Supporting Information

From Styrenes to Fluorinated Benzyl Bromides: A Photoinduced Difunctionalization via Atom Transfer Radical Addition

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1. General Considerations

1.1 General: For irradiation, blue LED strips (light-emitting diode, λ_{max} = 456 nm, purchased on superbrightleds.com – 2V LED Tape Light with LC2 Connector – 375 Lumens/ft) were placed 1.5 inches away from the reaction vials using the setup described in our previous publication.[1] NMR spectra (^{1}H, ^{11}B, ^{13}C, ^{19}F {^{1}H decoupled}) were obtained at 298 K using 400, 500, and 600 MHz spectrometers. Chemical shifts are referenced to residual, nondeuterated $CHCl_3$ (δ 7.26 in ^{1}H NMR and 77.3 in ^{13}C NMR). Reactions were monitored by GC/MS, ^{1}H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using phosphomolybdic acid, ninhydrin, *p*-anisaldehyde stain, and/or UV light. Flash chromatography was accomplished using an automated system (CombiFlash®, UV detector, λ = 254 nm and 280 nm) with RediSep® R_f silica gel disposable flash columns (60 Å porosity, 40–60 μm) or RediSep R_f Gold® silica gel disposable flash columns (60 Å porosity, 20–40 μm). Accurate mass measurement analyses were conducted using electron ionization (EI-TOF) or electrospray ionization (ESI-TOF). The signals were mass measured against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GCMS, and leucine enkephalin for ESI-LCMS. The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. The mass of the electron is not included. IR spectra were recorded on an FT-IR using either neat oil or solid products. Melting points (°C) are uncorrected. UV/vis studies were measured in a 1 cm quartz cuvette using a Genesys 150 UV/vis spectrophotometer from Thermo Scientific.

1.2 Chemicals: Deuterated NMR solvents were purchased and stored over 4Å molecular sieves. Dry MeCN and DMF were obtained from Acros Organics and used as received. THF and CH_2Cl_2 were purchased and dried *via* a solvent delivery system. Bulk solvents were purchased from Fisher Scientific. Styrenes and brominated radical precursors **2a** and **2b** were purchased from commercial suppliers and used as received. Compound **2c** was prepared using reported literature.[2] Photoredox-catalyzed reactions were performed using 8 mL Chemglass vials (2-dram, 17 x 60 mm, 15-425 Green Open Top Cap, TFE Septa).

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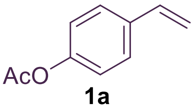
[1] Remeur, C.; Kelly, C. B.; Patel, N. R.; Molander, G. A. *ACS Catal.* **2017**, 7, 6065–6069.

[2] Engel-Andreasen, J.; Wellhöfer, I.; Wich, K.; Olsen, C. A. *J. Org. Chem.* **2017**, *82*, 11613–11619.

2. List of Styrenes

List of styrenes used in this study. Preparation of styrenes **1p-1u, 1w-z, 1ab** is described in **Section 3**.



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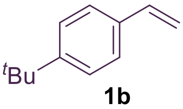

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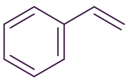

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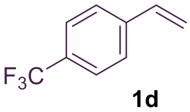

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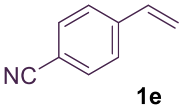

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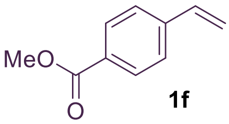

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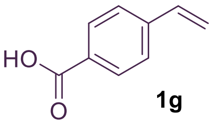

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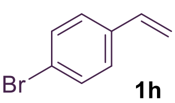

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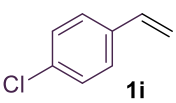

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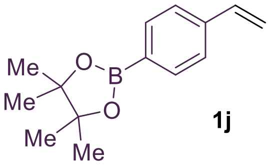

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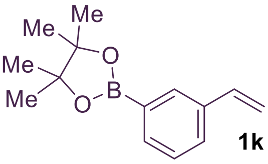

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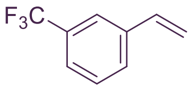

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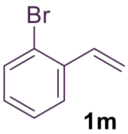

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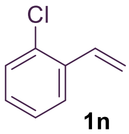

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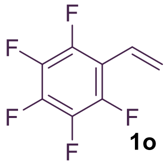

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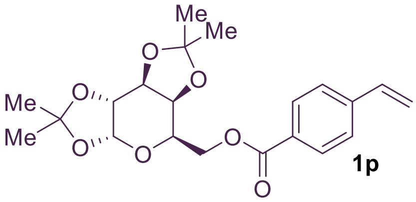

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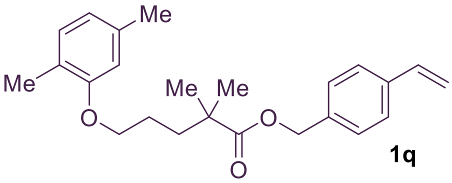

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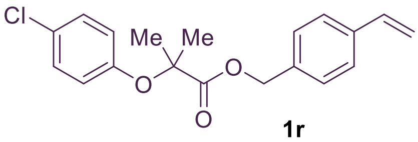

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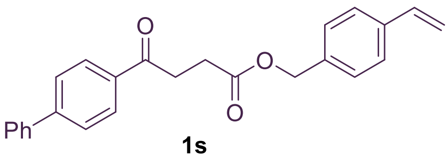

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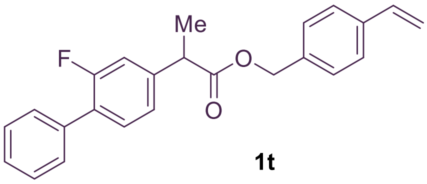

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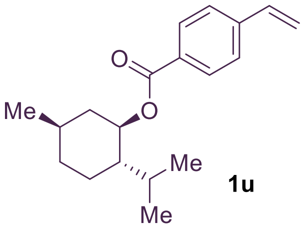

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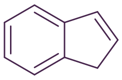

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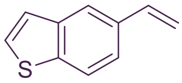

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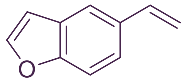

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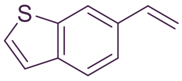

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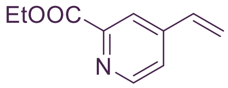

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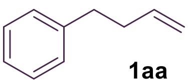

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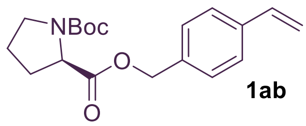

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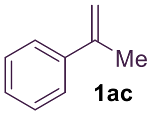

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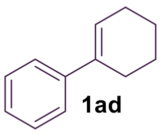
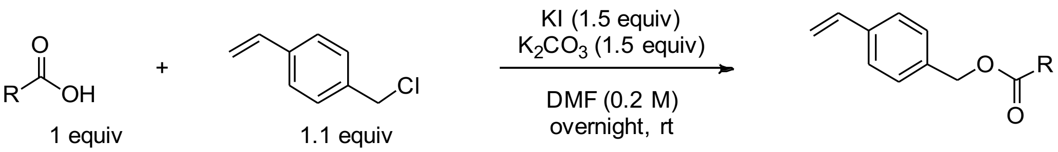


1ad

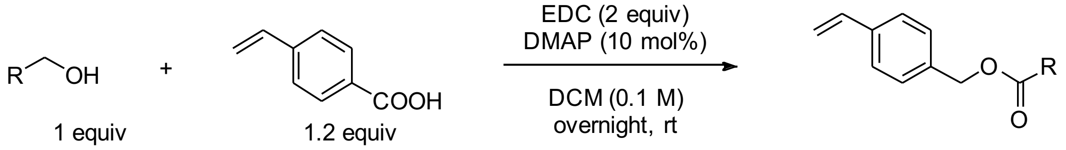
3. Preparation of Styrenes

Method A:



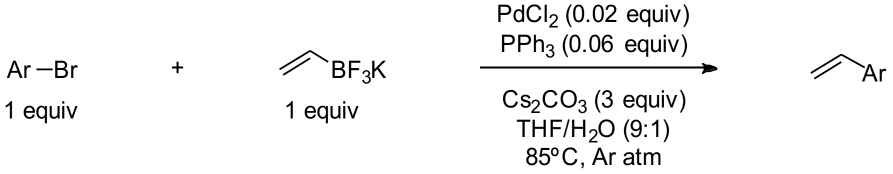
The styrenes were prepared following the adapted literature procedure:[3] In a dry round-bottomed flask, the corresponding carboxylic acid (1 mmol) was placed and DMF (5 mL) was added. Then, K_2CO_3 (207.3 mg, 1.5 mmol) and KI (249 mg, 1.5 mmol) were added and stirred. To this stirring suspension, 4-vinylbenzyl chloride (167.8 mg, 1.1 mmol) was added, and the reaction was allowed to proceed overnight at rt. Upon completion of the reaction, 10 mL of EtOAc were added, followed by 10 mL of H_2O. The reaction mixture was then extracted and washed three times with H_2O (10 mL). The organic layer was washed with satd NaCl soln (20 mL)., dried (Na_2SO_4), and the volatiles were removed under reduced pressure. The crude mixture was subjected to purification by automated flash column chromatography.

Method B:



The styrenes were prepared following the adapted literature procedure:[4] In a 25 mL round-bottom flask, 4-ethenylbenzoic acid (178 mg, 1.2 mmol), DMAP (12 mg, 0.1 mmol), CH_2Cl_2 (10 mL), *N*,*N*'-diisopropylcarbodiimide (EDC, 383 mg, 2 mmol) and the desired alcohol (1 mmol) were successively added. The mixture was stirred at rt overnight. The reaction was quenched with H_2O (5 mL) and extracted with EtOAc (3 × 30 mL). The organics were combined, dried (Na_2SO_4), and the volatiles were removed under reduced pressure. The crude mixture was subjected to short path silica filtration.

Method C:



The styrenes were prepared following the adapted literature procedure:[5] A stirred soln of potassium vinyltrifluoroborate (134 mg, 1.00 mmol), $PdCl_2$ (3.5 mg, 0.02 mmol), PPh_3 (16 mg, 0.06 mmol), Cs_2CO_3 (978 mg, 3.00 mmol), and the desired bromo arene (1.00 mmol) in THF/H_2O (9:1) (2 mL) was heated at 85 °C under an Ar atmosphere in a sealed tube. The reaction mixture was stirred at 85 °C overnight, then cooled to rt and diluted with H_2O (5 mL), followed by extraction with CH_2Cl_2 (3 x 15 mL). The solvent was removed in vacuo, and the crude product was purified by automated flash column chromatography.

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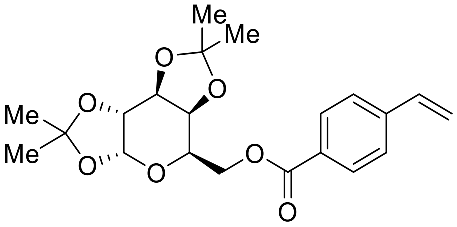
[3] K. C, S.; Dhungana, R. K.; Shrestha, B.; Thapa, S.; Khanal, N.; Basnet, P.; Lebrun, R. W.; Giri, R. *J. Am. Chem. Soc.* **2018**, *140*, 31, 9801–9805.

[4] Huang, J.; Ouyang, L.; Li, J.; Zheng, J.; Yan, W.; Wu, W.; Jiang, H. *Org. Lett.* **2018**, *20*, 5090–5093.

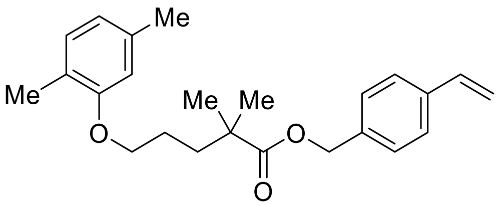
[5] Molander, G. A.; Brown, A. R. *J. Org. Chem.* **2006**, *71*, 9681–9686.

((3*R*,5*R*,5*S*,8*S*,8*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-d]pyran-5-yl)methyl 4-Vinylbenzoate (1p)



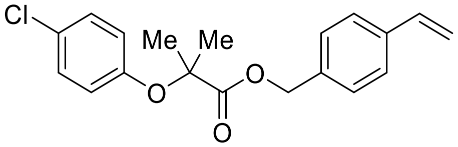
Prepared according to *Method B* from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (260 mg, 1.0 mmol, 1.0 equiv) and 4-vinylbenzoic acid (178 mg, 1.2 mmol, 2.0 equiv). After filtration through a short plug of silica, the title compound **1p** was obtained as a colorless, viscous oil (301 mg, 0.77 mmol, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 8.03 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.88 (dd, *J* = 17.5, 0.8 Hz, 1H), 5.59 (d, *J* = 4.9 Hz, 1H), 5.44 – 5.36 (m, 1H), 4.68 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.55 (dd, *J* = 11.5, 4.8 Hz, 1H), 4.44 (dd, *J* = 11.5, 7.5 Hz, 1H), 4.41 – 4.33 (m, 2H), 4.20 (ddd, *J* = 7.2, 4.9, 1.9 Hz, 1H), 1.54 (s, 3H), 1.50 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 166.2, 142.0, 136.1, 130.0 (2C), 129.2, 126.1 (2C), 116.4, 109.7, 108.8, 96.3, 71.2, 70.8, 70.6, 66.2, 63.9, 26.0, 26.0, 25.0, 24.5. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 3025, 2974, 1671, 1564, 1480, 1210, 1152. **HRMS (ESI)** calcd for $C_{21}H_{26}O_7Na$ $[M+Na]^+$: 413.1576, found 413.1580.

4-Vinylbenzyl 5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoate (1q)



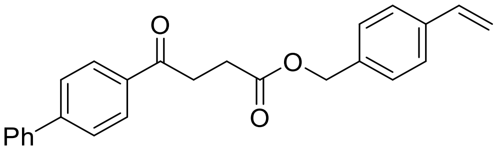
Prepared according to *Method A* from 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid (501 mg, 2.0 mmol, 1.0 equiv) and 1-(chloromethyl)-4-vinylbenzene (336 mg, 2.2 mmol, 1.1 equiv). After purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), the title compound **1q** was obtained as a colorless, viscous oil (460 mg, 1.26 mmol, 63%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.41 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.78 – 6.65 (m, 2H), 6.62 (s, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 5.12 (s, 2H), 3.91 (t, *J* = 5.4 Hz, 2H), 2.33 (s, 3H), 2.18 (s, 3H), 1.76 (s, 4H), 1.27 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 177.6, 157.9 137.4, 136.5, 136.4, 135.9, 130.3, 128.2 (2C), 128.1, 126.3 (2C), 123.6, 120.7, 114.2, 112.0, 67.9, 65.9, 42.2, 37.1, 25.2 (2C), 21.4, 15.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 3008, 2986, 1670, 1500, 1468, 1225, 1150. **HRMS (ESI)** calcd for $C_{24}H_{30}O_3Na$ $[M+Na]^+$: 389.2093, found 389.2093.

4-Vinylbenzyl 2-(4-Chlorophenoxy)-2-methylpropanoate (1r)



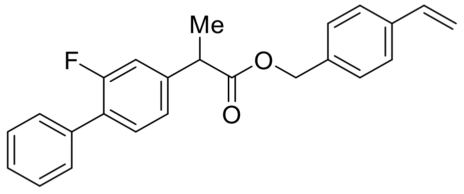
Prepared according to *Method A* from 2-(4-chlorophenoxy)-2-methylpropanoic acid (215 mg, 1.0 mmol, 1.0 equiv) and 1-(chloromethyl)-4-vinylbenzene (168 mg, 1.2 mmol, 1.2 equiv). After purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), the title compound **1r** was obtained as a colorless, viscous oil (270 mg, 0.82 mmol, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.40 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 9.0 Hz, 2H), 6.80 – 6.62 (m, 3H), 5.80 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.31 (dd, *J* = 10.9, 0.9 Hz, 1H), 5.21 (s, 2H), 1.62 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 173.7, 154.0, 137.8, 136.3, 134.7, 129.1 (2C), 128.8 (2C), 127.2, 126.4 (2C), 120.5 (2C), 114.6, 79.6, 67.0, 25.3 (2C). **FT-IR** (cm^{-1}, neat, ATR), ṽ = 3012, 2989, 1672, 1496, 1468, 1325, 1220, 1140. **HRMS (ESI)** calcd for $C_{19}H_{19}ClO_3Na$ $[M+Na]^+$: 353.0920, found 353.0926.

4-Vinylbenzyl 4-([1,1'-Biphenyl]-4-yl)-4-oxobutanoate (1s)



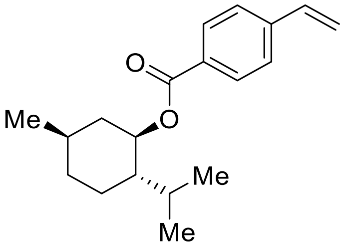
Prepared according to *Method A* from 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoic acid (254 mg, 1.0 mmol, 1.0 equiv) and 1-(chloromethyl)-4-vinylbenzene (168 mg, 1.1 mmol, 1.1 equiv). After purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), the title compound **1s** was obtained as a colorless, viscous oil (305 mg, 0.82 mmol, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = 8.06 (d, *J* = 7.2 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.40 (m, 3H), 7.33 (d, *J* = 7.8 Hz, 2H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (s, 1H), 5.27 (d, *J* = 11.8 Hz, 1H), 5.15 (s, 2H), 3.37 (d, *J* = 6.9 Hz, 2H), 2.85 (t, *J* = 6.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$), δ (ppm) = 197.7, 172.9, 146.1, 140.0, 137.7, 136.5, 135.5, 135.4, 129.1 (2C), 128.8 (2C), 128.6, 128.4, 127.4 (2C), 127.4, 126.5 (2C), 114.4, 66.4, 33.5, 28.5. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 3010, 2984, 1672, 1496, 1468, 1312, 1226, 1185, 1140. **HRMS (ESI)** calcd for $C_{25}H_{22}O_3Na$ $[M+Na]^+$: 393.1467, found 393.1467.

4-Vinylbenzyl 2-(2-Fluoro-[1,1'-biphenyl]-4-yl)propanoate (1t)



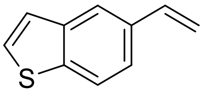
Prepared according to *Method A* from 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (244 mg, 1.0 mmol, 1.0 equiv) and 1-(chloromethyl)-4-vinylbenzene (168 mg, 1.1 mmol, 1.1 equiv). After purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), the title compound **1t** was obtained as a colorless, viscous oil (250 mg, 0.69 mmol, 69%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.63 – 7.53 (m, 2H), 7.47 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 4H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.18 – 7.10 (m, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H), 5.16 (q, *J* = 7.2 Hz, 2H), 3.83 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = - 117.2. **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 173.8, 159.7 (d, $J_{C\text{-}F}$ = 248.5 Hz), 141.6 (d, $J_{C\text{-}F}$ = 7.7 Hz), 137.6, 136.3, 135.5, 135.3, 130.8 (d, $J_{C\text{-}F}$ = 3.9 Hz), 128.9 (d, $J_{C\text{-}F}$ = 2.8 Hz), 128.4, 128.3, 127.9 (d, $J_{C\text{-}F}$ = 13.6 Hz), 127.7, 126.3, 123.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 115.3 (d, $J_{C\text{-}F}$ = 23.7 Hz), 114.4, 66.5, 45.0, 18.3. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2983, 1736, 1484, 1419, 1375, 1174, 1085. **HRMS (ESI)** calcd for $C_{24}H_{21}FO_2Na$ $[M+Na]^+$: 383.1423, found 383.1419.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-Vinylbenzoate (1u)



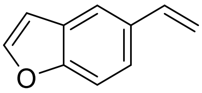
Prepared according to *Method B* from (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexan-1-ol (313 mg, 2.0 mmol, 1.0 equiv) and 4-vinylbenzoic acid (356 mg, 2.4 mmol, 2.0 equiv). After filtration through a short plug of silica, the title compound **1u** was obtained as a colorless, viscous oil (405 mg, 1.41 mmol, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 8.02 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 6.78 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.40 (d, *J* = 10.9 Hz, 1H), 4.95 (td, *J* = 10.9, 4.4 Hz, 1H), 2.23 – 2.11 (m, 2H), 1.99 (dt, *J* = 7.0, 3.5 Hz, 1H), 1.76 (dq, *J* = 14.9, 3.2 Hz, 2H), 1.67 – 1.45 (m, 2H), 1.24 – 1.09 (m, 2H), 0.98 – 0.92 (m, 6H), 0.82 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 165.9, 141.8, 136.1, 130.0, 129.9 (2C), 126.1 (2C), 116.3, 74.8, 47.3, 41.0, 34.4, 31.5, 26.6, 23.7, 22.1, 20.8, 16.6. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2914, 1670, 1481, 1251, 1126, 1100. **HRMS (ESI)** calcd for $C_{19}H_{26}O_2Na$ $[M+Na]^+$: 309.1830, found 308.1829.

5-Vinylbenzo[b]thiophene (1w)



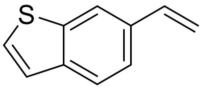
Prepared according to *Method C* from 5-bromobenzo[b]thiophene (213 mg, 1.0 mmol, 1.0 equiv). The spectral data matches those previously reported.[6] **^{1}H NMR** (500 MHz, CDCl$_3$), δ (ppm) = 7.85 – 7.76 (m, 2H), 7.47 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.44 (d, *J* = 5.4 Hz, 1H), 7.32 (d, *J* = 5.5 Hz, 1H), 5.28 (dd, *J* = 10.8, 0.9 Hz, 1H).

5-Vinylbenzofuran (1x)



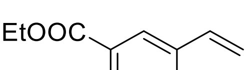
Prepared according to *Method C* from 5-bromobenzofuran (197 mg, 1.0 mmol, 1.0 equiv). The spectral data matches those previously reported.[7] **^{1}H NMR** (500 MHz, CDCl$_3$), δ (ppm) = 7.62 (dd, *J* = 4.7, 2.0 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.40 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.83 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.76 (dd, *J* = 2.2, 1.0 Hz, 1H), 5.74 (dd, *J* = 17.5, 0.9 Hz, 1H), 5.23 (dd, *J* = 10.9, 0.9 Hz, 1H).

6-Vinylbenzo[b]thiophene (1y)



Prepared according to *Method C* from 6-bromobenzo[b]thiophene (213 mg, 1.0 mmol, 1.0 equiv). The spectral data matches those previously reported.[8] **^{1}H NMR** (500 MHz, CDCl$_3$), δ (ppm) = 7.87 (d, *J* = 4.1 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.48 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.42 (d, *J* = 5.4 Hz, 1H), 7.31 (d, *J* = 5.2 Hz, 2H), 6.83 (ddd, *J* = 20.3, 10.8, 4.2 Hz, 2H), 5.82 (d, *J* = 17.5 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H).

Ethyl 4-Vinylpicolinate (1z)



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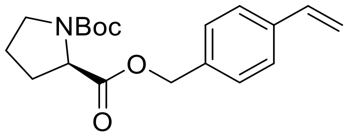
[6] Cooper, P.; Crisenza, G. E. M.; Feron, L. J.; Bower, J. F. *Angew. Chem. Int. Ed.* **2018**, *57*, 14198–14202.

[7] Zhou,Y.; Bandar, J. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **2017**, *139*, 8126–8129.

[8] Molloy, J. J.; Seath, C. P.; West, M. J.; McLaughlin, C.; Fazakerley, N. J.; Kennedy, A. R.; Nelson, D. J.; Watson, A. J. B. *J. Am. Chem. Soc.* **2018**, *140*, 126–130.

Prepared according to *Method C* from ethyl 4-bromopicolinate (70 mg, 0.3 mmol, 1.0 equiv). After purification by automated flash column chromatography (from hexanes to 25% EtOAc in hexanes), the title compound **1z** was obtained as a yellow, viscous oil (44.4 mg, 0.25 mmol, 83%). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = δ 8.68 (dd, *J* = 5.1, 2.6 Hz, 1H), 8.11 (d, *J* = 2.6 Hz, 1H), 7.41 (d, *J* = 5.1 Hz, 1H), 6.71 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.05 (d, *J* = 17.6 Hz, 1H), 5.56 (d, *J* = 10.8 Hz, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$), δ (ppm) ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 150.3, 148.9, 146.2, 134.2, 123.9, 122.3, 120.1, 62.1, 14.5. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2968, 1680, 1485, 1351, 1292, 1250, 1128, 1095. **HRMS (ESI)** calcd for $C_{10}H_{12}NO_2$ [M+H]$^+$: 178.0868, found 178.0860.

1-(*tert*-Butyl)-2-(4-vinylbenzyl) (*R*)-Pyrrolidine-1,2-dicarboxylate (1ab)



Prepared according to *Method A* from (*tert*-butoxycarbonyl)-*D*-proline (215 mg, 1.0 mmol, 1.0 equiv) and 1-(chloromethyl)-4-vinylbenzene (168 mg, 1.1 mmol, 1.1 equiv). After purification by automated flash column chromatography (from hexanes to 15% EtOAc in hexanes), the title compound **1ab** was obtained as a colorless, viscous oil (215 mg, 0.65 mmol, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = mixture of rotamers: 7.41 (dd, *J* = 7.2, 5.2 Hz, 2H), 7.37 – 7.31 (m, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.78 (d, *J* = 17.7 Hz, 1H), 5.32 – 5.05 (m, 3H), 4.34 (m, 1H), 3.62 – 3.41 (m, 2H), 2.36 – 2.21 (m, 1H), 2.03 – 1.85 (m, 3H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = mixture of rotamers: 173.0, 172.8, 153.8, 137.7, 137.4, 136.4, 136.3, 135.4, 135.1, 128.5, 128.3, 126.4, 126.3, 114.4, 114.2, 79.9, 66.3, 59.2, 58.9, 46.5, 46.3, 31.5, 30.9, 29.0, 28.5, 28.3, 24.3, 23.6, 22.7. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2965, 1685, 1489, 1354, 1290, 1251, 1128, 1095. **HRMS (ESI)** calcd for $C_{19}H_{25}NO_4Na$ [M+Na]$^+$: 354.1681, found 354.1680.

4. Synthesis of Fluorinated Benzyl Bromides: Reaction Workflow and Compound Characterization

A. Reaction Workflow:

All photoredox reactions were performed with blue LED strips (light-emitting diode, λ_{max} = 456 nm). The LEDs were placed 1.5 inches away from the reaction vials within a ventilated fume hood. A typical reaction setup is shown below.

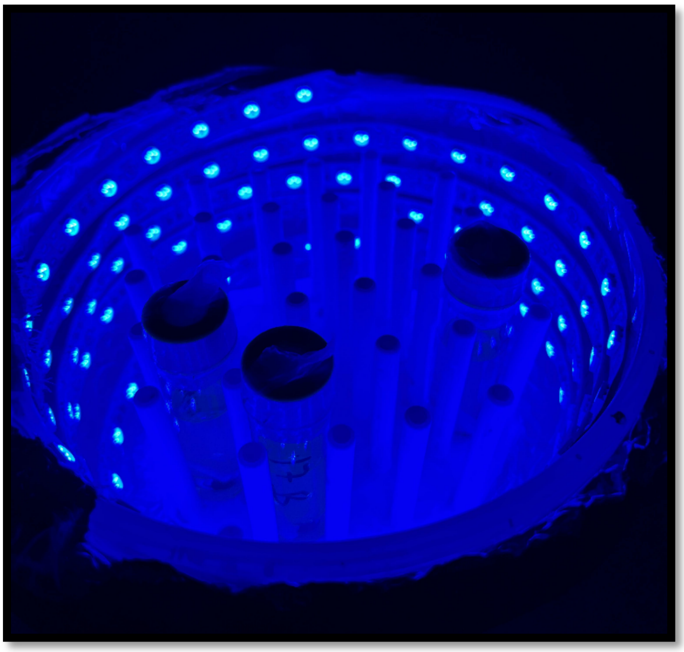
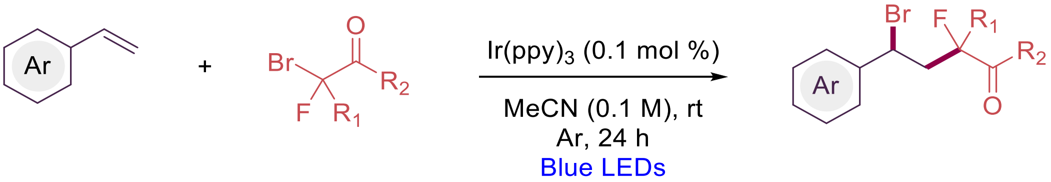


Figure S1. *Reaction setup for the photoinduced formation of fluorinated benzyl bromides*

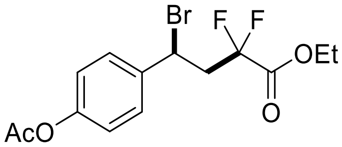
B. General Procedure:



To a flame-dried 8 mL vial equipped with a magnetic stir bar, if solid, styrene **1** (0.5 mmol, 1.0 equiv) was added, and the vial was subjected to 3 cycles of vacuum/argon degassing. Subsequently, 5 mL of a Ir(ppy)$_3$ stock solution in dry MeCN (1000 ppm/mL) were added under inert atmosphere. Subsequently, the α-bromocarbonyl compound was added via syringe (1.0 mmol, 2 equiv), and if liquid, styrene **1** (0.5 mmol, 1.0 equiv). The reaction mixture was irradiated (24 h) with blue LED strips (light-emitting diode, λ_{max} = 456 nm) as described in the "Workflow" section, with analysis by TLC. The temperature of the reaction was maintained at approximately 25 °C via a fan. Upon completion, the solvent was removed under reduced pressure. The crude mixture was subjected to short path silica filtration or purification by automated flash column chromatography using hexanes/EtOAc mixtures.

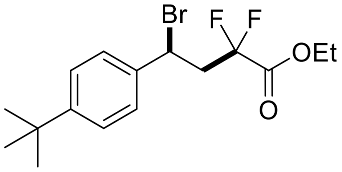
C. *Characterization Data:*

Ethyl 4-(4-Acetoxyphenyl)-4-bromo-2,2-difluorobutanoate (3a)



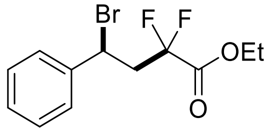
Prepared according to the *General Procedure* from the corresponding styrene **1a** (81.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After filtration through a short plug of silica, the title compound **3a** was obtained as a colorless oil (166 mg, 0.45 mmol, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.44 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.7 Hz, 2H), 5.18 (dd, J = 7.5, 6.1 Hz, 1H), 4.14 (q, J = 7.2, 2H), 3.25 – 3.05 (m, 2H), 2.32 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H).**^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -104.1 (d, J = 266.2 Hz), -104.7 (d, J = 266.2 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 169.1, 163.3 (d, $J_{C\text{-}F}$ = 32.3 Hz), 150.9, 137.8, 128.6 (2C), 122.0 (2C), 114.1 (t, $J_{C\text{-}F}$ = 253.5 Hz), 63.3, 44.7 (t, $J_{C\text{-}F}$ = 24.0 Hz), 43.5 (t, $J_{C\text{-}F}$ = 5.8 Hz), 21.1, 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2998, 1760, 1680, 1421, 1377, 1325, 1250, 1221, 1161, 1110. **HRMS (EI)** calcd for $C_{14}H_{15}F_2O_4$ [M-Br]: 285.0938, found 285.0941.

Ethyl 4-Bromo-4-(4-(*tert*-butyl)phenyl)-2,2-difluorobutanoate (3b)



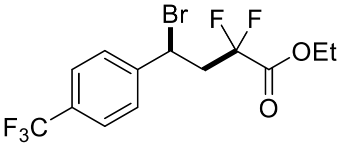
Prepared according to the *General Procedure* from the corresponding styrene **1b** (80 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **3b** was obtained as a colorless oil (134 mg, 0.37 mmol, 74%). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) 7.34 (m, 4H), 5.16 (t, J = 7.3 Hz, 1H), 4.05 (q, J = 7.2, 2H), 3.28 – 3.00 (m, 2H), 1.31 (s, 9H), 1.26 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -103.8 (d, J = 266.5 Hz), -104.6 (d, J = 266.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) 163.2 (t, $J_{C\text{-}F}$ = 32.1 Hz), 152.1, 137.3, 127.1 (2C), 125.7 (2C), 114.2 (t, $J_{C\text{-}F}$ = 252.2 Hz), 63.0, 45.0 – 44.3 (m), 34.7, 31.2 (3C), 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2964, 1761, 1466, 1417, 1395, 1373, 1337, 1299, 1268, 1212, 1187. **HRMS (EI)** calcd for $C_{15}H_{18}BrF_2O_2$ [M-CH_3]: 347.0458 found 347.0446.

Ethyl 4-Bromo-2,2-difluoro-4-phenylbutanoate (3c)



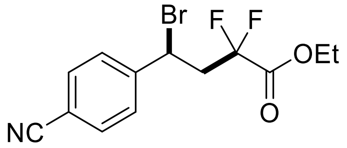
Prepared according to the *General Procedure* from the corresponding styrene **1c** (52 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After filtration through a short plug of silica, the title compound **3c** was obtained as a colorless oil (140 mg, 0.46 mmol, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) 7.55 – 7.35 (m, 5H), 5.19 (t, *J* = 7.3 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.17 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -103.9 (d, *J* = 266.4 Hz), -104.7 (d, $J_{F\text{-}F}$ = 266.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) 163.2 (t, $J_{C\text{-}F}$ = 32.0 Hz), 140.4, 129.0, 128.8 (2C), 127.4 (2C), 114.4 (t, $J_{C\text{-}F}$ = 256.5Hz), 63.1, 44.5 (m), 44.4 (m), 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 3032, 2985, 1760, 1495, 1455, 1374, 1338, 1301, 1181, 1068. **HRMS (EI)** calcd for $C_{12}H_{13}F_2O_2$ [M-Br]: 227.0884, found 227.0889.

Ethyl 4-Bromo-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)butanoate (3d)



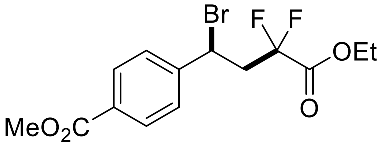
Prepared according to the *General Procedure* from the corresponding styrene **1d** (86.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After filtration through a short plug of silica, the title compound **3d** was obtained as a colorless oil (165 mg, 0.44 mmol, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.64 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 5.21 (dd, *J* = 8.0, 6.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.42 – 2.89 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H).**^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -62.9 (s), -103.8 (d, *J* = 267.3 Hz), -104.91 (d, *J* = 267.3 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 163.0 (t, $J_{C\text{-}F}$ = 31.9 Hz), 144.3, 131.0 (q, $J_{C\text{-}F}$ = 32.8 Hz), 127.8 (2C), 125.9 (q, $J_{C\text{-}F}$ = 3.7 Hz, 2C), 123.7 (q, $J_{C\text{-}F}$ = 272.4 Hz), 114.0 (t, $J_{C\text{-}F}$ = 253.0 Hz), 63.3, 44.2 (t, $J_{C\text{-}F}$ = 23.8 Hz), 42.7 (t, $J_{C\text{-}F}$ = 5.3 Hz), 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2998, 1759, 1423, 1377, 1325, 1221, 1161, 1117. **HRMS (EI)** calcd for $C_{13}H_{12}BrF_4O_3$ [M-F]: 354.9957, found 354.9960.

Ethyl 4-Bromo-4-(4-cyanophenyl)-2,2-difluorobutanoate (3e)



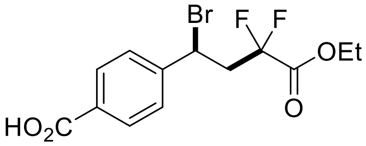
Prepared according to the *General Procedure* from the corresponding styrene **1e** (64.6 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After filtration through a short plug of silica, the title compound **3e** was obtained as a colorless oil (151 mg, 0.44 mmol, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.68 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 5.19 (dd, *J* = 8.2, 6.4 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.51 – 2.69 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.4 (d, *J* = 267.5 Hz), -105.4 (d, *J* = 267.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 163.0 (t, $J_{C\text{-}F}$ = 31.8 Hz), 145.5, 132.7 (2C), 128.2 (2C), 118.1, 113.9 (t, $J_{C\text{-}F}$ = 253.2 Hz), 112.7, 63.4, 44.0 (t, $J_{C\text{-}F}$ = 23.6 Hz), 42.4 ($J_{C\text{-}F}$, *J* = 5.0 Hz), 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2986, 2230, 1760, 1608, 1505, 1418, 1374, 1338, 1302, 1180, 1081. **HRMS (EI)** calcd for $C_{13}H_{12}F_2NO_2$ [M-Br]: 252.0836, found 252.0846.

Methyl 4-(1-Bromo-4-ethoxy-3,3-difluoro-4-oxobutyl)benzoate (3f)



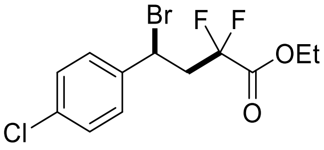
Prepared according to the *General Procedure* from the corresponding styrene **1f** (81.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **3f** was obtained as a colorless oil (144 mg, 0.39 mmol, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 8.04 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 5.21 (t, *J* = 7.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 3.21 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.7 (d, *J* = 266.5 Hz), -105.1 (d, *J* = 266.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 166.3, 163.1 (t, $J_{C\text{-}F}$ = 31.8 Hz), 145.1, 130.6, 130.1 (2C), 127.4 (2C), 114.1 (t, $J_{C\text{-}F}$ = 252.8 Hz), 63.3 52.3, 44.2 (t, $J_{C\text{-}F}$ = 23.8 Hz), 43.1 (t, $J_{C\text{-}F}$ = 5.3 Hz), 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 1761, 1720, 1611, 1435, 1419, 1374, 1337, 1277, 1180, 1109, 1080. **HRMS (EI)** calcd for $C_{14}H_{15}F_2O_4$ [M-Br]: 285.0938, found 285.0945.

4-(1-Bromo-4-ethoxy-3,3-difluoro-4-oxobutyl)benzoic Acid (3g)



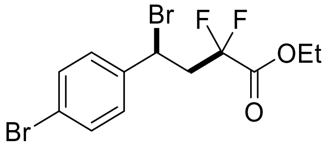
Prepared according to the *General Procedure* from the corresponding styrene **1g** (74.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 406 mg, 2.0 mmol, 4.0 equiv). After filtration through a short plug of silica, the title compound **3g** was obtained as a yellowish solid (168 mg, 0.48 mmol, 96%). **mp** 66-69 ºC. **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 9.29 (s, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 7.9 Hz, 2H), 5.13 (t, J = 7.2 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.13 – 3.05 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = 103.6 (d, J = 266.8 Hz), -105.1 (d, J = 266.8 Hz). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 171.1, 163.1 (t, J_{C-F} = 31.9 Hz), 146.2, 130.8 (2C), 129.6, 127.6 (2C), 114.1 (t, J_{C-F} = 252.9 Hz), 63.4, 44.1 (t, J_{C-F} = 23.7 Hz), 43.0 (t, J_{C-F} = 5.1 Hz), 13.8. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3285, 2988, 1766, 1691, 1610, 1426, 1316, 1284, 1247, 1216, 118, 1083. **HRMS (EI)** calcd for $C_{13}H_{13}BrF_2O_4$ [M]: 349.9965, found 349.9959.

Ethyl 4-Bromo-4-(4-chlorophenyl)-2,2-difluorobutanoate (3h)



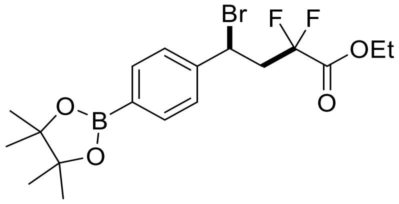
Prepared according to the *General Procedure* from the corresponding styrene **1h** (69.3 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After filtration through a short plug of silica, the title compound **3h** was obtained as a colorless oil (144 mg, 0.42 mmol, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.29 – 7.23 (m, 4H), 5.07 (dd, J = 8.1, 6.6 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 3.15 – 2.87 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H).**^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.8 (d, J = 266.7 Hz), -104.8 (d, J = 266.7 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 163.1 (t, J_{C-F} = 31.9 Hz), 139.0, 134.8, 129.0 (2C), 128.8 (2C), 114.1 (t, J_{C-F} = 252.7 Hz), 63.3, 44.4 (t, J_{C-F} = 23.8 Hz), 43.3 (t, J_{C-F} = 5.4 Hz), 13.8. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1760, 1476, 1444, 1374, 1338, 1302, 1237, 1180. **HRMS (EI)** calcd for $C_{12}H_{12}ClF_2O_2$ [M-Br]: 261.0494, found 261.0493.

Ethyl 4-Bromo-4-(4-bromophenyl)-2,2-difluorobutanoate (3i)



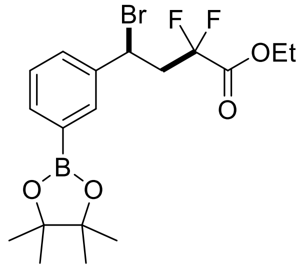
Prepared according to the *General Procedure* from the corresponding styrene **1i** (91.5 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After filtration through a short plug of silica, the title compound **3i** was obtained as a colorless oil (165 mg, 0.43 mmol, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.51 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.15 (dd, *J* = 8.0, 6.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.30 – 2.85 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).**^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.8 (d, *J* = 266.5 Hz), -104.8 (d, *J* = 266.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 163.1 (t, $J_{C\text{-}F}$ = 32.0 Hz), 139.5, 132.0 (2C), 129.0 (2C), 122.9, 114.1 (t, $J_{C\text{-}F}$ = 252.8 Hz), 63.3, 44.4 (t, $J_{C\text{-}F}$ = 23.8 Hz), 43.3 (t, $J_{C\text{-}F}$ = 5.4 Hz), 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 1759, 1472, 1440, 1374, 1337, 1301, 1236, 1178, 1130. **HRMS (EI)** calcd for $C_{12}H_{12}BrF_2O_2$ [M-Br]: 304.9989, found 304.9989.

Ethyl 4-Bromo-2,2-difluoro-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butanoate (3j)



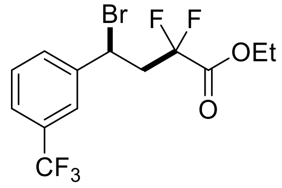
Prepared according to the *General Procedure* from the corresponding styrene **1j** (64.6 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 406 mg, 1.0 mmol, 4.0 equiv). After filtration through a short plug of silica, the title compound **3j** was obtained as a colorless oil (185 mg, 0.43 mmol, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.82 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 2H), 5.19 (t, *J* = 7.2 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.16 (m, 2H), 1.36 (s, 12H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -104.0 (d, *J* = 267.5 Hz), -105.0 (d, *J* = 267.5 Hz). **^{11}B NMR** (128 MHz, $CDCl_3$), δ (ppm) = 30.8. **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 163.2 (t, $J_{C\text{-}F}$ = 32.0 Hz), 143.2, 135.3 (2C), 127.7, 126.6 (2C), 114.2 (t, $J_{C\text{-}F}$ = 252.5 Hz), 84.0, 63.2 (2C), 44.0 – 44.1 (m, 2C), 24.9 (2C), 24.9 (2C), 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2979, 1760, 1611, 1398, 1358, 1324, 1271, 1211, 1167, 1142, 1087, 1020. **HRMS (EI)** calcd for $C_{18}H_{23}BF_2O_4$ [M-HBr]: 352.1657, found 352.1664.

Ethyl 4-Bromo-2,2-difluoro-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butanoate (3k)



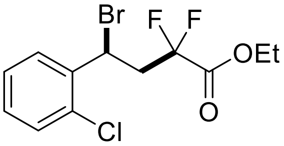
Prepared according to the *General Procedure* from the corresponding styrene **1k** (115 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **3k** was obtained as a colorless oil (169 mg, 0.39 mmol, 78%). **^{1}H NMR** (400 MHz, CDCl$_3$), δ (ppm) = 7.74 (d, J = 2.2 Hz, 1H), 7.67 (d, J = 7.4 Hz, 1H), 7.43 (dt, J = 7.9, 1.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 5.11 (t, J = 7.2 Hz, 1H), 4.05 (q, J = 7.3 Hz, 2H), 3.18 – 2.99 (m, 2H), 1.28 (d, J = 2.4 Hz, 12H), 1.22 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, CDCl$_3$), δ (ppm) = -104.1 (d, J = 266.5 Hz), -104.9 (d, J = 266.5 Hz). **^{11}B NMR** (128 MHz, CDCl$_3$), δ (ppm) = 30.4. **^{13}C NMR** (101 MHz, CDCl$_3$), δ (ppm) = 163.2 (t, $J_{C\text{-}F}$ = 32.1 Hz), 139.8, 135.4, 133.4, 132.5, 130.2, 128.3, 113.4 (t, $J_{C\text{-}F}$ = 252.1 Hz), 84.0 (2C), 63.1, 44.8 – 43.8 (m, 2C), 24.9 (2C), 24.9 (2C), 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2979, 1762, 1431, 1371, 1356, 1321, 1272, 1199, 1142, 1076. **HRMS (EI)** calcd for $C_{18}H_{23}BF_2O_4$ [M-HBr]: 352.1657, found 352.1664.

Ethyl 4-Bromo-2,2-difluoro-4-(3-(trifluoromethyl)phenyl)butanoate (3l)



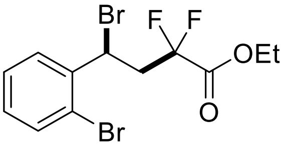
Prepared according to the *General Procedure* from the corresponding styrene **1l** (86.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After filtration through a short plug of silica, the title compound **3l** was obtained as a colorless oil (178 mg, 0.47 mmol, 95%). **^{1}H NMR** (400 MHz, CDCl$_3$), δ (ppm) = 7.69 (d, J = 1.9 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.51 (t, J = 7.8 Hz, 1H), 5.23 (dd, J = 8.0, 6.7 Hz, 1H), 4.50 – 4.12 (m, 2H), 3.17 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, CDCl$_3$), δ (ppm) = -62.8 (s), -103.7 (d, J = 266.5 Hz), -104.9 (d, J = 267.5 Hz). **^{13}C NMR** (101 MHz, CDCl$_3$), δ (ppm) = 163.0 (t, $J_{C\text{-}F}$ = 32.0 Hz), 141.5, 131.3 (q, $J_{C\text{-}F}$ = 32.6 Hz), 130.8, 129.5, 125.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.2 (q, $J_{C\text{-}F}$ = 3.6 Hz), 123.7 (t, $J_{C\text{-}F}$ = 272.7 Hz), 114.0 (t, $J_{C\text{-}F}$ = 252.9 Hz), 63.3, 44.3 (t, $J_{C\text{-}F}$ = 23.8 Hz), 42.9 (t, $J_{C\text{-}F}$ = 5.4 Hz), 13.7. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2988, 1761, 1452, 1375, 1327, 1165, 1124, 1106, 1073, 1035. **HRMS (EI)** calcd for $C_{13}H_{12}BrF_4O_3$ [M-F]: 354.9957, found 354.9959.

Ethyl 4-Bromo-4-(2-chlorophenyl)-2,2-difluorobutanoate (3m)



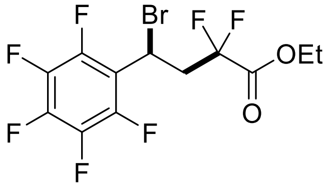
Prepared according to the *General Procedure* from the corresponding styrene **1m** (69.3 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After filtration through a short plug of silica, the title compound **3m** was obtained as a colorless oil (178 mg, 0.47 mmol, 94%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.59 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.40 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.33 (td, *J* = 7.6, 1.5 Hz, 1H), 7.30 – 7.23 (m, 1H), 5.73 (dd, *J* = 7.2, 6.7 Hz, 1H), 4.23 (q, *J* = 7.1, 2H), 3.44 – 2.98 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.2 (d, *J* = 266.3 Hz), -105.4 (d, *J* = 266.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 163.2 (t, $J_{C\text{-}F}$ = 32.0 Hz), 137.8, 132.7, 130.0, 129.9, 129.0, 127.5, 114.1 (t, $J_{C\text{-}F}$ = 272.7 Hz), 63.3, 43.4 (t, $J_{C\text{-}F}$ = 24.0 Hz), 39.6 (t, $J_{C\text{-}F}$ = 5.2 Hz), 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 1760, 1476, 1444, 1374, 1338, 1302, 1237, 1180. **HRMS (EI)** calcd for $C_{10}H_7BrClF_2O$ [M-OC_2H_5]: 294.9337, found 294.9343.

Ethyl 4-Bromo-4-(2-bromophenyl)-2,2-difluorobutanoate (3n)



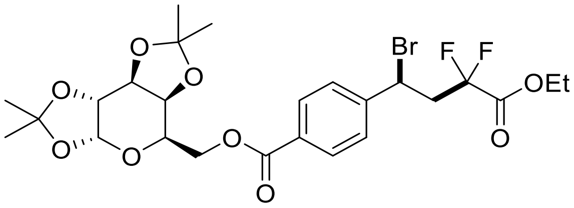
Prepared according to the *General Procedure* from the corresponding styrene **1n** (91.5 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **3n** was obtained as a colorless oil (168 mg, 0.44 mmol, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) = 7.94 – 7.51 (m, 2H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.19 (td, *J* = 7.7, 1.6 Hz, 1H), 5.72 (dd, *J* = 7.2, 6.4 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.68 – 2.86 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.0 (d, *J* = 266.7 Hz), -105.3 (d, *J* = 265.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 163.2 (t, $J_{C\text{-}F}$ = 32.1 Hz), 139.4, 133.3, 130.2, 129.1, 128.2, 123.0, 114.1 (t, $J_{C\text{-}F}$ = 272.7 Hz), 63.3, 43.5 (t, $J_{C\text{-}F}$ = 24.1 Hz), 42.5 (t, $J_{C\text{-}F}$ = 5.5 Hz), 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 1761, 1477, 1440, 1374, 1338, 1302, 1237, 1183. **HRMS (EI)** calcd for $C_{12}H_{12}BrF_2O_2$ [M-Br]: 304.9989, found 304.9984.

Ethyl 4-Bromo-2,2-difluoro-4-(perfluorophenyl)butanoate (3o)



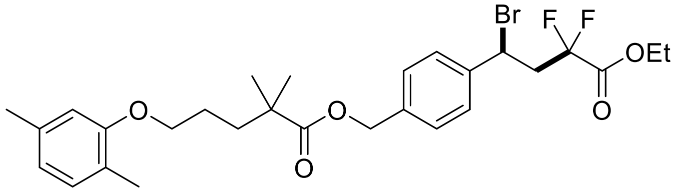
Prepared according to the *General Procedure* from the corresponding styrene **1o** (97.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 104 mg, 0.5 mmol, 2.0 equiv). After filtration through a short plug of silica, the title compound **3o** was obtained as a colorless oil (196 mg, 0.49 mmol, 99%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) 5.52 (dd, J = 9.6, 5.8 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.44 – 3.03 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -104.7 (d, J = 267.5 Hz), -107.2 (d, J = 267.6 Hz), -140.7 (bs), -151.4 – -153.8 (m), -159.9 – -161.6 (m). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) 162.7 (t, $J_{C\text{-}F}$ = 31.8 Hz), 144.8 (d, $J_{C\text{-}F}$ = 251.4 Hz), 142.86 – 139.88 (m, 2C), 139.29 – 135.55 (m, 2C), 114.5 (td, $J_{C\text{-}F}$ = 14.4, 4.3 Hz), 113.9 (t, $J_{C\text{-}F}$ = 253.4 Hz), 63.6, 41.7 (t, $J_{C\text{-}F}$ = 23.0 Hz), 28.7, 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 1761, 1654, 1523, 1504, 1426, 1301, 1240, 1223, 1185, 1152, 1133. **HRMS (EI)** calcd for $C_{12}H_8F_7O_2$ [M-Br]: 317.0413, found 317.0416.

((3*R*,5*R*,5*S*,8*S*,8*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 4-(1-bromo-4-ethoxy-3,3-difluoro-4-oxobutyl)benzoate (3p)



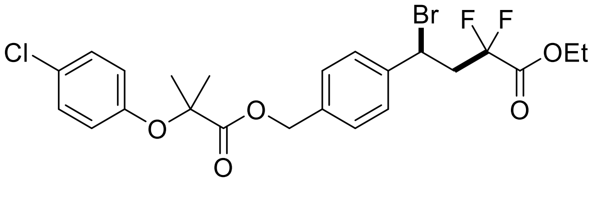
Prepared according to the *General Procedure* from the corresponding styrene **1p** (100 mg, 0.25 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 104 mg, 0.5 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 25% EtOAc in hexanes), the title compound **3p** was obtained as a colorless oil (131 mg, 0.21 mmol, 86%). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) 8.03 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 5.56 (d, J = 4.9 Hz, 1H), 5.18 (t, J = 7.2 Hz, 1H), 4.65 (dd, J = 7.9, 2.5 Hz, 1H), 4.52 (ddd, J = 11.6, 4.7, 2.1 Hz, 1H), 4.46 – 4.40 (m, 1H), 4.38 – 4.29 (m, 2H), 4.16 (m, 3H), 3.13 (m, 2H), 1.51 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -103.6 (d, J = 260.8 Hz), -105.0 (d, J = 260.8 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) 165.7, 163.1 (t, $J_{C\text{-}F}$ = 32.1 Hz), 145.2, 130.5, 130.2 (2C), 127.4 (2C), 114.1 (t, $J_{C\text{-}F}$ = 252.9 Hz), 109.7, 108.8, 96.3, 71.1, 70.8, 70.5, 66.1, 64.1, 63.3, 44.1 (t, $J_{C\text{-}F}$ = 23.8 Hz), 43.1 (t, $J_{C\text{-}F}$ = 5.3 Hz), 26.0, 26.0, 25.0, 24.5, 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2987, 1761, 1717, 1611, 1420, 1373, 1274, 1255, 1209, 1176, 1066. **HRMS (EI)** calcd for $C_{25}H_{31}F_2O_9$ [M-Br]: 513.1936, found 513.1939.

Ethyl 4-Bromo-4-(4-(((4-(2,5-dimethylphenoxy)-2,2-dimethylbutanoyl)oxy)methyl)phenyl)-2,2-difluorobutanoate (3q)



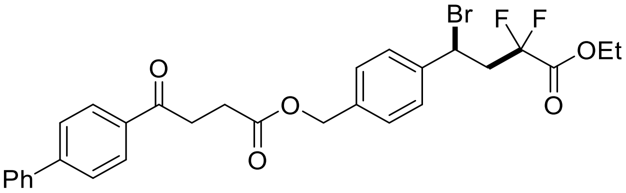
Prepared according to the *General Procedure* from the corresponding styrene **1q** (183 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 15% EtOAc in hexanes), the title compound **3q** was obtained as a colorless oil (202 mg, 0.39 mmol, 78%). **^{1}H NMR** (400 MHz, CDCl$_3$), δ (ppm) 7.42 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.03 (d, J = 7.4 Hz, 1H), 6.69 (d, J = 8.3 Hz, 1H), 6.63 (d, J = 1.6 Hz, 1H), 5.19 (t, J = 7.3 Hz, 1H), 5.12 (s, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.93 (t, J = 5.5 Hz, 2H), 3.39 – 2.97 (m, 2H), 2.33 (s, 3H), 2.19 (s, 3H), 1.90 – 1.74 (m, 4H), 1.32 (t, J = 7.2 Hz, 3H), 1.28 (s, 6H). **^{19}F NMR** (376 MHz, CDCl$_3$), δ (ppm) = -103.7 (d, J = 266.4 Hz), -104.9 (d, J = 265.5 Hz). **^{13}C NMR** (101 MHz, CDCl$_3$), δ (ppm) = 177.5, 163.2 (t, $J_{C\text{-}F}$ = 32.0 Hz), 157.0, 140.2, 137.3, 136.5, 130.3, 128.2 (2C), 127.6 (2C), 123.6, 120.8, 116.7, 114.3 (t, $J_{C\text{-}F}$ = 252.5 Hz), 112.0 67.9, 65.5, 63.2, 44.4 (t, $J_{C\text{-}F}$ = 23.8 Hz), 44.0 (t, $J_{C\text{-}F}$ = 5.5 Hz), 42.2, 37.2, 25.2 (2C), 21.4, 15.8, 13.8. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2950, 1768, 1727, 1508, 1473, 1390, 1374, 1337, 1306, 1284, 1263, 1188, 1156, 1129. **HRMS (ESI)** calcd for $C_{28}H_{35}BrF_2O_5Na$ [M+Na]$^+$: 591.1534, found 591.1534.

Ethyl 4-Bromo-4-(4-(((2-(4-chlorophenoxy)-2-methylpropanoyl)oxy)methyl)phenyl)-2,2-difluorobutanoate (3r)



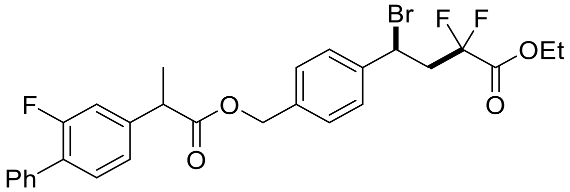
Prepared according to the *General Procedure* from the corresponding styrene **1r** (165.4 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), the title compound **3r** was obtained as a colorless oil (195 mg, 0.37 mmol, 74%). **^{1}H NMR** (400 MHz, CDCl$_3$), δ (ppm) = 7.39 (d, J = 7.8 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.15 (d, J = 8.7 Hz, 2H), 6.71 (d, J = 6.6 Hz, 2H), 5.19 (m, 3H), 4.17 (q, J = 7.7 Hz, 2H), 3.15 (m, 2H), 1.61 (s, 6H), 1.32 (t, J = 7.7 Hz, 3H). **^{19}F NMR** (376 MHz, CDCl$_3$), δ (ppm) = -103.0 (d, J = 266.7 Hz), -105.3 (d, J = 265.4 Hz). **^{13}C NMR** (101 MHz, CDCl$_3$), δ (ppm) = 173.7, 163.1 (t, $J_{C\text{-}F}$ = 32.0 Hz), 153.9, 140.7, 136.0, 129.1 (2C), 128.8 (2C), 127.6 (2C), 127.3, 120.3 (2C), 114.1 (t, $J_{C\text{-}F}$ = 252.6 Hz), 79.5, 66.5, 63.2, 44.3 (t, $J_{C\text{-}F}$ = 23.7 Hz), 43.8 (t, $J_{C\text{-}F}$ = 5.4 Hz), 25.3 (2C), 13.8. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1736, 1488, 1467, 1385, 1374, 1338, 1280, 1236, 1204, 1171, 1131, 1085. **HRMS (EI)** calcd for $C_{23}H_{23}ClF_2O_5$ [M-HBr]: 452.1202, found 452.1216.

Ethyl 4-Bromo-2,2-difluoro-4-(4-(((4-oxo-4-phenylbutanoyl)oxy)methyl)phenyl)butanoate (3s)



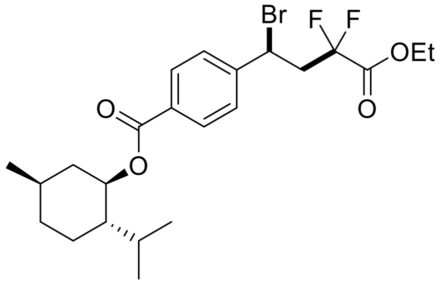
Prepared according to the *General Procedure* from the corresponding styrene **1s** (185 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), the title compound **3s** was obtained as a colorless oil (204 mg, 0.39 mmol, 78%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 8.08 (d, J = 8.3 Hz, 2H), 7.75 – 7.70 (m, 2H), 7.66 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.44 – 7.41 (m, 3H), 7.38 (d, J = 8.1 Hz, 2H), 5.21 – 5.14 (m, 3H), 4.16 (q, J = 7.2 Hz, 2H), 3.40 (t, J = 6.5 Hz, 2H), 3.16 (m, 2H), 2.88 (t, J = 6.4 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.0 (d, J = 266.7 Hz), -105.3 (d, J = 265.4 Hz). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 197.5, 172.7, 163.2 (t, J = 32.1 Hz), 146.0, 140.4, 139.8, 136.8, 135.2, 129.0 (2C), 128.7 (2C), 128.5 (2C), 128.3, 127.6 (2C), 127.3 (2C), 127.3 (2C), 114.2 (t, J = 252.4 Hz), 65.8, 63.2, 44.4 (t, J = 23.9 Hz), 43.9 (t, J = 5.5 Hz), 33.4, 28.3, 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 1764, 1747, 1736, 1677, 1326, 1307, 1272, 1215, 1203, 1173, 1143, 1083, 1015. **HRMS (ESI)** calcd for $C_{29}H_{27}BrF_2O_5Na$ $[M+Na]^+$: 595.0908, found 595.0911.

Ethyl 4-Bromo-2,2-difluoro-4-(4-(((2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoyl)oxy)methyl)phenyl) butanoate (3t)



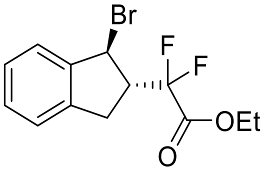
Prepared according to the *General Procedure* from the corresponding styrene **1t** (72.1 mg, 0.20 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 81 mg, 0.4 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), the title compound **3t** was obtained as a colorless oil (79 mg, 0.14 mmol, 70%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.46 (d, J = 8.3, 2H), 7.39 – 7.22 (m, 6H), 7.22 – 7.13 (m, 2H), 7.11 – 7.00 (m, 2H), 5.10 – 4.98 (m, 3H), 4.09 – 4.00 (m, 2H), 3.73 (q, J = 7.1 Hz, 1H), 3.14 – 2.94 (m, 2H), 1.48 (d, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.8 (d, J = 266.7 Hz), -104.9 (d, J = 265.4 Hz), -117.5 (s). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 173.8, 163.1 (t, $J_{C\text{-}F}$ = 32.0 Hz), 159.7 (d, $J_{C\text{-}F}$ = 248.6 Hz), 141.5 (d, $J_{C\text{-}F}$ = 7.8 Hz), 140.4, 136.7, 135.5, 130.9 (d, $J_{C\text{-}F}$ = 3.9 Hz), 129.0 (d, $J_{C\text{-}F}$ = 2.8 Hz), 128.5 (2C), 128.3 (2C), 128.0 (d, $J_{C\text{-}F}$ = 13.6 Hz) 127.7 (2C), 127.6 (2C), 123.6 (m), 115.3 (d, $J_{C\text{-}F}$ = 23.6 Hz), 114.2 (t, $J_{C\text{-}F}$ = 252.9 Hz), 66.0, 63.2, 45.0, 44.4 (t, $J_{C\text{-}F}$ = 23.9 Hz), 43.9 (t, $J_{C\text{-}F}$ = 5.4 Hz), 18.3, 13.8. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2982, 1766, 1736, 1624, 1582, 1516, 1484, 1450, 1419, 1375, 1335, 1173. **HRMS (EI)** calcd for $C_{28}H_{26}F_3O_4$ [M-Br]: 483.1783, found 483.1778.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-(1-bromo-4-ethoxy-3,3-difluoro-4-oxobutyl)benzoate (3u)



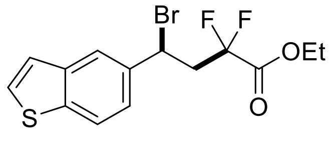
Prepared according to the *General Procedure* from the corresponding styrene **1s** (82 mg, 0.25 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 102 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), the title compound **3u** was obtained as a colorless oil (80 mg, 0.16 mmol, 66%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.95 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 5.12 (dd, J = 7.8, 6.6 Hz, 1H), 4.86 (td, J = 10.9, 4.5 Hz, 1H), 4.14 – 4.06 (m, 2H), 3.19 – 2.95 (m, 2H), 2.08 – 1.96 (m, 1H), 1.86 (ddd, J = 10.3, 6.8, 3.2 Hz, 1H), 1.70 – 1.62 (m, 2H), 1.54 – 1.44 (m, 2H), 1.22 (t, J = 7.1 Hz, 3H), 1.11 – 0.98 (m, 2H), 0.85 (dd, J = 9.6, 6.8 Hz, 7H), 0.72 (d, J = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.6 (d, J = 261.9 Hz), -105.7 (d, J = 261.9 Hz). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 165.3, 163.1 (t, $J_{C\text{-}F}$ = 31.8 Hz), 144.9 (d, $J_{C\text{-}F}$ = 3.3 Hz), 131.3, 130.1 (2C), 127.3 (2C), 114.1 (t, $J_{C\text{-}F}$ = 253.1 Hz), 75.1, 63.3, 47.3, 44.2 (t, $J_{C\text{-}F}$ = 23.7 Hz), 43.2 (q, $J_{C\text{-}F}$ = 4.9 Hz), 40.9, 34.3, 26.5 (d, $J_{C\text{-}F}$ = 4.8 Hz), 23.6 (d, $J_{C\text{-}F}$ = 4.2 Hz), 22.0, 20.8 (d, $J_{C\text{-}F}$ = 1.9 Hz), 16.5 (2C), 13.8. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2956, 1760, 1714, 1275, 1085, 1055. **HRMS (EI)** calcd for $C_{23}H_{31}F_2O_4$ [M-Br]: 409.2190, found 409.2184.

(±)Ethyl 2-(1-Bromo-2,3-dihydro-1H-inden-2-yl)-2,2-difluoroacetate (3v)



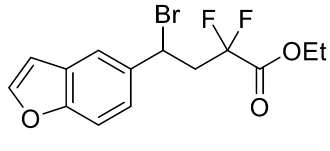
Prepared according to the *General Procedure* from the corresponding styrene **1w** (58 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **3v** was obtained as a colorless oil (155 mg, 0.48 mmol, 97%). ^{1}**H NMR** (600 MHz, CDCl$_3$), δ (ppm) = 7.35 – 7.31 (m, 1H), 7.21 – 7.18 (m, 2H), 7.15 – 7.12 (m, 1H), 5.57 (d, *J* = 4.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.55 – 3.41 (m, 1H), 3.28 (dd, *J* = 16.6, 9.0 Hz, 1H), 3.10 (dd, *J* = 16.6, 5.4 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{19}**F NMR** (376 MHz, CDCl$_3$), δ (ppm) = -110.2 (d, *J* = 256.4 Hz), -112.0 (d, *J* = 256.4 Hz). ^{13}**C NMR** (151 MHz, CDCl$_3$), δ (ppm) = 163.2 (t, $J_{C\text{-}F}$ = 32.4 Hz), 141.7, 140.0, 129.3, 127.9, 125.8, 124.6, 115.3 (t, $J_{C\text{-}F}$ = 253.7 Hz), 63.3, 54.2 (t, $J_{C\text{-}F}$ = 23.1 Hz), 49.3 (t, $J_{C\text{-}F}$ = 4.5 Hz), 31.1 (t, $J_{C\text{-}F}$ = 3.9 Hz), 13.9. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 1762, 1462, 1444, 1374, 1308, 1216, 1193, 1172, 1124, 1091. **HRMS (EI)** calcd for $C_{13}H_{13}F_2O_2$ [M-Br]: 239.0884, found 239.0900.

Ethyl 4-(Benzo[*b*]thiophen-5-yl)-4-bromo-2,2-difluorobutanoate (3w)



Prepared according to the *General Procedure* from the corresponding styrene **1w** (80.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **3w** was obtained as a colorless oil jointly with a small amount of the dehydrobrominated compound (75 mg, 0.21 mmol, 40%). ^{1}**H NMR** (600 MHz, CDCl$_3$), δ (ppm) = 7.90 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.50 (dd, *J* = 5.4, 2.3 Hz, 1H), 7.43 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.37 – 7.30 (m, 1H), 5.32 (t, *J* = 7.5 Hz, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.28 – 3.18 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{19}**F NMR** (376 MHz, CDCl$_3$), δ (ppm) = -103.9 (d, *J* = 256.4 Hz), -104.5 (d, *J* = 256.4 Hz). ^{13}**C NMR** (151 MHz, CDCl$_3$), δ (ppm) = 163.2 (t, $J_{C\text{-}F}$ = 32.0 Hz), 140.0, 139.8, 136.4, 128.1, 124.0, 123.8, 123.6, 121.3, 114.2 (t, $J_{C\text{-}F}$ = 252.6 Hz), 63.2, 45.0 – 44.8 (m), 44.7 – 44.6 (m), 13.7. **HRMS (ESI)** calcd for $C_{14}H_{12}F_2O_2S$ [M-HBr]: 282.0526, found 282.0546.

