Supporting Information

Key to Abbreviated Terms:

4CzIPN: 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile
bpy: 2,2′-bipyridyl
dtbbpy: 4,4′-di-*tert*-butyl-2,2′-dipyridyl
LED: Light-emitting diode
ppy: 2-(pyridinyl)phenyl

General Considerations:

General: All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 4- or 5-port dual-bank manifold. Argon or nitrogen was used to provide such an atmosphere. LED irradiation was accomplished using the LED reactors described in our previous reports or the new reactor design outlined here.[1] NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K. ^{1}H NMR spectra were referenced to residual non-deuterated chloroform (δ 7.26) in $CDCl_3$, residual DMSO-d_5 (δ 2.50) in DMSO-d_6, acetone-d_5 (δ 2.09) in acetone-d_6, and residual MeCN-d_2 (δ 1.94) in MeCN-d_3. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.30), DMSO-d_6 (δ 39.52), the carbonyl carbon of acetone (δ 205.87), or the nitrile carbon of MeCN-d_3 (δ 118.26), respectively ^{19}F NMR spectra were referenced to hexafluorobenzene (δ –164.9)[2] as an internal standard and are run with C-F/C-H decoupling. ^{11}B NMR spectra were obtained on a spectrometer equipped with the appropriate decoupling accessories. Reactions were monitored by HPLC, GC/MS, ^{1}H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using permanganate stain, Seebach's stain,[3] ninhydrin stain, and/or UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32-63 μm). Flash chromatography was accomplished using an automated system (monitoring at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 μm). Solvents were purified with drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected.

Chemicals: Deuterated NMR solvents were either used as purchased (MeCN-d_3, acetone-d_6, DMSO-d_6) or stored over 4Å molecular sieves and/or K_2CO_3 ($CDCl_3$). Na_2SO_4, $MgSO_4$, CH_2Cl_2, $CHCl_3$, EtOAc, pentane, hexanes, MeOH, Et_2O, and toluene were used as purchased. Et_3N was purchased from commercial suppliers and distilled from CaH_2 prior to use. THF was purchased and dried *via* a solvent delivery system. DMF (99.8%, extra dry) and DMSO (99.8%, extra dry)

[1] For information on these reactors and their construction see the supporting information of: (a) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764. (b) Jouffroy, M.; Kelly, C. B.; Molander, G. *Org. Lett.* **2016**, *18*, 876.
[2] Ravikumar, I.; Saha, S.; Ghosh, P. *Chem. Commun*. **2011**, *47*, 4721.
[3] Seebach, D.; Imwinkelried, R; Stucky, G. *Helv. Chim. Acta* **1987**, *70*, 448.

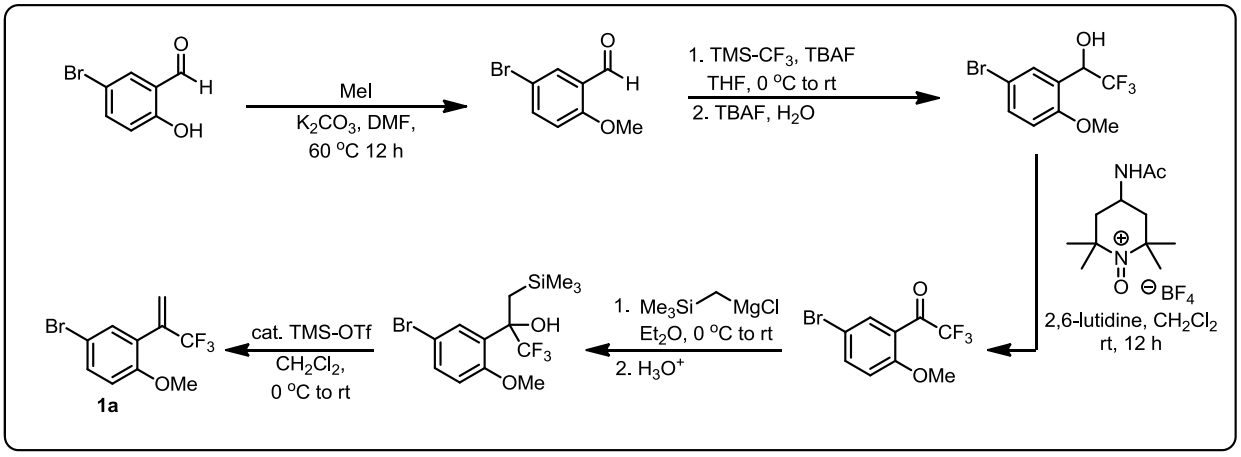
were purchased from commercial sources and stored over 4 Å molecular sieves. The transition metal photocatalysts $Ru(bpy)_3(PF_6)_2$ and $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ were prepared in-house by the procedure outlined in our previous publications.[1a,4] The organic photocatalyst 4CzIPN was prepared in-house by the procedure outlined in our previous publication.[5] Perfluoroalkyl-substituted alkenes were prepared in-house using the procedures outlined here. New organotrifluoroborates, α-silylamines, and alkylbis(catecholato)silicates were prepared in-house according to the procedures outlined here. Information (preparation protocols, characterization, etc.) for previously synthesized radical precursors (**2g**, **2k**, **2n**, **2p**, **2r**, **2s**, **2v**-**z**) can be found in our earlier reports.[5,6] All other radical precursors were purchased from commercial suppliers. Trifluoromethyl-substituted alkenes **1f**[7] and **1o**[8] were synthesized as outlined in previous reports. The oxoammonium salt 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium tetrafluoroborate ("Bobbitt's Salt") was prepared in the manner previously reported.[9]

Photochemistry: Irradiation of reaction vessels was accomplished using blue LEDs. LEDs were configured as outlined in the *Photochemical Reactor Design* section of our previous articles[1b,c] or using two 34 W blue LED lamps with the sample positioned ~ 6 cm from each lamp. A fan was employed to ensure reactions remained at or near rt when using LEDs.

[4] Tellis, J. C.; Primer, D. P.; Molander, G. A. *Science* **2014**, *345*, 433.
[5] Patel, N. P.; Kelly, C. B.; Siegenfeld, A. P.; Molander, G. A. *ACS Catal.* **2017**, *7*, 1766.
[6] ***Alkylsilicates*** (a) Jouffroy, M.; Primer, D.; Molander, G. A. *J. Am. Chem. Soc.* **2016**, *138*, 475; (b) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.*, **2016**, *18*, 764; (c) Jouffroy, M.; Davies, G. H. M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 1606; (d) Lin, K.; Wiles, R. J.; Kelly, C. B.; Davies, G. H. M.; Molander, G. A. *ACS Catal.* **2017**, *7*, 5129; ***Organotrifluoroborates*** (e) Molander, G. A.; Wisniewski, S. R. *J. Am. Chem. Soc.* **2012**, *134*, 16856. (f) Molander, G. A.; Canturk, B. *Org. Lett.* **2008**, *10*, 2135; (g) Primer, D. N.; Molander, G. A. *J. Am. Chem. Soc.* **2017**, *139*, 9847.
[7] Hamlin, T. A.; Kelly, C. B.; Cywar, R. M.; Leadbeater, N. E. *J. Org. Chem.* **2014**, *79*, 1145.
[8] Trost, B. M.; Debien, L. *J. Am. Chem. Soc.* **2015**, *137*, 11606.
[9] Mercadante, M. A.; Kelly, C. B.; Bobbitt, J. M.; Tilley, L. J.; Leadbeater, N. E. *Nat. Protoc.* **2013**, *8*, 666.

Synthesis of Perfluoroalkyl-Substituted Alkenes

Preparation of 4-bromo-1-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1a)



Methylation

5-Bromo-2-methoxybenzaldehyde[10]

This procedure is a modification of the procedure outlined by McQuaid et al.[11] To a 150 mL round bottom flask equipped with a stir bar was added K_2CO_3 (30.88 g, 0.223 mol, 3 equiv), DMF (75 mL) and 5-bromosalicylaldehyde (14.97 g, 0.0745 mol, 1 equiv). The solution became bright orange-yellow upon addition of the phenol. MeI (31.71 g, 13.91 mL, 0.223 mol, 3 equiv) was then added in one portion. The flask was equipped with an air-cooled reflux condenser and heated to 60 ºC in an oil bath. The solution was stirred at this temperature overnight.

At this time, the reaction mixture was transferred to a separatory funnel and diluted with a 50:50 by volume mixture of Et_2O (100 mL)[12] and EtOAc (100 mL). Deionized H_2O (200 mL) was added, and the layers were separated. The aq layer was extracted with a 1:1 by volume mixture of Et_2O/EtOAc (3 × 50 mL). The combined organic layers were washed with 2 M aq NaOH (150 mL), deionized H_2O (3 × 100 mL), and finally brine (100 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording the pure anisole (14.97 g, 94%) as a powdery pale-yellow solid (mp = 90-91 °C).

[10] Teichert, J. F.; Feringa, B. L. *Chem. Commun.* **2011**, *47*, 2679.
[11] McQuaid, K. M.; Long, J. Z.; Sames, D. *Org. Lett.* **2009**, 11, 2972.
[12] The desired methylation product is poorly soluble in Et_2O but is much more soluble in EtOAc. Conversely, DMF partitions better into EtOAc than into Et_2O. Thus, a split solvent system was used as a compromise to these two extremes.

^{1}H NMR δ 3.92 (s, 3H), 6.89 (d, *J* = 8.9 Hz, 1H), 7.63 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.92 (d, *J* = 2.6 Hz, 1H), 10.38 (s, 1H).

^{13}C NMR δ 56.3 (CH_3), 113.8 (C), 114.0 (CH), 126.4 (C), 131.4 (CH), 138.6 (CH), 161.0 (C), 188.6 (C).

Trifluoromethylation

1-(5-Bromo-2-methoxyphenyl)-2,2,2-trifluoroethanol[13]

The following is a modification of the procedure outline by Kelly et al.[14] To a 250 mL round bottom flask equipped with a stir bar was added 5-bromo-2-methoxybenzaldehyde (12.90 g, 0.060 mol, 1 equiv), THF (100 mL), and Me_3SiCF_3 (10.65 g, 0.075 mol, 1.25 equiv). The flask was sealed with a rubber septum and placed under an argon atmosphere *via* an inlet needle. The reaction mixture was cooled to 0 ^oC[15] in an ice-water bath. After stirring for approximately 10 min, TBAF (1 M in THF, 0.6 mL, 0.0006 mol, 0.01 equiv) was added dropwise *via* a syringe. After stirring for 10 min, the ice-bath was removed, and the solution was allowed to stir for approximately 8 h at rt.

To cleave the silyl ether formed by the reaction, H_2O (6 mL, 0.333 mol, ~ 5.5 equiv) was added *via* a syringe followed by TBAF (1 M in THF, 6 mL, 0.006 mol, 0.1 equiv). When the cleavage was judged to be complete,[16] the contents of the flask were transferred to a separatory funnel. Deionized H_2O (150 mL) and Et_2O (~150 mL) were added, and the layers were partitioned. The aq layer was extracted with Et_2O (3 × ~50 mL). The organic layers were combined, then washed once with deionized H_2O (150 mL) and brine (150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording crude 1-(5-bromo-2-methoxyphenyl)-2,2,2-trifluoroethanol. The crude product was purified by vacuum distillation

[13] Litvinas, N. D.; Brodsky, B. H.; Bois, J. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 4513.
[14] Kelly, C. B.; 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.
[15] Note that on small scales (< 20 mmol), the TBAF could be added relatively quickly. However, upon scale-up, the addition of TBAF is quite exothermic. Hence, it is recommended that the TBAF be added as slowly as possible, and/or cooling the reaction mixture to a temperature lower than that of 0 °C.
[16] It is recommended that this cleavage step be monitored by some form of spectroscopy or spectrometry (e.g., NMR or GC/MS).

(bp 98-100 °C @ 0.1 mmHg), giving the pure CF_3 alcohol (15.24 g, 89%) as a clear, pale-yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.40 (br s, 1H), 3.85 (s, 3H), 5.25 - 5.34 (m, 1H), 6.82 (d, J = 8.7 Hz, 1H), 7.46 (dd, J = 8.9, 2.4 Hz, 1H), 7.55 (d, J = 2.3 Hz, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 56.2 (CH_3), 68.3 (q, $J_{C\text{-}C\text{-}F}$ = 32.1 Hz, CH), 113.2 (CH), 113.4 (C), 124.5 (C), 124.6 (q, $J_{C\text{-}F}$ = 283.2 Hz, CF_3), 132.0 (CH), 133.5 (CH), 156.7 (C).
^{19}F NMR ($CDCl_3$, 471 MHz) δ -81.10 (s, 3F).

Oxidation

1-(5-Bromo-2-methoxyphenyl)-2,2,2-trifluoroethanone[17]

To a one-neck, 300 mL round bottom flask equipped with a stir bar was added 1-(5-bromo-2-methoxyphenyl)-2,2,2-trifluoroethanol (15.06 g, 0.053 mol, 1 equiv), 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium tetrafluoroborate (41.26 g, 0.137 mol, 2.6 equiv), and CH_2Cl_2 (130 mL). The mixture was allowed to stir at rt for approximately 5 min. At this time, 2,6-lutidine (12.78 g, 13.81 mL, 0.1193 mol, 2.25 equiv) was added all at once, and the flask was sealed with a rubber septum. The reaction mixture was stirred overnight at rt, gradually turning red. The solvent was removed *in vacuo* to afford a thick red residue. To this thick residue was added Et_2O (~125 mL), causing immediate precipitation of the spent oxidant. The heterogeneous solution was allowed to stir for 10 min, and the solids were filtered off through a medium porosity fritted funnel, washing with Et_2O (~150 mL). The solids were saved for oxidant reclamation,[18] and the solvent was removed from the filtrate *in vacuo* by rotary evaporation. The crude liquid material was then loaded atop a silica gel plug. The plug was eluted with Et_2O (~ 200 mL) to remove any of the residual spent oxidant. The solvent was removed from the filtrate *in vacuo* by rotary evaporation to give the crude trifluoromethyl ketone. Further purification was accomplished by vacuum distillation (bp 70-72 °C @ 0.1 mmHg), giving the pure CF_3 alcohol (12.10 g, 81%) as a clear yellow oil.

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[17] Litvinas, N. D.; Brodsky, B. H.; Bois, J. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 4513.
[18] Regeneration of the oxoammonium salt from the nitroxide, 4-acetamido-(2,2,6,6-tetramethyl-piperidin-1-yl)oxyl, can be performed as outlined in the published protocol, see: Mercadante, M. A.; Kelly, C. B.; Bobbitt, J. M.; Tilley, L. J.; Leadbeater, N. E. *Nat. Protoc.* **2013**, *8*, 666. It is recommended that the nitroxide be recrystallized from EtOAc first to remove lutidinium tetrafluoroborate.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.91 (s, 3H), 6.92 (d, *J* = 8.9 Hz, 1H), 7.67 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 56.5 (CH_3), 113.1 (C), 114.2 (CH), 116.1 (q, $J_{C\text{-}F}$ = 291.4 Hz, CF_3), 123.7 (C), 133.8 (CH), 138.5 (CH), 158.9 (C), 182.4 (q, $J_{C\text{-}C\text{-}F}$ = 38.5 Hz, C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -74.57 (s, 3F).

Alkylation

2-(5-Bromo-2-methoxyphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol

This procedure is a modification of the procedure outlined by Kelly et al.[19] To a 250 mL flame-dried round bottom flask equipped with a stir bar was added 1-(5-bromo-2-methoxyphenyl)-2,2,2-trifluoroethanone (11.96 g, 0.0425 mol, 1 equiv) in anhyd Et_2O (50 mL). The flask was cooled to 0 ^{o}C *via* an ice-water bath for 5 min. After this time, Me_3SiCH_2MgCl (1.3 M in THF, 48.75 mL, 0.0634 mol, 1.5 equiv) was added dropwise over 10 min *via* a syringe. The solution became bright yellow initially, then faded upon addition of the organomagnesium solution. After complete addition, the solution was stirred at 0 ^{o}C for 10 min, then warmed to rt. The reaction was allowed to stir at this temperature overnight.

After this time, the reaction mixture was cooled to 0 ^{o}C *via* an ice-water bath for 5 min. The reaction mixture was then *carefully* quenched dropwise with 2 M aq HCl (20 mL). ***CAUTION:*** *Exothermic, a vent needle is advisable*. After complete addition, the quenched reaction mixture was warmed to rt and transferred to a separatory funnel. Et_2O (100 mL) and deionized H_2O (100 mL) were added, and the layers were separated. The aq layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with 2 M aq HCl (100 mL), deionized H_2O (150 mL) and finally brine (150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation affording the pure 2-(5-bromo-2-methoxyphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (14.16 g, 90%) as a white solid (mp = 69 °C).

^{1}H NMR ($CDCl_3$, 500 MHz) δ -0.08 (s, 9H), 1.5 (d, *J* = 15.0 Hz, 1H), 1.6 (dd, *J* = 15.0, 2.4 Hz, 1H), 3.91 (s, 3H), 5.85 (br s, 1H), 6.86 (d, *J* = 8.7 Hz, 1H), 7.42 (s, 1H), 7.43 - 7.47 (m, 1H).

[19] Hamlin, T. A.; Kelly, C. B.; Cywar, R. M.; Leadbeater, N. E. *J. Org. Chem.* **2014**, *79*, 1145.

^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.5 (CH_3), 23.2 (CH_2), 57.0 (CH_3), 79.2 (q, $J_{C\text{-}C\text{-}F}$ = 29.0 Hz, C), 114.1 (C), 114.8 (CH), 126.1 (q, $J_{C\text{-}F}$ = 287.8 Hz, CF_3), 128.2 (C), 133.1 (CH), 133.6 (CH), 157.7 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -85.4 (s, 3F).

FT-IR (cm^{-1}, neat, ATR) 3458 (m), 2951 (m), 1242 (s), 1181 (s), 1152 (s), 1083 (s), 1019 (s), 837 (s), 810 (s), 692 (s), 561 (s).

HRMS (EI+) calcd for $C_{13}H_{18}BrF_3O_2Si$ $[M]^+$: 370.0212, found: 370.0241.

Peterson Elimination

4-Bromo-1-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene (1a)

To a 500 mL one neck round bottom was equipped with a stir bar was added 2-(5-bromo-2-methoxyphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (14.10 g, 0.038 mol, 1 equiv) and CH_2Cl_2 (190 mL).[20] The solution was cooled to 0 °C *via* an ice-water bath and stirred for 10 min at this temperature. After this time, TMSOTf (1.27 g, 1.03 mL, 0.15 equiv) was added to the flask dropwise over 5 min. The reaction mixture was stirred 0 °C for an additional 10 min upon complete addition of TMSOTf, then warmed to rt. The reaction mixture was stirred for 4 h at this temperature. After this time, the flask was cooled to rt and quenched with 100 mL of saturated aq $NaHCO_3$. The reaction mixture was transferred to a separatory funnel and diluted with Et_2O (~150 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with saturated aq $NaHCO_3$ (100 mL), deionized H_2O (100 mL), and finally brine (~150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation to give the crude CF_3 alkene. Further purification was accomplished by vacuum distillation (bp 59-61 °C @ 0.1 mmHg), giving pure **1a** (10.0 g, 94%) as a clear yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.80 (s, 3H), 5.65 (d, *J* = 1.1 Hz, 1H), 6.10 (d, *J* = 1.4 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.45 (dd, *J* = 8.9, 2.4 Hz, 1H).

[20] Hexanes can also be used in place of CH_2Cl_2.

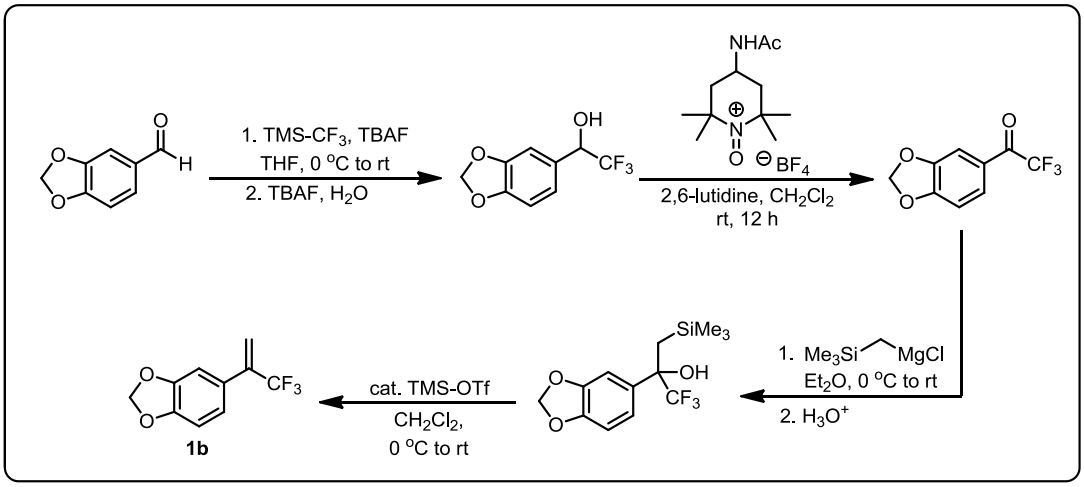
^{13}C NMR ($CDCl_3$, 125 MHz) δ 56.0 (CH_3), 112.6 (C), 113.2 (CH), 123.1 (q, $J_{C\text{-}F}$ = 274.0 Hz, CF_3), 124.4 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.2Hz, CH_2), 125.4 (C), 133.2 (CH), 133.5 (CH), 135.2 (q, $J_{C\text{-}C\text{-}F}$ = 32.1 Hz, C), 156.9 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -68.58 (s, 3F).

FT-IR (cm^{-1}, neat, ATR) 2942 (m), 2842 (m), 1283 (s), 1251 (s), 1166 (s), 1120 (s), 1071 (s), 1027 (s), 808 (s), 614 (s).

HRMS (EI+) calcd for $C_{10}H_8BrF_3O$ $[M]^+$: 279.9711, found: 279.9721

Preparation of 5-(3,3,3-Trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole (1b)



Trifluoromethylation

1-(Benzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethanol[21]

Synthesis of 1-(benzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethanol (5.94 g, 90%) was accomplished using the procedure for the preparation of 1-(5-bromo-2-methoxyphenyl)-2,2,2-trifluoroethanol, with ***the following modification***: The reaction was conducted using piperonal (4.50 g, 0.030 mol), and the quantities of other reagents were adjusted accordingly. The crude α-CF_3 alcohol was purified by vacuum distillation (89-91 °C @ 0.1 mmHg) and obtained as a viscous, colorless oil.

[21] Kelly, C. B.; Mercadante, M. A.; Hamlin, T. A.; Fletcher, M. H.; Leadbeater, N. E. *J. Org. Chem*. **2012**, 77, 8131.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.60 (br s, 1H), 4.93 (q, *J* = 6.6 Hz, 1H), 5.99 (s, 2H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.98 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 72.8 (q, $J_{C\text{-}C\text{-}F}$ = 32.1 Hz, CH), 101.6 (CH_2), 107.9 (CH), 108.5 (CH), 121.9 (CH), 124.5 (q, $J_{C\text{-}F}$ = 282.0 Hz, CF_3), 128.0 (C), 148.2 (C), 148.8 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -81.48 (s, 3F).

Oxidation

1-(Benzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethanone [22]

Synthesis of 1-(benzo[d][1,3]dioxol-5-yl)-2,2,2-trifluoroethanone (5.23 g, 92%) was accomplished using the procedure for the preparation of 1-(5-bromo-2-methoxyphenyl)-2,2,2-trifluoroethanone, with ***the following modification***: The reaction was conducted using 1-(benzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethanol (5.72 g, 0.026 mol), and the quantities of other reagents were adjusted accordingly. Further purification was accomplished by passing the crude material through a SiO_2 plug, eluting with 9:1 hexanes/EtOAc rather than vacuum distillation, giving the pure trifluoromethyl ketone as a clear, light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.11 (s, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 7.50 (s, 1H), 7.72 (dt, *J* = 8.4, 1.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 102.6 (CH_2), 108.5 (CH), 109.2 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, CH), 116.9 (q, $J_{C\text{-}F}$ = 290.5 Hz, CF_3), 124.4 (CH), 127.7 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 148.7 (C), 154.1 (C), 178.6 (q, $J_{C\text{-}C\text{-}F}$ = 34.8 Hz, C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -73.69 (s, 1F).

Alkylation

2-(Benzo[*d*][1,3]dioxol-5-yl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol

Synthesis of 2-(benzo[*d*][1,3]dioxol-5-yl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (6.64 g, 99%) was accomplished using the procedure for the preparation of 2-(5-bromo-2-methoxyphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, with ***the following modification***: The reaction was conducted using 1-(benzo[d][1,3]dioxol-5-yl)-2,2,2-trifluoroethanone (4.80 g,

[22] Kelly, C. B.; Mercadante, M. A.; Hamlin, T. A.; Fletcher, M. H.; Leadbeater, N. E. *J. Org. Chem*. **2012**, 77, 8131.

0.022 mol), and the quantities of other reagents were adjusted accordingly. The pure carbinol was obtained as a clear, light orange oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ -0.13 (s, 9 H), 1.42 (d, *J* = 14.9 Hz, 1H), 1.58 (d, *J* = 14.9 Hz, 1H), 2.26 (s, 1H), 5.98 (s, 2H), 6.80 (d, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 7.05 (s, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.1 (CH_3), 25.3 (CH_2), 77.4 (q, $J_{C\text{-}C\text{-}F}$ = 29.0 Hz, C), 101.5 (CH_2), 107.5 (CH), 108.0 (CH), 120.3 (CH), 126.1 (q, $J_{C\text{-}F}$ = 285.9 Hz, CF_3), 132.2 (C), 147.8 (C), 147.9 (C).
^{19}F NMR ($CDCl_3$, 471 MHz) δ -85.09 (s, 3F).
FT-IR (cm^{-1}, neat, ATR) 3523 (m), 2956 (m), 1241 (s), 1214 (s), 1157 (s), 1082 (s), 1040 (S), 864 (s), 836 (s), 815 (s).
HRMS (EI+) calcd for $C_{13}H_{17}F_3O_3Si$ $[M]^+$: 306.0899, found: 306.0923.

Peterson Elimination

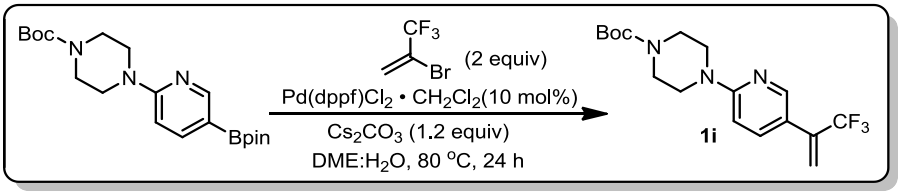
5-(3,3,3-Trifluoroprop-1-en-2-yl)benzo[*d*][1,3]dioxole (1b)[23]

Synthesis of 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole (0.966 g, 89%) was accomplished using the procedure for the preparation of 4-bromo-1-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene, with ***the following modification***: The reaction was conducted using 2-(benzo[*d*][1,3]dioxol-5-yl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1.53 g, 0.005 mol) and the quantities of other reagents were adjusted accordingly. Further purification was accomplished purified SiO_2 plug, eluting with 9:1 hexanes/EtOAc rather than vacuum distillation, giving the pure olefin as a clear, yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.69 (q, *J* = 1.6 Hz, 1H), 5.89 (q, *J* = 1.2 Hz, 1H), 5.99 (s, 2H), 6.82 (dd, *J* = 7.8, 0.6 Hz, 1H), 6.93 - 6.98 (m, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 101.7 (CH_2), 108.1 (CH), 108.6 (CH), 119.8 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.8 Hz, CH_2), 123.6 (q, $J_{C\text{-}F}$ = 274.9 Hz, CF_3), 121.8 (CH), 127.8 (C), 138.8 (q, $J_{C\text{-}C\text{-}F}$ = 30.2 Hz, C), 148.2 (C), 148.6 (C).
^{19}F NMR ($CDCl_3$, 471 MHz) δ -67.89 (s, 3F).

[23] Lebel, H.; Paquet, V. *Org. Lett.* **2002**, *4*, 1671.

Representative Procedure for Suzuki-Type Cross-Coupling of Aryl Boronates with 2-Bromo-3,3,3-trifluoroprop-1-ene



tert-Butyl 4-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-yl)piperazine-1-carboxylate (1i)

To a 50 mL microwave tube was added *tert*-butyl 4-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-yl)piperazine-1-carboxylate (1.00 g, 0.00257 mol, 1 equiv), Cs_2CO_3 (1.00 g, 0.0031 mol, 1.2 equiv), and Pd(dppf)Cl_2•CH_2Cl_2 (0.21 g, 0.00026 mol, 0.1 equiv). The tube was sealed with a crimp-top cap containing a TFE-lined silicone septum and placed under an argon atmosphere *via* an inlet needle. The tube was evacuated three times *via* an inlet needle, then purged with argon. A mixture of degassed DME (10 mL) and degassed, deionized H_2O (3 mL) were added *via* syringe, followed by 2-bromo-3,3,3-trifluoroprop-1-ene (0.899 g, 0.533 mL, 0.00514 mol).[24] The argon inlet needle was removed from the tube. The tube was heated to 80 ^oC. The reaction mixture was allowed to stir at this temperature for 24 h. Reaction progress was monitored by GC/MS. Once complete, the reaction was cooled to rt and diluted in EtOAc (25 mL). The reaction mixture was transferred to a separatory funnel and further diluted with deionized H_2O (25 mL). The layers were separated, and the aq layer was extracted with EtOAc (2 × 25 mL). The combined organic layers were washed with 1 M aq NaOH (25 mL), deionized H_2O (25 mL), and brine (25 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was achieved by SiO_2 column chromatography (gradient hexane/EtOAc) to give the desired olefin **1i** (0.718 g, 78%) as a light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.49 (s, 9H), 3.51 - 3.56 (m, 4H), 3.57 - 3.63 (m, 4H), 5.68 (d, *J* = 1.2 Hz, 1H), 5.84 (s, 1H), 6.63 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 8.28 (d, *J* = 2.2 Hz, 1H).

[24] Alternatively, the bromide may be pre-dissolved in the mixed solvent system.

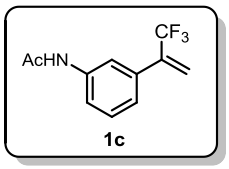
^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.7 (CH_3), 43.5 (br s, C), 44.8 (CH_2), 45.0 (CH_2), 80.3 (C), 106.4 (CH), 118.5 (q, $J_{C\text{-}F}$ = 5.8 Hz, CH_2), 119.3 (C), 123.6 (q, $J_{C\text{-}F}$ = 274.0 Hz, CF_3), 136.3 (q, $J_{C\text{-}F}$ = 30.2 Hz, C), 136.5 (CH), 147.1 (CH), 155.1 (C), 159.2 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -68.28 (s, 3F).

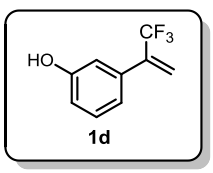
FT-IR (cm^{-1}, neat, ATR). 2979 (m), 2861 (m), 1690 (s), 1602 (s), 1406 (s), 1241 (s), 1196 (s), 1162 (s), 1119 (s), 1088 (s), 730 (s).

HRMS (ES+) calcd for $C_{17}H_{23}F_3N_3O_2$ $[M + H]^+$: 358.1725, found: 358.1742.

N*-(3-(3,3,3-Trifluoroprop-1-en-2-yl)phenyl)acetamide, 1c** (0.542 g, 79%) was prepared according to the general procedure from (3-acetamidophenyl)boronic acid (0.537 g, 0.003 mol) ***with the following modifications: 1) the reaction was carried out using $Pd(PPh_3)_2Cl_2$ (0.105 g, 0.00015 mol, 0.05 equiv) in place of $Pd(dppf)Cl_2•CH_2Cl_2$; 2) $AsPh_3$ (0.230 g, 0.00075 mol, 0.25 equiv) was used as a ligand; 3) A higher loading of Cs_2CO_3 was used (1.4 equiv); The reaction was performed in THF (10 mL) and H_2O (5 mL). The desired olefin **1c** was isolated as a powdery white solid (mp = 92 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.20 (s, 3H), 5.79 (q, J = 1.5 Hz, 1H), 5.97 (s, 1H), 7.21 (d, J = 7.6 Hz, 1H), 7.30 (br s, 1H), 7.35 (t, J = 7.9 Hz, 1H), 7.57 (s, 1H), 7.60 (d, J = 8.1 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.6 (CH_3), 119.3 (CH), 123.5 (q, $J_{C\text{-}F}$ = 274.0 Hz, CF_3), 121.0 (CH), 121.1 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 6.4 Hz, CH_2), 123.3 (CH), 129.4 (CH), 134.5 (C), 138.7 (q, $J_{C\text{-}C\text{-}F}$ = 29.3 Hz, C), 138.6 (C), 169.4 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -67.89 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 3258 (w, br), 3092 (m), 1660 (m), 1587 (s), 1359 (m), 1154 (vs), 1124 (s), 950 (m), 798 (s). **HRMS** (EI+) calcd for $C_{11}H_{10}F_3NO$ $[M]^+$: 229.0714, found: 229.0707.

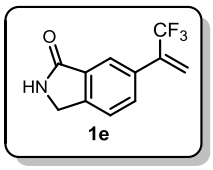


3-(3,3,3-Trifluoroprop-1-en-2-yl)phenol, 1d (0.511 g, 91%) was prepared according to the general procedure from potassium (3-hydroxyphenyl)trifluoroborate (0.600 g, 0.003 mol) ***with the following modification***s: 1) the reaction was carried out using $Pd(PPh_3)_2Cl_2$ (0.105 g, 0.00015 mol, 0.05 equiv) in place of $Pd(dppf)Cl_2•CH_2Cl_2$; 2) $AsPh_3$ (0.230 g, 0.00075 mol, 0.25 equiv) was used as a ligand; 3) A higher loading of Cs_2CO_3 was used (1.4 equiv); The reaction was performed in THF (10 mL) and H_2O (5 mL). 4) The reaction was quenched with 5 mL of 2 M aq HCl. The desired olefin **1d** was isolated as a pale orange oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 4.84 (br s,

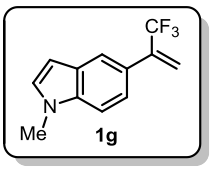


1H), 5.78 (q, *J* = 1.5 Hz, 1H), 5.96 (q, *J* = 1.0 Hz, 1H), 6.87 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.95 (s, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 8.3 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 114.8 (CH), 116.3 (CH), 123.5 (q, $J_{C\text{-}F}$ = 274.0 Hz, CF_3), 120.4 (CH), 121.0 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, CH_2), 130.2 (CH), 135.5 (C), 138.7 (q, $J_{C\text{-}C\text{-}F}$ = 31.2 Hz, C), 155.6 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -67.91 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 3341 (w, br), 1609 (m), 1357 (m), 1237 (m), 1158 (vs), 1117 (vs), 933 (s), 786 (m), 701 (m). **HRMS** (EI+) calcd for $C_9H_7F_3O$ $[M]^+$: 188.0449, found: 188.0451.

6-(3,3,3-Trifluoroprop-1-en-2-yl)isoindolin-1-one, 1e (0.353 g, 82%) was prepared according to the general procedure from 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isoindolin-1-one (0.500 g, 0.00192 mol), and the quantities of other reagents were adjusted accordingly. The desired olefin **1e** was isolated as brown semi-solid. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 4.53 (s, 2H), 5.87 (s, 1H), 6.06 (s, 1H), 7.04 (br s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.99 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 46.0 (CH_2), 123.4 (q, $J_{C\text{-}F}$ = 274.0 Hz, CF_3), 121.8 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, CH_2), 123.0 (CH), 123.8 (CH), 131.1 (CH), 133.1 (C), 134.1 (C), 138.6 (q, $J_{C\text{-}C\text{-}F}$ = 30.2 Hz, C), 144.5 (C), 171.9 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -68.01 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 3210 (w, br), 3077 (vw), 2852 (vw), 1681 (vs), 1457 (w), 1346 (w), 1165 (vs), 1103 (vs), 951 (w), 730 (m). **HRMS** (ES+) calcd for $C_{11}H_9F_3NO$ $[M + H]^+$: 228.0636, found: 228.0617.

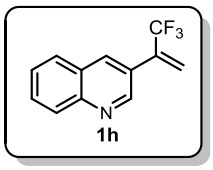


1-Methyl-5-(3,3,3-trifluoroprop-1-en-2-yl)-1*H*-indole, 1g (0.363 g, 54%) was prepared according to the general procedure from (1-methyl-1*H*-indol-5-yl)boronic acid (0.525 g, 0.003 mol) ***with the following modifications***: 1) the reaction was carried out using $Pd(PPh_3)_2Cl_2$ (0.105 g, 0.00015 mol, 0.05 equiv) in place of $Pd(dppf)Cl_2•CH_2Cl_2$; 2) $AsPh_3$ (0.230 g, 0.00075 mol, 0.25 equiv) was used as a ligand; 3) KOH (0.78 g, 0.0138 mol 4.6 equiv) was used in place of Cs_2CO_3; 4) The reaction was performed in THF (10 mL) and H_2O (5 mL); 5) The reaction was conducted at 100 °C rather than 80 °C. The desired olefin **1g** was isolated as light yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.81 (s, 3H), 5.75 (q, *J* = 1.4 Hz, 1H), 5.92 (s, 1H), 6.52 (d, *J* = 3.1 Hz, 1H), 7.09 (d, *J* = 3.1 Hz, 1H), 7.29 - 7.37 (m, 2H), 7.74 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 33.2 (CH_3), 101.8 (CH), 109.5 (CH), 119.2 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, CH_2), 120.5 (CH), 124.0 (q, $J_{C\text{-}F}$ = 274.3 Hz,

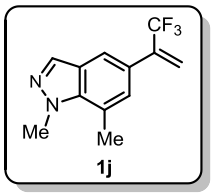


CF_3), 121.3 (CH), 125.3 (C), 128.7 (C), 130.1 (CH), 137.0 (C), 140.1 (q, $J_{C\text{-}C\text{-}F}$ =30.0 Hz, C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -67.72 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 2956 (vw), 1515 (w), 1324 (m), 1119 (vs), 721 (w). **HRMS** (EI+) calcd for $C_{12}H_{10}F_3N$ $[M]^+$: 225.0765, found: 225.0752.

3-(3,3,3-Trifluoroprop-1-en-2-yl)quinoline,[25] 1h (0.732 g, 82%) was prepared according to the general procedure from potassium trifluoro(quinolin-4-yl)borate (0.940 g, 0.004 mol) ***with the following modification***s: 1) the reaction was carried out using $Pd(PPh_3)_2Cl_2$ (0.140 g, 0.0002 mol, 0.05 equiv) in place of $Pd(dppf)Cl_2•CH_2Cl_2$; 2) $AsPh_3$ (0.306 g, 0.001 mol, 0.25 equiv) was used as a ligand; 3) KOH (1.03 g, 0.0184 mol 4.6 equiv) was used in place of Cs_2CO_3; 4) The reaction was performed in THF (12 mL) and H_2O (6 mL). The desired olefin **1h** was isolated as a light yellow solid (mp = 47–48 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 5.99 (d, *J* = 1.1 Hz, 1H), 6.16 (s, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.24 (s, 1H), 8.99 (d, *J* = 2.1 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 123.3 (q, $J_{C\text{-}F}$ = 274.0 Hz, CF_3), 122.4 (q, $J_{C\text{-}F}$ = 5.7 Hz, CH_2), 126.7 (C), 127.4 (C), 127.6 (CH), 128.6 (CH), 129.6 (CH), 130.6 (CH), 134.6 (CH) 136.6 (q, $J_{C\text{-}F}$ = 31.2 Hz, C), 148.2 (C), 149.2 (CH). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -68.13 (s, 3F).



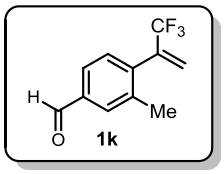
1,7-Dimethyl-5-(3,3,3-trifluoroprop-1-en-2-yl)-1*H*-indazole, 1j (0.117 g, 89%) was prepared according to the general procedure from (1,7-dimethyl-1*H*-indazol-5-yl)boronic acid (0.570 g, 0.003 mol) ***with the following modification***s: 1) the reaction was carried out using $Pd(PPh_3)_2Cl_2$ (0.105 g, 0.00015 mol, 0.05 equiv) in place of $Pd(dppf)Cl_2•CH_2Cl_2$; 2) $AsPh_3$ (0.230 g, 0.00075 mol, 0.25 equiv) was used as a ligand; 3) KOH (0.780 g, 0.0138 mol 4.6 equiv) was used in place of Cs_2CO_3; 4) The reaction was performed in THF (10 mL) and H_2O (5 mL). The desired olefin **1j** was isolated as pale orange oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.79 (s, 3H), 4.33 (s, 3H), 5.77 (q, *J* = 1.7 Hz, 1H), 5.94 (d, *J* = 1.0 Hz, 1H), 7.18 (s, 1H), 7.65 (s, 1H), 7.95 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 19.5 (CH_3), 39.3 (CH_3), 118.5 (CH), 119.9 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, CH_2), 123.8 (q, $J_{C\text{-}F}$ = 274.0 Hz, CF_3), 120.9 (C), 125.2 (CH), 126.7 (C), 127.5 (CH), 133.6 (CH),



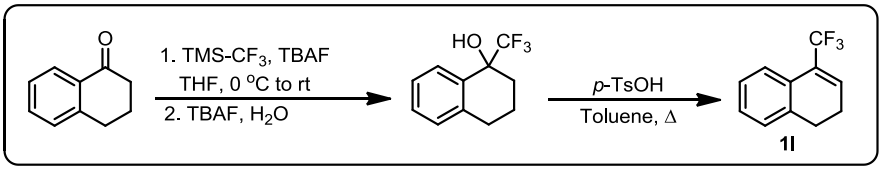
[25] Jimenez-Aquino, A.; Vega, J. A.; Trabanco, A. A.; Valdes, C. *Adv. Synth. Catal.* **2014**, *356*, 1079.

139.2 (q, $J_{C\text{-}C\text{-}F}$ = 30.2 Hz, C), 139.6 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -67.87 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 2951 (vw), 1506 (w), 1379 (w), 1247 (w), 1153 (vs), 1112 (vs), 1076 (s), 941 (m), 878 (m), 696 (m). **HRMS** (ES+) calcd for $C_{12}H_{12}F_3N_2$ $[M + H]^+$: 241.0953, found: 241.0939.

3-Methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzaldehyde, 1k (0.443 g, 70%) was prepared according to the general procedure from 3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (0.738 g, 0.003 mol). The desired olefin **1k** was isolated as pale orange oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.39 (s, 3H), 5.55 (s, 1H), 6.19 (s, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.78 (s, 1H), 10.02 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 19.9 (CH_3), 123.0 (q, $J_{C\text{-}F}$ = 274.0 Hz, CF_3), 123.5 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, CH_2), 127.0 (CH), 130.7 (CH), 131.5 (CH), 136.8 (C), 137.8 (q, $J_{C\text{-}C\text{-}F}$ = 31.2 Hz, C), 138.4 (C), 139.8 (C), 192.0 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -70.03 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 2972 (vw), 1697 (s), 1337 (w), 1168 (vs), 1120 (vs), 1067 (s), 958 (w), 827 (w), 613 (w) **HRMS** (EI+) calcd for $C_{11}H_9F_3O$ $[M + H]^+$: 214.0605, found: 214.0610.



Preparation of 5-(3,3,3-Trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole (1l)



Trifluoromethylation

1-(Trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-ol[26]

Synthesis of 1-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (2.51 g, 66%) was accomplished using the procedure for the preparation of 1-(5-bromo-2-methoxyphenyl)-2,2,2-trifluoroethanol, with ***the following modification***: The reaction was conducted using α-tetralone (2.56 g, 0.0175 mol, 1 equiv), and the quantities of other reagents were adjusted accordingly; 2) The reaction was judged to be incomplete after the first addition of TMS-CF_3. Thus, the reaction

[26] Bonnet-Delpon, D.; Charpentier-Morize, M.; Jacquot, R. *J. Org. Chem.* **1988**, *53*, 759.

was cooled to 0 °C, and additional TMS-CF_3 (1.24 g, 0.00875 mol, 0.5 equiv) and TBAF (0.1 mL, 0.0001 mol, 0.0057 equiv) were added. After this addition, the reaction mixture was warmed to rt and stirred for an additional 6 h, then quenched. After these modification, the crude α-CF_3 alcohol was isolated and purified by vacuum distillation (65-67 °C @ 0.1 mmHg) and obtained as a viscous, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.8 - 1.9 (m, 1H), 1.9 - 2.0 (m, 1H), 2.0 - 2.1 (m, 1H), 2.3 (ddd, *J* = 13.5, 9.7, 3.4 Hz, 1H), 2.4 (d, *J* = 1.4 Hz, 1H), 2.8 - 2.9 (m, 2H), 7.2 (d, *J* = 7.3 Hz, 1H), 7.2 - 7.3 (m, 2H), 7.7 (d, *J* = 7.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.8 (CH_2), 29.7 (CH_2), 32.7 (CH_2), 73.2 (q, $J_{C\text{-}C\text{-}F}$ = 27.8 Hz, C), 126.5 (q, $J_{C\text{-}F}$ = 285.9 Hz, CF_3), 126.8 (CH), 127.5 (CH), 129.2 (CH), 129.6 (CH), 133.3 (C), 139.0 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -81.1 (s, 3F).

Dehydration

4-(Trifluoromethyl)-1,2-dihydronaphthalene (1l)[27]

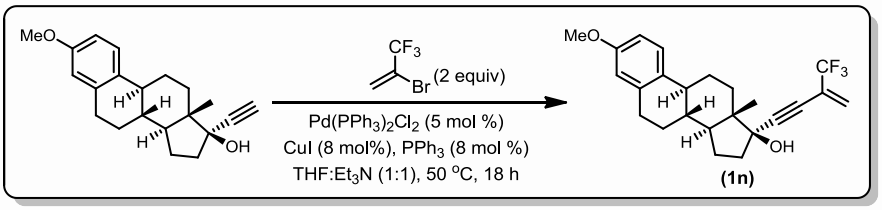
To a 150 mL one neck round bottom equipped with a stir bar was added 1-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (1.85 g, 8.65 mmol, 1 equiv), *p*-TsOH•H_2O (0.814 g, 4.28 mmol, 0.5 equiv), and toluene (61 mL).[28] The flask was equipped with a Dean-Stark apparatus (backfilled with ~10 mL of toluene) fitted with a reflux condenser. The reaction was heated to reflux for 36 h. Reaction progress was monitored by GC/MS. Once judged to be complete, the reaction was cooled rt and quenched with saturated aq $NaHCO_3$ (20 mL). The quenched mixture was stirred for 5 min, then transferred to a separatory funnel. The reaction mixture was diluted with pentane (100 mL) and saturated aq $NaHCO_3$ (100 mL). The layers were separated, and the aq layer was extracted with pentane (2 × 50 mL). The combined organic layers were washed with saturated aq $NaHCO_3$ (100 mL), deionized H_2O (100 mL), and finally brine (150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation to give the crude CF_3 alkene. Further purification was accomplished by passing the crude

[27] Bonnet-Delpon, D.; Charpentier-Morize, M.; Jacquot, R. *J. Org. Chem.* **1988**, *53*, 759.
[28] Hexanes can also be used in place of CH_2Cl_2.

material through a SiO_2 plug, eluting with pentane giving the pure olefin (1.456 g, 86%) as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.39 - 2.46 (m, 2H), 2.82 (t, *J* = 8.2 Hz, 2H), 6.72 (tq, *J* = 4.7, 1.4 Hz, 1H), 7.16 - 7.20 (m, 1H), 7.21 - 7.26 (m, 2H), 7.42 (dd, *J* = 4.6, 2.1 Hz, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.7 (CH_2), 27.5 (CH_2), 124.0 (q, $J_{C\text{-}F}$ = 273.1 Hz, CF_3), 124.4 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 127.1 (CH), 128.3 (CH), 128.5 (CH), 128.6 (C), 129.0 (q, $J_{C\text{-}C\text{-}F}$ = 29.3 Hz, C), 132.6 (q, $J_{C\text{-}F}$ = 6.4 Hz, CH), 136.2 (CH).
^{19}F NMR ($CDCl_3$, 471 MHz) δ -67.08 (s, 3F).

Representative Procedure for Sonogashira-Type Coupling of Alkynes with 2-Bromo-3,3,3-trifluoroprop-1-ene



(8*R*,9*S*,13*S*,14*S*,17*S*)-3-Methoxy-13-methyl-17-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (1n)

To an oven dried 20 mL microwave vial were added THF (3 mL) and Et_3N (3 mL). The solvents were sparged with nitrogen for 10 min. Mestranol (0.930 g, 3.0 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (0.105 g, 0.15 mmol, 0.05 equiv), CuI (0.045 g, 0.24 mmol, 0.08 equiv), and PPh_3 (0.063 g, 0.24 mmol, 0.08 equiv) were added sequentially to the vial. The vial was sealed with a crimp-top cap containing a TFE-lined silicone septum and placed under an argon atmosphere *via* an inlet needle. 2-Bromo-3,3,3-trifluoro-1-propene (1.05 g, 0.63 mL, 6.0 mmol) was added *via* a syringe. The argon inlet needle was removed from the tube. The reaction mixture was heated to 50 °C. The reaction was allowed to stir at this temperature for 18 h. Reaction progress was monitored by HPLC and ^{19}F NMR. Once complete, the reaction was cooled to rt and transferred to a separatory funnel. Deionized H_2O (50 mL) and EtOAc (50 mL) were added, and the layers were separated. The aq layer was extracted with EtOAc (2 × 25 mL). The combined organic layers were washed with brine (100 mL) and dried (Na_2SO_4). The solvent was removed *in vacuo* by rotary evaporation to give the crude coupling product. Further purification was accomplished by

SiO_2 column chromatography (gradient hexanes to 70:30 hexanes/EtOAc) to give the pure coupled product (0.844 g, 70%) as a light orange semisolid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.93 (s, 3H), 1.35 - 1.57 (m, 4H), 1.64 - 1.73 (m, 1H), 1.75 - 1.95 (m, 4H), 2.02 (s, 1H), 2.04 - 2.13 (m, 1H), 2.18 - 2.27 (m, 1H), 2.33 - 2.45 (m, 2H), 2.80 - 2.94 (m, 2H), 3.80 (s, 3H), 5.89 (s, 1H), 6.07 (s, 1H), 6.65 (s, 1H), 6.74 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 1H).

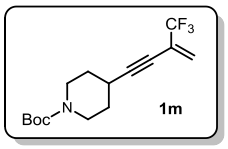
^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.1 (CH_3), 23.2 (CH_2), 26.7 (CH_2), 27.6 (CH_2), 30.1 (CH_2), 33.1 (CH_2), 39.1 (CH_2), 39.7 (CH_2), 43.9 (CH), 48.1 (CH), 50.1 (CH), 55.5 (CH_3), 78.7 (C), 80.5 (C), 97.5 (C), 111.8 (CH), 114.1 (CH), 121.6 (q, $J_{C\text{-}F}$ = 274.0 Hz, CF_3), 122.6 (q, $J_{C\text{-}C\text{-}F}$ = 35.7 Hz, C), 126.7 (CH), 127.0 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH_2), 132.7 (C), 138.2 (C), 157.8 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -71.19 (s, 3F).

FT-IR (cm^{-1}, neat, ATR) 3442 (br, w), 2932 (w), 2870 (w), 2230 (vw), 1609 (w), 1499 (m), 1254 (m), 1179 (s), 1138 (vs), 1037 (m), 908 (m), 732 (s).

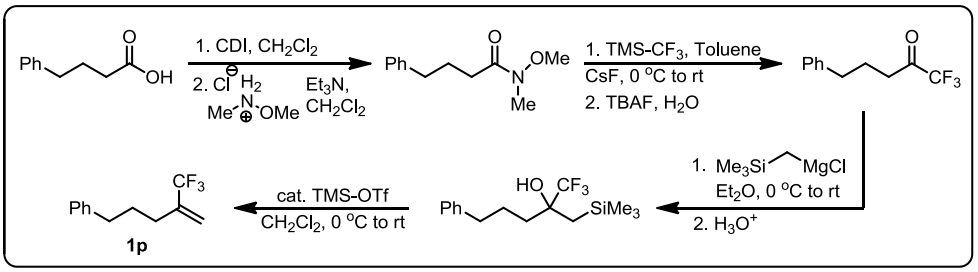
HRMS (ES+) calcd for $C_{24}H_{28}F_3O_2$ $[M + H]^+$: 405.2041, found: 405.2038.

***tert*-Butyl 4-(3-(Trifluoromethyl)but-3-en-1-yn-1-yl)piperidine-1-carboxylate, 1m** Synthesis



of *tert*-butyl 4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)piperidine-1-carboxylate (0.291 g, 32%) was accomplished using the above procedure with ***the following modification***: The reaction was conducted using *tert*-butyl 4-ethynylpiperidine-1-carboxylate (0.630 g, 3 mmol). Further purification was accomplished by SiO_2 column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to give the pure coupling product as a clear, light orange oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.48 (s, 9H), 1.67 (d, *J* = 3.8 Hz, 2H), 1.74 - 1.90 (m, 2H), 2.69 - 2.84 (m, 1H), 3.18 - 3.33 (m, 2H), 3.65 (s, 2H), 5.80 (d, *J* = 1.1 Hz, 1H), 6.00 (d, *J* = 1.3 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 27.3 (CH), 28.3 (CH_3), 30.8 (CH_2), 41.9 (CH_2), 74.5 (C), 79.5 (C), 96.3 (C), 121.2 (q, $J_{C\text{-}F}$ = 273.1 Hz, CF_3), 122.5 (q, $J_{C\text{-}C\text{-}F}$ = 35.7 Hz, C), 125.9 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH_2), 154.6 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -71.53 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 2951 (vw), 2928 (vw), 2870 (w), 2235 (vw), 1690 (s), 1420 (m), 1232 (m), 1137 (vs), 1002 (w), 936 (w), 872 (w), 768 (w). **HRMS** (EI+) calcd for $C_{15}H_{20}F_3NO_2$ $[M]^+$: 303.1446, found: 303.1461.

Preparation of (4-Trifluoromethyl)pent-4-en-1-yl)benzene (1q)



Weinreb Amide Synthesis

***N*-Methoxy-*N*-methyl-4-phenylbutanamide**[29]

To a 500 mL round bottom flask equipped with stir bar was added 4-phenylbutanoic acid (8.21 g, 0.050 mol, 1 equiv) and CH_2Cl_2 (170 mL). To this stirred solution was added 1,1′-carbonyldiimidazole (9.73 g, 0.060 mol, 1.2 equiv) in one portion, turning the solution a clear pale-yellow and resulting in the evolution of CO_2 gas. The reaction mixture was allowed to stir for 1 h at rt. After this time, *N*-*O*-dimethylhydroxylamine hydrochloride (5.85 g, 0.060 mol, 1.2 equiv) and Et_3N (12.65 g, 17.4 mL, 0.125 mol, 2.5 equiv) were added all at once, and the reaction mixture was stirred overnight. The reaction mixture was then quenched with 125 mL of 2 M aq HCl and stirred vigorously for 10 min. After this time, the solution was transferred to a separatory funnel, and the layers were separated. The aq layer was extracted with CH_2Cl_2 (3 × 75 mL). The combined organic layers were washed with 2 M aq HCl (150 mL), deionized H_2O (150 mL), saturated aq $NaHCO_3$ (2 × 100 mL), and brine (150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo via* rotary evaporation, affording the pure amide (9.77 g, 94%) as a clear, light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.89 - 2.00 (m, 2H), 2.34 - 2.46 (m, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 3.13 (d, *J* = 2.1 Hz, 3H), 3.57 (s, 3H), 7.09 - 7.19 (m, 3H), 7.21 - 7.29 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.0 (CH_2), 31.1 (CH_2), 32.1 (CH_2), 35.2 (CH_3), 61.0 (CH_3), 125.8 (CH), 128.3 (CH), 128.4 (CH), 141.7 (C), 174.2 (C).

[29] La Cruz, T. E.; Rychnovsky, S. D. *J. Org. Chem.* **2006**, *71*, 1068.

Trifluoromethylation

1,1,1-Trifluoro-5-phenylpentan-2-one[30]

To a 250 mL round bottom flask equipped with a stir bar was added *N*-methoxy-*N*-methyl-4-phenylbutanamide (8.29 g, 0.040 mol, 1 equiv). CsF (1.21 g, 0.008 mol, 0.2 equiv), followed by toluene (80 mL), was then added to the flask. The flask was sealed with a septum equipped with two inlet needles acting as exit valves. The flask was cooled to 0 ^{o}C for 15 min. TMS-CF_3 (11.36 g, 0.080 mol, 2 equiv) was added to the reaction mixture dropwise over a period of 10 min. After completion of the addition, the reaction mixture was allowed to stir for 10 min at 0 ^{o}C. The cooling bath was removed, and the reaction mixture was allowed to stir at rt overnight. **CAUTION:** *Upon reaching rt, a rapid reaction occurs that is mildly exothermic and evolves gas. Over this time period the solution became dark brown in color.* Reaction progress was monitored by ^{1}H NMR.[31]

Once complete conversion to the silylated, tetrahedral intermediate was confirmed, toluene was removed *in vacuo via* rotary evaporation. Hexanes (40 mL), followed by deionized H_2O (40 mL) followed by 1 M solution of TBAF in THF (40 mL, 0.040 mol, 1 equiv) were added to the reaction flask. The flask was equipped with an air-cooled reflux condenser and then heated to 50 ^{o}C in an oil bath for 8 h to facilitate cleavage of the silyl ether. Once the reaction was judge to be complete,[32] the reaction was cooled to rt. The reaction mixture was then diluted with Et_2O (125 mL) and deionized H_2O (100 mL), and then transferred to a separatory funnel. The layers were separated, and the aq layer was extracted with Et_2O (3 × 75 mL). The combined organic layers were washed with 2 M aq HCl (125 mL), deionized H_2O (150 mL), and brine (150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording the crude trifluoromethyl ketone. Further purification was accomplished by vacuum distillation (bp 79-81^{o}C @ 0.1 mmHg), affording the pure CF_3 ketone (6.74 g, 78%) as a clear, colorless oil.

[30] Li, Q.; Tochtrop, G. P. *Org. Lett.* **2014**, *16*, 1382.
[31] The *O*-silylated intermediate has characteristic peaks, and conversion can easily be determined by ^{1}H NMR. See Rudzinski, D. M.; Kelly C. B.; Leadbeater, N. E. *Chem. Commun*. **2012**, *48*, 9610 for further details.
[32] Conversion to the desired TFMK can be determined by examining the silyl region of the ^{1}H NMR with the *O*-silylated intermediate coming at ~ 0.25 ppm and $Me_3SiOSiMe_3$ coming at ~ 0.06 ppm .

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.98 - 2.06 (m, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.20 - 7.25 (m, 1H), 7.28 - 7.33 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.1 (CH_2), 34.8 (CH_2), 35.8 (CH_2), 115.8 (q, $J_{C\text{-}F}$ = 293.3 Hz, CF_3), 126.6 (CH), 128.7 (CH), 128.8 (CH), 140.9 (C), 191.6 (q, $J_{C\text{-}C\text{-}F}$ = 35.0 Hz, C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -82.32 (s, 3F).

Alkylation

1,1,1-Trifluoro-5-phenyl-2-((trimethylsilyl)methyl)pentan-2-ol

Synthesis of 1,1,1-trifluoro-5-phenyl-2-((trimethylsilyl)methyl)pentan-2-ol (7.98 g, 94%) was accomplished using the procedure for the preparation of 2-(5-bromo-2-methoxyphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, with ***the following modification***: The reaction was conducted using 1,1,1-trifluoro-5-phenylpentan-2-one (1.53 g, 0.005 mol), and the quantities of other reagents were adjusted accordingly. The carbinol was obtained as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.06 (s, 9H), 1.05 (d, *J* = 15.1 Hz, 1H), 1.14 (d, *J* = 15.1 Hz, 1H), 1.54 (br s, 1H), 1.71 - 1.77 (m, 4H), 2.59 - 2.67 (m, 2H), 7.16 - 7.22 (m, 3H), 7.27 - 7.32 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.3 (CH_3), 23.3 (CH_2), 25.4 (CH_2), 36.3 (CH_2), 36.4 (CH_2), 76.3 (q, $J_{C\text{-}C\text{-}F}$ = 28.4 Hz, C), 127.0 (q, $J_{C\text{-}F}$ = 286.5 Hz, CF_3), 126.3 (CH), 128.6 (CH), 128.7 (CH), 141.9 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -84.12 (s, 3F).

FT-IR (cm^{-1}, neat, ATR) 3476 (w), 3029 (m), 2954 (m), 1250 (s), 1218 (s), 1149 (s), 1100 (s), 839 (s), 750 (s), 698 (s).

HRMS (EI) calcd for $C_{14}H_{23}OSi$ $[M - CF_3]^+$: 235.1518, found: 235.1528.

Peterson Elimination

(4-(Trifluoromethyl)pent-4-en-1-yl)benzene (1p)[33]

Synthesis of (4-(trifluoromethyl)pent-4-en-1-yl)benzene (4.64 g, 83%) was accomplished using the procedure for the preparation of 4-bromo-1-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene, with ***the following modification***: 1) The reaction was conducted using 1,1,1-

[33] Fuchibe, K.; Hatta, H.; Oh, K.; Oki, R.; Ichikawa, J. *Angew. Chem., Int. Ed.* **2017**, *56*, 5890.

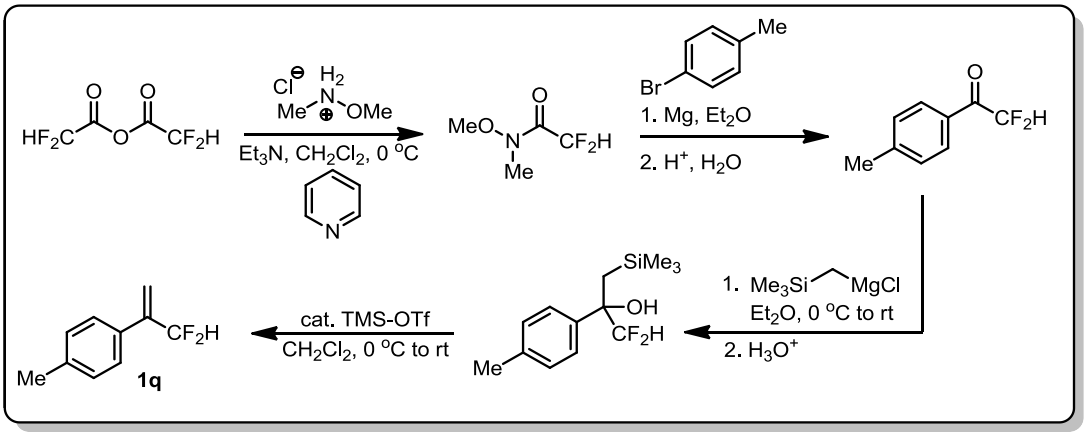
trifluoro-5-phenyl-2-((trimethylsilyl)methyl)pentan-2-ol (7.90 g, 0.005 mol), and the quantities of other reagents were adjusted accordingly; 2) 0.2 equiv of TMSOTf was used rather than 0.15 equiv; 3) After addition of TMSOTf, the reaction was heated to reflux for 5 h. Further purification was accomplished by passing the crude material through a SiO_2 plug, eluting with pentane rather than vacuum distillation, giving the pure olefin **1q** as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.79 - 1.94 (m, 2H), 2.25 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* = 7.7 Hz, 2H), 5.32 (d, *J* = 1.4 Hz, 1H), 5.68 (s, 1H), 7.18 - 7.24 (m, 3H), 7.28 - 7.33 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.3 (CH_2), 29.4 (CH_2), 35.5 (CH_2), 117.9 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.8 Hz, CH_2), 124.2 (q, $J_{C\text{-}F}$ = 274.0 Hz, CF_3), 126.3 (CH), 128.6 (CH), 128.7 (CH), 138.7 (q, $J_{C\text{-}C\text{-}F}$ = 28.4 Hz, C), 141.9 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -71.47 (s, 3F).

Preparation of 1-(3,3-Difluoroprop-1-en-2-yl)-4-methylbenzene (1q)



Weinreb Amide Synthesis

2,2-Difluoro-*N*-methoxy-*N*-methylacetamide [34]

To a 300 mL round bottom flask equipped with a stir bar was added difluoroacetic anhydride (8.70 g, 0.05 mol, 1 equiv), *N*,*O*-dimethylhydroxylamine hydrochloride (5.37 g, 0.055 mol, 1.1 equiv) and CH_2Cl_2 (125 mL) were added. The flask was cooled to 0 °C in an ice-water bath and allowed to stir for 5 min. After this time, pyridine (11.87 g, 12.1 mL, 0.150 mol, 3 equiv) and Et_3N (5.06 g, 6.97 mL, 0.050 mol 1 equiv) were added dropwise to the flask. After complete

[34] Pollock, J.; Borkin, D..; Lund, G.; Purohit, T.; Dyguda-Kazimierowicz, E.; Grembecka, J.; Cierpicki, T. *J. Med. Chem.* **2015**, *58*, 7465.

addition, the reaction mixture was allowed to stir at 0 °C for 4 h. After this time, the reaction mixture was quenched with saturated aq $NaHCO_3$ (75 mL), diluted with deionized H_2O (200 mL), and transferred to a separatory funnel. The layers were separated, and the aq layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with 2 M aq HCl (2 × 100 mL), saturated aq $NaHCO_3$, (100 mL) and brine (150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation to give the amide (3.16 g, 45%) as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.26 (s, 3H), 3.77 (s, 3H), 6.27 (t, J = 53.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 32.1 (CH_3), 62.2 (CH_3), 106.3 (t, $J_{C\text{-}F}$ = 244.7 Hz, CF_2H), 162.2 (t, $J_{C\text{-}\mathbf{C}\text{-}F}$ = 26.6 Hz, C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -129.9 (s, 100 F).

Weinreb Ketone Synthesis

2,2-Difluoro-1-(4-methylphenyl)ethanone[35]

To a 250 mL round bottom flask was added crushed Mg turnings (0.714 g, 0.0294 mol, 1.4 equiv) and a stir bar. The flask was sealed with a rubber septum, the atmosphere was evacuated from the flask *via* an inlet needle, and the flask was flame-dried under vacuum. The flask was flushed with argon and placed in a room temperature water bath. *p*-Bromotoluene (4.31 g, 0.0252 mol, 1.2 equiv) was dissolved in anhyd THF (42 mL) and added dropwise to the flask ***CAUTION***: *Mildly exothermic.* After complete addition, the solution was allowed to stir at rt for 90 min, and the mixture gradually became dark gray.

After this time, the flask was cooled to 0 °C for 5 min. 2,2-Difluoro-*N*-methoxy-*N*-methylacetamide (2.92 g, 0.021 mol, 1 equiv), dissolved in anhyd THF (21 mL), was then added to the flask dropwise. After complete addition of the amide, the reaction mixture was allowed to stir for 10 min at 0 °C. After this time, the ice bath was removed, and the reaction mixture was stirred at rt for 6 h. At this time, the solution was carefully quenched with an aq 2 M HCl solution (100 mL). ***CAUTION***: *Evolves H_2 Gas!* The quenched mixture was allowed to stir for

[35] Hamlin, T. A.; Kelly, C. B.; Ovian, J. M.; Wiles, R. J.; Tilley, L. J.; Leadbeater, N. E. *J. Org. Chem.* **2015**, *80*, 8150.

15 min, and after this time the contents of the flask were transferred to a separatory funnel. The layers were separated, and the aq layer was extracted with Et_2O (3 × 75 mL). The combined organic layers were washed with 2 M aq HCl (150 mL), deionized H_2O (150 mL), and brine (150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation to afford the crude ketone. Further purification was accomplished by washing the crude solid with pentane to give the pure difluoromethyl ketone (3.20 g, 90 %) as an off-white, powdery solid (mp = 50 °C).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.45 (s, 3H), 6.27 (t, J = 53.6 Hz, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.97 (d, J = 8.1 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.1 (CH_3), 111.4 (t, $J_{C\text{-}F}$ = 253.9 Hz, CF_2H), 129.3 (C), 129.9 (CH), 130.0 (CH), 146.5 (CH), 187.4 (t, $J_{C\text{-}C\text{-}F}$ = 24.7 Hz, C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -125.12 (s, 2F).

Alkylation

1,1-Difluoro-2-(*p*-tolyl)-3-(trimethylsilyl)propan-2-ol

Synthesis of 1,1-difluoro-2-(*p*-tolyl)-3-(trimethylsilyl)propan-2-ol (3.49 g, 75%) was accomplished using the procedure for the preparation of 2-(5-bromo-2-methoxyphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, with ***the following modification***: The reaction was conducted using 2,2-difluoro-1-(4-methylphenyl)ethanone (3.06 g, 0.018 mol), and the quantities of other reagents were adjusted accordingly. Further purification was accomplished by vacuum distillation (bp 89-91^{o}C @ 0.1 mmHg), affording the carbinol as a clear colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ -0.16 (s, 9H), 1.33 (d, J = 15.1 Hz, 1H), 1.43 (d, J = 14.8 Hz, 1H), 2.16 (s, 1H), 2.35 (s, 3H), 5.59 (t, J = 57.2 Hz, 1H), 7.17 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.3 (CH_3), 21.3 (CH_2), 23.9 (CH_3), 76.8 (t, $J_{C\text{-}C\text{-}F}$ = 21.1 Hz, C), 117.6 (t, $J_{C\text{-}F}$ = 250.2 Hz, CF_2H), 126.1 (CH), 129.1 (CH), 137.4 (C), 137.7 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -132.97 (s, 2F).

FT-IR (cm^{-1}, neat, ATR) 3605 (m), 2954 (m), 1249 (s), 1063 (s), 928 (s), 819 (s), 566 (s).

HRMS (EI+) calcd for $C_{13}H_{20}F_2OSi$ $[M]^+$: 258.1251, found: 258.1279.

Peterson Elimination

1-(3,3-Difluoroprop-1-en-2-yl)-4-methylbenzene (1q)[36]

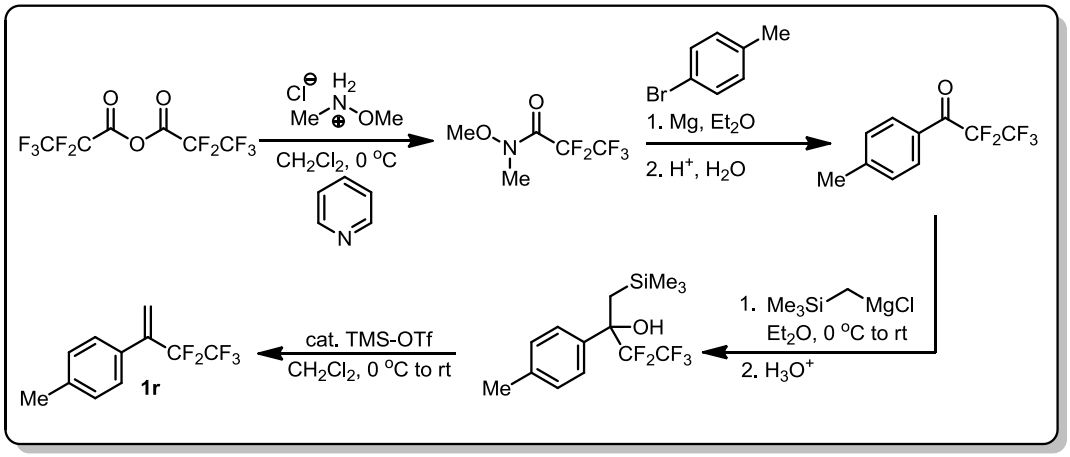
Synthesis of 1-(3,3-difluoroprop-1-en-2-yl)-4-methylbenzene (1.53 g, 91%) was accomplished using the procedure for the preparation of 4-bromo-1-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene, with ***the following modification***: The reaction was conducted using 1,1,1-trifluoro-5-phenyl-2-((trimethylsilyl)methyl)pentan-2-ol (2.58 g, 0.010 mol), and the quantities of the other reagents were adjusted accordingly. Further purification was accomplished by passing the crude material through a SiO_2 plug, eluting with pentane rather than vacuum distillation, giving the pure olefin as a clear, yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.37 (s, 3H), 5.62 (t, *J* = 2.1 Hz, 1H), 5.70 (t, *J* = 1.5 Hz, 1H), 6.39 (t, *J* = 55.5 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3 (CH_3), 115.8 (t, $J_{C\text{-}F}$ = 239.2 Hz, CF_2H), 118.2 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 9.2 Hz, CH_2), 127.0 (CH), 129.5 (CH), 132.1 (C), 138.8 (C), 142.1 (t, $J_{C\text{-}C\text{-}F}$ = 20.2 Hz, C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -116.10 (s, 2F).

Preparation of 1-Methyl-4-(3,3,4,4,4-pentafluorobut-1-en-2-yl)benzene (1r)



Weinreb Amide Synthesis

2,2,3,3,3-Pentafluoro-*N*-methoxy-*N*-methylpropanamide[37]

[36] Kazennikova, G. V.; Talalaeva, T. V.; Zimin, A. V.; Kocheshkov, K. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl)* **1961**, 985.

Synthesis of 2,2,3,3,3-pentafluoro-*N*-methoxy-*N*-methylpropanamide (5.97 g, 72%) was accomplished using the procedure for the preparation of 2,2-difluoro-*N*-methoxy-*N*-methylacetamide, with ***the following modification***: 1) The reaction was conducted using pentafluoropropionic anhydride (12.4 g, 0.040 mol), and the quantities of other reagents were adjusted accordingly; 2) No Et_3N was used in the synthesis of this amide. The Weinreb amide was obtained as a clear, pale-yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.28 (br s, 3H), 3.76 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 33.2 (CH_3) 62.4 (CH_3) 108.2 (tq, $J_{C\text{-}F}$ = 270.2, 38.9 Hz, CF_2) 118.3 (qt, $J_{C\text{-}F}$ = 288.4, 35.4 Hz, CF_3) 158.0 (br, C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -121.48 (s, 2F) -84.53 (s, 3F).

Weinreb Ketone Synthesis

2,2,3,3,3-Pentafluoro-1-(*p*-tolyl)propan-1-one[38]

Synthesis of 2,2,3,3,3-pentafluoro-1-(*p*-tolyl)propan-1-one (5.07 g, 76%) was accomplished using the procedure for the preparation of 2,2-difluoro-1-(4-methylphenyl)ethanone, with ***the following modification***: The reaction was conducted using 2,2,3,3,3-pentafluoro-*N*-methoxy-*N*-methylpropanamide (5.70 g, 0.028 mol), and the quantities of other reagents were adjusted accordingly. Further purification was accomplished by vacuum distillation (bp 88-90 ^{o}C @ 10 mmHg), affording the pentafluoroethyl ketone as a clear light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.46 (s, 3H), 7.34 (d, J = 8.2 Hz, 2H), 7.99 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.9 (CH_3) 109.1 (tq, $J_{C\text{-}F}$ = 269.0, 37.0 Hz, CF_2) 118.5 (qt, $J_{C\text{-}F}$ = 286.7, 33.9 Hz, CF_3) 128.9 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.5 Hz, C) 130.0 (CH) 130.5 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.1 Hz, CH) 147.4 (C) 183.0 (t, $J_{C\text{-}C\text{-}F}$ = 26.5 Hz, C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -118.51 (s, 2F), -84.67 (s, 3F).

Alkylation

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[37] Kelly, C. B.; Mercadante, M. A.; Carnaghan, E. R.; Doherty, M. J.; Fager, D. C.; Hauck, J. J.; Macinnis, A. E.; Tilley, L. J.; Leadbeater, N. E. *Eur. J. Org. Chem.* **2015**, 4071.

[38] Kelly, C. B.; Mercadante, M. A.; Carnaghan, E. R.; Doherty, M. J.; Fager, D. C.; Hauck, J. J.; Macinnis, A. E.; Tilley, L. J.; Leadbeater, N. E. *Eur. J. Org. Chem.* **2015**, 4071.

3,3,4,4,4-Pentafluoro-2-(*p*-tolyl)-1-(trimethylsilyl)butan-2-ol

Synthesis of 3,3,4,4,4-pentafluoro-2-(*p*-tolyl)-1-(trimethylsilyl)butan-2-ol (6.78 g, 89%) was accomplished using the procedure for the preparation of 2-(5-bromo-2-methoxyphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, with ***the following modification***: The reaction was conducted using 2,2,3,3,3-pentafluoro-1-(*p*-tolyl)propan-1-one (4.95 g, 0.0208 mol), and the quantities of other reagents were adjusted accordingly. Further purification was accomplished by vacuum distillation (bp 66-68 ^{o}C @ 0.1 mmHg), affording the carbinol as a clear, light yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ -0.20 (s, 9H), 1.50 (dd, *J* = 15.0, 0.9 Hz, 1H), 1.66 (dd, *J* = 15.0, 2.7 Hz, 1H), 2.27 (s, 1H), 2.35 (s, 3H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.1 (CH_3), 21.3 (CH_2), 25.1 (CH_3), 77.8 (t, $J_{C\text{-}C\text{-}F}$ = 23.8 Hz, C), 114.8 (tq, $J_{C\text{-}F}$ = 262.1, $J_{C\text{-}C\text{-}F}$ = 33.5 Hz, CF_2), 119.8 (qt, $J_{C\text{-}F}$ = 288.7, $J_{C\text{-}C\text{-}F}$ = 36.7 Hz, CF_3), 126.5 (CH), 129.0 (CH), 135.1 (C), 138.3 (C).
^{19}F NMR ($CDCl_3$, 471 MHz) δ -126.82 (d, *J* = 274.7 Hz, 1F), -123.45 (d, *J* = 274.7 Hz, 1F), -80.22 (s, 3F).
FT-IR (cm^{-1}, neat, ATR) 3621 (m), 2956 (m), 1211 (s), 1169 (s), 1131 (s), 1053 (s), 956 (s), 891 (s), 837 (s), 814 (s).
HRMS (EI) calcd for $C_{11}H_9F_5$ $[M - TMS - OH]^+$: 236.0624, found: 236.0628.

Peterson Elimination

1-Methyl-4-(3,3,4,4,4-pentafluorobut-1-en-2-yl)benzene (1r)

Synthesis of 1-methyl-4-(3,3,4,4,4-pentafluorobut-1-en-2-yl)benzene (3.23 g, 78%) was accomplished using the procedure for the preparation of 4-bromo-1-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene, with ***the following modification***: The reaction was conducted using 3,3,4,4,4-pentafluoro-2-(*p*-tolyl)-1-(trimethylsilyl)butan-2-ol (5.71 g, 0.0175 mol) and the quantities of other reagents were adjusted accordingly. Further purification was accomplished by passing the crude material through a SiO_2 plug, eluting with pentane rather than vacuum distillation, giving the pure olefin as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.38 (s, 3H), 5.76 (s, 1H), 5.97 (s, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.24 - 7.31 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3 (CH_3), 112.4 (tq, $J_{C\text{-}F}$ = 253.9, $J_{C\text{-}C\text{-}F}$ = 37.6 Hz, CF_2), 119.5 (qt, $J_{C\text{-}F}$ = 287.8, $J_{C\text{-}C\text{-}F}$ = 39.4 Hz, CF_3), 124.3 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ =8.2 Hz, CH_2), 128.7 (CH), 129.4 (CH), 132.3 (C), 138.9 (t, $J_{C\text{-}C\text{-}F}$ = 22.0 Hz, C), 139.2 (C).

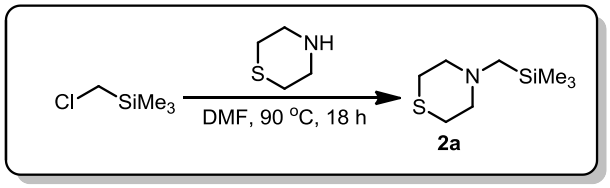
^{19}F NMR ($CDCl_3$, 471 MHz) δ -115.98 (s, 2F), -85.68 (s, 3F).

FT-IR (cm^{-1}, neat, ATR) 2928 (w), 1203 (s), 1162 (s), 1141 (s), 1084 (s), 1015 (s), 946 (s), 823 (s), 744 (s), 536 (s).

HRMS (EI) calcd for $C_{11}H_9F_5$ $[M]^+$: 236.0624, found: 236.0627.

Synthesis of Radical Precursors Employed in Defluorinative Alkylation

Representative Procedure for α-Silylamine Synthesis



4-((Trimethylsilyl)methyl)thiomorpholine, 2a

To a 100 mL round bottom flask equipped with a stir bar was added (chloromethyl)trimethylsilane (3.07 g, 25 mmol, 1 equiv) followed by DMF (25 mL) and thiomorpholine (5.42 g, 52.5 mmol, 2.1 equiv). The mixture was placed under an argon atmosphere and was heated to 90 °C in an oil bath overnight. Reaction progress was assessed by GC/MS and/or NMR. After this time, the reaction mixture was cooled to rt and was diluted with deionized H_2O (~50 mL). The solution was transferred to a separatory funnel, and Et_2O[39] (100 mL) was added. The layers were separated, and the aq layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with deionized H_2O (2 ×100 mL) and brine (150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording the crude α-silylamine. Further purification was accomplished by vacuum

[39] Alternatively, for rather non-polar amines, pentane can be used. Comparable yields can be obtained so long as one extra extraction is utilized (four total extractions rather than the three listed for Et_2O).

distillation (bp 49-51 °C @ 0.1 mmHg), giving pure **2a** as a clear pale-yellow oil (2.99 g, 63%).[40]

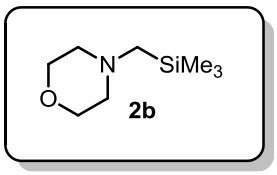
^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.04 (s, 9H), 1.91 (s, 2H), 2.59 - 2.67 (m, 8H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ -0.9 (CH_3), 28.4 (CH_2), 51.9 (CH_2), 58.6 (CH_2).

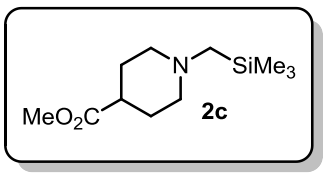
FT-IR (cm^{-1}, neat, ATR) 2953 (m), 2909 (m), 2790 (m), 2740 (m), 1294 (s), 849 (s), 837 (s), 777 (s), 761 (s), 703 (s).

HRMS (EI+) calcd for $C_8H_{19}NSSi$ $[M]^+$: 189.1007, found: 189.1007.

4-((Trimethylsilyl)methyl)morpholine,[41] 2b (1.39 g, 32%) was prepared according to the representative procedure ***with the following modification:*** 1) Morpholine (4.57 g, 52.5 mmol) was used in place of thiomorpholine. Further purification was accomplished by vacuum distillation (bp 59-61 °C @ 1 mmHg), giving pure **2b** as a clear colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.06 (s, 9H), 1.90 (s, 2H), 2.35 - 2.41 (m, 4H), 3.68 (t, J = 4.6 Hz, 4H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -0.9 (s, CH_3), 51.6 (CH_2), 57.6 (CH_2), 67.4 (CH_2).



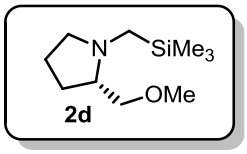
Methyl 1-((Trimethylsilyl)methyl)piperidine-4-carboxylate, 2c (2.25 g, 65%) was prepared according to the representative procedure ***with the following modification:*** 1) The reaction was conducted using (chloromethyl)trimethylsilane (1.84 g, 15 mmol, 1 equiv); 2) Methyl piperidine-4-carboxylate (4.29 g, 30 mmol, 1 equiv) was used in place of thiomorpholine. Further purification was accomplished by vacuum distillation (bp 58-60 °C @ 0.1 mmHg), giving pure **2c** as a clear colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.05 (s, 9H), 1.67 - 1.86 (m, 4H), 1.88 (s, 2H), 1.91 - 2.01 (m, 2H), 2.18 - 2.27 (m, 1H), 2.72 - 2.82 (m, 2H), 3.67 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -0.9 (CH_3), 28.8 (CH_2), 40.8 (CH), 51.3 (CH_2), 51.9 (CH_2), 57.1 (CH_3), 176.1 (C). **FT-IR** (cm^{-1}, neat, ATR) 2951 (m), 2779 (m), 1264



[40] In general, the peaks in ^{1}H NMR of α-silylamines appear broadened. We speculate that this may stem from an interaction between the deuterated solvent, $CDCl_3$, and the amine, although for some substrates this broadening can be resolved by increasing the relative concentration of the analyte in $CDCl_3$. See Lazareva, N. F.; Vakul'skaya, T. I.; Lazarev, I. M. *J. Phys. Org. Chem.* **2009**, *22*, 144. To alleviate this, more concentrated ^{1}H NMRs may be taken.
[41] Sato, Y.; Aoyama, T.; Shirai, H. *J. Organomet. Chem.* **1974**, *82*, 21.

(s), 1248 (s), 1193 (s), 1172 (s), 838 (s). **HRMS** (EI+) calcd for $C_{11}H_{23}NO_2Si$ $[M]^+$: 229.1498, found: 229.1495.

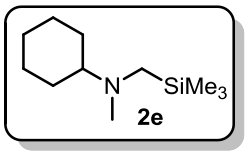
(*S*)-2-(Methoxymethyl)-1-((trimethylsilyl)methyl)pyrrolidine, 2d (0.98 g, 49%) was prepared



2d

according to the representative procedure ***with the following modification:*** 1) The reaction was conducted using (chloromethyl)trimethylsilane (1.23 g, 10 mmol, 1 equiv); 2) (*S*)-2-(methoxymethyl)pyrrolidine (2.36 g, 20.5 mmol, 2.05 equiv) was used in place of thiomorpholine. Further purification was accomplished by vacuum distillation (bp 68-70 °C @ 1 mmHg), giving pure **2d** as a clear colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.05 (s, 9H), 1.52 - 1.64 (m, 1H), 1.65 - 1.78 (m, 3H), 1.82 - 1.93 (m, 1H), 2.06 - 2.17 (m, 1H), 2.30 - 2.39 (m, 1H), 2.43 (d, *J* = 14.0 Hz, 1H), 3.02 - 3.12 (m, 1H), 3.17 - 3.28 (m, 1H), 3.35 (s, 3H), 3.39 - 3.46 (m, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -1.0 (CH_3), 1.7 (CH_2), 23.4 (CH_2), 28.7 (CH_2), 46.9 (br s, CH_2), 57.8 (CH), 59.4 (CH_3), 68.0 (br s, CH_2). **FT-IR** (cm^{-1}, neat, ATR) 2954 (m), 2874 (m), 2809 (m), 1247 (s), 1109 (s), 837 (s), 692 (s). **HRMS** (EI+) calcd for $C_{10}H_{23}NOSi$ $[M]^+$: 201.1549, found: 201.1563.

***N*-Methyl-*N*-((trimethylsilyl)methyl)cyclohexanamine,[42] 2e** (1.99 g, 67%) was prepared

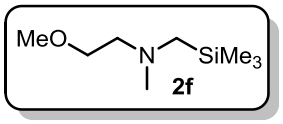


2e

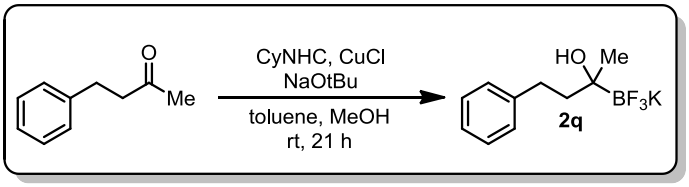
according to the representative procedure ***with the following modification:*** 1) The reaction was conducted using (chloromethyl)trimethylsilane (1.84 g, 15 mmol, 1 equiv); 2) *N*-methylcyclohexanamine (5.09 g, 45 mmol, 3 equiv) was used in place of thiomorpholine. Further purification was accomplished by vacuum distillation (bp 70-72 °C @ 1 mmHg), giving pure **2e** as a clear colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.05 (s, 9H), 1.03 - 1.11 (m, 1H), 1.11 - 1.26 (m, 4H), 1.58 - 1.64 (m, 1H), 1.72 - 1.81 (m, 4H), 1.95 (s, 2H), 2.24 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -1.1 (CH_3), 26.4 (CH_2), 26.8 (CH_2), 28.3 (CH_2), 42.0 (CH_2), 44.9 (CH_3), 65.2 (CH).

[42] Baciocchi, E.; Del Giacco, T.; Lapi, A. *Org. Lett.*, **2006** , *8*, 1783.

2-Methoxy-*N*-methyl-*N*-((trimethylsilyl)methyl)ethanamine, 2f (0.54 g, 35%) was prepared according to the representative procedure ***with the following modification:*** 1) The reaction was conducted using (chloromethyl)trimethylsilane (1.08 g, 8.8 mmol, 1 equiv); 2) 2-methoxy-*N*-methylethanamine (1.61 g, 18 mmol, 2.05 equiv) was used in place of thiomorpholine. Further purification was accomplished by vacuum distillation (bp 67-69 °C @ 1 mmHg), giving pure **2f** as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.06 (s, 9H), 1.94 (s, 2H), 2.26 (s, 3H), 2.52 (t, *J* = 6.0 Hz, 2H), 3.34 (s, 3H), 3.46 (t, *J* = 5.9 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -1.0 (CH_3), 47.2 (CH_2), 50.7 (CH_3), 59.1 (CH_2), 60.9 (CH_3), 71.2 (CH_2). **FT-IR** (cm^{-1}, neat, ATR) 2973 (m), 2877 (m), 2812 (m), 2769 (m), 1248 (s), 1123 (s), 763 (s), 693 (s). **HRMS** (EI) calcd for $C_8H_{21}NOSi$ $[M]^+$: 175.1392, found: 175.1380.



Procedure for the Synthesis of Potassium 2-Hydroxy-4-phenylbutyltrifluoroborate (2q)



The following procedure is a modification of the procedure outlined by Floreancig.[43] To a 250 mL round bottom flask equipped with a stir bar was charged with CuCl (140 mg, 1.4 mmol 0.2 equiv), $[CyNHC]BF_4$ (220 mg, 0.69 mmol, 0.1 equiv), bispinacolborane (1.93 g, 7.6 mmol, 1.1 equiv) and NaOtBu (130 mg, 1.3 mmol, 0.19 equiv). The flask was evacuated and purged three times with argon. Toluene (50 mL) was added *via* syringe, and the mixture was allowed to stir at rt for 30 min. 4-Phenylbutan-2-one (1.02 g, 6.9 mmol) and MeOH (442 mg, 0.56 mL, 13.8 mmol, 2 equiv) were added *via* syringe, and the mixture was allowed to stir at rt for 21 h. The reaction mixture was filtered through a plug of Celite® and then rinsed with EtOAc (3 × 40 mL). The filtrate was concentrated, and the resultant oil was dissolved in MeOH (50 mL) and transferred to a 150 mL round bottom flask. The flask was cooled to 0 ^{o}C in an ice bath, and then a solution of KHF_2 (4.5 M, 13.2 mL, 59.5 mmol, 8.62 equiv) was added dropwise over 10 min. **CAUTIONARY NOTE:** *KHF_2 solutions will etch glassware*. The mixture was warmed to rt and

[43] Hanna, R. D.; Naro, Y.; Deiters, A.; Floreancig, P. E. *J. Am. Chem. Soc.* **2016**, *138*, 13353.

stirred for 3.5 h. The solvent was removed *in vacuo* by rotary evaporation. The resultant solid was triturated and sonicated with hot acetone and filtered. This process was repeated three times. The filtrate was then concentrated to a minimal volume, and the alkyltrifluoroborate was precipitated through dropwise addition of cold Et_2O (~30 mL). The mixture was filtered, washed with cold Et_2O (~10 mL), and dried on high vacuum (< 0.5 mmHg) overnight to yield the desired organotrifluoroborate **2q** as a white powder (mp = >200 °C).

^{1}H NMR (acetone-d_6, 500 MHz) δ 1.04 (s, 3H), 1.56 - 1.65 (m, 1H), 1.65 - 1.73 (m, 1H), 2.71 (dd, J = 9.6, 8.4 Hz, 2H), 3.76 (s, 1H), 7.07 (t, J = 7.2 Hz, 1H), 7.13 - 7.24 (m, 4H).

^{13}C NMR (acetone-d_6, 125 MHz) δ 24.8 (CH_2), 24.9 (CH_2), 31.4 (CH_3), 44.0 (C), 125.8 (CH), 128.9 (CH), 129.3 (CH), 146.1 (C).

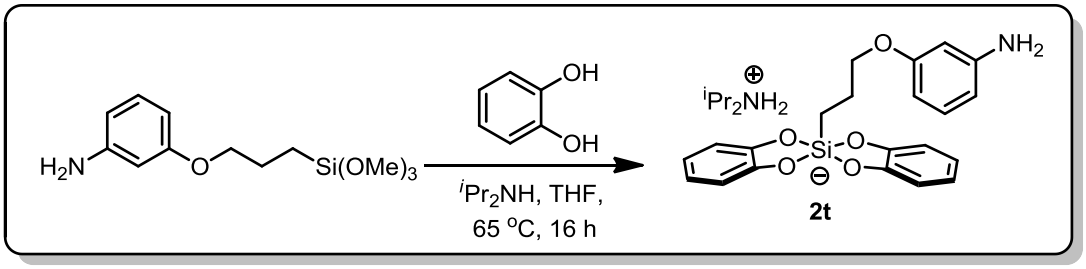
^{19}F NMR (acetone-d_6, 471 MHz) δ -153.16 (br s, 3F).

^{11}B NMR (acetone-d_6, 125 MHz) δ 5.92 (br s, 1B).

FT-IR (cm^{-1}, neat, ATR) 3542 (m), 2949 (m), 1602 (s), 1492 (s), 993 (s), 959 (s), 905 (s), 699 (s).

HRMS (ES–) calcd for $C_{10}H_{13}BF_3O$ $[M - K]^-$: 217.1012, found: 217.1022.

Representative Procedure for Alkylbis(catecholato)silicates



Diisopropylammonium Bis(catecholato) 3-(*m*-Aminophenoxy)propylsilicate (2t)

To an oven-dried, 100 mL round bottom flask equipped with a stir bar, reflux condenser, and gas inlet adapter was added catechol[44] (3.95 g, 35.9 mmol, 1.95 equiv) followed by THF (38 mL) and *i*-Pr_2NH[45] (2.24 g, 3.11 mL, 22.1 mmol, 1.2 equiv). The mixture was placed under an argon atmosphere and was allowed to stir at rt for 5 min. The solution became pale red. After this time,

[44] Recrystallized from hexane or heptane prior to use.
[45] A similar protocol can be used to prepare the more organic soluble triethylammonium salt, although precipitation may be more arduous. This salt works equally well in Ni/photoredox cross-coupling.

3-(3-(trimethoxysilyl)propoxy)aniline (5.00 g, 18.42 mmol, 1.0 equiv) was added. The solution immediately lightened to a golden yellow color. The solution was then heated to reflux in an oil bath and allowed to stir at this temperature overnight.[46] Once the reaction was judged to be complete by crude ^{1}H NMR analysis,[47] the solvent was removed *in vacuo* by rotary evaporation. The resulting powder was collected *via* filtration through a medium porosity fritted funnel. The powder was washed with Et_2O (~100 mL) and pentane (~50 mL). The solid was collected and dried further *in vacuo* to give the **2t** (6.129 g, 67%) as a powdery white solid (mp = 150 °C).

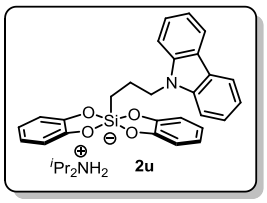
^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.54 (s, 2H), 1.18 (d, J = 6.4 Hz, 12H), 1.51 - 1.60 (m, 2H), 3.33 (br s, 2H), 3.63 (t, J = 7.2 Hz, 2H), 4.93 (s, 2H), 5.95 (dd, J = 8.1, 1.8 Hz, 1H), 6.01 (t, J = 2.0 Hz, 1H), 6.06 (dd, J = 7.8, 1.2 Hz, 1H), 6.43 (dd, J = 5.6, 3.4 Hz, 4H), 6.53 (dd, J = 5.5, 3.5 Hz, 4H), 6.80 (t, J = 7.9 Hz, 1H), 7.95 (br s, 2H).

^{13}C NMR (DMSO-d_6, 125 MHz) δ 14.0 (CH_2), 19.1 (CH_3), 24.4 (CH_2), 46.2 (CH_2), 69.8 (CH_2), 99.8 (CH), 102.1 (CH), 106.4 (CH), 109.5 (CH), 117.1 (CH), 129.3 (CH), 149.8 (C), 150.5 (C), 159.8 (C).

FT-IR (cm^{-1}, neat, ATR) 3046 (w), 1485 (s), 1239 (s), 813 (s), 742 (s), 687 (s), 506 (s).

HRMS (ES-) calcd for $C_{21}H_{20}NO_5Si$ [M – iPr$_2$NH$_2$]$^-$: 394.1096, found: 394.1111.

Diisopropylammonium Bis(catecholato)(3-carbazolylpropyl)silicate, 2u (1.87 g, 68%) was



prepared according to the general procedure from (3-carbazolylpropyltriethoxysilane (1.858 g, 5.00 mmol). The desired silicate **2u** was isolated as an off-white solid (mp = 154 °C). **^{1}H NMR** (DMSO-d_6, 500 MHz) δ 0.64 (t, J = 7.5 Hz, 2H), 1.19 (d, J = 6.4 Hz, 12H), 1.63 - 1.75 (m, 2H), 3.34 (br s, 2H), 4.21 (t, J = 7.6 Hz, 2H), 6.43 (dd, J = 5.5, 3.7 Hz, 4H), 6.55 (dd, J = 5.5, 3.5 Hz, 4H), 7.14 (t, J = 7.4 Hz, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 8.03 (br s, 2H), 8.09 (d, J = 7.6 Hz, 2H). **^{13}C NMR** (DMSO-d_6, 125 MHz) δ 15.2 (CH_2), 18.8 (CH_3), 24.0 (CH_2), 44.9 (CH), 46.3 (CH_2), 109.3 (CH), 109.7 (CH), 117.2 (CH), 118.4 (CH), 120.1 (CH), 121.8 (CH), 125.5 (C), 139.9 (C), 150.5 (C). **FT-IR** (cm^{-1}, neat, ATR) 3051 (vw, br) 1484 (s), 1239 (s), 818 (s), 740 (s), 721 (s), 666 (s), 585 (s), 507 (s). **HRMS** (ES+) calcd for $C_{27}H_{23}NaO_4Si$ [M + H + Na – iPr$_2$NH$_2$]$^+$: 476.1294, found: 476.1271.

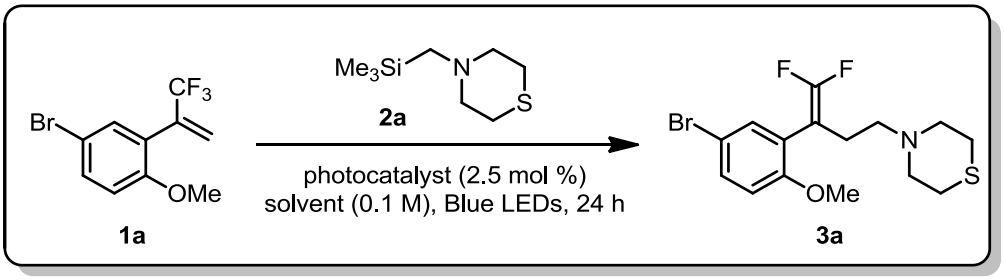
[46] Depending on the nature of the silicate and its solubility in THF, precipitation of the product would occur.
[47] For DIPA silicates, it is advisable to use acetone-d_6 or DMSO-d_6 as the NMR solvent, as these silicates have poor solubility in most other deuterated solvents.

Optimization and Control Studies for Various Radical Precursors

Procedure for optimization and control studies:

To a 4 mL reaction vial equipped with a stir bar was added photocatalyst [if $Ru(bpy)_3(PF_6)_2$, 0.0025 mmol, 0.025 equiv; if 4CzIPN, 0.005 mmol, 0.05 equiv] and the appropriate radical precursor (0.14 mmol, 1.4 equiv). The vial was sealed with a cap containing a TFE-lined silicone septum and placed under an Ar atmosphere through evacuating and purging with Ar three times *via* an inlet needle. The vial was then charged with the CF_3 alkene **1a** (28.1 mg, 0.1 mmol, 1.0 equiv) and anhyd DMSO (1 mL) *via* a syringe. The cap was sealed with Parafilm®, and the solution was either irradiated with blue LEDs in the aforementioned photoreactor or was wrapped in foil and placed in a light-free environment. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. The solution was stirred vigorously. Reaction progress was evaluated by GC/MS or HPLC after the addition of 4,4'-di-tert-butyl-1,1'-biphenyl (0.050 mL, 0.00001 mmol, 0.2 M in MeCN) as an internal standard (IS).

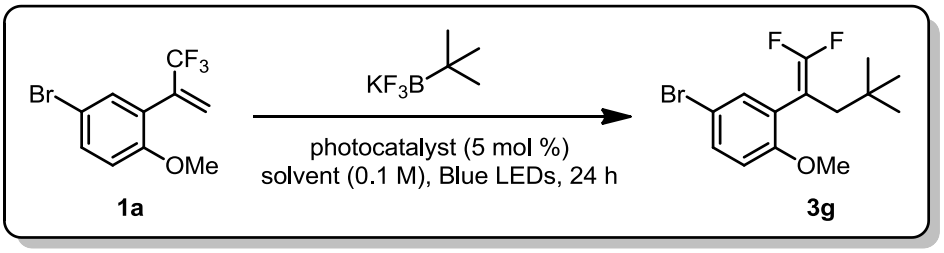
Table S1: Reaction Optimization of Defluorinative Radical Addition to CF_3 Alkenes using α-Silylamine 2a



Entry	Photocatalyst	Solvent	Prod : IS
1	$Ru(bpy)_3(PF_6)_2$	DMF	0.28
2	4CzIPN	DMF	0.27
3	$MesAcr^+BF_4^-$	DMF	—
4	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$	DMF	0.29
5	$Ru(bpy)_3(PF_6)_2$	DMSO	0.28
6	$Ru(bpy)_3(PF_6)_2$	MeCN	0.21
7	$Ru(bpy)_3(PF_6)_2$	EtOAc	—

[a] Prod:IS ratios were determined by HPLC integration.

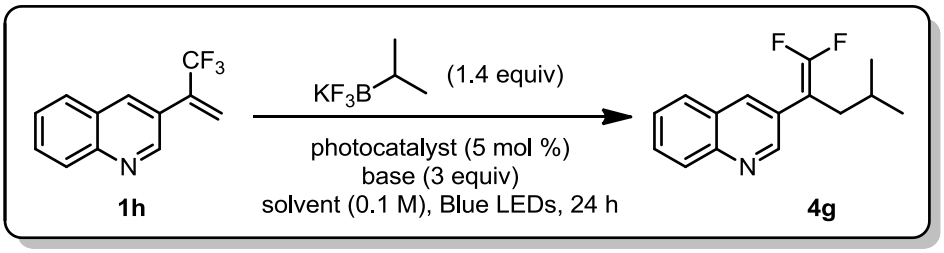
Table S2: Reaction Optimization of Defluorinative Radical Addition to CF_3 Alkenes using Organotrifluoroborate 2g



Entry	Photocatalyst	Solvent	Prod : IS
1	$Ru(bpy)_3(PF_6)_2$	DMSO	—
2	4CzIPN	DMSO	0.97
3	$MesAcr^+BF_4^-$	DMSO	—
4	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$	DMSO	Trace
5	4CzIPN	DMF	0.53
6	4CzIPN	MeCN	0.73
7	4CzIPN	EtOAc	0.63

[a] Prod:IS ratios were determined by HPLC integration.

Optimization of Radical Addition to Heteroaryl Trifluoromethyl Alkene Substrates with High Throughput Experimentation



High Throughput Experimentation was performed at the Penn/Merck Center for High Throughput Experimentation at the University of Pennsylvania. All solvents used in the screening center were dry and degassed. The screen was analyzed by UPLC with addition of an internal standard. The areas for the internal standard (IS), CF_3 alkene (SM), and product (P) from each of the screens are shown in the tables below. The ratios calculated are pertinent only to that specific screen; the ratios from one screen should not be quantitatively compared to those from a different screen. The results of the screens are summarized in two tables shown below, the first representing the ratio of product to internal standard and the second representing the ratio of starting material to internal standard both as determined by UPLC.

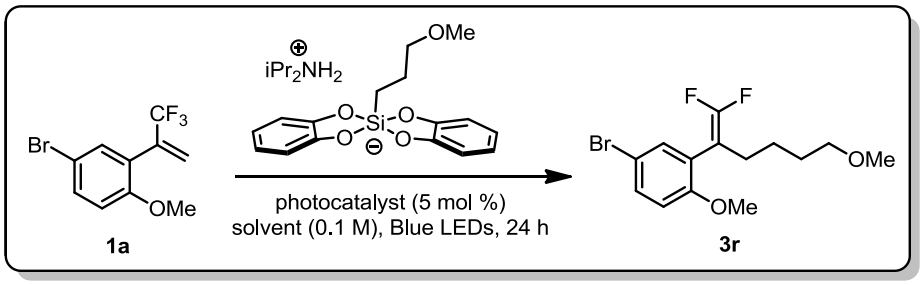
Procedure for Screen 1: Condition Optimization for Heteroaryl Substrates:

To a 96 well plate reactor containing 1 mL reaction vials equipped with a Teflon-coated magnetic stir bar in a glovebox was added sequentially: 1) solution of 5-(1,1-Difluoro-4-methylpent-1-en-2-yl)-1-methyl-1H-indole (**4g**) (10 μmol, 1.0 equiv) dissolved in MeCN (50 μL); 2) solution of isopropyl trifluoroborate (1.4 equiv) in MeCN (100 μL); (3) solution of inorganic base (3 equiv) in MeCN (100 μL) (to appropriate vials). The solvent was removed from the vials using a Genevac. To the appropriate vials was added sequentially: 1) solution of organic base (3 equiv) in the appropriate solvent (20 – 40 μL); 2) solution of photocatalyst (0.05 equiv) in the appropriate solvent (200 μL). The vials were sealed and stirred at rt under blue light irradiation for 24 h. After 24 h the reactions were opened to air, and diluted with 500 μL of MeCN. After stirring the diluted block for 15 min, 25 μL aliquots were then taken from the reaction vials and dosed into a 96-well UPLC block. These aliquots were further diluted by the addition of 700 μL of MeCN containing internal standard. The reaction mixtures were then analyzed by UPLC.

Product : IS	Diox	DMSO	DMF	MeCN	Diox	DMSO	DMF	MeCN	Diox	DMSO	DMF	MeCN
	$[Ir\{dF(CF_3)ppy\}_2(bpy)]PF_6$				$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$				4CzIPN			
Cs_2CO_3	5.85	0.00	2.74	0.00	1.89	0.00	0.00	0.00	0.00	1.28	1.55	1.94
K_2HPO_4	8.89	0.00	1.95	0.00	3.32	0.00	0.00	0.00	0.00	3.94	3.90	0.00
1:1 Li_2CO_3:DIPA	0.89	0.00	0.33	0.00	1.39	0.00	0.00	0.00	0.00	3.10	0.00	1.35
1:2 Cs_2CO_3:lutidine	4.33	0.00	0.95	0.00	7.17	0.00	0.00	0.00	0.00	1.15	1.92	2.80
lutidine	9.71	0.00	2.68	0.00	5.30	0.00	0.00	0.00	0.00	0.00	5.30	0.00
None	10.32	2.75	2.22	0.00	4.84	0.00	0.00	0.00	0.00	4.42	4.11	1.98
Na_2CO_3	10.53	0.00	2.52	0.00	9.51	0.00	0.00	0.00	0.00	0.00	5.18	0.00

SM : IS	Diox	DMSO	DMF	MeCN	Diox	DMSO	DMF	MeCN	Diox	DMSO	DMF	MeCN
	$[Ir\{dF(CF_3)ppy\}_2(bpy)]PF_6$				$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$				4CzIPN			
Cs_2CO_3	4.41	5.03	4.05	8.29	8.09	4.43	7.38	7.33	8.31	6.44	7.25	7.08
K_2HPO_4	0.77	2.23	3.74	5.58	6.27	1.07	4.24	5.19	9.67	4.50	4.62	6.25
1:1 Li_2CO_3:DIPA	6.99	4.32	7.62	6.52	6.95	2.90	7.05	6.56	1.93	6.35	2.50	7.18
1:2 Cs_2CO_3:lutidine	5.92	6.33	6.87	8.30	2.20	6.02	7.46	7.94	7.94	7.05	7.69	6.50
lutidine	0.00	3.11	2.97	5.22	2.85	1.84	3.44	6.02	8.77	5.98	3.31	8.99
None	0.00	0.32	3.18	6.54	4.22	1.35	4.93	5.46	10.11	3.12	4.34	5.69
Na_2CO_3	0.00	2.34	3.66	6.93	0.00	1.19	4.14	6.67	9.48	5.81	2.19	8.53

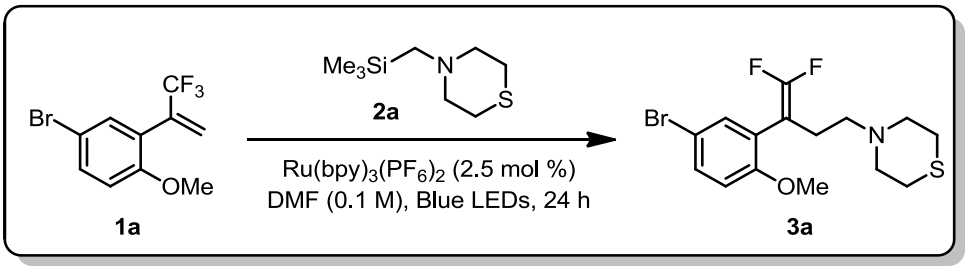
Table S3: Reaction Optimization of Defluorinative Radical Addition to CF_3 Alkenes using Alkyl(biscatecholato)silicate 2r



Entry	Photocatalyst	Solvent	Prod : IS
1	$Ru(bpy)_3(PF_6)_2$	DMF	0.28
2	4CzIPN	DMF	0.23
3	$MesAcr^+BF_4^-$	DMF	—
4	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$	DMF	0.28
5	$Ru(bpy)_3(PF_6)_2$	DMSO	0.30*
6	$Ru(bpy)_3(PF_6)_2$	MeCN	0.06
7	$Ru(bpy)_3(PF_6)_2$	EtOAc	—

*Note: while DMSO and DMF performed with nearly identical results, DMF was chosen as the solvent as later substrate screening determined it to result in more broad success across substrates. $Ru(bpy)_3(PF_6)_2$ and $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ resulted in the same Prod : IS but $Ru(bpy)_3(PF_6)_2$ was chosen for its lower cost per gram.

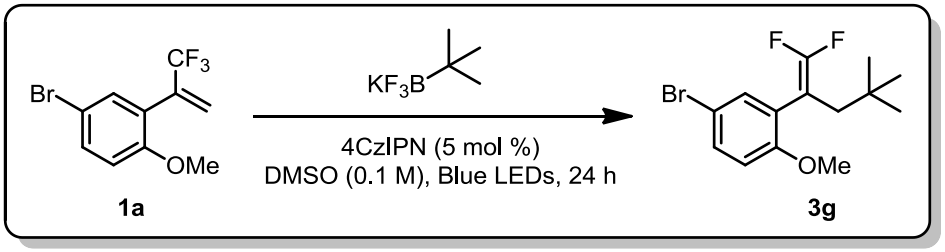
Table S4: Control Studies using α-Silylamine 2a



Entry	Deviation from procedure	% Conversion to 3a
1	*None*	99
2	*No $Ru(bpy)_3(PF_6)_2$*	0
3	*No light*	0

[a] Percent conversion was approximated based upon relative areas from the GC/MS trace of a given run.

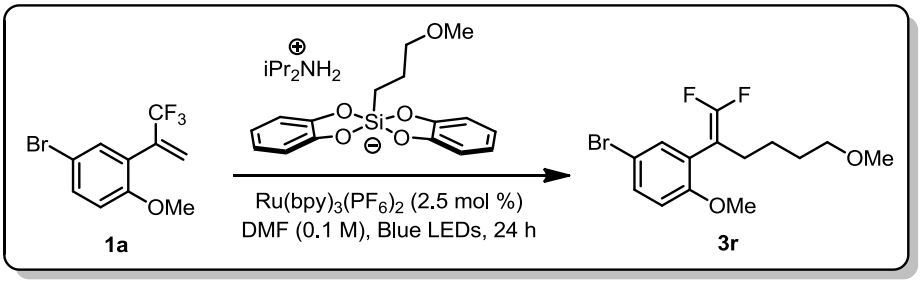
Table S5: Control Studies using Organotrifluoroborate 2g



Entry	Deviation from procedure	% Conversion to 3g
1	*None*	99
2	*No 4CzIPN*	0
3	*No light*	0

[a] Percent conversion was approximated based upon relative areas from the GC/MS trace of a given run.

Table S6: Control Studies using Alkyl(biscatecholato)silicate 2r

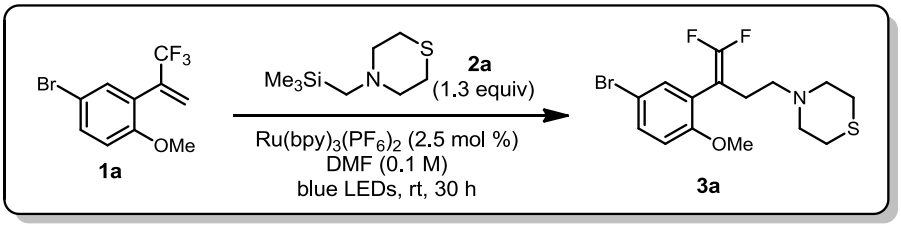


Entry	Deviation from procedure	% Conversion to 3r
1	*None*	99
2	*No Ru(bpy)$_3$(PF$_6$)$_2$*	0
3	*No light*	0

[a] Percent conversion was approximated based upon relative areas from the GC/MS trace of a given run.

General Procedures for Defluorinative Alkylation of Perfluoroalkyl-Substituted Alkenes

Representative Procedure for Defluorinative Alkylation using α-Silylamines



4-(3-(5-Bromo-2-methoxyphenyl)-4,4-difluorobut-3-en-1-yl)thiomorpholine (3a)

To an 8 mL reaction vial equipped with a stir bar was added $Ru(bpy)_3(PF_6)_2$ (0.011 g, 0.0125 mmol, 0.025 equiv). The vial was sealed with a cap containing a TFE-lined silicone septum and placed under an Ar atmosphere through evacuating and purging with Ar three times *via* an inlet needle. The vial was then charged with the α-silylamine **2a** (0.123 g, 0.65 mmol, 1.3 equiv) and CF_3 alkene **1a** (0.141 g, 0.5 mmol) in anhyd DMF (5 mL) *via* a syringe. The cap was sealed with Parafilm®, and the now bright red solution was irradiated with blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 ^oC *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by GC/MS.[48] Once judged to be complete, the now dark red-brown solution was transferred to a separatory funnel and diluted with deionized H_2O (20 mL), 2 M aq NaOH (5 mL) and Et_2O (~ 20 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 × ~20 mL). The combined organic layers were washed with deionized H_2O (2 × ~50 mL) followed by brine (~100 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient CH_2Cl_2/MeOH)[49] to give the desired difluoroalkene, **3a**, (0.165 g, 87%) as a pale-yellow oil.

[48] With some substrates, the reaction can stall after 24 h. To resolve this issue, additional $Ru(bpy)_3(PF_6)_2$ (0.0043 g, 0.0025 mmol, 0.005 equiv) and α-silylamine (0.2 equiv) are added. The reaction mixture is then irradiated for an additional 12 h.

[49] Alternatively, hexane/EtOAc (containing 1% Et_3N) may be used instead, although in some cases separation of the residual α-silylamine from the product is problematic with this solvent system.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.34 (t, *J* = 7.6 Hz, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 2.65 (d, *J* = 7.6 Hz, 8H), 3.79 (s, 3H), 6.76 (d, *J* = 8.7 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.5 Hz, 1H).

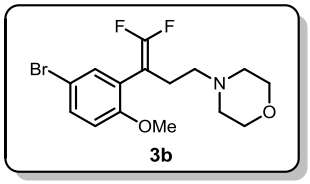
^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.9 (CH_2), 28.0 (CH_2), 54.9 (CH_2), 55.9 (CH_3), 56.8 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 87.2 (dd, $J_{C\text{-}C\text{-}F}$ = 23.8, 16.5 Hz, C), 112.6 (C), 112.8 (CH), 124.6 (dd, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5, 1.8 Hz, C), 132.0 (CH), 134.0 (CH), 153.6 (t, $J_{C\text{-}F}$ = 286.5 Hz, CF_2), 156.7 (C).

^{19}F NMR ($CDCl_3$, 377 MHz) δ -95.89 (d, *J* = 41.2 Hz, 1F), -91.83 (d, *J* = 41.2 Hz, F).

FT-IR (cm^{-1}, neat, ATR) 2912 (m), 2810 (m), 1742 (s), 1488 (s), 1282 (s), 1248 (s), 1225 (s), 1128 (s), 1027 (s), 908 (s), 807 (s), 729 (s).

HRMS (EI) calcd for $C_{15}H_{18}BrF_2NOS$ $[M]^+$: 377.0261, found: 377.0272.

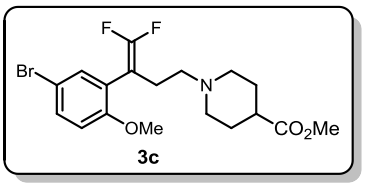
4-(3-(5-Bromo-2-methoxyphenyl)-4,4-difluorobut-3-en-1-yl)morpholine, 3b (0.118 g, 65%) was prepared according to the general procedure from α-silylamine **2b** (0.113 g, 0.65 mmol) ***with the following modification***s: 1) the reaction was run for 36 h; 2) Additional amine (0.018 g, 0.1 mmol 0.2 equiv) and $Ru(bpy)_3(PF_6)_2$ (0.0043 g, 0.0025 mmol, 0.005 equiv) were added after 24 h. The desired difluoroalkene **3b** was isolated as a clear, pale-yellow oil.



3b

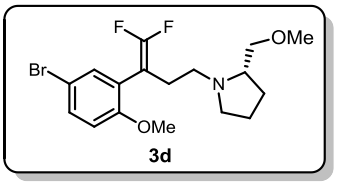
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.28 (t, *J* = 7.9 Hz, 2H), 2.33 - 2.40 (m, 4H), 2.44 - 2.50 (m, 2H), 3.66 (t, *J* = 4.6 Hz, 4H), 3.78 (s, 3H), 6.75 (d, *J* = 8.9 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 25.2 (CH_2), 53.7 (CH_2), 55.9 (CH_2), 56.4 - 57.1 (CH_2), 67.2 (CH_3), 87.3 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 17.4 Hz, C), 112.6 (CH), 112.8 (CH), 124.7 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 6.4 Hz, C), 132.0 (CH), 134.1 (C), 153.6 (t, $J_{C\text{-}F}$ = 287.8 Hz, CF_2), 156.8 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -95.97 (d, *J* = 41.2 Hz, 1F), -91.91 (d, *J* = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2900 (m), 2750 (m), 2700 (m), 1742 (s), 1489 (s), 1249 (s), 1231 (s), 1219 (s), 1115 (s), 1027 (s), 806 (s). **HRMS** (EI+) calcd for $C_{15}H_{18}BrF_2NO_2$ $[M]^+$: 361.0489, found: 361.0480.

Methyl 1-(3-(5-Bromo-2-methoxyphenyl)-4,4-difluorobut-3-en-1-yl)piperidine-4-carboxylate, 3c (0.148 g, 71%) was prepared according to the general procedure from α-silylamine **2c** (0.149 g, 0.65 mmol). The desired difluoroalkene **3c** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.68 - 1.78 (m, 2H), 1.88 (d, *J* = 11.3 Hz, 2H), 1.96 - 2.06 (m, 2H), 2.24 - 2.32 (m, 3H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.76 - 2.85 (m, 2H), 3.67 (s, 3H), 3.79 (s, 3H), 6.76 (d, *J* = 8.9 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.9, 2.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 25.5 (CH_2), 28.4 (CH_2), 41.1 (CH_2), 51.8 (CH_2), 53.0 (CH_2), 55.9 (CH_3), 56.4 (CH_3), 87.3 (dd, $J_{C\text{-}C\text{-}F}$ = 24.5, 17.3 Hz, C), 112.6 (CH), 112.7 (CH), 124.0 - 125.3 (m, C), 132.0 (CH), 134.0 (C), 153.5 (t, $J_{C\text{-}F}$ = 287.9 Hz, CF_2), 156.7 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 175.7 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -95.96 (d, *J* = 41.2 Hz, 1F), -91.93 (d, *J* = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2950 (w), 2800 (w), 1732 (s), 1249 (s), 1230 (s), 907 (vs), 728 (s). **HRMS** (EI+) calcd for $C_{20}H_{22}BrF_2NO_3$ $[M]^+$: 417.0747, found: 417.0751.



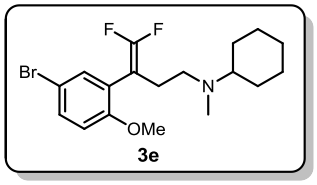
3c

(*S*)-1-(3-(5-Bromo-2-methoxyphenyl)-4,4-difluorobut-3-en-1-yl)-2-(methoxymethyl)pyrrolidine, 3d (0.142 g, 73%) was prepared according to the general procedure from α-silylamine **2d** (0.131 g, 0.65 mmol). The desired difluoroalkene **3d** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.60 (br s, 2H), 1.72 (br s, 2H), 1.81 - 1.91 (m, 1H), 2.16 (br s, 1H), 2.27 (br s, 1H), 2.48 - 2.57 (m, 2H), 2.76 - 2.81 (m, 1H), 3.12 (s, 1H), 3.21 (s, 1H), 3.24 - 3.28 (m, 1H), 3.29 (s, 3H), 3.80 (s, 3H), 6.76 (d, *J* = 8.9 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.38 (dd, *J* = 8.7, 2.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 23.2 (CH_2), 27.2 (CH_2), 28.7 (CH_2), 53.3 (CH_2), 54.4 (CH_2), 55.9 (CH_2), 59.3 (CH_2), 63.7 (CH_3), 76.4 (CH_3), 87.6 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 16.5 Hz, C), 112.6 (s, CH), 112.7 (C), 124.8 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.6 Hz, C), 132.0 (CH), 134.2 (CH), 153.6 (t, $J_{C\text{-}F}$ = 287.8 Hz, CF_2), 156.8 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -96.00 (d, *J* = 38.1 Hz, 1F), -92.13 (d, *J* = 38.1 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2950 (w), 2800 (w), 1742 (s), 1489 (s), 1247 (s), 1223 (s), 1122 (s), 1106 (s), 908 (s). **HRMS** (ES+) calcd for $C_{17}H_{22}BrF_2NO_2$ $[M + H]^+$: 390.0853, found: 390.0880.



3d

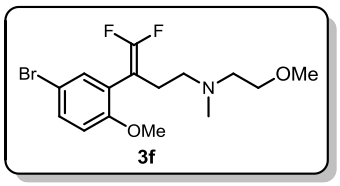
***N*-(3-(5-Bromo-2-methoxyphenyl)-4,4-difluorobut-3-en-1-yl)-*N*-methylcyclohexanamine, 3e**



3e

(0.097 g, 50%) was prepared according to the general procedure from α-silylamine **2e** (0.130 g, 0.65 mmol) ***with the following modifications***: 1) the reaction was run for 36 h; 2) Additional amine (0.020 g, 0.1 mmol 0.2 equiv) and $Ru(bpy)_3(PF_6)_2$ (0.0107 g, 0.0125 mmol, 0.025 equiv) The desired difluoroalkene **3e** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.02 - 1.27 (m, 5H), 1.60 (d, *J* = 13.0 Hz, 1H), 1.68 - 1.78 (m, 4H), 2.21 (s, 3H), 2.24 - 2.31 (m, 1H), 2.35 - 2.48 (m, 4H), 3.79 (s, 3H), 6.76 (d, *J* = 8.9 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 26.1 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 28.7 (CH_2), 37.3 (s, CH_2), 51.8 (CH), 55.8 (CH_3), 62.8 (CH_3), 87.5 (dd, $J_{C\text{-}C\text{-}F}$ = 24.5, 16.3 Hz, C), 112.5 (C), 112.6 (CH), 124.8 (C), 131.8 (CH), 134.0 (CH), 153.5 (t, $J_{C\text{-}F}$ = 287.9 Hz, CF_2), 156.6 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -96.03 (d, *J* = 44.3 Hz, 1F), -92.14 (d, *J* = 44.3 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2928 (s), 2853 (m), 1741 (s), 1489 (s), 1244 (s), 1223 (s), 1029 (s). **HRMS** (ES+) calcd for $C_{18}H_{25}BrF_2NO$ $[M + H]^+$: 388.1088, found: 388.1088.

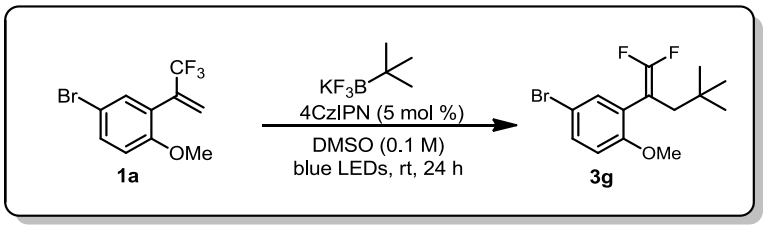
3-(5-Bromo-2-methoxyphenyl)-4,4-difluoro-*N*-(2-methoxyethyl)-*N*-methylbut-3-en-1-amine,



3f

3f (0.138 g, 76%) was prepared according to the general procedure from α-silylamine **2f** (0.114 g, 0.65 mmol). The desired difluoroalkene **3f** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.25 (s, 3H), 2.33 - 2.38 (m, 2H), 2.44 - 2.50 (m, 2H), 2.52 (t, *J* = 5.8 Hz, 2H), 3.32 (s, 3H), 3.41 (t, *J* = 5.8 Hz, 2H), 3.79 (s, 3H), 6.76 (d, *J* = 8.9 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 25.7 (CH_2), 42.6 (CH_2), 55.9 (CH_2), 56.0 (CH_2), 56.9 (CH_3), 59.1 (CH_3), 70.9 (CH_3), 87.4 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 16.5, C), 112.6 (C), 112.8 (CH), 124.8 (dd, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.6, 1.8 Hz, C), 132.0 (CH), 134.0 (CH), 153.57 (t, $J_{C\text{-}F}$ = 286.8 Hz, CF_2), 156.8 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -95.87 (d, *J* = 41.2 Hz, 1F), -91.94 (d, *J* = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2940 (m), 1742 (s), 1489 (s), 1281 (s), 1247 (s), 1234 (s), 1115 (s), 1027 (s), 806 (s). **HRMS** (EI+) calcd for $C_{15}H_{20}BrF_2NO_2$ $[M]^+$: 363.0663, found: 363.0645.

General Procedure for Defluorinative Alkylation using Potassium Organotrifluoroborates



4-Bromo-2-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-1-methoxybenzene (3g)

To an 8 mL reaction vial equipped with a stir bar was added 4CzIPN (19.7 mg, 0.025 mmol, 0.05 equiv) and potassium *tert*-butyltrifluoroborate **2g** (114.8 mg, 0.7 mmol, 1.4 equiv). The vial was sealed with a cap containing a TFE-lined silicone septum and placed under an Ar atmosphere through evacuating and purging with Ar three times *via* an inlet needle. The vial was then charged with the CF_3 alkene **1a** (140.5 mg, 0.5 mmol, 1 equiv) and anhyd DMSO (5 mL) *via* a syringe. The cap was sealed with Parafilm®, and the now bright yellow solution was irradiated with blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 ^{o}C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by GC/MS. Once judged to be complete, the now dark yellow-brown solution was transferred to a separatory funnel and diluted with deionized H_2O and Et_2O (~ 20 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 × ~20 mL). The combined organic layers were washed with deionized H_2O (2 × ~50 mL) followed by brine (~100 mL). The combined organic layers were dried ($MgSO_4$), filtered, and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient hexanes/EtOAc) to give the desired difluoroalkene, **3g**, (119.5 mg, 75%) as a clear colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.83 (s, 9H), 2.29 (s, 2H), 3.84 (s, 3H), 6.78 (d, J = 8.7 Hz, 1H), 7.31 (d, J = 2.3 Hz, 1H), 7.36 (dd, J = 8.7, 2.5 Hz, 1H).

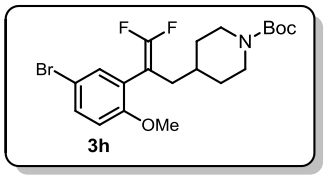
^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.8 (s, CH_3), 32.9 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.3 Hz, CH_2), 41.9 (C), 56.0 (CH_3), 86.7 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 15.6 Hz, C), 112.7 (C), 113.0 (CH), 127.2 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 131.6 (CH), 133.5 (CH), 154.8 (t, $J_{C\text{-}F}$ = 288.7 Hz, CF_2), 156.4 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -93.68 (d, J = 36.6 Hz, 1F), -90.62 (d, J = 35.1 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2954 (w), 1732 (s), 1489 (s), 1393 (m), 1253 (s), 1224 (vs), 1106 (m), 1029 (m), 973 (m), 807 (s), 624 (m).

HRMS (EI+) calcd for $C_{14}H_{17}BrF_2O$ $[M]^+$: 318.0431, found: 318.0439.

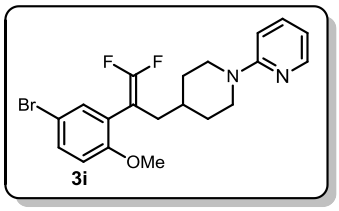
***tert*-Butyl 4-(2-(5-Bromo-2-methoxyphenyl)-3,3-difluoroallyl)piperidine-1-carboxylate, 3h**



3h

(191.1 mg, 86%) was prepared according to the general procedure from organotrifluoroborate **2h** (204 mg, 0.7 mmol) ***with the following modifications***: 1) the reaction was run for 36 h. The desired difluoroalkene **3h** was isolated as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.10 (qd, *J* = 12.2, 3.7 Hz, 2H), 1.26 - 1.36 (m, 1H), 1.45 (s, 9H), 1.65 (d, *J* = 12.2 Hz, 2H), 2.25 (dt, *J* = 6.8, 1.7 Hz, 2H), 2.61 (t, *J* = 12.5 Hz, 2H), 3.81 (s, 3H), 4.05 (d, *J* = 11.2 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.39 (dd, *J* = 8.8, 2.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 28.34 (CH_3), 31.6 (CH), 34.2 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 34.7 (CH_2), 43.7 (CH_3), 55.6 (CH_3), 79.1 (C), 86.3 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 16.5 Hz, C), 112.4 (C), 112.7 (CH), 124.8 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, C), 131.7 (CH), 133.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, CH), 153.5 (t, $J_{C\text{-}F}$ = 286.8 Hz, CF_2), 154.7 (C), 156.4 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, C). **^{19}F NMR** ($CDCl_3$, 471 MHz) -95.34 (d, *J* = 39.7 Hz, 1F), -91.08 (d, *J* = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2934 (w), 2845 (w), 1741 (m), 1686 (vs), 1489 (m), 1421 (s), 1229 (vs), 1166 (vs), 1028 (m), 974 (m), 808 (m), 732 (m). **HRMS** (ES+) calcd for $C_{15}H_{19}BrF_2NO$ $[M - C_5H_7O_2]^+$: 346.0618, found: 346.0620.

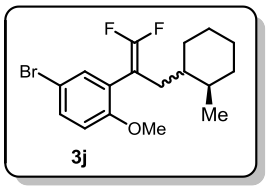
2-(4-(2-(5-Bromo-2-methoxyphenyl)-3,3-difluoroallyl)piperidin-1-yl)pyridine, 3i (169.3 mg, 80%) was prepared according to the general procedure from organotrifluoroborate **2i** (188 mg, 0.7 mmol). The desired difluoroalkene **3i** was isolated as a clear, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.26 (qd, *J* = 11.5, 3.5 Hz, 2 H), 1.36 - 1.52 (m, 1H), 1.77 (d, *J* = 12.7 Hz, 2H), 2.29 (d, *J* = 6.8 Hz, 2H), 2.76 (t, *J* = 11.7 Hz, 2H), 3.82 (s, 3H), 4.26 (d, *J* = 13.0 Hz, 2H), 6.57 (t, *J* = 6.2 Hz, 1H), 6.65 (d, *J* = 8.7 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 7.28 (s, 1H), 7.36 - 7.49 (m, 2H), 8.18 (d, *J* = 4.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 31.7 (CH_2), 34.8 (t, *J* = 2.7 Hz, CH_2), 35.1 (CH_2), 45.8 (CH_2), 56.0 (CH_3), 86.7 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 16.5 Hz, C), 107.4 (CH), 112.8 (C, CH), 113.0 (CH), 125.3 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 6.4 Hz, C),



3i

132.0 (CH), 133.6 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 137.6 (CH), 148.2 (CH), 153.8 (t, $J_{C\text{-}F}$ = 288.7 Hz, CF_2), 156.8 (C), 159.8 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) -95.38 (d, *J* = 39.7 Hz, 1F), -91.17 (d, *J* = 39.7 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2930 (w), 2843 (w), 1739 (m), 1592 (s), 1483 (vs), 1436 (s), 1249 (s), 1226 (vs), 1027 (m), 973 (m), 770 (m), 621 (m). **HRMS** (ES+) calcd for $C_{20}H_{22}BrF_2N_2O$ $[M + H]^+$: 423.0884, found: 423.0911.

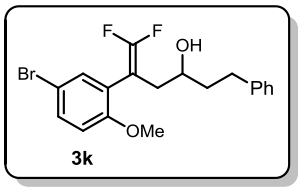
4-Bromo-2-(1,1-difluoro-3-(-2-methylcyclohexyl)prop-1-en-2-yl)-1-methoxybenzene, 3j



3j

(100.6 mg, 56%) was prepared according to the general procedure from organotrifluoroborate **2j** (143 mg, 0.7 mmol). The desired difluoroalkene **3j** was isolated as a clear, colorless oil.[50] **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.70 - 0.94 (m, 6H), 1.03 - 1.14 (m, 2H), 1.14 - 1.24 (m, 1H), 1.27 - 1.41 (m, 1H), 1.57 - 1.67 (m, 2H), 1.80 (d, *J* = 12.2 Hz, 1H), 1.94 - 2.05 (m, 1H), 2.67 (dq, *J* = 14.1, 3.5 Hz, 1H), 3.81 (s, 3H), 6.78 (d, *J* = 8.8 Hz, 1H), 7.25 (d, *J* = 2.2 Hz, 1H), 7.38 (dd, *J* = 8.7, 2.1 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 20.1 (CH_3), 26.2 (CH_2), 26.3 (CH_2), 31.4 (CH_2), 31.9 (CH_2), 35.5 (CH_2), 36.9 (CH), 42.2 (CH), 55.6 (CH_3), 87.4 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 14.7 Hz, C), 112.4 (C), 112.6 (CH), 125.2 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 4.6 Hz, C), 131.4 (CH), 133.3 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, C), 153.4 (t, $J_{C\text{-}F}$ = 287.8 Hz, CF_2), 156.4 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, C). **^{19}F NMR** ($CDCl_3$, 471 MHz) -96.13 (d, *J* = 41.2 Hz, 1F), -91.75 (d, *J* = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2922 (m), 2852 (w), 1738 (m), 1488 (s), 1247 (s), 1229 (vs), 1030 (m), 806 (s). **HRMS** (ES+) calcd for $C_{17}H_{22}BrF_2O$ $[M + H]^+$: 359.0822, found: 359.0821.

5-(5-Bromo-2-methoxyphenyl)-6,6-difluoro-1-phenylhex-5-en-3-ol, 3k (172.8 mg, 87%) was



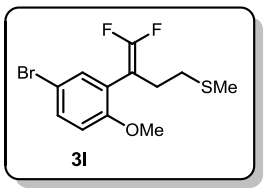
3k

prepared according to the general procedure from organotrifluoroborate **2k** (169 mg, 0.7 mmol). The desired difluoroalkene **3k** was isolated as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.69 - 1.84 (m, 2H), 2.11 - 2.28 (m, 1H), 2.38 (dq, *J* = 14.4, 3.2 Hz, 1H), 2.51 (ddd, *J* = 14.1, 9.5, 2.1 Hz, 1H), 2.62 (ddd, *J* = 13.7, 9.4, 6.2 Hz, 1H), 2.79 (ddd, *J* = 13.7, 9.4, 6.2 Hz, 1H), 3.48 (tt, *J* = 8.2, 4.2 Hz, 1H), 3.84 (s, 3H), 6.81 (d, *J* = 8.8 Hz, 1H), 7.13 - 7.20 (m, 3H), 7.24 - 7.29 (m, 3H), 7.42 (dd, *J* = 8.8, 2.4 Hz, 1H). **^{13}C NMR**

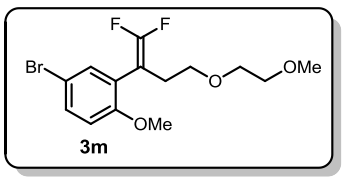
[50]Spectral data reflects the major *trans* diastereomer.

($CDCl_3$, 125 MHz) δ 32.3 (CH_2), 37.16 (CH_2), 38.5 (CH_2), 56.2 (CH_3), 68.8 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, CH), 84.9 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 18.3 Hz, C), 113.0 (CH), 113.4 (C), 124.7 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, 2 C), 126.0 (CH), 128.6 (2 × CH), 132.4 (CH), 133.7 (C), 142.2 (C), 154.3 (t, $J_{C\text{-}F}$ = 288.7 Hz, CF_2), 156.3 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) -94.38 (d, *J* = 36.6 Hz, 1F), -89.13 (d, *J* = 36.6 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 3349 (w, br), 3026 (vw), 2937 (w), 1742 (s), 1488 (s), 1232 (vs), 1111 (m), 1026 (m), 809 (m), 745 (m). **HRMS** (ES+) calcd for $C_{19}H_{20}BrF_2O_2$ $[M + H]^+$: 397.0615, found: 397.0613.

(3-(5-Bromo-2-methoxyphenyl)-4,4-difluorobut-3-en-1-yl)(methyl)sulfane, 3l (85.6 mg, 53%) was prepared according to the general procedure from organotrifluoroborate **2l** (118 mg, 0.7 mmol). The desired difluoroalkene **3l** was isolated as a clear, colorless, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.09 (s, 3H), 2.44 (t, *J* = 7.1 Hz, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 3.81 (s, 3H), 6.79 (d, *J* = 8.8 Hz, 1H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.40 (dd, *J* = 8.8, 2.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 15.1 (CH_3), 27.3 (CH_2), 31.9 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 55.6 (CH_3), 87.6 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 17.4 Hz, C), 112.4 (C), 112.5 (CH), 123.8 (dd, $J_{C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 4.6, 2.2 Hz, C), 131.9 (CH), 133.7 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 153.5 (t, $J_{C\text{-}F}$ = 289.6 Hz, CF_2), 156.5 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, C). **^{19}F NMR** ($CDCl_3$, 471 MHz) -95.04 (d, *J* = 39.7 Hz, 1F), -91.60 (d, *J* = 39.7 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2963(vw), 2917 (w), 2842 (vw), 1740 (m), 1488 (m), 1250 (s), 1228 (vs), 1029 (m), 806 (m). **HRMS** (EI+) calcd for $C_{12}H_{13}BrF_2OS$ $[M]^+$: 321.9839, found: 321.9821.

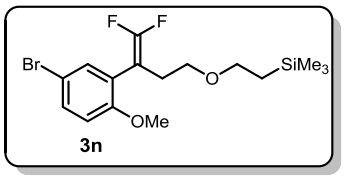


4-Bromo-2-(1,1-difluoro-4-(2-methoxyethoxy)but-1-en-2-yl)-1-methoxybenzene, 3m (98.3 mg, 56%) was prepared according to the general procedure from organotrifluoroborate **2m** (137 mg, 0.7 mmol). The desired difluoroalkene **3m** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.61 (tt, *J* = 7.1, 2.2 Hz, 2H), 3.38 (s, 3H), 3.41 (t, *J* = 7.1 Hz, 2H), 3.47 - 3.53 (m, 4H), 3.80 (s, 3H), 6.77 (d, *J* = 8.8 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.39 (dd, *J* =8.8, 2.7 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 28.2 (CH_2), 55.9 (CH_3), 59.3 (CH_3), 69.0 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 70.3 (CH_2), 72.2 (CH_2), 86.2 (dd, $J_{C\text{-}C\text{-}F}$ =24.7, 17.4 Hz, C), 112.7 (C), 112.8 (CH), 124.6 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, C), 132.1 (CH), 134.1 (t,



$J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, CH), 153.9 (t, $J_{C\text{-}F}$ = 288.7 Hz, CF_2), 156.8 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -95.34 (d, *J* = 41.2 Hz, 1F), -91.36 (d, *J* = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2874 (w), 1743 (s), 1489 (s), 1233 (vs), 1113 (vs), 1026 (s), 807 (s). **HRMS** (ES+) calcd for $C_{14}H_{18}BrF_2O_3$ $[M + H]^+$: 351.0407, found: 351.0411.

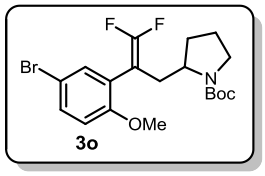
(2-((3-(5-Bromo-2-methoxyphenyl)-4,4-difluorobut-3-en-1-yl)oxy)ethyl)trimethylsilane, 3n



3n

(82.6 mg, 42%) was prepared according to the general procedure from organotrifluoroborate **2n** (167 mg, 0.7 mmol). The desired difluoroalkene **3n** was isolated as a clear, colorless, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ -0.01 - 0.02 (m, 9H), 0.82 - 0.96 (m, 2H), 2.58 (tt, *J* = 7.1, 2.2 Hz, 2H), 3.32 (t, *J* = 7.1 Hz, 2H), 3.38 - 3.46 (m, 2H), 3.80 (s, 3 H), 6.78 (d, *J* = 8.8 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.39 (dd, *J* = 8.8, 2.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ -1.1 (CH_3), 18.5 (CH_2), 28.4 (CH_2), 56.0 (CH_3), 67.8 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.5 Hz, CH_2), 68.2 (CH_2), 86.5 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 18.3 Hz, C), 112.7 (C), 112.8 (CH), 124.7 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, C), 132.1 (CH), 134.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, CH), 153.9 (t, $J_{C\text{-}F}$ = 288.7 Hz, CF_2), 156.8 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, CF_2). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -95.57 (d, *J* = 41.2 Hz, 1F), -91.53 (d, *J* = 39.7 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2954 (w), 2833 (w), 1743(s), 1488 (s), 1247 (vs), 1102 (s), 834 (vs). **HRMS** (EI+) calcd for $C_{11}H_{11}BrF_2O_2$ $[M - C_5H_{12}Si]^+$: 291.9910, found: 291.9924.

(*tert*-Butyl 2-(2-(5-Bromo-2-methoxyphenyl)-3,3-difluoroallyl)pyrrolidine-1-carboxylate, 3o



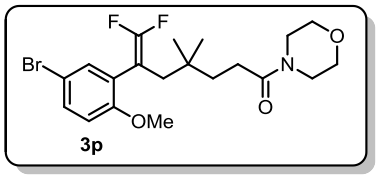
3o

(183.7 mg, 85%) was prepared according to the general procedure from organotrifluoroborate **2o** (194 mg, 0.7 mmol). The desired difluoroalkene **3o** was isolated as cloudy, colorless oil.[51] **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.38 (br s, 9H), 1.65 - 1.91 (m, 4H), 2.24 - 2.47 (m, 1H), 2.64 - 2.91 (m, 1H), 3.17 - 3.42 (m, 2H), 3.52 - 3.66 (m, 1H), 3.81 (s, 3H), 6.78 (d, *J* = 8.6 Hz, 1H), 7.16 - 7.47 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ **22.6 (br, CH_2), 23.4 (b, CH_2),** 28.3 (CH_3), **29.0 (s, 1 C), 29.7 (br, CH_2)**, **31.2 (br, CH_2), 32.4 (br, CH_2)**, **46.1 (br, CH), 46.5 (Br, CH),** 55.6 (CH_3), **78.8 (br, C), 79.1 (br, C),** 85.6 (br, C), 112.4 (C), 112.6 (CH), 124.4 (br, C), 131.7 (CH), 133.1

[51] NMR spectra of this compound indicates significant rotameric character; rotameric carbons are given in bold

(br, CH), 153.8 (t, $J_{C\text{-}F}$ = 288.7 Hz, CF_2), 154.2 (C), 156.2 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) -95.31 - -94.89 (m, 1F), -91.22 - -90.12 (m, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2973 (w), 2874 (w), 1739 (m), 1687 (vs), 1489(m), 1392 (vs), 1248 (m), 1161 (m) 1110 (m), 1027 (w), 731 (m). **HRMS** (ES+) calcd for $C_{19}H_{25}BrF_2NO_3$ $[M + H]^+$: 432.0986, found: 432.0962.

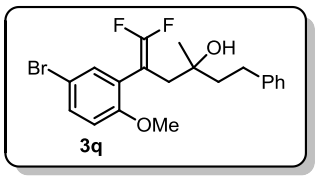
6-(5-Bromo-2-methoxyphenyl)-7,7-difluoro-4,4-dimethyl-1-morpholinohept-6-en-1-one, 3p



3p

(165 mg, 74%) was prepared according to the general procedure from organotrifluoroborate **2p** (204 mg, 0.7 mmol). The desired difluoroalkene **3p** was isolated as a pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.82 (s, 6H), 1.39 - 1.53 (m, 2H), 2.07 - 2.14 (m, 2H), 2.29 (s, 2H), 3.29 - 3.35 (m, 2H), 3.52 - 3.59 (m, 2H), 3.64 (t, *J* = 4.6 Hz, 4H), 3.83 (s, 3H), 6.76 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.35 (dd, *J* = 8.8, 2.2 Hz, 1H). **^{13}C NMR** 27.2 (CH_2), 28.3 (CH_2), 35.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_3), 36.9 (CH_3), 39.8 (CH_2), 42.2 (CH_2), 46.2 (C), 56.1 (CH_3), 68.9 (CH_2), 67.2 (CH_2), 86.0 (dd, $J_{C\text{-}C\text{-}F}$ = 23.8, 15.6 Hz, C), 112.7 (C), 113.2 (CH), 126.7 (dd, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.6, 1.8 Hz, C), 131.7 (CH), 133.3 (CH), 154.2 (t, $J_{C\text{-}F}$ = 288.7 Hz, CF_2), 156.3 (C), 172.1 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -92.93 (d, *J* = 36.6 Hz, 1F), -89.70 (d, *J* = 35.1 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2959 (w), 2857 (w), 1732 (s), 1643 (vs), 1489 (s), 1253 (s), 1253 (vs), 1113 (vs), 1027 (s), 810 (m), 623 (m). **HRMS** (EI+) calcd for $C_{20}H_{26}BrF_2NO_3$ $[M]^+$: 445.1064, found: 445.1055.

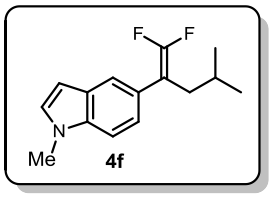
5-(5-Bromo-2-methoxyphenyl)-6,6-difluoro-3-methyl-1-phenylhex-5-en-3-ol, 3q (61.0 mg, 59%) was prepared according to the general procedure from organotrifluoroborate **2q** (89.6 mg, 0.35 mmol) and adjusting the quantities of the other reagents accordingly. The desired difluoroalkene **3q** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.20 (s, 3H), 1.55 (s, 1H), 1.65 - 1.75 (m, 3H), 2.55 - 2.63 (m, 3H), 3.83 (s, 3H), 6.79 (d, *J* = 8.9 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.23 - 7.27 (m, 2H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.39 (dd, *J* = 8.9, 2.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.0 (CH_2), 30.6 (CH_2), 40.6 (CH_2), 44.0 (CH_3), 56.2 (CH_3), 73.5 (C), 84.8 (dd, $J_{C\text{-}C\text{-}F}$ = 23.8, 17.4 Hz, C), 113.2 (CH), 113.3 (C), 126.0 (CH), 126.3 (C), 128.5 (CH), 128.6 (CH), 132.2 (CH), 133.6 (C), 142.6 (CH), 154.5 (t, $J_{C\text{-}F}$ = 291.0 Hz, CF_2), 156.0 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz)



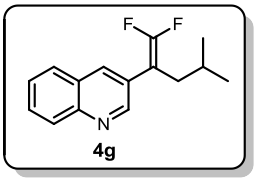
3q

δ -92.42 (d, *J* = 32.0 Hz, 1F), -88.78 (d, *J* = 32.0 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 3450 (b), 2950 (w), 1734 (s), 1489 (s), 1251 (s), 1223 (s), 809 (s), 732 (s), 699 (s). **HRMS** (ES+) calcd for $C_{20}H_{21}BrF_2NaO_2$ $[M + Na]^+$: 433.0600, found: 433.0591.

5-(1,1-Difluoro-4-methylpent-1-en-2-yl)-1-methyl-1H-indole, 4f (84.7 mg, 68%) was prepared according to the general procedure from organotrifluoroborate **2r** (105 mg, 0.7 mmol) and perfluoroalkyl-substituted alkene **1g** (112.6 mg, 0.5 mmol). The desired difluoroalkene **4f** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) 0.89 (d, *J* = 6.6 Hz, 6H), 1.60 (tspt, *J* = 13.7, 6.8 Hz, 1H), 2.31 (dt, *J* = 7.3, 2.4 Hz, 2H), 3.79 (s, 3H), 6.47 (dd, *J* = 3.1, 0.7 Hz, 1H), 7.05 (d, *J* = 2.9 Hz, 1H), 7.16 (dt, *J* = 8.6, 1.5 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.55 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 22.4 (CH_3), 26.6 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 33.1 (CH_3), 37.8 (CH_2), 92.5 (dd, $J_{C\text{-}C\text{-}F}$ = 21.1, 14.7 Hz, C), 101.3 (CH), 109.3 (CH), 121.1 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 122.4 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ =2.7 Hz, CH), 125.2 (dd, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.2, 2.2 Hz, C), 128.7 (C), 129.6 (CH), 136.2 (C), 154.2 (dd, $J_{C\text{-}F}$ = 286.8, 285.0 Hz, CF_2). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -97.03 (d, *J* = 50.4 Hz, 1F), -96.80 (d, *J* = 47.3 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2956 (w), 1727 (s), 1492 (m), 1227 (vs), 1132 (s), 980 (m), 754 (m), 719 (vs). **HRMS** (EI+) calcd for $C_{15}H_{17}F_2N$ $[M]^+$: 249.1329, found: 249.1321.

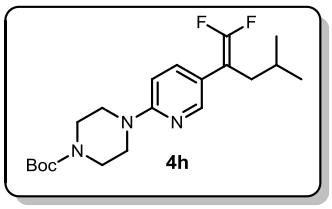


5-(1,1-Difluoro-4-methylpent-1-en-2-yl)-1-methyl-1*H*-indole, 4g (101.4 mg, 82%) was prepared according to the general procedure from organotrifluoroborate **2r** (105 mg, 0.7 mmol) and perfluoroalkyl-substituted alkene **1h** (111.6 mg, 0.5 mmol). The desired difluoroalkene **4g** was isolated as a clear, bright yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) 0.92 (d, *J* = 6.6 Hz, 6H), 1.62 (tspt, *J* = 13.8, 6.7 Hz, 1H), 2.40 (dt, *J* = 7.3, 2.3 Hz, 2H), 7.56 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.72 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 2.2 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 8.89 (t, *J* = 2.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 22.3 (CH_3), 26.8 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 36.6 (CH_2), 89.6 (dd, $J_{C\text{-}C\text{-}F}$ = 23.8, 12.8 Hz, C), 127.2 (CH), 127.9 (CH), 128.0 (C), 127.5 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.1 Hz, C), 129.5 (CH), 129.8 (CH), 135.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 147.3 (C), 150.6 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 154.9 (dd, $J_{C\text{-}F}$ = 290.5, 287.8 Hz, CF_2). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -93.40 (d, *J* = 41.2 Hz, 1F), -92.16 (d, *J* = 39.7 Hz, 1F). **FT-IR** (cm^{-}



[1], neat, ATR) 2958 (w), 1722 (s), 1490 (w), 1246 (s), 1134 (s), 1005 (w), 909 (m), 786 (m), 750 (s). **HRMS** (ES+) calcd for $C_{15}H_{16}F_2N$ $[M + H]^+$: 248.1251, found: 248.1260.

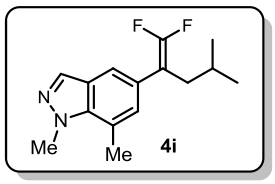
***tert*-Butyl 4-(5-(1,1-Difluoro-4-methylpent-1-en-2-yl)pyridin-2-yl)piperazine-1-carboxylate,**



4h

4h (156.4 mg, 82%) was prepared according to the general procedure from organotrifluoroborate **2r** (105 mg, 0.7 mmol) and perfluoroalkyl-substituted alkene **1i** (178.7 mg, 0.5 mmol). The desired difluoroalkene **4h** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.87 (d, *J* = 6.6 Hz, 6H), 1.49 (s, 9H), 1.58 (tspt, *J* = 13.7, 6.6 Hz, 1H), 2.21 (d, *J* = 6.9 Hz, 2H), 3.49 - 3.59 (m, 8H), 6.64 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H), 8.14 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 20.0 (CH), 22.2 (CH_3), 26.6 (CH_2), 28.6 (CH_3), 36.4 (CH_2), 45.2 (CH_2), 80.1 (C), 88.9 (dd, $J_{C\text{-}C\text{-}F}$ = 23.8, 12.8 Hz, C), 106.9 (CH), 119.4 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.1 Hz, C), 137.6 (CH), 147.4 (CH), 154.2 (t, $J_{C\text{-}F}$ = 288.1 Hz, CF_2), 155.0 (s, 4 C), 158.1 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -95.30 (d, *J* = 48.5 Hz, 1F), -94.58 (d, *J* = 48.5 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2950 (w), 1688 (s), 1237 (s), 1166 (s), 1126 (s), 908 (s), 729 (s). **HRMS** (EI+) calcd for $C_{20}H_{29}F_2N_3O_2$ $[M]^+$: 381.2228, found: 381.2220.

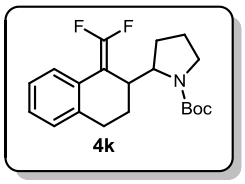
5-(1,1-Difluoro-4-methylpent-1-en-2-yl)-1,7-dimethyl-1H-indazole, 4i (111.4 mg, 89%) was



4i

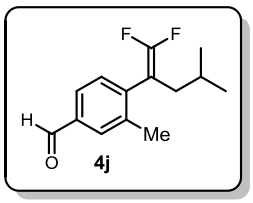
prepared according to the general procedure from organotrifluoroborate **2r** (105 mg, 0.7 mmol) and perfluoroalkyl-substituted alkene **1j** (120.1 mg, 0.5 mmol). The desired difluoroalkene **4i** was isolated as a clear, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) 0.89 (d, *J* = 6.6 Hz, 6H), 1.58 (tspt, *J* = 13.6, 6.8 Hz, 1H), 2.29 (dt, *J* = 7.3, 2.3 Hz, 2H), 2.76 (s, 3H), 4.31 (s, 3H), 7.02 (s, 1H), 7.45 (s, 1H), 7.89 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 19.5 (CH_3), 22.3 (CH_3), 26.6 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 37.4 (CH_2), 39.3 (CH_3), 91.8 (dd, $J_{C\text{-}C\text{-}F}$ = 22.0, 13.7 Hz, C), 118.9 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 120.6 (CH), 125.4 (C), 126.9 (dd, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.6, 2.8 Hz, C), 128.8 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 133.0 (CH), 138.9 (C), 154.3 (dd, $J_{C\text{-}F}$ = 287.8, 285.9 Hz, CF_2). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -96.01 (d, *J* = 47.3 Hz, 1F), -95.72 (d, *J* = 47.3 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2956 (m), 1725 (s), 1456 (m), 1371 (m), 1241 (vs), 1132 (s), 985 (m), 873 (m), 793 (s). **HRMS** (EI+) calcd for $C_{15}H_{19}F_2N_2$ $[M + H]^+$: 265.1516, found: 265.1539.

