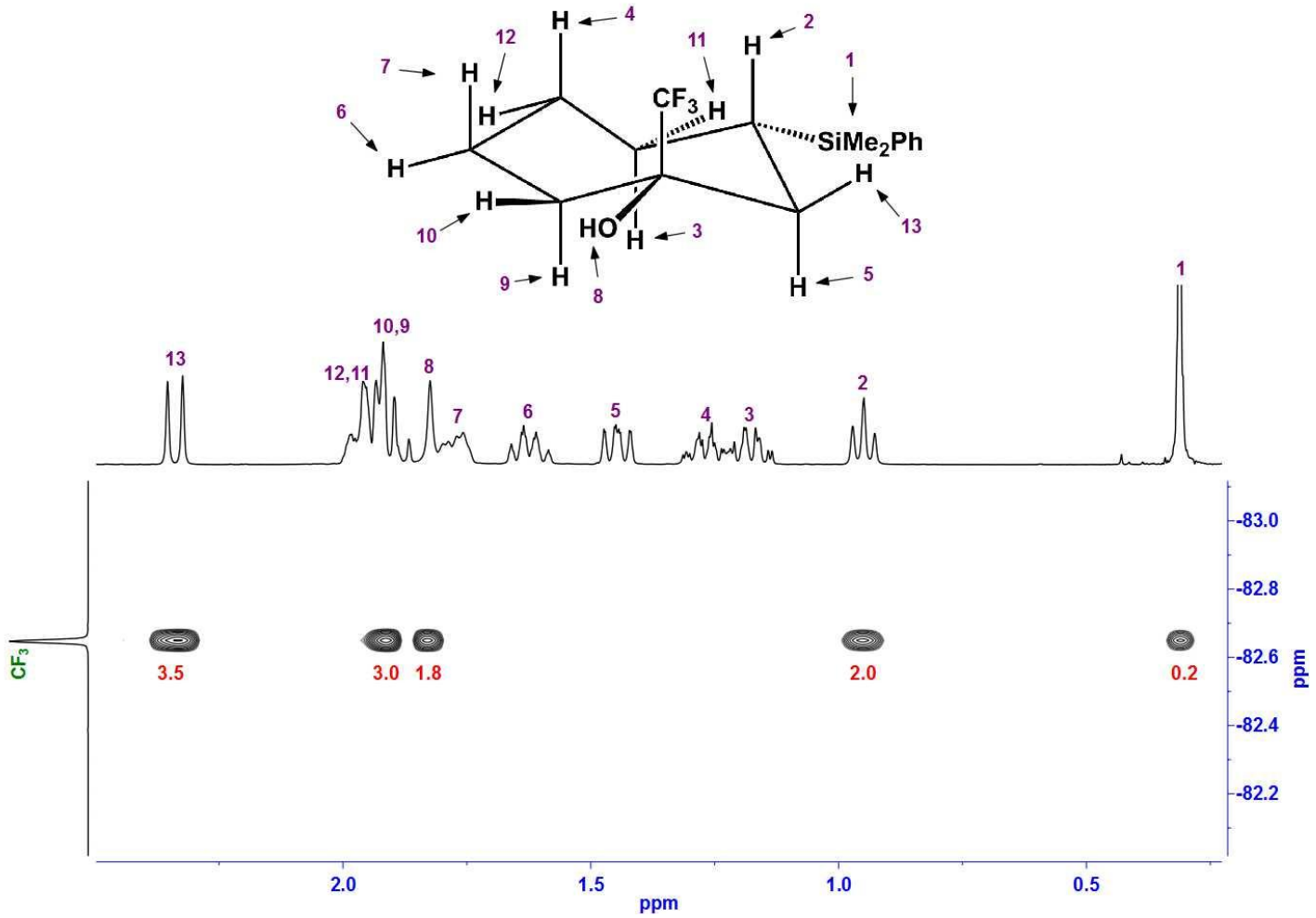
[1]H COSY of cyclohexanol **3l ′**. Processing was performed using MestReNova.



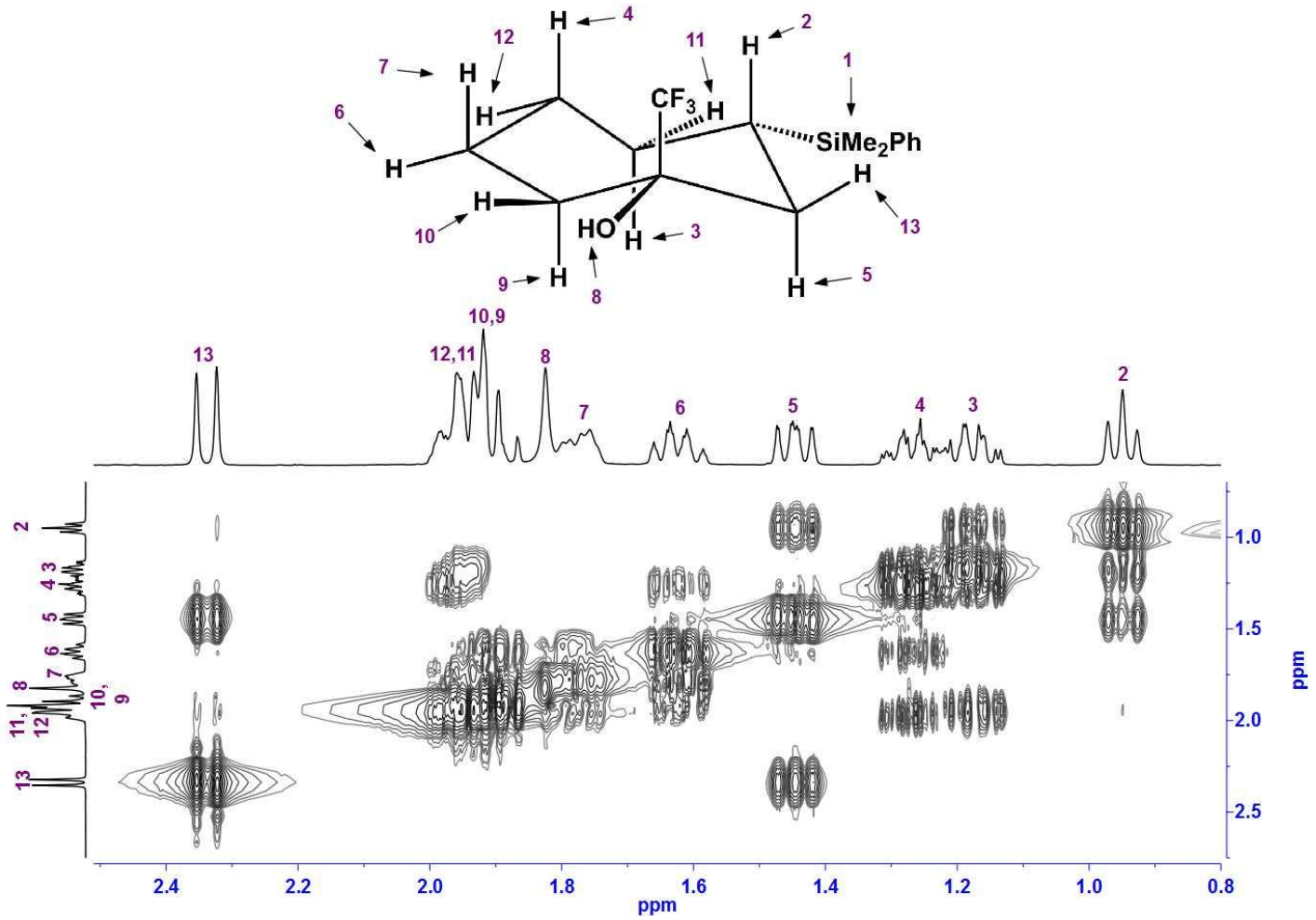
^{1}H NOESY of cyclohexanol **3l′**. Red indicates positive intensities while blue indicates negative intensities. Processing was performed using MestReNova.