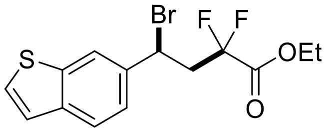
Ethyl 4-(Benzofuran-5-yl)-4-bromo-2,2-difluorobutanoate (3x)



Prepared according to the *General Procedure* from the corresponding styrene **1x** (72 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **3x** was obtained as a colorless oil jointly with a small amount of the dehydrobrominated compound (80 mg, 0.21 mmol, 45%). ^{1}**H NMR** (600 MHz, CDCl$_3$), δ (ppm) = 7.58 (dd, *J* = 7.1, 2.1 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.30 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.69 (dd, *J* = 2.3, 0.9 Hz, 1H), 5.24 (dd, *J* = 7.9, 6.7 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.14 (m, 2H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{19}**F NMR** (376 MHz, CDCl$_3$), δ (ppm) = -103.8 (d, *J* = 256.4 Hz), -104.2 (d, *J* = 256.4 Hz). ^{13}**C NMR**

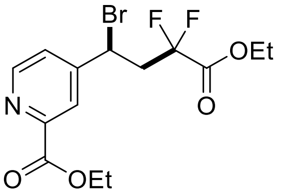
(151 MHz, CDCl$_3$), δ (ppm) = 163.2 (t, $J_{C\text{-}F}$ = 32.0 Hz), 154.8, 146.2, 135.1, 127.6, 123.9, 120.2, 114.2 (t, $J_{C\text{-}F}$ = 252.4 Hz), 111.8, 106.7, 63.1, 45.2 – 44.8 (m, 2C), 13.7. **HRMS (EI)** calcd for $C_{14}H_{13}BrF_2O_3$ [M]: 346.0016, found 346.0023.

Ethyl 4-(Benzo[*b*]thiophen-6-yl)-4-bromo-2,2-difluorobutanoate (3y)



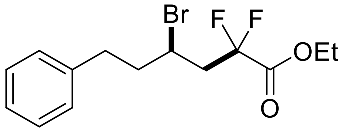
Prepared according to the *General Procedure* from the corresponding styrene **1y** (80.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **3y** was obtained as a colorless oil (91 mg, 0.25 mmol, 50%). **^{1}H NMR** (600 MHz, CDCl$_3$), δ (ppm) = 7.79 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 1.8 Hz, 1H), 7.42 (d, J = 5.4 Hz, 1H), 7.34 (dd, J = 8.4, 1.8 Hz, 1H), 7.25 (d, J = 0.9 Hz, 1H), 5.25 (t, J = 7.3 Hz, 1H), 3.95 (q, J = 7.1 Hz, 2H), 3.19 – 3.11 (ddt, J = 22.9, 15.8, 7.3 Hz, 2H), 1.14 (J = 7.3 Hz, 3H). **^{19}F NMR** (376 MHz, CDCl$_3$), δ (ppm) = -103.9 (d, J = 256.4 Hz), -104.5 (d, J = 256.4 Hz). **^{13}C NMR** (151 MHz, CDCl$_3$), δ (ppm) = 163.2 (t, $J_{C\text{-}F}$ = 31.9 Hz), 140.2, 139.6, 136.5, 127.8, 123.8, 123.5, 123.0, 122.3, 114.2 (t, $J_{C\text{-}F}$ = 252.6 Hz), 63.1, 45.0 – 44.6 (m, 2C), 13.7. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2983, 1740, 1610, 1513, 1442, 1248, 1210. **HRMS (EI)** calcd for $C_{14}H_{12}F_2O_2S$ [M-HBr]: 282.0526, found 282.0546.

Ethyl 4-(1-Bromo-4-ethoxy-3,3-difluoro-4-oxobutyl)picolinate (3z)



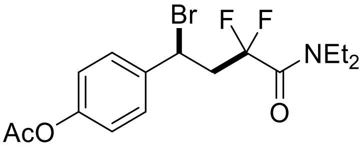
Prepared according to the *General Procedure* from the corresponding styrene **1z** (44.3 mg, 0.25 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 102 mg, 0.5 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **3z** was obtained as a colorless oil (55 mg, 0.14 mmol, 58%). **^{1}H NMR** (500 MHz, CDCl$_3$), δ (ppm) = 8.75 (d, J = 5.0 Hz, 1H), 8.16 (d, J = 1.8 Hz, 1H), 7.48 (dd, J = 5.0, 1.8 Hz, 1H), 5.15 (t, J = 8.0 Hz, 1H), 4.50 (q, J = 7.1 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 3.17 (d, J = 8.3 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, CDCl$_3$), δ (ppm) = -103.1 (d, J = 267.7 Hz), -105.5 (d, J = 267.7 Hz). **^{13}C NMR** (101 MHz, CDCl$_3$), δ (ppm) = 164.7, 162.9 (t, $J_{C\text{-}F}$ = 31.7 Hz), 150.6, 150.5, 149.2, 124.9, 123.3, 113.9 (t, $J_{C\text{-}F}$ = 253.6 Hz), 63.5, 62.3, 43.5 (t, $J_{C\text{-}F}$ = 23.7 Hz), 40.8 (t, $J_{C\text{-}F}$ = 4.9 Hz), 14.3, 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2983, 1741, 1665, 1610, 1575, 1513, 1448, 1368, 1355, 1250. **HRMS (ESI)** calcd for $C_{14}H_{17}BrF_2NO_4$ [M+H]$^+$: 380.0309, found 380.0311.

Ethyl 4-Bromo-2,2-difluoro-6-phenylhexanoate (3aa)



Prepared according to the *General Procedure* from the corresponding styrene **1aa** (66.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-*N*,*N*-diethyl-2,2-difluoroacetamide (**1a**, 203 mg, 1.0 mmol, 1.1 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **3z** was obtained as a colorless oil (158 mg, 0.35 mmol, 70%). The spectroscopic data matches with the reported literature.[9] **^{1}H NMR** (500 MHz, CDCl$_3$), δ (ppm) = 7.30 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 3H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.15 – 4.10 (m, 1H), 2.94 – 2.62 (m, 4H), 2.24 – 2.12 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$), δ (ppm) = 163.6 (t, *J* = 32.2 Hz), 140.3, 128.7 (2C), 128.7 (2C), 126.5, 114.9 (t, *J* = 253.7 Hz), 63.4, 45.6 (t, *J* = 5.8 Hz), 43.9 (t, *J* = 23.6 Hz), 40.8, 33.5, 14.0.

4-(1-Bromo-4-(diethylamino)-3,3-difluoro-4-oxobutyl)phenyl Acetate (4a)



Prepared according to the *General Procedure* from the corresponding styrene **1a** (81.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-*N*,*N*-diethyl-2,2-difluoroacetamide (**2b**, 127 mg, 0.55 mmol, 1.1 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **3a** was obtained as a colorless oil (168 mg, 0.43 mmol, 86%). **^{1}H NMR** (500 MHz, CDCl$_3$), δ (ppm) = 7.44 (d, *J* = 8.4 Hz, 2H), 7.09 – 7.02 (m, 2H), 5.35 (t, *J* = 6.9 Hz, 1H), 3.45 – 3.43 (m, 2H), 3.35 – 3.33 (m, 2H), 3.28 – 3.14 (m, 2H), 2.29 (s, 3H), 1.16 – 1.12 (m, 6H). **^{19}F NMR** (376 MHz, CDCl$_3$), δ (ppm) = -98.1 (d, *J* = 278.2 Hz), -99.0 (d, *J* = 278.2 Hz). **^{13}C NMR** (101 MHz, CDCl$_3$), δ (ppm) = 169.1, 161.9 (t, $J_{C\text{-}F}$ = 28.2 Hz), 150.5, 139.3, 128.4 (2C), 127.0, 122.5, 121.8 (2C), 117.9 (t, $J_{C\text{-}F}$ = 258.1 Hz), 45.05 – 44.05 (m), 41.8 (t, $J_{C\text{-}F}$ = 15.6 Hz), 21.1, 14.2, 12.3. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2983, 1740, 1668, 1611, 1596, 1513, 1444, 1387, 1361, 1259, 1210, 1172. **HRMS (EI)** calcd for $C_{16}H_{20}F_2NO_3$ [M-Br]: 312.1411, found 312.1418.

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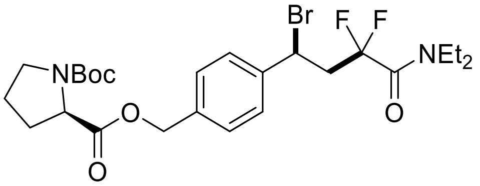
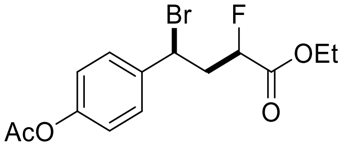
[9] Riente, P.; Pericàs, M. A. *ChemSusChem* **2015**, *8*, 1481–1844.

2-(4-(1-Bromo-4-(diethylamino)-3,3-difluoro-4-oxobutyl)benzyl) 1-(*tert*-Butyl)(2*R*)-pyrrolidine-1,2-dicarboxylate (4b)



Prepared according to the *General Procedure* from the corresponding styrene **1ab** (68 mg, 0.20 mmol, 1.0 equiv) and ethyl 2-bromo-*N*,*N*-diethyl-2,2-difluoroacetamide (**2b**, 63 mg, 0.28 mmol, 1.1 equiv). After purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), the title compound **4b** was obtained as a colorless oil (96 mg, 0.17 mmol, 85%). ^{1}**H NMR** (500 MHz, $CDCl_3$), δ (ppm) mixture of rotamers: 7.42 (m, 2H), 7.32 (m, 2H), 5.35 (t, *J* = 7.0 Hz, 1H), 5.26 – 5.03 (m, 2H), 4.39 – 4.21 (m, 1H), 3.59 – 3.07 (m, 8H), 2.31 – 2.16 (m, 1H), 2.00 – 1.81 (m, 3H), 1.46 – 1.33 (s, 9H), 1.20 – 1.08 (m, 6H).^{19}**F NMR** (376 MHz, $CDCl_3$), δ (ppm) mixture of rotamers: -98.6 (m), -98.8 (m). ^{13}**C NMR** (101 MHz, $CDCl_3$), δ (ppm) mixture of rotamers: 173.0, 173.0, 172.8, 161.9 (t, $J_{C\text{-}F}$ = 29.1 Hz), 154.4, 153.8, 153.7, 142.0, 141.7, 137.6, 137.3, 136.4, 136.3, 136.0, 129.0, 128.6, 128.6, 128.2, 127.5, 127.4, 126.0, 125.9, 118.0 (t, $J_{C\text{-}F}$ = 258.0 Hz), 79.9, 79.9, 79.8, 79.8, 66.0, 65.8, 59.1, 58.9, 58.9, 46.6, 46.4, 44.9 (t, $J_{C\text{-}F}$ = 32.1 Hz), 44.5 (t, $J_{C\text{-}F}$ = 22.6 Hz), 42.3, 41.8 (t, $J_{C\text{-}F}$ = 7.0 Hz), 47.1, 39.9 (t, $J_{C\text{-}F}$ = 21.5 Hz), 30.9, 29.9, 28.4, 28.2, 24.4, 24.3, 23.6, 14.2, 12.3, 11.2. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2974, 1811, 1745, 1692, 1464, 1393, 1367, 1322, 1249, 1226, 1158, 1123, 1081. **HRMS (ESI)** calcd for $C_{25}H_{35}BrF_2N_2O_5Na$ $[M+Na]^+$: 583.1595, found 583.1592.

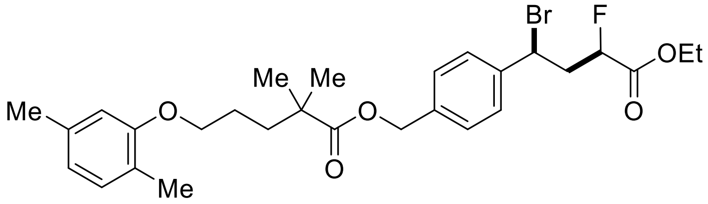
Ethyl 4-(4-Acetoxyphenyl)-4-bromo-2-fluorobutanoate (5a)



Prepared according to the *General Procedure* from the corresponding styrene **1a** (81.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2-fluoroacetate (**2c**, 185 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **5a** was obtained as a colorless oil (140 mg, 0.40 mmol, 81%). *dr*: 1:1. ^{1}**H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.48 – 7.44 (m, 2H), 7.24 – 6.96 (m, 2H), 5.37 – 4.54 (m, 2H), 4.38 – 4.19 (m, 2H), 2.94 – 2.47 (m, 2H), 2.33 (bs, 3H), 1.46 – 1.25 (m, 3H). ^{19}**F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -193.8 – -195.0 (m). ^{13}**C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 169.9 – 168.3 (m), 150.9, 150.8, 129.5, 128.7, 128.5, 122.2, 122.0, 121.8, 88.1 (d, $J_{C\text{-}F}$ = 185.9 Hz), 86.0 (d, $J_{C\text{-}F}$ = 185.9 Hz), 61.9, 48.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 46.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 42.8 (d, $J_{C\text{-}F}$ = 20.9 Hz), 42.6 (d, $J_{C\text{-}F}$ = 20.9 Hz), 21.1, 21.1, 14.1.

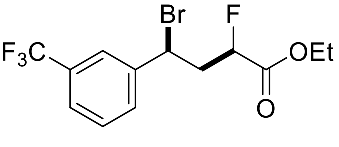
FT-IR (cm^{-1}, neat, ATR), ṽ = 1760, 1739, 1681, 1451, 1373, 1325, 1296, 1193, 1164, 1123. **HRMS (EI)** calcd for $C_{14}H_{16}FO_4$ [M-Br]: 267.1033, found 267.1044.

4-(1-Bromo-4-ethoxy-3-fluoro-4-oxobutyl)benzyl 5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoate (5b)



Prepared according to the *General Procedure* from the corresponding styrene **1q** (50 mg, 0.15 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 50 mg, 0.30 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **5b** was obtained as a colorless oil (64 mg, 0.12 mmol, 85%). *dr*: 1:1. **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.45 – 7.31 (m, 3H), 7.29 – 7.15 (m, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 4.9 Hz, 1H), 5.39 – 4.53 (m, 4H), 4.30 – 4.19 (m, 2H), 3.90 (td, *J* = 6.1, 2.8 Hz, 2H), 2.88 – 2.43 (m, 2H), 2.31 (s, 3H), 2.16 (s, 3H), 1.75 – 1.67 (m, 4H), 1.35 – 1.29 (m, 3H), 1.25 (t, *J* = 5.2 Hz, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -194.7, -195.9. **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 177.9 – 177.7 (m), 170.0 (d, J_{C-F} = 23.4 Hz), 169.3 (d, J_{C-F} = 22.9 Hz), 168.9 (d, J_{C-F} = 23.4 Hz), 157.2, 157.2, 140.9, 140.3, 139.7, 137.5, 137.4, 136.7, 134.7, 130.6, 128.9, 128.6, 128.5, 128.4, 128.0, 127.7, 123.8, 121.0, 112.2, 88.3 (d, J_{C-F} = 184.7 Hz), 87.4 (d, J_{C-F} = 185.8 Hz), 68.1, 66.2, 65.85, 62.2, 61.8, 49.6 (d, J_{C-F} = 2.7 Hz), 47.5 (d, J_{C-F} = 3.8 Hz), 42.9 (d, J_{C-F} = 21.3 Hz), 42.5 – 42.4 (m), 34.2 (d, J_{C-F} = 20.7 Hz), 30.8 (d, J_{C-F} = 3.3 Hz), 25.4, 21.7, 16.0, 14.4. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2951, 1761, 1728, 1508, 1472, 1415, 1390, 1373, 1263, 1211, 1190. **HRMS (ESI)** calcd for $C_{28}H_{37}BrF_5$ [M+H]$^+$: 551.1808, found 551.1801.

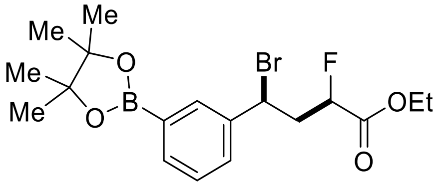
Ethyl 4-Bromo-2-fluoro-4-(3-(trifluoromethyl)phenyl)butanoate (5c)



Prepared according to the *General Procedure* from the corresponding styrene **1l** (68.9 mg, 0.40 mmol, 1.0 equiv) and ethyl 2-bromo-2-fluoroacetate (**2c**, 148 mg, 0.8 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **5c** was obtained as a colorless oil (115 mg, 0.32 mmol, 80%). *dr*: 1:1. **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.69 – 7.66 (m, 1H), 7.65 – 7.56 (m, 2H), 7.55 – 7.38 (m, 1H), 5.35 – 4.54 (m, 2H), 4.33 – 4.16 (m, 2H), 2.94 – 2.17 (m, 2H), 1.31 (m, 3H).**^{19}F NMR** (564 MHz, $CDCl_3$), δ (ppm) = -62.7 – -62.9 (m), -193.1 – -195.3 (m). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 169.8 (d, J_{C-F} = 23.4 Hz), 169.1 (d, J_{C-F} = 22.9 Hz), 168.7 (d, J_{C-F} = 23.4 Hz), 142.1, 141.4, 141.2, 132.2, 131.6 (d, J_{C-F} = 32.7 Hz), 131.0, 129.9, 129.8, 129.3, 126.0 (q, J_{C-F} = 3.5 Hz), 125.9 (q, J_{C-F} = 3.8 Hz), 125.5 (q, J_{C-F} = 3.8

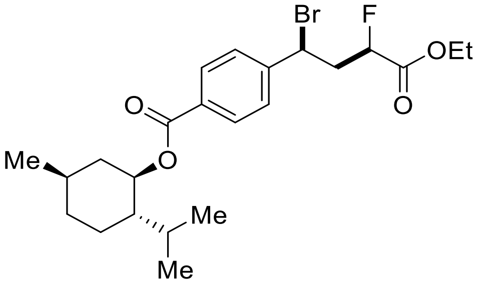
Hz), 124.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.7 (q, $J_{C\text{-}F}$ = 271.2 Hz), 123.5 (t, $J_{C\text{-}F}$ = 6.5 Hz Hz), 88.3 (d, $J_{C\text{-}F}$ = 186.4 Hz), 88.1 (d, $J_{C\text{-}F}$ = 186.4 Hz), 87.3 (d, $J_{C\text{-}F}$ = 186.4 Hz), 86.7 (d, $J_{C\text{-}F}$ = 186.4 Hz), 62.3, 61.9, 48.4 (d, $J_{C\text{-}F}$ = 3.3 Hz), 46.4 (d, $J_{C\text{-}F}$ = 3.8 Hz), 42.8 (d, $J_{C\text{-}F}$ = 20.7 Hz), 42.4 (d, $J_{C\text{-}F}$ = 20.7 Hz), 34.0 (d, $J_{C\text{-}F}$ = 21.3 Hz), 30.6 (d, $J_{C\text{-}F}$ = 3.8 Hz), 14.3. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 1760, 1739, 1451, 1373, 1325, 1296, 1193, 1164, 1123. **HRMS (EI)** calcd for $C_{13}H_{13}BrF_3O_2$ [M-F]: 337.0051, found 337.0049.

Ethyl 4-Bromo-2-fluoro-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butanoate (5d)



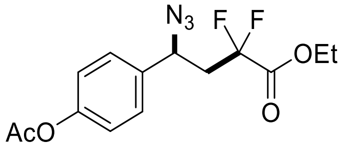
Prepared according to the *General Procedure* from the corresponding styrene **1k** (57.5 mg, 0.25 mmol, 1.0 equiv) and ethyl 2-bromo-2-fluoroacetate (**2c**, 185 mg, 1.0 mmol, 4.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **5d** was obtained as a colorless oil (80 mg, 0.19 mmol, 77%). *dr*: 1:1. **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.80 – 7.57 (m, 2H), 7.50 – 7.21 (m, 2H), 5.28 – 4.47 (m, 2H), 4.24 – 4.12 (m, 2H), 2.84 – 2.07 (m, 2H), 1.31 – 1.26 (m, 12H), 1.27 – 1.19 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -193.0 – -195.0 (m). **^{11}B NMR** (128 MHz, $CDCl_3$), δ (ppm) = 30.8. **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 169.9 (d, $J_{C\text{-}F}$ = 23.5 Hz), 169.2 (d, $J_{C\text{-}F}$ = 22.9 Hz), 140.2, 139.5, 139.1, 135.4, 135.3, 134.8, 133.8, 133.3, 132.8, 131.5, 130.3, 128.5, 128.4, 128.0, 88.3 (d, $J_{C\text{-}F}$ = 128.6 Hz), 87.5, 86.7 (d, J = 185.8 Hz), 86.7, 84.1, 83.8, 61.9, 61.5, 50.0 (d, $J_{C\text{-}F}$ = 2.8 Hz), 47.8 (d, $J_{C\text{-}F}$ = 3.8 Hz), 42.6 (d, $J_{C\text{-}F}$ = 21.0 Hz), 42.2 (d, $J_{C\text{-}F}$ = 20.5 Hz), 34.2 (d, $J_{C\text{-}F}$ = 20.9 Hz), 30.5 (d, $J_{C\text{-}F}$ = 3.3 Hz), 24.9, 24.9, 14.2, 14.1, 14.1. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2979, 1762, 1740, 1605, 1431, 1358, 1317, 1275, 1212, 1166, 1144. **HRMS (EI)** calcd for $C_{18}H_{25}BFO_4$ [M-Br]: 335.1830, found 335.1825.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-(1-Bromo-4-ethoxy-3-fluoro-4-oxobutyl)benzoate (5e)



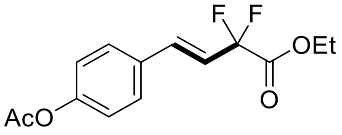
Prepared according to the *General Procedure* from the corresponding styrene **1u** (50 mg, 0.17 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 65 mg, 0.35 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **5e** was obtained as a colorless oil (72 mg, 0.15 mmol, 87%). *dr*: 1:1. **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 8.05 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 5.37 – 4.48 (m, 3H), 4.32 – 4.13 (m, 2H), 2.93 – 2.43 (m, 2H), 2.11 (dd, J = 10.3, 5.9 Hz, 1H), 1.94 (dt, J = 7.1, 3.4 Hz, 1H), 1.81 – 1.69 (m, 2H), 1.63 – 1.49 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.19 – 1.05 (m, 2H), 0.92 (d, J = 7.1 Hz, 6H), 0.79 (dd, J = 7.0, 3.0 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -194.7, -195.8 **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) =169.2 (d, $J_{C\text{-}F}$ = 22.9 Hz), 168.7 (d, $J_{C\text{-}F}$ = 22.9 Hz), 165.6, 145.6, 144.6, 131.7, 131.5, 130.6, 130.5, 127.8, 127.6, 86.9 (d, $J_{C\text{-}F}$ = 186.4 Hz), 86.7 (d, J = 186.4 Hz), 75.4 (d, $J_{C\text{-}F}$ = 3.3 Hz), 62.3 (d, $J_{C\text{-}F}$ = 3.8 Hz), 49.1 – 48.4 (m), 47.5, 47.0 – 46.5 (m), 42.7 (d, $J_{C\text{-}F}$ = 7.6 Hz), 42.1 (d, $J_{C\text{-}F}$ = 6.0 Hz), 41.2, 34.6, 31.7, 26.8 (d, $J_{C\text{-}F}$ = 2.7 Hz), 23.9 – 23.8 (m), 22.3, 21.0 (d, $J_{C\text{-}F}$ = 4.4 Hz), 16.8 – 16.7 (m), 14.4. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{v}$ = 2954, 2928, 1763, 1740, 1712, 1455, 1418, 1371, 1272, 1214. **HRMS (ESI)** calcd for $C_{23}H_{32}BrFO_4Na$ [M+Na]$^+$: 493.1366, found 493.1343.

Synthesis of Ethyl 4-(4-Acetoxyphenyl)-4-azido-2,2-difluorobutanoate (6)



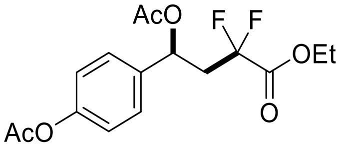
The bromide was prepared according to the *General Procedure* from the corresponding styrene **1a** (81.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After filtration through a short plug of silica and solvent evaporation, the crude was dissolved in 5 mL of dry DMSO in the presence of NaN_3 (49 mg, 0.75 mmol, 1.5 equiv). The reaction was stirred overnight at rt. Upon completion, the reaction was poured into H_2O (10 mL) and the mixture was extracted with EtOAc (3 x 10 mL). The organic phase was washed with H_2O (20 mL), and satd aq NaCl (20 mL), and the layers were separated. The organic phase was dried with Na_2SO_4 anh. After solvent removal, the crude was subjected to purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), yielding the title compound **6** as a colorless oil (95 mg, 0.30 mmol, 58%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.27 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 4.69 (dd, J = 9.5, 4.4 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 2.68 – 2.32 (m, 2H), 2.23 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -102.7 (d, J = 264.6 Hz), -106.8 (d, J = 265.2 Hz). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 169.2, 163.5 (t, $J_{C\text{-}F}$ = 32.1 Hz), 151.0, 135.5, 127.9 (2C), 122.3 (2C), 114.4 (t, $J_{C\text{-}F}$ = 255.4 Hz), 63.2, 59.5 (m), 41.2 (t, $J_{C\text{-}F}$ = 23.8 Hz), 21.1, 13.9. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{v}$ = 2985, 2105, 1760, 1508, 1425, 1371, 1340, 1303, 1189, 1167, 1085. **HRMS (EI)** calcd for $C_{14}H_{15}F_2O_4$ [M-N_3]: 285.0938, found 285.0988.

Ethyl (*E*)-4-(4-Acetoxyphenyl)-2,2-difluorobut-3-enoate (7)



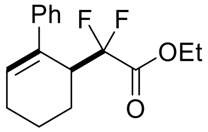
The bromide was prepared according to the *General Procedure* from the corresponding styrene **1a** (81.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After filtration through a short plug of silica and solvent evaporation, the crude was dissolved in 5 mL of dry EtOH in the presence of EtONa (170 mg, 2.5 mmol, 5.0 equiv). The reaction was stirred overnight at rt. Upon completion, the reaction was poured in H_2O (10 mL) and the mixture was extracted with EtOAc (3 x 10 mL). The organics were washed with H_2O and dried over Na_2SO_4 anh. After solvent removal, the crude was subjected to purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), yielding the title compound **8** as a colorless oil (72 mg, 0.26 mmol, 51%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.38 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.98 (dt, *J* = 16.1, 2.5 Hz, 1H), 6.18 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.23 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.3 (s). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 169.2, 163.8 (t, $J_{C\text{-}F}$ = 34.9 Hz), 151.6, 135.8 (t, $J_{C\text{-}F}$ = 9.5 Hz), 131.8, 128.6 (2C), 122.1 (2C), 119.1 (t, $J_{C\text{-}F}$ = 25.0 Hz), 112.6 (t, $J_{C\text{-}F}$ = 248.7 Hz), 63.2, 21.1, 14.0. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 1761, 1656, 1604, 1508, 1418, 1371, 1299, 1268, 1195, 1167, 1075. **HRMS (ESI)** calcd for $C_{14}H_{15}F_2O_4$ $[M+H]^+$: 285.0938, found 285.0938.

Ethyl 4-Acetoxy-4-(4-acetoxyphenyl)-2,2-difluorobutanoate (8)



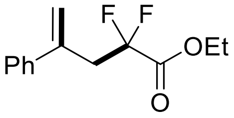
The bromide was prepared according to the *General Procedure* from the corresponding styrene **1a** (81.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After filtration through a short plug of silica, AgOAc (83 mg, 0.5 mmol, 1.0 equiv) was added, and the mixture was heated at 50 ºC for 4 h. Upon completion, the reaction was poured into H_2O (10 mL) and the mixture was extracted with EtOAc (3 x 10 mL). The organics were washed with H_2O and dried over Na_2SO_4 anh. After solvent removal, the crude was subjected to purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), yielding the title compound **8** as a colorless oil (100 mg, 0.29 mmol, 59%). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) = ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.04 (dd, *J* = 9.7, 3.9 Hz, 1H), 4.27 (q, *J* = 7.1, 2H), 2.82 (m, 1H), 2.51 (m, 1H), 2.29 (s, 3H), 2.03 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.6 (d, *J* = 266.5 Hz), -105.7 (d, *J* = 267.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) = 169.4, 169.3, 163.5 (t, *J* = 32.3 Hz), 150.7, 136.5, 127.7 (2C), 121.9 (2C), 117.5 114.2 (t, $J_{C\text{-}F}$ = 252.6 Hz), 69.2 (t, $J_{C\text{-}F}$ = 5.1 Hz), 63.01, 40.9 (t, *J* = 23.4 Hz), 21.1, 20.9, 13.9. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 1761, 1659, 1656, 1600, 1501, 1418, 1371, 1300, 1268, 1195, 1165. **HRMS (ESI)** calcd for $C_{16}H_{18}F_2O_6Na$ [M+Na]$^+$: 367.0969, found 367.0962.

Ethyl 2,2-Difluoro-2-(2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)acetate (9)



Prepared according to the *General Procedure* from the corresponding styrene **1ac** (79.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **9** was obtained as a colorless oil (57 mg, 0.20 mmol, 41%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.30 – 7.04 (m, 5H), 6.00 (t, *J* = 6.0 Hz, 3H), 3.74 – 3.58 (m, 2H), 3.55 – 3.41 (m, 1H), 2.33 – 2.06 (m, 4H), 1.96 – 1.56 (m, 4H), 1.07 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -105.4 (d, *J* = 250.5 Hz), -108.4 (d, *J* = 250.1 Hz). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 164.4 (t, $J_{C\text{-}F}$ = 32.6 Hz), 142.1, 133.2, 128.0 (2C), 127.0 (2C), 116.5 (t, $J_{C\text{-}F}$ = 257.8 Hz), 62.5, 39.9 (dd, $J_{C\text{-}F}$ = 23.1, 21.0 Hz), 25.3, 22.4 (2C), 18.1 (2C), 13.6. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 3025, 2941, 1759, 1492, 1445, 1372, 1295, 1265, 1207, 1185, 1145, 1109. **HRMS (ESI)** calcd for $C_{16}H_{18}F_2O_2Na$ [M+Na]$^+$: 303.1173, found 303.1171.

Ethyl 2,2-Difluoro-4-phenylpent-4-enoate (10)

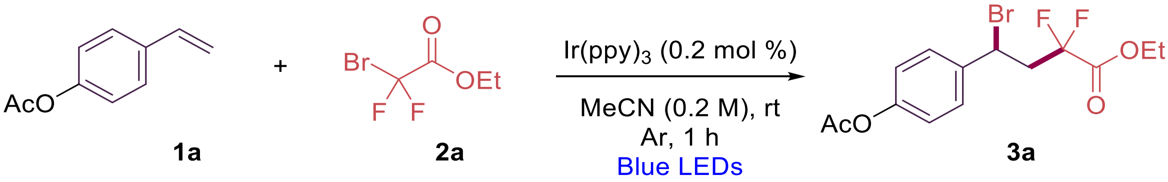


Prepared according to the *General Procedure* from the corresponding styrene **1ad** (59.1 mg, 0.50 mmol, 1.0 equiv) and ethyl 2-bromo-2,2-difluoroacetate (**2a**, 203 mg, 1.0 mmol, 2.0 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **10** was obtained as a colorless oil (38 mg, 0.16 mmol, 32%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) = 7.33 – 7.21 (m, 5H), 5.43 (bs, 1H), 5.24 (bs, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.23 (td, *J* = 15.6, 1.0 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) = -103.3 (s). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) = 163.8 (t, $J_{C\text{-}F}$ = 32.5 Hz), 140.2, 128.4 (2C), 128.2, 127.9, 126.4 (2C), 119.3, 115.1 (t, $J_{C\text{-}F}$ = 252.3 Hz), 62.8, 40.3, 13.8. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 3041, 2990, 1760, 1495, 1446, 1374, 1335, 1292, 1221, 1183, 1116, 1074. **HRMS (ESI)** calcd for $C_{13}H_{14}F_2O_2Na$ [M+Na]$^+$: 263.0860, found 263.0852.

5. Mechanistic Investigations

A. *Quantum yield*

The quantum yield of the reaction was determined using the procedure reported previously:[10] Styrene **1a** and ethyl bromodifluoroacetate **2a** were used as model substrates to determinate the quantum yield of this transformation, using 1,3,5-trimethoxybenzene as internal standard in a proportion 1:1 with **1a**.



The quantum yield of the reaction is defined as:

$$\Phi(\text{reaction at 456 nm}) = \frac{\text{mol of formed product}}{\text{mol of photon flux} \cdot \text{t} \cdot \text{f}} \qquad (1)$$

where Φ is the quantum yield of the reaction, t is the time of the reaction (s), and f is the incident light absorbed by the $Ir(ppy)_3$ photocatalyst at 456 nm. The photon flux is calculated by standard ferrioxalate actinometry[11] (see Section *A.3*).

A.1. Incident light absorbed by $Ir(ppy)_3$

The fraction of light, f, absorbed was determined according to equation 2:

$$\text{F} = 1 - 10^{-\text{A}} \qquad (2)$$

Where A is the absorbance of the $Ir(ppy)_3$ in MeCN at 456 nm. The wavelength of 458 nm was chosen based on the known absolute $\Phi(Fe^{+2})$ value. The absorbance of the reaction components (**1a**: 0.2 M, **2a**: 0.4 M and $Ir(ppy)_3$: 0.2 mM) in MeCN (1 mL) to a cuvette equipped with a Teflon-coated magnetic stir bar and stirred for 30 seconds. The absorbance was recorded. The absorbance (A) at 458 nm was determined to be 1.067 (*Figure S2*), thus indicating the fraction of light absorbed is 0.91 according to equation 2.

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[10] El Khatib, M.; Serafim, R. A. M.; Molander, G. A. *Angew. Chem. Int. Ed.* **2016**, *55*, 254.

[11] Demas, J. N.; Bowman, W. D.; Zalewski, E. F.; Velapoidl, R. *J. Phys. Chem.* **1981**, *85*, 2766.

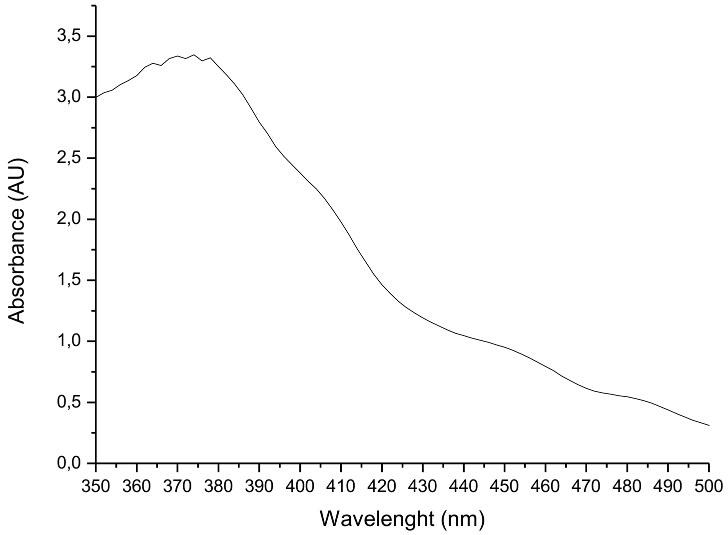


Figure S2. *UV-Vis spectra of all reaction components (**1a**: 0.2 M, **2a**: 0.4 M and Ir(ppy)$_3$: 0.2 mM) in MeCN*

A.2. The photoredox reaction

The photoredox transformation was developed using the general procedure for 60 min. Afterwards, 1,3,5-trimethoxybenzene was added as internal standard, and the solvent was evaporated. The yield of the reaction was determined by ^{1}H NMR (*Figure S3*), where 0.024 mmols (12%) of the desired compound were obtained.

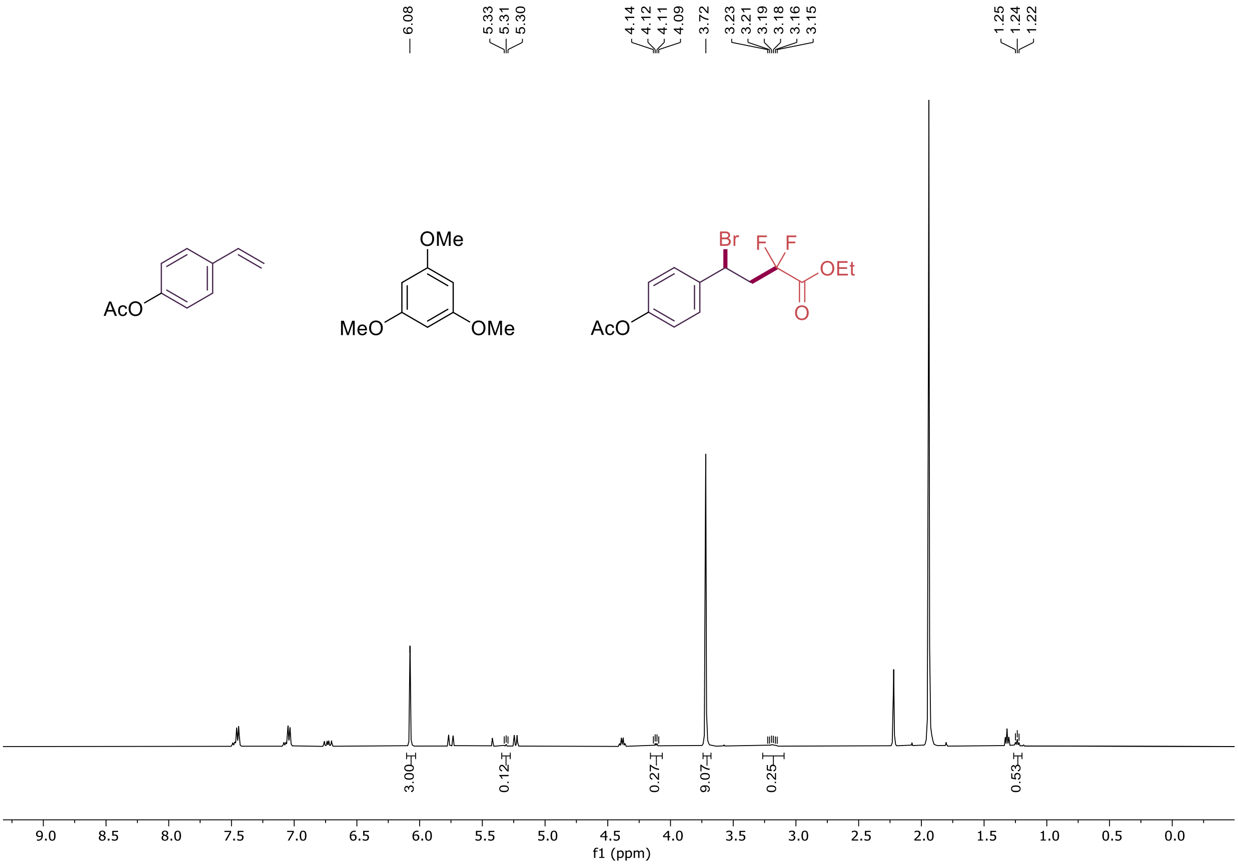


Figure S3. ^{1}H NMR (500 MHz, CDCl$_3$) of the reaction after 60 min in the presence of 1,3,5-trimethoxybenzene

A.3. Photon flux at 458 nm

Standard ferrioxalate actinometry was used to determine the photon flux of the spectrophotometer using equations 3 and 4. For the ferrioxalate actinometer, the production of iron(II) ions proceeds by the following reactions:[3]

$$[Fe(C_2O_4)n]^{+(3-2n)} \xrightarrow{\text{light}} Fe^{+2} + (n-1)(C_2O_4)^{-2} + C_2O_4^{-}$$

$$[Fe(C_2O_4)n]^{+(3-2n)} + C_2O_4^{-} \longrightarrow Fe^{+2} + n(C_2O_4)^{-2} + 2\,CO_2$$

The moles of Fe^{+2} formed are determined spectrophotometrically by development with 1,10-phenanthroline (phen) to form the red $[Fe(phen)_3]^{+2}$ moiety ($\lambda = 510$ nm).[3] The photon flux is defined as shown in equation 3:

$$\text{Photon flux} = \frac{\text{mol Fe}^{+2}}{\Phi(\text{Fe}^{+2}) \cdot \text{t} \cdot \text{f}} \qquad (3)$$

where Φ is the quantum yield for the ferrioxalate actinometer (0.84 at $\lambda = 458$ nm), t is the time (s), f ~1, and the mol of Fe^{+2} are calculated according to equation 4.

$$\text{mol (Fe}^{+2}) = \frac{\text{V} \cdot \Delta\text{A}}{\text{l} \cdot \epsilon} \qquad (4)$$

where V is the total volume of the solution, ΔA is the difference in absorbance between irradiated and nonirradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11110 L mol^{-1} cm^{-1}).[3]

B.4. Experimental

The following solutions were prepared in the dark (flasks were wrapped in aluminum foil) and stored in the dark at room temperature:

– Ferrioxalate solution (0.15 M): Potassium ferrioxalate hydrate (1.312 g) was added to a flask wrapped in aluminum foil containing H_2SO_4 (20 mL, 0.05 M). The flask was stirred for complete solvation of the green solid in complete darkness. It is noteworthy that the solution should not be exposed to any incident light.

– Developer solution: 1,10-Phenanthroline (50 mg) and NaOAc (11.25 g) was added to a flask containing H_2SO_4 (50 mL, 0.5 M) and sonicated until completely solvated.

The absorbance of the non-irradiated sample. The buffered solution of phen (350 μL) was added to a ferrioxalate solution (2.0 mL) in a vial that had been covered with aluminum foil and with the lights of the laboratory switched off. The vial was capped and allowed to rest for 1 h and then transferred to a cuvette. The absorbance of the non-irradiated solution was measured at 510 nm to be 0.32 (average of two determinations, see *Figure S4*).

The absorbance of the irradiated sample. In a cuvette equipped with a stir bar was added the ferrioxalate solution (2.0 mL), and the stirred solution was irradiated for 90 s at λ = 458 nm with an excitation slit width = 10.0 nm. After irradiation, the buffered phen solution (350 µL) was added to the cuvette and allowed to rest for 1 h in the dark to allow the ferrous ions to coordinate completely to phen. The absorbance was measured at 510 nm to be 1.80 (average of two determinations, *Figure S4*).

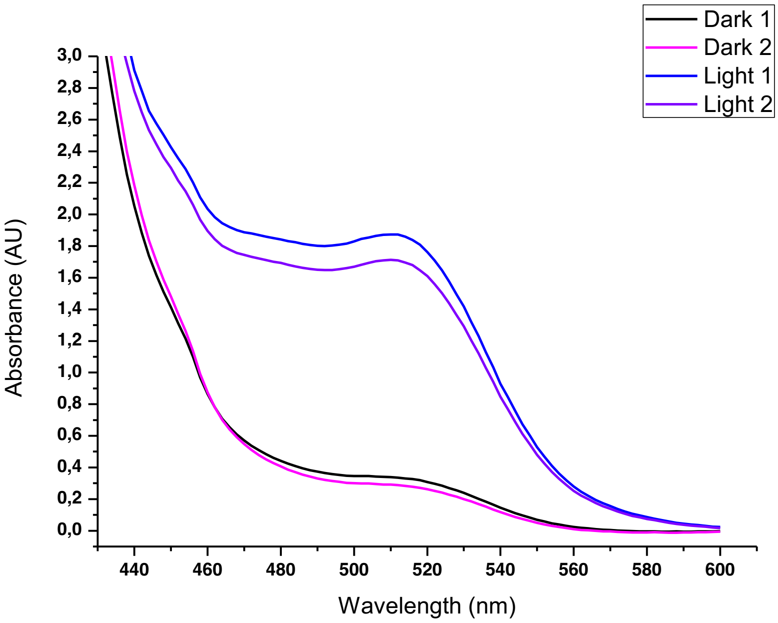


Figure S4. *Absorption spectra for irradiated and non-irradiated samples of red [Fe(phen)$_3$]$^{+2}$*

Photon flux sample calculation. Sample calculation:

$$\text{mol (Fe}^{+2}) = \frac{\text{V} \cdot \Delta\text{A}}{\text{l} \cdot \epsilon} \qquad (4)$$

$$\text{mol (Fe}^{+2}) = \frac{0.00235\ \text{L} \cdot 1.48}{1.0\ \text{cm} \cdot 11100\ \text{L} \cdot \text{mol}^{-1}\text{cm}^{-1}} = 3.13\text{x}10^{-7}\text{mol}$$

$$\text{Photon flux} = \frac{\text{mol Fe}^{+2}}{\Phi(\text{Fe}^{+2}) \cdot \text{t} \cdot \text{f}} \qquad (3)$$

$$\text{Photon flux} = \frac{3.13\text{x}10^{-7}\text{mol}}{0.84 \cdot 90\ \text{s} \cdot 1} = \mathbf{4.14x10^{-9}\ einstein\ s^{-1}}$$

A.5. Quantum yield of the photoinduced transformation

Therefore, the quantum yield of the reaction was determined to be:

$$\Phi(\text{reaction at 458 nm}) = \text{mol of formed}\frac{\text{product}}{\text{mol of photon flux} \cdot \text{t} \cdot \text{f}} \qquad (1)$$

$$\boldsymbol{\Phi}(\textbf{reaction at 458 nm}) = \frac{2.4\text{x}10^{-5}\ \text{mol}}{4.14\text{x}10^{-9}\ \text{einstein s}^{-1} \cdot 3600\ \text{s} \cdot 0.91} = \mathbf{1.8}$$

The quantum yield studies indicate that this is a radical-chain process as evidenced by the Φ value. In other words, the quantum yield value indicated that 1.8 equivalents of product are formed for every photon absorbed, which is a result that could only be consistent with a radical chain mechanism.

B. Light-off experiment

To determine the necessity of constant light irradiation with the optimized conditions, a reaction mixture was irradiated for 10 min, and then the light source was removed. The reaction was allowed to proceed overnight, after which a ^{1}H NMR crude analysis showed only 10% yield. Given the low photochemical quantum yield value obtained through our experiments (1.8) and very low photocatalyst loading (1000 ppm), the reaction requires a longer time to proceed to complete conversion, thus requiring constant LED irradiation.

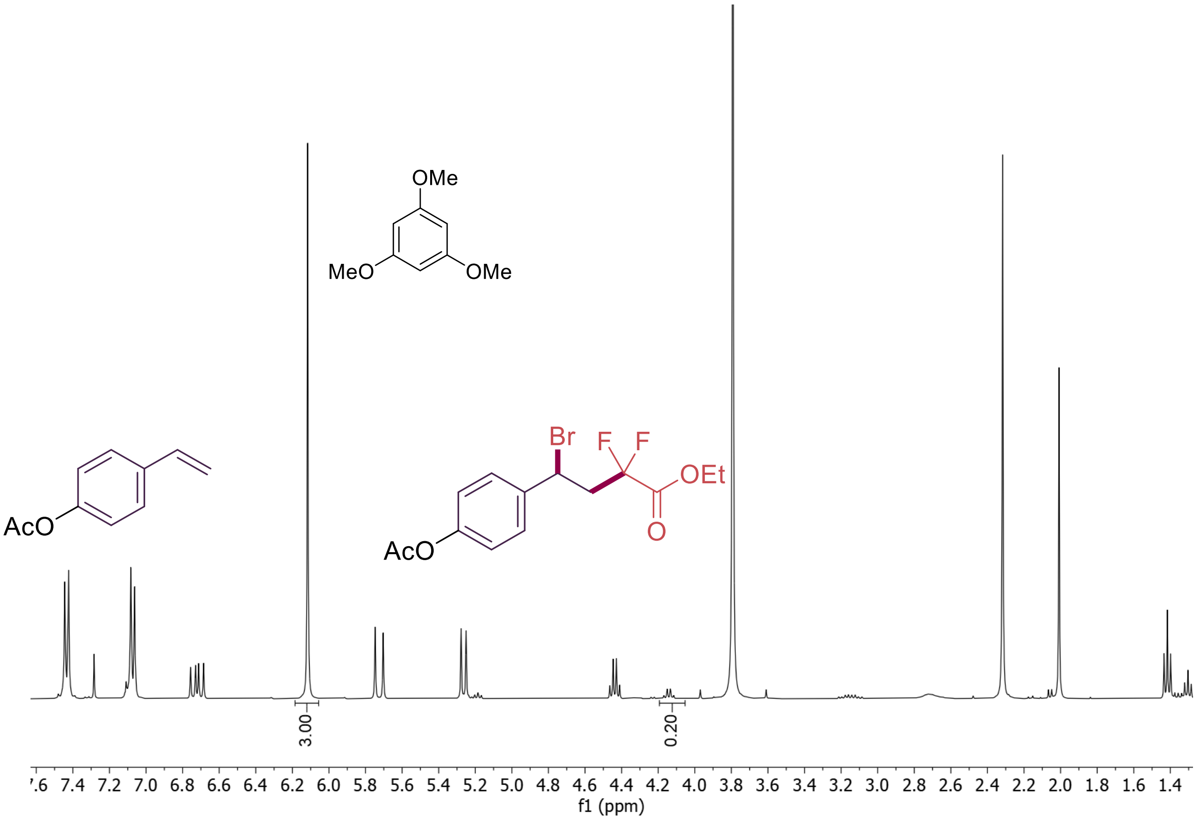
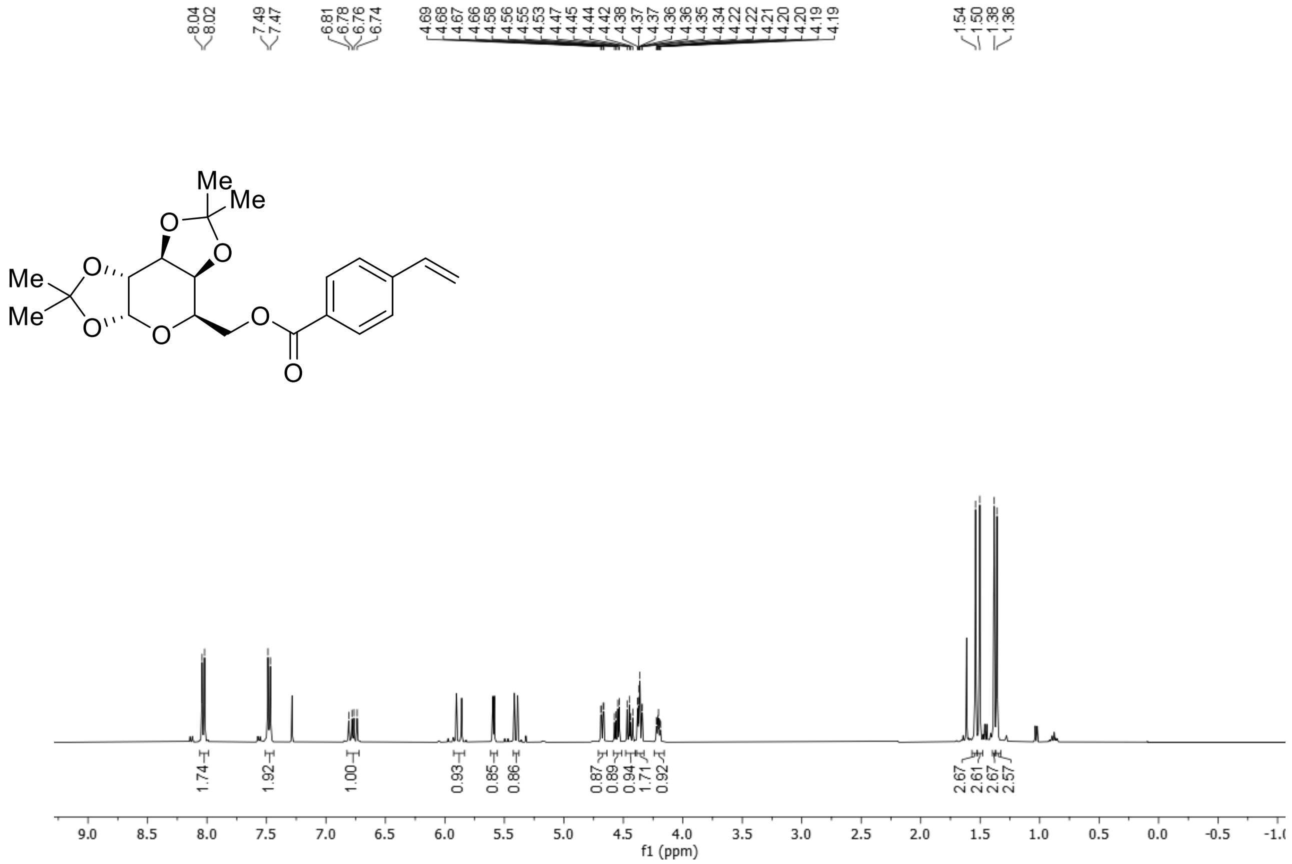
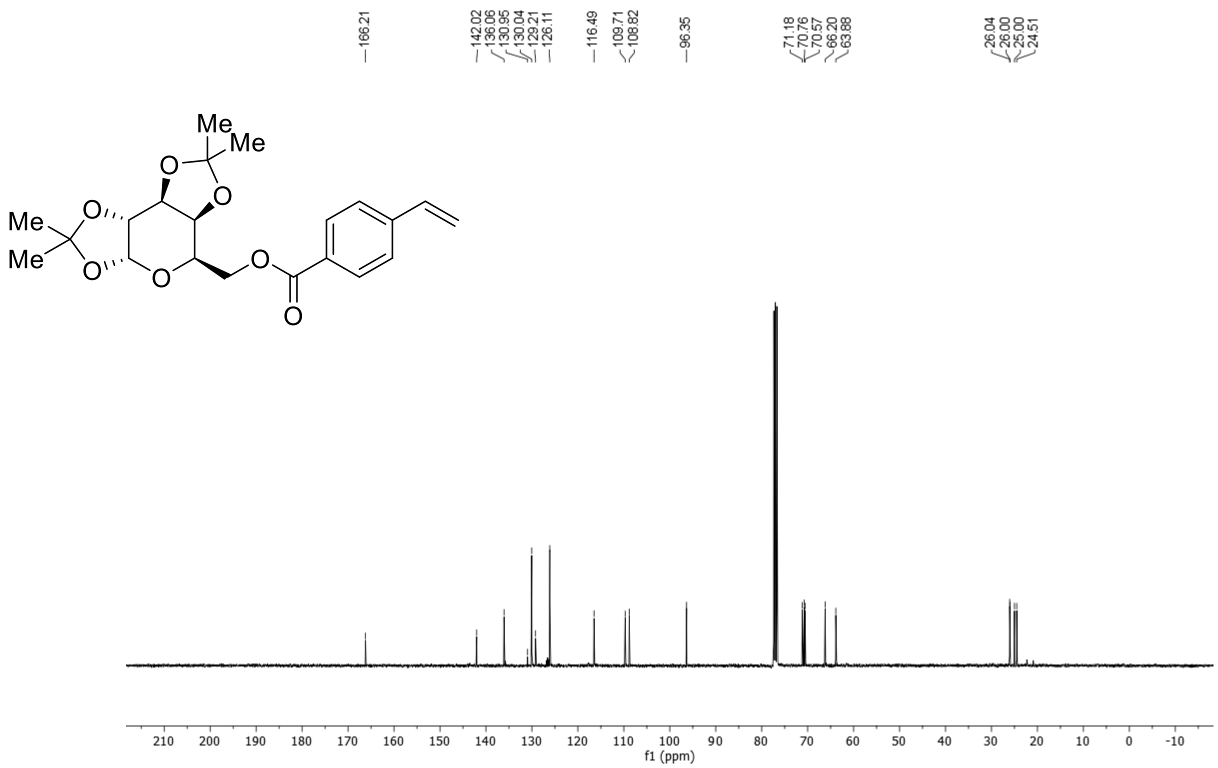


Figure S5. ^{1}H NMR (400 MHz, CDCl$_3$) of the reaction (10 min irradiation and 15h stirring without irradiation) in the presence of 1,3,5-trimethoxybenzene

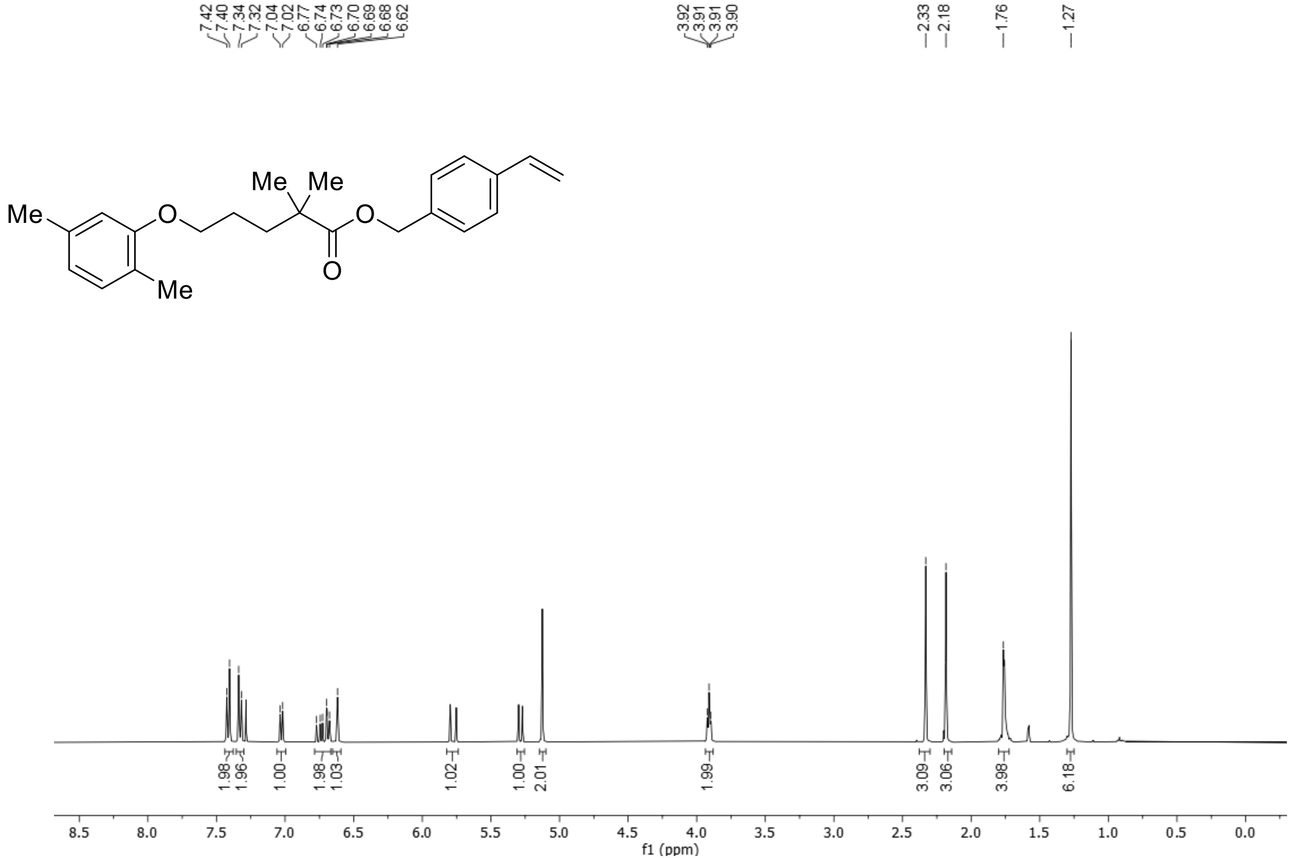
6. NMR spectra



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

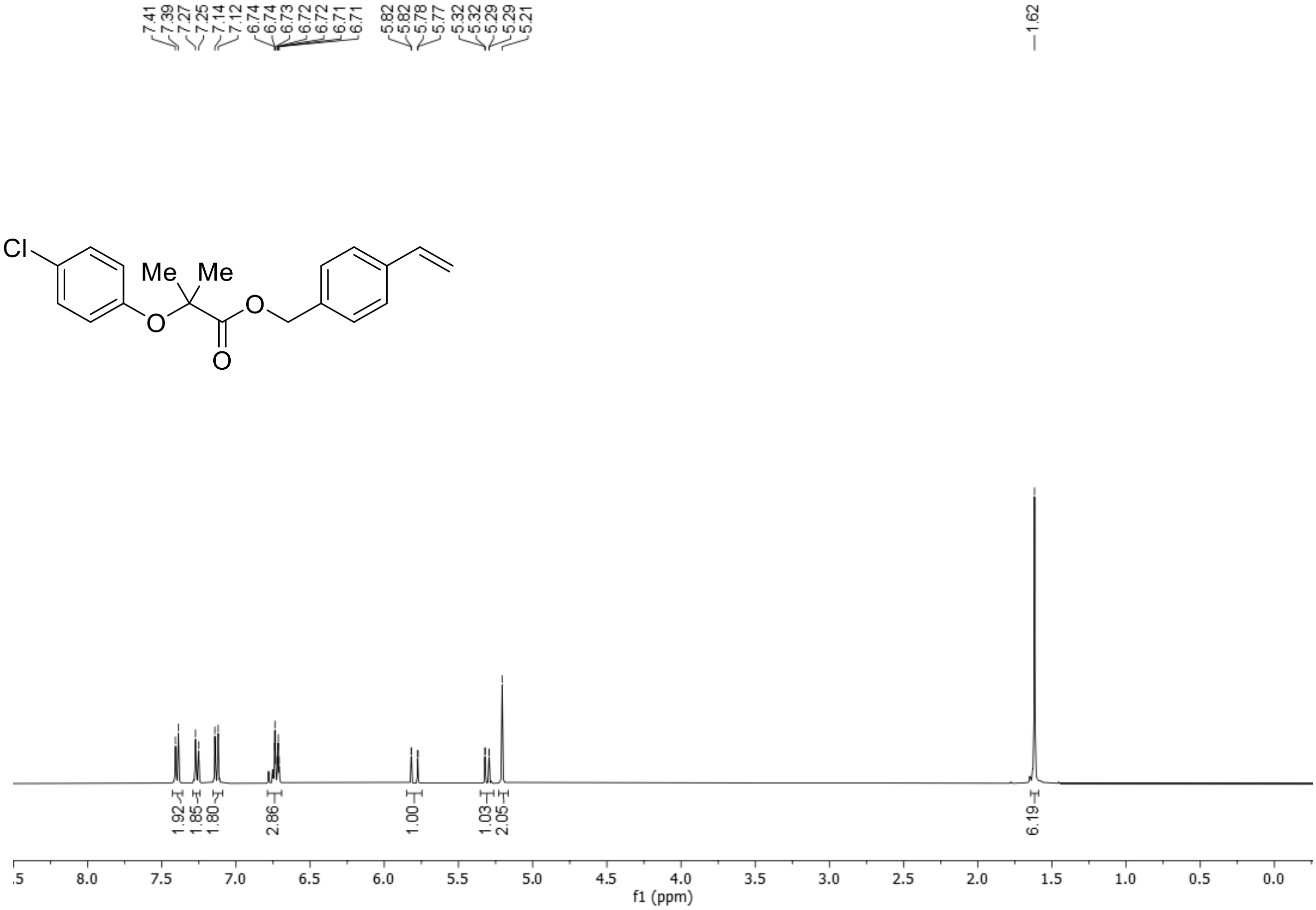


^{13}C NMR (101 MHz, CDCl$_3$) of compound **1p.**

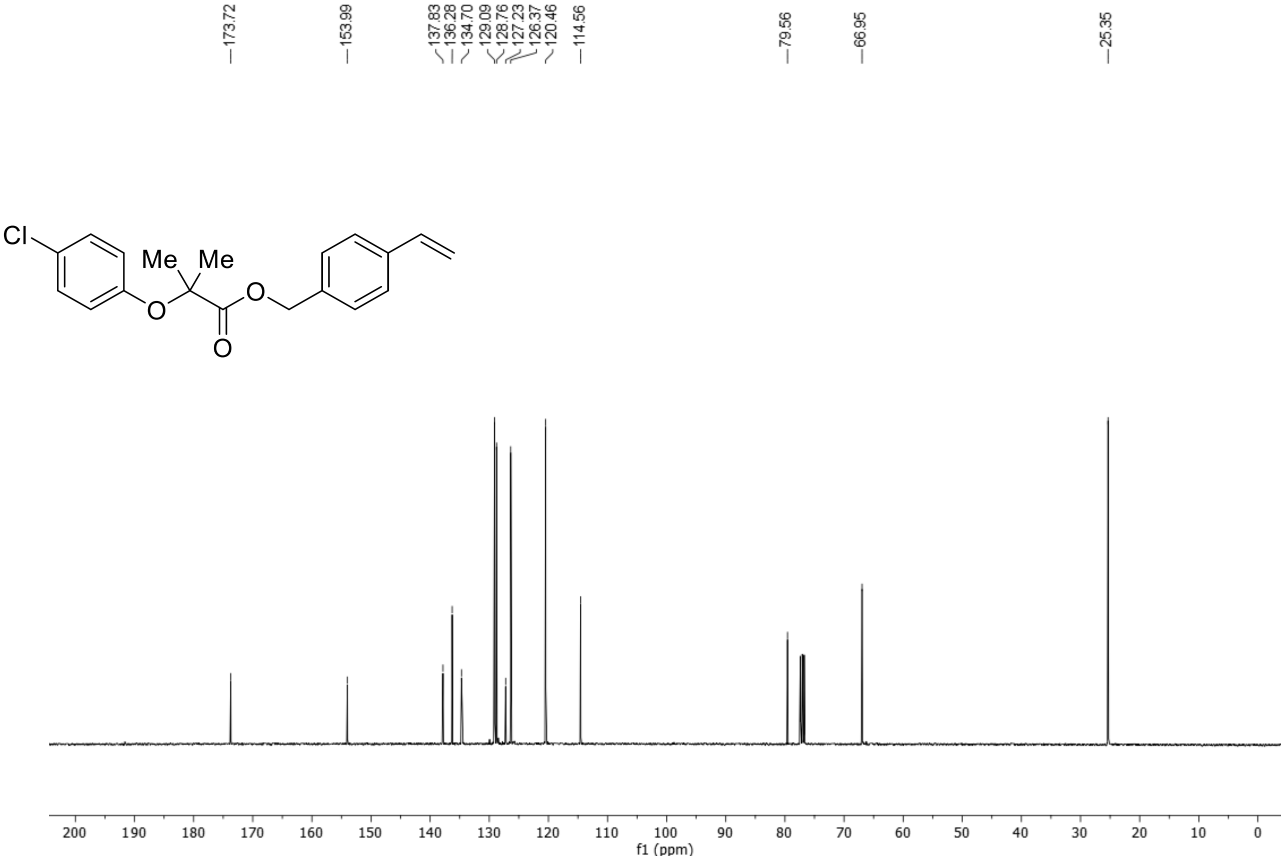


^{1}H NMR (400 MHz, CDCl$_3$) of compound **1q**.

