Supporting Information

Photocatalyst-free Light-Mediated Three-Component Alkoxy-, Hydroxy-, and Azidotrifluoromethylation of Alkenes

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1. General Considerations

1.1 General: All chemical transformations requiring inert atmosphere were done using Schlenk line techniques. For purple light irradiation a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) was placed 4 cm away from the reaction vials. Photoredox-catalyzed reactions were performed using 4 or 8 mL Screw Neck Vial (clear glass, 45 x 14.7 mm) with screw cap 13 mm black Sil/PTFE septum, or using 4 or 8 mL Chemglass vials (15-425 Green Open Top Cap, TFE Septa). NMR spectra (^{1}H, ^{13}C, ^{19}F, ^{31}P) were performed in the *Servei de Ressonància Magnètica Nuclear* (UAB) using NEO 300, NEO 400, NEO 500, or NEO 600 spectrometers, or in *Laboratorio de RMN Jesús H. Rodríguez Ramos* (UAM), using a Bruker Avance 300 and 500 MHz spectrometers. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, δ_H = 7.26 ppm, δ_C = 77.16 ppm). ^{13}C NMR and ^{19}F spectra were acquired on a broad band decoupled mode. The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), bs (broad singlet). Reactions were monitored by ^{1}H NMR, and/or TLC. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (60 Å porosity, 250 μm thickness) in heptane/AcOEt as the eluent, and visualized using potassium permanganate stain, and/or UV light. Flash column chromatography was accomplished using silica gel Merck-60 from Aldrich. High Resolution Mass Spectrometry (HRMS) were registered in a spectrometer Bruker maXis IITM (Q-TOF) or a GCT Agilent Technologies 6890 N using Atmospheric Pressure Chemical Ionization (APCI) or Electrospray Ionization (ESI) method. HRMS (ESI+) and elemental analyses were also done by the *Servei d'Anàlisi Química* of UAB and *Parque Científico Tecnológico* of UBU. HRMS was done using a Bruker microTOF-QII mass spectrometer (fly time analyzer) through positive electrospray ionization Melting points (°C) were measure using Büchi Melting Point B-540 apparatus in open capillary tubes, and the values are uncorrected.

1.2 Chemicals: Deuterated NMR solvents were purchased from Sigma Aldrich or Eurisotop. Dry acetone, DMA, DMF, DMSO MeCN, THF and CH_2Cl_2 were obtained from Sigma Aldrich, ThermoFisher or Carlo Erba, and used as received. 1,2-DCE was purchased from ThermoFisher, and dried over 4Å molecular sieves. Alcohols, $TMSN_3$, were purchased from commercial suppliers and used as received. Alkenes were commercially available or prepared as reported[1] and trifluoromethyl-thianthrenium salt (TT-CF_3^+ OTf^-)[2] were synthesized according to a literature procedure.

[1] a) Z. Wang, Y. Yang, *RSC Adv.*, **2020**,*10*, 29263-29267; b) A. Granados, R. K. Dhungana, M. Sharique, J. Majhi, G. A. Molander, *Org. Lett.* **2022**, *24*, 4750-4755.
[2] H. Jia, A. P. Häring, F. Berger, L. Zhang, T. Ritter, *J. Am. Chem. Soc.* **2021**, *143*, 7623–7628.

2. Photoinduced Reactions

2.1. Reaction Workflow:

All photoredox reactions were performed with a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm). The lamp was placed 4 cm away from the reaction vials and cooled at 25ºC by an external fan. A typical reaction setup is shown below.

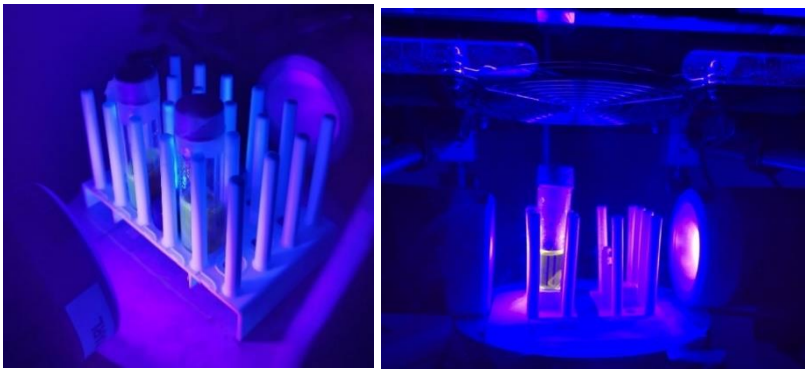


Figure S1. *Reaction setup for the visible light-assisted alcoxy-, hydroxy-, and azidotrifluoromethylation of alkenes*

2.2. Synthesis of 1,2-Trifluoromethyl Ethers

2.2.1. Reaction Optimization:

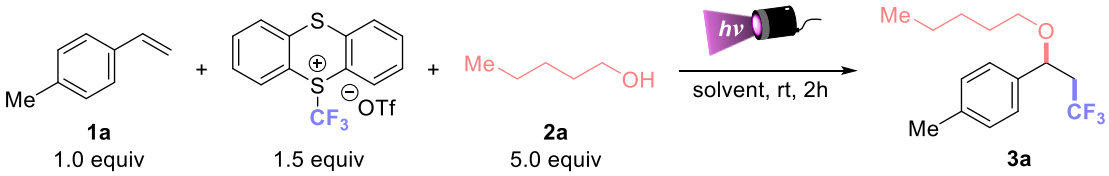


Table S1. Solvent[a]

Entry	Solvent	Concentration (M)	3a (%)[b]
1	CH_2Cl_2	0.05	80
2	CH_2Cl_2	0.1	80
3	1,2-dichloroethane	0.1	95 (73)[c]
4	MeCN	0.1	55
5	acetone	0.1	23
6	DMSO	0.1	34
7	DMF	0.1	nd
8	DMA	0.1	nd

[a]Optimization reactions were performed using 1-methyl-4-vinylbenzene (**1a**, 0.05 mmol), trifluoromethyl-thianthrenium salt TT-CF_3^+ OTf^- (1.5 equiv) and pentan-1-ol (**2a**, 5.0 equiv), in dry degassed solvent (1.0 mL, c = 0.1 M) under purple Kessil irradiation (λ_{max} = 390 nm) for 2 hours at rt. [b]Yields were determined by ^{19}F-NMR analysis using trifluorotoluene as internal standard. [c]Isolated yield. Abbreviations: nd, no detected.

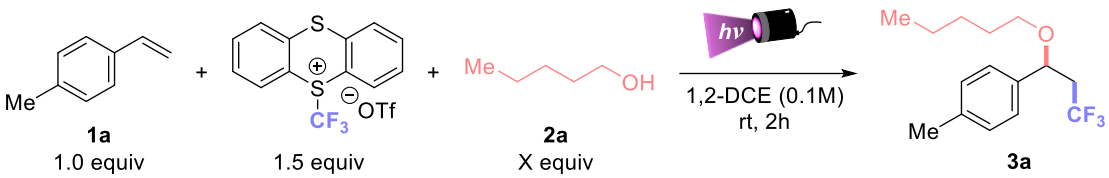


Table S2. Equivalents of pentan-1-ol[a]

Entry	Equiv of 2a	3a (%)[b]
1	1.1	18
2	1.5	22
3	2.0	23
4	3.0	56
5	4.0	90
6	**5.0**	**95 (73)[c]**

[a]Optimization reactions were performed using 1-methyl-4-vinylbenzene (**1a**, 0.05 mmol), trifluoromethyl-thianthrenium salt TT-CF_3^+ OTf^- (1.5 equiv) and pentan-1-ol (**2a**), in dry degassed 1,2-dichloroethane (1.0 mL, c = 0.1 M) under purple Kessil irradiation (λ_{max} = 390 nm) for 2 hours at rt. [b]Yields were determined by ^{19}F-NMR analysis using trifluorotoluene as internal standard. [c]Isolated yield.

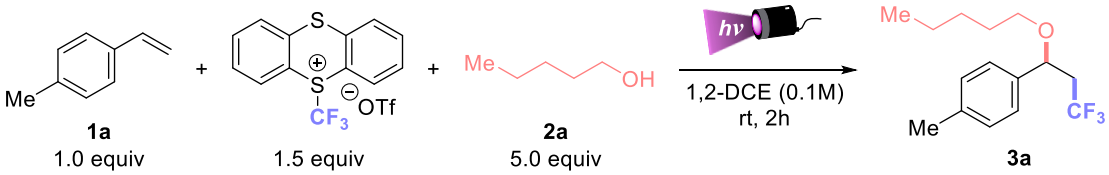
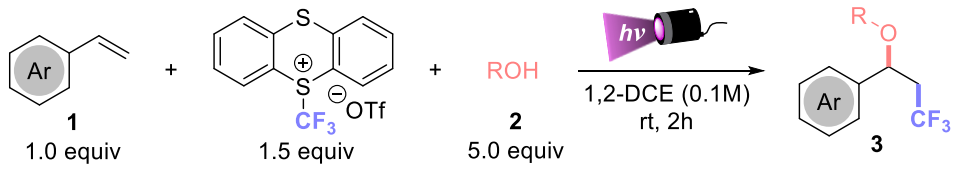


Table S3. Control experiments[a]

Entry	Equiv of 2a	3a (%)[b]
1	No TT-CF_3	nr
2	No alcohol	nd
3	No light	nr

[a]Optimization reactions were performed using 1-methyl-4-vinylbenzene (**1a**, 0.05 mmol), trifluoromethyl-thianthrenium salt TT-CF_3^+ OTf^- (1.5 equiv) and pentan-1-ol (**2a**, 5.0 equiv), in dry degassed 1,2-dichloroethane (1.0 mL, c = 0.1 M) under purple Kessil irradiation (λ_{max} = 390 nm) for 2 hours at rt. [b]All the reactions were analyzed by ^{19}F-NMR and 1H-NMR. Abbreviations: nr, no reaction; nd, no detected.

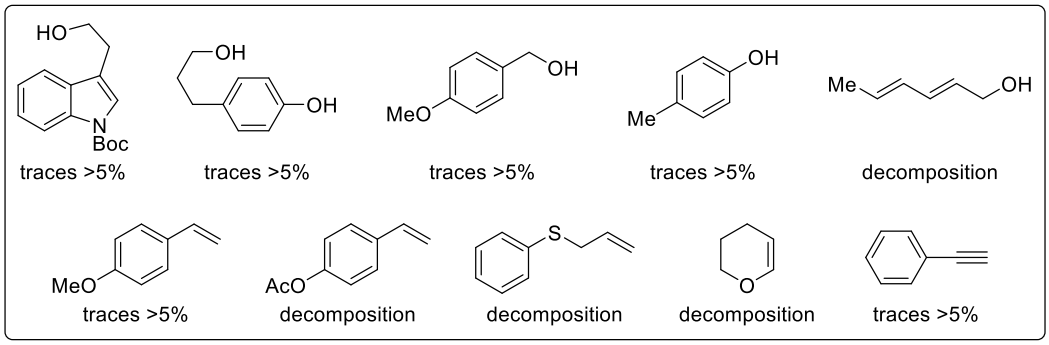
2.2.2. General Procedure A:



To an 8 mL vial equipped with a magnetic stir bar was added alcohol **2** (1.25 mmol, 5.0 equiv, *if solid*), styrene **1** (0.25 mmol, 1.0 equiv, *if solid*) and trifluoromethyl-thianthrenium salt TT-CF_3^+ OTf^- (163 mg, 0.38 mmol, 1.5 equiv). The vial was sealed with a cap containing a Sil/PTFE septum, evacuated, and backfilled with nitrogen. After this process was repeated 3 times, anhydrous degassed 1,2-dichloroethane (2.5 mL, *c* = 0.1 M), alcohol **2** (1.25 mmol, 5.0 equiv, *if liquid*), and styrene **1** (0.25 mmol, 1.0 equiv, *if liquid*) were added via syringe. The reaction mixture was irradiated with a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) for 2 hours as described in the "Workflow" section. The lamp was placed 4 cm away from the reaction vials and cooled at room temperature by an external fan. Upon completion, the volatiles were removed under reduced pressure, and the crude mixture was subjected to purification by column chromatography to afford compound **3**.

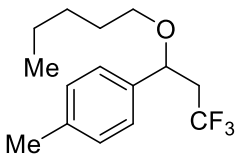
2.2.3. Unsuccessful Reagents:

All the crude mixtures were analyzed by ^{1}H-NMR.



2.2.4. Characterization Data:

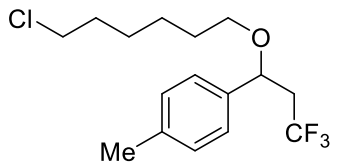
1-Methyl-4-(3,3,3-trifluoro-1-(pentyloxy)propyl)benzene (3a)



Prepared according to the *General Procedure A* from pentan-1-ol (110 mg, 1.25 mmol, 5.0 equiv) and 1-methyl-4-vinylbenzene (30 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (0-2% CH_2Cl_2 in heptane), the title compound **3a** was obtained as a yellow oil (50 mg, 0.18 mmol, 73%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.25 – 7.19 (m, 2H), 7.19 – 7.09 (m, 2H) 4.51 (dd, *J* = 8.7, 4.1 Hz, 1H), 3.36 – 3.17 (m, 2H), 2.75 – 2.51 (m, 1H), 2.40 – 2.24 (m, 1H), 2.35 (s, 3H), 1.57 – 1.51 (m, 2H), 1.34 – 1.22 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$), δ (ppm) = 137.9, 137.8, 129.4 (2C), 126.4 (2C), 125.8 (q, $J_{C\text{-}F}$ = 277.4 Hz), 75.9 (q, $J_{C\text{-}F}$ = 3.2 Hz), 69.0, 42.4 (q, $J_{C\text{-}F}$ = 27.3 Hz), 29.4, 28.2, 22.5, 21.2, 14.0. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.6

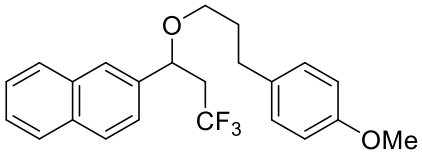
(s, 3F). **IR** (ATR) ν (cm^{-1}): 2956, 2930, 2865, 1513, 1427, 1376, 1284, 1247, 1202, 1124, 1103. **HRMS (ESI)** calcd for $C_{15}H_{21}F_3NaO$ $[M+Na]^+$: 297.1437, found 297.1431.

1-(1-((6-Chlorohexyl)oxy)-3,3,3-trifluoropropyl)-4-methylbenzene (3b)



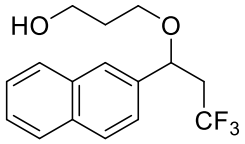
Prepared according to the *General Procedure A* from 6-chlorohexan-1-ol (171 mg, 1.25 mmol, 5.0 equiv) and 1-methyl-4-vinylbenzene (30 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (0-2% CH_2Cl_2 in heptane), the title compound **3b** was obtained as a yellow oil (58 mg, 0.18 mmol, 72%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.25 – 7.20 (m, 2H), 7.20 – 7.10 (m, 2H), 4.52 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.52 (t, *J* = 6.7 Hz, 2H), 3.40 – 3.19 (m, 2H), 2.76 – 2.52 (m, 1H), 2.43 – 2.23 (m, 1H), 2.37 (s, 3H), 1.81 – 1.72 (m, 2H), 1.60 – 1.52 (m, 2H), 1.50 – 1.32 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$), δ (ppm) = 138.1, 137.8, 129.5 (2C), 126.5 (2C), 125.9 (q, $J_{C\text{-}F}$ = 277.5 Hz), 76.1 (q, $J_{C\text{-}F}$ = 3.2 Hz), 68.8, 45.1, 42.5 (q, $J_{C\text{-}F}$ = 27.3 Hz), 32.7, 29.6, 26.7, 25.5, 21.3. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.61 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2933, 2863, 1512, 1427, 1376, 1320, 1284, 1247, 1202, 1125, 1104. **HRMS (APCI)** calcd for $C_{16}H_{22}ClF_3O$ $[M]^+$: 322.1306, found 322.1312.

2-(3,3,3-trifluoro-1-(3-(4-methoxyphenyl)propoxy)propyl)Naphthalene (3c)



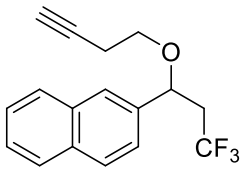
Prepared according to the *General Procedure A* from 3-(4-methoxyphenyl)propan-1-ol (208 mg, 1.25 mmol, 5.0 equiv) and 2-vinylnaphthalene (39 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (0-5% AcOEt in heptane), the title compound **3c** was obtained as a yellow oil (64 mg, 0.17 mmol, 66%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.95 – 7.83 (m, 3H), 7.81 – 7.75 (m, 1H), 7.56 – 7.46 (m, 3H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.75 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.79 (s, 3H), 3.47 – 3.27 (m, 2H), 2.90 – 2.74 (m, 1H), 2.75 – 2.58 (m, 2H), 2.55 – 2.41 (m, 1H), 1.95 – 1.80 (m, 2H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 157.9, 138.1, 134.1, 133.5, 133.3, 129.5 (2C), 129.0, 128.1, 127.9, 126.6, 126.4, 126.0, 125.96 (q, $J_{C\text{-}F}$ = 277.5 Hz), 124.0, 113.9 (2C), 76.4 (q, $J_{C\text{-}F}$ = 3.2 Hz), 68.2, 55.3, 42.3 (q, $J_{C\text{-}F}$ = 27.5 Hz), 31.7, 31.4. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.4 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2915, 1610, 1509, 1465, 1440, 1376, 1270, 1242, 1174, 1114, 1035. **HRMS (APCI)** calcd for $C_{23}H_{23}F_3O_2$ $[M]^+$: 388.1645, found 388.1650.

3-(3,3,3-Trifluoro-1-(naphthalen-2-yl)propoxy)propan-1-ol (3d)



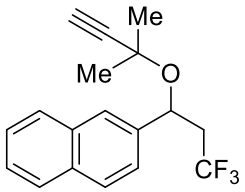
Prepared according to the *General Procedure A* from propane-1,3-diol (95 mg, 1.25 mmol, 5.0 equiv) and 2-vinylnaphthalene (39 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (10-40% AcOEt in heptane), the title compound **3d** was obtained as a yellow oil (47 mg, 0.16 mmol, 64%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.92 – 7.82 (m, 3H), 7.80 – 7.82 (m, 1H), 7.75 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.76 (dd, *J* = 9.0, 3.8 Hz, 1H), 3.78 (t, *J* = 5.7 Hz, 2H), 3.51 (t, *J* = 5.8 Hz, 2H), 2.88 – 2.63 (m, 1H), 2.56 – 2.36 (m, 1H), 2.09 (s, 1H), 1.86 – 1.79 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 137.5, 133.5, 133.3, 129.2, 128.1, 127.9, 126.7, 126.5, 126.1, 125.9 (q, $J_{C\text{-}F}$ = 277.5 Hz), 123.7, 76.9 (q, $J_{C\text{-}F}$ = 3.2 Hz), 67.9, 61.6, 42.3 (q, $J_{C\text{-}F}$ = 27.6 Hz), 32.3. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.52 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2944, 2881, 1731, 1601, 1508, 1426, 1376, 1249, 1201, 1173, 1115, 1051. **HRMS (APCI)** calcd for $C_{16}H_{17}F_3O_2$ $[M]^+$: 298.1175, found 298.1178.

2-(1-(But-3-yn-1-yloxy)-3,3,3-trifluoropropyl)naphthalene (3e)



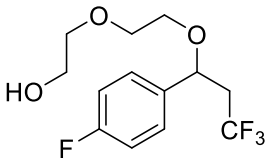
Prepared according to the *General Procedure A* from but-3-yn-1-ol (88 mg, 1.25 mmol, 5.0 equiv) and 2-vinylnaphthalene (39 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (0-10% CH_2Cl_2 in heptane), the title compound **3e** was obtained as a yellow oil (45 mg, 0.16 mmol, 62%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.92 – 7.78 (m, 4H), 7.56 – 7.43 (m, 3H), 4.79 (dd, *J* = 8.5, 4.2 Hz, 1H), 3.49 (td, *J* = 7.0, 1.1 Hz, 2H), 2.89 – 2.65 (m, 1H), 2.55 – 2.38 (m, 3H), 1.96 (t, *J* = 2.7 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$), δ (ppm) = 137.6, 133.5, 133.3, 129.1, 128.1, 127.9, 126.6, 126.5, 126.1, 125.8 (q, $J_{C\text{-}F}$ = 277.5 Hz), 123.9, 81.2, 76.6 (q, $J_{C\text{-}F}$ = 3.4 Hz), 69.5, 67.2, 42.3 (q, $J_{C\text{-}F}$ = 27.6 Hz), 20.0. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.6 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2950, 1729, 1602, 1508, 1426, 1376, 1249, 1201, 1173, 1115. **HRMS (APCI)** calcd for $C_{17}H_{15}F_3O$ $[M]^+$: 292.1070, found 292.1070.

2-(3,3,3-Trifluoro-1-((2-methylbut-3-yn-2-yl)oxy)propyl)naphthalene (3f)



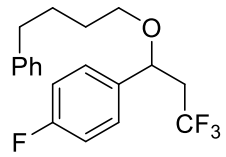
Prepared according to the *General Procedure A* from 2-methylbut-3-yn-2-ol (105 mg, 1.25 mmol, 5.0 equiv) and 2-vinylnaphthalene (39 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (0-5% CH_2Cl_2 in heptane), the title compound **3f** was obtained as a yellow oil (10 mg, 0.03 mmol, 13%). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = 7.80 – 7.71 (m, 4H), 7.45 – 7.39 (m, 3H), 5.26 (dd, *J* = 8.5, 4.4 Hz, 1H), 2.69 – 2.59 (m, 1H), 2.40 – 2.28 (m, 1H), 2.31 (s, 1H), 1.49 (s, 3H), 1.14 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 140.8, 133.4, 133.2, 129.0, 128.5, 128.1, 127.9, 126.4, 126.1, 125.7 (q, $J_{C\text{-}F}$ = 277.5 Hz), 125.4, 124.3, 73.3, 71.8, 71.7 (q, $J_{C\text{-}F}$ = 2.9 Hz), 43.4 (q, $J_{C\text{-}F}$ = 27.1 Hz), 30.3, 30.1. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.0 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2924, 1426, 1379, 1250, 1129, 1029. **HRMS (APCI)** calcd for $C_{18}H_{17}F_3O$ $[M]^+$: 306.1226, found 306.1230.

2-(2-(3,3,3-Trifluoro-1-(4-fluorophenyl)propoxy)ethoxy)ethan-1-ol (3g)



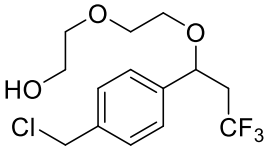
Prepared according to the *General Procedure A* from diethylene glycol (133 mg, 1.25 mmol, 5.0 equiv) and 1-fluoro-4-vinylbenzene (31 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (10-40% AcOEt in heptane), the title compound **3g** was obtained as a yellow oil (54 mg, 0.18 mmol, 73%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.37 – 7.24 (m, 2H), 7.10 – 7.00 (m, 2H), 4.62 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.75 – 3.67 (m, 2H), 3.66 – 3.59 (m, 2H), 3.58 – 3.53 (m, 2H), 3.50 – 3.41 (m, 2H), 2.79 – 2.55 (m, 1H), 2.44 – 2.29 (m, 1H), 2.26 (bs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 162.8 (d, $J_{C\text{-}F}$ = 246.9 Hz), 136.0 (d, $J_{C\text{-}F}$ = 3.2 Hz), 128.3 (d, $J_{C\text{-}F}$ = 8.2 Hz, 2C), 125.7 (q, $J_{C\text{-}F}$ = 277.5 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.6 Hz, 2C), 76.0 (q, $J_{C\text{-}F}$ = 3.3 Hz), 72.4, 70.4, 68.3, 61.9, 42.4 (q, $J_{C\text{-}F}$ = 27.6 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.6 (s, 3F), -113.55 (s, 1F). **IR** (ATR) ν (cm^{-1}): 2915, 1604, 1508, 1380, 1248, 1222, 1121, 1091, 1060. **HRMS (APCI)** calcd for $C_{13}H_{17}F_4O_3$ $[M+H]^+$: 297.1108, found 297.1114.

1-Fluoro-4-(3,3,3-trifluoro-1-(4-phenylbutoxy)propyl)benzene (3h)



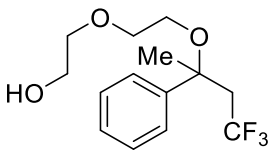
Prepared according to the *General Procedure A* from 4-phenylbutan-1-ol (189 mg, 1.26 mmol, 5.0 equiv) and 1-fluoro-4-vinylbenzene (31 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (0-5% CH_2Cl_2 in heptane), the title compound **3h** was obtained as a yellow oil (68 mg, 0.20 mmol, 80%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.38 – 7.24 (m, 4H), 7.24 – 7.15 (m, 3H), 7.11 – 7.03 (m, 2H), 4.54 (dd, *J* = 8.5, 4.3 Hz, 1H), 3.41 – 3.23 (m, 2H), 2.75 – 2.55 (m, 3H), 2.44 – 2.25 (m, 1H), 1.75 – 1.57 (m, 4H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 162.7 (d, $J_{C\text{-}F}$ = 246.5 Hz), 142.5, 136.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 128.5 (2C), 128.4 (2C), 128.2 (d, $J_{C\text{-}F}$ = 8.2 Hz, 2C), 125.9, 125.8 (q, $J_{C\text{-}F}$ = 277.4 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21.5 Hz, 2C), 75.7 (q, $J_{C\text{-}F}$ = 3.3 Hz), 68.9, 42.5 (q, $J_{C\text{-}F}$ = 27.4 Hz), 35.7, 29.4, 28.0. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.5 (s, 3F), -113.86 (s, 1F). **IR** (ATR) ν (cm^{-1}): 2938, 2860, 1604, 1508, 1378, 1319, 1285, 1248, 1222, 1127, 1090. **HRMS (ESI)** calcd for $C_{19}H_{20}F_4NaO$ $[M+Na]^+$: 363.1342, found 363.1337.

2-(2-(1-(4-(Chloromethyl)phenyl)-3,3,3-trifluoropropoxy)ethoxy)ethan-1-ol (3i)



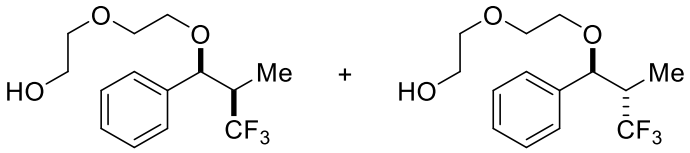
Prepared according to the *General Procedure A* from diethylene glycol (132 mg, 1.24 mmol, 5.0 equiv) and 1-(chloromethyl)-4-vinylbenzene (38 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (10-40% AcOEt in heptane), the title compound **3i** was obtained as a yellow oil (58 mg, 0.18 mmol, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.44 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 4.64 (dd, *J* = 8.6, 4.1 Hz, 1H), 4.58 (s, 2H), 3.76 – 3.67 (m, 2H), 3.68 – 3.58 (m, 2H), 3.59 – 3.54 (m, 2H), 3.53 – 3.43 (m, 2H), 2.76 – 2.57 (m, 1H), 2.45 – 2.30 (m, 1H), 2.22 (bs, 1H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 140.6, 137.9, 129.2 (2C), 127.0 (2C), 125.7 (q, $J_{C\text{-}F}$ = 277.4 Hz), 76.4 (q, $J_{C\text{-}F}$ = 3.2 Hz), 72.4, 70.4, 68.5, 61.9, 45.8, 42.3 (q, $J_{C\text{-}F}$ = 27.6 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.6 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2873, 1424, 1379, 1247, 1204, 1122, 1100, 1057. **HRMS (ESI)** calcd for $C_{14}H_{18}ClF_3NaO_3$ $[M+Na]^+$: 349.0789, found 349.0785.

2-(2-((4,4,4-Trifluoro-2-phenylbutan-2-yl)oxy)ethoxy)ethan-1-ol (3j)



Prepared according to the *General Procedure A* from diethylene glycol (135 mg, 1.27 mmol, 5.0 equiv) and prop-1-en-2-ylbenzene (30 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (10-40% AcOEt in heptane), the title compound **3j** was obtained as a yellow oil (51 mg, 0.18 mmol, 69%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.45 – 7.26 (m, 5H), 3.73 (s, 2H), 3.66 – 3.56 (m, 4H), 3.49 – 3.37 (m, 1H), 3.28 – 3.16 (m, 1H), 2.76 – 2.47 (m, 2H), 2.44 (bs, 1H), 1.76 (d, J = 1.3 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$), δ (ppm) = 143.2, 128.6 (2C), 127.9, 126.2 (2C), 125.5 (q, $J_{C\text{-}F}$ = 278.1 Hz), 76.3 (q, $J_{C\text{-}F}$ = 2.3 Hz), 72.4, 70.7, 62.0, 61.9, 46.8 (q, $J_{C\text{-}F}$ = 26.4 Hz), 22.3 (q, $J_{C\text{-}F}$ = 1.9 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ (ppm) = -59.96 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2871, 1447, 1365, 1260, 1234, 1169, 1117, 1061. **HRMS (ESI)** calcd for $C_{14}H_{19}F_3NaO_3$ $[M+Na]^+$: 315.1178, found 315.1172.

2-(2-(3,3,3-Trifluoro-2-methyl-1-phenylpropoxy)ethoxy)ethan-1-ol (3k)



***syn*-3k** ***anti*-3k'**

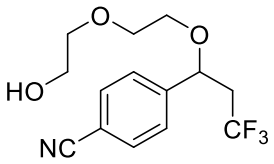
Prepared according to the *General Procedure A* from diethylene glycol (131 mg, 1.23 mmol, 5.0 equiv) and (*E*)-prop-1-en-1-ylbenzene (29 mg, 0.25 mmol, 1.0 equiv). The title compound was obtained as mixture of diastereomers (1:1), and after a chromatographic purification (10-40% AcOEt in heptane) ***syn*-3k** was obtained as a yellow oil (26 mg, 0.09 mmol, 37%) and ***anti*-3k'** was obtained as a yellow oil (24 mg, 0.08 mmol, 34%).

Data of ***syn*-3k. ^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.42 – 7.26 (m, 5H), 4.71 (d, *J* = 3.3 Hz, 1H), 3.75 – 3.68 (m, 2H), 3.68 – 3.63 (m, 2H), 3.62 – 3.55 (m, 3H), 3.56 – 3.44 (m, 1H), 2.51 – 2.27 (m, 1H), 2.10 (t, *J* = 6.2 Hz, 1H), 1.10 (d, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 139.7, 128.6 (2C), 128.0, 127.6 (q, $J_{C\text{-}F}$ = 280.6 Hz), 126.7 (2C), 79.1 (q, $J_{C\text{-}F}$ = 2.7 Hz), 72.4, 70.6, 69.2, 62.0, 45.4 (q, $J_{C\text{-}F}$ = 25.0 Hz), 7.0 (q, $J_{C\text{-}F}$ = 2.5 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -69.90 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2944, 1727, 1584, 1508, 1465, 1376, 1248, 1200, 1123, 1063, 1029. **HRMS (ESI)** calcd for $C_{14}H_{19}F_3NaO_3$ $[M+Na]^+$: 315.1178, found 315.1170.

Data of ***anti*-3k'**. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.41 – 7.27 (m, 5H), 4.40 (d, *J* = 8.0 Hz, 1H), 3.77 – 3.66 (m, 2H), 3.64 – 3.59 (m, 2H), 3.58 – 3.54 (m, 2H), 3.49 – 3.40 (m, 2H), 2.74 – 2.59 (m, 1H), 2.15 (t, *J* = 6.2 Hz, 1H), 0.84 (d, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 138.7, 128.6 (2C), 128.6, 127.9

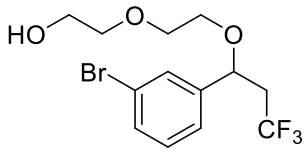
(2C), 127.6 (q, J_{C-F} = 280.6 Hz), 81.6 (q, J_{C-F} = 1.8 Hz), 72.3, 70.5, 68.5, 62.0, 44.2 (q, J_{C-F} = 25.0 Hz), 10.5 (q, J_{C-F} = 3.2 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -68.8 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2944, 1727, 1584, 1508, 1465, 1376, 1248, 1200, 1123, 1063, 1029. **HRMS (ESI)** calcd for $C_{14}H_{19}F_3NaO_3$ $[M+Na]^+$: 315.1178, found 315.1178.

4-(3,3,3-Trifluoro-1-(2-(2-hydroxyethoxy)ethoxy)propyl)benzonitrile (3l)



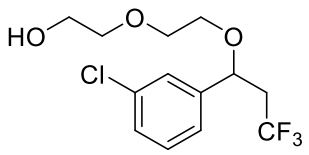
Prepared according to the *General Procedure A* from diethylene glycol (132 mg, 1.24 mmol, 5.0 equiv) and 4-vinylbenzonitrile (32 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (10-40% AcOEt in heptane), the title compound **3l** was obtained as a yellow oil (31 mg, 0.10 mmol, 42%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.75 – 7.61 (m, 2H), 7.52 – 7.42 (m, 2H), 4.71 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.73 (t, *J* = 4.5 Hz, 2H), 3.67 – 3.61 (m, 2H), 3.60 – 3.54 (m, 2H), 3.54 – 3.46 (m, 2H), 2.79 – 2.55 (m, 1H), 2.47 – 2.24 (m, 1H), 2.04 (bs, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$), δ (ppm) = 145.6, 132.7 (2C), 125.3 (q, J_{C-F} = 277.4 Hz), 127.2 (2C), 118.4, 112.5, 76.1 (q, J_{C-F} = 3.3 Hz), 72.3, 70.3, 68.8, 61.8, 42.1 (q, J_{C-F} = 28.0 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.5 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2874, 2228, 1609, 1380, 1283, 1248, 12041, 1122, 1102, 1058. **HRMS (ESI)** calcd for $C_{14}H_{16}F_3NNaO_3$ $[M+Na]^+$: 326.0974, found 326.0966.

2-(2-(1-(3-Bromophenyl)-3,3,3-trifluoropropoxy)ethoxy)ethan-1-ol (3m)



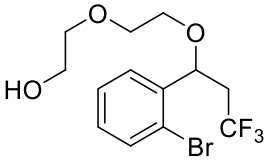
Prepared according to the *General Procedure A* from diethylene glycol (130 mg, 1.30 mmol, 5.0 equiv) and 1-bromo-3-vinylbenzene (46 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (10-40% AcOEt in heptane), the title compound **3m** was obtained as a yellow oil (53 mg, 0.15 mmol, 59%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.55 – 7.47 (m, 1H), 7.52 – 7.39 (m, 1H), 7.28 – 7.21 (m, 2H), 4.60 (dd, *J* = 8.7, 4.1 Hz, 1H), 3.77 – 3.70 (m, 2H), 3.68 – 3.60 (m, 2H), 3.59 – 3.54 (m, 2H), 3.53 – 3.45 (m, 2H), 2.77 – 2.53 (m, 1H), 2.45 – 2.24 (m, 1H), 2.19 (bs, 1H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 142.8, 131.7, 130.6, 129.7, 125.6 (q, J_{C-F} = 277.5 Hz), 125.2, 123.1, 76.1 (q, J_{C-F} = 3.2 Hz), 72.4, 70.4, 68.7, 61.9, 42.3 (q, J_{C-F} = 27.8 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.6 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2874, 1473, 1428, 1378, 1281, 1245, 1198, 1121, 1068. **HRMS (ESI)** calcd for $C_{13}H_{16}BrF_3NaO_3$ $[M+Na]^+$: 379.0127, found 379.0119.

2-(2-(1-(3-Chlorophenyl)-3,3,3-trifluoropropoxy)ethoxy)ethan-1-ol (3n)



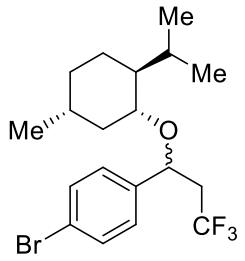
Prepared according to the *General Procedure A* from diethylene glycol (134 mg, 1.30 mmol, 5.0 equiv) and 1-chloro-3-vinylbenzene (35 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (10-40% AcOEt in heptane), the title compound **3n** was obtained as a yellow oil (53 mg, 0.15 mmol, 67%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.43 – 7.35 (m, 1H), 7.36 – 7.31 (m, 2H), 7.32 – 7.21 (m, 1H), 4.66 (dd, J = 8.6, 4.1 Hz, 1H), 3.79 – 3.74 (m, 2H), 3.72 – 3.64 (m, 2H), 3.63 – 3.59 (m, 2H), 3.58 – 3.49 (m, 2H), 2.82 – 2.58 (m, 1H), 2.48 – 2.35 (m, 1H), 2.34 – 2.28 (m, 1H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 142.5, 134.9, 130.3, 128.7, 126.7, 125.6 (q, $J_{C\text{-}F}$ = 277.5 Hz),124.8, 76.1 (q, $J_{C\text{-}F}$ = 3.2 Hz), 72.4, 70.4, 68.6, 61.9, 42.3 (q, $J_{C\text{-}F}$ = 27.8 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.7 (s, 3F). **HRMS (ESI)** calcd for $C_{13}H_{16}ClF_3NaO_3$ $[M+Na]^+$: 335.0632, found 335.0630.

2-(2-(1-(2-Bromophenyl)-3,3,3-trifluoropropoxy)ethoxy)ethan-1-ol (3o)



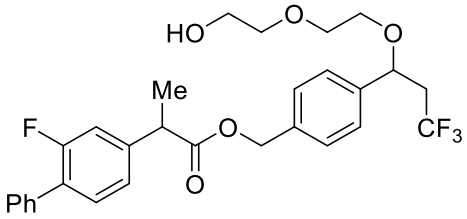
Prepared according to the *General Procedure A* from diethylene glycol (135 mg, 1.27 mmol, 5.0 equiv) and 1-bromo-2-vinylbenzene (47 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (10-40% AcOEt in heptane), the title compound **3o** was obtained as a yellow oil (55 mg, 0.15 mmol, 61%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.54 (dt, *J* = 7.7, 1.5 Hz, 2H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.23 – 7.12 (m, 1H), 5.11 (dd, *J* = 7.7, 4.6 Hz, 1H), 3.76 – 3.68 (m, 2H), 3.68 – 3.60 (m, 2H), 3.59 – 3.49 (m, 4H), 2.55 – 2.38 (m, 2H), 2.25 (bs, 1H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 139.4, 133.2, 129.8, 128.2, 127.7, 125.7 (q, $J_{C\text{-}F}$ = 277.9 Hz), 122.5, 75.4 (q, $J_{C\text{-}F}$ = 3.3 Hz), 72.4, 70.5, 68.9, 61.9, 40.9 (q, $J_{C\text{-}F}$ = 28.0 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.8 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2868, 1438, 1379, 1283, 1246, 1199, 1125, 1103, 1060, 1024. **HRMS (ESI)** calcd for $C_{13}H_{16}BrF_3NaO_3$ $[M+Na]^+$: 379.0127, found 379.0125.

1-Bromo-4-(3,3,3-trifluoro-1-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)propyl)benzene (3p)



Prepared according to the *General Procedure A* from L-menthol (195 mg, 1.25 mmol, 5.0 equiv) and 1-bromo-4-vinylbenzene (46 mg, 0.25 mmol, 1.0 equiv). The title compound was obtained as mixture of diastereomers (1:1), and after a chromatographic purification (0-5% CH_2Cl_2 in heptane) the inseparable mixture **3p** was obtained as a yellow oil (51 mg, 0.13 mmol, 50%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.52 – 7.44 (m, 4H), 7.26 – 7.18 (m, 4H), 4.71 (dd, *J* = 8.0, 4.9 Hz, 1H), 4.59 (dd, *J* = 7.1, 5.5 Hz, 1H), 3.19 (td, *J* = 10.5, 4.2 Hz, 1H), 2.87 (td, *J* = 10.4, 4.1 Hz, 1H), 2.77 – 2.52 (m, 2H), 2.44 – 2.24 (m, 3H), 2.25 – 2.08 (m, 2H), 1.68 – 1.47 (m, 5H), 1.33 – 1.09 (m, 4H), 0.97 – 0.61 (m, 21H), 0.27 (d, J = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 142.0, 139.9, 131.9 (2C), 131.8 (2C), 129.1 (2C), 128.4 (2C), 125.7 (q, $J_{C\text{-}F}$ = 277.3 Hz), 125.7 (q, $J_{C\text{-}F}$ = 277.2 Hz), 122.4, 122.0, 80.0, 75.3, 75.1 (q, $J_{C\text{-}F}$ = 3.2 Hz), 71.2 (q, $J_{C\text{-}F}$ = 3.3 Hz), 49.2, 48.4, 42.7 (q, $J_{C\text{-}F}$ = 27.2 Hz), 42.5, 42.2 (q, $J_{C\text{-}F}$ = 27.3 Hz), 39.4, 34.5, 34.4, 31.7, 31.5, 25.1, 25.0, 23.0, 22.8, 22.5, 22.4, 21.5, 21.4, 16.0, 15.5. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.1 (s, 3F), -63.2 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2950, 1729, 1602, 1508, 1426, 1376, 1249, 1201, 1173, 1115. **HRMS (ESI)** calcd for $C_{19}H_{26}BrF_3NaO$ $[M+Na]^+$: 429.1011, found 429.1002.

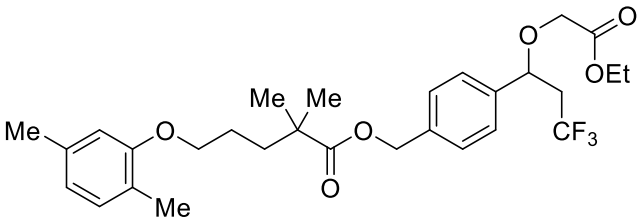
4-(3,3,3-Trifluoro-1-(2-(2-hydroxyethoxy)ethoxy)propyl)benzyl 2-(2-Fluoro-[1,1'-biphenyl]-4-yl)propanoate (3q)



Prepared according to the *General Procedure A* from diethylene glycol (133 mg, 1,25 mmol, 5.0 equiv) and 4-vinylbenzyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (90 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (10-40% AcOEt in heptane), the title compound **3q** was obtained as a yellow oil (94 mg, 0.18 mmol, 70%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.59 – 7.49 (m, 2H), 7.48 – 7.35 (m, 4H), 7.34 – 7.27 (m, 4H), 7.19 – 7.07 (m, 2H), 5.17 and 5.12 (AB system, Δν = 15.4 Hz, *J* = 12.7 Hz, 2H), 4.64 (dd, *J* = 8.6, 4.1 Hz, 1H), 3.82 (q, *J* = 7.2 Hz, 1H), 3.71 (t, *J* = 4.5 Hz, 2H), 3.65 – 3.59 (m, 2H), 3.59 – 3.54 (m, 2H), 3.51 – 3.43 (m, 2H), 2.77 – 2.57 (m, 1H), 2.47 – 2.24 (m, 2H), 1.56 (d, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 173.8, 159.8 (d, $J_{C\text{-}F}$ = 248.4 Hz), 141.7 (d, $J_{C\text{-}F}$ = 7.7 Hz), 140.3, 136.2, 135.5 (d, $J_{C\text{-}F}$ = 1.3 Hz), 130.9 (d, $J_{C\text{-}F}$ = 4.0 Hz), 129.0 (d, $J_{C\text{-}F}$ = 2.9 Hz), 128.6 (2C), 128.5 (2C), 128.0 (d, $J_{C\text{-}F}$ = 13.6 Hz), 127.8, 126.8 (2C), 125.7 (q, $J_{C\text{-}F}$ = 277.4

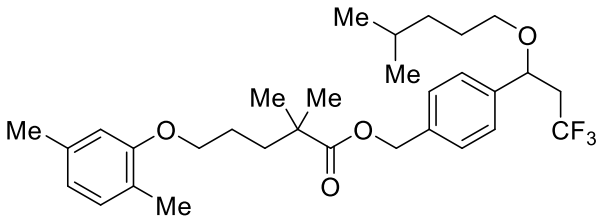
Hz), 123.7 (d, J_{C-F} = 3.3 Hz), 115.3 (d, J_{C-F} = 23.7 Hz), 76.4 (q, J_{C-F} = 3.2 Hz), 72.4, 70.3, 68.4, 66.3, 61.8, 45.1, 45.1, 42.2 (q, J_{C-F} = 27.6 Hz),18.4. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.6 (s, 3F), -117.6 (s, 1F). **IR** (ATR) ν (cm^{-1}): 2878, 1733, 1483, 1418, 1378, 1325, 1247, 1125, 1059. **HRMS (ESI)** calcd for $C_{29}H_{30}F_4NaO_5$ $[M+Na]^+$: 557.1922, found 557.1917.

4-(1-(2-Ethoxy-2-oxoethoxy)-3,3,3-trifluoropropyl)benzyl 5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoate (3r)



Prepared according to the *General Procedure A* from ethyl 2-hydroxyacetate (130 mg, 1.25 mmol, 5.0 equiv) and 4-vinylbenzyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (92 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (0-10% AcOEt in heptane), the title compound **3r** was obtained as a yellow oil (18 mg, 0.03 mmol, 13%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.38 – 7.34 (m, 2H), 7.33 – 7.29 (m, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.59 (s, 1H), 5.11 (s, 2H), 4.77 (dd, *J* = 7.8, 5.0 Hz, 1H), 4.18 (qd, *J* = 7.1, 1.2 Hz, 2H), 3.97 (d, *J* = 16.2 Hz, 1H), 3.90 (t, *J* = 5.4 Hz, 2H), 3.84 (d, *J* = 16.2 Hz, 1H), 2.91 – 2.67 (m, 1H), 2.54 – 2.33 (m, 1H), 2.30 (s, 3H), 2.15 (s, 3H), 1.76 – 1.67 (m, 4H), 1.25 (s, 6H), 1.25 (t, *J* = 7.0, 3H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 177.7, 169.9, 157.1, 138.9, 137.2, 136.6, 130.5, 128.4 (2C), 127.4 (2C), 125.5 (q, J_{C-F} = 278.0 Hz), 123.7, 120.9, 112.1, 76.2 (q, J_{C-F} = 3.4 Hz), 68.0, 65.9, 65.8, 61.1, 42.3, 42.1 (q, J_{C-F} = 28.0 Hz),37.3, 25.3 (3C), 21.5, 15.9, 14.2. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.5 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2874, 1726, 1614, 1584, 1508, 1472, 1426, 1380, 1248, 1198, 1123, 1046. **HRMS (ESI)** calcd for $C_{29}H_{37}F_3NaO_6$ $[M+Na]^+$: 561.2434, found 561.2428.

4-(3,3,3-Trifluoro-1-((4-methylpentyl)oxy)propyl)benzyl 5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoate (3s)



Prepared according to the *General Procedure A* from 4-methylpentan-1-ol (128 mg, 1.25 mmol, 5.0 equiv) and 4-vinylbenzyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (92 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (0-10% AcOEt in heptane), the title compound **3s** was obtained as a yellow oil (52 mg, 0.10 mmol, 39%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.38 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 7.00 (d,

J = 7.5 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 5.12 (s, 2H), 4.54 (dd, *J* = 8.7, 4.0 Hz, 1H), 3.90 (t, *J* = 5.4 Hz, 2H), 3.35 – 3.18 (m, 2H), 2.75 – 2.51 (m, 1H), 2.42 – 2.26 (m, 1H), 2.31 (s, 3H), 2.16 (s, 3H), 1.80 – 1.70 (m, 4H), 1.58 – 1.44 (m, 3H), 1.26 (s, 6H), 1.23 – 1.16 (m, 2H), 0.87 (dd, *J* = 6.6, 1.2 Hz, 6H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 177.7, 157.1, 140.8, 136.6, 136.5, 130.5, 128.3 (2C), 125.8 (q, $J_{C\text{-}F}$ = 277.5 Hz), 126.7 (2C), 123.7, 120.9, 112.1, 76.0 (q, $J_{C\text{-}F}$ = 3.1 Hz), 69.6, 68.0, 65.9, 42.5 (q, $J_{C\text{-}F}$ = 27.4 Hz), 42.3, 37.3, 35.2, 27.9, 27.6, 25.3 (3C), 22.7 (2C), 21.5, 15.9. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ (ppm) = -63.6 (s, 3F). **IR** (ATR) ν (cm^{-1}): 2953, 2868, 1727, 1614, 1584, 1508, 1472, 1424, 1383, 1320, 1248, 1189, 1126, 1047. **HRMS (ESI)** calcd for $C_{31}H_{43}F_3NaO_4$ $[M+Na]^+$: 559.3006, found 559.2995.

2.3. Synthesis of 1,2-Trifluoromethyl Alcohols:

2.3.1. Reaction Optimization:

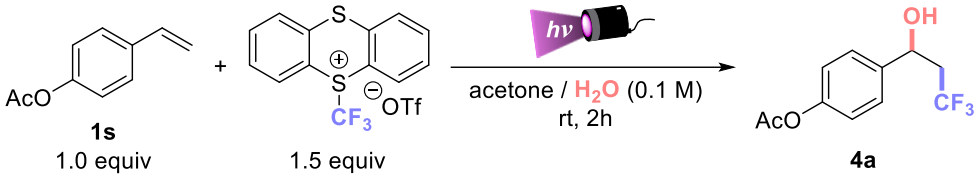
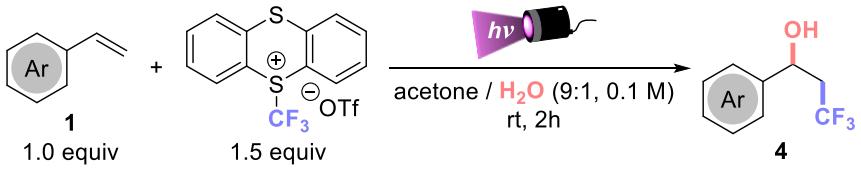


Table S4. Proportion acetone/H_2O[a]

Entry	Acetone / H_2O	3a (%)[b]
1	10 equiv of H_2O	75
2	**9:1**	**77 (67)**[c]
3	9:2	77
4	4:1	70
5	9:0	traces

[a]Optimization reactions were performed using 4-vinylphenyl acetate (0.05 mmol) and trifluoromethyl-thianthrenium salt TT-CF_3^+ OTf^- (1.5 equiv), in dry degassed mixture of acetone/water (1.0 mL, c = 0.1 M) under purple Kessil irradiation (λ_{max} = 390 nm) for 2 hours at rt. [b]Yields were determined by ^{19}F-NMR analysis using trifluorotoluene as internal standard. [c]Isolated yield.

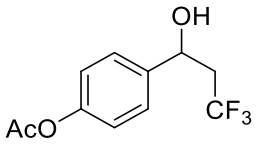
2.3.2. General Procedure B:



To an 8 mL vial equipped with a magnetic stir bar was added styrene **1** (0.25 mmol, 1.0 equiv, *if solid*) and trifluoromethyl-thianthrenium salt TT-CF_3^+ OTf^- (163 mg, 0.38 mmol, 1.5 equiv). The vial was sealed with a cap containing a Sil/PTFE septum, evacuated, and backfilled with nitrogen. After this process was repeated 3 times, degassed acetone and degassed distilled water (9:1, 2.5 mL, *c* = 0.1 M), and styrene **1** (0.25 mmol, 1.0 equiv, *if liquid*) were added via syringe. The reaction mixture was irradiated with a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) for 2 hours as described in the "Workflow" section. The lamp was placed 4 cm away from the reaction vials and cooled at room temperature by an external fan. Upon completion, the volatiles were removed under reduced pressure, and the crude mixture was subjected to purification by column chromatography to afford compound **4**.

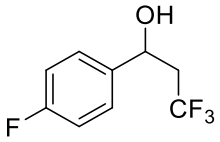
2.3.3. Characterization Data:

3,3,3-Trifluoro-1-(4-acetoxyphenyl)-1-propanol (4a)



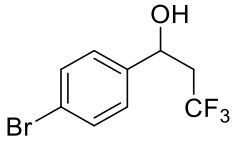
Prepared according to the *General Procedure B* from 4-vinylphenyl acetate (42 mg, 0.26 mmol, 1.0 equiv). After a chromatographic purification (2-10% AcOEt in heptane), the title compound **4a** was obtained as white solid (43 mg, 0.17 mmol, 67 %). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = 7.36 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 5.04 (dd, *J* = 9.1, 3.6 Hz, 1H), 2.65-2.53 (m, 1H), 2.47-2.36 (m, 1H), 2.29 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 169.8, 150.6, 140.1, 127.0 (2C), 125.9 (q, $J_{C\text{-}F}$ = 277.5 Hz), 122.1 (2C), 68.3 (q, $J_{C\text{-}F}$ = 3.3 Hz), 42.9 (q, $J_{C\text{-}F}$ = 26.9 Hz), 21.2. **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$), δ (ppm) = -63.7 (s, 3F). The data is in agreement with those previously reported.[3]

3,3,3-Trifluoro-1-(4-fluorophenyl)-1-propanol (4b)



Prepared according to the *General Procedure B* from 1-fluoro-4-vinylbenzene (31 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (2-20% AcOEt in heptane), the title compound **4b** was obtained as a colourless oil (87 mg, 0.10 mmol, 40 %). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.36 (dd, *J* = 8.4, 5.3 Hz, 2H), 7.07 (t, *J* = 8.7 Hz, 2H), 5.08 (dt, *J* = 8.8, 3.4 Hz, 1H), 2.71-2.34 (m, 2H), 2.18 (d, *J* = 3.2 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 162.8 (d, $J_{C\text{-}F}$ = 246.9 Hz), 127.6 (d, $J_{C\text{-}F}$ = 8.3 Hz, 2C)), 125.9 (q, $J_{C\text{-}F}$ = 277.6 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.6 Hz, 2C), 68.4 (q, $J_{C\text{-}F}$ = 3.2 Hz), 43.2 (q, $J_{C\text{-}F}$ = 27.0 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -63.7 (s, 3F), -113.6 (s, 1F). The data is in agreement with those previously reported.[3]

3,3,3-Trifluoro-1-(4-bromophenyl)-1-propanol (4c)

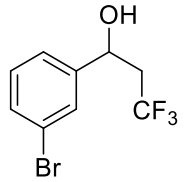


Prepared according to the *General Procedure B* from 1-bromo-4-vinylbenzene (47 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (2-20% AcOEt in heptane), the title compound **4c** was obtained as a colourless

[3] Y. Yasu, T. Koike, M. Akita. *Angew. Chem. Int. Ed.* **2012**, *51*, 9567-9571.

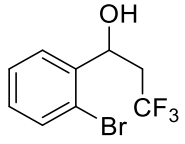
oil (29.6 mg, 0.11 mmol, 44 %). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.52 (d, *J* = 8.1 Hz, 2 H), 7.26 (d, *J* = 8.1, 2 H), 5.08-5.05 (m, 1 H), 2.70-2.55 (m, 1 H), 2.51-2.34 (m, 1 H), 2.17 (d, *J* = 3.1 Hz, 1 H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$), δ (ppm) = 141.4, 132.1 (2C), 127.5 (2C), 125.9 (q, $J_{C\text{-}F}$ = 277.4 Hz), 122.4, 68.4 (q, $J_{C\text{-}F}$ = 3.1 Hz), 43.0 (q, $J_{C\text{-}F}$ = 27.0 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -63.7 (s, 3F). The data is in agreement with those previously reported.[3]

3,3,3-Trifluoro-1-(3-bromophenyl)-1-propanol (4d)



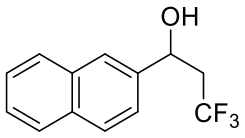
Prepared according to the *General Procedure B* from 1-bromo-3-vinylbenzene (47 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (2-20% AcOEt in heptane), the title compound **4d** was obtained as a yellow oil (56.5 mg, 0.21 mmol, 84 %). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.56-7.55 (m, 1H), 7.46 (dt, *J* = 7.3, 1.8 Hz, 1H),7.31-7.22 (m, 2H), 5.05 (dd, *J*= 8.9, 3.6 Hz, 1H), 2.69-2.51 (m, 1H), 2.49-2.35 (m, 1H), 2.16 (bs, 1 H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 144.6, 131.6, 130.6, 129.0, 125.9 (q, $J_{C\text{-}F}$ = 277.4 Hz),124.4, 123.1, 68.3 (q, $J_{C\text{-}F}$ = 3.3 Hz), 43.0 (q, $J_{C\text{-}F}$ = 27.1 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -63.7 (s, 3F). The data is in agreement with those previously reported.[3]

3,3,3-Trifluoro-1-(2-bromophenyl)-1-propanol (4e)



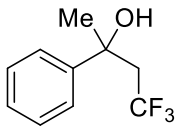
Prepared according to the *General Procedure B* from 1-bromo-2-vinylbenzene (47 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (2-20% AcOEt in heptane), the title compound **4e** was obtained as a colorless oil (21.5 mg, 0.08 mmol, 32 %). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.63 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.38 (tdd, *J* = 7.8, 1.3, 0.5 Hz, 1H), 7.19 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 5.47 (dt, *J* = 9.5, 3.1 Hz, 1H), 2.66-2.36 (m, 2H), 2.30 (d, *J*= 3.7 Hz, 1 H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 141.3, 133.1, 129.8, 128.2, 127.4, 126.0 (q, $J_{C\text{-}F}$ = 277.8 Hz), 121.4, 67.8 (q, $J_{C\text{-}F}$ = 3.3 Hz), 41.5 (q, $J_{C\text{-}F}$ = 27.1 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -63.8 (s, 3F). The data is in agreement with those previously reported.[3]

3,3,3-Trifluoro-1-(naphthalen-6-yl)propan-1-ol) (4f)



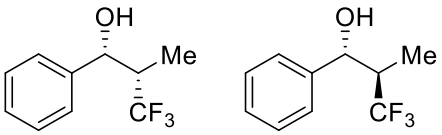
Prepared according to the *General Procedure B* from 2-vinylnaphthalene (39 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (2-30 % AcOEt in heptane), the title compound **4f** was obtained as a colorless oil (45.6 mg, 0.19 mmol, 74 %). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.89-7.83 (m, 4H), 7.53-7.46 (m, 3 H), 5.26 (dd, *J*= 10.0, 3.0 Hz, 1H), 2.82-2.63 (m, 1H), 2.64-2.47 (m, 1H), 2.29 (brs, 1H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 139.8, 133.4 (2C), 129.0, 128.2, 127.9, 126.6, 126.5, 126.1 (q, $J_{C\text{-}F}$ = 276.0 Hz), 124.8, 123.5, 69.1 (q, $J_{C\text{-}F}$ = 3.3 Hz), 42.9 (q, $J_{C\text{-}F}$ = 27.0 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -63.6 (s, 3F). The data is in agreement with those previously reported.[3]

3,3,3-Trifluoro-1-methyl-1-pheny-1-propanol (4g)



Prepared according to the *General Procedure B* from prop-1-en-2-ylbenzene (30 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (2-15 % AcOEt in heptane), the title compound **4g** was obtained as a colorless oil (38.8 mg, 0.19 mmol, 75 %). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.47 (d, *J*= 7.5 Hz, 2H), 7.37 (t, *J*= 7.4 Hz, 2H), 7.30 (d, *J*= 7.1 Hz, 1H), 2.77-2.59 (m, 2H), 2.17 (bs, 1H), 1.72 (s, 3H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 146.4, 128.6 (2C), 127.5, 125.9 (q, $J_{C\text{-}F}$ = 277.9 Hz), 124.5 (2C), 72.1 (q, $J_{C\text{-}F}$ = 2.2 Hz), 46.8 (q, $J_{C\text{-}F}$ = 25.6 Hz), 29.8. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = 60.1 (s, 3F). The data is in agreement with those previously reported.[3]

3,3,3-Trifluoro-2-methyl-1-phenylpropanol (4h)



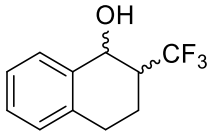
***syn*-4h** ***anti*-4h'**

Prepared according to the *General Procedure B* from (*E*)-prop-1-en-1-ylbenzene (29 mg, 0.25 mmol, 1.0 equiv). The title compound was obtained as mixture of diastereomers (1:1.3), and after a chromatographic purification (2-10 % AcOEt in heptane) ***syn*-4h** was obtained as a colorless oil (29 mg, 0.14 mmol, 55%) and ***anti*-4h'** was obtained as a colorless oil (22 mg, 0.11 mmol, 43%). The data is in agreement with those previously reported.[3]

Data of ***syn*-4h. ^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.42-7.30 (m, 5H), 4.81 (dd, *J* = 8.2, 2.5 Hz, 1H), 2.71-2.58 (m, 1H), 2.17 (d, *J* = 3.0 Hz, 1H), 0.87 (d, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 141.1, 128.8 (2C), 128.7, 127.9 (q, $J_{C\text{-}F}$ = 280.7 Hz), 127.1 (2C), 74.2 (q, $J_{C\text{-}F}$ = 2.0 Hz), 44.9 (q, $J_{C\text{-}F}$ = 24.4 Hz), 10.7 (q, $J_{C\text{-}F}$ = 3.0 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -68.6 (s, 3F).

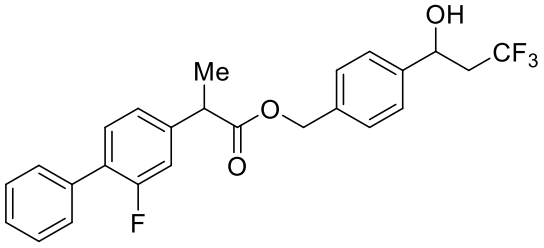
Data of ***anti*-4h'**. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.41-7.28 (m, 5H), 5.23 (d, *J* = 2.7 Hz, 1H), 2.56-2.38 (m, 1H), 1.93 (bs, 1H), 1.09 (d, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 141.1, 128.8 (2C), 128.7, 127.8 (q, $J_{C\text{-}F}$ = 280.7 Hz),127.1 (2C), 74.2 (q, $J_{C\text{-}F}$ = 2.0 Hz), 44.9 (q, $J_{C\text{-}F}$ = 24.4 Hz), 10.7 (q, $J_{C\text{-}F}$ = 3.1 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -70.1 (s, 3F).