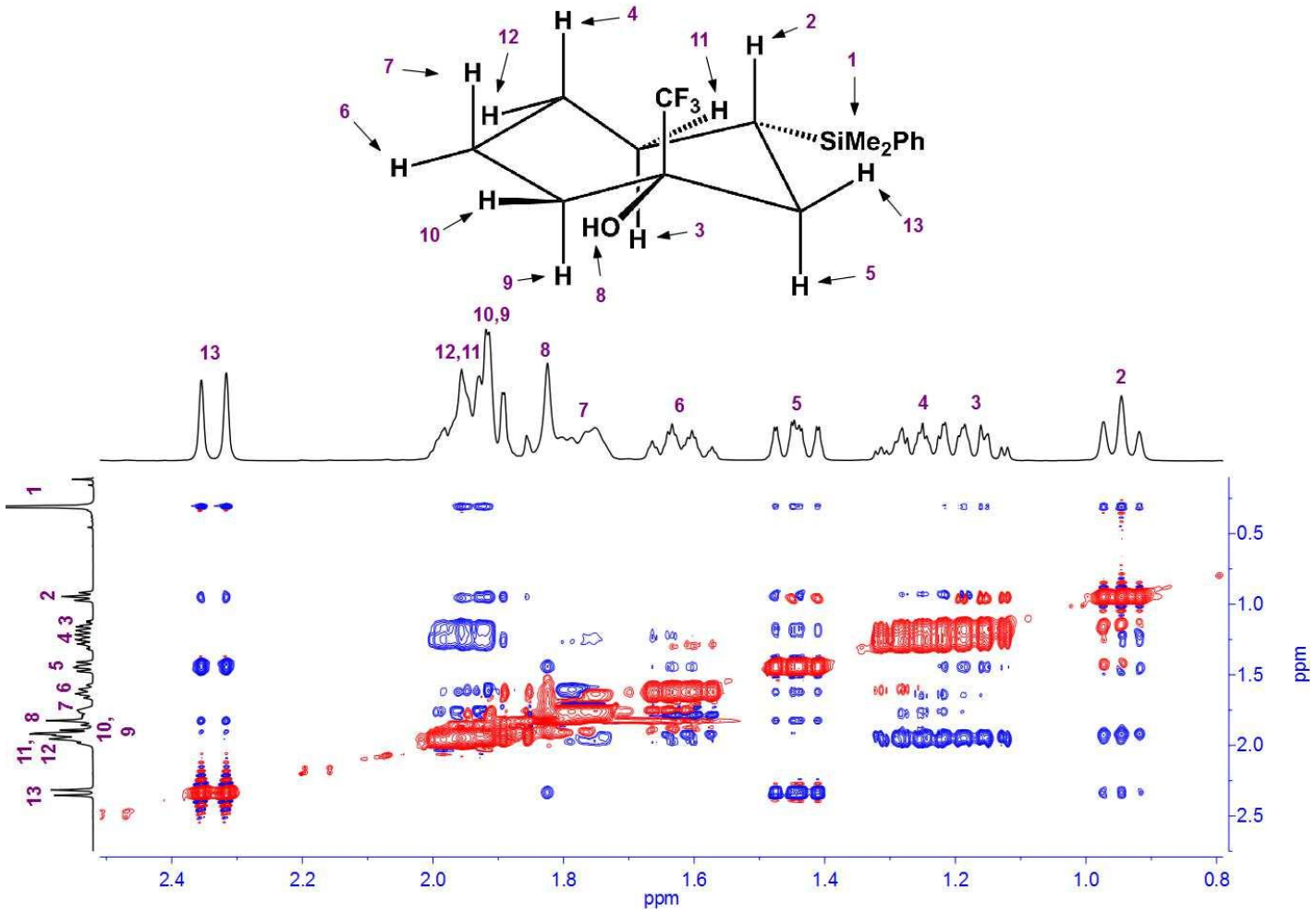
^{1}H-^{13}C HSQC of cyclohexanol **3l′**. Processing was performed using MestReNova.



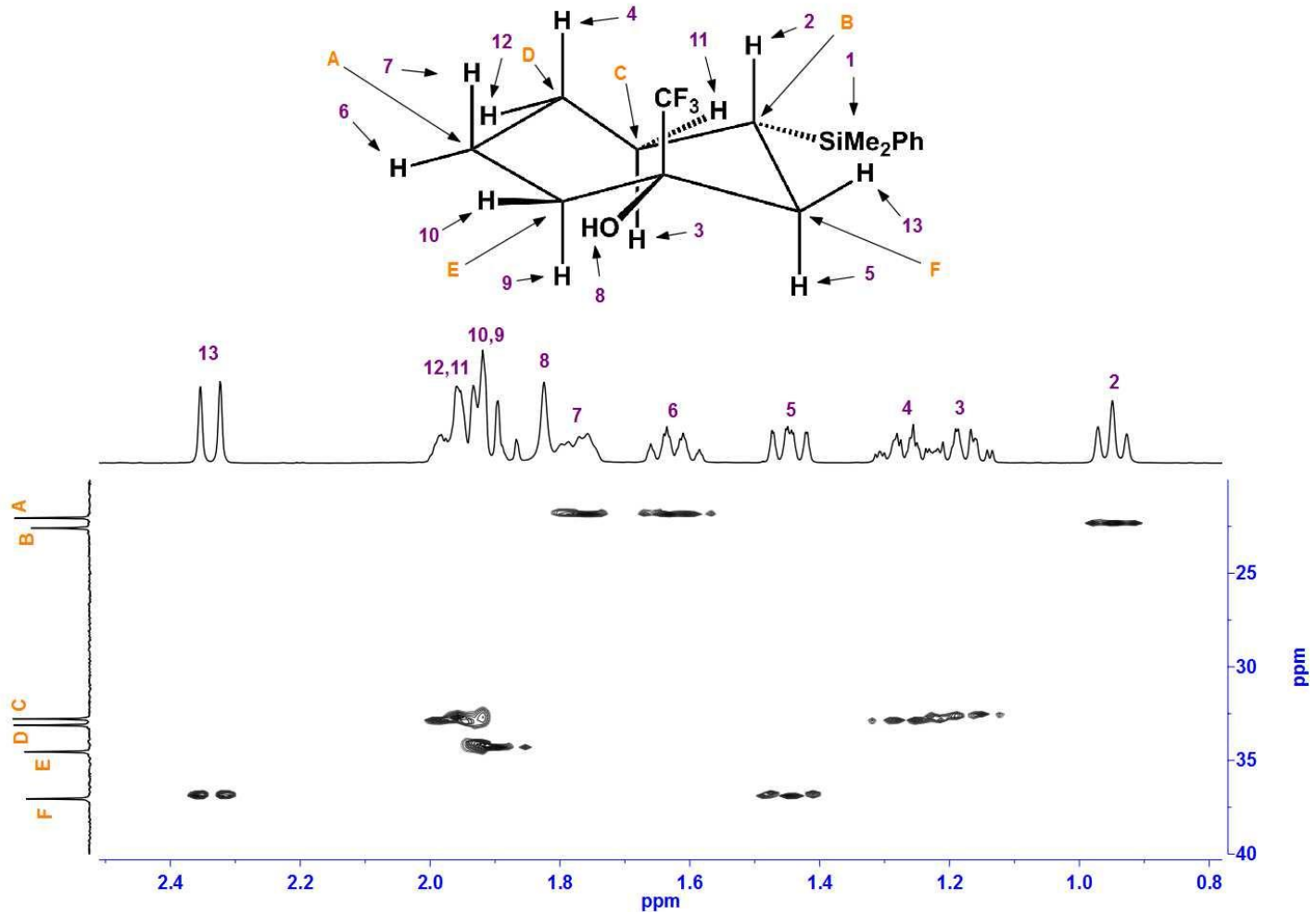
^{1}H-^{19}F HOESY of cycloheptanol **3m**. The red numbers correspond to the intensity of the cross peak normalized to the weakest signal followed by normalization to the number of proton corresponding to that signal. The HOESY spectrum was collected on a Brüker DRX-400 400 MHz NMR spectrometer. A hoseyph pulse sequence was used with 96 scans of a 2k X 128 matrix collected. The spectrum was obtained using a relaxation delay of 2.2 s, mixing time of 2.4 s, and a phase-sensitive TPPI method. Processing was performed using MestReNova.