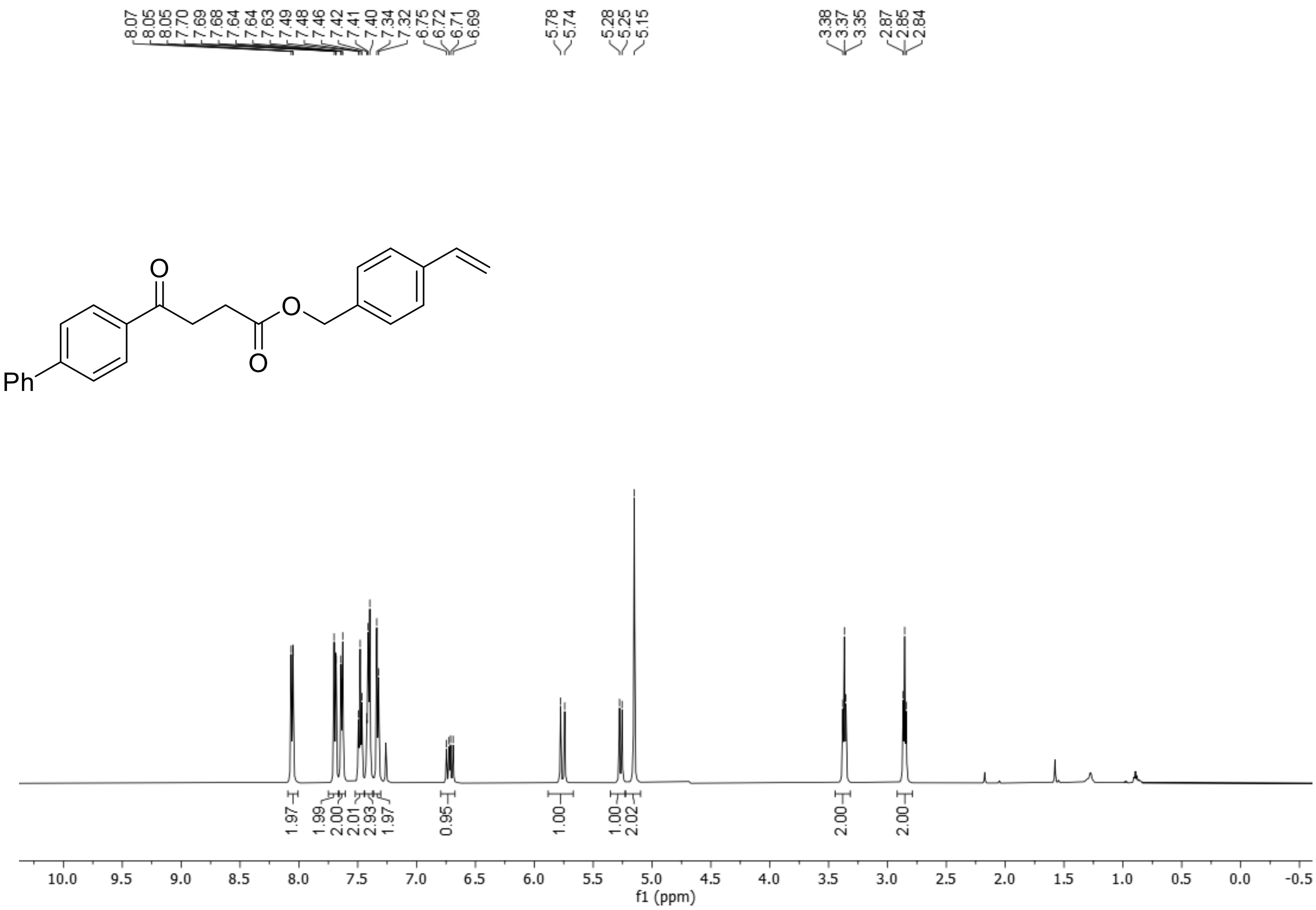
^{13}C NMR (101 MHz, CDCl$_3$) of compound **1q.**



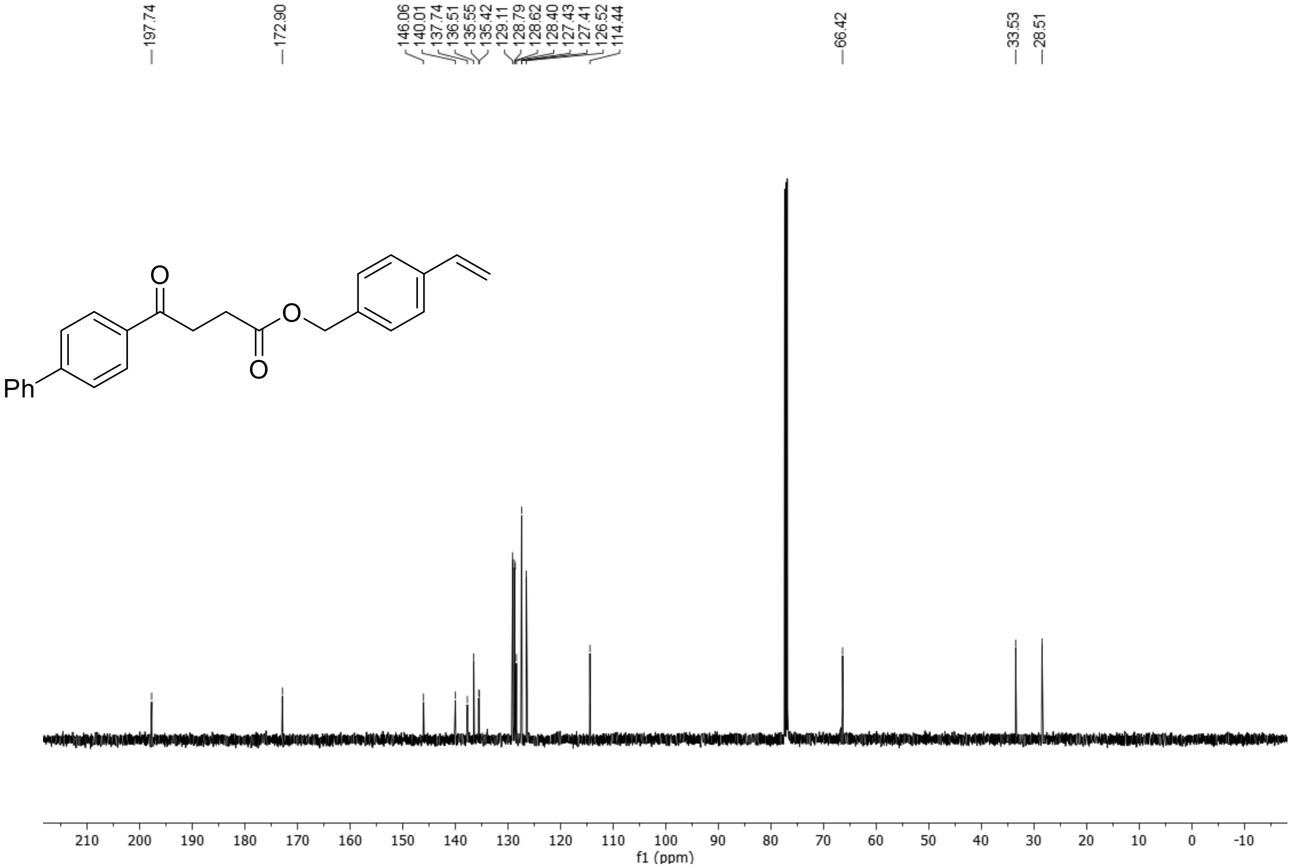
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1r**.



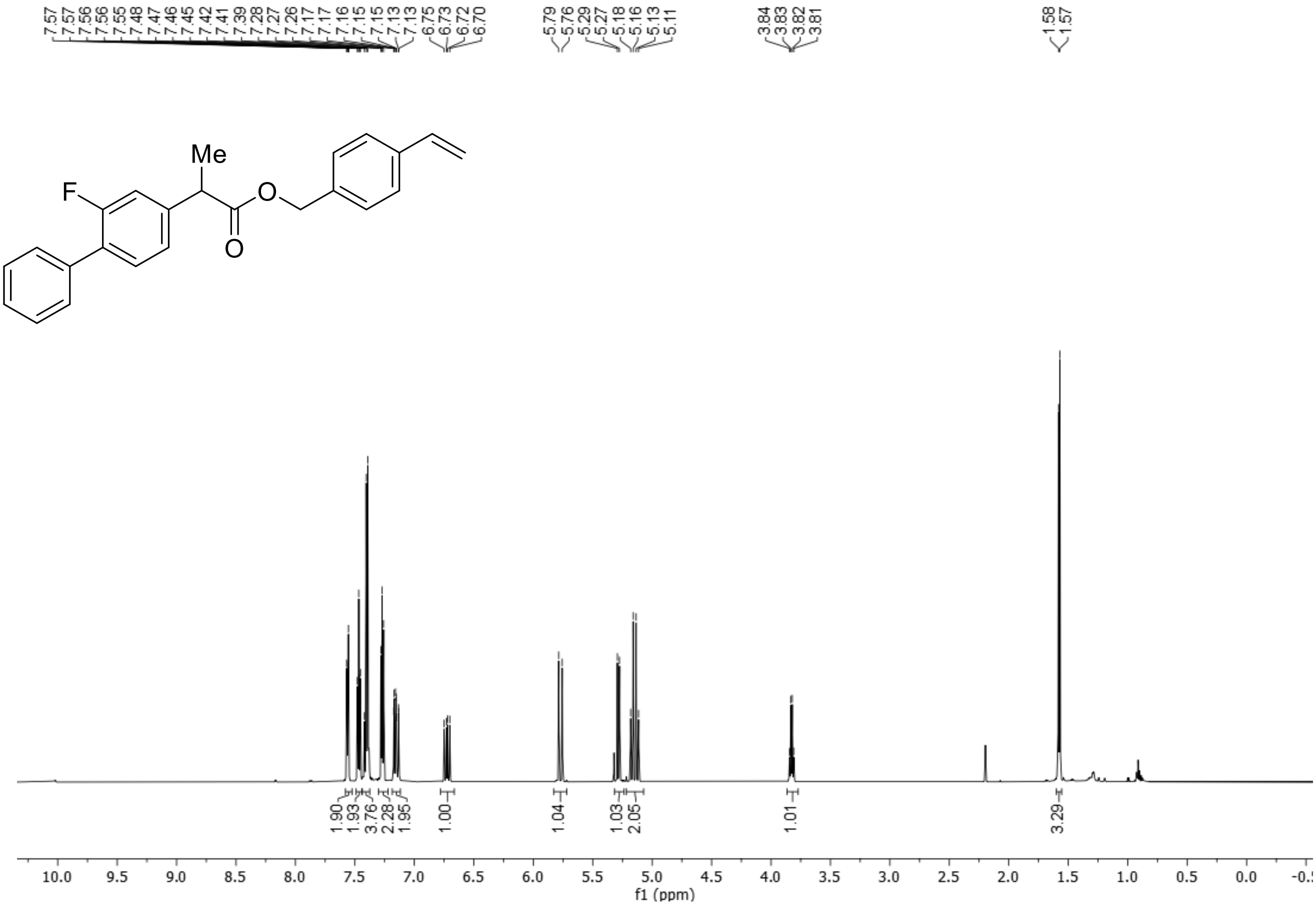
^{13}C NMR (101 MHz, CDCl$_3$) of compound **1r.**



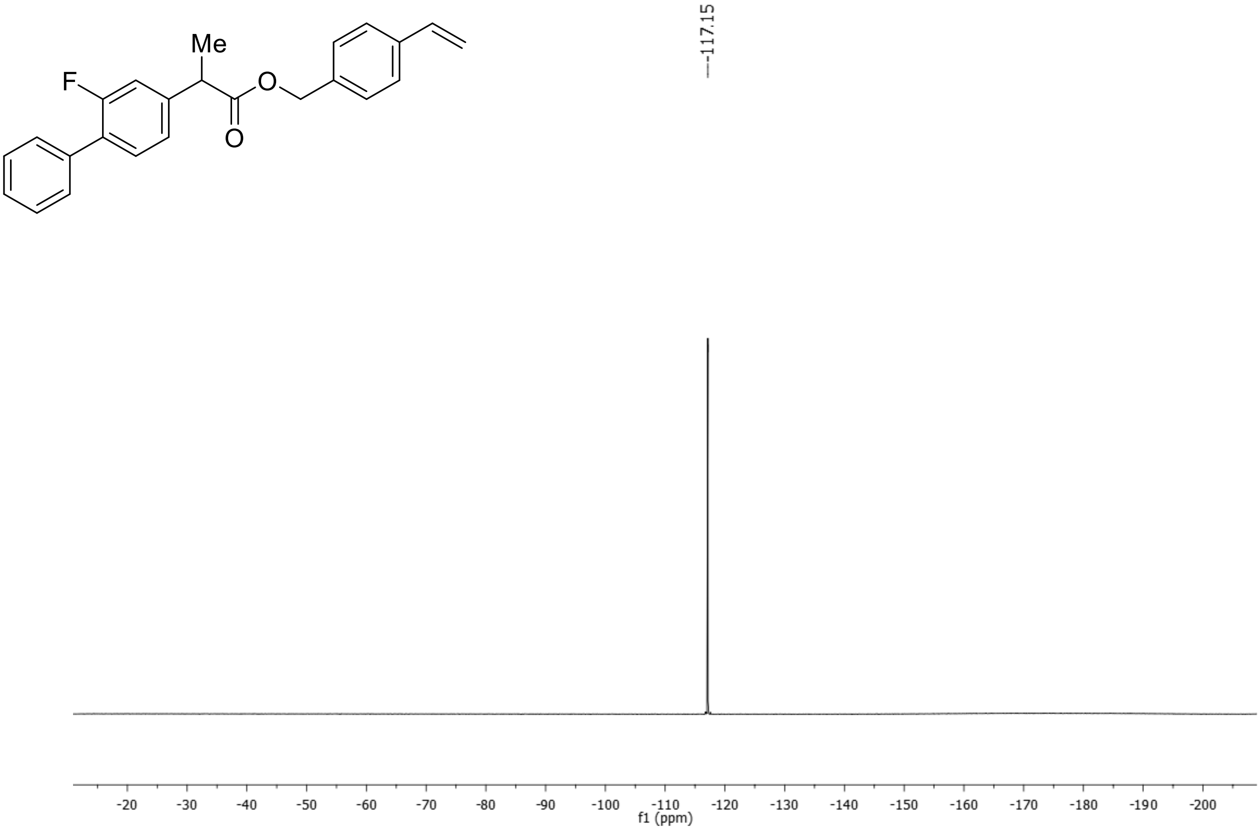
^{1}H NMR (500 MHz, CDCl$_3$) of compound **1s**.



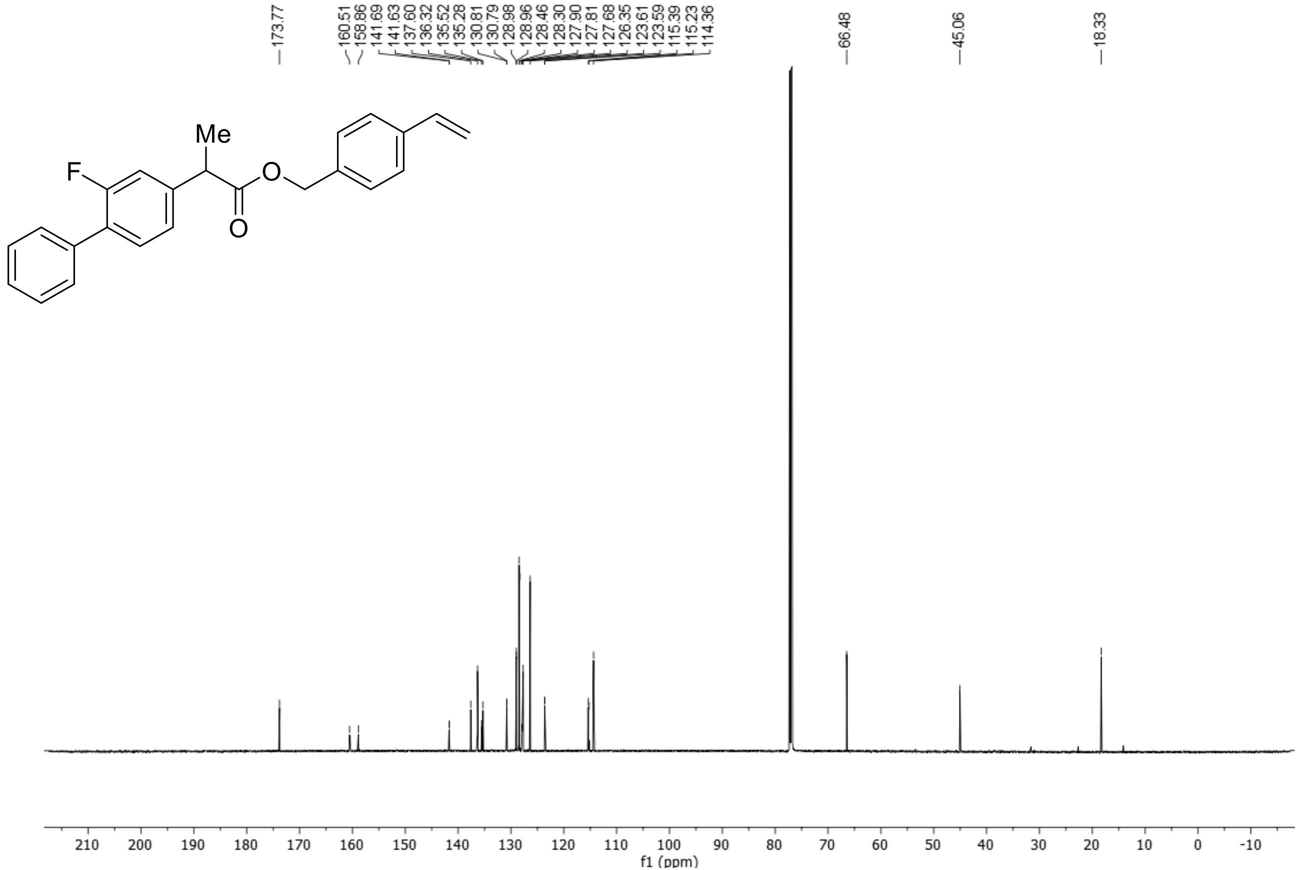
^{13}C NMR (126 MHz, CDCl$_3$) of compound **1s.**



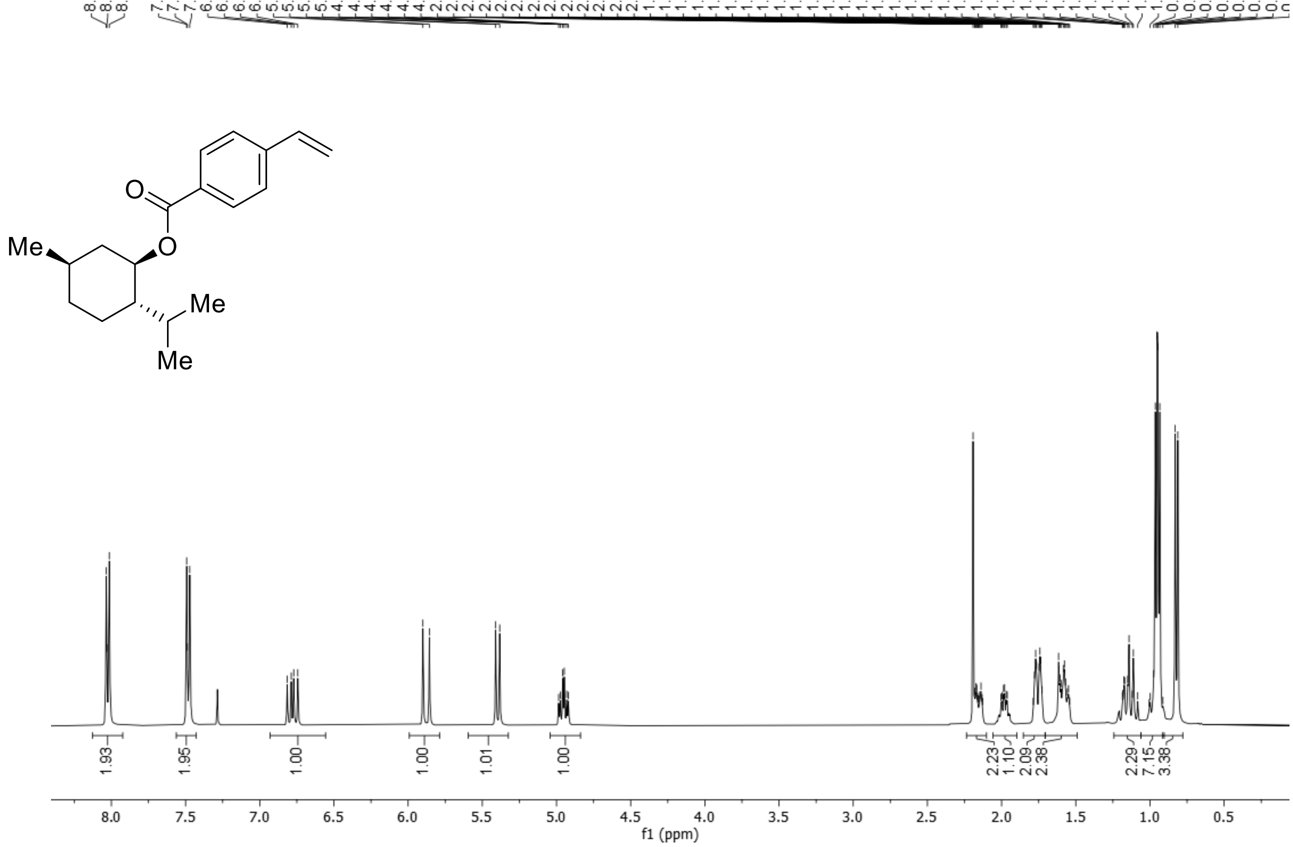
^{1}H NMR (600 MHz, CDCl$_3$) of compound **1t**.



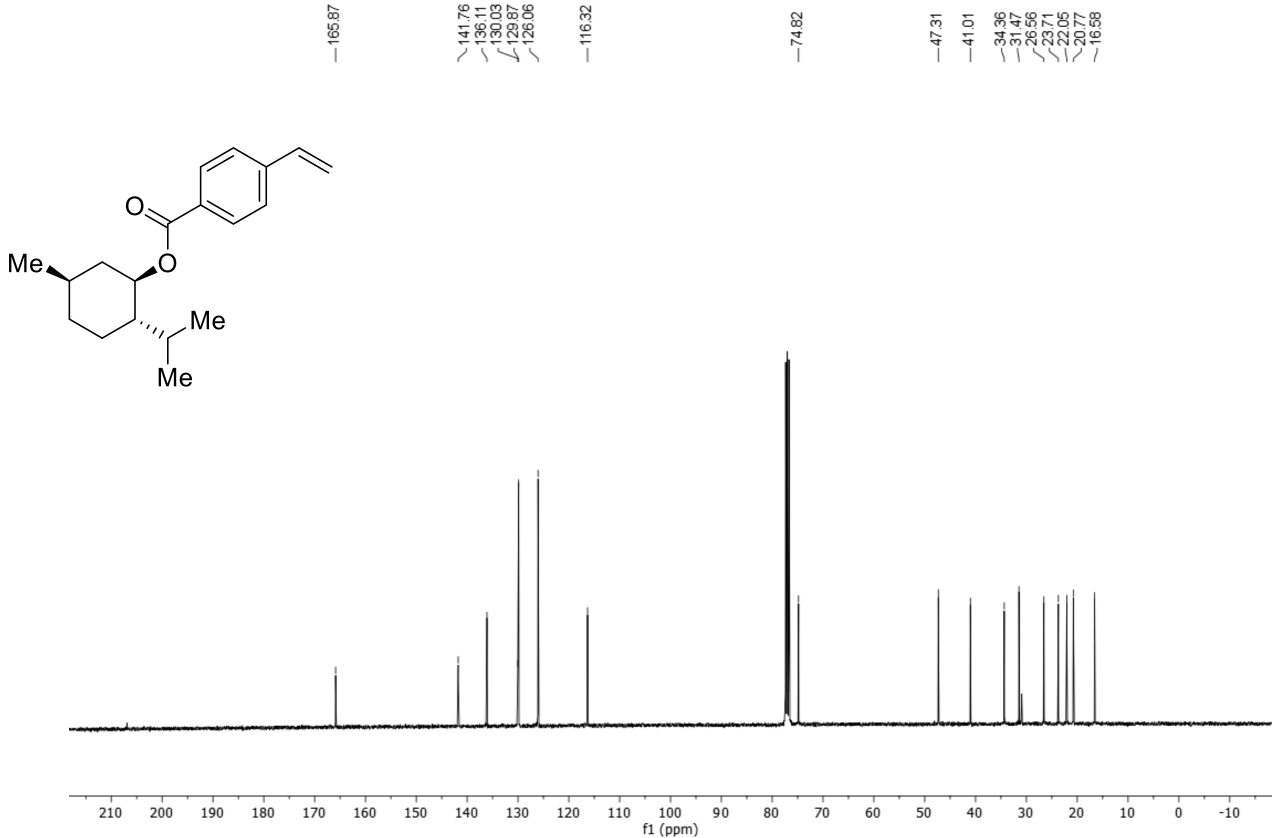
^{19}F NMR (376 MHz, CDCl$_3$) of compound **1t**.



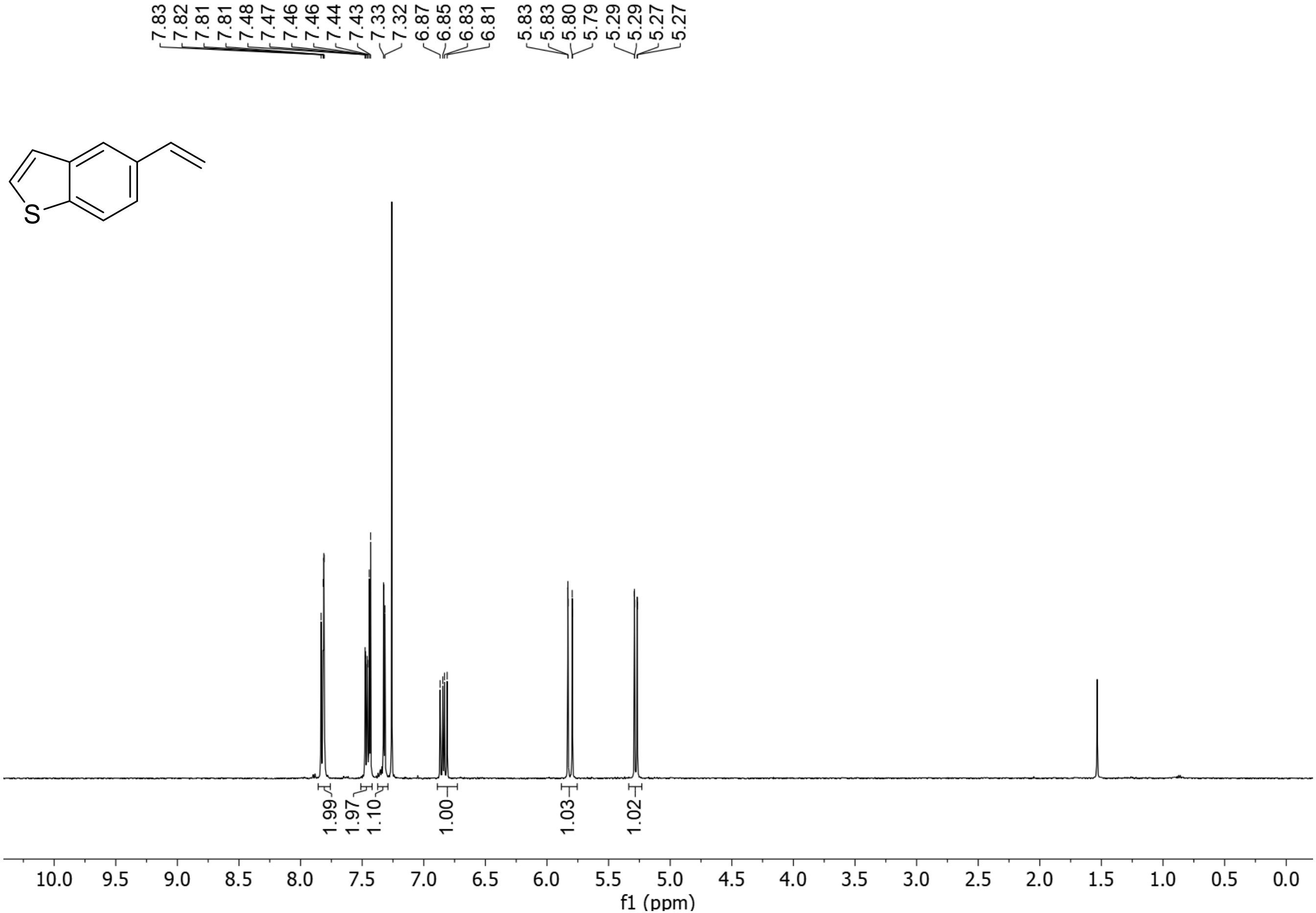
^{13}C NMR (151 MHz, CDCl$_3$) of compound **1t.**



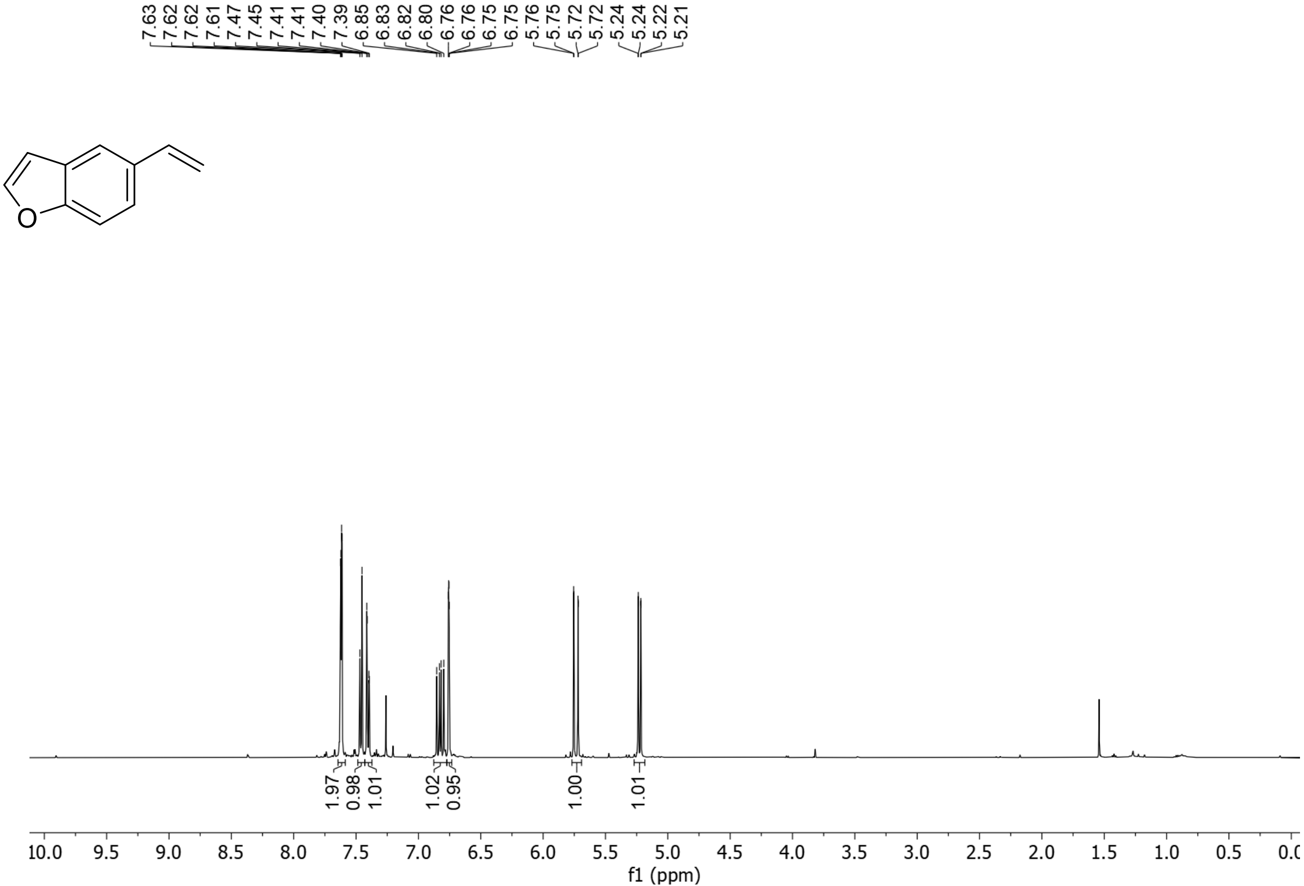
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1u**.



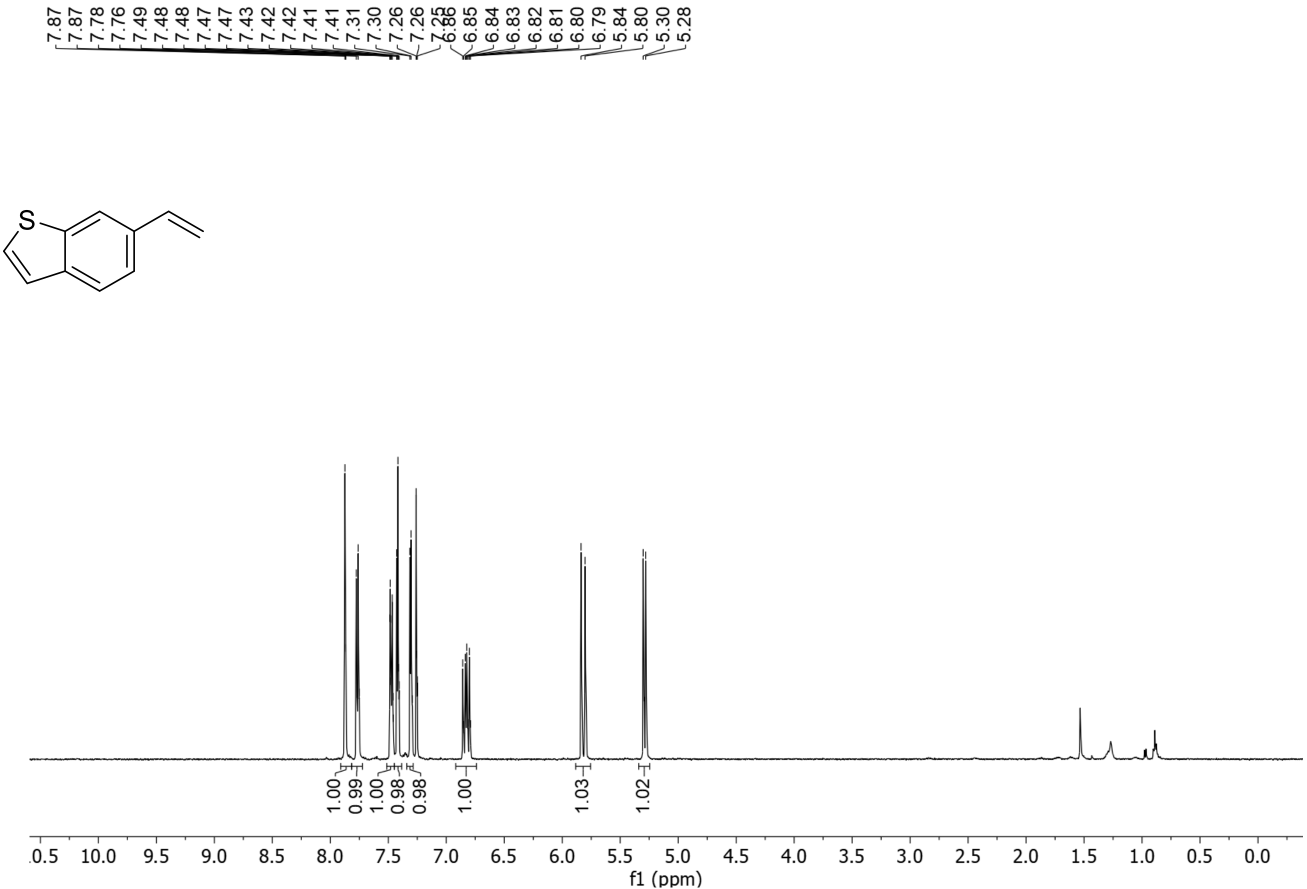
^{13}C NMR (101 MHz, CDCl$_3$) of compound **1u.**



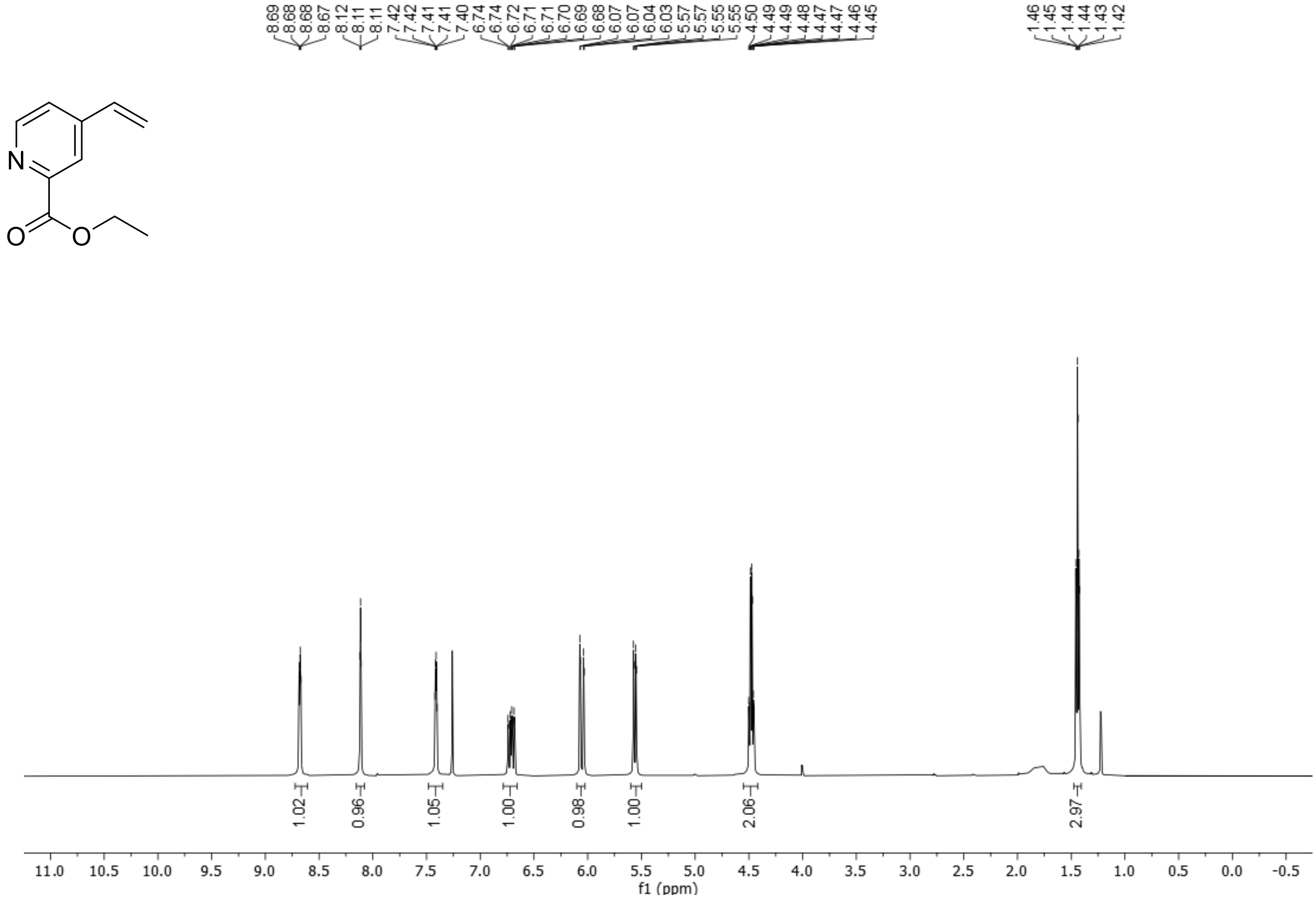
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1w**.



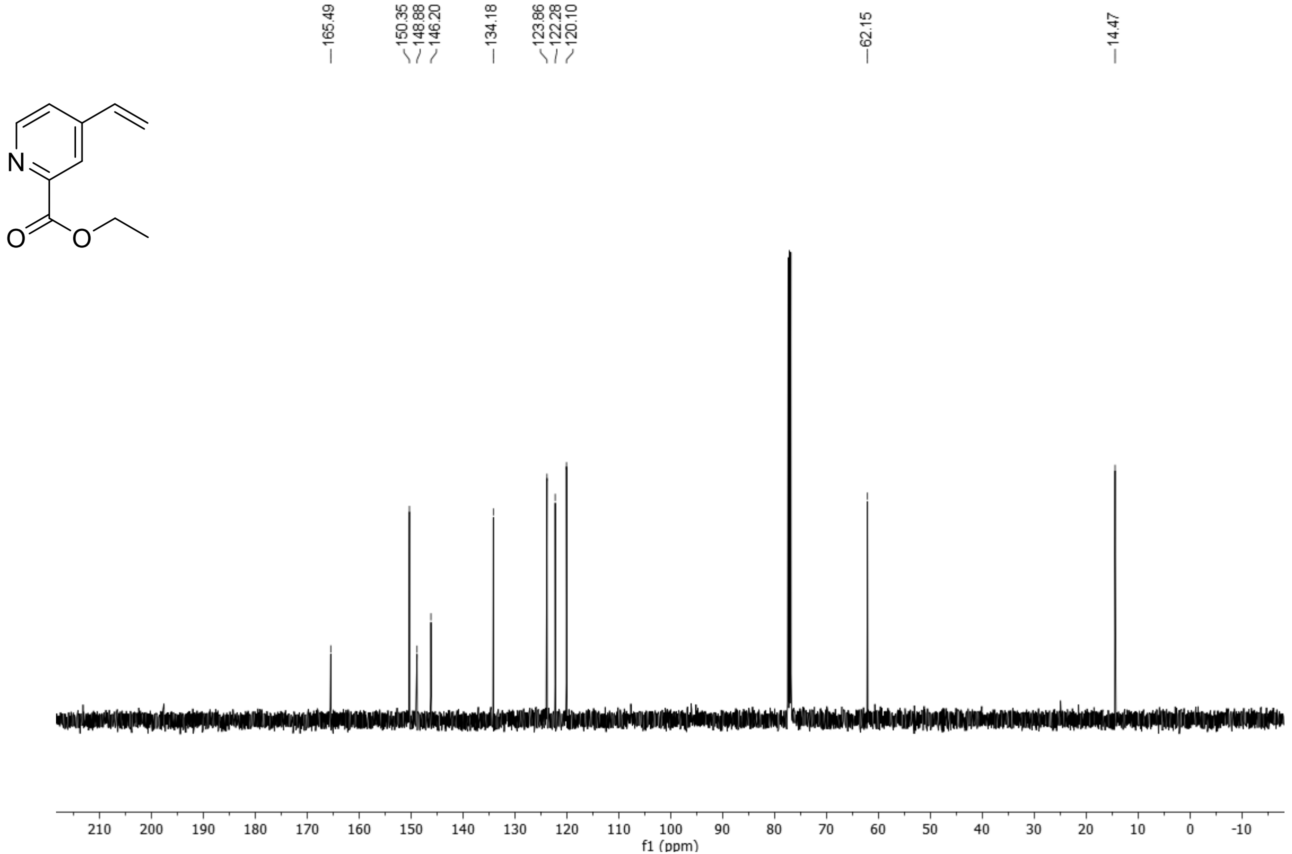
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1x**.



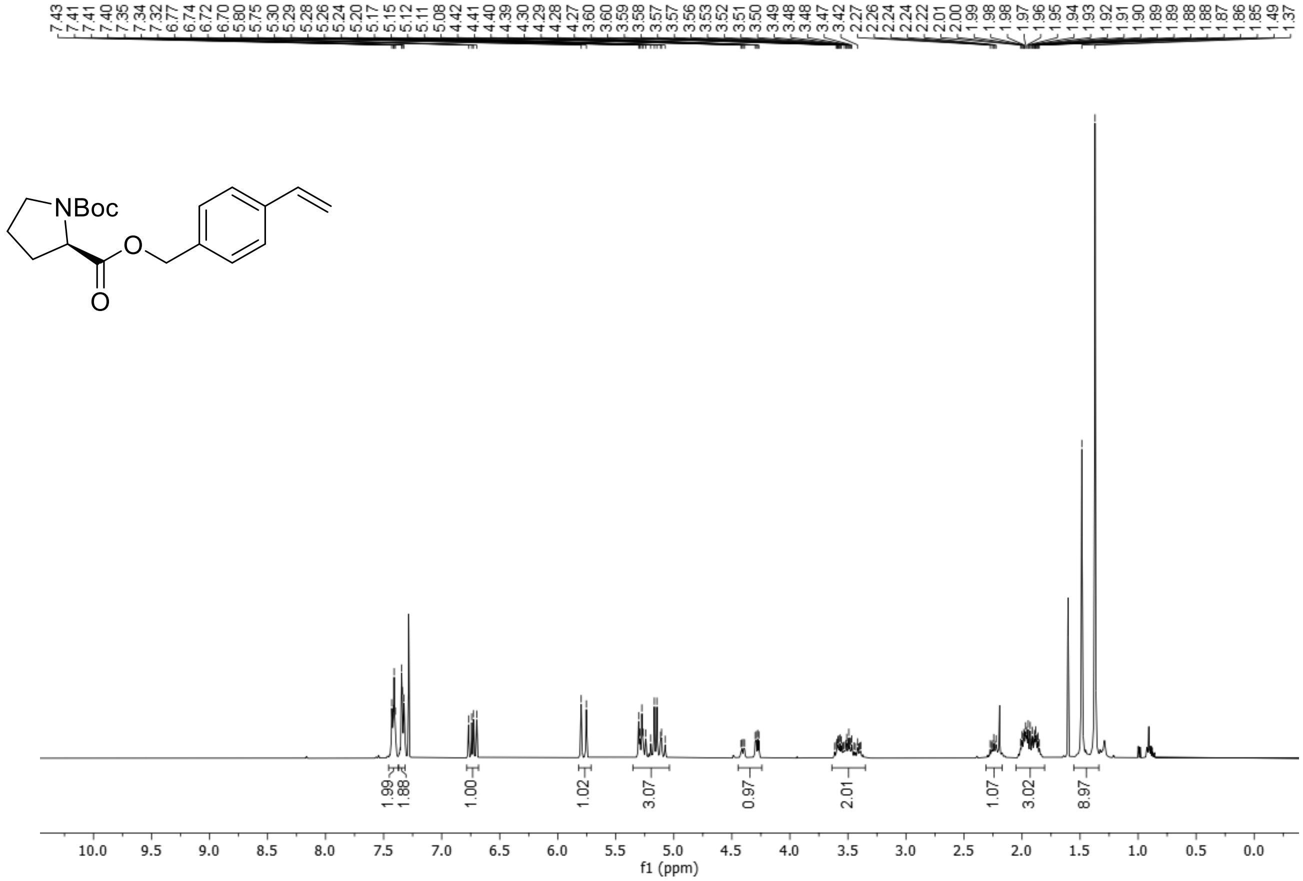
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1y**.



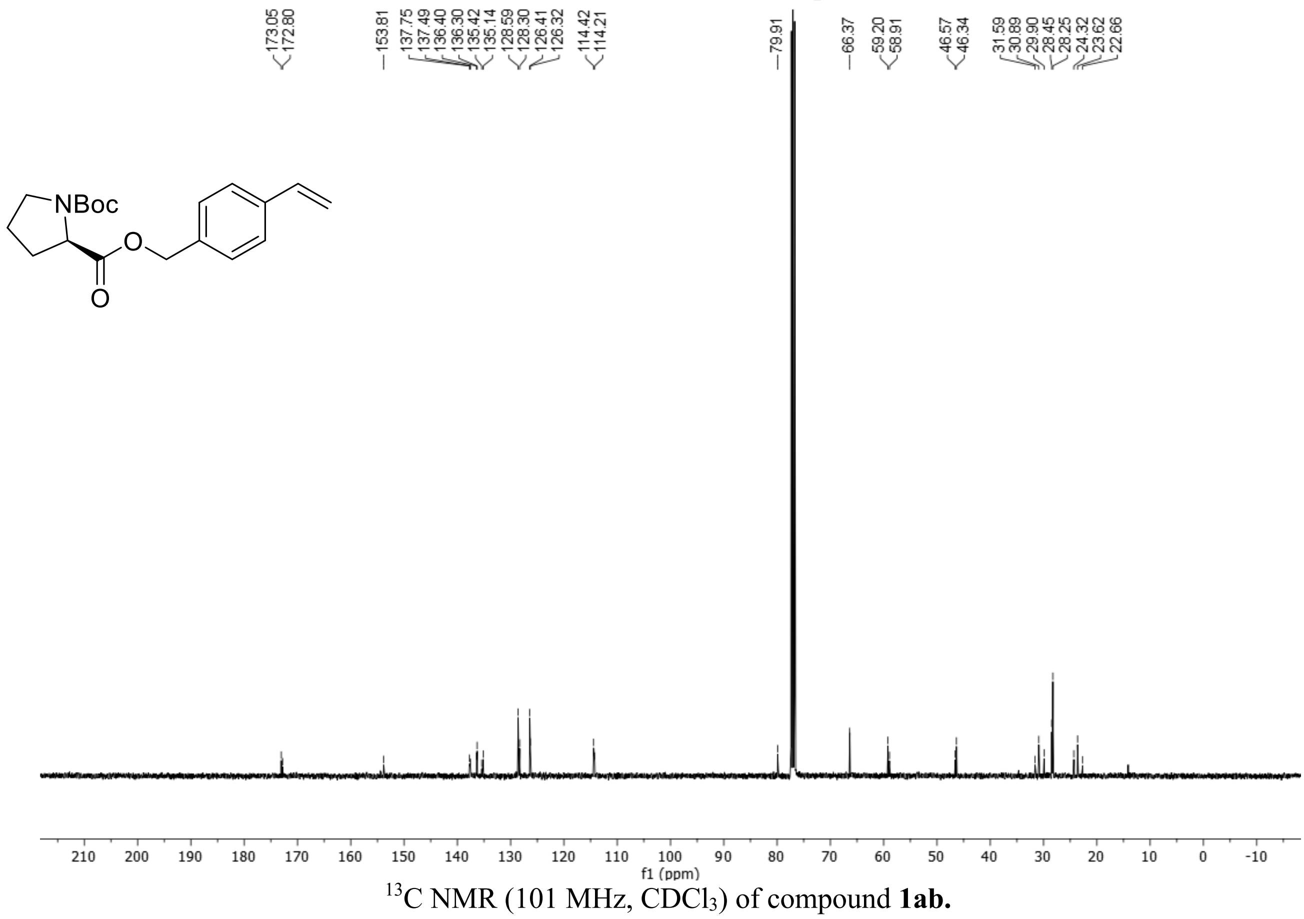
^{1}H NMR (500 MHz, CDCl$_3$) of compound **1z**.



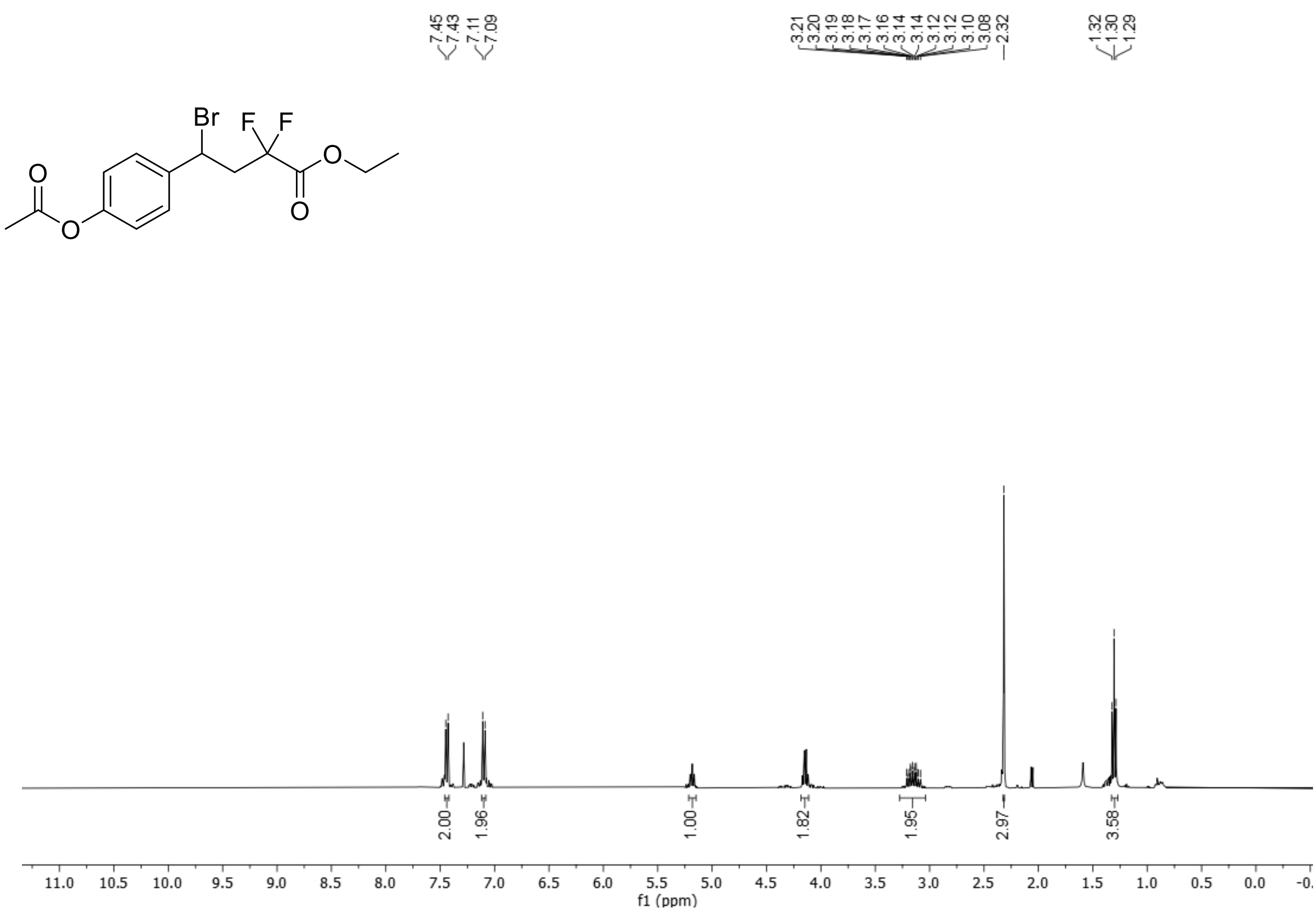
^{13}C NMR (126 MHz, CDCl$_3$) of compound **1z.**



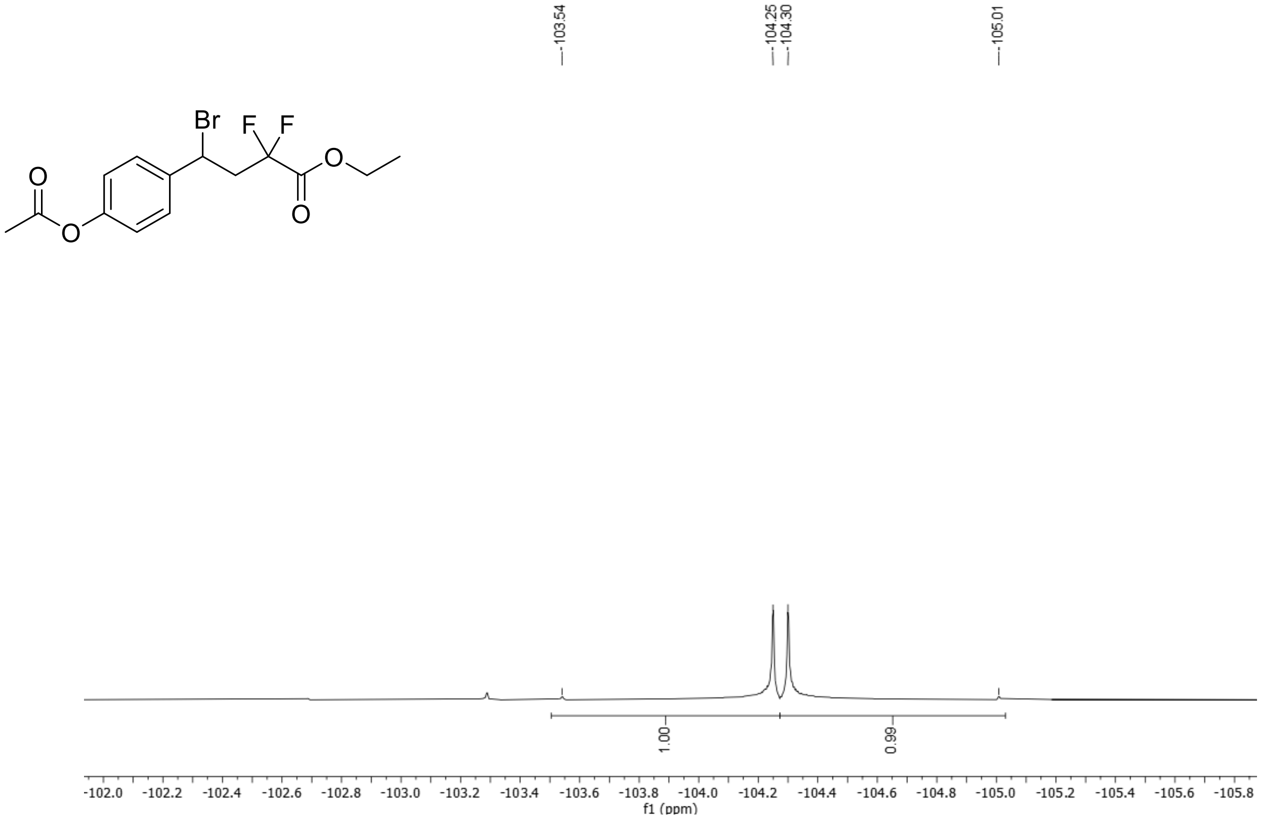
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1ab**.



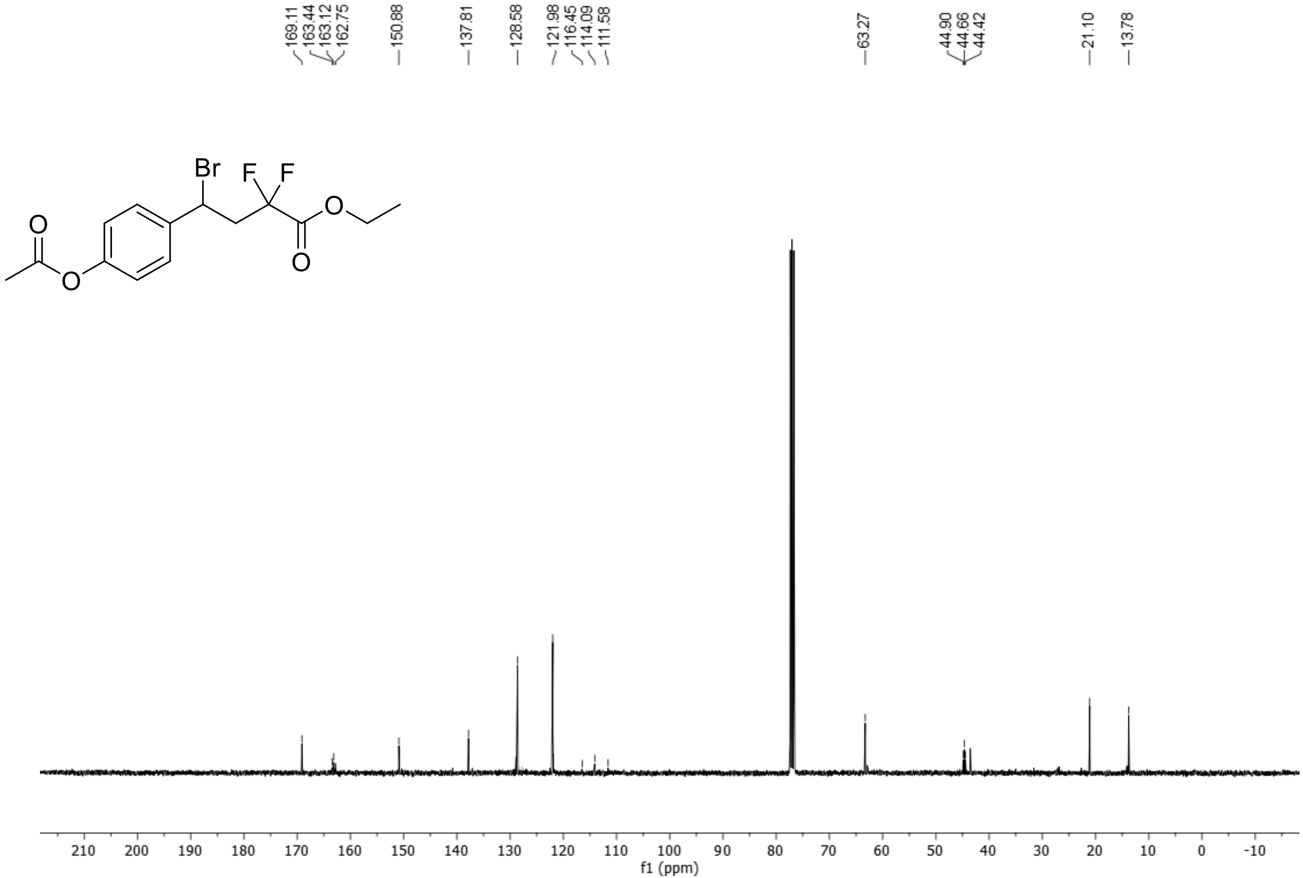
^{13}C NMR (101 MHz, CDCl$_3$) of compound **1ab.**



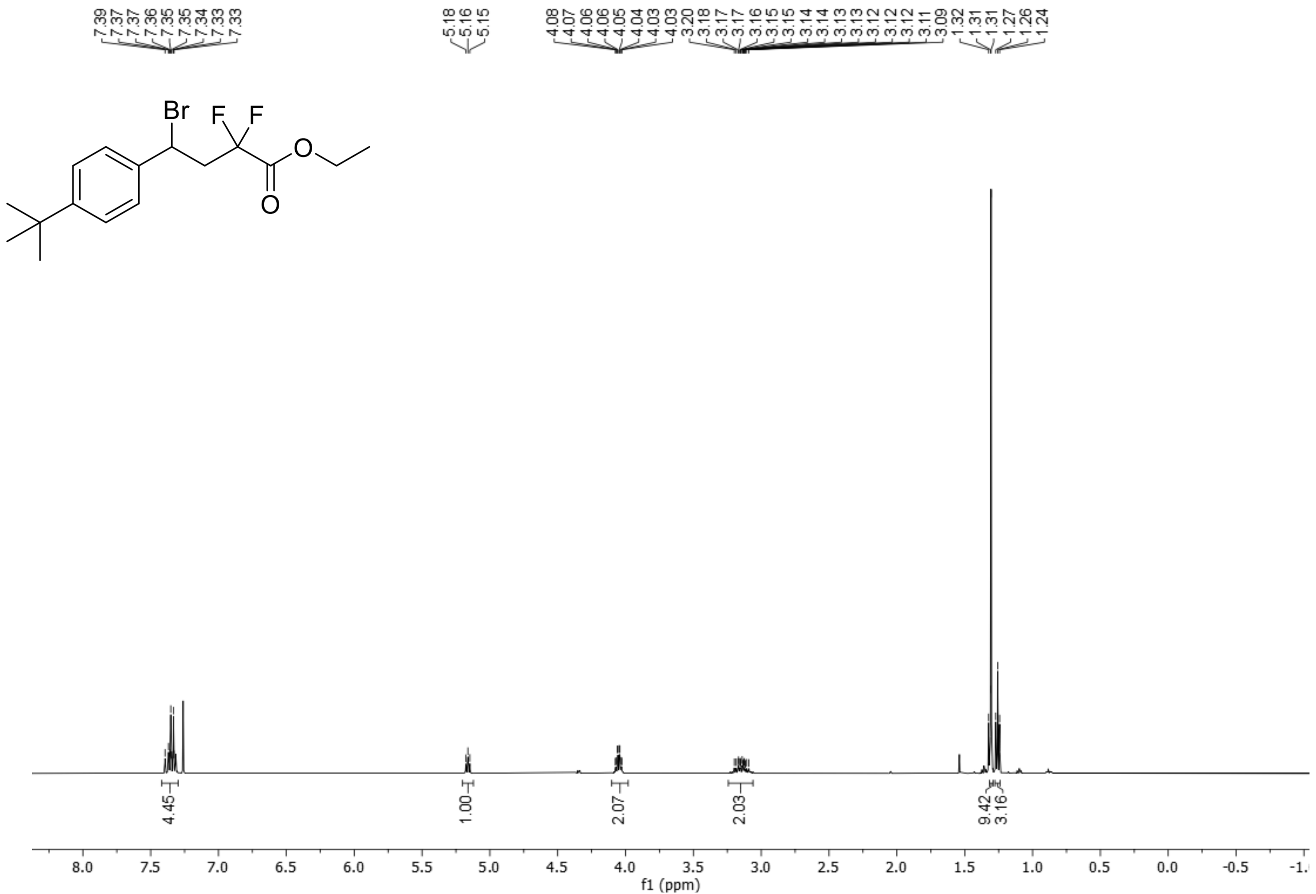
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3a**.



