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# Rapid Access to Diverse, Trifluoromethyl-Substituted Alkenes Using Complementary Strategies

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# Supporting Information

## Key to Abbreviated Terms:

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] Unless otherwise noted, NMR spectra ($^{1}$H, $^{11}$B, $^{13}$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 77.3), DMSO-$d_6$ (δ 39.5), the carbonyl carbon of acetone (δ 205.9), or the nitrile carbon of MeCN-$d_3$ (δ 118.3), 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 reported 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] α-$CF_3$-β-TMS-alcohols were prepared in-house using the procedures outlined here. Information for previously synthesized radical precursors (preparation protocols, characterization, etc.) can be found in our earlier reports.[5] All other radical precursors were purchased from commercial suppliers. 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.[6]

**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 34W blue (470 nm) 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.

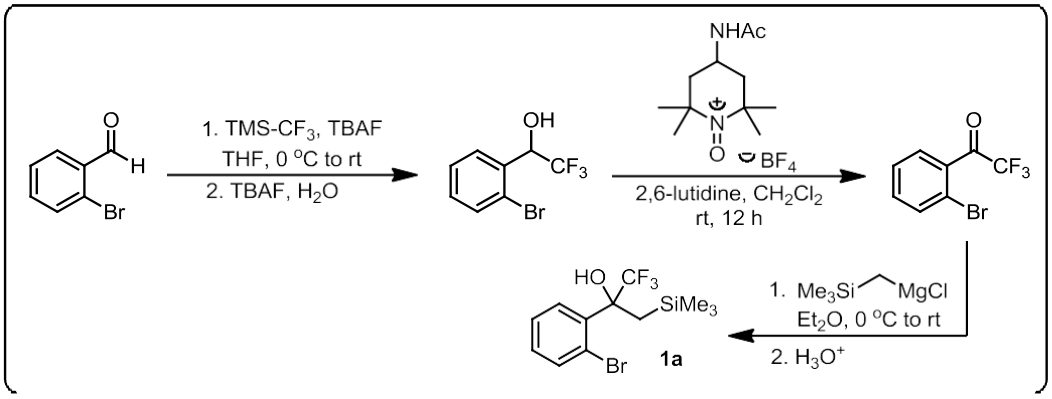
[4] Tellis, J. C.; Primer, D. P.; Molander, G. A. *Science* **2014**, *345*, 433.

[5] ***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) Patel, N. R.; Kelly, C. B.; Siegenfeld, A. P.; Molander, G. A. *ACS Catal.* **2017**, *7*, 1766. ***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. ***α-Silylamines*** (f) Remeur, C.; Kelly, C. B.; Patel, N. R.; Molander, G. A. *ACS Catal.*, **2017**, *7*, 6065.

[6] Mercadante, M. A.; Kelly, C. B.; Bobbitt, J. M.; Tilley, L. J.; Leadbeater, N. E. *Nat. Protoc.* **2013**, *8*, 666.

# Synthesis of α-$CF_3$-β-TMS-Alcohols

***Preparation of 2-(2-bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1a)***




*Trifluoromethylation*

**1-(2-Bromophenyl)-2,2,2-trifluoroethanol[7]**

The following is a modification of the procedure outline by Kelly et al.[8] To a 250 mL round bottom flask equipped with a stir bar was added 2-bromobenzaldehyde (7.40 g, 40 mmol, 1 equiv), THF (60 mL), and TMS–$CF_3$ (7.38 g, 52 mmol, 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 °C[9] in an ice-water bath. After stirring for approximately 10 min, TBAF (1 M in THF, 0.4 mL, 0.4 mmol, 0.01 equiv) was added dropwise *via* a syringe. After stirring for 10 min, the ice-bath was removed and the soln was allowed to stir for approximately 8 h at rt.

To cleave the silyl ether formed by the reaction, $H_2O$ (4 mL, ~5.5 equiv) was added *via* a syringe followed by TBAF (1 M in THF, 4 mL, 4 mmol, 0.1 equiv). When the cleavage was judged to be complete,[10] the contents of the flask were transferred to a separatory funnel. Deionized $H_2O$ (100 mL) and $Et_2O$ (~100 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 $H_2O$ (100 mL) and brine (100 mL). The organic layer was dried ($Na_2SO_4$),

[7] Baumann, M; Baxendale, I. R.; Martin, L. J.; Ley, S. V. *Tetrahedron*, **2009**, *65*, 6611.
[8] 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.
[9] Note that on small scales (< 20 mmol), the TBAF could be added relatively fast. However, upon scale-up the addition of TBAF is quite exothermic. Hence, it is recommended that the TBAF be added as slow as possible and/or cooling the reaction mixture to a temperature lower than that of 0 °C.
[10] It is recommended that this cleavage step be monitored by some form of spectroscopy (e.g., GC/MS or NMR).

and the solvent was removed *in vacuo* by rotary evaporation affording crude 1-(2-bromophenyl)-2,2,2-trifluoroethanol. The crude product was purified by vacuum distillation (bp 59-61 °C @ 0.1 mmHg) giving the pure $CF_3$ alcohol (9.02 g, 88%) as a clear, pale-yellow oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 2.70 (d, *J* = 4.9 Hz, 1H), 5.63 (dt, *J* = 11.4, 6.3 Hz, 1H), 7.27 (td, *J* = 7.9, 1.7 Hz, 1H), 7.41 (td, *J* = 7.6, 1.1 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H).
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 71.5 (q, $J_{C\text{-}C\text{-}F}$ =32.1 Hz, CH), 124.6 (q, $J_{C\text{-}F}$ = 282.3 Hz, $CF_3$), 124.1 (C), 128.1 (CH), 129.5 (CH), 131.2 (CH), 133.3 (CH), 134.1 (C).
**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -80.71 (s, 3F).

*Oxidation*

**1-(2-Bromophenyl)-2,2,2-trifluoroethanone[11]**

The following is a modification of the procedure outline by Kelly et al.[12] To a one-neck 300 mL round bottom flask equipped with a stir bar was added 1-(2-bromophenyl)-2,2,2-trifluoroethanol (8.16 g, 32 mmol, 1 equiv), 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidin-1-ium tetrafluoroborate (24.01 g, 80 mmol, 2.6 equiv), and $CH_2Cl_2$ (80 mL). The mixture was allowed to stir at rt for approximately 5 min. At this time, 2,6-lutidine (7.72 g, 8.34 mL, 72 mmol, 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 and gradually turned red. The solvent was removed *in vacuo* to afford a thick red residue. To this thick residue was added $Et_2O$ (~100 mL), causing immediate precipitation of the spent oxidant. The heterogeneous soln was allowed to stir for 10 min, and the solids were filtered off through a medium porosity fritted funnel, washing with $Et_2O$ (~100 mL). The solvent was removed from the filtrate *in vacuo* by rotary evaporation. The crude material was then loaded atop a silica gel plug. The plug was eluted with $Et_2O$ (~150 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 65- 67 °C @ 0.1 mmHg), giving the pure $CF_3$ ketone (7.04 g, 87%) as a clear, yellow oil.

[11] Van Der Mei, F. W.; Qin, C.; Morrison, R. J.; Hoveyda, A. H. *J. Am. Chem. Soc*, **2017**, *139*, 9053.
[12] 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 7.43 - 7.50 (m, 2H), 7.70 (dtt, $J$ = 5.8, 2.9, 1.4 Hz, 1H), 7.76 (s, 1H).

**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 115.9 (q, $J_{\mathbf{C\text{-}F}}$ = 292.3 Hz, $CF_3$), 121.9 (C), 127.6 (CH), 130.1 (CH), 132.7 (C), 134.3 (CH), 135.2 (CH), 182.5 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 36.7 Hz, C).

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -76.26 (s, 3F).

*Alkylation*

**2-(2-Bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1a)**

This procedure is a modification of the procedure outlined by Kelly et al.[13] To a 100 mL flame-dried round bottom flask equipped with a stir bar was added 1-(2-bromophenyl)-2,2,2-trifluoroethanone (4.43 g, 0.0175 mol, 1 equiv) in anhyd $Et_2O$ (22 mL). The flask was cooled to 0 °C *via* an ice-water bath for 5 min. After this time, $Me_3SiCH_2MgCl$ (1.3 M in THF, 20.2 mL, 0.0263 mol) was added dropwise over 10 min *via* a syringe. The soln became bright yellow initially, then faded upon addition of additional organomagnesium reagent. After complete addition, the soln was stirred at 0 °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 °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*. 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. Further purification was accomplished by vacuum distillation (bp 68-70 °C @ 0.1 mmHg), affording 2-(2-bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol **1a** (4.46 g, 83%) as a colorless oil.

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

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ -0.12 (s, 9H), 1.52 (s, 1H), 1.55 (s, 1H), 2.09 (br s, 1H), 7.19 (ddd, *J* = 8.2, 7.2, 1.7 Hz, 1H), 7.35 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 7.61 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H).

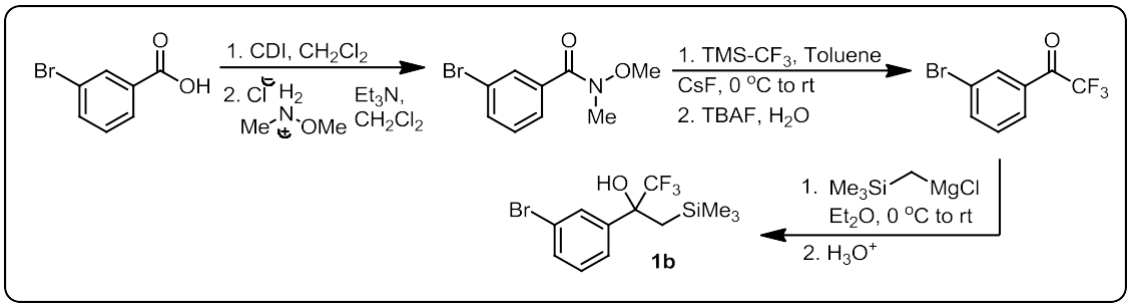
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ -0.1 ($CH_3$), 23.5 ($CH_2$), 79.3 (q, $J_{C\text{-}C\text{-}F}$ = 30.2 Hz, C), 120.6 (C), 125.7 (q, $J_{C\text{-}F}$ = 287.8 Hz, $CF_3$), 127.2 (CH), 130.0 (CH), 131.1 (CH), 135.7 (CH), 135.8 (C).

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -83.15 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3531 (w), 2955 (w), 2899 (w), 1354 (s), 1249 (s), 1210 (s), 1156 (s), 1077 (s), 919 (s), 837 (s), 757 (s).

**HRMS** (EI+) calcd for $C_{11}H_{16}BrOSi$ $[M - CF_3]^+$: 271.0154, found: 271.0173.

***Preparation of 2-(3-bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1b)***




*Weinreb Amide Synthesis*

**3-Bromo-*N*-methoxy-*N*-methylbenzamide[14]**

To a 500 mL round bottom flask equipped with a stir bar was added 3-bromobenzoic acid (10.05 g, 0.050 mol, 1 equiv) and $CH_2Cl_2$ (170 mL). To this stirred soln was added 1,1'-carbonyldiimidazole (9.73 g, 0.060 mol, 1.2 equiv) in one portion, turning the soln 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 soln 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),

[14] Gabriel, C. M.; Keener, M.; Gallou, F.; Lipshutz, B. H. *Org.Lett*, **2015**, *17*, 3968.

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 (11.21 g, 92%) as a clear light yellow oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 3.36 (s, 3H), 3.55 (s, 3H), 7.28 (t, *J* = 7.9 Hz, 1H), 7.58 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.82 (t, *J* = 1.6 Hz, 1H).
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 33.6 ($CH_3$), 61.2 ($CH_3$), 122.0 (C), 126.8 (CH), 129.7 (CH), 131.2 (CH), 133.6 (CH), 136.1 (C), 168.2 (C).

*Trifluoromethylation*

**1-(3-Bromophenyl)-2,2,2-trifluoroethanone[15]**

To a 250 mL round bottom flask equipped with a stir bar was added 3-bromo-*N*-methoxy-*N*-methylbenzamide (10.05 g, 0.041 mol, 1 equiv). CsF (1.51 g, 0.010 mol, 0.2 equiv) followed by toluene (100 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 °C for 15 min. TMS–$CF_3$ (14.2 g, 0.100 mol, 2 equiv) was added to the reaction mixture dropwise over a period of 10 min. After completion of addition, the reaction mixture was allowed to stir for 10 min at 0 °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 soln became dark brown in color.* Reaction progress was monitored by $^1$H NMR.[16]

Once complete conversion to the silylated tetrahedral intermediate was confirmed, the toluene was removed *in vacuo via* rotary evaporation. Hexanes (50 mL), followed by deionized $H_2O$ (50 mL) followed by 1 M soln of TBAF in THF (50 mL, 0.050 mol, 1 equiv) were added to the reaction flask. The flask was equipped with an air-cooled reflux condenser and then heated to 50 °C in an oil bath for 8 h to facilitate cleavage of the silyl ether. Once the reaction was judge to be

[15] Wu, W.; Tian, Q.; Chen, T.; Weng, Z. *Chem. Eur J.*, **2016**, *22*, 16455.
[16] 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.

complete,[17] the reaction was cooled to rt. The reaction mixture was then diluted with $Et_2O$ (125 mL) and deionized $H_2O$ (100 mL) and 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 69-71 °C @ 1 mmHg), affording the pure $CF_3$ ketone (4.93g, 47%) as a clear colorless oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 7.45 (t, *J* = 7.9 Hz, 1H), 7.85 (ddd, *J* = 8.1, 1.8, 0.9 Hz, 1H), 8.00 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.20 (s, 1H).
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 116.7 (q, $J_{C\text{-}F}$ = 291.4 Hz, $CF_3$), 123.7 (C), 128.8 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, C), 130.9 (CH), 131.9 (CH), 133.2 (CH), 138.7 (CH), 179.7 (q, $J_{C\text{-}C\text{-}F}$ = 35.7 Hz, C).
**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -74.71 (s, 3F).

*Alkylation*

**2-(3-Bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1b)**

Synthesis of 2-(3-bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (4.36 g, 73%) was accomplished using the procedure for the preparation of 2-(2-bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, with the following modification: The reaction was conducted using 1-(3-bromophenyl)-2,2,2-trifluoroethanone (4.43 g, 0.0175 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly. The crude carbinol was further purified by vacuum distillation (bp 70-72 °C @ 0.1 mmHg), affording the pure carbinol as a colorless oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ -0.16 (s, 9H), 1.44 (d, *J* = 15.3 Hz, 1H), 1.58 (d, *J* = 11.1 Hz, 1H), 2.30 (s, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 7.45 - 7.51 (m, 2H), 7.73 (s, 1H).

[17] 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 hexamethdisiloxane coming at ≈ 0.06 ppm.

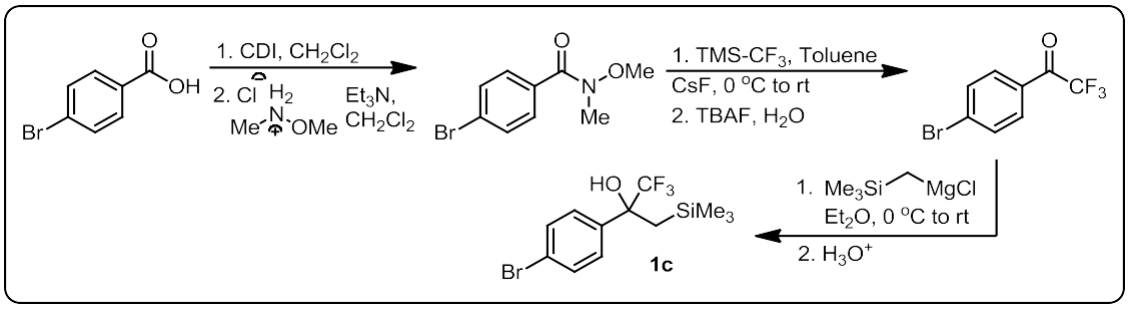
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 0.0 ($CH_3$), 25.3 ($CH_2$), 77.3 (q, $J_{C\text{-}C\text{-}F}$ = 29.3 Hz, C), 122.7 (C), 125.9 (q, $J_{C\text{-}F}$ = 285.9 Hz, $CF_3$), 125.3 (app d, two overlapping CH signals), 129.9 (CH), 131.8 (CH), 140.7 (C).

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -85.02 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3615 (w), 2955 (w), 2899 (w), 1597 (s), 1215 (s), 1152 (s), 837 (s), 786 (s), 768 (s), 710 (s), 699 (s).

**HRMS** (EI+) calcd for $C_{11}H_{16}BrOSi$ $[M - CF_3]^+$: 271.0154, found: 271.0159.

***2-(4-Bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1c)***




*Weinreb Amide Synthesis*

**4-Bromo-*N*-methoxy-*N*-methylbenzamide[18]**

Synthesis of 4-bromo-*N*-methoxy-*N*-methylbenzamide (7.68 g, 90%) was accomplished using the procedure for the preparation of 3-bromo-*N*-methoxy-*N*-methylbenzamide, with the following modification: The reaction was conducted using 4-bromobenzoic acid (7.03 g, 0.035 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly. The desired amide was obtained as a clear, light yellow oil.

**$^{1}$H NMR** ($CDCl_3$, 500 MHz) δ 3.36 (s, 3H), 3.53 (s, 3H), 7.52 - 7.56 (m, 2H), 7.56 - 7.60 (m, 2H).

**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 33.7 (br s, $CH_3$), 61.3 ($CH_3$), 125.3 (C), 130.1 (CH), 131.4 (CH), 133.0 (C), 168.8 (C).

*Trifluoromethylation*

[18] Muir, C. W.; Kennedy, A. R.; Redmond, J. M.; Watson, A. J. B. – *Org. Biomol. Chem.*, **2013**, *11*, 3337.

**1-(4-Bromophenyl)-2,2,2-trifluoroethanone**[15]

Synthesis of 1-(4-Bromophenyl)-2,2,2-trifluoroethanone (5.15 g, 68%) was accomplished using the procedure for the preparation of 1-(3-bromophenyl)-2,2,2-trifluoroethanone, with the following modification: The reaction was conducted using 4-bromo-*N*-methoxy-*N*-methylbenzamide (7.32 g, 0.0305 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly. The crude $CF_3$ ketone was further purified by vacuum distillation (bp 69-71 °C @ 1 mmHg), affording the pure $CF_3$ ketone as a clear colorless oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 7.69 - 7.74 (m, 2H), 7.93 (d, $J$ = 7.9 Hz, 2H).
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 116.8 (q, $J_{C\text{-}F}$ = 291.4 Hz, $CF_3$), 129.0 (C), 131.7 (C), 131.7 (CH), 132.9 (CH), 180.0 (q, $J_{C\text{-}C\text{-}F}$ = 35.7 Hz, C).
**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -74.69 (s, 3F).

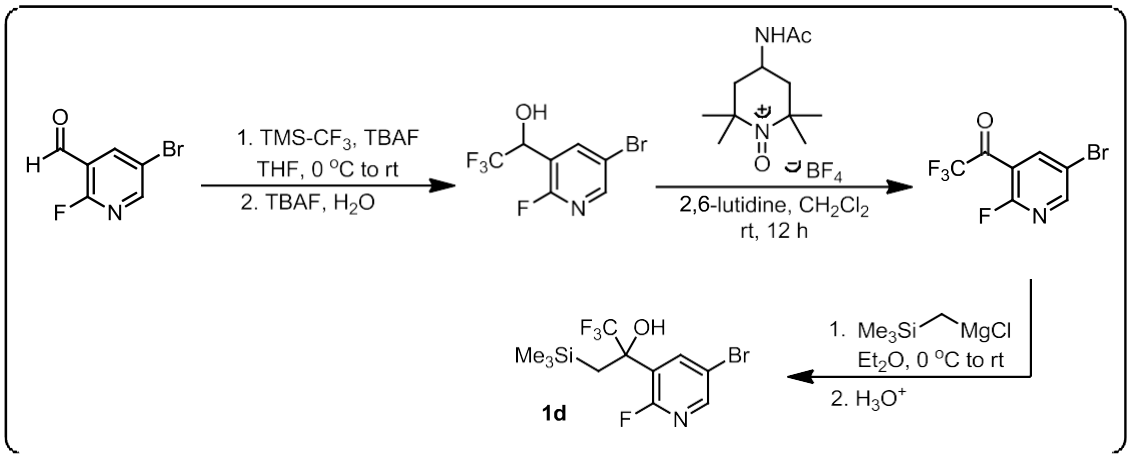
*Alkylation*

**2-(4-Bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1c)**
Synthesis of 2-(4-bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (5.07 g, 85%) was accomplished using the procedure for the preparation of 2-(2-bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, with the following modification: The reaction was conducted using 1-(4-bromophenyl)-2,2,2-trifluoroethanone (4.81 g, 0.017 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly. The crude carbinol was further purified by vacuum distillation (bp 73-75 °C @ 0.1 mmHg), affording the pure carbinol as a colorless oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ -0.16 (s, 9H), 1.43 (d, $J$ = 15.1 Hz, 1H), 1.58 (d, $J$ = 16.3 Hz, 1H), 2.28 (s, 1H), 7.40 - 7.46 (m, 2H), 7.48 - 7.53 (m, 2H).
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 0.1 ($CF_3$), 25.1 ($CH_2$), 77.5 (signal overlaps with the solent peaks; q, $J_{C\text{-}C\text{-}F}$ = 63.9 Hz, C), 123.0 (C), 125.8 (q, $J_{C\text{-}F}$ = 285.9 Hz, $CF_3$), 128.4 (CH), 131.6 (CH), 137.4 (C).
**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -85.23 (s, 3F).
**FT-IR** ($cm^{-1}$, neat, ATR) 3614 (w), 2955 (w), 2898 (w), 1489 (m), 1215 (s), 1167 (s), 1150 (s), 1075 (s), 989 (s), 914 (s), 839 (s), 820 (s).

**HRMS** (EI+) calcd for $C_{11}H_{16}BrO_3Si$ [M – $CF_3$]$^+$: 271.0140, found: 271.0157.

***Preparation of 2-(5-bromo-2-fluoropyridin-3-yl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1d)***




*Trifluoromethylation*

**1-(5-Bromo-2-fluoropyridin-3-yl)-2,2,2-trifluoroethanol**

Synthesis of 1-(5-bromo-2-fluoropyridin-3-yl)-2,2,2-trifluoroethanol (5.86 g, 54%) was accomplished using the procedure for the preparation of 1-(2-bromophenyl)-2,2,2-trifluoroethanol, with the following modification: The reaction was conducted using 5-bromo-2-fluoronicotinaldehyde (6.12 g, 0.030 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly. The crude product was purified by silica gel plug using 80/20 hexane/EtOAc as the eluent, giving the pure $CF_3$ alcohol as a pale-yellow solid (mp = 69-71 °C).

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 3.23 (br s, 1H), 5.35 (q, *J* = 6.1 Hz, 1H), 8.20 (dd, *J* = 7.9, 2.4 Hz, 1H), 8.31 (dd, *J* = 2.4, 1.3 Hz, 1H).

**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 65.9 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 33.9 Hz, CH), 117.4 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 4.6 Hz, CH), 119.2 (d, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 30.2 Hz, C), 123.9 (q, $J_{\mathbf{C\text{-}F}}$ = 283.2 Hz, $CF_3$), 143.2 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}C\text{-}F}}$ = 4.6 Hz, C), 149.4 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ =15.6 Hz, CH), 159.8 (d, $J_{\mathbf{C\text{-}F}}$ = 241.9 Hz, CF).

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -81.79 (d, *J* = 6.1 Hz, 3F), -77.31 (d, *J* = 4.6 Hz, 1F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3304 (w, br), 3095 (w), 1440 (s), 1154 (s), 1120 (s), 1109 (s), 629 (s).

**HRMS** (EI+) calcd for $C_7H_4BrF_4NO$ [M]$^+$: 272.9412, found: 272.9409.

*Oxidation*

**1-(5-Bromo-2-fluoropyridin-3-yl)-2,2,2-trifluoroethanone**

Synthesis of 1-(5-bromo-2-fluoropyridin-3-yl)-2,2,2-trifluoroethanone[19] (3.30 g, 62%) was accomplished using the procedure for the preparation of 1-(2-bromophenyl)-2,2,2-trifluoroethanone, with the following modification: The reaction was conducted using 1-(5-bromo-2-fluoropyridin-3-yl)-2,2,2-trifluoroethanol (5.48 g, 0.020 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly. The crude product was further purified by eluting the crude compound through a plug of silica gel using $Et_2O$ as the eluent, followed by precipitating the product upon the addition of pentane, giving the desired compound as its hydrate (1.90 g, 66%) as an orange solid (mp = 94-96 °C).

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 8.42 (dd, $J$ = 7.9, 2.4 Hz, 1H), 8.58 (dd, $J$ = 2.4, 1.1 Hz, 1H).

**$^{13}$C NMR** (DMSO-$d_6$, 125 MHz) δ 91.0 (qd, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 33.0, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 6.4 Hz, C), 115.7 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 4.6 Hz, CH), 122.9 (q, $J_{\mathbf{C\text{-}F}}$ = 287.8 Hz, $CF_3$), 122.5 (d, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 28.4 Hz, C), 143.6 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}C\text{-}F}}$ = 2.8 Hz, C), 149.3 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ =15.6 Hz, CH), 159.3 (d, $J_{\mathbf{C\text{-}F}}$ = 244.7 Hz, CF).

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -84.94 (d, $J$ = 12.2 Hz, 1F), -66.55 (d, $J$ = 12.2 Hz, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3508 (m), 3164 (m, br), 1443 (s), 1182 (s), 1165 (s), 1145 (s), 765 (s), 753 (s), 688 (s), 654 (s).

**HRMS** (EI+) calcd for $C_7H_2BrF_4NO$ $[M]^+$: 270.9256, found: 270.9264.

*Alkylation*

**2-(5-Bromo-2-fluoropyridin-3-yl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1d)**

Synthesis of 2-(5-bromo-2-fluoropyridin-3-yl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (2.90 g, 70%) was accomplished using the procedure for the preparation of 2-(2-bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, with the following modifications: 1) The reaction was conducted using 1-(5-bromo-2-fluoropyridin-3-yl)-2,2,2-trifluoroethanone (2.90 g, 10.0 mmol, 1 equiv) and the quantities of other reagents were adjusted accordingly; 2) Because this material exists predominately in its hydrate form, it must first be dehydrated. This can easily be

[19] Isolated mostly in it hydrate form. This is reflected in the calculated yield.

performed by azeotropic removal of water in benzene[20] just prior to reacting the ketone; 3) A lower loading (1.05 equiv) of the Grignard solution was used; 4) Dilute HCl (0.5 M) was used during the workup. The pure carbinol was obtained without any further purification as a white solid (mp = 137-139 °C).

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ -0.11 (s, 9H), 1.38 (dd, $J$ = 15.4, 1.2 Hz, 1H), 2.03 (d, $J$ = 15.3 Hz, 1H), 2.68 (s, 1H), 8.26 - 8.29 (m, 1H), 8.29 - 8.32 (m, 1H).

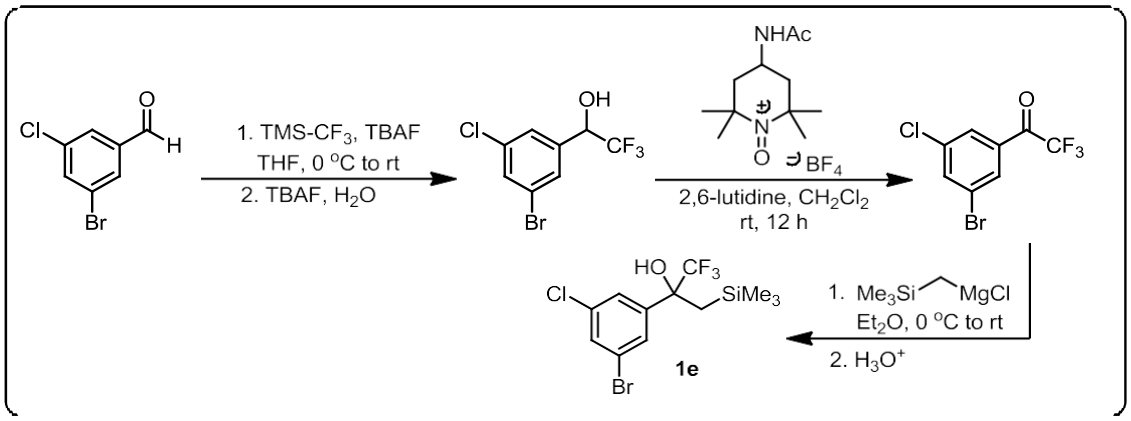
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 0.0 ($CH_3$), 22.6 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 5.4 Hz, $CH_2$), 75.9 (qd, $J_{C\text{-}C\text{-}F}$ = 30.9, $J_{C\text{-}C\text{-}C\text{-}F}$ = 7.3 Hz, C), 117.1 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.5 Hz, CH), 125.2 (qd, $J_{C\text{-}F}$ = 286.1, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, $CF_3$), 122.4 (d, $J_{C\text{-}C\text{-}F}$ = 28.2 Hz, C), 143.5 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 3.6 Hz, C), 149.1 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 15.4 Hz, CH), 159.3 (d, $J_{C\text{-}F}$ = 240.7 Hz, CF).

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -85.16 (d, $J$ = 15.3 Hz, 3F), -68.03 (q, $J$ = 13.7 Hz, 1F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3347 (m, br), 3091 (w), 1447 (s), 1220 (s), 993 (s), 861 (s), 849 (s), 839 (s).

**HRMS** (EI+) calcd for $C_{11}H_{14}BrF_4NOSi$ $[M]^+$: 358.9964, found: 358.9950.

***Preparation of 2-(3-bromo-5-chlorophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1e)***




*Trifluoromethylation*

[20] The *gem*-diol/ketone mixture was first dissolved in ≈ 50 mL of benzene in a 100 mL round bottom flask. The flask was then equipped with a graduated Dean Stark trap along with a reflux condenser. The reaction mixture was heated to reflux for about 1.5 h. Crude $^1$H and $^{19}$F NMR confirmed that the mixture was >95% of the ketone form. The Dean-Stark was then removed and the volume was decreased to about a fourth of the initial volume. The reaction was then executed as previously described.

**1-(3-Bromo-5-chlorophenyl)-2,2,2-trifluoroethanol[21]**

Synthesis of 1-(3-bromo-5-chlorophenyl)-2,2,2-trifluoroethanol (4.48 g, 77%) was accomplished using the procedure for the preparation of 1-(2-bromophenyl)-2,2,2-trifluoroethanol, with the following modification: The reaction was conducted using 3-bromo-5-chlorobenzaldehyde (4.39 g, 0.020 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly. The crude product was purified by vacuum distillation (bp 65-67 °C @ 0.1 mmHg), giving the pure $CF_3$ alcohol as a clear, pale-yellow oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 2.74 (d, *J* = 3.8 Hz, 1H), 5.00 (dt, *J* = 9.6, 6.3 Hz, 1H), 7.43 (s, 1H), 7.53 (s, 1H), 7.56 (t, *J* = 1.8 Hz, 1H).
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 71.8 (q, $J_{C\text{-}C\text{-}F}$ = 32.1 Hz, CH), 124.0 (q, $J_{C\text{-}F}$ = 283.2 Hz, $CF_3$), 123.2 (C), 126.8 (CH), 129.1 (CH), 132.8 (CH), 135.7 (C), 137.5 (C).
**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -81.40 (s, 3F).

*Oxidation*

**1-(3-Bromo-5-chlorophenyl)-2,2,2-trifluoroethanone**

Synthesis of 1-(3-bromo-5-chlorophenyl)-2,2,2-trifluoroethanone (3.53 g, 79%) was accomplished using the procedure for the preparation of 1-(2-bromophenyl)-2,2,2-trifluoroethanone, with the following modification: The reaction was conducted using 1-(3-bromo-5-chlorophenyl)-2,2,2-trifluoroethanol (4.49 g, 0.0155 mol, 1 equiv). The crude product was further purified by first passage of the crude material over a pad of silica eluting with $Et_2O$ followed by vacuum distillation (bp 51-53 °C @ 0.1 mmHg) to give the pure $CF_3$ ketone as a clear yellow oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 7.86 (t, *J* = 1.8 Hz, 1H), 7.96 (d, *J* = 0.6 Hz, 1H), 8.07 (d, *J* = 0.6 Hz, 1H).
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 116.4 (q, $J_{C\text{-}F}$ = 291.4 Hz, $CF_3$), 124.1 (C), 128.9 (CH), 131.4 (CH), 132.7 (C), 136.7 (C), 138.3 (CH), 178.7 (q, $J_{C\text{-}C\text{-}F}$ = 36.7 Hz, C).

[21] Lo, W. C.; Hunter, J. E.; Watson, G. B.; Patny, A.; Iyer, P. S.; Boruwa, J. Pesticidal compositions and processes related thereto. Patent: US2014/171314 A1, 2014.

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -74.82 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3079 (w), 1731 (s), 1560 (s), 1208 (s), 1179 (s), 1142 (s), 997 (s), 982 (s), 761 (s), 703 (s), 660 (s).

**HRMS** (EI+) calcd for $C_8H_3BrClF_3O$ $[M]^+$: 285.9008, found: 285.9021.

*Alkylation*

**2-(3-Bromo-5-chlorophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1e)**

Synthesis of 2-(3-bromo-5-chlorophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (3.02 g, 71%) was accomplished using the procedure for the preparation of 2-(2-bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, with the following modifications: 1) The reaction was conducted using 1-(3-bromo-5-chlorophenyl)-2,2,2-trifluoroethanone (3.25 g, 0.0113 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly; 2) A lower loading (1.05 equiv) of the Grignard solution was used; Further purification was accomplished by vacuum distillation (bp 82-85 °C @ 0.1 mmHg), affording the pure carbinol (3.02 g, 71%) as a clear, colorless oil.

**$^{1}$H NMR** ($CDCl_3$, 500 MHz) δ -0.13 (s, 9H), 1.43 (d, $J$ = 15.3 Hz, 1H), 1.57 (d, $J$ = 15.3 Hz, 1H), 2.31 (s, 1H), 7.50 (s, 1H), 7.52 (t, $J$ = 1.7 Hz, 1H), 7.61 (s, 1H).

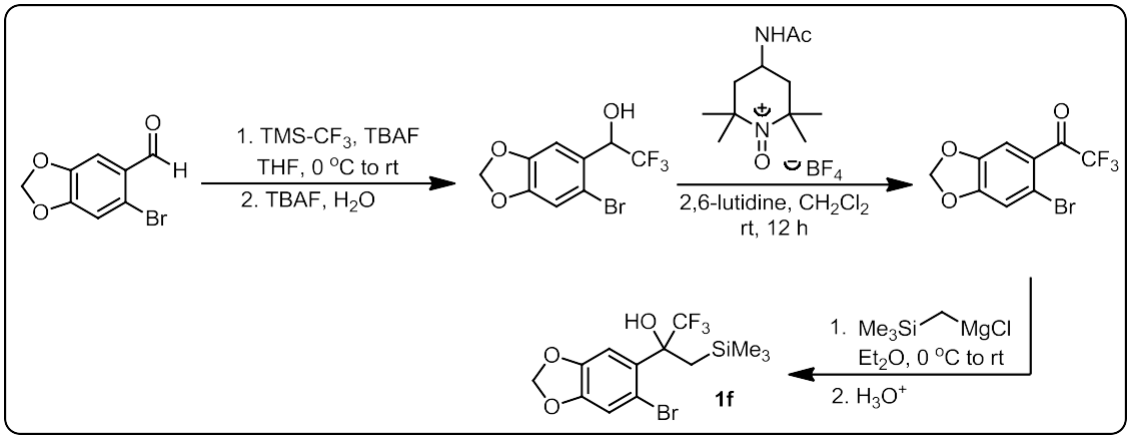
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 0.1 ($CH_3$), 25.3 ($CH_2$), 77.1 (q, $J_{C\text{-}C\text{-}F}$ = 29.3 Hz, C), 125.6 (q, $J_{C\text{-}F}$ = 286.8 Hz, $CF_3$), 122.9 (C), 126.0 (CH), 128.4 (CH), 131.7 (CH), 135.4 (C), 142.0 (C).

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -84.92 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3613 (w), 2955 (w), 1562 (s), 1214 (s), 1157 (s), 1116 (s), 999 (s), 838 (s), 791 (s), 764 (s), 713 (s).

**HRMS** (EI+) calcd for $C_{11}H_{15}BrClOSi$ $[M - CF_3]^+$: 304.9764, found: 304.9785.

***Preparation of 2-(6-bromobenzo[d][1,3]dioxol-5-yl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1f)***




*Trifluoromethylation*

**1-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethanol**

Synthesis of 1-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethanol (4.49 g, 75%) was accomplished using the procedure for the preparation of 1-(2-bromophenyl)-2,2,2-trifluoroethanol, with the following modifications: 1)The reaction was conducted using 6-bromobenzo[*d*][1,3]dioxole-5-carbaldehyde (4.58 g, 0.020 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly 2) After 8 h the trifluoromethylation step was judged to be incomplete. Thus the reaction mixture was cooled and additional TMS–$CF_3$ (1 equiv) was added followed by TBAF (0.01 equiv). The crude product was purified by vacuum distillation (bp 100-102 °C @ 0.1 mmHg), giving the pure $CF_3$ alcohol as a clear, pale-yellow oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 2.56 (d, $J$ = 4.4 Hz, 1H), 5.44 - 5.61 (m, 1H), 6.02 (dd, $J$ = 8.0, 1.3 Hz, 2H), 7.02 (s, 1H), 7.14 (s, 1H).

**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 71.5 (q, $J_{\mathbf{C-C-F}}$ = 32.1 Hz, CH), 102.5 ($CH_2$), 109.0 (CH), 112.9 (CH), 115.1 (C), 124.5 (q, $J_{\mathbf{C-F}}$ = 282.3 Hz, $CF_3$), 127.0 (C), 148.2 (C), 149.6 (C).

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -80.76 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3448 (w br), 2907 (w), 1479 (s), 1236 (s), 1168 (s), 1114 (s), 1070 (s), 1036 (s), 930 (s), 846 (s).

**HRMS** (EI+) calcd for $C_9H_6BrF_3O_3$ $[M]^+$: 297.9452, found: 297.9460.

*Oxidation*

**1-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethanone**

Synthesis of 1-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethanone (3.53 g, 79%) was accomplished using the procedure for the preparation of 1-(2-bromophenyl)-2,2,2-trifluoroethanone, with the following modification: The reaction was conducted using 1-(6-bromobenzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethanol (4.19 g, 0.014 mol, 1 equiv). The crude product was further purified by first passage of the crude material over a pad of silica eluting with $Et_2O$ followed by vacuum distillation (bp 95-97 °C @ 0.1 mmHg) giving the pure $CF_3$ ketone (3.88 g, 93%) as a clear, yellow oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 6.13 (s, 2H), 7.20 (s, 1H), 7.23 (d, $J$ = 1.4 Hz, 1H).

**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 103.5 ($CH_2$), 110.0 (q, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 3.7 Hz, C), 116.1 (q, $J_{\mathbf{C\text{-}F}}$ = 292.3 Hz, $CF_3$), 115.7 (CH), 116.9 (C), 124.1 (CH), 147.6 (C), 152.7 (C), 179.8 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 35.7 Hz, C).

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -75.17 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 2916 (w), 1720 (s), 1507 (s), 1485 (s), 1196 (s), 1177 (s), 1138 (s), 1114 (s), 1036 (s), 994 (s), 930 (s).

**HRMS** (EI+) calcd for $C_9H_4BrF_3O_3$ $[M]^+$: 295.9296, found: 295.9305.

*Alkylation*

**2-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (1f)**

Synthesis of 2-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (2.95 g, 70%) was accomplished using the procedure for the preparation of 2-(2-bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, with the following modifications: 1) The reaction was conducted using 1-(6-bromobenzo[*d*][1,3]dioxol-5-yl)-2,2,2-trifluoroethanone (3.26 g, 0.011 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly; 2) A lower loading (1.05 equiv) of the Grignard solution was used; Further purification was accomplished by vacuum distillation (bp 95-97 °C @ 0.1 mmHg), affording the pure carbinol (2.95 g, 70%) as a colorless oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ -0.07 (s, 9H), 1.42 (d, *J* = 15.6 Hz, 1H), 1.55 (s, 1H), 2.08 (br s, 1H), 6.02 (dd, *J* = 3.4, 1.2 Hz, 2H), 7.04 (s, 1H), 7.19 (br s, 1H).

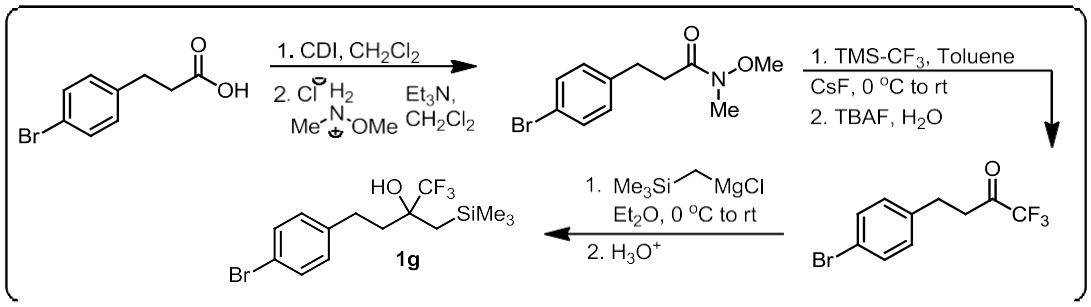
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 0.2 ($CH_3$), 23.9 ($CH_2$), 79.3 (q, $J_{C-C-F}$ = 28.4 Hz, C), 102.6 ($CH_2$), 110.9 (CH), 111.9 (C), 115.4 (CH), 126.0 (q, $J_{C-F}$ = 286.8 Hz, $CF_3$), 129.6 (C), 147.8 (C), 148.6 (C).

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -83.19 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3532 (w), 2956 (w), 2899 (w), 1482 (s), 1233 (s), 1213 (s), 1162 (s), 1038 (s), 837 (s).

**HRMS** (EI+) calcd for $C_{13}H_{16}BrF_3O_3Si$ $[M]^+$: 384.0004, found: 383.9981.

***Preparation of 4-(4-bromophenyl)-1,1,1-trifluoro-2-((trimethylsilyl)methyl)butan-2-ol (1g)***




*Weinreb Amide Synthesis*

**3-(4-Bromophenyl)-*N*-methoxy-*N*-methylpropanamide[22]**

Synthesis of 3-(4-Bromophenyl)-*N*-methoxy-*N*-methylpropanamide (4.156 g, 87%) was accomplished using the procedure for the preparation of 3-bromo-*N*-methoxy-*N*-methylbenzamide, with the following modification: The reaction was conducted using 3-(4-bromophenyl)propanoic acid (4.00 g, 0.0175 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly. The desired amide was obtained as a clear, light yellow oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 2.72 (t, *J* = 7.5 Hz, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 3.17 (s, 3H), 3.61 (s, 3H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H).

**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 30.0 ($CH_2$), 32.3 ($CH_2$), 33.5 ($CH_3$), 61.3 ($CH_3$), 119.9 (C), 130.3 (CH), 131.5 (CH), 140.4 (C), 173.3 (C).

[22] Kumar, K.; Natarajan, A. *Tetrahedron*, **2008**, *49*, 2103.

*Trifluoromethylation*

**4-(4-Bromophenyl)-1,1,1-trifluorobutan-2-one**

Synthesis of 4-(4-bromophenyl)-1,1,1-trifluorobutan-2-one (2.321 g, 60%) was accomplished using the procedure for the preparation of 1-(3-bromophenyl)-2,2,2-trifluoroethanone, with the following modification: The reaction was conducted using 3-(4-bromophenyl)-*N*-methoxy-*N*-methylpropanamide (3.75 g, 0.0138 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly. The crude $CF_3$ ketone was further purified by vacuum distillation (bp 79-81 °C @ 0.1 mmHg), affording the pure $CF_3$ ketone as a clear, colorless oil.

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 2.95 (t, $J$ = 7.0 Hz, 2H), 3.03 (t, $J$ = 7.0 Hz, 2H), 7.04 - 7.11 (m, 2H), 7.40 - 7.45 (m, 2H).
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 27.9 ($CH_2$), 38.0 ($CH_2$), 115.7 (q, $J_{C-F}$ = 291.6 Hz, $CF_3$), 120.7 (C), 130.3 (CH), 132.0 (CH), 138.5 (C), 190.6 (q, $J_{C-C-F}$ = 34.5 Hz, C).
**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -82.40 (s, 3F).
**FT-IR** ($cm^{-1}$, neat, ATR) 2939 (w), 1763 (s), 1489 (s), 1204 (s), 1169 (s), 1136 (s), 1057 (s), 1012 (s), 990 (s), 812 (s).
**HRMS** (EI+) calcd for $C_{10}H_8BrF_3O$ $[M]^+$: 279.9711, found: 279.9706.

*Alkylation*

**4-(4-Bromophenyl)-1,1,1-trifluoro-2-((trimethylsilyl)methyl)butan-2-ol (1g)**

Synthesis of 4-(4-bromophenyl)-1,1,1-trifluoro-2-((trimethylsilyl)methyl)butan-2-ol (1.00 g, 38%) was accomplished using the procedure for the preparation of 2-(2-bromophenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, with the following modification: The reaction was conducted using 4-(4-bromophenyl)-1,1,1-trifluorobutan-2-one (2.00 g, 0.00711 mol, 1 equiv) and the quantities of other reagents were adjusted accordingly. The crude carbinol was further purified by column chromatography (gradient hexanes to 80:20 hexanes/EtOAc), affording the pure carbinol as a clear colorless oil.

**$^{1}$H NMR** ($CDCl_3$, 500 MHz) δ 0.13 (s, 9H), 1.13 (d, *J* = 15.3 Hz, 1H), 1.23 (d, *J* = 15.3 Hz, 1H), 1.85 (s, 1H), 1.93 - 2.01 (m, 2H), 2.63 - 2.73 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H).

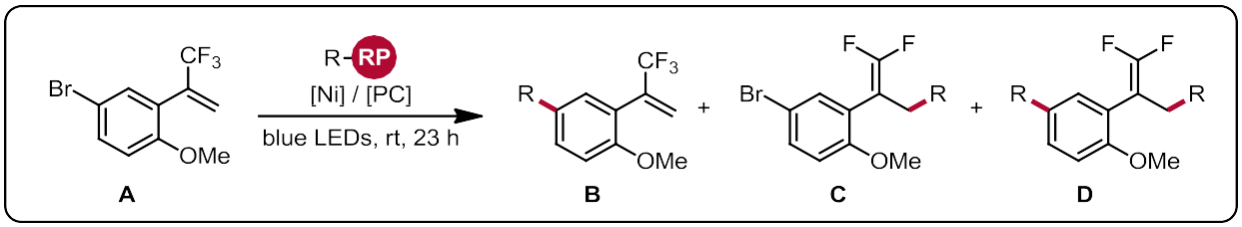
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 0.4 ($CH_3$), 23.7 ($CH_2$), 29.3 ($CH_2$), 38.5 ($CH_2$), 76.2 (q, $J_{C\text{-}C\text{-}F}$ = 28.2 Hz, C), 120.2 (C), 126.9 (q, $J_{C\text{-}F}$ = 287.9 Hz, $CF_3$), 130.3 (CH), 131.9 (CH), 140.5 (C).

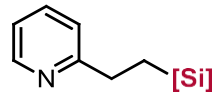
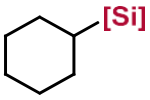
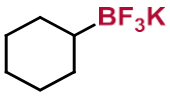
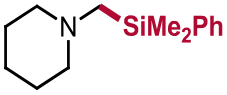
**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -84.09 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3467 (w), 2953 (w), 1489 (s), 1251 (s), 1151 (s), 1072 (s), 1011 (s), 838 (s), 805 (s).

**HRMS** (EI+) calcd for $C_{14}H_{20}BrF_3OSi$ $[M]^+$: 368.0419, found: 368.0425.

## Cross-Coupling vs. Radical Addition Competition Reactions

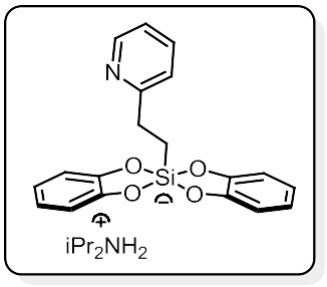



| R-RP | Relative Ratio[a] A : B : C : D | | | |
|---|---|---|---|---|
|  | 54 | 24 | 18 | 4 |
|  | 0 | 75 | 0 | 25 |
|  | 13 | 38 | 22 | 27 |
|  | 0 | 38 | 0 | 62 |
|  | 46 | 53 | 2 | 0 |

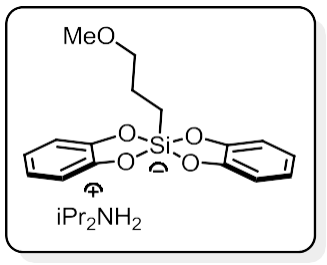
[a] Determined by $^{19}$F NMR

***Representative Procedure for Silicate Radical Precursor***

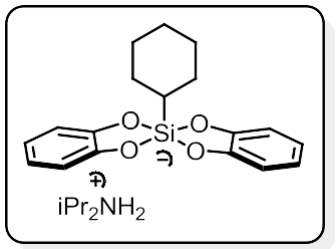
A 4 mL vial was charged with $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (2.4 mg, 0.0050 mmol, 5.0 mol %), $[Ru(bpy)_3](PF_6)_2$ (2.1 mg, 0.0025 mmol, 2.5 mol %), and silicate (0.12 mmol, 1.2 equiv). The vial was evacuated and backfilled with argon three times. A degassed soln of 4-bromo-1-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene **A** (28.1 mg, 0.10 mmol, 1.0 equiv) in DMF (1.0 mL, 0.10 M) was then added, and the vial was sealed and irradiated with blue light for 23 h. Upon completion, the reaction was diluted with $Et_2O$ (5 mL) and washed with 1 M aq NaOH (2 × 3 mL) and brine (3 mL), dried ($Na_2SO_4$), filtered, and concentrated. The crude material was then dissolved in $CDCl_3$, and the product distribution was examined by $^{19}$F NMR.




Set up according to the general procedure using diisopropylammonium 2-(pyridin-2-yl)ethylbis(catecholato)silicate (54.3 mg, 0.12 mmol 1.2 equiv).

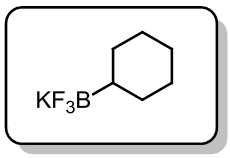



Set up according to the general procedure using diisopropylammonium 3-methoxypropylbis(catecholato)silicate (50.3 mg, 0.12 mmol 1.2 equiv).



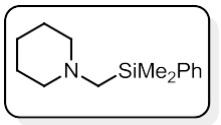

Set up according to the general procedure using diisopropylammonium cyclohexylbis(catecholato)silicate (51.6 mg, 0.12 mmol 1.2 equiv).

***Procedure for Trifluoroborate Radical Precursor***




A 4 mL vial was charged with $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (2.4 mg, 0.0050 mmol, 5.0 mol %), $[Ir(dFCF_3ppy)(bpy)](PF_6)$ (2.5 mg, 0.0025 mmol, 2.5 mol %), potassium cyclohexyltrifluoroborate (16.4 mg, 0.150 mmol, 1.50 equiv), and $Cs_2CO_3$ (48.9 mg, 0.15 mmol, 1.50 equiv). The vial was evacuated and backfilled with argon three times. A degassed soln of 4-bromo-1-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene **A** (28.1 mg, 0.10 mmol, 1.0 equiv) in dioxane (2.0 mL, 0.050 M) was then added, and the vial was sealed and irradiated with blue light for 23 h. Upon completion, the reaction was diluted with $Et_2O$ (5 mL) and washed with $H_2O$ (2 × 3 mL) and brine (3 mL), dried ($Na_2SO_4$), filtered, and concentrated. The crude material was then dissolved in $CDCl_3$, and the product distribution was examined by $^{19}F$ NMR.

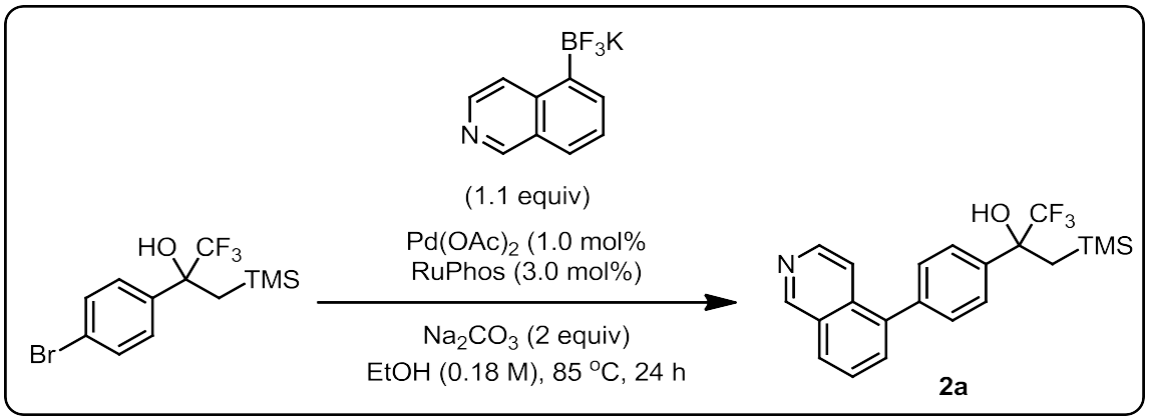
***Procedure for Silylamine Radical Precursor***




A 4 mL vial was charged with $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (2.4 mg, 0.0050 mmol, 5.0 mol %) and $[Ru(bpy)_3](PF_6)_2$ (2.1 mg, 0.0025 mmol, 2.5 mol %). The vial was evacuated and backfilled with argon three times. Degassed solns of 1-((dimethyl(phenyl)silyl)methyl)piperidine (28 mg 0.12 mmol, 1.2 equiv) in DMF (0.50 mL, 0.24 M) and 4-bromo-1-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene **A** (28.1 mg, 0.10 mmol, 1.0 equiv) in DMF (0.5 mL, 0.2 *M*) were then added (final reaction concentration 0.1 M relative to aryl bromide) and the vial was sealed and irradiated with blue light for 23 h. Upon completion, the reaction was diluted with $Et_2O$ (5 mL) and washed with $H_2O$ (2 × 3 mL) and brine (3 mL), dried ($Na_2SO_4$), filtered, and concentrated. The crude material was then dissolved in $CDCl_3$ and the product distribution was examined by $^{19}F$ NMR.

## General Procedures for Diversification of α-$CF_3$-β-TMS-Alcohols

***Representative Procedure for Suzuki Cross-Coupling***



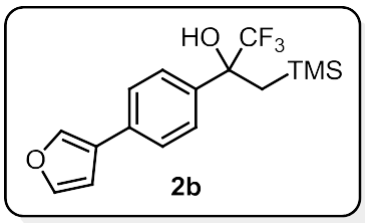

**1,1,1-Trifluoro-2-(4-(isoquinolin-5-yl)phenyl)-3-(trimethylsilyl)propan-2-ol (2a)**

A 20 mL microwave vial was charged with potassium isoquinoline-5-trifluoroborate (517 mg, 2.20 mmol, 1.10 equiv), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 1.0 mol %), RuPhos (28 mg, 0.060 mmol, 3.0 mol %), and $Na_2CO_3$ (424 mg, 4.00 mmol, 2.00 equiv). The vial was evacuated and backfilled with argon three times. Degassed EtOH (11.1 mL, 0.18 M relative to aryl bromide) was added followed by α-$CF_3$-β-TMS-alcohol **1c** (683 mg, 2.00 mmol, 1.00 equiv). The microwave vial was then sealed and heated in an 85 °C oil bath for 24 h. Upon completion, the vial was cooled to rt, diluted with EtOAc, and eluted through a plug of Celite®. The crude

material was then purified by column chromatography (gradient hexanes to EtOAc 1% v/v $Et_3N$) to afford title compound **2a** (732 mg, 1.88 mmol, 94% yield) as a white solid (mp = 165-166 ºC).

**$^1$H NMR** (500 MHz, acetone-$d_6$) δ -0.11 (s, 9H), 1.64 (d, $J$ = 14.8 Hz, 1H), 1.84 (d, $J$ = 14.8 Hz, 1H), 5.59 (s, 1H), 7.55 - 7.60 (m, 2H), 7.69 (dt, $J$ = 6.0, 1.0 Hz, 1H), 7.75 - 7.79 (m, 2H), 7.87 (d, $J$ = 8.1 Hz, 2H), 8.16 (ddd, $J$ = 7.0, 2.4, 0.6 Hz, 1H), 8.50 (d, $J$ = 6.0 Hz, 1H), 9.37 (s, 1H).
**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.2 ($CH_3$), 25.0 ($CH_2$), 77.5 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 29.1 Hz, C), 118.8 (CH), 127.5 (q, $J_{\mathbf{C\text{-}F}}$ = 287.0 Hz, $CF_3$), 128.0 (CH), 128.0 (CH), 128.3 (CH), 130.1 (CH), 130.3 (CH), 131.9 (CH), 134.7 (C), 139.5 (C), 139.7 (C), 139.8 (C), 144.6 (CH), 153.9 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 2.7 Hz, C).
**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ –84.86 (s, 3F).
**FT-IR** ($cm^{-1}$, neat, ATR) 3137 (br w), 2954 (w), 1152 (vs), 924 (s), 833 (s).
**HRMS** (EI) calcd for $C_{21}H_{22}F_3NOSi[M]^+$: 390.1501; found: 390.1521.

**1,1,1-Trifluoro-2-(4-(furan-3-yl)phenyl)-3-(trimethylsilyl)propan-2-ol, 2b** (633 mg, 96% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **1c** (683 mg, 2.00 mmol, 1.00 equiv), potassium furan-3-trifluoroborate (383 mg, 2.20 mmol, 1.10 equiv), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 1.0 mol %), RuPhos (28 mg, 0.060 mmol, 3.0 mol %), $Na_2CO_3$ (424 mg, 4.00 mmol, 2.00 equiv), and degassed EtOH (11.1 mL, 0.18 M). The title compound **2b** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a yellow oil. **$^1$H NMR** (500 MHz, $CD_3OD$ w/ 0.05 % TMS) δ -0.20 (s, 9H), 1.46 (d, $J$ = 14.7 Hz, 1H), 1.62 (d, $J$ = 14.9 Hz, 1H), 6.75 - 6.82 (m, 1H), 7.45 - 7.64 (m, 5H), 7.90 (s, 1H).[23] **$^{13}$C NMR** (126 MHz, $CD_3OD$ w/ 0.05 % TMS) δ 0.2 ($CH_3$), 25.2 ($CH_2$), 77.8 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 28.4 Hz, C), 109.7 (CH), 126.3 (CH), 127.9 (d, $J_{\mathbf{C\text{-}F}}$ = 286.8 Hz, $CF_3$), 127.4 (C), 128.5 (CH), 133.7 (C), 139.2 (C), 140.3 (CH), 145.2 (CH). **$^{19}$F NMR** (471 MHz, $CD_3OD$ w/ 0.05 % TMS) δ -85.14 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 3566 (br w), 2955 (w), 2808 (w), 1521 (w), 1421 (w), 1275 (w), 1250 (s), 1215 (s), 1152 (vs), 988 (s), 915

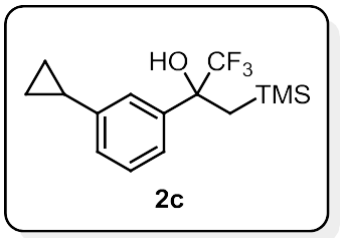


**2b**

[23] No OH proton is observed due to deuterium exchange with the solvent.

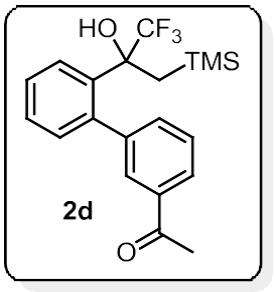
(s), 836 (vs), 784 (vs), 741 (s), 623 (s), 596 (s). **HRMS** (EI) calcd for $C_{16}H_{19}F_3O_2Si$ [M]$^+$: 328.1106, found: 328.1094.

**2-(3-Cyclopropylphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, 2c** (403 mg, 67% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **1b** (683 mg, 2.00 mmol, 1.00 equiv) with the following modifications: potassium cyclopropyltrifluoroborate (355 mg, 2.40 mmol, 1.20 equiv), XPhos Pd G2 (47 mg, 0.060 mmol, 3.0 mol %), $K_2CO_3$ (829 mg, 6.00 mmol, 3.00 equiv), and degassed 10:1 CPME/$H_2O$ (8.0 mL, 0.25 M). After heating at 100 ºC for 24 h, the reaction was stopped and worked up as described in the general procedure. The title compound **2c** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a yellow oil. **$^1$H NMR** (500 MHz, acetone-$d_6$) δ -0.20 (s, 9H), 0.62 - 0.74 (m, 2H), 0.96 (dq, $J$ = 8.3, 2.0 Hz, 2H), 1.52 (d, $J$ = 14.7 Hz, 1H), 1.71 (d, $J$ = 14.9 Hz, 1H), 1.96 (tt, $J$ = 8.4, 5.1 Hz, 1H), 5.28 (s, 1H), 7.07 (d, $J$ = 7.6 Hz, 1H), 7.26 (t, $J$ = 7.7 Hz, 1H), 7.37 - 7.43 (m, 2H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.2 ($CH_3$), 9.65 ($CH_2$), 9.79 ($CH_2$), 16.1 ($CH_2$), 24.8 (CH), 77.4 (q, $J_{C\text{-}C\text{-}F}$ = 28.2 Hz, C), 124.7 (CH), 124.8 (CH), 126.1 (CH), 127.5 (q, $J_{C\text{-}F}$ = 286.1 Hz, $CF_3$), 128.7 (CH), 139.8 (C), 144.5 (C). **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -82.05 (s, 3F). **FT-IR** (cm$^{-1}$, neat, ATR) 3612 (br w), 2956 (w), 1250 (s), 1214 (s), 1163 (vs), 994 (s), 841 (vs), 712 (s). **HRMS** (EI) calcd for $C_{15}H_{21}F_3OSi$ [M]$^+$: 302.1314, observed: 302.1306.



2c

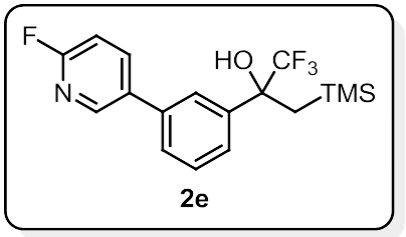
**1-(2'-(1,1,1-Trifluoro-2-hydroxy-3-(trimethylsilyl)propan-2-yl)-[1,1'-biphenyl]-3-yl)ethan-1-one, 2d** (669 mg, 88% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **1a** (683 mg, 2.00 mmol, 1.00 equiv) and potassium (3-acetylphenyl)trifluoroborate (497 mg, 2.20 mmol, 1.10 equiv) with the following modifications: (1) $Pd(OAc)_2$ (22 mg, 0.10 mmol, 5.0 mol %), (2) QPhos (171 mg, 0.24 mmol, 12 mol %), (3) $K_2CO_3$ (138 mg, 4.00 mmol, 2.00 equiv), and (4) degassed 2:1 dioxane/$H_2O$ (10 mL, 0.2 M). The title compound **2d** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a white solid (mp = 125-126 ºC). **$^1$H NMR** (500 MHz, DMSO-$d_6$) δ -0.25 (s, 9H), 1.22 (d, $J$ = 14.7 Hz, 1H), 1.75 (d, $J$ = 14.6 Hz, 1H), 2.55 (s,



2d

3H), 5.77 (s, 1H), 7.03 (app d, 1H), 7.47 – 7.29 (m, 4H), 7.53 (app d, $J$ = 7.9 Hz, 1H), 7.75 (s, 1H), 7.85 (app d, $J$ = 7.5 Hz, 1H). Peaks appear broad due to restricted rotation about $C_{sp2}$–$C_{sp2}$ bond on NMR timescale. **$^{13}$C NMR** (126 MHz, **taken at 300K**, DMSO-$d_6$) δ 0.0 ($CH_3$), 24.9 (br s, $CH_2$), 26.6 ($CH_3$), 77.8 (q, $J_{C\text{-}C\text{-}F}$ = 28.2 Hz, C), 126.3 (q, $J_{C\text{-}F}$ = 288.8 Hz, $CF_3$), 125.6 (app d, $J$ = 21.8 Hz, CH), 126.7 (C), 127.1 (CH), 127.6 (CH), 128.7 (C), 129.2 (CH), 132.7 (CH), 133.5 (C), 135.1 (app d, $J$ = 33.6 Hz, CH), 135.6 (CH), 140.9 (CH), 145.6 (C), 197.8 (C). Some peaks are doublets and some appear broad due to restricted rotation about $C_{sp2}$–$C_{sp2}$ bond on NMR timescale, peaks coalesced at 333K. **$^{13}$C NMR** (126 MHz, **taken at 333K**, DMSO-$d_6$) δ -0.3 ($CH_3$), 24.9 ($CH_2$), 26.3 ($CH_3$), 77.8 (q, $J_{C\text{-}C\text{-}F}$ = 28.2 Hz, C), 126.1 (q, $J_{C\text{-}F}$ = 289.3 Hz, $CF_3$), 125.3 (CH), 126.6 (br s, C), 126.8 (CH), 127.3 (CH), 128.1 (br s, C), 128.8 (br s, CH), 132.5 (CH), 132.9 (br s, C), 135.1 (CH), 135.5 (CH), 140.7 (CH), 145.3 (C), 197.5 (C). **$^{19}$F NMR** (471 MHz, DMSO-$d_6$, **taken at 300K**) δ -81.37 (app d, $J$ = 83.6 Hz, 3F). **$^{19}$F NMR** (471 MHz, DMSO-$d_6$, **taken at 313K**) δ -81.10 (s, 3F). **FT-IR** (cm$^{-1}$, neat, ATR) 3446 (br s), 2959 (w), 1672 (s), 1424 (s), 1203 (s), 1149 (vs), 993 (s), 918 (s), 839 (vs), 758 (s), 695 (s), 587 (s). **HRMS** (EI) calcd for $C_{20}H_{23}F_3O_2Si$ [M]$^+$: 380.1419, found: 380.1424.

**1,1,1-Trifluoro-2-(3-(6-fluoropyridin-3-yl)phenyl)-3-(trimethylsilyl)propan-2-ol, 2e** (641 mg, 90% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **1b** (683 mg, 2.00 mmol, 1.00 equiv), potassium 6-fluoropyridin-3-yltrifluoroborate (447 mg, 2.20 mmol, 1.10 equiv), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 1.0 mol %), RuPhos (28 mg, 0.060 mmol, 3.0 mol %), $Na_2CO_3$ (424 mg, 4.00 mmol, 2.00 equiv), and degassed EtOH (11.1 mL, 0.18 M). The title compound **2e** was purified by column chromatography (gradient hexanes to EtOAc 1% v/v $Et_3N$) and isolated as a white solid (mp = 88-89 ºC). **$^1$H NMR** (500 MHz, $CDCl_3$) δ -0.17 (s, 9H), 1.60 (d, $J$ = 14.9 Hz, 1H), 1.87 (d, $J$ = 14.9 Hz, 1H), 5.52 (s, 1H), 7.19 (dd, $J$ = 8.3, 2.9 Hz, 1H), 7.56 (t, $J$ = 7.8 Hz, 1H), 7.72 (dd, $J$ = 23.0, 7.6 Hz, 2H), 7.98 (s, 1H), 8.24 (td, $J$ = 7.8, 2.4 Hz, 1H), 8.51 (d, $J$ = 1.5 Hz, 1H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.2 ($CH_3$), 24.7 ($CH_2$), 77.5 (q, $J_{C\text{-}C\text{-}F}$ = 28.2 Hz, C), 110.4 (d, $J_{C\text{-}C\text{-}F}$ = 38.1 Hz, CH), 127.4 (q, $J_{C\text{-}F}$ = 287.0 Hz, $CF_3$), 126.3 (CH), 127.5 (CH), 127.7 (CH), 129.8 (CH), 135.7 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.5 Hz, C), 137.3 (C), 141.1 (C), 141.1 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.5 Hz, CH), 146.7 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 15.4 Hz, CH), 164.2 (d, $J_{C\text{-}F}$



**2e**

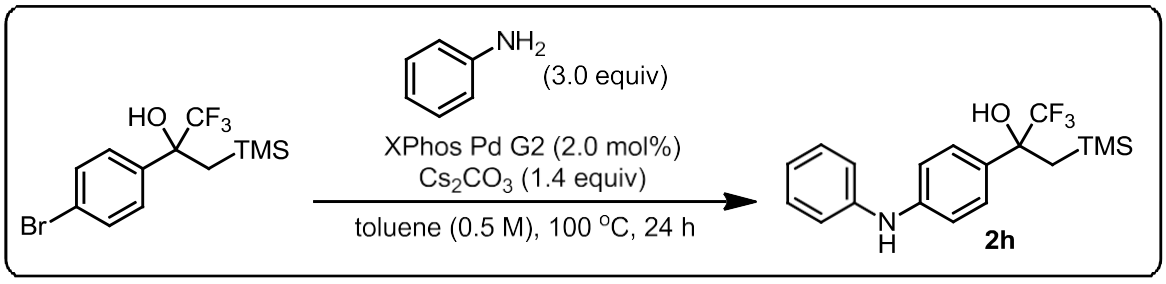
= 236.1 Hz, CF). **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -82.08 (s, 3F), -72.54 (s, 1F). **FT-IR** (cm$^{-1}$, neat, ATR) 3283 (br s), 2956 (w), 1603 (w), 1480 (s), 1252 (s), 1166 (vs), 945 (s), 839 (vs), 799 (s), 712 (s), 585 (s). **HRMS** (ESI) calcd for $C_{17}H_{20}F_4NOSi$ $[M + H]^+$: 358.1250, found: 358.1245.

**1-(4'-(1,1,1-Trifluoro-2-hydroxy-3-(trimethylsilyl)propan-2-yl)-[1,1'-biphenyl]-3-yl)ethan-1-one, 2f** (697 mg, 92% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **1c** (683 mg, 2.00 mmol, 1.00 equiv), (3-acetylphenyl)trifluoroborate (497 mg, 2.20 mmol, 1.10 equiv), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 1.0 mol %), RuPhos (28 mg, 0.060 mmol, 3.0 mol %), $Na_2CO_3$ (424 mg, 4.00 mmol, 2.00 equiv), and degassed EtOH (11.1 mL, 0.18 M). The title compound **2f** was purified by column chromatography (gradient 0 to 100 % EtOAc in hexanes) and isolated as a white solid (mp = 139-140 ºC). **$^1$H NMR** (500 MHz, $CDCl_3$) δ -0.14 (s, 9H), 1.51 (d, $J$ = 15.0 Hz, 1H), 1.70 (d, $J$ = 14.8 Hz, 1H), 2.63 (s, 1H), 2.67 (s, 3H), 7.55 (t, $J$ = 7.8 Hz, 1H), 7.61 - 7.70 (m, 4H), 7.82 (dq, $J$ = 7.8, 1.1 Hz, 1H), 7.95 (dt, $J$ = 7.8, 1.1 Hz, 1H), 8.21 (t, $J$ = 1.6 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 0.1 ($CH_3$), 25.1 ($CH_2$), 27.0 ($CH_3$), 77.5 (q, $J_{C\text{-}C\text{-}F}$ = 29.1 Hz, C), 126.1 (q, $J_{C\text{-}F}$ = 285.2 Hz, $CF_3$), 127.1 (CH), 127.1 (CH), 127.2 (CH), 127.8 (CH), 129.4 (CH), 132.0 (CH), 137.9 (C), 138.0 (C), 140.3 (C), 141.2 (C), 198.5 (C). **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -85.07 (s, 3F). **FT-IR** (cm$^{-1}$, neat, ATR) 3458 (br w), 2955 (w), 1678 (s), 1239 (s), 1154 (vs), 847 (s). **HRMS** (EI) calcd for $C_{20}H_{23}F_3O_2Si$ $[M]^+$: 380.1419, found: 380.1432.

**1-(3-(6-(1,1,1-Trifluoro-2-hydroxy-3-(trimethylsilyl)propan-2-yl)benzo[d][1,3]dioxol-5-yl)phenyl)ethan-1-one, 2g** (252 mg, 59% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **1f** (385 mg, 1.00 mmol, 1.00 equiv) and potassium (3-acetylphenyl)trifluoroborate (249 mg, 1.10 mmol, 1.10 equiv) with the following modifications: (1) $Pd(OAc)_2$ (11 mg, 0.050 mmol, 5.0 mol %), (2) QPhos (85 mg, 0.12 mmol, 12 mol %), (3) $K_2CO_3$ (276 mg, 2.00 mmol, 2.00 equiv), and (4) degassed 2:1 dioxane/$H_2O$ (5 mL, 0.2 M). The title

compound **2g** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a yellow oil. **$^1$H NMR** (500 MHz, **taken at 343.15 K**, DMSO-$d_6$) δ -0.17 (s, 9H), 1.18 (d, $J$ = 15.0 Hz, 1H), 1.68 (d, $J$ = 15.0 Hz, 1H), 2.54 (s, 3H), 6.06 (s, 1H), 6.09 (d, $J$ = 0.6 Hz, 1H), 6.53 (s, 1H), 7.05 (s, 1H), 7.35 - 7.46 (m, 2H), 7.74 (s, 1H), 7.82 (d, $J$ = 7.6 Hz, 1H).[16] **$^{13}$C NMR** (126 MHz, **taken at 343.15 K**, DMSO-$d_6$) δ -0.3 ($CH_3$), 24.8 ($CH_2$), 26.1 ($CH_3$), 77.6 (q, $J_{C-C-F}$ = 27.2 Hz, C), 101.3 ($CH_2$), 108.5 (C), 111.7 (CH), 125.9 (q, $J_{C-F}$ = 288.8 Hz, $CF_3$), 125.2 (CH), 126.5 (C), 128.3 (br s, CH), 129.0 (C), 133.0 (br s, CH), 134.5 (C), 135.1 (br s, C), 144.8 (C), 145.9 (CH), 146.2 (CH), 197.4 (C). **$^{19}$F NMR** (471 MHz, **taken at 300K**, DMSO-$d_6$) δ -81.52 (app d, $J$ = 87.7 Hz, 3F). **$^{19}$F NMR** (471 MHz, **taken at 350K**, DMSO-$d_6$) δ -80.57 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 3432 (br s), 2956 (w), 2892 (w), 1671 (s), 1508 (s), 1163 (vs), 843 (vs), 692 (s), 587 (s). **HRMS** (ESI) calcd for $C_{21}H_{23}F_3O_4Si$ [M + Na]$^+$: 447.1215, found: 447.1234.

***Procedures for Buchwald-Hartwig Aminations***




**1,1,1-Trifluoro-2-(4-(phenylamino)phenyl)-3-(trimethylsilyl)propan-2-ol (2h)** A 20 mL microwave vial was charged with $Cs_2CO_3$ (1.34 g, 4.20 mmol, 1.40 equiv), and flame dried under vacuum, and cooled to rt under a positive pressure of argon. The vial was then charged with XPhos Pd-G2 (47 mg, 0.060 mmol, 2.0 mol %) and evacuated and backfilled with argon three times. Anhyd toluene (6.0 mL, 0.5 *M* relative to aryl bromide) was then added followed by aryl bromide **1c** (1.02 g, 3.00 mmol, 1.00 equiv). The vial was then sealed and heated at 100 ºC in an oil bath for 24 h. Upon completion, the vial was cooled to rt, diluted with EtOAc, eluted through a plug of Celite®, and concentrated. The crude material was then purified by column chromatography (gradient hexanes to EtOAc 1% v/v $Et_3N$) to afford title compound **2h** (1.05 g, 1.88 mmol, 94% yield) as a yellow oil.

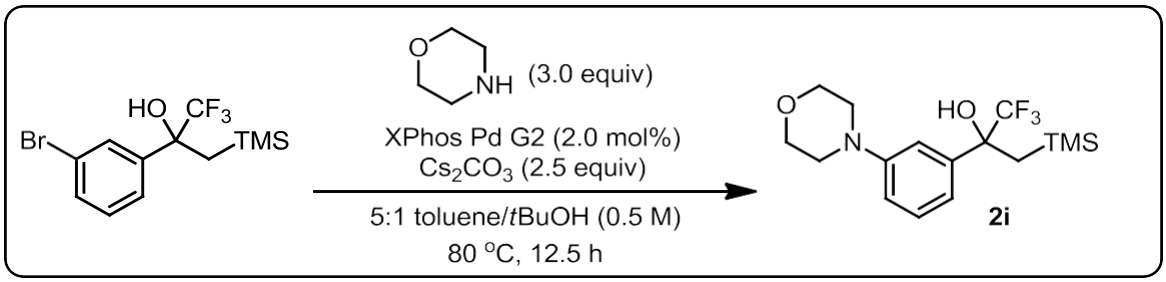
**$^1$H NMR** (500 MHz, $CDCl_3$) δ -0.14 (s, 9H), 1.52 (d, *J* = 14.7 Hz, 1H), 1.69 (d, *J* = 14.7 Hz, 1H), 5.19 (s, 1H), 6.87 (t, *J* = 7.3 Hz, 1H), 7.14 (dd, *J* = 7.9, 5.7 Hz, 4H), 7.25 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.45 (br s, 1H), 7.51 (d, *J* = 8.6 Hz, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 0.3 ($CH_3$), 24.8 ($CH_2$), 77.2 (signal overlaps with solvent peaks; q, $J_{C-C-F}$ = 28.4 Hz, C), 117.0 (CH), 118.5 (CH), 121.3 (CH), 127.6 (q, $J_{C-F}$ = 286.8 Hz, $CF_3$), 128.6 (CH), 130.1 (CH), 131.2 (C), 144.4 (C), 144.6 (C).

**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -82.38 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3137 (br w), 2954 (w), 1152 (s), 924 (s), 833 (s).

**HRMS** (ESI) calcd for $C_{18}H_{23}F_3NOSi$ $[M + H]^+$: 354.1501, found: 354.1519.




**1,1,1-Trifluoro-2-(3-morpholinophenyl)-3-(trimethylsilyl)propan-2-ol (2i)** A 20 mL microwave vial was charged with $Cs_2CO_3$ (1.64 g, 5.00 mmol, 2.50 equiv) and XPhos Pd-G2 (31 mg, 0.040 mmol, 2.0 mol %) and evacuated and backfilled with argon three times. anhyd toluene (4.0 mL) was then added followed by degassed *t*-BuOH (0.80 mL, final reaction concentration 0.42 M). Aryl bromide **1b** (682 mg, 2.00 mmol, 1.00 equiv) and morpholine (0.26 mL, 1.5 mmol, 3.0 equiv, degassed and eluted through basic alumina) were the added. The vial was then sealed and heated at 80 ºC in an oil bath overnight (12.5 h). Upon completion, the reaction mixture was cooled to rt, diluted with EtOAc, eluted through a plug of Celite®, and concentrated. The crude material was then purified by column chromatography (gradient hexanes to EtOAc 1% v/v $Et_3N$) to afford title compound **2i** (636 mg, 1.83 mmol, 92% yield) as a white solid (99-100 ºC).

**$^1$H NMR** (500 MHz, acetone-$d_6$) δ -0.18 (s, 9H), 1.51 (d, *J* = 14.8 Hz, 1H), 1.71 (d, *J* = 14.6 Hz, 1H), 3.08 - 3.21 (m, 4H), 3.73 - 3.86 (m, 4H), 5.30 (s, 1H), 6.94 (ddd, *J* = 8.1, 2.5, 0.6 Hz, 1H), 7.10 (dd, *J* = 7.8, 0.5 Hz, 1H), 7.25 (t, *J* = 7.9 Hz, 1H), 7.29 (s, 1H).

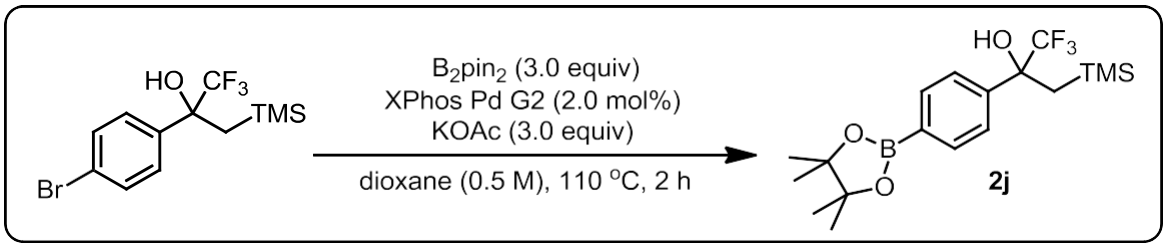
**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.2 ($CH_3$), 24.9 ($CH_2$), 50.3 ($CH_2$), 67.5 ($CH_2$), 77.6 (q, $J_{C-C-F}$ = 27.5 Hz, C), 115.2 (CH), 116.1 (CH), 119.1 (CH), 127.5 (q, $J_{C-F}$ = 285.9 Hz, $CF_3$), 129.4 (CH), 140.7 (C), 152.4 (C).

**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -81.93 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3358 (br w), 1146 (vs), 918 (s), 842 (s), 712 (s).

**HRMS** (ESI) calcd for $C_{16}H_{25}F_3NO_2Si$ $[M + H]^+$: 348.1607, found 348.1577.

***Procedures for Borylation of Aryl Bromides***




**1,1,1-Trifluoro-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-3-(trimethylsilyl)propan-2-ol (2j)** A 20 mL microwave vial was charged with bis(pinacolato)diboron (1.52 g, 6.00 mmol, 3.00 equiv), XPhos Pd-G2 (31 mg, 0.040 mmol, 2.0 mol %), and KOAc (589 mg, 6.00 mmol, 3.00 equiv). The vial was then evacuated and backfilled with argon three times. Anhyd dioxane (4.0 mL, 0.5 M) and aryl bromide **1c** (682 mg, 2.00 mmol, 1.0 equiv) were then added. The vial was sealed and heated at 110 ºC for 2 h. Upon completion, the vial was cooled to rt, diluted with EtOAc, eluted through a plug of Celite®, and concentrated. The crude material was then purified by column chromatography (gradient hexanes to EtOAc) to afford title compound **2j** (629 mg, 1.62 mmol, 81% yield) as a white solid (mp = 90-92 ºC).

**$^{1}$H NMR** (360 MHz, acetone-$d_6$) δ -0.20 (s, 9H), 1.34 (s, 12H), 1.56 (d, $J$ = 14.8 Hz, 1H), 1.75 (d, $J$ = 14.8 Hz, 1H), 5.41 (s, 1H), 7.65 - 7.71 (m, 2H), 7.75 - 7.79 (m, 2H).

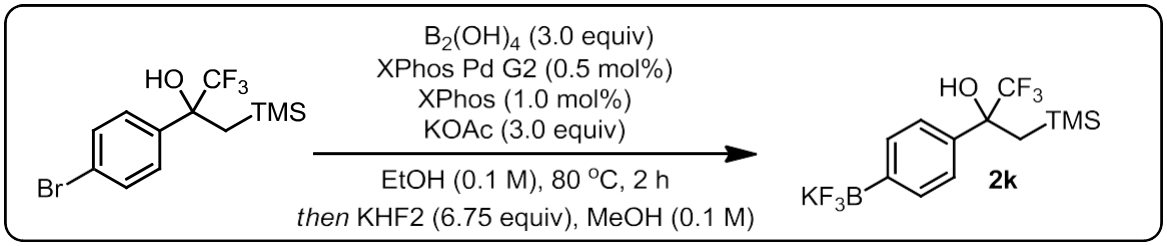
**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.2 ($CH_3$), 24.6 (d, $J$ = 8.2 Hz, $CH_2$), 25.3 (d, $J$ = 5.5 Hz, $CH_3$), 77.6 (q, $J_{C-C-F}$ = 27.9 Hz, C), 84.7 (C), 127.4 (q, $J_{C-F}$ = 285.9 Hz, $CF_3$), 127.0 (CH), 135.1 (CH), 142.9 (C), 143.0 (C).

**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -82.06 (s, 3F).

**$^{11}$B NMR** (128 MHz, acetone-$d_6$) δ 30.5 (s, 1B).

**FT-IR** (cm$^{-1}$, neat, ATR) 3488 (br w), 2982 (br w), 1361 (vs), 1152 (vs), 1078 (vs), 854 (vs), 658 (vs).

**HRMS** (EI) calcd for $C_{18}H_{28}BF_3O_3Si$ [M]$^+$: 372.1654, found: 372.1658.




**Potassium (4-(1,1,1-Trifluoro-2-hydroxy-3-(trimethylsilyl)propan-2-yl)phenyl)trifluoroborate (2k)**

***Borylation***

A 20 mL microwave vial was charged with XPhos Pd-G2 (7.9 mg, 0.010 mmol, 0.50 mol %), XPhos (9.5 mg, 0.020 mmol, 1.0 mol %), $B_2(OH)_4$ (538 mg, 6.00 mmol, 3.00 equiv), and KOAc (589 mg, 6.00 mmol, 3.00 equiv). The vial was evacuated and backfilled with argon three times. Degassed EtOH (20 mL, 0.1 M relative to aryl bromide) was then added followed by aryl bromide **1c** (682 mg, 2.00 mmol, 1.00 equiv). The vial was sealed and heated at 80 ºC until the reaction turned orange and starting material was consumed (as monitored by HPLC). The reaction was then cooled to rt, filtered through a pad of Celite® with EtOAc (~100 mL), and concentrated. The crude mixture was then dissolved in EtOAc (20 mL) and transferred to a separatory funnel. The organic layer was washed with $H_2O$ (1 x 20 mL) and brine (1 x 20 mL). The combined aq layers were then extracted with EtOAc (3 x 10 mL).

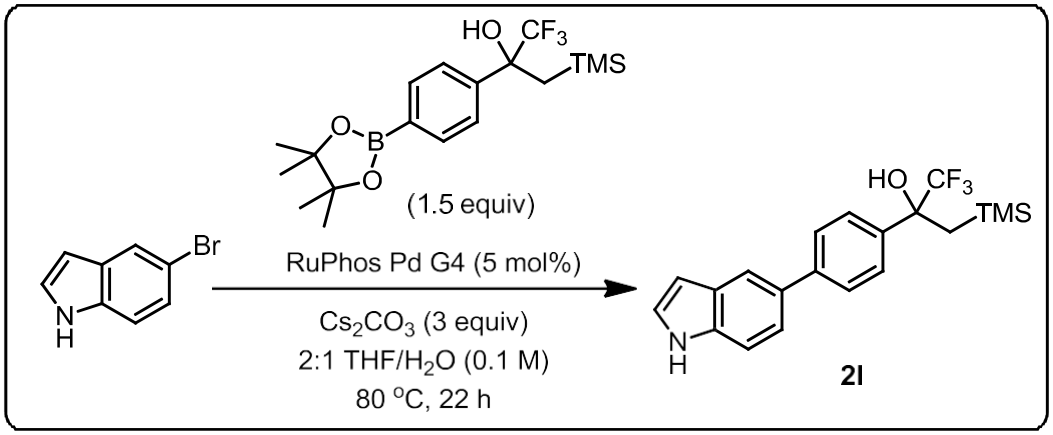
***Synthesis of Trifluoroborate***

The combined organic layers were dried ($Na_2SO_4$), filtered, and concentrated. The crude material was then dissolved in MeOH (20 mL, 0.1 M relative to aryl bromide) and cooled to 0 ºC in an ice bath. Once equilibrated, 4.5 M aq $KHF_2$ (3.00 mL, 13.5 mmol, 6.75 equiv) was added dropwise. The reaction was stirred for 10 min at 0 ºC, after which the ice bath was removed and the reaction was stirred at ambient temperature for 1.5 h (conversion to the corresponding trifluoroborate was determined by $^{11}$B NMR). The resulting mixture was then concentrated and

lyophilized overnight to remove any trace water. Acetone (~50 mL) was then added to the dry solid, the resulting slurry was then filtered to remove inorganic salts, and the acetone soln was concentrated to obtain a sticky yellow oil. The oil was dissolved in a minimal amount of $CH_2Cl_2$ (~5 mL) and precipitated by addition of pentane (~50 mL). A sticky brown semisolid was then collected and placed under hi-vac at 50 °C for 8 h to obtain title compound **2k** (626 mg, 1.70 mmol, 85% yield, average of three reactions) as a fine yellow powder (decomp. >150 °C).

**$^1$H NMR** (360 MHz, acetone-$d_6$) δ -0.19 (s, 9H), 1.48 (d, $J$ = 14.8 Hz, 1H), 1.68 (d, $J$ = 14.5 Hz, 1H), 4.96 (br s, 1H), 7.38 (d, $J$ = 7.7 Hz, 2H), 7.50 (d, $J$ = 7.9 Hz, 2H).
**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.3 ($CH_3$), 24.8 ($CH_2$), 77.5 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 28.4 Hz, C), 125.5 (CH), 127.7 (q, $J_{\mathbf{C\text{-}F}}$ = 286.5 Hz, $CF_3$), 132.0 (CH), 136.4 (C).
**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -142.75 – -143.22 (m, 3F), -82.11 (s, 3F).
**$^{11}$B NMR** (128 MHz, acetone-$d_6$) δ 5.8 (br s, 1B).
**FT-IR** ($cm^{-1}$, neat, ATR) 3613 (br w), 2956 (br w), 1216 (s), 1165 (s), 957 (vs), 916 (vs), 825 (vs), 747 (s), 697 (w), 639 (w), 551 (w).
**HRMS** (ESI) calcd for $C_{12}H_{16}BF_6OSi$ [M – K]$^-$: 329.0968; found: 329.0973.

***Procedures for the Suzuki Cross-Coupling of Borylated α-$CF_3$-β-TMS-Alcohols***




**2-(4-(1*H*-Indol-5-yl)phenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (2l)** A 20 mL microwave vial was charged with 5-bromoindole (98.0 mg, 0.500 mmol, 1.00 equiv), aryl Bpin **2j** (291 mg, 0.750 mmol, 1.50 equiv), RuPhos Pd G4 (21.3 mg, 0.025 mmol, 5.0 mol %), and

$Cs_2CO_3$ (489 mg, 1.50 mmol, 3.00 equiv). The vial was evacuated and backfilled with argon three times. Degassed 2:1 THF/$H_2O$ (5.0 mL, 0.1 M relative to aryl bromide) was added. The microwave vial was then sealed and heated in an 80 ºC oil bath for 22 h. Upon completion, the vial was cooled to rt, diluted with EtOAc, and eluted through a plug of Celite®. The crude material was then purified by column chromatography (gradient hexanes to EtOAc) to afford title compound **2l** (186.7 mg, 0.495 mmol, 99% yield) as a white solid (mp = 99-101 ºC).

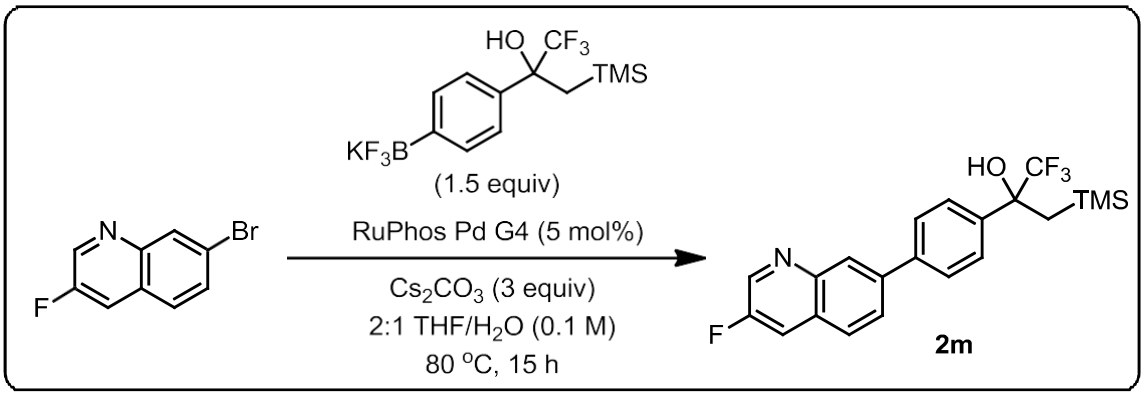
**$^1$H NMR** (500 MHz, acetone-$d_6$) δ -0.15 (s, 9H), 1.58 (d, $J$ = 14.8 Hz, 1H), 1.78 (d, $J$ = 14.8 Hz, 1H), 5.40 (s, 1H), 6.55 (t, $J$ = 2.1 Hz, 1H), 7.37 (t, $J$ = 2.7 Hz, 1H), 7.46 (dd, $J$ = 8.5, 1.7 Hz, 1H), 7.52 (d, $J$ = 8.4 Hz, 1H), 7.72 (s, 3H), 7.90 (d, $J$ = 0.9 Hz, 1H), 10.30 (br s, 1H).[16]

**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.3 ($CH_3$), 24.8 ($CH_2$), 77.4 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 28.2 Hz, C), 103.0 (CH), 112.6 (CH), 119.6 (CH), 121.7 (CH), 127.6 (q, $J_{\mathbf{C\text{-}F}}$ = 286.1 Hz, $CF_3$), 126.5 (CH), 127.2 (CH), 128.0 (CH), 129.8 (C), 132.6 (C), 137.0 (C), 137.7 (C), 143.3 (C).

**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -82.08 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3417 (br s), 2955 (s), 1469 (s), 1418 (s), 1250 (s), 1215 (s), 1154 (vs), 1096 (s), 989 (s), 921 (s), 844 (vs), 805 (s).

**HRMS** (ESI) calcd for $C_{20}H_{23}F_3NOSi[M + H]^+$: 378.1501; found: 378.1502.




**1,1,1-Trifluoro-2-(4-(3-fluoroquinolin-7-yl)phenyl)-3-(trimethylsilyl)propan-2-ol (2m)**

A 20 mL microwave vial was charged with 7-bromo-3-fluoroquinoline (134 mg, 0.500 mmol, 1.00 equiv), aryl trifluoroborate **2k** (276 mg, 0.750 mmol, 1.50 equiv), RuPhos Pd G4 (21.3 mg, 0.025 mmol, 5.0 mol %), and $Cs_2CO_3$ (489 mg, 1.50 mmol, 3.00 equiv). The vial was evacuated and backfilled with argon three times. Degassed 2:1 THF/$H_2O$ (5.0 mL, 0.1 M relative to aryl bromide) was added. The microwave vial was then sealed and heated in an 80 ºC oil bath for 15

h. Upon completion, the vial was cooled to rt, diluted with EtOAc, eluted through a plug of Celite®, and concentrated. The crude material was then purified by column chromatography (gradient hexanes to EtOAc 0.1% v/v $Et_3N$) to afford title compound **2m** (161 mg, 0.395 mmol, 79% yield) as a white solid (mp =145-146 °C).

**$^1$H NMR** (500 MHz, acetone-$d_6$) δ -0.14 (s, 9H), 1.62 (d, $J$ = 14.9 Hz, 1H), 1.82 (d, $J$ = 14.7 Hz, 1H), 5.48 (s, 1H), 7.82 - 7.86 (m, 2H), 7.89 - 7.94 (m, 2H), 8.04 (dq, $J$ = 8.6, 1.0 Hz, 1H), 8.07 - 8.11 (m, 1H), 8.16 (m, 1H), 8.38 (m, 1H), 8.90 (d, $J$ = 2.7 Hz, 1H).

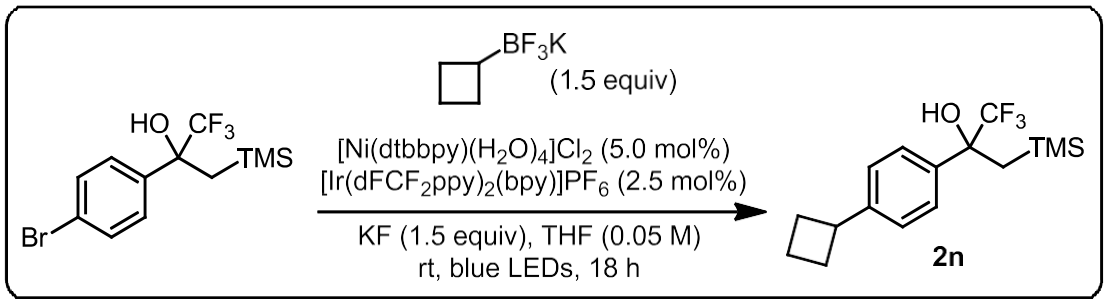
**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.2 ($CH_3$), 24.8 ($CH_2$), 77.5 (q, $J_{C\text{-}C\text{-}F}$ = 28.1 Hz, C), 119.0 (d, $J_{C\text{-}C\text{-}F}$ = 16.5 Hz, CH), 127.5 (q, $J_{C\text{-}F}$ = 287.8 Hz, $CF_3$), 127.7 (CH), 128.0 (CH), 128.3 (C), 128.5 (CH), 128.8 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ =5.5 Hz, C), 129.2 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 4.6 Hz, C), 139.9 (CH), 140.5 (CH), 141.5 (br s, C), 142.8 (d, $J_{C\text{-}C\text{-}F}$ = 27.5 Hz, CH), 146.9 (C), 157.4 (d, $J_{C\text{-}F}$ = 254.8 Hz, CF).

**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -130.17 (s, 1F), -82.02 (s, 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 3225 (br w), 2954 (w), 1614 (s), 1337 (s), 1249 (s), 1217 (s), 1153 (vs), 1100 (s), 996 (s), 919 (s), 847 (s).

**HRMS** (EI) calcd for $C_{21}H_{21}F_4NOSi$ $[M]^+$: 408.1407, observed: 408.1419.

***Representative Procedure for $C_{sp2}$–$C_{sp3}$ Cross-Coupling using Trifluoroborates***



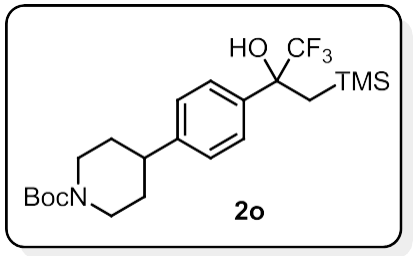

**2-(4-Cyclobutylphenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (2n)**

A stir bar-equipped 8 mL vial was charged with $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (5.9 mg, 0.0125 mmol, 5.0 mol %), $[Ir(dFCF_3ppy)_2(bpy)](PF_6)$ (6.3 mg, 0.00625 mmol, 2.5 mol %), KF (21.8 mg, 0.375 mmol, 1.50 equiv), and potassium cyclobutyltrifluoroborate (60.8 mg, 0.375 mmol, 1.50 equiv). The vial was sealed and via an inlet needle evacuated and backfilled with argon three times. Anhyd, degassed THF (5.0 mL, 0.05 M) was then added, followed by α-$CF_3$-β-TMS-alcohol **1c** (85.3 mg, 0.250 mmol, 1.0 equiv). The vial was sealed with Parafilm® and irradiated with blue

LEDs while rapidly stirring. The temperature of the reaction was maintained at ~28 ºC using a fan. After 19 h, the reaction was judged to be done by GC/MS and was diluted with EtOAc and filtered through Celite®. The filtrate was concentrated and purified by column chromatography (gradient hexanes to EtOAc) to afford title compound **2n** (55.4 mg, 0.175 mmol, 70% yield, average yield of two reactions) as a colorless oil.

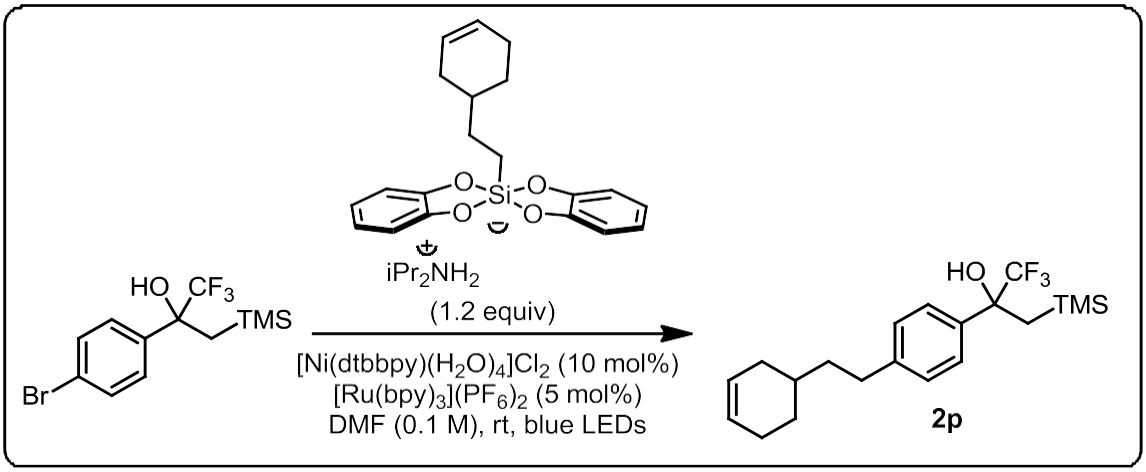
**$^{1}$H NMR** (500 MHz, acetone-$d_6$) δ -0.21 (s, 9H), 1.53 (d, $J$ = 14.8 Hz, 1H), 1.71 (d, $J$ = 14.8 Hz, 1H), 1.80 - 1.89 (m, 1H), 1.97 - 2.04 (m, 1H), 2.09 - 2.19 (m, 2H), 2.33 (qt, $J$ = 8.5, 2.4 Hz, 2H), 3.50 - 3.65 (m, 1H), 5.31 (s, 1H), 7.26 (d, $J$ = 8.1 Hz, 2H), 7.57 (d, $J$ = 8.2 Hz, 2H).
**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.1 ($CH_3$), 18.7 ($CH_2$), 24.6 ($CH_2$), 30.4 (CH), 40.8 ($CH_2$), 77.1 (q, $J_{C\text{-}C\text{-}F}$ = 28.4 Hz, C), 127.5 (q, $J_{C\text{-}F}$ = 286.5 Hz, $CF_3$), 126.4 (CH), 127.5 (CH), 137.4 (C), 146.7 (C).
**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -82.17 (s, 3F).
**FT-IR** ($cm^{-1}$, neat, ATR) 3613 (br w), 2958 (br w), 1214 (s), 1149 (vs), 989 (s), 917 (s), 839 (vs), 697 (s), 623 (s).
**HRMS** (EI) calcd for $C_{16}H_{23}F_3OSi[M]^+$: 316.1470, found: 316.1472.

***tert*-Butyl 4-(4-(1,1,1-Trifluoro-2-hydroxy-3-(trimethylsilyl)propan-2-yl)phenyl)piperidine-1-carboxylate, 2o** (84.3 mg, 76% yield, average yield of two reactions) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **1c** (85.3 mg, 0.250 mmol, 1.00 equiv), $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (5.9 mg, 0.0125 mmol, 5.0 mol %), $[Ir(dFCF_3ppy)_2(bpy)](PF_6)$ (6.3 mg, 0.00625 mmol, 2.5 mol %), KF (21.8 mg, 0.375 mmol, 1.50 equiv), and potassium *N*-Boc-piperidinyl-4-trifluoroborate (109 mg, 0.375 mmol, 1.50 equiv), and degassed THF (5.0 mL, 0.05 M). The title compound **2o** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a white solid (mp = 130-131 ºC). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ -0.20 (s, 9H), 1.43 (d, $J$ = 14.9 Hz, 1H), 1.48 (s, 9H), 1.56 - 1.68 (m, 3H), 1.82 (d, $J$ = 13.0 Hz, 2H), 2.29 (s, 1H), 2.66 (tt, $J$ = 12.2, 2.9 Hz, 1H), 2.72 - 2.90 (m, 2H), 4.26 (br s, 2H), 7.20 (d, $J$ = 8.3 Hz, 2H), 7.47 (d, $J$ = 8.3 Hz, 2H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.1 ($CH_3$), 24.8 ($CH_2$), 28.7 ($CH_3$), 34.0 ($CH_2$), 42.8 ($CH_2$), 77.2 (q, $J_{C\text{-}C\text{-}F}$ = 27.5 Hz, C), 79.6 (C),



127.5 (q, $J_{C-F}$ = 286.8 Hz, $CF_3$), 127.1 (CH), 127.7 (CH), 137.9 (CH), 146.8 (C), 155.3 (C), 207.6 (br s, C). **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -85.08 (s, 3F). **FT-IR** (cm$^{-1}$, neat, ATR) 3349 (br w), 2942 (br w), 1665 (s), 1428 (s), 1149 (vs), 838 (s), 623 (s). **HRMS (**ESI) calcd for $C_{22}H_{34}F_3NNaO_3Si$ [M + Na]$^+$: 468.2158, found: 468.2178.

***Representative Procedure for $C_{sp2}$–$C_{sp3}$ Cross-Coupling using Silicates***




**2-(4-(2-(Cyclohex-3-en-1-yl)ethyl)phenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol (2p).** A stir bar-equipped 8 mL vial was charged with $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (23.5 mg, 0.050 mmol, 10.0 mol %), $[Ru(bpy)_3](PF_6)$ (21 mg, 0.025 mmol, 5.0 mol %), and ethyl cyclohexyl silicate (273 mg, 0.600 mmol, 1.20 equiv). The vial was sealed and *via* an inlet needle evacuated and backfilled with argon three times. Anhyd DMF (5.0 mL, 0.1 M) was then added, followed by α-$CF_3$-β-TMS-alcohol **1c** (171 mg, 0.500 mmol, 1.00 equiv). The vial was sealed with Parafilm® and irradiated with two blue Kessil lamps while rapidly stirring. The Kessil lamps were positioned ~4 inches away on opposite sides of the reaction vial. The temperature of the reaction was maintained at ~30 ºC using a fan. After 48 h, the reaction was transferred to a separatory funnel and diluted with $Et_2O$ (~20 mL). The organic layer was then washed with saturated aq $Na_2CO_3$ (2 x 10 mL) and brine (1 x 10 mL). The combined aq layers were then back extracted with $Et_2O$ (3 x 20 mL). The combined organic layers were concentrated, and the crude material was then purified by column chromatography (gradient hexanes to EtOAc 1% v/v $Et_3N$) to afford title compound **2p** (132.4 mg, 0.36 mmol, 71% yield) as a colorless oil.

**$^{1}$H NMR** (500 MHz, acetone-$d_6$) δ -0.21 (s, 9H), 1.19 - 1.29 (m, 1H), 1.52 (d, $J$ = 14.8 Hz, 1H), 1.55 - 1.64 (m, 3H), 1.65 - 1.74 (m, 2H), 1.76 - 1.83 (m, 1H), 1.98 - 2.03 (m, 2H), 2.11 - 2.19 (m, 1H), 2.69 (t, $J$ = 7.6 Hz, 2H), 5.30 (s, 1H), 5.63 (d, $J$ = 2.1 Hz, 2H), 7.25 (d, $J$ = 8.2 Hz, 2H), 7.55 (d, $J$ = 8.1 Hz, 2H).

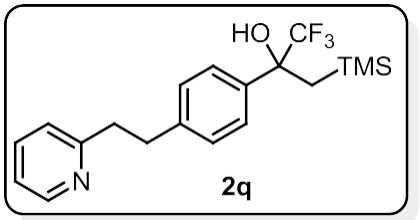
**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.1 ($CH_3$), 24.8 ($CH_2$), 25.9 ($CH_2$), 29.6 (CH), 32.5 ($CH_2$), 33.4 ($CH_2$), 33.9 ($CH_2$), 39.3 (d, $J$ = 2.7 Hz, $CH_2$), 77.2 (q, $J_{C\text{-}C\text{-}F}$ = 28.2 Hz, C), 127.5 (q, $J_{C\text{-}F}$ = 287.0 Hz, $CF_3$), 127.2 (CH), 127.6 (CH), 127.6 (CH), 128.7 (CH), 137.3 (C), 143.6 (C).

**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -82.16 (s, 3F).

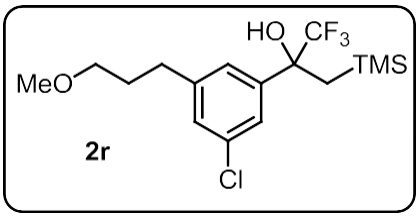
**FT-IR** ($cm^{-1}$, neat, ATR) 3613 (br w), 2914 (br s), 1250 (s), 1215 (s), 1148 (vs), 917 (s), 841 (vs), 653 (s).

**HRMS (**EI) calcd for $C_{20}H_{29}F_3OSi[M]^+$: 370.1940, found 370.1929.

**1,1,1-Trifluoro-2-(4-(2-(pyridin-2-yl)ethyl)phenyl)-3-(trimethylsilyl)propan-2-ol, 2q** (135.4 mg, 0.37 mmol, 74% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **1c** (171 mg, 0.500 mmol, 1.00 equiv), ethyl pyridyl silicate (272 mg, 0.60 mmol, 1.20 equiv), and DMF (5.0 mL, 0.1 M) with the following modifications: [Ni(dtbbpy)($H_2O$)$_4$]$Cl_2$ (12.0 mg, 0.0250 mmol, 5.0 mol %) and [Ru(bpy)$_3$]($PF_6$) (11 mg, 0.013 mmol, 2.5 mol %). The crude material was purified by column chromatography (gradient hexanes to EtOAc) to afford title compound **2p** as a white solid (mp = 121-122 ºC). **$^{1}$H NMR** (500 MHz, acetone-$d_6$) δ -0.22 (s, 9H), 1.52 (d, $J$ = 14.8 Hz, 1H), 1.70 (d, $J$ = 14.8 Hz, 1H), 3.07 (app s, 4H), 5.31 (s, 1 H), 7.11 - 7.18 (m, 2 H), 7.24 (d, $J$ = 8.4 Hz, 2H), 7.54 (d, $J$ = 8.1 Hz, 2H), 7.61 (td, $J$ = 7.8, 2.1 Hz, 1H), 8.49 - 8.53 (m, 1H).**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.1 ($CH_3$), 24.6 ($CH_2$), 36.0 ($CH_2$), 40.4 ($CH_2$), 77.1 (q, $J_{C\text{-}C\text{-}F}$ = 28.2 Hz, C), 122.2 (CH), 124.0 (CH), 127.4 (q, $J_{C\text{-}F}$ = 286.1 Hz, $CF_3$), 127.5 (CH), 128.7 (CH), 137.4 (CH), 137.5 (C), 142.3 (C), 149.8 (CH), 161.7 (C). **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -82.19 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 2951 (br w), 1599 (w), 1150 (vs), 920 (s), 843 (s), 759 (s), 697 (s), 534 (s). **HRMS (**ESI) calcd for $C_{19}H_{25}F_3NOSi$ [M + H]$^+$: 368.1658, found 368.1645.

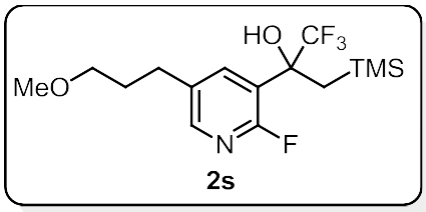


**2-(3-Chloro-5-(3-methoxypropyl)phenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol, 2r**




(129 mg, 0.35 mmol, 70% yield, average of two reactions) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **1e** (188 mg, 0.500 mmol, 1.00 equiv), propyl methoxy silicate (252 mg, 0.600 mmol, 1.20 equiv), and DMF (5.0 mL, 1.0 M). The crude material was purified by column chromatography (gradient hexanes to EtOAc) to afford title compound **2r** as a white solid (mp = 56-57 ºC). **$^1$H NMR** (500 MHz, acetone-$d_6$) δ -0.17 (s, 9H), 1.55 (d, $J$ = 14.9 Hz, 1H), 1.76 (d, $J$ = 14.9 Hz, 1H), 1.80 - 1.92 (m, 2H), 2.72 (t, $J$ = 7.6 Hz, 2H), 3.27 (s, 3H), 3.35 (t, $J$ = 6.0 Hz, 2H), 5.52 (br s, 1H), 7.26 (s, 1H), 7.45 (s, 1H), 7.52 (s, 1H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.2 ($CH_3$), 24.6 ($CH_2$), 32.1 ($CH_2$), 32.8 ($CH_2$), 58.6 ($CH_2$), 72.0 ($CH_3$), 77.2 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 28.2 Hz, C), 125.3 (CH), 127.2 (q, $J_{\mathbf{C\text{-}F}}$ = 287.0 Hz, $CF_3$), 126.6 (CH), 129.0 (CH), 134.3 (C), 142.2 (C), 145.2 (C). **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -82.11 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 3369 (br w), 2951 (br w), 1580 (s), 1250 (s), 1213 (s), 1170 (vs), 1009 (s), 845 (vs), 718 (s). **HRMS** (EI) calcd for $C_{15}H_{20}ClF_3OSi$ $[M - CH_3OH]^+$: 336.0924, found: 336.0945; calcd for $C_{15}H_{24}ClO_2Si$ $[M - CF_3]$: 299.1234, found: 299.1230.

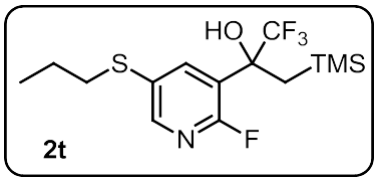
**1,1,1-Trifluoro-2-(2-fluoro-5-(3-methoxypropyl)pyridin-3-yl)-3-(trimethylsilyl)propan-2-ol,**




**2s** (151.2 mg, 0.43 mmol, 86% yield, average of two reactions) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **1d** (183 mg, 0.500 mmol, 1.00 equiv), propyl methoxy silicate (252 mg, 0.600 mmol, 1.20 equiv), and DMF (5.0 mL, 1.0 M). The crude material was purified by column chromatography (gradient hexanes to EtOAc) to afford title compound **2s** as a white solid (mp = 82-83 ºC). **$^1$H NMR** (500 MHz, acetone-$d_6$) δ -0.16 (s, 9H), 1.53 (dd, $J$ = 15.2, 1.5 Hz, 1H), 1.83 – 1.90 (m, 2H), 2.78 - 2.82 (m, 3H), 3.27 (s, 3H), 3.35 (t, $J$ = 6.2 Hz, 2H), 5.77 (s, 1H), 8.08 (s, 1H), 8.20 (dd, $J$ = 9.5, 2.2 Hz, 1H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ -0.1 ($CH_3$), 22.4 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}C\text{-}F}}$ = 6.4 Hz, $CH_2$), 29.0 ($CH_2$), 32.0 ($CH_2$), 58.6 ($CH_2$), 71.7 ($CH_3$), 75.8 (qd, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 30.2, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 7.3 Hz, C), 121.1 (d, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 29.3 Hz, C), 126.8 (q, $J_{\mathbf{C\text{-}F}}$ = 286.8 Hz, $CF_3$), 136.7 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 4.6 Hz, CH), 141.7 (C), 148.1 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 15.6 Hz, CH),

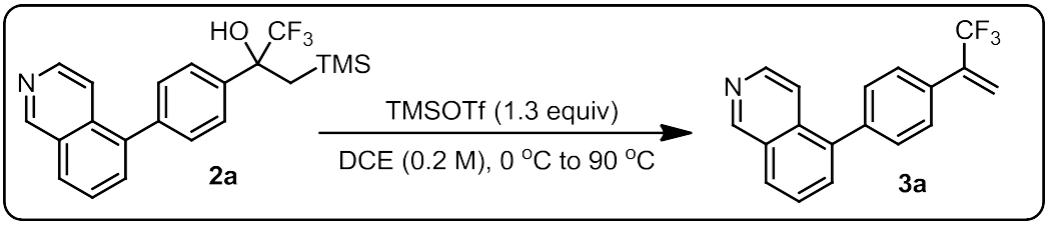
159.7 (d, $J_{C\text{-}F}$ = 234.6 Hz, CF). **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -82.41 (dd, $J$ = 18.1, 4.5 Hz, 3F), -67.60 (qd, $J$ = 18.3, 6.0 Hz, 1F). **FT-IR** (cm$^{-1}$, neat, ATR) 3313 (br w), 2853 (br w), 1591 (w), 1454 (s), 1169 (vs), 947 (s), 836 (vs), 764 (s), 698 (w). **HRMS** (ESI) calcd for $C_{15}H_{24}F_3NO_2Si$[M + H]$^+$: 354.1512, found: 354.1517.

**1,1,1-Trifluoro-2-(2-fluoro-5-(propylthio)pyridin-3-yl)-3-(trimethylsilyl)propan-2-ol, 2t**




(147 mg, 0.41 mmol, 83% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **1d** (180 mg, 0.500 mmol, 1.00 equiv), propyl thiol silicate (316.2 mg, 0.750 mmol, 1.50 equiv), and DMF (5.0 mL, 0.1 M). After 24 h, the reaction was worked up as described in the general procedure and purified by column chromatography (gradient hexanes to EtOAc) to afford title compound **2t** as a white solid (mp = 75-76 ºC). **$^1$H NMR** (500 MHz, acetone-$d_6$) δ -0.15 (s, 9H), 1.01 (t, $J$ = 7.3 Hz, 3H), 1.54 (dd, $J$ = 15.0, 1.8 Hz, 1H), 1.63 (tq, $J$ = 14.8, 7.3 Hz, 2H), 2.01 (dd, $J$ = 15.0, 2.1 Hz, 1H), 2.99 (t, $J$ = 7.2 Hz, 2H), 5.96 (s, 1H), 8.23 (dd, $J$ = 2.3, 1.5 Hz, 1H), 8.33 (dd, $J$ = 9.0, 2.6 Hz, 1H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ -0.1 ($CH_3$), 13.4 ($CH_2$), 22.3 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 6.4 Hz, $CH_2$), 23.2 ($CH_2$), 37.0 ($CH_2$), 75.8 (qd, $J_{C\text{-}C\text{-}F}$ = 30.2, $J_{C\text{-}C\text{-}C\text{-}F}$ = 6.4 Hz, C), 122.2 (d, $J_{C\text{-}C\text{-}F}$ = 29.3 Hz, C), 126.7 (qd, $J_{C\text{-}F}$ = 286.8, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, $CF_3$), 132.4 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 4.6 Hz, CH), 143.2 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 4.6 Hz, C), 149.3 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 15.6 Hz, CH), 159.9 (d, $J_{C\text{-}F}$ = 238.3 Hz, CF). **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -82.38 (d, $J$ = 18.1 Hz, 3F), -66.80 (q, $J$ = 18.4 Hz, 1F). **FT-IR** (cm$^{-1}$, neat, ATR) 3322 (br w), 2962 (br w), 1443 (s), 1251 (s), 1175 (vs), 999 (s), 865 (s). **HRMS** (ESI) calcd for $C_{14}H_{22}F_4NOSSi$[M + H]$^+$: 354.1512, found: 354.1517.

## General Procedure for the Elimination of α-$CF_3$-β-TMS-alcohols to $CF_3$ Alkenes




**5-(4-(3,3,3-Trifluoroprop-1-en-2-yl)phenyl)isoquinoline (3a)**

***General Procedure***

A flame-dried 50 mL round-bottom flask equipped with a stir bar was charged with alcohol **2a** (707 mg, 1.82 mmol, 1.00 equiv) and DCE (9.1 mL, 0.2 M). The resulting heterogeneous soln was chilled to 0 ºC in an ice bath. Once equilibrated, TMSOTf (0.43 mL, 2.37 mmol, 1.3 equiv) was added dropwise (~1 drop/second). The ice bath was then removed, and the reaction was stirred at rt for 1 h. The flask was then equipped with a reflux condenser and refluxed at 90 ºC for 3 h. Once judged done by $^1$H and $^{19}$F NMR, the reaction was cooled to rt and quenched with 10 mL of saturated aq $NH_4Cl$. After stirring for 10 min at rt, the reaction mixture was transferred to a separatory funnel and diluted with EtOAc (50 mL). The layers were then separated, and the organic layer was washed with saturated aq $NaHCO_3$ (2 x 25 mL) and brine (1 x 25 mL) and concentrated. The crude material was purified by column chromatography (gradient hexanes to EtOAc 1% v/v $Et_3N$) to afford title compound **3a** (462.5 mg, 1.55 mmol, 85% yield) as a viscous colorless oil.

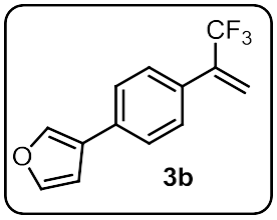
***Modification: 1 equiv HCl, 60 mol % TMSOTf***

An 8 mL microwave vial equipped with a stir bar was charged with alcohol **2a** (195 mg, 0.500 mmol, 1.00 equiv) and DCE (5 mL, 0.1 M). The resulting heterogeneous soln was chilled to 0 ºC in an ice bath. Once equilibrated, 4 N HCl in dioxane (0.13 mL, 0.500 mmol, 1.00 equiv) was added followed by dropwise addition of TMSOTf (33 µL, 0.15 mmol, 30 mol %). The ice bath was then removed, and the reaction was heated at 90 ºC for 3 h, after which TMSOTf (33 µL, 0.15 mmol, 30 mol %) was again added. The reaction was then stirred overnight at 90 ºC (17 h). Once judged done by $^1$H and $^{19}$F NMR, the reaction was cooled to 0 ºC and quenched with 5 mL of saturated aq $NaHCO_3$. After stirring for 10 min at rt, the reaction mixture was transferred to a

separatory funnel and diluted with EtOAc (20 mL). The layers were then separated, and the organic layer was washed with saturated aq $NaHCO_3$ (2 x 15 mL) and brine (1 x 15 mL) and concentrated. The crude material was purified by column chromatography (gradient hexanes to EtOAc 1% v/v $Et_3N$) to afford title compound **3a** (123.9 mg, 1.55 mmol, 83% yield) as a viscous, colorless oil.

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.90 (d, *J* = 1.7 Hz, 1H), 6.05 (d, *J* = 1.2 Hz, 1H), 7.49 - 7.56 (m, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.66 - 7.71 (m, 2H), 7.73 (dd, *J* = 6.0, 0.8 Hz, 1H), 8.02 (dd, *J* = 6.2, 3.3 Hz, 1H), 8.51 (d, *J* = 6.1 Hz, 1H), 9.33 (s, 1H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 118.5 (CH), 120.9 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 123.6 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 127.0 (CH), 127.7 (CH), 127.7 (CH), 129.2 (C), 130.3 (CH), 131.1 (CH), 133.2 (C), 134.1 (C), 138.7 (q, $J_{C\text{-}C\text{-}F}$ = 30.1 Hz, C), 138.5 (C), 140.0 (C), 143.8 (CH), 153.2 (CH).
**$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -67.77 (s, 3F).
**FT-IR** ($cm^{-1}$, neat, ATR) 3036 (br w), 1585 (s), 1352 (s), 1163 (vs), 1117 (s), 829 (w).
**HRMS (**ESI) calcd for $C_{18}H_{13}F_3N$ $[M + H]^+$: 300.1000; found: 300.0992.

**3-(4-(3,3,3-Trifluoroprop-1-en-2-yl)phenyl)furan, 3b** (98.1 mg, 0.41 mmol, 41% yield) was



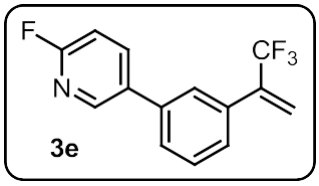
**3b**

prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2b** (328 mg, 1.00 mmol, 1.00 equiv) and DCE (5.0 mL, 0.2 M) with the following modifications: TMSOTf (18 μL, 0.10 mmol, 0.10 equiv). After stirring for 24 h, the reaction was judged to be done by $^1$H and $^{19}$F NMR and quenched according to the general procedure. The title compound **3b** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a white solid (mp = 79-80 ºC). **$^1$H NMR** (500 MHz, acetone-$d_6$) δ 6.04 (t, *J* = 1.6 Hz, 2H), 6.94 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.67 (t, *J* = 1.7 Hz, 1H), 7.70 (dt, *J* = 8.5, 2.1 Hz, 2H), 8.11 (br s, 1H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 109.5 (CH), 121.5 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 6.0 Hz, $CH_2$), 124.7 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 126.7 (C), 126.9 (CH), 128.6 (CH), 132.7 (C), 134.4 (C), 139.0 (q, $J_{C\text{-}C\text{-}F}$ = 30.2 Hz, C), 140.6 (CH), 145.3 (CH). **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -85.14 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 3127 (w), 1520 (w), 1347 (s), 1120 (vs), 841 (vs), 789 (vs), 595 (s). **HRMS (**EI) calcd for $C_{13}H_9F_3O$ $[M]^+$: 238.0605 found: 238.0596.

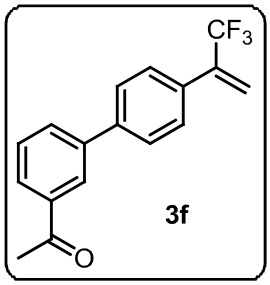
**1-Cyclopropyl-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene, 3c** (78.5 mg, 0.370 mmol, 74% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2c** (151 mg, 0.50 mmol, 1.00 equiv) and DCE (2.5 mL, 0.2 M) with the following modifications: TMSOTf (18 μL, 0.10 mmol, 0.20 equiv). After stirring for 90 min at rt, the reaction was quenched and worked up as described. The title compound **3c** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 0.68 - 0.75 (m, 2H), 0.96 - 1.02 (m, 2H), 1.92 (tt, *J* = 8.5, 5.2 Hz, 1H), 5.74 (d, *J* = 1.5 Hz, 1H), 5.94 (d, *J* = 1.2 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.17 (s, 1H), 7.20 - 7.30 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 9.6 ($CH_2$), 15.7 (CH), 120.6 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 6.1 Hz, $CH_2$), 123.7 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 124.8 (CH), 125.4 (CH), 126.4 (CH), 128.8 (CH), 134.0 (C), 139.5 (q, $J_{C\text{-}C\text{-}F}$ = 30.2 Hz, C), 144.7 (C). **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ - 67.83 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 3010 (br w), 1345 (s), 1157 (s), 1120 (vs), 1092 (vs), 701 (s). **HRMS (**EI) calcd for $C_{12}H_{11}F_3$ $[M]^+$: 212.0813, found: 212.0820.

**1-(2'-(3,3,3-Trifluoroprop-1-en-2-yl)-[1,1'-biphenyl]-3-yl)ethan-1-one, 3d** (80.3 mg, 1.55 mmol, 55% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2d** (190 mg, 0.500 mmol, 1.00 equiv) and DCE (2.5 mL, 0.2 M) with the following modifications: TMSOTf (18 μL, 0.10 mmol, 0.20 equiv). After stirring at rt for a total of 1.5 h, the reaction was judged to be done by $^1$H and $^{19}$F NMR and quenched according to the general procedure. The title compound **3d** was purified by column chromatography (gradient hexanes EtOAc) and isolated as a colorless oil. **$^1$H NMR** (500 MHz, acetone-$d_6$) δ 2.60 (s, 3H), 5.48 - 5.60 (m, 1H), 6.03 (q, *J* = 1.4 Hz, 1H), 7.42 - 7.47 (m, 2H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.53 - 7.59 (m, 3H), 7.93 - 7.95 (m, 1H), 7.97 (dt, *J* = 7.1, 1.8 Hz, 1H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 26.8 ($CH_3$), 124.2 (q, $J_{C\text{-}F}$ = 273.4 Hz, $CF_3$), 126.5 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.4 Hz, $CH_2$), 127.8 (CH), 128.7 (CH), 129.4 (CH), 130.2 (CH), 130.3 (CH), 131.0 (C), 131.6 (C), 133.4 (C), 134.7 (C), 138.3 (q, $J_{C\text{-}C\text{-}F}$ = 30.9 Hz, C), 138.0 (CH), 142.3 (C), 197.8 (C). (Only 16 $^{13}$C NMR peaks are observed due to overlapping quaternary aromatic carbons) **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -66.36 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 3064 (br w), 1685 (s), 1343 (s), 1165 (vs), 1120 (vs), 760 (s), 613 (s). **HRMS** (EI) calcd for $C_{17}H_{13}F_3O$ $[M]^+$: 290.0918, found: 290.0900.

**2-Fluoro-5-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)pyridine, 3e** (244 mg, 0.91 mmol, 91% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2e** (343 mg, 1.00 mmol, 1.00 equiv) and DCE (5.0 mL, 0.2 M) with the following modifications: TMSOTf (53 µL, 0.29 mmol, 0.20 equiv). After heating at 90 ºC for 3 h, an additional TMSOTf (18 µL, 0.10 mmol, 0.10 equiv) was added to the reaction. After stirring at 90 ºC for a total of 10 h, the reaction was judged to be done by $^1$H and $^{19}$F NMR and quenched according to the general procedure. The title compound **3e** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a white solid (mp = 42-43 ºC). **$^1$H NMR** (500 MHz, acetone-$d_6$) δ 6.14 (d, $J$ = 1.2 Hz, 1H), 6.16 (d, $J$ = 1.7 Hz, 1H), 7.21 (dd, $J$ = 8.5, 3.0 Hz, 1H), 7.51 - 7.66 (m, 2H), 7.78 (dt, $J$ = 7.4, 1.6 Hz, 1H), 7.82 (s, 1H), 8.29 (td, $J$ = 8.1, 2.4 Hz, 1H), 8.55 (d, $J$ = 2.0 Hz, 1H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 110.4 (d, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 38.5 Hz, CH), 122.9 (q, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 5.5 Hz, $CH_2$), 124.6 (q, $J_{\mathbf{C\text{-}F}}$ = 273.1 Hz, $CF_3$), 127.1 (CH), 127.8 (CH), 128.8 (CH), 130.5 (CH), 135.2 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}C\text{-}F}}$ = 4.6 Hz, C), 135.3 (C), 138.3 (C), 139.0 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 29.3 Hz, C), 141.3 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 8.2 Hz, CH), 146.9 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 16.5 Hz, CH), 164.3 (d, $J_{\mathbf{C\text{-}F}}$ = 236.5 Hz, CF). **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -72.18 (s 1F), -65.33 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 3017 (w), 1255 (s), 1095 (vs), 954 (s), 840 (s), 576 (s). **HRMS** (ESI) $C_{14}H_{10}F_4N$ $[M + H]^+$: 268.0749, found: 268.0745.

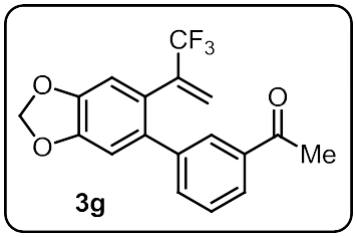



**1-(4'-(3,3,3-Trifluoroprop-1-en-2-yl)-[1,1'-biphenyl]-3-yl)ethan-1-one, 3f** (329.6 mg, 1.14 mmol, 76% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2f** (535 mg, 1.46 mmol, 1.00 equiv) and DCE (7.5 mL, 0.2 *M*) with the following modifications: TMSOTf (53 µL, 0.29 mmol, 0.20 equiv). After stirring for 10 min at rt, the reaction was quenched and worked up as described. The title compound **3f** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a white solid (mp = 44-45 ºC). **$^1$H NMR** (500 MHz, acetone-$d_6$) δ 2.67 (s, 3H), 6.12 – 6.08 (m, 2H), 7.60 - 7.69 (m, 3H), 7.79 - 7.85 (m, 2H), 7.96 (ddd, $J$ = 7.7, 1.9, 1.1 Hz, 1H), 8.02 (dt, $J$ = 7.7, 1.3 Hz, 1H), 8.26 - 8.31 (m, 1H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 27.0 ($CH_3$), 122.1 (q, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 6.4 Hz, $CH_2$), 124.7 (q, $J_{\mathbf{C\text{-}F}}$ = 274.0 Hz, $CF_3$), 127.5 (CH), 128.3 (CH), 128.5



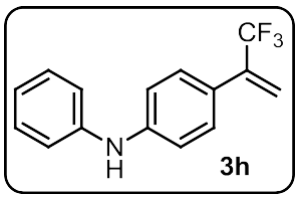
(CH), 128.8 (CH), 130.3 (CH), 132.2 (CH), 133.7 (C), 138.9 (q, $J_{C\text{-}C\text{-}F}$ = 29.8 Hz, C), 139.0 (C), 141.3 (C), 141.8 (C), 198.0 (C). **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -65.09 (s, 3F). **FT-IR** (cm$^{-1}$, neat, ATR) 3043 (br w), 1681 (vs), 1352 (s), 1157 (vs), 1109 (s), 948 (s), 803 (s), 686 (s), 586(s). **HRMS (**EI) calcd for $C_{17}H_{13}F_3O$ [M]$^+$: 290.0918, found: 290.0890.

**1-(3-(6-(3,3,3-Trifluoroprop-1-en-2-yl)benzo[*d*][1,3]dioxol-5-yl)phenyl)ethan-1-one, 3g**



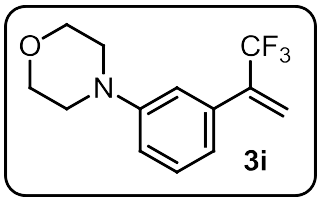

(123.5 mg, 0.369 mmol, 94% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2g** (167 mg, 0.393 mmol, 1.00 equiv) and DCE (2.0 mL, 0.2 M) with the following modifications: TMSOTf (14 μL, 0.0787 mmol, 0.20 equiv). After stirring for 1 h at room temperature, the reaction was judged to be done by $^1$H and $^{19}$F NMR and quenched according to the general procedure. The title compound **3g** was purified by column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) and isolated as an off-white solid (mp = 90–91 ºC). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 2.59 (s, 3H), 5.25 – 5.17 (m, 1H), 5.87 – 5.82 (m, 1H), 6.05 (s, 2H), 6.84 (s, 1H), 6.89 (s, 1H), 7.48 – 7.41 (m, 2H), 7.86 – 7.83 (m, 1H), 7.92 – 7.87 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 26.7 ($CH_3$), 101.8 ($CH_2$), 109.8 (CH), 110.7 (CH), 123.1 (q, $J_{C\text{-}F}$ = 273.9 Hz, $CF_3$), 125.6 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.3 Hz, $CH_2$), 126.1 (C), 126.9 (CH), 128.5 (CH), 129.8 (CH), 134.2 (CH), 135.7 (C), 137.1 (C), 137.1 (q, $J_{C\text{-}C\text{-}F}$ = 30.4 Hz), 141.4 (C), 147.2 (C), 148.2 (C), 198.0 (C). **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -68.90 (s, 3F). **FT-IR** (cm$^{-1}$, neat, ATR) 2896 (w), 1679 (s), 1113 (vs), 1032 (s), 591 (s). **HRMS (**EI) calcd for $C_{18}H_{13}F_3O_3$ [M]$^+$: 334.0817 found: 334.0828.

***N*-Phenyl-4-(3,3,3-trifluoroprop-1-en-2-yl)aniline, 3h** ((377 mg, 1.43 mmol, 89% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2h** (580 mg, 1.60 mmol, 1.00 equiv) and DCE (8.0 mL, 0.2 M) with the following modifications: TMSOTf (89 μL, 0.49 mmol, 0.30 equiv). After stirring at 90 ºC for a total of 3 h, the reaction was judged to be done by $^1$H and $^{19}$F NMR and quenched accorded to the general procedure. The title compound **3h** was purified by column chromatography (gradient hexanes to EtOAc 1% v/v $Et_3N$) and isolated as a yellow oil. **$^1$H NMR** (500 MHz, acetone-$d_6$) δ 5.85 - 5.91 (m, 2H), 6.93



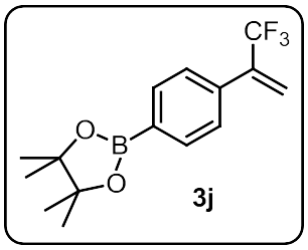
(t, $J$ = 7.3 Hz, 1H), 7.12 - 7.17 (m, 2H), 7.17 - 7.21 (m, 2H), 7.25 - 7.32 (m, 2H), 7.40 (d, $J$ = 8.5 Hz, 2H), 7.69 (br s, 1H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 116.9 (CH), 118.7 (q, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 6.0 Hz, $CH_2$), 119.4 (CH), 122.1 (CH), 124.9 (q, $J_{\mathbf{C\text{-}F}}$ = 273.4 Hz, $CF_3$), 125.0 (C), 129.1 (CH), 130.2 (CH), 138.9 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 29.1 Hz, C), 143.6 (C), 146.0 (C). Additional weak signals to the right of some carbon signals is observed due to hydrogen deuterium exchange. **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -65.22 (s, 3F). **FT-IR** (cm$^{-1}$, neat, ATR) 3396 (br w), 3044 (br w), 1726 (w), 1596 (s), 1519 (vs), 1315 (s), 1162 (vs), 1115 (vs), 743 (s), 694 (s), 609 (s). **HRMS** (EI) calcd for $C_{15}H_{12}F_3N$ [M]$^+$: 263.0922, found: 263.0900.

**4-(3-(3,3,3-Trifluoroprop-1-en-2-yl)phenyl)morpholine, 3i** (73.4 mg, 0.285 mmol, 95% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2i** (105 mg, 0.30 mmol, 1.00 equiv) and DCE (1.5 mL, 0.2 M) with the following modifications: TMSOTf (16 μL, 0.090 mmol, 0.30 equiv). After stirring for 3 h at 90 ºC TMSOTf (16 μL, 0.090 mmol, 0.30 equiv) was added and the reaction was stirred for 4 h at 90 ºC at which time TMSOTf (16 μL, 0.090 mmol, 0.30 equiv) was added. The reaction was then allowed to stir overnight (15 h), after which the reaction was judged to be done by $^1$H and $^{19}$F NMR and quenched according to the general procedure. The title compound **3i** was purified by column chromatography (gradient hexanes to 50:50 hexanes/EtOAc) and isolated as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 3.20 – 3.17 (m, 4H), 3.89 – 3.85 (m, 4H), 5.76 – 5.73 (m, 1H), 5.96 – 5.92 (m, 1H), 6.98 – 6.91 (m, 3H), 7.32 – 7.27 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 49.3 ($CH_2$), 67.0 ($CH_2$), 114.9 (CH), 116.3 (CH), 119.3 (CH), 120.6 (q, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 5.7 Hz, $CH_2$), 123.5 (q, $J_{\mathbf{C\text{-}F}}$ = 273.9 Hz, $CF_3$), 129.5 (CH), 134.8 (C), 139.5 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 30.0 Hz, C), 151.5 (C). **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -67.90 (s, 3F). **FT-IR** (cm$^{-1}$, neat, ATR) 2856 (w), 1599 (w), 1362 (s), 1114 (vs), 963 (s), 700 (w). **HRMS (**EI) calcd for $C_{13}H_{14}F_3NO$ [M]$^+$: 257.1027 found: 257.1019.



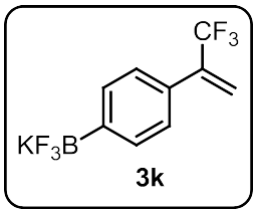
**3i**

**4,4,5,5-Tetramethyl-2-(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)-1,3,2-dioxaborolane, 3j**



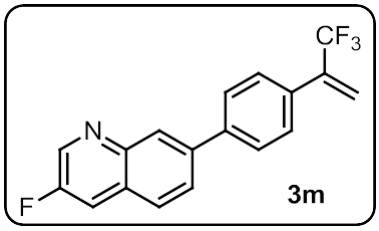

(102 mg, 0.341 mmol, 68% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2j** (194 mg, 0.50 mmol, 1.00 equiv) and DCE (2.5 mL, 0.2 M) with the following modifications: TMSOTf (30 μL, 0.15 mmol, 0.30 equiv). After stirring for 30 min at rt, the reaction was quenched and worked up as described. The title compound **3j** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$ w/ 0.05 % TMS) δ 1.35 (s, 6H), 1.35 (s, 6H), 5.80 (t, $J$ = 1.4 Hz, 1H), 5.98 (t, $J$ = 1.1 Hz, 1H), 7.45 (d, $J$ = 8.2 Hz, 2H), 7.82 (d, $J$ = 7.6 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$ w/ 0.05 % TMS) δ 25.1 ($CH_3$), 84.3 (C), 121.1 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 123.6 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_2$), 126.9 (CH), 135.2 (CH), 136.5 (C), 139.4 (q, $J_{C\text{-}C\text{-}F}$ = 30.2 Hz, C). **$^{19}$F NMR** (471 MHz, $CDCl_3$ w/ 0.05 % TMS) δ -67.77 (s, 3F). **$^{11}$B NMR** (128 MHz, $CDCl_3$ w/ 0.05 % TMS) δ 30.6 (br s, 1B). **FT-IR** ($cm^{-1}$, neat, ATR) 2981 (w), 1613 (m), 1400 (s), 1362 (s), 1167 (m), 1129 (m), 1095 (m), 859 (m), 657 (m). **HRMS (**EI) cald for $C_{15}H_{18}BF_3O_2$ $[M]^+$: 298.1352, found: 298.1339.

**Potassium 4-(3,3,3-Trifluoroprop-1-en-2-yl)phenyltrifluoroborate, 3k.** An 8 mL microwave vial was charged with α-$CF_3$-β-TMS-alcohol **2k** (368 mg, 1.00 mmol, 1.00 equiv) and DCE (5.0 mL, 0.2 M). The resulting soln was chilled to 0 ºC in an ice bath. Once equilibrated, TMSOTf (0.36 mL, 2.0 mmol, 2.0 equiv) was added dropwise (~1 drop/second). The ice bath was then removed, and the reaction was stirred at rt for 24 h. The crude reaction was then diluted with EtOAc (25 mL) and transferred to a separatory funnel. The organic layer was then washed with $H_2O$ (2 x 5 mL) and brine (1 x 5 mL) and then concentrated. The crude material was then dissolved in MeOH (10 mL, 0.1 M) and chilled to 0 ºC in an ice bath. Once equilibrated, aq 4.5 M $KHF_2$ (1.40 mL, 6.75 mmol, 6.75 equiv) was then added dropwise. The reaction mixture was then stirred at rt for 1 h, after which the reaction mixture was concentrated and lyophilized overnight to remove trace water. Acetone (25 mL) was then added to the solid and the mixture was filtered to remove inorganic salts. Concentration of the filtered soln afforded the title compound **3k** (272 mg, 0.978 mmol, 98% yield) as a waxy tan solid (decomp. > 130 ºC). **$^1$H NMR** (500 MHz, acetone-$d_6$) δ 5.83 (d, $J$ = 1.7 Hz, 1H), 5.87 (d, $J$ = 1.5 Hz, 1H), 7.24 (d, $J$ =

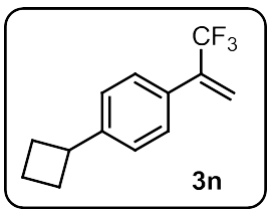


7.3 Hz, 2H), 7.53 (d, $J$ = 7.8 Hz, 2H). **$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 119.6 (q, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 5.4 Hz, $CH_2$), 122.8 (q, $J_{\mathbf{C\text{-}F}}$ = 273.4 Hz, $CF_3$), 126.0 (s, CH), 131.1 (C), 132.8 (CH), 140.5 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 29.1 Hz, C). **$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -143.11 – -144.06 (m, 4F), -65.16 (s, 3F). **$^{11}$B NMR** (128 MHz, acetone-$d_6$) δ 8.33 – 0.14 (m, 1B). **FT-IR** ($cm^{-1}$, neat, ATR) 3646 (w), 1351 (w), 1167 (s), 1118 (s), 945 (vs), 832 (s), 754 (s), 619 (s). **HRMS (**ESI) calcd for $C_9H_6BF_6$ [M – K]$^-$: 239.0467, found: 239.0465.