***tert*-Butyl 2-(1-(Difluoromethylene)-1,2,3,4-tetrahydronaphthalen-2-yl)pyrrolidine-1-carboxylate, 4k** (121.0 mg, 69%) was prepared according to the general procedure from organotrifluoroborate **2o** (194 mg, 0.7 mmol) and perfluoroalkyl-substituted alkene **1l** (99.1 mg, 0.5 mmol). The desired difluoroalkene **4k** was isolated as a clear, pale-yellow oil. *Diastereomeric ratio*: 1:1.4.[52,53] **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.42 - 1.52 (m, 9H), 1.61 - 1.71 (m, 1H), 1.78 (dd, *J* = 14.0, 6.9 Hz, 2H), 1.81 - 1.91 (m, 2H), 2.47 - 2.60 (m, 1H), 2.70 - 2.86 (m, 1H), 2.93 - 3.08 (m, 1H), 3.19 (d, *J* = 10.8 Hz, 1H), 3.32 - 3.40 (m, 1H), 3.52 - 3.62 (m, 1H), 3.81 - 3.99 (m, 1H), 7.07 - 7.23 (m, 4H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ **23.5 (br, CH_2),** 23.9 - 24.5 (br, CH_2), 25.1 - 25.7 (br, CH_2), **27.3 (CH_2),** 27.5 - 27.7 (CH_2), **27.8 (CH_2),** 28.4 - 28.6 (CH_3), **28.8 (CH_3),** 35.7 (CH_2), **36.3 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 20.9 Hz, CH_2),** 46.8 - 46.9 (br, CH), **47.1 (d, $J_{C\text{-}C\text{-}F}$ = 29.1 Hz, CH),** 58.8 (CH_2), **59.3 (CH_2),** 79.2 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 24.5 Hz, CH), **79.8 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 37.2 Hz, CH),** 89.8 (br, C), **90.5 (br, C),** 110.9 (C), **119.6 (C),** 120.6 (C), **126.2 (C),** 126.6 (CH), **127.0 (CH),** 127.3 (CH), **127.5 (CH),** 127.7 (CH), **127.8 (CH),** 128.2 (CH), **128.6 (CH),** 130.3 (q, $J_{C\text{-}C\text{-}F}$ = 48.1 Hz, C), **138.9 (q, $J_{C\text{-}F}$ = 35.0 Hz, C),** 152.9 (q, $J_{C\text{-}F}$ = 287.0 Hz, CF_3), **155.3 (q, $J_{C\text{-}F}$ = 287.0 Hz, CF_3),** 155.2 (C), **155.4 (C).** **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -93.98 (d, *J* = 41.2 Hz, 1F), **-93.14 (d, *J* = 41.2 Hz, 1F),** -92.70 (d, *J* = 41.2 Hz, 1F), -92.32 (d, *J* = 41.2 Hz, 1F), **-91.96 (d, *J* = 41.2 Hz, 1F),** -91.69 (d, *J* = 41.2 Hz, 1F), **-91.34 (d, *J* = 39.7 Hz, 1F), -89.89 (d, *J* = 39.7 Hz, 1F).** **FT-IR** (cm^{-1}, neat, ATR). 2974 (m), 1689 (s), 1391 (s), 1366 (s), 1232 (s), 1164 (s), 1112 (s), 763 (s), 729 (s). **HRMS** (EI) calcd for $C_{20}H_{25}F_2NNaO_2$ $[M + Na]^+$: 372.1756, found: 372.1751.



4k

4-(1,1-Difluoro-4-methylpent-1-en-2-yl)-3-methylbenzaldehyde, 4j (94.1 mg, 79%) was prepared according to the general procedure from organotrifluoroborate **2r** (105 mg, 0.7 mmol) and perfluoroalkyl-substituted alkene **1k** (107.1 mg, 0.5 mmol). The desired difluoroalkene **4j** was isolated as a clear yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.91 (d, *J* = 6.6 Hz, 6H), 1.52 (tspt, *J* = 13.9, 6.8 Hz, 1H), 2.21 (dt, *J* = 7.1, 2.0 Hz, 2H), 2.38 (s, 3H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.73 (s, 1H), 9.98 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 19.4 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, CH_3), 22.2 (CH_3), 26.4 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, CH), 37.7 (CH_2), 90.0 (dd, *J* = 22.9, 16.5

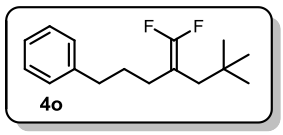


4j

[52] Major diastereomer values given in bold.
[53] For clarity, only an image of the major diastereomer is provided for the ^{1}H NMR.

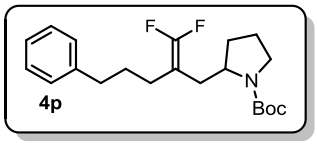
Hz, C), 126.9 (CH), 130.3 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, CH), 131.5 (CH), 135.6 (C), 137.8 (C), 140.2 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.6 Hz, C), 152.8 (t, $J_{C\text{-}F}$ = 289.6 Hz, CF_2), 191.8 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -95.81 (d, *J* = 41.2 Hz, 1F), -90.93 (d, *J* = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2960 (w), 1738 (s), 1701 (vs), 1606 (w), 1247 (s), 1220 (s), 1134 (s), 972 (w), 831 (m). **HRMS** (ES+) calcd for $C_{14}H_{17}F_2O$ $[M + H]^+$: 239.1247, found: 239.1258.

(4-(Difluoromethylene)-6,6-dimethylheptyl)benzene, 4o (102.2 mg, 81%) was prepared



according to the general procedure from organotrifluoroborate **2g** (98.4 mg, 0.6 mmol) and perfluoroalkyl-substituted alkene **1p** (107.1 mg, 0.5 mmol) ***with the following modification***: $LiBF_4$ (56.3 mg, 0.6 mmol, 1.2 equiv) was added as a fluoride scavenger to enhance the rate of fluoride elimination which was necessary to suppress the formation of the CF_3 alkane by-product. The desired difluoroalkene **4o** was isolated as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.92 (s, 9H), 1.71 - 1.80 (m, 2H), 1.87 (t, *J* = 2.2 Hz, 2H), 2.08 (tt, *J* = 8.1, 2.4 Hz, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 7.17 - 7.23 (m, 3H), 7.28 - 7.33 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 28.3 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 29.7 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 30.1 (CH_3), 33.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 35.7 (CH_2), 39.6 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}F}$ =1.8 Hz, CH_2), 87.7 (t, $J_{C\text{-}C\text{-}F}$ = 16.5 Hz, C), 126.1 (CH), 128.6 (CH), 128.6 (CH), 142.4 (C), 154.9 (t, $J_{C\text{-}F}$ = 284.1 Hz, CF_2). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -97.57 (d, *J* = 53.4 Hz, 1F), -95.07 (d, *J* = 53.4 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2953 (m), 2867 (w), 1738 (vs), 1478 (w), 1365 (w), 1259 (m), 1208 (vs), 1089 (m), 747 (m), 697 (s). **HRMS** (EI+) calcd for $C_{16}H_{22}F_2$ $[M]^+$: 252.1690, found: 252.1712.

***tert*-Butyl 2-(2-(Difluoromethylene)-5-phenylpentyl)pyrrolidine-1-carboxylate, 4p** (82.1 mg,

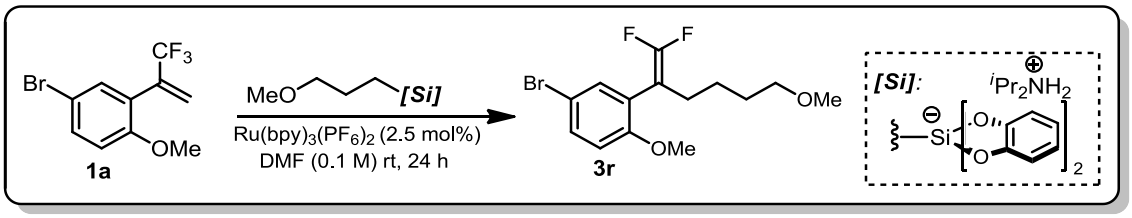


90%) was prepared according to the general procedure from organotrifluoroborate **2o (**97.0 mg, 0.35 mmol) and perfluoroalkyl-substituted alkene **1p** (53.6 mg, 0.25 mmol) ***with the following modification***: 1) A higher loading of 4CzIPN was used (19.7 mg, 0.025 mmol, 0.1 equiv) 2) Two 34W blue LEDs were used for irradiation. The desired difluoroalkene **4p** was isolated as a clear, pale-yellow oil.[54] **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.47 (s, 9H), 1.60 - 1.92 (m, 6H), 1.95 - 2.12

[54] NMR spectra of this compound indicates significant rotameric character; rotameric carbons and fluorines are given in bold

(m, 3H), 2.19 - 2.47 (m, 1H), 2.61 (t, *J* = 7.3 Hz, 2H), 3.24 - 3.46 (m, 2H), 3.76 - 4.06 (m, 1H), 7.13 - 7.22 (m, 3H), 7.24 - 7.32 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ **22.5 (br, CH_2), 23.4 (br, CH_2), 26.0 (br, CH_2)**, 28.5 (CH_3), **29.1 (br, CH_2), 29.3 (br, CH_2), 29.7 (br, CH_2), 29.9 (br, CH_2),** 30.4 (CH_2), 35.3 (CH_2), **46.0 (br, CH_2), 46.4 (br, CH_2)**, 55.4 (br, CH_3), 78.5 - 79.0 (C), 79.3 (br, CH), 86.1 - 87.1 (C), **125.6 (br, CH), 125.8 (br, CH),** 128.2 (br, 2 × CH), **141.7 (br, C), 141.8 - 142.1 (br, C),** 154.3 (t, $J_{C\text{-}F}$ = 284.1 Hz, CF_2), 154.3 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ **-98.27 (d, *J* = 56.5 Hz, 1F), -97.65 (d, *J* = 58.0 Hz, 1F), -97.43 (d, *J* = 54.9 Hz, 1F), -97.22 (d, *J* = 53.4 Hz, 1F)**. **FT-IR** (cm^{-1}, neat, ATR) 2973 (w), 1745 (m), 1689 (vs), 1391 (vs), 1365 (s), 1167 (s), 1103 (s), 746 (m), 699 (m). **HRMS** (ES+) calcd for $C_{21}H_{29}NNaF_2O_2$ [M + Na]$^+$: 388.2094, found: 388.2064.

General Procedure for Defluorinative Alkylation using Ammonium Alkylbis(catecholato)silicates



4-Bromo-2-(1,1-difluoro-6-methoxyhex-1-en-2-yl)-1-methoxybenzene (3a)

To an 8 mL reaction vial equipped with a stir bar was added $Ru(bpy)_3(PF_6)_2$ (0.011 g, 0.0125 mmol, 0.025 equiv) and 3-methoxypropylsilicate **2r** (0.294 g, 0.7 mmol, 1.4 equiv). The vial was sealed with a cap containing a TFE-lined silicone septum and placed under an Ar atmosphere through evacuating and purging with Ar three times *via* an inlet needle. The vial was then charged with the CF_3 alkene **1a** (0.141 g, 0.5 mmol) in anhyd DMF (5 mL) *via* a syringe. The cap was sealed with Parafilm®, and the now bright red solution was irradiated with blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by GC/MS. Once judged to be complete, the now dark red-brown solution was transferred to a separatory funnel and diluted with Et_2O (50 mL) and 2 M aq

NaOH (50 mL).[55] The layers were separated, and the aq layer was extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with 2 M aq NaOH (50 mL), deionized H_2O (2 × 50 mL), followed by brine (100 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient 100:0 to 9:1 hexanes/EtOAc)[56] to give the desired difluoroalkene, **3r**, (0.130 g, 78%) as a pale-yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.30 - 1.39 (m, 2H), 1.53 - 1.61 (m, 2H), 2.33 (tt, *J* = 7.6, 2.2 Hz, 2H), 3.31 (s, 3H), 3.34 (t, *J* = 6.5 Hz, 2H), 3.80 (s, 3H), 6.78 (d, *J* = 8.8 Hz, 1H), 7.25 (d, *J* = 2.4 Hz, 1H), 7.38 (dd, *J* = 8.8, 2.4 Hz, 1H).

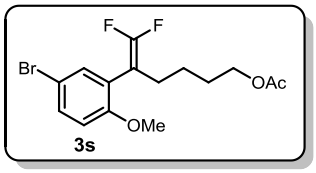
^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.4 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 27.8 (CH_2), 29.2 (CH_2), 56.0 (CH_3), 58.8 (CH_3), 72.7 (CH_2), 88.6 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 15.6 Hz, C), 112.7 (C), 112.9 (CH), 125.0 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, C), 132.0 (CH), 133.8 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, CH), 153.4 (t, $J_{C\text{-}F}$ = 287.8 Hz, CF_2), 156.9 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -96.38 (d, *J* = 42.7 Hz, 1F), -92.36 (d, *J* = 42.7 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2936 (w), 2865 (w), 1741 (s), 1489 (s), 1280 (m), 1116 (vs), 1028 (s), 970 (w), 807 (s), 624(w).

HRMS (ES+) calcd for $C_{14}H_{18}BrF_2O_2$ $[M + H]^+$: 335.0458, found: 335.0481.

5-(5-Bromo-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl Acetate, 3s (0.097 g, 53%) was



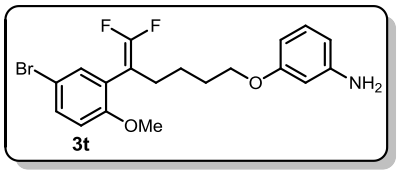
3s

prepared according to the general procedure from propylacetoxy silicate **2s** (0.313 mg, 0.7 mmol, 1.4 equiv). The desired difluoroalkene **3s** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.30 - 1.38 (m, 2H), 1.56 - 1.65 (m, 2H), 2.02 (s, 3H), 2.34 (t, *J* = 7.5 Hz, 2H), 3.80 (s, 3H), 4.02 (t, *J* = 6.6 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 2.1 Hz, 1H), 7.38 (dd, *J* = 8.9, 2.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.2 (CH_2), 24.1 (br s, CH_2), 27.5 (CH_2), 28.1 (CH_3), 56.0 (CH_2), 64.4 (CH_3), 88.3 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 15.6 Hz, C), 112.7 (C), 112.9 (CH), 124.8 (br s, C), 132.1 (CH), 133.7 (br s, CH), 153.4 (t, $J_{C\text{-}F}$ = 287.8 Hz, CF_2), 156.8 (C), 171.3 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -96.16 (d, *J* = 44.3 Hz, 1F),

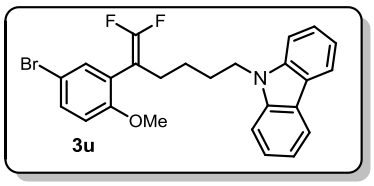
[55] Note that the aq layer will turn dark brown and become warm likely due to the reaction between catechol (or the orthosilicate byproduct) and hydroxide.
[56] For substrates containing basic residues, hexane/EtOAc (containing 1% Et_3N) was used instead.

-91.99 (d, *J* = 44.3 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2950 (w), 1734 (s), 1489 (s), 1226 (s), 1027 (s), 808 (s), 732 (s). **HRMS** (EI+) calcd for $C_{15}H_{17}BrF_2O_3$ $[M]^+$: 362.0329, found: 362.0335.

3-((5-(5-Bromo-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl)oxy)aniline, 3t (0.134 g, 65%) was prepared according to the general procedure from aniline silicate **2t** (0.348 g, 0.7 mmol, 1.4 equiv). The desired difluoroalkene **3t** was isolated as a viscous, clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.37 - 1.48 (m, 2H), 1.70 - 1.79 (m, 2H), 2.37 (tt, *J* = 7.8, 1.8 Hz, 2H), 3.78 (s, 3H), 3.87 (t, *J* = 6.4 Hz, 2H), 3.99 (br s, 2H), 6.21 - 6.26 (m, 1H), 6.30 (dd, *J* = 8.0, 2.4 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 1H), 7.04 (t, *J* = 8.1 Hz, 1H), 7.24 - 7.26 (m, 1H), 7.38 (dd, *J* = 8.8, 2.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.2 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 27.6 (CH_2), 28.8 (CH_2), 56.0 (CH_2), 67.5 (CH_3), 88.5 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 16.5 Hz, C), 101.9 (CH), 104.8 (CH), 108.1 (CH), 112.7 (C), 112.9 (CH), 124.9 (dd, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5, 1.8 Hz, C), 130.3 (CH), 132.0 (CH), 133.7 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 148.0 (C), 153.4 (t, $J_{C\text{-}F}$ = 288.7 Hz, CF_2), 156.8 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, C), 160.4 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -96.18 (d, *J* = 41.2 Hz, 1F), -92.12 (d, *J* = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2940 (w), 1488 (s), 1251 (s), 1166 (s), 1120 (s), 1071 (s), 1027 (s), 808 (s). **HRMS** (EI+) calcd for $C_{19}H_{20}BrF_2NO_2$ $[M]^+$: 411.0645, found: 411.0630.

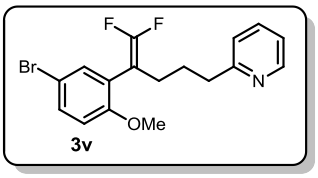


9-(5-(5-Bromo-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl)-9H-carbazole, 3u (0.158 g, 67%) was prepared according to the general procedure from carbozyl silicate **2u** (0.388 g, 0.7 mmol, 1.4 equiv) ***with the following modifications***: 1) the reaction was run for 36 h. The desired difluoroalkene **3u** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.34 - 1.42 (m, 2H), 1.81 - 1.90 (m, 2H), 2.31 - 2.37 (m, 2H), 3.66 (s, 3H), 4.25 (t, *J* = 7.2 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 1H), 7.18 (d, *J* = 2.2 Hz, 1H), 7.19 - 7.24 (m, 2H), 7.32 - 7.39 (m, 3H), 7.42 - 7.47 (m, 2H), 8.09 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 25.4 (CH_2), 27.6 (CH_2), 28.5 (CH_2), 43.0 (CH_2), 55.9 (CH_3), 88.1 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 16.0 Hz, C), 108.8 (CH), 112.7 (C), 112.9 (CH), 119.0 (CH), 120.6 (CH), 123.1 (C), 124.7 (C), 125.9 (CH), 132.1 (CH), 133.7 (br s, C), 140.6 (CH), 153.4 (t, $J_{C\text{-}F}$ = 287.8 Hz, CF_2),



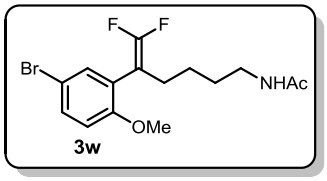
156.8 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -95.96 (d, *J* = 41.2 Hz, 1F), -91.79 (d, *J* = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2940 (w), 1741 (s), 1484 (s), 1462 (s), 1452 (s), 1249 (s), 1225 (s), 748 (s), 722 (s). **HRMS** (EI+) calcd for $C_{25}H_{22}BrF_2NO$ $[M]^+$: 469.0853, found: 469.0865.

2-(4-(5-Bromo-2-methoxyphenyl)-5,5-difluoropent-4-en-1-yl)pyridine, 3v (0.107 g, 58%) was prepared according to the general procedure from pyridyl silicate **2v** (0.317 g, 0.7 mmol, 1.4 equiv). The desired difluoroalkene **3v** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.69 - 1.77 (m, 2H), 2.36 - 2.41 (m, 2H), 2.78 (t, *J* = 7.8 Hz, 2H), 3.78 (s, 3H), 6.76 (d, *J* = 8.9 Hz, 1H), 7.05 - 7.12 (m, 2H), 7.23 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 8.51 (d, *J* = 4.3 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.6 (CH_2), 27.8 (CH_2), 37.9 (CH_2), 55.9 (CH_3), 88.5 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 16.5 Hz, 3 C), 112.7 (CH), 112.9 (CH), 121.2 (CH), 122.9 (CH), 124.9 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, C), 132.0 (CH), 133.8 (C), 136.5 (CH), 149.5 (CH), 153.4 (t, $J_{C\text{-}F}$ = 286.8 Hz, CF_2), 156.8 (C), 161.9 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -95.97 (d, *J* = 42.7 Hz, 1F), -92.08 (d, *J* = 42.7 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2950 (w), 1740 (s), 1489 (s), 1249 (s), 1225 (s), 1027 (s), 806 (s). **HRMS** (EI+) calcd for $C_{17}H_{16}BrF_2NO$ $[M]^+$: 367.0383, found: 367.0384.



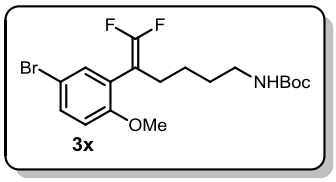
3v

***N*-(5-(5-Bromo-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl)acetamide, 3w** (0.125 g, 69%) was prepared according to the general procedure from propylamido silicate **2w** (0.313 g, 0.7 mmol, 1.4 equiv). The desired difluoroalkene **3w** was isolated as a white solid (mp = 91-92 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.24 - 1.34 (m, 2H), 1.44 - 1.53 (m, 2H), 1.94 (s, 3H), 2.29 - 2.35 (m, 2H), 3.18 (q, *J* = 6.9 Hz, 2H), 3.79 (s, 3H), 5.43 (br s, 1H), 6.78 (d, *J* = 8.9 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.38 (dd, *J* = 8.9, 2.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 23.3 (CH_2), 24.9 (CH_2), 27.4 (CH_2), 29.0 (CH_3), 39.5 (CH_2), 55.9 (CH_3), 88.3 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 16.5 Hz, C), 112.6 (C), 112.9 (CH), 124.7 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, C), 132.0 (CH), 133.6 (br s, CH), 153.3 (t, $J_{C\text{-}F}$ = 286.8 Hz, CF_2), 156.8 (C), 170.3 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -96.15 (d, *J* = 41.2 Hz, 1F), -92.04 (d, *J* = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 3250 (m), 3075 (m), 2940 (m), 2870 (m), 1749 (s), 1489 (s), 1248 (s), 1233 (s), 1219 (s), 803 (s). **HRMS** (EI+) calcd for $C_{15}H_{18}BrF_2NO_2$ $[M]^+$: 361.0489, found: 361.0468.



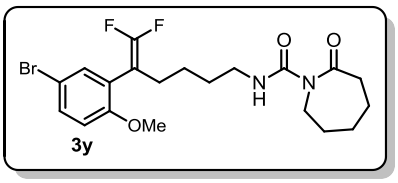
3w

tert*-Butyl (5-(5-Bromo-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl)carbamate, 3x** (0.092 g, 44%) was prepared according to the general procedure from alkylsilicate **2x** (0.353 g, 0.7 mmol, 1.4 equiv) ***with the following modifications: 1) the reaction was run for 48 h. The desired difluoroalkene **3x** was isolated as a clear pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.25 - 1.34 (m, 2H), 1.43 (s, 9H), 2.31 (t, *J* = 7.5 Hz, 2H), 3.07 (d, *J* = 5.4 Hz, 2H), 3.80 (s, 3H), 4.39 - 4.50 (m, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 7.22 (d, *J* = 2.2 Hz, 1H), 7.38 (dd, *J* = 8.7, 2.3 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.9 (CH_2), 27.6 (CH_2), 28.6 (CH_3), 29.7 (CH_2), 40.5 (CH_2), 56.0 (CH_3), 79.3 (C), 88.4 (dd, $J_{C\text{-}C\text{-}F}$ = 25.0, 16.0 Hz, C), 112.7 (C), 112.9 (CH), 124.9 (C), 132.0 (CH), 133.7 (CH), 153.4 (t, $J_{C\text{-}F}$ = 287.0 Hz, CF_2), 156.2 (C), 156.8 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -96.17 (d, *J* = 41.2 Hz, 1F), -92.14 (d, *J* = 41.2 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 3350 (w), 2940 (m), 1694 (s), 1489 (s), 1247 (s), 1227 (s), 1168 (s). **HRMS** (EI+) calcd for $C_{18}H_{22}BrF_2NO_3$ $[M]^+$: 419.0908, found: 419.0928.



3x

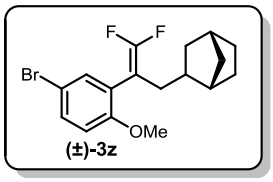
N*-(5-(5-Bromo-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl)-2-oxoazepane-1-carboxamide, 3y** (0.149 g, 65%) was prepared according to the general procedure from silicate **2y** (0.285 g, 0.53 mmol, 1.05 equiv) ***with the following modification: the reaction was run for 72 h. The desired difluoroalkene **3y** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.27 - 1.36 (m, 2H), 1.50 - 1.58 (m, 2H), 1.65 - 1.81 (m, 6H), 2.28 - 2.36 (m, 2H), 2.64 - 2.73 (m, 2H), 3.18 - 3.28 (m, 2H), 3.79 (s, 3H), 3.93 - 4.01 (m, 2H), 6.77 (d, *J* = 8.9 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.7, 2.4 Hz, 1H), 9.23 (br. s., 1 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 23.8 (CH_2), 25.1 (t, t, $J_{C\text{-}C\text{-}C\text{-}F}$ =2.7 Hz, CH_2), 27.6 (CH_2), 28.6 (CH_2), 29.1 (CH_2), 29.4 (CH_2), 40.0 (CH_2), 40.5 (CH_2), 44.0 (CH_2), 56.0 (CH_2), 88.4 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 16.5 Hz, C), 112.7 (C), 112.9 (CH), 125.0 (dd, $J_{C\text{-}C\text{-}C\text{-}F}$ =4.6, 1.8 Hz, C), 132.0 (CH), 133.8 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, CH), 153.4 (t, $J_{C\text{-}F}$ = 287.8 Hz, CF_2), 155.1 (C), 156.9 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, C), 179.9 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -96.16 (d, *J* = 42.7 Hz, 1F), -92.18 (d, *J* = 41.2 Hz, F). **FT-IR** (cm^{-1}, neat, ATR) 3273 (m), 2934 (m), 2861 (m), 1739 (s),



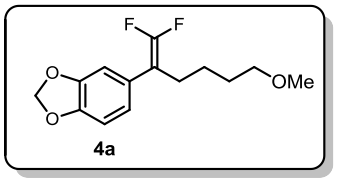
3y

1697 (s), 1651 (s), 1530 (s), 1489 (s), 1396 (s), 1247 (s), 1227 (s), 1214 (s), 1179 (s), 1164 (s), 970 (s). **HRMS** (ES+) calcd for $C_{20}H_{25}BrF_2N_2NaO_3$ $[M + Na]^+$: 481.0914, found: 481.0926.

(±)-**2-(2-(5-Bromo-2-methoxyphenyl)-3,3-difluoroallyl)bicyclo[2.2.1]heptane, 3z** (0.158 g, 88%) was prepared according to the general procedure from bicycloheptyl silicate **2z** (0.309 g, 0.7 mmol, 1.4 equiv). The desired difluoroalkene **3z** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.98 - 1.05 (m, 3H), 1.07 (d, *J* = 9.8 Hz, 1H), 1.21 - 1.31 (m, 2H), 1.34 (d, *J* = 9.8 Hz, 1H), 1.44 (ddd, *J* = 11.0, 7.5, 3.5 Hz, 2H), 1.96 (br s, 1H), 2.02 - 2.09 (m, 1H), 2.18 (br s, 1H), 2.23 - 2.29 (m, 1H), 3.79 (s, 3H), 6.77 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.9, 2.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 29.0 (CH_2), 30.0 (CH_2), 34.6 (CH_2), 35.5 (CH_2), 37.1 (CH_2), 37.7 (CH), 40.2 (CH), 40.9 (CH_2), 56.0 (CH_3), 88.0 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 15.6 Hz, C), 112.7 (C), 112.9 (CH), 125.4 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, C), 131.9 (CH), 133.8 (CH), 153.9 (t, $J_{C\text{-}F}$ = 287.8 Hz, CF_2), 156.9 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -96.78 (d, *J* = 42.7 Hz, 1F), -92.63 (d, *J* = 42.7 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2948 (s), 2875 (w), 1742 (s), 1489 (s), 1247 (s), 1235 (s), 1222 (s), 1029 (s), 806 (s). **HRMS** (EI+) calcd for $C_{17}H_{19}BrF_2O$ $[M]^+$: 356.0587, found: 356.0574.

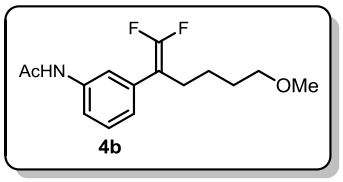


5-(1,1-Difluoro-6-methoxyhex-1-en-2-yl)benzo[*d*][1,3]dioxole, 4a (0.106 g, 78%) was prepared according to the general procedure from 3-methoxypropylsilicate **2r** (0.294 g, 0.7 mmol, 1.4 equiv) ***with the following modification***: CF_3 alkene **1b** (0.108 g, 0.5 mmol, 1 equiv) was used in place of **1a**. The desired difluoroalkene **4a** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.38 - 1.48 (m, 2H), 1.54 - 1.61 (m, 2H), 2.36 (tt, *J* = 7.5, 2.4 Hz, 2H), 3.31 (s, 3H), 3.34 (t, *J* = 6.5 Hz, 2H), 5.97 (s, 2H), 6.75 - 6.82 (m, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.5 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 28.0 (s, CH_2), 29.2 (CH_2), 58.8 (CH_3), 72.7 (CH_2), 92.2 (dd, $J_{C\text{-}C\text{-}F}$ = 22.9, 13.7 Hz, C), 101.4 (CH_2), 108.5 (CH), 109.1 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, C), 122.0 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 127.5 (dd, $J_{C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 4.6, 2.5 Hz, C), 147.0 (C), 148.0 (C), 153.8 (dd, $J_{C\text{-}F}$ = 288.7, 285.9 Hz, CF_2). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -95.54 (d, *J* = 45.8 Hz, 1F), -95.18 (d, *J* = 45.8 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2929



(w), 2868 (w), 1727 (m), 1491 (m), 1438 (m), 1237 (vs), 1116 (s), 1038 (s), 935 (m), 861 (m), 811 (m). **HRMS** (EI+) calcd for $C_{14}H_{16}F_2O_3$ $[M]^+$: 270.1068, found: 270.1086.

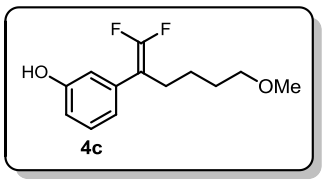
***N*-(3-(1,1-Difluoro-6-methoxyhex-1-en-2-yl)phenyl)acetamide, 4b** (0.115 g, 81%) was



4b

prepared according to the general procedure from 3-methoxypropylsilicate **2r** (0.294 g, 0.7 mmol, 1.4 equiv) ***with the following modification***: CF_3 alkene **1c** (0.115 g, 0.5 mmol, 1 equiv) was used in place of **1a**. The desired difluoroalkene **4b** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.36 - 1.47 (m, 2H), 1.50 - 1.61 (m, 2H), 2.18 (s, 3H), 2.40 (ddd, *J* = 9.8, 7.6, 2.0 Hz, 2H), 3.29 (s, 3H), 3.33 (t, *J* = 6.5 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.20 (br s, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.41 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.6 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, CH_2), 24.7 (CH_3), 27.6 (CH_2), 29.2 (CH_2), 58.7 (CH_3), 72.7 (CH_2), 92.3 (dd, $J_{C\text{-}C\text{-}F}$ = 22.0, 13.7 Hz, C), 119.1 (CH), 119.9 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 124.4 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, CH), 129.3 (CH), 134.7 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, C), 138.5 (C), 153.9 (dd, $J_{C\text{-}F}$ = 289.6, 286.8 Hz, CF_2), 168.9 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -94.42 (d, *J* = 42.7 Hz, 1F), -94.21 (d, *J* = 44.3 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 3305 (w, br), 2930 (w) 2866 (w), 1728 (m), 1698 (s), 1551 (s), 1489 (m), 1429 (m), 1240 (vs), 1118 (vs) 791 (s), 698 (s). **HRMS** (EI+) calcd for $C_{15}H_{20}F_2NO_2$ $[M]^+$: 284.1462, found: 284.1475.

3-(1,1-Difluoro-6-methoxyhex-1-en-2-yl)phenol, 4c (0.092 g, 76%) was prepared according to

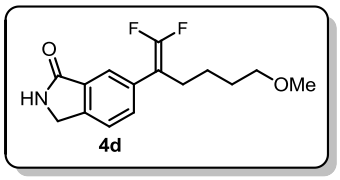


4c

the general procedure from 3-methoxypropylsilicate **2r** (0.294 g, 0.7 mmol, 1.4 equiv) ***with the following modification***: CF_3 alkene **1d** (0.094 g, 0.5 mmol, 1 equiv) was used in place of **1a**. The desired difluoroalkene **4c** was isolated as a clear yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.39 - 1.49 (m, 2H), 1.54 - 1.63 (m, 2H), 2.40 (tt, *J* = 7.6, 2.0 Hz, 2H), 3.32 (s, 3H), 3.36 (t, *J* = 6.5 Hz, 2H), 4.99 (br s, 1H), 6.74 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.79 (s, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.5 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 27.6 (CH_2), 29.0 (CH_2), 58.6 (CH_3), 72.8 (CH_2), 92.2 (dd, $J_{C\text{-}C\text{-}F}$ = 22.0, 11.9 Hz, C), 114.6 (CH), 115.5 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 120.7 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, CH), 129.9 (CH), 135.4 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.6 Hz, C), 153.9 (dd, $J_{C\text{-}F}$ = 290.5, 285.9 Hz, 7 C), 156.2 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -94.39 (d, *J* = 42.7 Hz, 1F), -94.02 (d, *J* = 42.7 Hz, 1F). **FT-IR** (cm^{-1}, neat,

ATR) 3293 (w, br), 2937 (w), 1727 (s), 1583 (m), 1448 (m), 1248 (vs), 1119 (vs), 999 (w), 850 (s), 783 (s), 696 (m). **HRMS** (EI+) calcd for $C_{13}H_{16}F_2O_2$ $[M]^+$: 242.118, found: 242.1122.

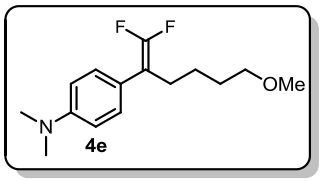
6-(1,1-Difluoro-6-methoxyhex-1-en-2-yl)isoindolin-1-one, 4d (0.136 g, 96%) was prepared



4d

according to the general procedure from 3-methoxypropylsilicate **2r** (0.294 g, 0.7 mmol, 1.4 equiv) ***with the following modification***: CF_3 alkene **1e** (0.120 g, 0.5 mmol, 1 equiv)[57] was used in place of **1a** 2) CH_2Cl_2/*i*-PrOH was used in place of hexane/EtOAc during column chromatography. The desired difluoroalkene **4d** was isolated as a clear, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.38 - 1.47 (m, 2H), 1.53 - 1.62 (m, 2H), 2.48 (tt, *J* = 7.3, 2.0 Hz, 2H), 3.30 (s, 3H), 3.33 (t, *J* = 6.5 Hz, 2H), 4.47 (s, 2H), 6.85 (br s, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.82 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.6 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 27.7 (CH_2), 29.2 (CH_2), 45.9 (CH_2), 58.8 (CH_3), 72.6 (CH_2), 92.1 (dd, $J_{C\text{-}C\text{-}F}$ = 22.9, 12.8 Hz, C), 123.5 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ =2.7 Hz, CH), 123.6 (CH), 132.2 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ =2.8 Hz, CH), 132.8 (C), 134.2 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, C), 142.9 (C), 154.0 (dd, $J_{C\text{-}F}$ =290.5, 286.8 Hz, CF_2), 172.2 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -94.15 (d, *J* = 41.2 Hz, 1F), -93.76 (d, *J* = 42.7 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 3227 (w, br) 2929 (w), 2865 (w), 1690 (vs), 1294 (m), 1234 (s), 1116 (s), 774 (m), 587 (m). **HRMS** (ES+) calcd for $C_{15}H_{18}F_2NO_2$ $[M + H]^+$: 282.1306, found: 282.1290.

4-(1,1-Difluoro-6-methoxyhex-1-en-2-yl)-*N*,*N*-dimethylaniline, 4e (0.107 g, 80%) was



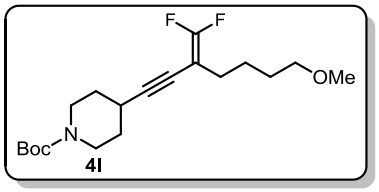
4e

prepared according to the general procedure from 3-methoxypropylsilicate **2r** (0.294 g, 0.7 mmol, 1.4 equiv) ***with the following modification***: CF_3 alkene **1f** (0.108 g, 0.5 mmol, 1 equiv) was used in place of **1a**. The desired difluoroalkene **4e** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.38 - 1.47 (m, 2H), 1.52 - 1.61 (m, 2H), 2.38 (tt, *J* = 7.4, 2.3 Hz, 2H), 2.96 (s, 6H), 3.30 (s, 3H), 3.33 (t, *J* = 6.6 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.6 (CH_2), 27.6 (CH_2), 29.2 (CH_2), 40.6 (CH_3), 58.7 (CH_2), 72.7 (CH_3), 92.0 (dd, $J_{C\text{-}C\text{-}F}$ = 18.8, 16.0 Hz, C), 112.5 (CH), 121.4 (CH), 129.1 (t, $J_{C\text{-}F}$ = 3.2 Hz, C), 149.8 (C), 153.7 (t, $J_{C\text{-}F}$ = 287.8 Hz, CF_2). **^{19}F NMR**

[57] As noted previously, this CF_3 alkene was found to be ~95% pure and thus the mass was adjusted accordingly.

($CDCl_3$, 471 MHz) δ -96.56 (s, 2F). **FT-IR** (cm^{-1}, neat, ATR) 2930 (m), 2865 (m), 1724 (s), 1613 (s), 1524 (s), 1228 (s), 1115 (s), 908 (s), 817 (s). **HRMS** (EI+) calcd for $C_{15}H_{21}F_2NO$ $[M]^+$: 269.1591, found: 269.1582.

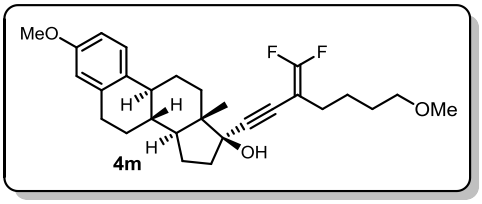
***tert*-Butyl 4-(3-(Difluoromethylene)-7-methoxyhept-1-yn-1-yl)piperidine-1-carboxylate, 4l**



4l

(0.118 g, 66%) was prepared according to the general procedure from 3-methoxypropylsilicate **2r** (0.262 g, 0.625 mmol, 1.25 equiv) ***with the following modification***: CF_3 alkene **1m** (0.152 g, 0.5 mmol, 1 equiv) was used in place of **1a**. The desired difluoroalkene **4l** was isolated as a clear, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.48 (s, 9H), 1.51 - 1.68 (m, 6H), 1.72 - 1.87 (m, 2H), 2.03 - 2.13 (m, 2H), 2.68 - 2.80 (m, 1H), 3.19 - 3.32 (m, 2H), 3.35 (s, 3H), 3.37 - 3.45 (m, 2H), 3.60 - 3.72 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 24.5 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.3 Hz, CH_2), 27.2 (CH), 27.8 (CH_2), 28.7 (CH_3), 28.9 (CH_2), 31.6 (br s, CH_2), 42.1 (br, CH_2), 58.8 (CH_3), 72.6 (CH_2), 73.8 (dd, $J_{C\text{-}C\text{-}C\text{-}F}$ = 8.2, 3.7 Hz, C), 78.3 (dd, $J_{C\text{-}C\text{-}F}$ = 34.8, 15.6 Hz, C), 79.7 (C), 96.3 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 6.0 Hz, C), 155.0 (C), 159.1 (dd, $J_{C\text{-}F}$ = 295.1, 291.4 Hz, CF_2). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -90.1 (d, *J* = 22.9 Hz, 1F), -85.2 (d, *J* = 22.9 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2928 (w), 2863 (w), 1718 (s), 1693 (vs), 1419 (s), 1231 (s), 1166 (vs), 1118 (vs), 1020 (w), 864 (w). **HRMS** (EI+) calcd for $C_{14}H_{20}F_2NO$ $[M - Boc]^+$: 256.1513, found: 256.1514.

(8*R*,9*S*,13*S*,14*S*,17*S*)-17-(3-(Difluoromethylene)-7-methoxyhept-1-yn-1-yl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol, 4m



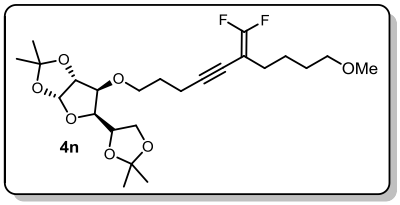
4m

(0.137 g, 60%) was prepared according to the general procedure from 3-methoxypropylsilicate **2r** (0.262 g, 0.625 mmol, 1.25 equiv) ***with the following modification***: CF_3 alkene **1m** (0.202 g, 0.5 mmol, 1 equiv) dissolved[58] in 2.4 mL of anhyd DMF was used in place of **1a**. The desired difluoroalkene **4m** was isolated as a clear, pale-yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.91 (s, 3H), 1.33 - 1.55 (m, 4H), 1.62 (t, *J* = 3.1 Hz, 4H), 1.65 - 1.93 (m,

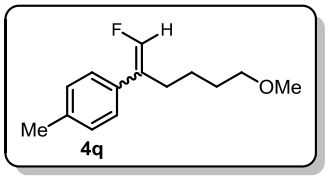
[58] The neat starting alkene is unstable over extended periods. Storage of these enynes as dilute solution in DMF (~0.2 M) allows them to be stored at 0 °C for at least one week without appreciable degradation.

5H), 1.94 - 2.02 (m, 1H), 2.06 (td, *J* = 12.5, 3.2 Hz, 1H), 2.11 - 2.17 (m, 2H), 2.21 (td, *J* = 12.2, 3.9 Hz, 1H), 2.28 - 2.41 (m, 2H), 2.79 - 2.94 (m, 2H), 3.32 (s, 3H), 3.36 - 3.42 (m, 2H), 3.79 (s, 3H), 6.64 (d, *J* = 2.4 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 13.1 (CH_3), 23.1 (CH_2), 24.5 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.4 Hz, CH_2), 26.7 (CH_2), 26.8 (CH_2), 27.6 (CH_2), 28.9 (CH_2), 30.1 (CH_2), 33.2 (CH_2), 39.3 (CH_2), 39.7 (CH_2), 43.9 (CH), 47.8 (CH), 50.0 (CH), 55.4 (CH_3), 58.8 (CH_3), 72.7 (CH_2), 77.9 (dd, $J_{C\text{-}C\text{-}C\text{-}F}$ = 8.2, 3.7 Hz, C), 78.1 (dd, $J_{C\text{-}C\text{-}F}$ = 33.9, 14.7 Hz, C), 80.5 (C), 97.7 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ =6.0 Hz, C), 111.8 (CH), 114.1 (CH), 126.6 (CH), 132.8 (C), 138.2 (C), 159.1 (dd, $J_{C\text{-}F}$ = 295.1, 292.3 Hz, CF_2), 157.7 (C). **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -88.75 (d, *J* = 19.6 Hz, 1F), -83.63 (d, *J* = 19.6 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2928 (m), 2865 (m), 2051 (w), 1774 (m), 1664 (s), 1499 (m), 1256 (s) 1116 (s), 908 (m), 730 (vs). **HRMS** (ES+) calcd for $C_{28}H_{36}F_2NaO_3$ $[M + Na]^+$: 481.2530 found: 481.2537.

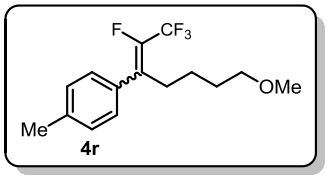
(3a*R*,5*R*,6*S*,6a*R*)-6-((6-(Difluoromethylene)-10-methoxydec-4-yn-1-yl)oxy)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxole, 4n (0.117 g, 49%) was prepared according to the general procedure from 3-methoxypropylsilicate **2r** (0.262 g, 0.625 mmol, 1.25 equiv) ***with the following modification***: CF_3 alkene **1o** (0.210 g, 0.5 mmol, 1 equiv) was used in place of **1a**. The desired difluoroalkene **4n** was isolated as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.32 (s, 3H), 1.36 (s, 3H), 1.43 (s, 3H), 1.50 (s, 3H), 1.53 - 1.65 (m, 4H), 1.71 - 1.87 (m, 2H), 2.03 - 2.09 (m, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 3.34 (s, 3H), 3.39 (t, *J* = 6.1 Hz, 2H), 3.61 (dt, *J* = 9.5, 5.8 Hz, 1H), 3.73 (ddd, *J* = 9.4, 7.2, 5.4 Hz, 1H), 3.88 (d, *J* = 2.9 Hz, 1H), 3.99 (dd, *J* = 8.6, 5.6 Hz, 1H), 4.09 (dd, *J* = 8.6, 6.1 Hz, 1H), 4.12 (dd, *J* = 7.7, 3.1 Hz, 1H), 4.30 (dt, *J* = 7.6, 6.0 Hz, 1H), 4.55 (d, *J* = 3.7 Hz, 1H), 5.87 (d, *J* = 3.7 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 16.3 (CH_2), 24.6 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 25.6 (CH_3), 26.5 (CH_3), 27.0 (CH_3), 27.1 (CH_3), 27.3 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 58.8 (CH_3), 67.6 (CH_2), 68.9 (CH_2), 72.7 (dd, $J_{C\text{-}C\text{-}C\text{-}F}$ = 11.9, 8.2 Hz, C), 72.6 (CH_2), 72.8 (CH_2), 78.4 (dd, $J_{C\text{-}C\text{-}F}$ = 34.8, 14.7 Hz, C), 81.4 (CH), 82.4 (CH), 82.7 (CH), 93.7 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, C), 105.6 (CH), 109.2 (C), 112.0 (C), 159.2 (dd, $J_{C\text{-}F}$ = 293.3, 291.4 Hz, CF_2). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -90.49 (d, *J* = 22.9 Hz, 1F), -85.83 (d, *J* = 22.9 Hz, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2985 (w), 2870 (w), 1842 (vw), 1719 (m), 1372 (m), 1214 (m), 1120 (s), 1071 (vs), 1017 (s), 847 (m). **HRMS** (ES+) calcd for $C_{24}H_{37}F_2O_7$ $[M + H]^+$: 475.2507 found: 475.2498.



1-(1-Fluoro-6-methoxyhex-1-en-2-yl)-4-methylbenzene, 4q (0.076 g, 68%) was prepared according to the general procedure from 3-methoxypropylsilicate **2r** (0.294 g, 0.7 mmol, 1.4 equiv) ***with the following modification***s: 1) CF_2H alkene **1q** (0.084 g, 0.5 mmol, 1 equiv) was used in place of **1a**; 2) A higher loading of $Ru(bpy)_3(PF_6)_2$ (0.0215 g, 0.025 mmol, 0.05 equiv) was used 3) The reaction was run for 48 h. The desired fluoroalkene **4q** was isolated as a clear, colorless oil. *E*/*Z* ratio: 5.7:1.[59] **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.38 - 1.47 (m, 2H), 1.53 - 1.62 (m, 2H), 2.34 (s, 3H), 2.55 (td, *J* = 7.5, 2.9 Hz, 2H), 3.30 (s, 3H), 3.34 (t, *J* = 6.6 Hz, 2H), 6.77 (d, *J* = 85.6 Hz, 1H), 7.12 - 7.18 (m, 4H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.3 (CH_2), 24.5 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 26.5 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH_2), 29.4 (CH_3), 58.7 (CH_3), 72.8 (CH_2), 126.9 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH), 128.3 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.6 Hz, C), 129.5 (CH), 133.7 (d, $J_{C\text{-}C\text{-}F}$ = 9.2 Hz, C), 137.4 (C), 145.8 (d, $J_{C\text{-}F}$ = 258.4 Hz, CFH). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -135.06 (s, 1F). **FT-IR** (cm^{-1}, neat, ATR) 2962 (w), 2865 (w), 1657 (s), 1513 (s), 1452 (s), 1118 (s), 808 (s), 502 (s). **HRMS** (EI+) calcd for $C_{14}H_{19}FO$ $[M]^+$: 222.1422, found: 222.1420.



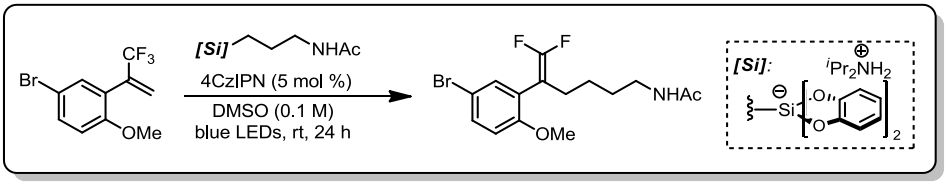
1-Methyl-4-(1,1,1,2-tetrafluoro-7-methoxyhept-2-en-3-yl)benzene, 4r (0.082 g, 57%) was prepared according to the general procedure from 3-methoxypropylsilicate **2r** (0.419 g, 1.0 mmol, 2 equiv) ***with the following modification***s: 1) CF_2CF_3 alkene **1r** (0.118 g, 0.5 mmol, 1 equiv) was used in place of **1a**; 2) A higher loading of $Ru(bpy)_3(PF_6)_2$ (0.0323 g, 0.0375 mmol, 0.075 equiv) was used 3) The reaction was run for 48 h. The desired (fluoro)trifluoromethyl alkene **4r** was isolated as a clear, colorless oil. *E*/*Z* ratio: 1.6:1.[59] **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.34 - 1.42 (m, 2H), 1.50 - 1.60 (m, 2H), 2.36 (s, 3H), 2.46 - 2.52 (m, 2H), 3.29 (s, 3H), 3.33 (t, *J* = 6.4 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.5 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 23.5 (CH_2), 29.3 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 31.8 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.5 Hz, CH_2), 58.8 (CH_2), 72.6 (CH_3), 119.4 (qd, $J_{C\text{-}F}$ = 273.4, $J_{C\text{-}C\text{-}F}$ = 43.6 Hz, CF_3), 128.3 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, CH), 129.2 (CH), 131.5 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, C), 138.4 (C), 142.3 (dq, $J_{C\text{-}F}$ = 251.6, $J_{C\text{-}C\text{-}F}$ = 36.5 Hz, CF). **^{19}F NMR**



[59] Characterization data for only the major *E* isomer is given. Major diastereomer determined by J-coupling constants in ^{1}H and ^{13}C NMR

($CDCl_3$, 471 MHz) δ -134.29 (q, *J* = 9.2 Hz, 1F), -67.92 (d, *J* = 9.2 Hz, 3F). **FT-IR** (cm^{-1}, neat, ATR) 2929 (w), 2869 (w), 1347 (s), 1335 (s), 1193 (s), 1120 (s), 818 (s). **HRMS** (EI+) calcd for $C_{15}H_{18}F_4O$ $[M]^+$: 290.1308, found: 290.1294.

Representative Procedure for Large Scale Defluorinative Alkylation



***N*-(5-(5-Bromo-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl)acetamide (3w)**

To an oven dried, 100 mL round bottom flask equipped with a stir bar were added 4CzIPN (0.118 g, 0.15 mmol, 0.05 equiv) and propylacetamidosilicate **2r** (1.876 g, 4.2 mmol, 1.4 equiv). The flask was sealed with a rubber septum and was evacuated and purged with argon three times *via* an inlet needle. The flask was then charged with CF_3 alkene **1a** (0.843 g, 3 mmol, 1 equiv) dissolved in anhyd DMSO (30 mL) *via* a syringe. The now bright yellow solution was irradiated by blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 ^oC *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by GC/MS. Once complete (~ 24 h), the now dark yellow-brown solution was transferred to a separatory funnel and diluted with deionized H_2O (100 mL) and Et_2O (~ 100 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 × ~50 mL). The combined organic layers were washed with deionized H_2O (2 × ~150 mL) followed by brine (~100 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hex:EtOAc) to give the desired difluoroalkene **3w** (0.678 g, 63%) as a pale-yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.24 - 1.34 (m, 2H), 1.44 - 1.53 (m, 2H), 1.94 (s, 3H), 2.29 - 2.35 (m, 2H), 3.18 (q, *J* = 6.9 Hz, 2H), 3.79 (s, 3H), 5.43 (br s, 1H), 6.78 (d, *J* = 8.9 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.38 (dd, *J* = 8.9, 2.4 Hz, 1H).

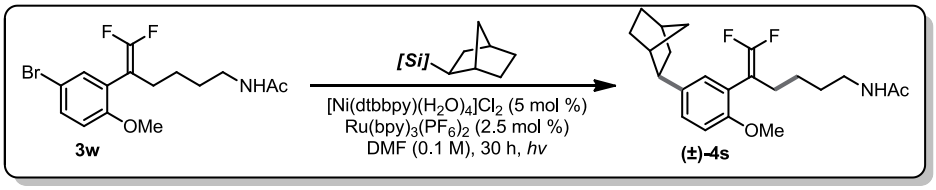
^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.3 (CH_2), 24.9 (CH_2), 27.4 (CH_2), 29.0 (CH_3), 39.5 (CH_2), 55.9 (CH_3), 88.3 (dd, $J_{C\text{-}C\text{-}F}$ = 24.7, 16.5 Hz, C), 112.6 (C), 112.9 (CH), 124.7 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, C), 132.0 (CH), 133.6 (br s, CH), 153.3 (t, $J_{C\text{-}F}$ = 286.8 Hz, CF_2), 156.8 (C), 170.3 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -96.15 (d, J = 41.2 Hz, 1F), -92.04 (d, J = 41.2 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 3250 (m), 3075 (m), 2940 (m), 2870 (m), 1749 (s), 1489 (s), 1248 (s), 1233 (s), 1219 (s), 803 (s).

HRMS (EI+) calcd for $C_{15}H_{18}BrF_2NO_2$ $[M]^+$: 361.0489, found: 361.0468.

Ni/Photoredox Cross-Coupling of *Gem*-Difluoroalkene 4s



***N*-(5-(5-((±)-Bicyclo[2.2.1]heptan-2-yl)-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl)acetamide, 4s**

To an 20 mL reaction vial equipped with a stir bar were added [(±)-bicyclo[2.2.1]heptan-2-yl silicate **2z** (0.530 g, 1.2 mmol, 1.2 equiv], $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (23.6 mg, 0.05 mmol, 0.05 equiv),[60] difluoroalkene **1a** (0.362 g, 1 mmol, 1 equiv), and $Ru(bpy)_3(PF_6)$ (0.0215 g, 0.025 mmol, 0.025 equiv). The vial was sealed with a cap containing a TFE-lined silicone septum. The vial was evacuated three times *via* an inlet needle, then purged with argon. The vial was then charged *via* a syringe with dry DMF (10 mL). The cap was sealed with Parafilm®, and the now bright red solution was irradiated in the aforementioned LED reactor. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by HPLC. Once judged to be complete, the now opaque, milky-brown solution was transferred to a separatory funnel and diluted with deionized H_2O (~ 20 mL) and Et_2O (~ 20 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 × ~20 mL). The combined organic layers were washed with 2 M aq

[60] In previous reports, we either pre-complexed the dtbbpy ligand to nickel *in situ* or conducted the reaction without pre-complexation. We recently found that preparation of $[Ni(dtbbpy)(H_2O)_4]Cl_2$ simplifies the process entirely. This complex can easily be prepared by reacting dtbbpy (1.05 equiv) with $NiCl_2 \cdot 6H_2O$ in refluxing EtOH (0.1 M) for 12 h. Once cooled to rt, the solvent can be removed *in vacuo* by rotary evaporation, and the resulting mint green solid can be washed with Et_2O followed by pentane to remove any residual ligand. This complex can be stored on the bench for an indefinite period of time.

NaOH (2 × ~30 mL), 2 M aq HCl (~30 mL), deionized H_2O (~30 mL), and brine (~50 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by flash column chromatography (gradient hexane/EtOAc) to give the desired coupling product, **4s**, (0.236 g, 63%) as a viscous, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.16 (d, *J* = 9.8 Hz, 1H), 1.22 - 1.38 (m, 4H), 1.44 - 1.53 (m, 3H), 1.54 - 1.65 (m, 3H), 1.74 (ddd, *J* = 11.4, 9.5, 2.4 Hz, 1H), 1.92 (s, 3H), 2.26 - 2.31 (m, 1H), 2.32 - 2.38 (m, 3H), 2.68 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.18 (q, *J* = 6.5 Hz, 2H), 3.79 (s, 3H), 5.35 (br s, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.94 (d, *J* = 2.1 Hz, 1H), 7.12 (dd, *J* = 8.5, 2.3 Hz, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.5 (CH), 25.0 (br. s., CH_2), 27.7 (CH), 29.1 (CH_2), 29.2 (CH_2), 30.7 (CH_2), 36.2 (CH_2), 37.1 (CH_2), 39.3 (CH_2), 39.7 (CH), 43.4 (CH_3), 46.7 (CH_2), 55.9 (CH_3), 89.3 (dd, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 23.8, 16.5 Hz, C), 111.2 (CH), 122.3 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ =3.7 Hz, C), 127.6 (CH), 130.1 (CH_2), 139.9 (CH), 153.4 (t, $J_{\mathbf{C\text{-}F}}$ = 285.9 Hz, CF_2), 155.4 (C), 170.2 (C).

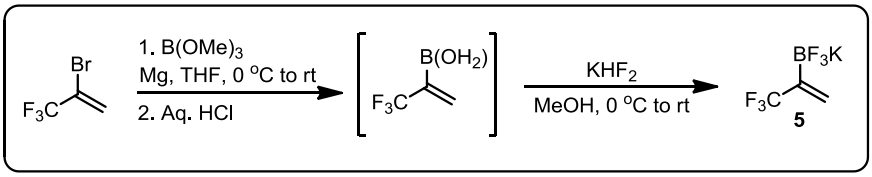
^{19}F NMR ($CDCl_3$, 471 MHz) δ -97.30 (d, *J* = 45.8 Hz, 1F), -93.35 (d, *J* = 45.8 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 3287 (m), 3087 (m), 2949 (m), 2869 (m), 1742 (s), 1650 (s), 1500 (s), 1280 (s), 1248 (s), 1231 (s), 1031 (s).

HRMS (ES+) calcd for $C_{22}H_{30}F_2NO_2$ $[M + H]^+$: 378.2242, found: 378.2245.

Synthesis and Utilization of Potassium Trifluoro(3,3,3-trifluoroprop-1-en-2-yl)borate

Synthesis of Potassium Trifluoro(3,3,3-trifluoroprop-1-en-2-yl)borate (5)



Stage One

To a 250 mL Schlenk flask equipped with a stir bar was added activated[61] Mg powder (0.850 g, 35.0 mmol). The flask was sealed with a septum and flame-dried under vacuum. The flask was purged with argon and was charged with THF (60 mL) *via* a syringe. The solution was cooled to 0 °C *via* ice-water bath. To the cooled solution was added trimethyl borate (9.75 mL, 77.5 mmol) *via* syringe, and the solution was stirred vigorously. A solution of 2-bromo-3,3,3-trifluoro-1-propene (3.1 mL, 29.2 mmol) in THF (7.5 mL) was then added slowly in 3 portions over 30 min. After the addition was complete, the heterogeneous solution turned dark grey. The solution was stirred at 0 °C for 6 h and then was allowed to warm to rt and stirred overnight.

Stage Two

The solution was cooled to 0 °C and was quenched with 6 M aq HCl (~ 20 mL) *via* slow addition through a syringe. **CAUTION:** *Evolves hydrogen gas, the use of several vent needles is recommended!* The mixture was allowed to stir at 0 °C for 1 h. The solution was transferred to a 500 mL separatory funnel and diluted with deionized H_2O (~100 mL) and Et_2O (~60 mL). The layers were separated, and the aq layer was extracted with Et_2O (2 × ~60 mL). The combined organic layers were transferred to a 500 mL round bottom flask and were cooled to 0 °C. To the flask was slowly added 4.5 M aq KHF_2 in MeOH (40 mL). **CAUTIONARY NOTE:** *KHF_2 solutions will etch glassware*. The solution was allowed to warm to rt and stirred overnight. The solvent was removed *in vacuo* to afford the crude organotrifluoroborate. The solids were washed with hot acetone (4 × ~60 mL), and the filtrate was collected in a round bottom flask. The solvent was removed *in vacuo* to give an oily brown solid. The solid was triturated with cold

[61] Magnesium powder was activated *via* successive washes with 2 M aq HCl (3 × ~ 10 mL) followed by a wash with Et_2O (~ 20 mL).

Et_2O (~80 mL) and filtered to yield organotrifluoroborate **5** as a white crystalline solid (1.26 g for the first crop, 0.557 g for the second crop, 31% over 3 steps).

^{1}H NMR (acetone-d_6, 500 MHz) δ 5.57 (br s, 1H), 5.68 (br s, 1H).

^{13}C NMR (acetone-d_6, 125 MHz) 121.8 (dtd, $J_{C\text{-}C\text{-}C\text{-}F}$ = 10.8, 7.2, 2.3 Hz, CH_2), 126.2 (q, $J_{C\text{-}F}$ = 271.3 Hz, CF_3), 143.6 (br s, C).

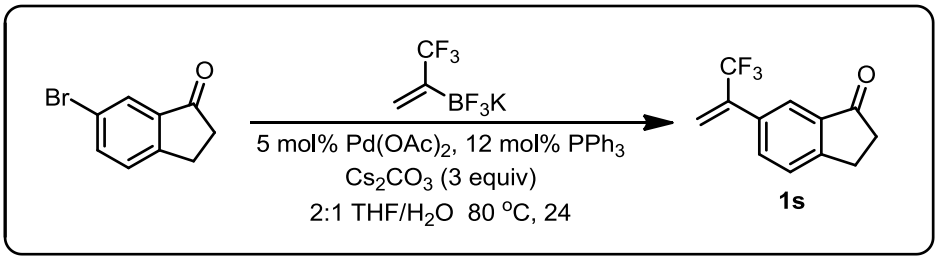
^{19}F NMR (acetone-d_6, 471 MHz) δ -143.92 (dd, J = 94.6, 48.8 Hz, 3F), -64.05 (s, 3F).

^{11}B NMR (acetone-d_6, 128 MHz) δ 1.15 (q, J = 46.7 Hz, 1B).

FT-IR (cm^{-1}, neat, ATR) 1640 (m), 1322 (s), 1170 (s), 1080 (s), 998 (s), 974 (s), 945 (s), 831 (s), 715 (s), 616 (s).

HRMS (ES-) calcd for $C_3H_2BF_6$ $[M - K]^-$: 163.0149, found: 163.0154.

Suzuki Cross-Coupling using Potassium Trifluoro(3,3,3-trifluoroprop-1-en-2-yl)borate and 6-Bromo-2,3-dihydro-1H-inden-1-one



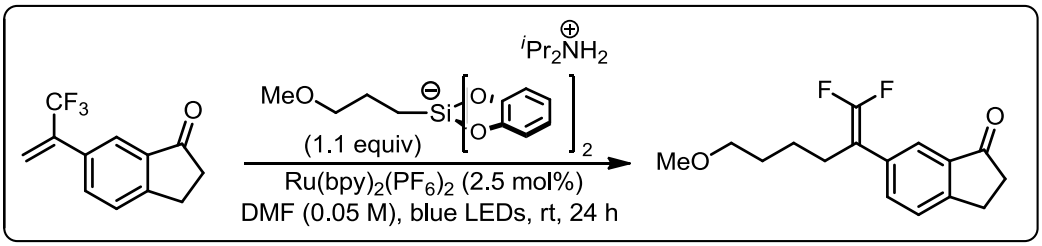
6-(3,3,3-Trifluoroprop-1-en-2-yl)-2,3-dihydro-1*H*-inden-1-one, 1s

To a 20 mL microwave tube was added 6-bromo-2,3-dihydro-1H-inden-1-one (0.211 g, 1 mmol, 1 equiv), organotrifluoroborate **5** (0.303 g, 1.5 mmol, 1.5 equiv), Cs_2CO_3 (0.979 g, 3 mmol, 3 equiv), PPh_3 (0.032 g, 0.12 mmol, 0.12 equiv) and $Pd(OAc)_2$ (0.011 g, 0.05 mmol, 0.05 equiv). The tube was sealed with a crimp-top cap containing a TFE-lined silicone septum and placed under an argon atmosphere *via* an inlet needle. The tube was evacuated three times *via* an inlet needle, then purged with argon. A mixture of degassed THF (6 mL) and degassed deionized H_2O (3 mL) were added *via* syringe. The argon inlet needle was removed from the tube. The tube was heated to 80 ^oC. The reaction mixture was allowed to stir at this temperature for 24 h. Reaction progress was monitored by GC/MS. Once complete, the reaction was cooled to rt and diluted in EtOAc (25 mL). The reaction mixture was transferred to a separatory funnel and further diluted with deionized H_2O (25 mL). The layers were separated, and the aq layer was extracted with

EtOAc (2 × 25 mL). The combined organic layers were washed with 1 M aq NaOH (25 mL), deionized H_2O (25 mL), and brine (25 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was achieved by SiO_2 column chromatography (gradient hexane/EtOAc) to give the desired olefin **1s** (0.172 g, 76%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.74 (t, J = 6.3 Hz, 2H), 3.18 (t, J = 5.8 Hz, 2H), 5.83 (q, J = 1.4 Hz, 1H), 6.02 (s, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.85 (s, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.9 (CH_2), 36.7 (CH_2), 123.4 (q, $J_{C\text{-}F}$ = 274.3 Hz, CF_3), 121.7 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, CH_2), 123.0 (CH), 127.3 (CH), 133.3 (C), 133.8 (CH), 137.7 (C), 138.4 (q, $J_{C\text{-}C\text{-}F}$ = 30.5 Hz, C), 155.9 (C), 206.7 (C).
^{19}F NMR ($CDCl_3$, 471 MHz) δ -68.07 (s, 3F).
FT-IR (cm^{-1}, neat, ATR) 2934 (vw), 1712 (vs), 1617 (w), 1348 (w), 1116 (vs), 951 (w), 842 (w).
HRMS (EI+) calcd for $C_{12}H_9F_3O$ $[M]^+$: 226.0605, found: 226.0594.

Radical Defluorinative Alkylation of 6-(3,3,3-Trifluoroprop-1-en-2-yl)-2,3-dihydro-1H-inden-1-one using Alkylsilicate 2r



6-(1,1-Difluoro-6-methoxyhex-1-en-2-yl)-2,3-dihydro-1*H*-inden-1-one, 1s

To two 8 mL reaction vials equipped with stir bars were added $Ru(bpy)_3(PF_6)_2$ (0.0054 g, 0.0125 mmol, 0.025 equiv) and 3-methoxypropylsilicate **2r** (0.147 g, 0.35 mmol, 1.4 equiv). The vials were sealed with caps containing a TFE-lined silicone septum and placed under an Ar atmosphere through evacuating and purging with Ar three times *via* inlet needles. The vials were then each charged with the CF_3 alkene **1s** (0.057 g, 0.25 mmol) in anhyd DMF (2.5 mL) *via* a syringe. The capped vials were sealed with Parafilm®, and the now bright red solutions were irradiated with blue LEDs in the aforementioned photoreactor. The temperatures of these reactions were maintained at approximately 27 °C *via* a fan. The solutions were stirred

vigorously while being irradiated. Reaction progress was monitored by GC/MS. Once both were judged to be complete, the now dark red-brown solutions were combined and transferred to a separatory funnel. The combined solution was diluted with Et_2O (50 mL) and 2 M aq NaOH (50 mL).[62] The layers were separated, and the aq layer was extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with 2 M aq NaOH (50 mL) and deionized H_2O (2 × 50 mL), followed by brine (100 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient hexanes/EtOAc) to give the desired difluoroalkene, **4t**, (0.108 g, 77%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.35 - 1.44 (m, 2H), 1.52 - 1.59 (m, 2H), 2.44 (tt, *J* = 7.5, 1.8 Hz, 2H), 2.69 - 2.75 (m, 2H), 3.14 (t, *J* = 6.0 Hz, 2H), 3.29 (s, 3H), 3.32 (t, *J* = 6.4 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.54 (dt, *J* = 8.1, 1.5 Hz, 1H), 7.68 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.6 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, CH_2), 25.8 (CH_2), 27.6 (CH_2), 29.2 (CH_2), 36.7 (CH_2), 58.8 (CH_3), 72.5 (CH_2), 91.9 (dd, $J_{C\text{-}C\text{-}F}$ = 22.9, 12.8 Hz, C), 123.4 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 127.0 (CH), 133.4 (t, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, C), 135.0 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.7 Hz, CH), 137.6 (C), 154.0 (dd, $J_{C\text{-}F}$ = 291.4, 287.8 Hz, CF_2), 154.3 (C), 206.9 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -94.17 (d, *J* = 42.7 Hz, 1F), -93.83 (d, *J* = 41.2 Hz, 1F).

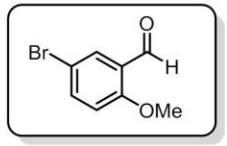
FT-IR (cm^{-1}, neat, ATR) 2928 (vw), 2866 (vw), 1711 (vs), 1645 (vw), 1225 (m), 1117 (s), 838 (m).

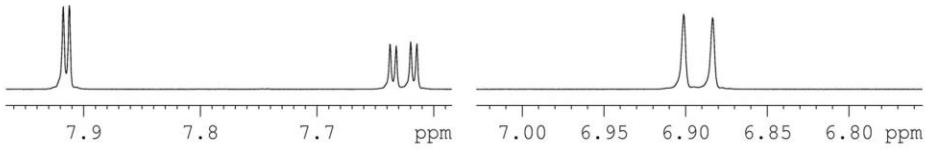
HRMS (EI+) calcd for $C_{16}H_{19}F_2O_2$ $[M + H]^+$: 281.1353, found: 281.1337.

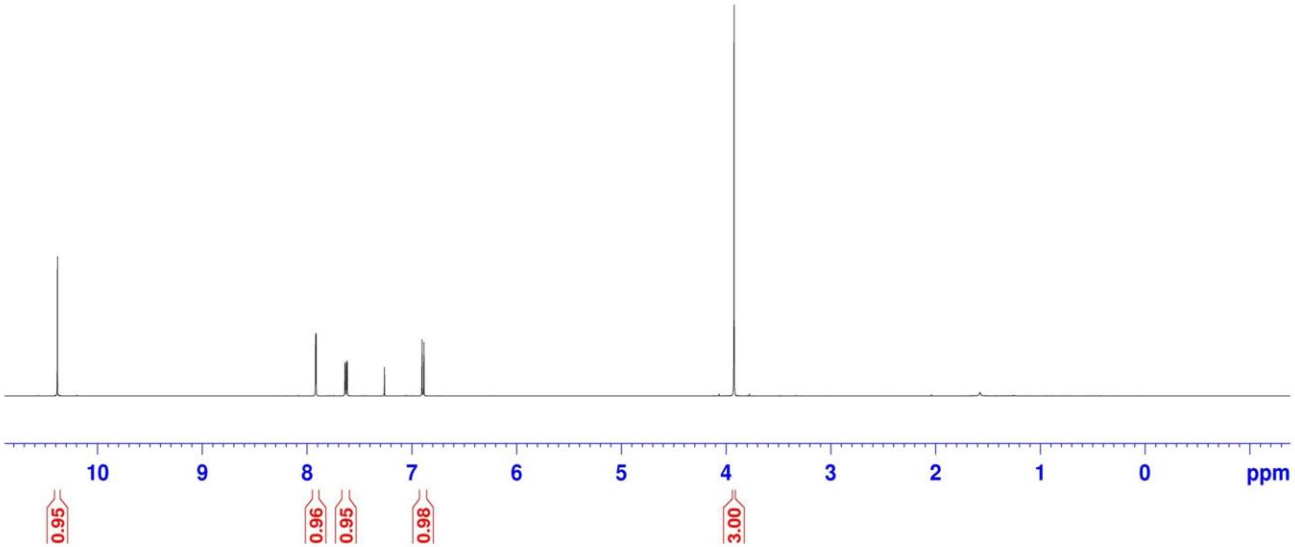
[62] Note that the aq layer will turn dark brown and become warm, likely because of the reaction between catechol (or the orthosilicate byproduct) and hydroxide.

Spectra of Synthesized Compounds – Listed by Order of Appearance

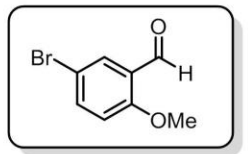
5–bromo–2–methoxybenzaldehyde
500 MHZ, CDCl3

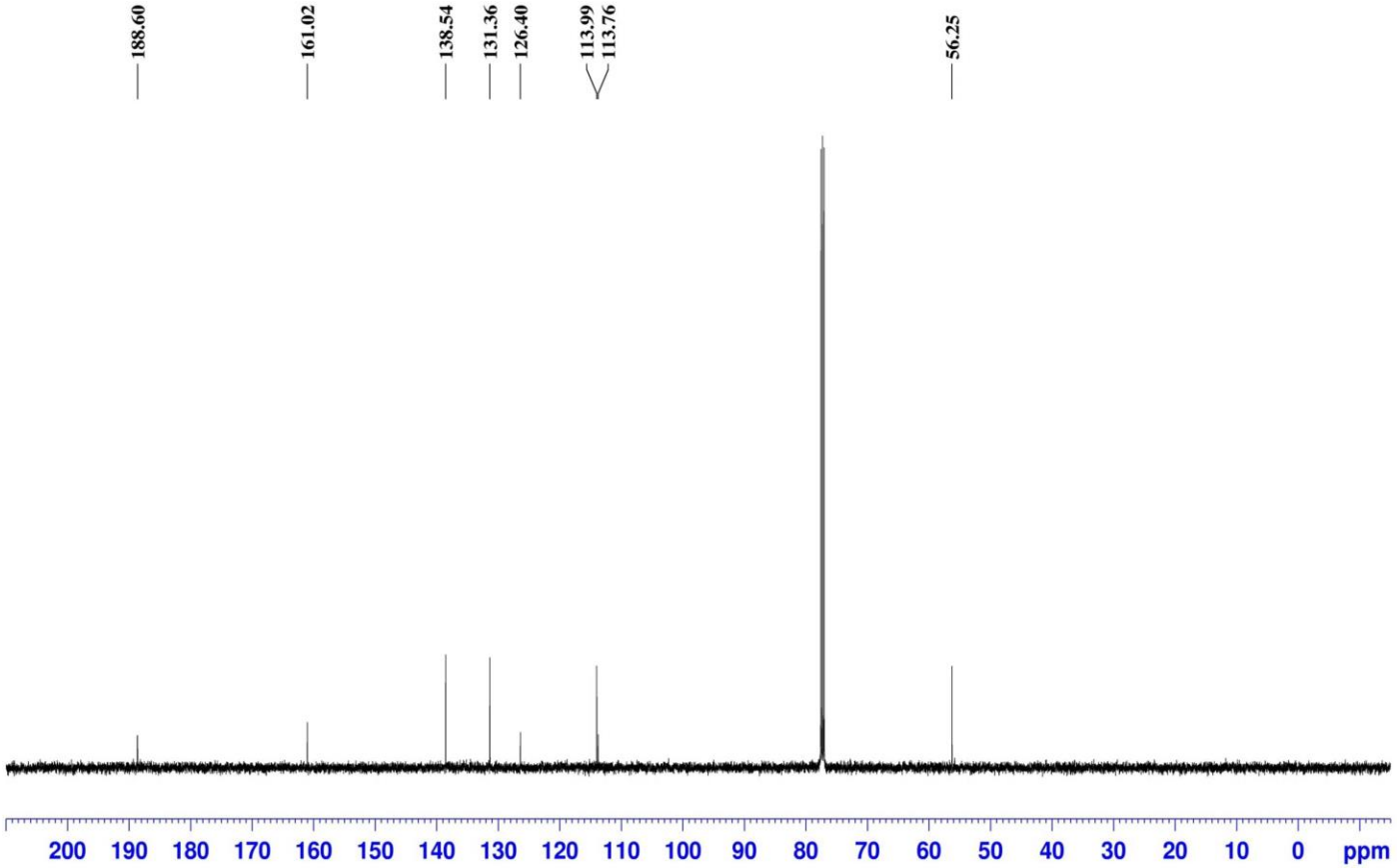




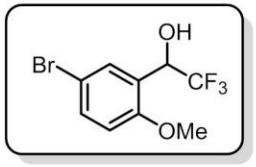


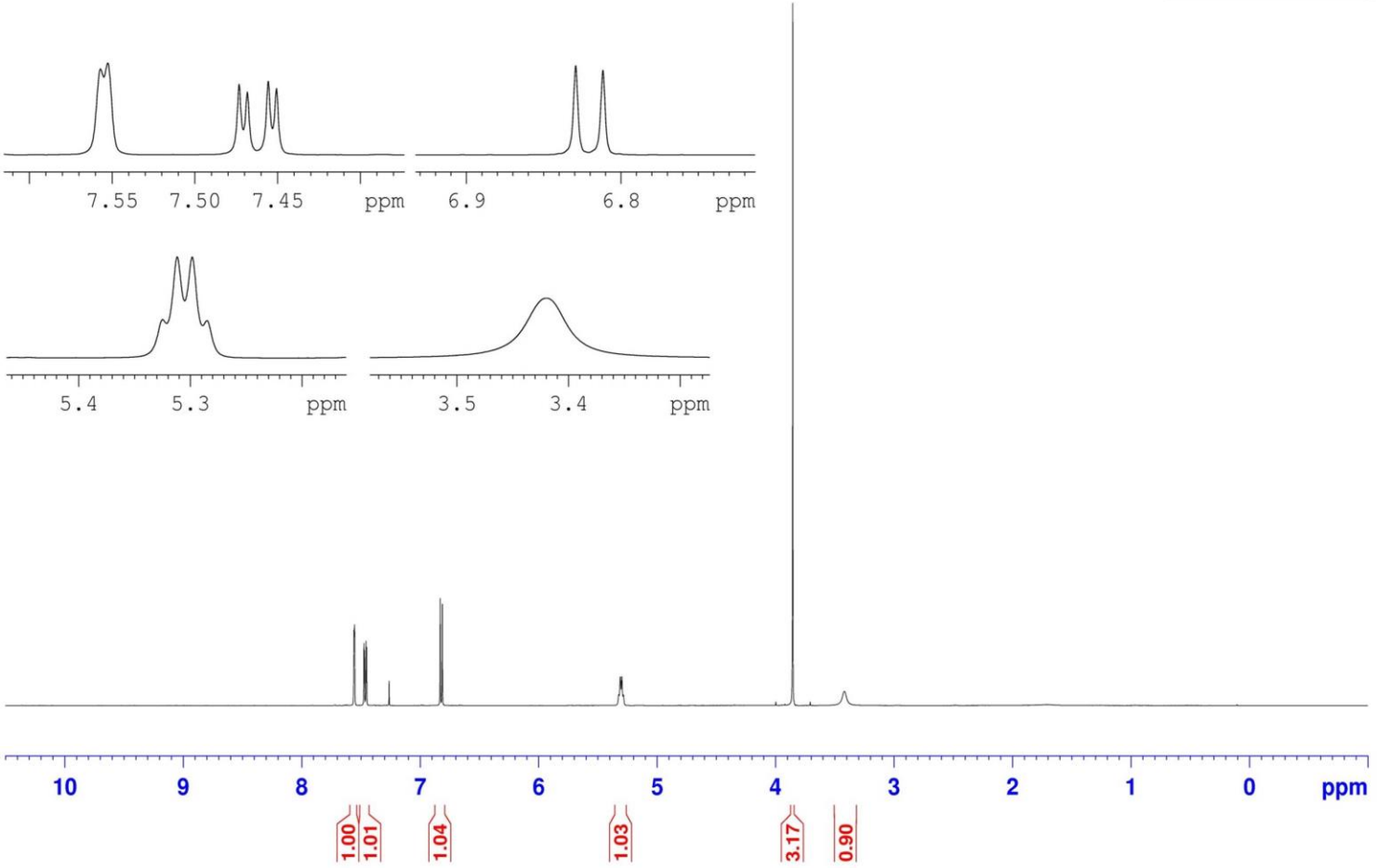
5–bromo–2–methoxybenzaldehyde
125 MHz, CDCl3



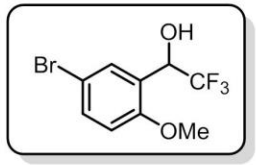


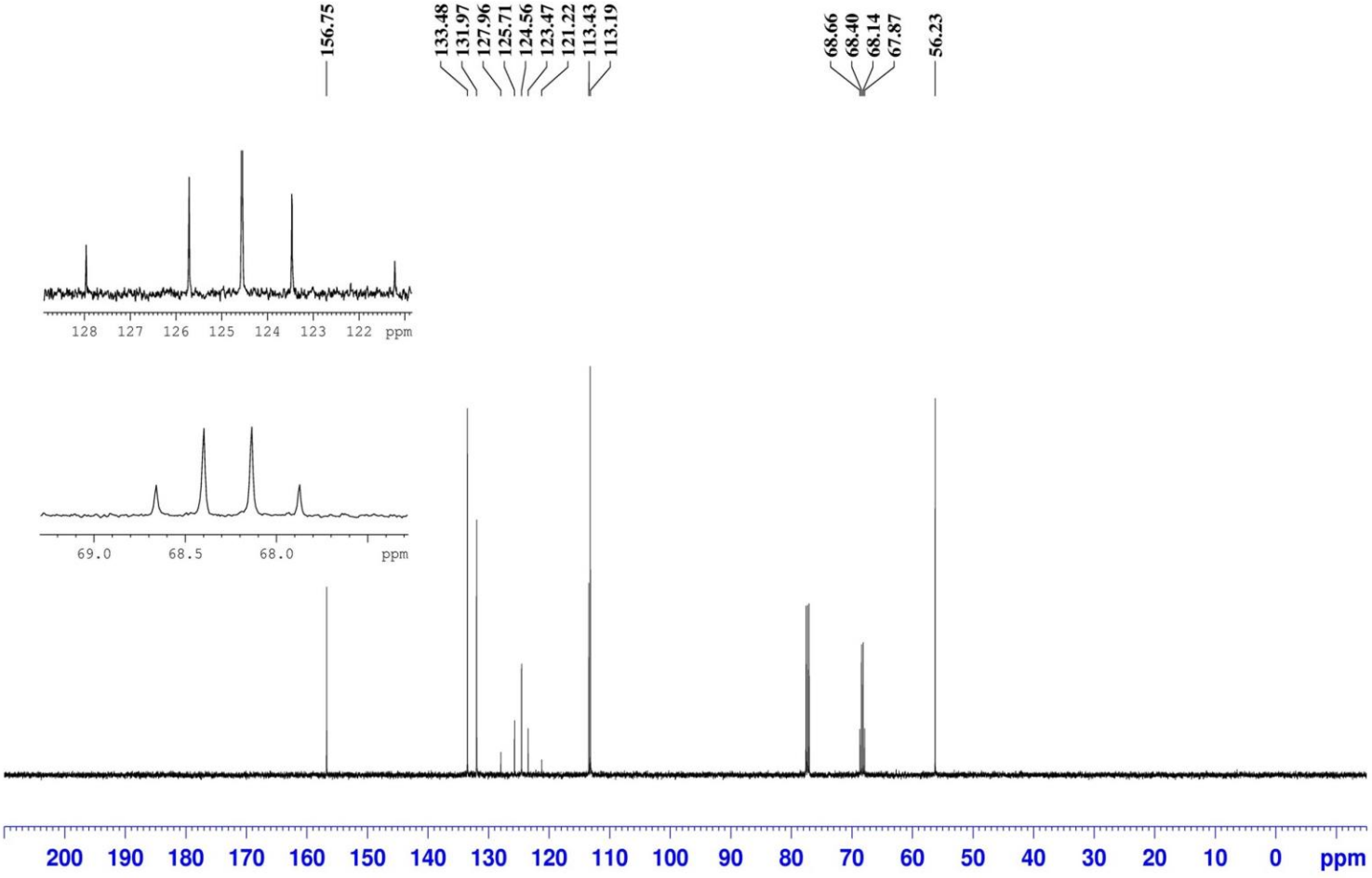
1–(5–bromo–2–methoxyphenyl)–2,2,2–trifluoroethanol
500 MHz. CDCl3



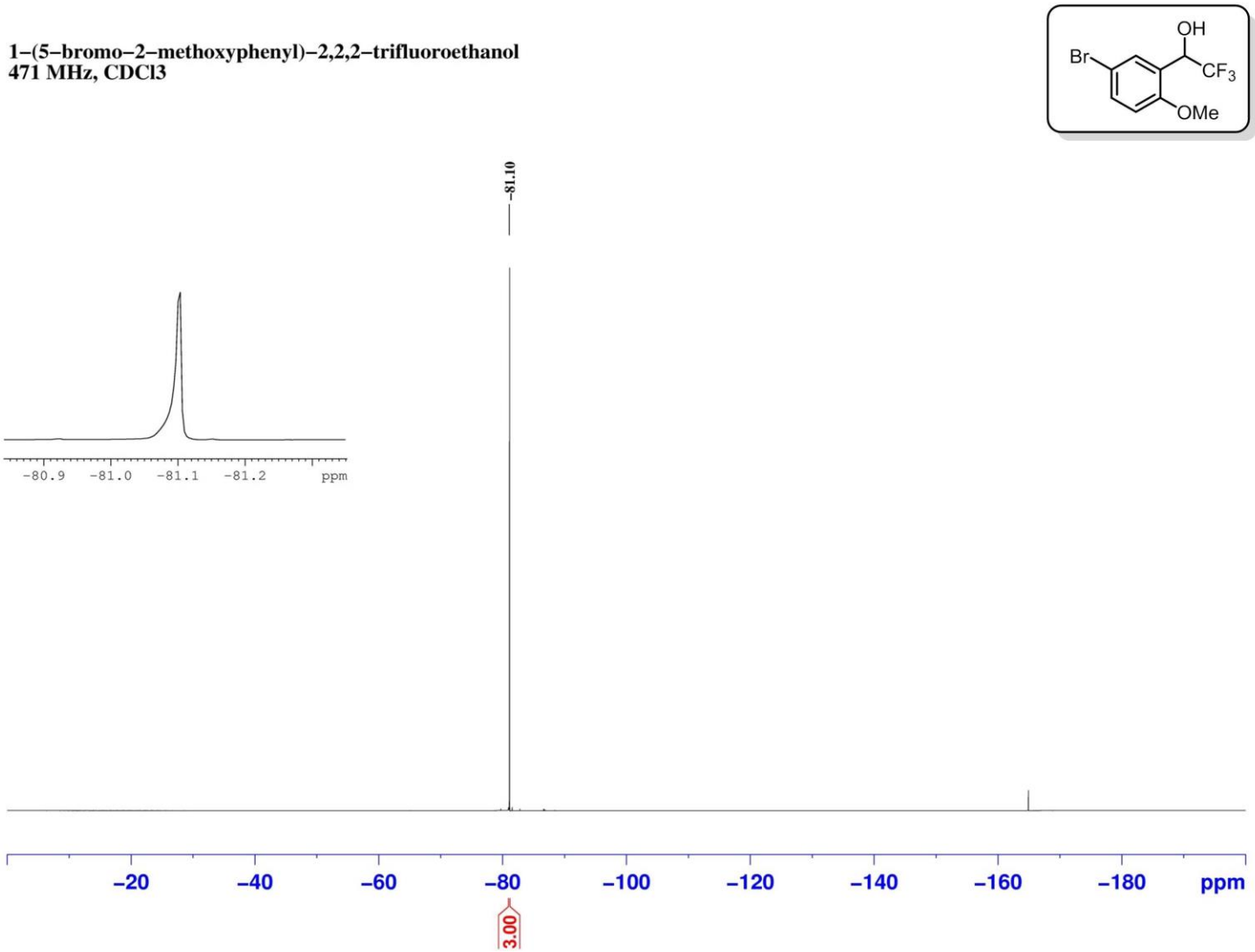


1–(5–bromo–2–methoxyphenyl)–2,2,2–trifluoroethanol
125 MHz, CDCl3

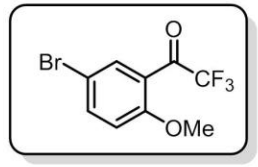


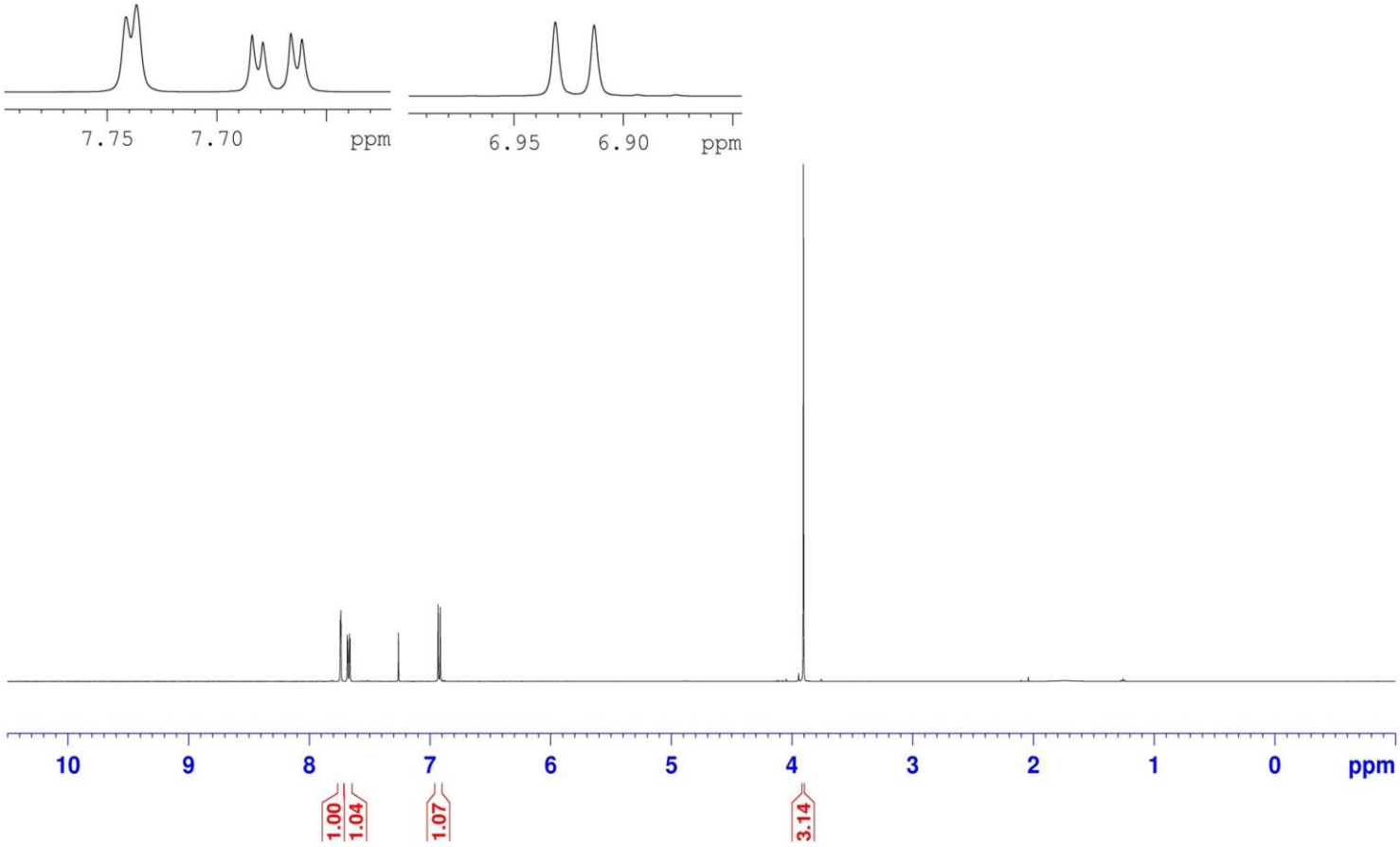


1–(5–bromo–2–methoxyphenyl)–2,2,2–trifluoroethanol
471 MHz, CDCl3

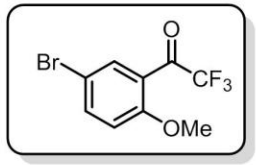


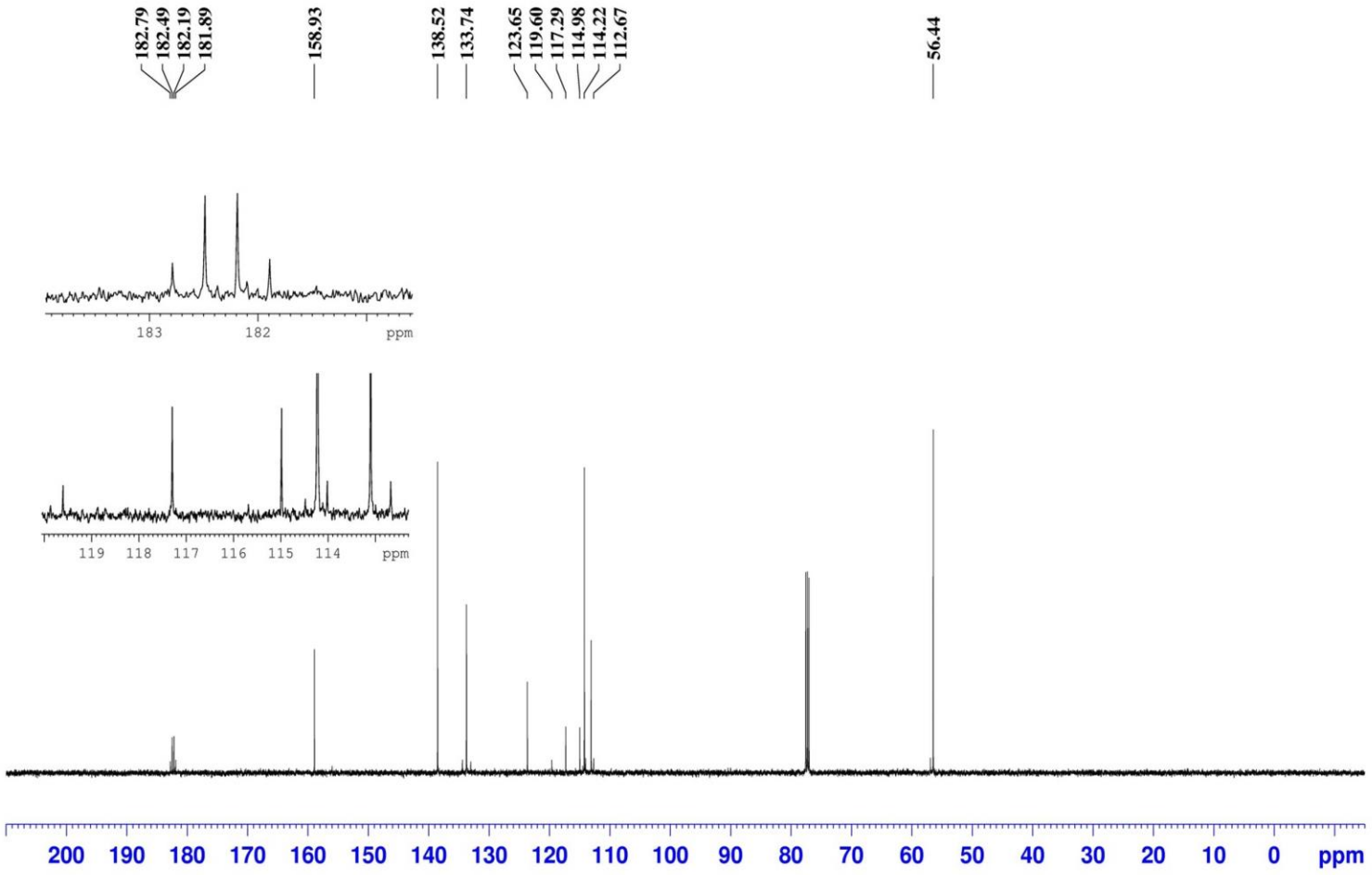
1–(5–bromo–2–methoxyphenyl)–2,2,2–trifluoroethanone
500 MHz, CDCl3



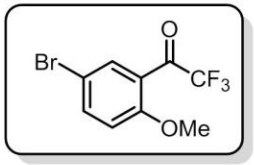


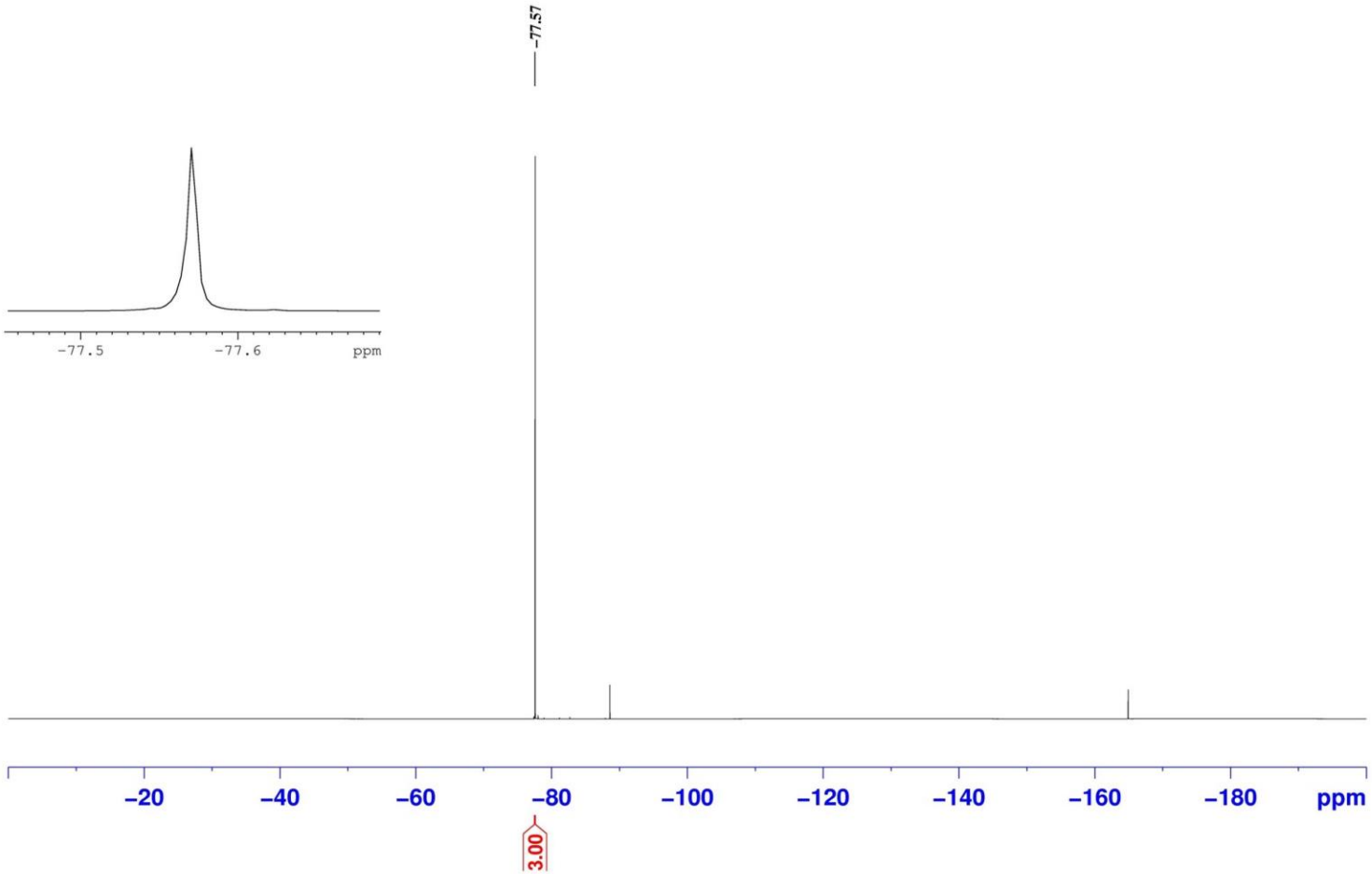
1–(5–bromo–2–methoxyphenyl)–2,2,2–trifluoroethanone
125 MHz, CDCl3



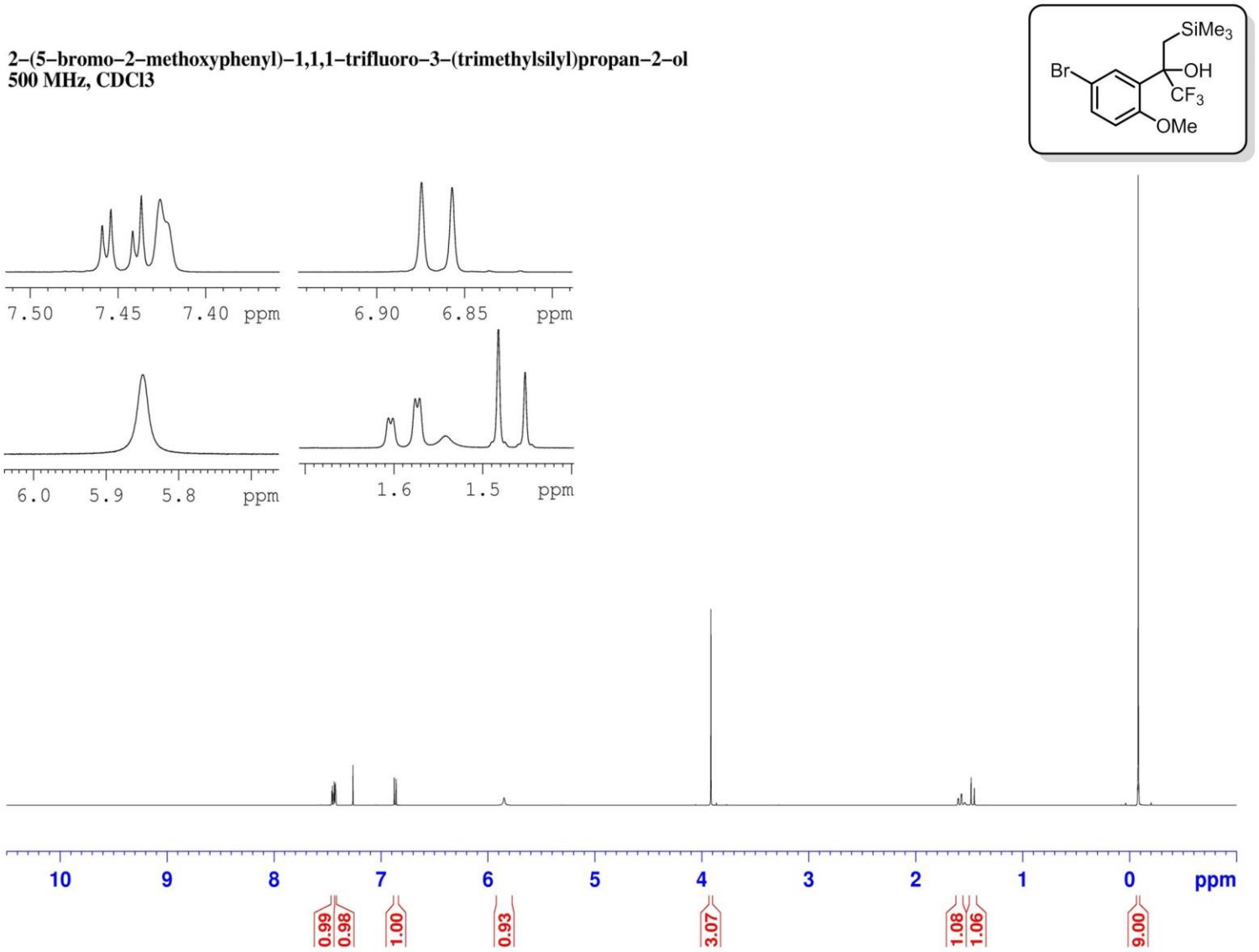


1–(5–bromo–2–methoxyphenyl)–2,2,2–trifluoroethanone
471 MHz, CDCl3

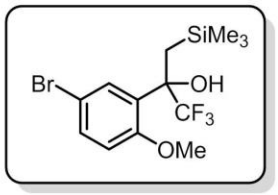


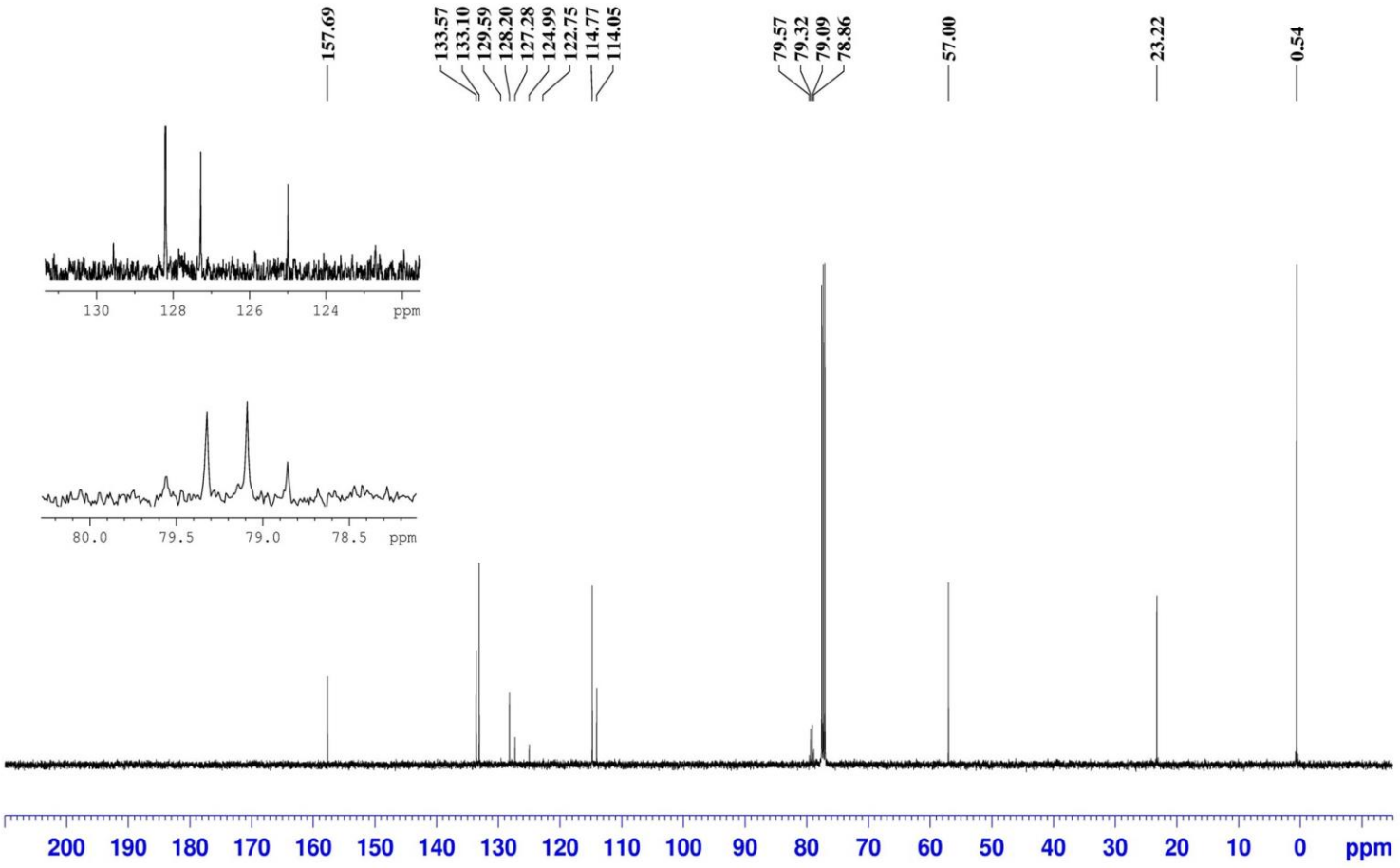


2–(5–bromo–2–methoxyphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
500 MHz, CDCl3

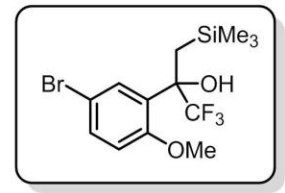


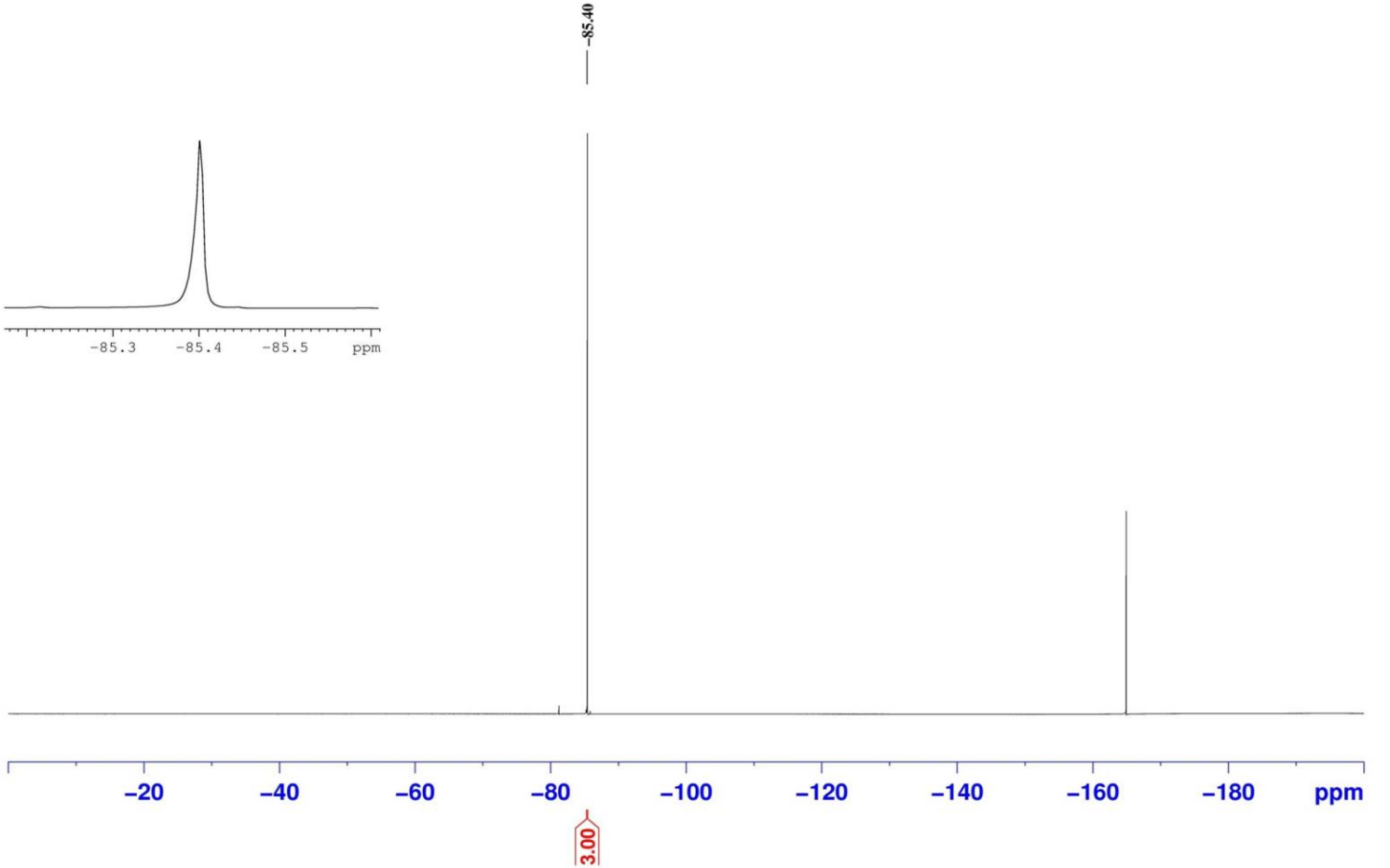
2–(5–bromo–2–methoxyphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
125 MHz, CDCl3



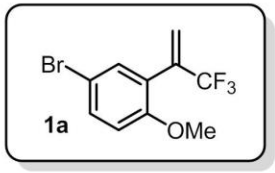


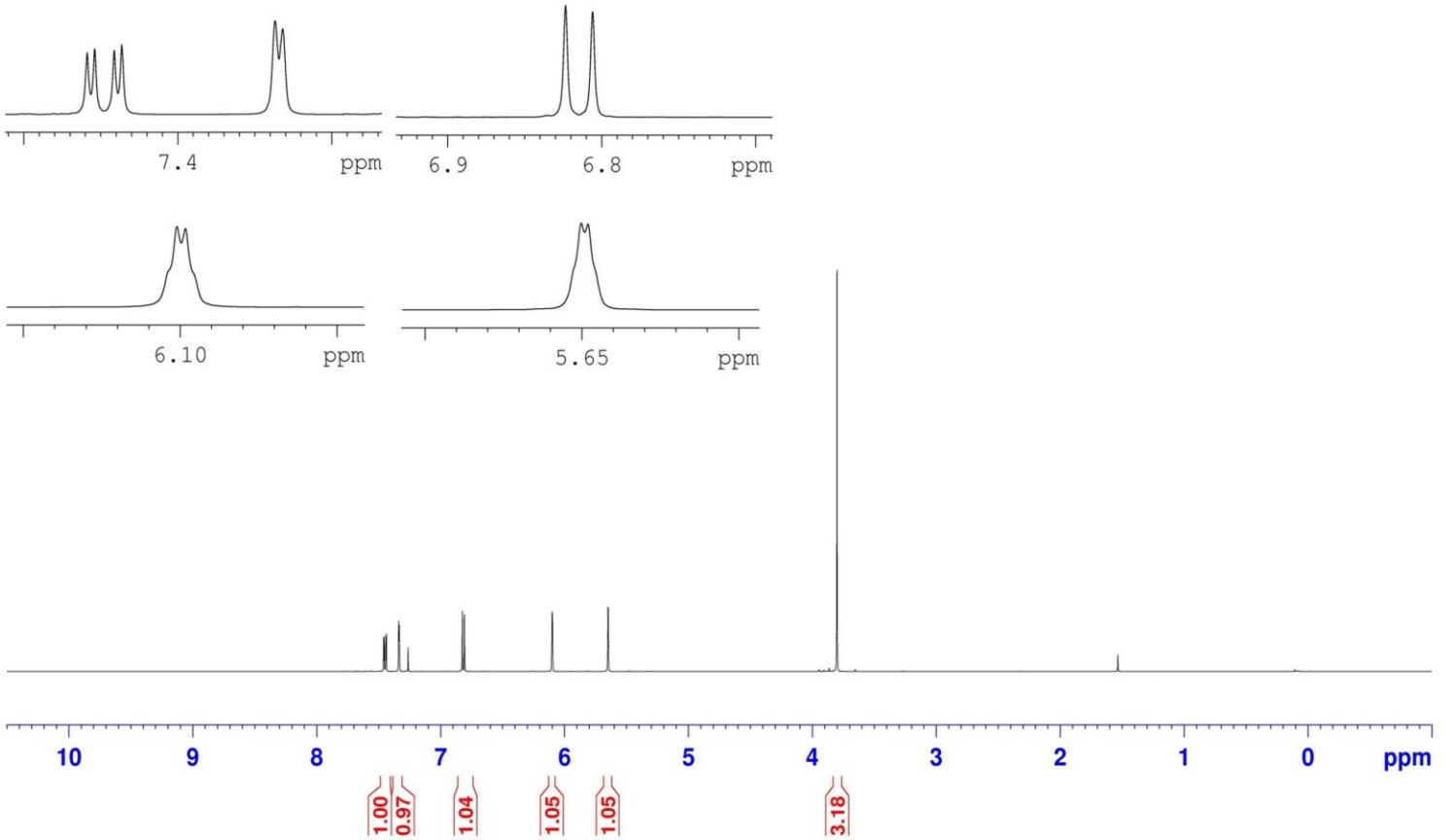
2–(5–bromo–2–methoxyphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
471 MHz, CDCl3



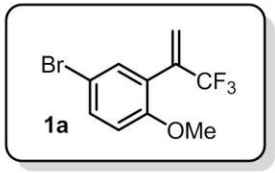


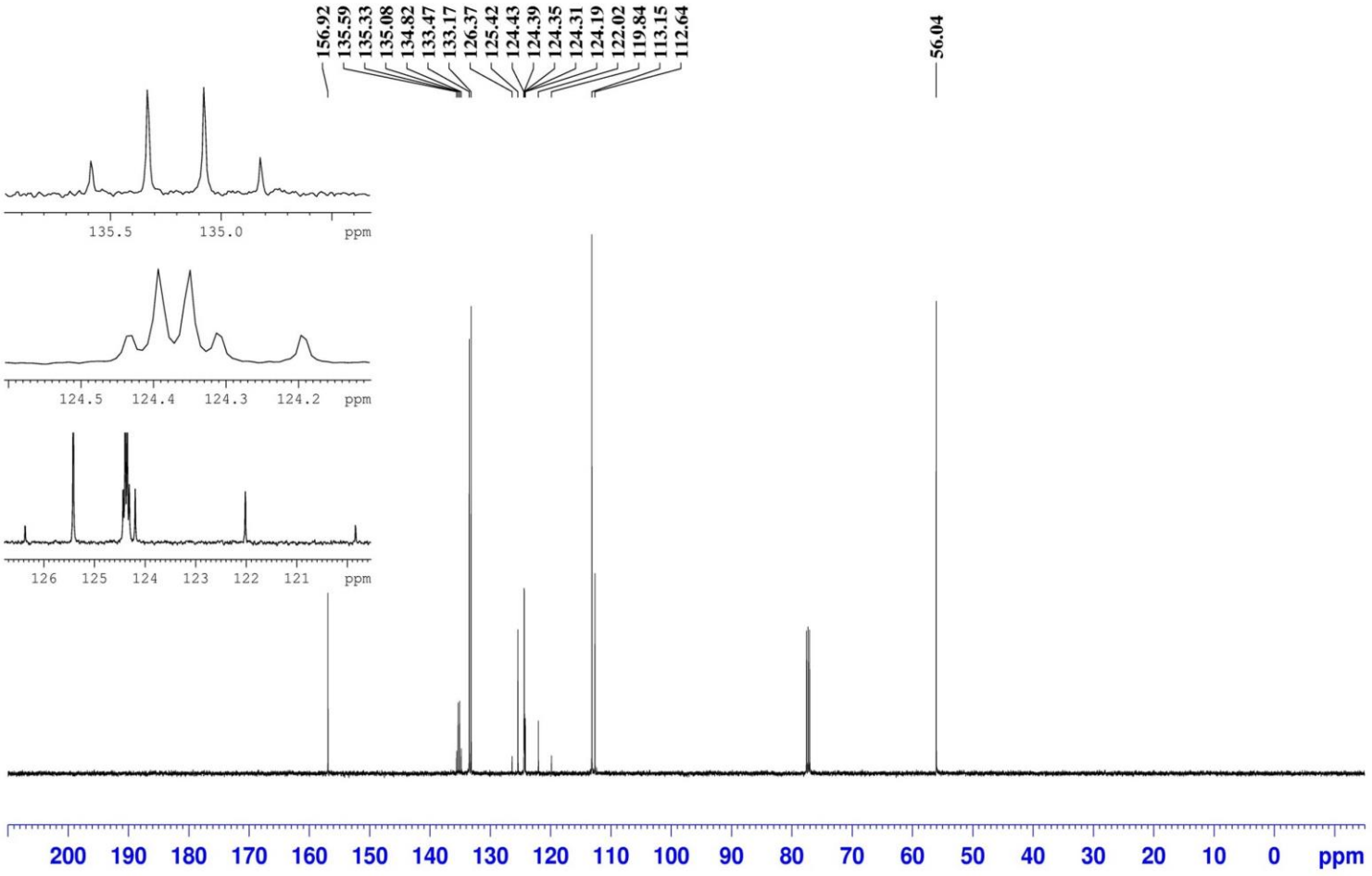
4–bromo–1–methoxy–2–(3,3,3–trifluoroprop–1–en–2–yl)benzene
500 MHz, CDCl3



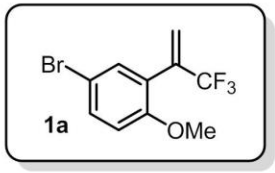


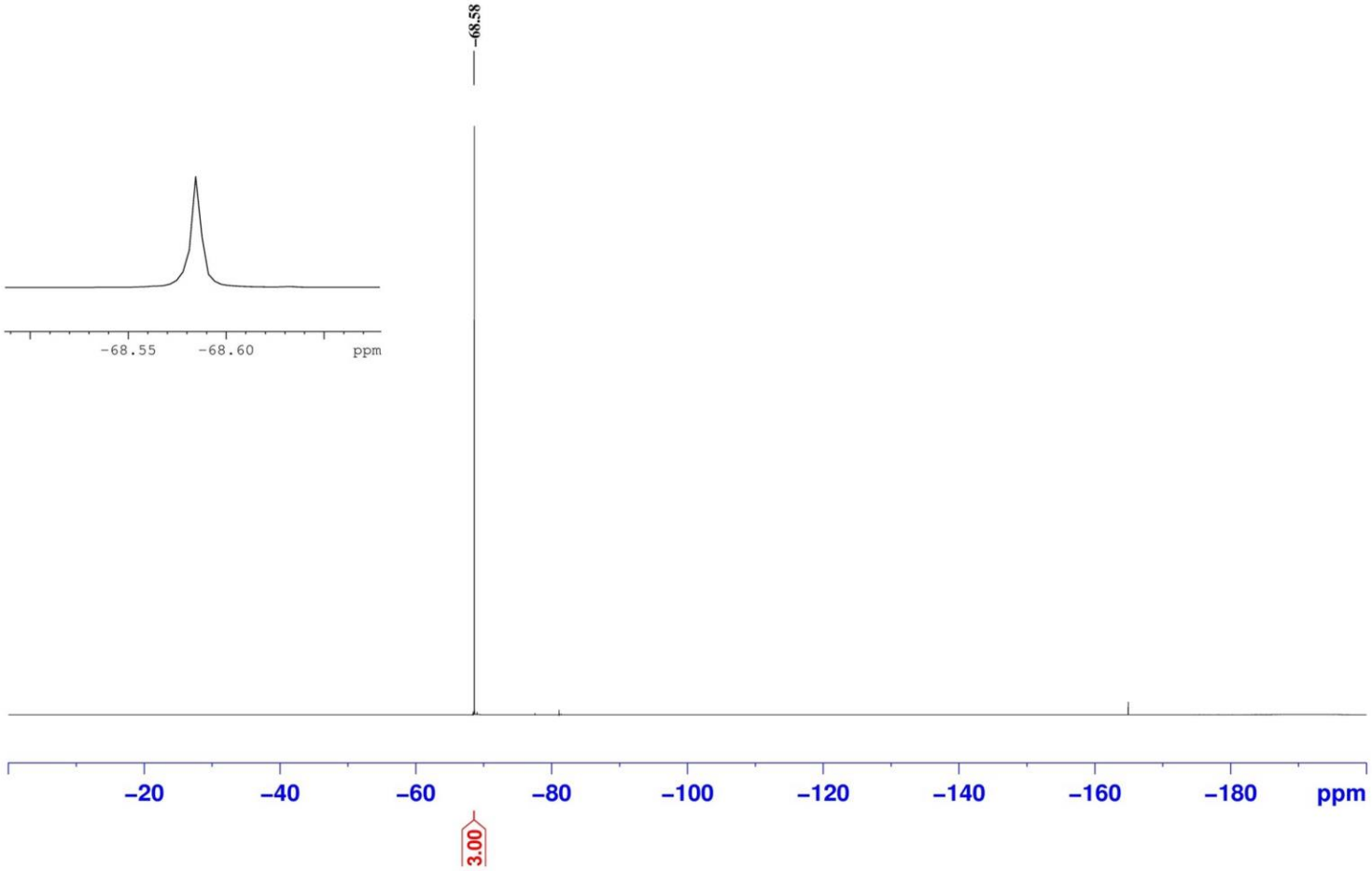
4–bromo–1–methoxy–2–(3,3,3–trifluoroprop–1–en–2–yl)benzene
125 MHz, CDCl3



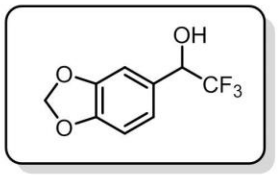


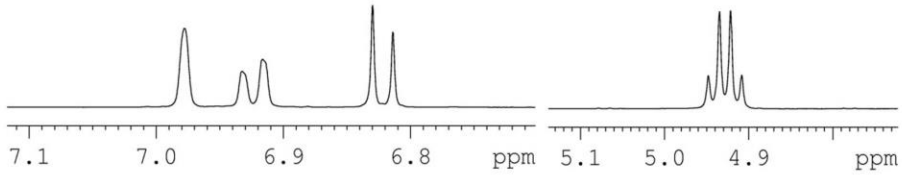
4–bromo–1–methoxy–2–(3,3,3–trifluoroprop–1–en–2–yl)benzene
471 MHz, CDCl3

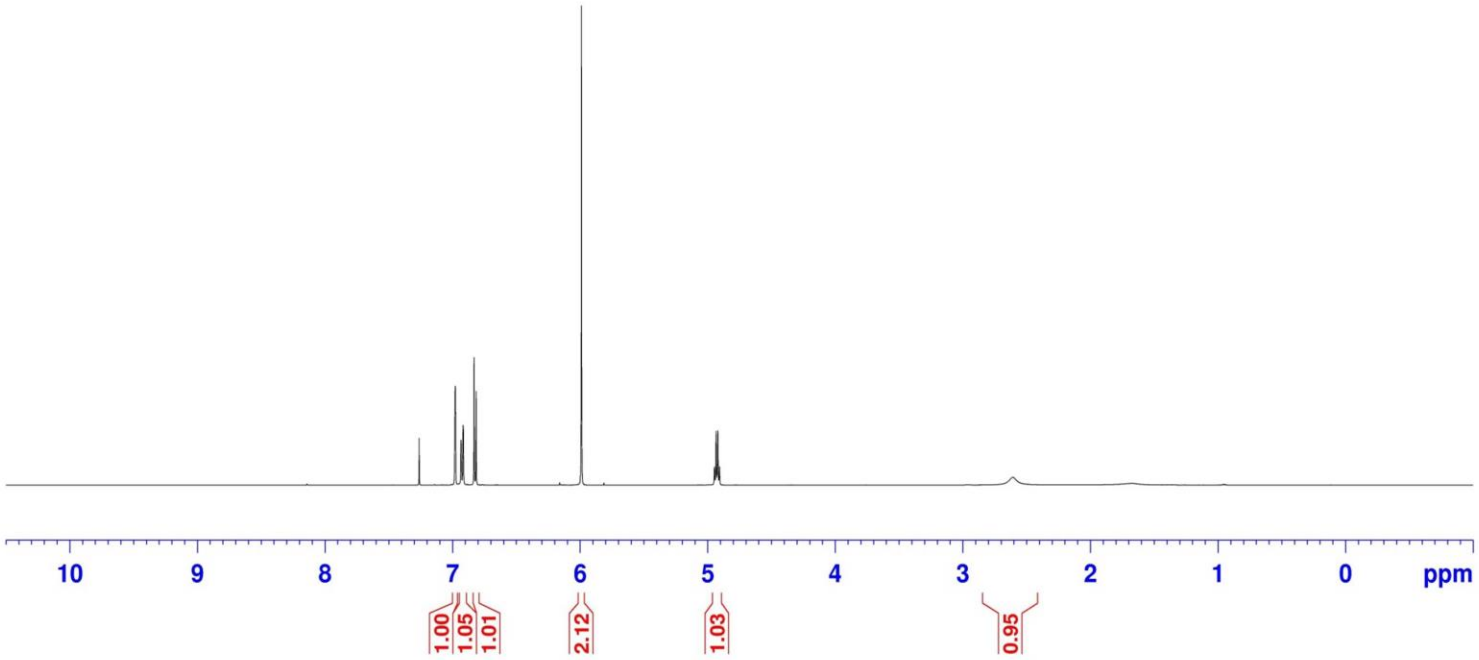




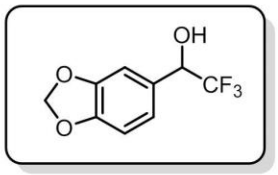
1–(benzo[d][1,3]dioxol–5–yl)–2,2,2–trifluoroethanol
500 MHz, CDCl3

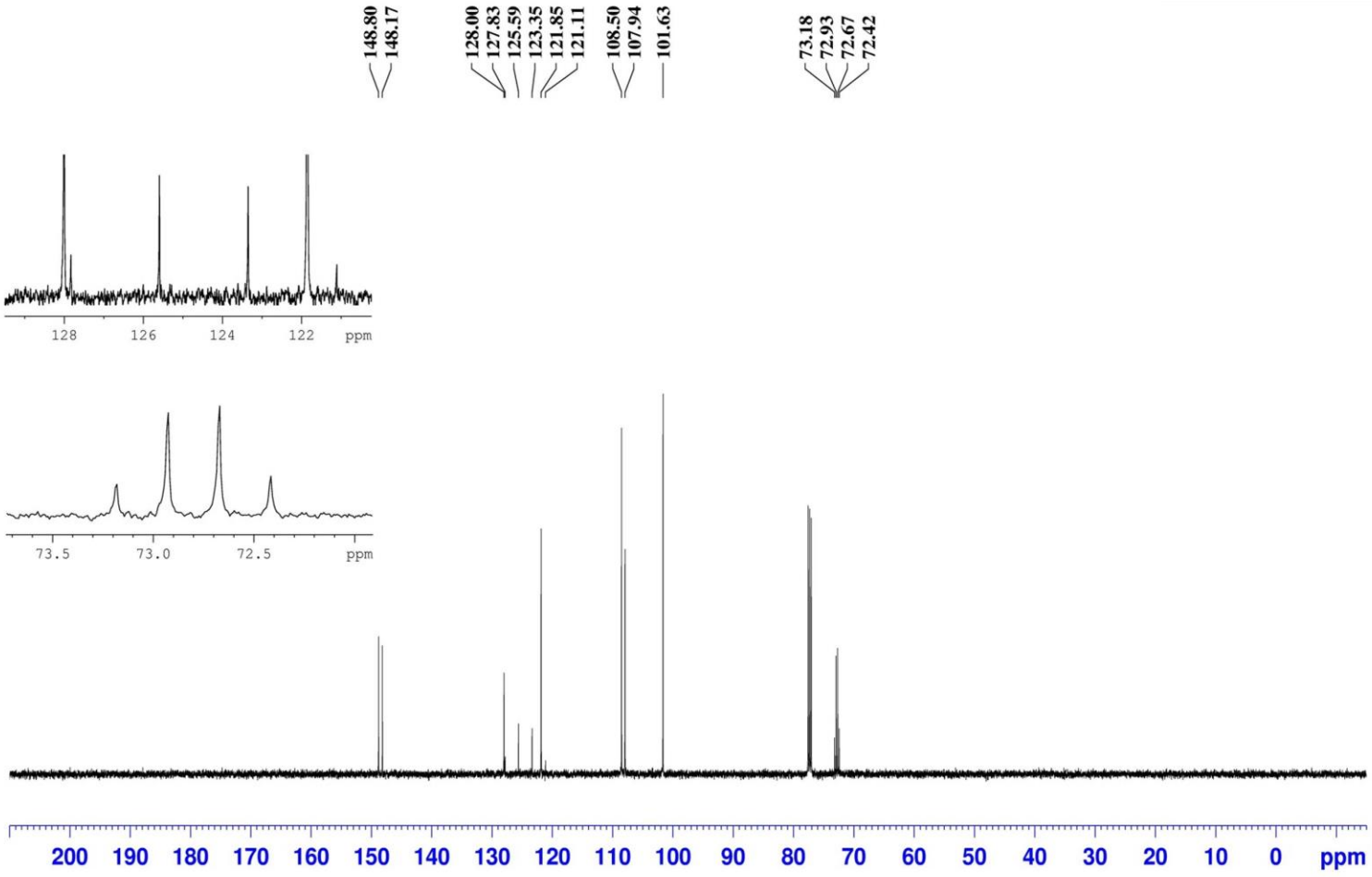




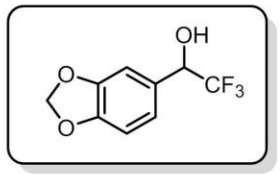


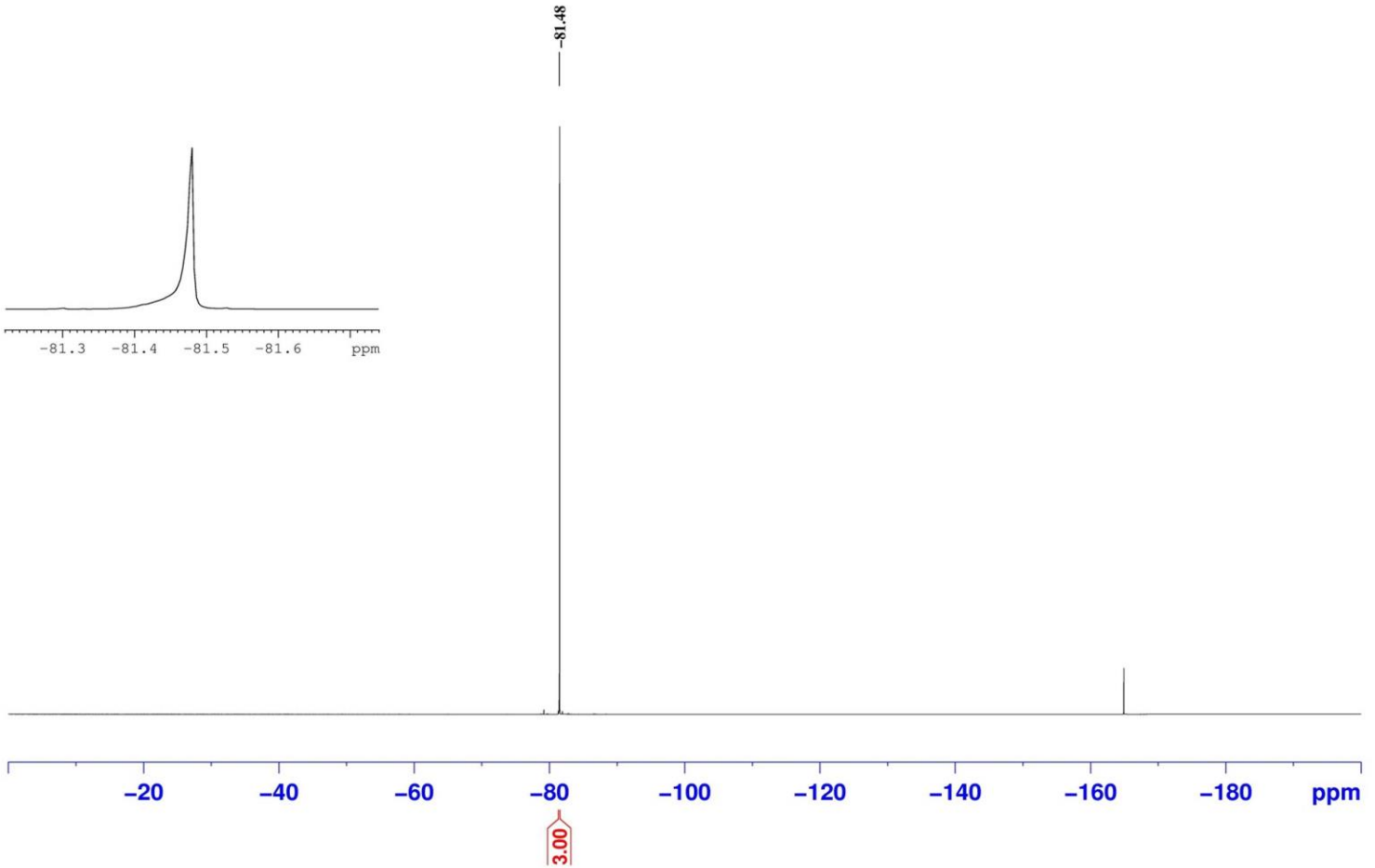
1−(benzo[d][1,3]dioxol−5−yl)−2,2,2−trifluoroethanol
125 MHz, CDCl3



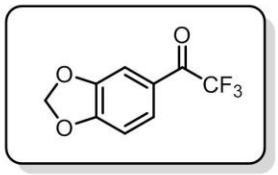


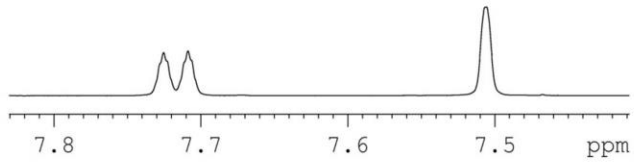
1–(benzo[d][1,3]dioxol–5–yl)–2,2,2–trifluoroethanol
471 MHz, CDCl3

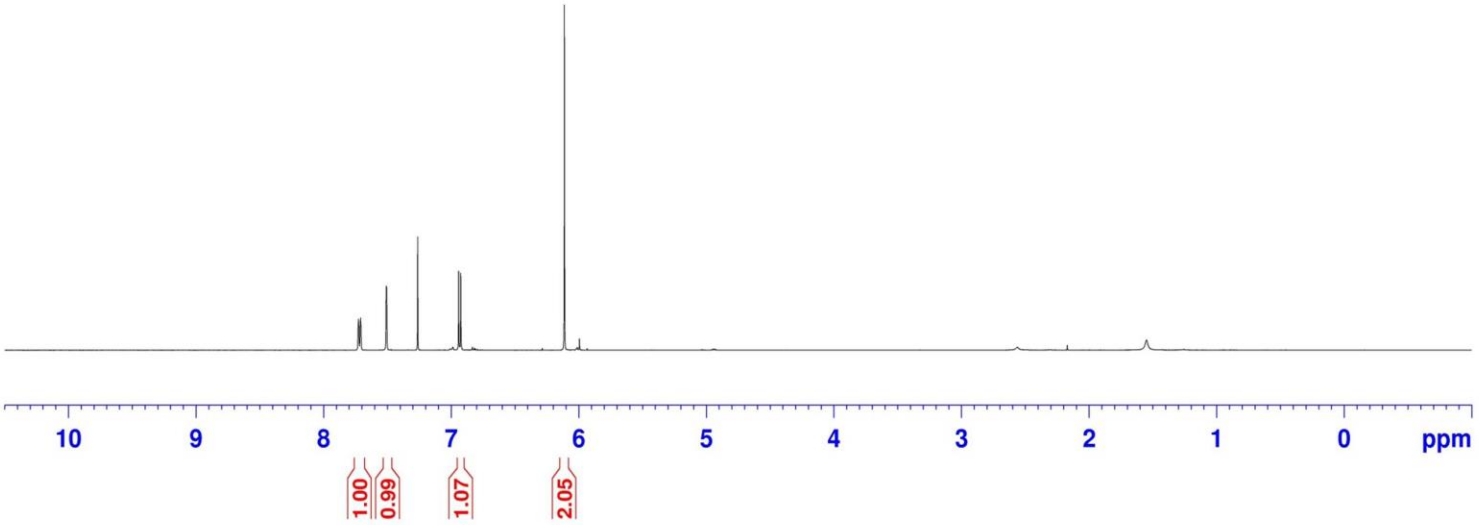




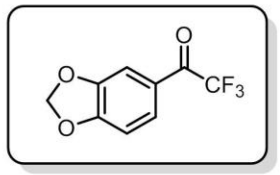
1–(benzo[d][1,3]dioxol–5–yl)–2,2,2–trifluoroethanone
500 MHz, CDCl3

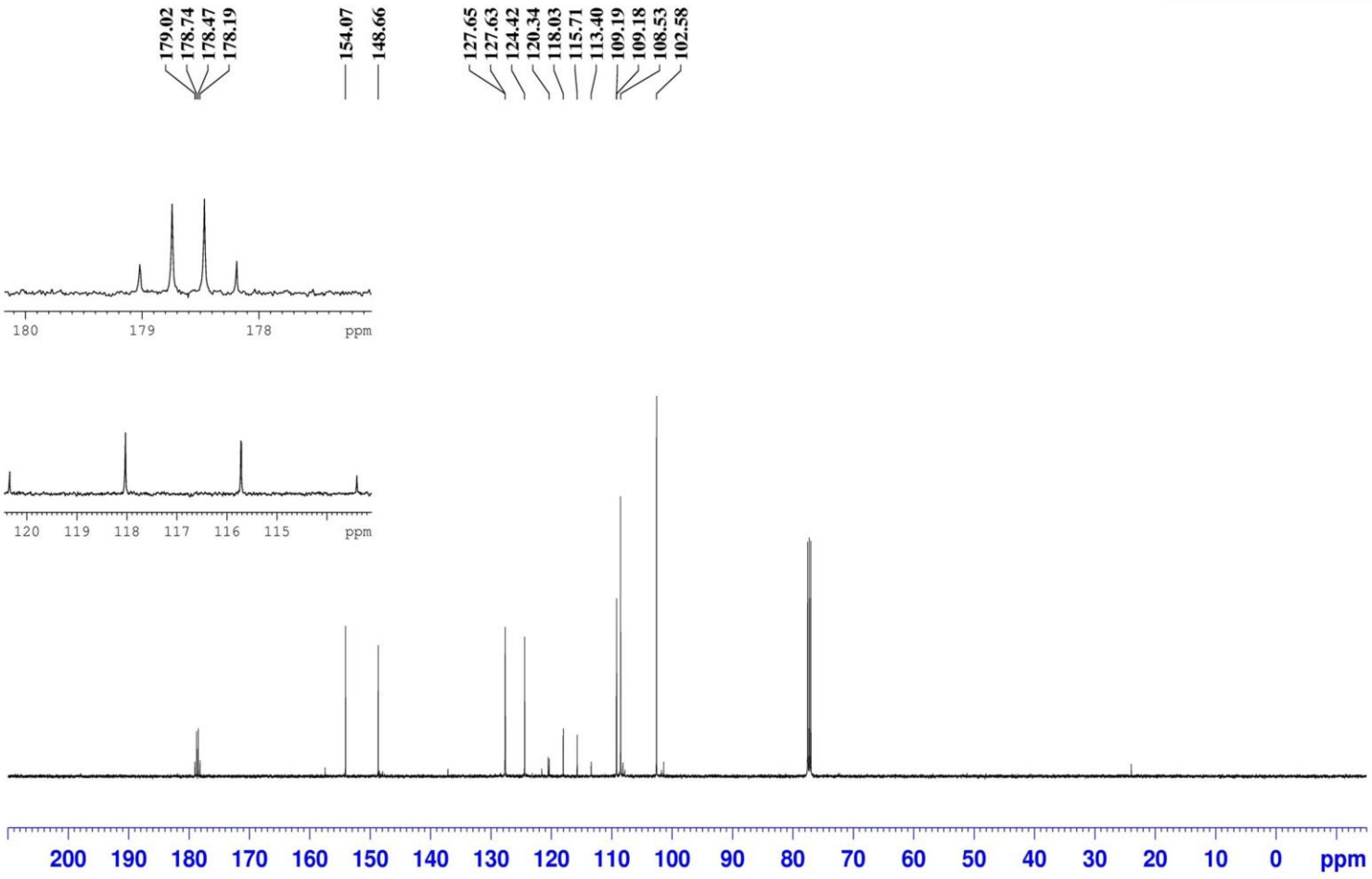




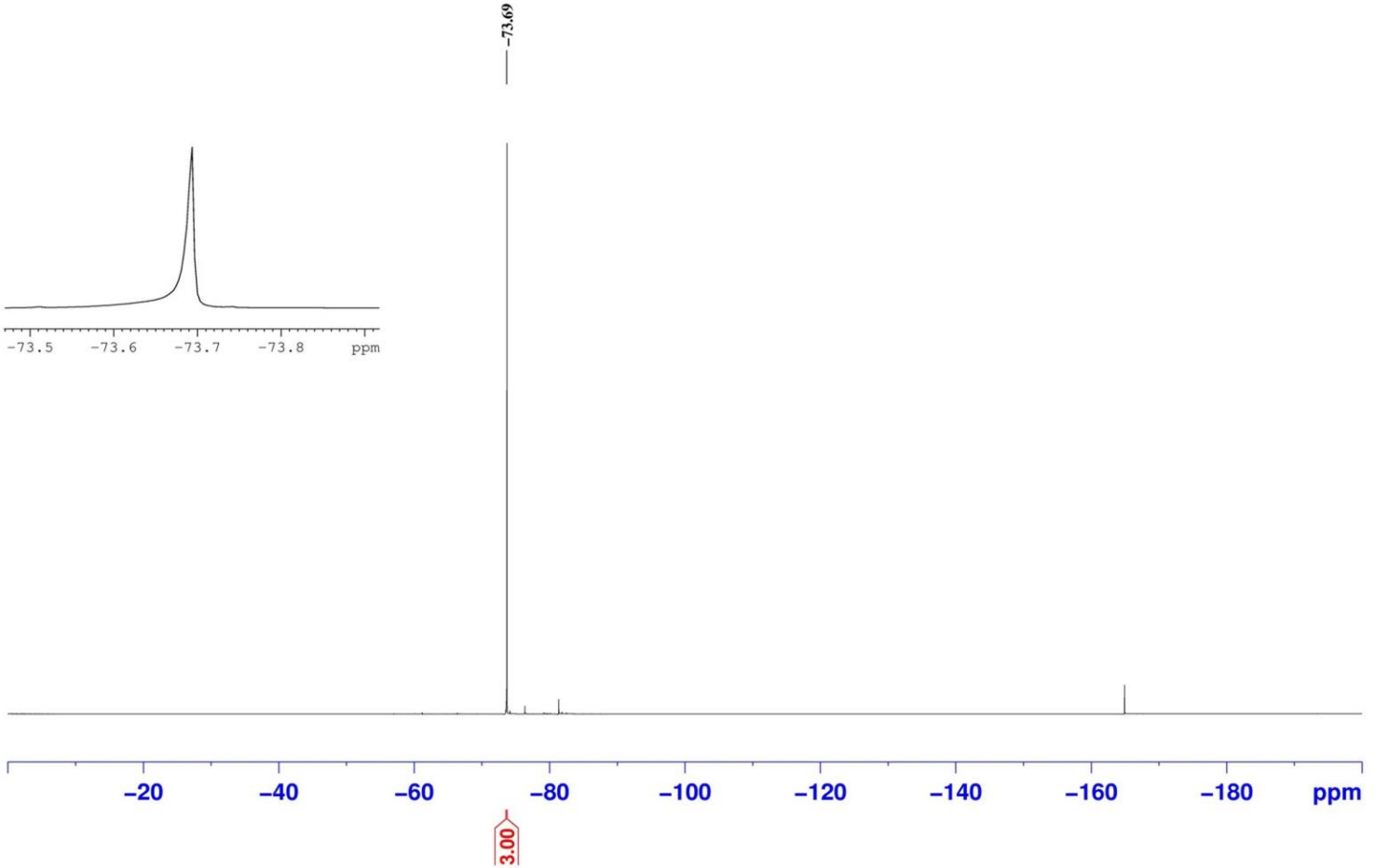


1–(benzo[d][1,3]dioxol–5–yl)–2,2,2–trifluoroethanone
125 MHz, CDCl3

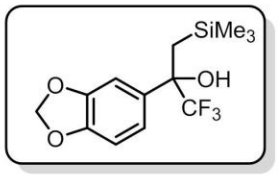


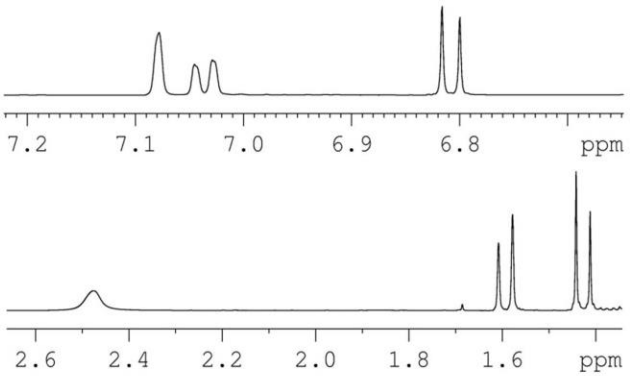


1–(benzo[d][1,3]dioxol–5–yl)–2,2,2–trifluoroethanone
471 MHz, CDCl3

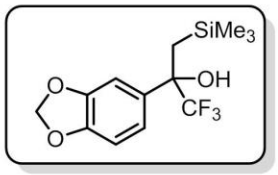


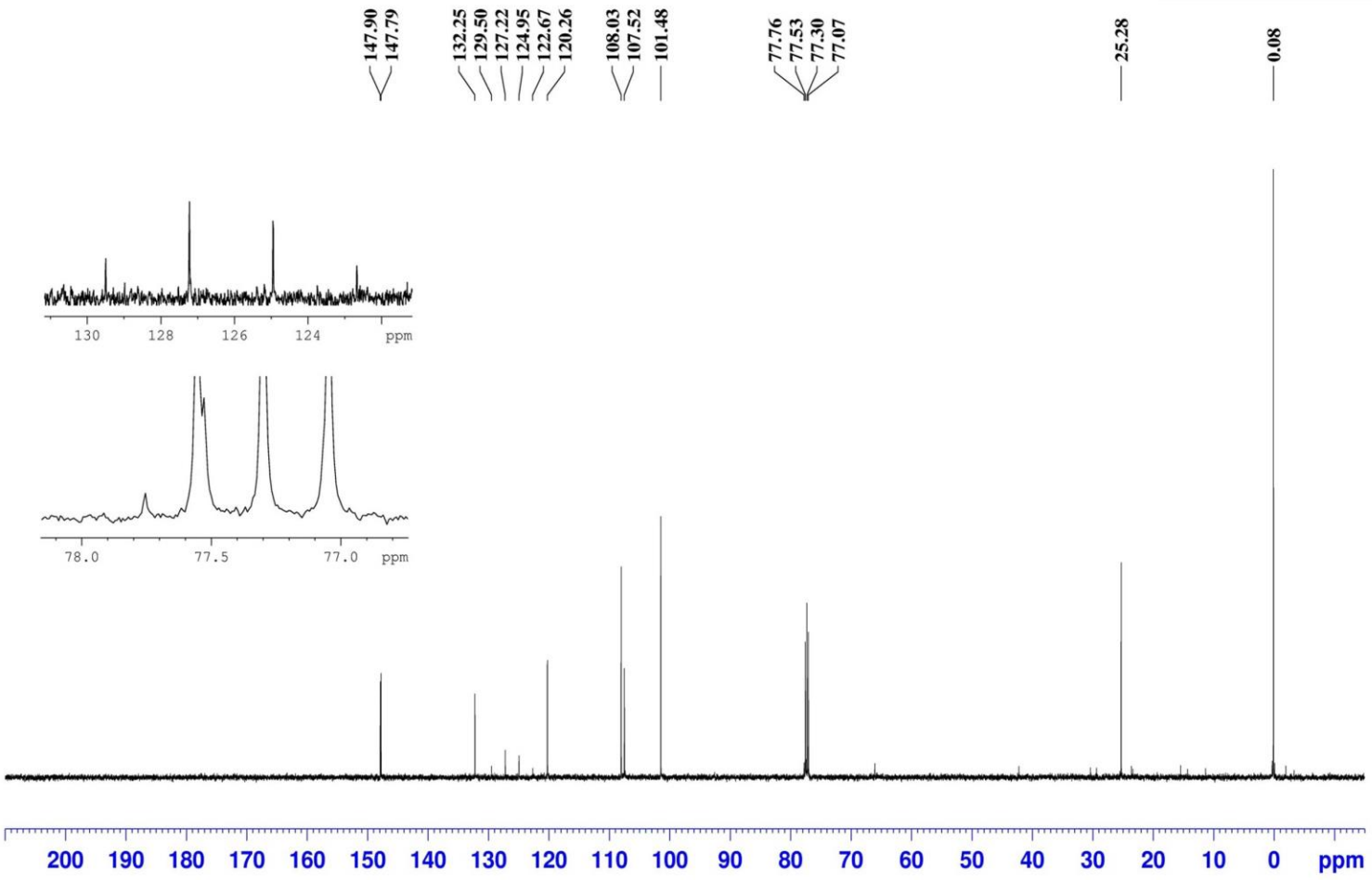
2–(benzo[d][1,3]dioxol–5–yl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
500 MHz, CDCl3



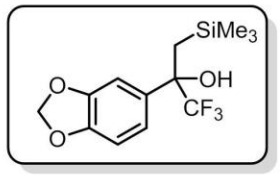


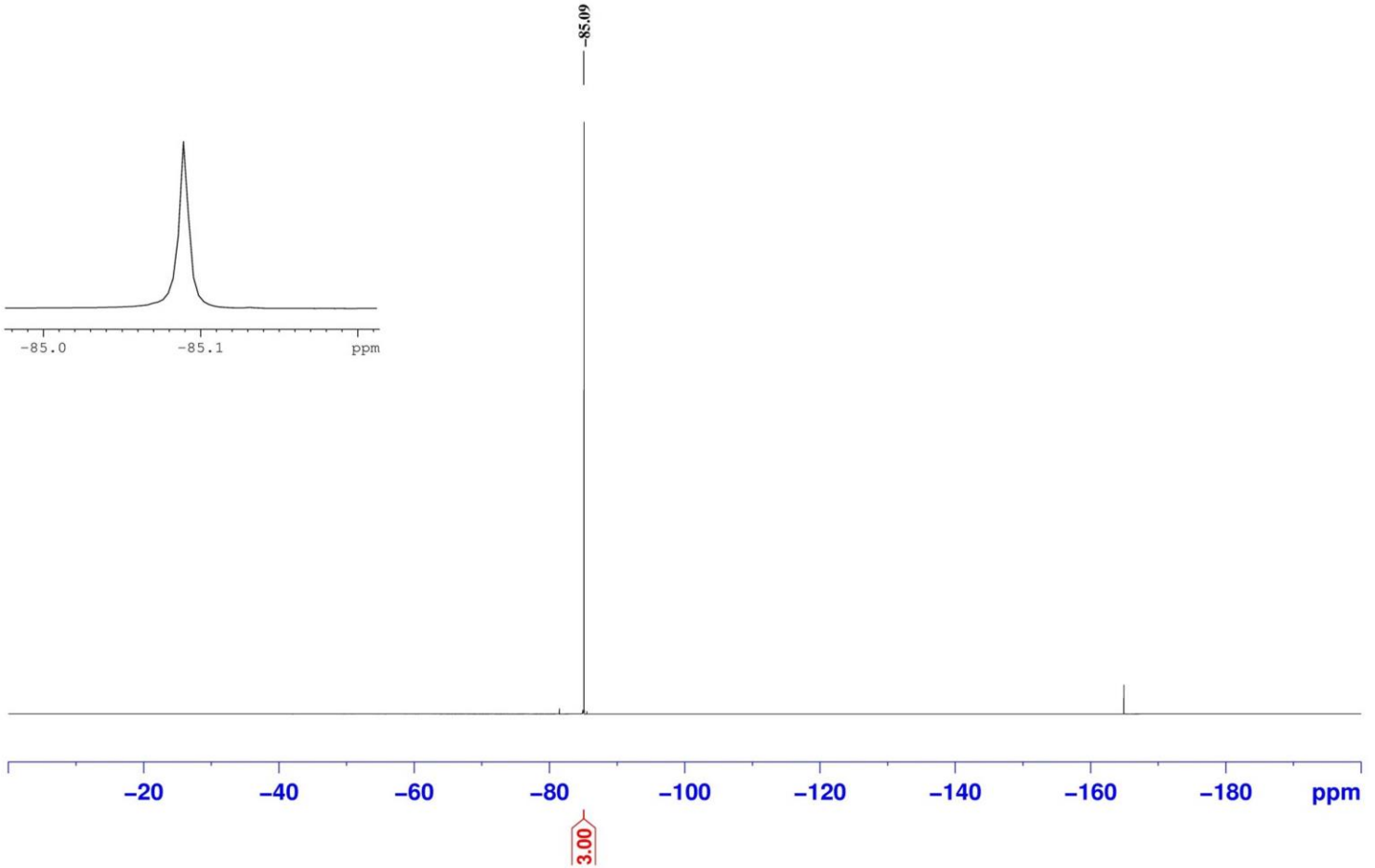
2–(benzo[d][1,3]dioxol–5–yl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
125 MHz, CDCl3



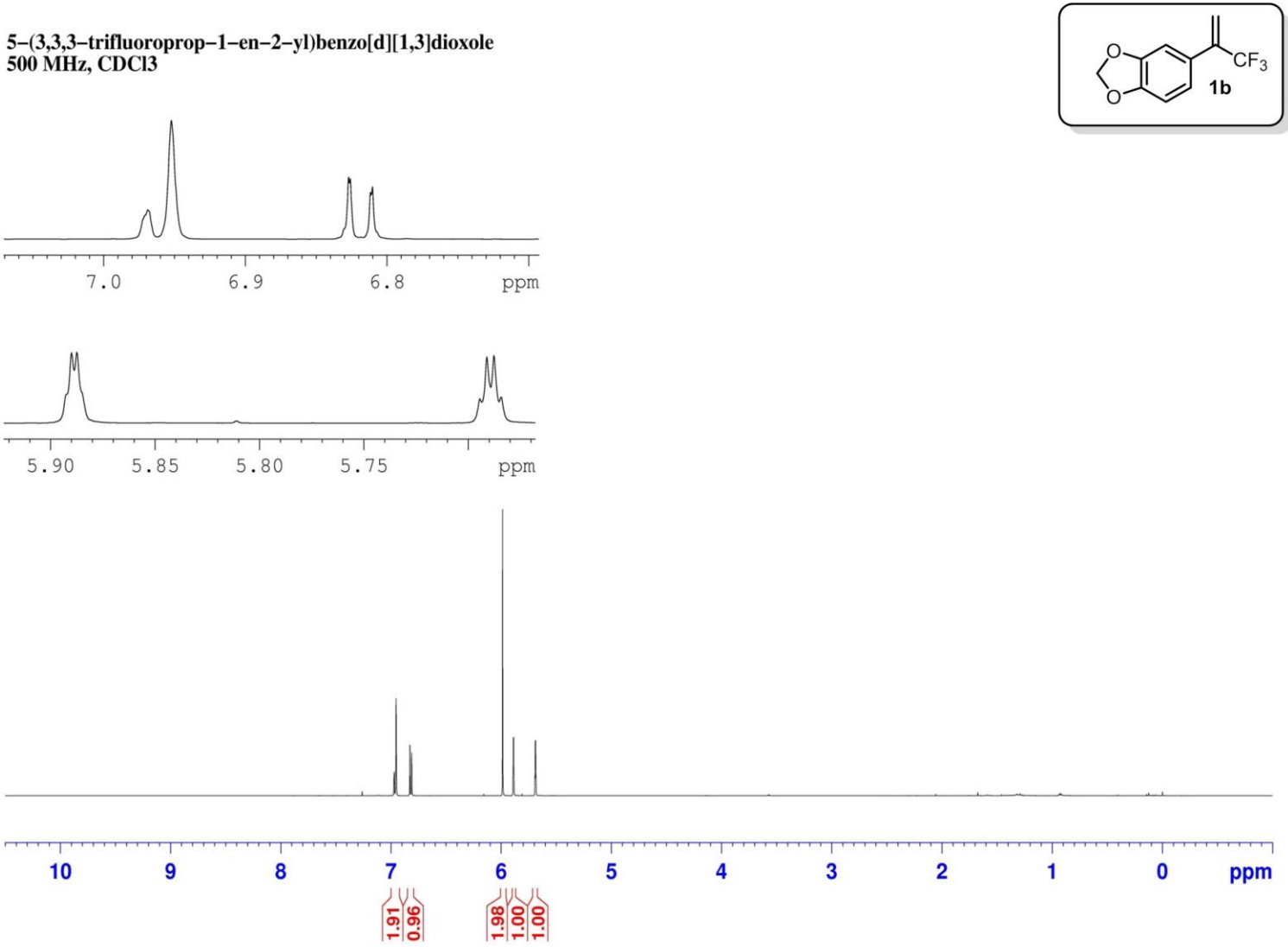


2–(benzo[d][1,3]dioxol–5–yl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol
471 MHz, CDCl3