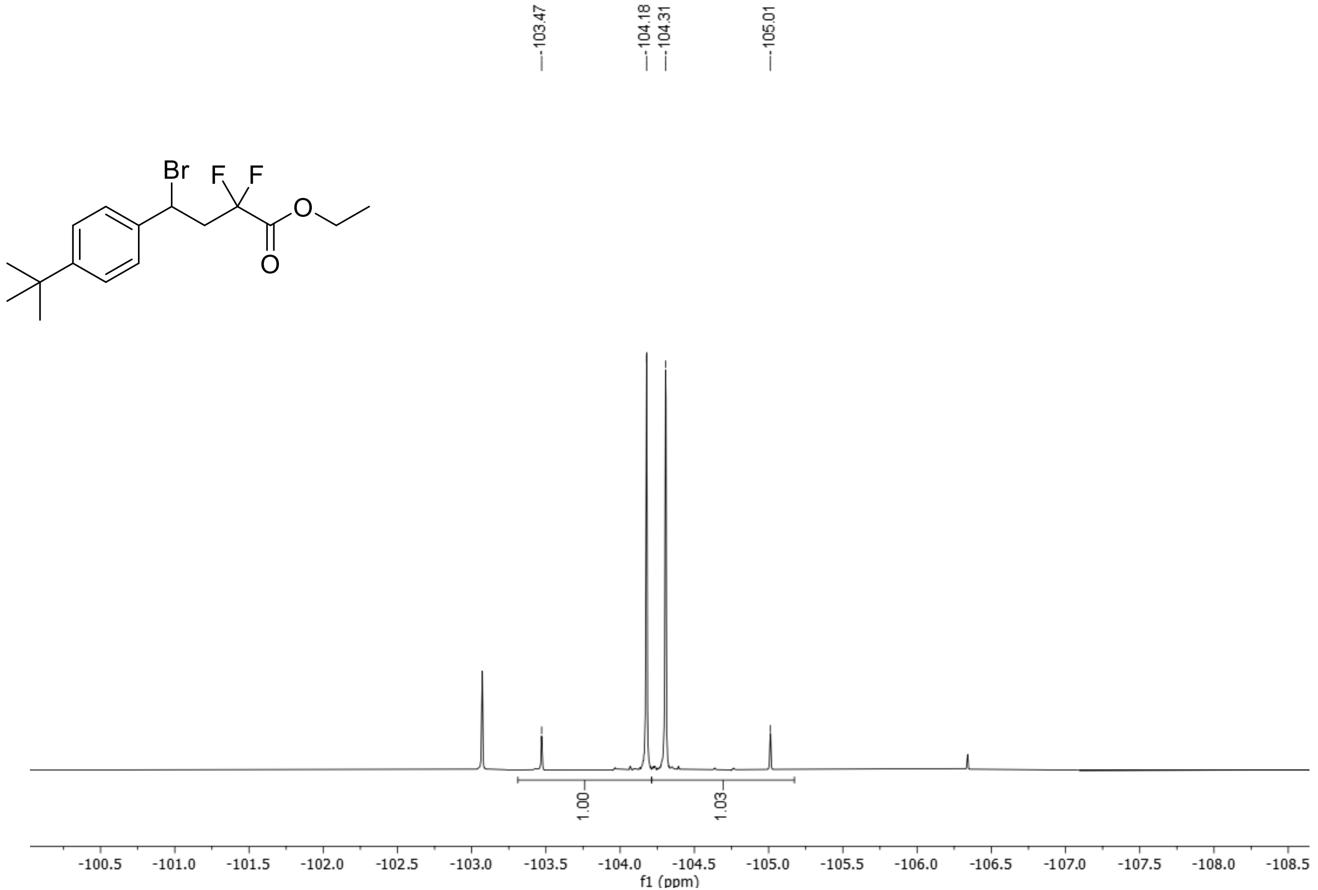
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3a.**



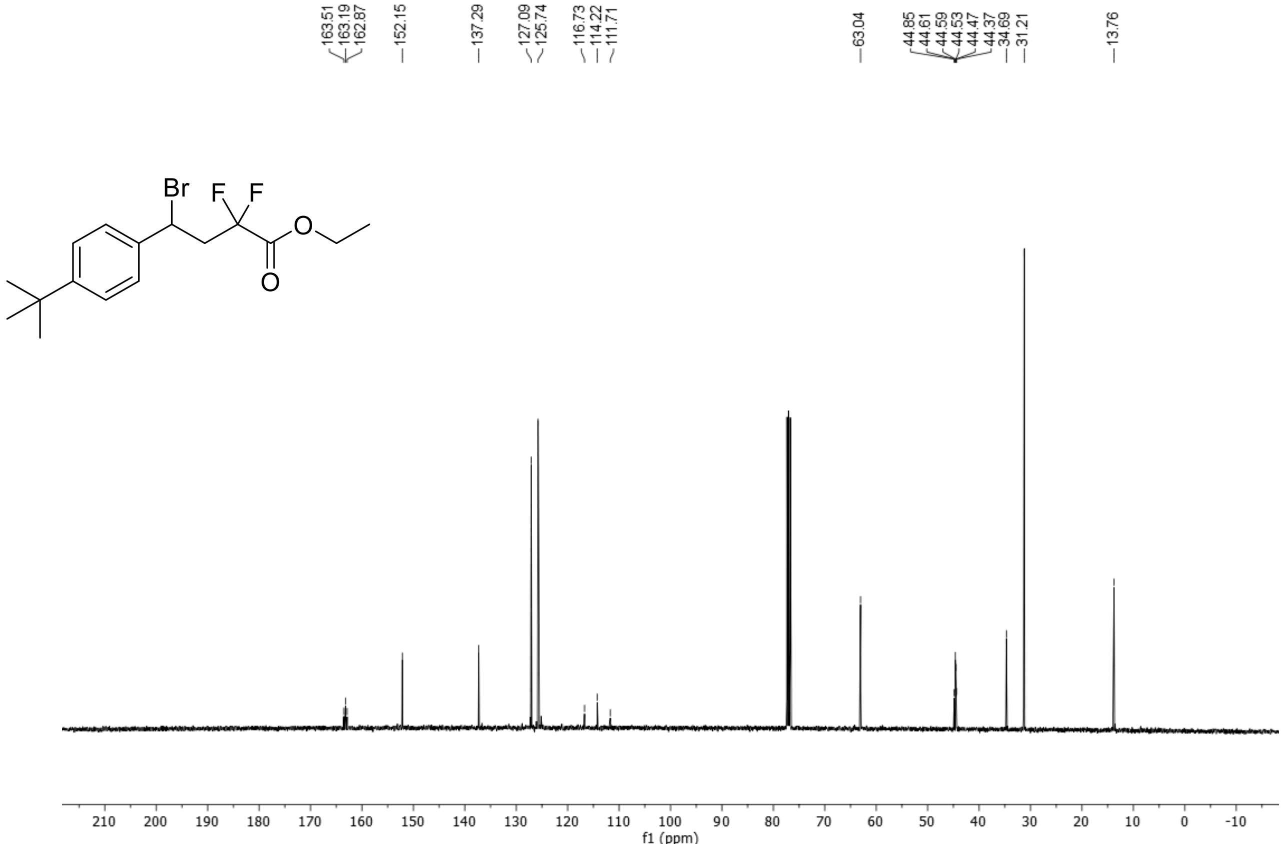
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3a.**



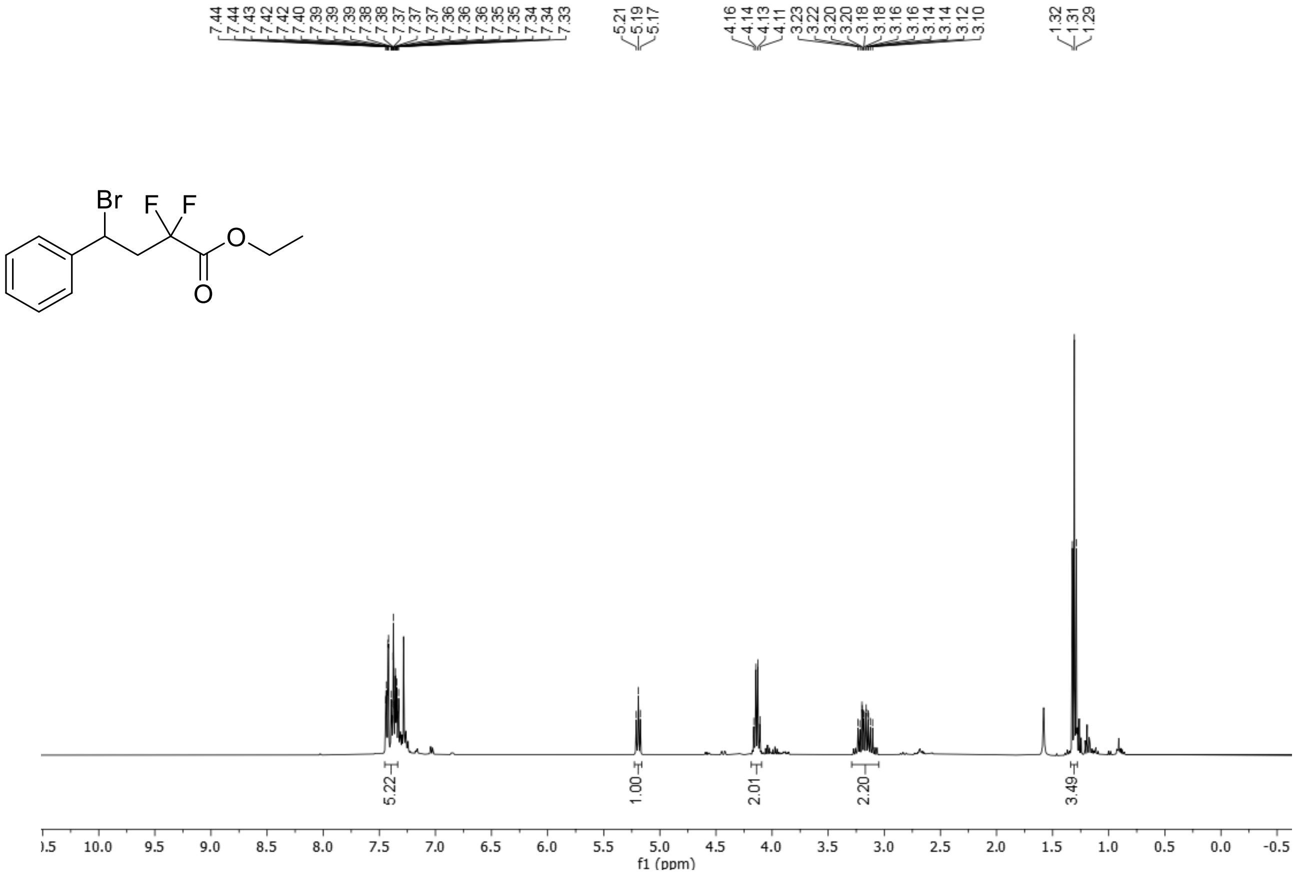
^{1}H NMR (500 MHz, CDCl$_3$) of compound **3b**.



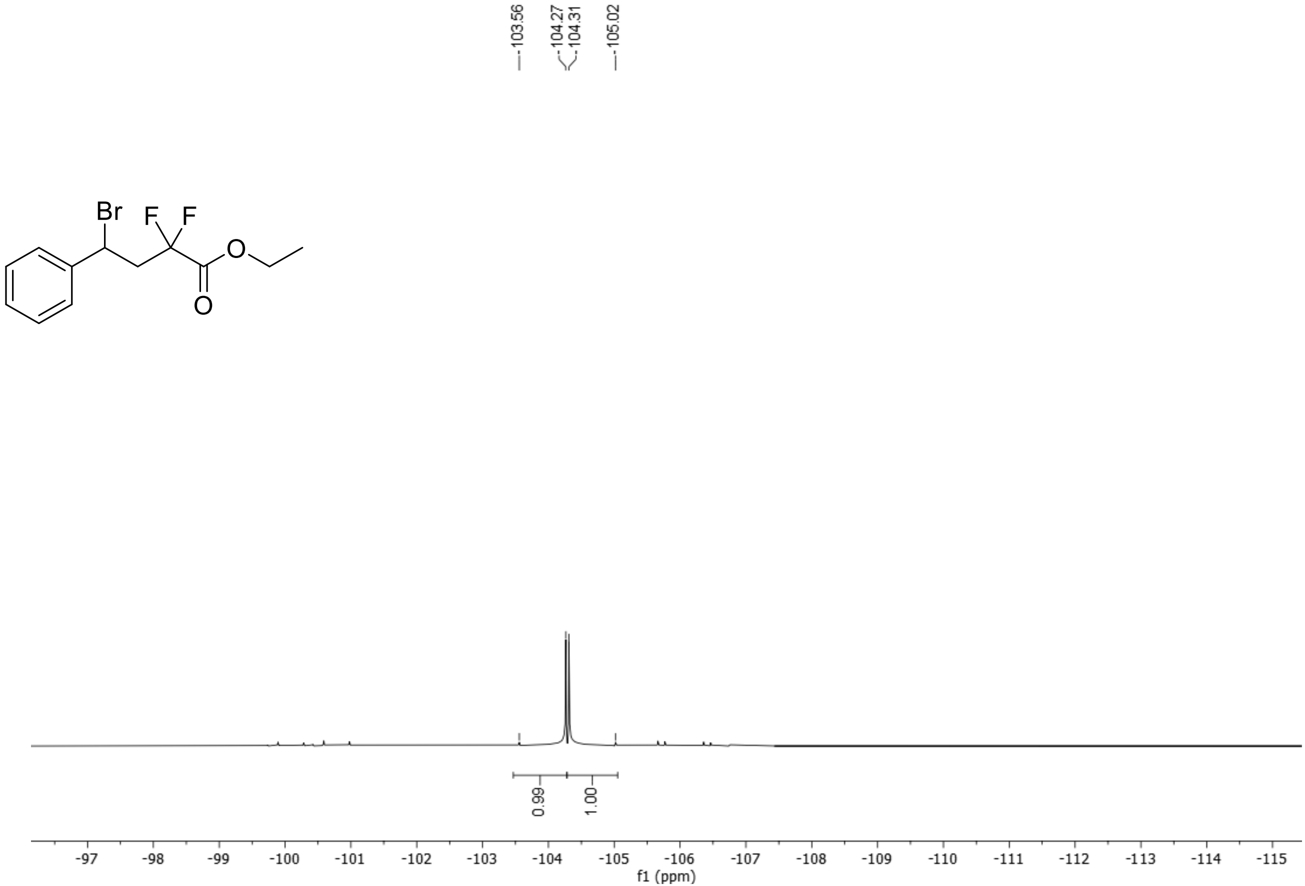
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3b.**



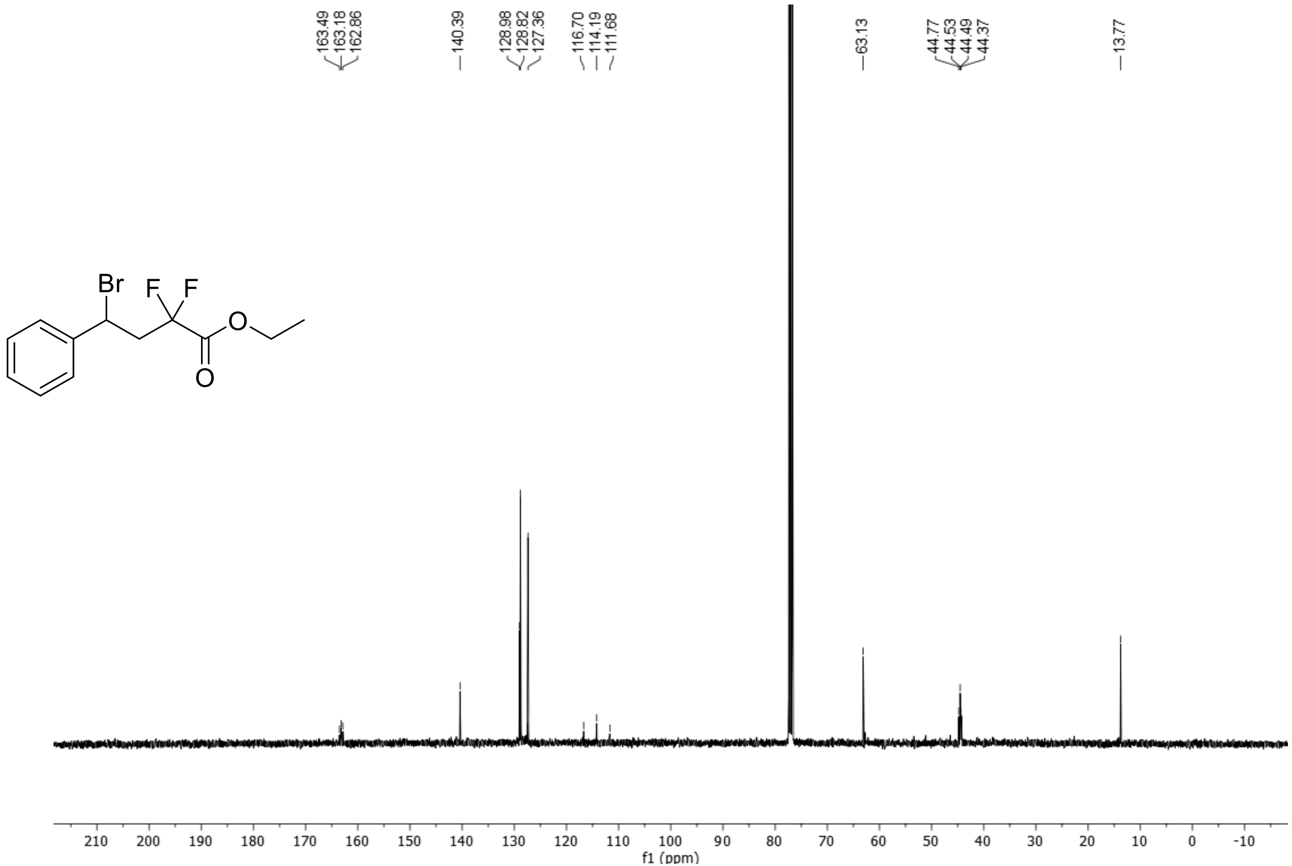
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3b.**



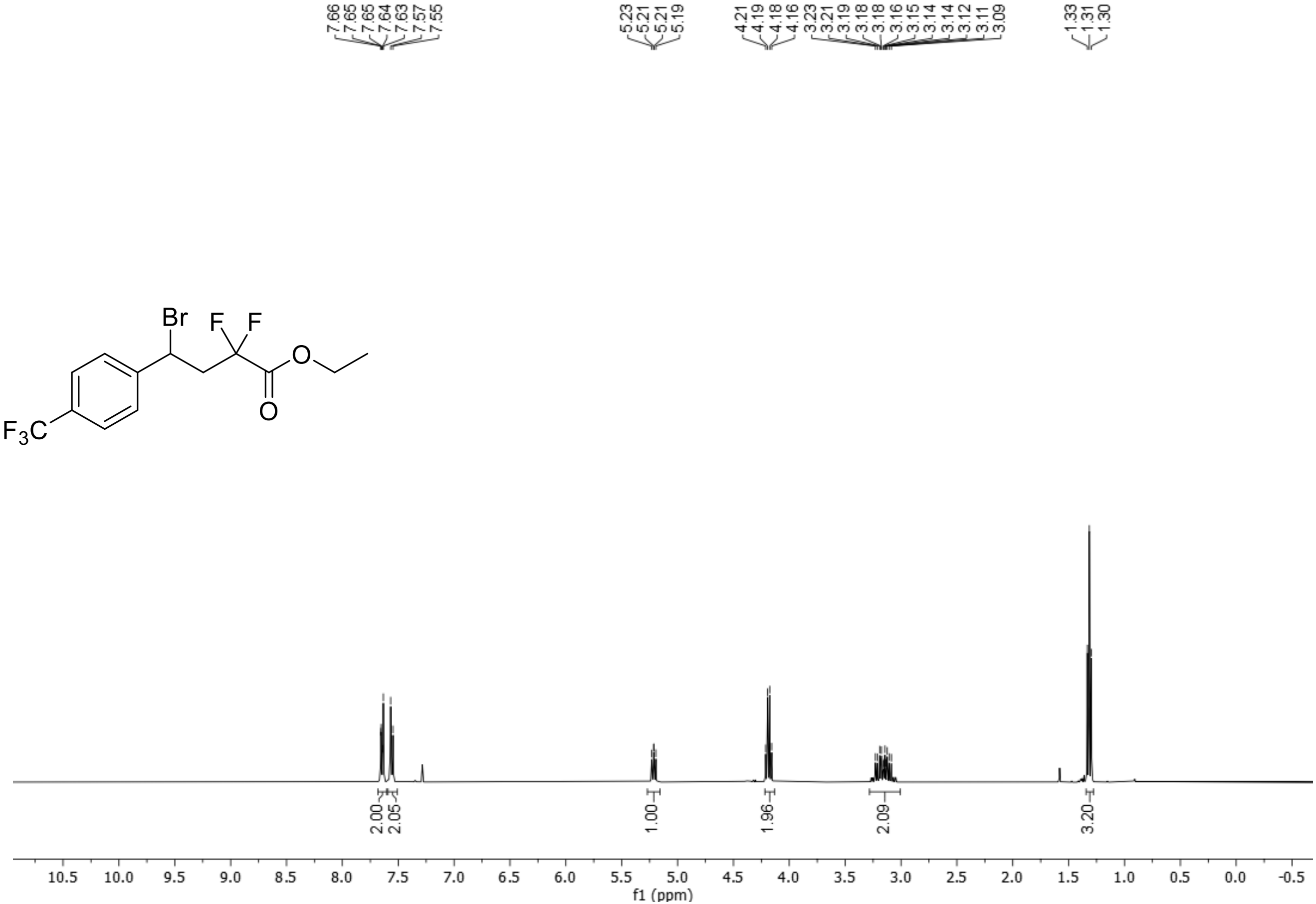
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3c**.



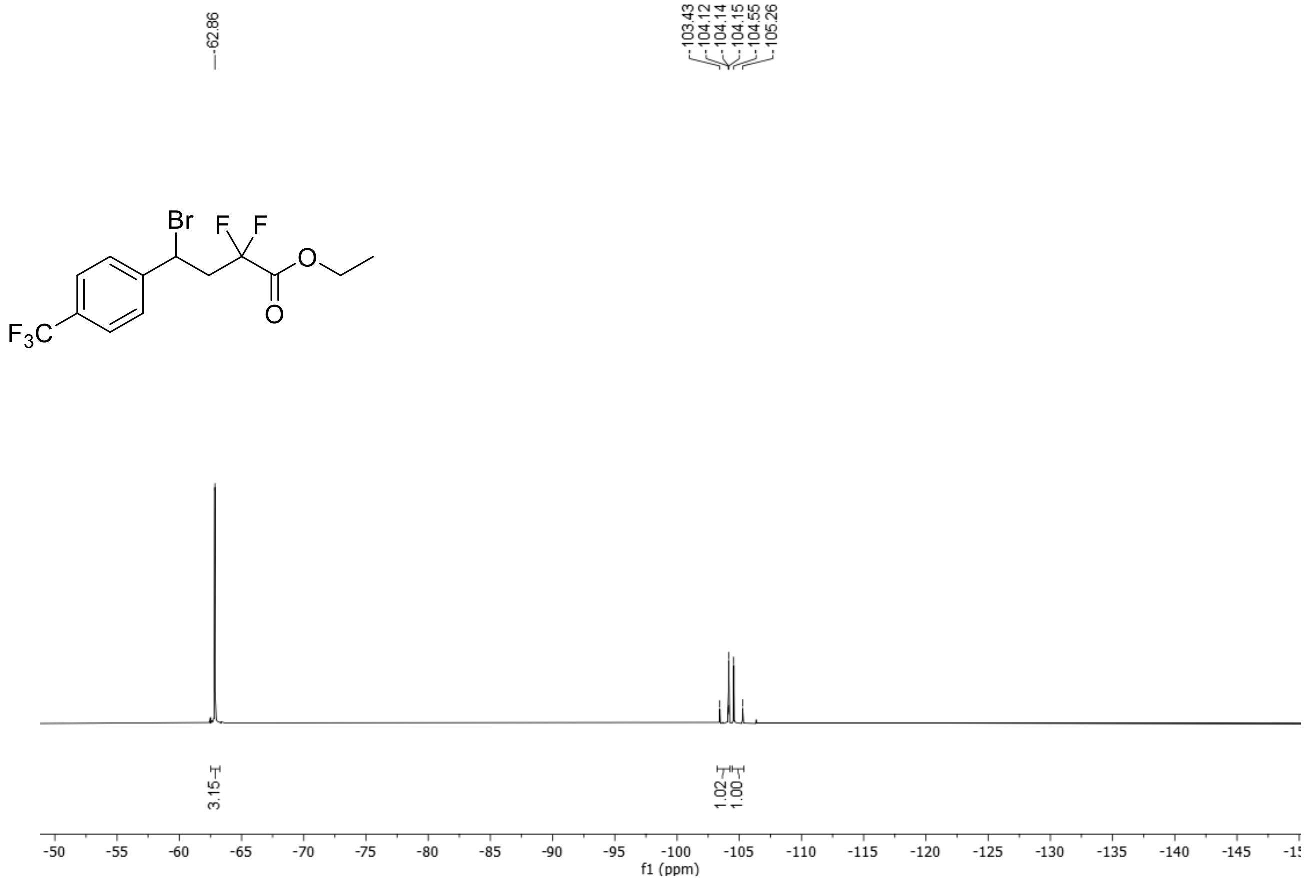
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3c.**



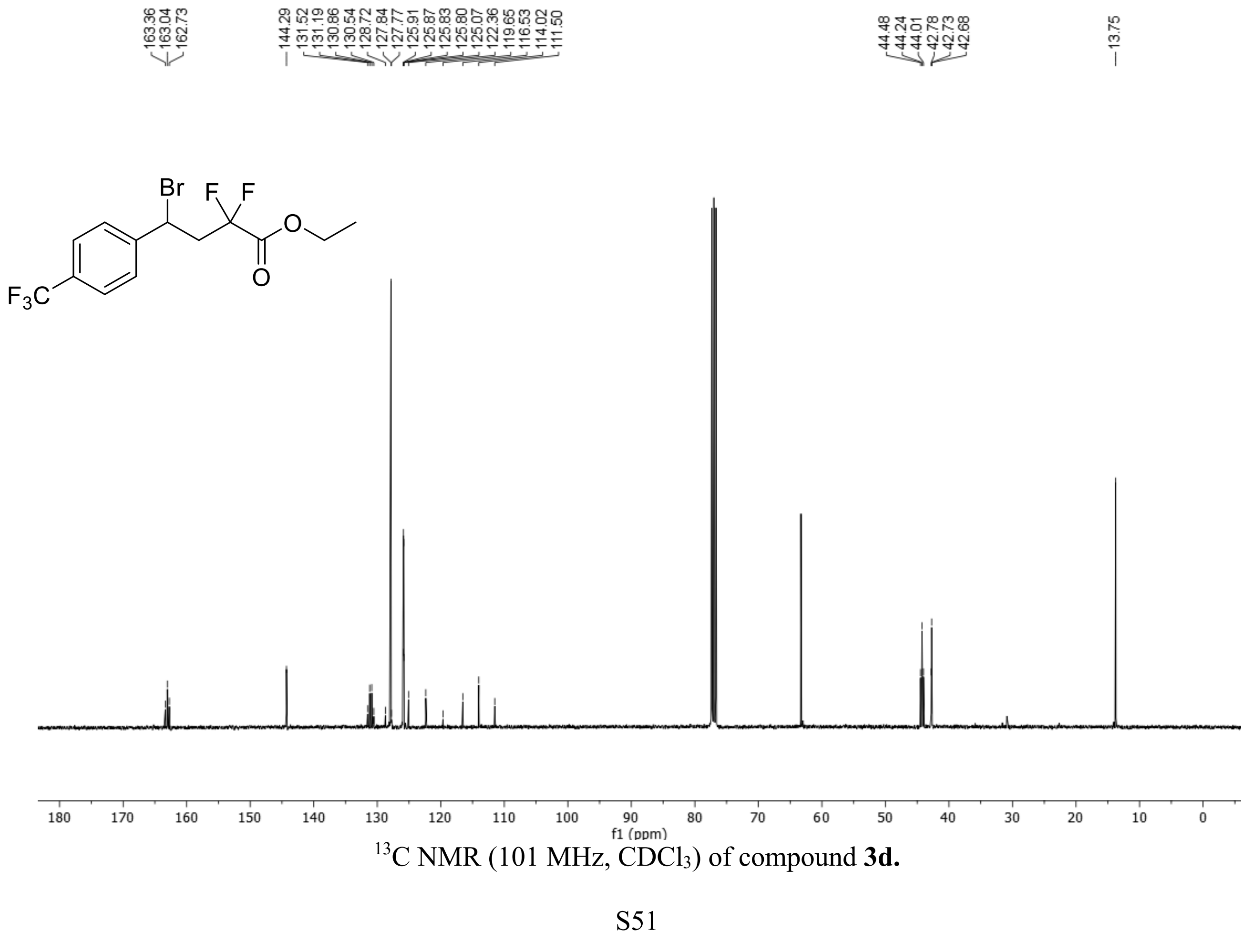
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3c.**



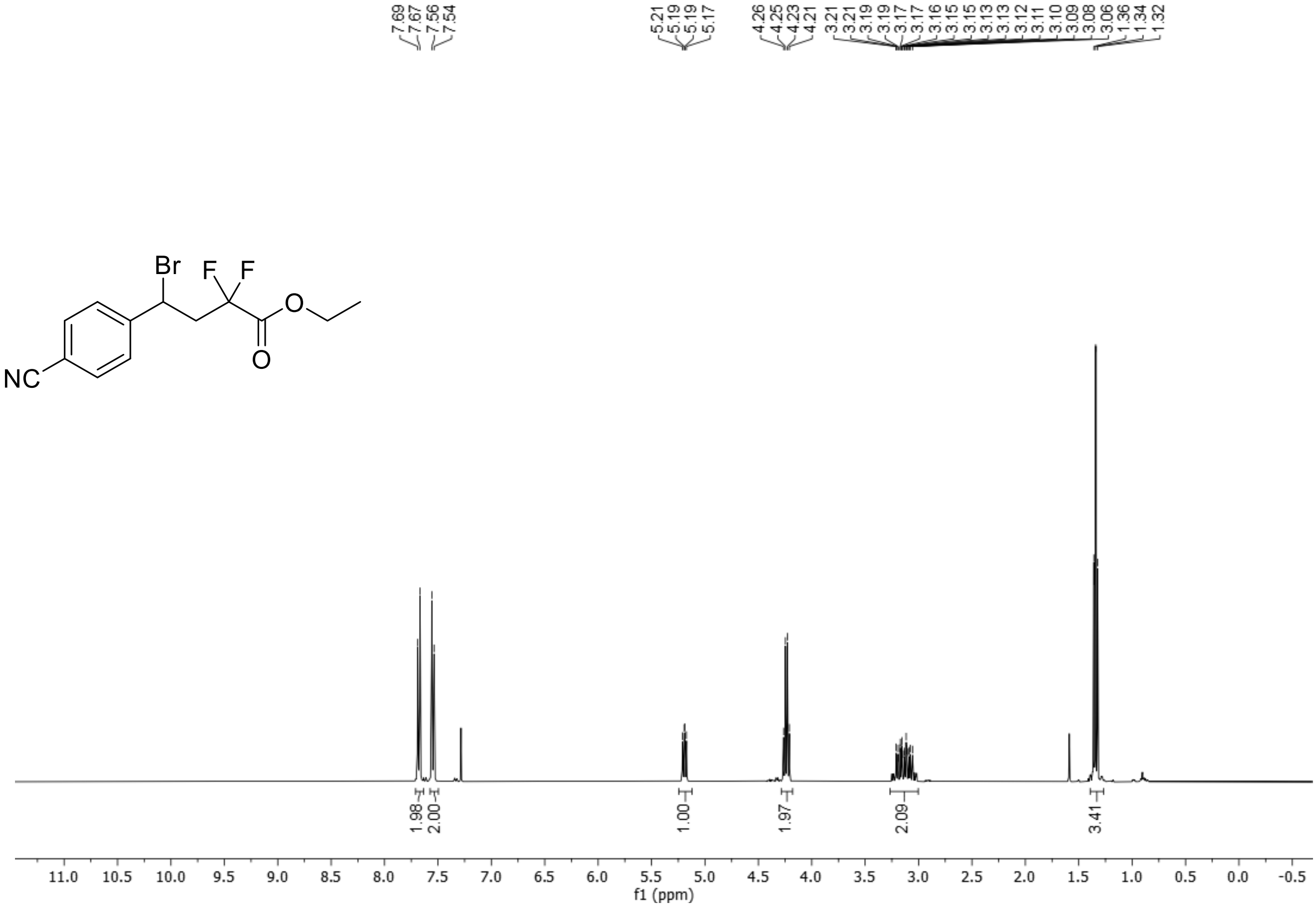
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**.



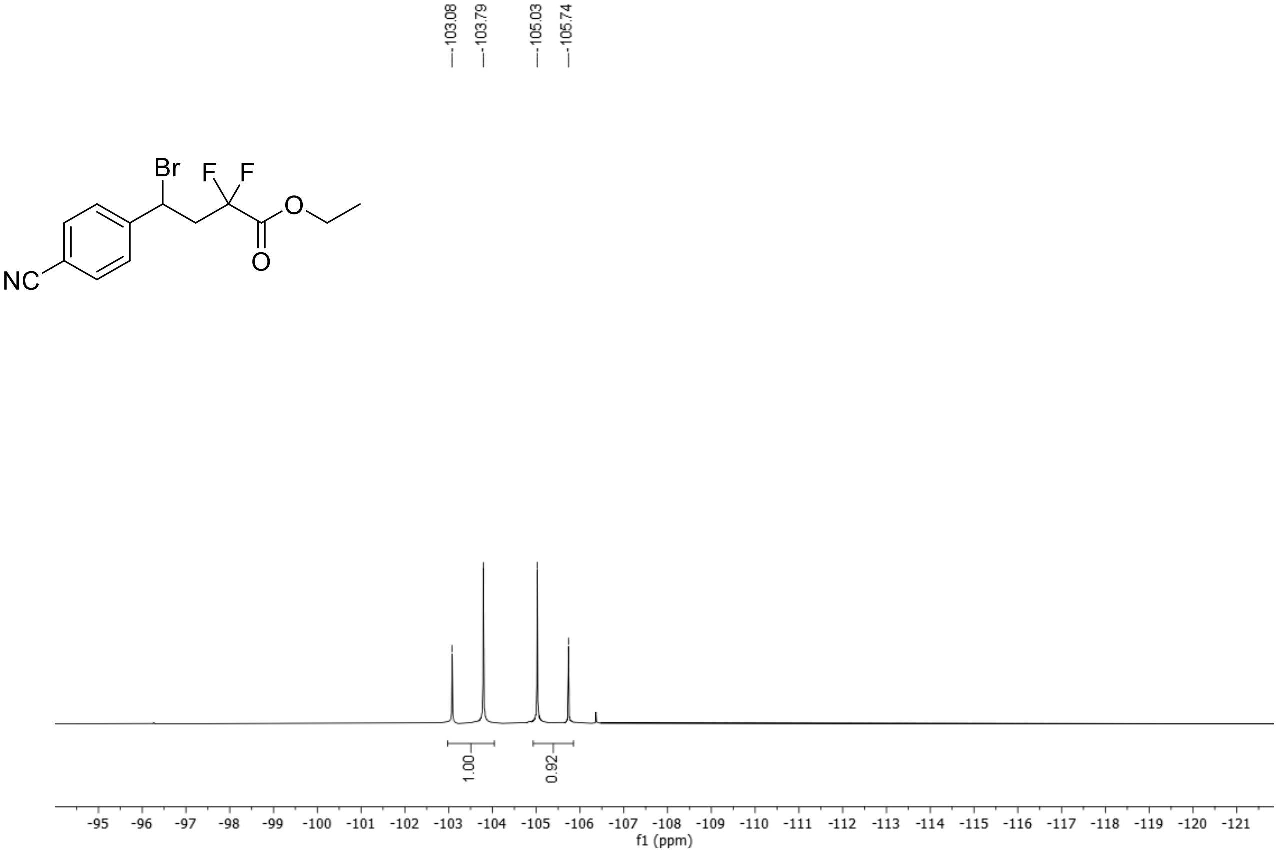
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3d.**



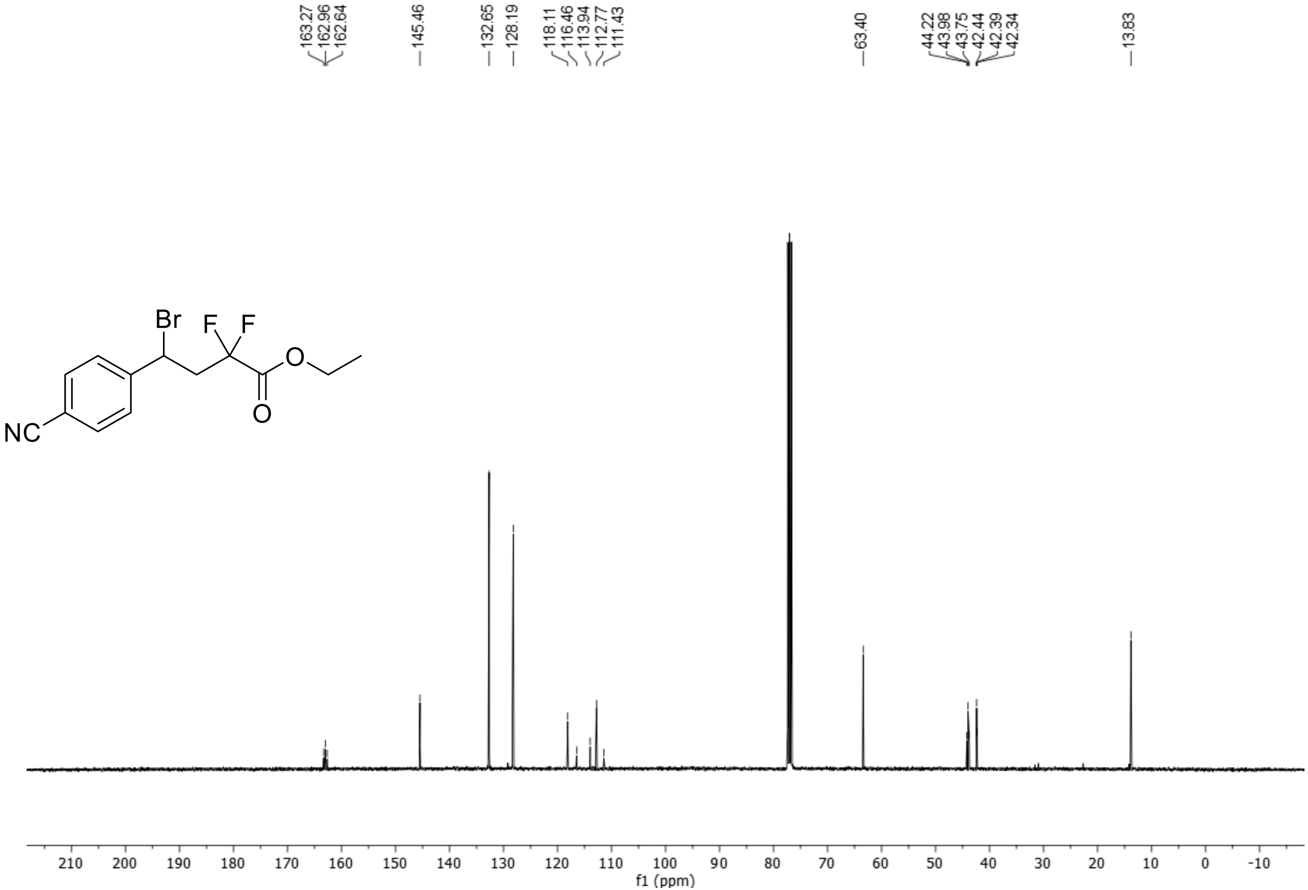
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3d.**



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

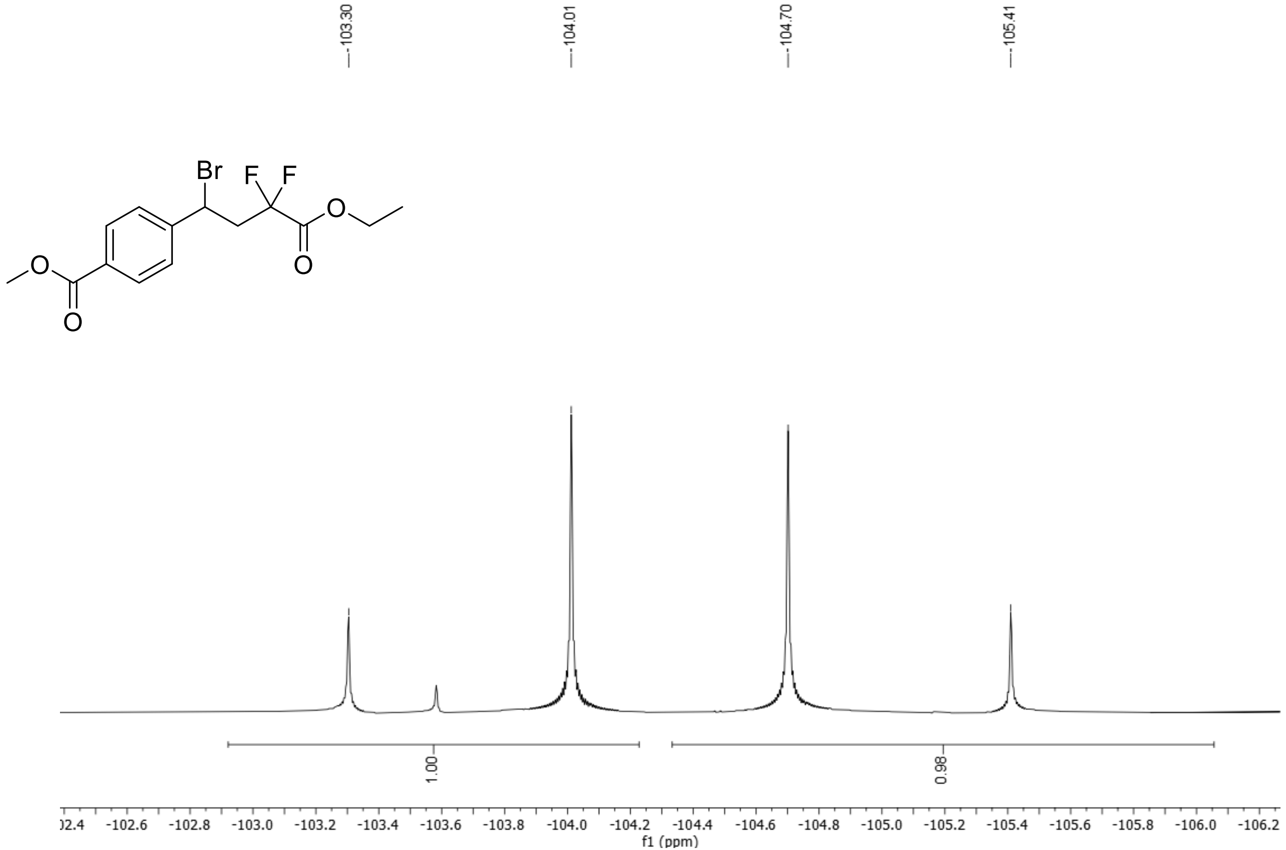


^{19}F NMR (376 MHz, $CDCl_3$) of compound **3e.**



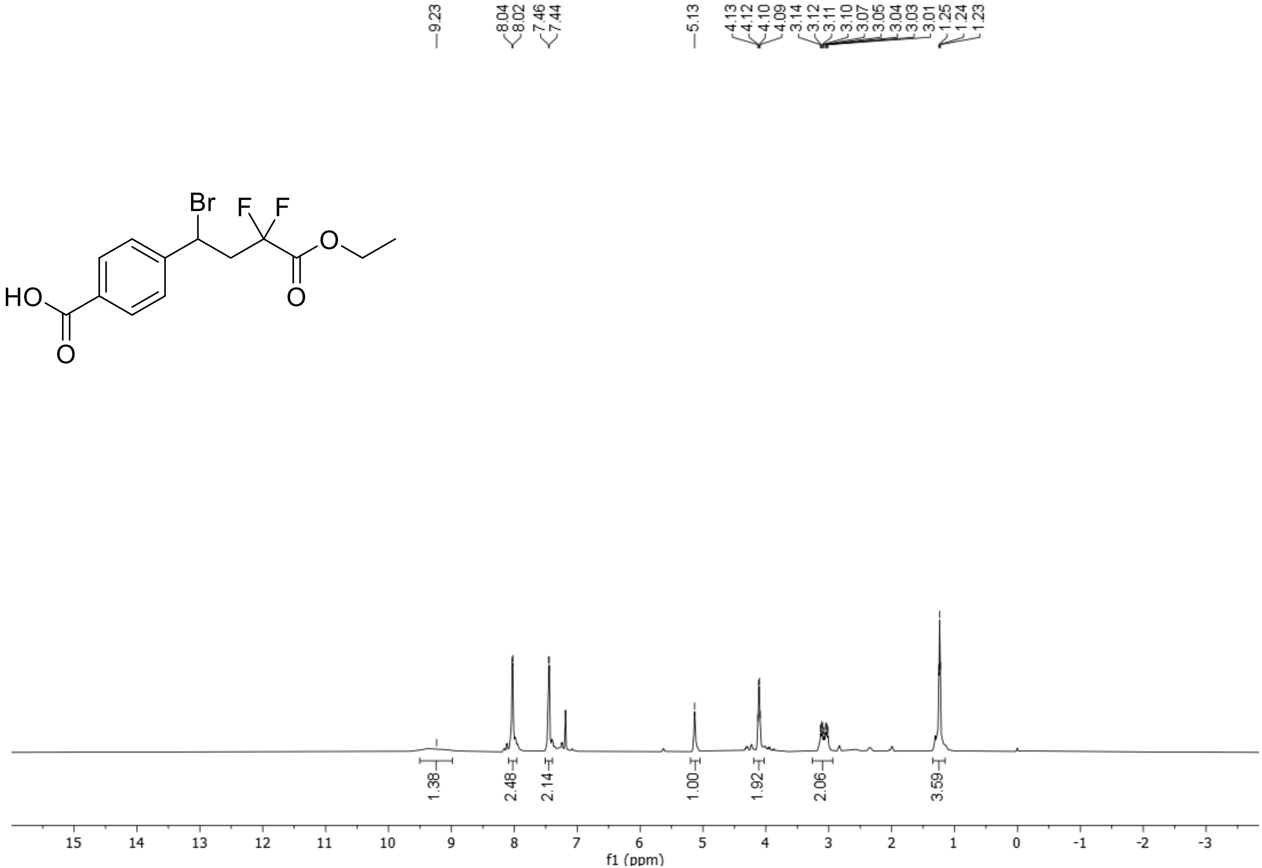
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3e.**

^{1}H NMR (400 MHz, CDCl$_3$) of compound **3f**.

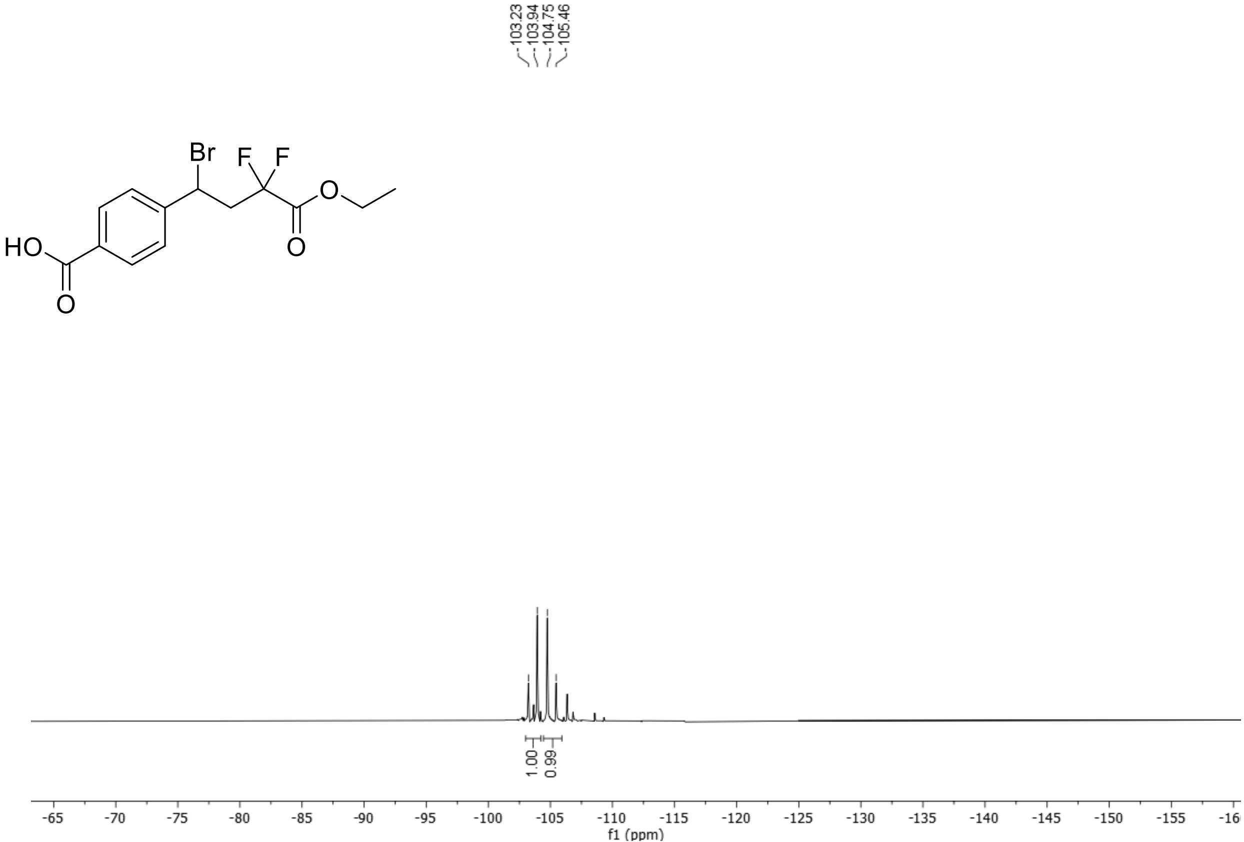


^{19}F NMR (376 MHz, CDCl$_3$) of compound **3f.**

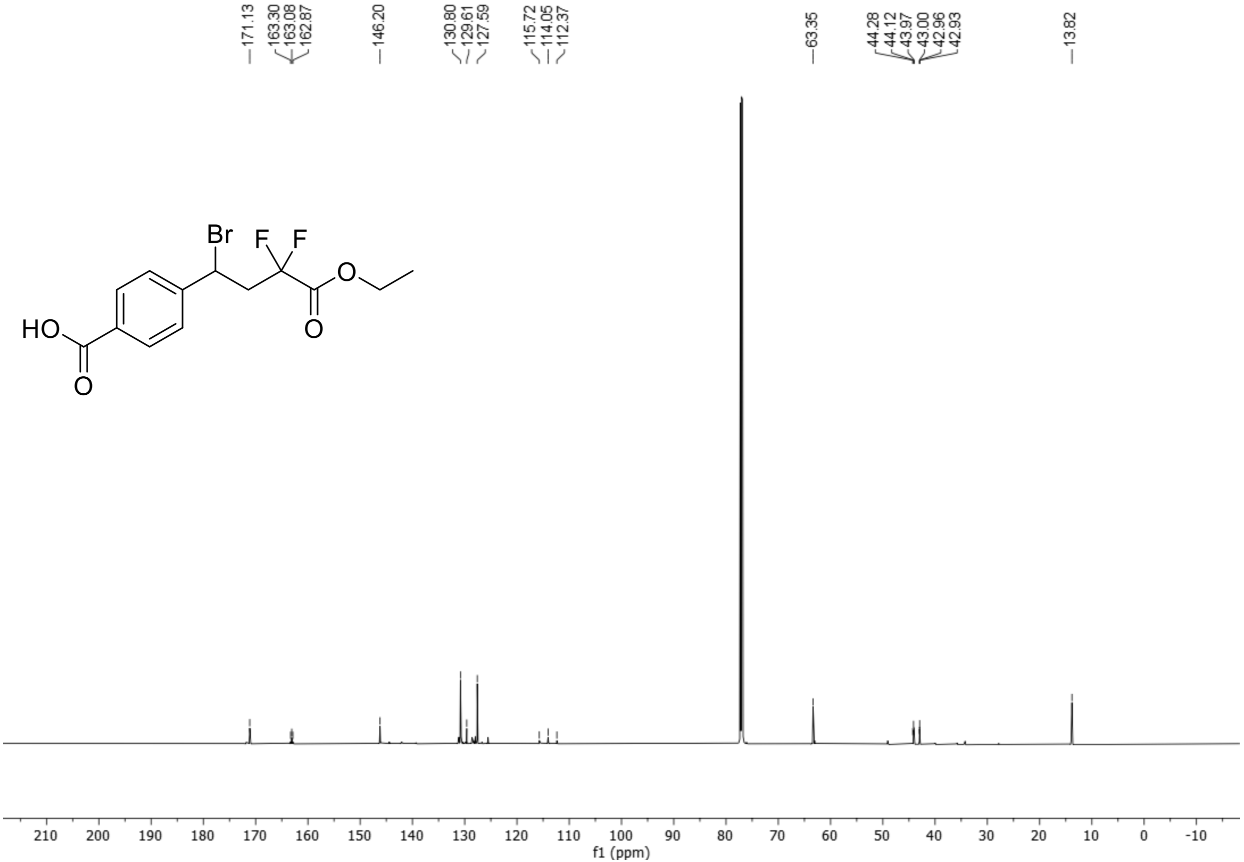
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3f.**



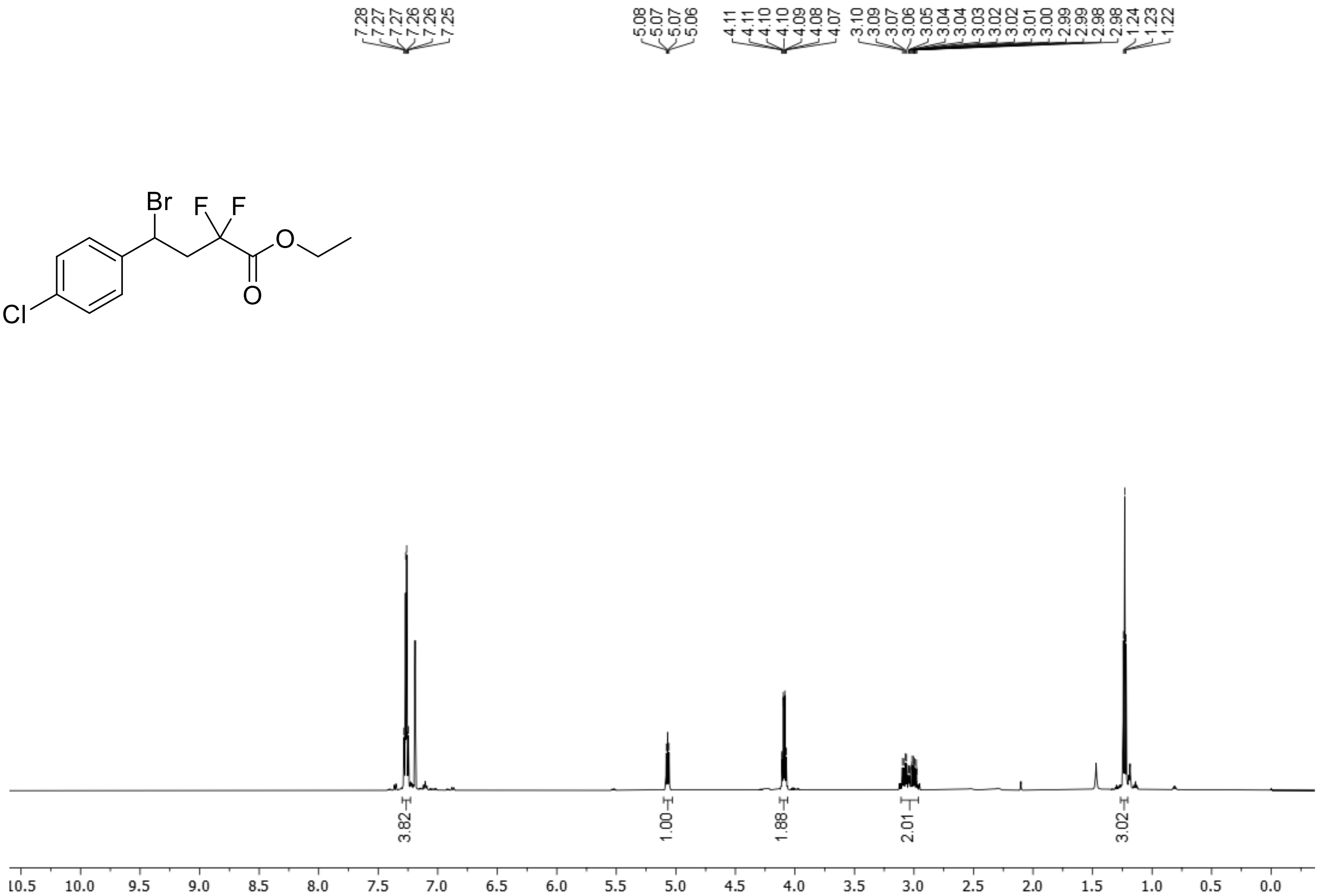
^{1}H NMR (600 MHz, CDCl$_3$) of compound **3g**.



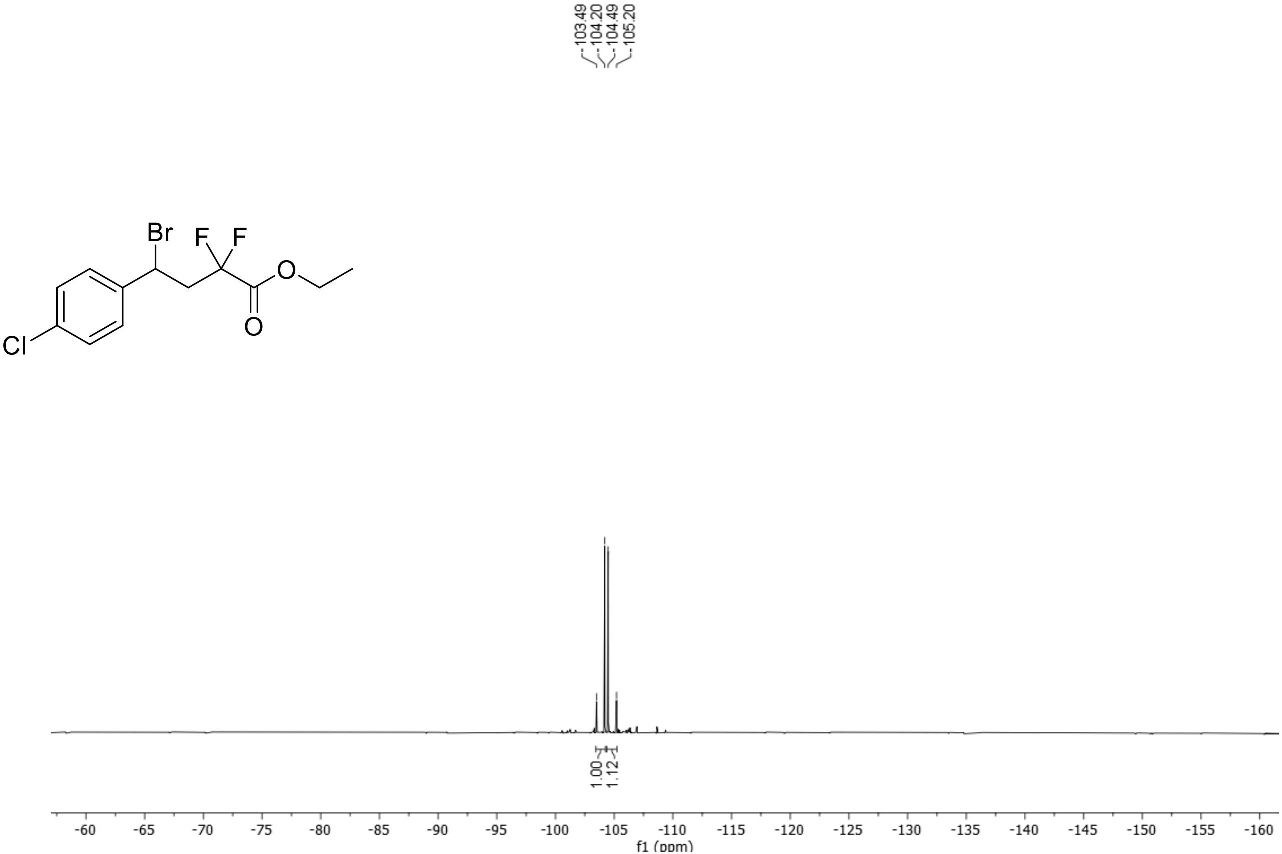
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3g.**



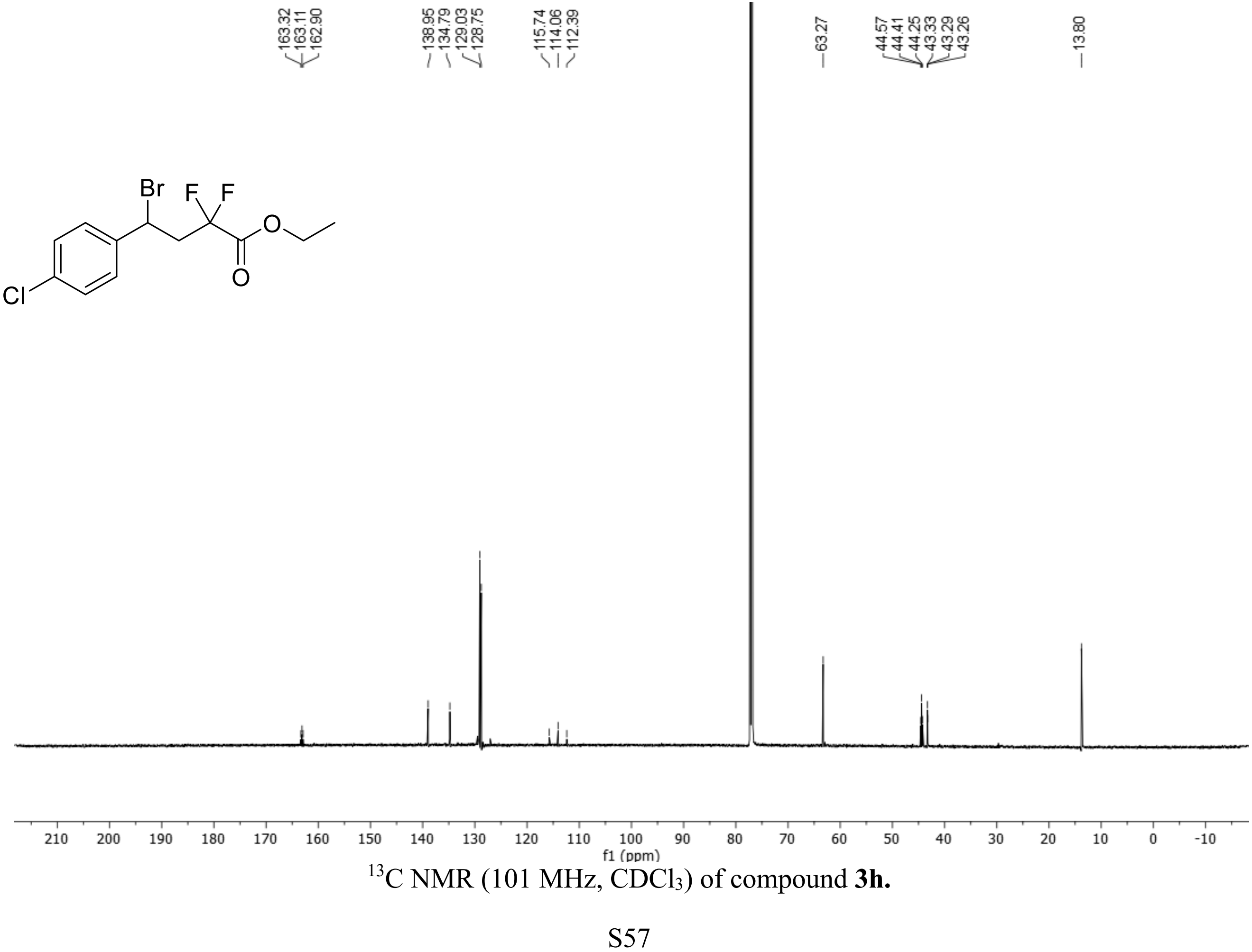
^{13}C NMR (151 MHz, CDCl$_3$) of compound **3g.**



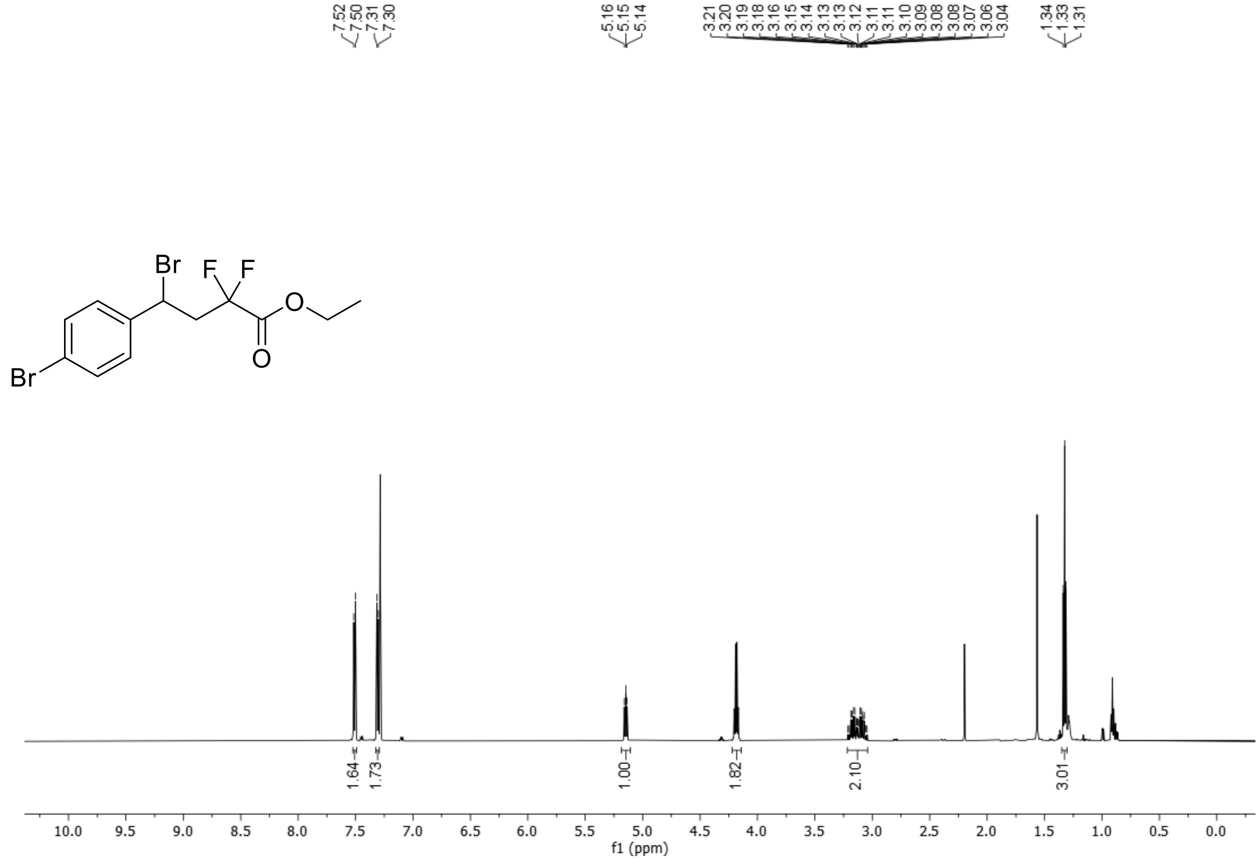
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3h**.