**3-Fluoro-7-(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)quinoline, 3m** (74.2 mg, 0.23 mmol, 97% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2m** (99 mg, 0.24 mmol, 1.00 equiv) and DCE (1.2 mL, 0.2 M) with the following modifications: TMSOTf (13 μL, 0.073 mmol, 0.30 equiv). After stirring for 13.5 h at 90 ºC, the reaction was judged to be done by $^1$H and $^{19}$F NMR and quenched according to the general procedure. The title compound **3m** was purified by column chromatography (gradient hexanes to 50:50 hexanes/EtOAc) and isolated as a white solid (mp = 107–108 ºC). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.89 – 5.86 (m, 1H), 6.04 – 6.01 (m, 1H), 7.61 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.81 (dd, J = 8.6, 2.8 Hz, 1H), 7.92 – 7.85 (m, 2H), 8.36 (s, 1H), 8.86 (d, J = 2.8 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 118.3 (d, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 16.6 Hz, CH), 120.7 (q, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 5.7 Hz, $CH_2$), 123.5 (q, $J_{\mathbf{C\text{-}F}}$ = 274.0 Hz, $CF_3$), 127.21 (CH), 27.3 (CH), 127.6 (CH), 127.9 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}F}}$ = 5.4 Hz, C), 128.0 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}C\text{-}F}}$ = 5.1 Hz, CH), 128.1 (CH), 133.3 (C), 138.6 (q, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 30.4 Hz, C), 140.5 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}C\text{-}F}}$ = 2.9 Hz, C), 140.7 (C), 142.3 (d, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 27.2 Hz, CH), 145.8 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 1.8 Hz, C), 156.5 (d, $J_{\mathbf{C\text{-}F}}$ = 256.8 Hz, CF). **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -67.78 (s, 3F), -130.91 (s, 1F). **FT-IR** ($cm^{-1}$, neat, ATR) 1611 (w), 1450 (w), 1355 (s), 1158 (vs), 1115 (vs), 894 (s), 817 (s). **HRMS (**EI) calcd for $C_{18}H_{11}F_4N$ [M]$^+$: 317.0828 found: 317.0838.

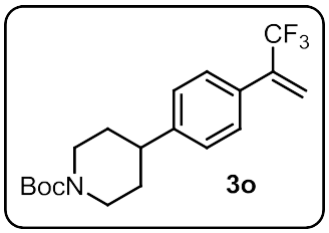



**1-Cyclobutyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene, 3n** (63.0 mg, 0.278 mmol, 63% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2n** (140 mg, 0.442 mmol, 1.00 equiv) and DCE (2.21 mL, 0.2 M) with the following modifications: TMSOTf (16.1 μL, 0.088 mmol, 0.20 equiv). After stirring for 2 h at rt, the reaction was quenched and worked



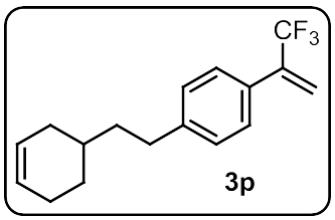
up as described. The title compound **3n** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 1.82 - 1.93 (m, 1H), 1.98 - 2.10 (m, 1H), 2.11 - 2.23 (m, 2H), 2.37 (qt, $J$ = 8.4, 2.5 Hz, 2H), 3.51 - 3.63 (m, 1H), 5.75 (d, $J$ = 1.5 Hz, 1H), 5.92 (d, $J$ = 1.2 Hz, 1H), 7.24 (d, $J$ = 8.3 Hz, 2H), 7.40 (d, $J$ = 8.1 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 18.6 (s, $CH_2$), 30.0 (s, $CH_2$), 40.3 (s, CH), 119.9 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 6.0 Hz, $CH_2$), 123.7 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 126.8 (CH), 127.5 (CH), 131.3 (C), 139.1 (q, $J_{C\text{-}C\text{-}F}$ = 29.3 Hz, C), 147.5 (C). **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -67.90 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 2975 (br w), 1350 (s), 1166 (vs), 1123 (vs), 970 (s), 915 (s). **HRMS (**EI) calcd for $C_{13}H_{13}F_3$ $[M]^+$: 226.0965, found: 226.0984.

***tert*-Butyl 4-(4-(3,3,3-Trifluoroprop-1-en-2-yl)phenyl)piperidine-1-carboxylate, 3o** (101 mg, 0.285 mmol, 57% yield) was prepared according to the following procedure: α-$CF_3$-β-TMS-alcohol **2o** (223 mg, 0.50 mmol, 1.00 equiv) was dissolved in DCE (2.5 mL, 0.2 M) and chilled to 0 ºC in an ice bath. Once equilibrated, TMSOTf (0.11 mL, 0.60 mmol, 1.2 equiv) was added dropwise, and the ice bath was removed. After stirring for 1 h at rt, TMSOTf (90 μL, 0.50 mmol, 1 equiv) was added, and the reaction was stirred at rt for 1 h. The reaction was quenched with saturated aq $NaHCO_3$ (5 mL) and diluted with EtOAc (5 mL). The aq layer was washed with EtOAc (3 x 5 mL). The combined organic layers were dried ($Na_2SO_4$), filtered, and concentrated. The resulting oil was transferred to a 1 dram vial, dissolved in THF (1 mL, 0.5 M), and chilled to 0 ºC. Once equilibrated, DMAP (61 mg, 0.50 mmol, 1.0 equiv) and $Et_3N$ (0.14 mL, 1.0 mmol, 2.0 equiv) were added followed by dropwise addition of di-*tert*-butyl dicarbonate (164 mg, 0.750 mmol, 1.50 equiv) in THF (0.38 mL, 2.0 M). The reaction was allowed to warm to rt. After stirring overnight, the reaction was diluted with brine (5 mL) and EtOAc (5 mL). The organic layer was then concentrated, and the resulting crude material was purified by column chromatography (gradient hexanes to EtOAc) to afford title compound **3o** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$ w/ 0.05% TMS) δ 1.49 (s, 9H), 1.58 – 1.69 (m, 2H), 1.83 (d, $J$ = 13.4 Hz, 2H), 2.67 (tt, $J$ = 12.2, 3.4 Hz, 1H), 2.81 (t, $J$ = 12.0 Hz, 2H), 4.26 (br s, 2H), 5.75 (q, $J$ = 1.5 Hz, 1H), 5.92 (d, $J$ = 1.2 Hz, 1H), 7.22 (d, $J$ = 8.1 Hz, 2H), 7.40 (d, $J$ = 8.1 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$ w/ 0.05% TMS) δ 28.7 ($CH_3$), 33.3 (CH), 42.7 ($CH_2$), 44.5 (br s, $CH_2$), 79.8 (C), 120.2 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 123.6 (q, $J_{C\text{-}}$

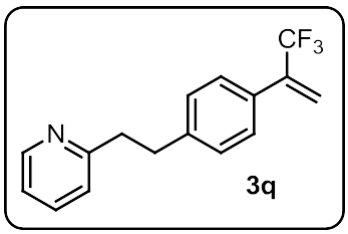


$_{F}$ = 274.3 Hz, $CF_3$), 127.3 (CH), 127.7 (CH), 131.9 (C), 138.9 (q, $J_{C\text{-}C\text{-}F}$ = 30.0 Hz, C), 147.0 (C), 155.1 (C). **$^{19}$F NMR** (471 MHz, $CDCl_3$ w/ 0.05% TMS) δ -67.89 (s, 3F). **FT-IR** (cm$^{-1}$, neat, ATR) 2977 (br w), 2934 (br w), 2854 (br w), 1688 (s), 1422 (s), 1160 (vs), 1120 (vs), 1078 (s), 838 (s), 613 (s). **HRMS (**ESI) calcd for $C_{19}H_{24}F_3NO_2$ $[M]^+$: 355.1759, found: 355.1774; calcd for $C_{15}H_{16}F_3NO_2$ [M – $C(CH_3)_3$ + H]: 299.1133, found: 299.1141; calcd for $C_{14}H_{16}F_3N$ [M – Boc + H]: 255.1235, found: 255.1243.

**1-(2-(Cyclohex-3-en-1-yl)ethyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene, 3p** (117 mg, 0.42 mmol, 84% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2p** (99 mg, 0.50 mmol, 1.00 equiv) and DCE (2.5 mL, 0.2 M) with the following modifications: TMSOTf (20 μL, 0.15 mmol, 0.30 equiv). After stirring for 1 h at rt, the reaction was judged to be done by $^1$H and $^{19}$F NMR and quenched according to the general procedure. The title compound **3p** was purified by column chromatography (100% pentane) and isolated as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 1.33 – 1.23 (m, 1H), 1.65 – 1.55 (m, 3H), 1.76 – 1.68 (m, 1H), 1.84 – 1.76 (m, 1H), 2.12 – 1.97 (m, 2H), 2.22 – 2.13 (m, 1H), 2.71 – 2.63 (m, 2H), 5.70 – 5.64 (m, 2H), 5.76 – 5.73 (m, 1H), 5.93 – 5.90 (m, 1H), 7.21 (d, $J$ = 8.1 Hz, 2H), 7.37 (d, $J$ = 8.0 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 25.3 ($CH_2$), 29.0 ($CH_2$), 32.0 ($CH_2$), 33.1 ($CH_2$), 33.3 (CH), 38.4 ($CH_2$), 119.7 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.9 Hz, $CH_2$), 123.6 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 126.6 (CH), 127.2 (CH), 127.4 (CH), 128.7 (CH), 131.1 (C), 139.0 (q, $J_{C\text{-}C\text{-}F}$ = 29.8 Hz, C), 144.1 (C). **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -67.89 (s, 3F). **FT-IR** (cm$^{-1}$, neat, ATR) 2914 (w), 1351 (w), 1164 (s), 1120 (vs), 1079 (s), 990 (s), 654 (w). **HRMS (**EI) calcd for $C_{17}H_{19}F_3$ $[M]^+$: 280.1439 found: 280.1420.

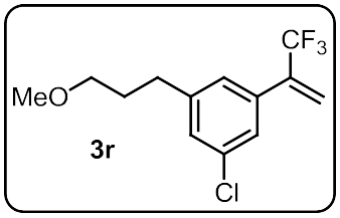



**2-(4-(3,3,3-Trifluoroprop-1-en-2-yl)phenethyl)pyridine, 3q** (55.0 mg, 0.184 mmol, 82% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2q** (89 mg, 0.242 mmol, 1.00 equiv) and DCE (1.21 mL, 0.2 M) with the following modifications: TMSOTf (52.9 μL, 0.291 mmol, 1.2 equiv). After stirring for 3 h at rt, the reaction was quenched and worked up as described. The title compound **3q** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a colorless



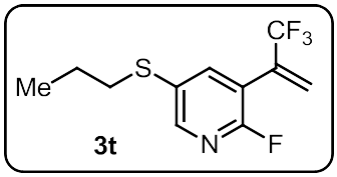
oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 3.02 - 3.15 (m, 4H), 5.74 (d, *J* = 1.5 Hz, 1H), 5.91 (d, *J* = 1.1 Hz, 1H), 7.05 - 7.16 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.56 (td, *J* = 7.6, 1.8 Hz, 1H), 8.57 (dd, *J* = 4.7, 0.8 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 35.8 ($CH_2$), 40.2 ($CH_2$), 120.0 (q, $J_{C-F}$ = 5.5 Hz, $CH_2$), 121.5 (CH), 123.7 (q, $J_{C-F}$ = 274.0 Hz, $CF_3$), 123.2 (CH), 127.6 (CH), 128.9 (CH), 131.5 (C), 136.6 (CH), 139.0 (q, $J_{C-F}$ = 30.2 Hz, C), 142.9 (C), 149.6 (CH), 161.2 (C). **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -67.86 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 2928 (br w), 1351 (s), 1162 (vs), 1116 (vs), 1077 (s), 828 (s). **HRMS (**EI) calcd for $C_{16}H_{14}F_3N$ $[M]^+$: 277.1078, found: 277.1089.

**1-Chloro-3-(3-methoxypropyl)-5-(3,3,3-trifluoroprop-1-en-2-yl)benzene, 3r** (130.2 mg, 0.467 mmol, 93% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2r** (185 mg, 0.50 mmol, 1.00 equiv) and DCE (2.5 mL, 0.2 M) with the following modifications: TMSOTf (18 μL, 0.10 mmol, 0.20 equiv). After stirring for 45 min at 90 ºC, the reaction was quenched and worked up as described. The title compound **3r** was purified by column chromatography (gradient hexanes to EtOAc) and isolated as a colorless oil.



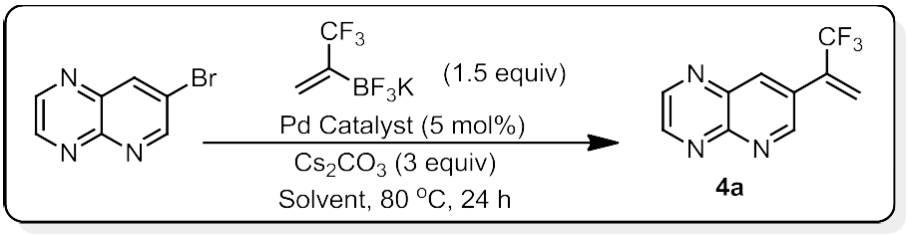

**$^1$H NMR** (500 MHz, $CDCl_3$ w/ 0.05 % TMS) δ 1.84 - 1.92 (m, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 3.34 (s, 3H), 3.38 (t, *J* = 6.2 Hz, 2H), 5.77 (q, *J* = 1.5 Hz, 1H), 5.98 (d, *J* = 1.4 Hz, 1H), 7.15 (s, 1H), 7.20 - 7.23 (m, 1H), 7.26 - 7.29 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$ w/ 0.05 % TMS) δ 31.2 ($CH_2$), 32.3 ($CH_2$), 58.8 ($CH_2$), 71.7 ($CH_3$), 121.5 (q, $J_{C-C-C-F}$ = 5.5 Hz, $CH_2$), 123.3 (q, $J_{C-F}$ = 273.1 Hz, $CF_3$), 125.4 (CH), 126.2 (CH), 129.4 (CH), 134.7 (C), 135.5 (C), 138.4 (q, $J_{C-C-F}$ = 30.2 Hz, C), 144.6 (C). **$^{19}$F NMR** (471 MHz, $CDCl_3$ w/ 0.05 % TMS) δ -67.95 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 2927 (br w), 2869 (br w), 1574 (w), 1352 (w), 1163 (s), 1119 (vs), 874 (w), 658(w). **HRMS (**EI) cald for $C_{13}H_{12}ClF_3O$ $[M - 2H]^-$: 276.0529, found: 276.0549; $C_{12}H_{10}ClF_3$ $[M - CH_3OH]$: 246.0423, found: 246.0416.

**2-Fluoro-5-(propylthio)-3-(3,3,3-trifluoroprop-1-en-2-yl)pyridine, 3t** (76.7 mg, 0.289 mmol, 65% yield) was prepared according to the general procedure using α-$CF_3$-β-TMS-alcohol **2t** (159 mg, 0.447 mmol, 1.00 equiv) and DCE (2.2 mL, 0.2 M) with the following modifications: TMSOTf (0.19 mL, 1.07 mmol, 2.4 equiv). The reaction was then stirred for 3



d at 90 ºC with additional TMSOTf (0.10 mL, 0.54 mmol, 1.2 equiv) being added after 1 day, 1.5 days, and 2 days (a total of 6.0 equiv of TMSOTf was added). Once the reaction was judged to be done by $^{1}H$ and $^{19}F$ NMR, it was quenched and worked-up according to the general procedure. The title compound **3t** was purified by column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) and isolated as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 1.03 (t, $J$ = 7.3 Hz, 3H), 1.71 – 1.62 (m, 2H), 2.88 (t, $J$ = 7.3 Hz, 2H), 5.94 – 5.89 (m, 1H), 6.29 – 6.25 (m, 1H), 7.78 – 7.73 (m, 1H), 8.20 – 8.17 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 13.3 ($CH_3$), 22.6 ($CH_2$), 37.0 ($CH_2$), 116.6 (d, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 30.8 Hz, C), 122.5 (q, $J_{\mathbf{C\text{-}F}}$ = 273.8 Hz, $CF_3$), 126.0 – 126.2 (m, $CH_2$), 131.3 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}C\text{-}F}}$ = 4.9 Hz, C), 131.4 (qd, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 32.1, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 4.9 Hz, C), 142.5 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 2.5 Hz, CH), 148.8 (d, $J_{\mathbf{C\text{-}N\text{-}C\text{-}F}}$ = 14.9 Hz, CH), 159.5 (d, $J_{\mathbf{C\text{-}F}}$ = 241.2 Hz, CF). **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -75.32 (s, 1F), -68.84 (d, $J$ = 4.0 Hz, $CF_3$). **FT-IR** ($cm^{-1}$, neat, ATR) 2967 (w), 1437 (s), 1171 (vs), 1127 (vs), 755 (s). **HRMS (**EI) calcd for $C_{11}H_{11}F_4NS$ $[M]^+$: 265.0548 found: 265.0556.

## General Procedure for the Cross-Coupling with Trifluoroborate 6




**7-(3,3,3-Trifluoroprop-1-en-2-yl)pyrido[2,3-b]pyrazine (4a)**

To a 50 mL microwave tube was added 7-bromopyrido[2,3-b]pyrazine (210 mg, 1.0 mmol, 1 equiv), $Cs_2CO_3$ (978 mg, 3.0 mmol, 3 equiv), potassium trifluoro(3,3,3-trifluoroprop-1-en-2-yl)borate **6** (303 mg, 1.5 mmol, 1.5 equiv), $Pd(OAc)_2$ (11 mg, 0.05 mmol, 0.05 equiv), and $PPh_3$ (32 mg, 0.12 mmol, 0.12 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 reaction mixture was allowed to stir at 80 °C 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 hexanes to 80:20 hexanes/EtOAc) to give the desired olefin **4a** (0.197 g, 88%) as an orange powder (mp = 113 – 115 °C).

**$^1$H NMR** ($CDCl_3$, 500 MHz) δ 6.13 (s, 1H), 6.30 (s, 1H), 8.58 (s, 1H), 9.00 (s, 1H), 9.11 (s, 1H), 9.28 (d, $J$ = 2.0 Hz, 1H).

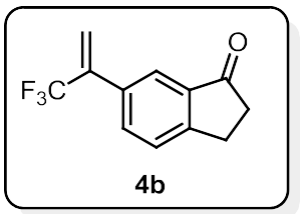
**$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 122.9 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 124.2 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 131.0 (C), 135.3 (q, $J_{C\text{-}C\text{-}F}$ = 31.2 Hz, C), 136.9 (CH), 137.6 (C), 147.1 (CH), 148.5 (CH), 151.3 (C), 152.9 (CH).

**$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -68.16 (s, 3F).

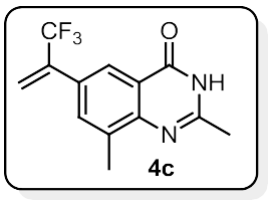
**FT-IR** ($cm^{-1}$, neat, ATR) 1153 (s), 1116 (s), 1027 (m), 905 (s), 727 (s), 720 (s).

**HRMS** (ES+) calcd for $C_{10}H_7F_3N_3$ $[M + H]^+$: 226.0592, found: 226.0583.

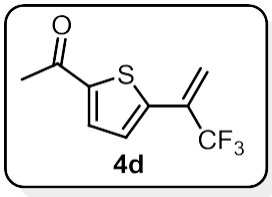
**6-(3,3,3-Trifluoroprop-1-en-2-yl)-2,3-dihydro-1H-inden-1-one, 4b** (160 mg, 76%) was prepared according to the general procedure from (3-6-bromo-2,3-dihydro-1H-inden-1-one (211 mg, 1.00 mmol.) The desired olefin **4b** was isolated as a yellow oil. **$^1$H NMR** ($CDCl_3$, 500 MHz) δ 2.74 (t, *J* = 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).




**2,8-Dimethyl-6-(3,3,3-trifluoroprop-1-en-2-yl)quinazolin-4(3H)-one, 4c** (82.7 mg, 78%) was prepared according to the general procedure from 6-bromo-2,8-dimethylquinazolin-4(3H)-one (100 mg, 0.39 mmol) ***with the following modification***: the reaction was using $PCy_3$ Pd-G4 (13.1 mg, 0.02 mmol, 0.05 equiv) in place of $Pd(OAc)_2$. The desired olefin **4c** was isolated as a powdery white solid (mp = >190 °C). **$^1$H NMR** ($CDCl_3$, 500 MHz) δ 2.59 (s, 3H), 2.64 (s, 3H), 5.89 (d, *J* = 1.5 Hz, 1H), 6.04 (d, *J* = 1.2 Hz, 1H), 7.69 (s, 1H), 8.21 (s, 1H), 10.64 (br s, 1H). **$^{13}$C NMR** (DMSO-$d_6$, 125 MHz) δ 17.2 ($CH_3$), 21.8 ($CH_3$), 120.4 (C), 121.4 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 11.9 Hz, CH), 122.5 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 123.4 (q, $J_{C\text{-}F}$ = 275.0 Hz, $CF_3$), 128.9 (C), 132.9 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 7.3 Hz, C), 135.6 (C), 135.9 (q, $J_{C\text{-}C\text{-}F}$ = 29.3 Hz, C), 147.9 (C), 154.4 (CH), 161.8 (C). **$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -67.78 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 2875 (w), 1682 (s), 1624 (s), 1611 (s), 1164 (s), 1146 (s), 1114 (s), 1096 (s). **HRMS** (ES+) calcd for $C_{13}H_{12}F_3N_2O$ $[M + H]^+$: 269.0902, found: 269.0883.

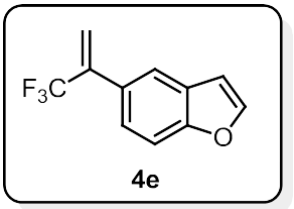



**1-(5-(3,3,3-Trifluoroprop-1-en-2-yl)thiophen-2-yl)ethanone, 4d** (141 mg, 64%) was prepared according to the general procedure from 1-(5-bromothiophen-2-yl)ethanone (205 mg, 0.001 mol). The desired olefin **4d** was isolated as a light-yellow oil. **$^1$H NMR** ($CDCl_3$, 500 MHz) δ 2.55 (s, 3H), 5.96 (s,



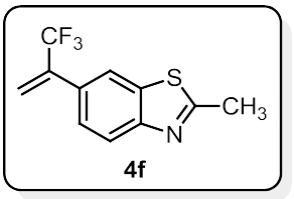
1H), 5.99 (s, 1H), 7.20 (d, $J$ = 2.7 Hz, 1H), 7.59 (d, $J$ = 3.9 Hz, 1H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 26.9 ($CH_3$), 122.5 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 120.9 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 127.7 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, C), 132.6 (q, $J_{C\text{-}C\text{-}F}$ = 32.1 Hz, C), 132.9 (CH), 143.2 (CH), 144.5 (C), 190.7 (C). **$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -68.97 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 1663 (s), 1269 (s), 1169 (s), 1123 (s), 931 (s), 810 (s). **HRMS** (EI+) calcd for $C_9H_8F_3OS$ $[M + H]^+$: 221.0248, found: 221.0254.

**5-(3,3,3-Trifluoroprop-1-en-2-yl)benzofuran, 4e** (186 mg, 88%) was prepared according to the general procedure from 5-bromobenzofuran (197 mg, 1.00 mmol) ***with the following modification***: RuPhos (33 mg, 0.07 mmol, 0.07 equiv) was used as a ligand. The desired olefin **4e** was isolated as a colorless oil. **$^{1}$H NMR** ($CDCl_3$, 500 MHz) δ 5.76 (d, $J$ = 1.5 Hz, 1H), 5.98 (s, 1H), 6.80 (s, 1H), 7.39 (d, $J$ = 8.6 Hz, 1H), 7.51 (d, $J$ = 8.6 Hz, 1H), 7.66 (d, $J$ = 2.2 Hz, 1H), 7.70 (s, 1H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 107.0 (CH), 111.7 (CH), 123.8 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 120.6 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 120.8 (CH), 124.3 (CH), 128.0 (C), 129.0 (C), 139.5 (q, $J_{C\text{-}C\text{-}F}$ = 30.2 Hz, C), 146.2 (CH), 155.4 (C). **$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -68.05 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 1255 (s), 1167 (s), 1146 (s), 1109 (s), 885 (s), 769 (s), 741 (s). **HRMS** (EI+) calcd for $C_{11}H_7F_3O$ $[M]^+$: 212.0449, found: 212.0442.



4e

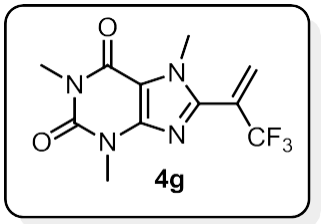
**2-Methyl-6-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d]thiazole, 4f** (65.3 mg, 61%) was prepared according to the general procedure from 6-bromo-2-methylbenzo[*d*]thiazole (100 mg, 4.4 mmol) ***with the following modification***: the reaction was using SPhos Pd-G4 (17.5 mg, 0.022 mmol, 0.05 equiv) in place of $Pd(OAc)_2$. The desired olefin **4f** was isolated as a light-yellow oil with an 8% impurity of the internal alkene isomer. **$^{1}$H NMR** ($CDCl_3$, 500 MHz) δ 2.86 (s, 3H), 5.83 (d, $J$ = 1.5 Hz, 1H), 6.03 (d, $J$ = 1.2 Hz, 1H), 7.54 (dd, $J$ = 8.5, 1.2 Hz, 1H), 7.92 (s, 1H), 7.94 (d, $J$ = 8.5 Hz, 1H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 20.5 ($CH_3$), 120.6 (CH), 121.3 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 123.5 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 122.6 (CH), 125.8 (CH), 130.5 (C), 136.4 (C), 138.8 (q, $J_{C\text{-}C\text{-}F}$ = 30.2 Hz, C), 153.9 (C), 168.7 (C). **$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -67.89 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 1195 (s),



4f

1161 (s), 1116 (s), 1089 (s), 944 (s), 827 (s), 643 (s). **HRMS** (EI+) calcd for $C_{11}H_8F_3NS$ $[M]^+$: 243.0330, found: 243.0322.

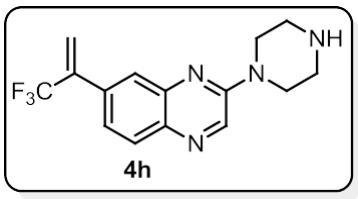
**1,3,7-Trimethyl-8-(3,3,3-trifluoroprop-1-en-2-yl)-1H-purine-2,6(3H,7H)-dione, 4g**



4g

(210 mg, 73%) was prepared according to the general procedure from 8-bromo-1,3,7-trimethyl-1*H*-purine-2,6(3*H*,7*H*)-dione (273 mg, 1.00 mmol). The desired olefin **4g** was isolated as a light tan powder (mp = 143-145 °C). **$^1$H NMR** ($CDCl_3$, 500 MHz) δ 3.41 (s, 3H), 3.58 (s, 3H), 3.98 (s, 3H), 6.03 (s, 1H), 6.52 (s, 1H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 28.2 ($CH_3$), 30.0 ($CH_3$), 33.5 ($CH_3$), 108.9 (C), 121.7 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 128.8 (q, $J_{C\text{-}C\text{-}F}$ = 33.9 Hz, C), 129.4 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.0 Hz, $CH_2$), 144.3 (C), 147.9 (C), 151.7 (C), 155.6 (C). **$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -68.46 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 2959 (w), 1704 (s), 1661 (s), 1438 (s), 1307 (s), 1179 (s), 1165 (s), 1136 (s), 1087 (s), 977 (s), 743 (s). **HRMS** (ES+) calcd for $C_{11}H_{12}F_3N_4O_2$ $[M + H]^+$: 289.0912, found: 289.0919.

**2-(Piperazin-1-yl)-7-(3,3,3-trifluoroprop-1-en-2-yl)quinoxaline, 4h** (129 mg, 84%) was prepared according to the general procedure from 7-bromo-2-(piperazin-1-yl)quinoxaline (147 mg, 1.00 mmol) ***with the following modifications***: 1) the reaction was using $PCy_3$ Pd-G4 precomplex (0.017 g, 0.05 mmol, 0.05 equiv) in place of $Pd(OAc)_2$; 2) no additional ligands were added. The desired olefin **4h** was isolated as a viscous, yellow oil. **$^1$H NMR** ($CDCl_3$, 500 MHz) δ 2.09 (s, 1H), 3.04 (t, *J* = 5.0 Hz, 4H), 3.79 (t, *J* = 4.9 Hz, 4H), 5.92 (s, 1H), 6.05 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.78 (s, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 8.58 (s, 1H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 45.9 ($CH_2$), 46.1 ($CH_2$), 123.5 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 121.7 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 123.9 (CH), 125.8 (CH), 129.1 (CH), 135.3 (C), 136.6 (CH), 137.0 (C), 138.9 (q, $J_{C\text{-}C\text{-}F}$ = 30.2 Hz, C), 141.7 (C), 152.9 (C). **$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -67.62 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 3295 (m), 2946 (m), 2841 (m), 1574 (s), 1543 (s), 1397 (s), 1231 (s), 1161 (s), 824 (s), 732 (s). **HRMS** (ES+) calcd for $C_{15}H_{16}F_3N_4$ $[M + H]^+$: 309.1327, found: 309.1339.

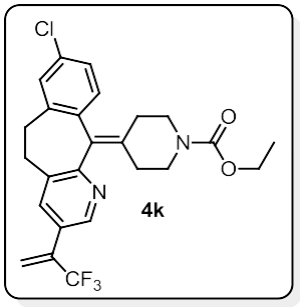


4h

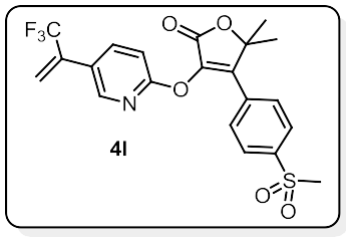
**2-(1H-Imidazol-1-yl)-5-(3,3,3-trifluoroprop-1-en-2-yl)pyrimidine, 4i** (361.7 mg, 75%) was prepared according to the general procedure from 5-bromo-2-(1H-imidazol-1-yl)pyrimidine (450 mg, 2.0 mmol) ***with the following modifications***: 1) the reaction was using XPhos Pd-G4 (78.0 mg, 0.1 mmol, 0.05 equiv) in place of $Pd(OAc)_2$; 2) the reaction was purified by column chromatography (gradient hexanes to 80:20 hexanes/EtOAc 1% v/v $Et_3N$). The desired olefin **4i** was isolated as a powdery white solid (mp = 124 °C). **$^1$H NMR** ($CDCl_3$, 500 MHz) δ 5.94 (s, 1H), 6.17 (s, 1H), 7.19 (s, 1H), 7.90 (s, 1H), 8.64 (s, 1H), 8.77 (s, 2H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 116.8 (CH), 122.7 (q, $J_{C\text{-}F}$ = 273 Hz, $CF_3$), 123.4 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5 Hz, $CH_2$), 125.5 (C), 131.3 (CH), 133.2 (q, $J_{C\text{-}C\text{-}F}$ = 32 Hz, C), 136.6 (CH), 155.0 (C), 157.5 (CH). **$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -68.59 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 3120 (w), 1480 (s), 1456 (s), 1208 (s), 1174 (s), 1164 (s), 1136 (s), 1122 (s), 1089 (s), 1046 (s), 978 (s). **HRMS** (ES+) calcd for $C_{10}H_8F_3N_4$ $[M + H]^+$: 241.0701, found: 241.0690.

***tert*-Butyl 4-(5-(3,3,3-Trifluoroprop-1-en-2-yl)pyrimidin-2-yl)piperazine-1-carboxylate, 4j** (57.6 mg, 80%) was prepared according to the general procedure from *tert*-butyl 4-(5-bromopyrimidin-2-yl)piperazine-1-carboxylate (68.6 mg, 0.2 mmol) ***with the following modification***: the reaction was using XPhos Pd-G4 (8.6 mg, 0.01 mmol, 0.05 equiv) in place of $Pd(OAc)_2$. The desired olefin **4j** was isolated as a powdery white solid (mp = 86 °C). **$^1$H NMR** ($CDCl_3$, 500 MHz) δ 1.49 (s, 9H), 3.44 - 3.56 (m, 4H), 3.78 - 3.92 (m, 4H), 5.69 (d, $J$ = 1.5 Hz, 1H), 5.87 (s, 1H), 8.40 (s, 2H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 28.7 ($CH_3$), 30.0 (C), 43.9 ($CH_2$), 80.4 ($CH_2$), 116.5 (C), 119.1 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 123.3 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 134.3 (q, $J_{C\text{-}C\text{-}F}$ = 31.2 Hz, C), 155.1 (C), 156.6 (CH), 161.5 (C). **$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -68.75 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 2975 (w), 2880 (w), 1686 (s), 1600 (s), 1415 (s), 1246 (s), 1204 (s), 1162 (s), 1117 (s), 1096 (s). **HRMS** (EI+) calcd for $C_{16}H_{21}F_3N_4O_2$ $[M]^+$: 358.1617, found: 358.1628.

**Ethyl 4-(8-Chloro-3-(3,3,3-trifluoroprop-1-en-2-yl)-5*H*-benzo[5,6]cyclohepta[1,2-b]pyridin-11(6*H*)-ylidene)piperidine-1-carboxylate, 4k** (94 mg, 79%) was prepared according to the general procedure from ethyl 4-(3-bromo-8-chloro-5H-benzo[5,6]cyclohepta[1,2-b]pyridin-11(6H)-ylidene)piperidine-1-carboxylate (115 mg, 0.25 mmol) ***with the following modification***: the reaction was using Pd-G4 dimer (5 mg, 0.00625 mmol, 0.025 equiv) in place of $Pd(OAc)_2$. The desired olefin **4k** was isolated as a white foam. **$^1$H NMR** ($CDCl_3$, 500 MHz) δ 1.25 (t, *J* = 7.1 Hz, 3H), 2.25 - 2.56 (m, 4H), 2.77 - 2.94 (m, 2H), 3.12 - 3.22 (m, 2H), 3.31 - 3.46 (m, 2H), 3.72 - 3.89 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 5.80 (s, 1H), 6.02 (s, 1H), 7.09 - 7.13 (m, 1H), 7.13 - 7.18 (m, 1H), 7.19 (d, *J* = 1.5 Hz, 1H), 7.51 (s, 1H), 8.47 (s, 1H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 15.0 ($CH_3$), 31.0 (d, *J* = 26.6 Hz, $CH_2$), 31.7 ($CH_2$), 32.0 ($CH_2$), 45.1 ($CH_2$), 61.6 ($CH_2$), 121.9 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 123.2 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 126.6 (C), 128.4 (C), 129.2 (CH), 130.8 (CH), 133.3 (C), 133.4 (C), 133.9 (C), 136.2 (q, $J_{C\text{-}C\text{-}F}$ = 31.2 Hz, C), 136.5 (CH), 137.8 (C), 138.7 (CH), 139.7 (C), 145.5 (CH), 155.8 (C), 157.7 (C). **$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -68.20 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 2981 (m), 2910 (m), 1692 (s), 1430 (s), 1226 (s), 1169 (s), 1121 (s), 1091 (s), 997 (s), 732 (s). **HRMS** (EI+) calcd for $C_{25}H_{24}ClF_3N_2O_2$ $[M]^+$: 476.1478, found: 476.1454.

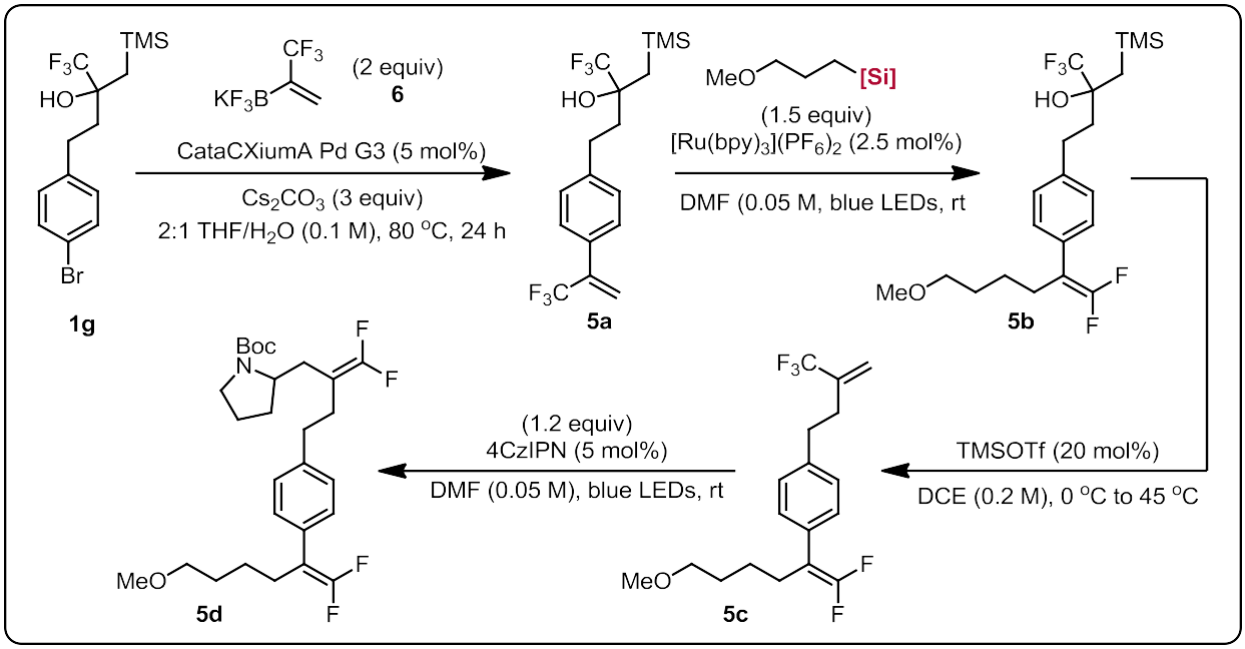



**5,5-Dimethyl-4-(4-(methylsulfonyl)phenyl)-3-((5-(3,3,3-trifluoroprop-1-en-2-yl)pyridin-2-yl)oxy)furan-2(5*H*)-one, 4l** (81.4 mg, 72%) was prepared according to the general procedure from 3-((5-bromopyridin-2-yl)oxy)-5,5-dimethyl-4-(4-(methylsulfonyl)phenyl)furan-2(5*H*)-one (110 mg, 0.200 mmol) ***with the following modification***: the reaction was using Catacxium A-Pd G3 (9.1 mg, 0.0125 mmol, 0.05 equiv) in place of $Pd(OAc)_2$. The desired olefin **4l** was isolated as a light-yellow oil. **$^1$H NMR** ($CDCl_3$, 500 MHz) δ 1.77 (s, 6H), 3.07 (s, 3H), 5.78 (d, *J* = 1.4 Hz, 1H), 6.01 (d, *J* = 1.1 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.80 (dd, *J* = 8.5, 2.1 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 2H), 8.21 (d, *J* = 2.3 Hz, 1H). **$^{13}$C NMR** ($CDCl_3$, 125 MHz) δ 26.5 ($CH_3$), 44.6 ($CH_3$), 84.7 (C), 111.1 (C), 121.9 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.5 Hz, $CH_2$), 123.1 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 126.2 (CH), 128.2 (CH), 129.2 (CH), 135.0 (C), 135.6 (q, $J_{C\text{-}C\text{-}F}$ = 31.2 Hz, C), 137.8 (C), 139.1 (CH), 141.8 (C), 146.5 (CH), 149.3 (C), 161.7 (C), 165.9 (C). **$^{19}$F NMR** ($CDCl_3$, 471 MHz) δ -



68.49 (s, 3F). **FT-IR** ($cm^{-1}$, neat, ATR) 2980 (w), 1766 (s), 1315 (s), 1245 (s), 1194 (s), 1173 (s), 1150 (s), 1123 (s), 1085 (s), 772 (s), 728 (s), 551 (s), 533 (s). **HRMS** (ES+) calcd for $C_{21}H_{19}F_3NO_5S$ $[M + H]^+$: 454.0936, found: 454.0924.

## Procedures for diversification of alkyl masked α-$CF_3$-β-TMS-alcohol




*Suzuki Cross-Coupling*

**1,1,1-Trifluoro-4-(4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)-2-((trimethylsilyl)methyl)butan-2-ol (5a)** A 20 mL microwave vial was charged with trifluoroborate **6** (606 mg, 3.00 mmol, 2.00 equiv), Pd-G3-CataCXiumA (55 mg, 0.075 mmol, 5.0 mol %), and $Cs_2CO_3$ (1.47 g, 4.50 mmol, 3.00 equiv). The vial was evacuated and backfilled with argon three times. Degassed 2:1 THF/$H_2O$ (13.6 mL, 0.1 M relative to aryl bromide) was added followed by aryl bromide **1g** (554 mg, 1.50 mmol, 1.00 equiv). The microwave vial was then sealed and heated in an 80 °C oil bath for 24 h and monitored by GC/MS. Upon completion, the vial was cooled to rt, diluted with EtOAc, eluted through a plug of Celite®, and concentrated. The crude material was then purified by column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to afford title compound **5a** as a yellow oil (425 mg, 1.11 mmol, 74% yield).

**$^1$H NMR** (500 MHz, acetone-$d_6$) δ 0.14 (s, 9H), 1.28 (d, $J$ = 4.6 Hz, 2H), 2.02 - 2.08 (m, 2H, peak overlaps with solvent peak), 2.85 (ddd, $J$ = 11.7, 6.4, 2.6 Hz, 2H), 4.78 (s, 1H), 5.96 (d, $J$ = 1.5 Hz, 1H), 6.00 (d, $J$ = 1.2 Hz, 1H), 7.33 (d, $J$ = 8.1 Hz, 2H), 7.46 (d, $J$ = 8.1 Hz, 2H).
**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 0.6 ($CH_3$), 23.5 ($CH_2$), 29.9 (obscured by solvent signal, observed by DEPT135 experiment), 39.5 ($CH_2$), 76.1 (q, $J_{C\text{-}C\text{-}F}$ = 27.5 Hz, C), 121.3 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 6.2 Hz, $CH_2$), 124.7 (q, $J_{C\text{-}F}$ = 274.0 Hz, $CF_3$), 128.3 (q, $J_{C\text{-}F}$ = 285.9 Hz, $CF_3$), 128.4 (CH), 129.6 (CH), 132.1 (C), 139.2 (q, $J_{C\text{-}C\text{-}F}$ = 29.3 Hz, C), 144.2 (C).
**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -81.56 (s, 3F), -65.42 (s, 3F).
**FT-IR** ($cm^{-1}$, neat, ATR) 2955 (w), 1353 (w), 1164 (vs), 1129 (s), 842 (s).
**HRMS** (EI) calcd $C_{17}H_{22}F_6OSi$ $[M]^+$: 384.1344, found: 384.1353.

*Radical Alkylation*

**4-(4-(1,1-Difluoro-6-methoxyhex-1-en-2-yl)phenyl)-1,1,1-trifluoro-2-((trimethylsilyl)methyl)butan-2-ol (5b)** An 8 mL screw cap vial was charged with $[Ru(bpy)_3](PF_6)_2$ (5.4 mg, 0.0063 mmol, 2.5 mol %) and propyl methoxy silicate (157 mg, 0.375 mmol, 1.50 equiv). The vial was evacuated and backfilled with argon three times. A degassed soln of trifluoromethyl alkene **5a** (96.1 mg, 0.250 mmol, 1.00 equiv) in DMF (5.0 mL, 0.050 M relative to alkene **5a**) was then added *via* syringe. The vial was sealed and irradiated with blue light (34W, 470 nm) at rt for 2 d and monitored by GC/MS. Upon completion, the reaction was diluted with EtOAc (15 mL), and the organic layer was washed with saturated aq $NaHCO_3$ (2 x 10 mL) and brine (1 x 10 mL). The combined aq layers were then back extracted with EtOAc (2 x 10 mL). The combined organic layers were dried ($Na_2SO_4$), filtered, and concentrated. The crude material was then purified by column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to afford title compound **5b** (83.3 mg, 0.190 mmol, 76% yield, average of two reactions) as a colorless oil.

**$^1$H NMR** (500 MHz, acetone-$d_6$) δ 0.13 (s, 9H), 1.26 (d, $J$ = 3.1 Hz, 2H), 1.36 - 1.45 (m, 2H), 1.54 (dq, $J$ = 8.6, 6.5 Hz, 2H), 1.98 - 2.04 (m, 2H), 2.44 (tt, $J$ = 7.8, 2.3 Hz, 2H), 2.76 - 2.82 (m, 2H), 3.21 (s, 3H), 3.29 (t, $J$ = 6.3 Hz, 2H), 4.79 (s, 1H), 7.28 (d, $J$ = 8.2 Hz, 2H), 7.31 (d, $J$ = 8.1 Hz, 2H).
**$^{13}$C NMR** (126 MHz, acetone-$d$) δ 0.6 ($CH_3$), 23.5 ($CH_2$), 25.2 (br s, $CH_2$), 28.1 ($CH_2$), 29.9 (obscured by solvent signal, observed via DEPT 135 experiment), 29.7 (obscured by solvent

signal, observed via DEPT 135 experiment), 39.6 ($CH_2$), 58.5 ($CH_2$), 72.8 ($CH_3$), 76.1 (q, $J_{C\text{-}C\text{-}F}$ = 27.5 Hz, C), 93.5 (dd, $J_{C\text{-}C\text{-}F}$ = 21.1, 13.7 Hz, C), 128.3 (q, $J_{C\text{-}F}$ = 285.0 Hz, $CF_3$), 129.1 - 129.8 (m, CH), 132.1 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.8 Hz, C), 142.2 (CH), 154.5 (dd, $J_{C\text{-}F}$ = 287.8, 285.0 Hz, $CF_2$).

**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ 248.24 (s, 3F), 235.40 (d, $J$ = 49.2 Hz, 1F), 235.19 (d, $J$ = 49.2 Hz, 1F)

**FT-IR** ($cm^{-1}$, neat, ATR) 3401 (br w), 2947 (br w), 1727 (s), 1231 (s), 1152 (vs), 1110 (s), 840 (vs), 692 (w).

**HRMS** (EI) calcd for $C_{21}H_{31}F_5O_2Si$ $[M]^+$: 438.2013, found: 438.2029.

*Peterson Elimination*

**1-(1,1-Difluoro-6-methoxyhex-1-en-2-yl)-4-(3-(trifluoromethyl)but-3-en-1-yl)benzene (5c)**

An 8 mL microwave vial was charged with α-$CF_3$-β-TMS-alcohol **5b** (118 mg, 0.270 mmol, 1.00 equiv) and DCE (1.4 mL, 0.2 M). The resulting soln was chilled to 0 ºC in an ice bath. Once equilibrated, TMSOTf (11 μL, 0.060 mmol, 20 mol %) was added dropwise (~1 drop/second). The ice bath was then removed, and the reaction was stirred at 45 ºC for 3.5 h. Once judged done by $^1$H NMR, the reaction was cooled to rt and quenched with 5 mL of saturated aq $NaHCO_3$. After stirring for 10 min at rt, the reaction mixture was transferred to a separatory funnel and diluted with EtOAc (10 mL). The layers were then separated, and the organic layer was washed with saturated aq $NaHCO_3$ (2 x 5 mL) and brine (1 x 5 mL). The organic layers were then concentrated, and the crude material was purified by column chromatography (gradient hexanes to 80:20 hexanes/EtOAc) to afford title compound **5c** (72.3 mg, 0.207 mmol, 77% yield) as a colorless oil.

**$^1$H NMR** (500 MHz, acetone-$d_6$) δ 1.34 - 1.47 (m, 2H), 1.49 - 1.58 (m, 2H), 2.45 (tt, = 7.6, 2.4 Hz, 2H), 2.56 (t, $J$ = 8.0 Hz, 2H), 2.88 (t, $J$ = 7.8 Hz, 2H), 3.21 (s, 3H), 3.29 (t, $J$ = 6.3 Hz, 2H), 5.54 (d, $J$ = 1.2 Hz, 1H), 5.75 (br s, 1H), 7.26 - 7.35 (m, 4H).

**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 25.2 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 2.3 Hz, $CH_2$), 28.1 ($CH_2$), 29.7 ($CH_2$), 31.7 ($CH_2$), 34.1 ($CH_2$), 58.5 ($CH_2$), 72.8 ($CH_3$), 93.5 (dd, $J_{C\text{-}C\text{-}F}$ = 20.9, 13.6 Hz, C), 119.6 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ = 5.9 Hz, $CH_2$), 125.1 (q, $J_{C\text{-}F}$ = 273.4 Hz, $CF_3$), 129.3 (t, $J_{C\text{-}C\text{-}C\text{-}F}$ = 3.2 Hz, C), 129.5 (CH), 132.3 (q, $J_{C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 1.8 Hz, C), 138.5 (q, $J_{C\text{-}C\text{-}F}$ = 29.2 Hz, C), 141.0 (CH), 154.4 (dd, $J_{C\text{-}F}$ = 287.9, 284.3 Hz, $CF_2$).

**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -94.54 (d, $J$ = 49.0 Hz, 1F), -94.33 (d, $J$ = 49.0 Hz, 1F), -69.17 (s 3F).

**FT-IR** ($cm^{-1}$, neat, ATR) 2933 (br w), 2868 (br w), 1727 (s), 1232 (s), 1165 (vs), 1116 (vs), 942 (s), 822 (s).

**HRMS** (EI) cald for $C_{18}H_{21}F_5O$ $[M]^+$: 348.1513, found: 348.1519.

*2nd Radical Alkylation*

***tert*-Butyl 2-(4-(4-(1,1-Difluoro-6-methoxyhex-1-en-2-yl)phenyl)-2-(difluoromethylene)butyl)pyrrolidine-1-carboxylate (5d)** An 8 mL screw cap vial was charged with 4CzIPN (15 mg, 0.19 mmol, 10 mol %) and potassium 1-*N*-Boc-pyrrolidin-2-yltrifluoroborate (74 mg, 0.27 mmol, 1.4 equiv). The vial was evacuated and backfilled with argon three times. A degassed soln of trifluoromethyl alkene **5c** (66 mg, 0.19 mmol, 1.00 equiv) in DMSO (3.8 mL, 0.050 M relative to alkene **5c**) was then added via syringe. The vial was sealed and irradiated with blue light (34W, 470 nm) at rt for 24 h. Upon completion, the reaction was diluted with EtOAc (10 mL) and the organic layer was washed with saturated aq $NaHCO_3$ (2 x 5 mL) and brine (1 x 5 mL). The combined aq layers were then back extracted with EtOAc (2 x 5 mL). The combined organic layers were dried ($Na_2SO_4$), filtered, and concentrated. The crude material was then purified by column chromatography (gradient hexanes to 80:20 hexanes/EtOAc). The title compound coeluted with 4CzIPN. The mixed material was triturated with $Et_2O$ and filtered to remove the insoluble 4CzIPN. The title compound **5d** (44.9 mg, 95:5 ratio of product to starting material alkene, 0.086 mmol, 45% yield) as a colorless oil. Rotamers observed by NMR, reported major resonances.

**$^1$H NMR** (500 MHz, acetone-$d_6$) δ 1.34 - 1.43 (m, 3H), 1.46 (app d, $J$ = 7.5 Hz, 9H), 1.50 - 1.57 (m, 2H), 1.59 - 1.71 (m, 1H), 1.77 - 1.87 (m, 1H), 1.87 - 1.95 (m, 2H), 2.06 - 2.13 (m, 1H), 2.32 - 2.41 (m, 3H), 2.44 (ddt, $J$ = 9.9, 5.1, 2.3 Hz, 2H), 2.71 - 2.81 (m, 1H), 3.21 (s, 3H), 3.29 (t, $J$ = 6.3 Hz, 2H), 3.31 - 3.37 (m, 2H), 3.94 (br s, 1H), 7.20 - 7.35 (m, 4H).

**$^{13}$C NMR** (126 MHz, acetone-$d_6$) δ 23.7 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 122.6 Hz, $CH_2$), 25.1 (t, $J$ = 2.3 Hz, $CH_2$), 28.0 ($CH_2$), 28.7 (d, $J$ = 5.4 Hz, $CH_2$), 29.1 ($CH_2$), 29.4 ($CH_2$), 29.6 ($CH_3$), 30.6 (s, 1 C), 33.9 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 44.5 Hz, $CH_2$), 47.0 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}C\text{-}F}}$ = 40.9 Hz, CH), 56.1 (d, $J$ = 16.3 Hz, $CH_2$), 58.4 ($CH_2$), 72.7 ($CH_3$), 79.2 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 29.1 Hz, $CH_2$), 87.9 (q, $J$ = 16.0 Hz, C), 93.5 (dd, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 21.8, 13.6 Hz, C), 129.2 (CH), 129.4 (CH), 132.0 (q, $J$ = 10.0 Hz, C), 141.5 (d, $J_{\mathbf{C\text{-}C\text{-}F}}$ = 35.4 Hz,

C), 155.2 (dd, $J_{\mathbf{C\text{-}F}}$ = 287.9, 286.1 Hz, $CF_2$), 154.7 (d, $J_{\mathbf{C\text{-}F}}$ = 40.0 Hz, $CF_2$), 155.3 (d, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 17.3 Hz, C).

**$^{19}$F NMR** (471 MHz, acetone-$d_6$) δ -96.72 (app dd, $J$ = 484.5, 59.5 Hz, 1F), -96.09 (app dd, $J$ = 346.6, 57.6 Hz, 1F), -94.18 – -94.80 (m).

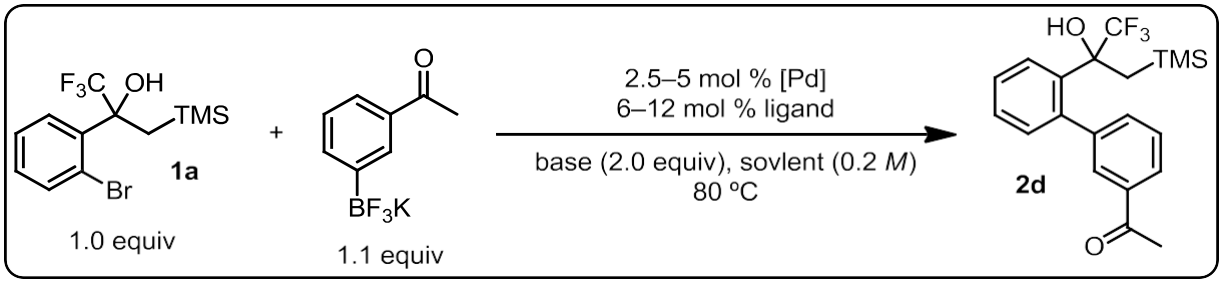
**FT-IR** ($cm^{-1}$, neat, ATR) 2932 (br s), 2869 (br s), 1744 (s), 1690 (vs), 1391 (vs), 1229 (vs), 1168 (vs), 1100 (vs), 905 (w), 772 (w).

**HRMS** (ESI) calcd for $C_{27}H_{37}F_4NNaO_3$ $[M + Na]^+$: 522.2607; found: 522.2593.

# Optimization of Suzuki Cross-Coupling with High Throughput Experimentation

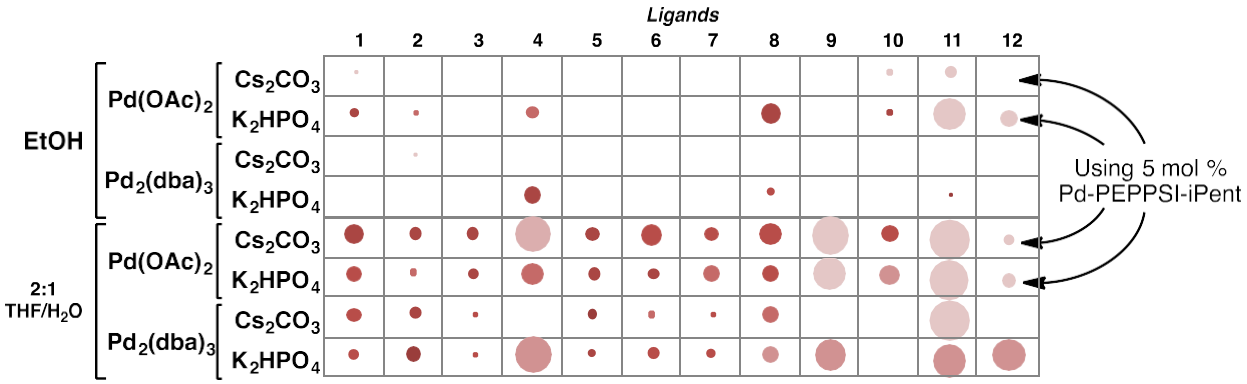
High Throughput Experimentation was performed at the Penn/Merck Center for High Throughput Experimentation at the University of Pennsylvania. All solvents used in the screening center were dry and degassed. The screens were analyzed by UPLC with addition of an internal standard. The areas for the internal standard (IS), aryl bromide (ArBr), 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 illustrated in a heat map. The information conveyed in these heat maps is two-fold. First, the size of the circle corresponds to the amount of product. The larger the circle, the more product formed during the reaction. Secondly, the shade of the circle corresponds to the amount of starting material, in this case aryl bromide, remaining. The lighter the circle, the less aryl bromide remaining after 24 h. Therefore, for a reaction resulting in high conversion and product formation, the circle will be both large and light.

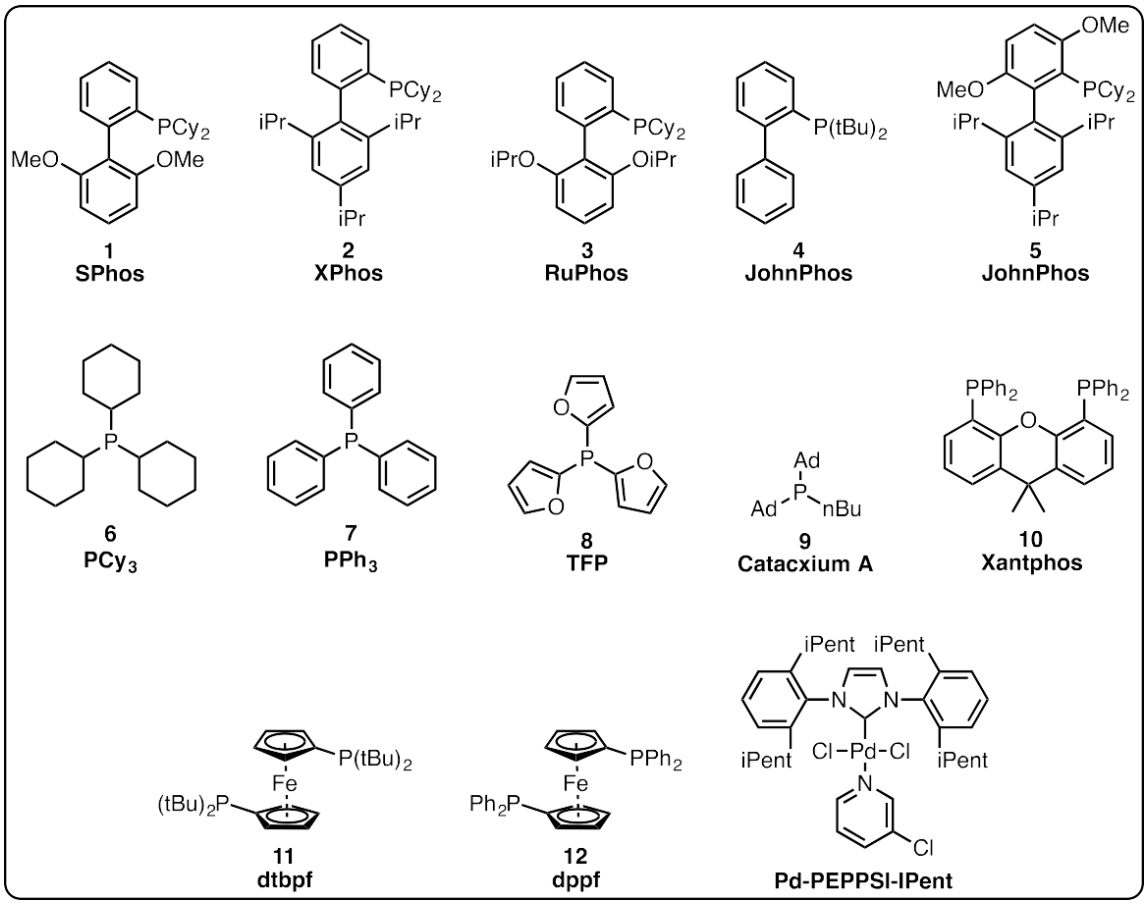
***Procedure for Screen 1: Ligand Optimization for Substrate 2d:***



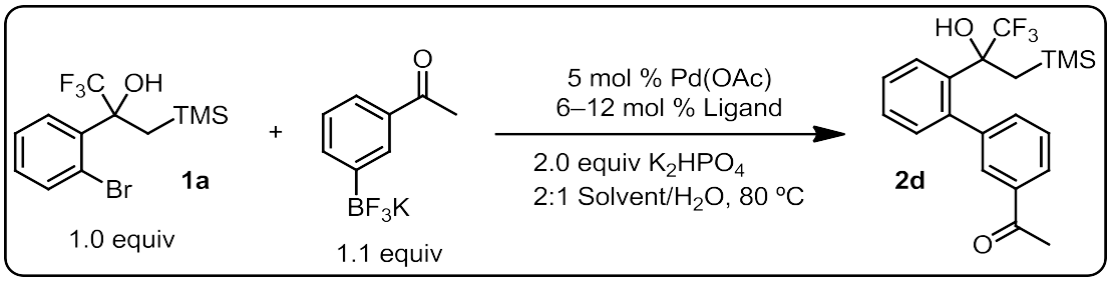

To a 96 well plate reactor containing 1 mL reaction vials equipped with a Teflon-coated magnetic stir bar in a glovebox was added sequentially: 1) $Pd(OAc)_2$ (0.05 equiv) dissolved in THF (100 µL); 2) $Pd_2(dba)_3$ (0.025 equiv) dissolved in THF (100 µL); 3) soln of ligand (0.06 equiv for all bidentate ligands; 0.12 equiv for all monodentate ligands) in THF (100 µL); 4) slurry of $Cs_2CO_3$ (2.00 equiv) in THF (200 µL); 5) slurry of $K_2HPO_4$ (2.00 equiv) in THF (200 µL). The solvent was then removed in the glovebox by Genovac evaporation before the

following steps. Next, 1) *ortho*-aryl bromide **2d** (1.00 equiv) and aryl $BF_3K$ (1.10 equiv) in EtOH (200 µL); 2) *ortho*-aryl bromide **2d** (1.00 equiv) and aryl $BF_3K$ (1.10 equiv) in THF (133 µL); 3) deionized $H_2O$ (67 µL) were added sequentially. The vials were sealed and stirred at 80 °C. After 18 h the reactions were cooled to rt, 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. The reaction mixtures were then analyzed by UPLC.

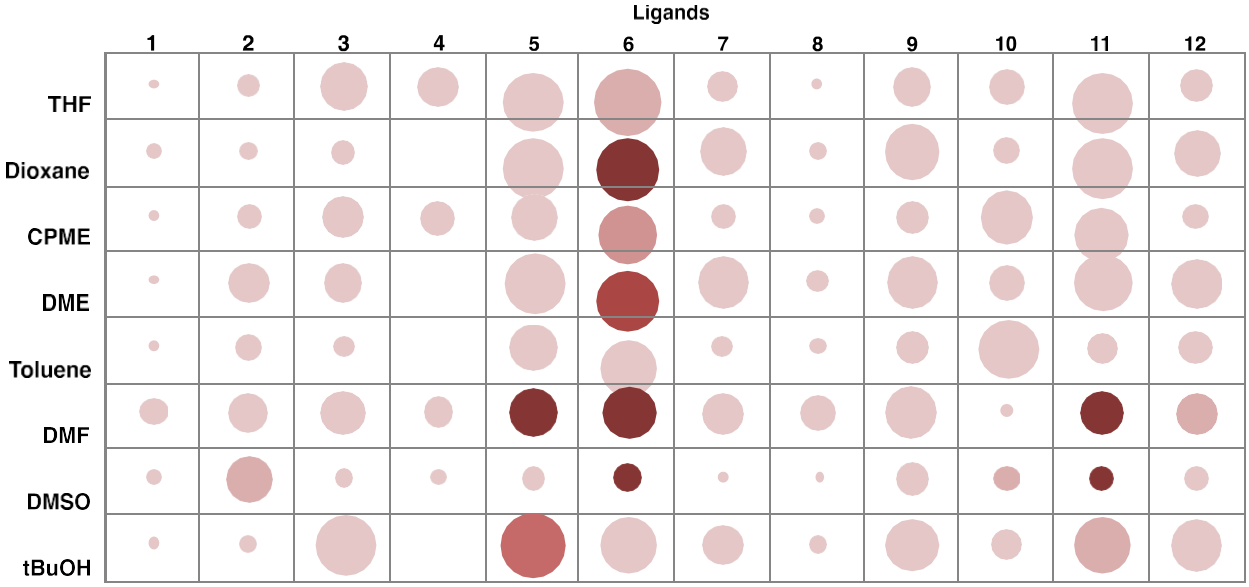


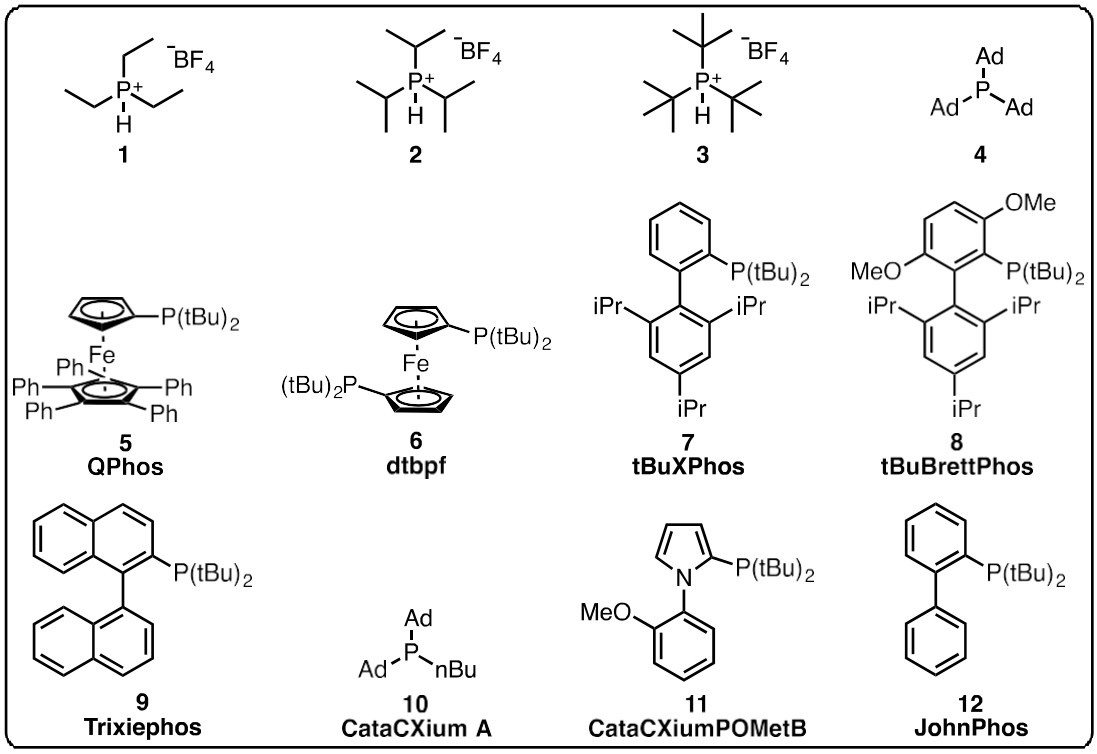



***Procedure for Screen 2: Ligand Optimization for Substrate 2d:***

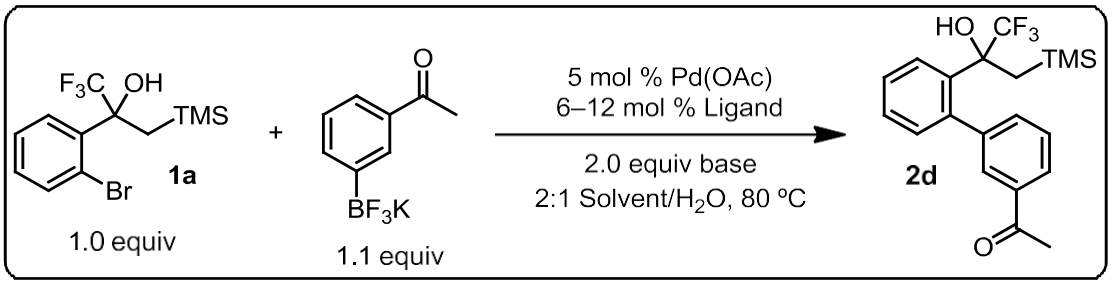



To a 96 well plate reactor containing 1 mL reaction vials equipped with a Teflon-coated magnetic stir bar in a glovebox was added sequentially: 1) $Pd(OAc)_2$ (0.05 equiv) dissolved in THF (100 µL); 2) a soln of ligand (0.06 equiv for all bidentate ligands; 0.12 equiv for all monodentate ligands) in THF (100 µL). The solvent was then removed in the glovebox by Genovac evaporation. Next, 1) aryl $BF_3K$ (1.10 equiv) in THF (100 µL); 2) a slurry of $K_2HPO_4$ (2.00 equiv) in THF (100 µL) were then added followed by Genovac evaporation of the solvent in the glovebox. Then, 1) *ortho*-aryl bromide **2d** (1.00 equiv) in the reaction solvent (133 µL); 3) deionized $H_2O$ (67 µL) were added sequentially. The vials were sealed and stirred at 80 °C. After 18 h the reactions were cooled to rt, 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. The reaction mixtures were then analyzed by UPLC.



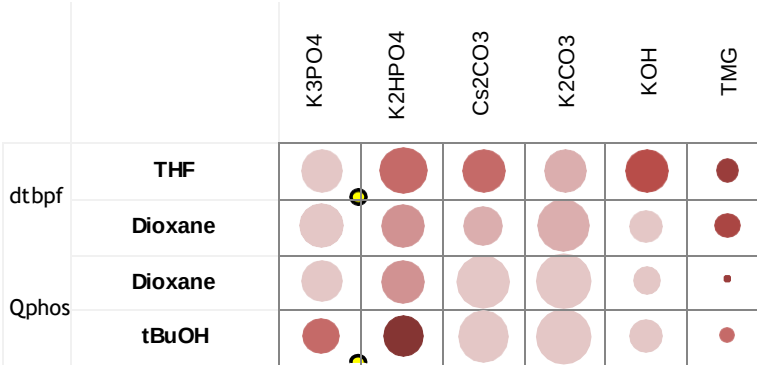



***Procedure for Screen 3: Ligand Optimization for Substrate 2d:***

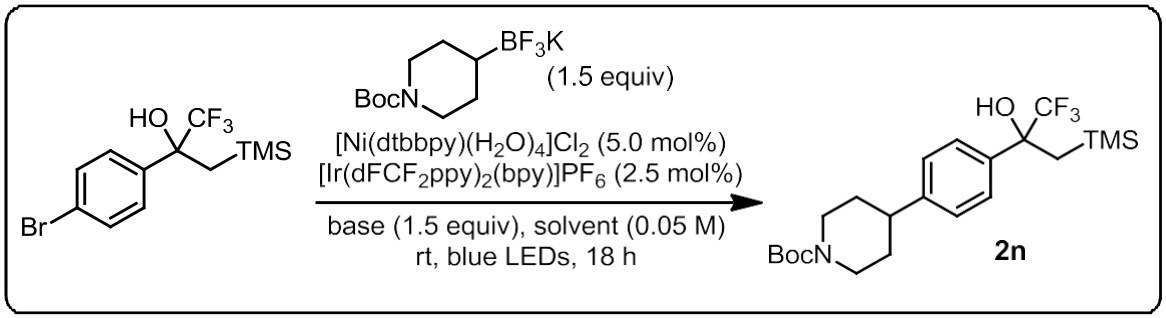



To a 24 well plate reactor containing 1 mL reaction vials equipped with a Teflon-coated magnetic stir bar in a glovebox was added sequentially: 1) $Pd(OAc)_2$ (0.05 equiv) dissolved in THF (50 µL); 2) soln of ligand (0.06 equiv for all bidentate ligands; 0.12 equiv for all monodentate ligands) in THF (50 µL); 3) aryl $BF_3K$ (1.10 equiv) in THF (250 µL). The solvent was then removed in the glovebox by Genovac evaporation. All the bases (2 equiv), except TMG, were then added as solids to each reaction vial. TMG was added via micropipette. Next, 1) *ortho*-aryl bromide **1a** (1.00 equiv) in the reaction solvent (133 µL); 2) deionized $H_2O$ (67 µL) were added sequentially across the reaction vials. The vials were sealed and stirred at 80 ºC. After 18 h the reactions were cooled to rt, opened to air, and diluted with 500 µL of MeCN. After

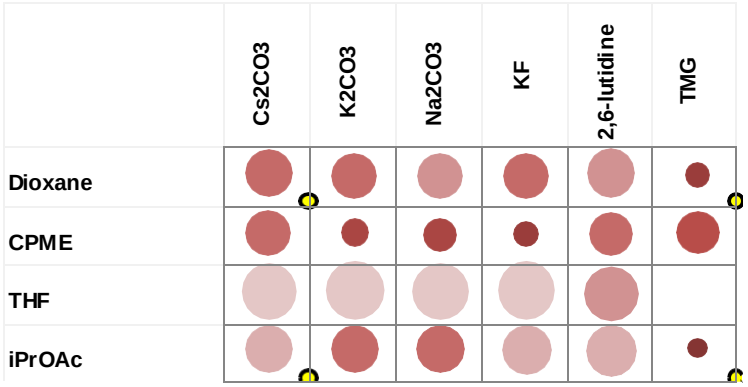
stirring the diluted block for 15 min, 25 µL aliquots were then taken from the reaction vials and dosed into a 96-well UPLC block. These aliquots were further diluted by the addition of 700 µL of MeCN. The reaction mixtures were then analyzed by UPLC.




***Procedure for Screen 4: Ligand Optimization for Substrate 2o:***



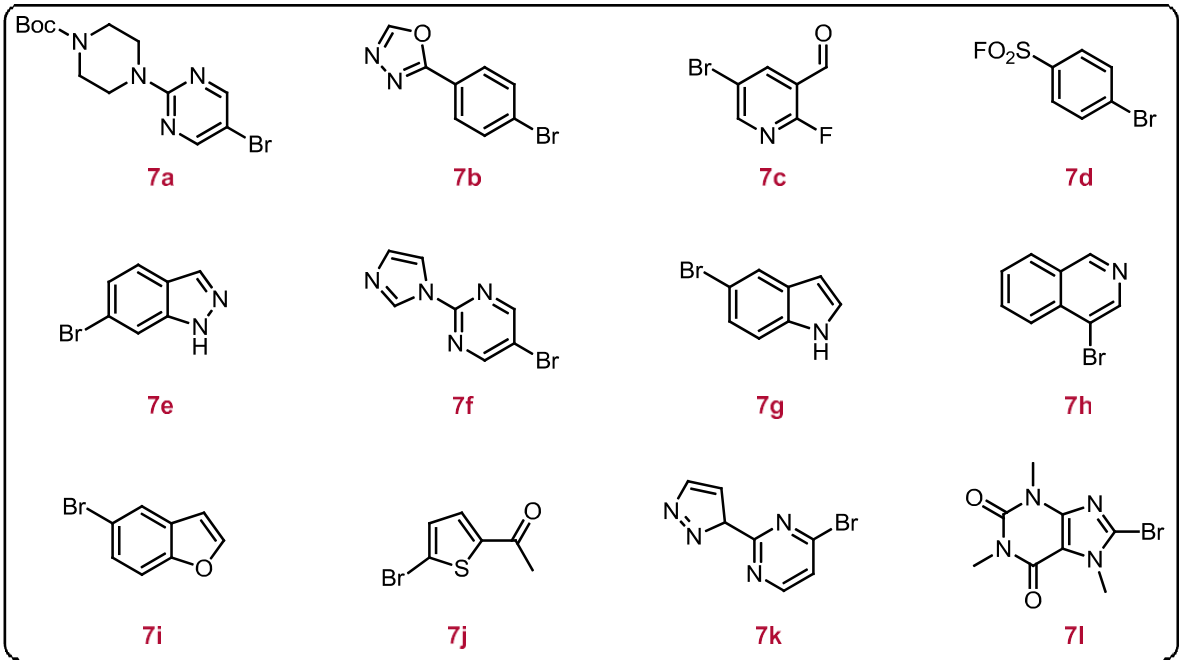

To a 24 well plate reactor containing 1 mL reaction vials equipped with a Teflon-coated magnetic stir bar in a glovebox was added potassium *N*-Boc-piperidinyl-4-trifluoroborate (1.50 equiv) and $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (0.05 equiv) in acetone (300 µL). The solvent was then removed in the glovebox by Genovac evaporation. All the bases (1.50 equiv), except 2,6-lutidine and TMG, were then added as solids to each reaction vial. 2,6-Lutidine and TMG was added via micropipette. Next, *para*-aryl bromide **1c** (1.00 equiv) and $[Ir(dFCF_3ppy)_2(bpy)]PF_6$ (0.025 equiv) in the reaction solvent (50 µL) were added sequentially across the reaction vials. The vials were sealed and irradiated with blue LEDs while stirring at rt (~24 ºC). 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. The reaction mixtures were then analyzed by UPLC.




***Procedure for Screen 5: Ligand Optimization for Substrates 7a – 7l:***

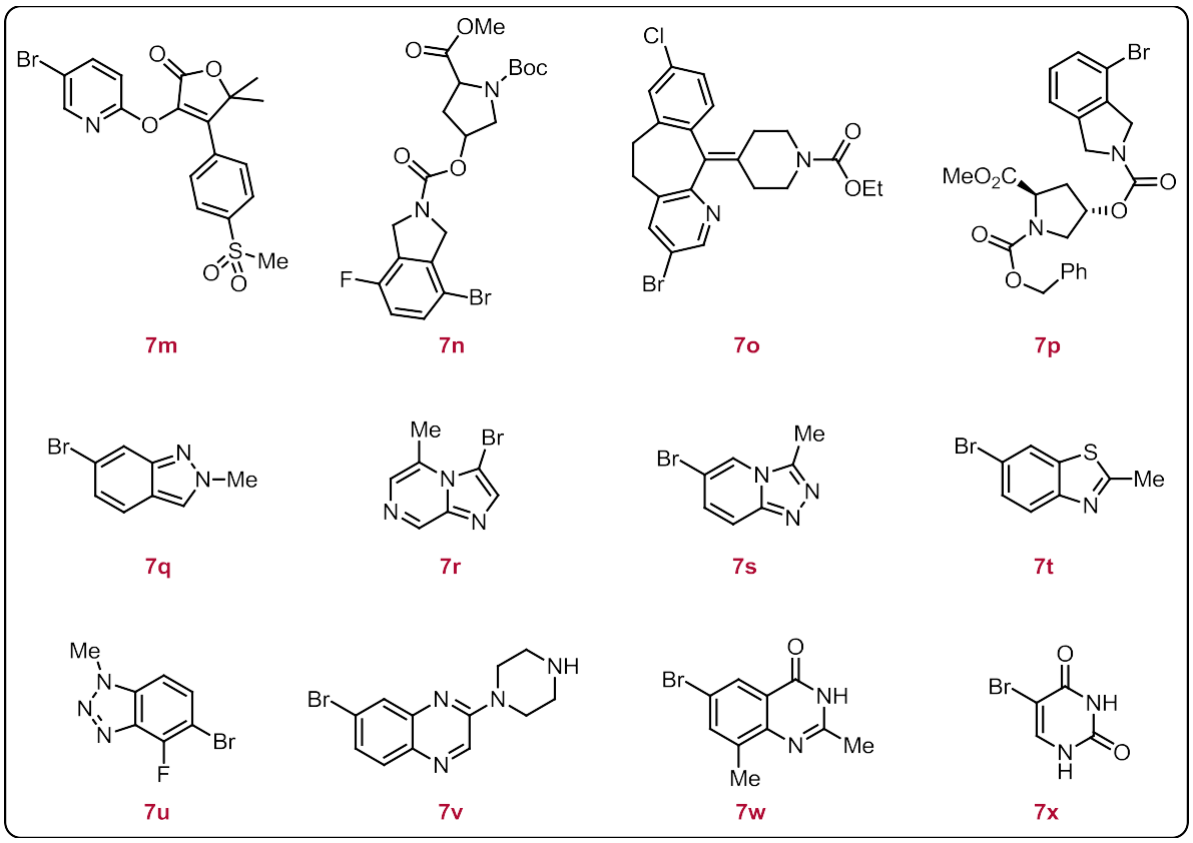
To a 96 well plate reactor containing 1 mL reaction vials equipped with a Teflon-coated magnetic stir bar in a glovebox was added sequentially: 1) $Pd_2(dba)_3$ (0.025 equiv) dissolved in THF (50 µL); 2) soln of ligand (0.07 equiv for all bidentate ligands; 0.12 equiv for all monodentate ligands) in THF (50 µL); (3) soln of aryl bromide (10 µmol, 1 equiv) in THF (50 µL); (4) soln of potassium trifluoro(3,3,3-trifluoroprop-1-en-2-yl)borate (15 µL, 1.5 equiv) in THF (50 µL); (5) soln of $Cs_2CO_3$ (30 µmol, 3 equiv) in deionized $H_2O$ (100 µL). The vials were sealed and stirred at 80 °C for 24 h. After 24 h the reactions were cooled to rt, 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. The reaction mixtures were then analyzed by UPLC.

| Ligand | 7a | 7b | 7c | 7d | 7e | 7f | 7g | 7h | 7i | 7j | 7k | 7l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| XPhos | | | | | | | | | | | | |
| XantPhos | | | | | | | | | | | | |
| QPhos | | | | | | | | | | | | |
| SPhos | | | | | | | | | | | | |
| RuPhos | | | | | | | | | | | | |
| $PPh_3$ | | | | | | | | | | | | |
| Catacxium A | | | | | | | | | | | | |
| dppf | | | | | | | | | | | | |




***Procedure for Screen 6: Ligand Optimization for Substrates 7m – 7x:***

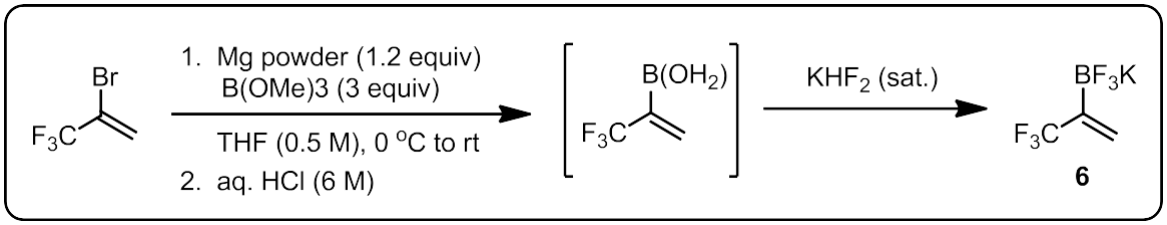
To a 96 well plate reactor containing 1 mL reaction vials equipped with a Teflon-coated magnetic stir bar in a glovebox was added sequentially: 1) Pd precomplex (0.05 equiv) dissolved in THF (50 µL) or $Pd_2(dba)_3$ (0.025 equiv) dissolved in THF (25 µL) and ligand (0.07 equiv for bidentate ligand and 0.12 equiv for monodentate ligand) dissolved in THF (25 µL); (2) soln of aryl bromide (10 µmol, 1 equiv) in THF (50 µL); (3) soln of potassium trifluoro(3,3,3-trifluoroprop-1-en-2-yl)borate (15 µL, 1.5 equiv) in THF (50 µL); (4) soln of $Cs_2CO_3$ (30 µmol, 3 equiv) in deionized $H_2O$ (100 µL). The vials were sealed and stirred at 80 °C for 24 h. After 24 h the reactions were cooled to rt, 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. The reaction mixtures were then analyzed by UPLC.




| Precatalyst | 7m | 7n | 7o | 7p | 7q | 7r | 7s | 7t | 7u | 7v | 7w | 7x |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| XPhos Pd G4 | | | | | | | | | | | | |
| Sphos Pd G4 | | | | | | | | | | | | |
| $PCy_3$ Pd G4 | | | | | | | | | | | | |
| Catacxium A Pd G3 | | | | | | | | | | | | |
| XantPhos Pd G4 | | | | | | | | | | | | |
| RuPhos Pd G4 | | | | | | | | | | | | |
| Qphos + $Pd_2(dba)_3$ | | | | | | | | | | | | |
| $PPh_3$ + $Pd_2(dba)_3$ | | | | | | | | | | | | |

# 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***




*Stage One*

Mg powder was activated *via* successive washes with 2 M aq HCl (3 x ~10 mL) followed by a wash with $Et_2O$ (~20 mL). To a 250 mL Schlenk flask equipped with a stir bar was added activated Mg powder (0.85 g, 35.0 mmol). The flask was sealed with a septum and flame-dried under vacuum with an acetylene torch. The flask was purged with argon and allowed to cool to rt. To the flask was added THF (60 mL). The soln was cooled to 0 °C with an ice bath. To the cooled soln was added $B(OMe)_3$ (9.75 mL, 77.5 mmol) *via* syringe, and the soln was stirred vigorously. The flask stopcock was closed, and a soln of 2-bromo-3,3,3-trifluoro-1-propene (3.1 mL, 29.2 mmol) in THF (7.5 mL) was added slowly in 3 portions over 30 min. After the addition was complete, the heterogeneous soln turned dark grey. The soln was stirred at 0 °C for 6 h and then was allowed to warm to rt and stirred overnight.

*Stage Two*

The soln was cooled to 0 °C and was quenched with 6 M aq HCl (~20 mL) *via* a slow addition through a syringe. The mixture was allowed to stir at 0 °C for 1 h. The soln 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 $KHF_2$ (40 mL). The soln was allowed to warm to rt and stirred overnight. The solvent was removed *in vacuo* to afford a crude solid. 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, which was dried on a vacuum line for

5 min. The solid was triturated with cold $Et_2O$ (~80 mL) and filtered to yield 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) 121.78 (dtd, $J_{\mathbf{C\text{-}C\text{-}C\text{-}F}}$ = 10.8, 7.2, 2.3 Hz, $CH_2$), 126.25 (q, $J_{\mathbf{C\text{-}F}}$ = 271.3 Hz, $CF_3$), 143.65 (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).

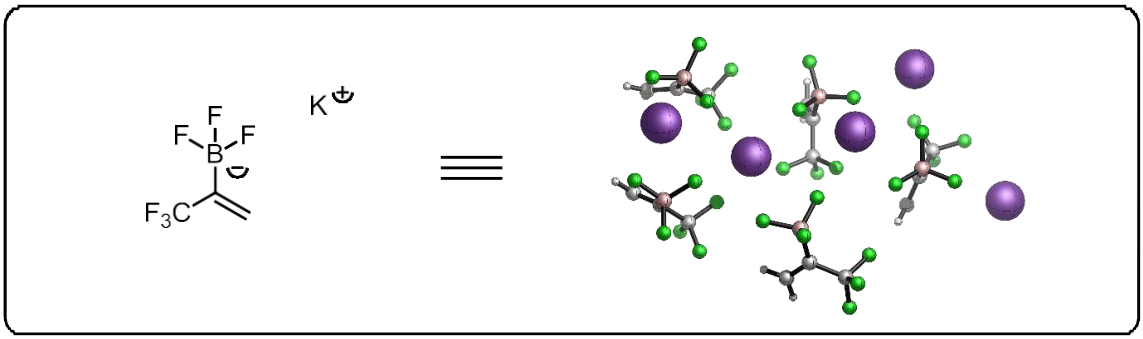
**$^{11}$B NMR** (acetone-$d_6$, 128 MHz) δ 1.15 (q, $J$ = 46.7 Hz, 1B).

**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.

# X-Ray Crystal Structure Data

***X-Ray Structure Determination of Potassium trifluoro(3,3,3-trifluoroprop-1-en-2-yl)borate (6)***



$C_{15}H_{10}B_5F_{30}K_5$, crystallizes in the triclinic space group P1 with a = 10.9621(4)Å, b = 12.9672(5)Å, c = 13.9252(5)Å, α = 111.325(2)°, β = 99.442(2)°, γ = 105.532(2)°, V = 1699.53(11)Å$^3$, Z = 2, and $d_{calc}$ = 1.973 g/cm$^3$. X-ray intensity data were collected on a Bruker APEXII [1] CCD area detector employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at a temperature of 100 K. Preliminary indexing was performed from a series of thirty six 0.5° rotation frames with exposures of 10 seconds. A total of 3218 frames were collected with a crystal to detector distance of 49.8 mm, rotation widths of 0.5° and exposures of 10 seconds:

| scan type | 2θ | ω | φ | X | Frames |
|---|---|---|---|---|---|
| ω | -33.00 | 262.32 | 59.98 | 28.88 | 178 |
| φ | -30.50 | 251.25 | 9.11 | 21.36 | 739 |
| φ | 23.00 | 346.20 | 14.21 | 32.61 | 739 |
| ω | 22.00 | 322.28 | 240.21 | 72.15 | 138 |
| φ | 24.50 | 68.74 | 340.76 | -42.87 | 739 |
| ω | 29.50 | 351.94 | 183.80 | 85.83 | 81 |
| ω | 32.00 | 128.29 | 101.21 | -99.65 | 153 |
| ω | 34.50 | 311.43 | 168.18 | 97.50 | 168 |
| ω | -33.00 | 319.37 | 31.77 | -99.82 | 127 |
| ω | 22.00 | 315.12 | 74.22 | 94.02 | 156 |

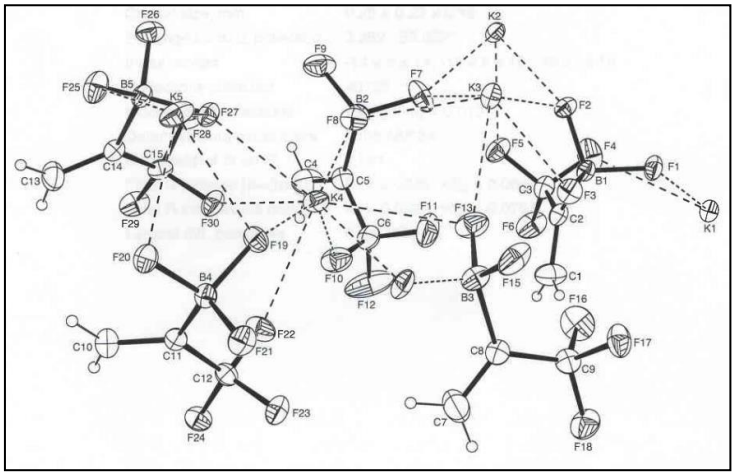
Rotation frames were integrated using SAINT [2], producing a listing of unaveraged $F^2$ and $\sigma(F^2)$ values. A total of 40795 reflections were measured over the ranges $3.282 < 2\theta < 55.092°$, $-14 \le h \le 14$, $-16 \le k \le 16$, $-18 \le l \le 18$ yielding 7808 unique reflections ($R_{int}$ = 0.0197). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.6720, 0.7456). The structure was solved by direct methods - SHELXT [4]. The asymmetric unit consists of five formula units of the title compound. Refinement was by full-matrix least squares based on $F^2$ using SHELXL-2014 [5].

All reflections were used during refinement. The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 1.5672P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1 = 0.0283 and wR2 = 0.0680 for 7096 observed reflections for which $F > 4\sigma(F)$ and R1 = 0.0320 and wR2 = 0.0704 and GOF = 1.081 for all 7808 unique, non-zero reflections and 524 variables. The maximum $\Delta/\sigma$ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.85 and -0.55 e/Å$^3$.

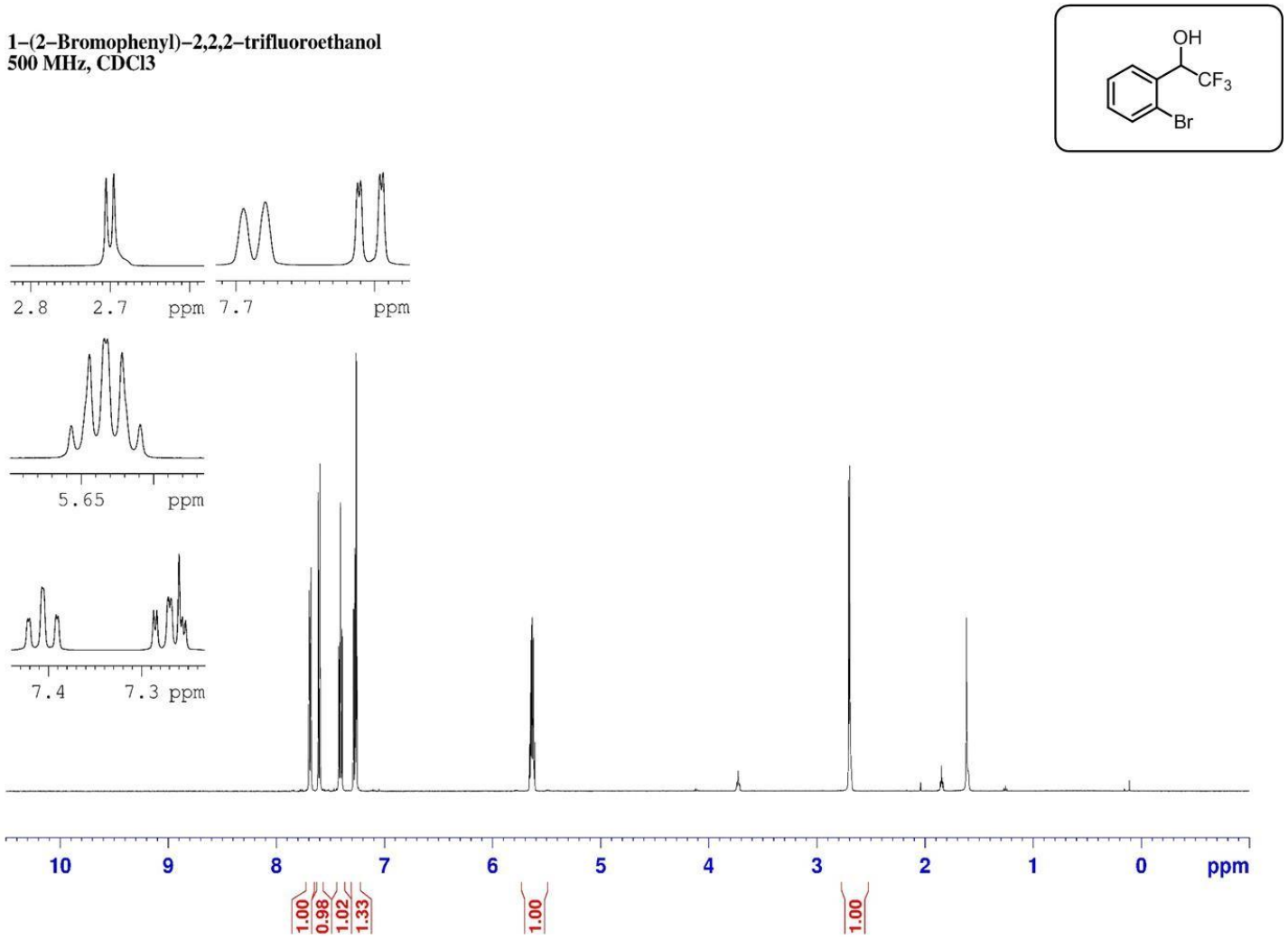
**Table S.1.** Summary of Structure Determination of Potassium Trifluoro(3,3,3-trifluoroprop-1-en-2-yl)borate (**6**):

| | |
|---|---|
| Empirical formula | $C_{15}H_{10}B_5F_{30}K_5$ |
| Formula weight | 1009.78 |
| Temperature/K | 100 |
| Crystal System | Triclinic |
| Space group | P1 |
| a | 10.9621(4)Å |
| b | 12.9672(5)Å |
| c | 13.9252(5)Å |
| α | 111.325(2)Å |
| β | 99.442(2)Å |
| γ | 105.532(2)Å |
| Volume | 1699.53(11)Å$^3$ |
| Z | 2 |
| $d_{calc}$ | 1.973 g/cm$^3$ |
| μ | 0.825 mm$^{-1}$ |
| F(000) | 980.0 |
| Crystal size, mm | 0.25 x 0.23 x 0.13 |
| 2θ range for data collection | 3.282 – 55.092° |
| Index ranges | $-14 \le h \le 14$, $-16 \le k \le 16$, $-18 \le l \le 18$ |
| Reflections collected | 40795 |
| Independent reflections | 7808[R(int) = 0.0197 |
| Data/restraints/parameters | 7808/48/524 |
| Goodness-of-fit on $F^2$ | 1.081 |
| Final R indexes [I>=2σ (I)] | $R_1 = 0.0283$, $wR_2 = 0.0680$ |
| Final R indexes [all data] | $R_1 = 0.0320$, $wR_2 = 0.0704$ |
| Largest diff. peak/hole | 0.85/-0.55 eÅ$^{-3}$ |

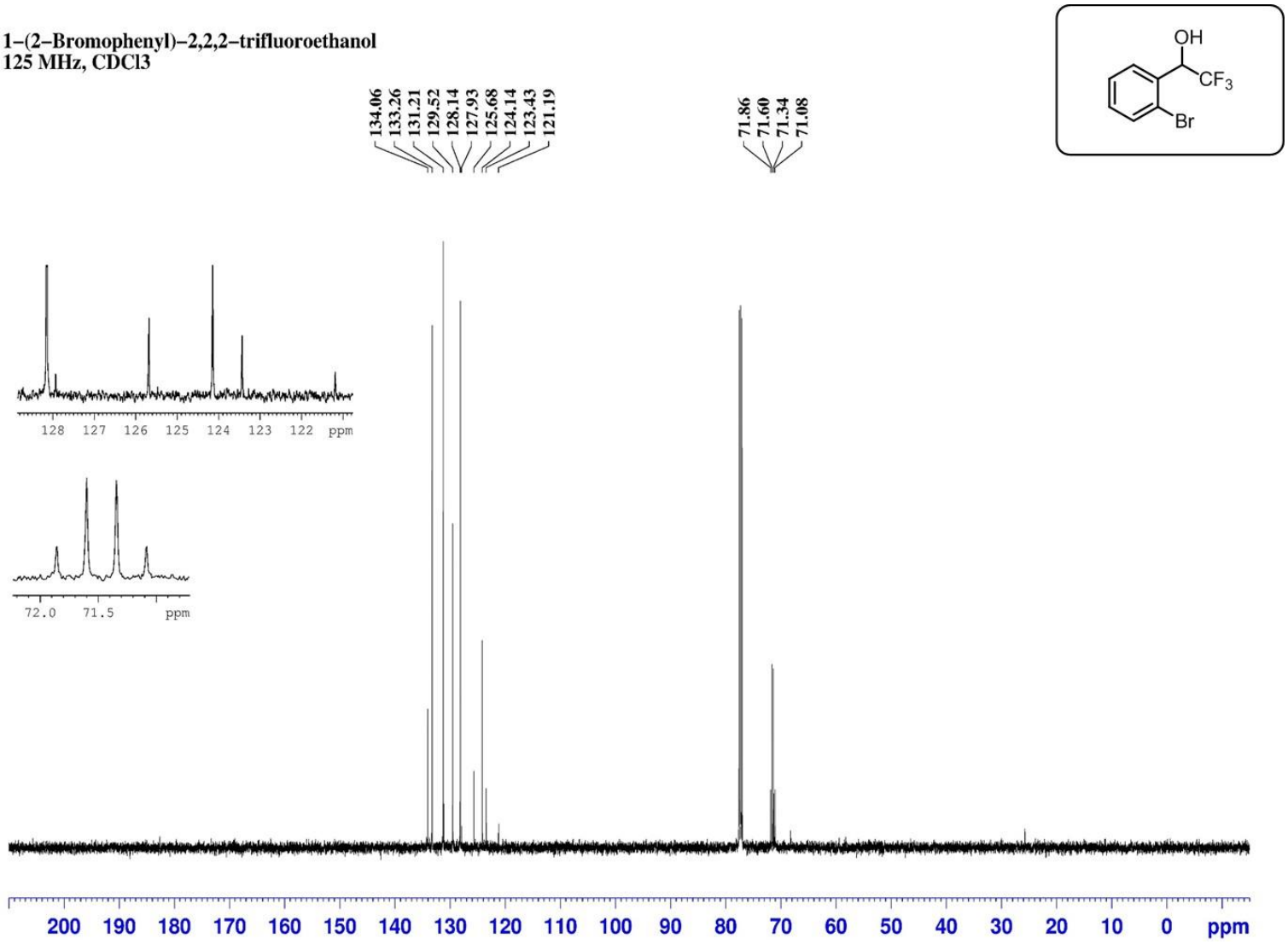
**Figure S.1** is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.



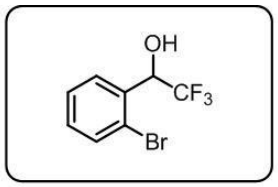
## NMR Spectra of Synthesized Compound

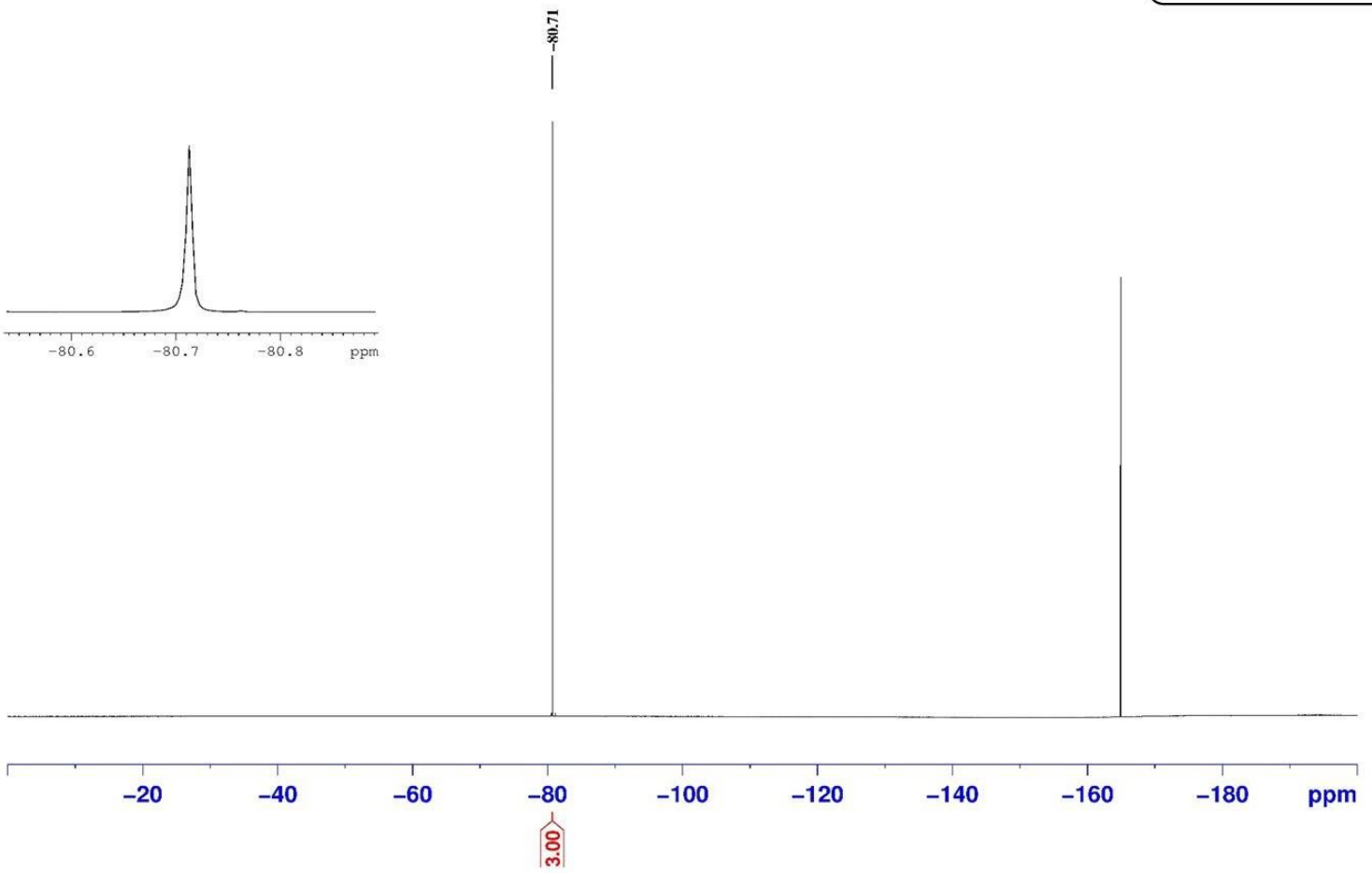


**1–(2–Bromophenyl)–2,2,2–trifluoroethanol**
**125 MHz, CDCl3**

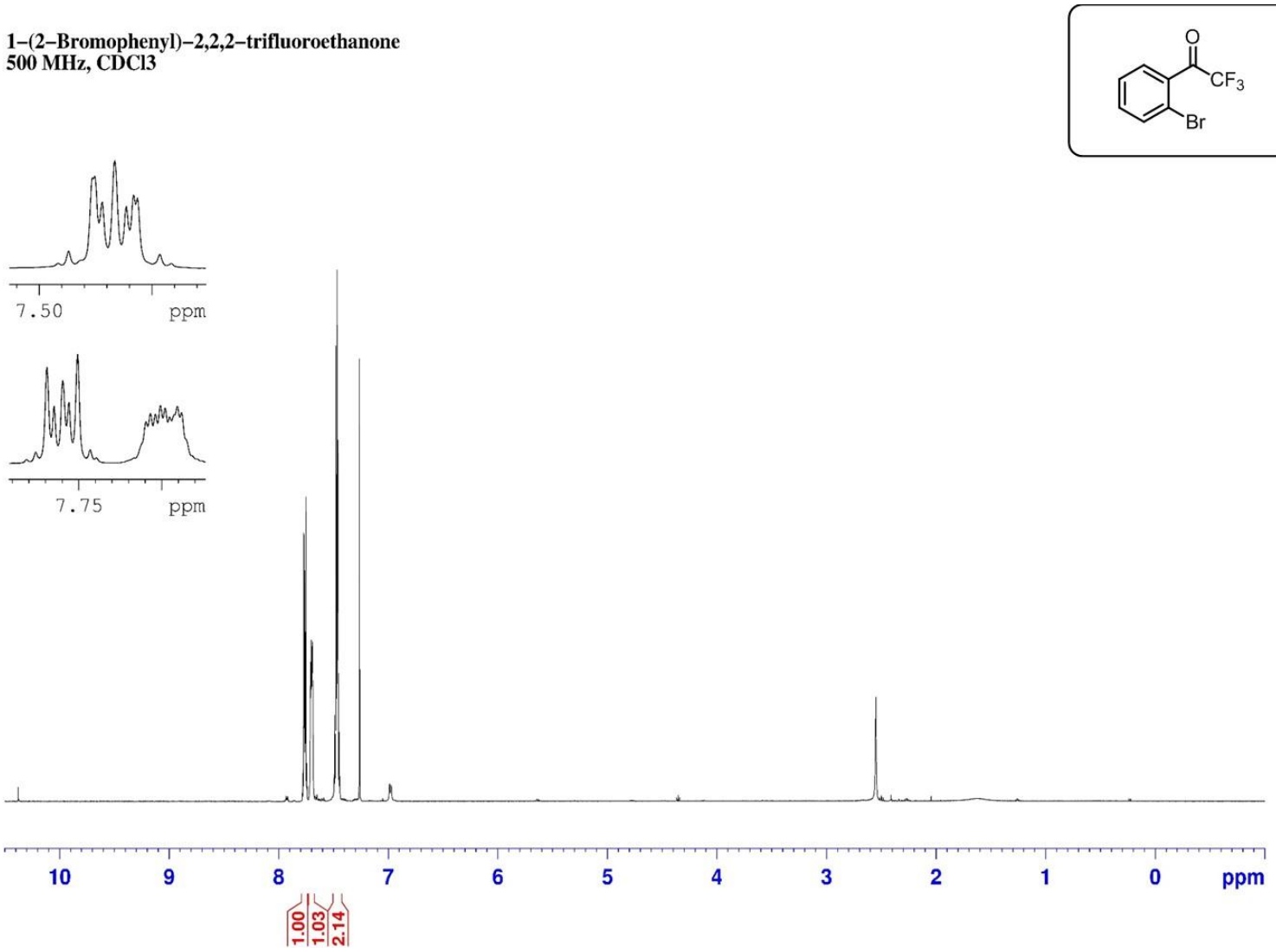


**1−(2−bromophenyl)−2,2,2−trifluoroethanol**
**CDCl3, 500 MHz**

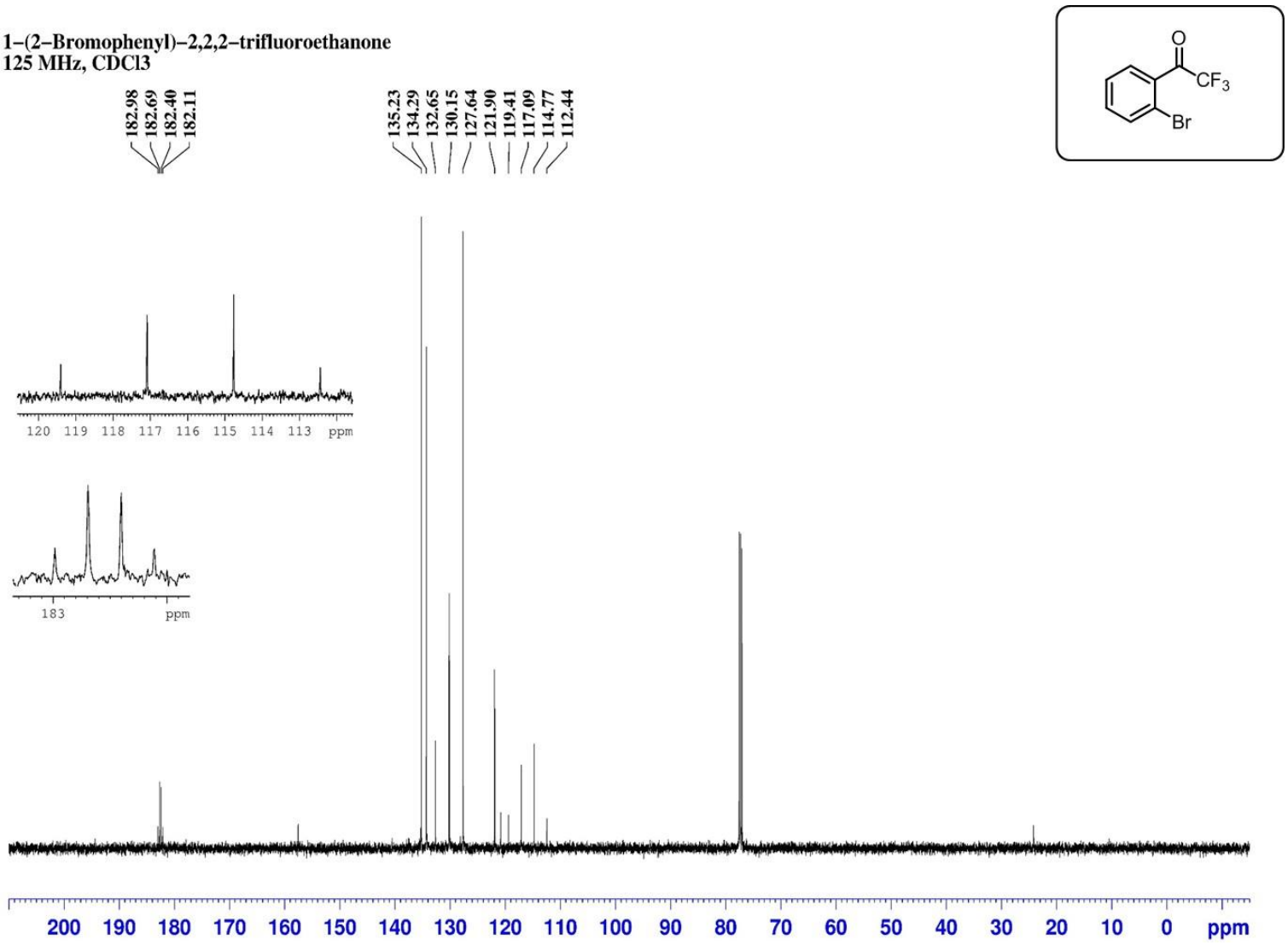


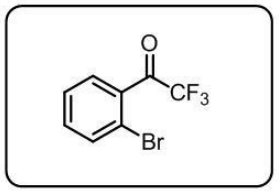
**1–(2–Bromophenyl)–2,2,2–trifluoroethanone**
**500 MHz, CDCl3**

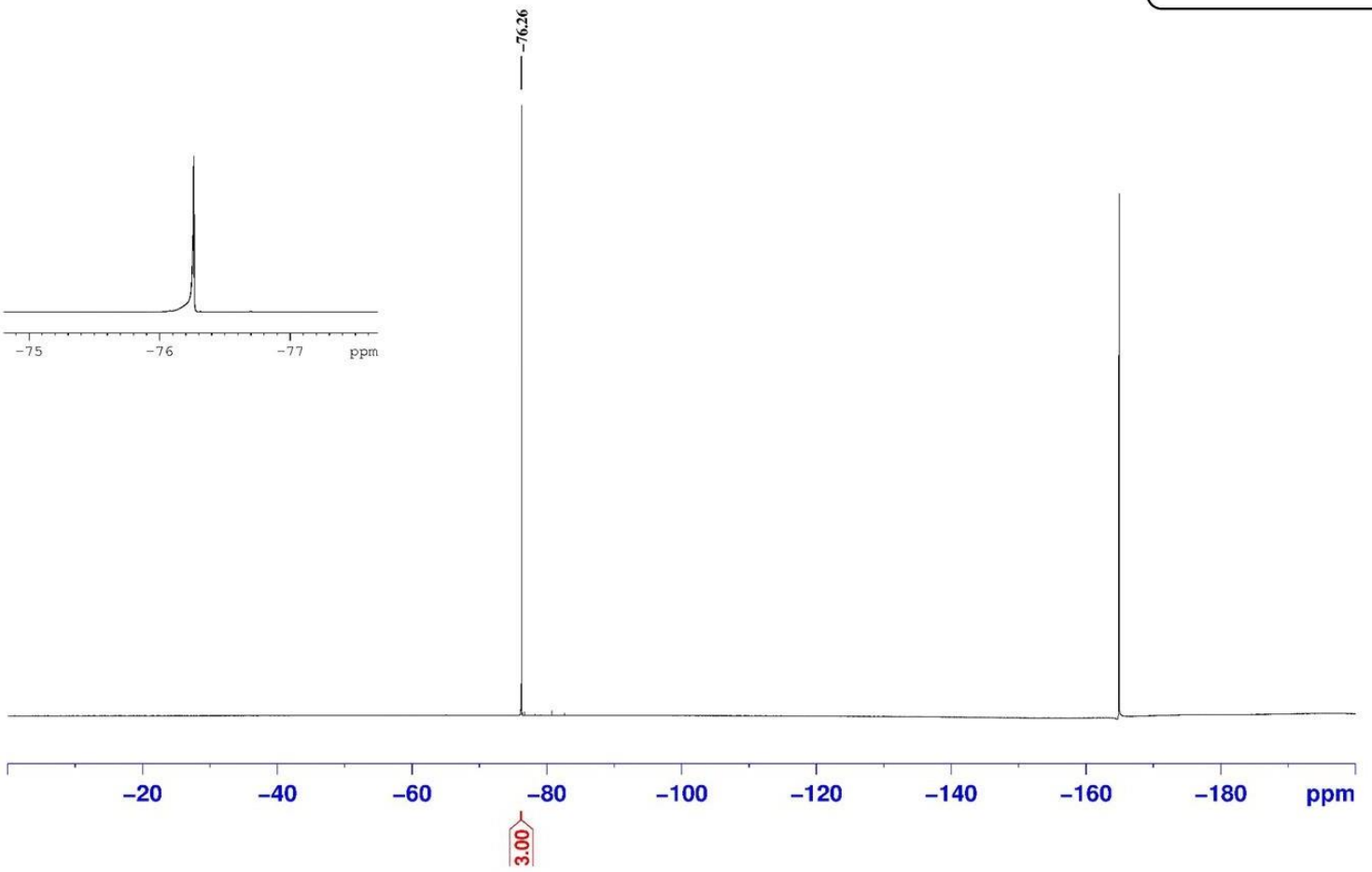


**1–(2–Bromophenyl)–2,2,2–trifluoroethanone**
**125 MHz, CDCl3**

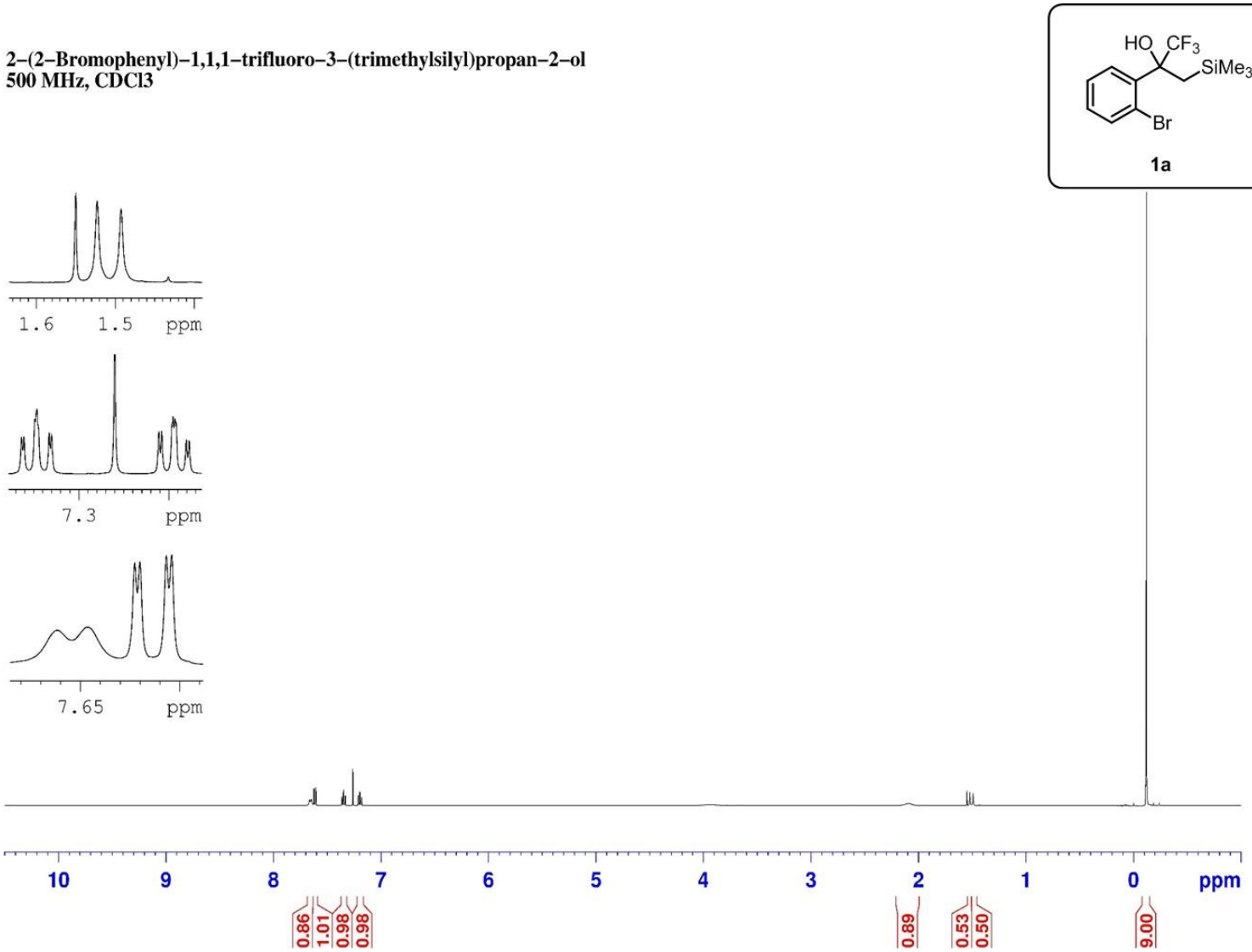


**1–(2–bromophenyl)–2,2,2–trifluoroethanone**
**CDCl3, 471 MHz**

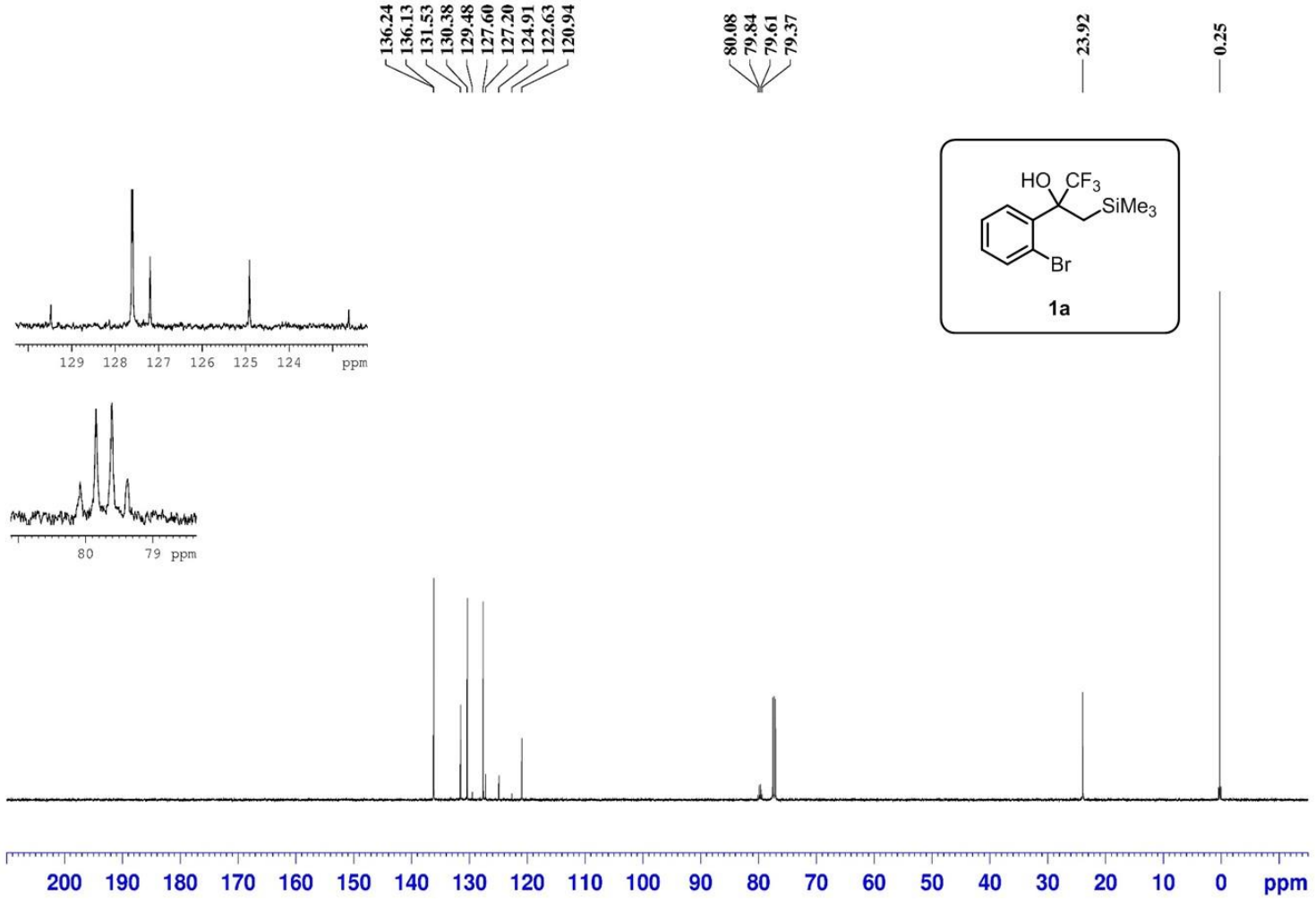


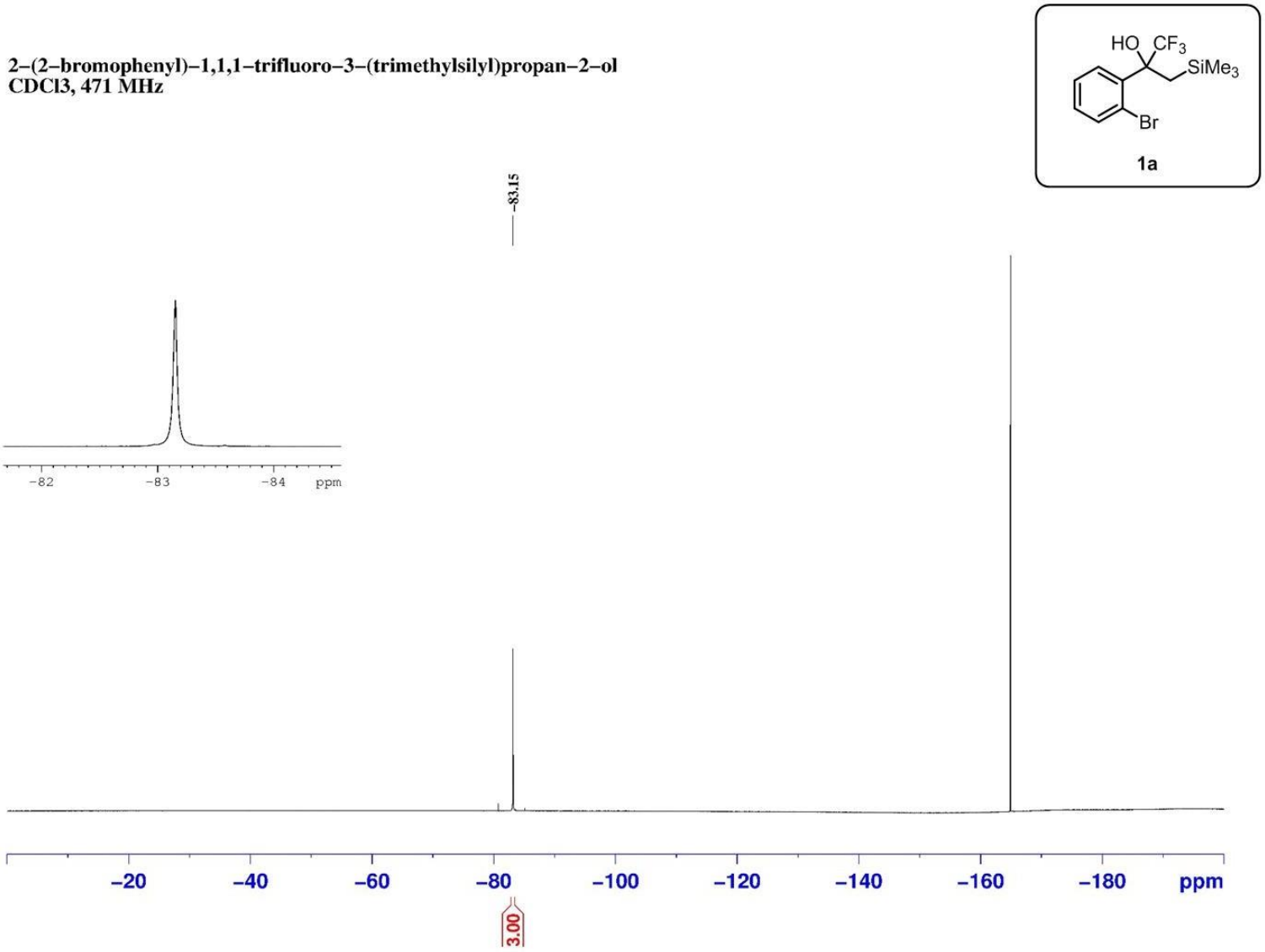
**2–(2–Bromophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**500 MHz, CDCl3**



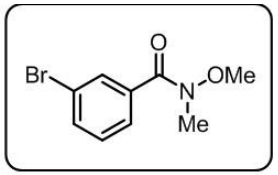
**2–(2–Bromophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**125 MHz, CDCl3**

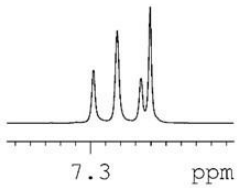


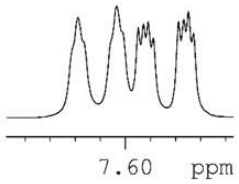
**2–(2–bromophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**CDCl3, 471 MHz**



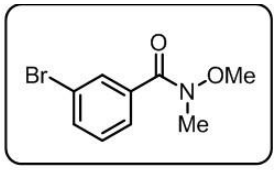
**3–Bromo–N–methoxy–N–methylbenzamide**
**500 MHz, CDCl3**

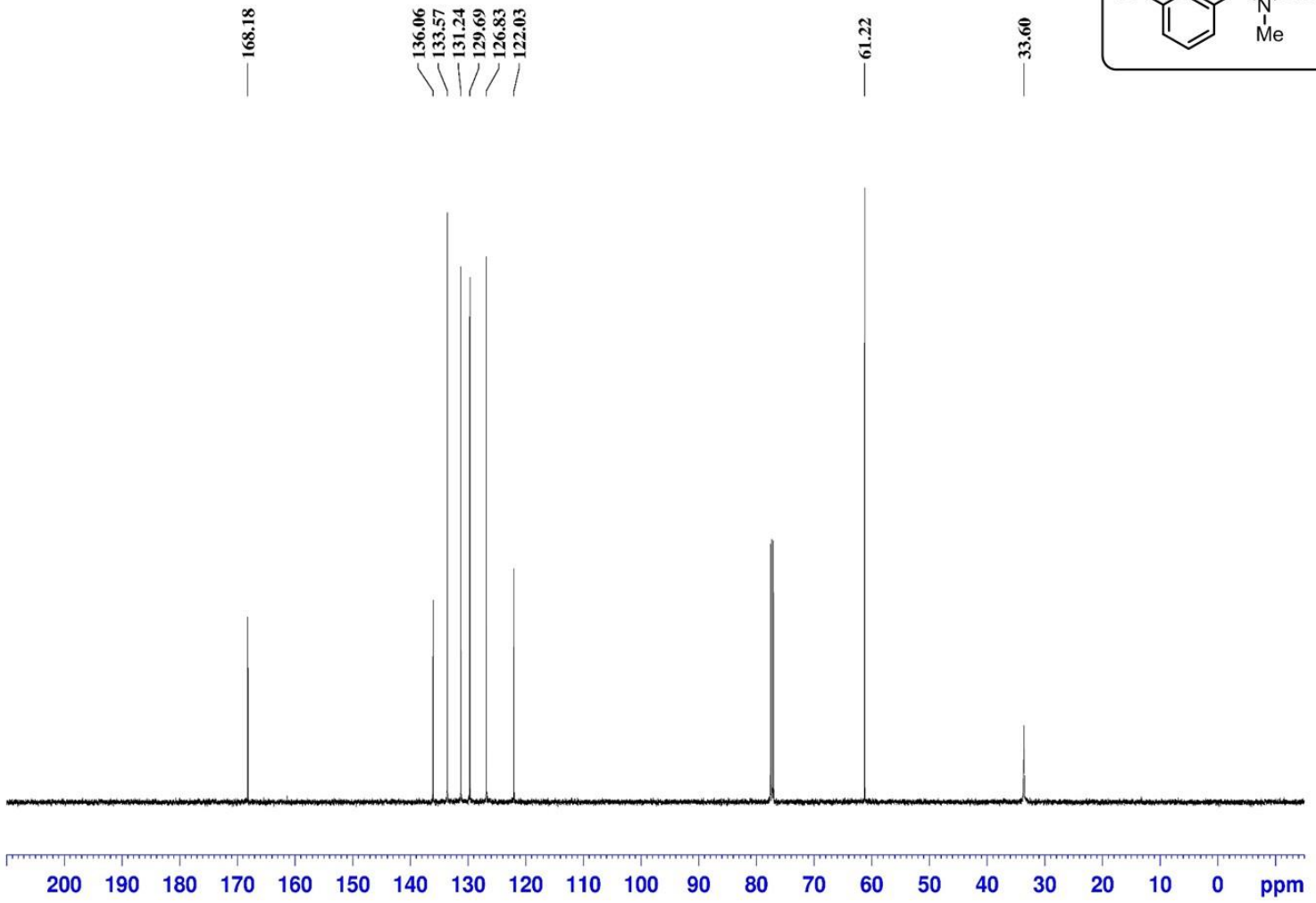


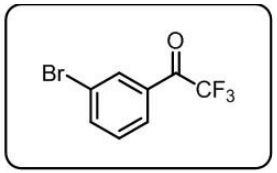



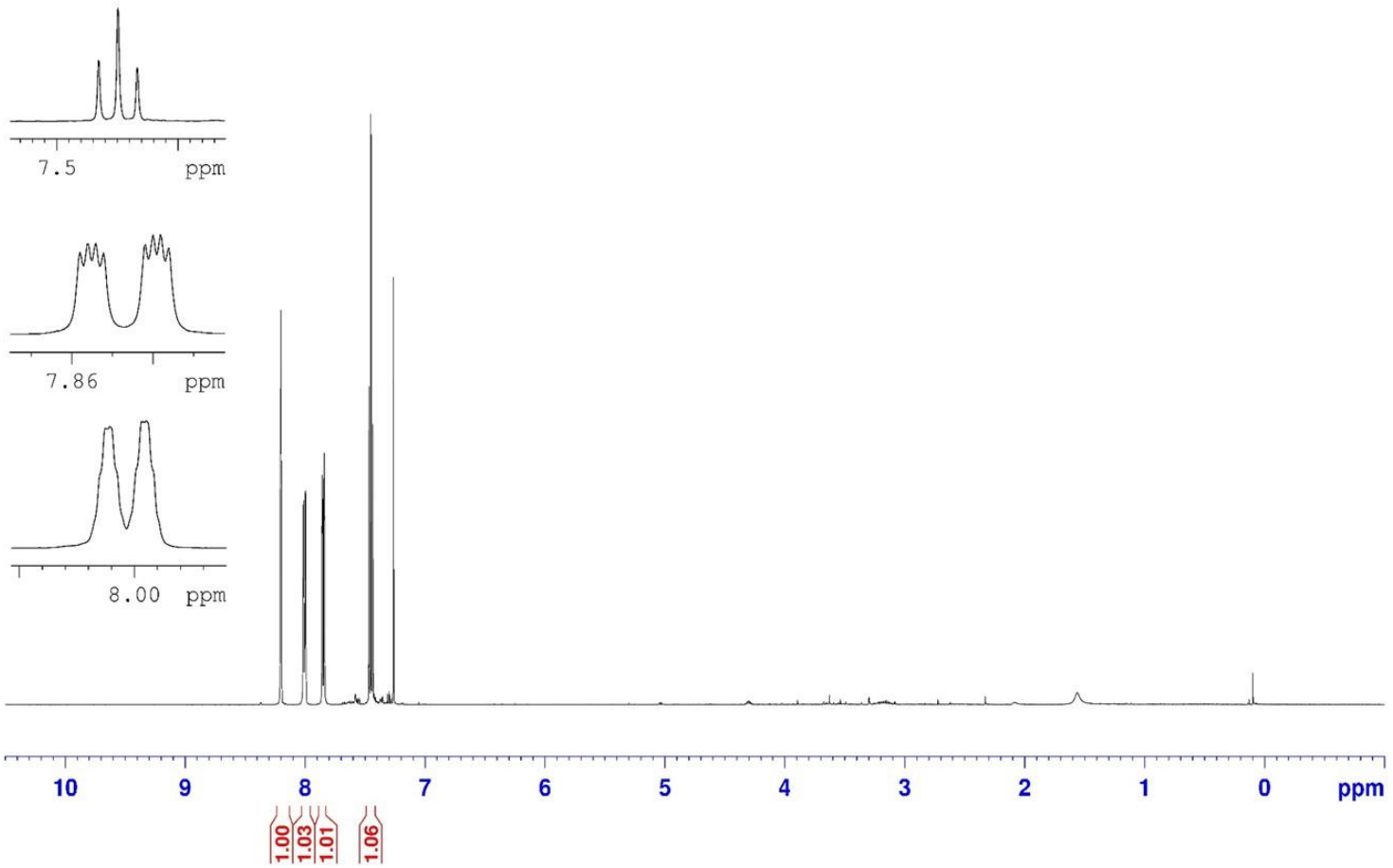
**3–Bromo–N–methoxy–N–methylbenzamide**
**125 MHz, CDCl3**