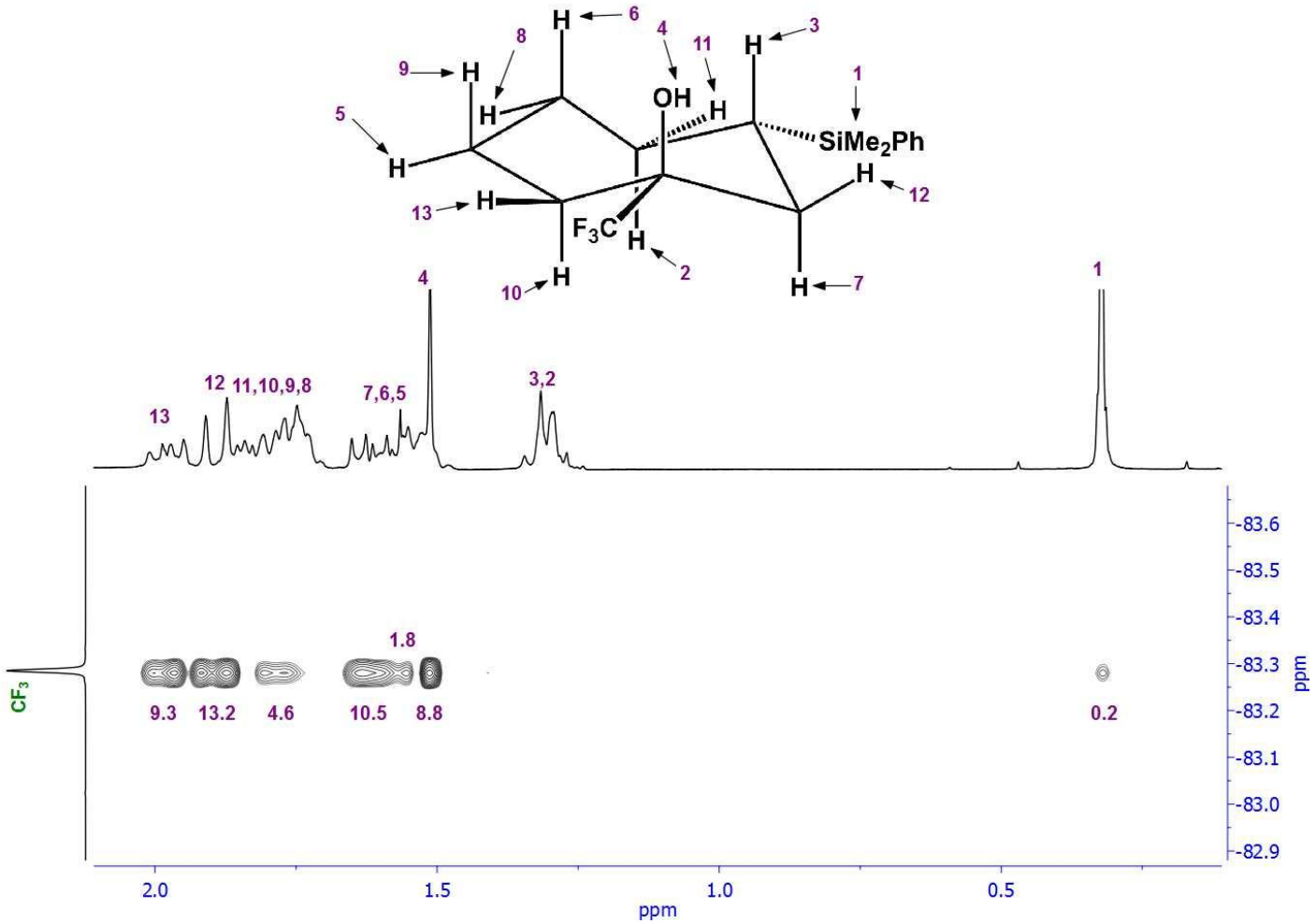
^{1}H COSY of cycloheptanol **3m**. Processing was performed using MestReNova.



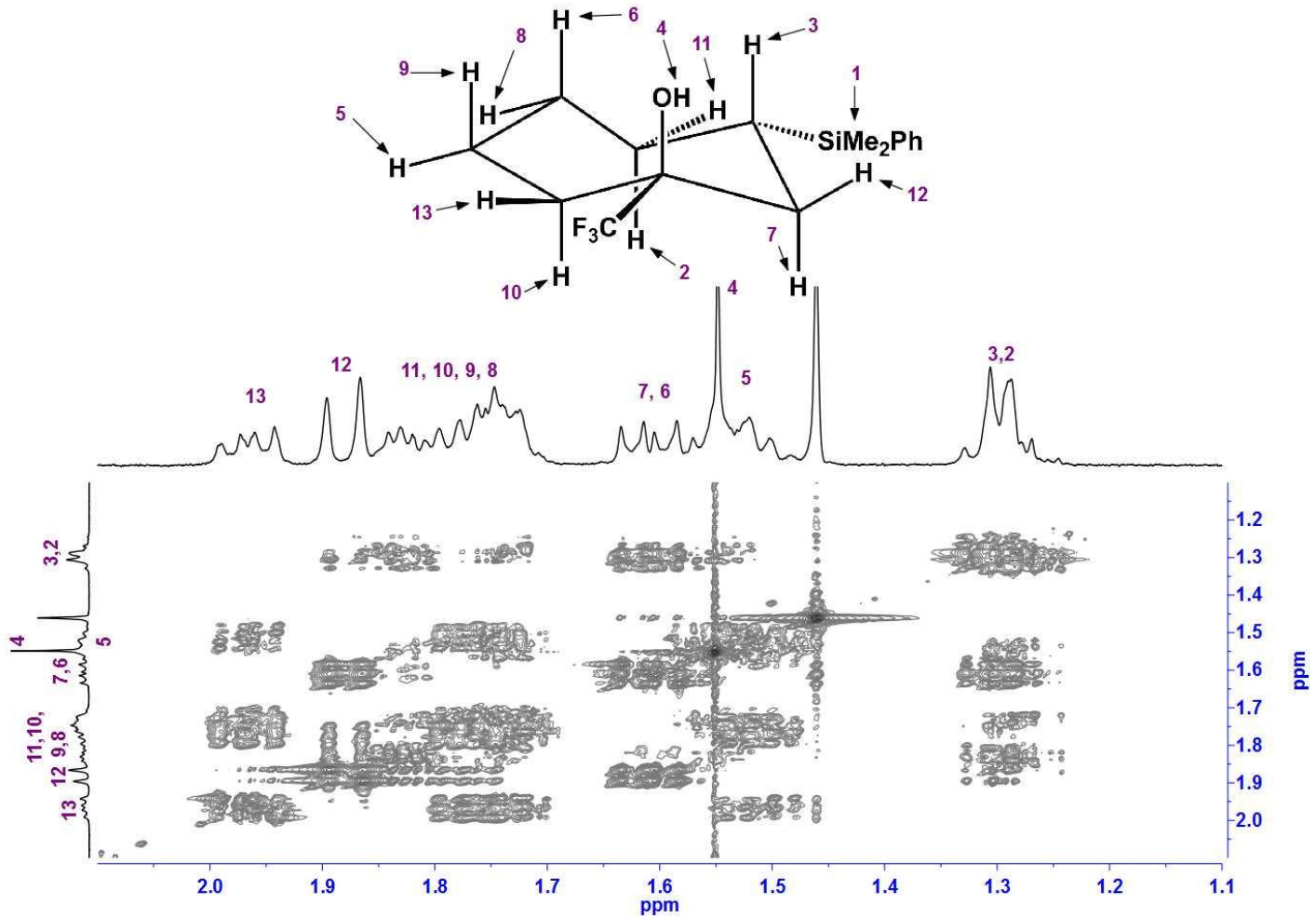
^{1}H NOESY of cycloheptanol **3m**. Red indicates positive intensities while blue indicates negative intensities. Processing was performed using MestReNova.



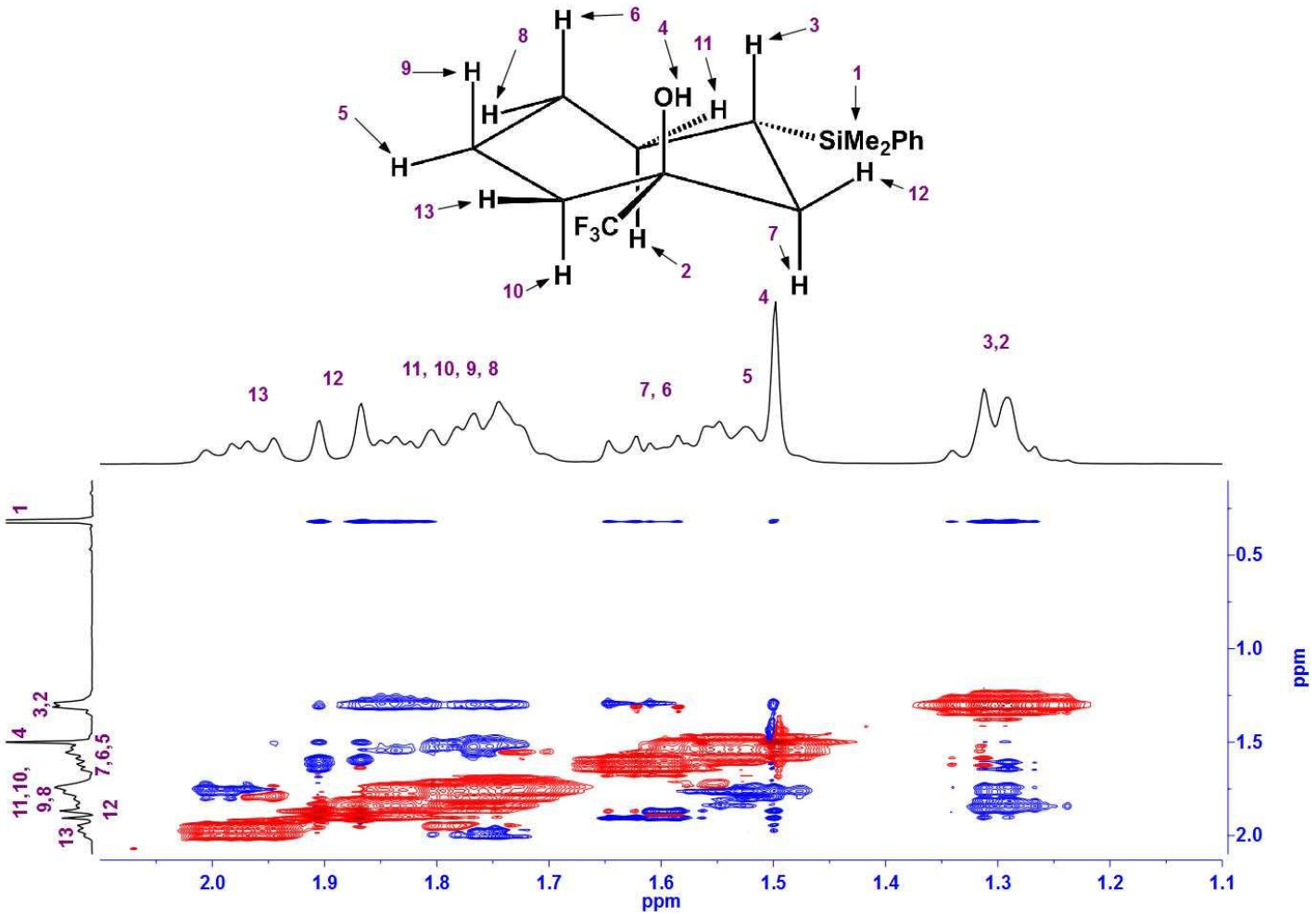
^{1}H-^{13}C HSQC of cycloheptanol **3m**. Processing was performed using MestReNova.