2-(Trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (4i)



Prepared according to the *General Procedure B* from 1,2-dihydronaphthalene (35 mg, 0.27 mmol, 1.0 equiv). The title compound was obtained as mixture of diastereomers (1:1), and after a chromatographic purification (0-5% CH_2Cl_2 in heptane) the inseparable mixture **4i** was obtained as a colorless oil (38.8 mg, 0.19 mmol, 75 %). The combined data for both isomers is detailed. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.56 (dd, *J*= 7.3, 1.9 Hz, 1H), 7.36-7.25 (m, 3H), 7.24-7.09 (m, 4H), 5.04-5.00 (m, 2H), 3.06-2.80 (m, 5H), 2.63-2.38 (m, 2H), 2.26-2.00 (m, 4H), 1.88-1.80 (m, 1H). **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$), δ (ppm) = 136.8, 136.4, 136.1, 135.8, 130.2, 129.3, 129.0, 128.5, 128.1, 128.0, 127.8 (q, $J_{C\text{-}F}$ = 280.1 Hz), 127.3 (q, $J_{C\text{-}F}$ = 279.4 Hz), 127.0, 126.9, 67.6 (q, $J_{C\text{-}F}$ = 3.3, 2.0 Hz), 65.9 (q, $J_{C\text{-}F}$ = 2.9 Hz), 47.3 (q, $J_{C\text{-}F}$ = 24.3 Hz), 44.7 (q, $J_{C\text{-}F}$ = 25.7 Hz), 28.3, 27.7, 21.1 (q, $J_{C\text{-}F}$ = 2.9 Hz), 16.5 (q, $J_{C\text{-}F}$ = 2.5 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm) = -68.7 (s, 3F), -69.8 (s, 3F). The data is in agreement with those previously reported.[3]

4-(3,3,3-Trifluoro-1-hydroxypropyl)Benzyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (4j)



Prepared according to the *General Procedure B* from 4-vinylbenzyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (90 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (2-15 % AcOEt in heptane), the title compound **4j** was obtained as a colourless oil (63 mg, 0.14 mmol, 56 %). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 1H NMR (300 MHz, Chloroform-d) δ 7.58 – 7.48 (m, 2H), 7.50 – 7.39 (m, 2H), 7.41 – 7.27 (m, 6H), 7.17 – 7.04 (m, 2H), 5.14 (s, 2H), 5.08 (dt, *J* = 8.9, 3.3 Hz, 1H), 3.80 (q, *J* = 7.2 Hz, 1H), 2.69 – 2.52 (m, 1H), 2.52 – 2.35 (m,

1H), 2.10 (d, J = 3.2 Hz, 1H), 1.55 (d, J = 7.8 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm) = 173.9, 159.8 (d, $J_{C\text{-}F}$ = 248.5 Hz), 142.5, 141.7 (d, $J_{C\text{-}F}$ = 7.8 Hz), 136.2, 135.6, 130.9 (d, $J_{C\text{-}F}$ = 4.0 Hz), 129.1 (d, $J_{C\text{-}F}$ = 3.0 Hz, 2C), 128.6 (4C), 127.9, 128.0 (d, $J_{C\text{-}F}$ = 13.4 Hz), 126.0 (2C), 126.0 (q, $J_{C\text{-}F}$ = 277.8 Hz), 123.7 (d, $J_{C\text{-}F}$ = 3.5 Hz), 115.4 (d, $J_{C\text{-}F}$ = 23.5 Hz), 68.7 (q, $J_{C\text{-}F}$ = 3.3 Hz), 66.4, 45.2, 43.0 (q, $J_{C\text{-}F}$ = 27.0 Hz), 18.4. **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$), δ (ppm) = -63.7 (s, 3F), -117.6 (s, 1F). **IR** (ATR) ν (cm^{-1}): 1716, 1623, 1483, 1418, 1369, 1326, 1247, 1169, 1126, 1019. **HRMS (APCI)** calcd for $C_{25}H_{22}F_4O_3$ $[M]^+$: 446.1500, found 446.1495.

2.4. Synthesis of 1,2-Trifluoromethyl Azides and 1,2-Trifluoromethyl Amines:

2.4.1. Reaction Optimization:

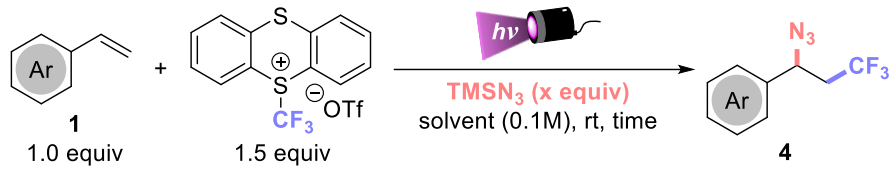
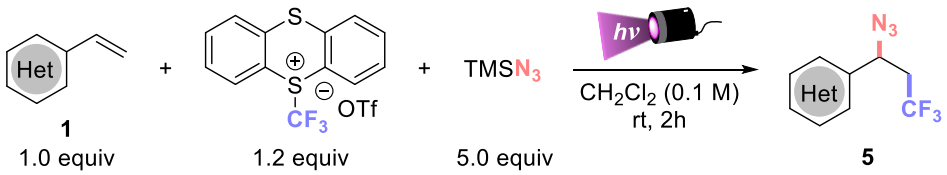


Table S5. Exploration of reaction conditions

Entry	Equiv. TT-CF_3	Equiv Styrene	Equiv azide	Conc. of styrene	Solvent	Time	Yield[a]
1	1.5	1	5	0.1 M	MeCN	2 h	58%
2	1.5	1	5	0.1 M	Acetone	2 h	0%
3	1.5	1	5	0.1 M	DCM	2 h	90%
4	1.5	1	5	0.1 M	DCE	2 h	74 %
5	1.5	1	5	0.1 M	THF	2 h	46%
6	1.5	1	5	0.1 M	DME	2 h	68%
7	1.2	1	5	0.1 M	DCM	2 h	95%
8	1.2	1	3.5	0.1 M	DCM	2 h	94%
9	1.2	1	2.5	0.1 M	DCM	2 h	83%
10	**1.2**	**1**	**3.5**	**0.1 M**	**DCM**	**1 h**	**96%**
11	1.2	1	3.5	0.1 M	DCM	1 h	0%[b]

[a]Calculated by ^{1}H-NMR adding 0.1 mmol of 1,3,5-trimethoxybenzene. [b]No light or 427 nm Kessil or 456 nm Kessil.

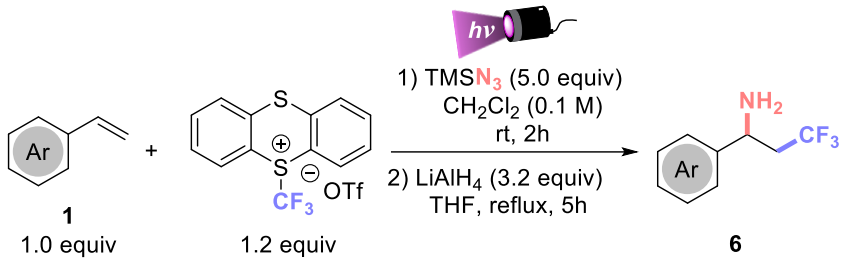
2.4.2. General Procedure C:



To an 8 mL vial equipped with a magnetic stir bar was added styrene **1** (0.5 mmol, 1.0 equiv, *if solid*) and trifluoromethyl-thianthrenium salt TT-CF_3^+ OTf^- (326 mg, 0.6 mmol, 1.2 equiv). The vial was sealed with a cap containing a Sil/PTFE septum, evacuated, and backfilled with nitrogen. After this process was repeated 3 times, anhydrous degassed CH_2Cl_2 (5 mL, *c* = 0.1 M), $TMSN_3$ (2.5 mmol, 5 equiv) and styrene **1** (0.5 mmol, 1.0 equiv, *if liquid*) were added via syringe. The reaction mixture was irradiated with a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) for 1 hour as described in the "Workflow" section. The lamp was placed 4 cm away from the reaction vials and cooled at room temperature by an external fan. Upon completion, the

volatiles were removed under reduced pressure, and the crude mixture was subjected to purification by column chromatography to afford compound **5**.

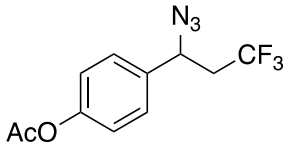
2.4.3. General Procedure D:



To an 8 mL vial equipped with a magnetic stir bar was added styrene **1** (0.5 mmol, 1.0 equiv, *if solid*) and trifluoromethyl-thianthrenium salt TT-CF_3^+ OTf^- (326 mg, 0.6 mmol, 1.2 equiv). The vial was sealed with a cap containing a Sil/PTFE septum, evacuated, and backfilled with nitrogen. After this process was repeated 3 times, anhydrous degassed CH_2Cl_2 (5 mL, *c* = 0.1 M), $TMSN_3$ (2.5 mmol, 5 equiv) and styrene **1** (0.5 mmol, 1.0 equiv, *if liquid*) were added via syringe. The reaction mixture was irradiated with a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) for 1 hour as described in the "Workflow" section. The lamp was placed 4 cm away from the reaction vials and cooled at room temperature by an external fan. Upon completion, the volatiles were removed under reduced pressure, and to the crude mixture, $LiAlH_4$ 1 M in THF (1.6 mmol, 3.2 equiv.) was added at room temperature.[4] After 5h reflux, the reaction mixture was carefully quenched with H_2O (72 µL), 15 % aq NaOH (216 µL), and H_2O (72 µL). Then, the solution was diluted with ethyl acetate, filter the solution through celite and dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by column chromatography to afford compound **5**.

2.4.4. Characterization Data:

4-(1-Azido-3,3,3-trifluoropropyl)phenyl Acetate (5a)

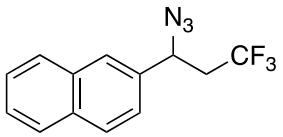


Compound **5a** was prepared according to the *General Procedure C* from 4-vinylphenyl acetate (81.1 mg, 0.5 mmol). After purification by column chromatography through silica gel (from hexane:AcOEt, 9.5:0.5 to 9:1), the title compound **5a** was obtained as a light-yellow oil (93.8 mg, 0.34 mmol, 69% yield). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm): 7.34 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 4.79 (dd, *J* = 8.7, 4.9 Hz, 1H), 2.68 – 2.55 (m, 1H), 2.47 (m, 1H), 2.30 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 169.2, 151.1, 135.3, 127.8, 125.2 (q,

[4] H. Liu, Q. Geo, C. Chen, M. Wang, Z. Xu, *Org. Chem. Front.* **2018**, *5*, 1522-1526.

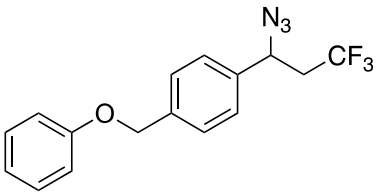
J = 275.3 Hz), 122.4, 59.4 (q, *J* = 3.1 Hz), 40.5 (q, *J* = 28.3 Hz), 21.1. **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm): -64.1. The data is in agreement with those previously reported.[5]

2-(1-Azido-3,3,3-trifluoropropyl)naphthalene (5b)



Compound **5b** was prepared according to the *General Procedure C* from 2-vinylnaphthalene (77.1 mg, 0.5 mmol). After purification by column chromatography through silica gel (hexane:AcOEt, 9.5:0.5), the title compound **5x** was obtained as a colorless oil (141.1 mg, 0.33 mmol, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 7.92 (d, *J* = 8.5 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.80 (s, 1H), 7.58 – 7.52 (m, 2H), 7.43 (d, *J* = 8.5 Hz, 1H), 4.97 (dd, *J* = 8.5, 5.2 Hz, 1H), 2.72 (m, 1H), 2.60 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 134.9, 133.5, 133.1, 129.4, 128.7, 128.1, 127.8, 126.8, 126.4, 126.3, 125.3 (q, *J* = 277.2 Hz), 124.2, 123.7, 122.0, 60.2 (q, *J* = 3.0 Hz), 60.19, 40.4 (q, *J* = 28.3 Hz). **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm): -64.0. The data is in agreement with those previously reported.[5]

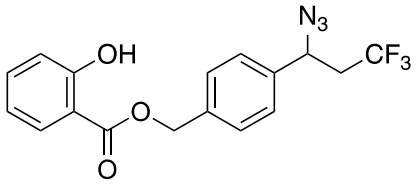
1-(1-Azido-3,3,3-trifluoropropyl)-4-(phenoxymethyl)benzene (5c)



Compound **5c** was prepared according to the *General Procedure C* from 1-(benzyloxy)-4-vinylbenzene (105.1 mg, 0.5 mmol). After purification by column chromatography through silica gel (hexane:AcOEt, 9.5:0.5), the title compound **5c** was obtained as a colorless oil (71.5 mg, 0.34 mmol, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 7.50 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.00 – 6.97 (m, 3H), 5.09 (s, 2H), 4.80 (dd, *J* = 8.6, 5.1 Hz, 1H), 2.69 – 2.58 (m, 1H), 2.50 (m, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 158.6, 138.2, 137.4, 129.6, 128.2, 127.0, 125.2 (q, *J* = 277.2 Hz), 121.2, 114.8, 69.3, 59.7, 40.4 (q, *J* = 27.7 Hz); **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm): -64.0; **IR** (ATR) ν (cm^{-1}): 3003, 2927, 2107, 1710, 1598, 1495, 1358, 1219, 1137; **HRMS** (ESI+) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{14}F_3N_3ONa$ 344.0987; found 344.0982.

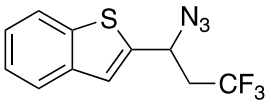
[5] F. Wang, X. Qi, Z. Liang, P. Chen, G. Liu, *Angew. Chem*. **2014**, *126*, 1881-1886.

4-(1-Azido-3,3,3-trifluoropropyl)benzyl 2-Hydroxybenzoate (5d)



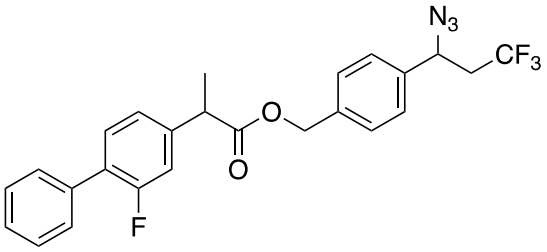
Compound **5d** was prepared according to the *General Procedure C* from 4-vinylbenzyl 2-acetoxybenzoate (148.2 mg, 0.5 mmol). After purification by column chromatography through silica gel (hexane:AcOEt, 9.5:0.5), the title compound **5d** was obtained as a yellow oil (76.5 mg, 0.21 mmol, 42% yield). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 10.70 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 7.8, 5.8 Hz, 2H), 7-49-7.45 (m, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.89 (dd, *J* = 8.1, 7.2 Hz, 1H), 5.40 (s, 2H), 4.82 (dd, *J* = 8.5, 5.1 Hz, 1H), 2.64 (m, 1H), 2.51 (m, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 170.0, 161.8, 138.1, 136.4, 136.0, 130.0, 129.0, 127.1, 125.2 (q, *J* = 278.5 Hz), 119.3, 117.7, 112.3, 66.3, 59.6, 40.4 (q, *J* = 29.0 Hz); **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm): -64.0; **IR** (ATR) ν (cm^{-1}): 3194, 2956, 2104, 1674, 1613, 1484, 1382, 1296, 1245, 1209, 1128, 1084; **HRMS** (ESI+) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{14}F_3N_3O_2Na$ 366.1060; found 366.1075.

2-(1-Azido-3,3,3-trifluoropropyl)benzo[*b*]thiophene (5e)



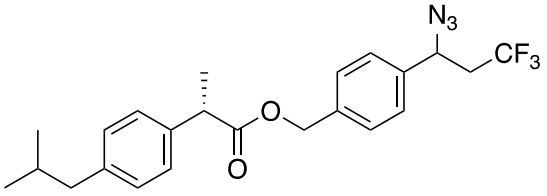
Compound **5e** was prepared according to the *General Procedure C* from 2-vinylbenzo[*b*]thiophene (80.1 mg, 0.5 mmol). After purification by column chromatography through silica gel in hexane, the title compound **5e** was obtained as a colorless oil (27.7 mg, 0.10 mmol, 20% yield). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 7.84 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.32 (s, 1H), 5.14 (dd, *J* = 8.1, 5.5 Hz, 1H), 2.80 – 2.62 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 140.9, 139.6, 138.8, 125.3, 125.0 (q, *J* = 278.5 Hz), 124.9, 124.1, 123.0, 122.6, 56.1, 40.6 (q, *J* = 29.0 Hz); **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm): -64.1; **IR** (ATR) ν (cm^{-1}): 2925, 2854, 2107, 1384, 1320, 1244, 1151, 1126; **HRMS** (ESI+) m/z: $[M+H]^+$ Calcd. for $C_{11}H_9F_3N_3S$ 272.0469; found 272.0460.

4-(1-Azido-3,3,3-trifluoropropyl)benzyl 2-(2-Fluoro-[1,1'-biphenyl]-4-yl)propanoate (5f)



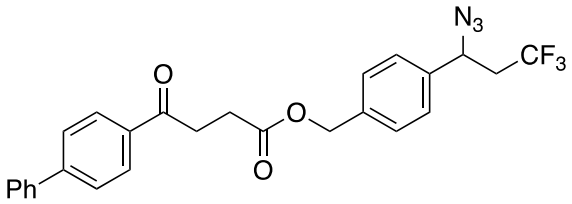
Compound **5f** was prepared according to the *General Procedure C* from 4-vinylbenzyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (180.2 mg, 0.5 mmol). After purification by column chromatography through silica gel (hexane:AcOEt, 9:1, Rf = 0.35), the title compound **5f** was obtained as a colorless oil (185.5 mg, 0.39 mmol, 79% yield), mp: 58 – 60 ºC. **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm): 7.54 (d, *J* = 8.2 Hz, 2H), 7.45 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.16 – 7.09 (m, 2H), 5.16 (s, 2H), 4.78 (dd, *J* = 8.6, 5.1 Hz, 1H), 3.83 (q, *J* = 7.2 Hz, 1H), 2.61 (m, 1H), 2.47 (m, 1H), 1.57 (d, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$), δ (ppm): 173.7, 159.7 (d, *J* = 249.2 Hz), 141.5, 137.7, 136.8, 135.4, 130.8, 129.0, 128.9, 128.6 (d, *J* = 30.2 Hz), 127.8 (d, *J* = 31.7 Hz), 127.8, 126.9, 125.2 (q, *J* = 277.8 Hz), 123.6, 66.0, 59.6, 45.0, 40.4 (q, *J* = 28.7 Hz), 18.3; **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm): -64.0 (s, 3F), -117.5 (s, 1F); **IR** (ATR) ν (cm^{-1}): 2936, 2104, 1733, 1484, 1418, 1379, 1244, 1128; **HRMS** (ESI+) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{21}F_4N_3O_2Na$ 494.1462; found 494.1467.

4-(1-Azido-3,3,3-trifluoropropyl)Benzyl 2-(4-Isobutylphenyl)propanoate (5g)



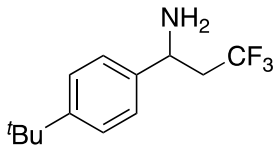
Compound **5g** was prepared according to the *General Procedure C* from 4-vinylbenzyl (*S*)-2-(4-isobutylphenyl)propanoate (161.2 mg, 0.5 mmol). After purification by column chromatography through silica gel (hexane:AcOEt, 9.5:0.5, Rf = 0.3), the title compound **5g** was obtained as a colorless oil (141.1 mg, 0.33 mmol, 65% yield**). ^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 7.26 (s, 4H), 7.20 (d, *J* = 6.8Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 5.12 (s, 2H), 4.77 (dd, *J* = 8.6, 5.1 Hz, 1H), 3.77 (q, *J* = 7.2 Hz, 1H), 2.64 – 2.55 (m, 1H), 2.57-2.46 (m, 3H), 1.87 (m, 1H), 1.5 (d, *J* = 7.2 Hz, 3H), 1.0 (d, *J* = 6.7 Hz, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 174.4, 140.7, 137.5, 137.41, 137.2, 129.4, 128.4, 127.2, 126.8, 125,2 (q, *J* = 278.5 Hz), 65.6, 59.7, 59.6 (q, *J* = 2.5 Hz), 45.1, 45.0, 40.4 (q, *J* = 29.0 Hz), 30.2, 22.4, 18.4; **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm): -64.1; **IR** (ATR) ν (cm^{-1}): 2958, 2104, 1734, 1513, 1381, 1245, 1137, 1106; **HRMS** (ESI+) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{26}F_3N_3O_2Na$ 456.1869; found 456.1880.

4-(1-Azido-3,3,3-trifluoropropyl)benzyl 4-([1,1'-Biphenyl]-4-yl)-4-oxobutanoate (5h)



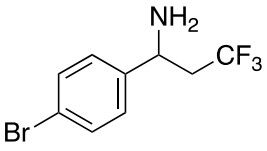
Compound **5h** was prepared according to the *General Procedure C* from 4-vinylbenzyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (185.2 mg, 0.5 mmol). After purification by column chromatography through silica gel (gradient from 10% to 50% AcOEt in hexane), the title compound **5h** was obtained as a colorless oil (145.7 mg, 0.30 mmol, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 8.06 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42 (dd, *J* = 7.7, 5.3 Hz, 3H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.18 (s, 2H), 4.79 (dd, *J* = 8.6, 5.1 Hz, 1H), 3.38 (t, *J* = 6.7 Hz, 2H), 2.87 (t, *J* = 6.6 Hz, 2H), 2.62 (m, 1H), 2.49 (m, 1H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 197.6, 172.7, 146.0, 139.8, 137.6, 137.0, 135.2, 129.0, 128.9, 128.3, 127.3, 127.0, 126.9, 125.5 (q, *J* = 278.5 Hz), 65.8, 59.6, 40.4 (q, *J* = 25.2 Hz), 33.4, 28.3; **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm): -64.0 (s, 3F); **IR** (ATR) ν (cm^{-1}): 2917, 2101, 1732, 1676, 1600, 1387, 1355, 1244, 1125, 1102; **HRMS** (ESI+) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{22}F_3N_3O_3Na$ 504.1505; found 504.1515.

1-(4-(*tert*-Butyl)phenyl)-3,3,3-trifluoropropan-1-amine (6a)



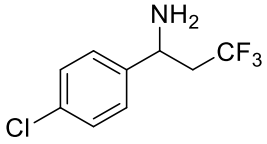
Compound **6a** was prepared according to the *General Procedure D* from 4-*tert*-butyl-styrene (80.1 mg, 0.5 mmol). After purification by column chromatography through silica gel (from hexane:AcOEt, 8:2 to hexane:EtOAc, 1:1 (with 2% of NEt_3), the title compound **6a** was obtained as a brown oil (78.3 mg, 0.32 mmol, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 7.40 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.35 (dd, *J* = 8.4, 4.6 Hz, 1H), 2.52 - 2.41 (m, 2H), 1.70 (s, 2H), 1.34 (s, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 150.8, 141.1, 126.5 (q, *J* = 278.5 Hz), 125.8 (2C), 50.3, 43.3 (q, *J* = 25.2 Hz), 34.5, 31.3; **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm): -63.7; **IR** (ATR) ν (cm^{-1}): 2963, 2905, 2870, 1511, 1395, 1384, 1329, 1251, 1134; **HRMS** (ESI+) m/z: $[M+Na]^+$ Calcd. for $C_{13}H_{18}F_3NNa$ 268.1284; found 268.1286.

1-(4-Bromophenyl)-3,3,3-trifluoropropan-1-amine (6b)



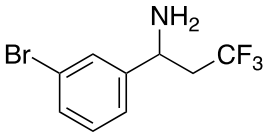
Compound **6b** was prepared according to the *General Procedure D* from 4-bromostyrene (91.5 mg, 0.5 mmol). After purification by column chromatography through silica gel (from 20% to 100% AcOEt in hexane), the title compound **6b** was obtained as a brown oil (80.4 mg, 0.30 mmol, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.41 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J*= 8.5 Hz, 2H), 4.27 (dd, *J* = 8.2, 4.7 Hz, 2H), 2.43 – 2.29 (m, 2H), 1.60 (s, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$), δ (ppm): 142.9, 131.9, 128.0, 126.0 (q, *J* = 277.8 Hz), 121.6, 50.2, 42.2 (q, *J* = 26.3 Hz); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$), δ (ppm): -63.7; **IR** (ATR) ν (cm^{-1}): 2923, 2853, 1685, 1488, 1390, 1253, 1137; **HRMS** (ESI+) m/z: $[M+Na]^+$ Calcd. for $C_9H_{10}BrF_3N$ 267.9943; found 267.9941.

1-(4-Chlorophenyl)-3,3,3-trifluoropropan-1-amine (6c)



Compound **6c** was prepared according to the *General Procedure D* from 4-Chlorostyrene (69.3 mg, 0.5 mmol). After purification by column chromatography through silica gel (from 20% to 50% AcOEt in hexane), the title compound **6c** was obtained as a brown oil (64.1 mg, 0.29 mmol, 57% yield). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 7.25 – 7.28 (m, 4 H), 4.35 (dd, *J* = 8.5, 4.5 Hz, 2 H), 2.49 – 2.34 (m, 2 H), 1.81 (s, 2 H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 142.4, 133.5, 129.0, 127.7, 126.2 (q, *J* = 278.5 Hz), 50.1 (q, *J* = 2.5 Hz), 43.2 (q, *J* = 26.5 Hz); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$), δ (ppm): -63.7 (s, 3F).

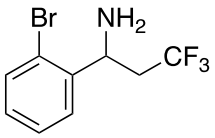
1-(3-Bromophenyl)-3,3,3-trifluoropropan-1-amine (6d)



Compound **6d** was prepared according to the *General Procedure D* from 3-bromostyrene (91.5 mg, 0.5 mmol). After purification by column chromatography through silica gel (from 20% to 50% (with 2% of NEt_3) AcOEt in hexane), the title compound **6d** was obtained as a brown oil (59.0 mg, 0.22 mmol, 44% yield).**^{11}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 7.55 (s, 1H), 7.42 (d, *J*= 8.2 Hz, 1H), 7.29 (d, *J*= 7.6 Hz, 1H), 7.22 (t, *J*= 7.8 Hz, 1H), 4.33 (dd, *J* = 8.2, 4.9 Hz, 2H), 2.48 – 2.38 (m, 2H), 1.68 (s, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 146.3, 131.0, 130.4, 129.4, 126.1 (q, *J* = 278.4 Hz), 125.0, 122.8, 50.3, 43.2 (q, *J* = 26.5 Hz); **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$),

δ (ppm): -63.7; **IR** (ATR) ν (cm^{-1}): 3394, 3311, 2925, 1570, 1473, 1430, 1382, 1260, 1133; **HRMS** (ESI+) m/z: $[M+Na]^+$ Calcd. for $C_9H_{10}BrF_3N$ 267.9943; found 267.9945.

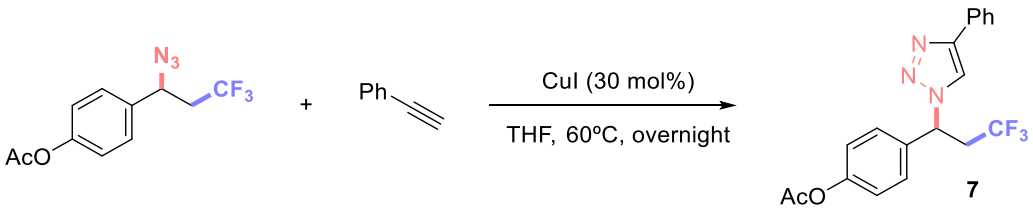
1-(2-Bromophenyl)-3,3,3-trifluoropropan-1-amine (6e)



Compound **6e** was prepared according to the *General Procedure D* from 2-bromostyrene (91.5 mg, 0.5 mmol). After purification by column chromatography through silica gel (from 20% to 40% (with 2% of NEt_3) AcOEt in hexane), the title compound **6e** was obtained as a brown oil (69.7 mg, 0.26 mmol, 52% yield). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 7.50 – 7.53 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.17 - 7.12 (m, 1H), 4.79 (dd, *J* = 9.5, 3.2 Hz, 1H), 2.59 - 2.48 (m, 1H), 2.41 – 2.30 (m, 1H), 1.71 (s, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 142.5, 133.2, 129.2, 128.1, 127.5, 126.3 (q, *J* = 278.5 Hz), 122.7, 49.4, 41.6 (q, *J* = 26.5 Hz); **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm): -63.6; **IR** (ATR) ν (cm^{-1}): 3399, 3321, 2925, 1568, 1468, 1432, 1384, 1324, 1251, 1130; **HRMS** (ESI+) m/z: $[M+Na]^+$ Calcd. for $C_9H_9BrF_3NNa$ 289.9763; found 289.8764.

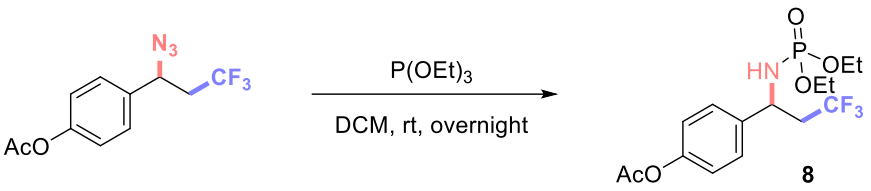
2.5. Derivatization Reactions

Click reaction



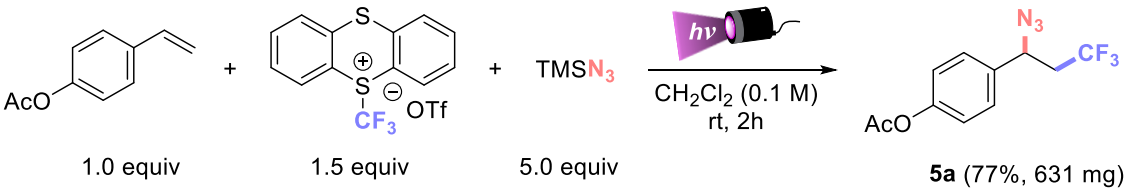
The product was prepared following the adapted literature procedure[3]: Under inert atmosphere, a Schlenk flash with a magnetic stirring bar, the compound **7** (136.6 mg, 0.5 mmol, 1 equiv.) and THF (5 mL) was added. Then, phenylacetylene (165 µL, 1.5 mmol, 3 equiv.) and CuI (30.3 mg, 0.13 mmol, 0.3 equiv.) was added and stirred overnight at 60 ºC. Then, the mixture was concentrated under vacuum, and after purification through a short plug of silica, the title compound **7** was obtained as pure white solid (187.3 mg, 0.5 mmol, 99%), **mp**: 113 – 115 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm): 7.74 (d, *J* = 7.2 Hz, 2H), 7.69 (s, 1H), 7.37 – 7.31 (m, 4H), 7.29 – 7.23 (m, 1H), 7.06 (d, *J* = 8.6 Hz, 2H), 5.80 (dd, *J* = 8.4, 5.7 Hz, 1H), 3.72 – 3.57 (m, 1H), 3.01 (m, 1H), 2.23 (s , 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$), δ (ppm): 169.2, 151.3, 149.1, 134.7, 130.2, 128.9 128.4, 128.0, 125.8, 125.1 (q, *J* = 278.8 Hz), 122.6, 119.6, 58.9, 39.5 (q, *J* = 29.3 Hz), 21.1; **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$), δ (ppm): -64.5; **IR** (ATR) ν (cm^{-1}): 3084, 1784, 1514, 1432, 1370, 1256, 1214, 1139; **HRMS** (ESI+) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{16}F_3N_3O_2Na$ 398.1087; found 398.1094.

Formation of iminophosphorane



A round bottom flask with a magnetic stirring bar, to a dry dichloromethane solution (2.5 mL) of the compound **8** (68.3 mg, 0.25 mmol, 1 equiv.) was added triethylphosphite (77.6 µL, 0.5 mmol, 2.0 equiv.) dropwise in 3 min. The reaction mixture was allowed to stir overnight at room temperature, then concentrated under vacuum. After purification by column chromatography through silica gel (from 20% of AcOEt in hexane to AcOEt), the title compound **8** was obtained as a white solid (81.3 mg, 0.21 mmol, 85% yield). **mp**: 177 – 179 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 7.34 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 4.50 – 4.41 (m, 1H), 4.24 (t, *J* = 10.2 Hz, 1H), 4.08 – 3.96 (m, 2H), 3.90 – 3.83 (m, 1H), 3.63 – 3.56 (m, 1H), 2.70 - 2.64 (m, 1H), 2.63 - 2.45 (m, 1H), 2.28 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$), δ (ppm): 169.3, 150.2, 139.9, 127.3, 125.4 (q, $^{1}J_{F\text{-}C}$ = 277.2 Hz), 121.8, 68.3, 68.1, 62.5 (d, $^{3}J_{P\text{-}C}$ = 5.0 Hz), 62.2 (d, $^{3}J_{P\text{-}C}$ = 5.0 Hz), 42.1 (qd, $^{2}J_{F\text{-}C}$ = 27.7 Hz, $^{3}J_{P\text{-}C}$ = 8.5 Hz, 1C), 21.1, 16.1 (d, $^{2}J_{P\text{-}C}$ = 6.3 Hz), 15.8 (d, $^{2}J_{P\text{-}C}$ = 6.3 Hz); **^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$), δ (ppm): -63.4; **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$), δ (ppm): 6.1 Hz; **IR** (ATR) ν (cm^{-1}): 3180, 2983, 2915, 1759, 1373, 1217, 1197, 1140; **HRMS** (ESI+) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{22}F_3N_3O_3Na$ 504.1505; found 504.1515.

2.6. Large Scale Synthesis of 5a

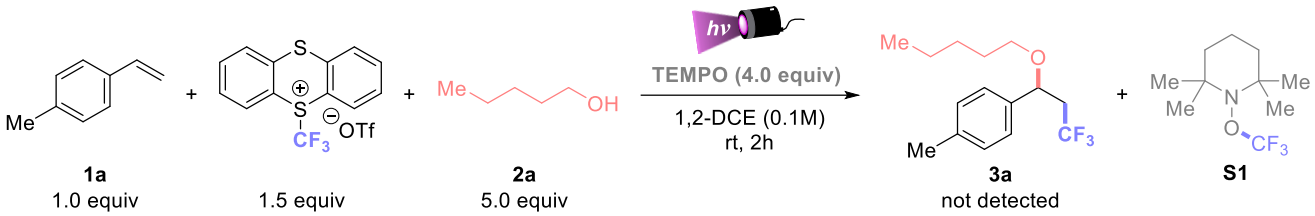


To a 100 mL Schlenk flask with a magnetic stir bar was added trifluoromethyl-thianthrenium salt TT-CF_3^+ OTf^- (1.56 g, 3.60 mmol, 1.2 equiv). The flask was sealed with a cap containing a Sil/PTFE septum, evacuated, and backfilled with nitrogen. After this process was repeated 3 times, anhydrous degassed CH_2Cl_2 (30 mL, *c* = 0.1 M), $TMSN_3$ (2 mL, 15.00 mmol, 5.0 equiv) and styrene **1** (487 mg, 3.00 mmol, 1.0 equiv) were added via syringe. The reaction mixture was irradiated with a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) for 16 hours. The lamp was placed 4 cm away from the reaction vials, and cooled at room temperature by an external fan. Upon completion, the volatiles were removed under reduced pressure, and the crude mixture was subjected to purification by flash column chromatography (9.5:0.5 to 9:1% AcOEt in hexane). The title compound **5a** was obtained as a brown oil (631 mg, 2.31 mmol, 77%). **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm):

7.34 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 4.79 (dd, *J* = 8.7, 4.9 Hz, 1H), 2.68 – 2.55 (m, 1H), 2.47 (m, 1H), 2.30 (s, 3H). The data is in agreement with those previously reported.[5]

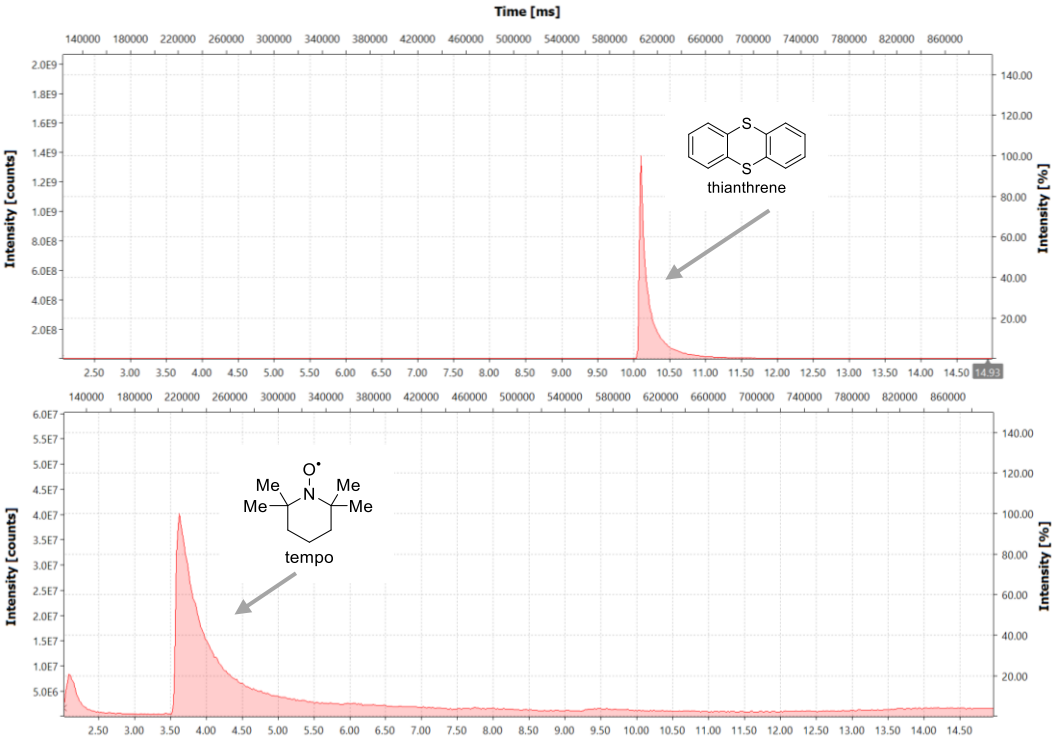
3 Mechanistic Investigations

3.1 TEMPO Trapping Experiment



1a 1.0 equiv | 1.5 equiv | **2a** 5.0 equiv | **3a** not detected | **S1**

To test the intermediacy of radical species, a trapping experiment was performed using TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] as a radical scavenger. The reaction was performed according to the *General Procedure A* using pentan-1-ol (23 mg, 0.27 mmol, 5.0 equiv) and 1-methyl-4-vinylbenzene (6 mg, 0.05 mmol, 1.0 equiv) in the presence of TEMPO (33 mg, 0.21vmmol, 4.0 equiv). The reaction was analyzed by ^{1}H-NMR and GC-MS. The formation of **3a** was completely inhibited, and 1-methyl-4-vinylbenzene and pentan-1-ol were recovered intact. The generated trifluoromethyl radical was successfully trapped, and the tempo adduct **S1** was detected by GC-MS.



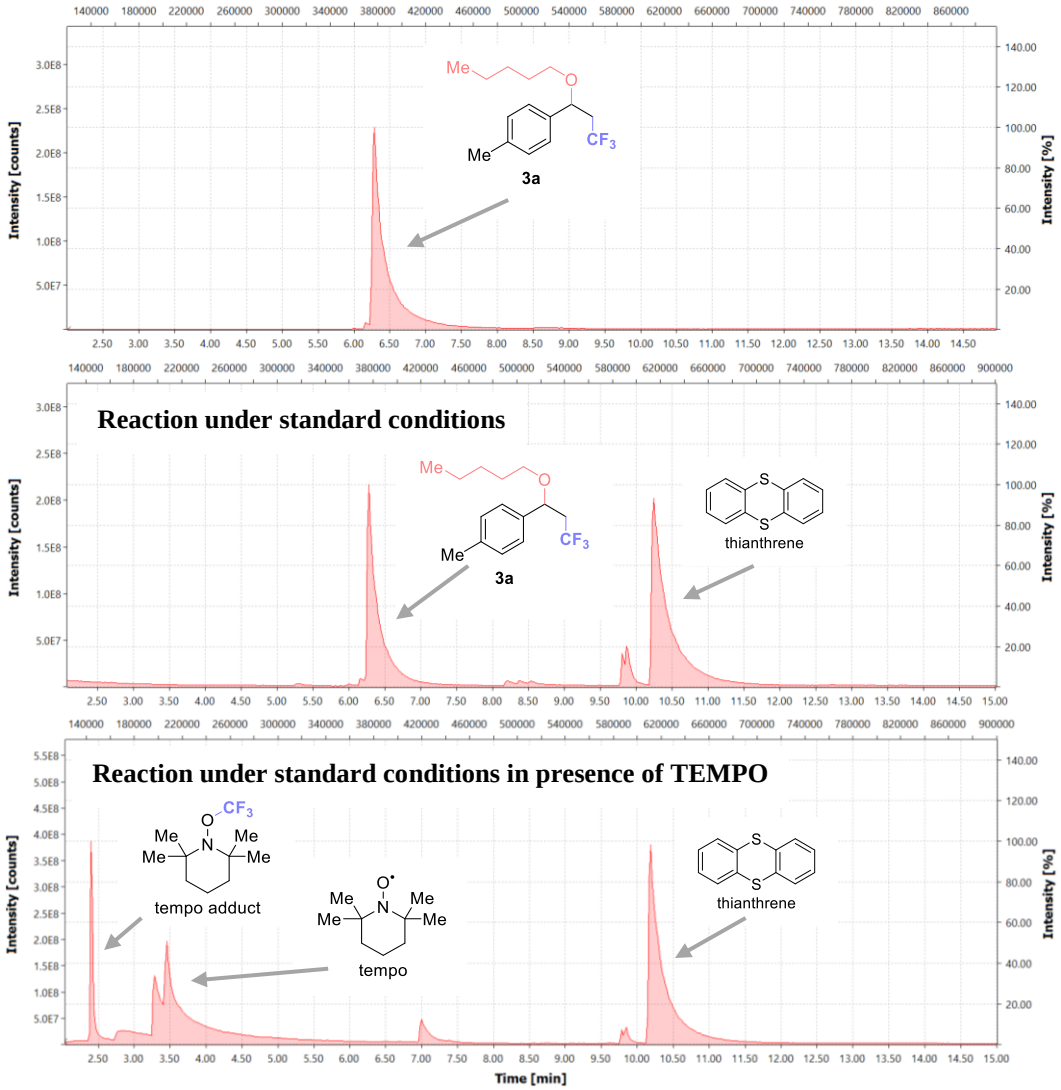
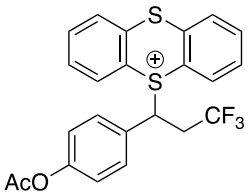


Figure S1. GC-MS spectra of various components and reaction mixture with and without TEMPO.

3.2 Detection of Intermediate D



Theoretical mass: 447,0695
Found: 447.0689

Figure S2. Structure with the corresponding m/z of the intermediate.

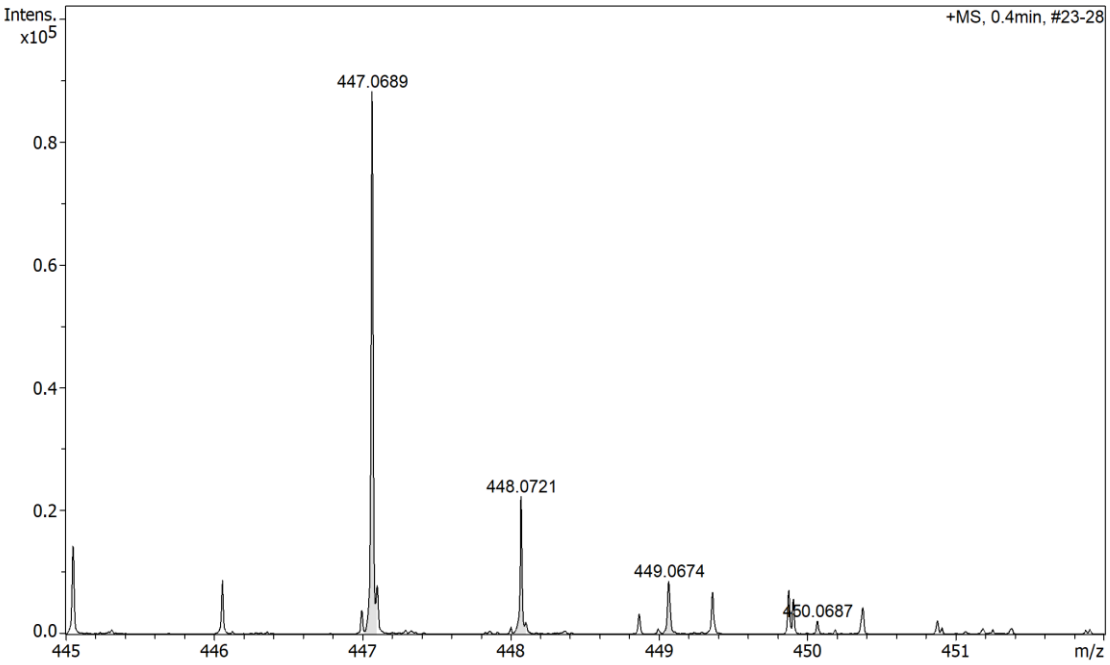
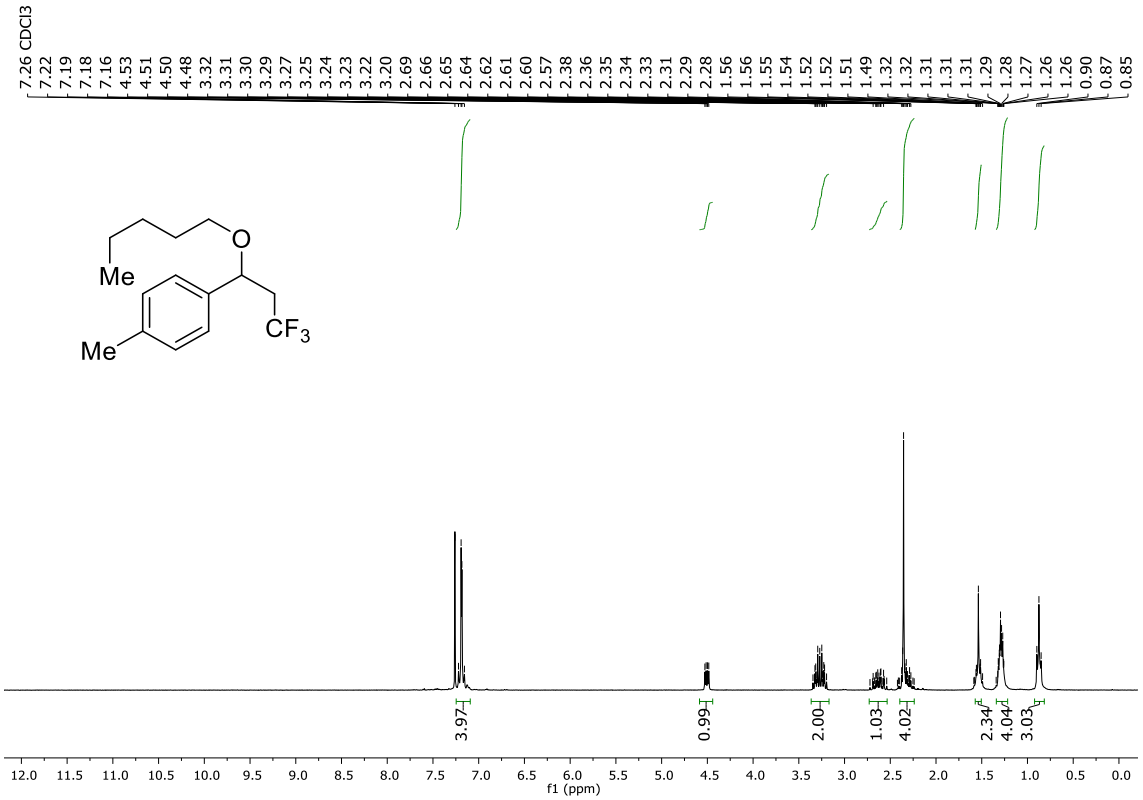
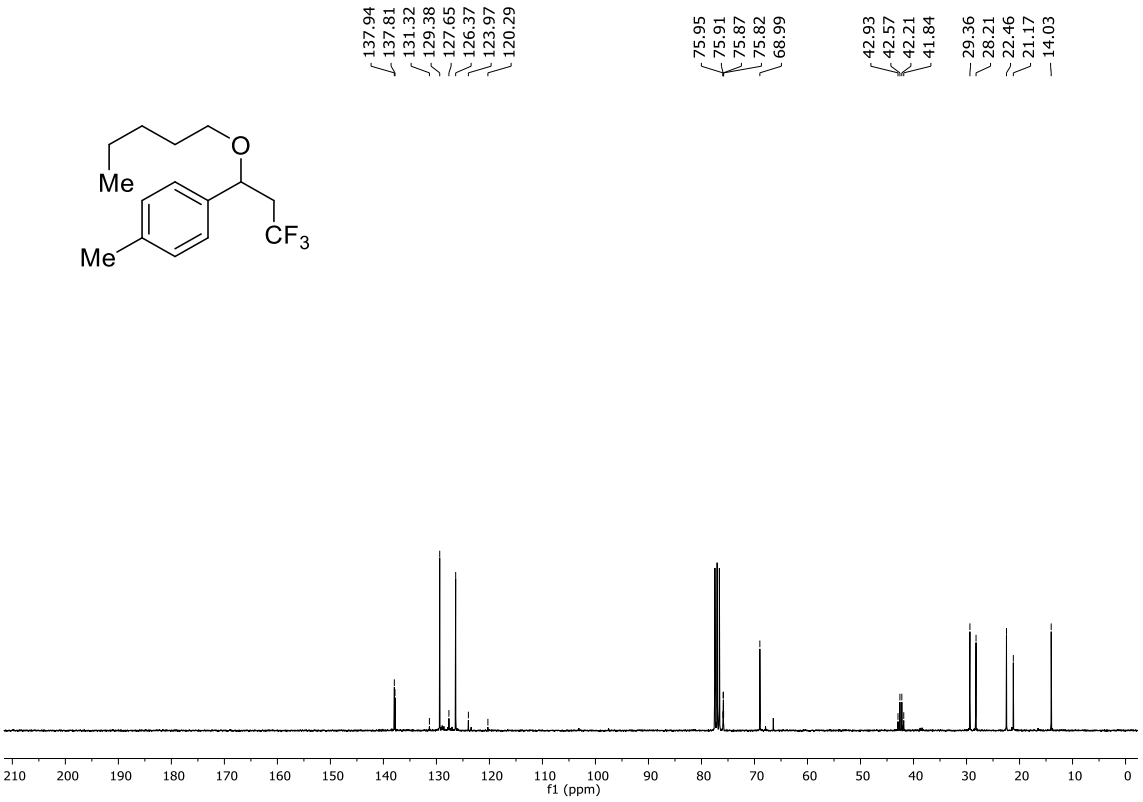


Figure S3. Mass spectrum of the intermediate **B**.

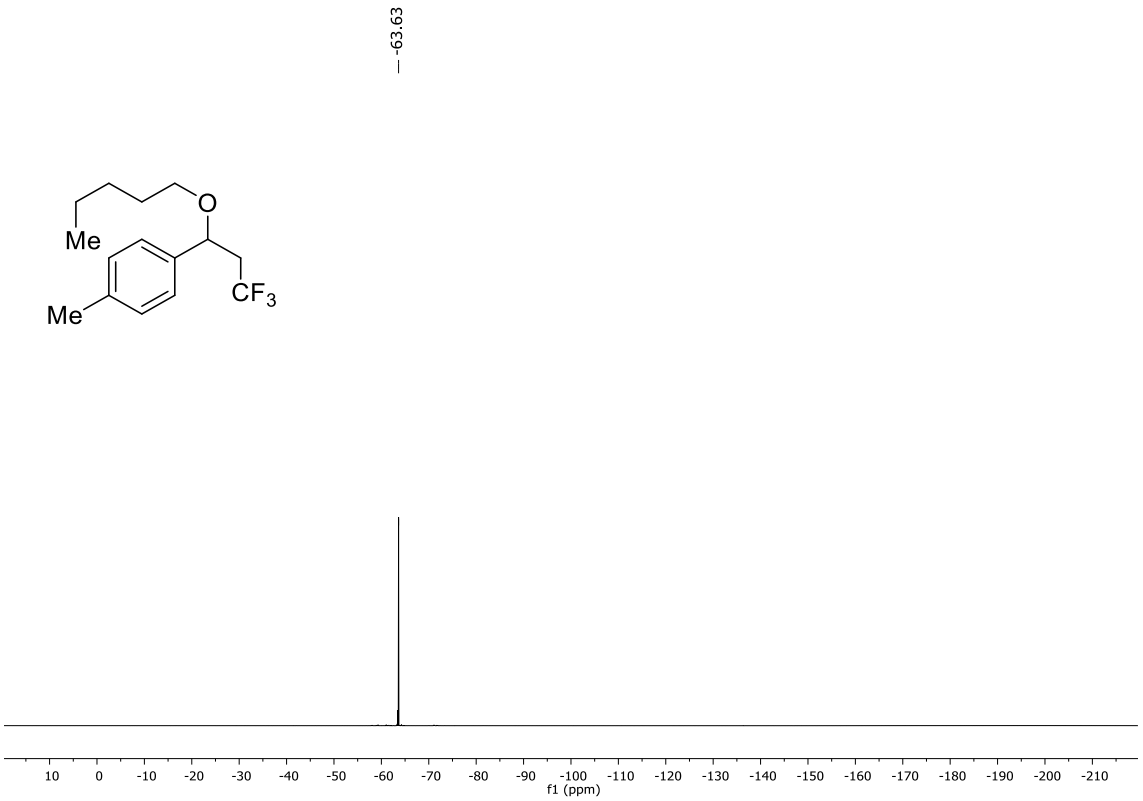
4 NMR Spectra



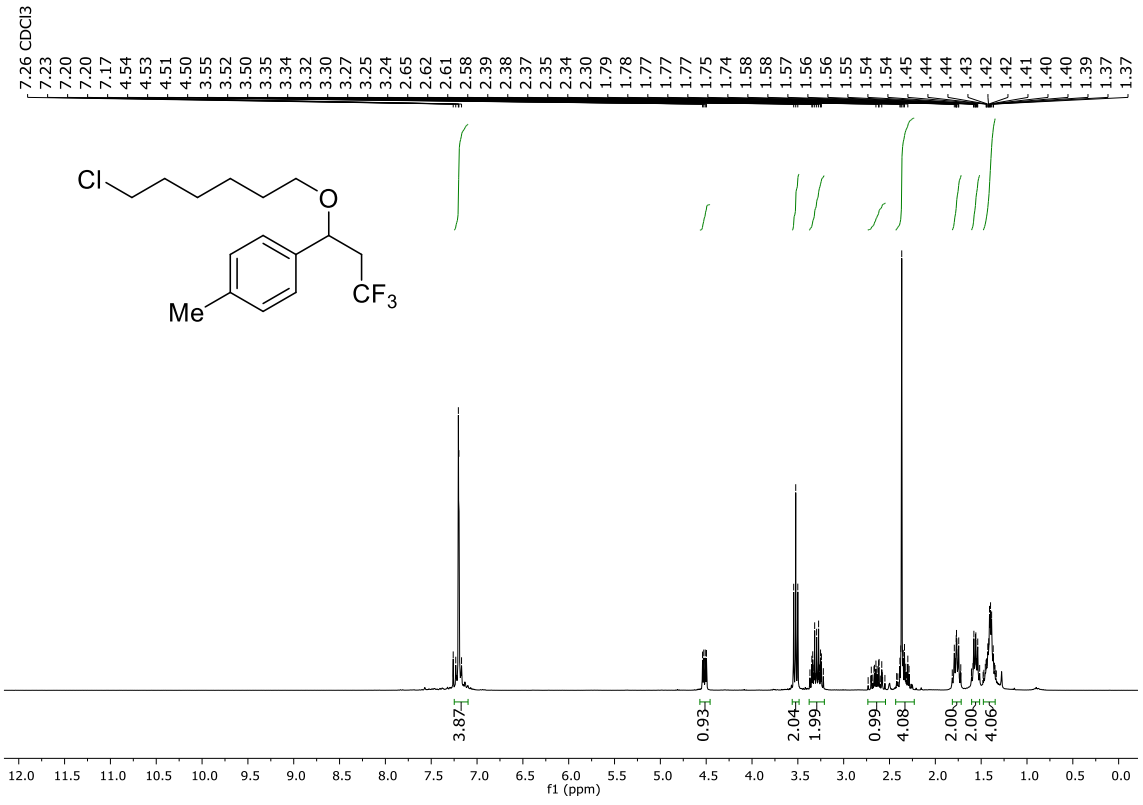
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3a**.



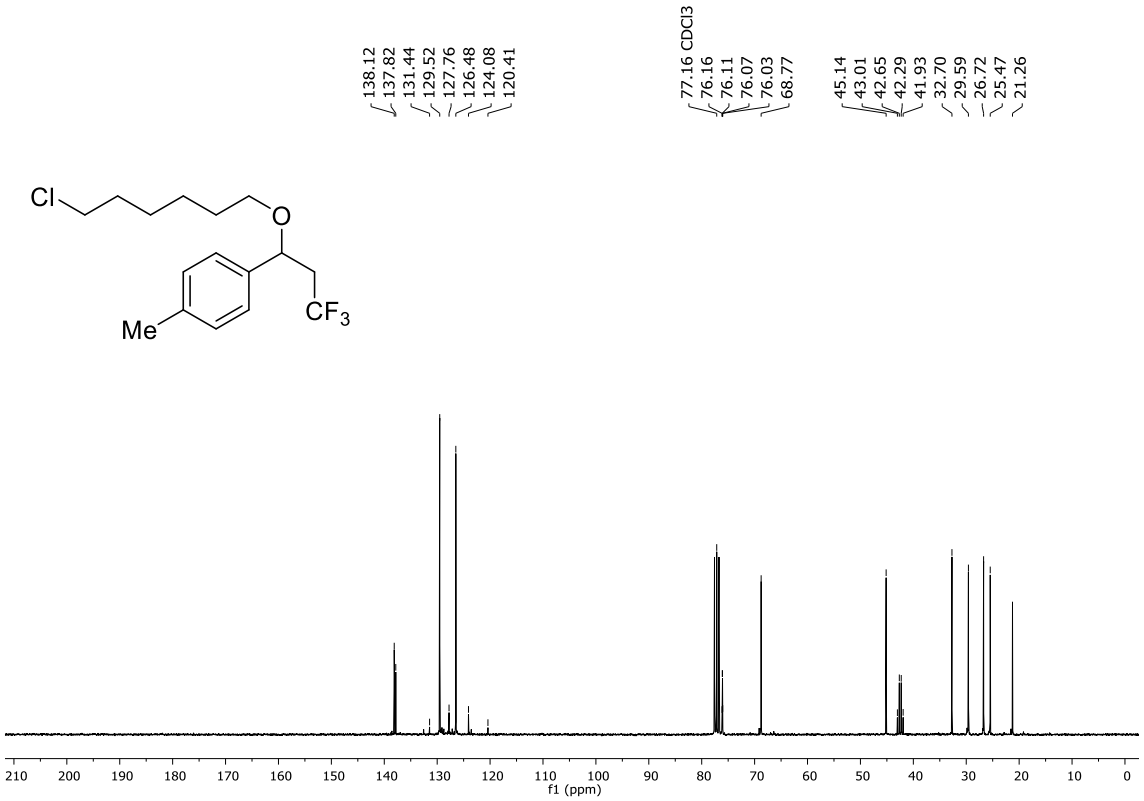
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of compound **3a.**



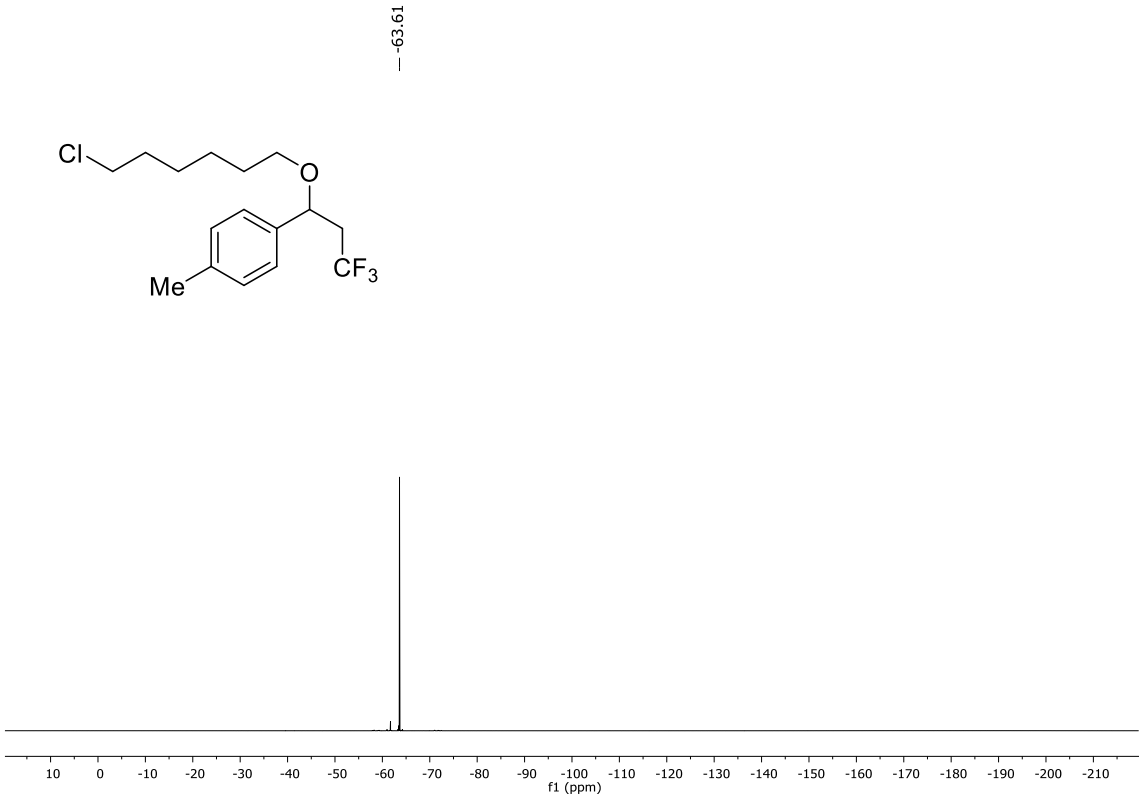
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3a.**



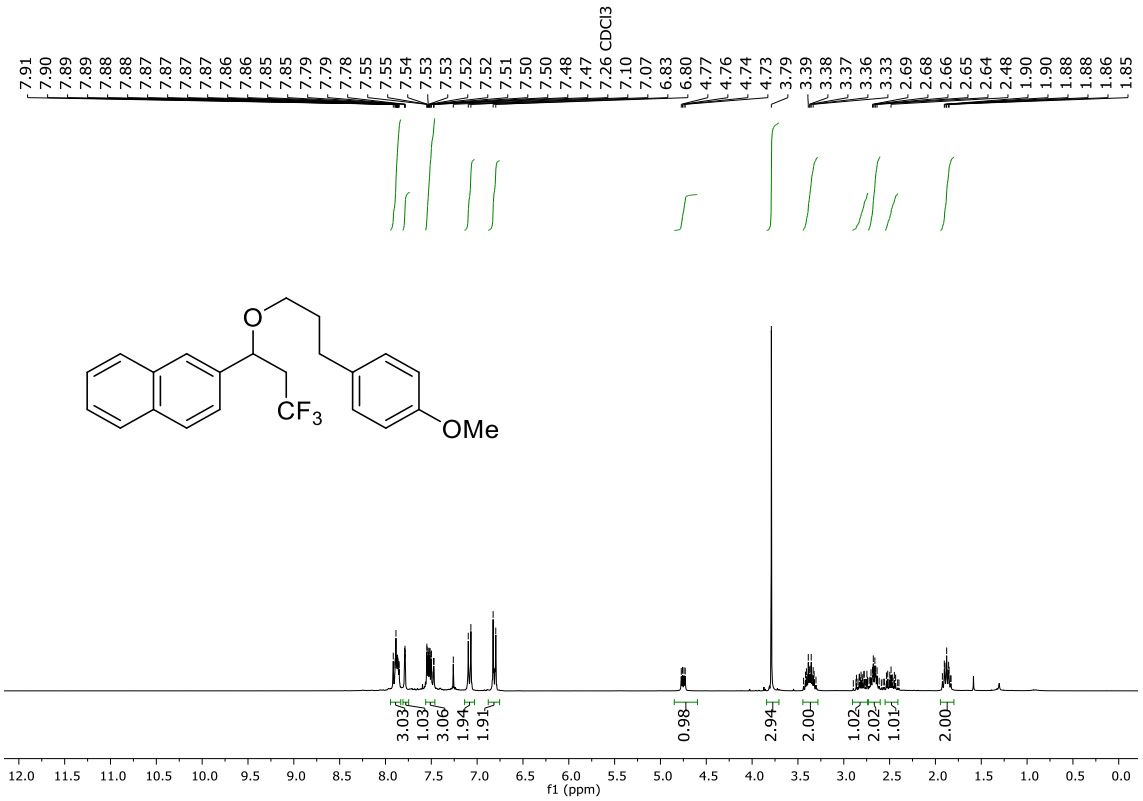
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3b**.