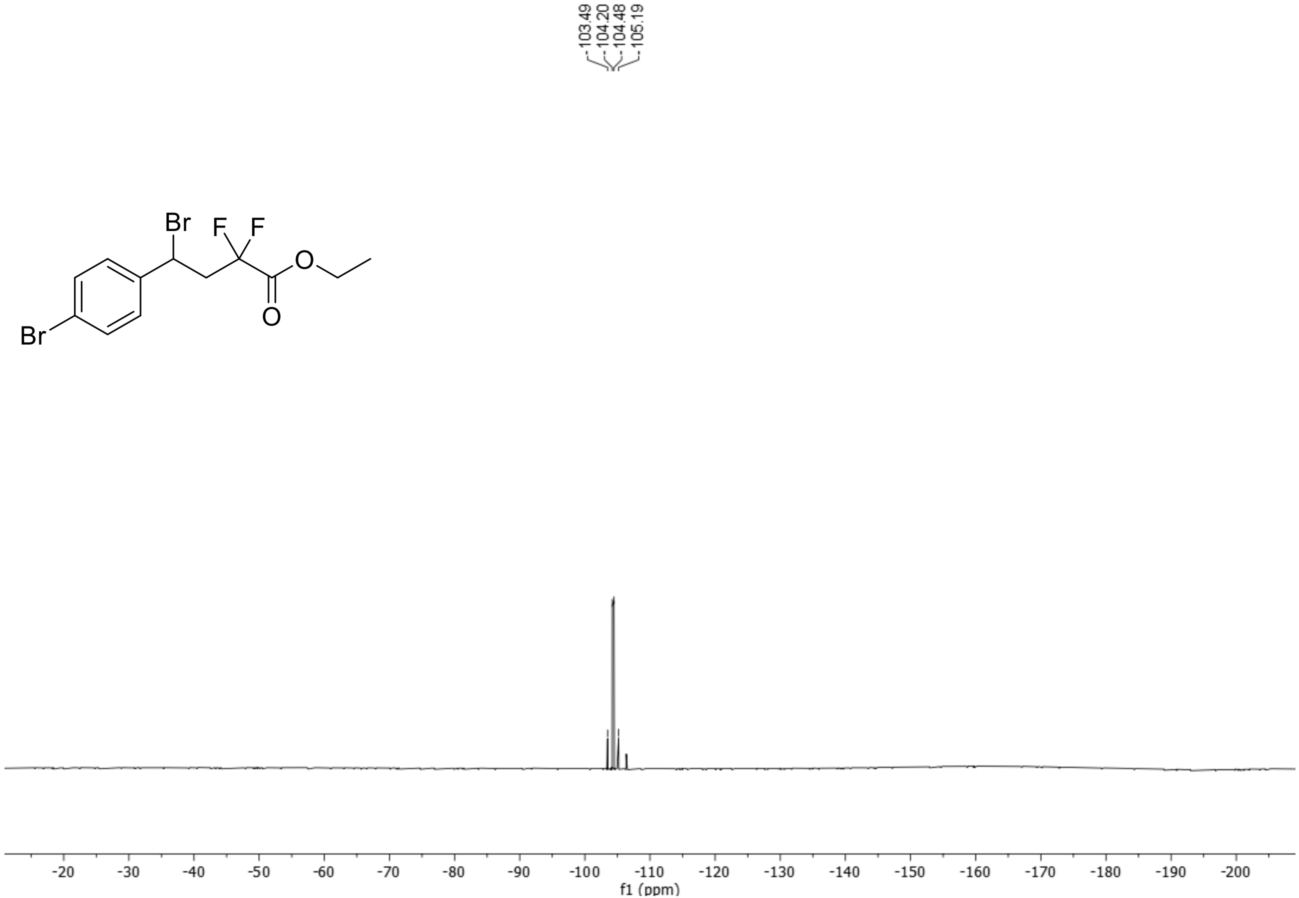
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3h.**



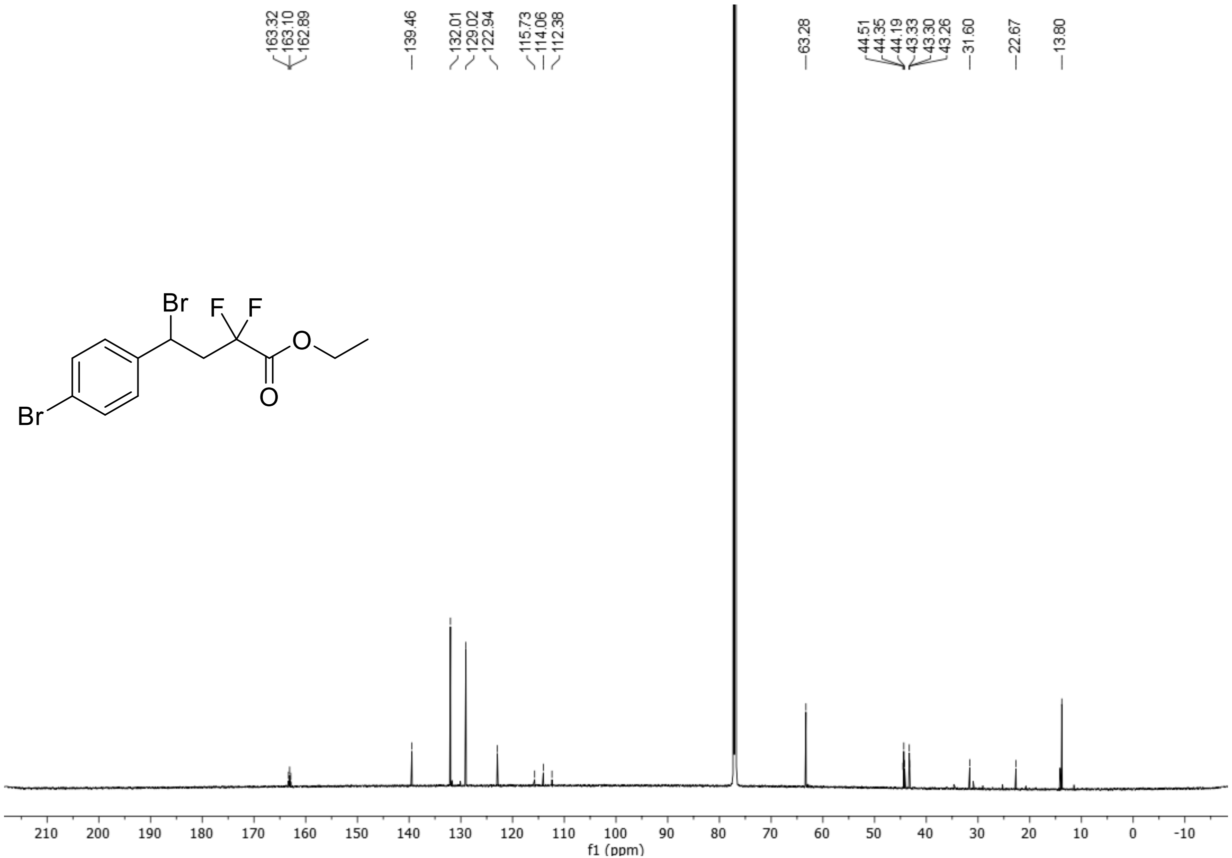
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3h.**



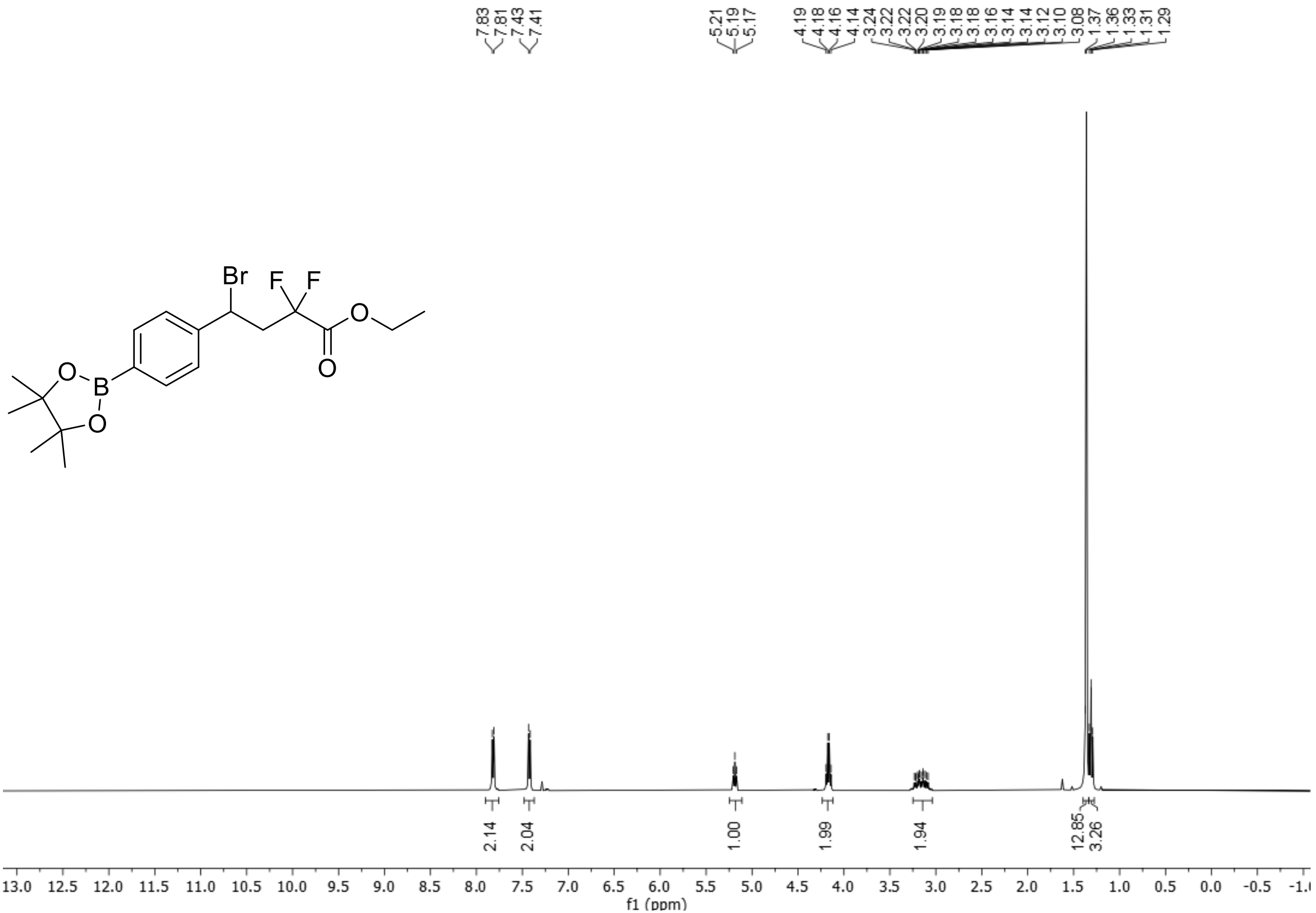
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3i**.



^{19}F NMR (376 MHz, CDCl$_3$) of compound **3i.**

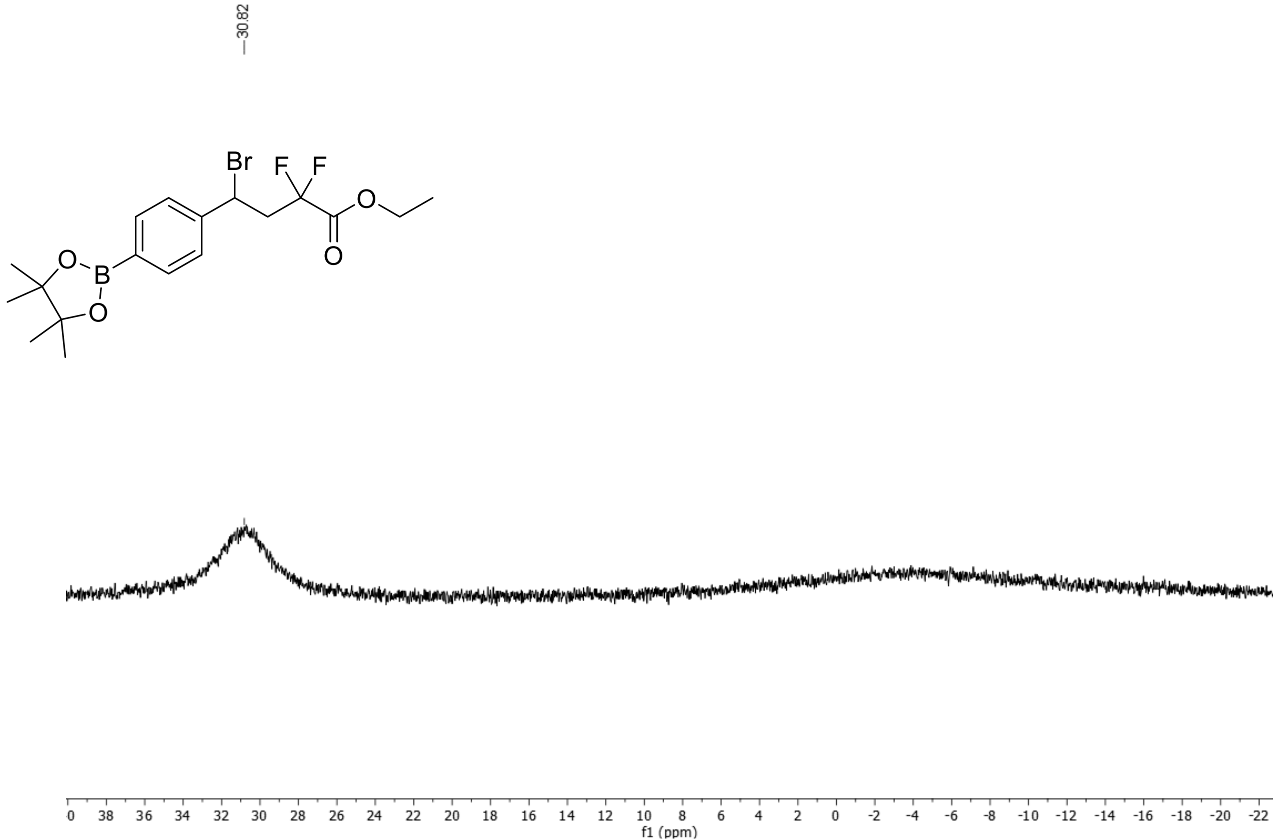


^{13}C NMR (101 MHz, CDCl$_3$) of compound **3i.**

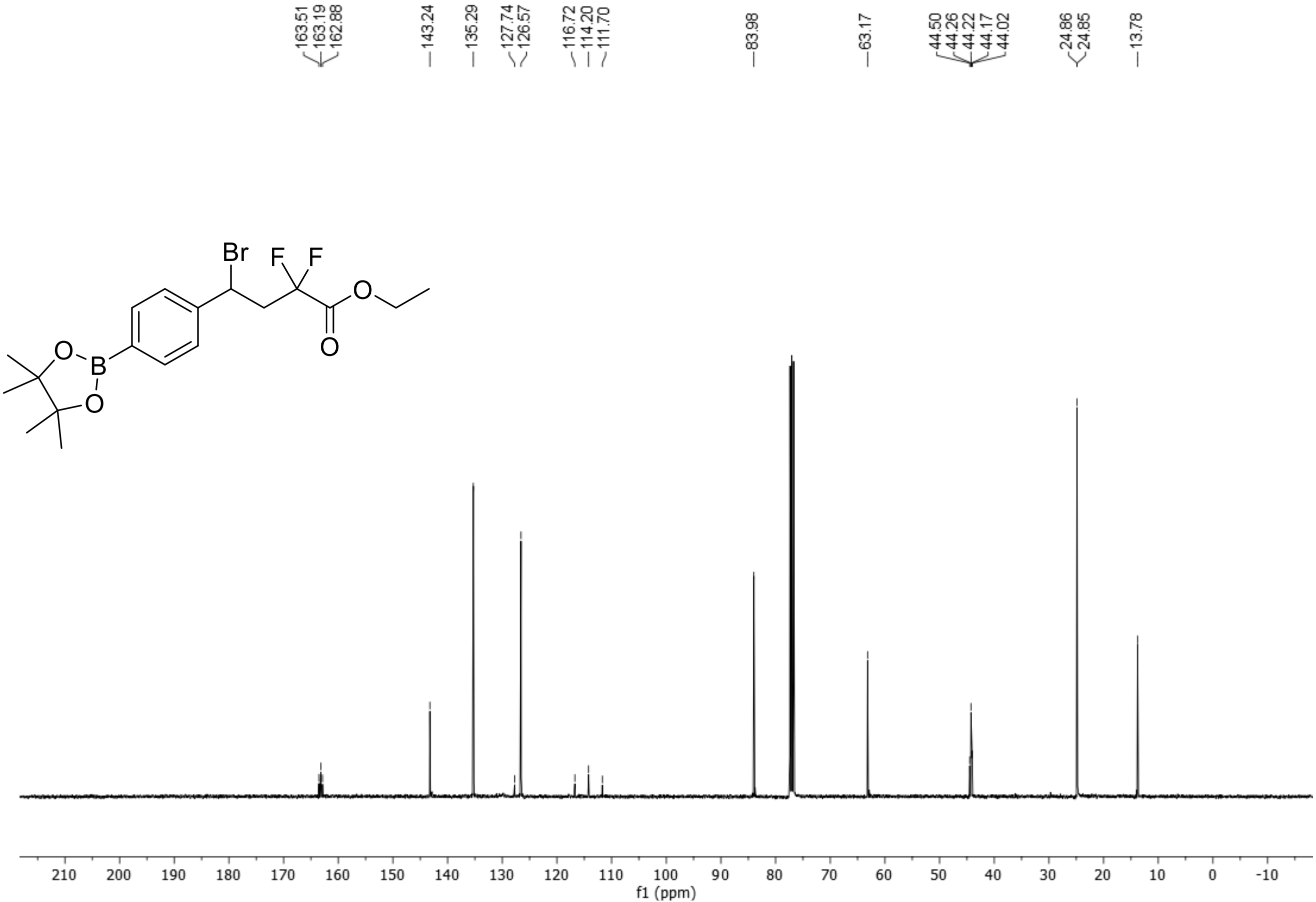


^{1}H NMR (400 MHz, CDCl$_3$) of compound **3j**.

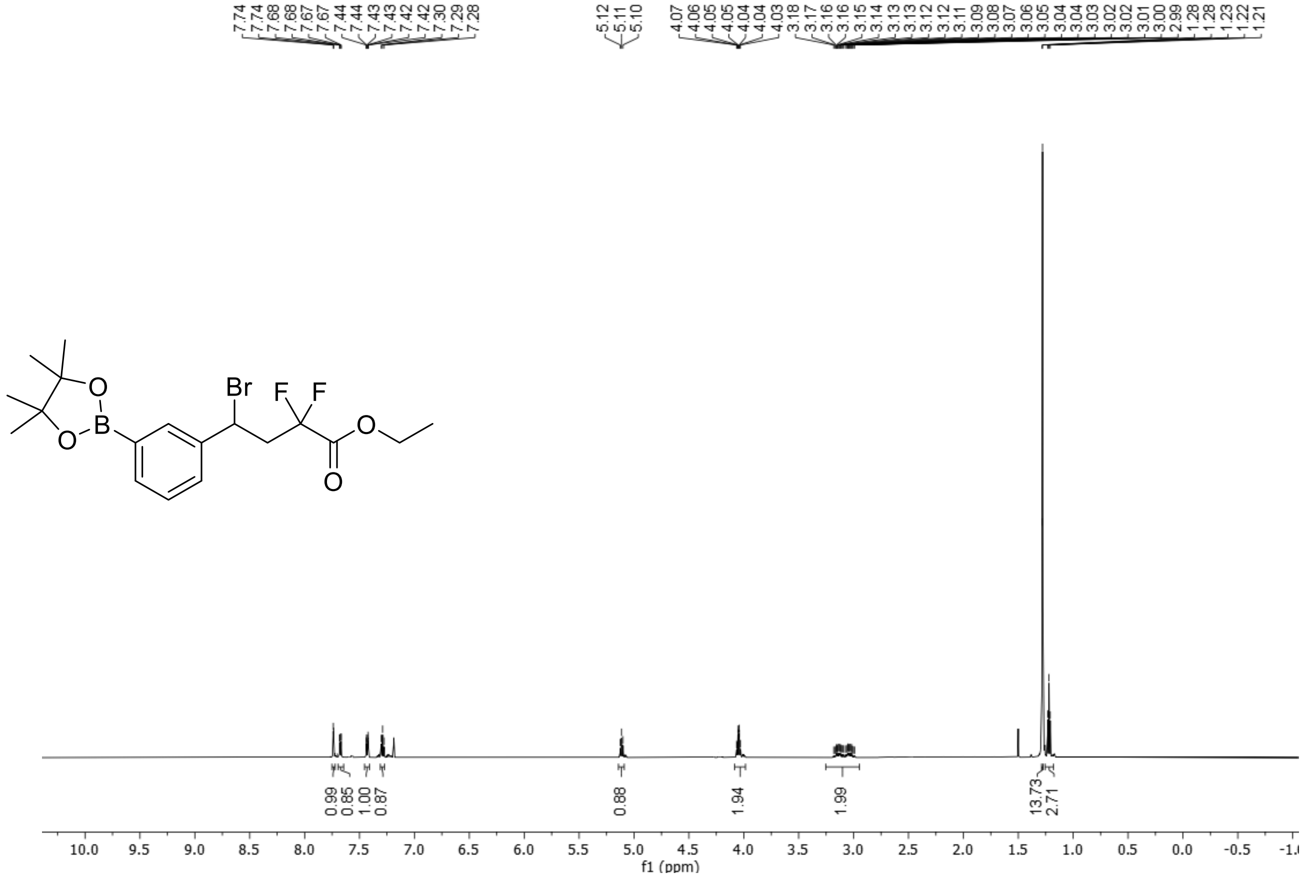
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3j.**



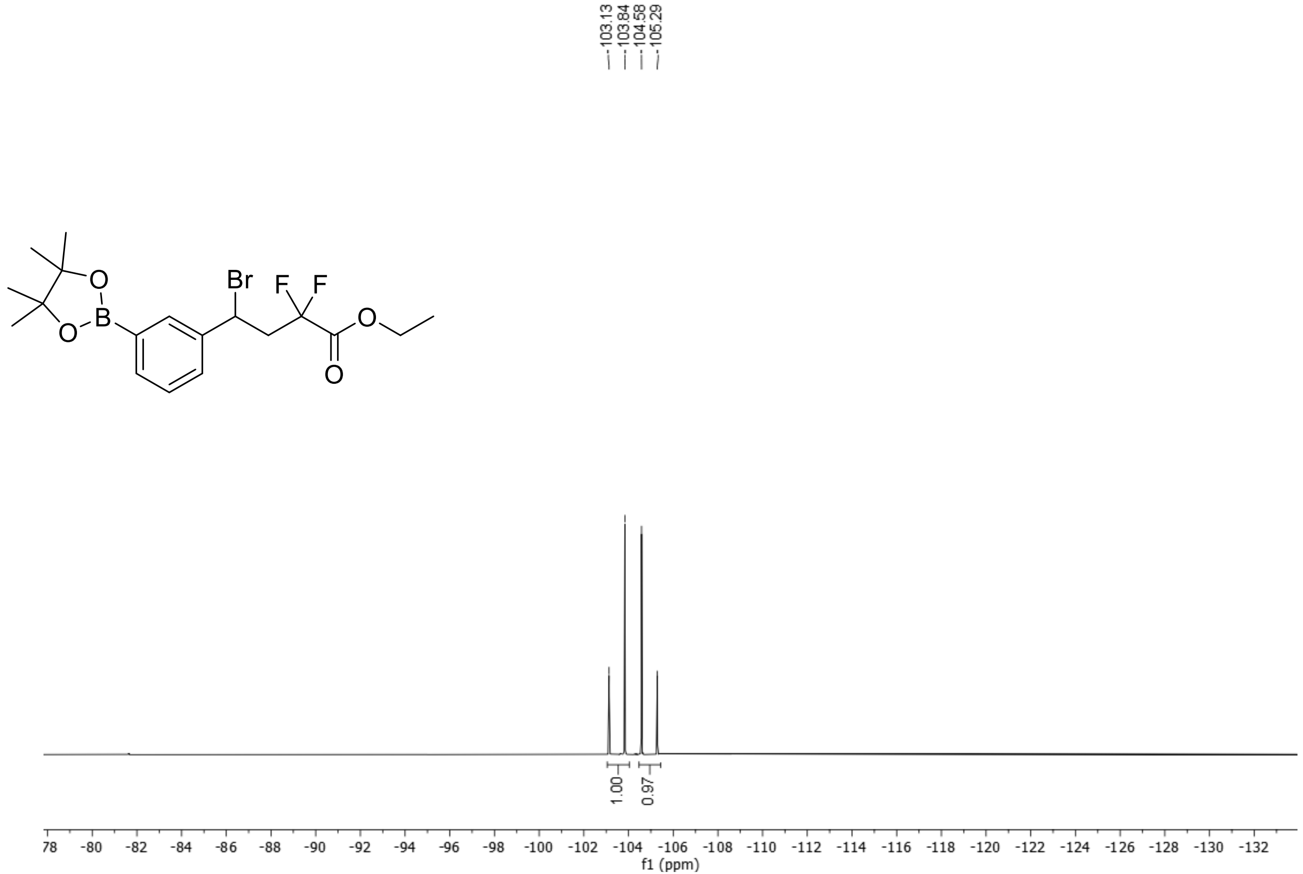
^{11}B NMR (128 MHz, CDCl$_3$) of compound **3k.**



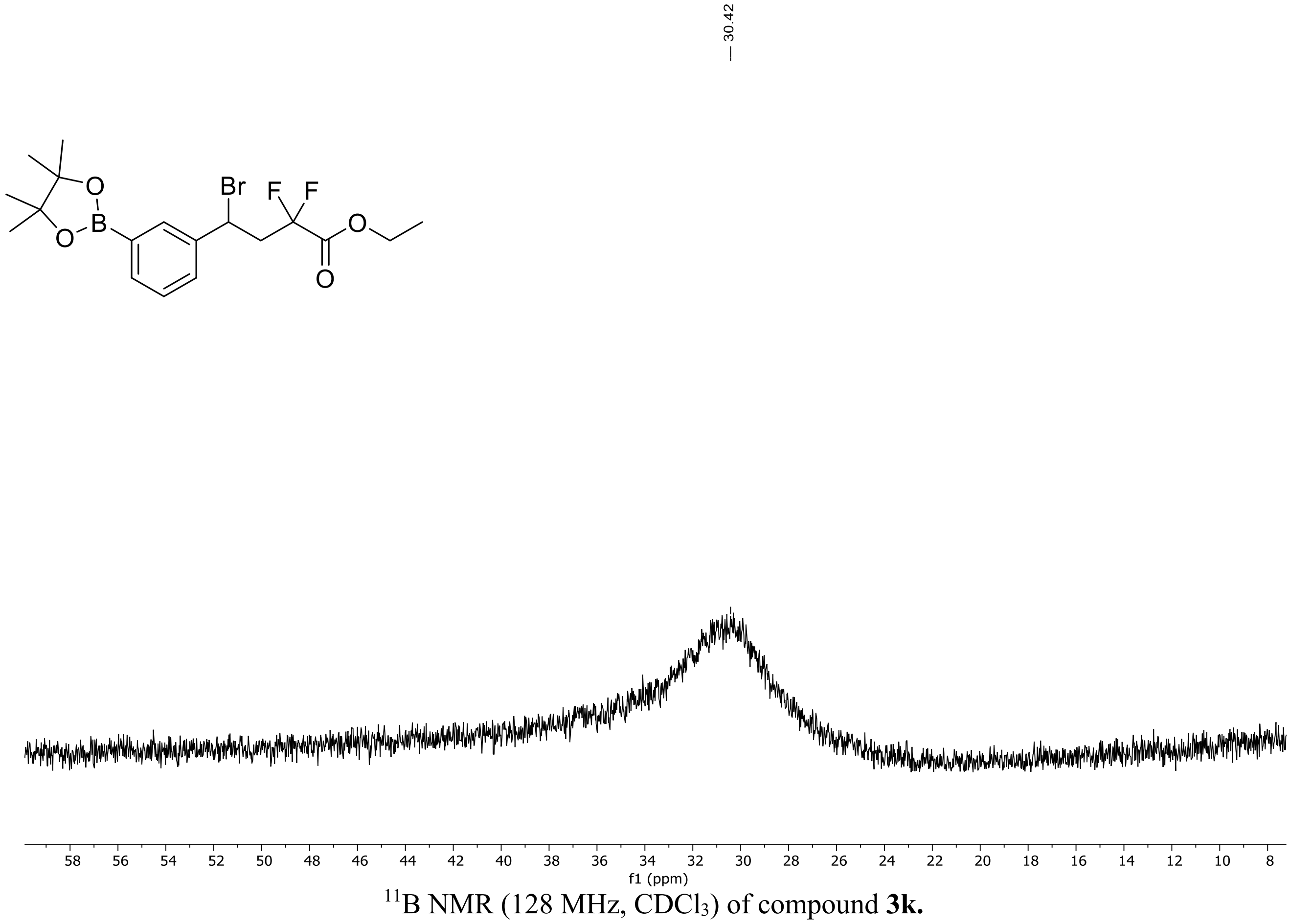
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3j.**



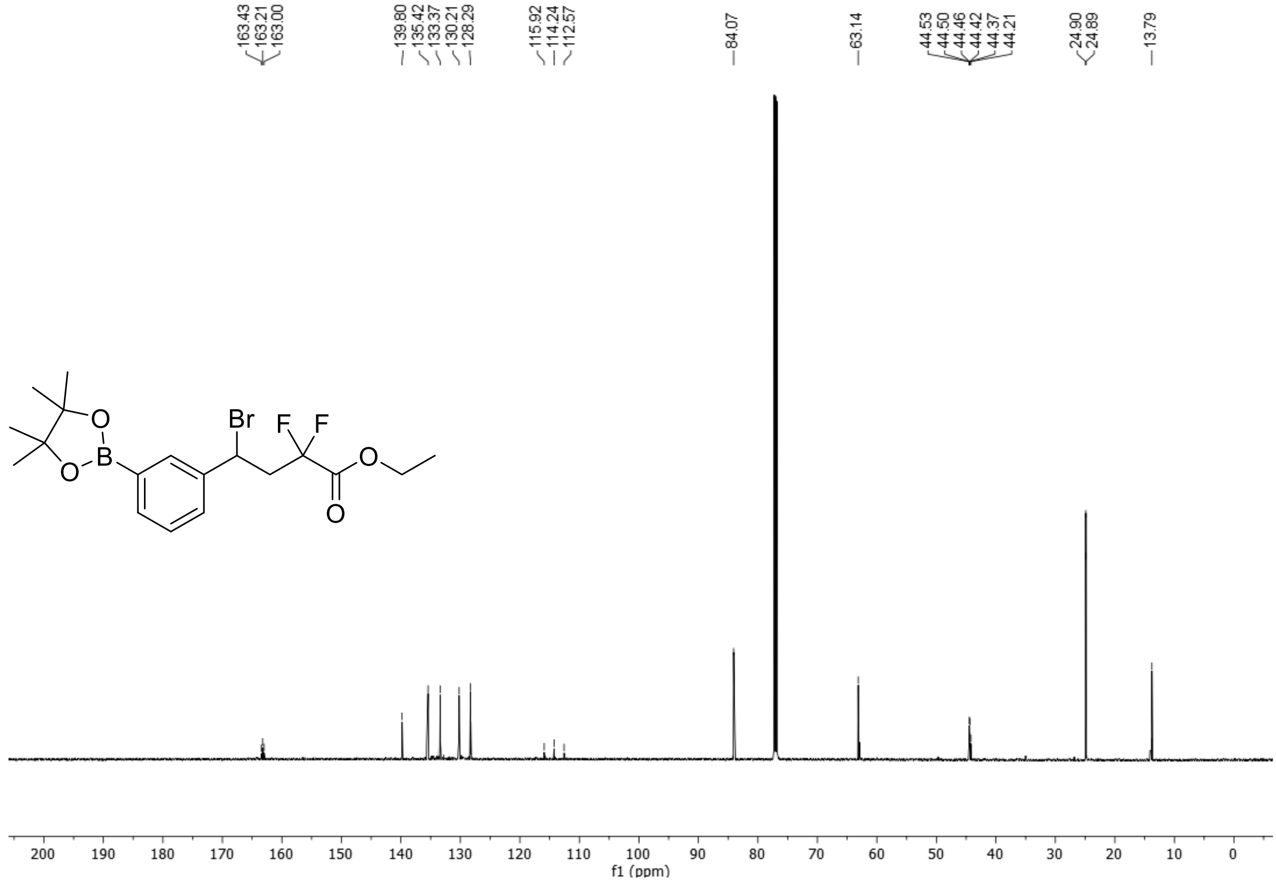
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3k**.



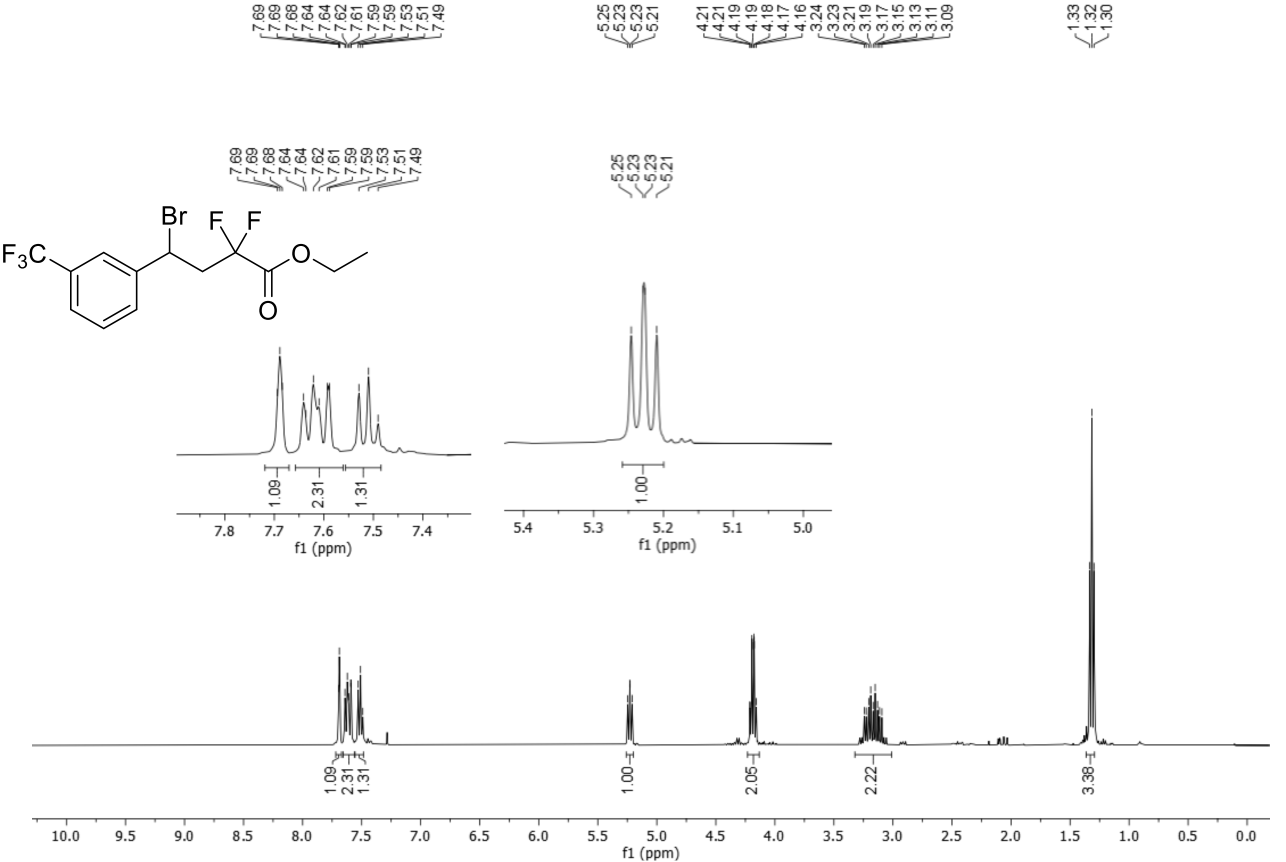
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3k.**



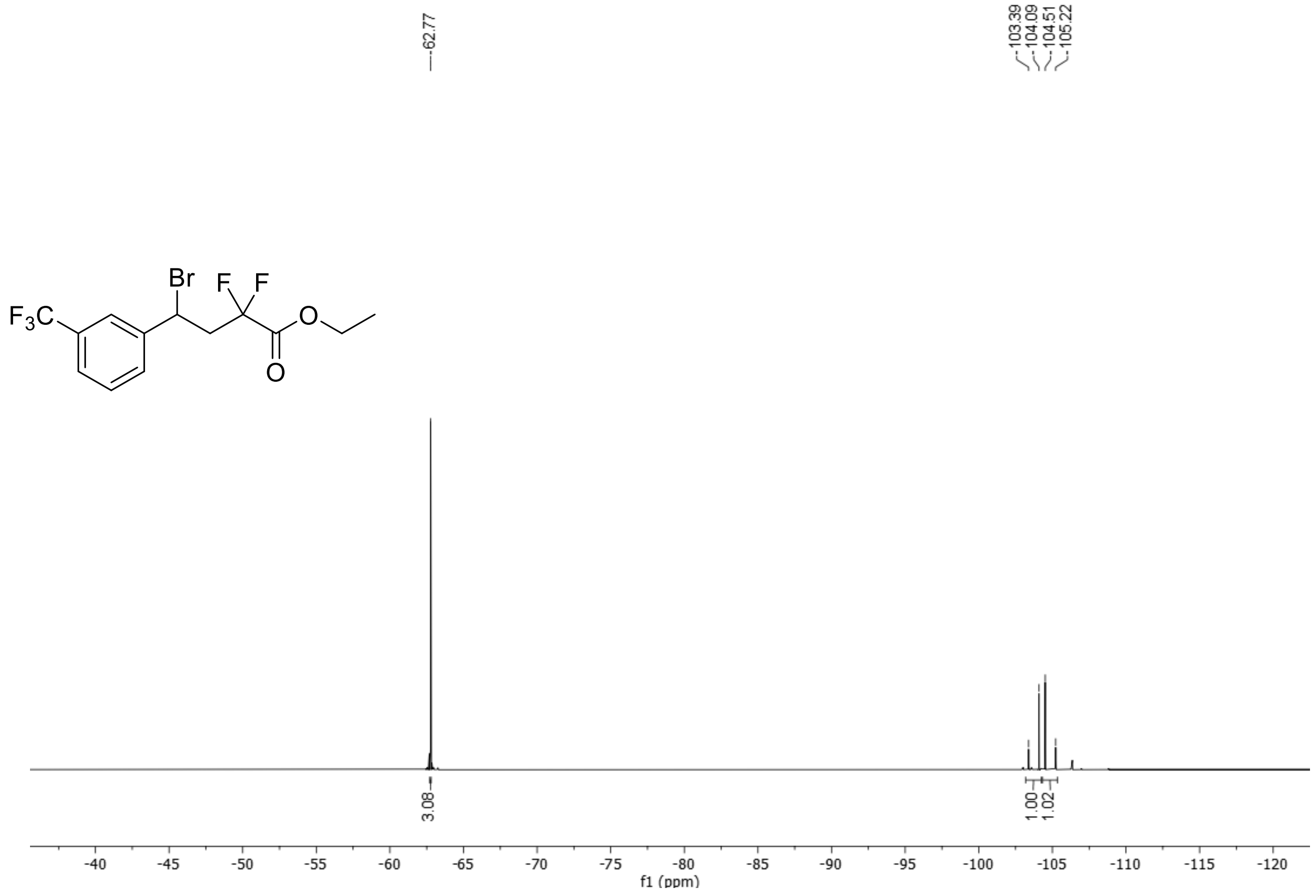
^{11}B NMR (128 MHz, CDCl$_3$) of compound **3k.**



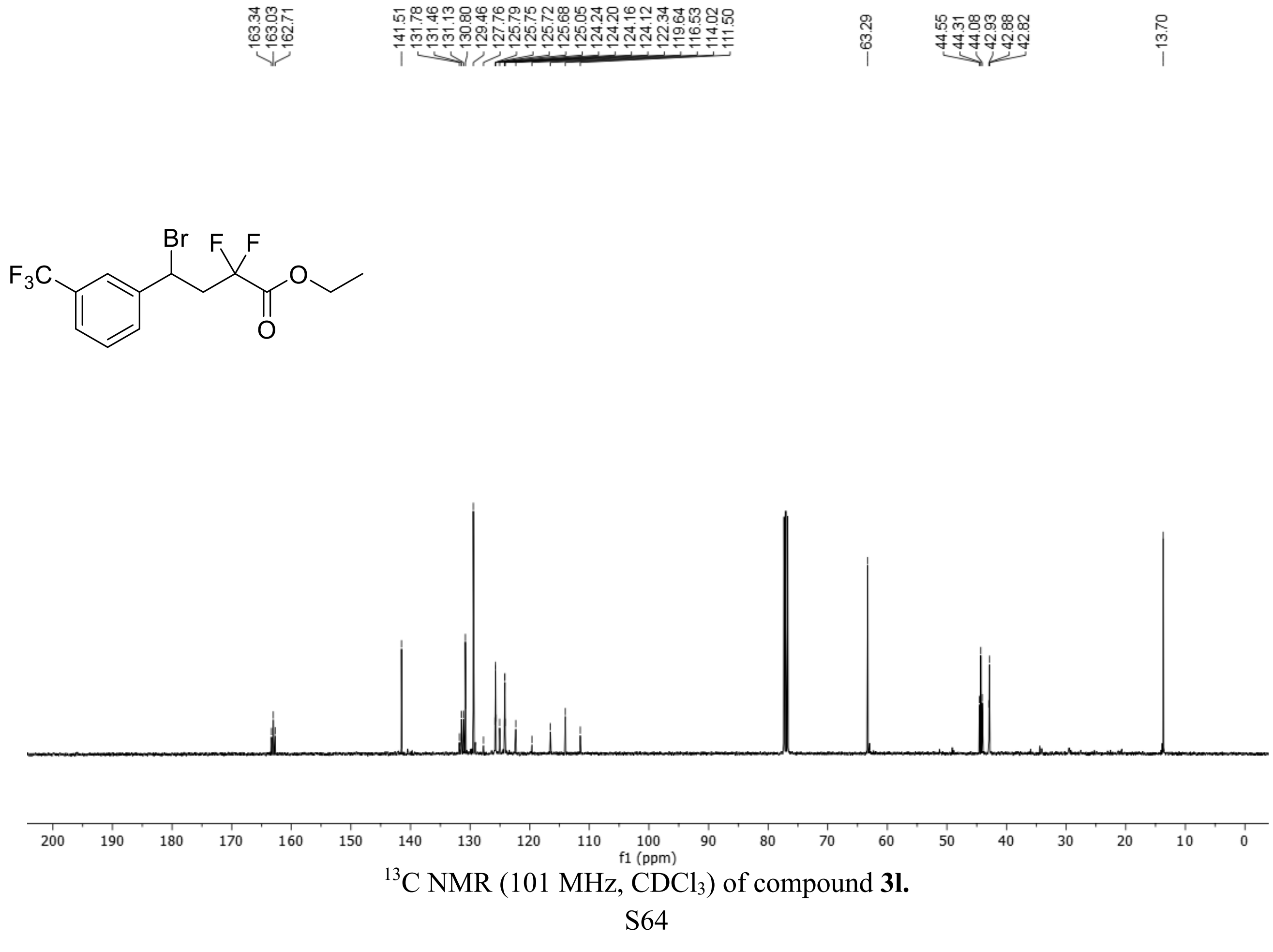
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3k.**



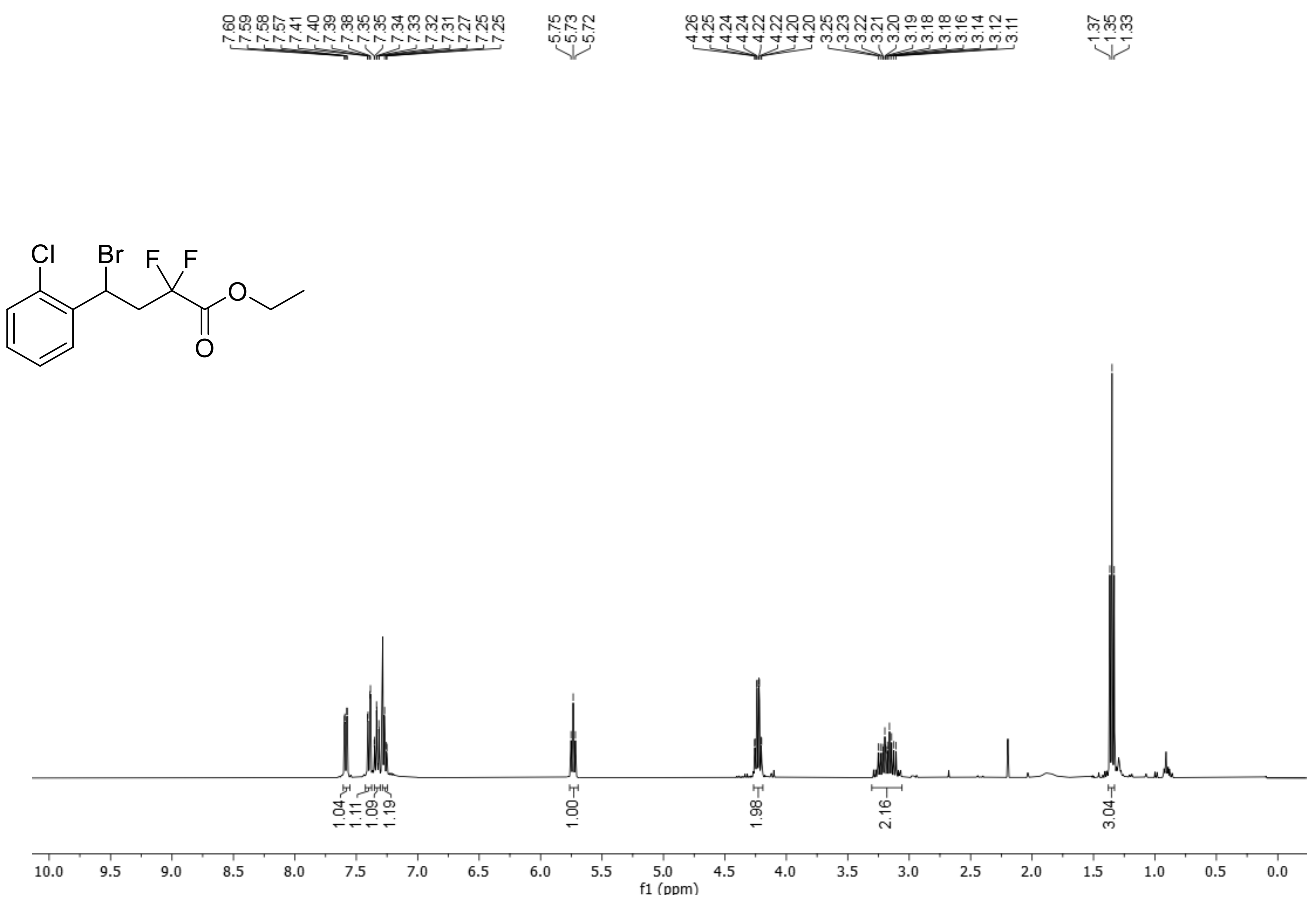
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3l**.



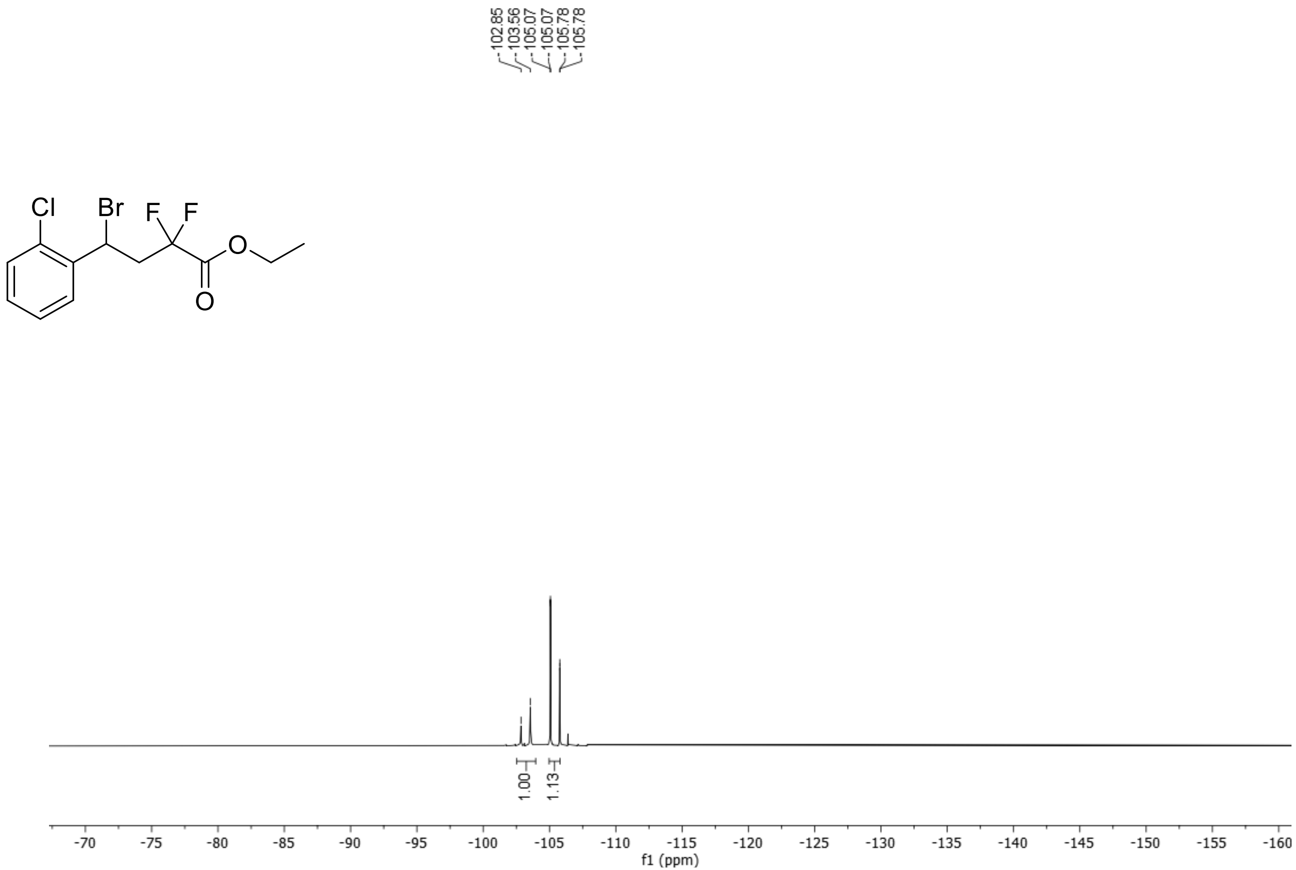
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3l.**



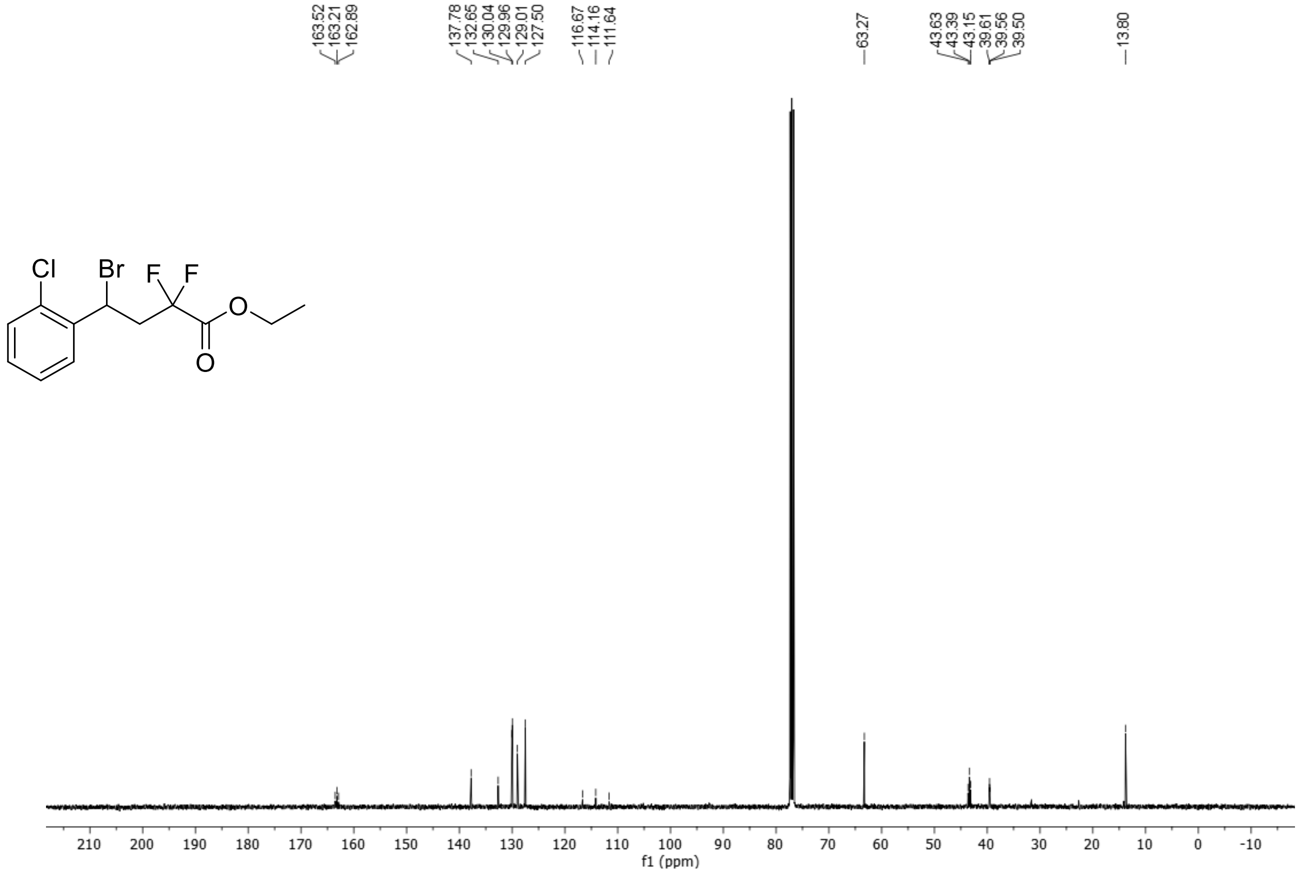
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3l.**



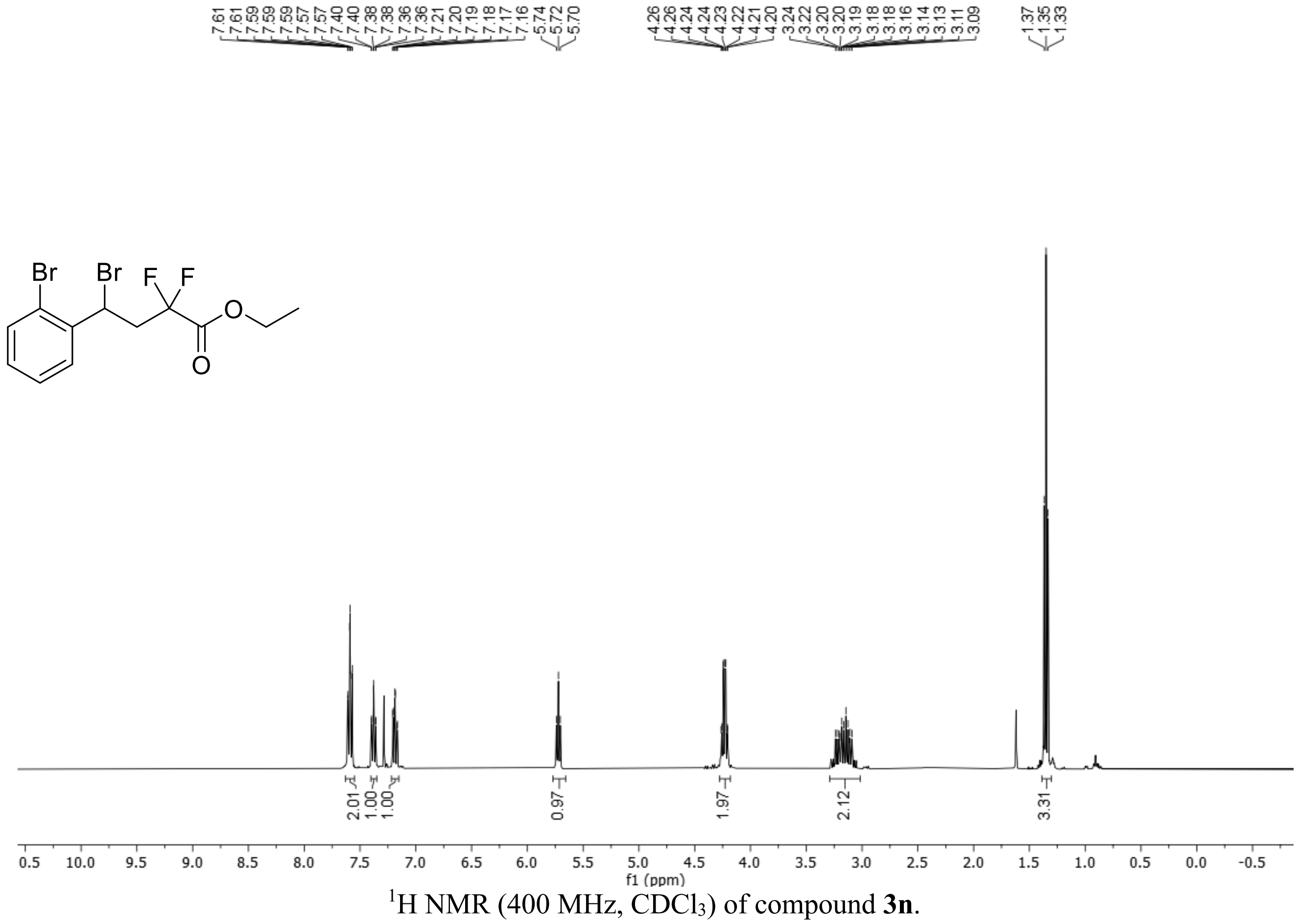
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3m**.



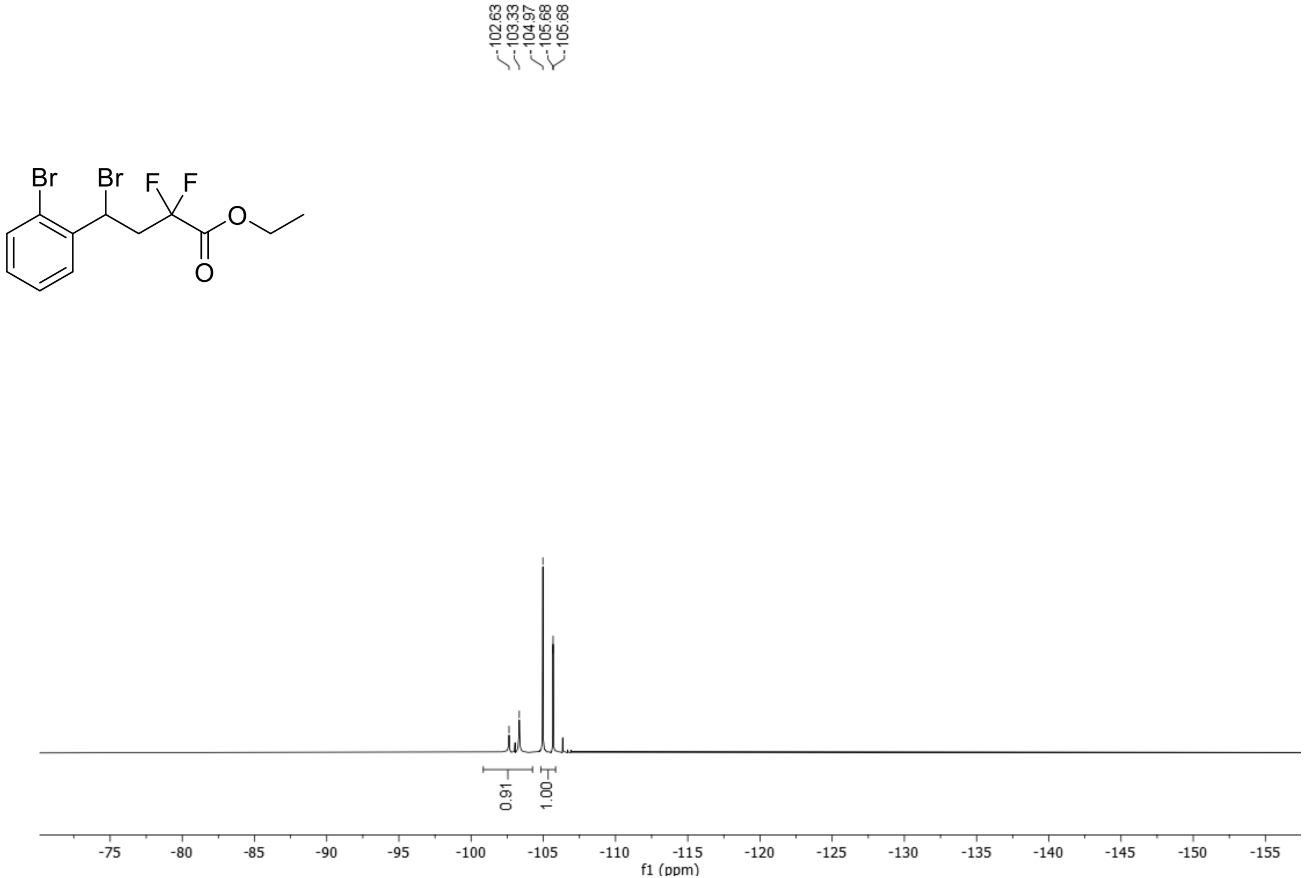
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3m.**



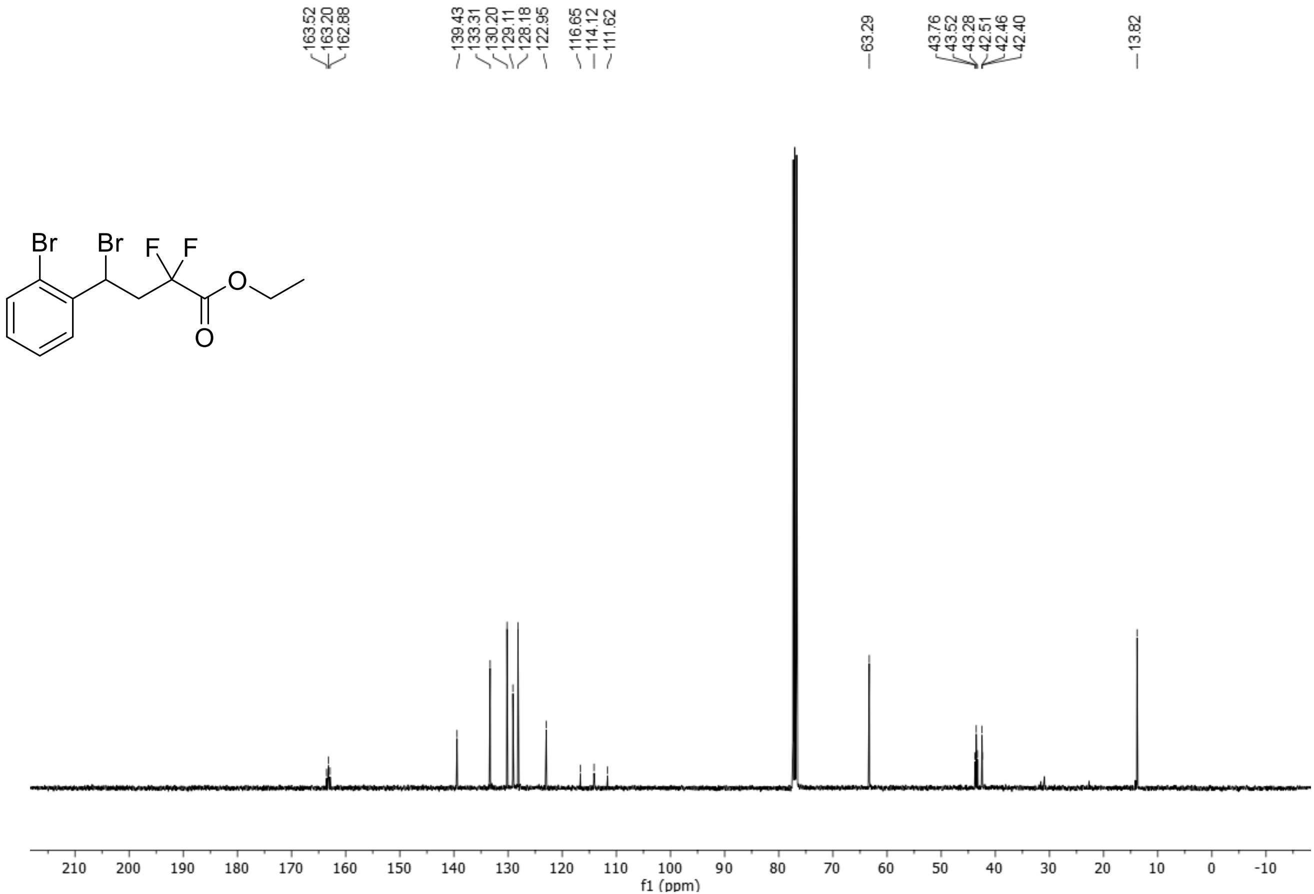
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3m.**



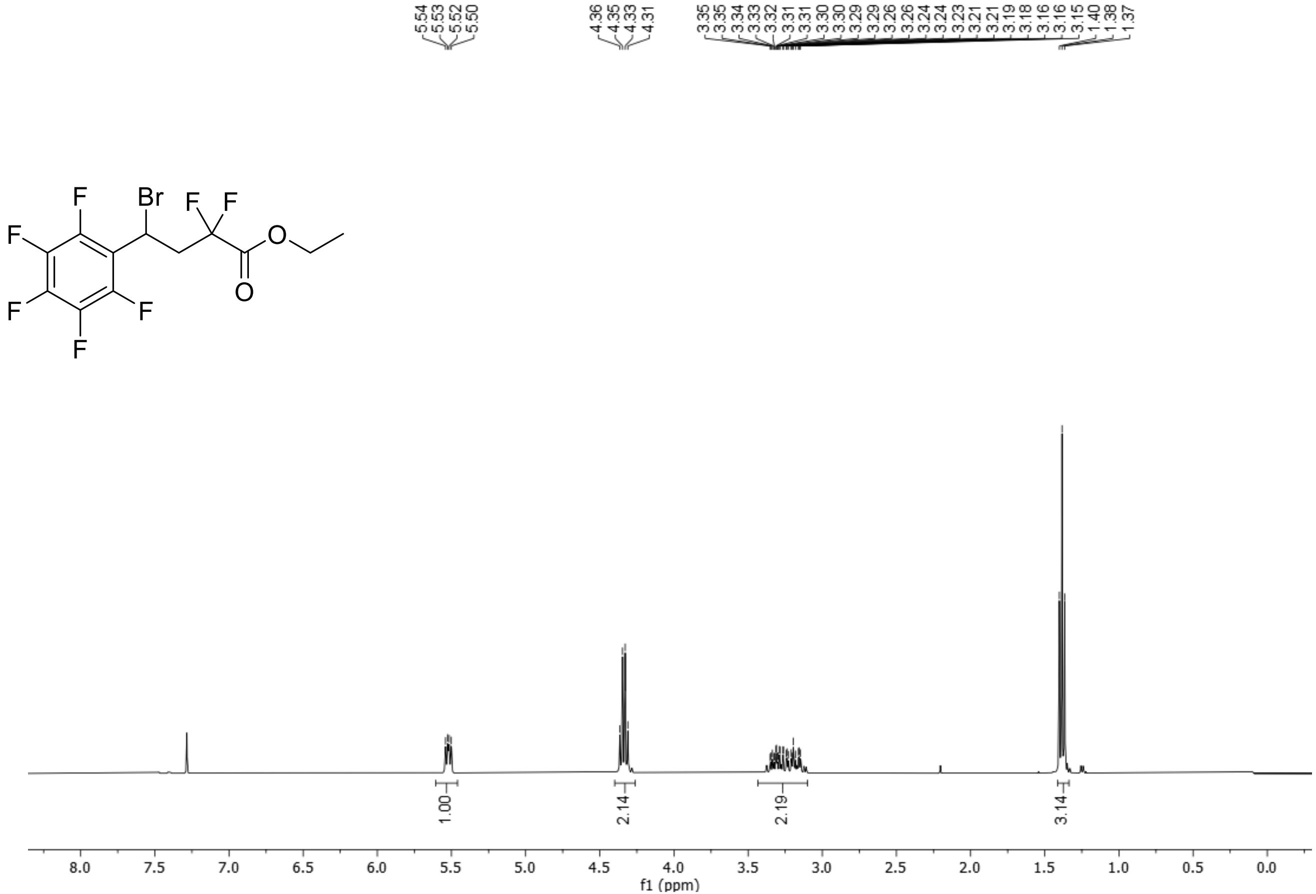
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3n**.