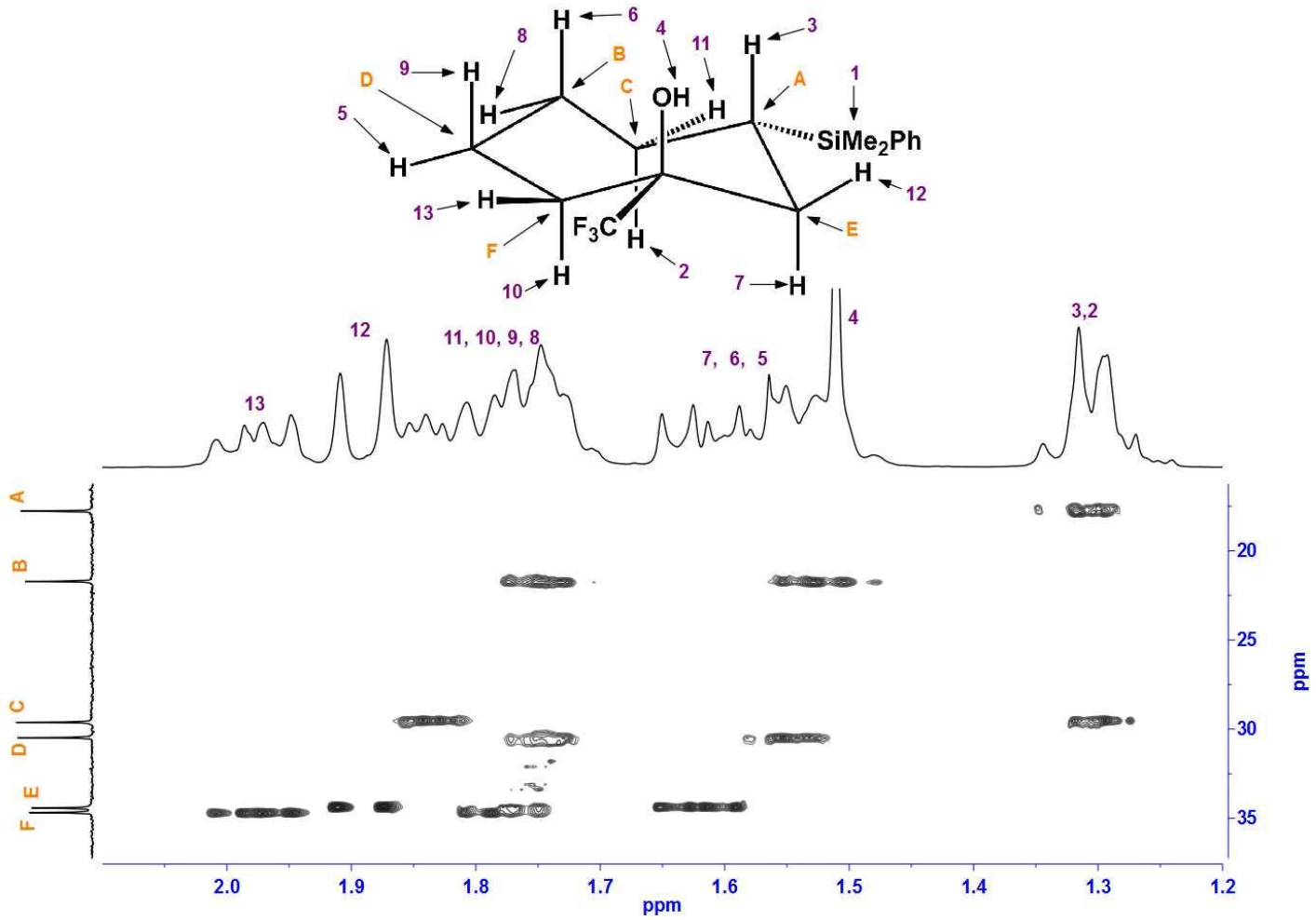
^{1}H-^{19}F HOESY of cycloheptanol **3m′**. The red numbers correspond to the intensity of the cross peak normalized to the weakest signal followed by normalization to the number of proton corresponding to that signal. The HOESY spectrum was collected on a Brüker DRX-400 400 MHz NMR spectrometer. A hoseyph pulse sequence was used with 96 scans of a 2k X 128 matrix collected. The spectrum was obtained using a relaxation delay of 2.2 s, mixing time of 2.4 s, and a phase-sensitive TPPI method. Processing was performed using MestReNova.



[1]H COSY of cycloheptanol **3m′**. Processing was performed using MestReNova.

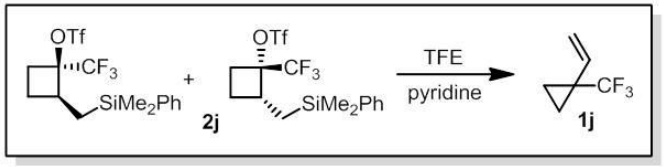


^{1}H NOESY of cycloheptanol **3m′**. Red indicates positive intensities while blue indicates negative intensities. Processing was performed using MestReNova.

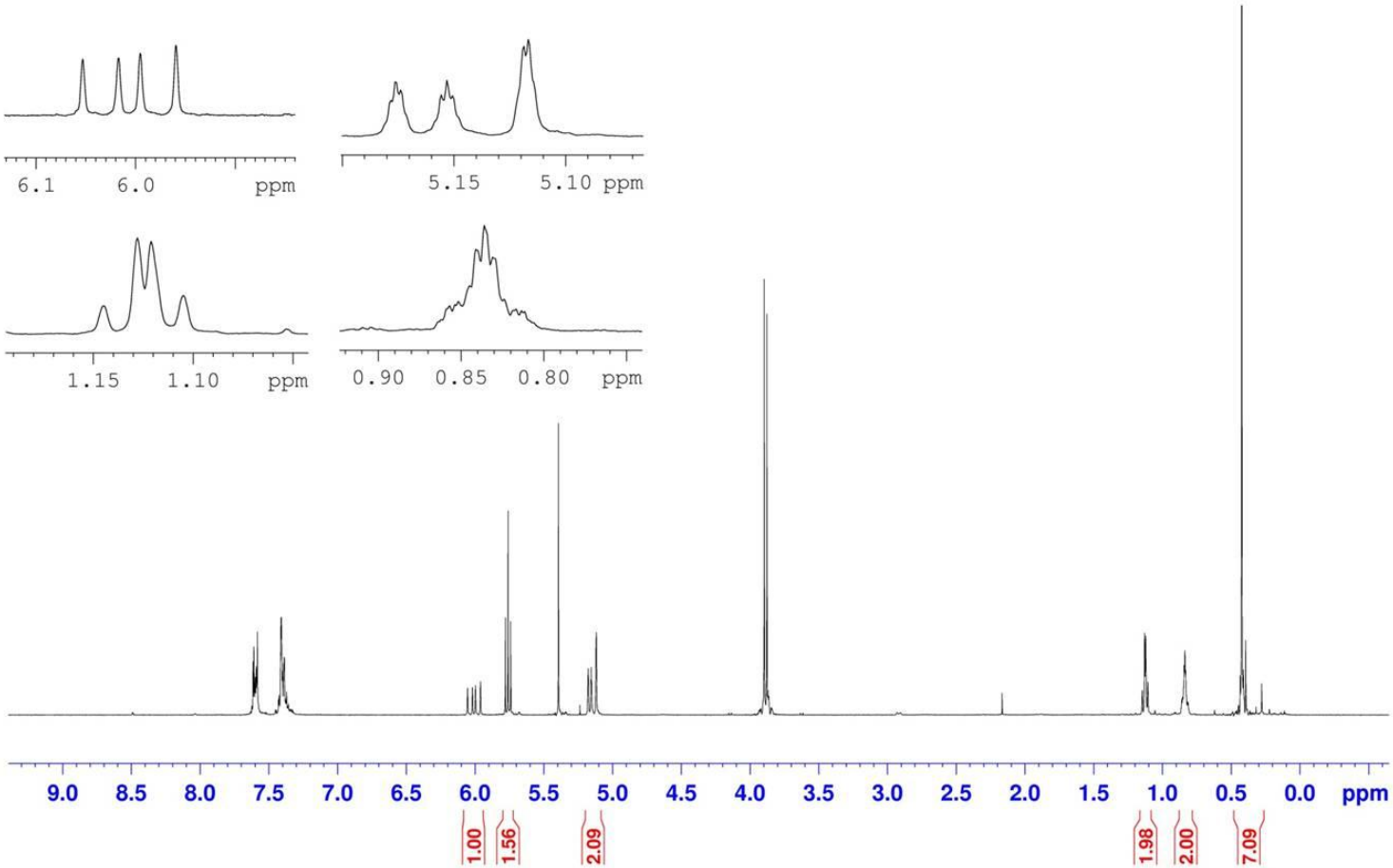


^{1}H-^{13}C HSQC of cycloheptanol **3m′**. Processing was performed using MestReNova.