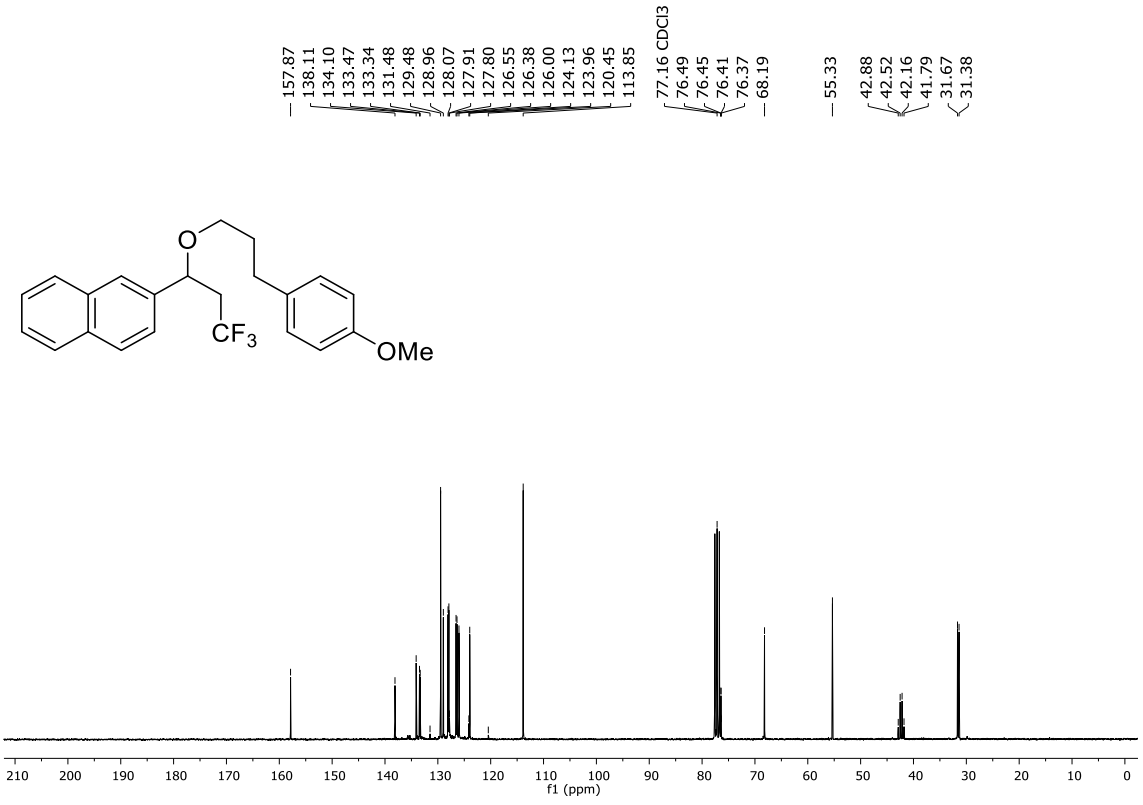
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of compound **3b.**



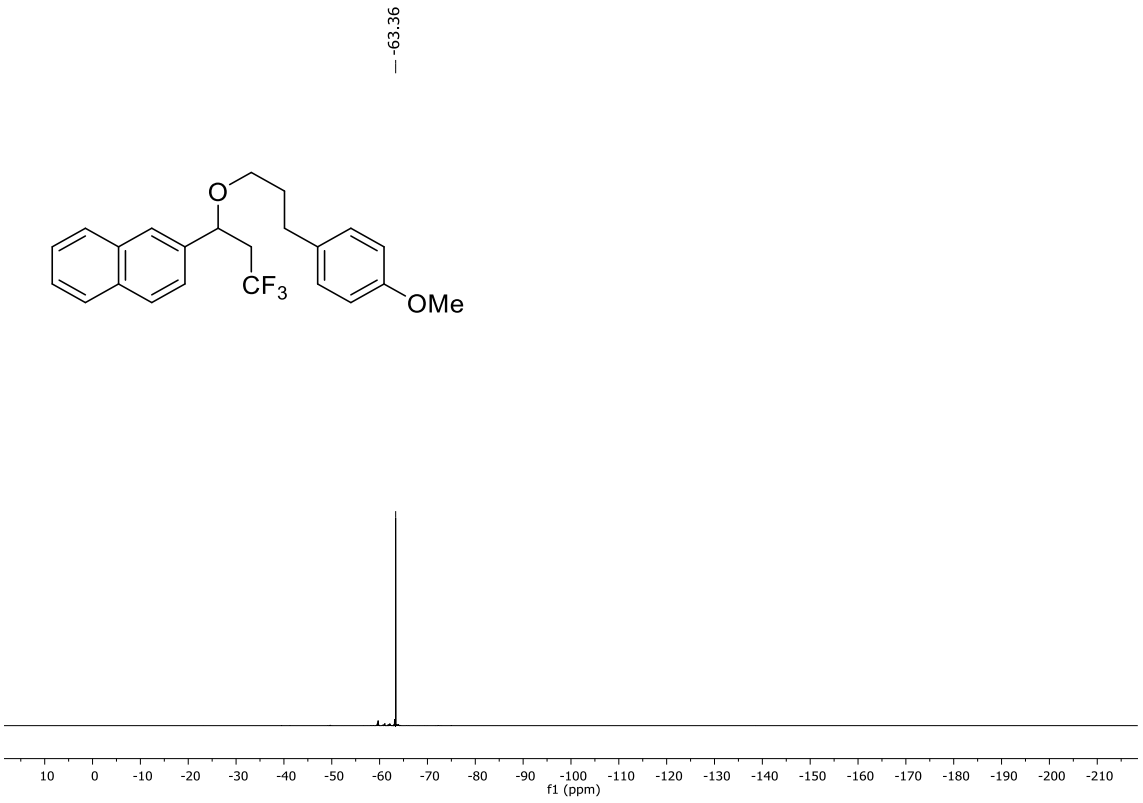
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3b.**



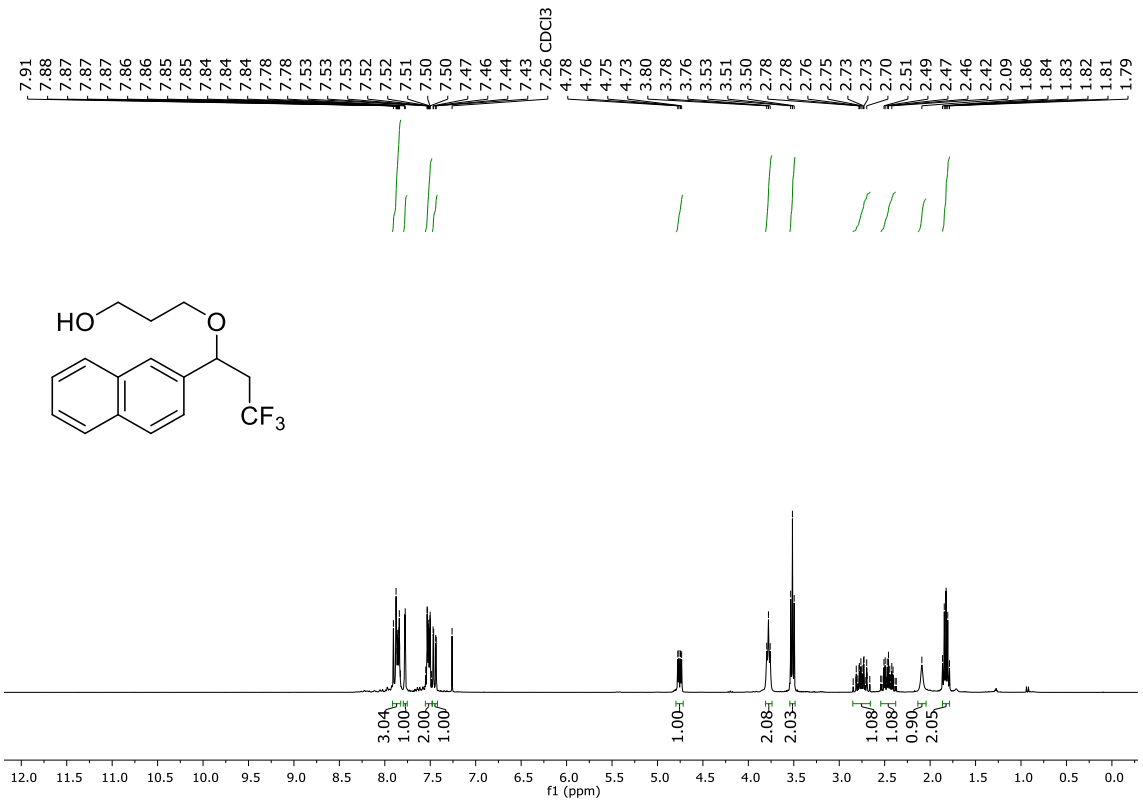
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3c**.



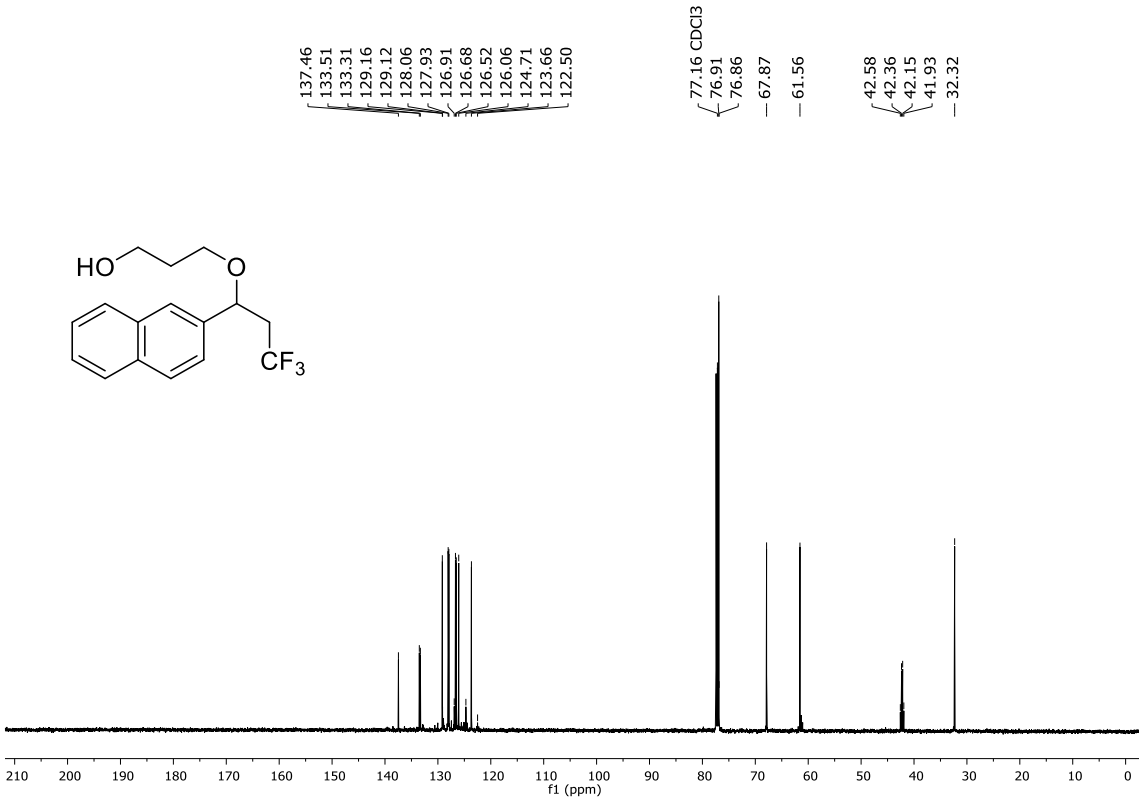
^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$) of compound **3c.**



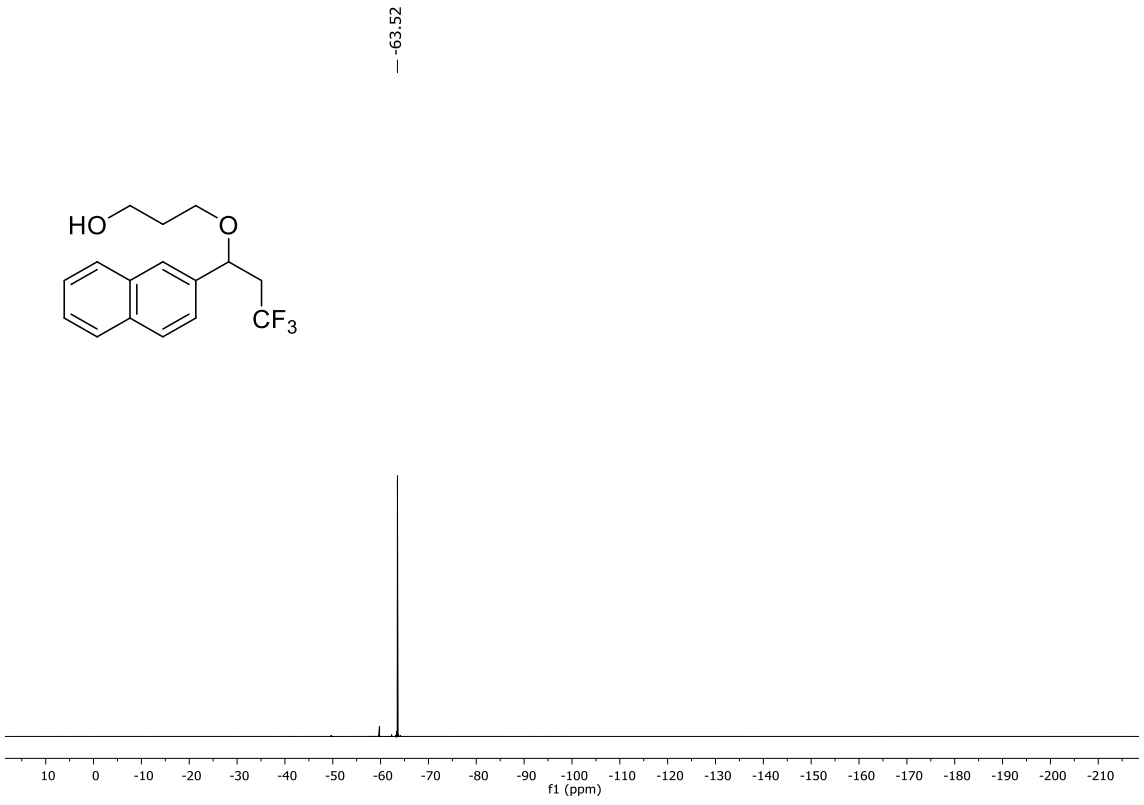
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3c.**



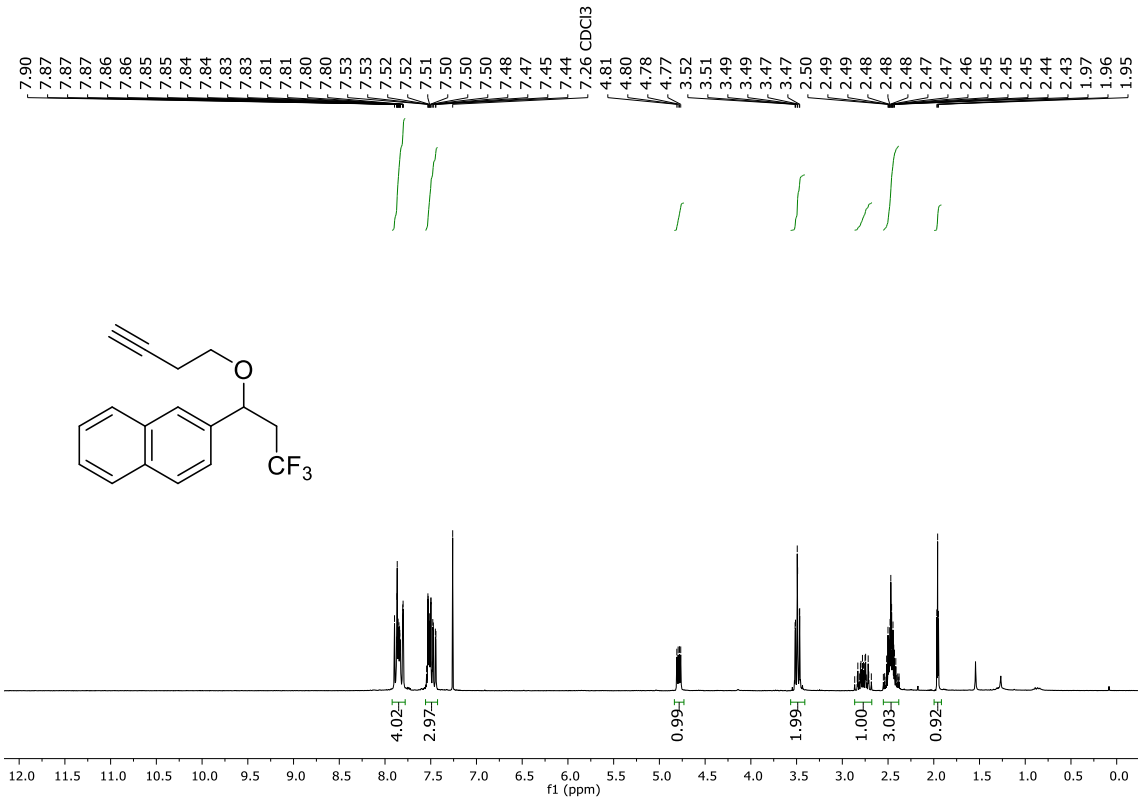
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3d**.



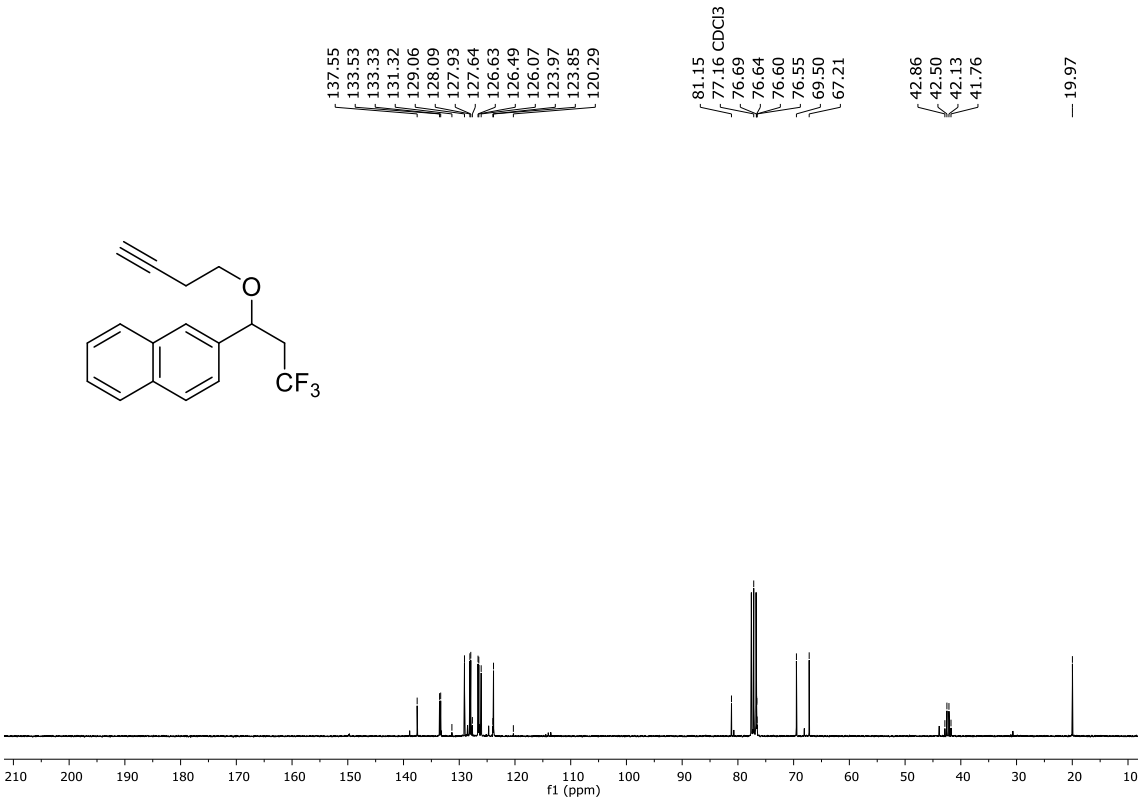
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3d.**



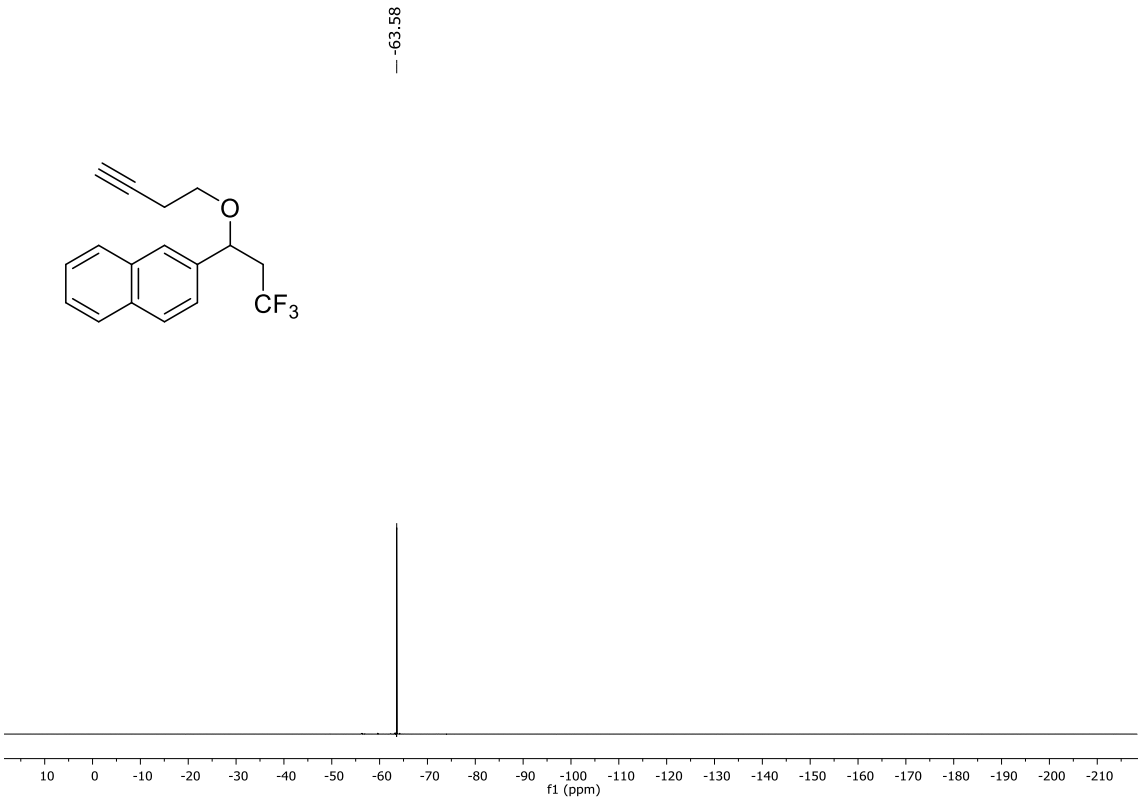
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3d.**



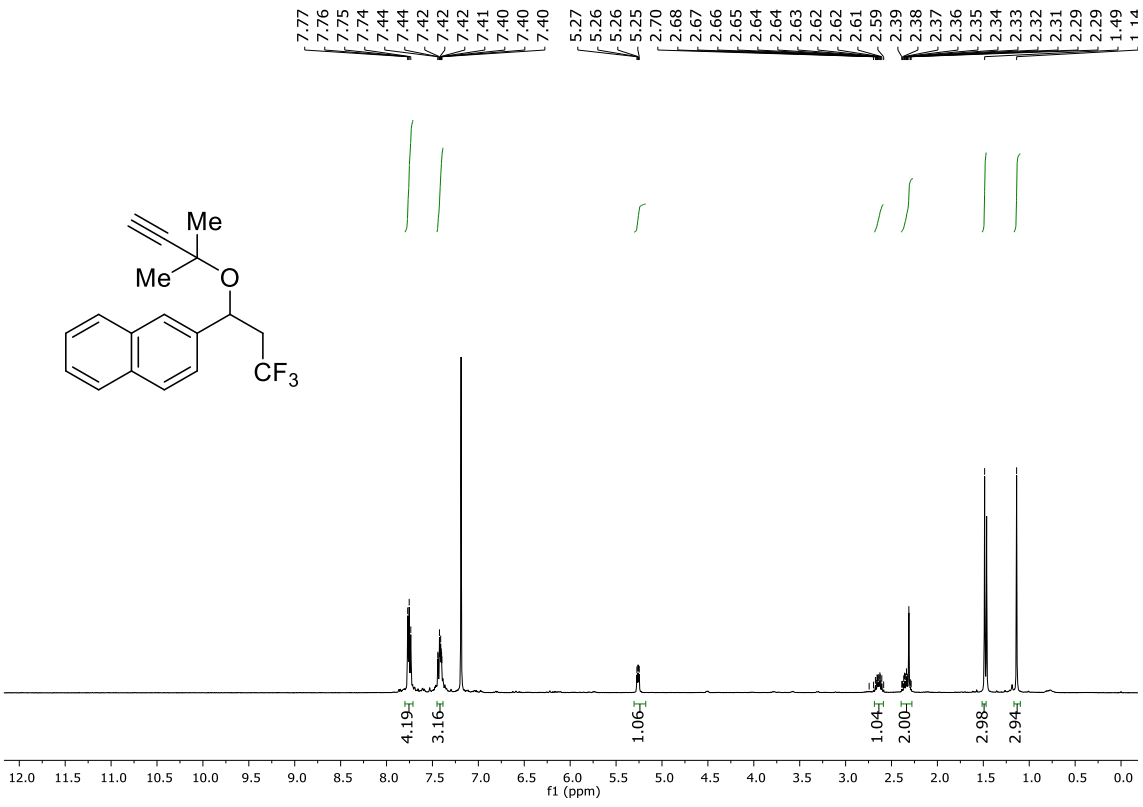
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3e**.



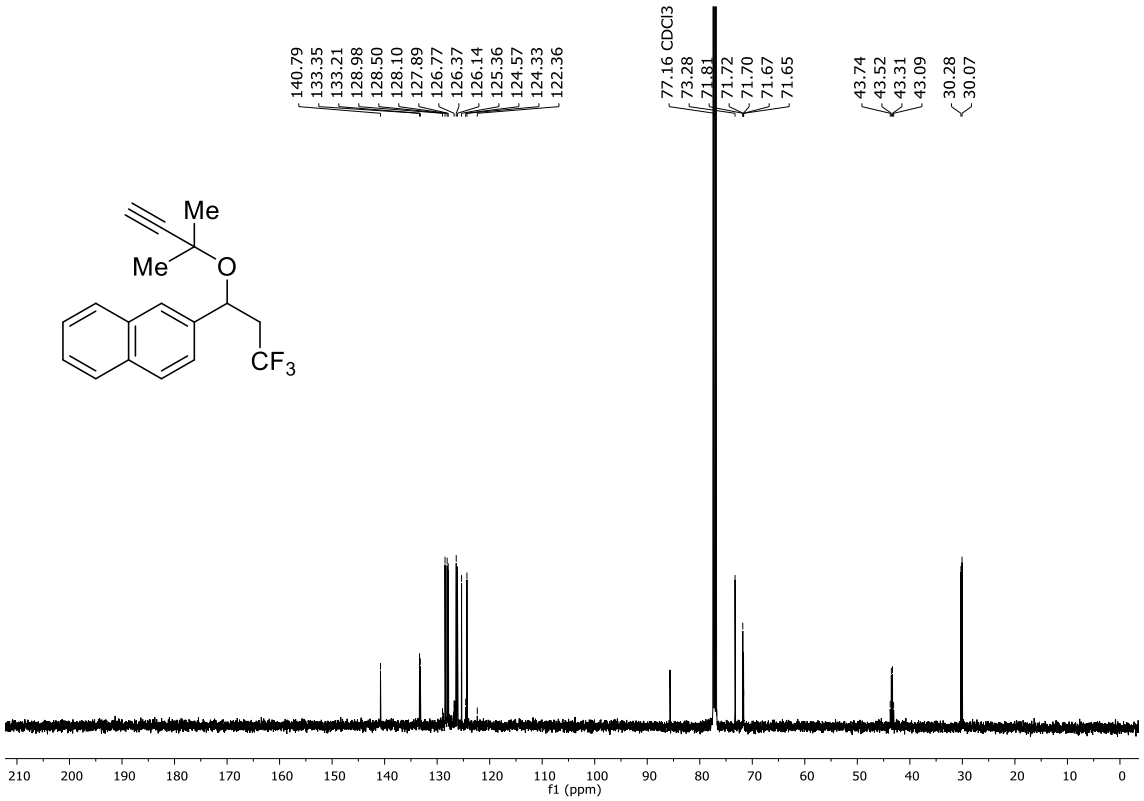
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of compound **3e.**



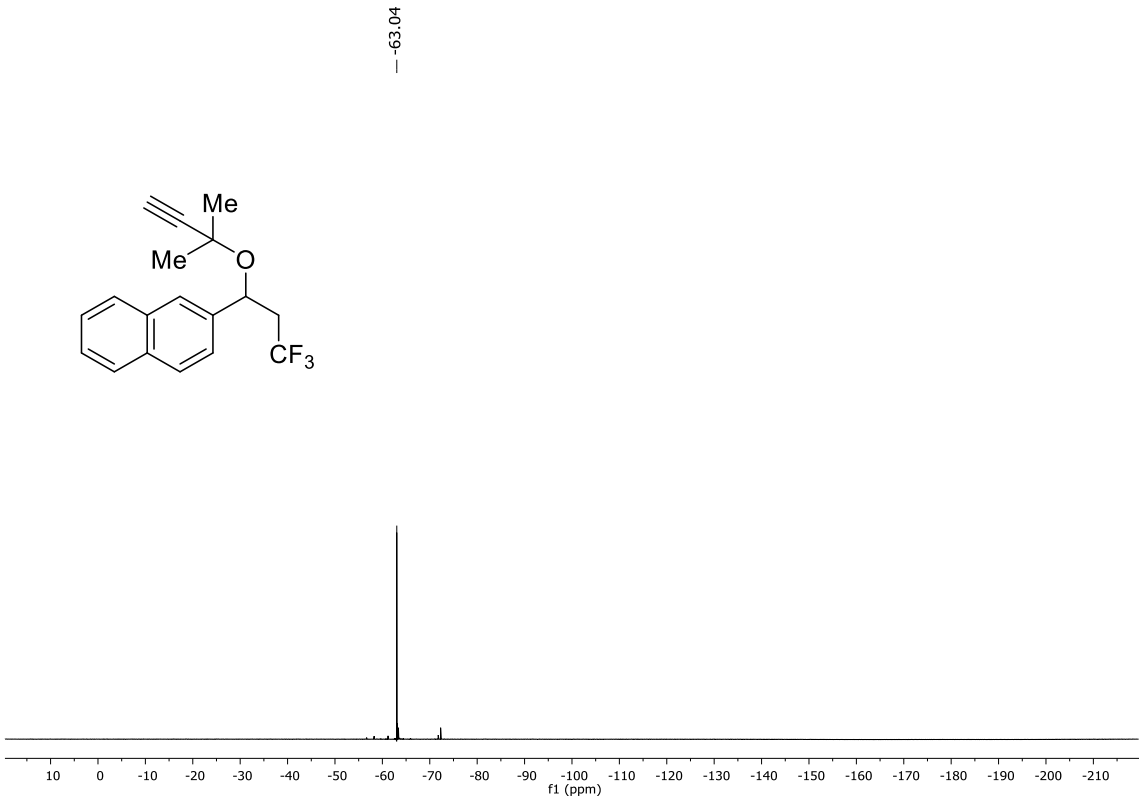
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3e.**



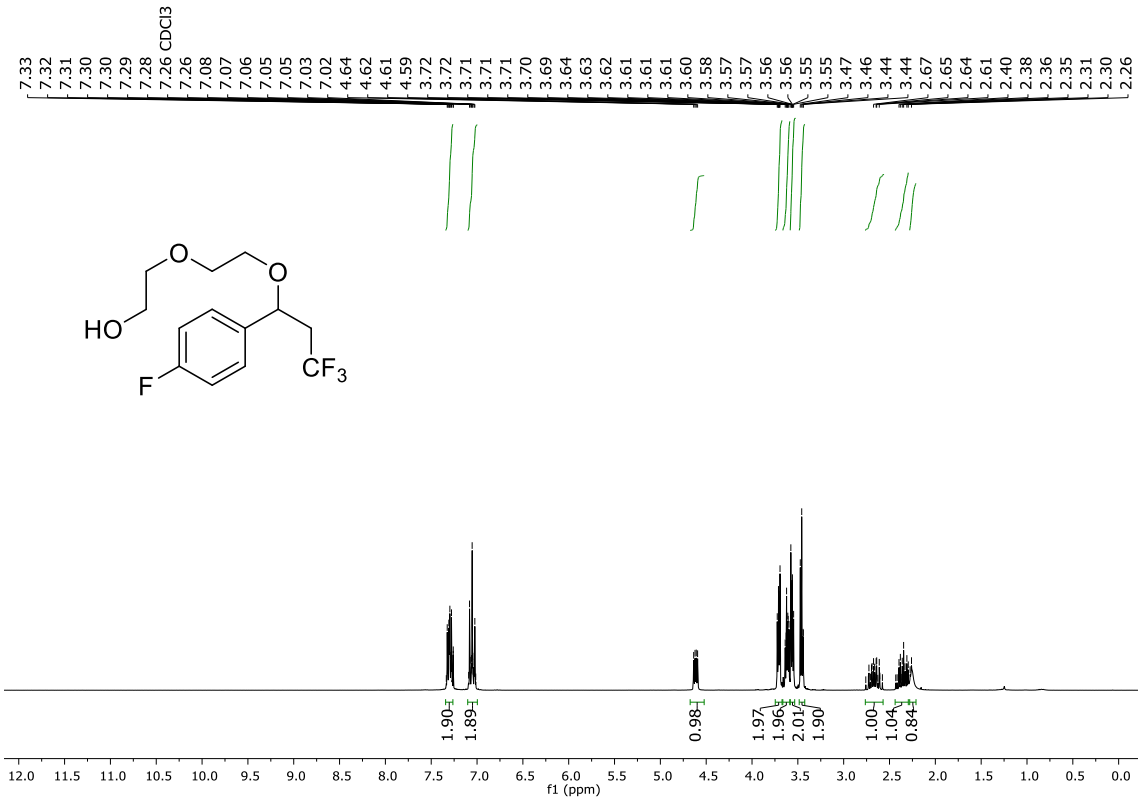
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3f**.



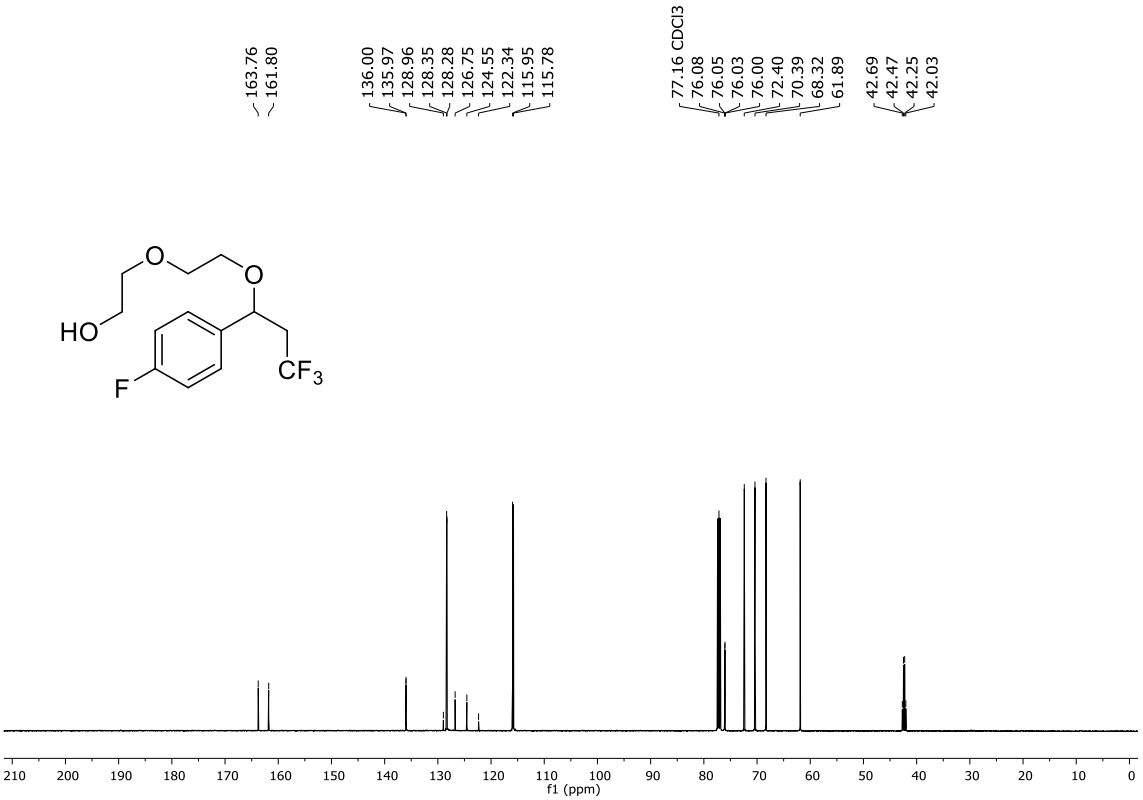
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **3f.**



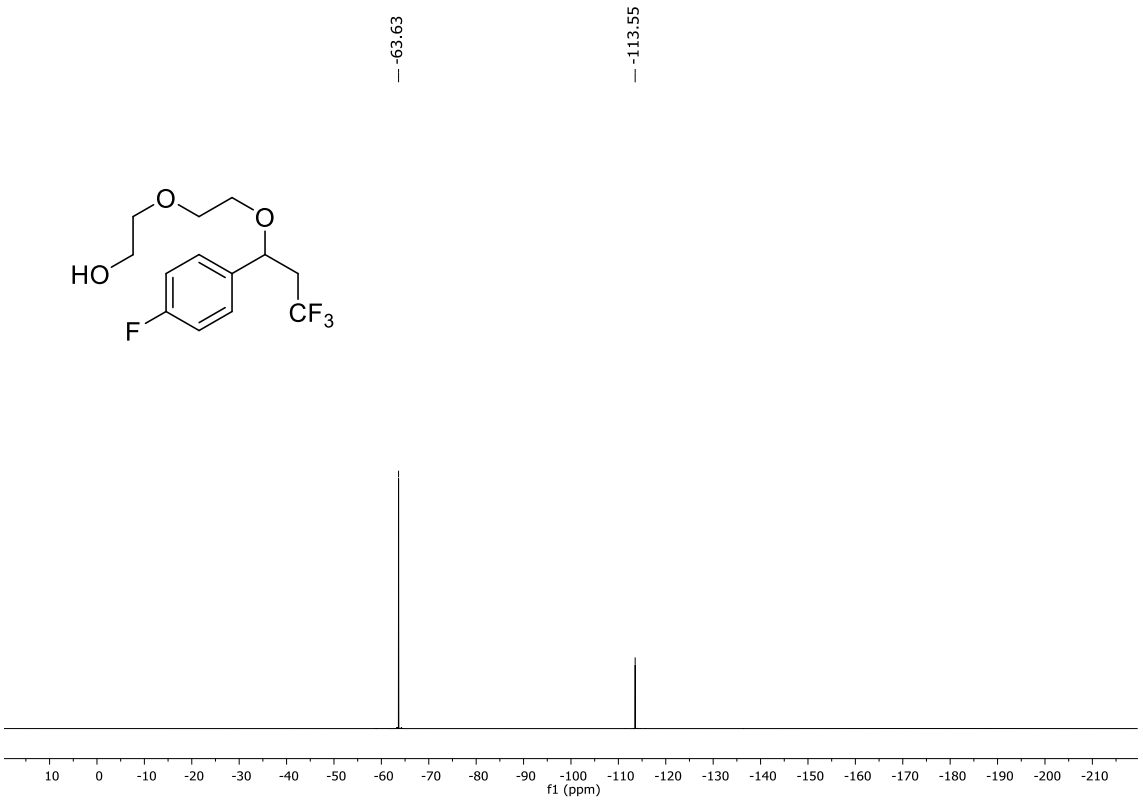
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3f.**



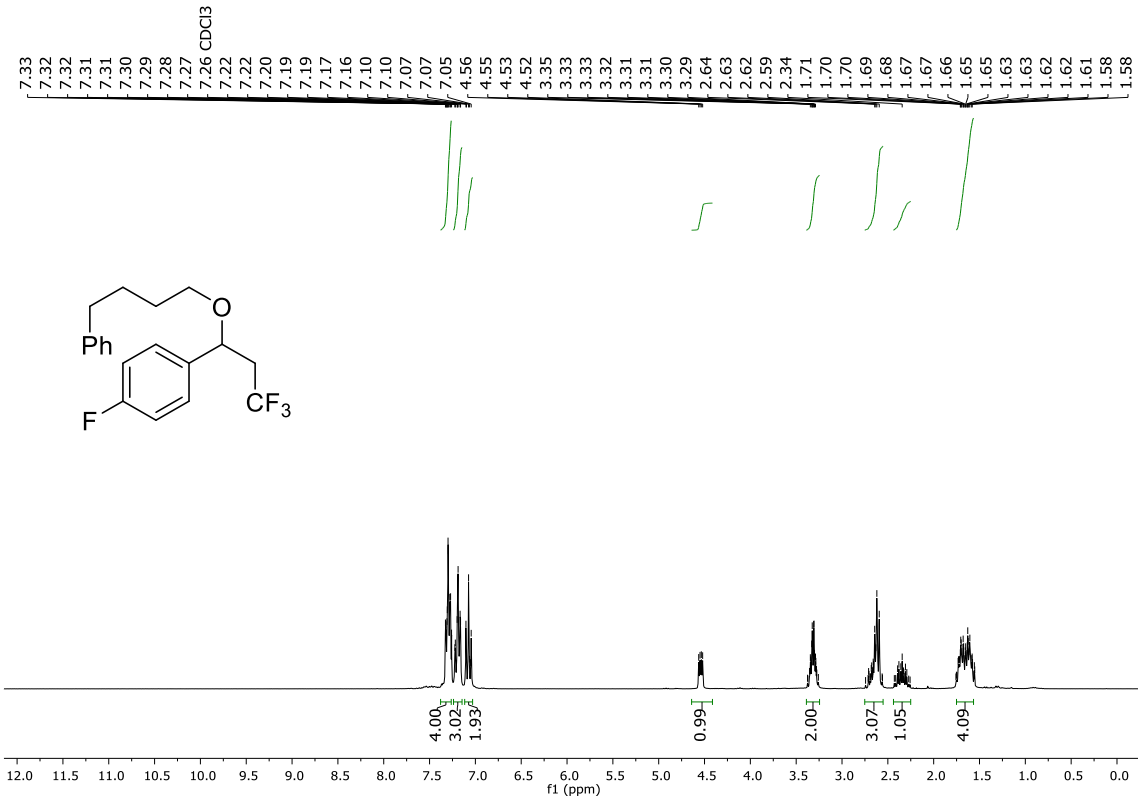
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3g**.



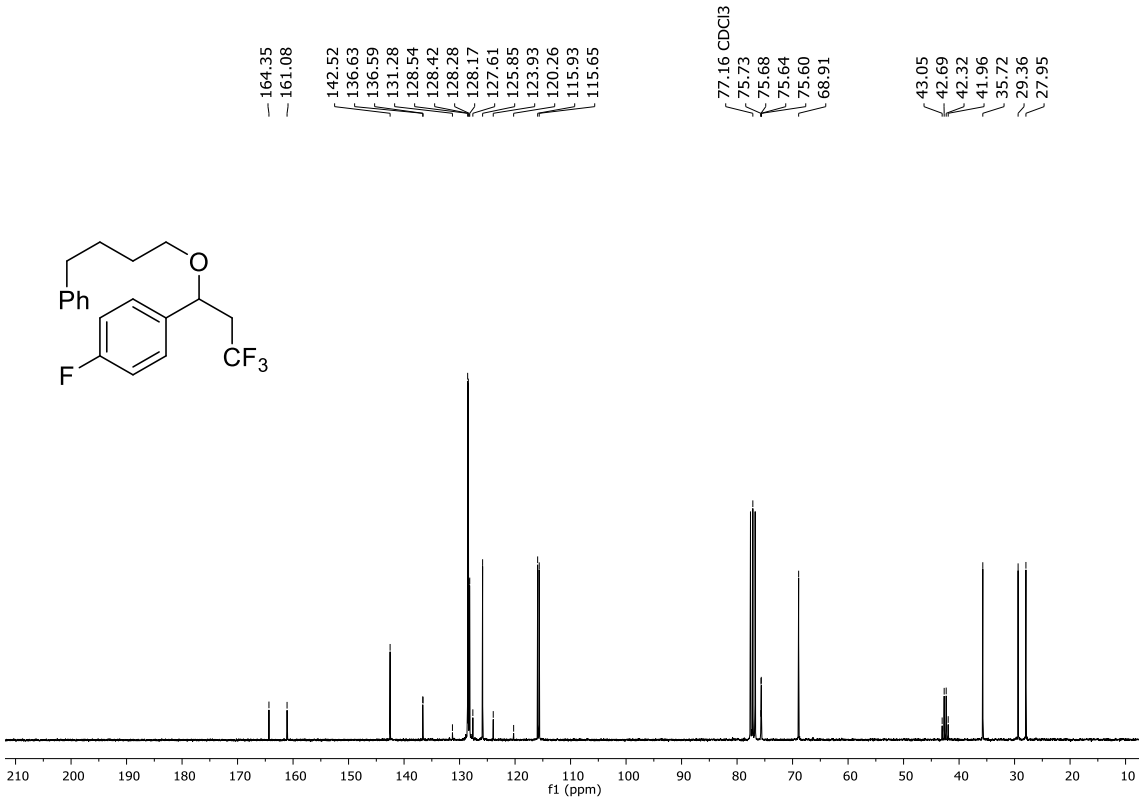
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3g.**



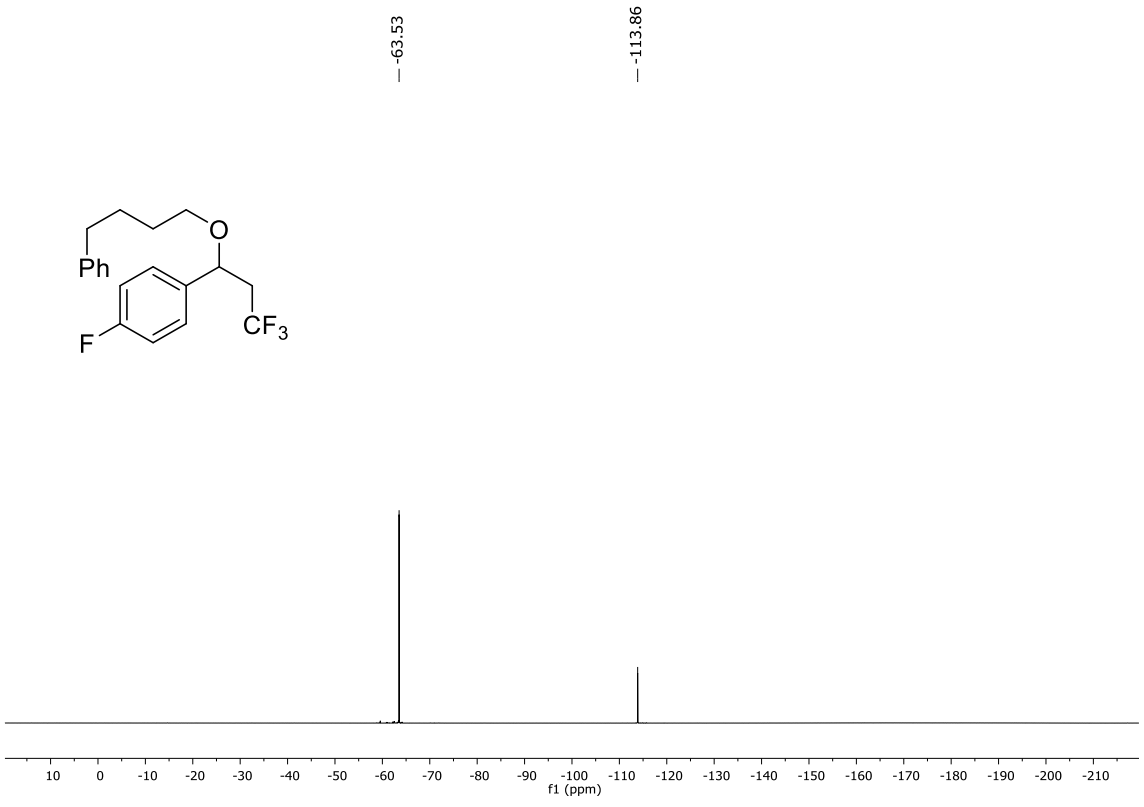
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3g.**



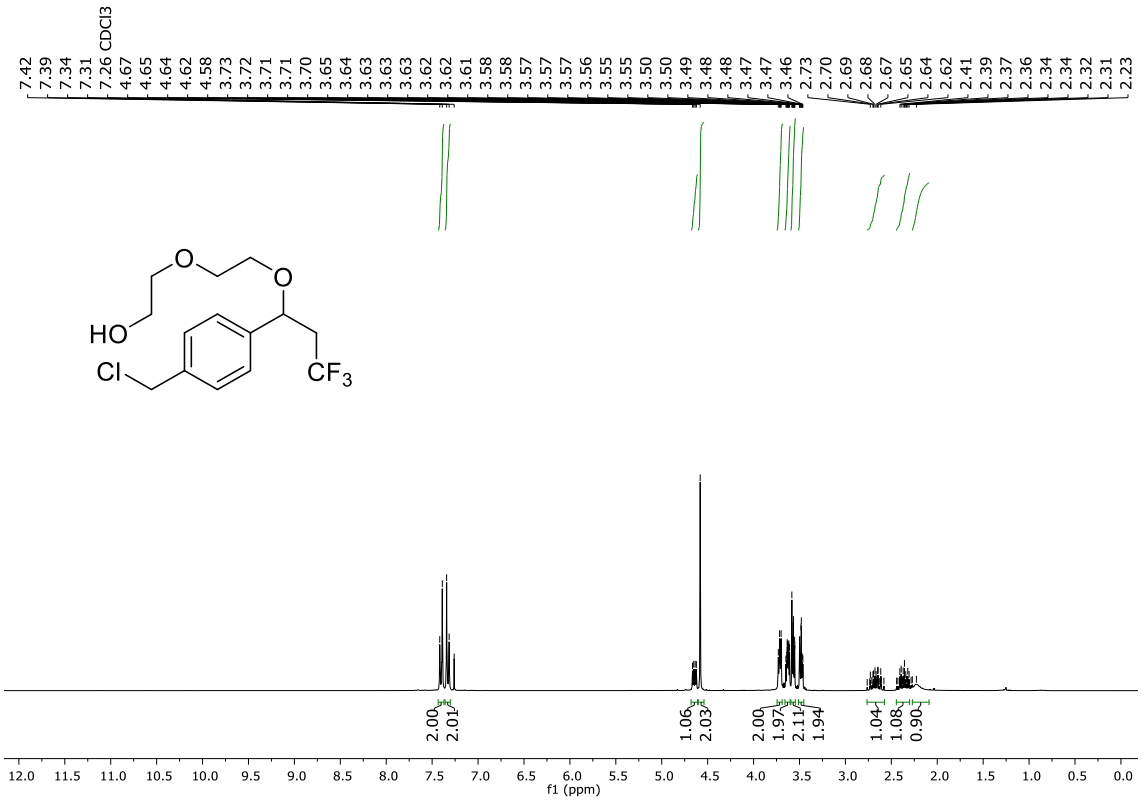
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3h**.



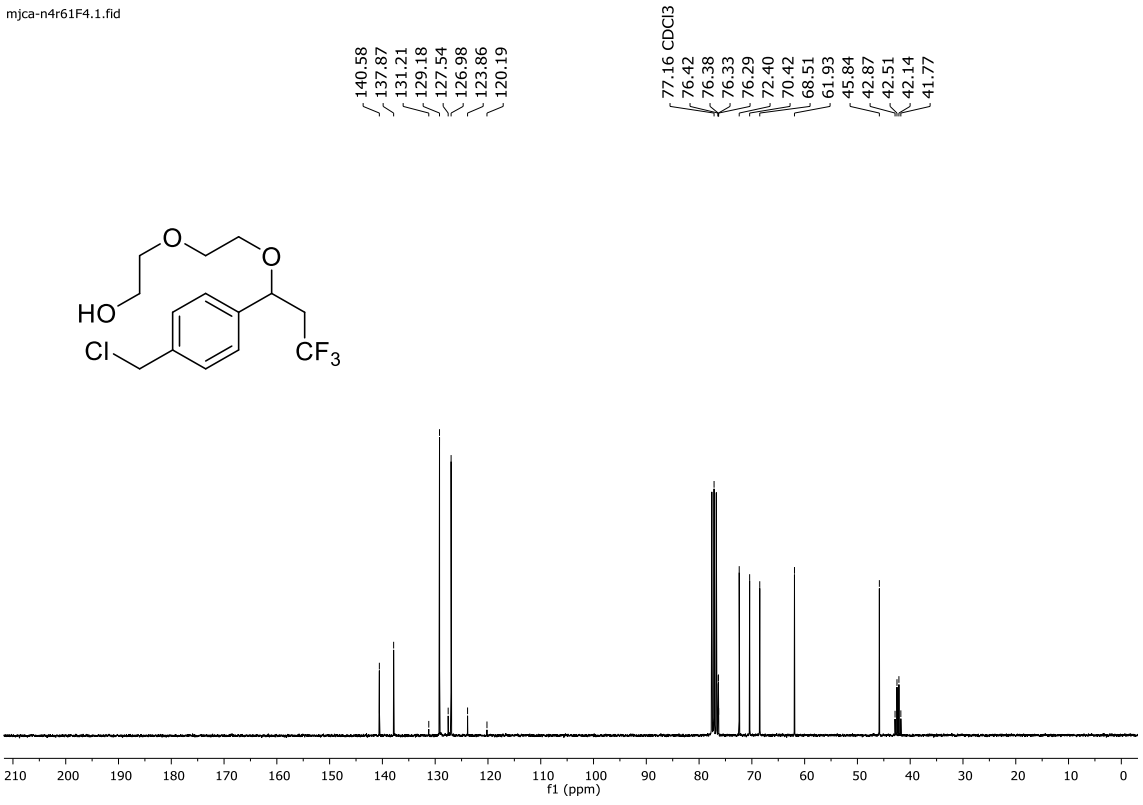
$^{13}C\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) of compound **3h.**



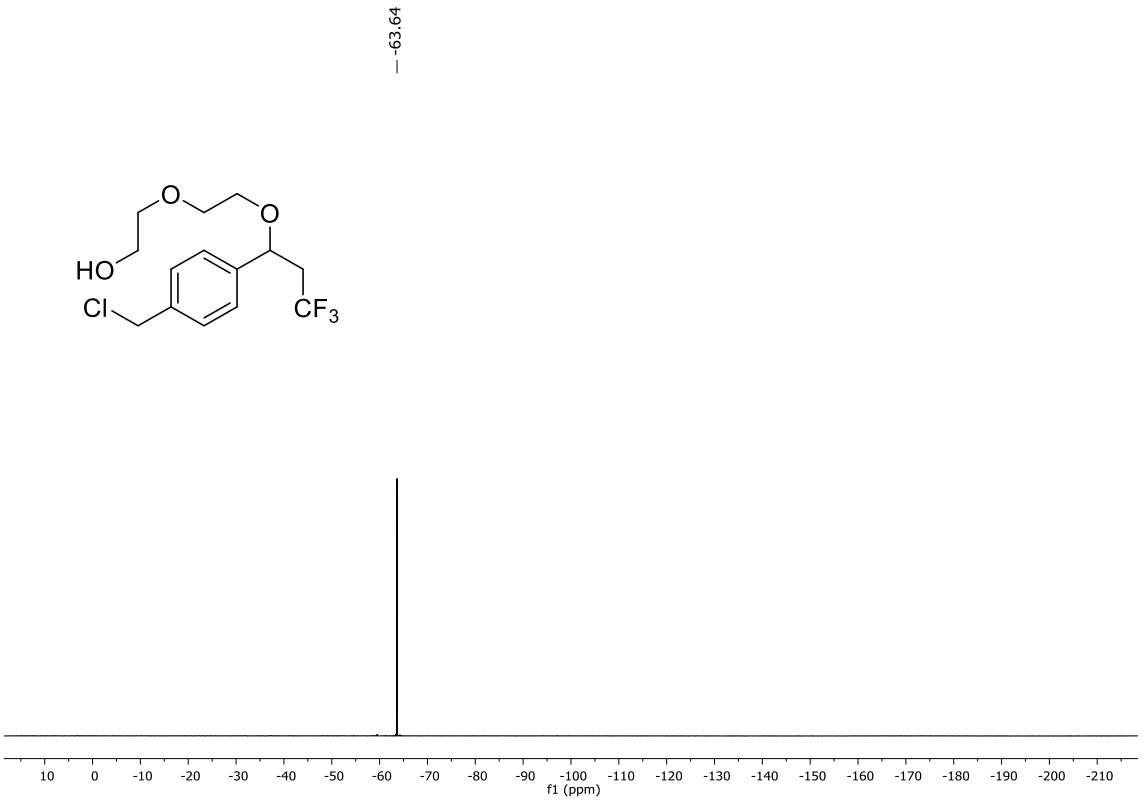
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3h.**



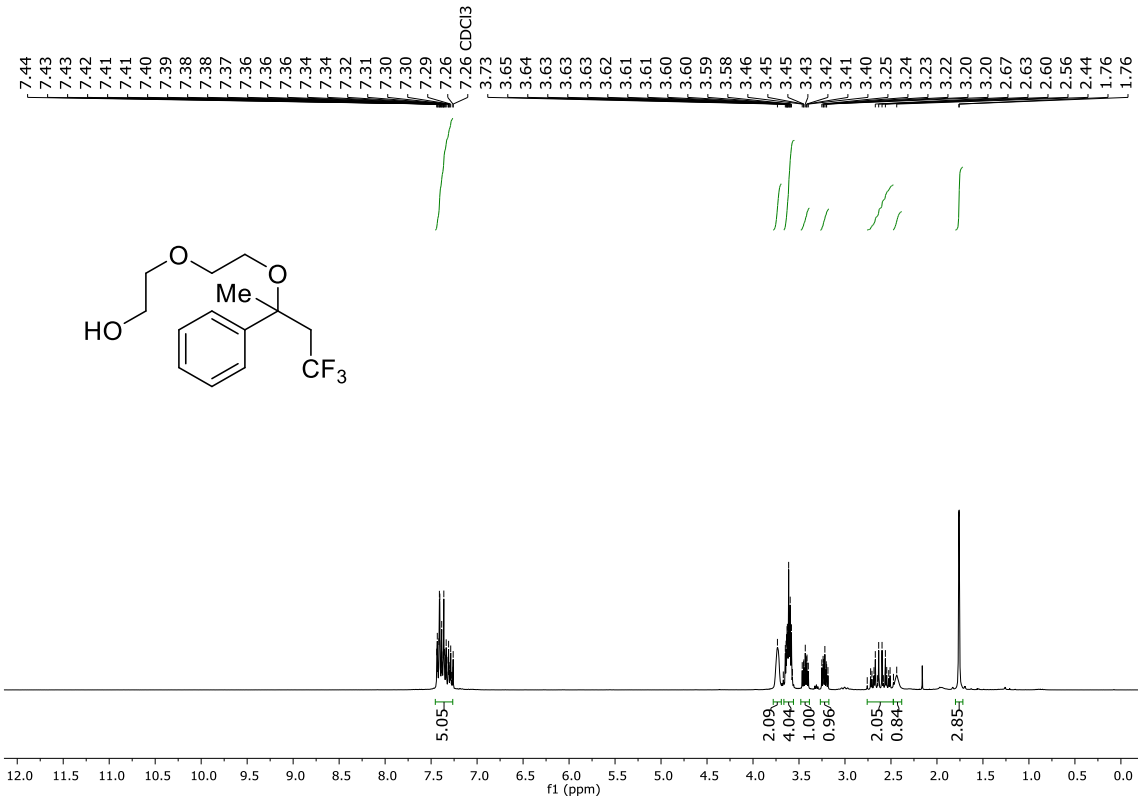
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3i**.