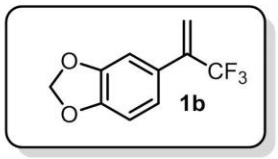


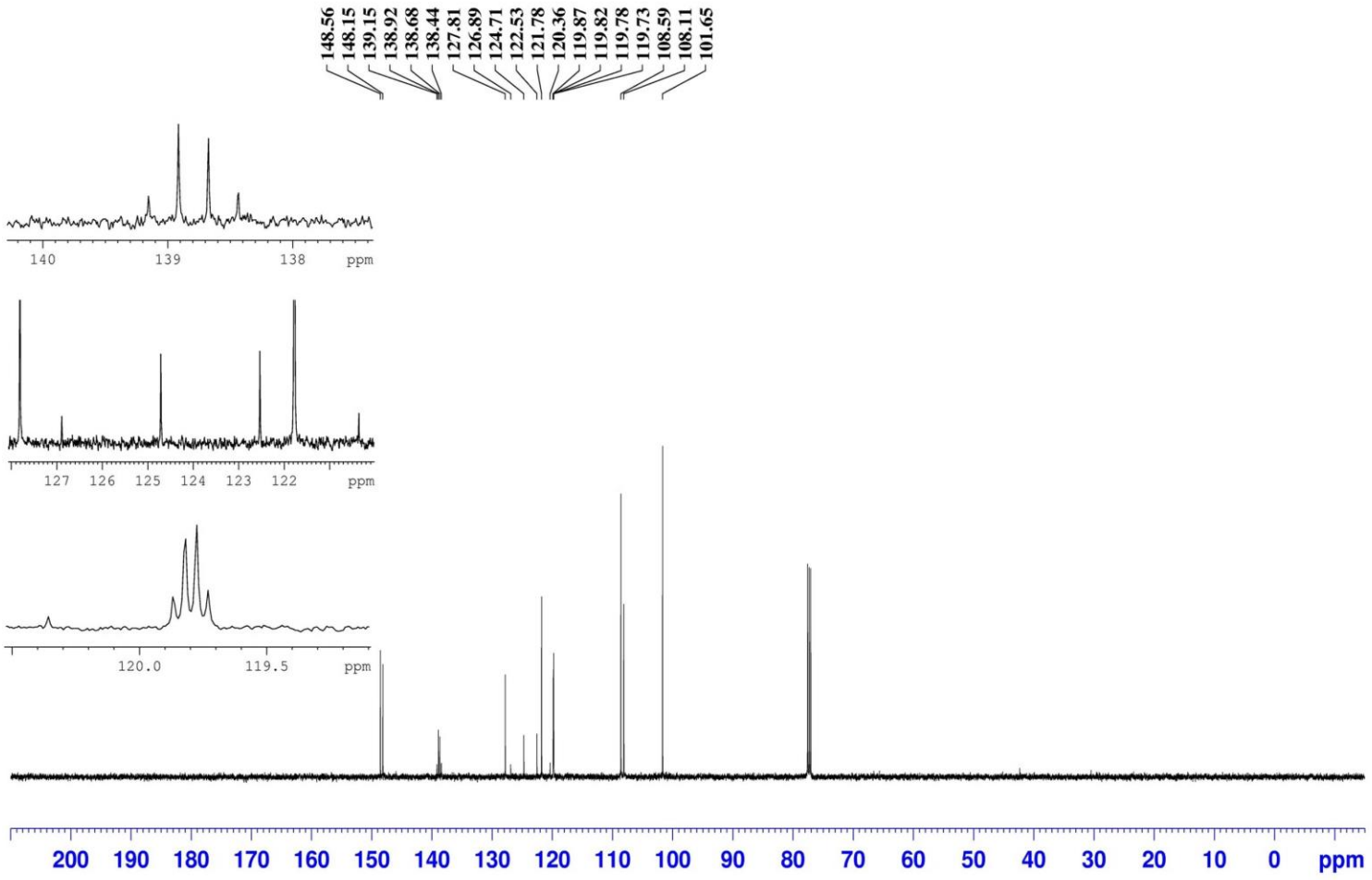


5−(3,3,3−trifluoroprop−1−en−2−yl)benzo[d][1,3]dioxole
500 MHz, CDCl3

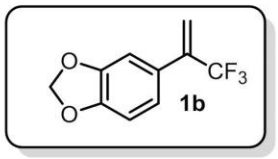


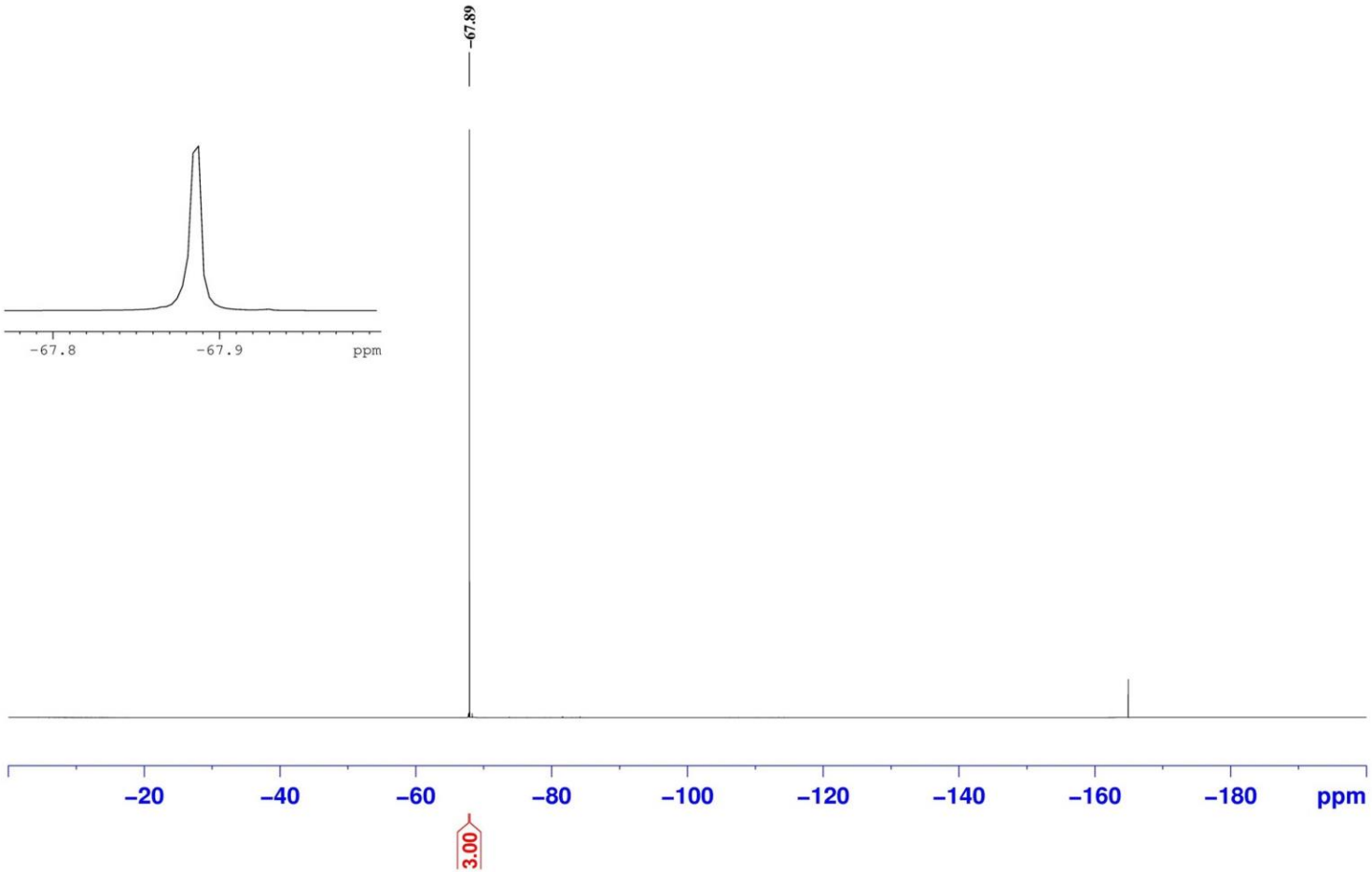
5–(3,3,3–trifluoroprop–1–en–2–yl)benzo[d][1,3]dioxole
125 MHz, CDCl3



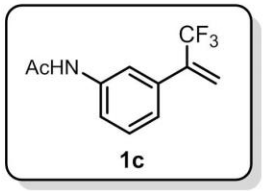


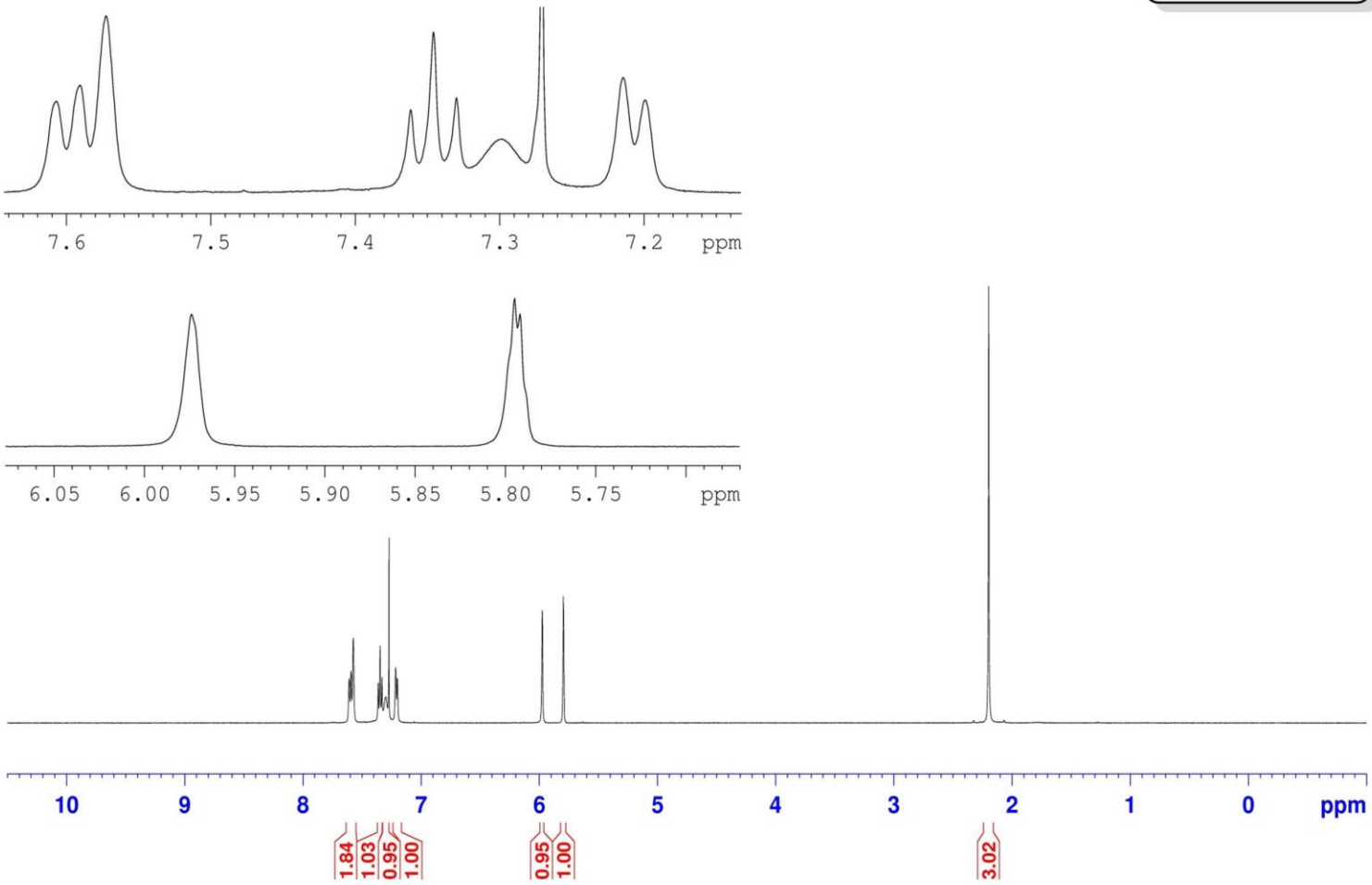
5–(3,3,3–trifluoroprop–1–en–2–yl)benzo[d][1,3]dioxole
471 MHz, CDCl3



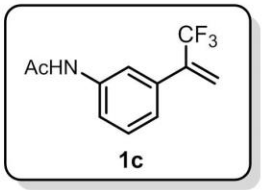


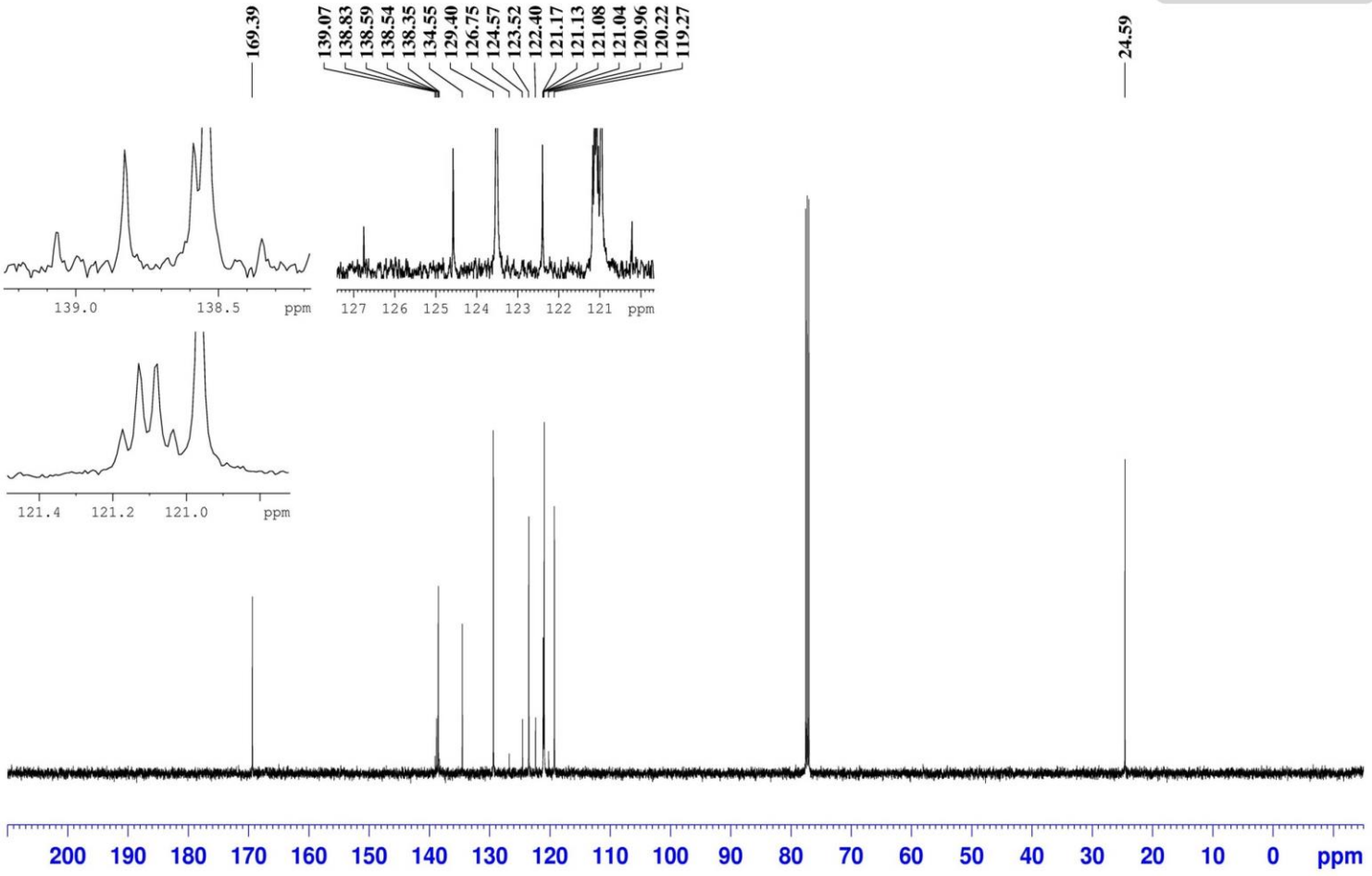
N–(3–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)acetamide
500 MHz, CDCl3



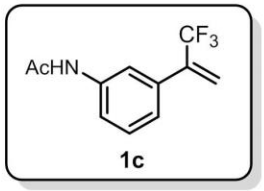


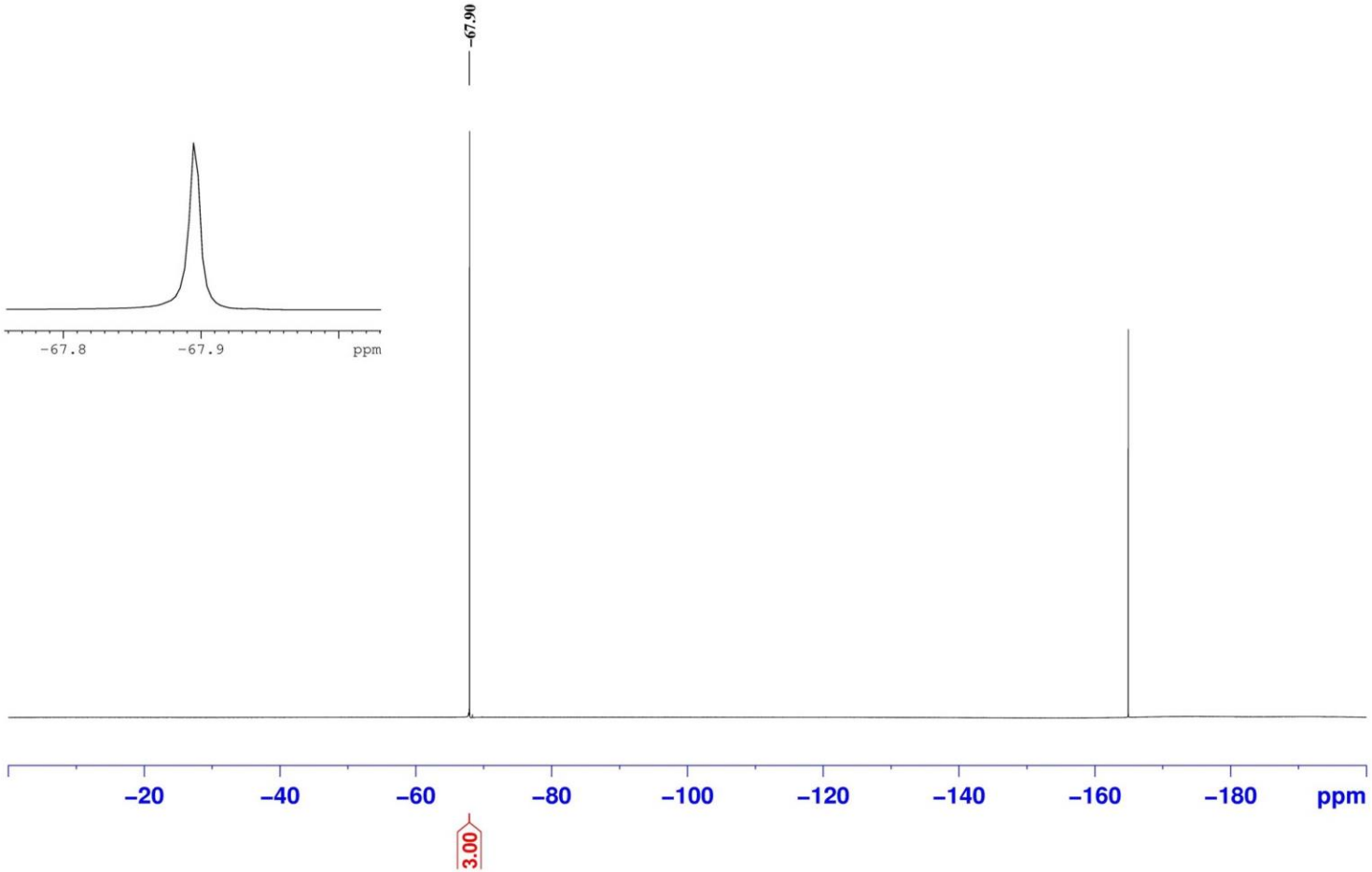
N–(3–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)acetamide
125 MHz, CDCl



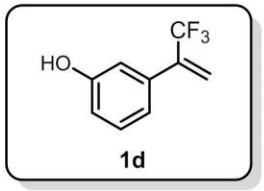


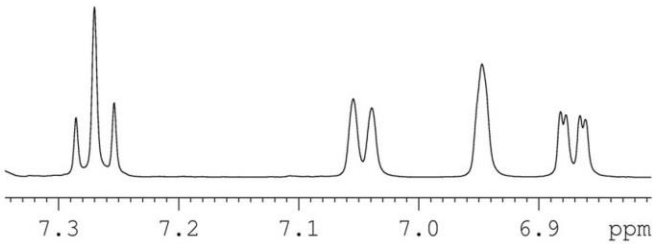
N–(3–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)acetamide
471 MHz, CDCl3

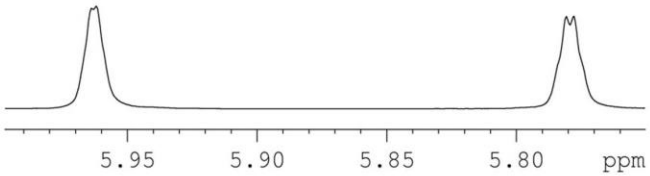


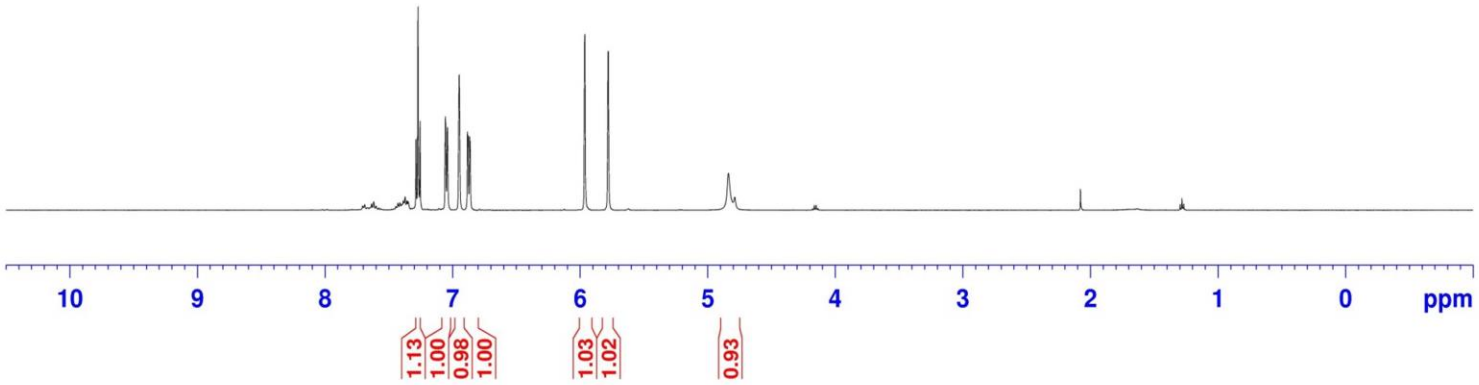


3–(3,3,3–trifluoroprop–1–en–2–yl)phenol
500 MHz, CDCl3

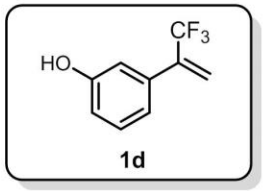


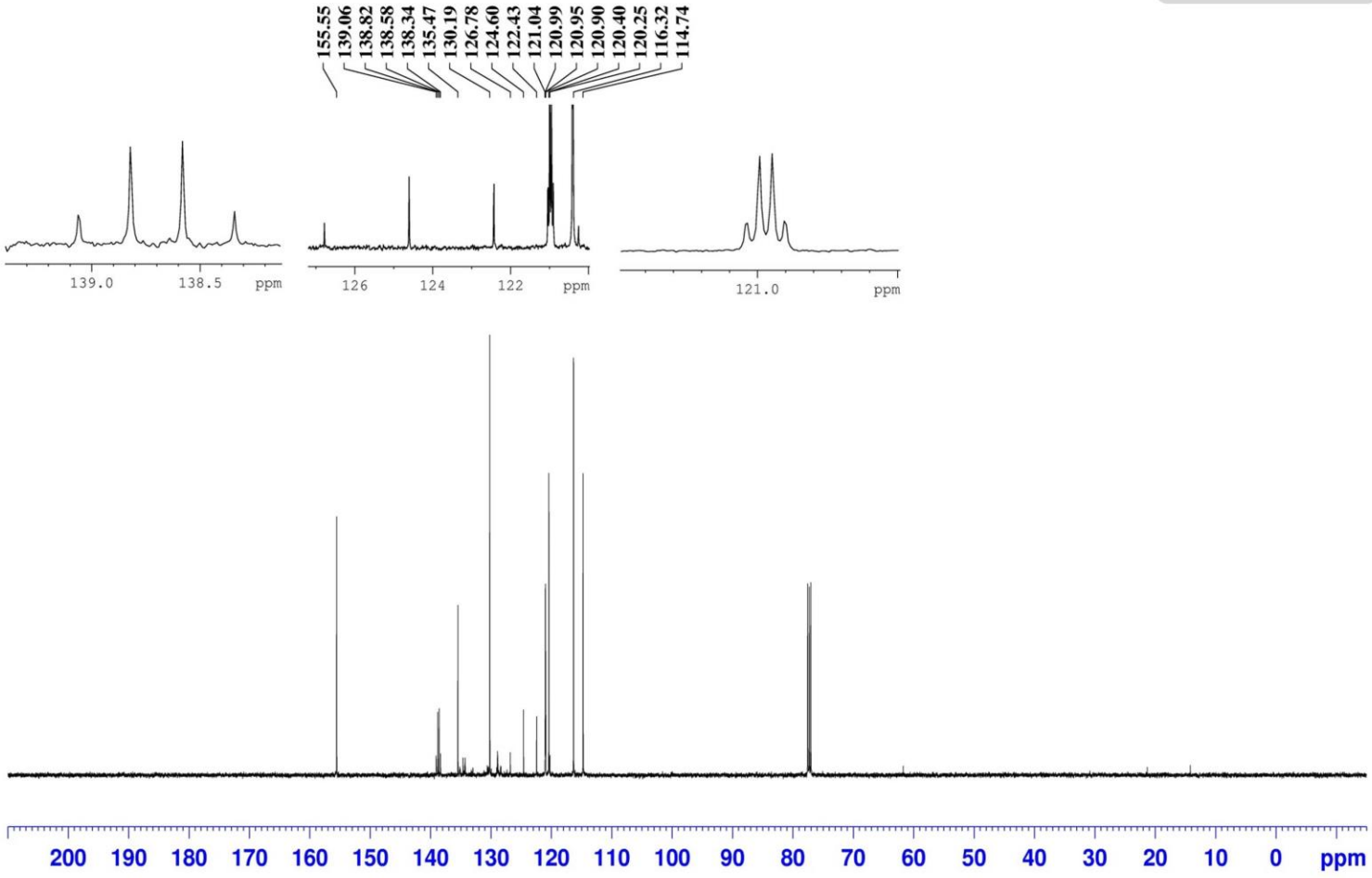




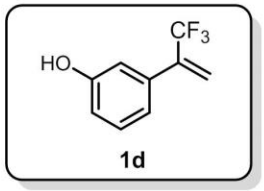


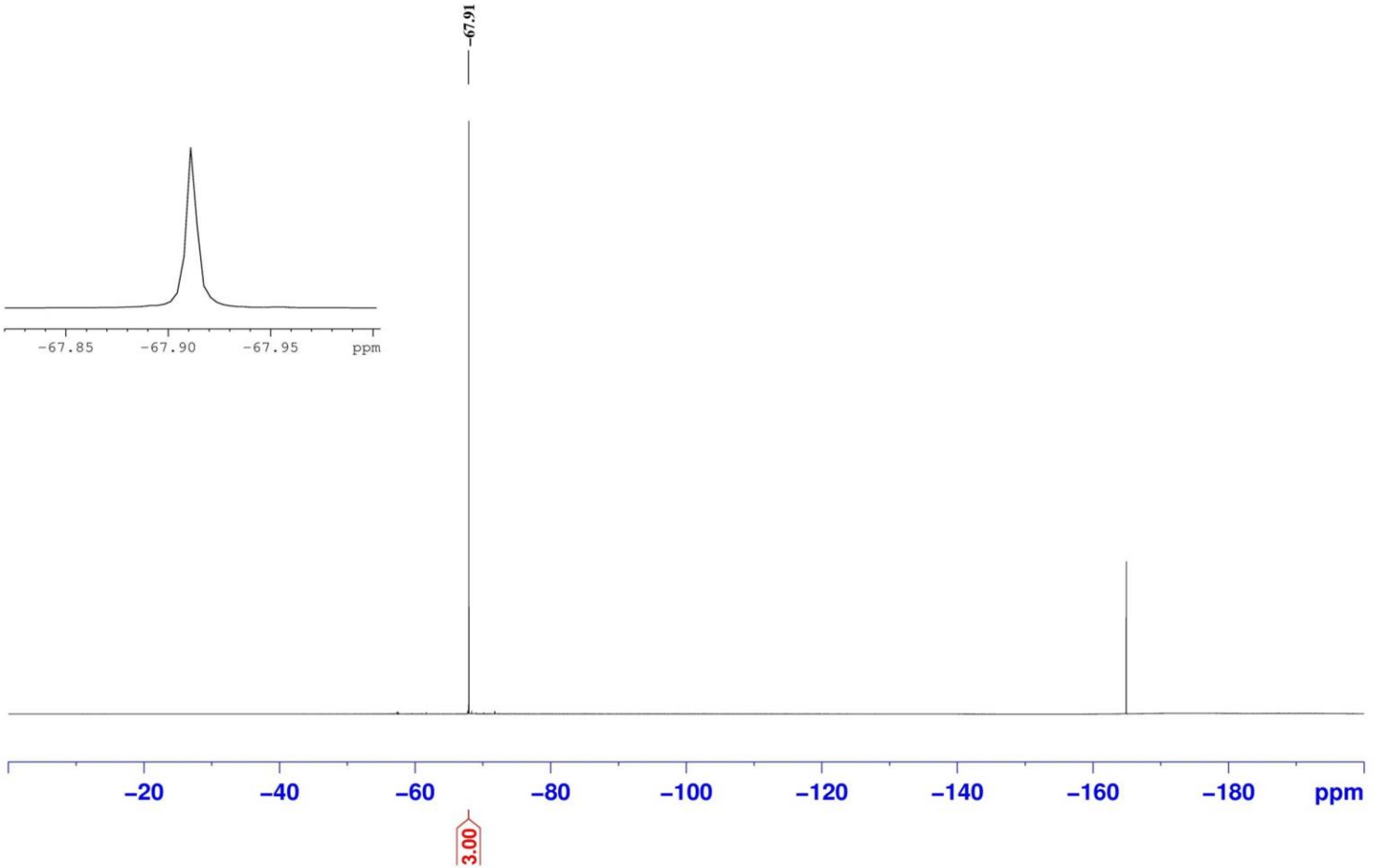
3–(3,3,3–trifluoroprop–1–en–2–yl)phenol
125 MHz, CDCl3



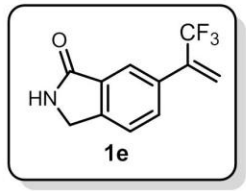


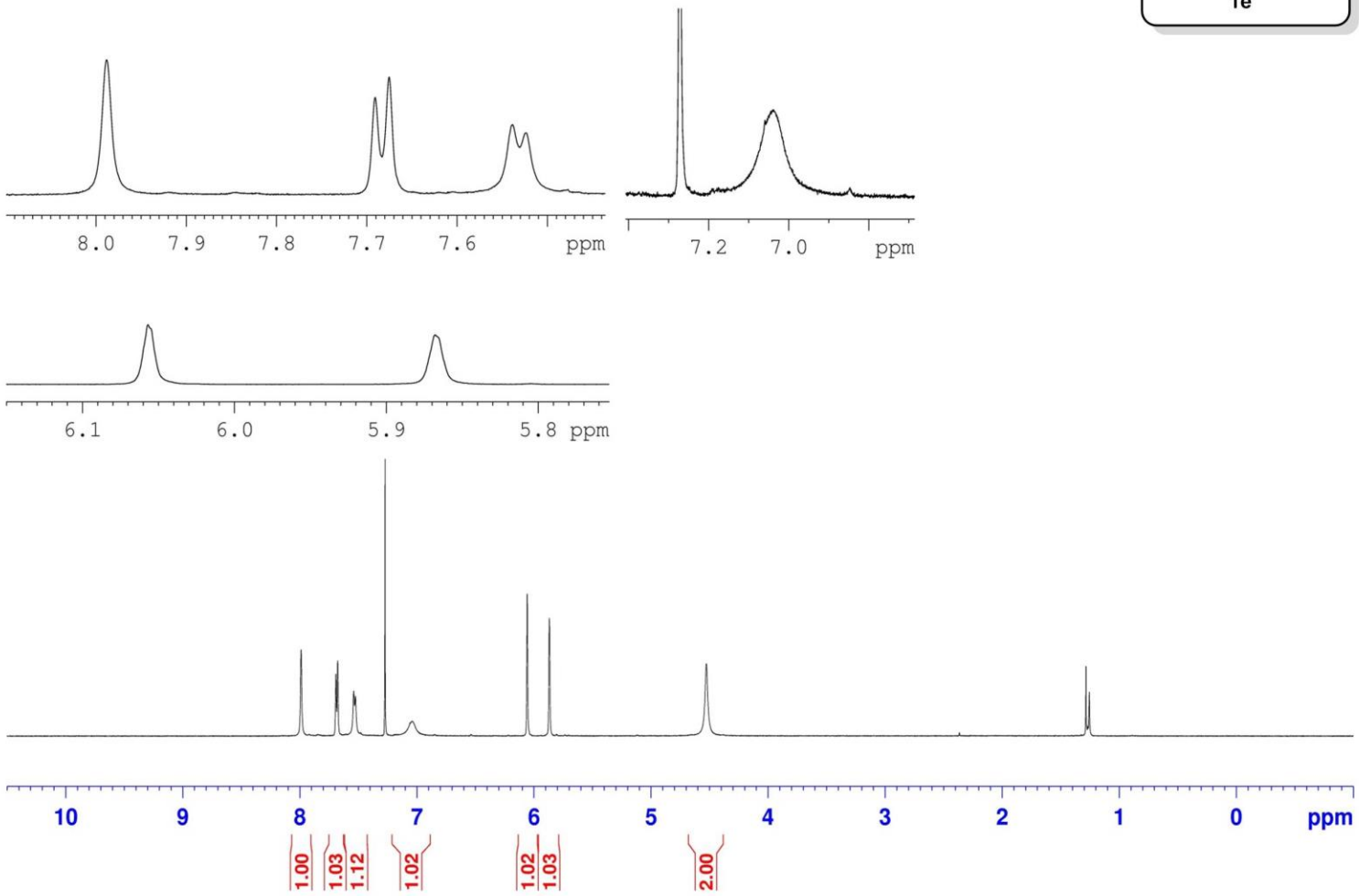
3–(3,3,3–trifluoroprop–1–en–2–yl)phenol
471 MHz, CDCl3



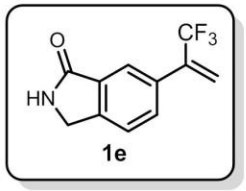


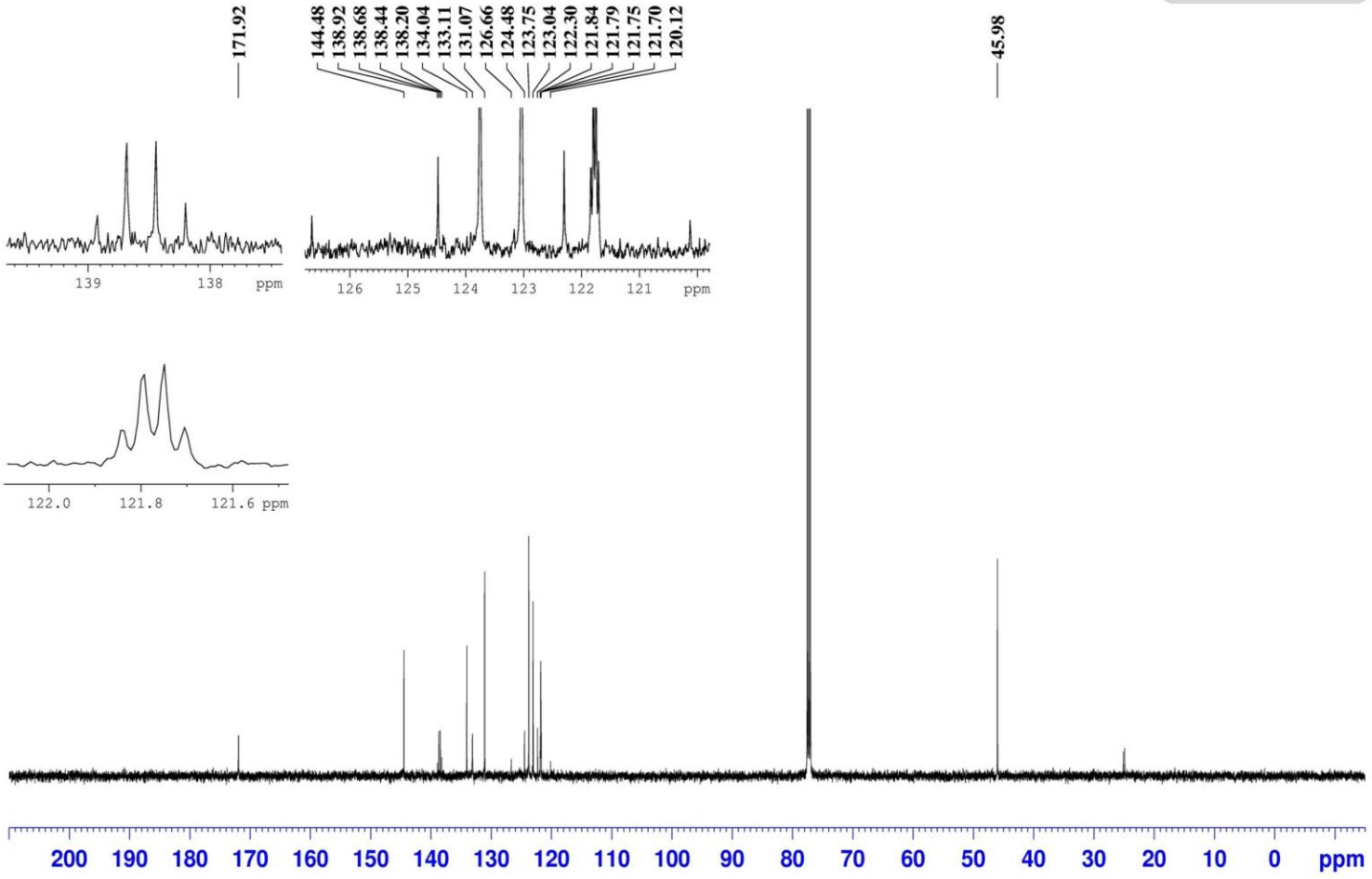
6−(3,3,3−trifluoroprop−1−en−2−yl)isoindolin−1−one
500 MHz, CDCl3



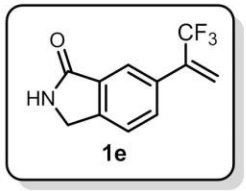


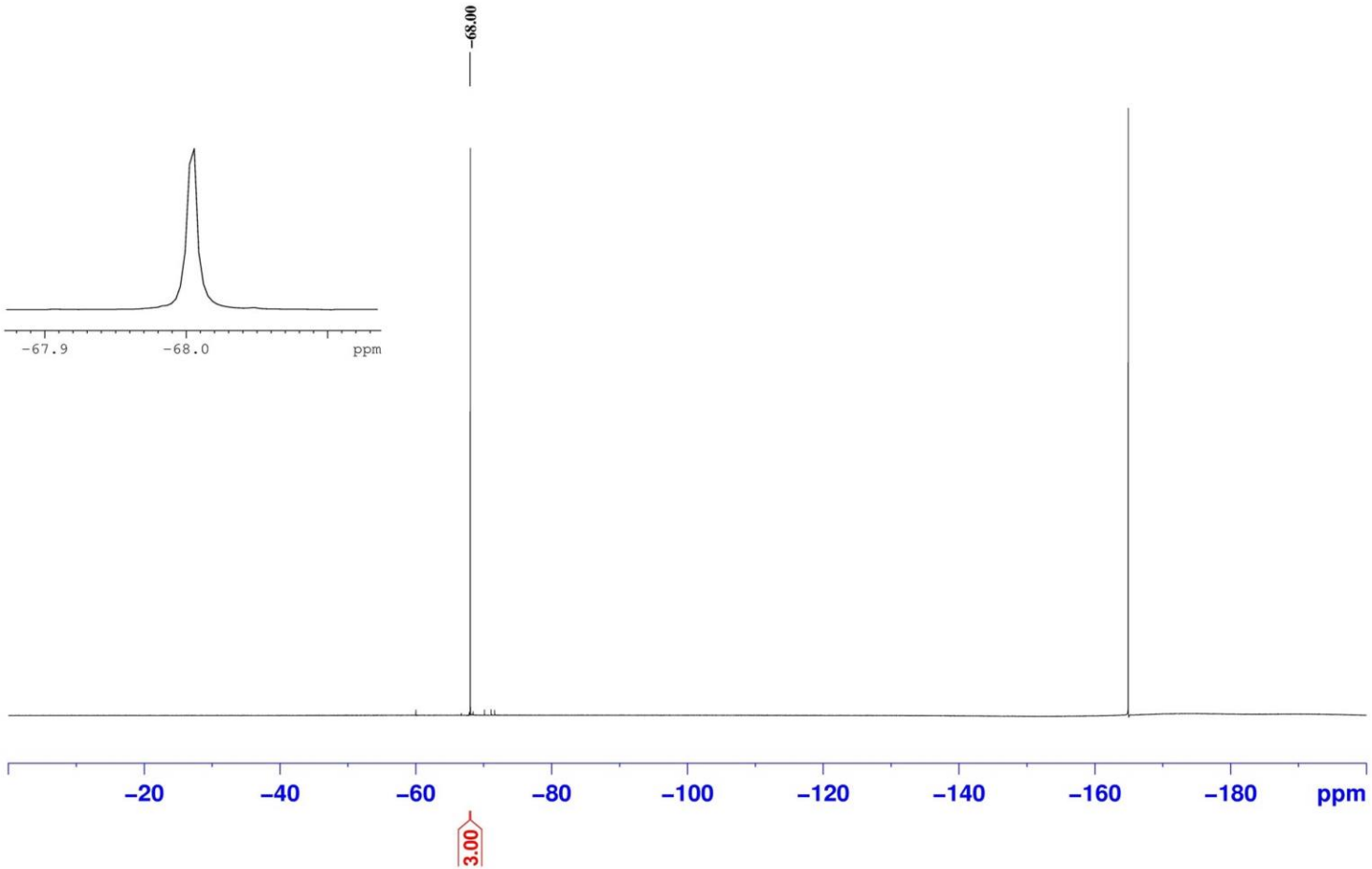
13C NMR6−(3,3,3−trifluoroprop−1−en−2−yl)isoindolin−1−one
125 MHz, CDCl3



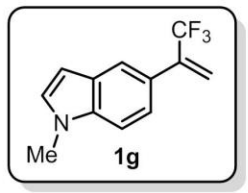


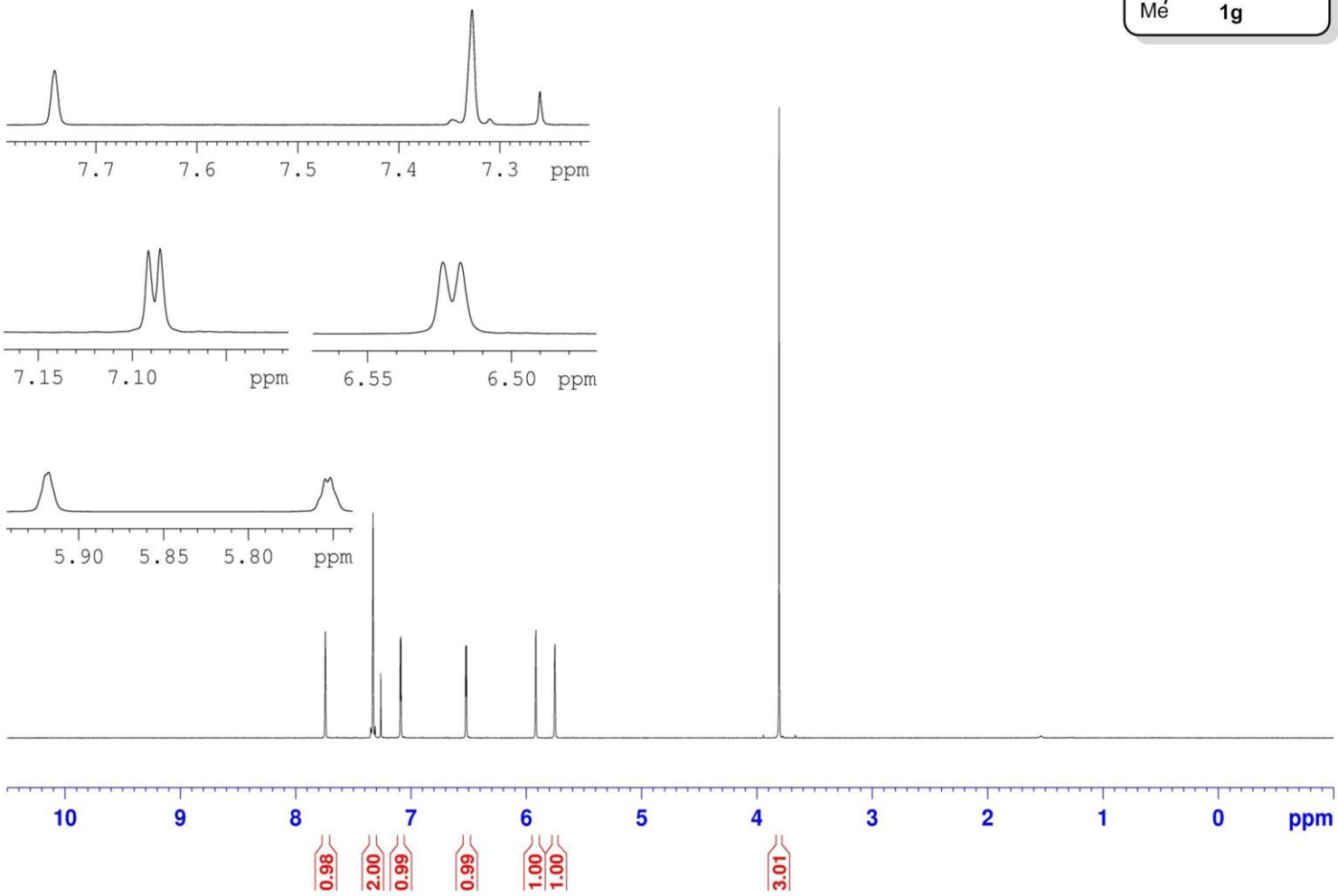
6−(3,3,3−trifluoroprop−1−en−2−yl)isoindolin−1−one
471 MHz, CDCl3



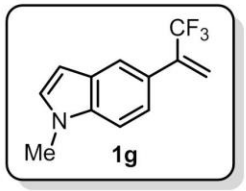


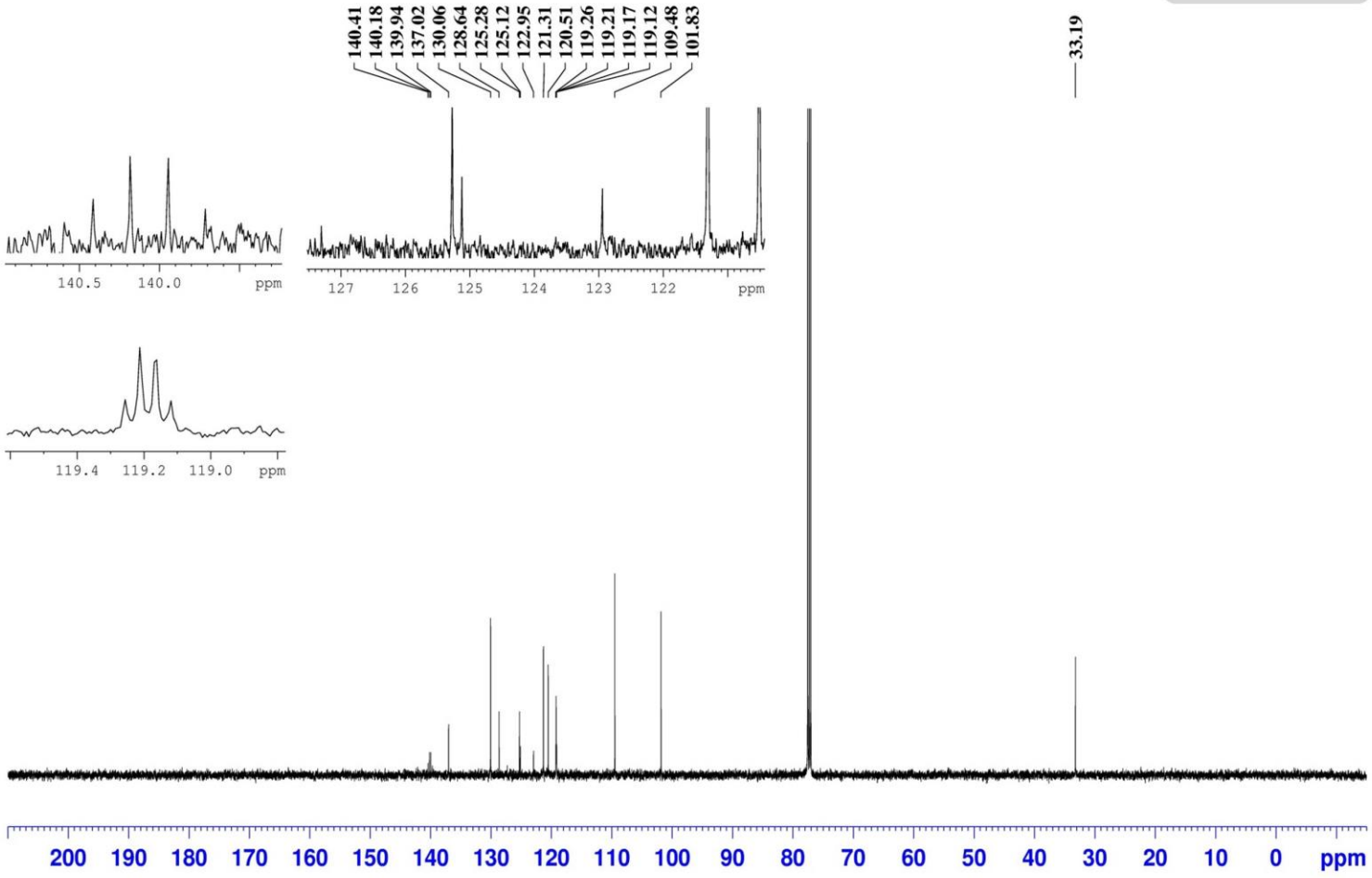
1−methyl−5−(3,3,3−trifluoroprop−1−en−2−yl)−1H−indole
500 MHz, CDCl3



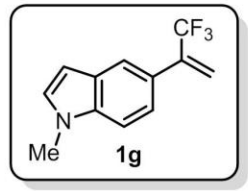


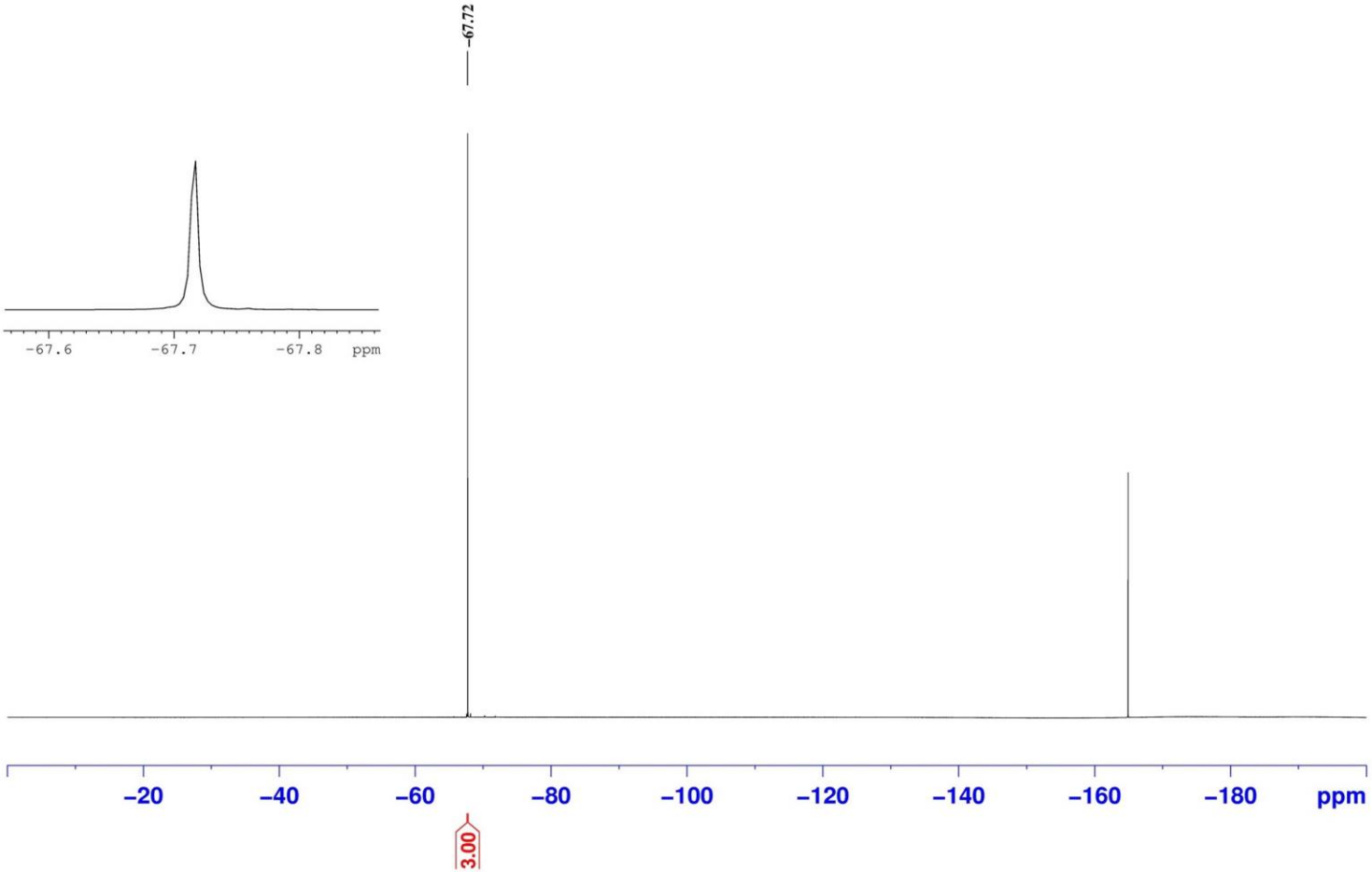
1−methyl−5−(3,3,3−trifluoroprop−1−en−2−yl)−1H−indole
125 MHz, CDCl3



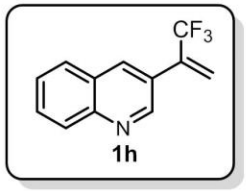


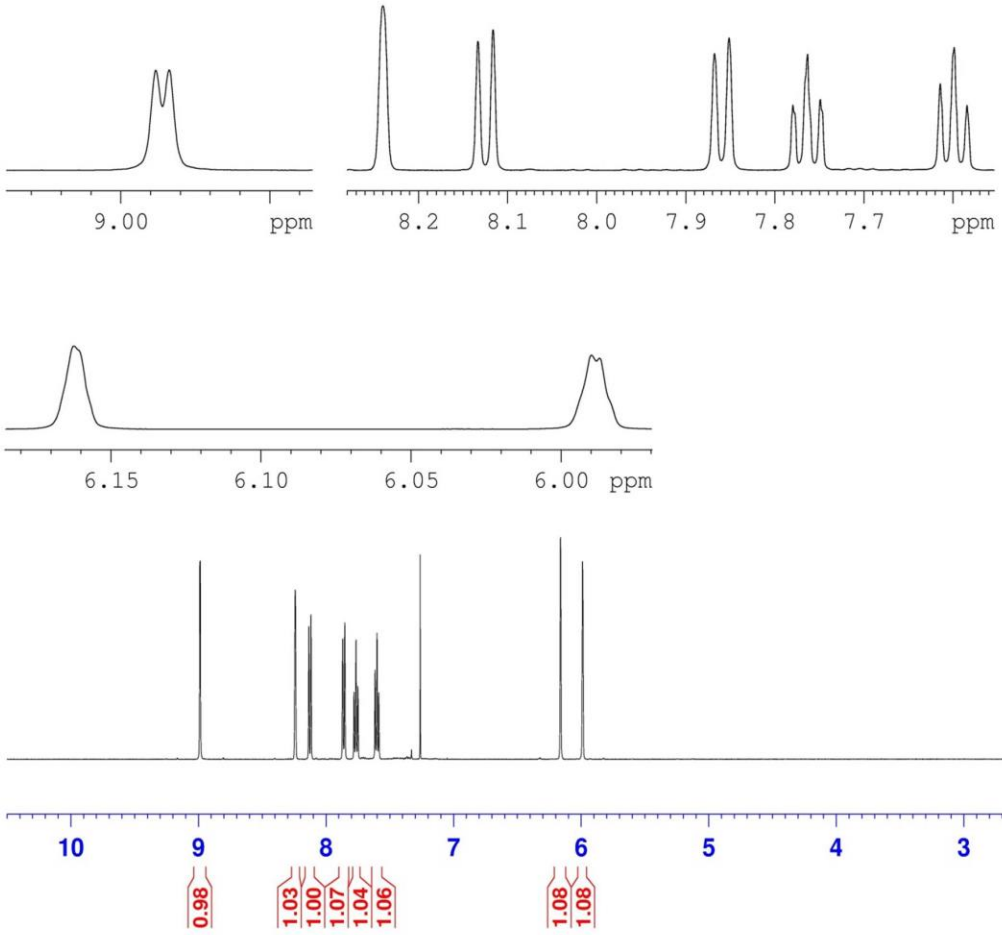
1–methyl–5–(3,3,3–trifluoroprop–1–en–2–yl)–1H–indole
471 MHz, CDCl3



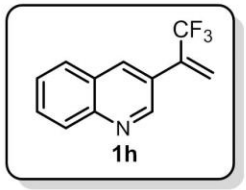


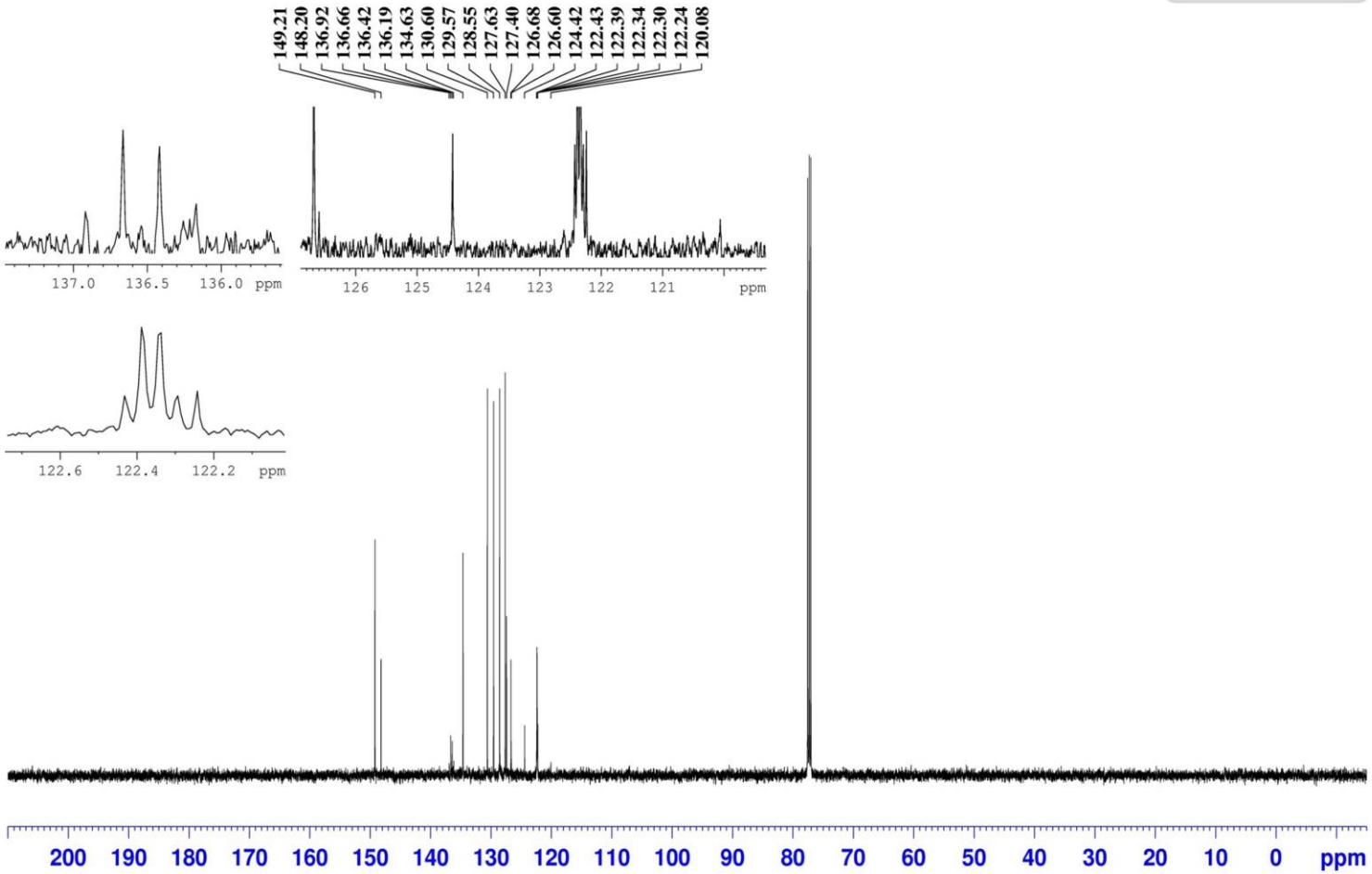
3–(3,3,3–trifluoroprop–1–en–2–yl)quinoline
500 MHz, CDCl3



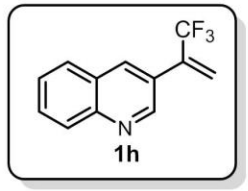


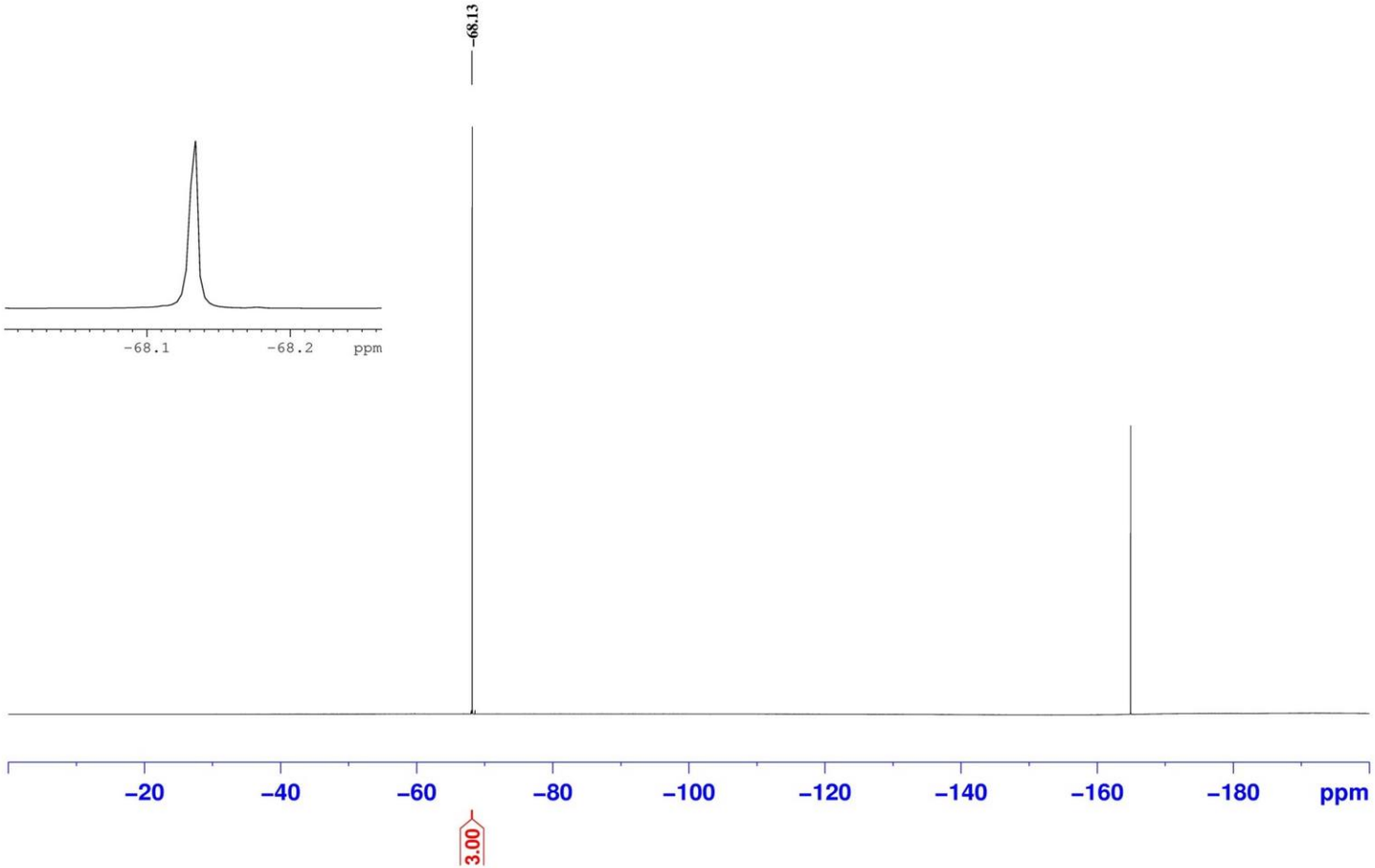
3–(3,3,3–trifluoroprop–1–en–2–yl)quinoline
125 MHz, CDCl3



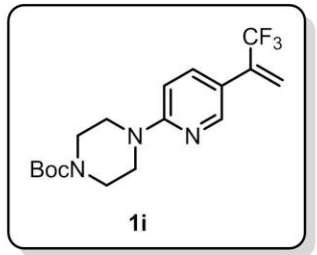


3–(3,3,3–trifluoroprop–1–en–2–yl)quinoline
471 MHz, CDCl3

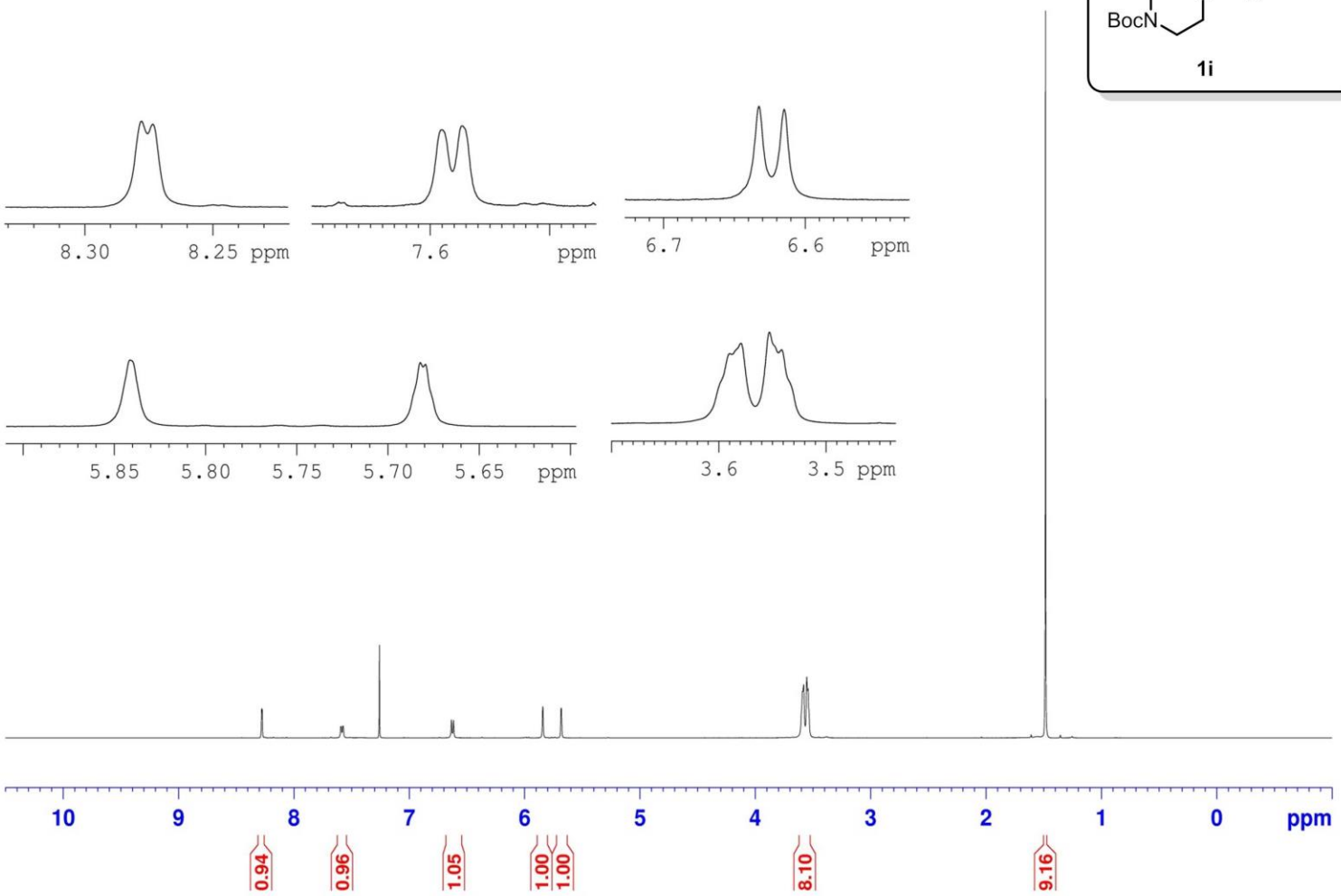




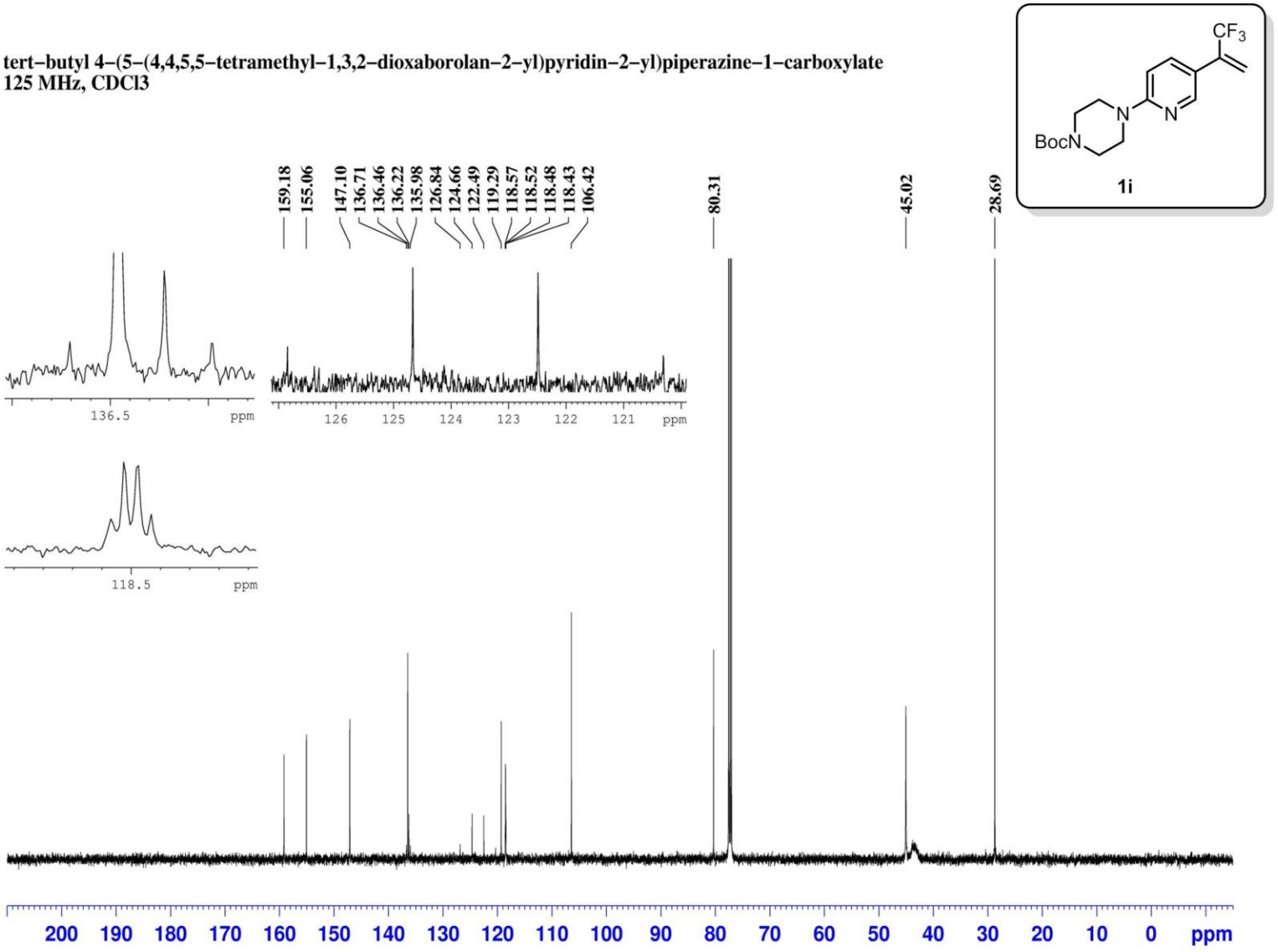
tert−butyl 4−(5−(4,4,5,5−tetramethyl−1,3,2−dioxaborolan−2−yl)pyridin−2−yl)piperazine−1−carboxylate
500 MHz, CDCl3



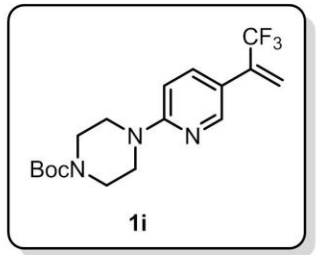
1i



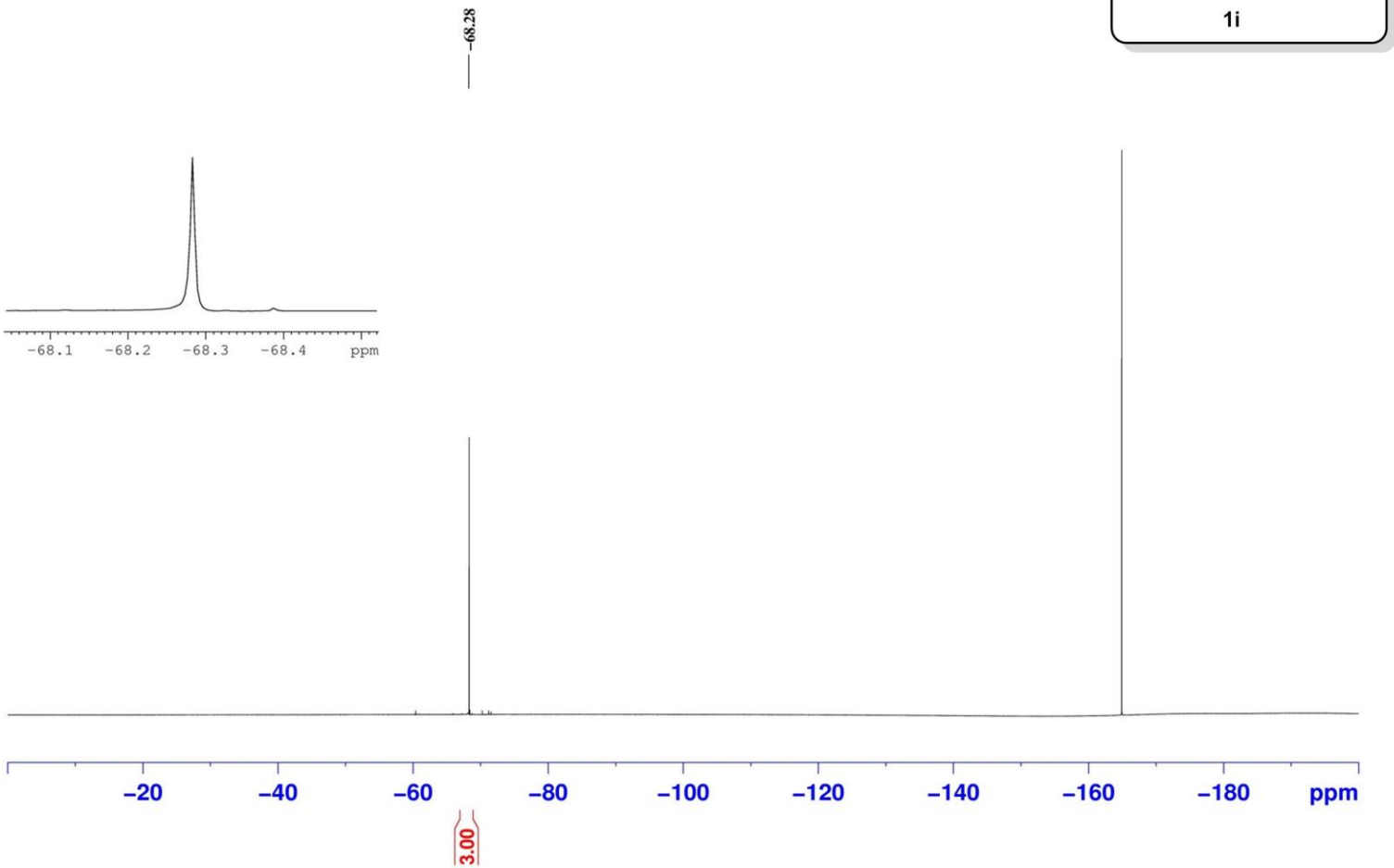
tert−butyl 4−(5−(4,4,5,5−tetramethyl−1,3,2−dioxaborolan−2−yl)pyridin−2−yl)piperazine−1−carboxylate
125 MHz, CDCl3



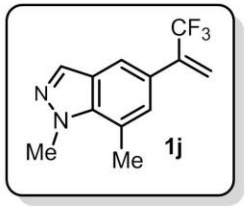
tert−butyl 4−(5−(4,4,5,5−tetramethyl−1,3,2−dioxaborolan−2−yl)pyridin−2−yl)piperazine−1−carboxylate
471 MHz, CDCl3

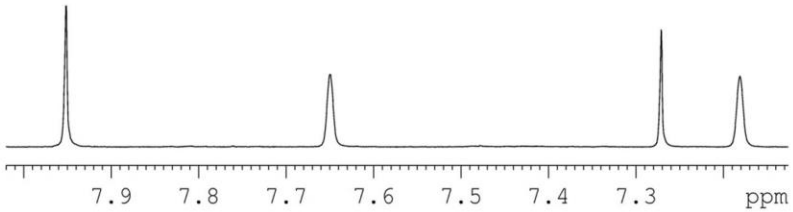


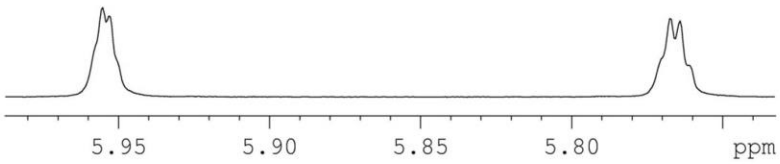
1i

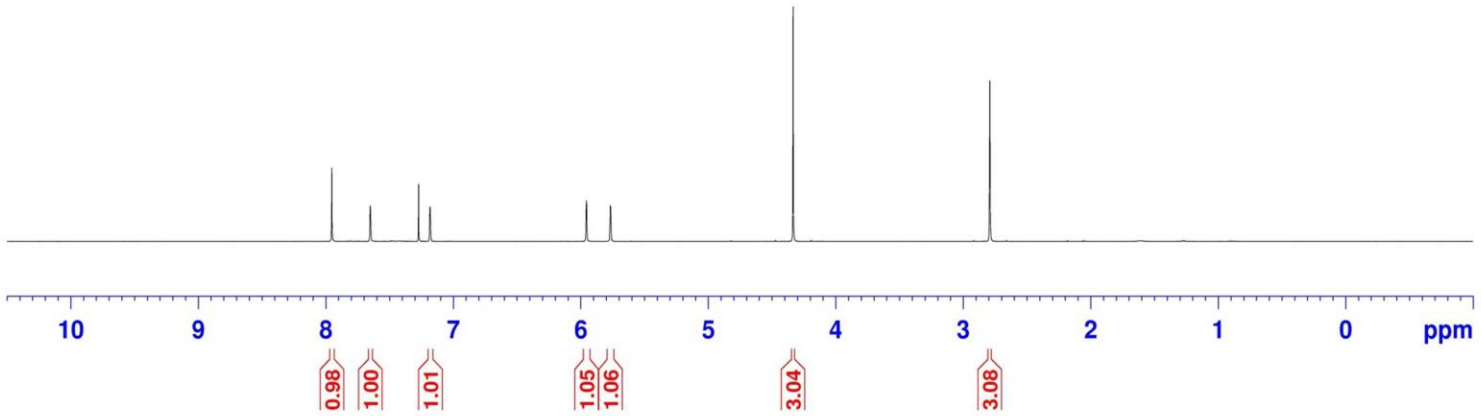


1,7–dimethyl–5–(3,3,3–trifluoroprop–1–en–2–yl)–1H–indazole
500 MHz, CDCl3

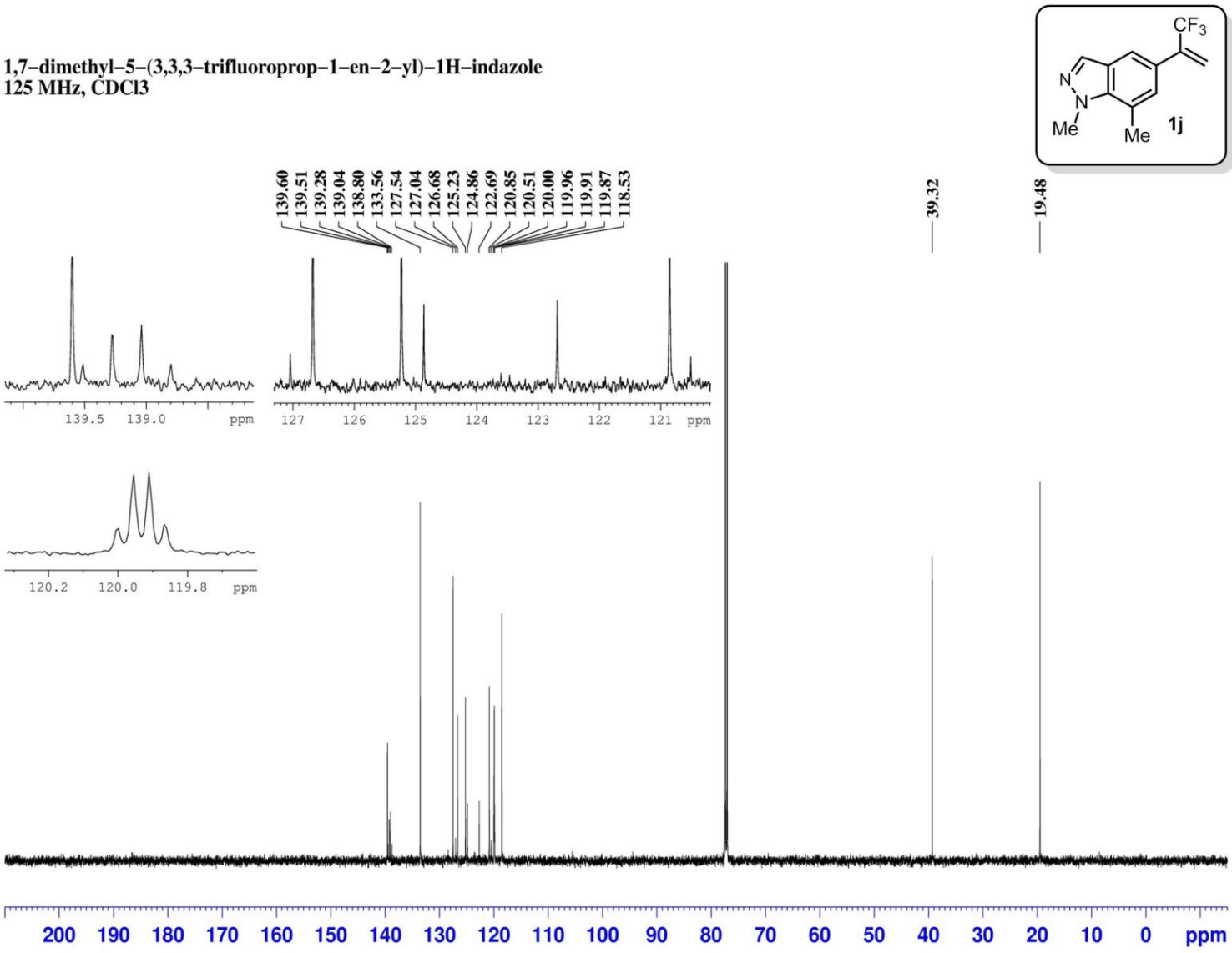




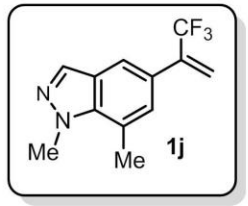


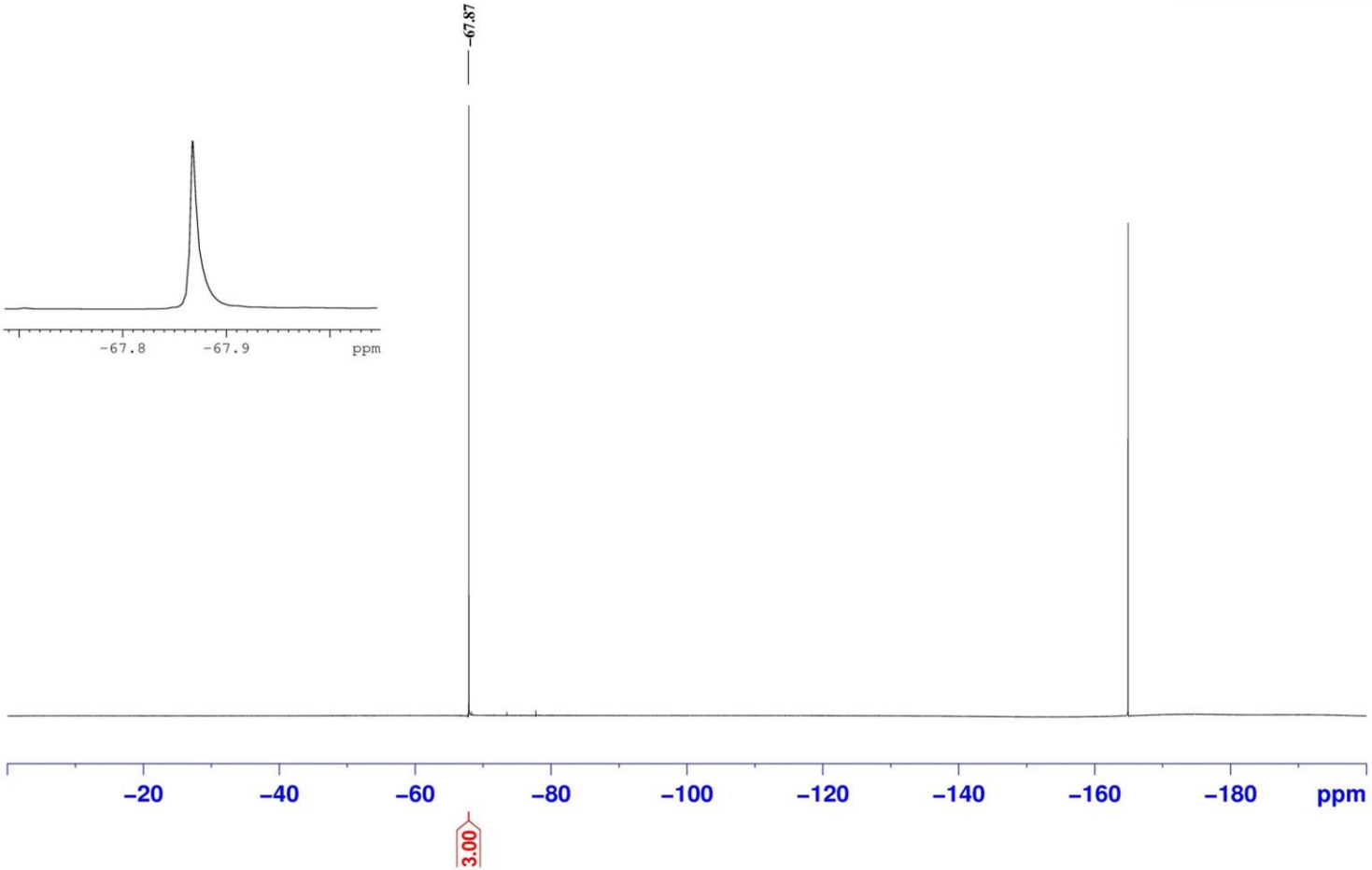


1,7–dimethyl–5–(3,3,3–trifluoroprop–1–en–2–yl)–1H–indazole
125 MHz, CDCl3

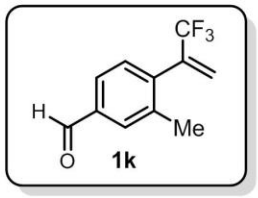


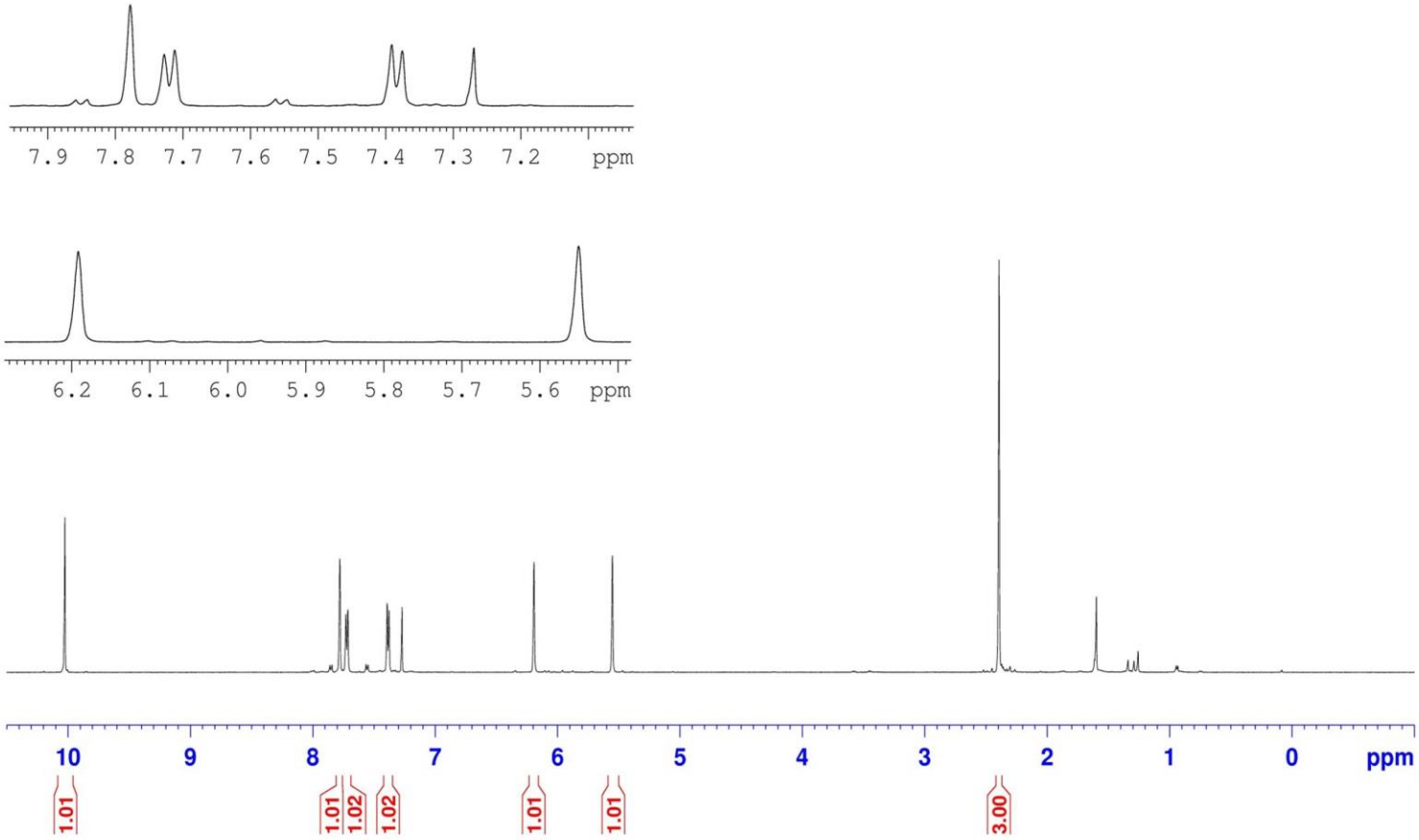
1,7–dimethyl–5–(3,3,3–trifluoroprop–1–en–2–yl)–1H–indazole
471 MHz, CDCl3



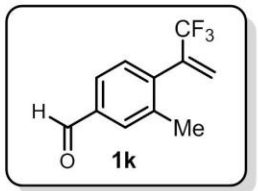


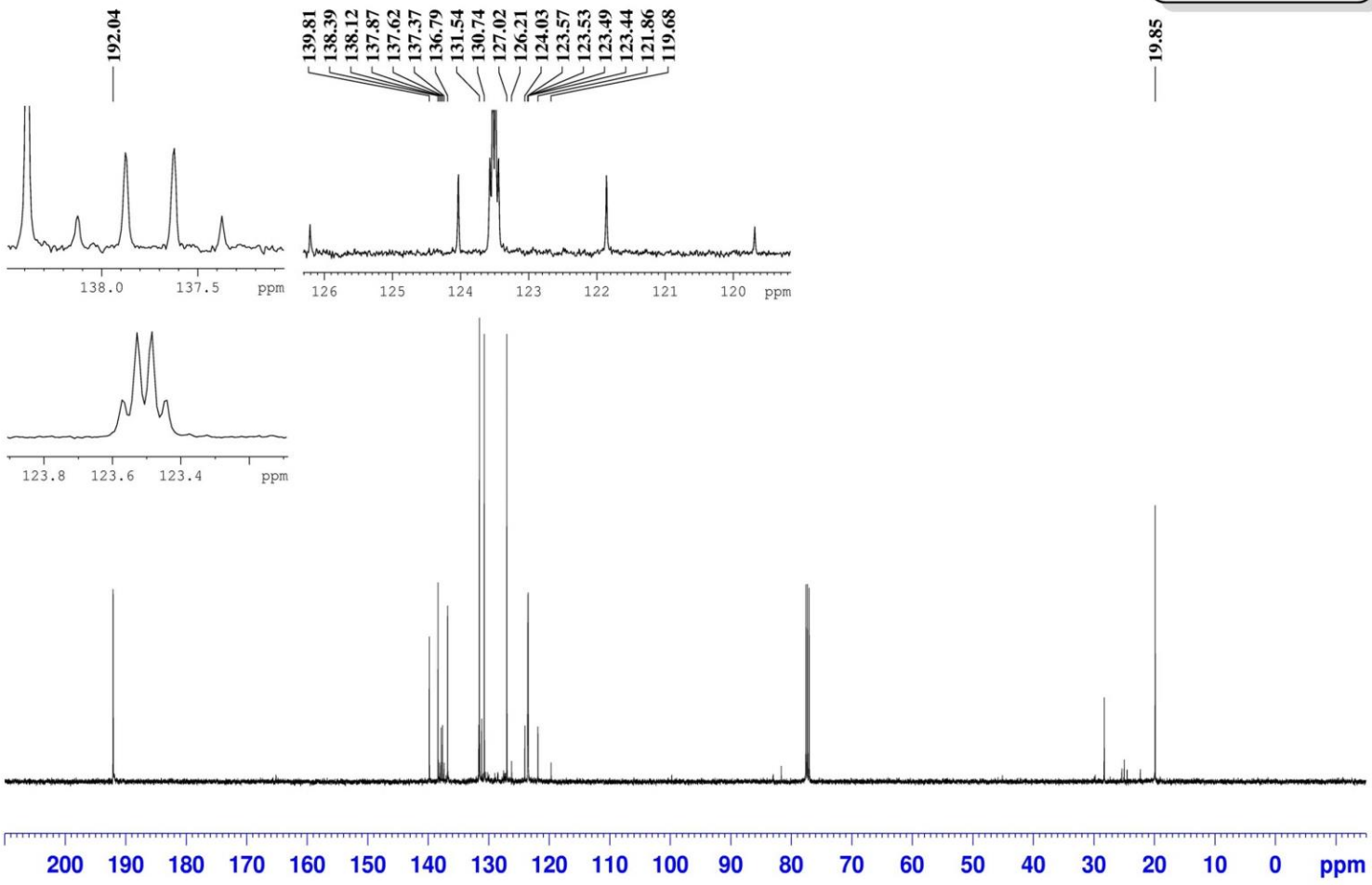
3–methyl–4–(3,3,3–trifluoroprop–1–en–2–yl)benzaldehyde
500 MHz, CDCl3



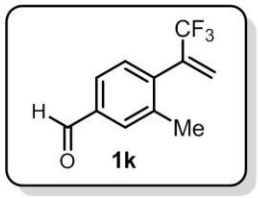


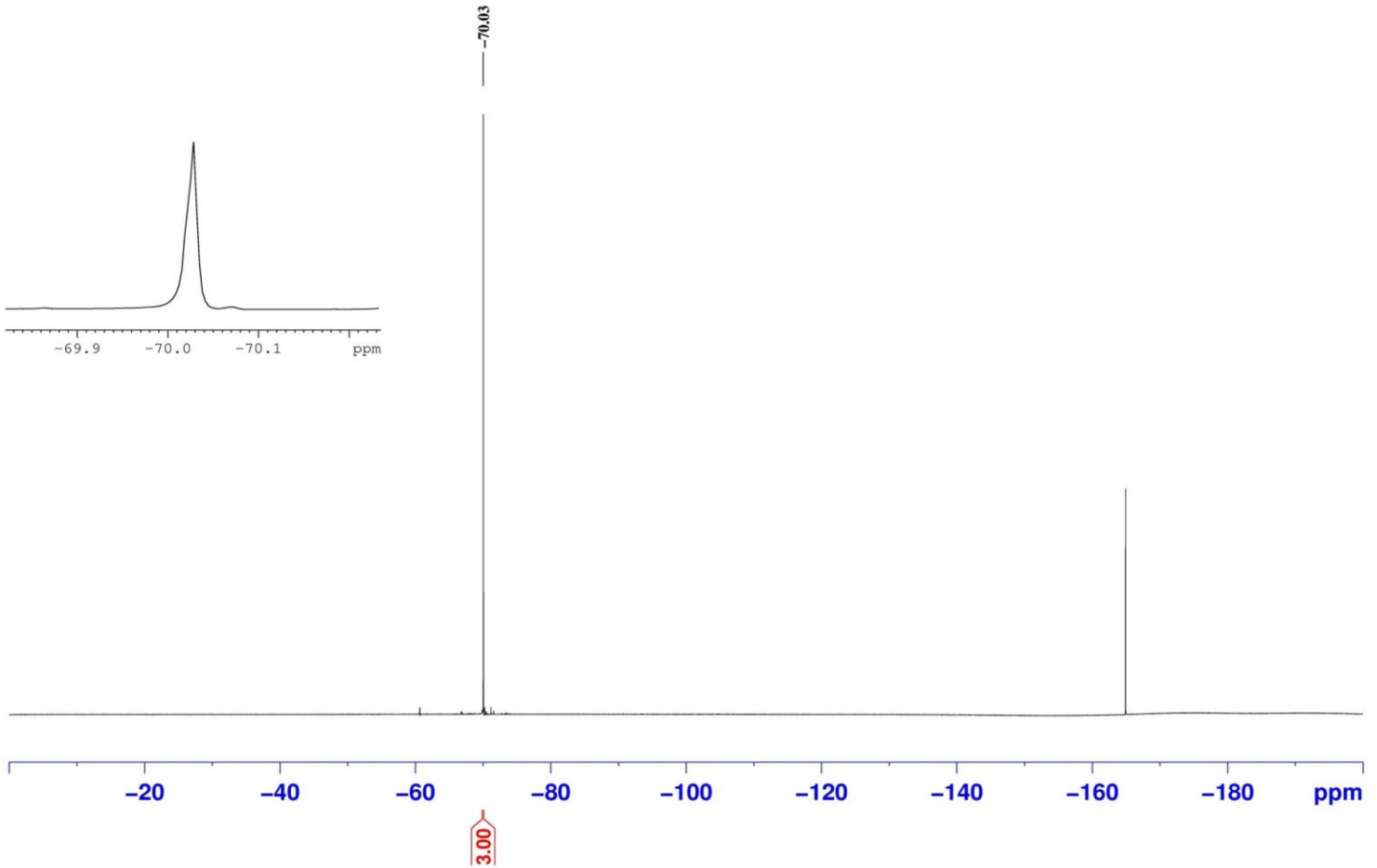
3–methyl–4–(3,3,3–trifluoroprop–1–en–2–yl)benzaldehyde
125 MHz. CDCl3



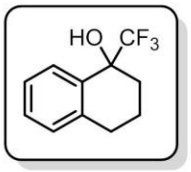


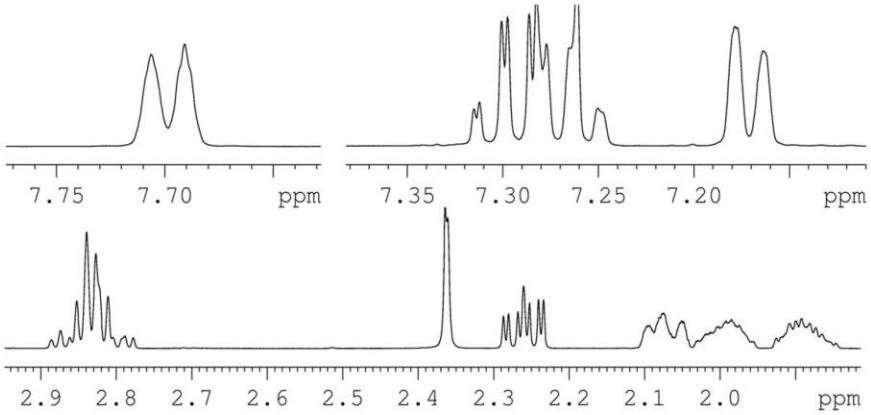
3–methyl–4–(3,3,3–trifluoroprop–1–en–2–yl)benzaldehyde
471 MHz, CDCl3

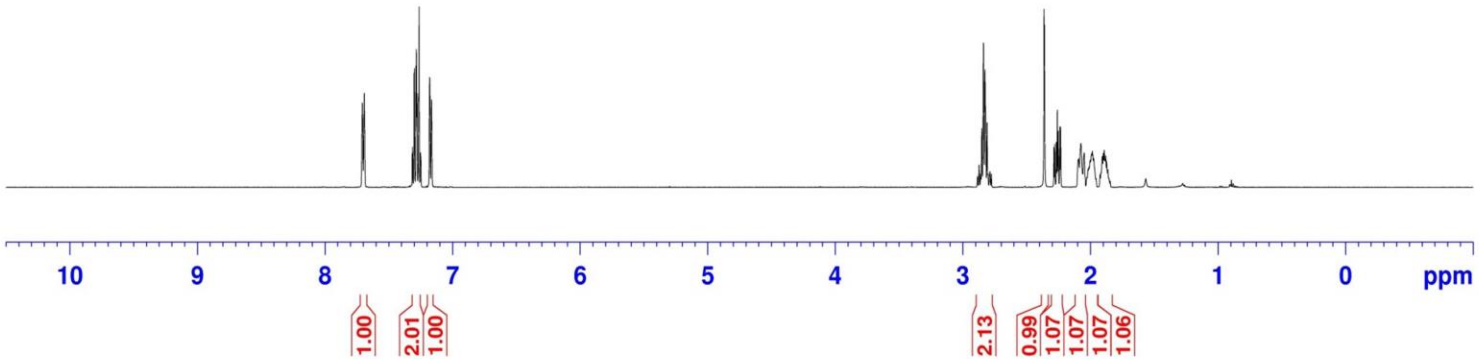




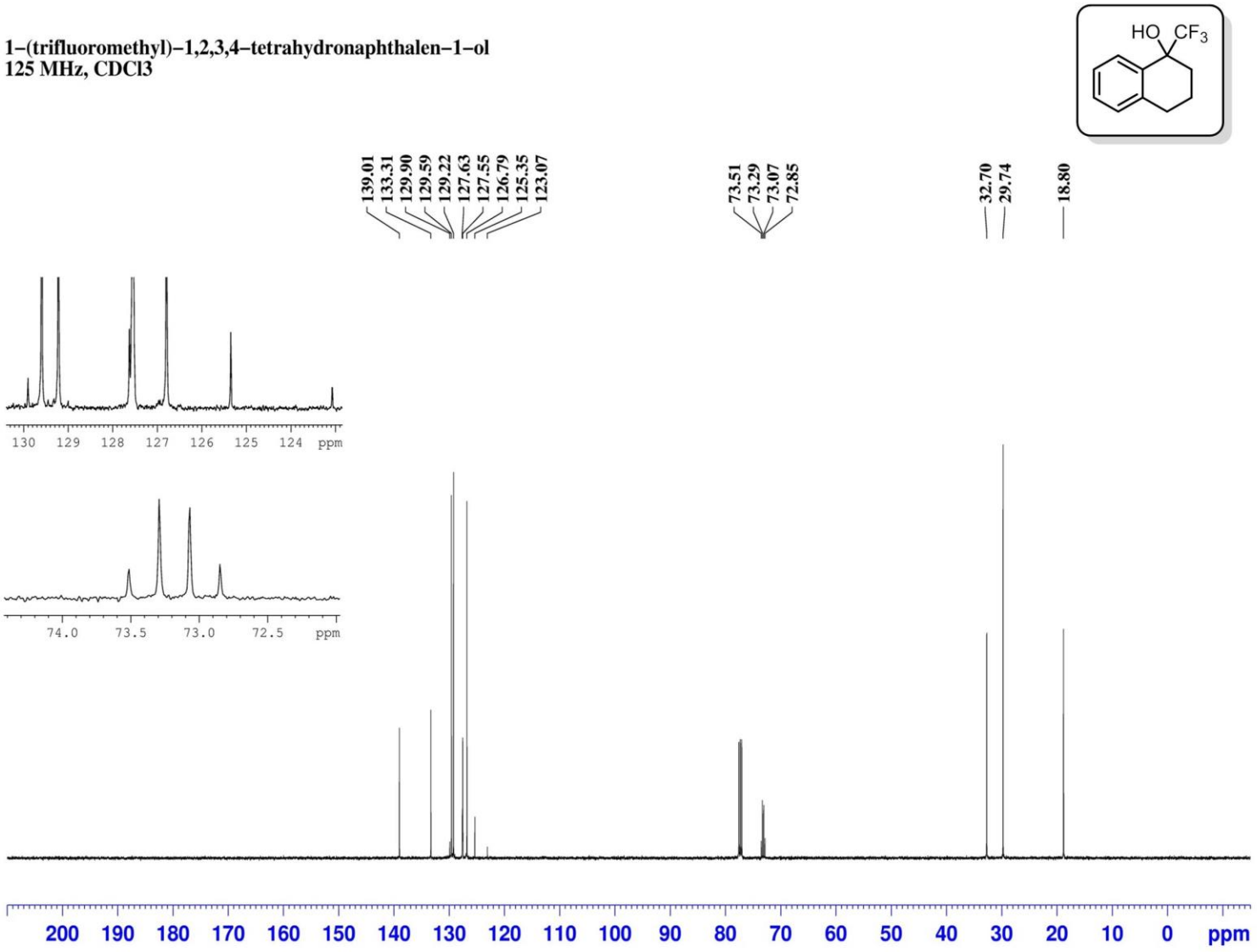
1−(trifluoromethyl)−1,2,3,4−tetrahydronaphthalen−1−ol
500 MHz, CDCl3



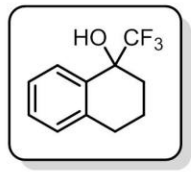


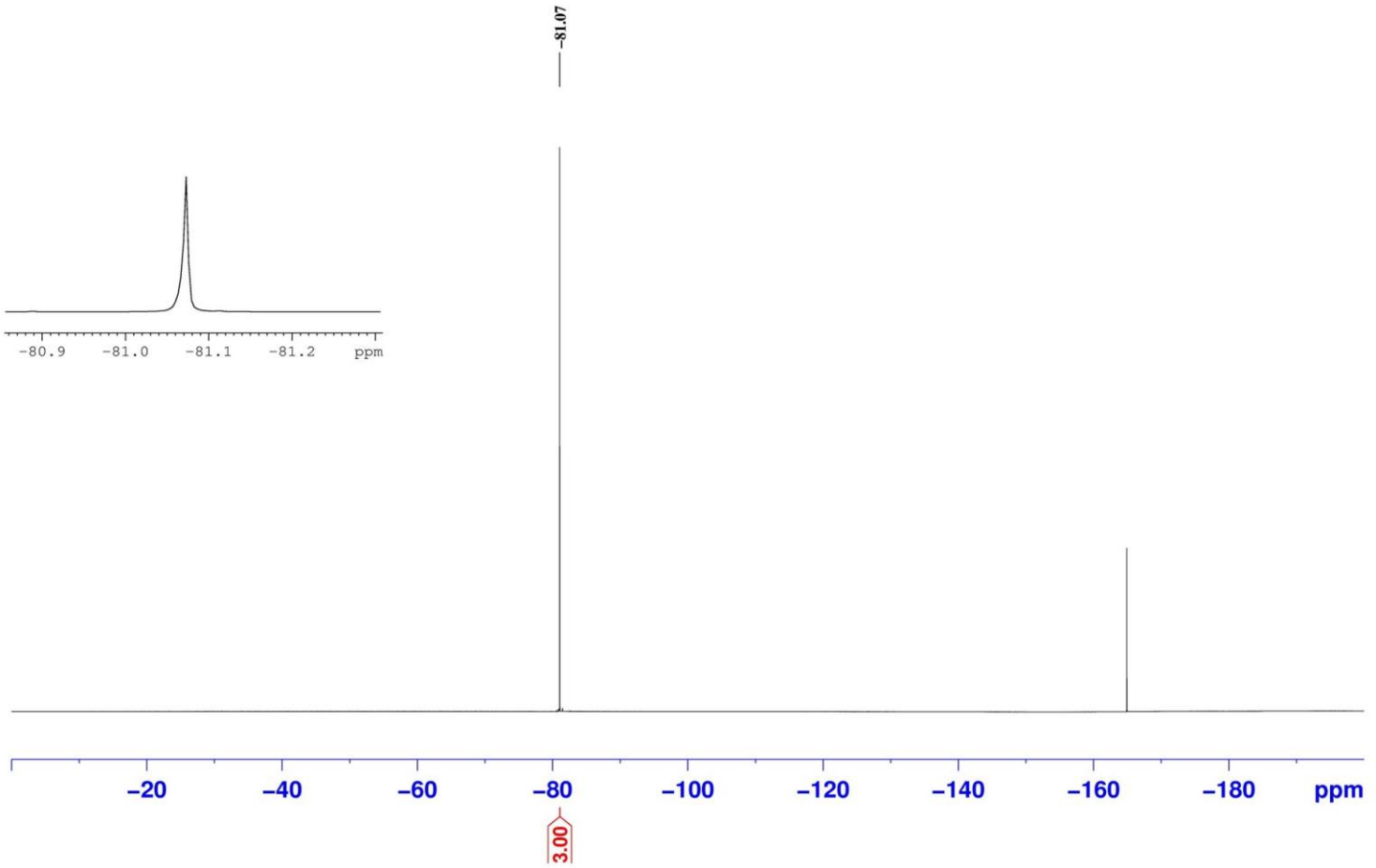


1−(trifluoromethyl)−1,2,3,4−tetrahydronaphthalen−1−ol
125 MHz, CDCl3

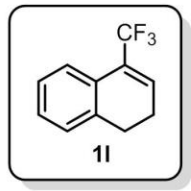


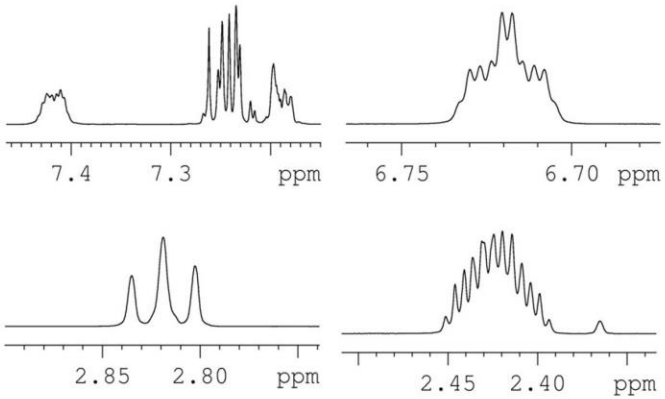
1–(trifluoromethyl)–1,2,3,4–tetrahydronaphthalen–1–ol
471 MHz, CDCl3

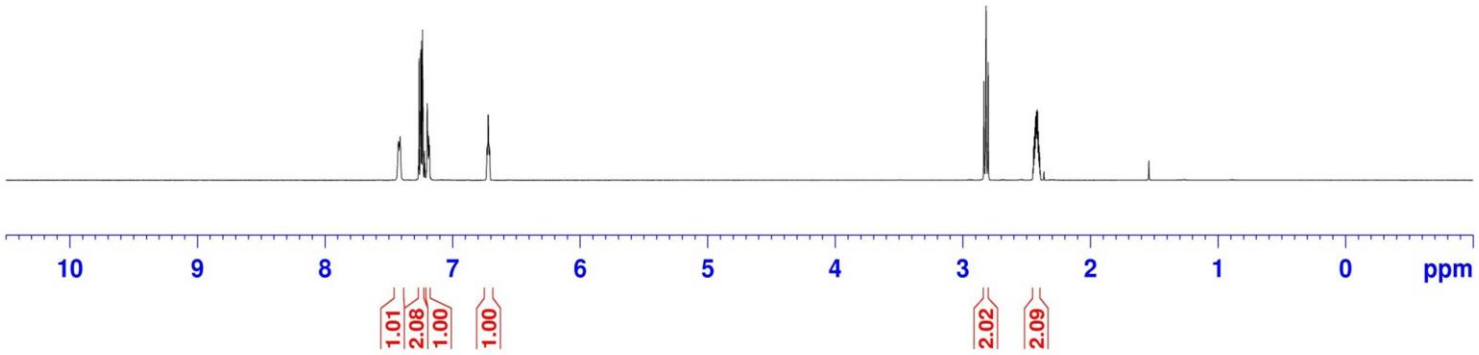




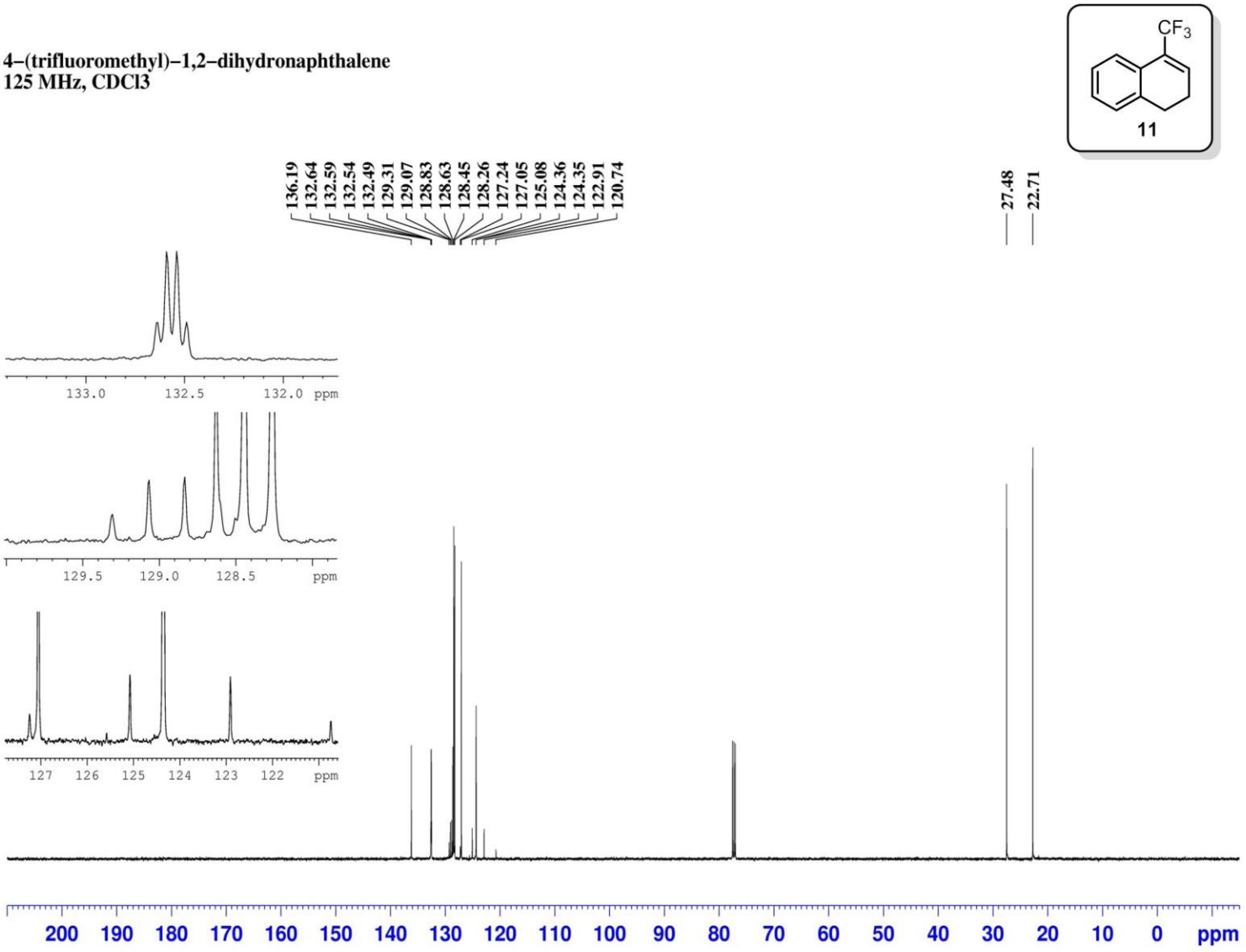
4–(trifluoromethyl)–1,2–dihydronaphthalene
500 MHz, CDCl3



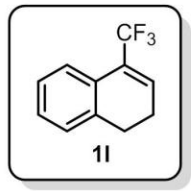


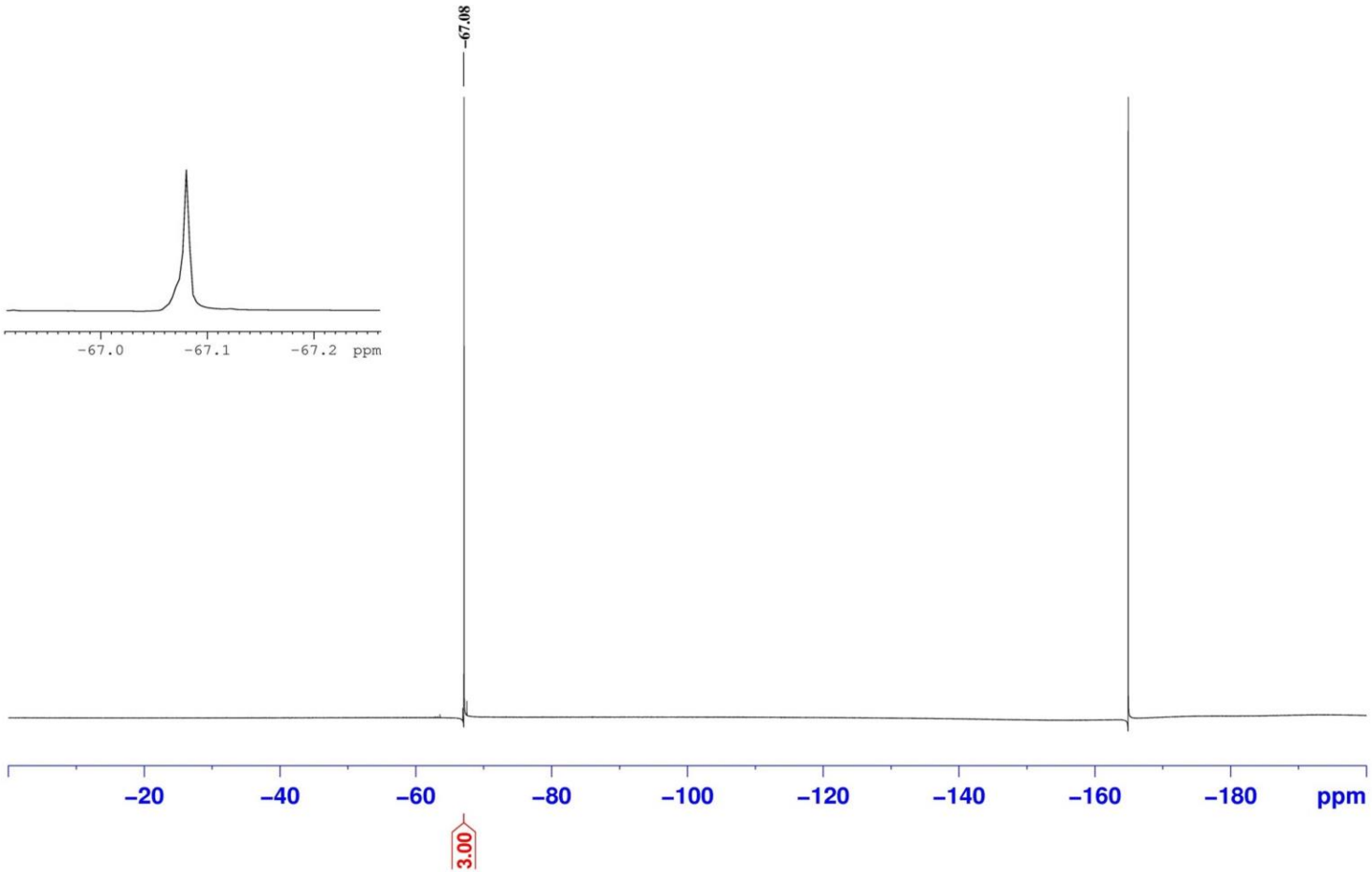


4–(trifluoromethyl)–1,2–dihydronaphthalene
125 MHz, CDCl3

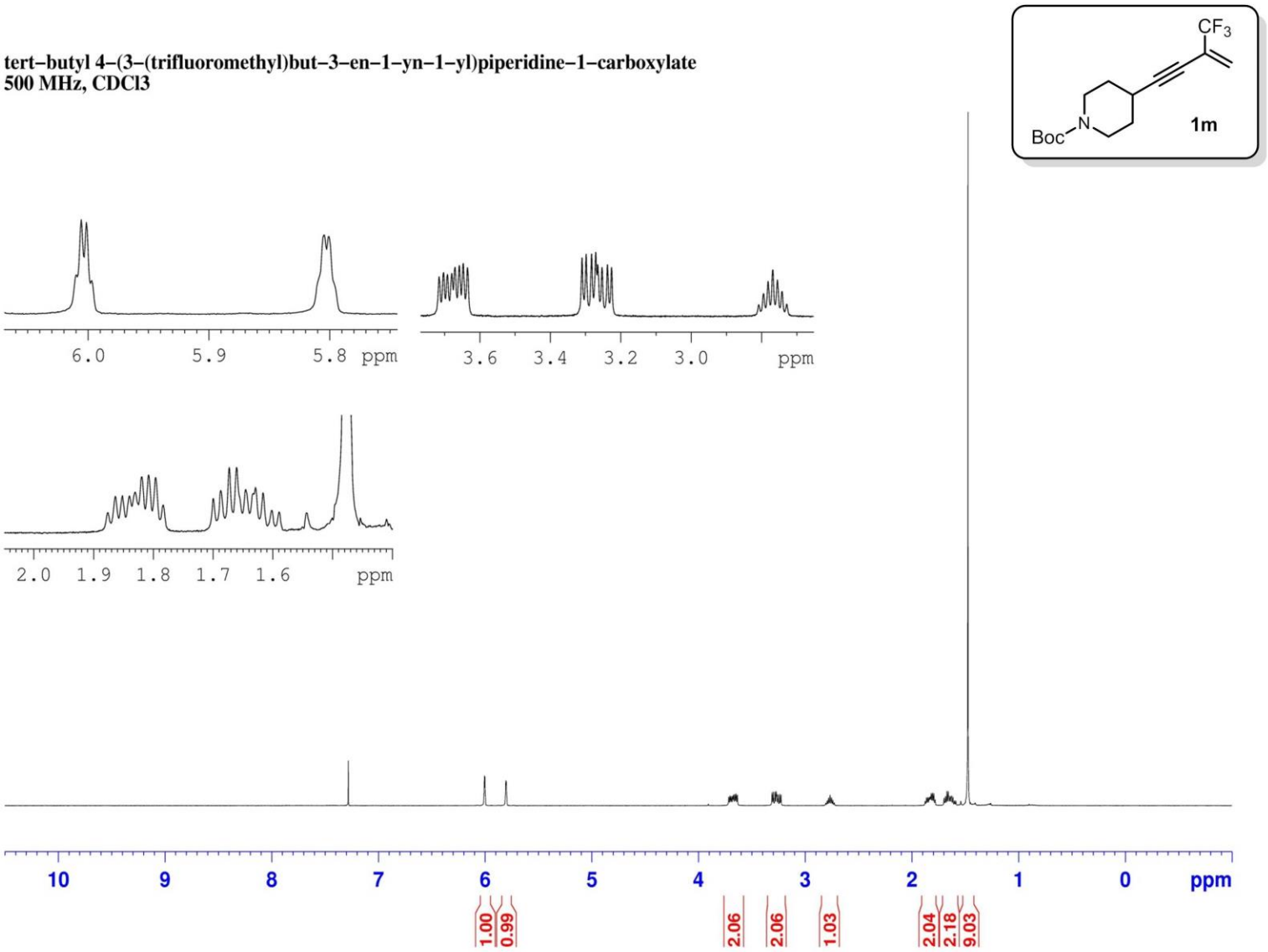


4–(trifluoromethyl)–1,2–dihydronaphthalene
471 MHz, CDCl3

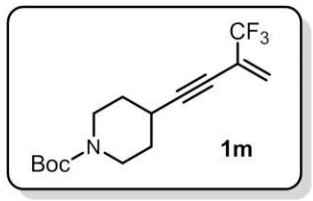


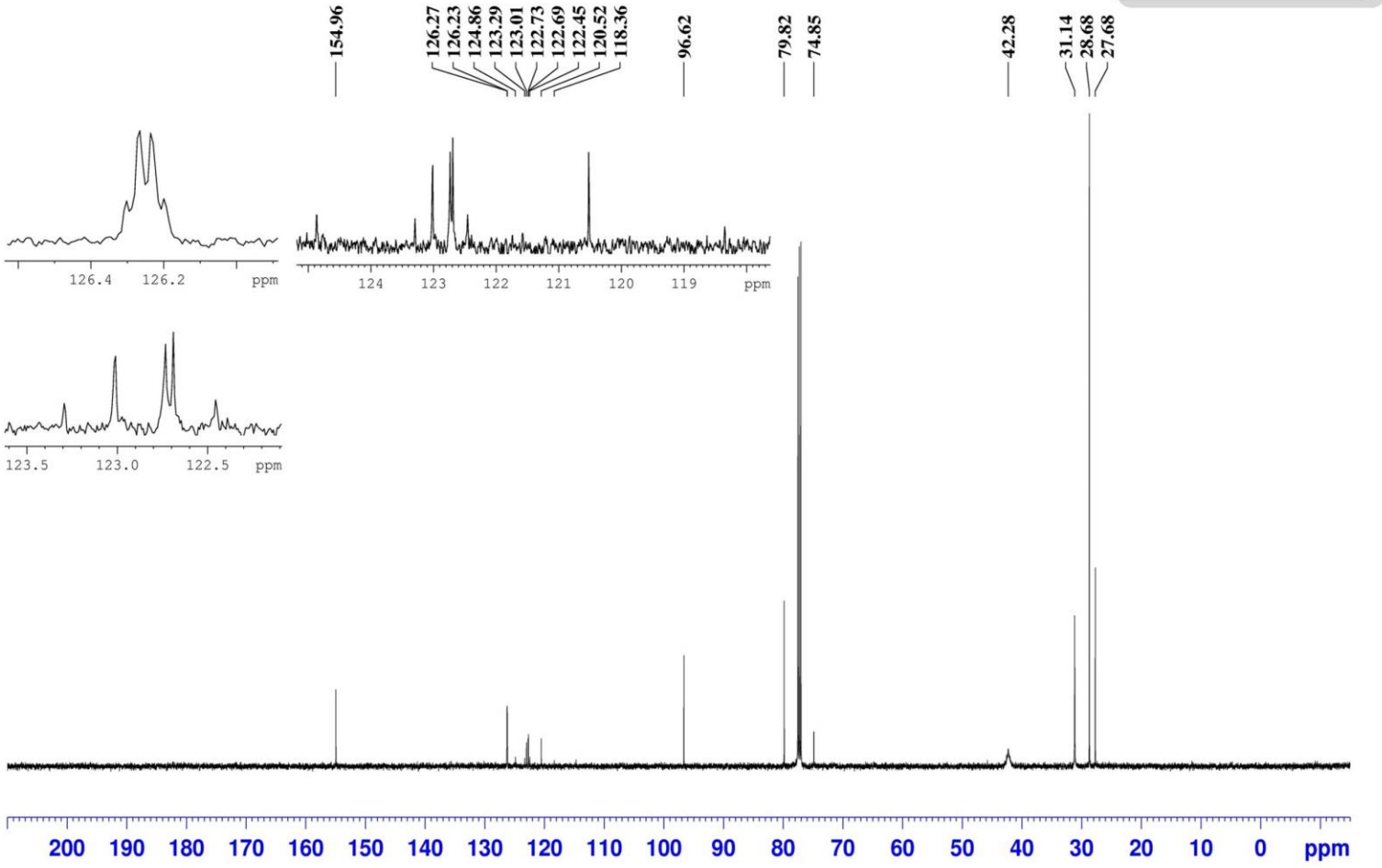


tert−butyl 4−(3−(trifluoromethyl)but−3−en−1−yn−1−yl)piperidine−1−carboxylate
500 MHz, CDCl3

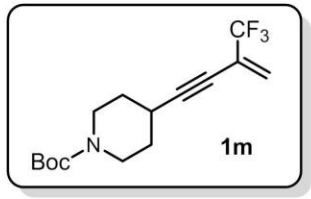


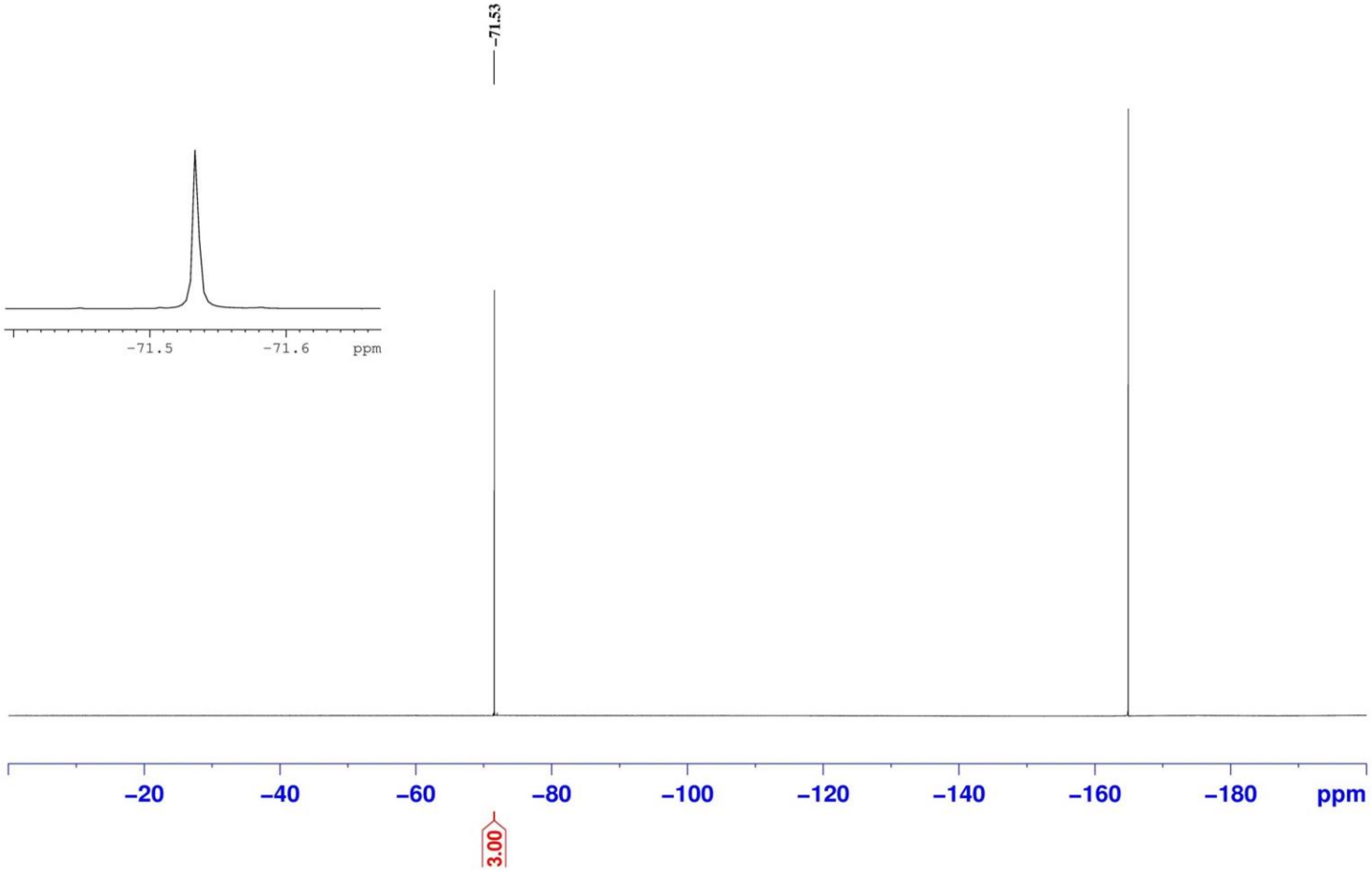
tert−butyl 4−(3−(trifluoromethyl)but−3−en−1−yn−1−yl)piperidine−1−carboxylate
125 MHz, CDCl3



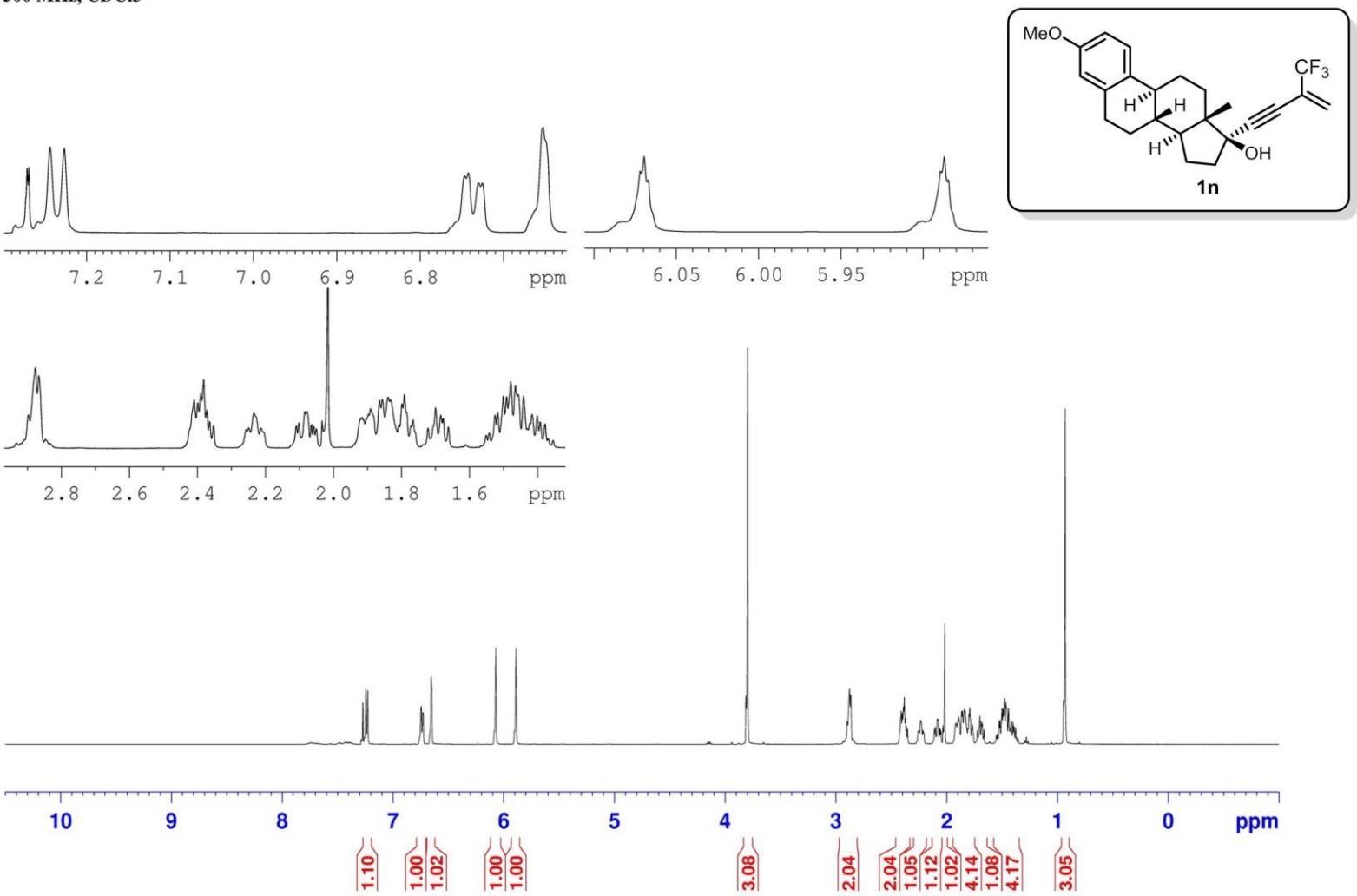


tert–butyl 4–(3–(trifluoromethyl)but–3–en–1–yn–1–yl)piperidine–1–carboxylate
471 MHz, CDCl3

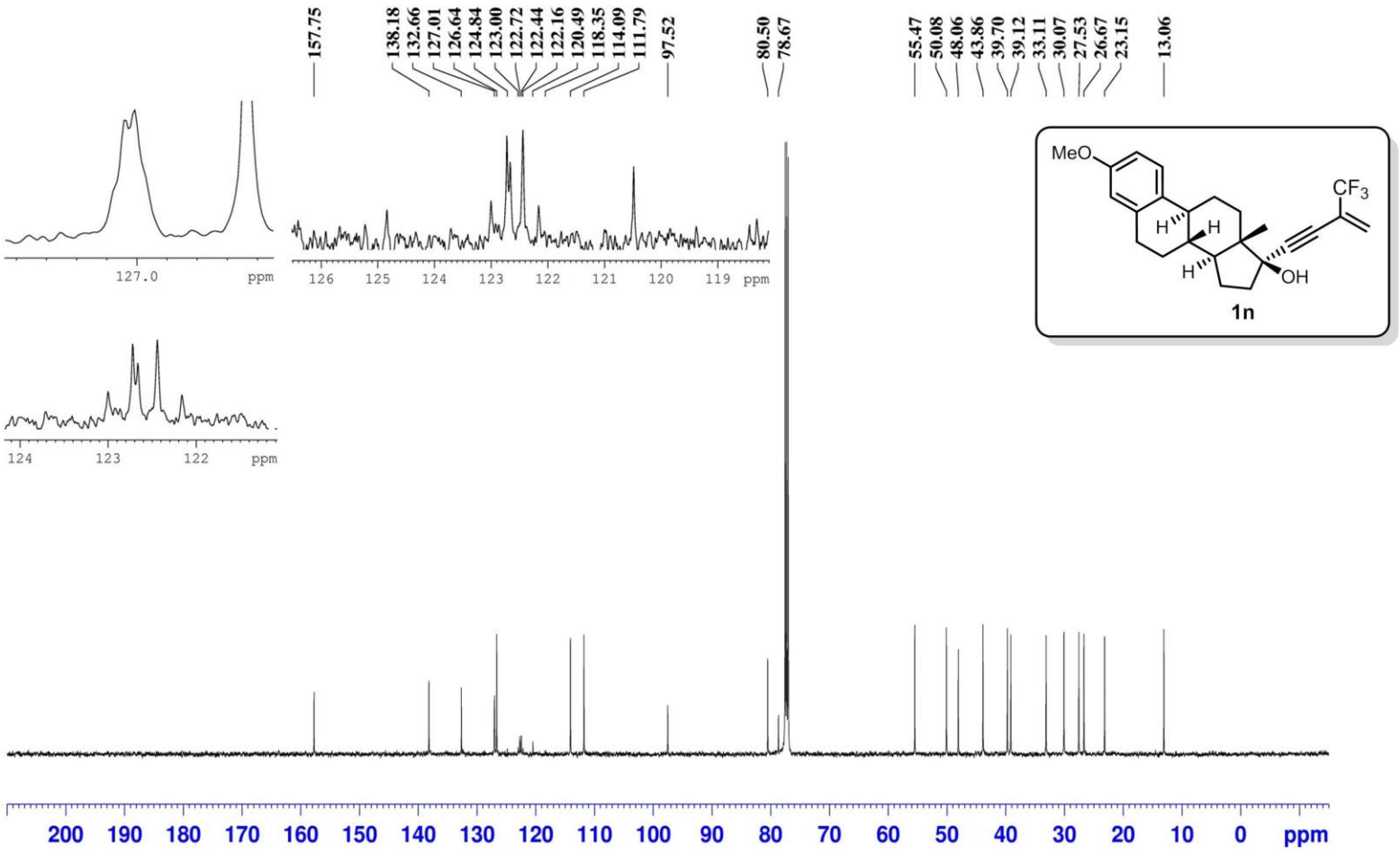




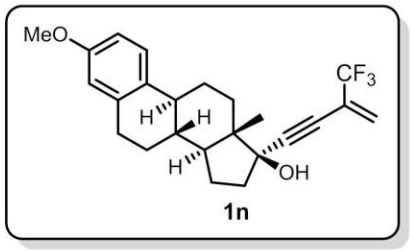
(8R,9S,13S,14S,17S)−3−methoxy−13−methyl−17−(3−(trifluoromethyl)but−3−en−1−yn−1−yl)−7,8,9,11,12,13,14,15,16,17−decahydro−6H−cyclopenta[a]phenantl
500 MHz, CDCl3



(8R,9S,13S,14S,17S)−3−methoxy−13−methyl−17−(3−(trifluoromethyl)but−3−en−1−yn−1−yl)−7,8,9,11,12,13,14,15,16,17−decahydro−6H−cyclopenta[a]phenanthı
125 MHz, CDCl3

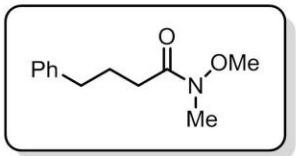


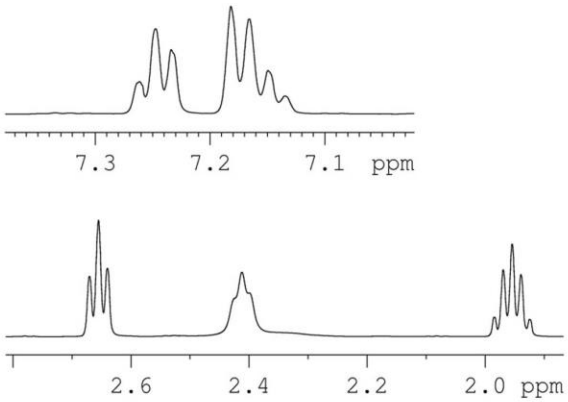
(8R,9S,13S,14S,17S)−3−methoxy−13−methyl−17−(3−(trifluoromethyl)but−3−en−1−yn−1−yl)−7,8,9,11,12,13,14,15,16,17−decahydro−6H−cyclopenta[a]phenanthren−17−ol
471 MHz, CDCl3

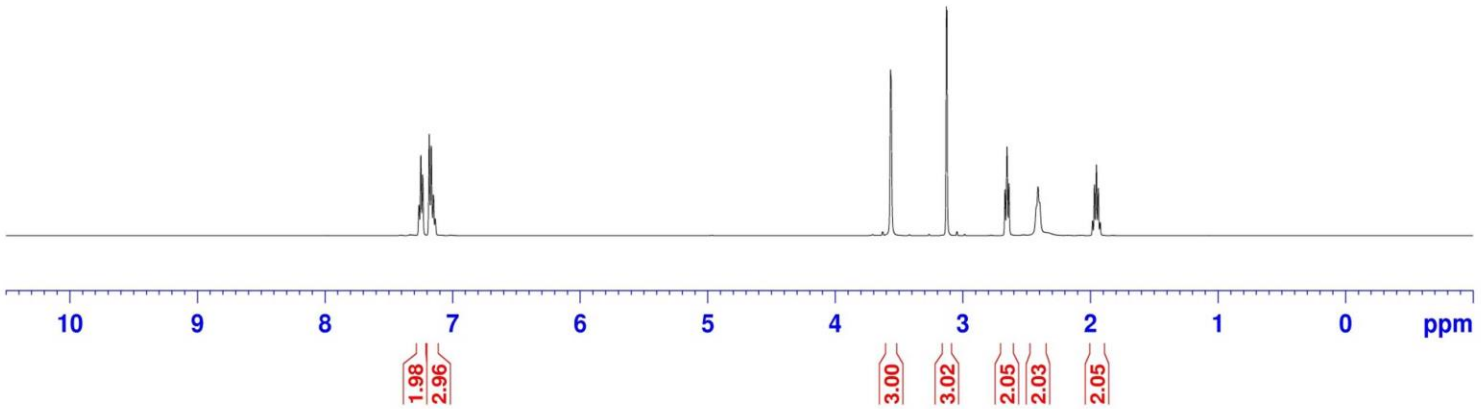


1n

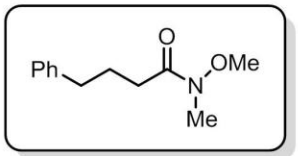
N–methoxy–N–methyl–4–phenylbutanamide
500 MHz, CDCl3

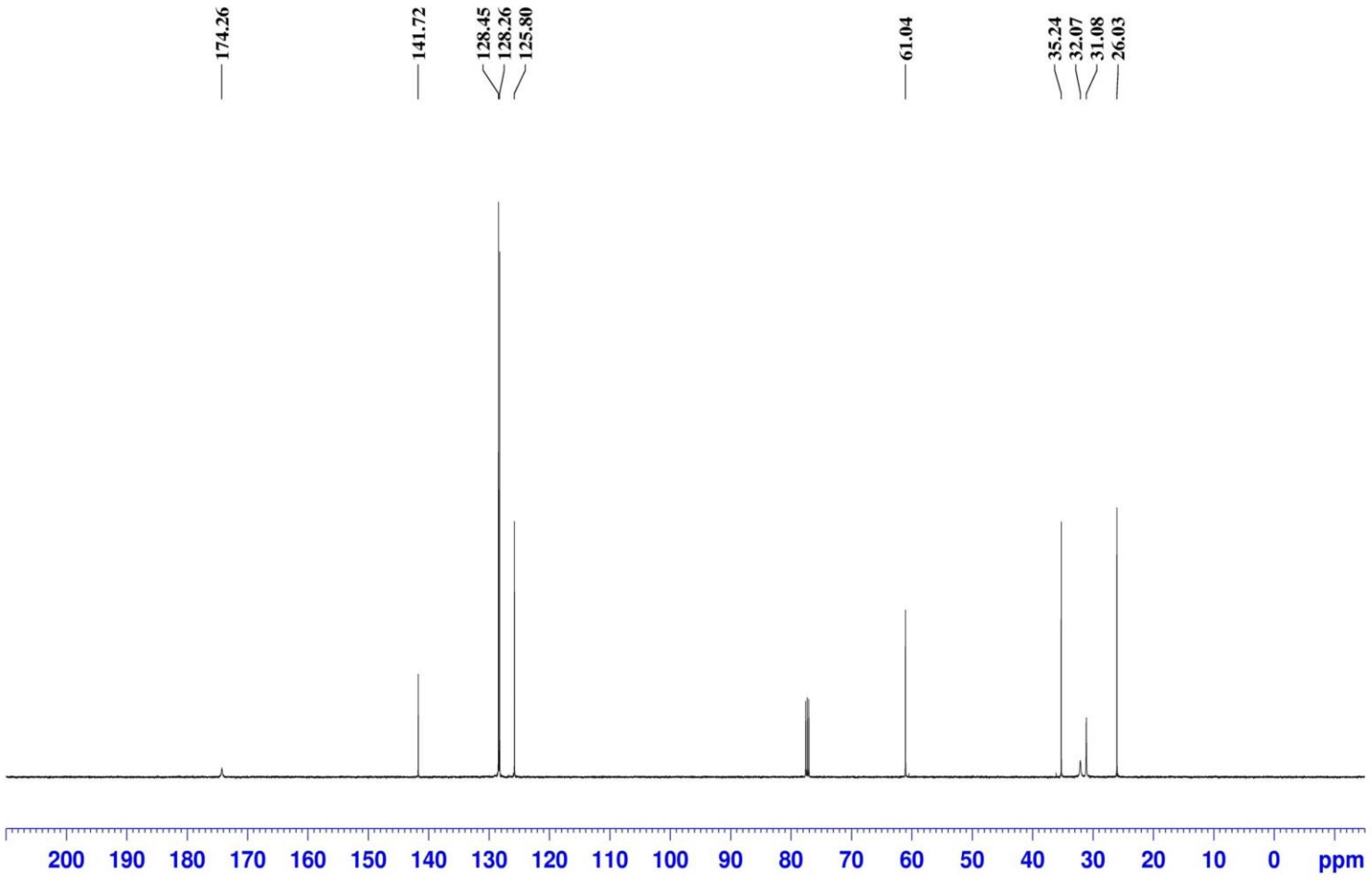




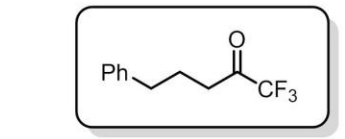


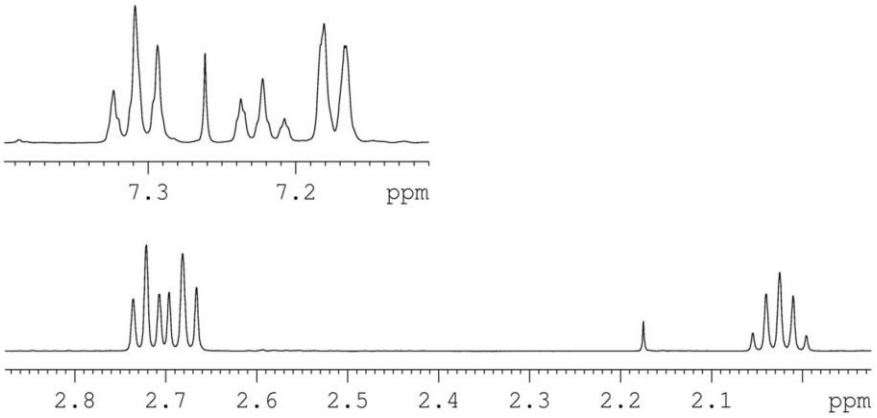
N–methoxy–N–methyl–4–phenylbutanamide
125 MHz, CDCl3

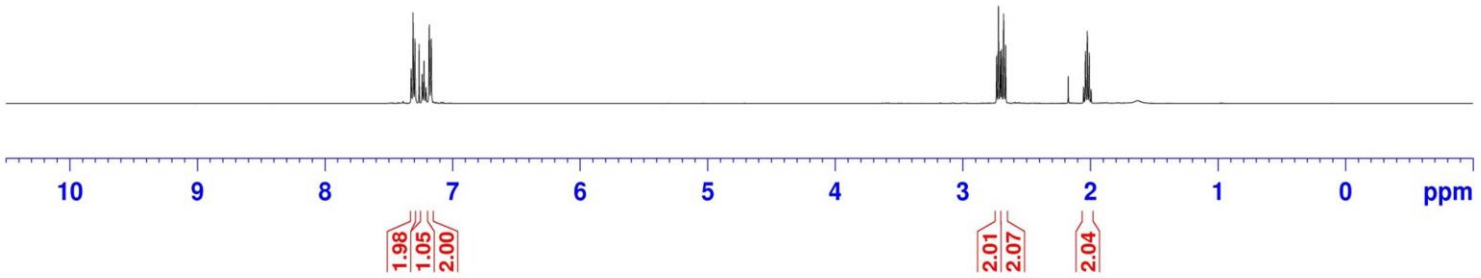




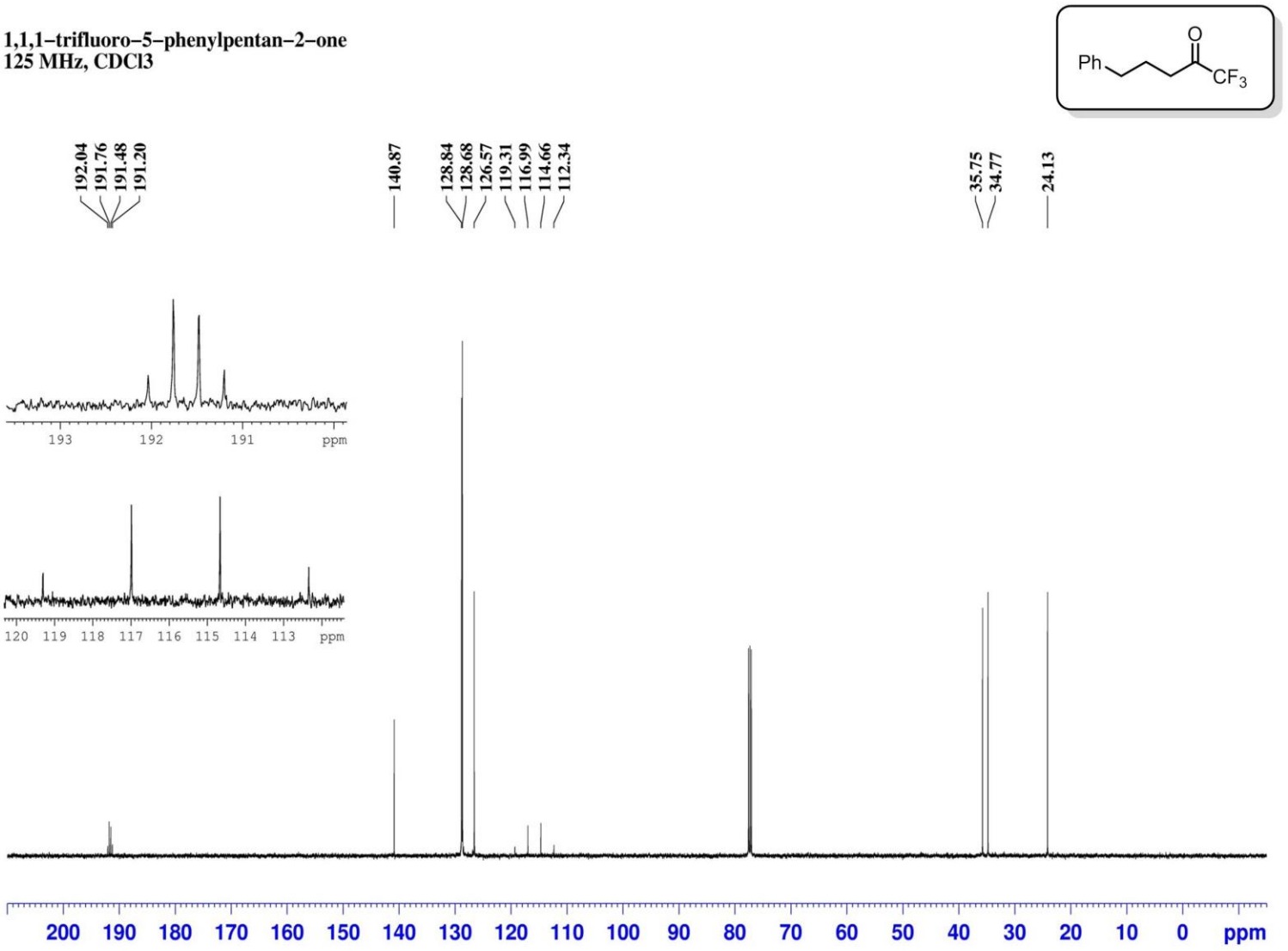
1,1,1–trifluoro–5–phenylpentan–2–one
500 MHz, CDCl3