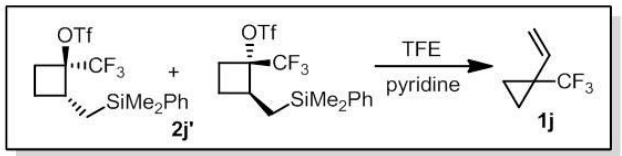
^{1}H-NMR Spectra of Solvolysis Studies

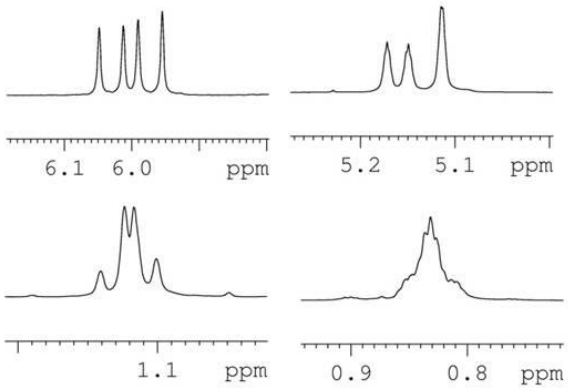


Solvolysis Mixture, 1–(trifluoromethyl)–1–vinylcyclopropane
TCE Method for Yield Determination
300 MHz, CF3CD2OD

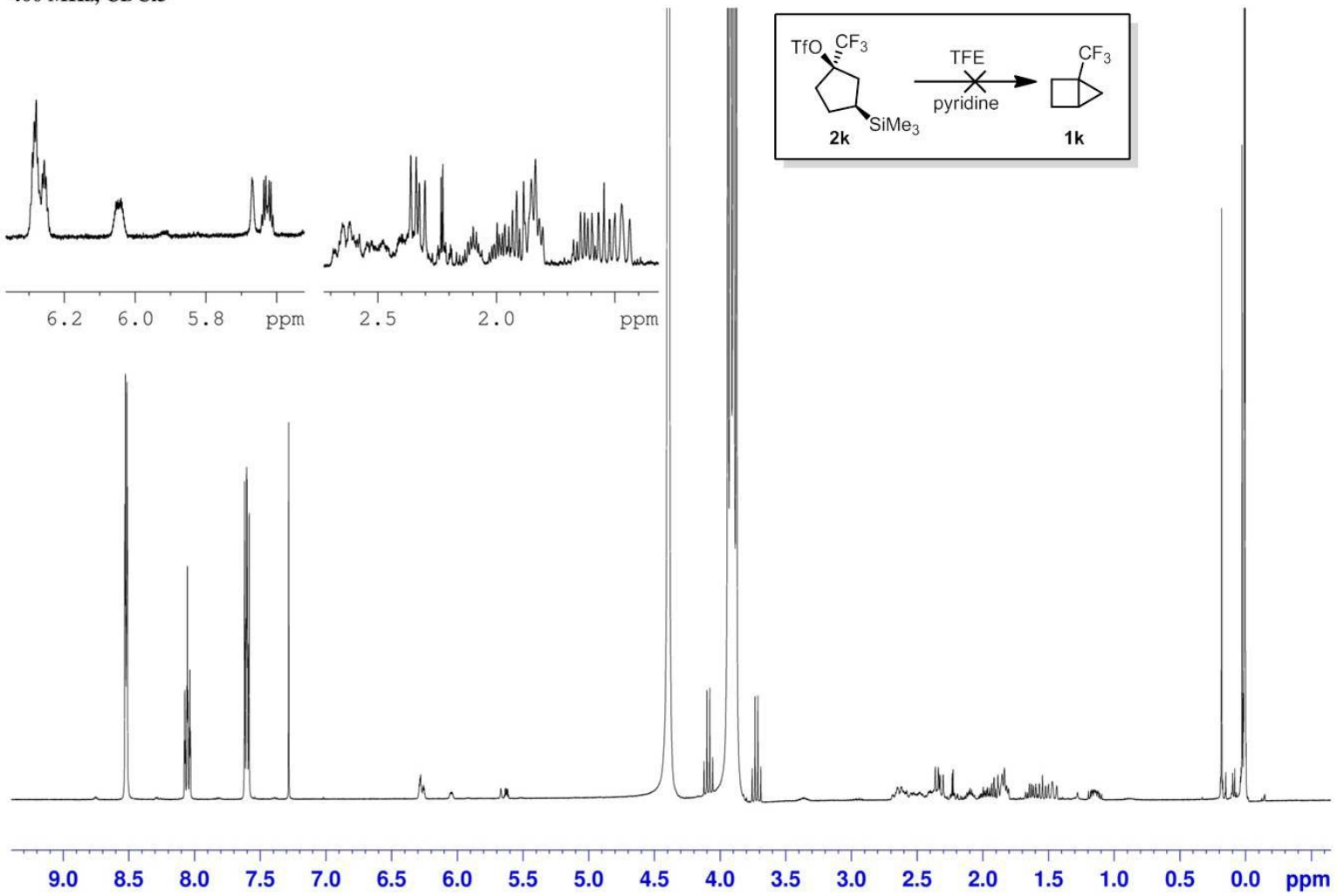


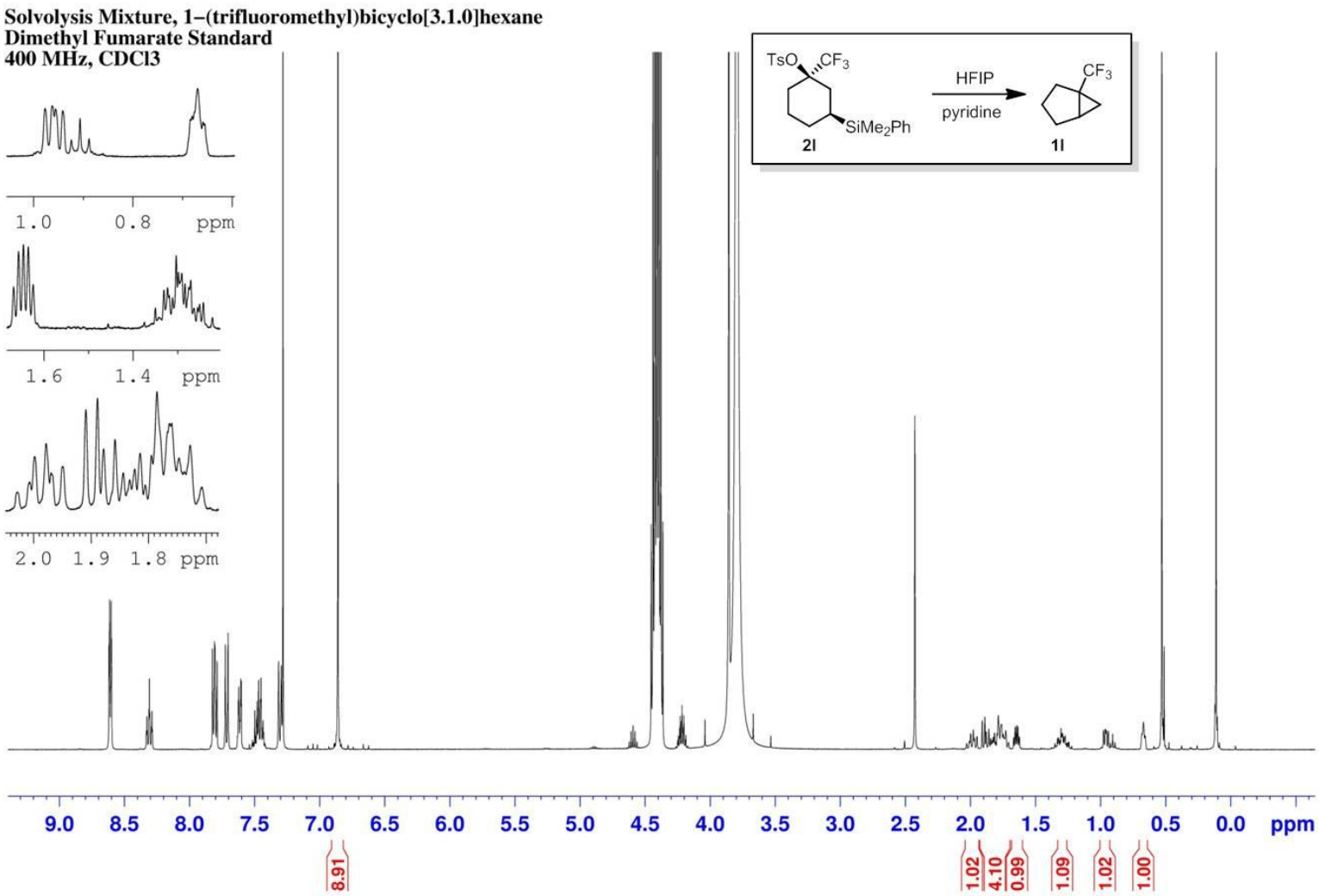
Solvolysis Mixture, 1–(trifluoromethyl)–1–vinylcyclopropane
TCE Method for Yield Determination
300 MHz, CF3CD2OD