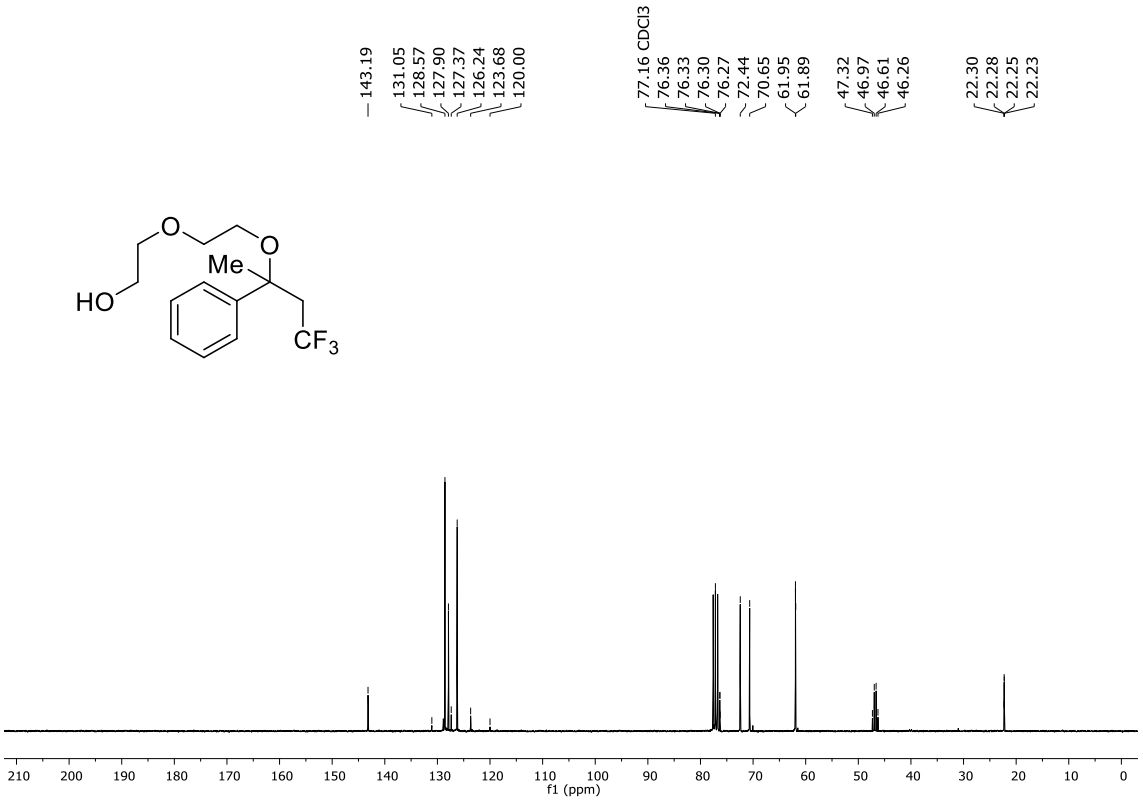
^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$) of compound **3i.**



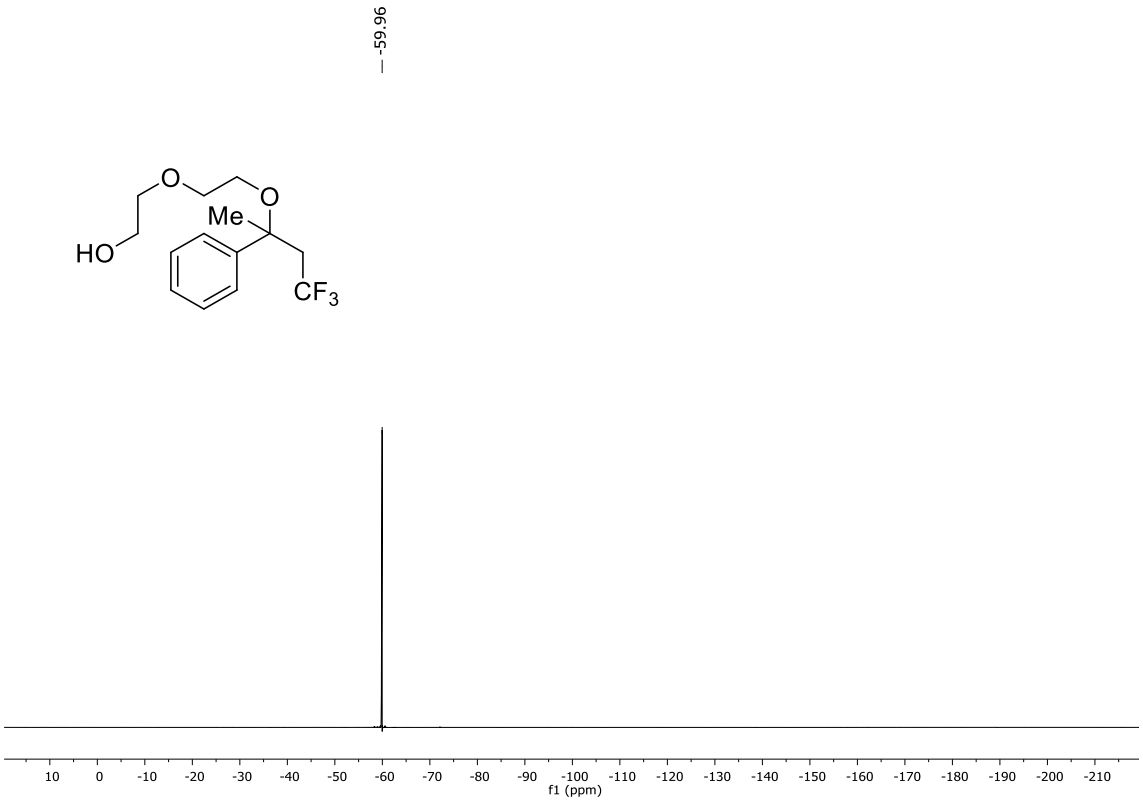
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3i.**



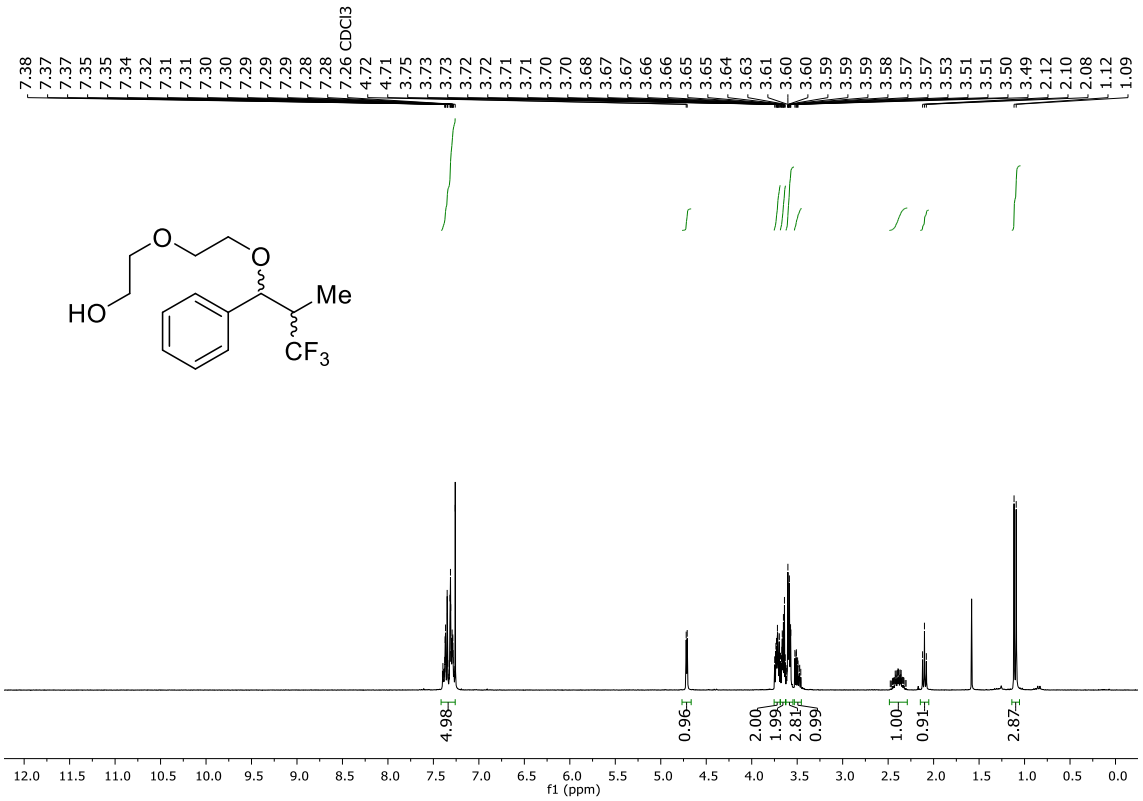
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3j**.



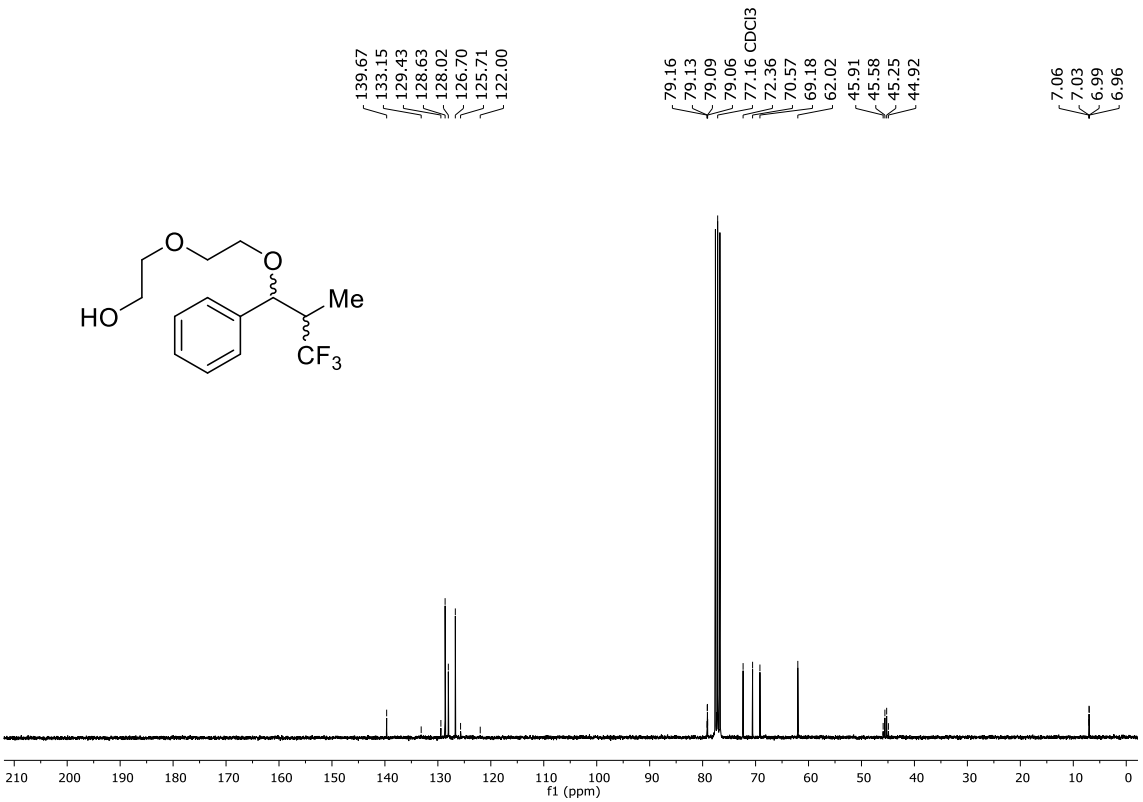
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of compound **3j.**



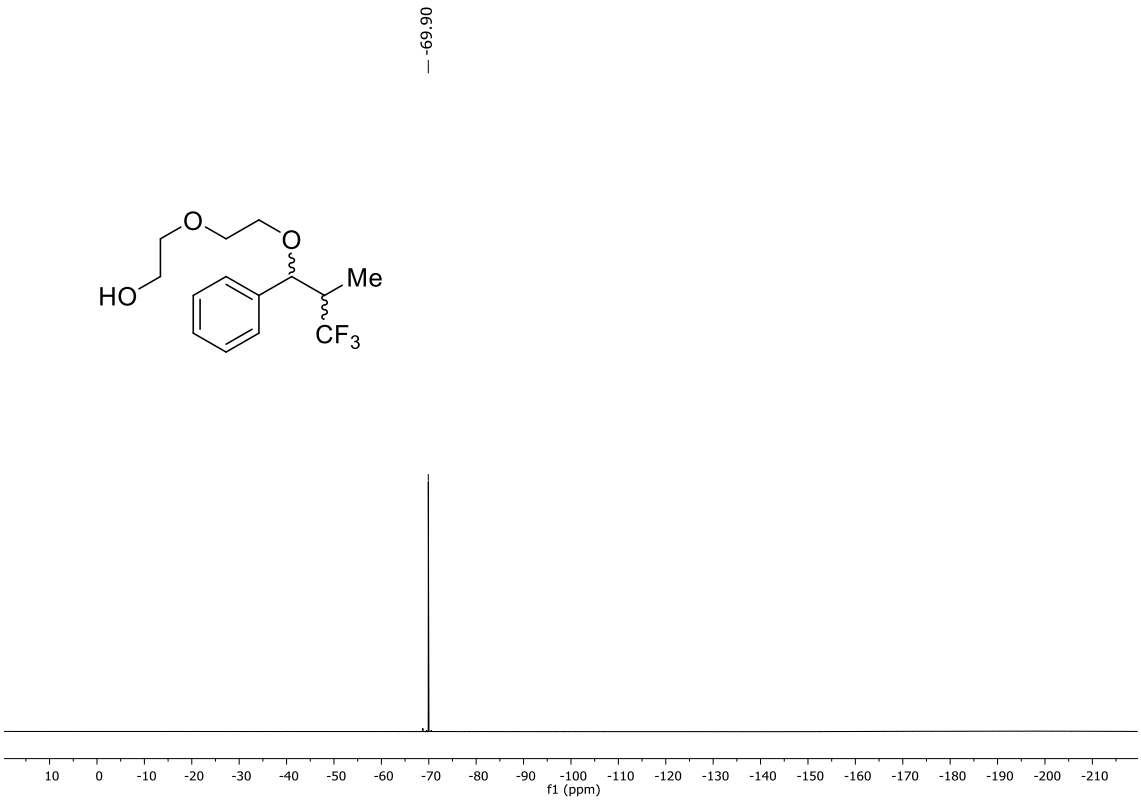
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3j.**



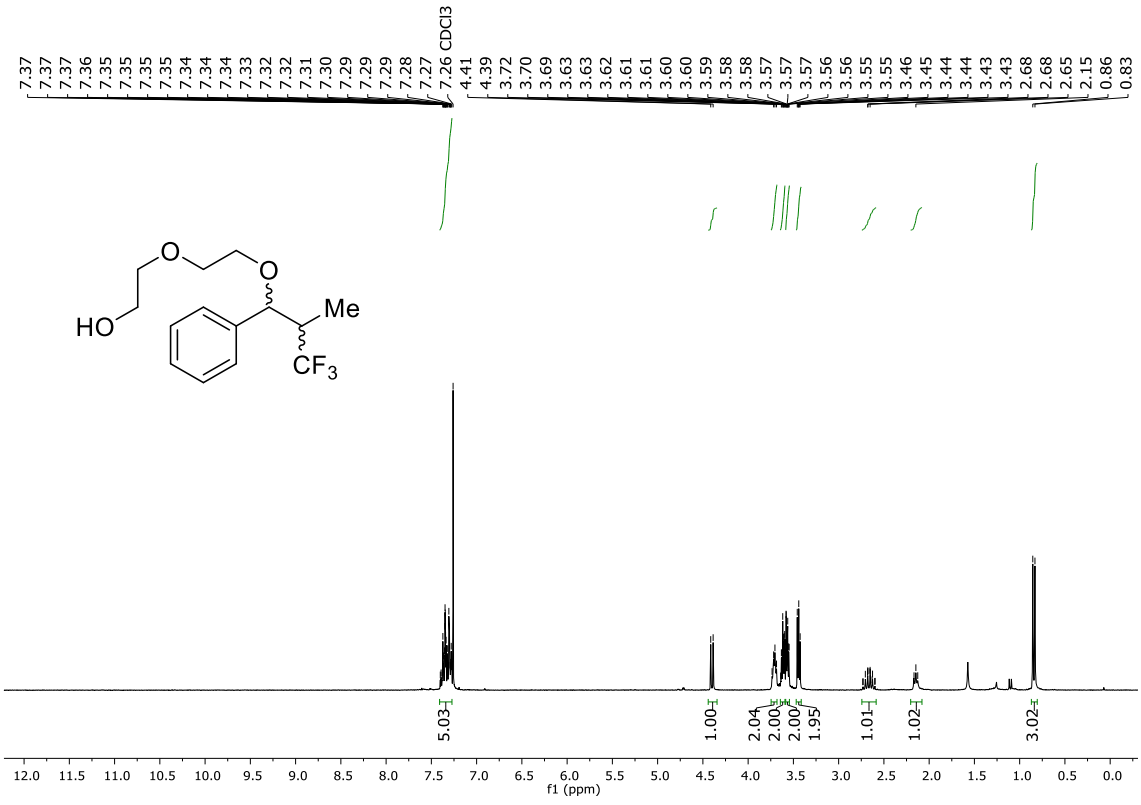
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3k**.



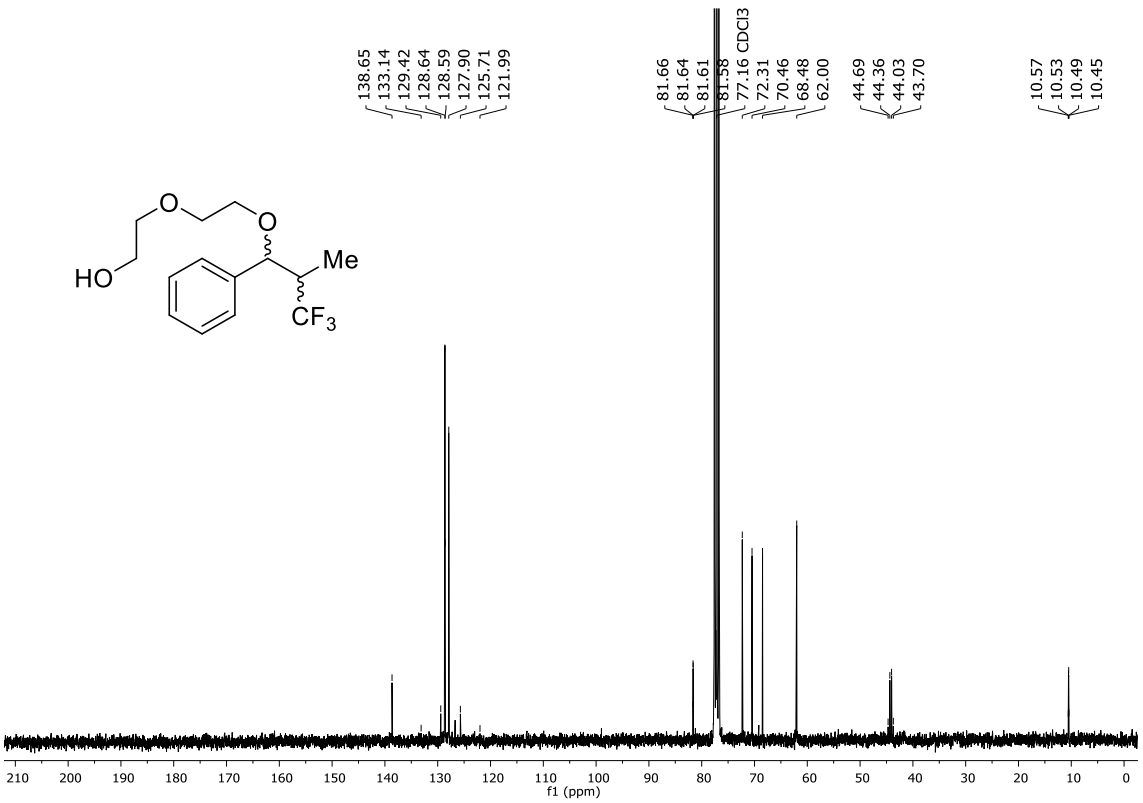
^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$) of compound **3k.**



$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3k.**

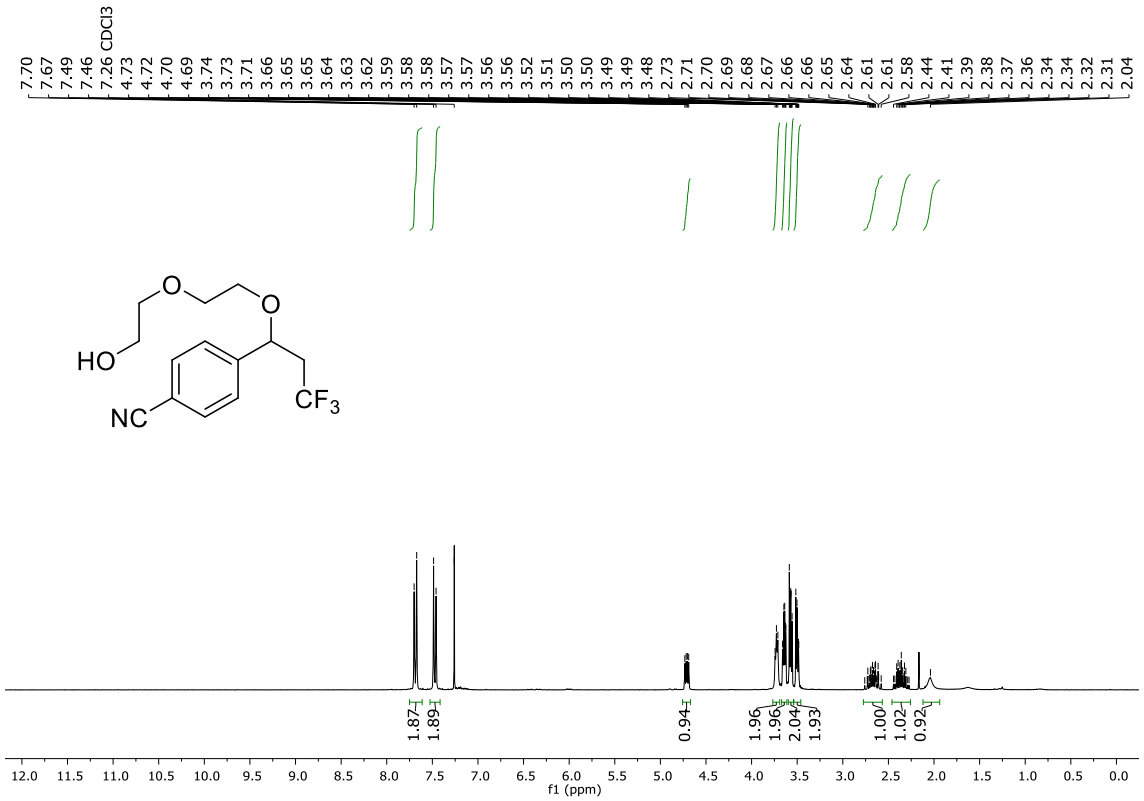


^{1}H NMR (300 MHz, $CDCl_3$) of compound **3k'**.

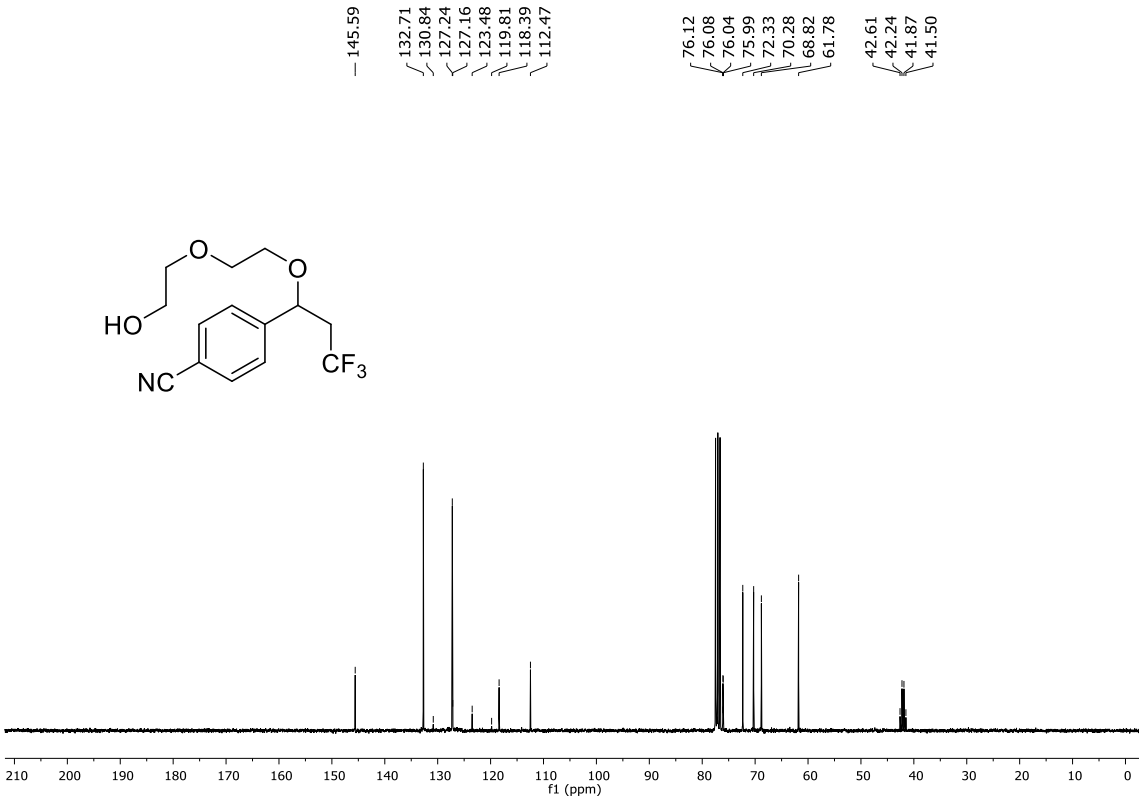


$^{13}C\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) of compound **3k'.**

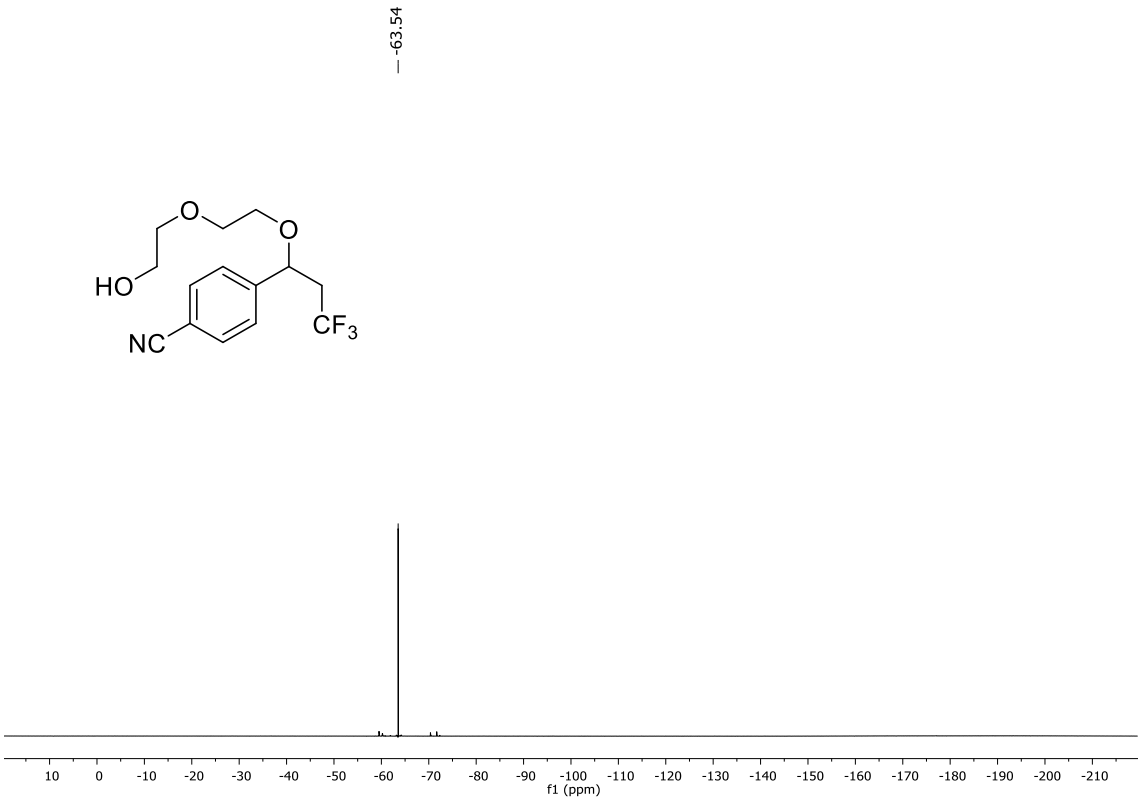
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3k'.**



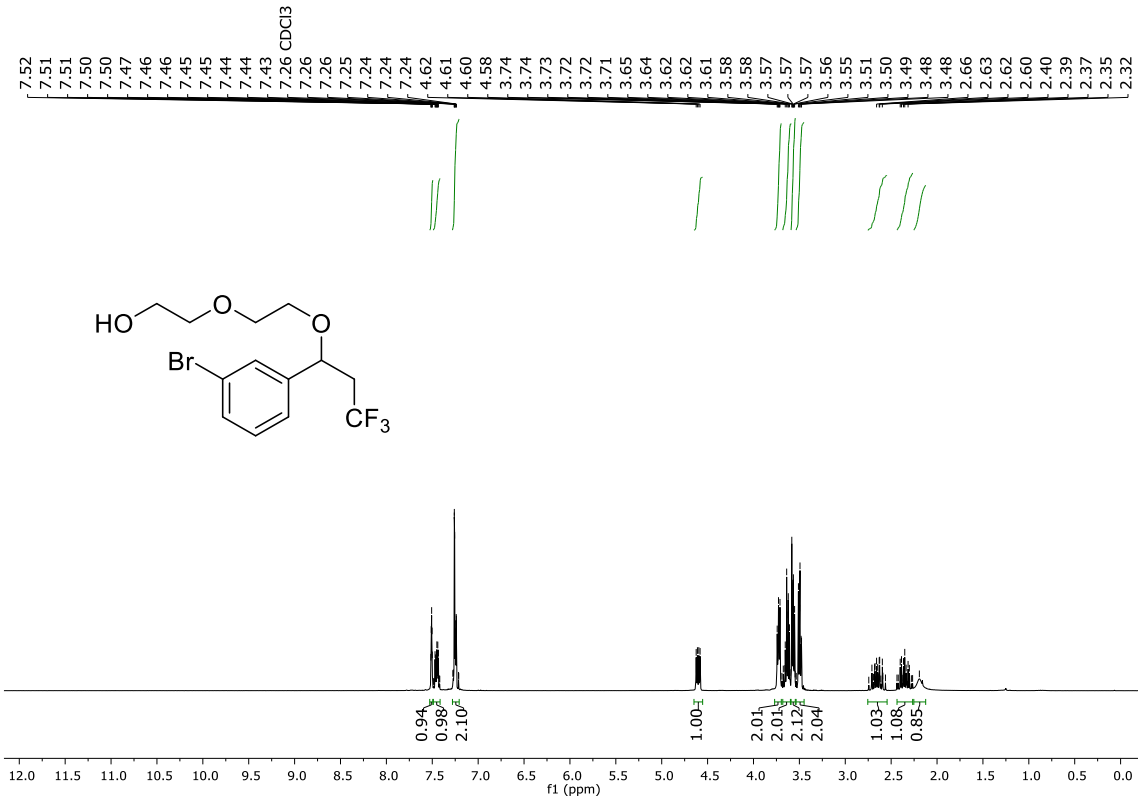
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3l**.



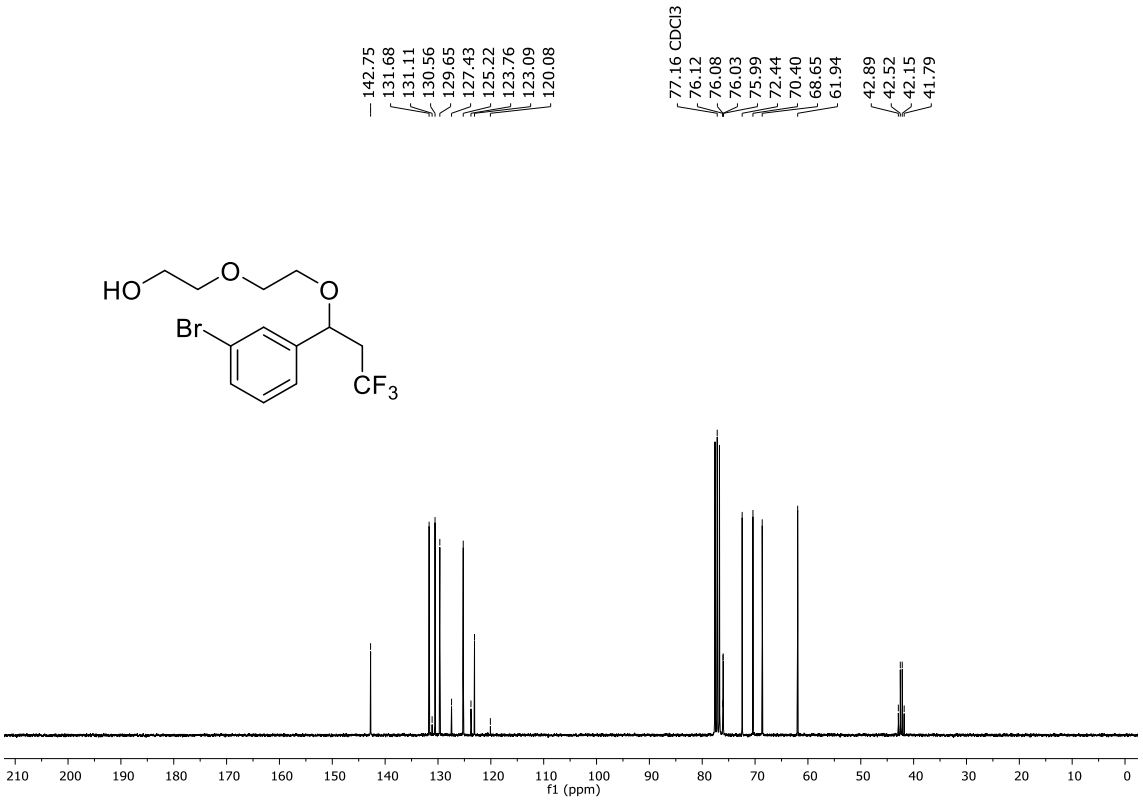
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of compound **3l.**



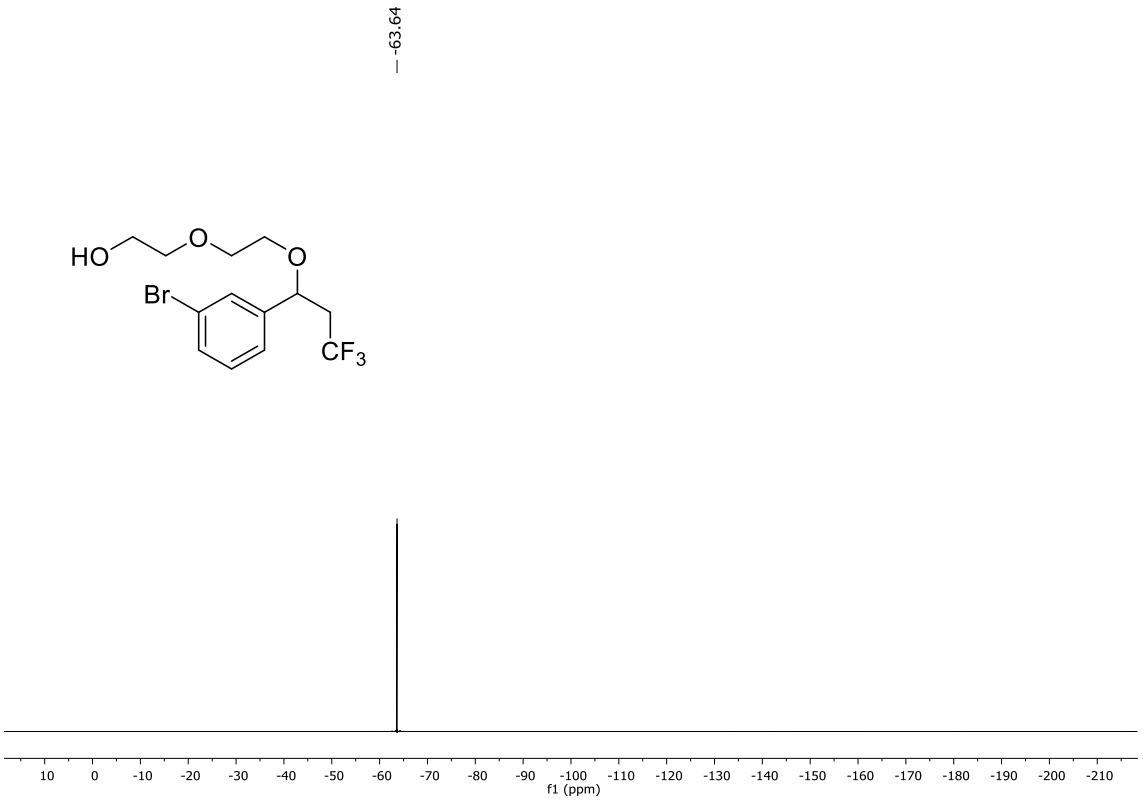
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3l.**



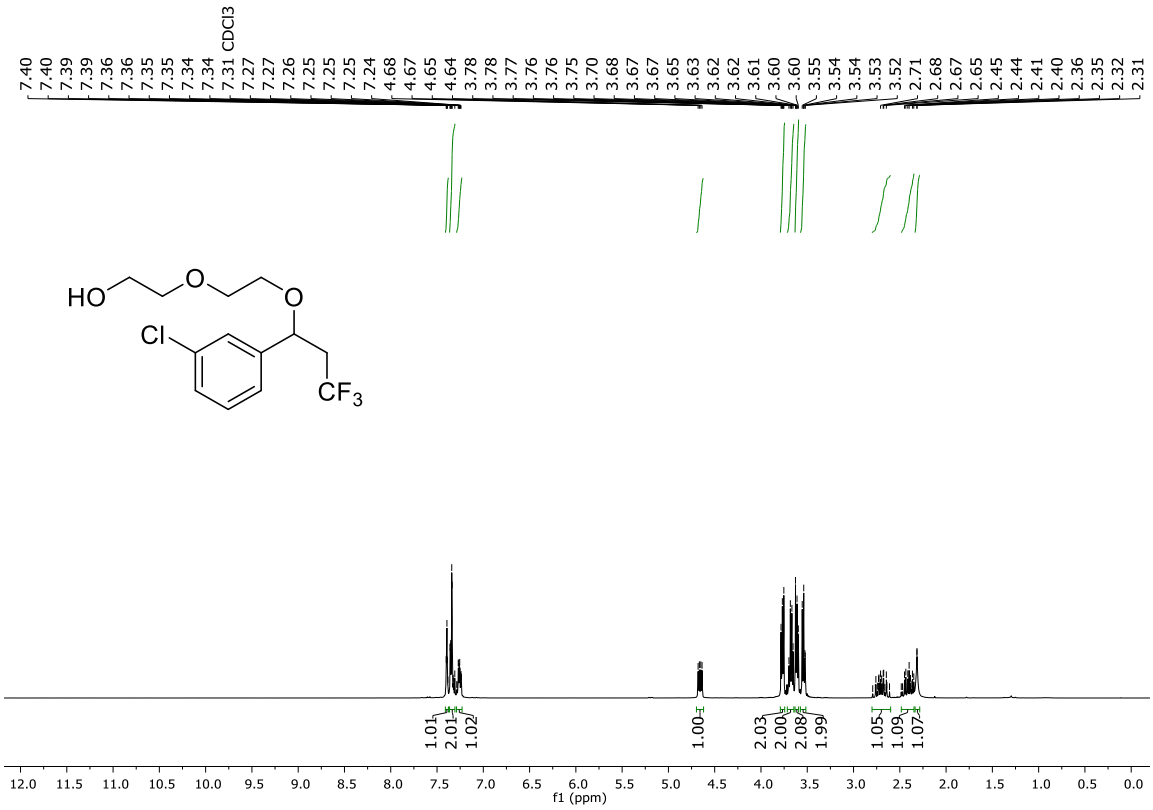
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3m**.



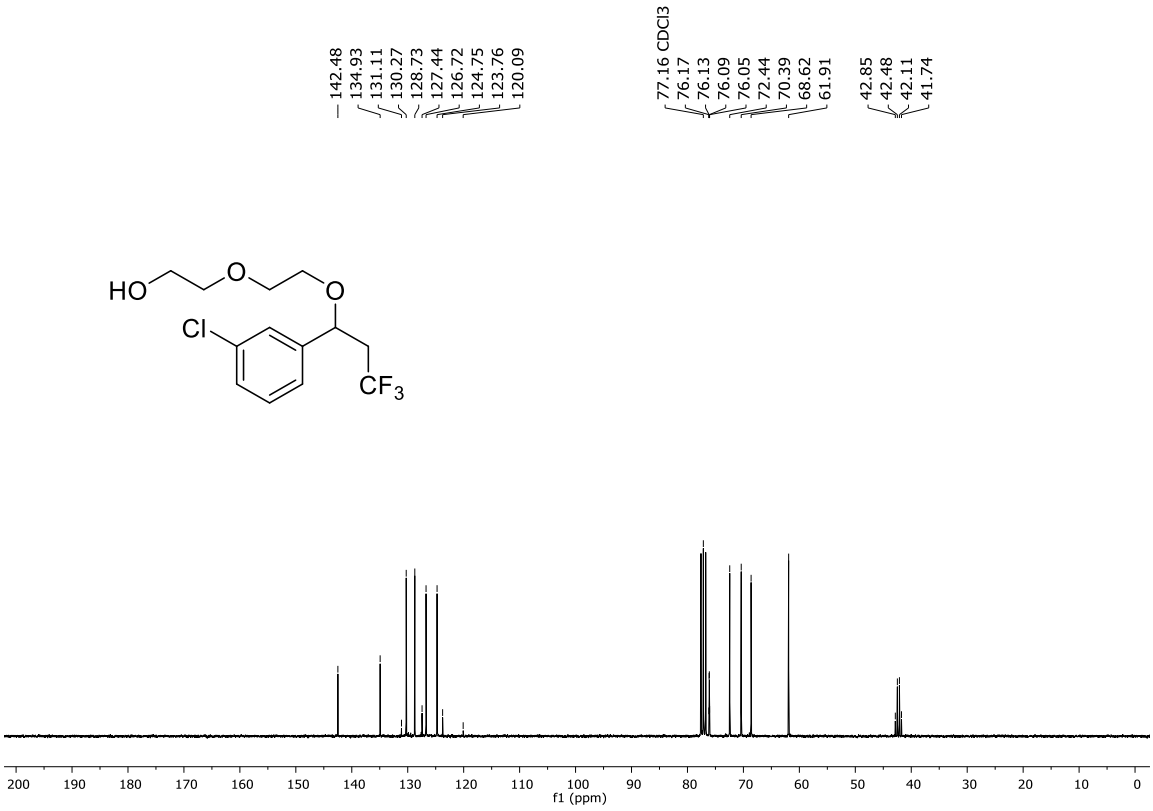
$^{13}C\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) of compound **3m.**



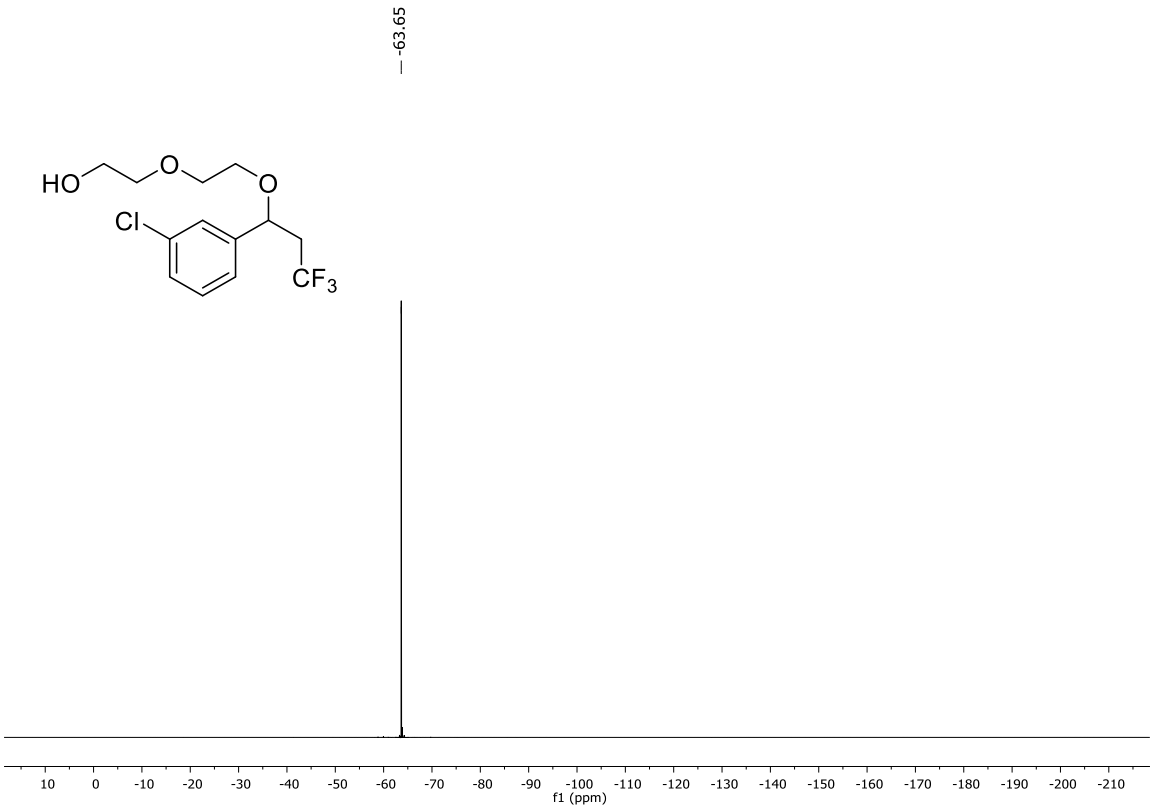
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3m.**



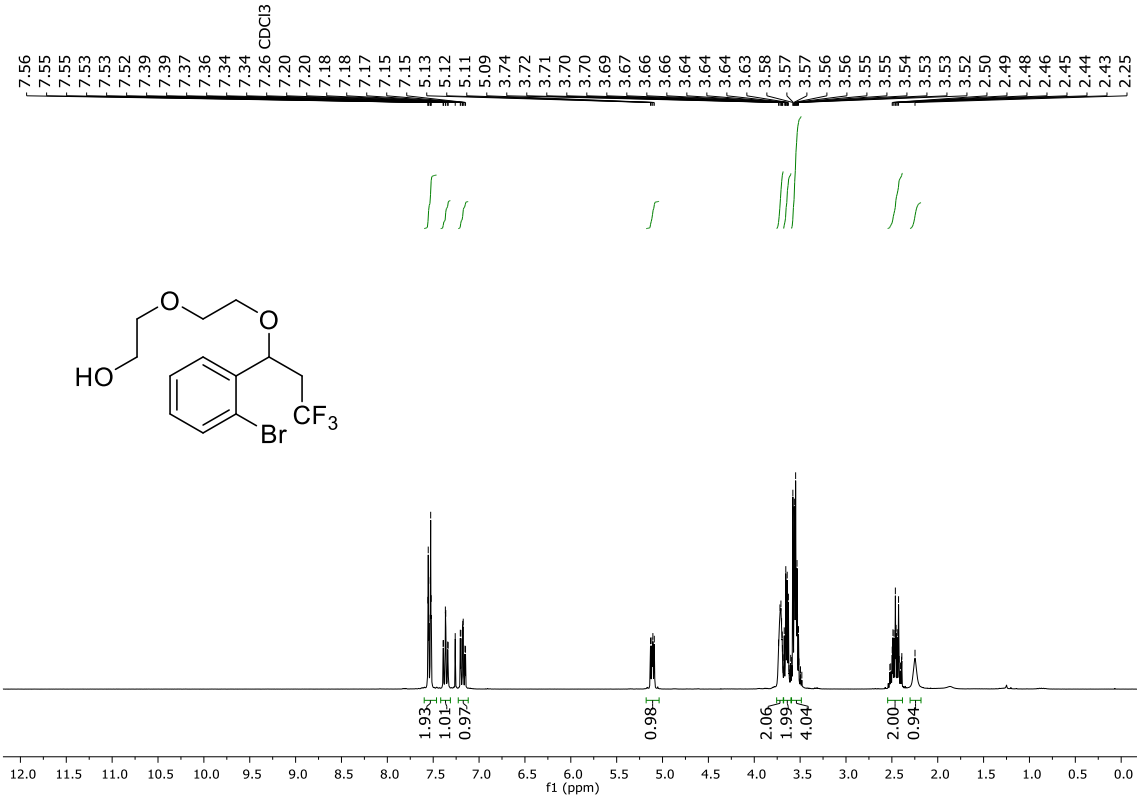
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3n**.



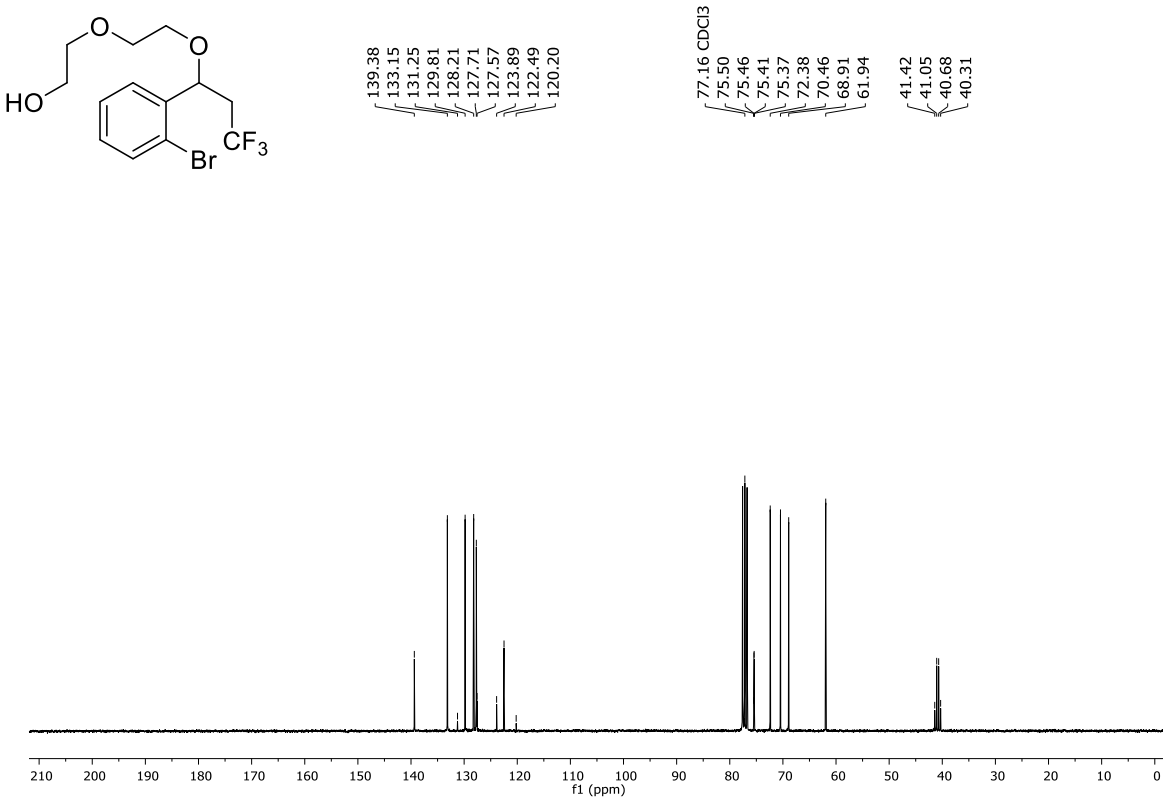
^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$) of compound **3n.**



$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3n.**

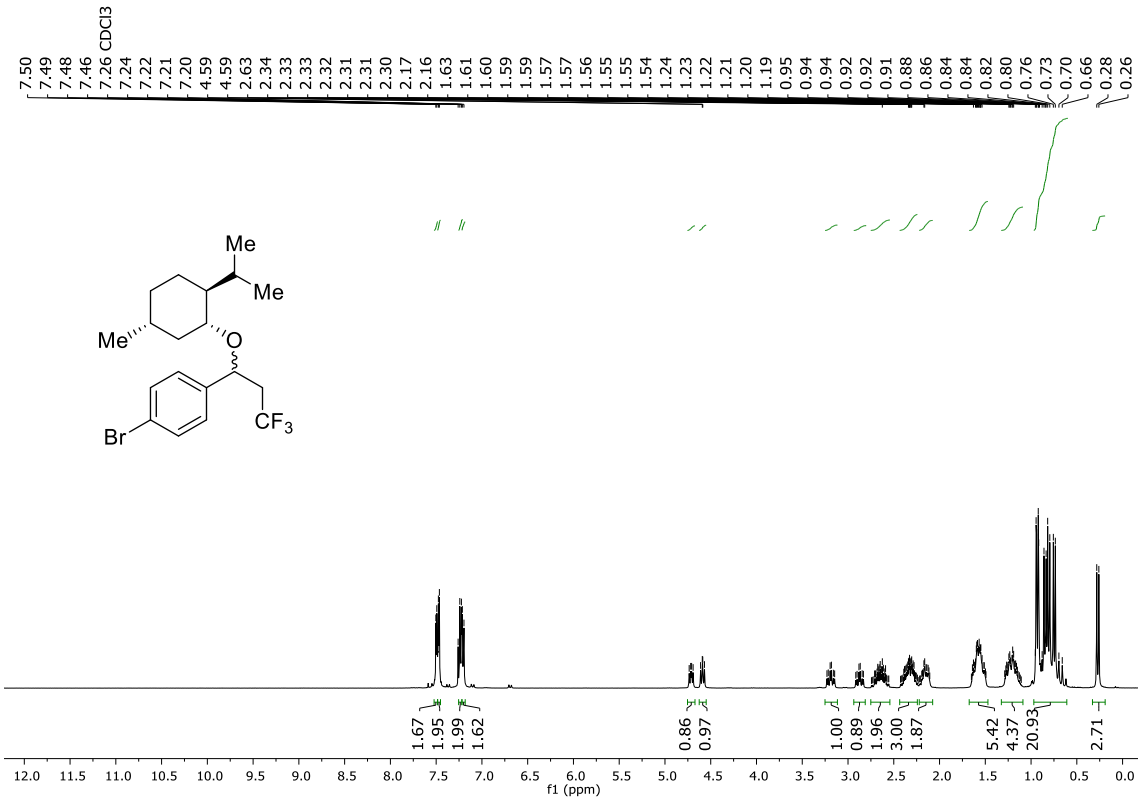


^{1}H NMR (300 MHz, $CDCl_3$) of compound **3o**.

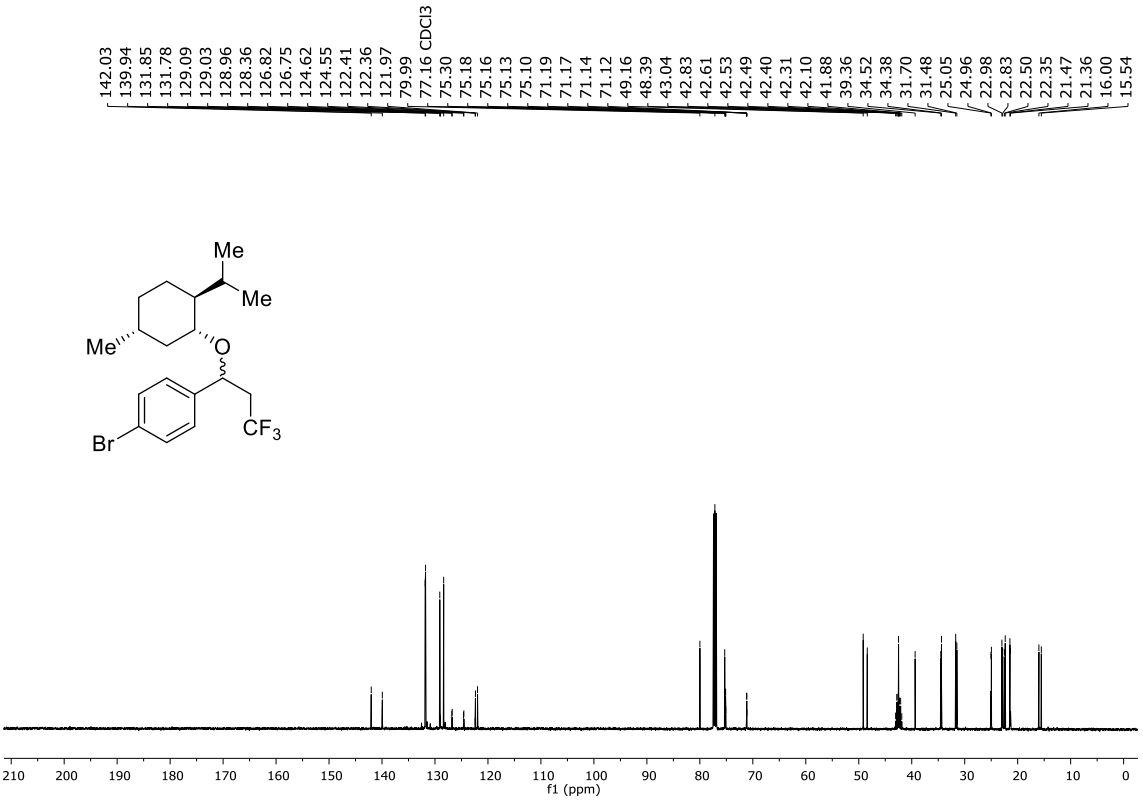


$^{13}C\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) of compound **3o.**

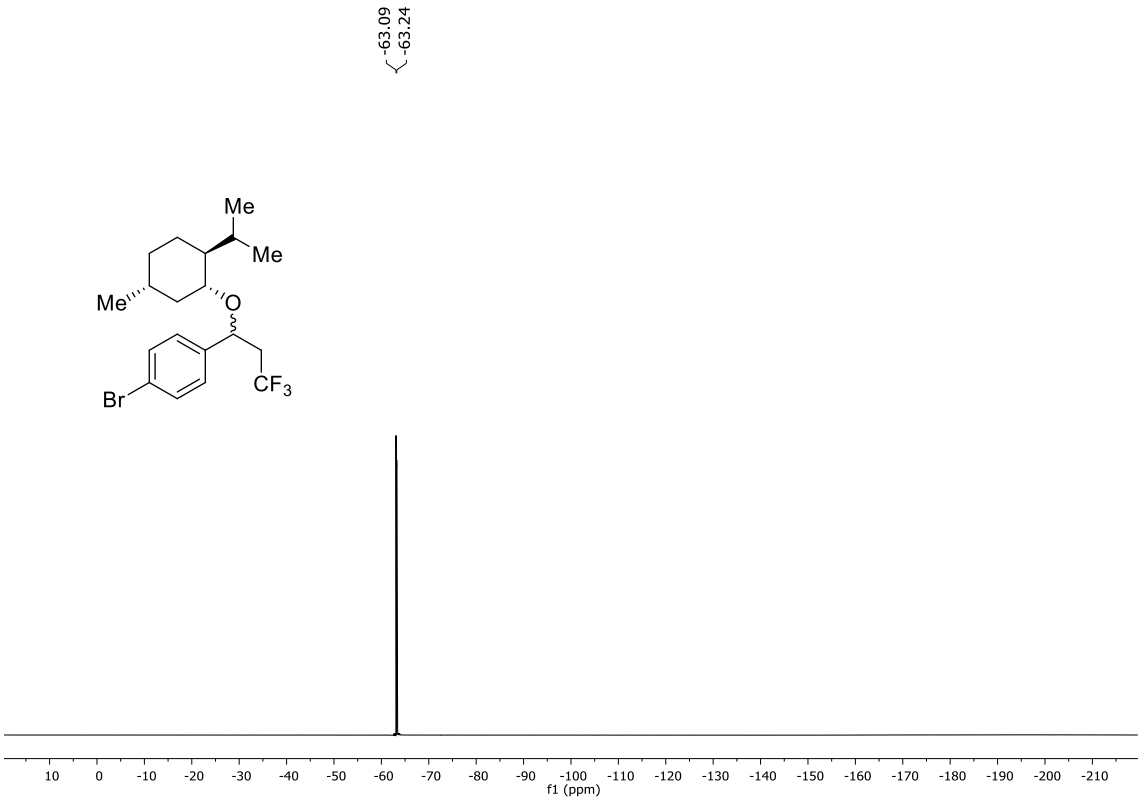
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3o.**



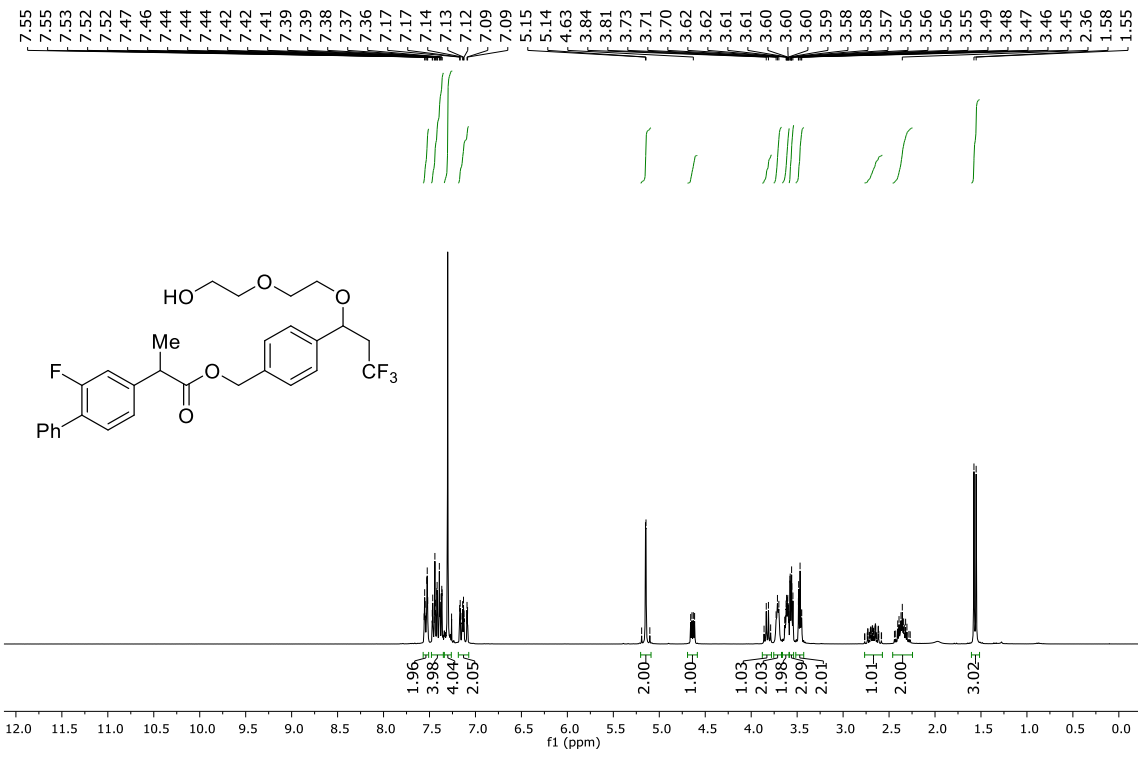
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3p**.