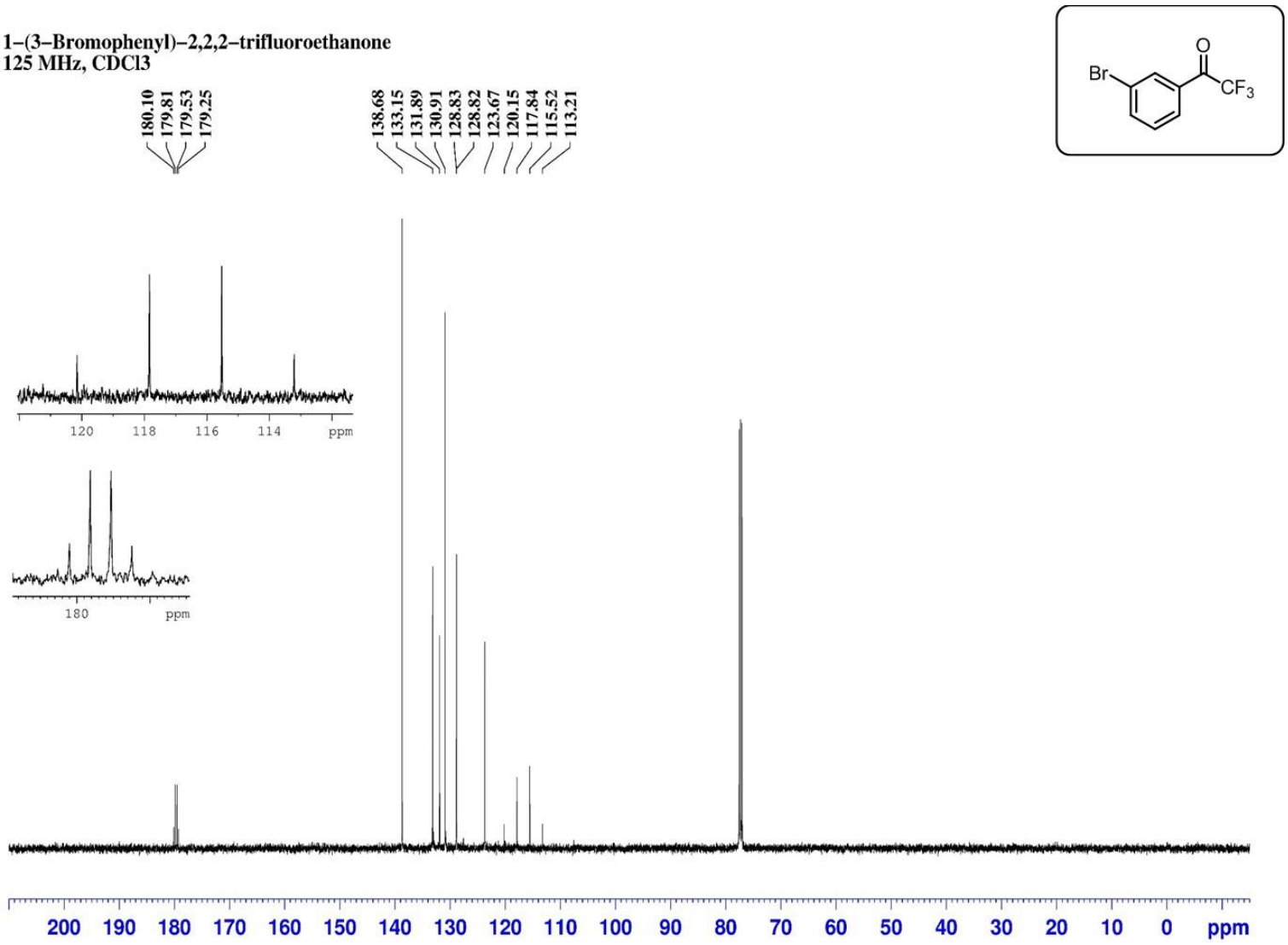



**1–(3–Bromophenyl)–2,2,2–trifluoroethanone**
**500 MHz, CDCl3**

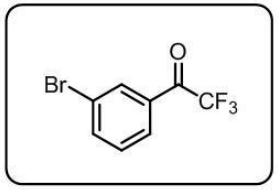


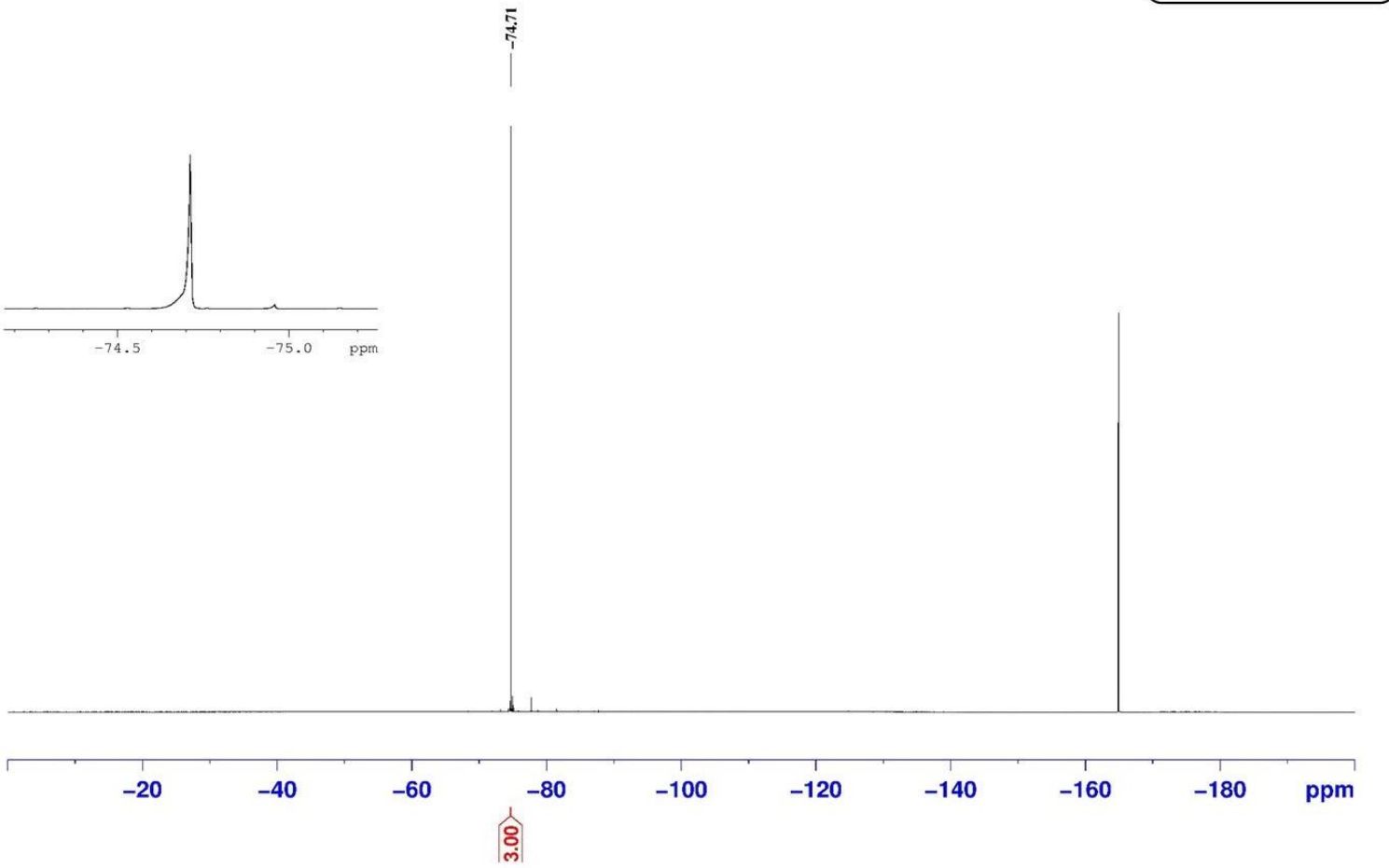



**1–(3–Bromophenyl)–2,2,2–trifluoroethanone**
**125 MHz, CDCl3**

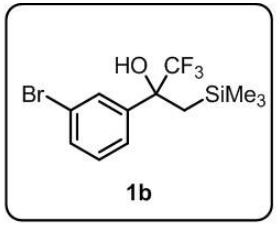


**1–(3–bromophenyl)–2,2,2–trifluoroethanone**
**CDCl3, 471 MHz**

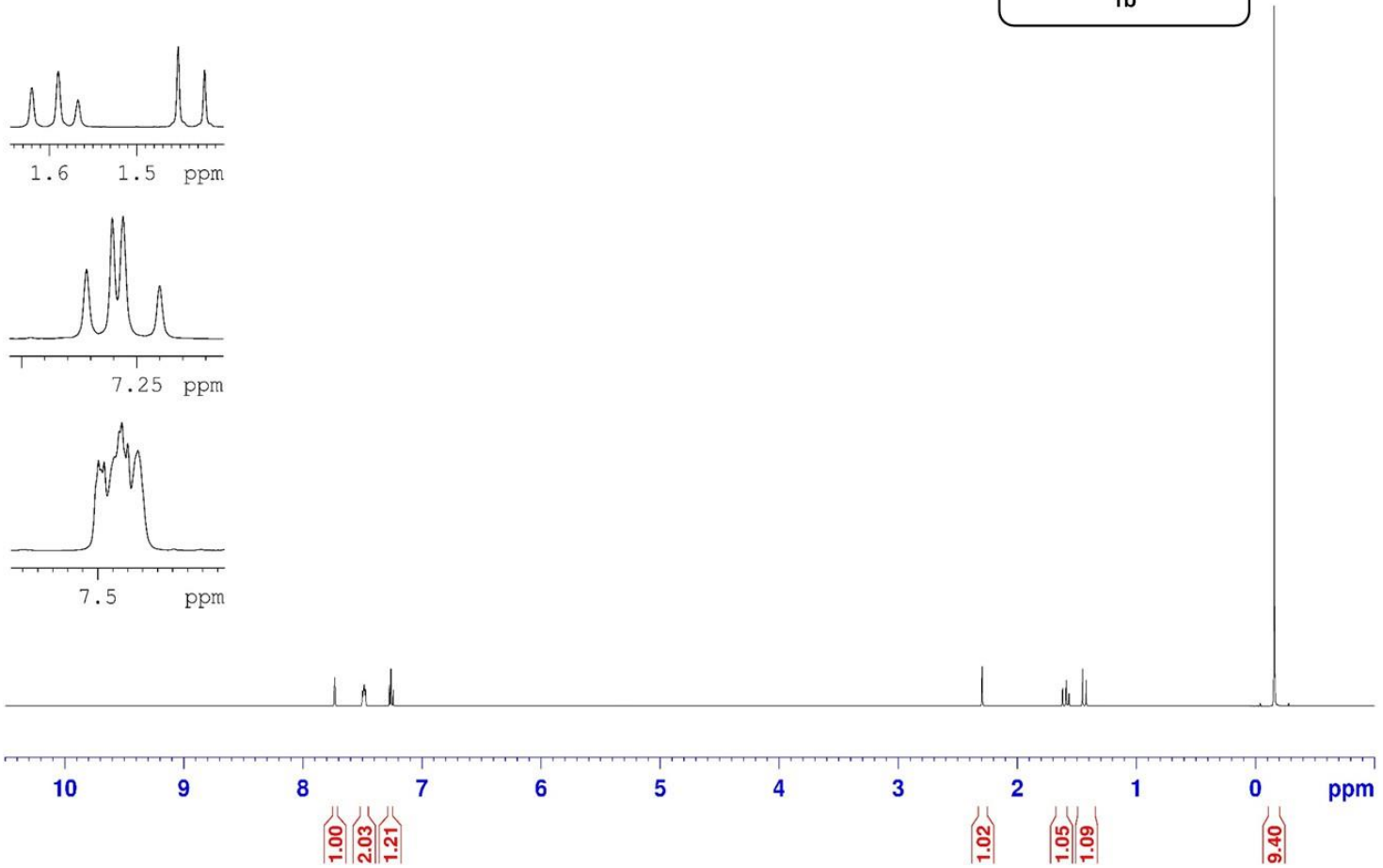


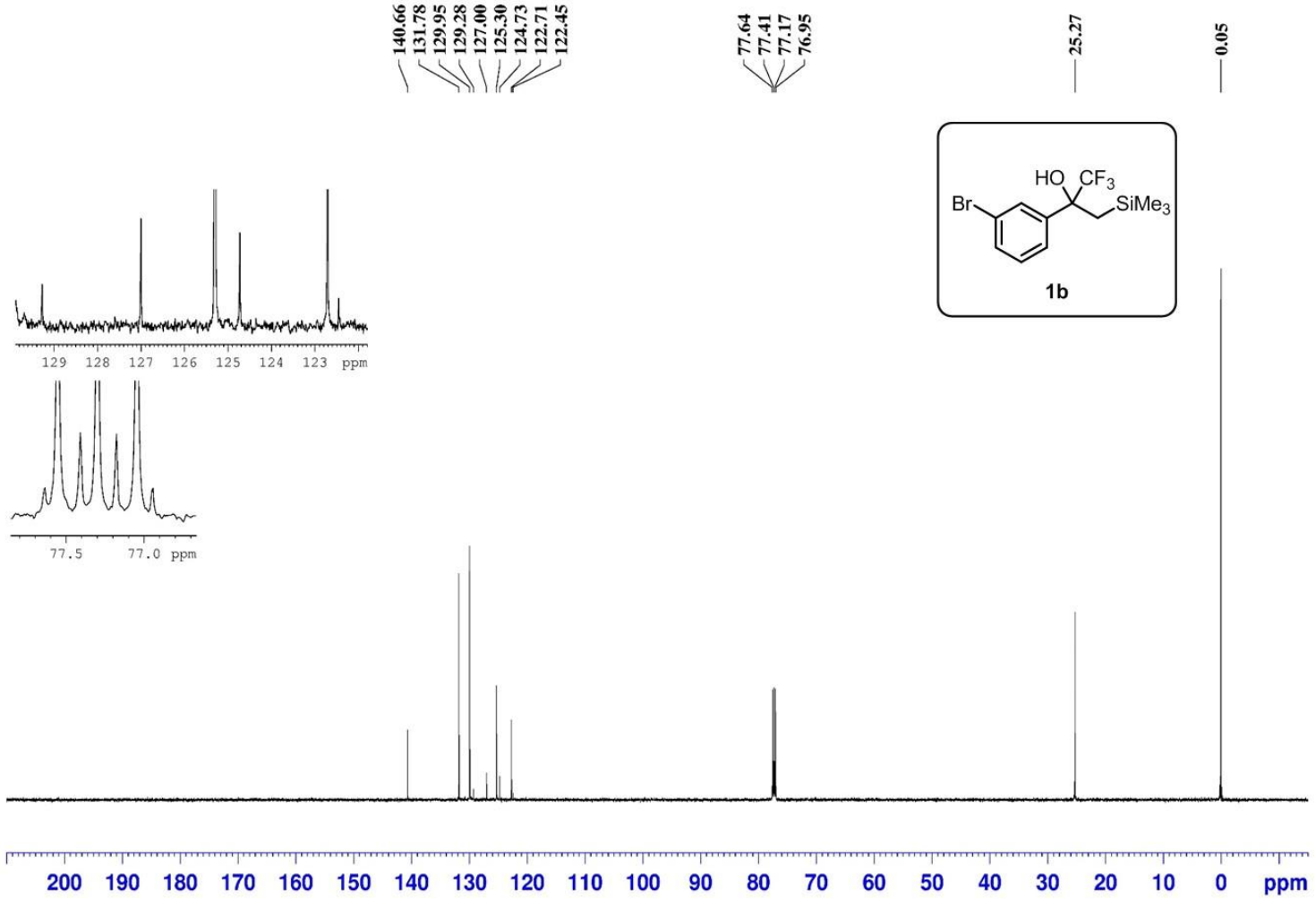
**2–(3–Bromophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**500 MHz, CDCl3**



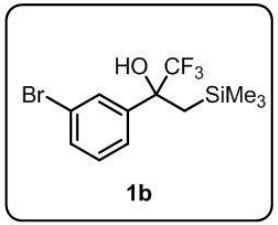

**1b**



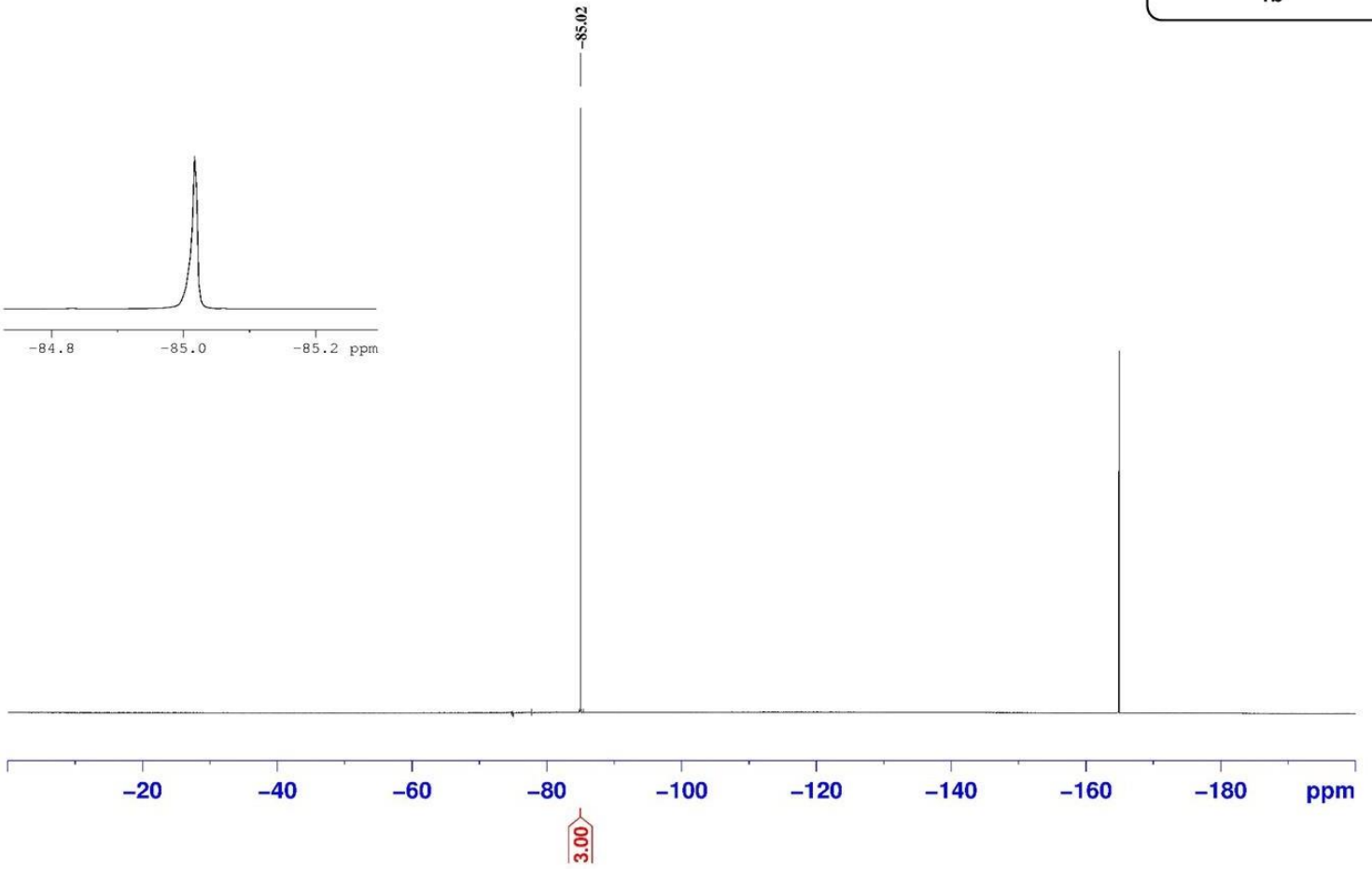
**2–(3–Bromophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**125 MHz, CDCl3**



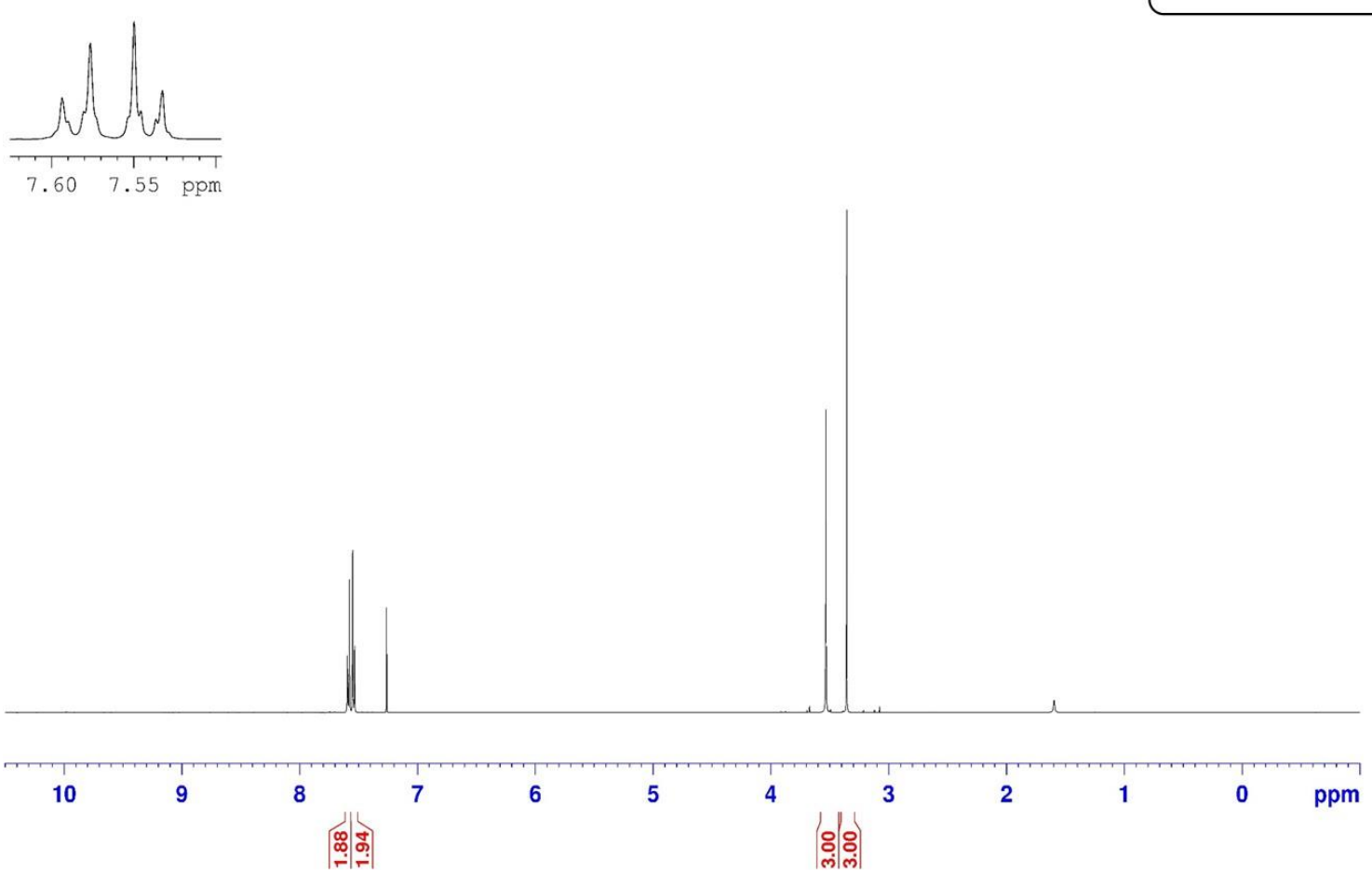
**2–(3–bromophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**CDCl3, 471 MHz**



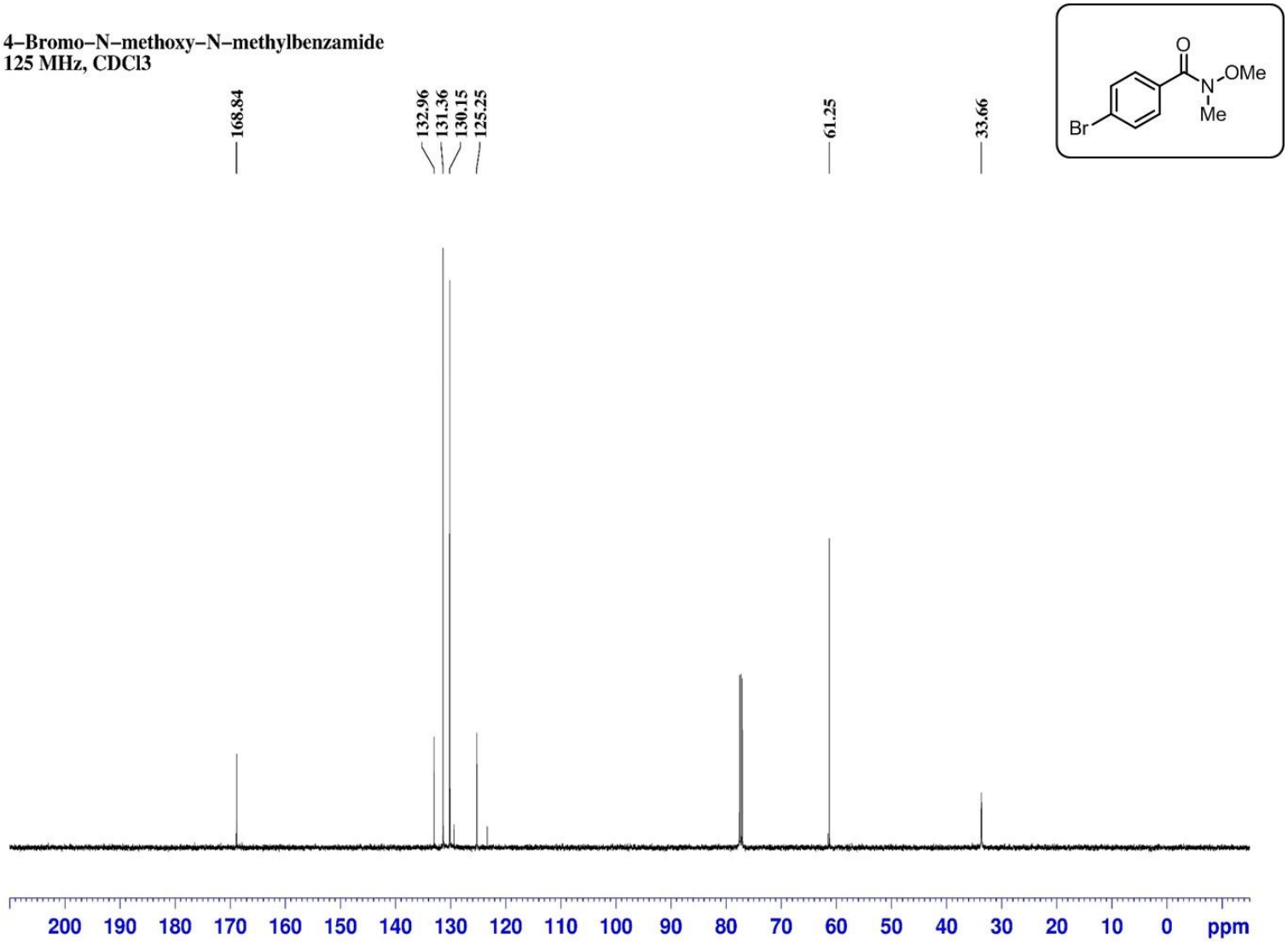

**1b**



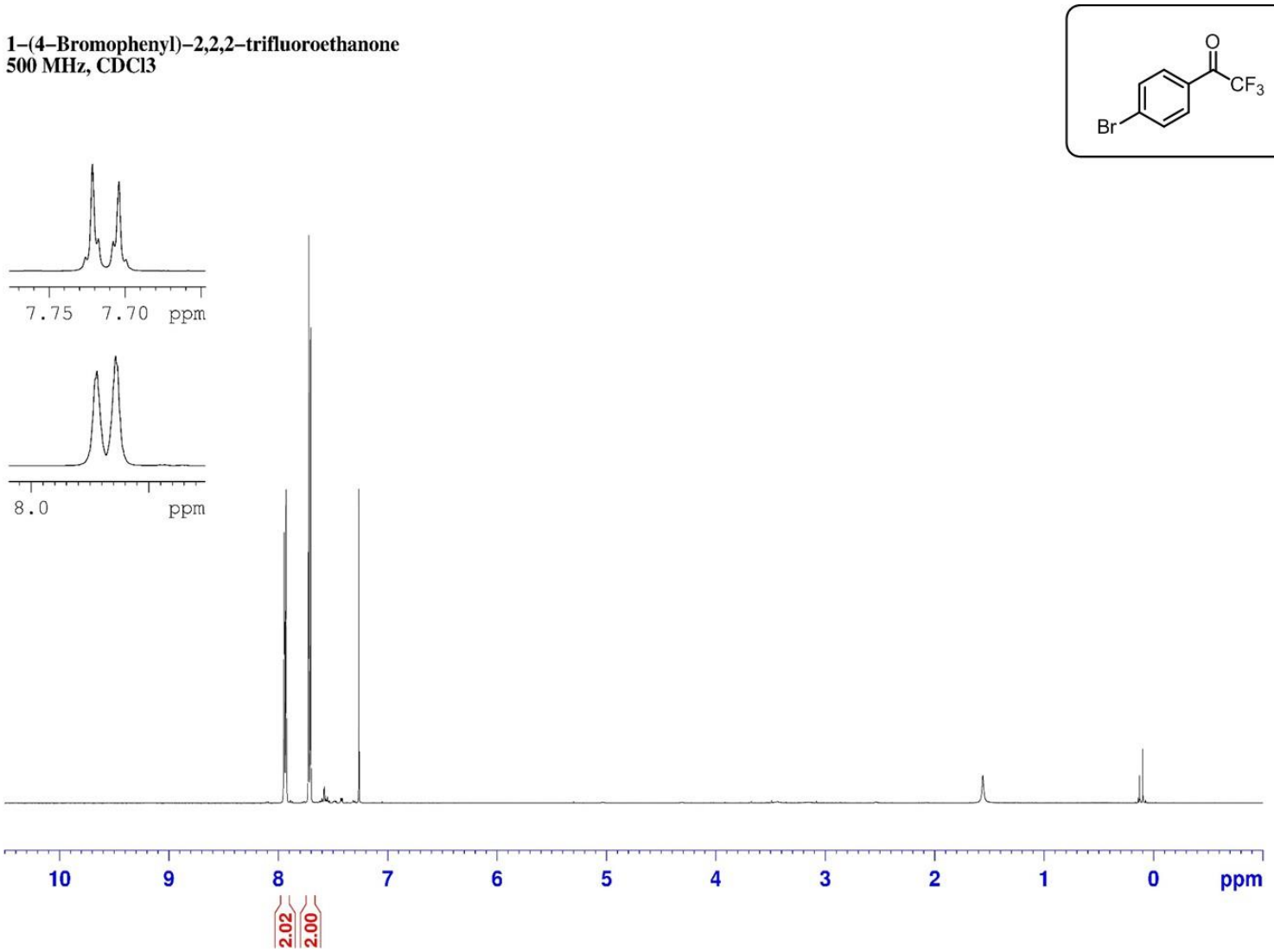
**4–Bromo–N–methoxy–N–methylbenzamide**
**500 MHz, CDCl3**



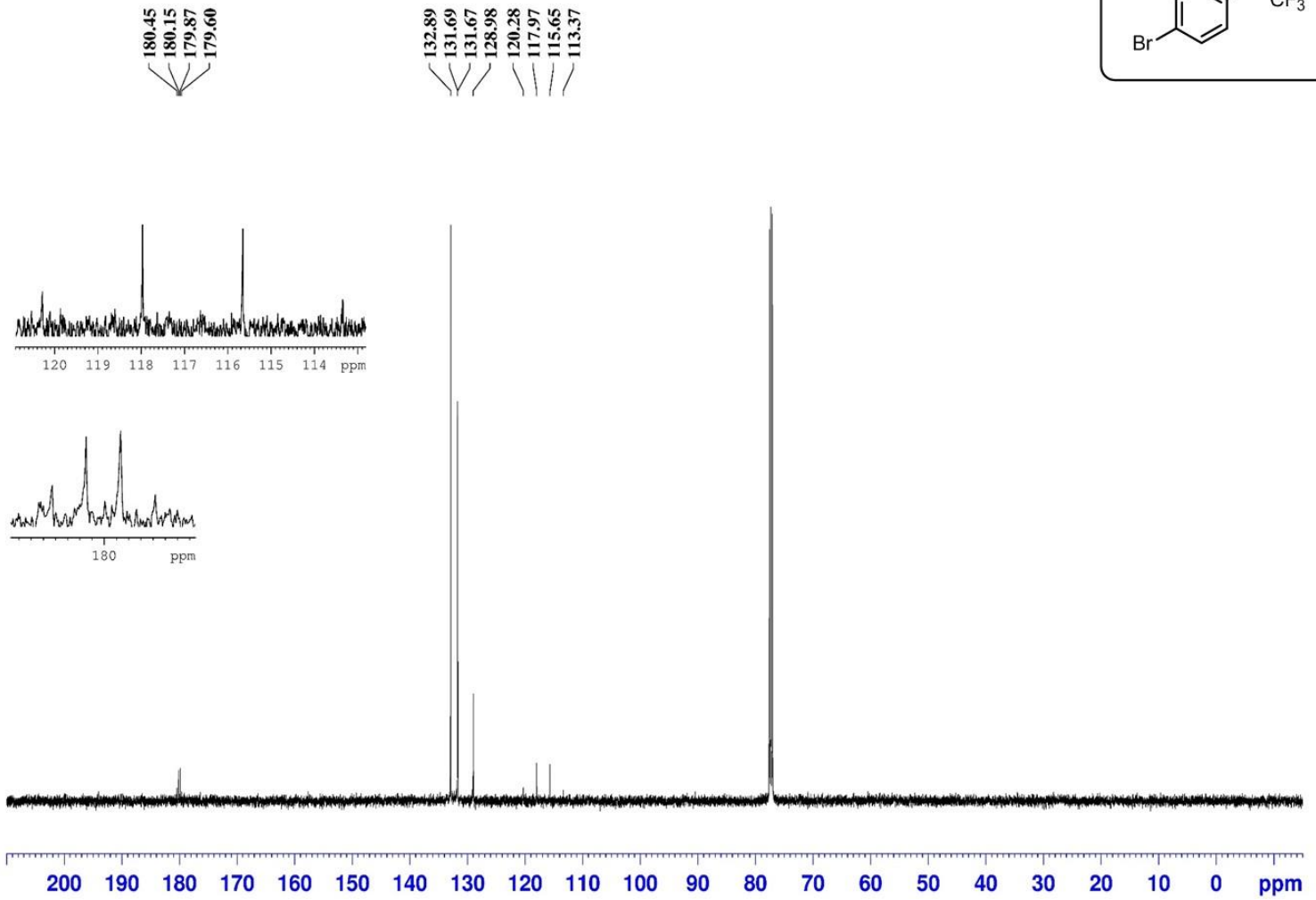
**4–Bromo–N–methoxy–N–methylbenzamide**
**125 MHz, CDCl3**

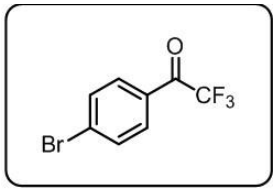


**1–(4–Bromophenyl)–2,2,2–trifluoroethanone**
**500 MHz, CDCl3**

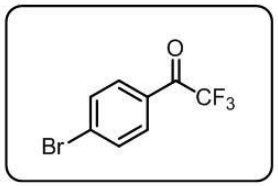


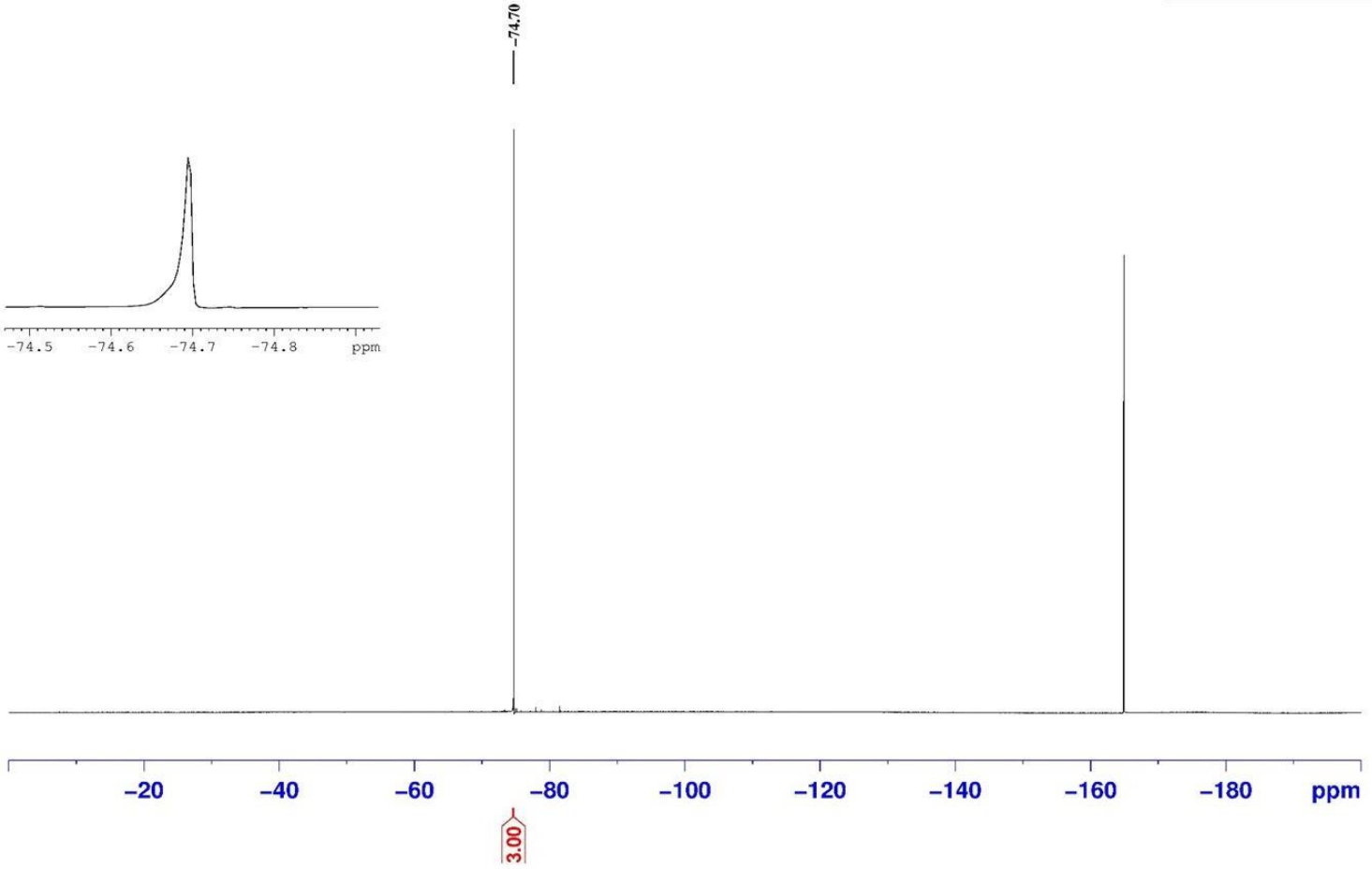
**1–(4–Bromophenyl)–2,2,2–trifluoroethanone**
**125 MHz, CDCl3**



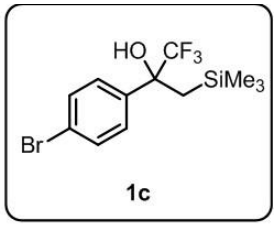



**1–(4–bromophenyl)–2,2,2–trifluoroethanone**
**CDCl3, 471 MHz**

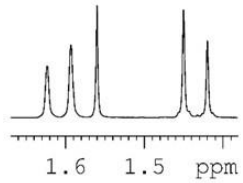


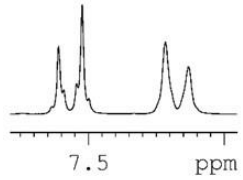



**2–(4–Bromophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**500 MHz, CDCl3**

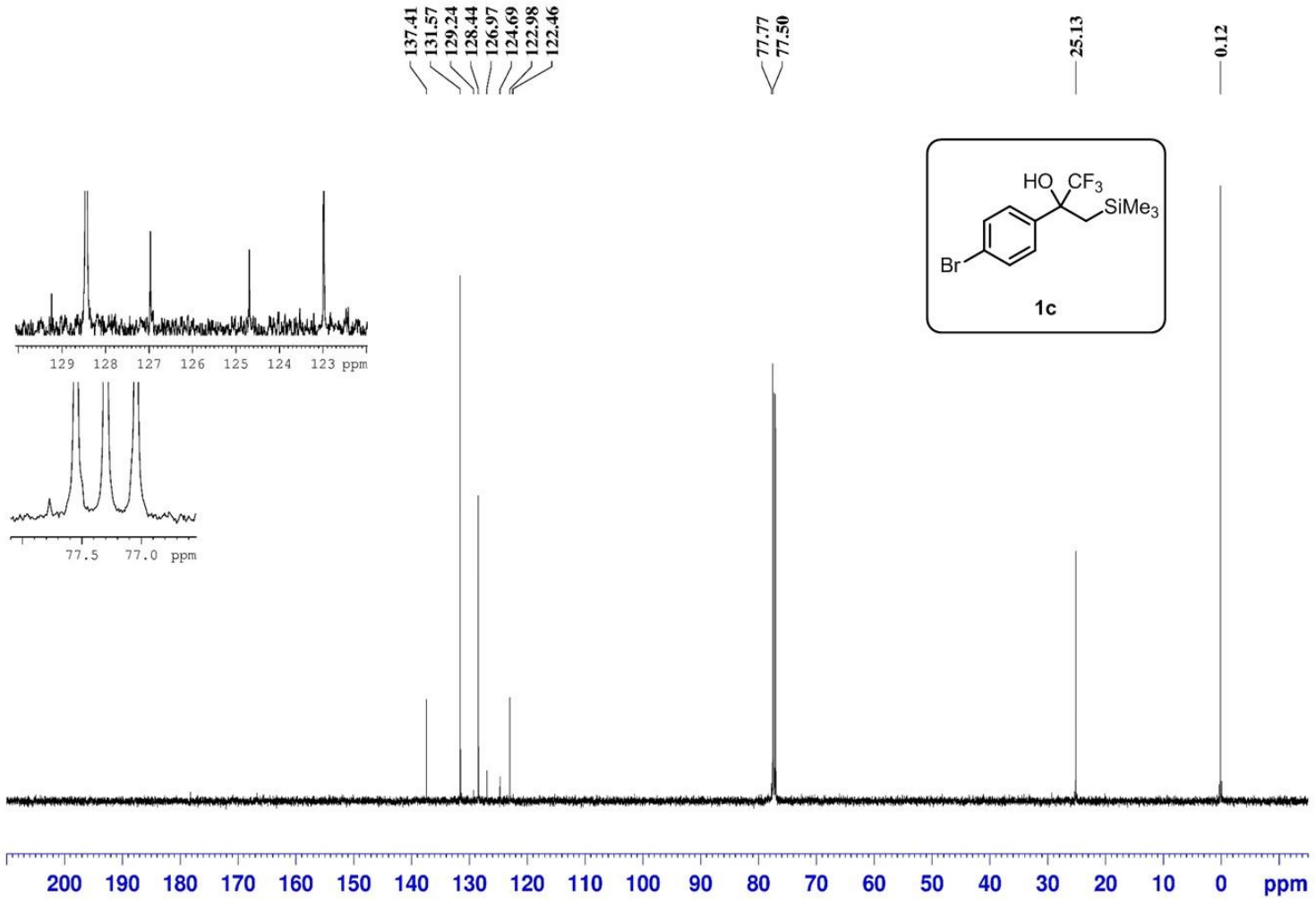



**1c**

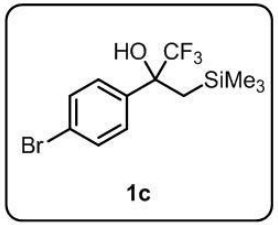


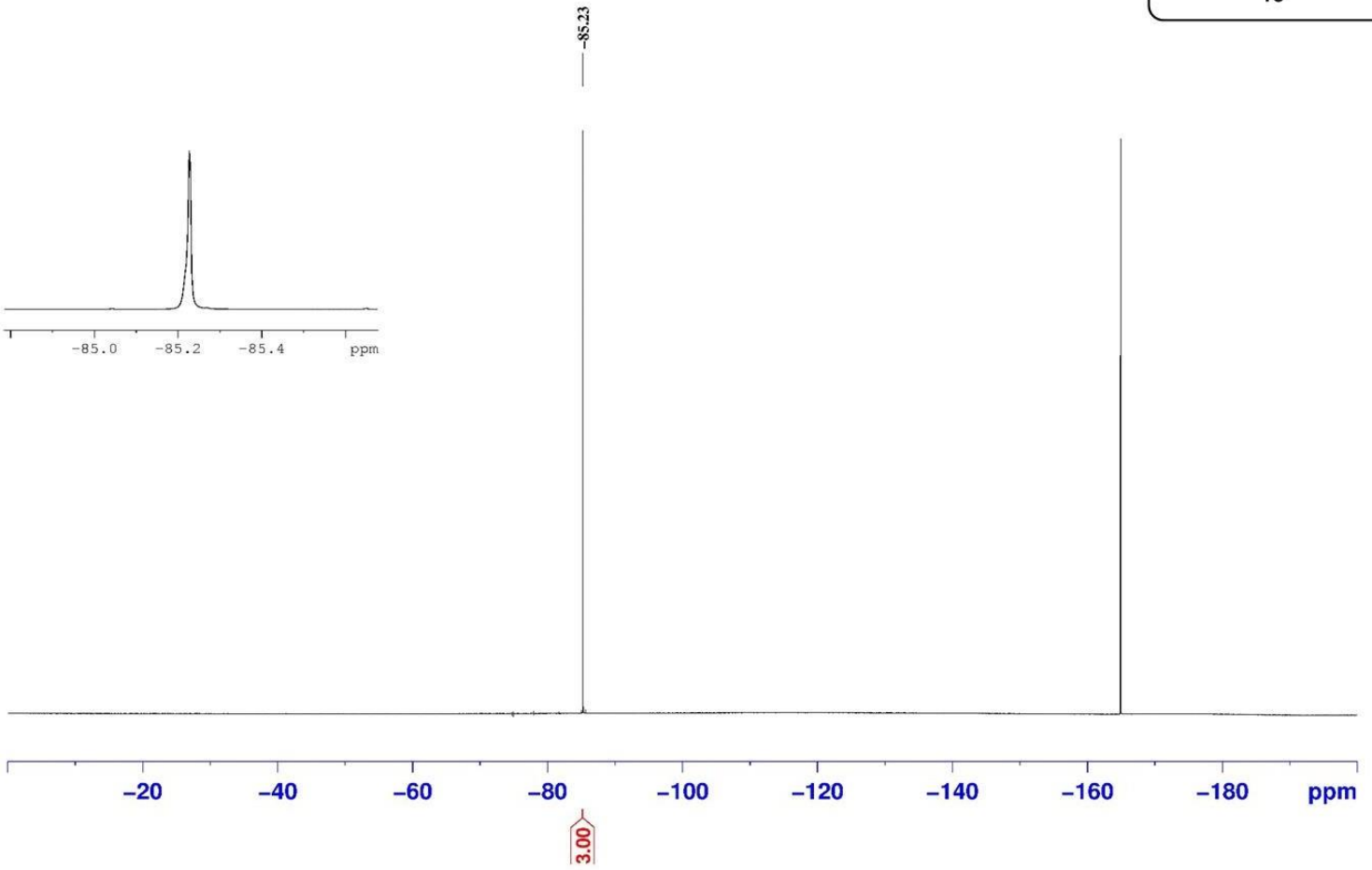



**2–(4–Bromophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**125 MHz, CDCl3**

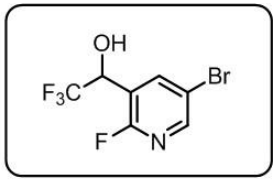


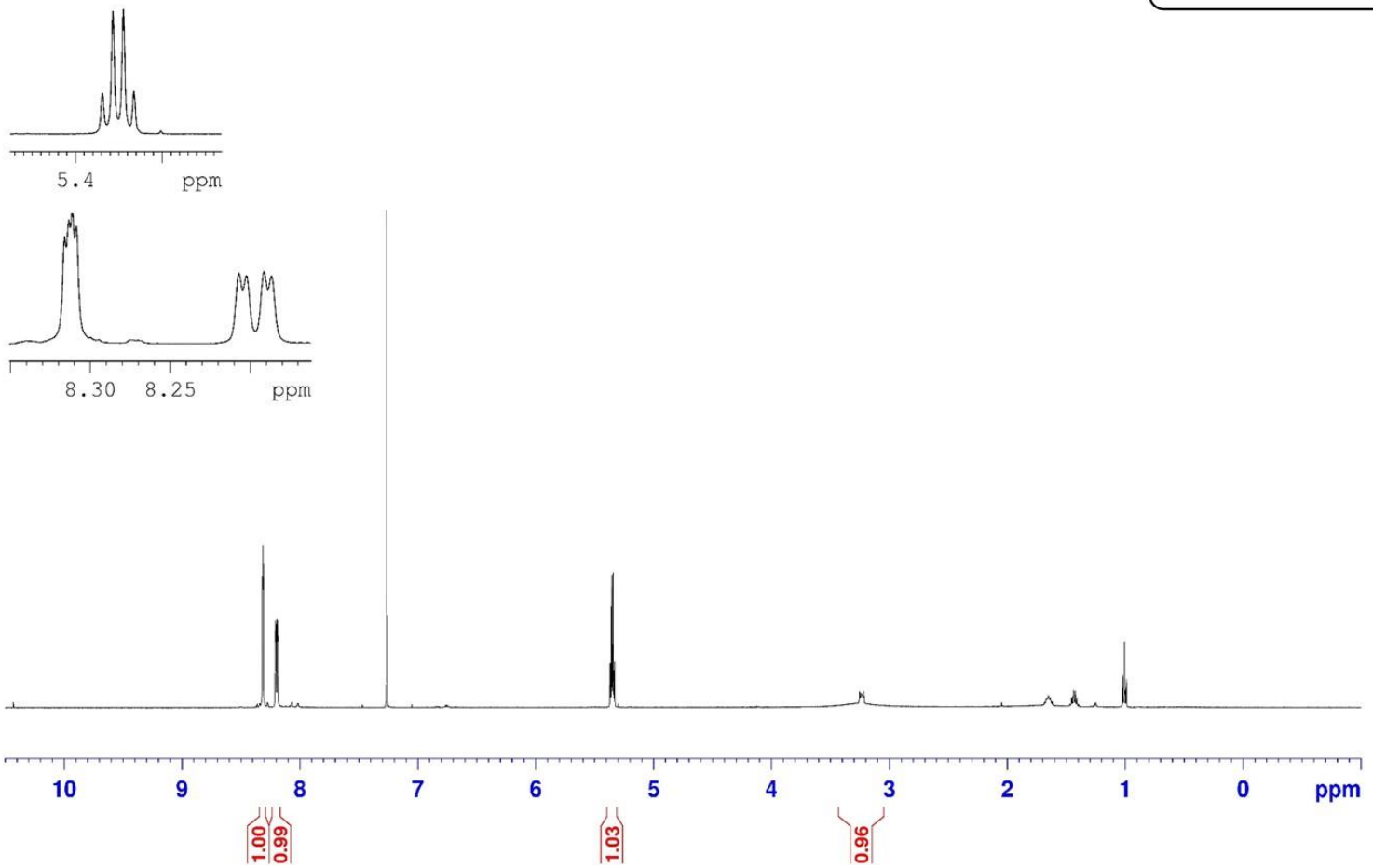
**2–(4–bromophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**CDCl3, 471 MHz**



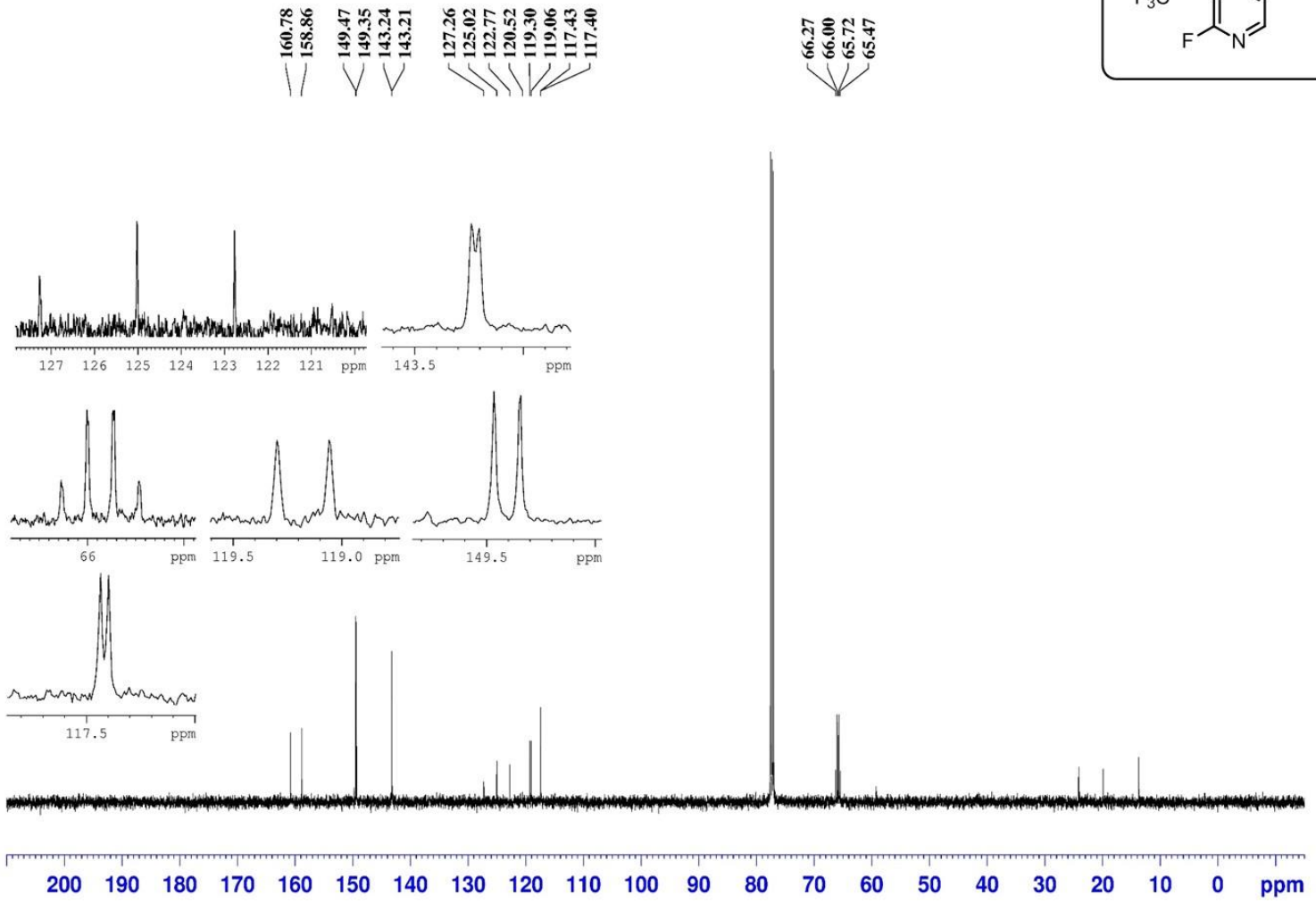



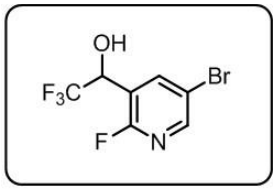
**1–(5–Bromo–2–fluoropyridin–3–yl)–2,2,2–trifluoroethanol**
**500 MHz, CDCl3**



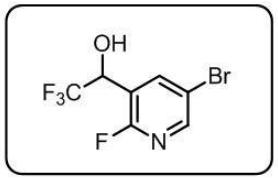



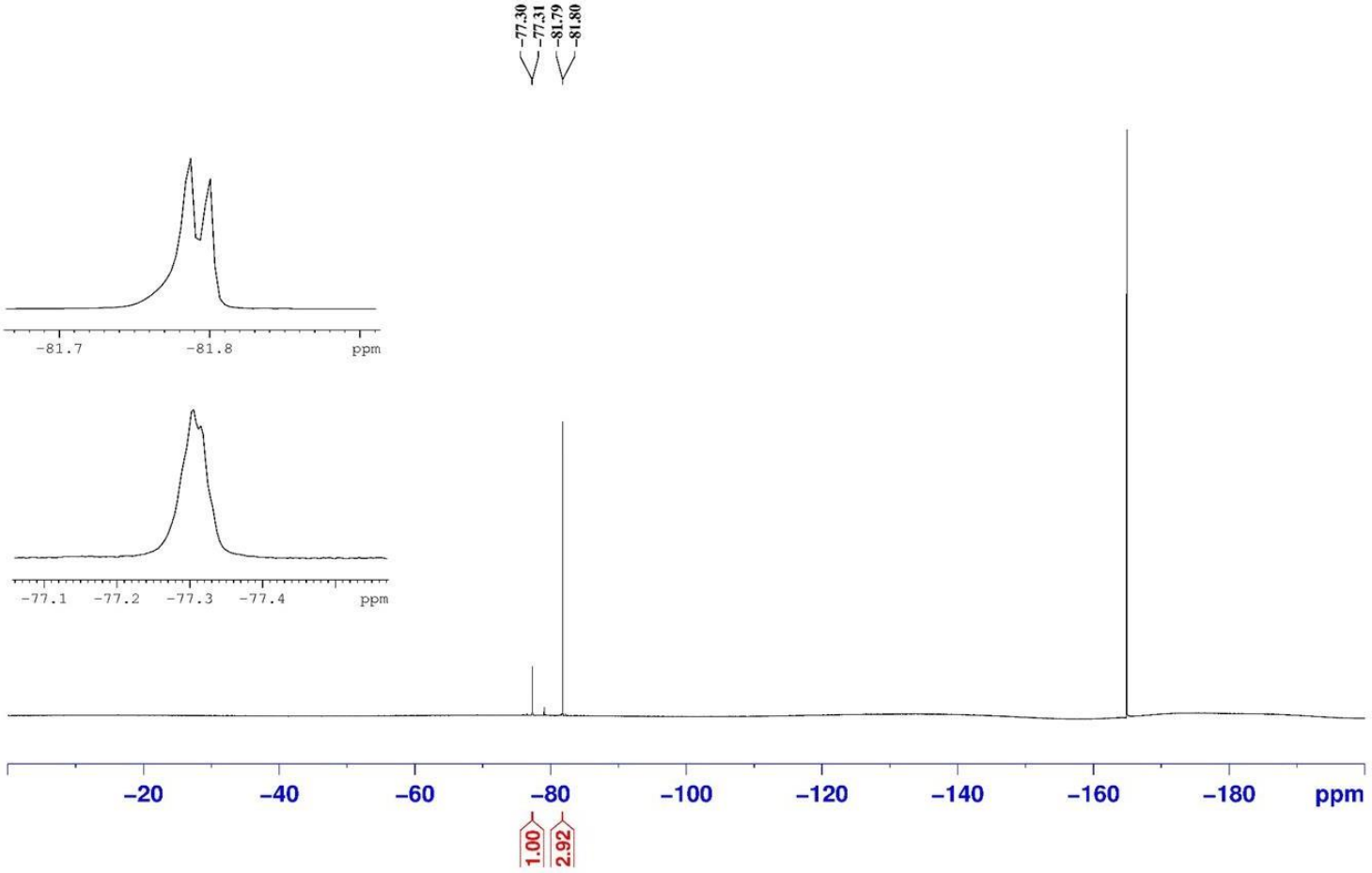
**1–(5–Bromo–2–fluoropyridin–3–yl)–2,2,2–trifluoroethanol**
**125 MHz, CDCl3**



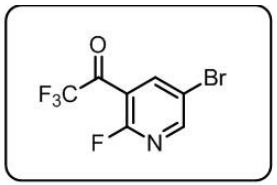



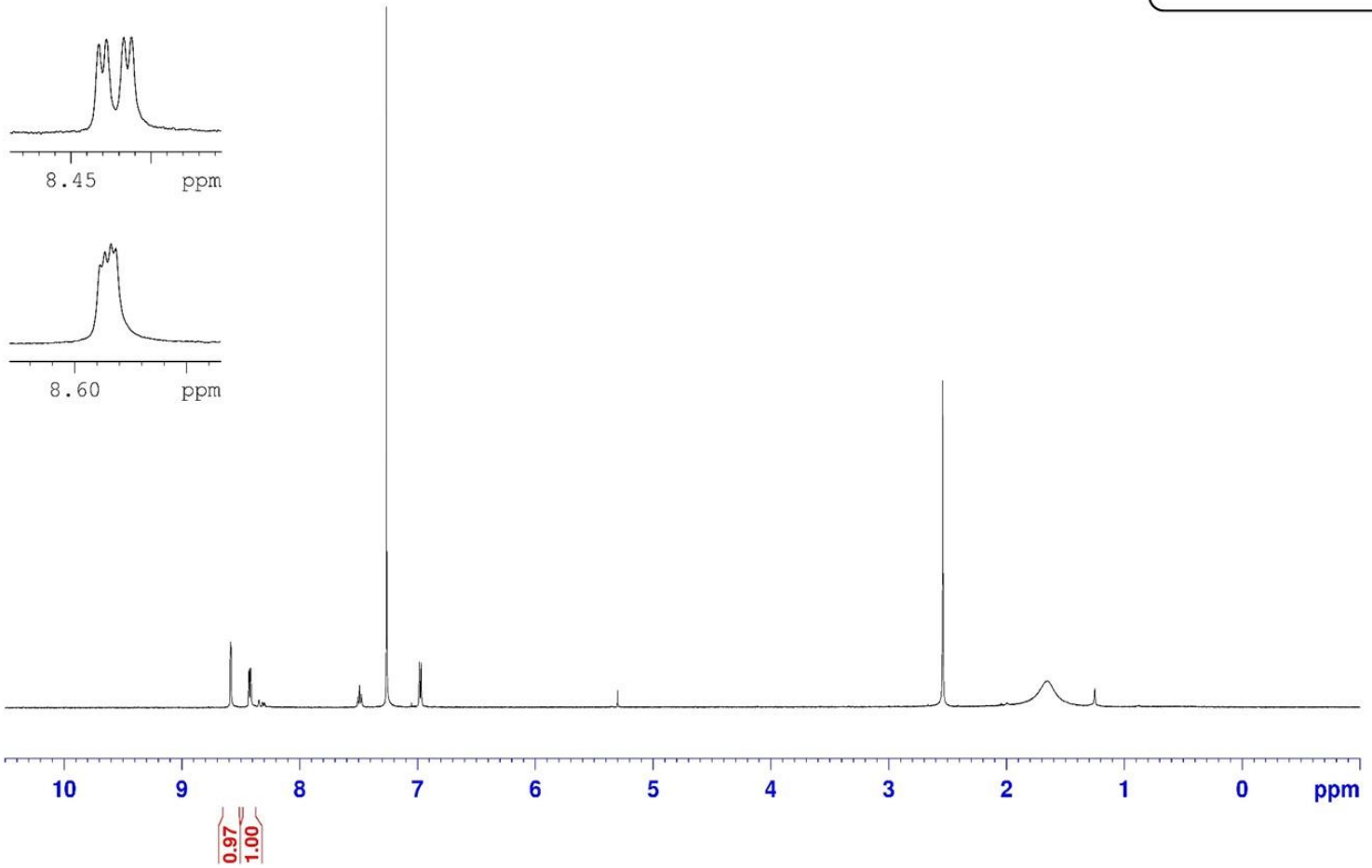
**Trifluoromethylation**
**CDCl3, 471 MHz**



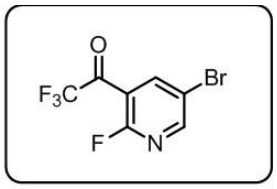



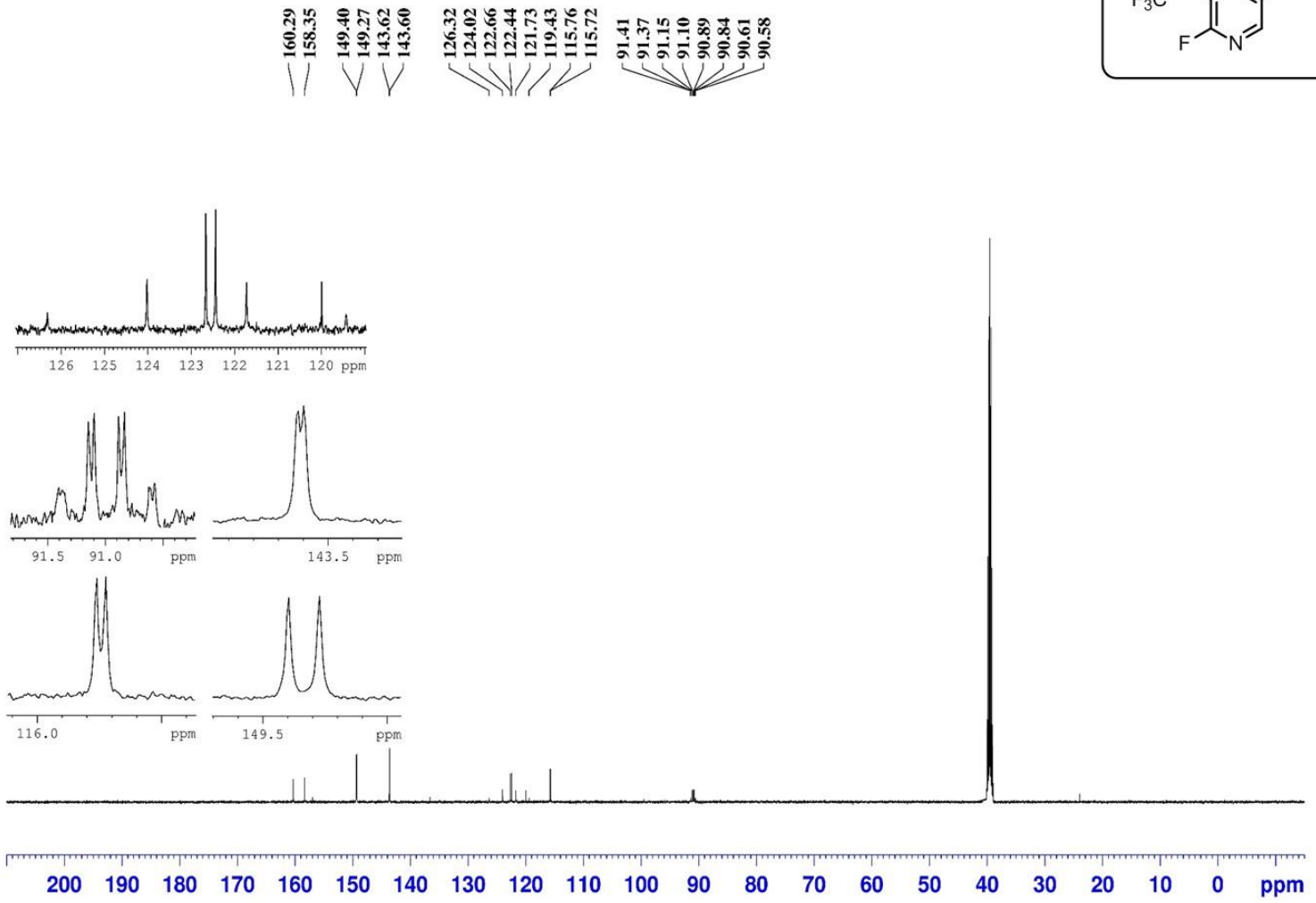
**1–(5–Bromo–2–fluoropyridin–3–yl)–2,2,2–trifluoroethanone**
**500 MHz, CDCl3**



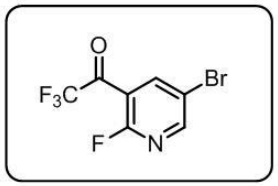



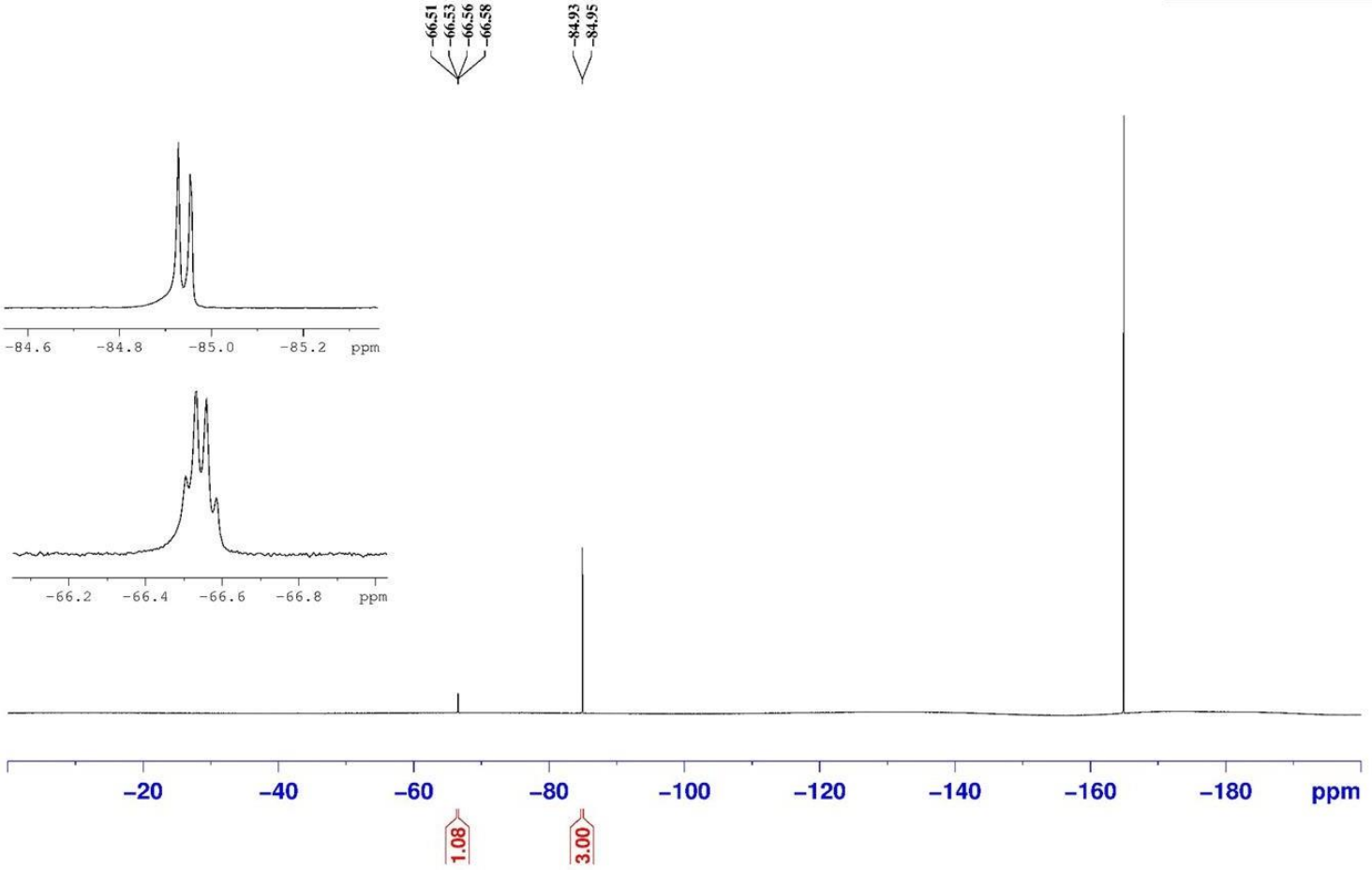
**1–(5–Bromo–2–fluoropyridin–3–yl)–2,2,2–trifluoroethanone**
**125 MHz, DMSO–d6**



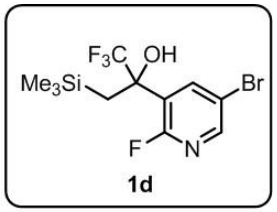



**1–(5–bromo–2–fluoropyridin–3–yl)–2,2,2–trifluoroethanone**
**CDCl3, 471 MHz**

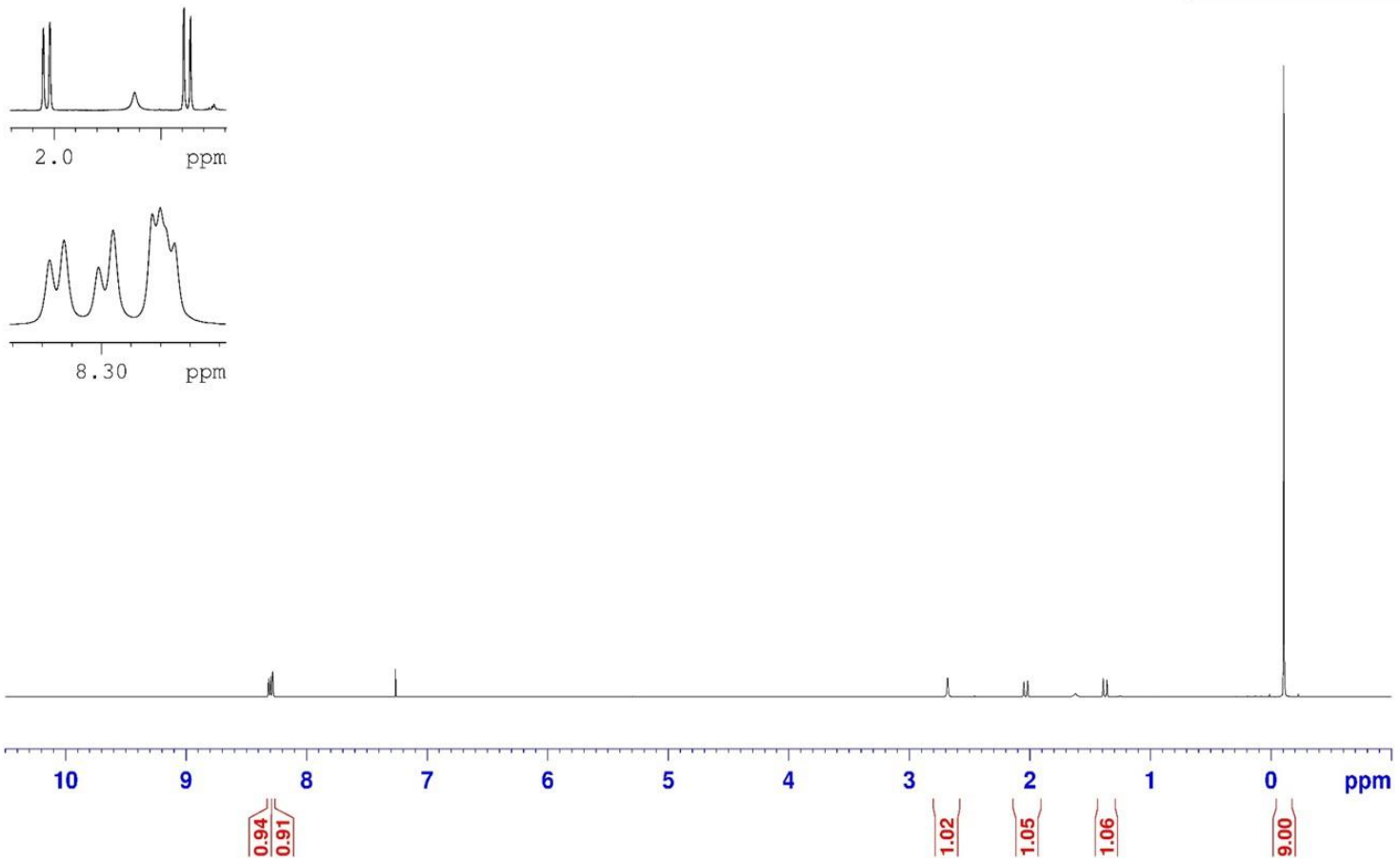


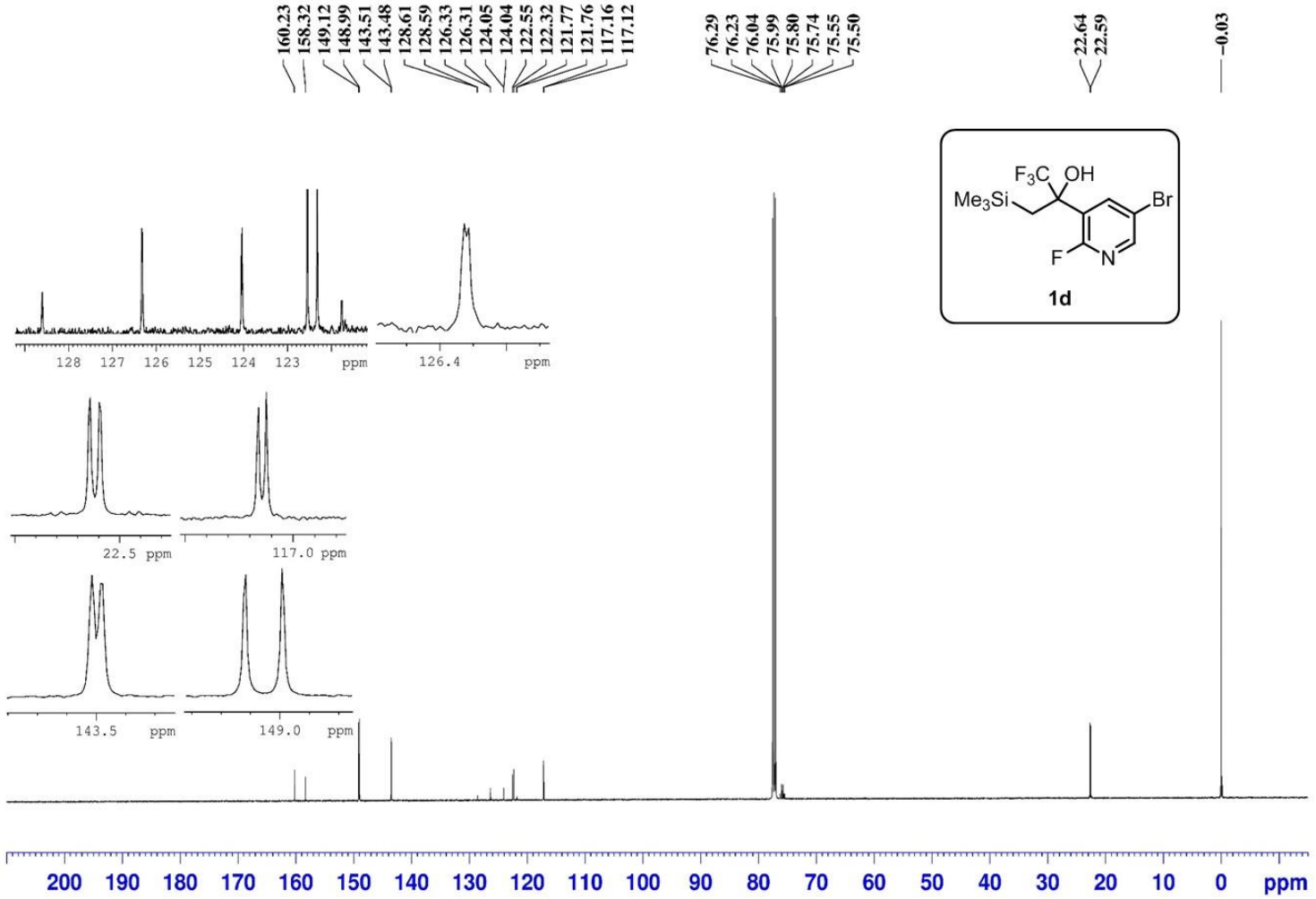
**2–(5–Bromo–2–fluoropyridin–3–yl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**500 MHz, CDCl3**



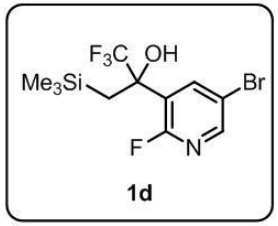
**1d**

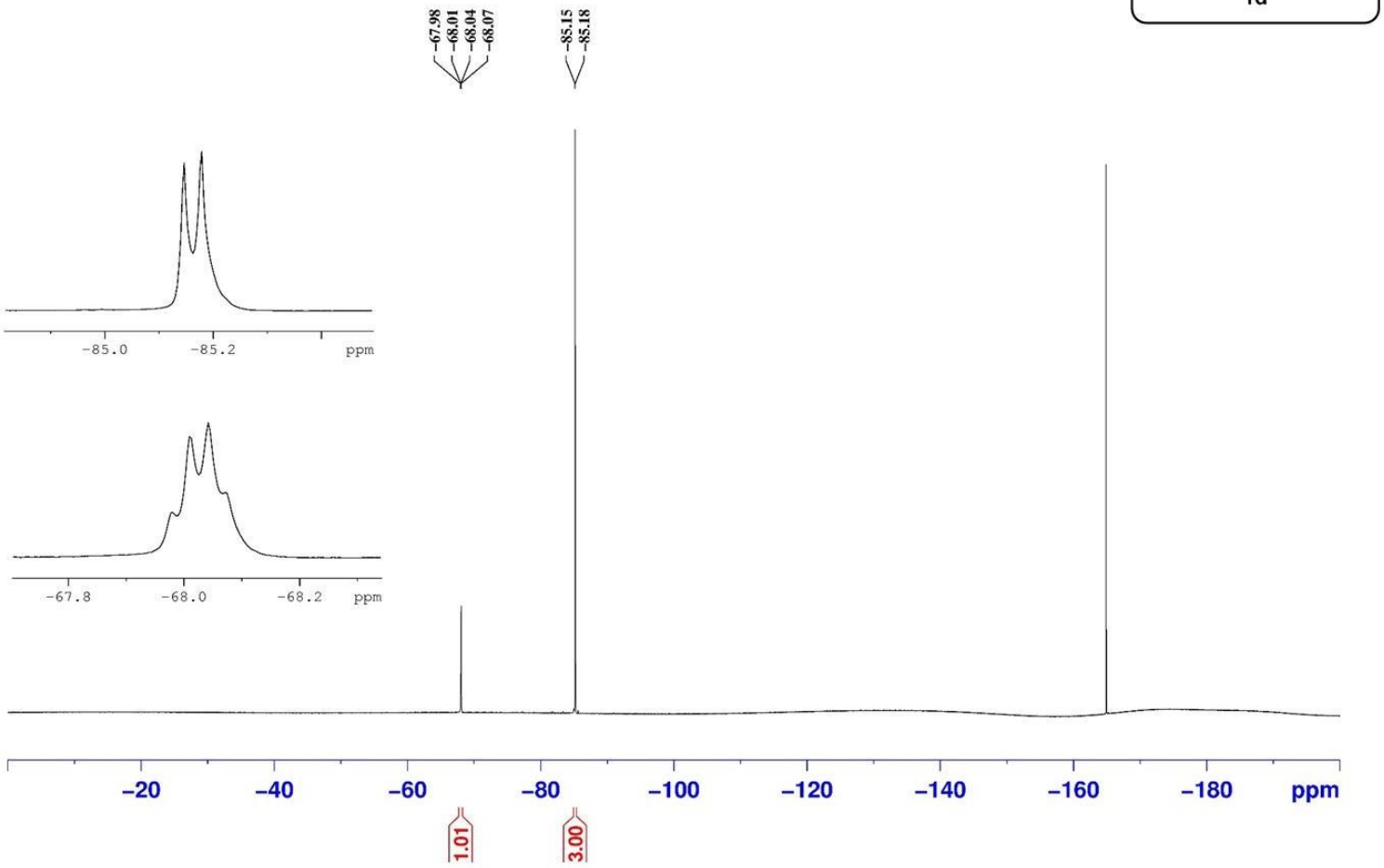


**2–(5–Bromo–2–fluoropyridin–3–yl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**125 MHz, CDCl3**

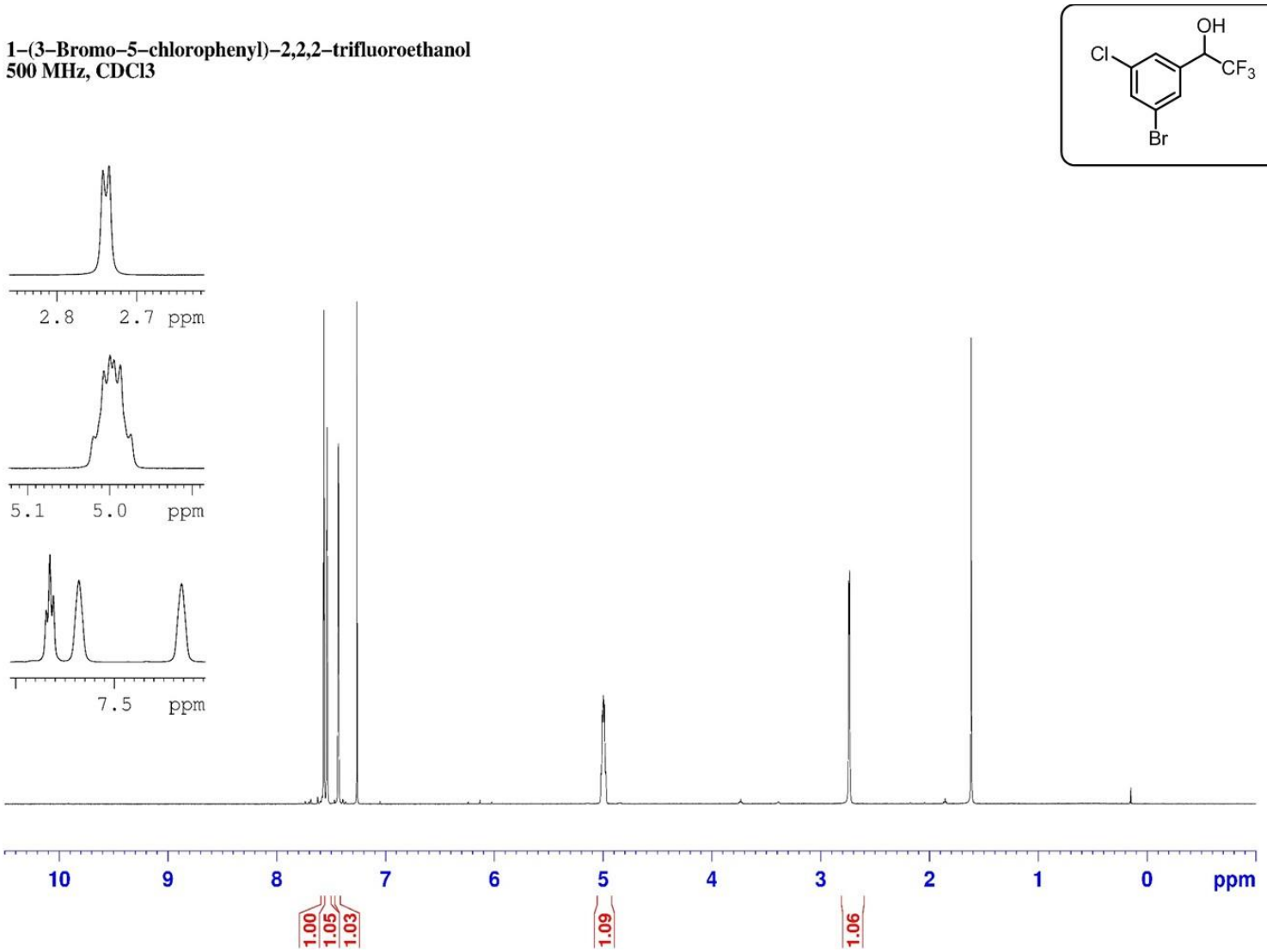


**2–(5–bromo–2–fluoropyridin–3–yl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**CDCl3, 471 MHz**

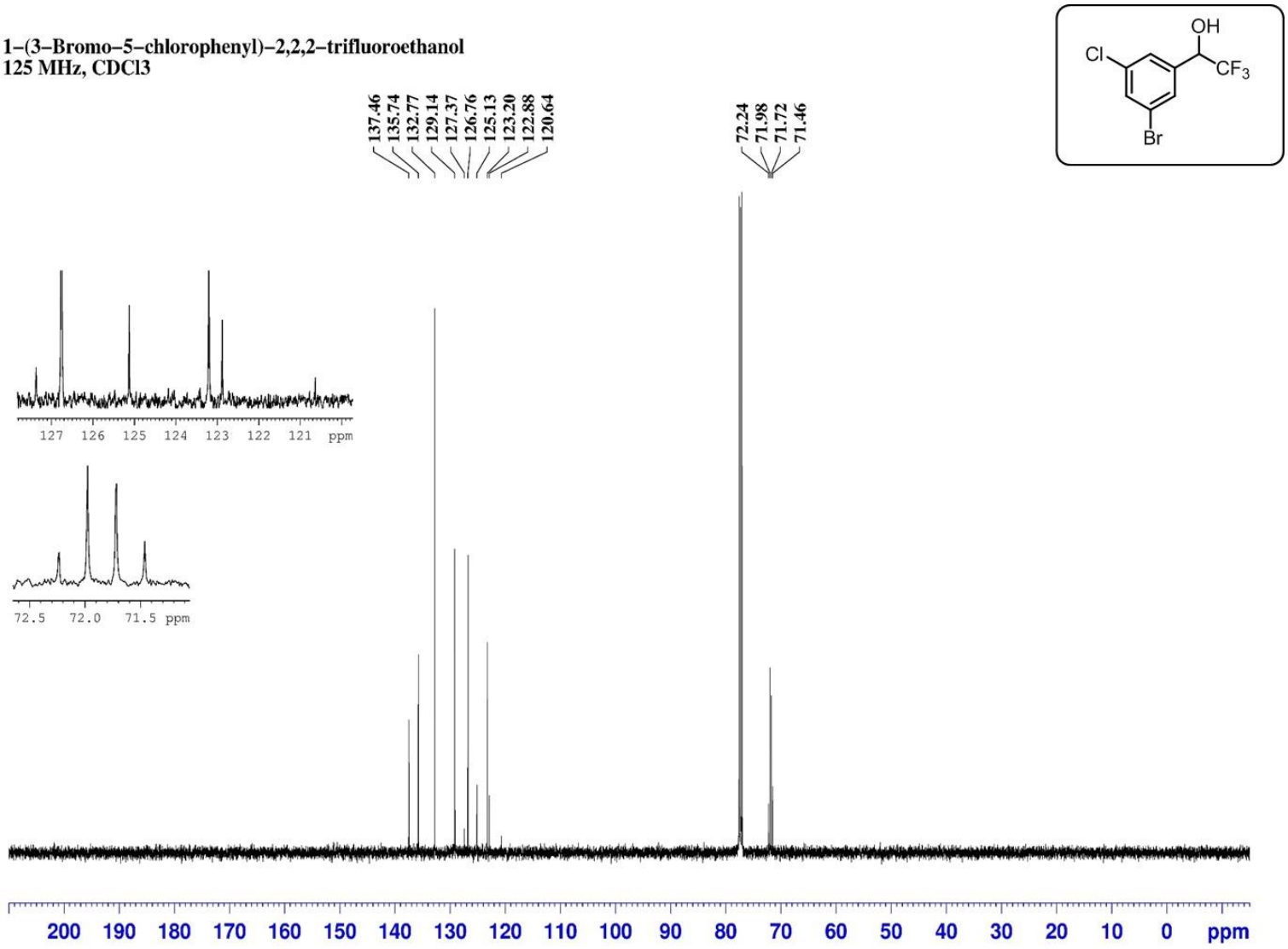


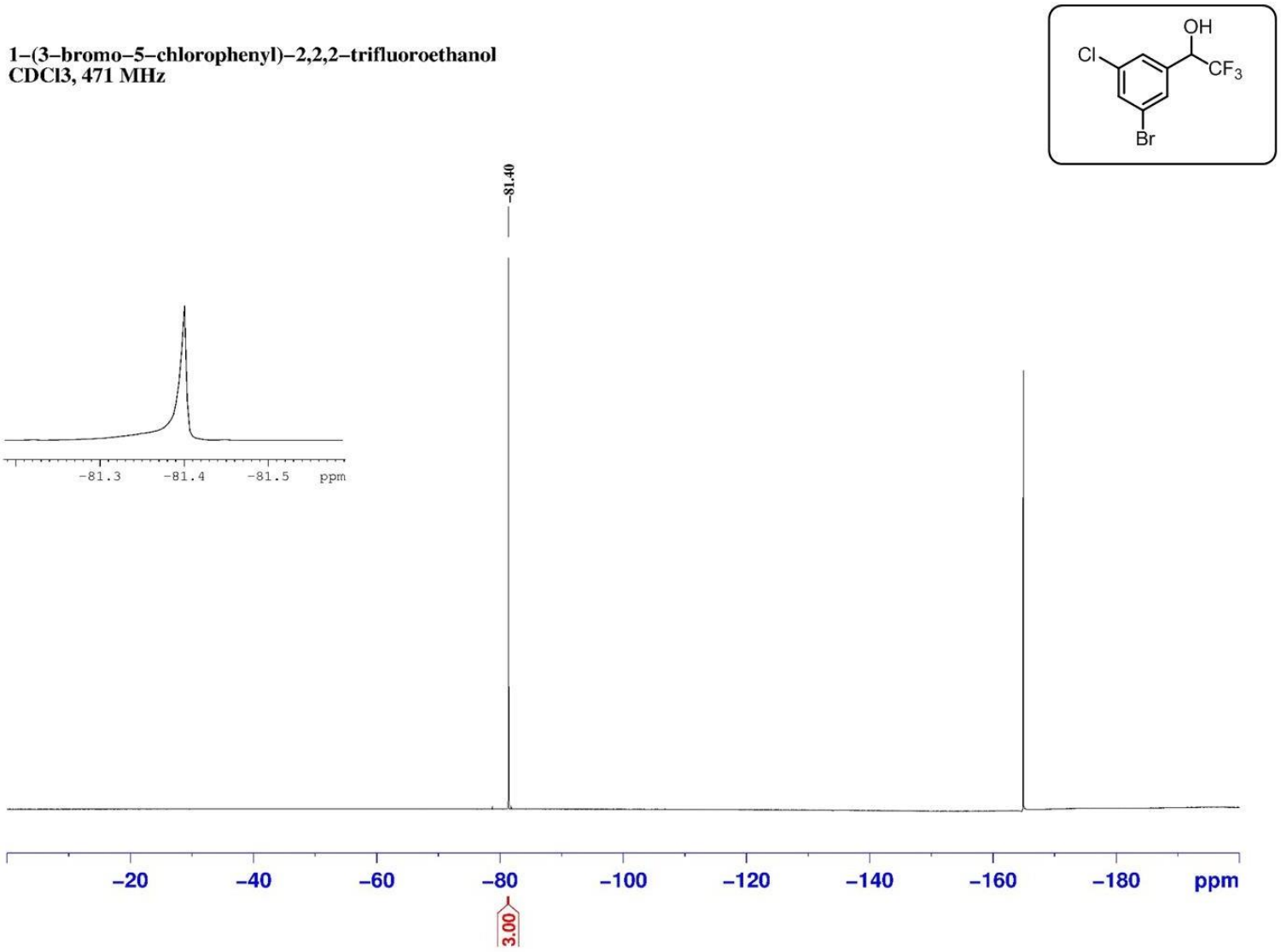
**1–(3–Bromo–5–chlorophenyl)–2,2,2–trifluoroethanol**
**500 MHz, CDCl3**



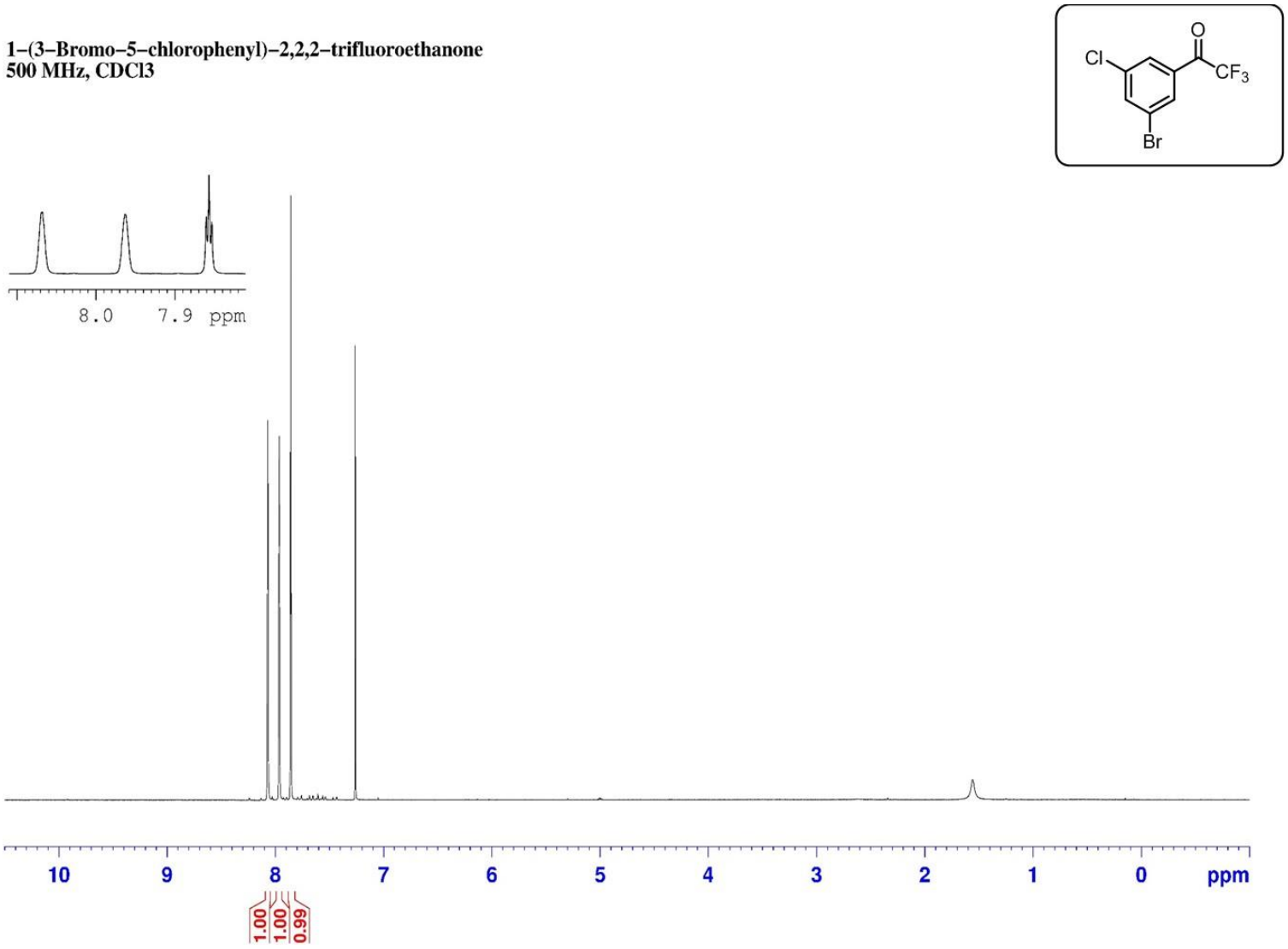
**1–(3–Bromo–5–chlorophenyl)–2,2,2–trifluoroethanol**
**125 MHz, CDCl3**



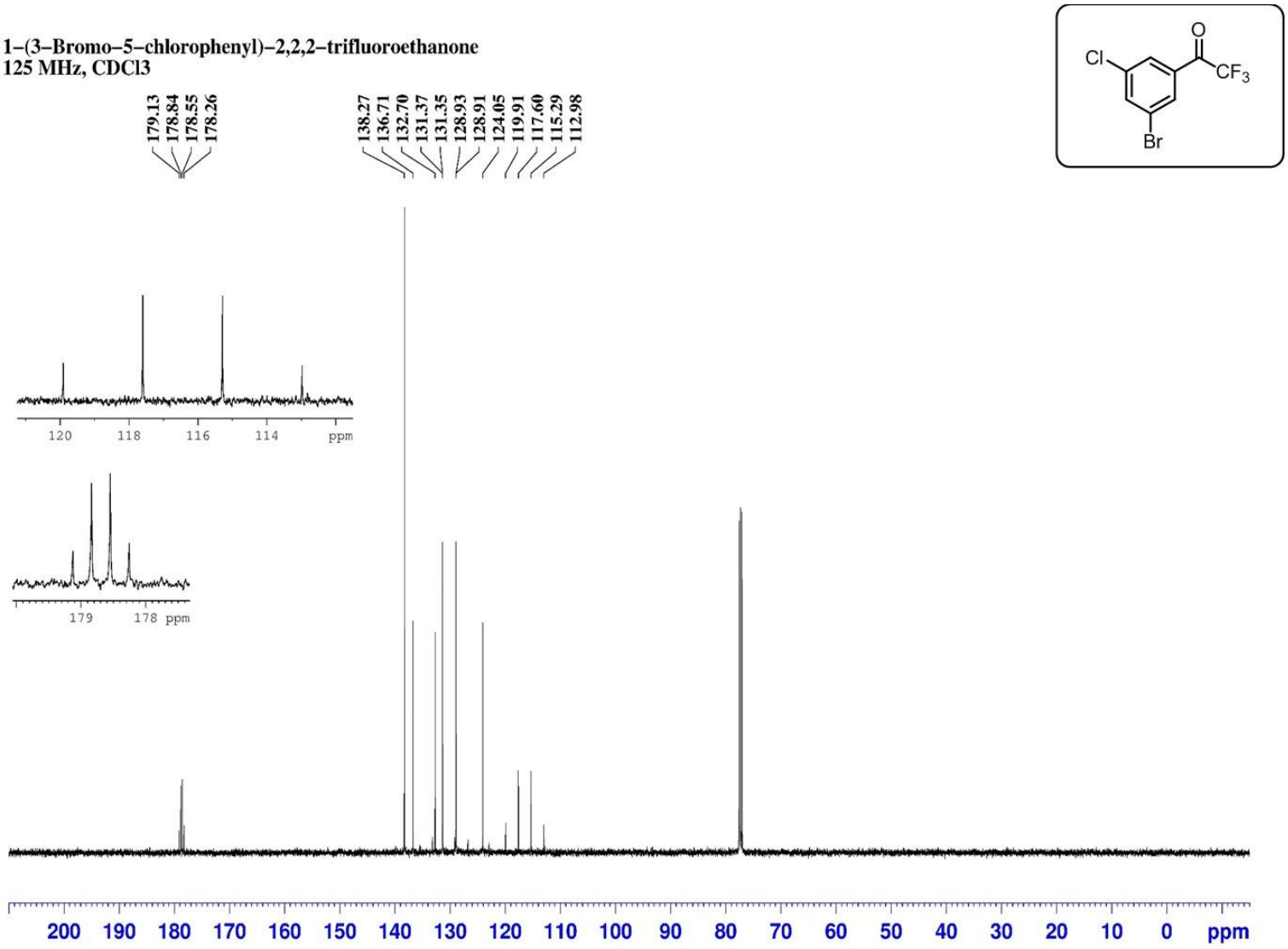
**1–(3–bromo–5–chlorophenyl)–2,2,2–trifluoroethanol**
**CDCl3, 471 MHz**



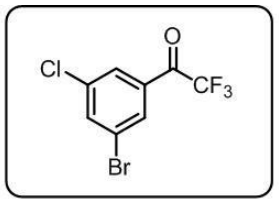
**1–(3–Bromo–5–chlorophenyl)–2,2,2–trifluoroethanone**
**500 MHz, CDCl3**

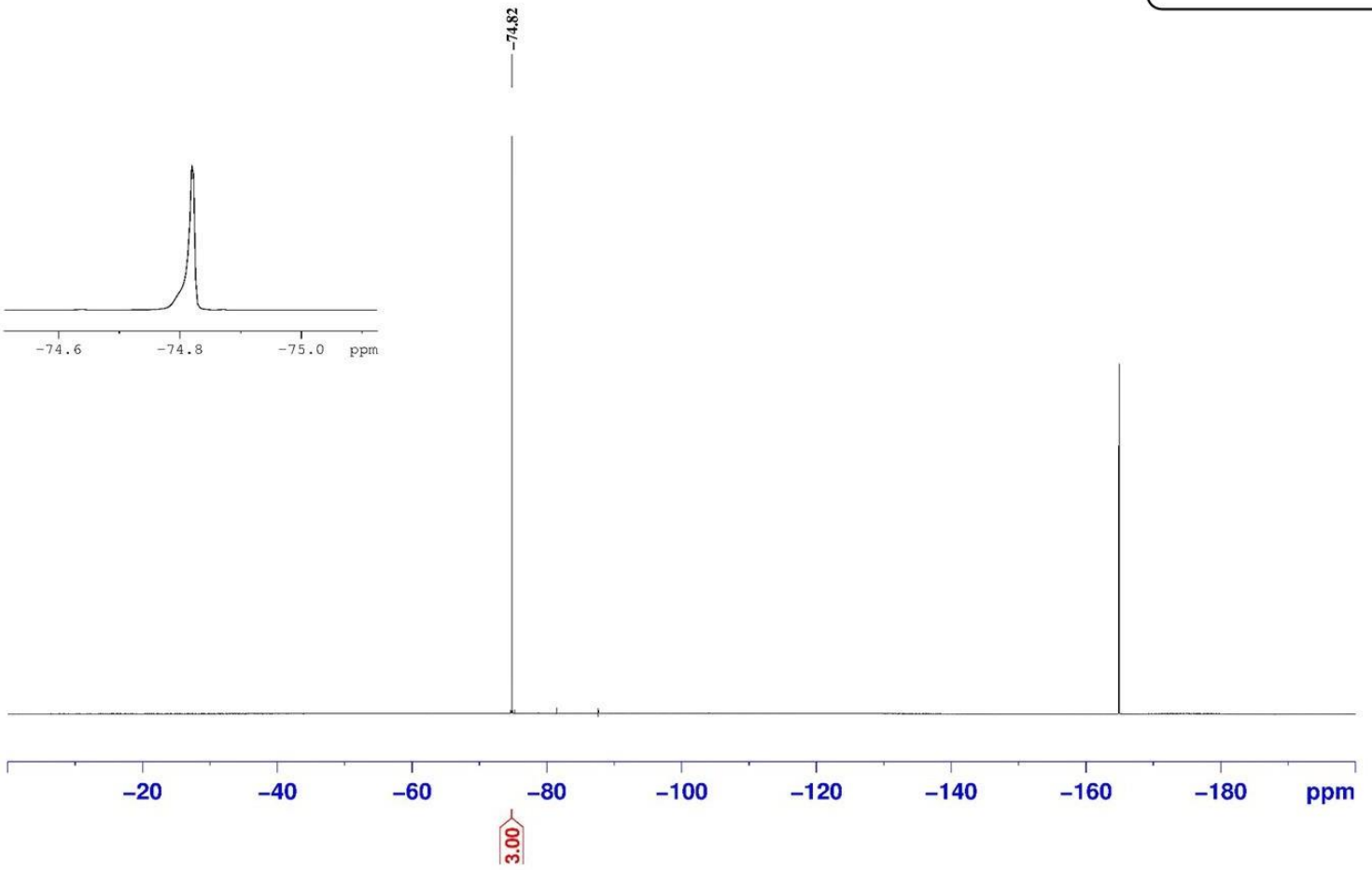


**1–(3–Bromo–5–chlorophenyl)–2,2,2–trifluoroethanone**
**125 MHz, CDCl3**

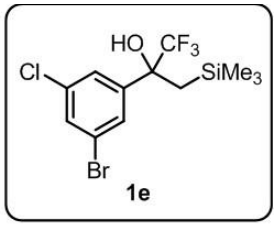


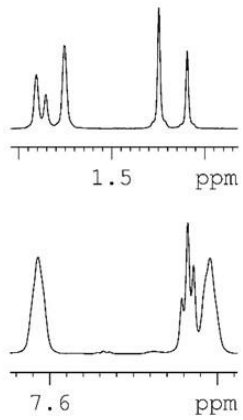
**1–(3–bromo–5–chlorophenyl)–2,2,2–trifluoroethanone**
**CDCl3, 471 MHz**



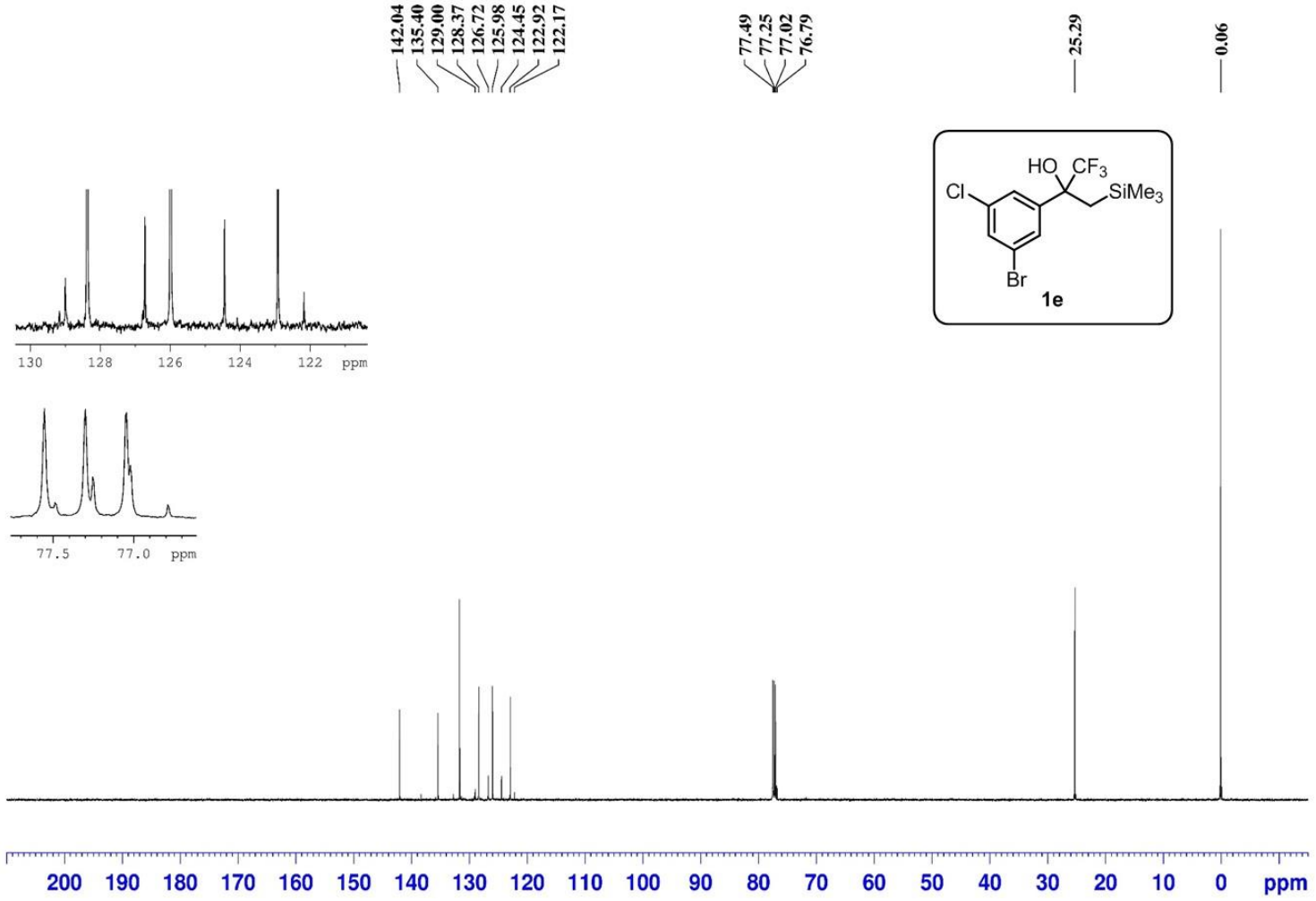



**2–(3–Bromo–5–chlorophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**500 MHz, CDCl3**

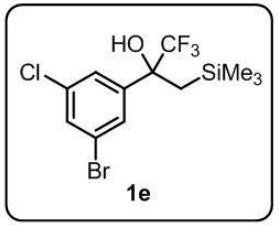


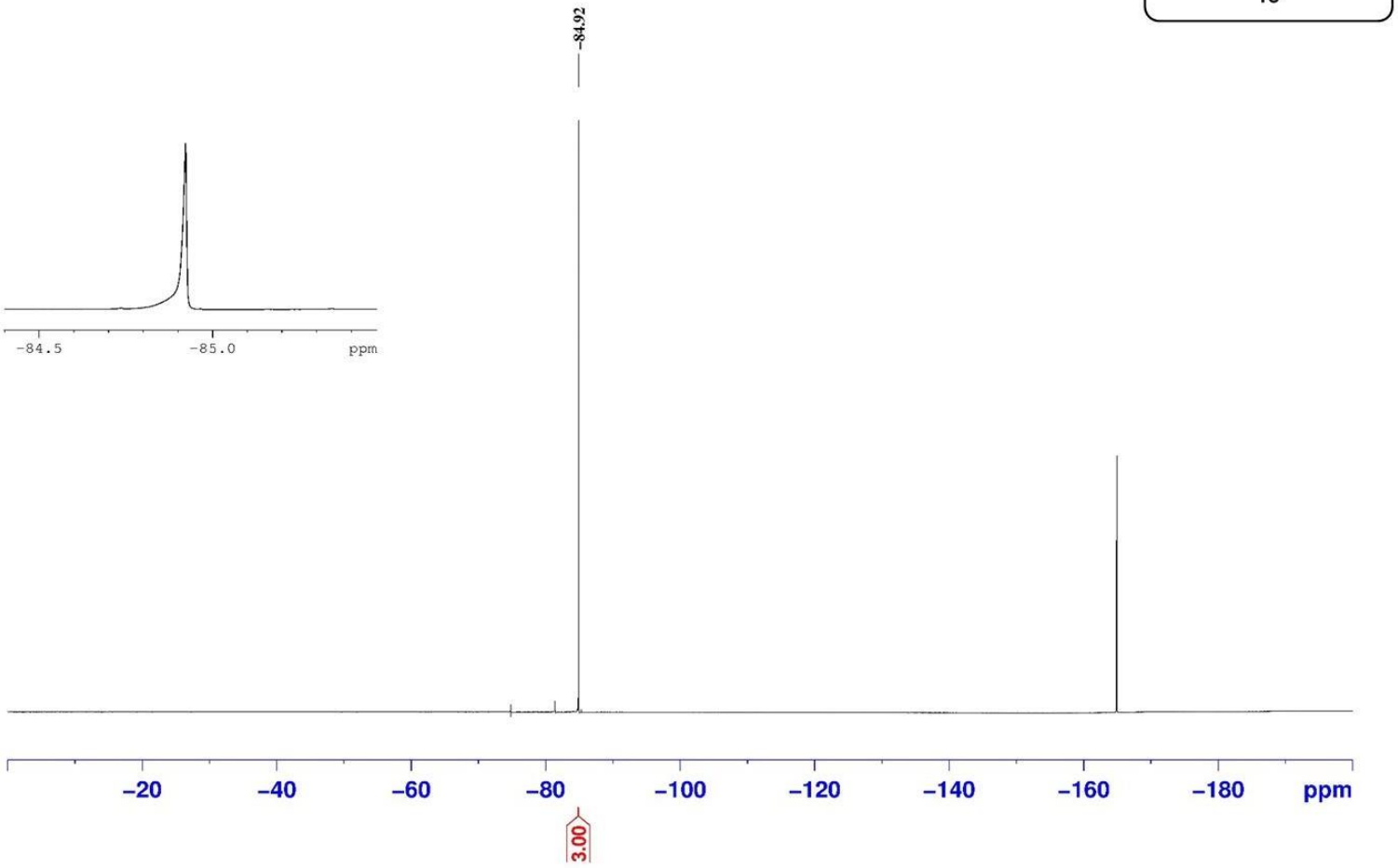



**2–(3–Bromo–5–chlorophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**125 MHz, CDCl3**

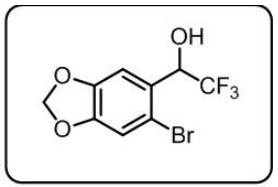


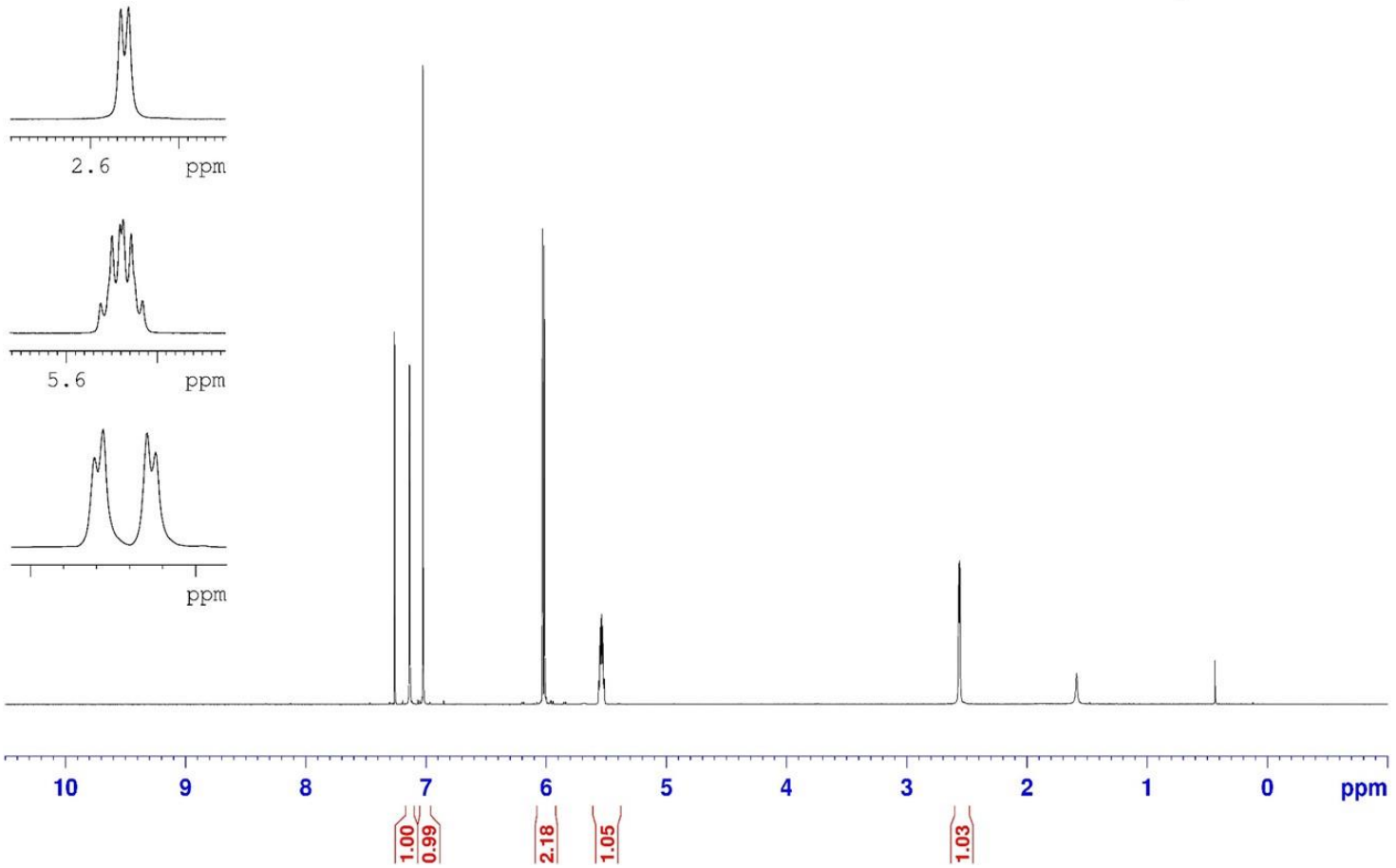
**2–(3–bromo–5–chlorophenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**CDCl3, 471 MHz**



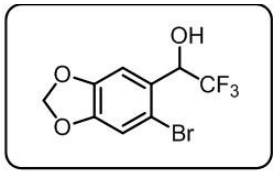



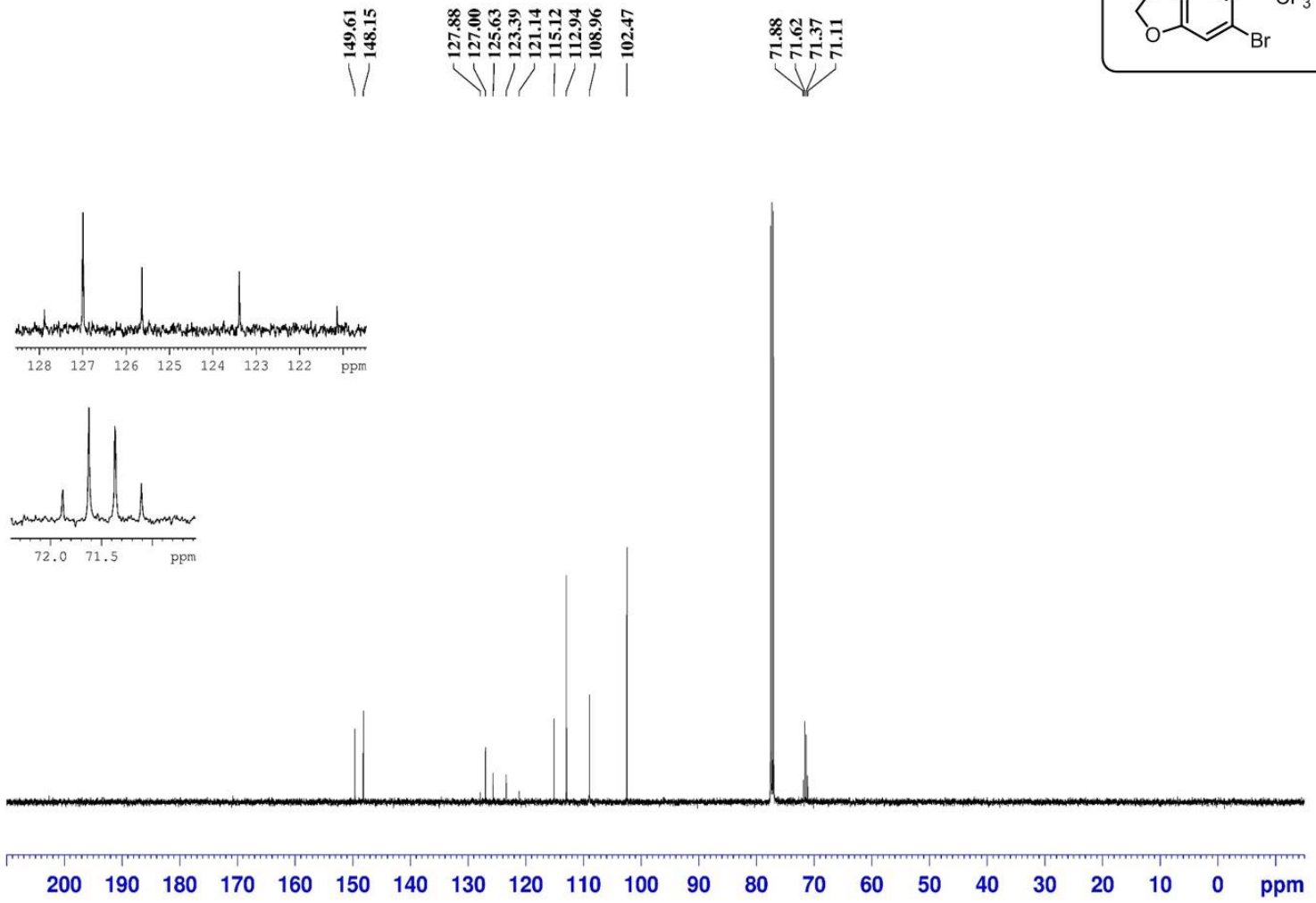
**1-(6-Bromobenzo[d][1,3]dioxol-5-yl)-2,2,2-trifluoroethanol**
**500 MHz, CDCl3**



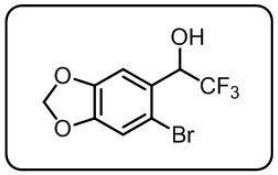



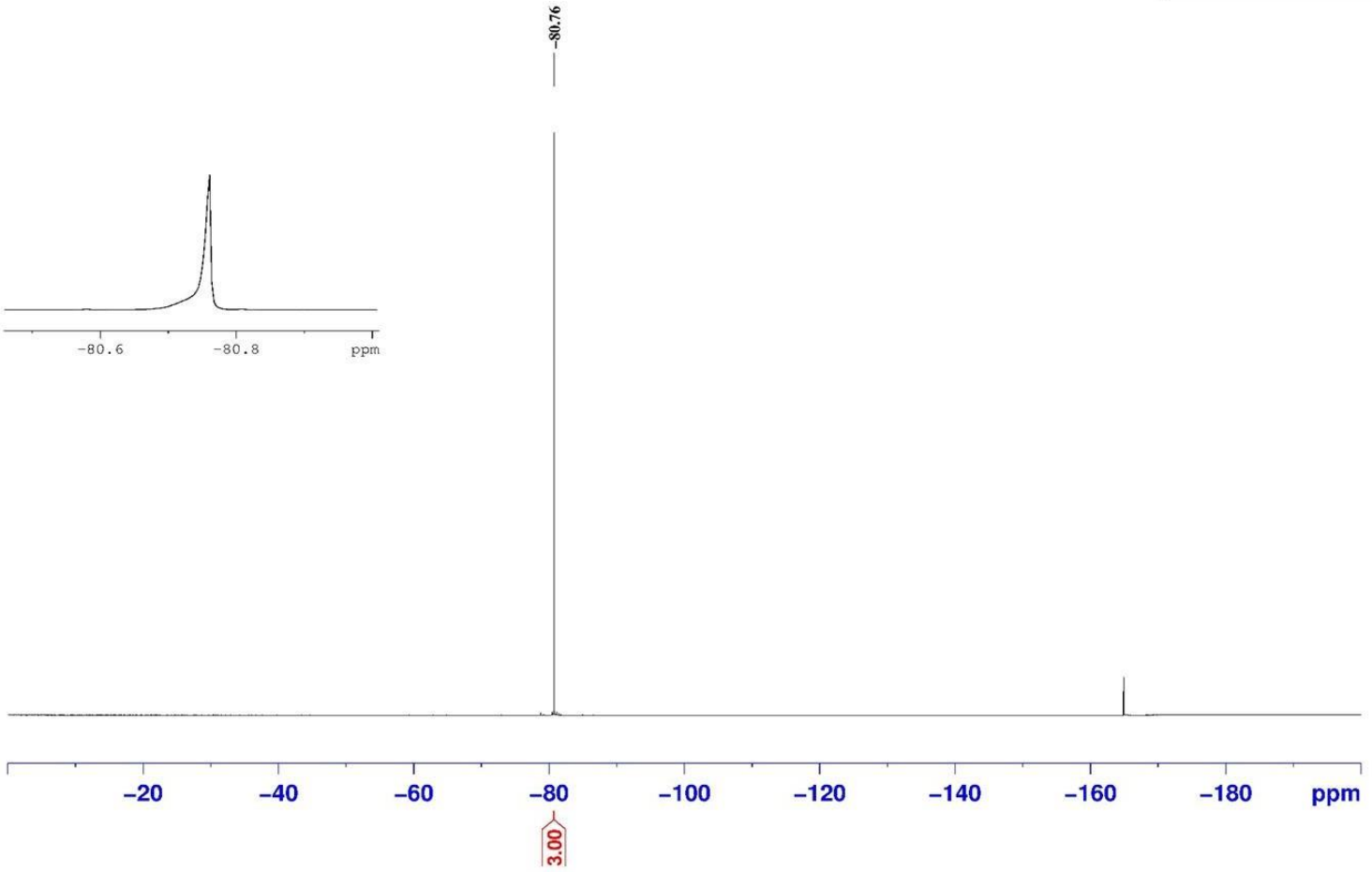
**1–(6–Bromobenzo[d][1,3]dioxol–5–yl)–2,2,2–trifluoroethanol**
**125 MHz, CDCl3**



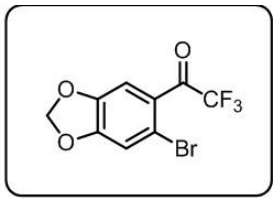



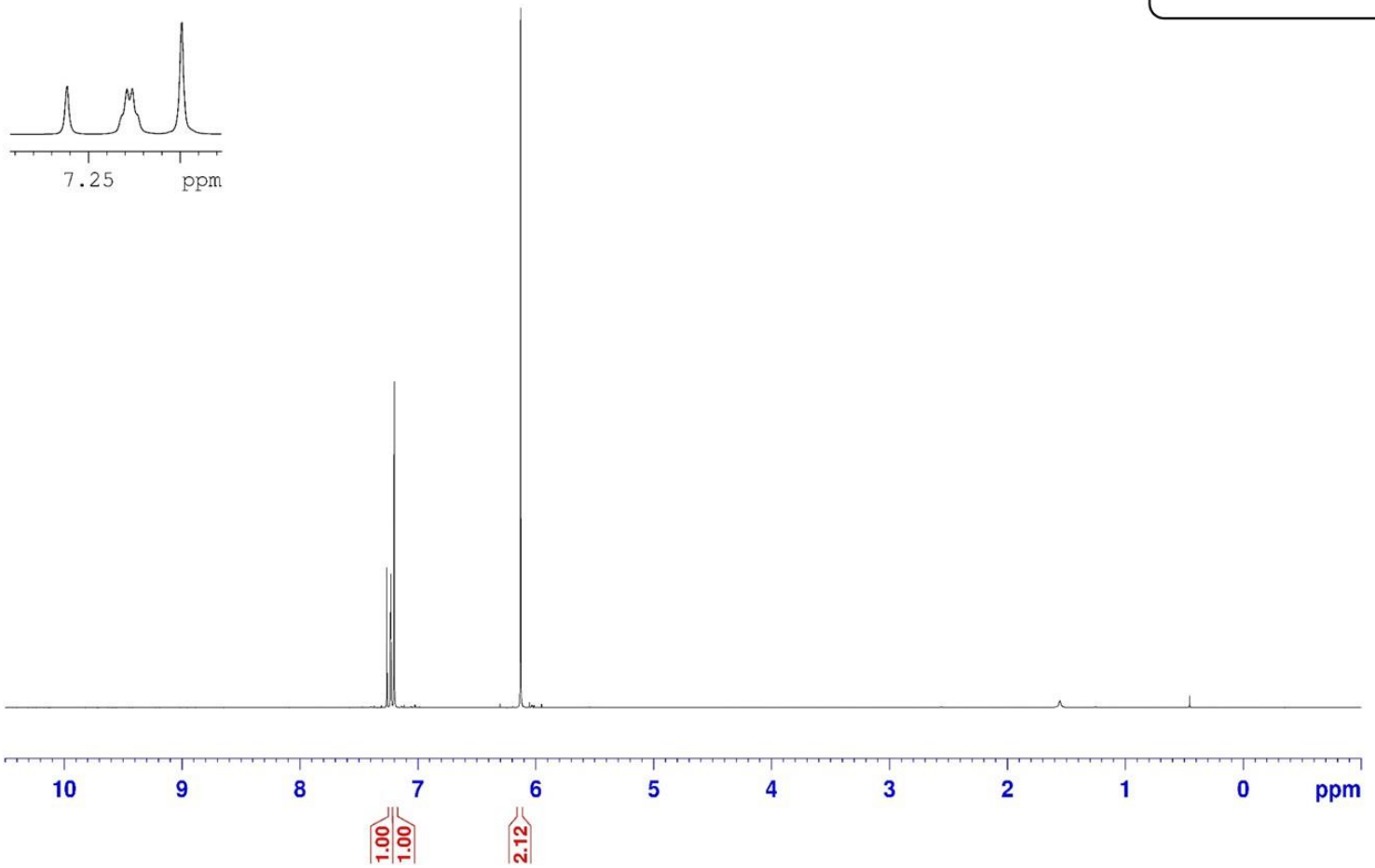
**1–(6–bromobenzo[d][1,3]dioxol–5–yl)–2,2,2–trifluoroethanol**
**CDCl3, 471 MHz**



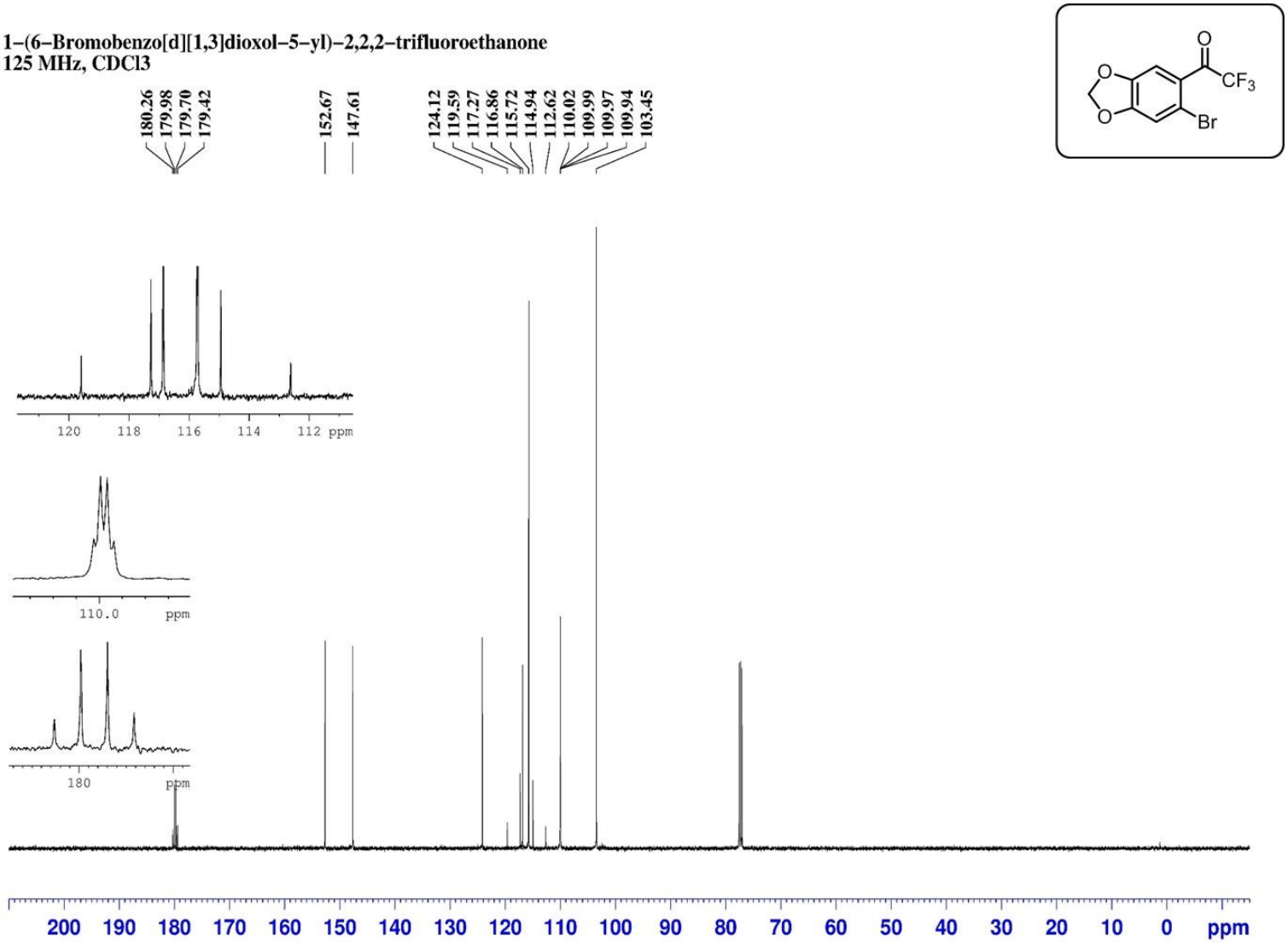



**1-(6-Bromobenzo[d][1,3]dioxol-5-yl)-2,2,2-trifluoroethanone**
**500 MHz, CDCl3**

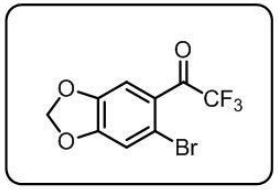


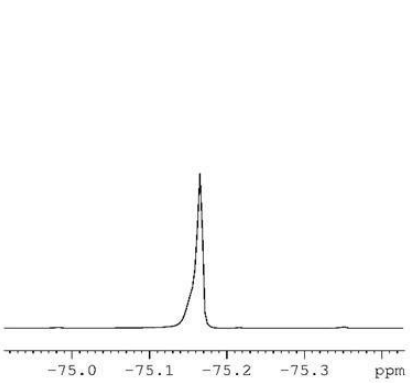



**1–(6–Bromobenzo[d][1,3]dioxol–5–yl)–2,2,2–trifluoroethanone**
**125 MHz, CDCl3**

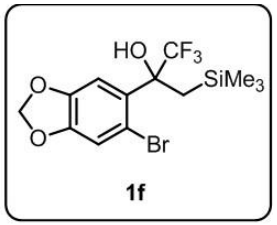


**1–(6–bromobenzo[d][1,3]dioxol–5–yl)–2,2,2–trifluoroethanone**
**CDCl3, 471 MHz**

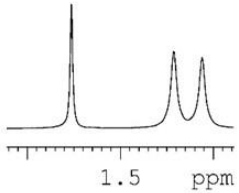


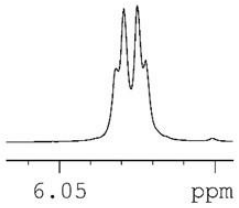



**2-(6-Bromobenzo[d][1,3]dioxol-5-yl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol**
**500 MHz, CDCl3**

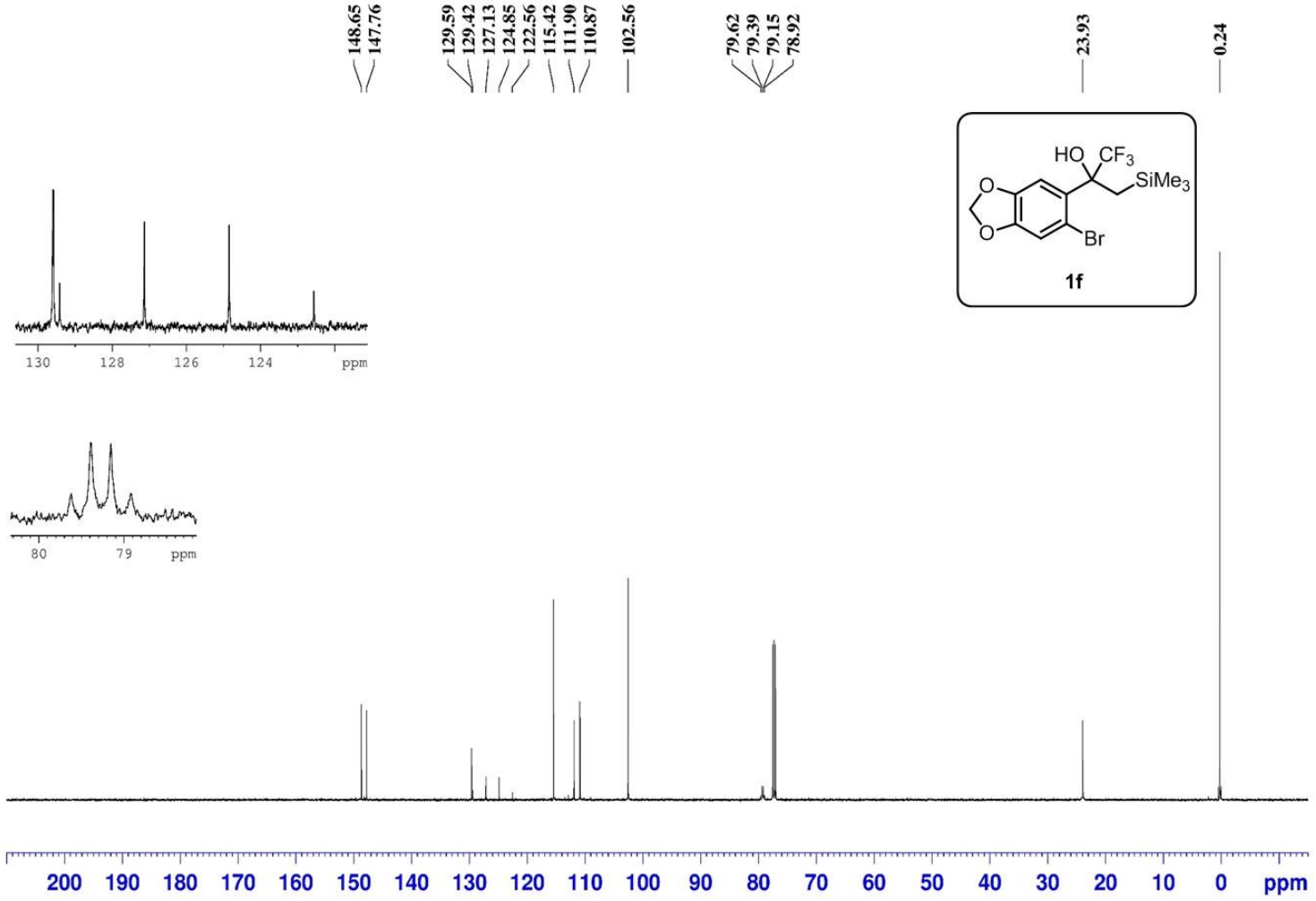



**1f**

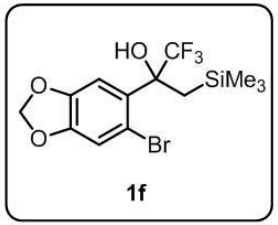


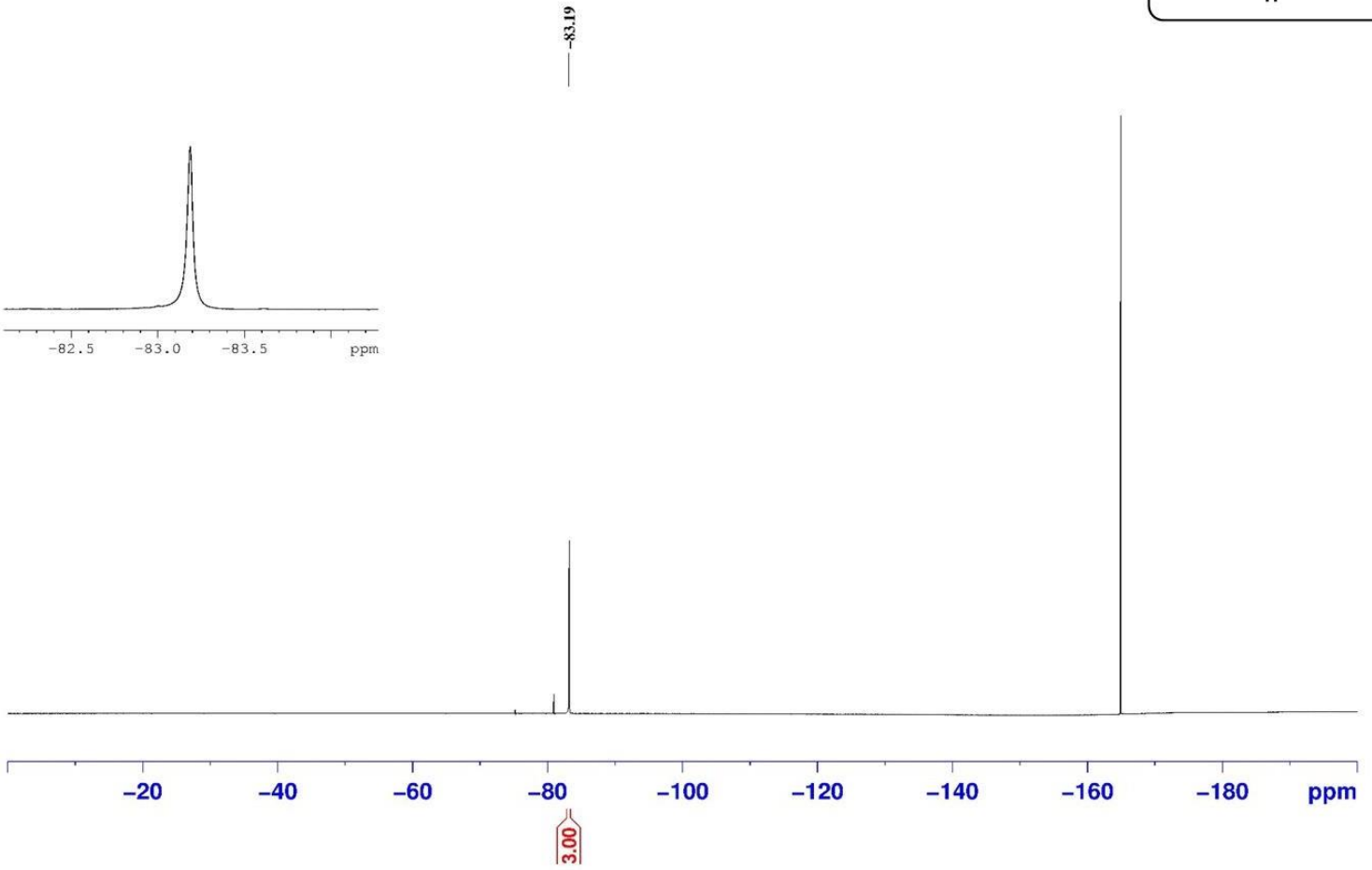
**2–(6–Bromobenzo[d][1,3]dioxol–5–yl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**125 MHz, CDCl3**



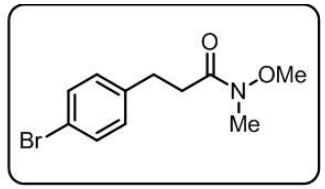
**2–(6–bromobenzo[d][1,3]dioxol–5–yl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**CDCl3, 471 MHz**