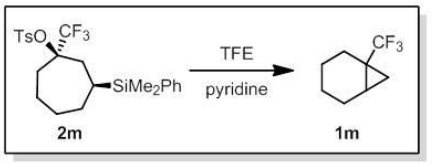


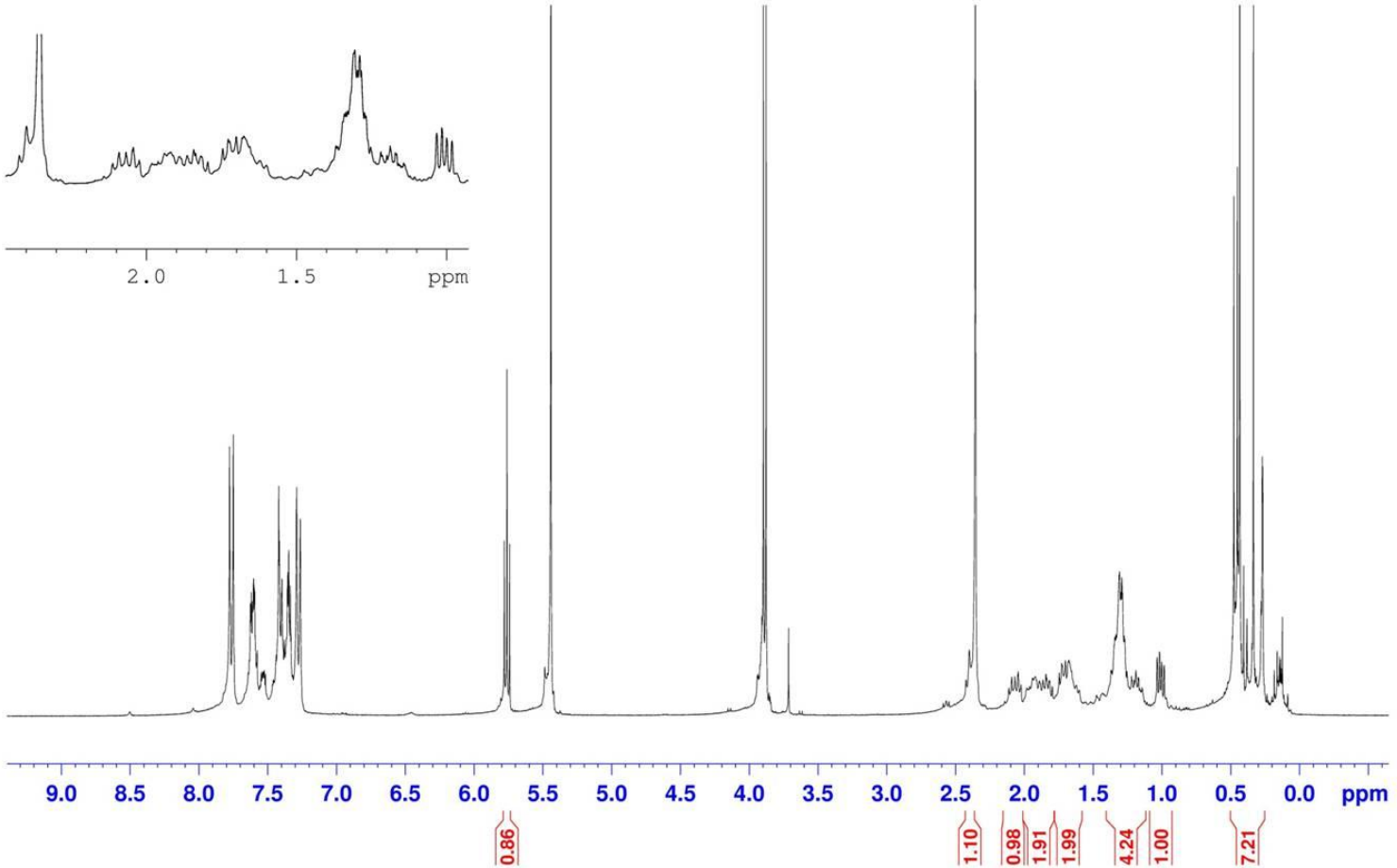
Solvolysis Mixture, Attempted Solvolysis of 1−(trifluoromethyl)−3−(trimethylsilyl)cyclopentyl trifluoromethanesulfonate "Cis"
400 MHz, CDCl3