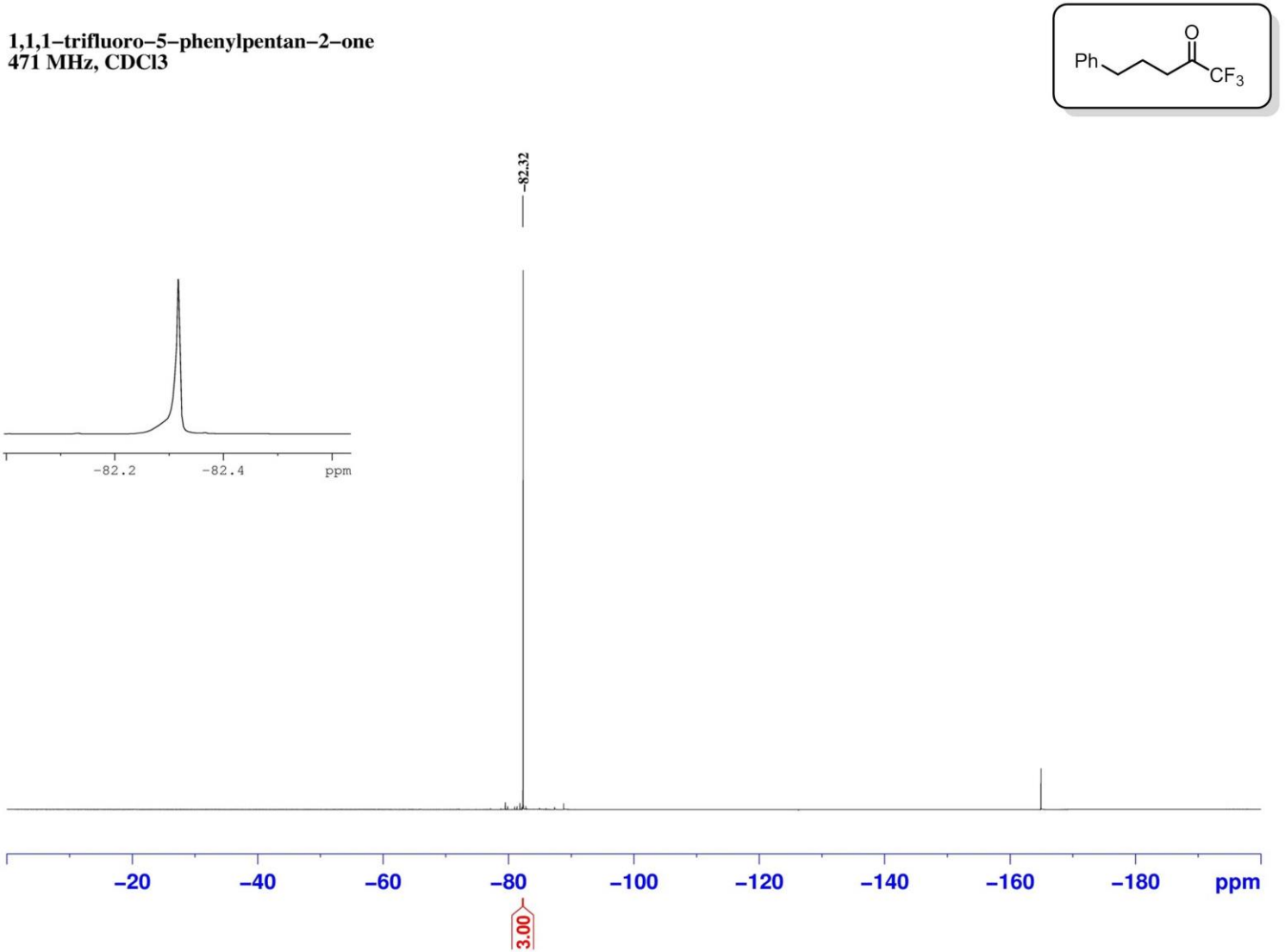




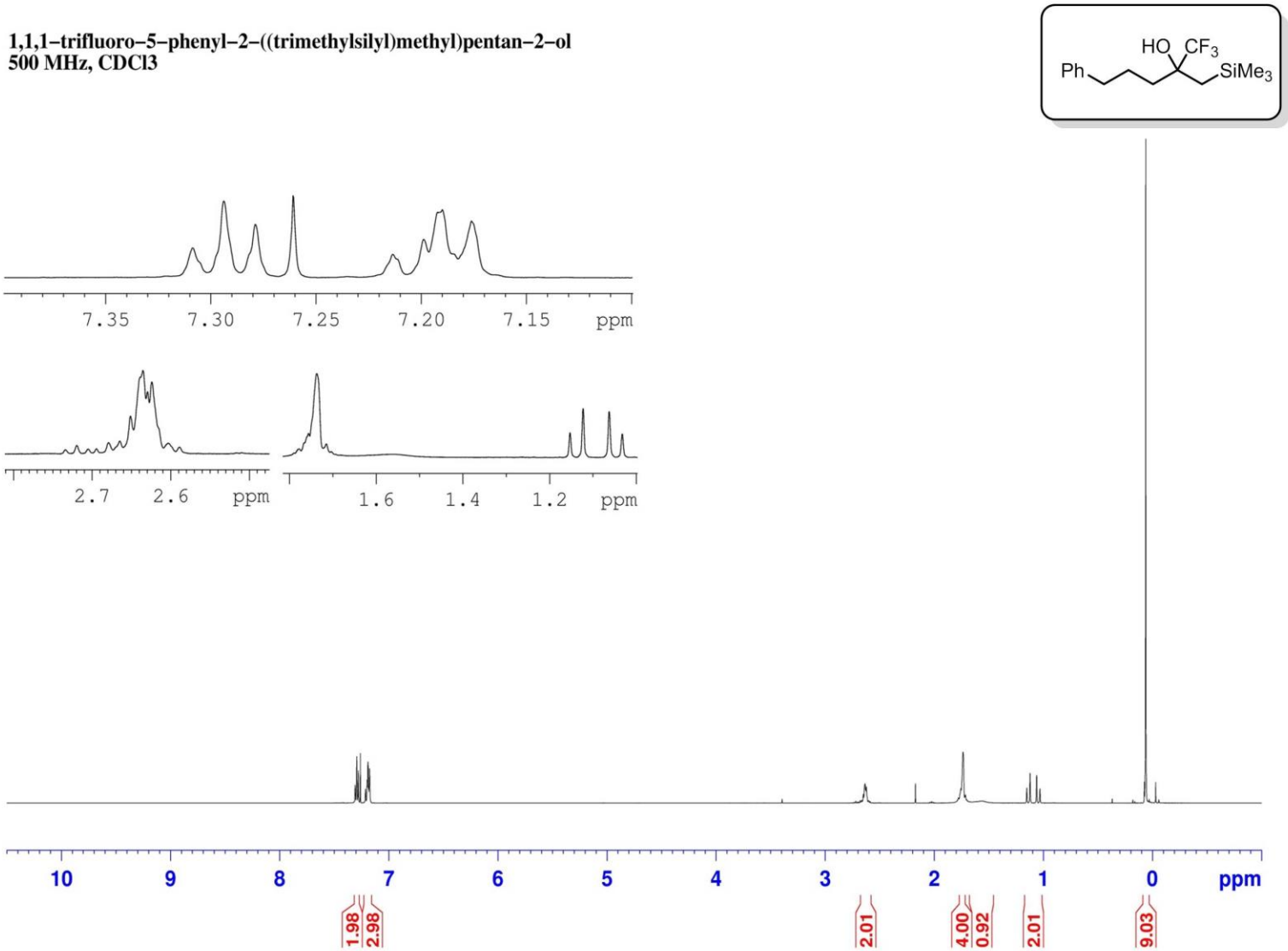
1,1,1–trifluoro–5–phenylpentan–2–one
125 MHz, CDCl3



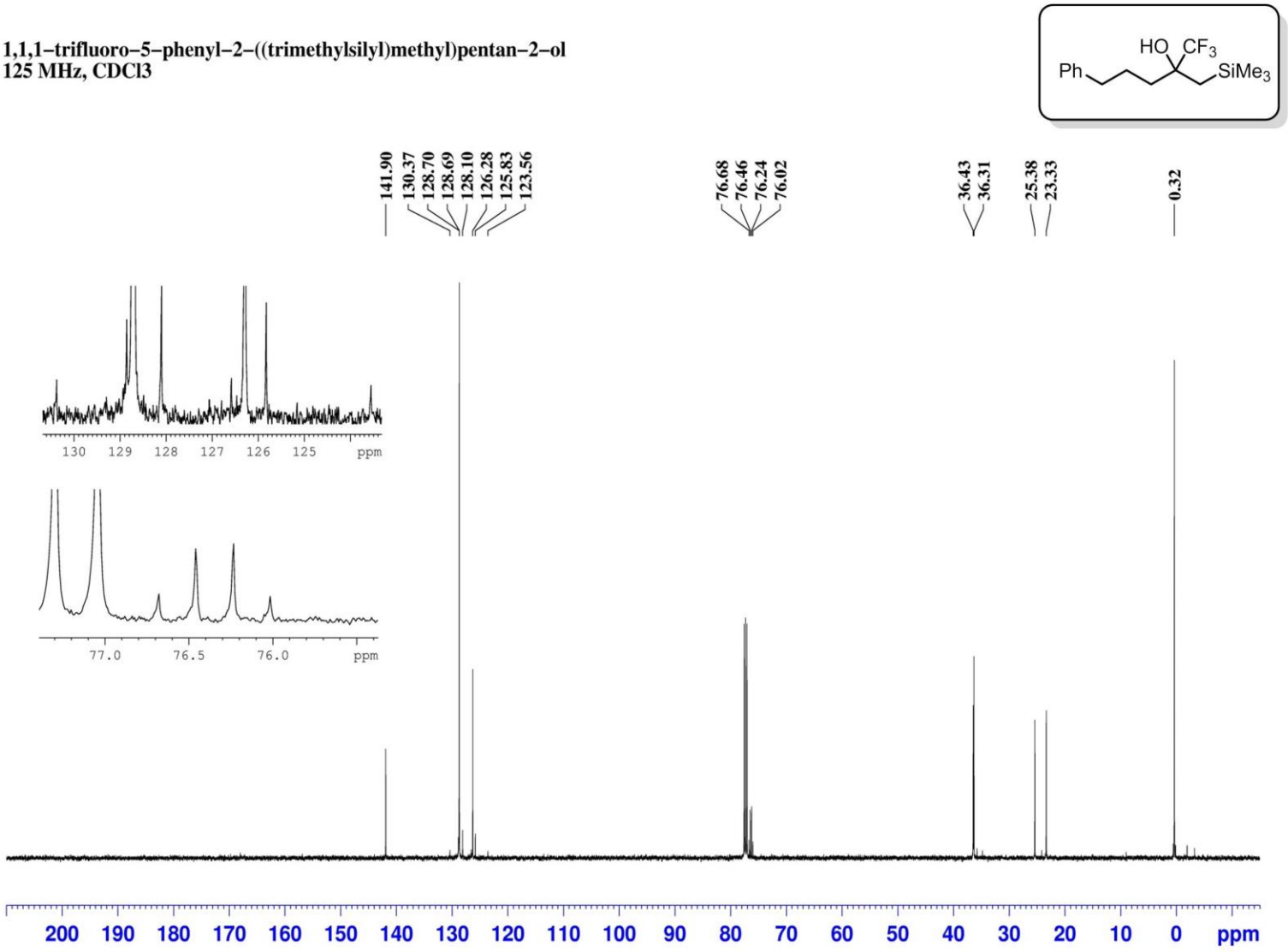
1,1,1–trifluoro–5–phenylpentan–2–one
471 MHz, CDCl3



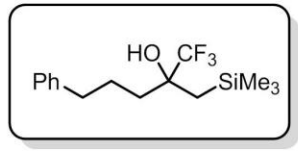
1,1,1−trifluoro−5−phenyl−2−((trimethylsilyl)methyl)pentan−2−ol
500 MHz, CDCl3

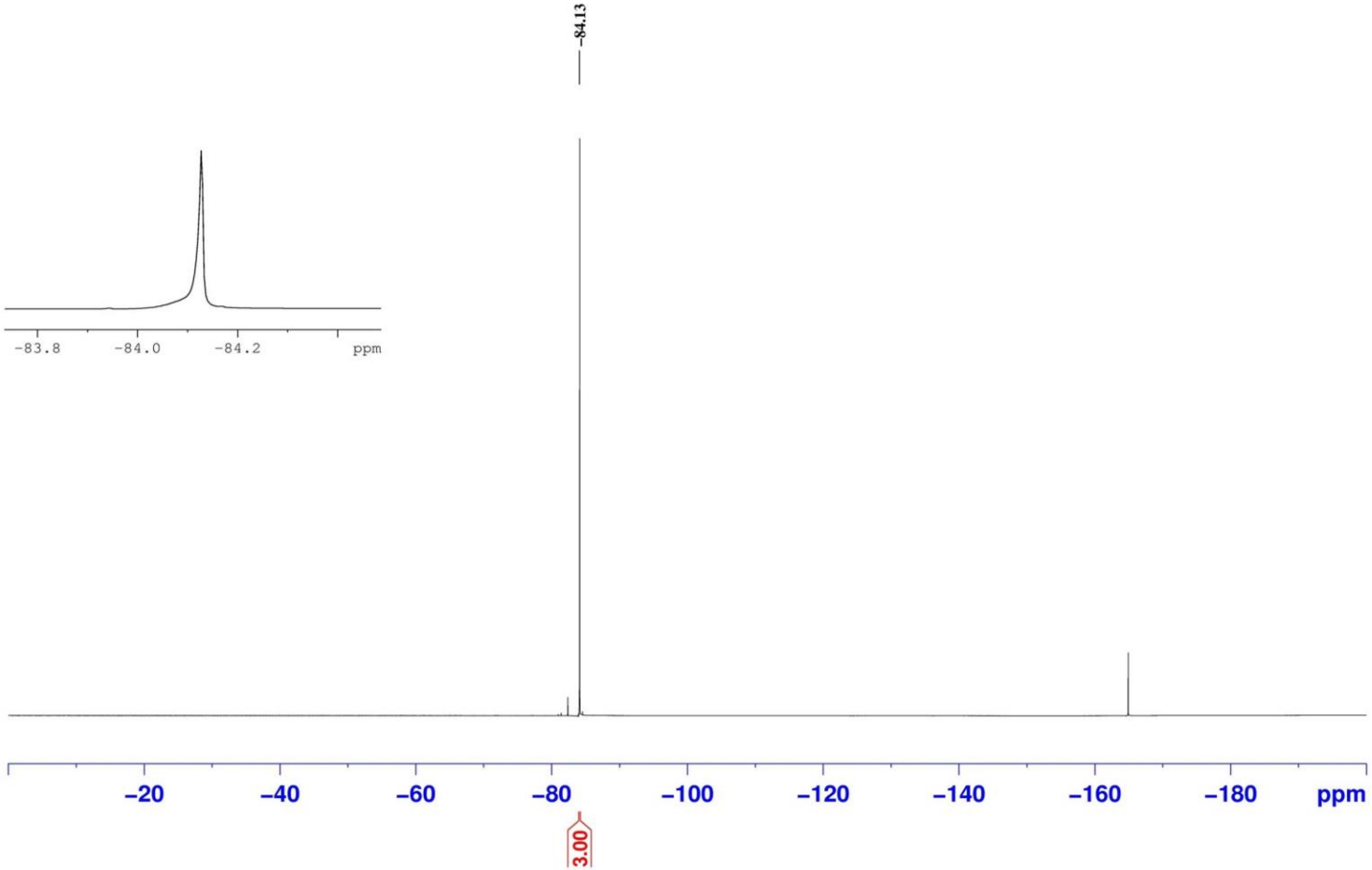


1,1,1−trifluoro−5−phenyl−2−((trimethylsilyl)methyl)pentan−2−ol
125 MHz, CDCl3

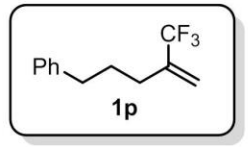


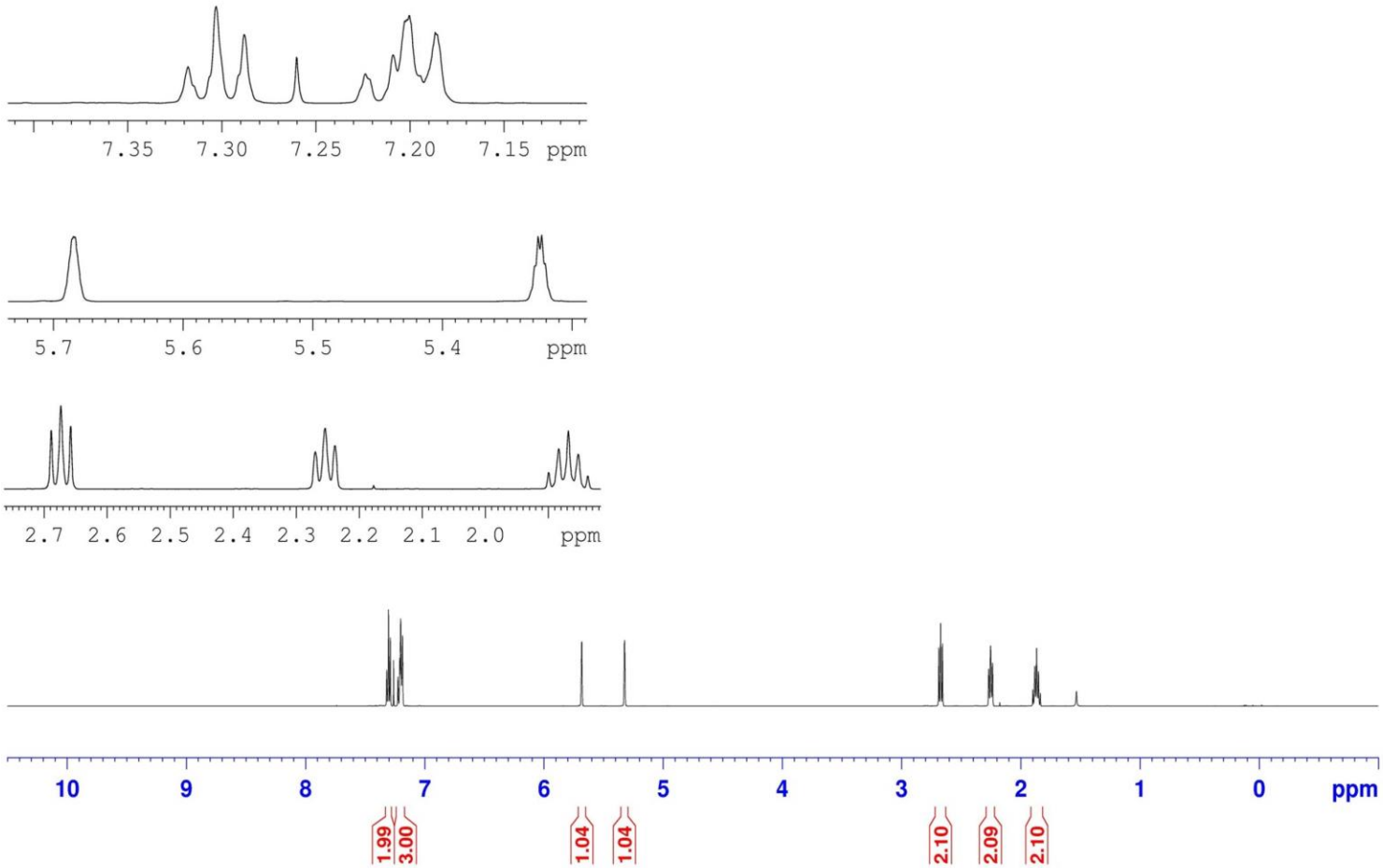
1,1,1−trifluoro−5−phenyl−2−((trimethylsilyl)methyl)pentan−2−ol
471 MHz, CDCl3



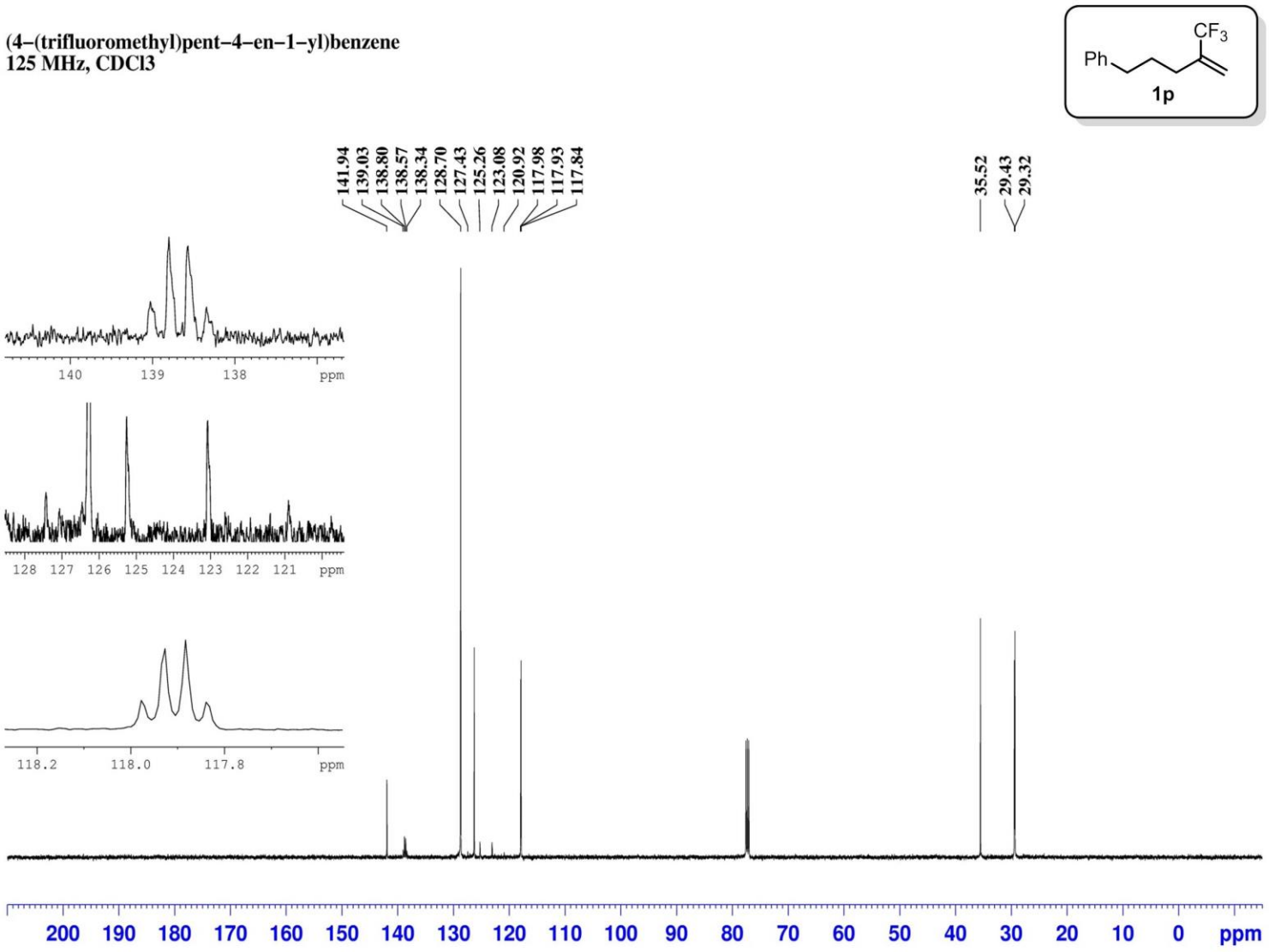


(4–(trifluoromethyl)pent–4–en–1–yl)benzene
500 MHz, CDCl3

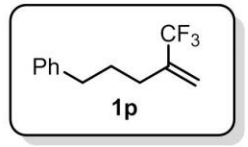


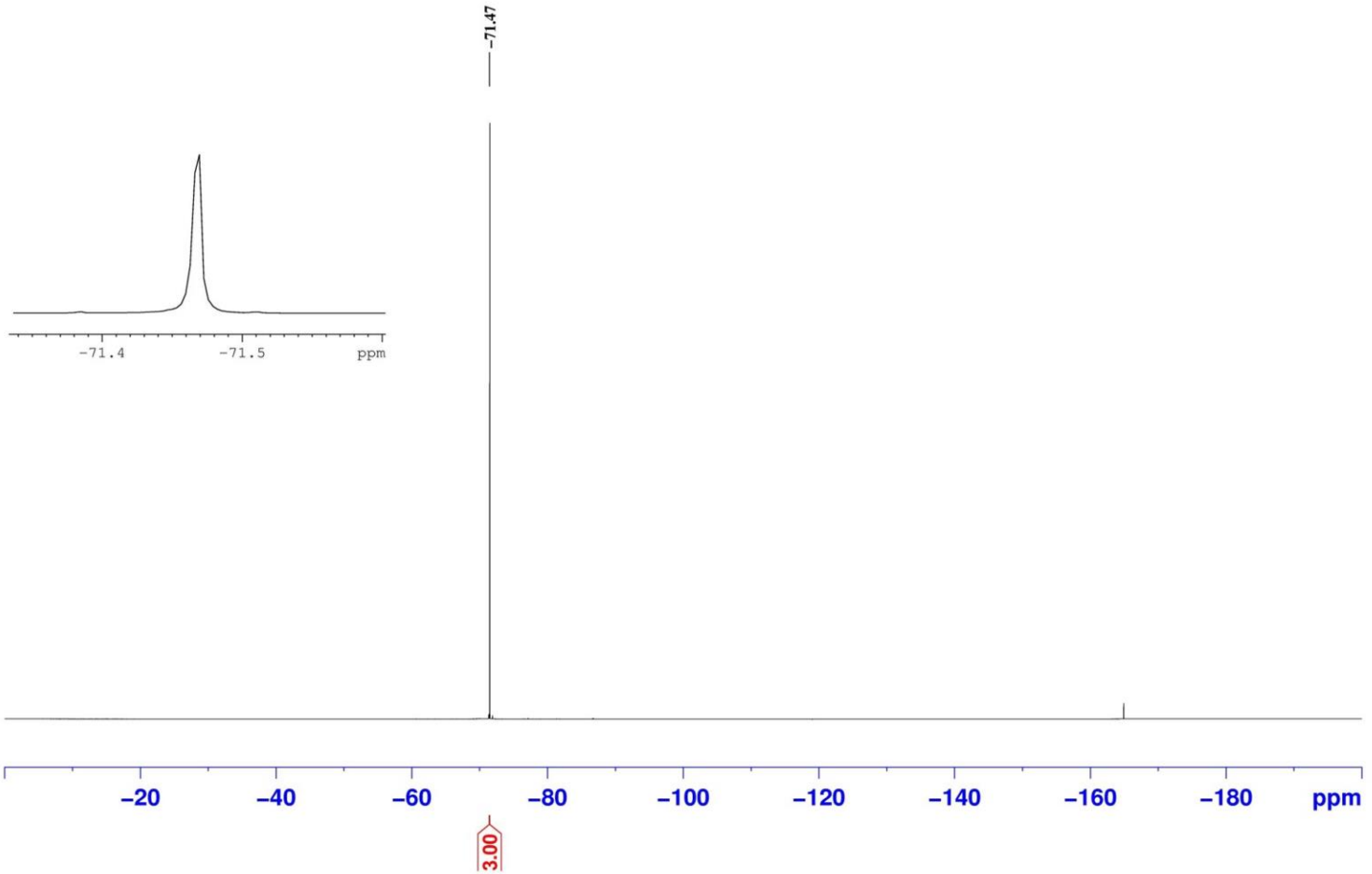


(4–(trifluoromethyl)pent–4–en–1–yl)benzene
125 MHz, CDCl3

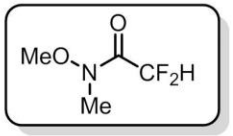


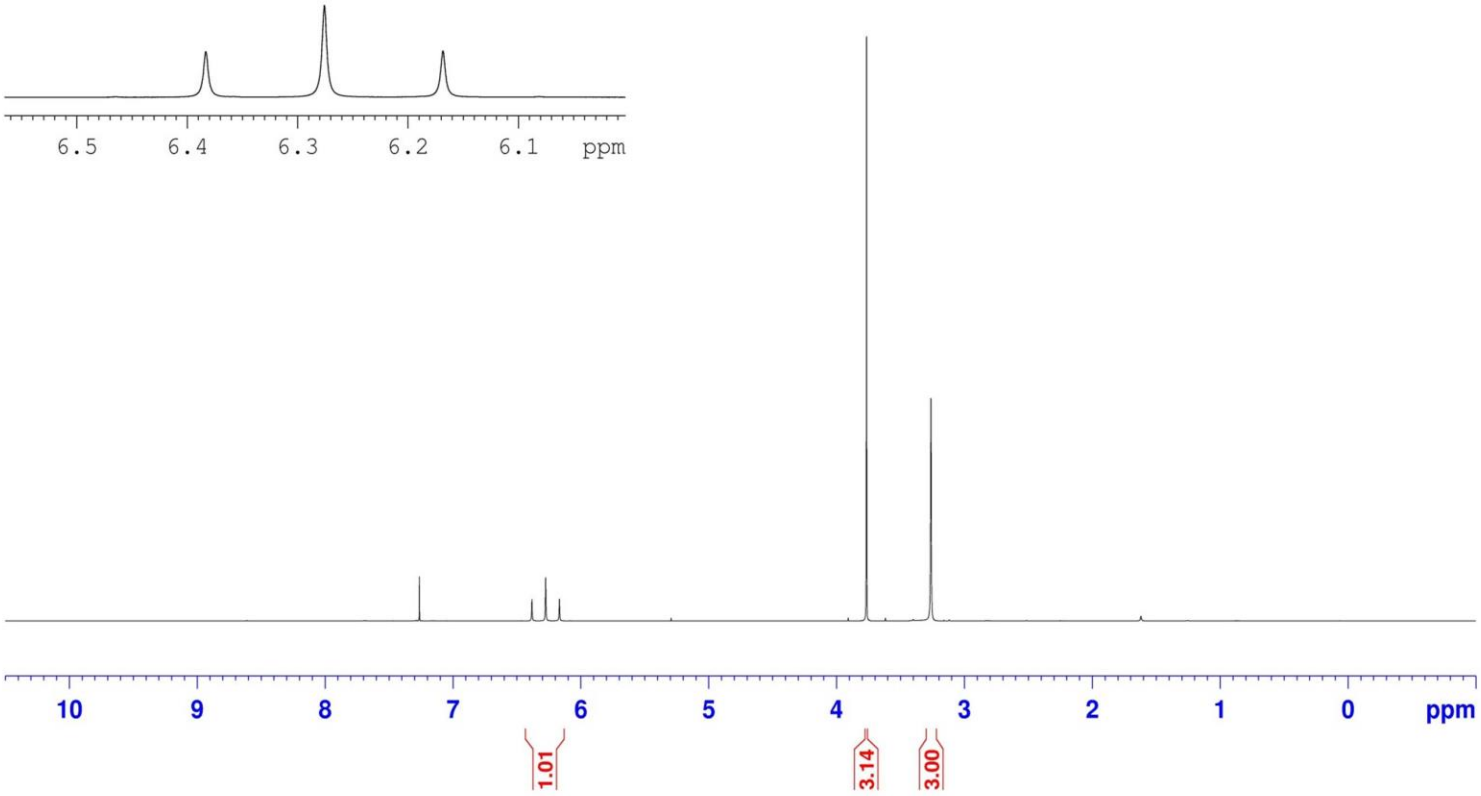
(4–(trifluoromethyl)pent–4–en–1–yl)benzene
471 MHz, CDCl3



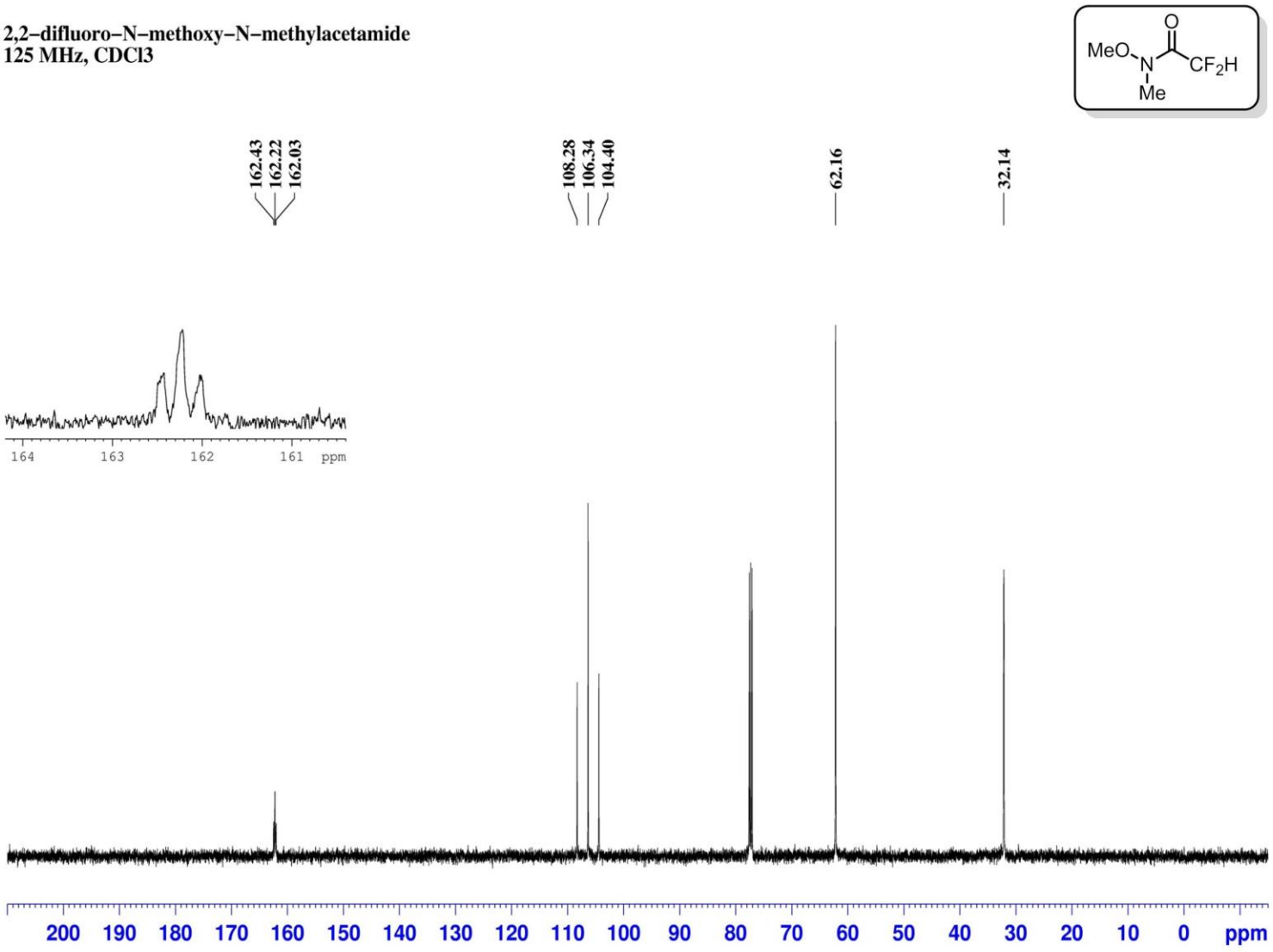


2,2–difluoro–N–methoxy–N–methylacetamide
500 MHz, CDCl3

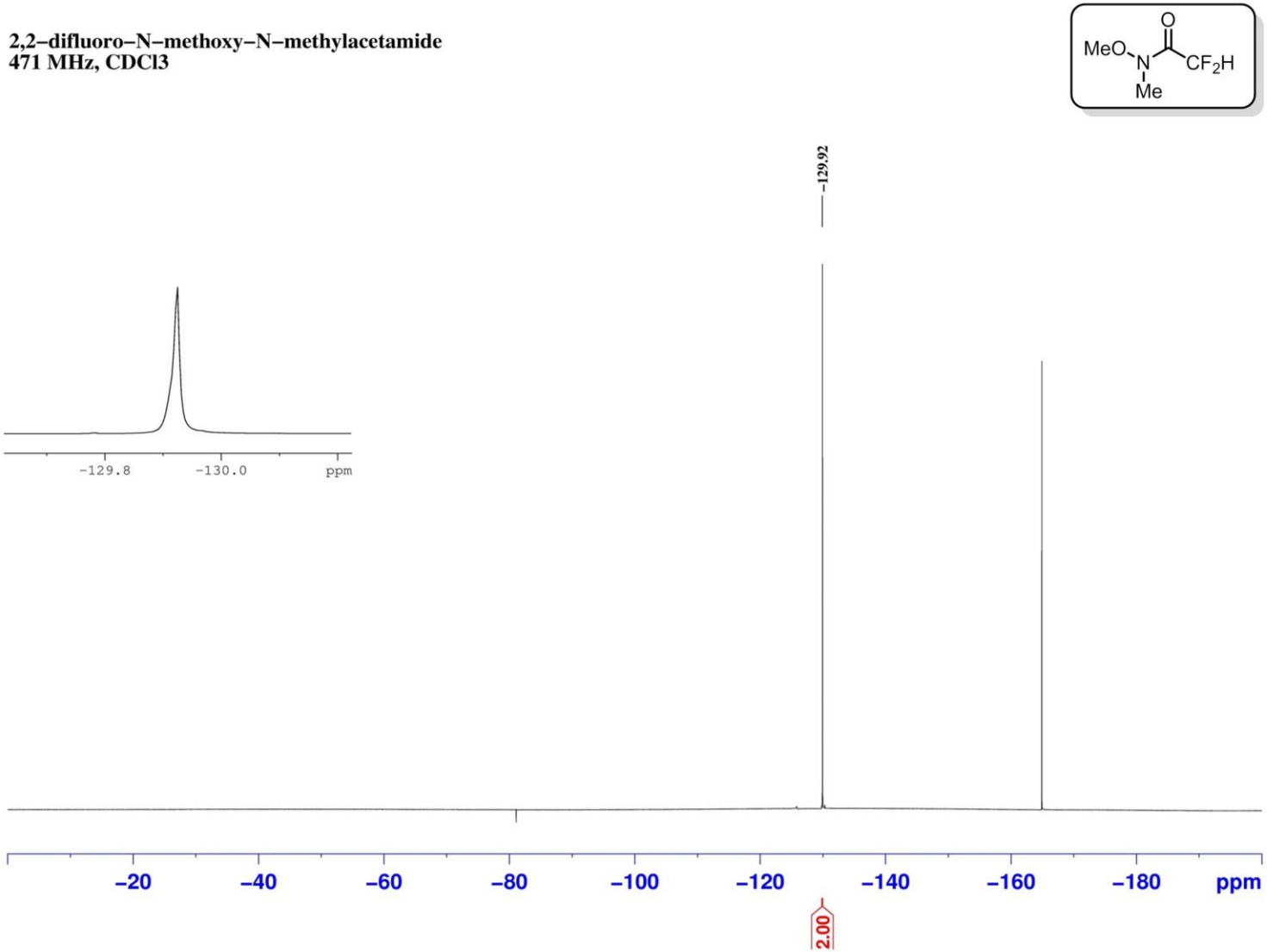




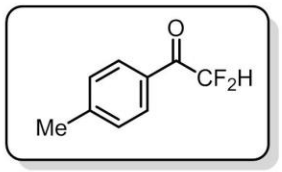
2,2–difluoro–N–methoxy–N–methylacetamide
125 MHz, CDCl3

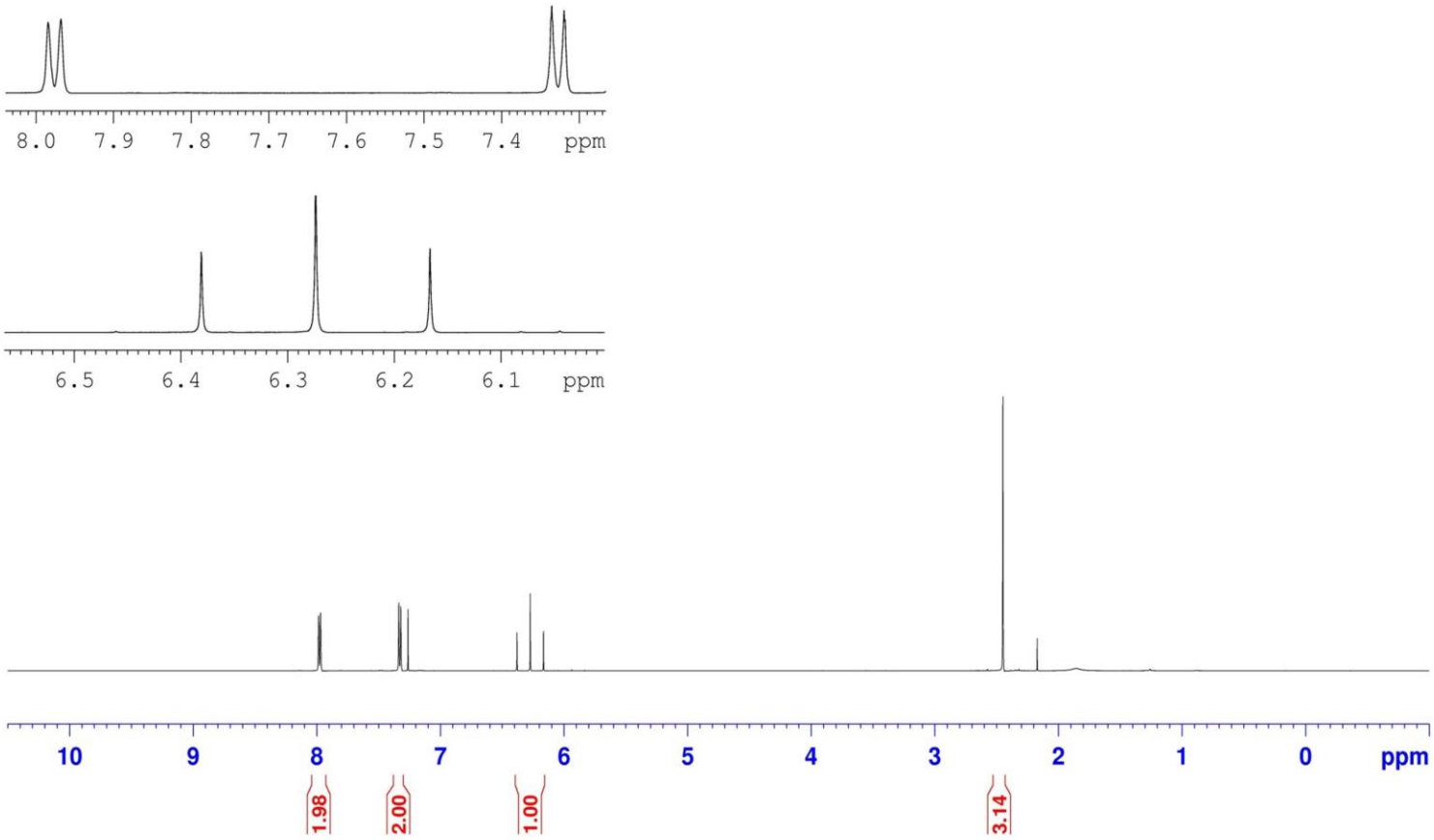


2,2–difluoro–N–methoxy–N–methylacetamide
471 MHz, CDCl3

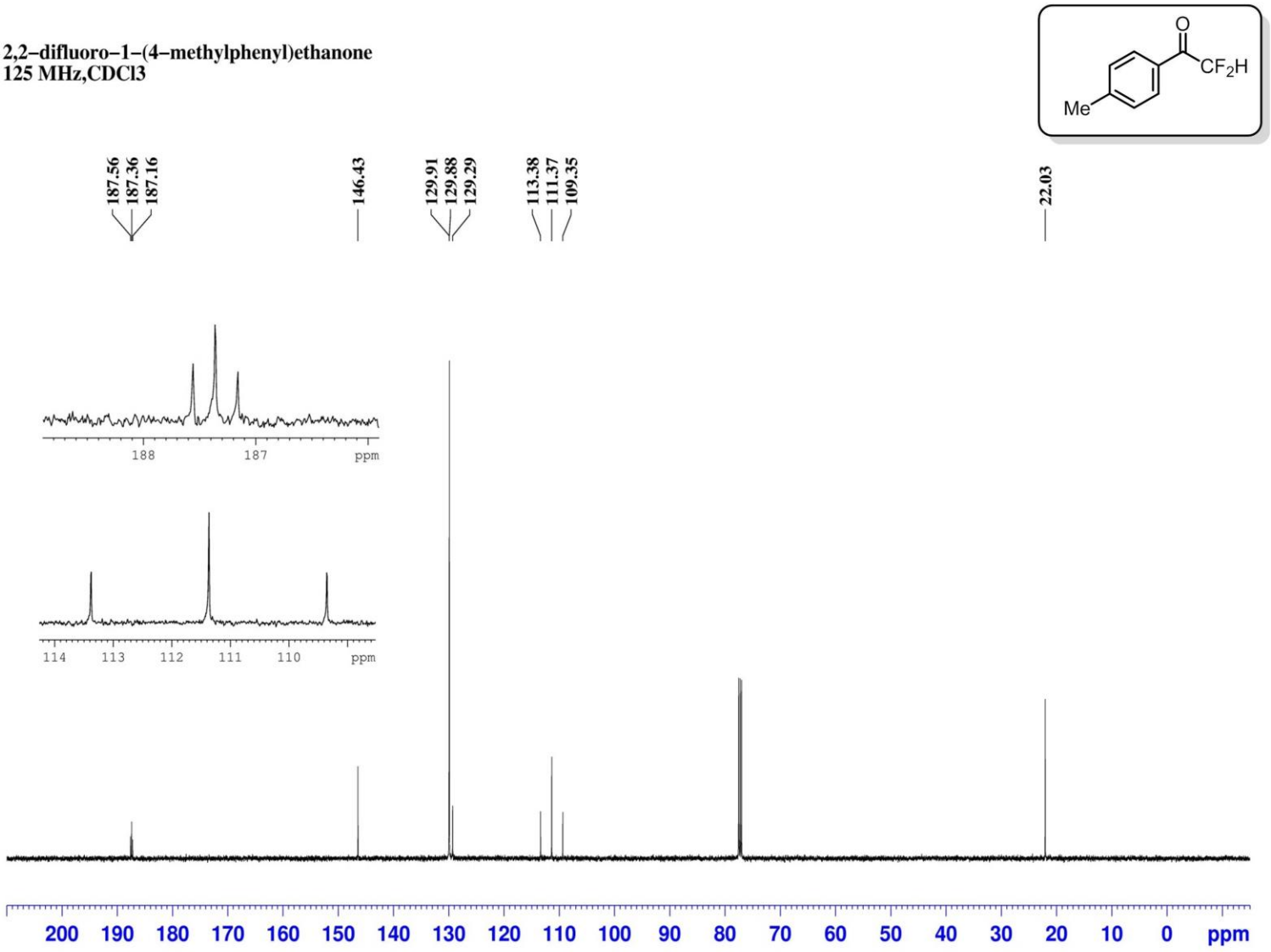


2,2–difluoro–1–(4–methylphenyl)ethanone
500 MHz, CDCl3

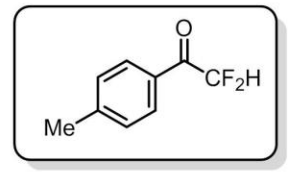


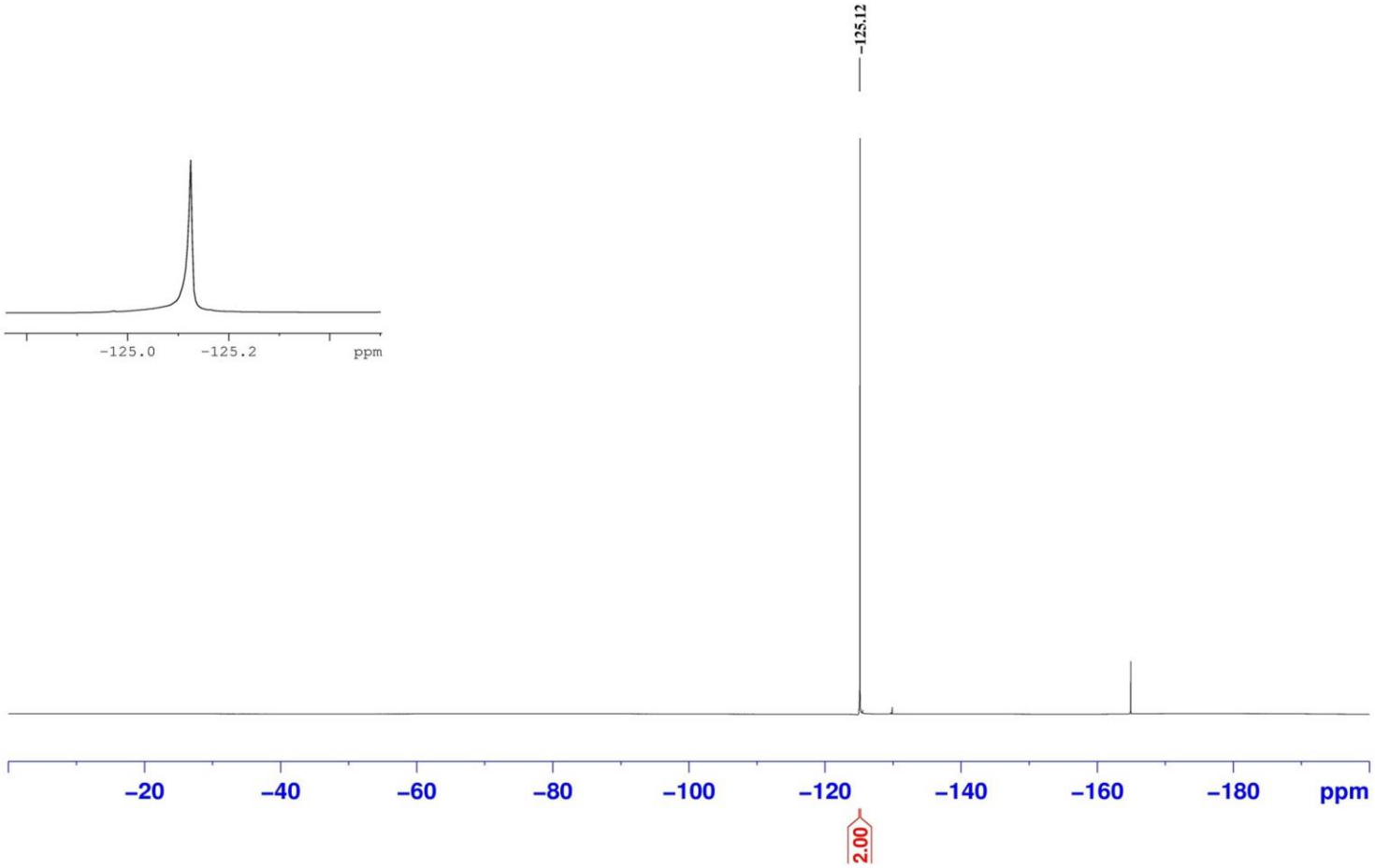


2,2–difluoro–1–(4–methylphenyl)ethanone
125 MHz,CDCl3

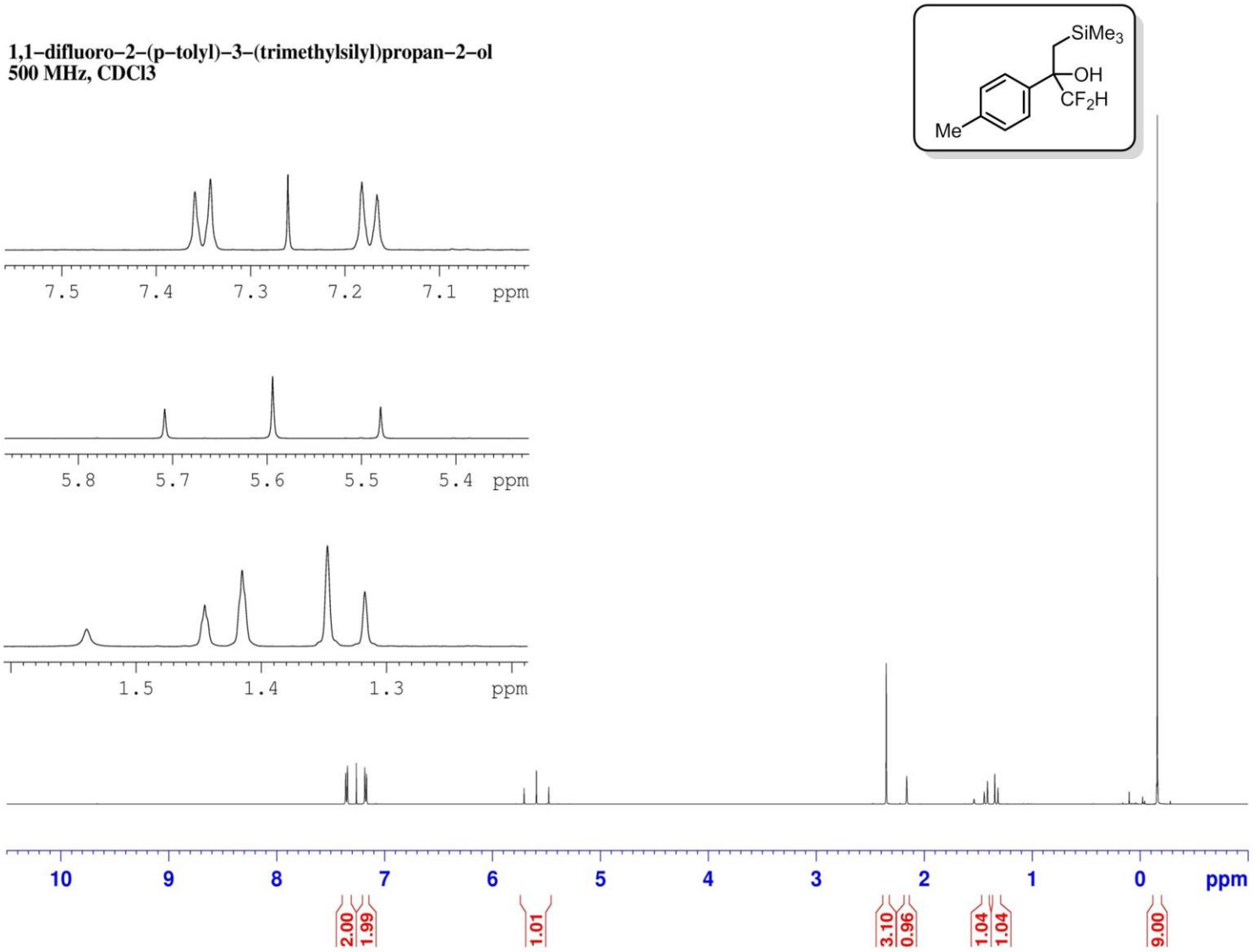


2,2–difluoro–1–(4–methylphenyl)ethanone
471 MHz, CDCl3

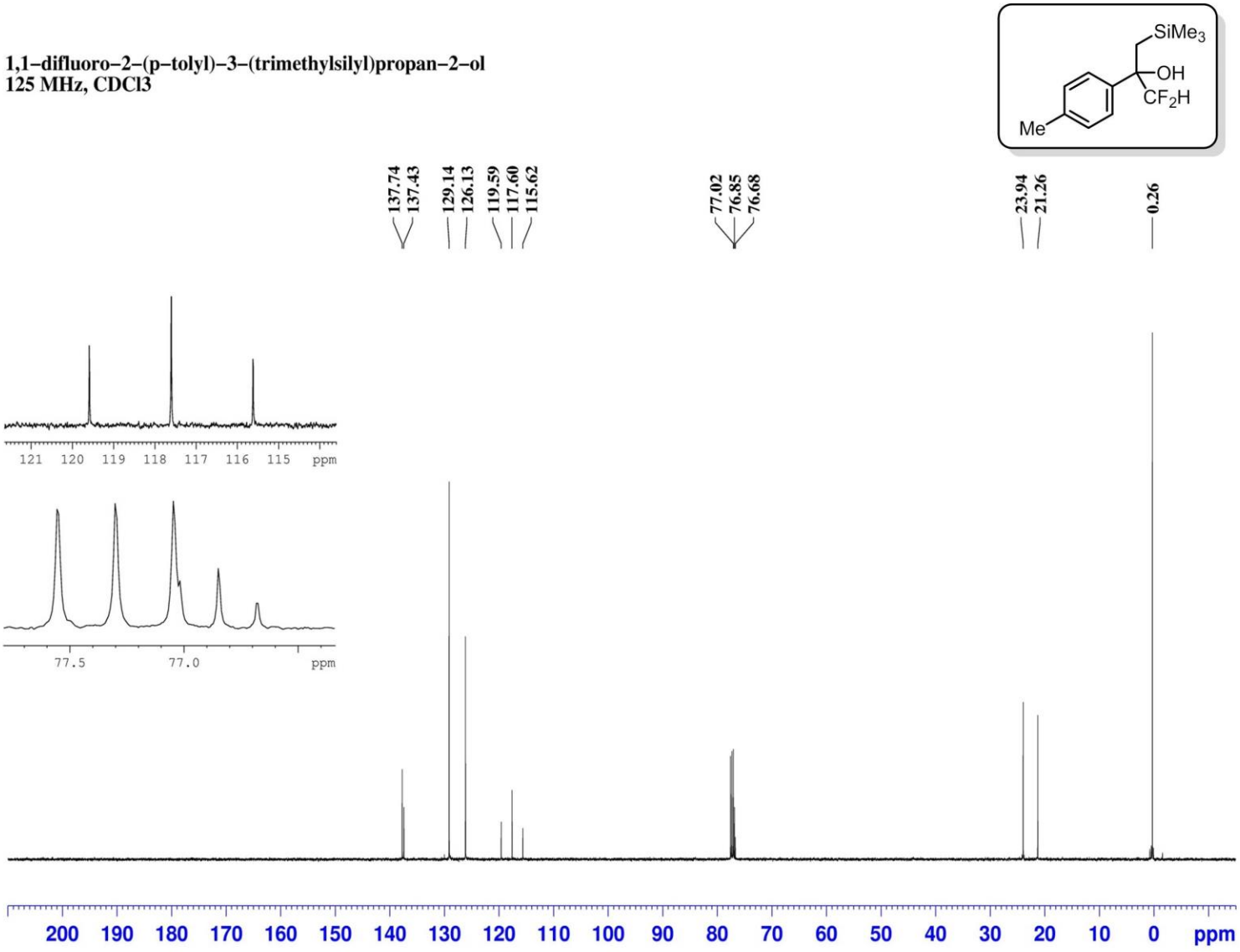




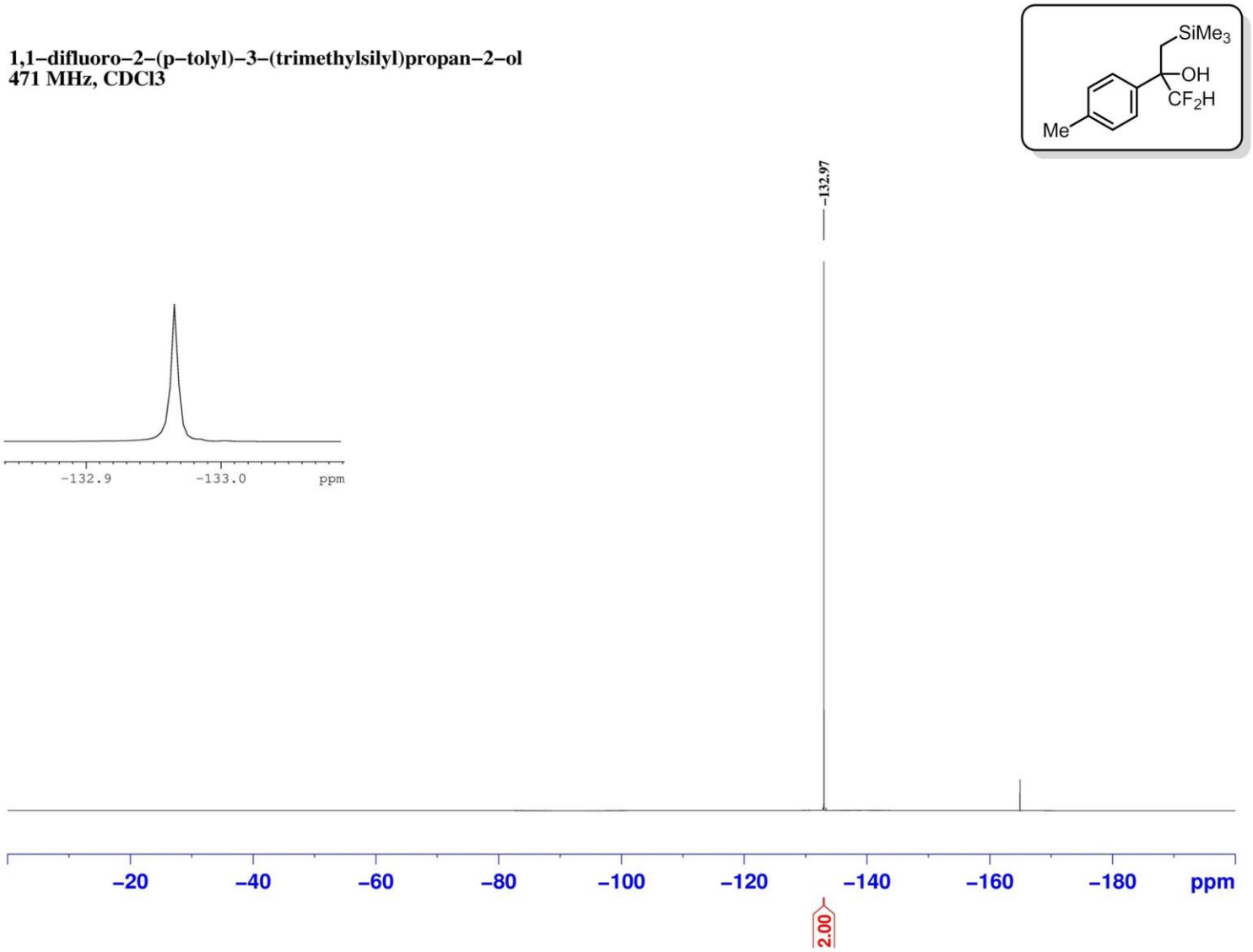
1,1–difluoro–2–(p–tolyl)–3–(trimethylsilyl)propan–2–ol
500 MHz, CDCl3



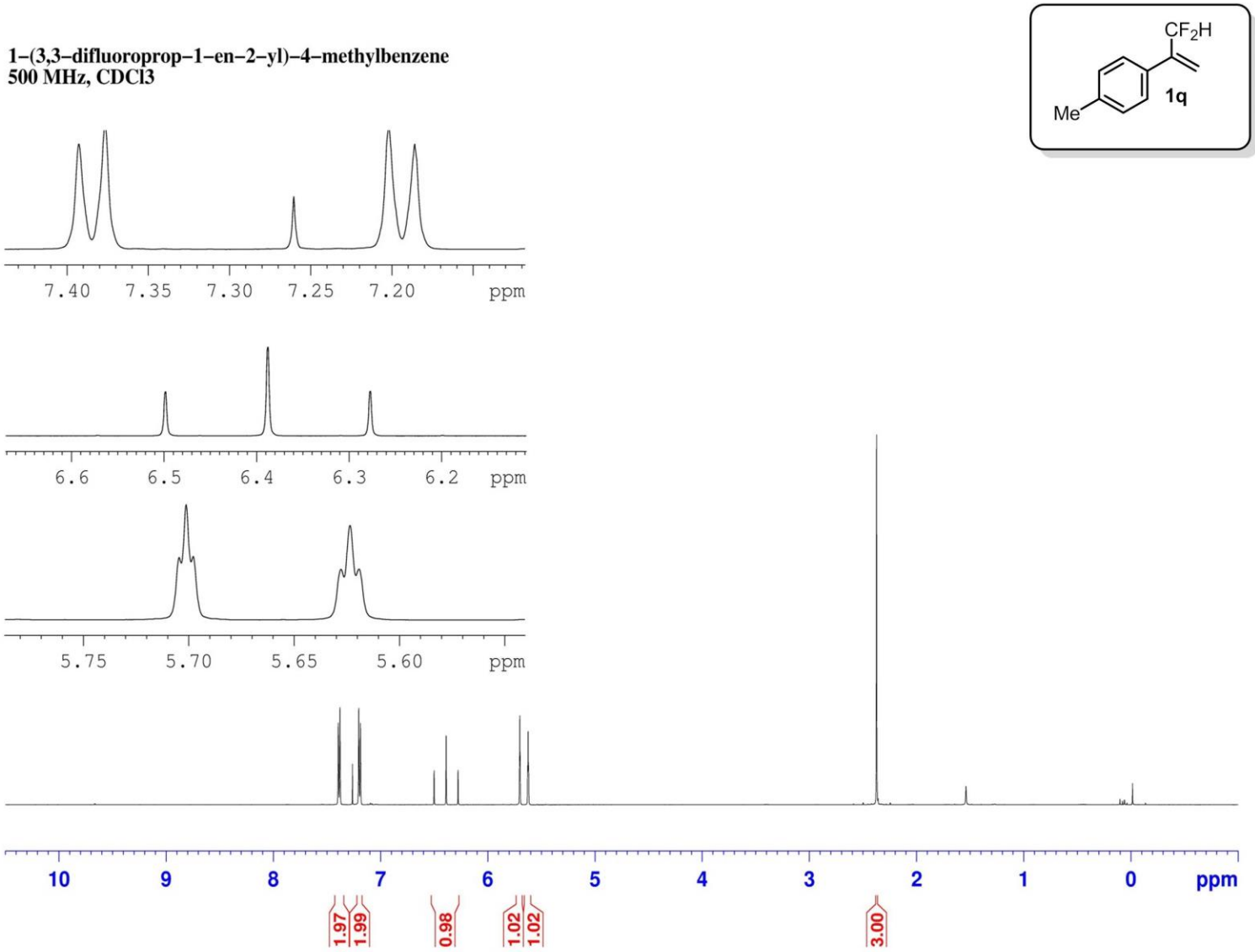
1,1–difluoro–2–(p–tolyl)–3–(trimethylsilyl)propan–2–ol
125 MHz, CDCl3



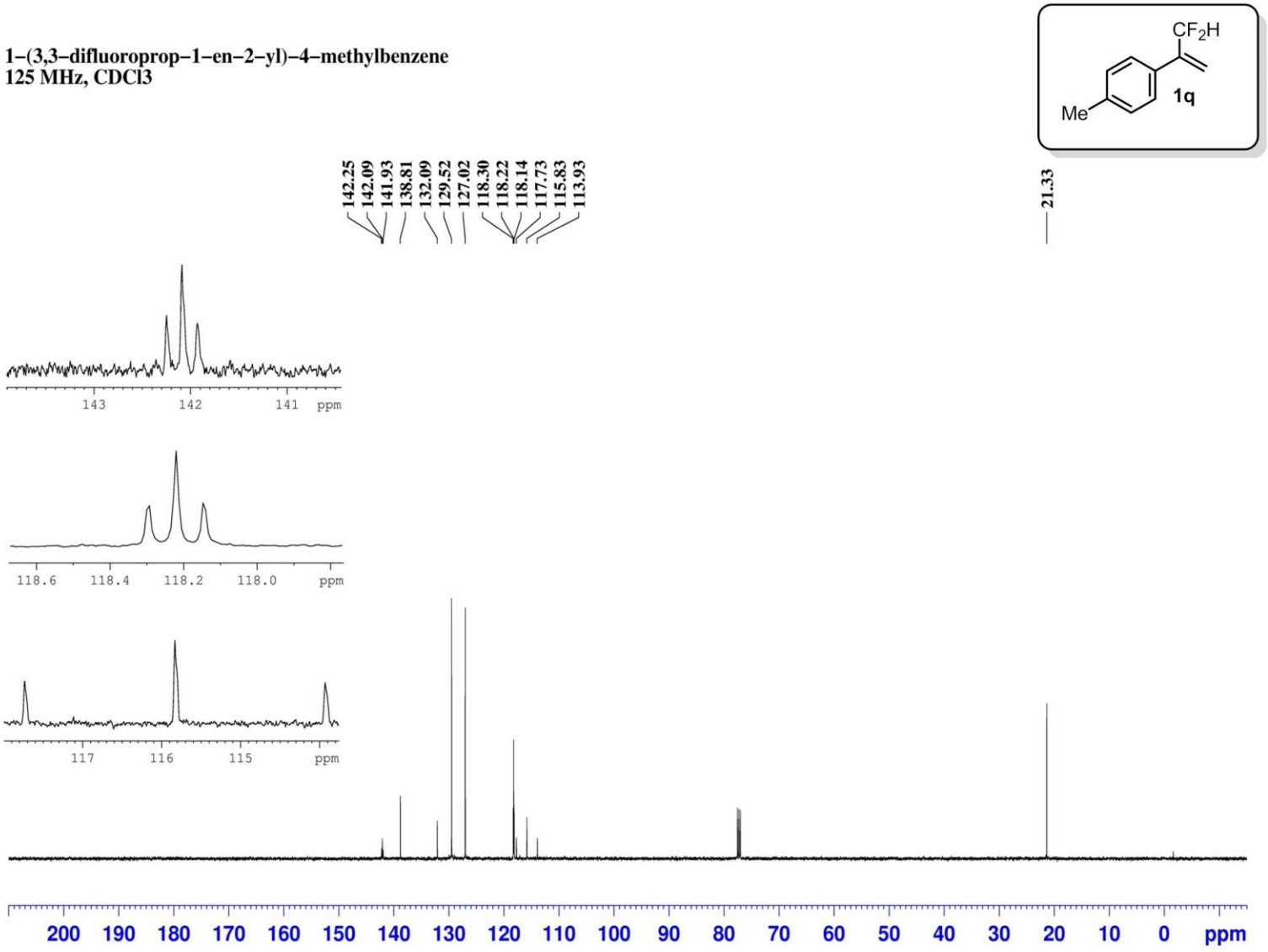
1,1–difluoro–2–(p–tolyl)–3–(trimethylsilyl)propan–2–ol
471 MHz, CDCl3



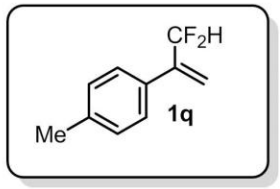
1–(3,3–difluoroprop–1–en–2–yl)–4–methylbenzene
500 MHz, CDCl3

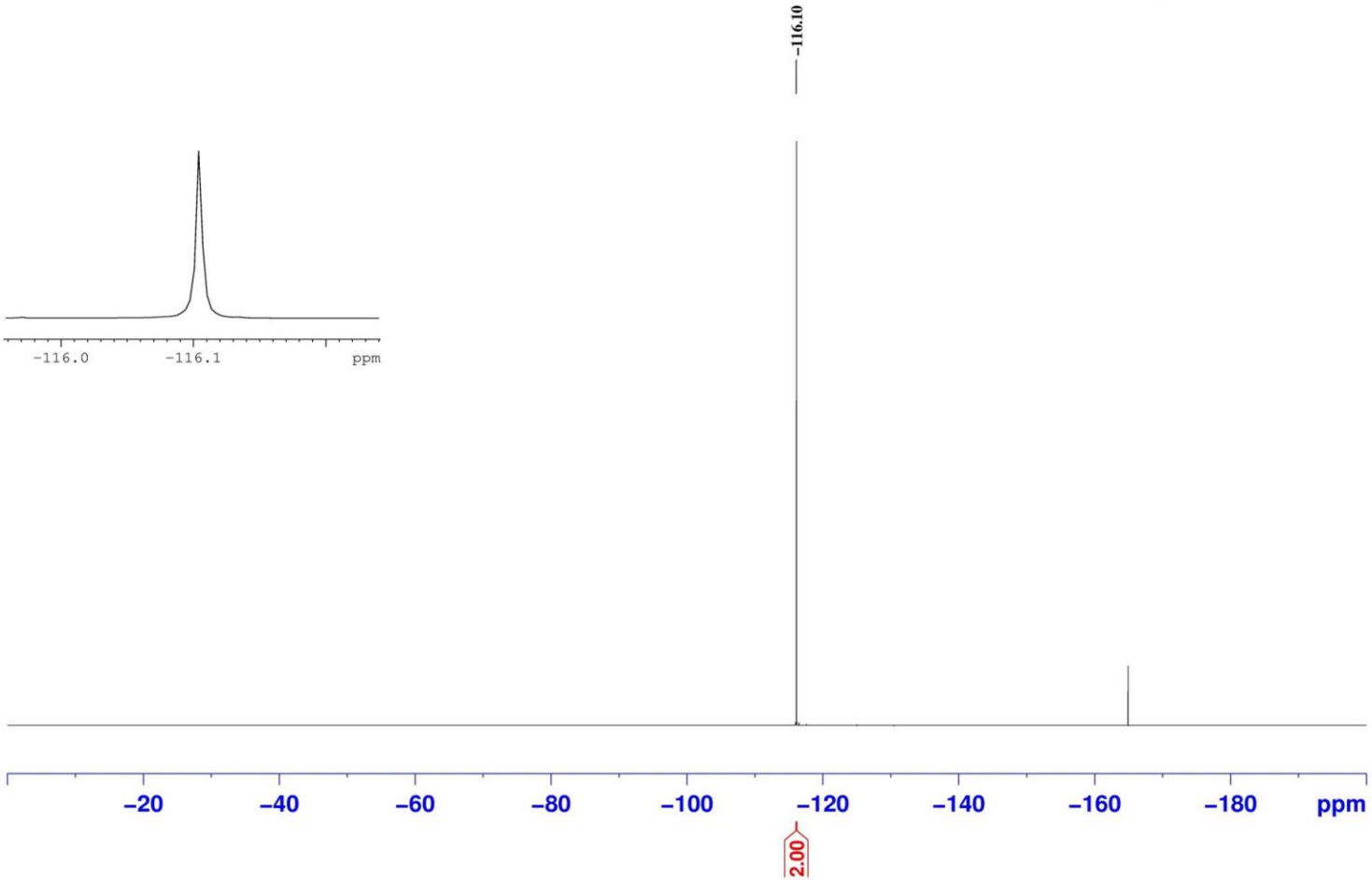


1–(3,3–difluoroprop–1–en–2–yl)–4–methylbenzene
125 MHz, CDCl3



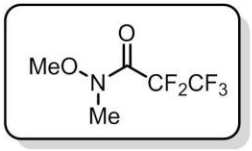
1–(3,3–difluoroprop–1–en–2–yl)–4–methylbenzene
471 MHz, CDCl3

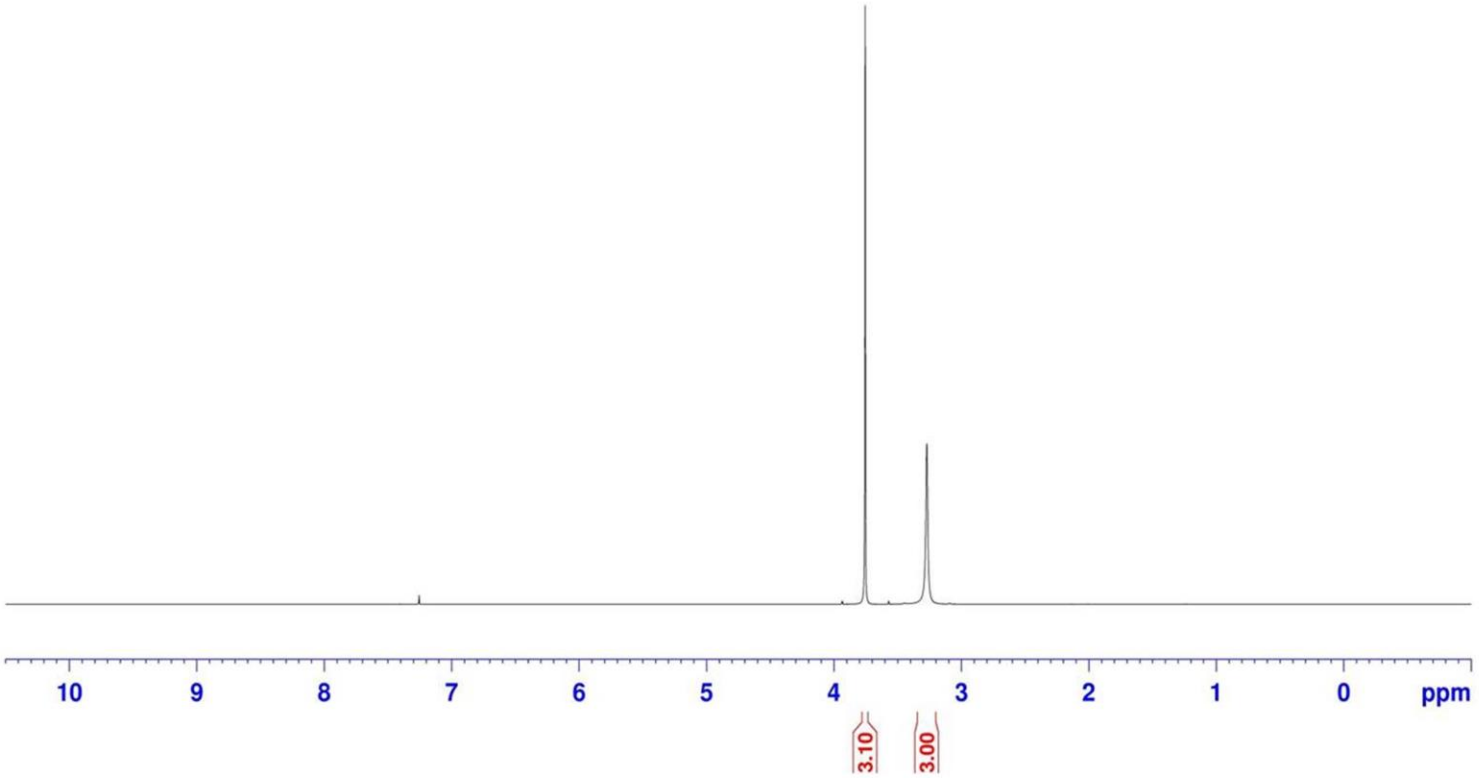




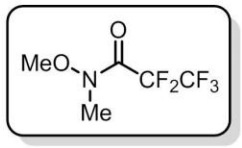
2,2,3,3,3–pentafluoro–N–methoxy–N–methylpropanamide

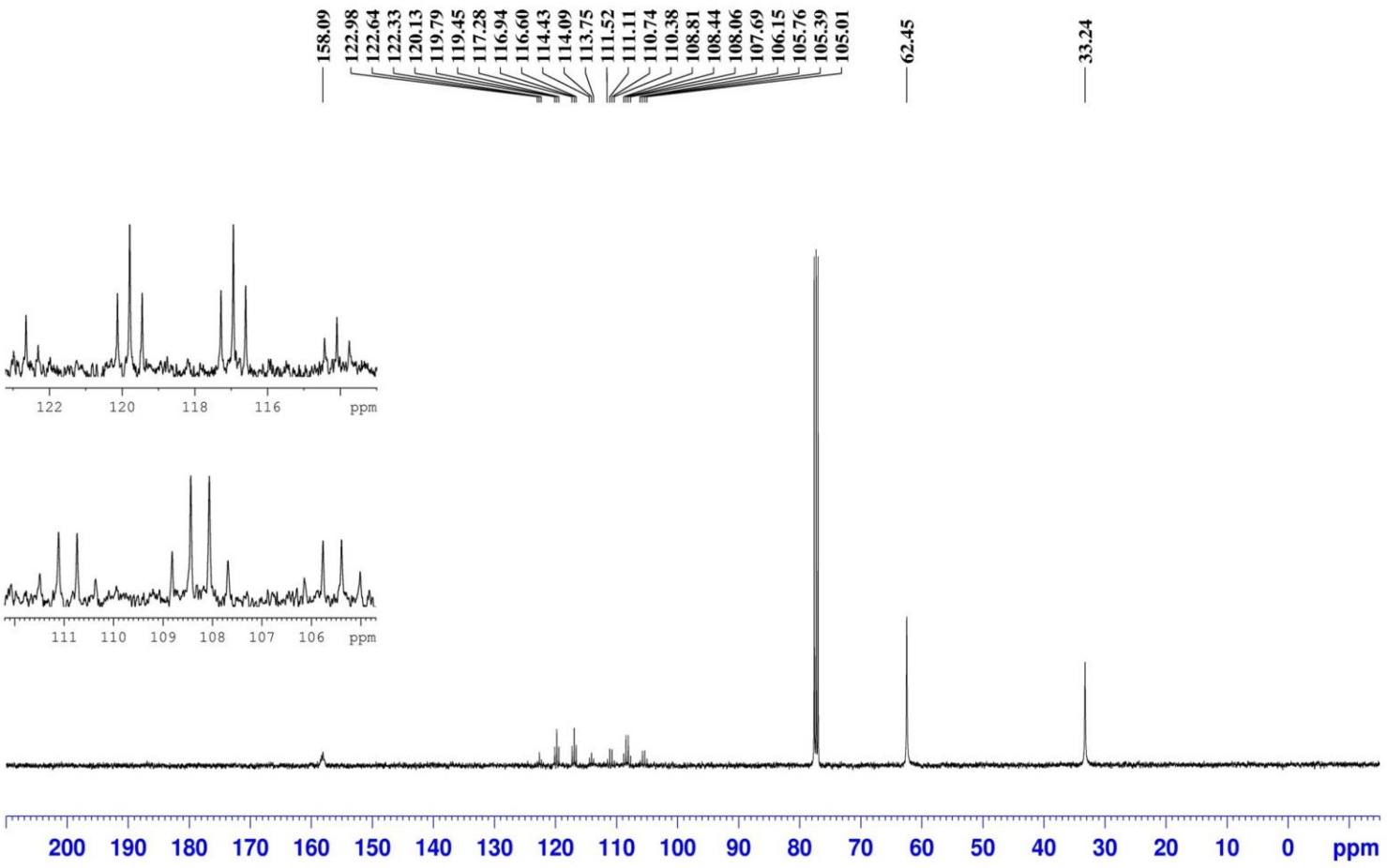
500 MHz, CDCl3



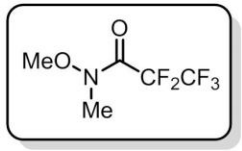


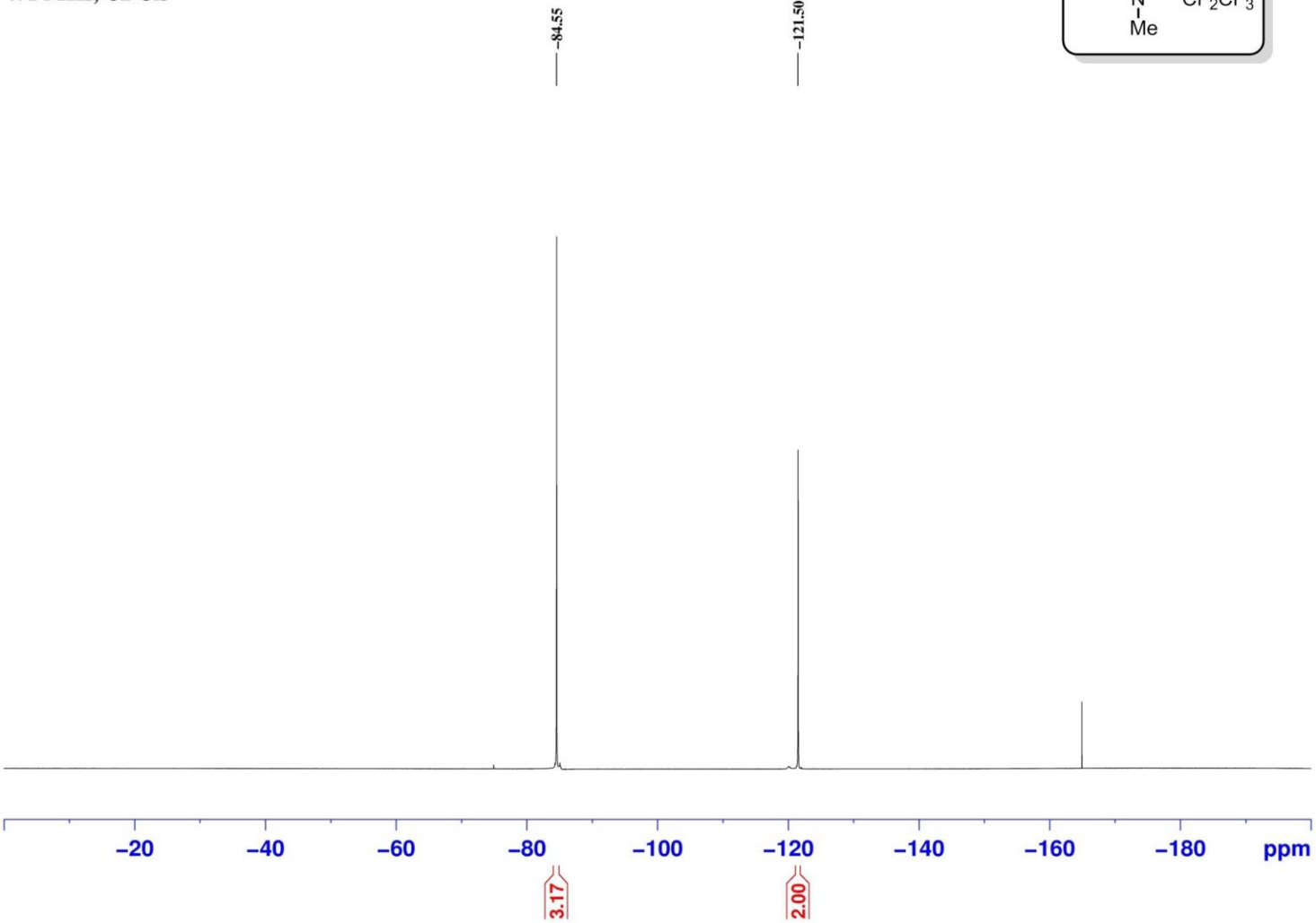
2,2,3,3,3–pentafluoro–N–methoxy–N–methylpropanamide
125 MHz, CDCl3



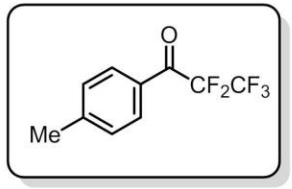


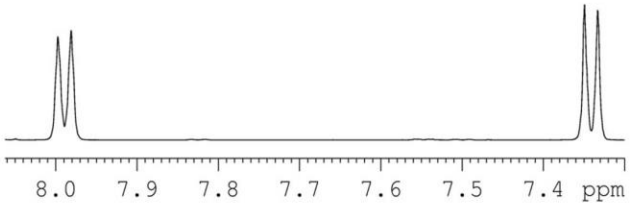
2,2,3,3,3–pentafluoro–N–methoxy–N–methylpropanamide
471 MHz, CDCl3

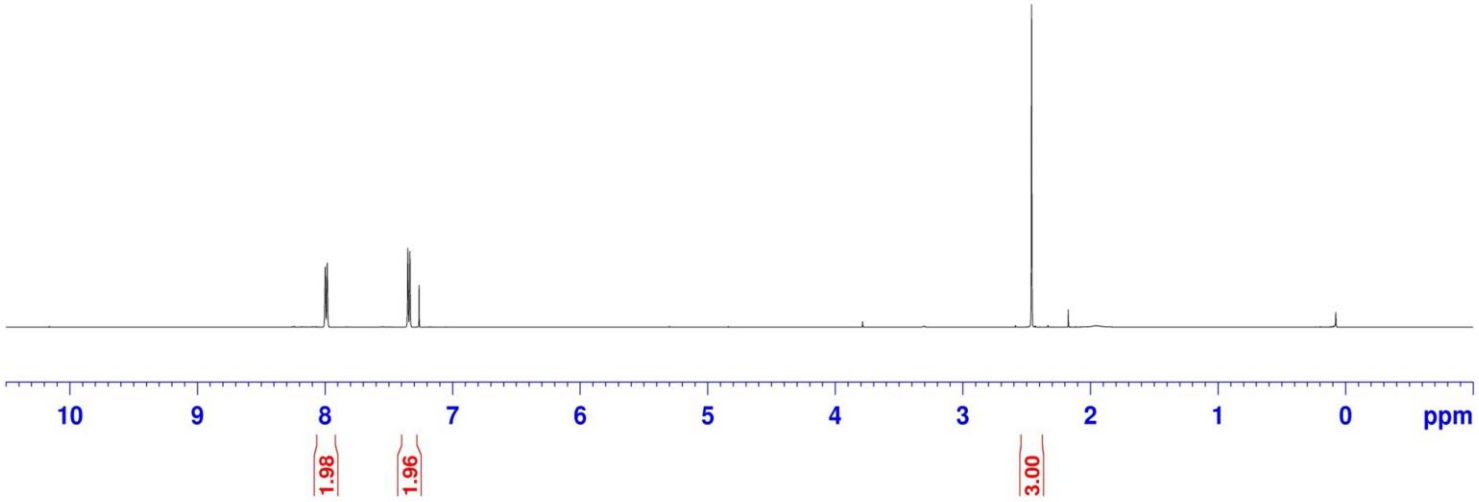




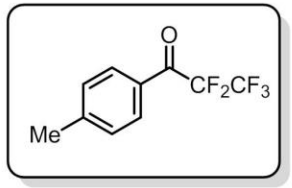
2,2,3,3,3–pentafluoro–1–(p–tolyl)propan–1–one
500 MHz, CDCl3

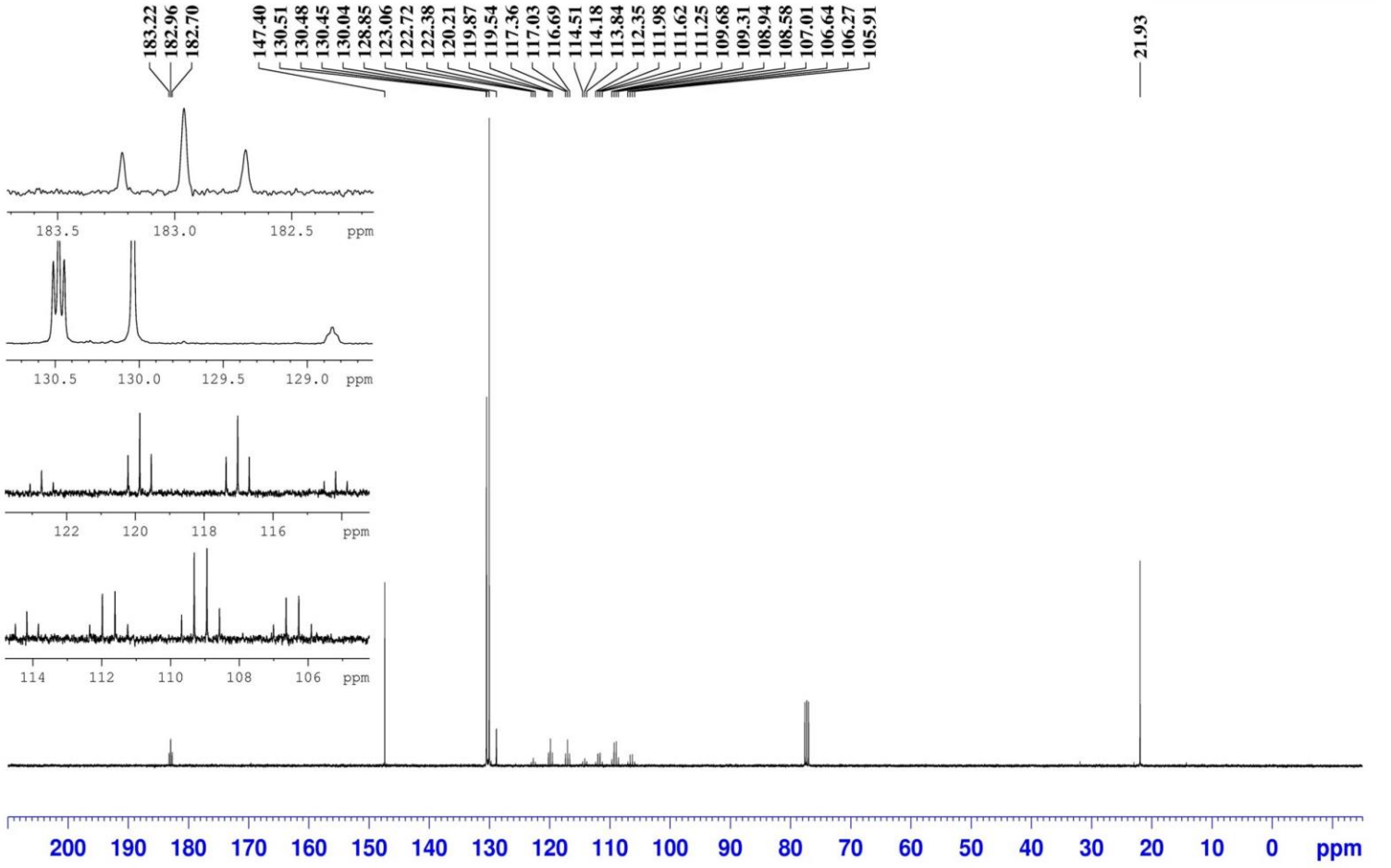




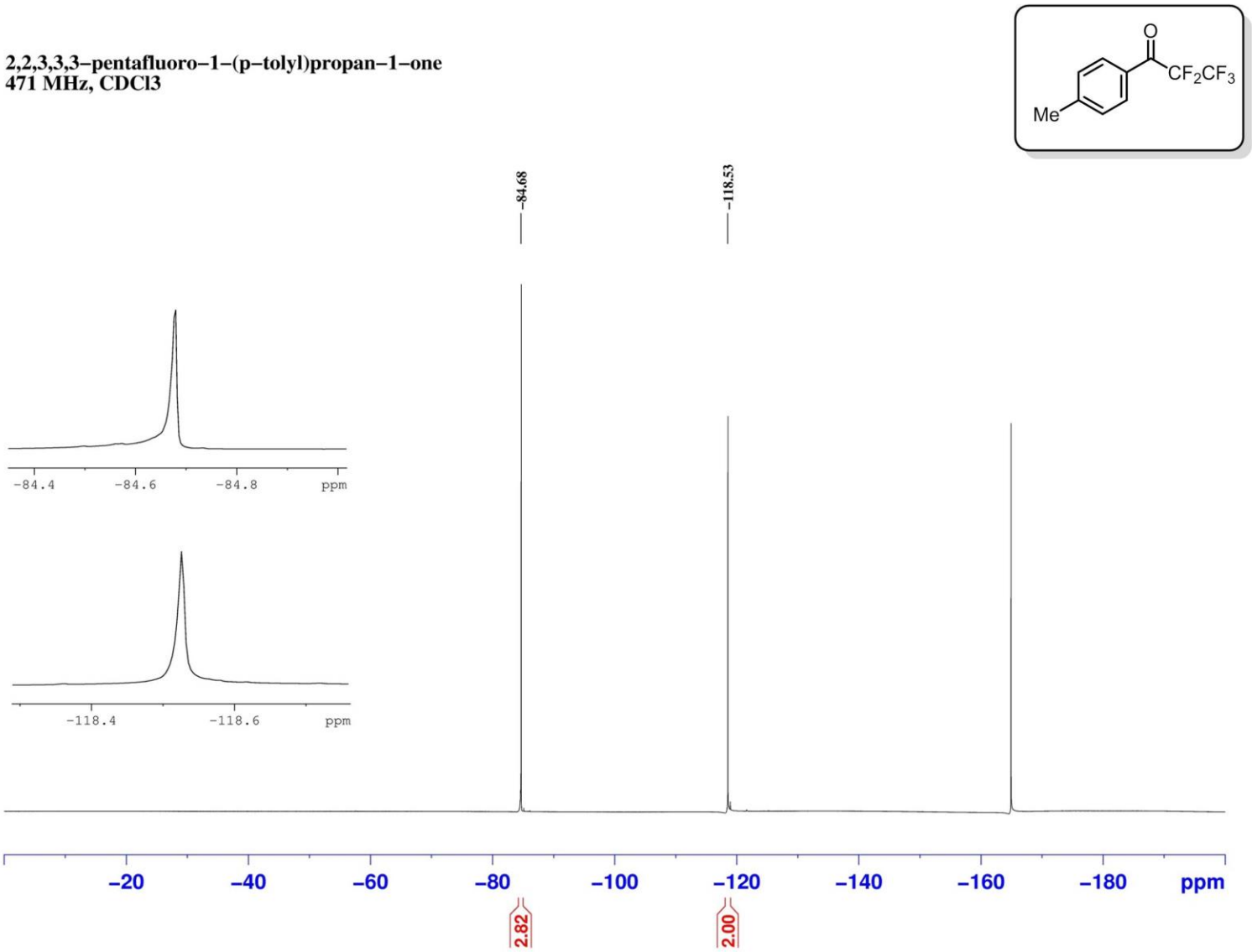


2,2,3,3,3–pentafluoro–1–(p–tolyl)propan–1–one
125 MHz, CDCl3

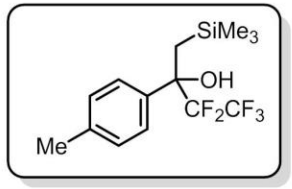


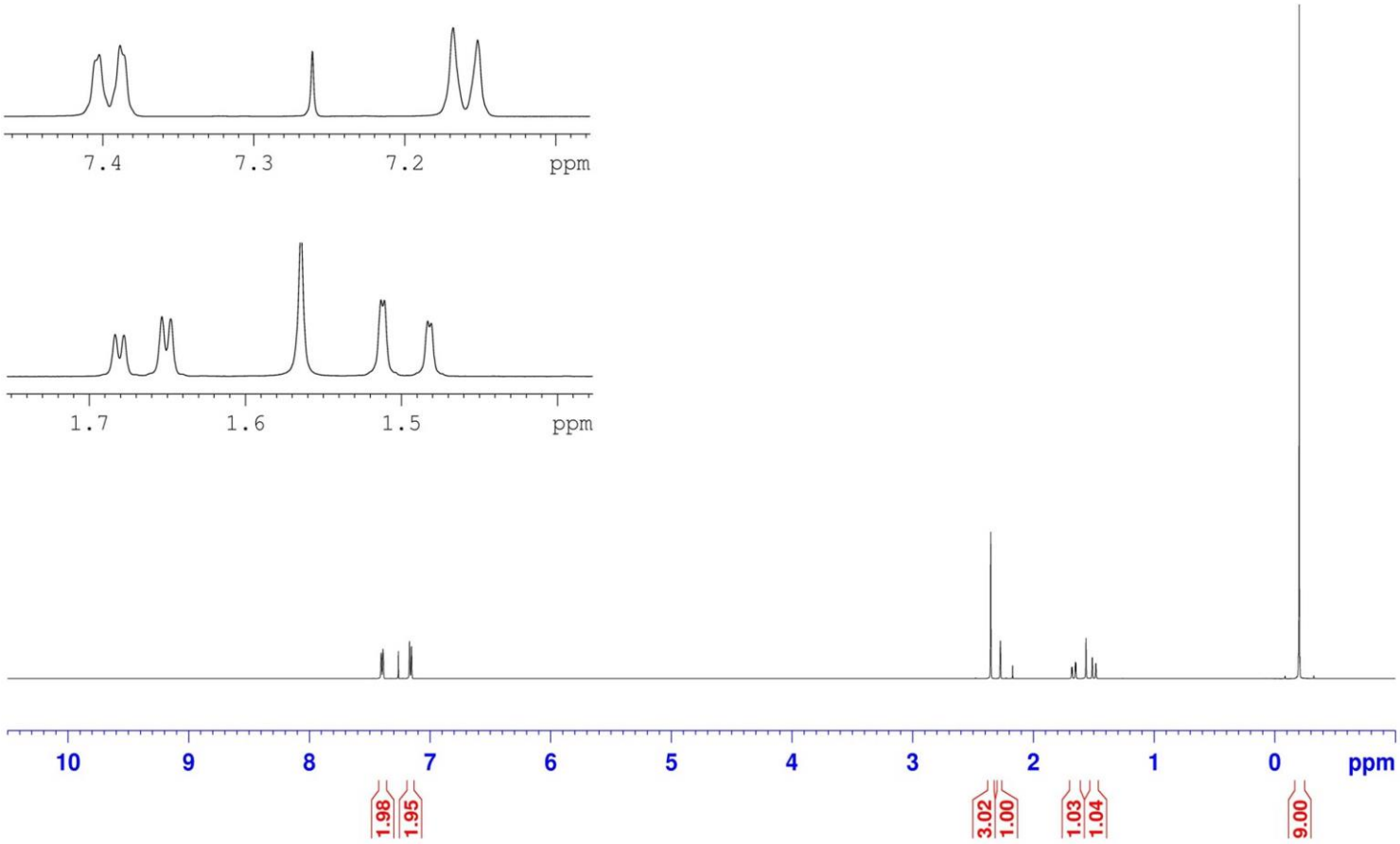


2,2,3,3,3–pentafluoro–1–(p–tolyl)propan–1–one
471 MHz, CDCl3

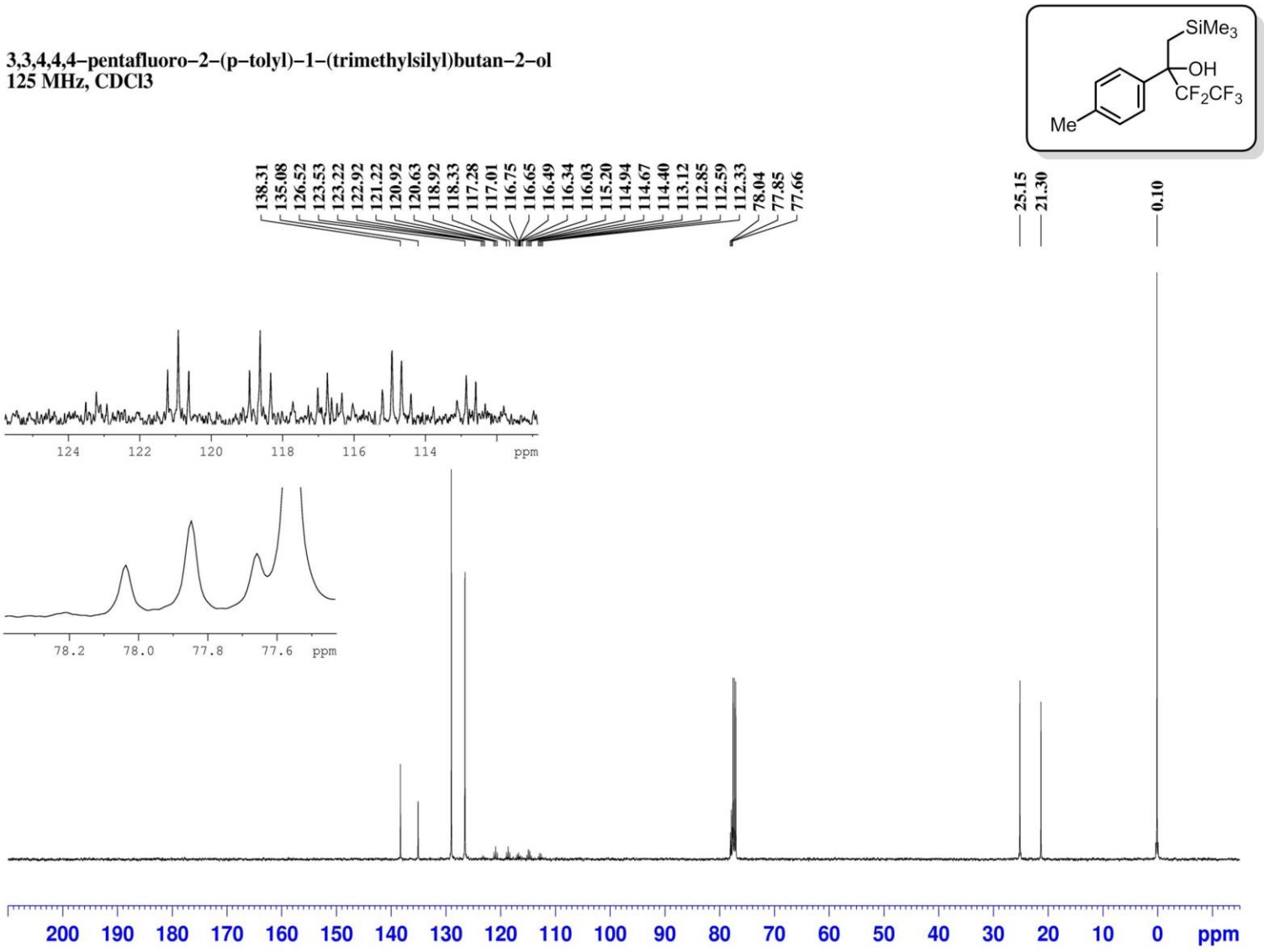


3,3,4,4,4–pentafluoro–2–(p–tolyl)–1–(trimethylsilyl)butan–2–ol
500 MHz, CDCl3

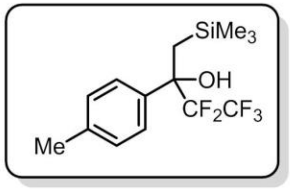


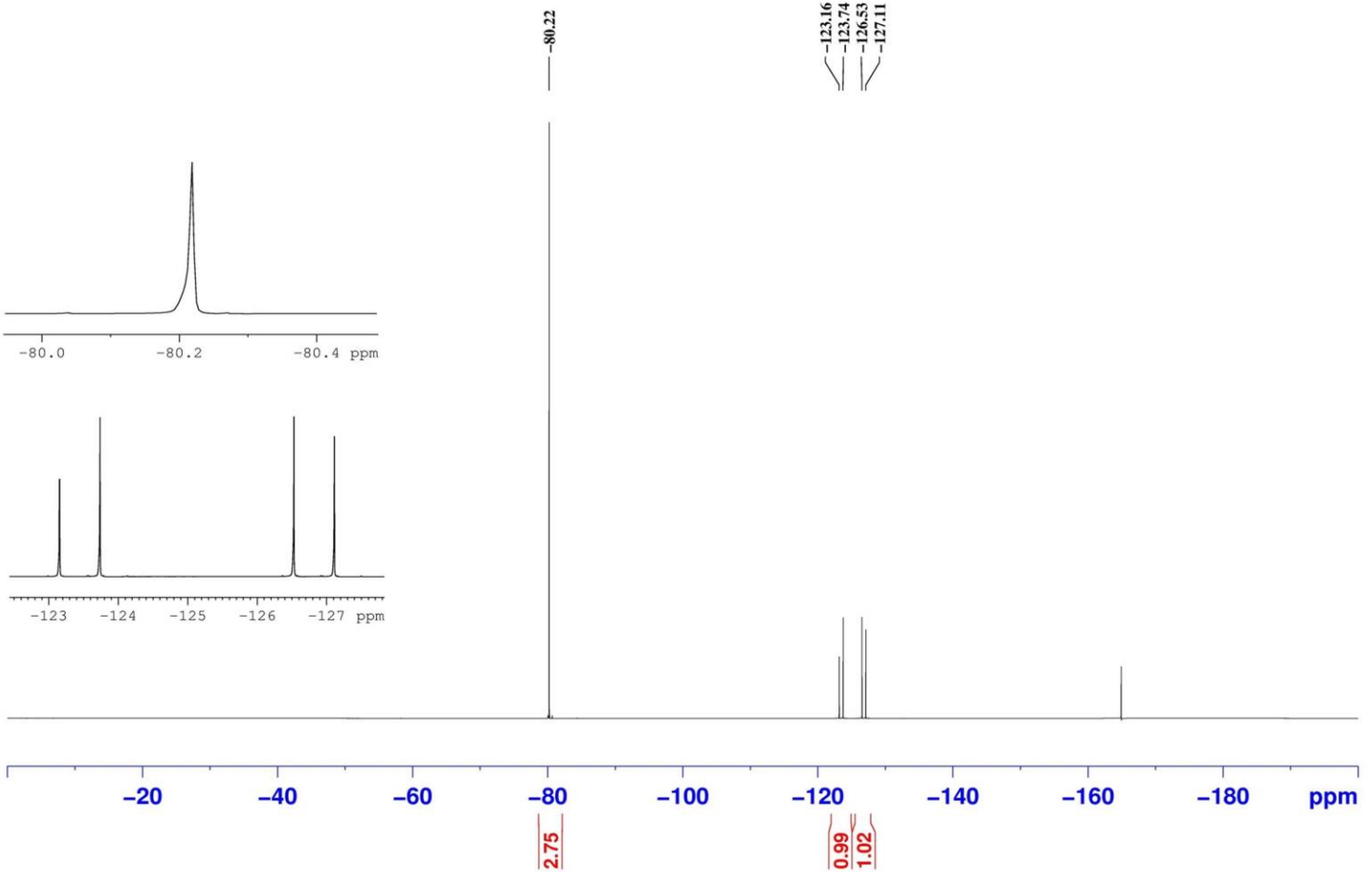


3,3,4,4,4–pentafluoro–2–(p–tolyl)–1–(trimethylsilyl)butan–2–ol
125 MHz, CDCl3

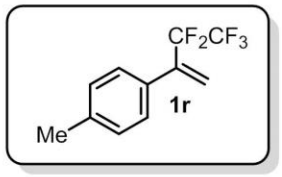


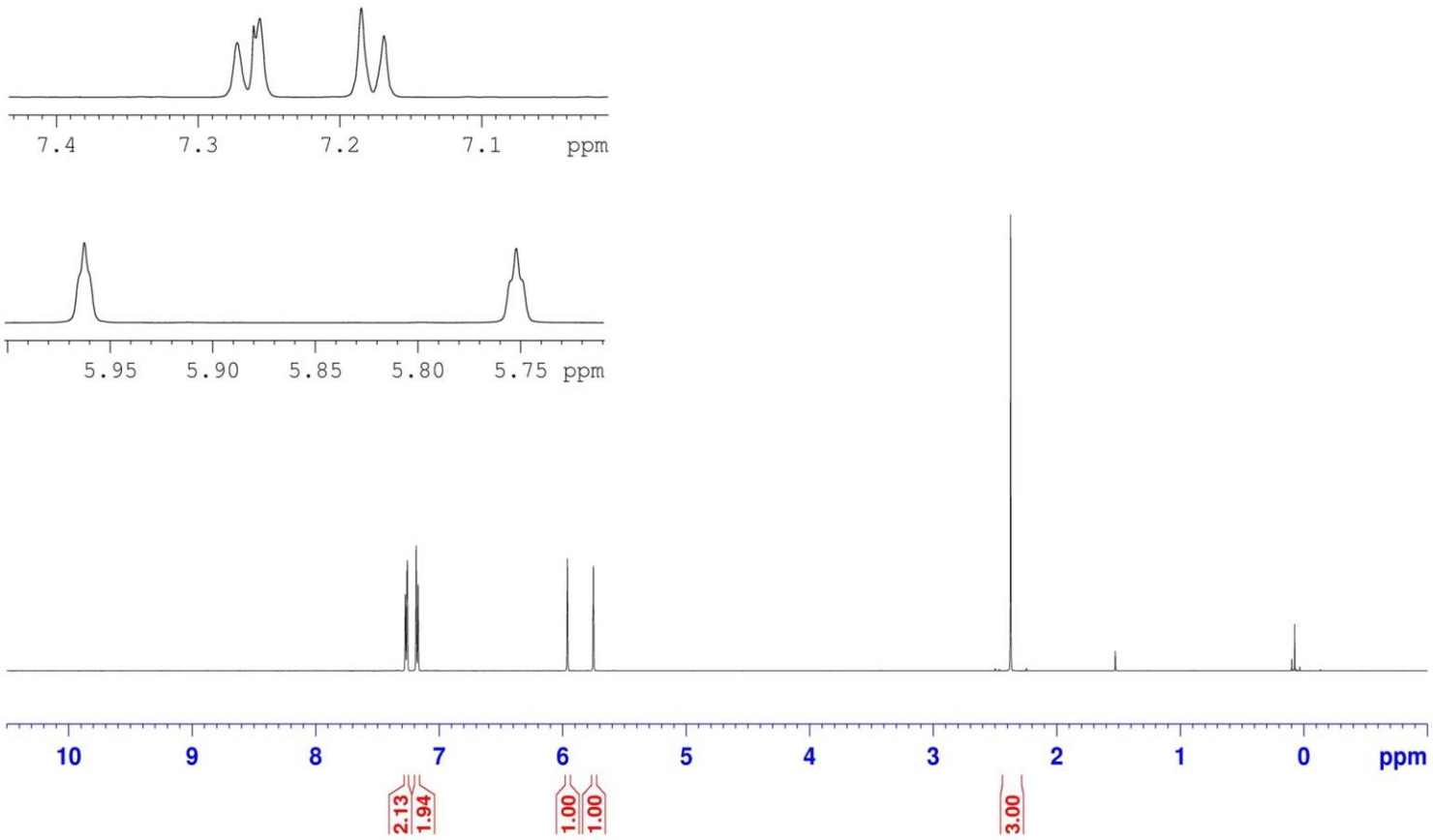
3,3,4,4,4–pentafluoro–2–(p–tolyl)–1–(trimethylsilyl)butan–2–ol
471 MHz, CDCl3



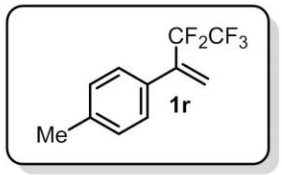


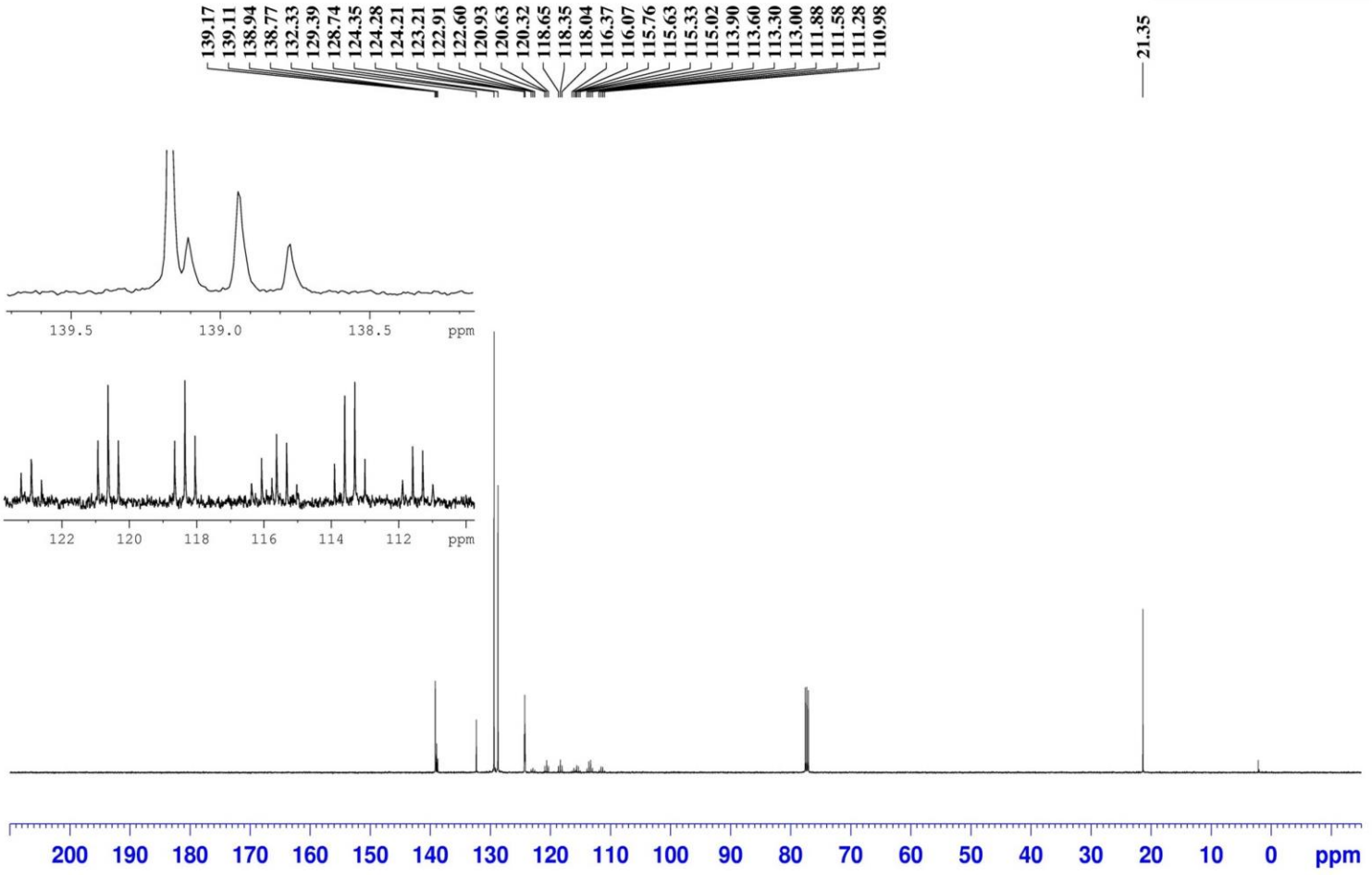
1–methyl–4–(3,3,4,4,4–pentafluorobut–1–en–2–yl)benzene
500 MHz, CDCl3



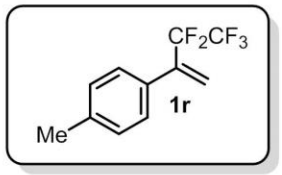


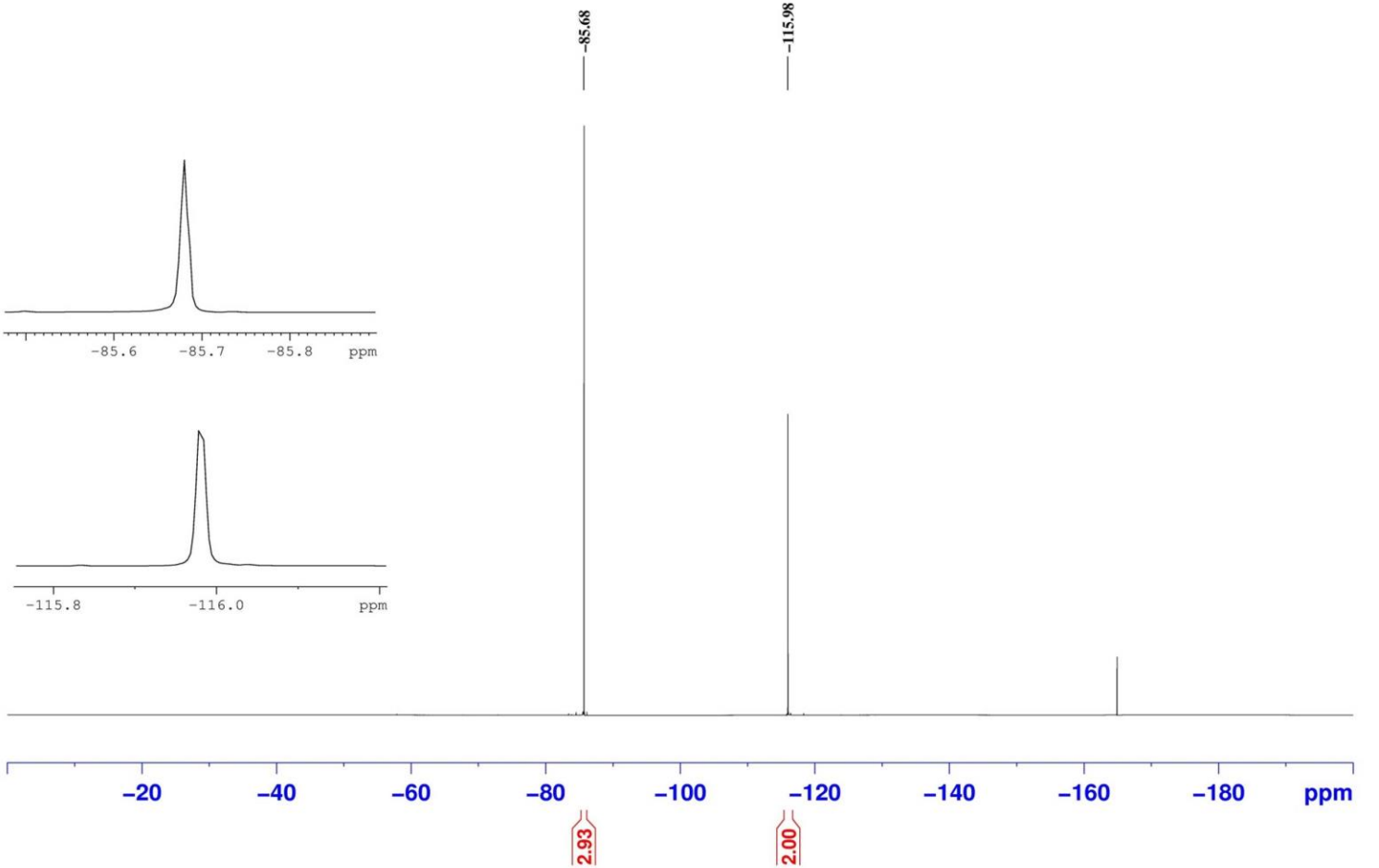
1−methyl−4−(3,3,4,4,4−pentafluorobut−1−en−2−yl)benzene
125 MHz, CDCl3



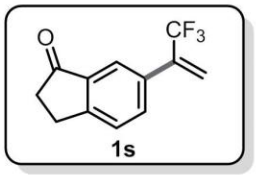


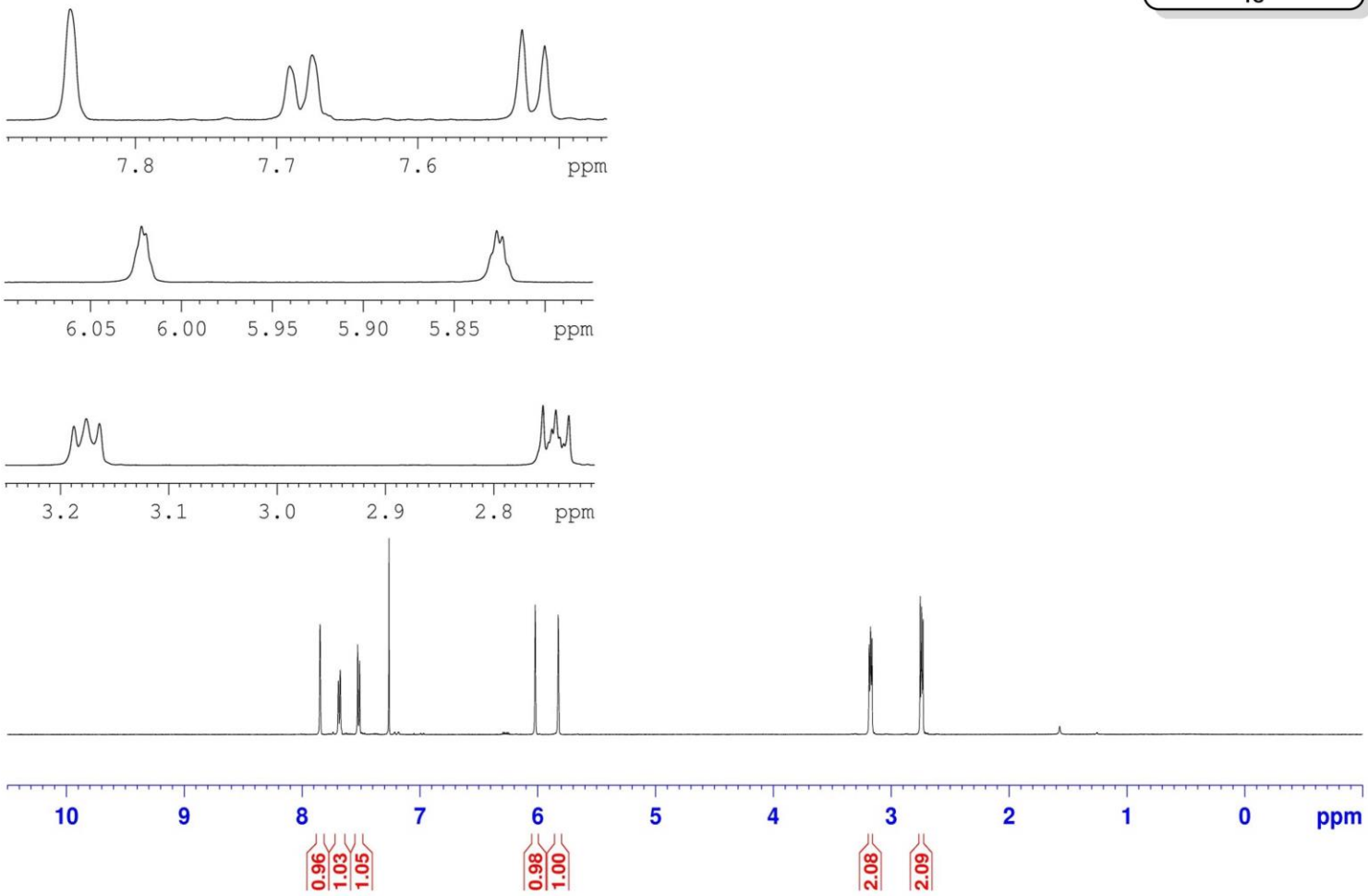
1−methyl−4−(3,3,4,4,4−pentafluorobut−1−en−2−yl)benzene
471 MHz, CDCl3



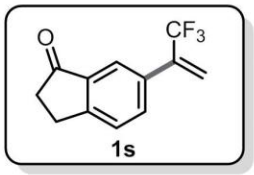


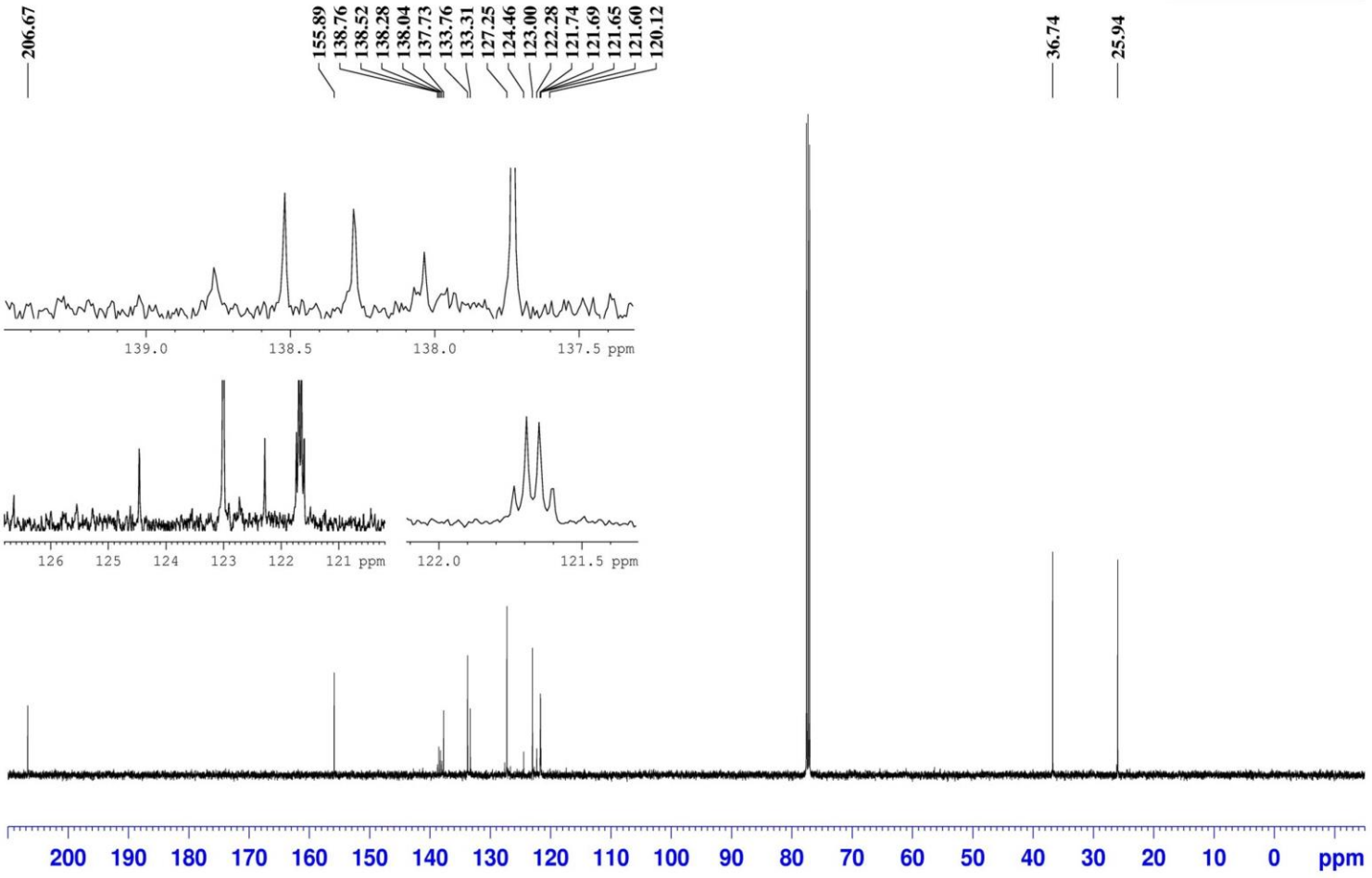
6–(3,3,3–trifluoroprop–1–en–2–yl)–2,3–dihydro–1H–inden–1–one
500 MHz, CDCl3



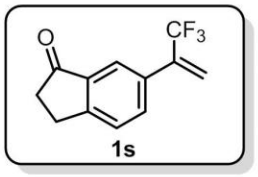


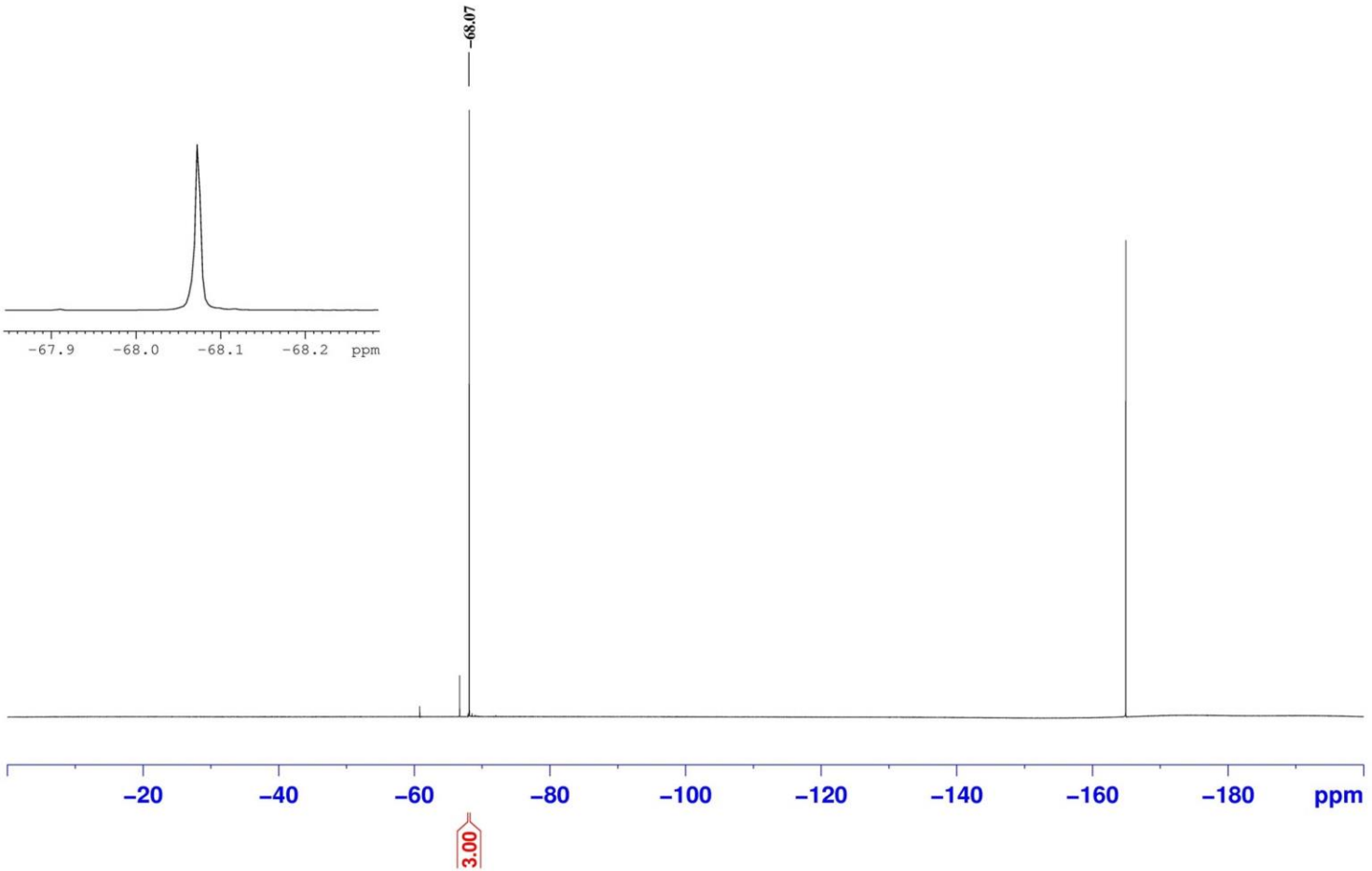
6–(3,3,3–trifluoroprop–1–en–2–yl)–2,3–dihydro–1H–inden–1–one
125 MHz, CDCl3



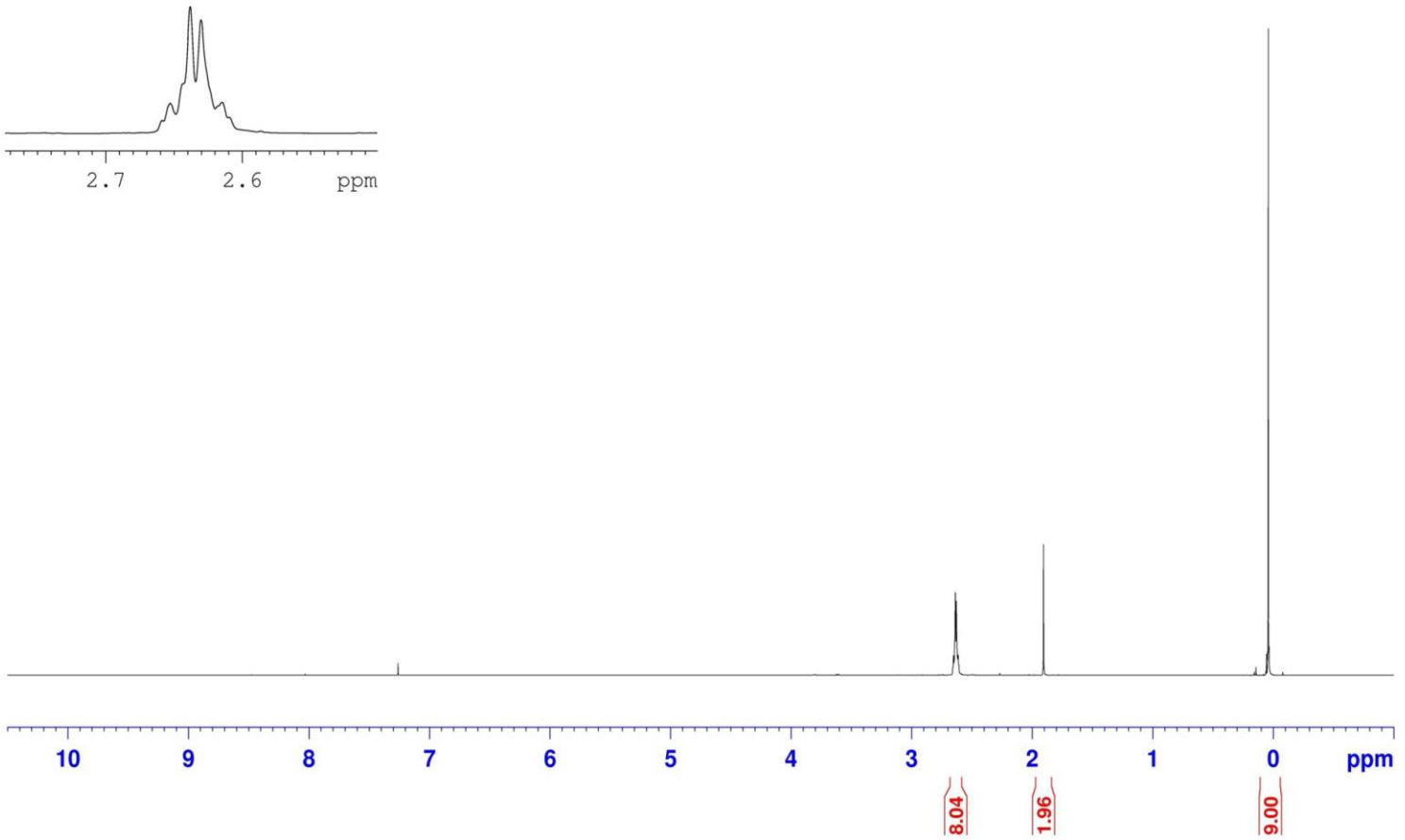


6–(3,3,3–trifluoroprop–1–en–2–yl)–2,3–dihydro–1H–inden–1–one
471 MHz, CDCl3

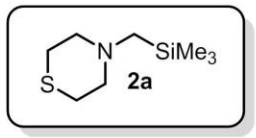


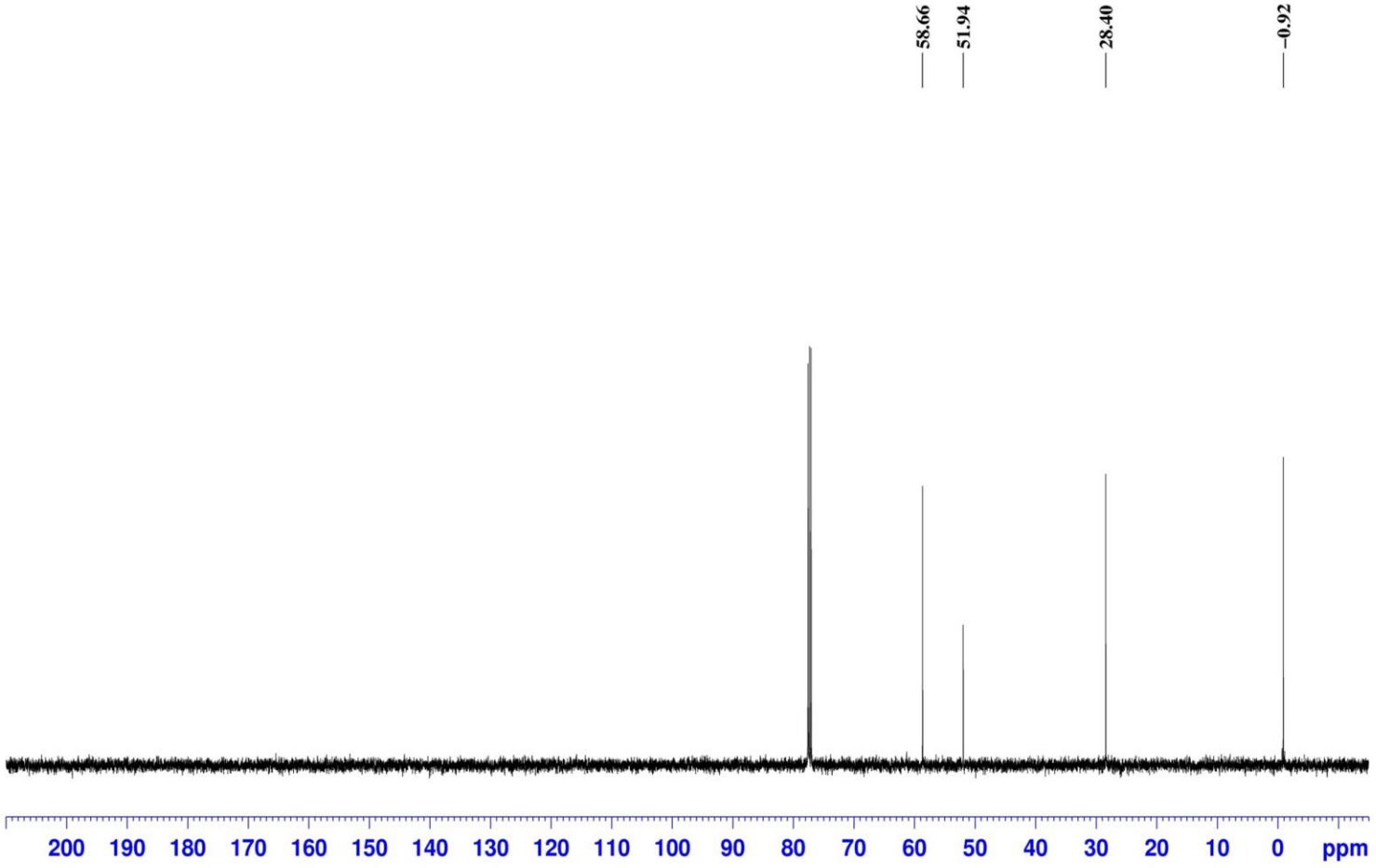


4–((trimethylsilyl)methyl)thiomorpholine
500 MHz, CDCl3

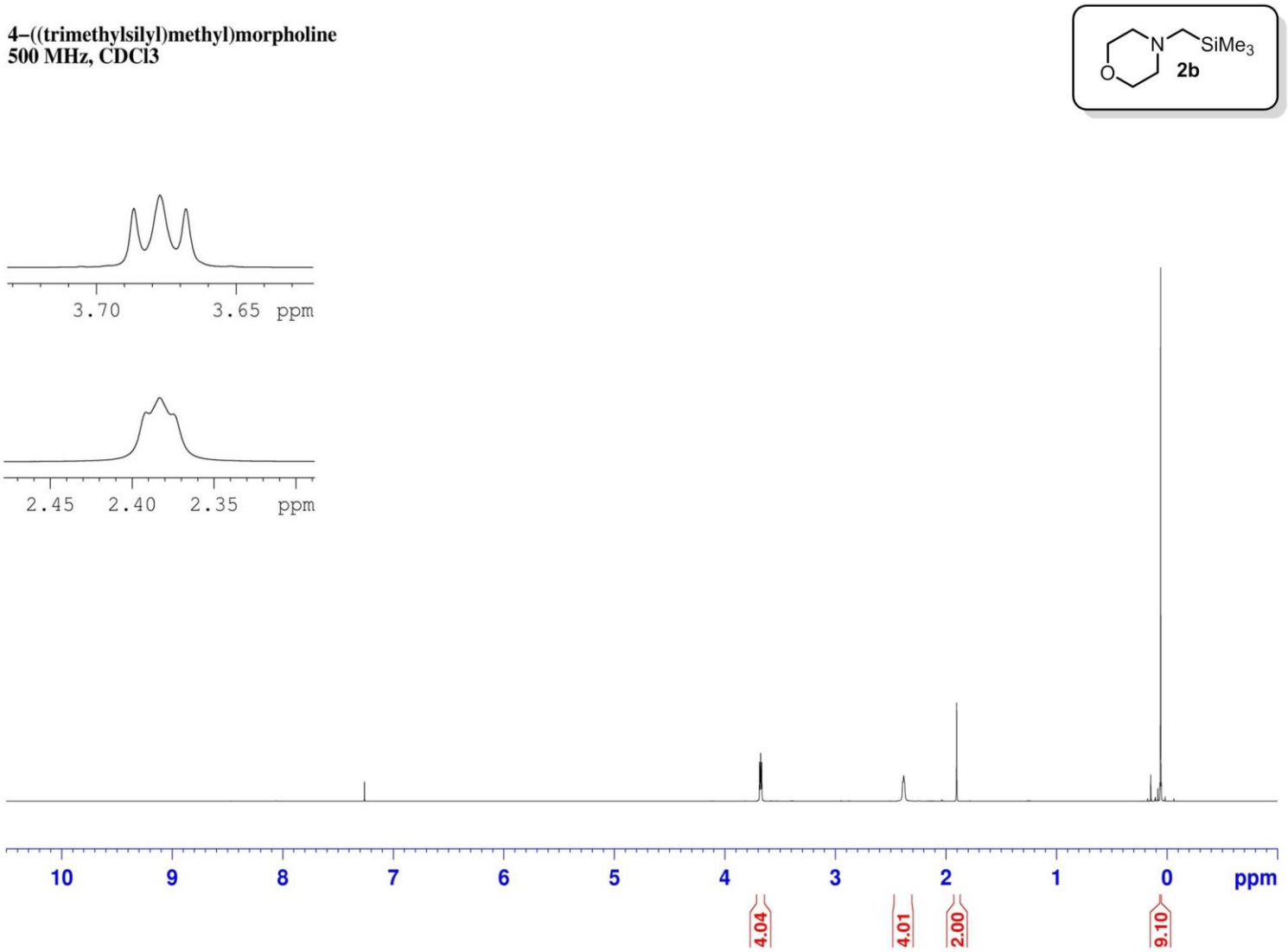


4–((trimethylsilyl)methyl)thiomorpholine
125 MHz, CDCl3

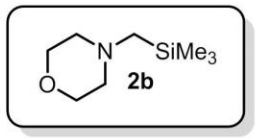


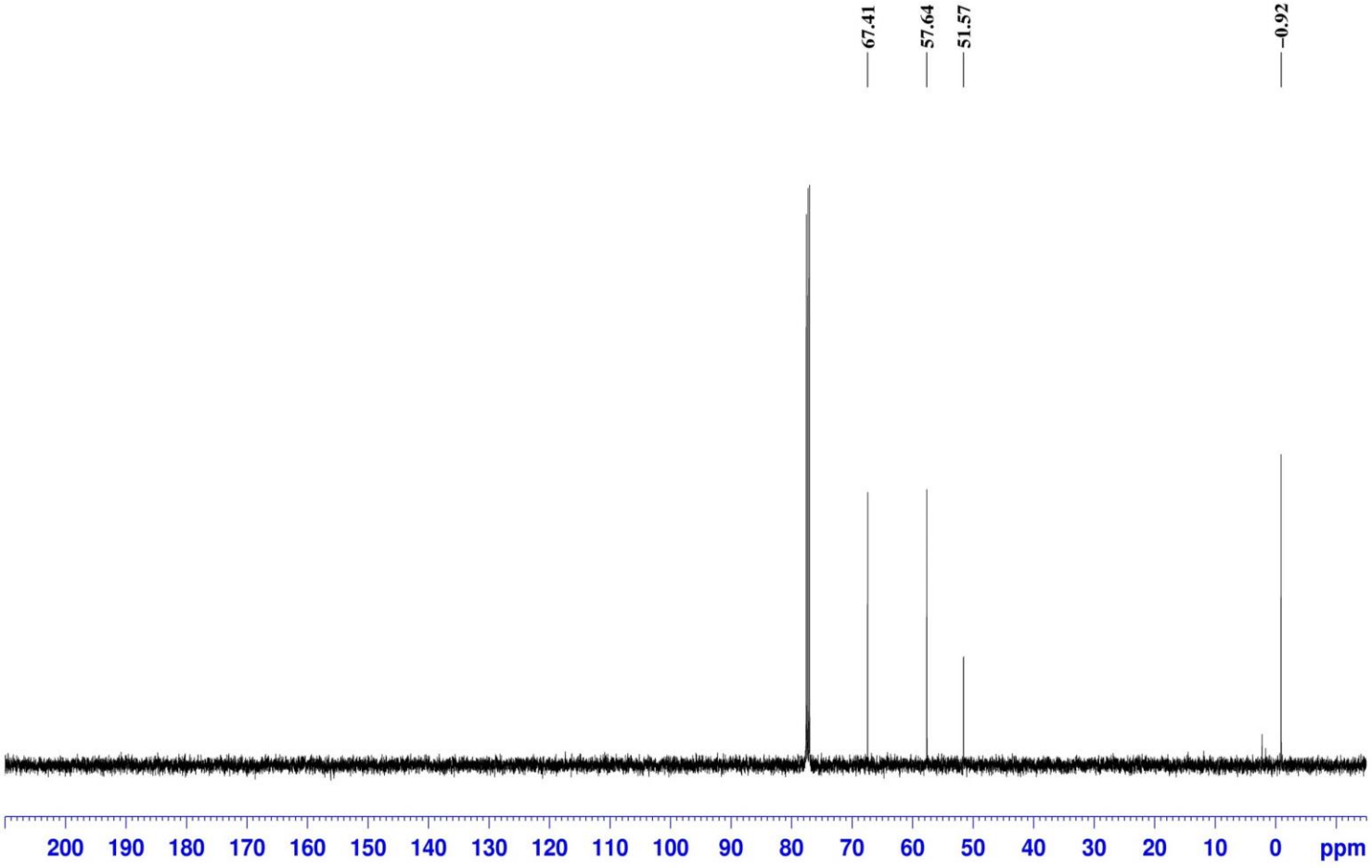


4–((trimethylsilyl)methyl)morpholine
500 MHz, CDCl3

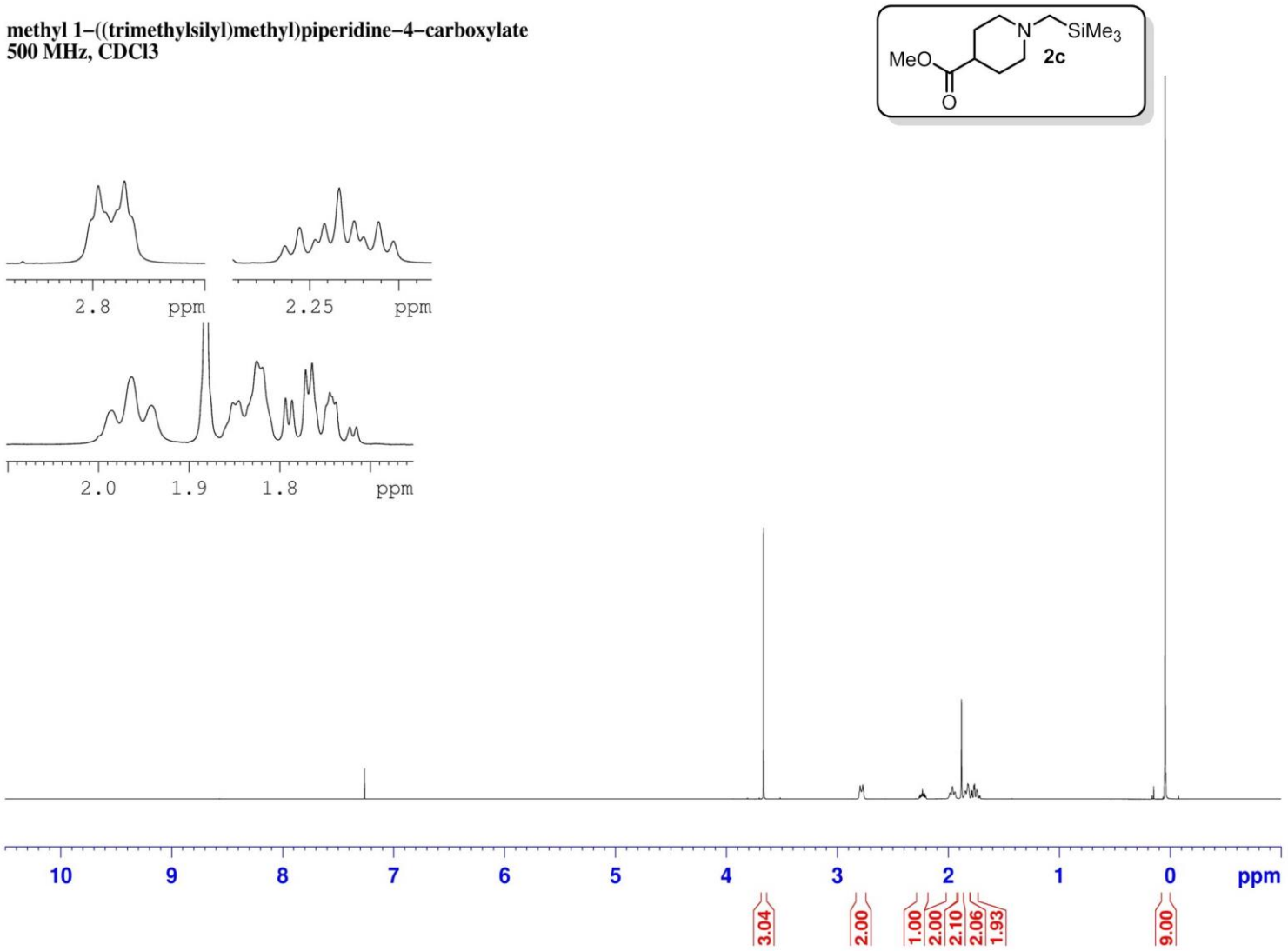


4–((trimethylsilyl)methyl)morpholine
125 MHz, CDCl3

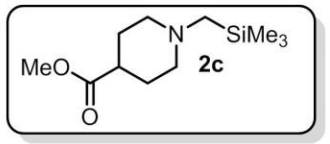


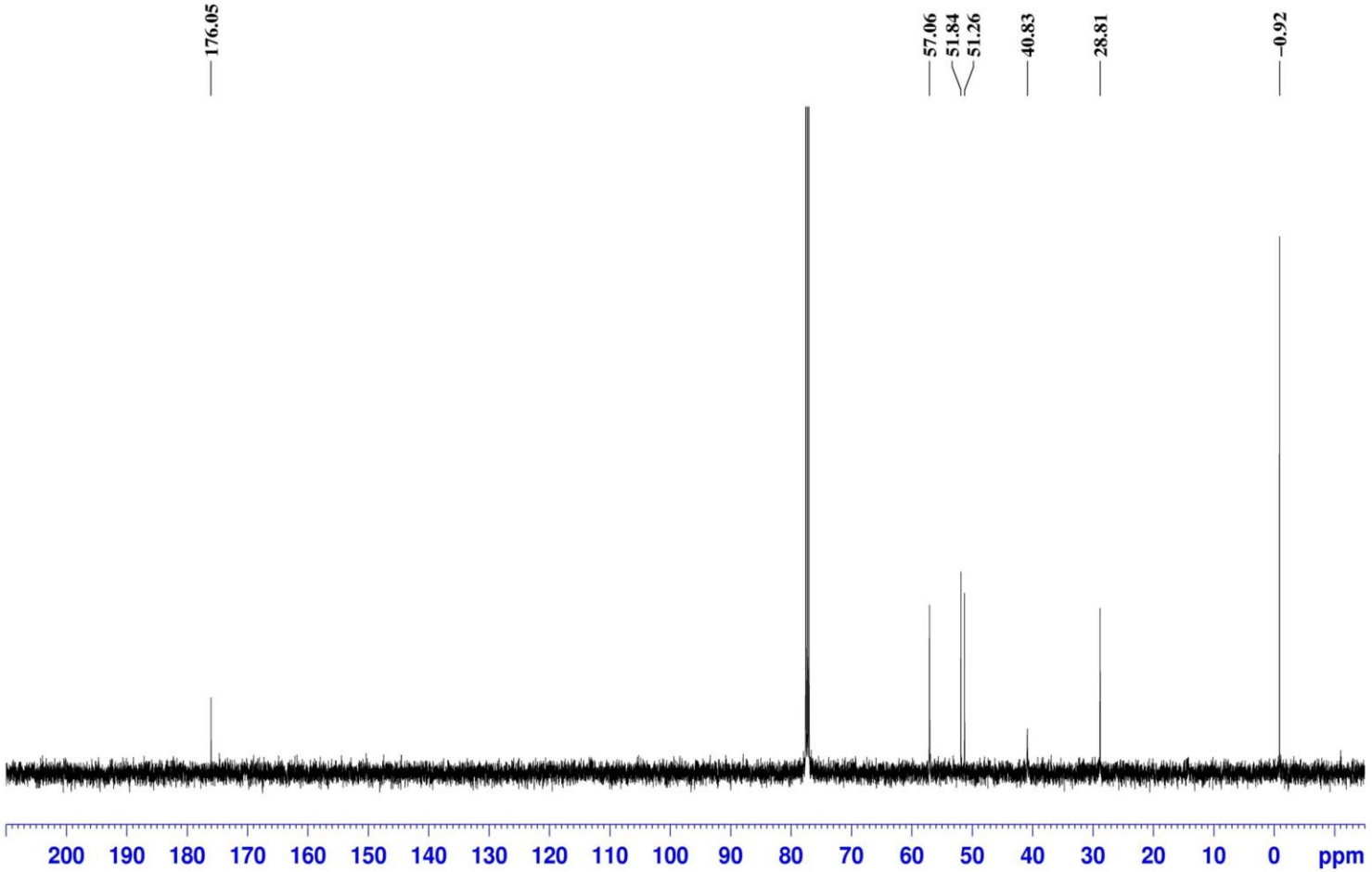


methyl 1–((trimethylsilyl)methyl)piperidine–4–carboxylate
500 MHz, CDCl3

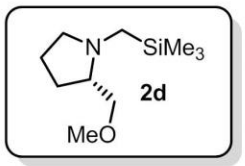


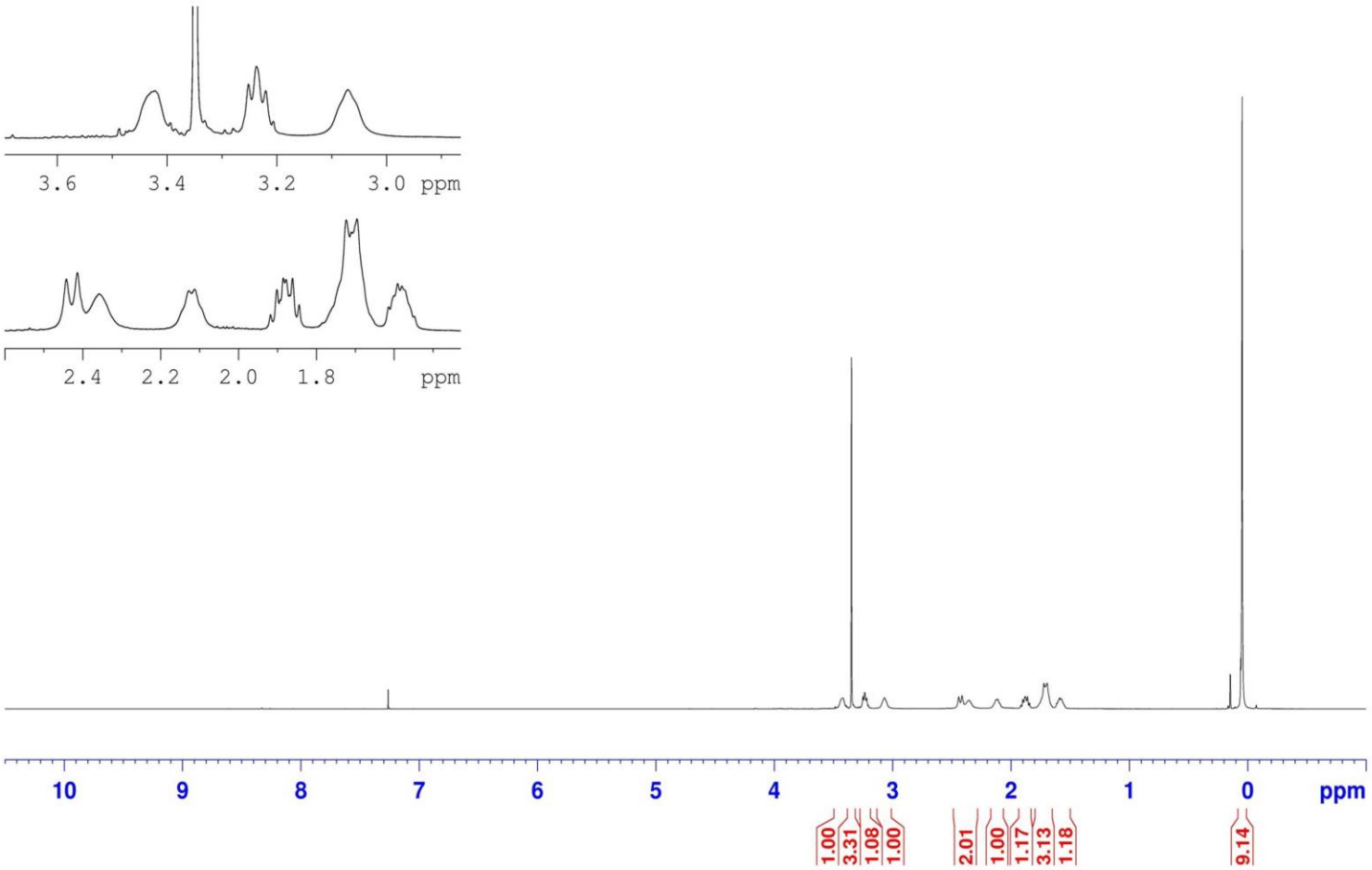
methyl 1−((trimethylsilyl)methyl)piperidine−4−carboxylate
125 MHz, CDCl3