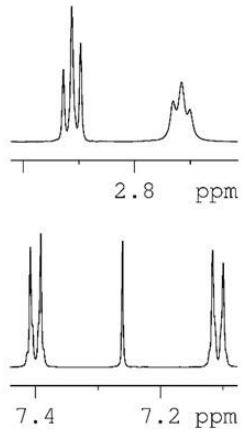


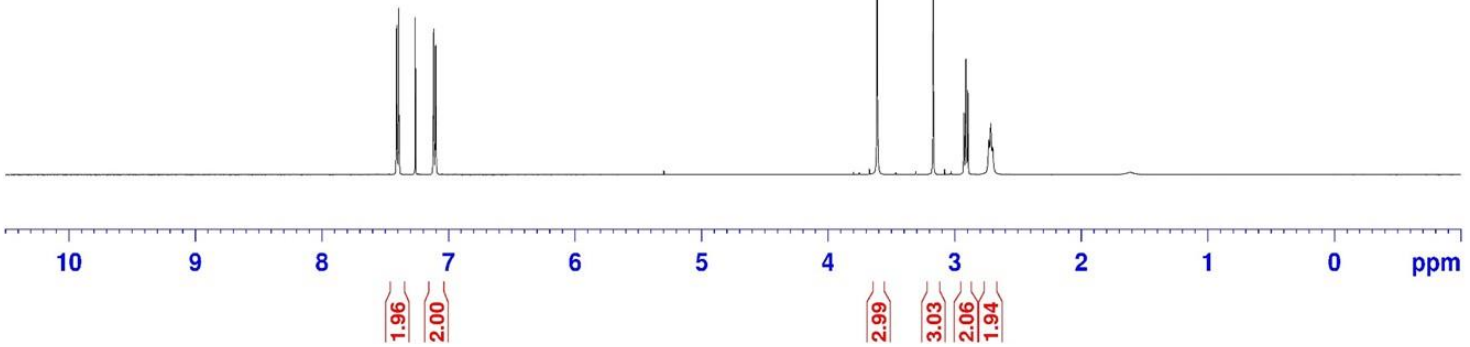

**1f**



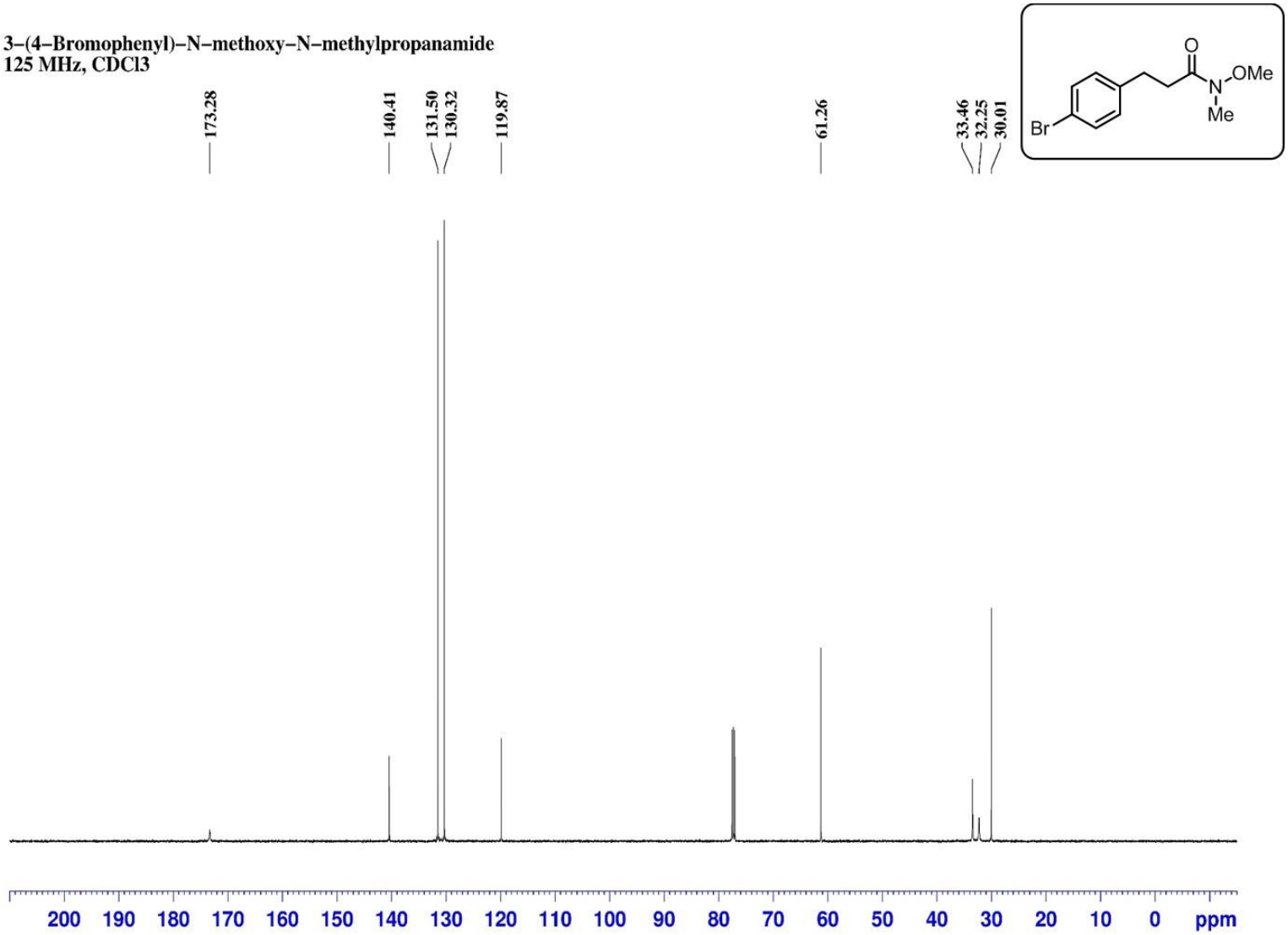
**3–(4–Bromophenyl)–N–methoxy–N–methylpropanamide**
**500 MHz, CDCl3**



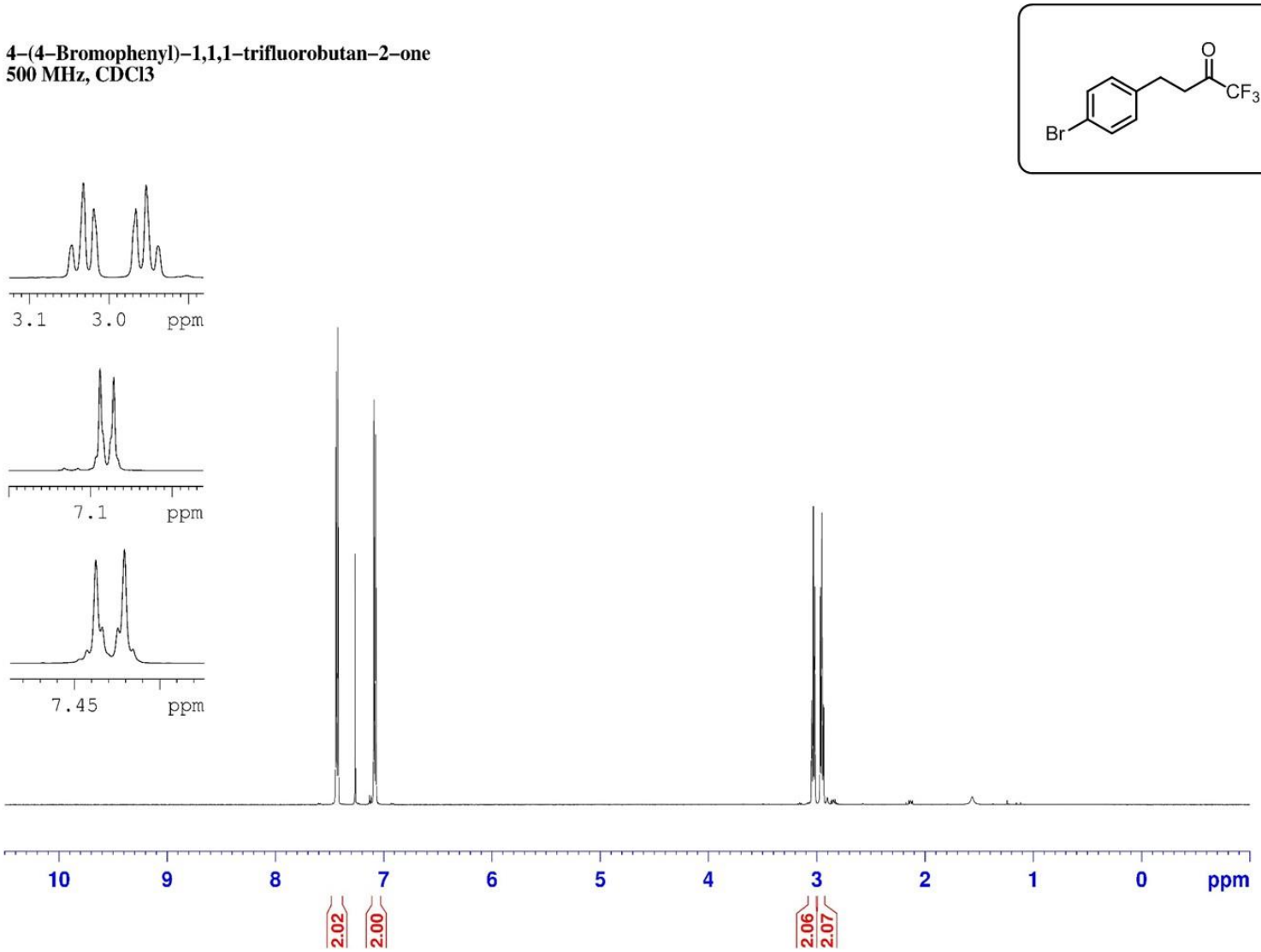



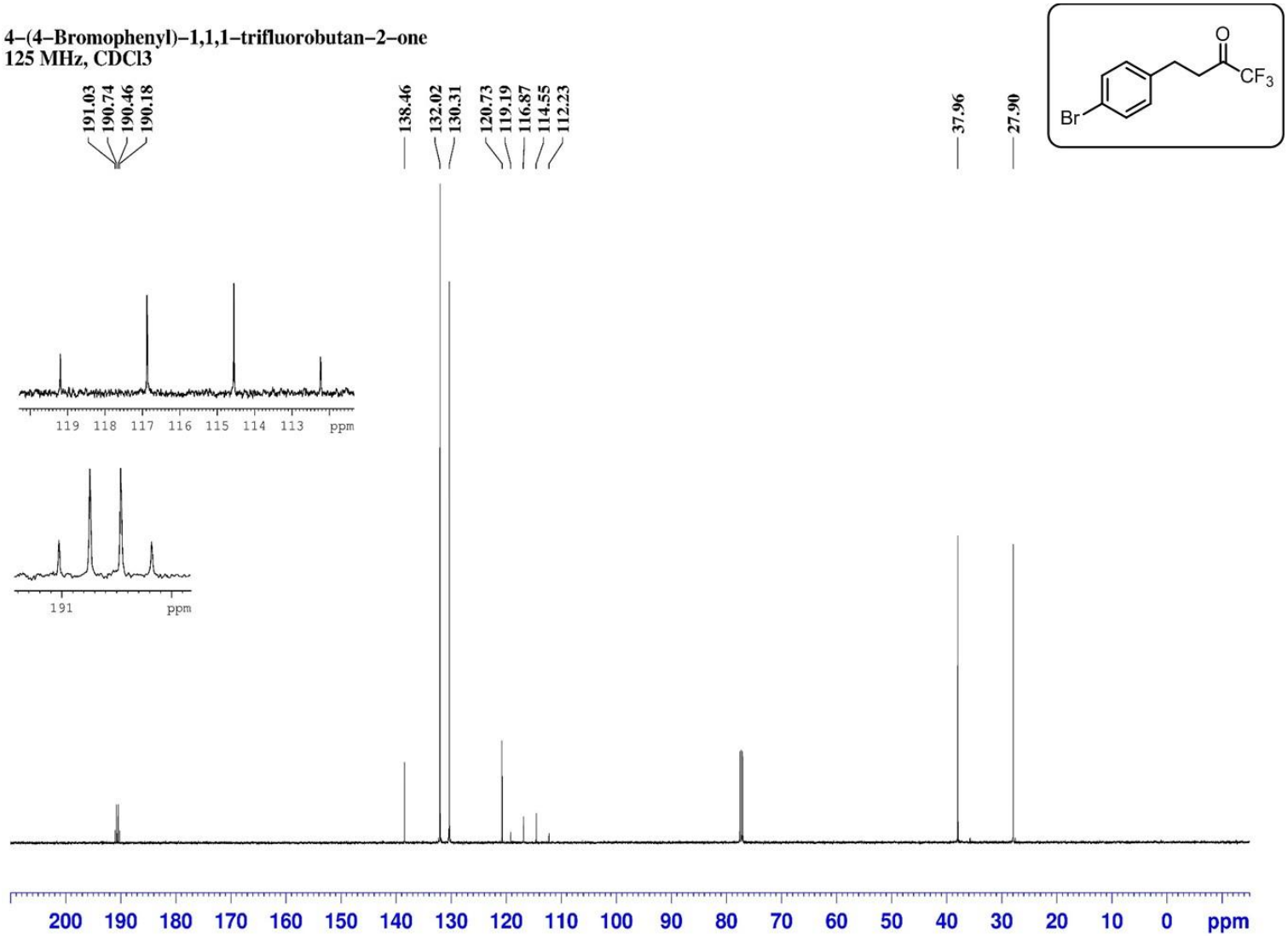



**3–(4–Bromophenyl)–N–methoxy–N–methylpropanamide**
**125 MHz, CDCl3**

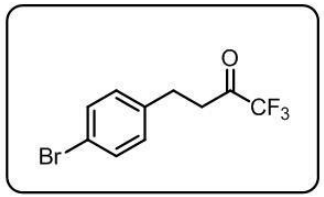


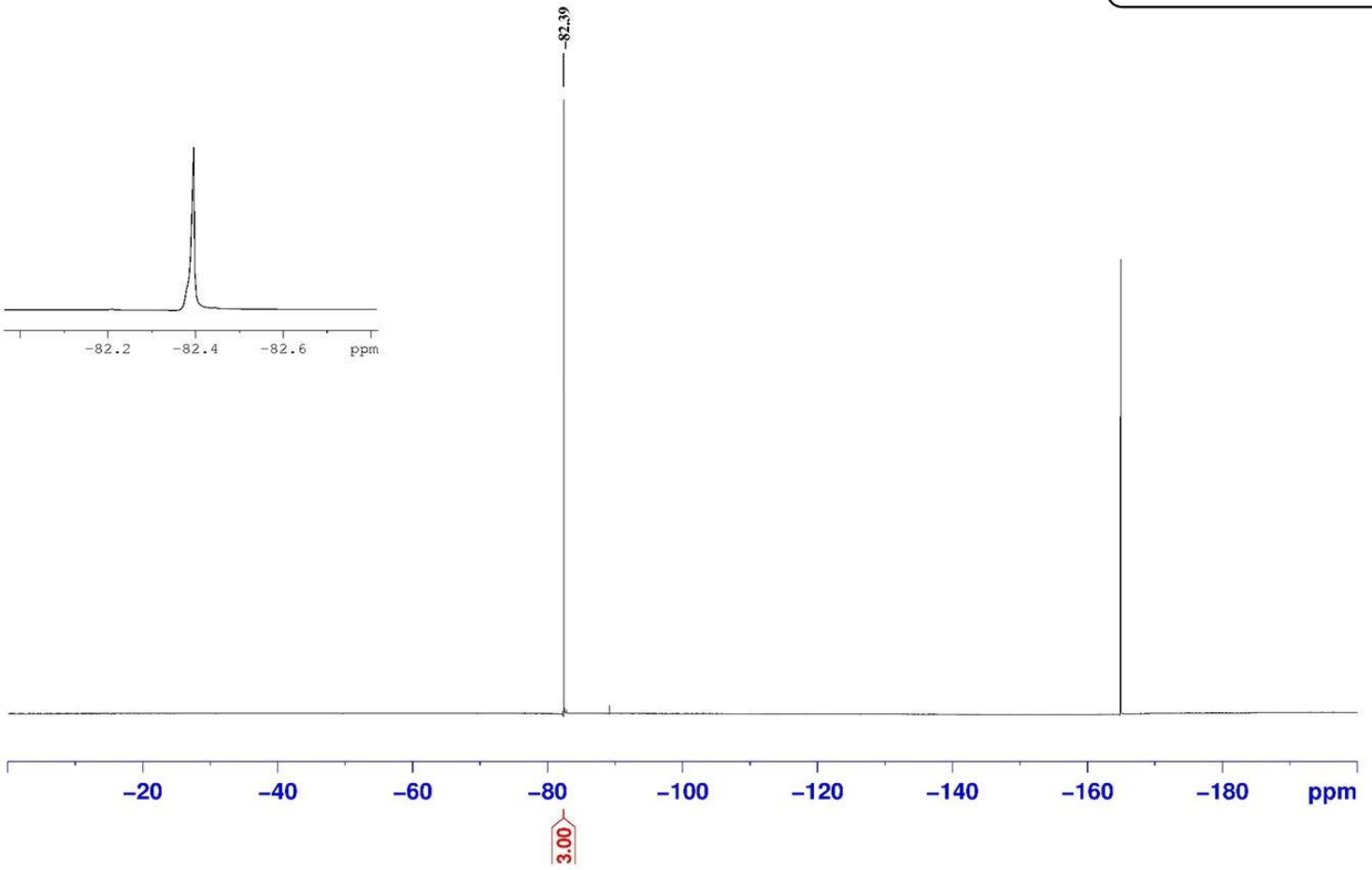
**4–(4–Bromophenyl)–1,1,1–trifluorobutan–2–one**
**500 MHz, CDCl3**



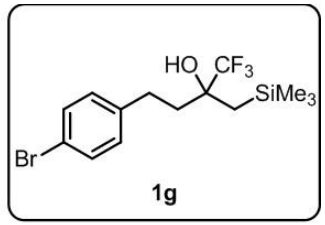

4–(4–Bromophenyl)–1,1,1–trifluorobutan–2–one
125 MHz, CDCl3
191.03
190.74
190.46
190.18
138.46
132.02
130.31
120.73
119.19
116.87
114.55
112.23
37.96
27.90
O
CF3
Br
119 118 117 116 115 114 113 ppm
191 ppm
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

**4–(4–bromophenyl)–1,1,1–trifluorobutan–2–one**
**CDCl3, 471 MHz**

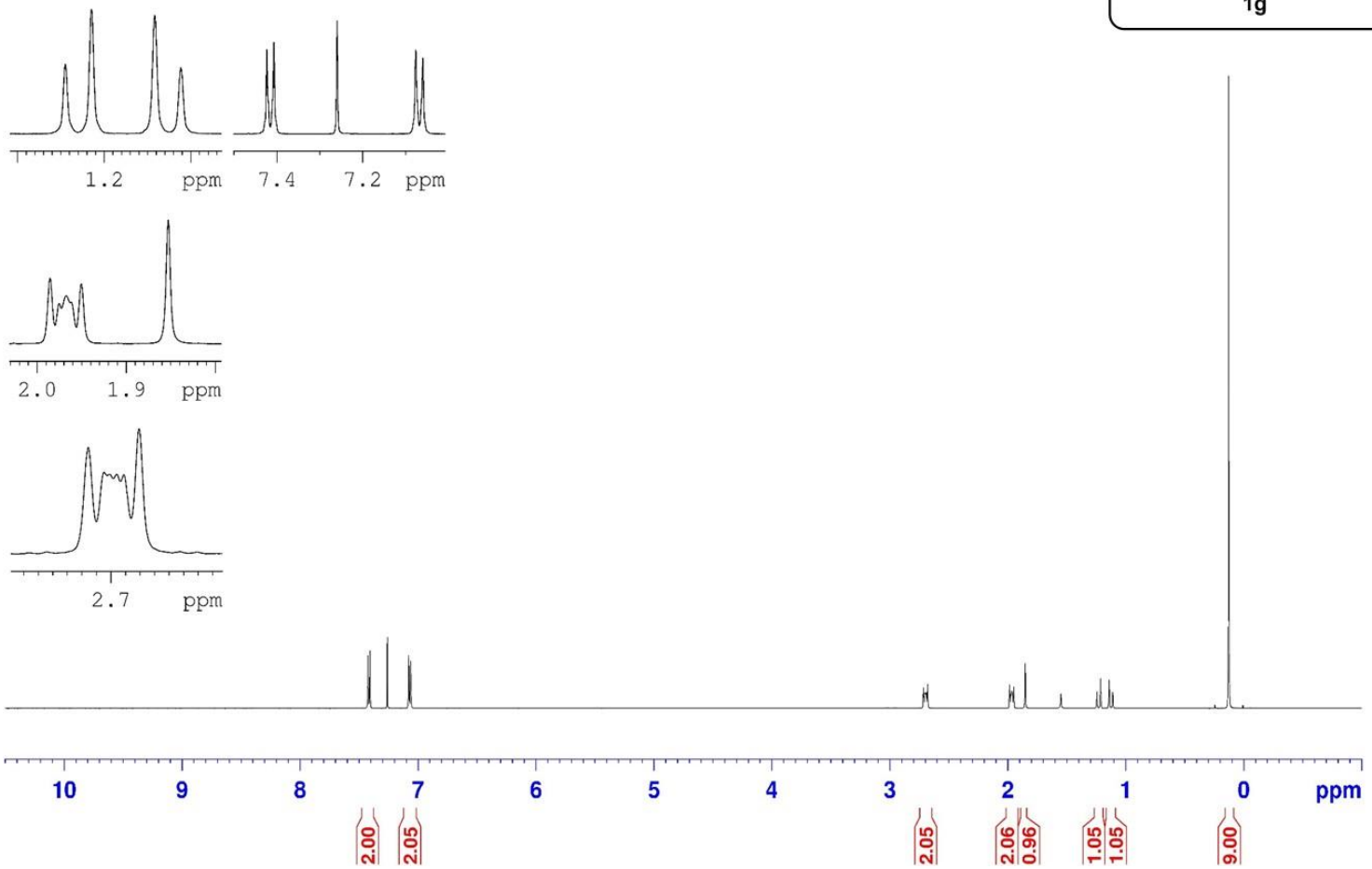


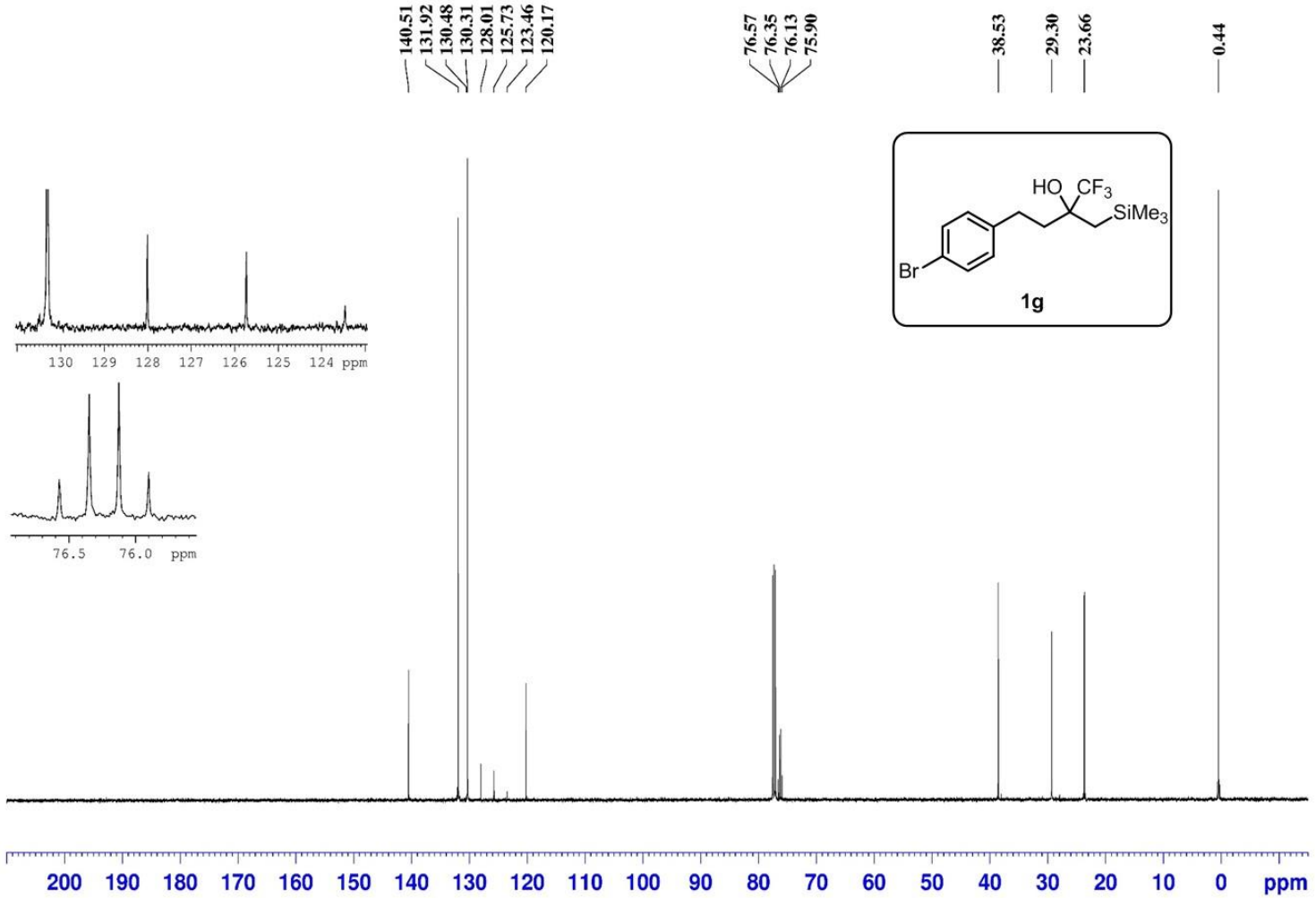
**4–(4–Bromophenyl)–1,1,1–trifluoro–2–((trimethylsilyl)methyl)butan–2–ol**
**500 MHz, CDCl3**



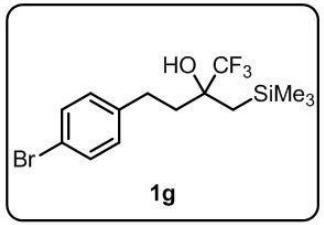

**1g**



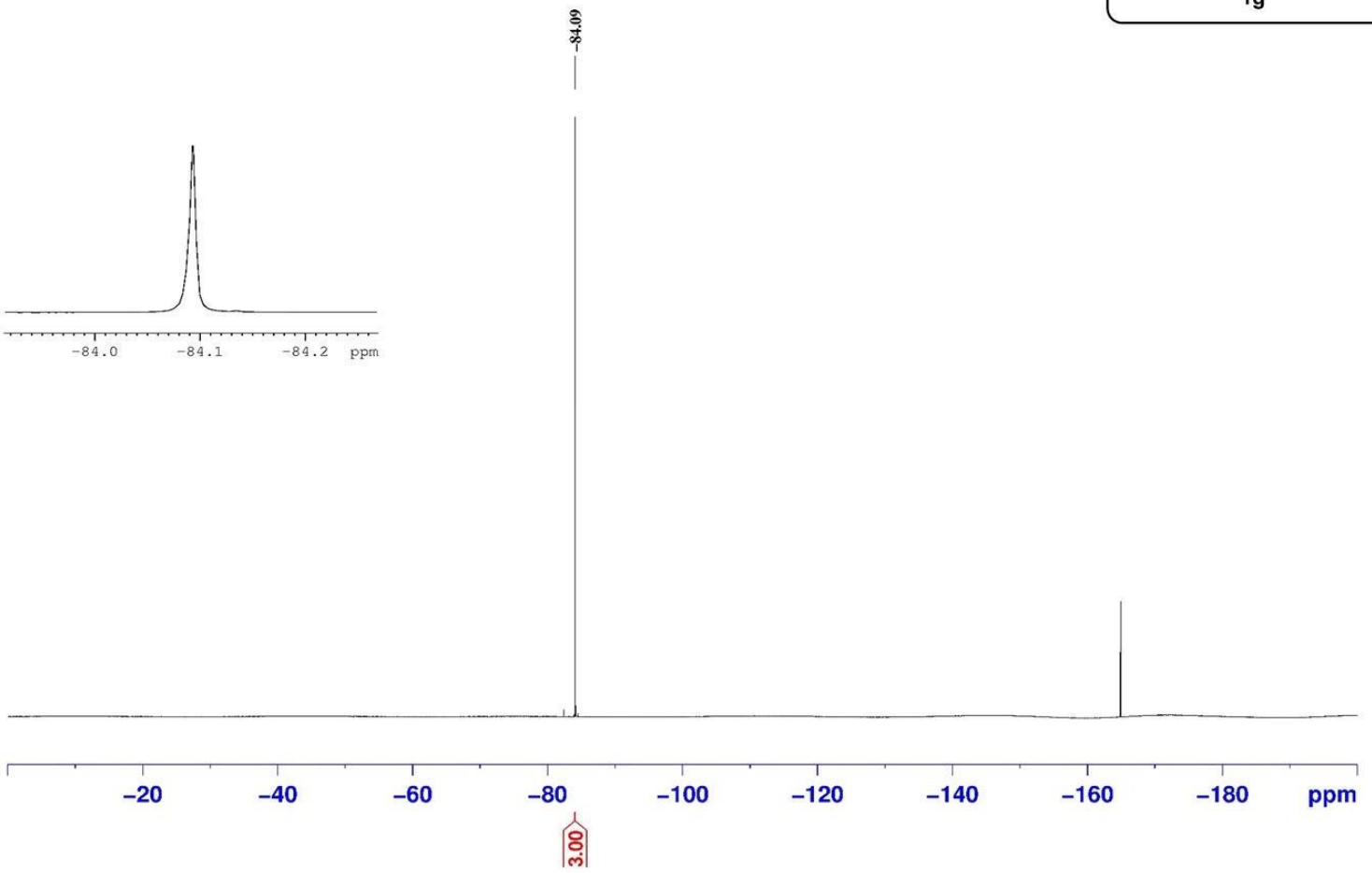
**4–(4–Bromophenyl)–1,1,1–trifluoro–2–((trimethylsilyl)methyl)butan–2–ol**
**125 MHz, CDCl3**



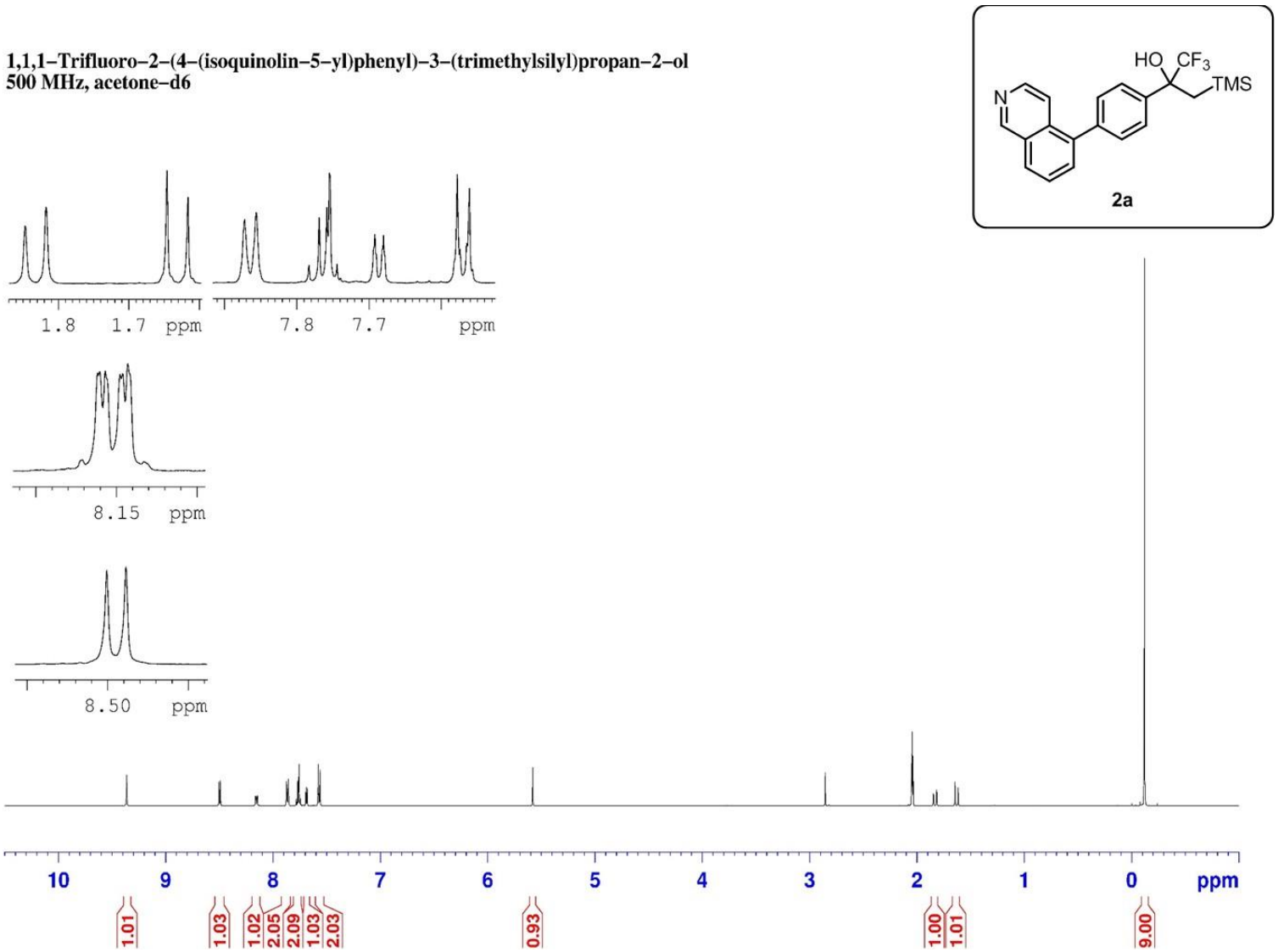
**4–(4–bromophenyl)–1,1,1–trifluoro–2–((trimethylsilyl)methyl)butan–2–ol**
**CDCl3, 471 MHz**



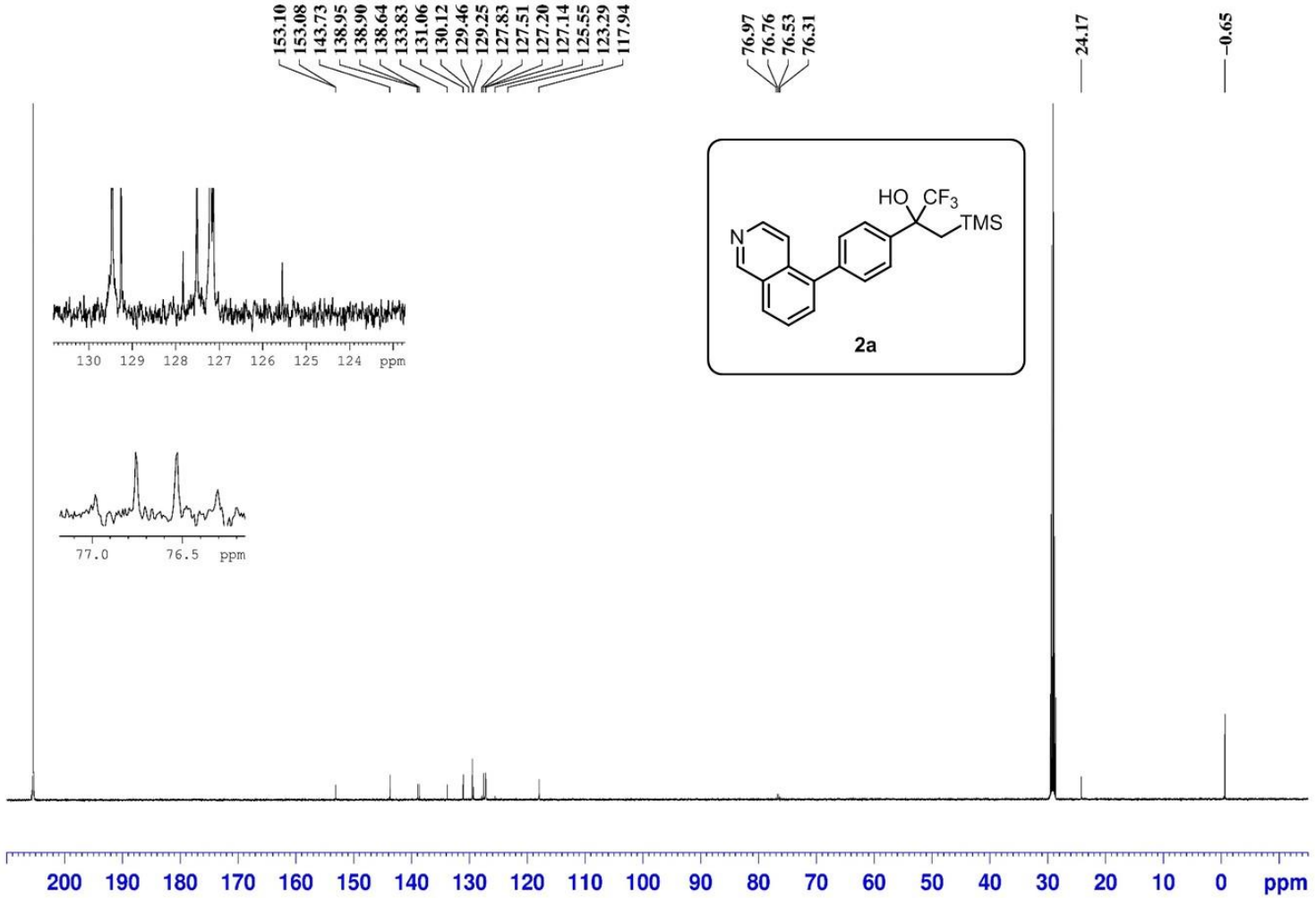

**1g**



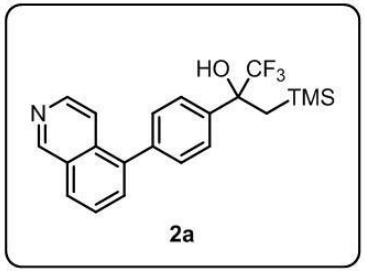
**1,1,1–Trifluoro–2–(4–(isoquinolin–5–yl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**500 MHz, acetone–d6**

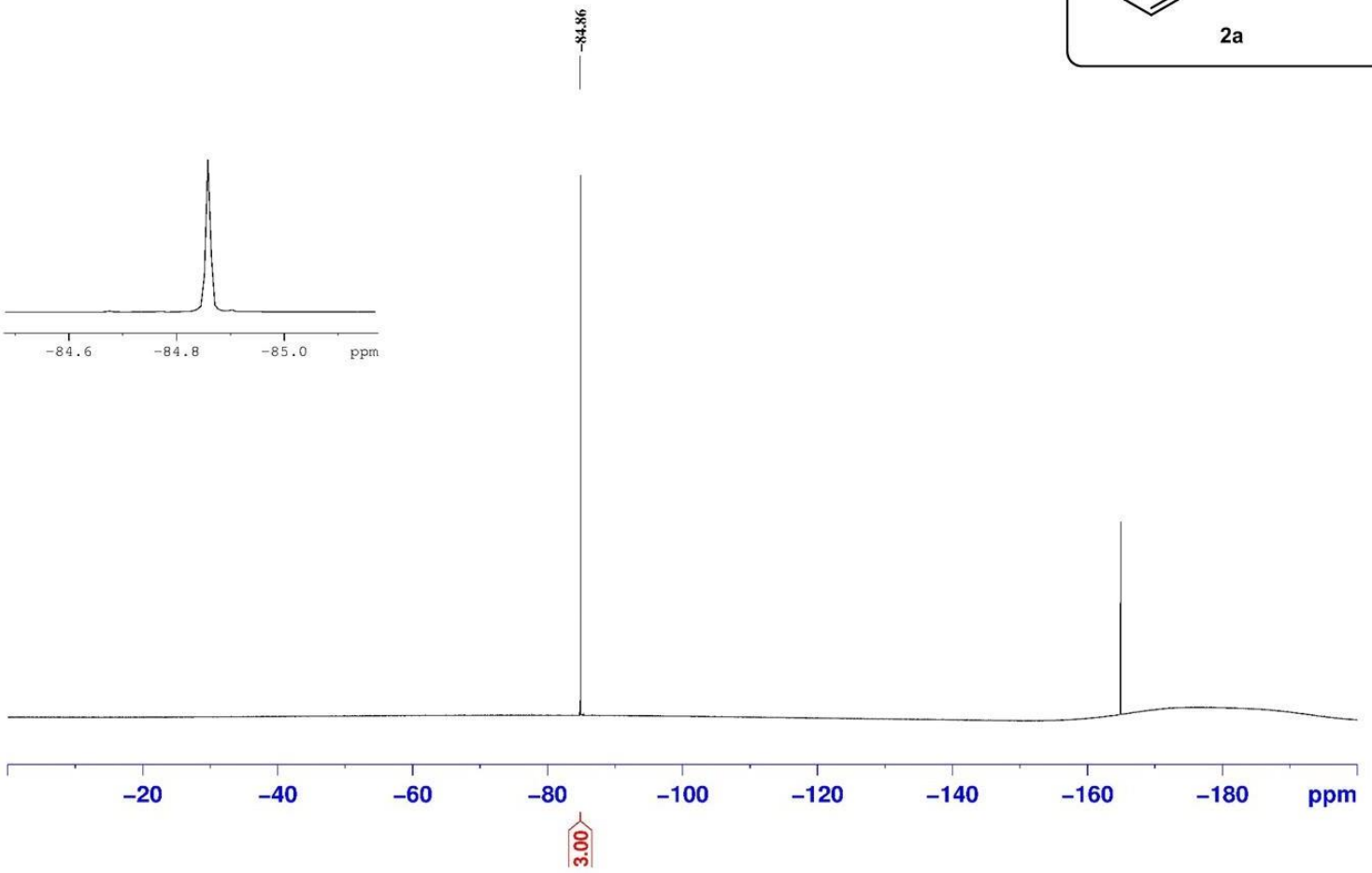


**1,1,1–Trifluoro–2–(4–(isoquinolin–5–yl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**125 MHz, acetone–d6**

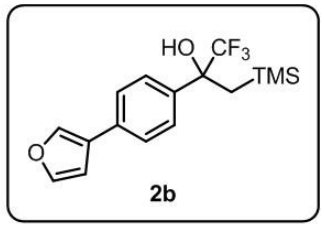


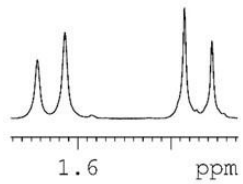
**1,1,1–trifluoro–2–(4–(isoquinolin–5–yl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**Acetone–d6, 471 MHz**

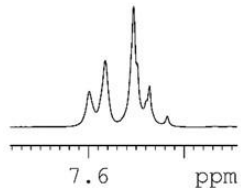


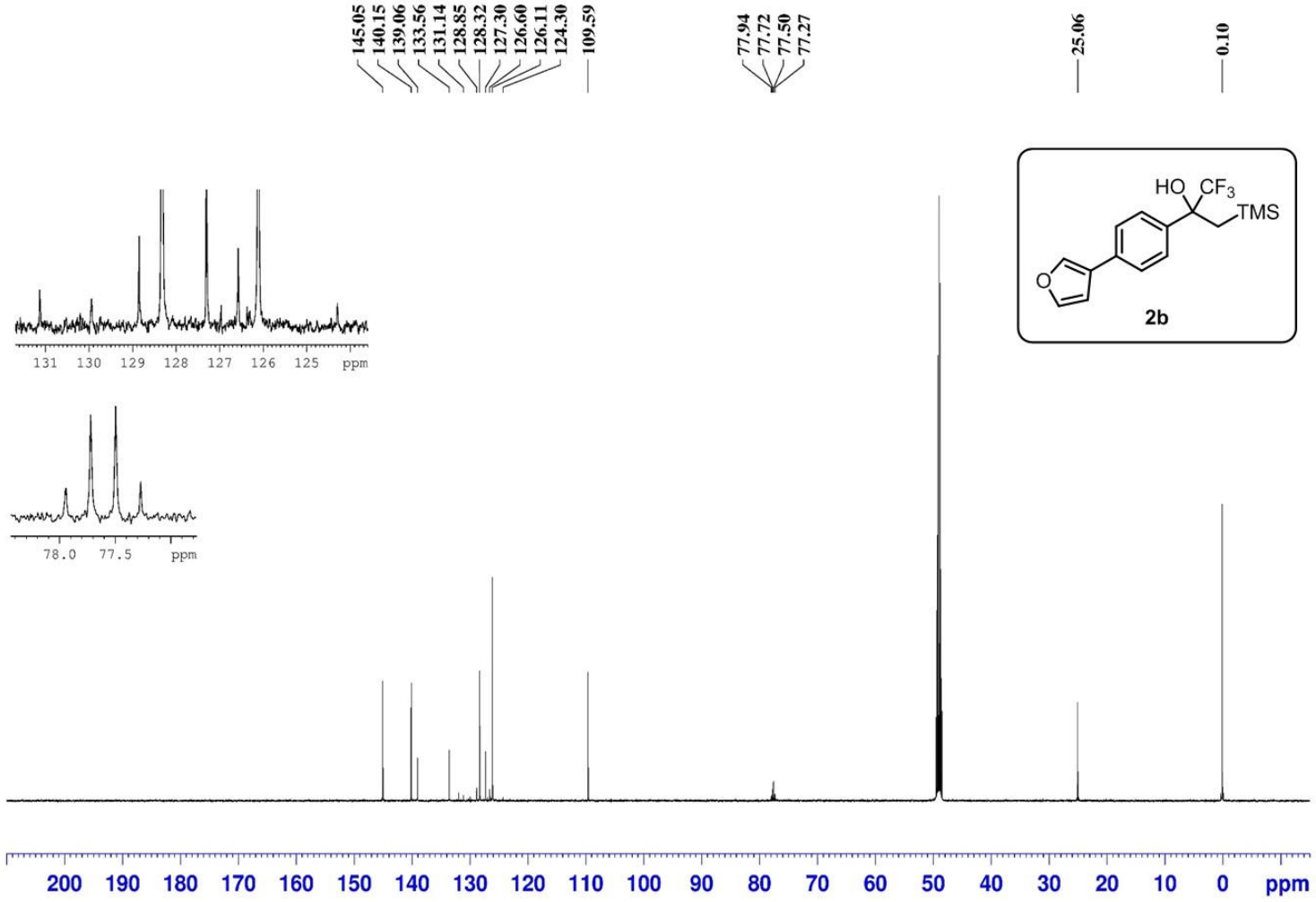
**1,1,1–Trifluoro–2–(4–(furan–3–yl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**500 MHz, CD3OD**



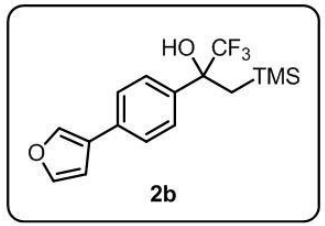



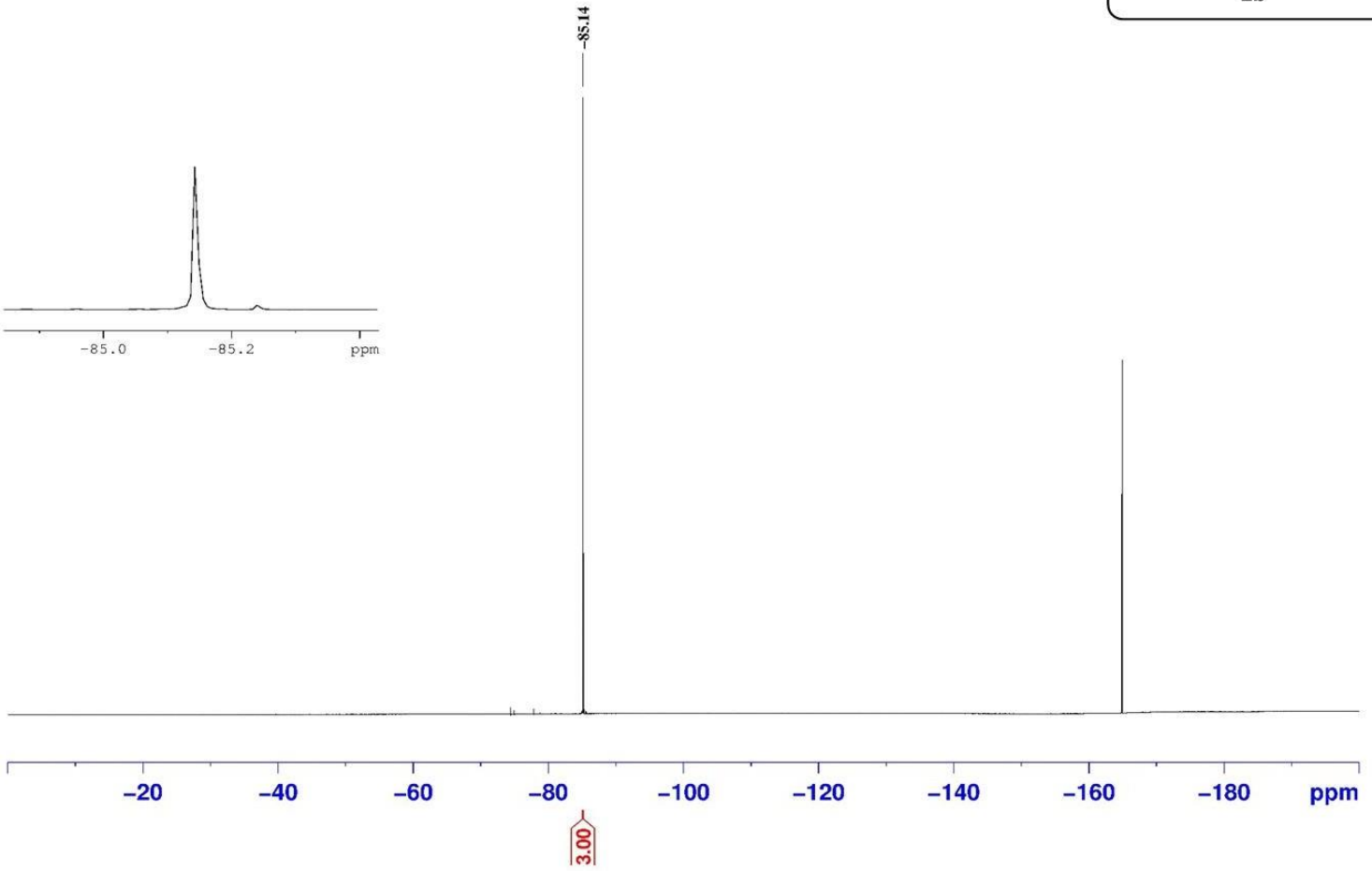



**1,1,1–Trifluoro–2–(4–(furan–3–yl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**125 MHz, CD3OD**

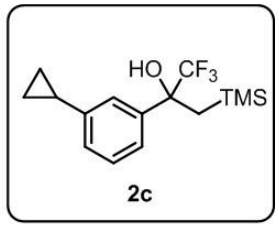


**1,1,1–trifluoro–2–(4–(furan–3–yl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**CD3OD, 471 MHz**

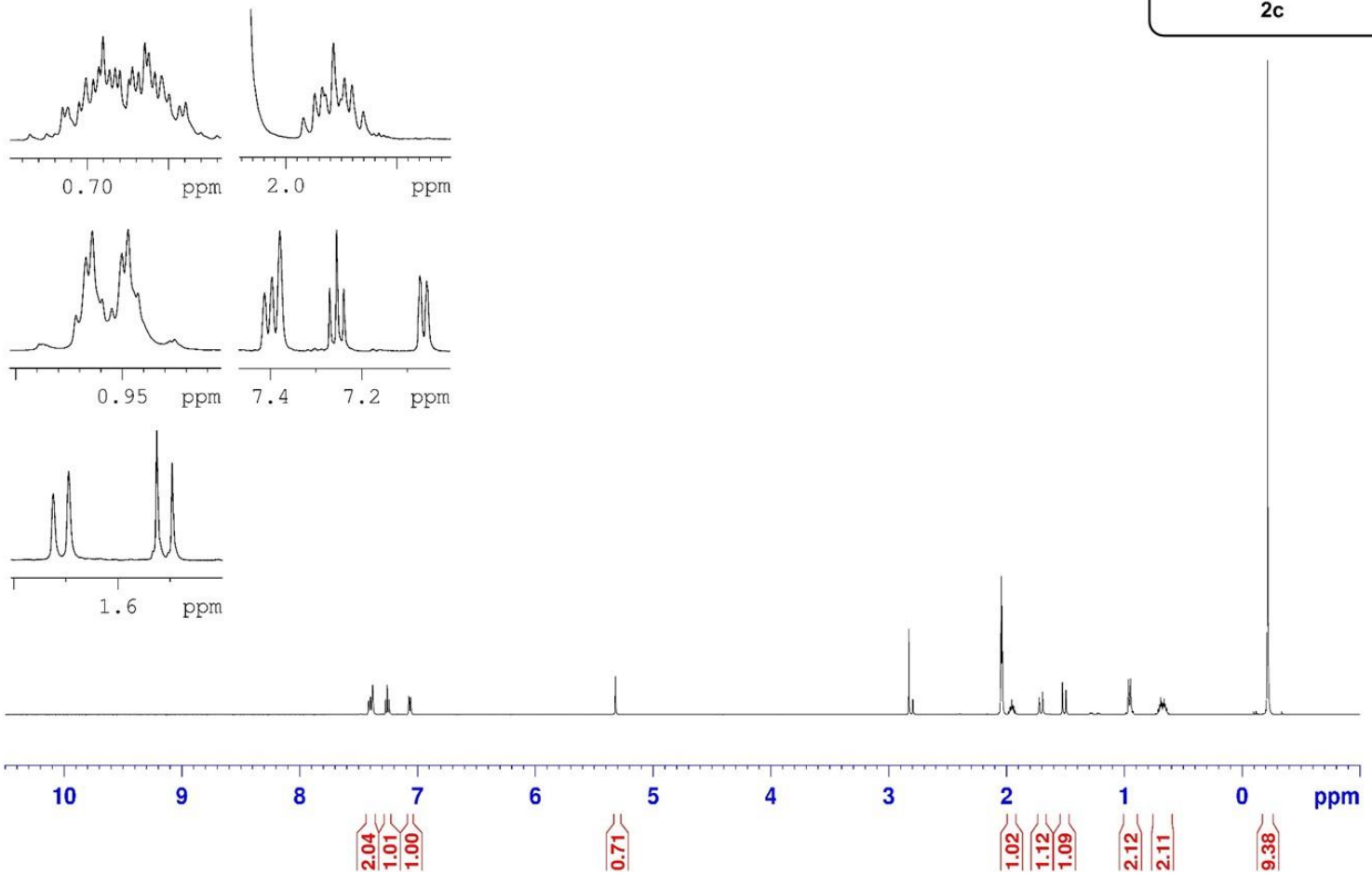


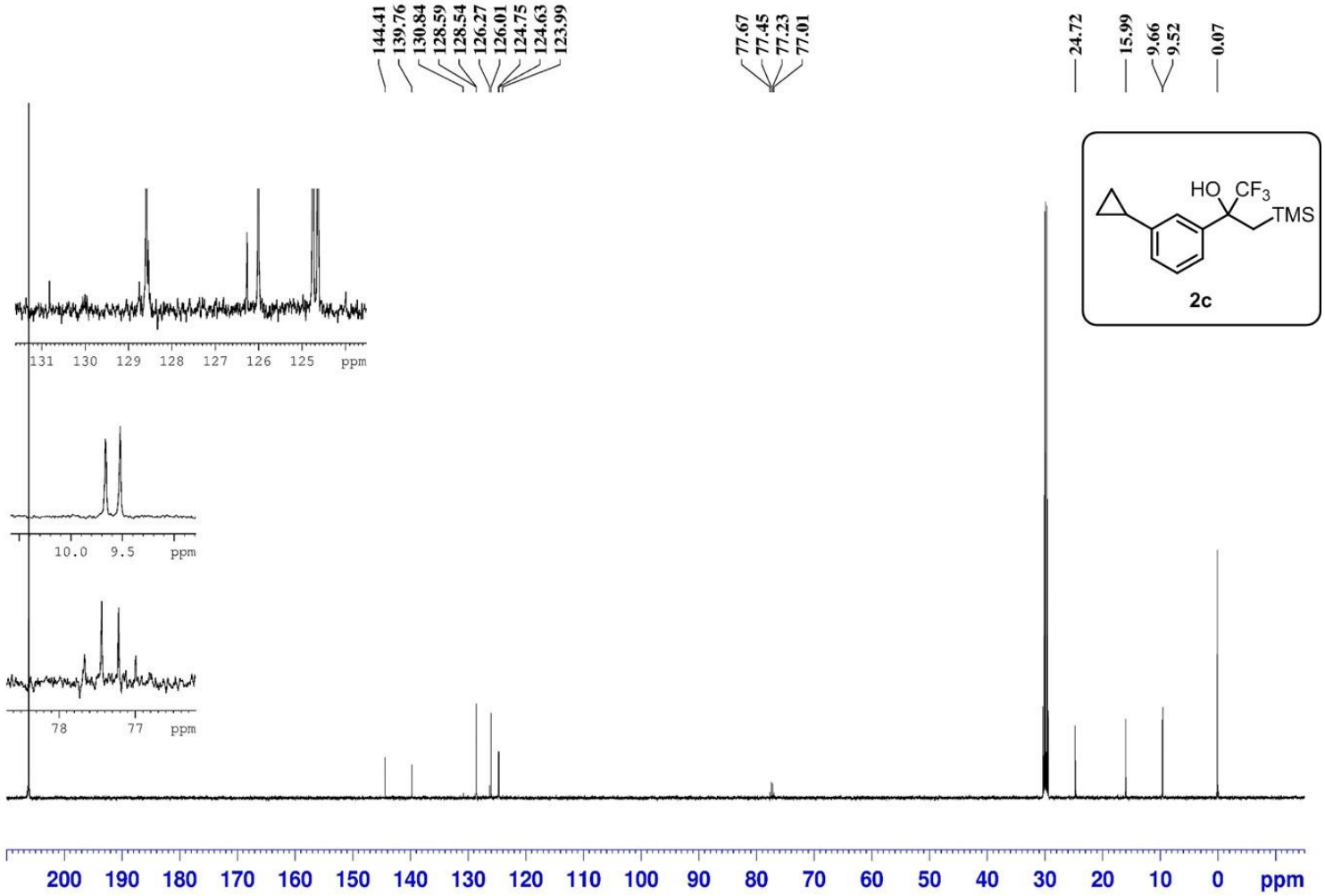
**2–(3–Cyclopropylphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**500 MHz, acetone–d6**



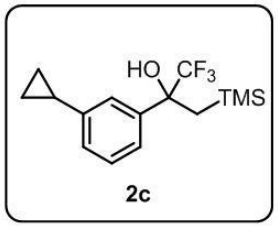

**2c**



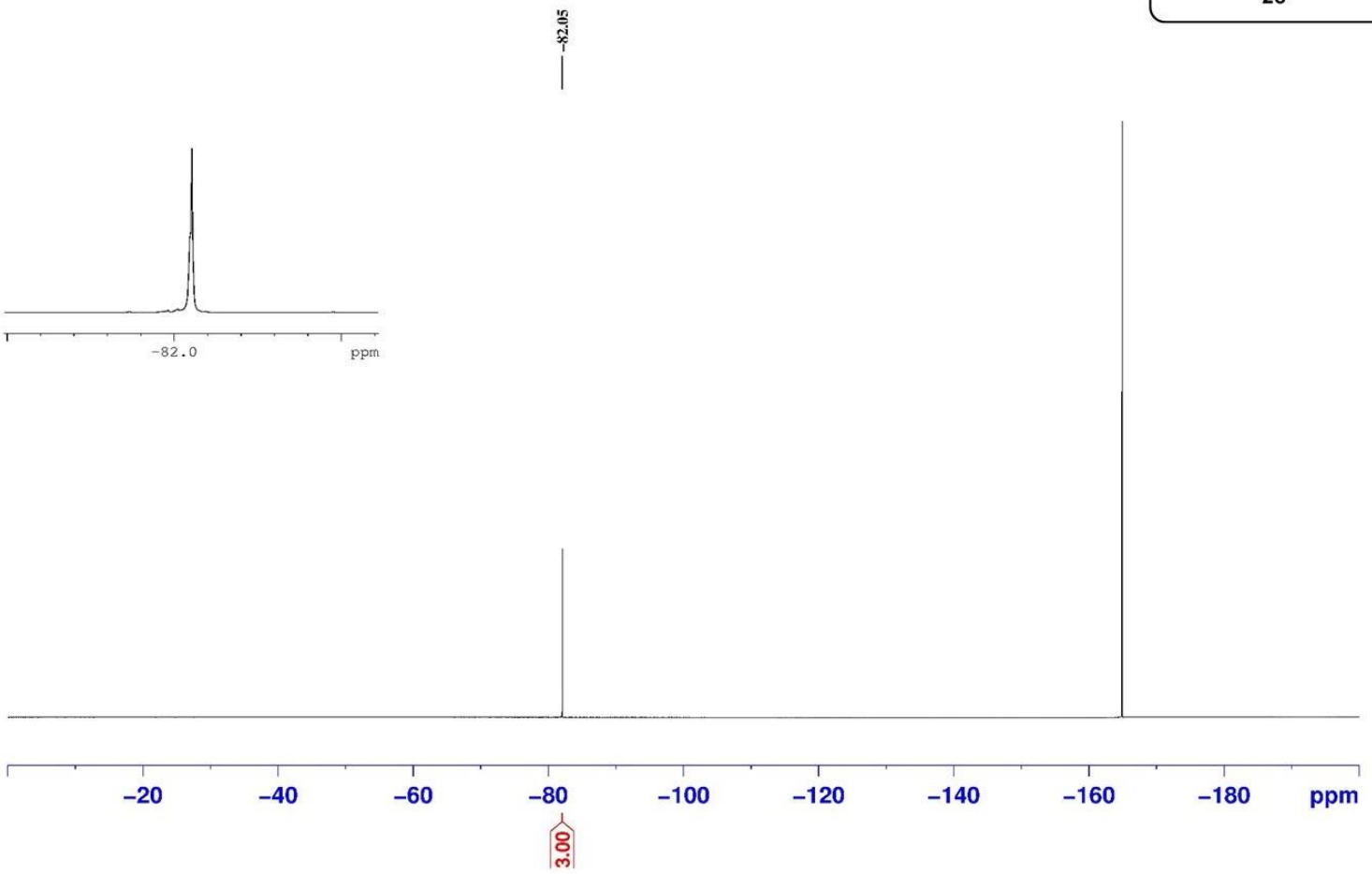
**2–(3–Cyclopropylphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**125 MHz, acetone–d6**



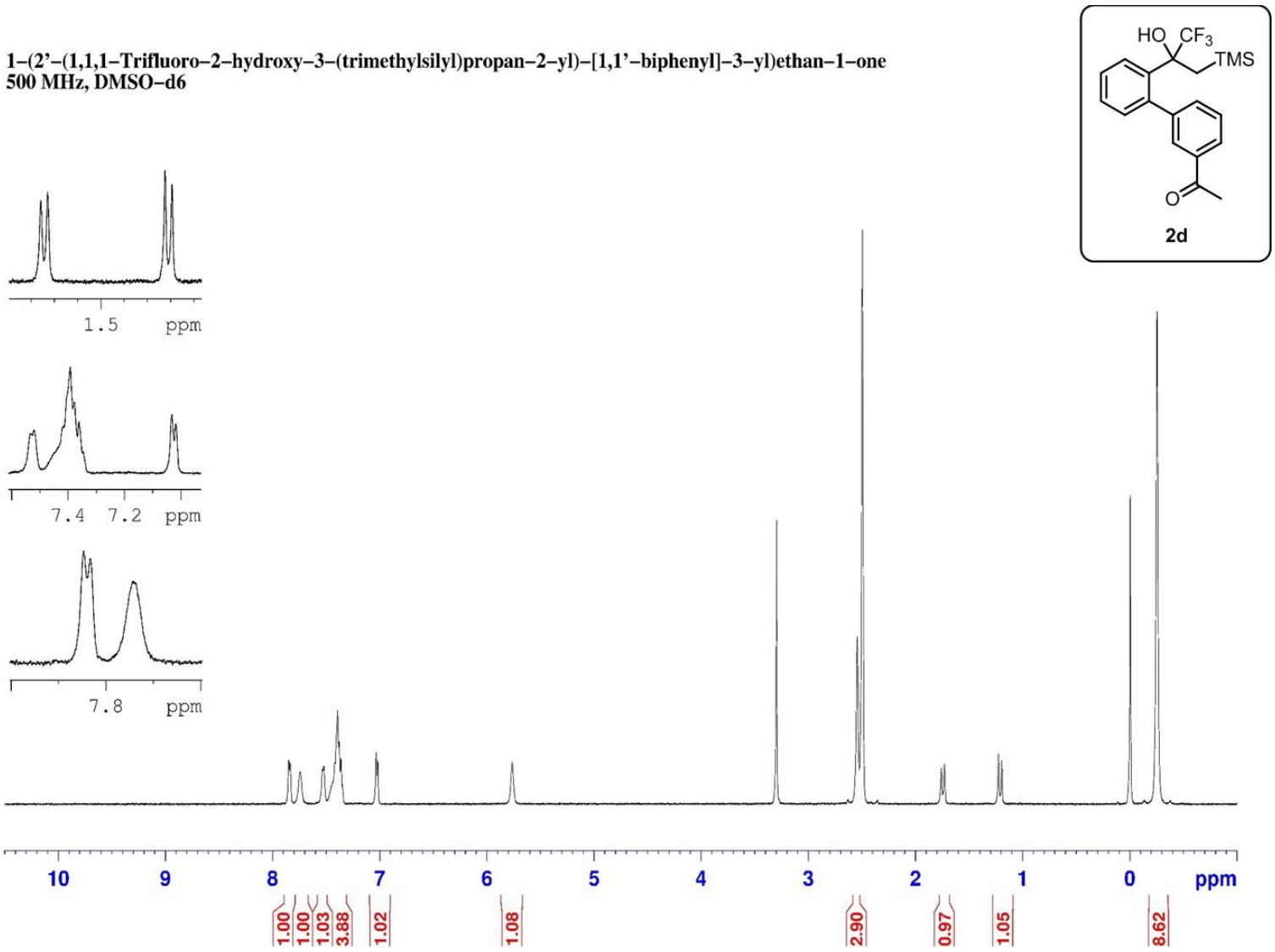
**2–(3–cyclopropylphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**CDCl3, 471 MHz**



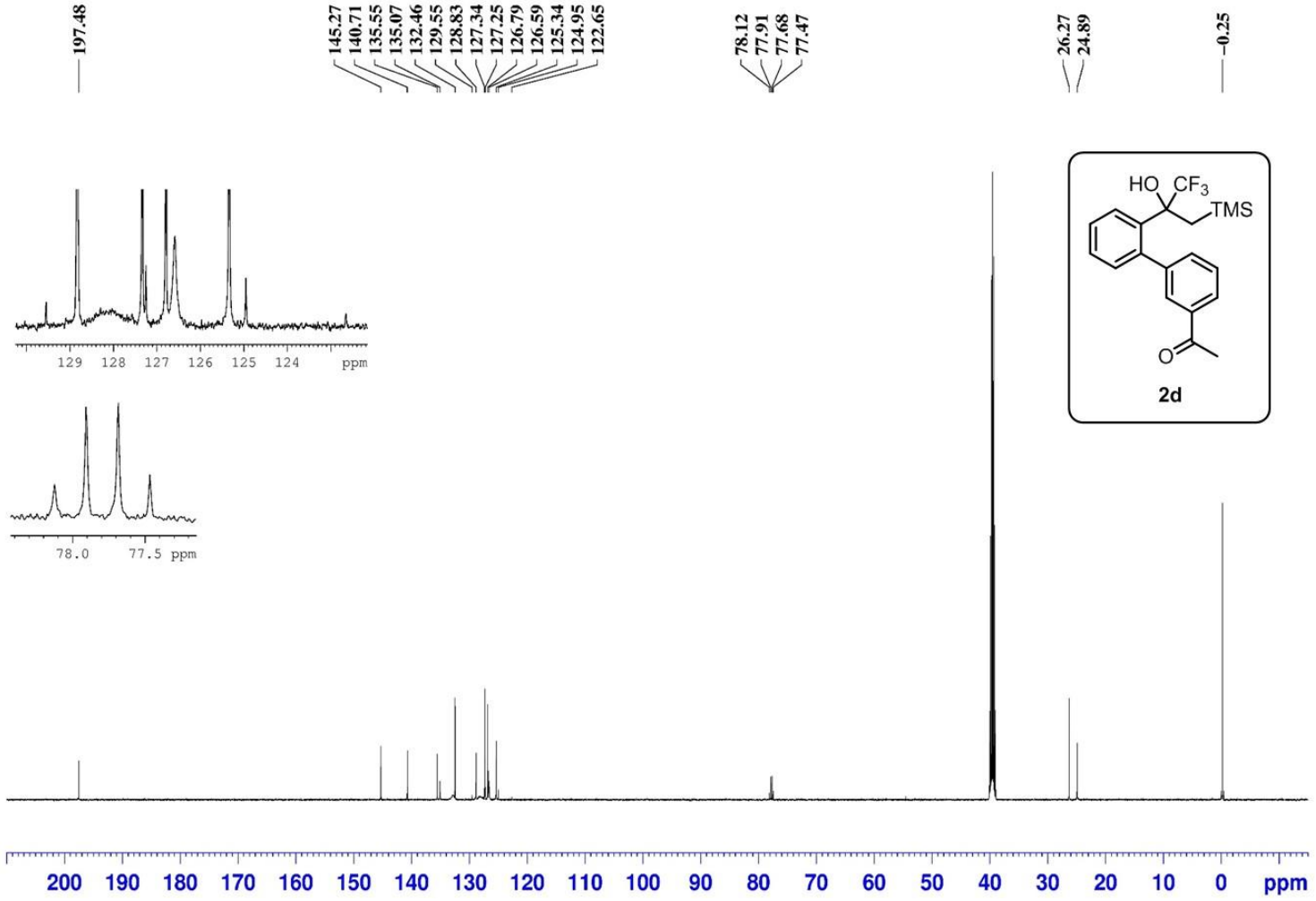

**2c**



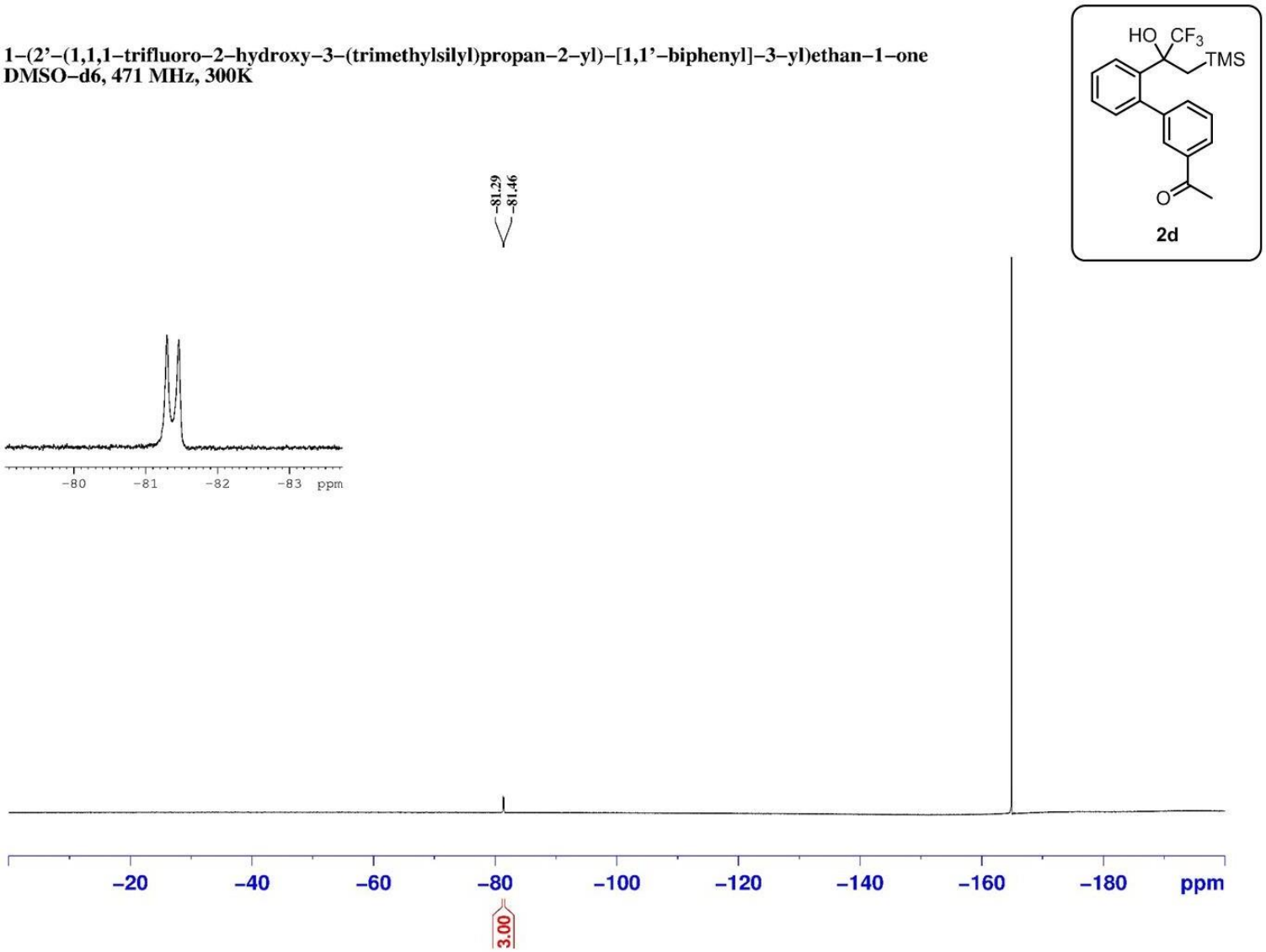
**1–(2'–(1,1,1–Trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**500 MHz, DMSO–d6**



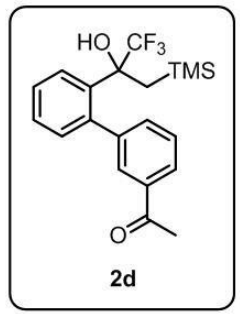
**1–(2'–(1,1,1–Trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**125 MHz, DMSO–d6, 333 K**



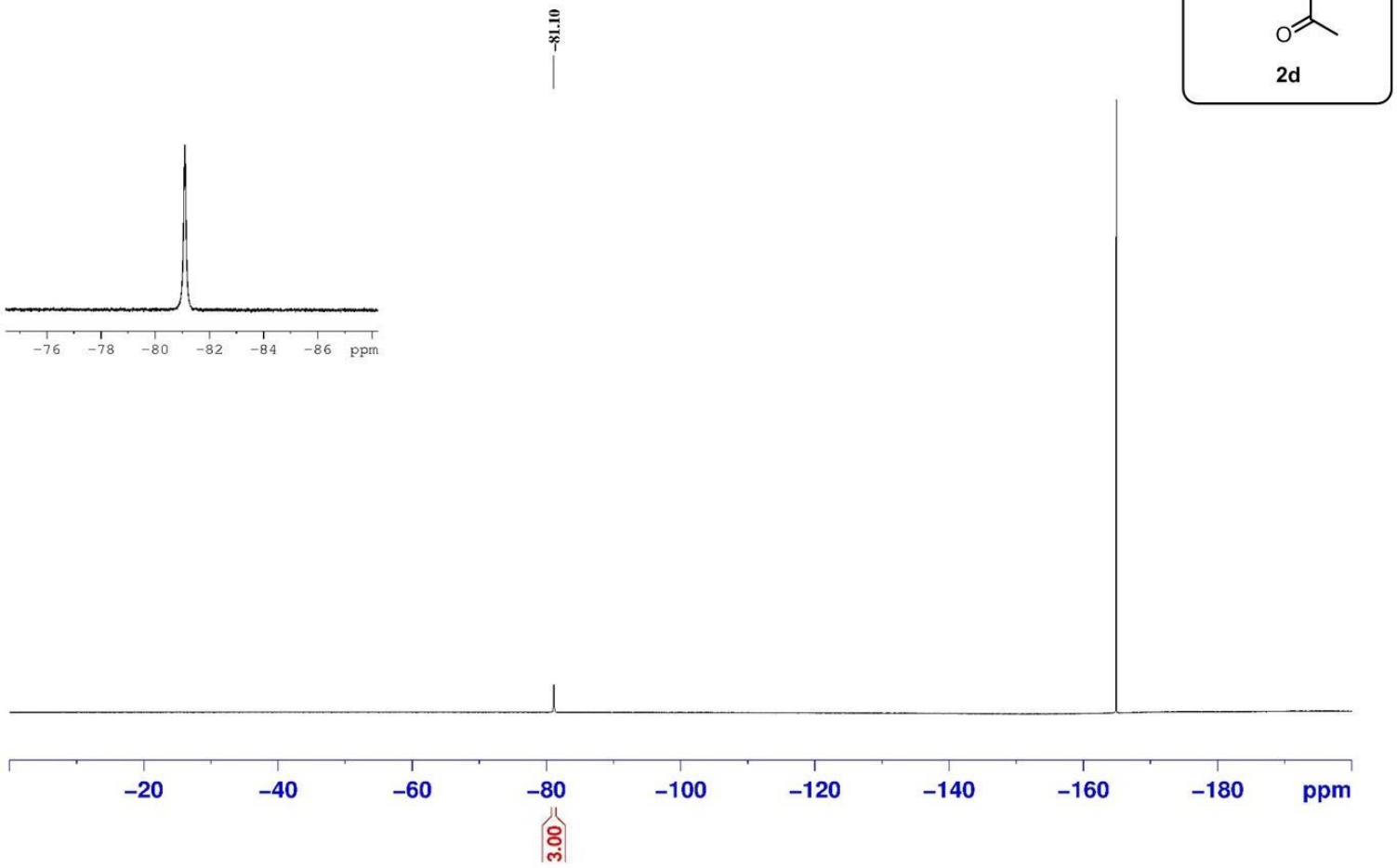
**1–(2'–(1,1,1–trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**DMSO–d6, 471 MHz, 300K**



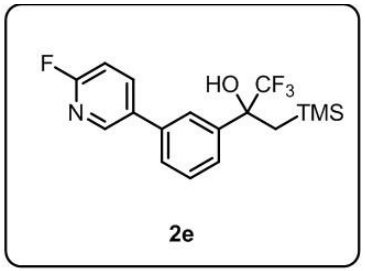
**1–(2'–(1,1,1–trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**DMSO–d6, 471 MHz, 313K**



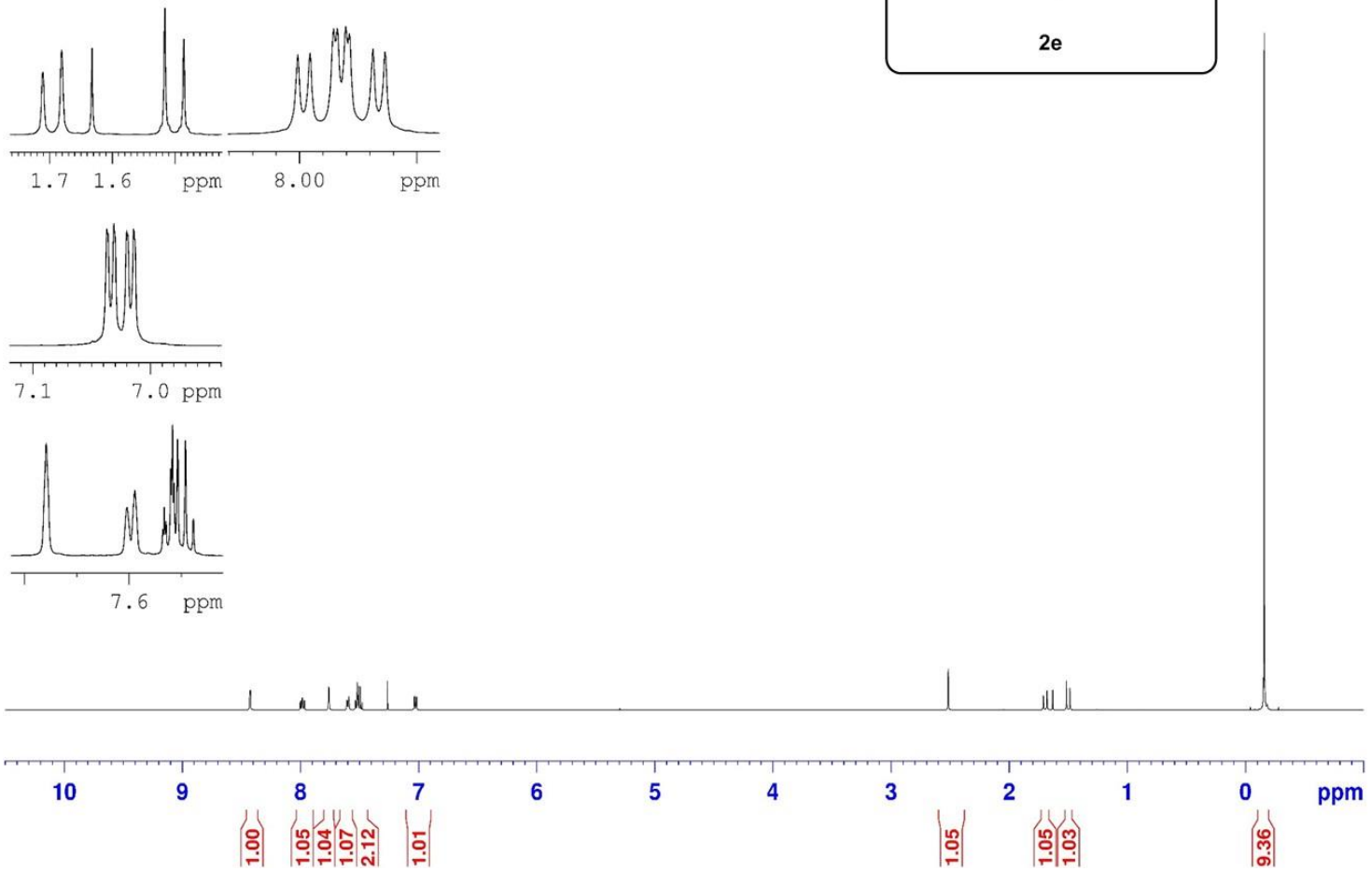

**2d**



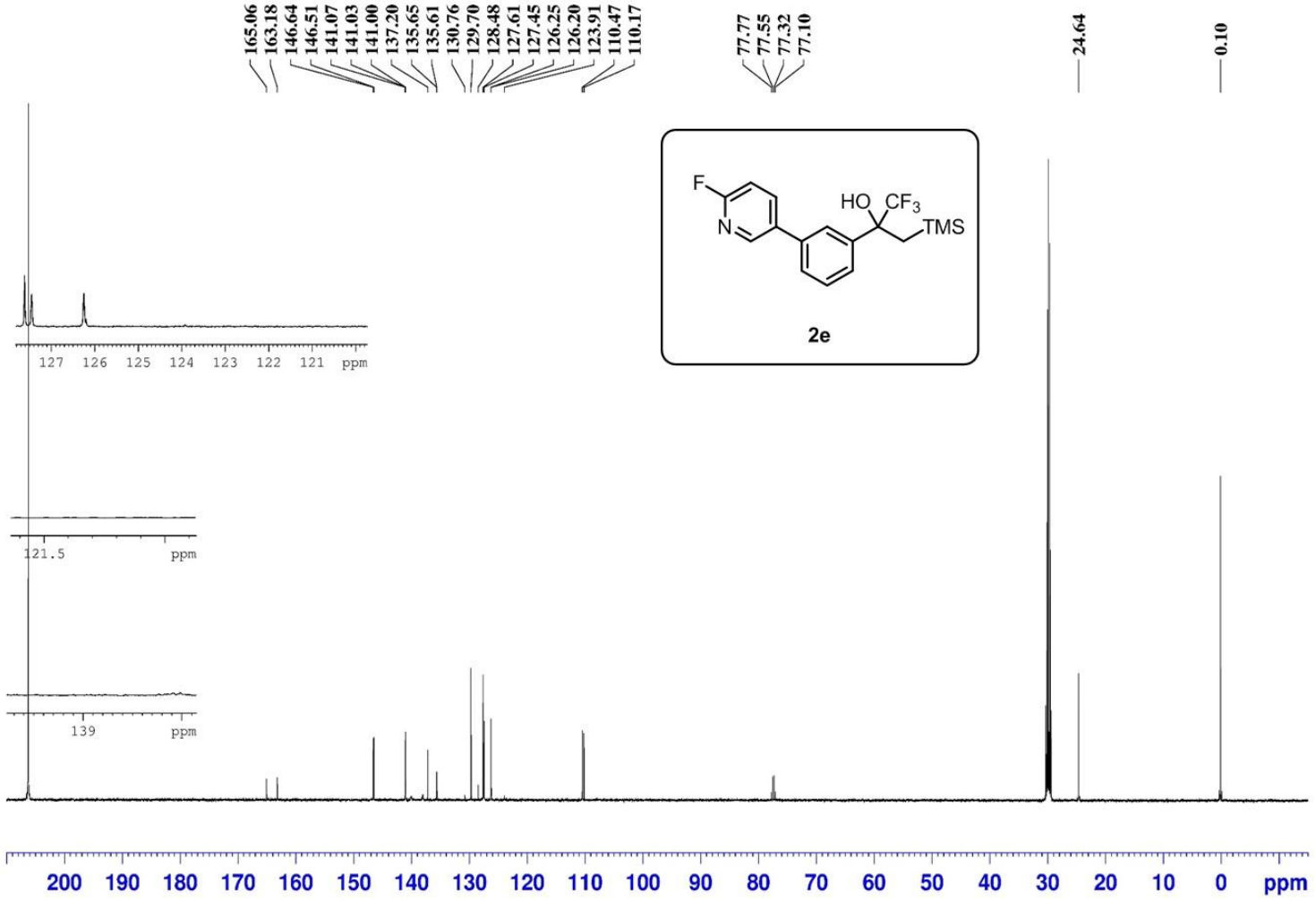
**1,1,1−Trifluoro−2−(3−(6−fluoropyridin−3−yl)phenyl)−3−(trimethylsilyl)propan−2−ol**
**500 MHz, CDCl3**



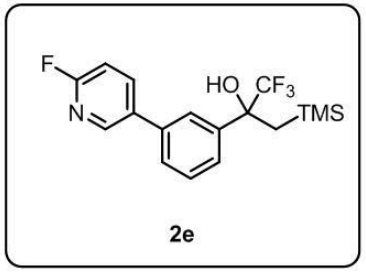

**2e**

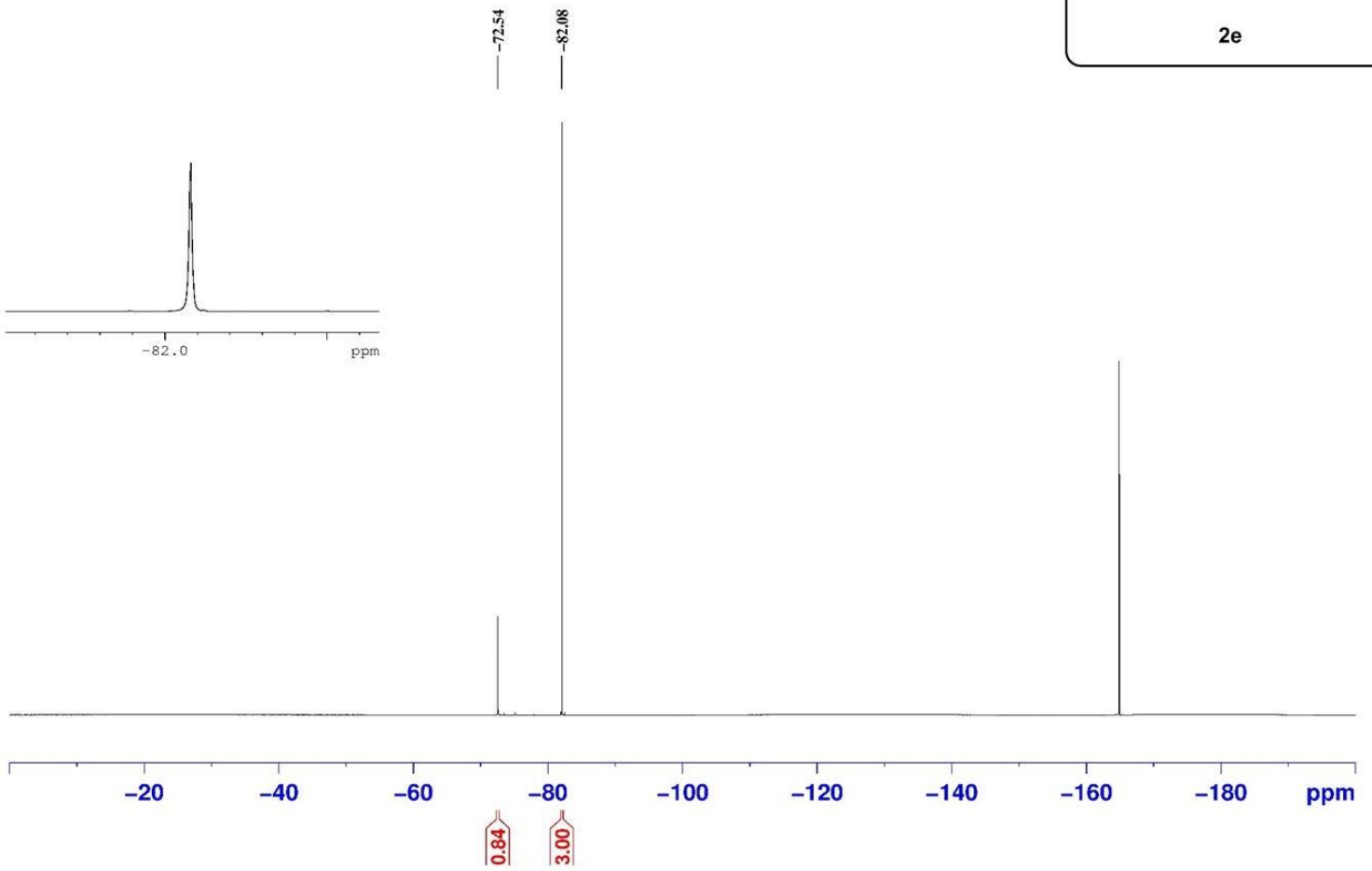


**1,1,1–Trifluoro–2–(3–(6–fluoropyridin–3–yl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**125 MHz, acetone–d6**

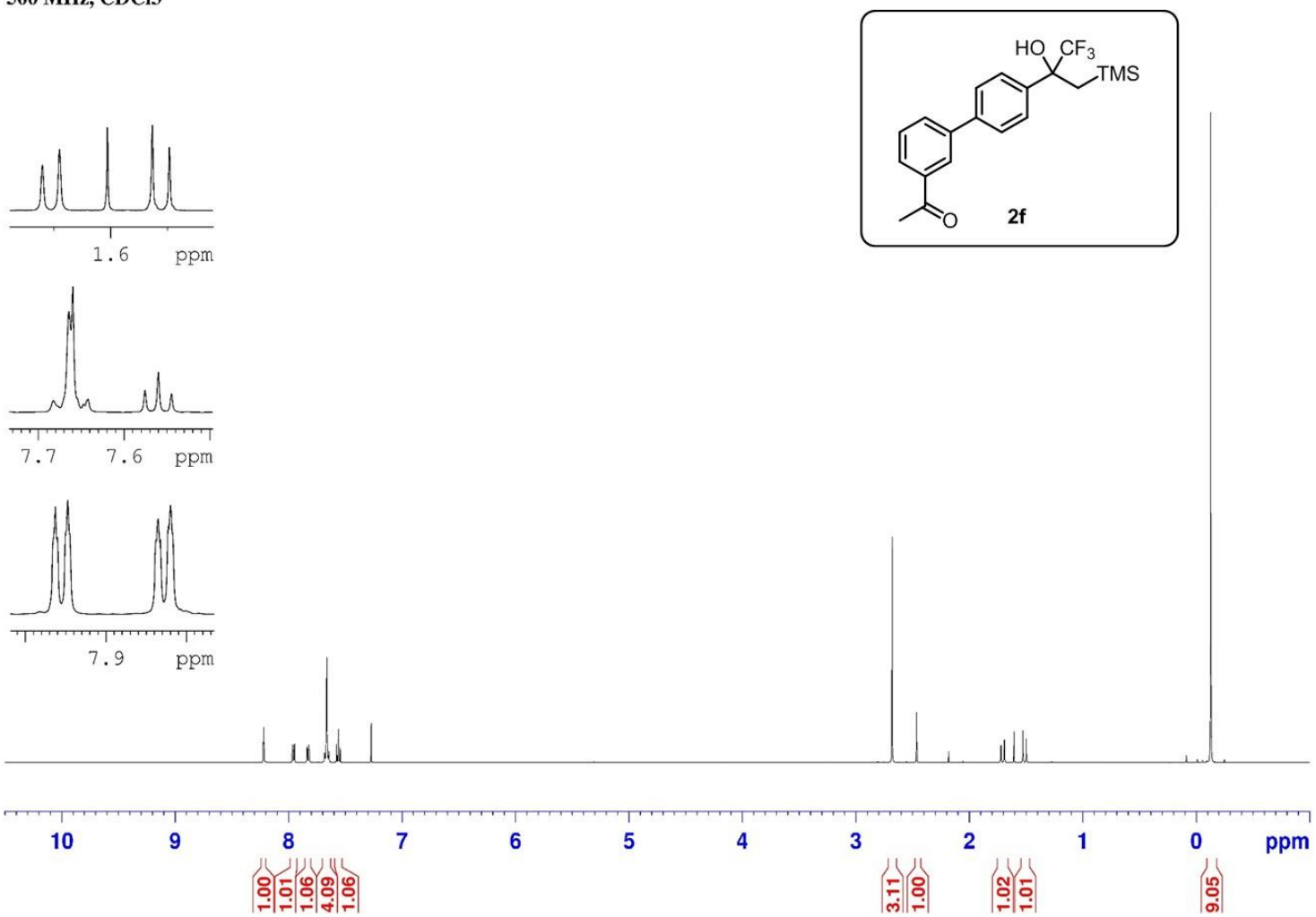


**1,1,1–trifluoro–2–(3–(6–fluoropyridin–3–yl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**Acetone–d6, 471 MHz**

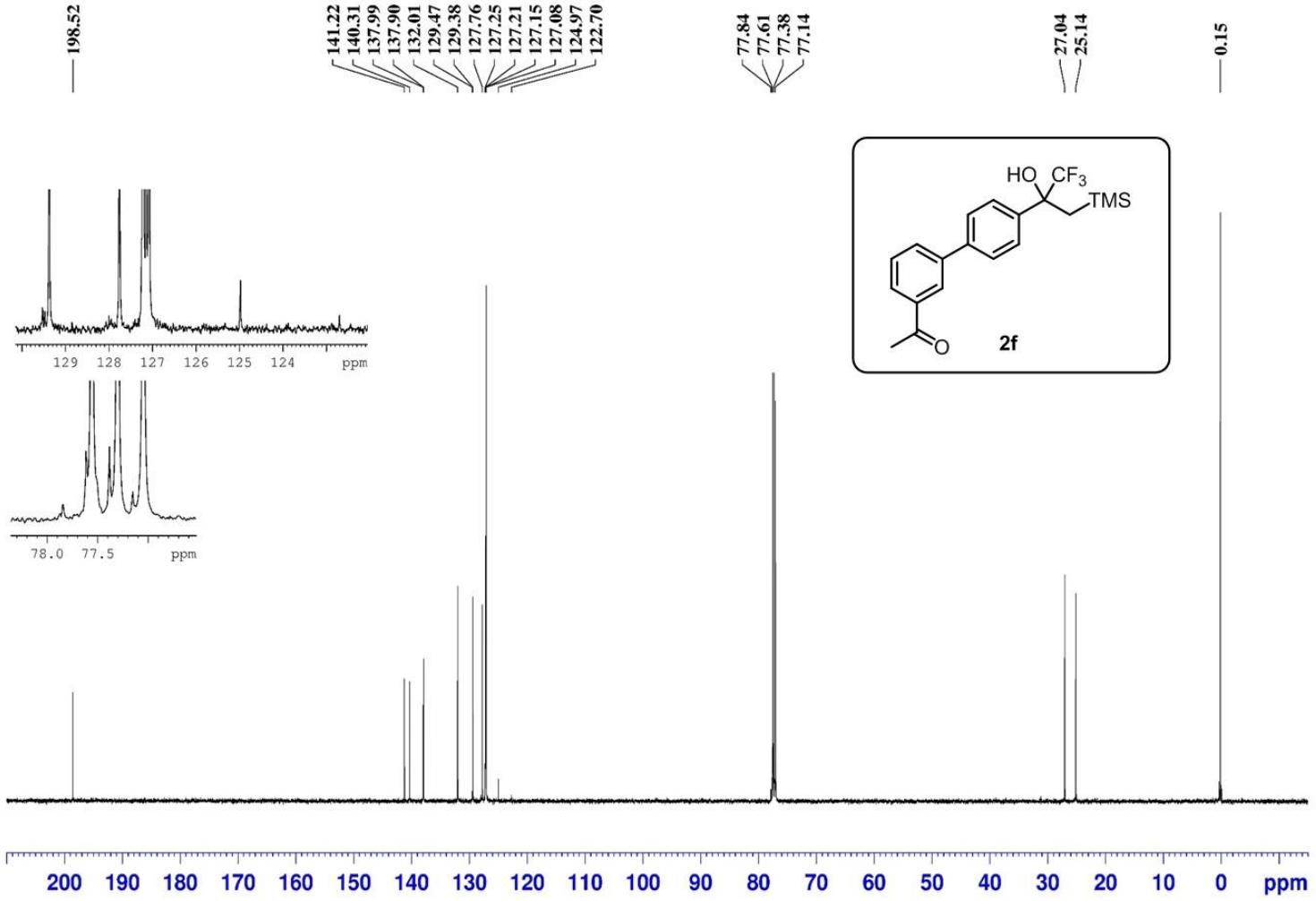


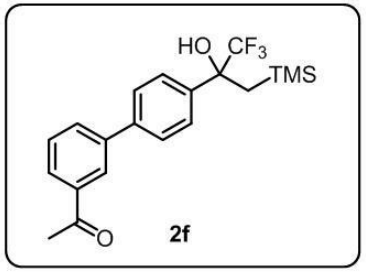
**1–(4'–(1,1,1–Trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**500 MHz, CDCl3**

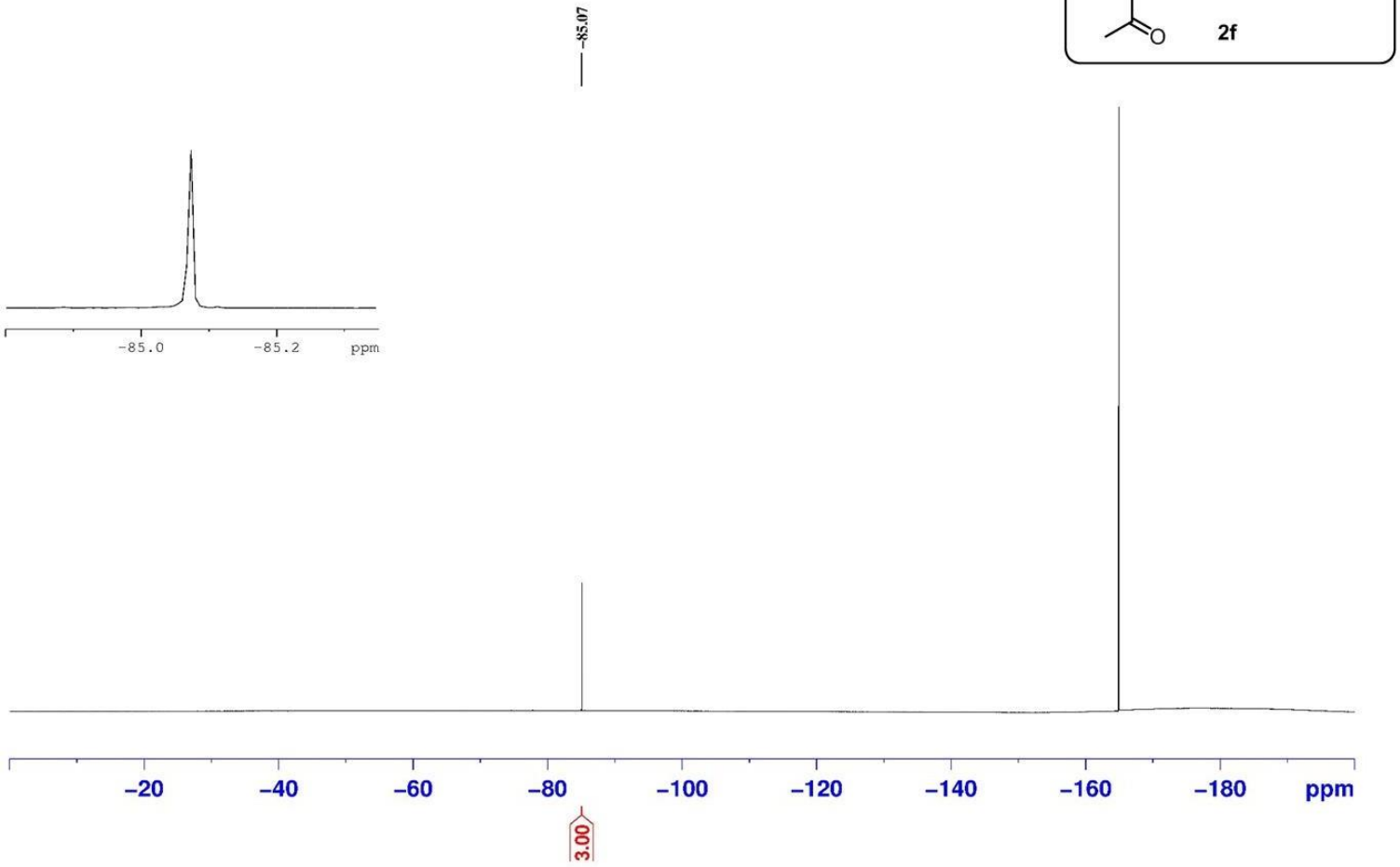


**1–(4'–(1,1,1–Trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**125 MHz, CDCl3**

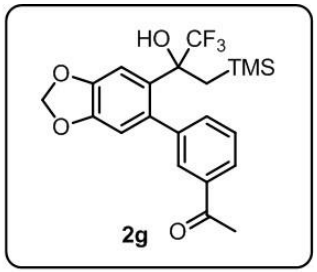


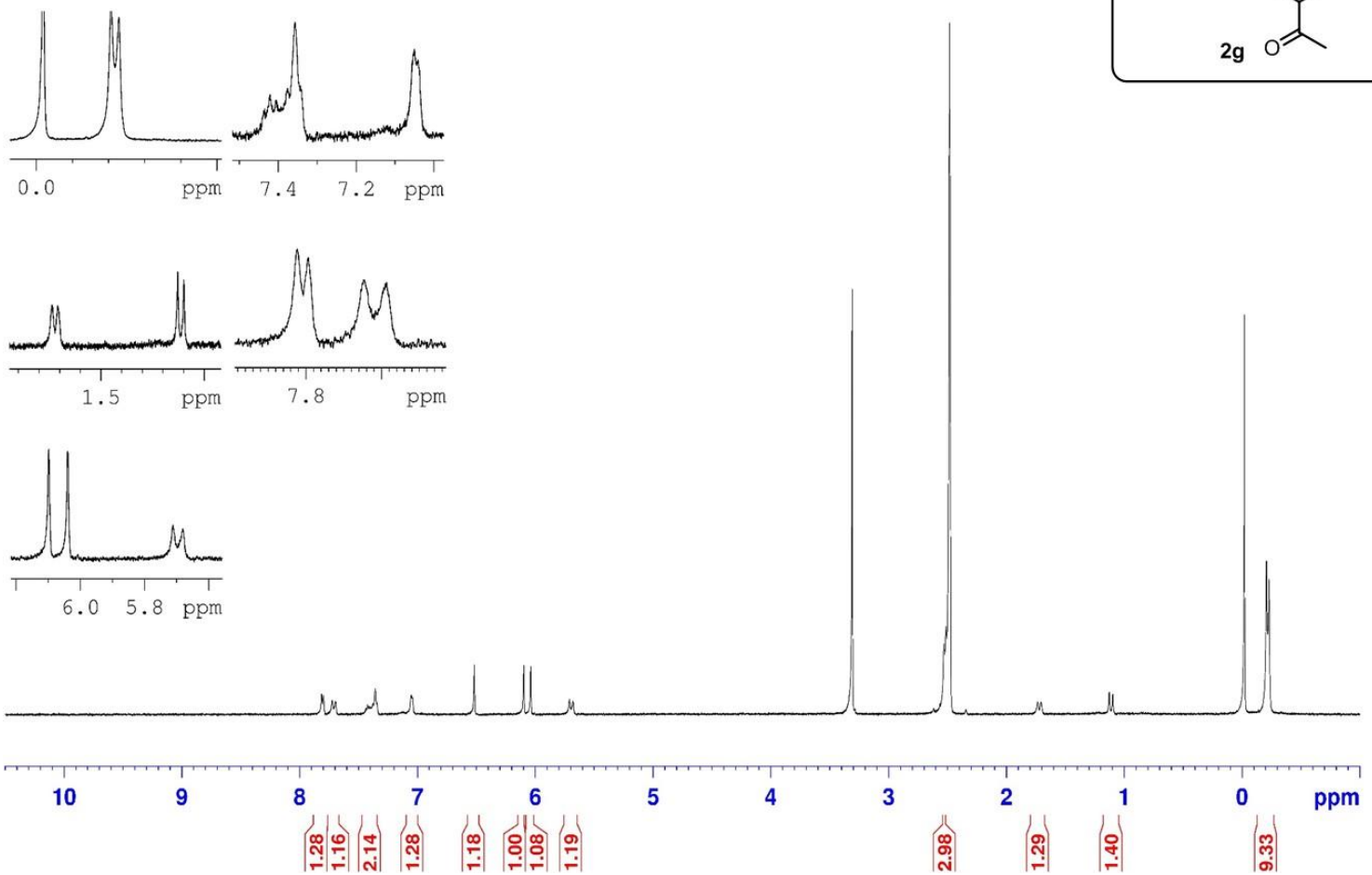
**1–(4'–(1,1,1–trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**CDCl3, 471 MHz**



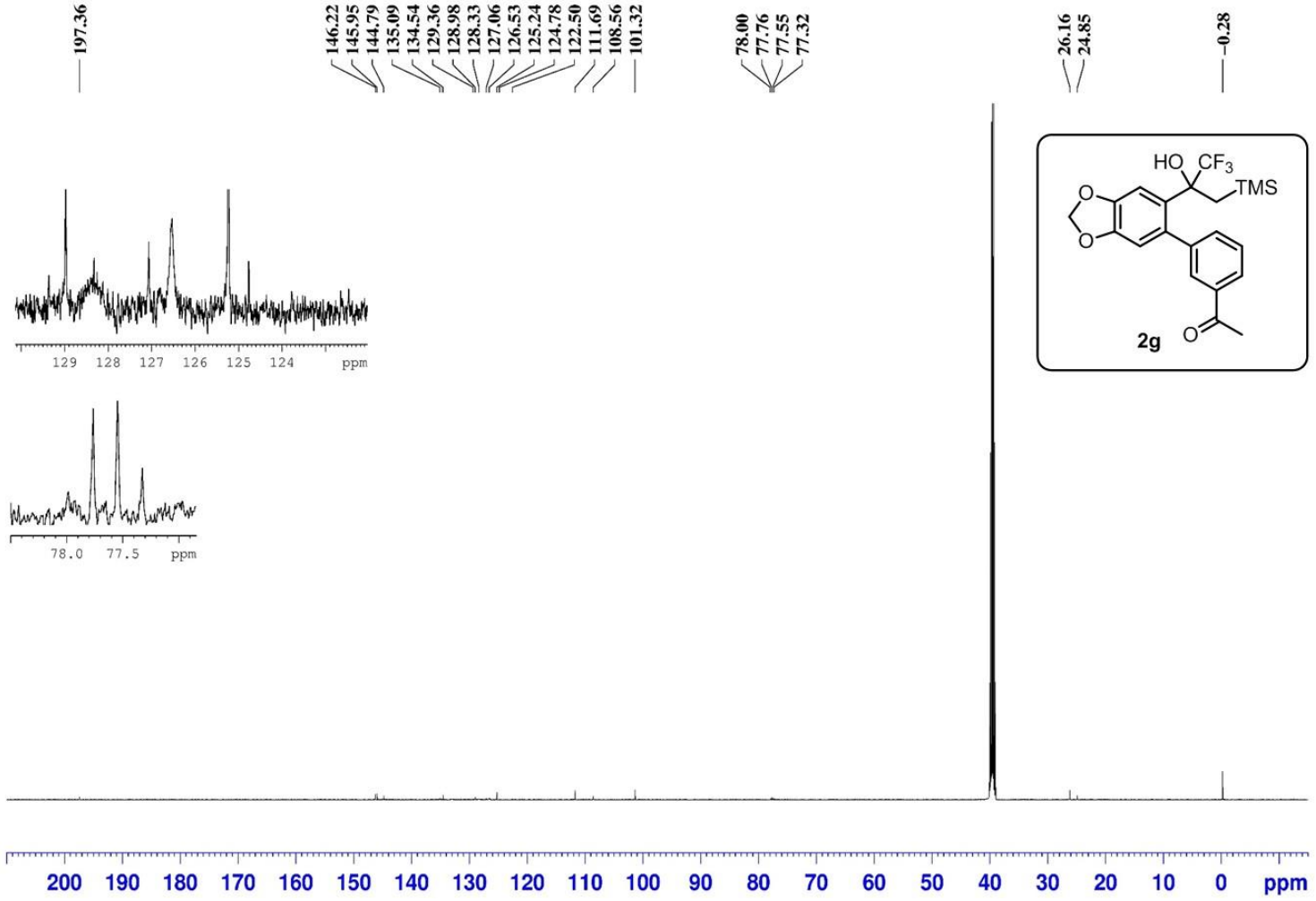



**1-(3-(6-(1,1,1-Trifluoro-2-hydroxy-3-(trimethylsilyl)propan-2-yl)benzo[d][1,3]dioxol-5-yl)phenyl)ethan-1-one**
**500 MHz, DMSO-d6**

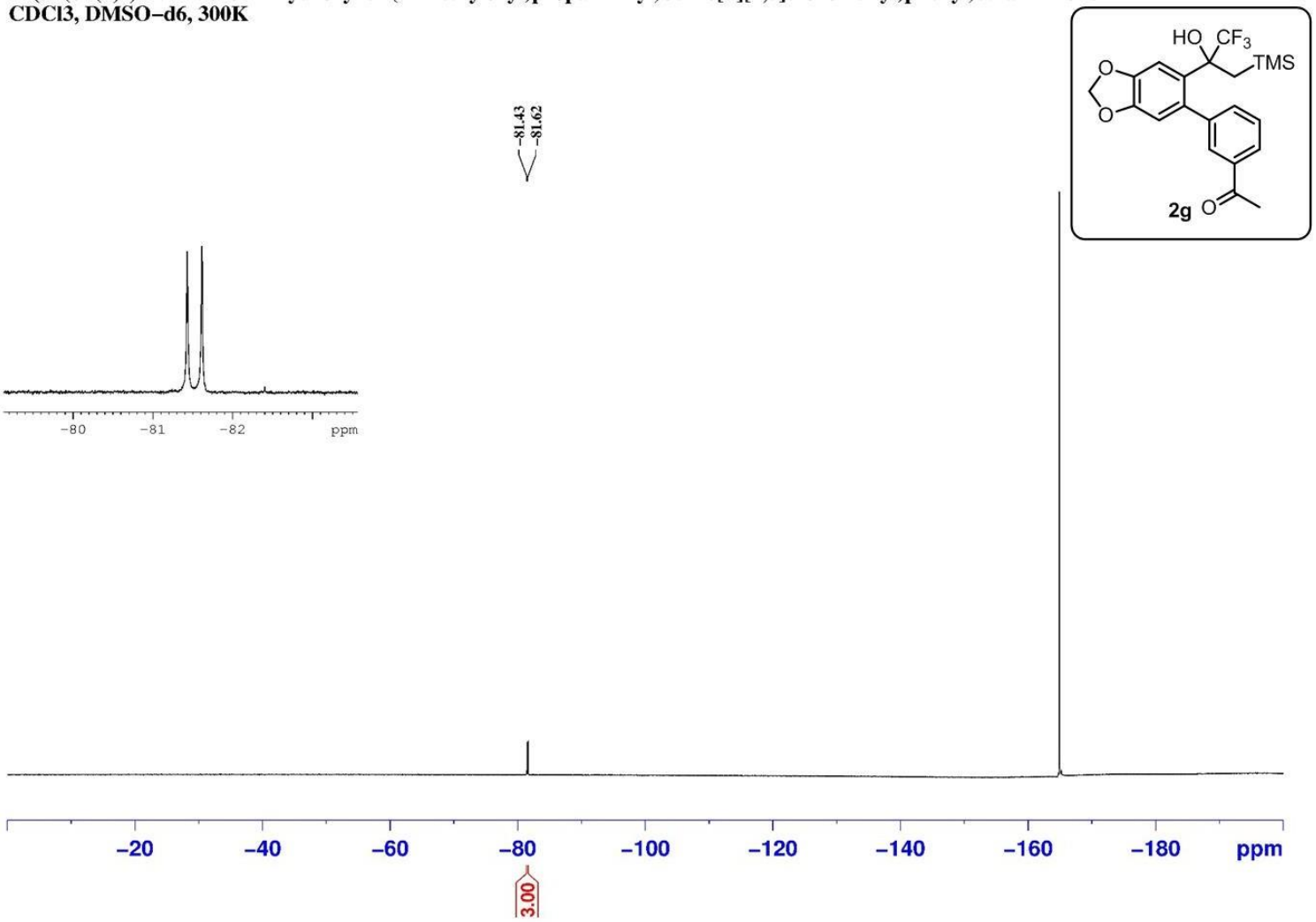


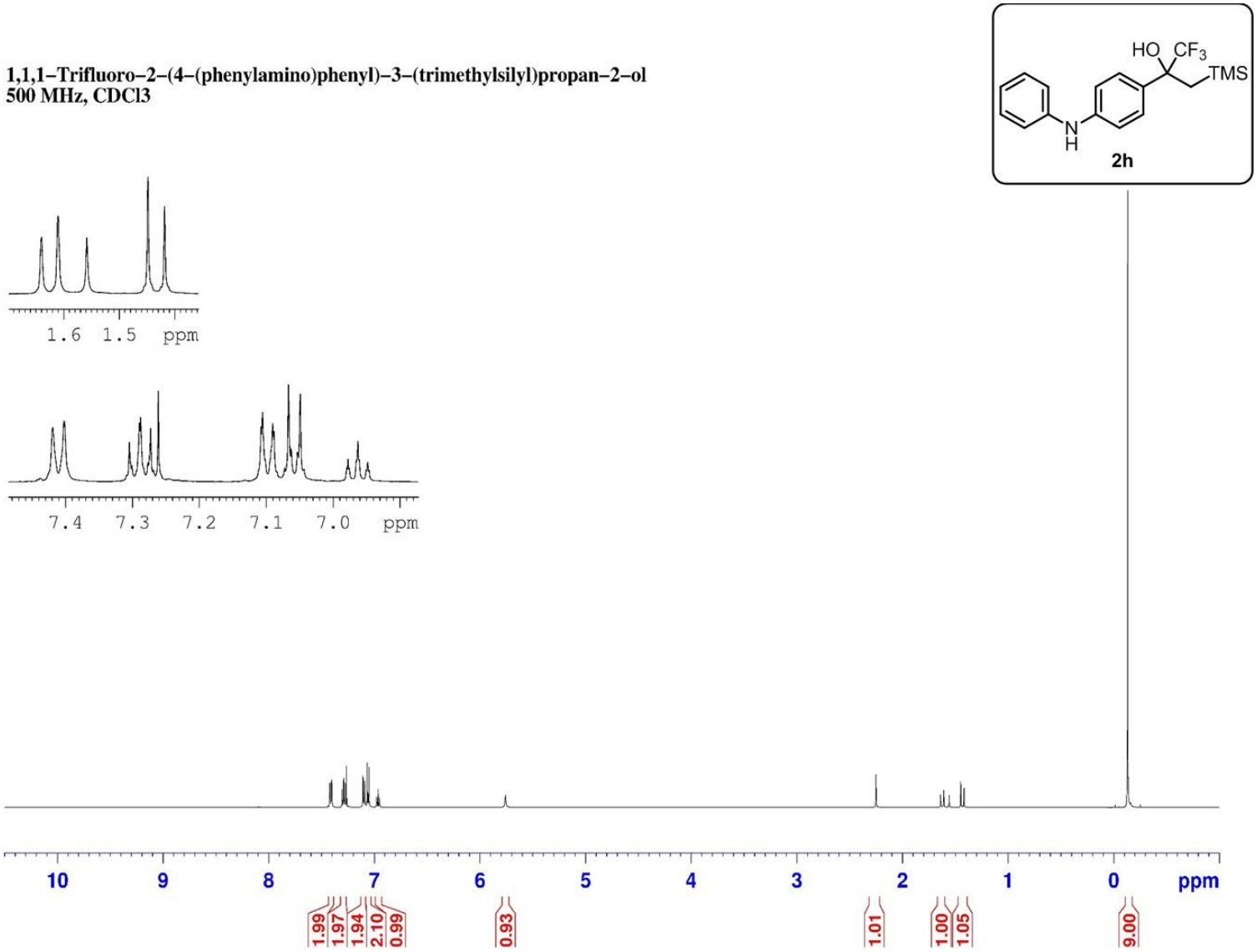
**1–(3–(6–(1,1,1–Trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)benzo[d][1,3]dioxol–5–yl)phenyl)ethan–1–one**
**125 MHz, DMSO–d6, 343 K**



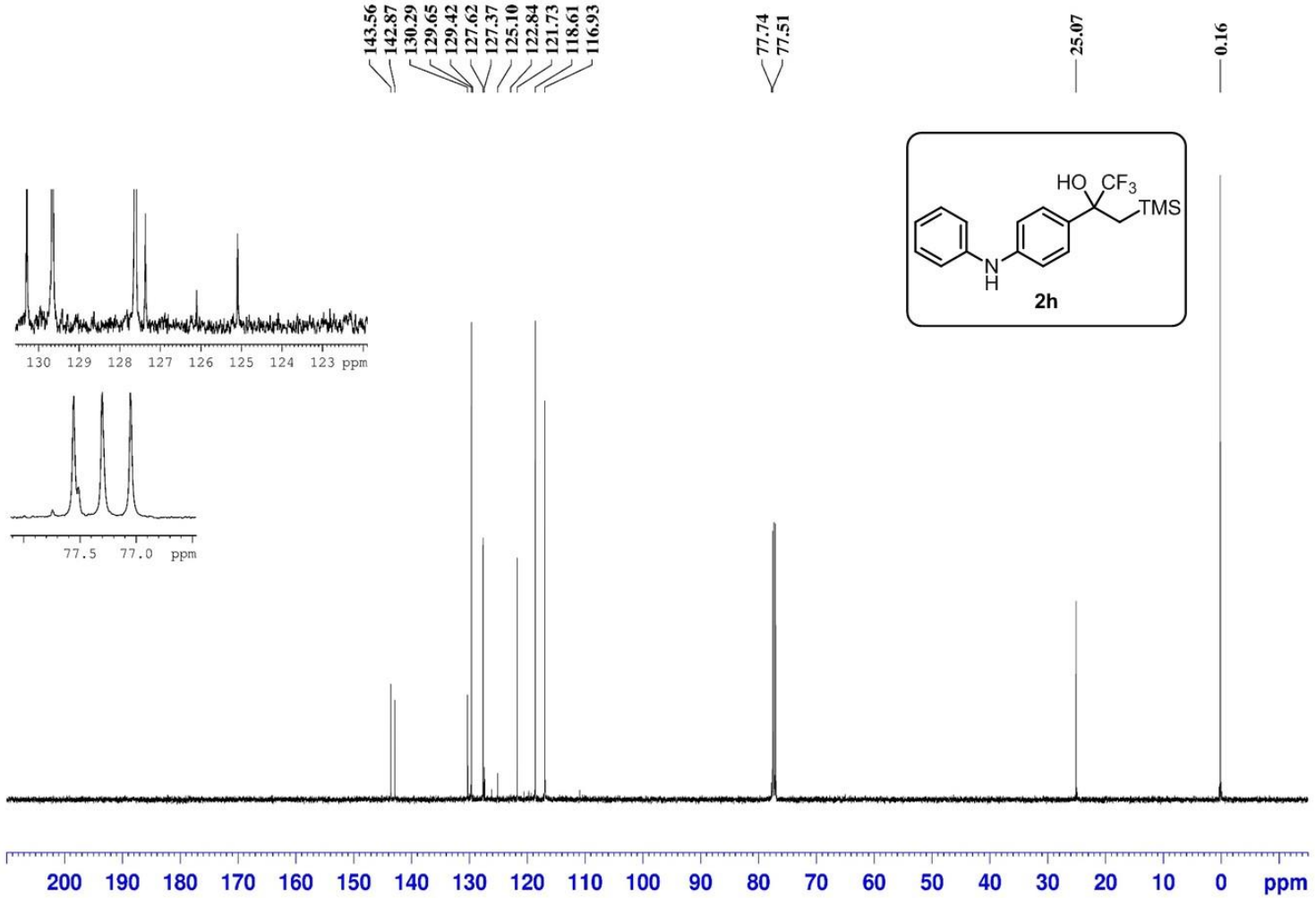
**1–(3–(6–(1,1,1–trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)benzo[d][1,3]dioxol–5–yl)phenyl)ethan–1–one**
**CDCl3, DMSO–d6, 300K**



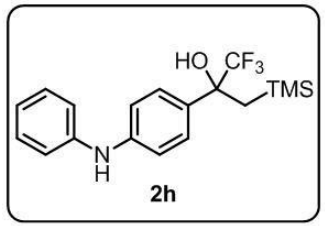
**1,1,1−Trifluoro−2−(4−(phenylamino)phenyl)−3−(trimethylsilyl)propan−2−ol**
**500 MHz, CDCl3**



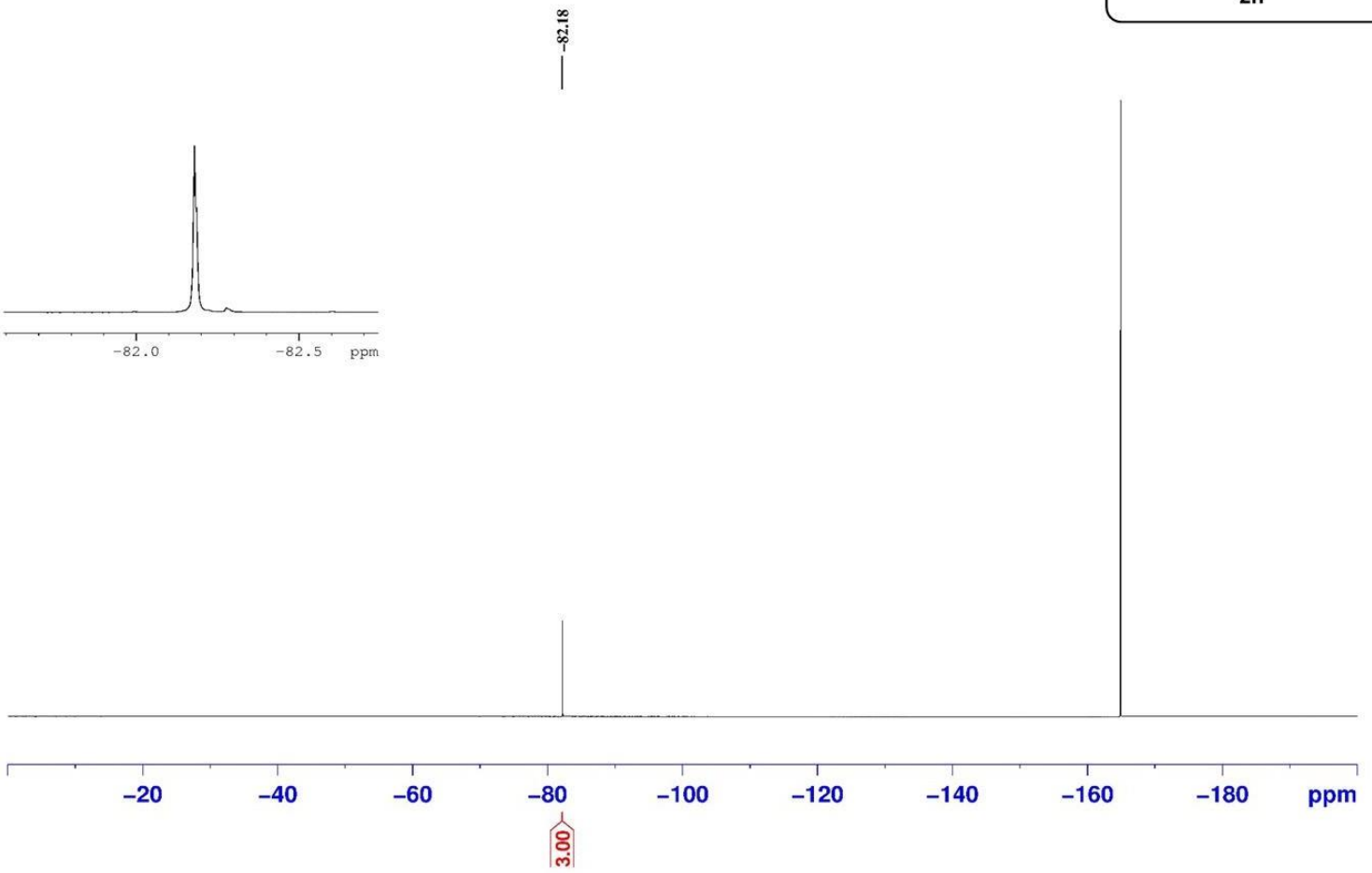
**1,1,1–Trifluoro–2–(4–(phenylamino)phenyl)–3–(trimethylsilyl)propan–2–ol**
**125 MHz, CDCl3**



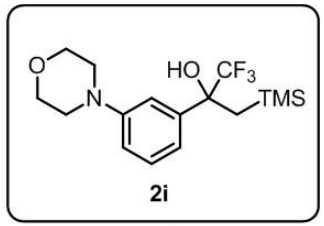
**1,1,1–trifluoro–2–(4–(phenylamino)phenyl)–3–(trimethylsilyl)propan–2–ol**
**Acetone–d6, 471 MHz**



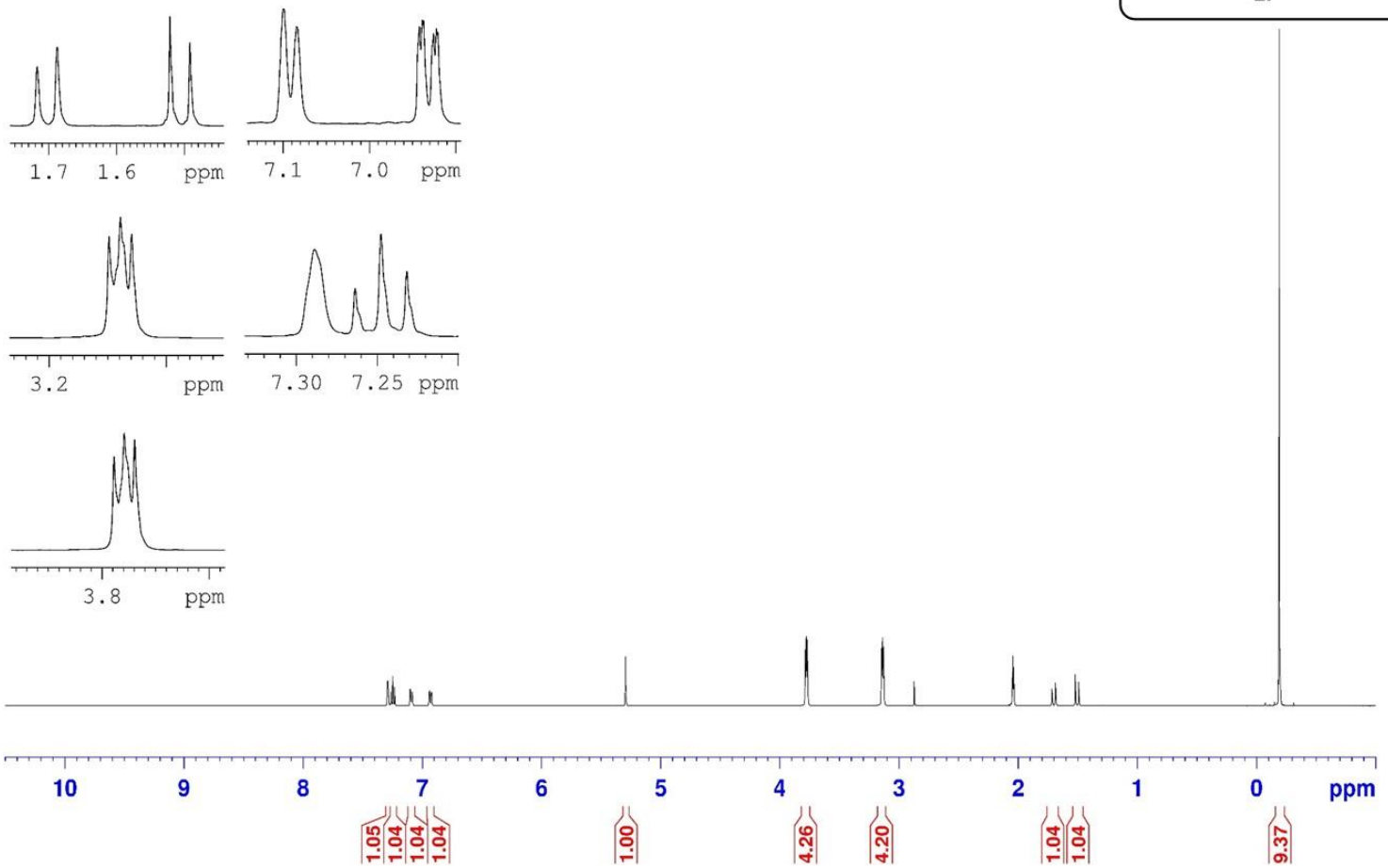
**2h**



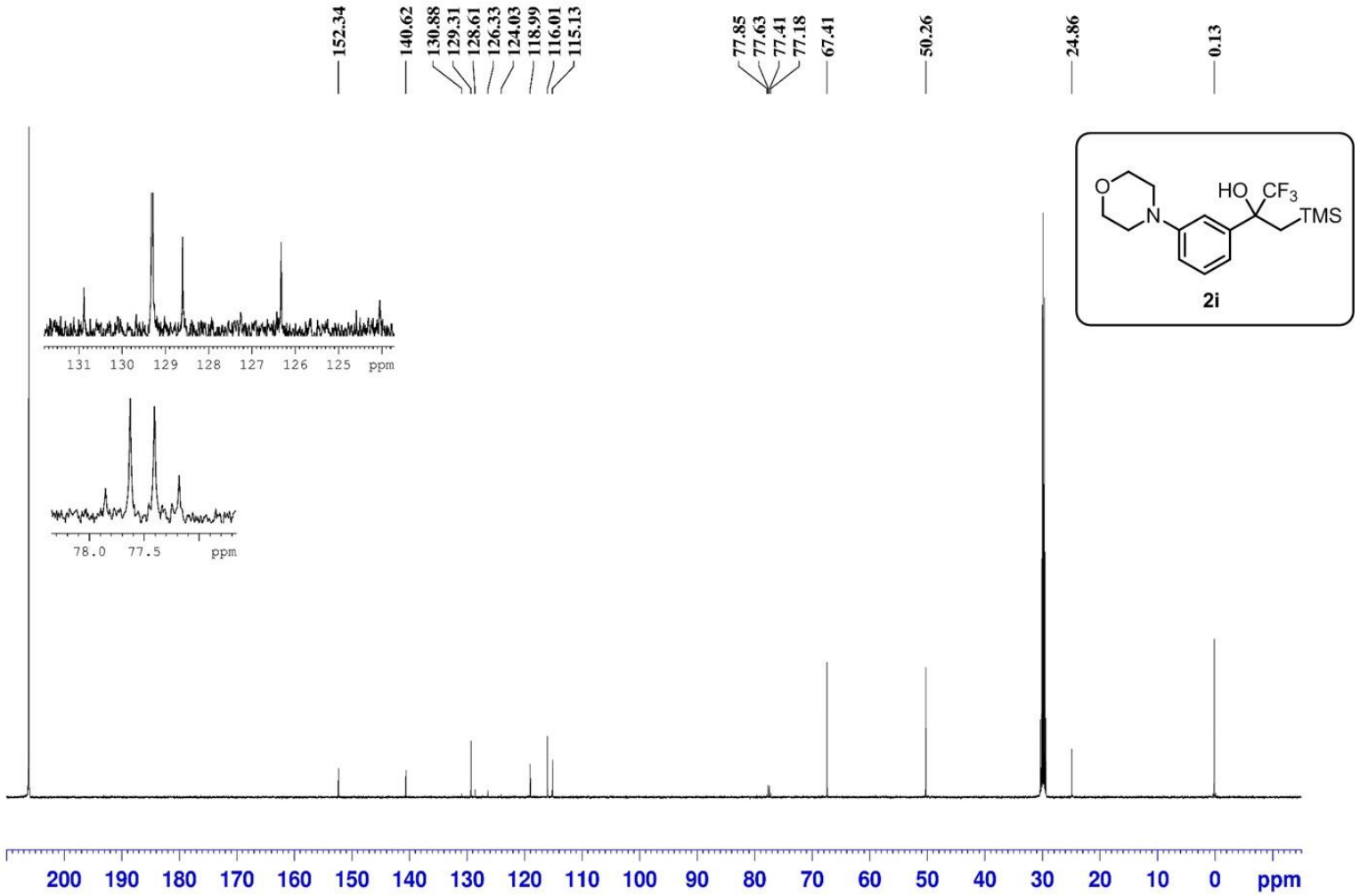
**1,1,1−Trifluoro−2−(3−morpholinophenyl)−3−(trimethylsilyl)propan−2−ol**
**500 MHz, acetone_d6**



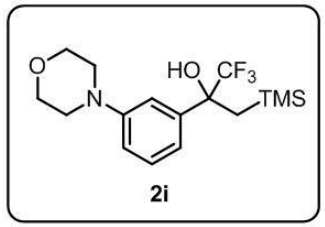

**2i**



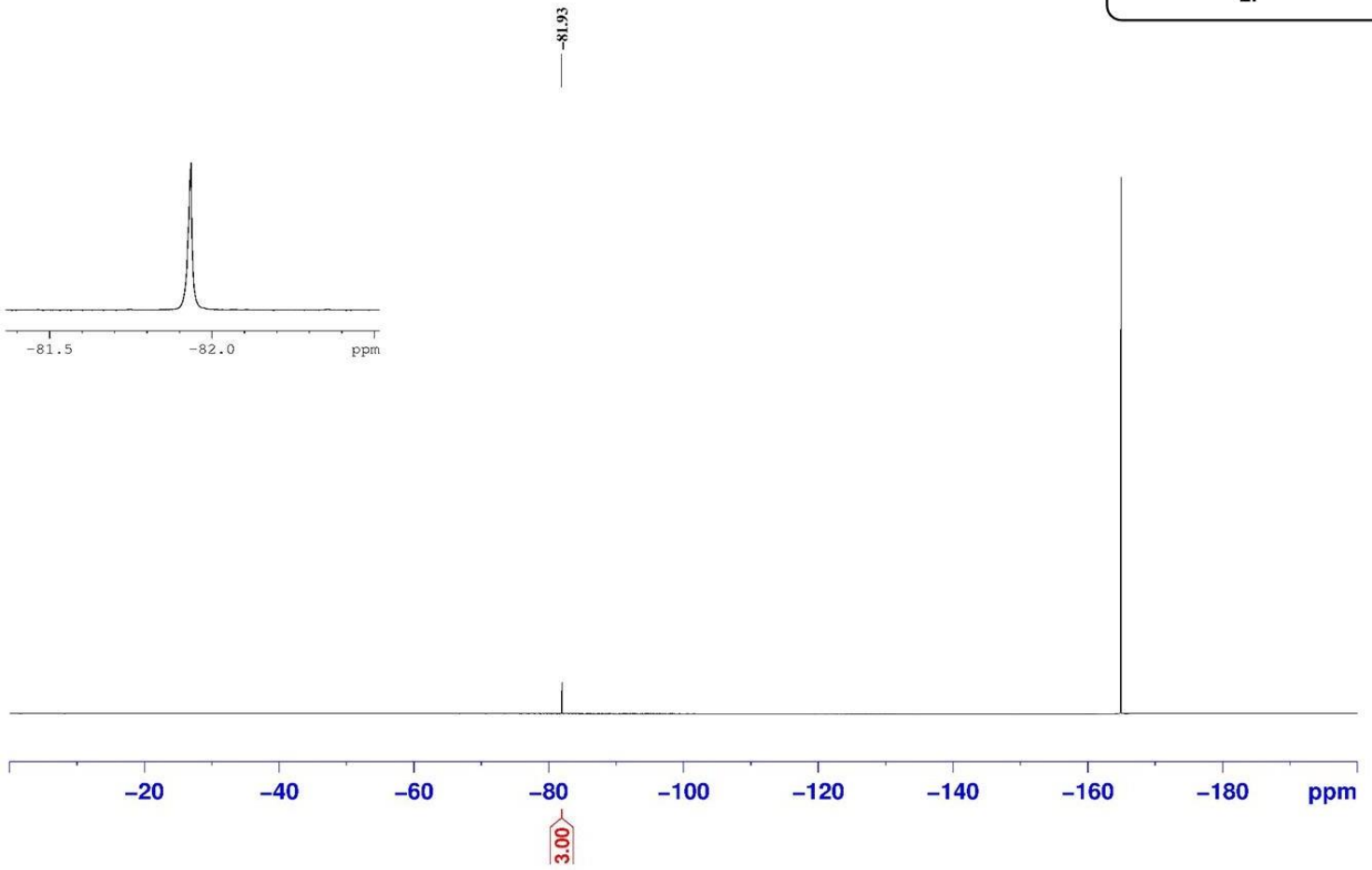
**1,1,1–Trifluoro–2–(3–morpholinophenyl)–3–(trimethylsilyl)propan–2–ol**
**125 MHz, acetone–d6**



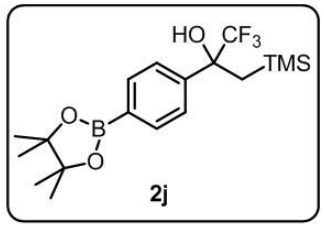
**1,1,1–trifluoro–2–(3–morpholinophenyl)–3–(trimethylsilyl)propan–2–ol**
**Acetone–d6, 471 MHz**

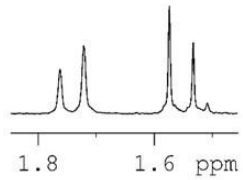


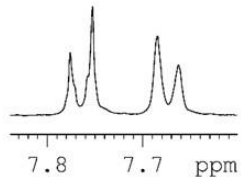

**2i**



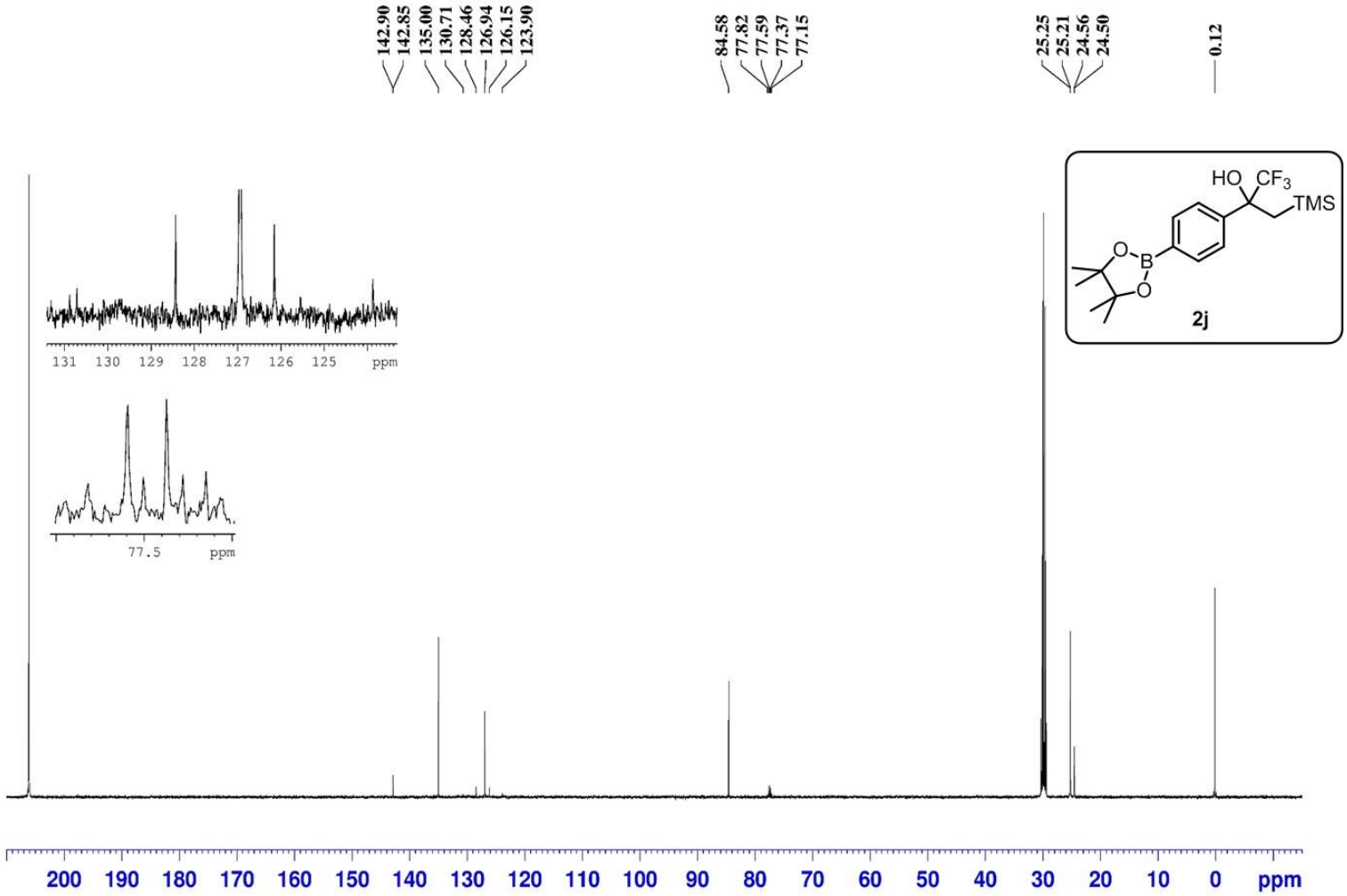
**1,1,1−Trifluoro−2−(4−(4,4,5,5−tetramethyl−1,3,2−dioxaborolan−2−yl)phenyl)−3−(trimethylsilyl)propan−2−ol**
**500 MHz, acetone−d6**