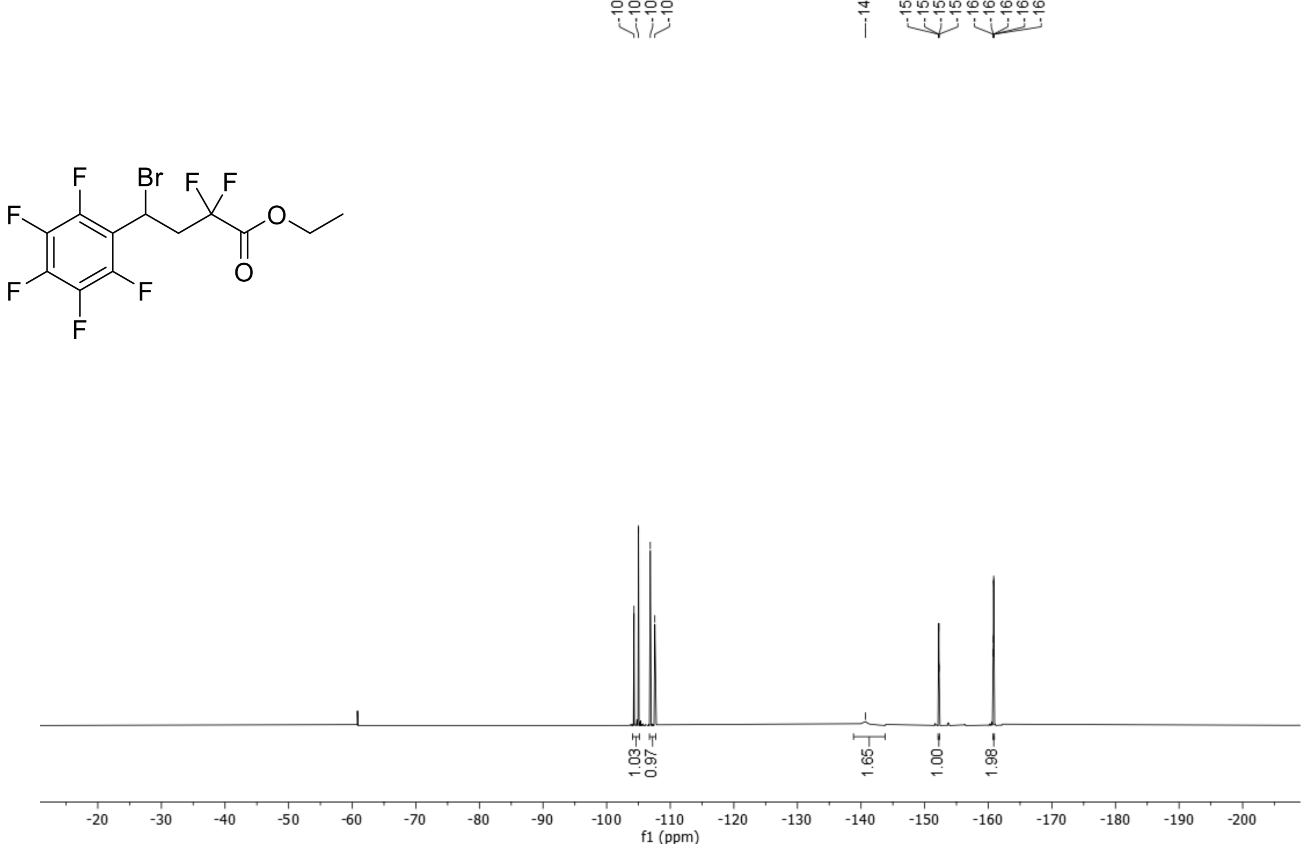
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3n.**



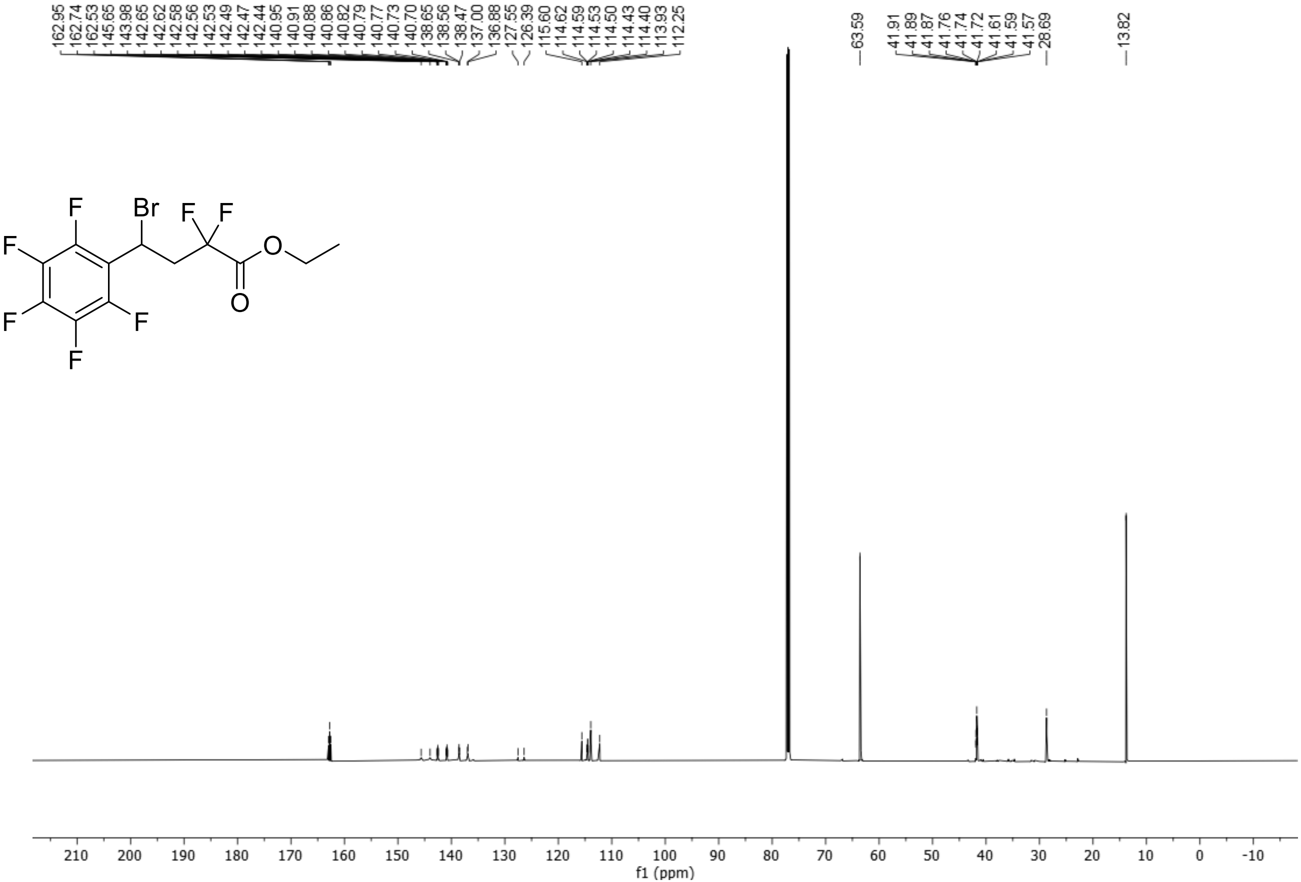
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3n.**



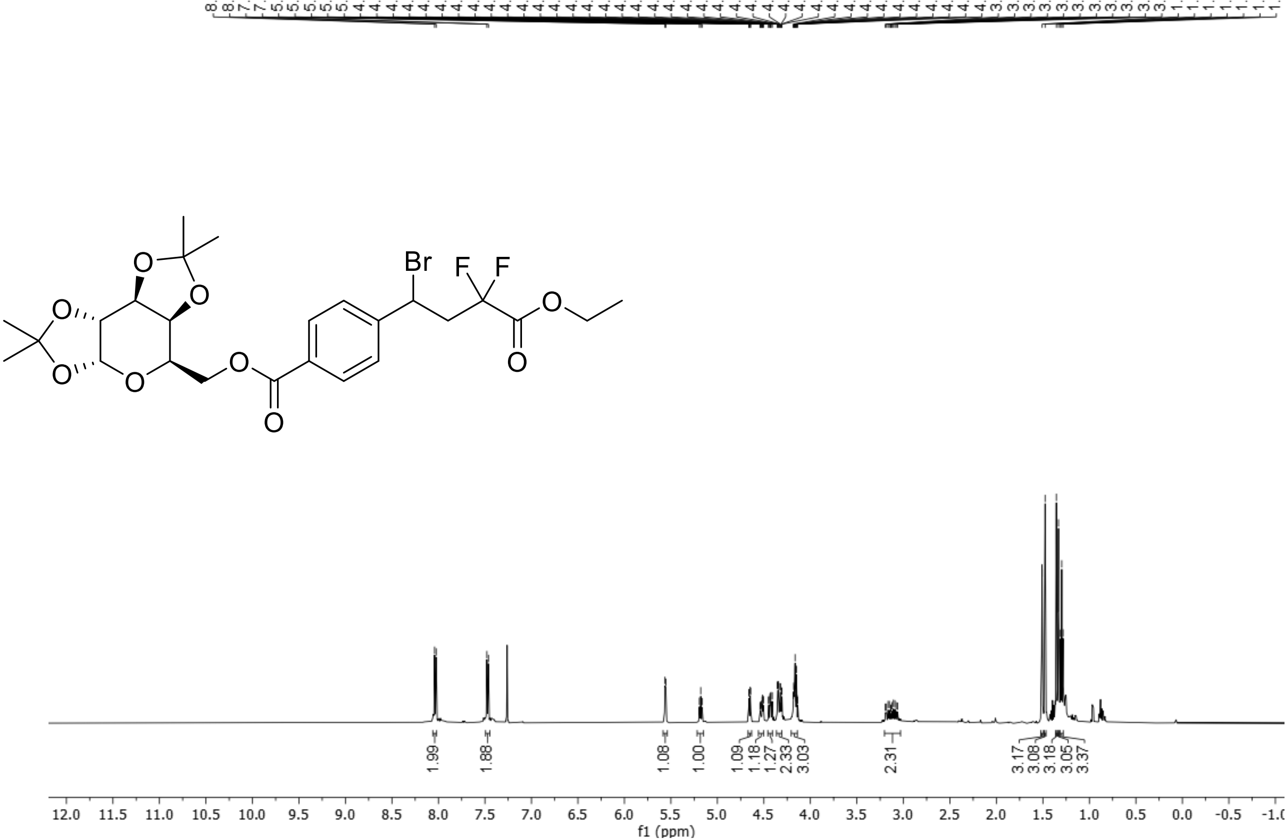
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3o**.



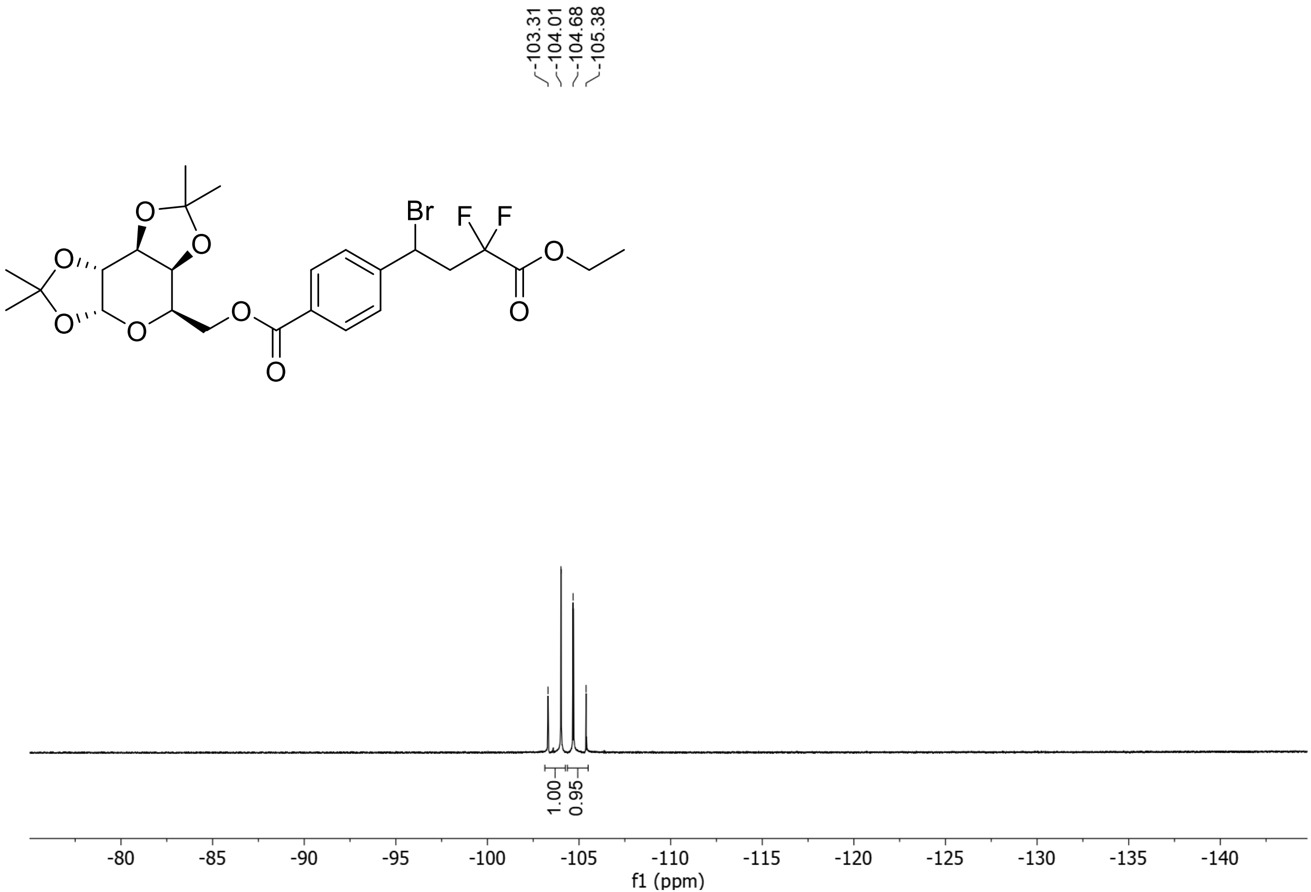
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3o.**



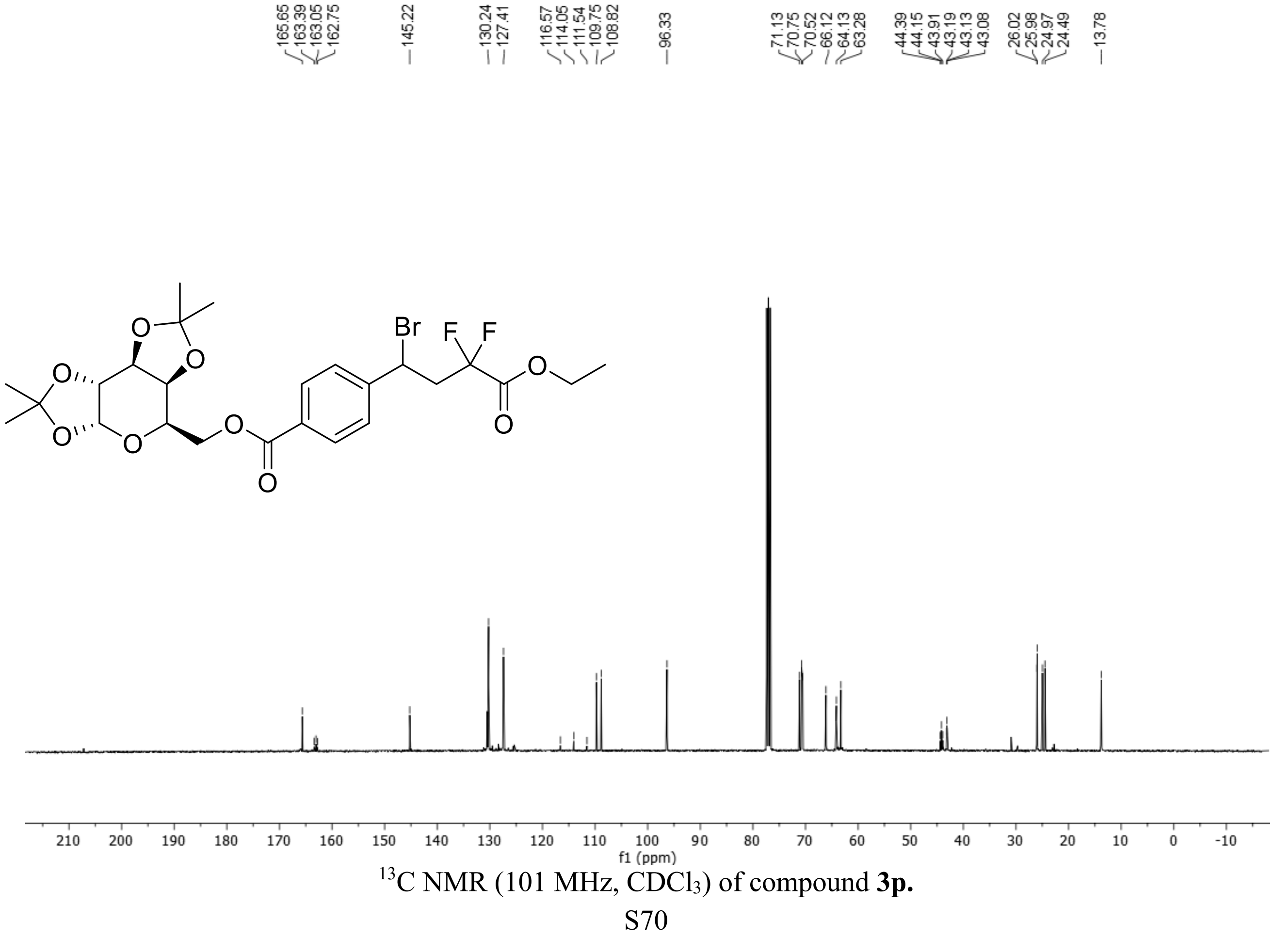
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3o.**



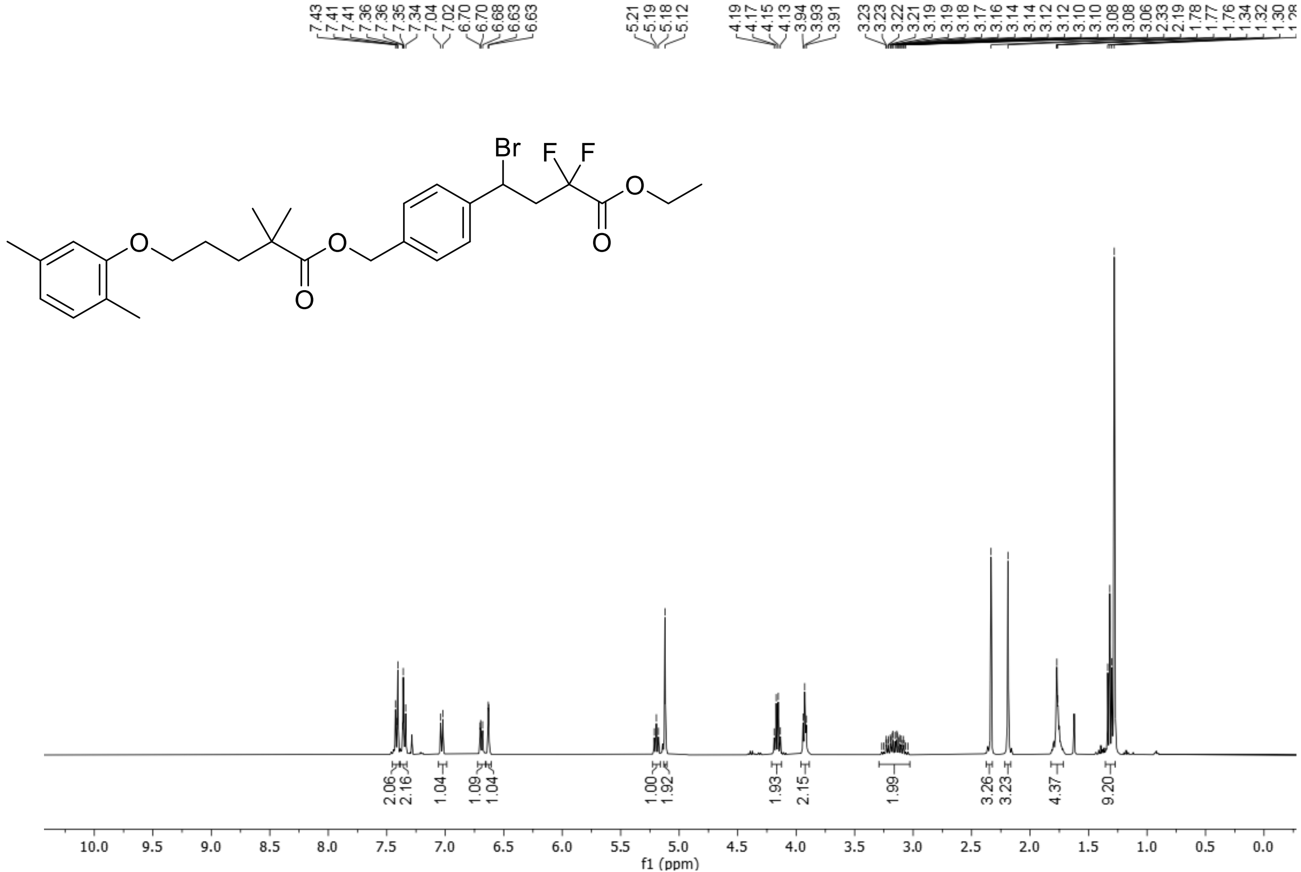
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3p**.



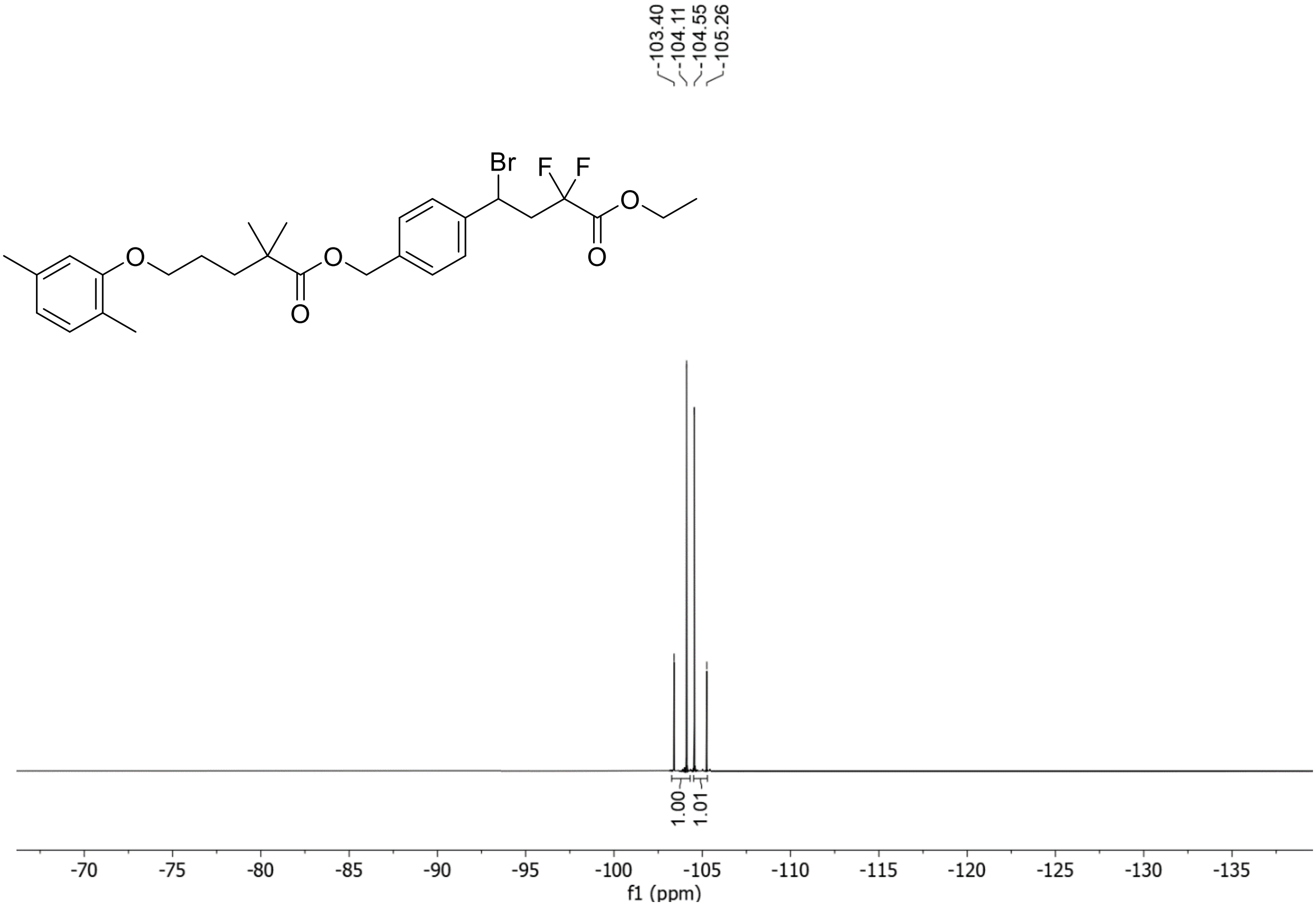
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3p.**



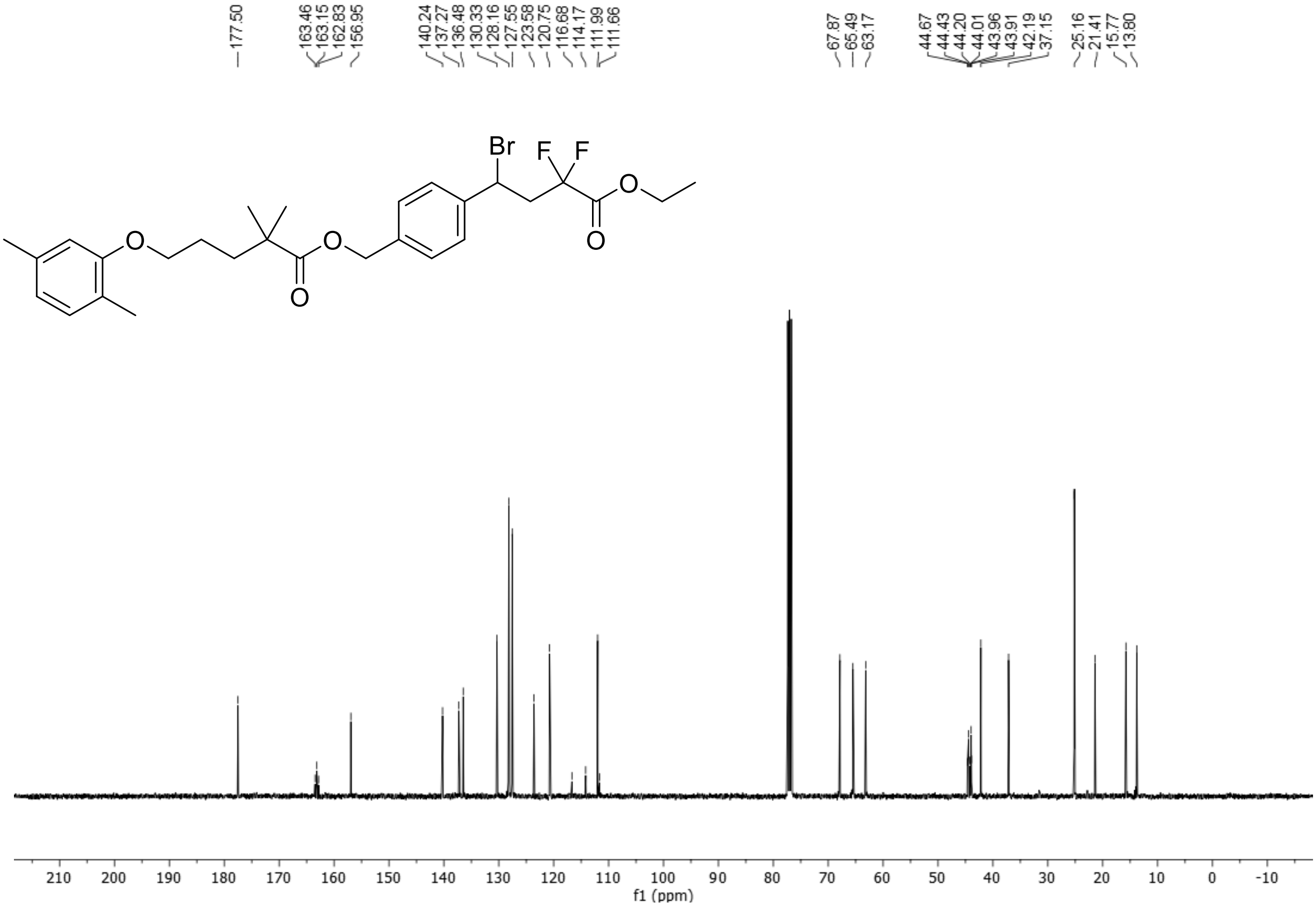
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3p.**



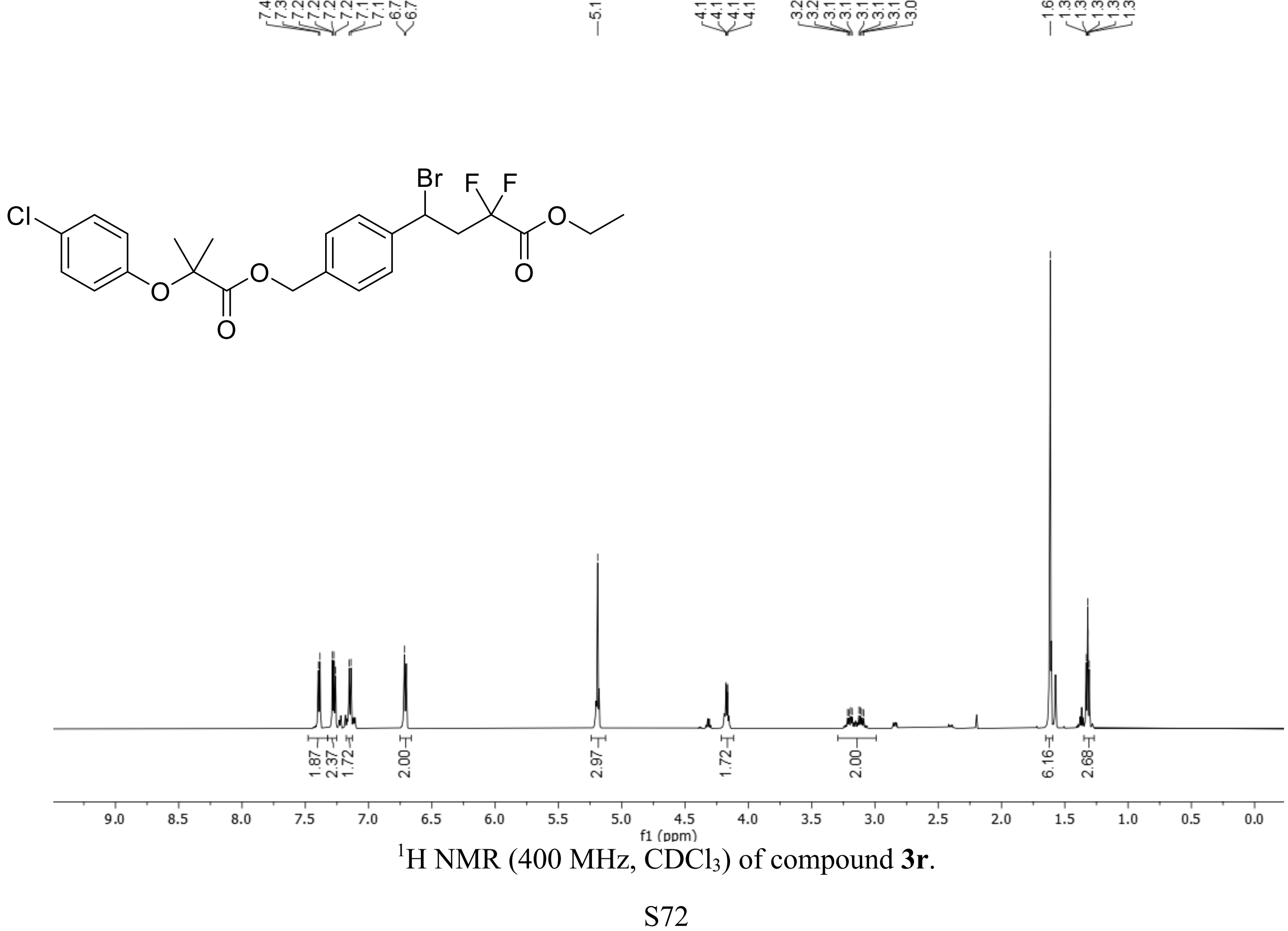
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3q**.



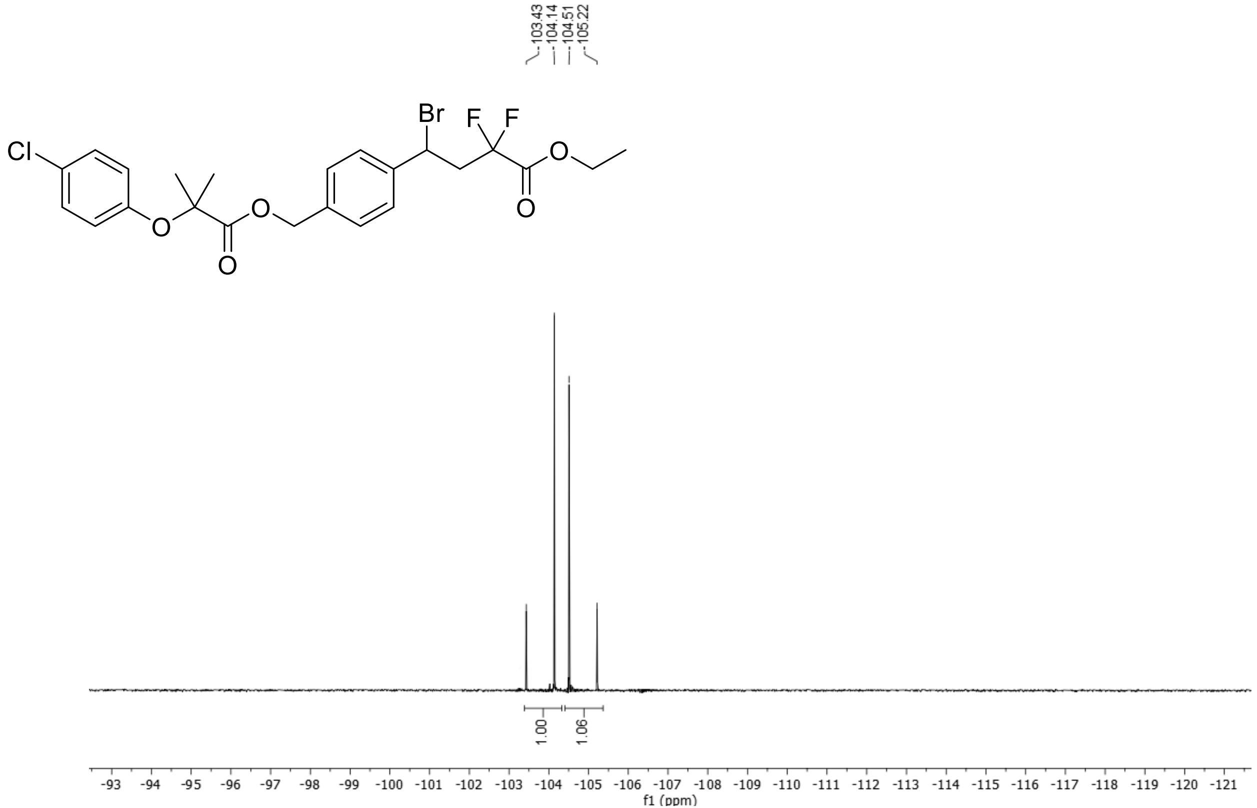
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3q.**



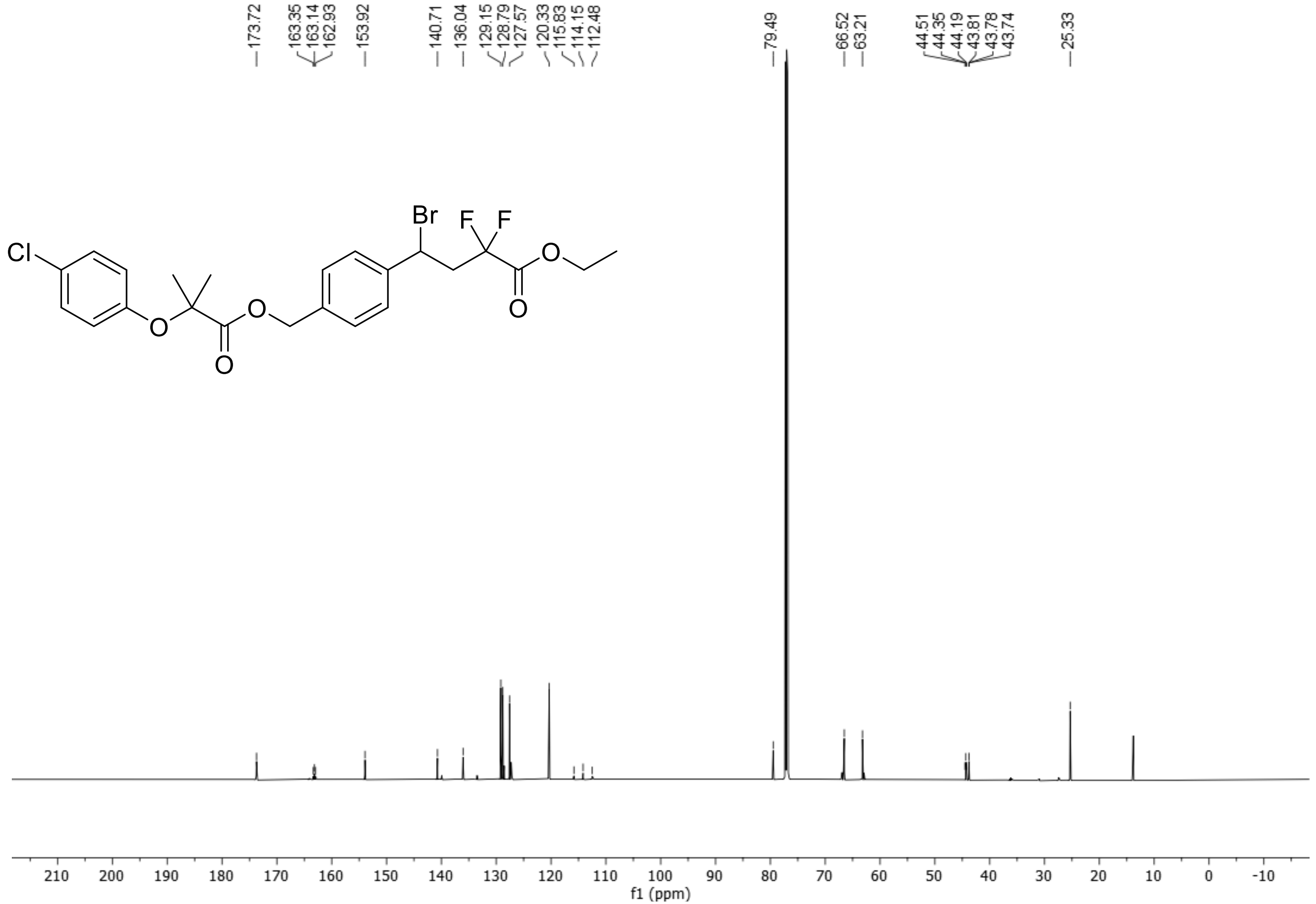
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3q.**



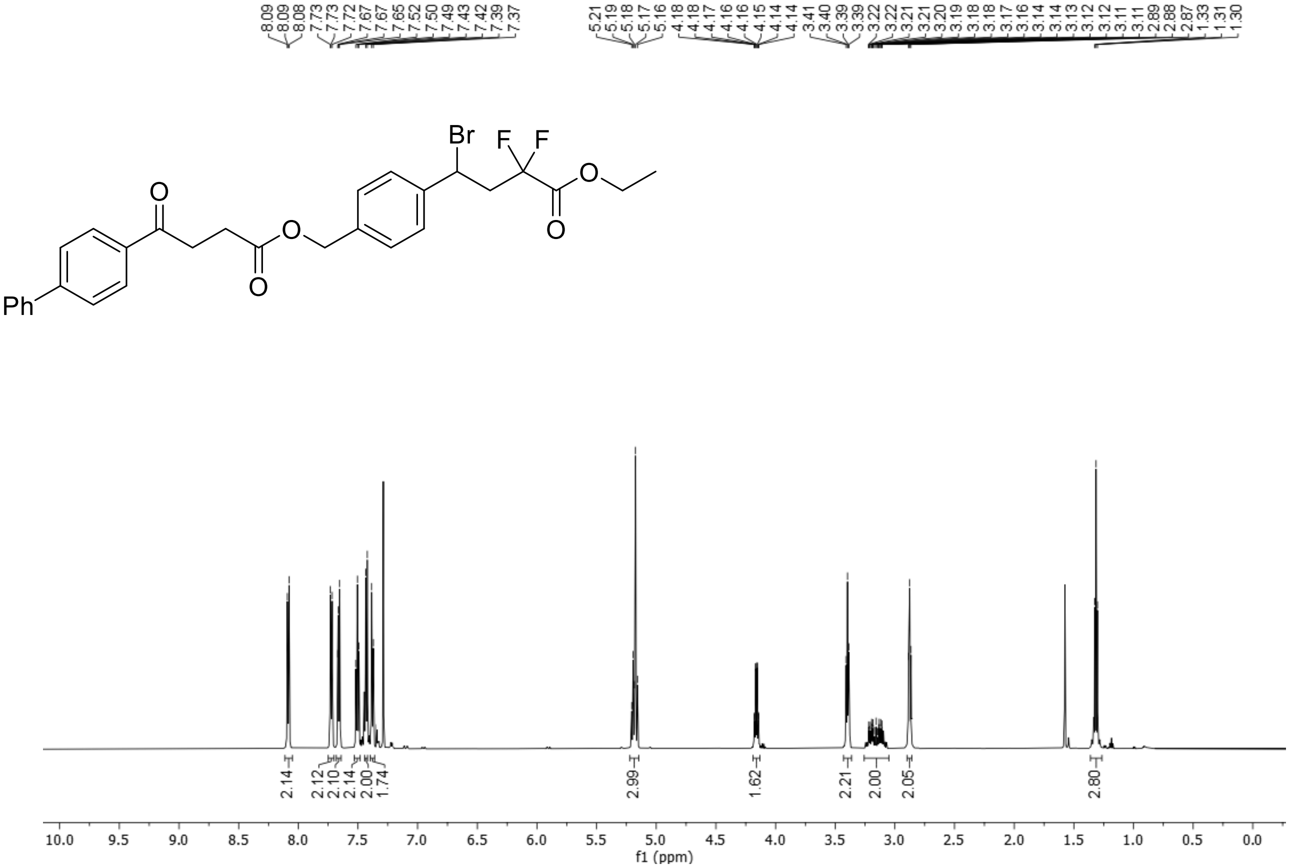
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3r**.



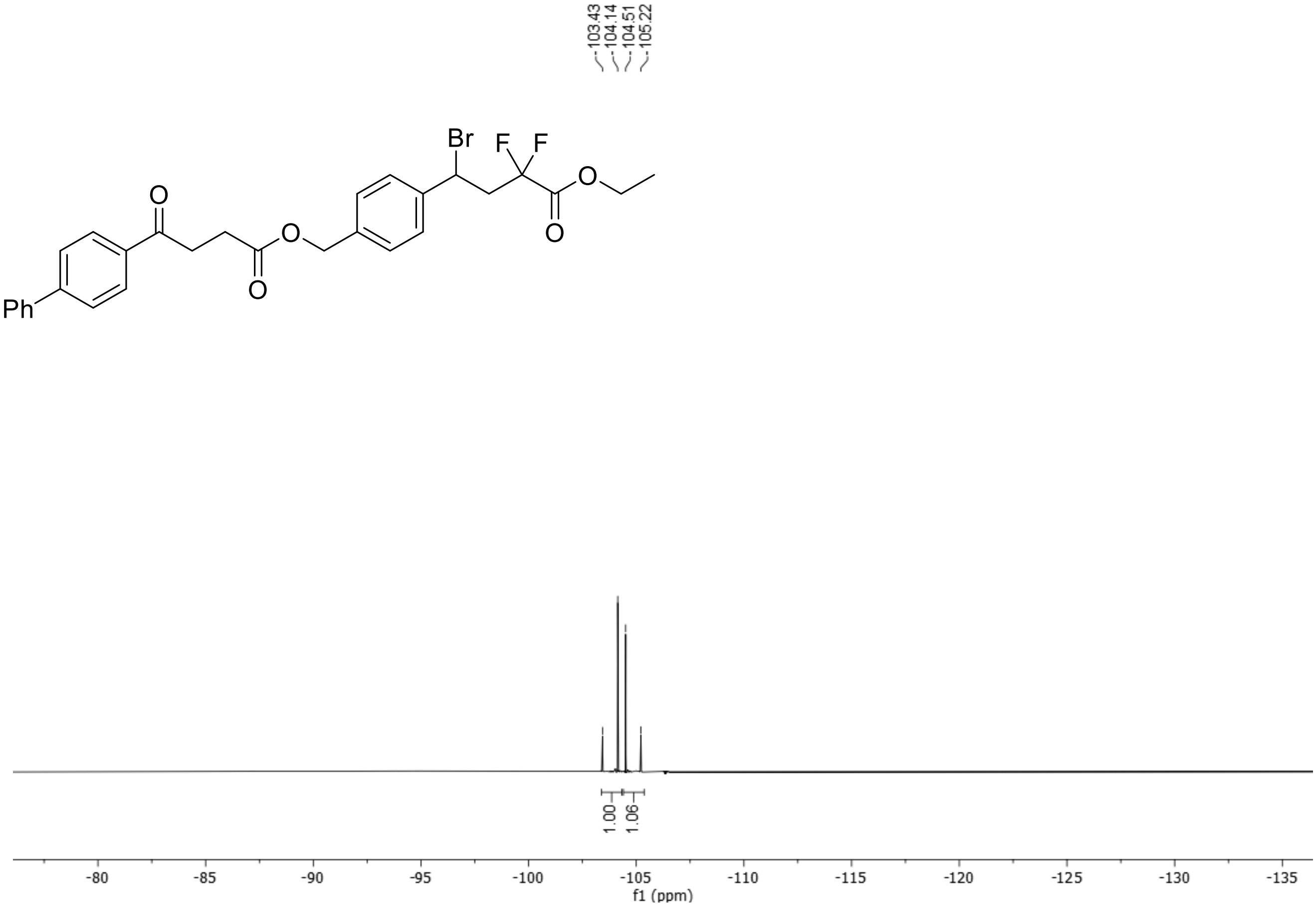
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3r.**



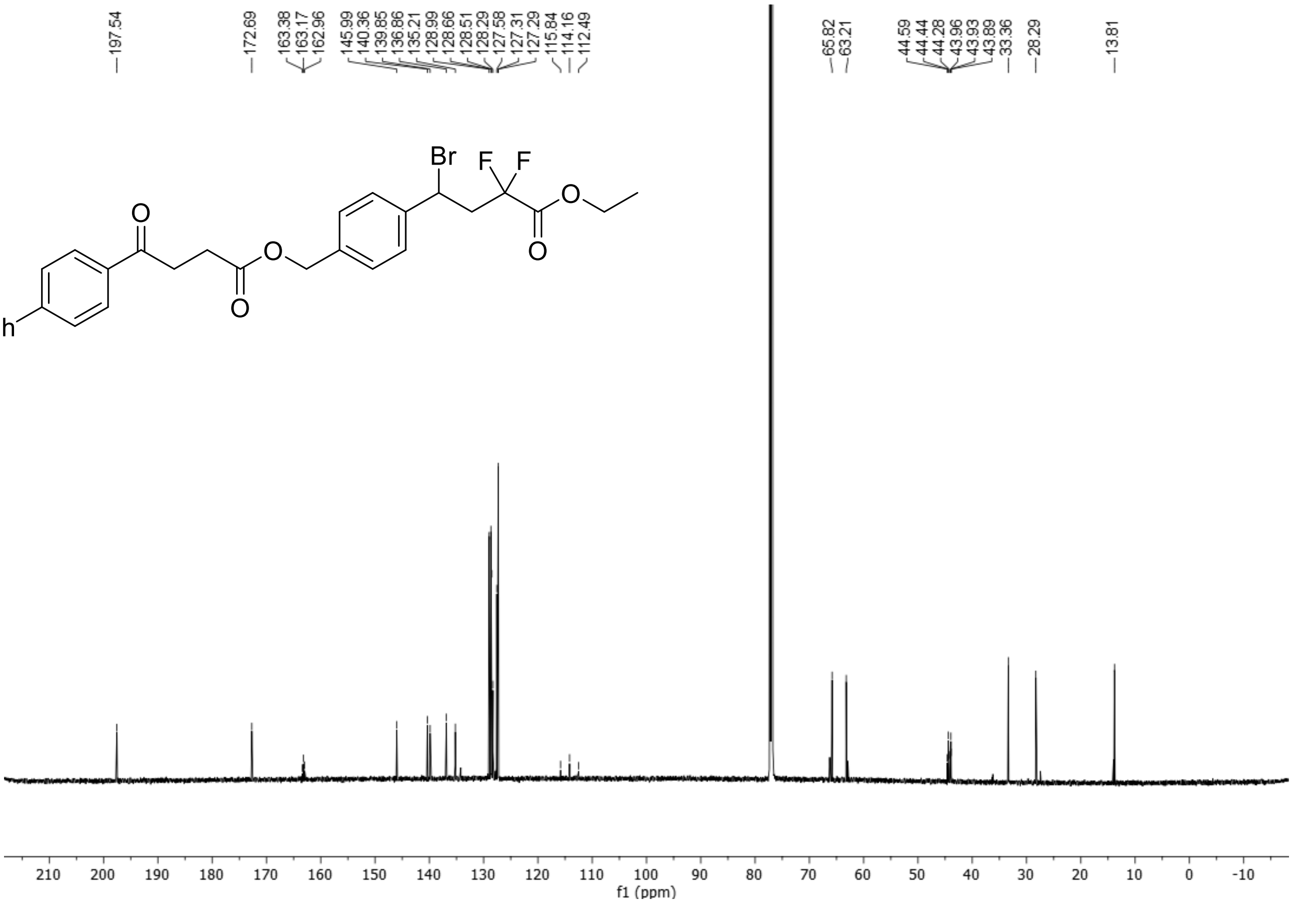
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3r.**



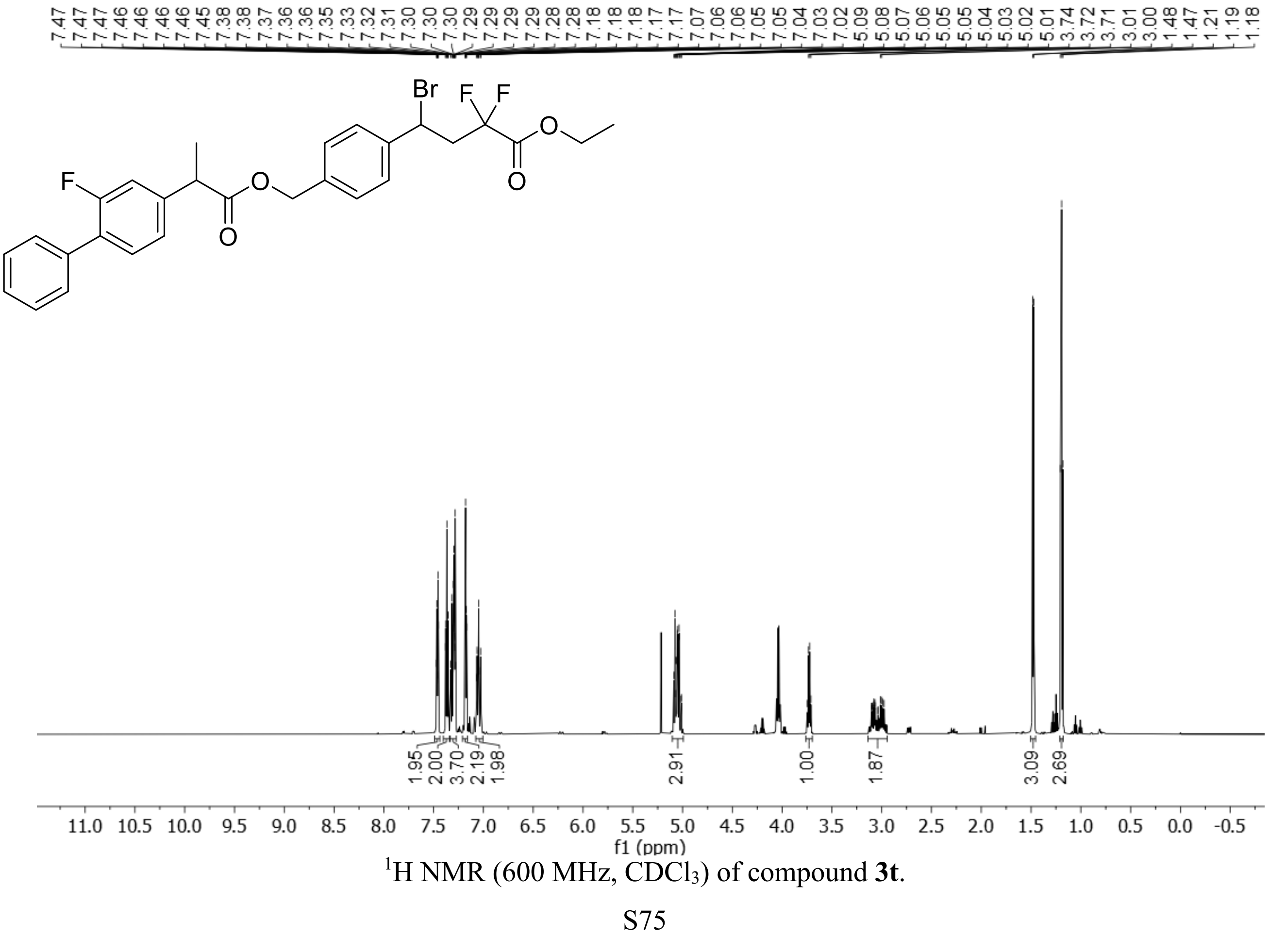
^{1}H NMR (600 MHz, CDCl$_3$) of compound **3s**.



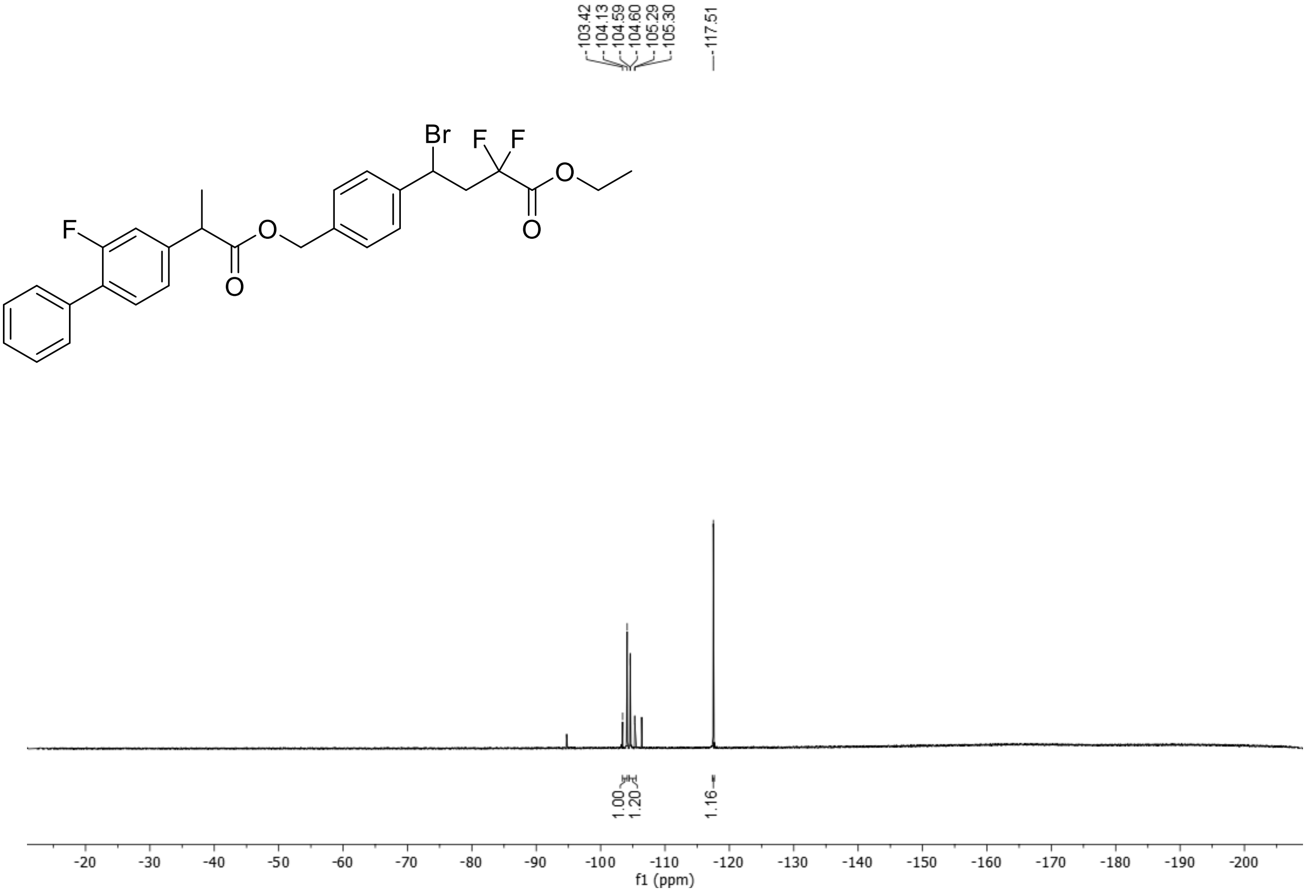
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3s.**



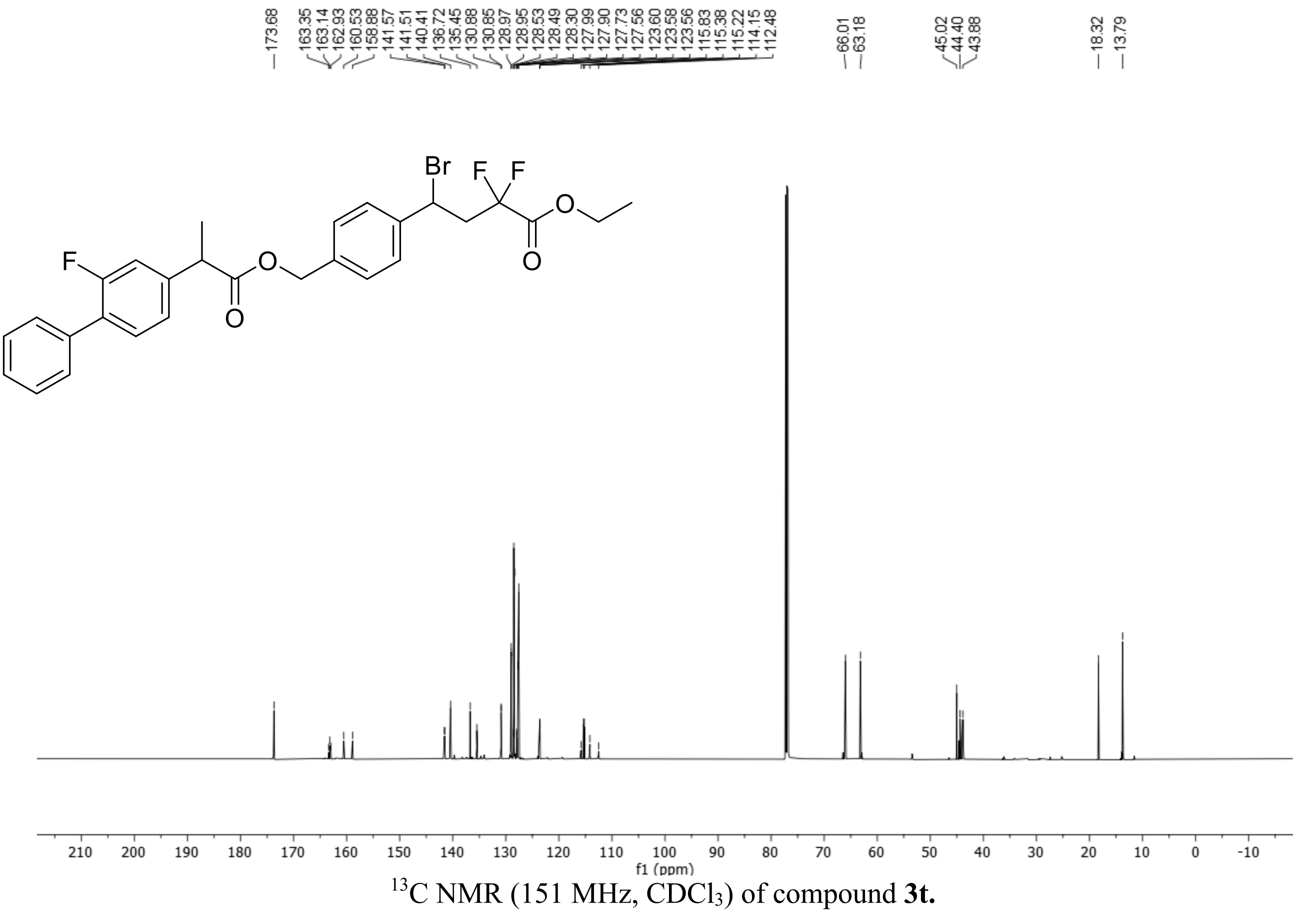
^{13}C NMR (151 MHz, CDCl$_3$) of compound **3s.**



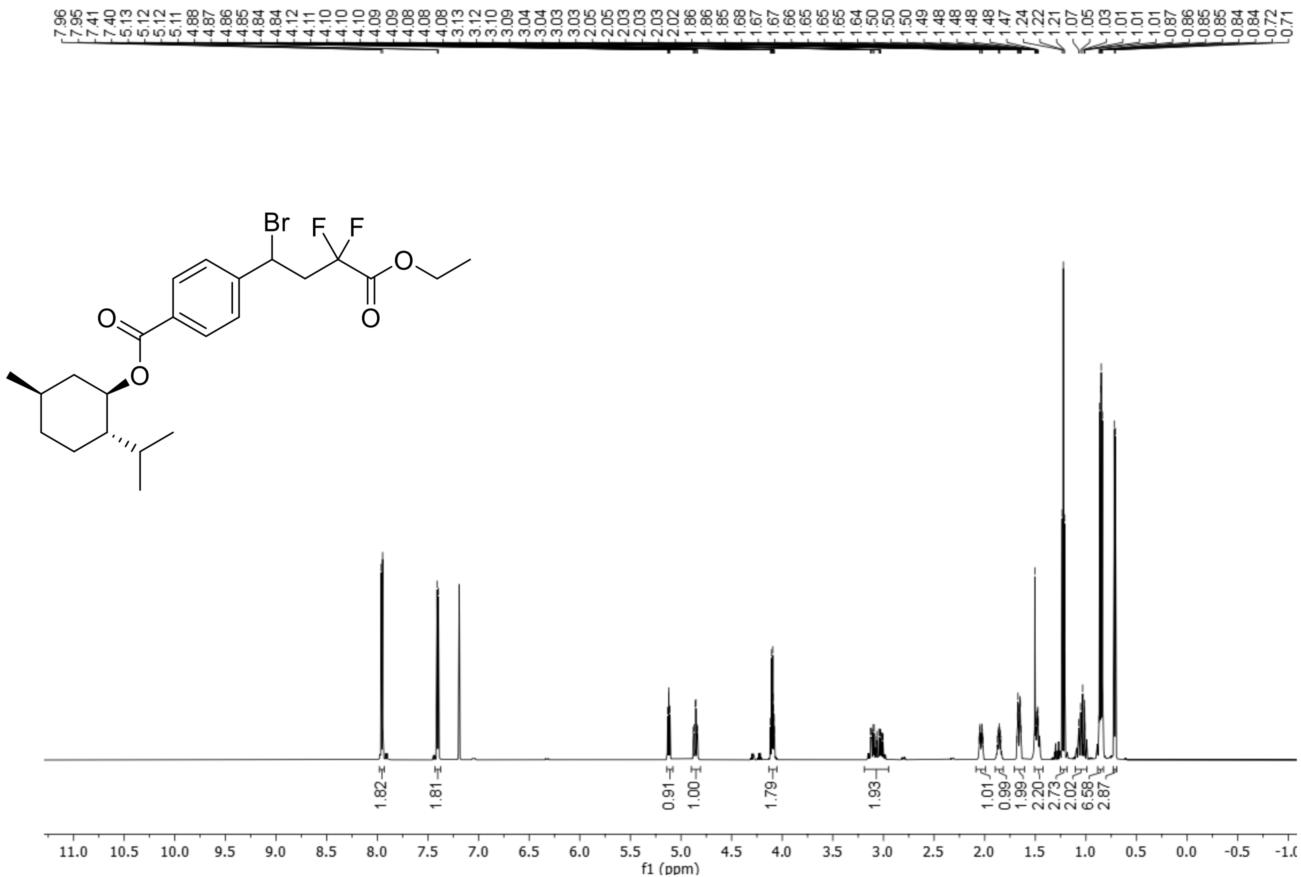
^{1}H NMR (600 MHz, CDCl$_3$) of compound **3t**.