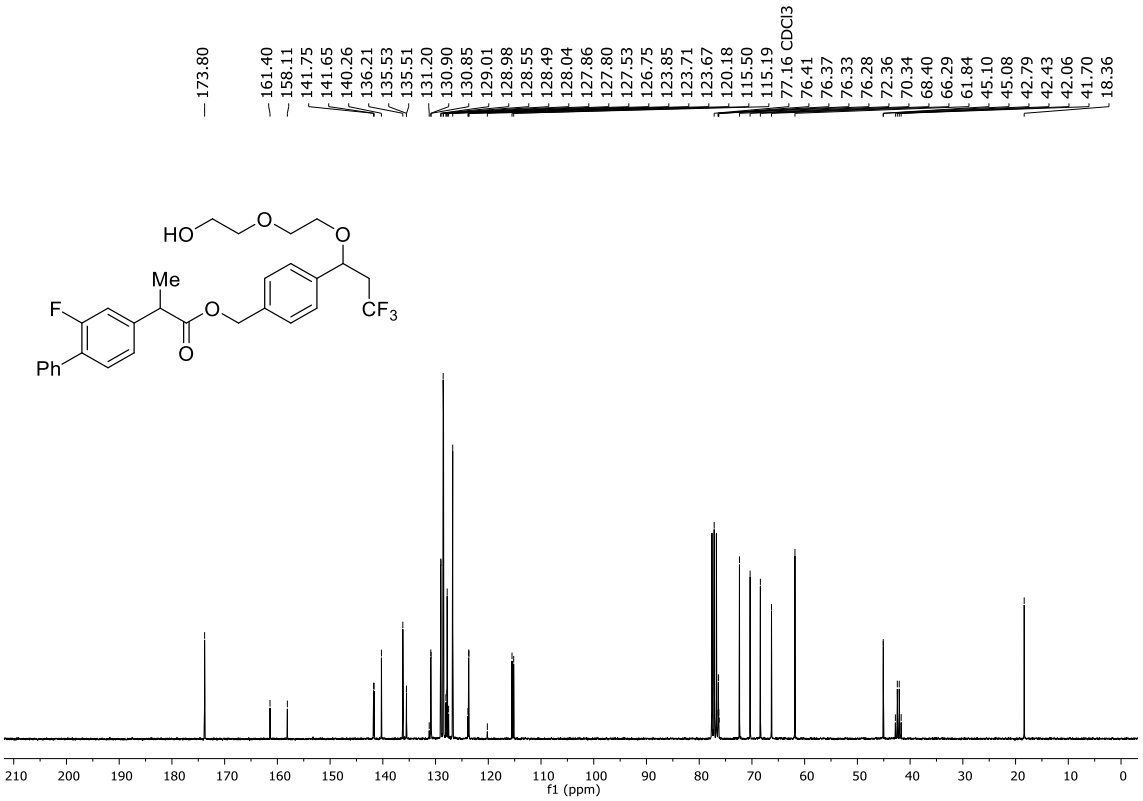
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3p.**



$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3p.**

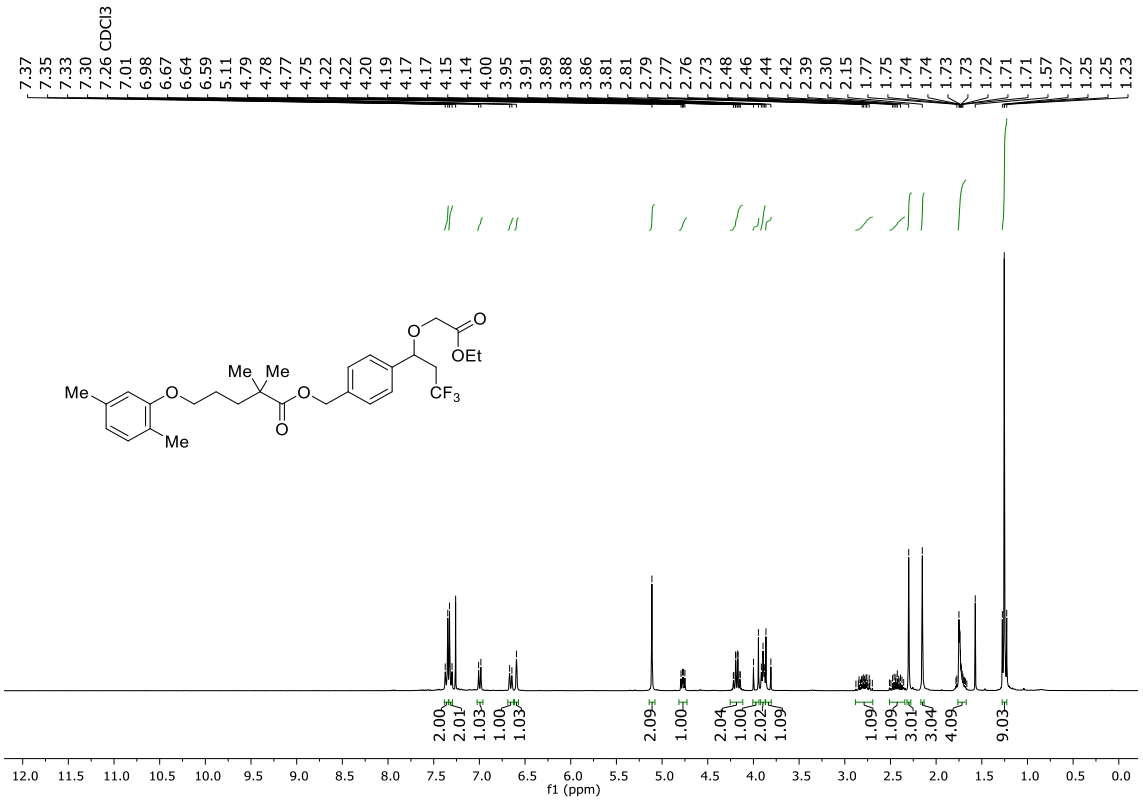


^{1}H NMR (300 MHz, $CDCl_3$) of compound **3q**.

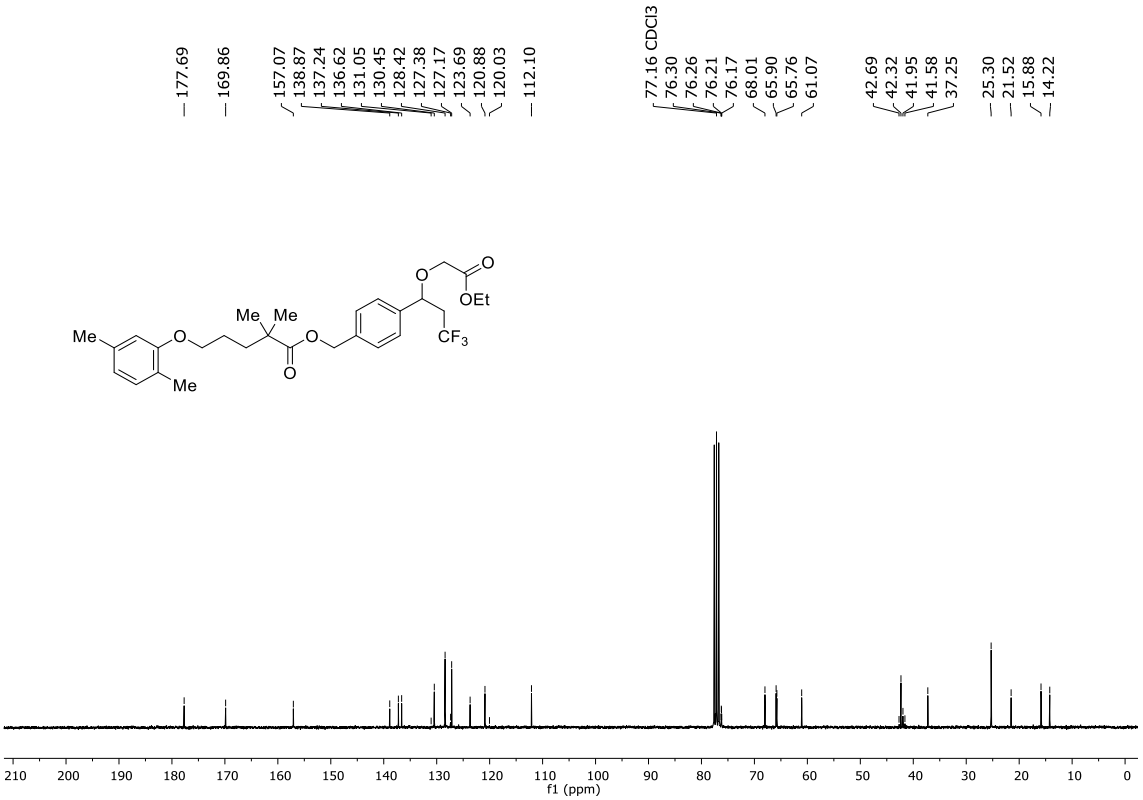


$^{13}C\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) of compound **3q.**

$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3q.**

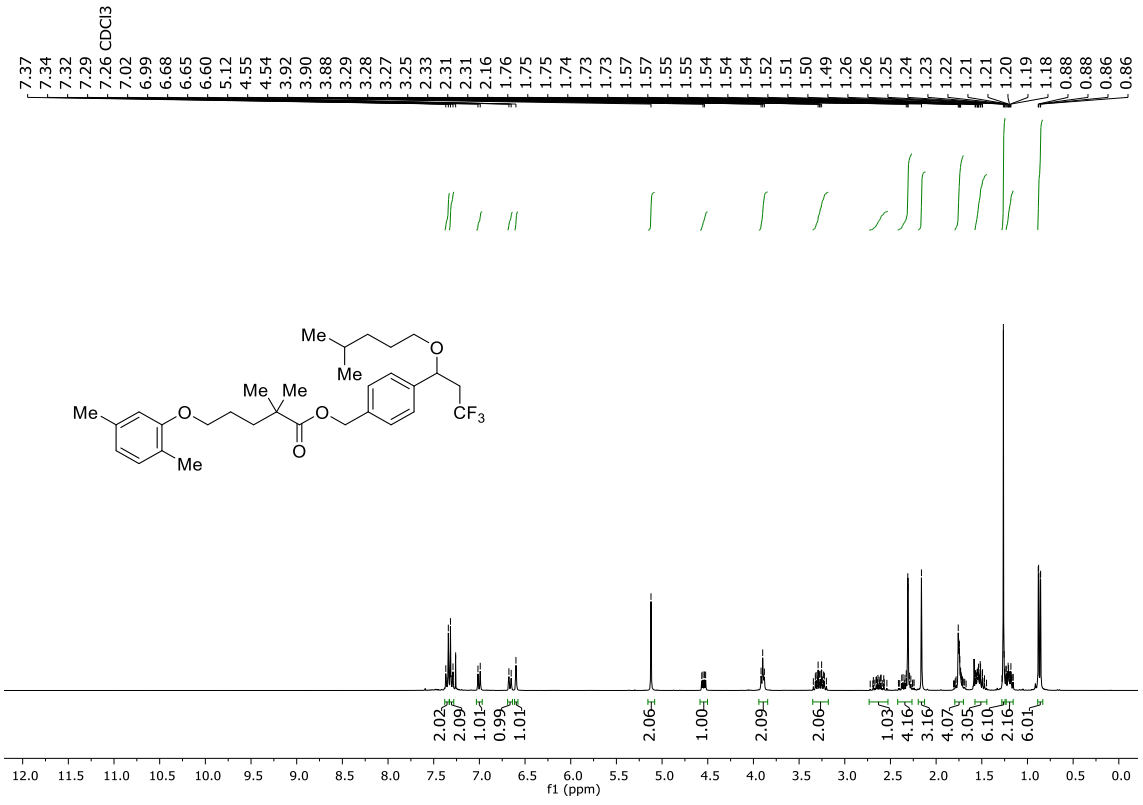


^{1}H NMR (300 MHz, $CDCl_3$) of compound **3r**.

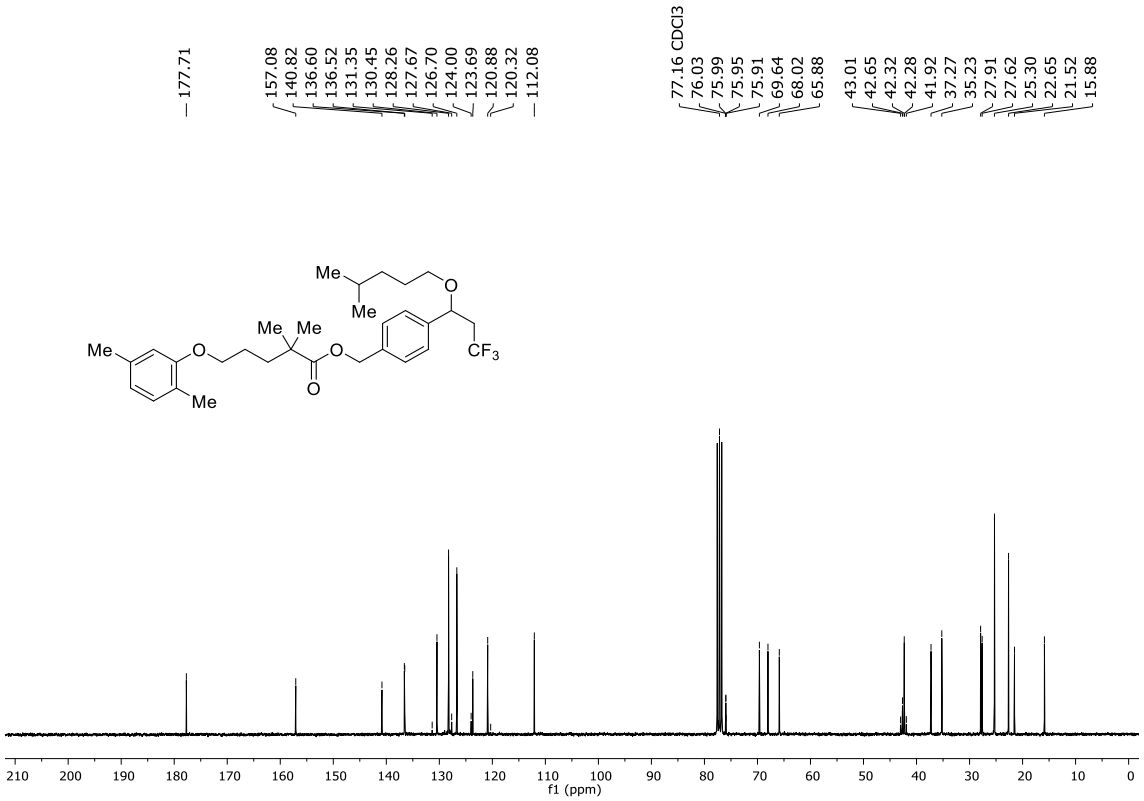


^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$) of compound **3r.**

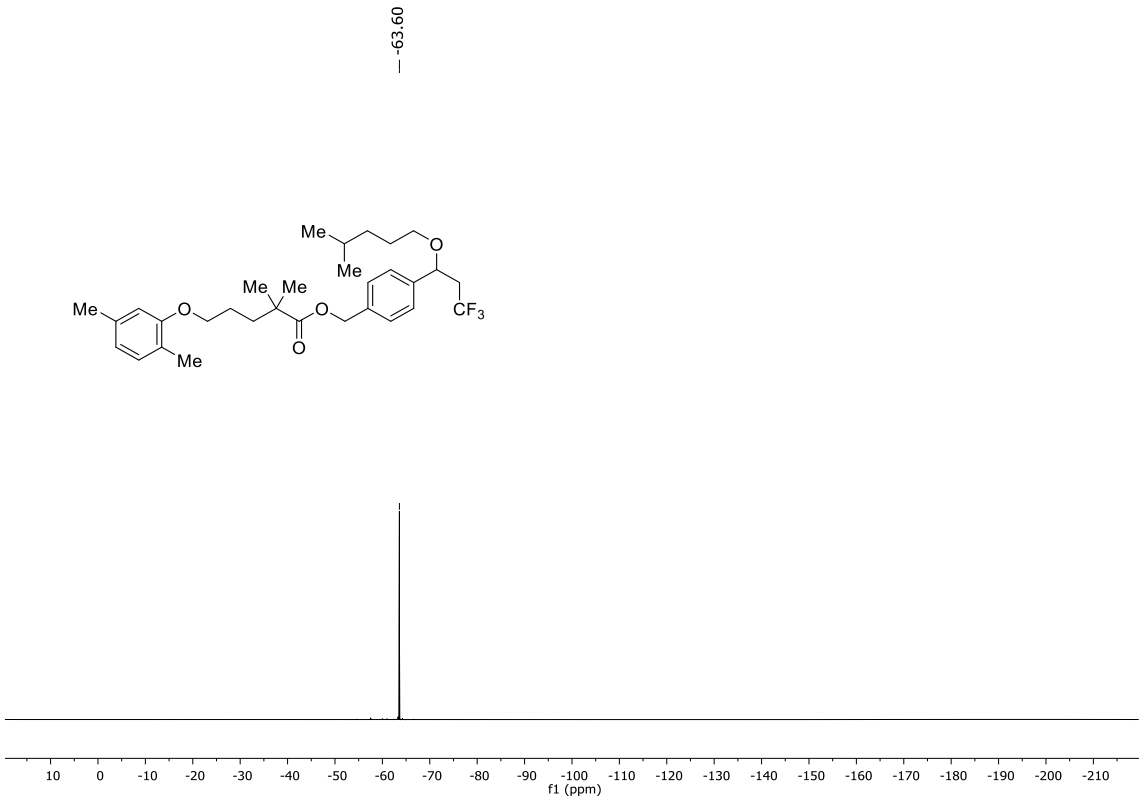
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3r.**



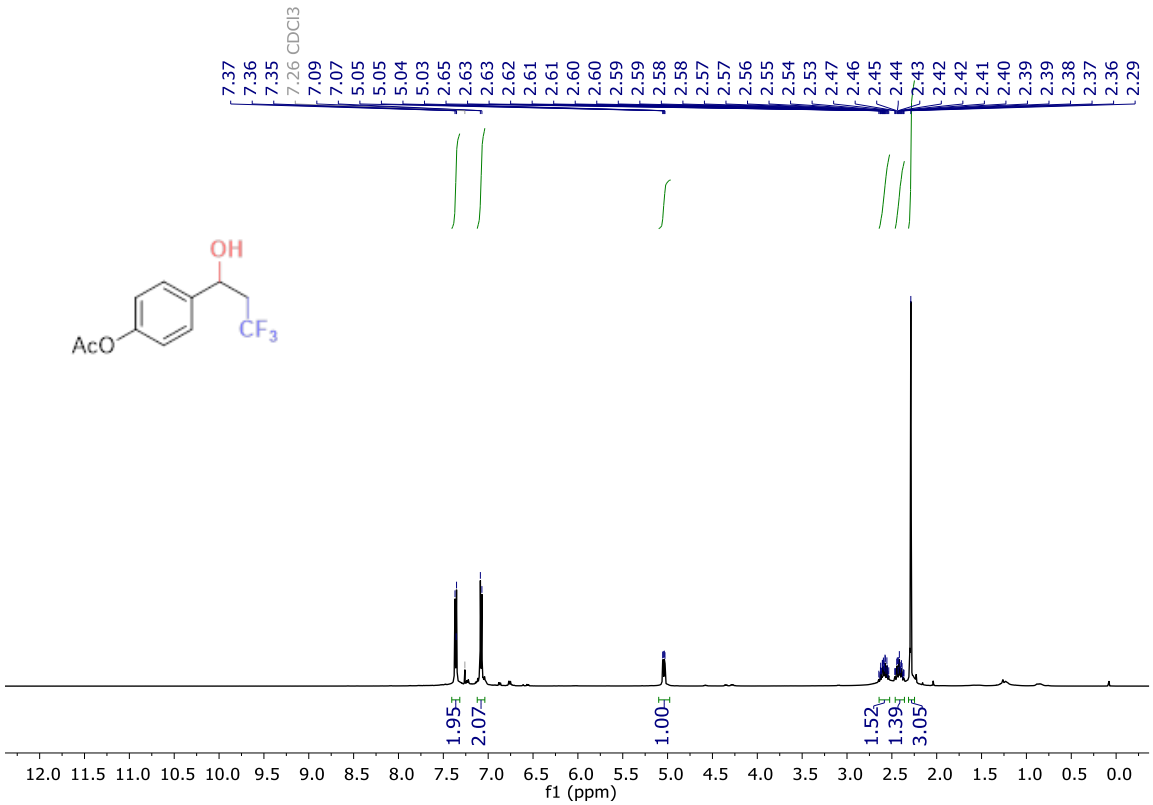
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3s**.



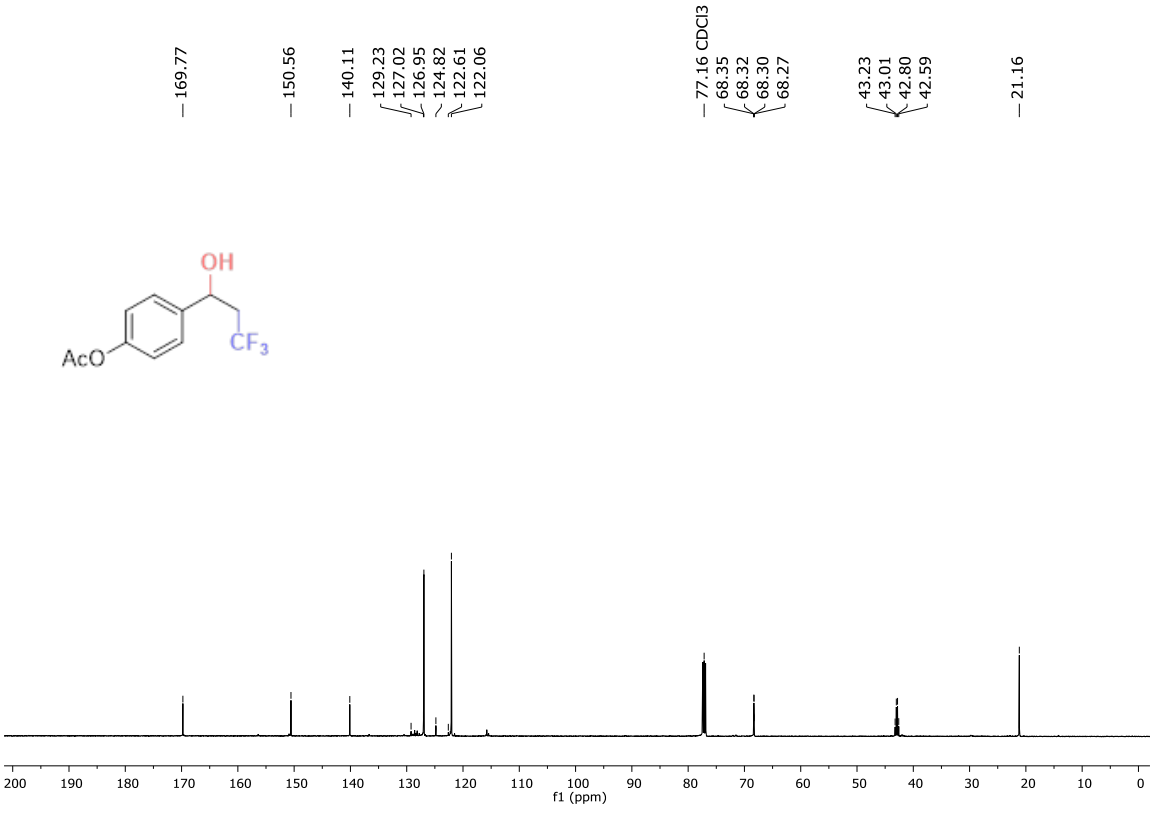
$^{13}C\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) of compound **3s.**



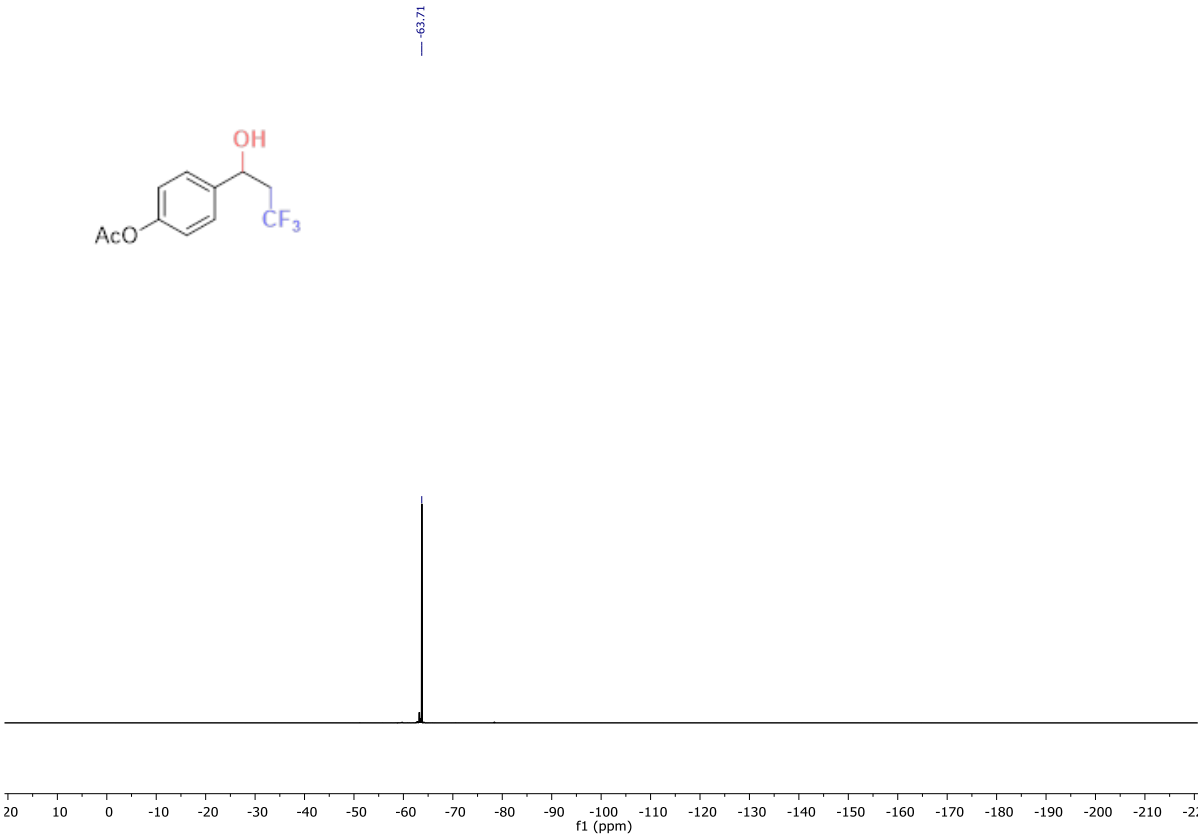
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **3s.**



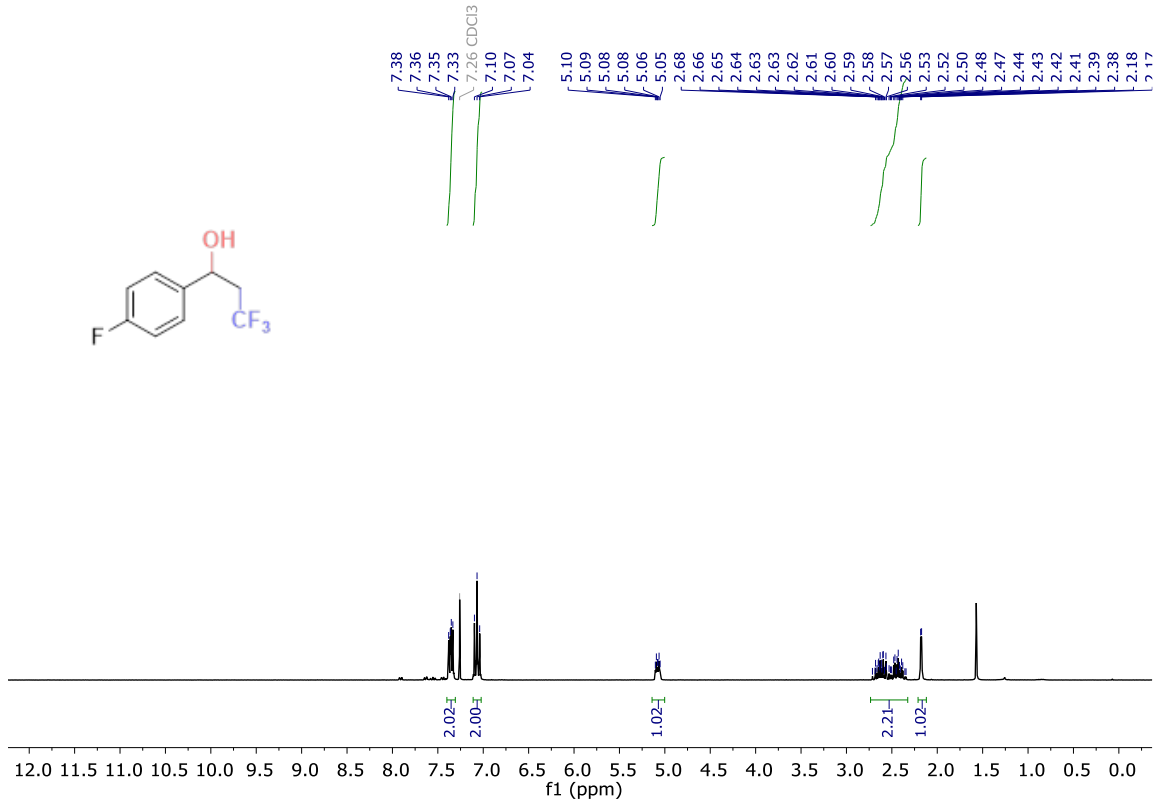
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4a**



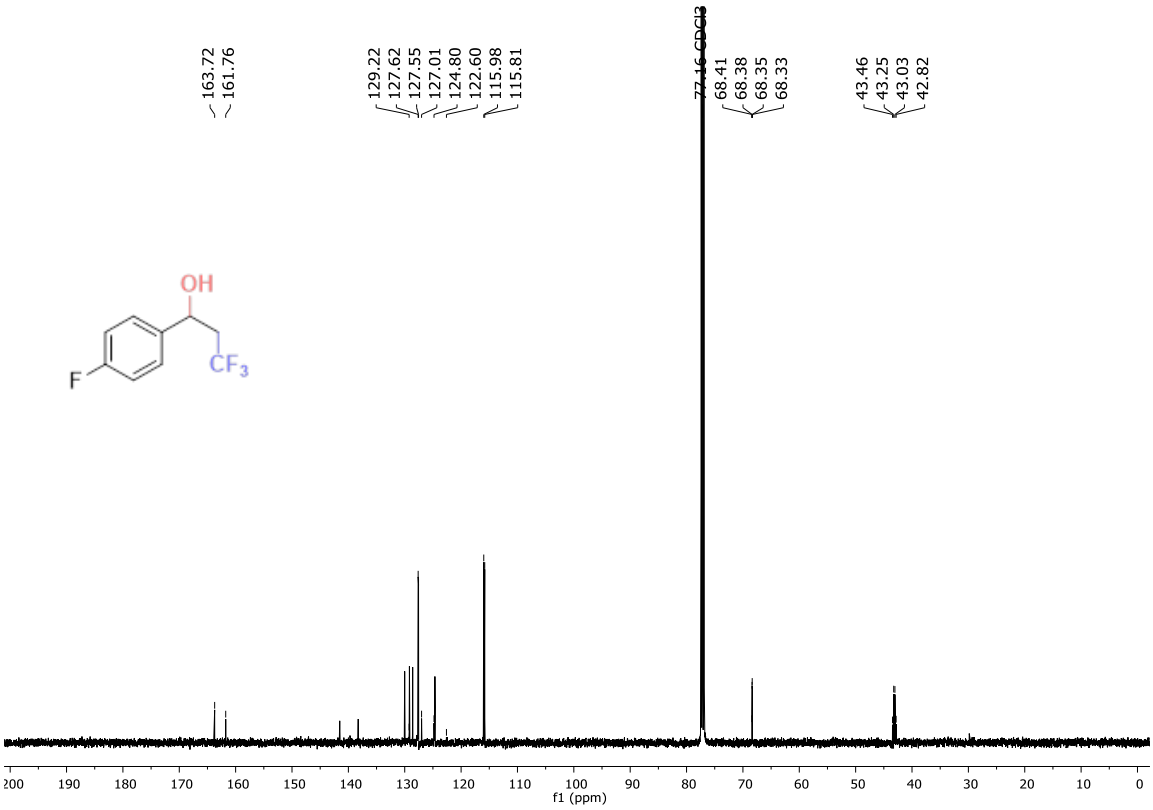
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **4a.**



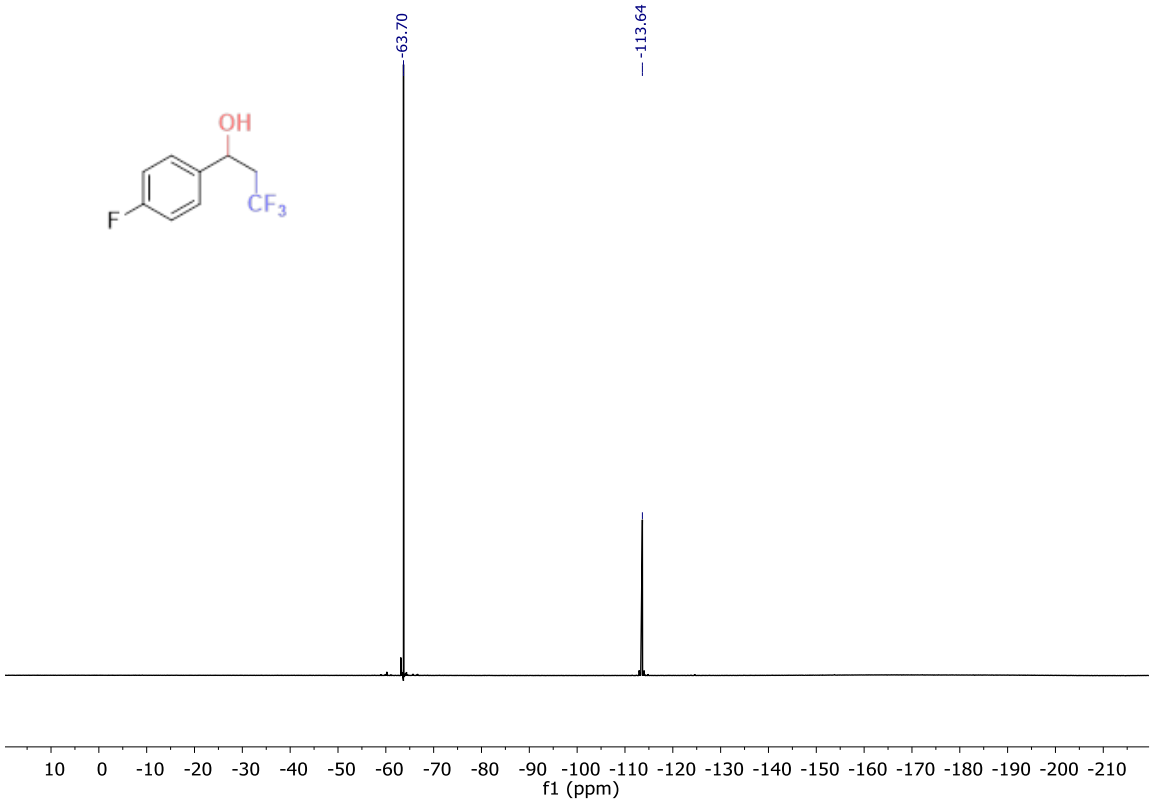
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) of compound **4a**



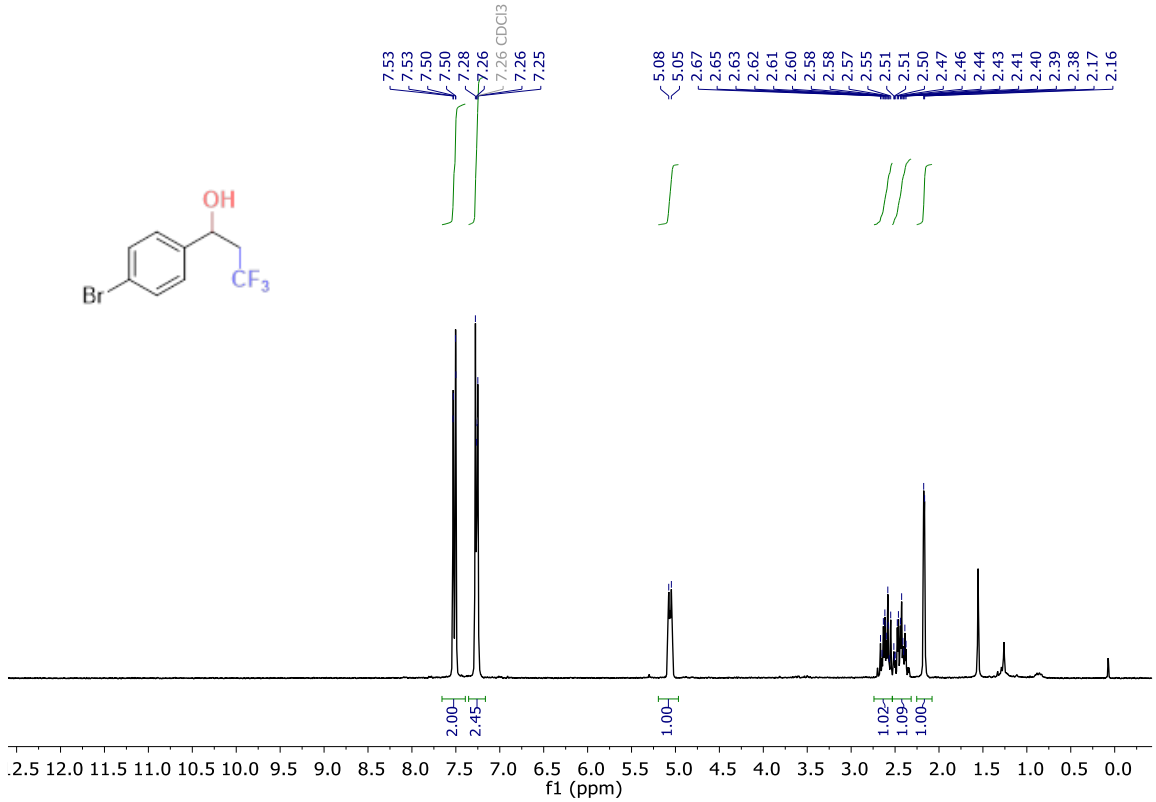
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4b**



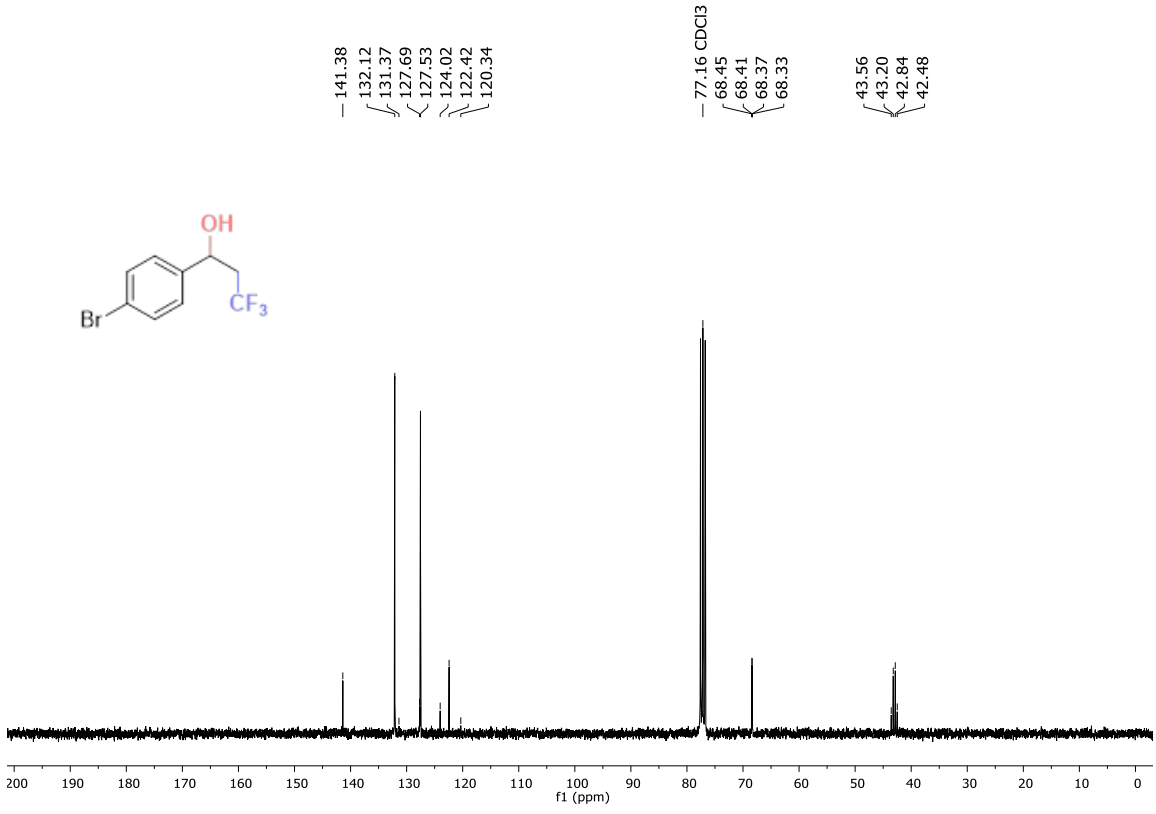
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **4b.**



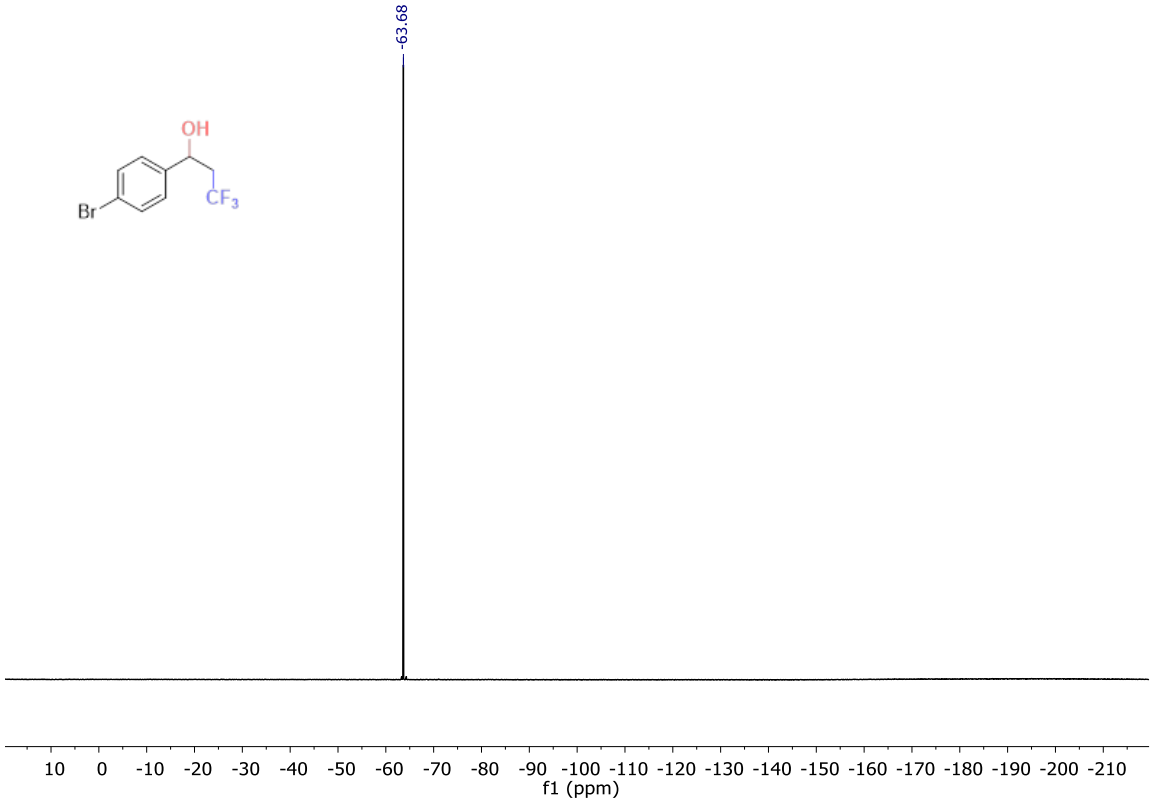
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **4b**



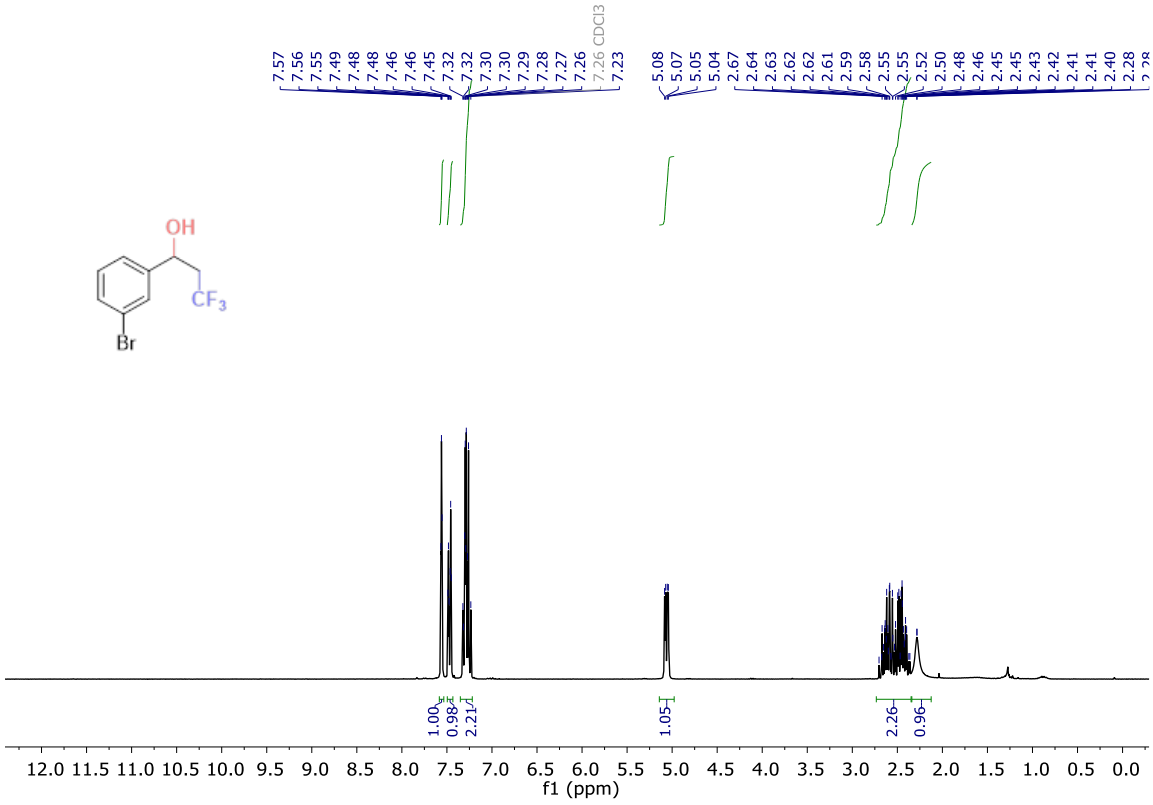
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4c**



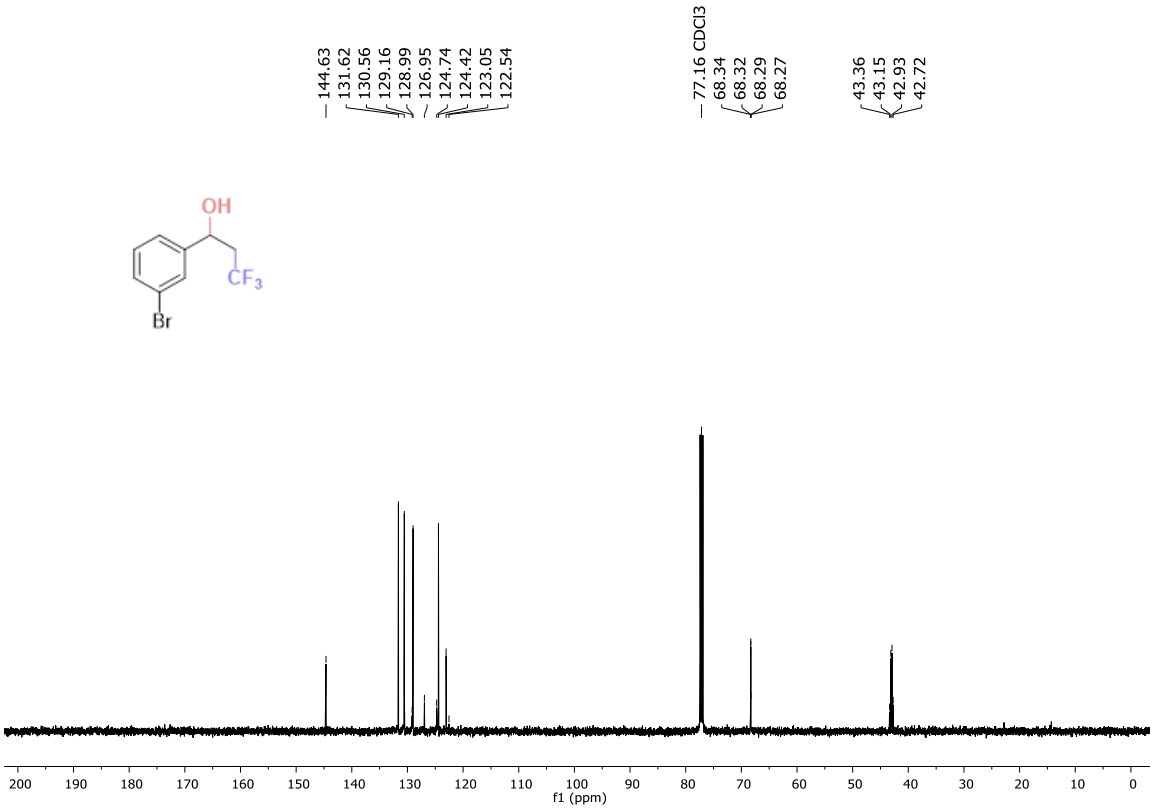
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **4c.**



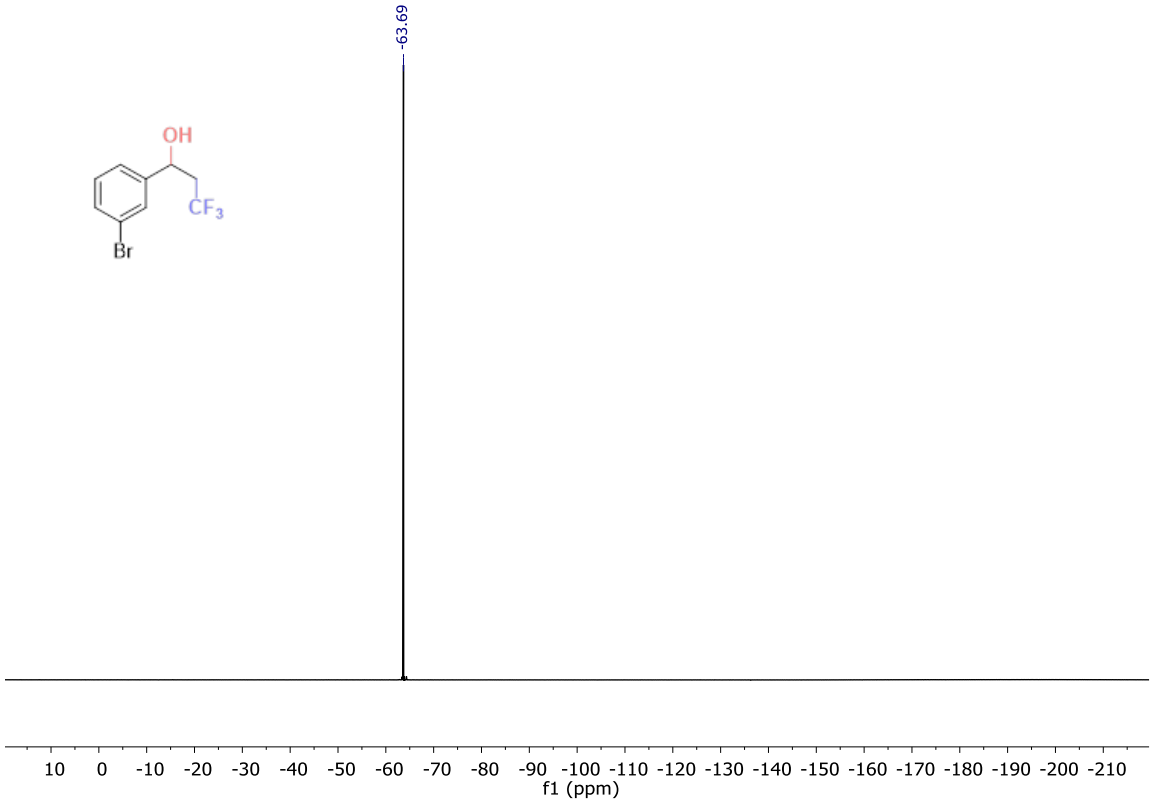
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **4c**



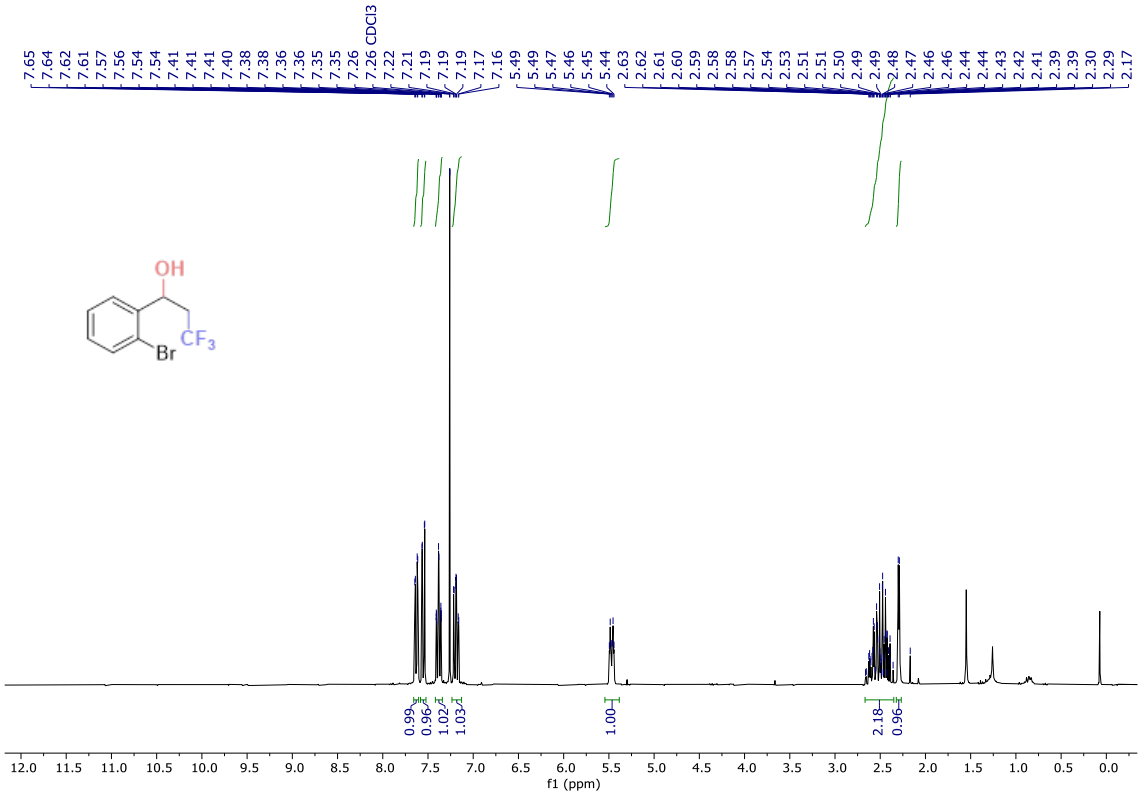
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4d**



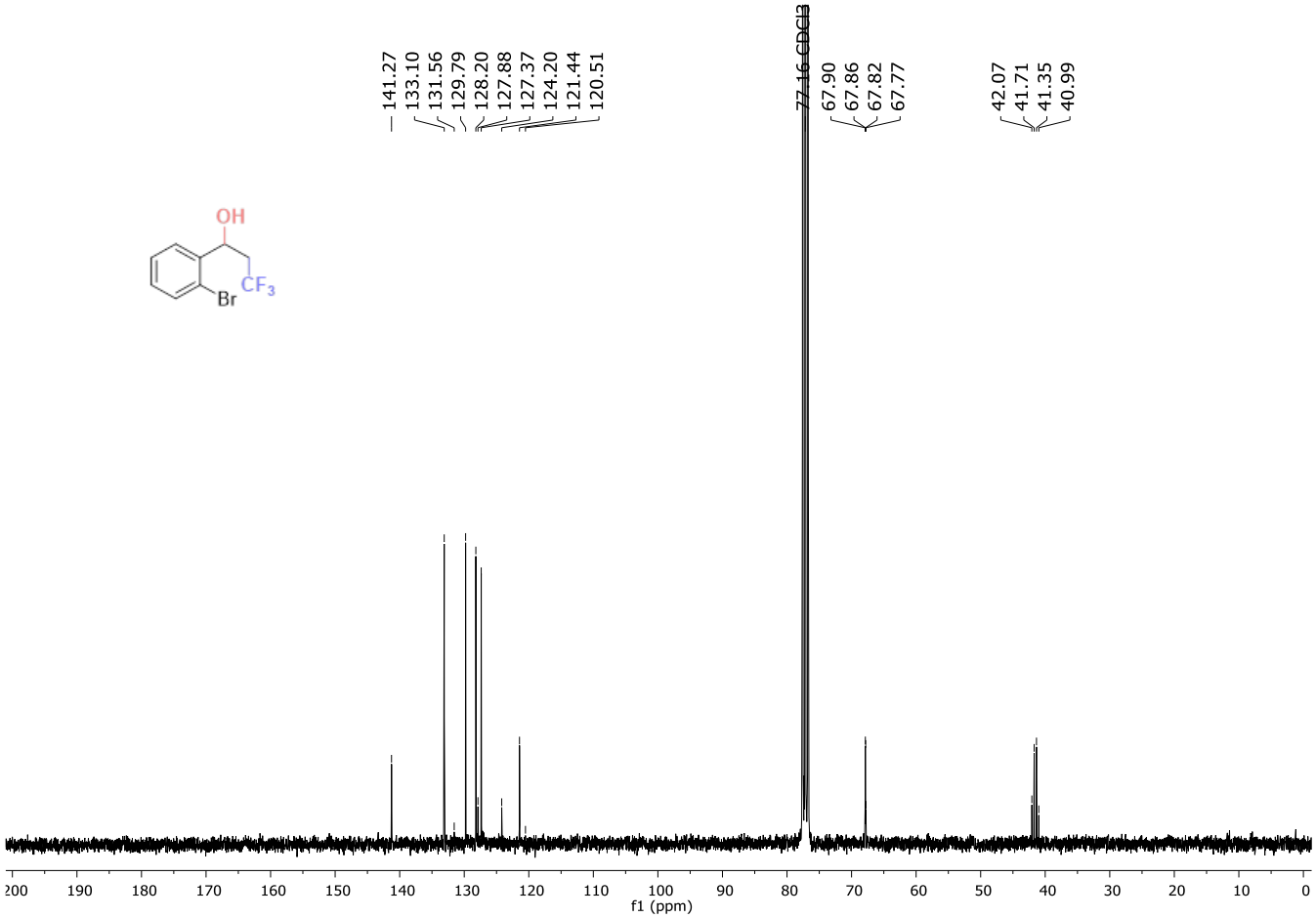
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **4d.**