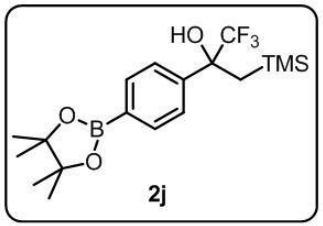



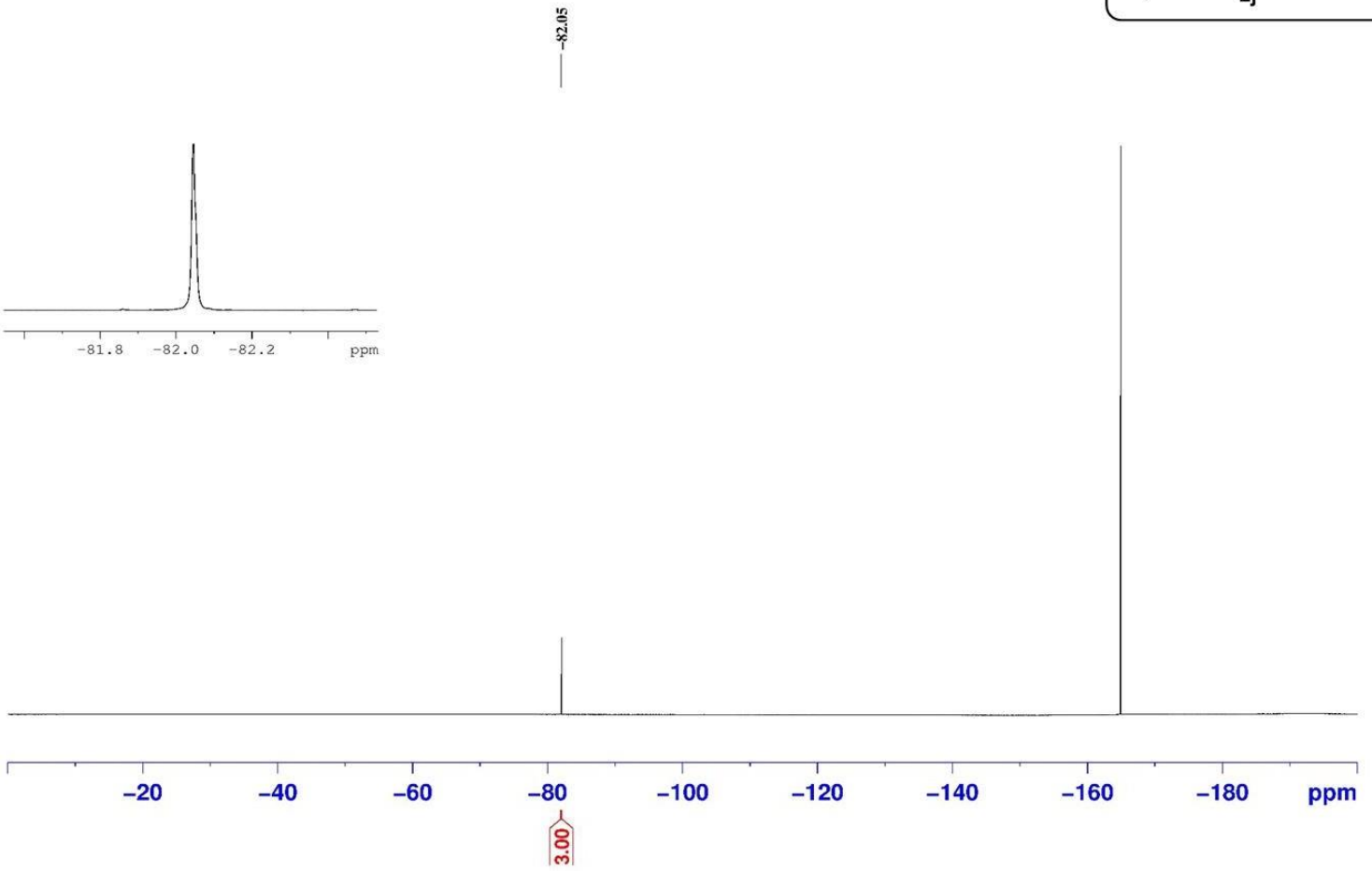



**1,1,1−Trifluoro−2−(4−(4,4,5,5−tetramethyl−1,3,2−dioxaborolan−2−yl)phenyl)−3−(trimethylsilyl)propan−2−ol**
**125 MHz, acetone−d6**

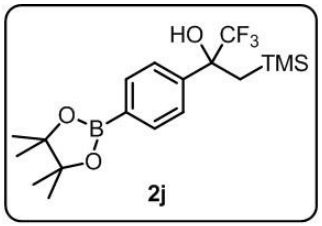


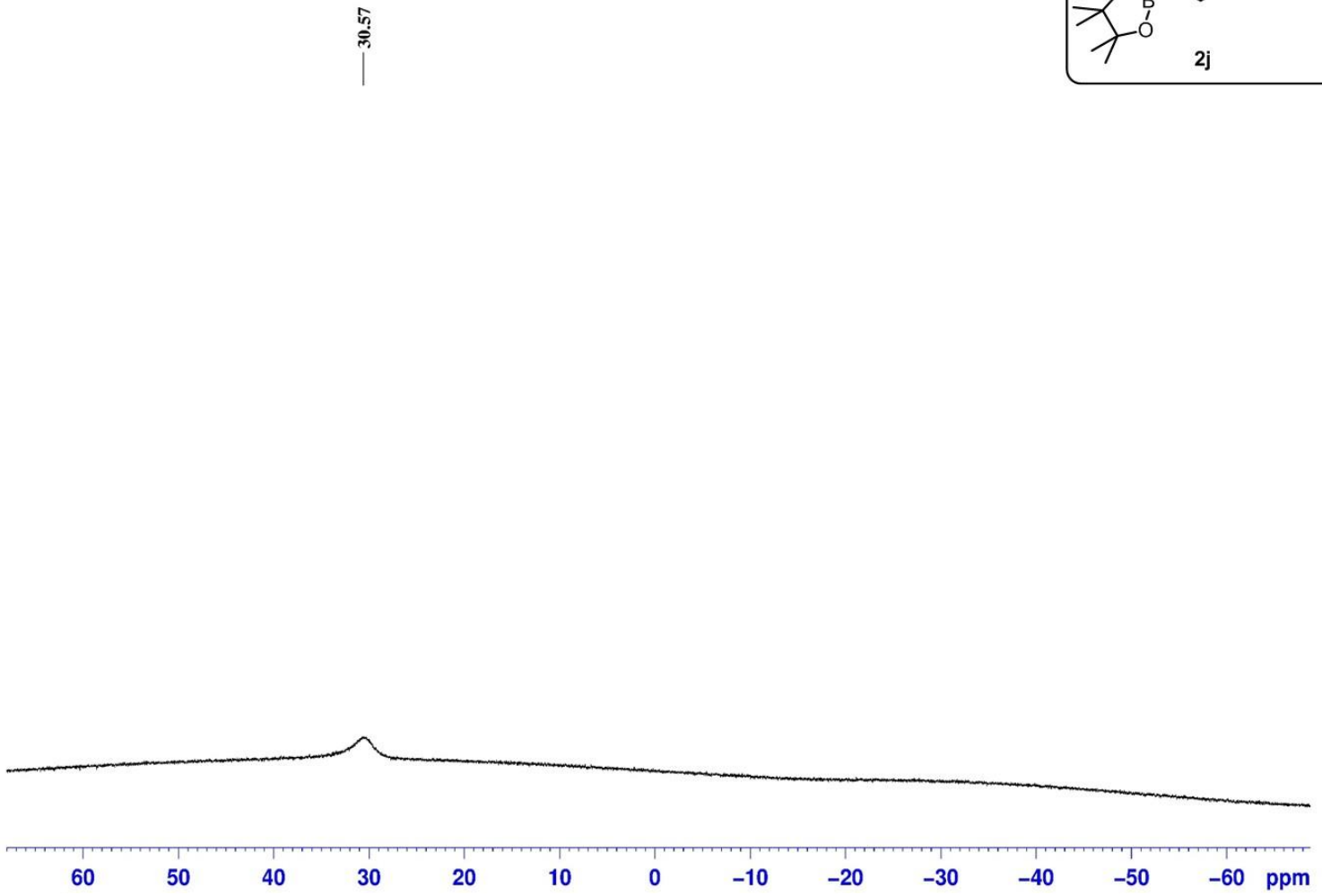
**1,1,1−trifluoro−2−(4−(4,4,5,5−tetramethyl−1,3,2−dioxaborolan−2−yl)phenyl)−3−(trimethylsilyl)propan−2−ol**
**CDCl3, 471 MHz**



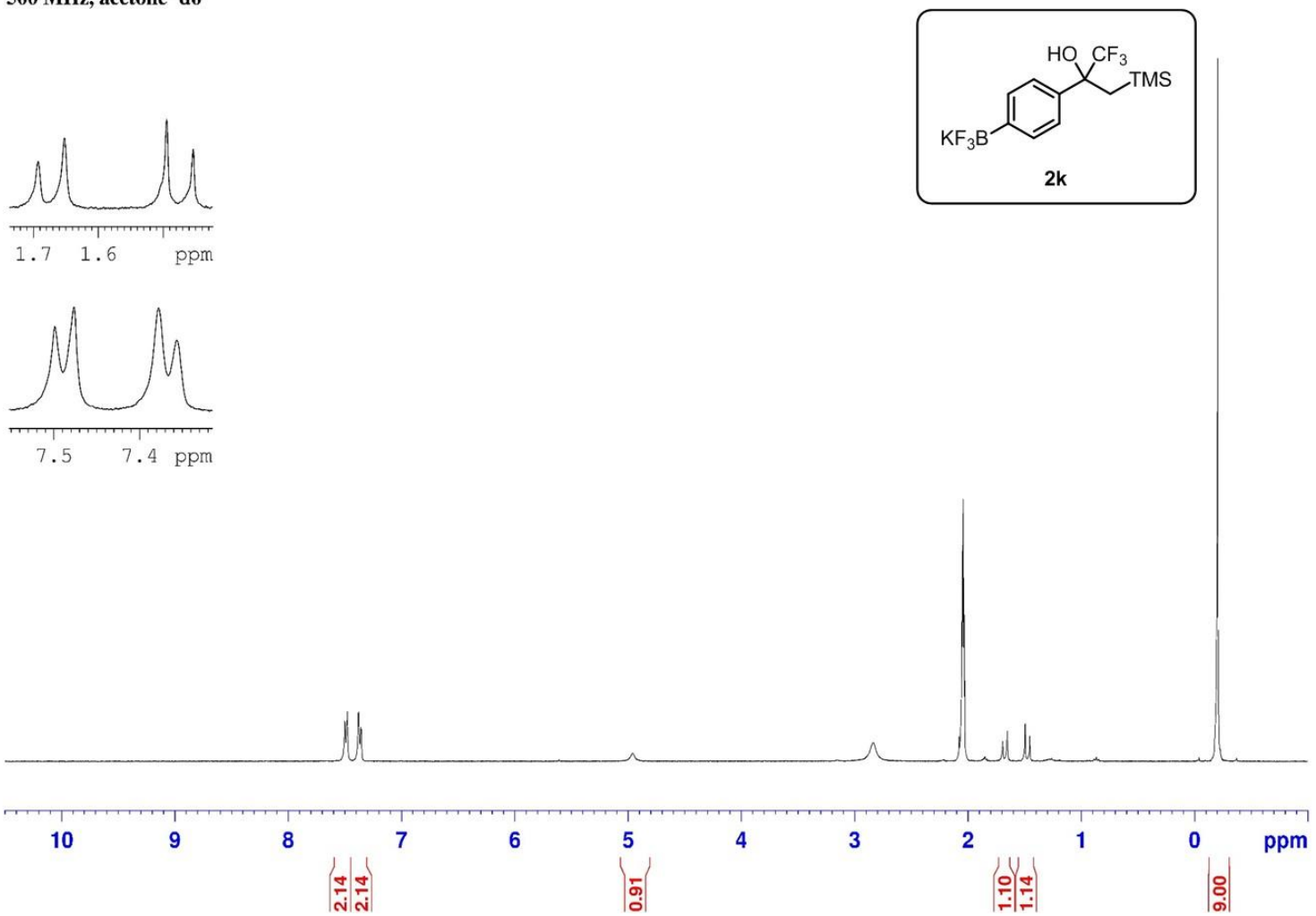



**1,1,1−Trifluoro−2−(4−(4,4,5,5−tetramethyl−1,3,2−dioxaborolan−2−yl)phenyl)−3−(trimethylsilyl)propan−2−ol**
**11B NMR with 1H decoupling**

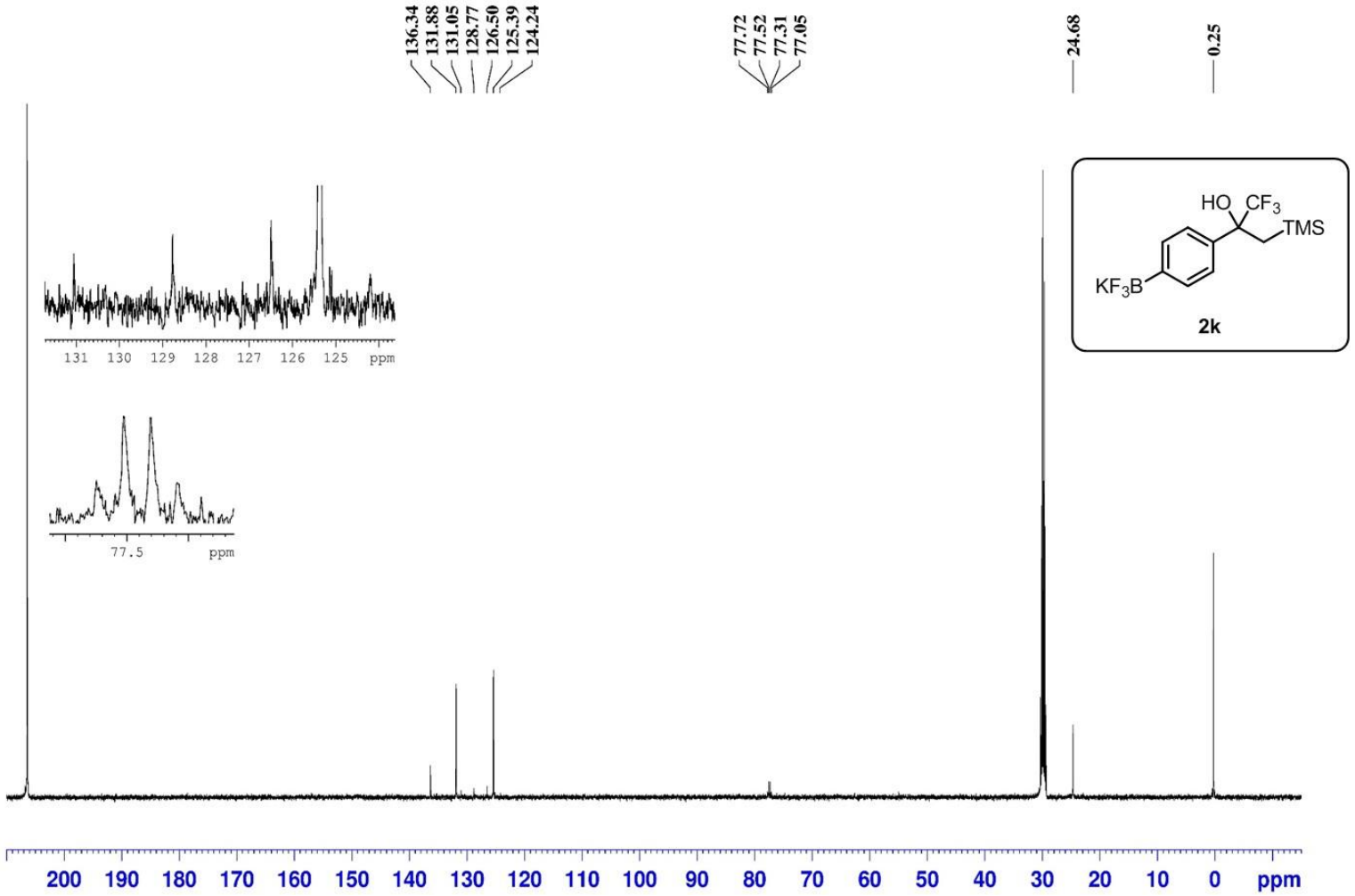


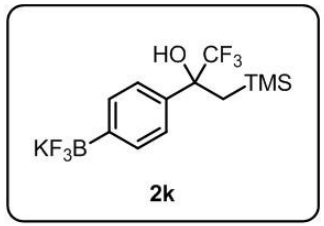
**Potassium (4–(1,1,1–Trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)phenyl)trifluoroborate**
**500 MHz, acetone–d6**



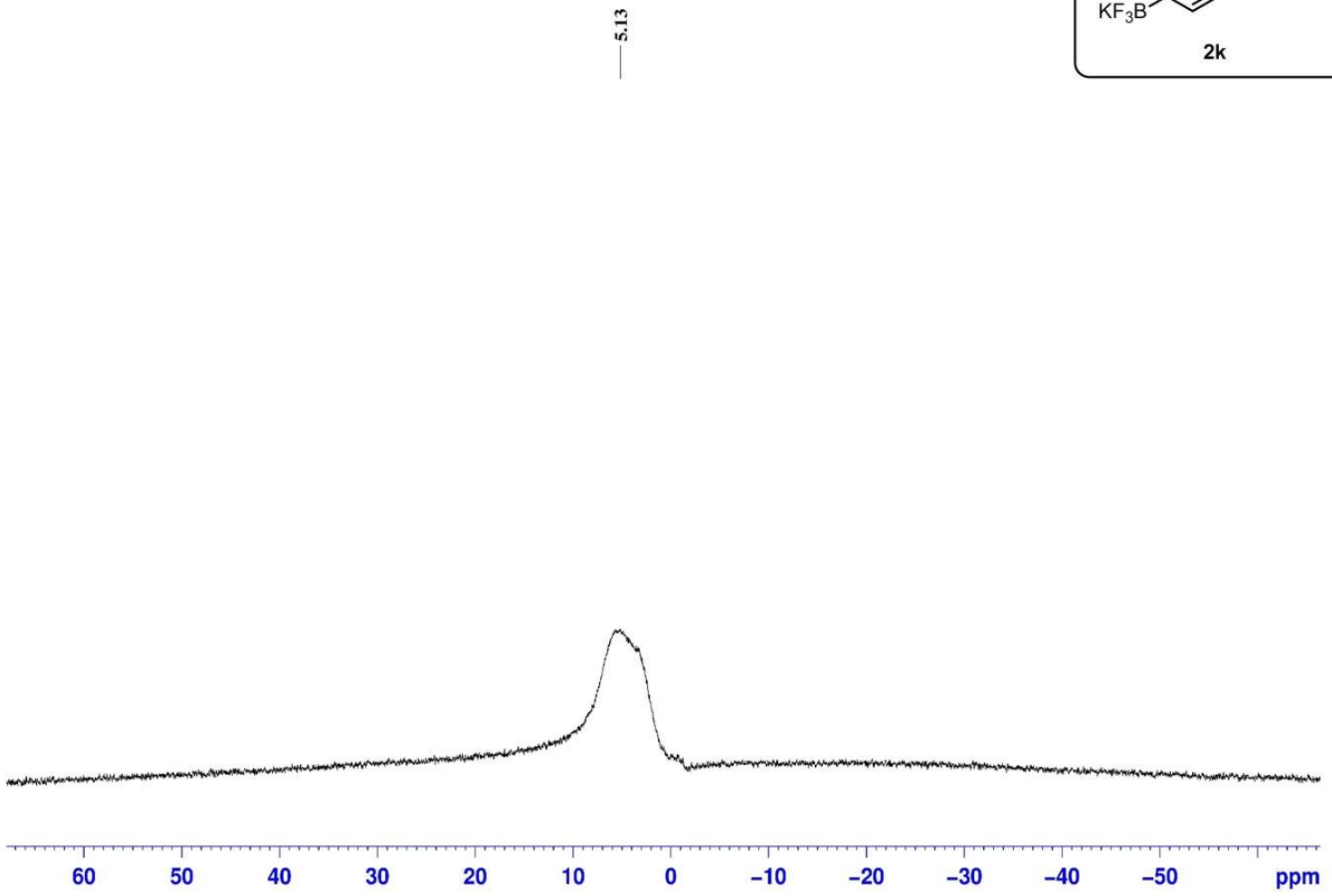
**Potassium (4–(1,1,1–Trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)phenyl)trifluoroborate**
**125 MHz, acetone–d6**



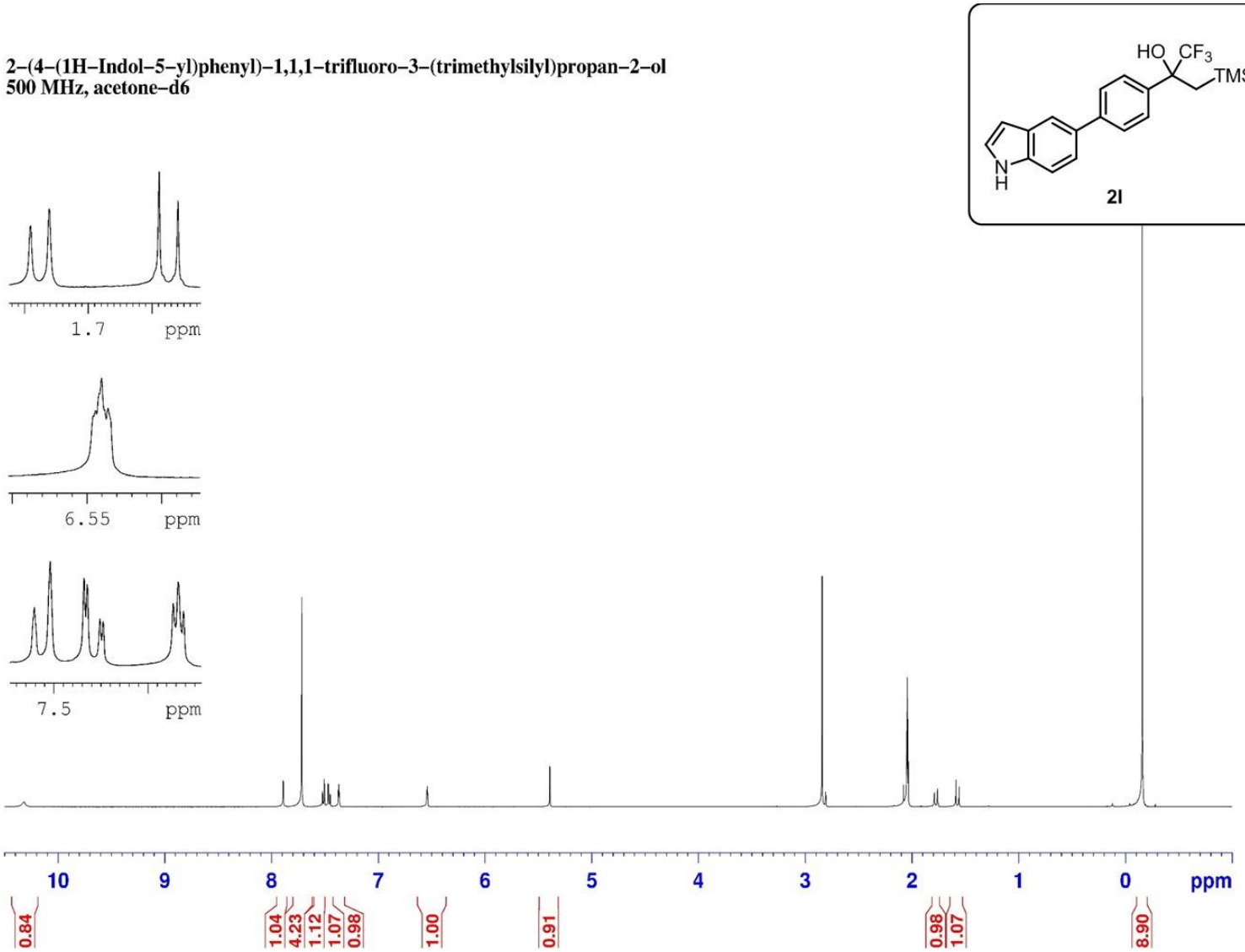
**Potassium (4–(1,1,1–Trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)phenyl)trifluoroborate**
**11B NMR**



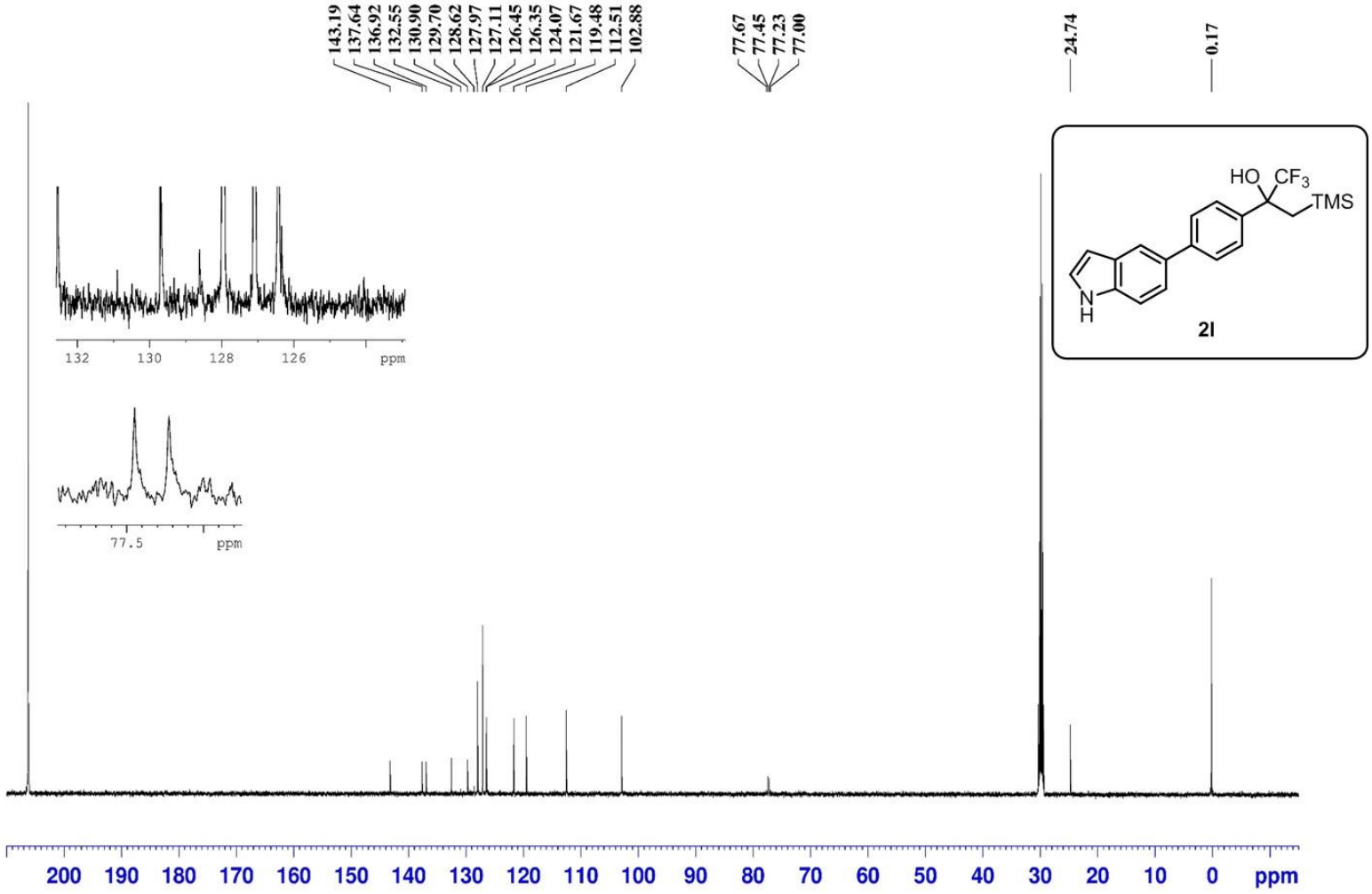
**2k**



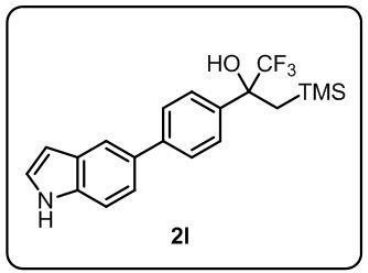
**2-(4-(1H-Indol-5-yl)phenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol**
**500 MHz, acetone-d6**



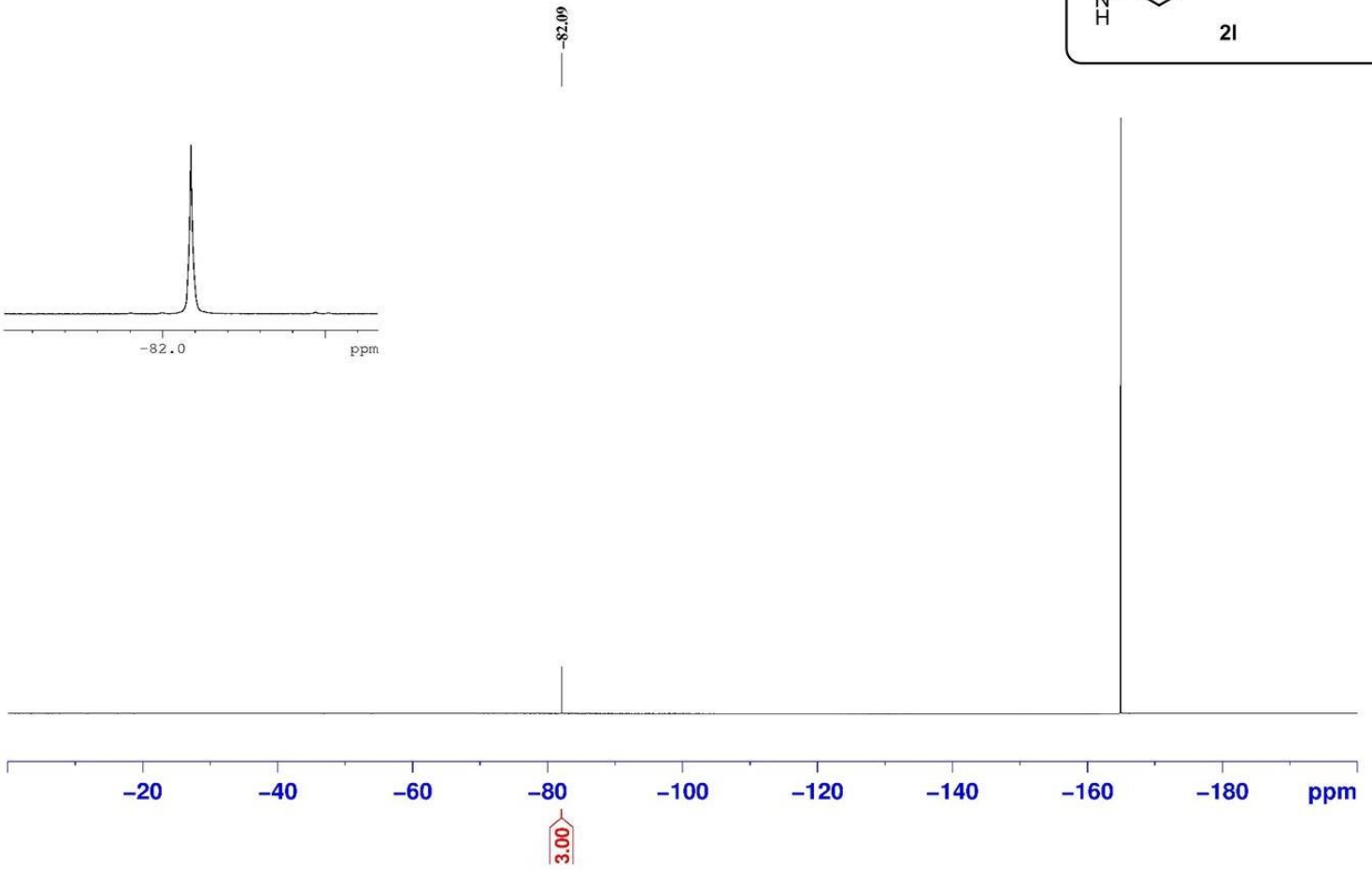
**2–(4–(1H–Indol–5–yl)phenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**125 MHz, acetone–d6**



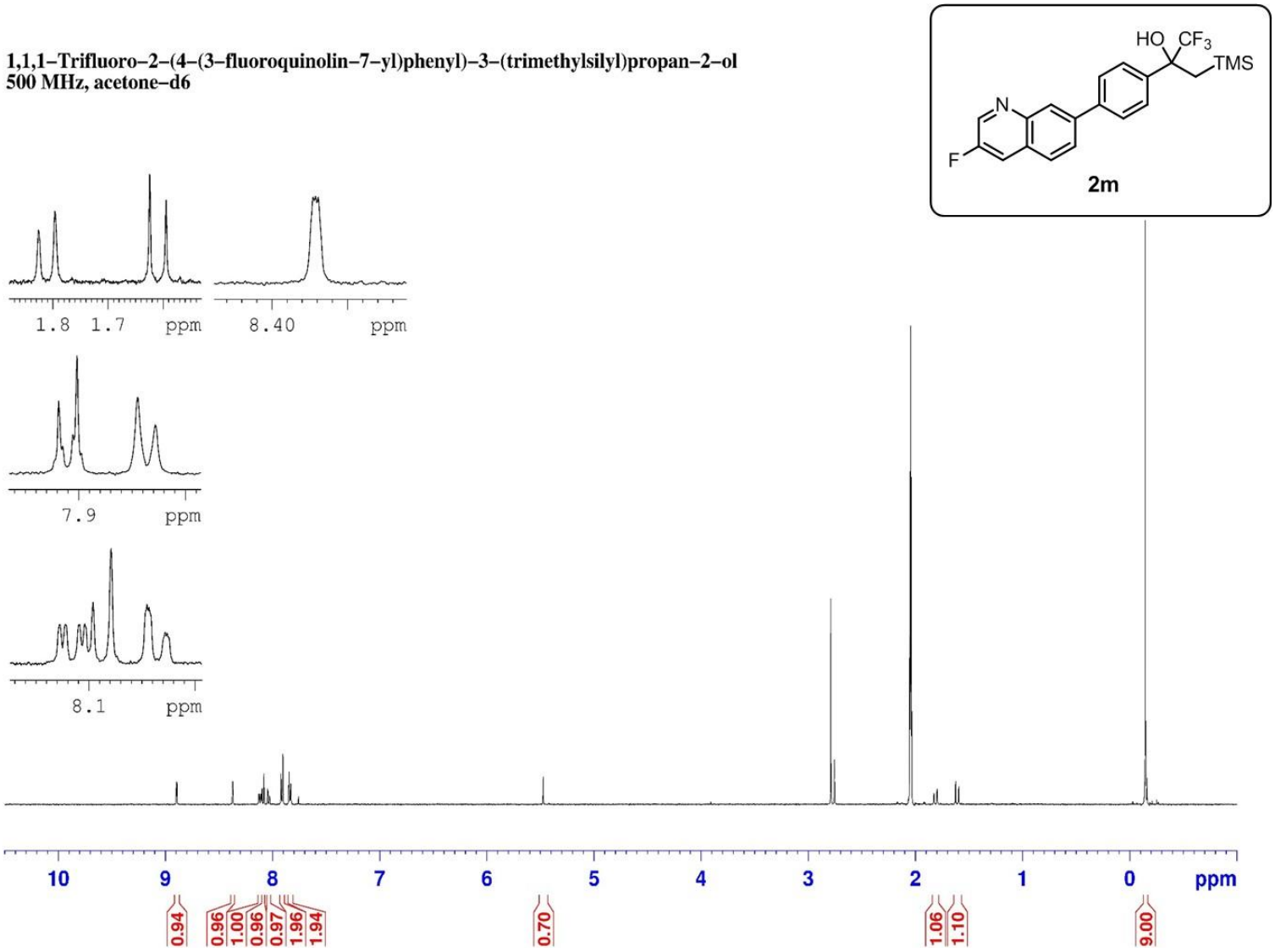
**2-(4-(1H-indol-5-yl)phenyl)-1,1,1-trifluoro-3-(trimethylsilyl)propan-2-ol**
**Acetone-d6, 471 MHz**



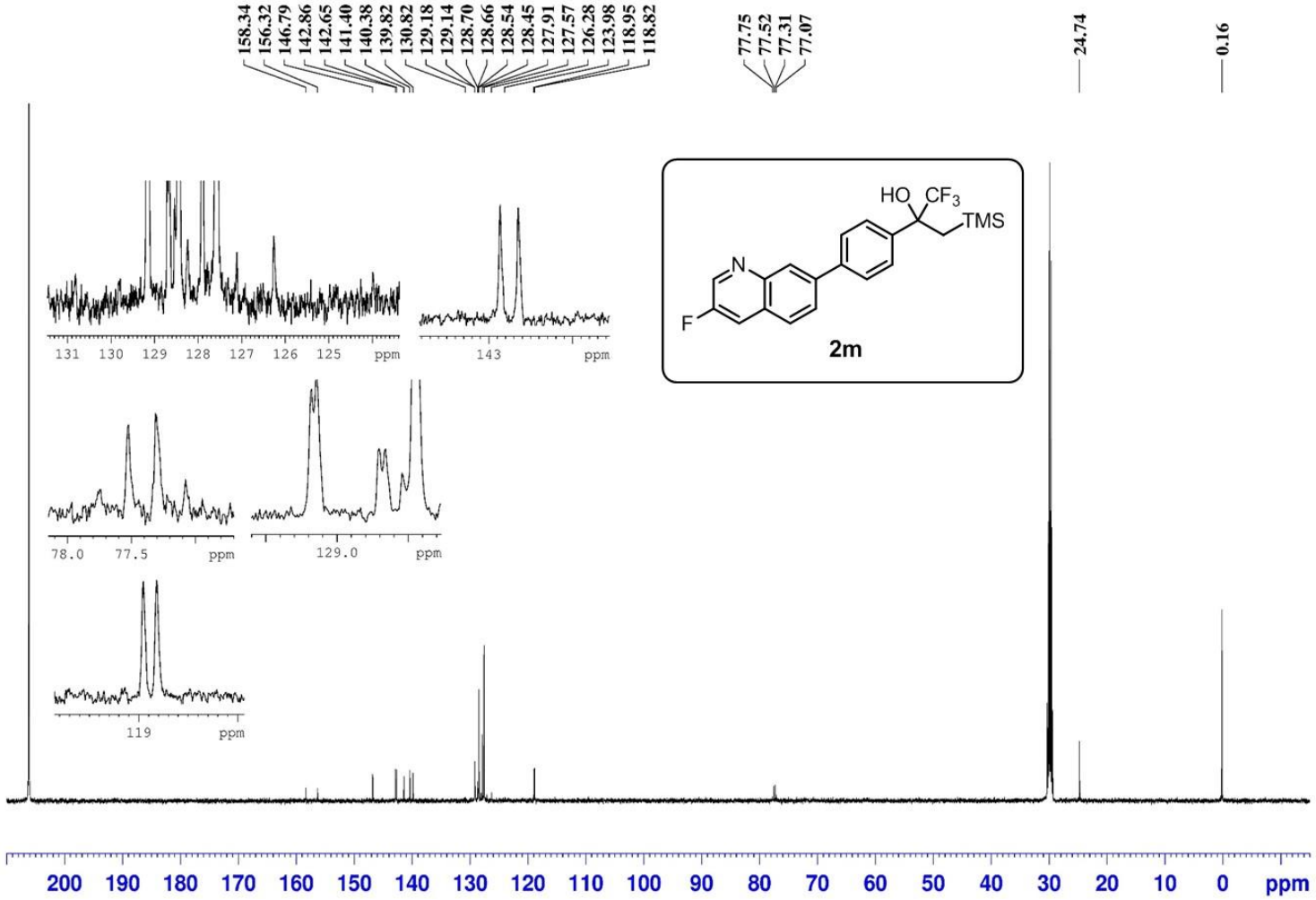

**2l**



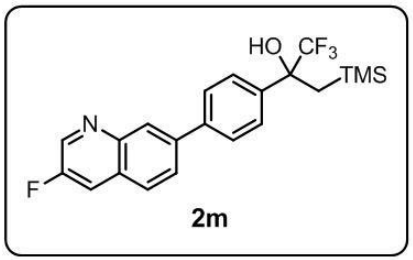
**1,1,1–Trifluoro–2–(4–(3–fluoroquinolin–7–yl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**500 MHz, acetone–d6**



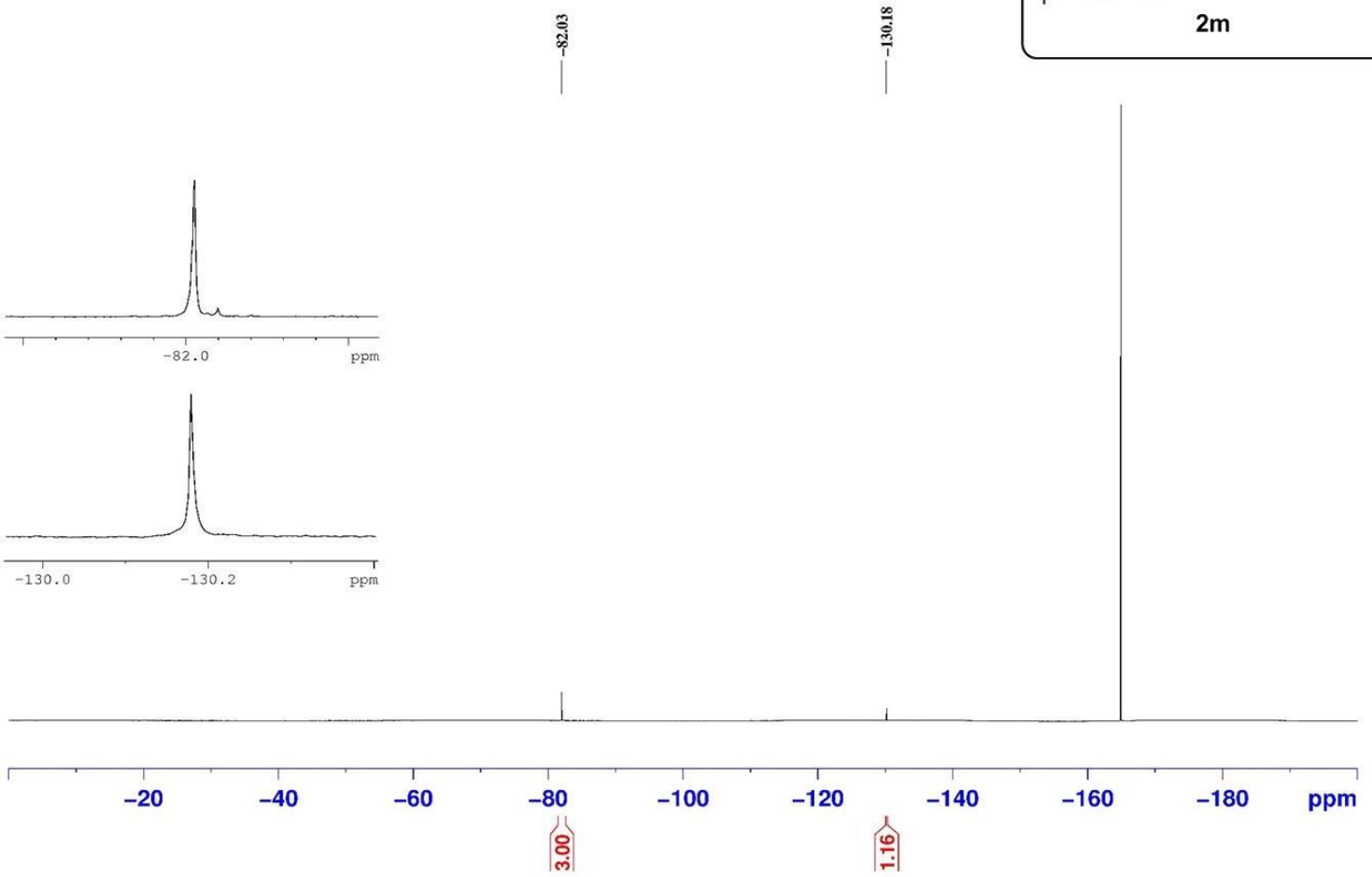
**1,1,1–Trifluoro–2–(4–(3–fluoroquinolin–7–yl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**125 MHz, acetone–d6**



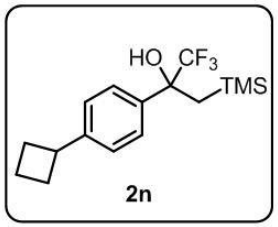
**1,1,1–trifluoro–2–(4–(3–fluoroquinolin–7–yl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**Acetone–d6, 471 MHz**

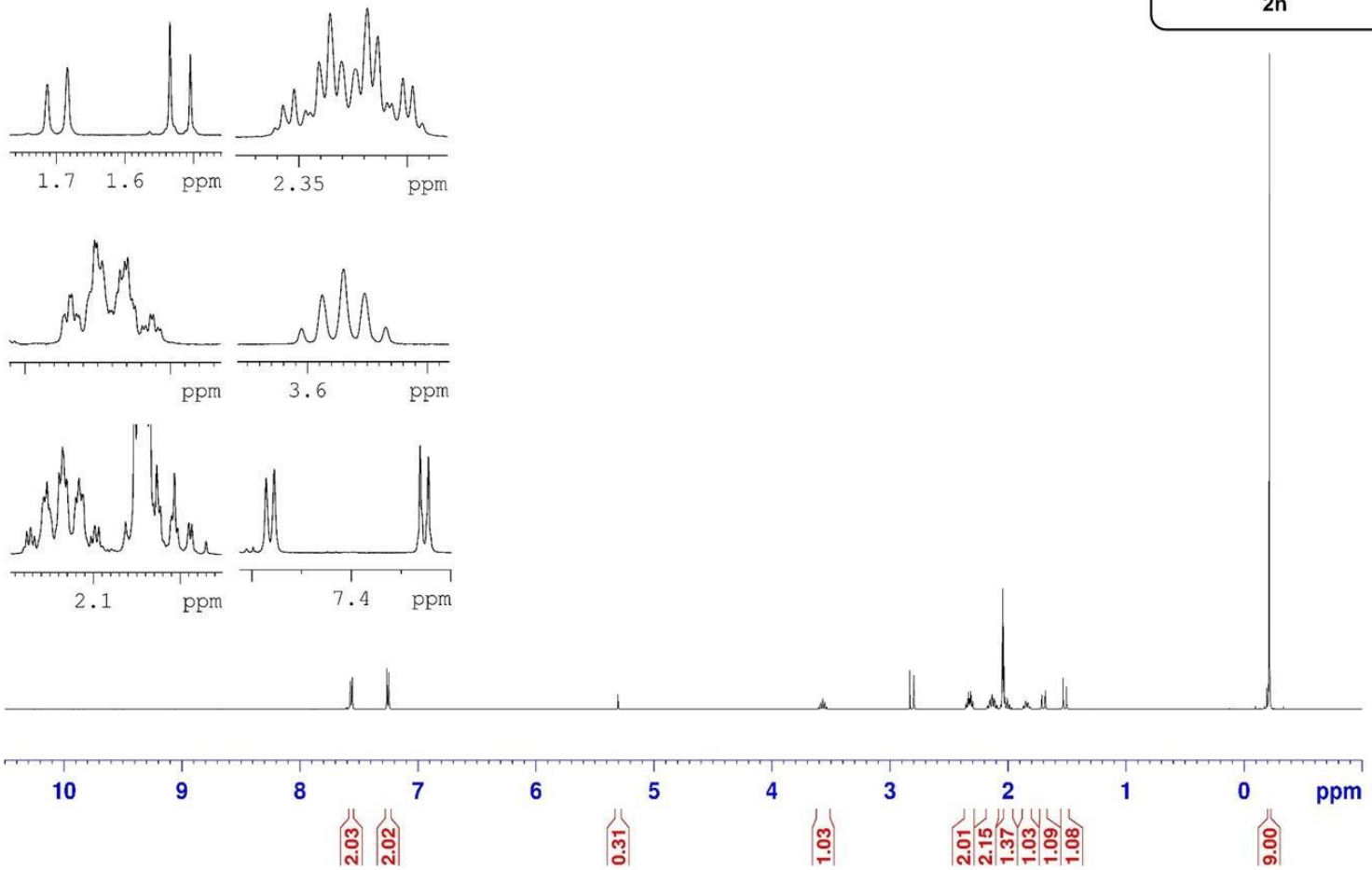



**2m**

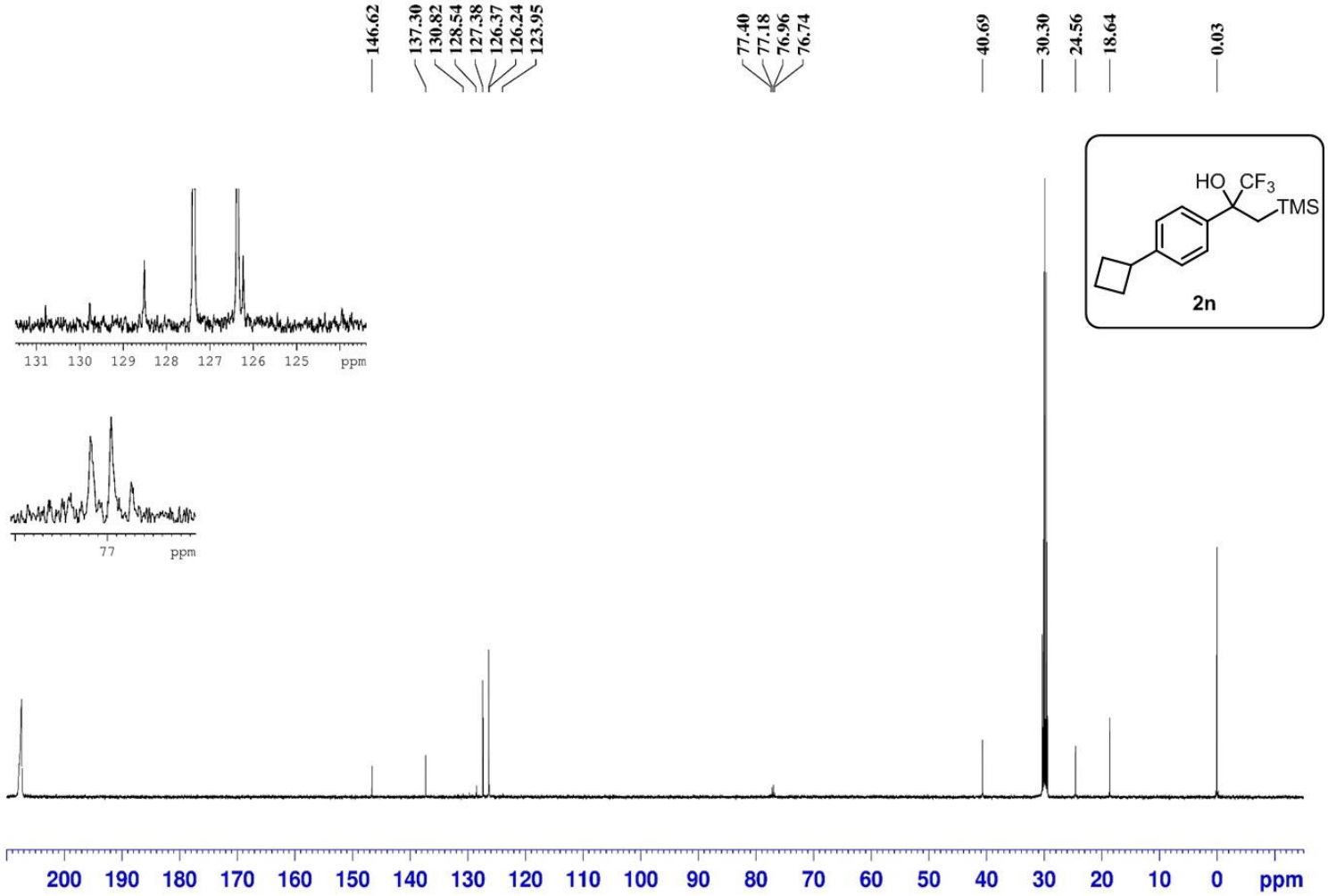


**2–(4–Cyclobutylphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**500 MHz, acetone–d6**

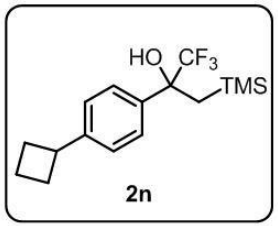


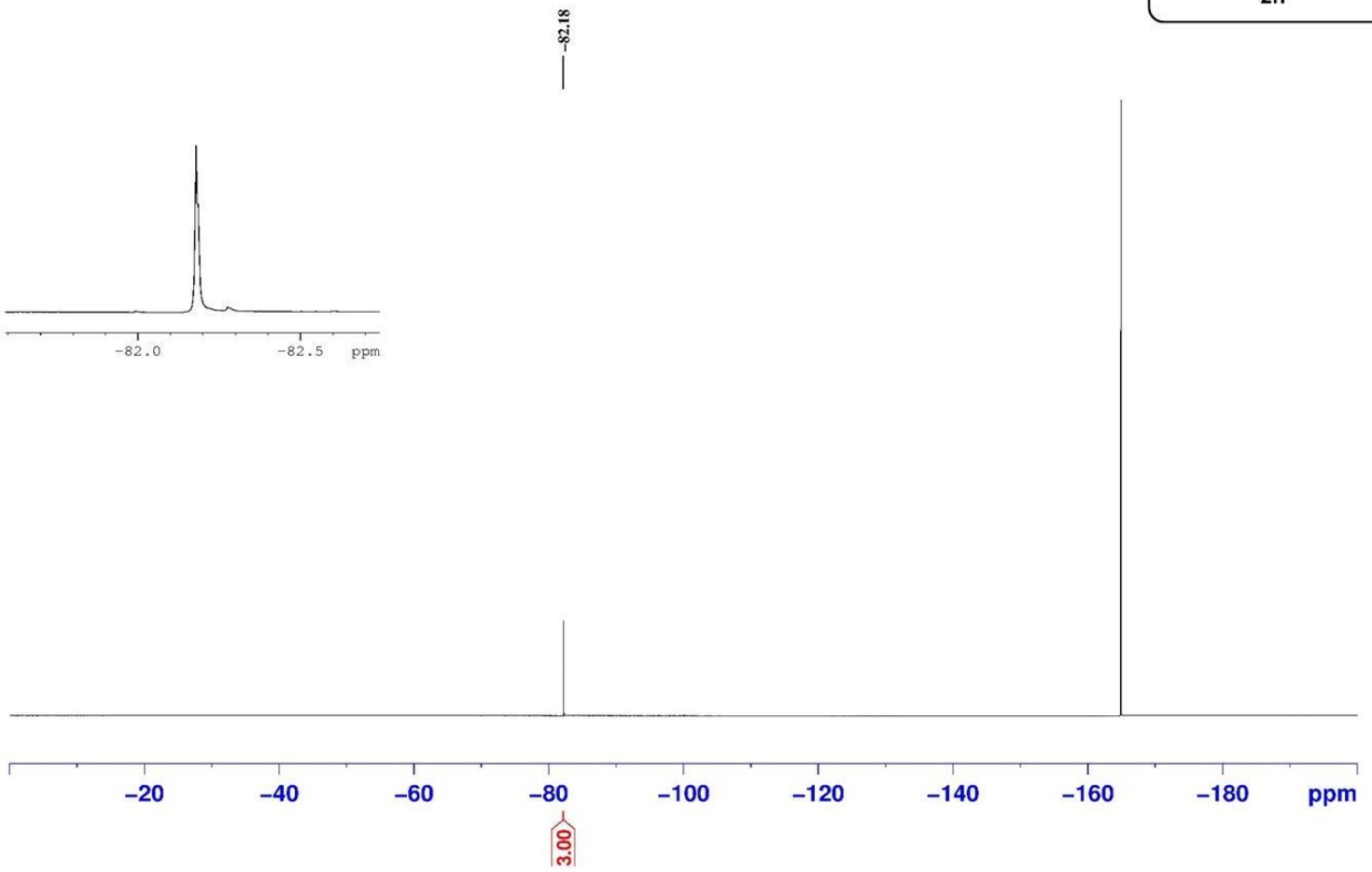



**2–(4–Cyclobutylphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**125 MHz, acetone–d6**

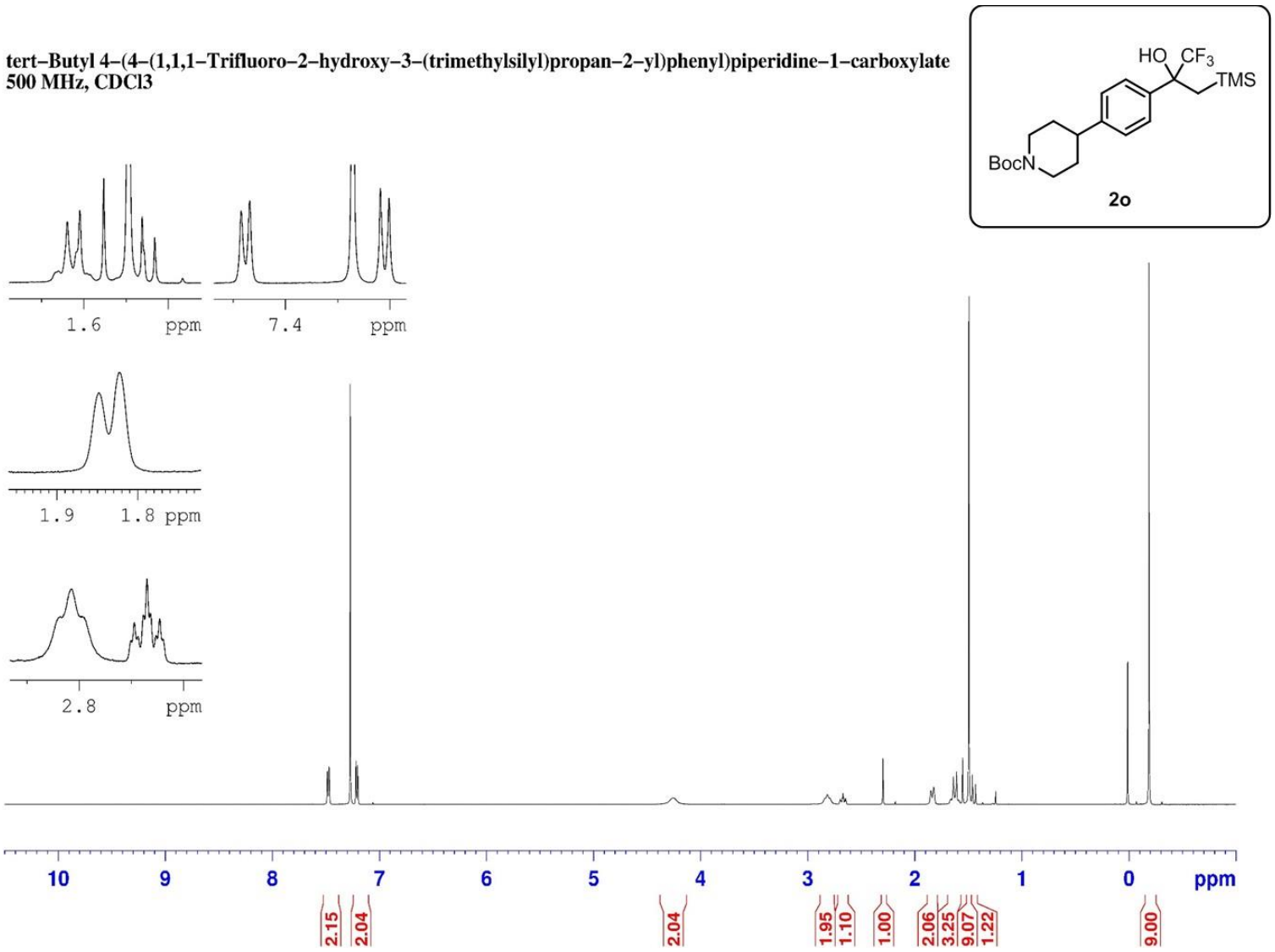


**2–(4–cyclobutylphenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**Acetone–d6, 471 MHz**

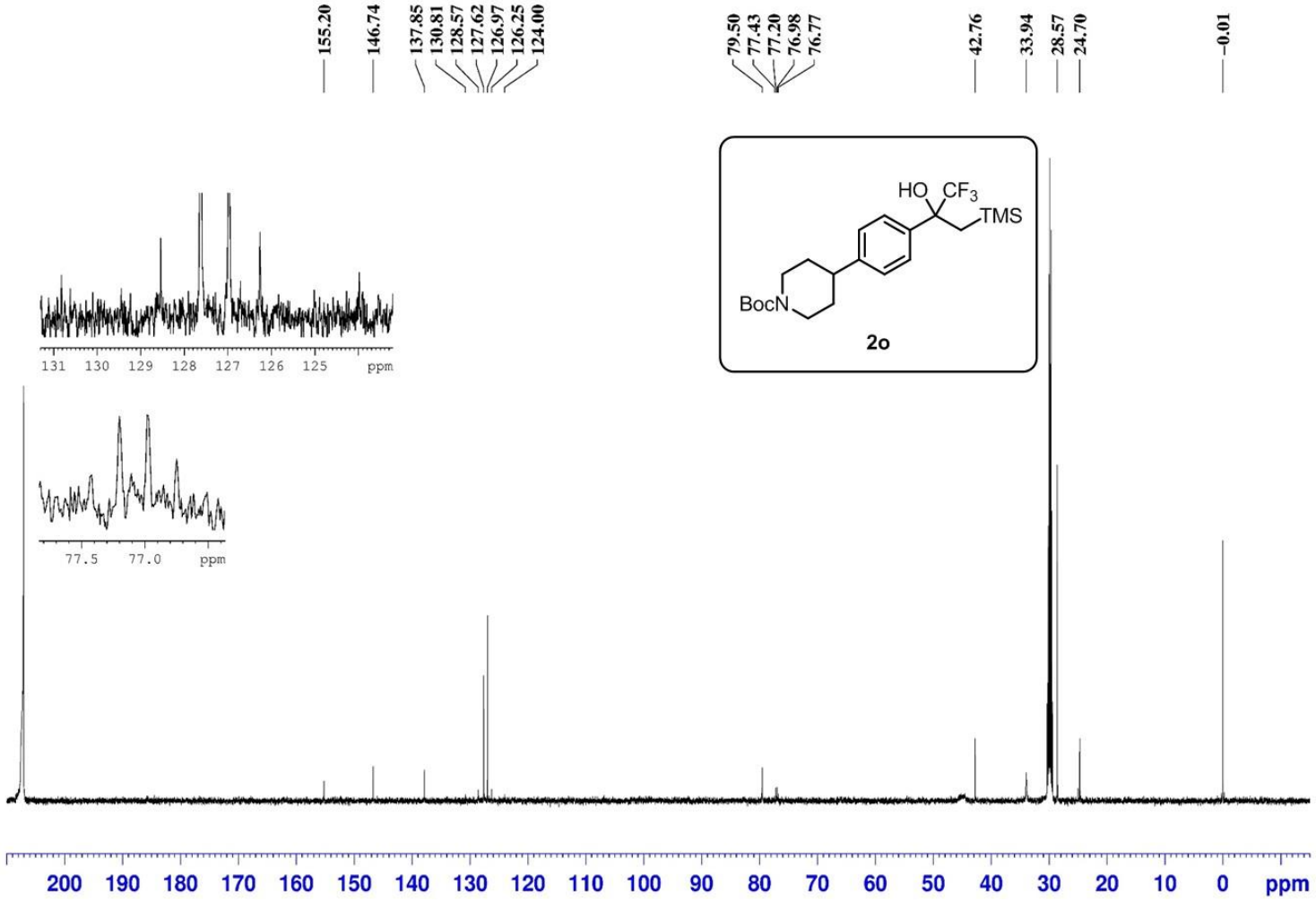


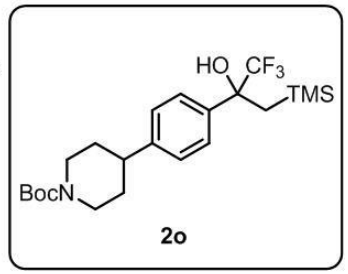
**tert–Butyl 4–(4–(1,1,1–Trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)phenyl)piperidine–1–carboxylate**
**500 MHz, CDCl3**



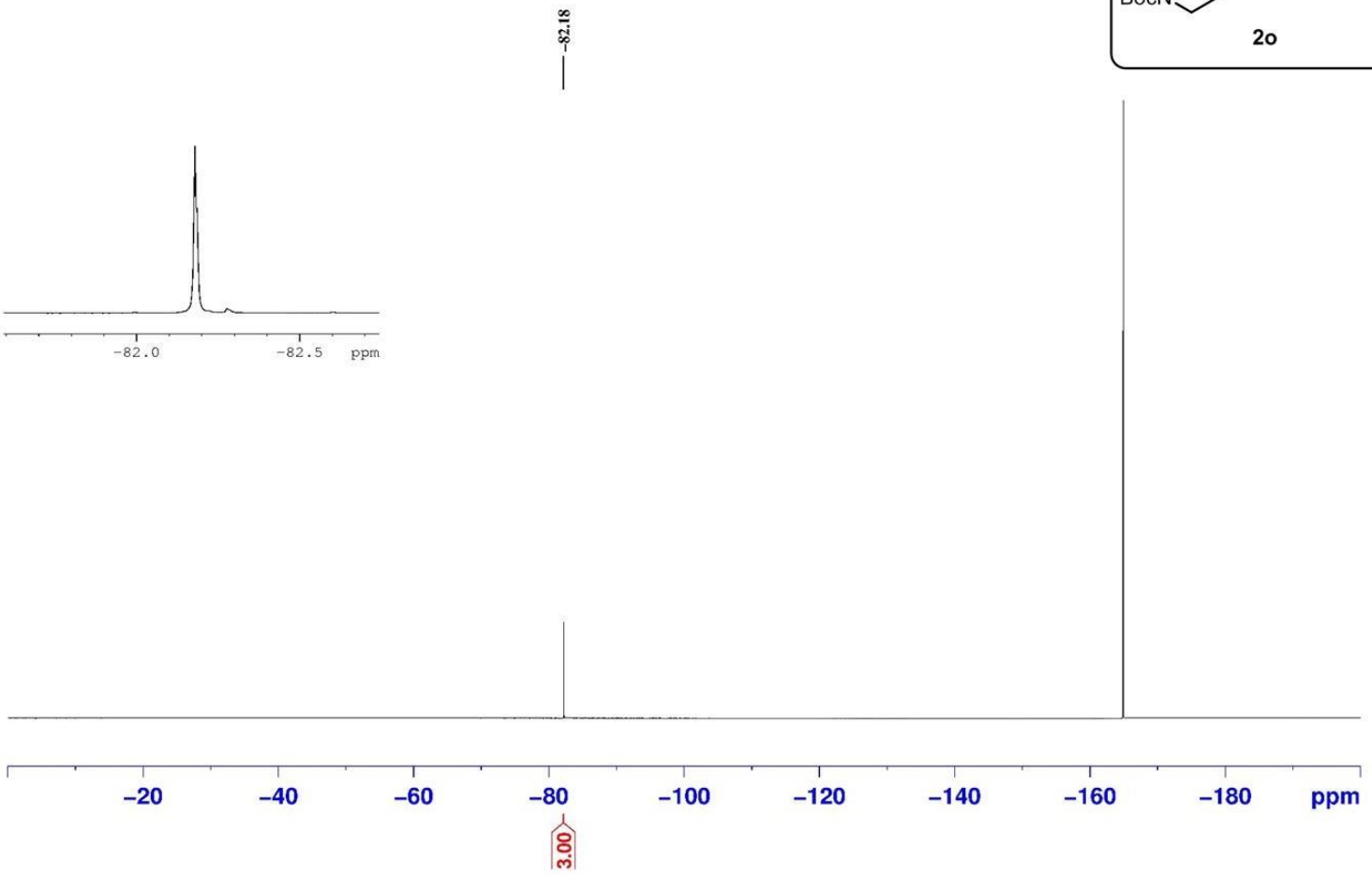
**tert–Butyl 4–(4–(1,1,1–Trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)phenyl)piperidine–1–carboxylate**
**125 MHz, acetone–d6**



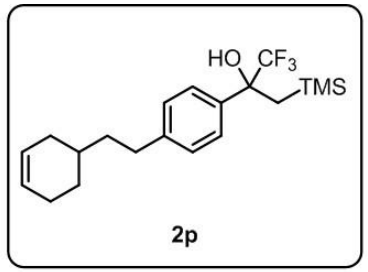
**tert–butyl 4–(4–(1,1,1–trifluoro–2–hydroxy–3–(trimethylsilyl)propan–2–yl)phenyl)piperidine–1–carboxylate**
**Acetone–d6, 471 MHz**



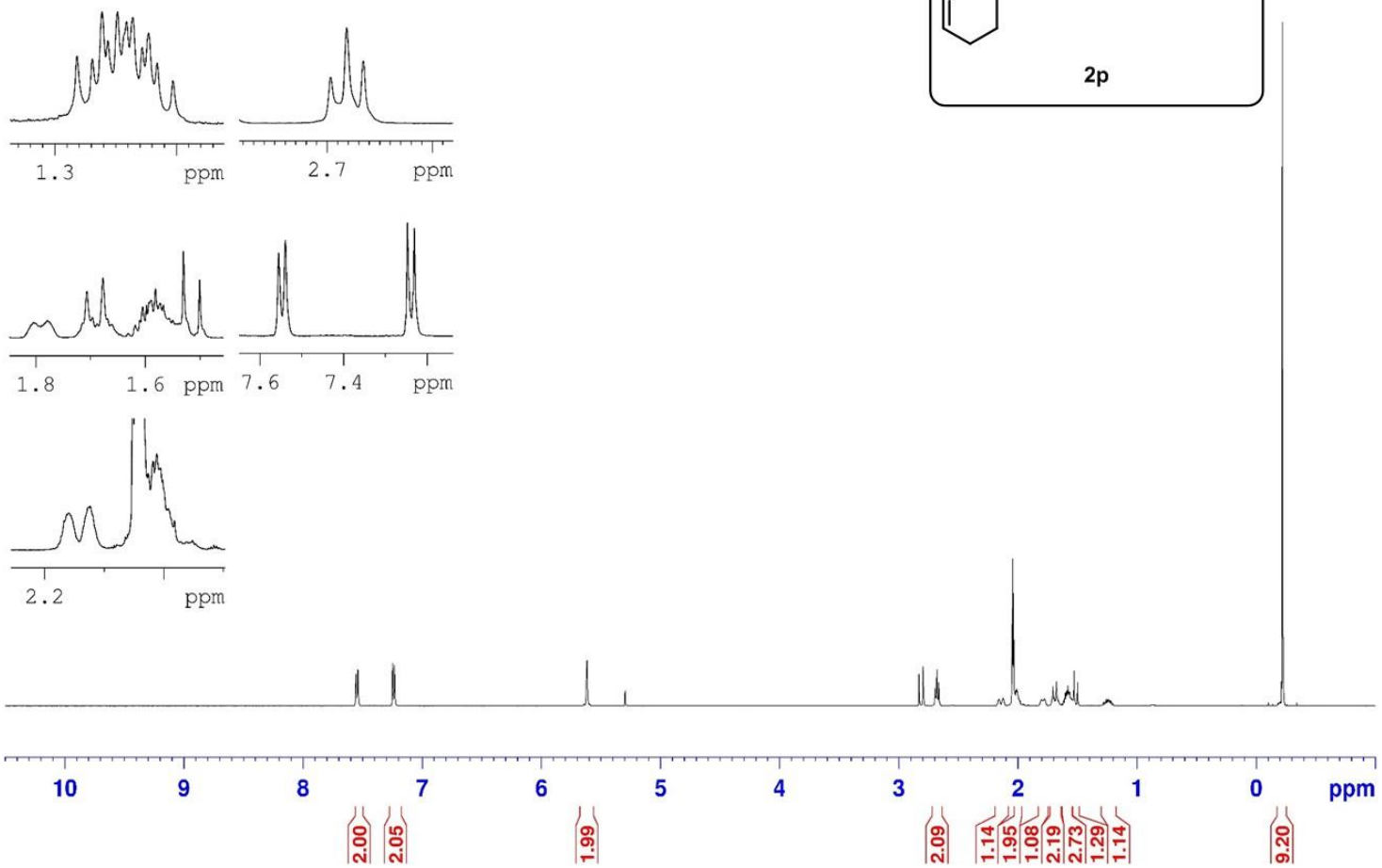

**2o**



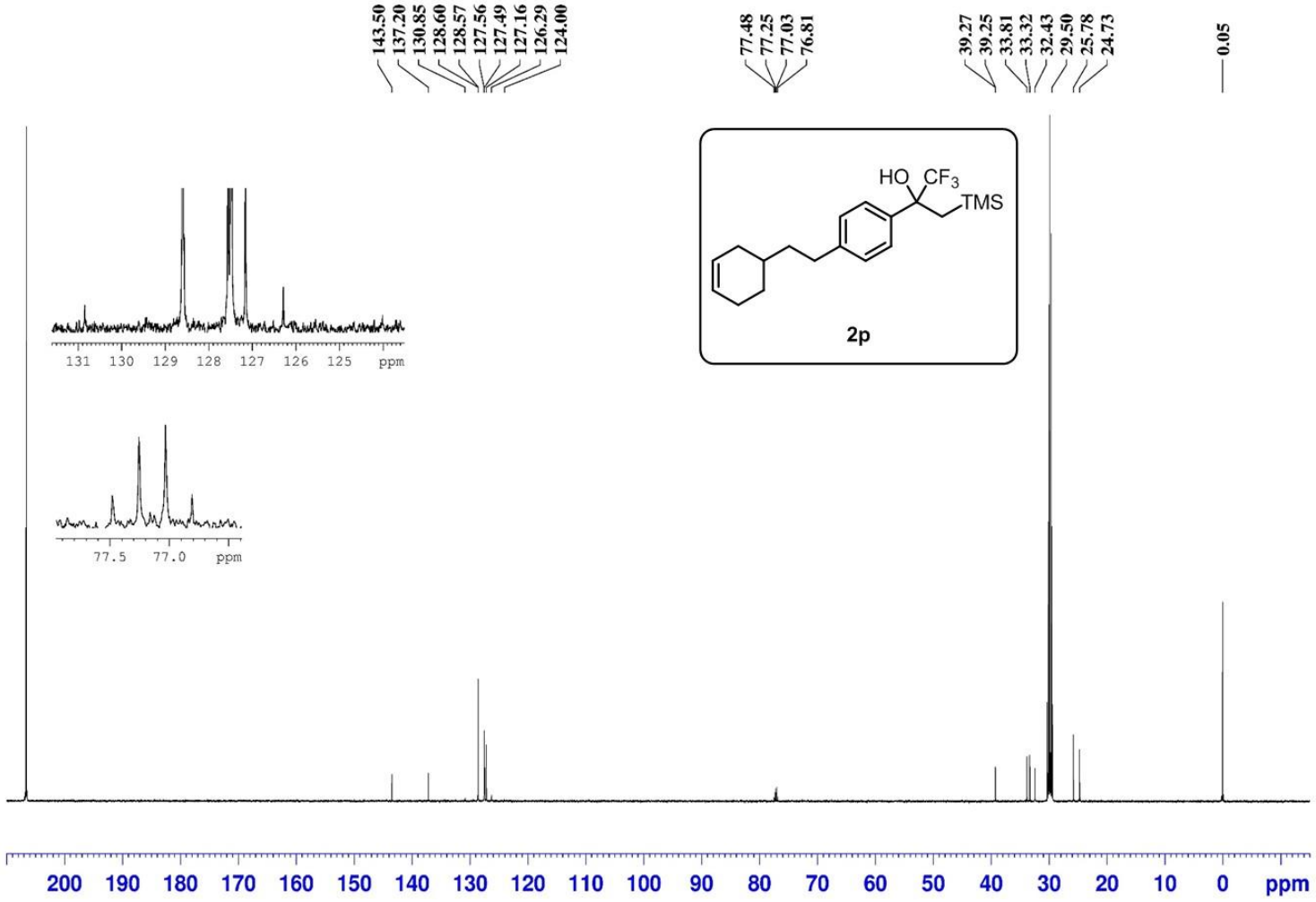
**2–(4–(2–(Cyclohex–3–en–1–yl)ethyl)phenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**500 MHz, acetone–d6**



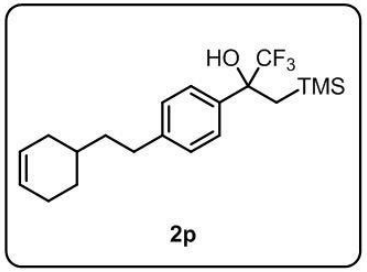

**2p**

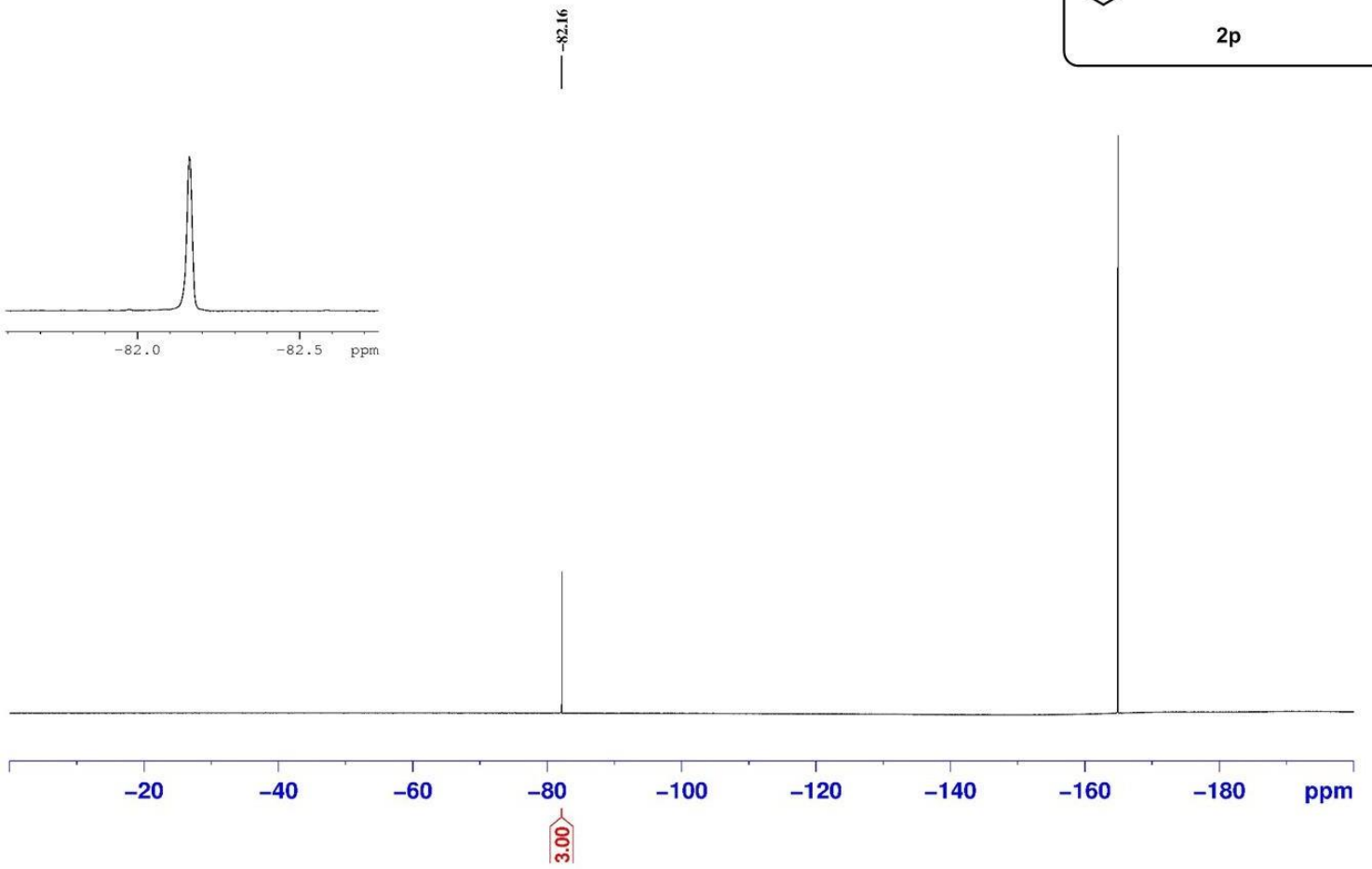


**2–(4–(2–(Cyclohex–3–en–1–yl)ethyl)phenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**125 MHz, acetone–d6**

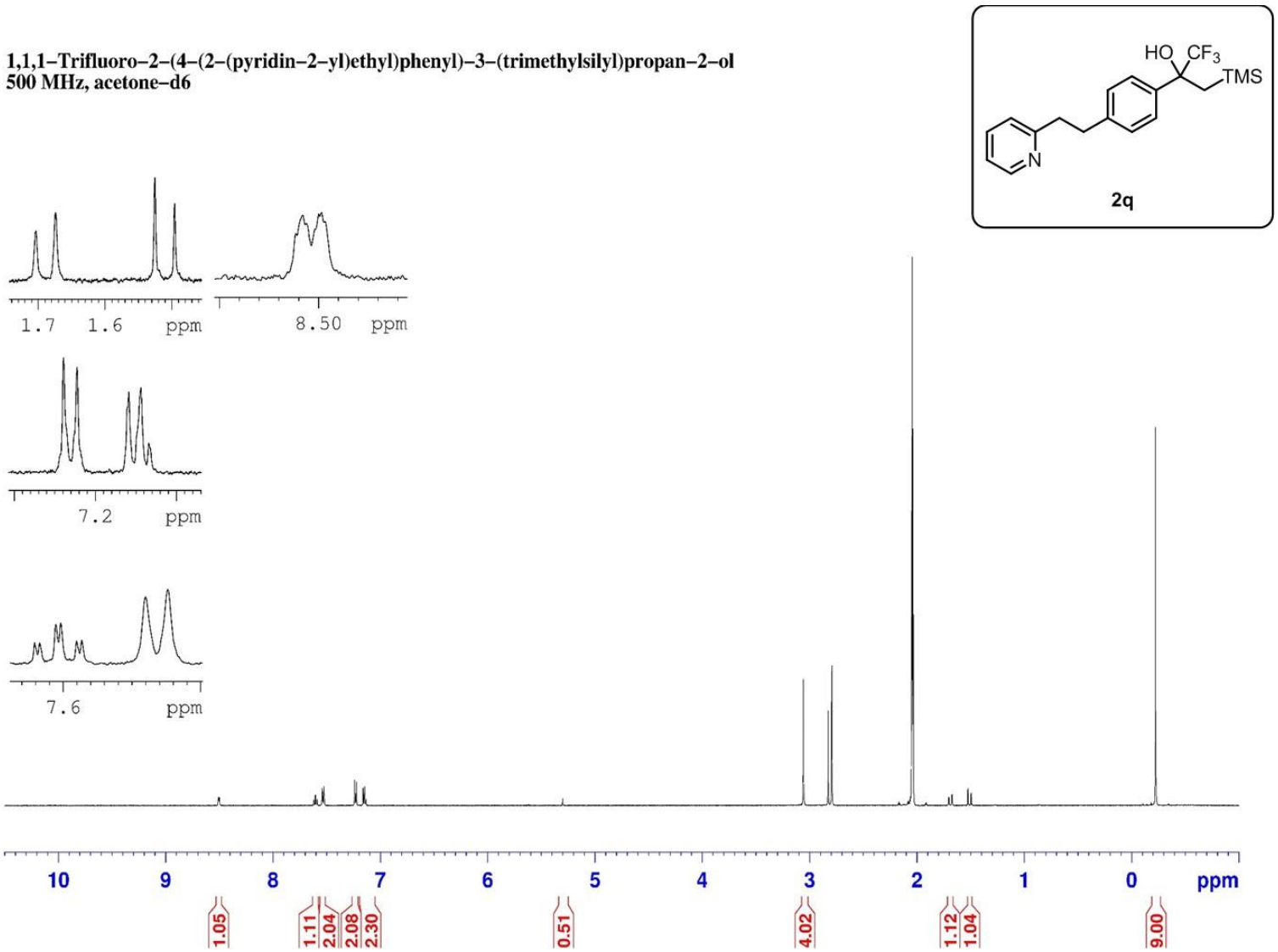


**2–(4–(2–(cyclohex–3–en–1–yl)ethyl)phenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**Acetone–d6, 471 MHz**

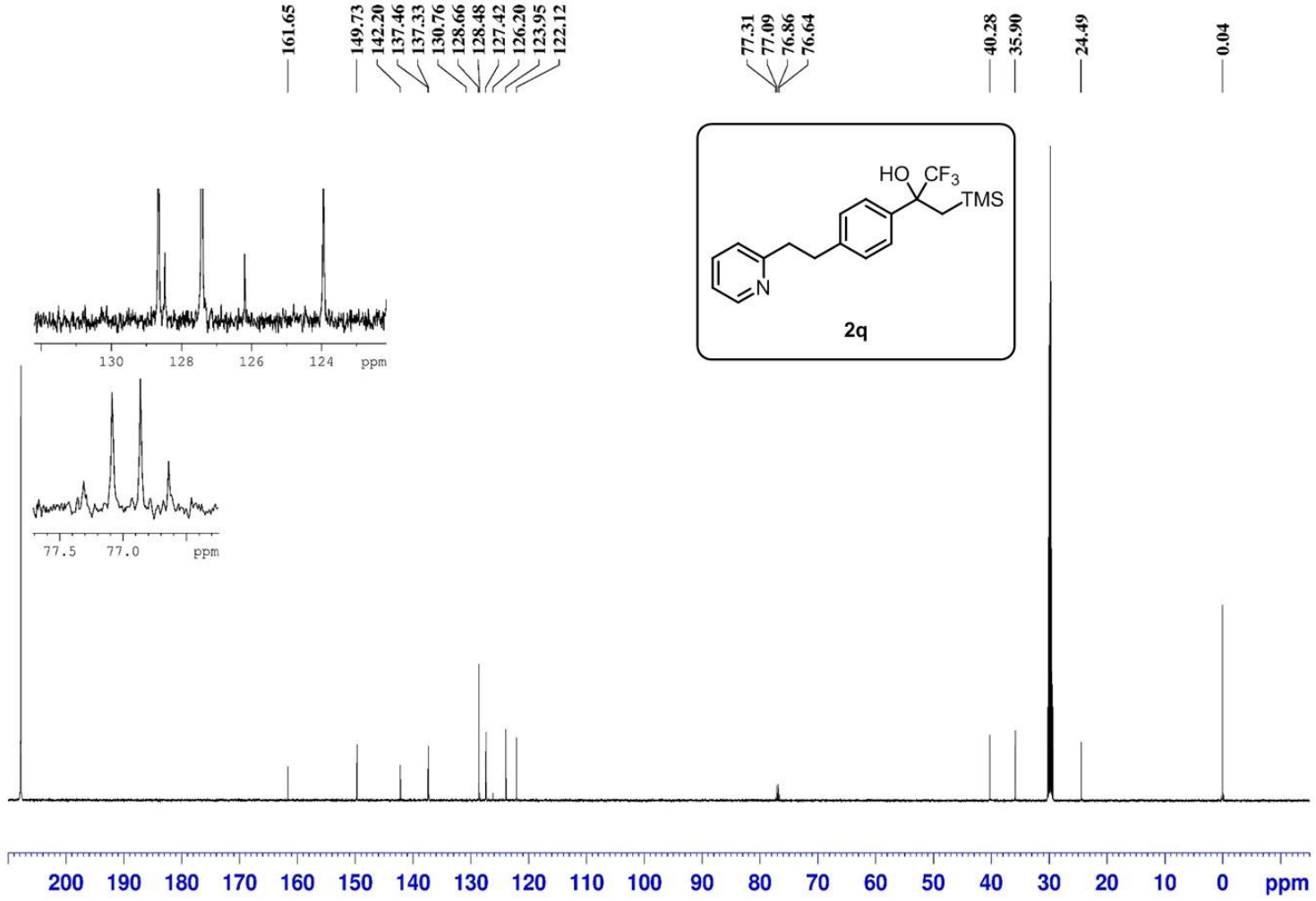


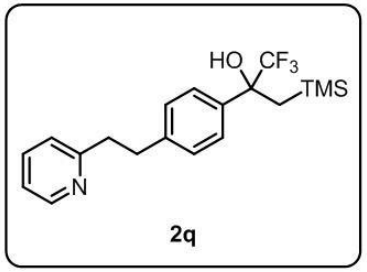
**1,1,1−Trifluoro−2−(4−(2−(pyridin−2−yl)ethyl)phenyl)−3−(trimethylsilyl)propan−2−ol**
**500 MHz, acetone−d6**



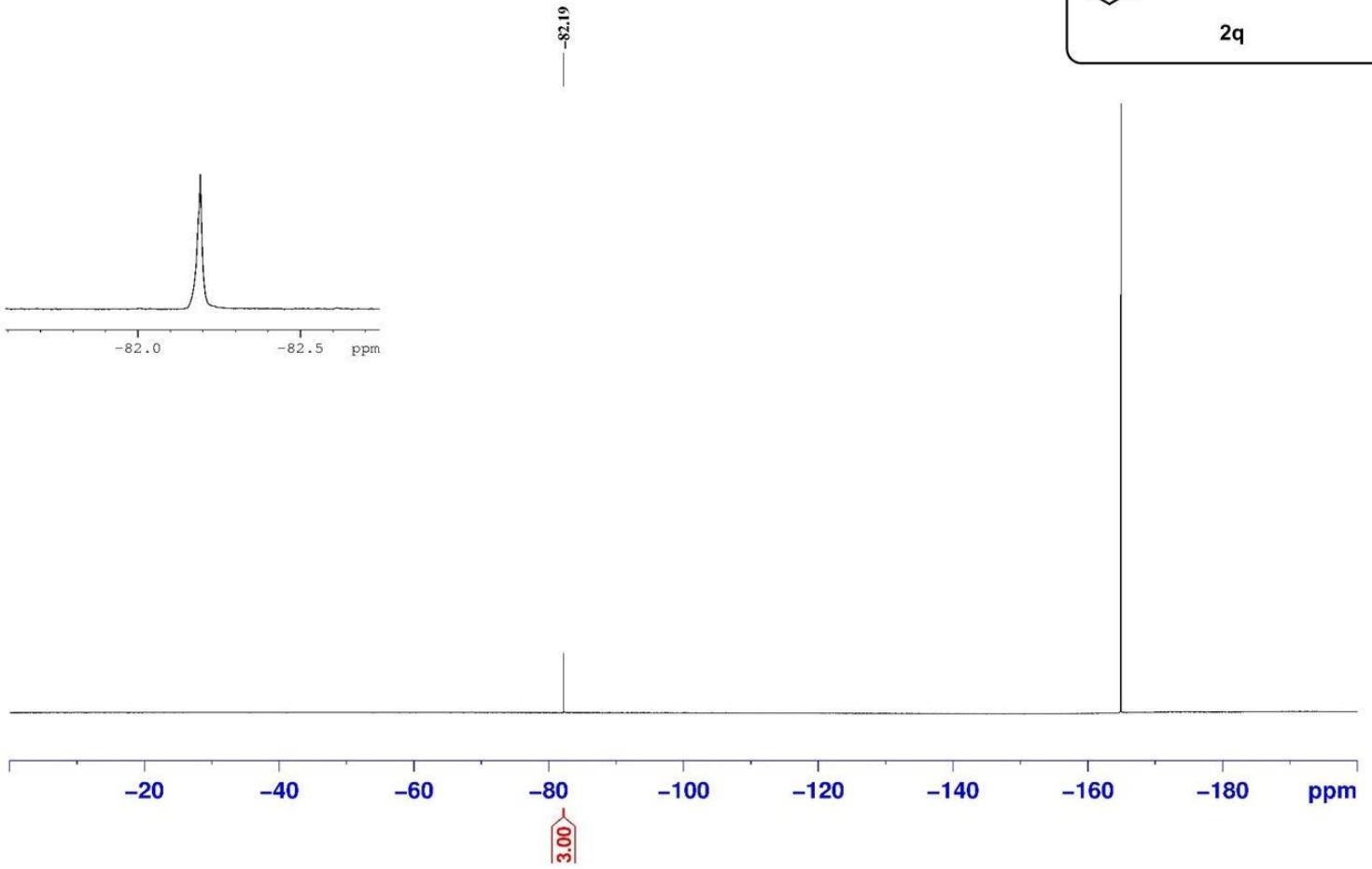
**1,1,1–Trifluoro–2–(4–(2–(pyridin–2–yl)ethyl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**125 MHz, acetone–d6**



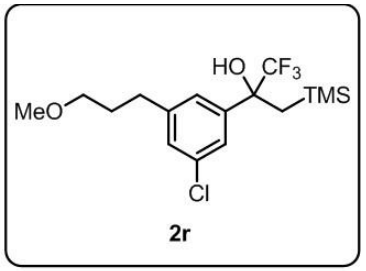
**1,1,1–trifluoro–2–(4–(2–(pyridin–2–yl)ethyl)phenyl)–3–(trimethylsilyl)propan–2–ol**
**Acetone–d6, 471 MHz**



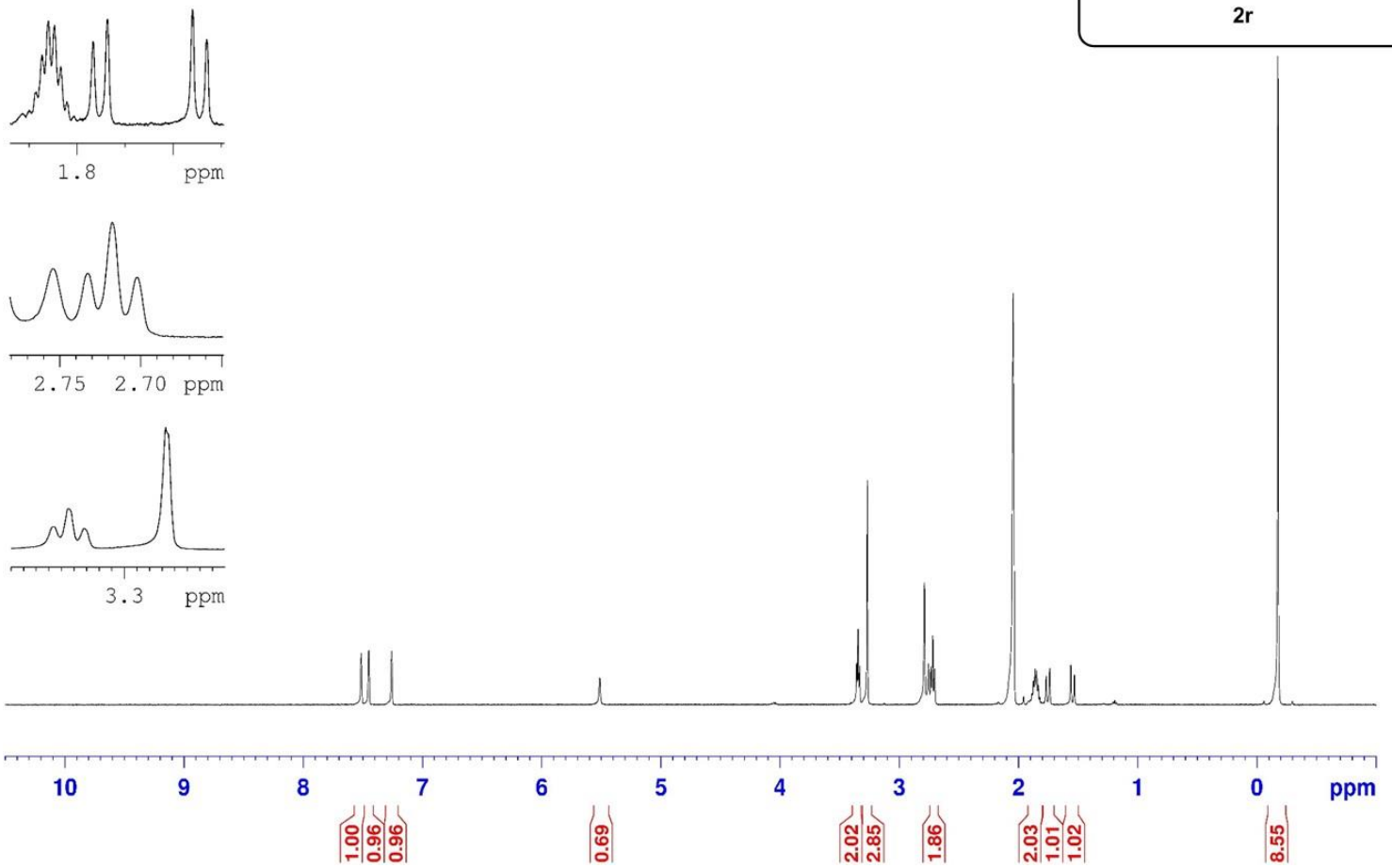

**2q**



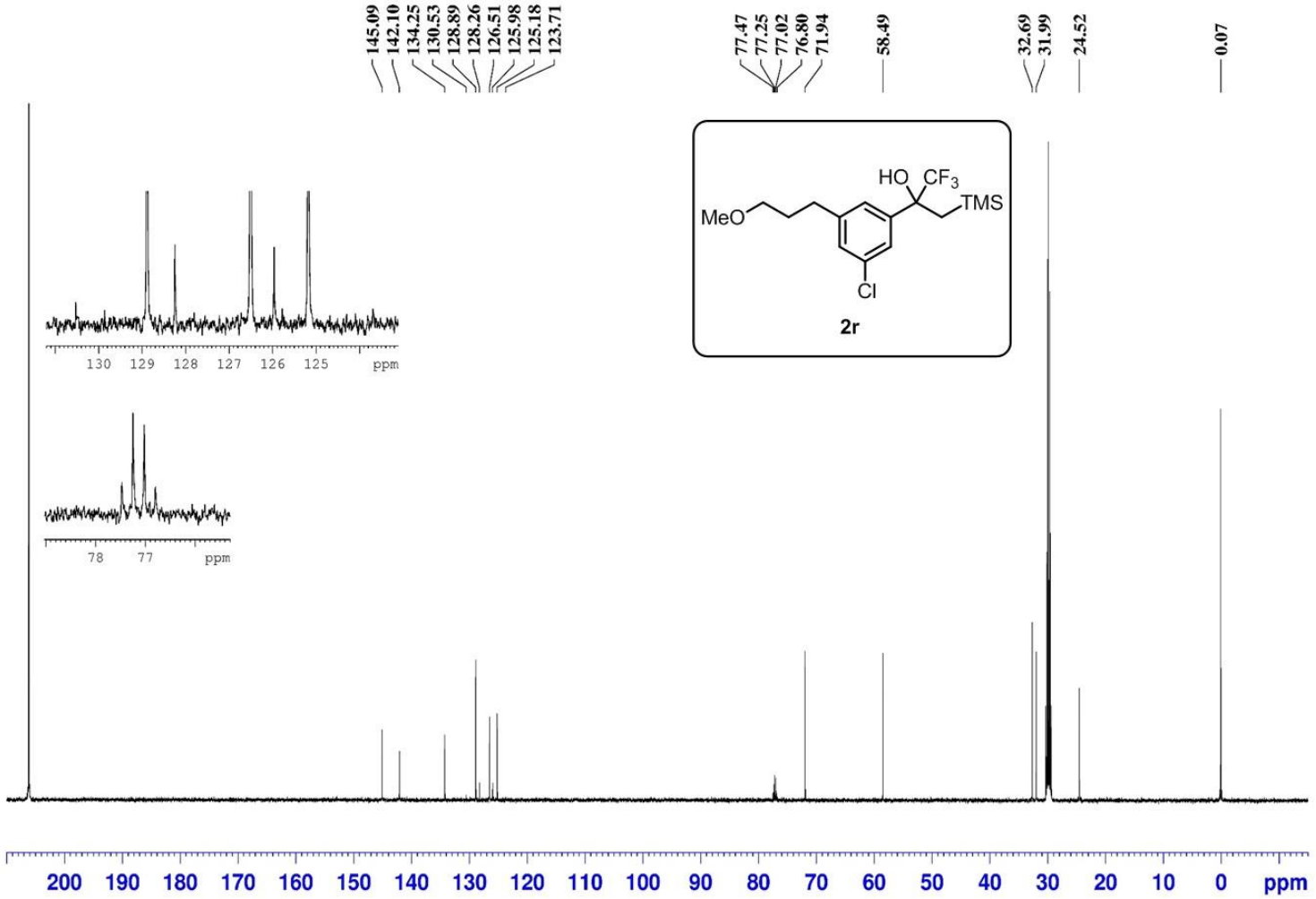
**2–(3–Chloro–5–(3–methoxypropyl)phenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**500 MHz, acetone–d6**



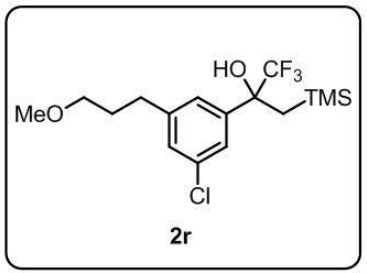

**2r**



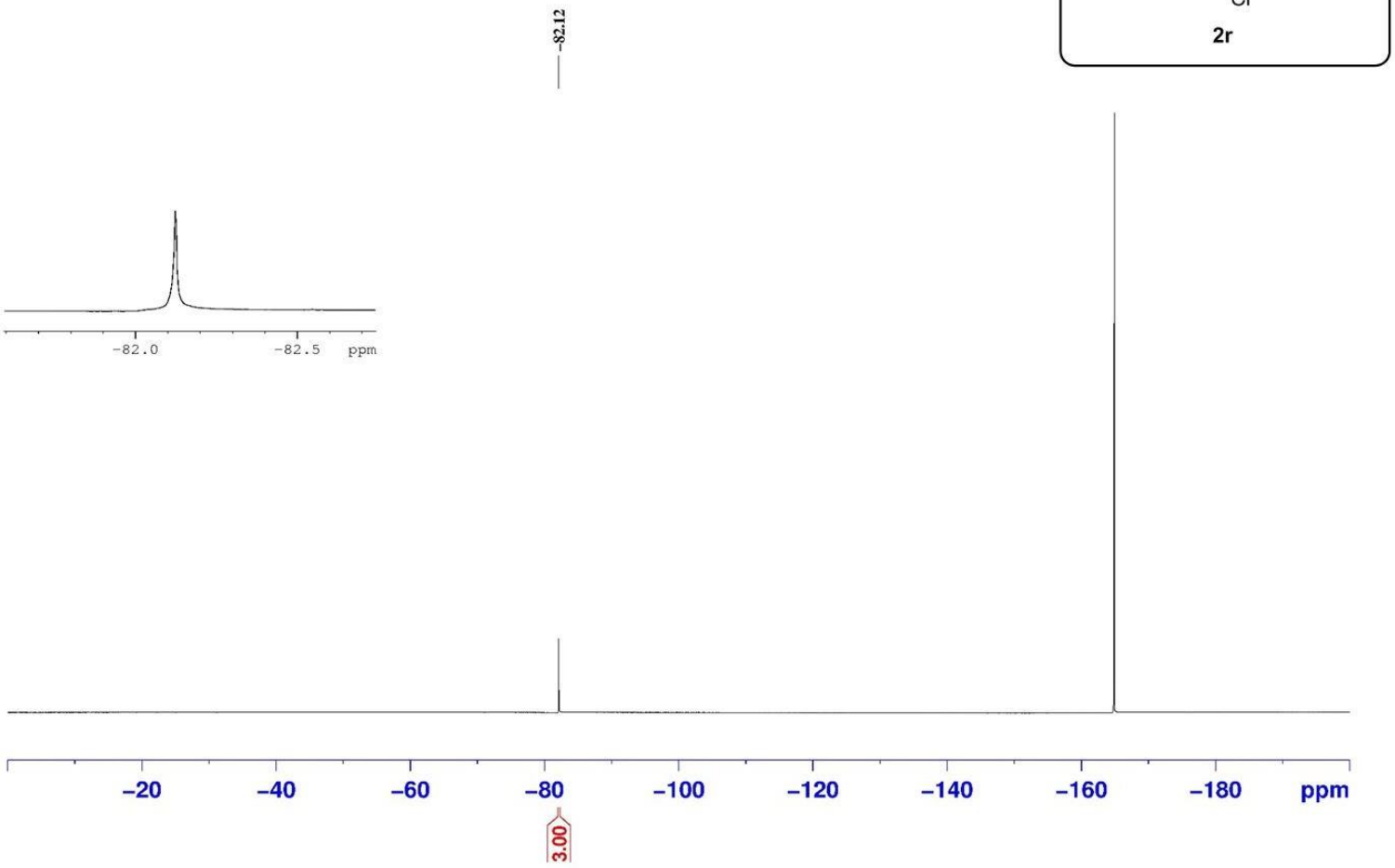
**2–(3–Chloro–5–(3–methoxypropyl)phenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**125 MHz, acetone–d6**



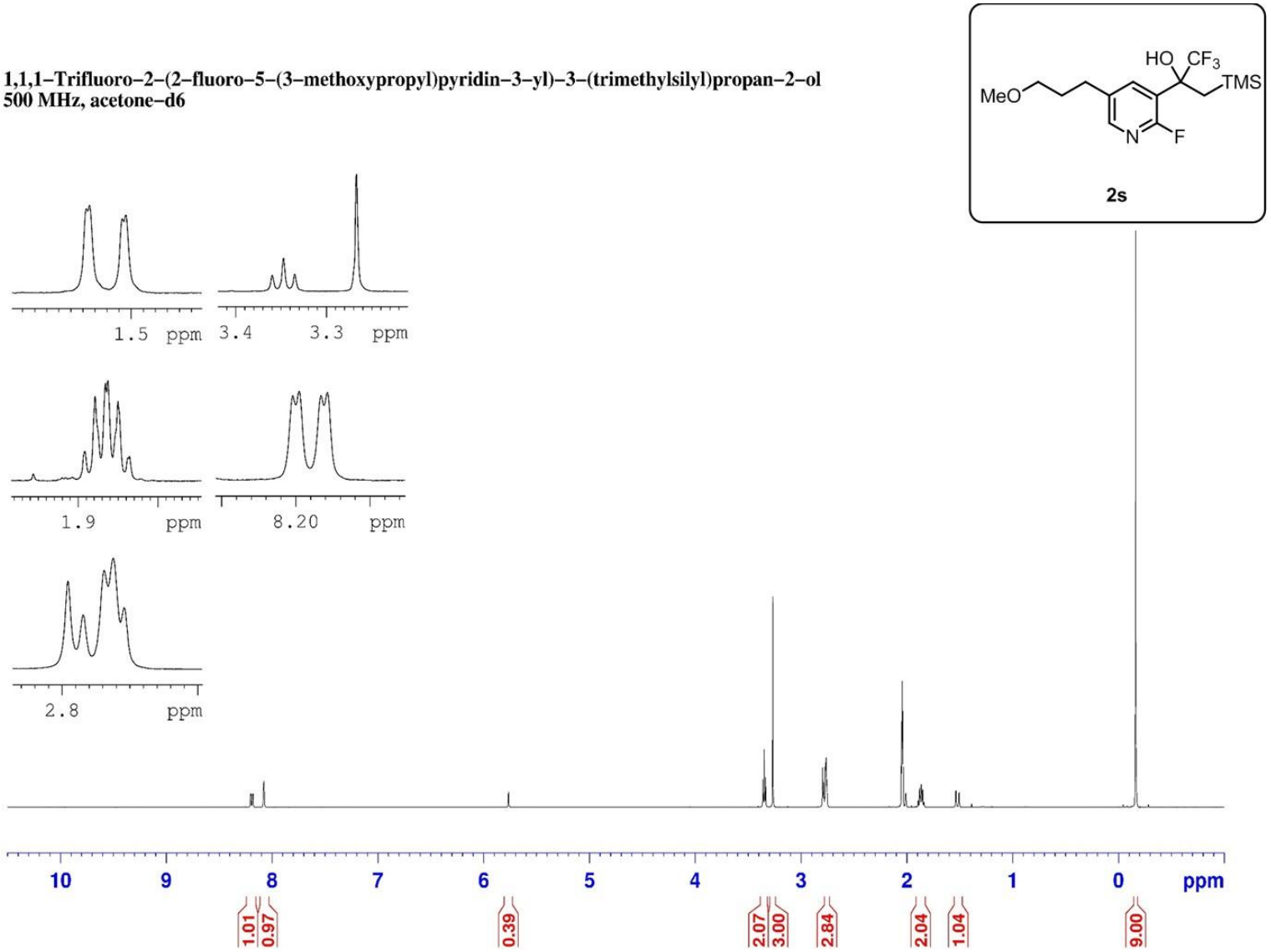
**2–(3–chloro–5–(3–methoxypropyl)phenyl)–1,1,1–trifluoro–3–(trimethylsilyl)propan–2–ol**
**Acetone–d6, 471 MHz**



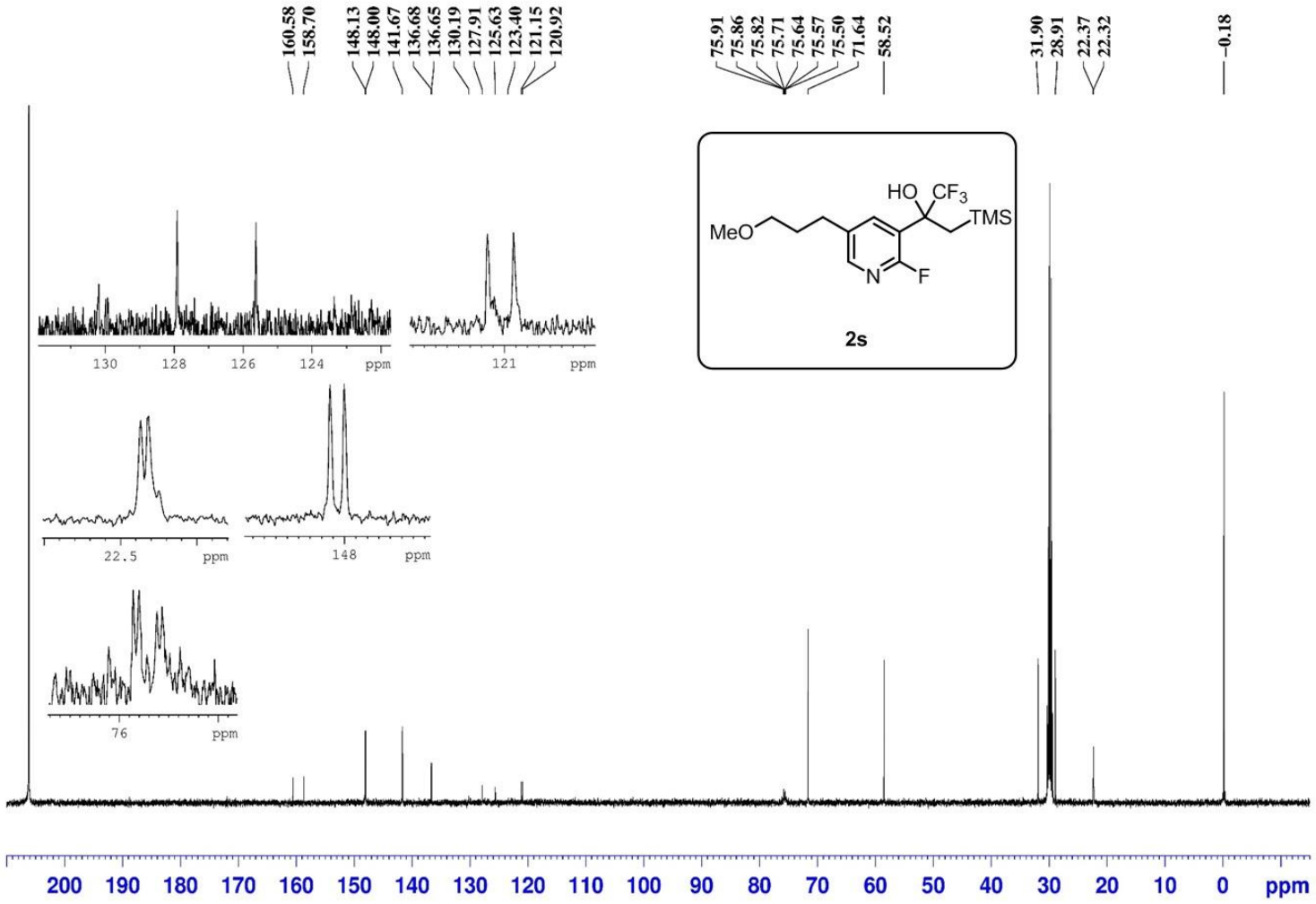

**2r**



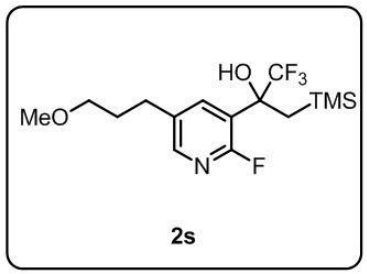
**1,1,1−Trifluoro−2−(2−fluoro−5−(3−methoxypropyl)pyridin−3−yl)−3−(trimethylsilyl)propan−2−ol**
**500 MHz, acetone−d6**



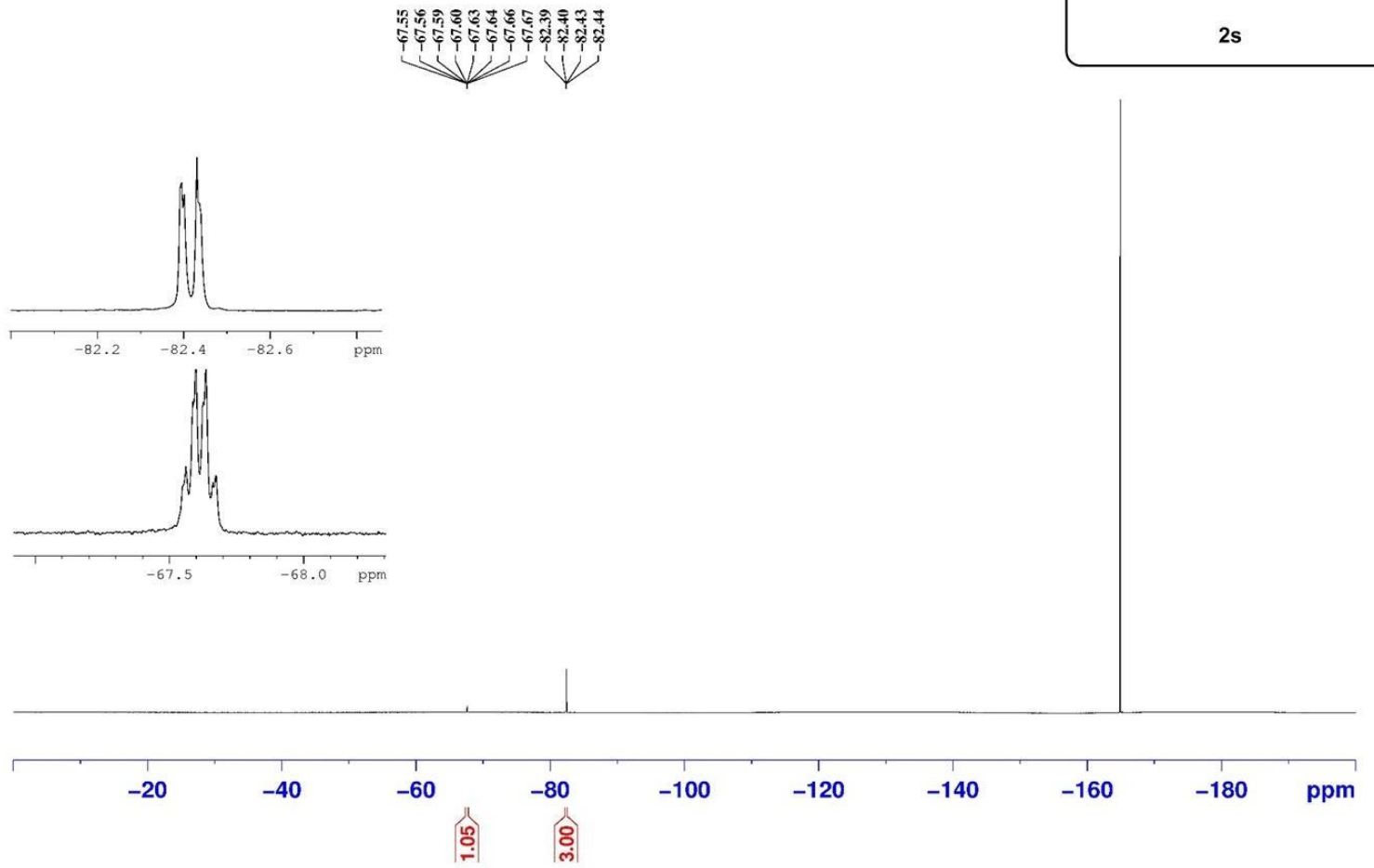
**1,1,1–Trifluoro–2–(2–fluoro–5–(3–methoxypropyl)pyridin–3–yl)–3–(trimethylsilyl)propan–2–ol**
**125 MHz, acetone–d6**



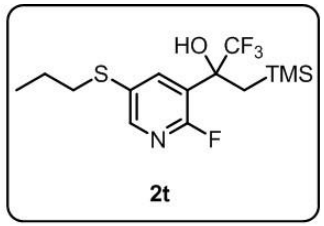
**1,1,1–trifluoro–2–(2–fluoro–5–(3–methoxypropyl)pyridin–3–yl)–3–(trimethylsilyl)propan–2–ol**
**Acetone–d6, 471 MHz**



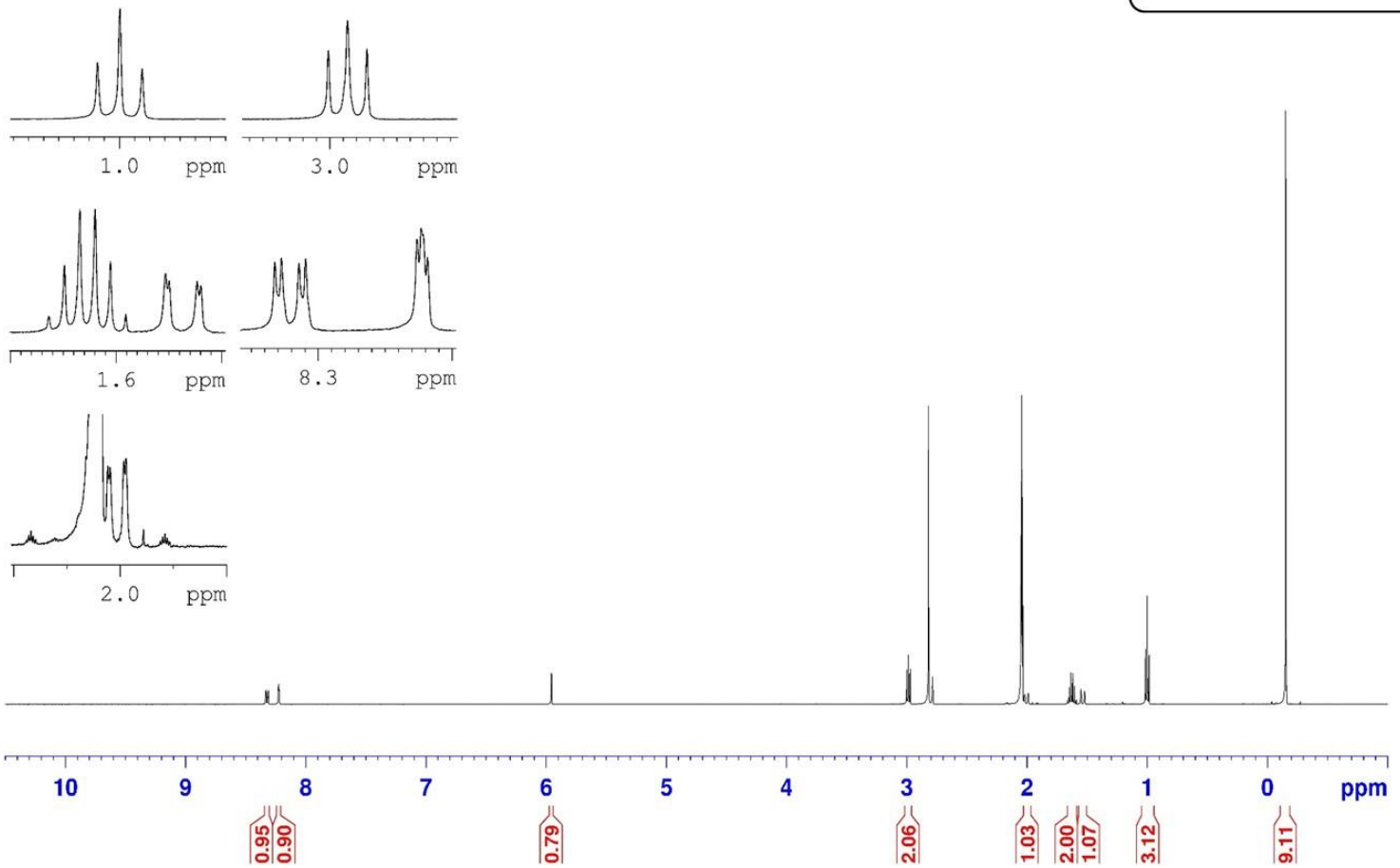

**2s**



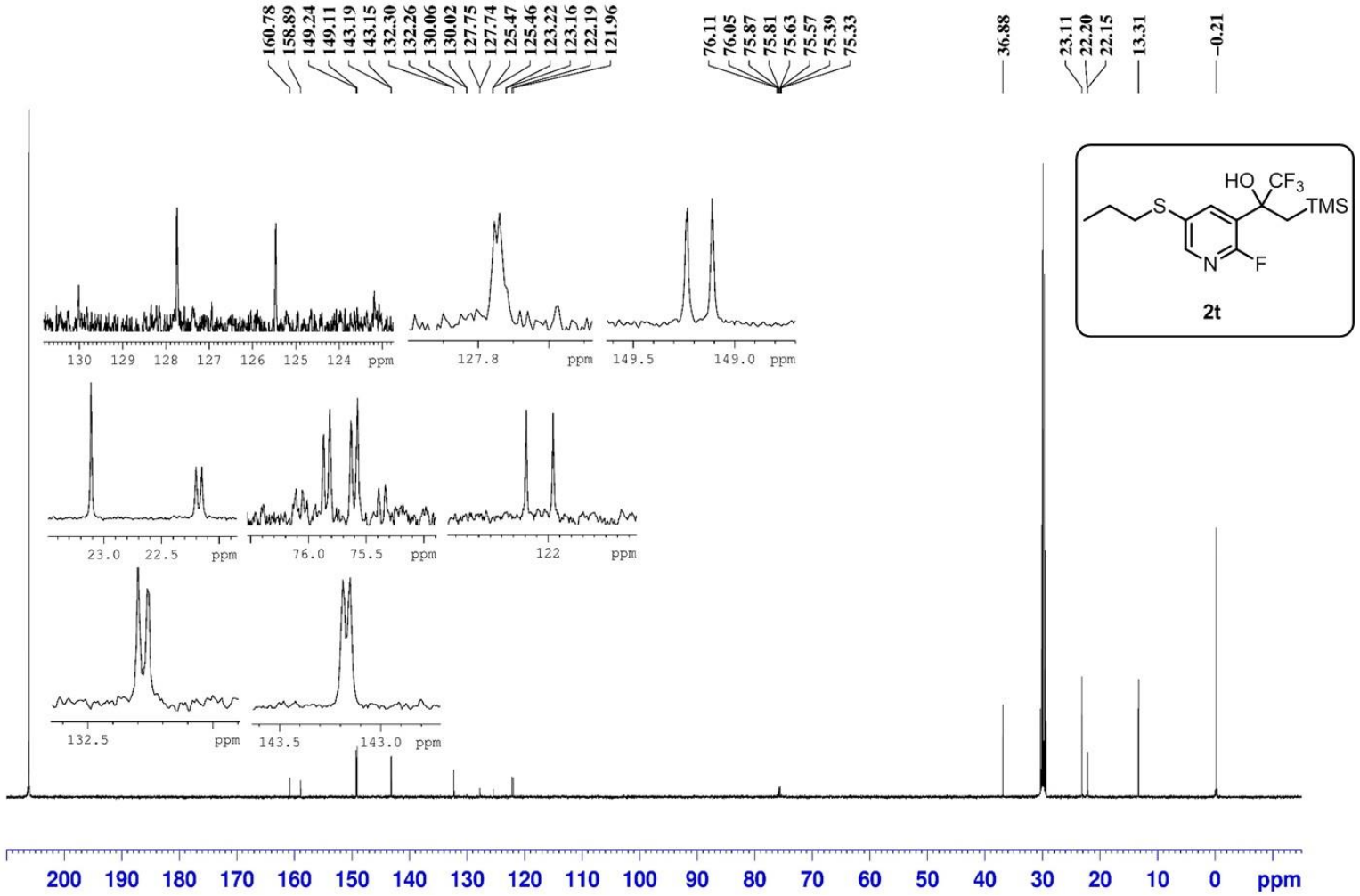
**1,1,1–Trifluoro–2–(2–fluoro–5–(propylthio)pyridin–3–yl)–3–(trimethylsilyl)propan–2–ol**
**500 MHz, acetone–d6**



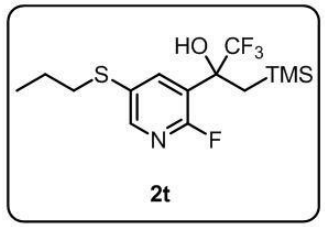
**2t**



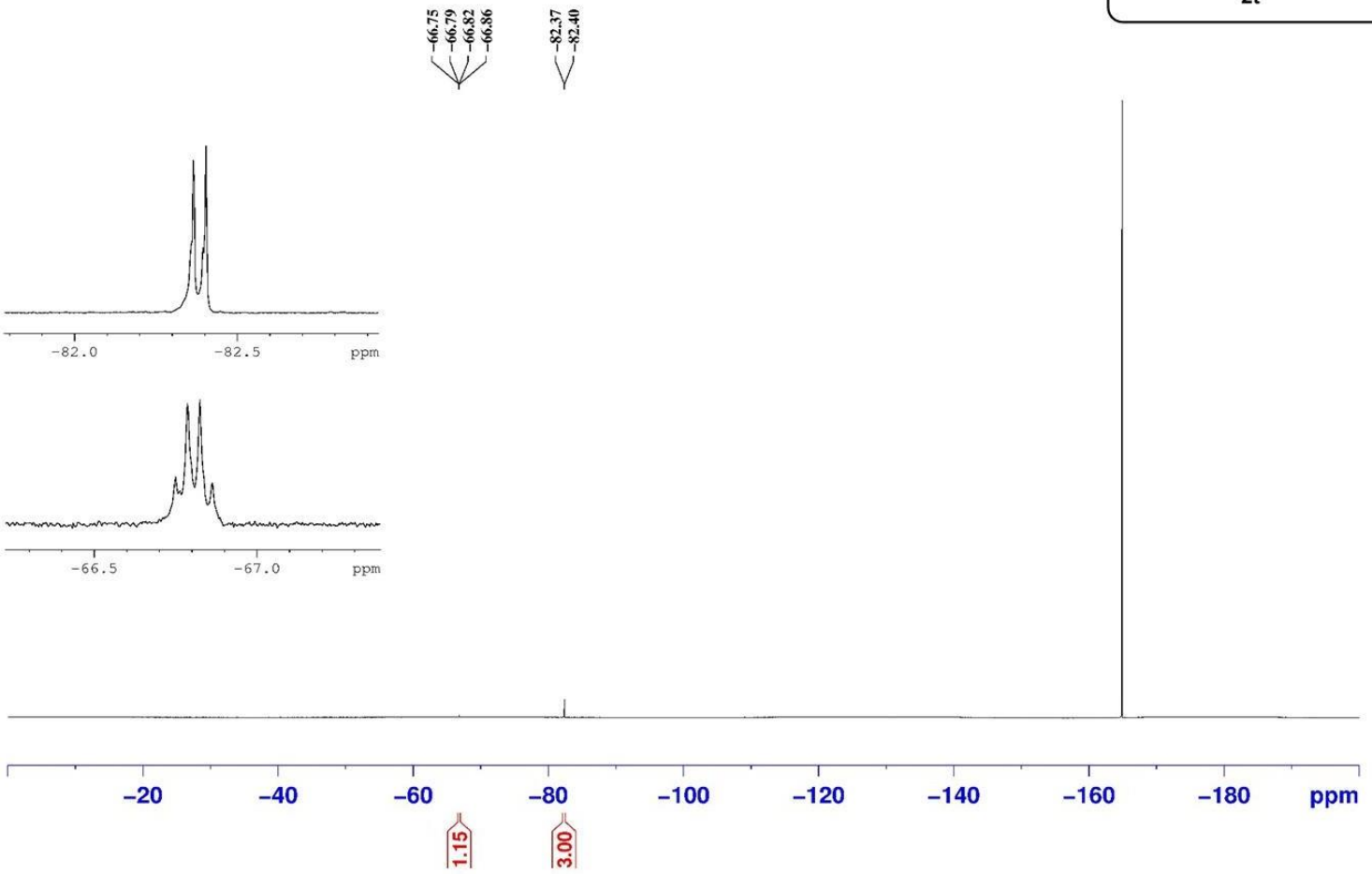
**1,1,1−Trifluoro−2−(2−fluoro−5−(propylthio)pyridin−3−yl)−3−(trimethylsilyl)propan−2−ol**
**125 MHz, acetone−d6**



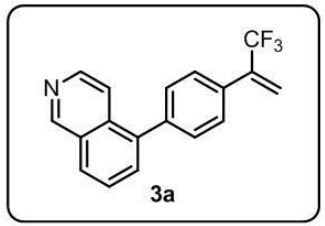
**1,1,1–trifluoro–2–(2–fluoro–5–(propylthio)pyridin–3–yl)–3–(trimethylsilyl)propan–2–ol**
**Acetone–d6, 471 MHz**

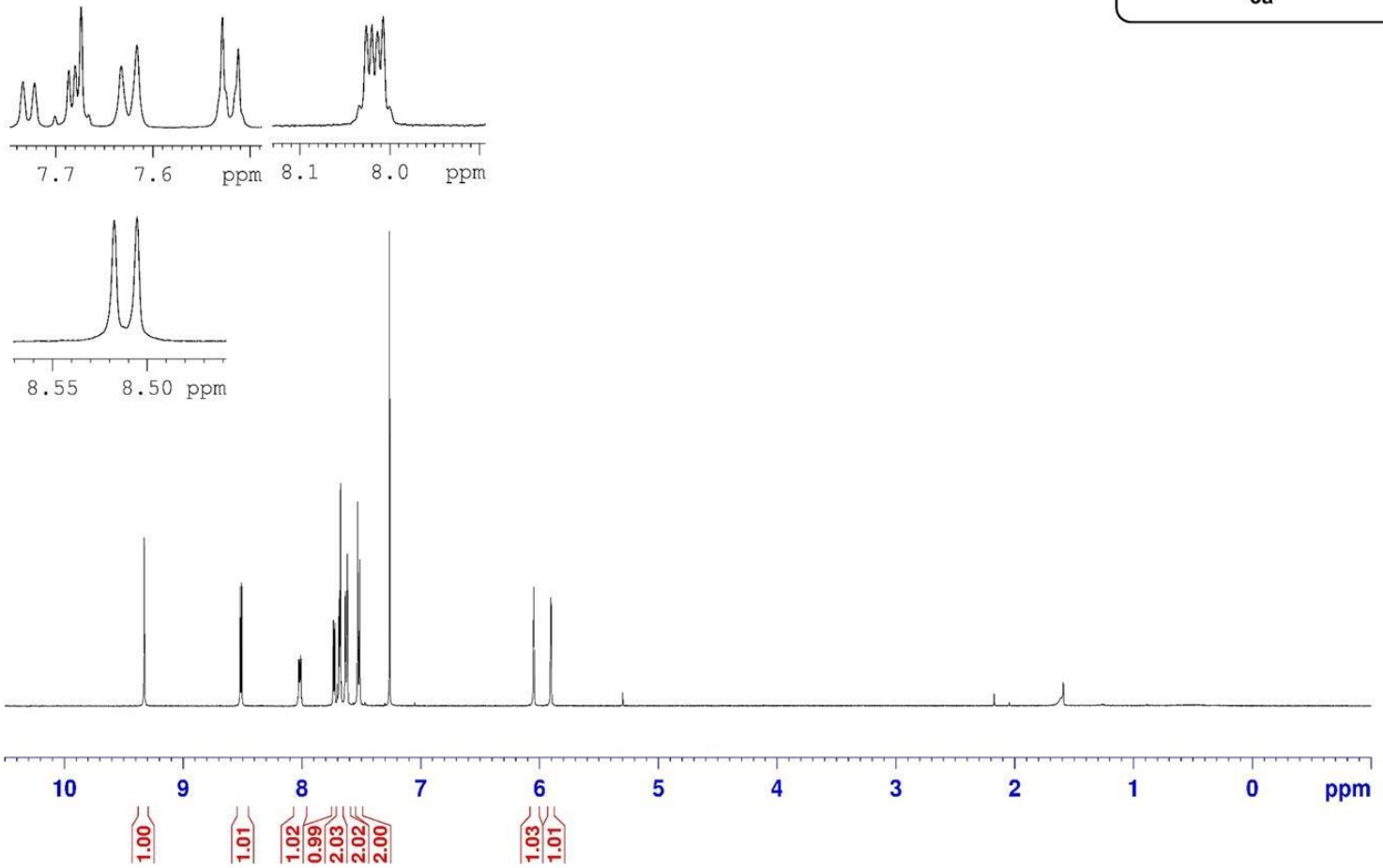



**2t**

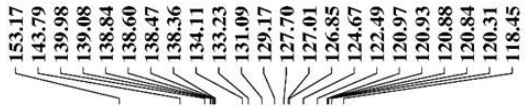


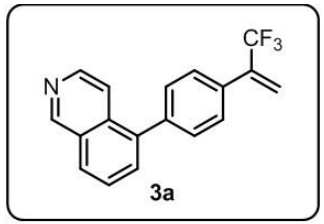
**5–(4–(3,3,3–Trifluoroprop–1–en–2–yl)phenyl)isoquinoline**
**500 MHz, CDCl3**

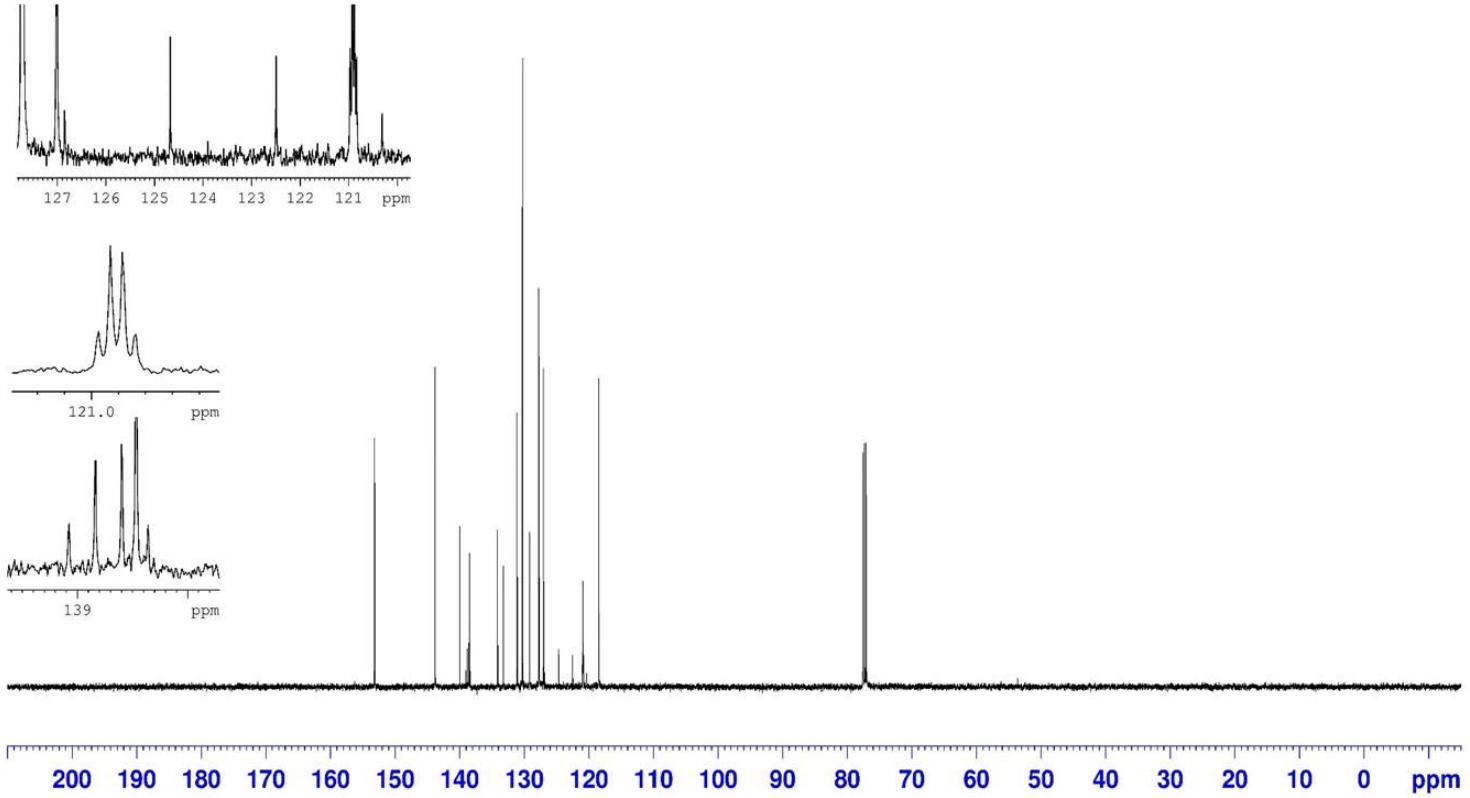


**5–(4–(3,3,3–Trifluoroprop–1–en–2–yl)phenyl)isoquinoline**
**125 MHz, CDCl3**

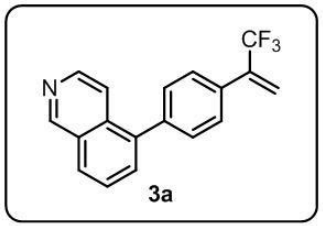


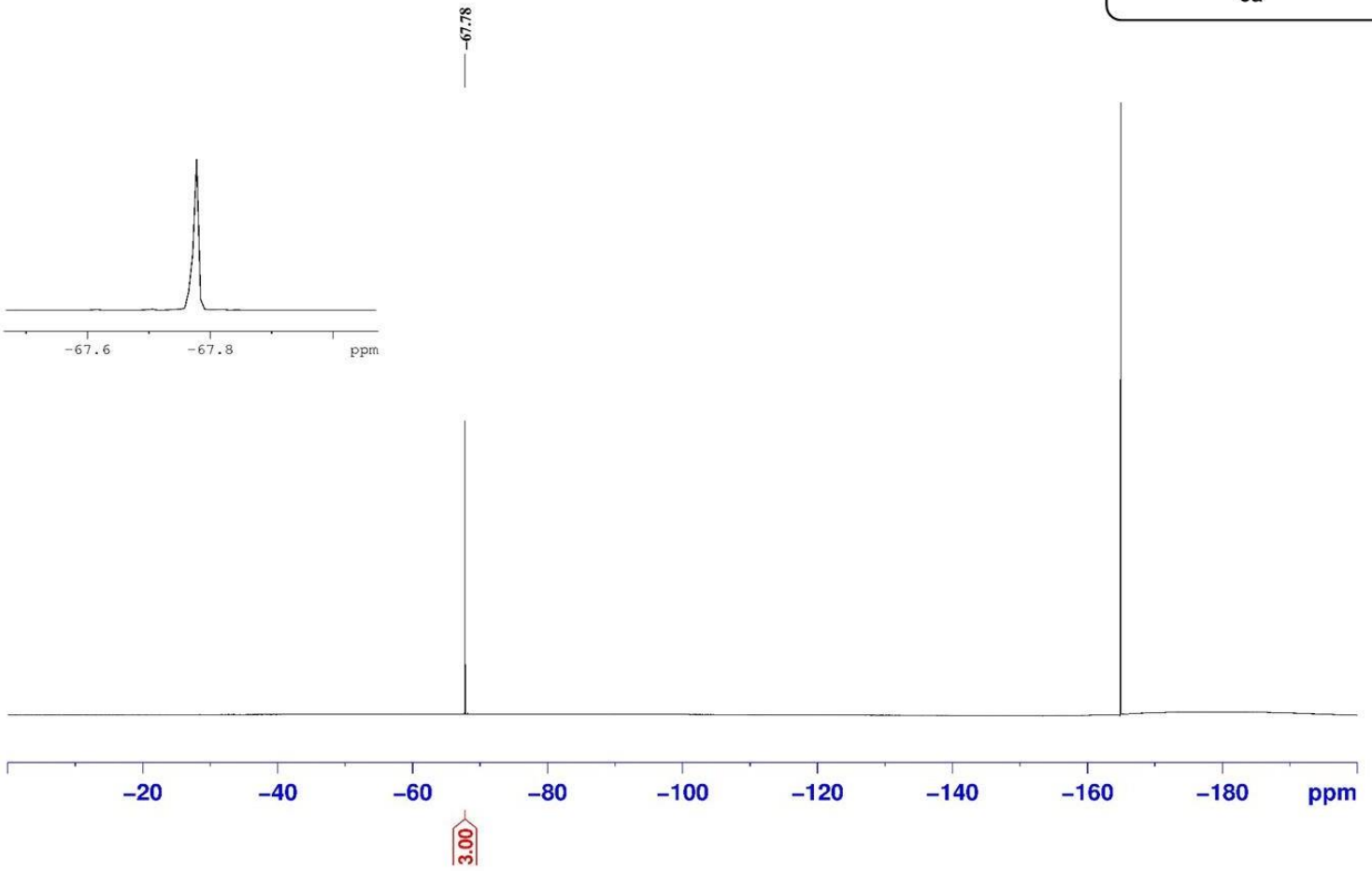



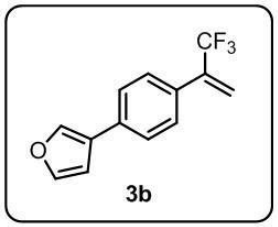

6.5

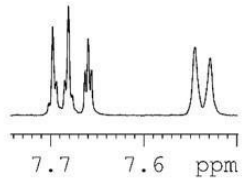
**5–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)isoquinoline**
**CDCl3, 471 MHz**