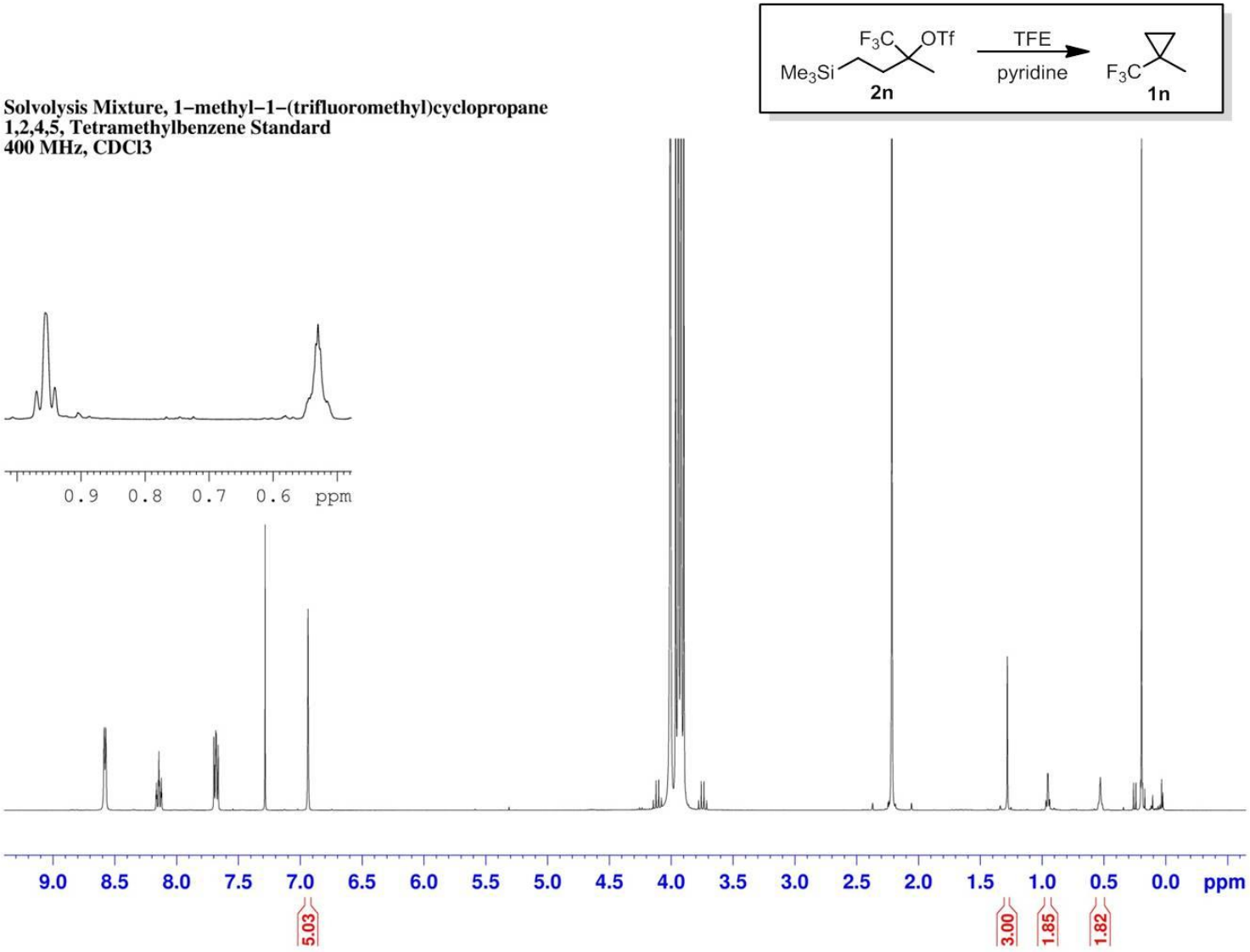


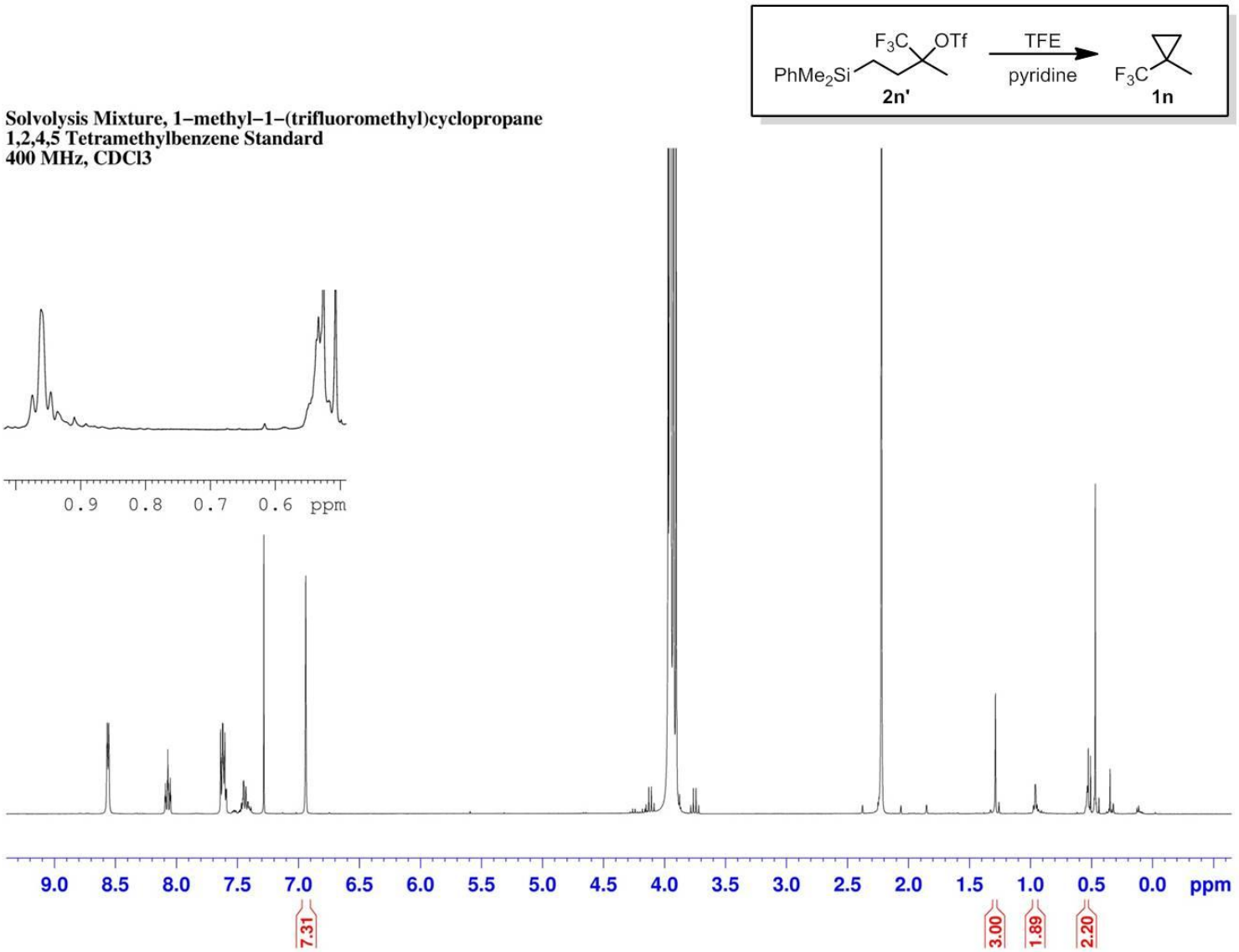

Solvolysis Mixture, 1−(trifluoromethyl)bicyclo[3.1.0]hexane
Dimethyl Fumarate Standard
400 MHz, CDCl3
TsO
CF3
SiMe2Ph
2l
HFIP
pyridine
CF3
1l
1.0
0.8
ppm
1.6
1.4
ppm
2.0
1.9
1.8
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
8.91
1.02
4.10
0.99
1.09
1.02
1.00

Solvolysis Mixture, 1–(trifluoromethyl)bicyclo[4.1.0]heptane
TCE Method for Yield Determination
300 MHz, CF3CD2OD