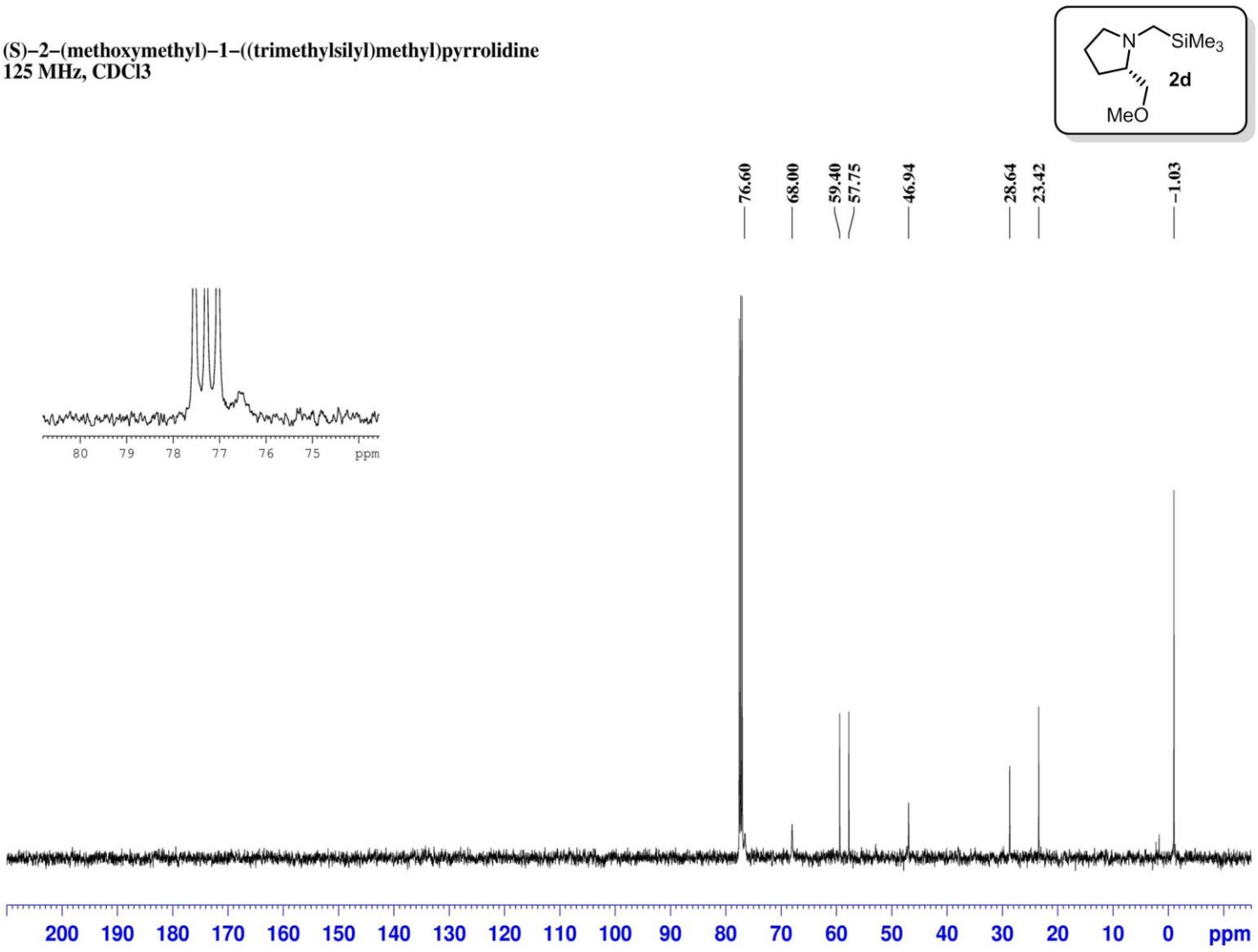


(S)−2−(methoxymethyl)−1−((trimethylsilyl)methyl)pyrrolidine
500 MHz, CDCl3

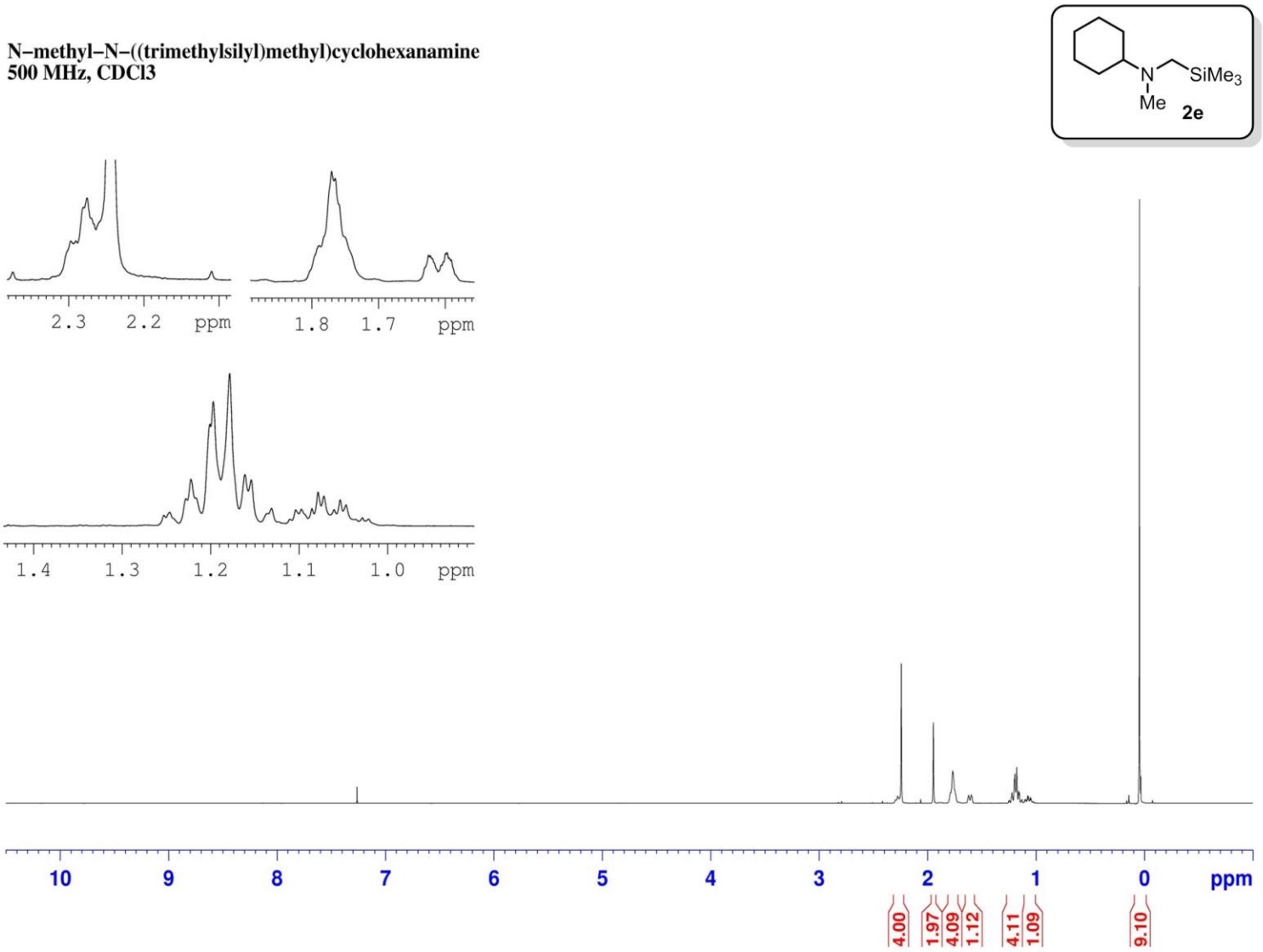




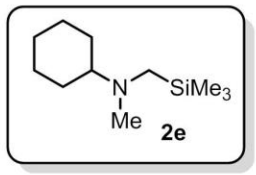
(S)−2−(methoxymethyl)−1−((trimethylsilyl)methyl)pyrrolidine
125 MHz, CDCl3

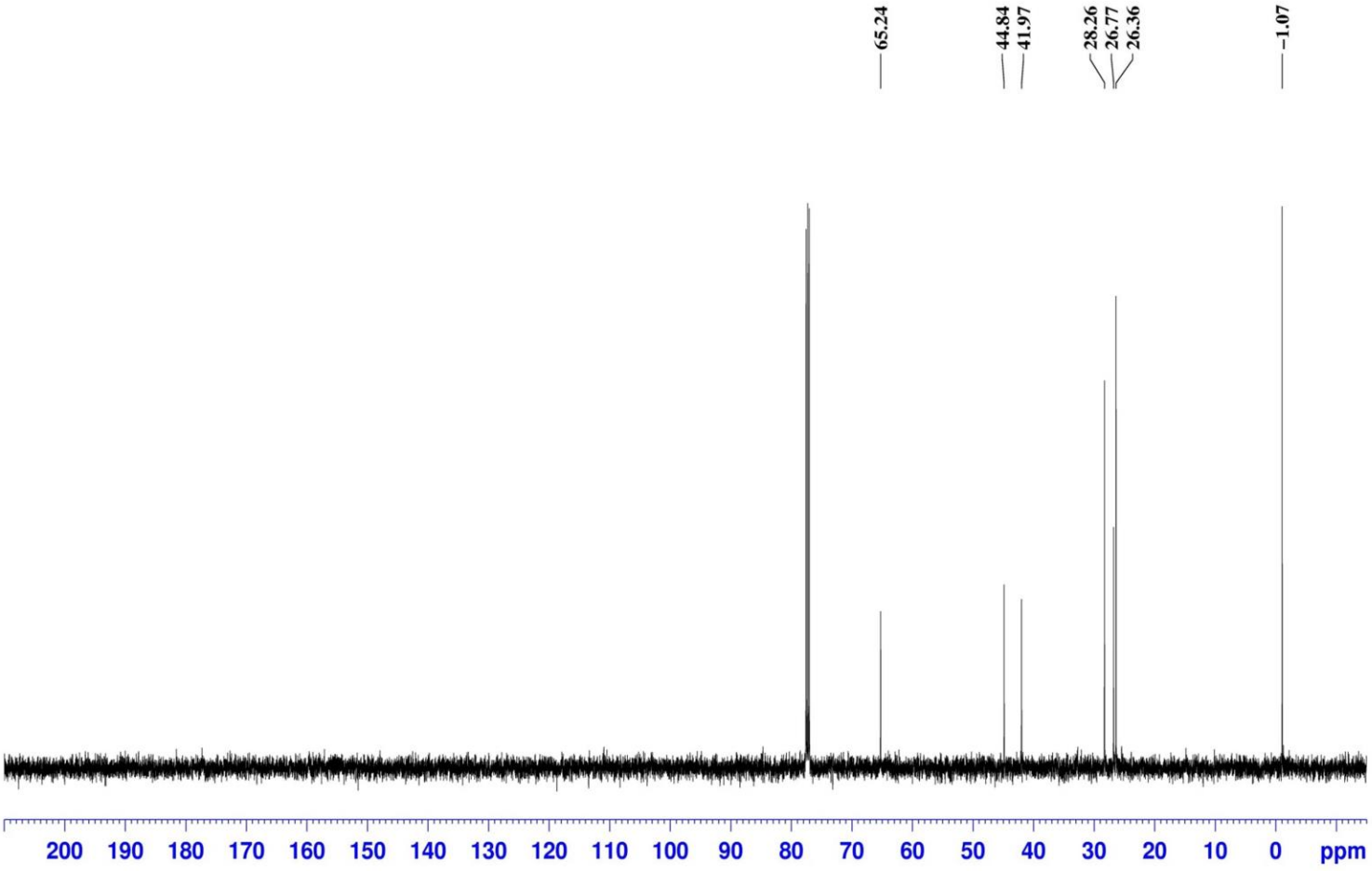


N–methyl–N–((trimethylsilyl)methyl)cyclohexanamine
500 MHz, CDCl3

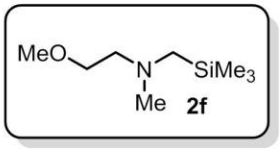


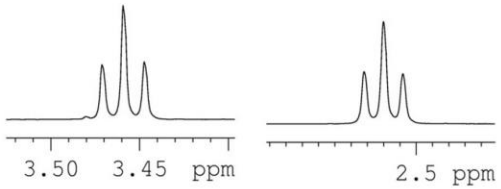
N–methyl–N–((trimethylsilyl)methyl)cyclohexanamine
125 MHz, CDCl3

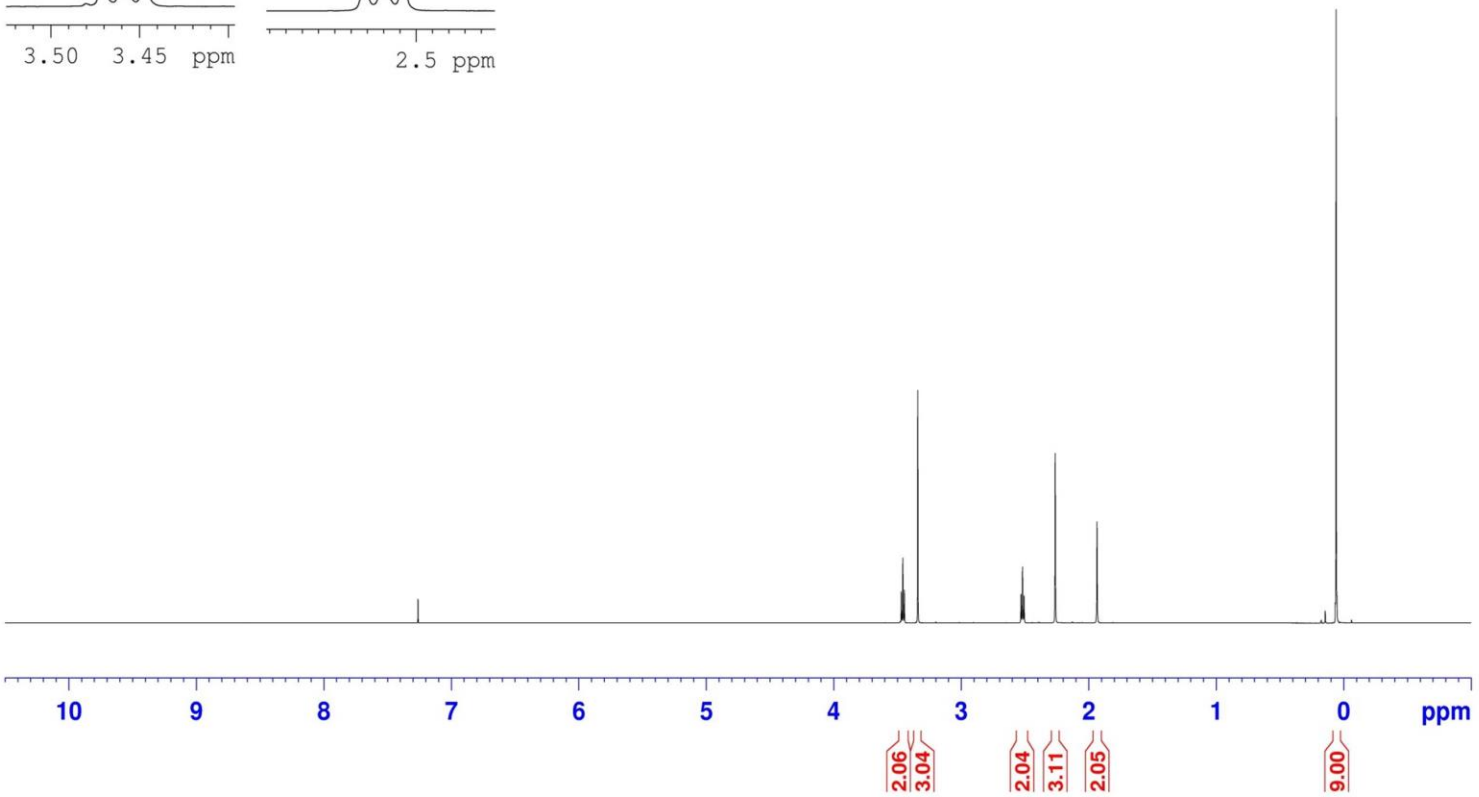




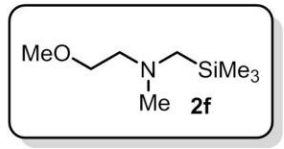
2–methoxy–N–methyl–N–((trimethylsilyl)methyl)ethanamine
500 MHz, CDCl3

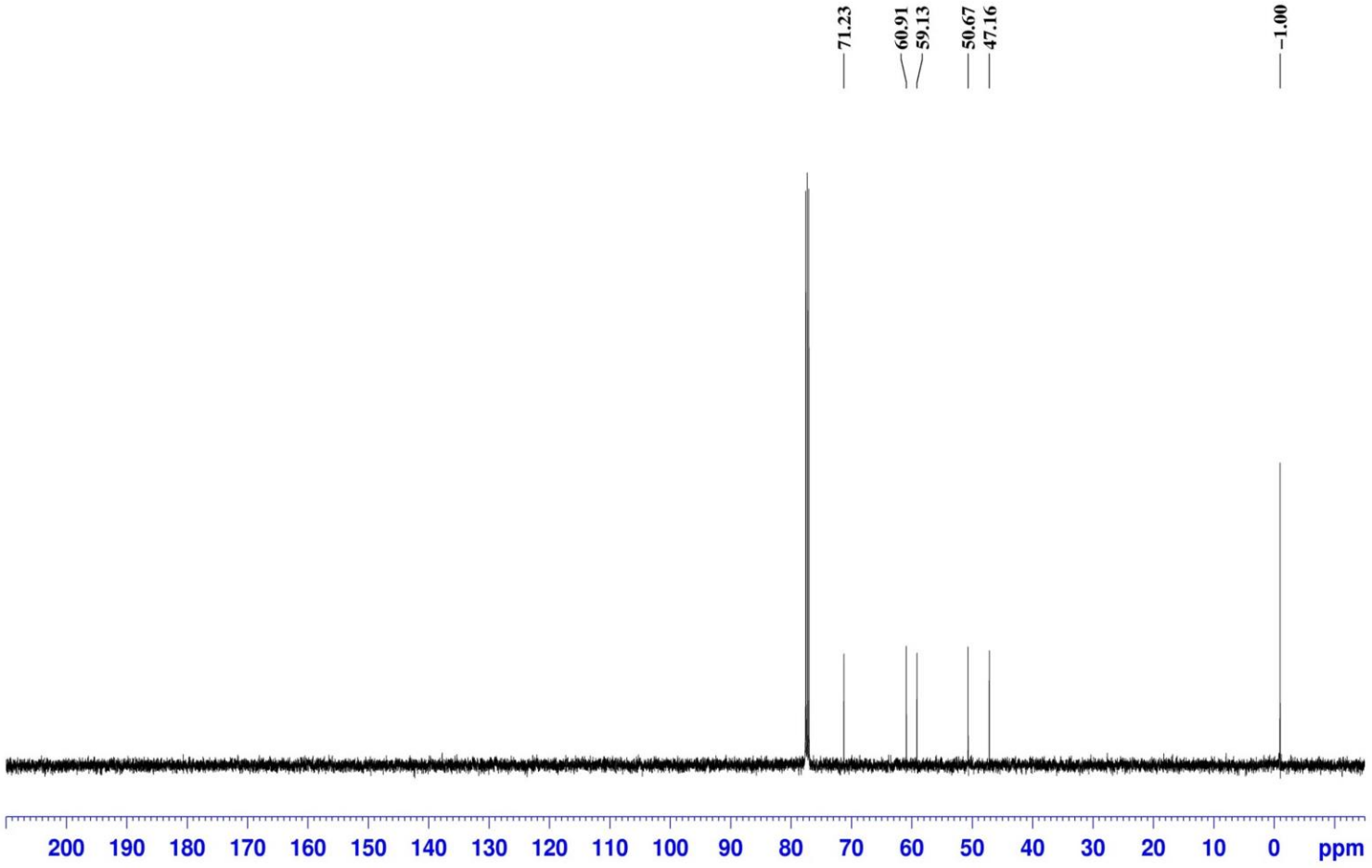


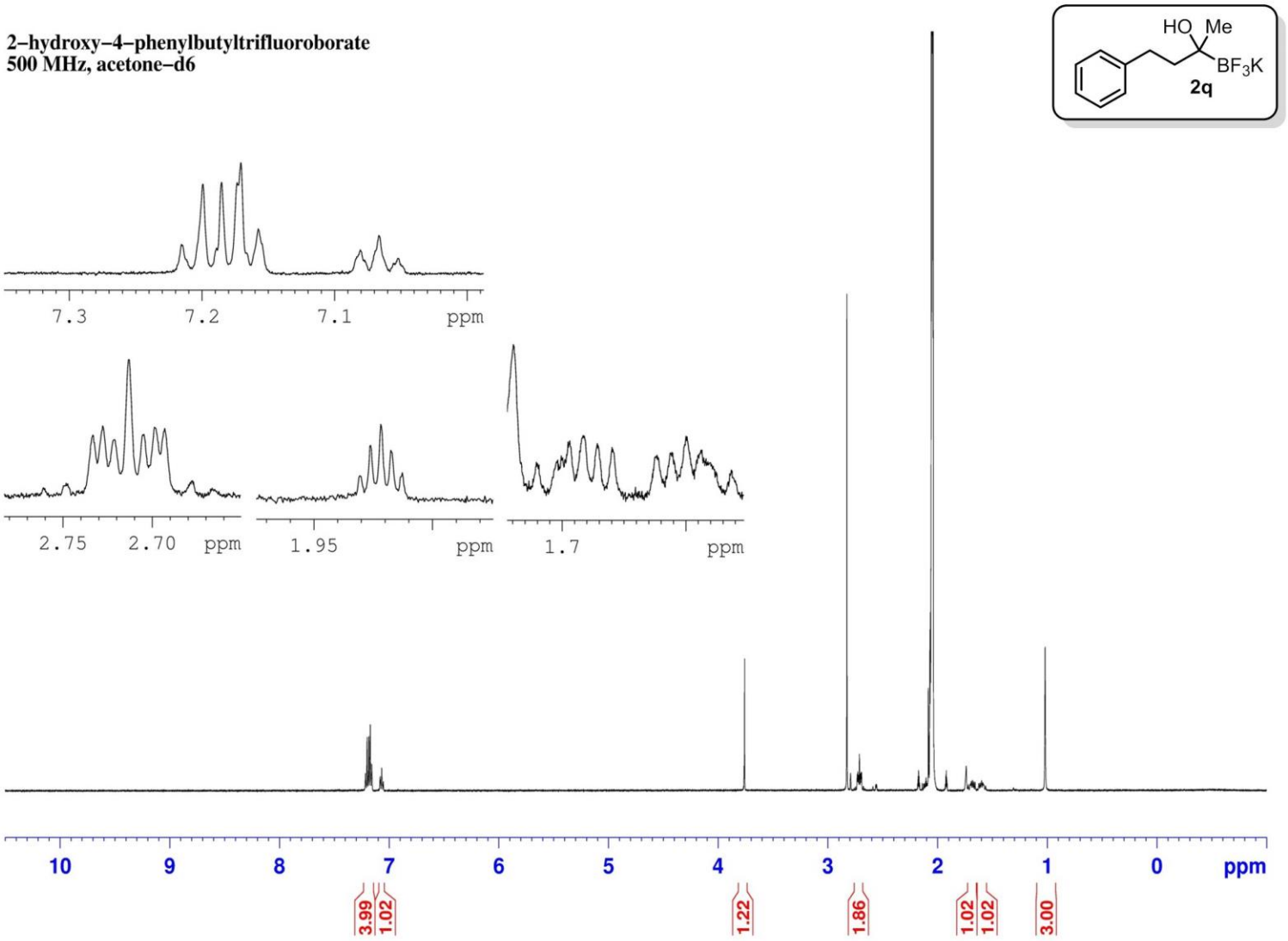




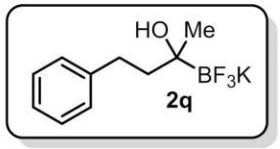
2–methoxy–N–methyl–N–((trimethylsilyl)methyl)ethanamine
125 MHz, CDCl3

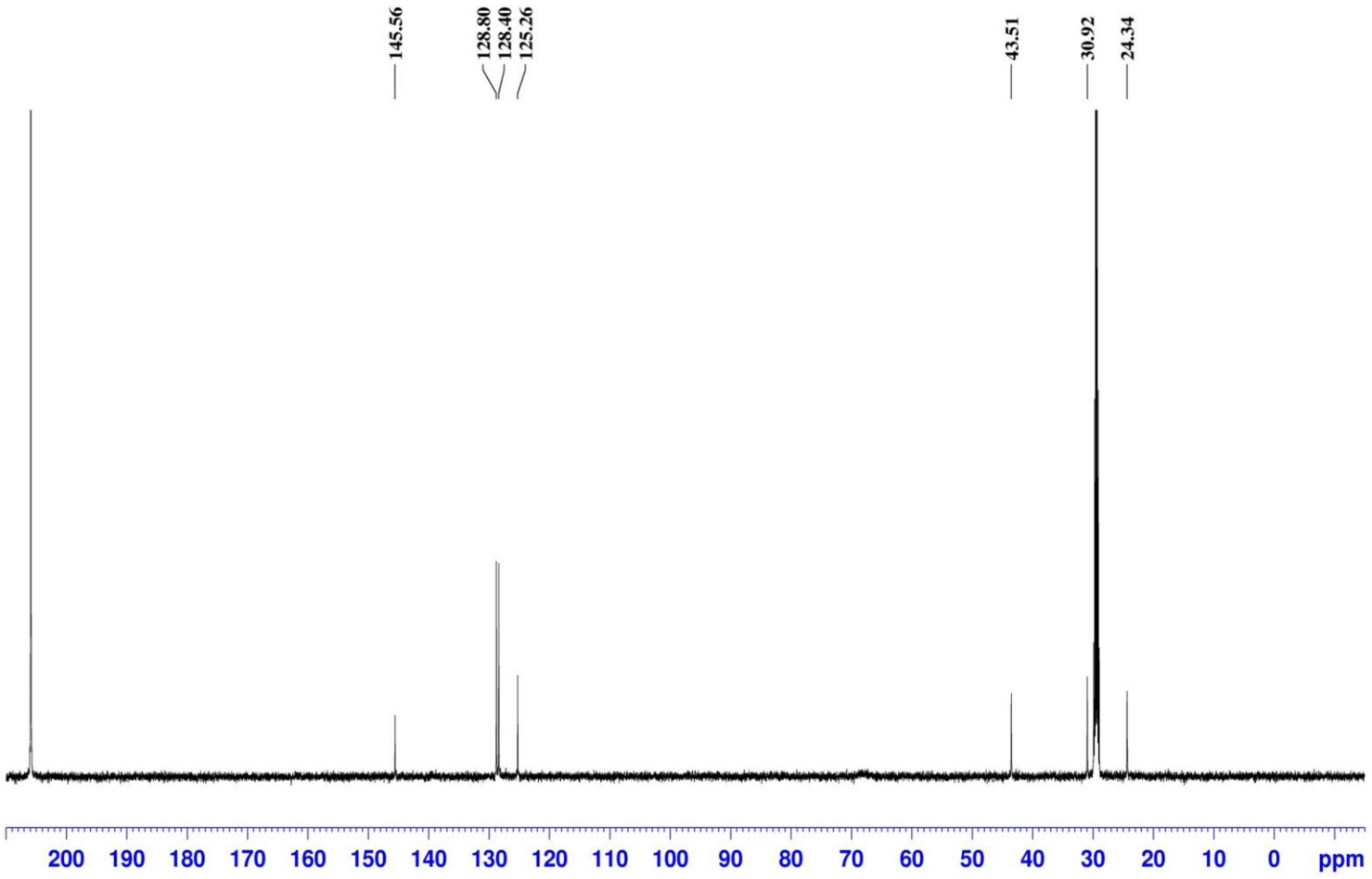




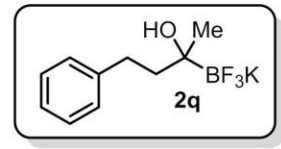

2–hydroxy–4–phenylbutyltrifluoroborate
500 MHz, acetone–d6
HO
Me
BF3K
2q
7.3
7.2
7.1
ppm
2.75
2.70
ppm
1.95
ppm
1.7
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
3.99
1.02
1.22
1.86
1.02
1.02
3.00

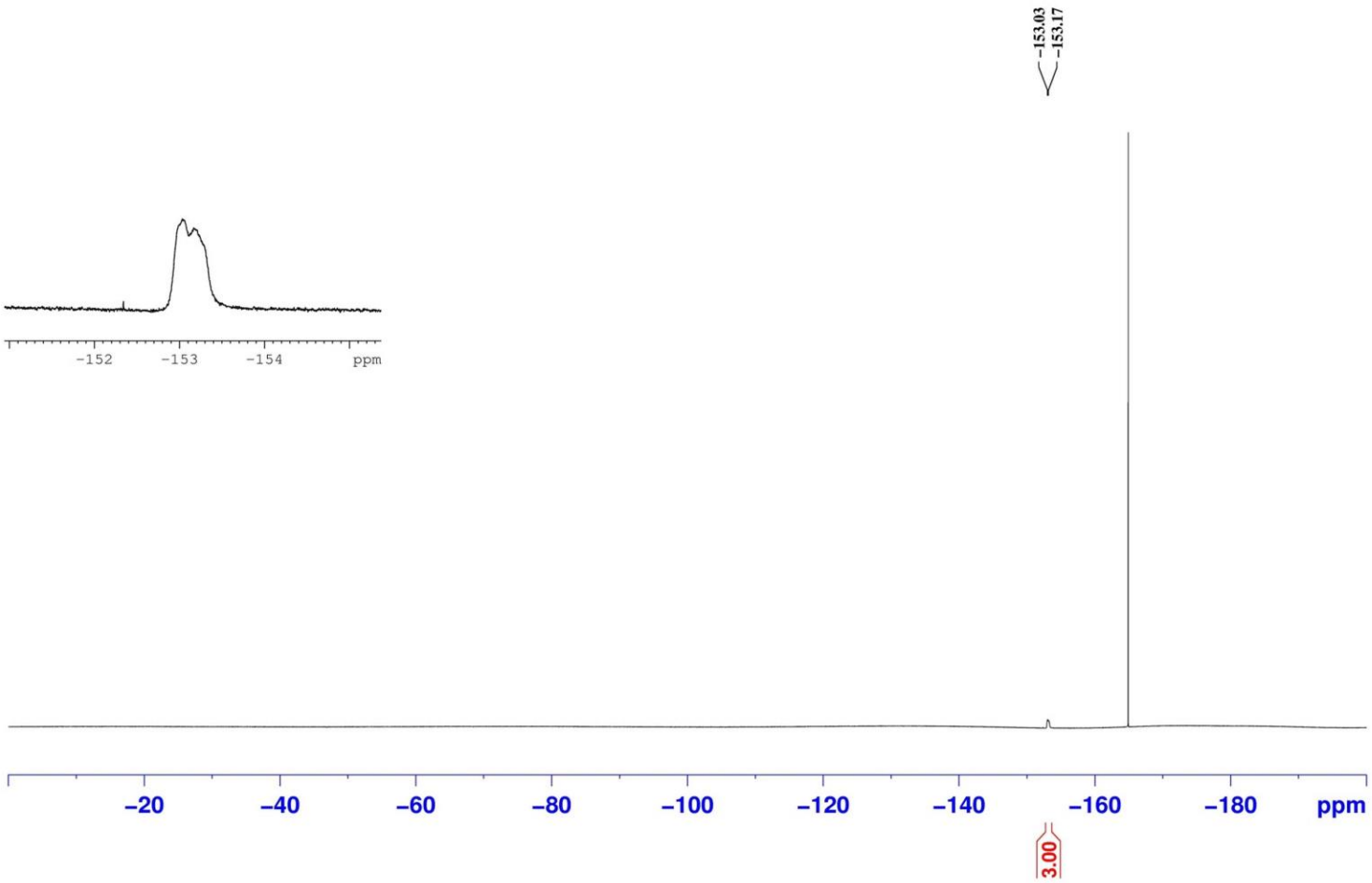
potassium 2–hydroxy–4–phenylbutyltrifluoroborate
125 MHz, acetone–d6



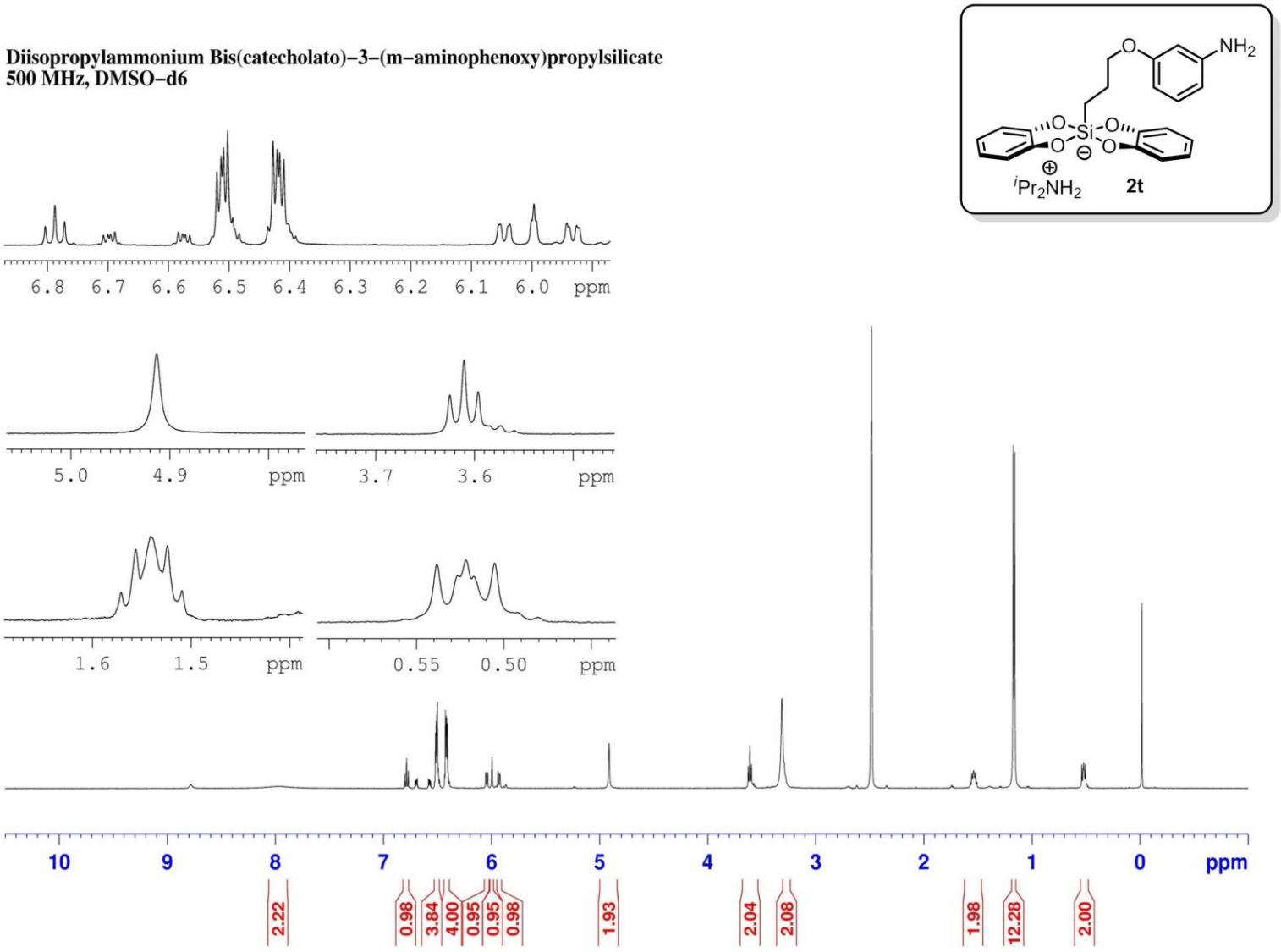


Potassium trifluoro(2–hydroxy–4–phenylbutan–2–yl)borate
471 MHz, CDCl3

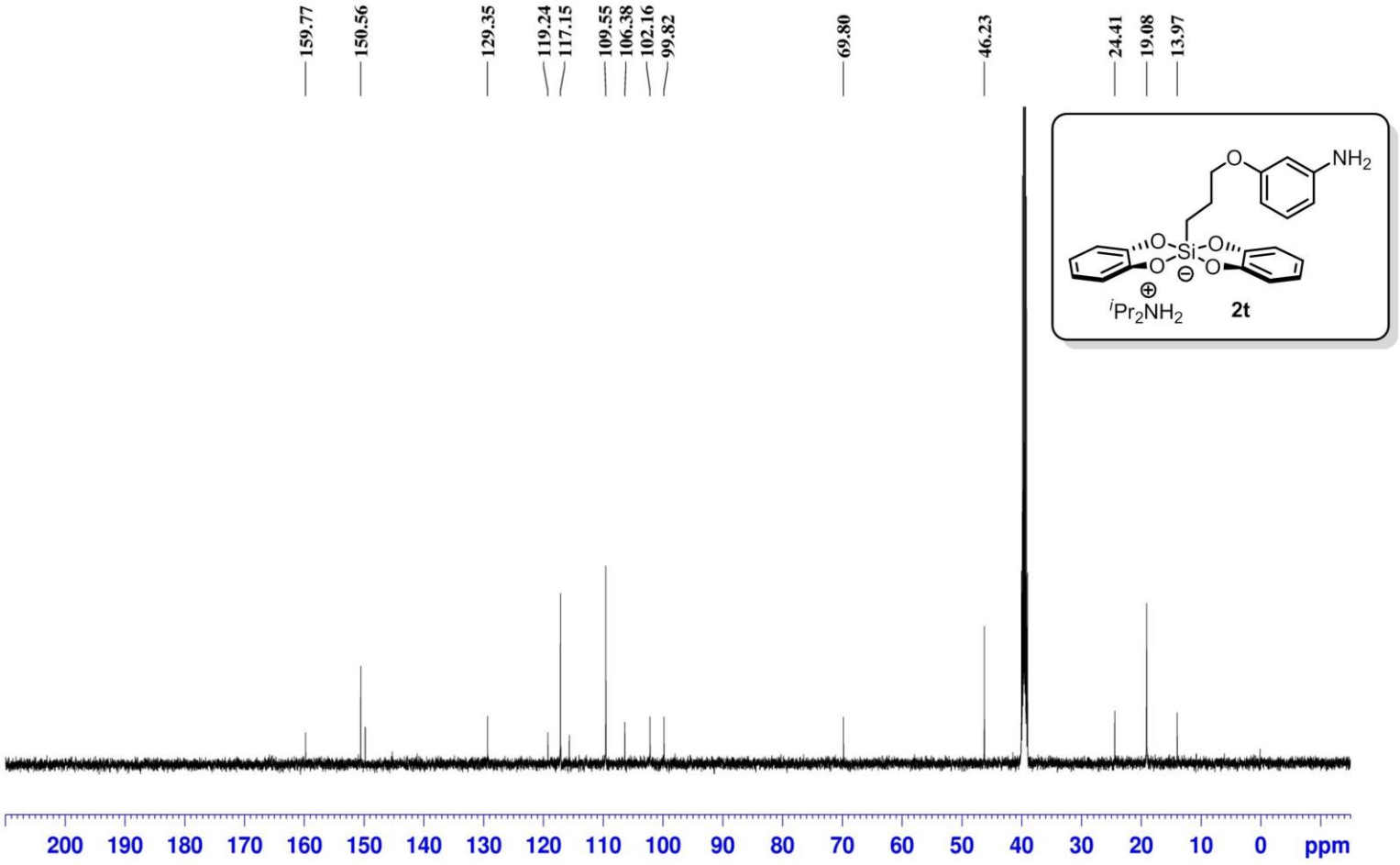




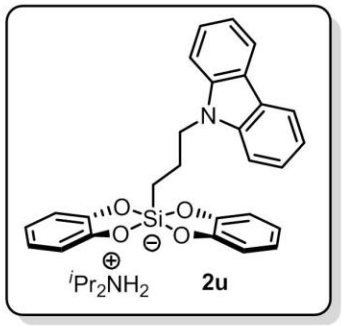
Diisopropylammonium Bis(catecholato)−3−(m−aminophenoxy)propylsilicate
500 MHz, DMSO−d6

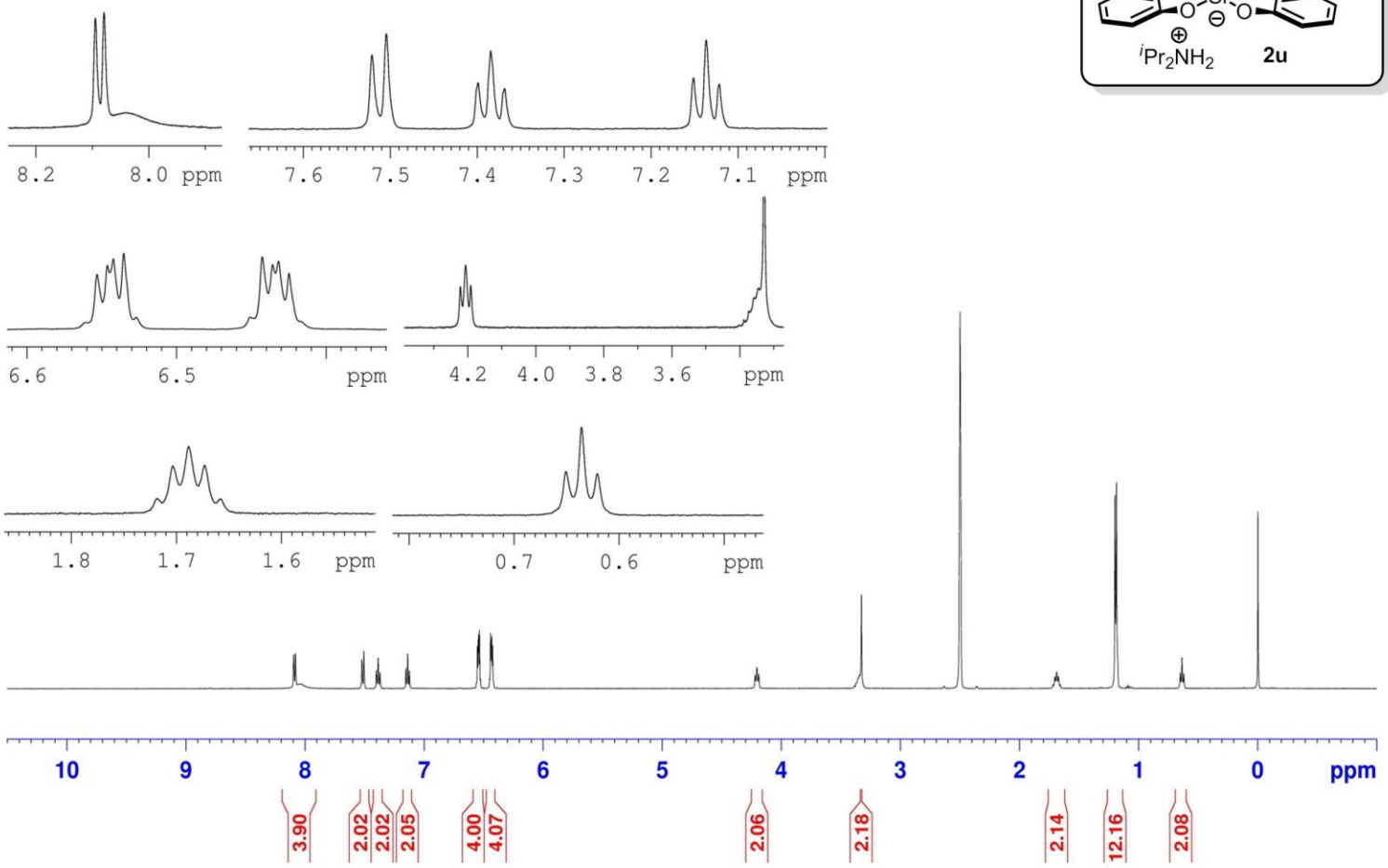


Diisopropylammonium Bis(catecholato) 3–(m–aminophenoxy)propyl silicate
125 MHz, DMSO–d6

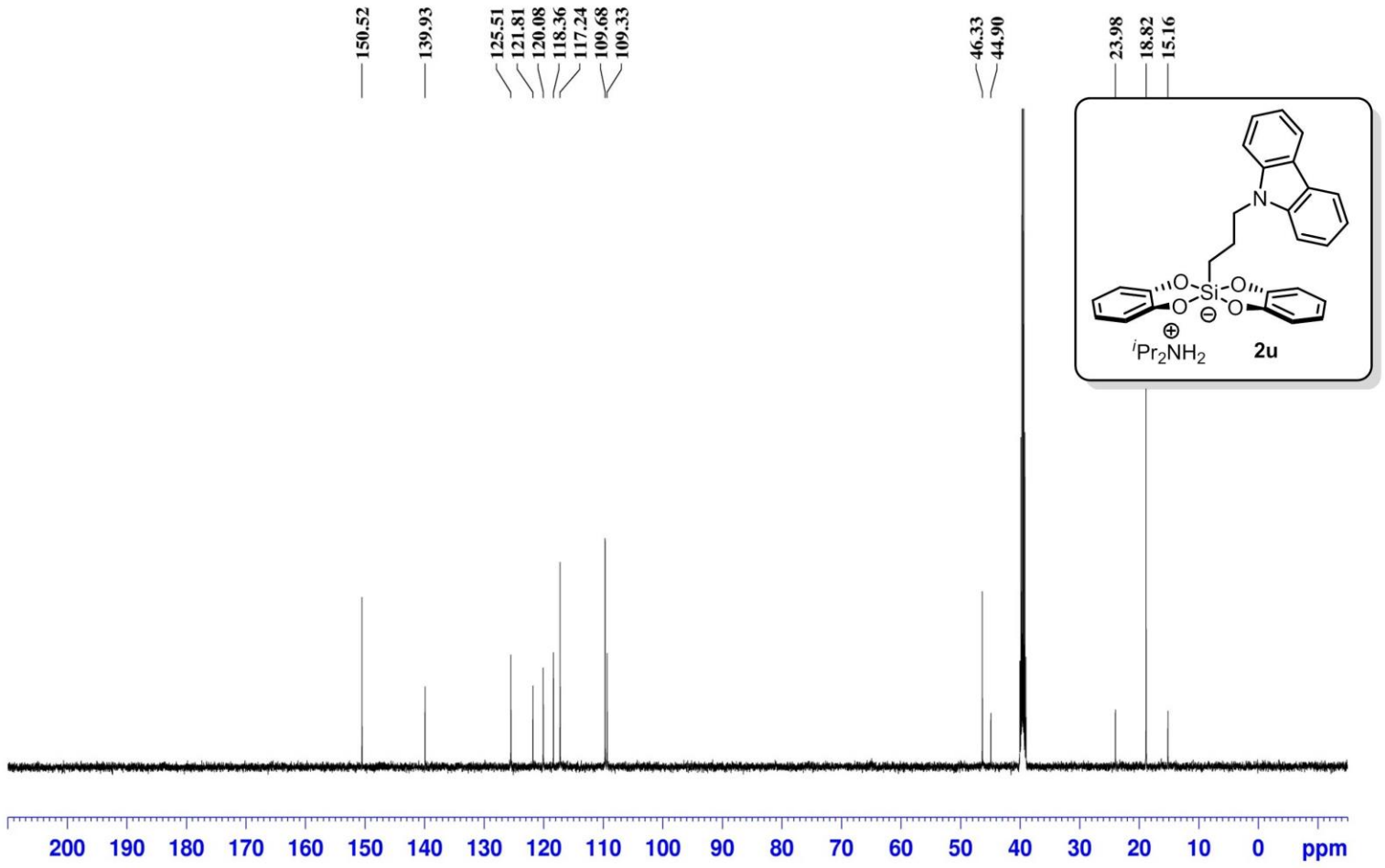


Diisopropylammonium Bis(catecholato)(3−carbazolylpropyl)silicate
500 MHz, DMSO−d6

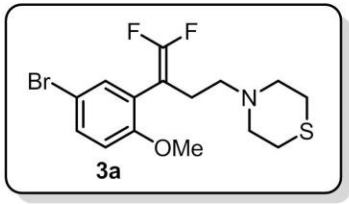




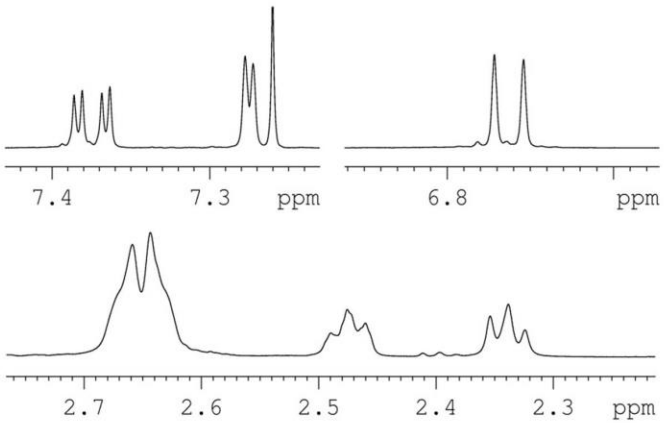
Diisopropylammonium Bis(catecholato)(3−carbazolylpropyl)silicate
125 MHz, DMSO−d6

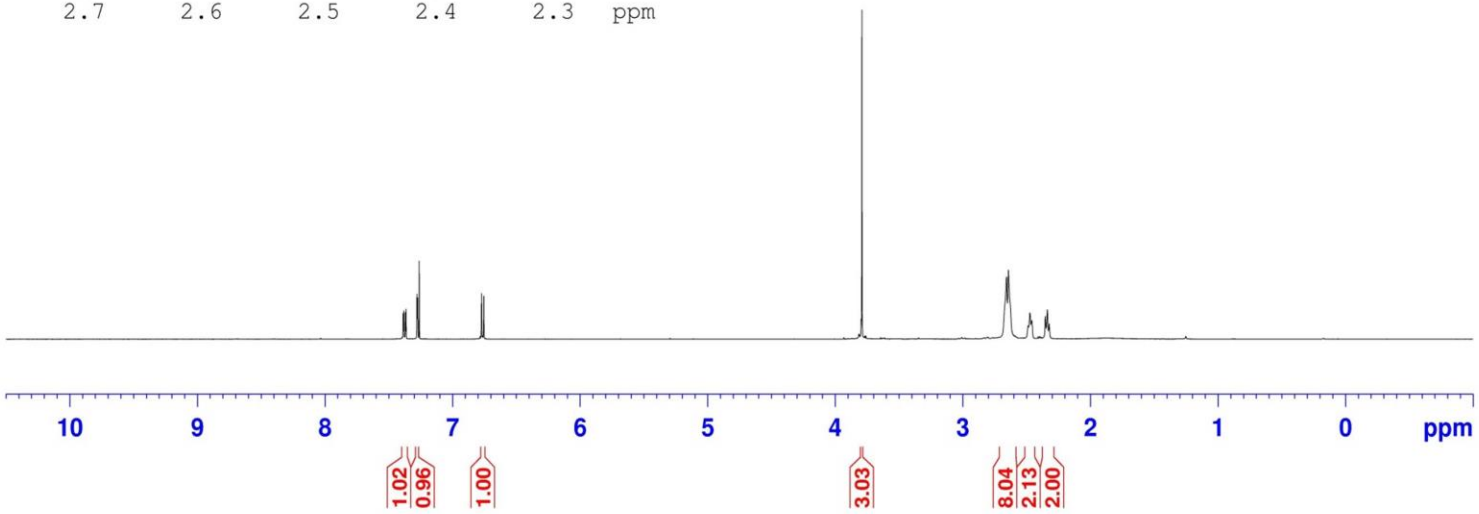


4–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)thiomorpholine
500 MHz, CDCl3

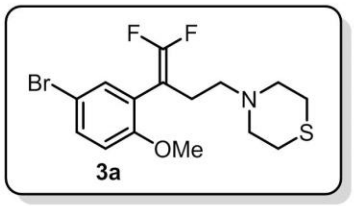


3a

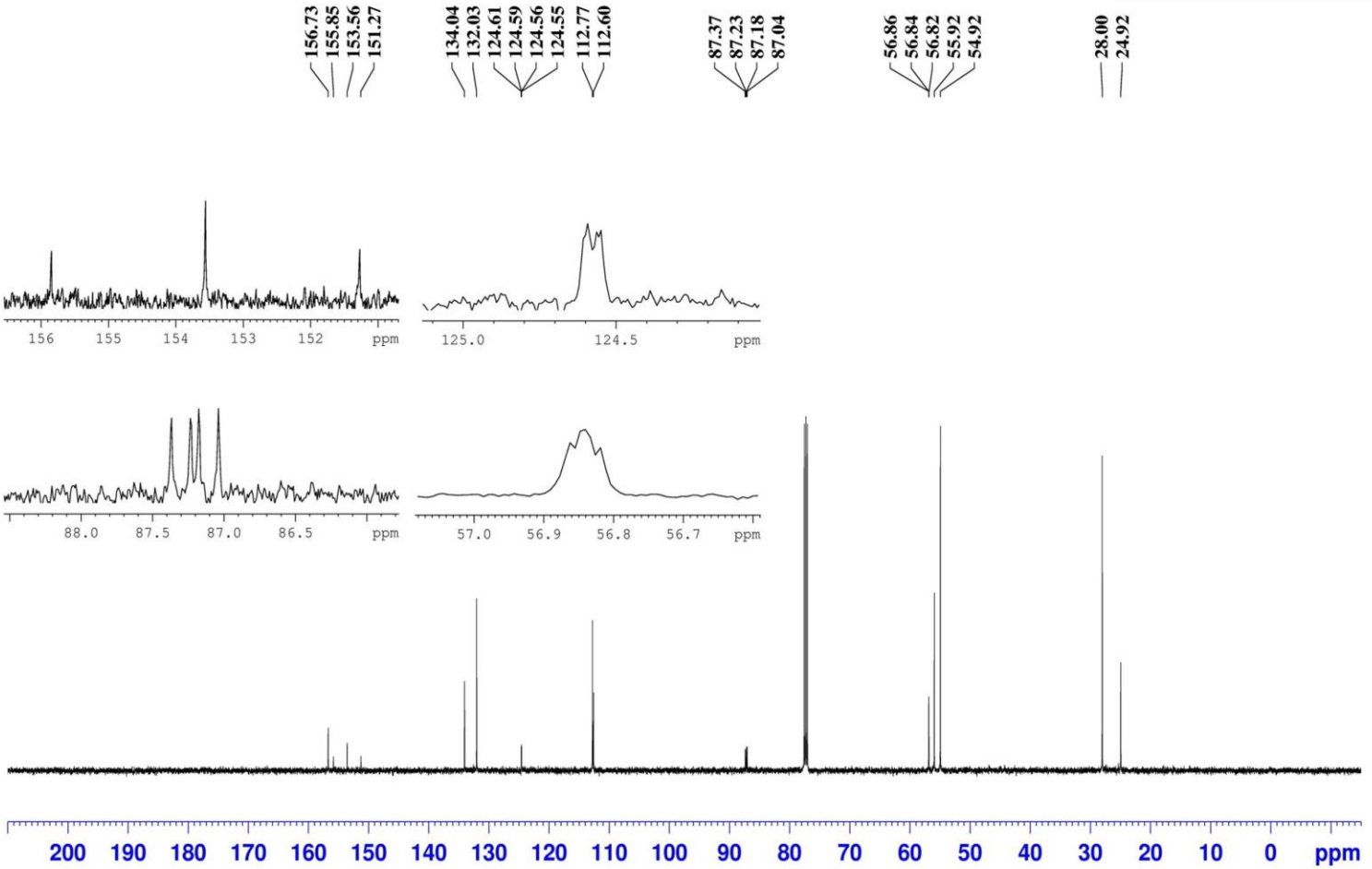




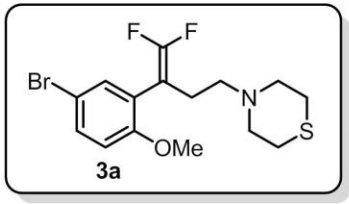
4–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)thiomorpholine
125 MHz, CDCl3



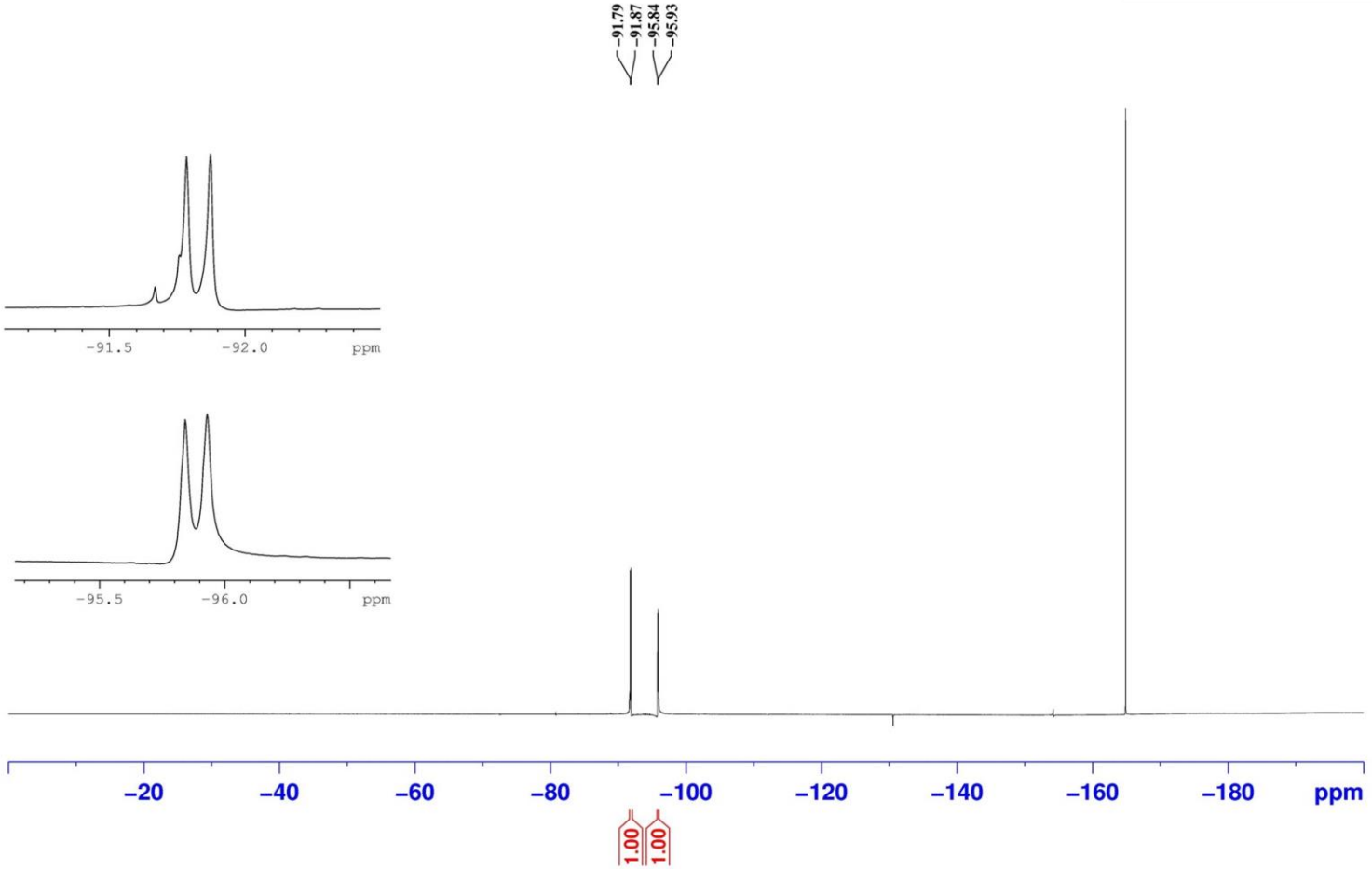
3a



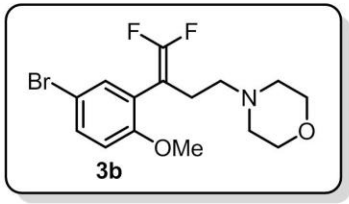
4–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)thiomorpholine
471 MHz, CDCl3



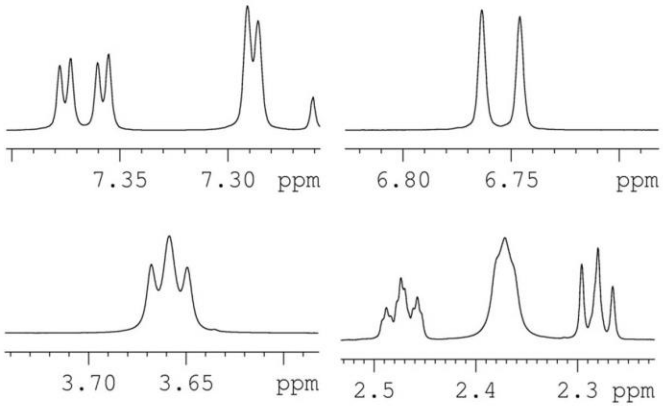
3a

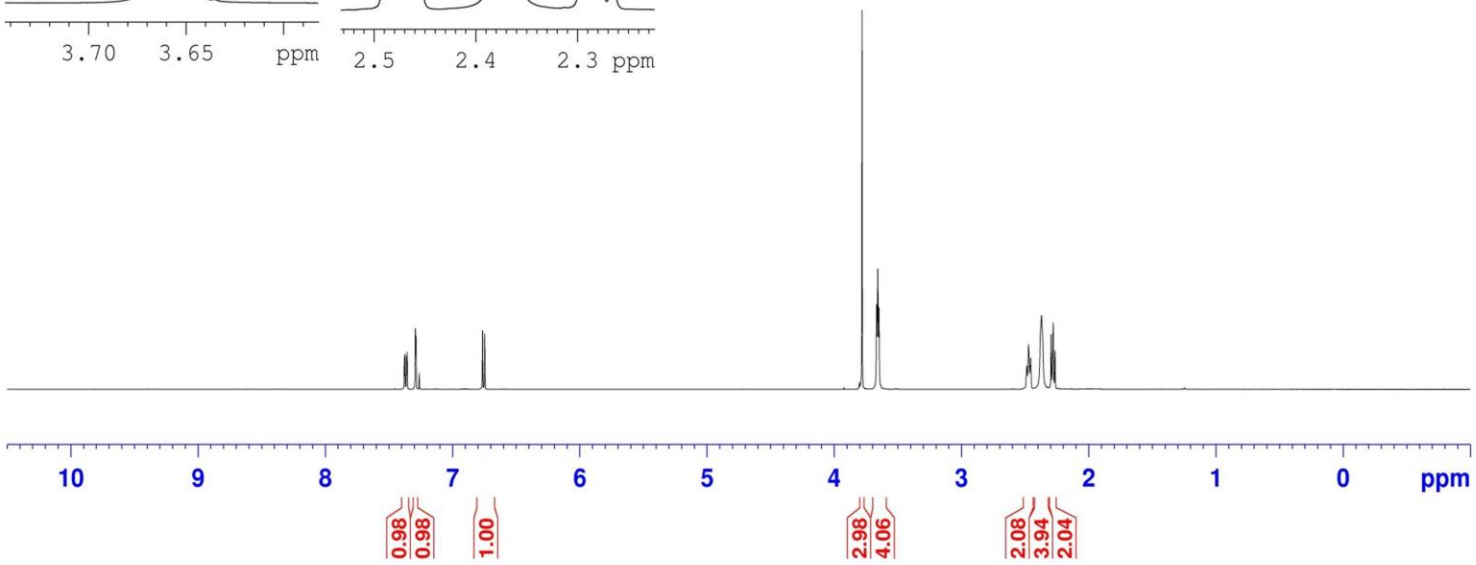


4–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)morpholine
500 MHz, CDCl3

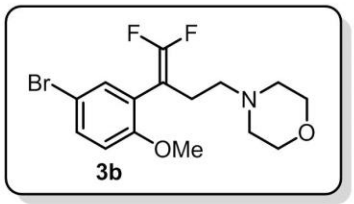


3b

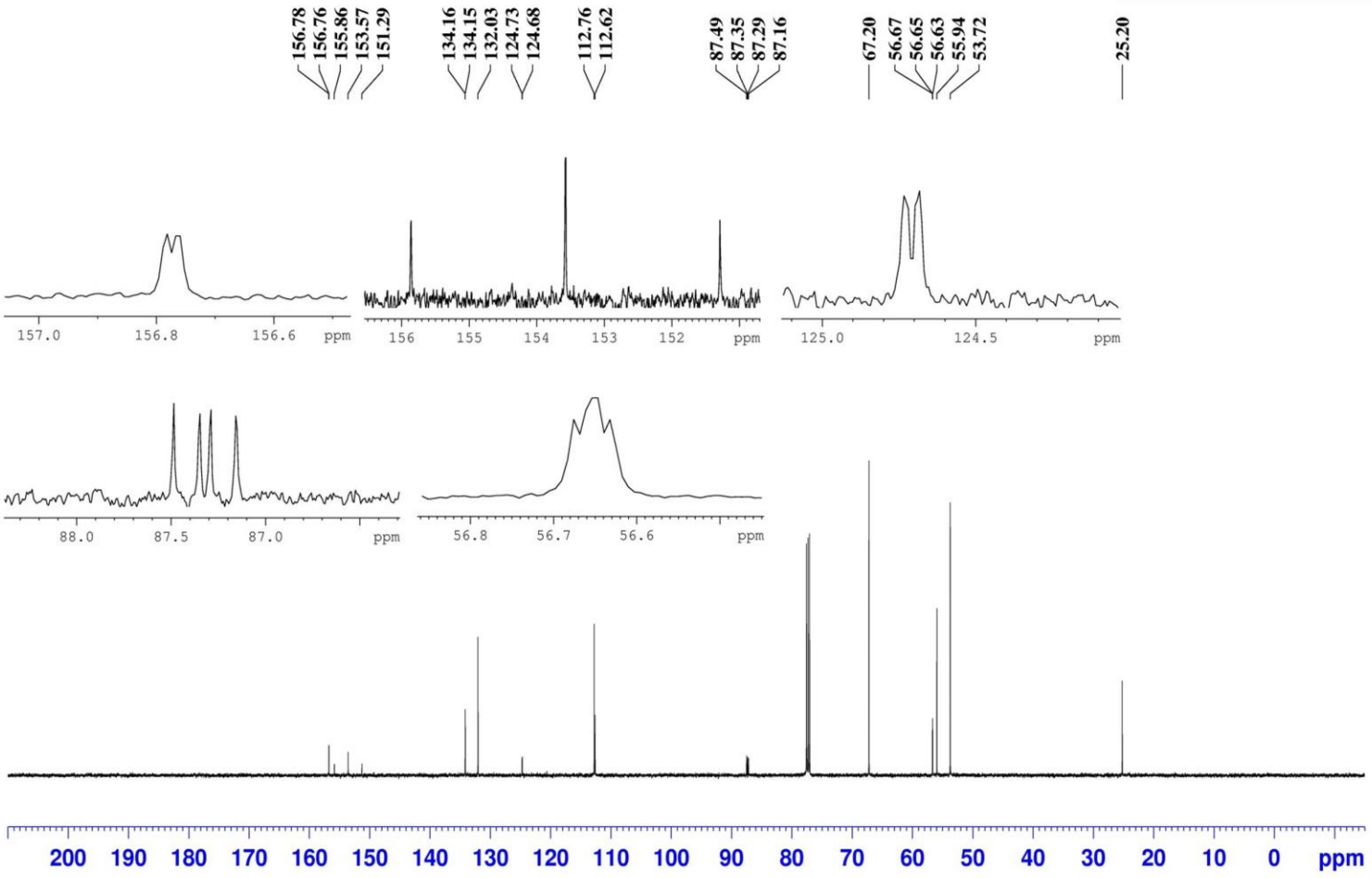




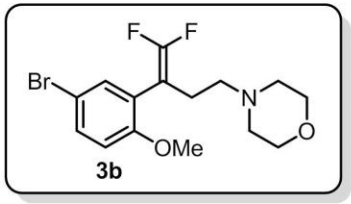
4–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)morpholine
125 MHz, CDCl3



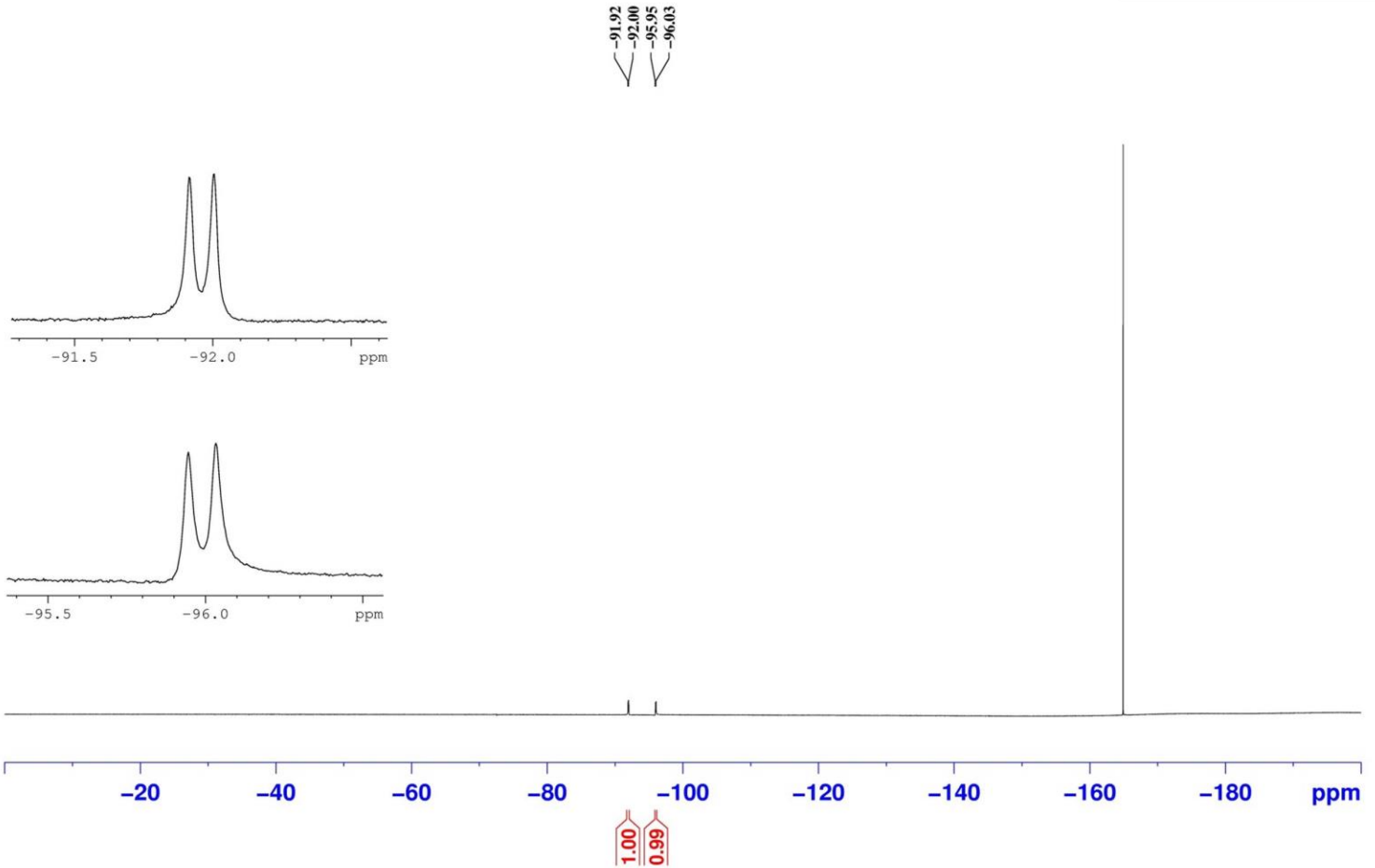
3b



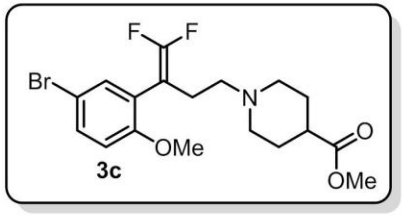
4–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)morpholine
471 MHz, CDCl3

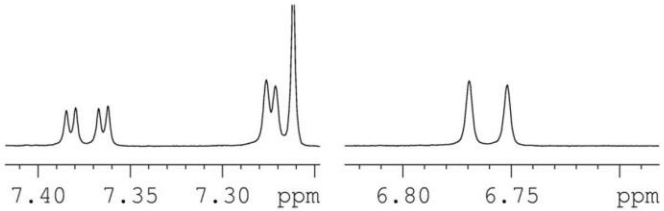


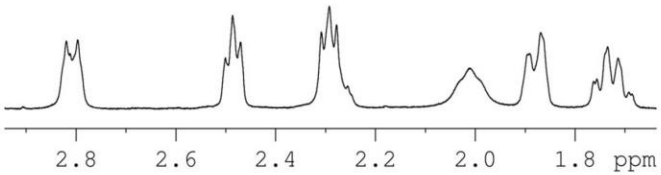
3b

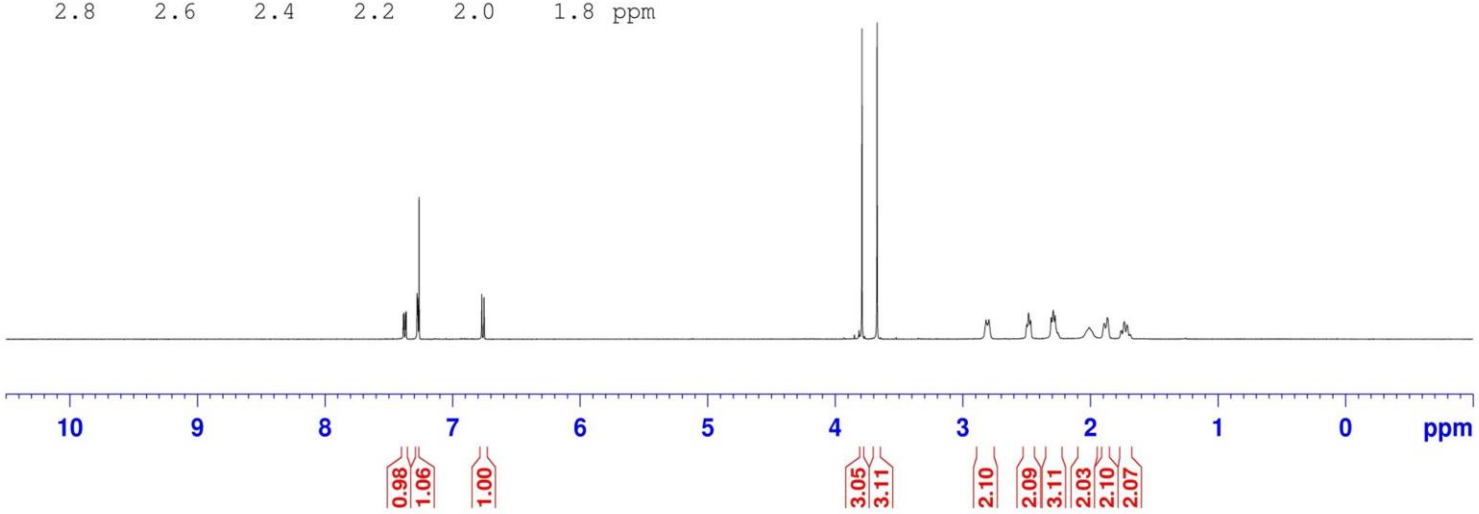


methyl 1–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)piperidine–4–carboxylate
500 MHz, CDCl3

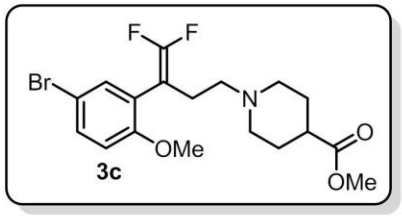


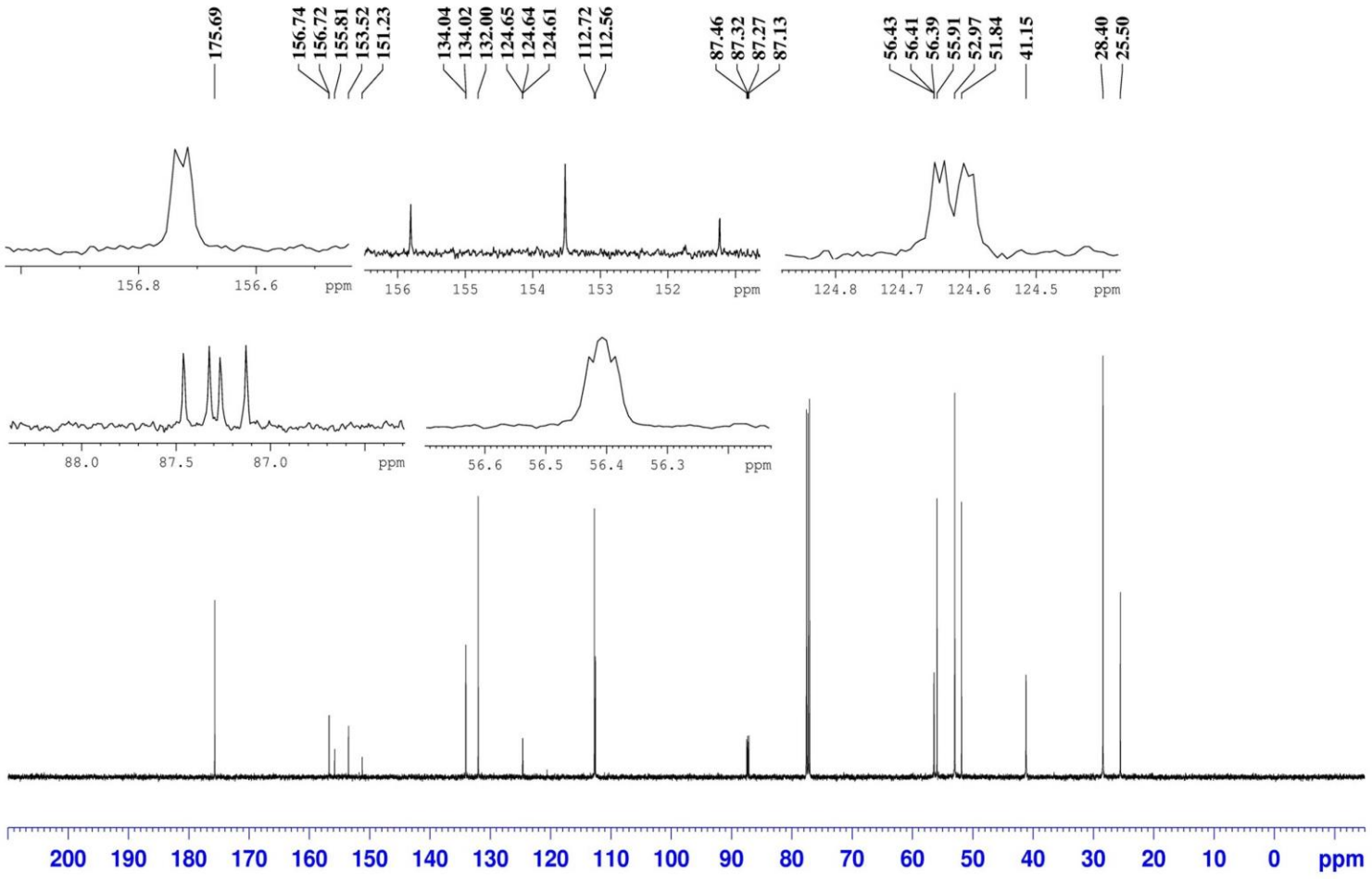




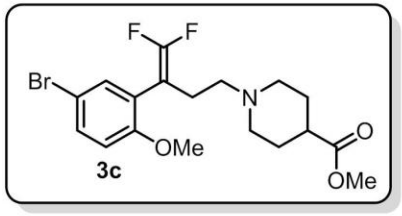


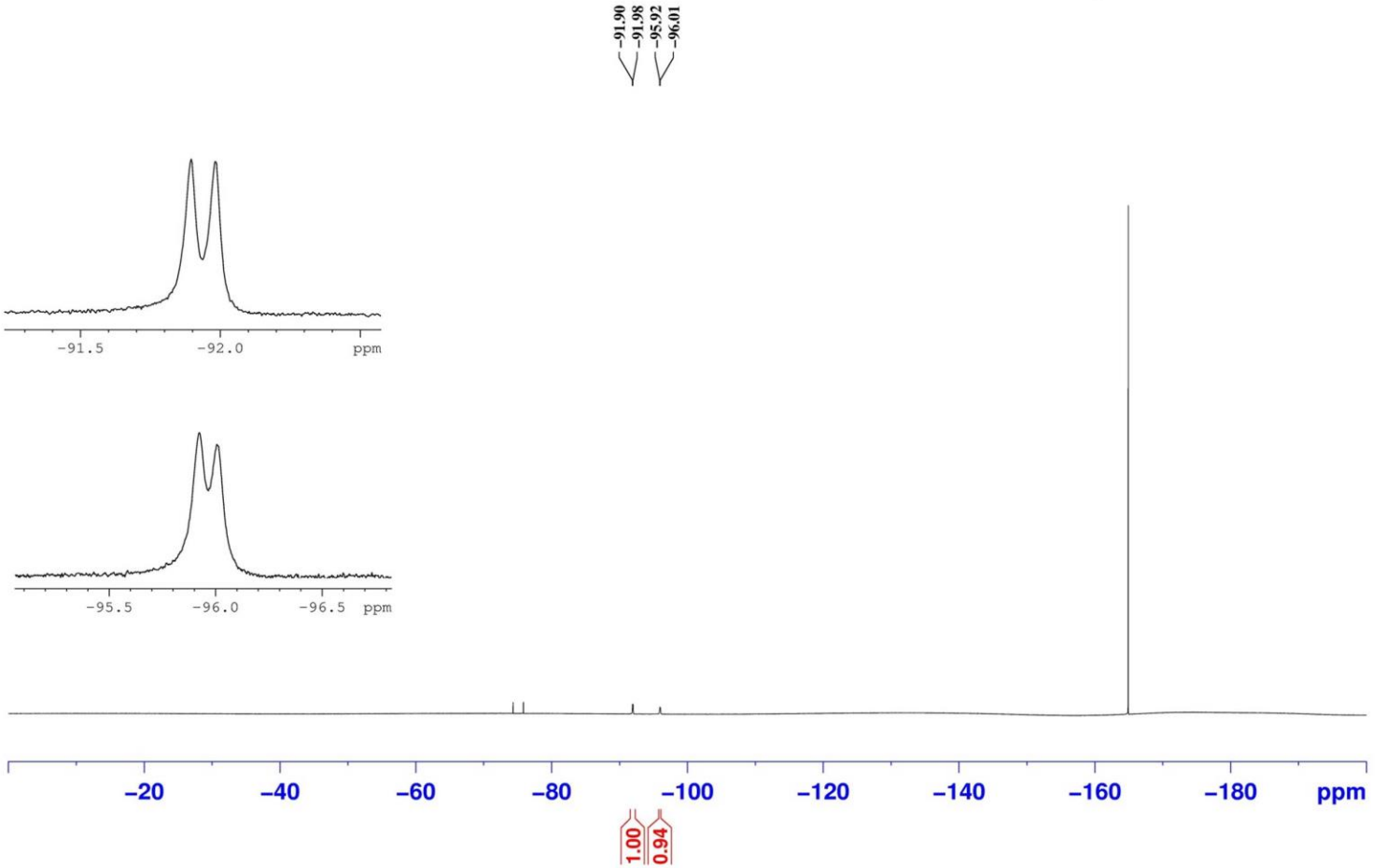
methyl 1–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)piperidine–4–carboxylate
125 MHz, CDCl3



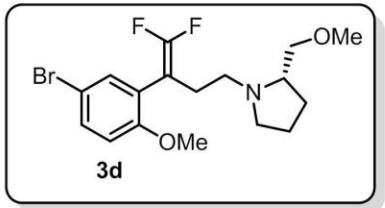


methyl 1–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)piperidine–4–carboxylate
471 MHz, CDCl3

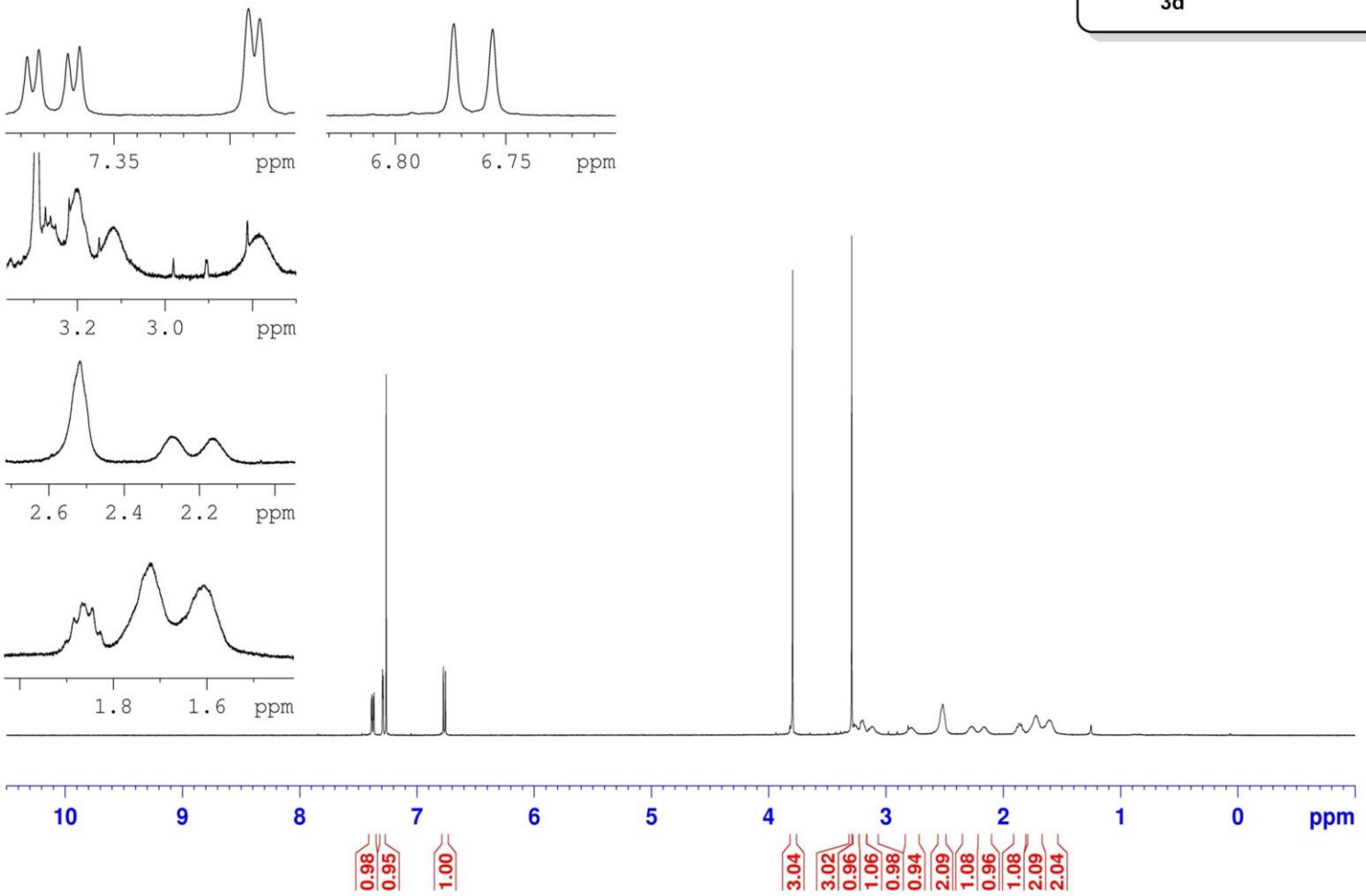




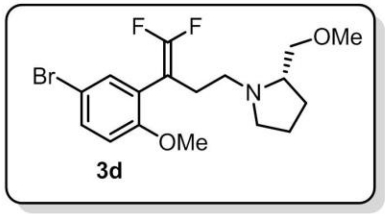
(S)−1−(3−(5−bromo−2−methoxyphenyl)−4,4−difluorobut−3−en−1−yl)−2−(methoxymethyl)pyrrolidine
500 MHz, CDCl3



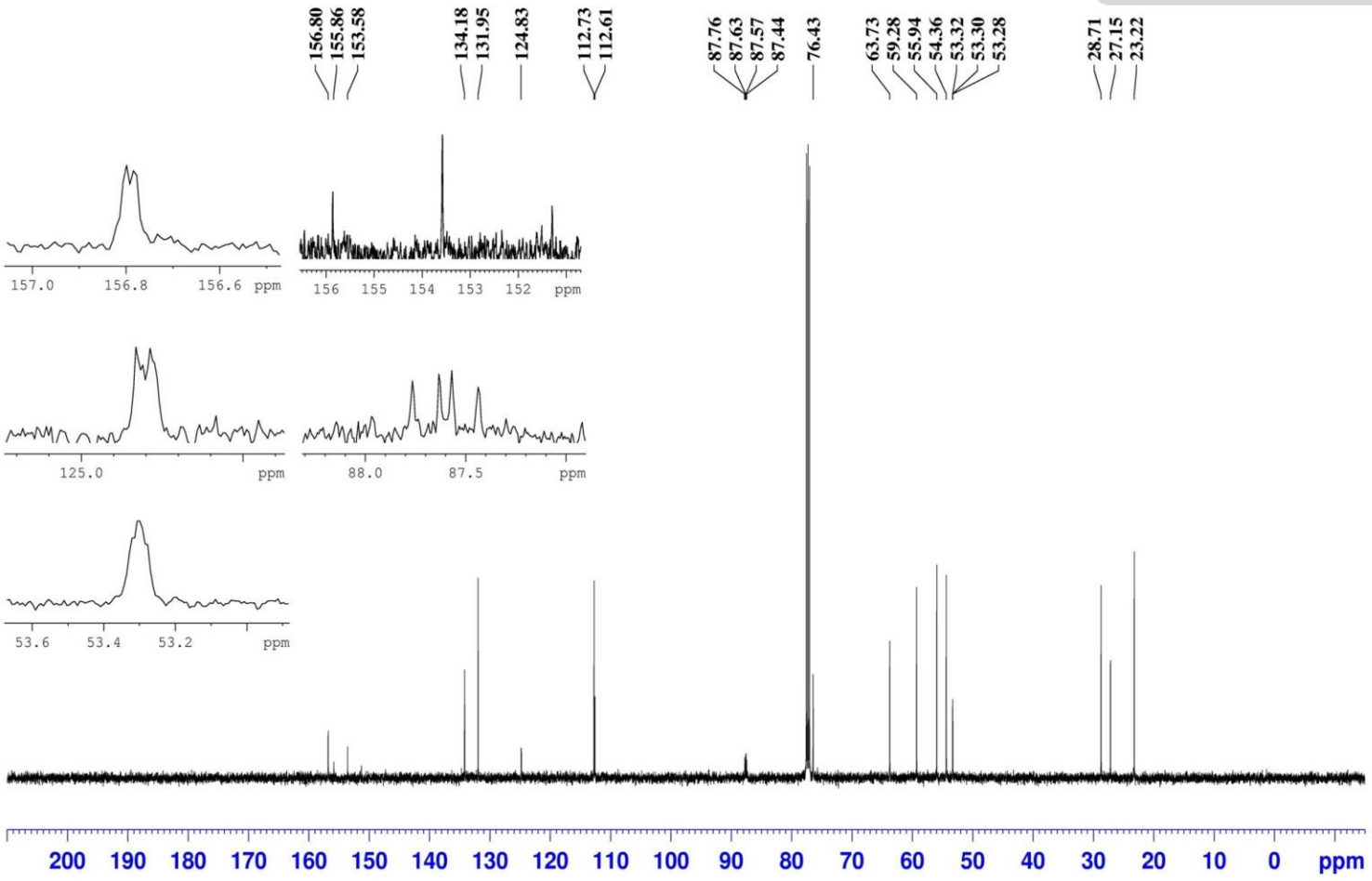
3d



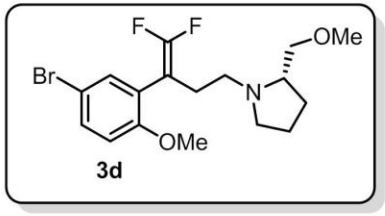
(S)−1−(3−(5−bromo−2−methoxyphenyl)−4,4−difluorobut−3−en−1−yl)−2−(methoxymethyl)pyrrolidine
125 MHz, CDCl3



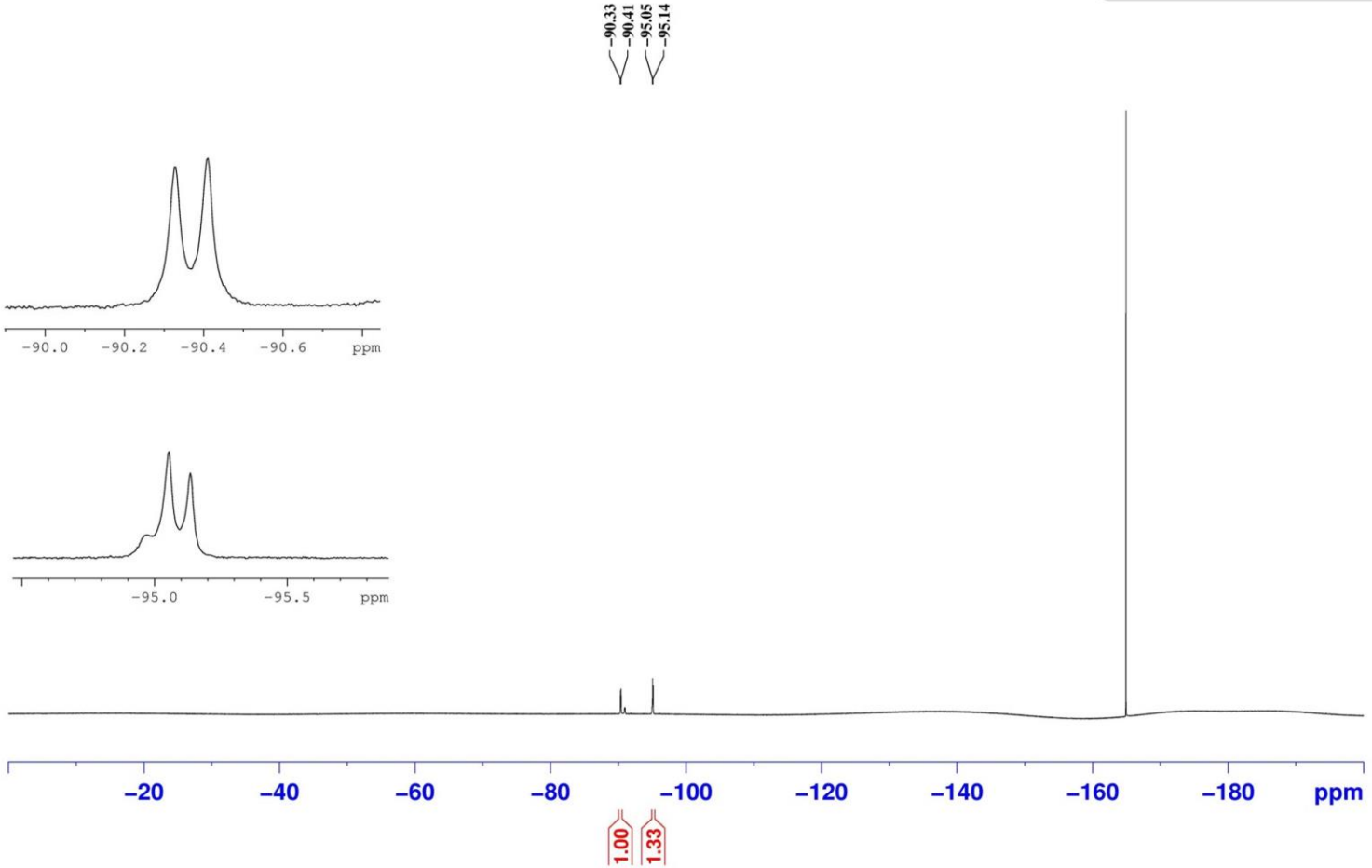
3d



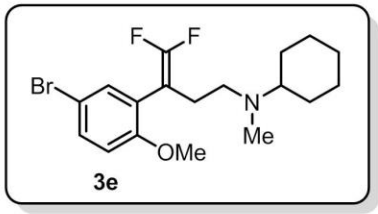
(S)−1−(3−(5−bromo−2−methoxyphenyl)−4,4−difluorobut−3−en−1−yl)−2−(methoxymethyl)pyrrolidine
471 MHz, CDCl3



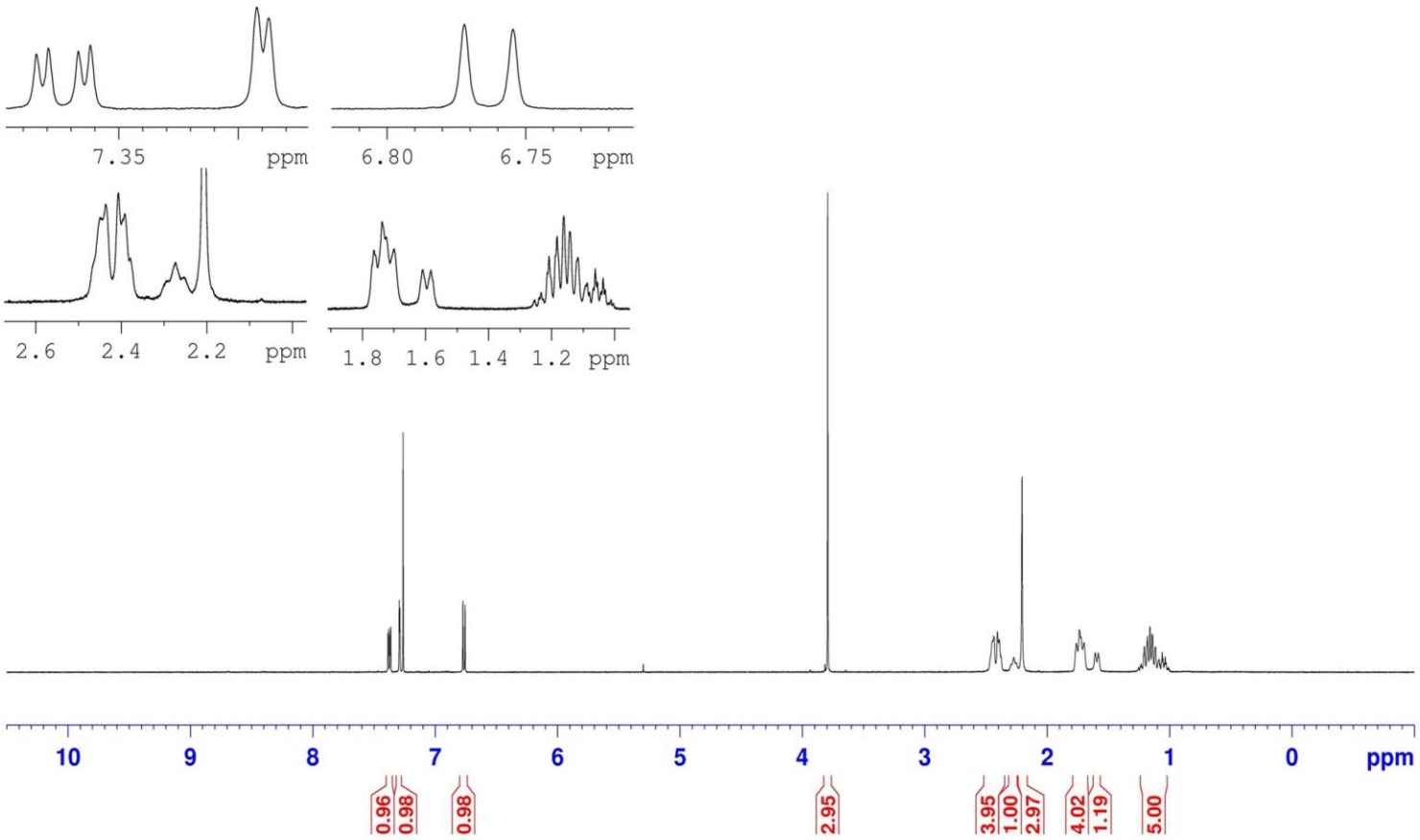
3d



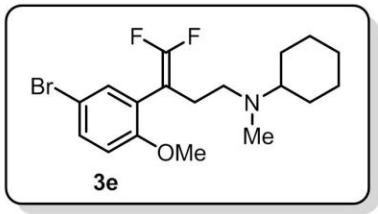
N–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)–N–methylcyclohexanamine
500 MHz, CDCl3



3e



N–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)–N–methylcyclohexanamine
125 MHz, CDCl3



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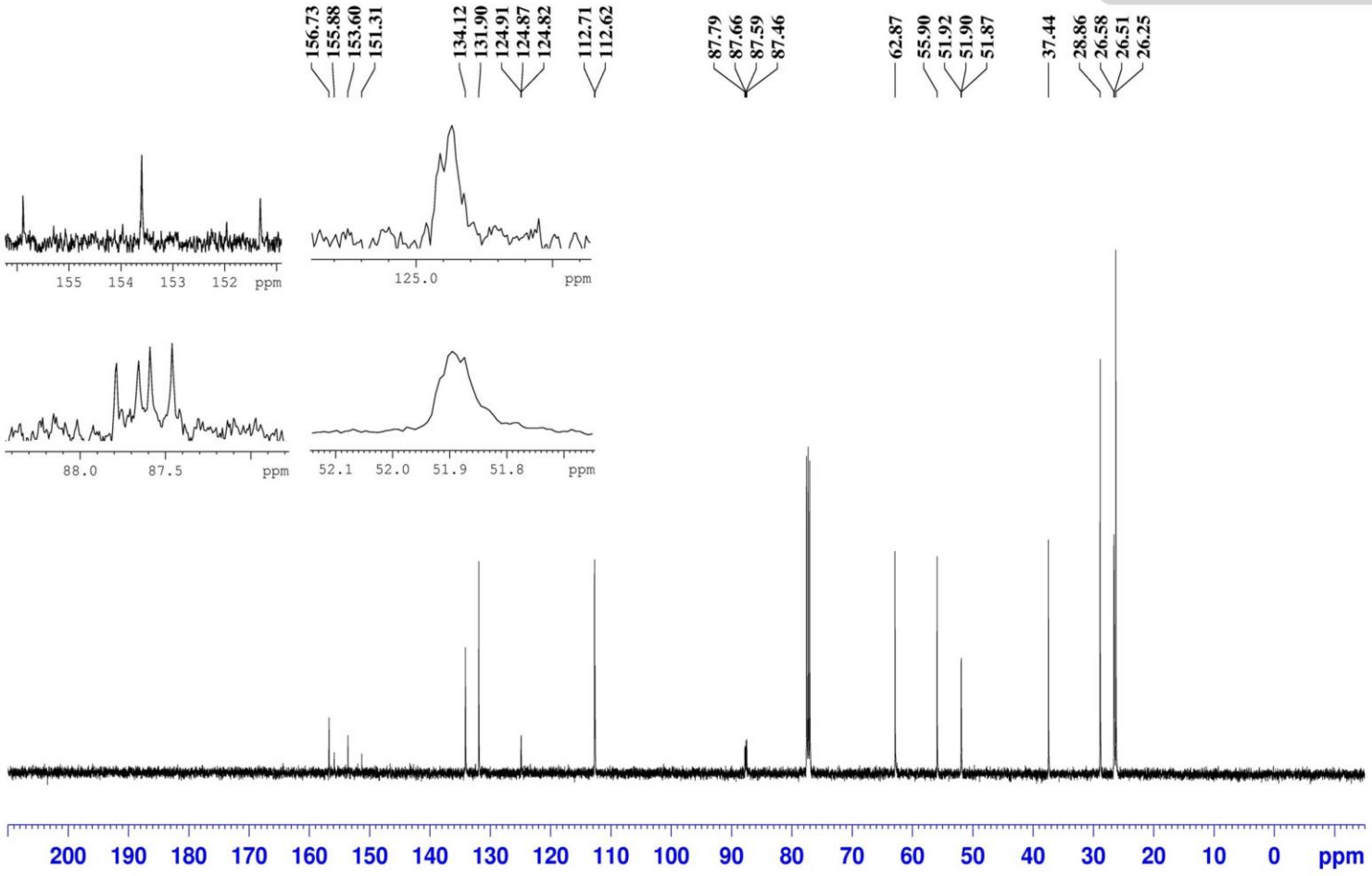
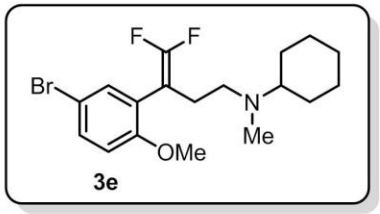
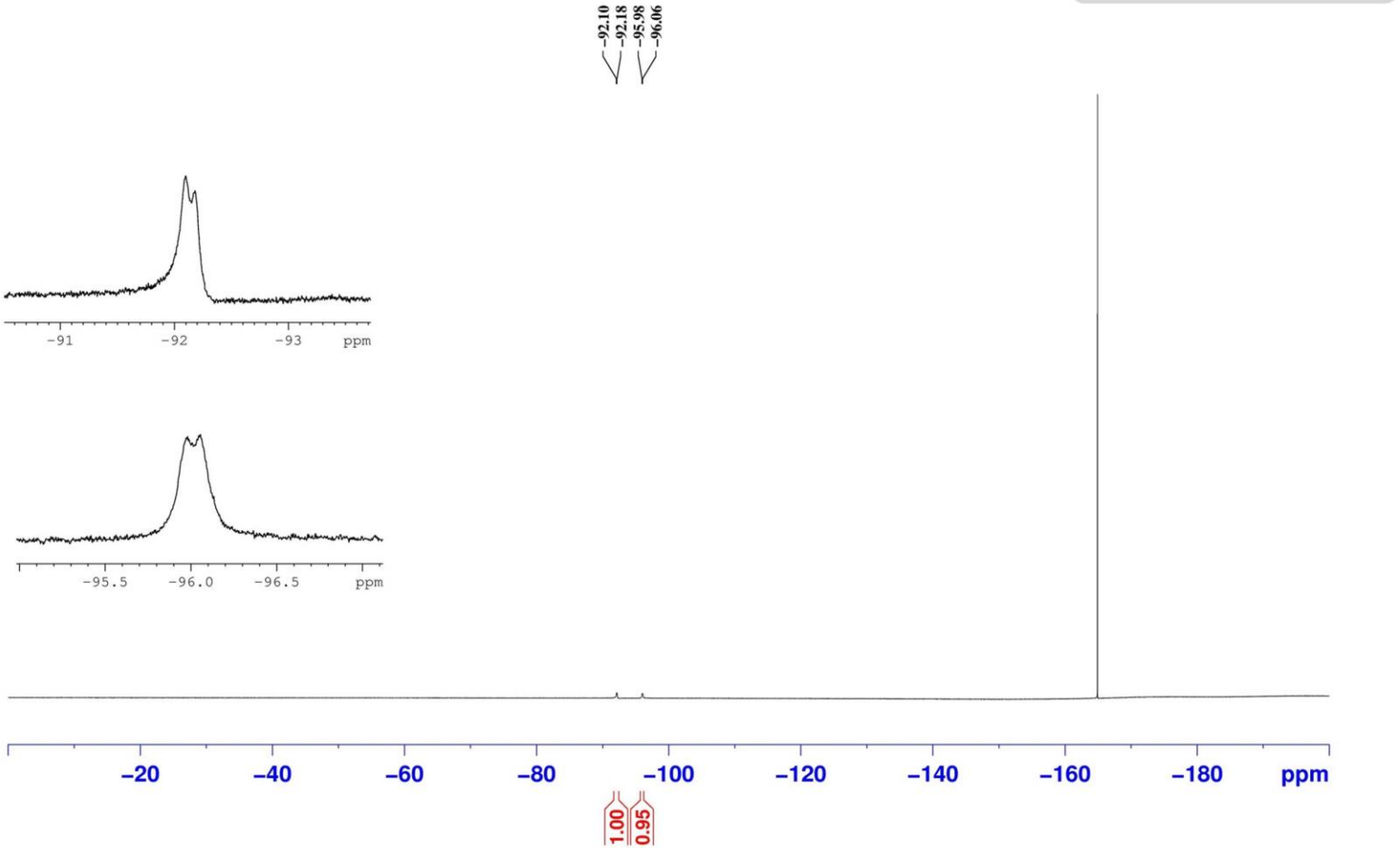


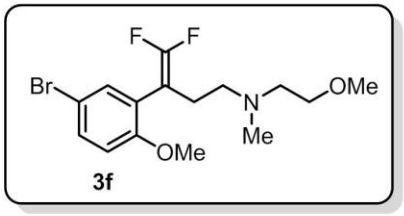
N–(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)–N–methylcyclohexanamine
471 MHz, CDCl3



3e



3–(5–bromo–2–methoxyphenyl)–4,4–difluoro–N–(2–methoxyethyl)–N–methylbut–3–en–1–amine
500 MHz, CDCl3



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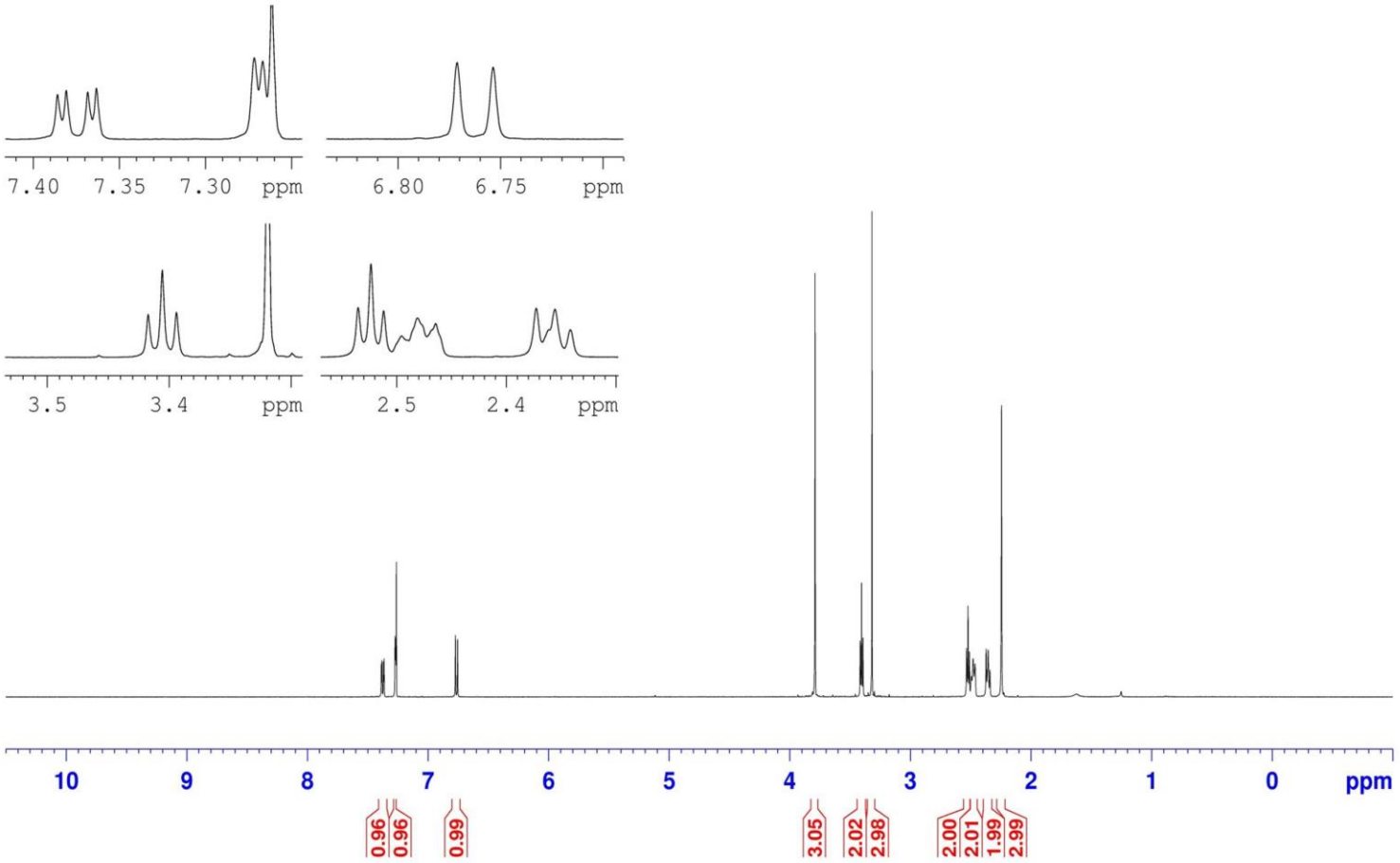
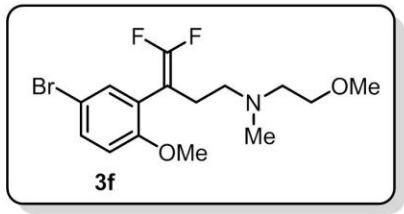


3–(5–bromo–2–methoxyphenyl)–4,4–difluoro–N–(2–methoxyethyl)–N–methylbut–3–en–1–amine
125 MHz, CDCl3



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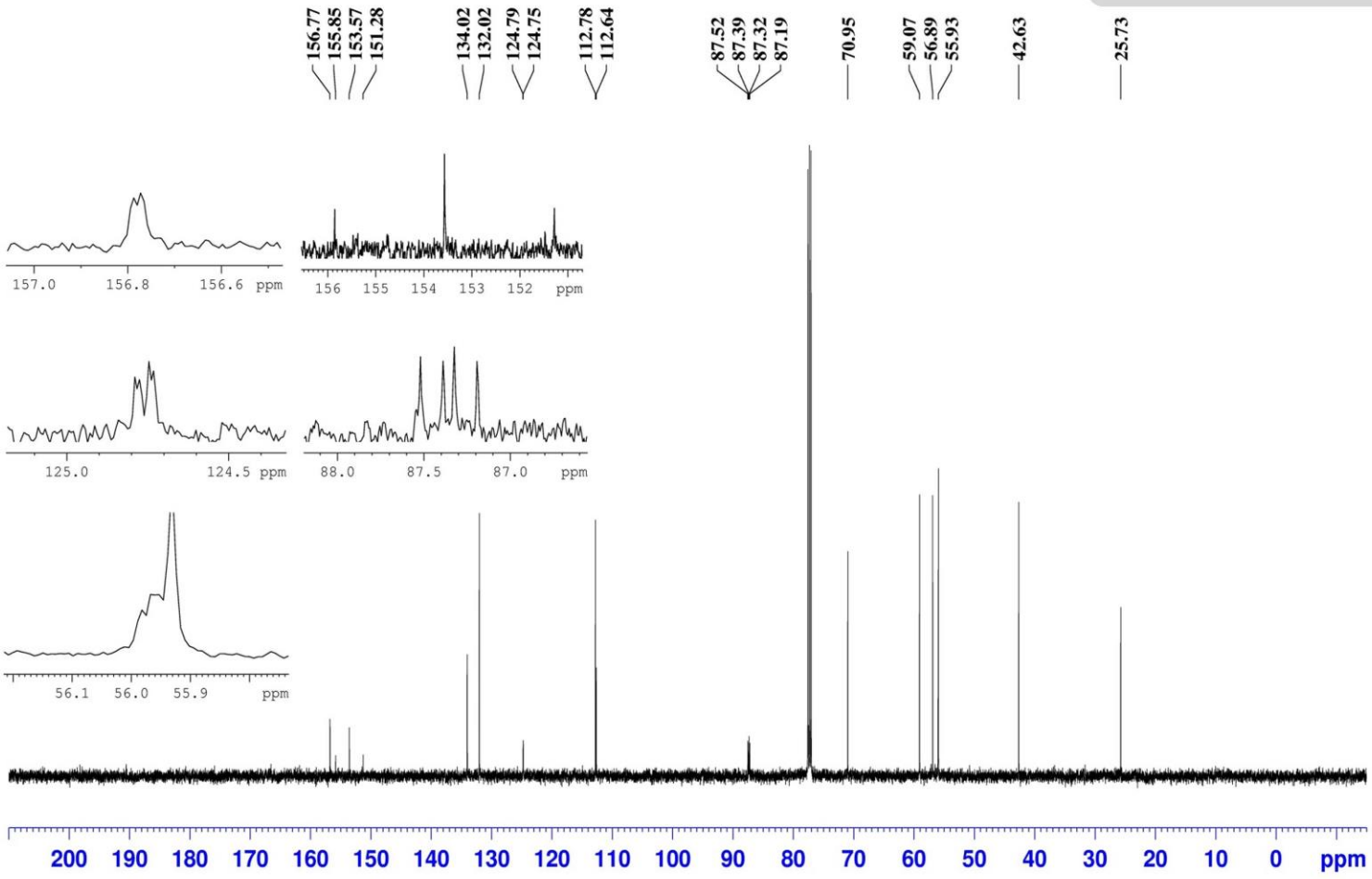
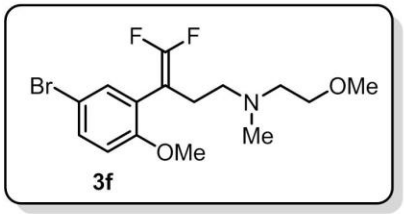


3–(5–bromo–2–methoxyphenyl)–4,4–difluoro–N–(2–methoxyethyl)–N–methylbut–3–en–1–amine
471 MHz, CDCl3



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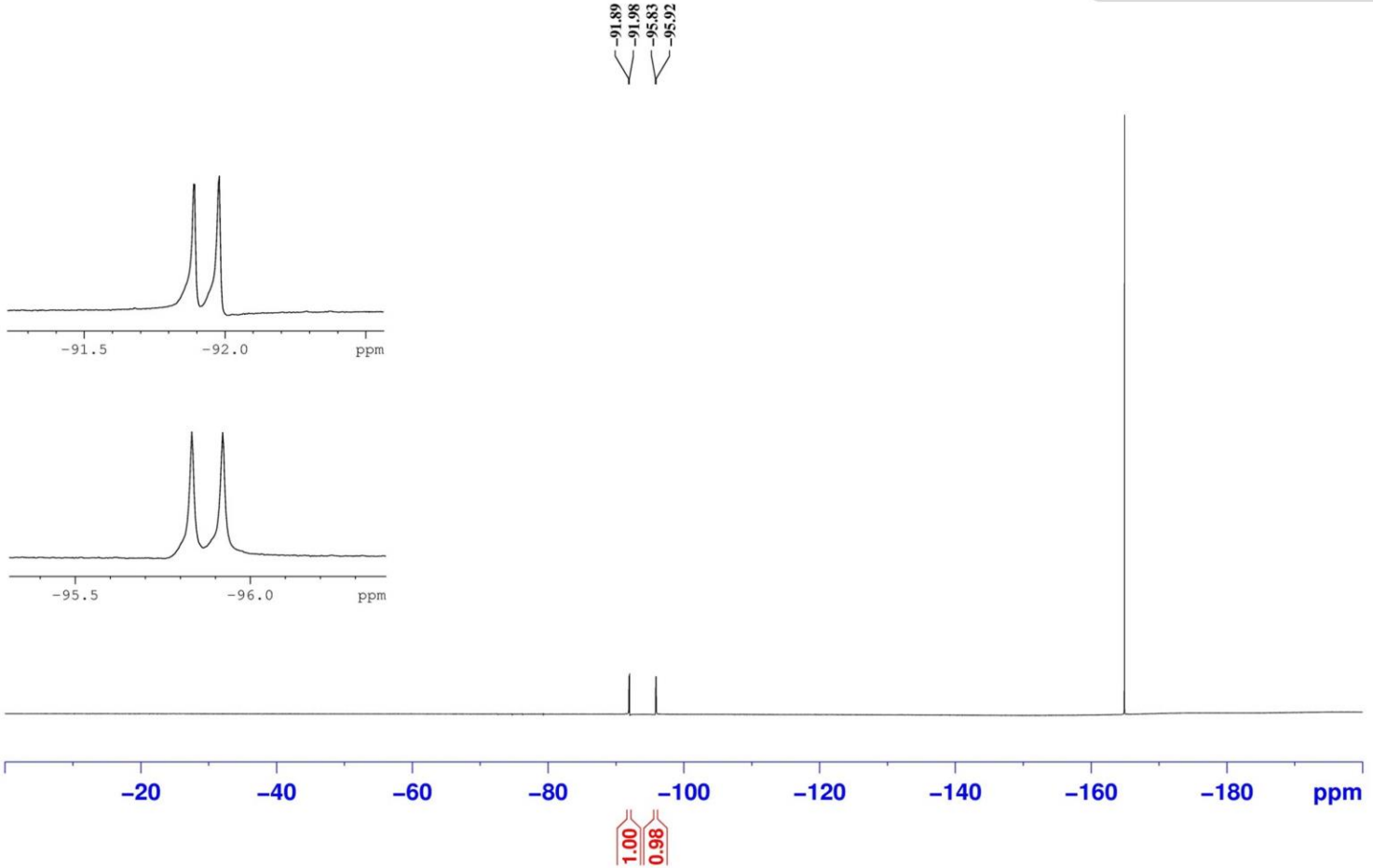
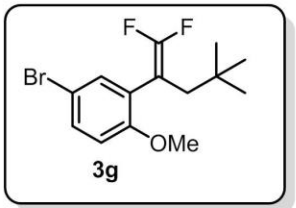
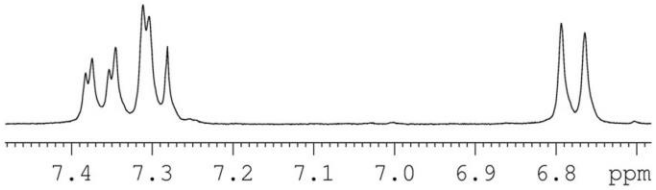
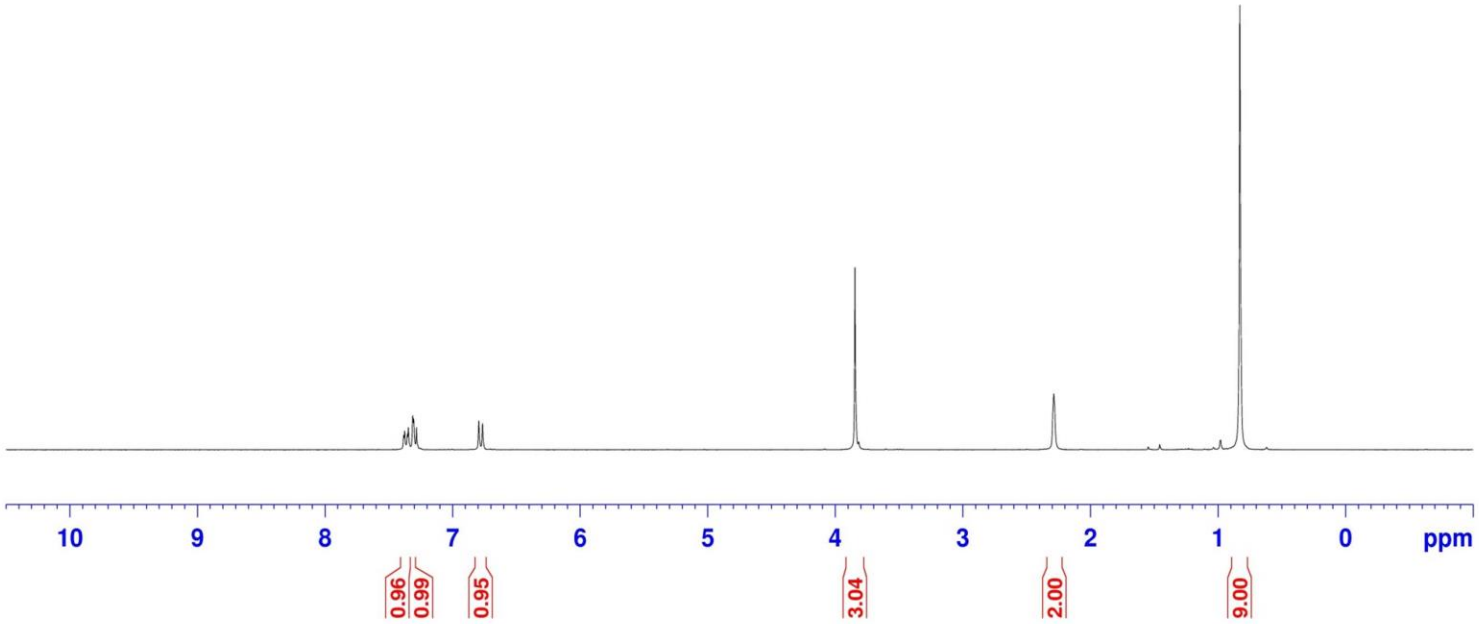


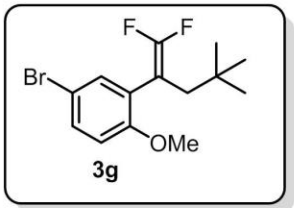
4–bromo–2–(1,1–difluoro–4,4–dimethylpent–1–en–2–yl)–1–methoxybenzene
500 MHz, CDCl3



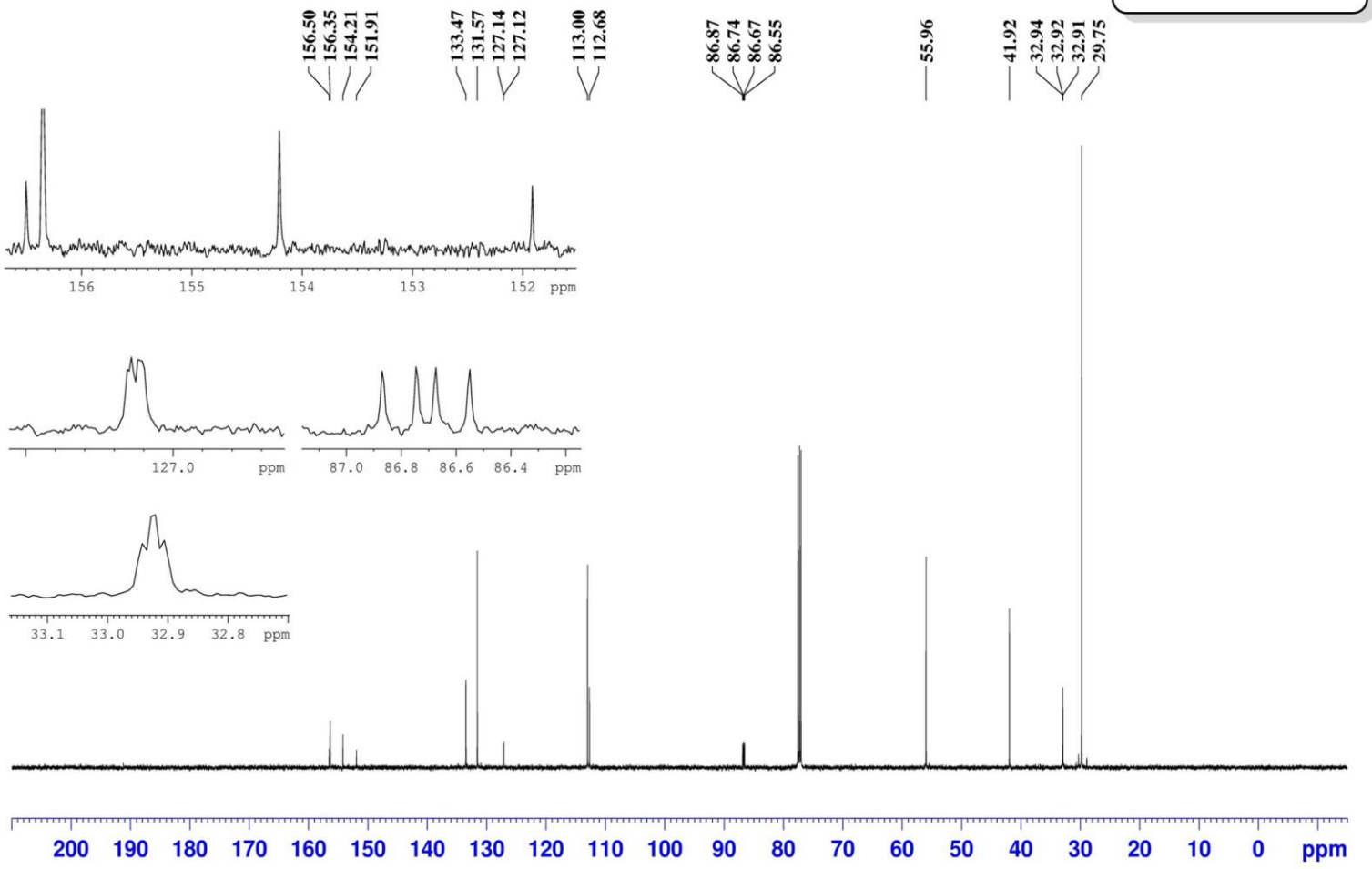




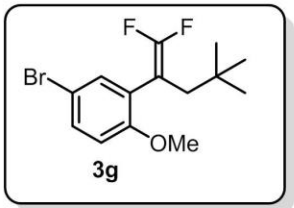
4–bromo–2–(1,1–difluoro–4,4–dimethylpent–1–en–2–yl)–1–methoxybenzene
125 MHz, CDCl3



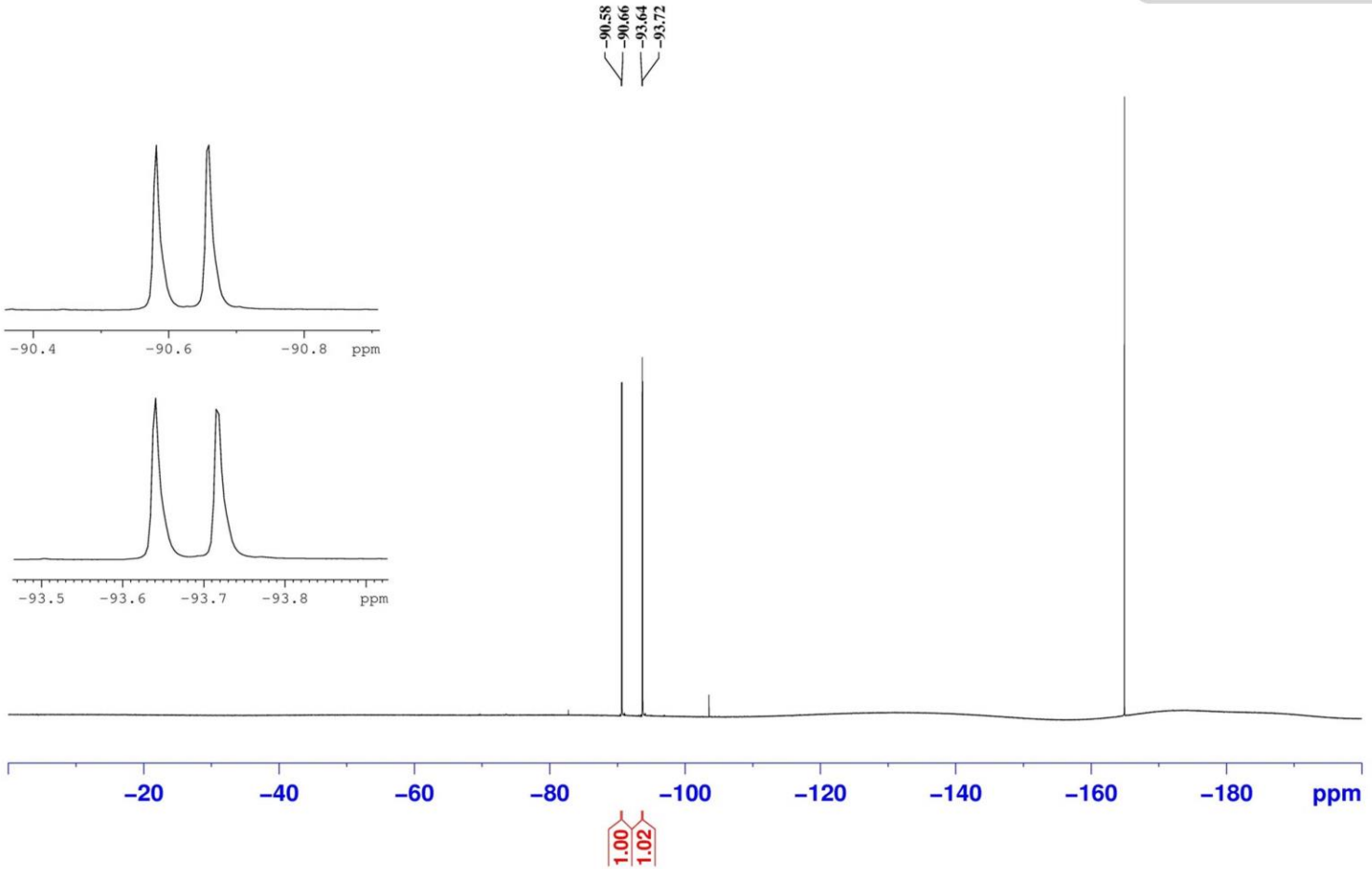
3g



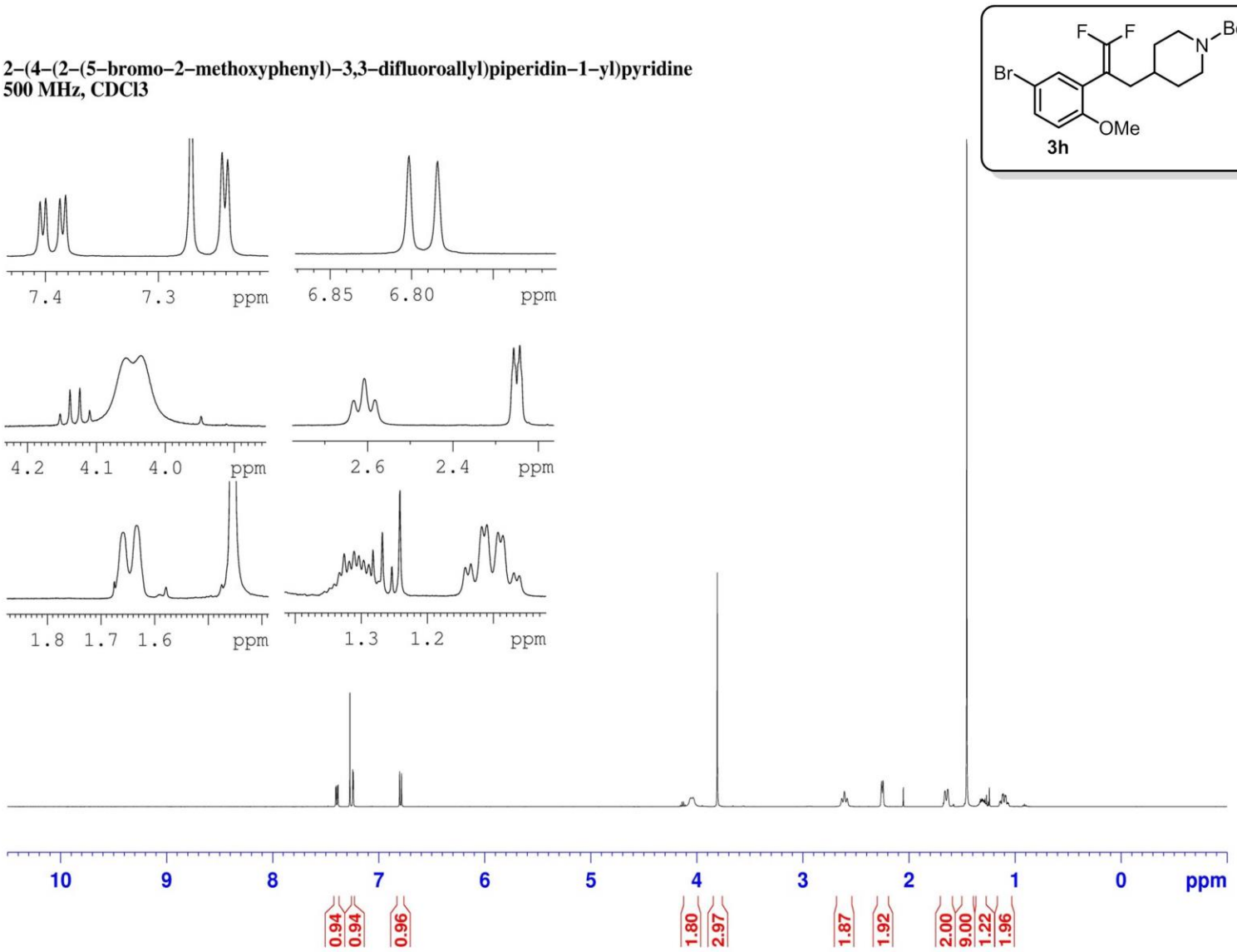
4–bromo–2–(1,1–difluoro–4,4–dimethylpent–1–en–2–yl)–1–methoxybenzene
471 MHz, CDCl3



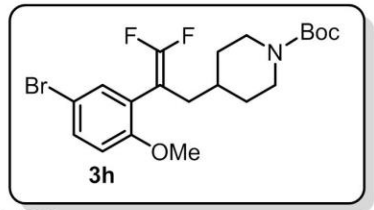
3g

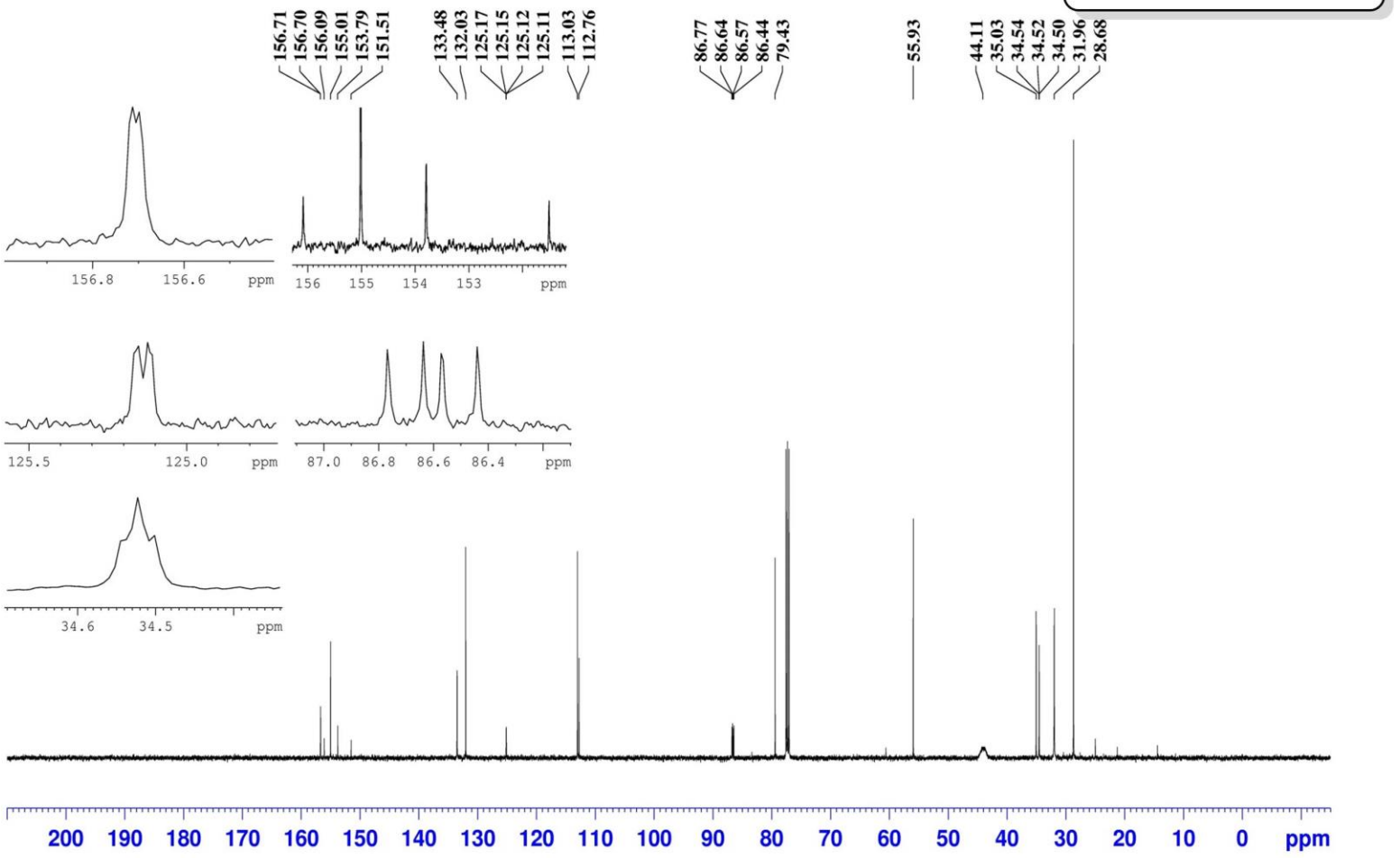


2–(4–(2–(5–bromo–2–methoxyphenyl)–3,3–difluoroallyl)piperidin–1–yl)pyridine
500 MHz, CDCl3

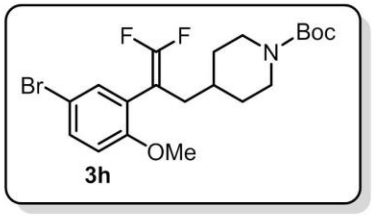


tert−butyl 4−(2−(5−bromo−2−methoxyphenyl)−3,3−difluoroallyl)piperidine−1−carboxylate
125 MHz, CDCl3

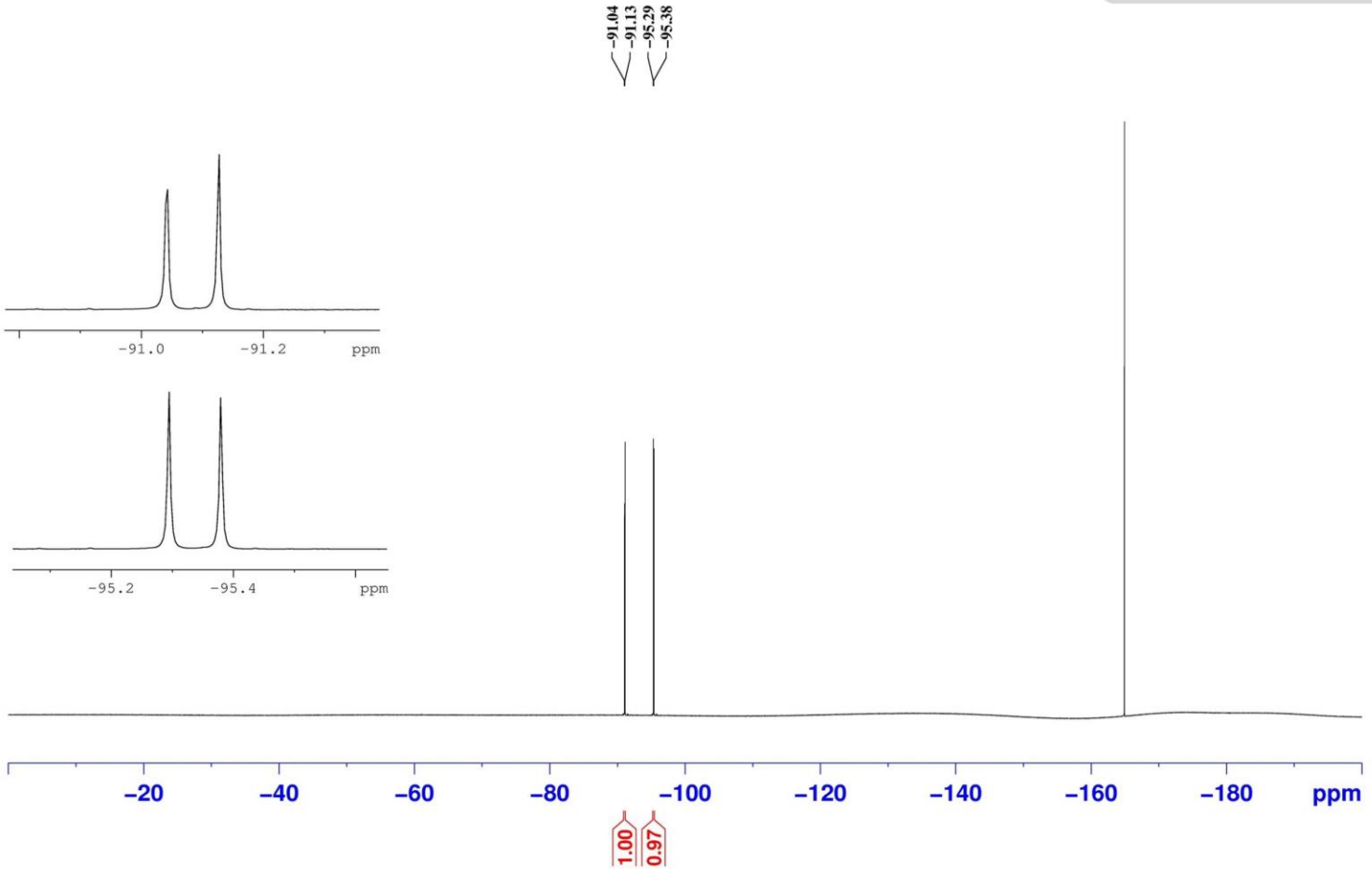




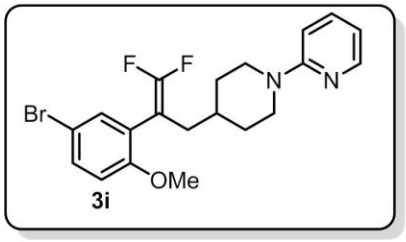
tert-butyl 4-(2-(5-bromo-2-methoxyphenyl)-3,3-difluoroallyl)piperidine-1-carboxylate
471 MHz, CDCl3

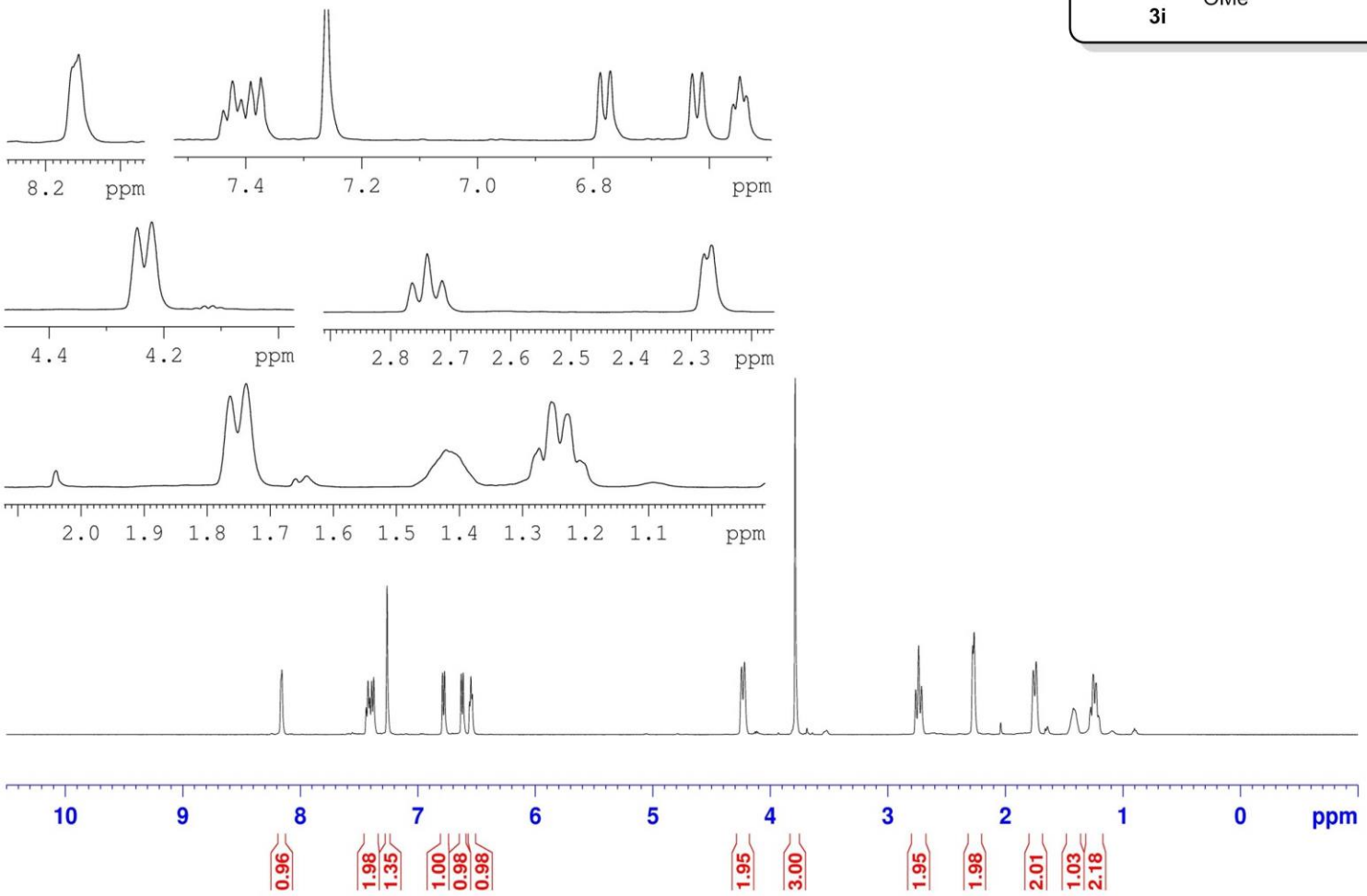


3h

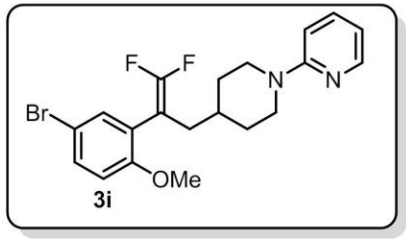


2–(4–(2–(5–bromo–2–methoxyphenyl)–3,3–difluoroallyl)piperidin–1–yl)pyridine
500 MHz, CDCl3

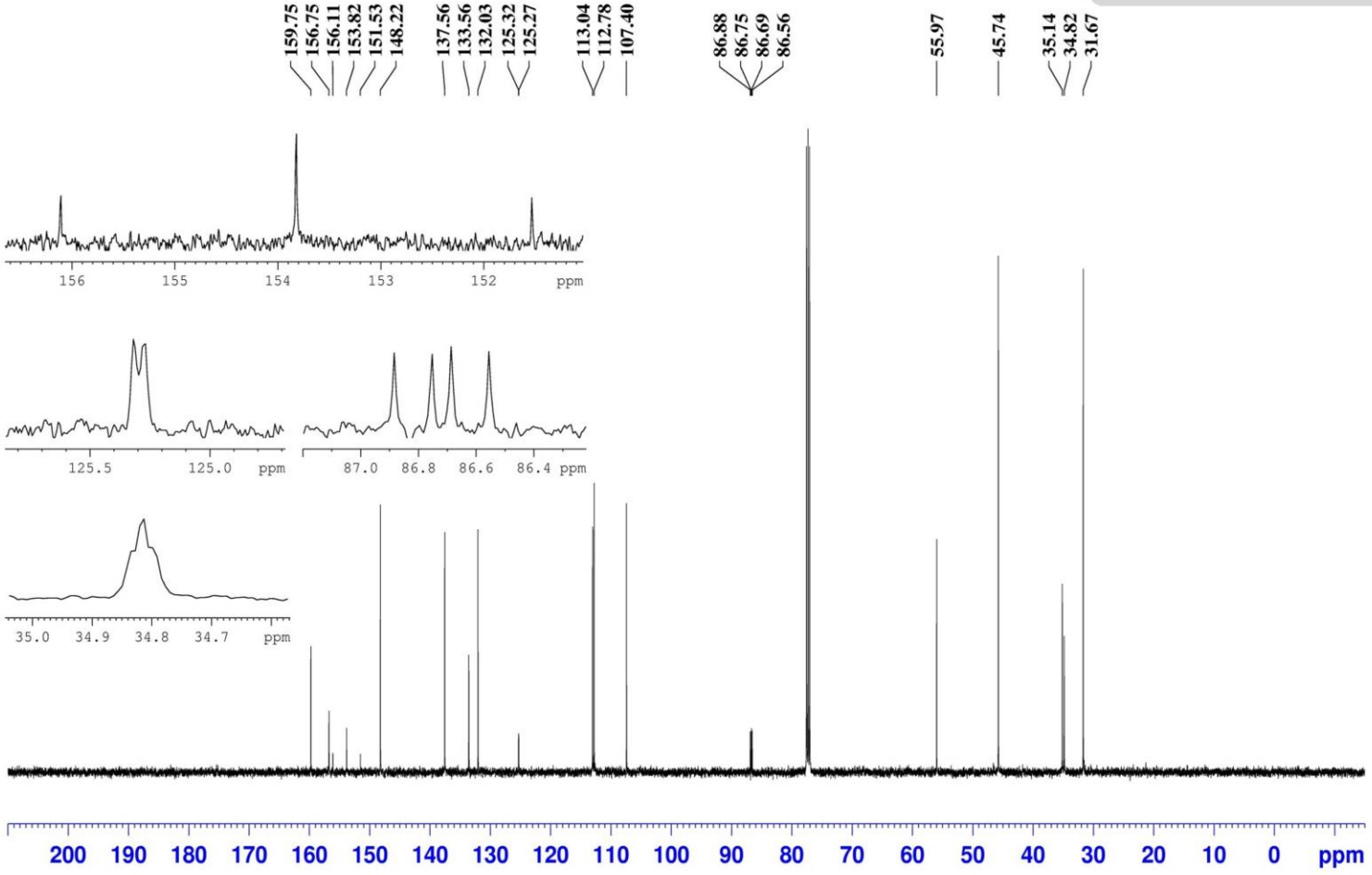




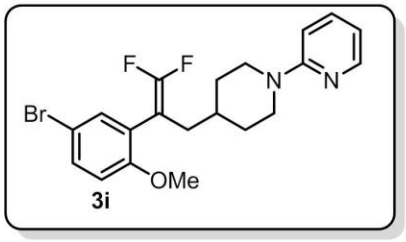
2–(4–(2–(5–bromo–2–methoxyphenyl)–3,3–difluoroallyl)piperidin–1–yl)pyridine
125 MHz, CDCl3