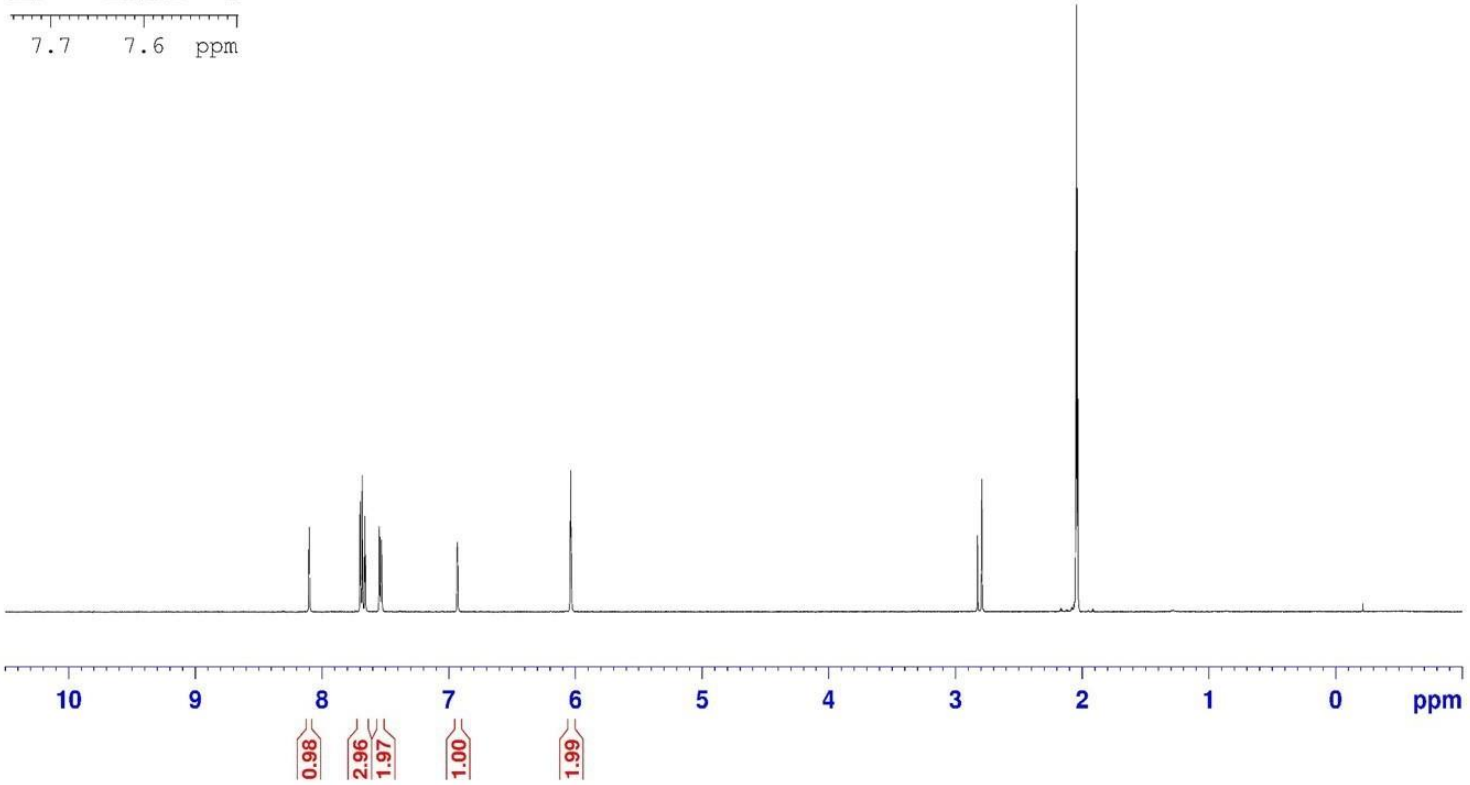


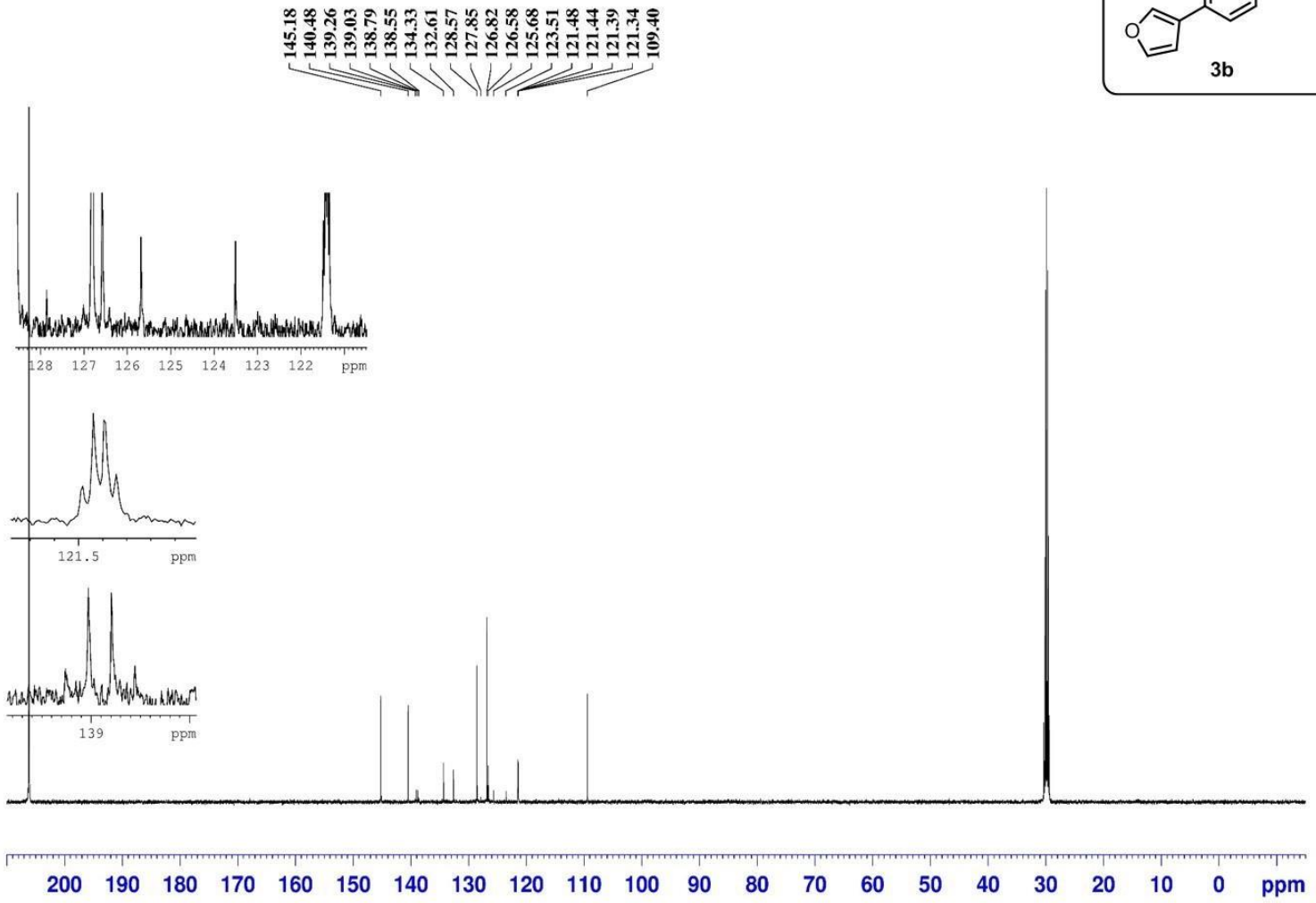
**3–(4–(3,3,3–Trifluoroprop–1–en–2–yl)phenyl)furan**
**500 MHz, acetone–d6**

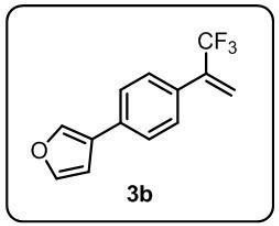


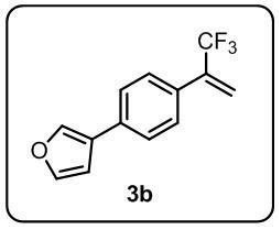



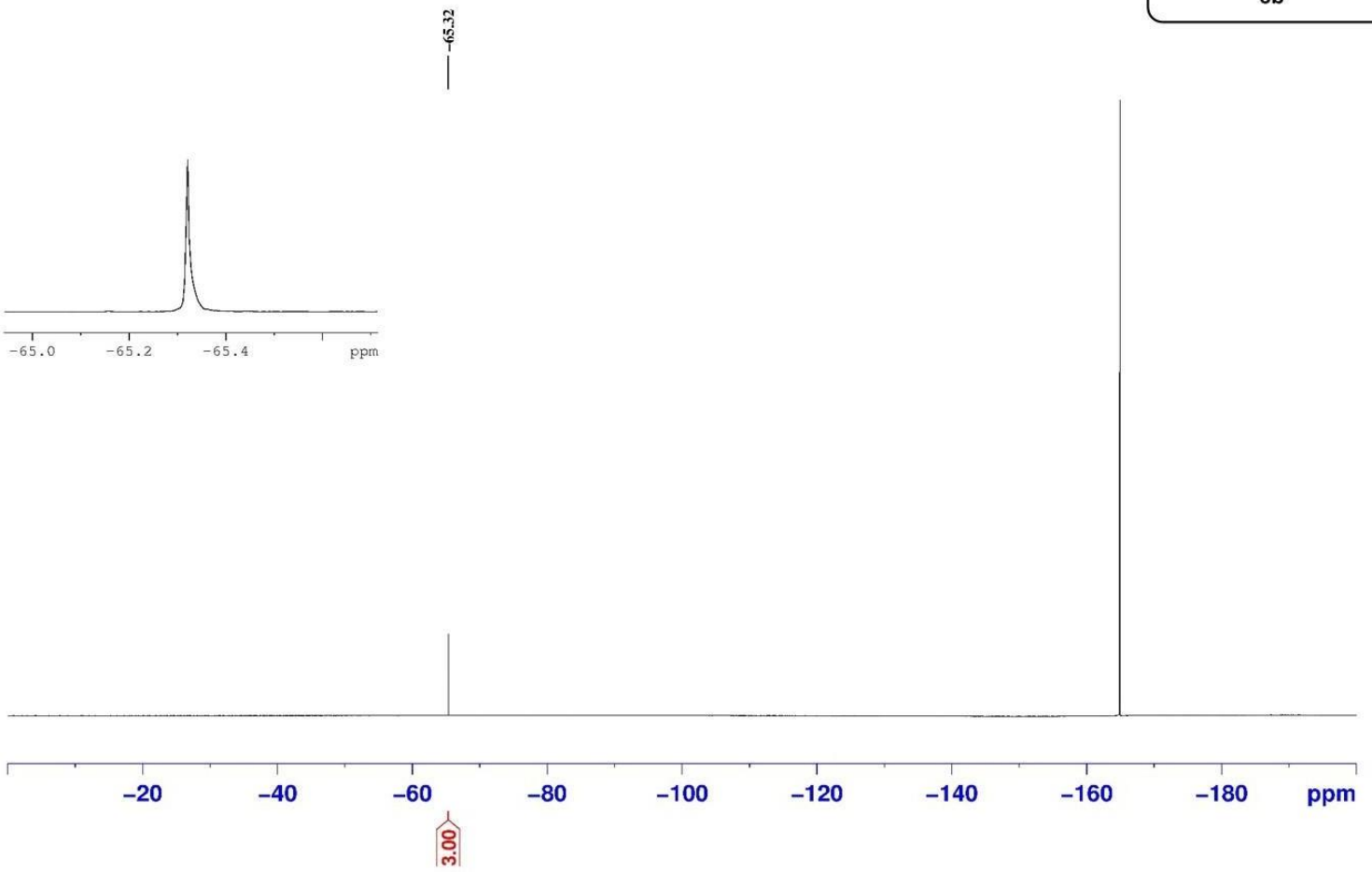
**3–(4–(3,3,3–Trifluoroprop–1–en–2–yl)phenyl)furan**
**125 MHz, acetone–d6**



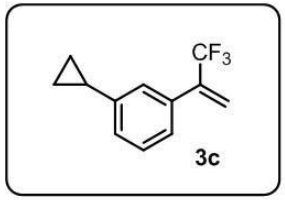



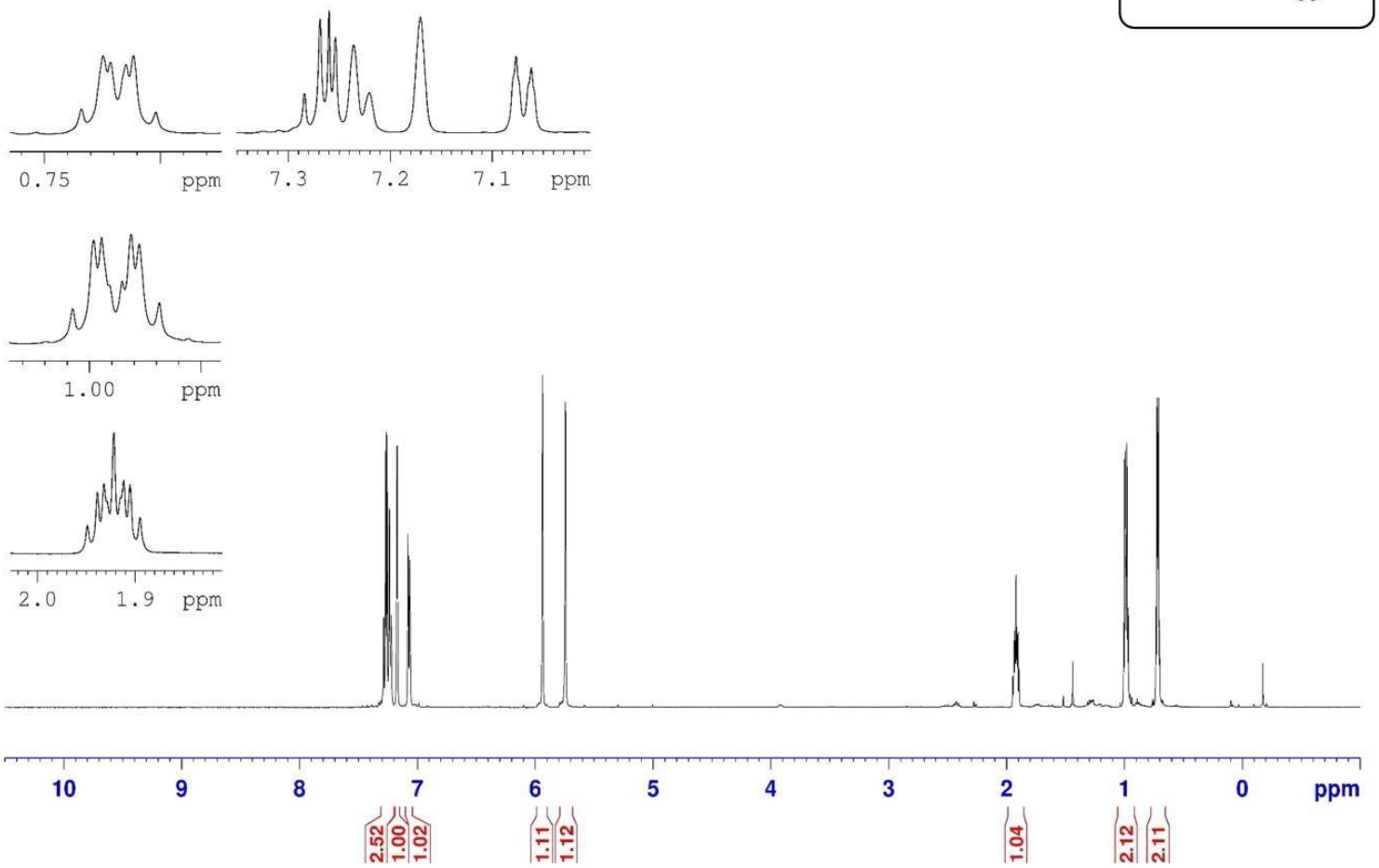
**3–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)furan**
**Acetone–d6, 471 MHz**



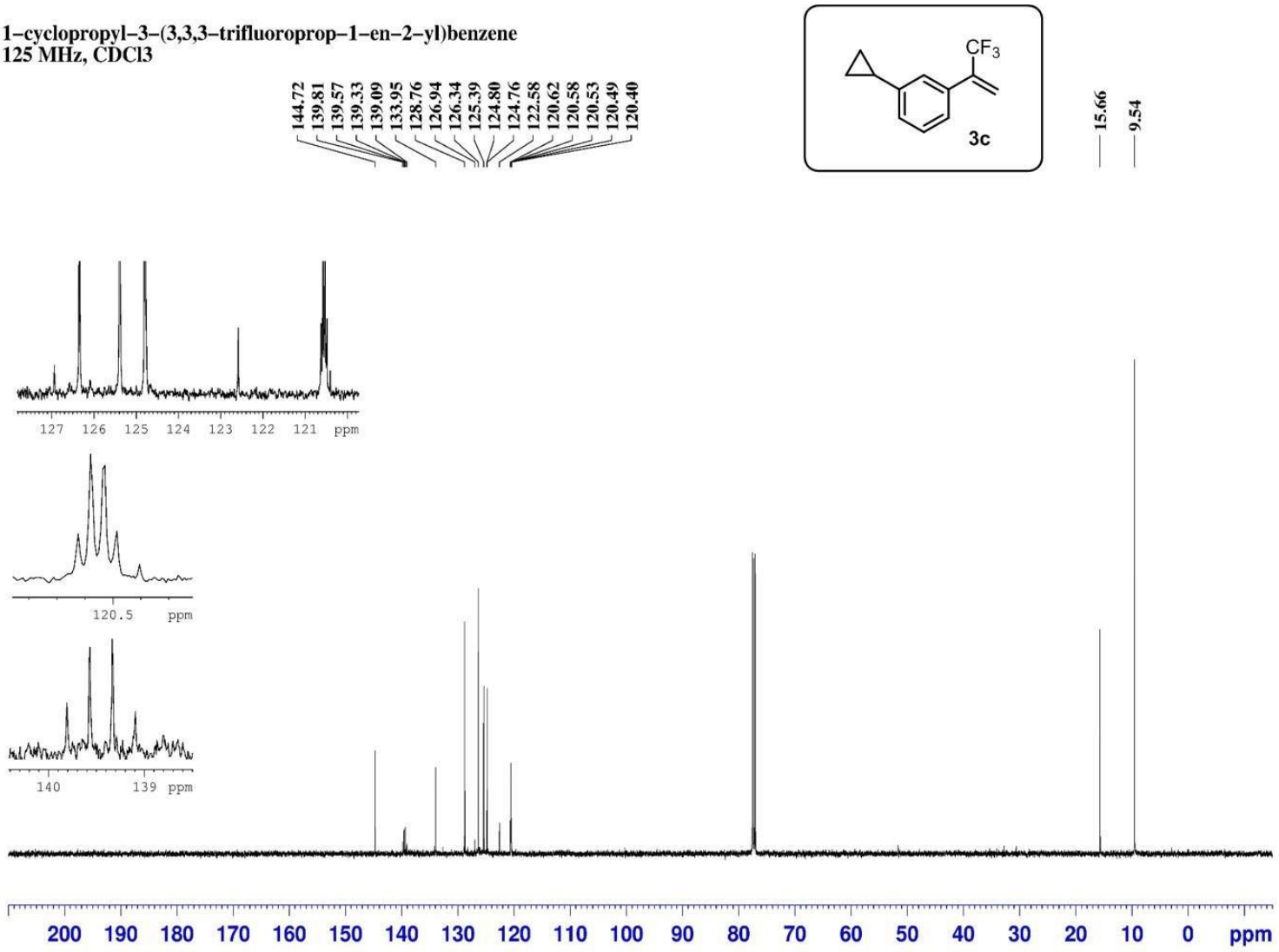



**1−cyclopropyl−3−(3,3,3−trifluoroprop−1−en−2−yl)benzene**
**500 MHz, CDCl3**

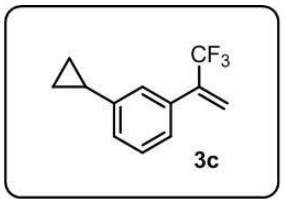


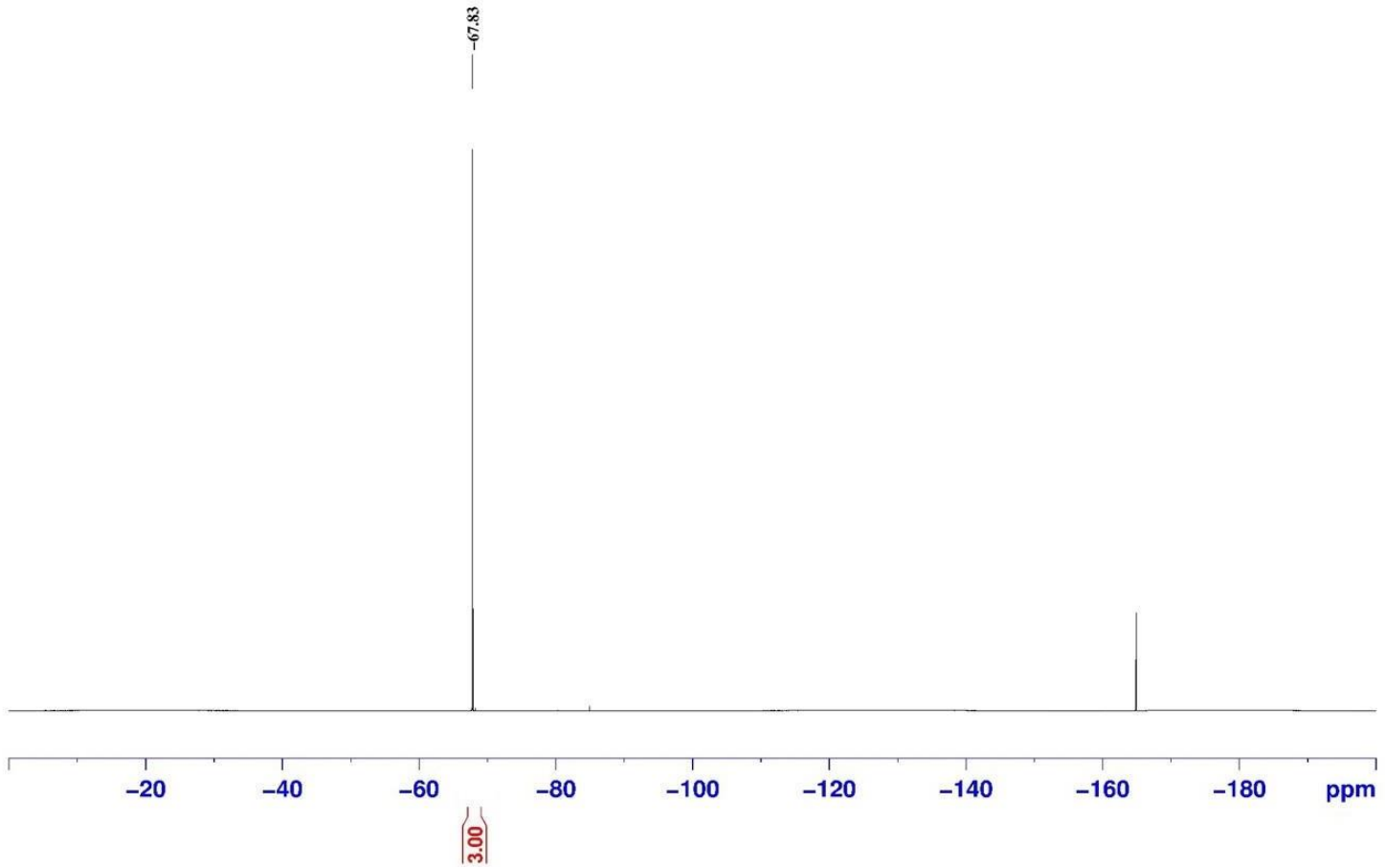



**1–cyclopropyl–3–(3,3,3–trifluoroprop–1–en–2–yl)benzene**
**125 MHz, CDCl3**

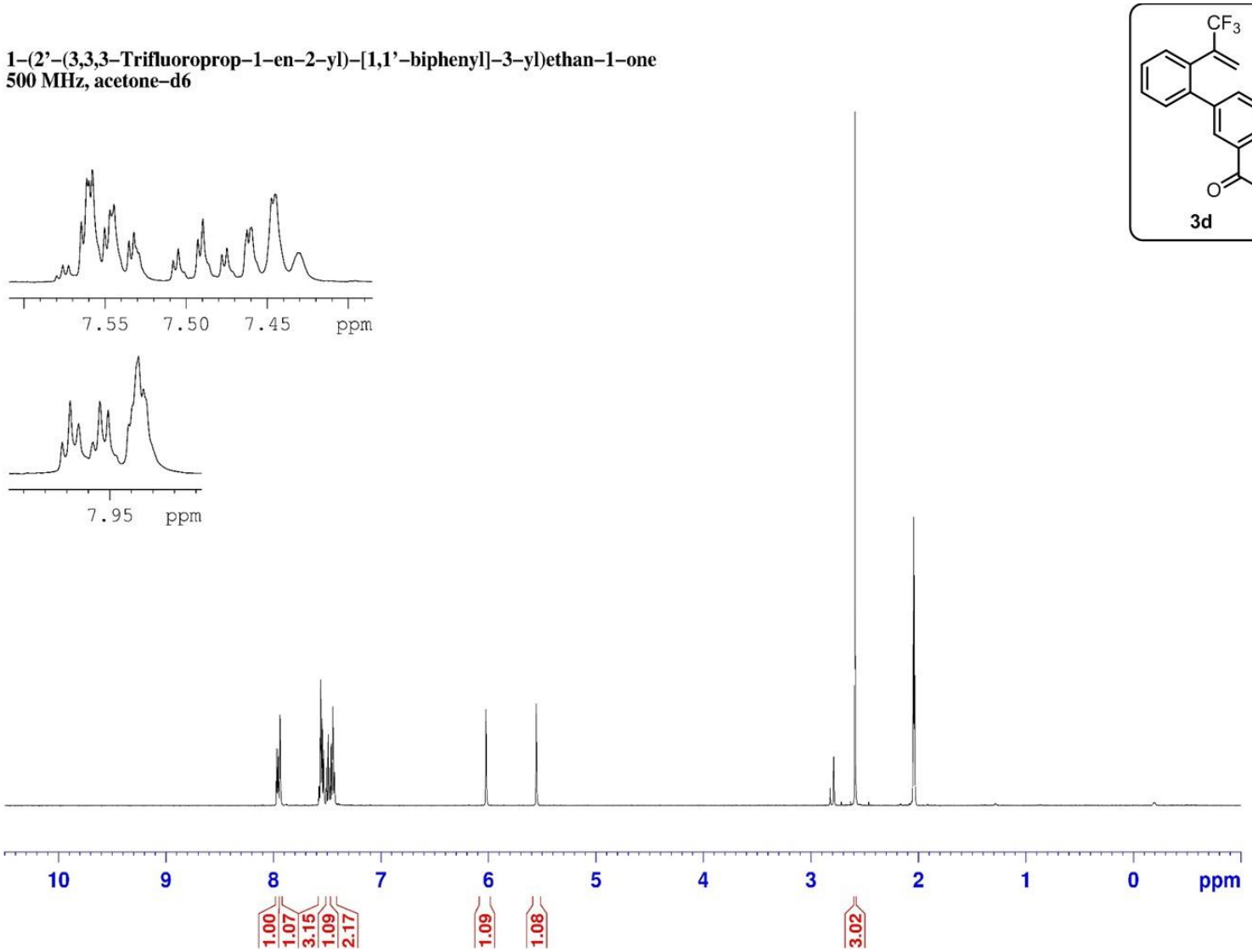


**1−cyclopropyl−3−(3,3,3−trifluoroprop−1−en−2−yl)benzene**
**471 MHz, CDCl3**

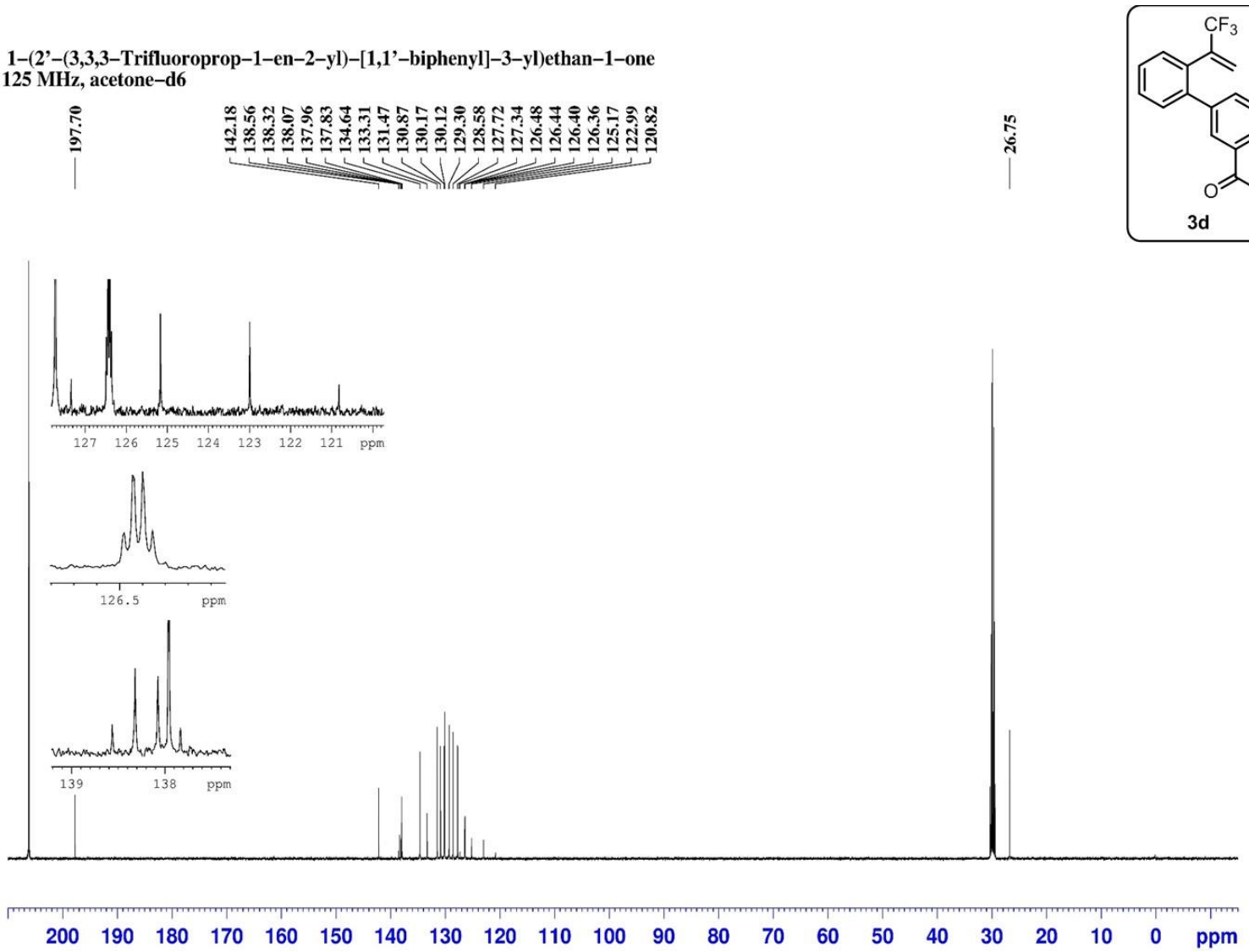


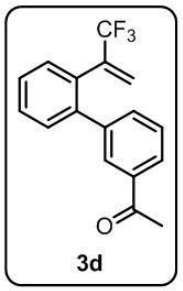
**1–(2'–(3,3,3–Trifluoroprop–1–en–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**500 MHz, acetone–d6**

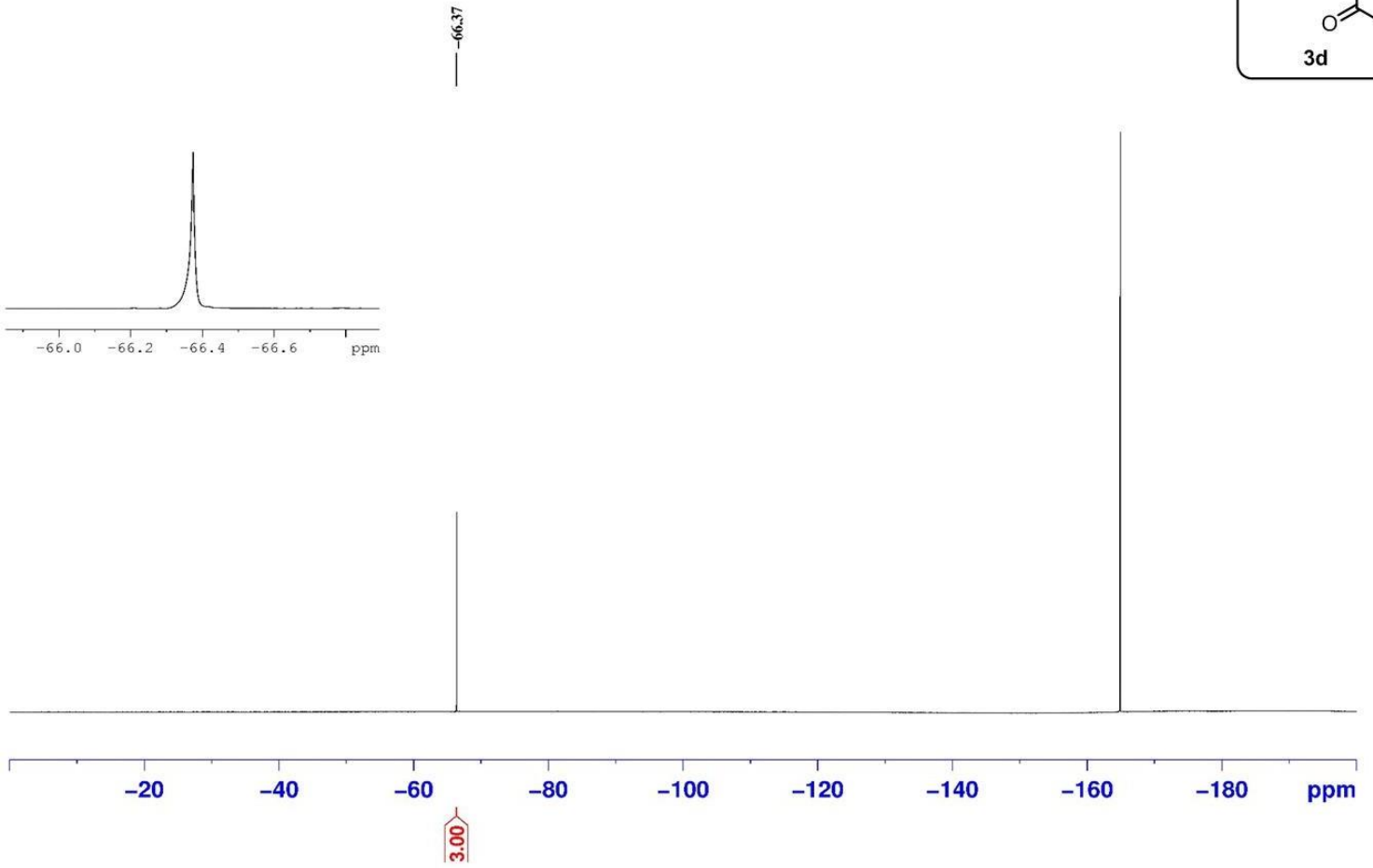


**1–(2'–(3,3,3–Trifluoroprop–1–en–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**125 MHz, acetone–d6**

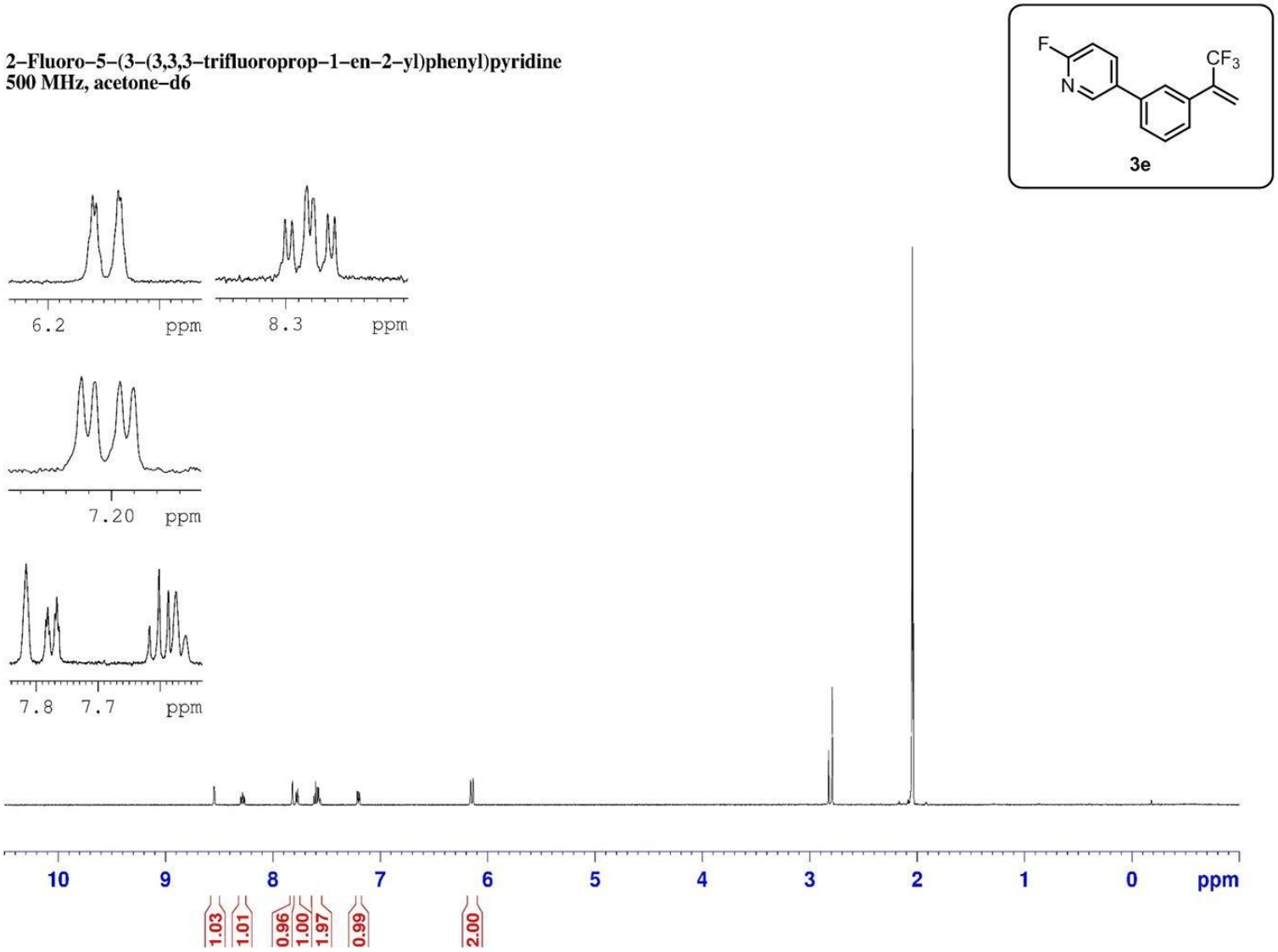


**1–(2'–(3,3,3–trifluoroprop–1–en–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**Acetone–d6, 471 MHz**

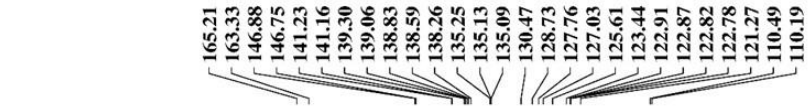


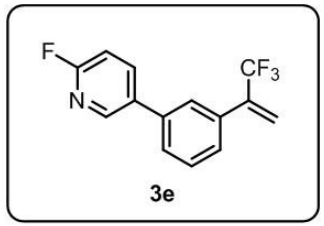



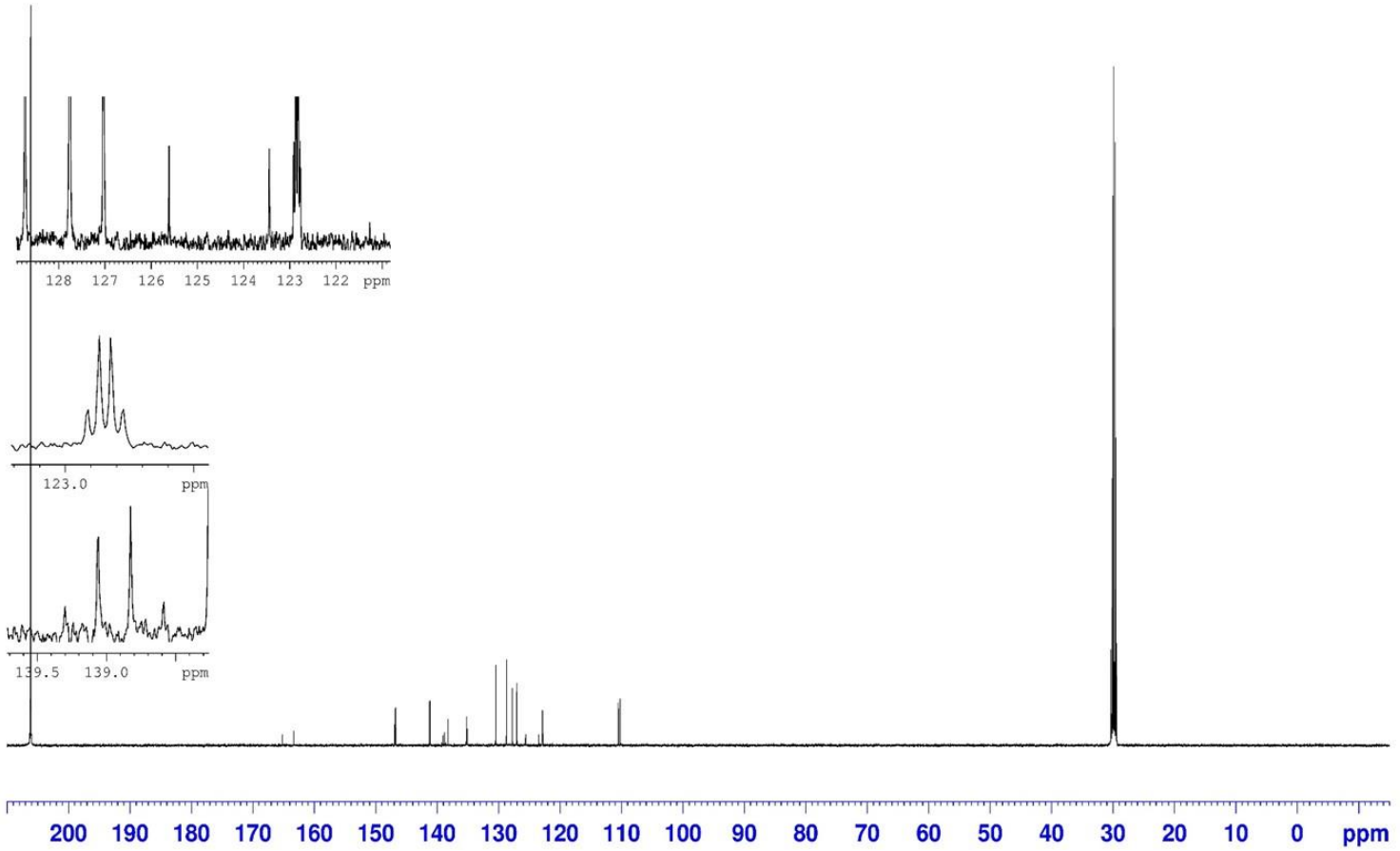
**2–Fluoro–5–(3–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)pyridine**
**500 MHz, acetone–d6**



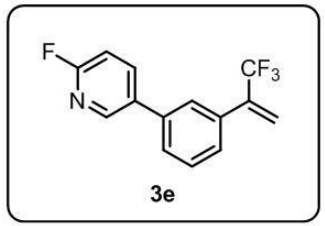
**2–Fluoro–5–(3–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)pyridine**
**125 MHz, acetone–d6**



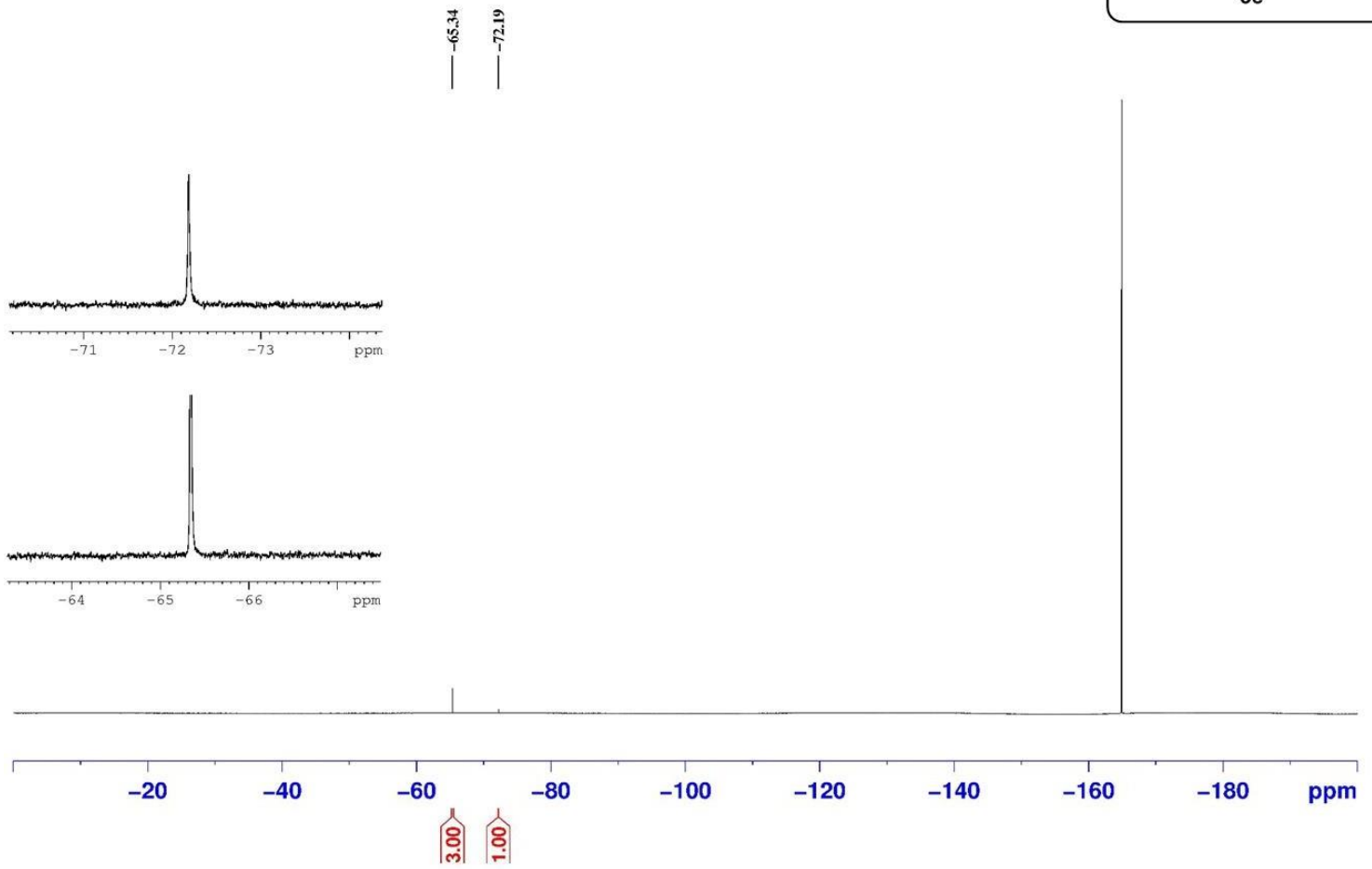



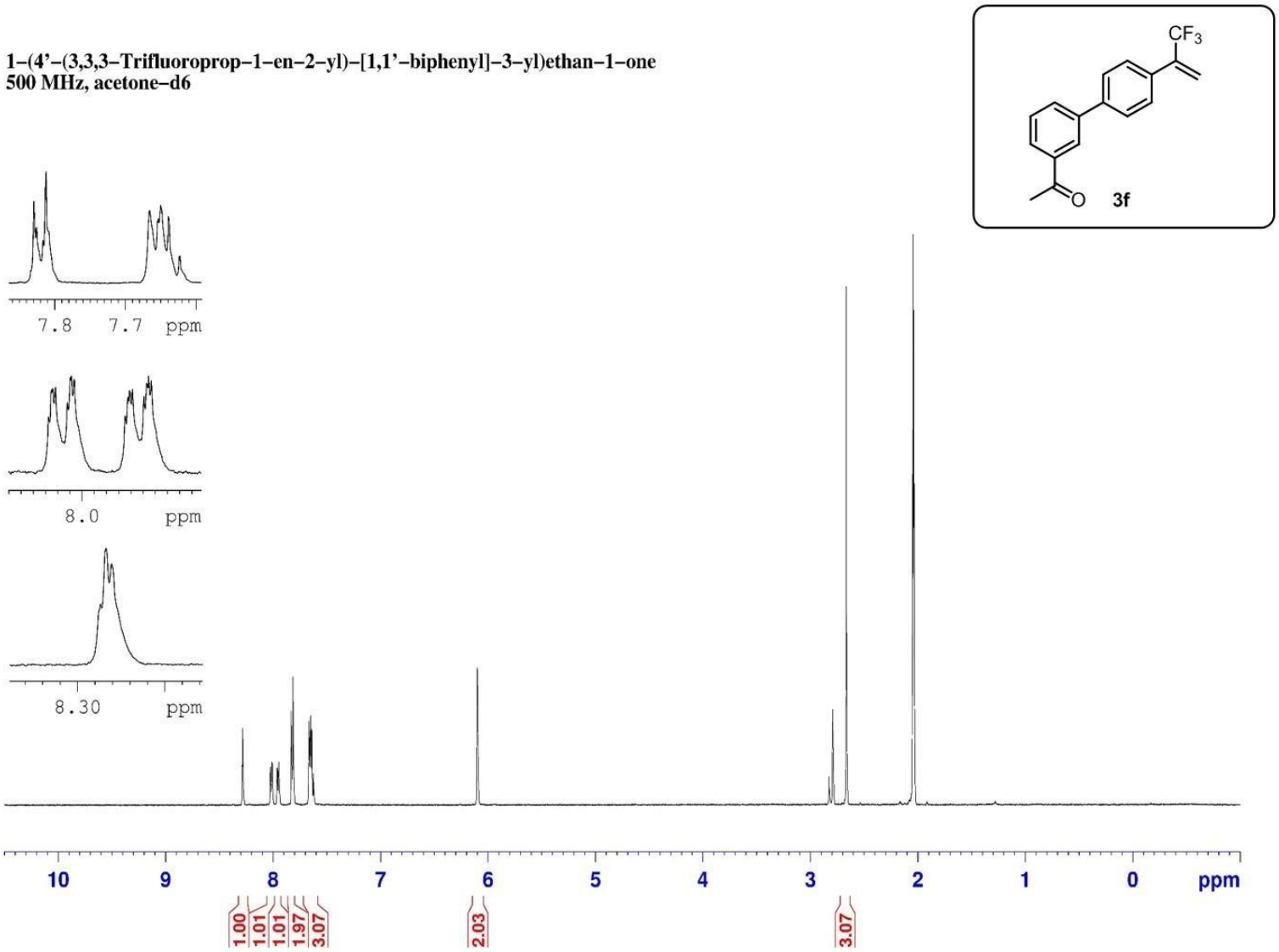
**2–fluoro–5–(3–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)pyridine**
**Acetone–d6, 471 MHz**



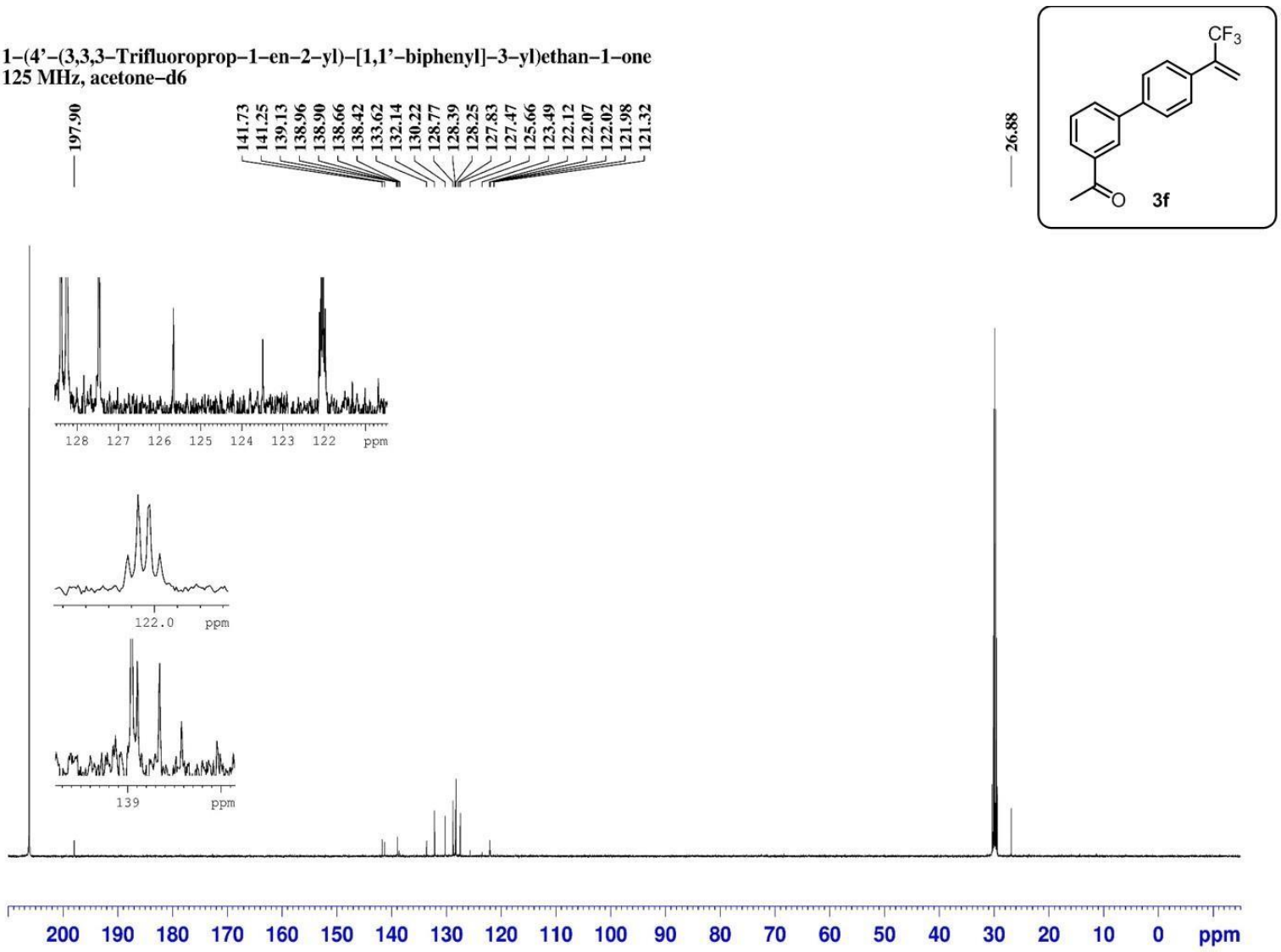

**3e**



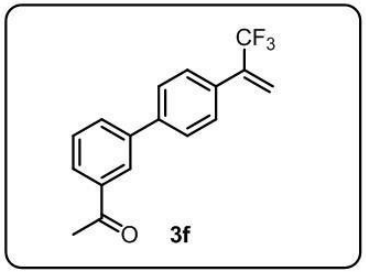
**1–(4'–(3,3,3–Trifluoroprop–1–en–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**500 MHz, acetone–d6**

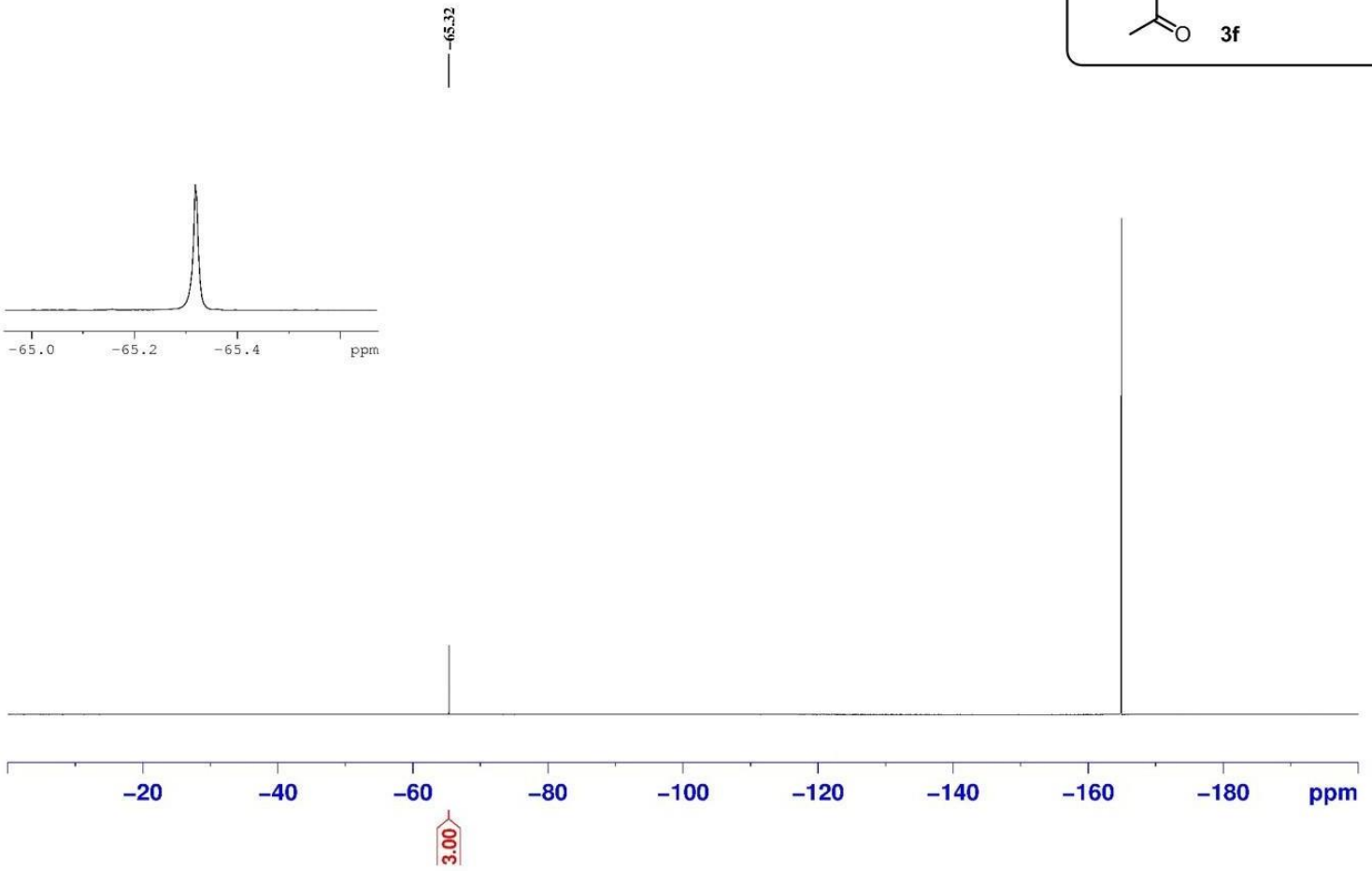


**1–(4'–(3,3,3–Trifluoroprop–1–en–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**125 MHz, acetone–d6**

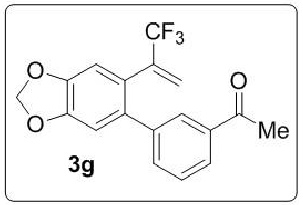


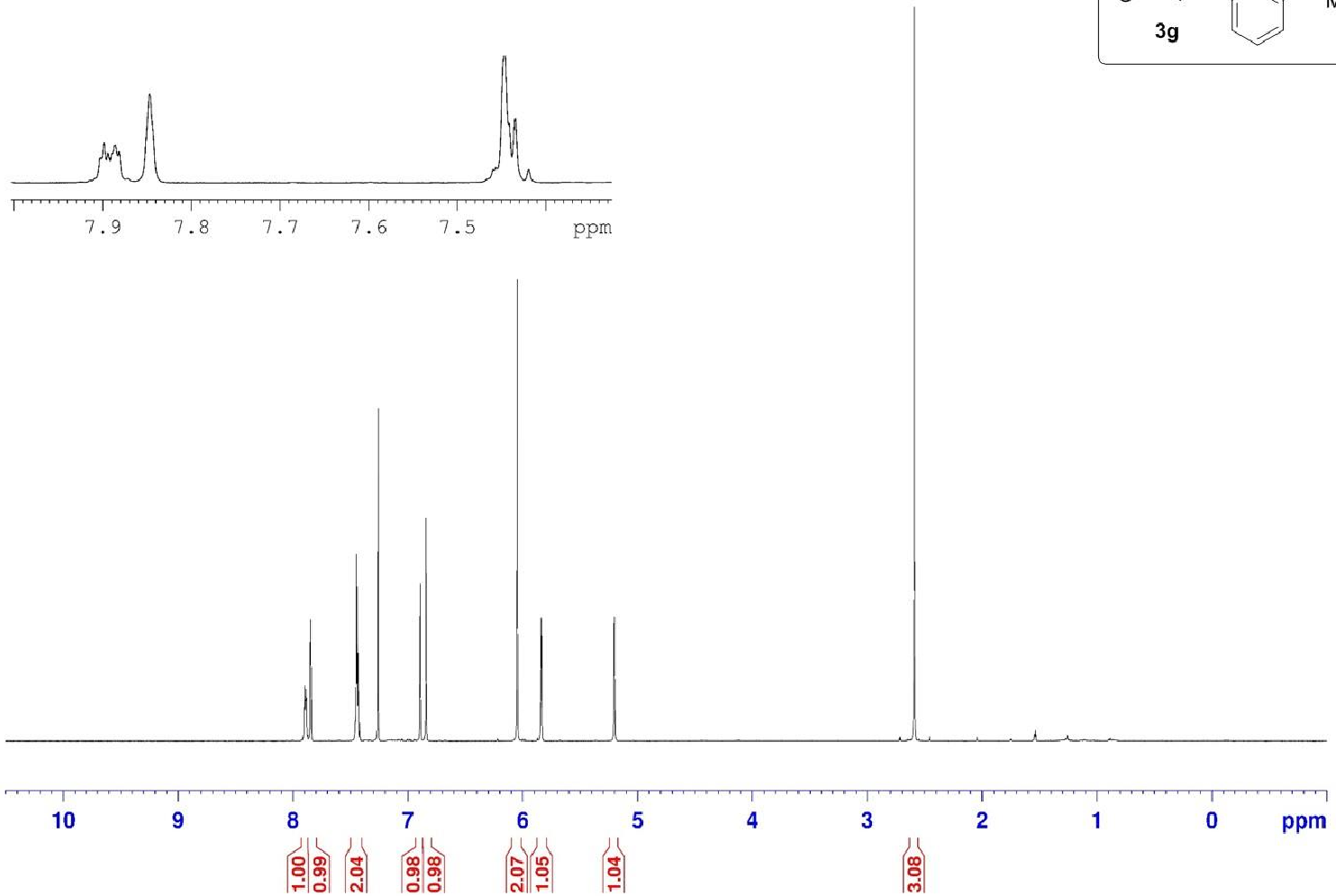
**1–(4'–(3,3,3–trifluoroprop–1–en–2–yl)–[1,1'–biphenyl]–3–yl)ethan–1–one**
**Acetone–d6, 471 MHz**



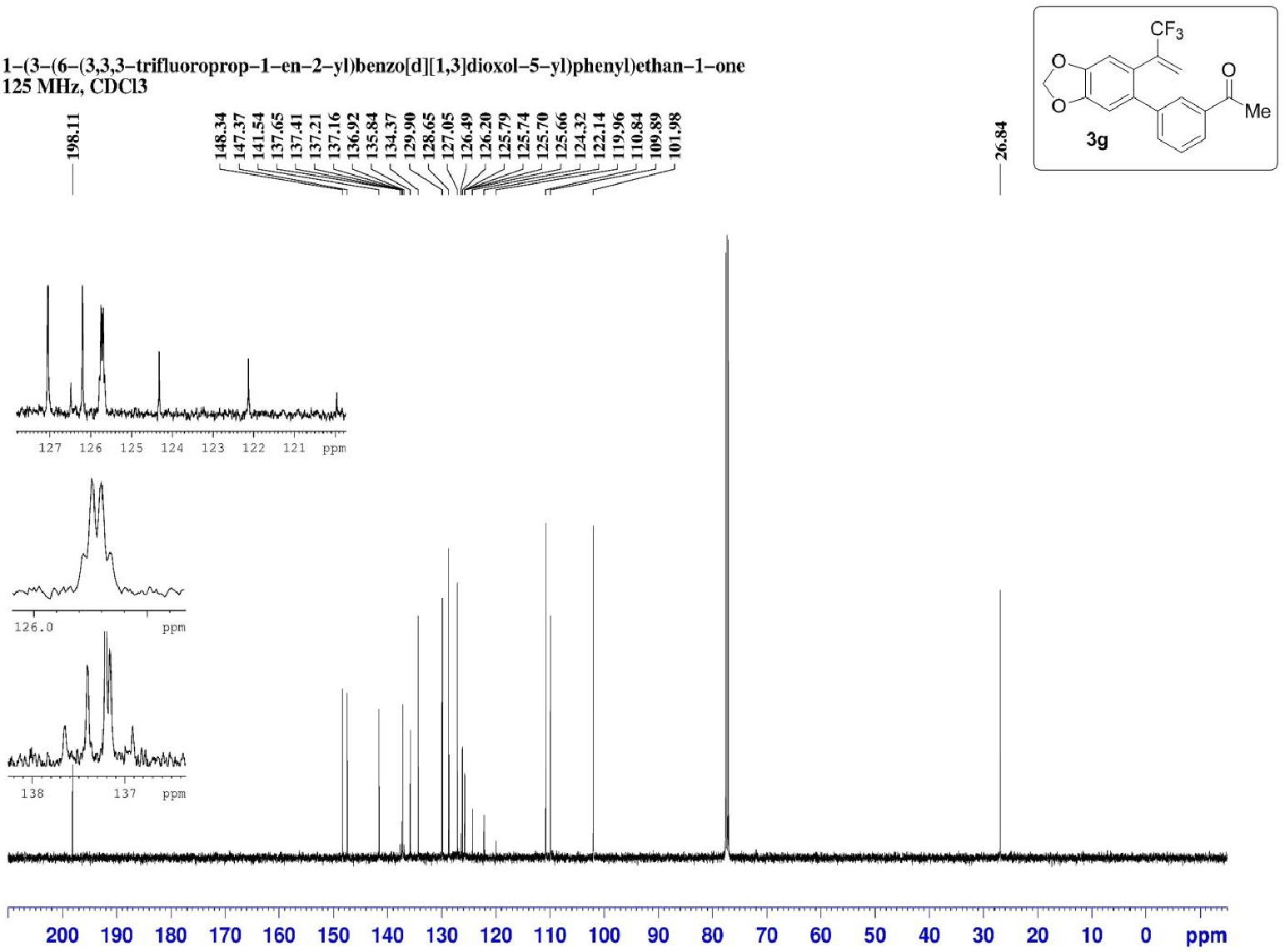



**1-(3-(6-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxol-5-yl)phenyl)ethan-1-one**
**500 MHz, CDCl3**

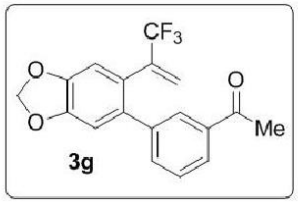


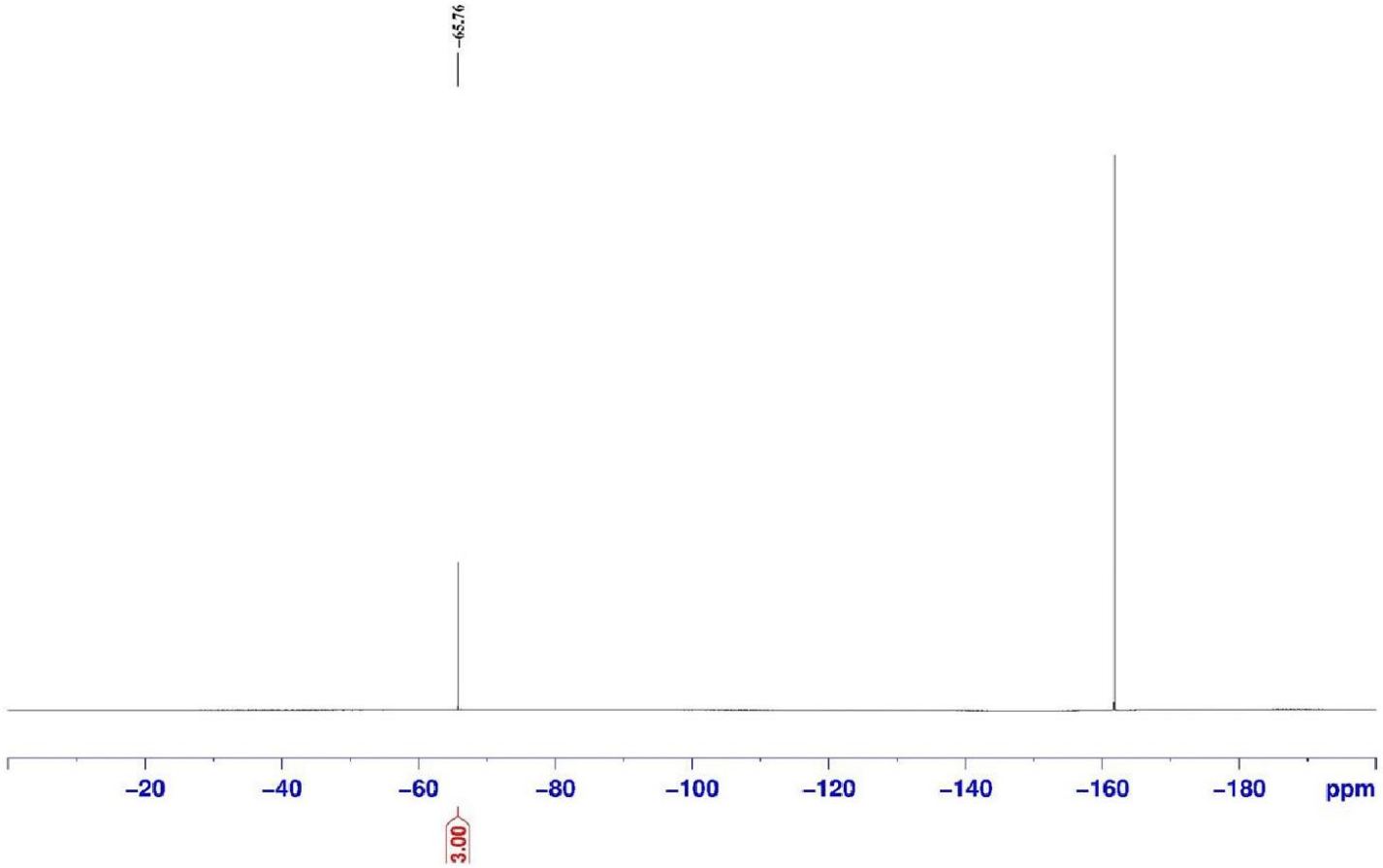
**1-(3-(6-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxol-5-yl)phenyl)ethan-1-one**
**125 MHz, CDCl3**



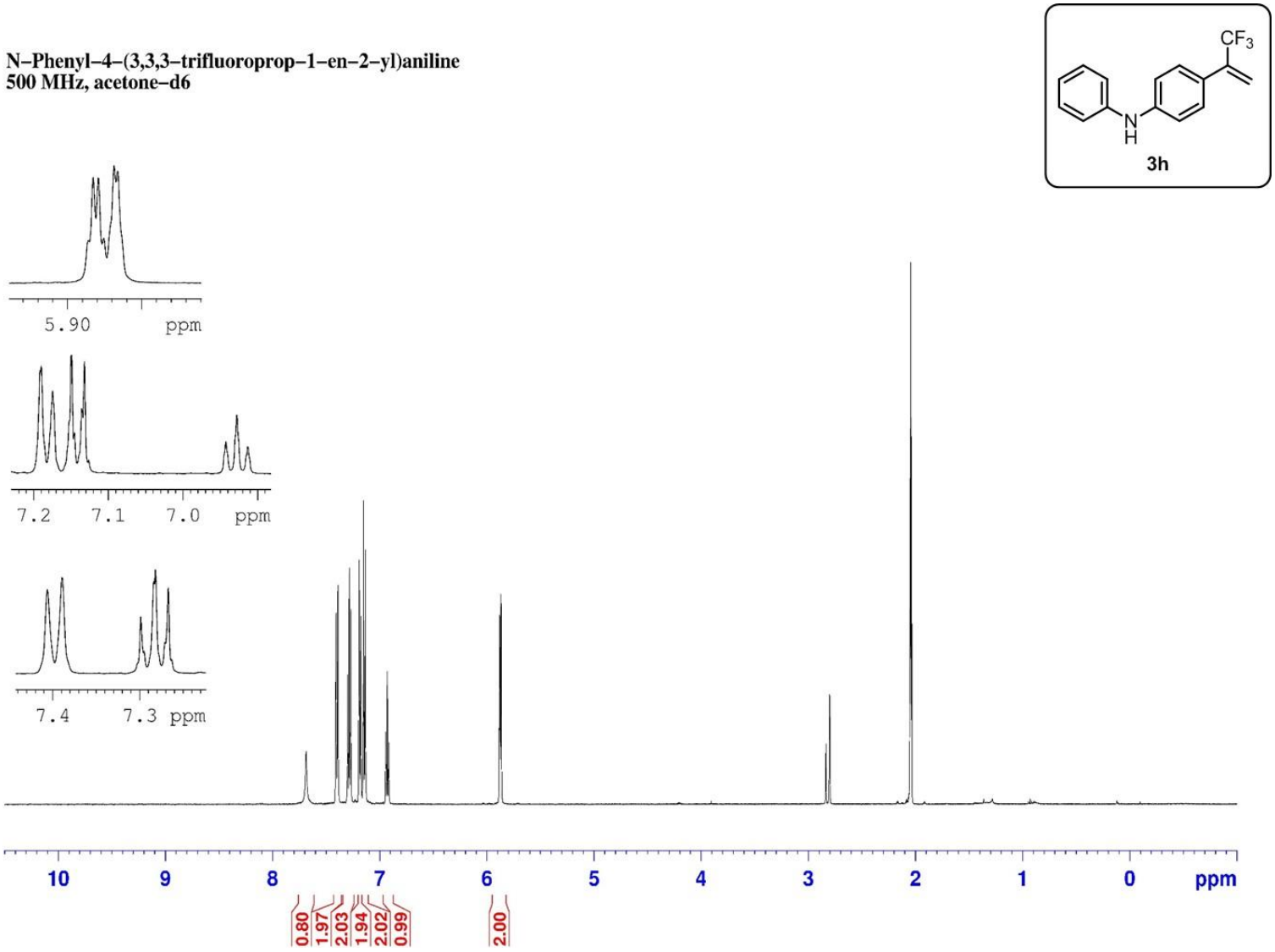
**1-(3-(6-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxol-5-yl)phenyl)ethan-1-one**
**471 MHz, CDCl3**



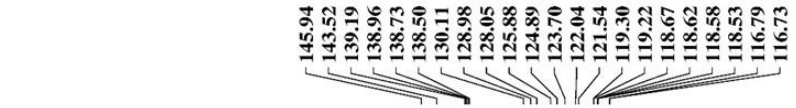
**3g**

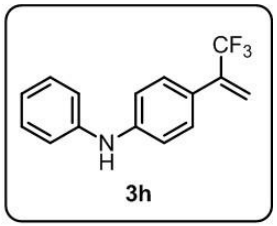


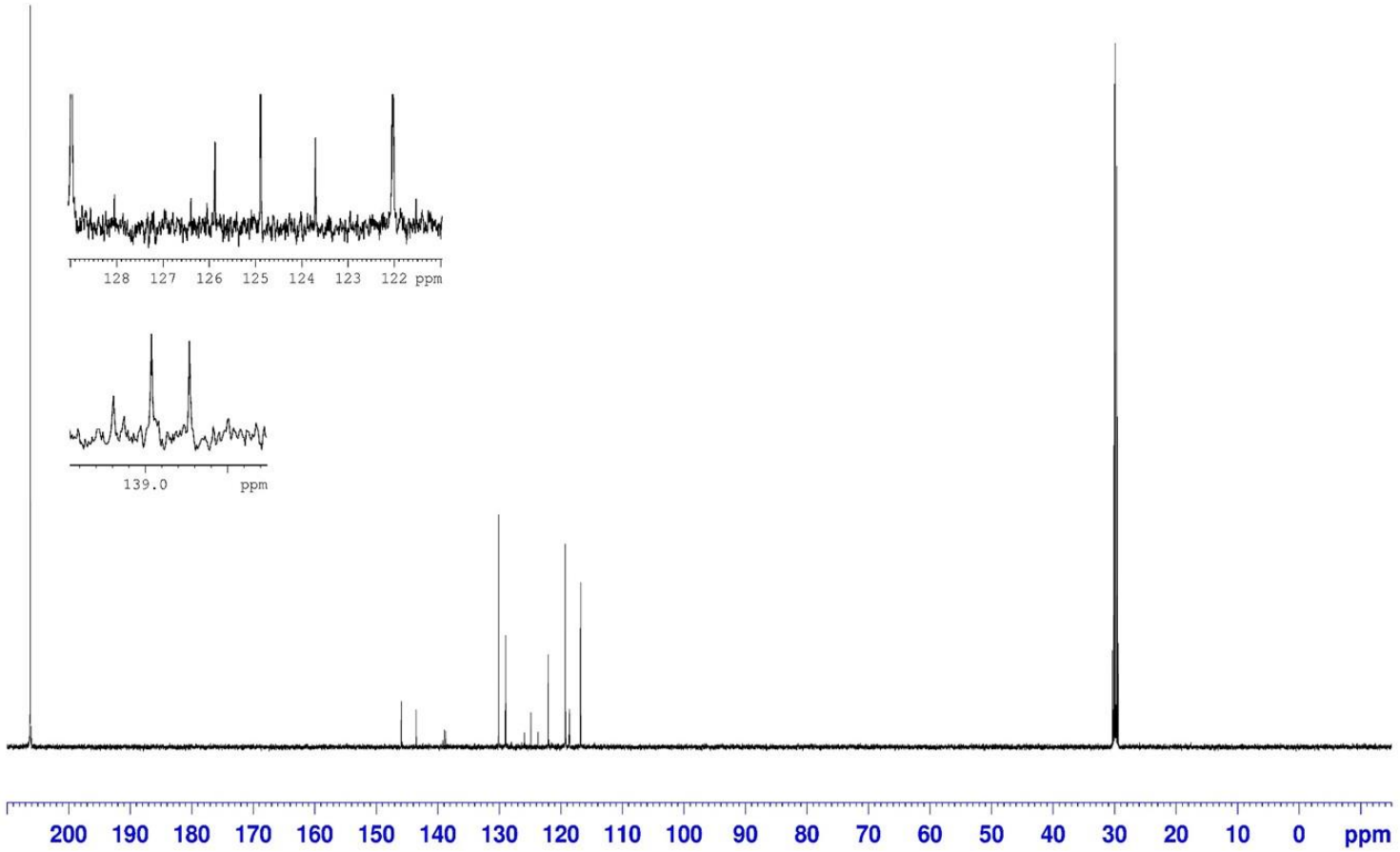
**N–Phenyl–4–(3,3,3–trifluoroprop–1–en–2–yl)aniline**
**500 MHz, acetone–d6**



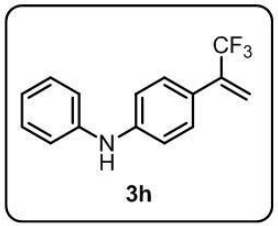
**N–Phenyl–4–(3,3,3–trifluoroprop–1–en–2–yl)aniline**
**125 MHz, acetone–d6**



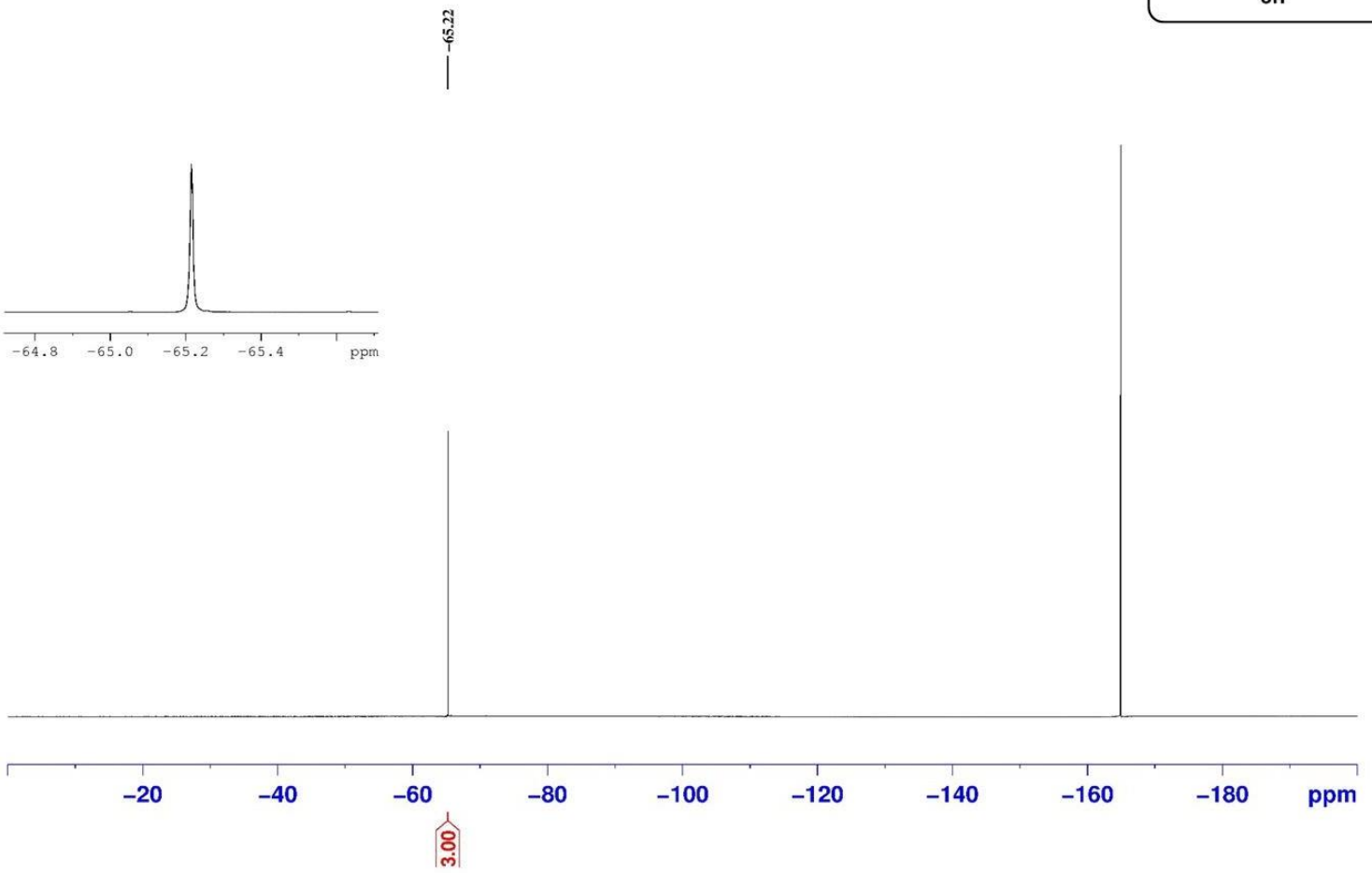



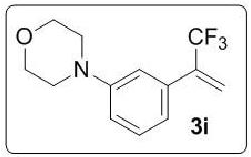
**N–phenyl–4–(3,3,3–trifluoroprop–1–en–2–yl)aniline**
**Acetone–d6, 471 MHz**

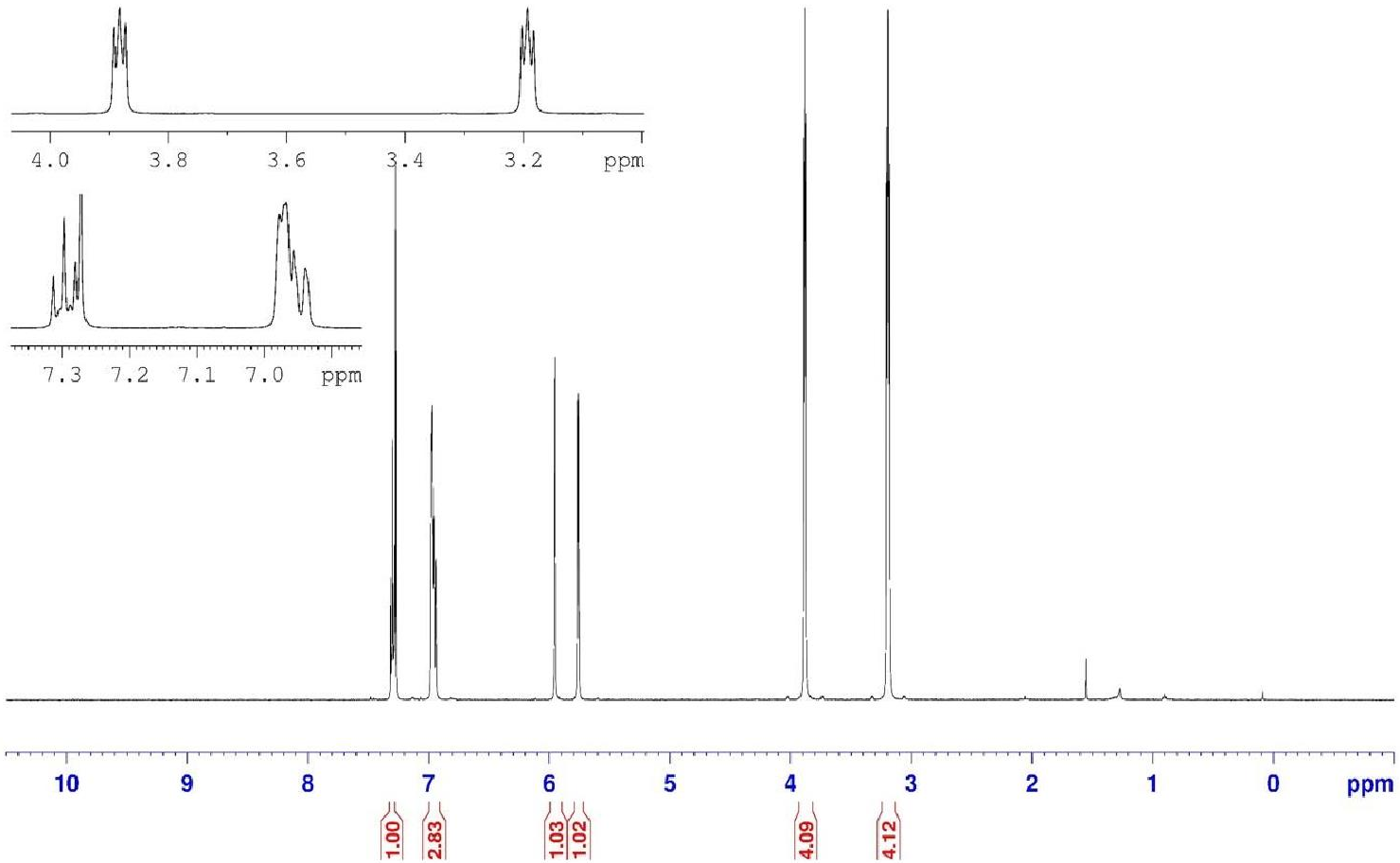



3h

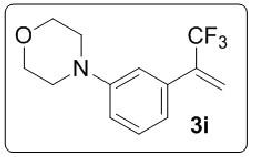


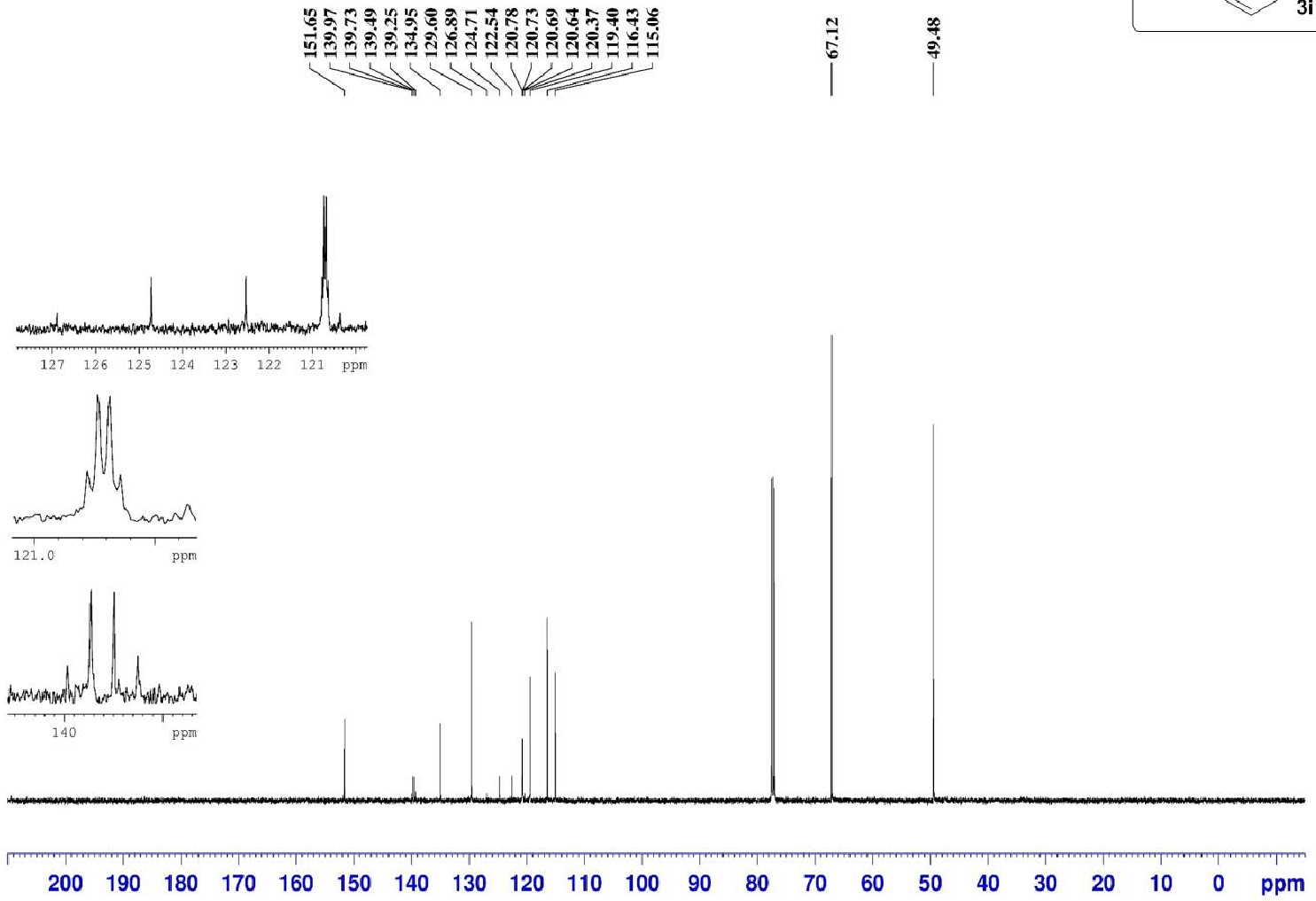
**4–(3–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)morpholine**
**500 MHz, CDCl3**



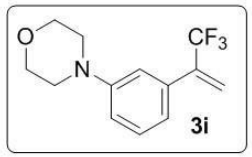



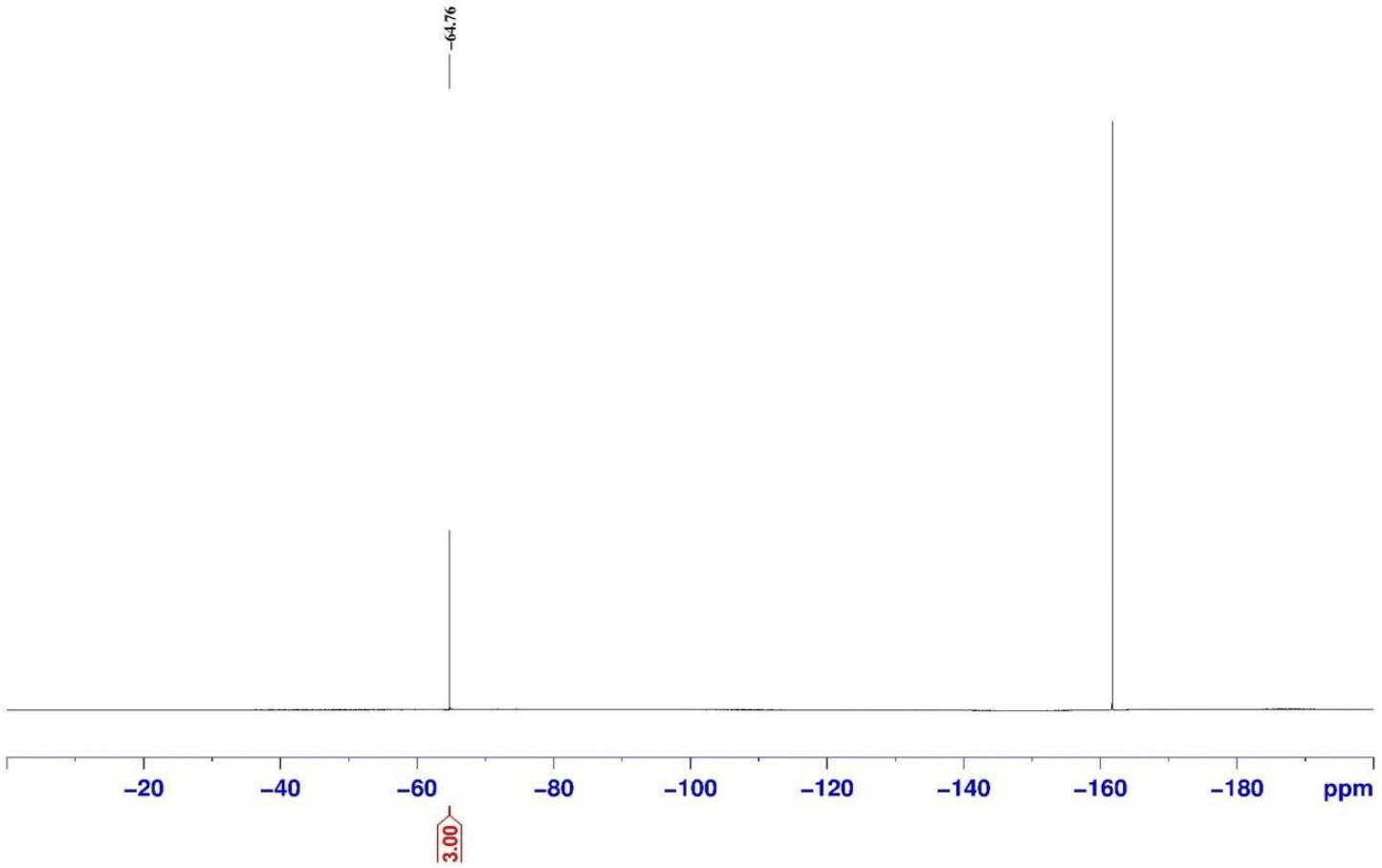
**4–(3–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)morpholine**
**125 MHz, CDCl3**



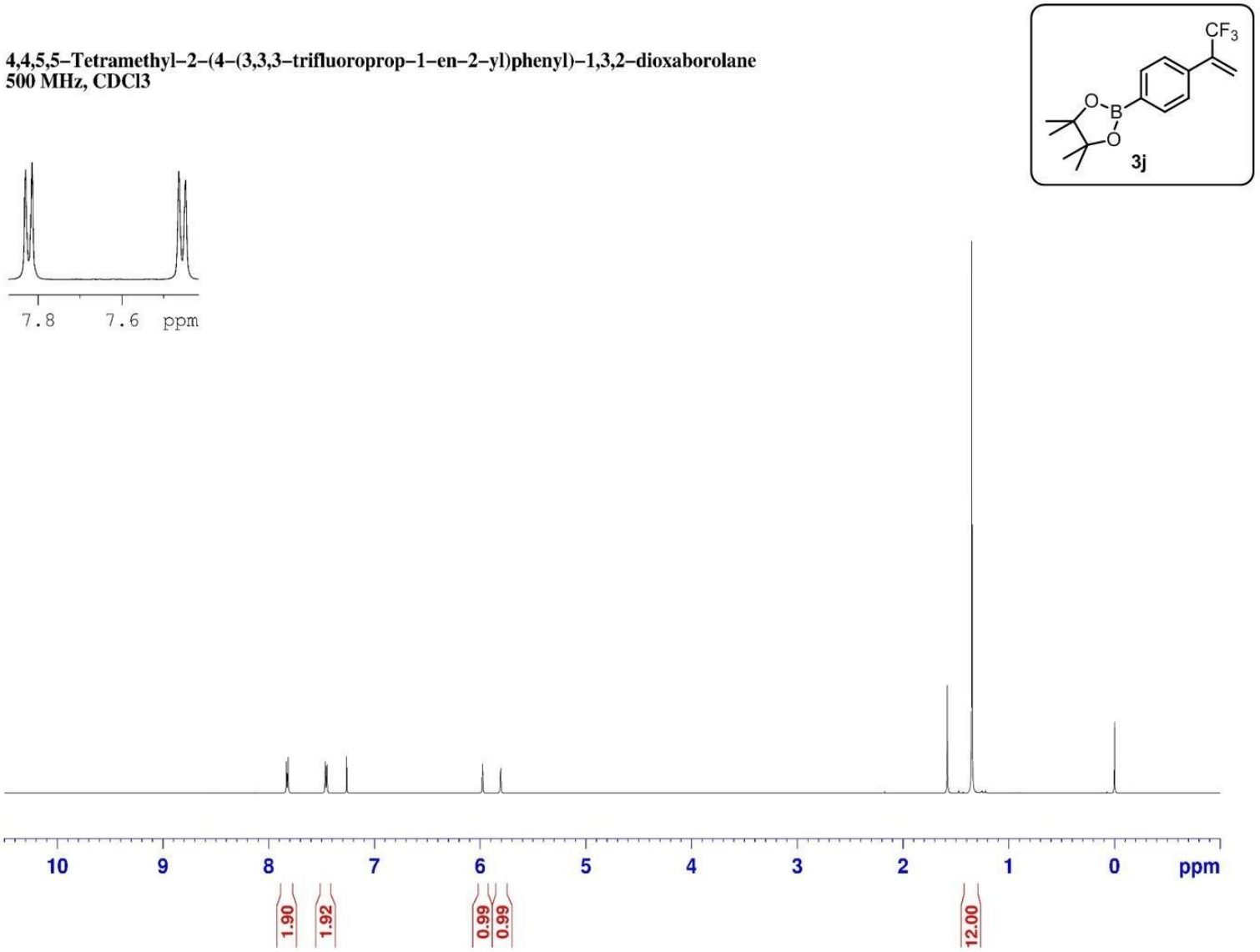



**4–(3–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)morpholine**
**471 MHz, CDCl3**

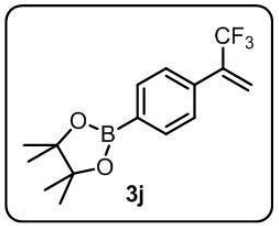


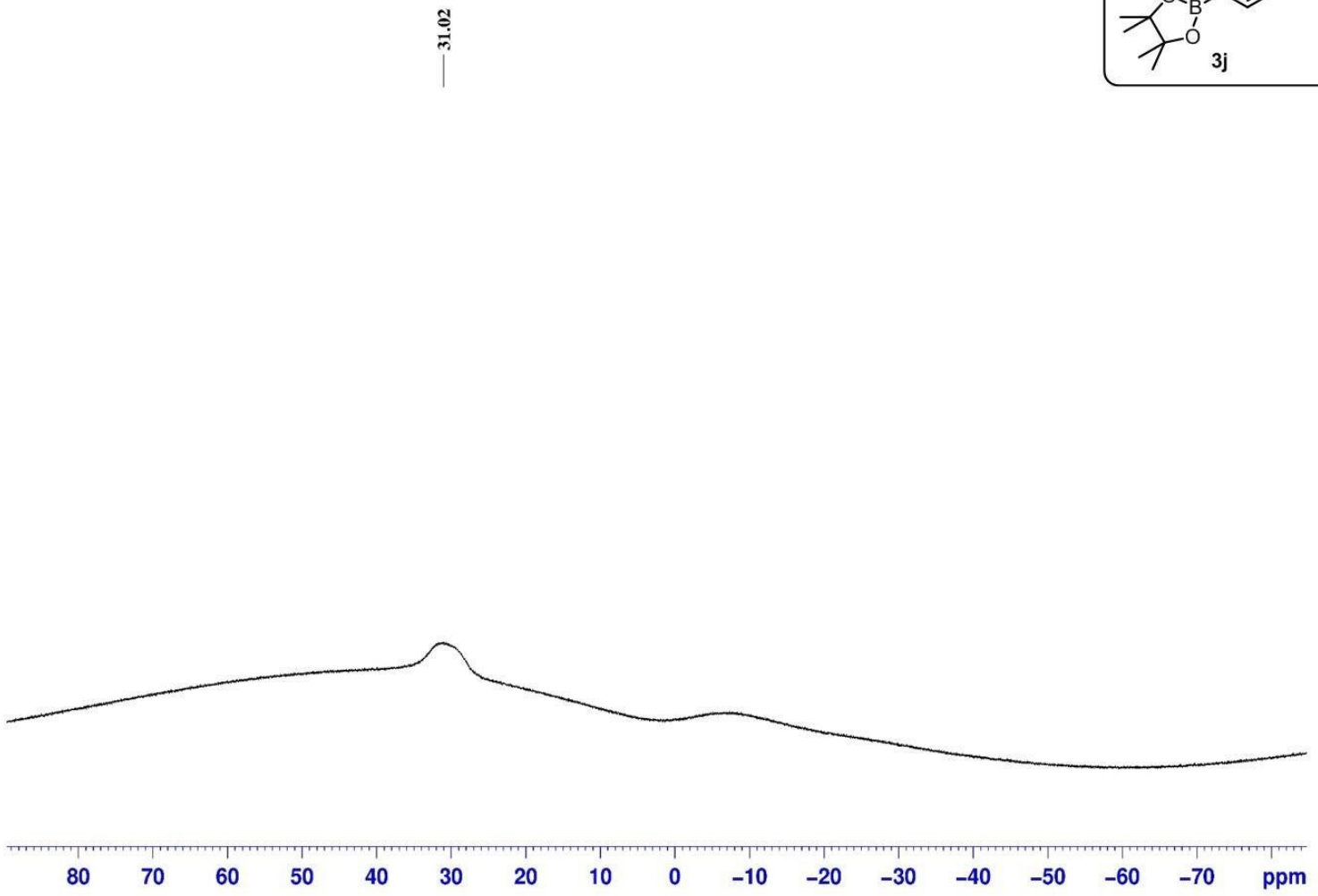



**4,4,5,5–Tetramethyl–2–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)–1,3,2–dioxaborolane**
**500 MHz, CDCl3**

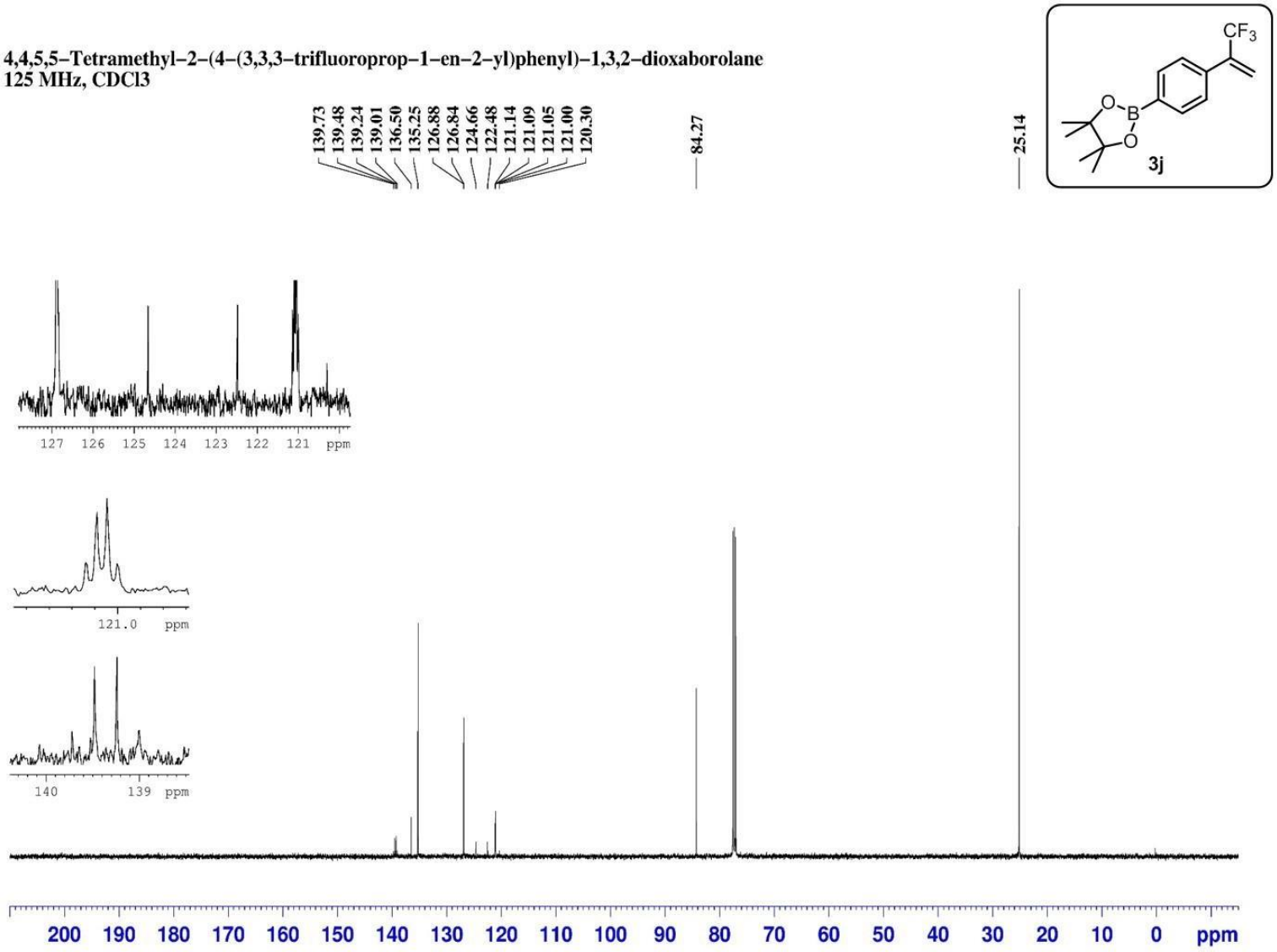


**4,4,5,5–Tetramethyl–2–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)–1,3,2–dioxaborolane**
**128 MHz, acetone–d6**

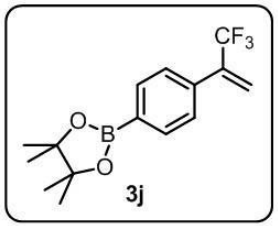


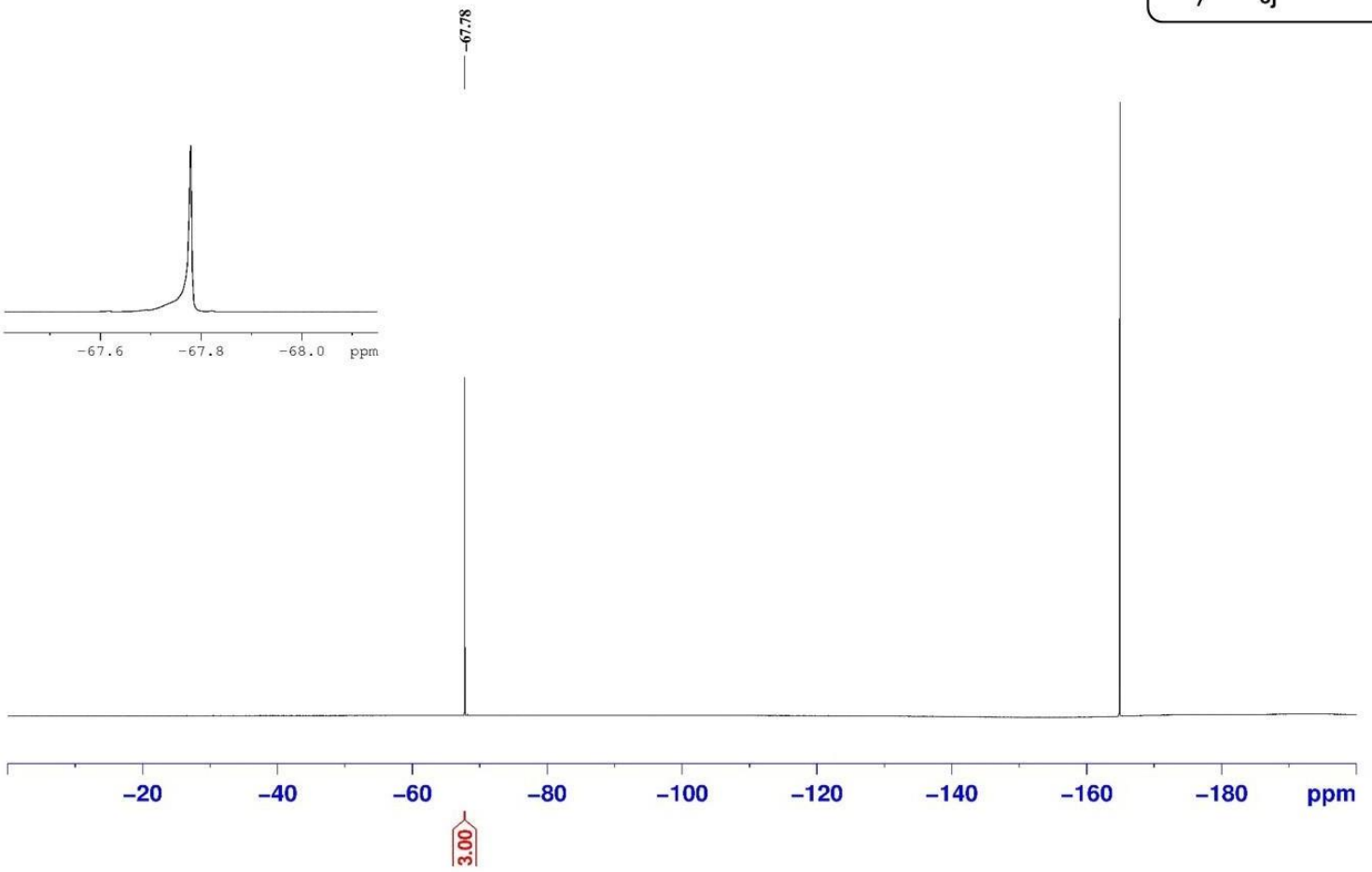



**4,4,5,5–Tetramethyl–2–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)–1,3,2–dioxaborolane**
**125 MHz, CDCl3**

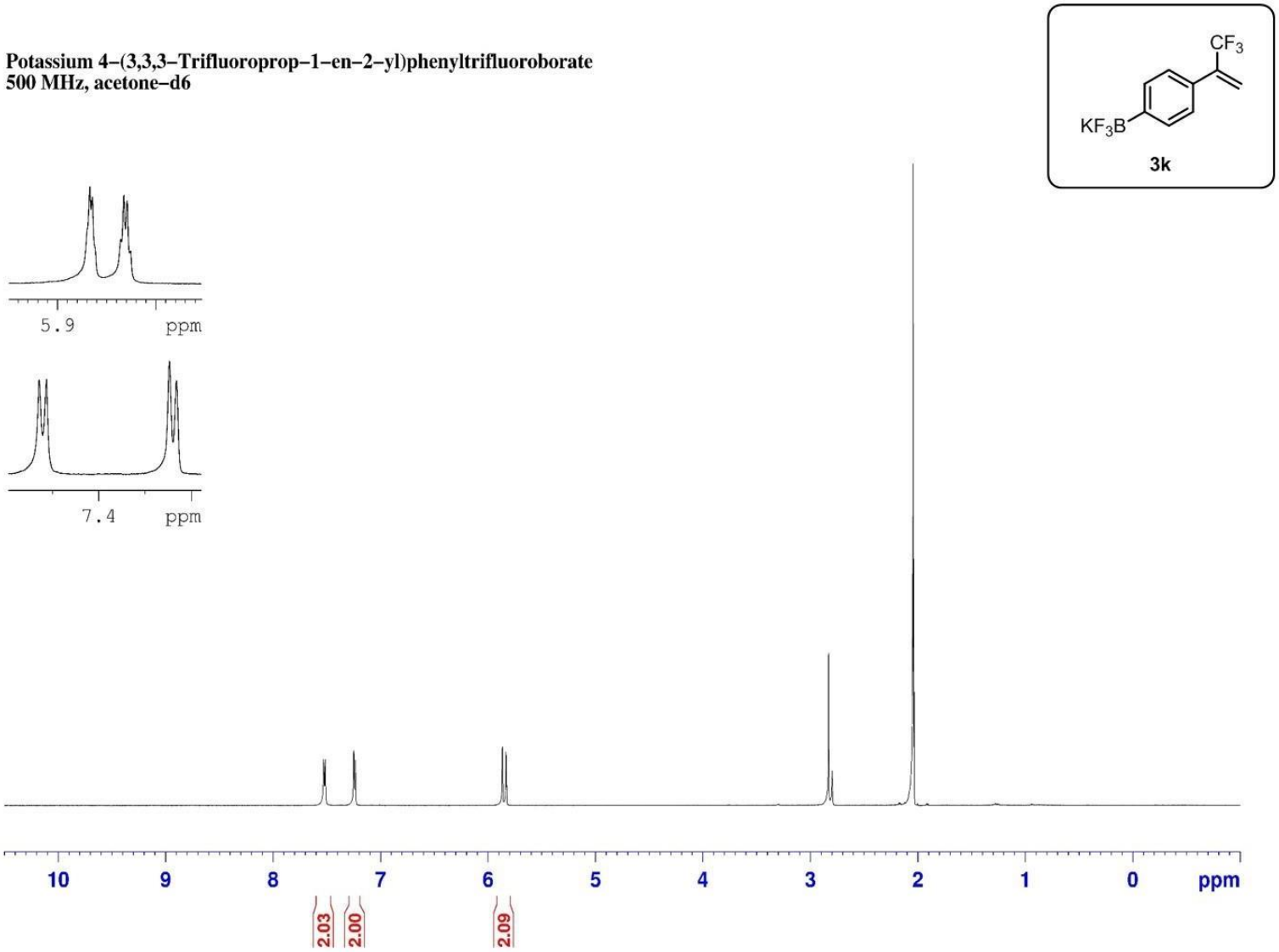


**4,4,5,5–tetramethyl–2–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)–1,3,2–dioxaborolane**
**CDCl3, 471 MHz**

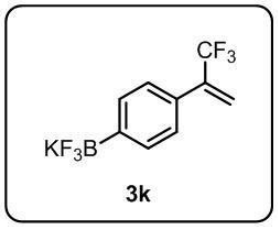


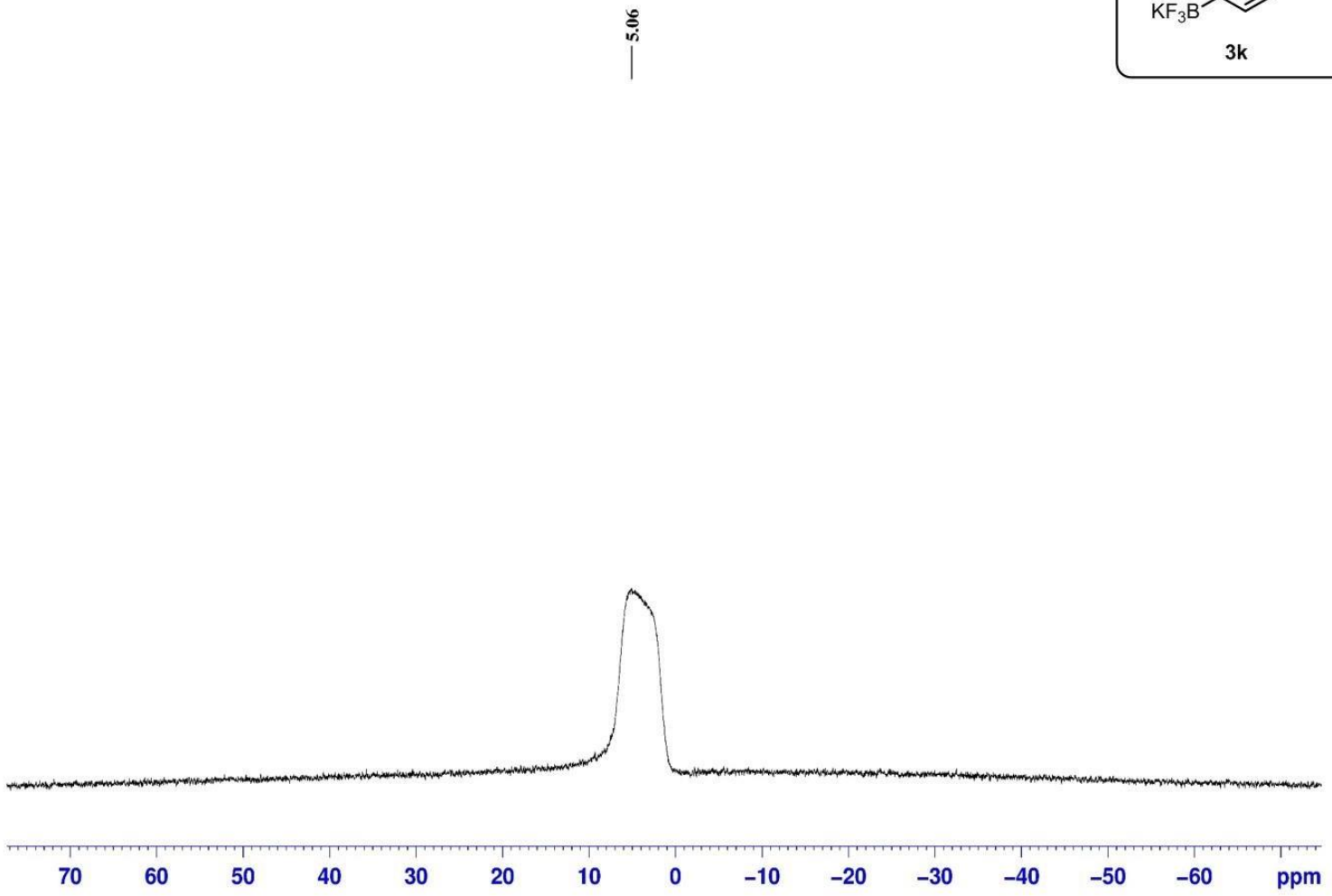



**Potassium 4–(3,3,3–Trifluoroprop–1–en–2–yl)phenyltrifluoroborate**
**500 MHz, acetone–d6**

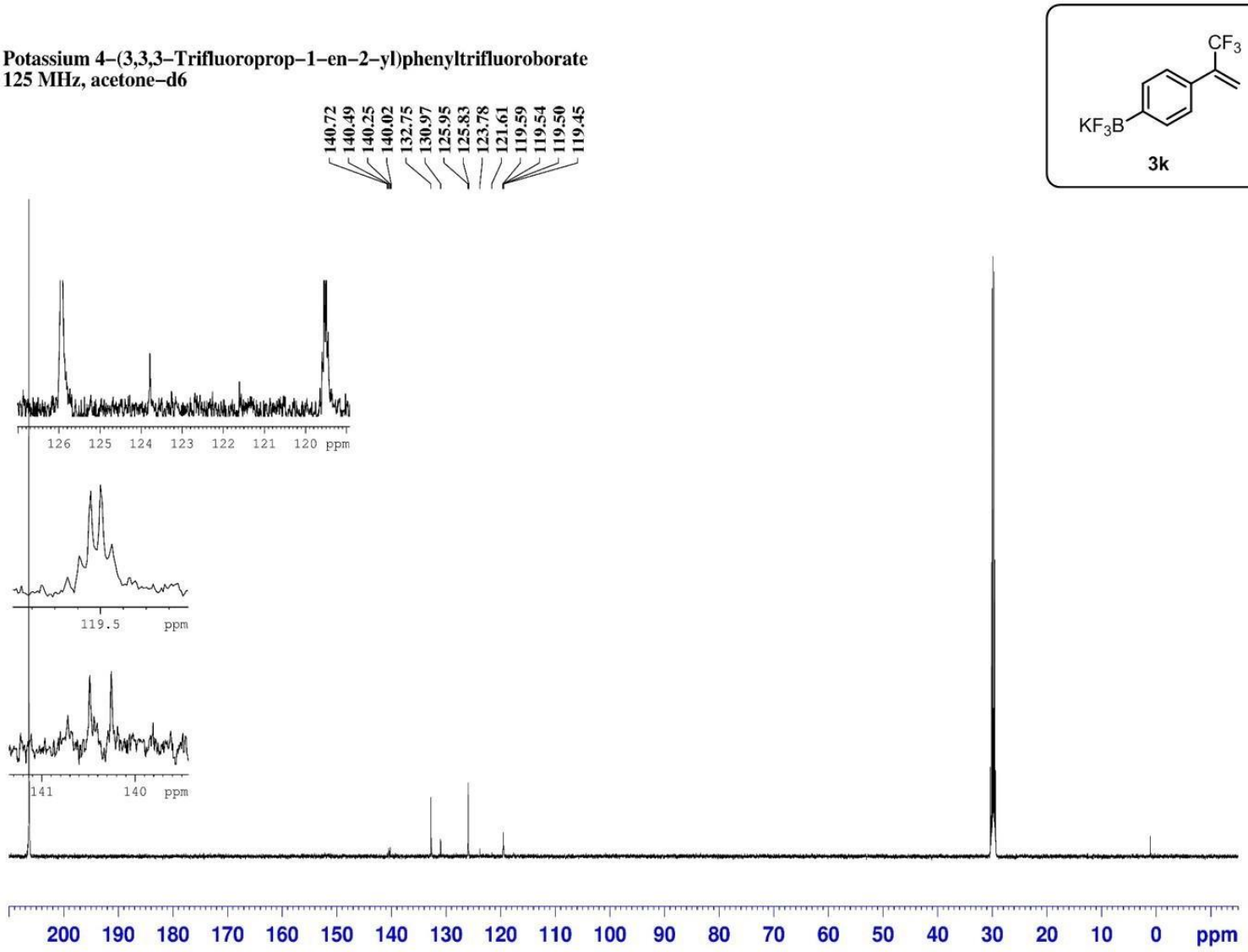


**Potassium 4–(3,3,3–Trifluoroprop–1–en–2–yl)phenyltrifluoroborate**
**11B NMR ECHO**

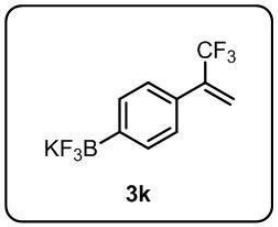


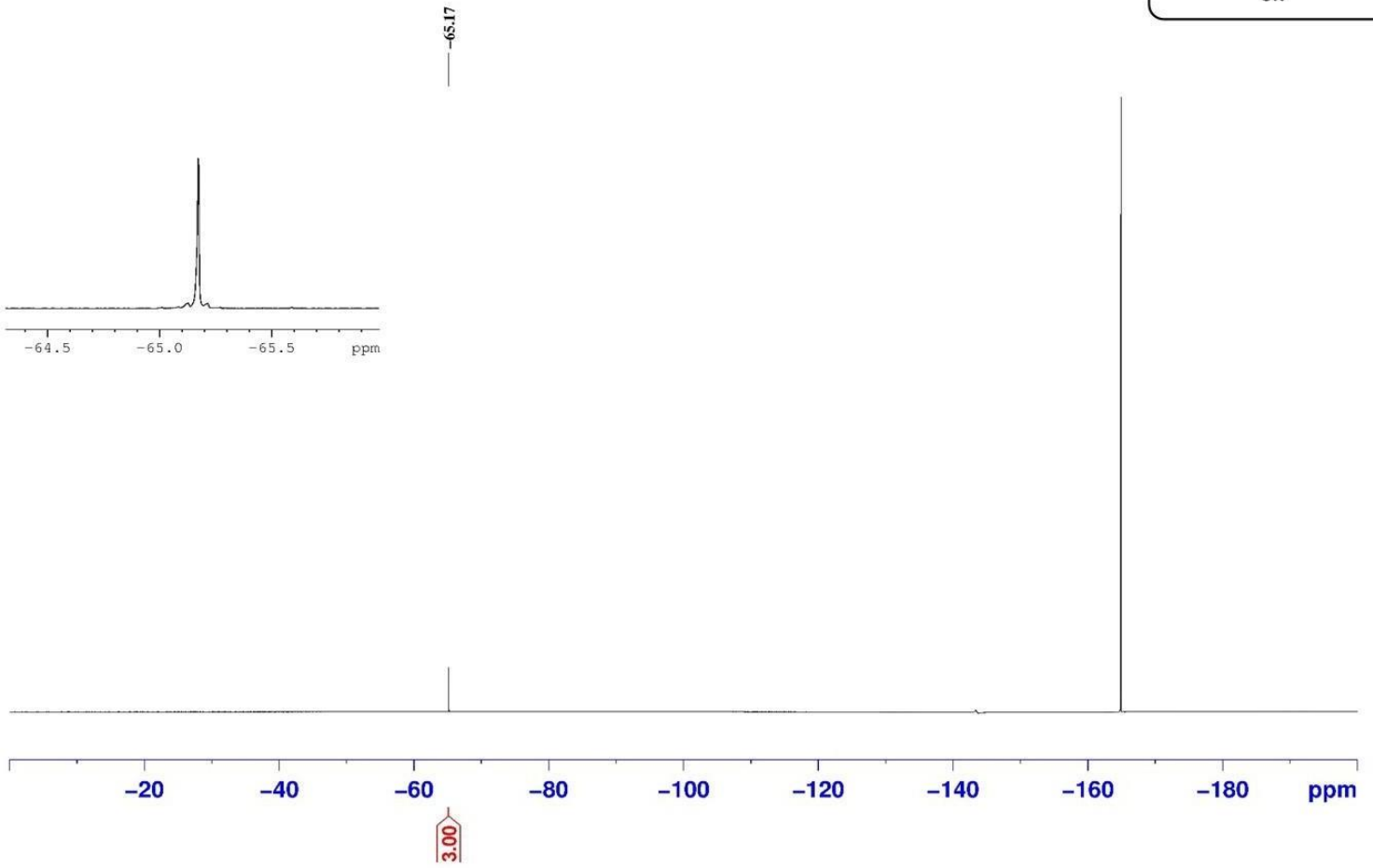
**Potassium 4–(3,3,3–Trifluoroprop–1–en–2–yl)phenyltrifluoroborate**
**125 MHz, acetone–d6**



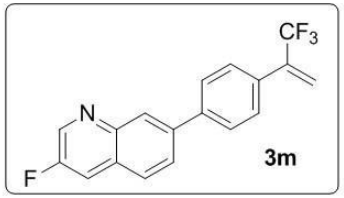
**Potassium 4–(3,3,3–trifluoroprop–1–en–2–yl)phenyltrifluoroborate**
**Acetone–d6, 471 MHz**

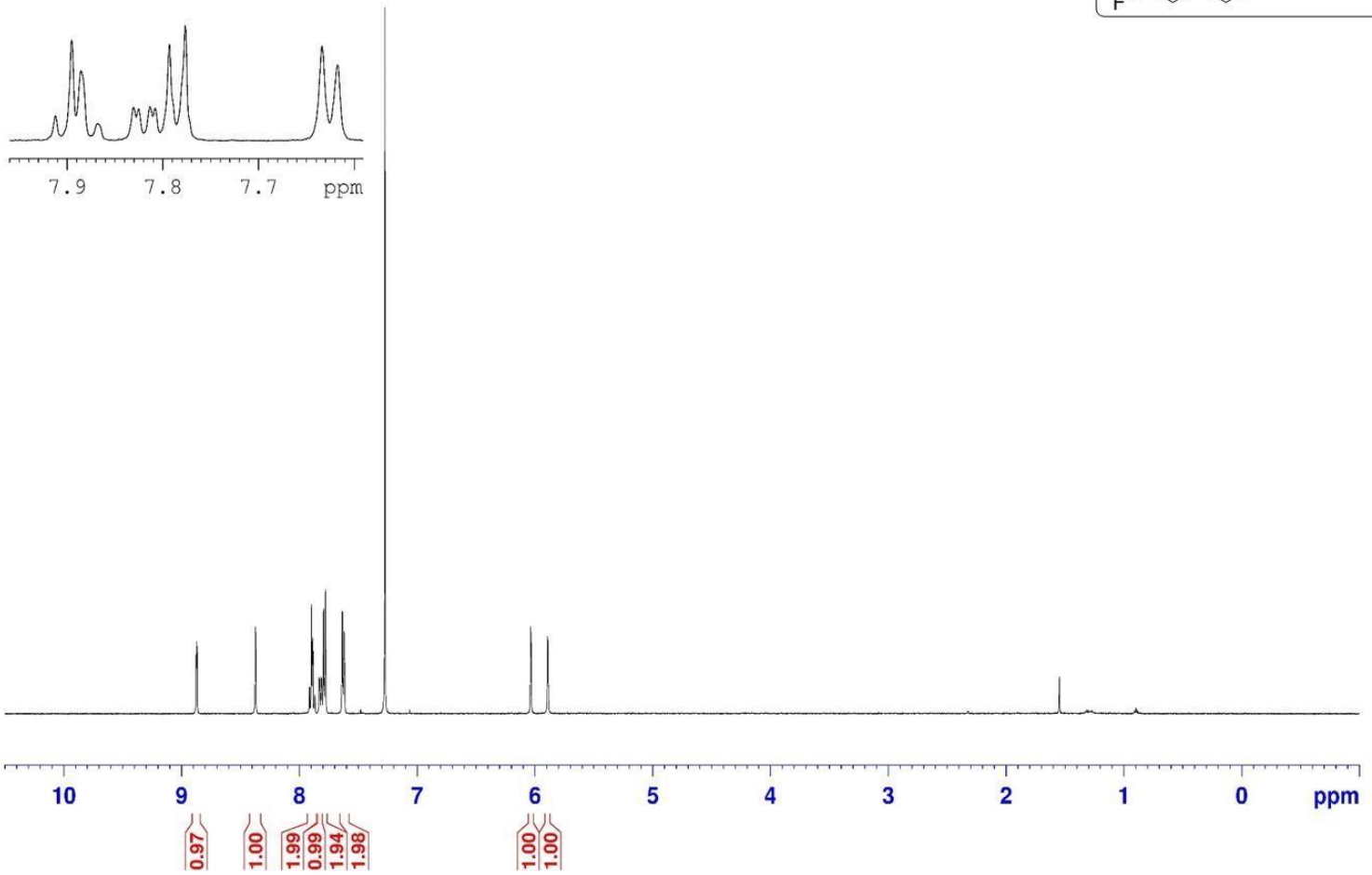



**3k**

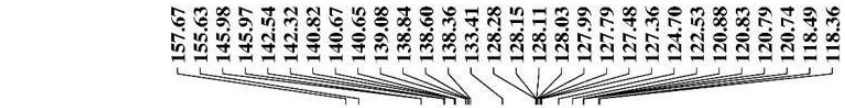


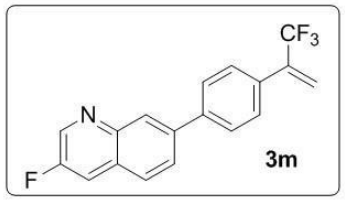
**3–fluoro–7–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)quinoline**
**500 MHz, CDCl3**

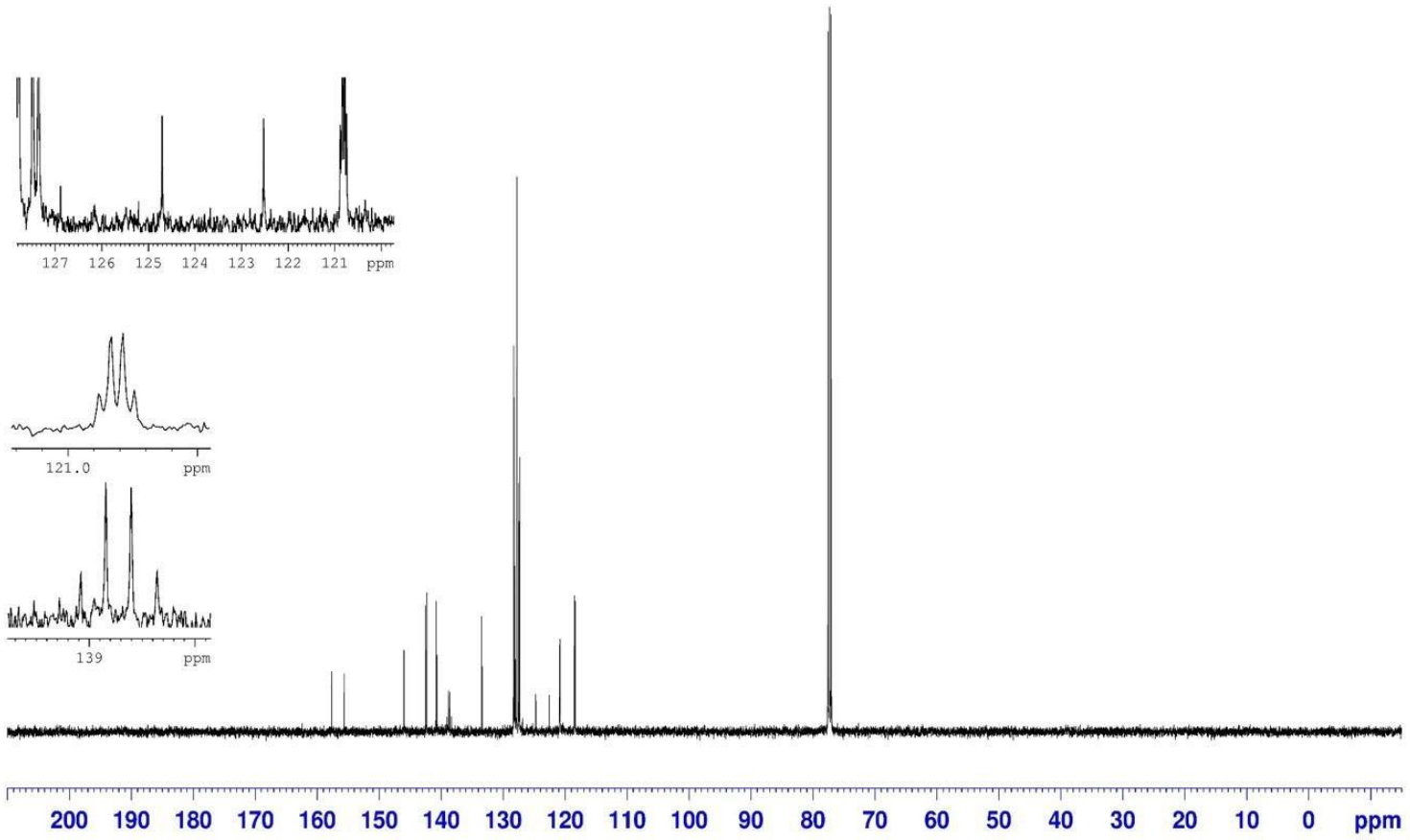


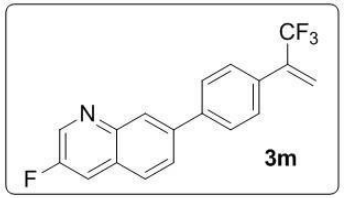
**3–fluoro–7–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)quinoline**
**125 MHz, CDCl3**