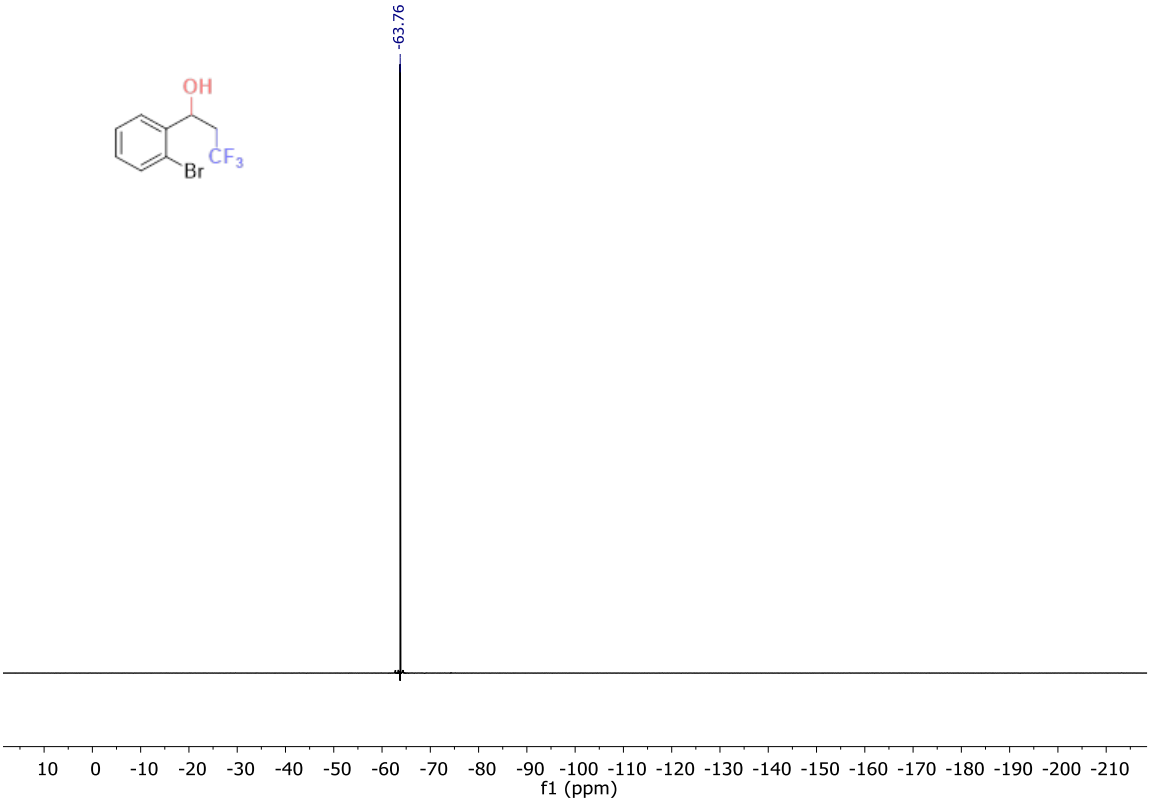
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **4d**



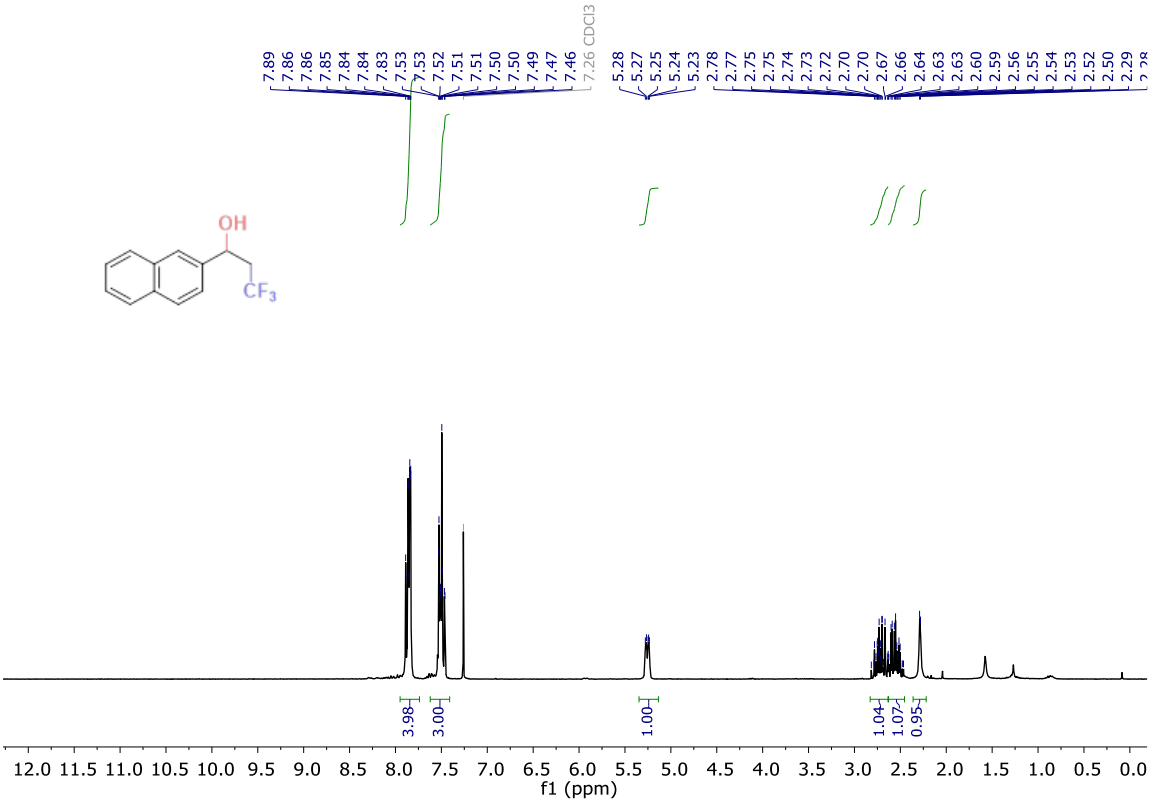
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4e**



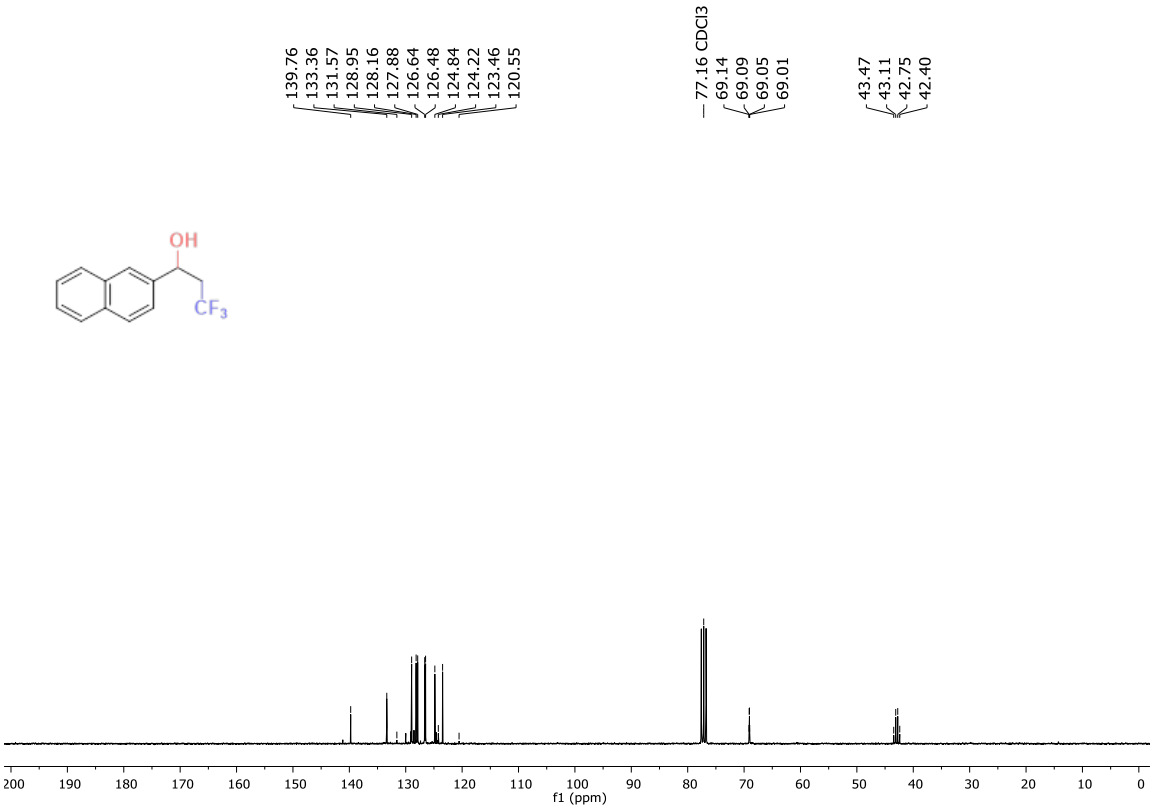
^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$) of compound **4e.**



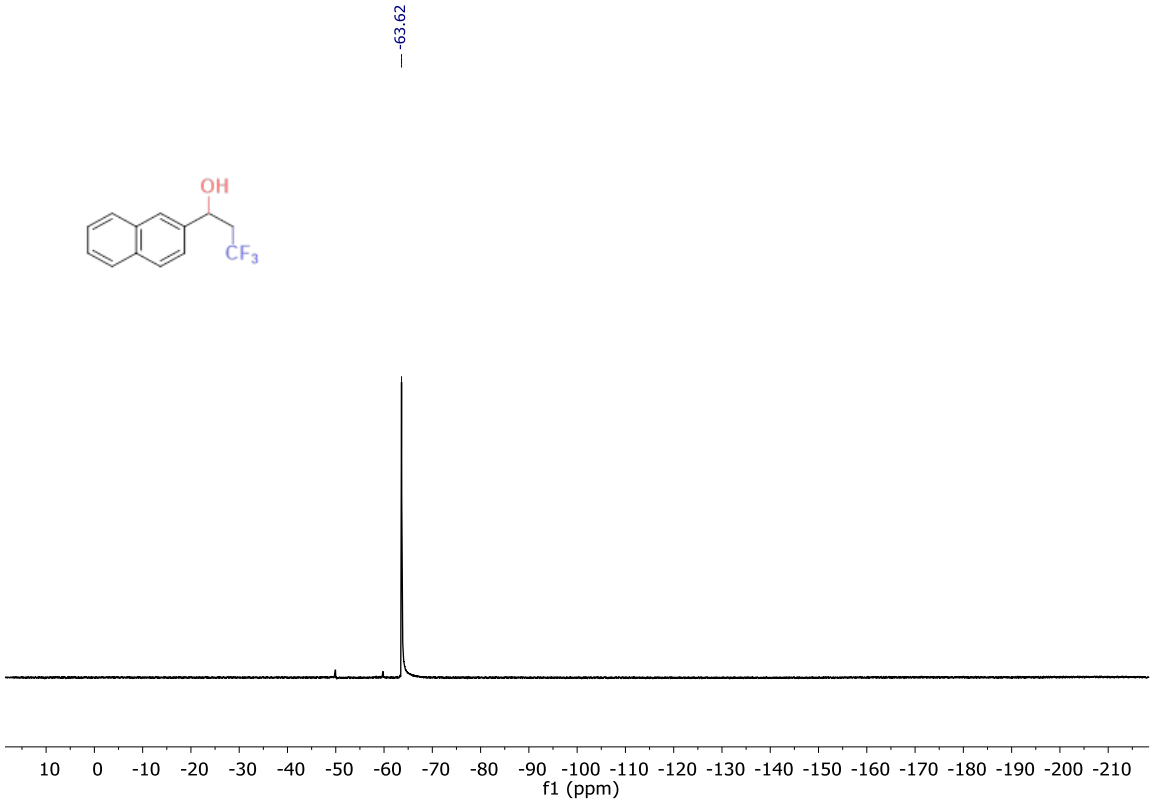
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **4e**



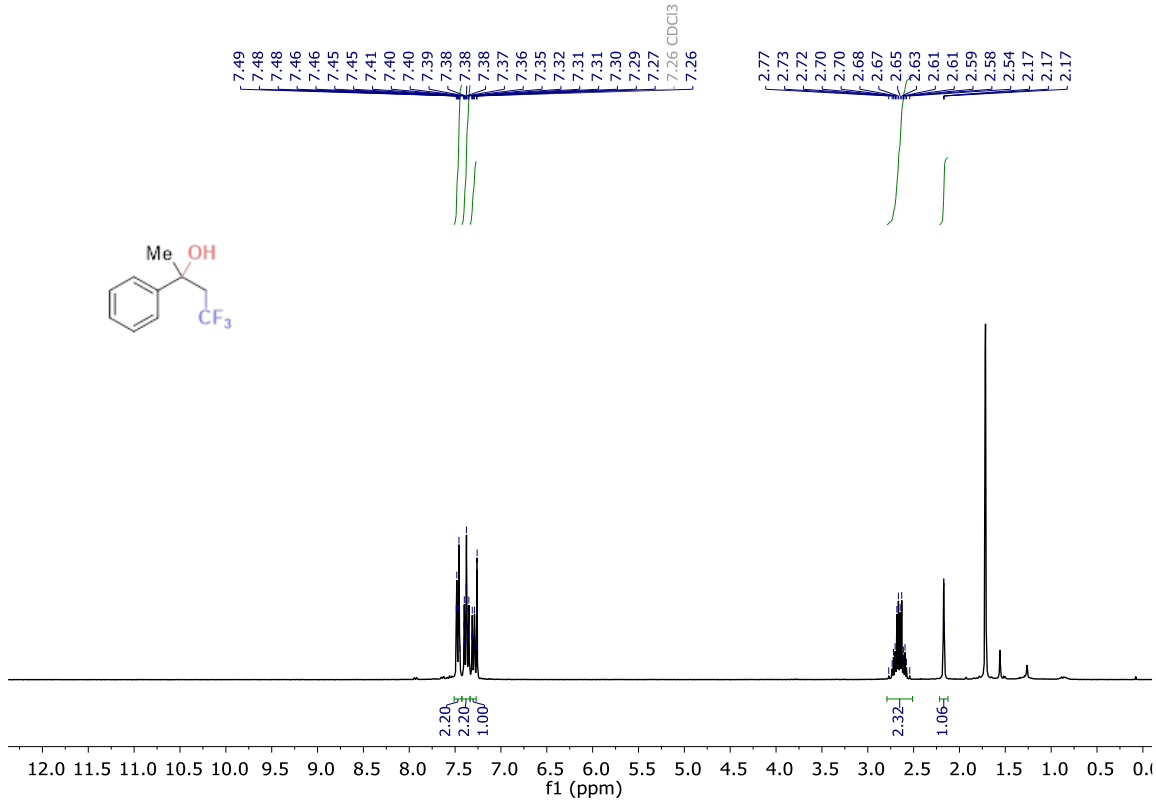
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4f**



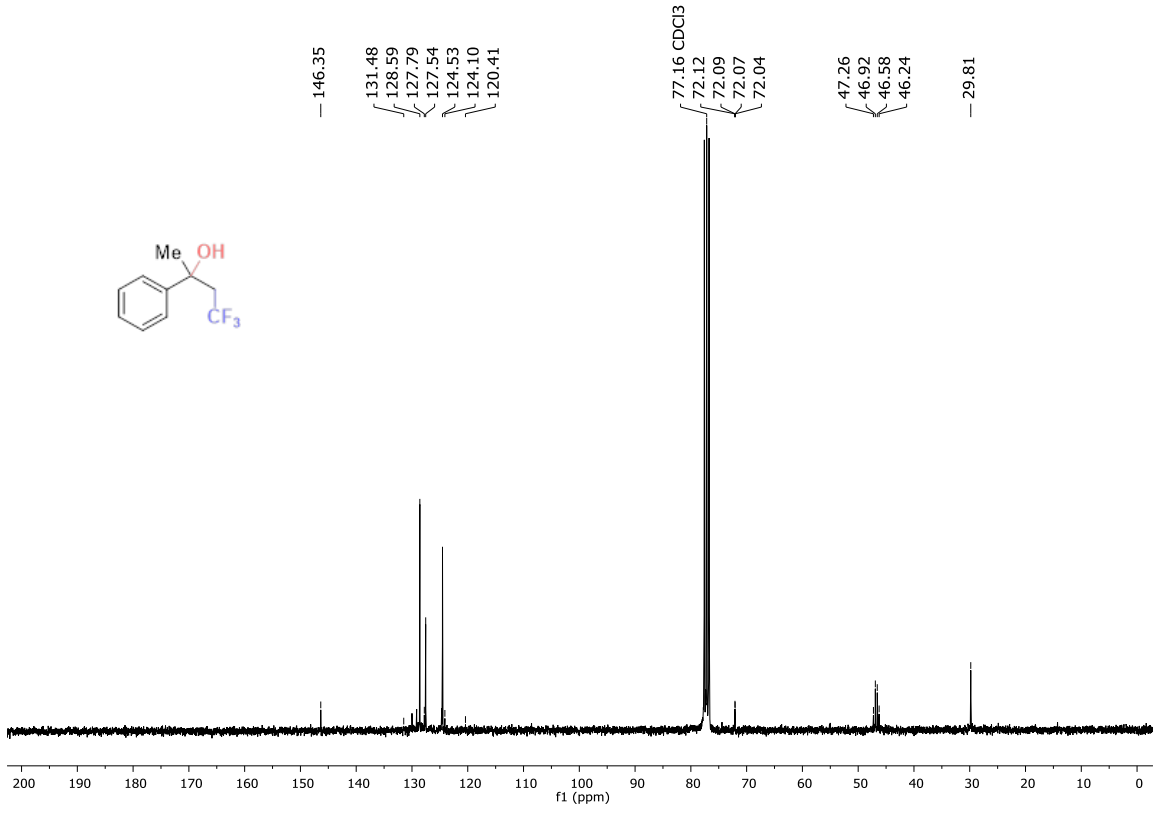
$^{13}C\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) of compound **4f.**



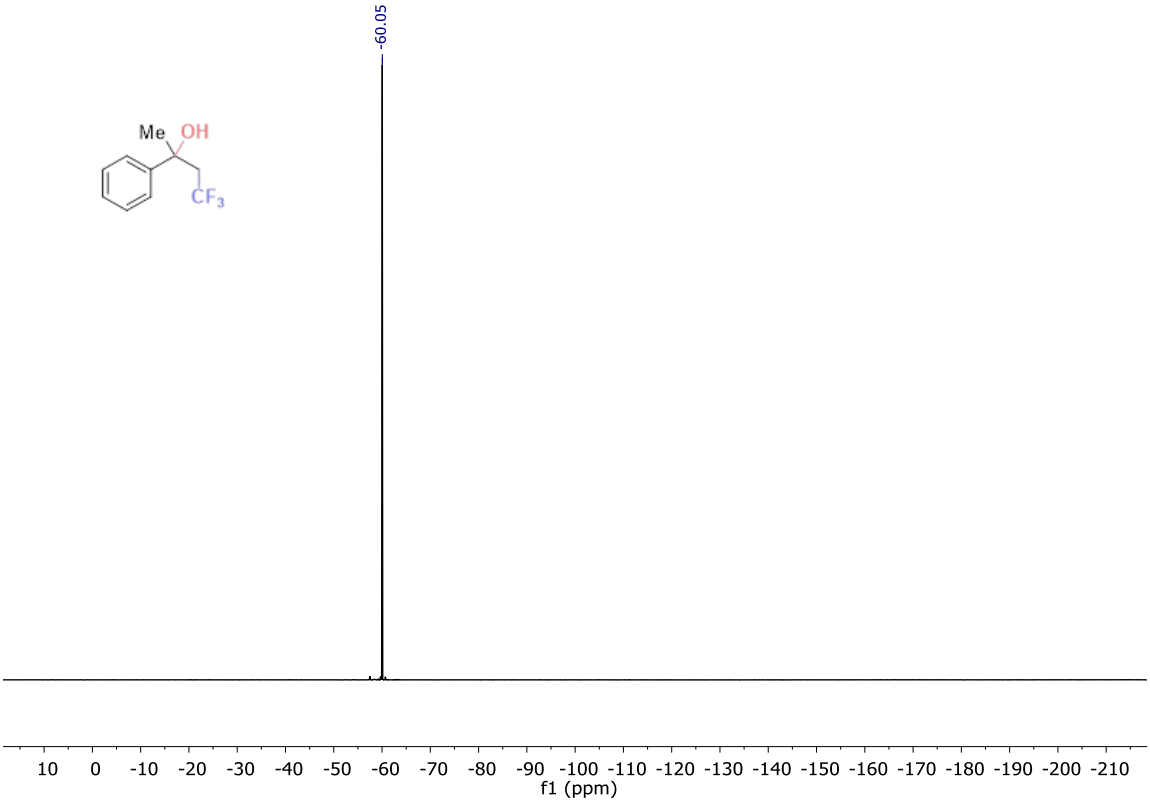
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **4e**



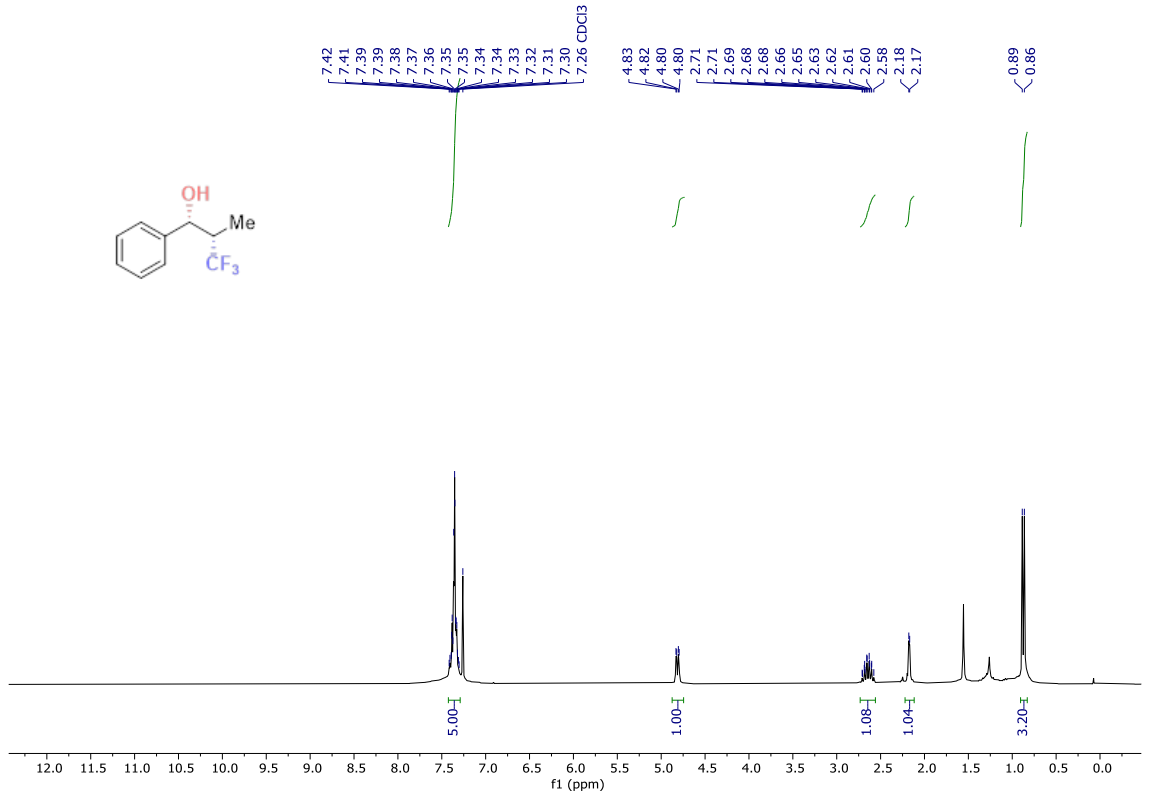
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4g**



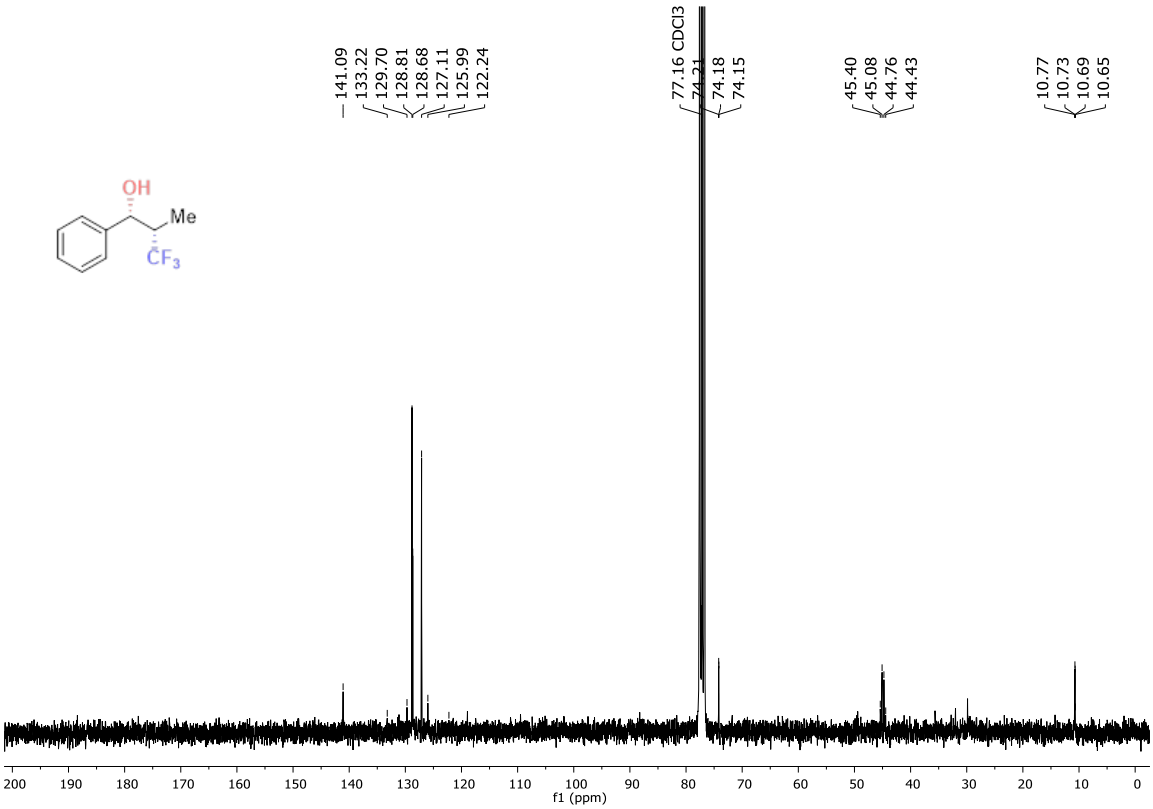
^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$) of compound **4g**



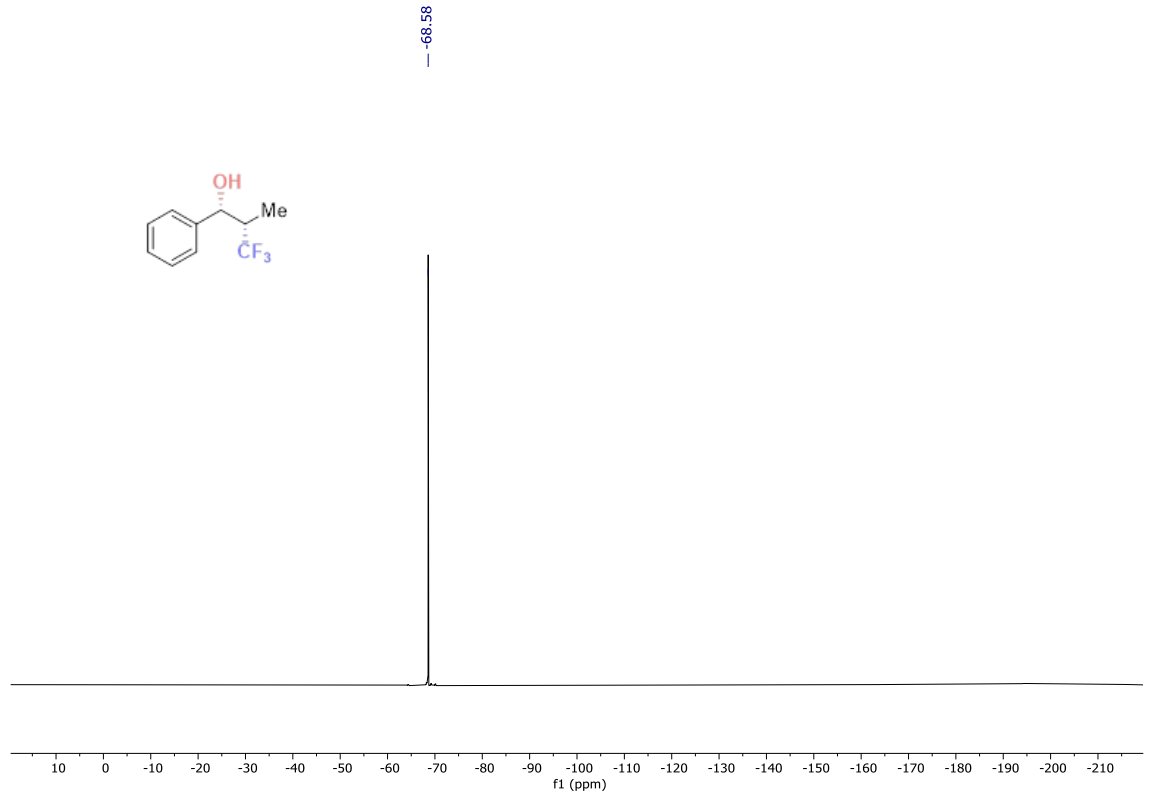
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **4g**



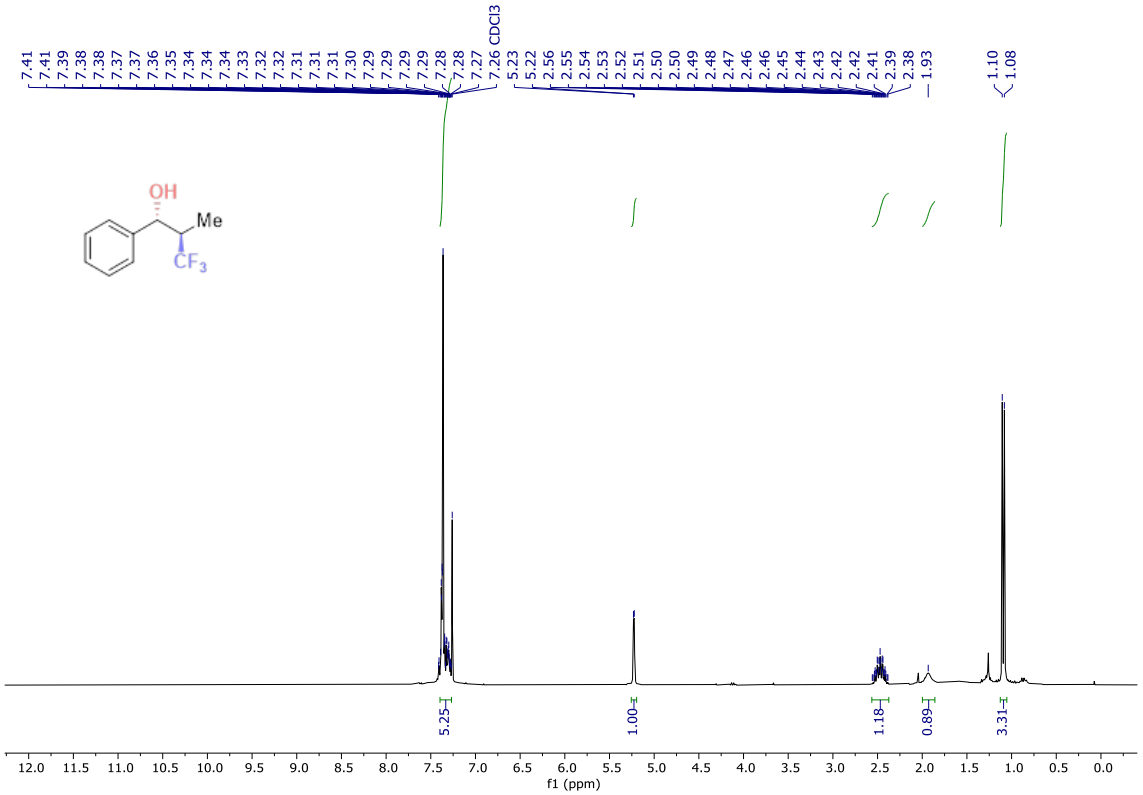
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4h (*syn* isomer)**



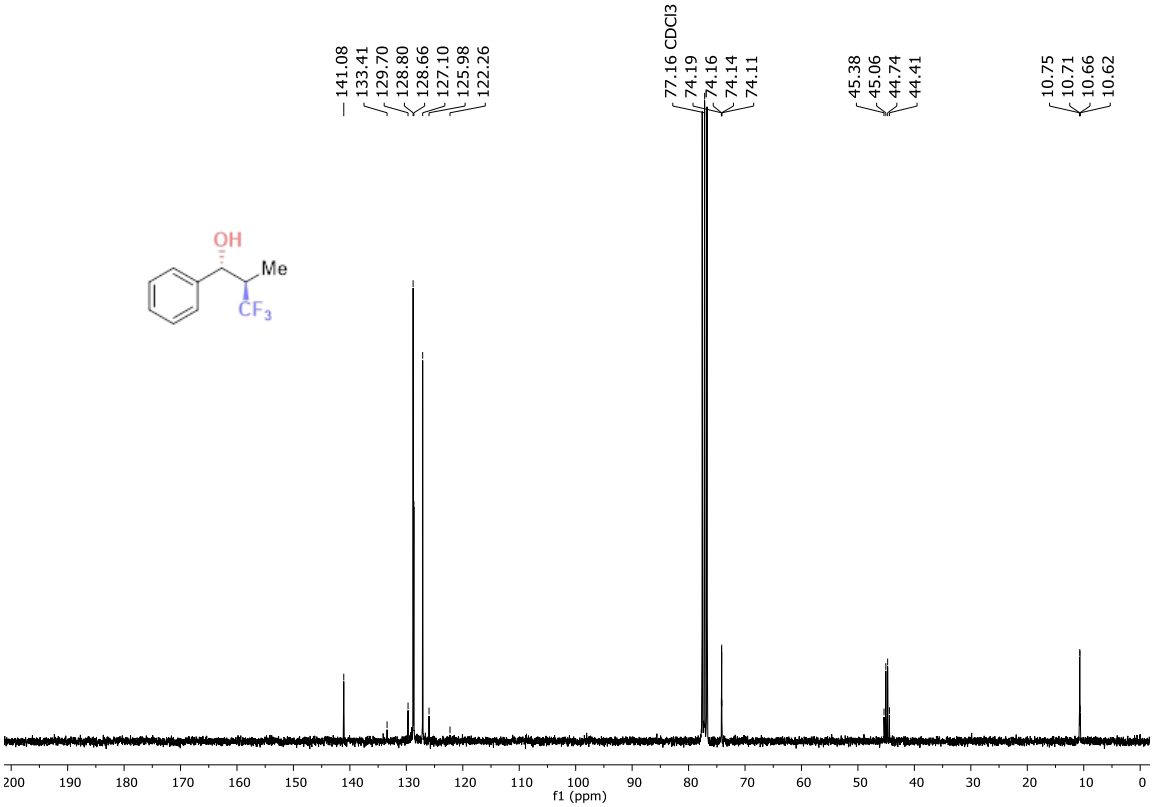
$^{13}C\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) of compound **4h (*syn* isomer)**



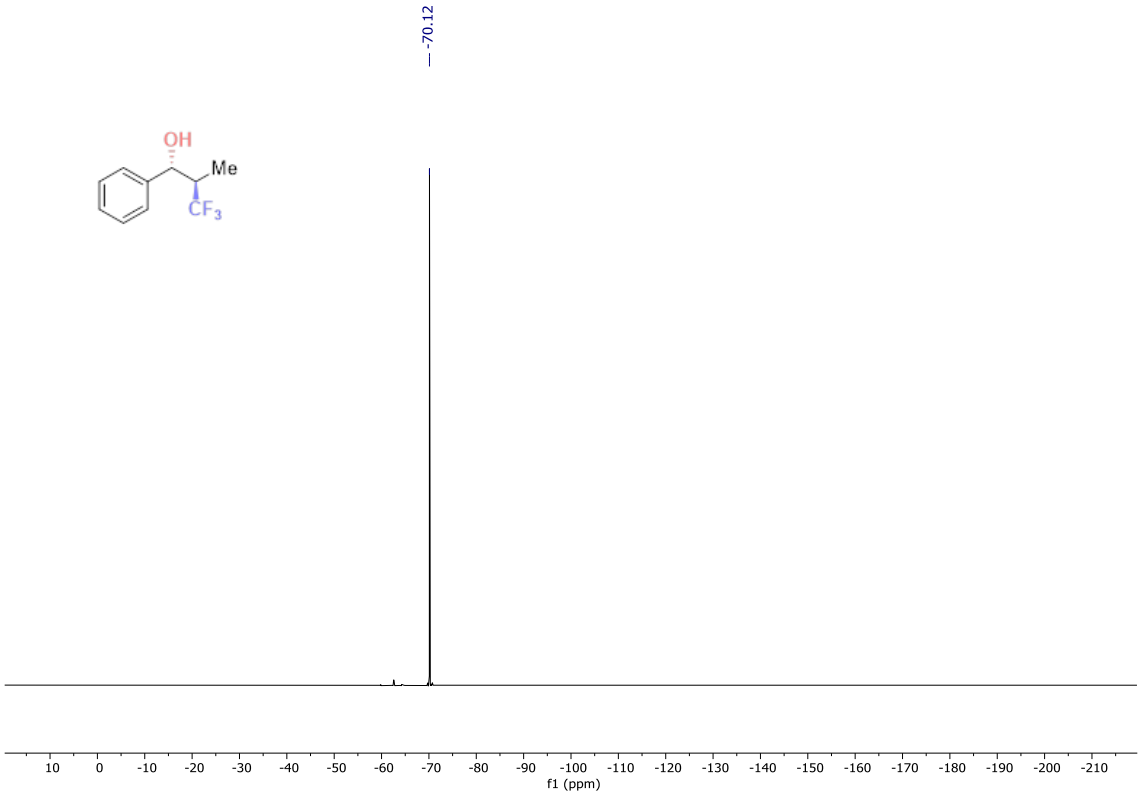
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **4h (*syn* isomer)**



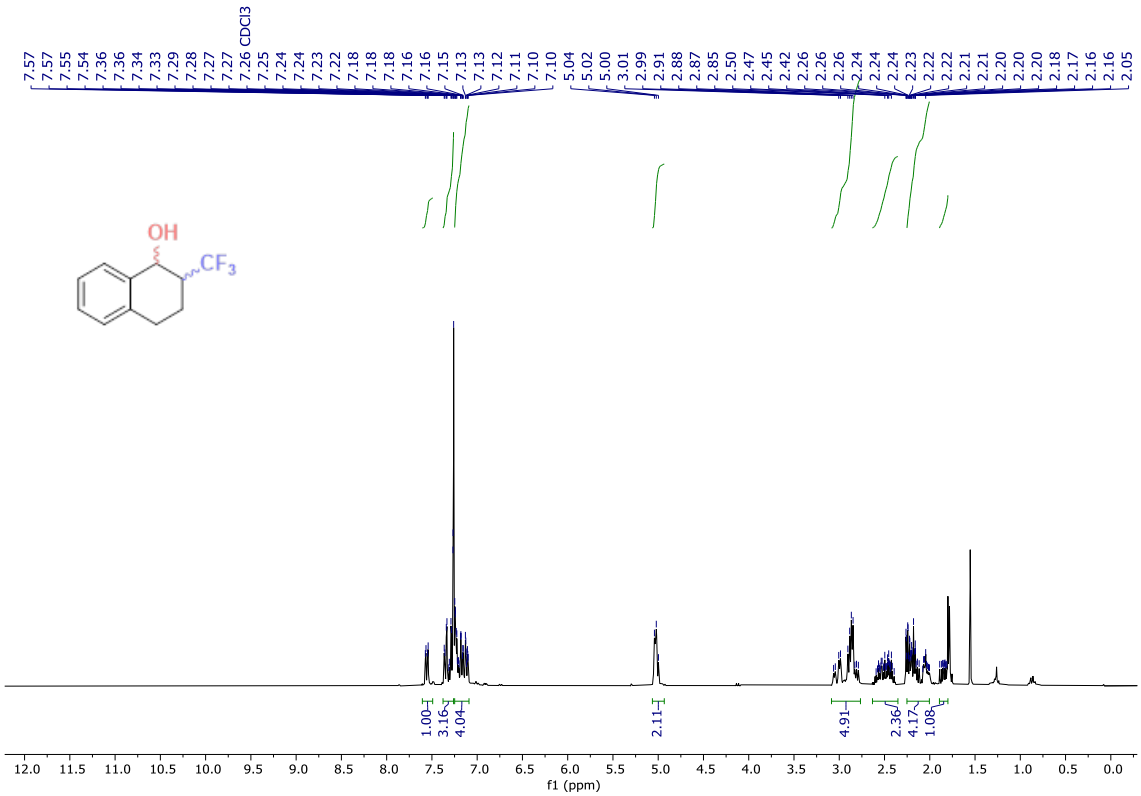
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4h (*anti* isomer)**



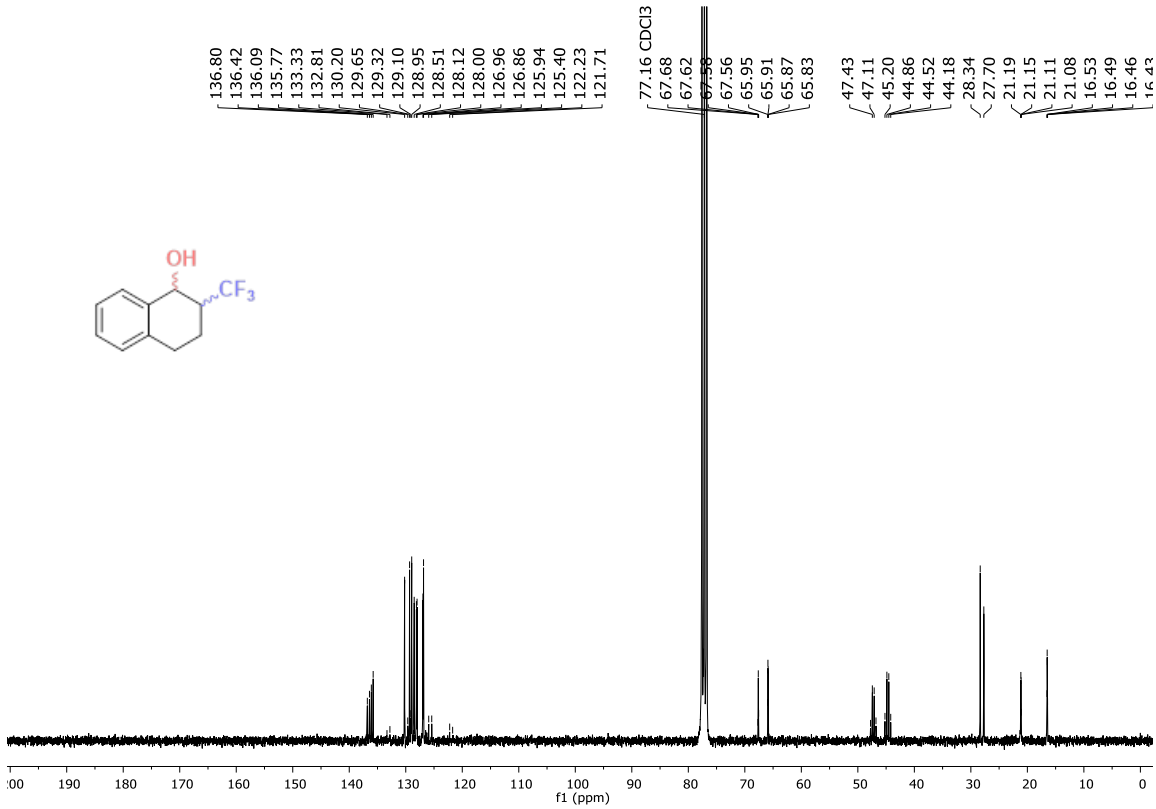
^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$) of compound **4h (*anti* isomer)**



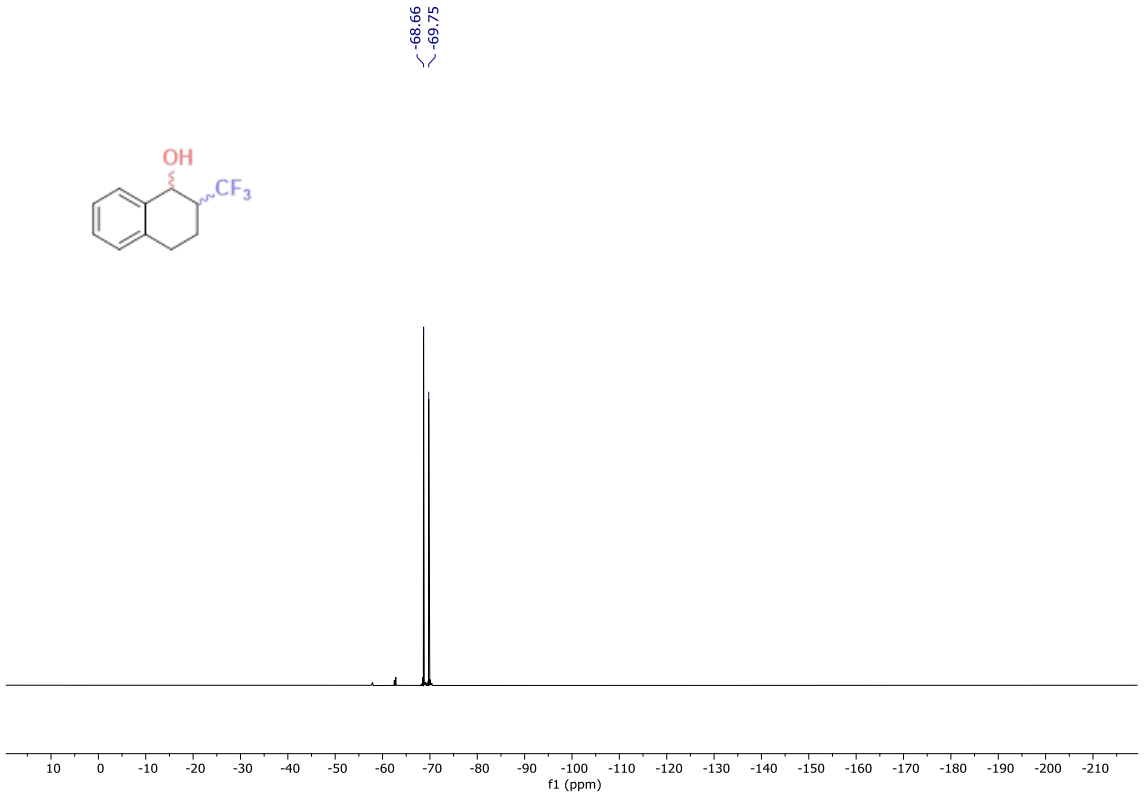
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **4h (*anti* isomer)**



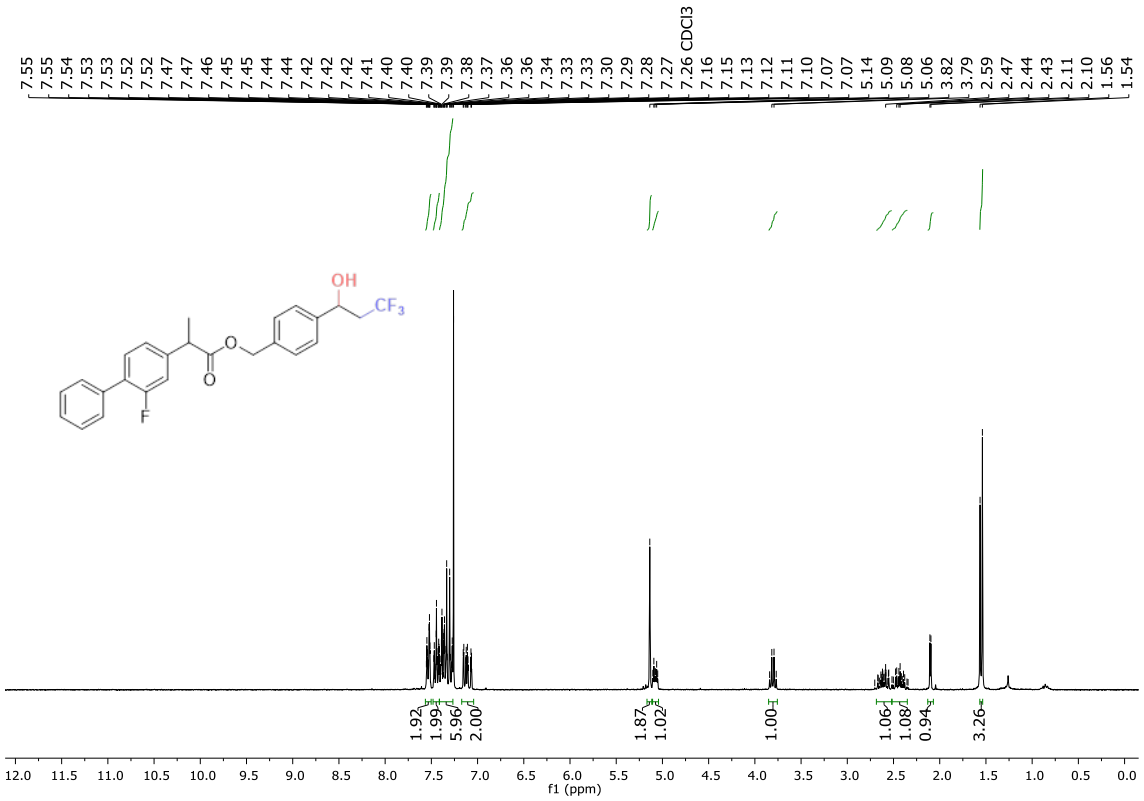
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4i**



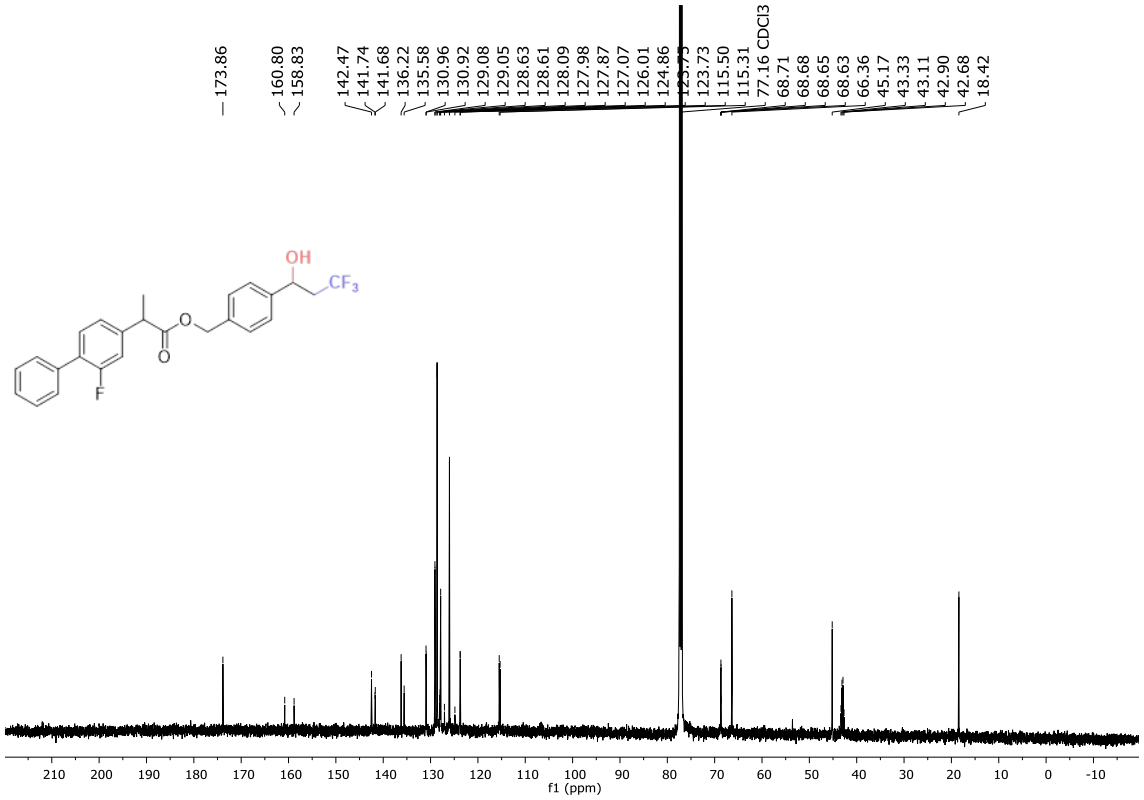
$^{13}C\{^{1}H\}$ NMR (76 MHz, $CDCl_3$) of compound **4i**



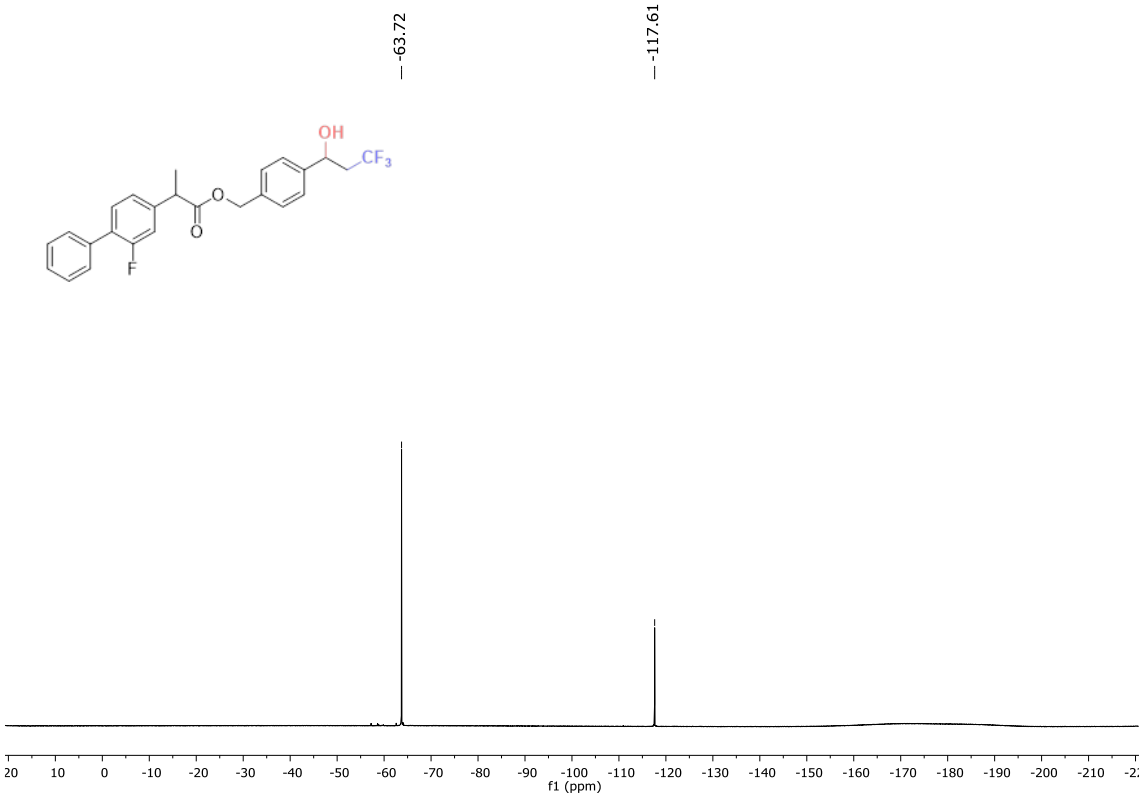
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **4i**



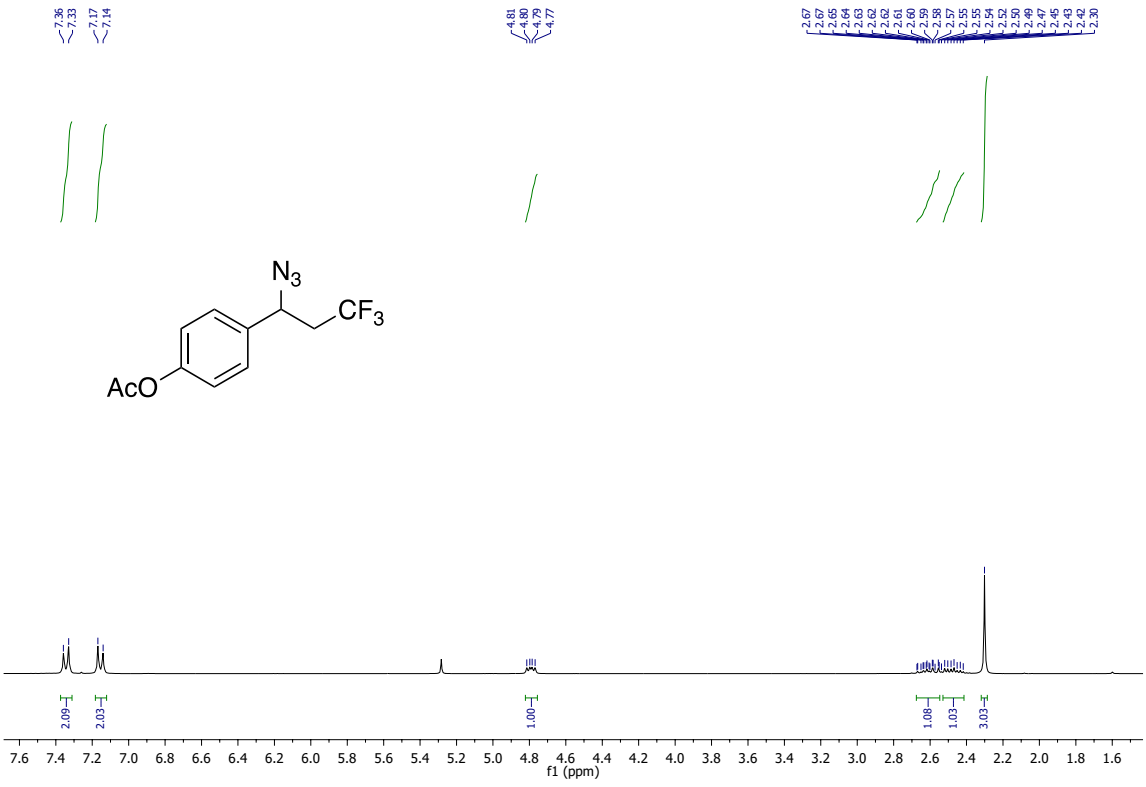
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4j**



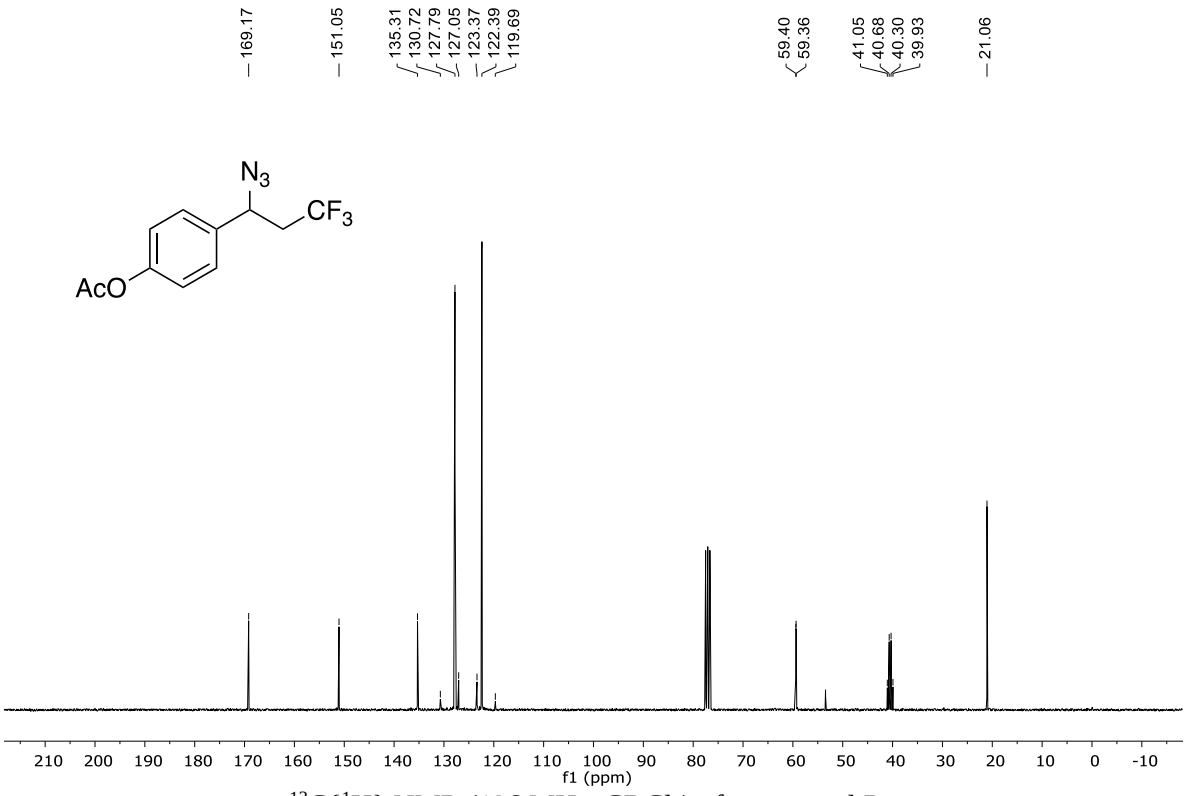
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **4j.**



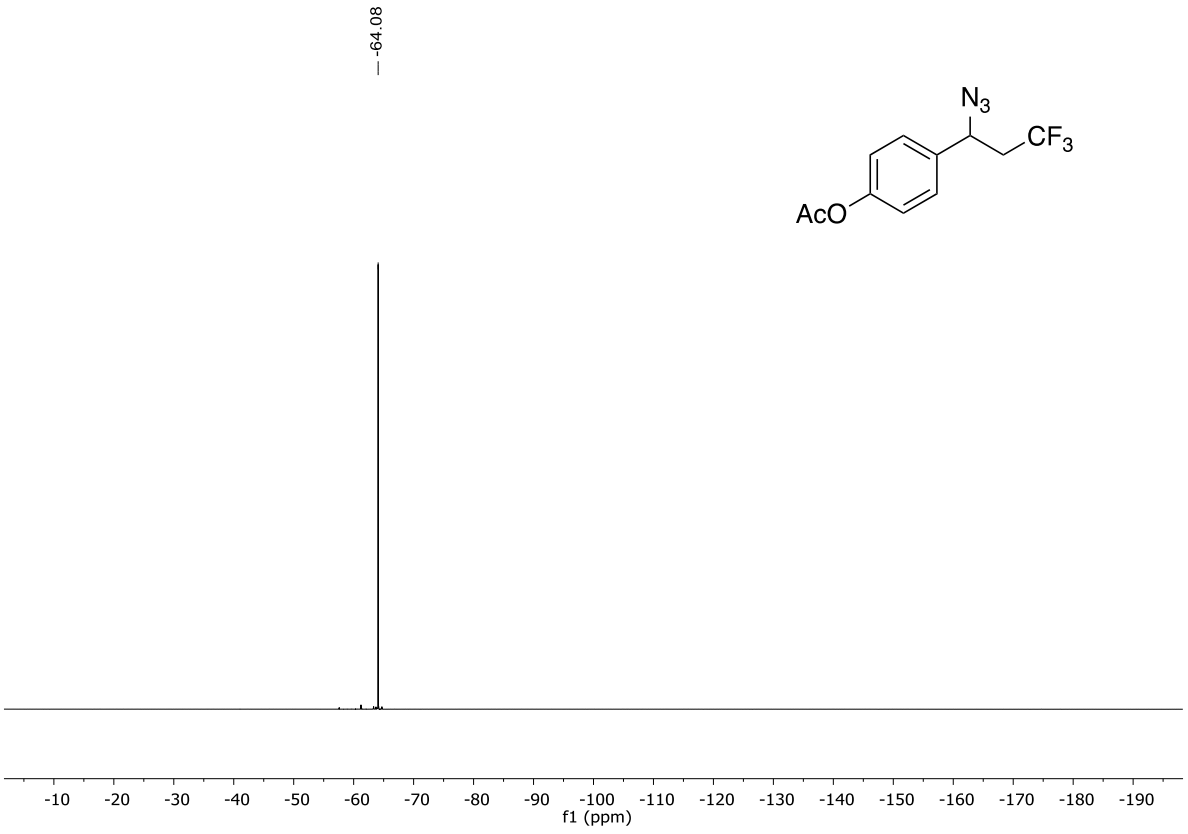
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) of compound **4j**



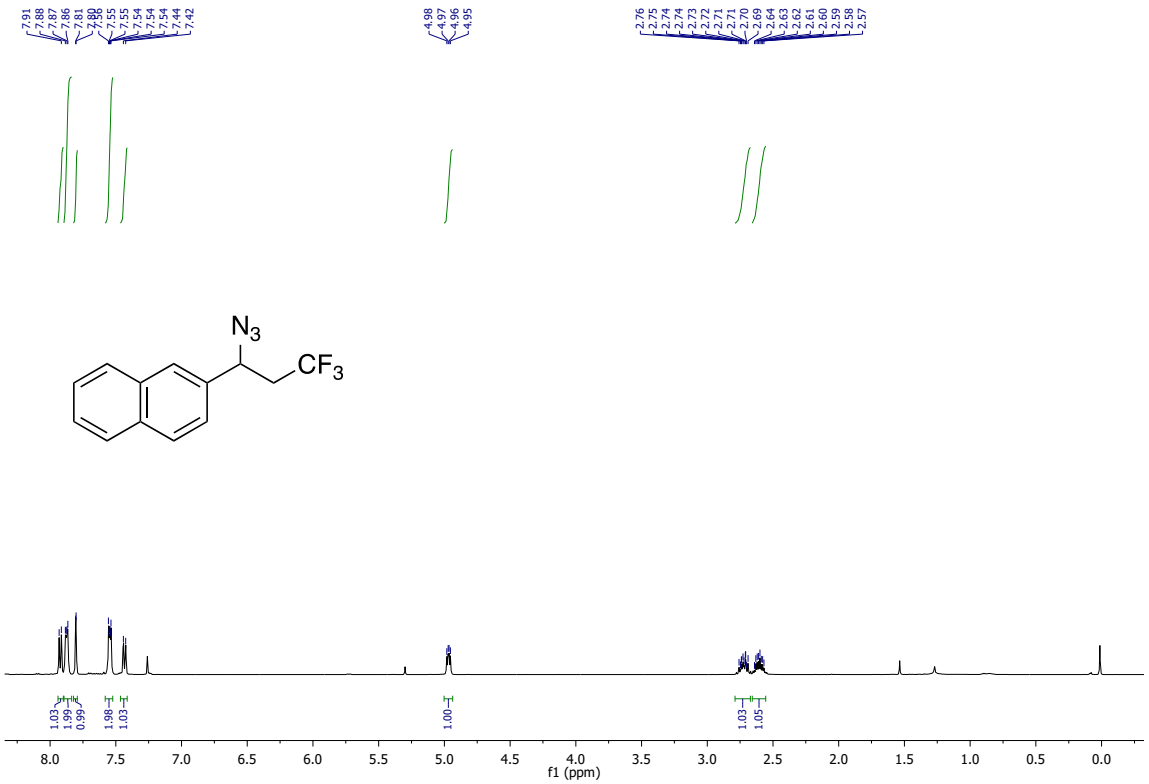
^{1}H NMR (300 MHz, $CDCl_3$) of compound **5a**.