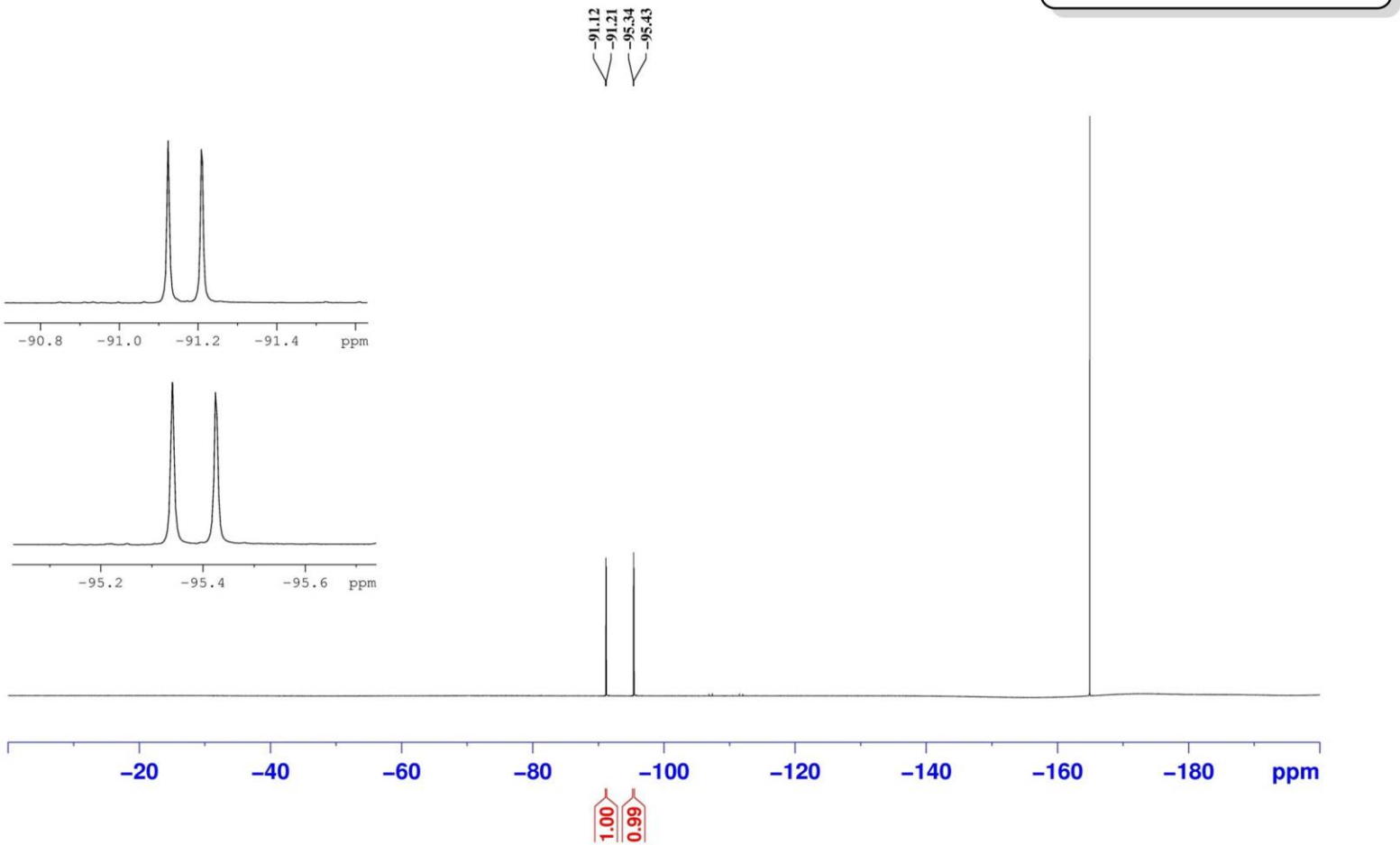


3i

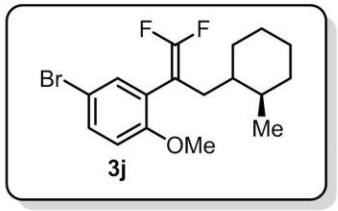


2–(4–(2–(5–bromo–2–methoxyphenyl)–3,3–difluoroallyl)piperidin–1–yl)pyridine
471 MHz, CDCl3

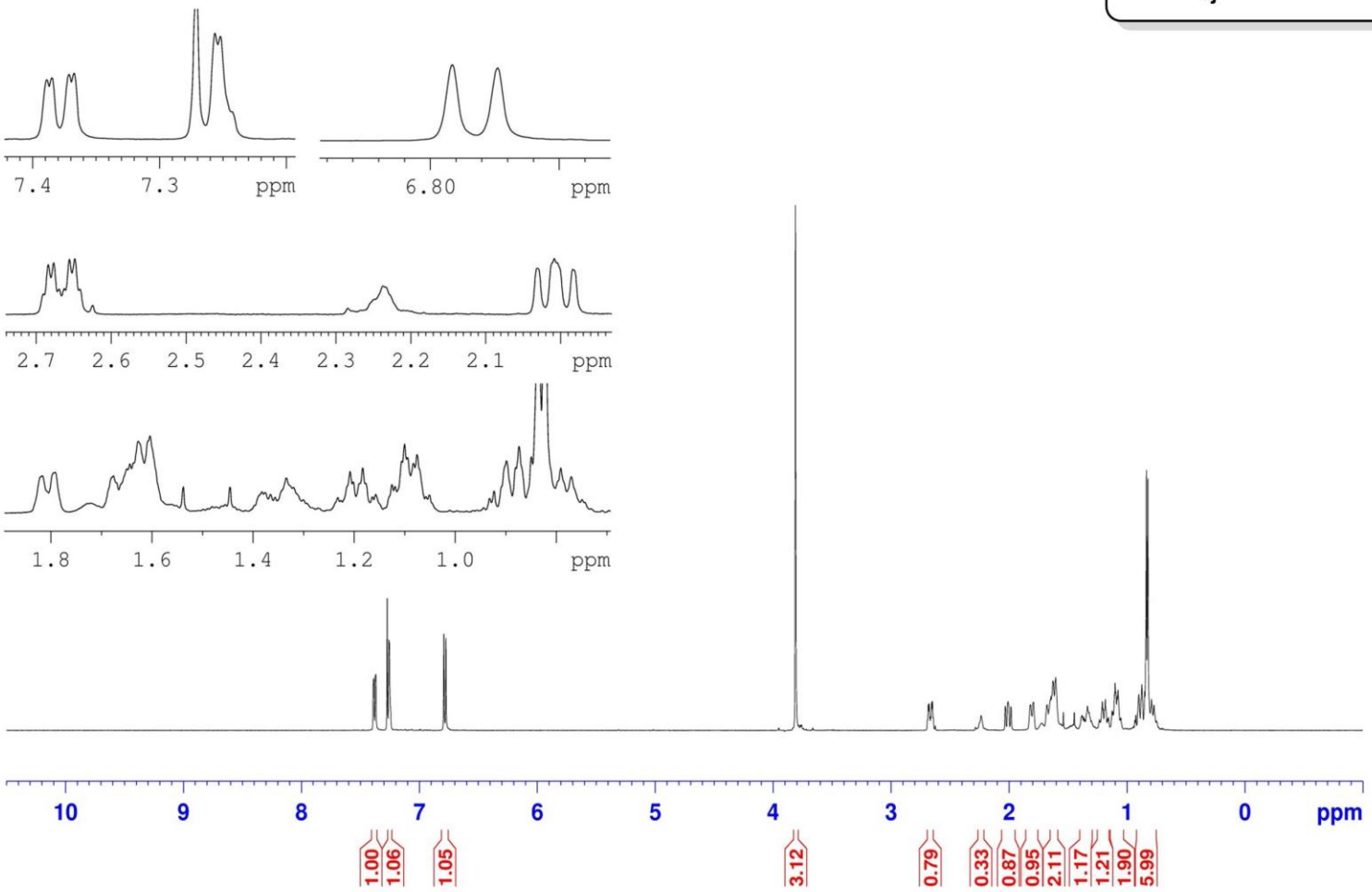




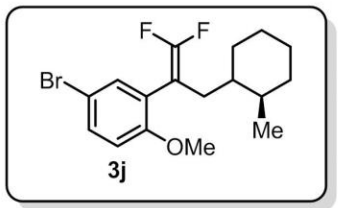
4-bromo-2-(1,1-difluoro-3-(-2-methylcyclohexyl)prop-1-en-2-yl)-1-methoxybenzene
500 MHz, CDCl3



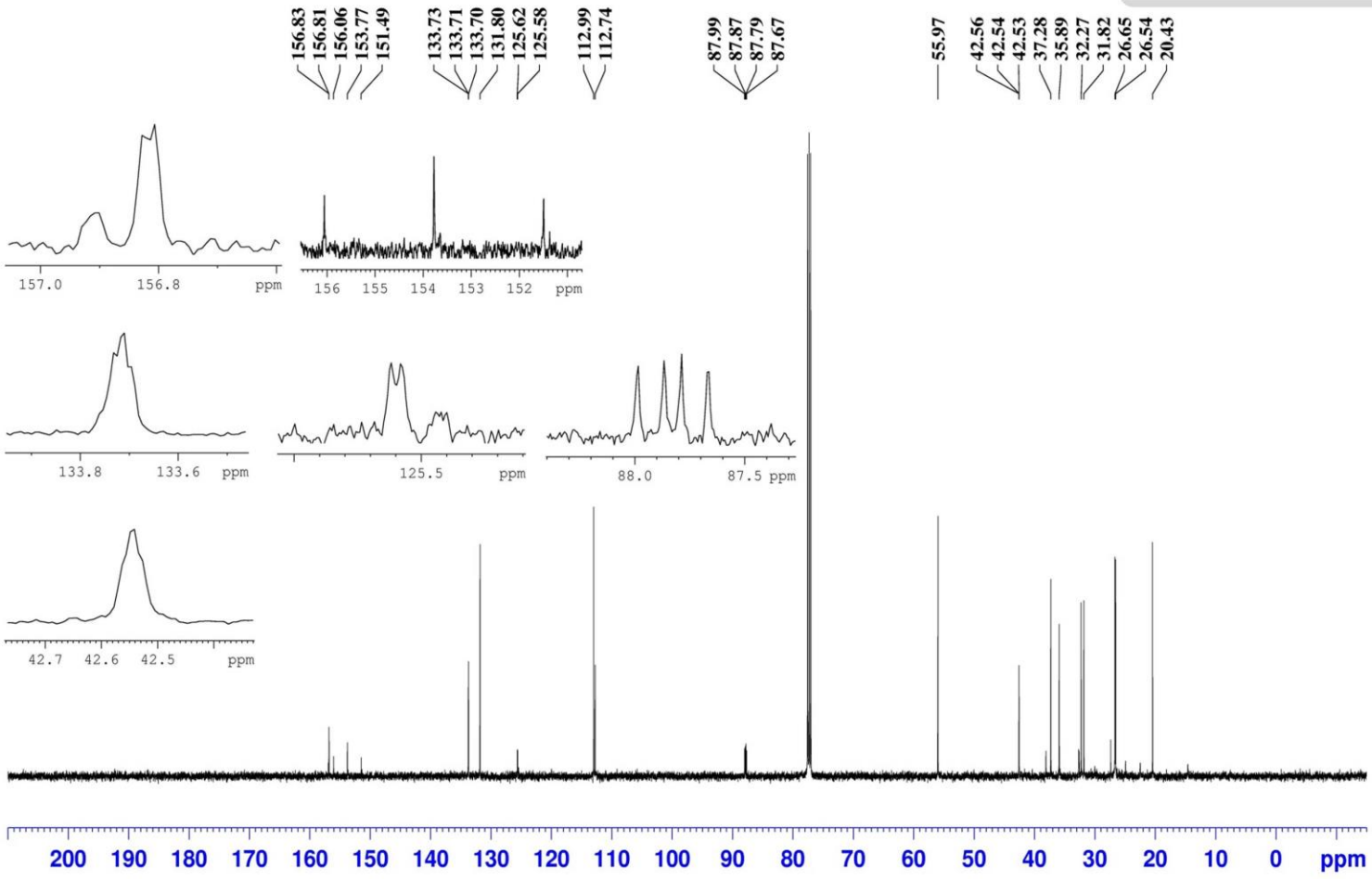
3j



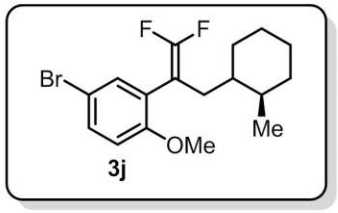
4–bromo–2–(1,1–difluoro–3–(–2–methylcyclohexyl)prop–1–en–2–yl)–1–methoxybenzene
125 MHz, CDCl3



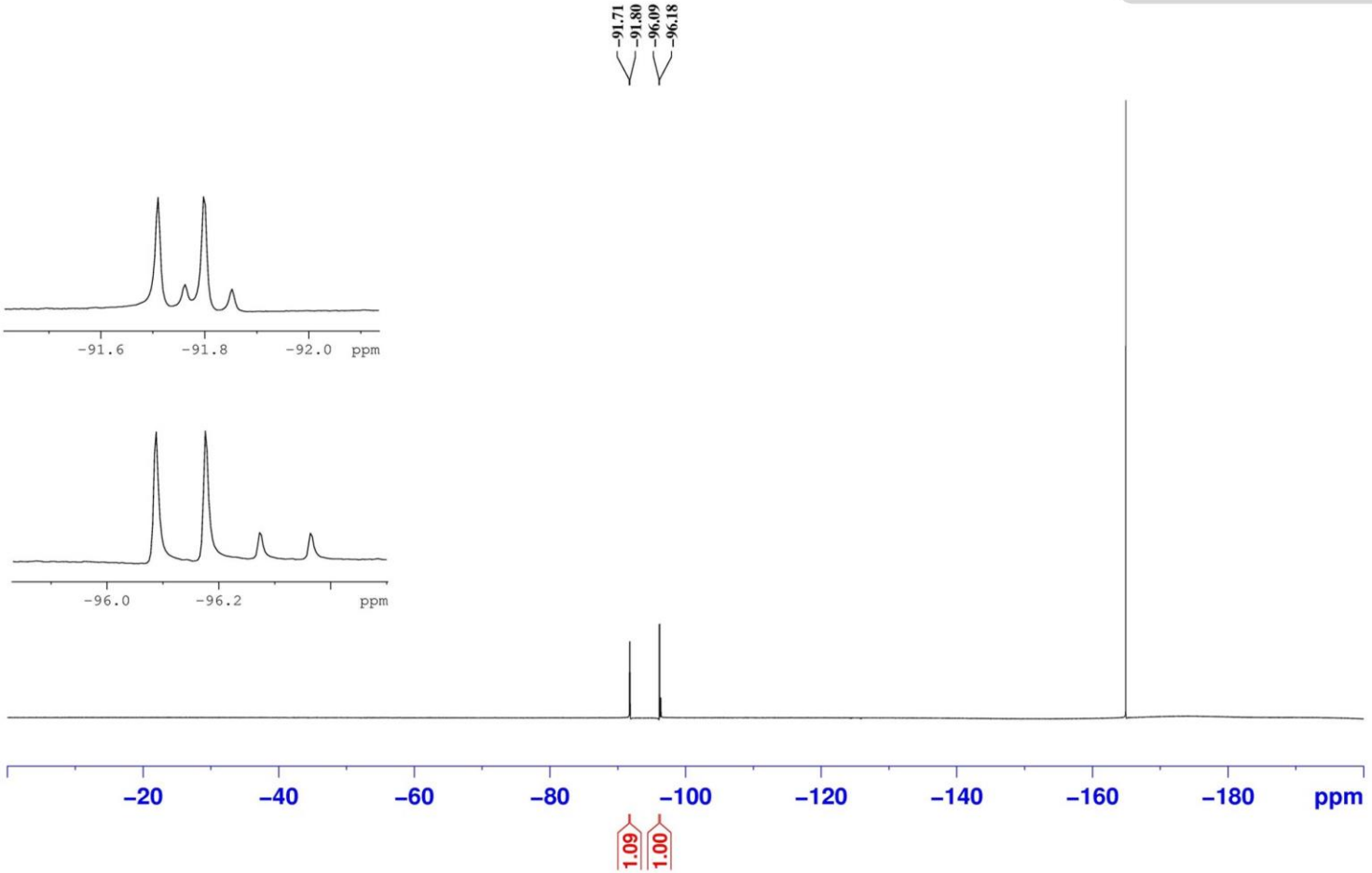
3j



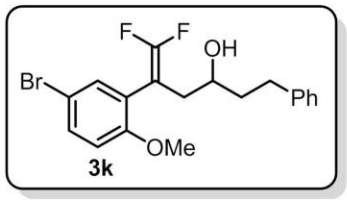
4–bromo–2–(1,1–difluoro–3–(–2–methylcyclohexyl)prop–1–en–2–yl)–1–methoxybenzene
471 MHz, CDCl3

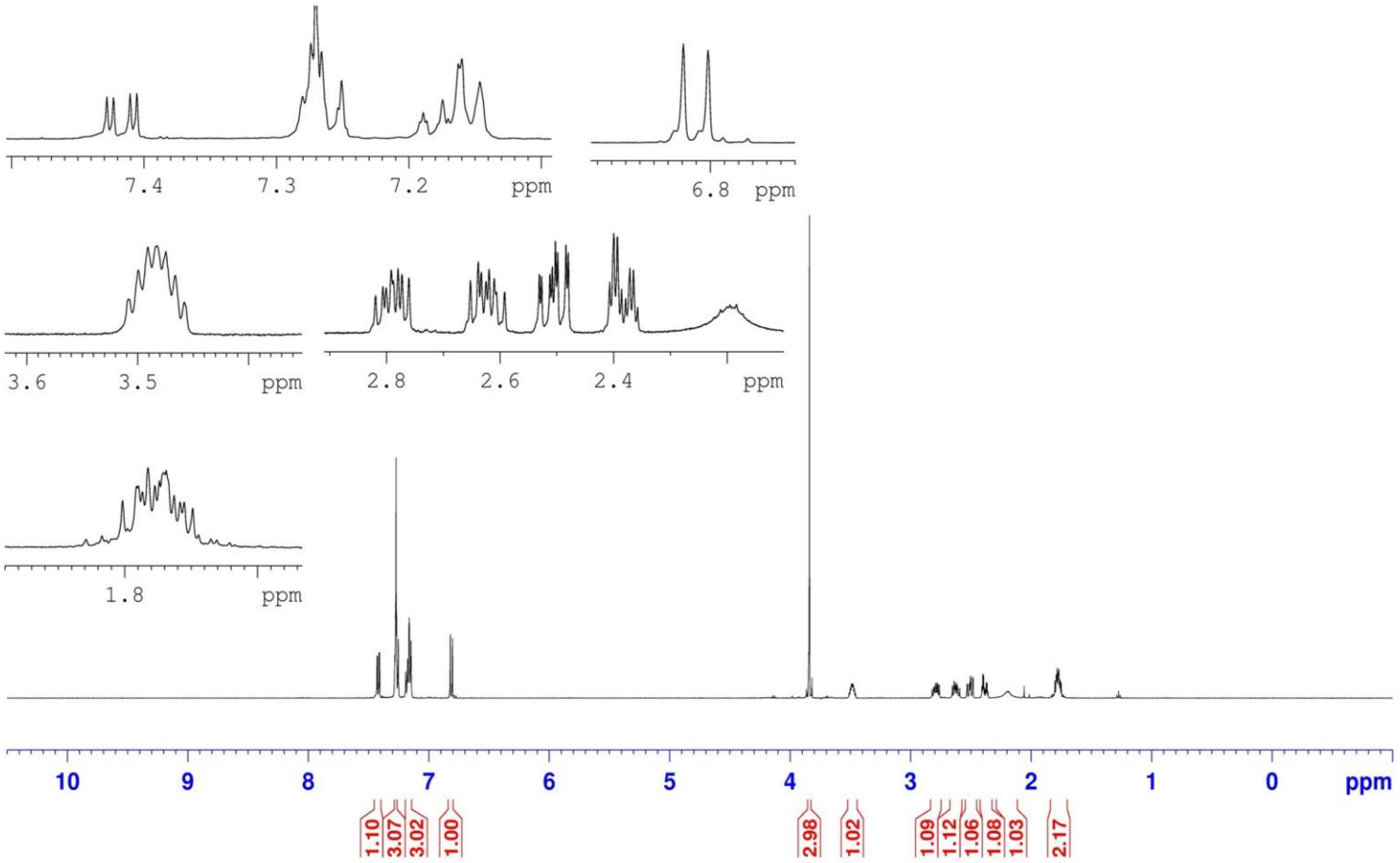


3j

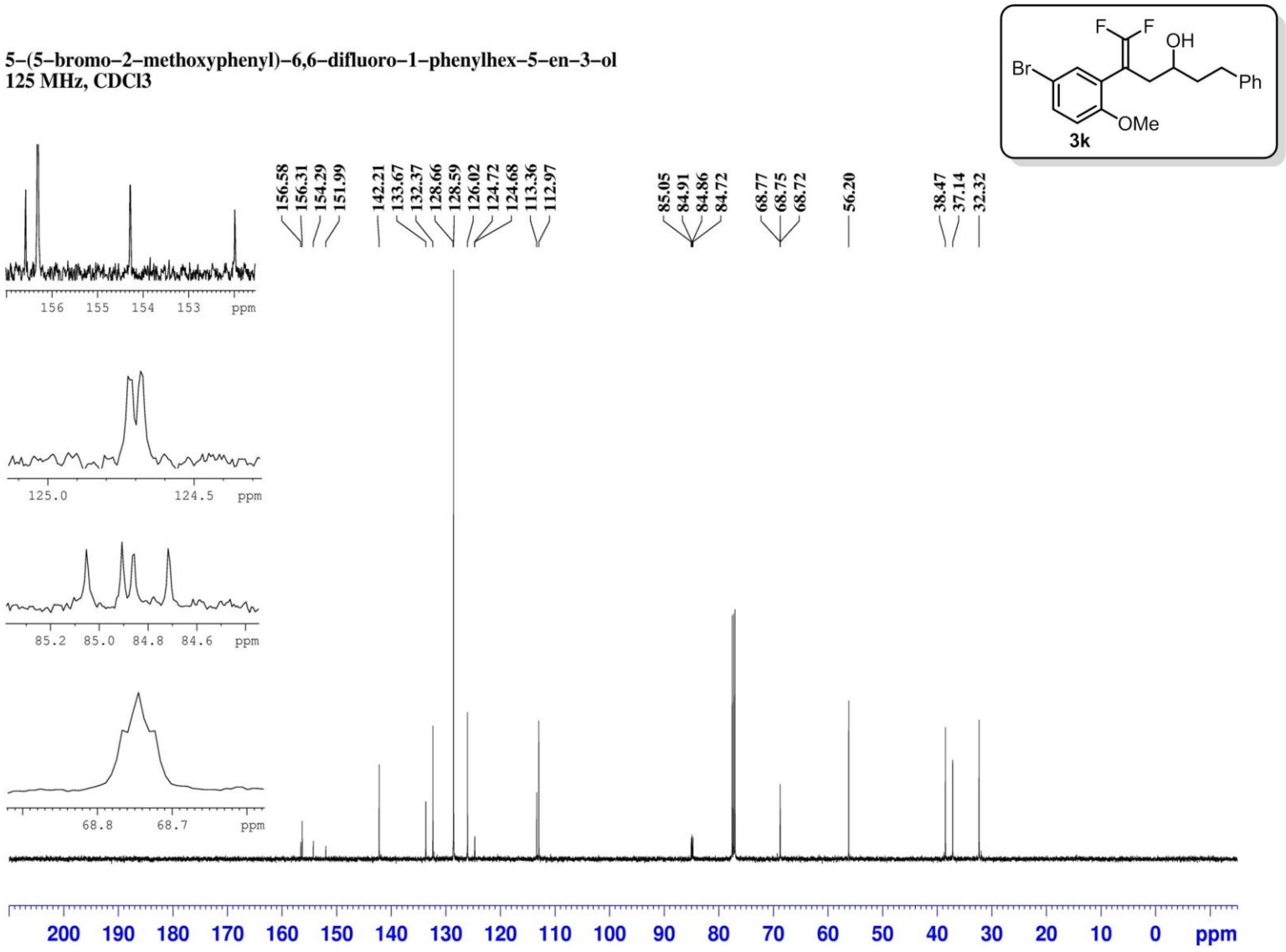


5–(5–bromo–2–methoxyphenyl)–6,6–difluoro–1–phenylhex–5–en–3–ol
500 MHz, CDCl3

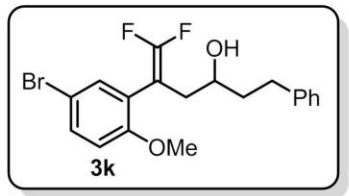




5–(5–bromo–2–methoxyphenyl)–6,6–difluoro–1–phenylhex–5–en–3–ol
125 MHz, CDCl3



5–(5–bromo–2–methoxyphenyl)–6,6–difluoro–1–phenylhex–5–en–3–ol
471 MHz, CDCl3



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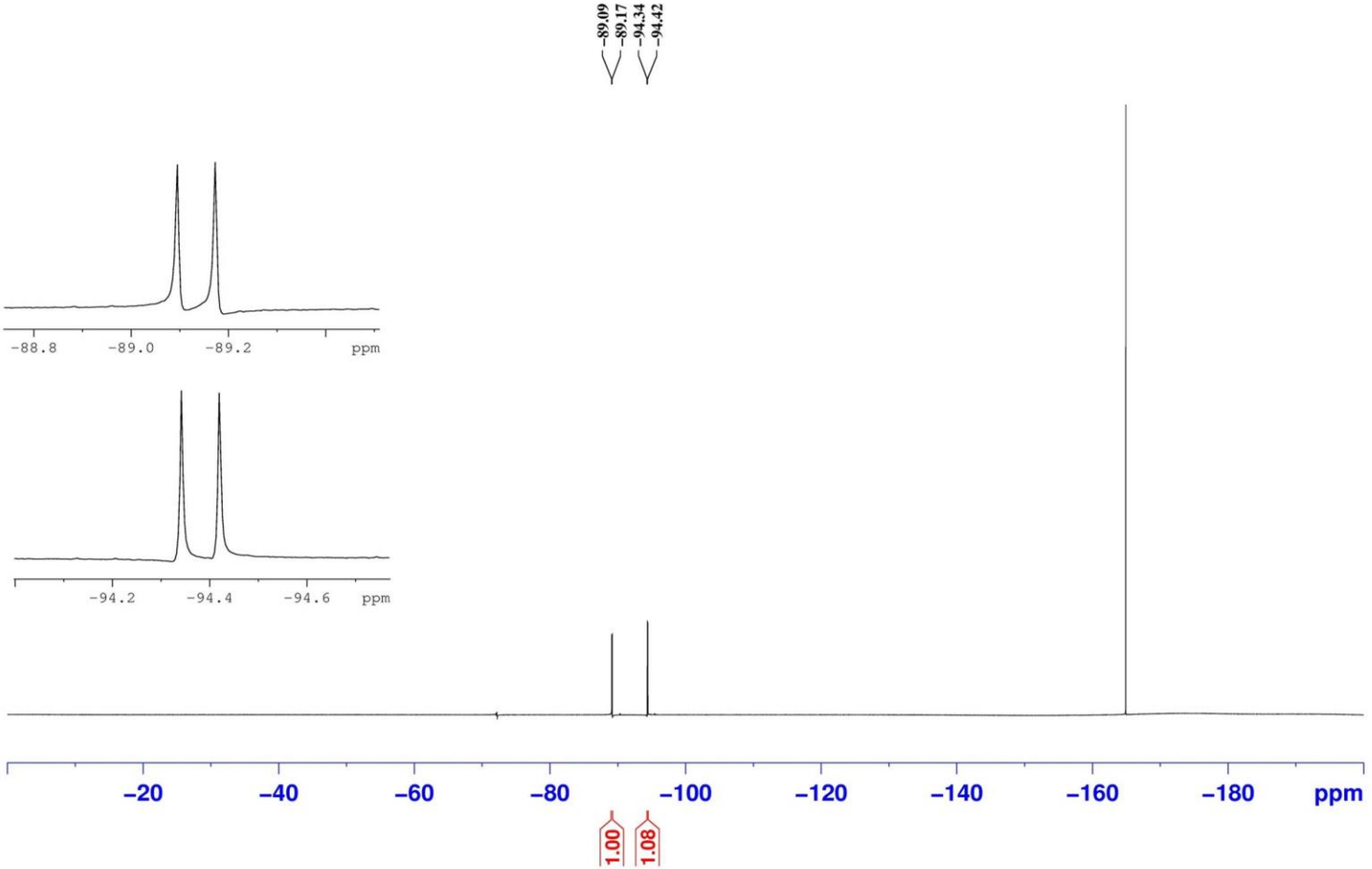
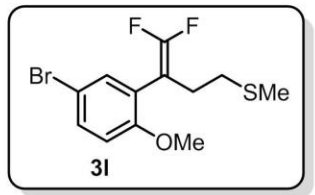


(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)(methyl)sulfane
500 MHz, CDCl3



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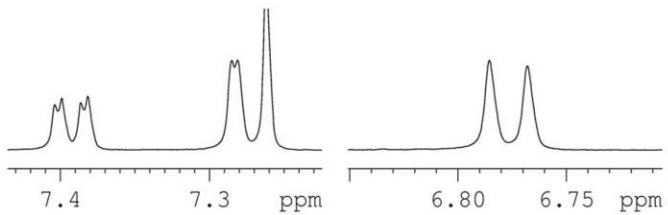
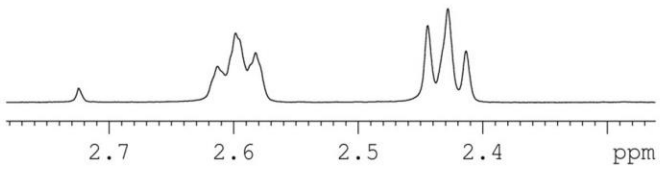
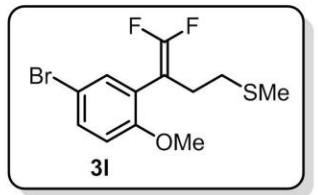




(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)(methyl)sulfane
125 MHz, CDCl3



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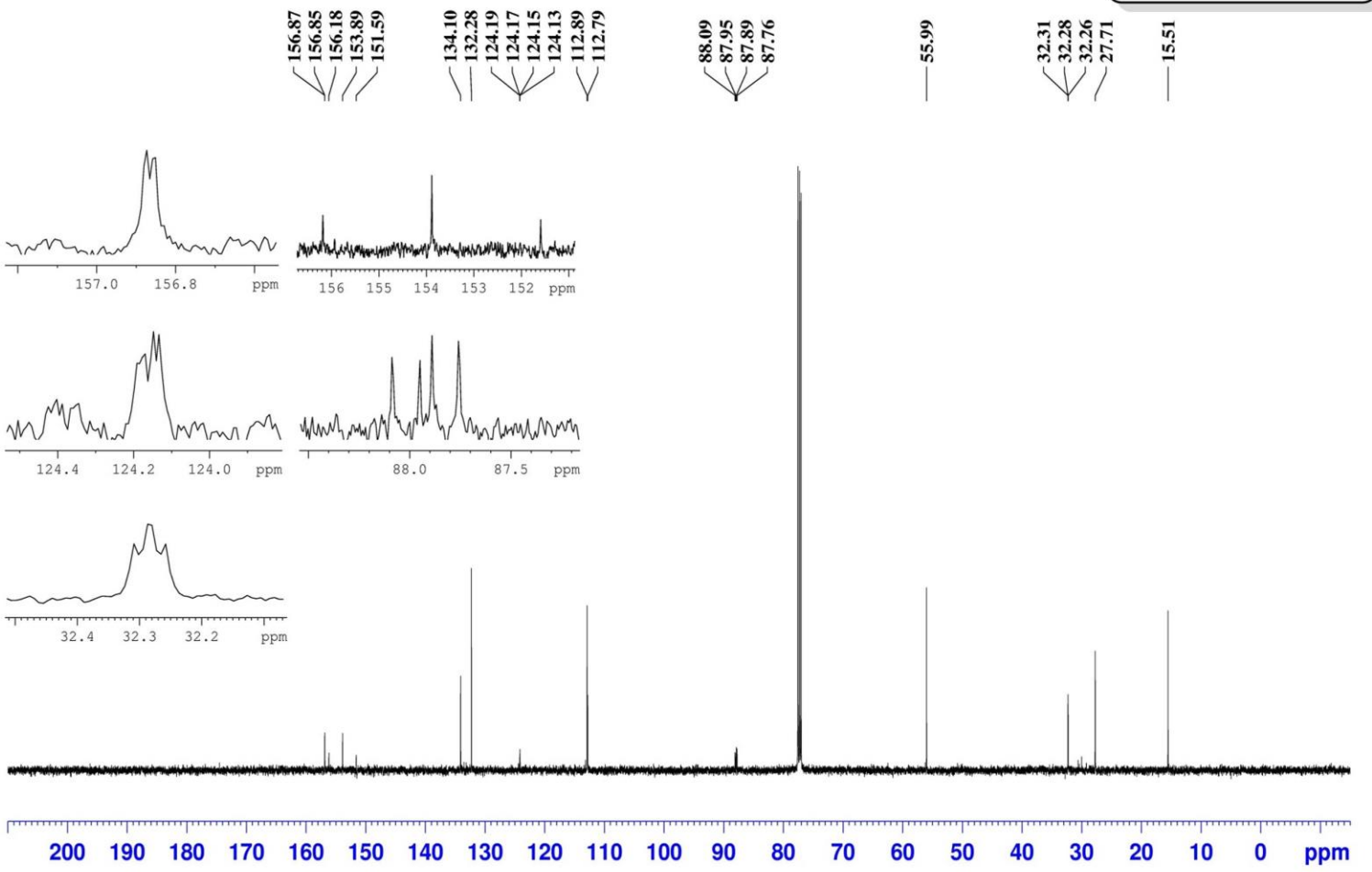
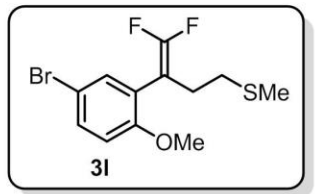


(3–(5–bromo–2–methoxyphenyl)–4,4–difluorobut–3–en–1–yl)(methyl)sulfane
471 MHz, CDCl3



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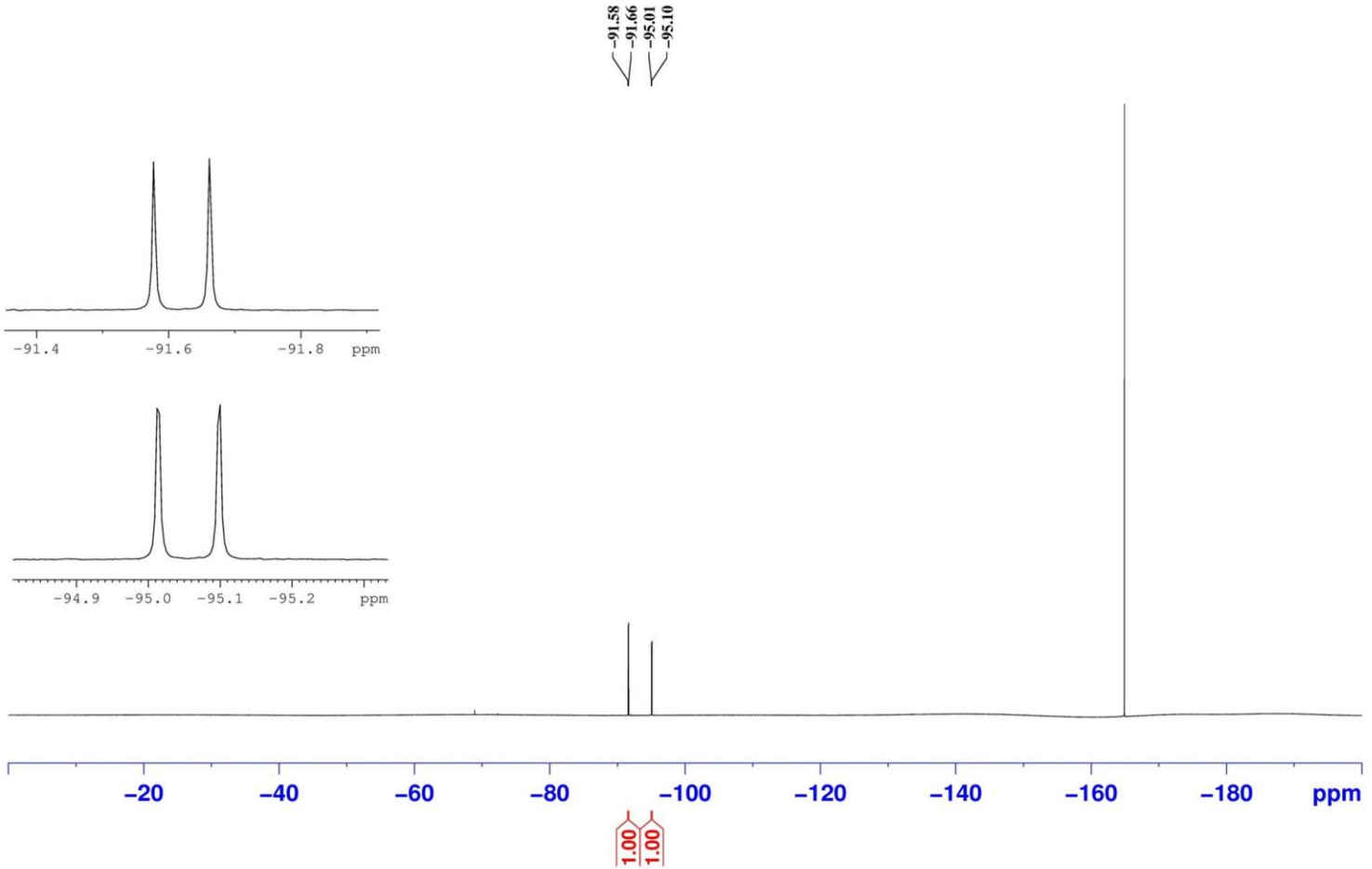
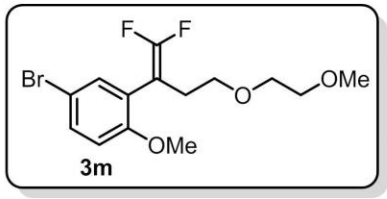
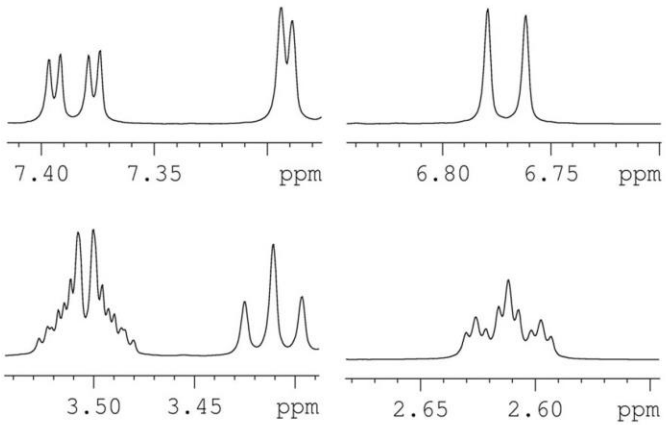
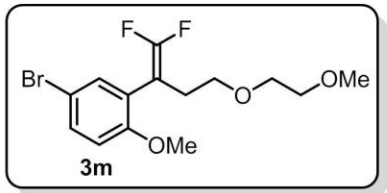


4–bromo–2–(1,1–difluoro–4–(2–methoxyethoxy)but–1–en–2–yl)–1–methoxybenzene
500 MHz, CDCl3





4–bromo–2–(1,1–difluoro–4–(2–methoxyethoxy)but–1–en–2–yl)–1–methoxybenzene
125 MHz, CDCl3



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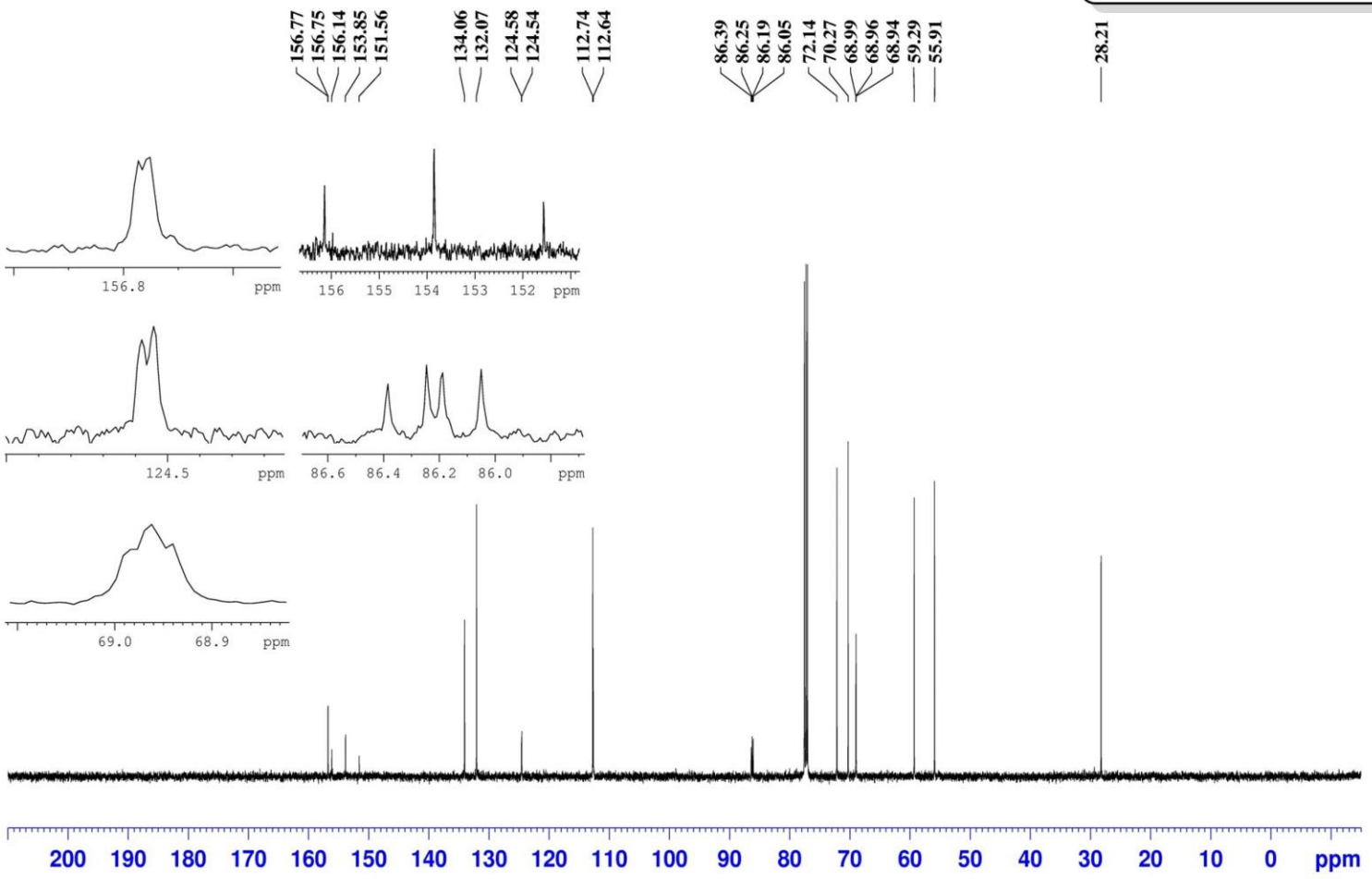
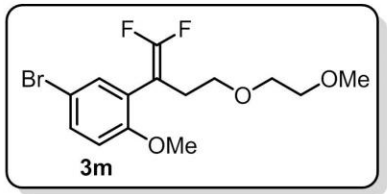
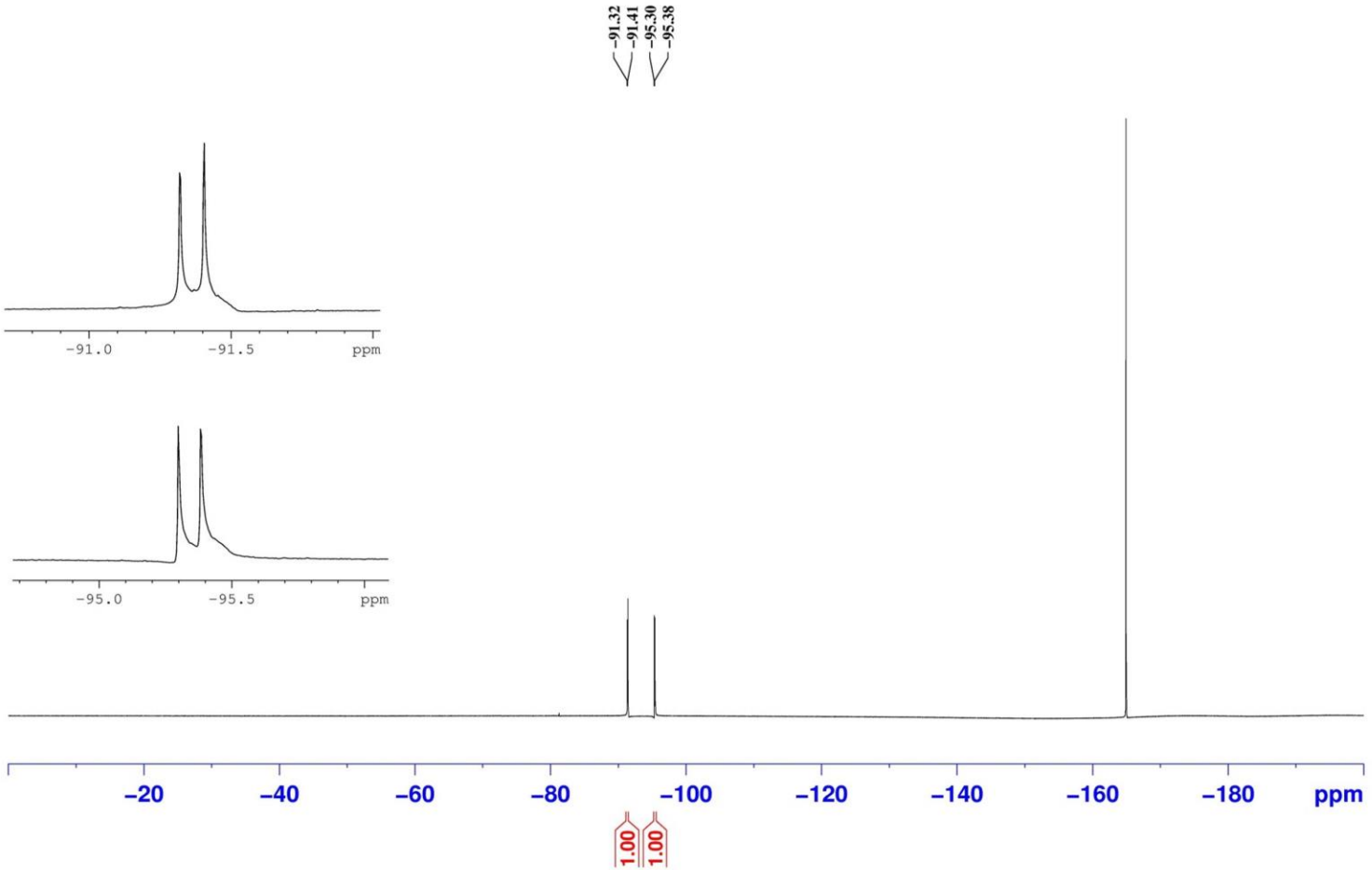


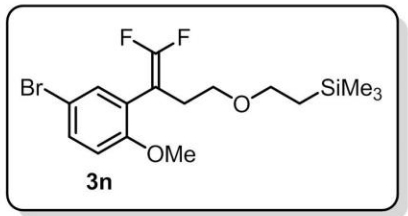
4–bromo–2–(1,1–difluoro–4–(2–methoxyethoxy)but–1–en–2–yl)–1–methoxybenzene
471 MHz, CDCl3

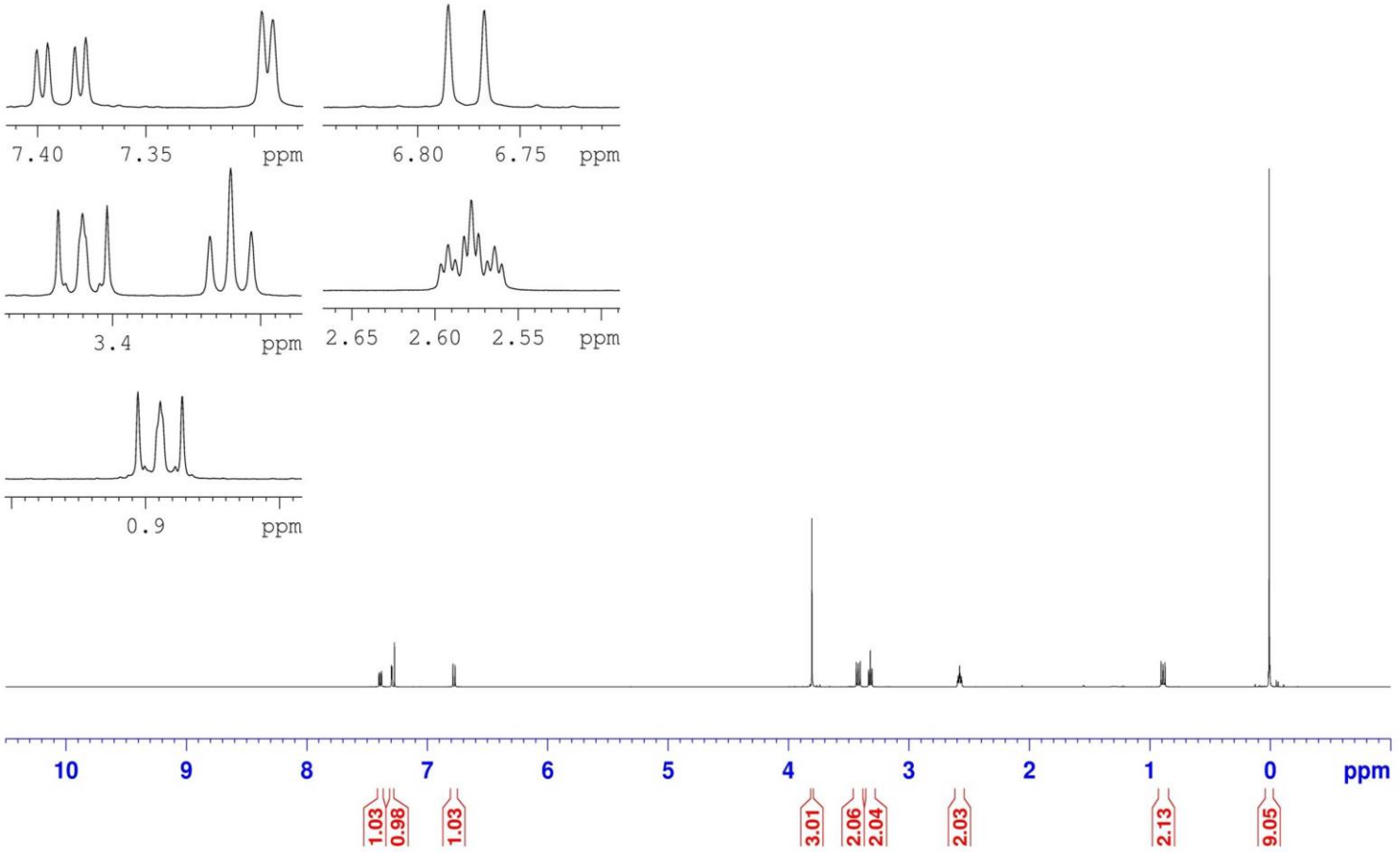


3m

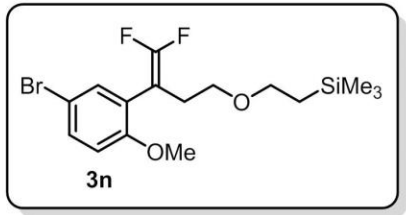


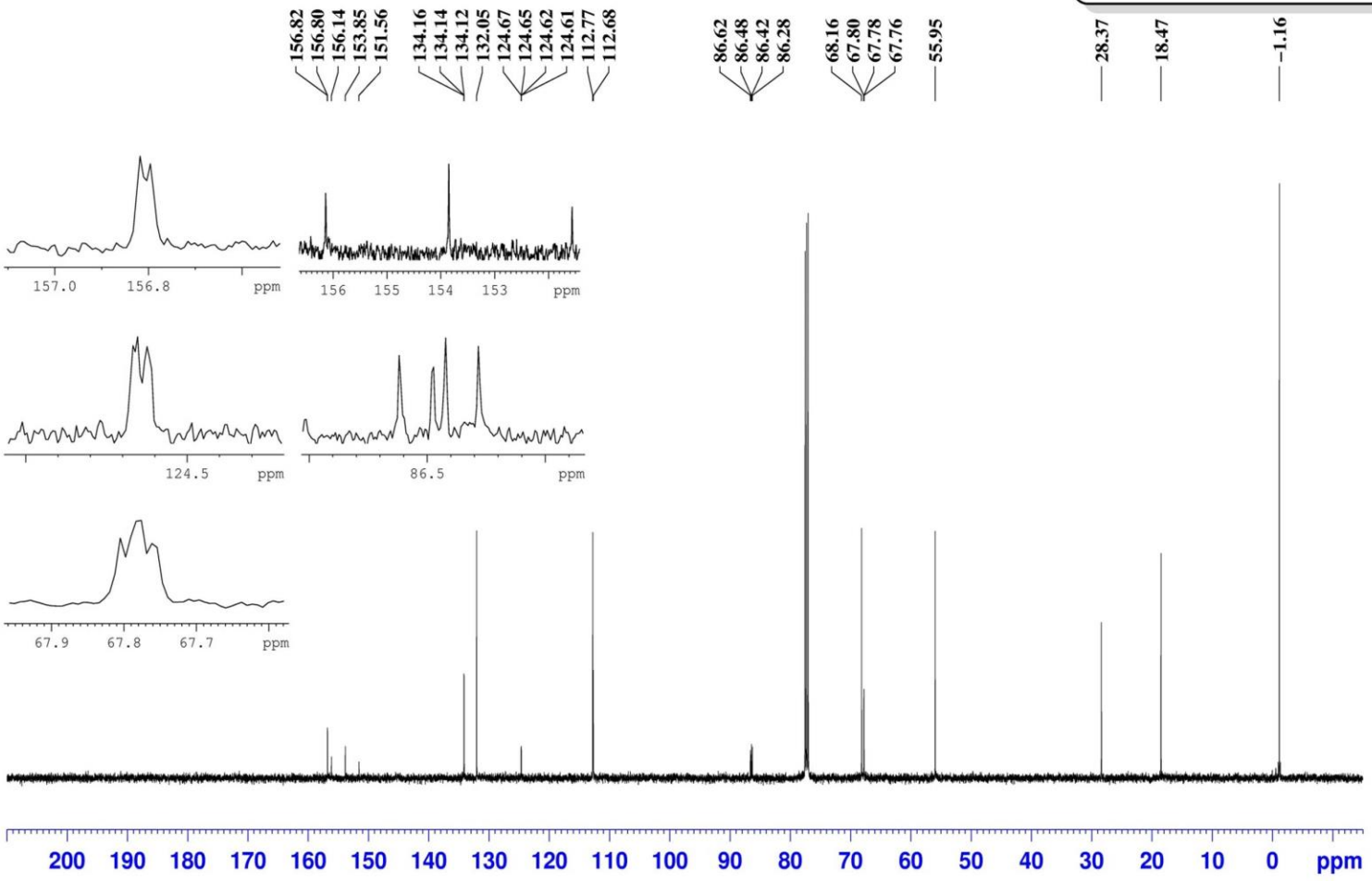
(2-((3-(5-bromo-2-methoxyphenyl)-4,4-difluorobut-3-en-1-yl)oxy)ethyl)trimethylsilane
500 MHz, CDCl3



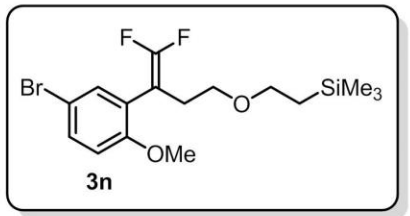


(2-((3-(5-bromo-2-methoxyphenyl)-4,4-difluorobut-3-en-1-yl)oxy)ethyl)trimethylsilane
125 MHz, CDCl3





(2-((3-(5-bromo-2-methoxyphenyl)-4,4-difluorobut-3-en-1-yl)oxy)ethyl)trimethylsilane
471 MHz, CDCl3



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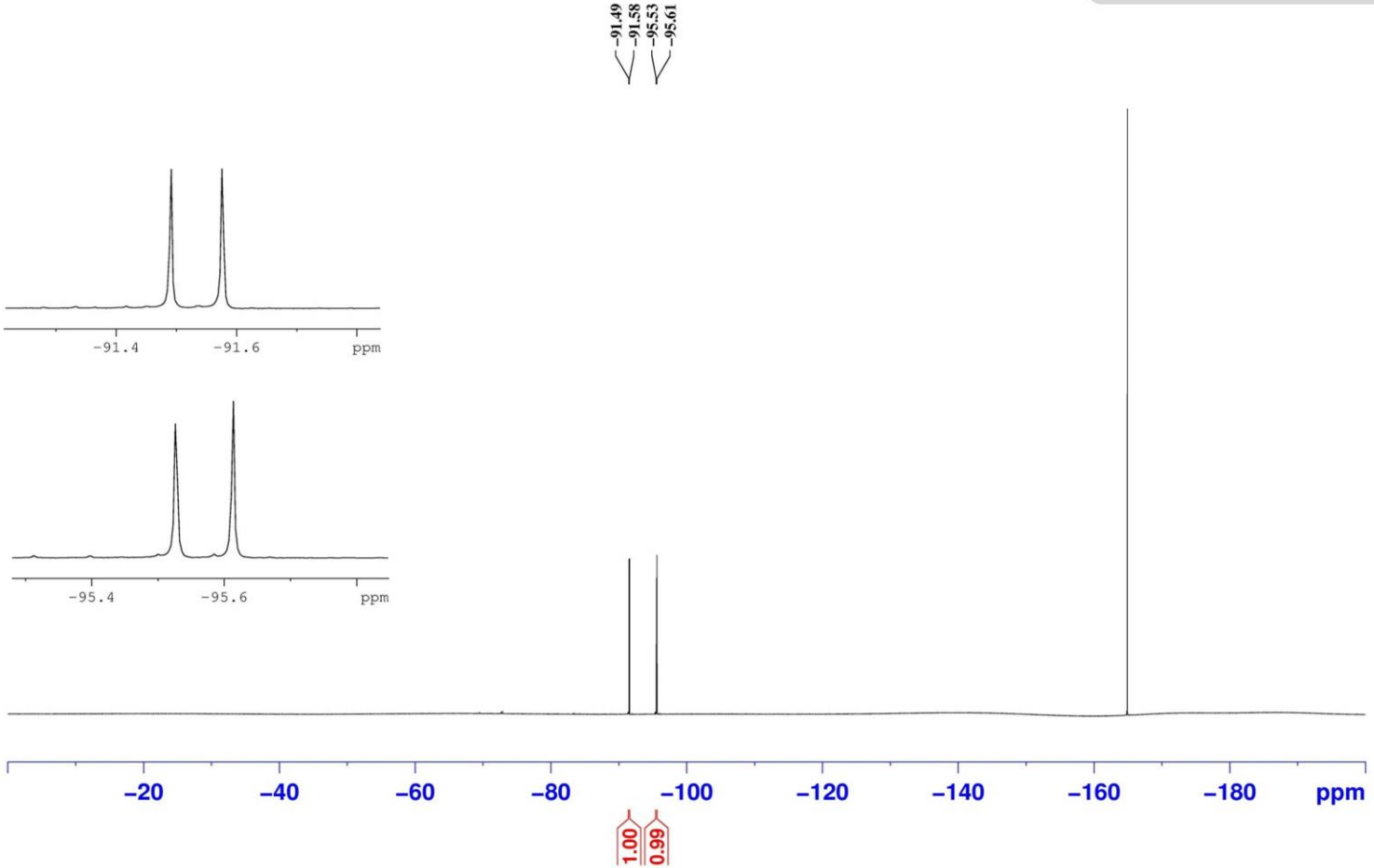
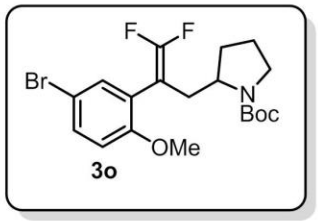
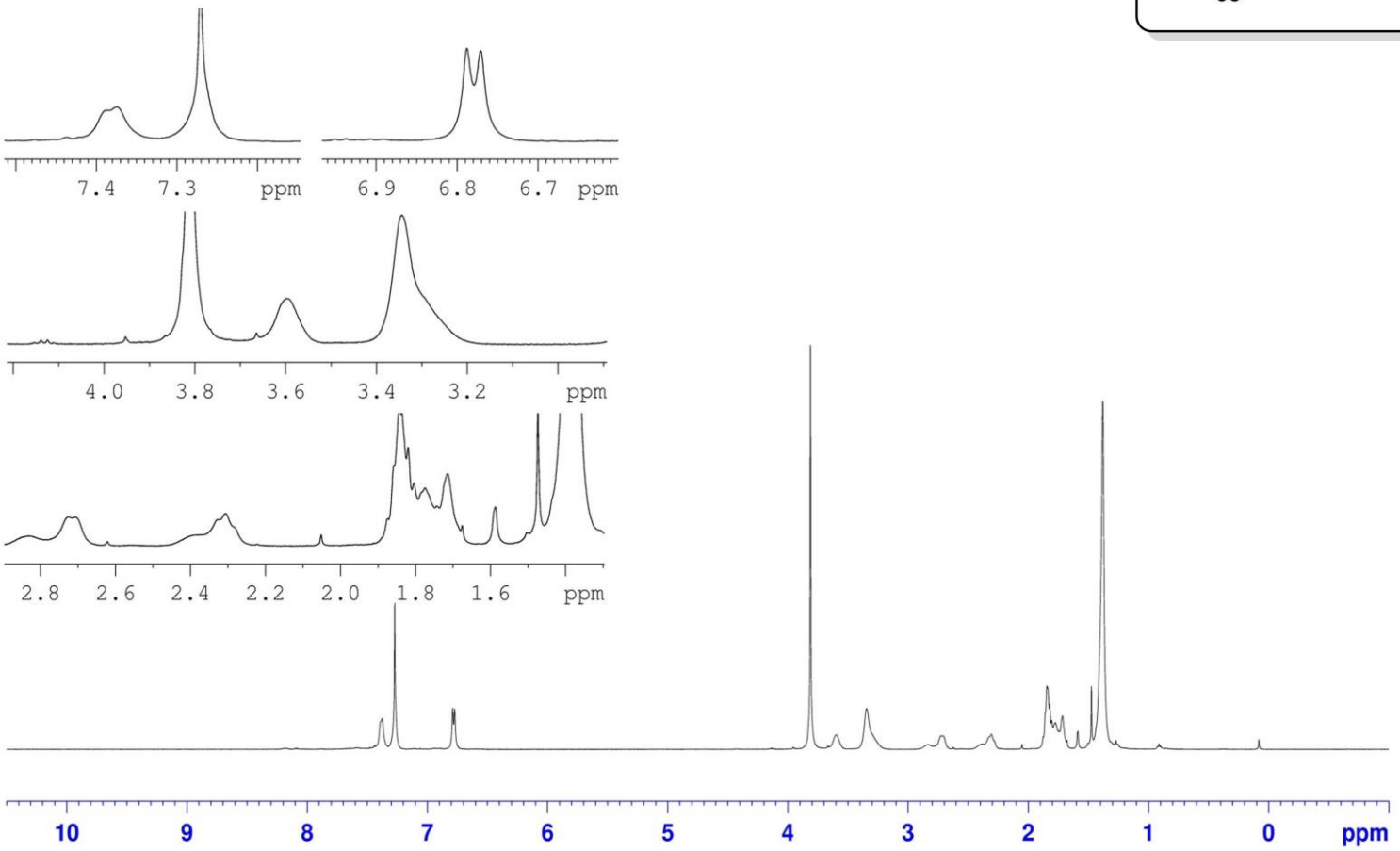
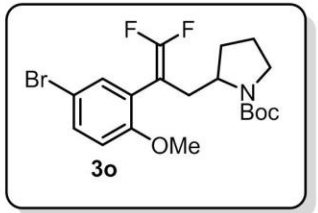


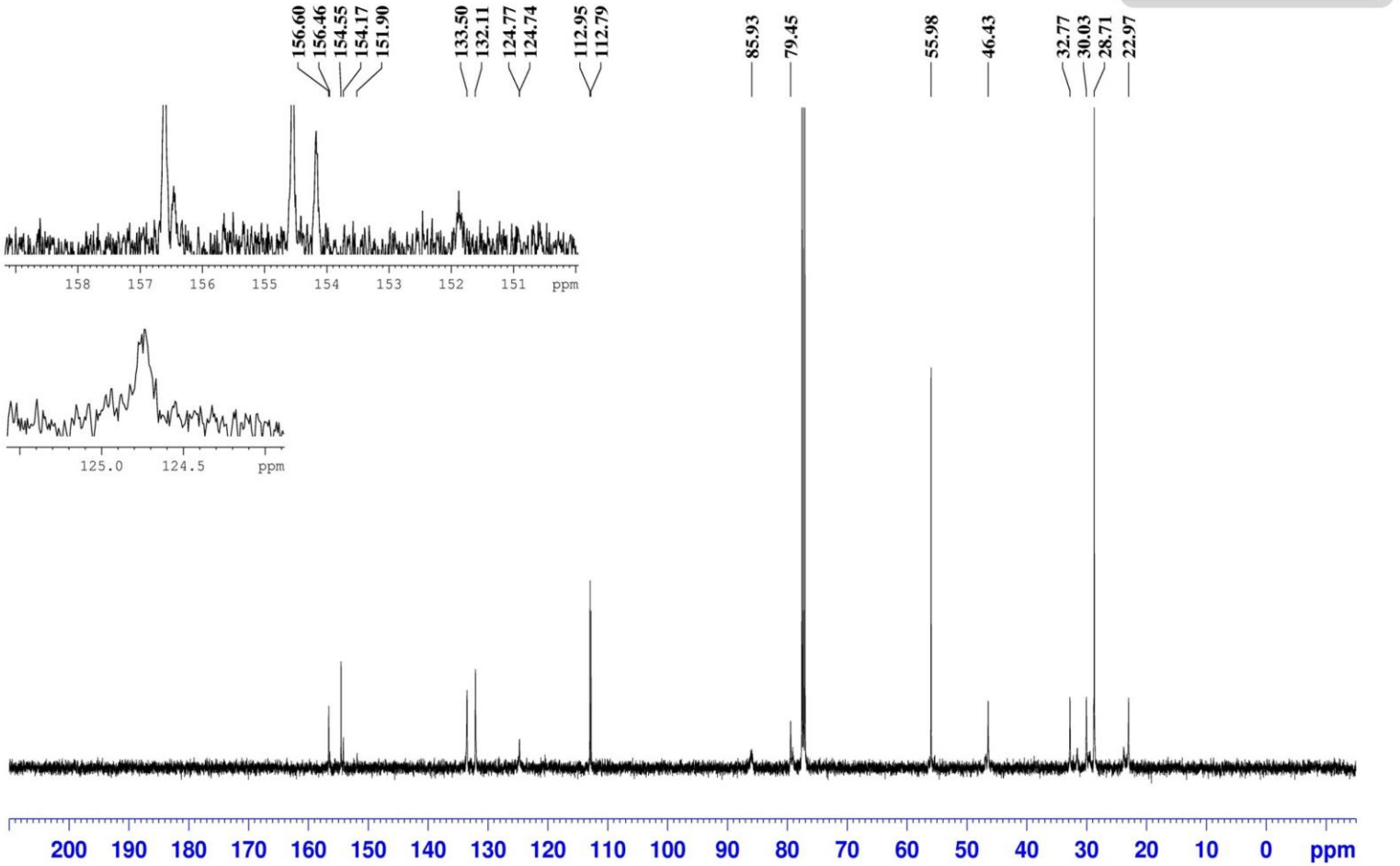
(tert−butyl 2−(2−(5−bromo−2−methoxyphenyl)−3,3−difluoroallyl)pyrrolidine−1−carboxylate
500 MHz, CDCl3



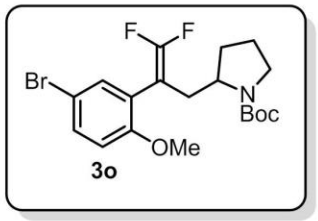


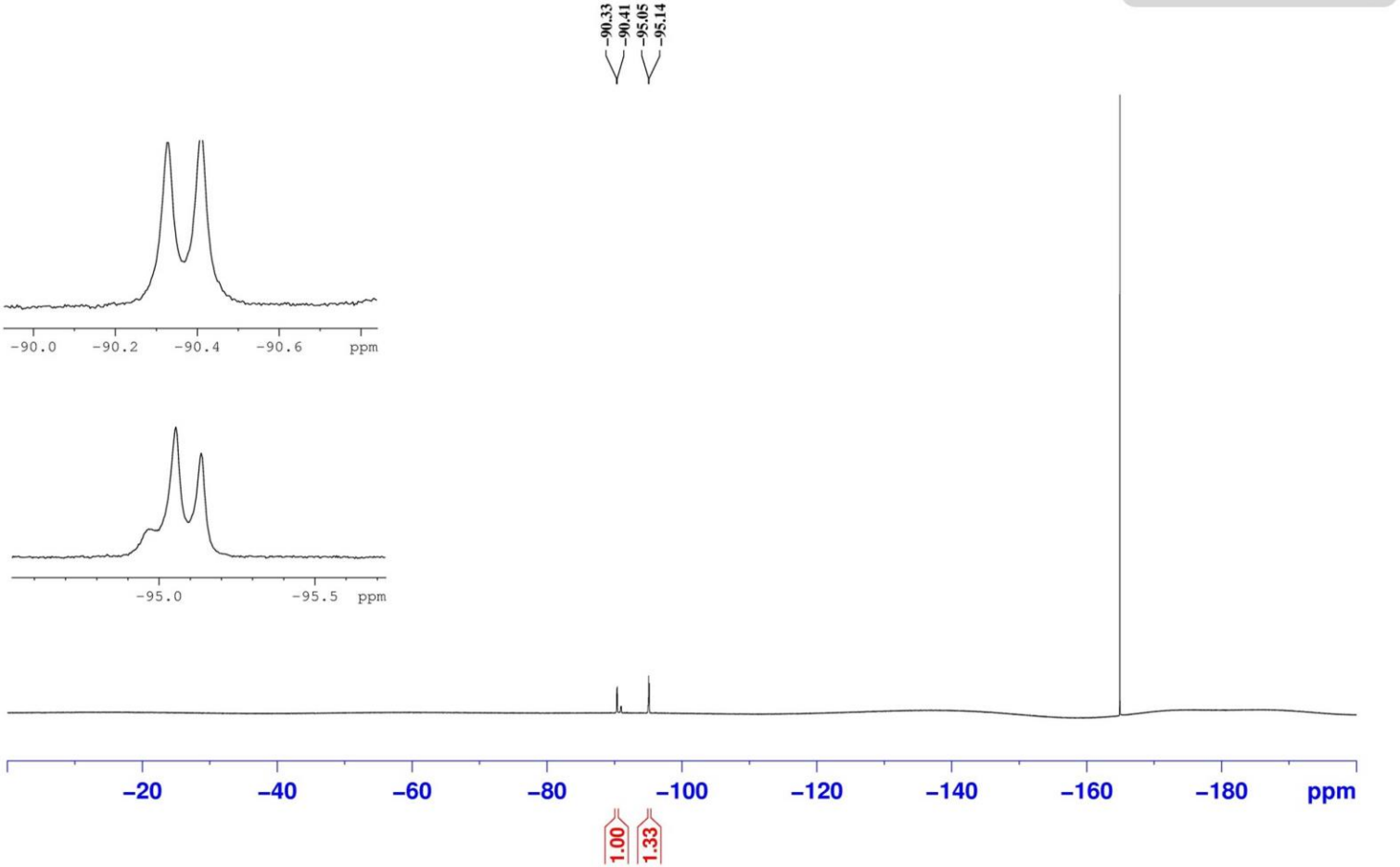
tert−butyl 4−(5−(1,1−difluoro−4−methylpent−1−en−2−yl)pyridin−2−yl)piperazine−1−carboxylate
125 MHz, CDCl3



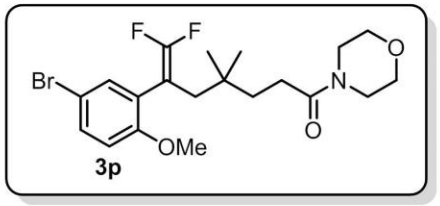


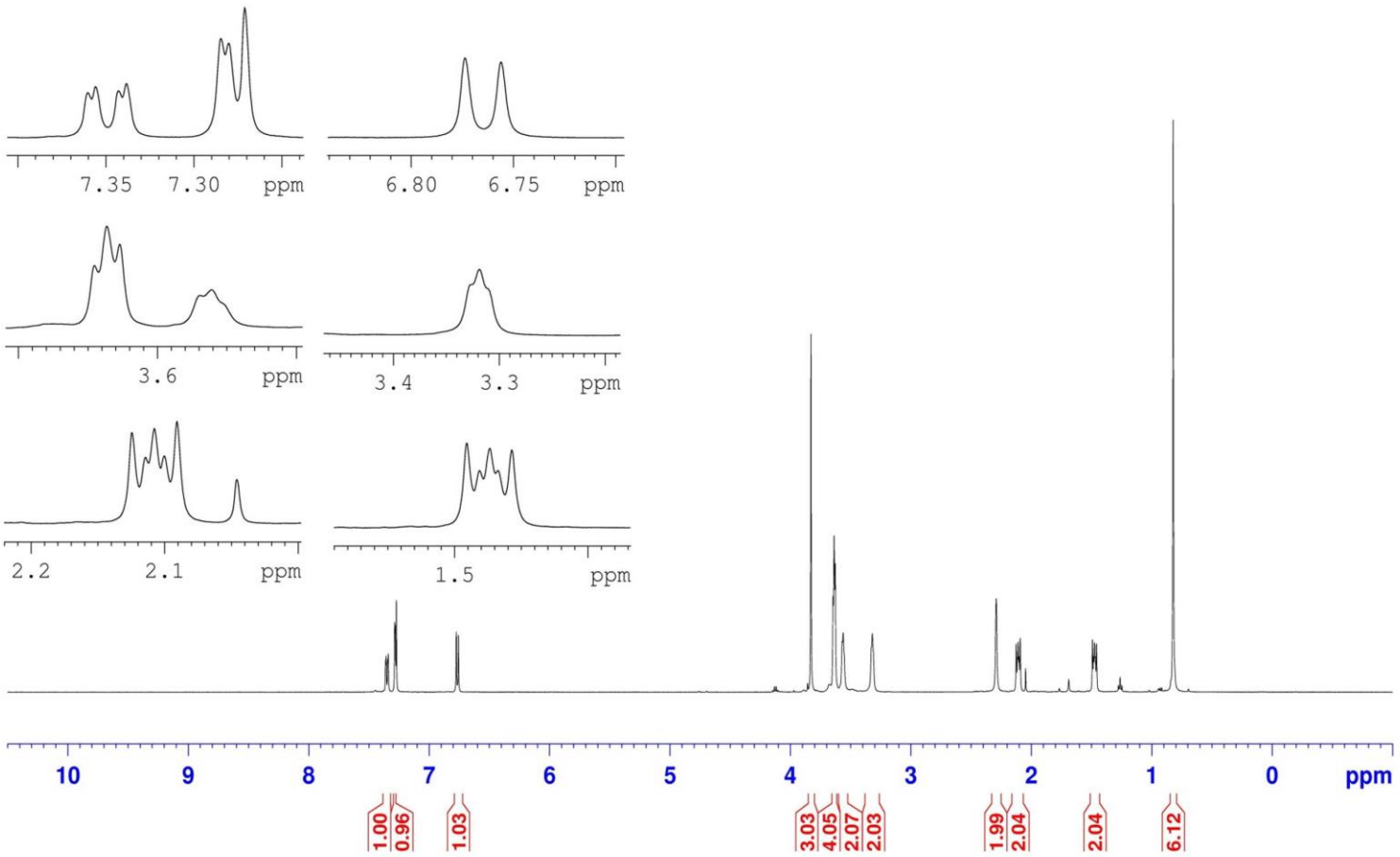
(tert–butyl 2–(2–(5–bromo–2–methoxyphenyl)–3,3–difluoroallyl)pyrrolidine–1–carboxylate
471 MHz, CDCl3



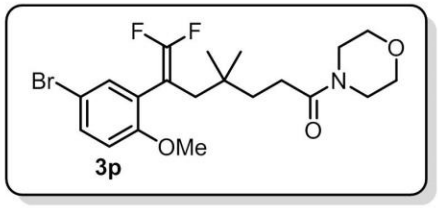


6–(5–bromo–2–methoxyphenyl)–7,7–difluoro–4,4–dimethyl–1–morpholinohept–6–en–1–one
500 MHz, CDCl3





6–(5–bromo–2–methoxyphenyl)–7,7–difluoro–4,4–dimethyl–1–morpholinohept–6–en–1–one
125 MHz, CDCl3



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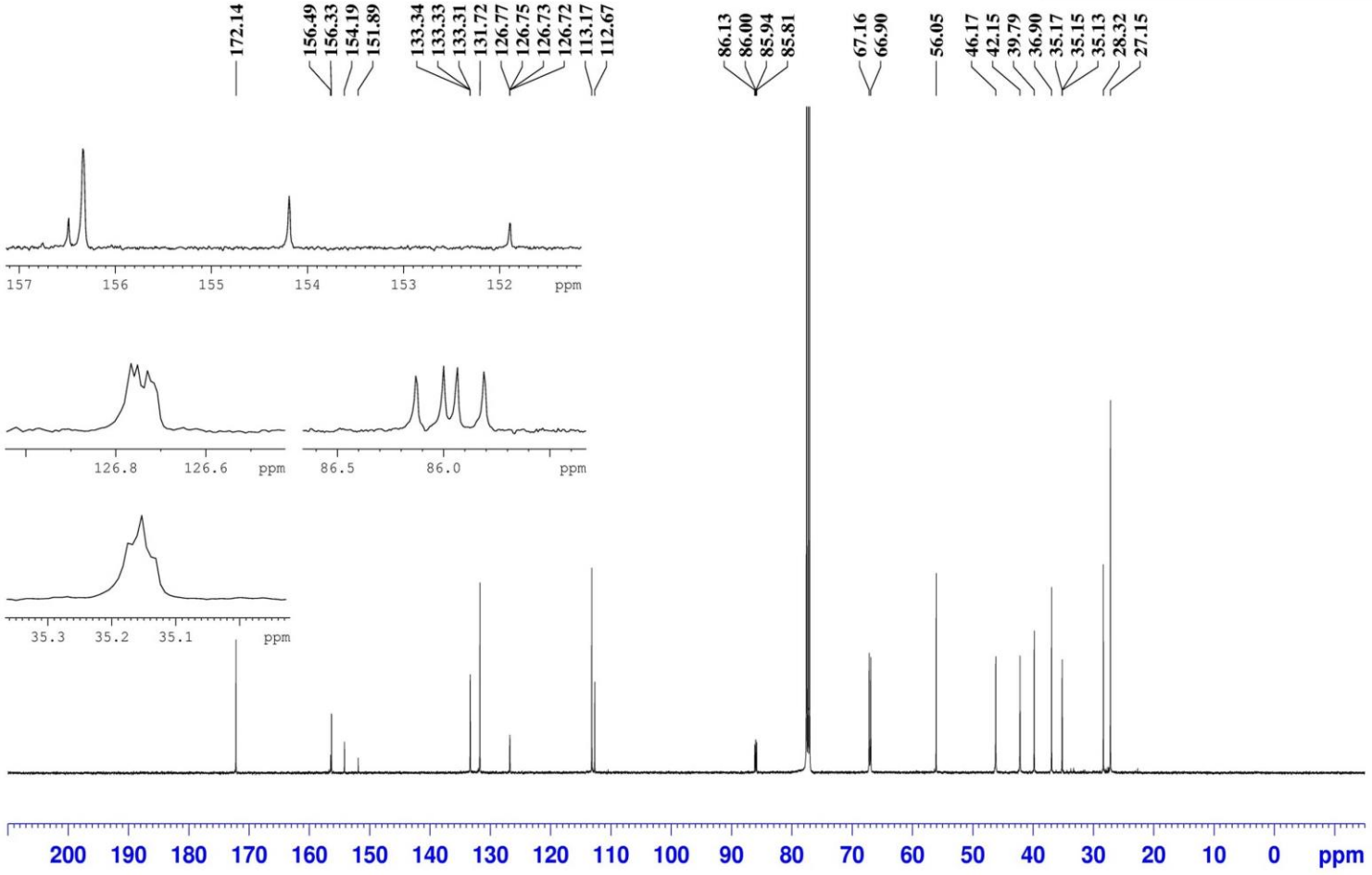
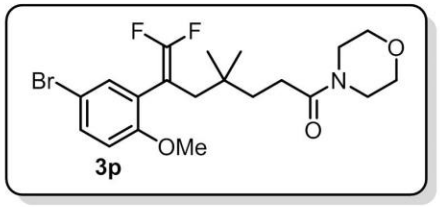


6–(5–bromo–2–methoxyphenyl)–7,7–difluoro–4,4–dimethyl–1–morpholinohept–6–en–1–one
471 MHz, CDCl3



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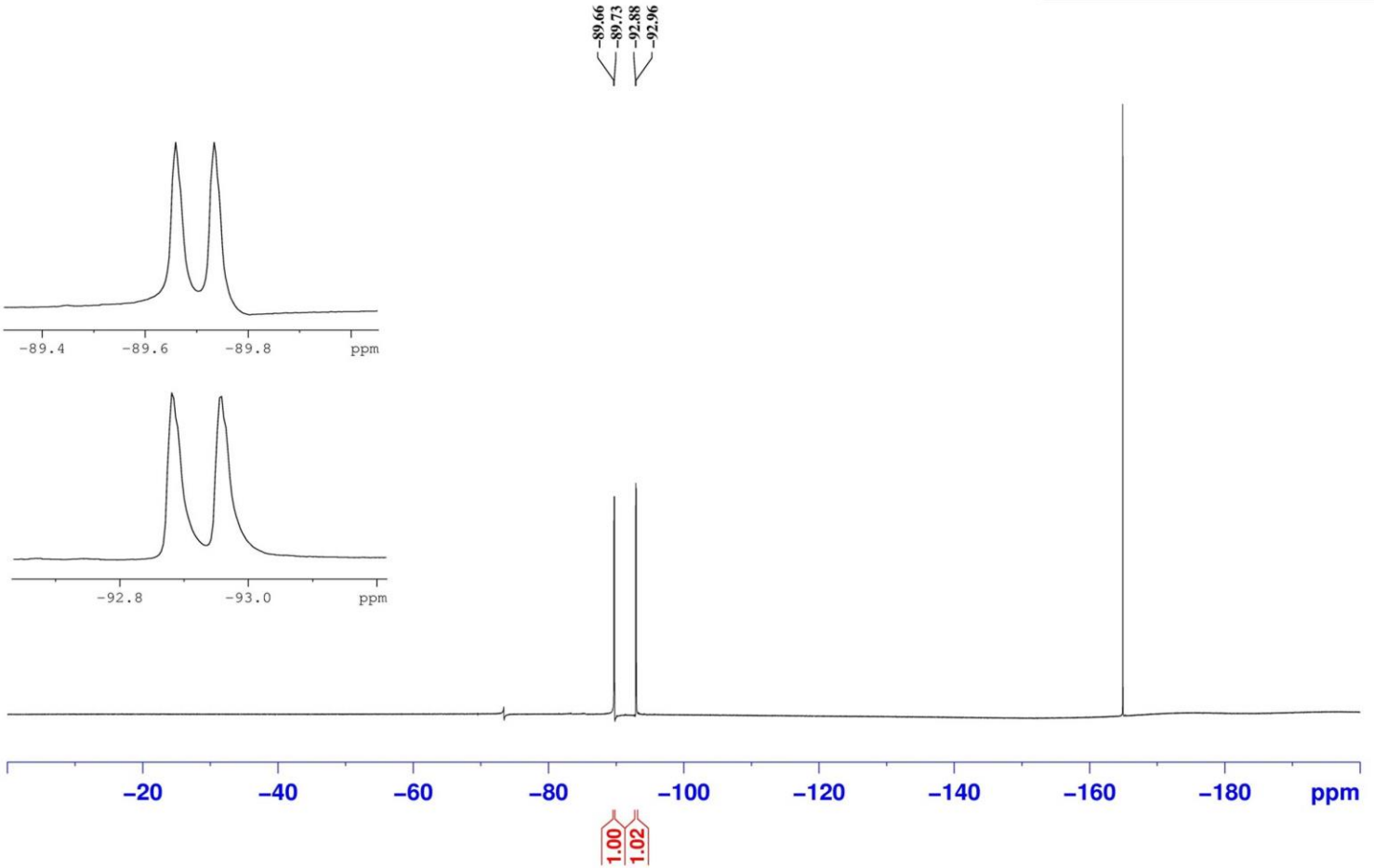
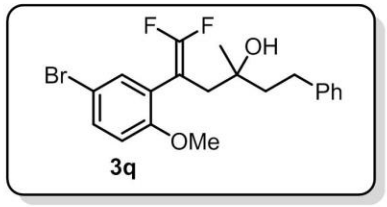


5–(5–bromo–2–methoxyphenyl)–6,6–difluoro–3–methyl–1–phenylhex–5–en–3–ol
500 MHz, CDCl3



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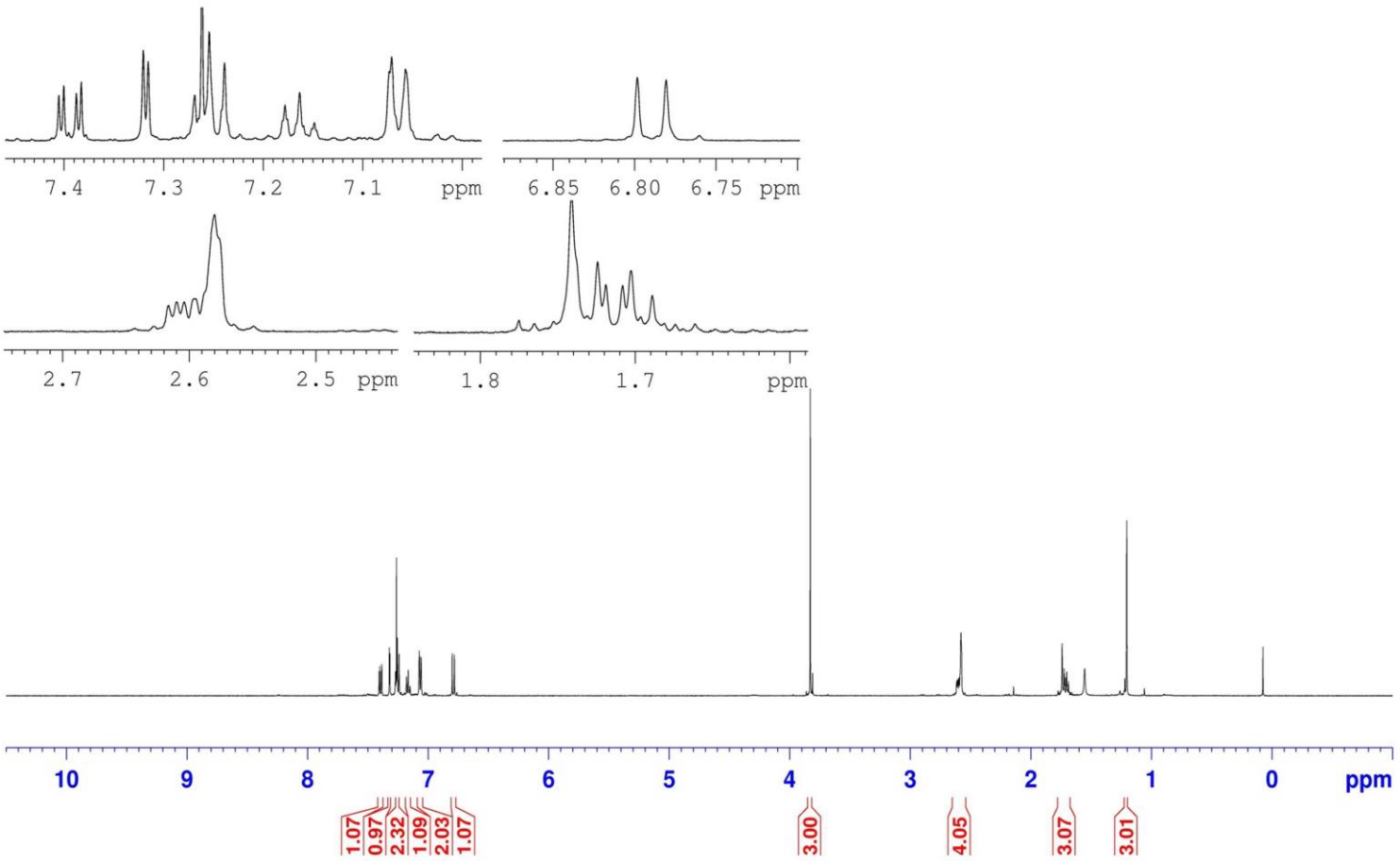
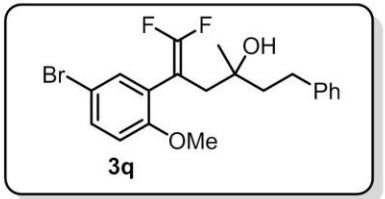


5–(5–bromo–2–methoxyphenyl)–6,6–difluoro–3–methyl–1–phenylhex–5–en–3–ol
125 MHz, CDCl3



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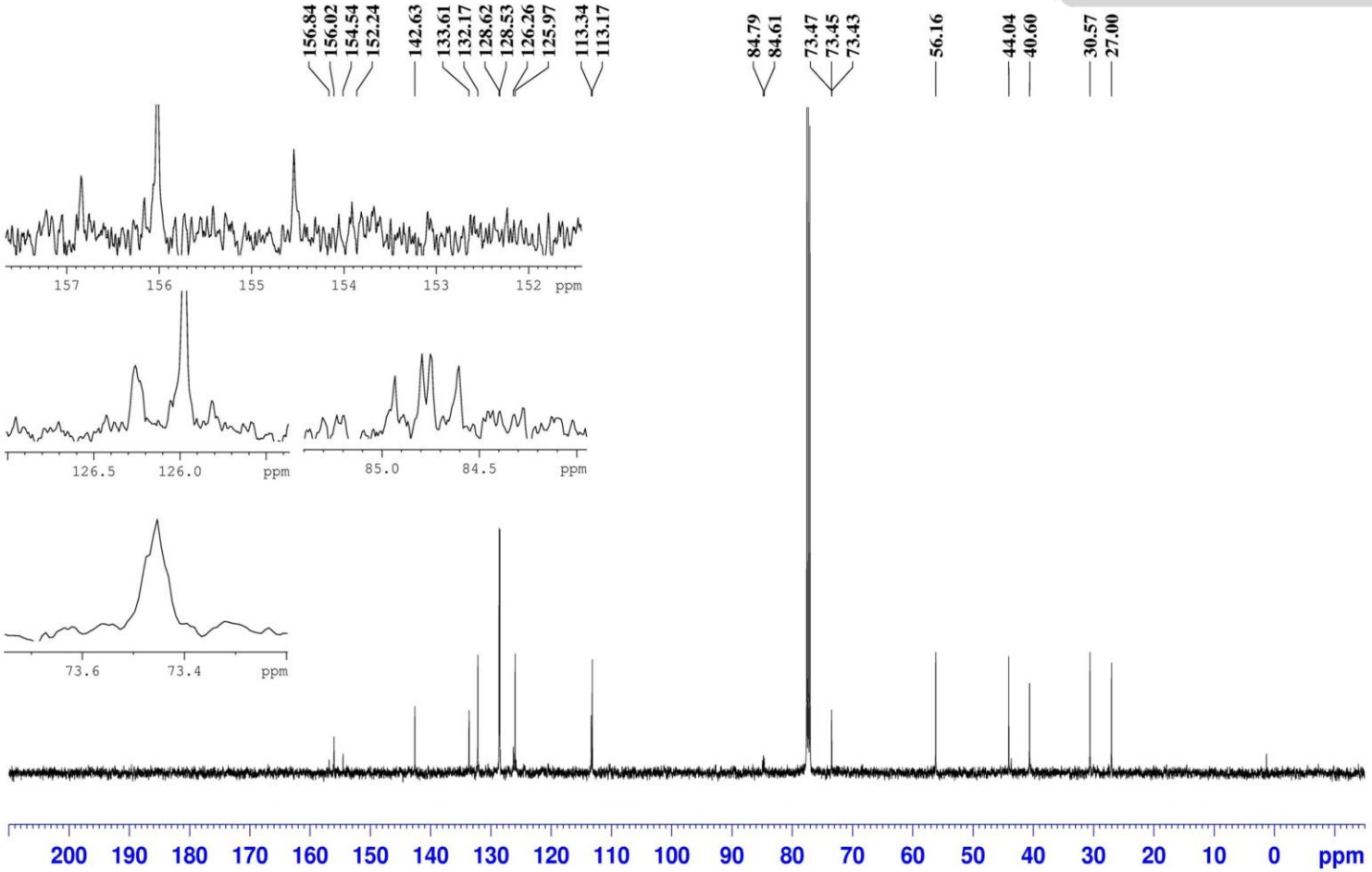
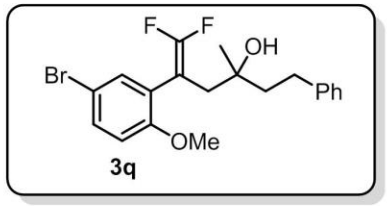
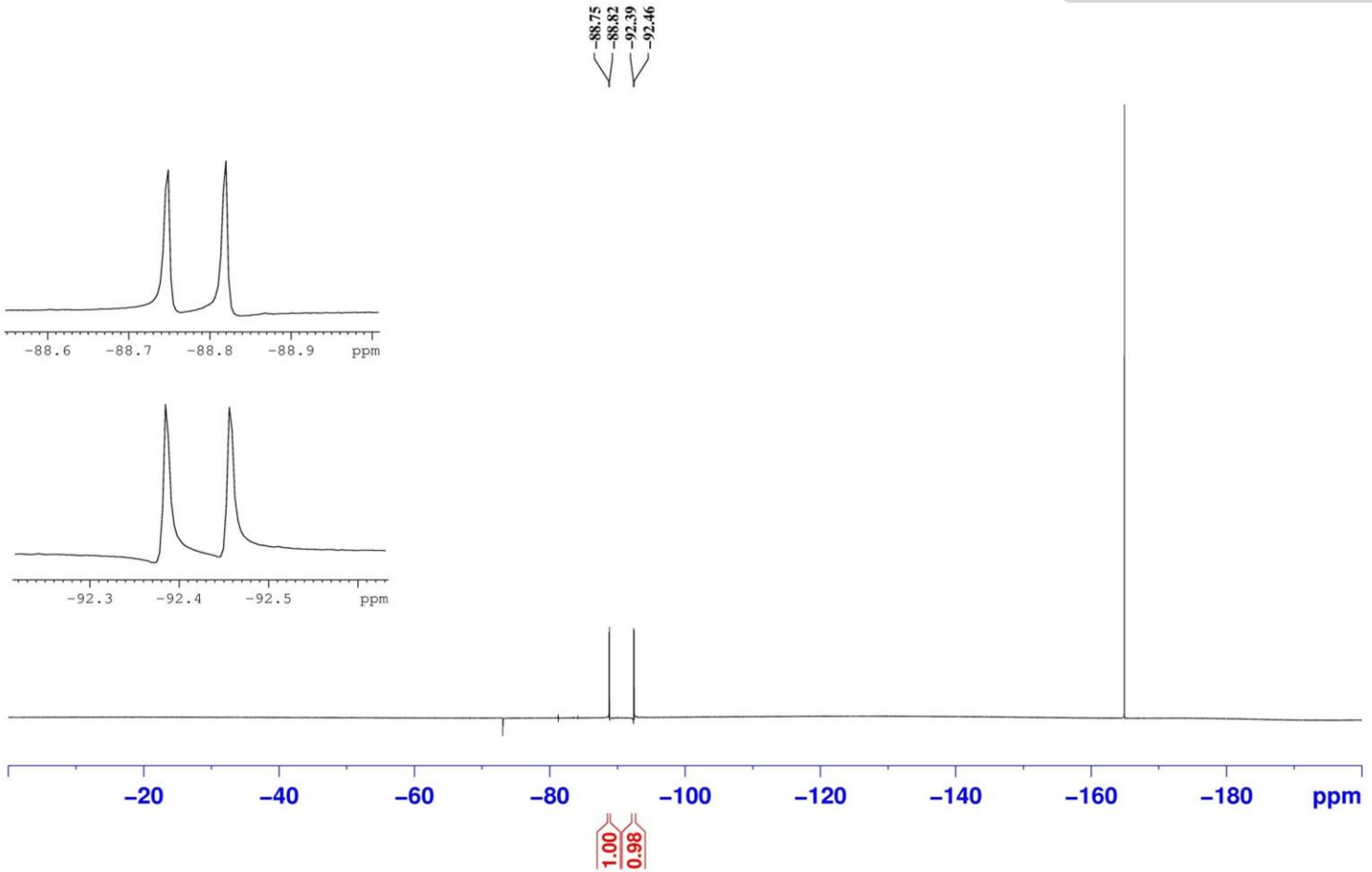


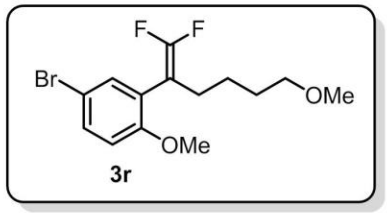
5–(5–bromo–2–methoxyphenyl)–6,6–difluoro–3–methyl–1–phenylhex–5–en–3–ol
471 MHz, CDCl3



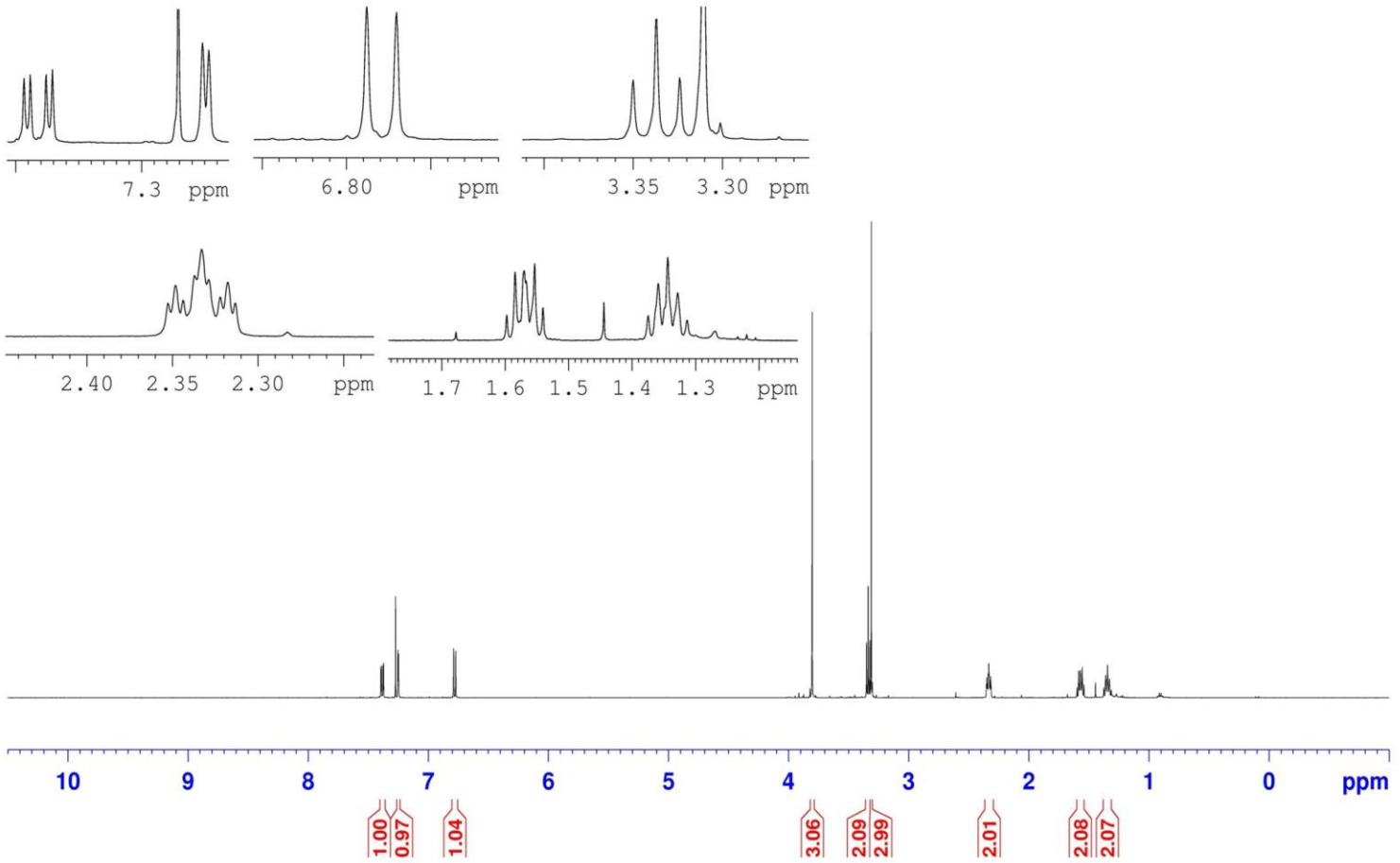
3q



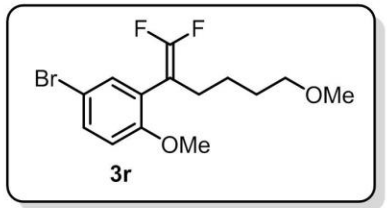
4–bromo–2–(1,1–difluoro–6–methoxyhex–1–en–2–yl)–1–methoxybenzene
500 Mhz, CDCl3



3r



4–bromo–2–(1,1–difluoro–6–methoxyhex–1–en–2–yl)–1–methoxybenzene
125 MHz, CDCl3



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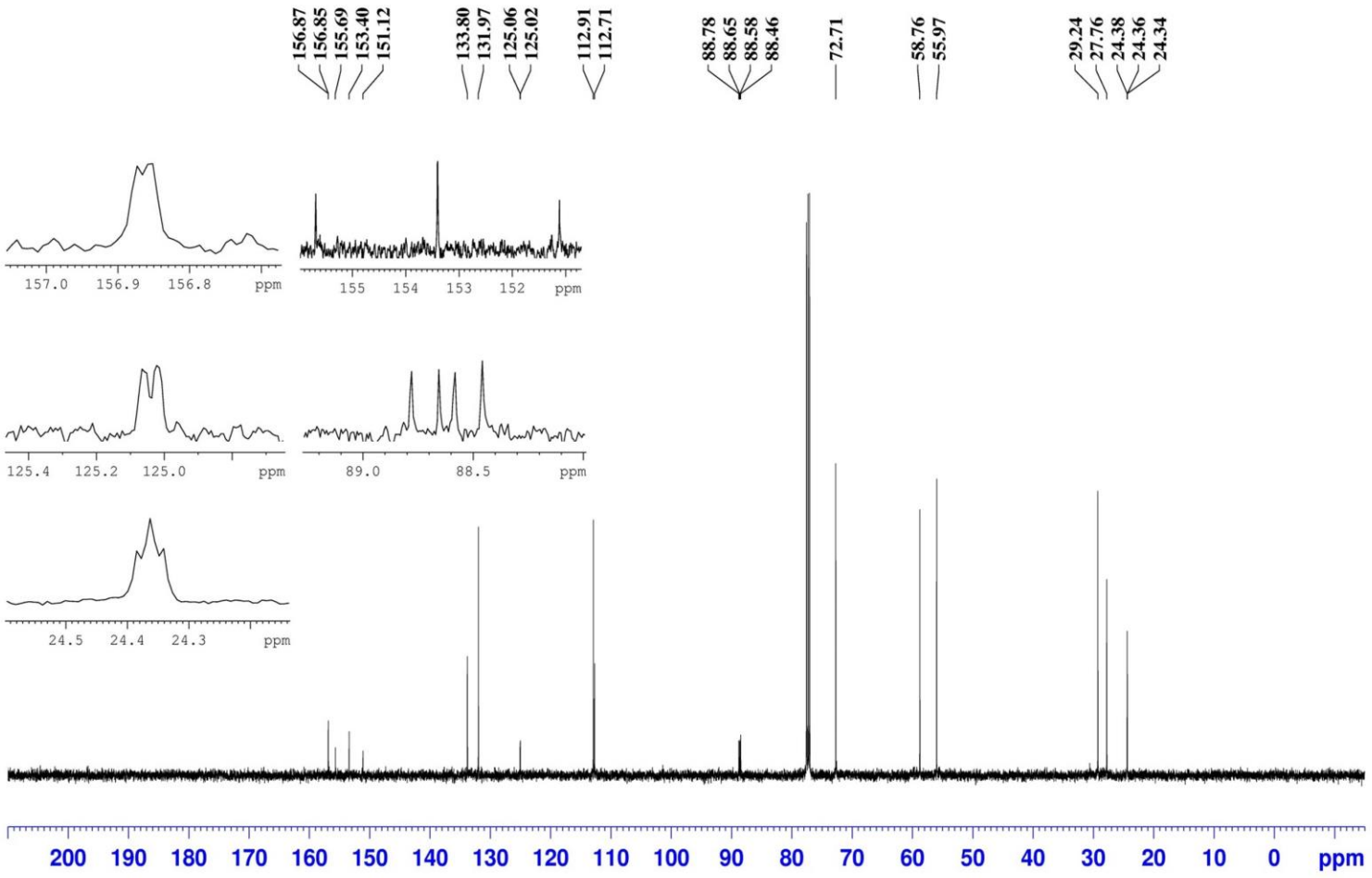
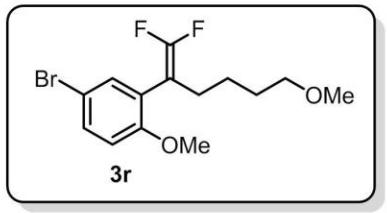


4–bromo–2–(1,1–difluoro–6–methoxyhex–1–en–2–yl)–1–methoxybenzene
471 MHz, CDCl3



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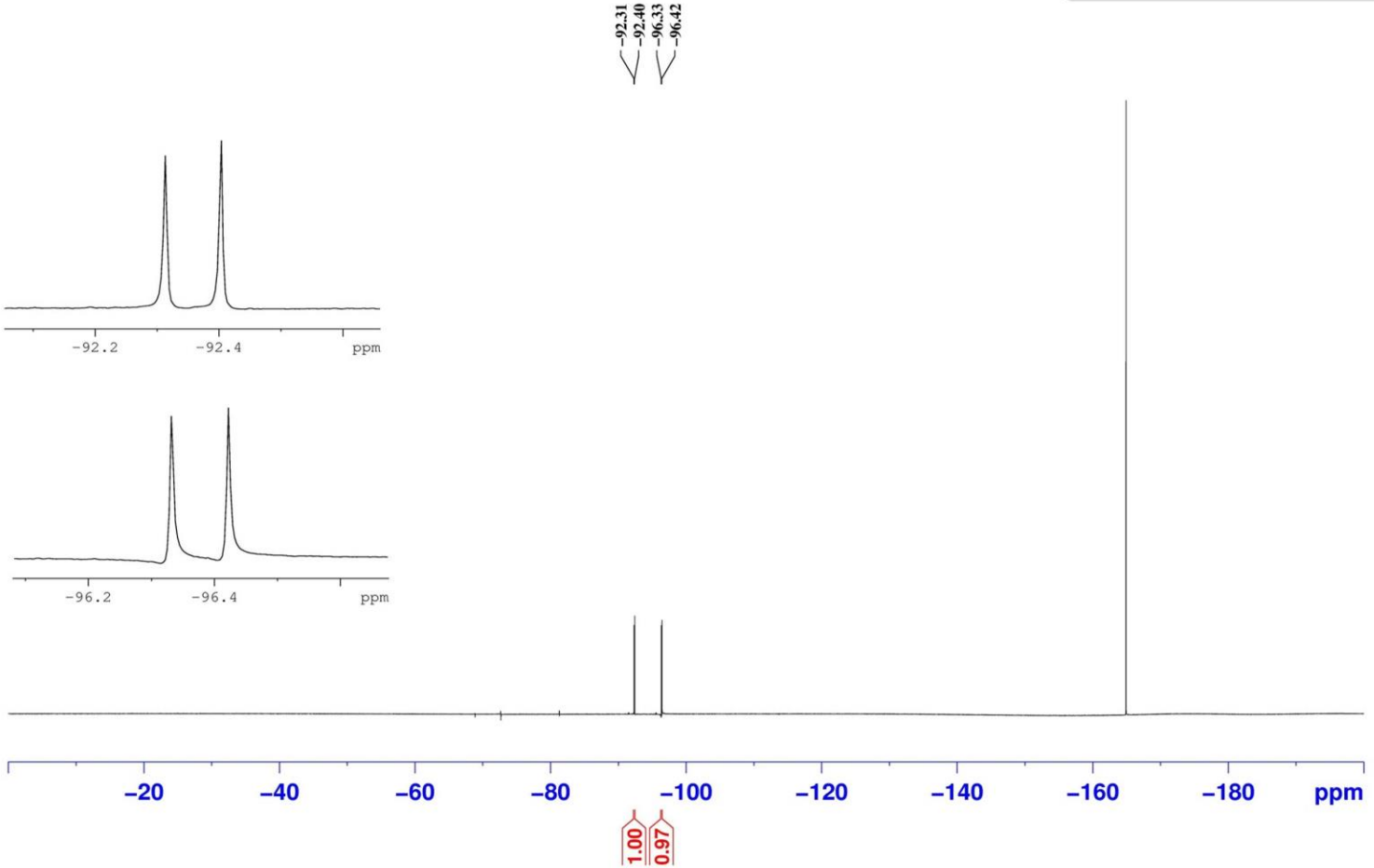
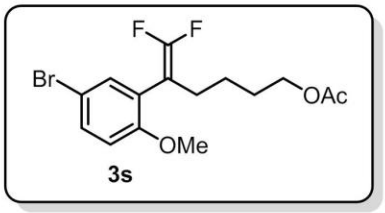
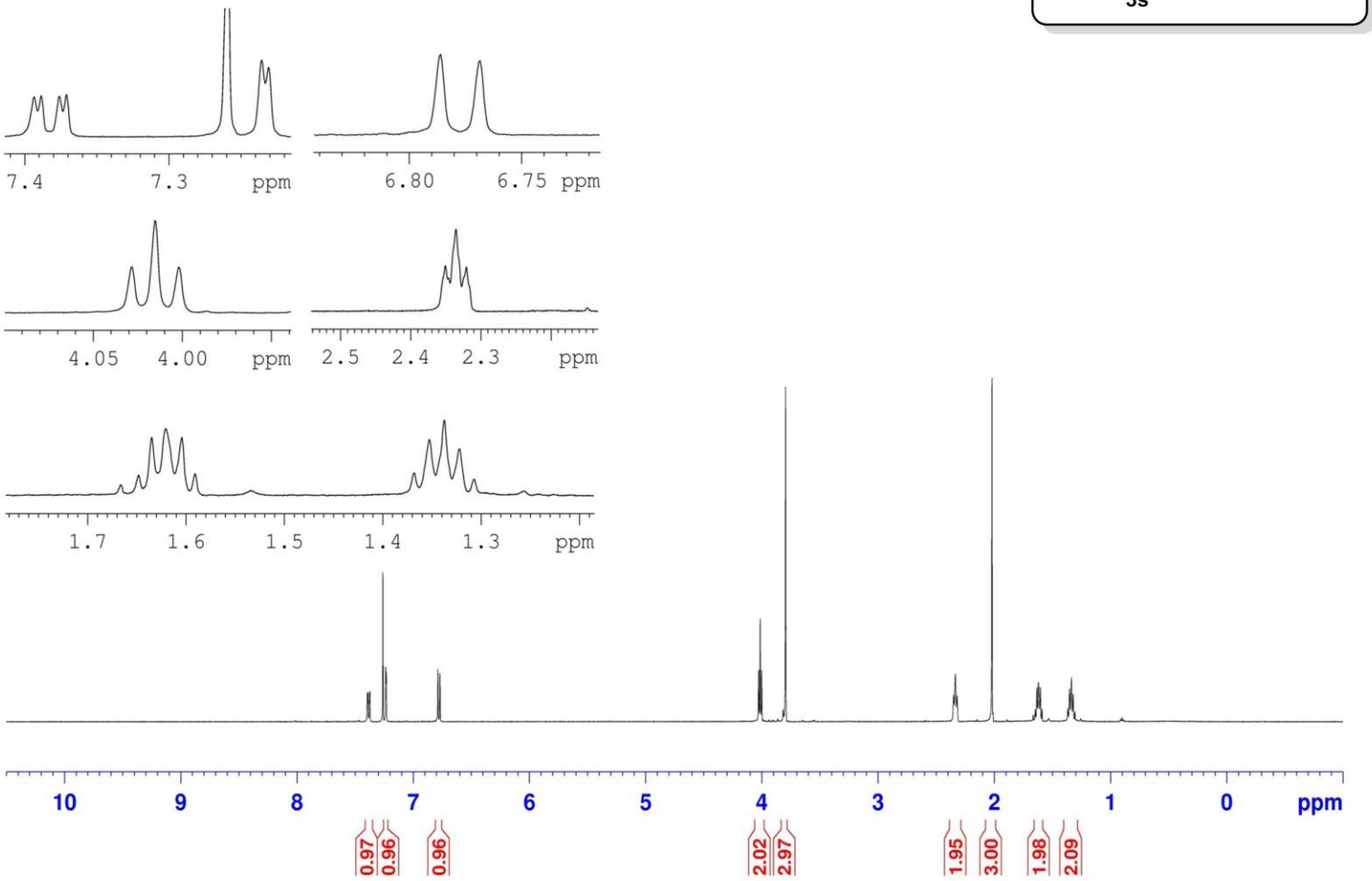


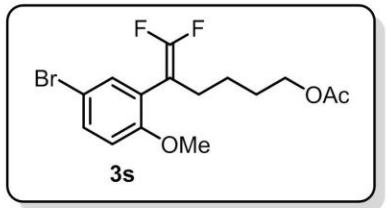
5–(5–bromo–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl acetate
500 MHz, CDCl3



3s



5–(5–bromo–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl acetate
125 MHz, CDCl3



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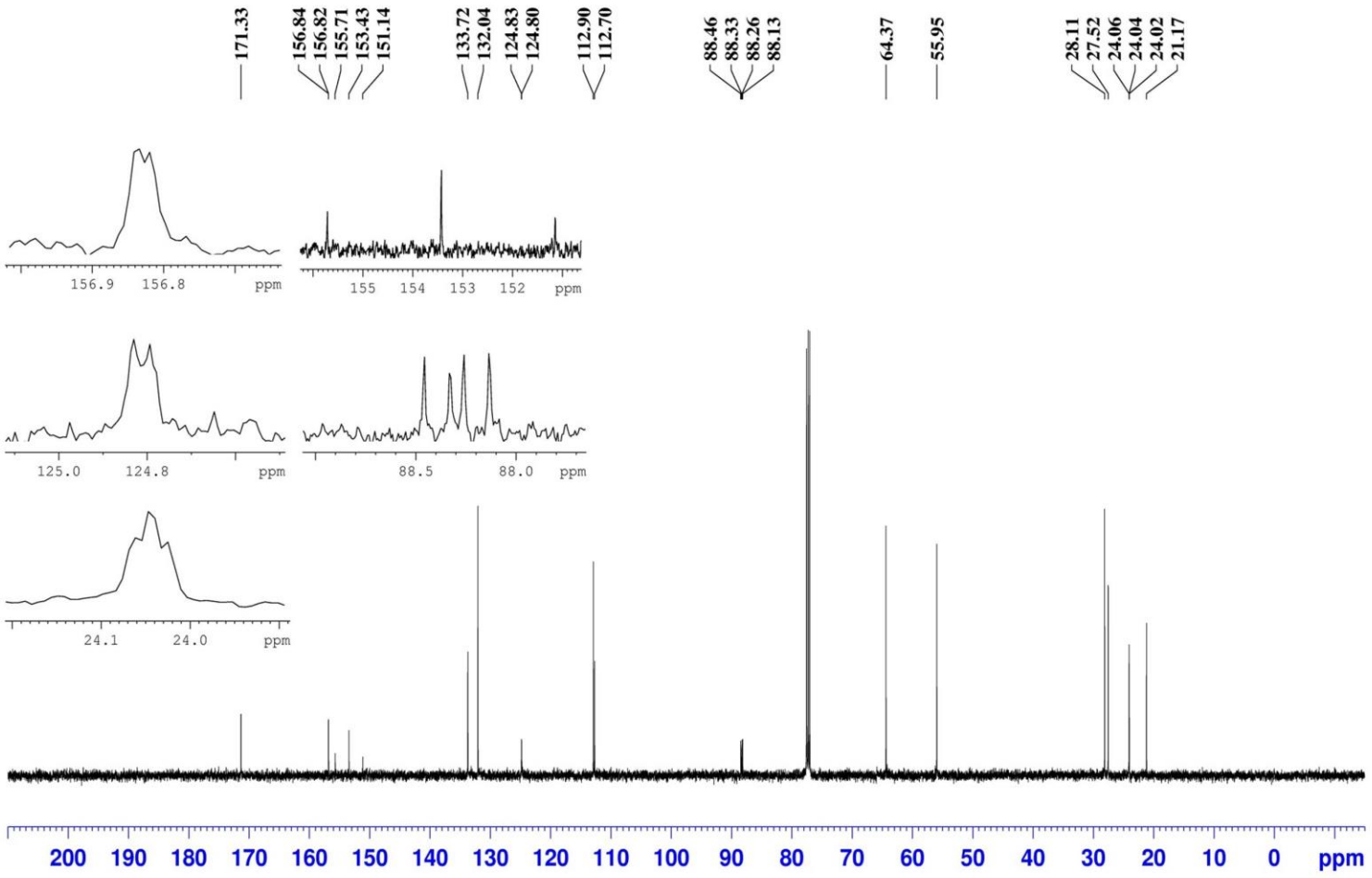
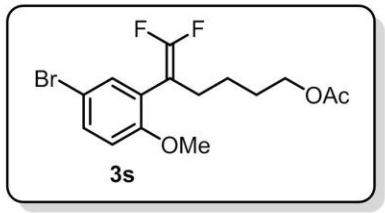


5–(5–bromo–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl acetate
471 MHz, CDCl3



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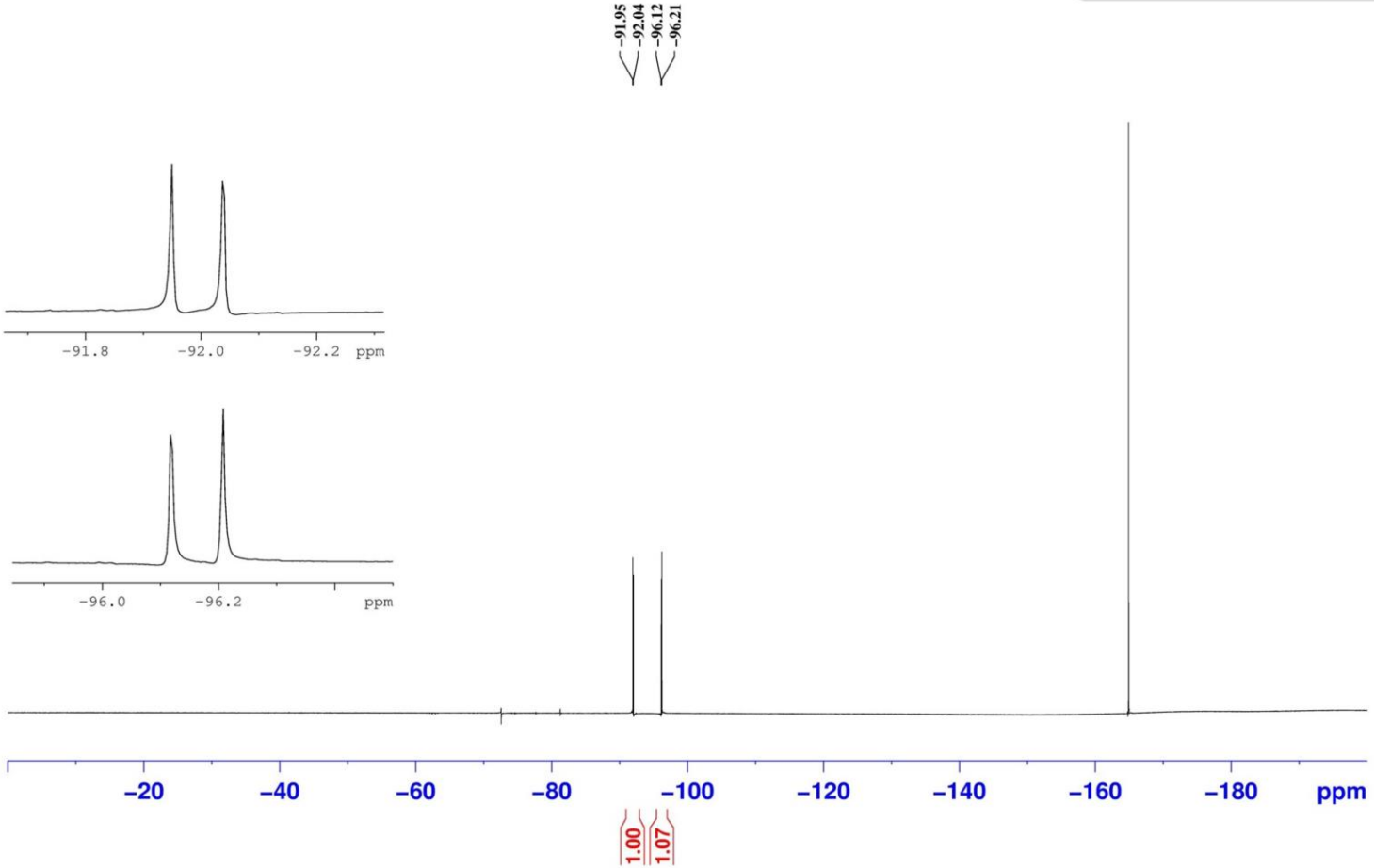
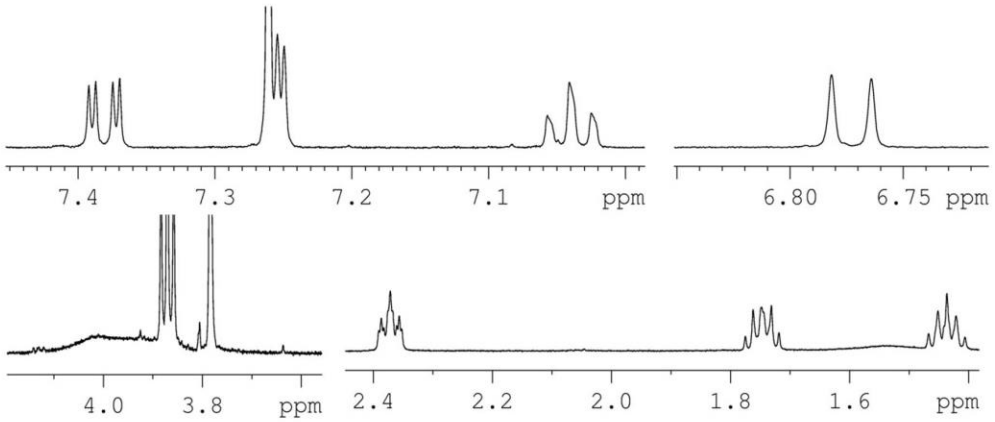
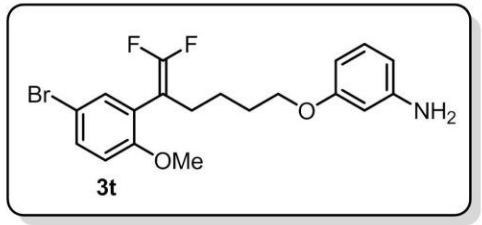


3-((5-(5-bromo-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl)oxy)aniline
500 MHz, CDCl3





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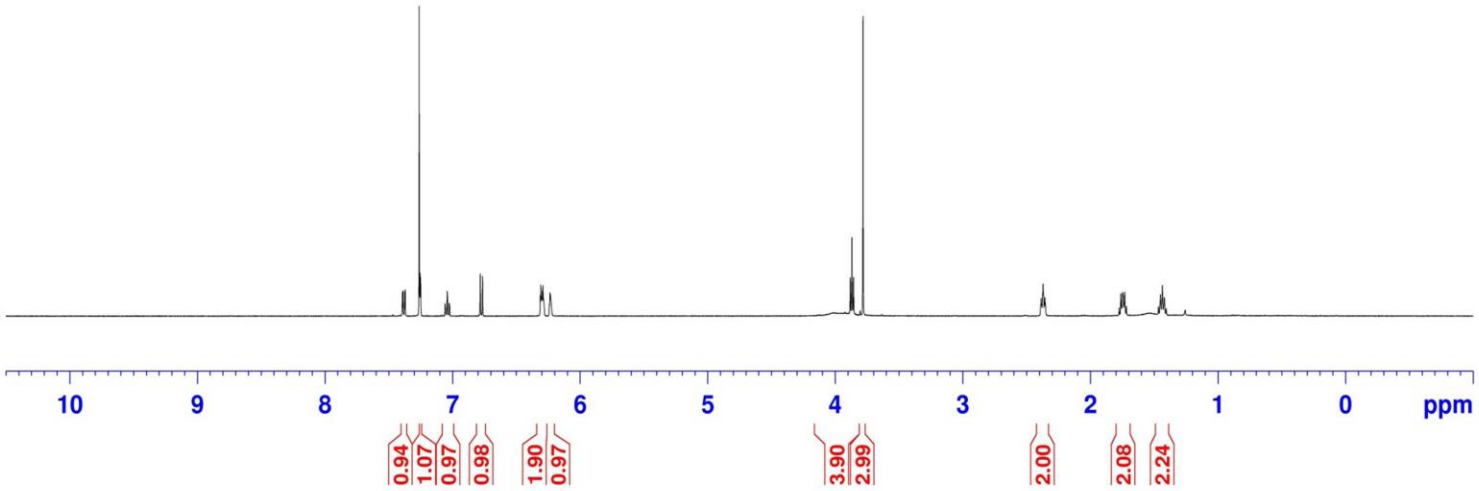
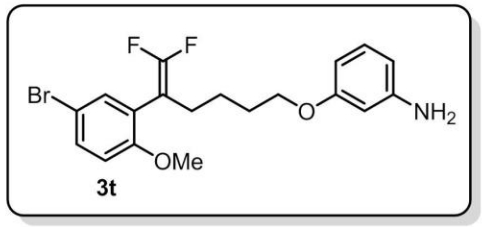


3-((5-(5-bromo-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl)oxy)aniline
125 MHz, CDCl3



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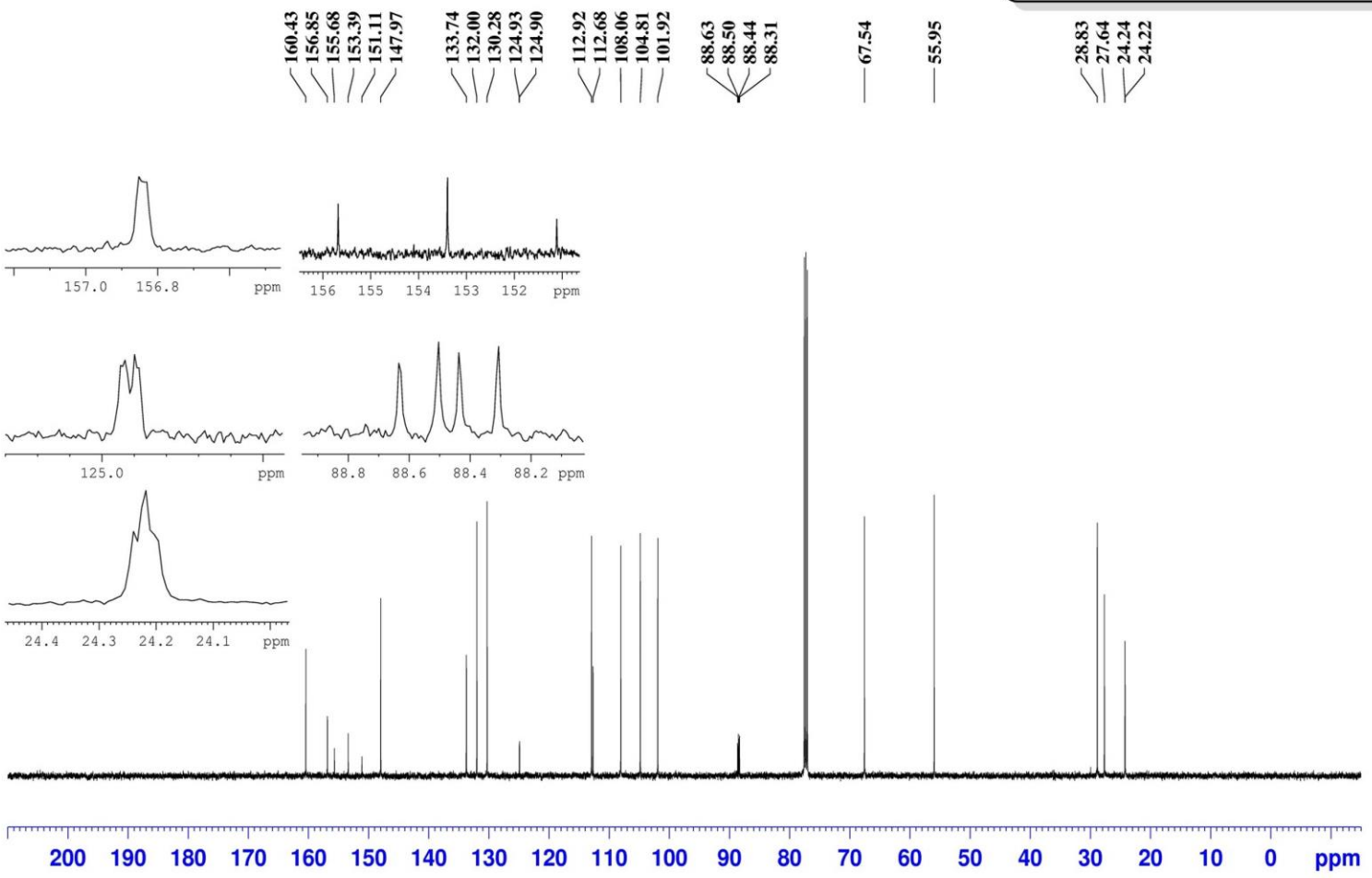
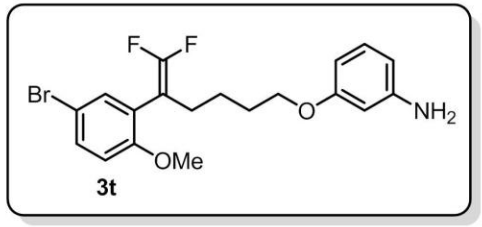


3-((5-(5-bromo-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl)oxy)aniline
471 MHz, CDCl3



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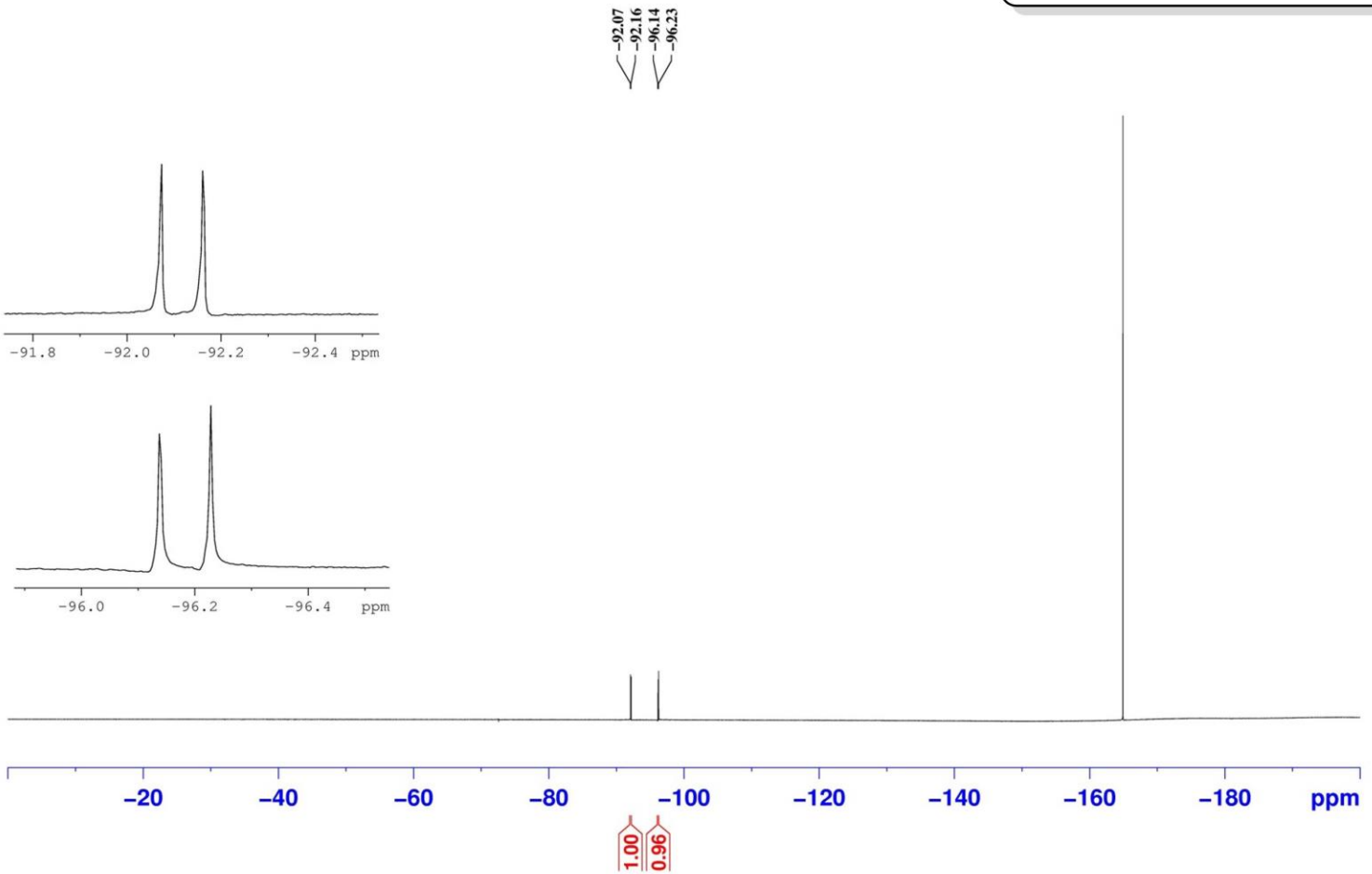
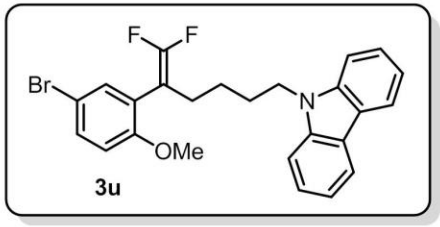
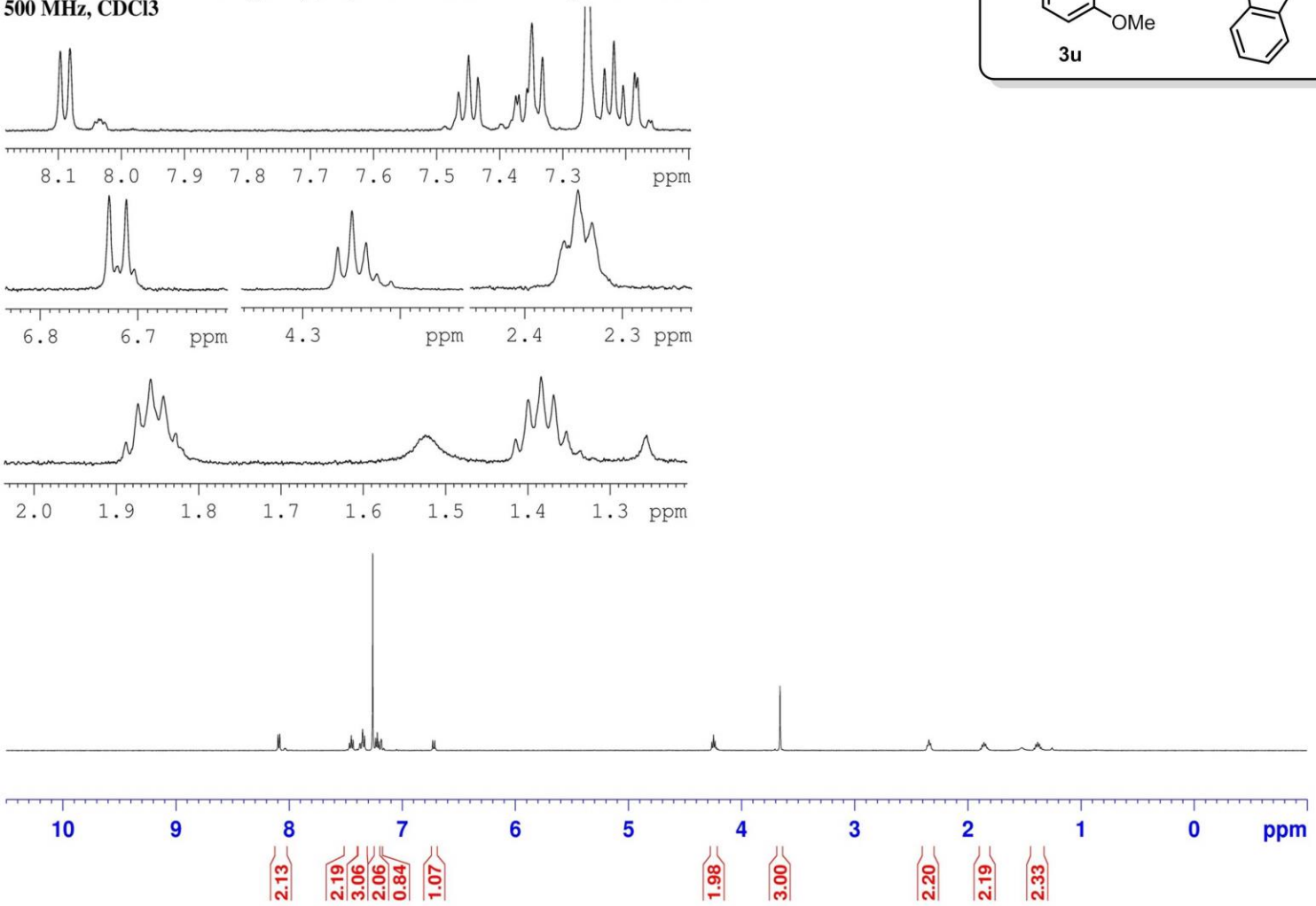
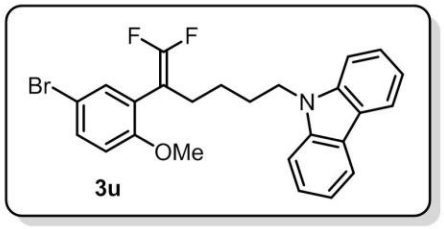




9–(5–(5–bromo–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl)–9H–carbazole
500 MHz, CDCl3



9-(5-(5-bromo-2-methoxyphenyl)-6,6-difluorohex-5-en-1-yl)-9H-carbazole
125 MHz, CDCl3



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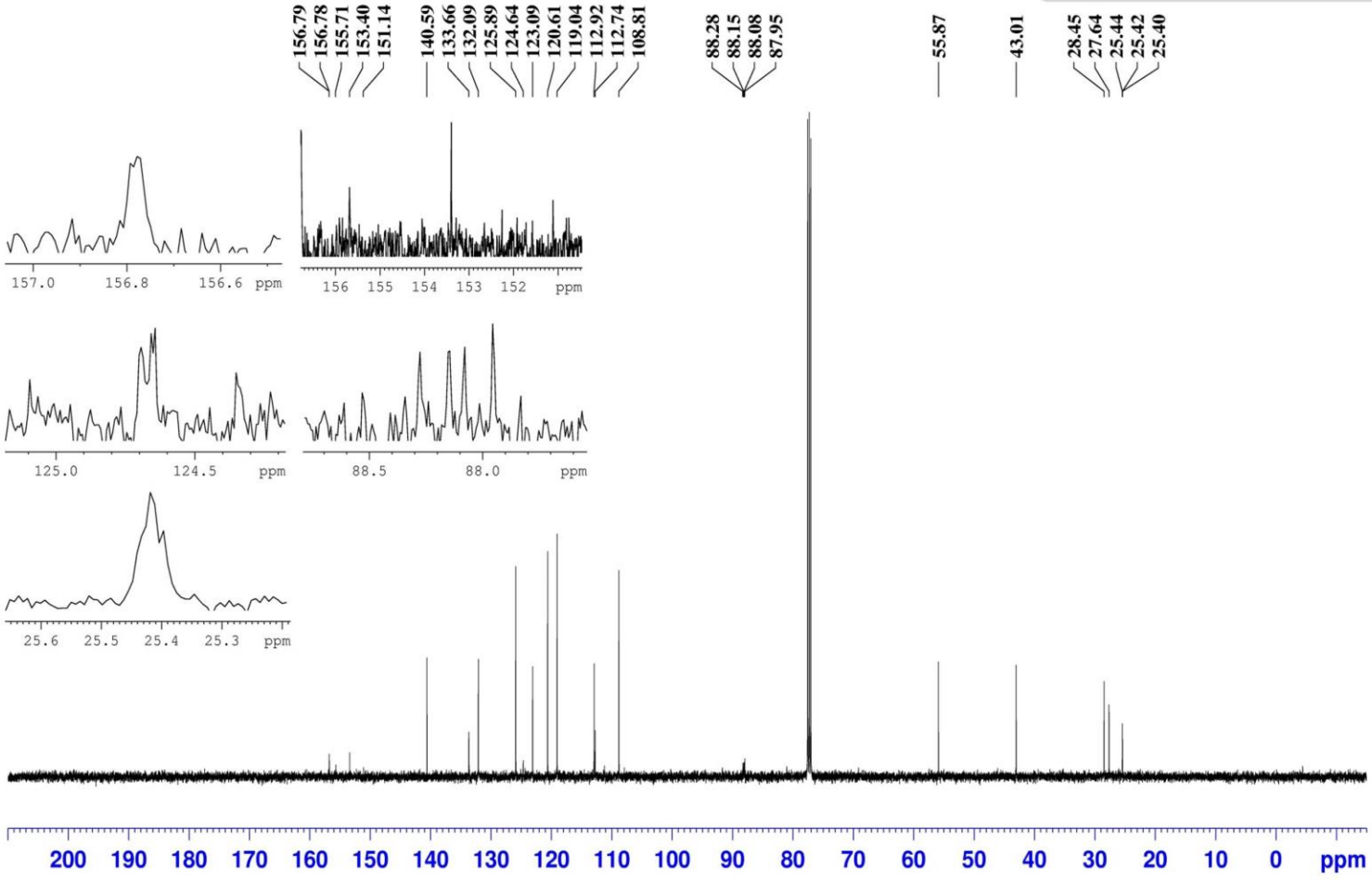
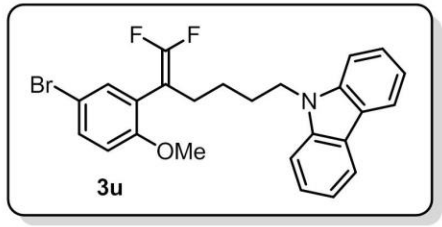
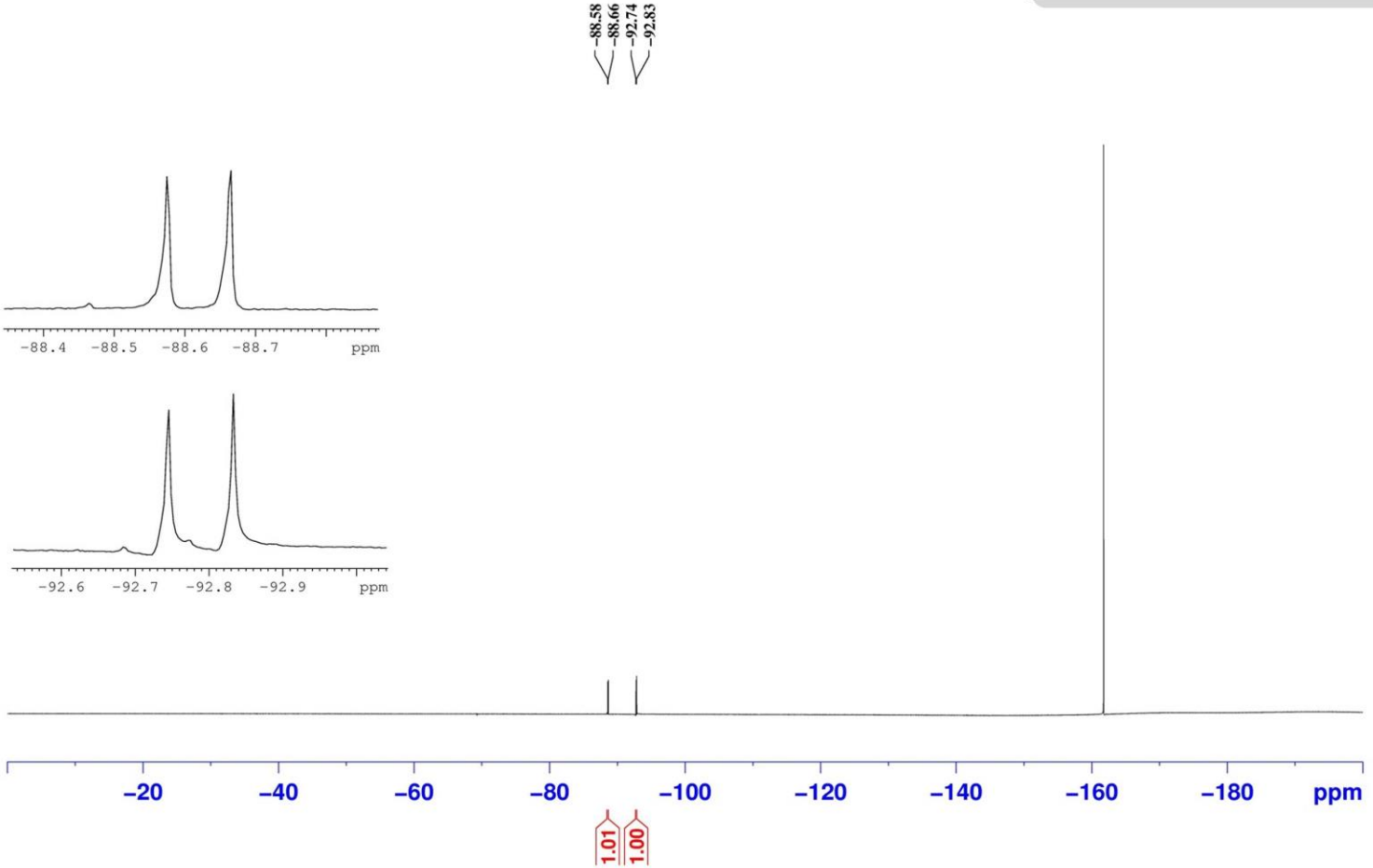


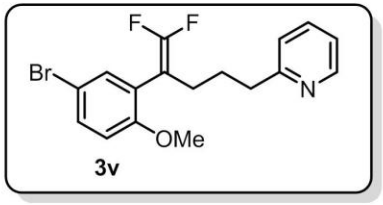
9–(5–(5–bromo–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl)–9H–carbazole
471 MHz, CDCl3



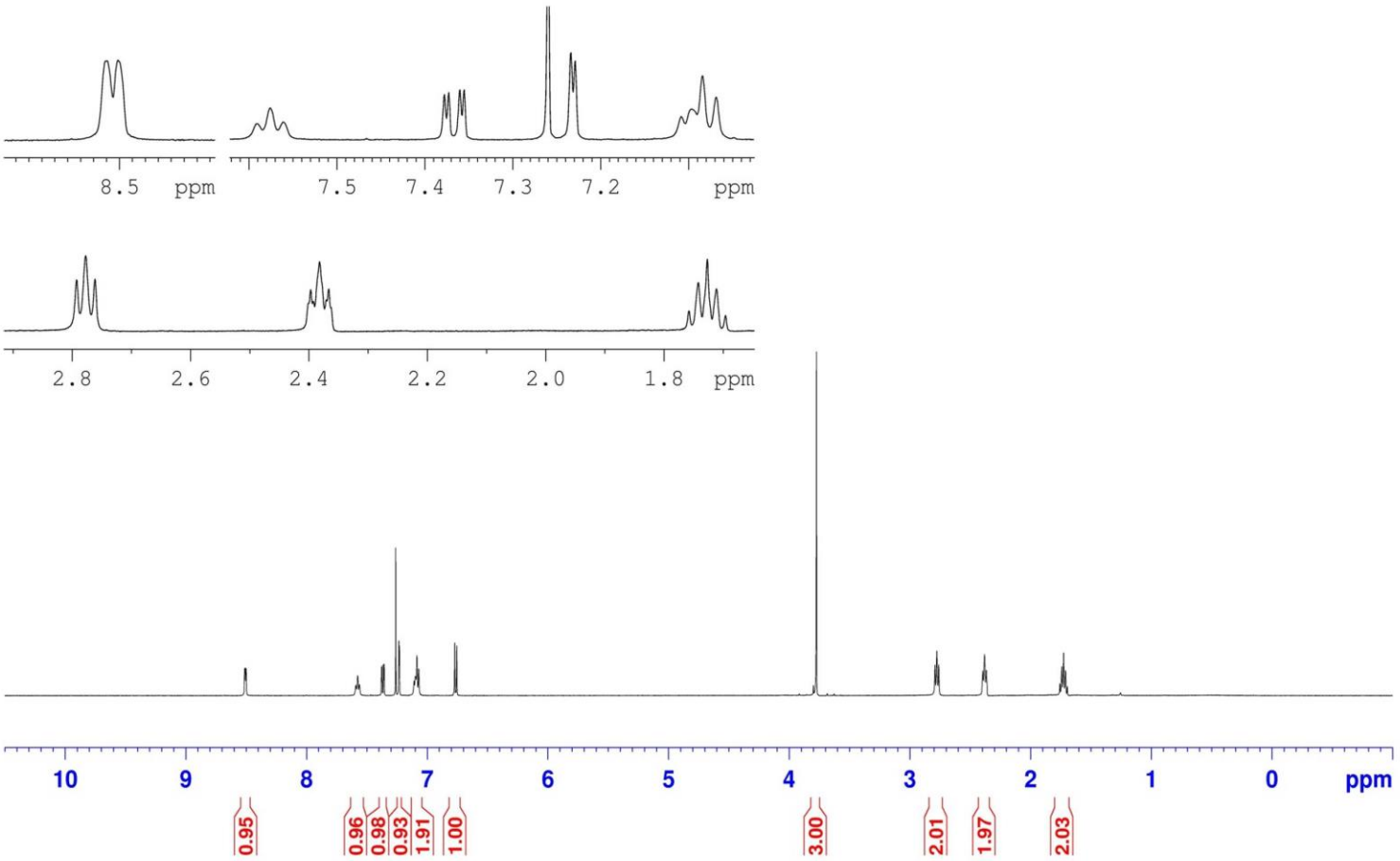
3u



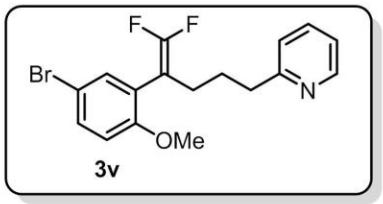
2-(4-(5-bromo-2-methoxyphenyl)-5,5-difluoropent-4-en-1-yl)pyridine
500 MHz, CDCl3



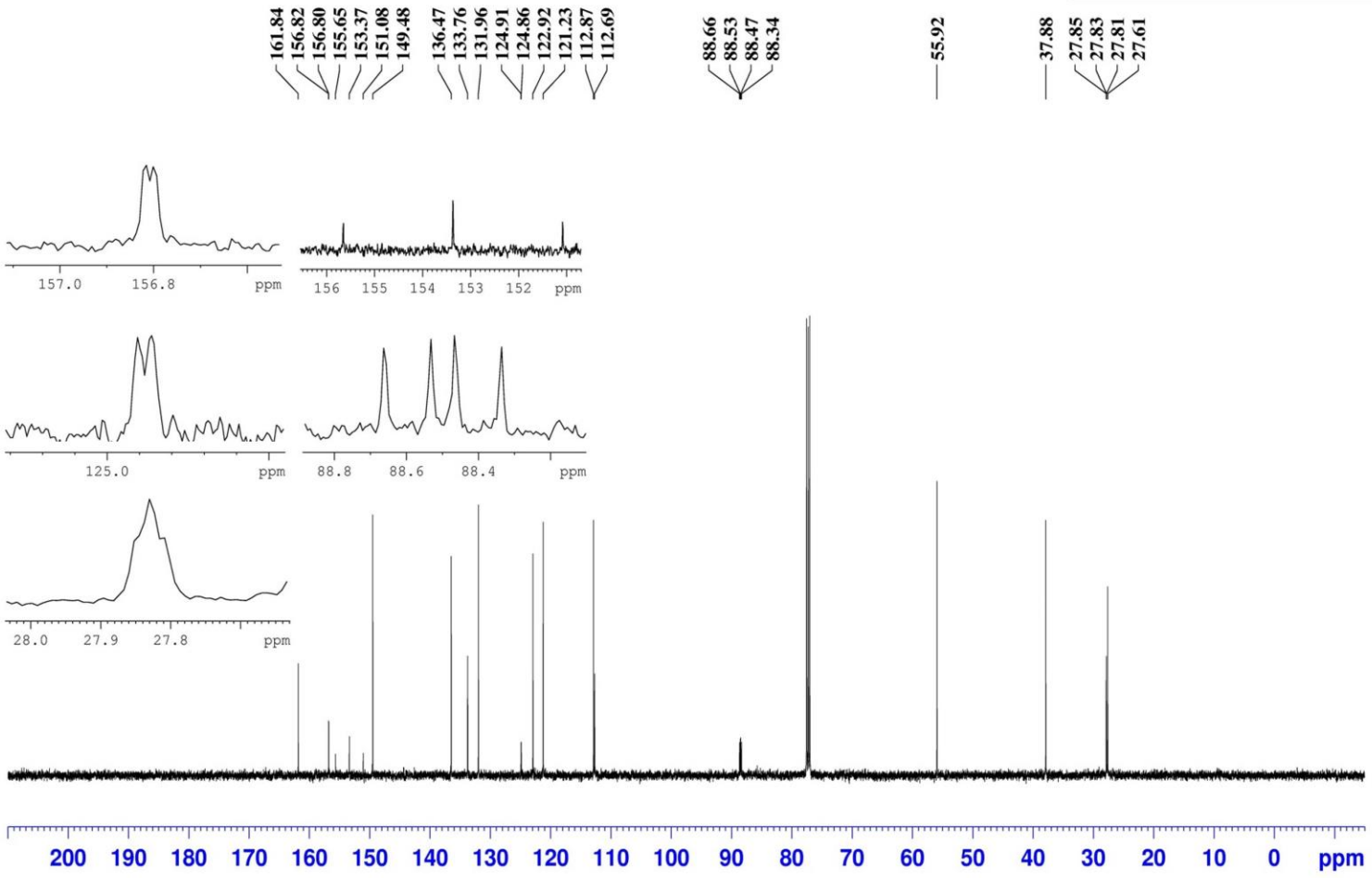
3v



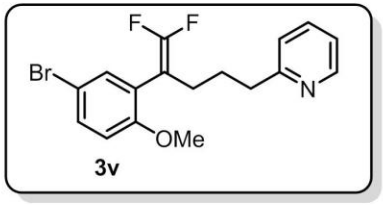
2–(4–(5–bromo–2–methoxyphenyl)–5,5–difluoropent–4–en–1–yl)pyridine
125 MHz, CDCl3