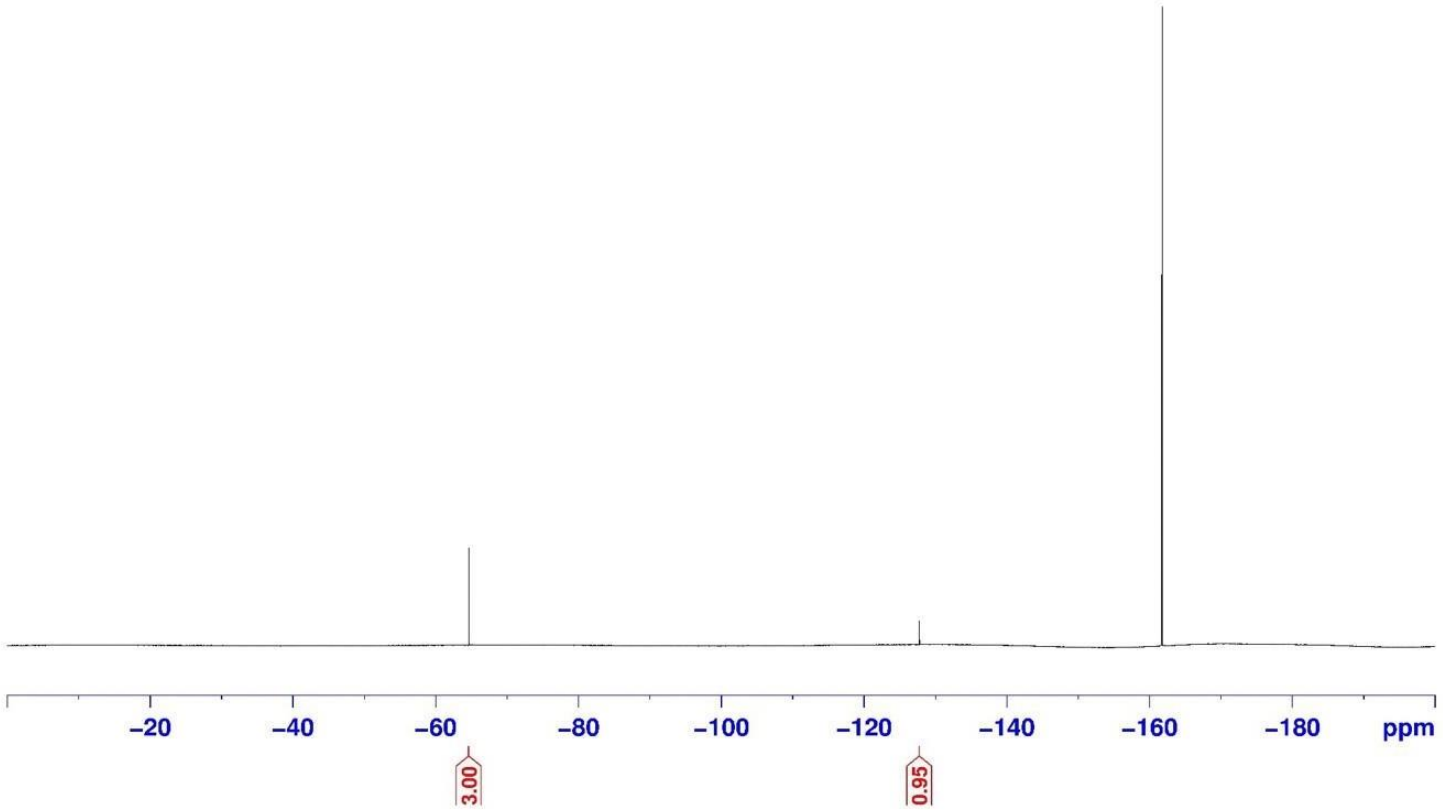


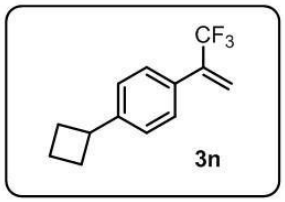



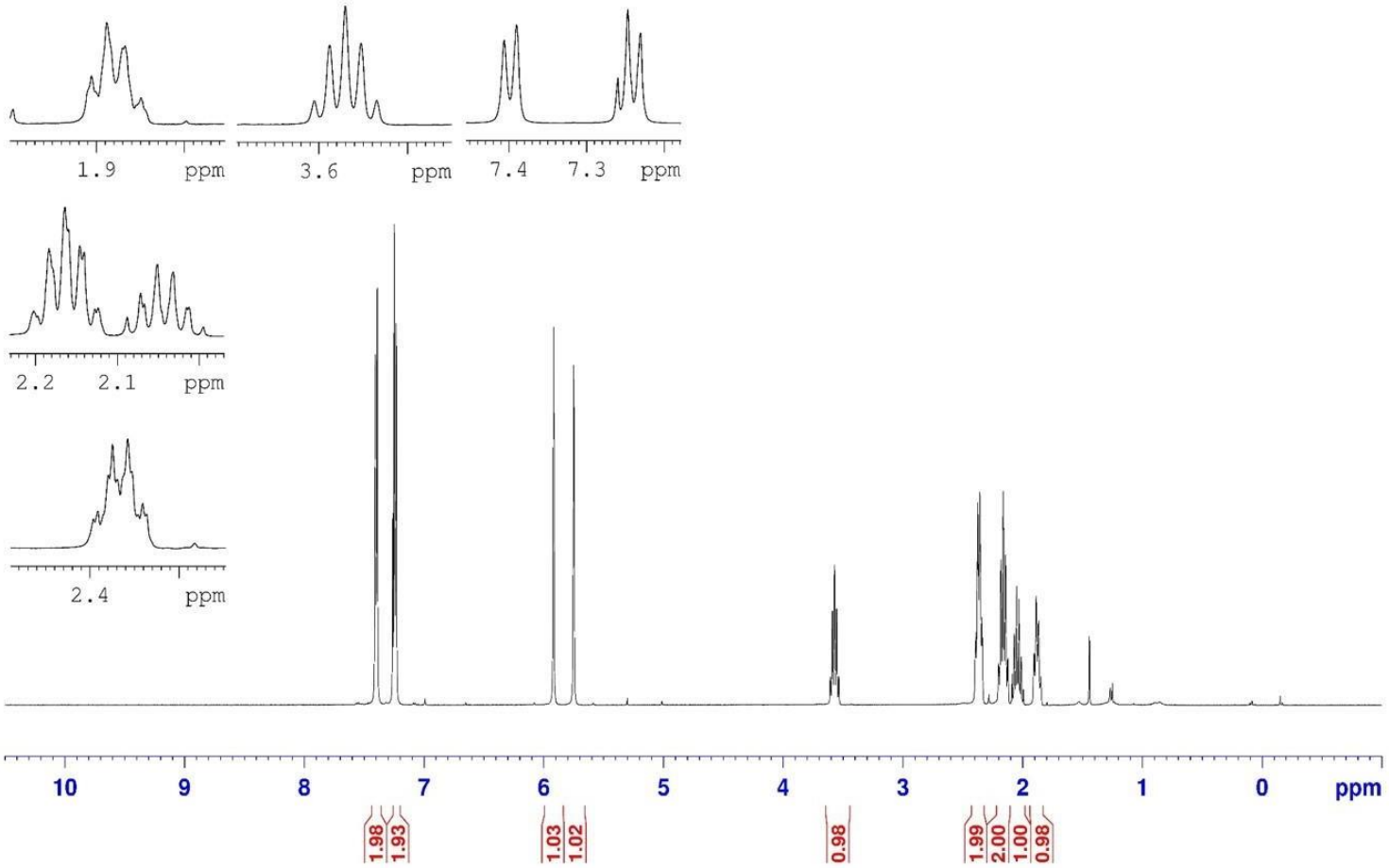
**3–fluoro–7–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)quinoline**
**471 MHz, CDCl3**



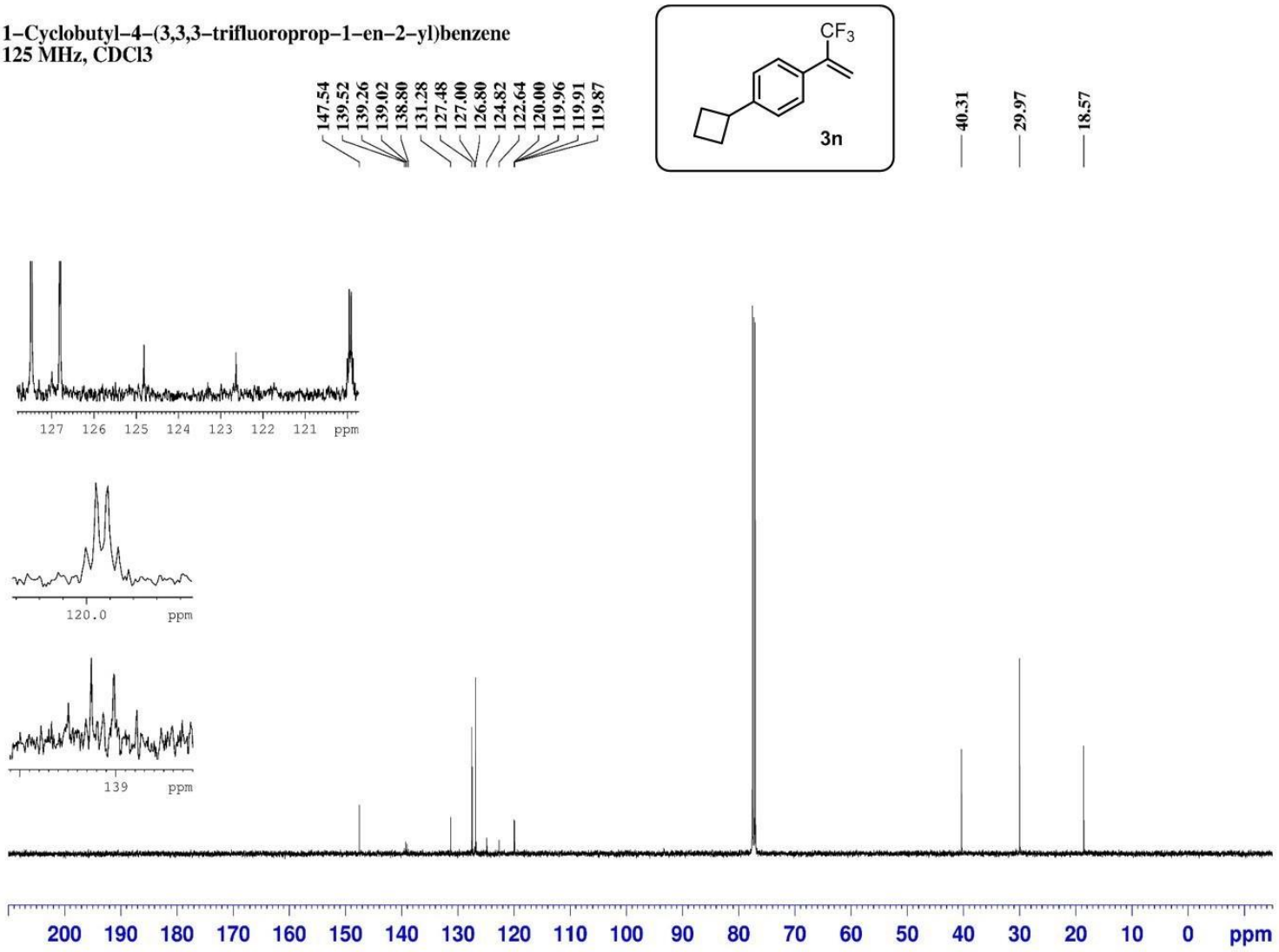



**1–Cyclobutyl–4–(3,3,3–trifluoroprop–1–en–2–yl)benzene**
**500 MHz, CDCl3**

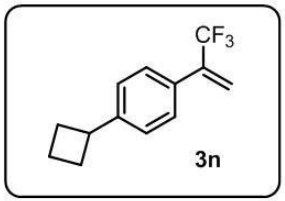


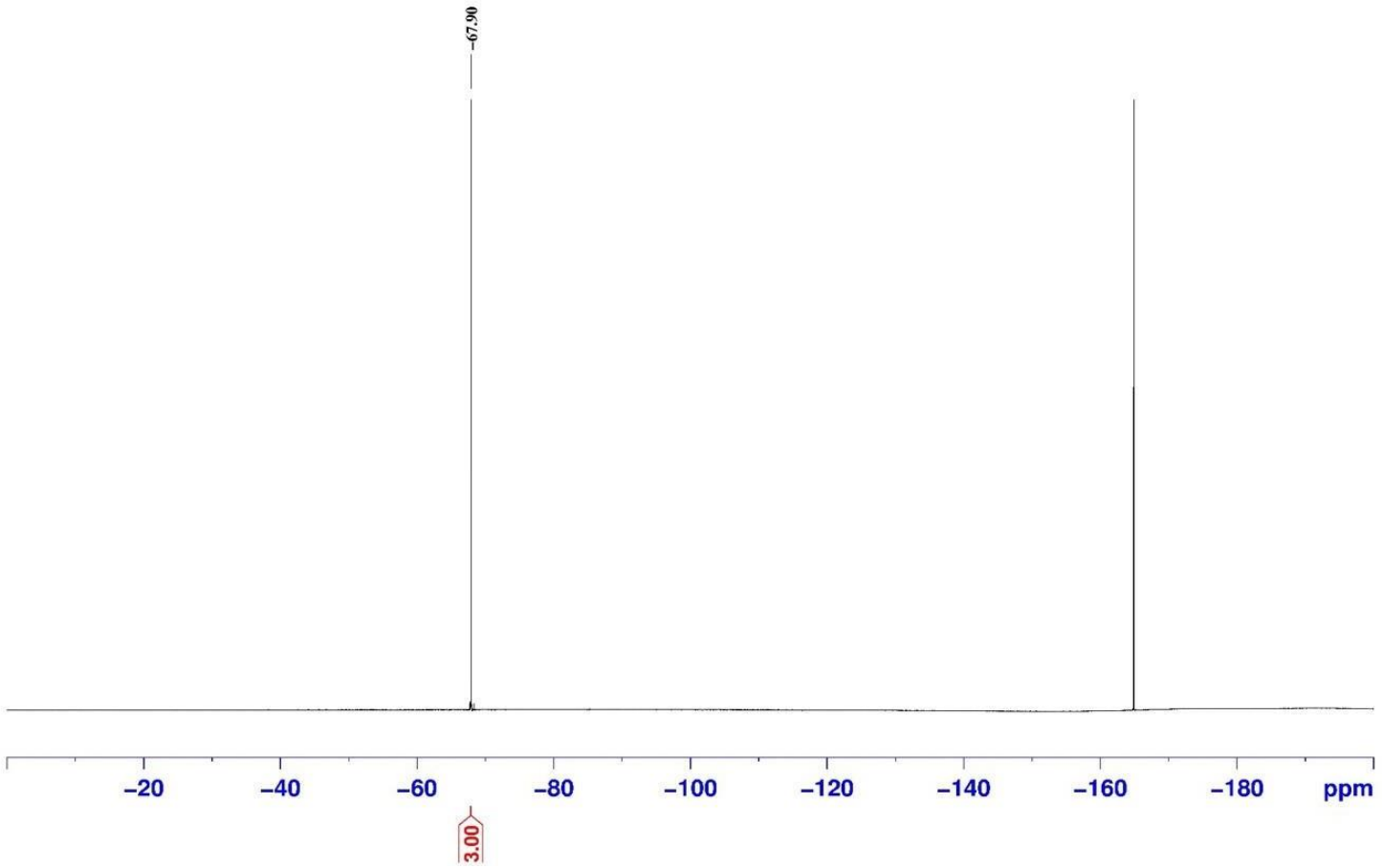



**1–Cyclobutyl–4–(3,3,3–trifluoroprop–1–en–2–yl)benzene**
**125 MHz, CDCl3**

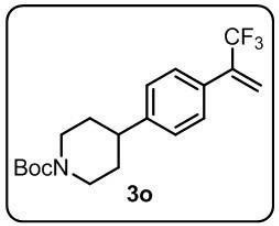


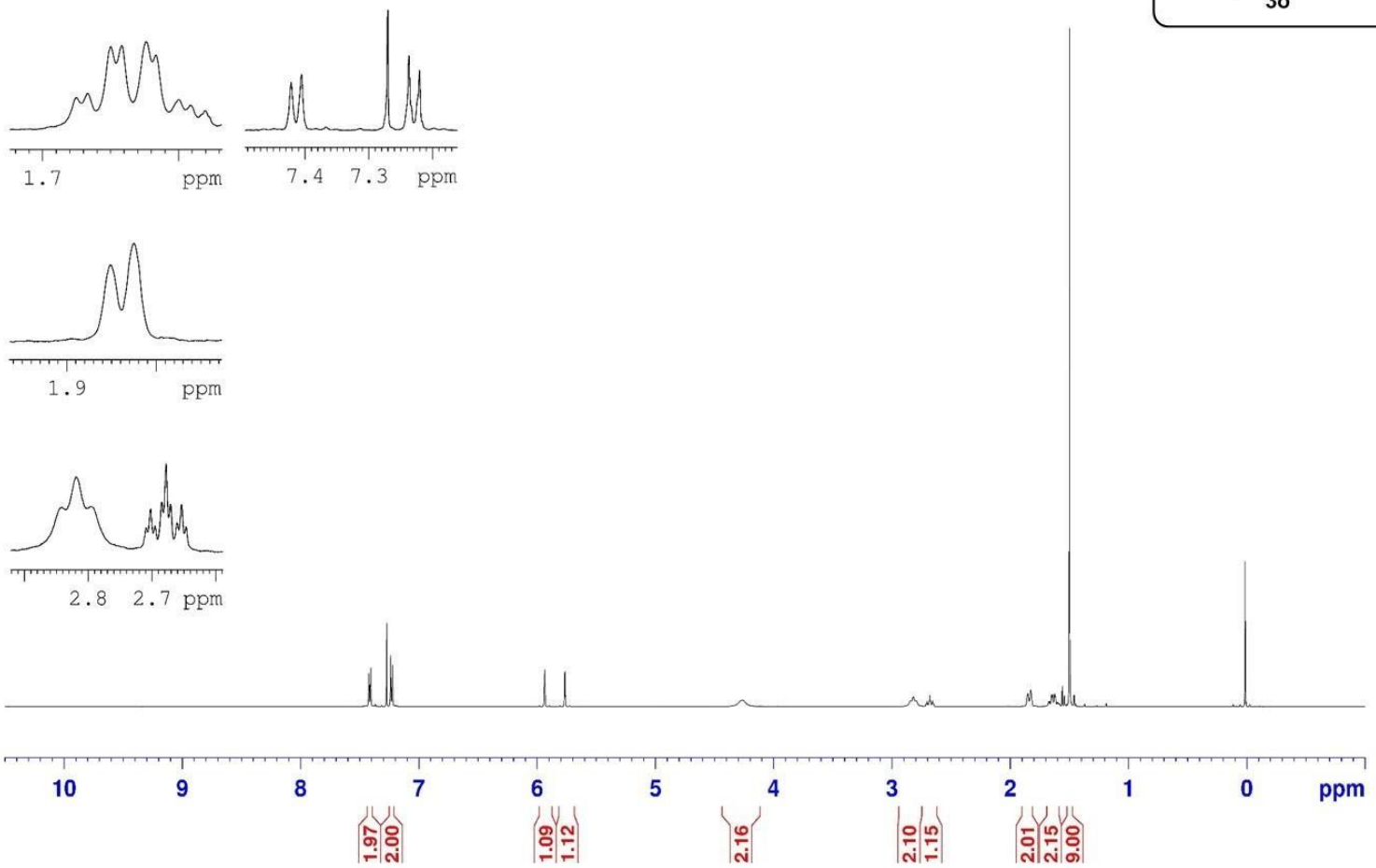
**1–Cyclobutyl–4–(3,3,3–trifluoroprop–1–en–2–yl)benzene**
**471 MHz, CDCl3**



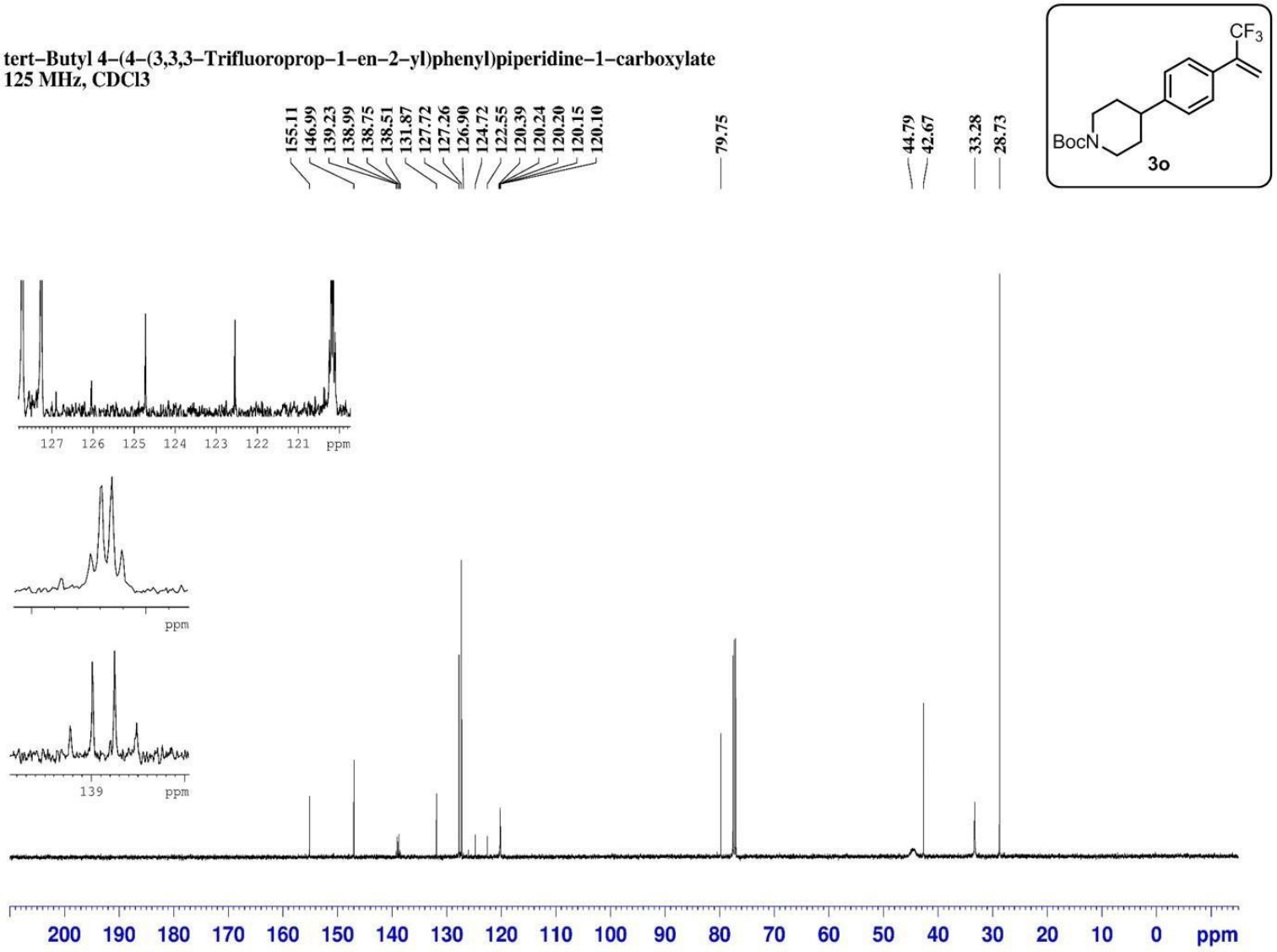



**tert–Butyl 4–(4–(3,3,3–Trifluoroprop–1–en–2–yl)phenyl)piperidine–1–carboxylate**
**500 MHz, CDCl3**

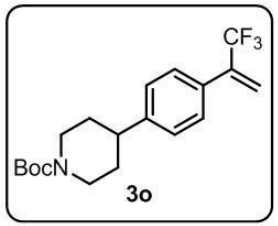


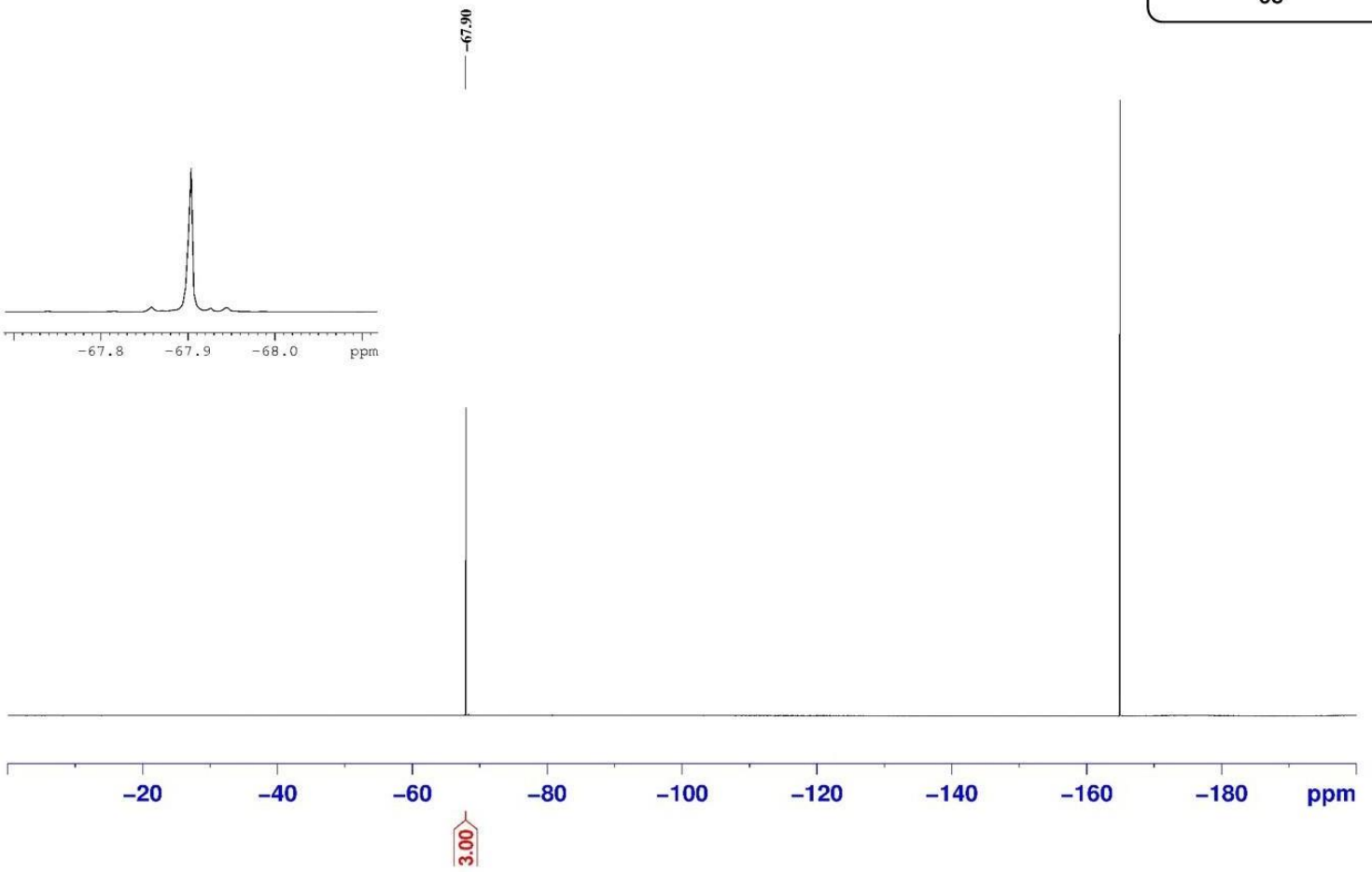



**tert–Butyl 4–(4–(3,3,3–Trifluoroprop–1–en–2–yl)phenyl)piperidine–1–carboxylate**
**125 MHz, CDCl3**

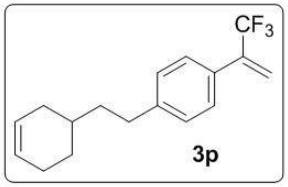


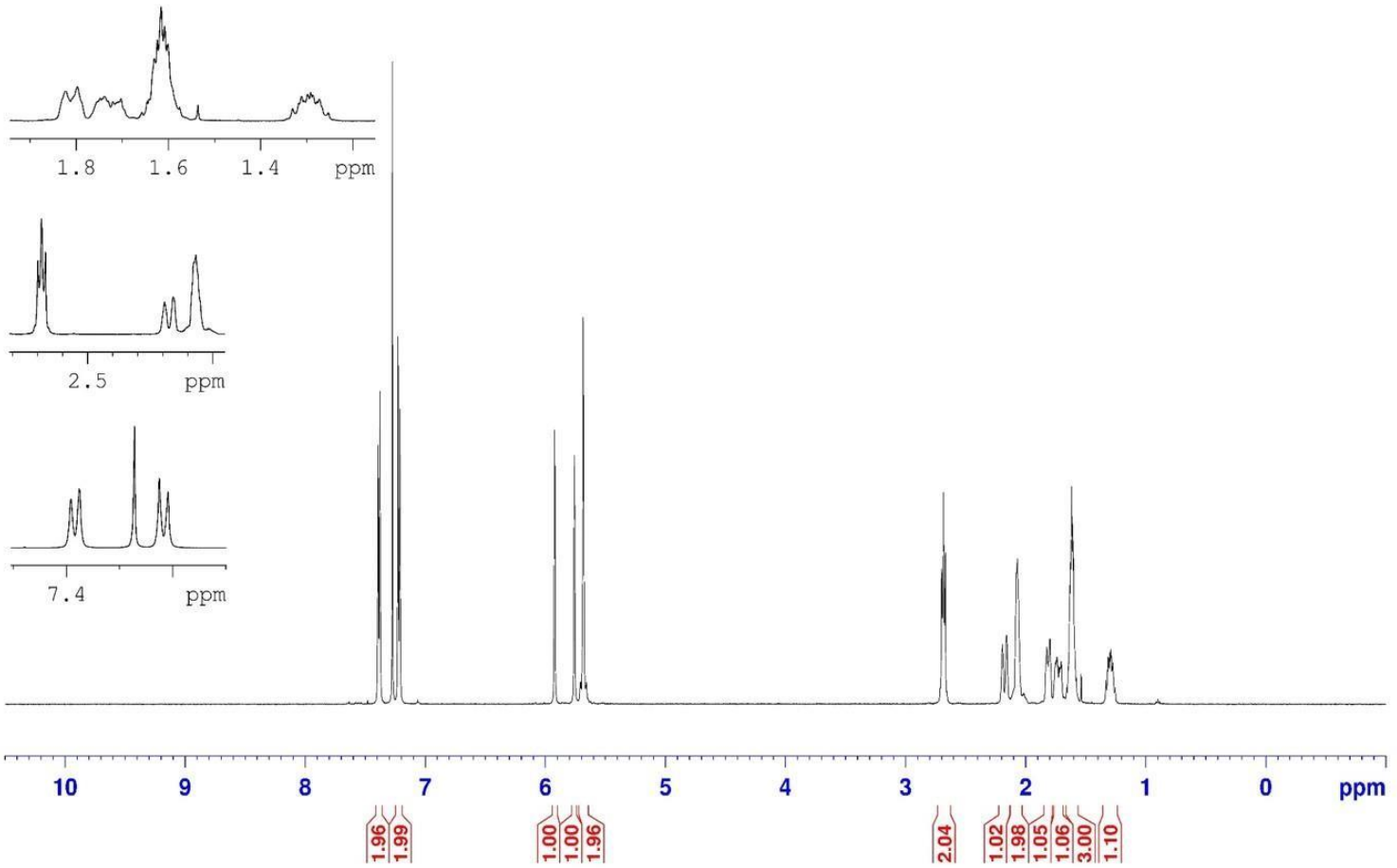
**tert–butyl 4–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)piperidine–1–carboxylate**
**CDCl3, 471 MHz**



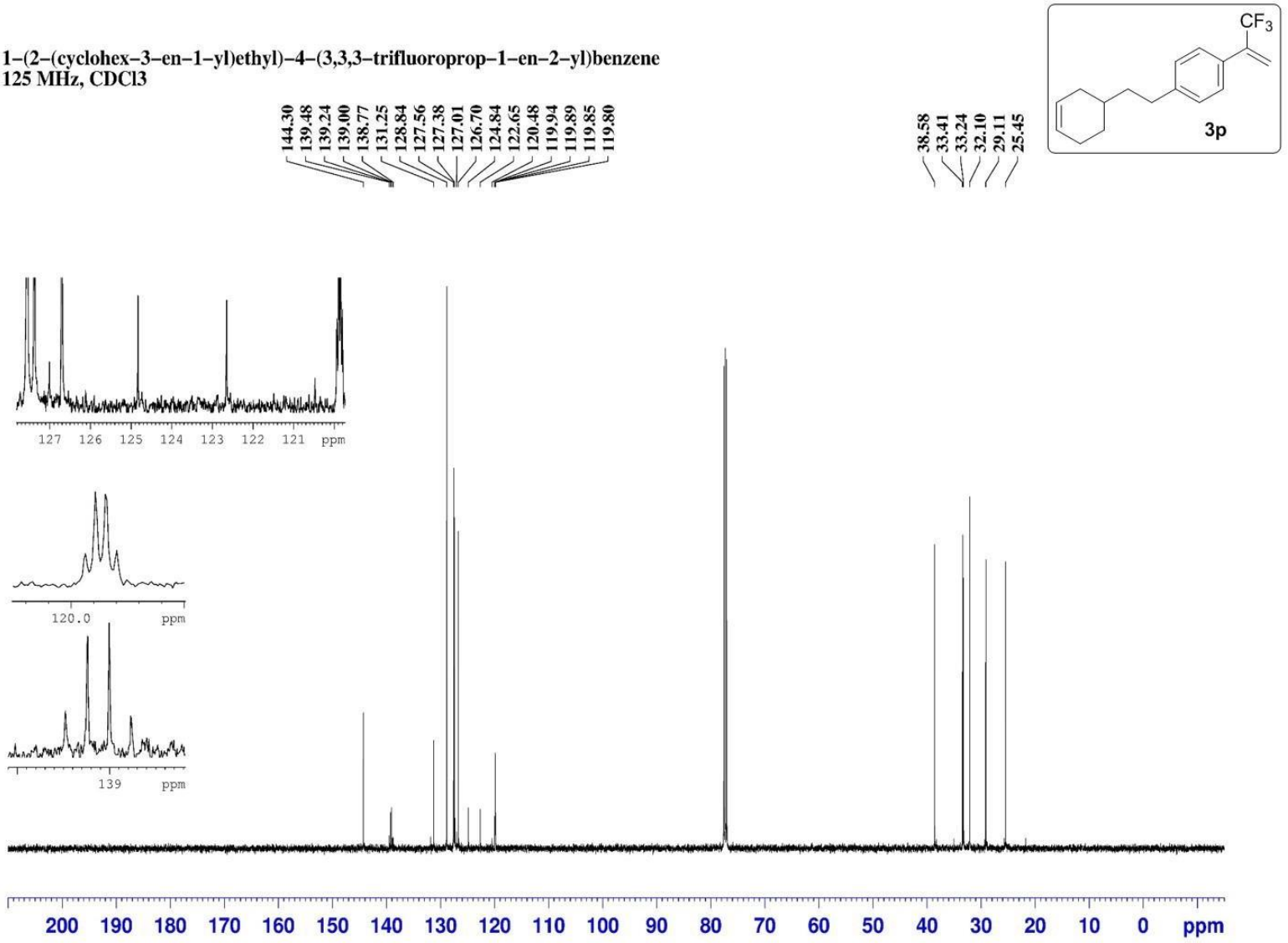



**1–(2–(cyclohex–3–en–1–yl)ethyl)–4–(3,3,3–trifluoroprop–1–en–2–yl)benzene**
**500 MHz, CDCl3**

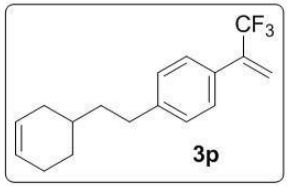


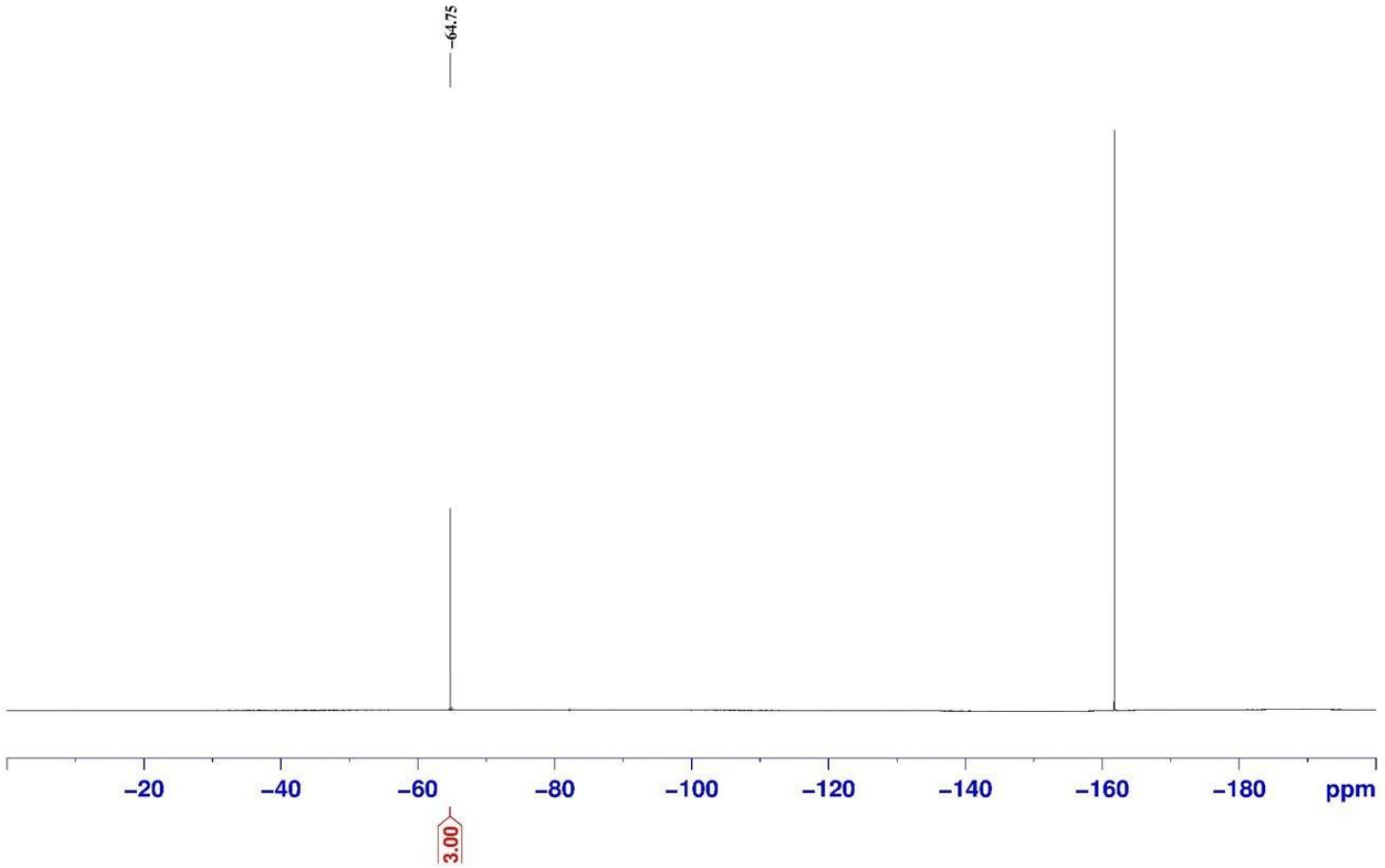



**1–(2–(cyclohex–3–en–1–yl)ethyl)–4–(3,3,3–trifluoroprop–1–en–2–yl)benzene**
**125 MHz, CDCl3**

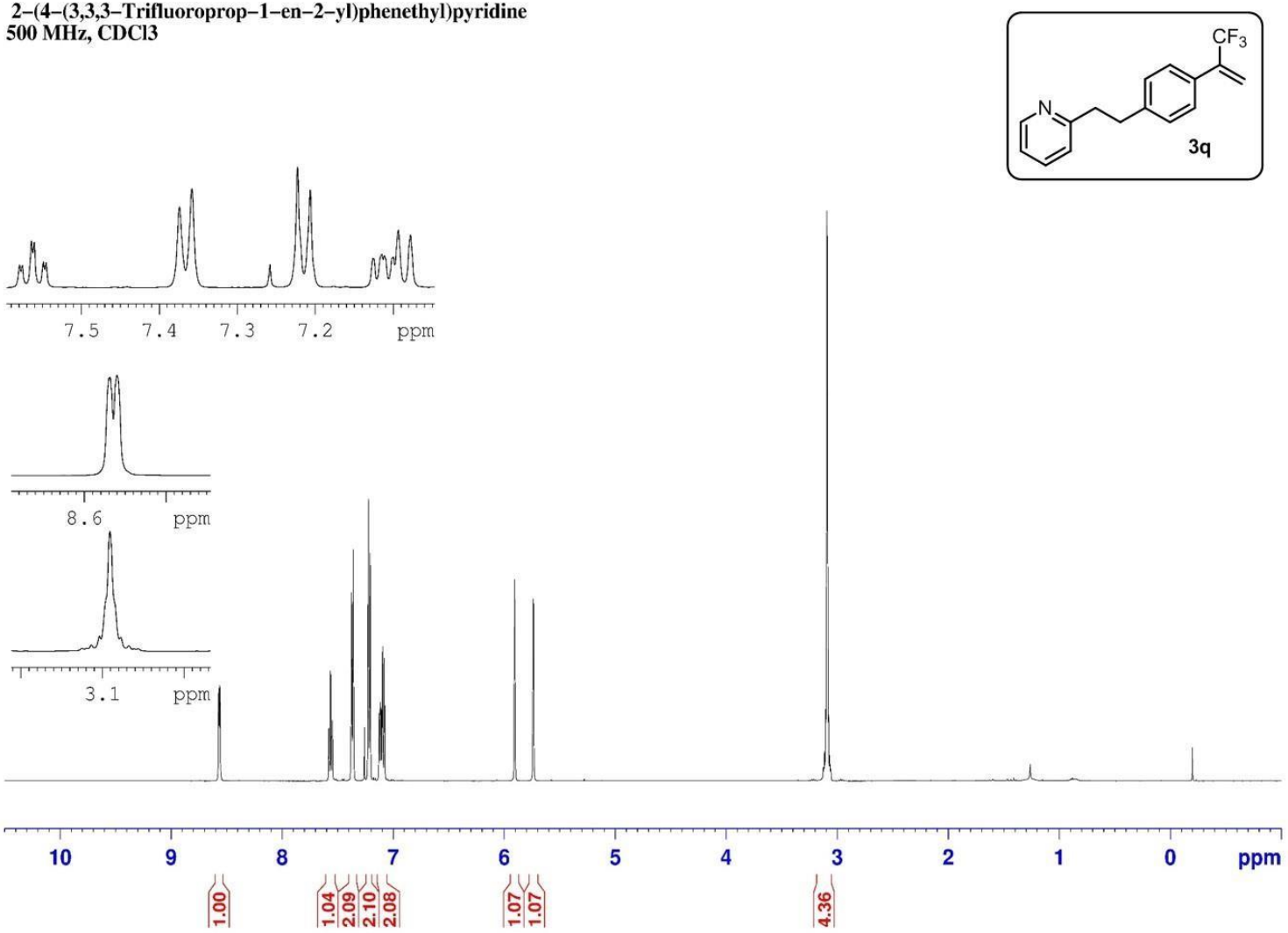


**1-(2-(cyclohex-3-en-1-yl)ethyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene**
**471 MHz, CDCl3**

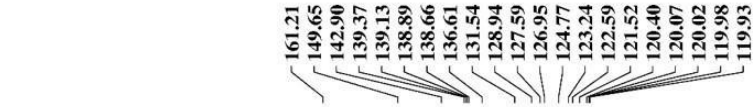


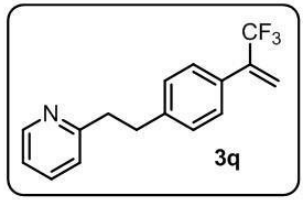



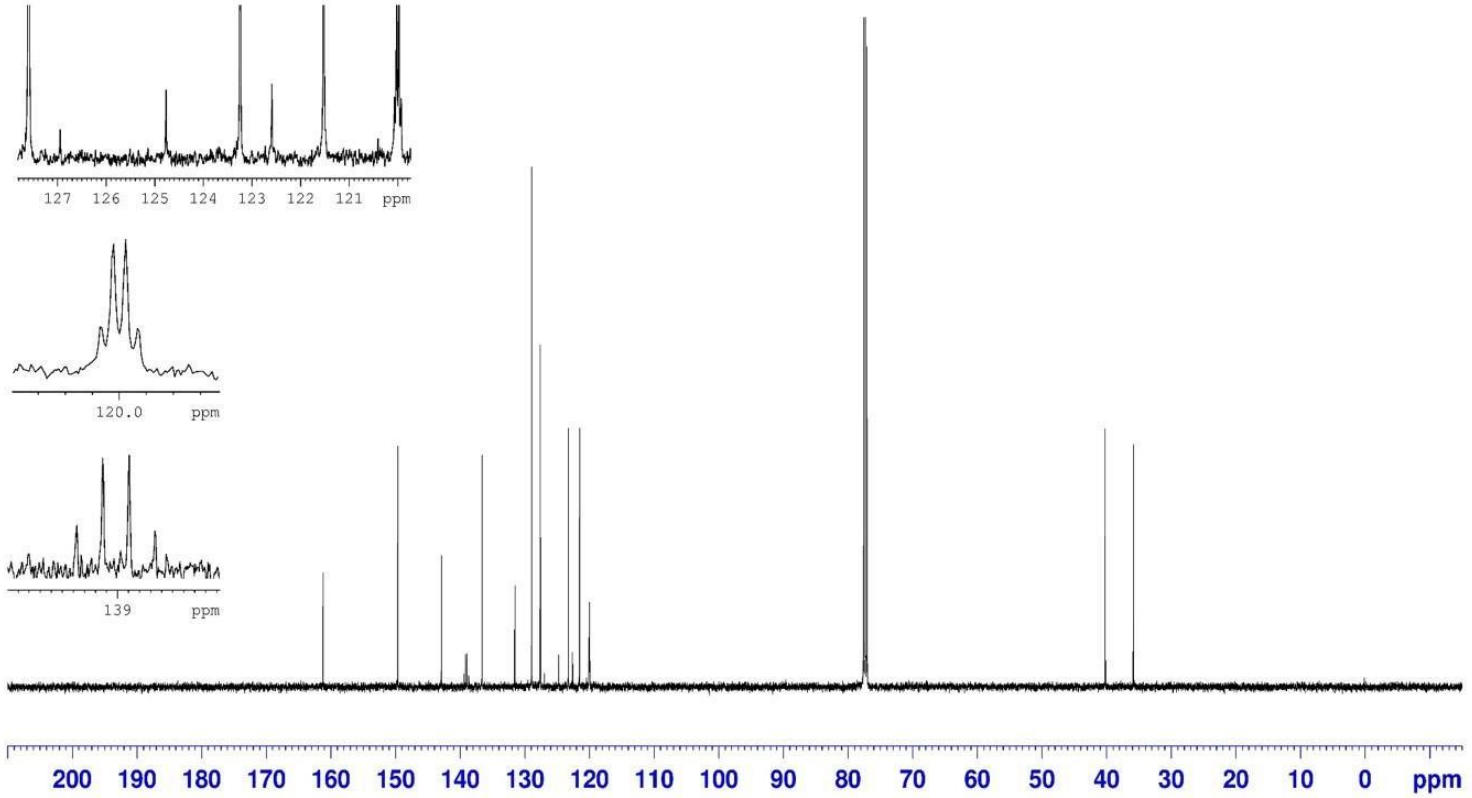
**2–(4–(3,3,3–Trifluoroprop–1–en–2–yl)phenethyl)pyridine**
**500 MHz, CDCl3**



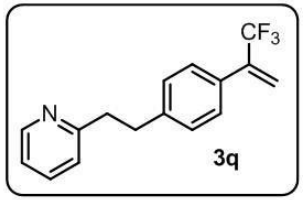
**2-(4-(3,3,3-Trifluoroprop-1-en-2-yl)phenethyl)pyridine**
**125 MHz, CDCl3**

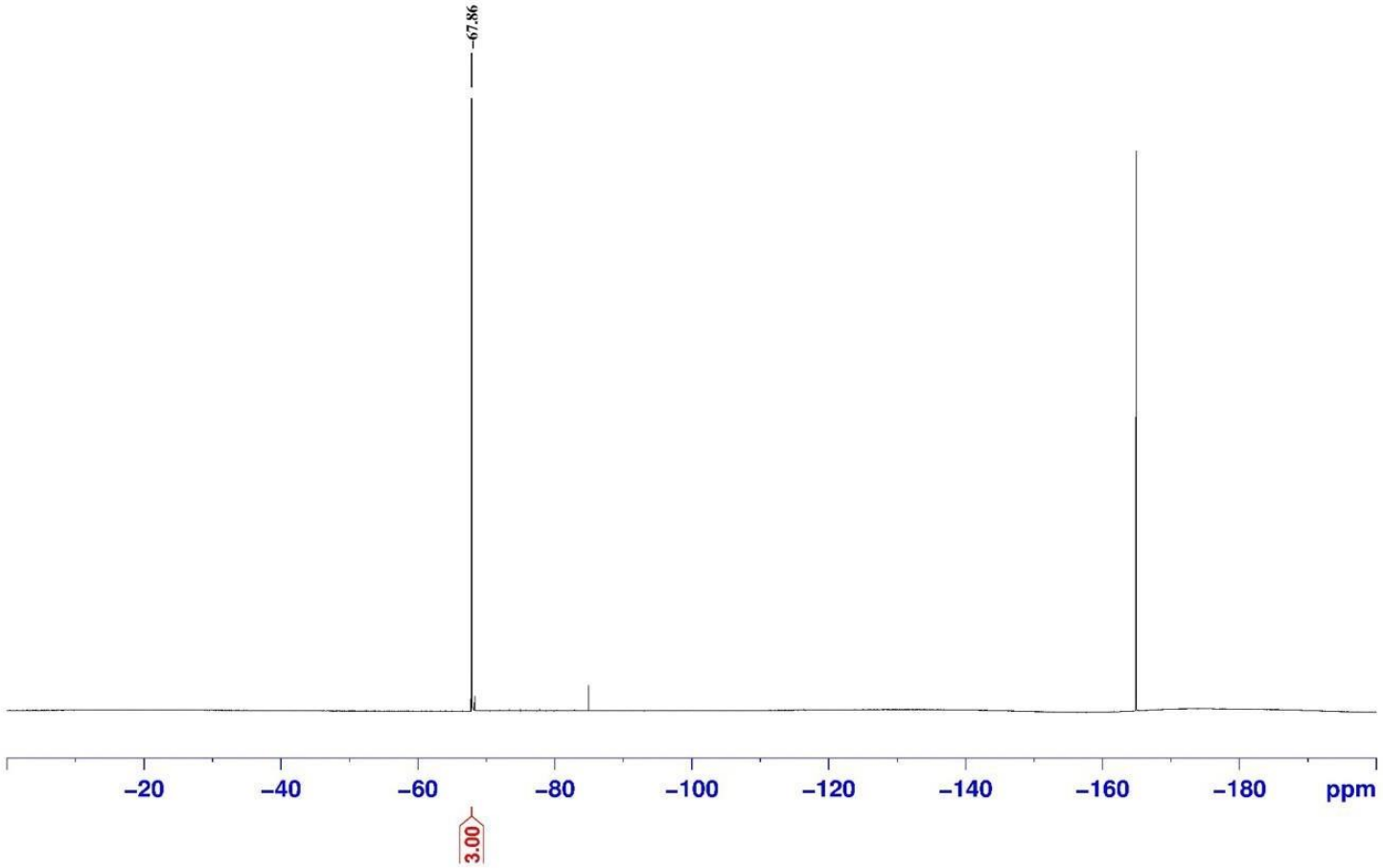


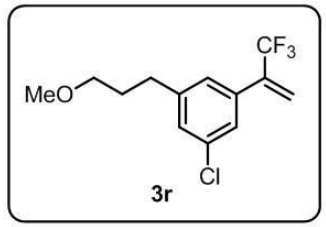



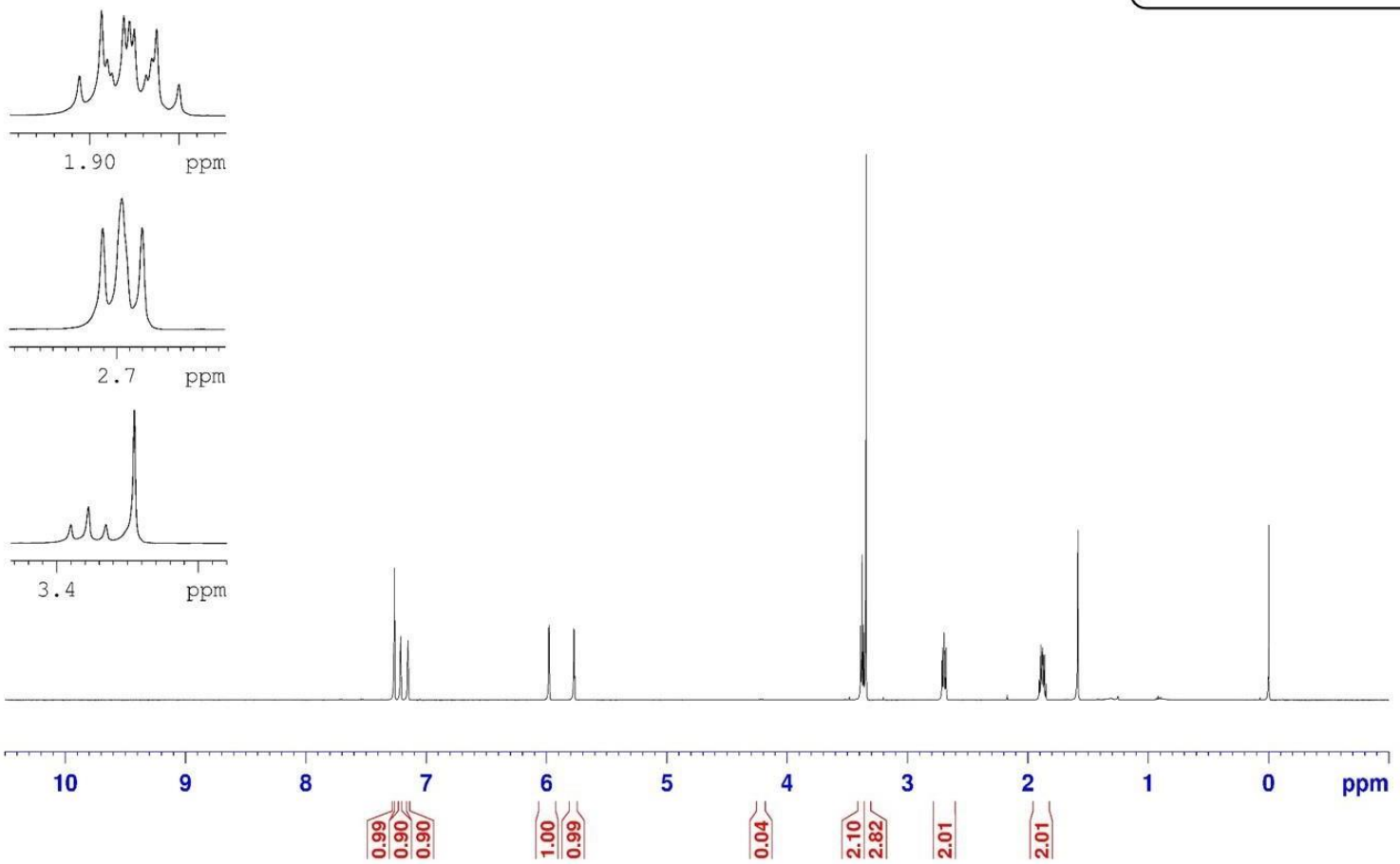
**2–(4–(3,3,3–Trifluoroprop–1–en–2–yl)phenethyl)pyridine**
**471 MHz, CDCl3**



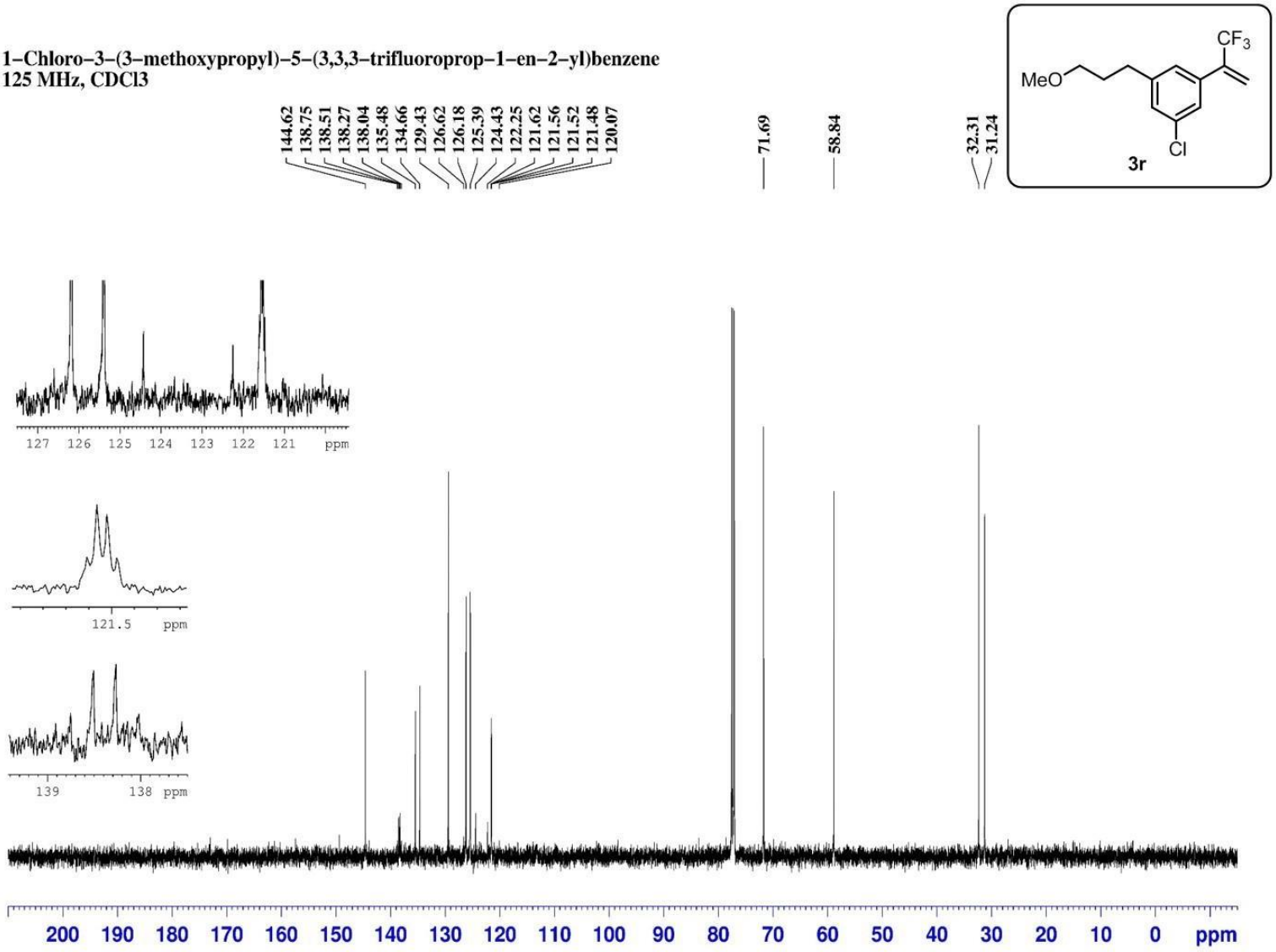



**1–Chloro–3–(3–methoxypropyl)–5–(3,3,3–trifluoroprop–1–en–2–yl)benzene**
**500 MHz, CDCl3**

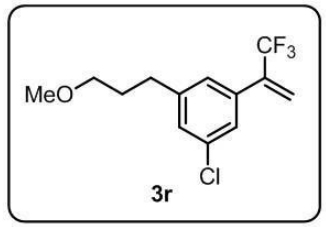


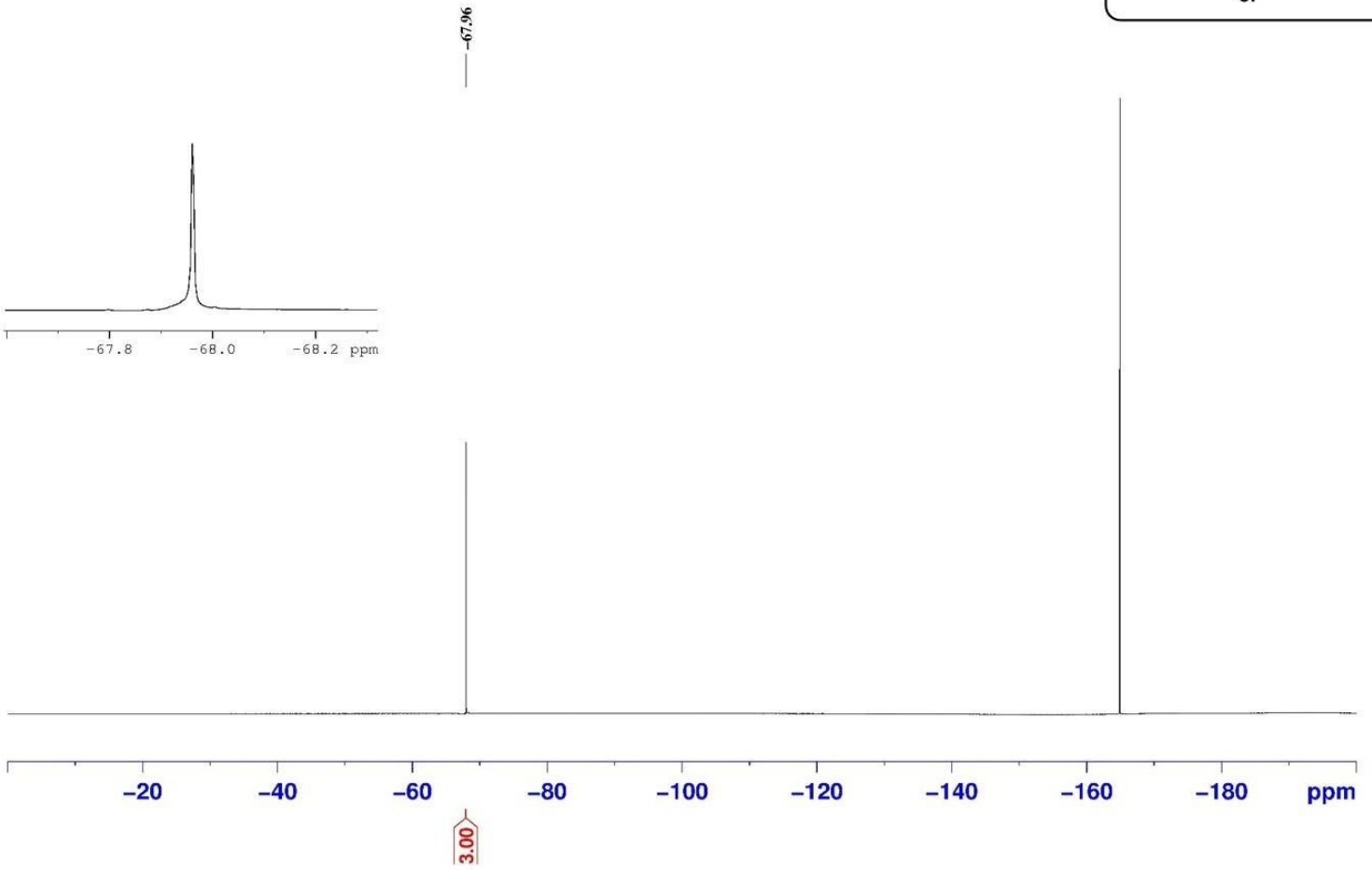



**1–Chloro–3–(3–methoxypropyl)–5–(3,3,3–trifluoroprop–1–en–2–yl)benzene**
**125 MHz, CDCl3**

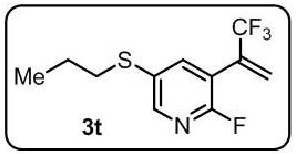


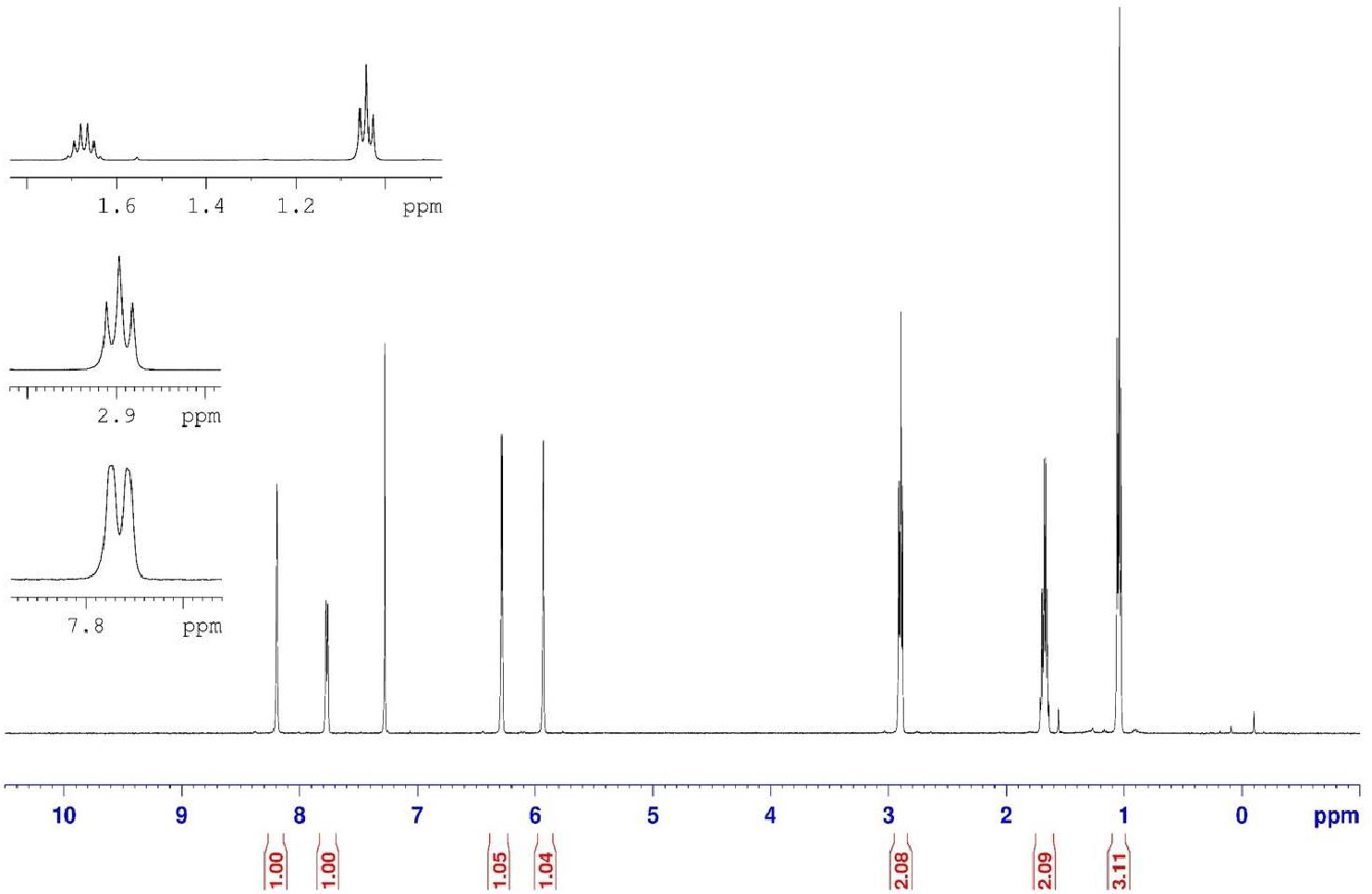
**1–chloro–3–(3–methoxypropyl)–5–(3,3,3–trifluoroprop–1–en–2–yl)benzene**
**CDCl3, 471 MHz**



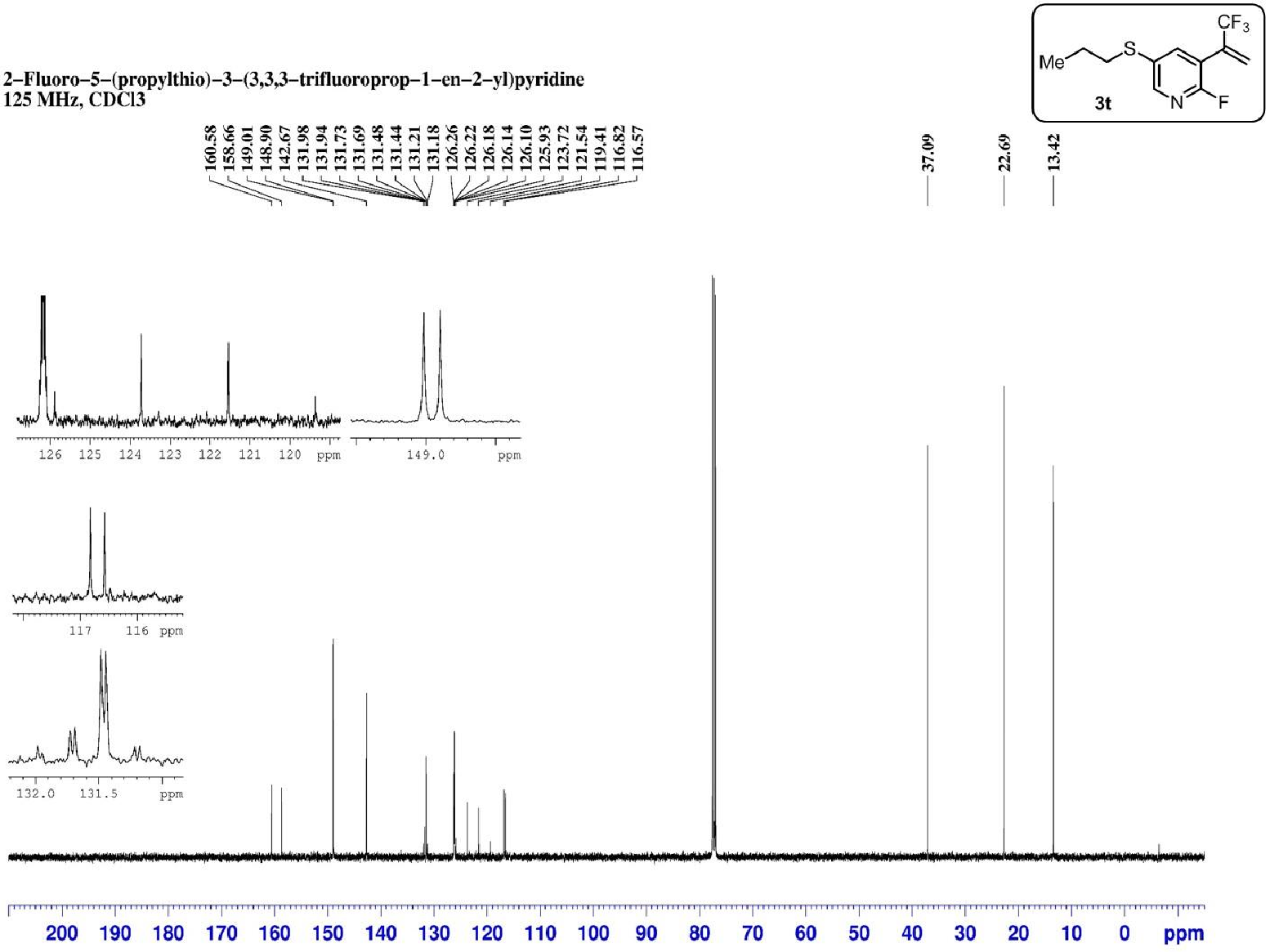



**2-Fluoro-5-(propylthio)-3-(3,3,3-trifluoroprop-1-en-2-yl)pyridine**
**500 MHz, CDCl3**

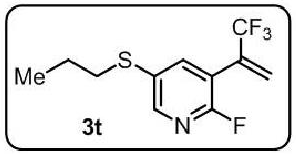


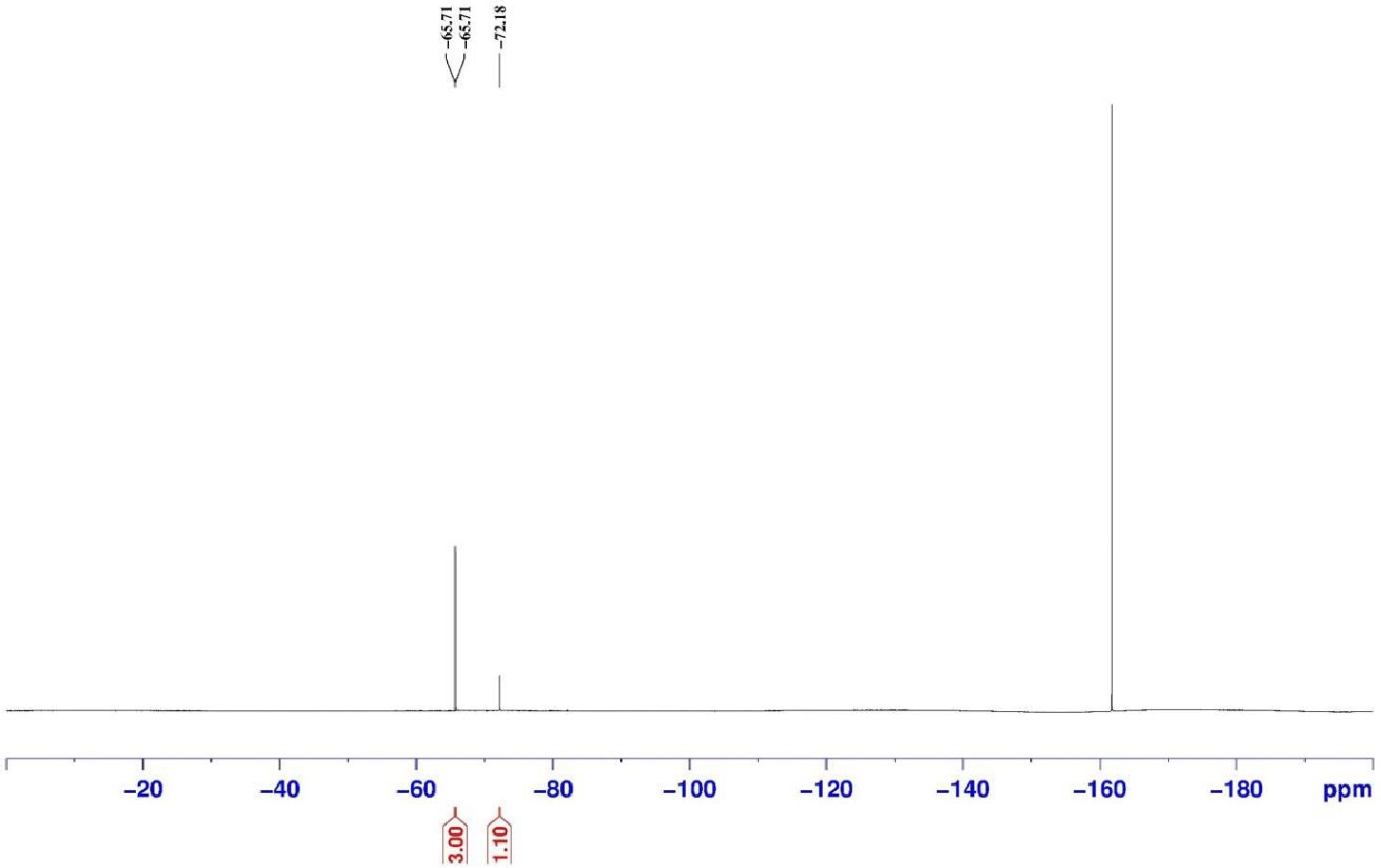



**2–Fluoro–5–(propylthio)–3–(3,3,3–trifluoroprop–1–en–2–yl)pyridine**
**125 MHz, CDCl3**

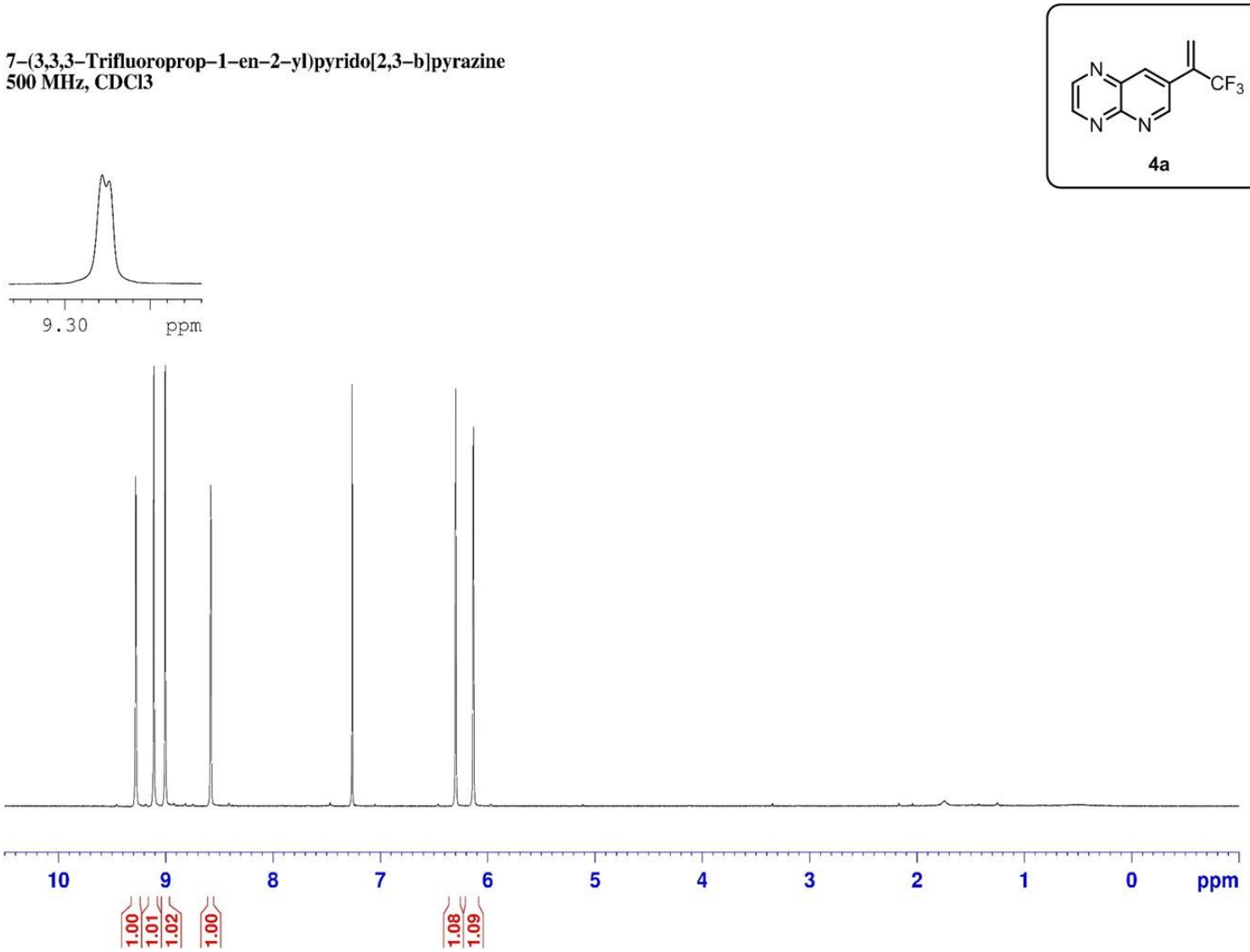


**2–Fluoro–5–(propylthio)–3–(3,3,3–trifluoroprop–1–en–2–yl)pyridine**
**471 MHz, CDCl3**



**7–(3,3,3–Trifluoroprop–1–en–2–yl)pyrido[2,3–b]pyrazine**
**500 MHz, CDCl3**

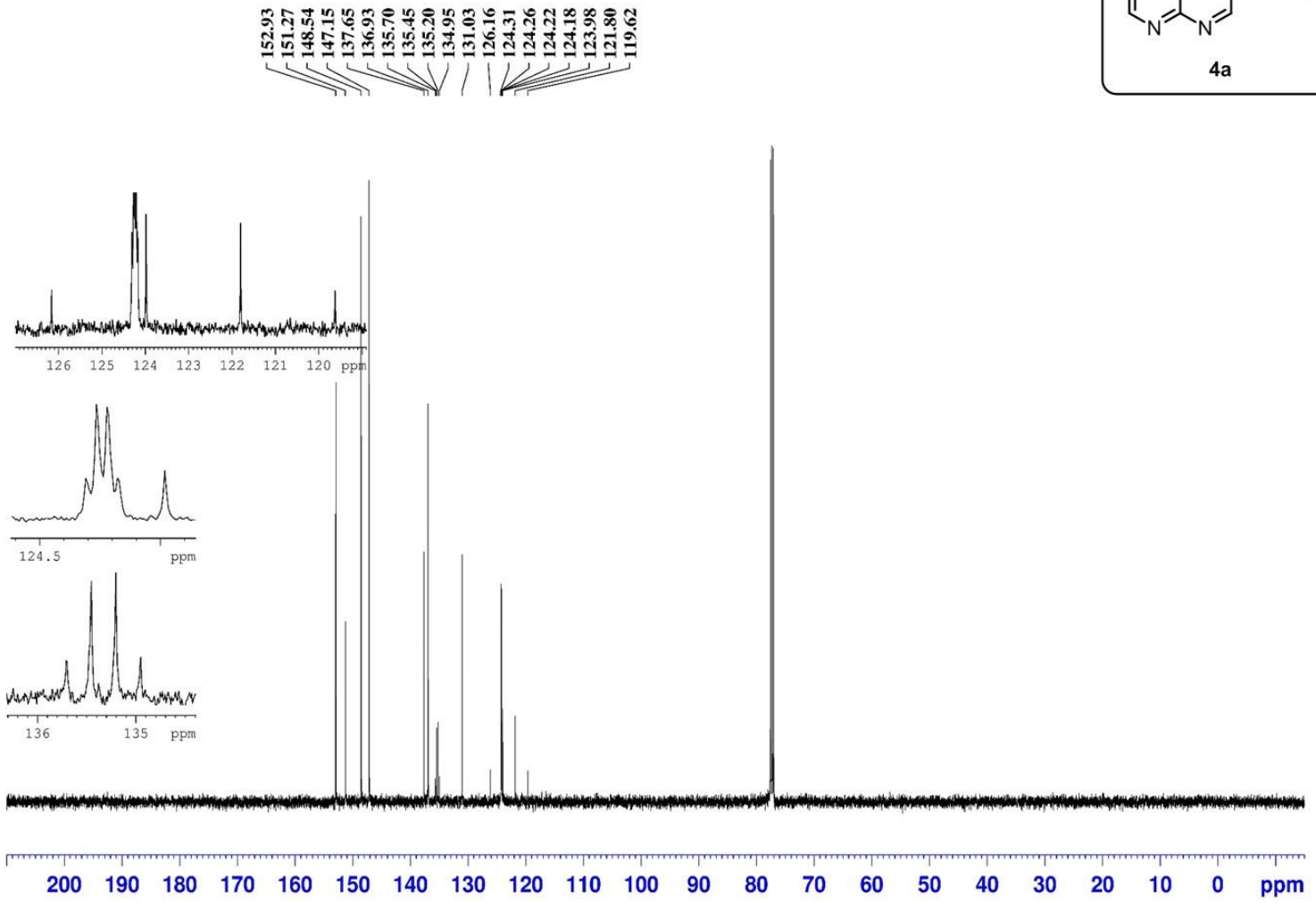


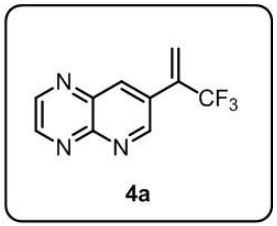




**4a**

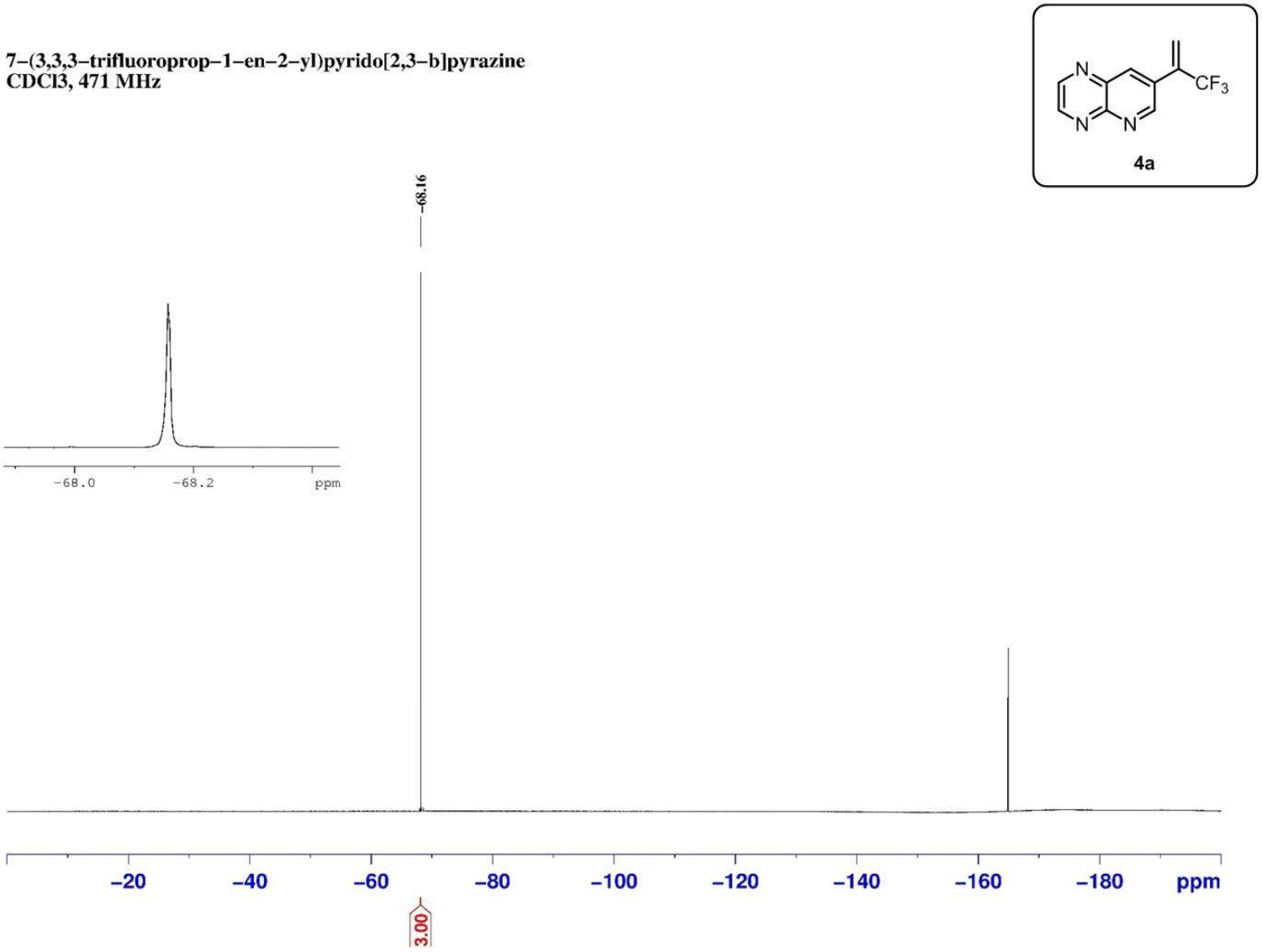
**7–(3,3,3–Trifluoroprop–1–en–2–yl)pyrido[2,3–b]pyrazine**
**125 MHz, CDCl3**



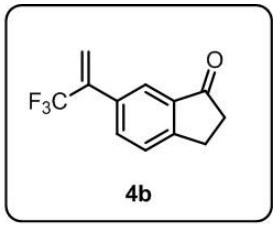




**4a**

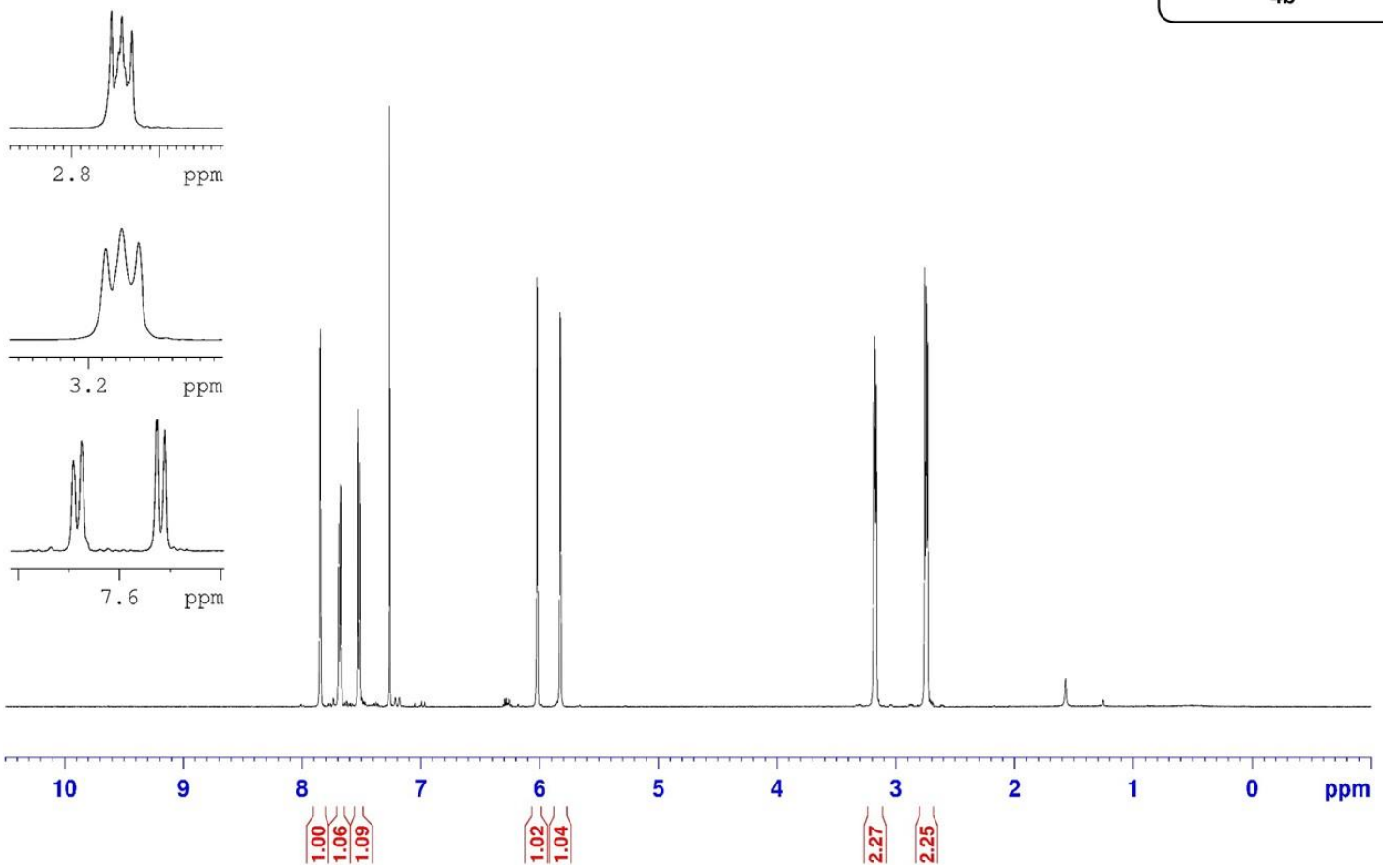
**7–(3,3,3–trifluoroprop–1–en–2–yl)pyrido[2,3–b]pyrazine**
**CDCl3, 471 MHz**



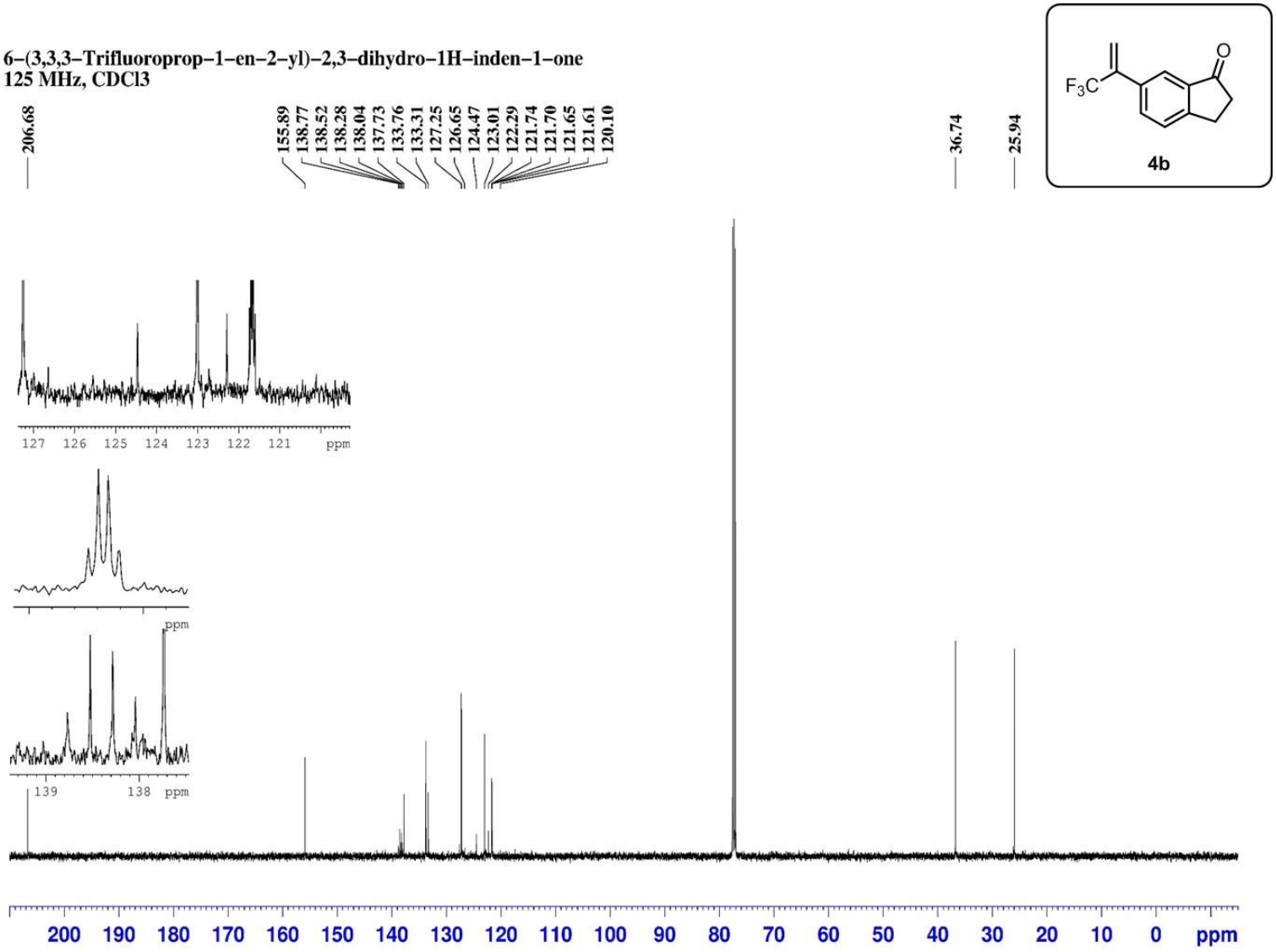
**6–(3,3,3–Trifluoroprop–1–en–2–yl)–2,3–dihydro–1H–inden–1–one**
**500 MHz, CDCl3**



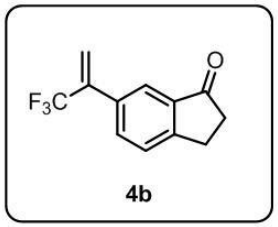

**4b**



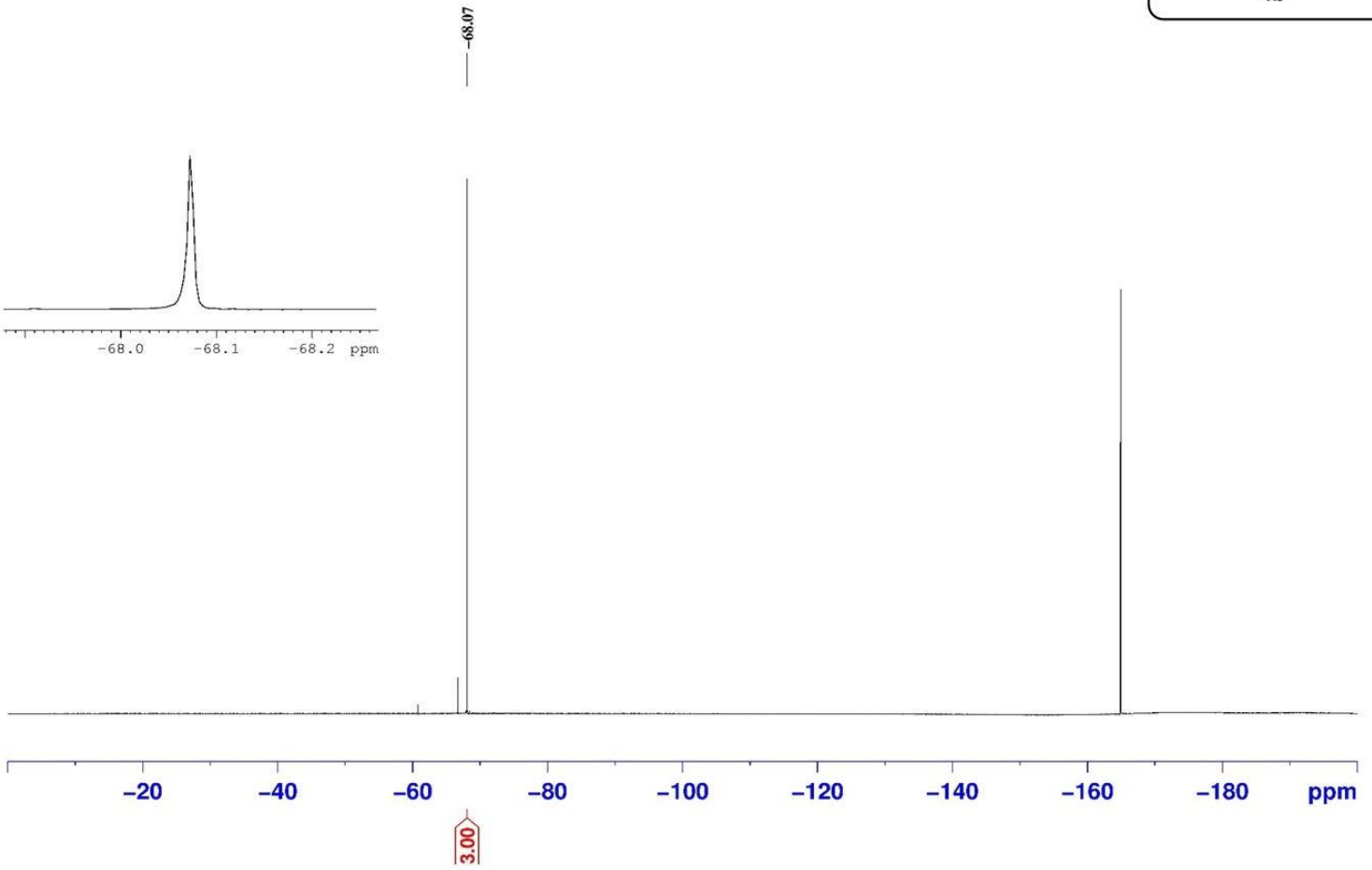
**6–(3,3,3–Trifluoroprop–1–en–2–yl)–2,3–dihydro–1H–inden–1–one**
**125 MHz, CDCl3**



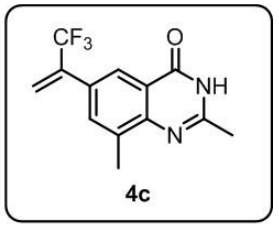
**6–(3,3,3–trifluoroprop–1–en–2–yl)–2,3–dihydro–1H–inden–1–one**
**CDCl3, 471 MHz**



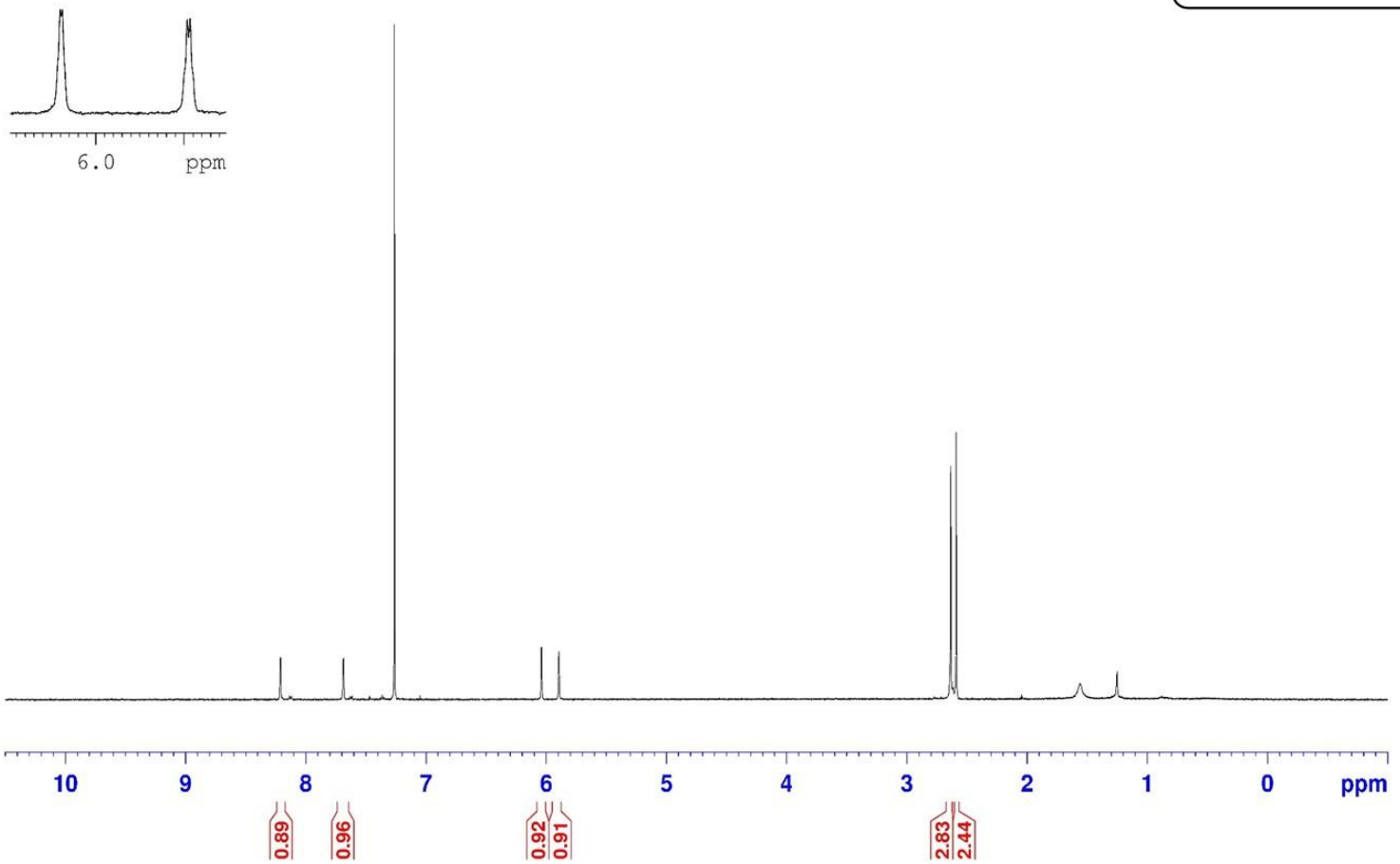

**4b**



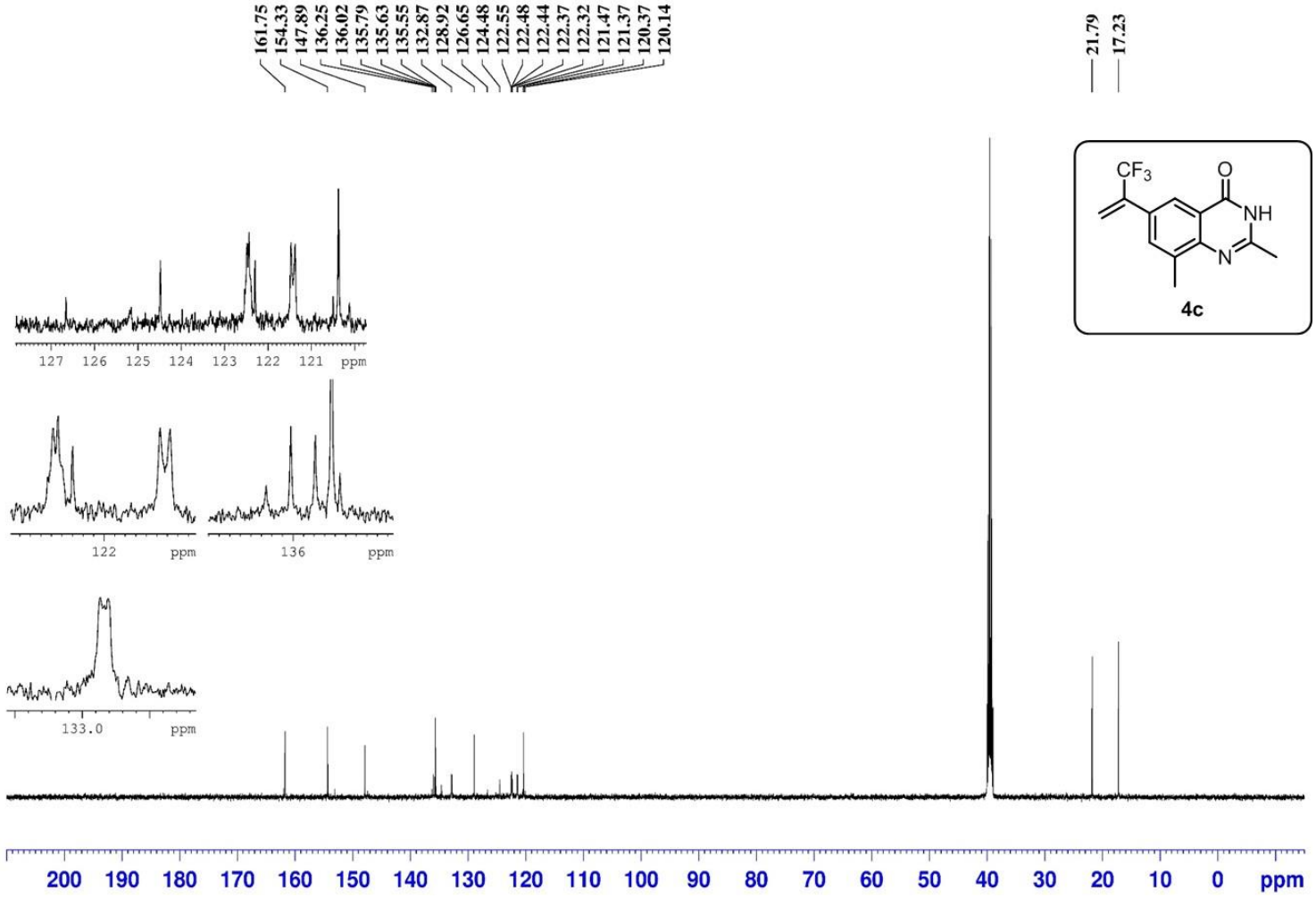
**2,8–Dimethyl–6–(3,3,3–trifluoroprop–1–en–2–yl)quinazolin–4(3H)–one**
**500 MHz, CDCl3**



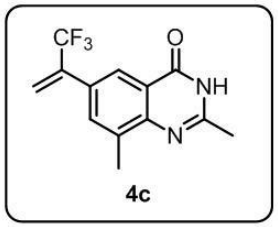
**4c**



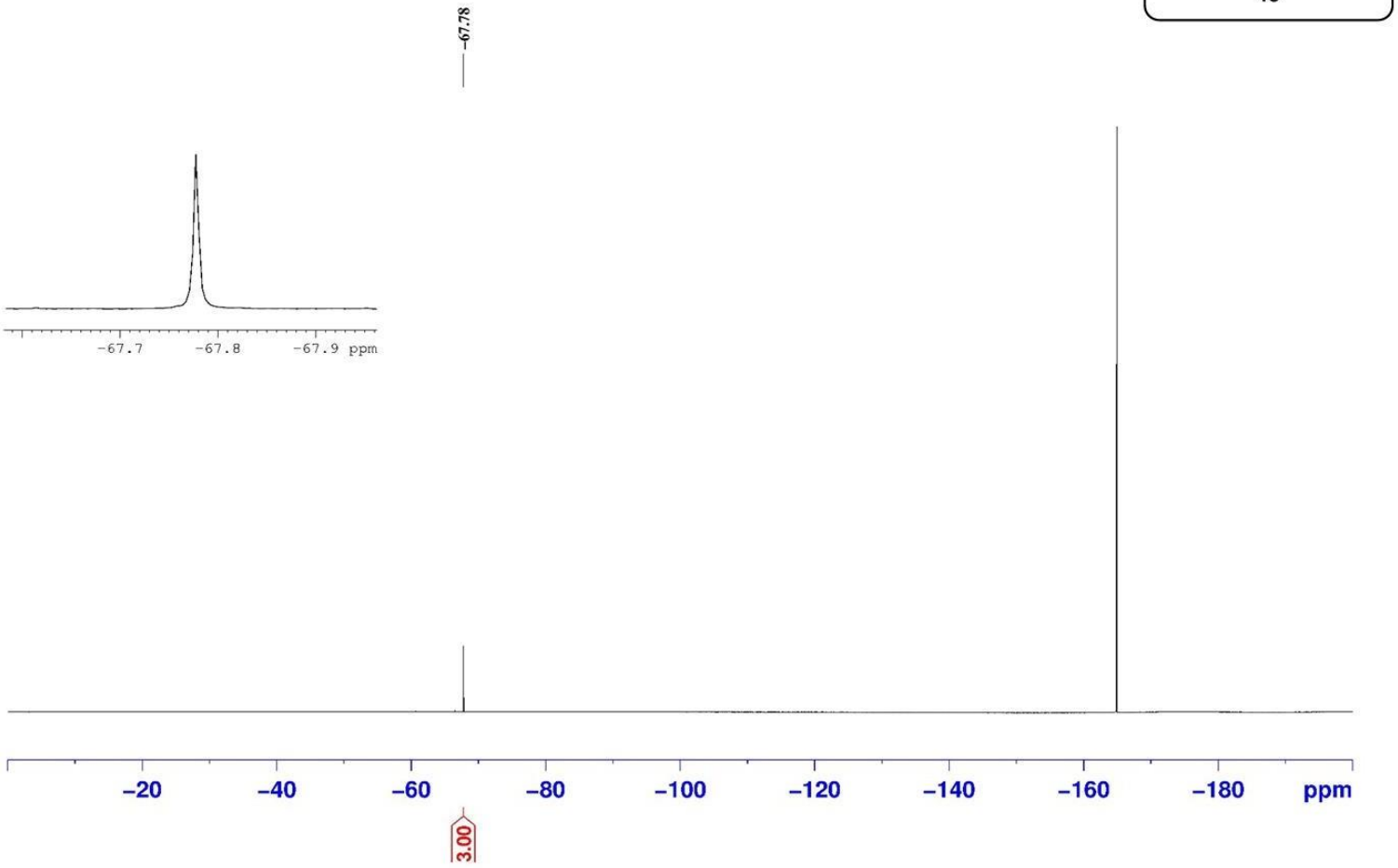
**2,8–Dimethyl–6–(3,3,3–trifluoroprop–1–en–2–yl)quinazolin–4(3H)–one**
**125 MHz, DMSO–d6**



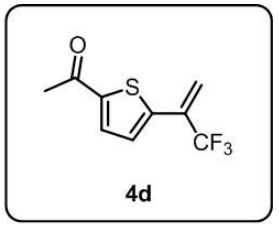
**2,8−dimethyl−6−(3,3,3−trifluoroprop−1−en−2−yl)quinazolin−4(3H)−one**
**CDCl3, 471 MHz**



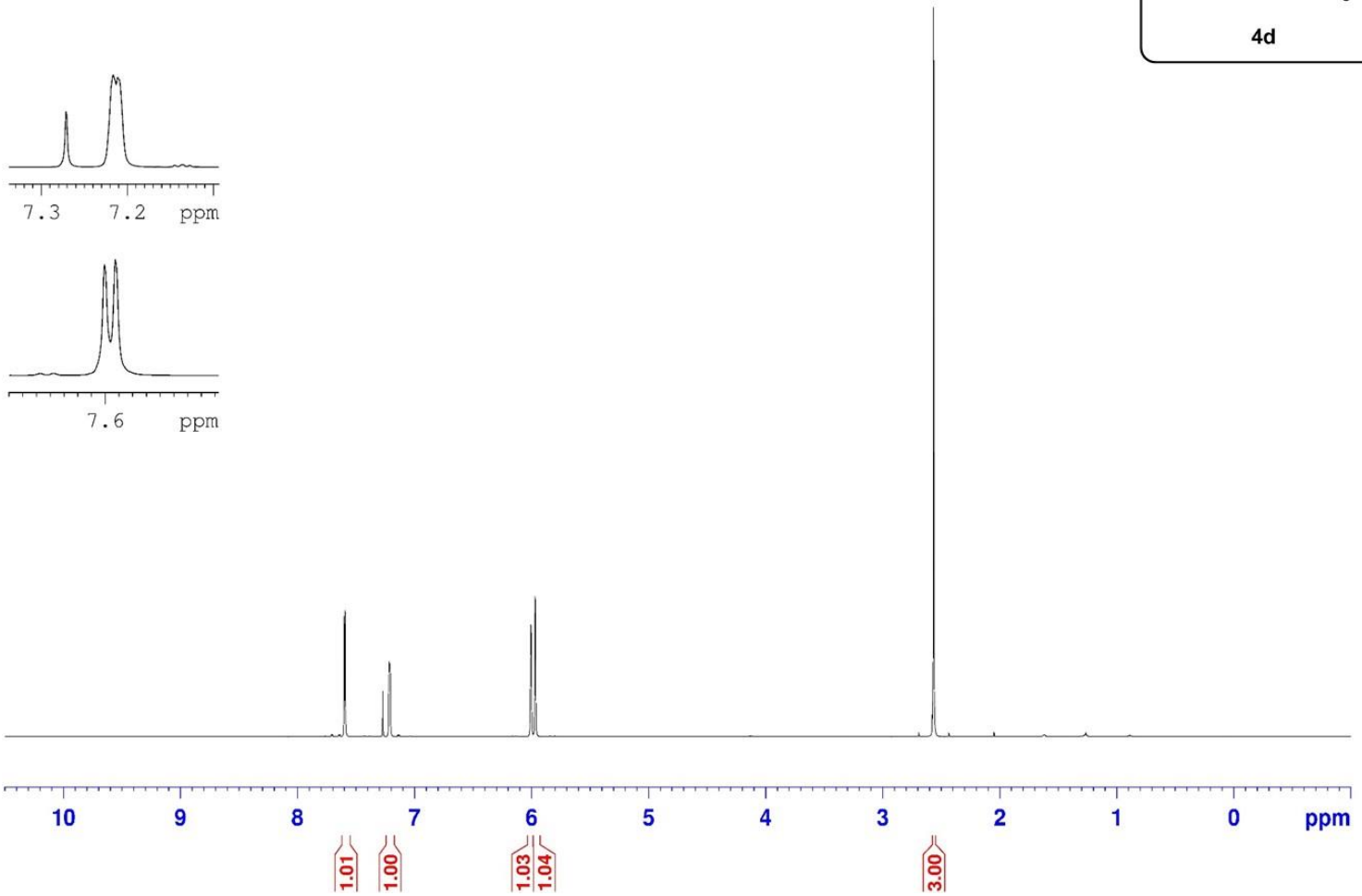
**4c**



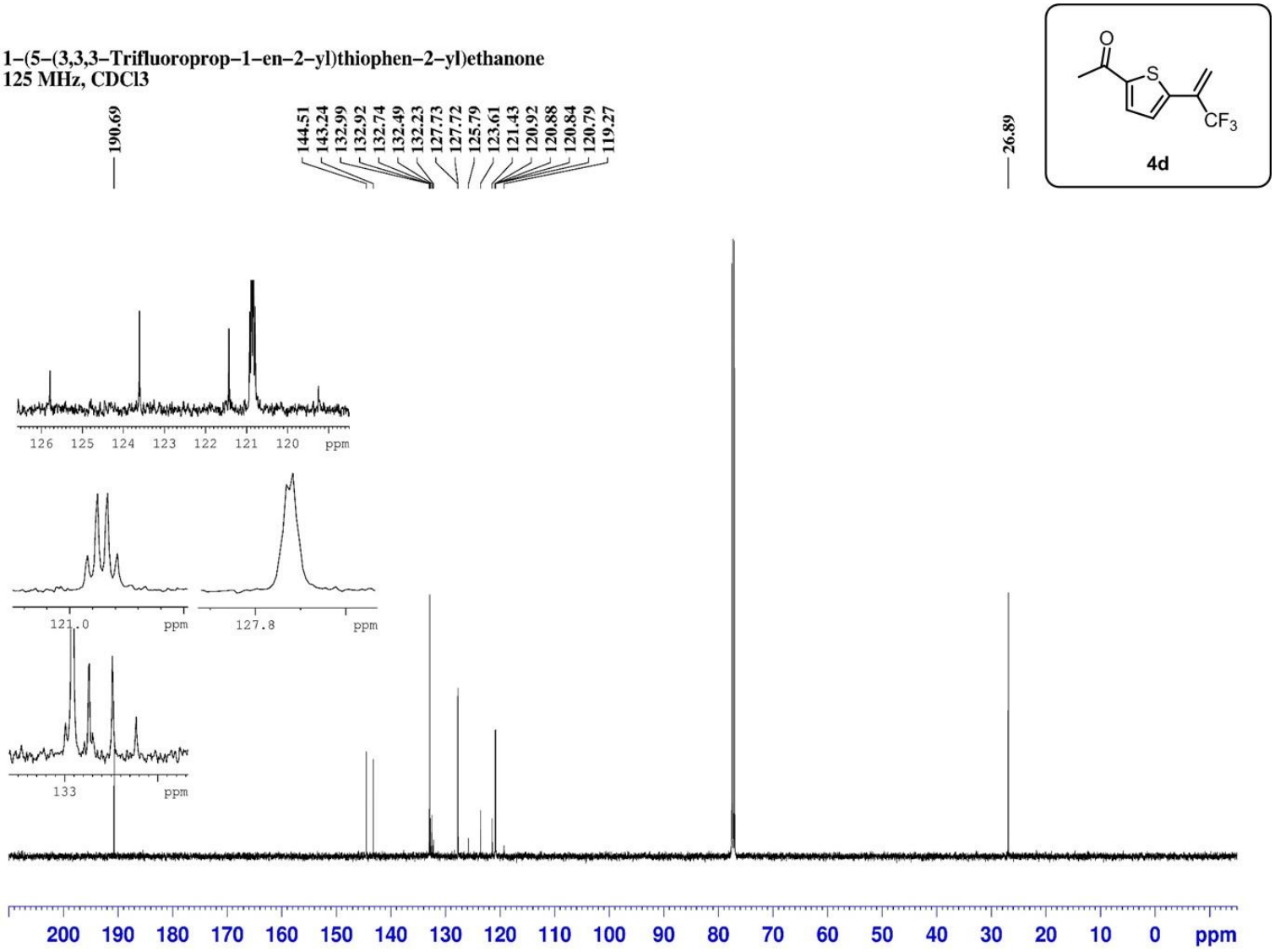
**1–(5–(3,3,3–Trifluoroprop–1–en–2–yl)thiophen–2–yl)ethanone**
**500 MHz, CDCl3**



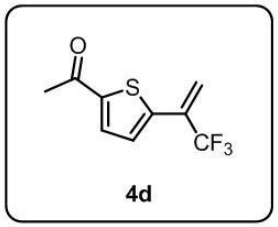

**4d**



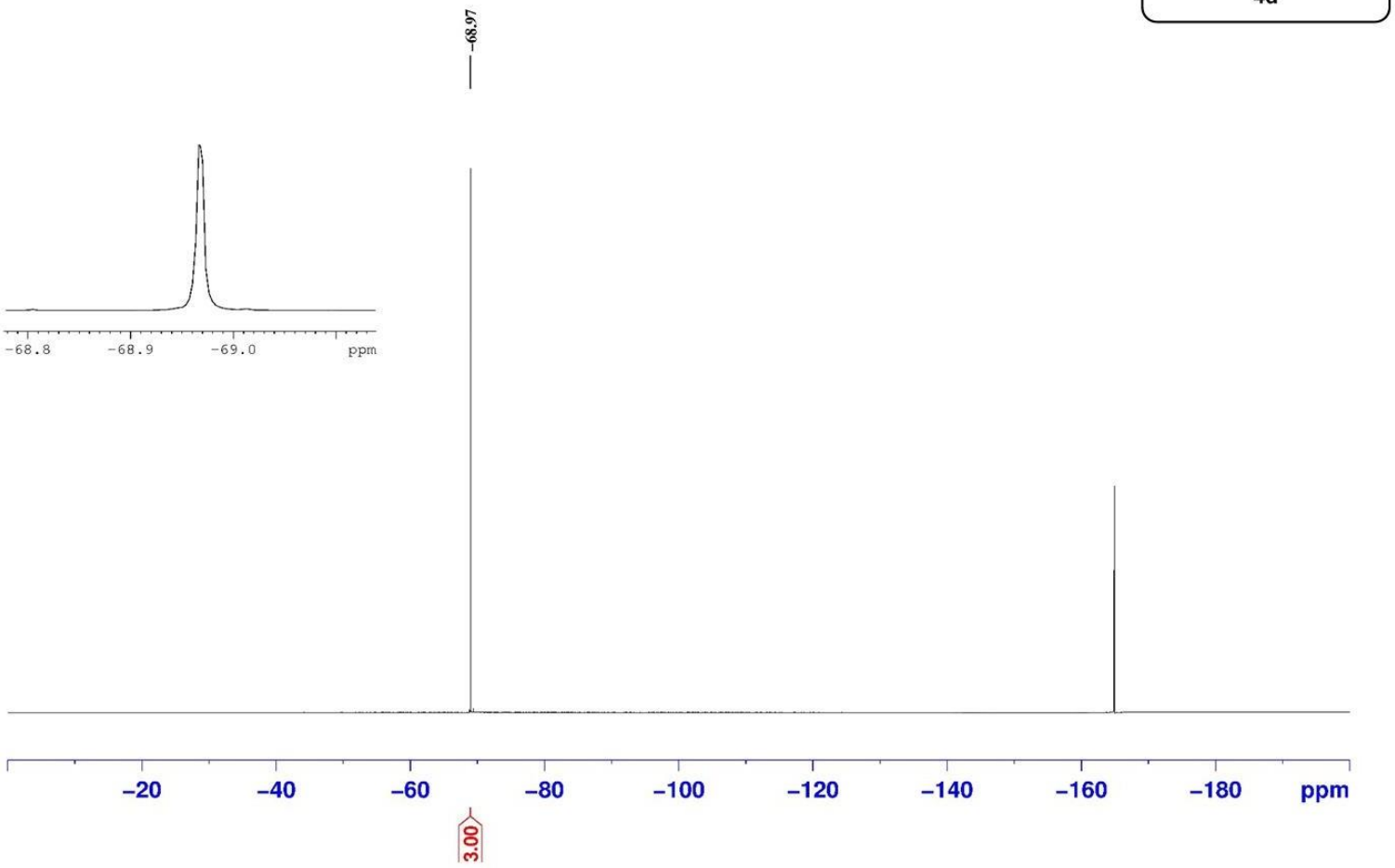
**1–(5–(3,3,3–Trifluoroprop–1–en–2–yl)thiophen–2–yl)ethanone**
**125 MHz, CDCl3**



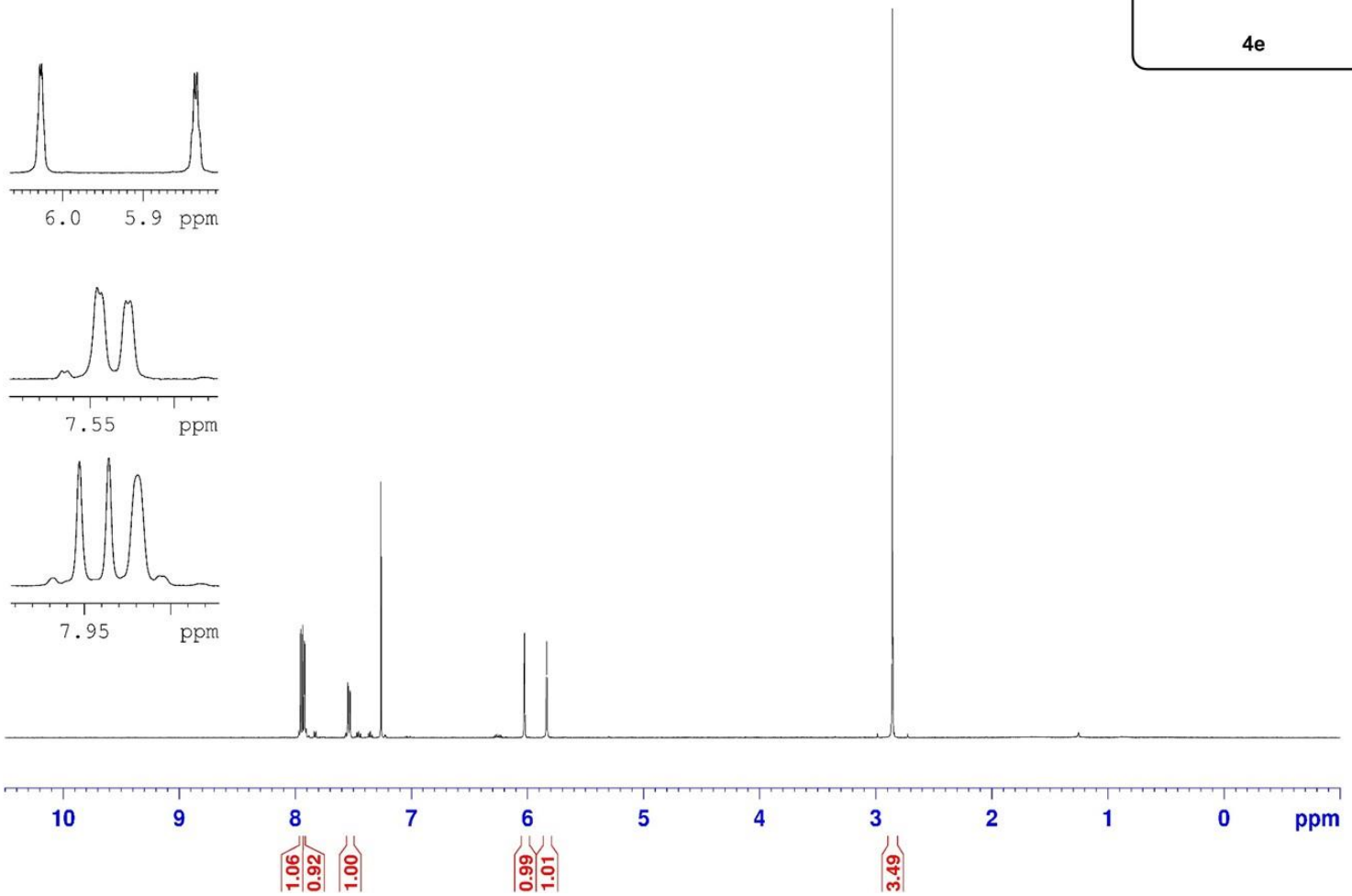
**1–(5–(3,3,3–trifluoroprop–1–en–2–yl)thiophen–2–yl)ethanone**
**CDCl3, 471 MHz**

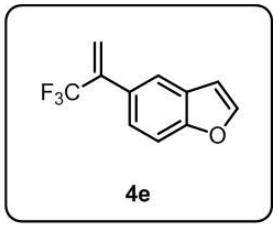



**4d**



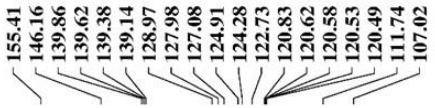
**2–Methyl–6–(3,3,3–trifluoroprop–1–en–2–yl)benzo[d] thiazole**
**500 MHz, CDCl3**

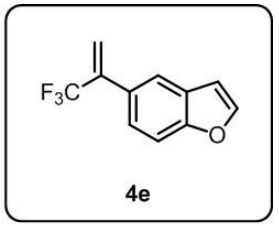


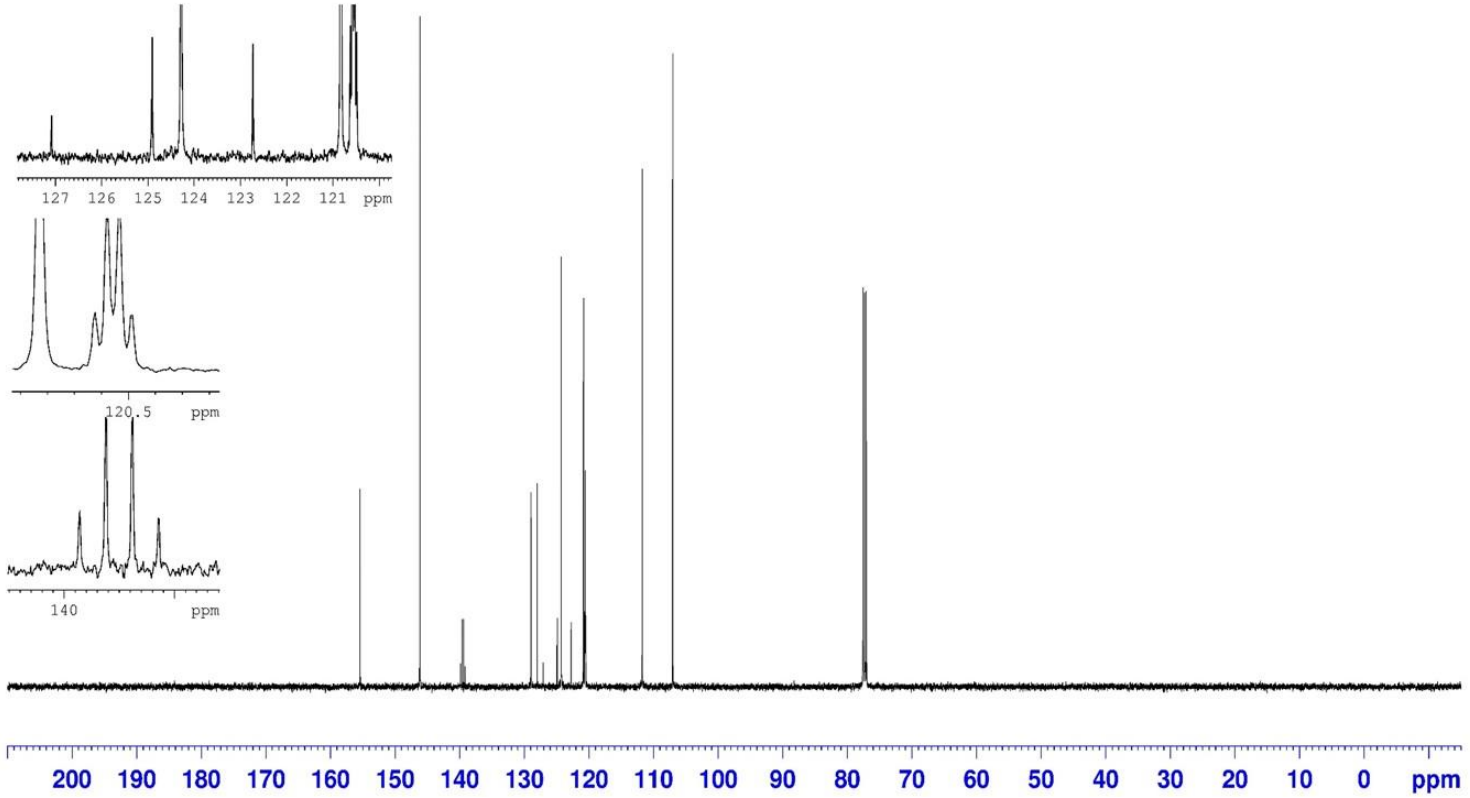




**4e**

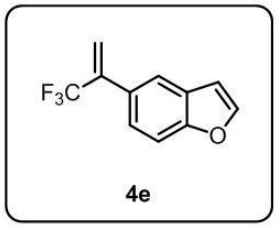
**5–(3,3,3–Trifluoroprop–1–en–2–yl)benzofuran**
**125 MHz, CDCl3**

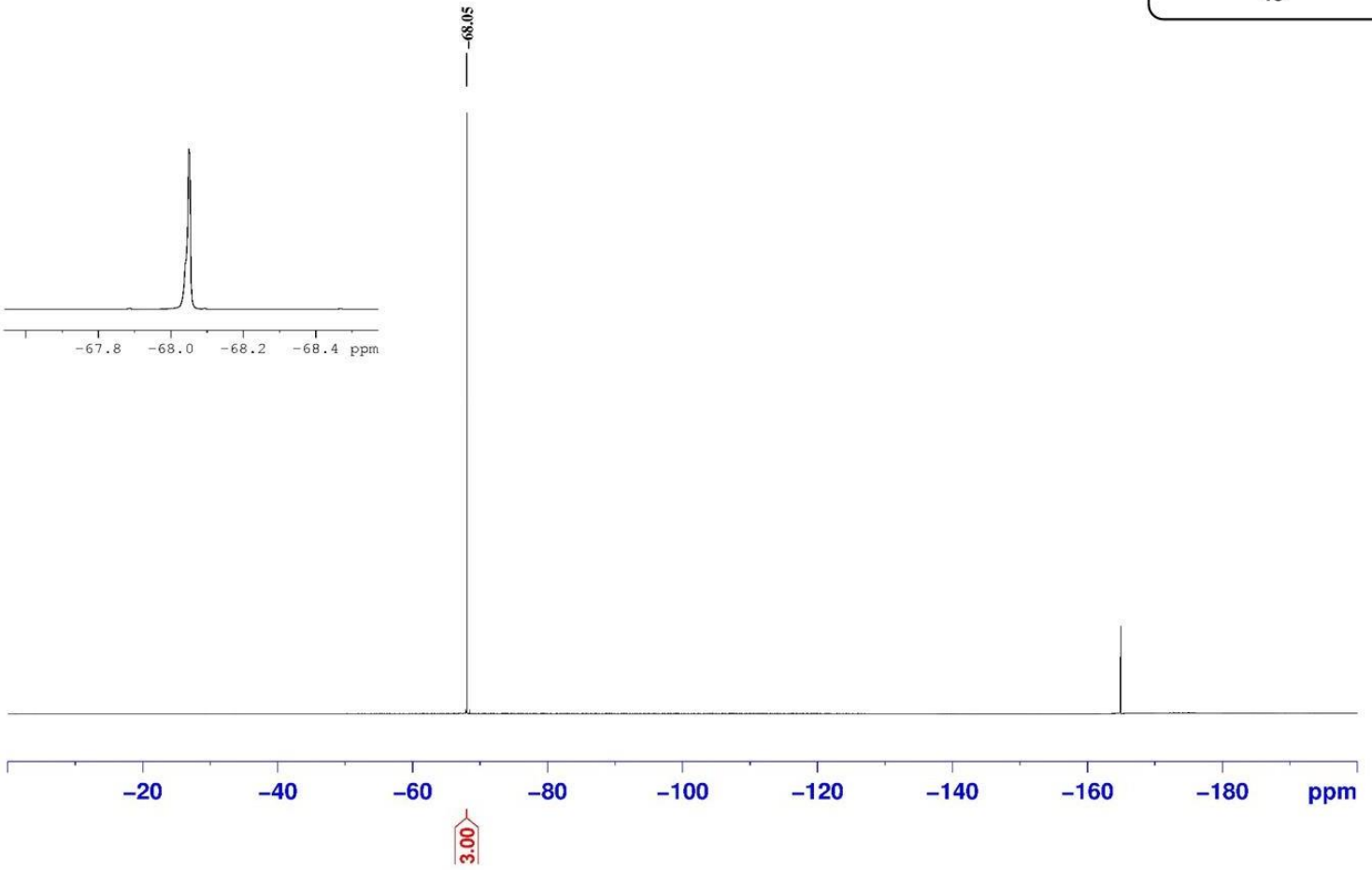


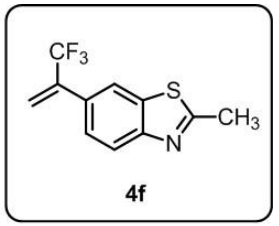



**5−(3,3,3−trifluoroprop−1−en−2−yl)benzofuran**
**CDCl3, 471 MHz**

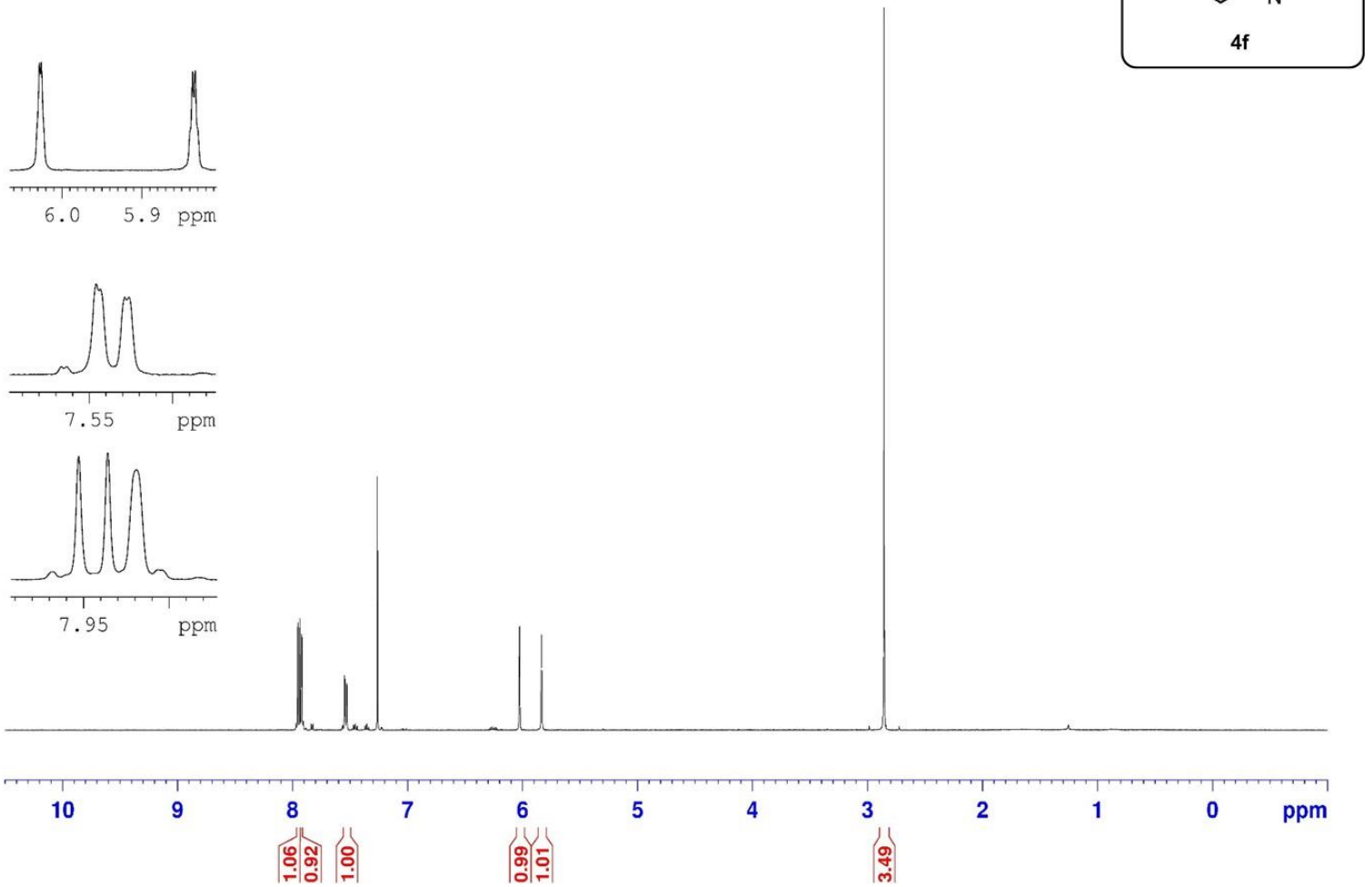


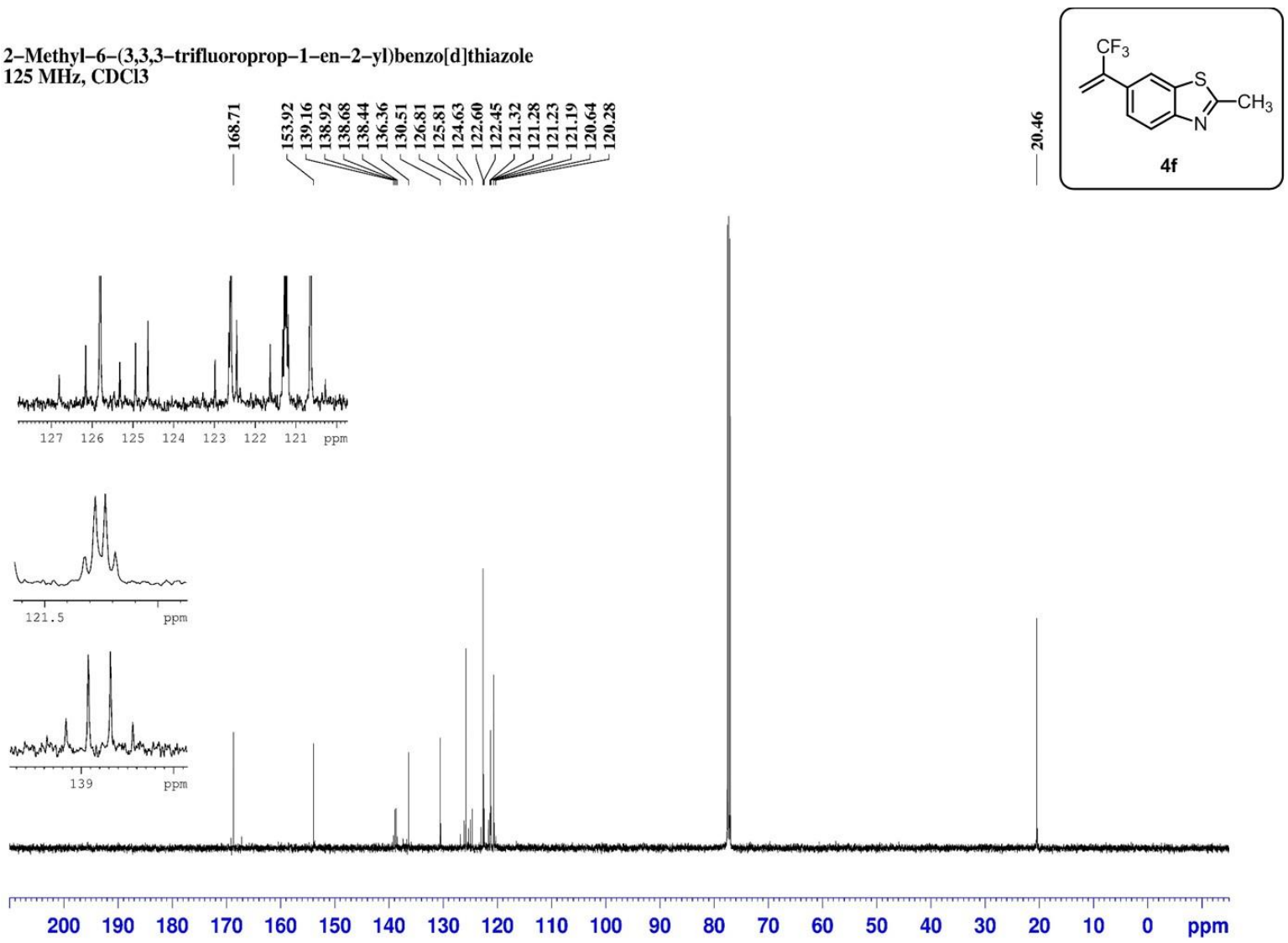
**2–Methyl–6–(3,3,3–trifluoroprop–1–en–2–yl)benzo[d] thiazole**
**500 MHz, CDCl3**