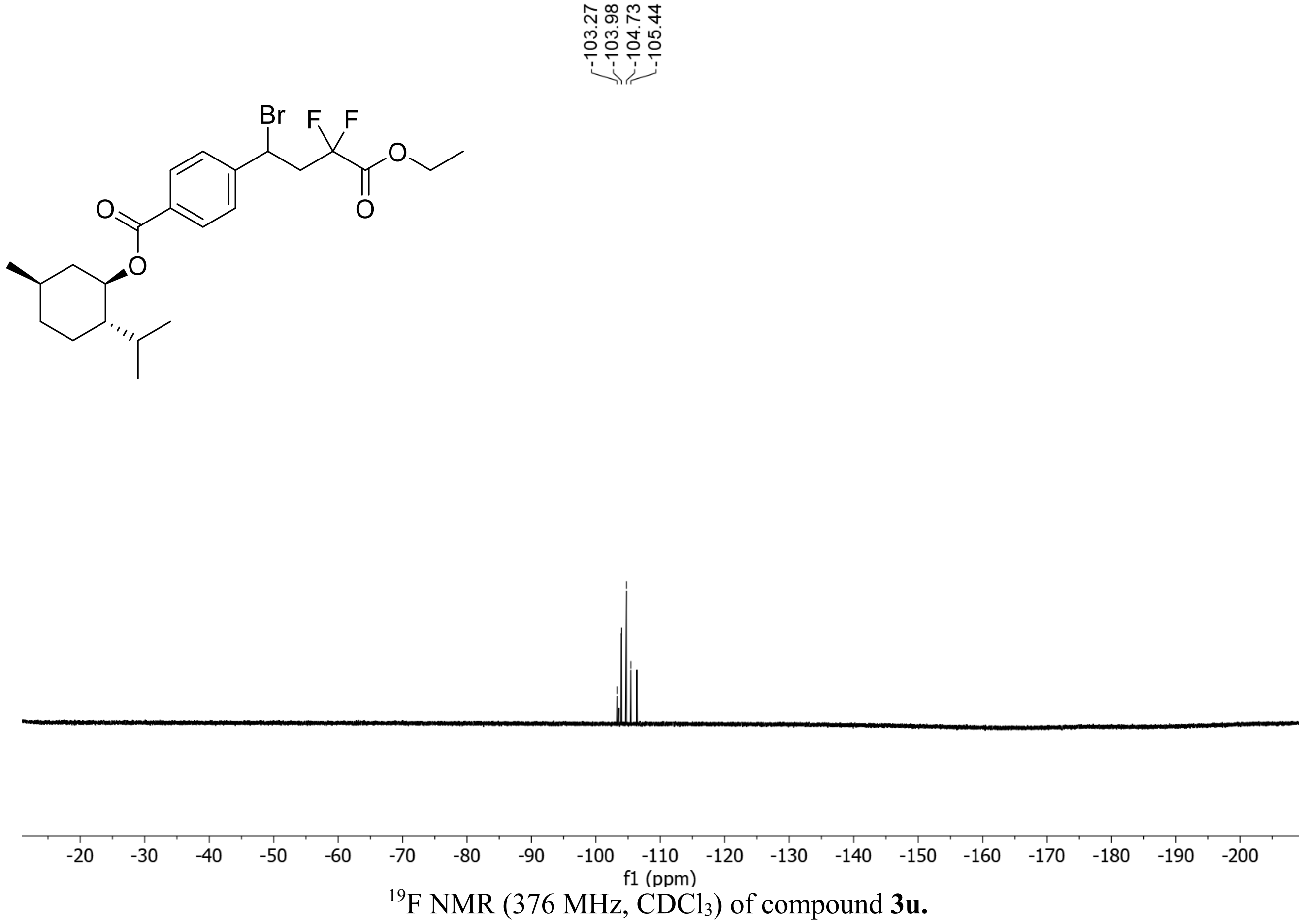
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3t.**



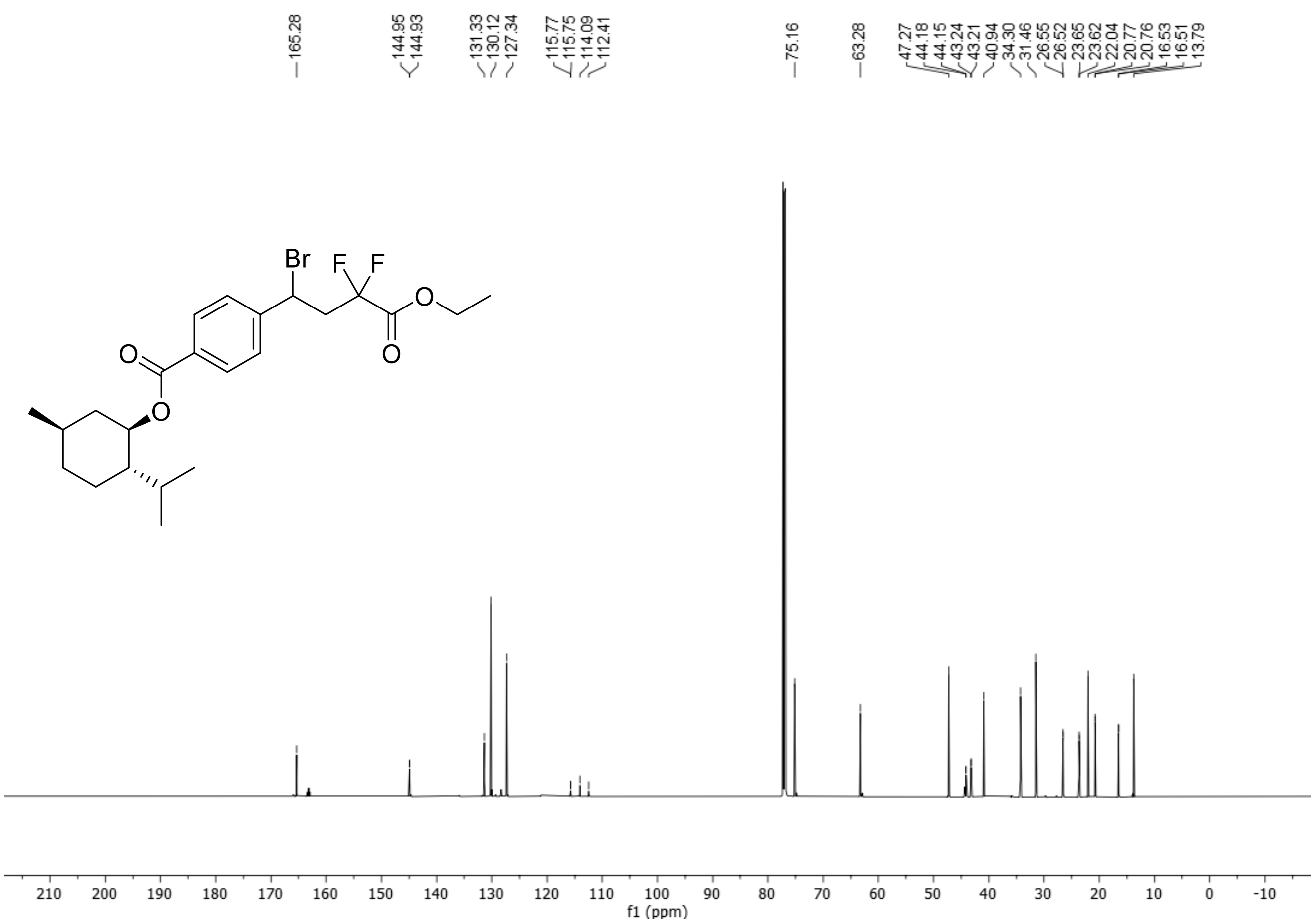
^{13}C NMR (151 MHz, CDCl$_3$) of compound **3t.**



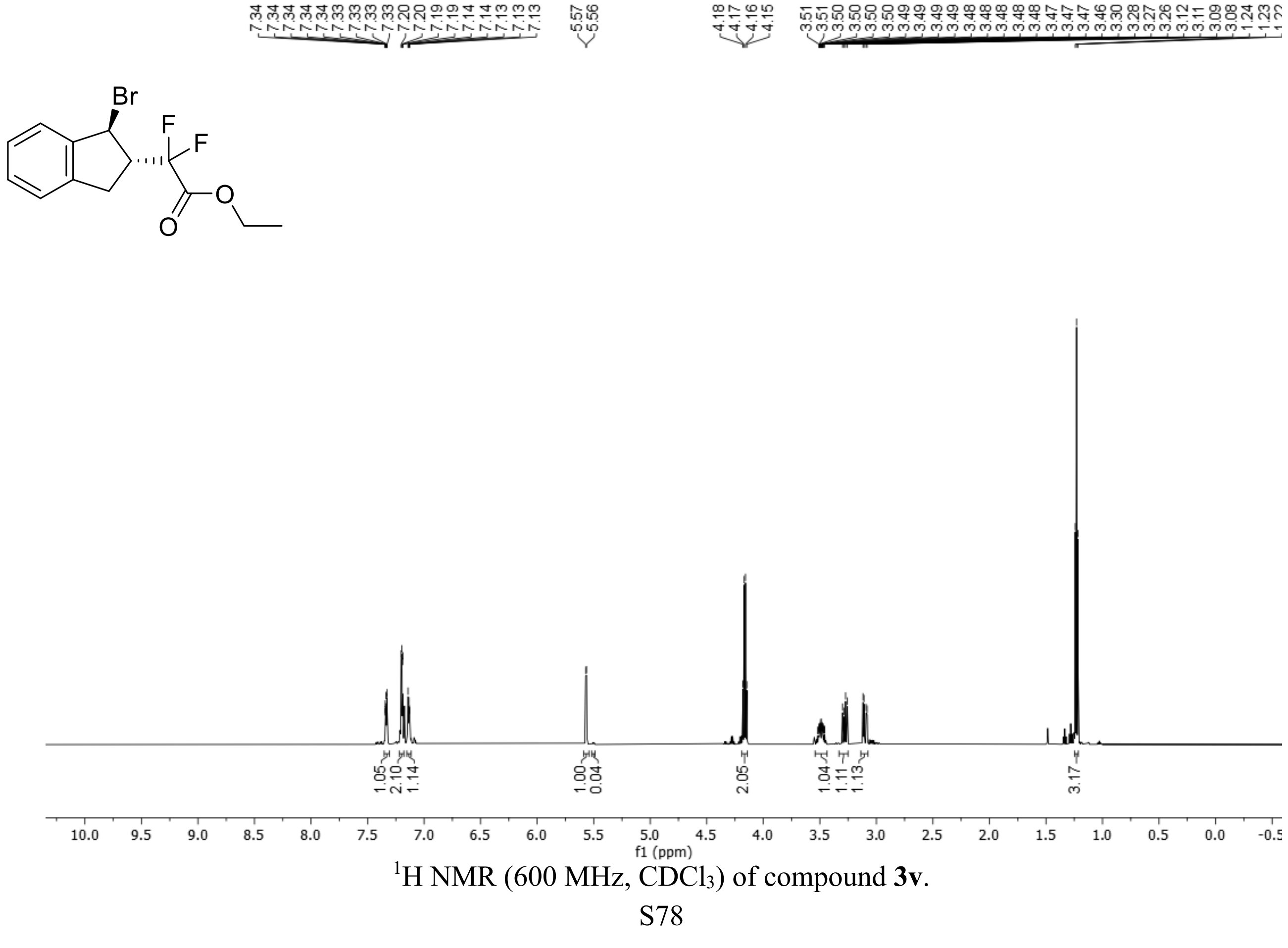
^{1}H NMR (600 MHz, CDCl$_3$) of compound **3u**.



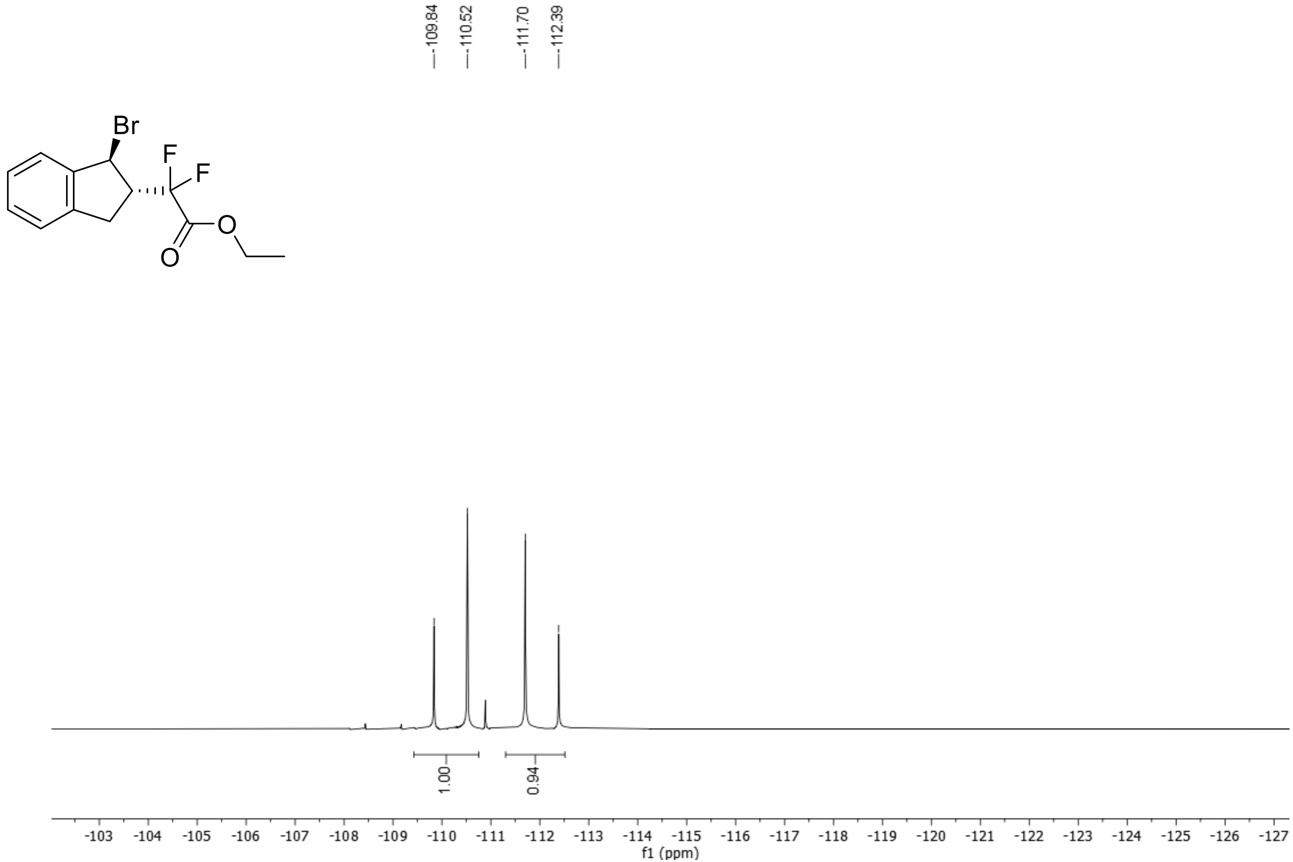
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3u.**



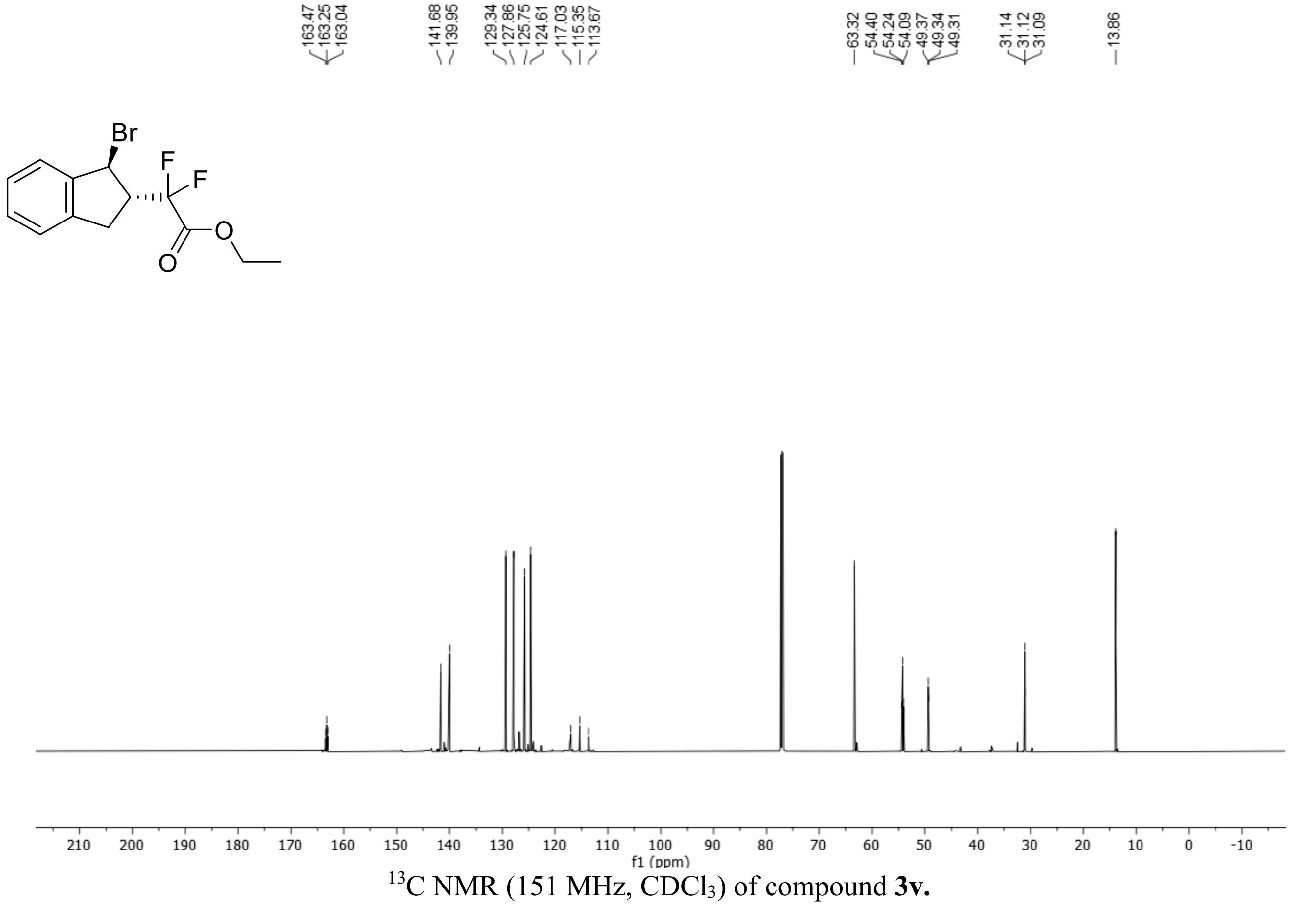
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3u.**



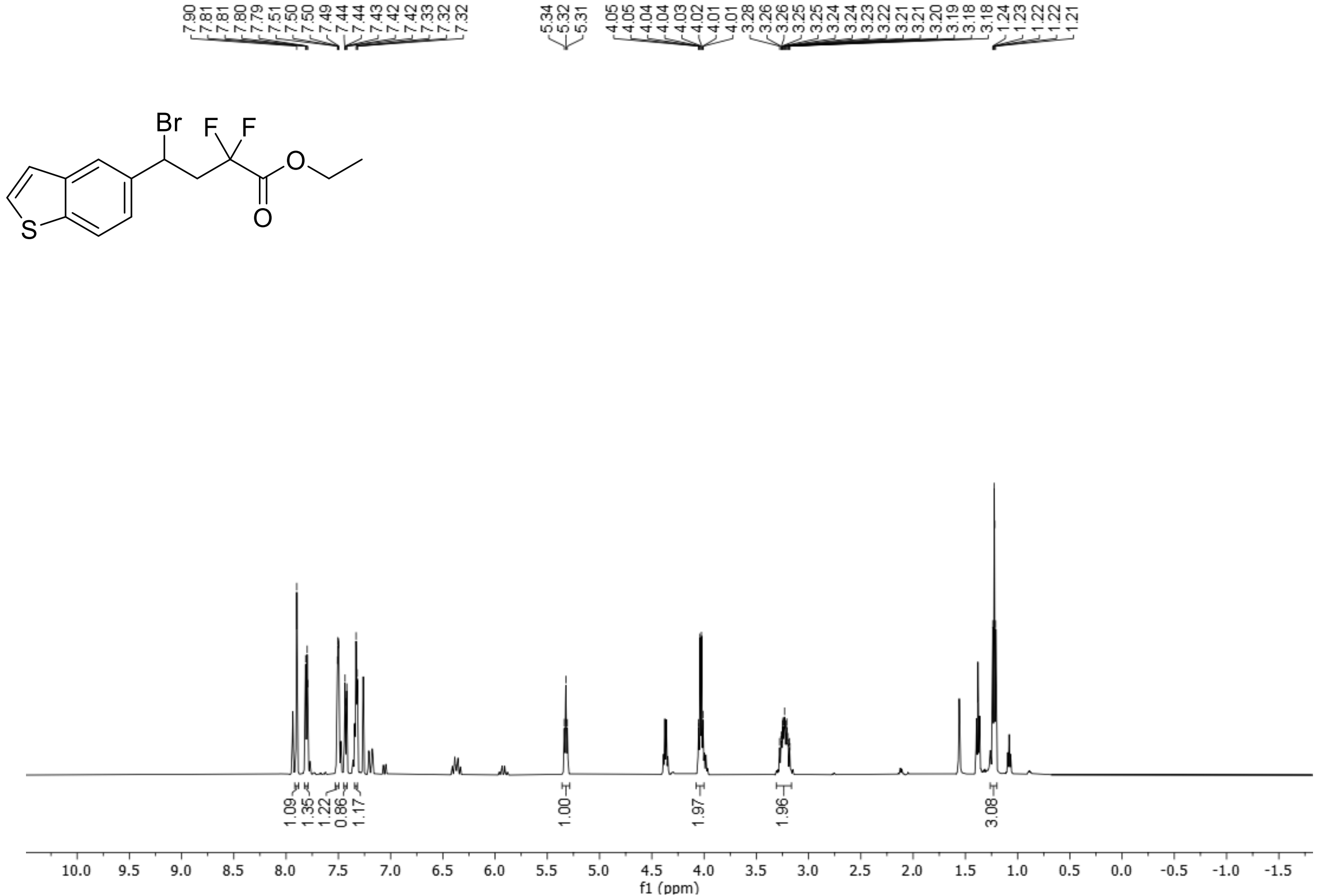
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3v**.



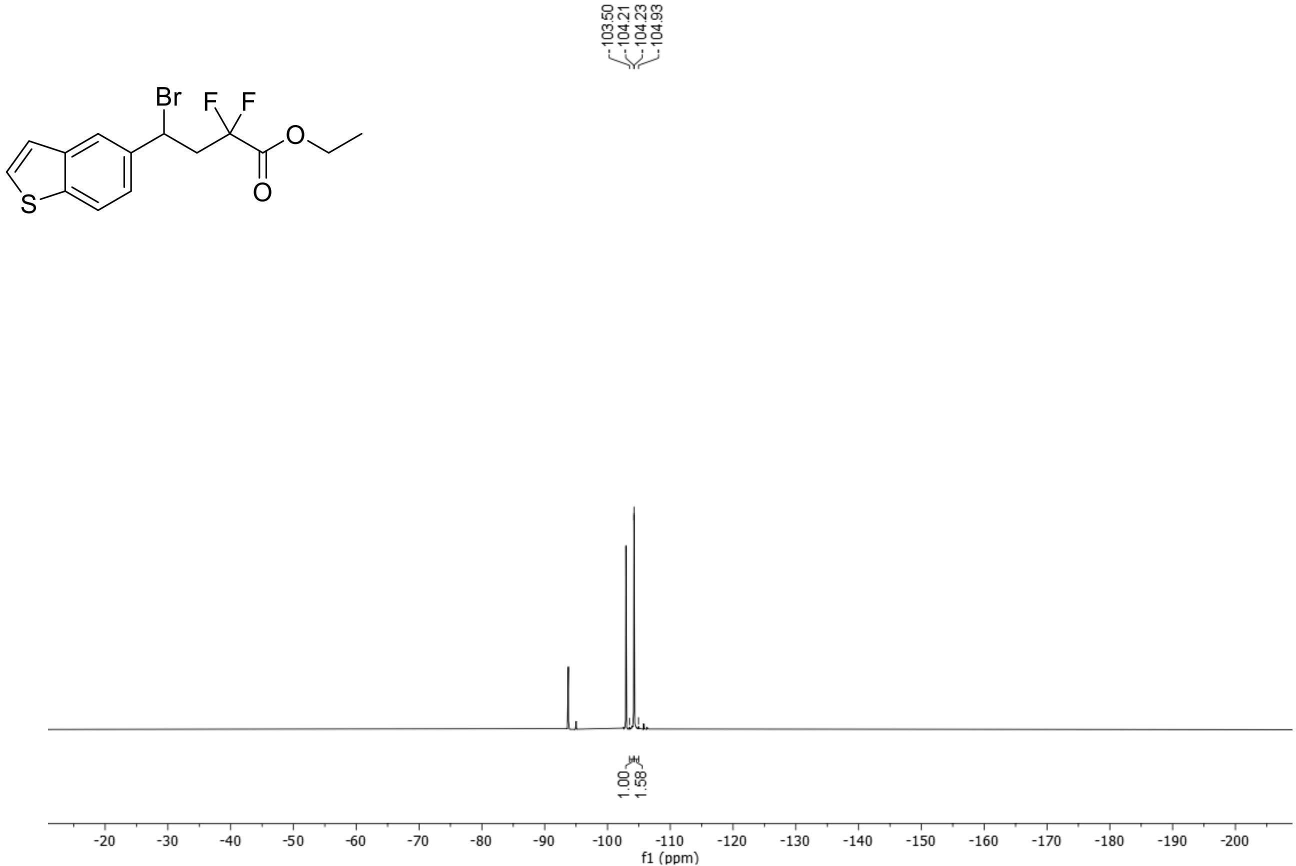
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3v.**



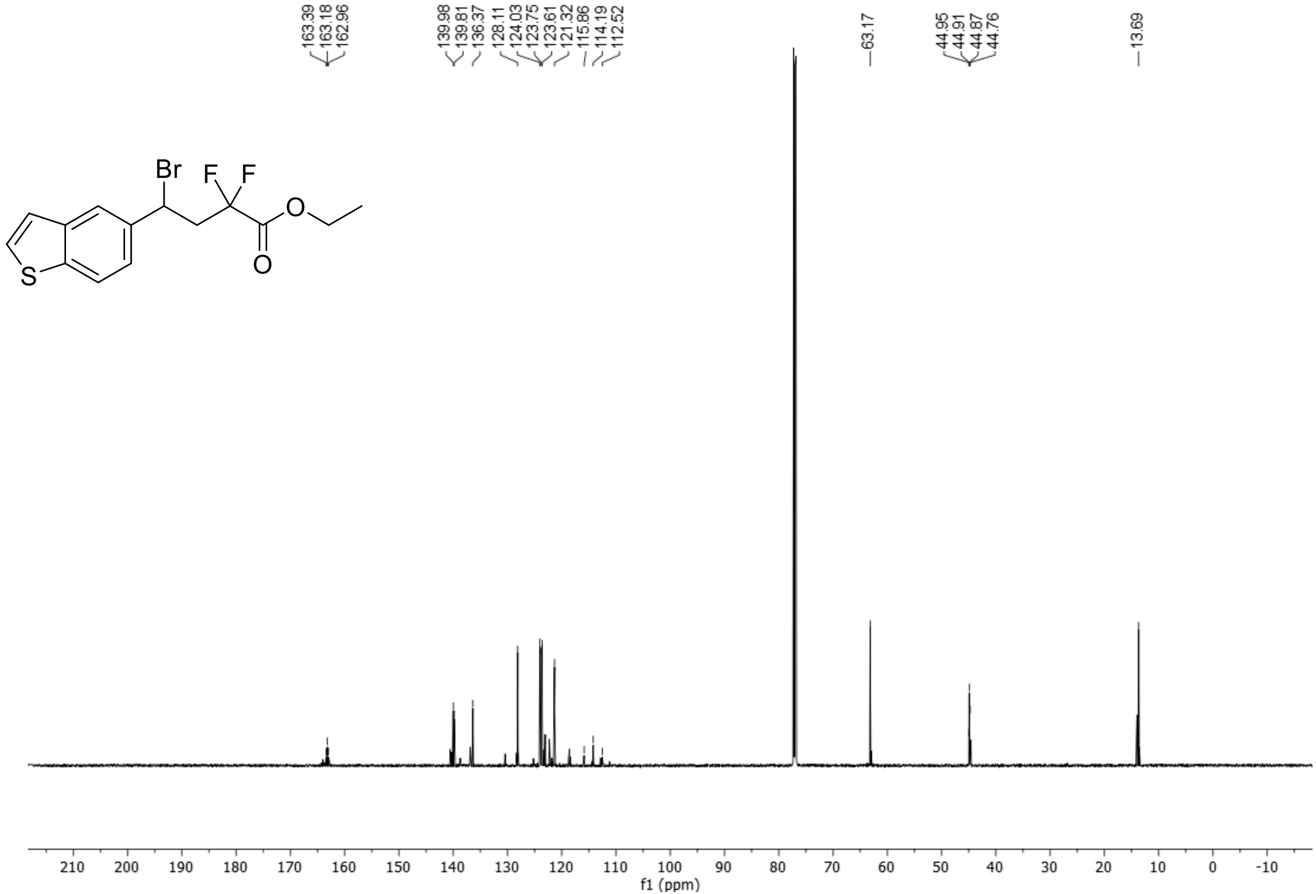
^{13}C NMR (151 MHz, CDCl$_3$) of compound **3v.**



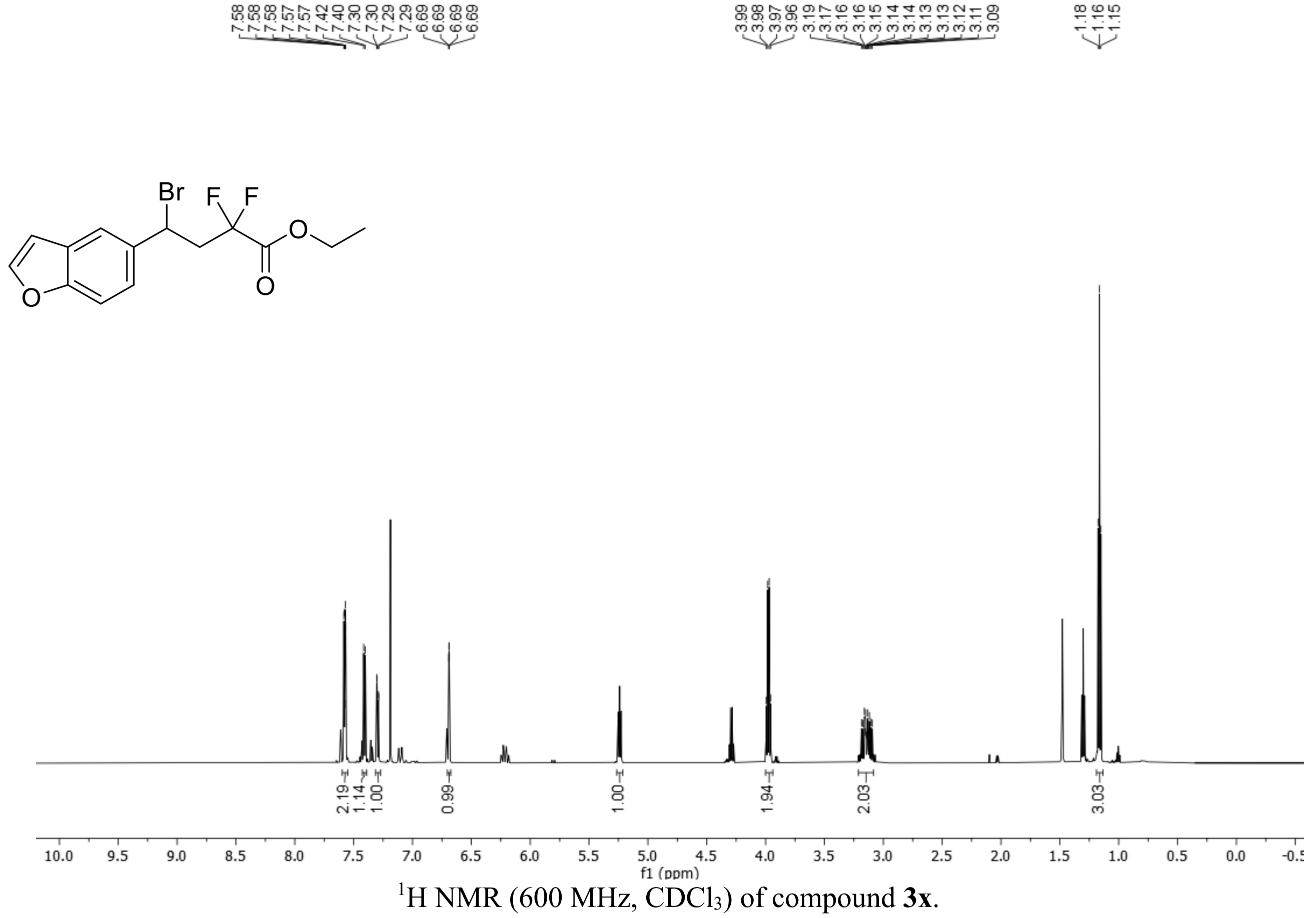
^{1}H NMR (600 MHz, CDCl$_3$) of compound **3w**.



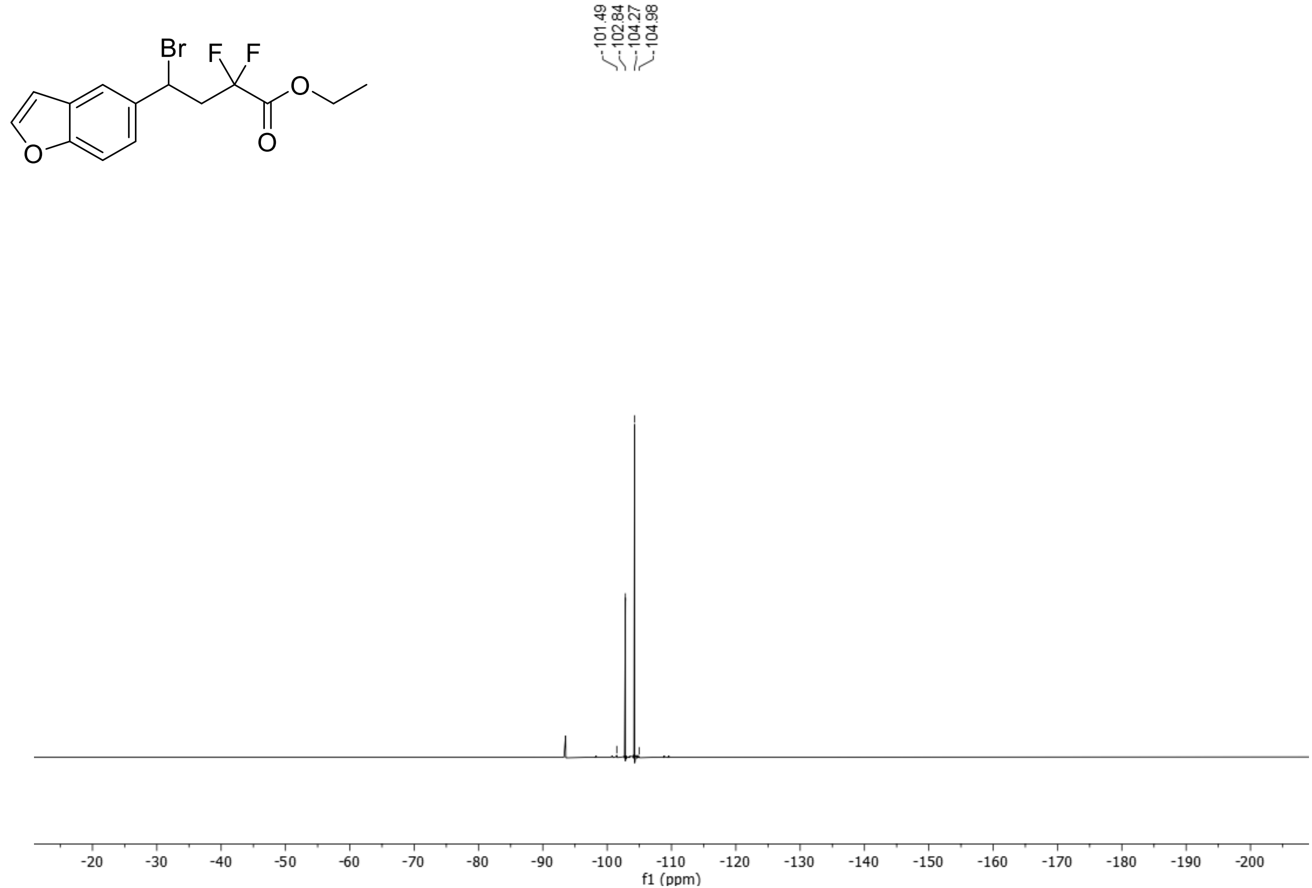
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3w.**



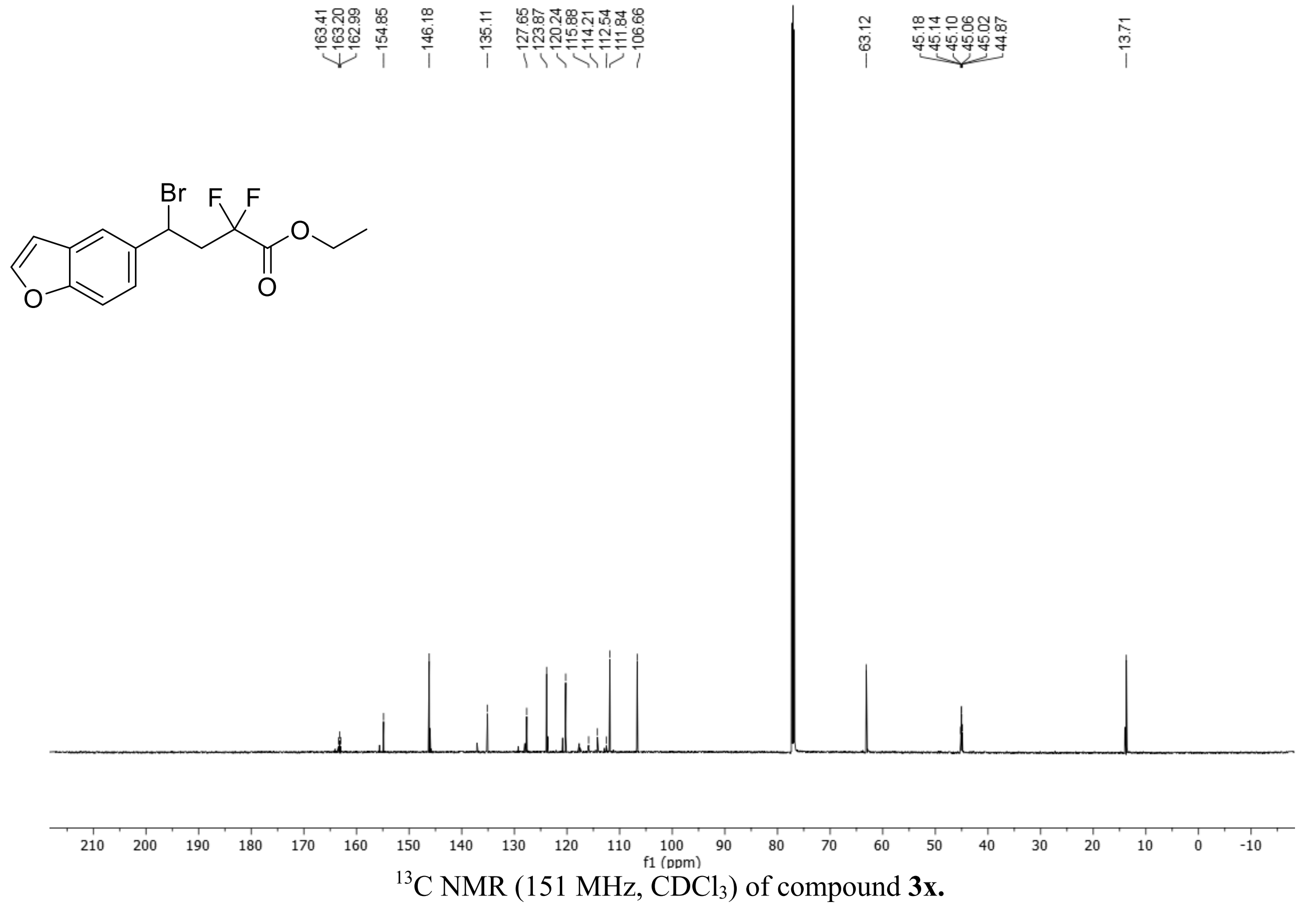
^{13}C NMR (151 MHz, CDCl$_3$) of compound **3w.**



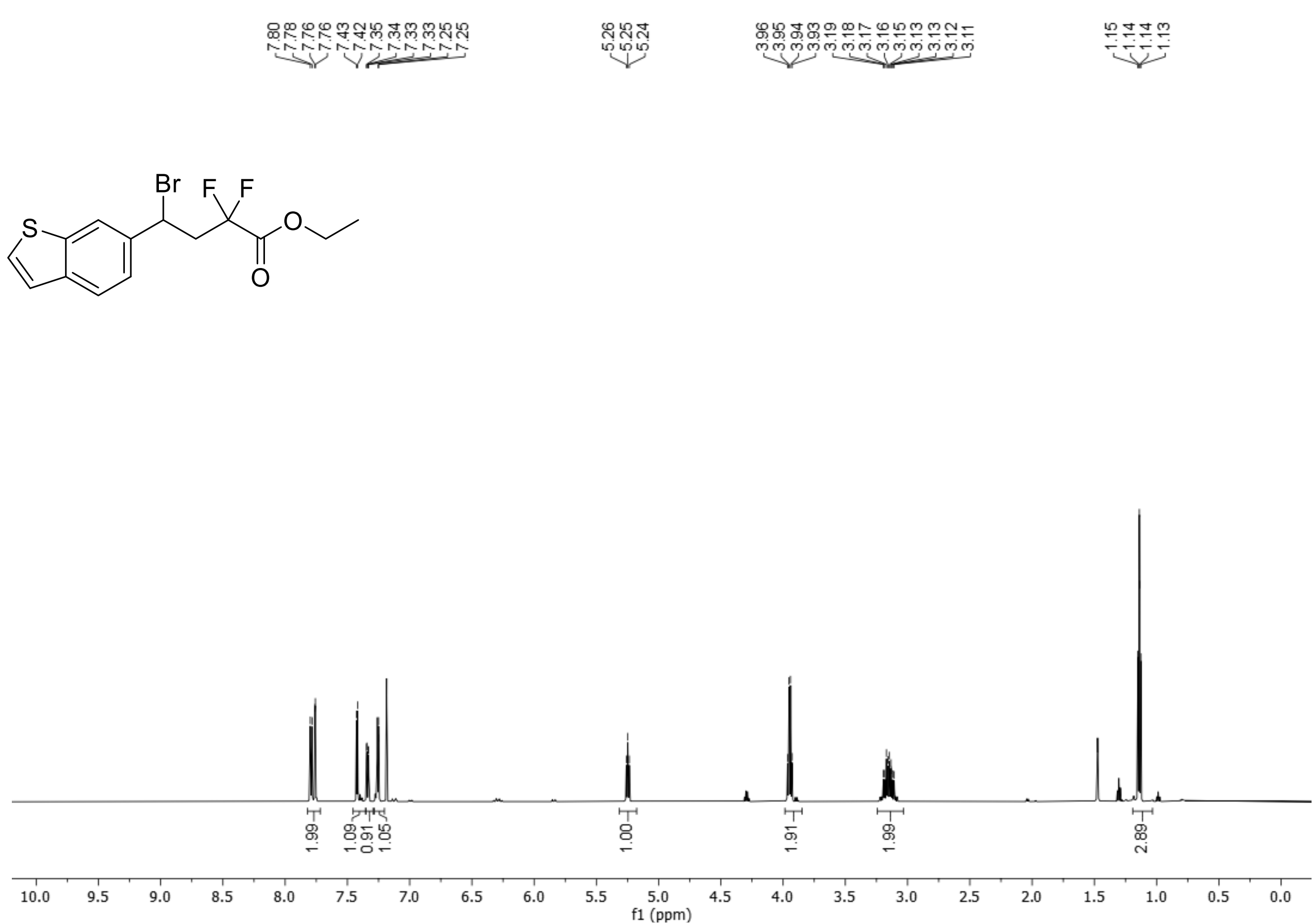
^{1}H NMR (600 MHz, CDCl$_3$) of compound **3x**.



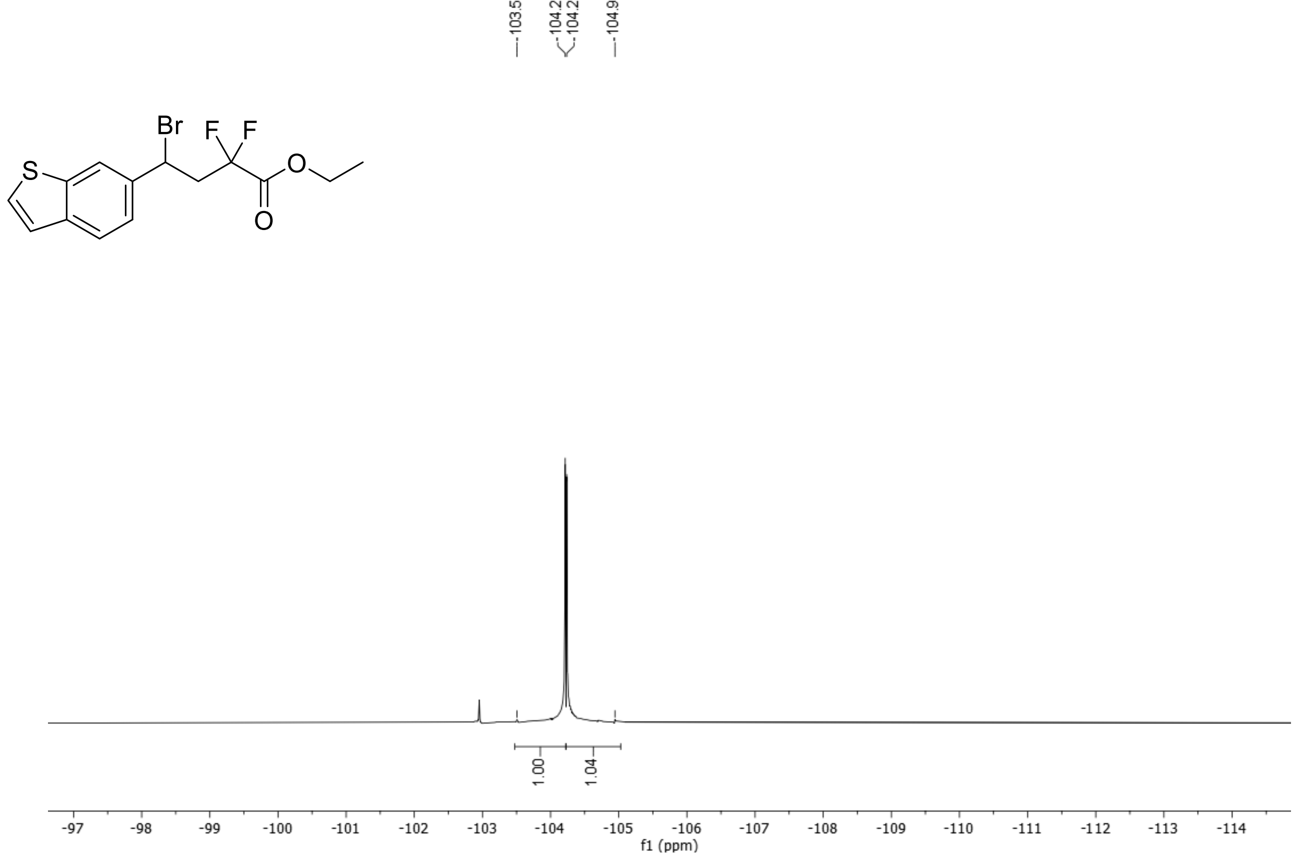
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3x.**



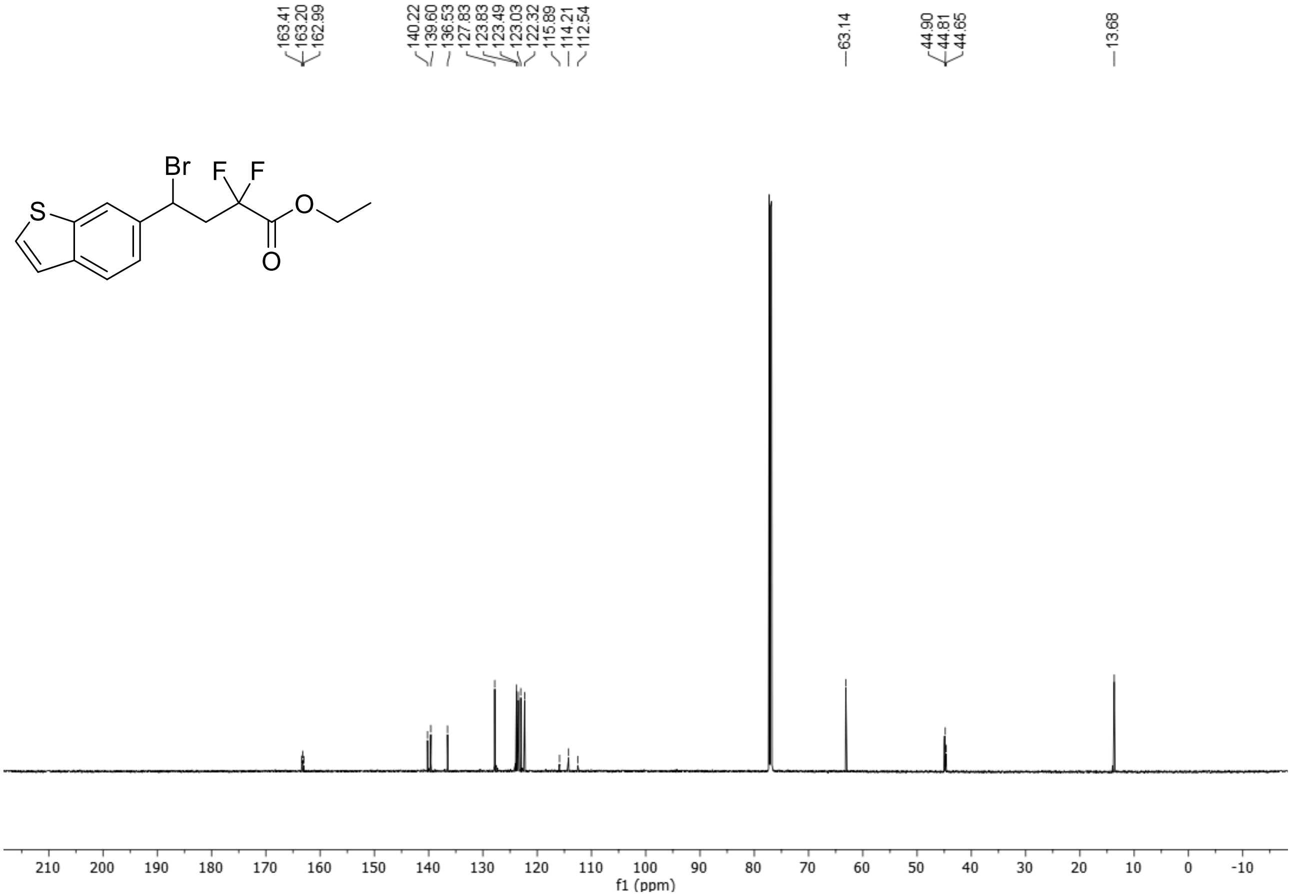
^{13}C NMR (151 MHz, CDCl$_3$) of compound **3x.**



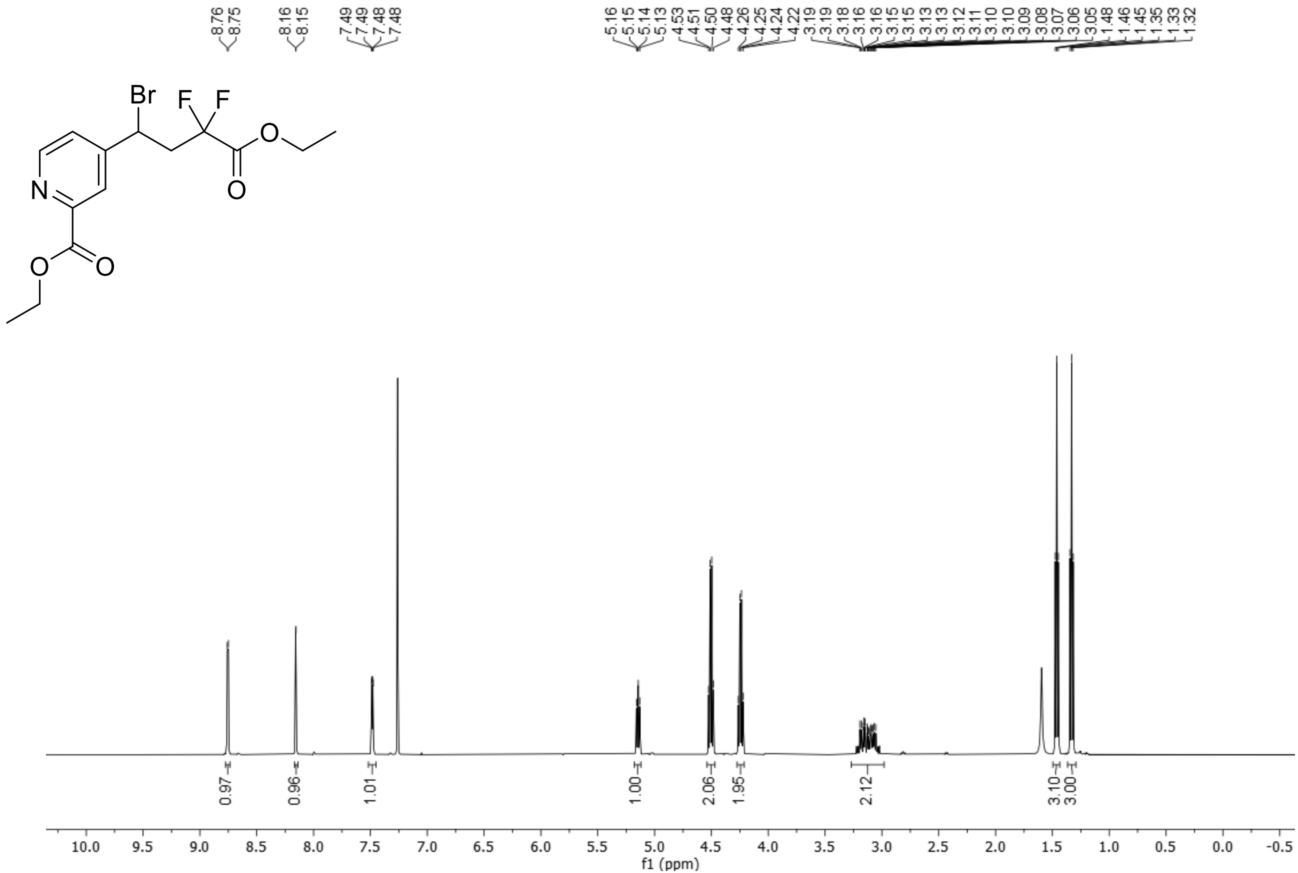
^{1}H NMR (600 MHz, CDCl$_3$) of compound **3y**.



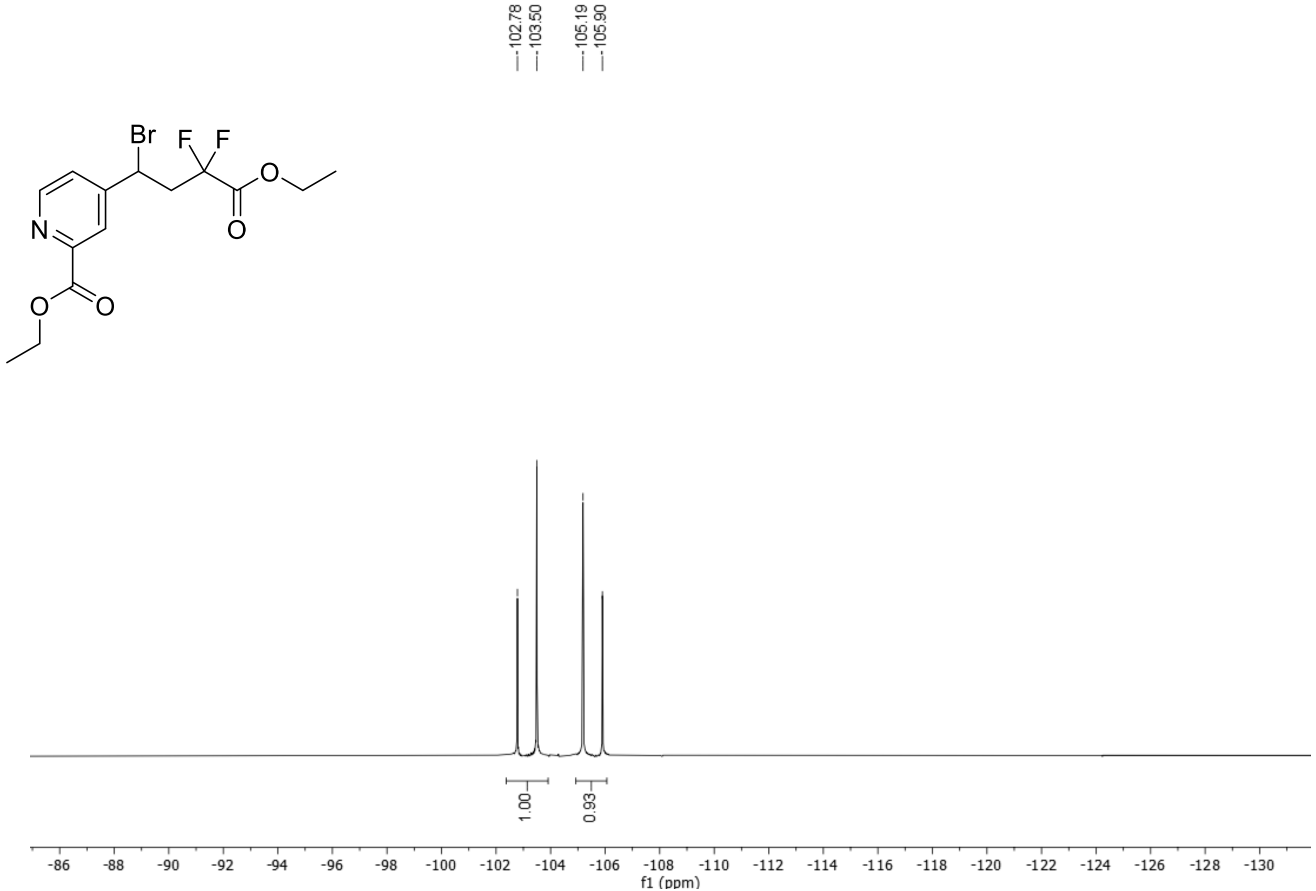
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3y.**



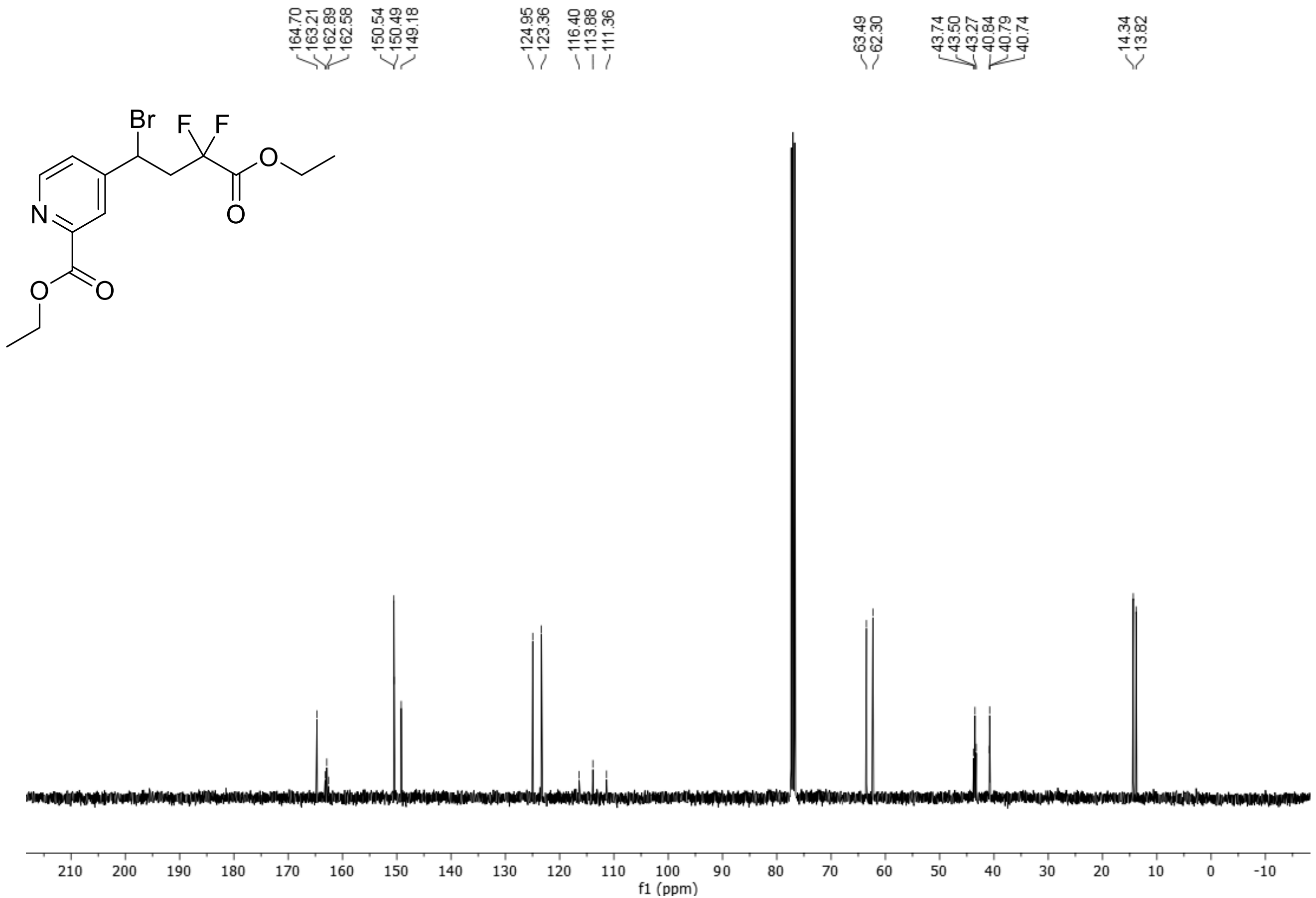
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3y.**



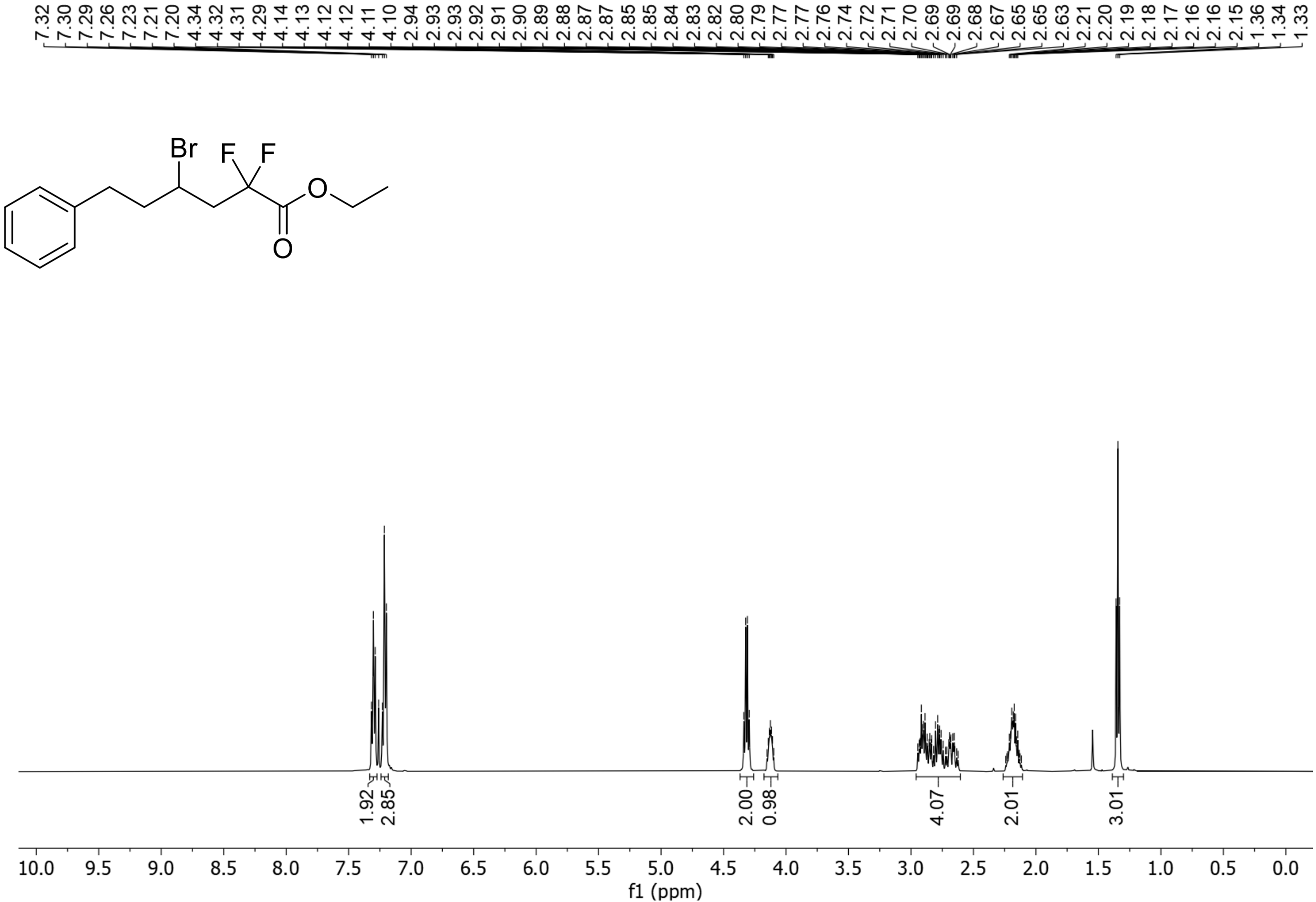
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3z**.



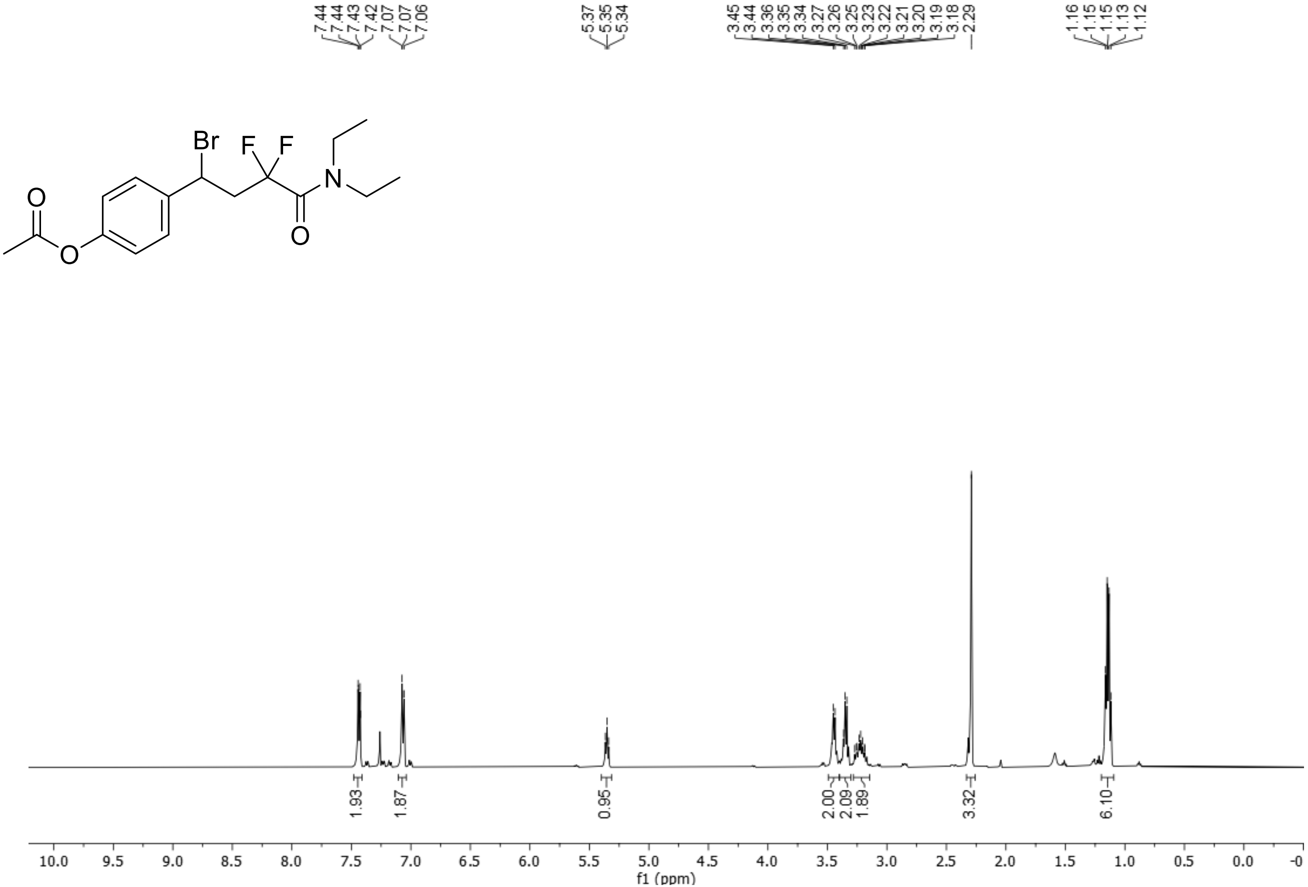
^{19}F NMR (376 MHz, CDCl$_3$) of compound **3z.**



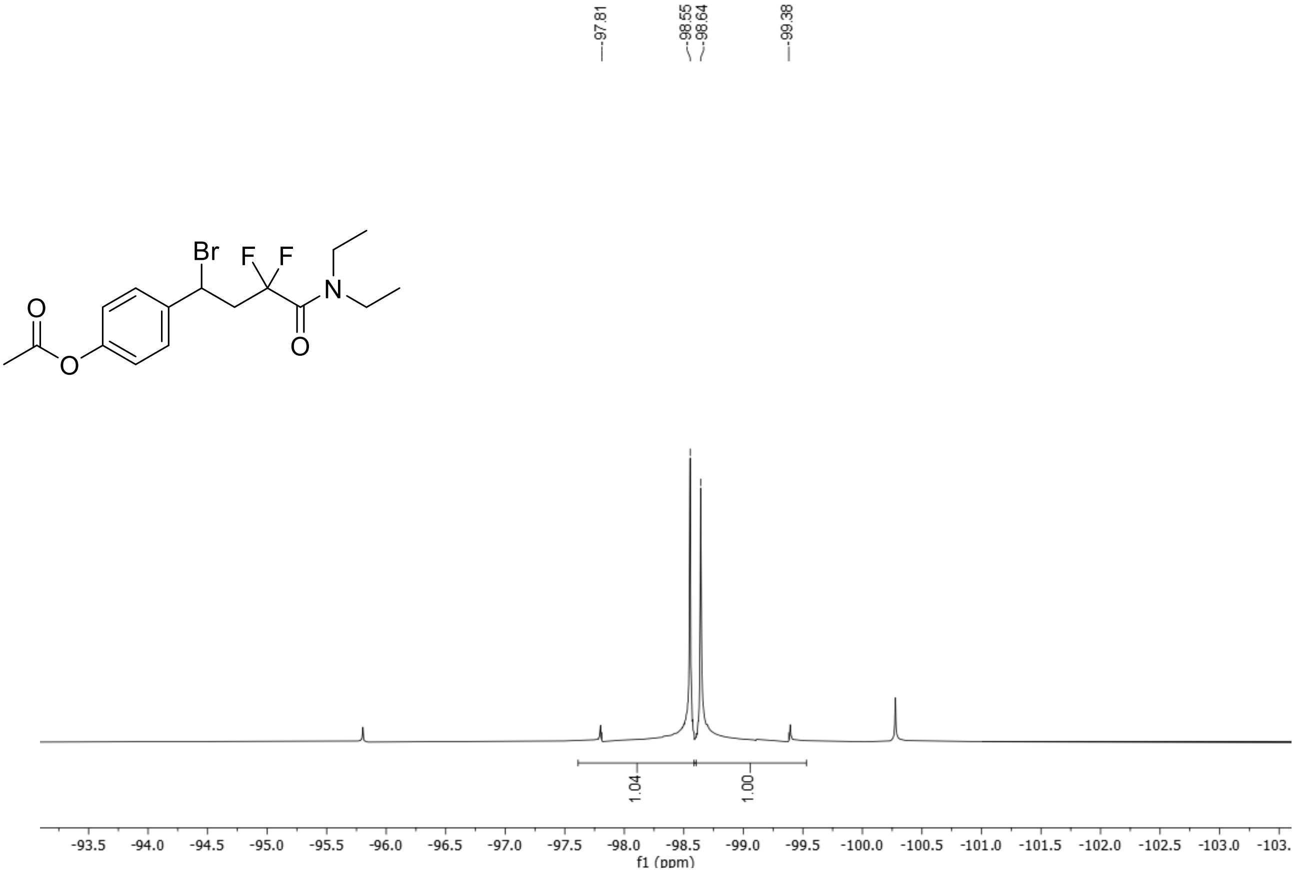
^{13}C NMR (101 MHz, CDCl$_3$) of compound **3z.**



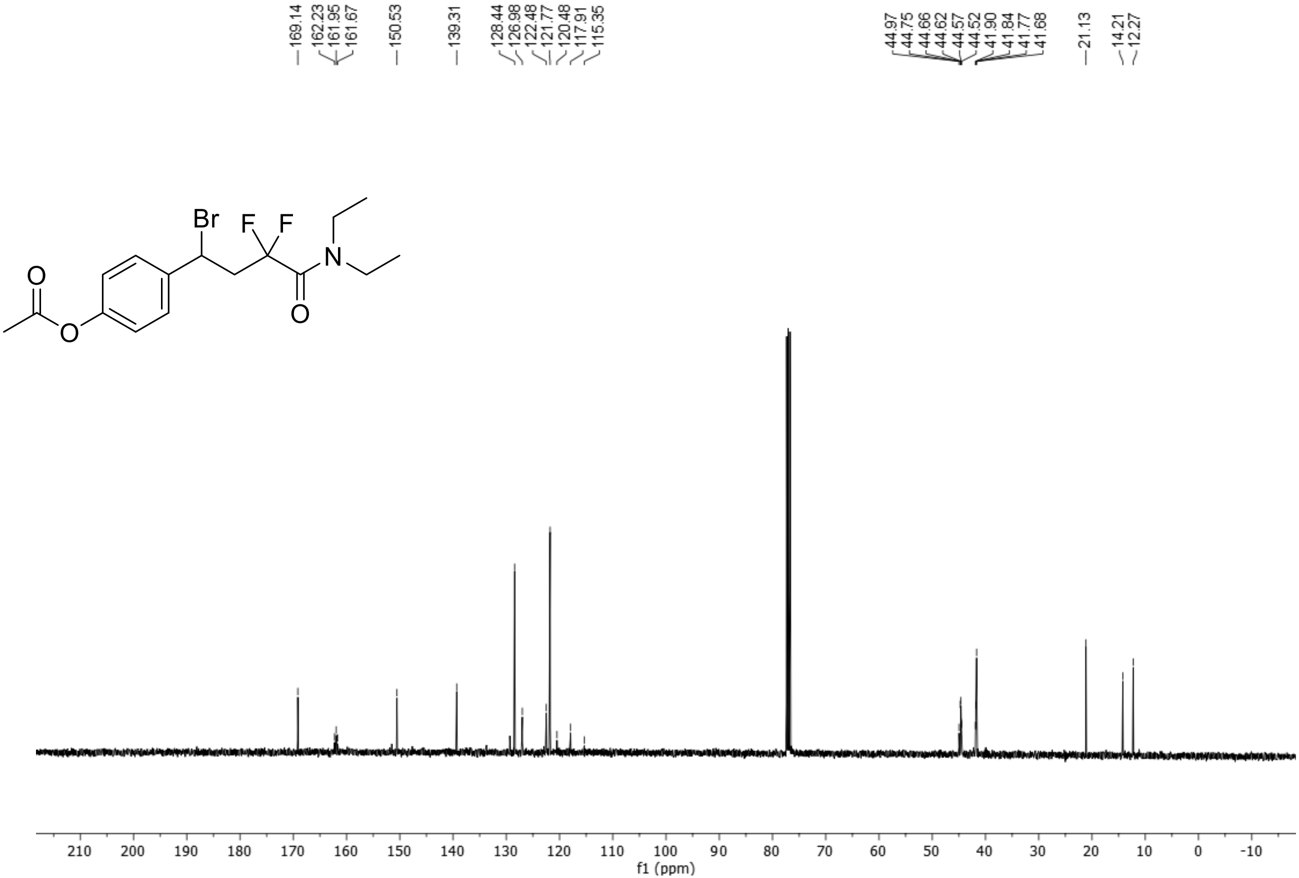
^{1}H NMR (500 MHz, CDCl$_3$) of compound **3aa**.