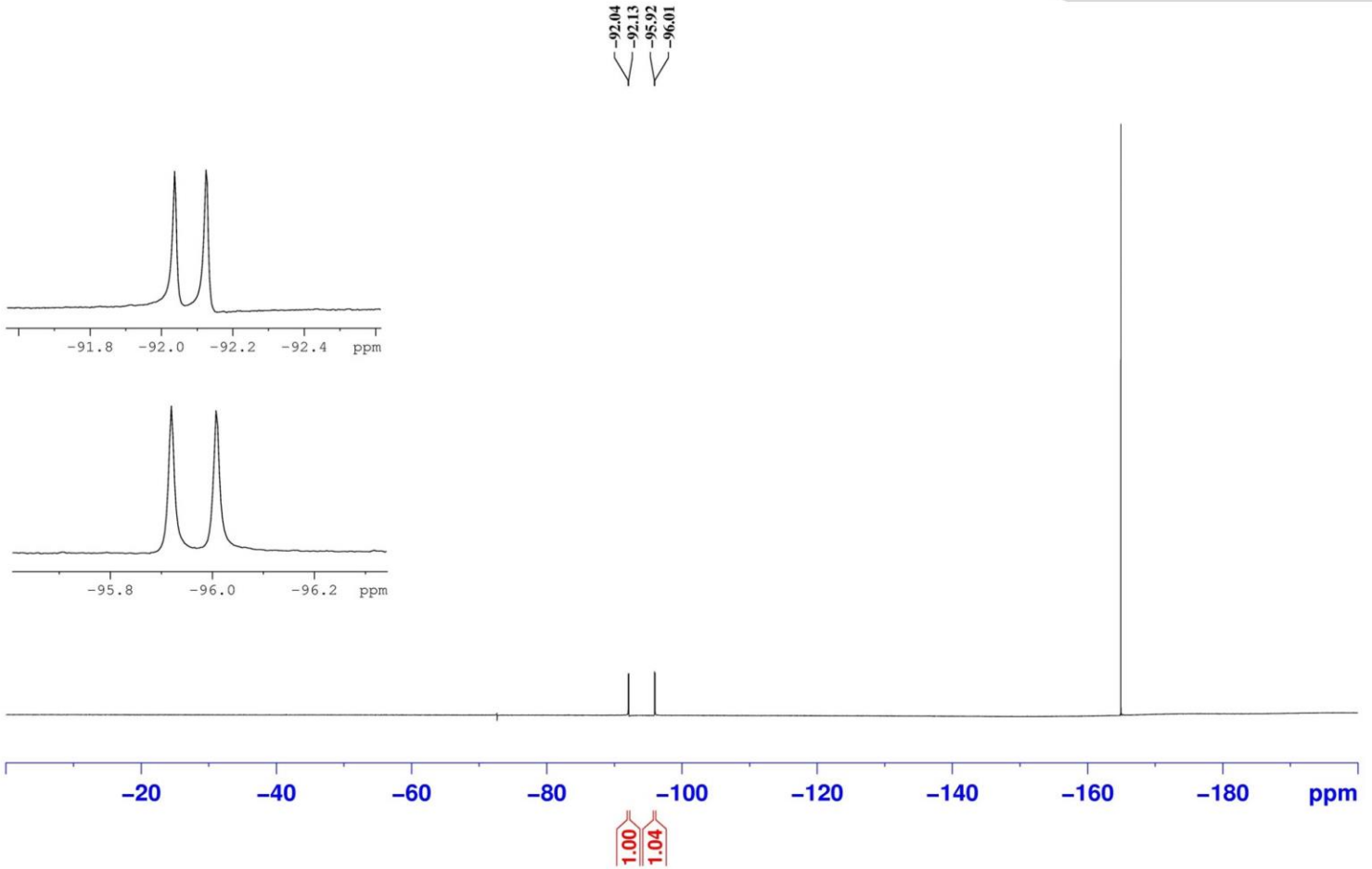
3v



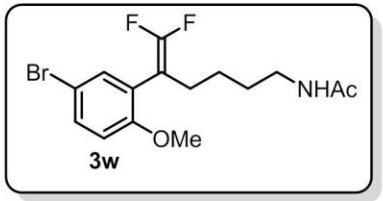
2–(4–(5–bromo–2–methoxyphenyl)–5,5–difluoropent–4–en–1–yl)pyridine
471 MHz, CDCl3

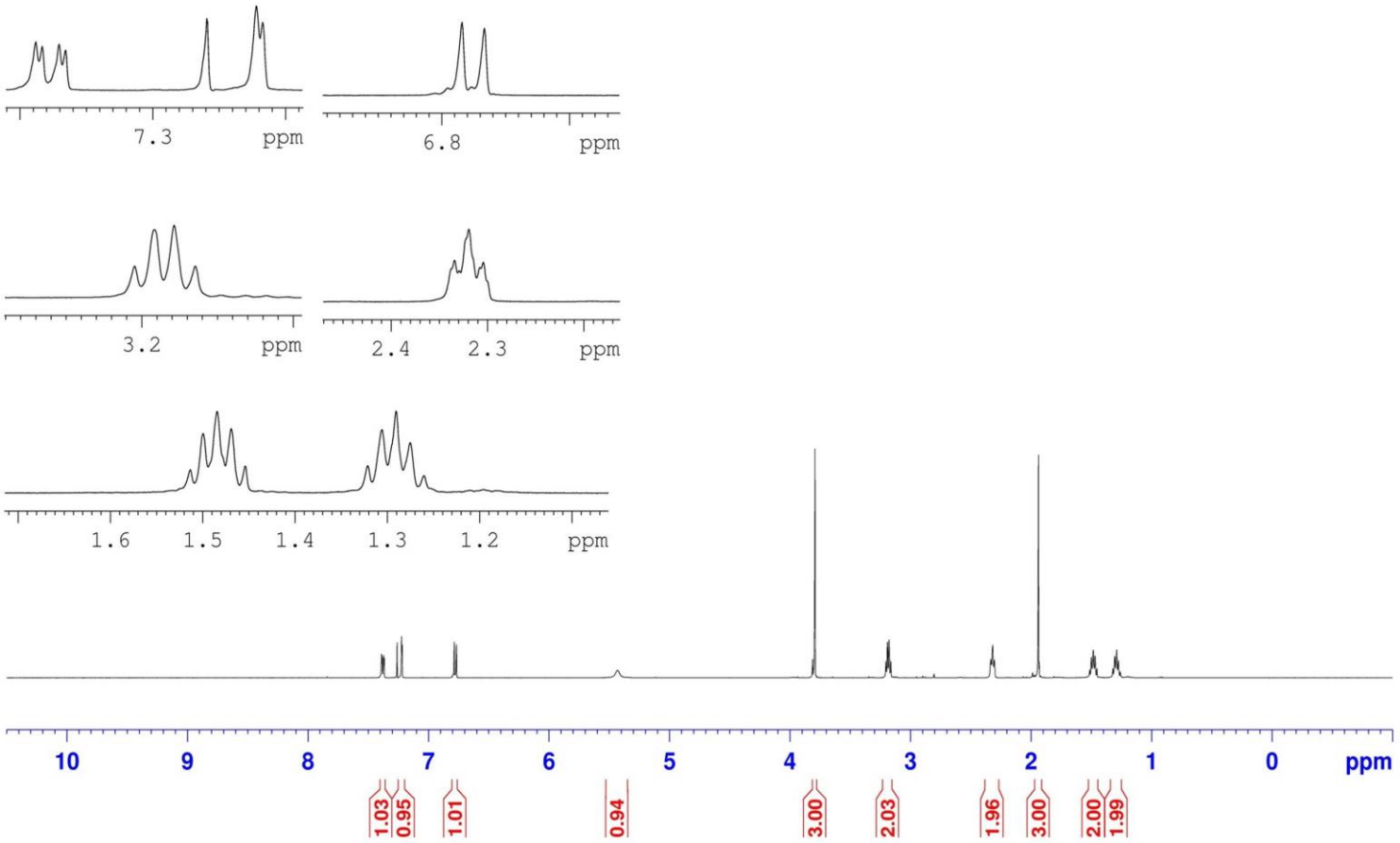


3v

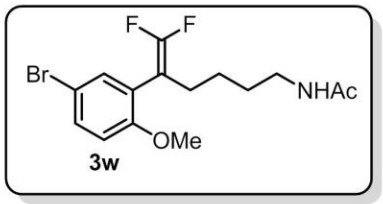


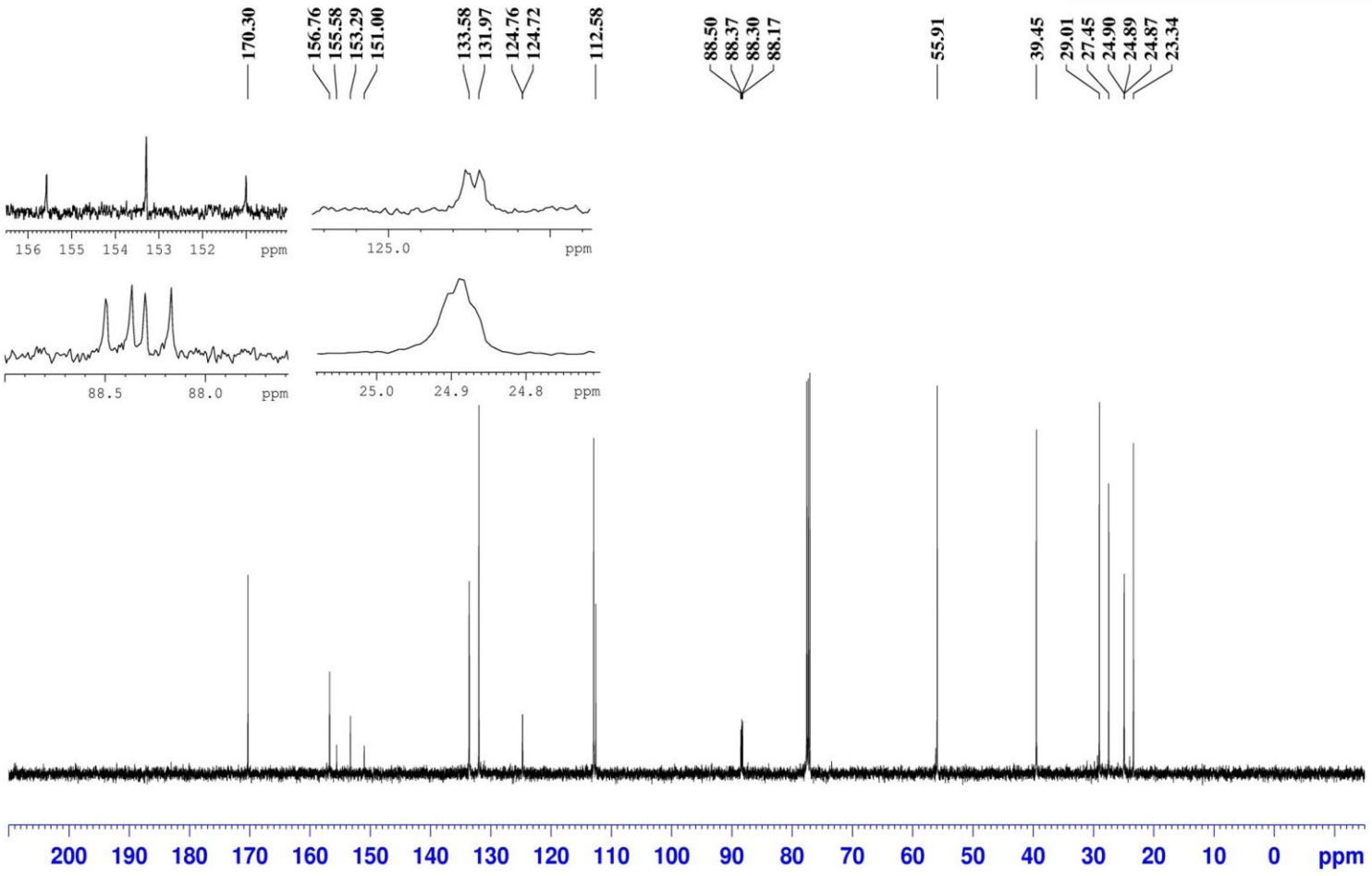
2-(4-(5-bromo-2-methoxyphenyl)-5,5-difluoropent-4-en-1-yl)pyridine
500 MHz, CDCl3



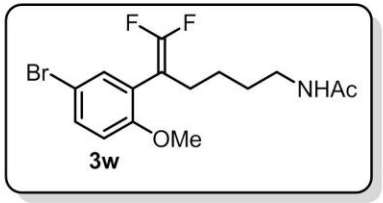


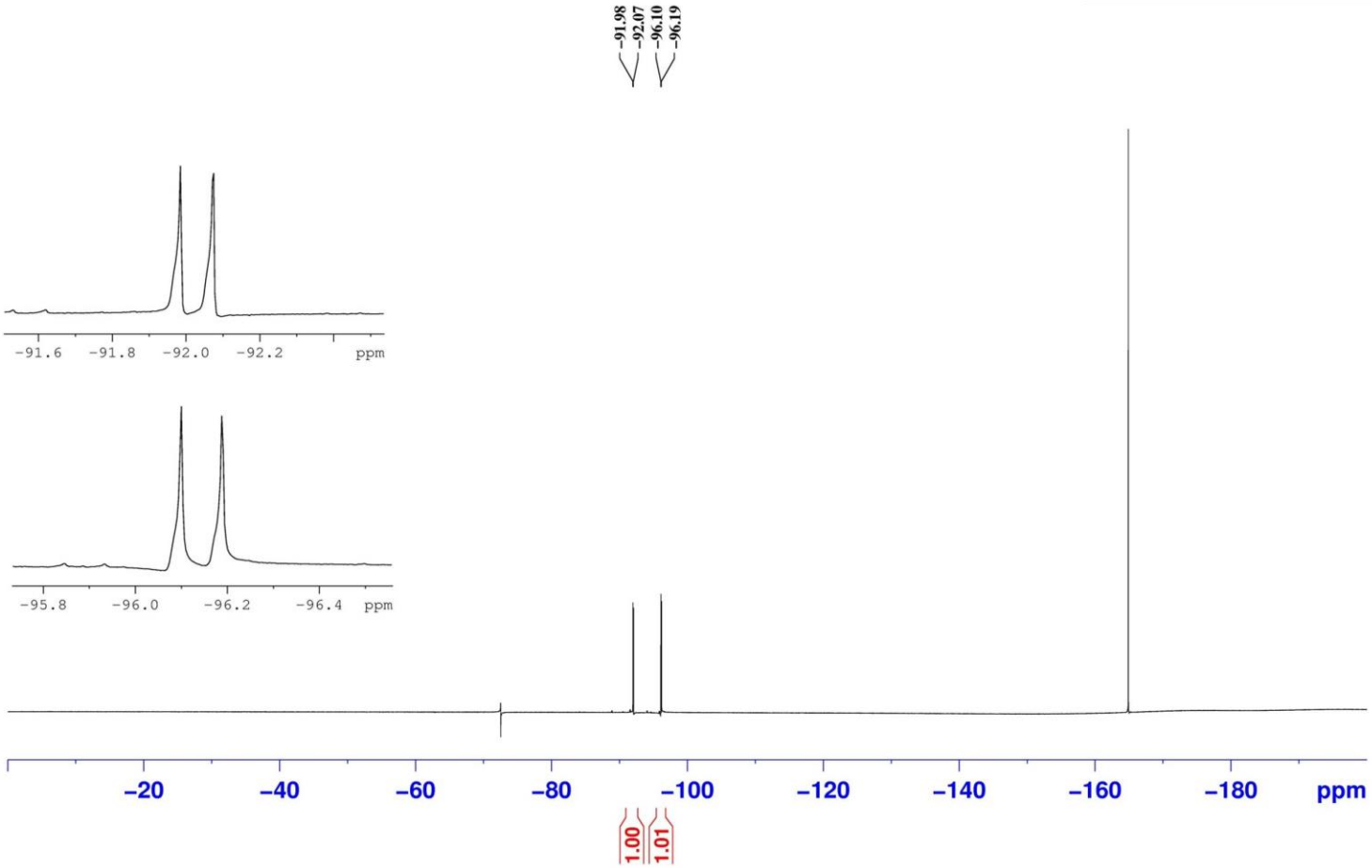
N–(5–(5–bromo–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl)acetamide
125 MHz, CDCl3



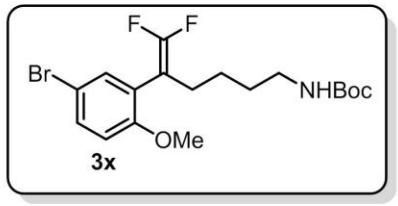


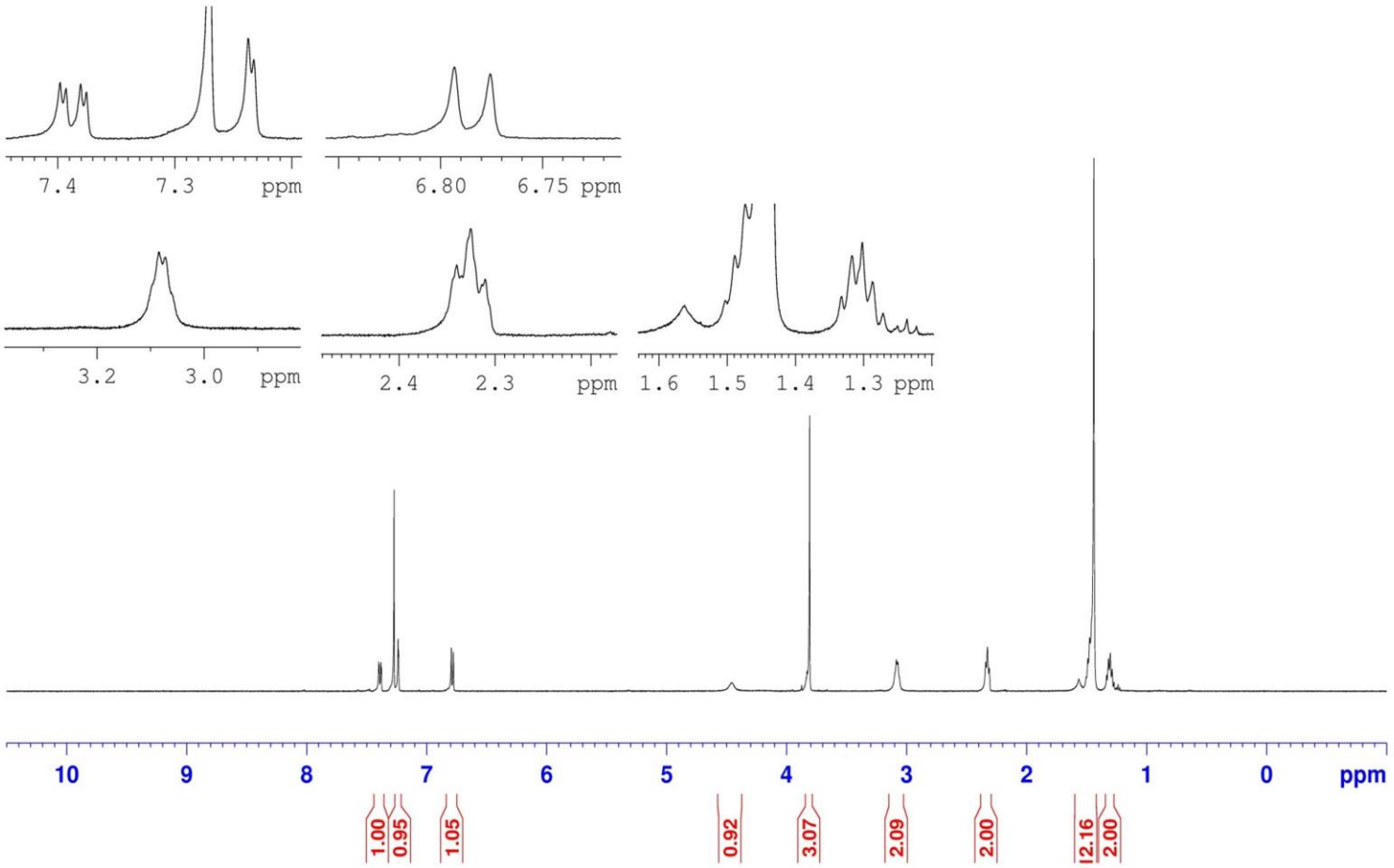
N–(5–(5–bromo–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl)acetamide
471 MHz, CDCl3



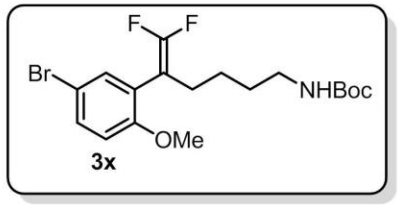


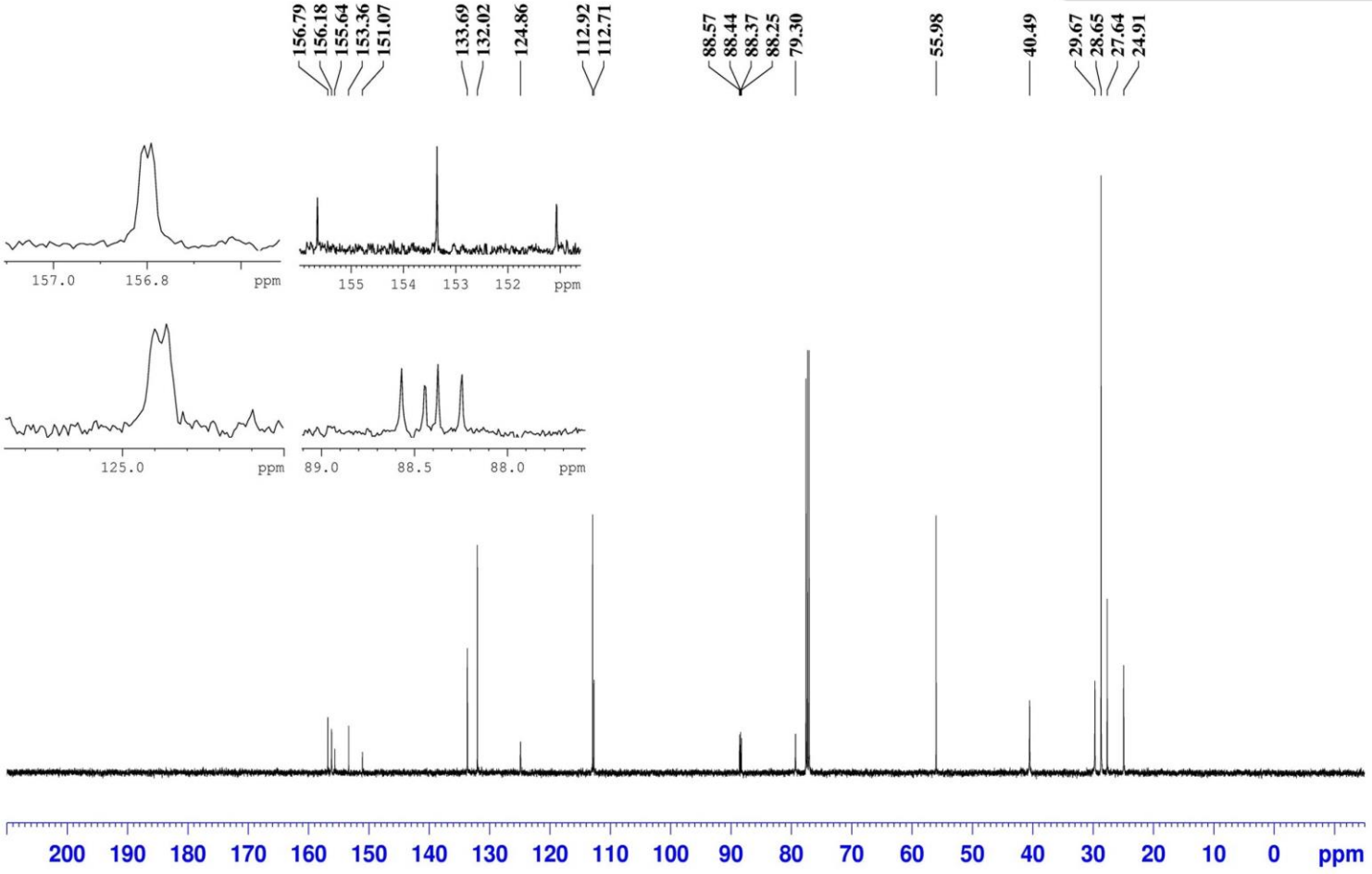
tert−butyl (5−(5−bromo−2−methoxyphenyl)−6,6−difluorohex−5−en−1−yl)carbamate
500 MHz, CDCl3



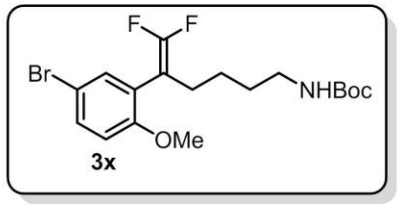


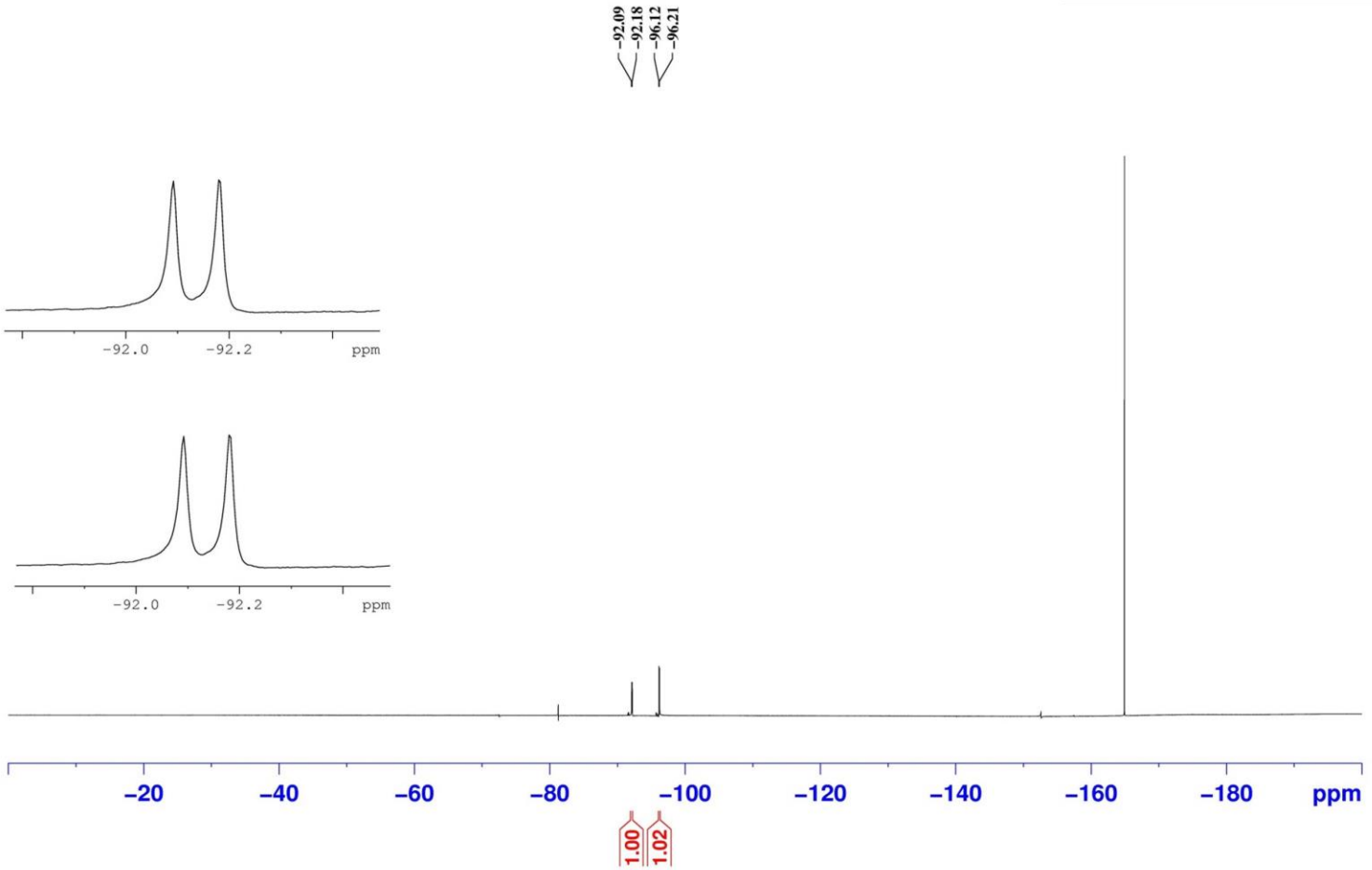
tert−butyl (5−(5−bromo−2−methoxyphenyl)−6,6−difluorohex−5−en−1−yl)carbamate
125 MHz, CDCl3



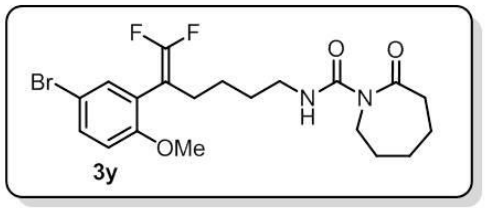


tert–butyl (5–(5–bromo–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl)carbamate
471 MHz, CDCl3

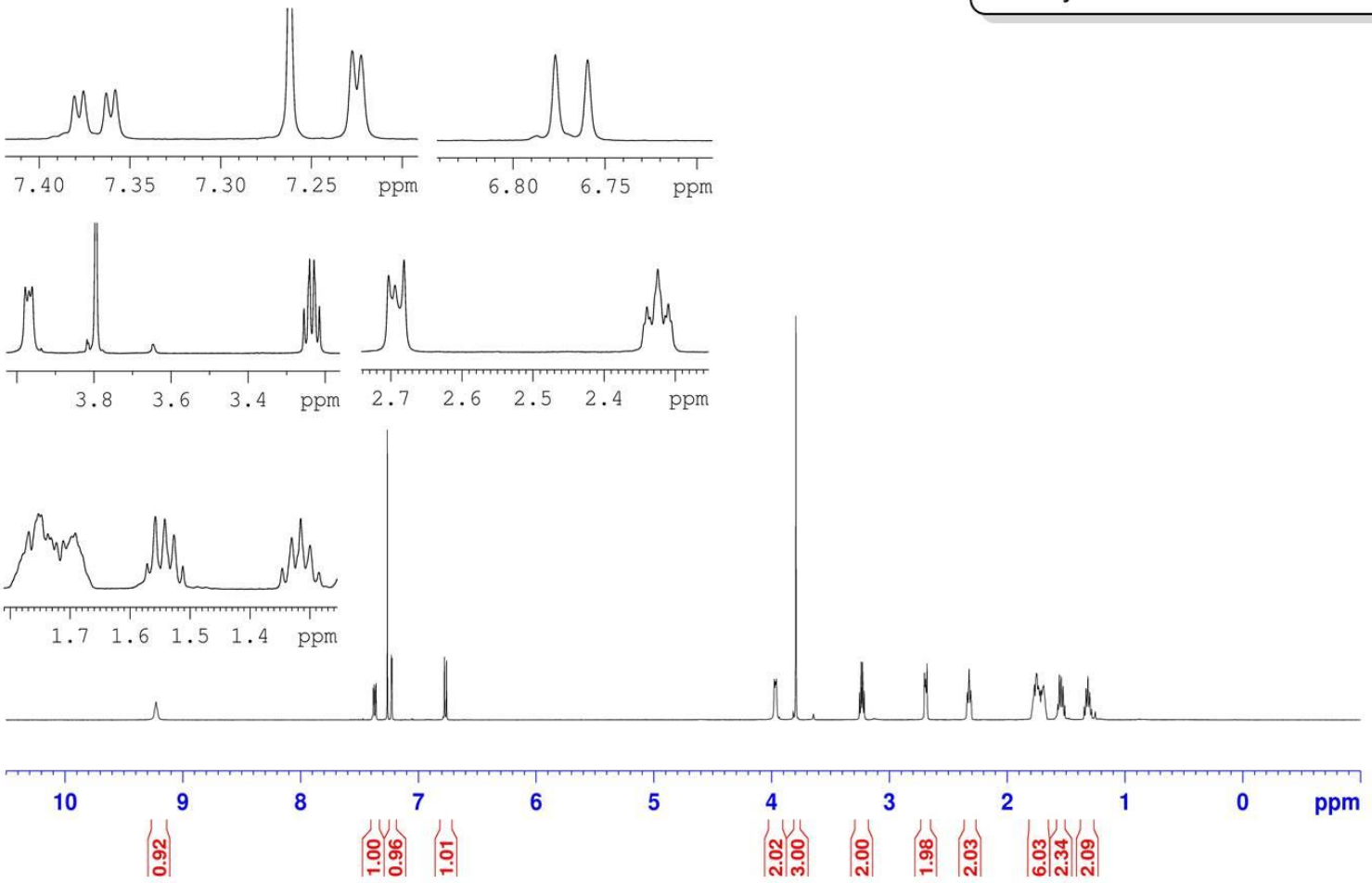




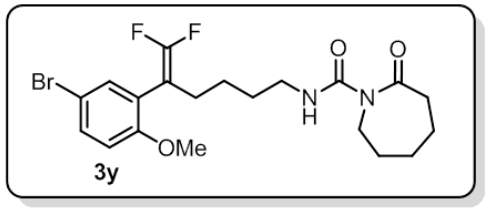
N–(5–(5–Bromo–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl)–2–oxoazepane–1–carboxamide
500 MHz, CDCl3

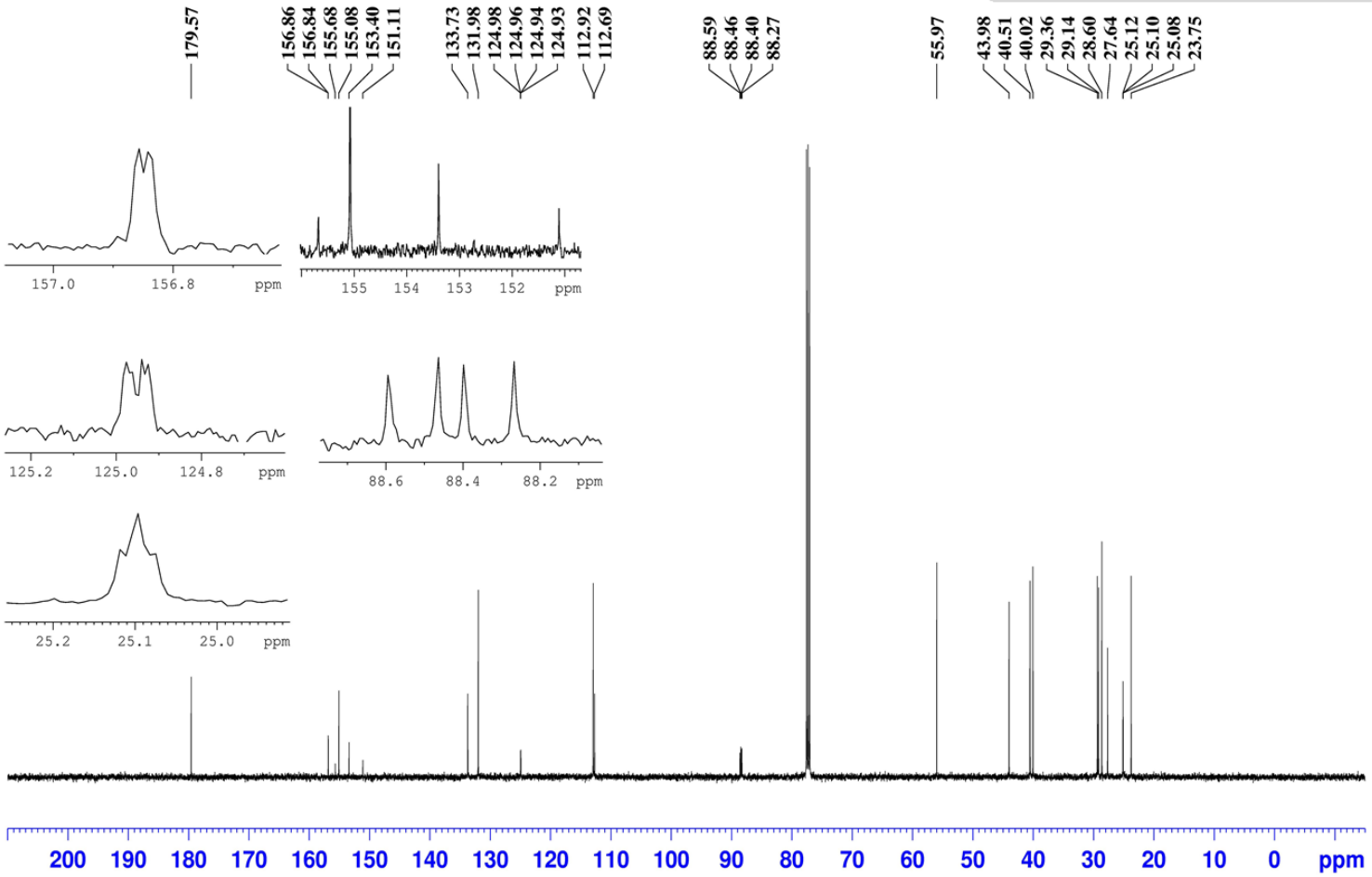


3y

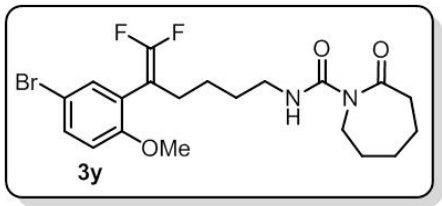


N–(5–(5–Bromo–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl)–2–oxoazepane–1–carboxamide
125 MHz, CDCl3

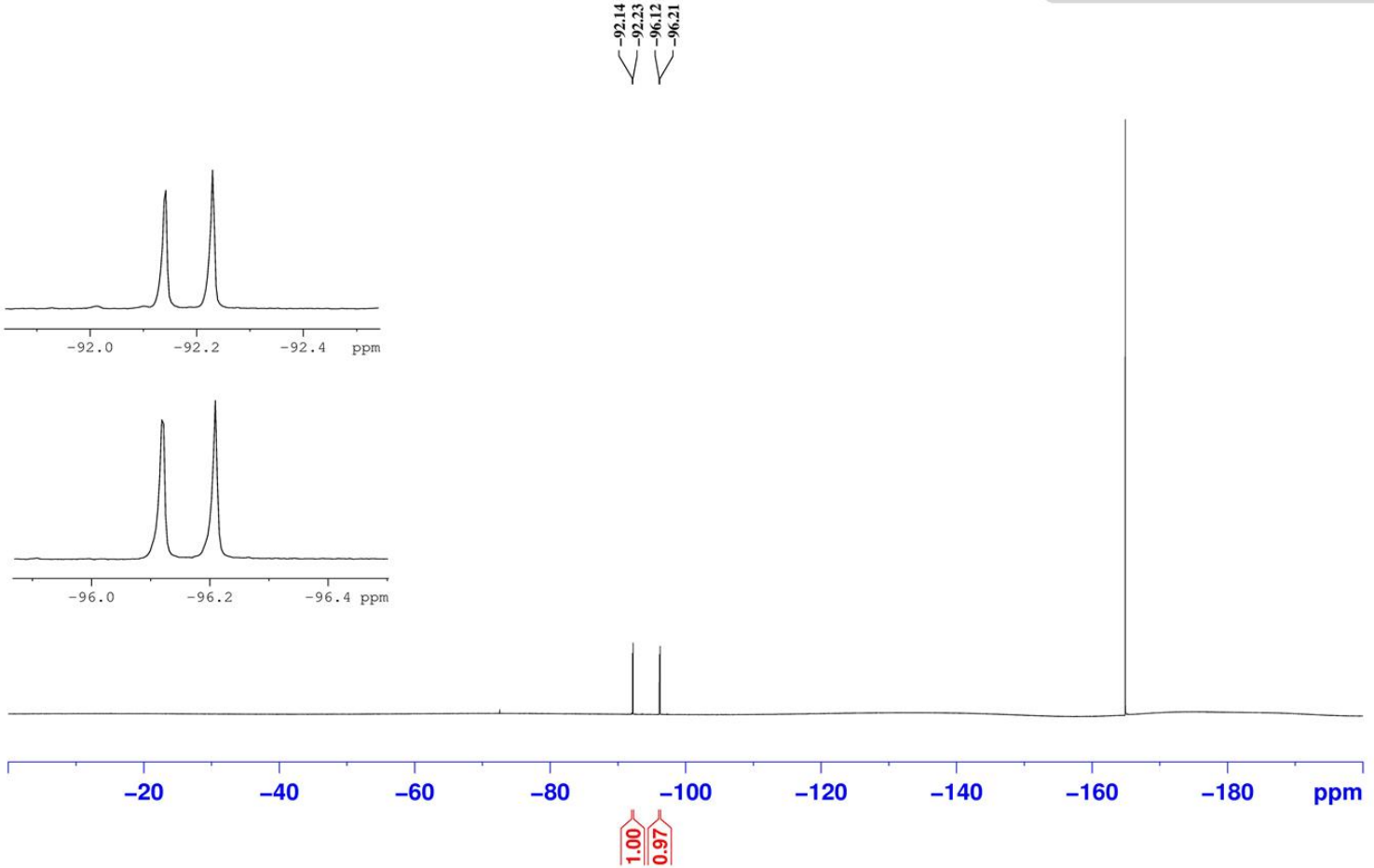




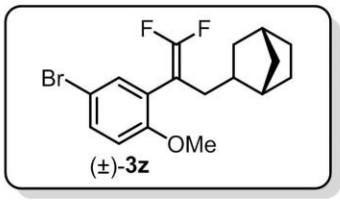
N–(5–(5–bromo–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl)–2–oxoazepane–1–carboxamide
471 MHz, CDCl3



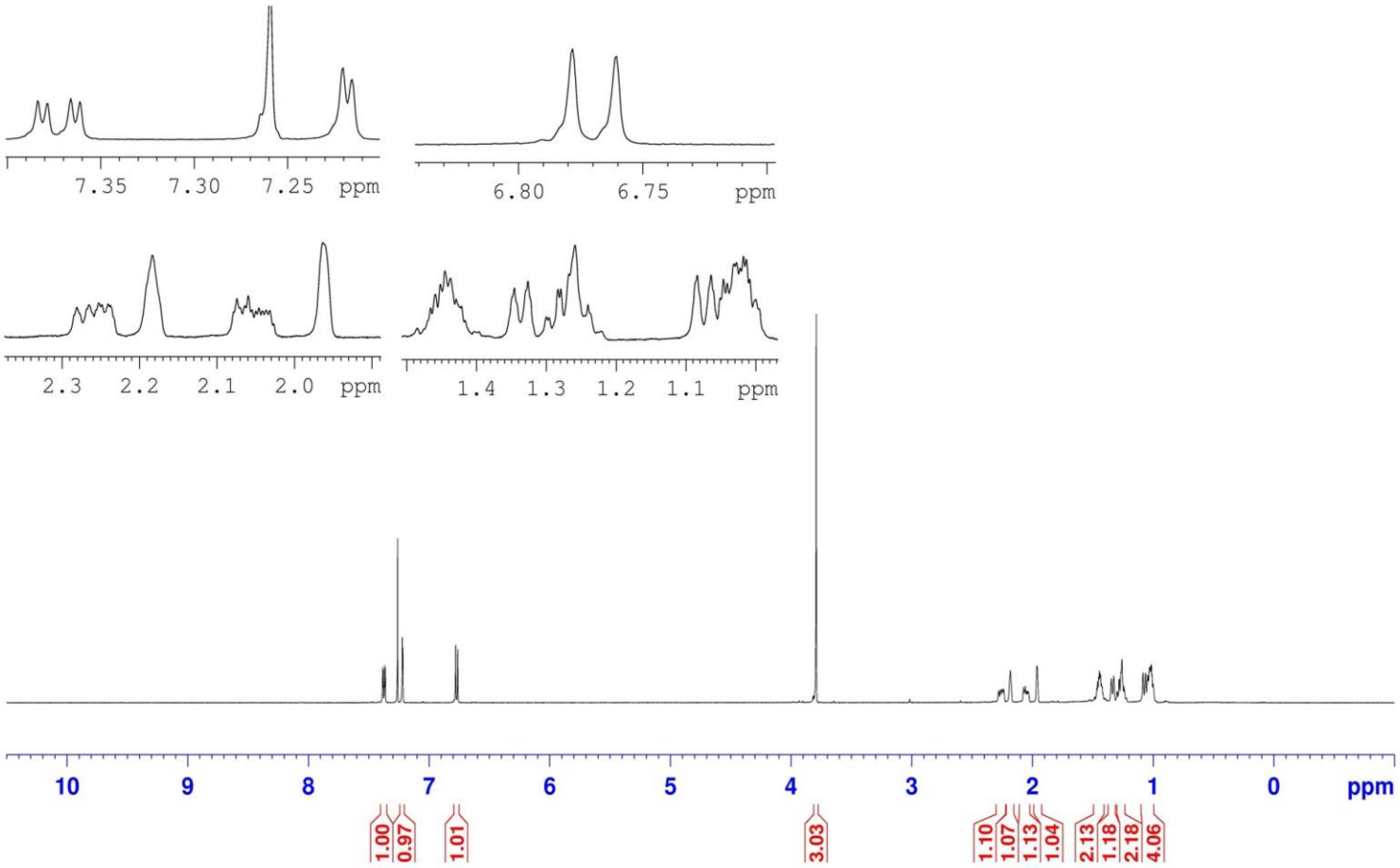
3y



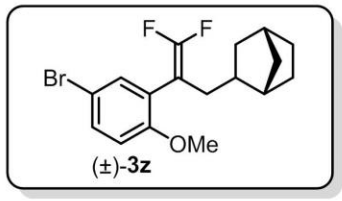
(±)−2−(2−(5−bromo−2−methoxyphenyl)−3,3−difluoroallyl)bicyclo[2.2.1]heptane
500 MHz, CDCl3



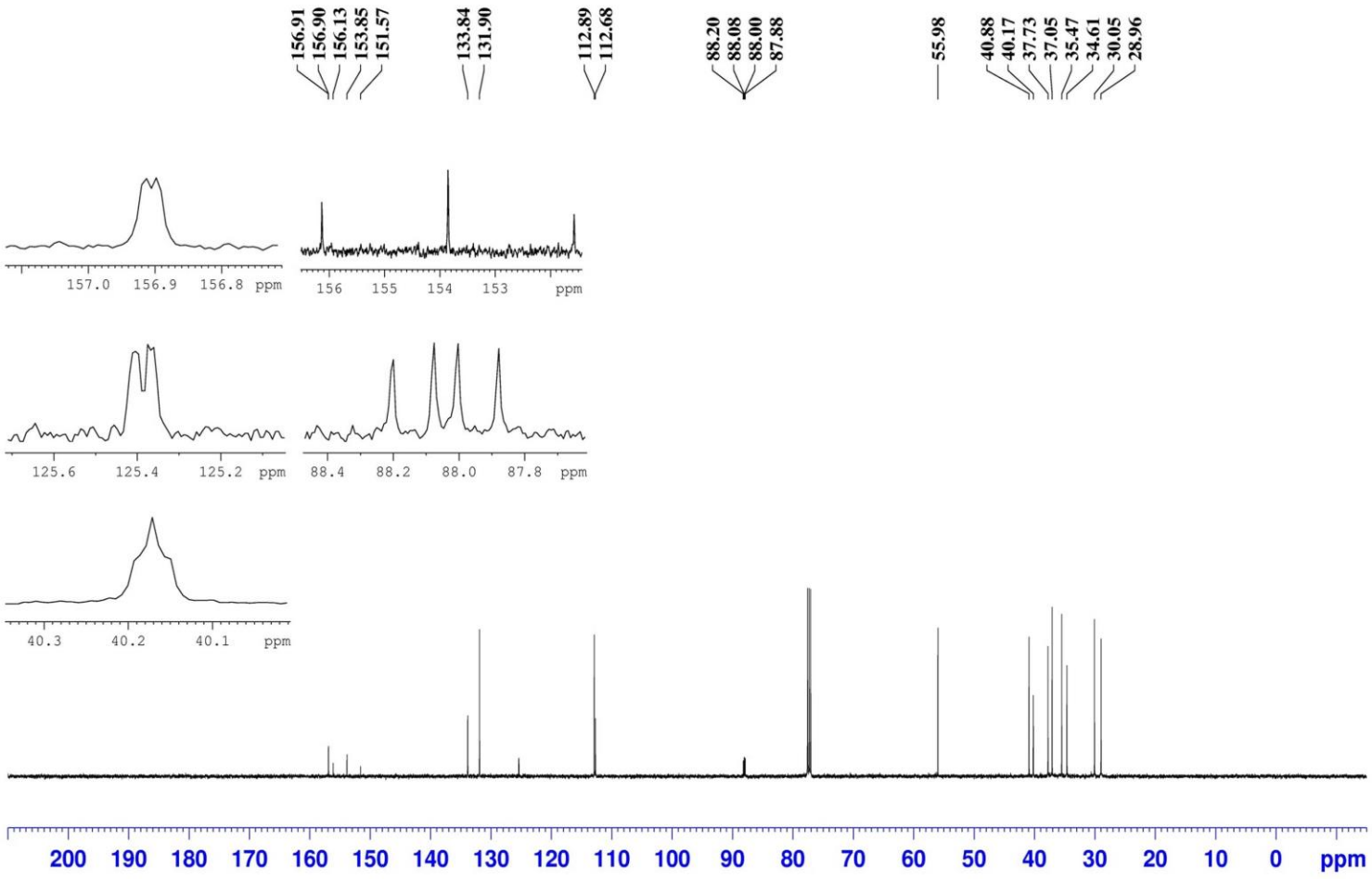
(±)-**3z**



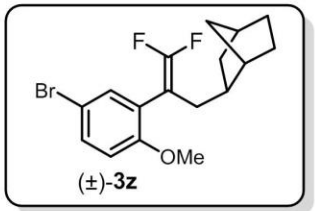
(±)−2−(2−(5−bromo−2−methoxyphenyl)−3,3−difluoroallyl)bicyclo[2.2.1]heptane
125 MHz, CDCl3



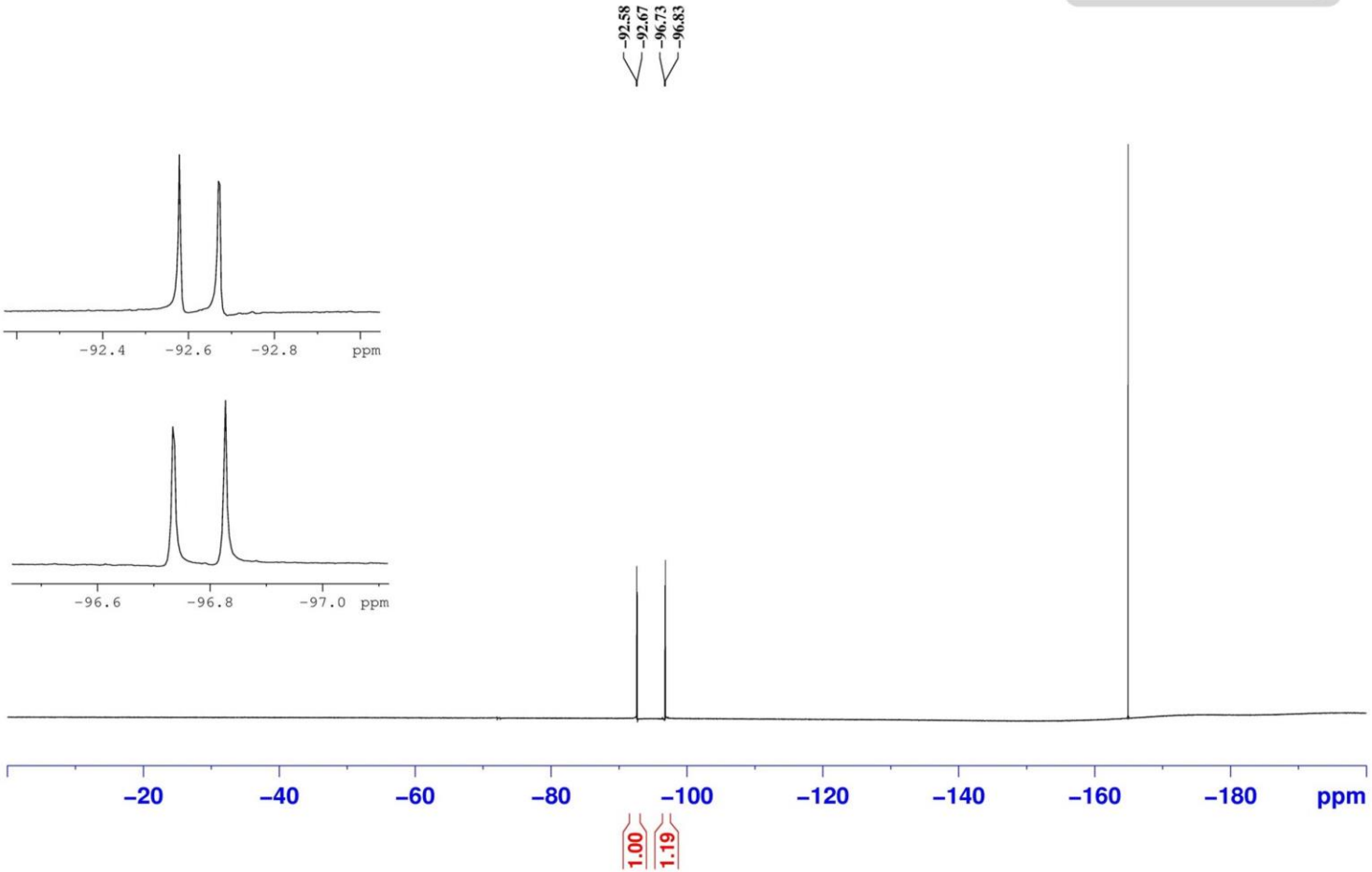
(±)-**3z**



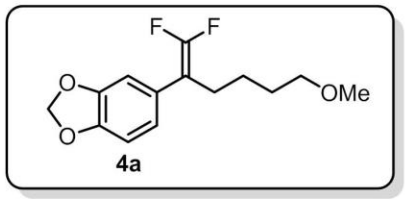
(±)−2−(2−(5−bromo−2−methoxyphenyl)−3,3−difluoroallyl)bicyclo[2.2.1]heptane
471 MHz, CDCl3



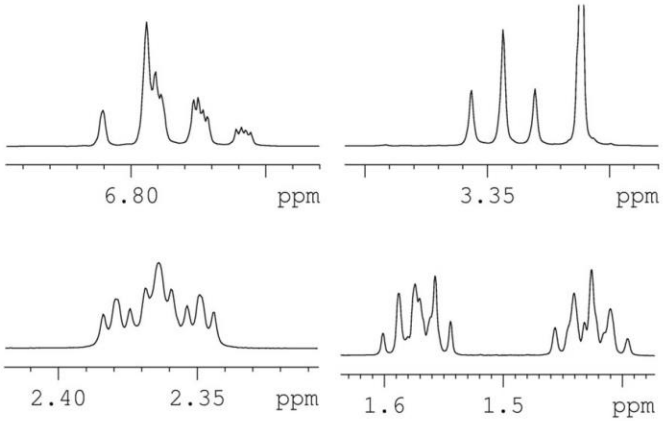
(±)-**3z**

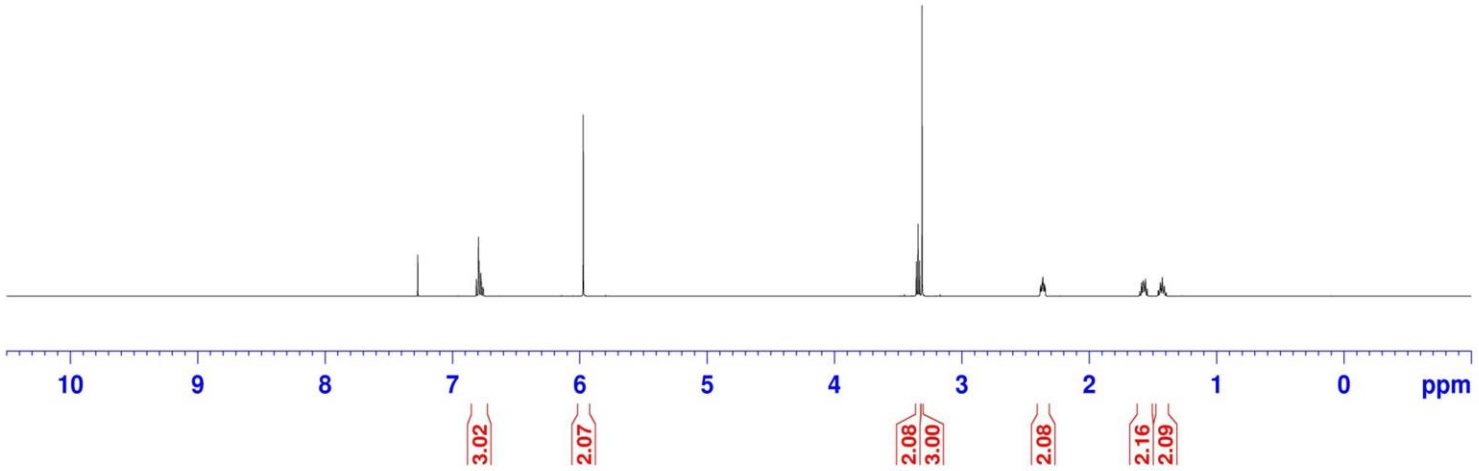


5–(1,1–difluoro–6–methoxyhex–1–en–2–yl)benzo[d][1,3]dioxole
500 MHz. CDCl3

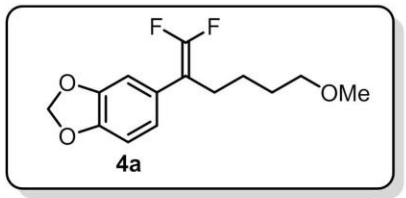


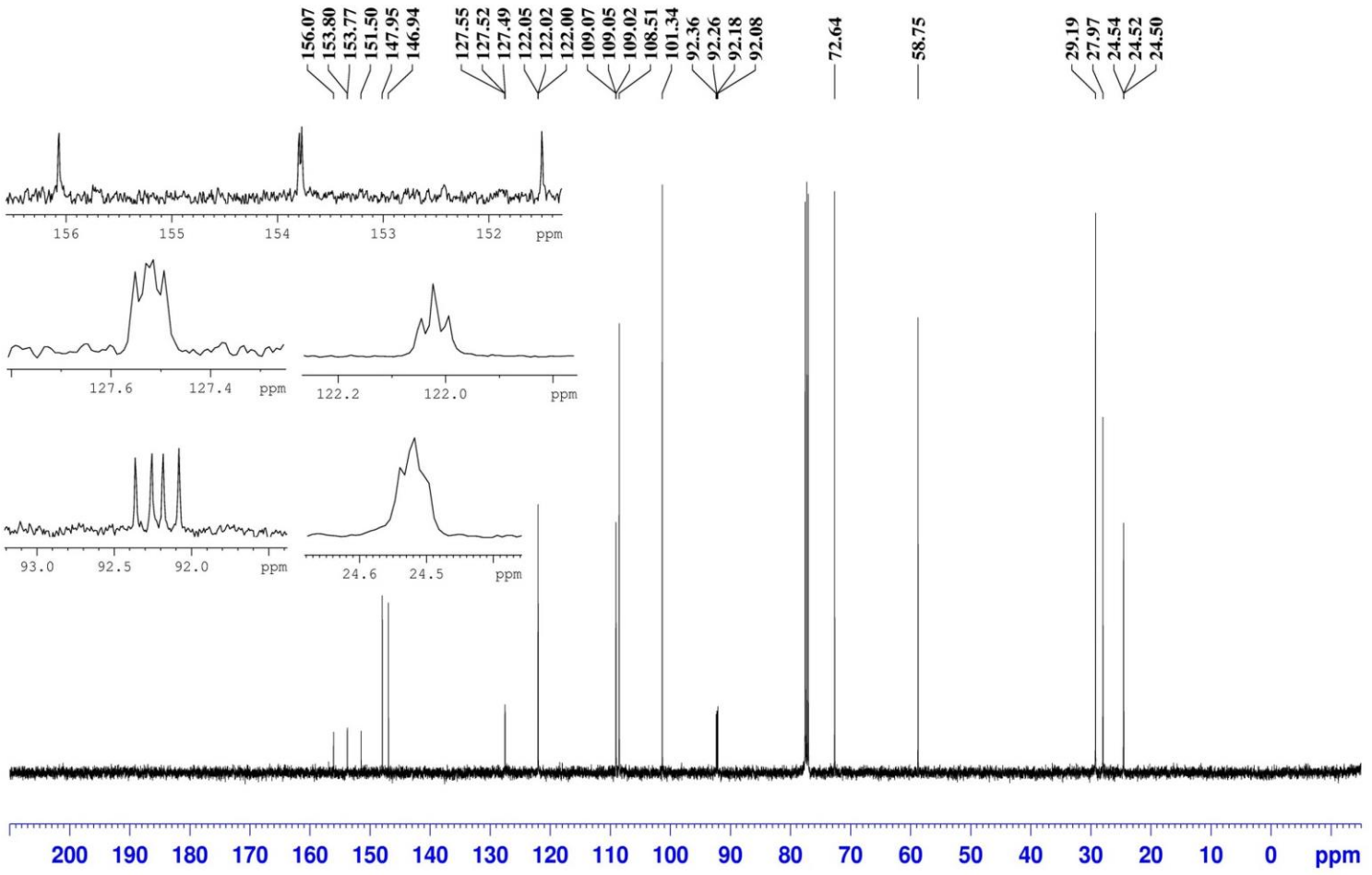
4a



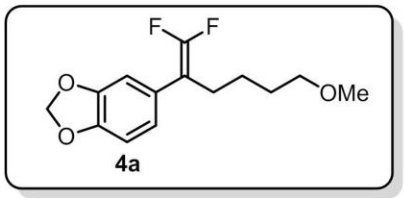


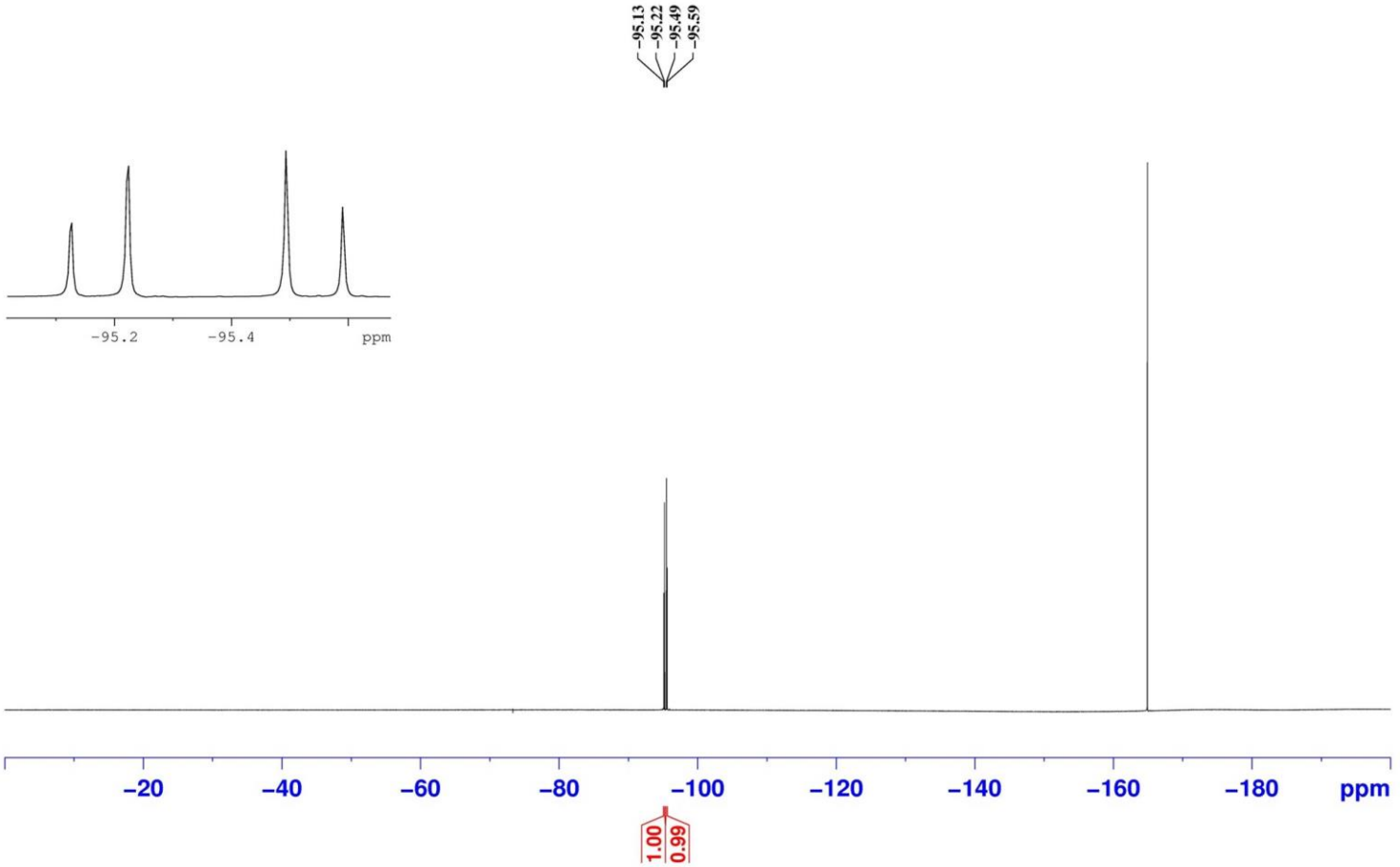
5–(1,1–difluoro–6–methoxyhex–1–en–2–yl)benzo[d][1,3]dioxole
125 MHz, CDCl3



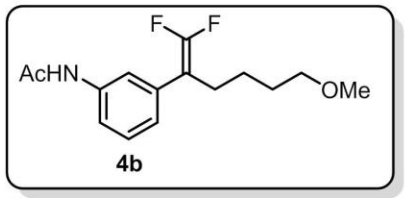


5–(1,1–Difluoro–6–methoxyhex–1–en–2–yl)benzo[d][1,3]dioxole
471 MHz, CDCl3

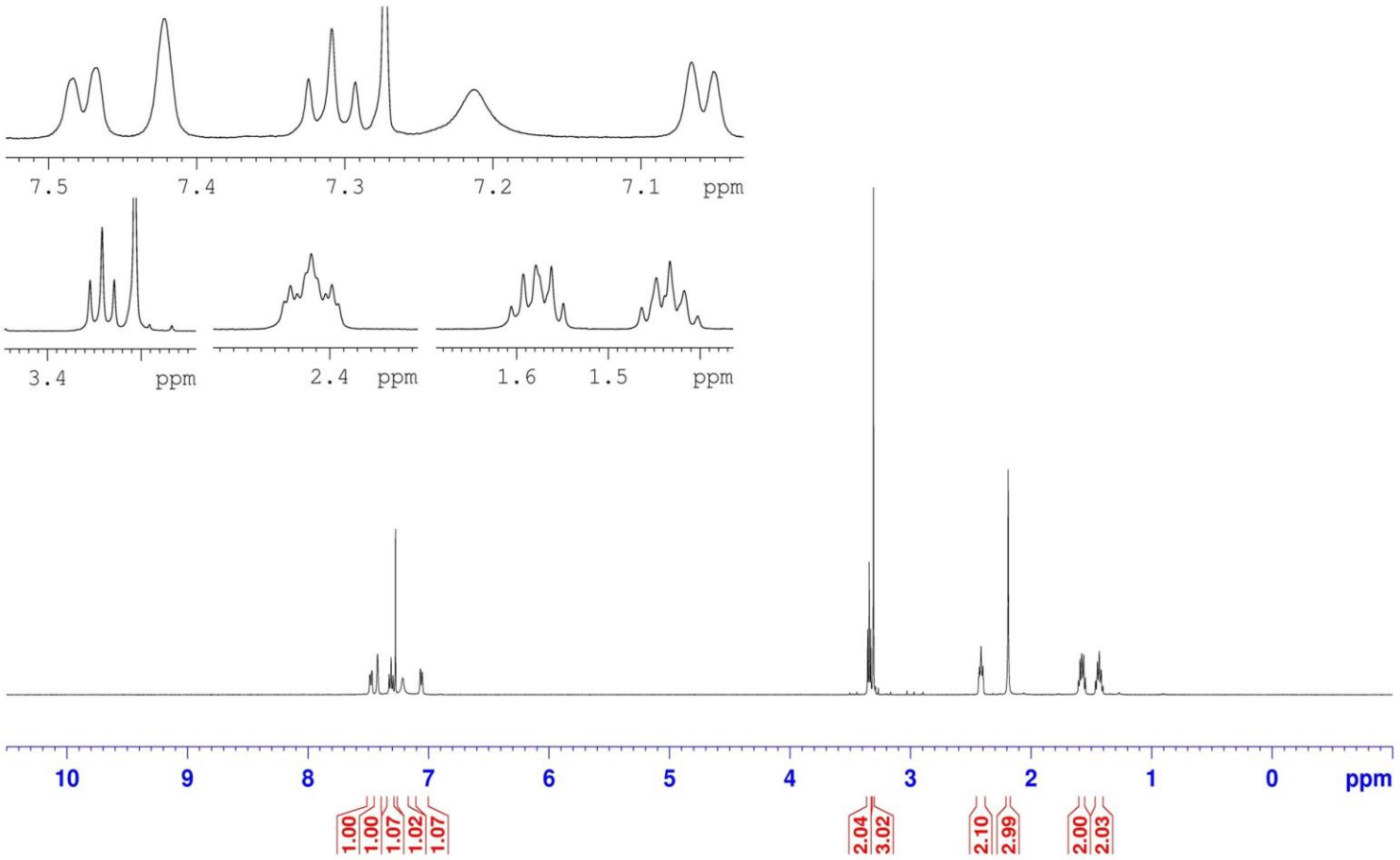




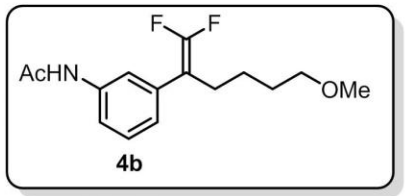
N–(3–(1,1–difluoro–6–methoxyhex–1–en–2–yl)phenyl)acetamide
500 MHz, CDCl3

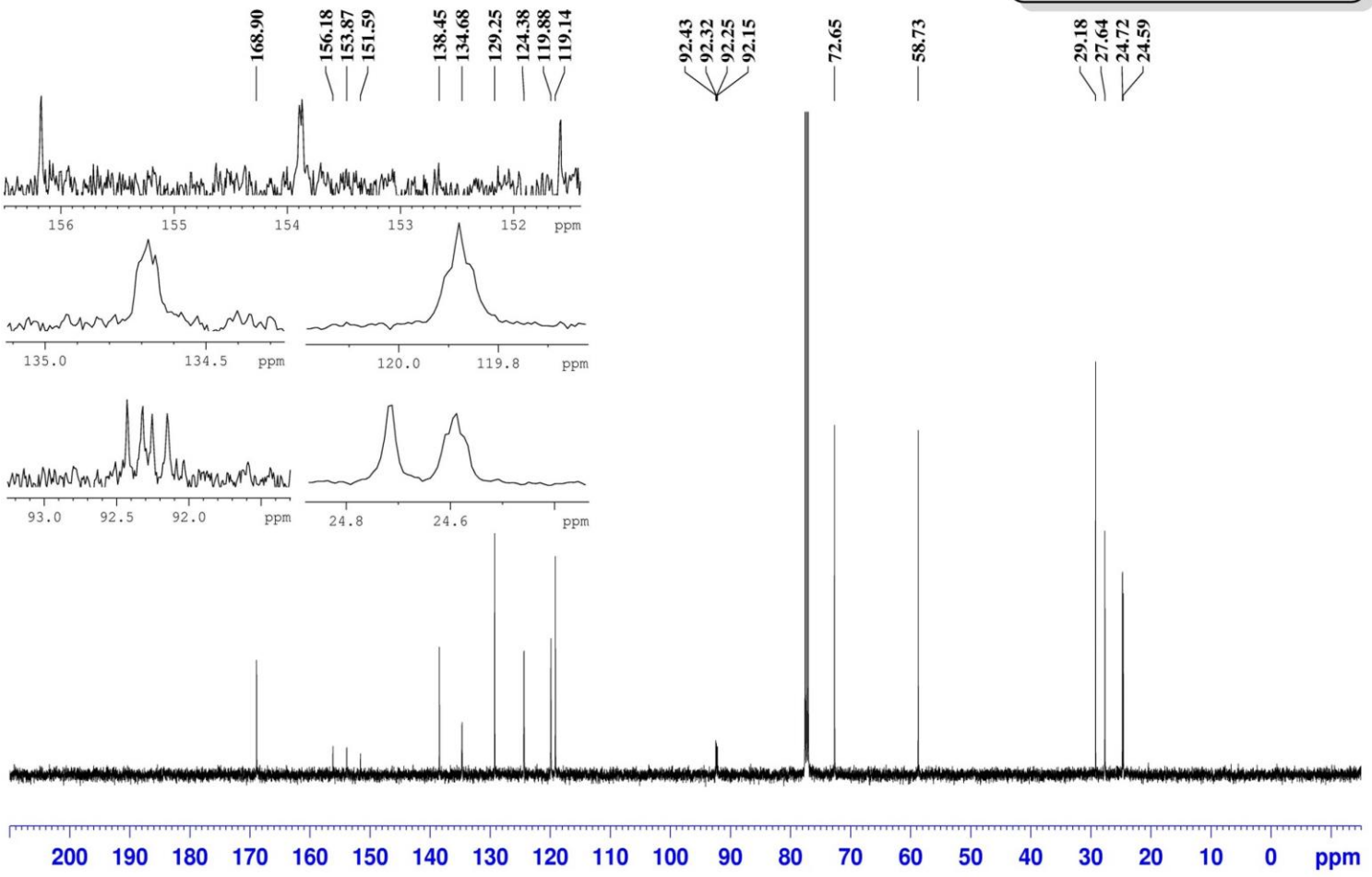


4b

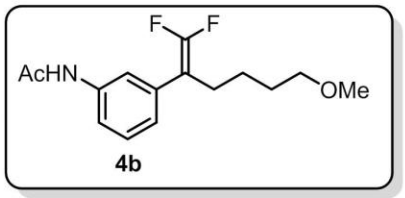


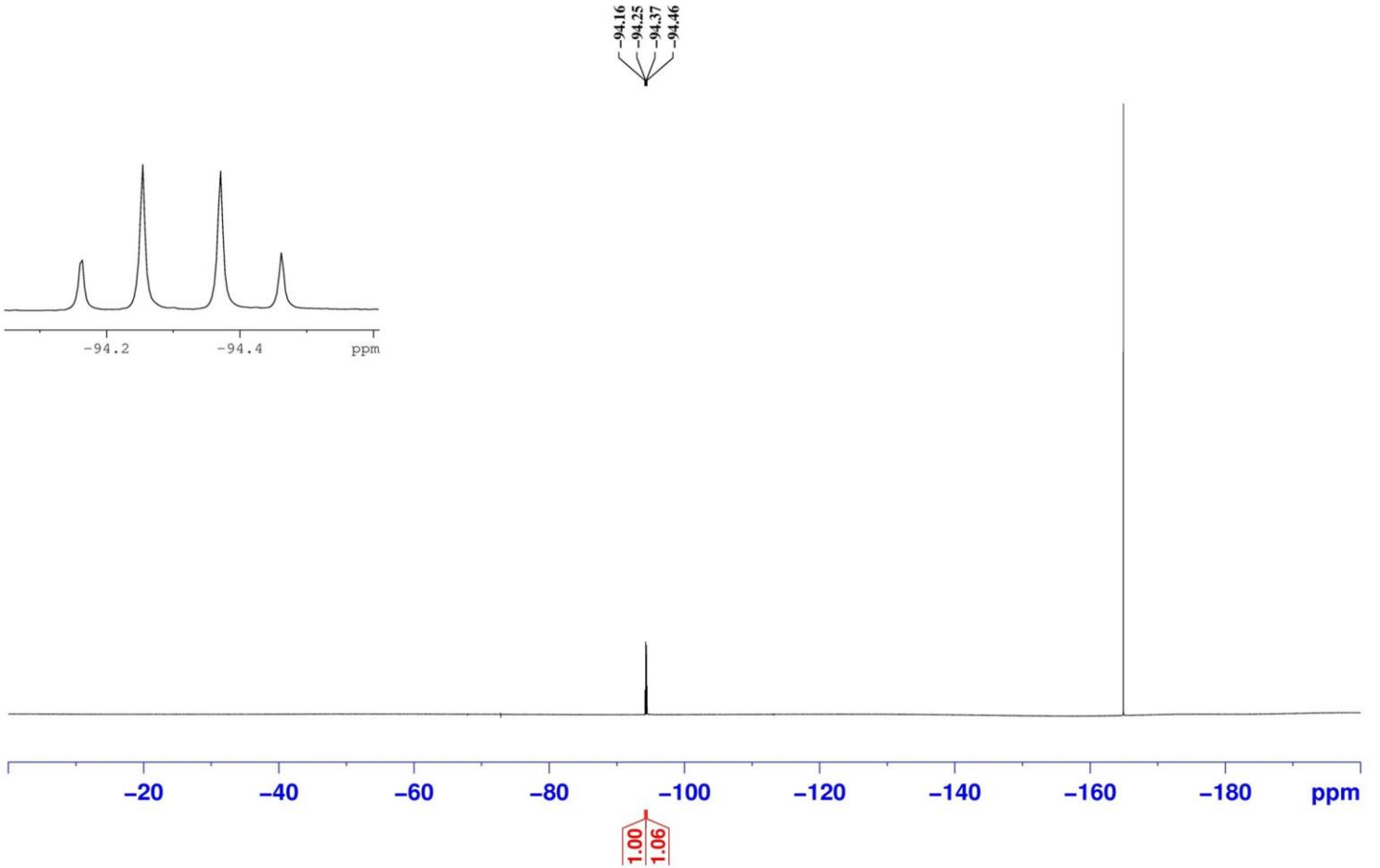
N–(3–(1,1–difluoro–6–methoxyhex–1–en–2–yl)phenyl)acetamide
125 MHz, CDCl3



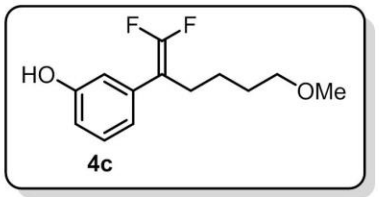


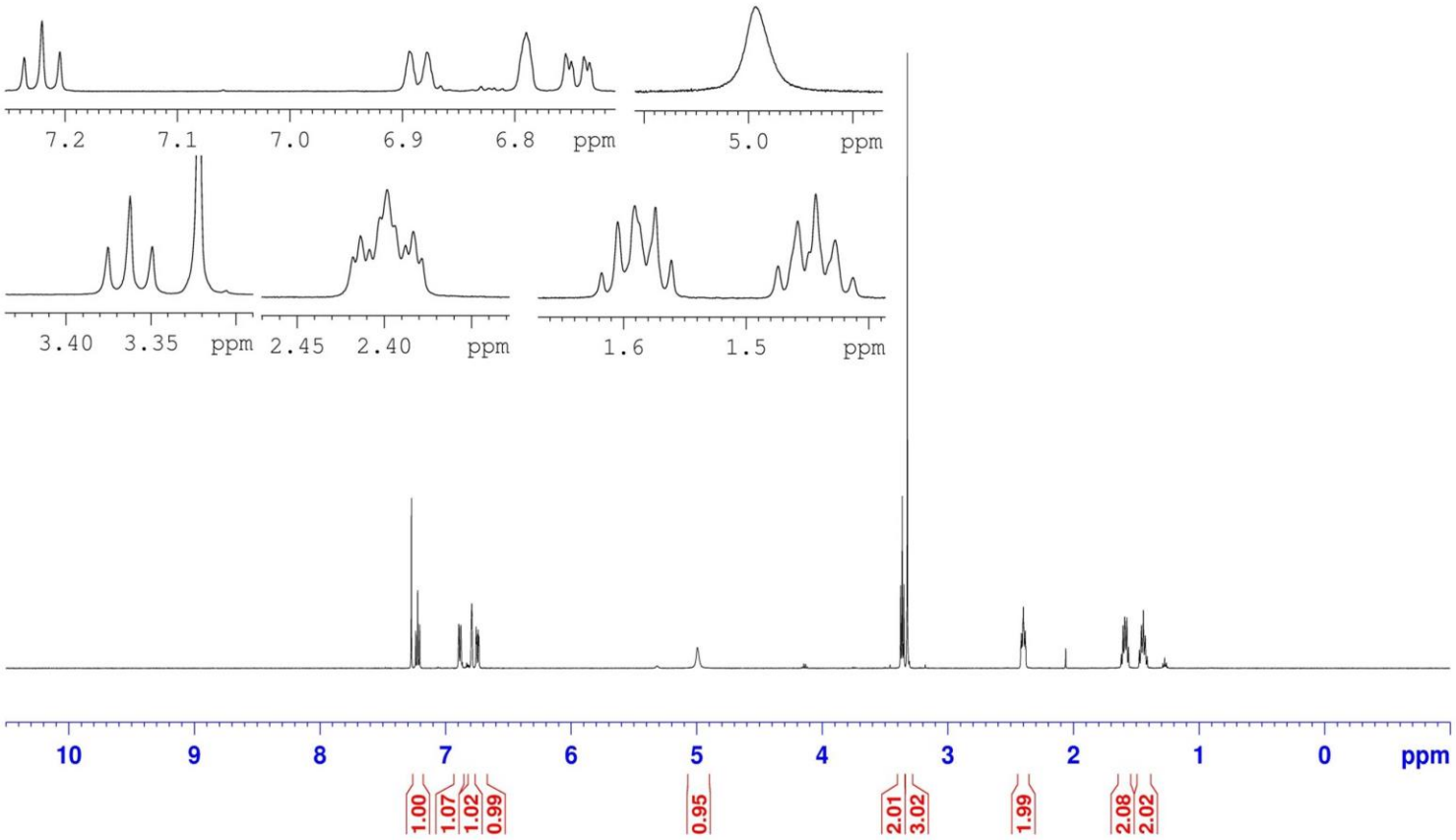
N–(3–(1,1–difluoro–6–methoxyhex–1–en–2–yl)phenyl)acetamide
471 MHz, CDCl3



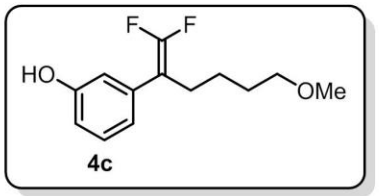


3–(1,1–difluoro–6–methoxyhex–1–en–2–yl)phenol
500 MHz, CDCl3

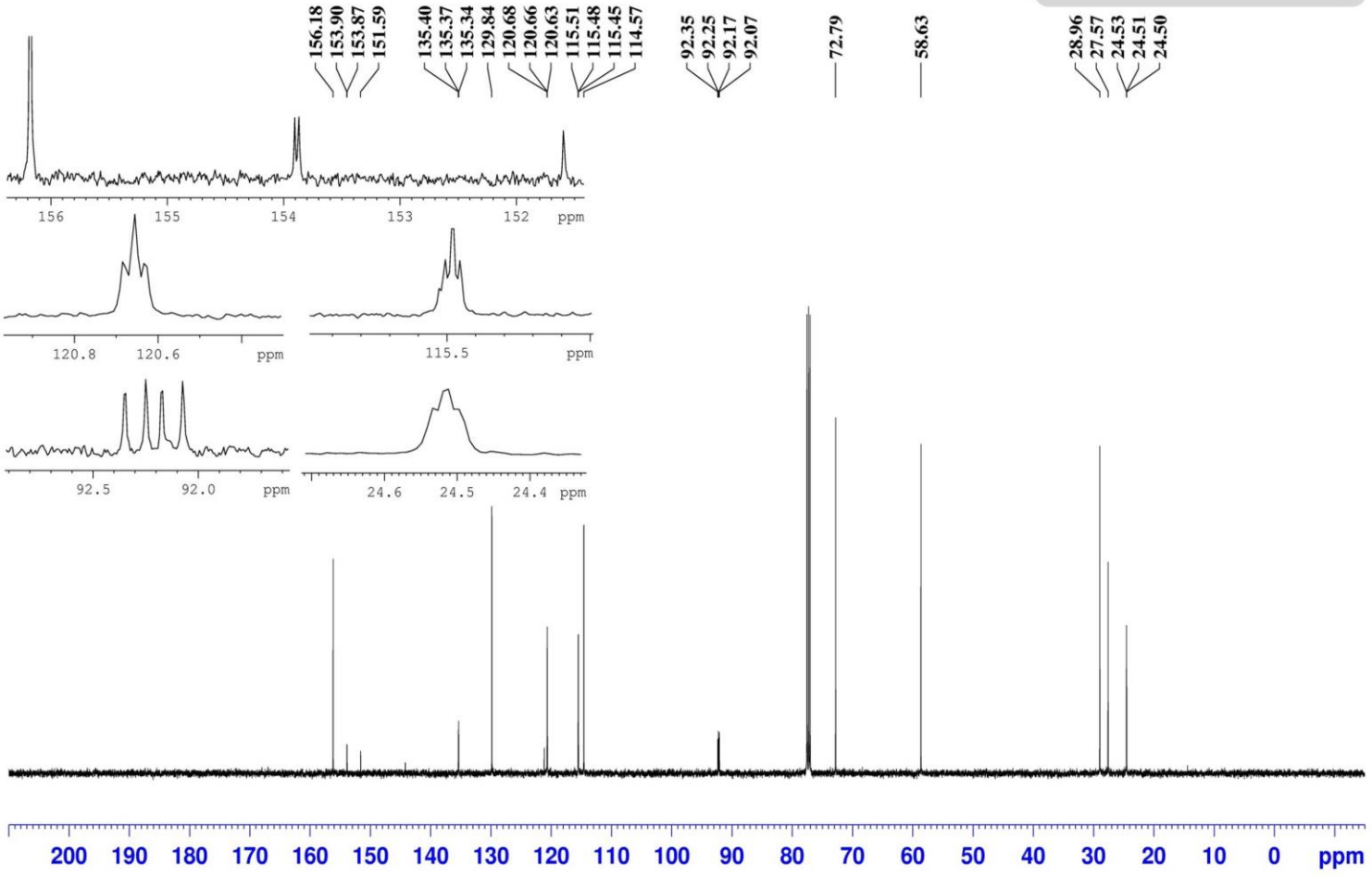




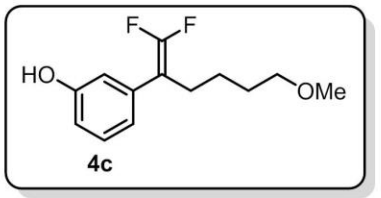
3–(1,1–difluoro–6–methoxyhex–1–en–2–yl)phenol
125 MHz, CDCl3



4c



3–(1,1–difluoro–6–methoxyhex–1–en–2–yl)phenol
471 MHz, CDCl3



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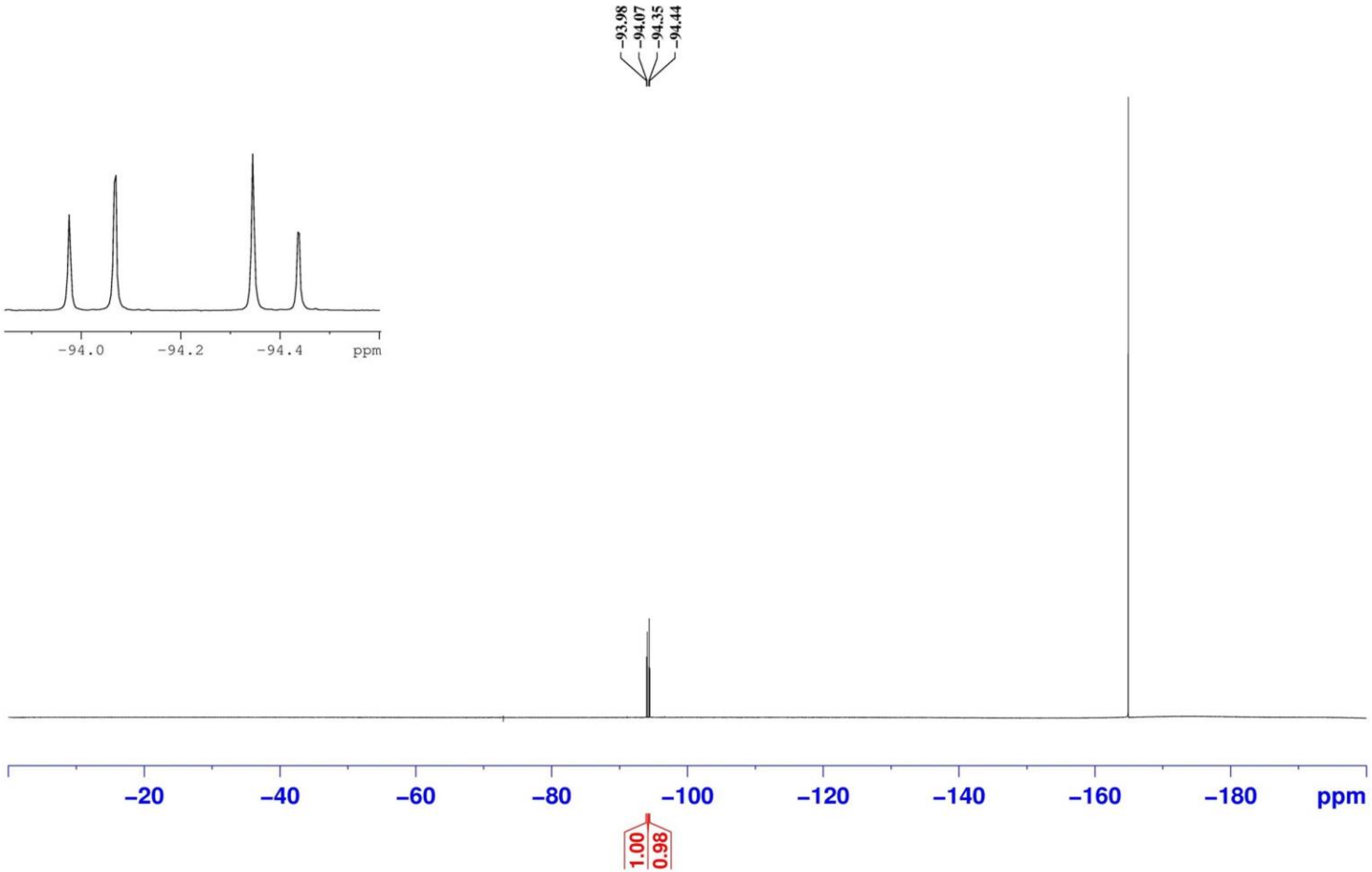
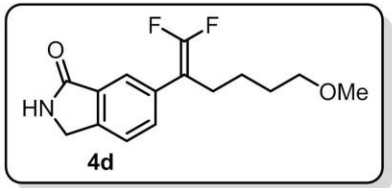
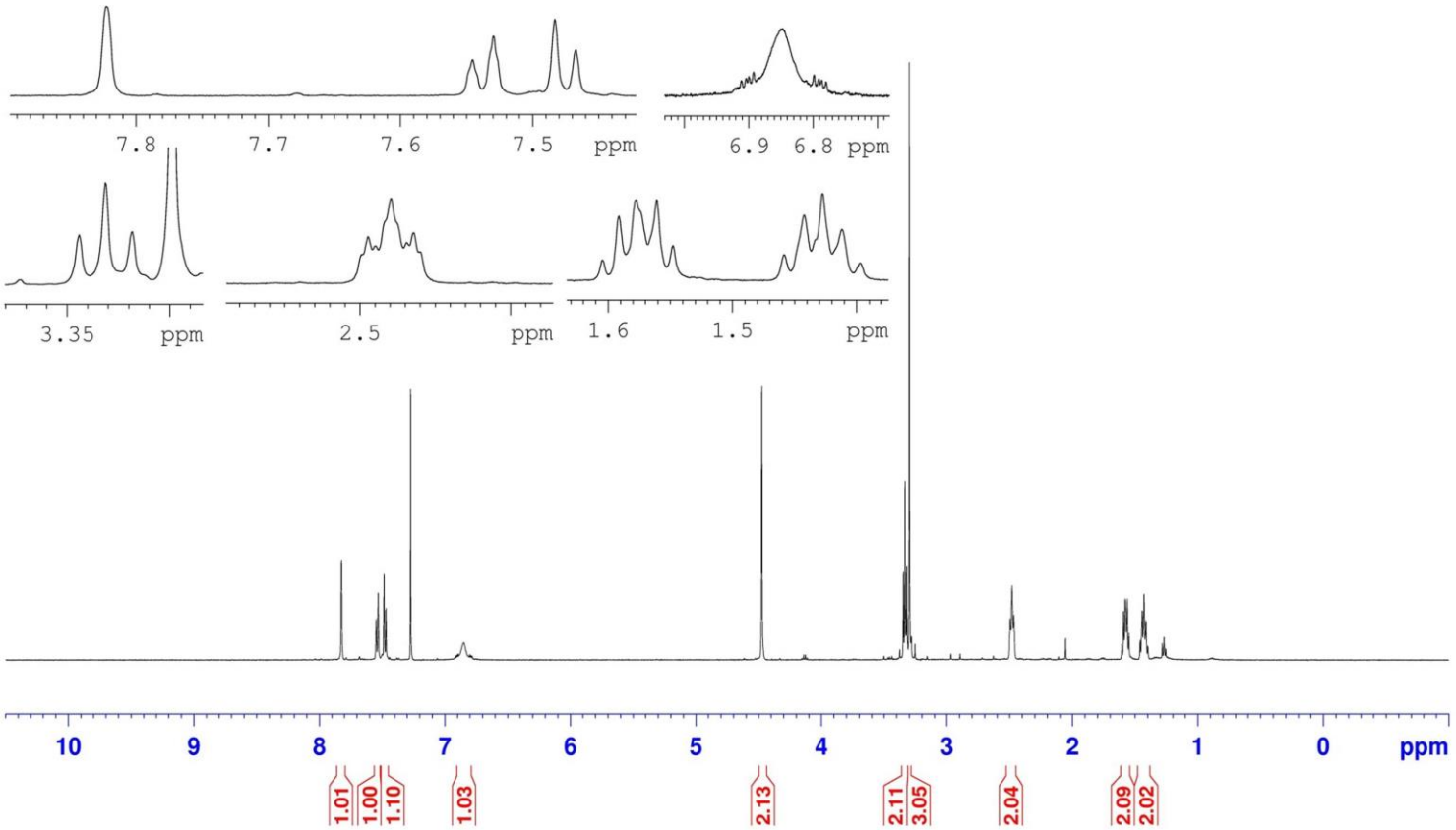


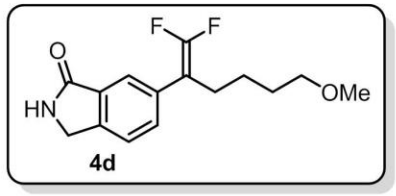
6–(1,1–difluoro–6–methoxyhex–1–en–2–yl)isoindolin–1–one
500 MHz, CDCl3



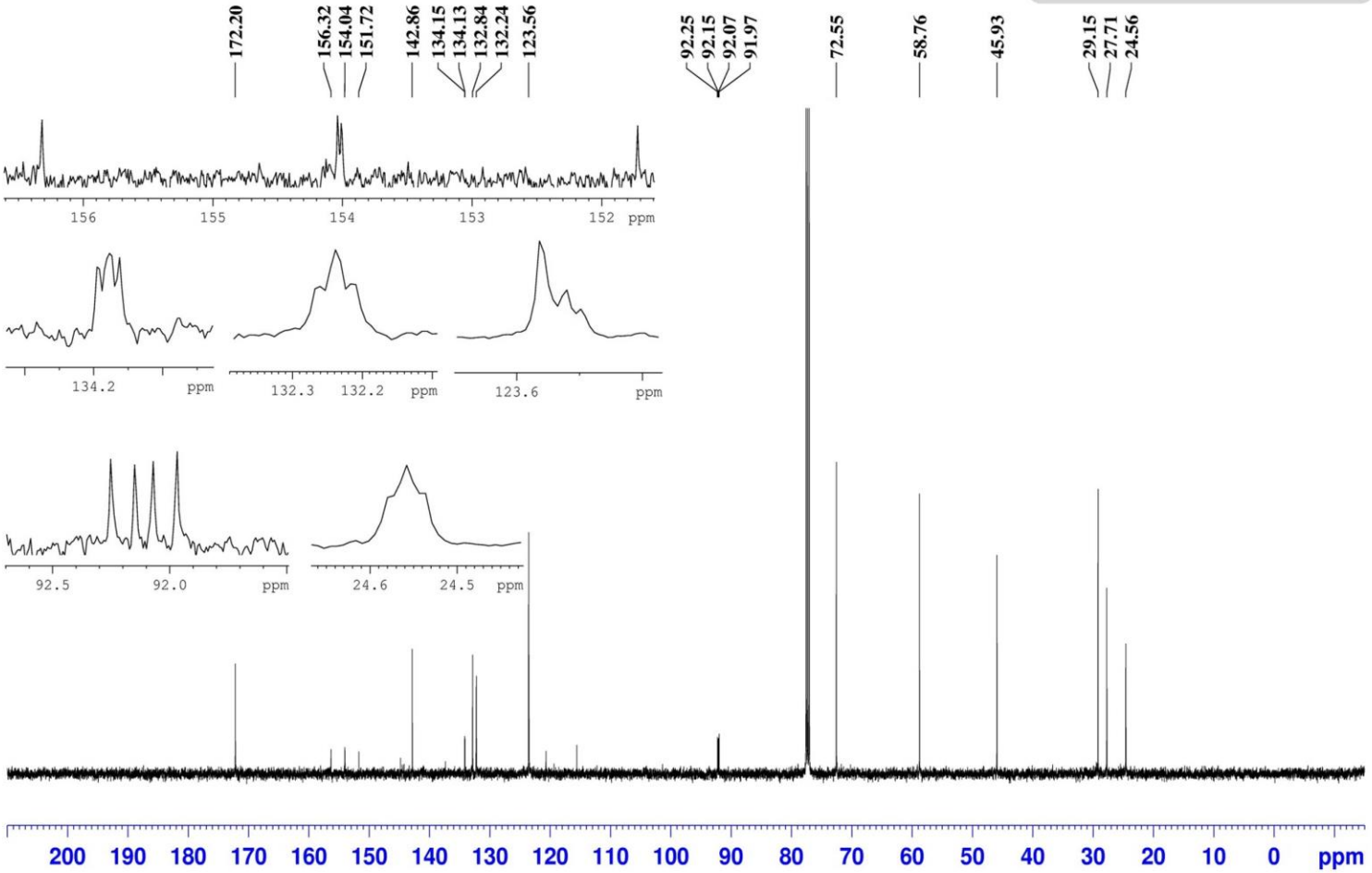
4d



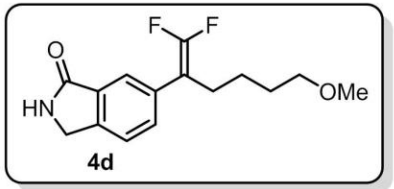
6-(1,1-difluoro-6-methoxyhex-1-en-2-yl)isoindolin-1-one
125 MHz, CDCl3

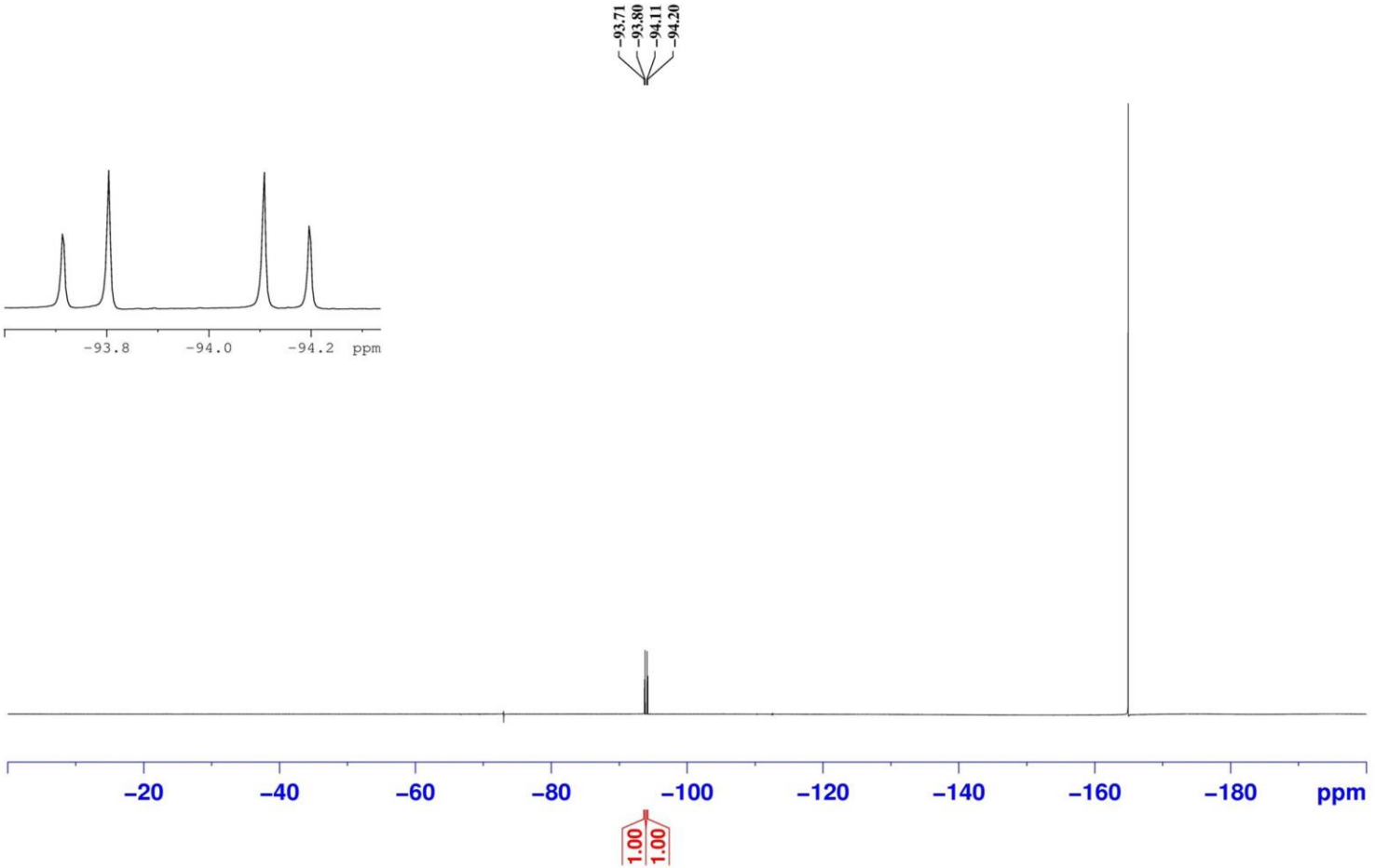


4d

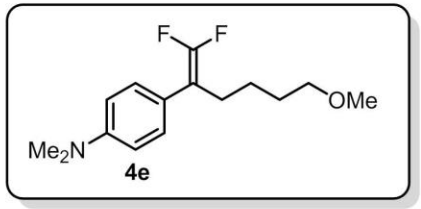


6–(1,1–difluoro–6–methoxyhex–1–en–2–yl)isoindolin–1–one
471 MHz, CDCl3

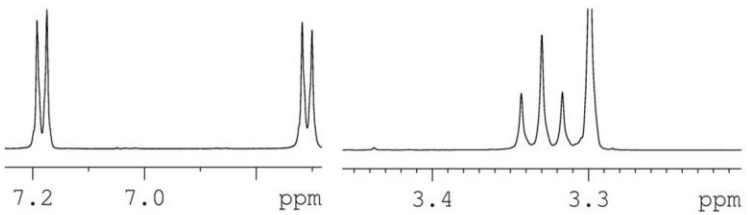


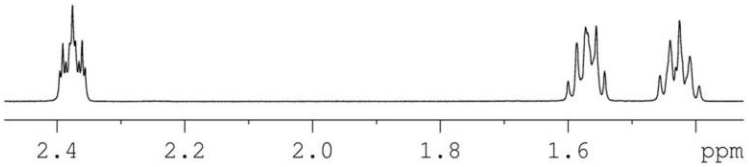


4–(1,1–difluoro–6–methoxyhex–1–en–2–yl)–N,N–dimethylaniline
500 MHz, CDCl3

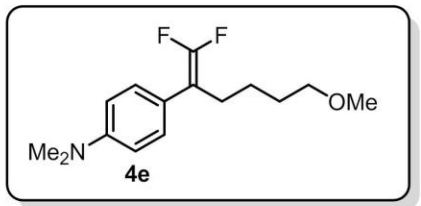


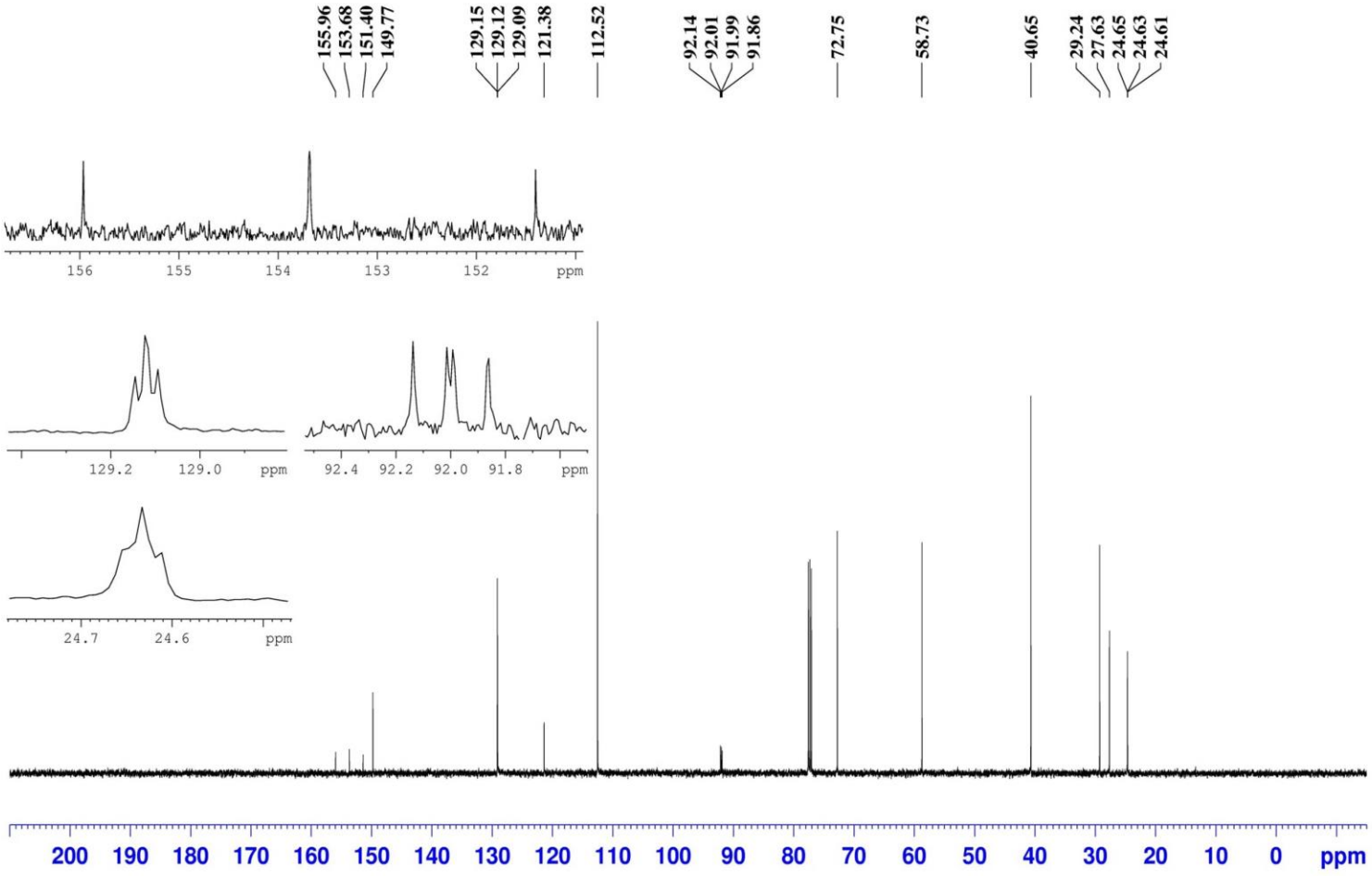
4e



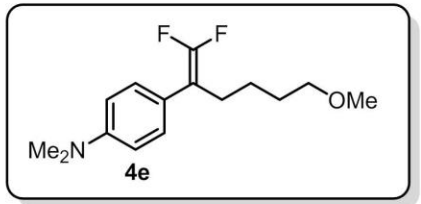


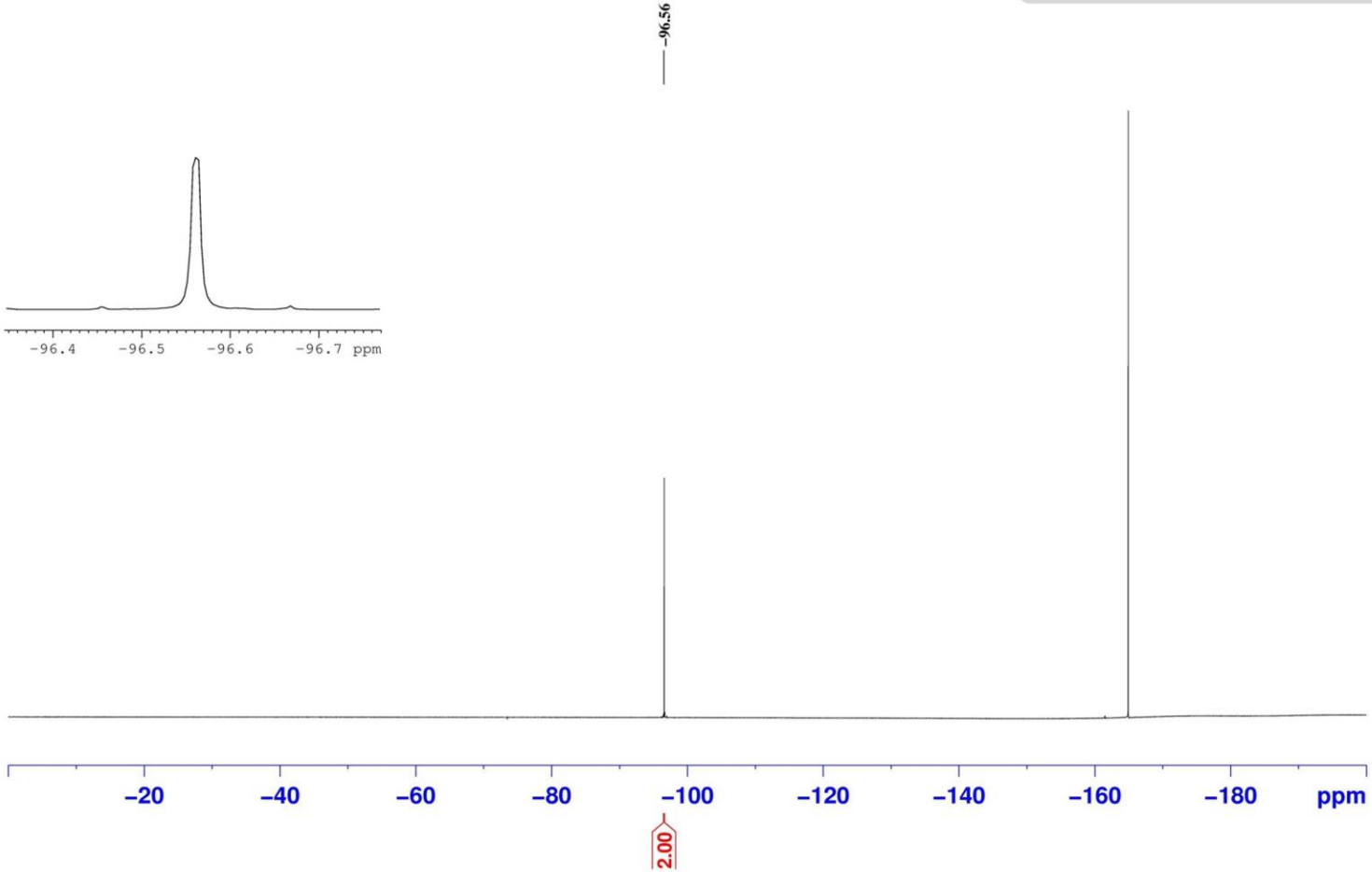
4–(1,1–difluoro–6–methoxyhex–1–en–2–yl)–N,N–dimethylaniline
125 MHz, CDCl3



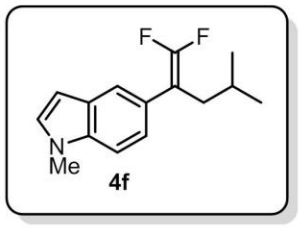


4–(1,1–difluoro–6–methoxyhex–1–en–2–yl)–N,N–dimethylaniline
471 MHz, CDCl3

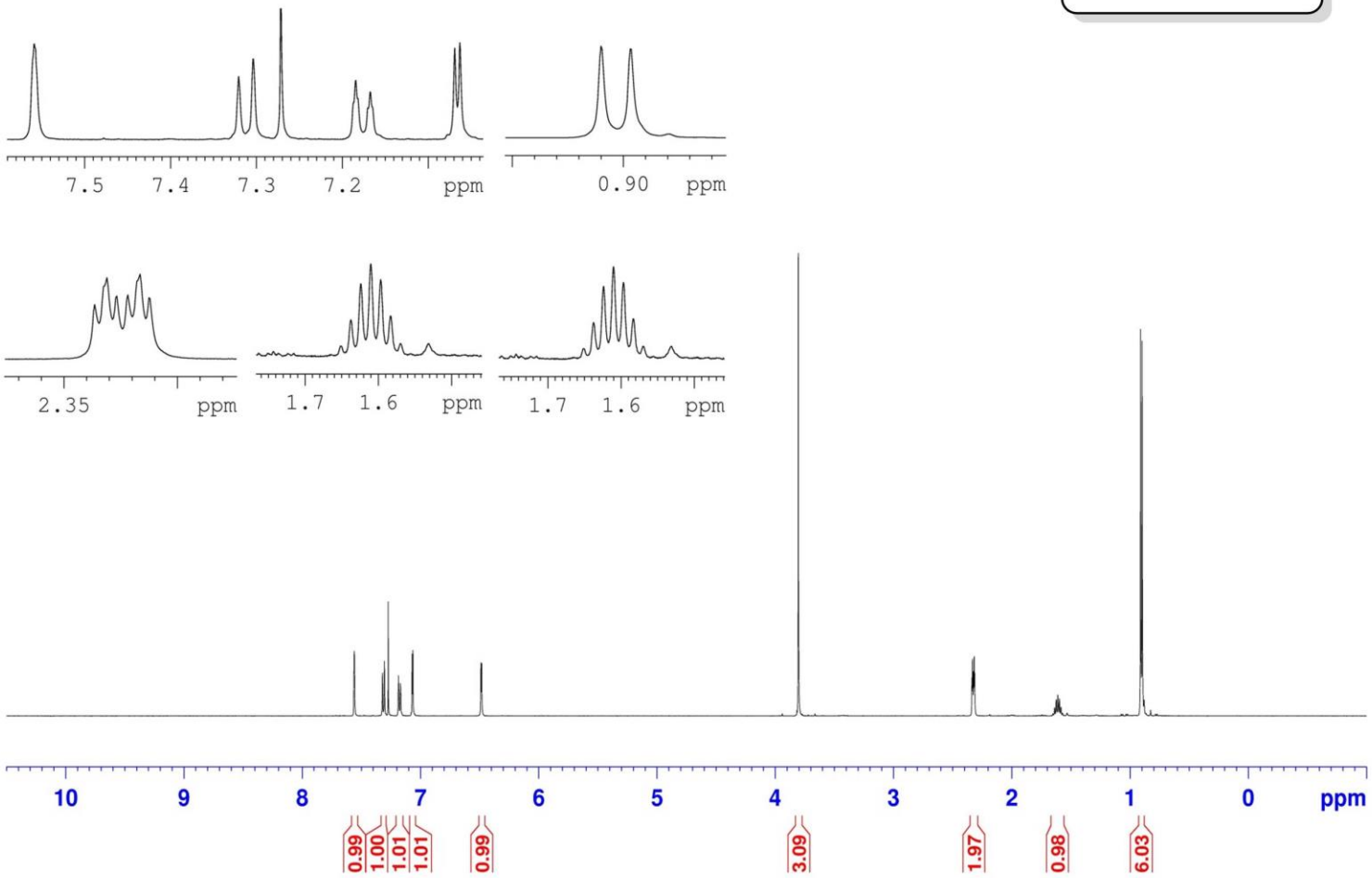




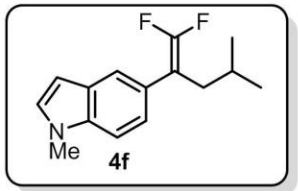
5–(1,1–difluoro–4–methylpent–1–en–2–yl)–1–methyl–1H–indole
500 MHz, CDCl3

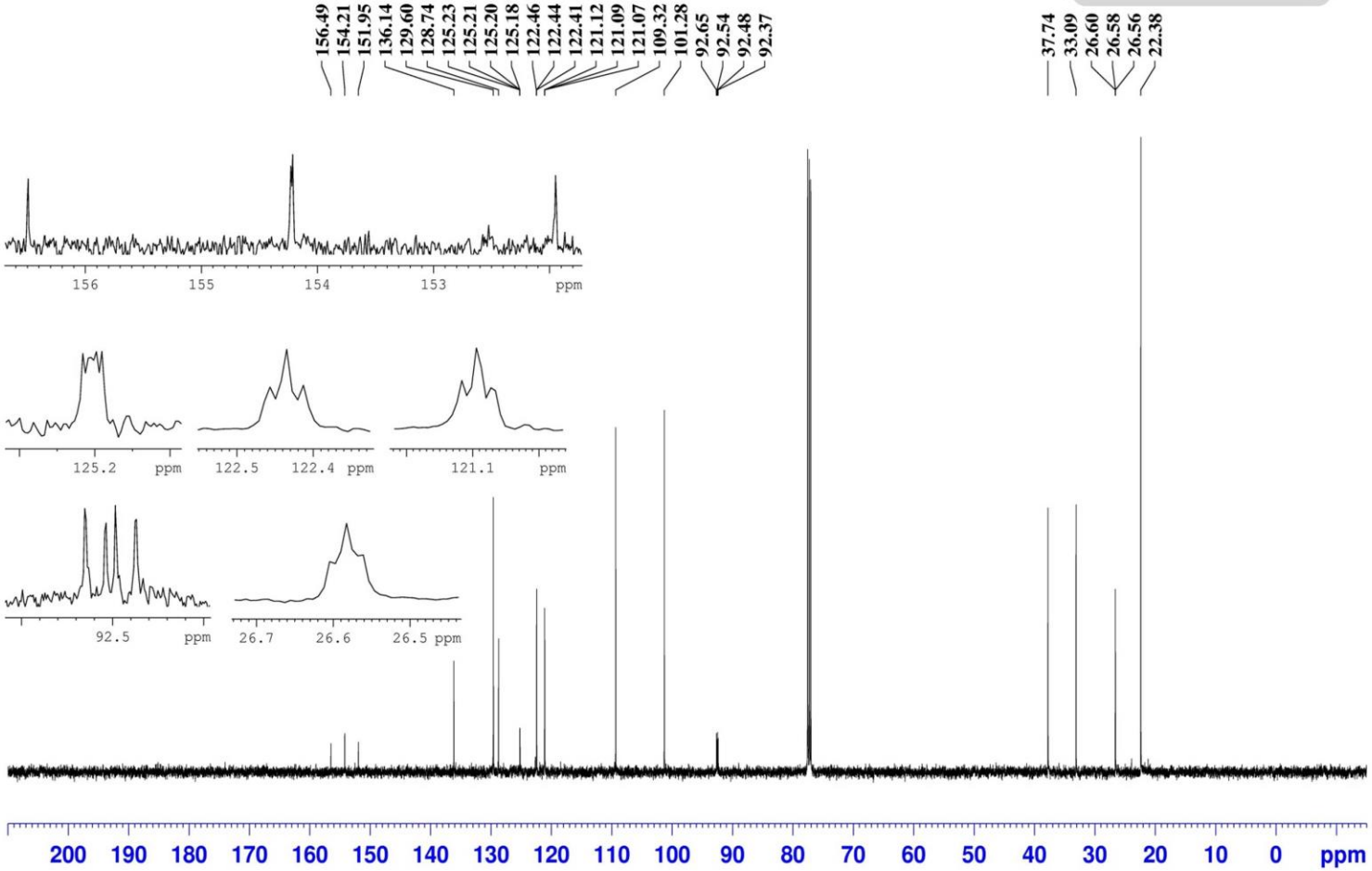


4f

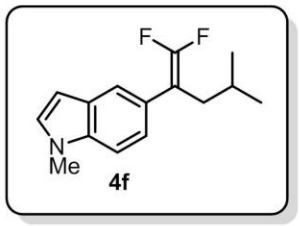


5–(1,1–difluoro–4–methylpent–1–en–2–yl)–1–methyl–1H–indole
125 MHz, CDCl3

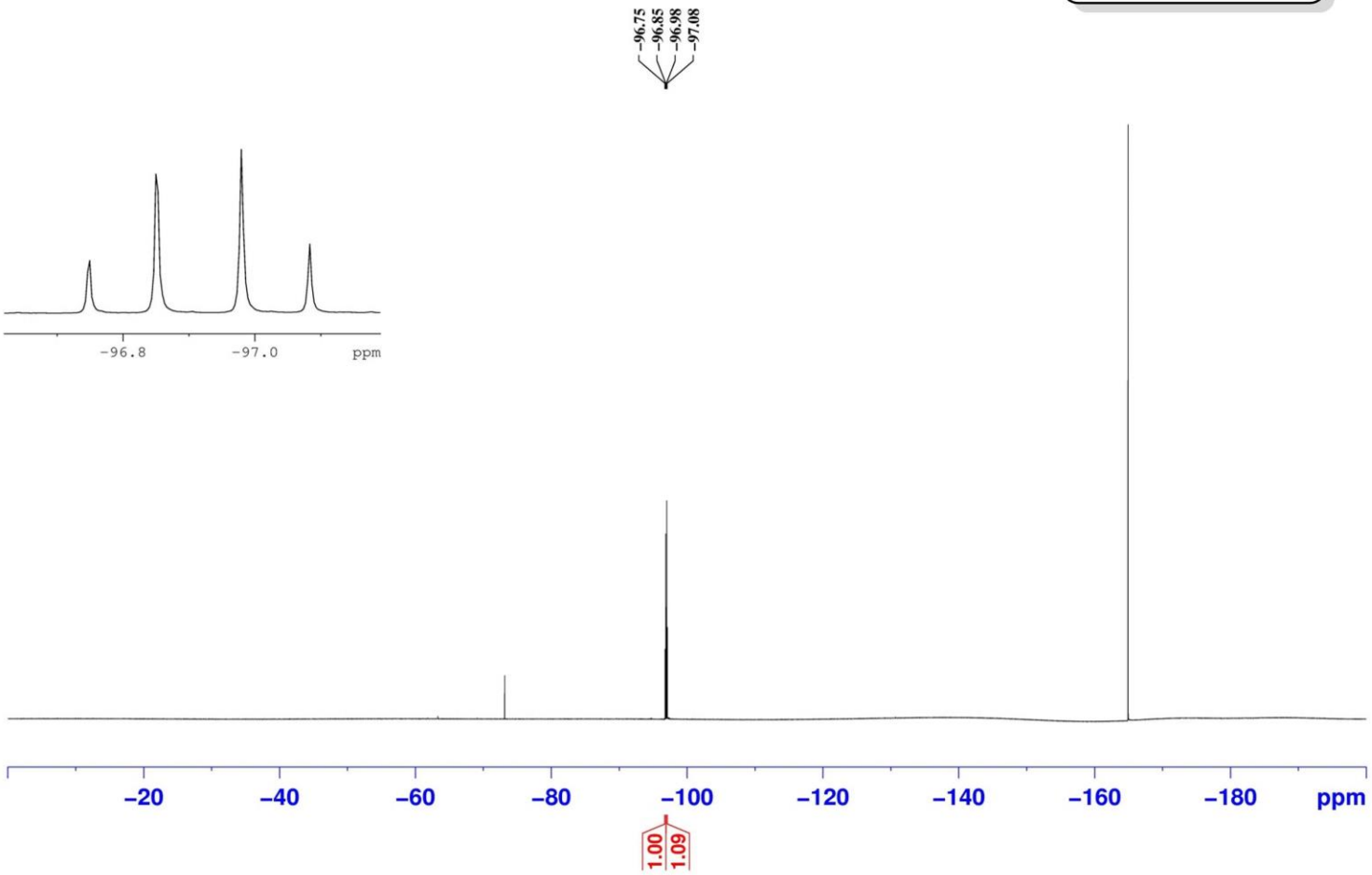




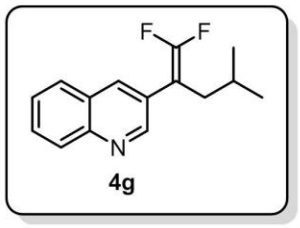
5–(1,1–difluoro–4–methylpent–1–en–2–yl)–1–methyl–1H–indole
471 MHz, CDCl3

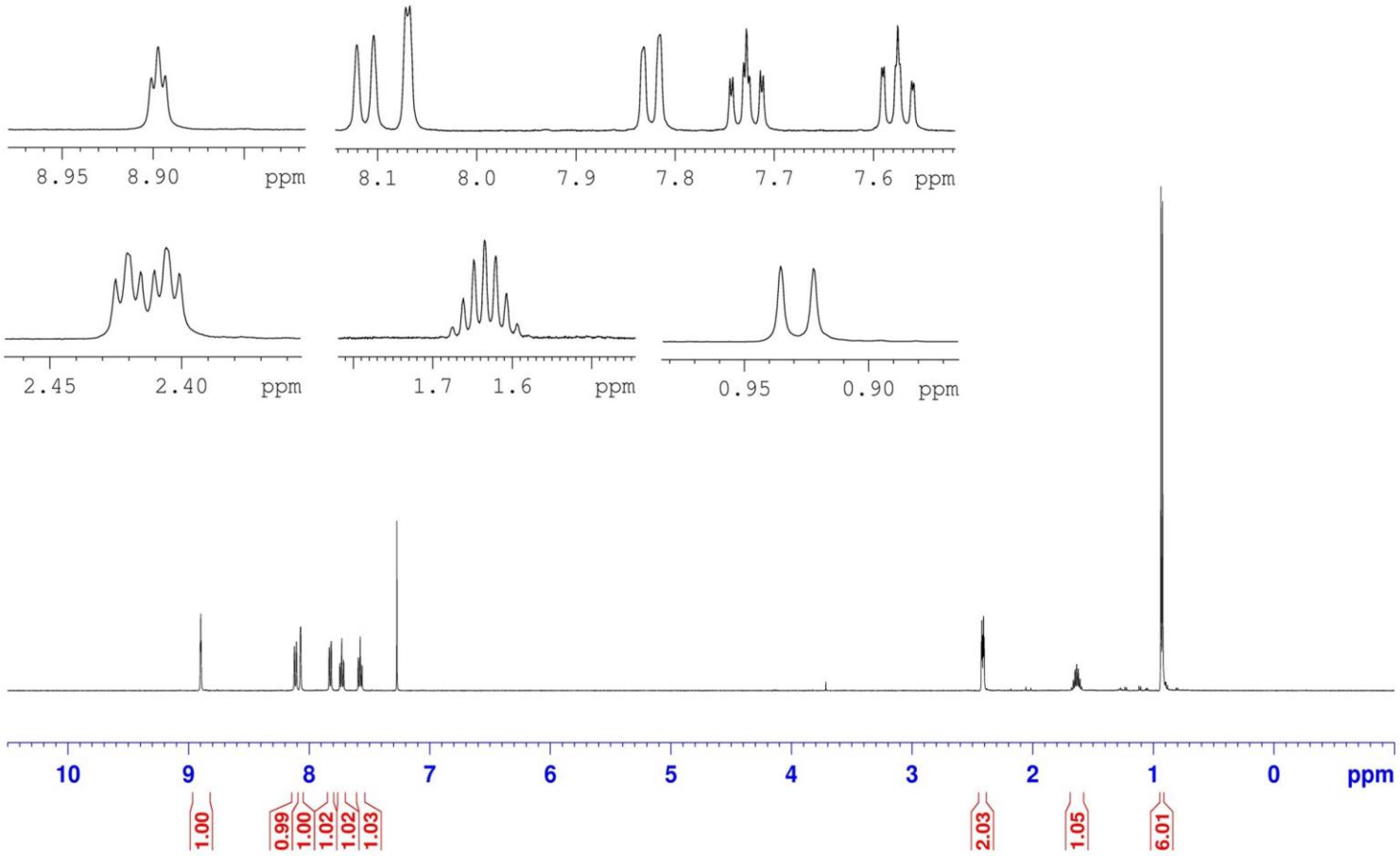


4f

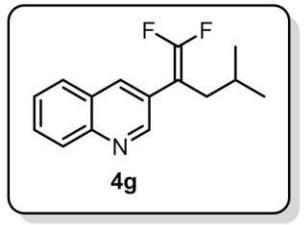


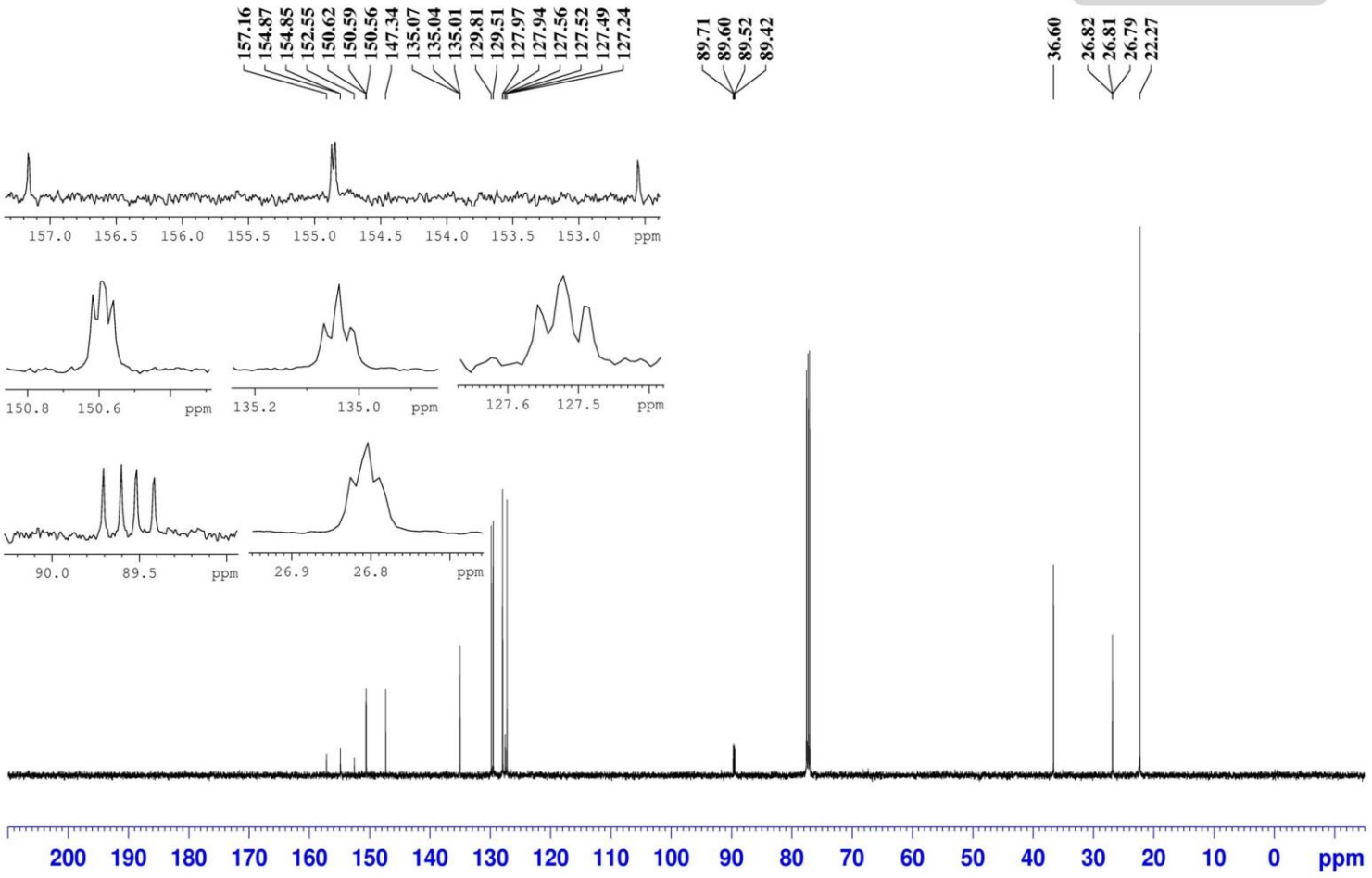
3–(1,1–difluoro–4–methylpent–1–en–2–yl)quinoline
500 MHz, CDCl3



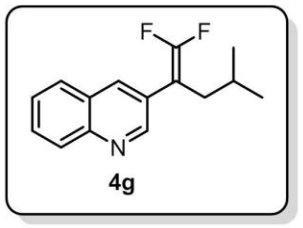


3–(1,1–difluoro–4–methylpent–1–en–2–yl)quinoline
125 MHz, CDCl3

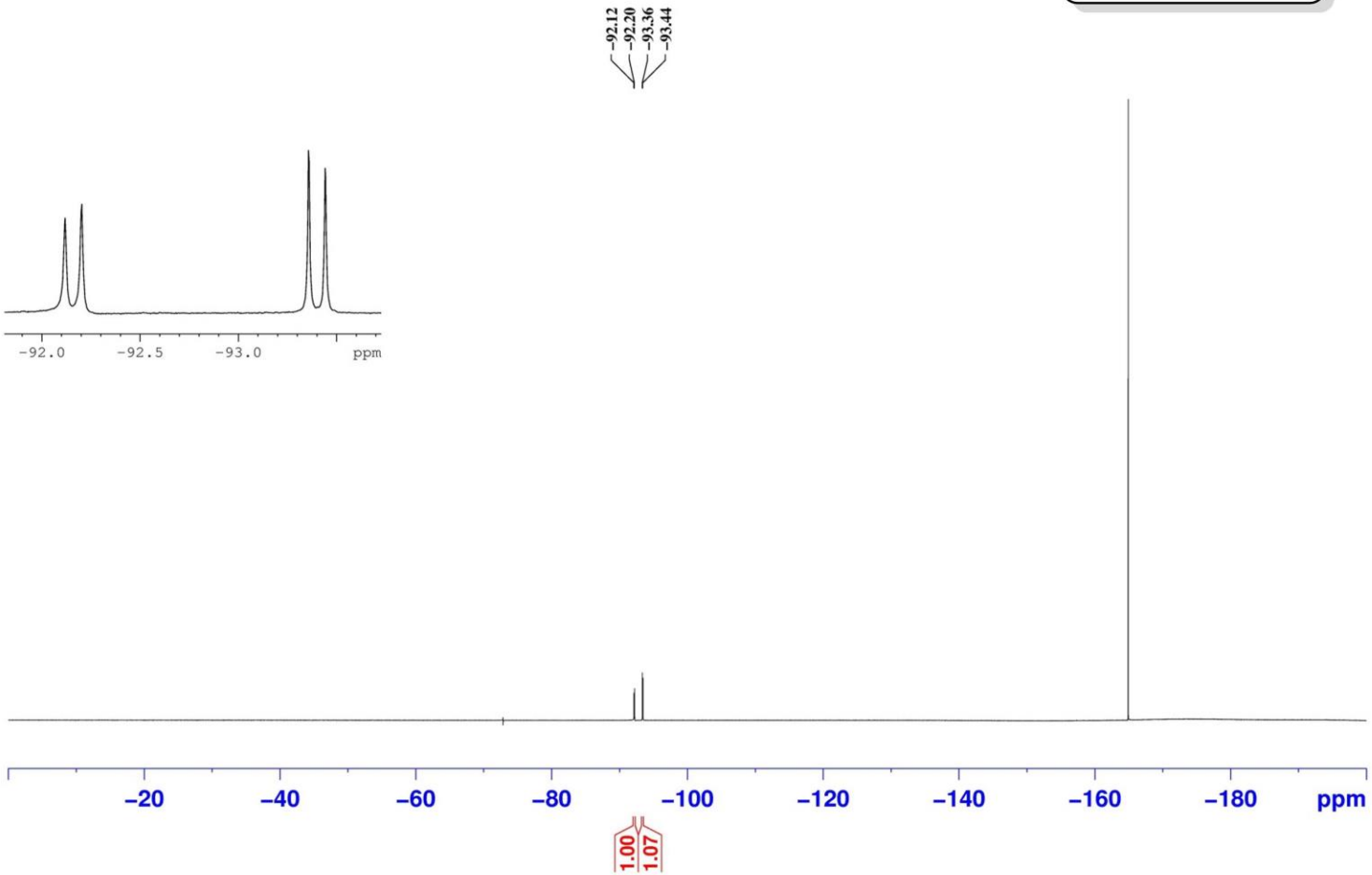




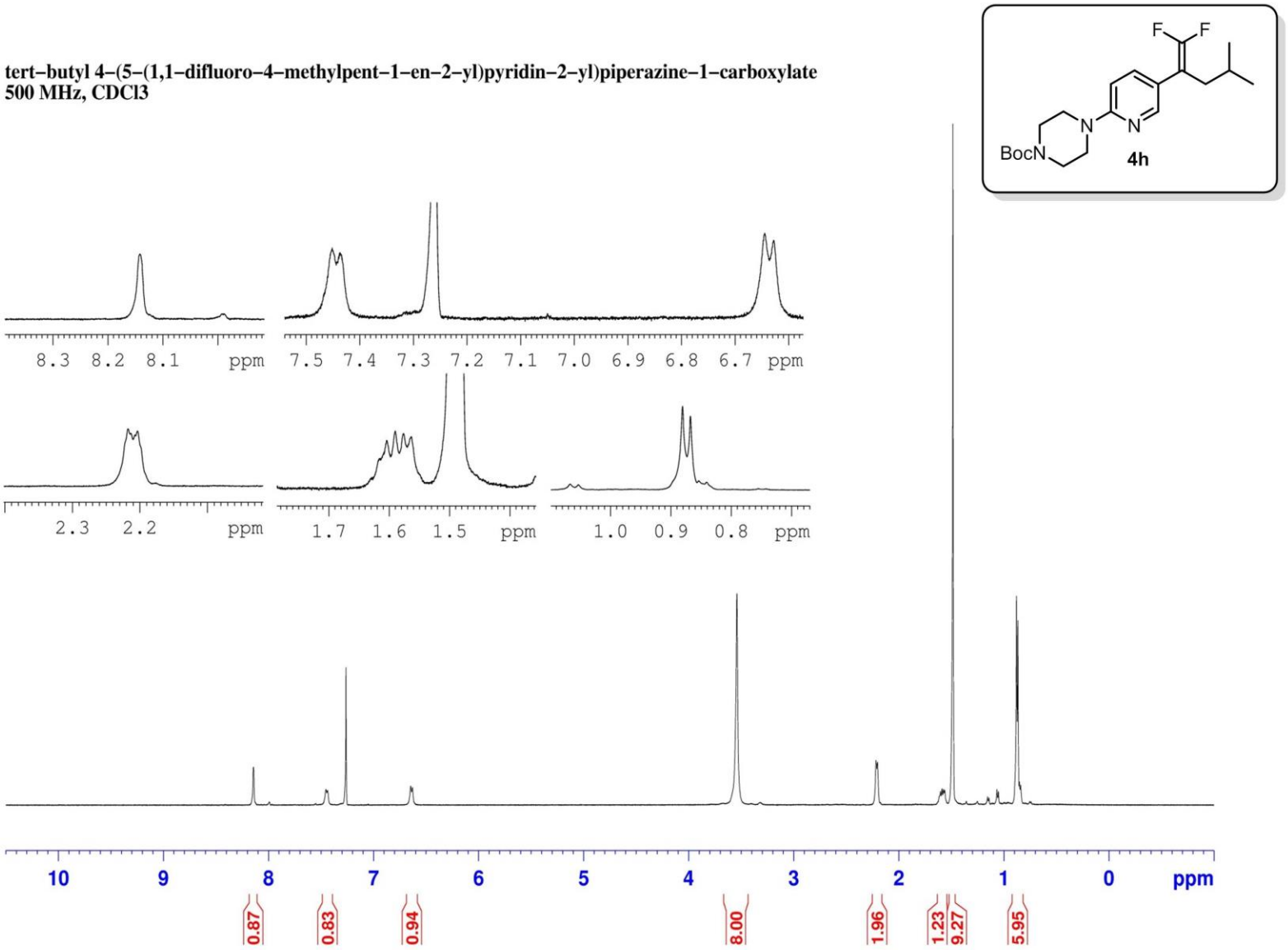
5–(1,1–difluoro–4–methylpent–1–en–2–yl)–1–methyl–1H–indole
471 MHz, CDCl3



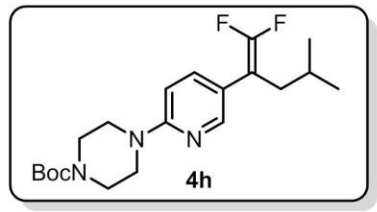
4g

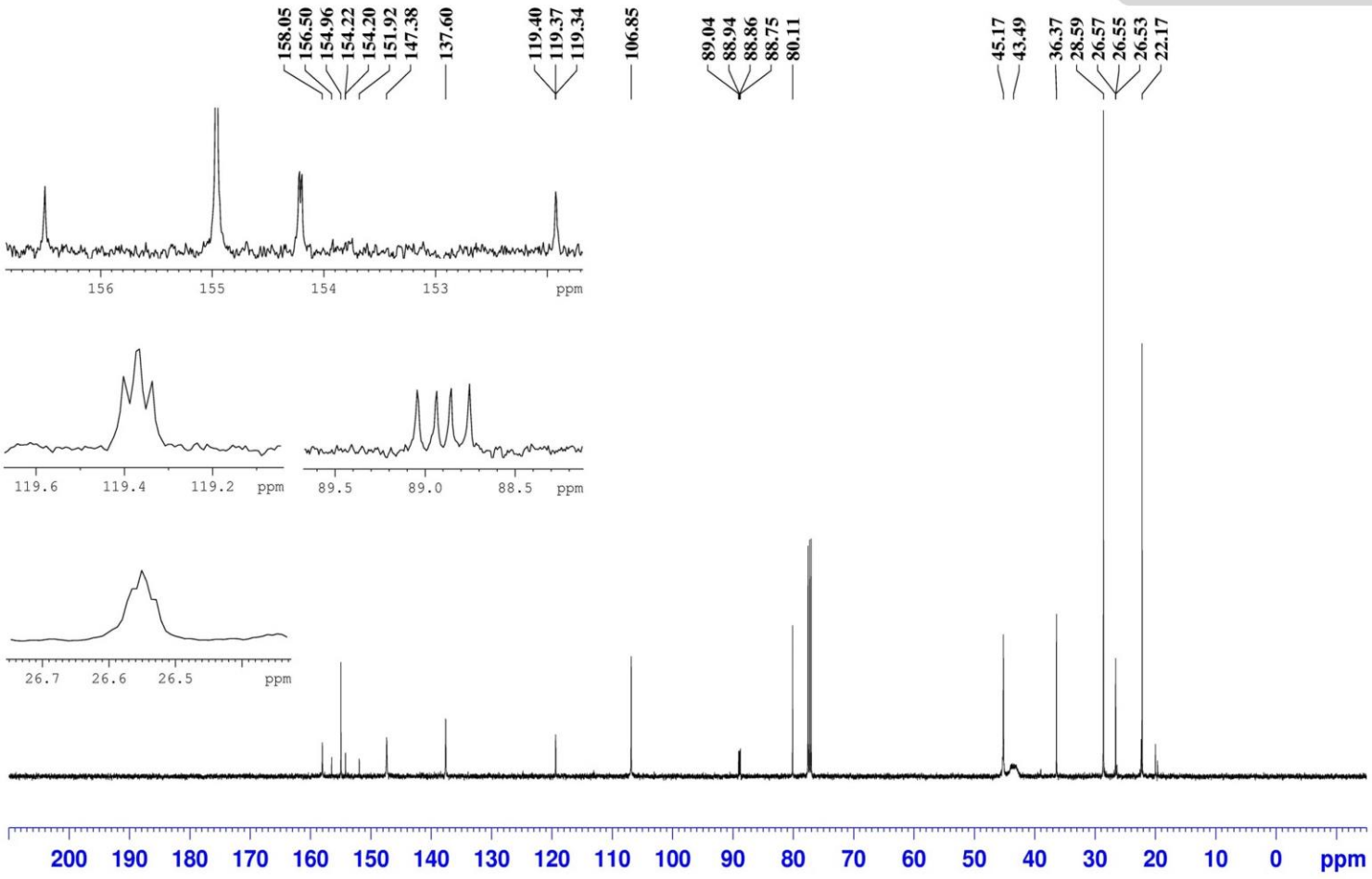


tert–butyl 4–(5–(1,1–difluoro–4–methylpent–1–en–2–yl)pyridin–2–yl)piperazine–1–carboxylate
500 MHz, CDCl3

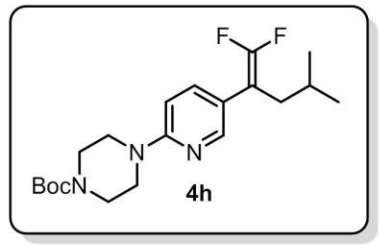


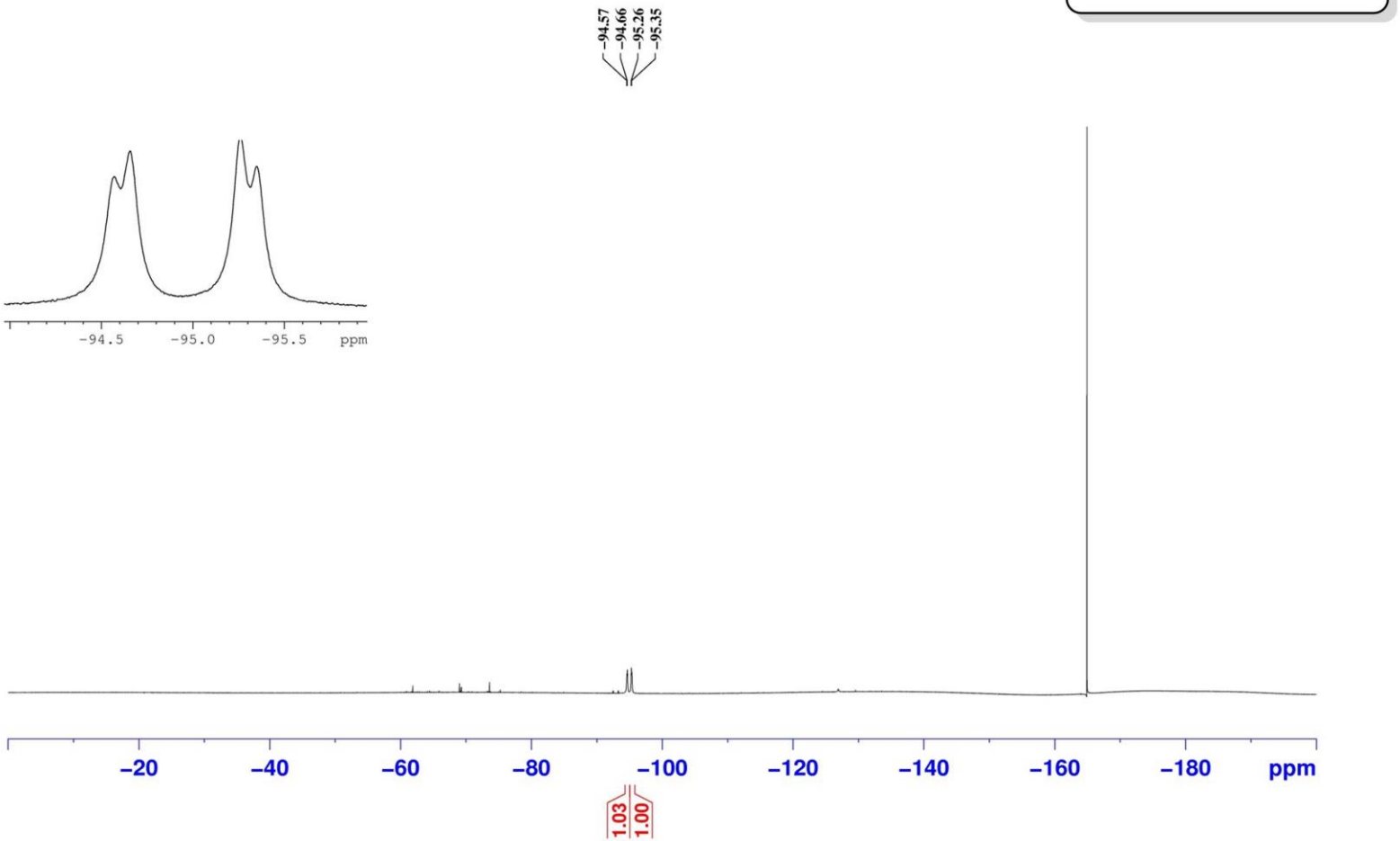
tert−butyl 4−(5−(1,1−difluoro−4−methylpent−1−en−2−yl)pyridin−2−yl)piperazine−1−carboxylate
125 MHz, CDCl3



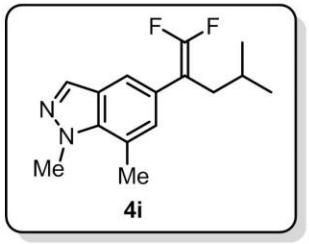


tert−butyl 4−(5−(1,1−difluoro−4−methylpent−1−en−2−yl)pyridin−2−yl)piperazine−1−carboxylate
471 MHz, CDCl3

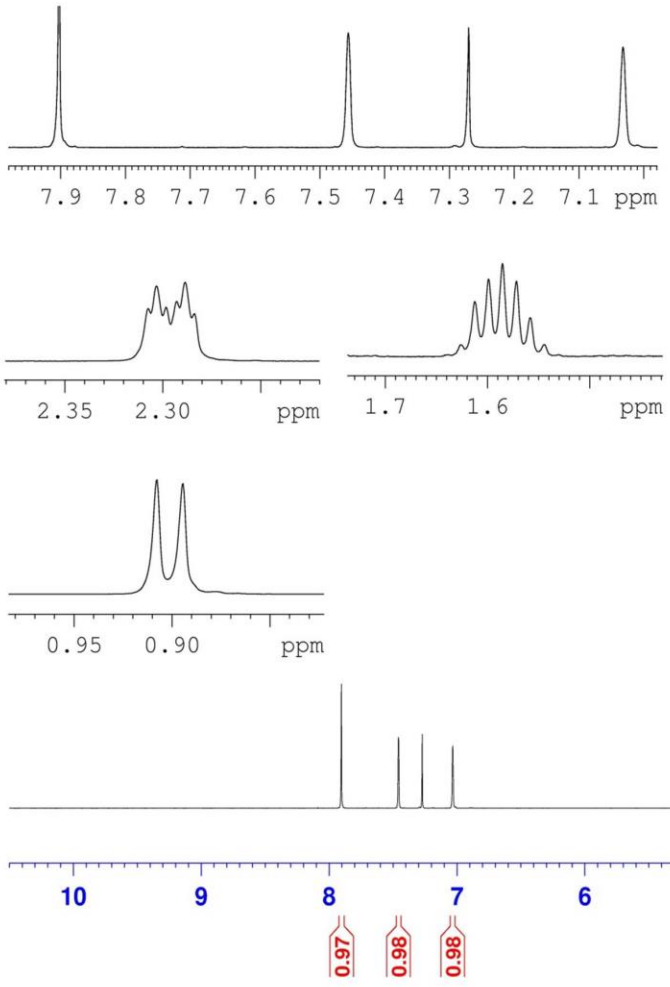




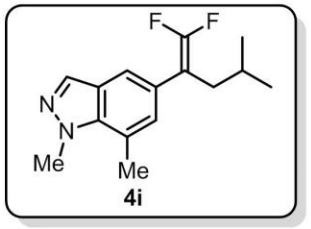
5–(1,1–difluoro–4–methylpent–1–en–2–yl)–1,7–dimethyl–1H–indazole
500 MHz, CDCl3



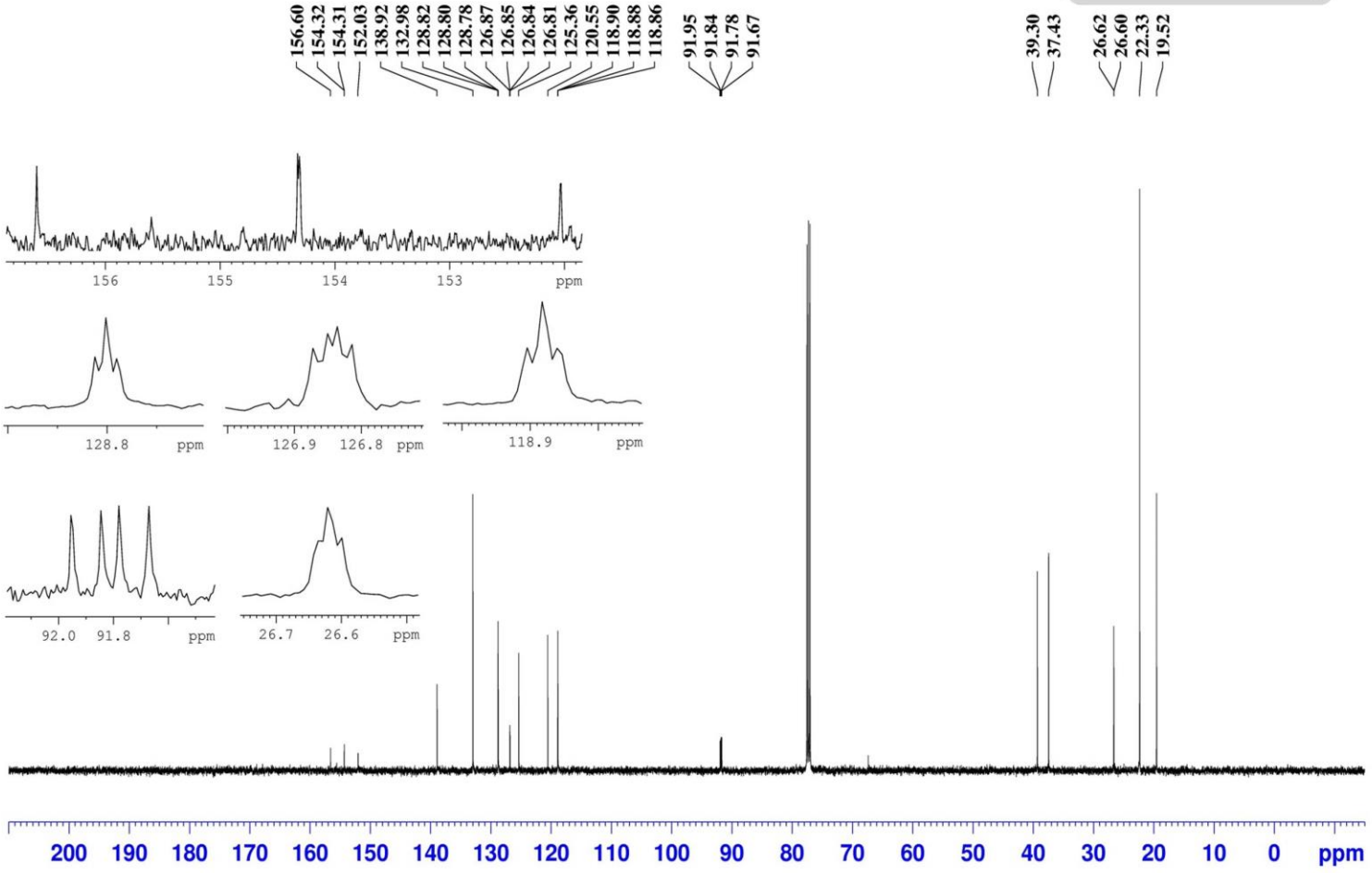
4i



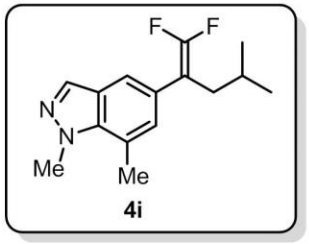
5–(1,1–difluoro–4–methylpent–1–en–2–yl)–1,7–dimethyl–1H–indazole
125 MHz, CDCl3



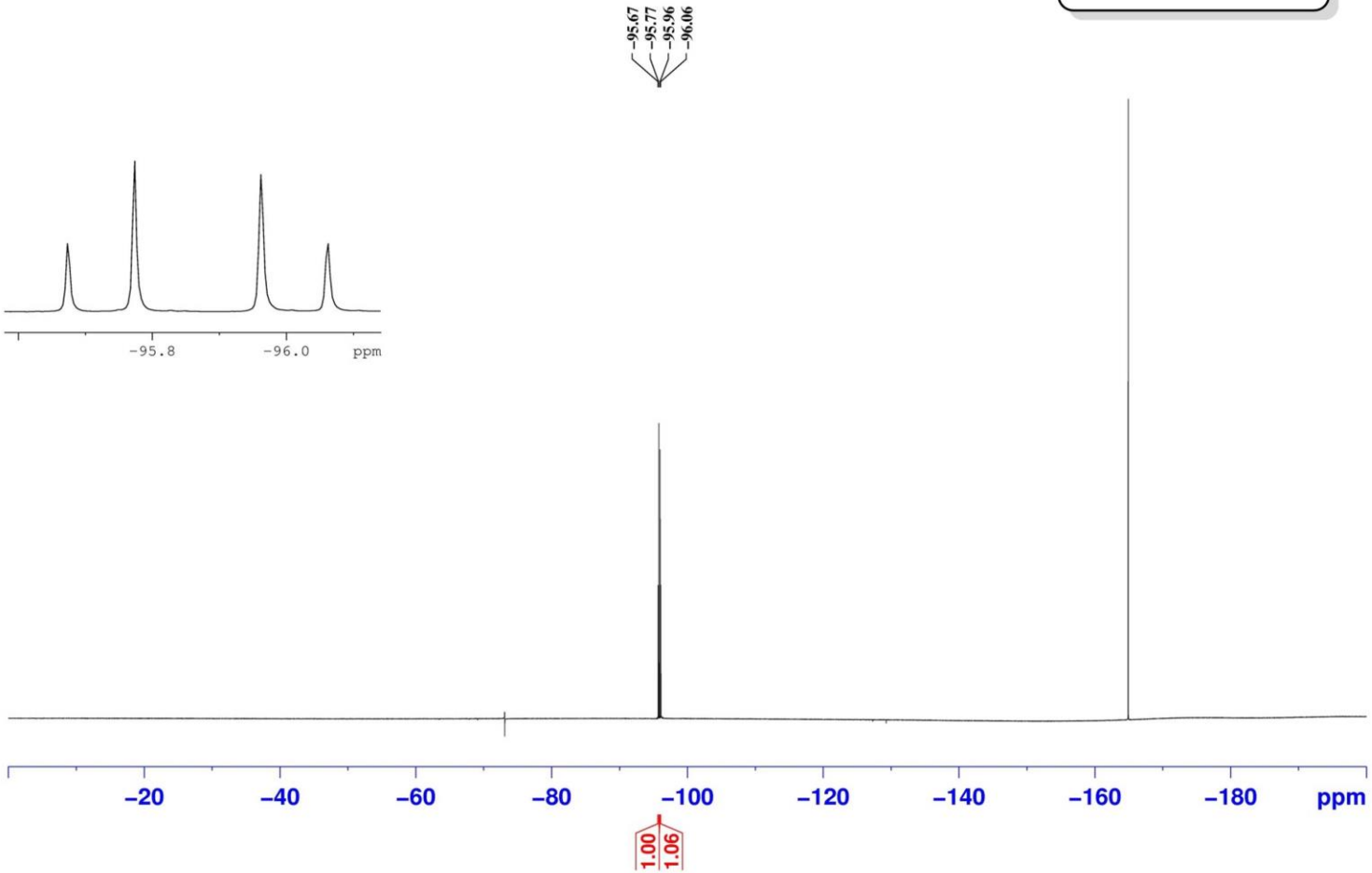
4i



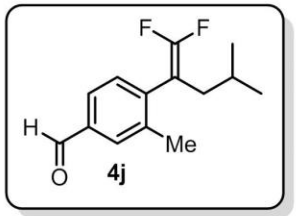
5-(1,1-difluoro-4-methylpent-1-en-2-yl)-1,7-dimethyl-1H-indazole
471 MHz, CDCl3