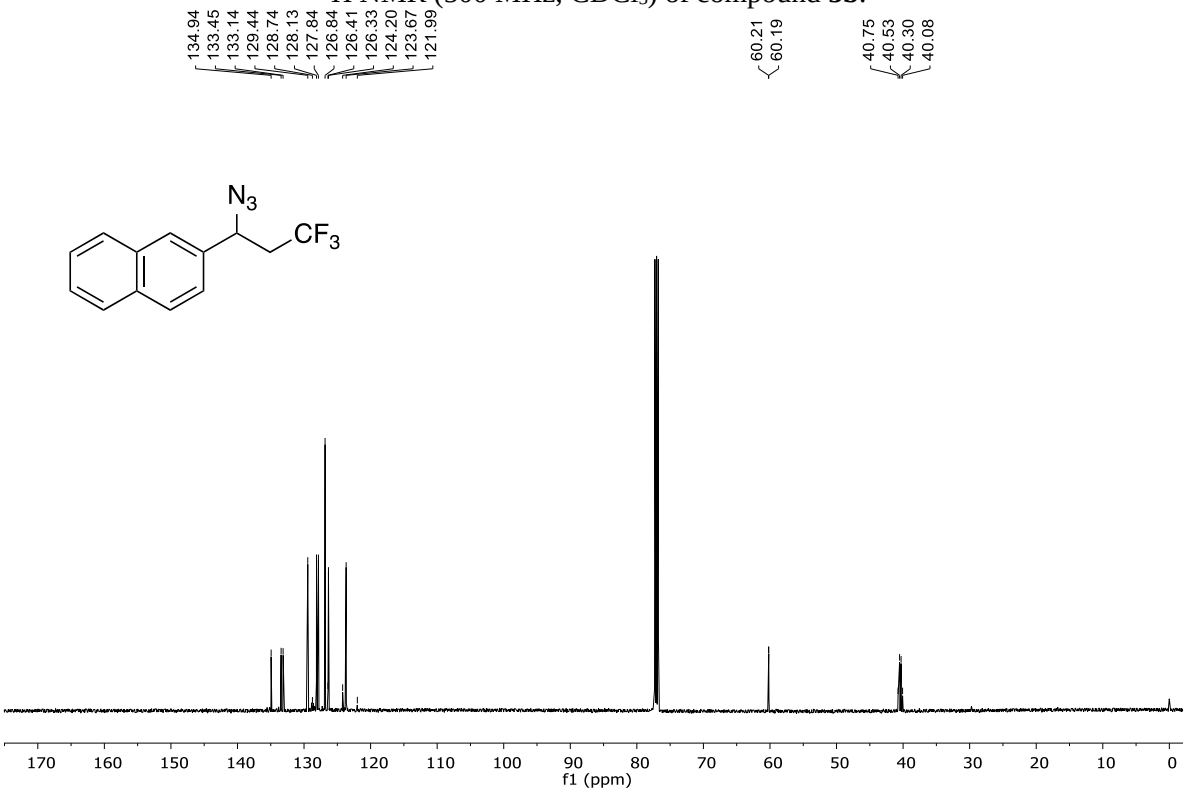
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **5a.**



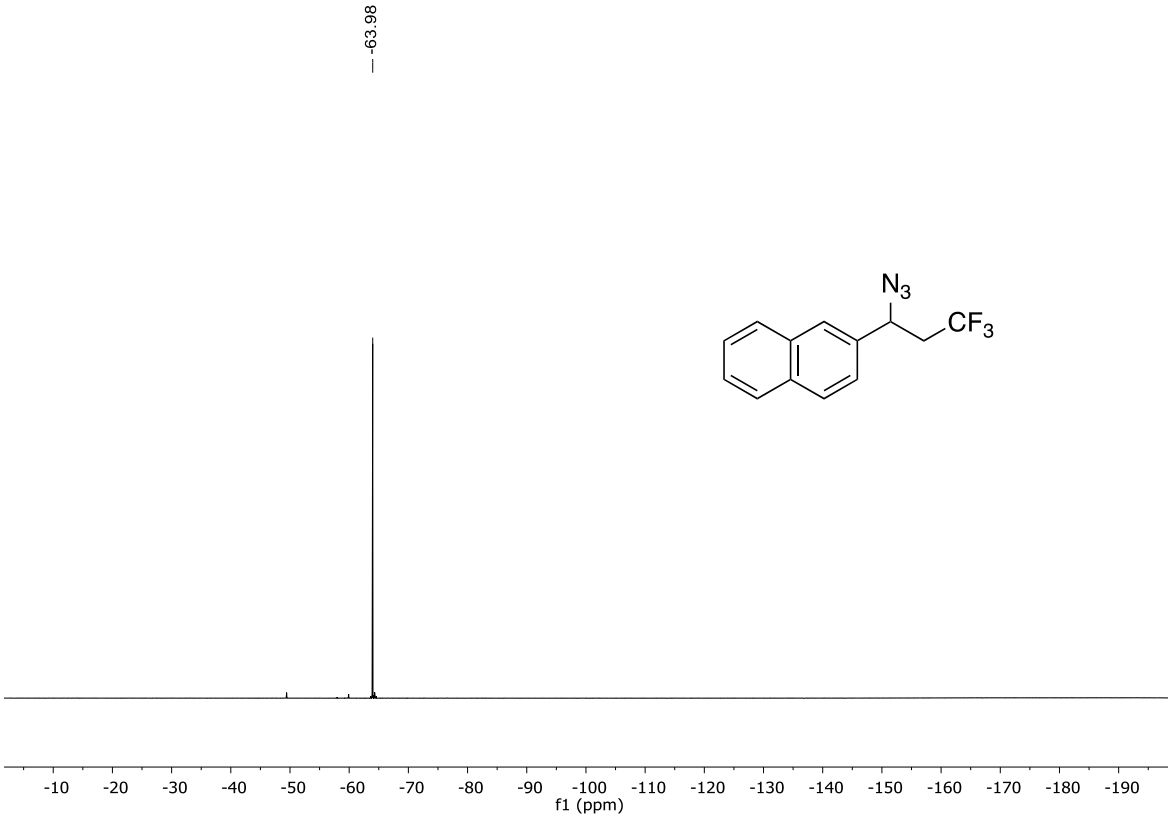
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **5a.**



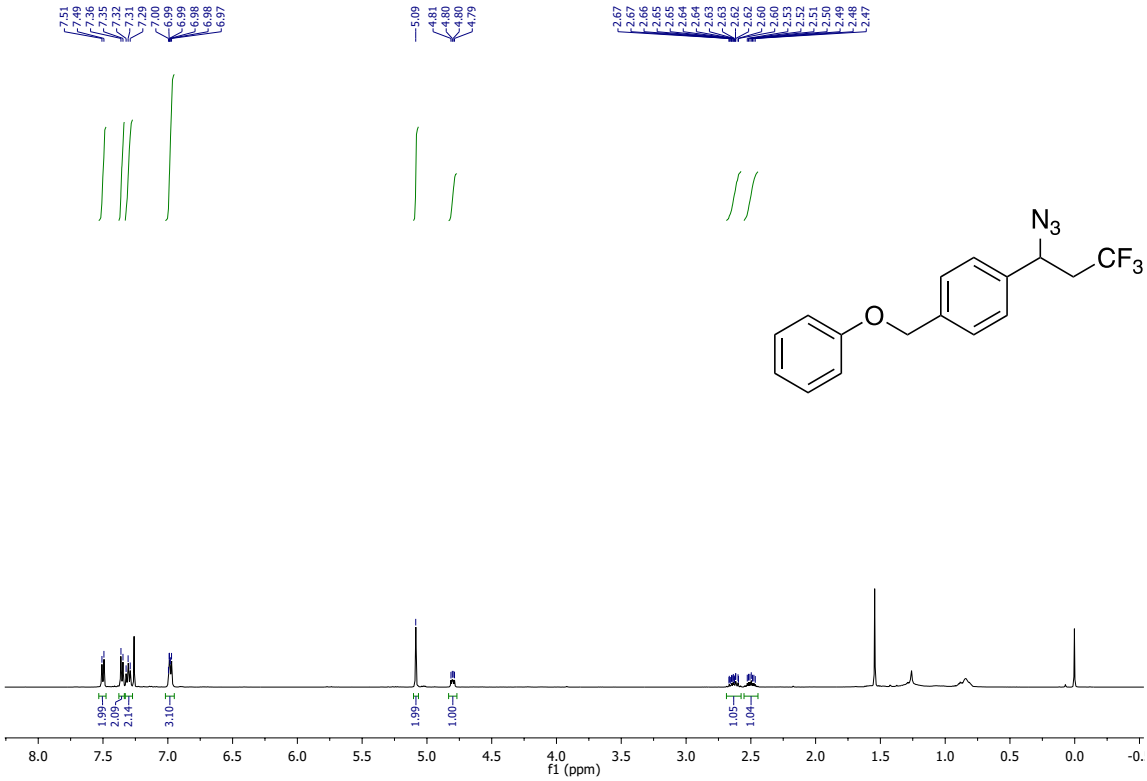
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5b**.



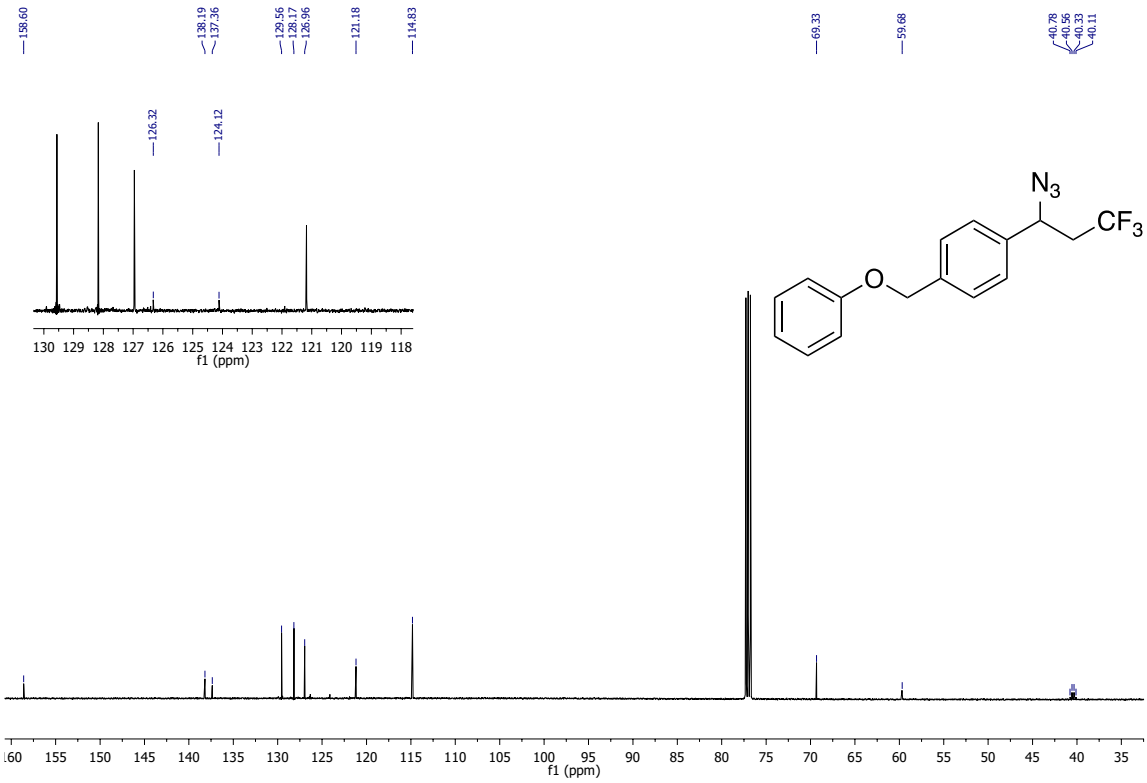
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **5b.**



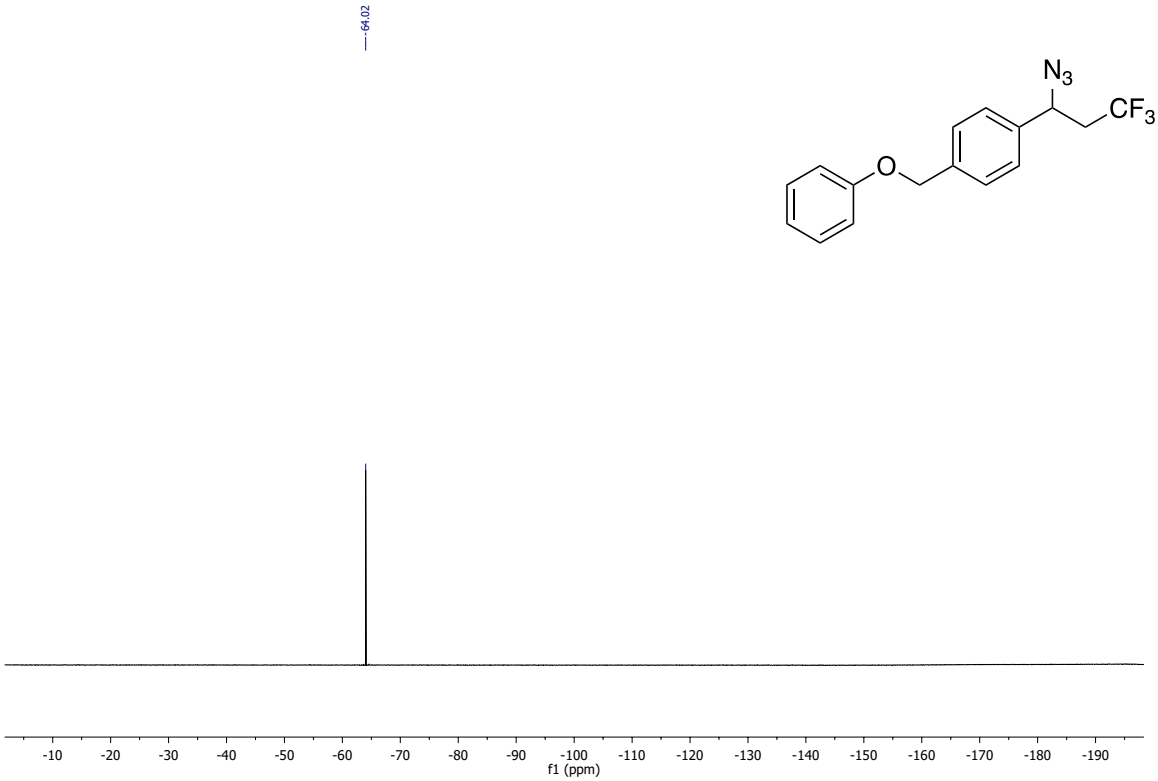
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **5b.**



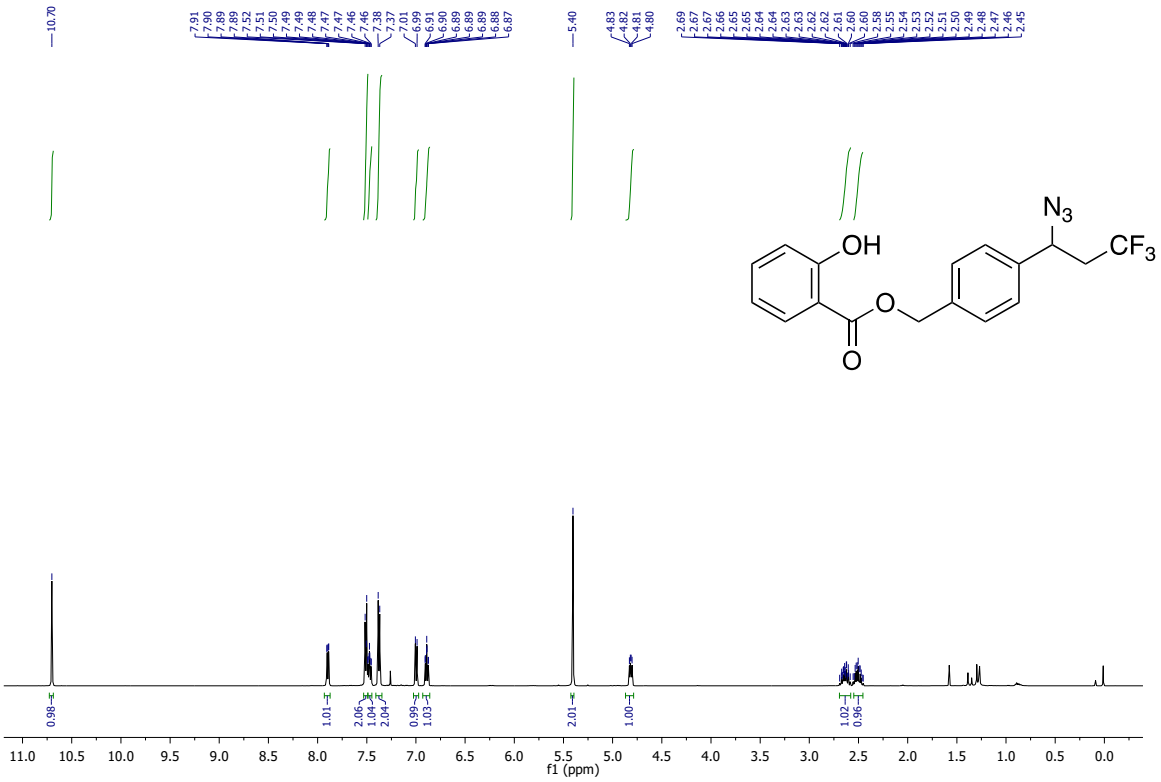
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5c**.



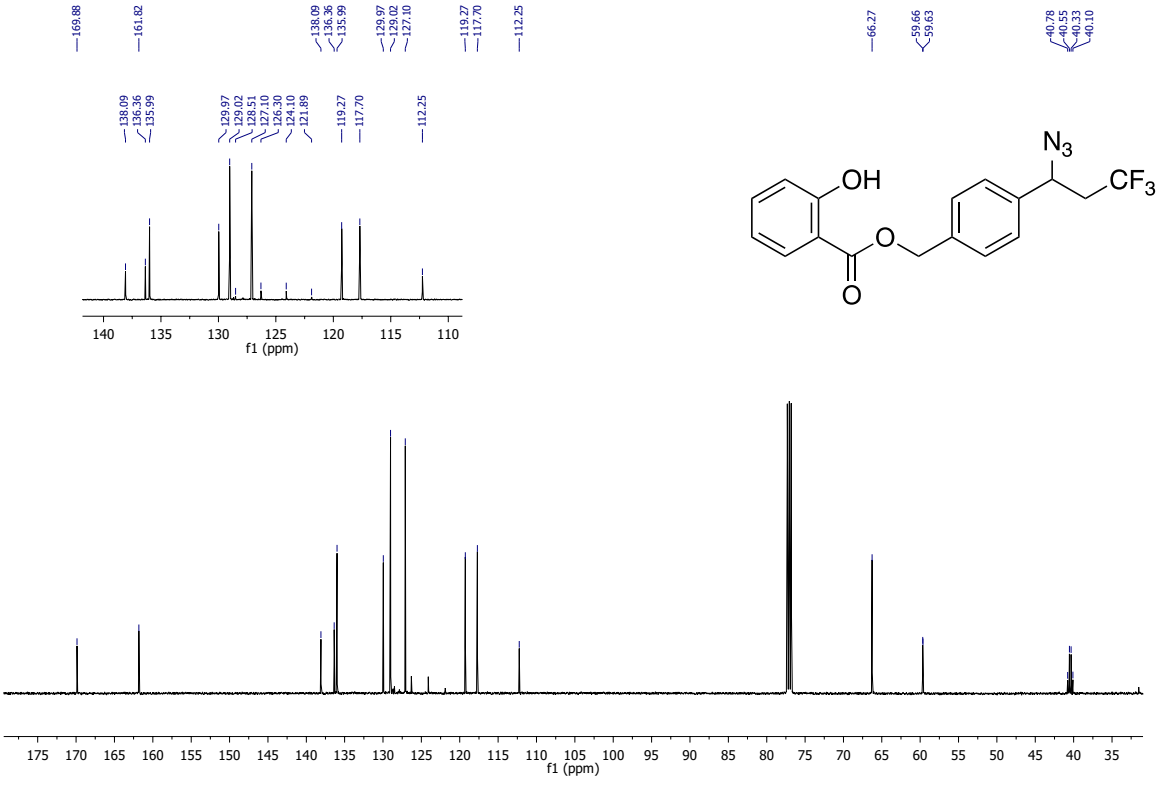
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **5c.**



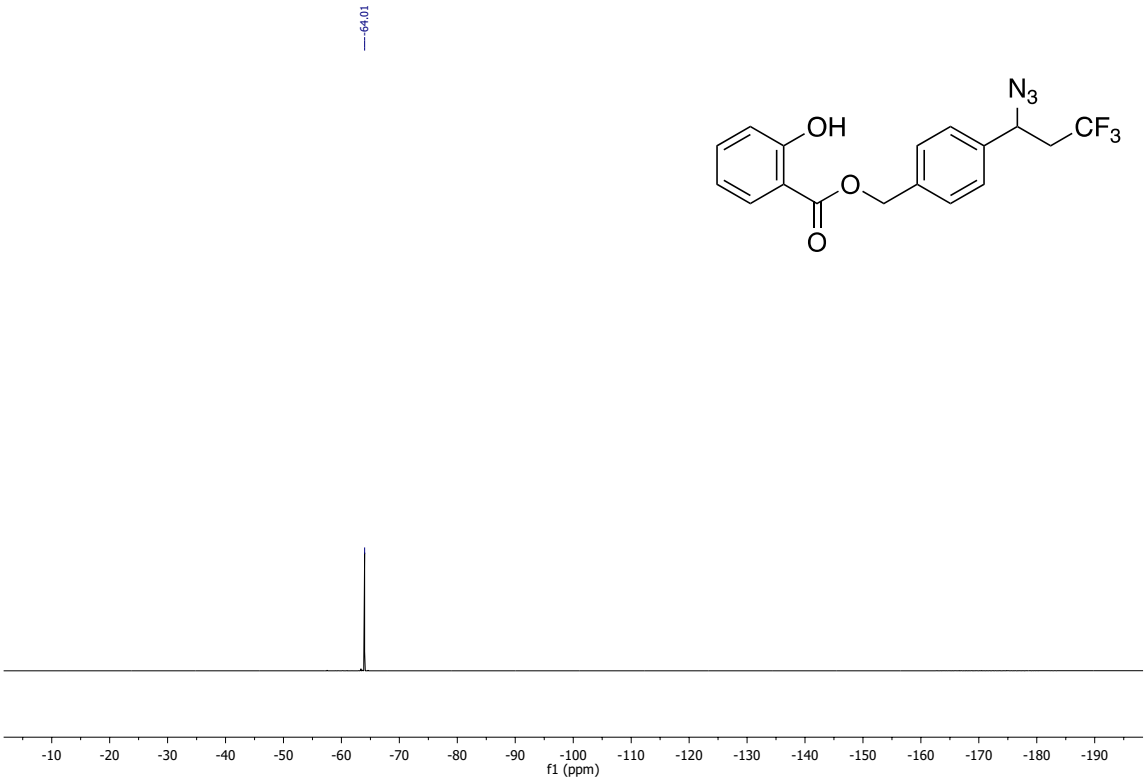
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **5c.**



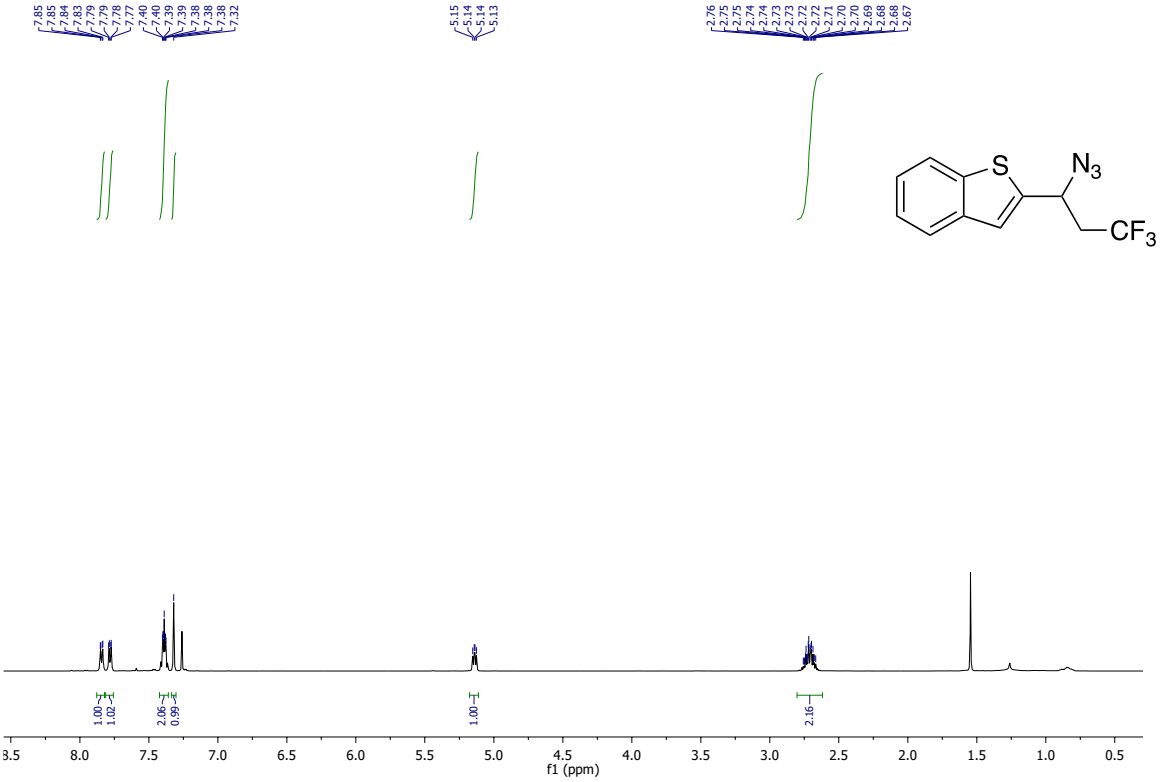
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5d**.



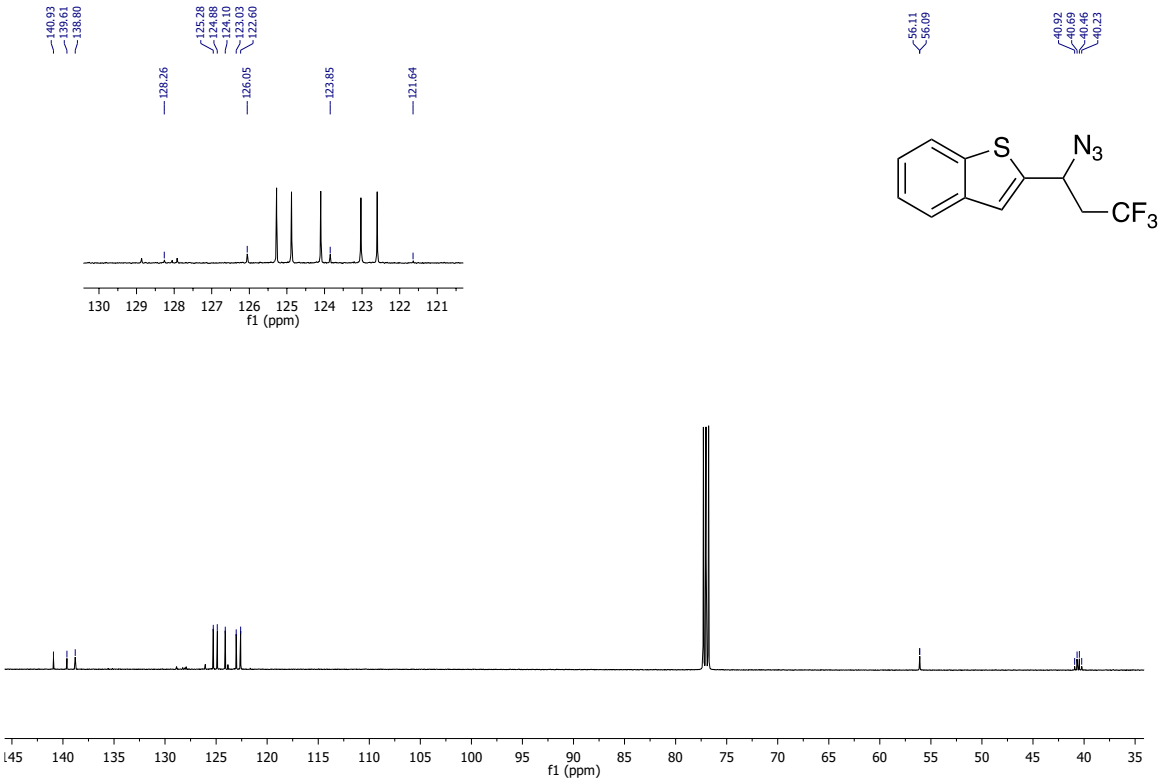
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **5d.**



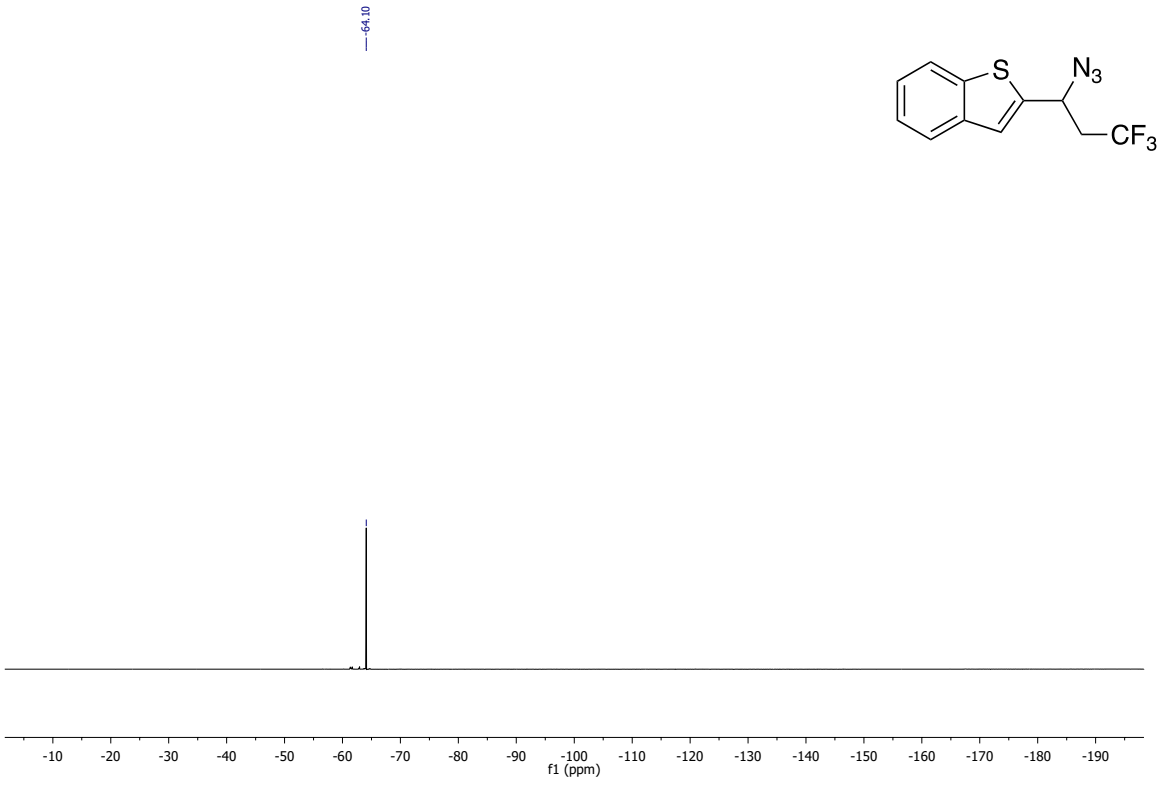
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **5d.**



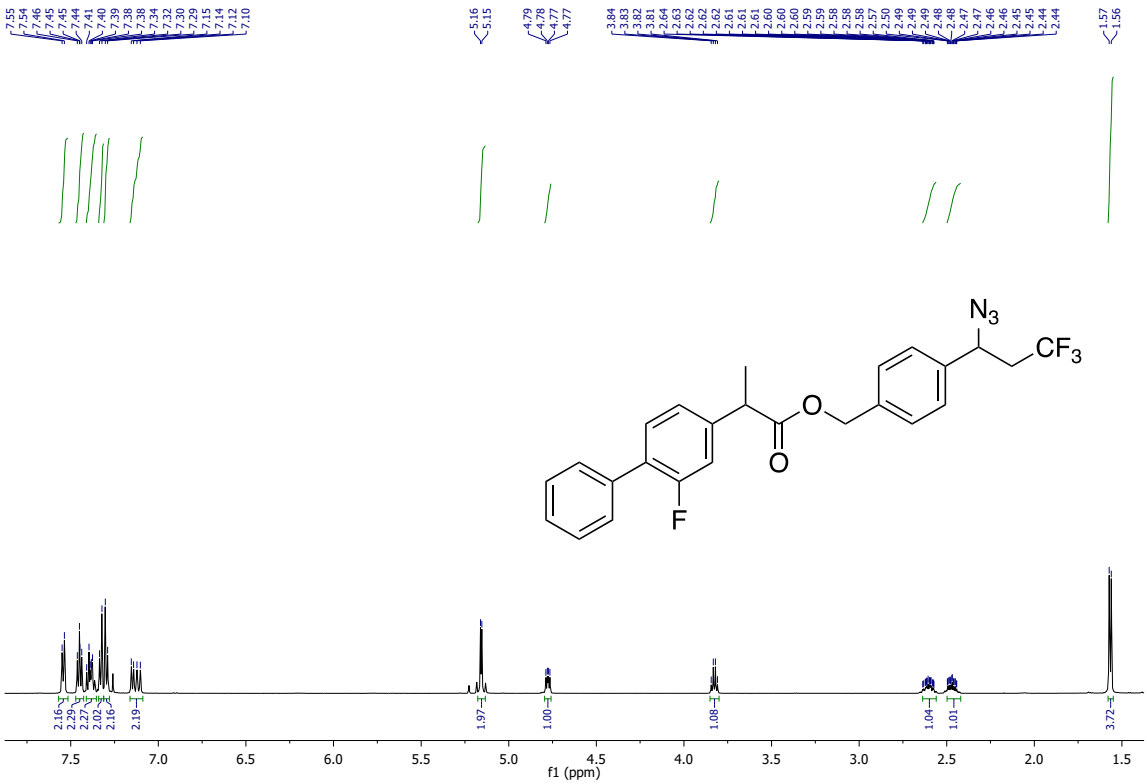
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5e**.



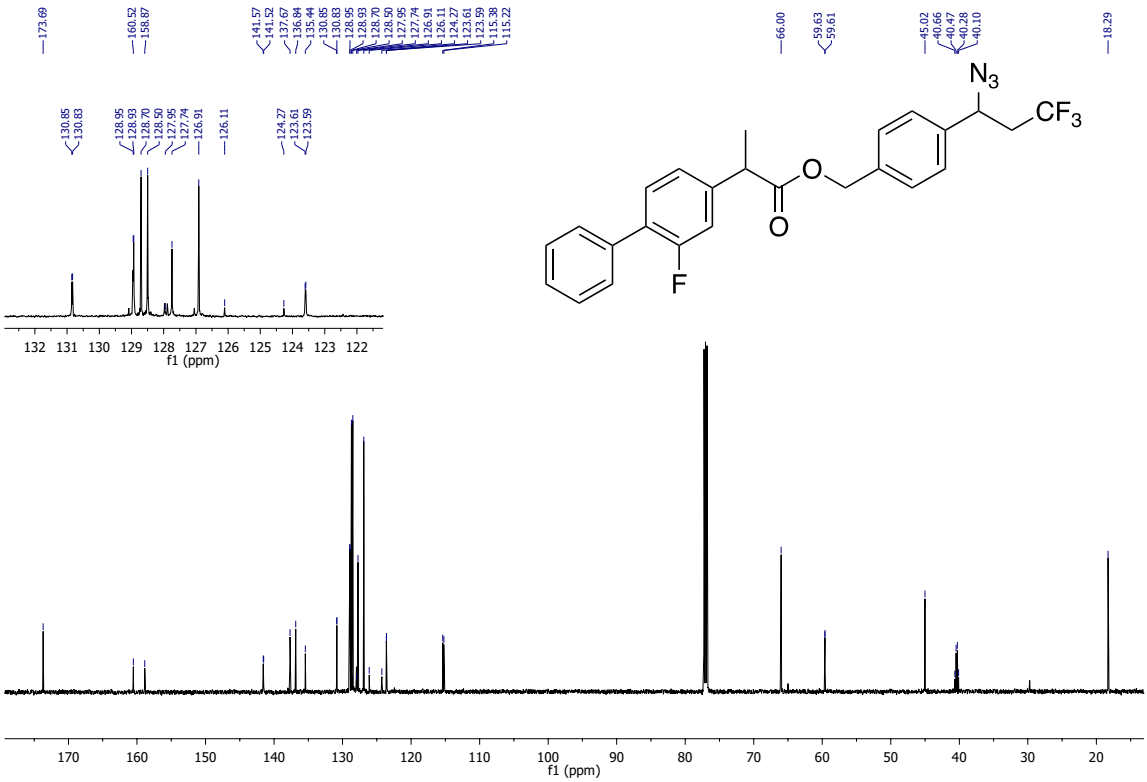
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **5e.**



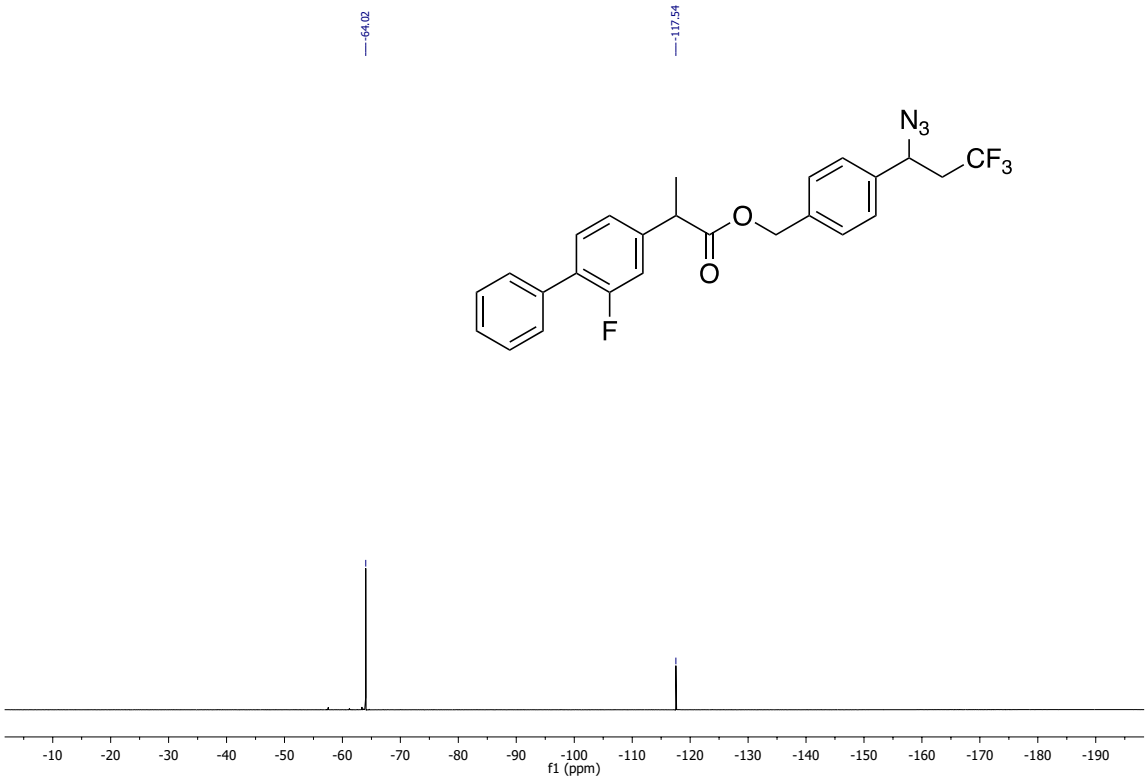
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **5e.**



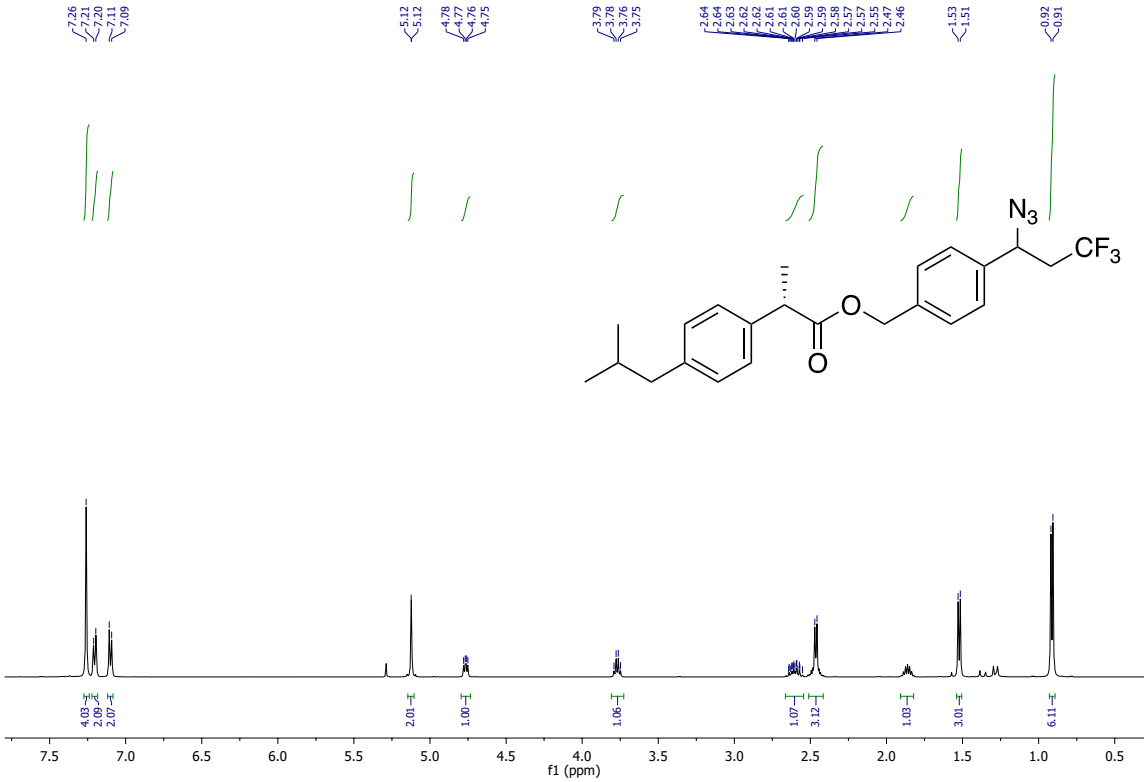
^{1}H NMR (600 MHz, $CDCl_3$) of compound **5f**.



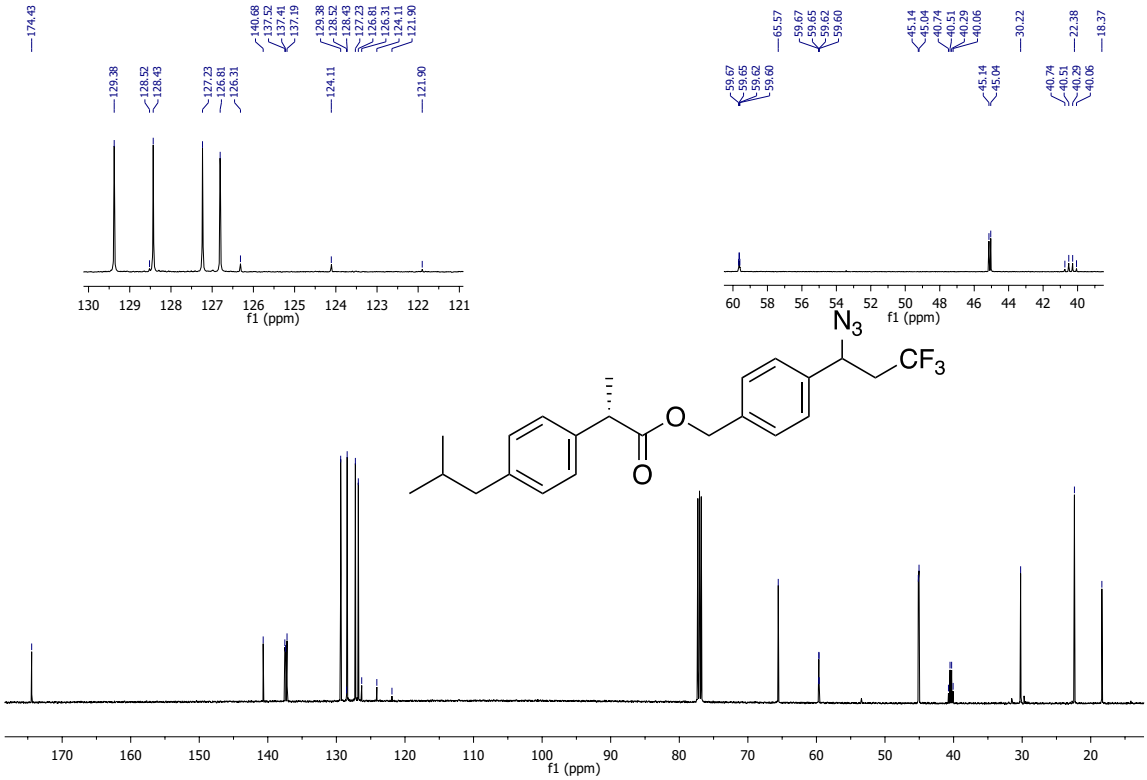
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of compound **5f**.



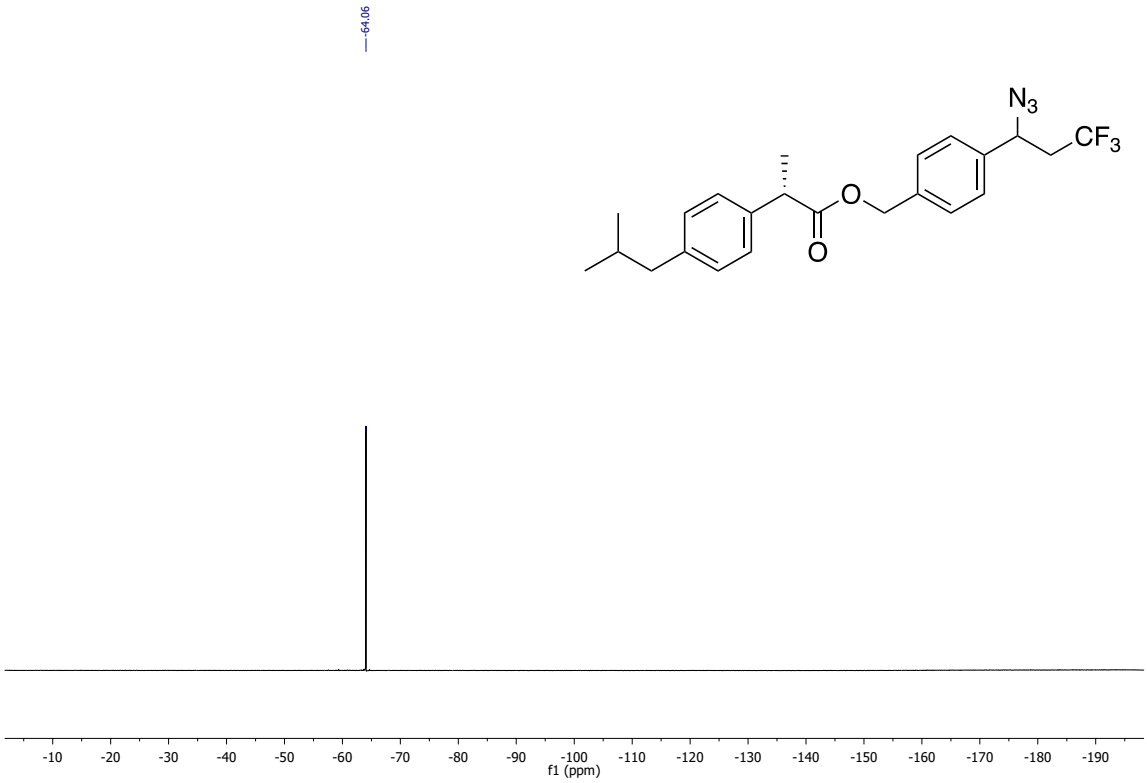
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **5f.**



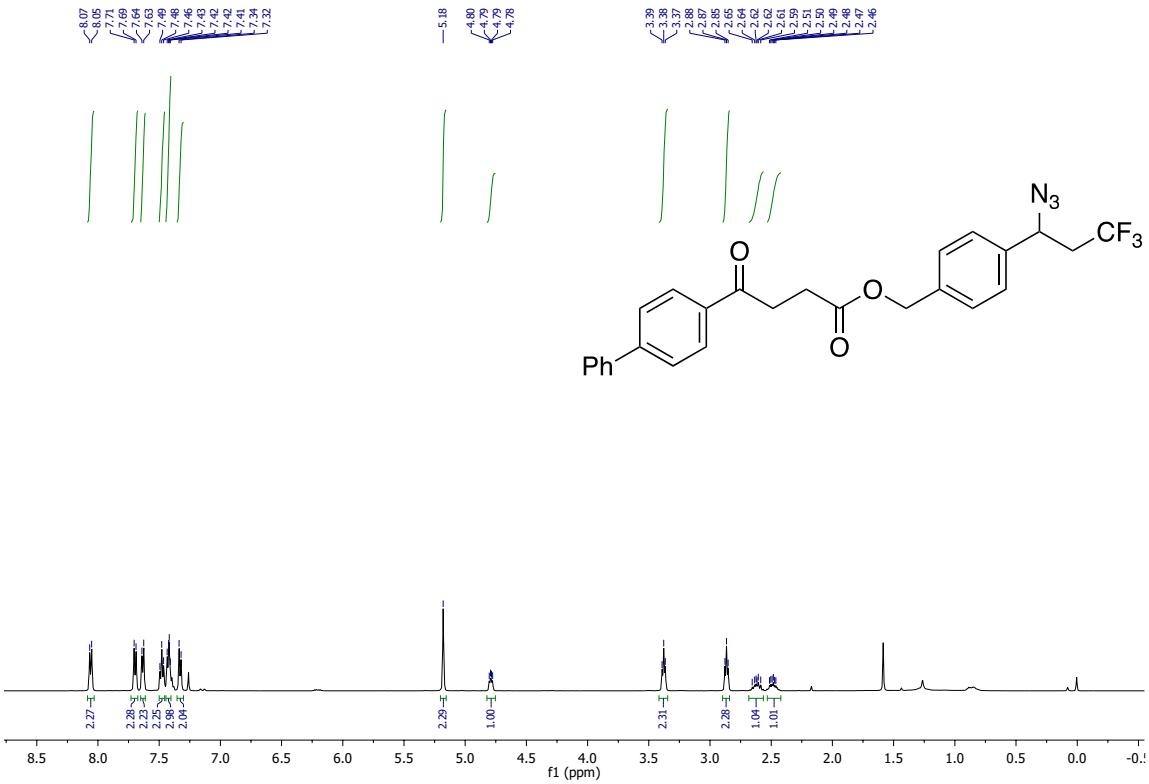
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5g**.



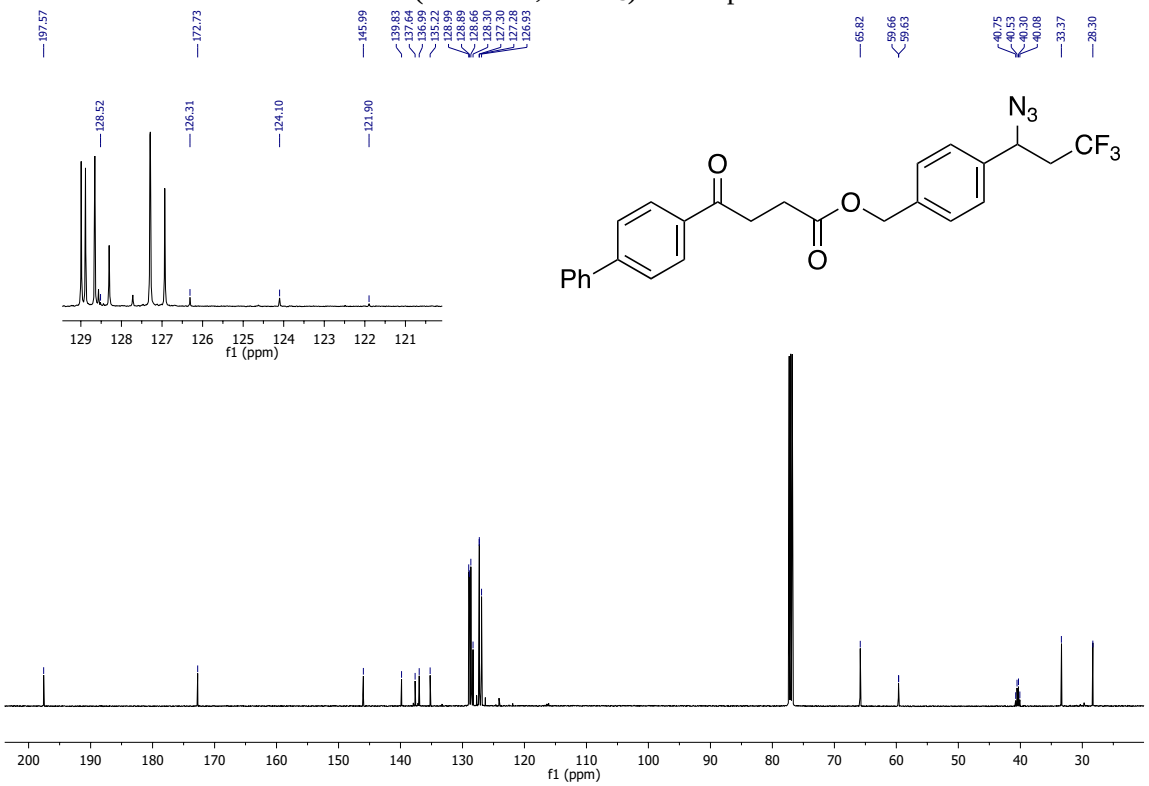
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **5g.**



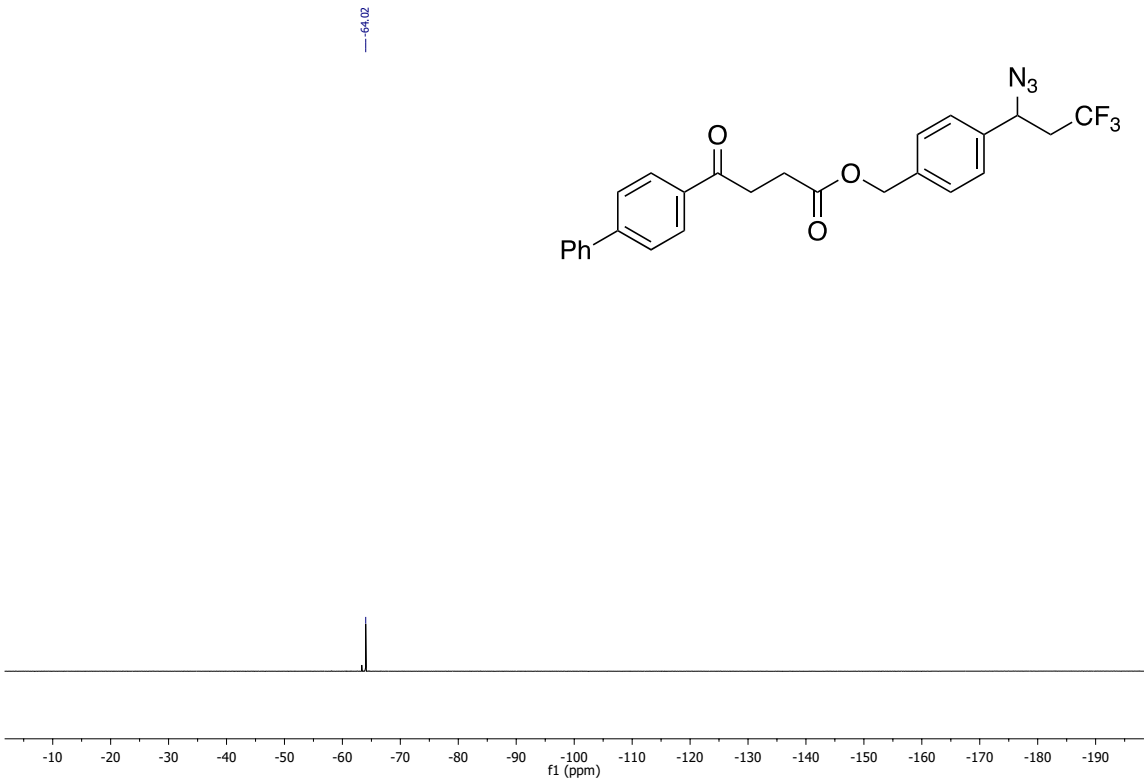
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **5g.**



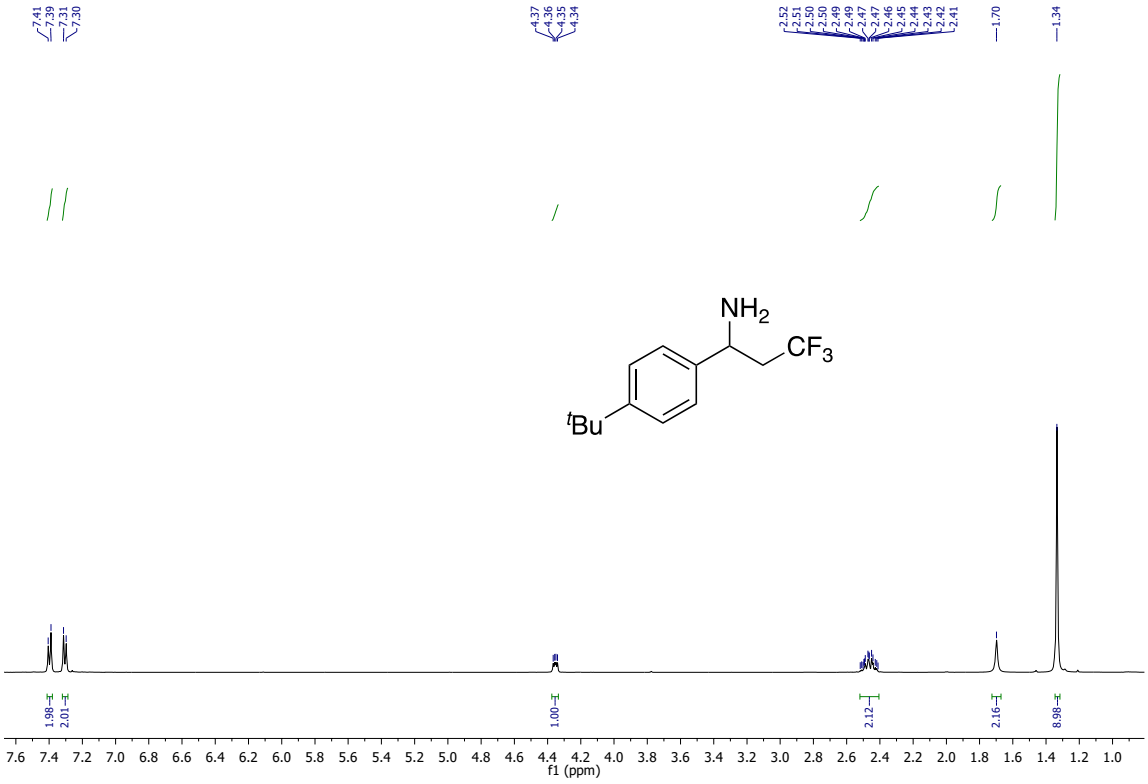
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5h**.