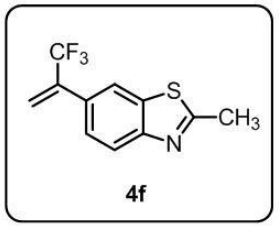
**4f**



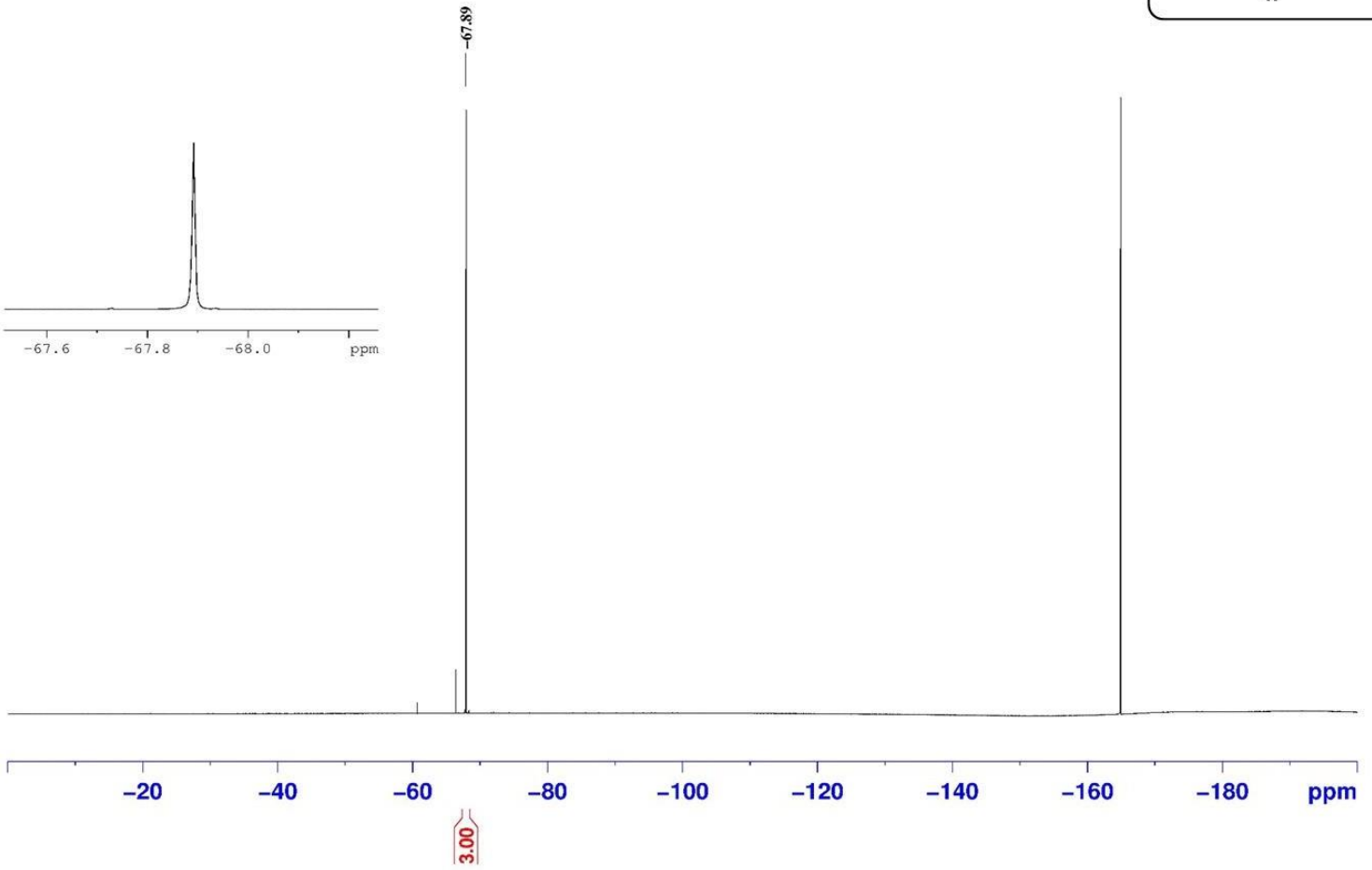
**2–Methyl–6–(3,3,3–trifluoroprop–1–en–2–yl)benzo[d]thiazole**
**125 MHz, CDCl3**



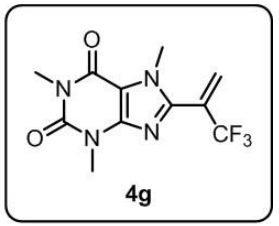
**2–methyl–6–(3,3,3–trifluoroprop–1–en–2–yl)benzo[d] thiazole**
**CDCl3, 471 MHz**



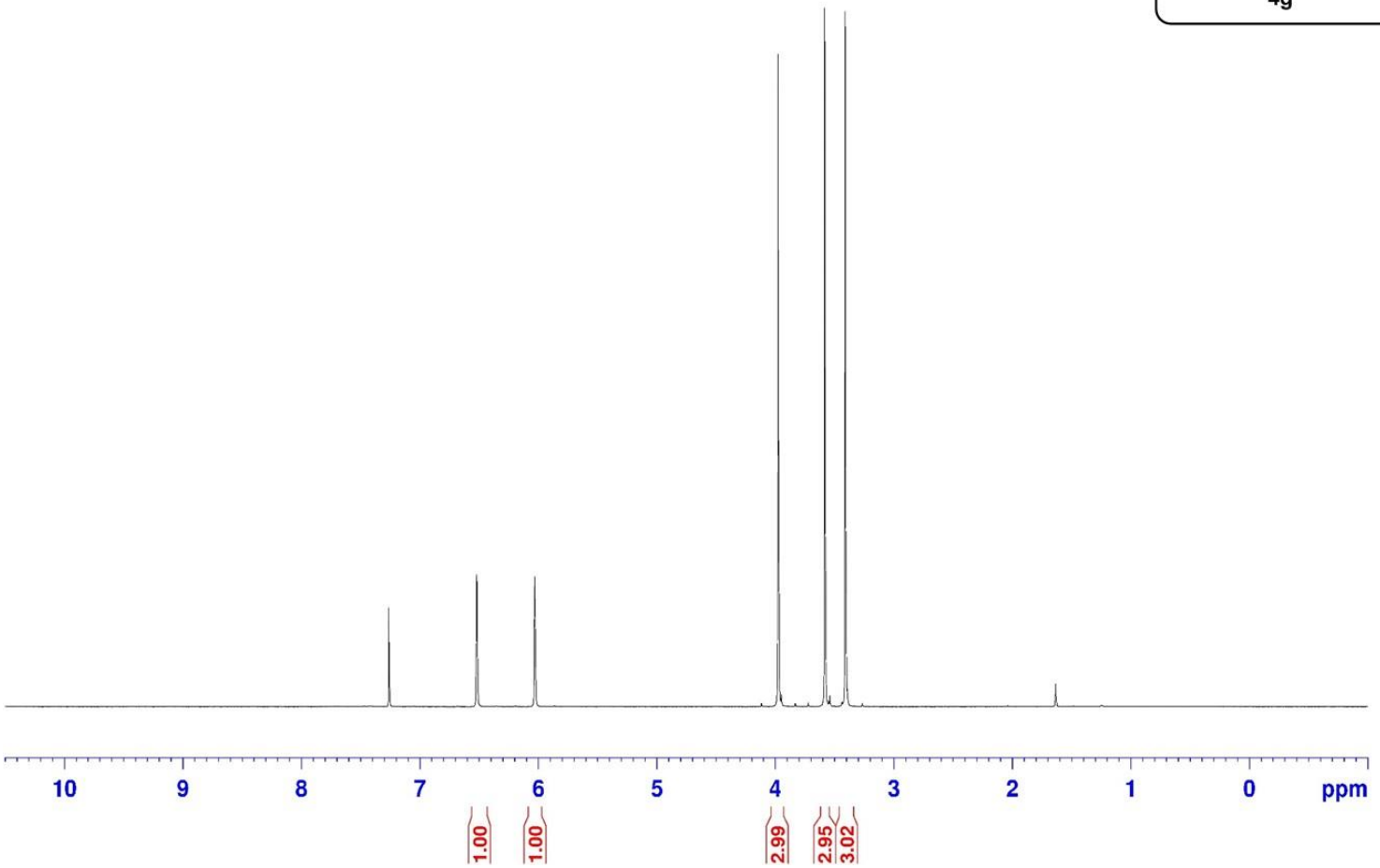

**4f**



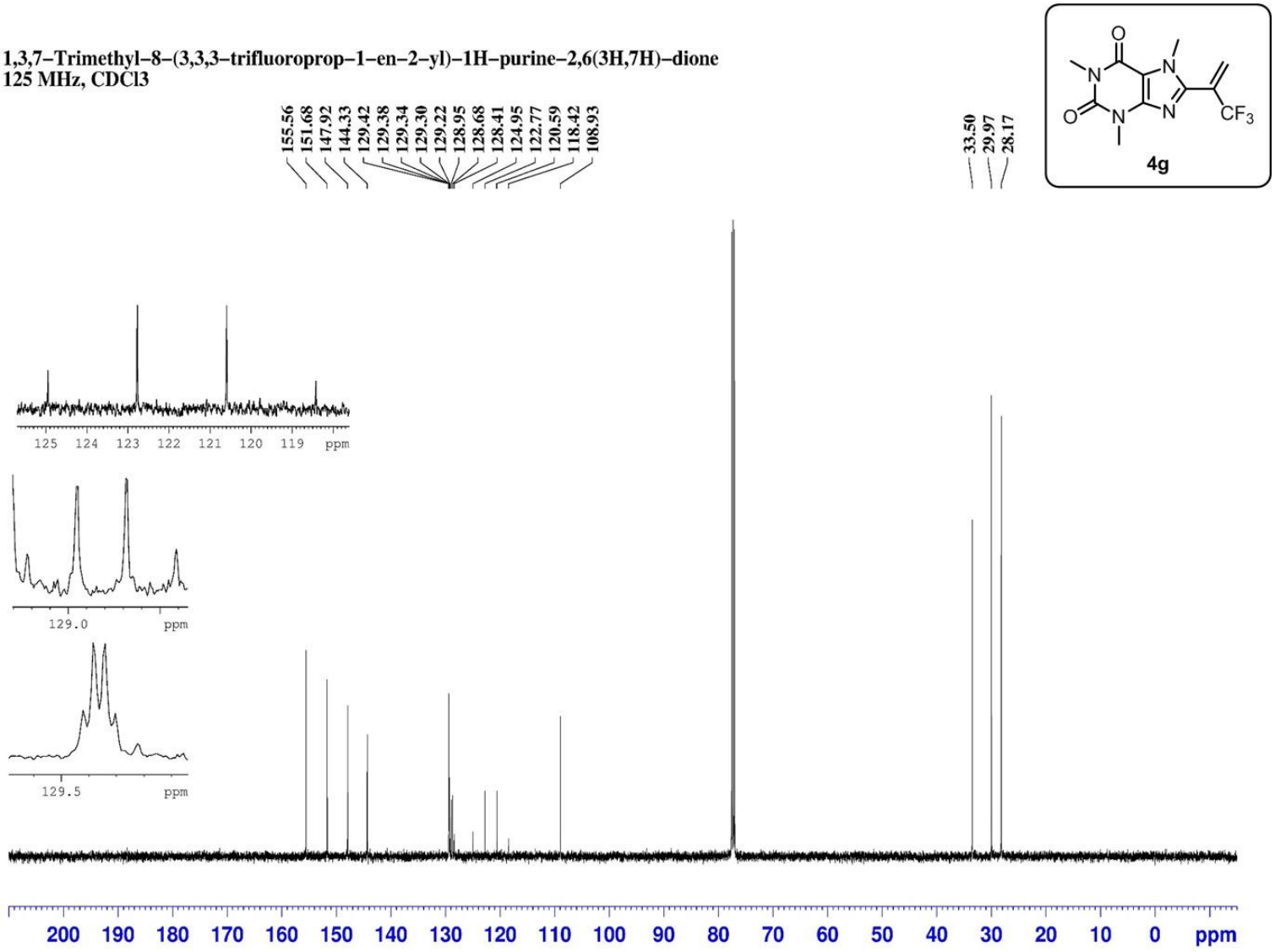
**1,3,7–Trimethyl–8–(3,3,3–trifluoroprop–1–en–2–yl)–1H–purine–2,6(3H,7H)–dione**
**500 MHz, CDCl3**



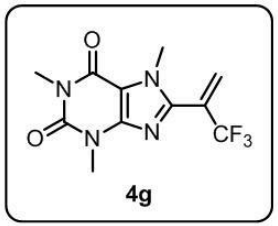
**4g**



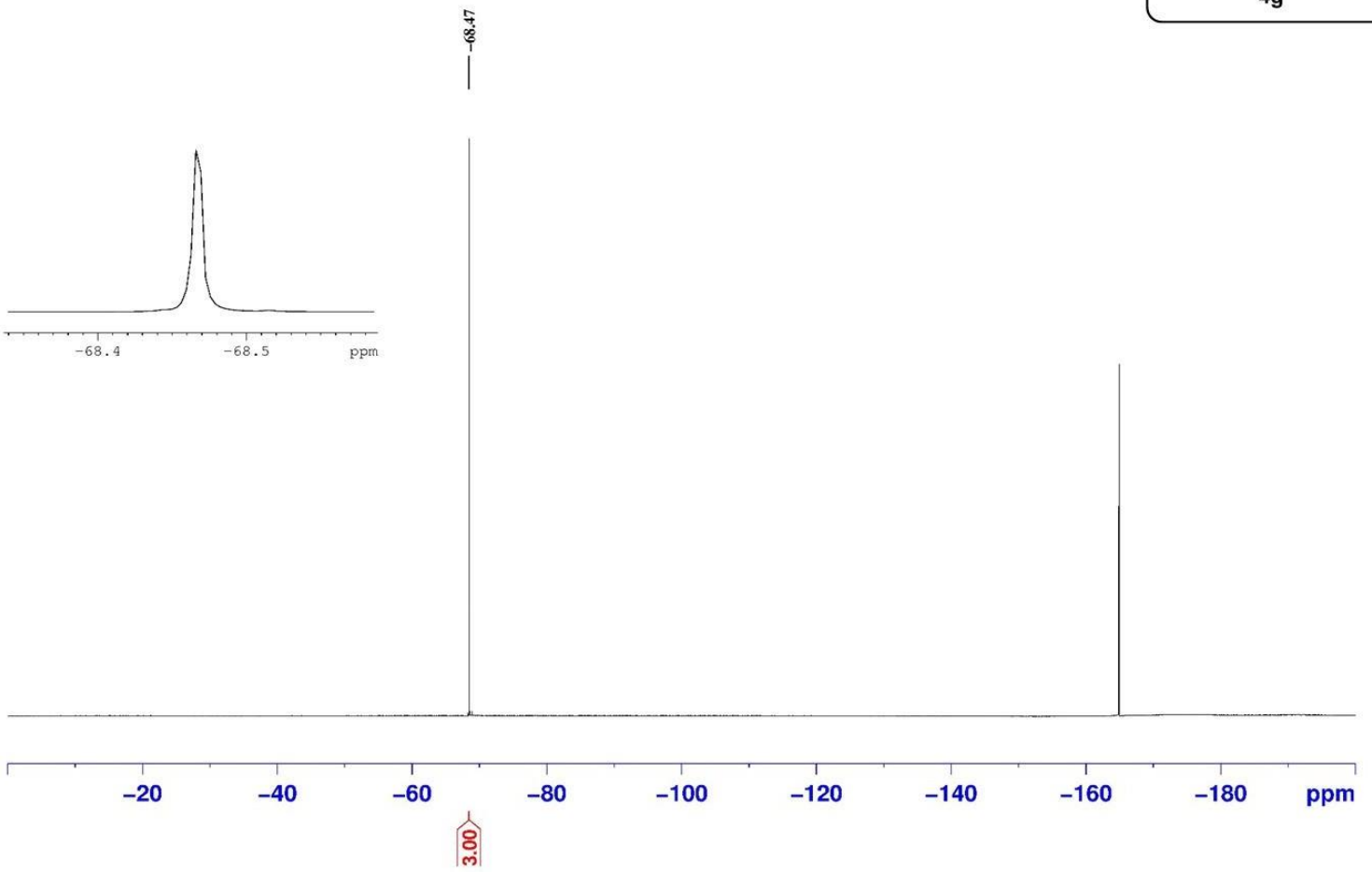
**1,3,7−Trimethyl−8−(3,3,3−trifluoroprop−1−en−2−yl)−1H−purine−2,6(3H,7H)−dione**
**125 MHz, CDCl3**



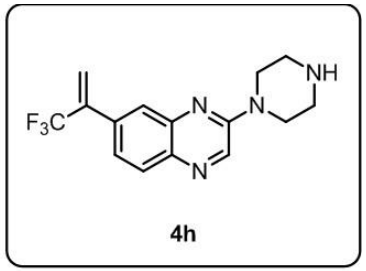
**1,3,7–trimethyl–8–(3,3,3–trifluoroprop–1–en–2–yl)–1H–purine–2,6(3H,7H)–dione**
**CDCl3, 471 MHz**



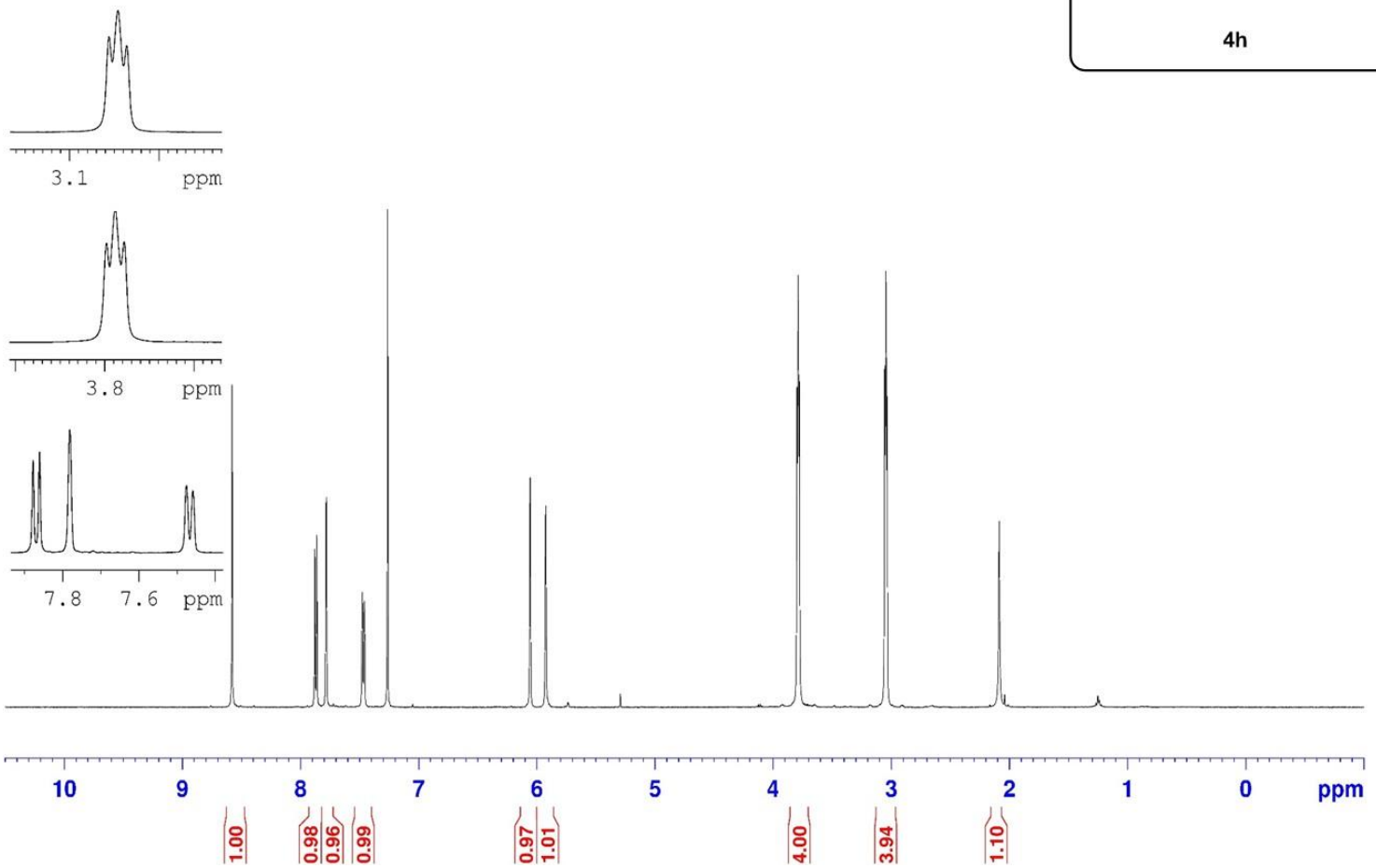

**4g**

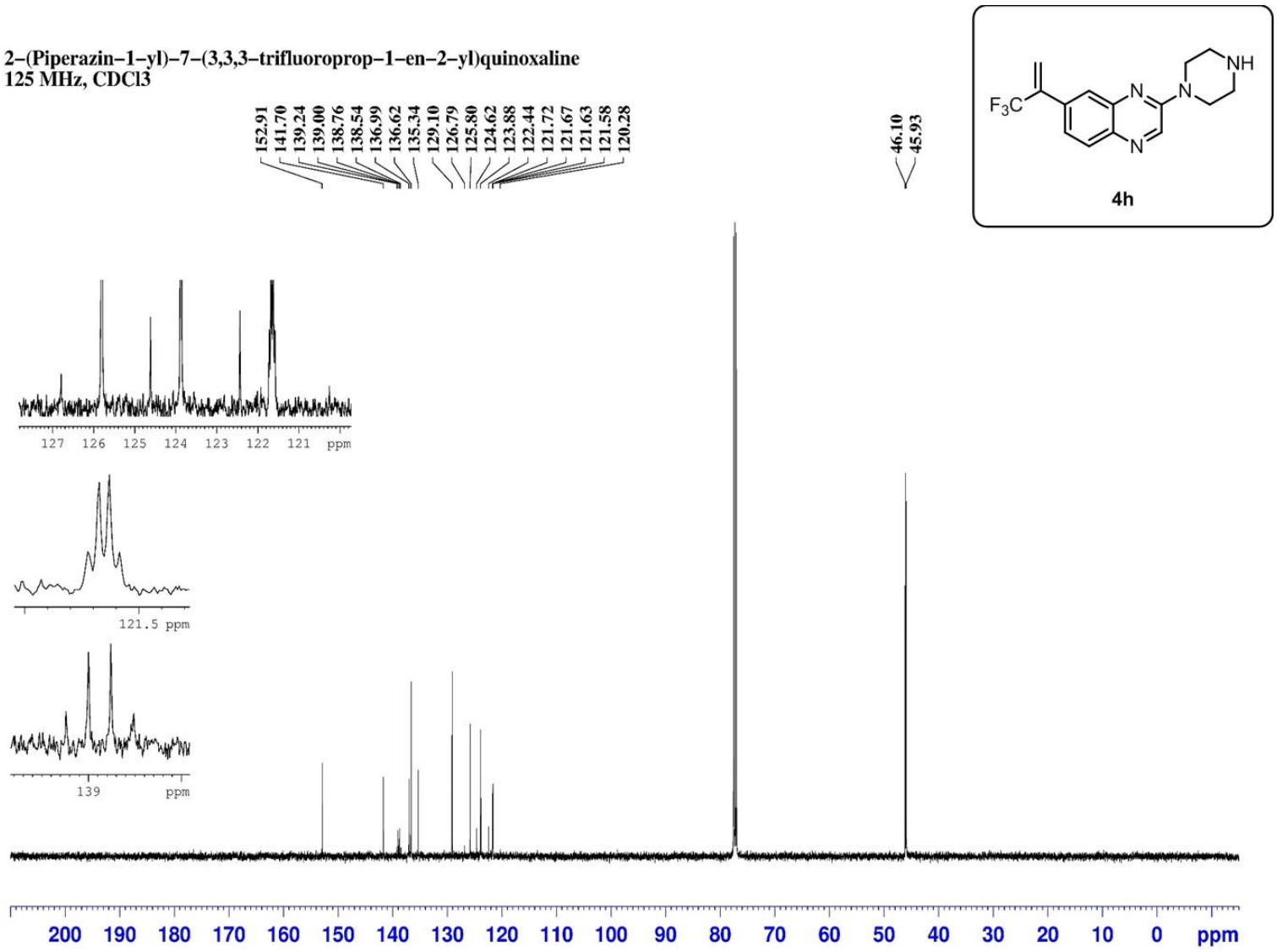


**2–(Piperazin–1–yl)–7–(3,3,3–trifluoroprop–1–en–2–yl)quinoxaline**
**500 MHz, CDCl3**

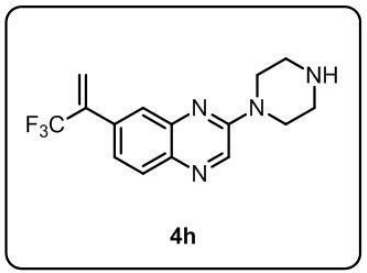



**4h**

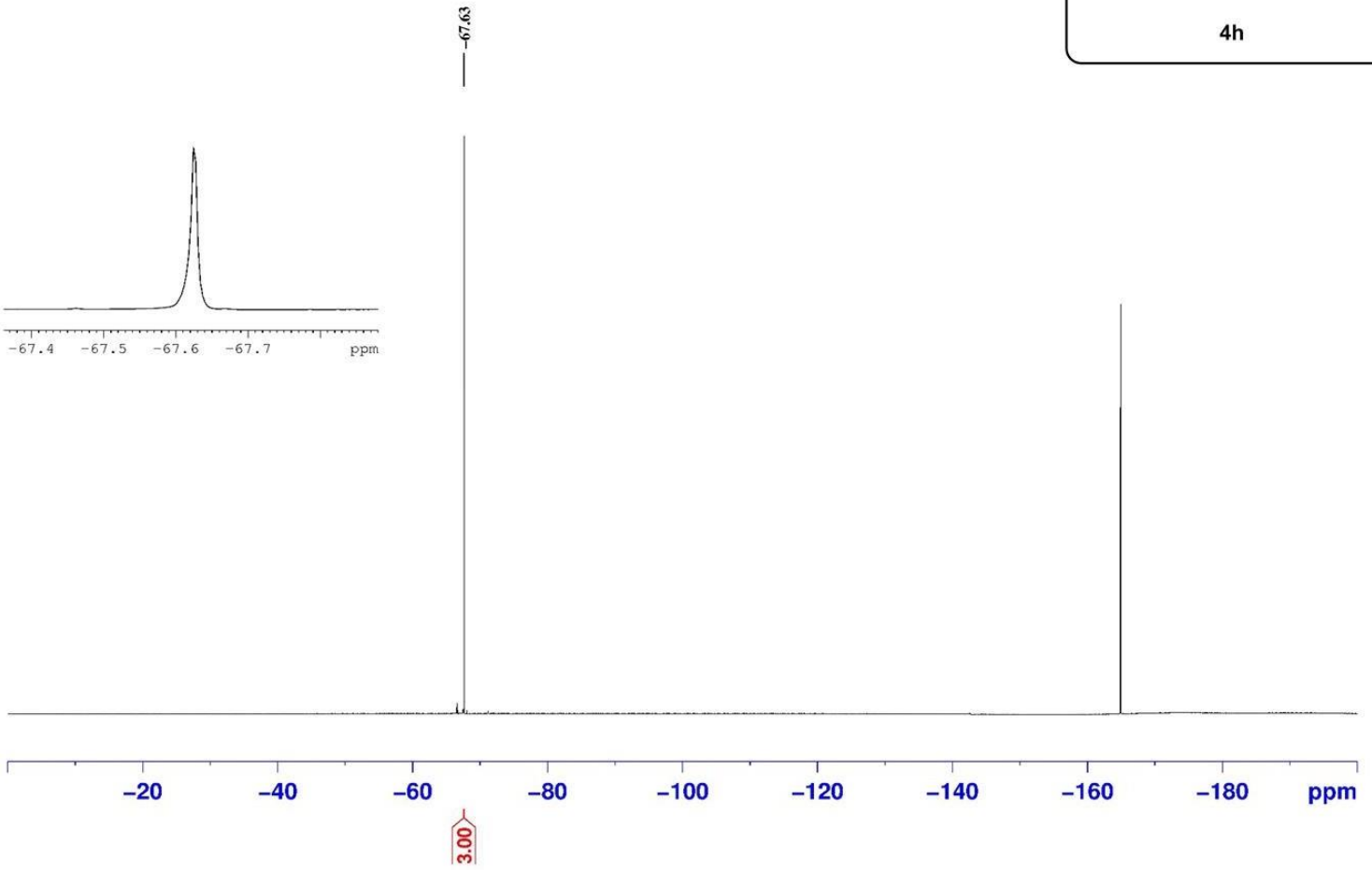



2–(Piperazin–1–yl)–7–(3,3,3–trifluoroprop–1–en–2–yl)quinoxaline
125 MHz, CDCl3
152.91
141.70
139.24
139.00
138.76
138.54
136.99
136.62
135.34
129.10
126.79
125.80
124.62
123.88
122.44
121.72
121.67
121.63
121.58
120.28
46.10
45.93
4h
127 126 125 124 123 122 121 ppm
121.5 ppm
139 ppm
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

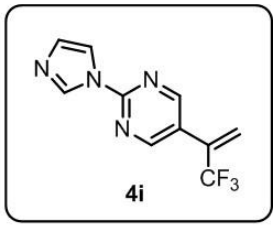
**2–(piperazin–1–yl)–7–(3,3,3–trifluoroprop–1–en–2–yl)quinoxaline**
**CDCl3, 471 MHz**



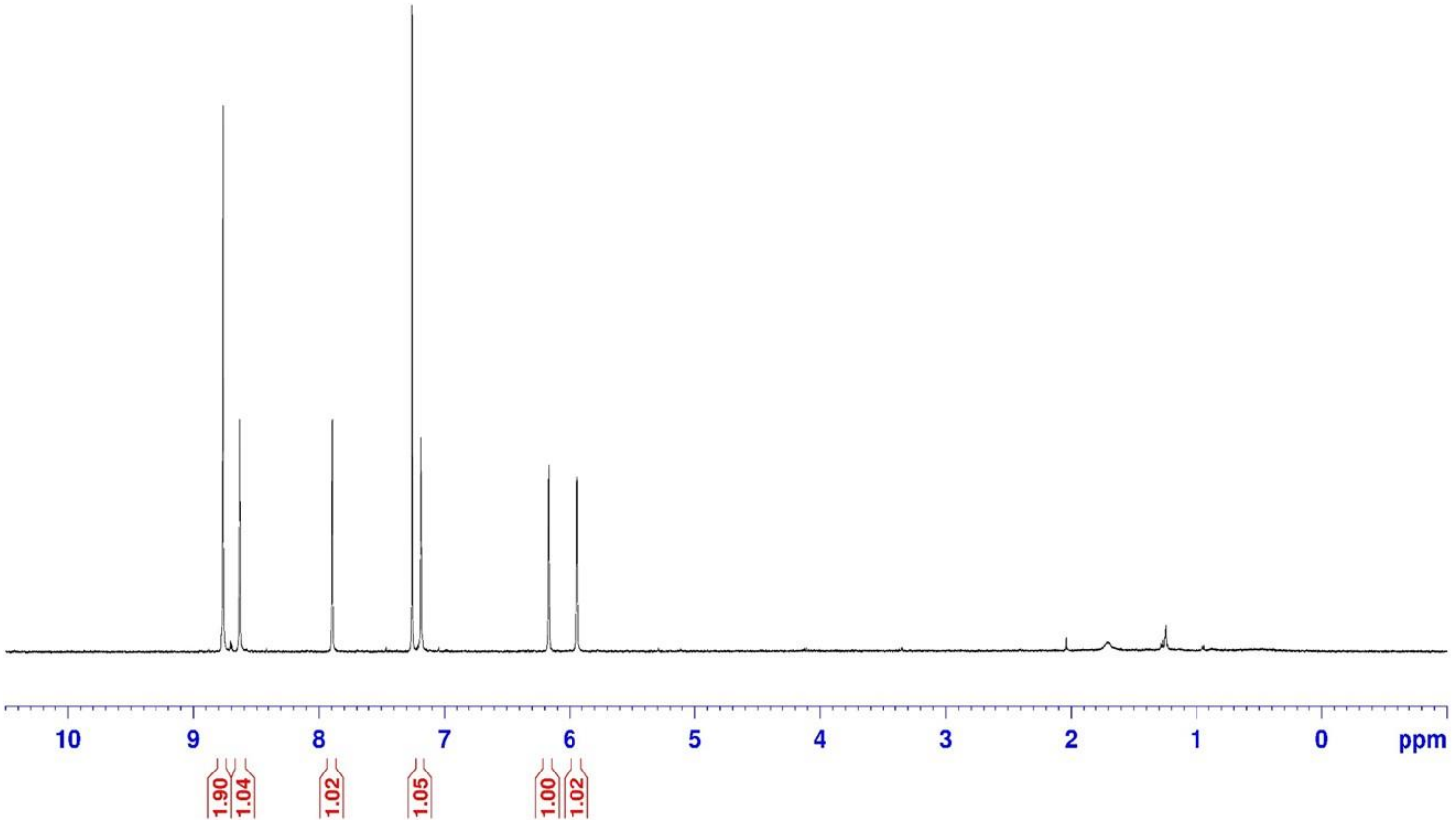

**4h**



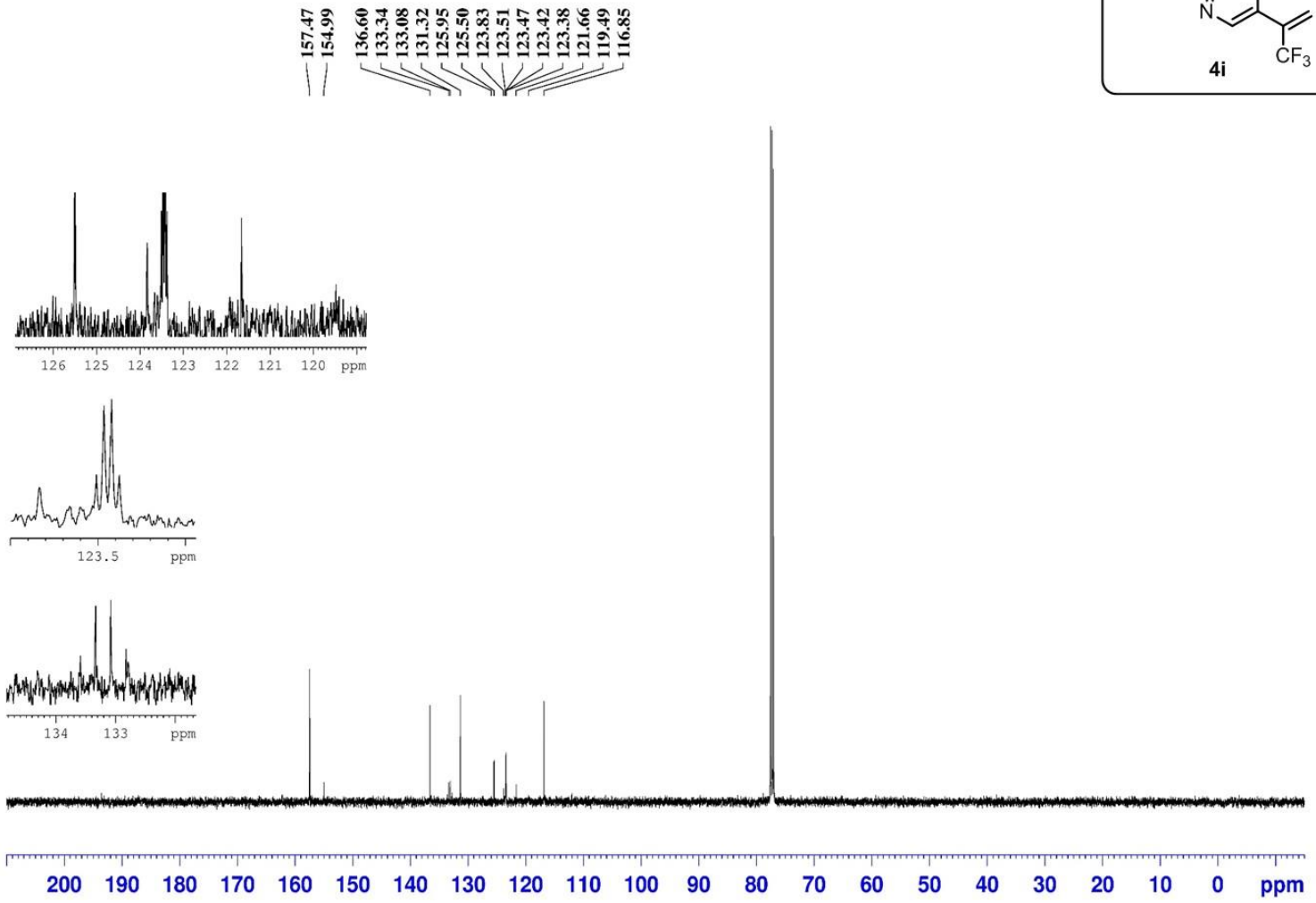
**2–(1H–Imidazol–1–yl)–5–(3,3,3–trifluoroprop–1–en–2–yl)pyrimidine**
**500 MHz, CDCl3**

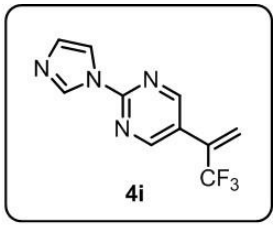


**4i**

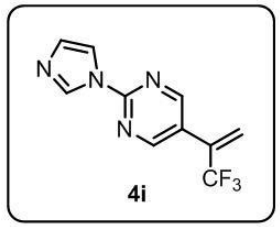


**2–(1H–Imidazol–1–yl)–5–(3,3,3–trifluoroprop–1–en–2–yl)pyrimidine**
**125 MHz, CDCl3**

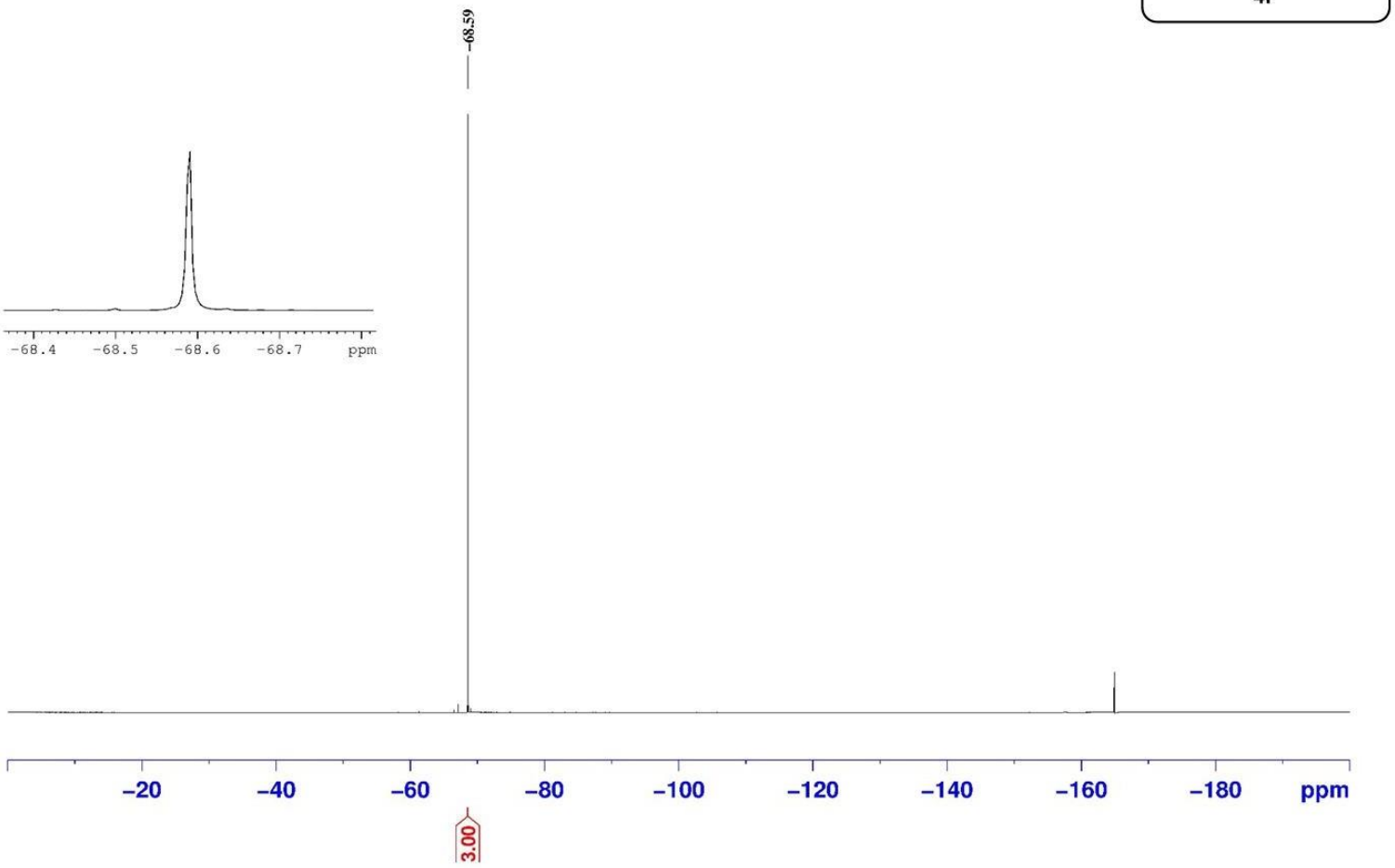


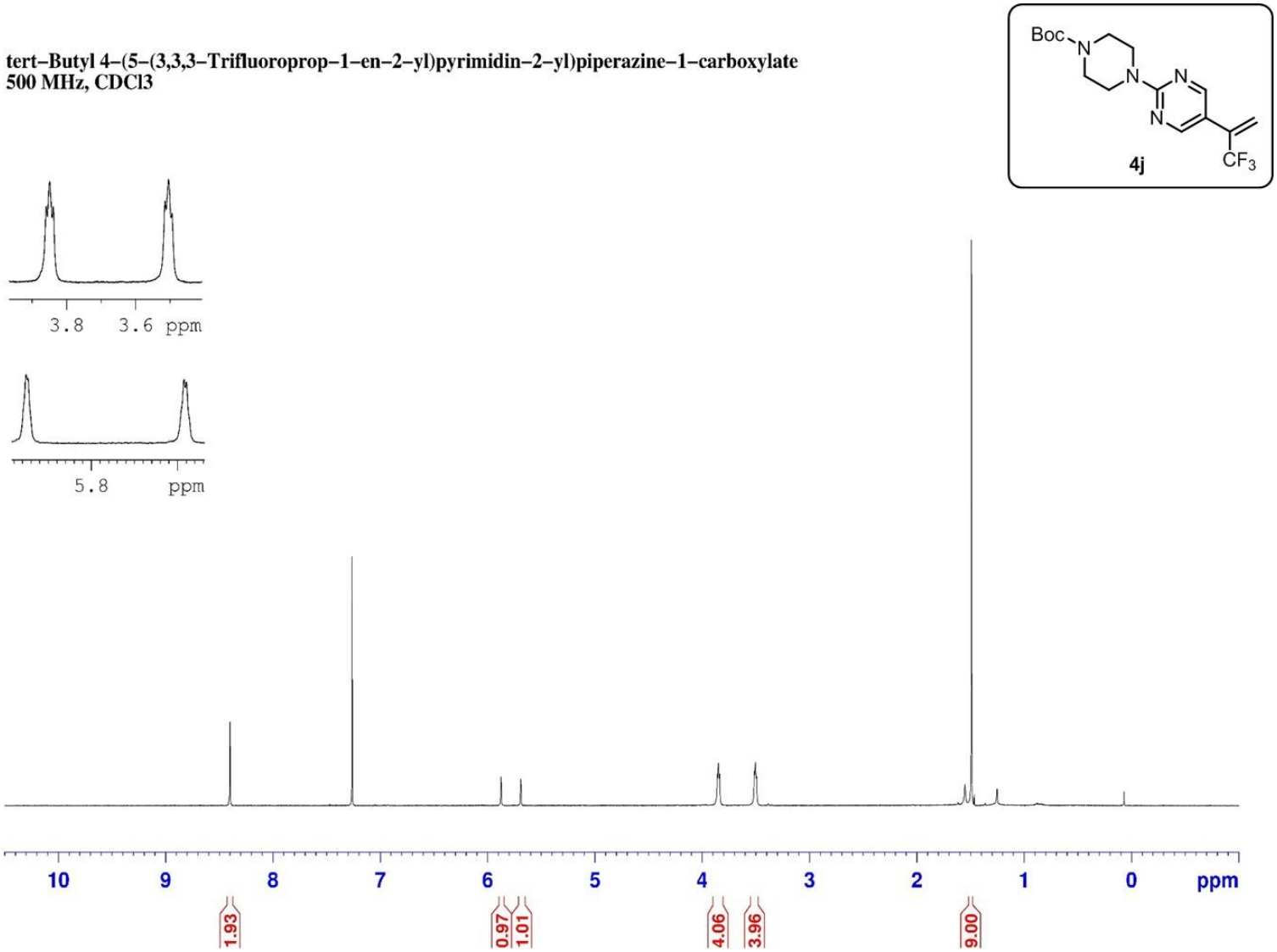
**2–(1H–imidazol–1–yl)–5–(3,3,3–trifluoroprop–1–en–2–yl)pyrimidine**
**CDCl3, 471 MHz**



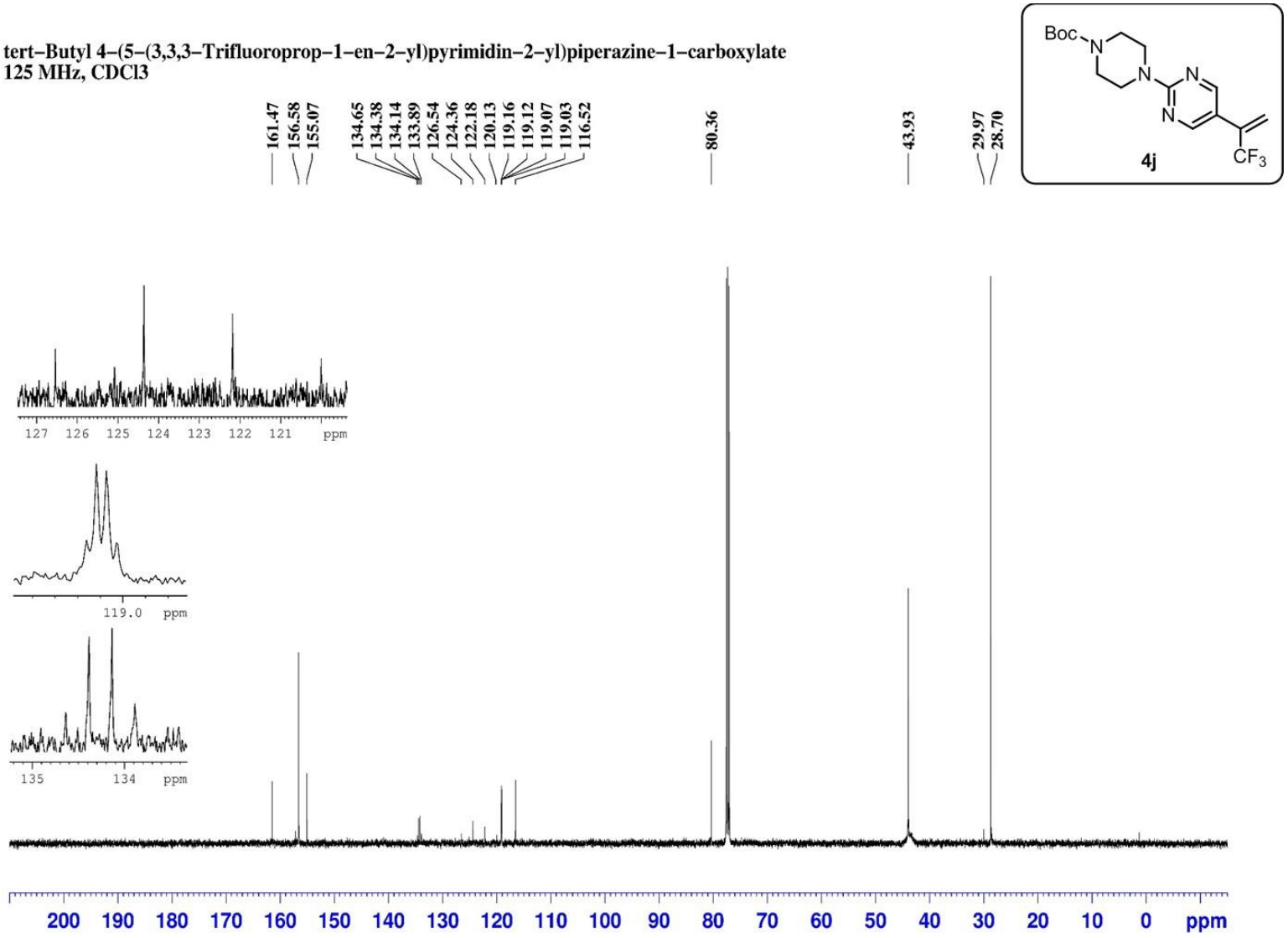
**4i**



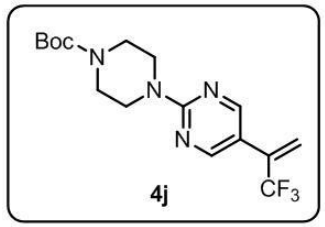
**tert–Butyl 4–(5–(3,3,3–Trifluoroprop–1–en–2–yl)pyrimidin–2–yl)piperazine–1–carboxylate**
**500 MHz, CDCl3**



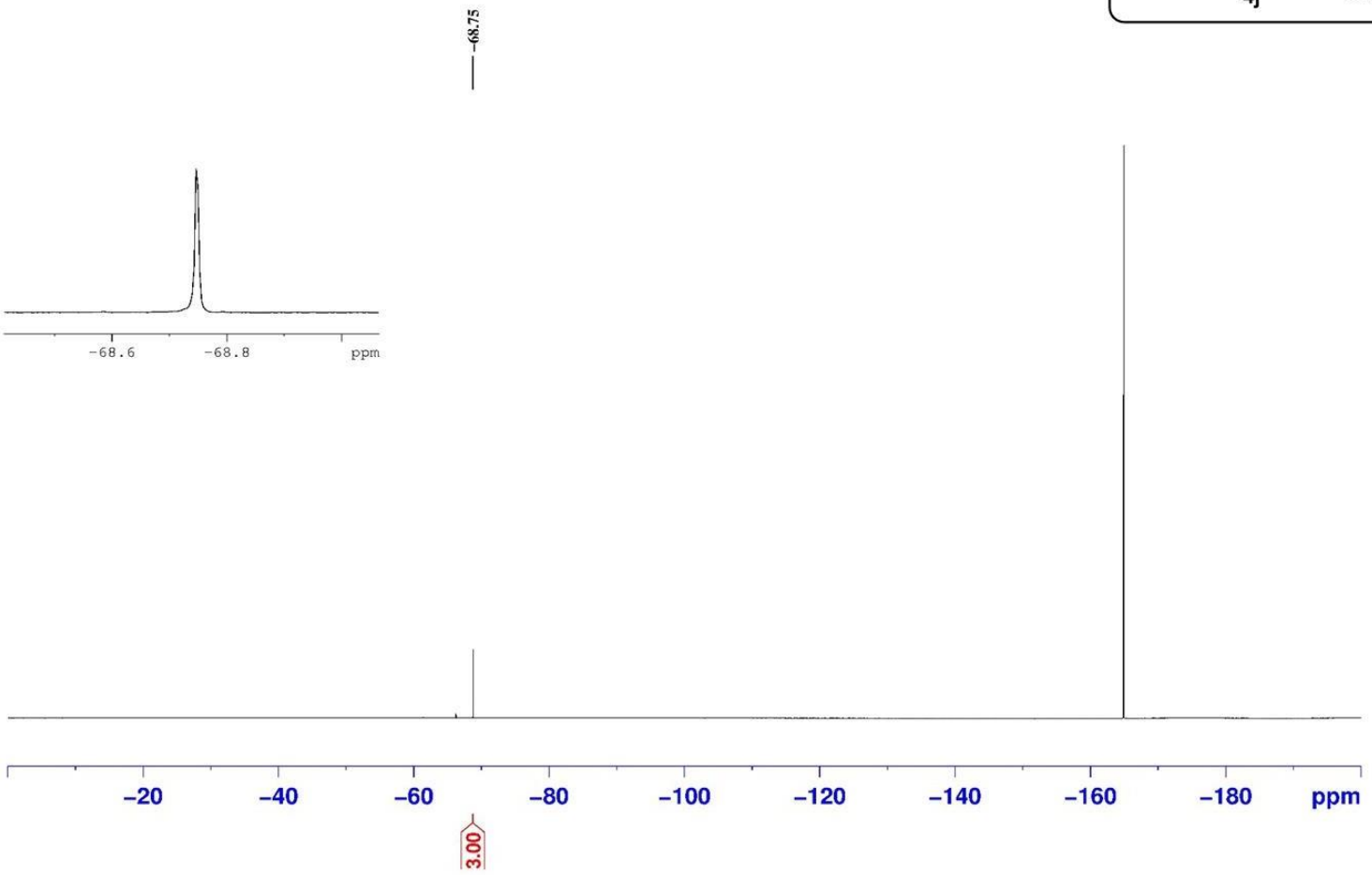
**tert-Butyl 4-(5-(3,3,3-Trifluoroprop-1-en-2-yl)pyrimidin-2-yl)piperazine-1-carboxylate**
**125 MHz, CDCl3**



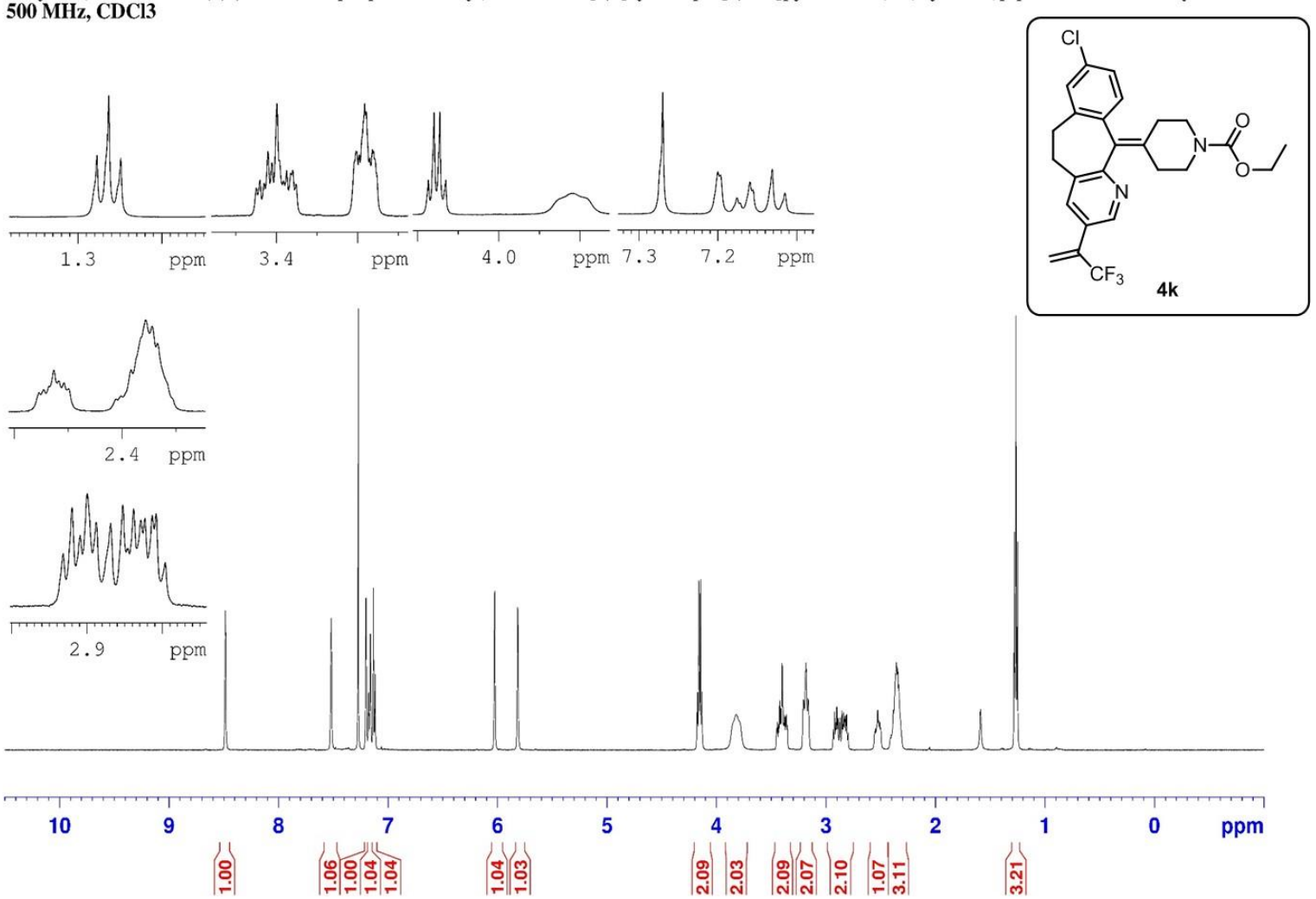
**tert-butyl 4-(5-(3,3,3-trifluoroprop-1-en-2-yl)pyrimidin-2-yl)piperazine-1-carboxylate**
**CDCl3, 471 MHz**



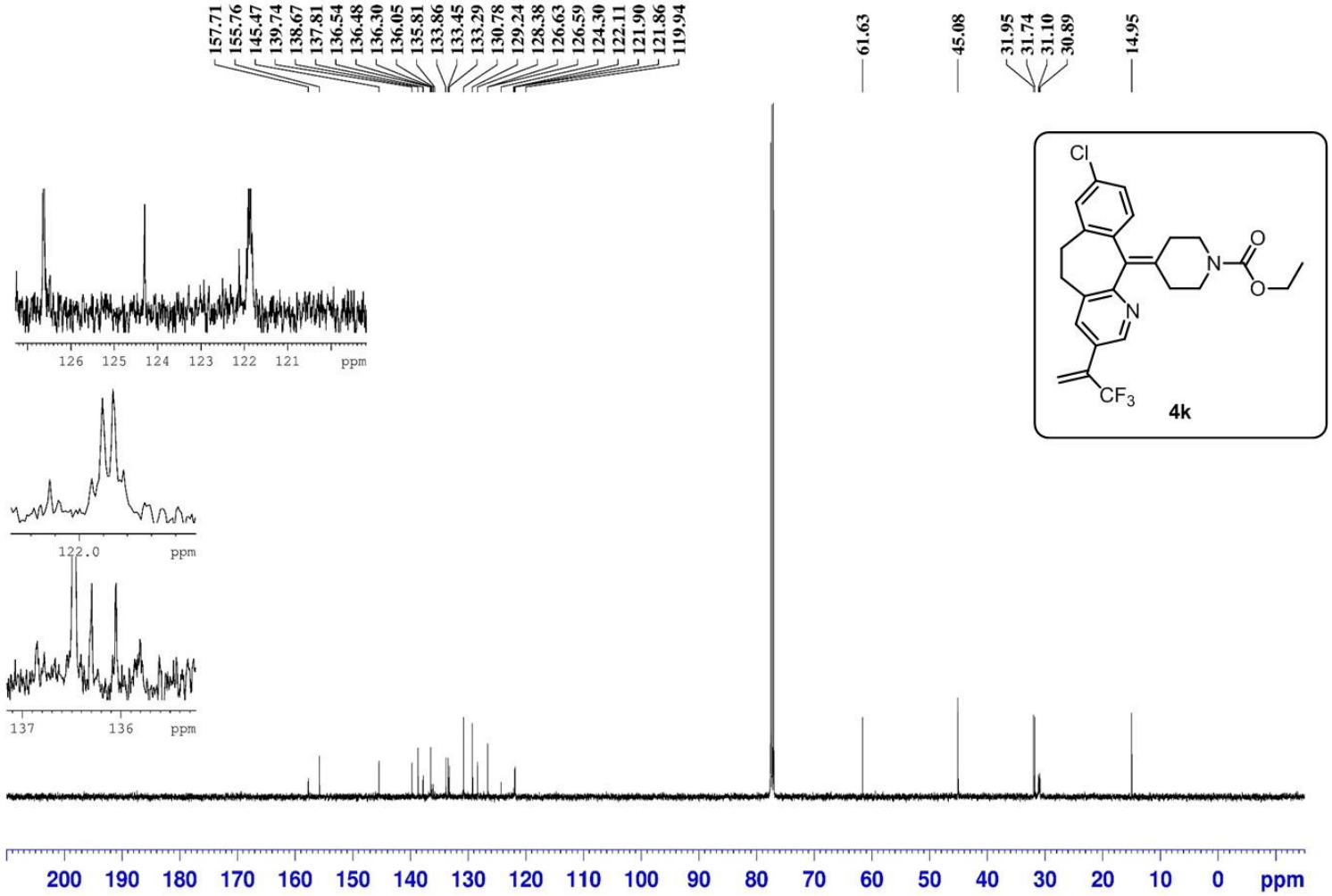

**4j**



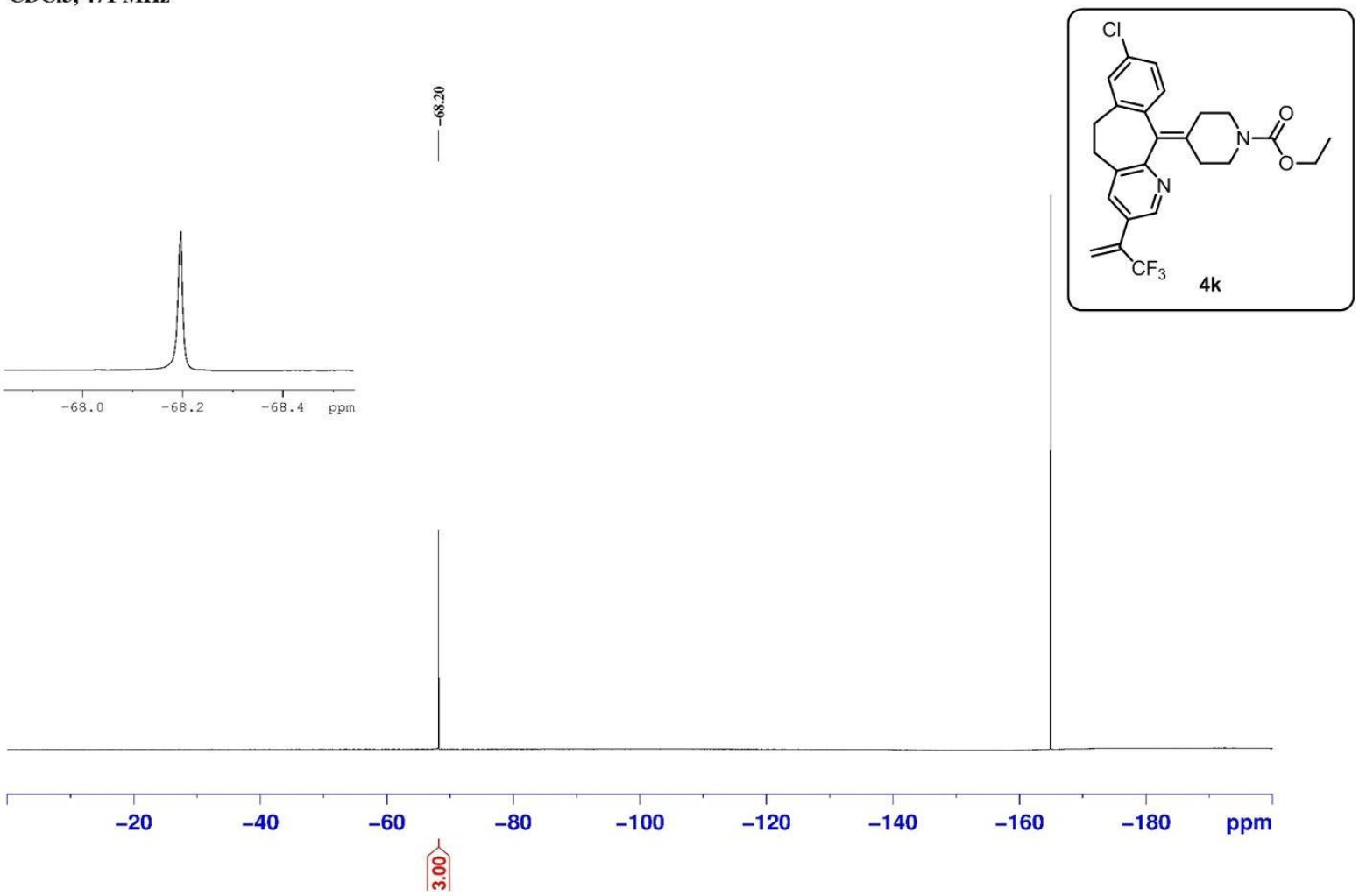
**Ethyl 4–(8–Chloro–3–(3,3,3–trifluoroprop–1–en–2–yl)–5H–benzo[5,6]cyclohepta[1,2–b]pyridin–11(6H)–ylidene)piperidine–1–carboxylate**
**500 MHz, CDCl3**



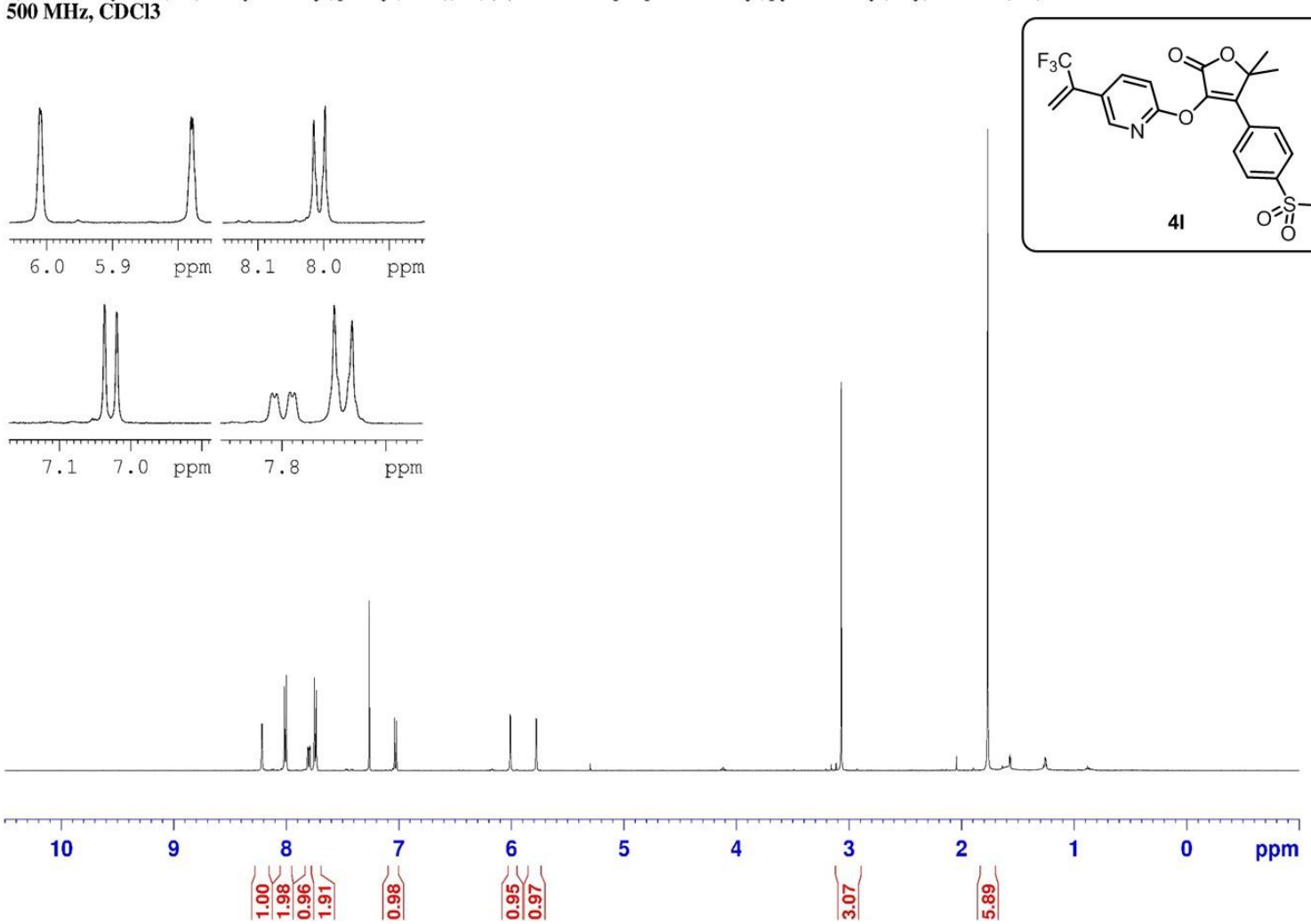
**Ethyl 4−(8−Chloro−3−(3,3,3−trifluoroprop−1−en−2−yl)−5H−benzo[5,6]cyclohepta[1,2−b]pyridin−11(6H)−ylidene)piperidine−1−carboxylate**
**125 MHz, CDCl3**



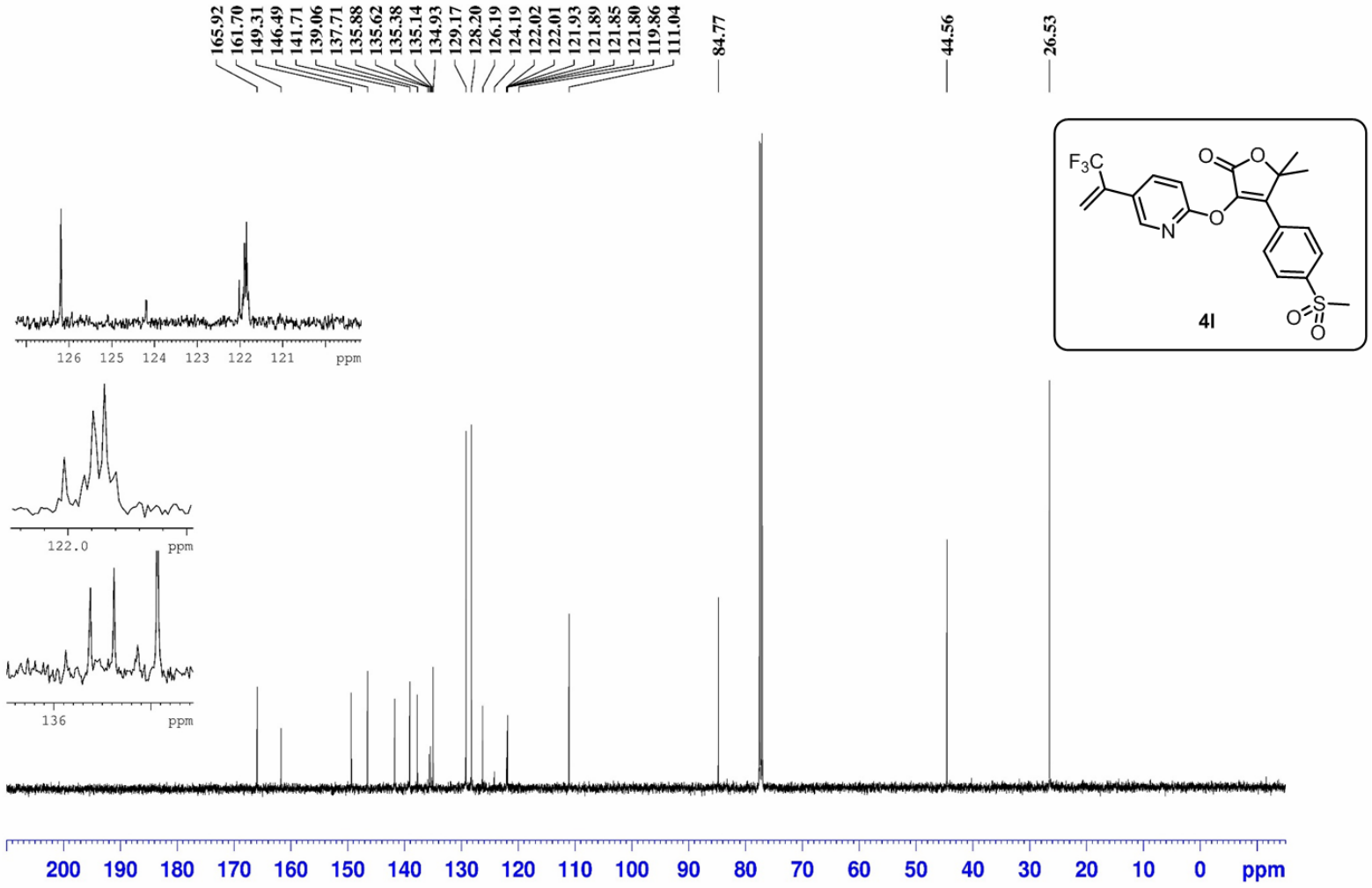
**Ethyl 4–(8–chloro–3–(3,3,3–trifluoroprop–1–en–2–yl)–5H–benzo[5,6]cyclohepta[1,2–b]pyridin–11(6H)–ylidene)piperidine–1–carboxyl**
**CDCl3, 471 MHz**



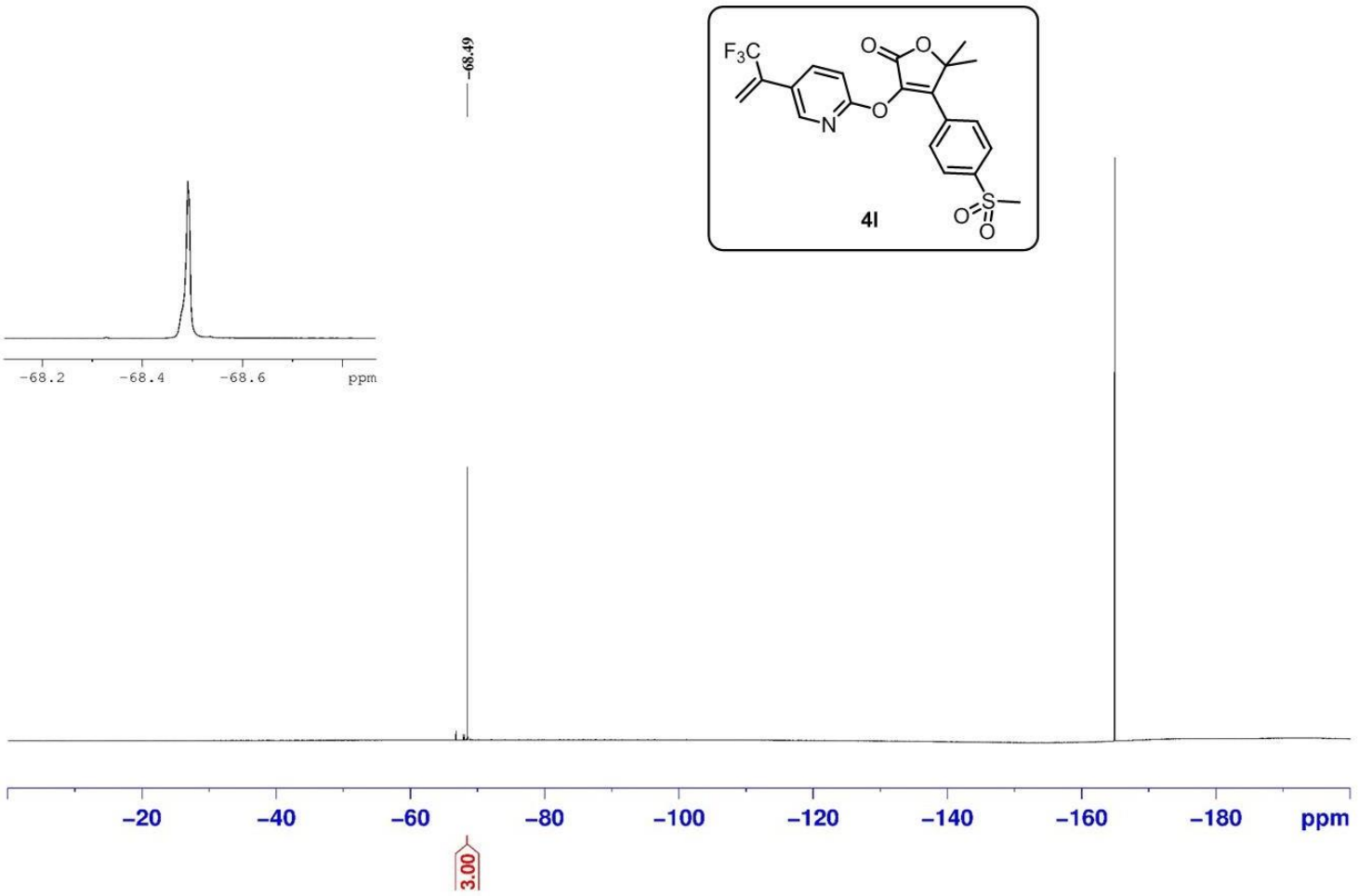
**5,5–Dimethyl–4–(4–(methylsulfonyl)phenyl)–3–((5–(3,3,3–trifluoroprop–1–en–2–yl)pyridin–2–yl)oxy)furan–2(5H)–one**
**500 MHz, CDCl3**



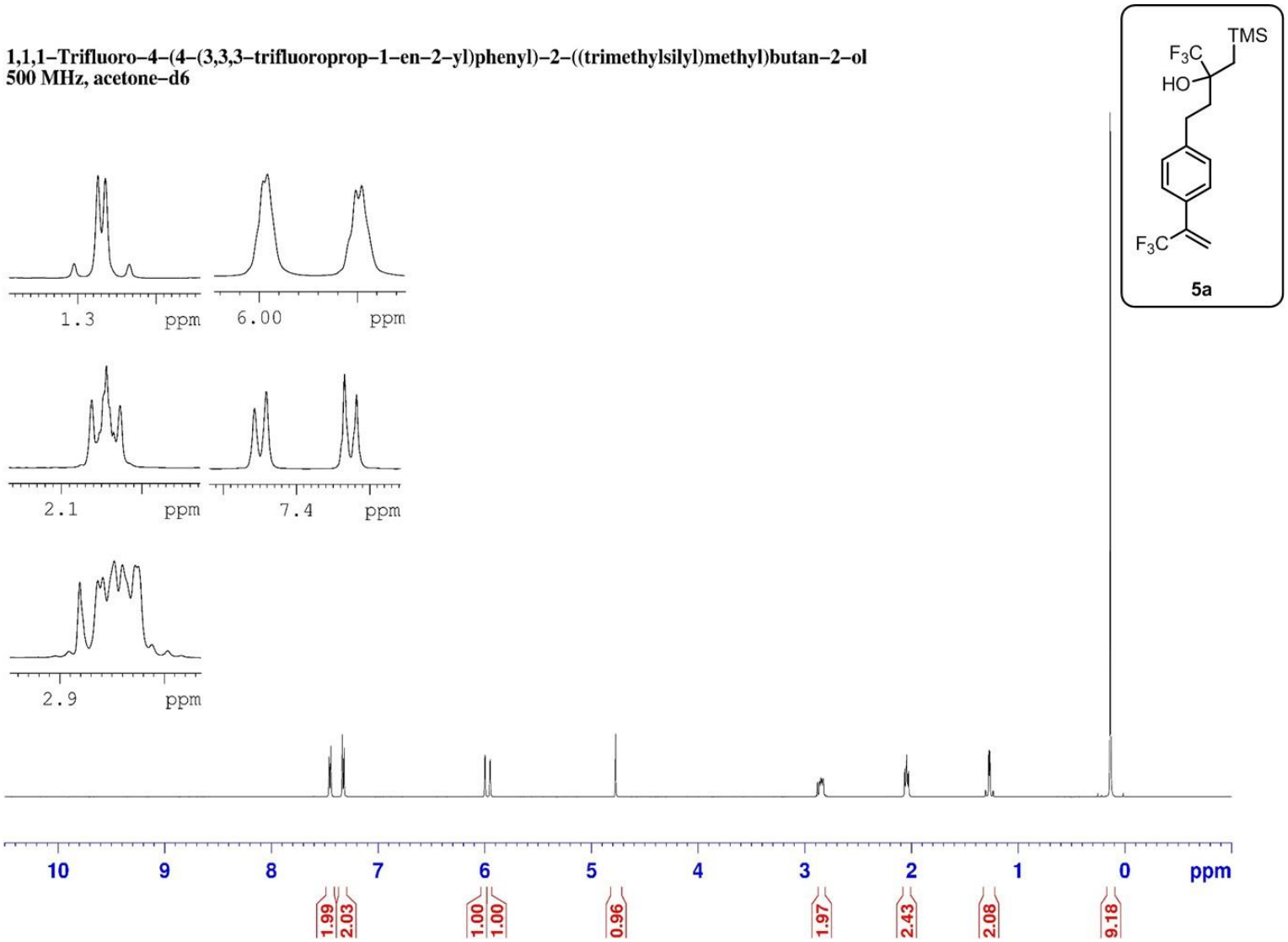
**5,5–Dimethyl–4–(4–(methylsulfonyl)phenyl)–3–((5–(3,3,3–trifluoroprop–1–en–2–yl)pyridin–2–yl)oxy)furan–2(5H)–one**
**125 MHz, CDCl3**



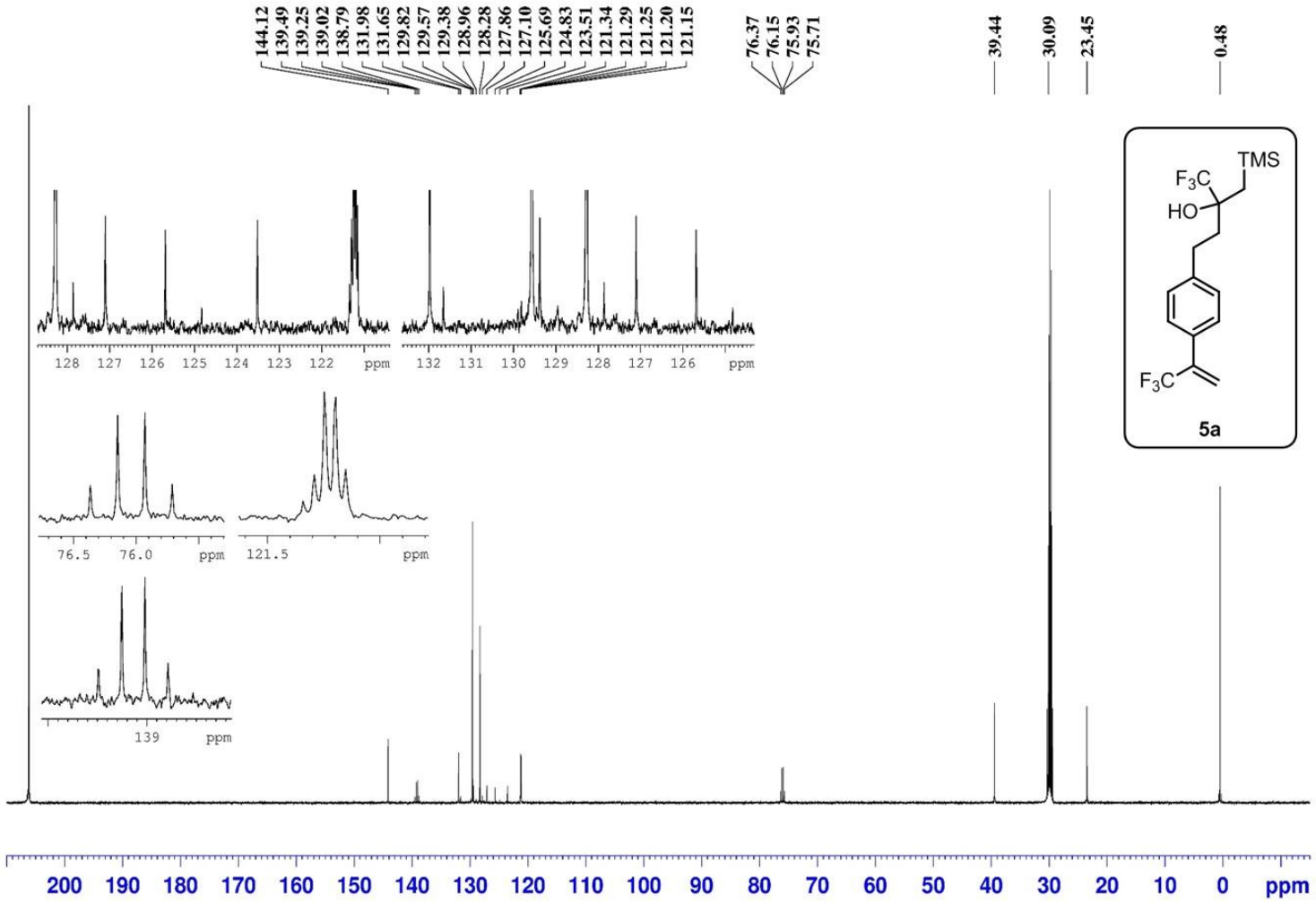
**5,5−dimethyl−4−(4−(methylsulfonyl)phenyl)−3−((5−(3,3,3−trifluoroprop−1−en−2−yl)pyridin−2−yl)oxy)furan−2(5H)−one**
**CDCl3, 471 MHz**



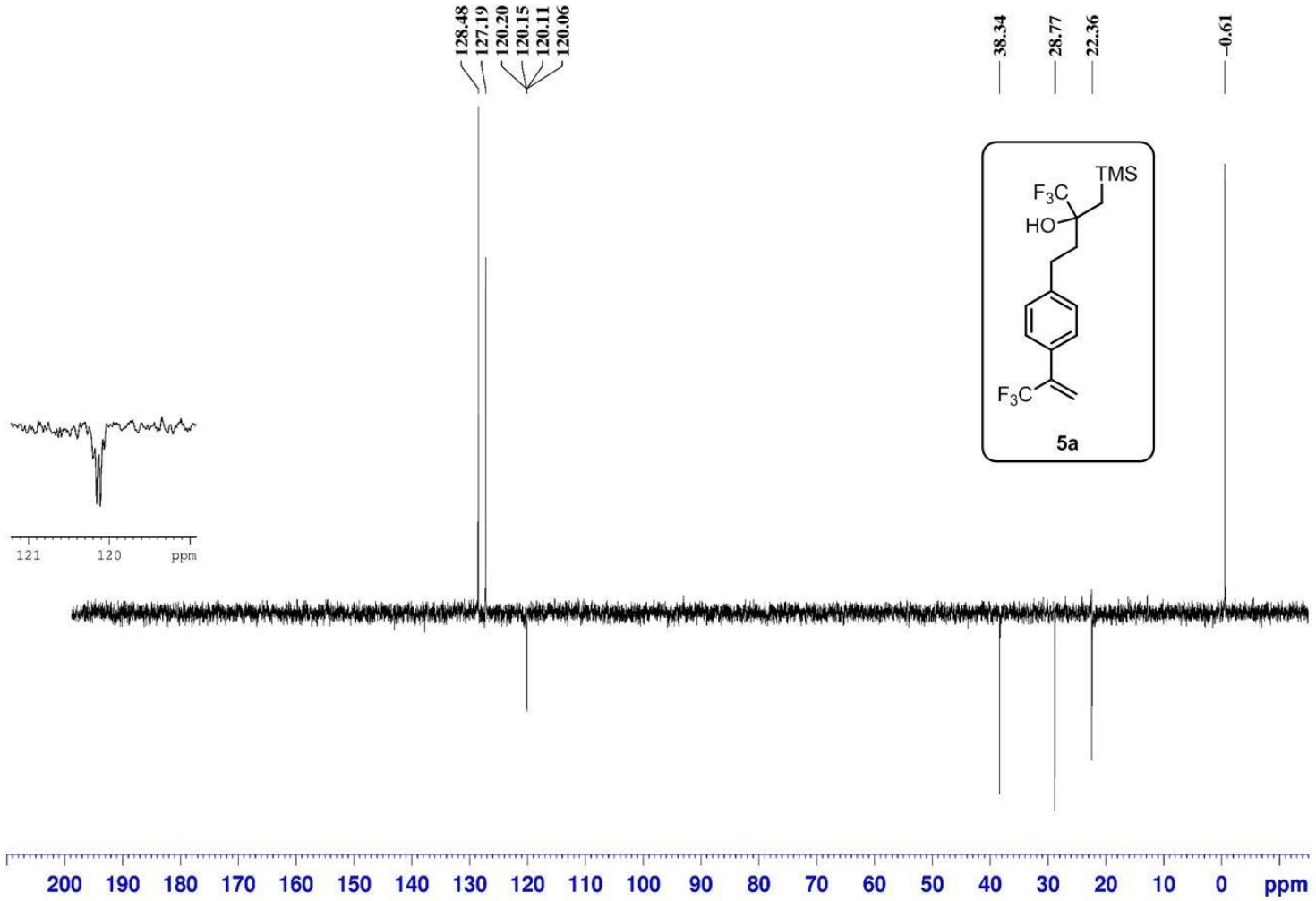
**1,1,1–Trifluoro–4–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)–2–((trimethylsilyl)methyl)butan–2–ol**
**500 MHz, acetone–d6**



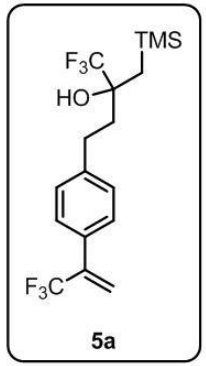
**1,1,1–Trifluoro–4–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)–2–((trimethylsilyl)methyl)butan–2–ol**
**125 MHz, acetone–d6**

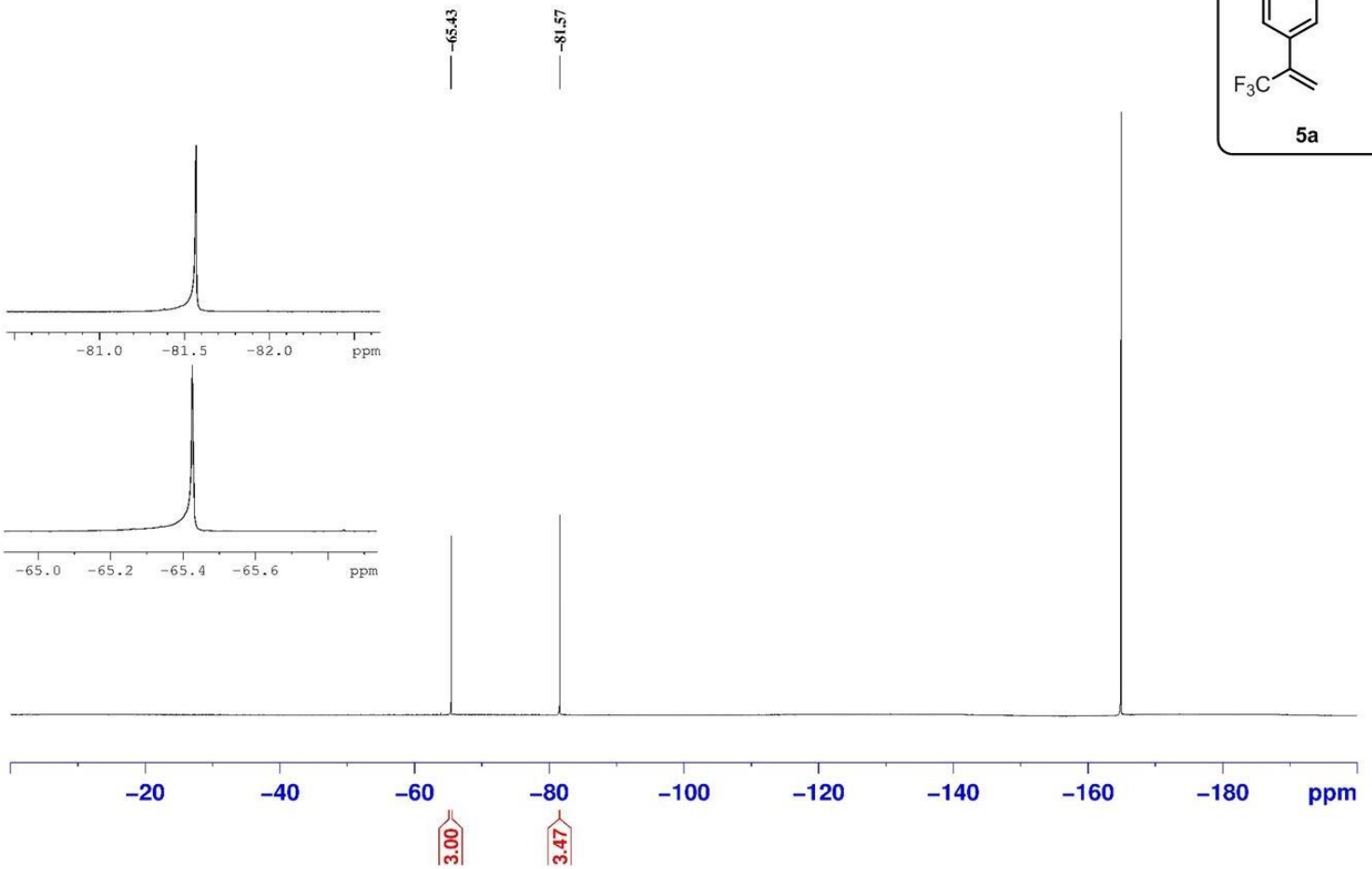


**1,1,1–Trifluoro–4–(4–(3,3,3–trifluoroprop–1–en–2–yl)phenyl)–2–((trimethylsilyl)methyl)butan–2–ol**
**125 MHz, acetone–d6, DEPT135**

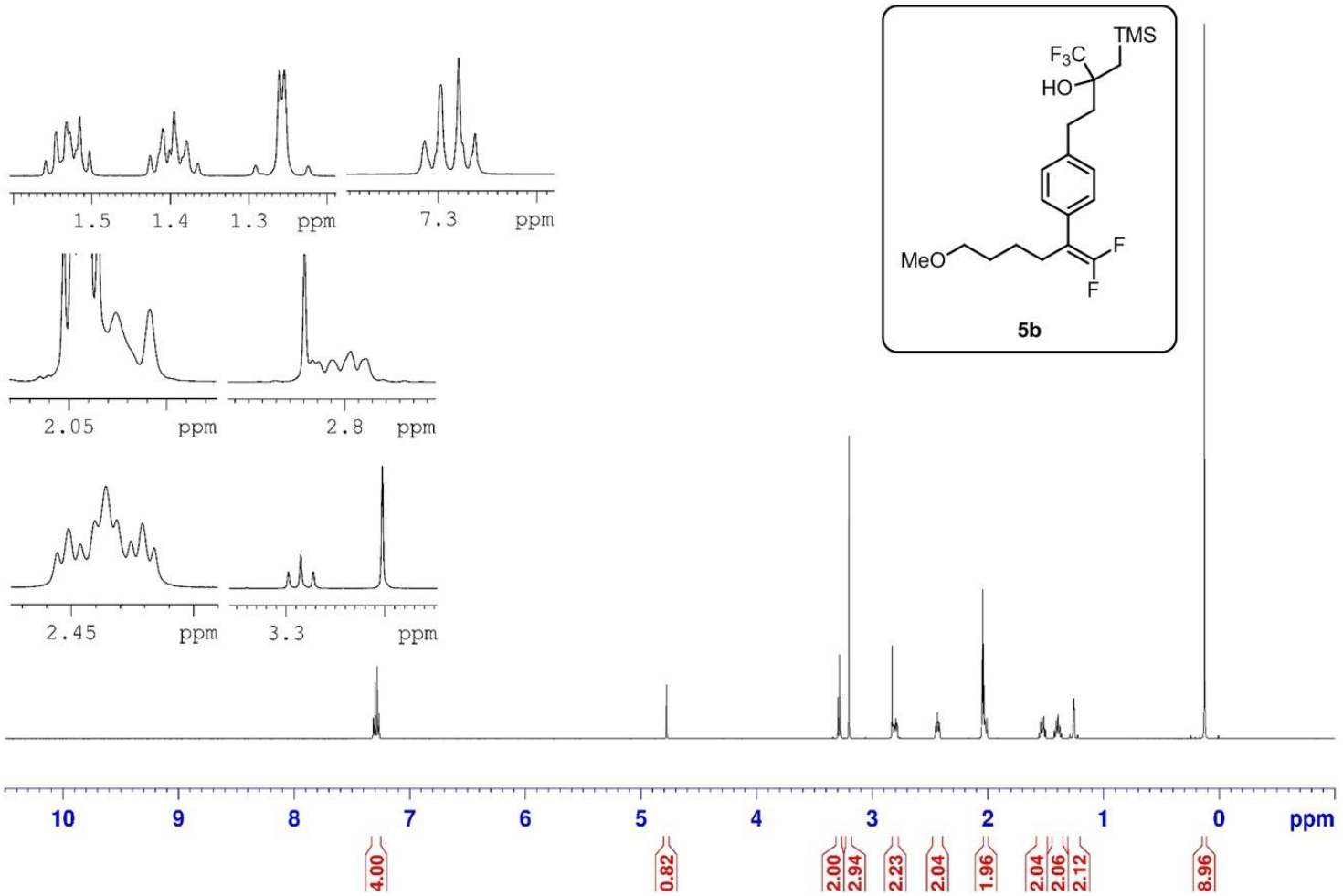


**1,1,1−trifluoro−4−(4−(3,3,3−trifluoroprop−1−en−2−yl)phenyl)−2−((trimethylsilyl)methyl)butan−2−ol**
**Acetone−d6, 471 MHz**

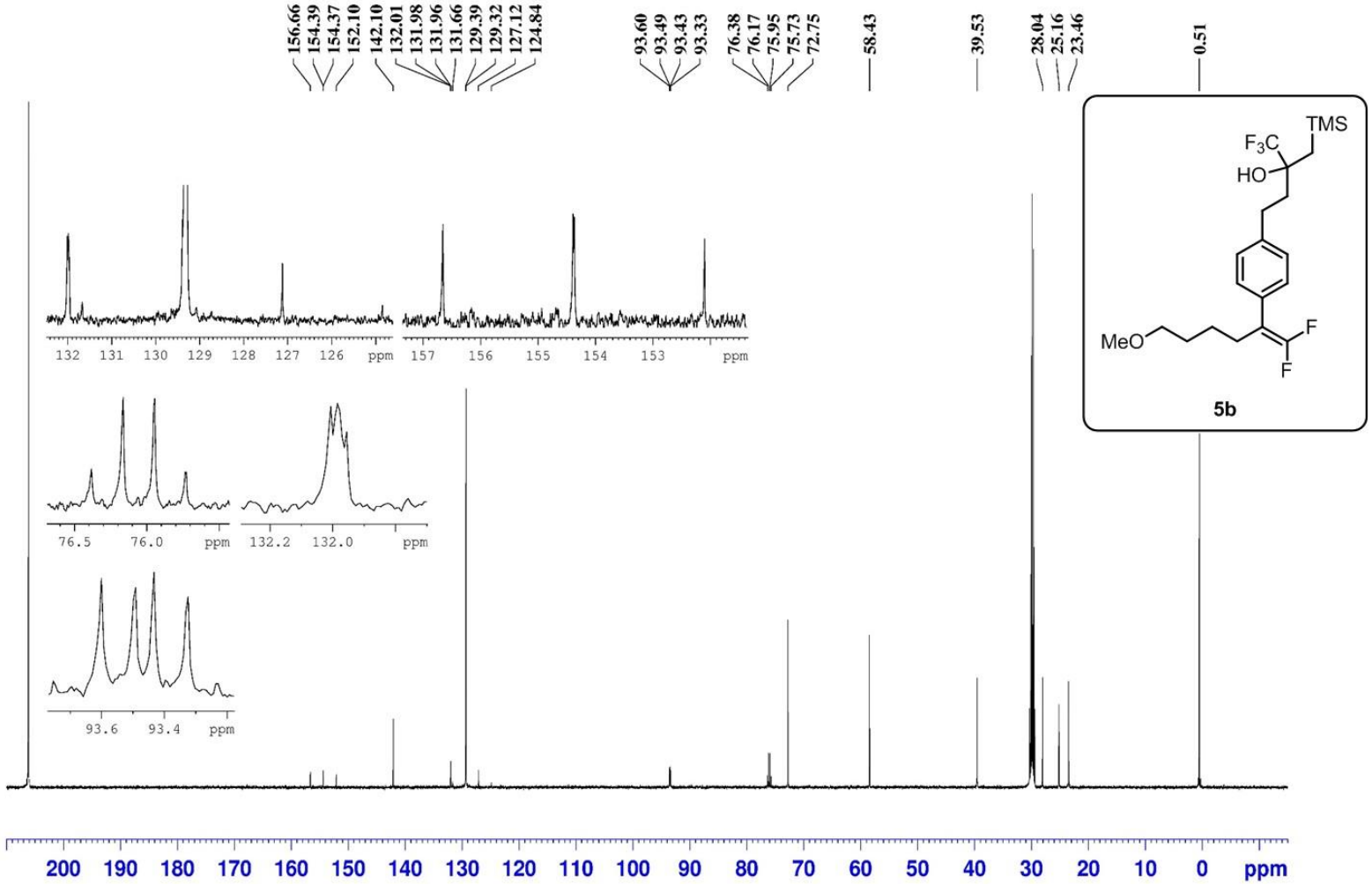


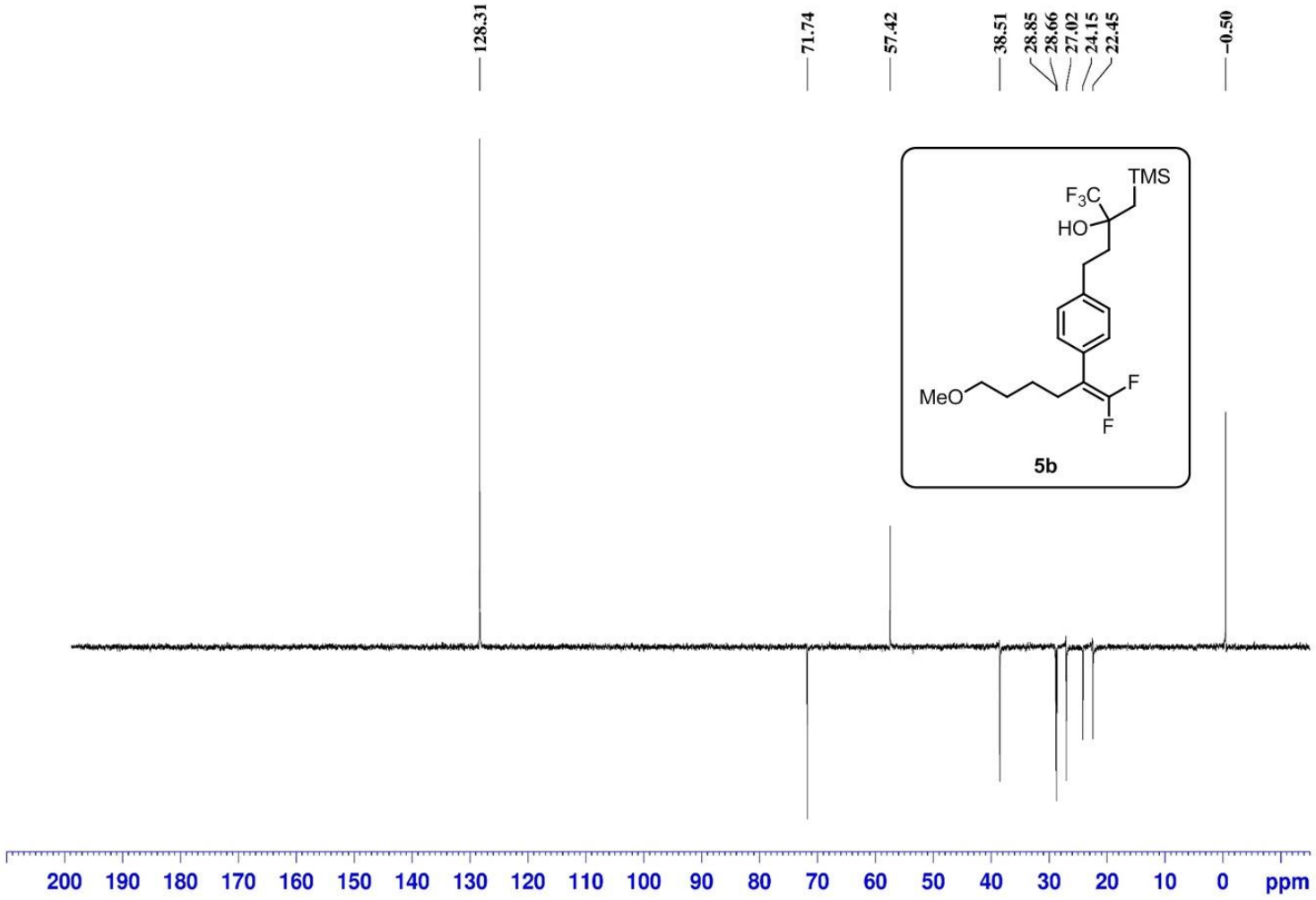
**4–(4–(1,1–Difluoro–6–methoxyhex–1–en–2–yl)phenyl)–1,1,1–trifluoro–2–((trimethylsilyl)methyl)butan–2–ol**
**500 MHz, acetone–d6**



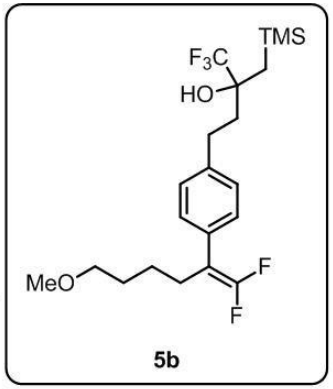
**4–(4–(1,1–Difluoro–6–methoxyhex–1–en–2–yl)phenyl)–1,1,1–trifluoro–2–((trimethylsilyl)methyl)butan–2–ol**
**125 MHz, acetone–d6**



**4–(4–(1,1–Difluoro–6–methoxyhex–1–en–2–yl)phenyl)–1,1,1–trifluoro–2–((trimethylsilyl)methyl)butan–2–ol**
**125 MHz, acetone–d6, DEPT135**

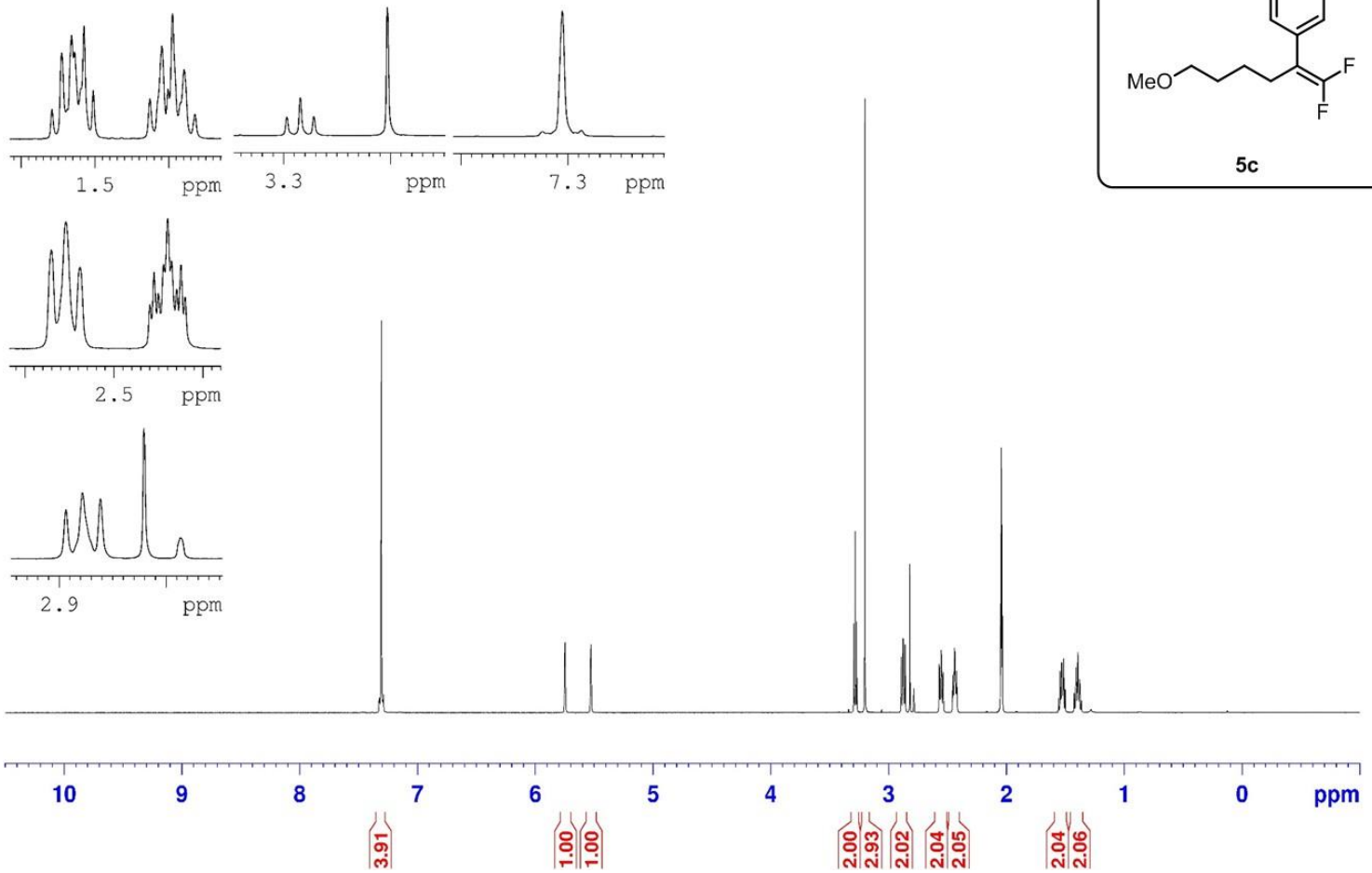


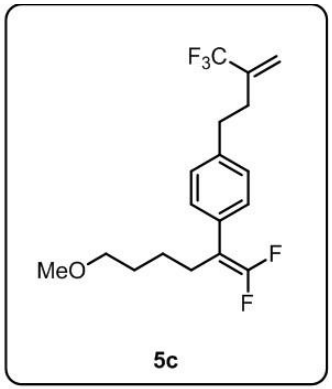
**4–(4–(1,1–difluoro–6–methoxyhex–1–en–2–yl)phenyl)–1,1,1–trifluoro–2–((trimethylsilyl)methyl)butan–2–ol**
**Acetone–d6, 471 MHz**




**5b**

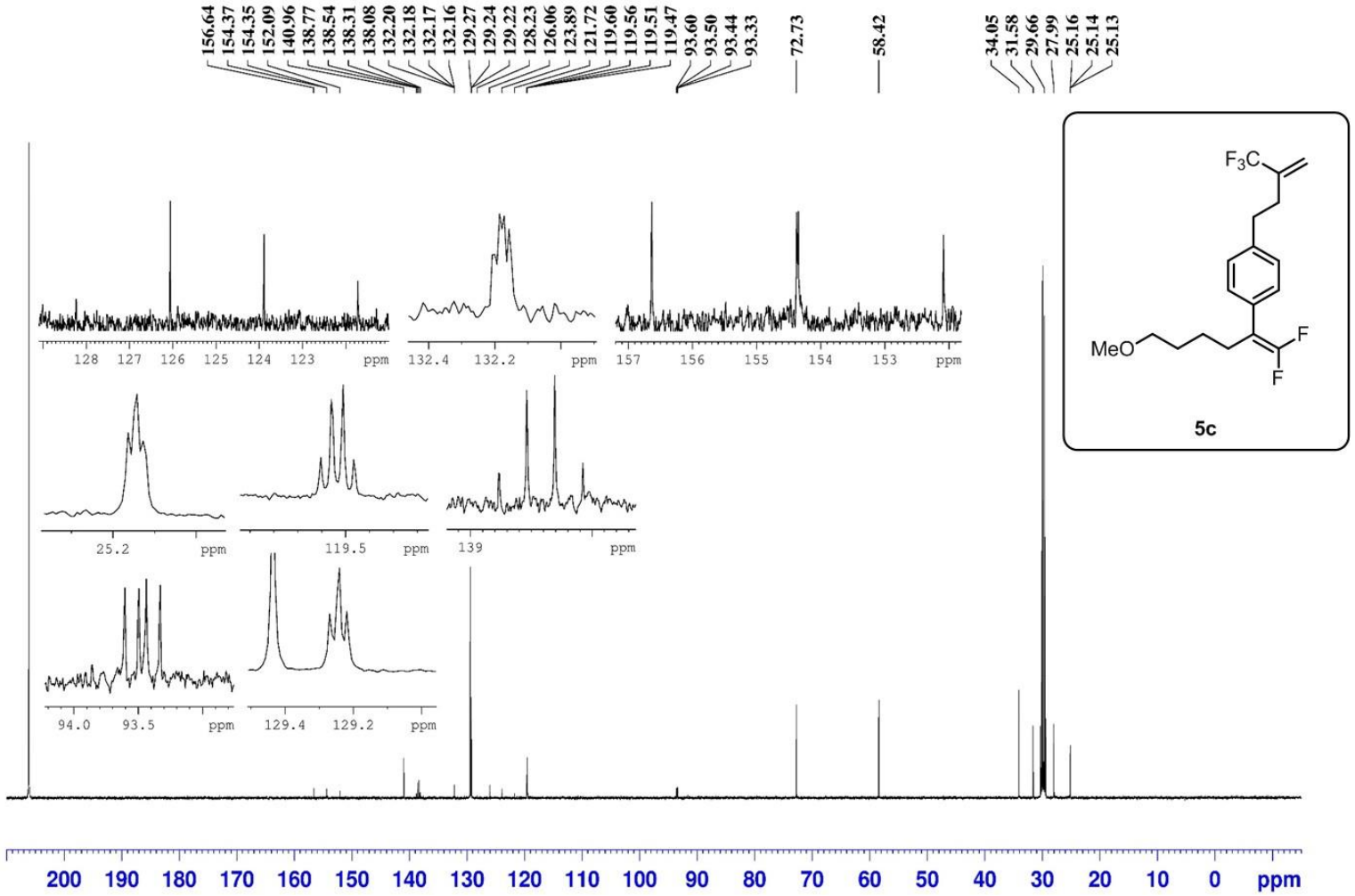
**1–(1,1–Difluoro–6–methoxyhex–1–en–2–yl)–4–(3–(trifluoromethyl)but–3–en–1–yl)benzene**
**500 MHz, acetone–d6**



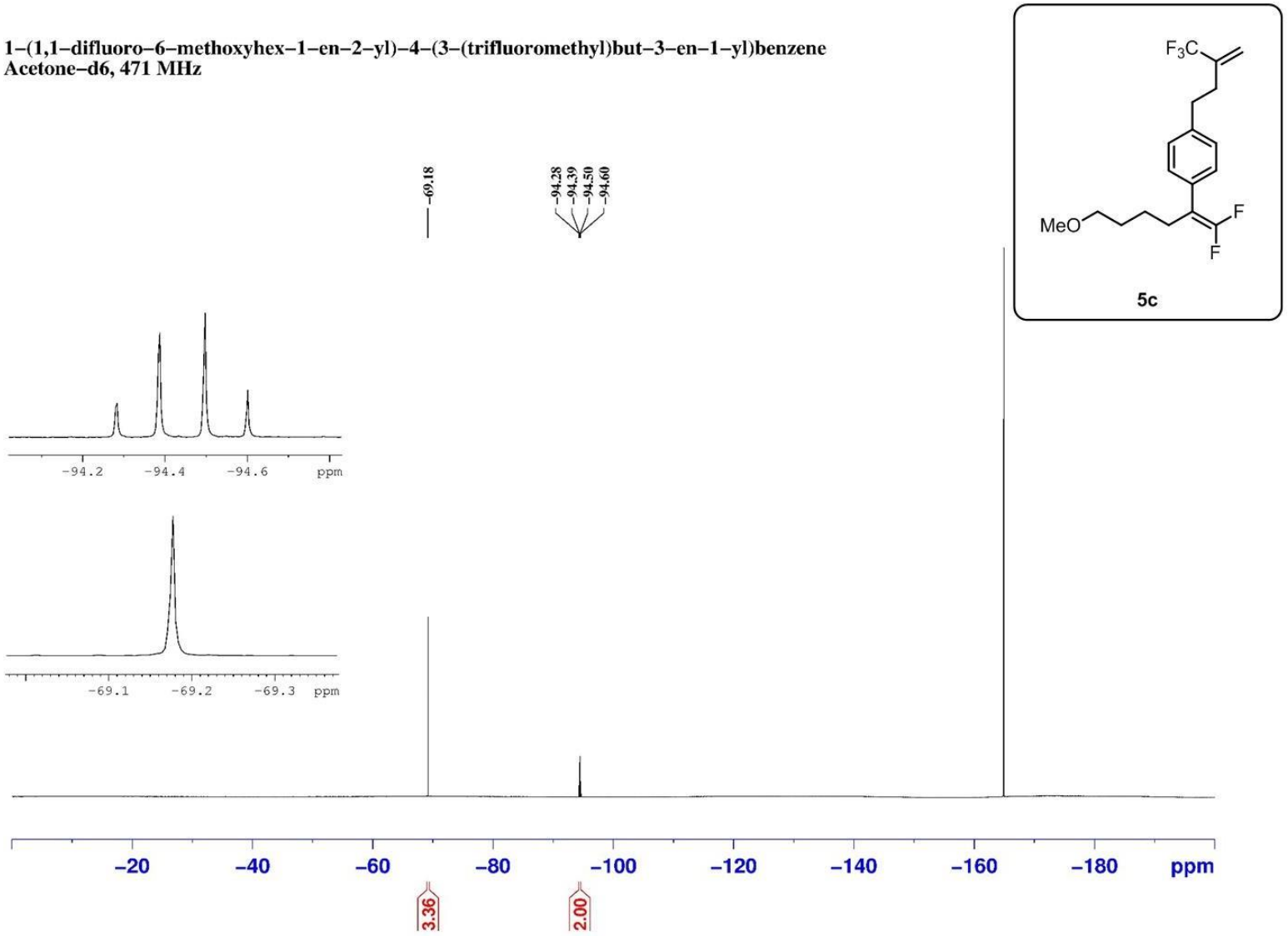




**5c**

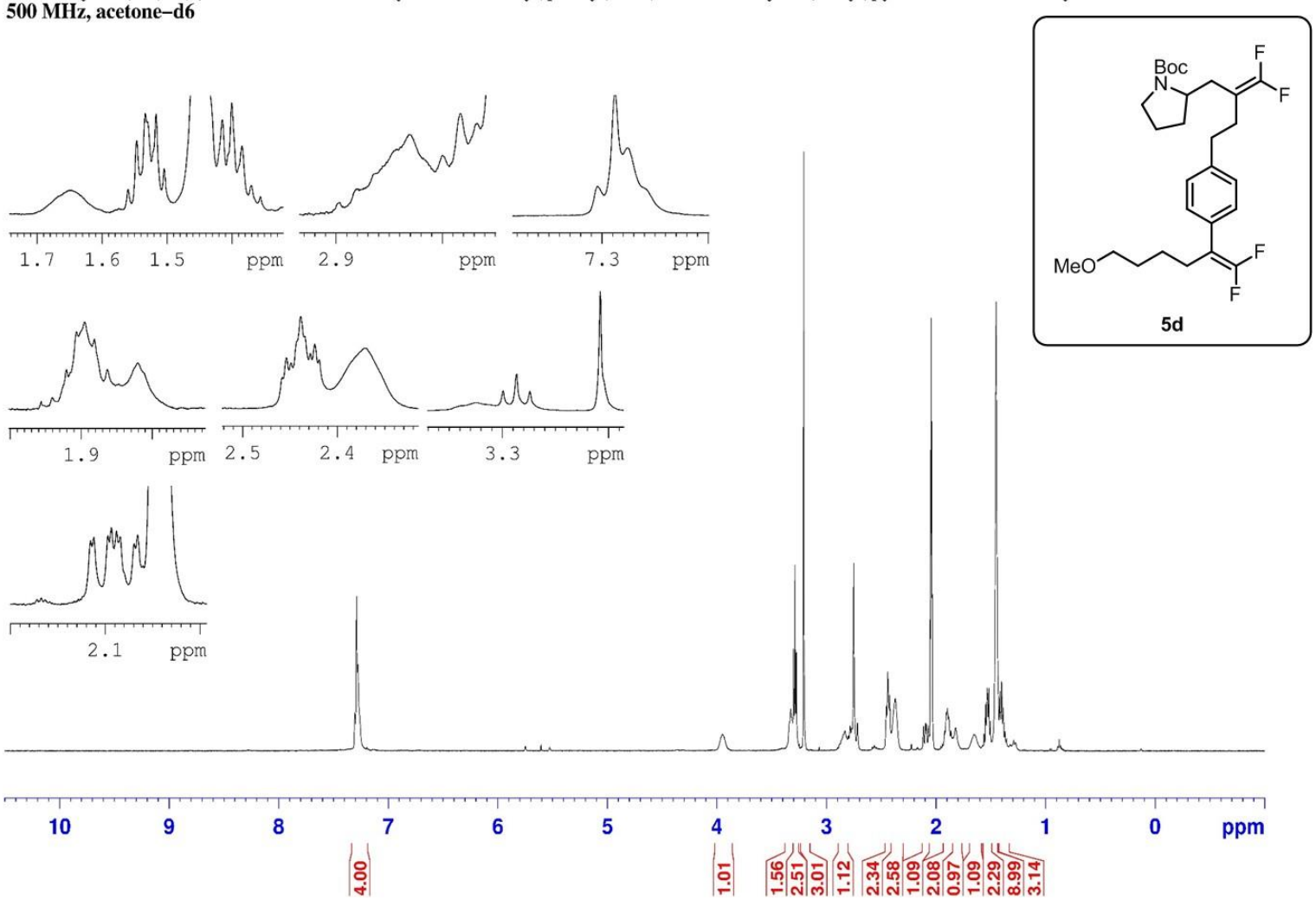
**1–(1,1–Difluoro–6–methoxyhex–1–en–2–yl)–4–(3–(trifluoromethyl)but–3–en–1–yl)benzene**
**125 MHz, acetone–d6**



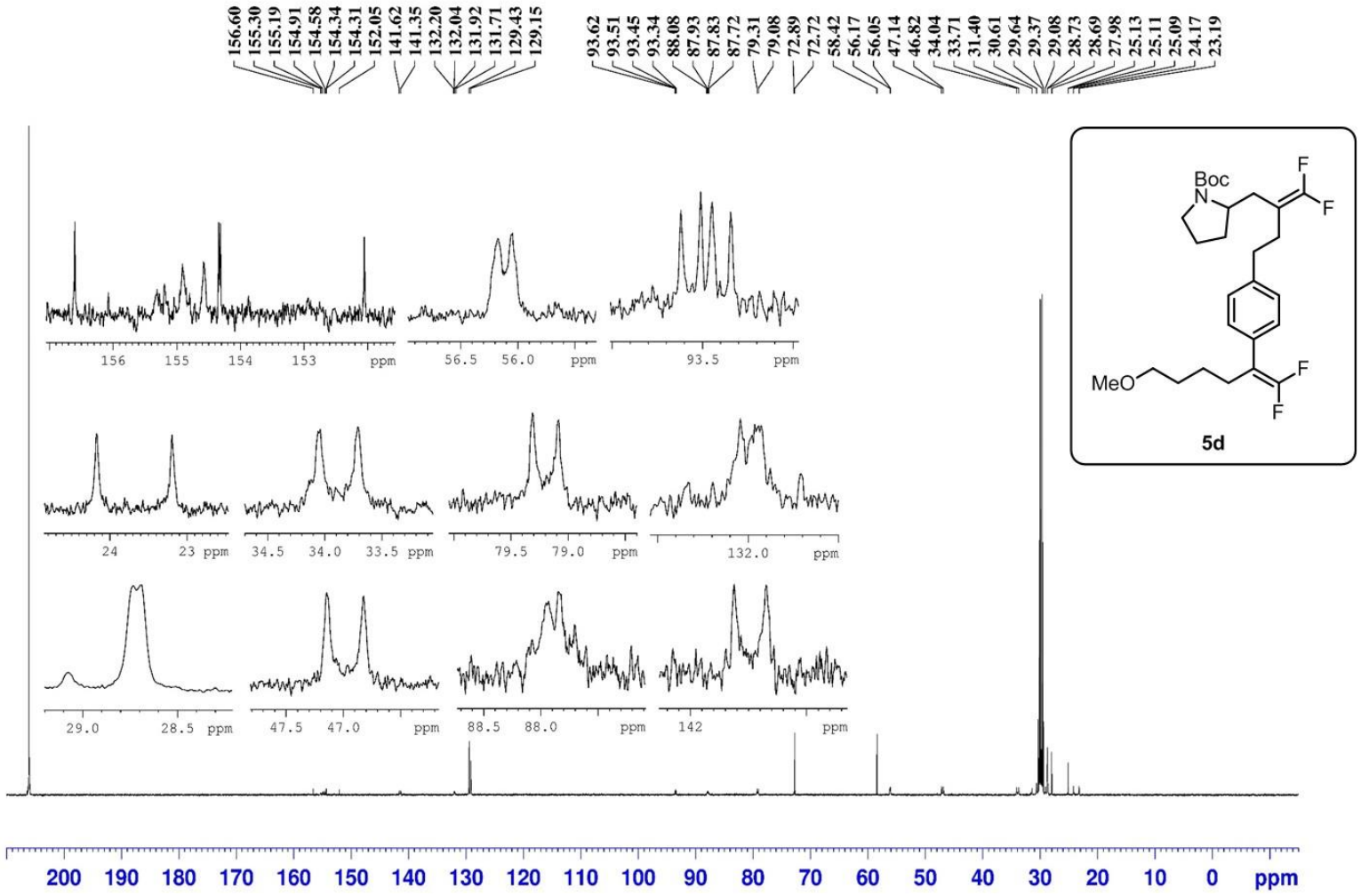
**1–(1,1–difluoro–6–methoxyhex–1–en–2–yl)–4–(3–(trifluoromethyl)but–3–en–1–yl)benzene**
**Acetone–d6, 471 MHz**



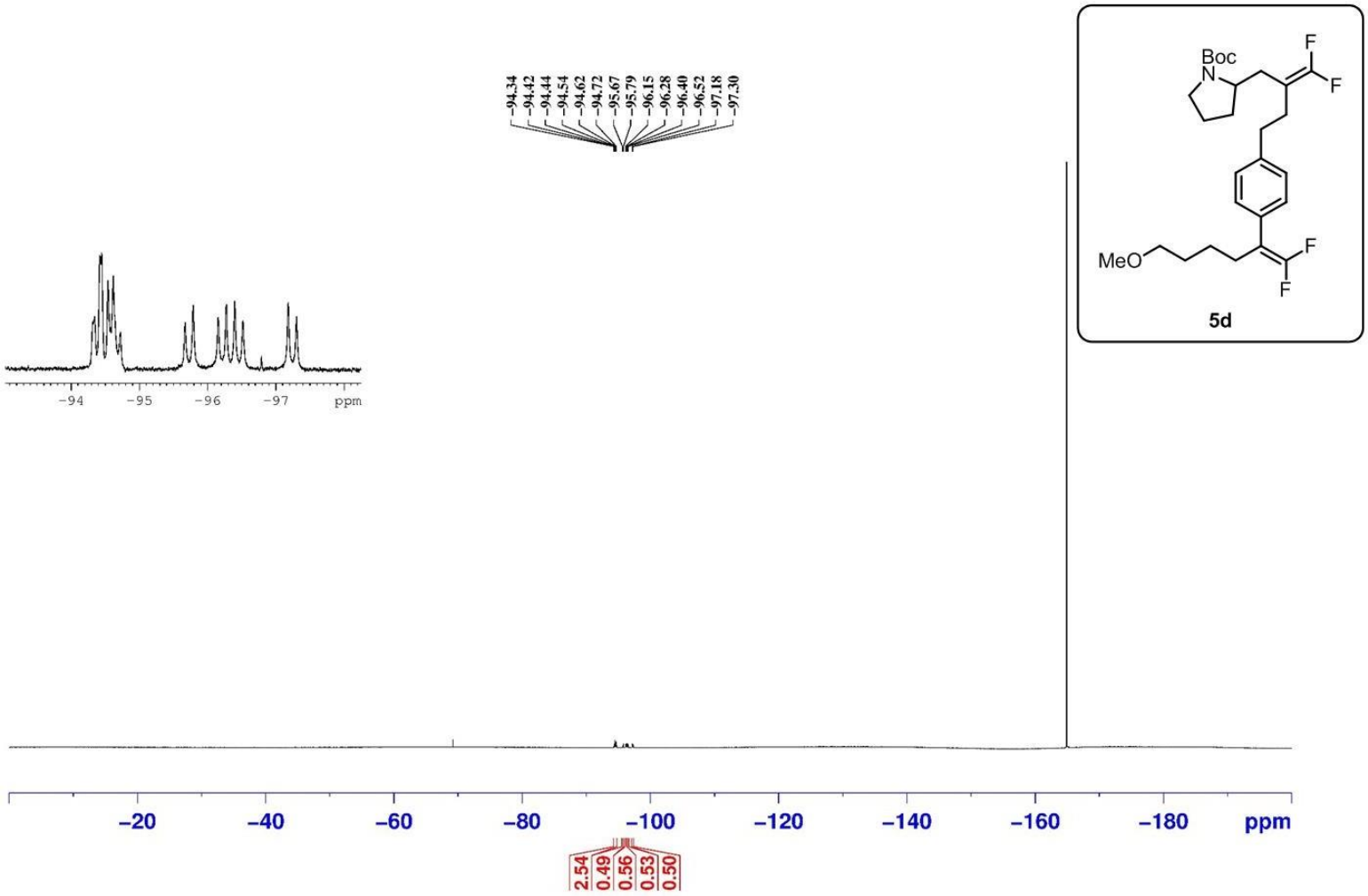
**tert–Butyl 2–(4–(4–(1,1–Difluoro–6–methoxyhex–1–en–2–yl)phenyl)–2–(difluoromethylene)butyl)pyrrolidine–1–carboxylate**
**500 MHz, acetone–d6**



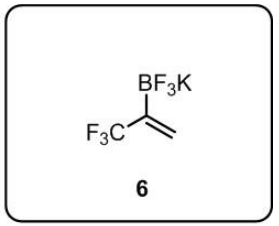
**tert–Butyl 2–(4–(4–(1,1–Difluoro–6–methoxyhex–1–en–2–yl)phenyl)–2–(difluoromethylene)butyl)pyrrolidine–1–carboxylate**
**125 Mhz, acetone–d6**



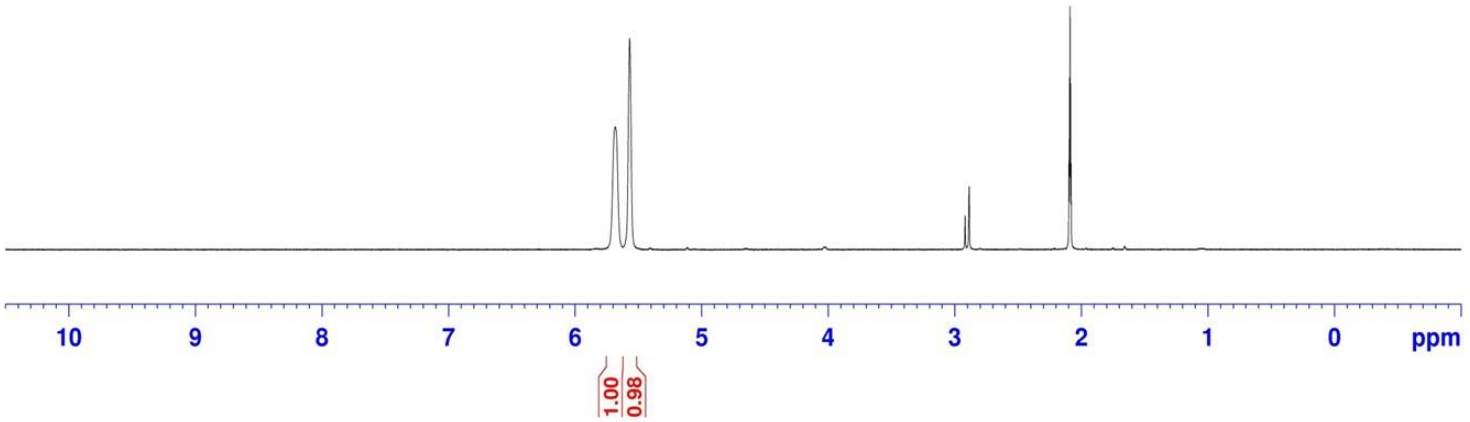
**tert–Butyl 2–(4–(4–(1,1–difluoro–6–methoxyhex–1–en–2–yl)phenyl)–2–(difluoromethylene)butyl)pyrrolidine–1–carboxylate**
**Acetone–d6, 471 MHz**



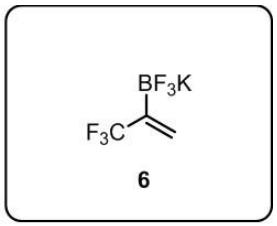
**Potassium Trifluoro(3,3,3−trifluoroprop−1−en−2−yl)borate**
**500 MHz, acetone−d6**

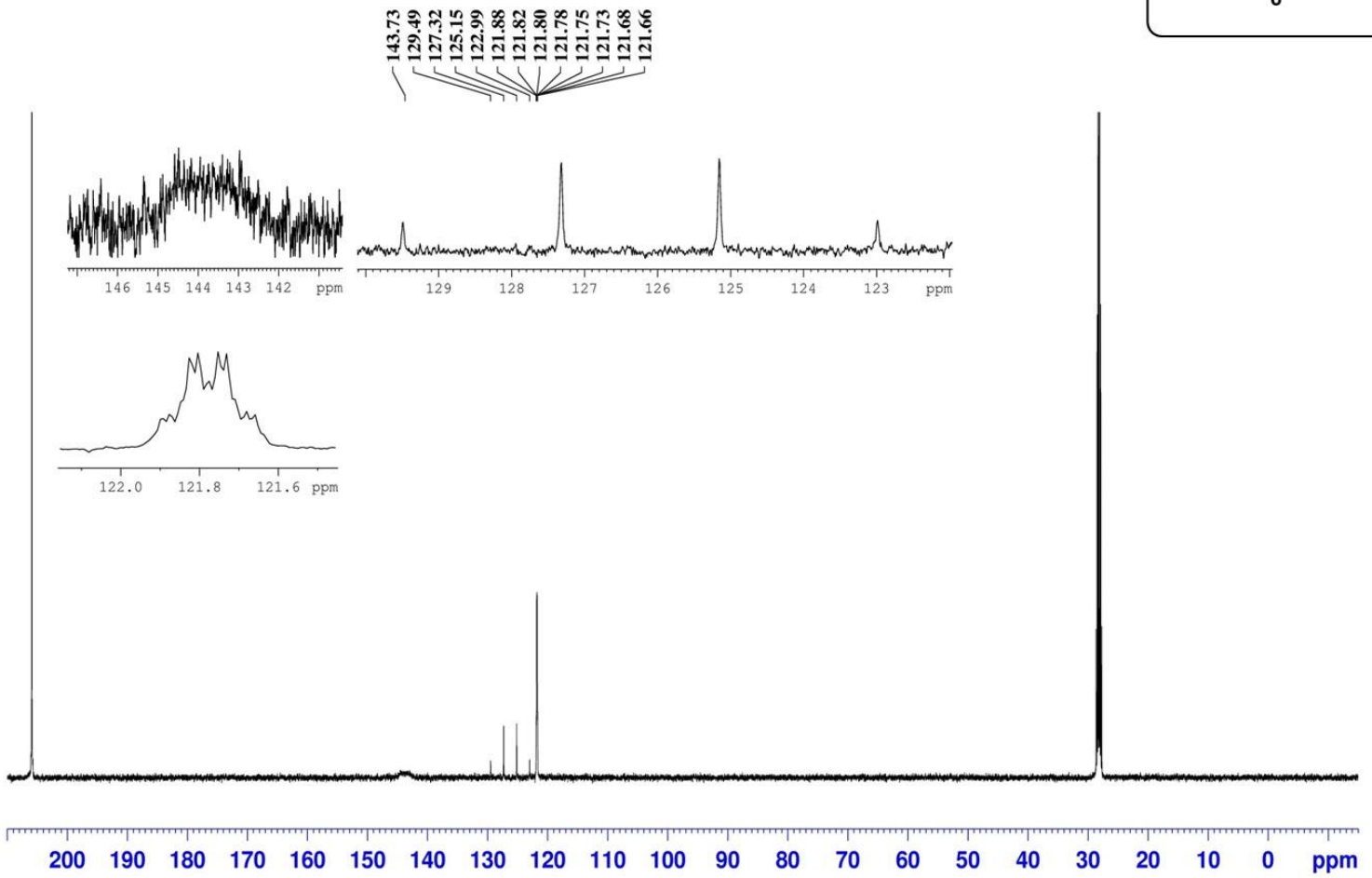



**6**

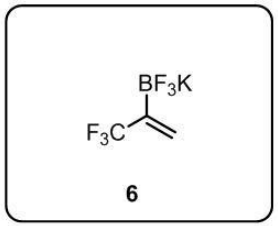


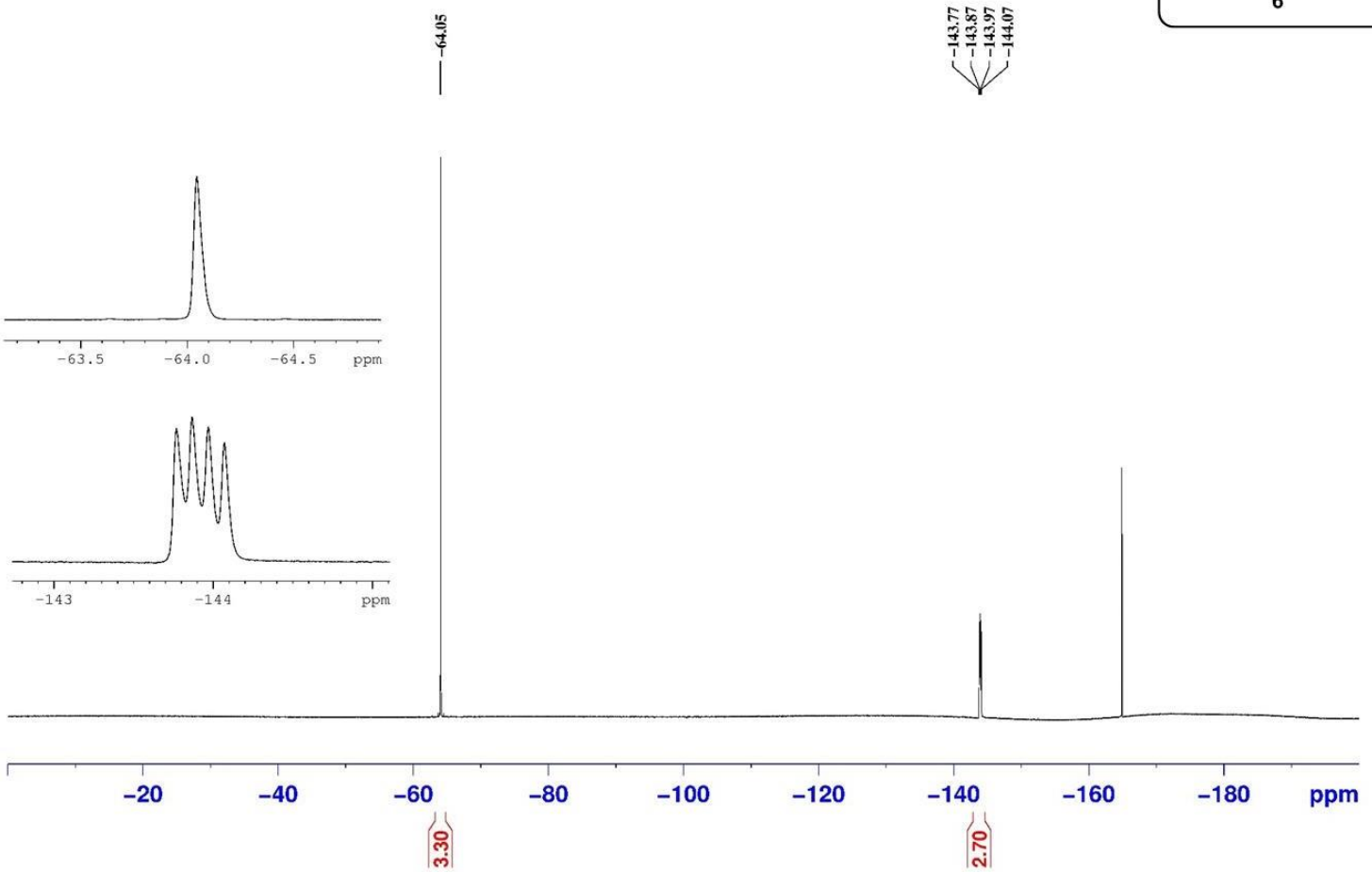
**Potassium Trifluoro(3,3,3−trifluoroprop−1−en−2−yl)borate**
**125 MHz, acetone−d6**



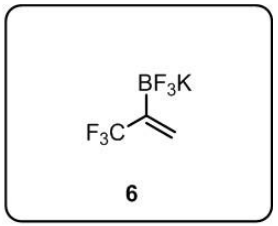
**Potassium Trifluoro(3,3,3−trifluoroprop−1−en−2−yl)borate**
**471 MHz, CDCl3**



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

1.70
1.34
0.97
0.61




**6**