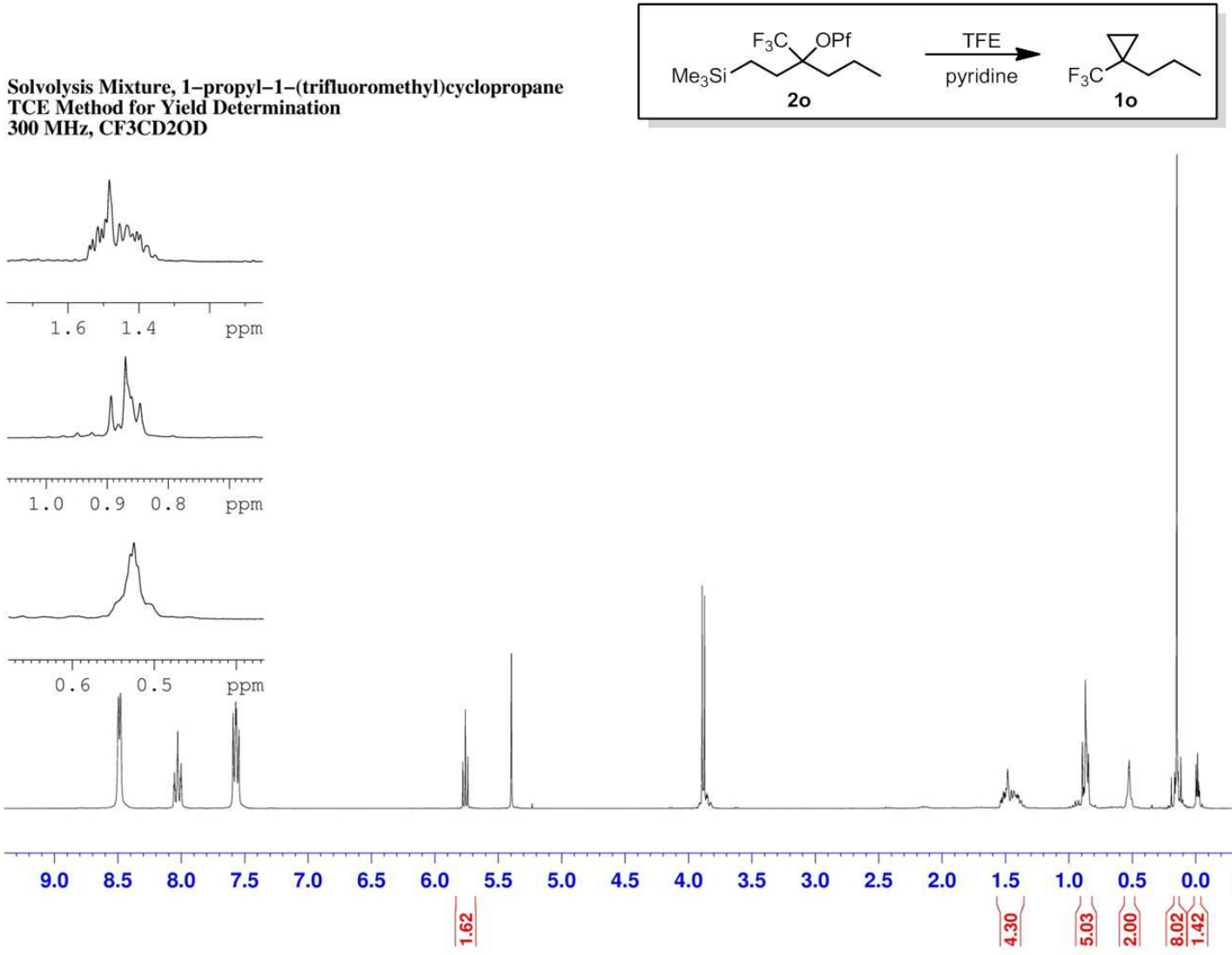


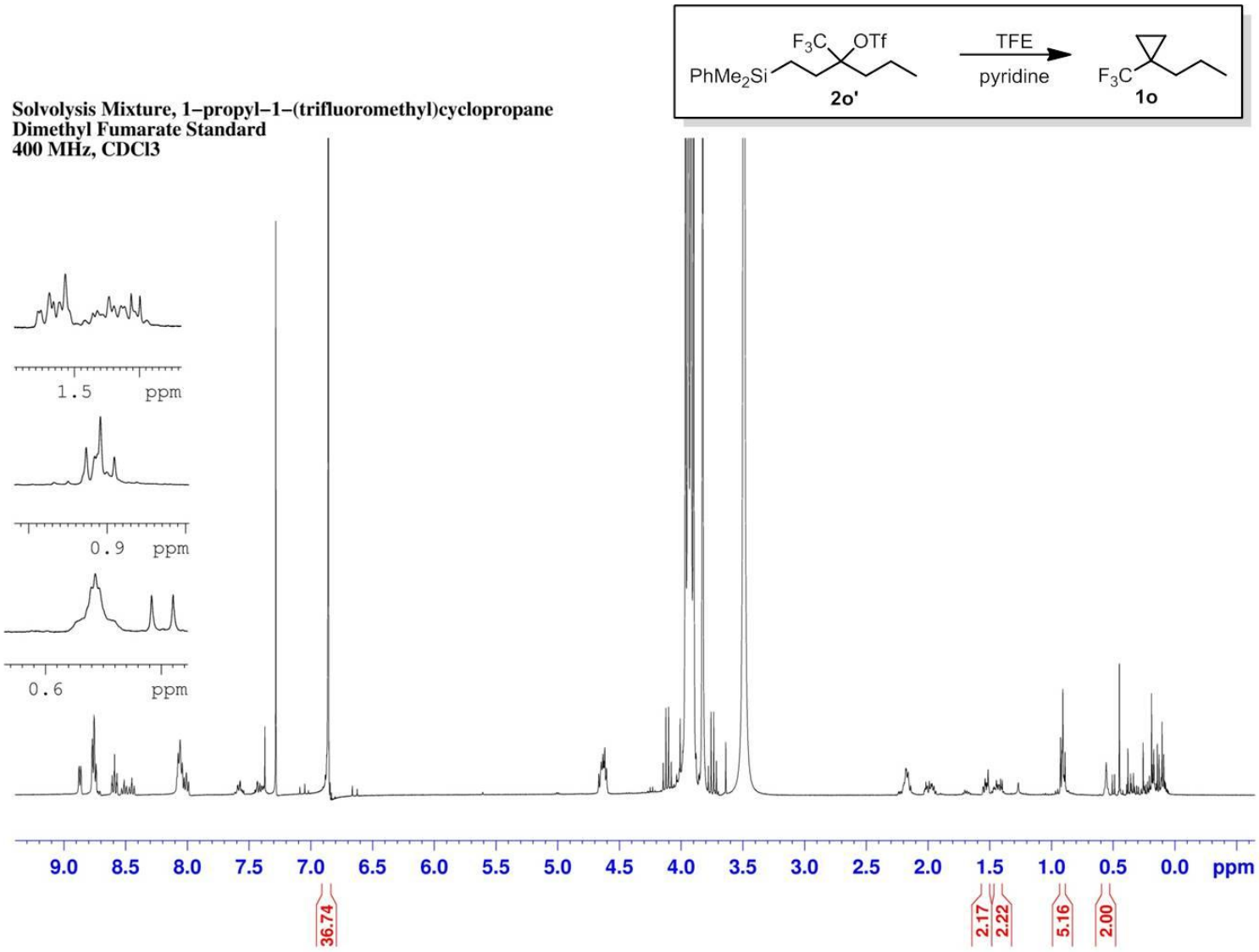


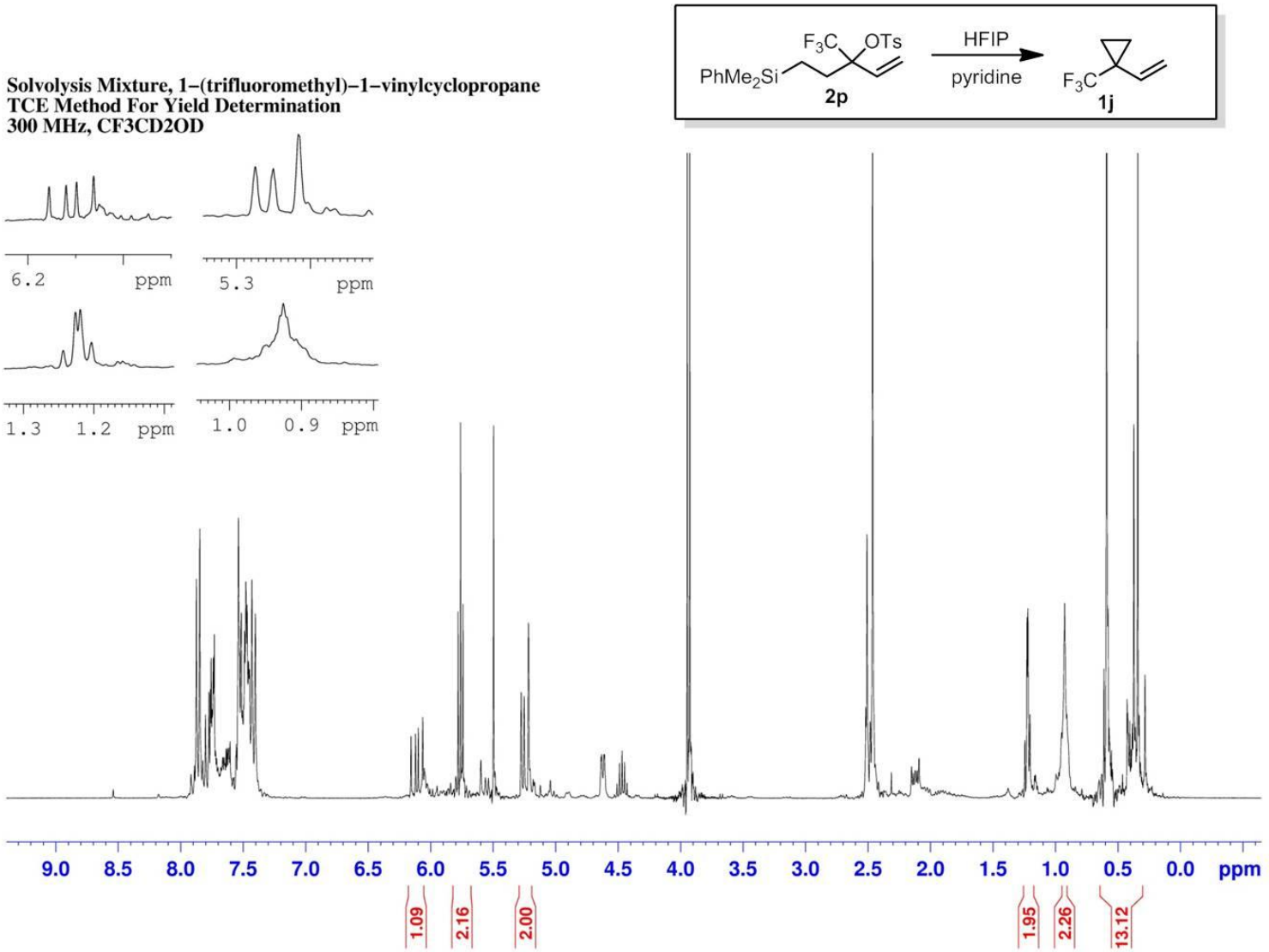

F3C
OTf
Me3Si
2n
TFE
pyridine
F3C
1n
Solvolysis Mixture, 1−methyl−1−(trifluoromethyl)cyclopropane
1,2,4,5, Tetramethylbenzene Standard
400 MHz, CDCl3
0.9 0.8 0.7 0.6 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.03
3.00
1.85
1.82


F3C
OTf
PhMe2Si
2n'
TFE
pyridine
F3C
1n
Solvolysis Mixture, 1−methyl−1−(trifluoromethyl)cyclopropane
1,2,4,5 Tetramethylbenzene Standard
400 MHz, CDCl3
0.9 0.8 0.7 0.6 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
7.31
3.00
1.89
2.20

Solvolysis Mixture, 1–propyl–1–(trifluoromethyl)cyclopropane
TCE Method for Yield Determination
300 MHz, CF3CD2OD




F3C OTf
PhMe2Si
2o'
TFE
pyridine
F3C
1o
Solvolysis Mixture, 1–propyl–1–(trifluoromethyl)cyclopropane
Dimethyl Fumarate Standard
400 MHz, CDCl3
1.5 ppm
0.9 ppm
0.6 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
36.74
2.17
2.22
5.16
2.00


Solvolysis Mixture, 1–(trifluoromethyl)–1–vinylcyclopropane
TCE Method For Yield Determination
300 MHz, CF3CD2OD
F3C
OTs
PhMe2Si
2p
HFIP
pyridine
F3C
1j
6.2
ppm
5.3
ppm
1.3
1.2
ppm
1.0
0.9
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.09
2.16
2.00
1.95
2.26
13.12