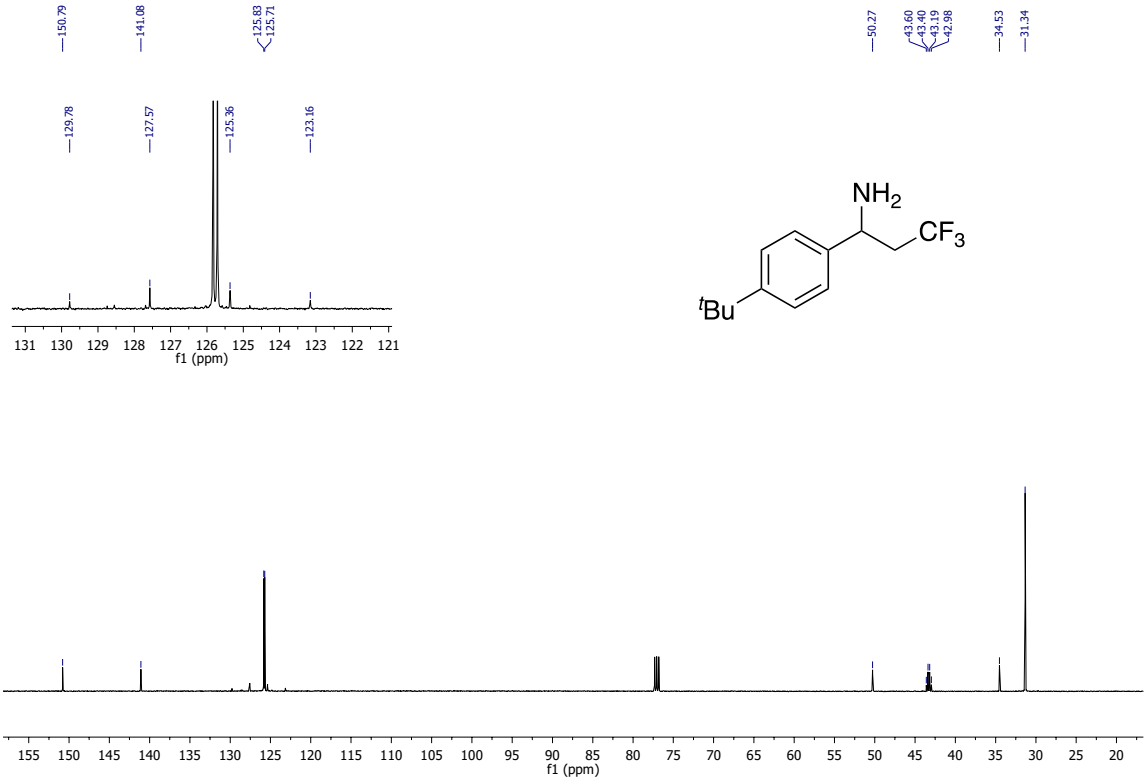
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **5h**.



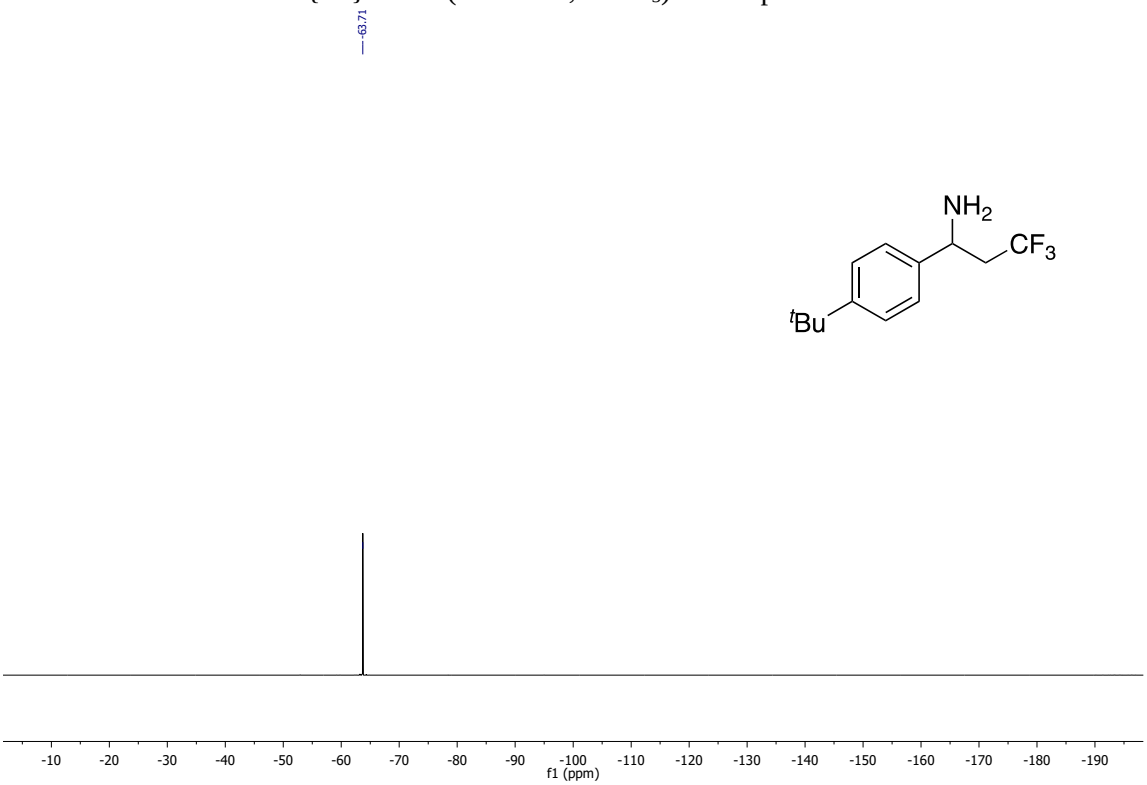
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **5h.**



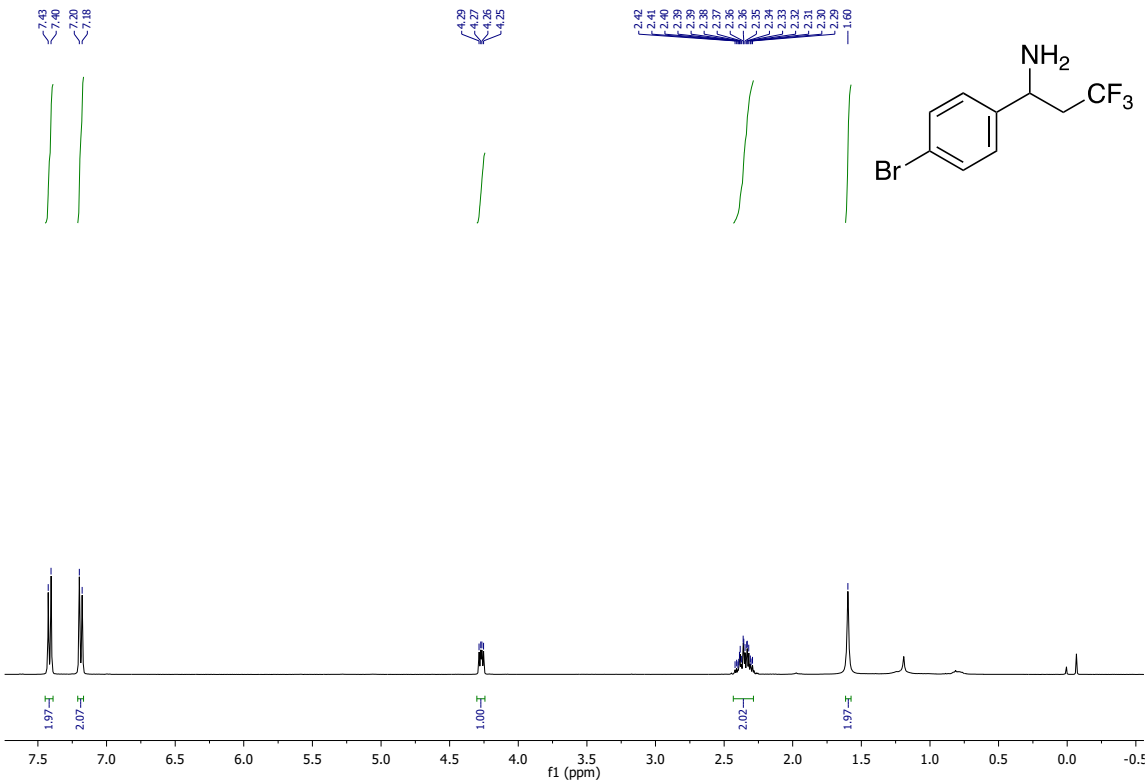
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6a**.



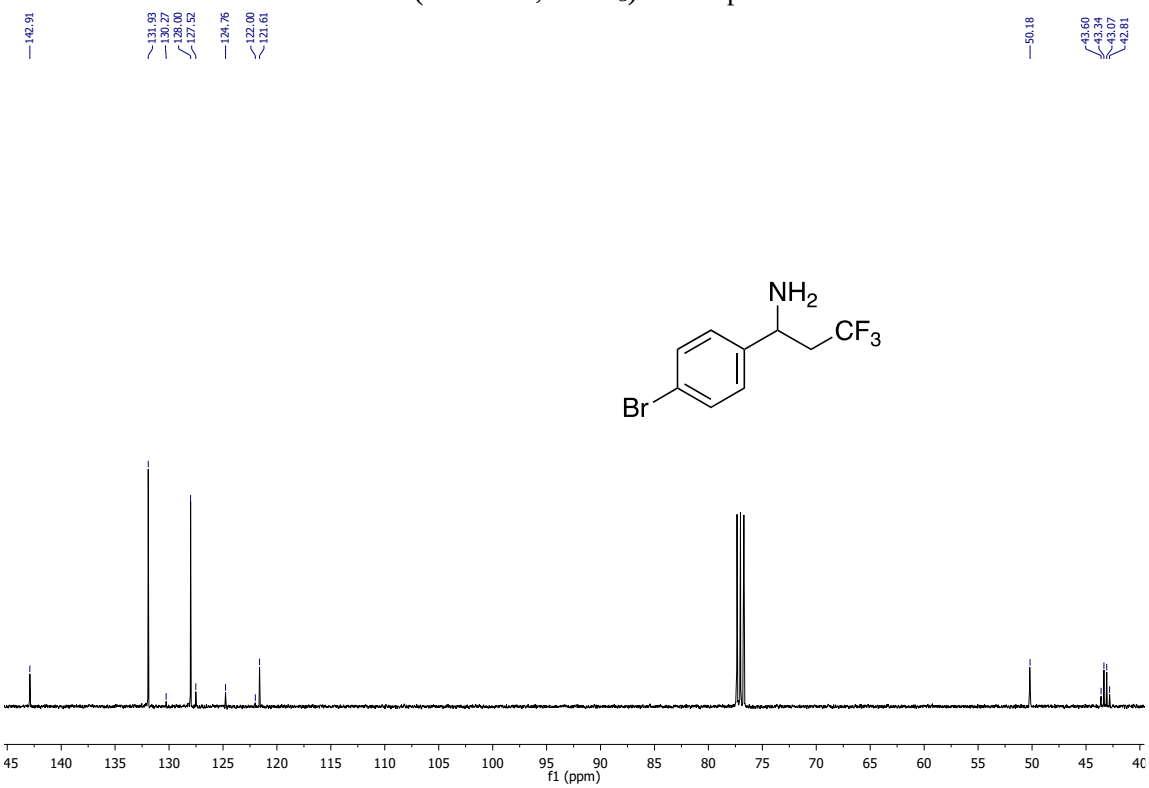
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **6a**.



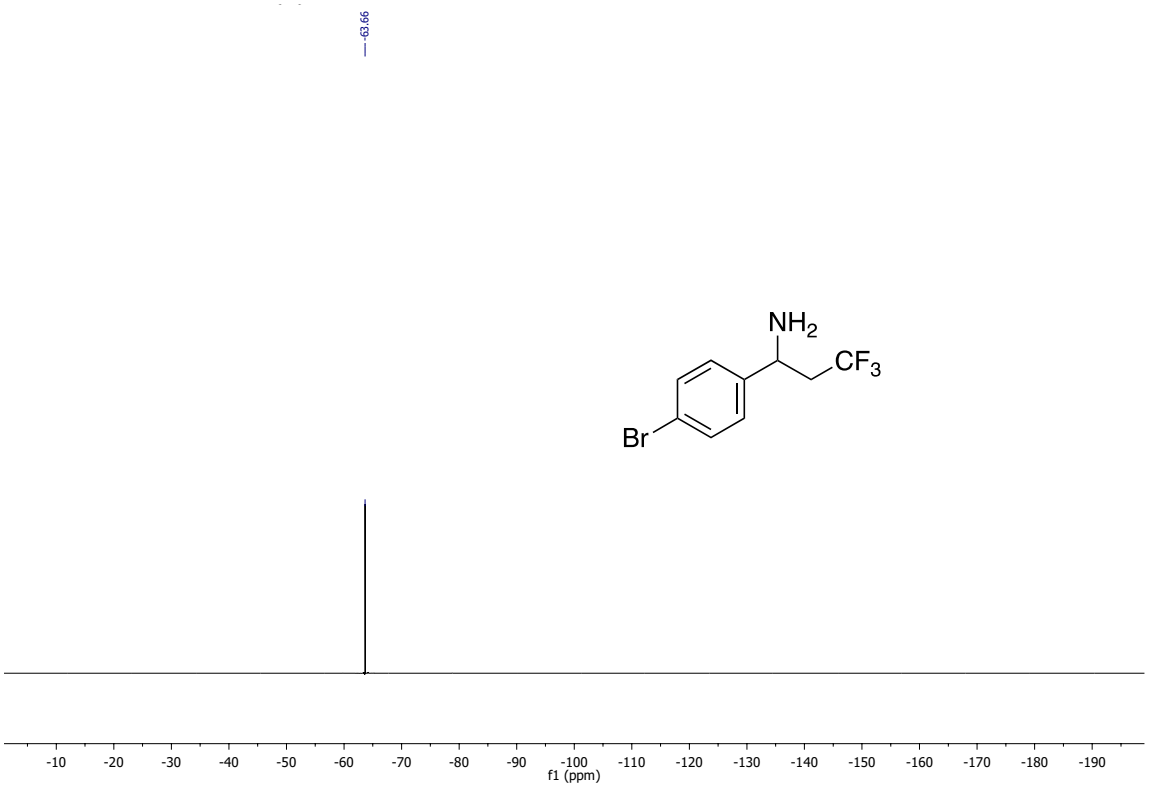
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **6a.**



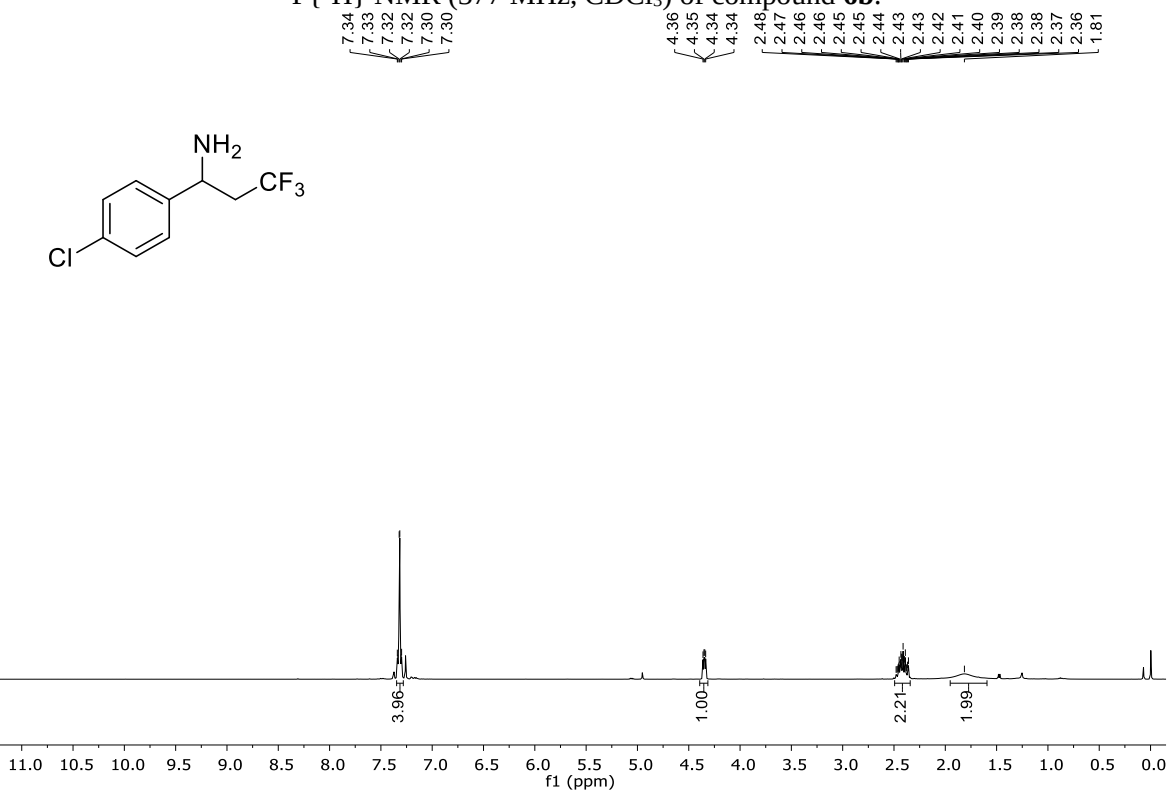
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6b**.



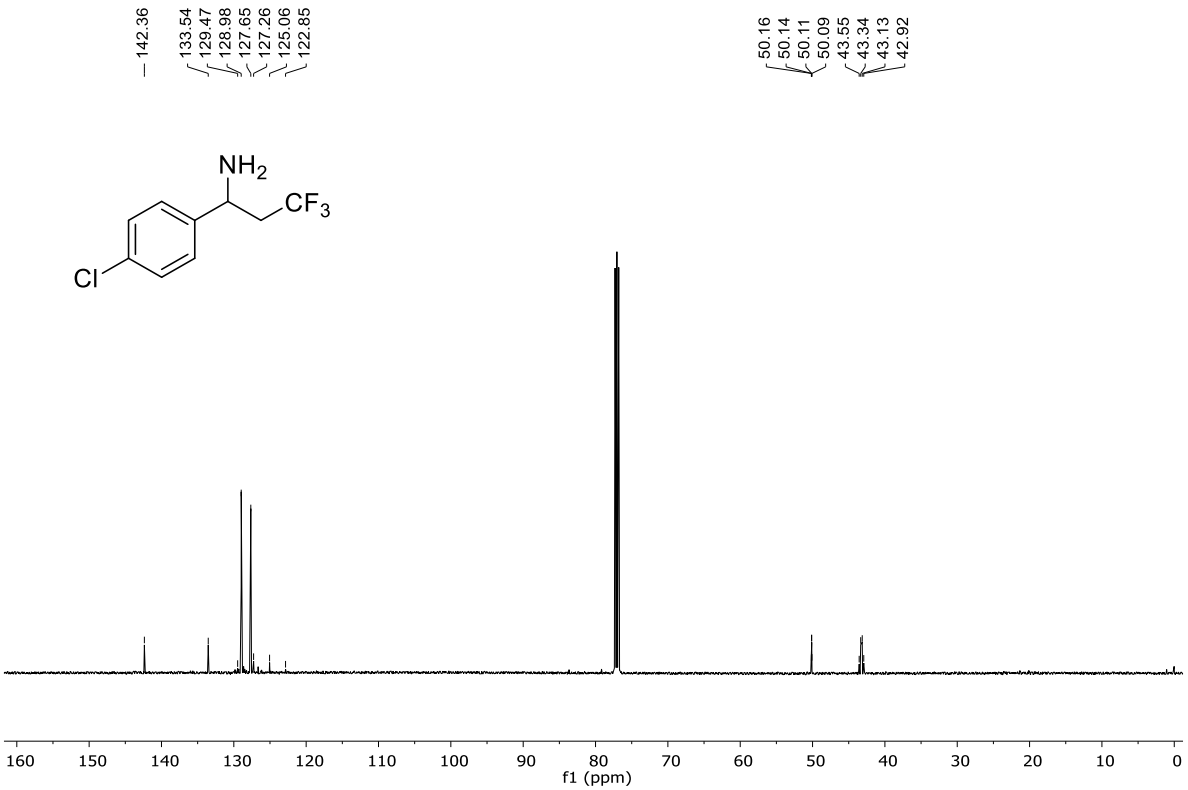
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **6b**.



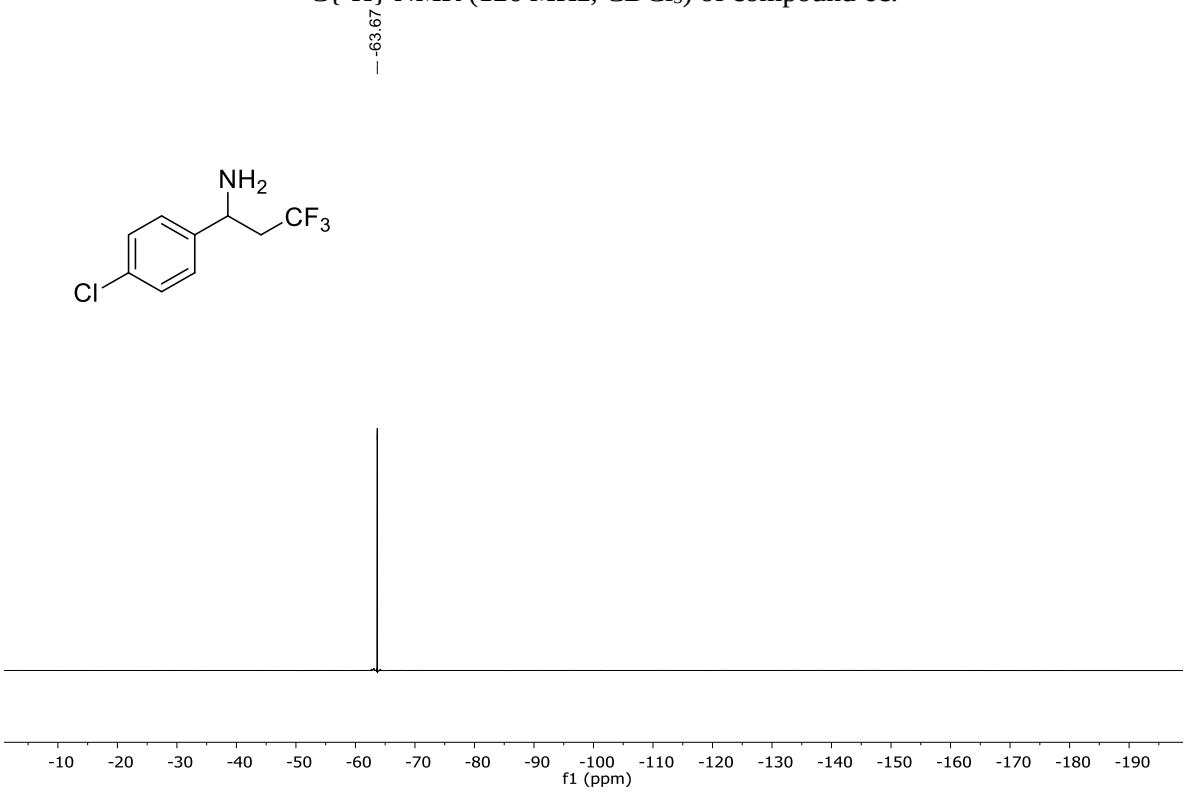
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) of compound **6b**.



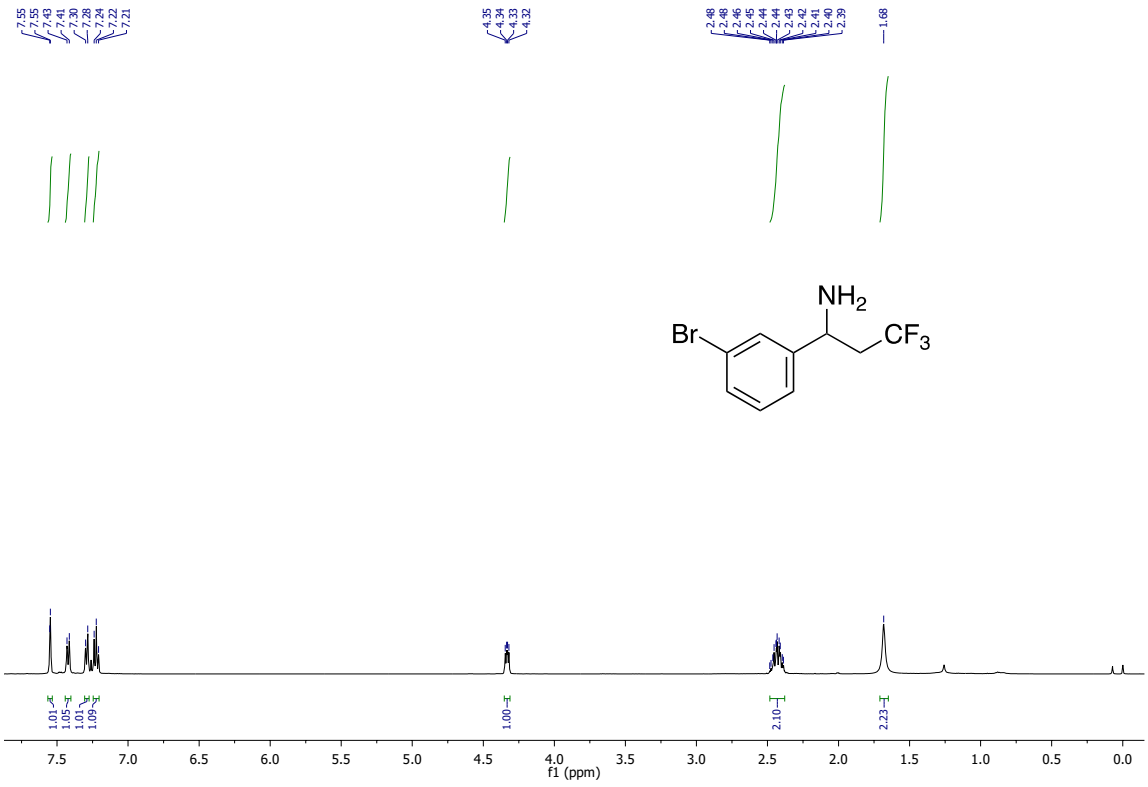
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6c**.



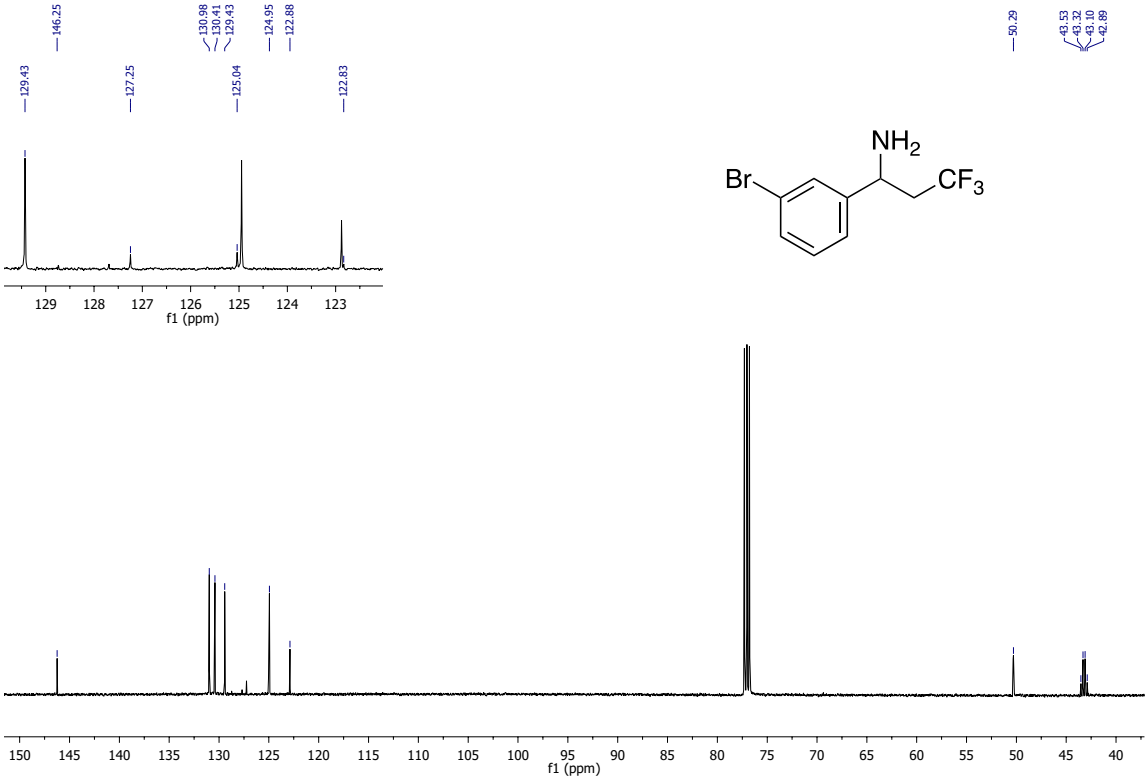
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **6c**.



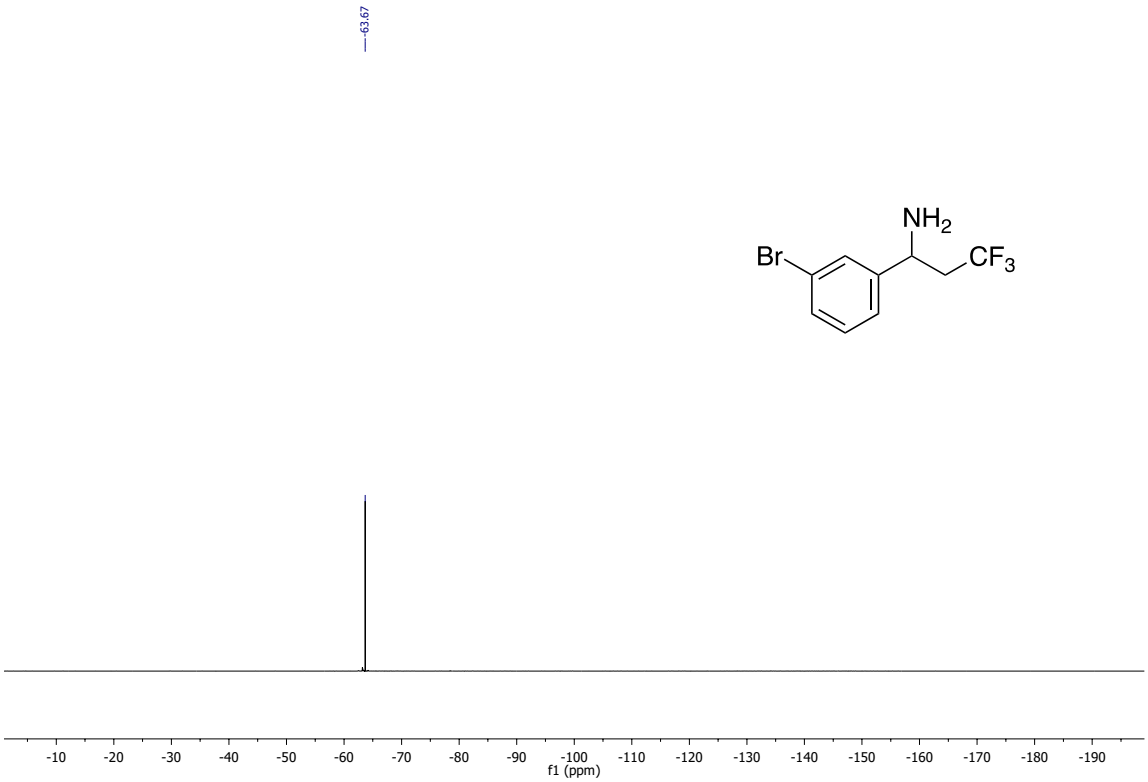
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) of compound **6c**.



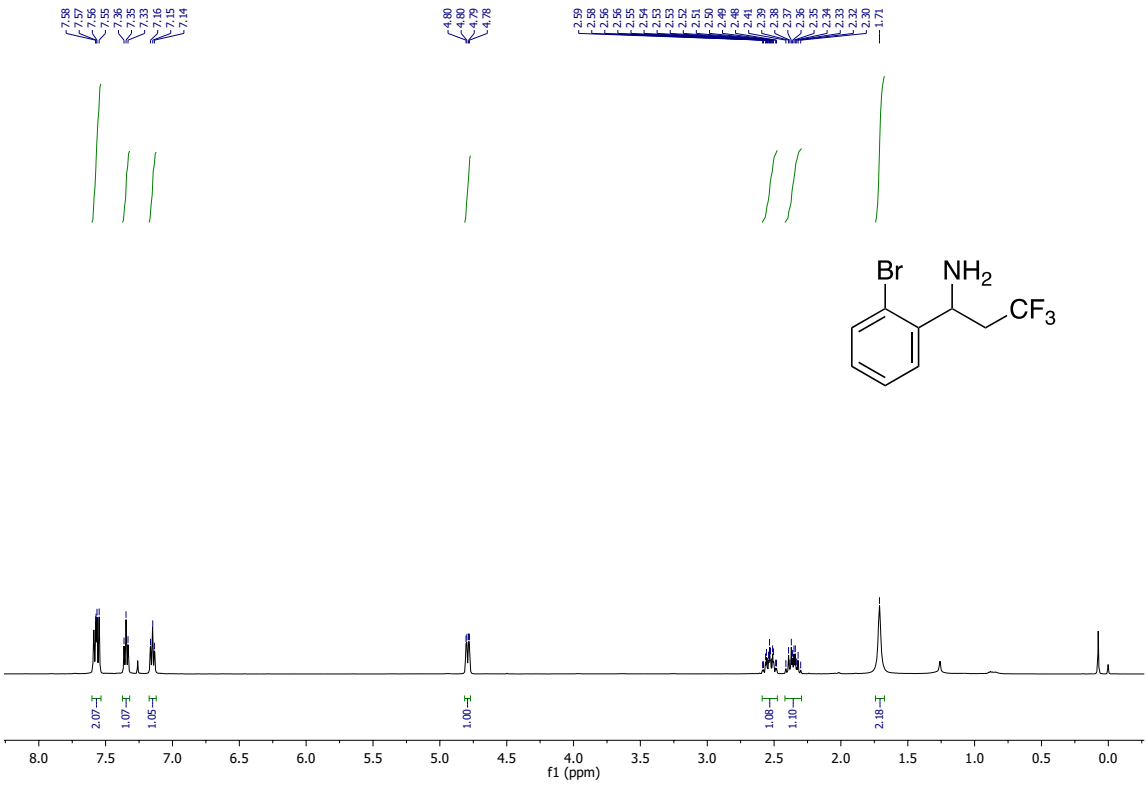
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6d**.



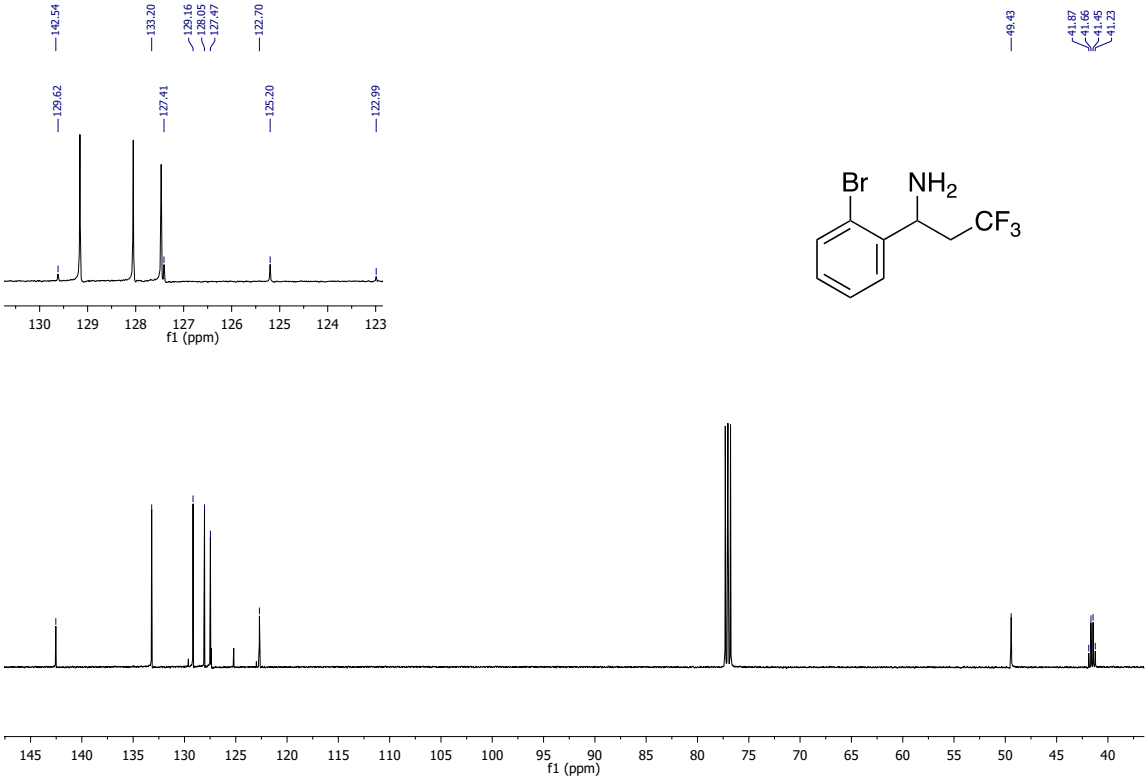
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **6d**.



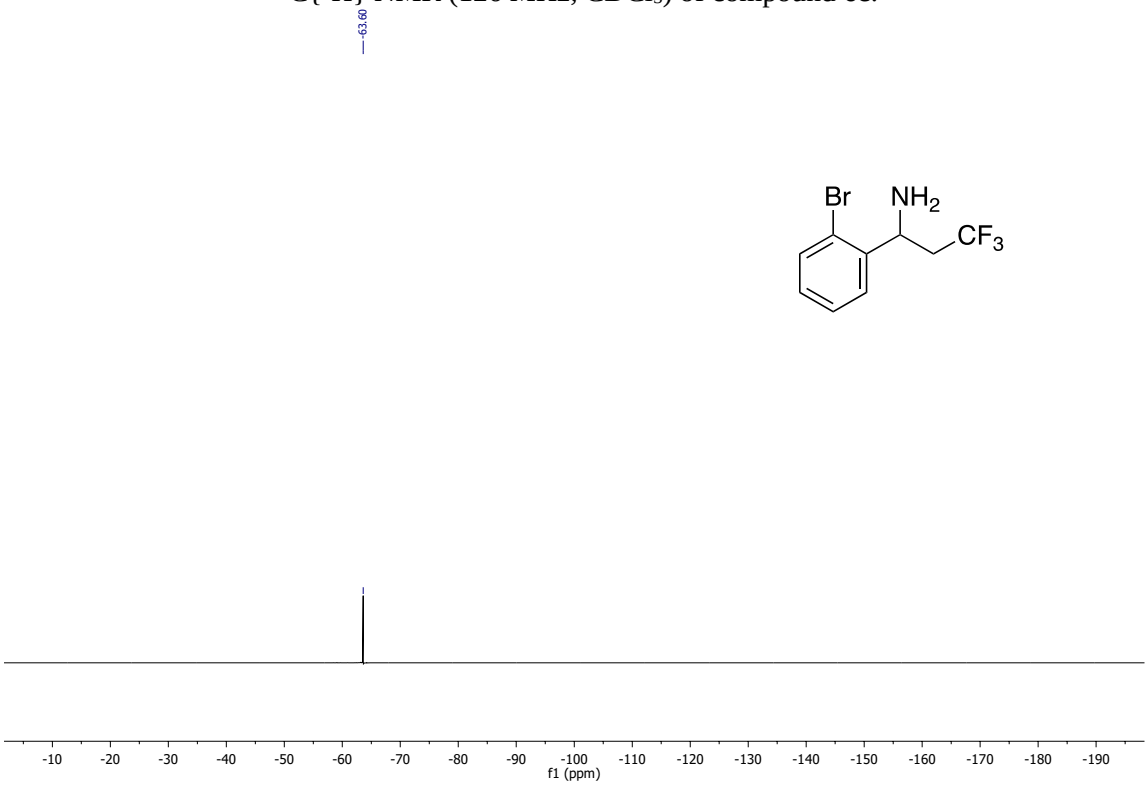
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) of compound **6d.**



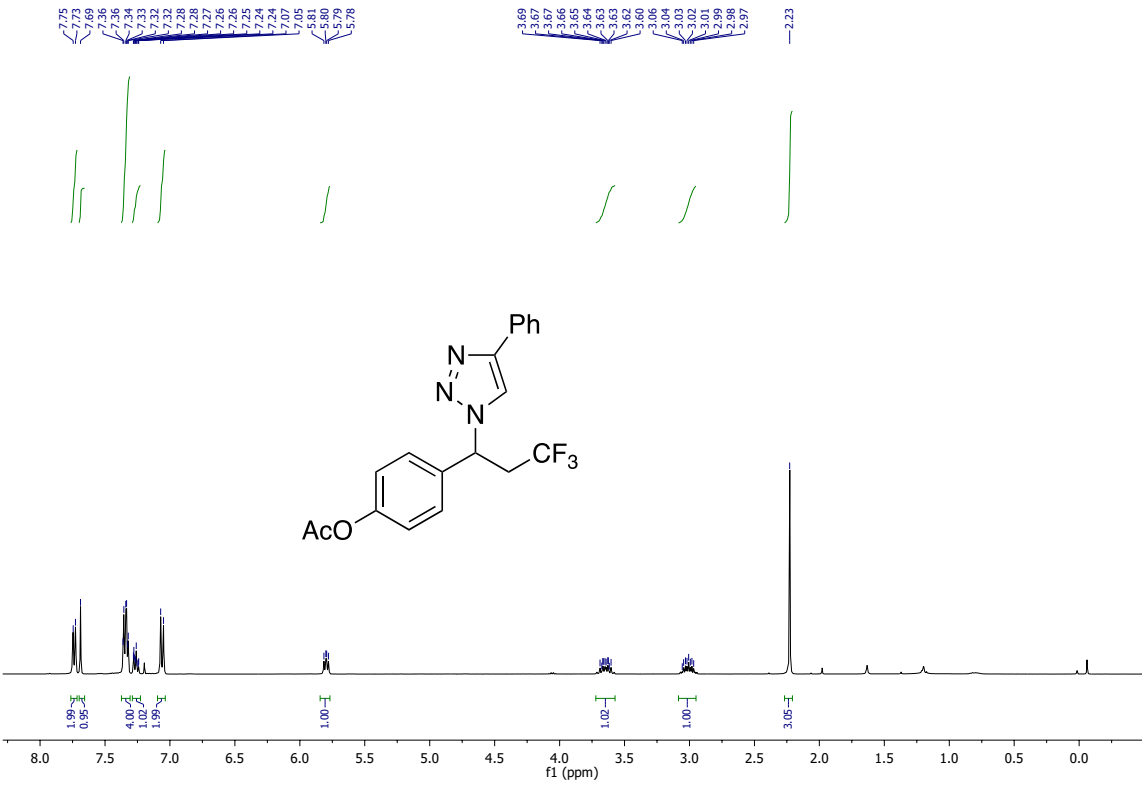
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6e**.



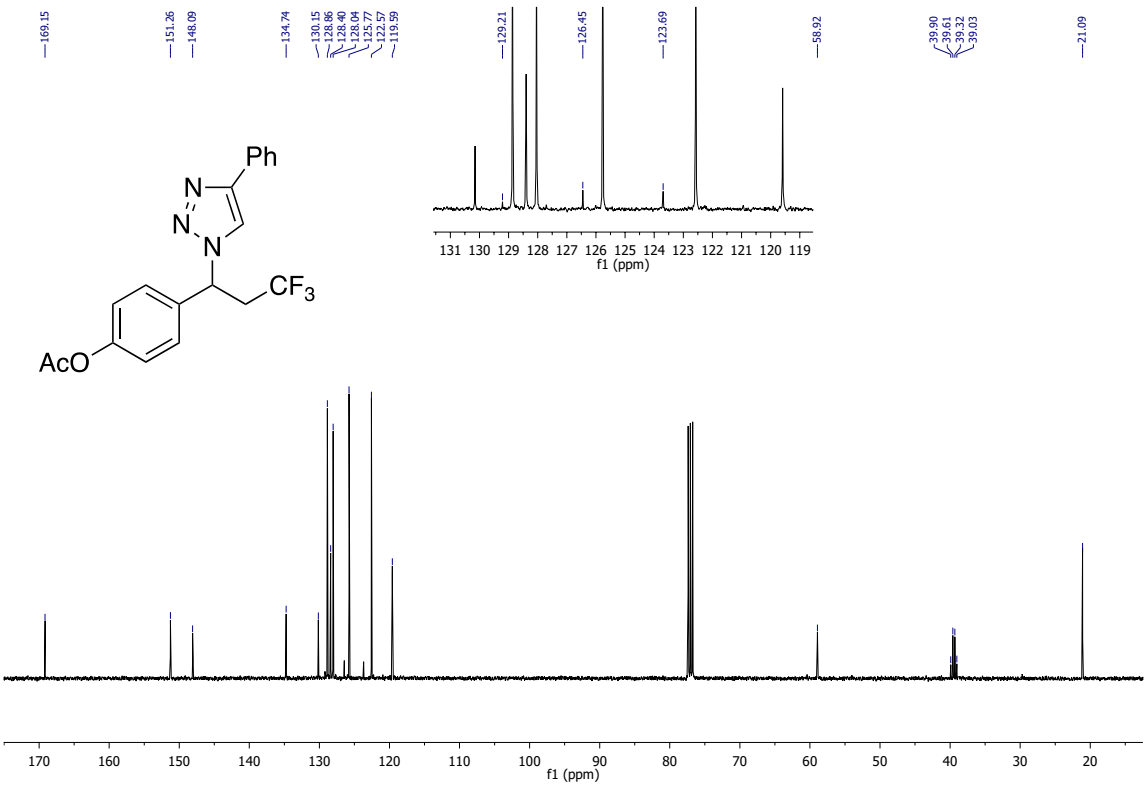
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **6e**.



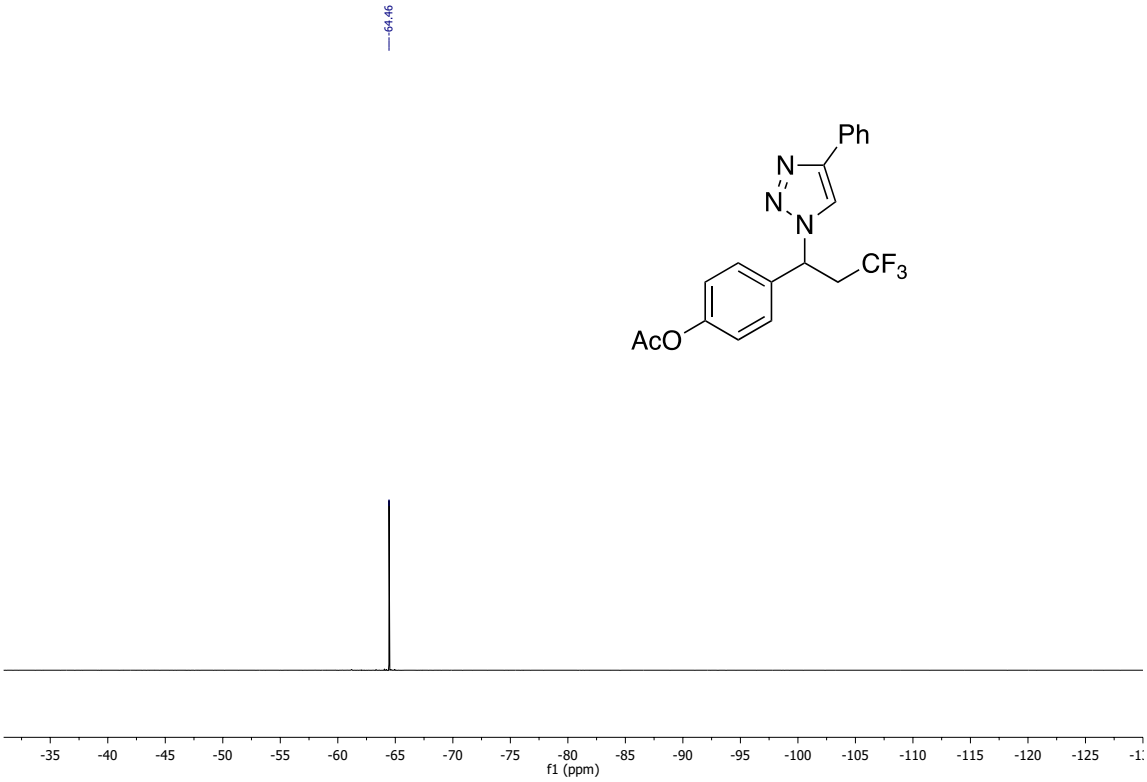
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **6e.**



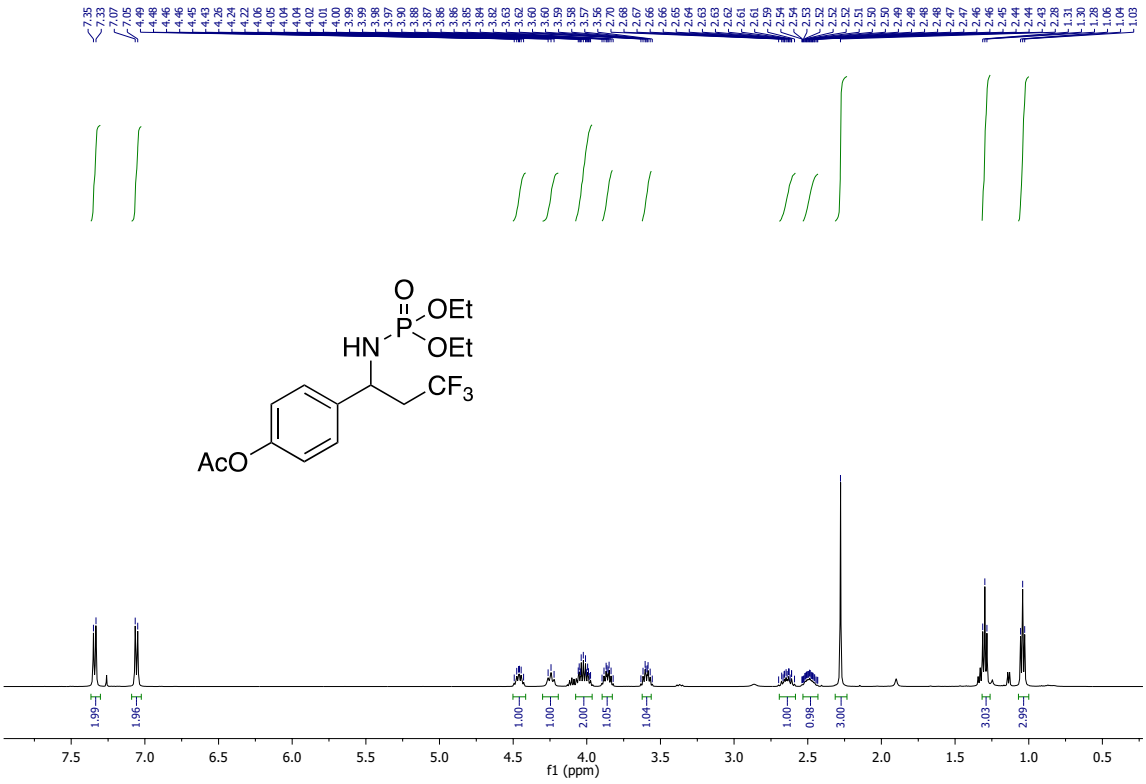
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7**.



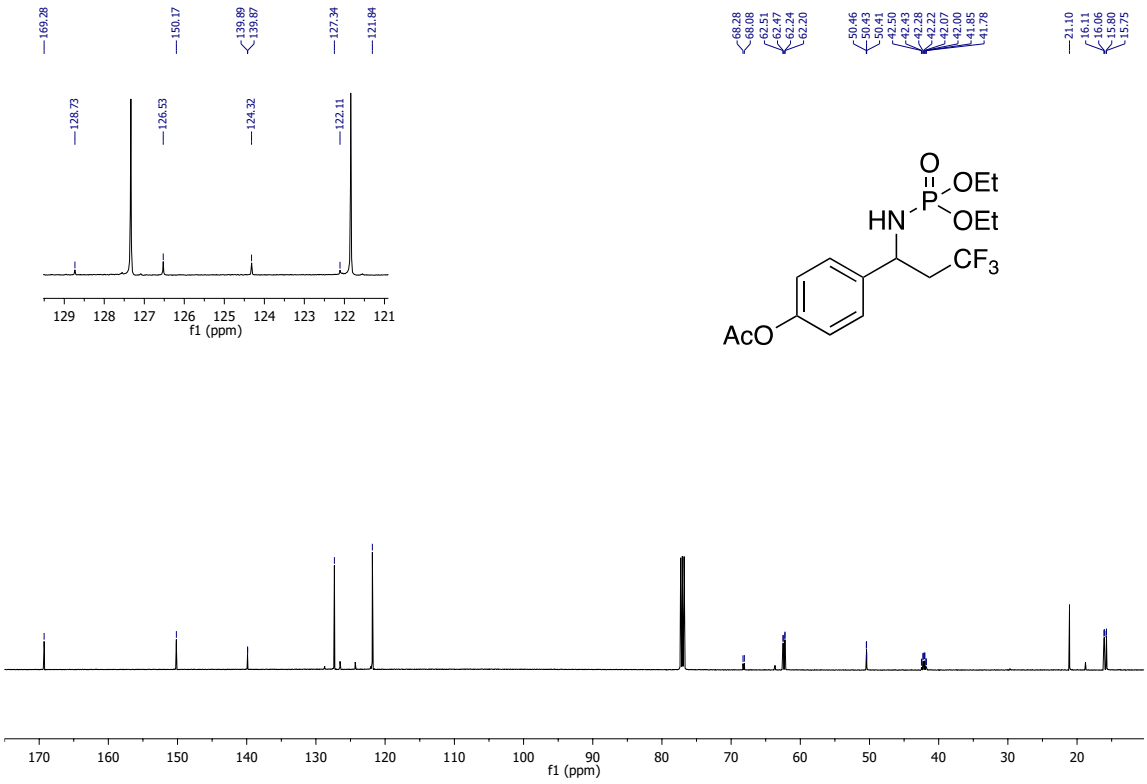
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of compound **7**.



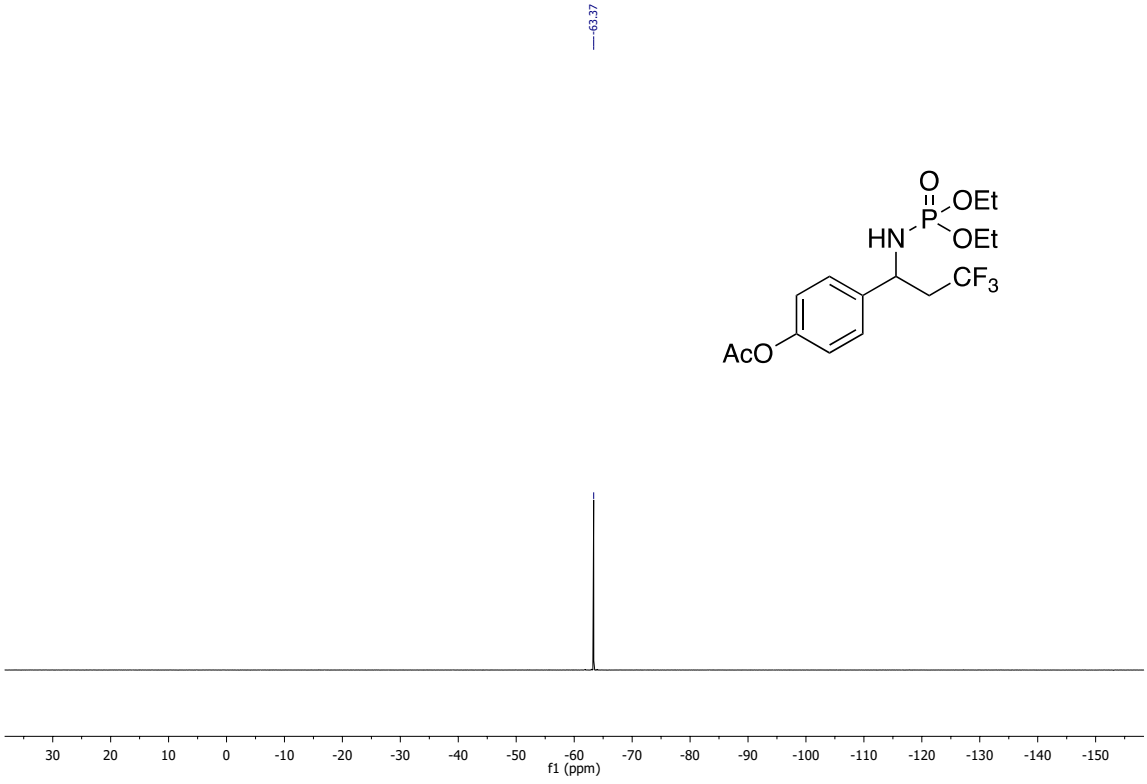
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) of compound **7**.



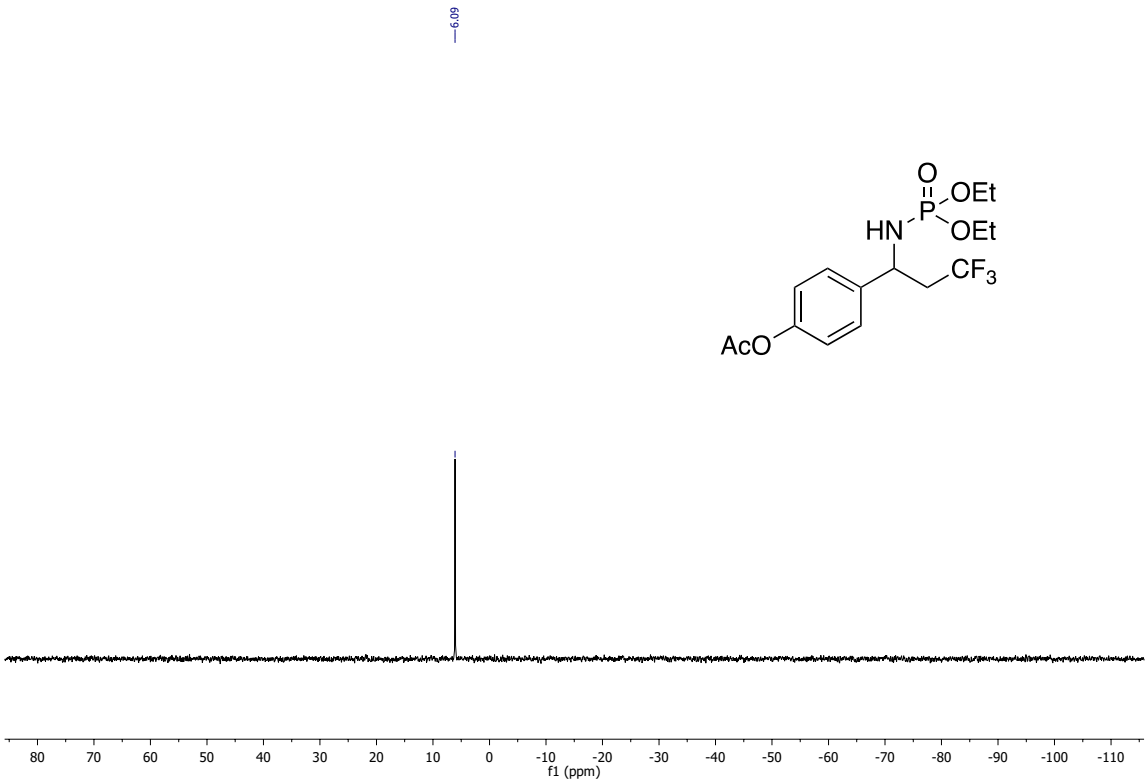
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**.



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of compound **8**.



$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of compound **8**.



^{31}P NMR (162 MHz, $CDCl_3$) of compound **8**.