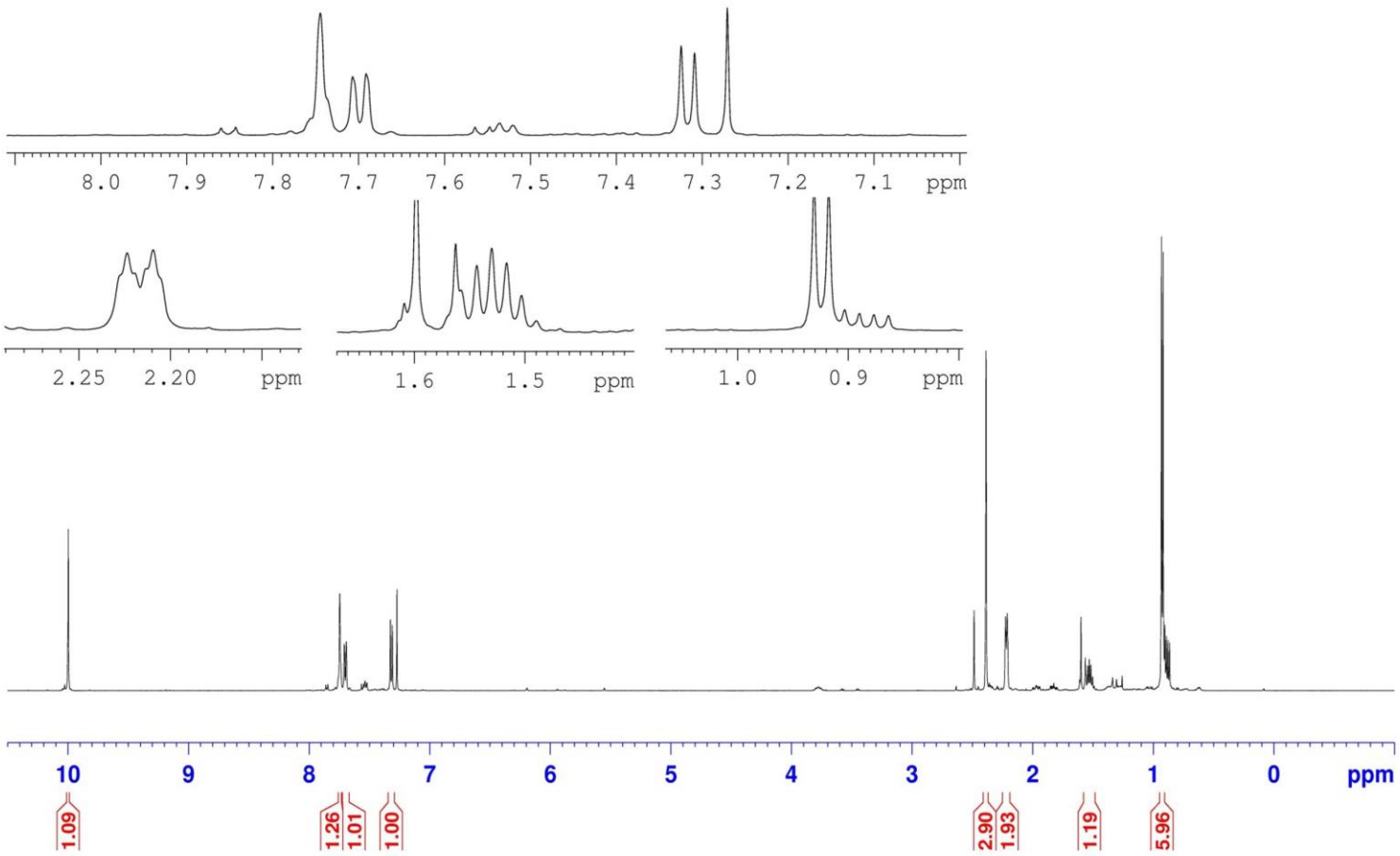


4i

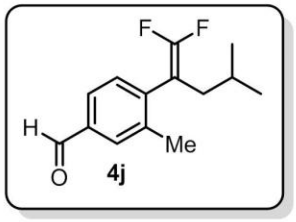


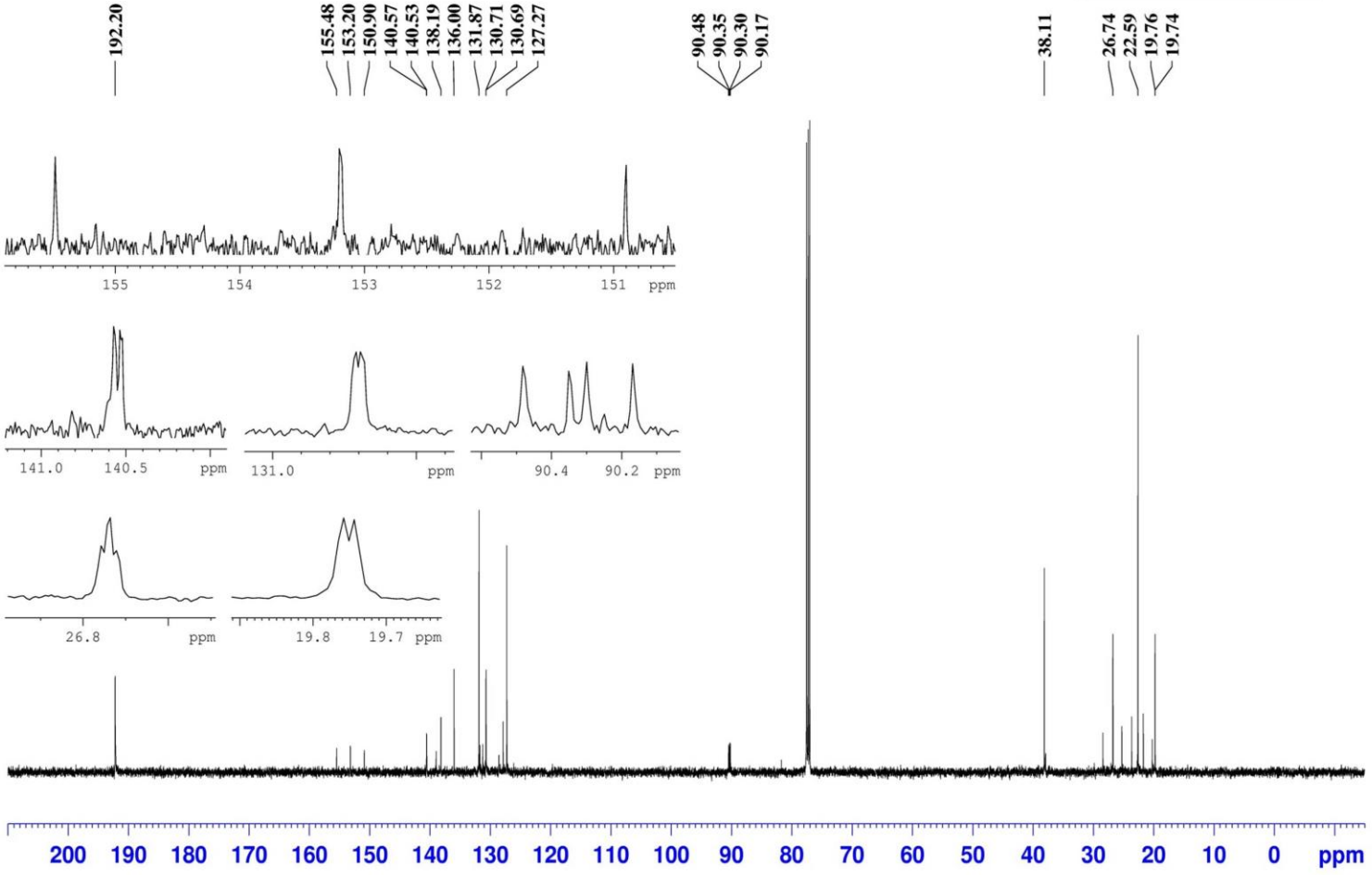
4–(1,1–difluoro–4–methylpent–1–en–2–yl)–3–methylbenzaldehyde
500 MHz, CDCl3



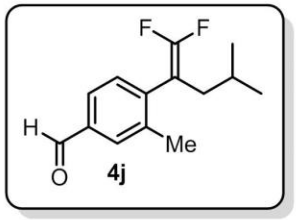


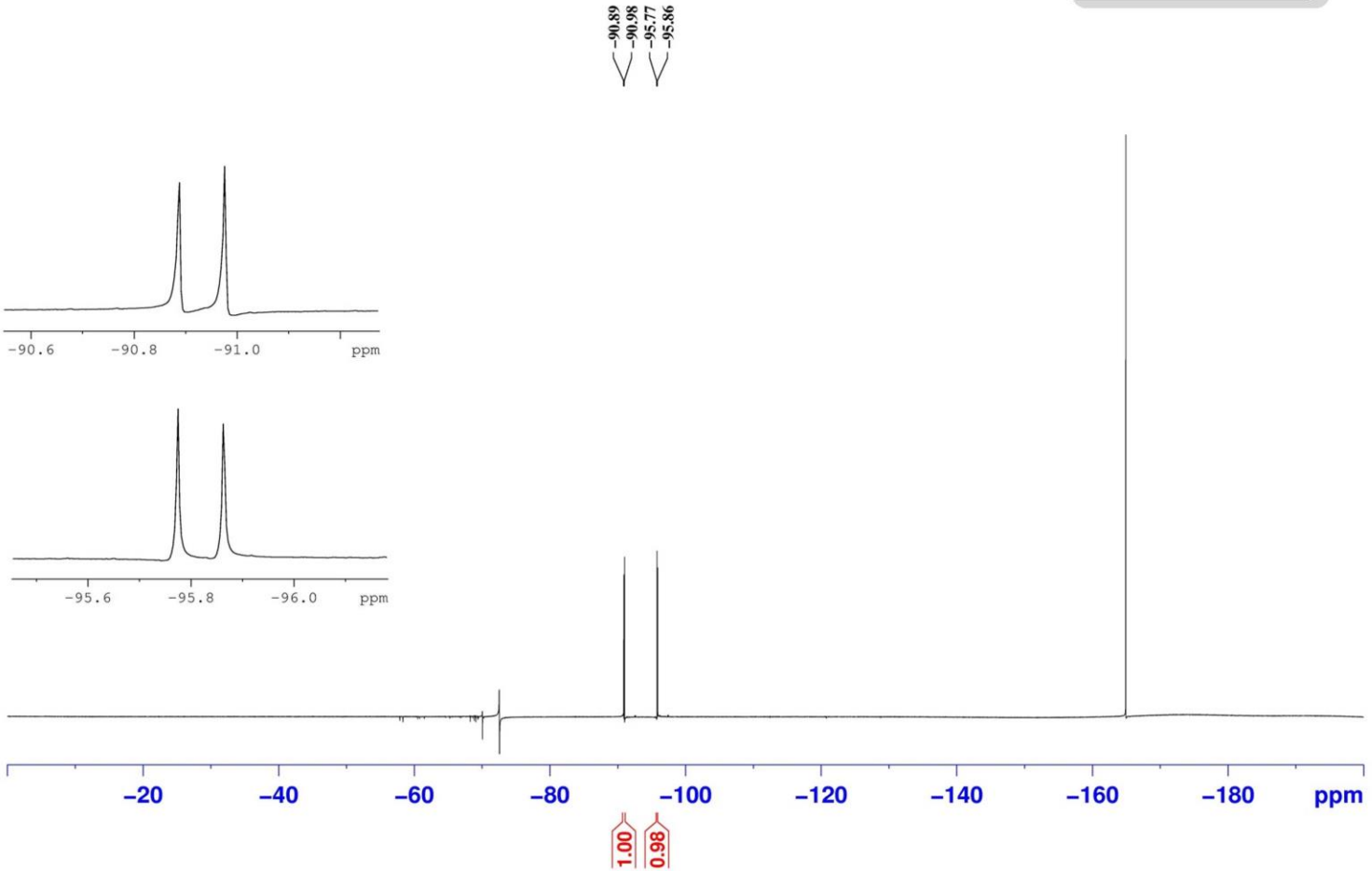
4–(1,1–difluoro–4–methylpent–1–en–2–yl)–3–methylbenzaldehyde
125 MHz, CDCl3



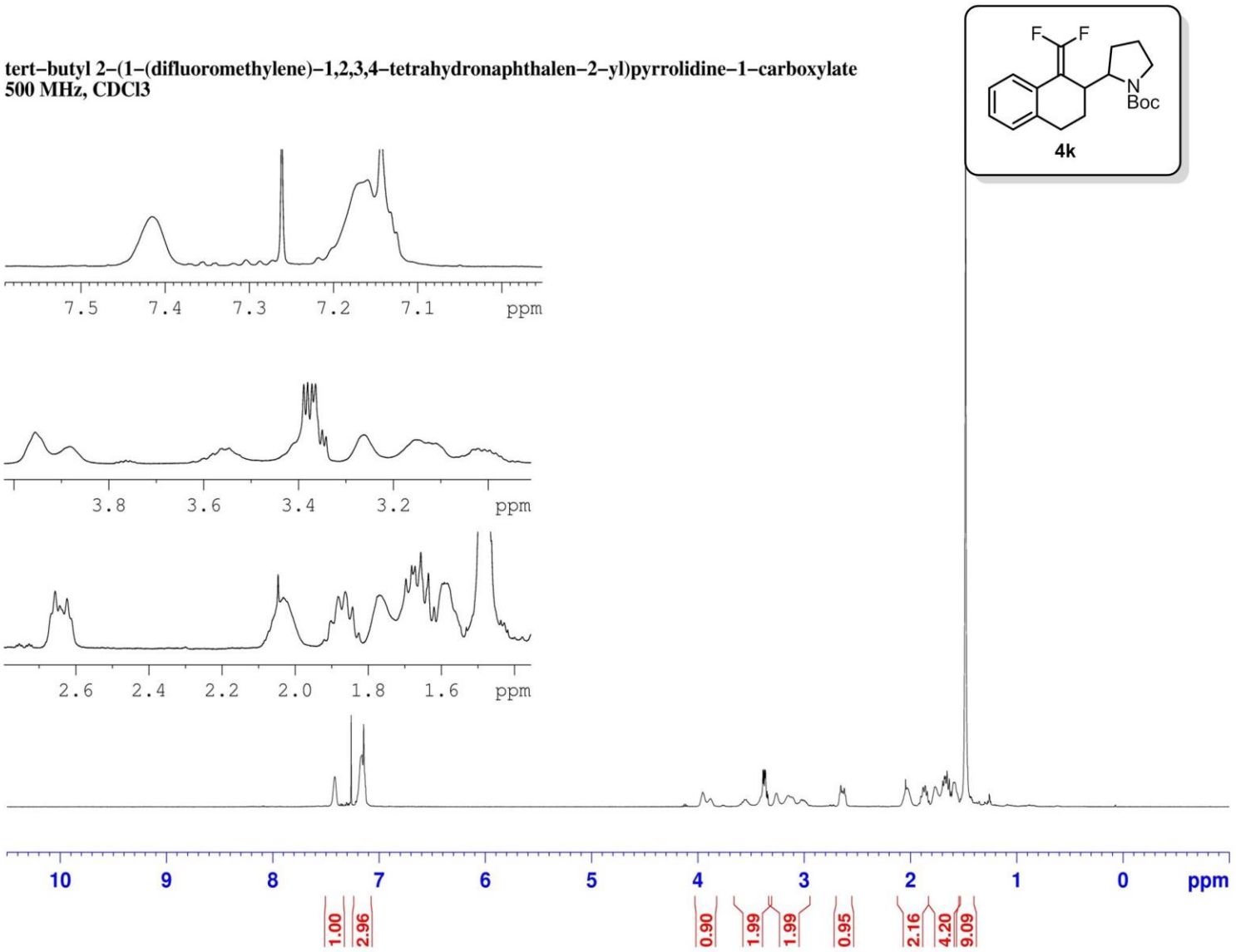


4–(1,1–difluoro–4–methylpent–1–en–2–yl)–3–methylbenzaldehyde
471 MHz, CDCl3

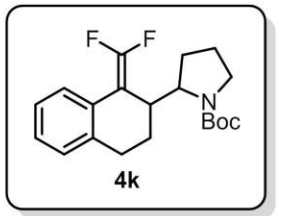




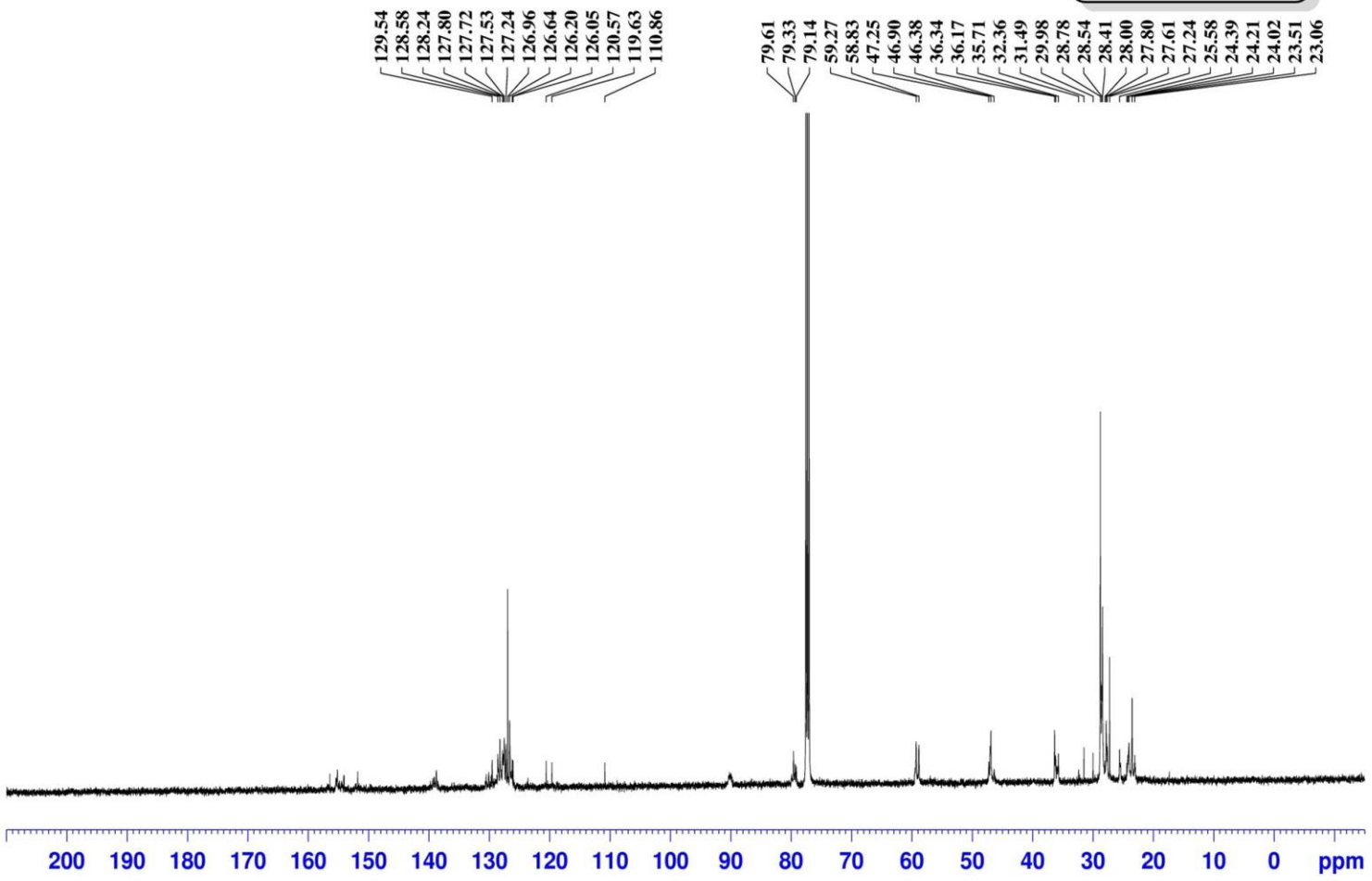
tert−butyl 2−(1−(difluoromethylene)−1,2,3,4−tetrahydronaphthalen−2−yl)pyrrolidine−1−carboxylate
500 MHz, CDCl3



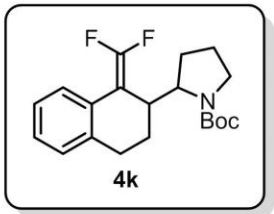
tert−butyl 2−(1−(difluoromethylene)−1,2,3,4−tetrahydronaphthalen−2−yl)pyrrolidine−1−carboxylate
125 MHz, CDCl3



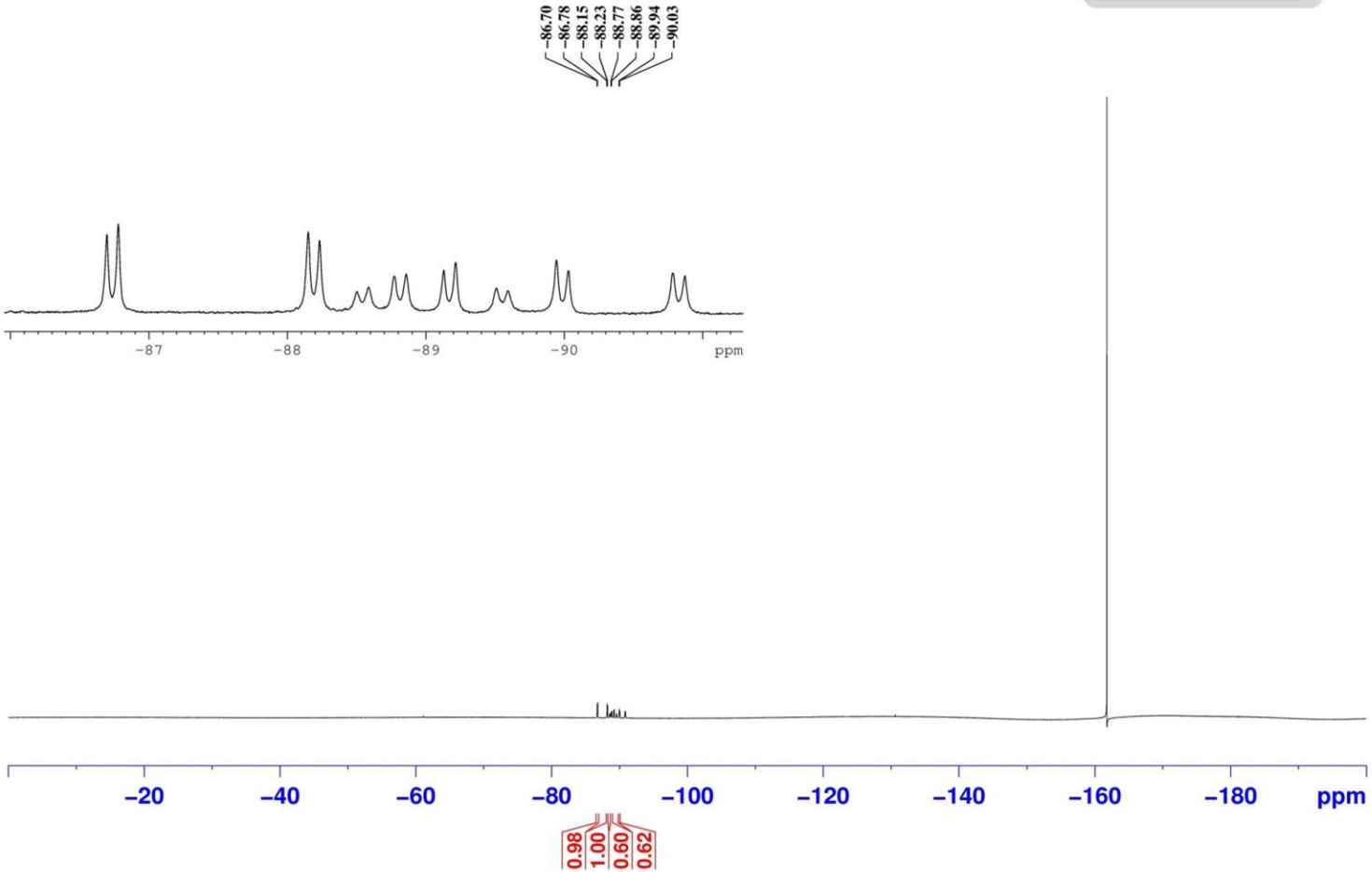
4k



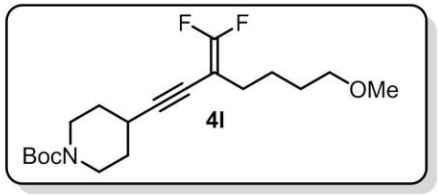
tert−butyl 2−(1−(difluoromethylene)−1,2,3,4−tetrahydronaphthalen−2−yl)pyrrolidine−1−carboxylate
471 MHz, CDCl3

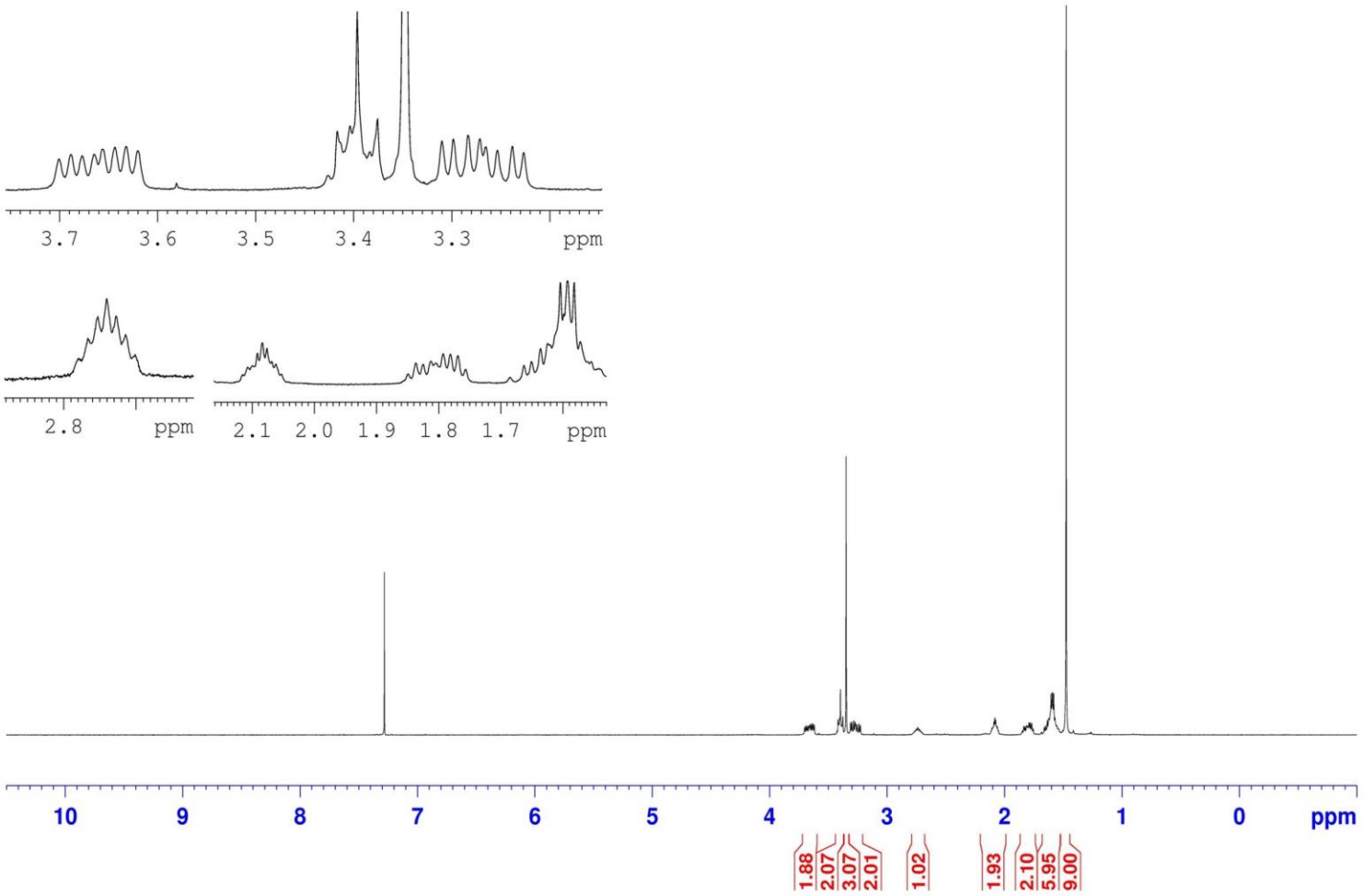


4k

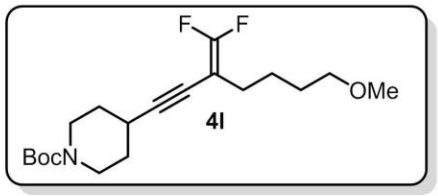


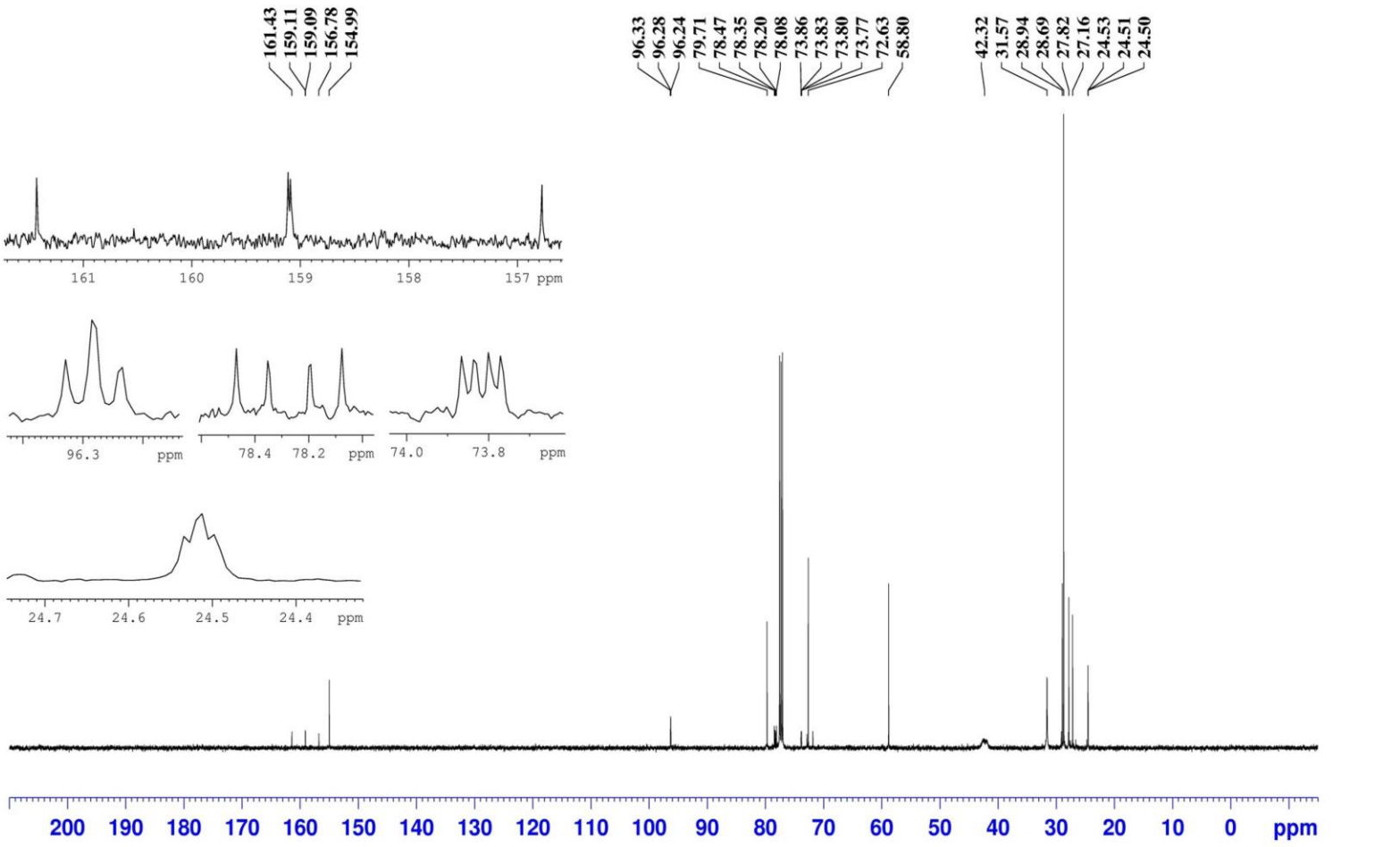
tert−butyl 4−(3−(difluoromethylene)−7−methoxyhept−1−yn−1−yl)piperidine−1−carboxylate
500 MHz, CDCl3



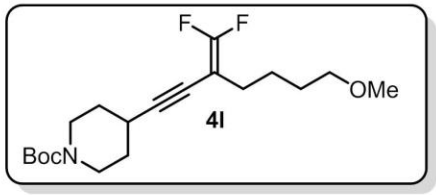


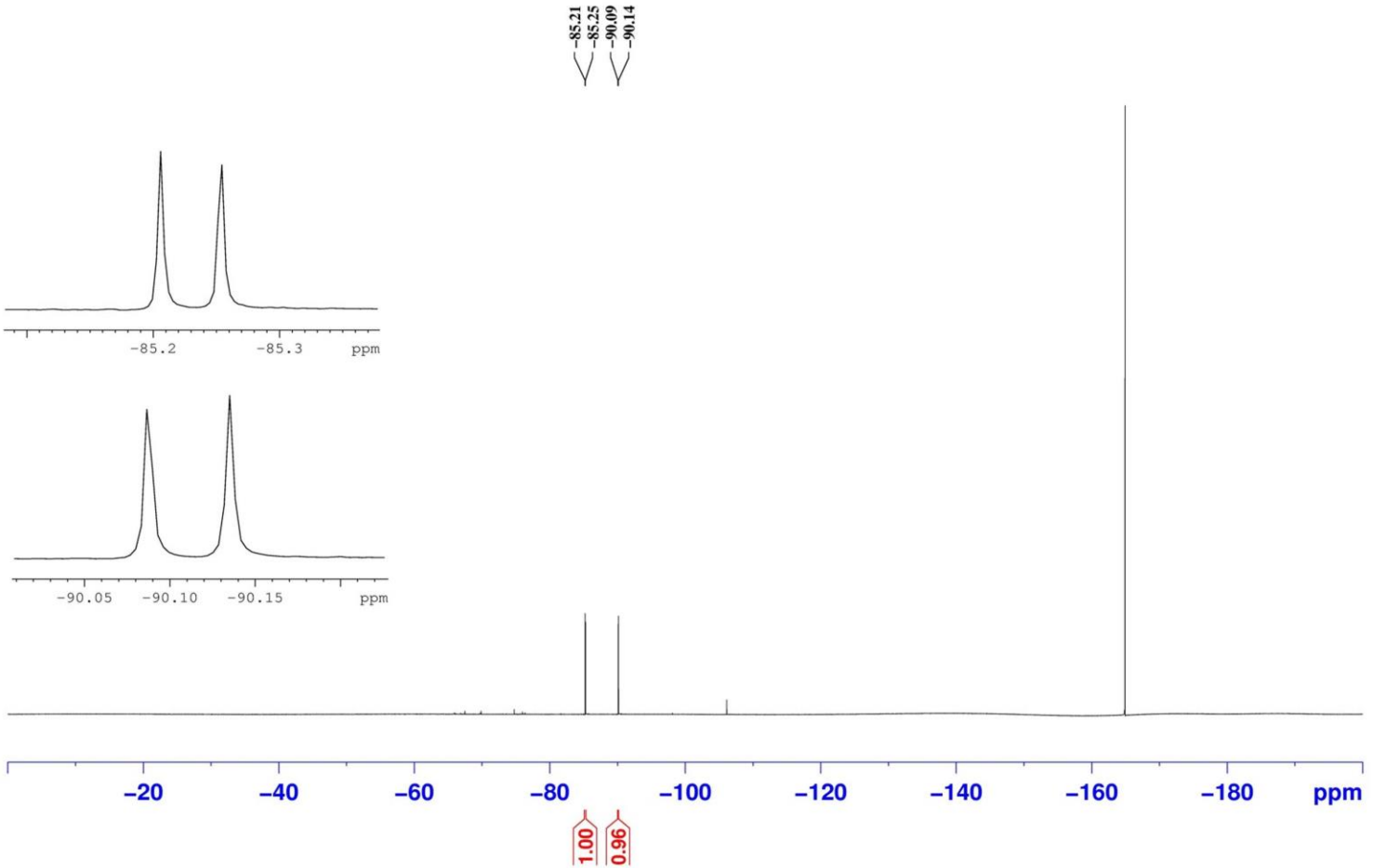
tert−butyl 4−(3−(difluoromethylene)−7−methoxyhept−1−yn−1−yl)piperidine−1−carboxylate
125 MHz, CDCl3



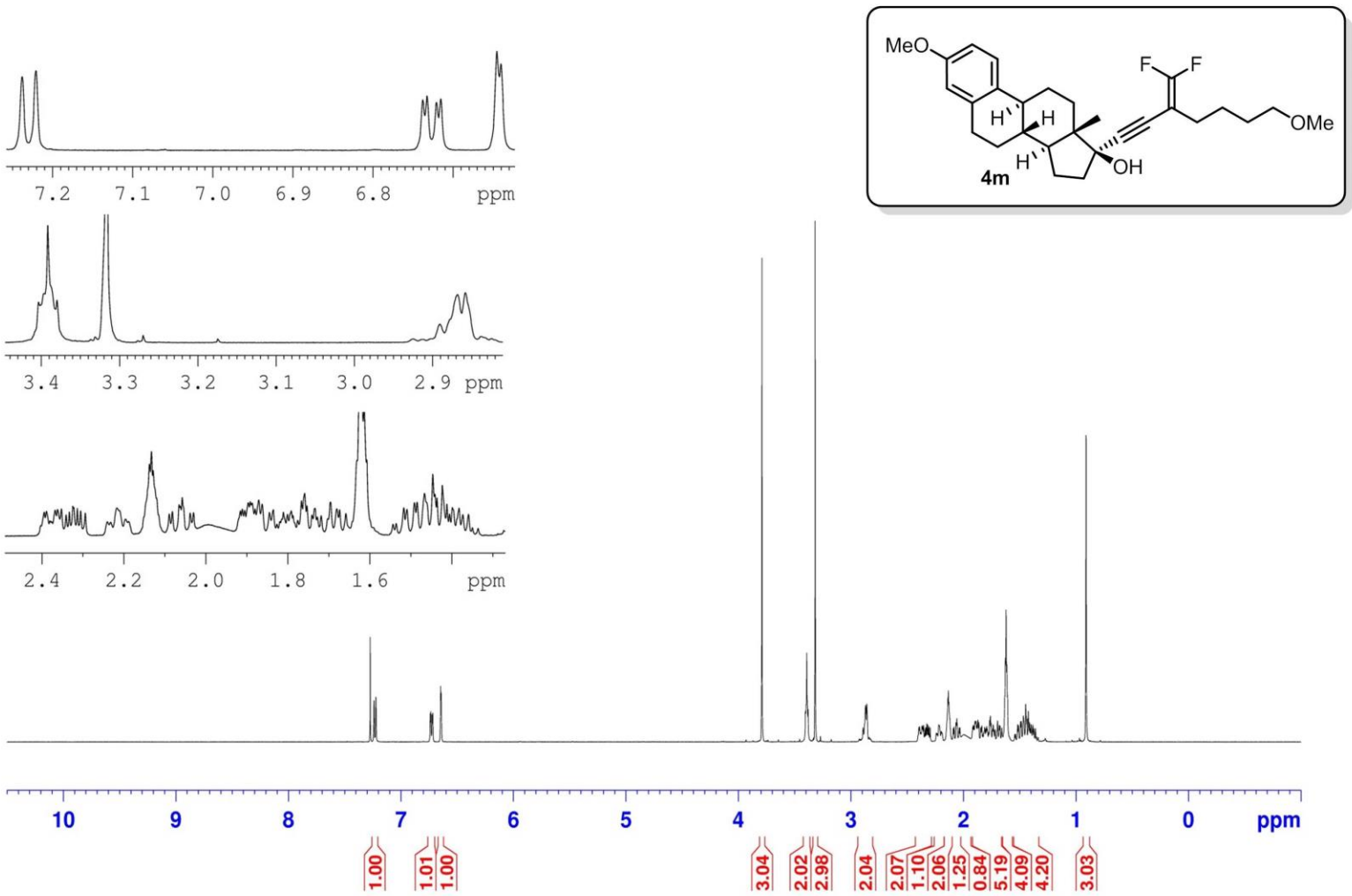


tert–butyl 4–(3–(difluoromethylene)–7–methoxyhept–1–yn–1–yl)piperidine–1–carboxylate
471 MHz, CDCl3

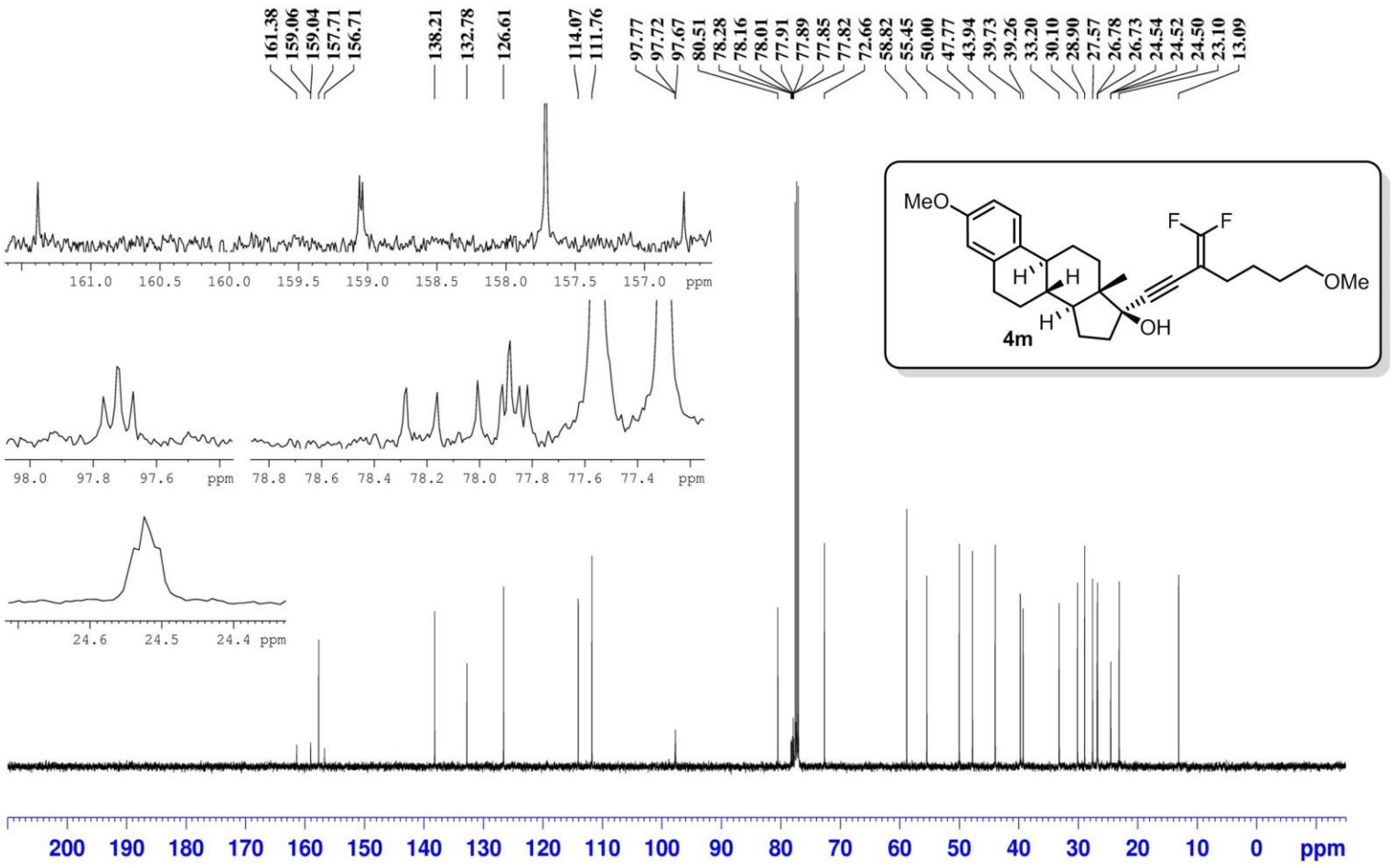




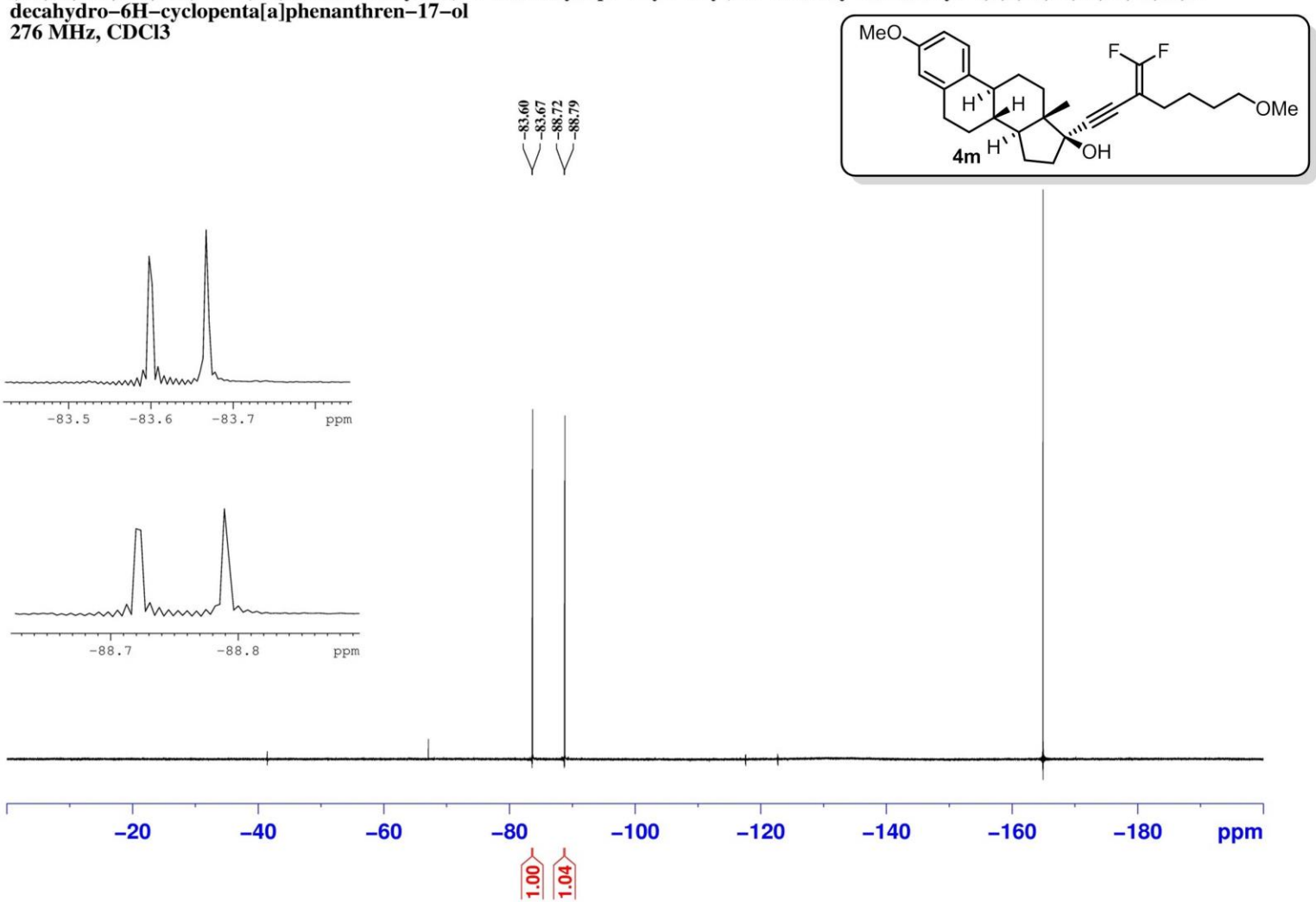
(8R,9S,13S,14S,17S)−17−(3−(difluoromethylene)−7−methoxyhept−1−yn−1−yl)−3−methoxy−13−methyl−7,8,9,11,12,13,14,15,16,17−decahydro−6H−cyclopenta[a]phenanthren−17
500 MHz, CDCl3



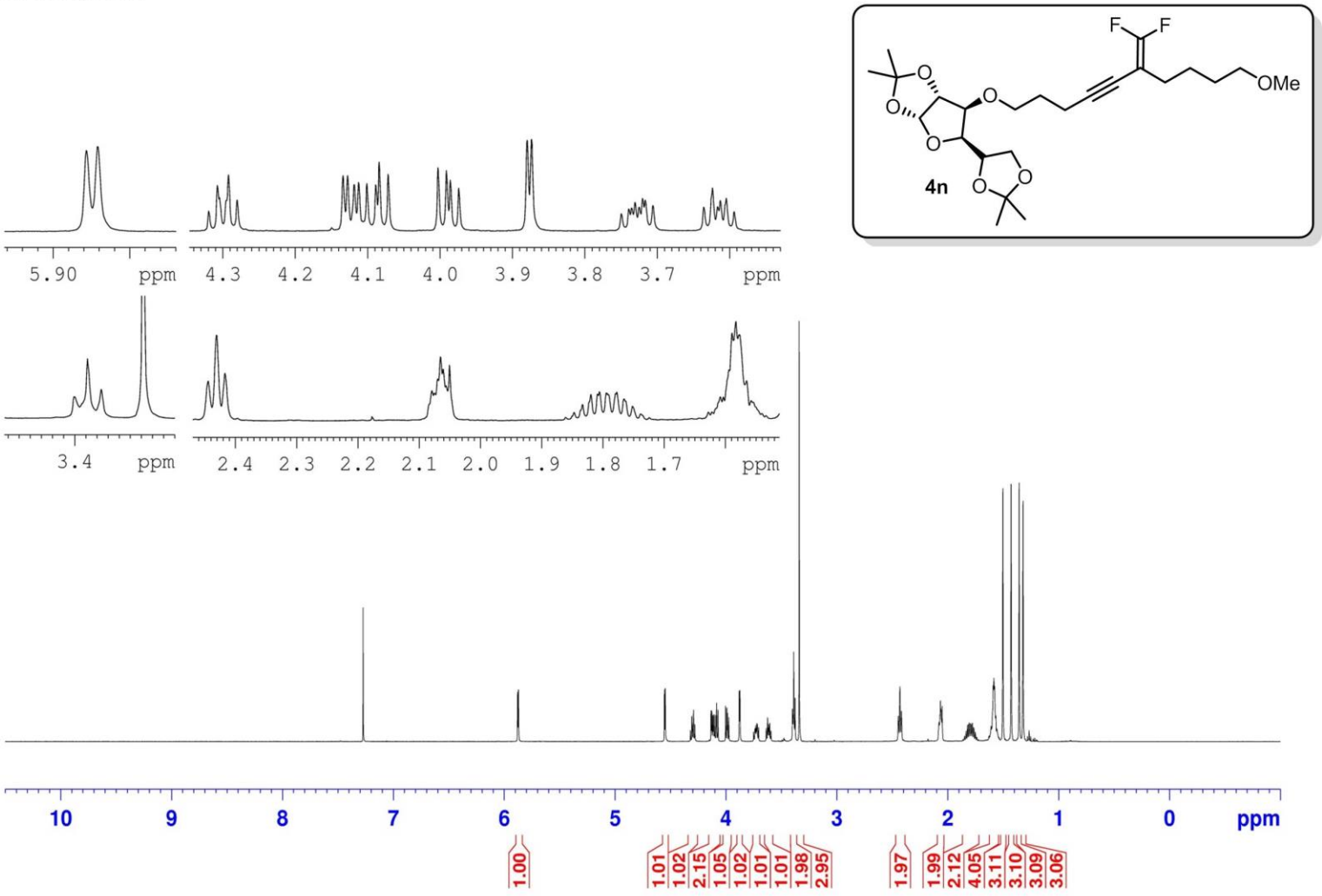
(8R,9S,13S,14S,17S)−17−(3−(difluoromethylene)−7−methoxyhept−1−yn−1−yl)−3−methoxy−13−methyl−7,8,9,11,12,13,14,15,16,17−decahydro−6H−cyclopenta[a]phenanthren−1
125 MHz, CDCl3



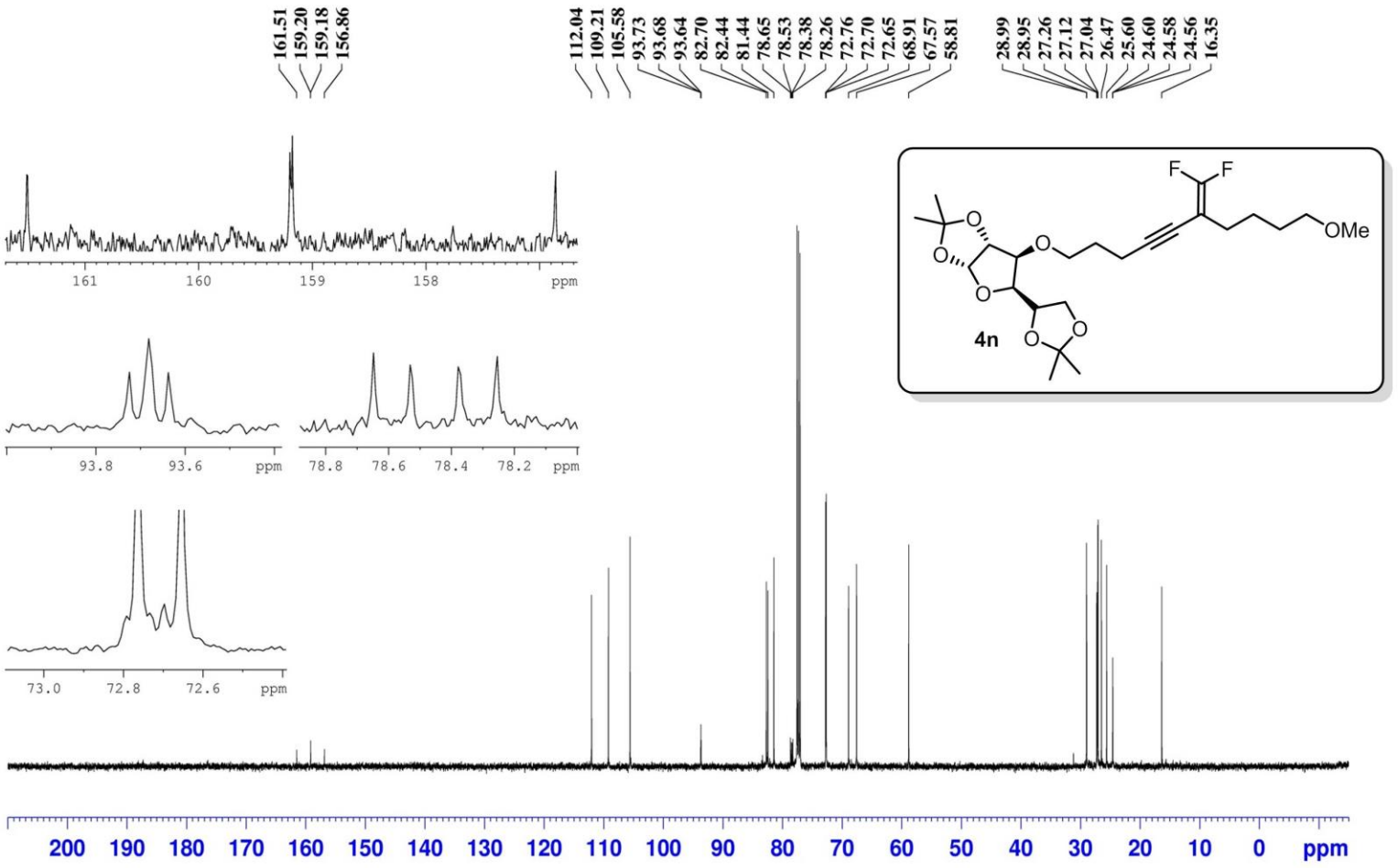
(8R,9S,13S,14S,17S)−17−(3−(difluoromethylene)−7−methoxyhept−1−yn−1−yl)−3−methoxy−13−methyl−7,8,9,11,12,13,14,15,16,17−decahydro−6H−cyclopenta[a]phenanthren−17−ol
276 MHz, CDCl3



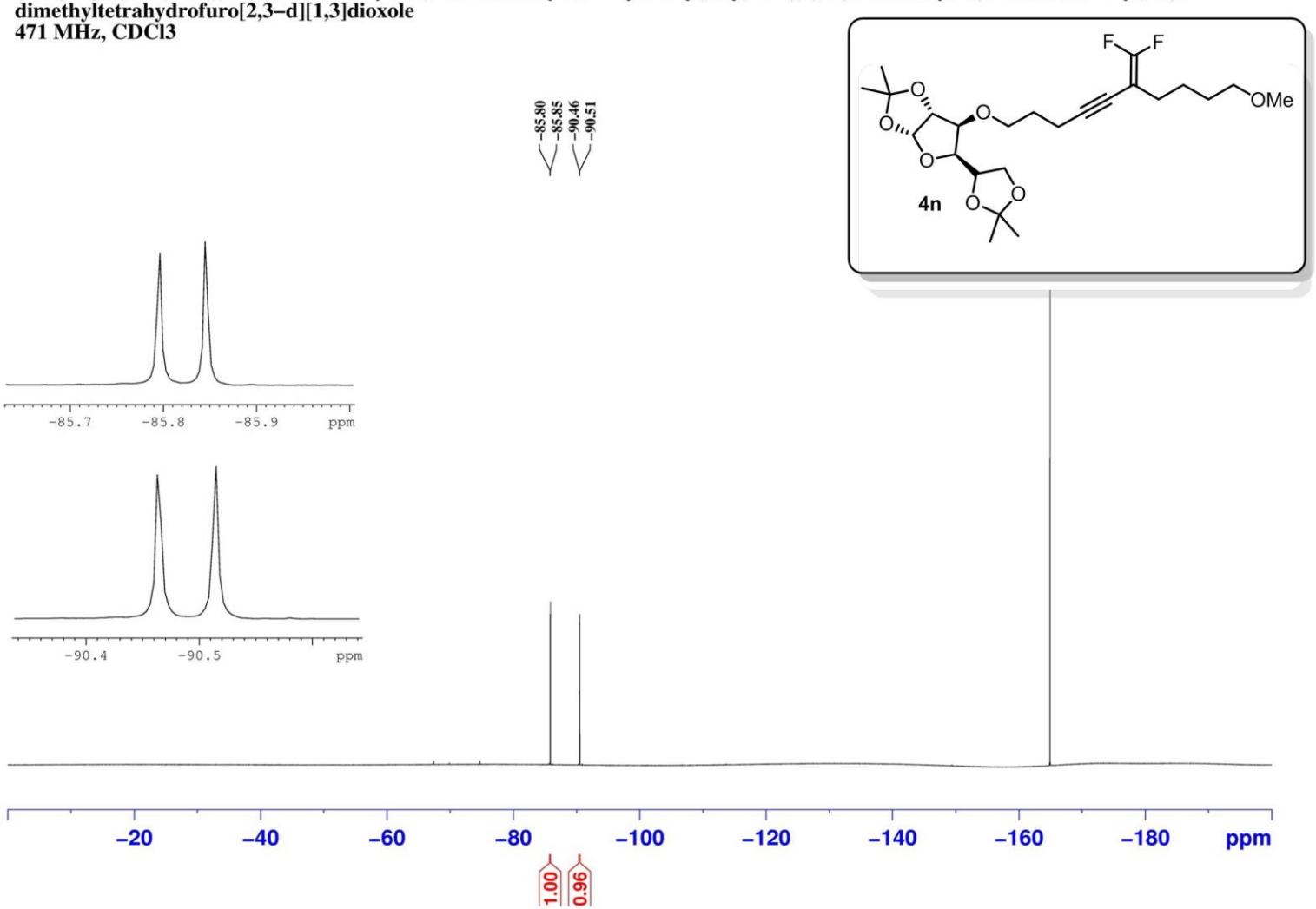
(3aR,5R,6S,6aR)−6−((6−(difluoromethylene)−10−methoxydec−4−yn−1−yl)oxy)−5−((S)−2,2−dimethyl−1,3−dioxolan−4−yl)−2,2−dimethyltetrahydrofuro[2,3−d][1
500 MHz, CDCl3



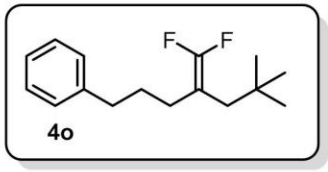
(3aR,5R,6S,6aR)−6−((6−(difluoromethylene)−10−methoxydec−4−yn−1−yl)oxy)−5−((S)−2,2−dimethyl−1,3−dioxolan−4−yl)−2,2−dimethyltetrahydrofuro[2,3−d][1
125 MHz, CDCl3

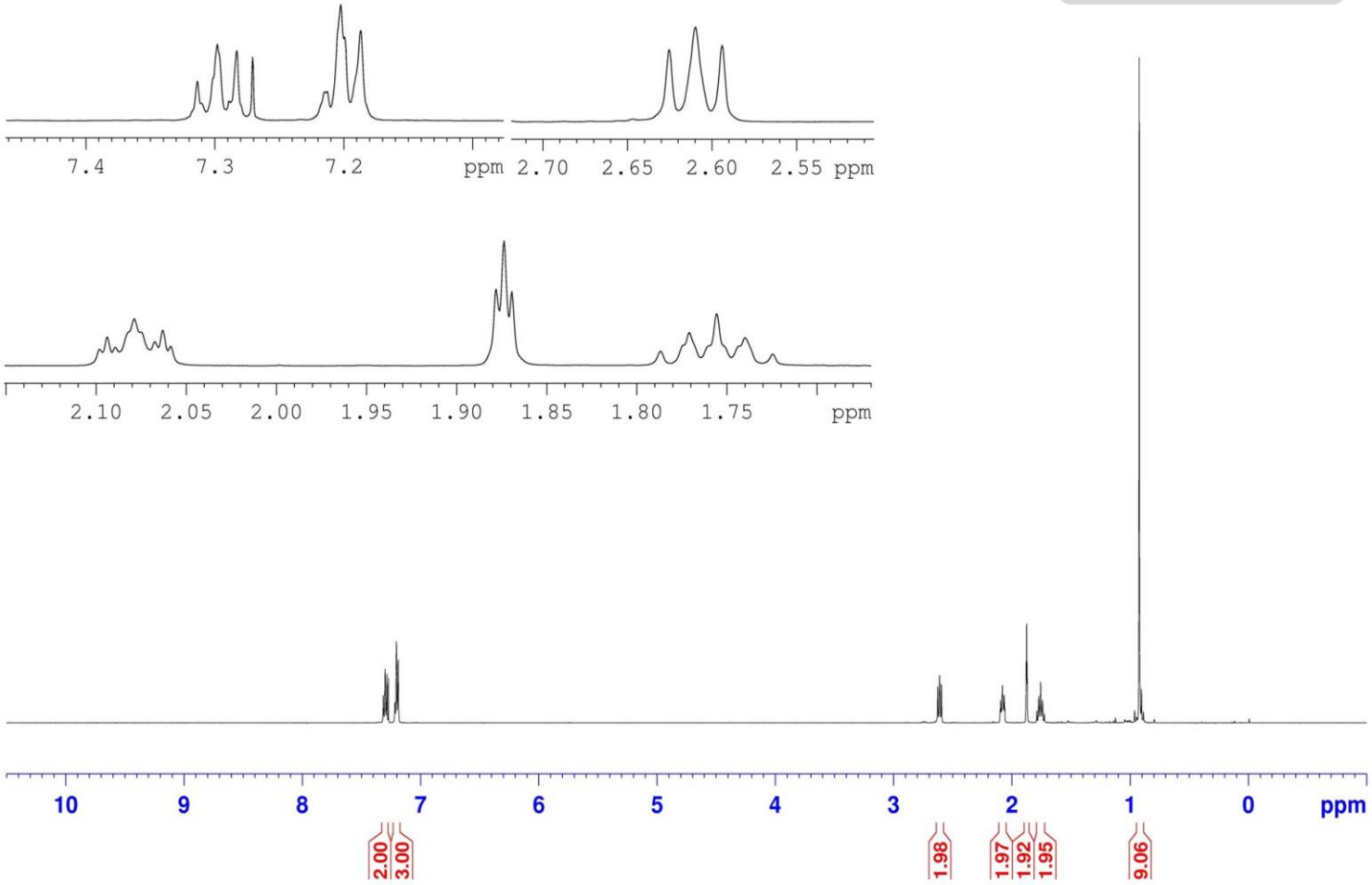


(3aR,5R,6S,6aR)−6−((6−(difluoromethylene)−10−methoxydec−4−yn−1−yl)oxy)−5−((S)−2,2−dimethyl−1,3−dioxolan−4−yl)−2,2−dimethyltetrahydrofuro[2,3−d][1,3]dioxole
471 MHz, CDCl3

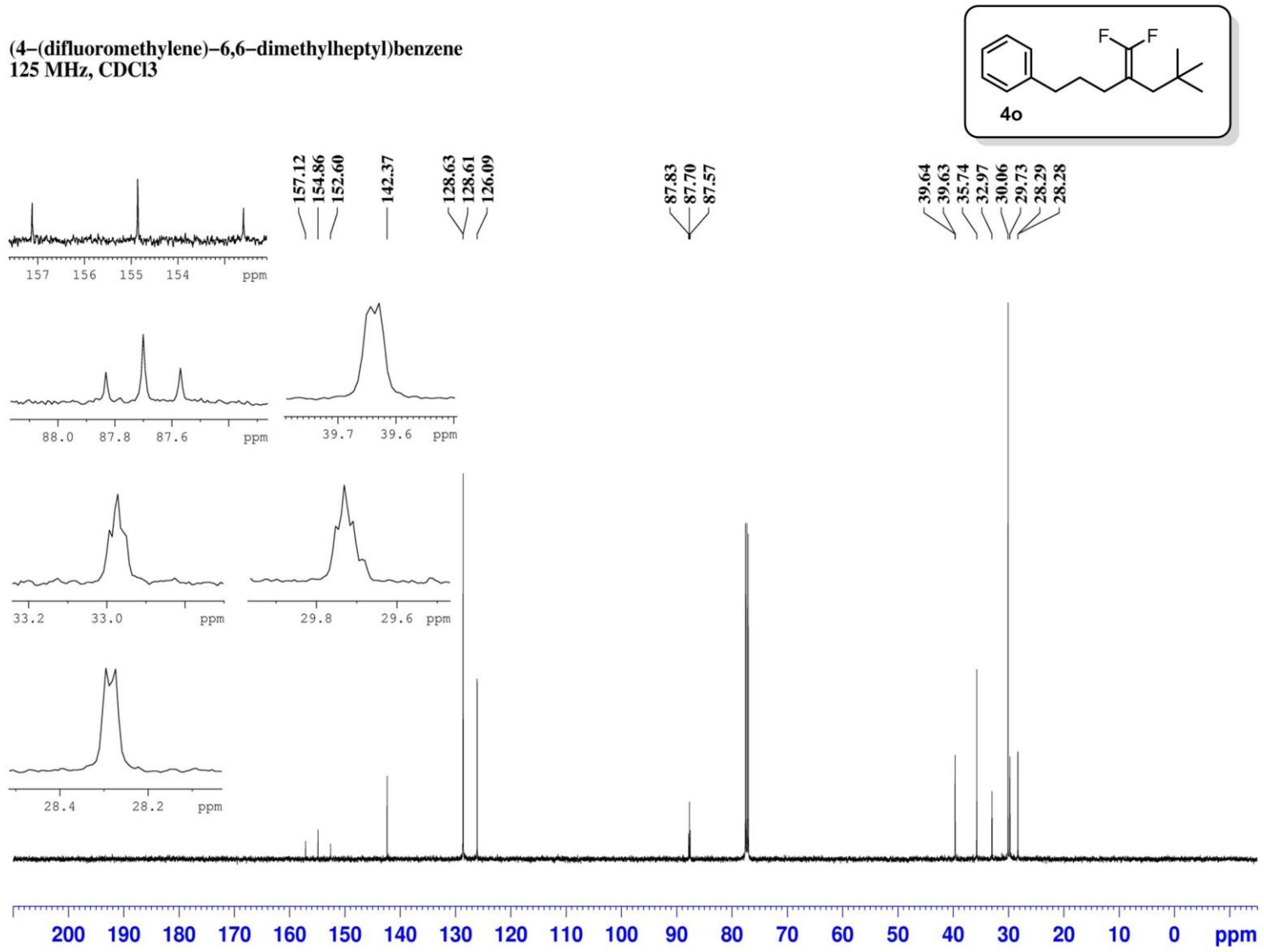


(4–(difluoromethylene)–6,6–dimethylheptyl)benzene
500 MHz, CDCl3

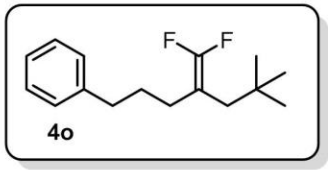


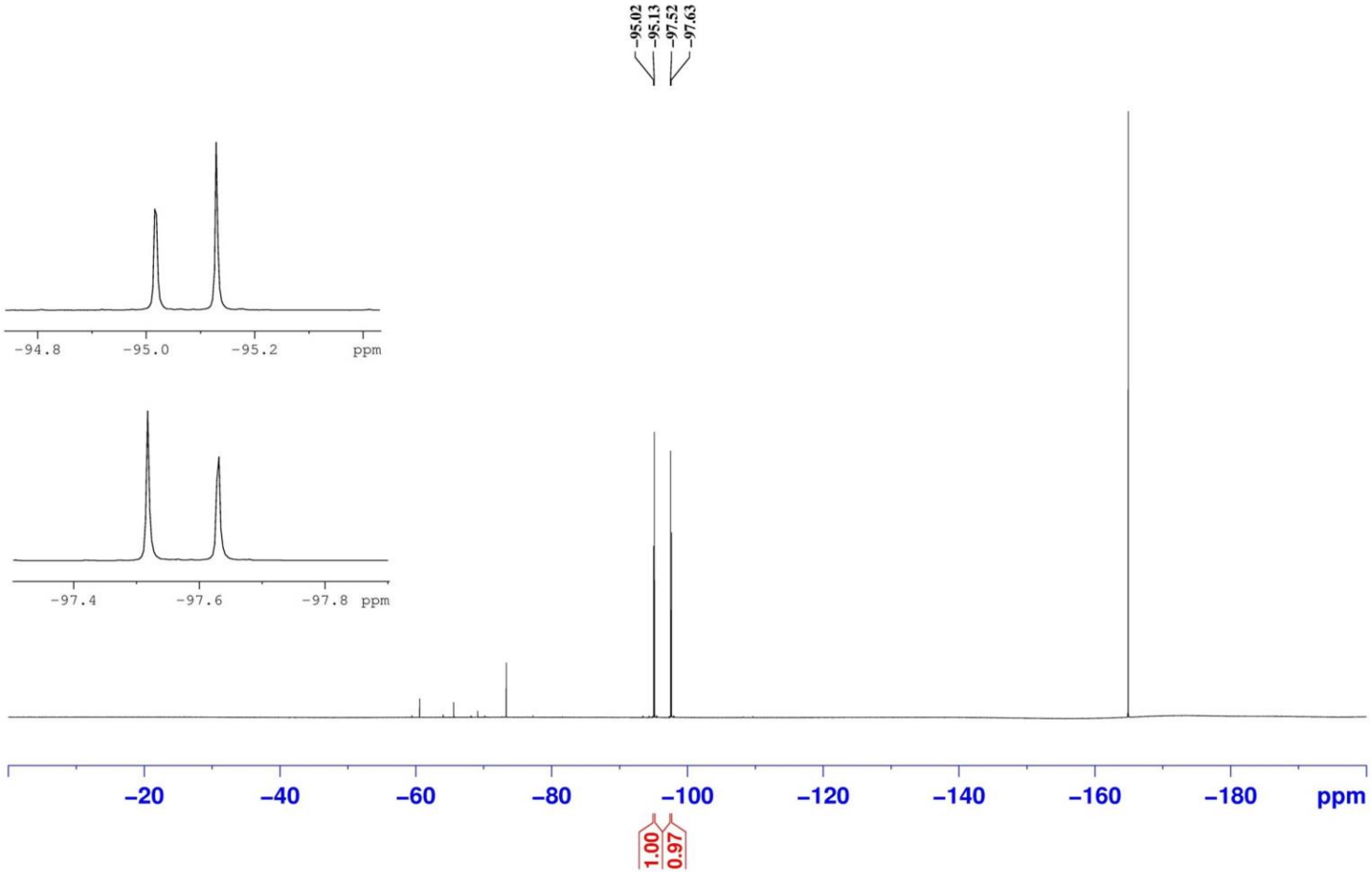


(4–(difluoromethylene)–6,6–dimethylheptyl)benzene
125 MHz, CDCl3

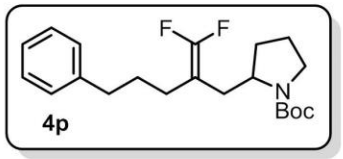


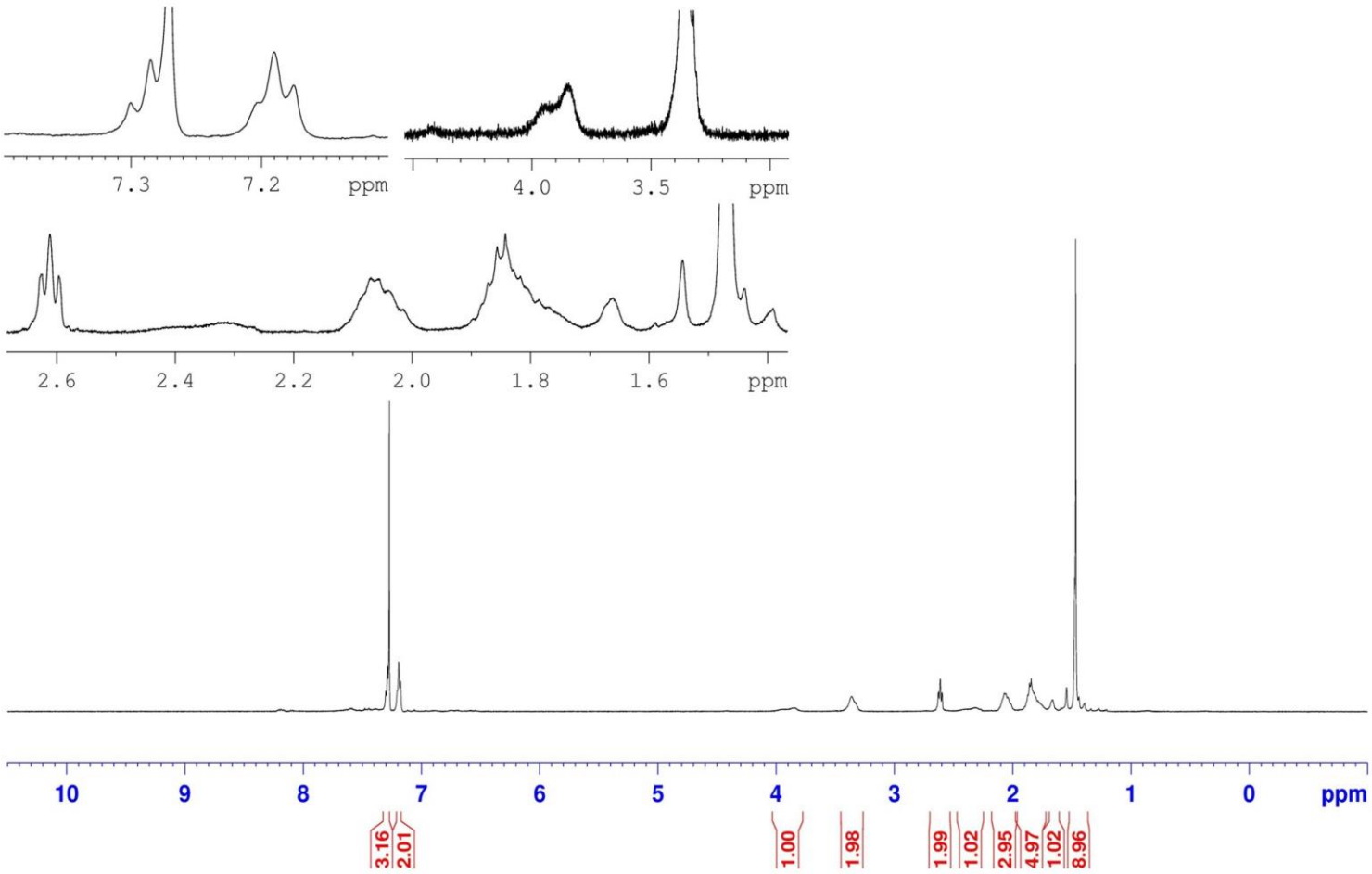
(4–(difluoromethylene)–6,6–dimethylheptyl)benzene
471 MHz, CDCl3



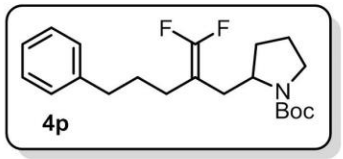


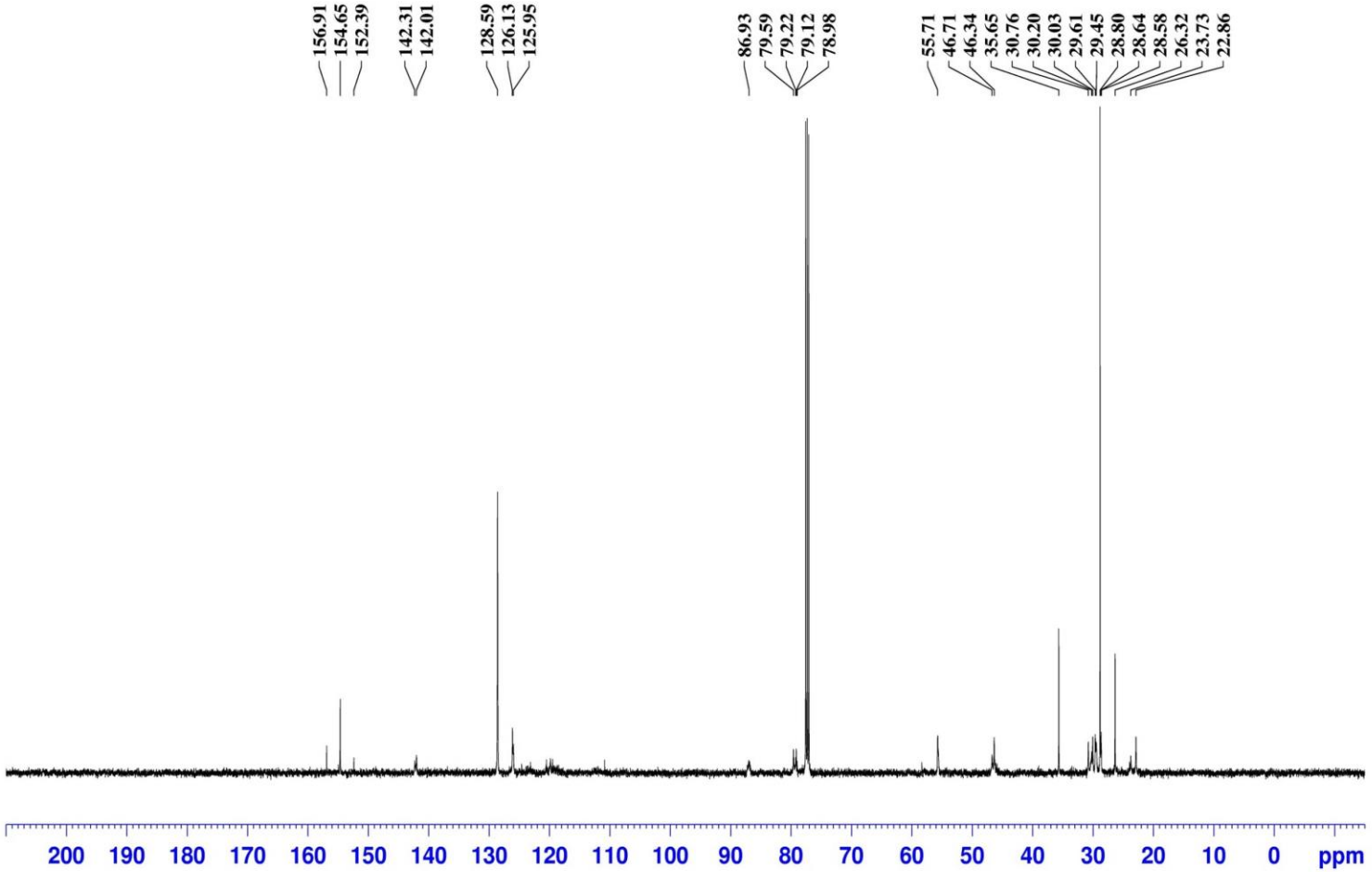
tert−butyl 2−(2−(difluoromethylene)−5−phenylpentyl)pyrrolidine−1−carboxylate
500 MHz, CDCl3



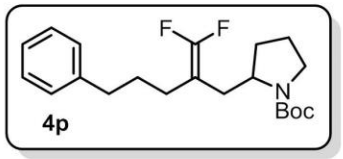


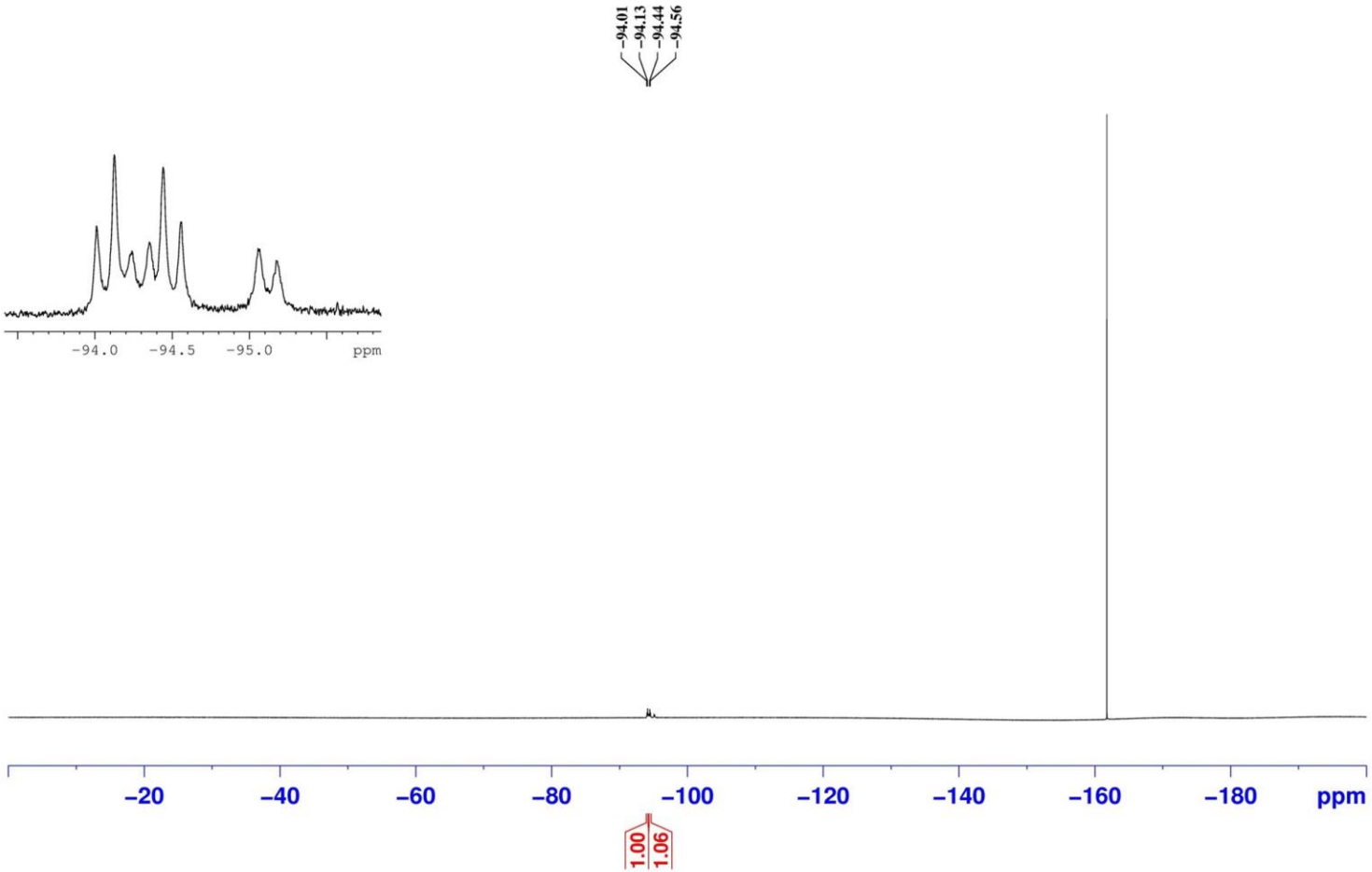
tert−butyl 2−(2−(difluoromethylene)−5−phenylpentyl)pyrrolidine−1−carboxylate
125 MHz, CDCl3



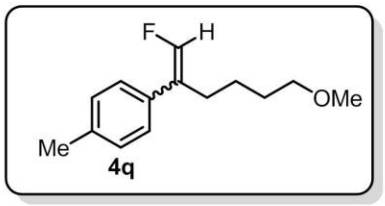


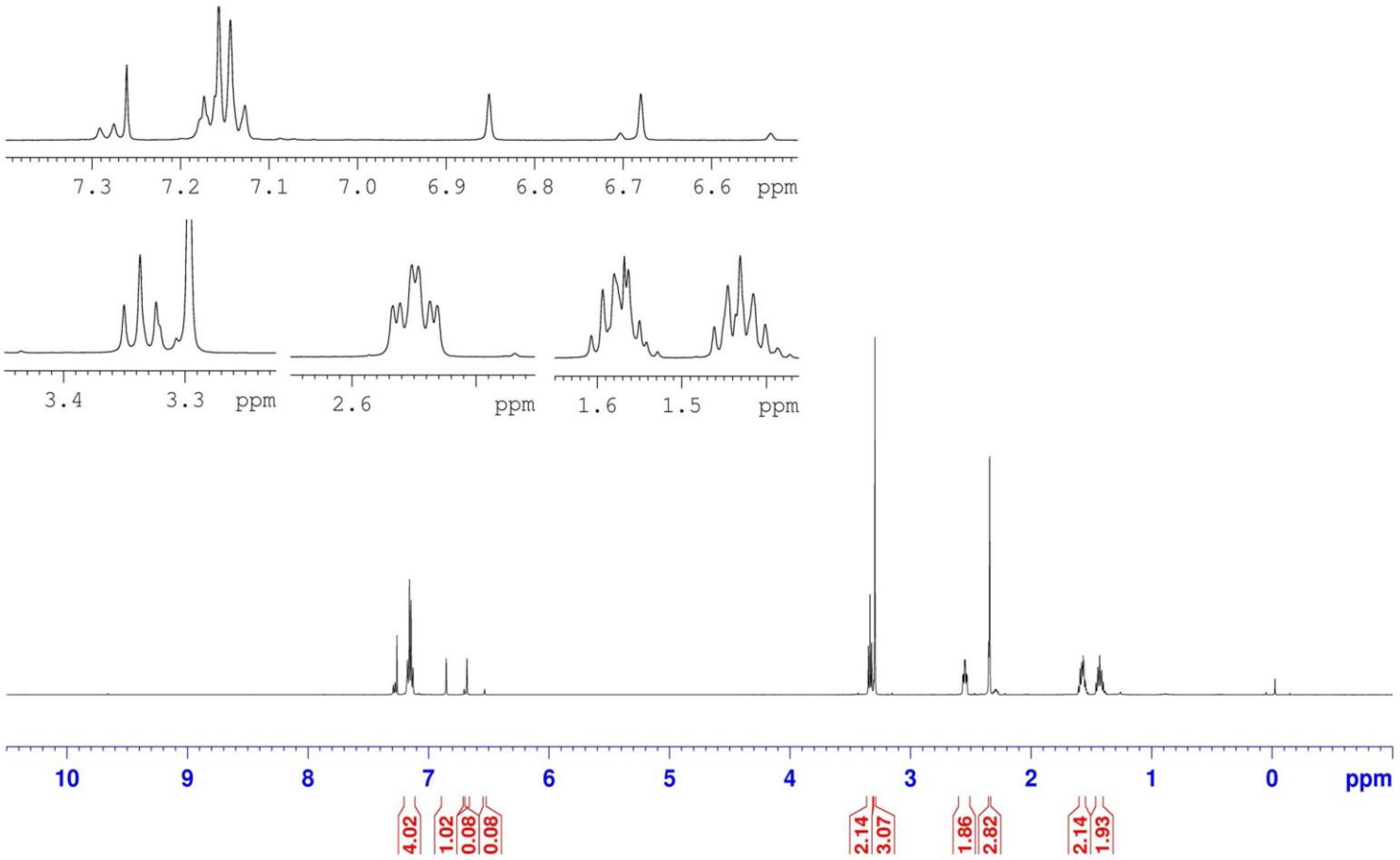
tert−butyl 2−(2−(difluoromethylene)−5−phenylpentyl)pyrrolidine−1−carboxylate
471 MHz, CDCl3



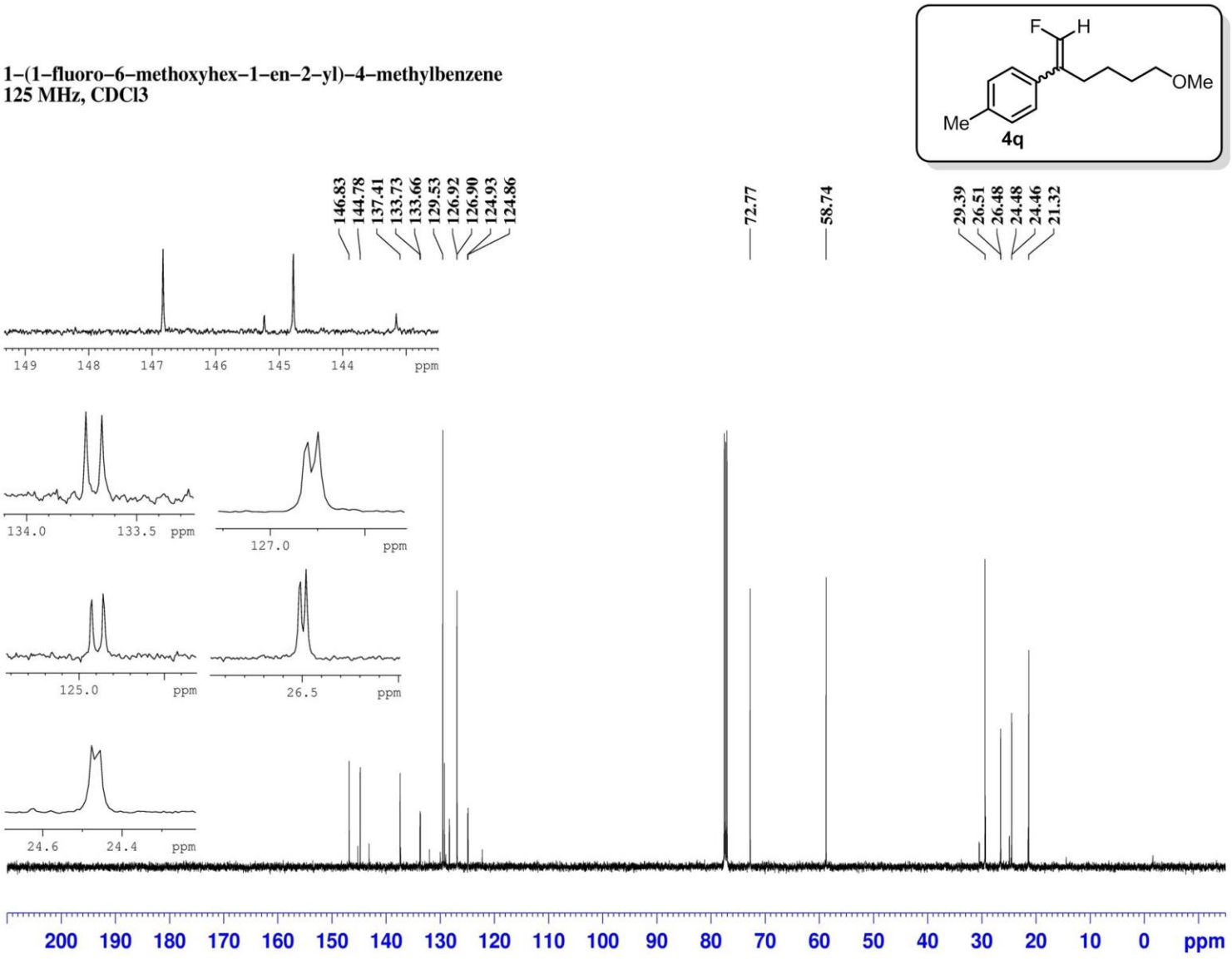


1–(1–fluoro–6–methoxyhex–1–en–2–yl)–4–methylbenzene
500 MHz, CDCl3

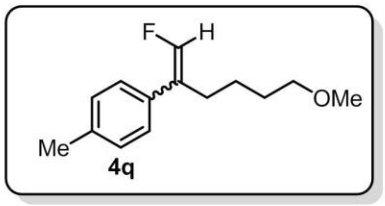


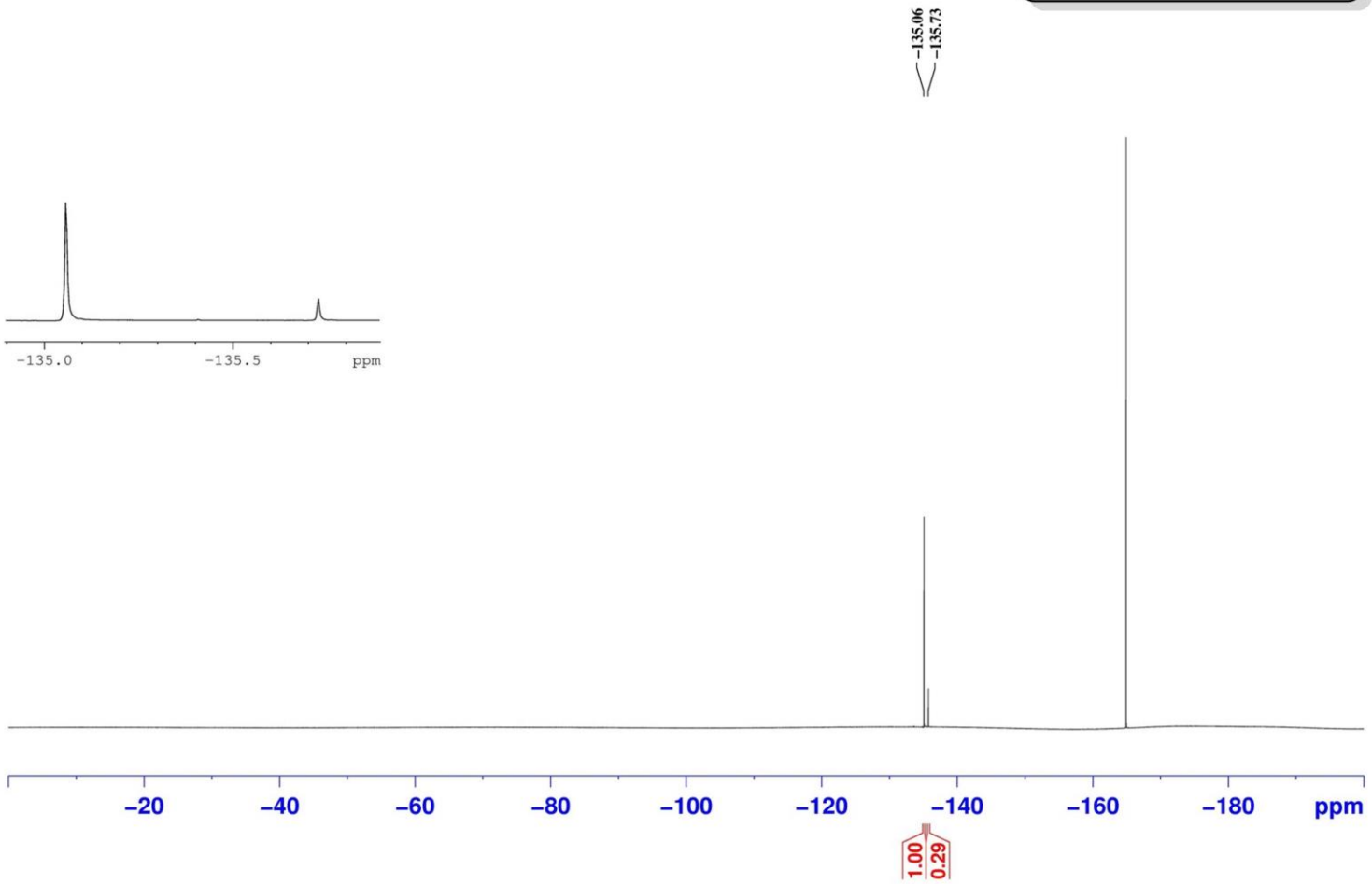


1–(1–fluoro–6–methoxyhex–1–en–2–yl)–4–methylbenzene
125 MHz, CDCl3

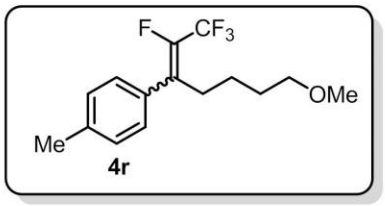


1–(1–fluoro–6–methoxyhex–1–en–2–yl)–4–methylbenzene
471 MHz, CDCl3

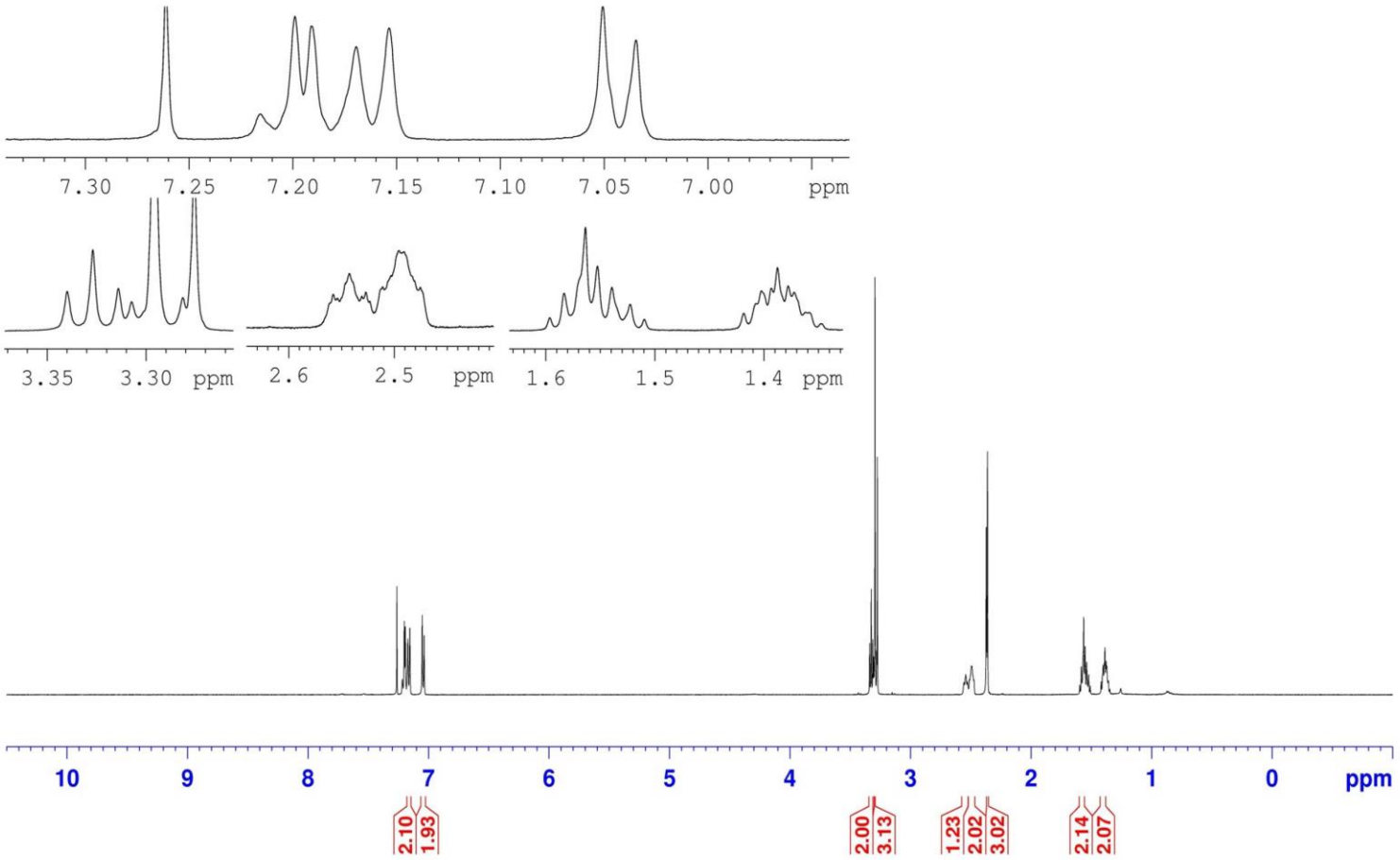




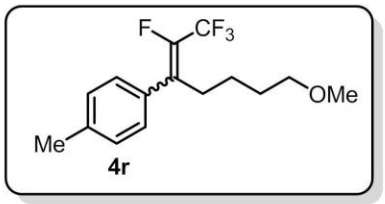
1−methyl−4−(1,1,1,2−tetrafluoro−7−methoxyhept−2−en−3−yl)benzene
500 MHz, CDCl3



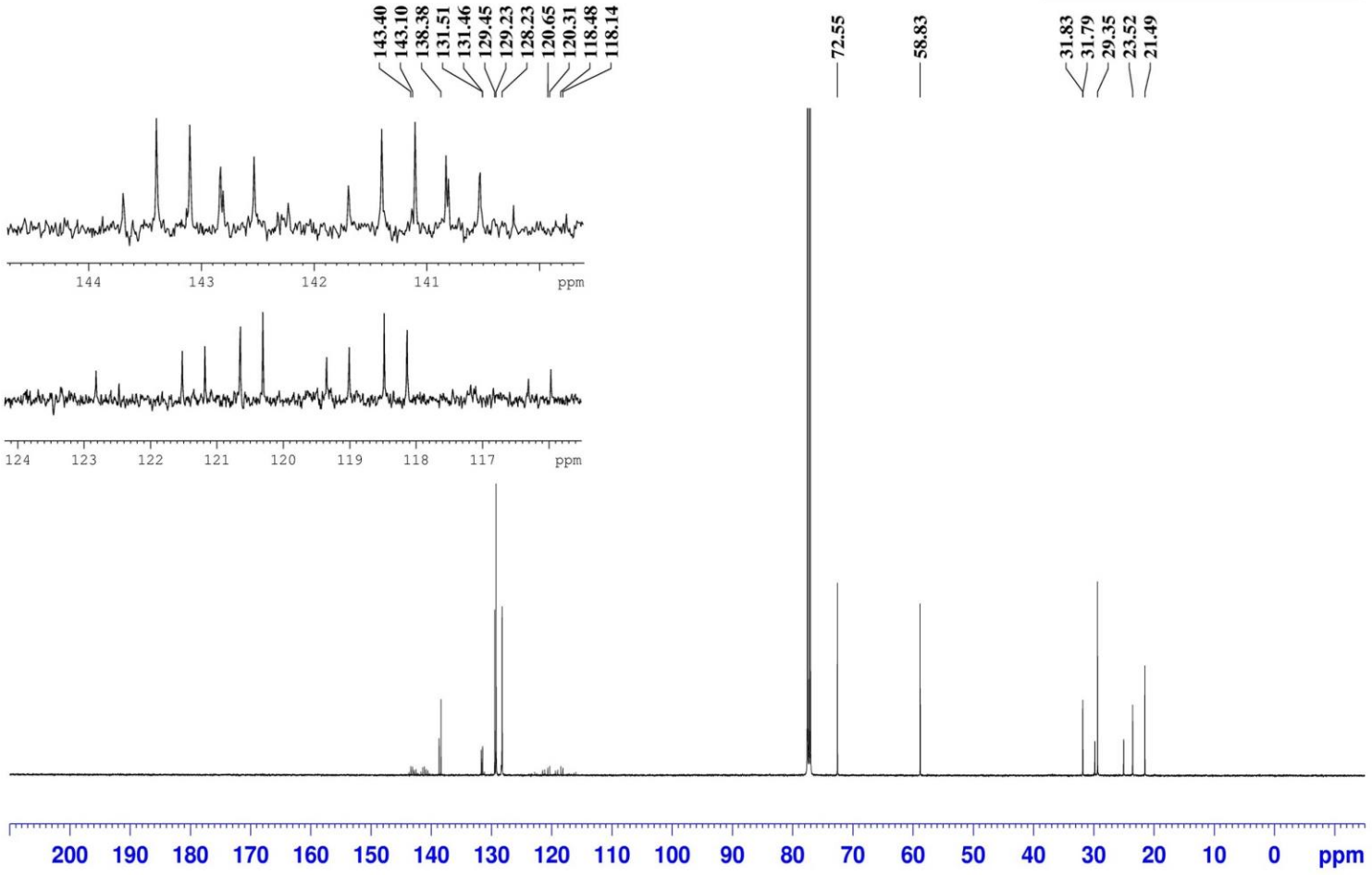
4r



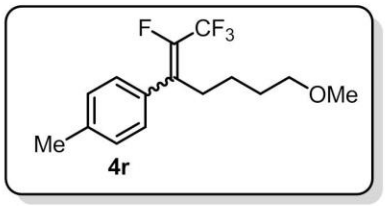
1–methyl–4–(1,1,1,2–tetrafluoro–7–methoxyhept–2–en–3–yl)benzene
125 MHz, CDCl3

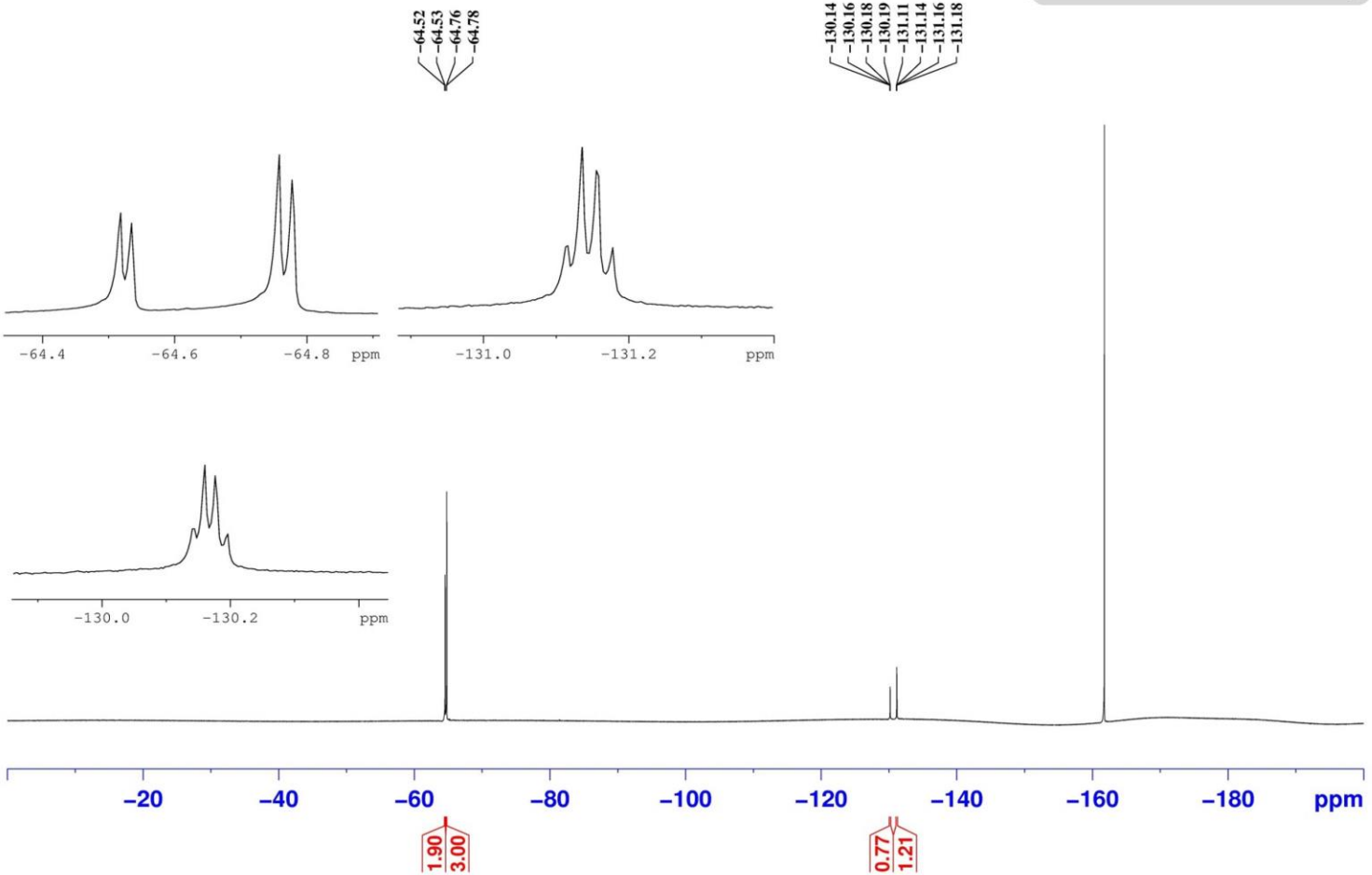


4r

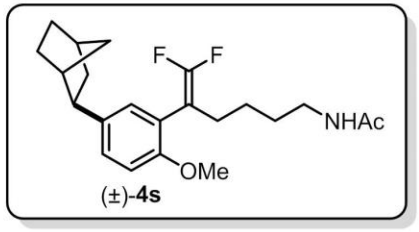


1−methyl−4−(1,1,1,2−tetrafluoro−7−methoxyhept−2−en−3−yl)benzene
471 MHz, CDCl3

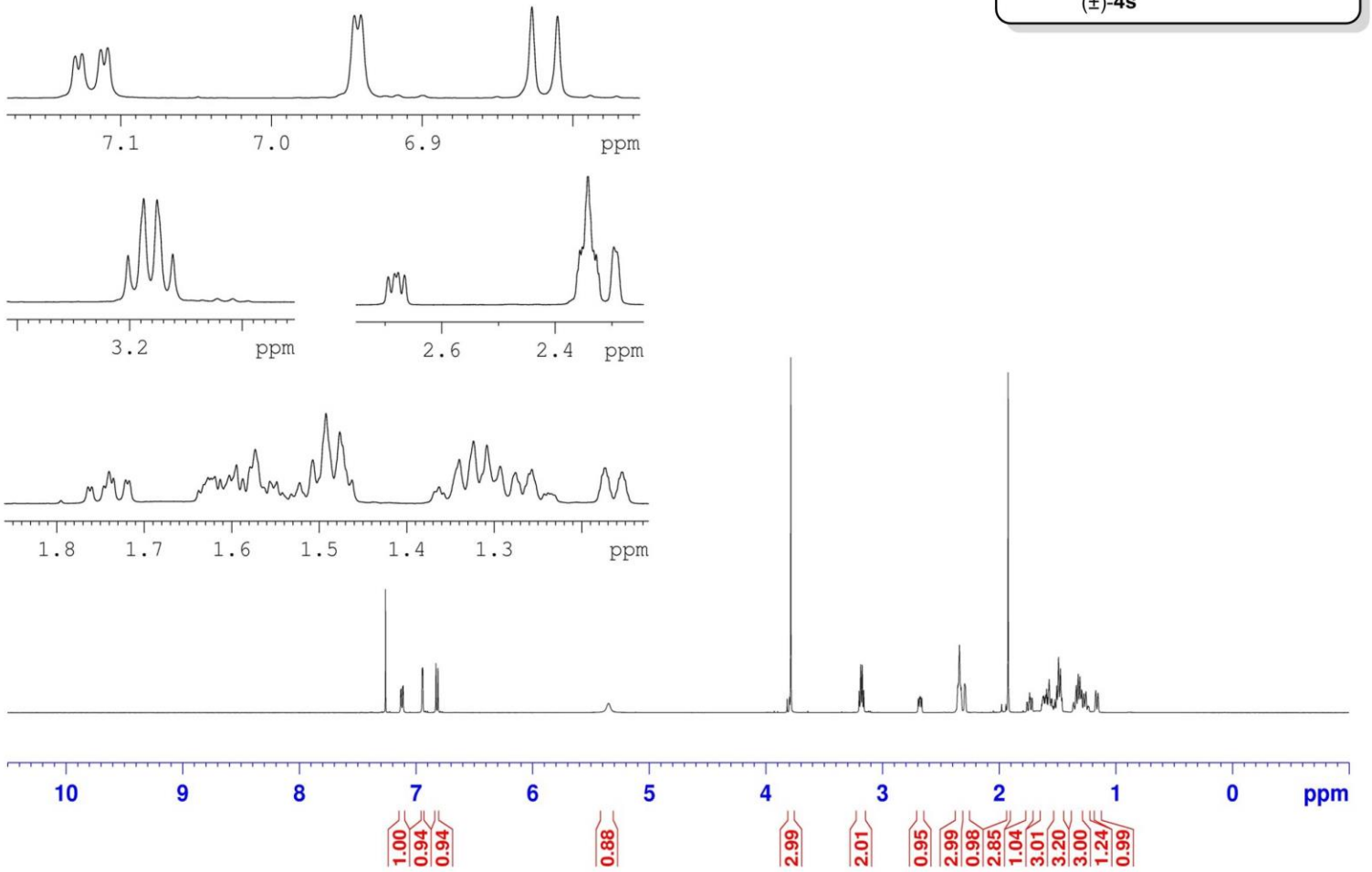




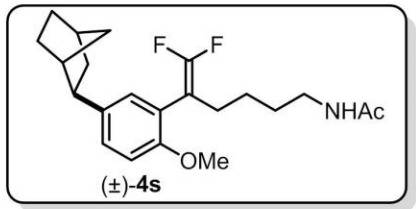
N–(5–(5–((±)–bicyclo[2.2.1]heptan–2–yl)–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl)acetamide
500 MHz, CDCl3



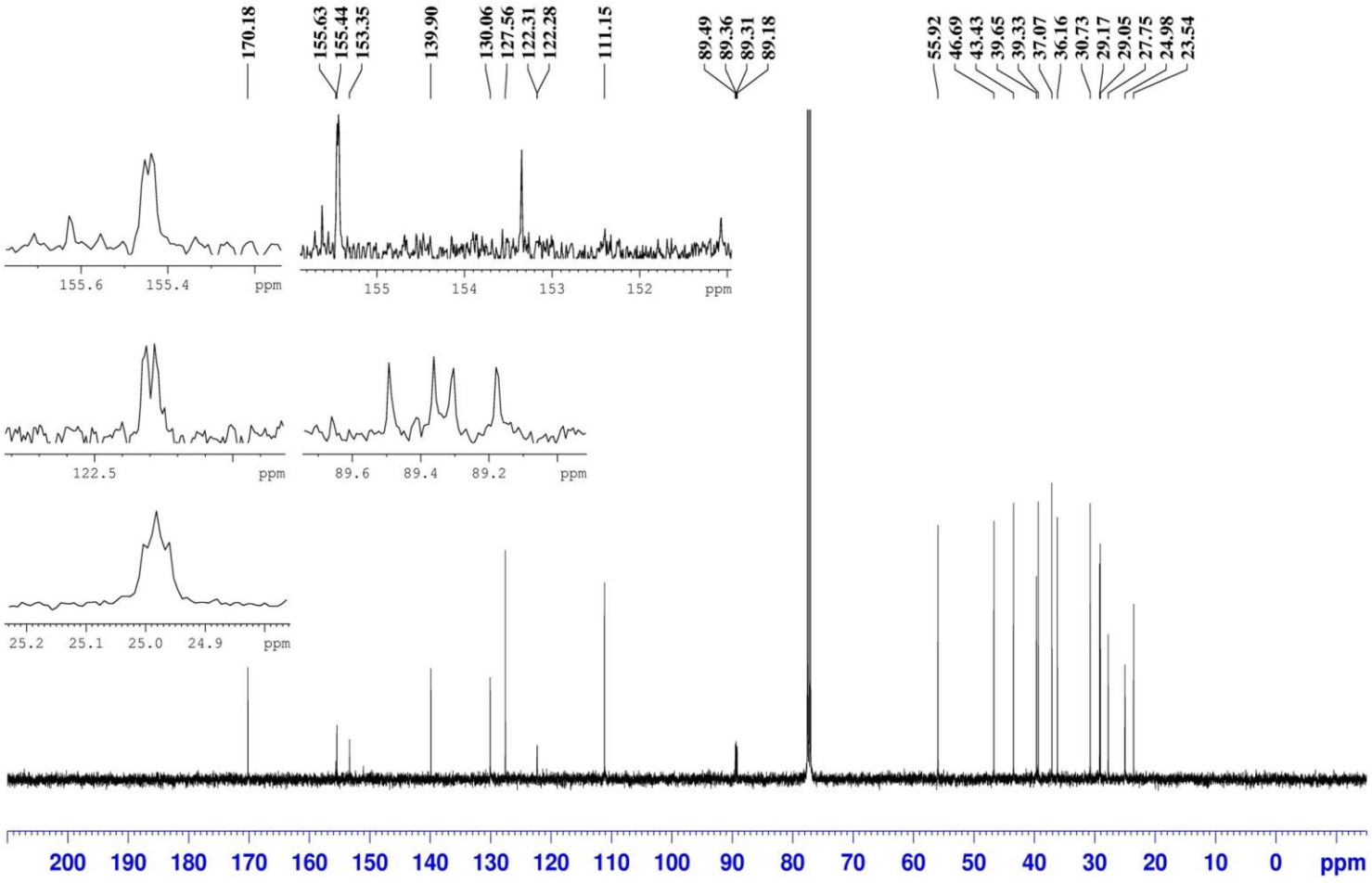
(±)-**4s**



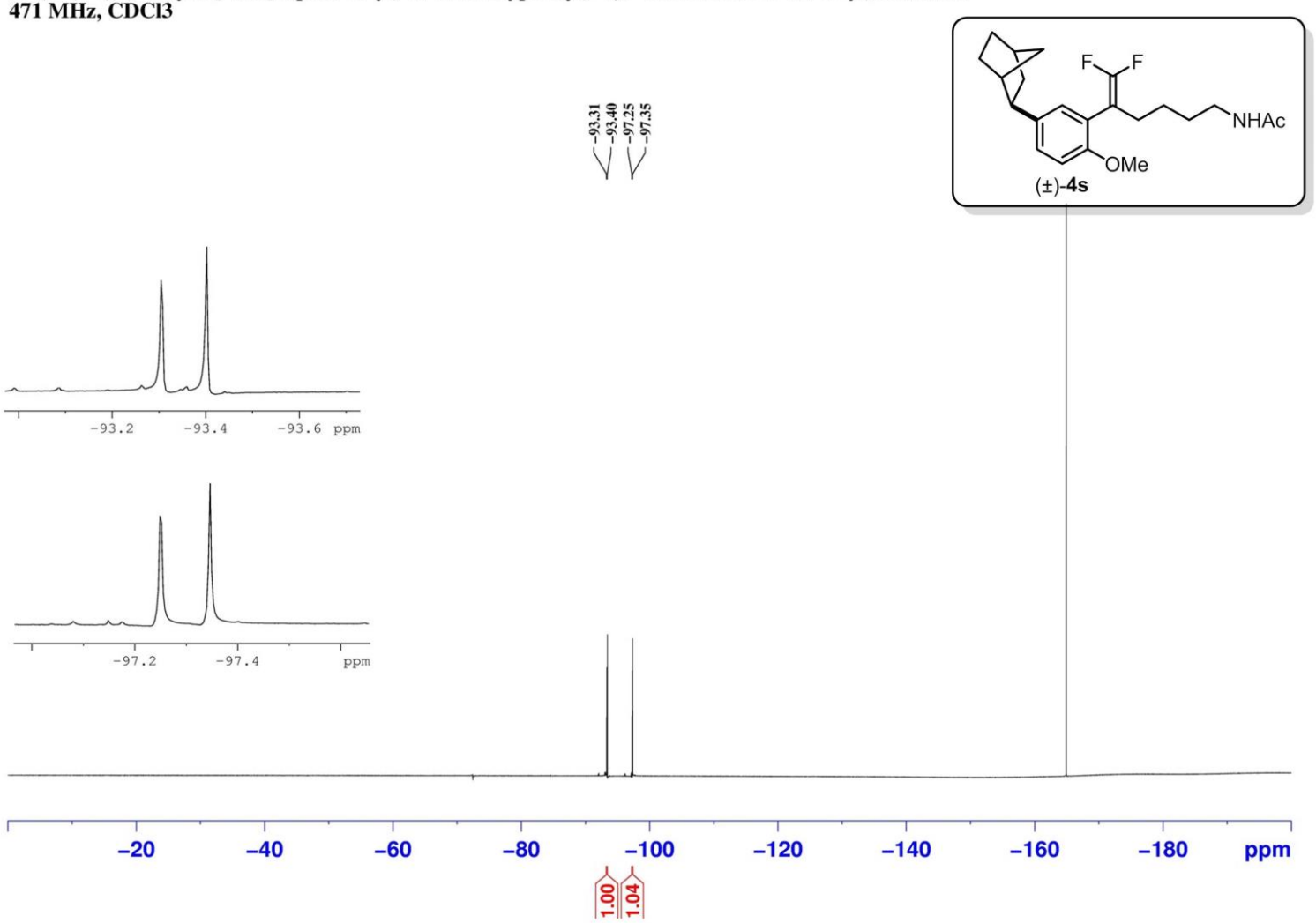
N–(5–(5–((±)–bicyclo[2.2.1]heptan–2–yl)–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl)acetamide
125 MHz, CDCl3



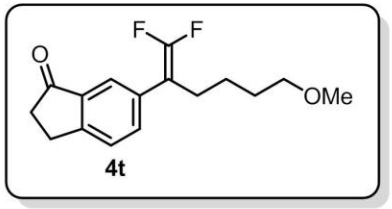
(±)-**4s**



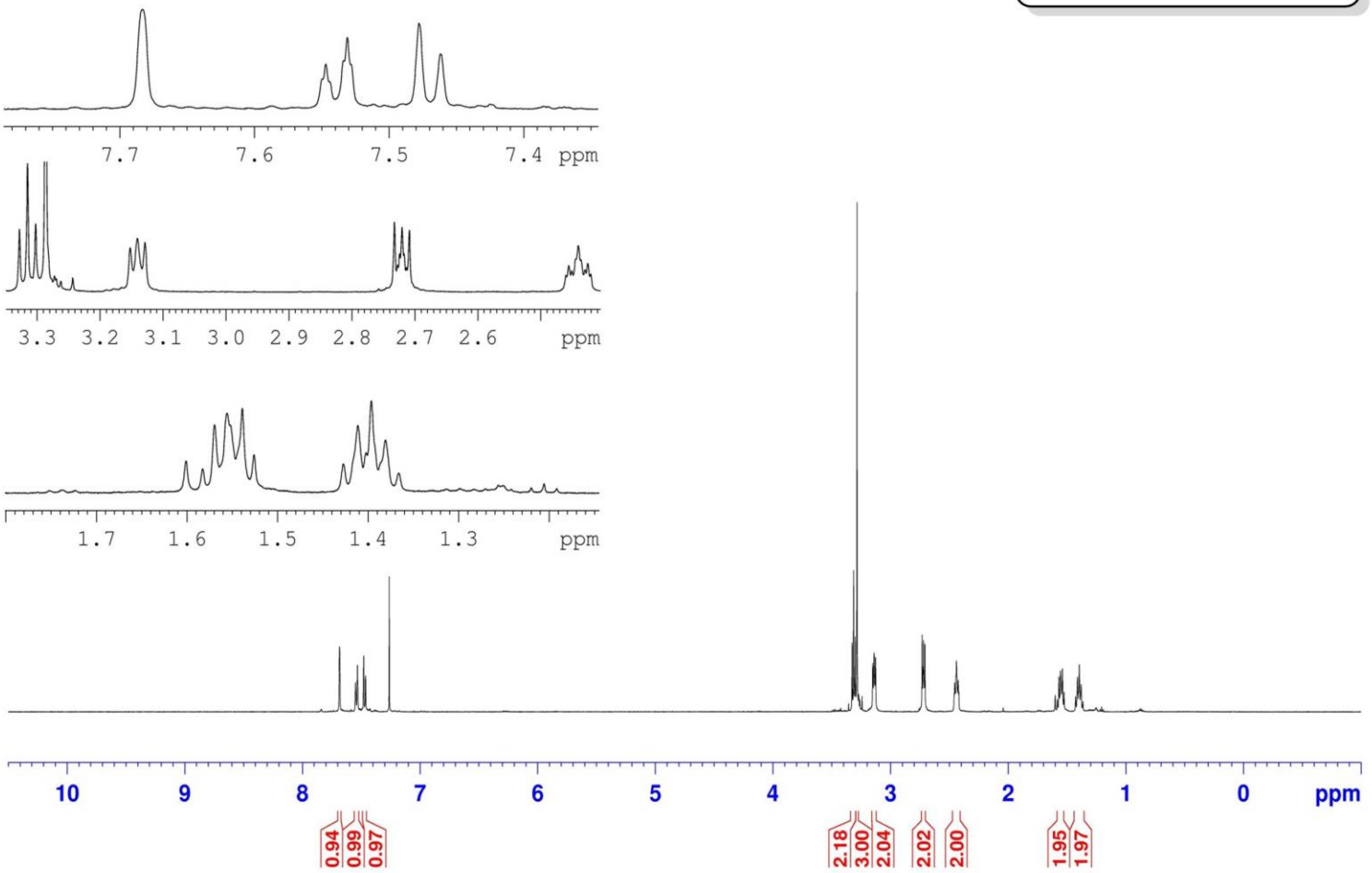
N–(5–(5–((±)–bicyclo[2.2.1]heptan–2–yl)–2–methoxyphenyl)–6,6–difluorohex–5–en–1–yl)acetamide
471 MHz, CDCl3



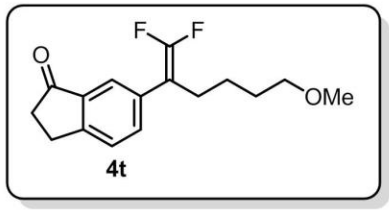
6−(3,3,3−trifluoroprop−1−en−2−yl)−2,3−dihydro−1H−inden−1−one
500 MHz, CDCl3



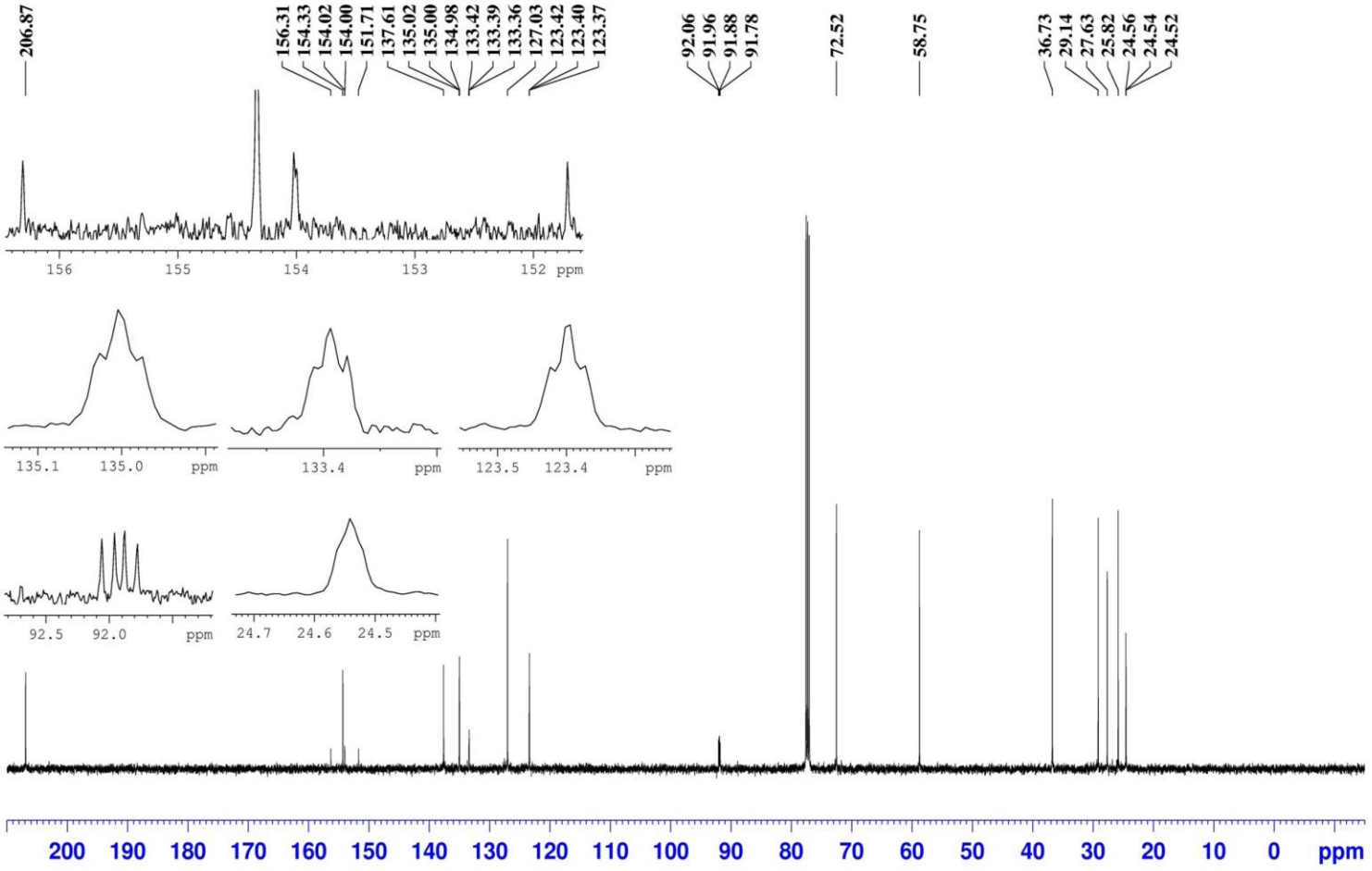
4t



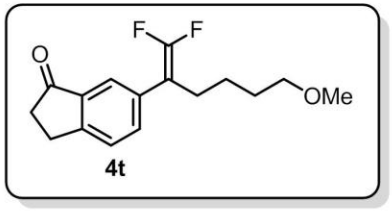
6–(1,1–difluoro–6–methoxyhex–1–en–2–yl)–2,3–dihydro–1H–inden–1–one
125 MHz, CDCl3



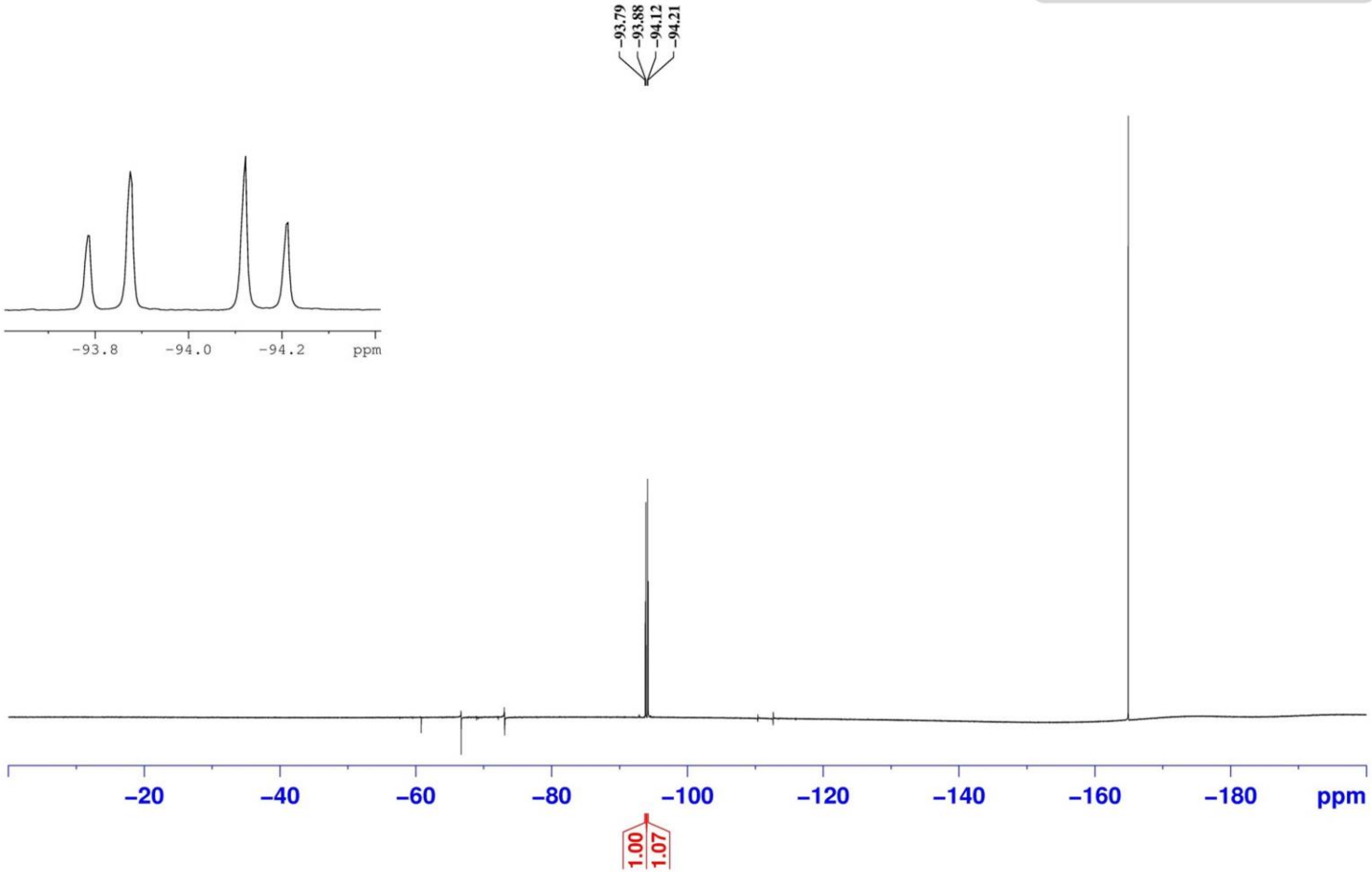
4t



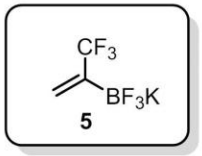
6–(1,1–difluoro–6–methoxyhex–1–en–2–yl)–2,3–dihydro–1H–inden–1–one
471 MHz, CDCl3

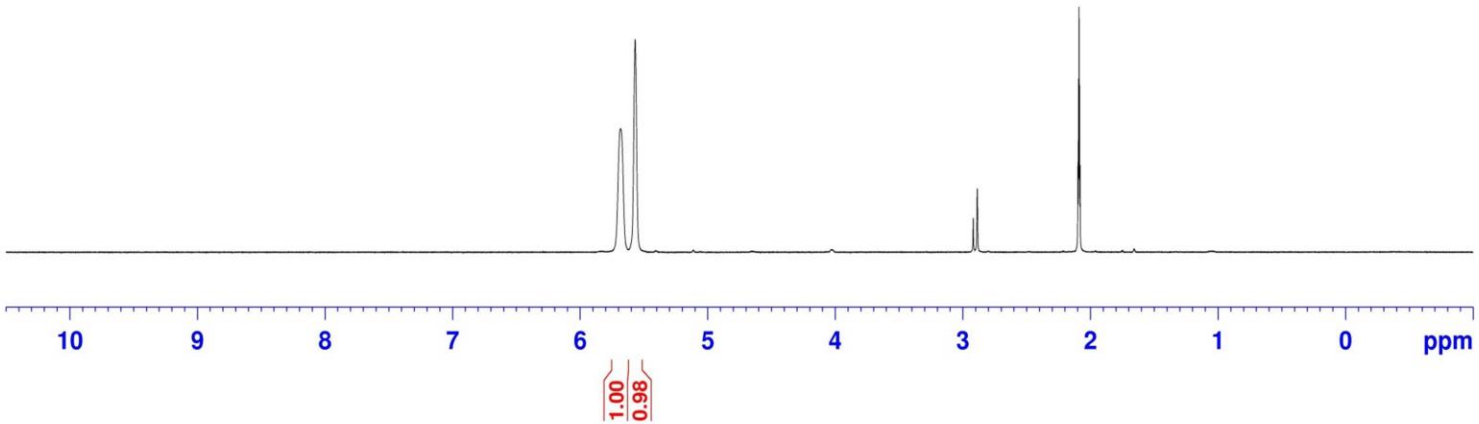


4t

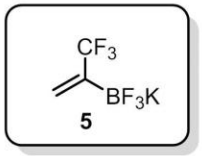


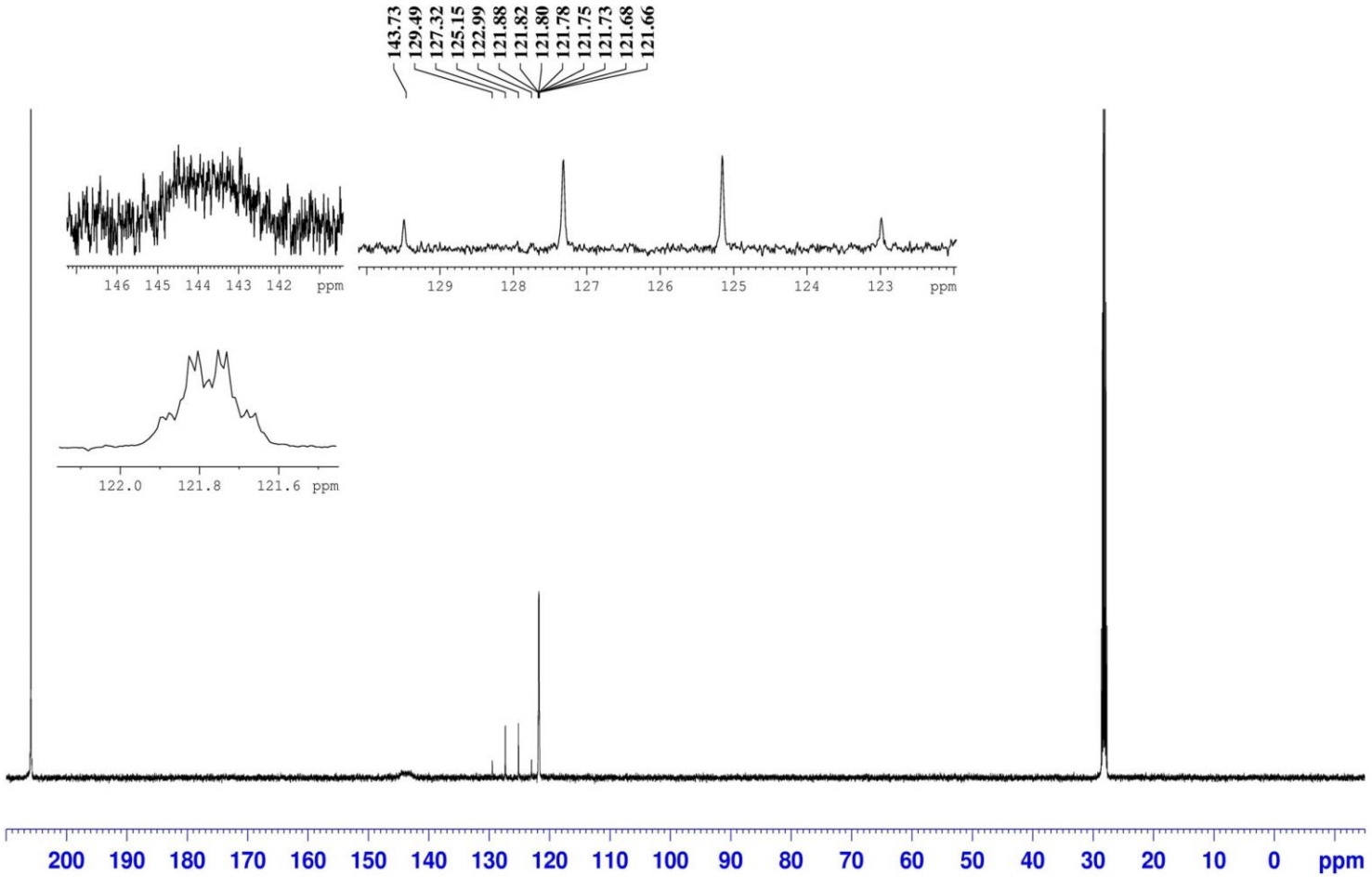
Potassium Trifluoro(3,3,3−trifluoroprop−1−en−2−yl)borate
500 MHz, acetone−d6



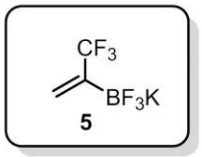


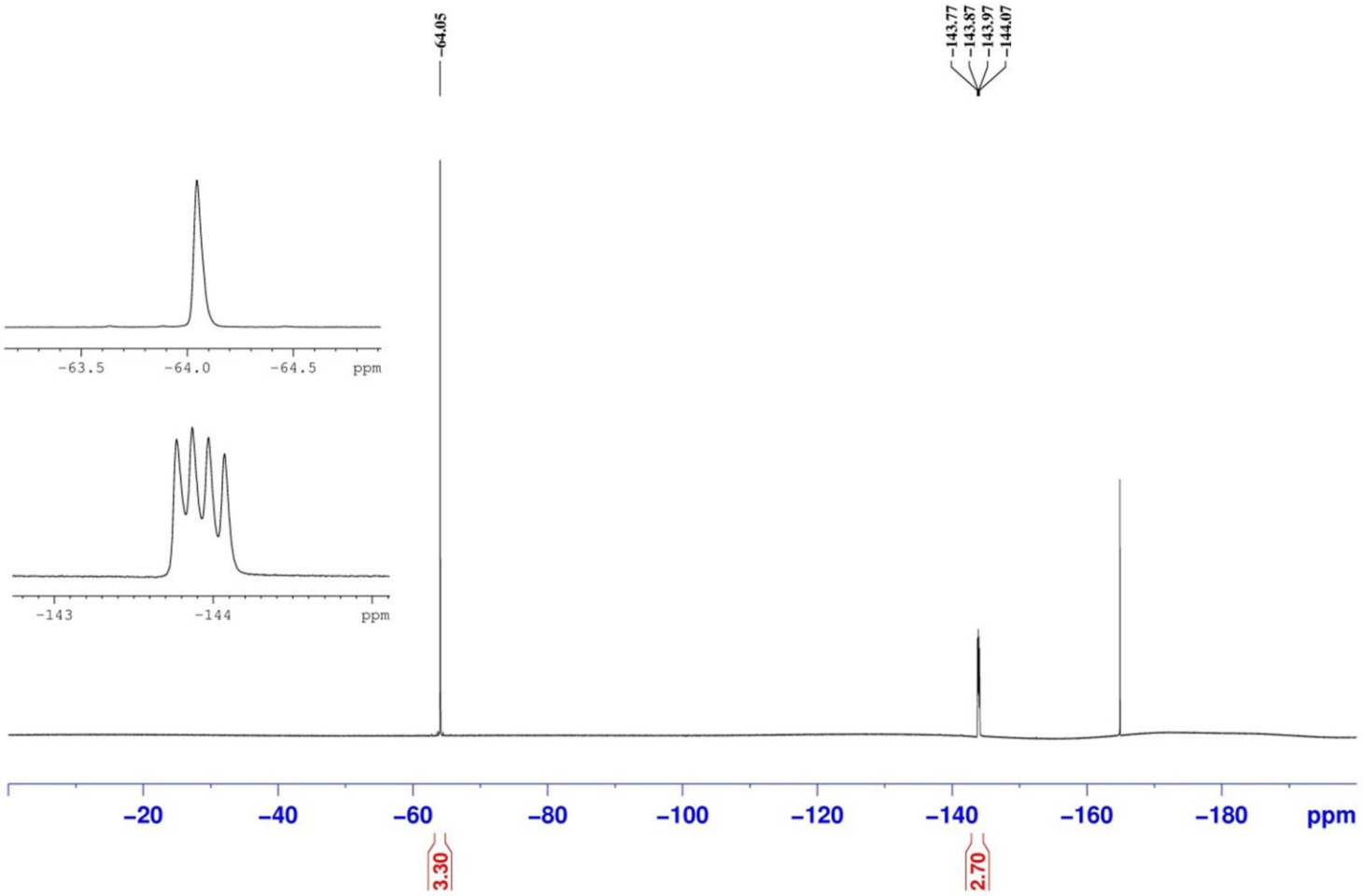
Potassium Trifluoro(3,3,3−trifluoroprop−1−en−2−yl)borate
125 MHz, acetone−d6





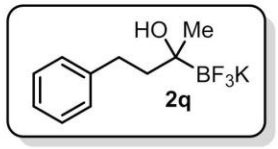
Potassium Trifluoro(3,3,3−trifluoroprop−1−en−2−yl)borate
471 MHz, CDCl3

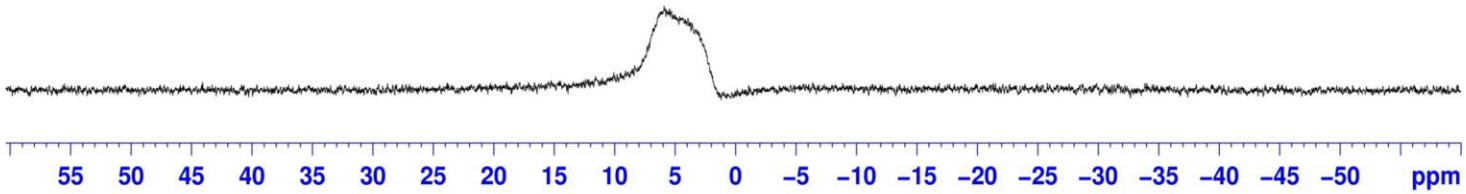




Potassium 2–Hydroxy–4–phenylbutyltrifluoroborate
125 MHz, acetone–d6

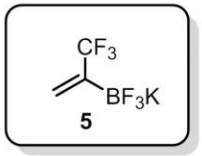
5.92



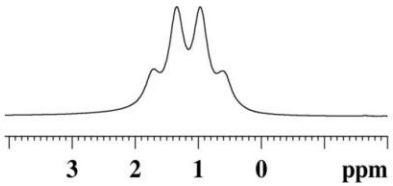


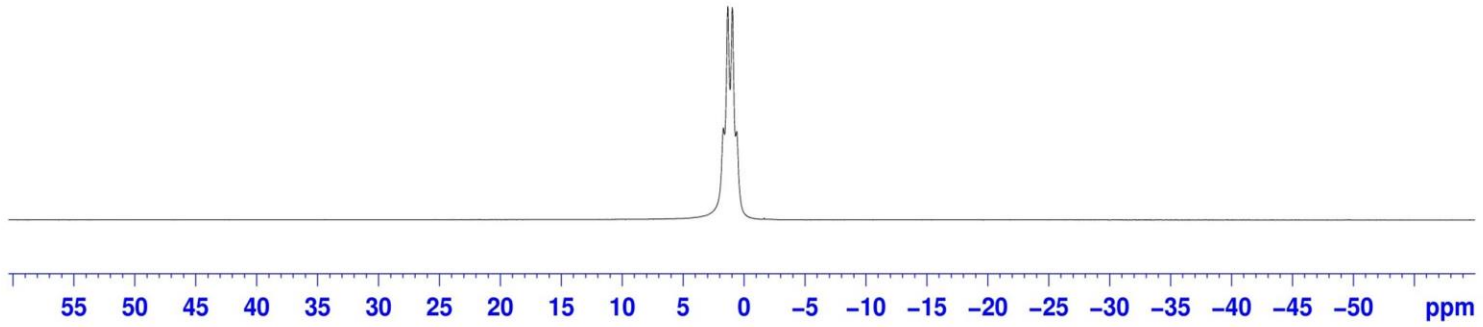
Potassium Trifluoro(3,3,3−trifluoroprop−1−en−2−yl)borate
128 MHz, acetone−d6

1.70
1.34
0.97
0.61

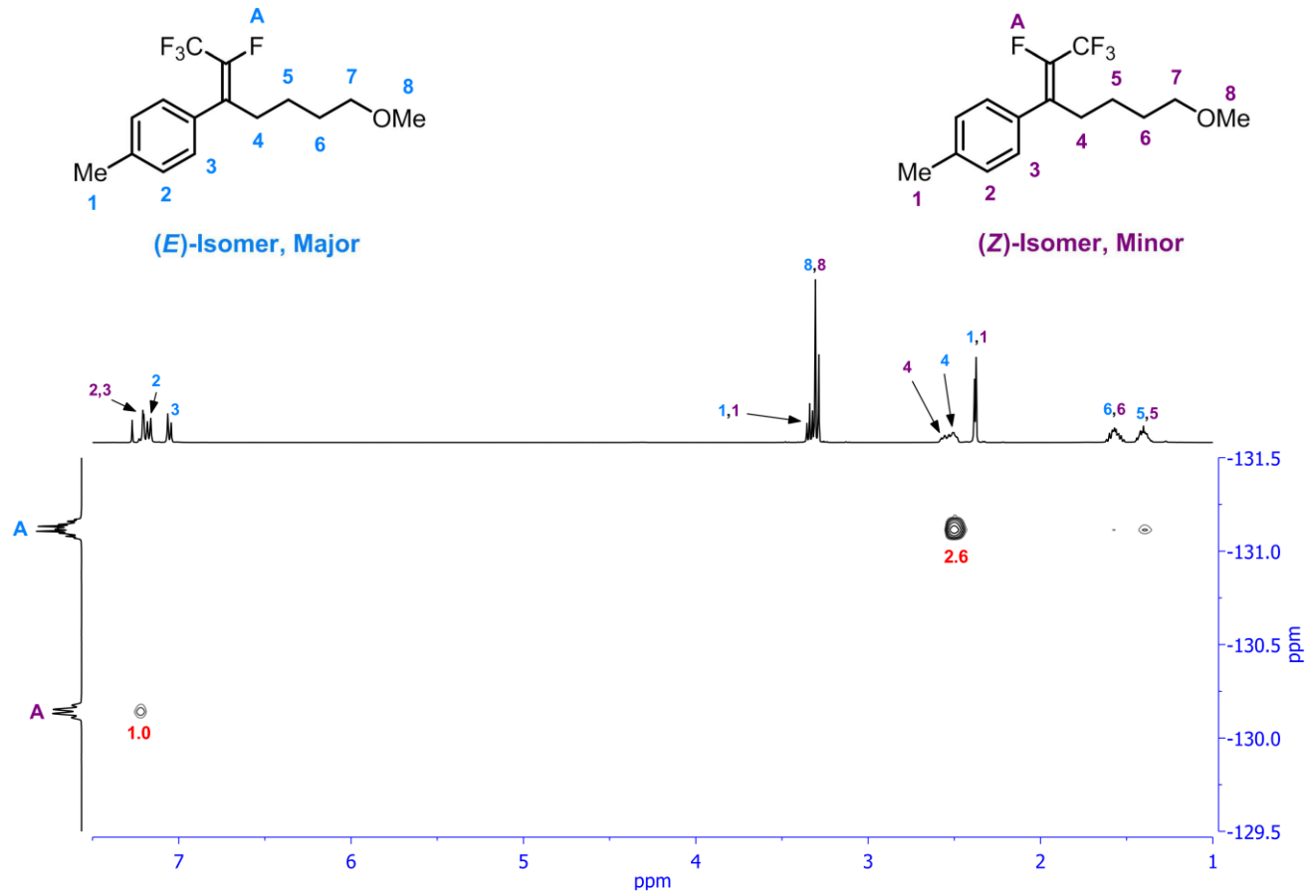


5

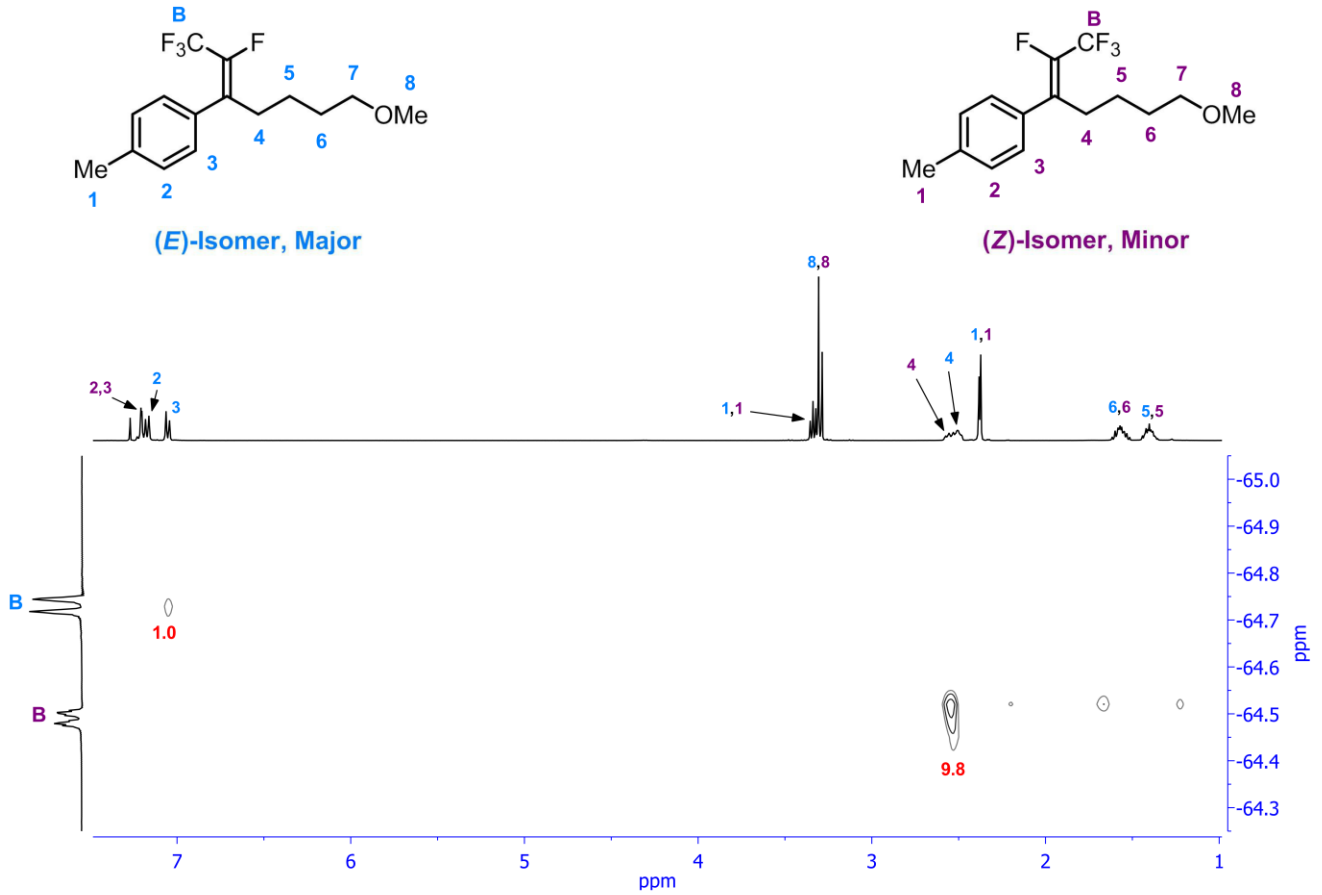




^{1}H-^{19}F HOESY Spectra of 4r Isomers



^{1}H- ^{19}F HOESY of the "F" region of the isomers of **4r**. 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 500 MHz NMR spectrometer. A hoseyph pulse sequence was used with 8 scans of a 4k X 256 matrix collected. The spectrum was obtained using a relaxation delay of 1 s, mixing time of 0.8 s, and a phase-sensitive TPPI method. The fluorine spectrum *was not* calibrated to hexafluorobenzene. Processing was performed using MestReNova.



^{1}H- ^{19}F HOESY of the "CF_3" region of the isomers of **4r**. 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 500 MHz NMR spectrometer. A hoseyph pulse sequence was used with 8 scans of a 4k X 256 matrix collected. The spectrum was obtained using a relaxation delay of 1 s, mixing time of 0.8 s, and a phase-sensitive TPPI method. The fluorine spectrum *was not* calibrated to hexafluorobenzene. Processing was performed using MestReNova.