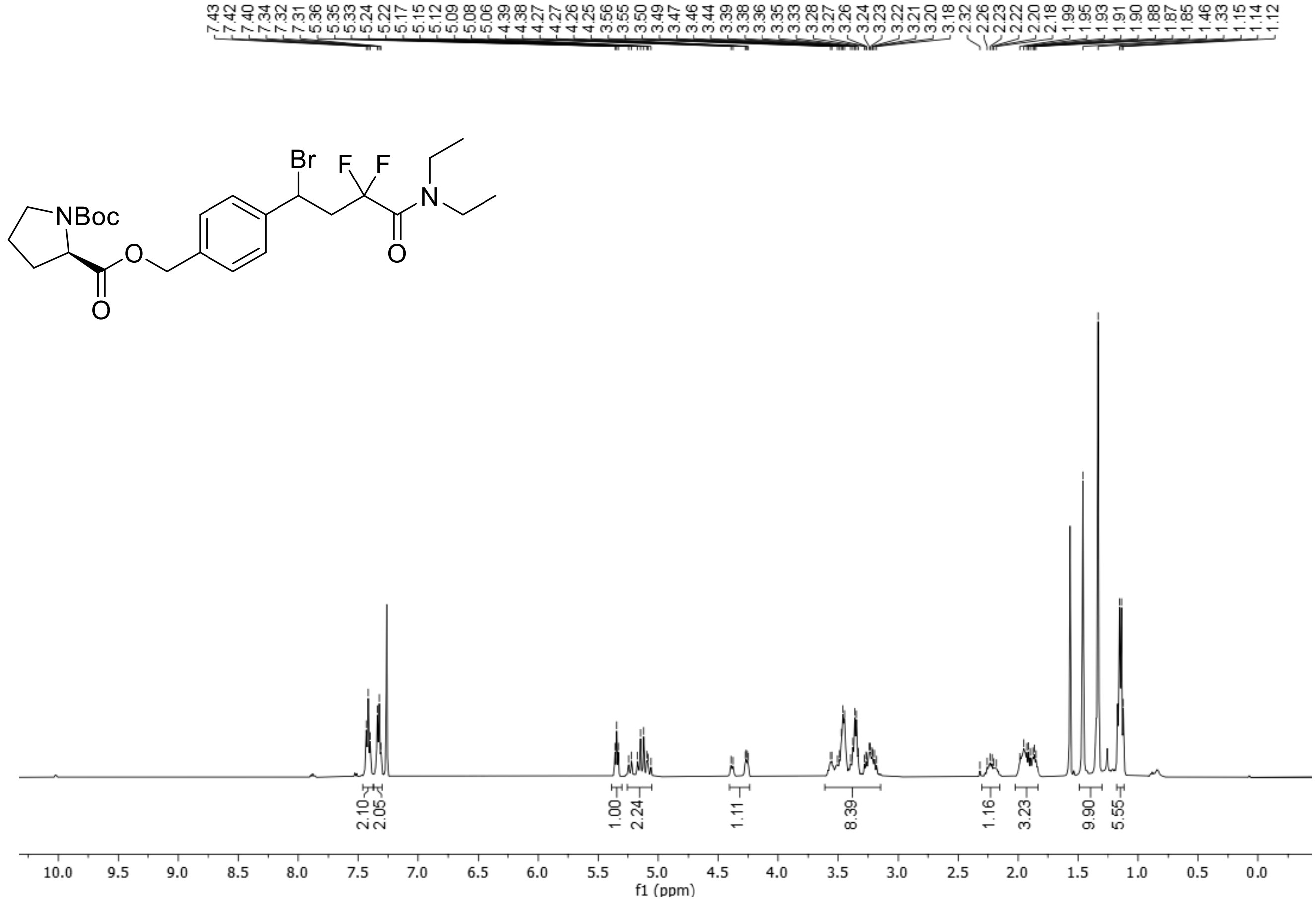
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4a**.



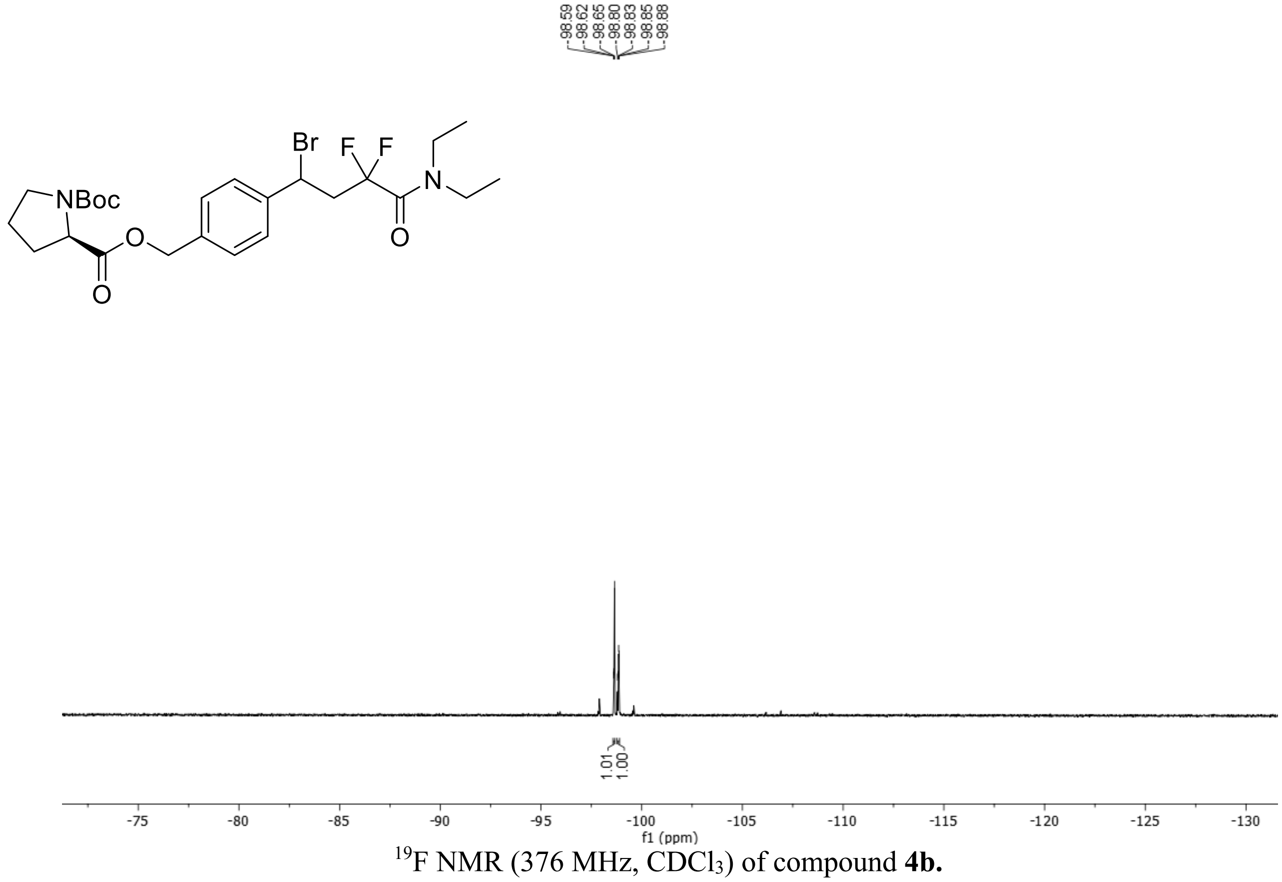
^{19}F NMR (376 MHz, CDCl$_3$) of compound **4a.**



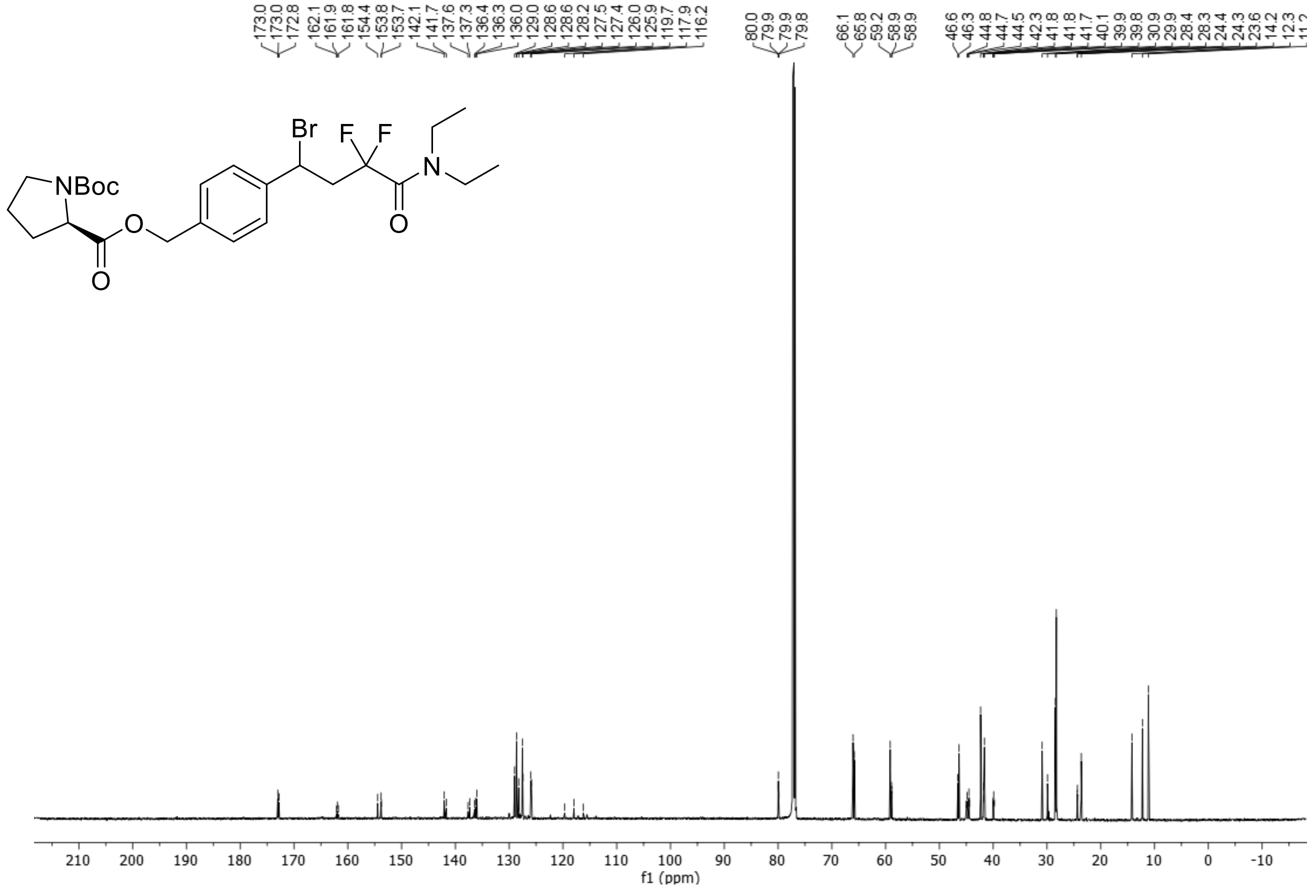
^{13}C NMR (101 MHz, CDCl$_3$) of compound **4a.**



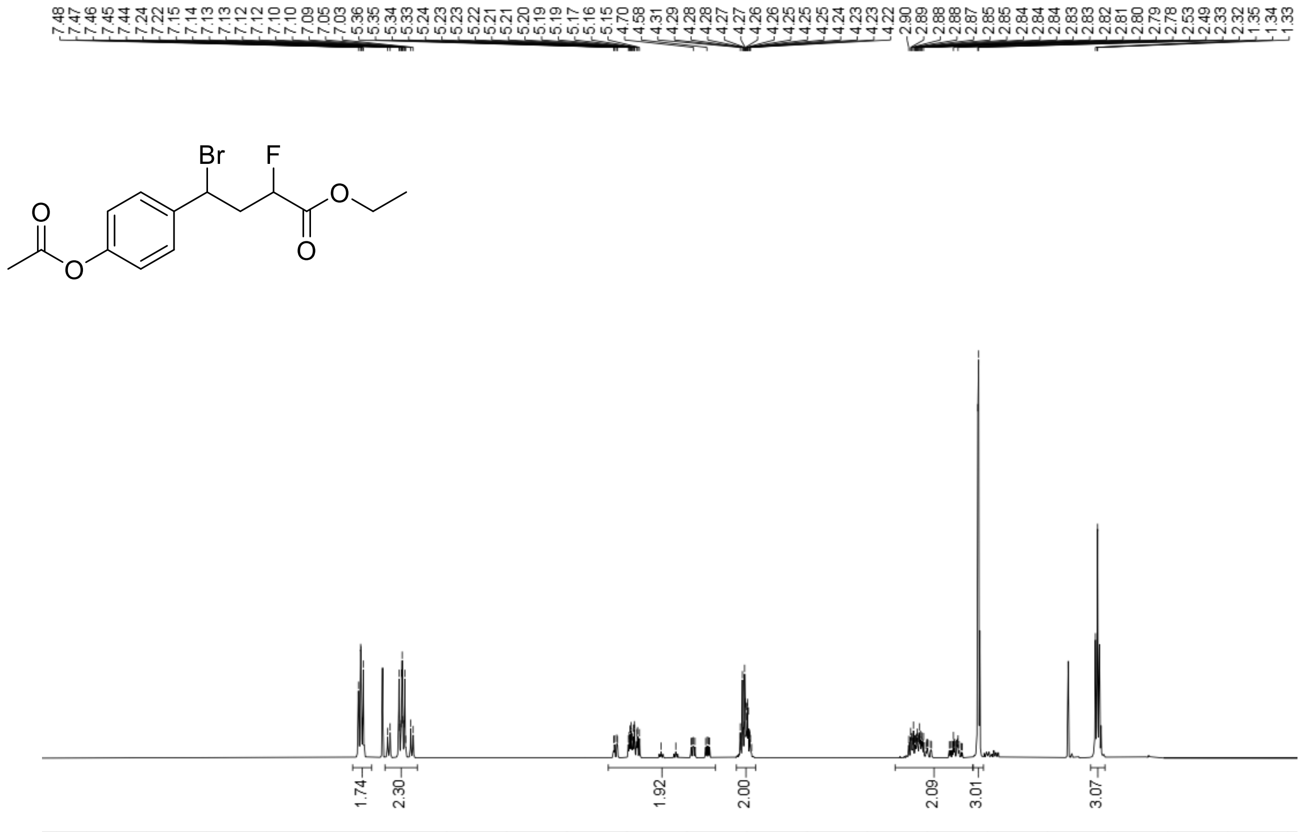
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4b**.



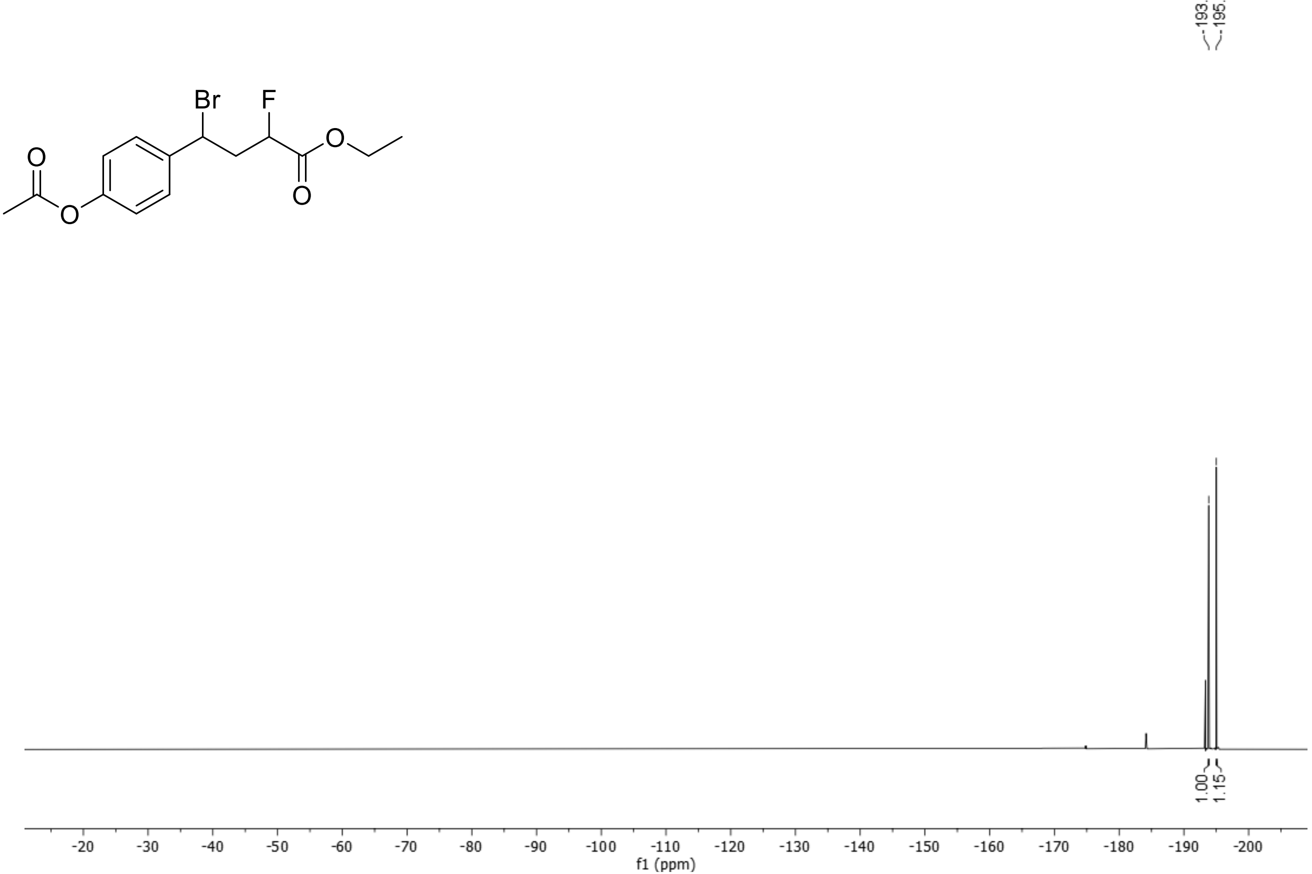
^{19}F NMR (376 MHz, CDCl$_3$) of compound **4b.**



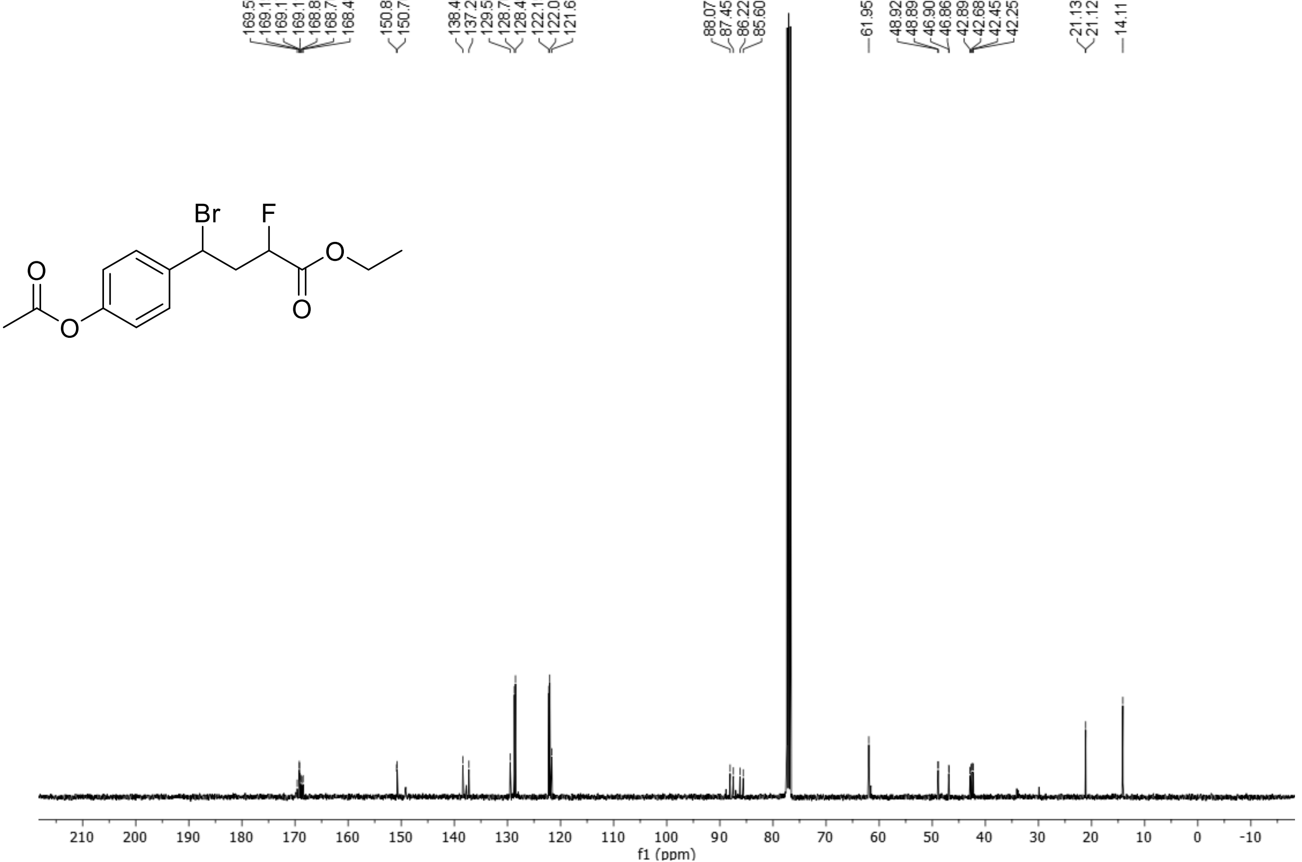
^{13}C NMR (101 MHz, CDCl$_3$) of compound **4b.**



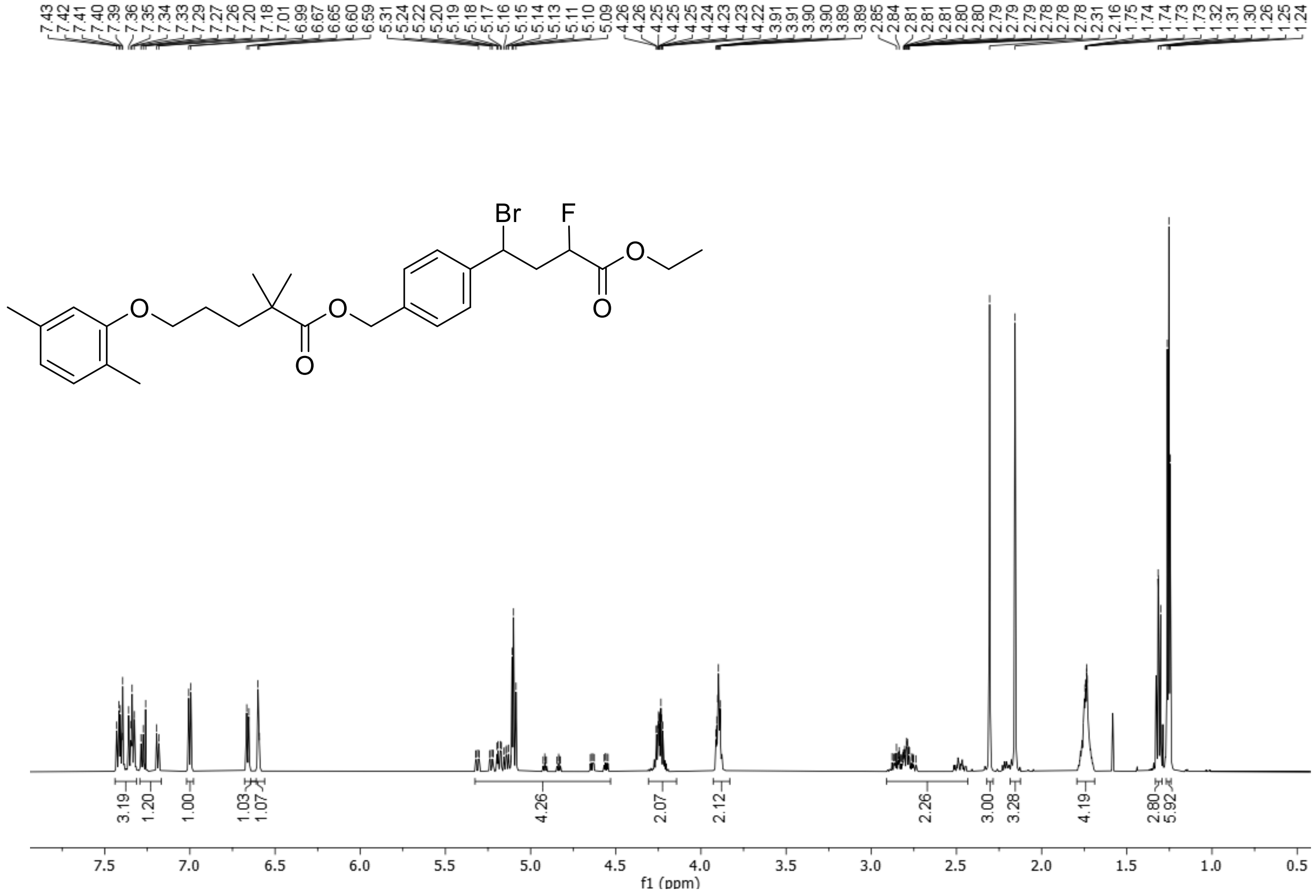
^{1}H NMR (600 MHz, CDCl$_3$) of compound **5a**.



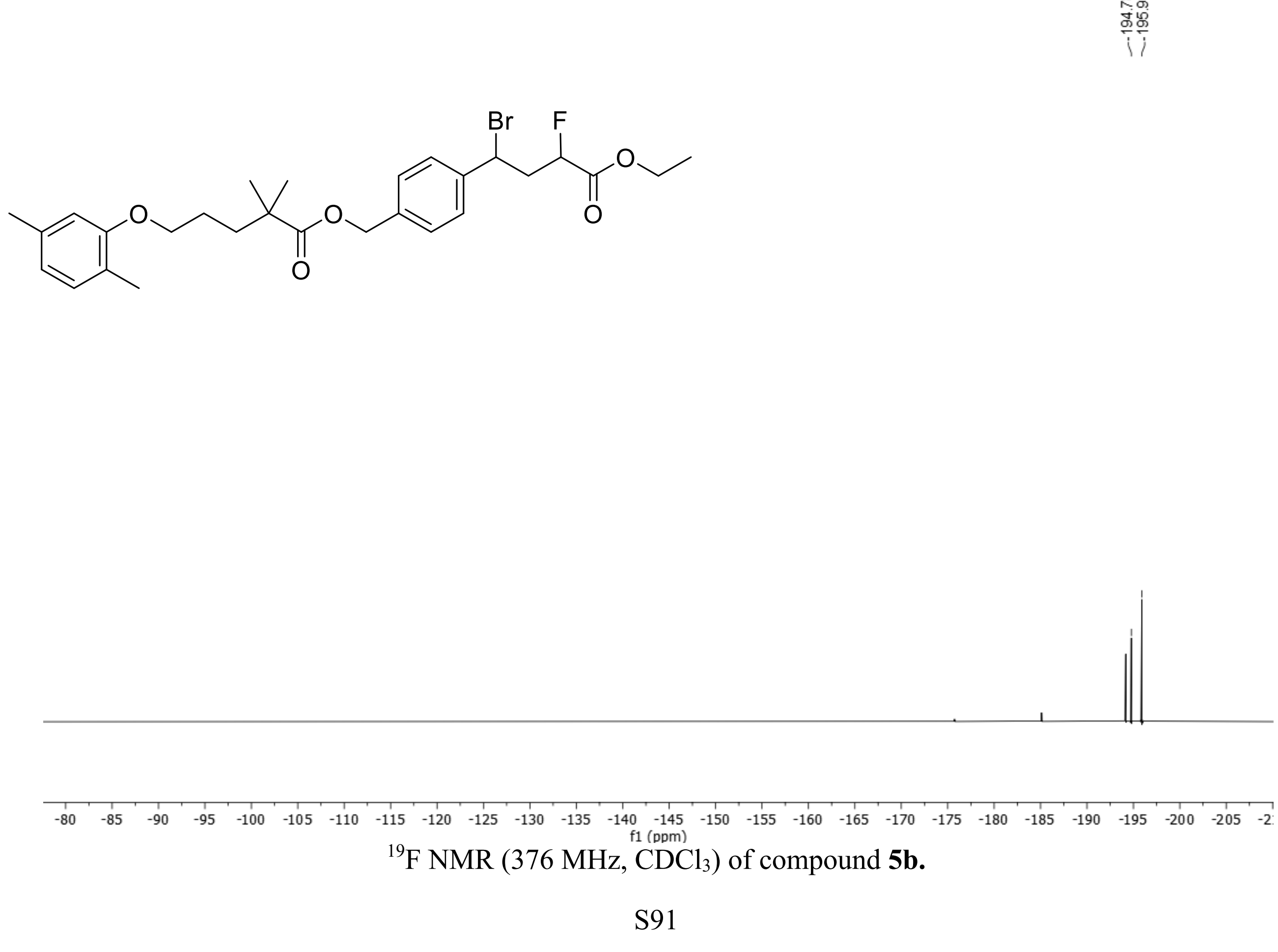
^{19}F NMR (376 MHz, CDCl$_3$) of compound **5a.**



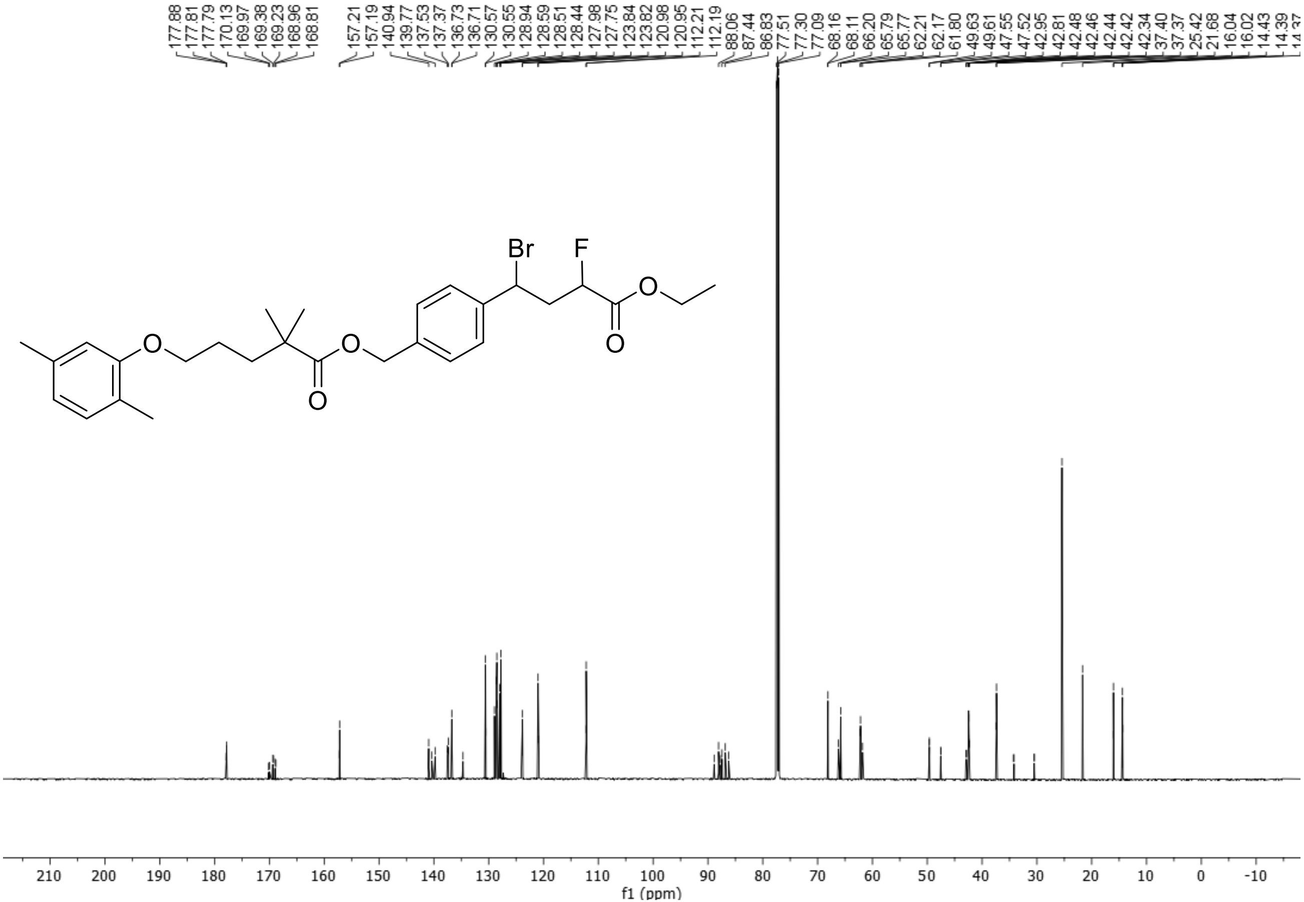
^{13}C NMR (151 MHz, CDCl$_3$) of compound **5a.**



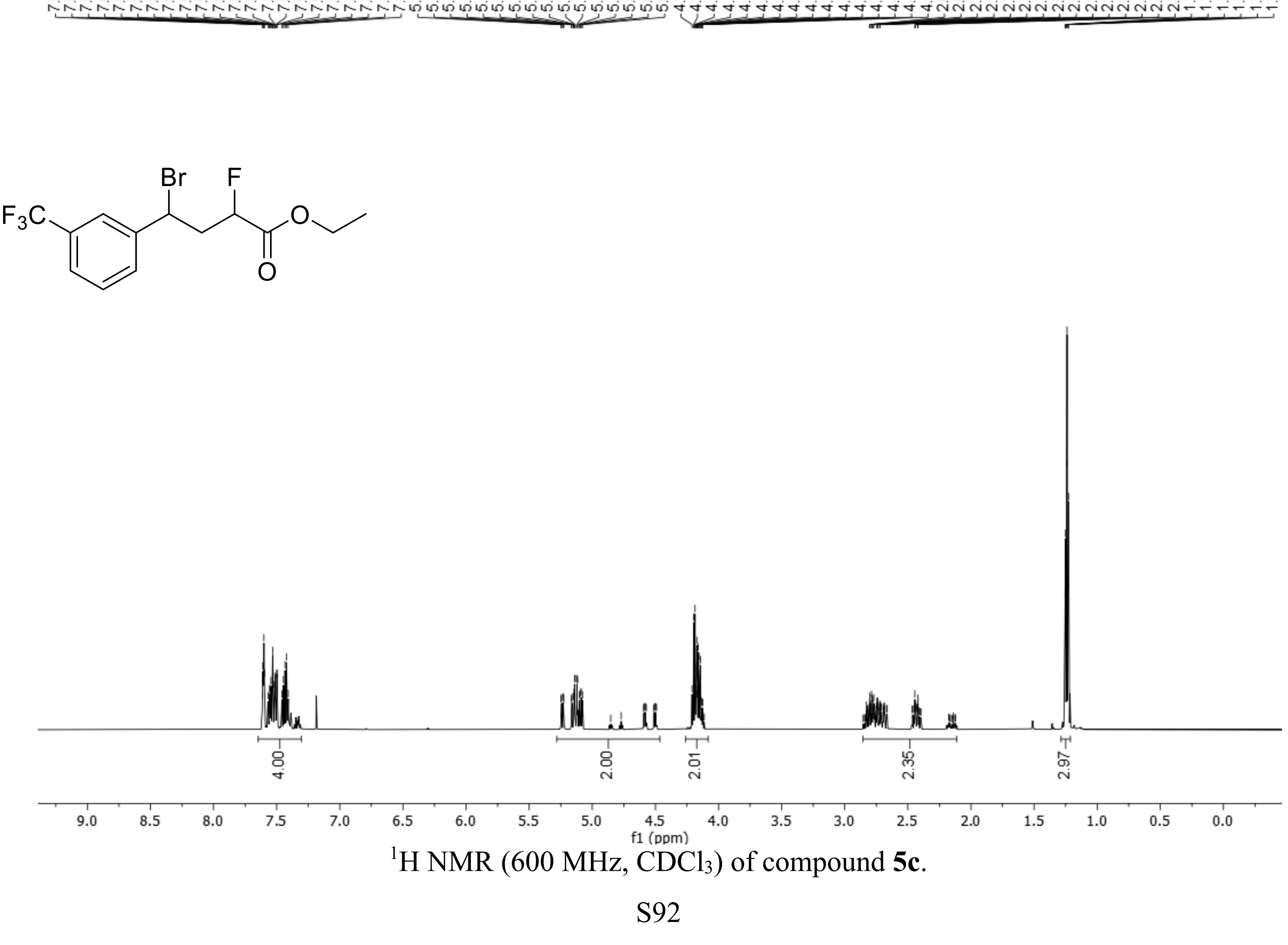
^{1}H NMR (600 MHz, CDCl$_3$) of compound **5b**.



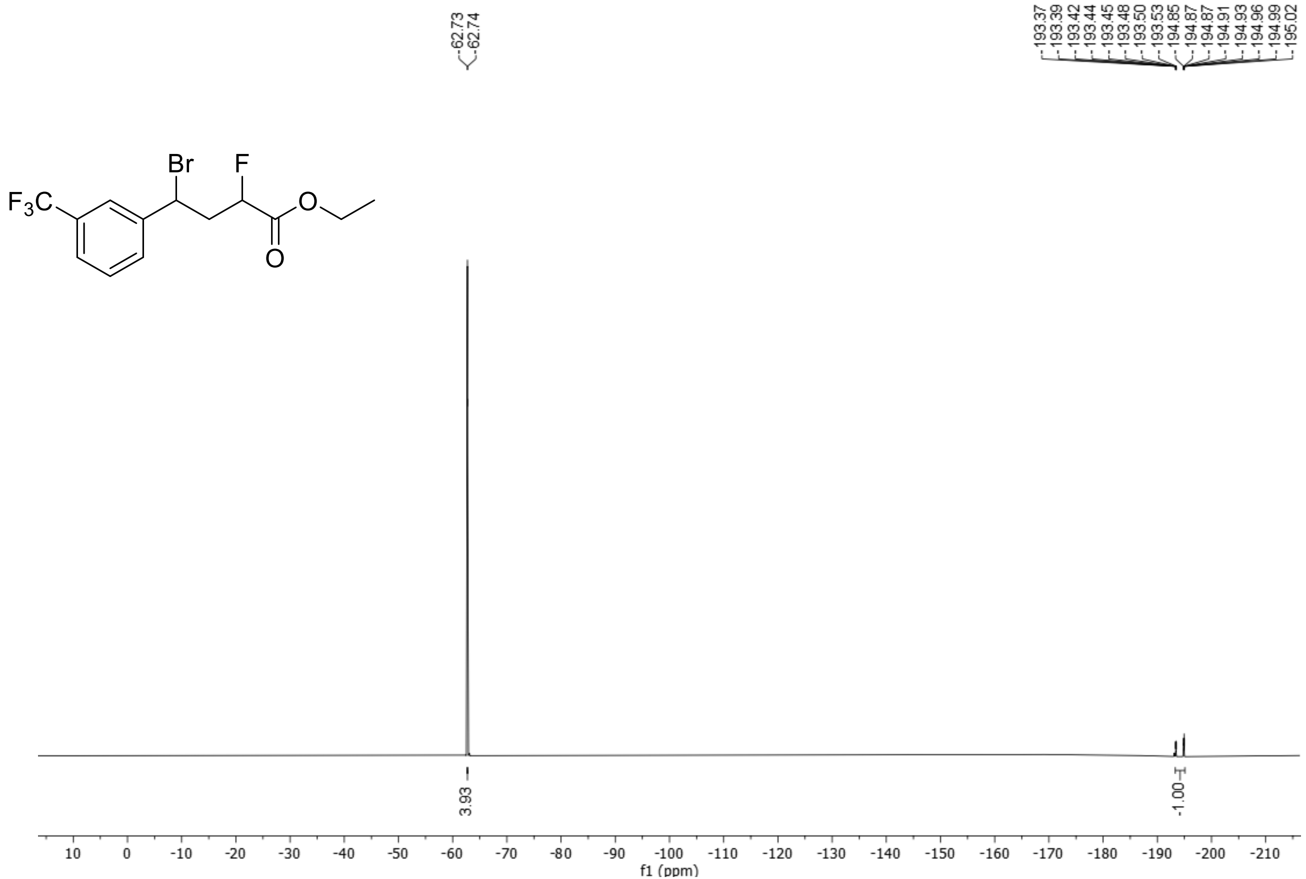
^{19}F NMR (376 MHz, CDCl$_3$) of compound **5b.**



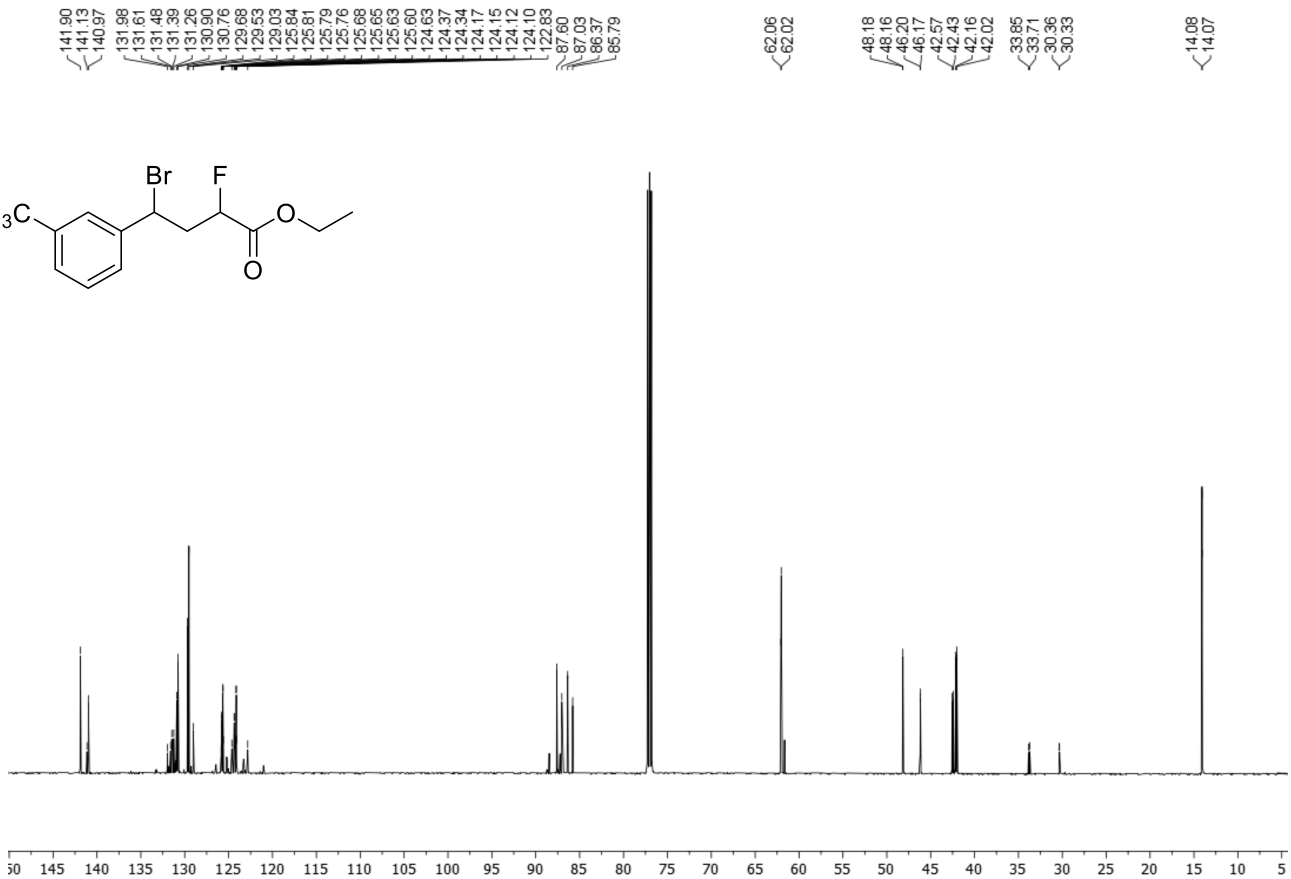
^{13}C NMR (151 MHz, $CDCl_3$) of compound **5b.**



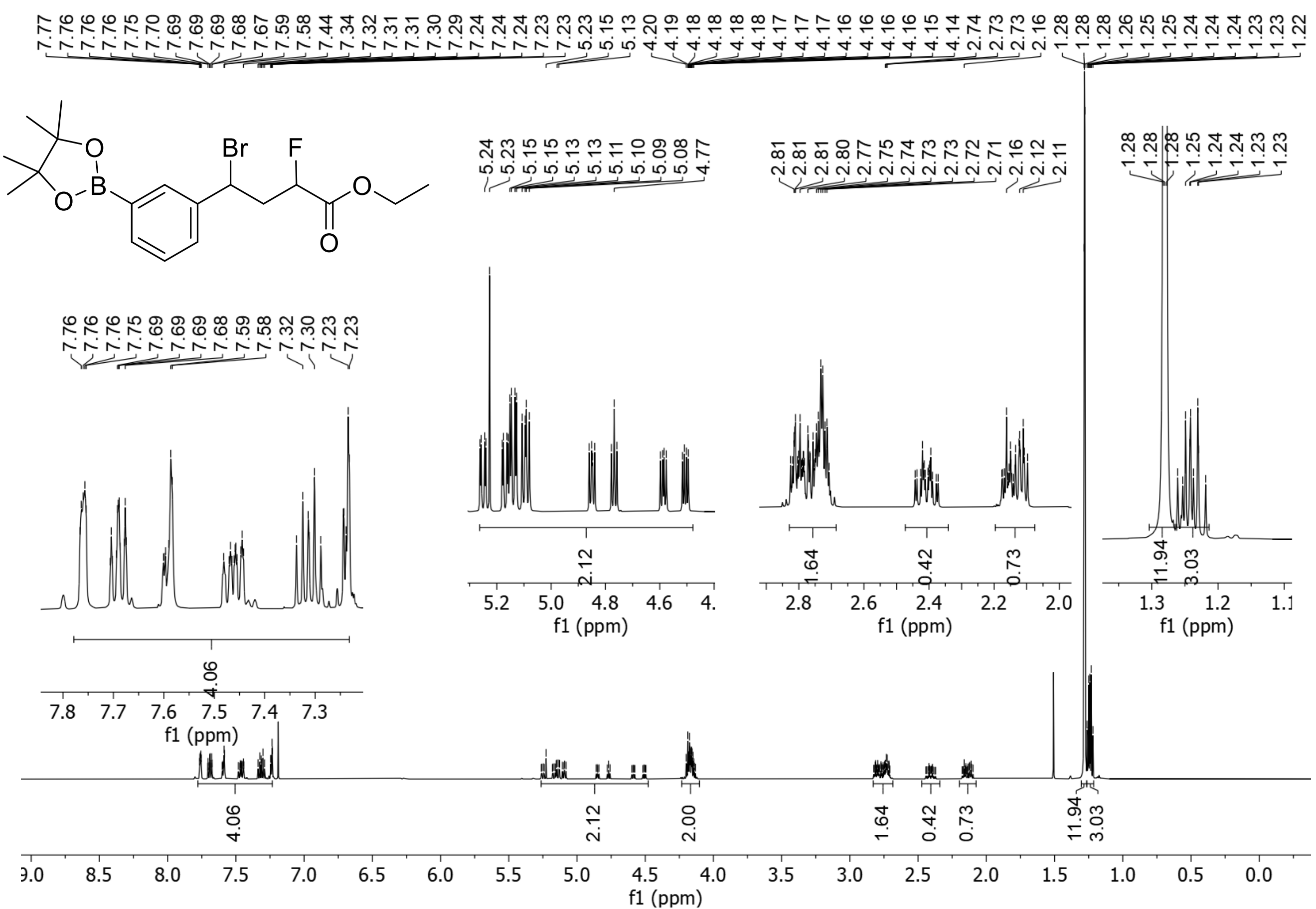
^{1}H NMR (600 MHz, $CDCl_3$) of compound **5c**.



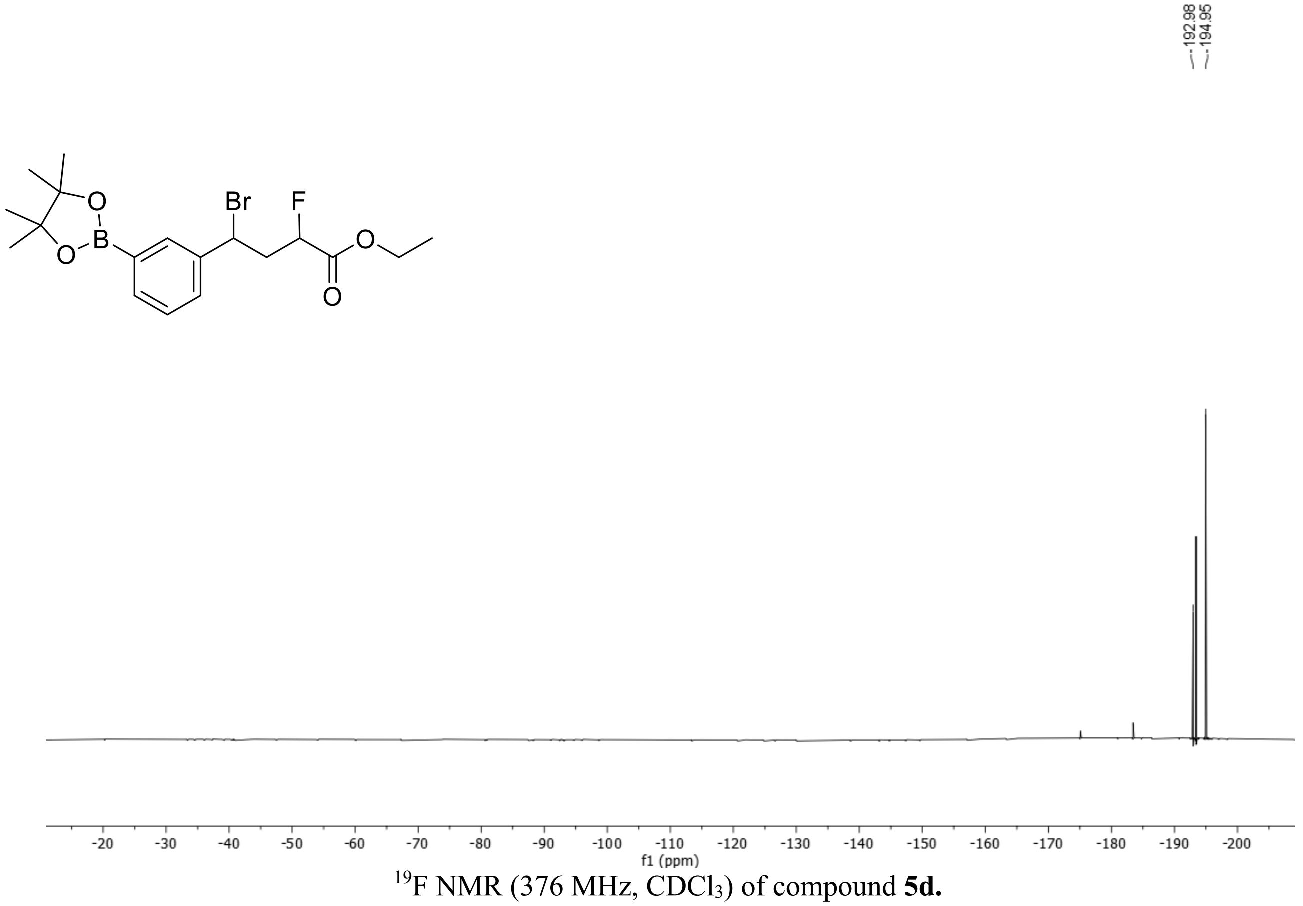
^{19}F NMR (564 MHz, CDCl$_3$) of compound **5c.**



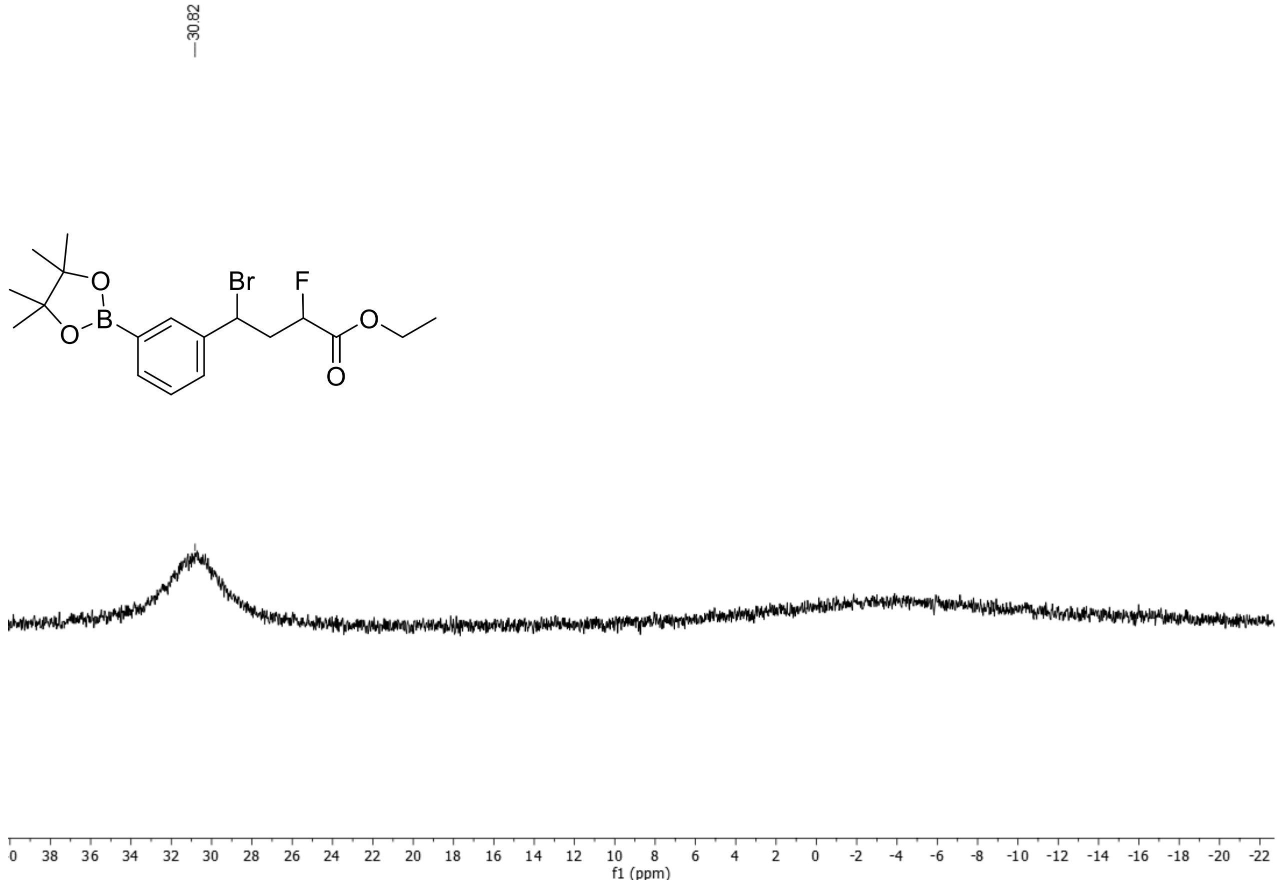
^{13}C NMR (151 MHz, CDCl$_3$) of compound **5c.**



^{1}H NMR (600 MHz, CDCl$_3$) of compound **5d**.

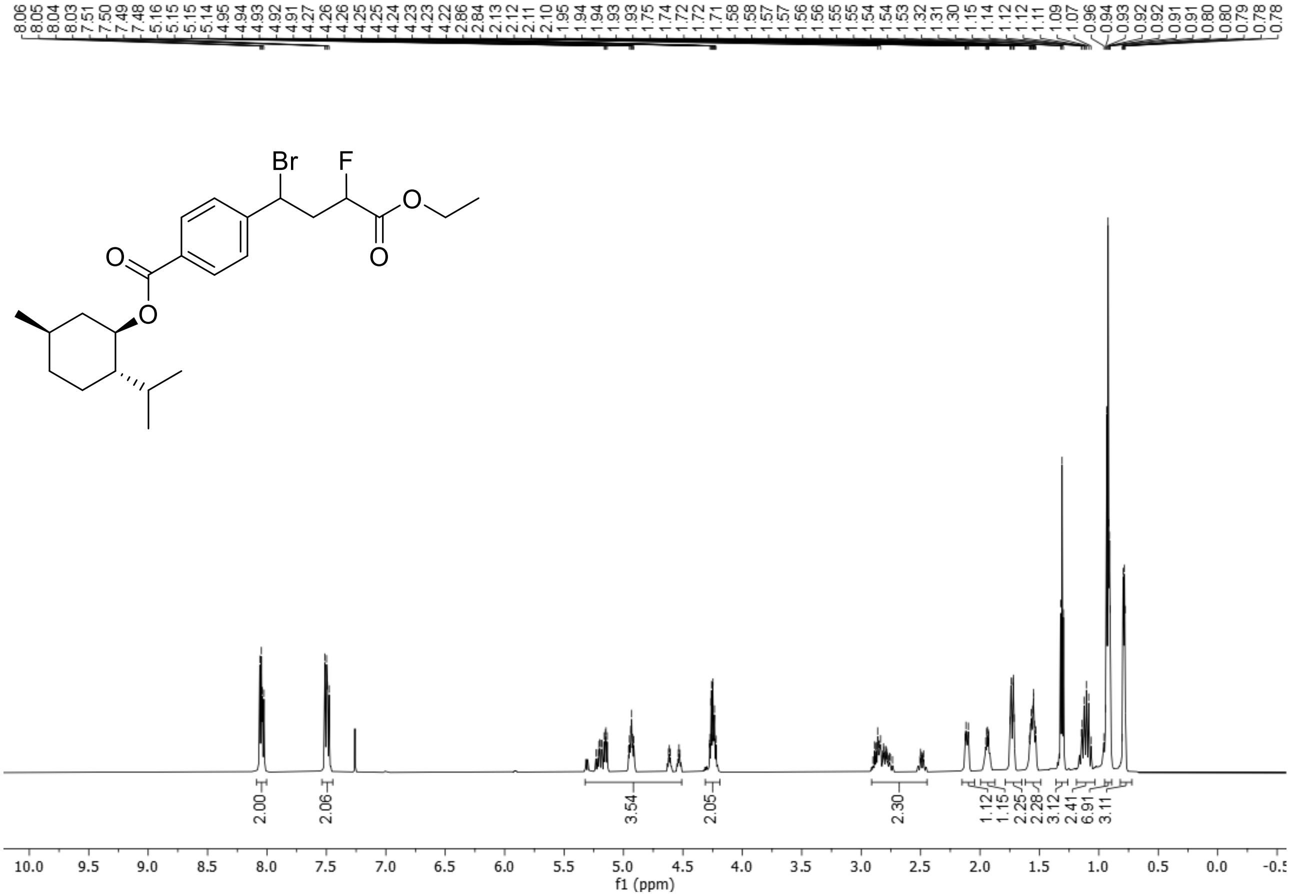


^{19}F NMR (376 MHz, CDCl$_3$) of compound **5d.**

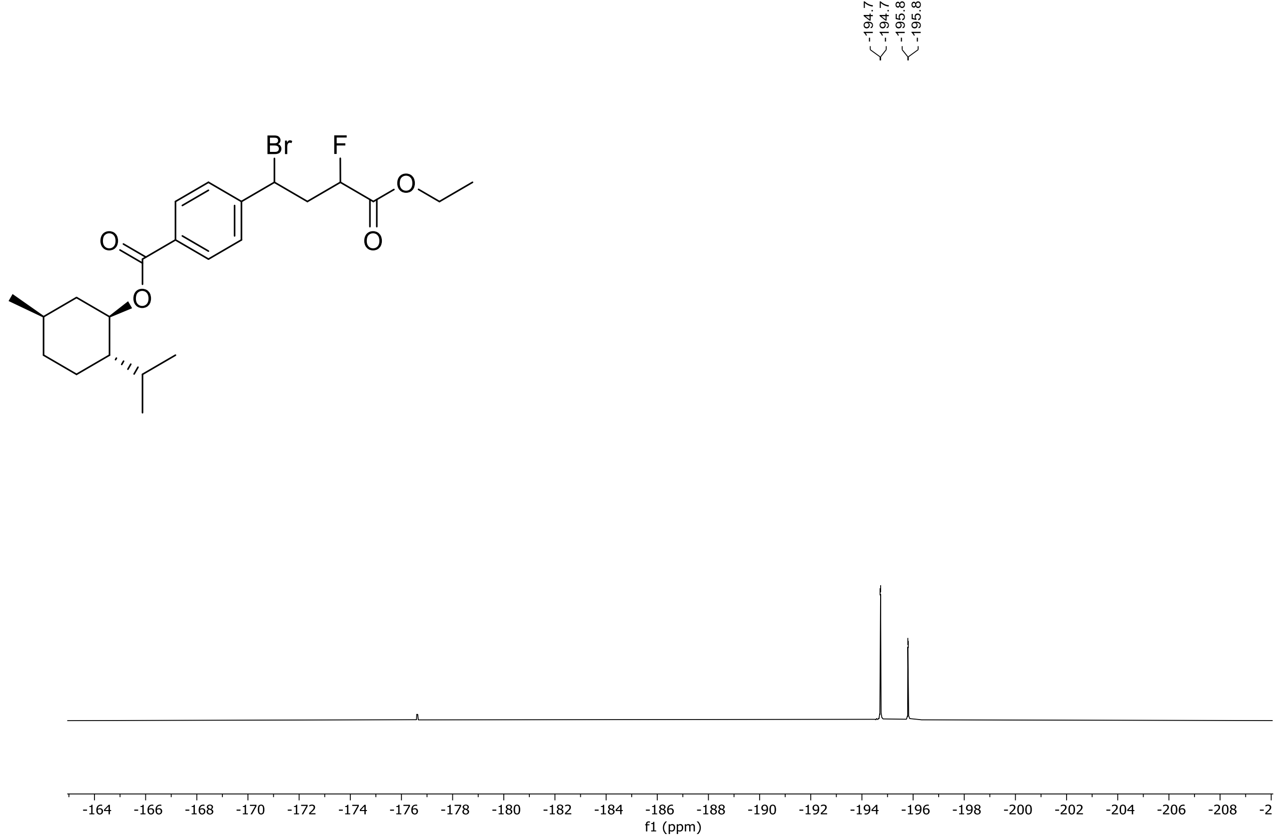


^{11}B NMR (128 MHz, CDCl$_3$) of compound **5d.**

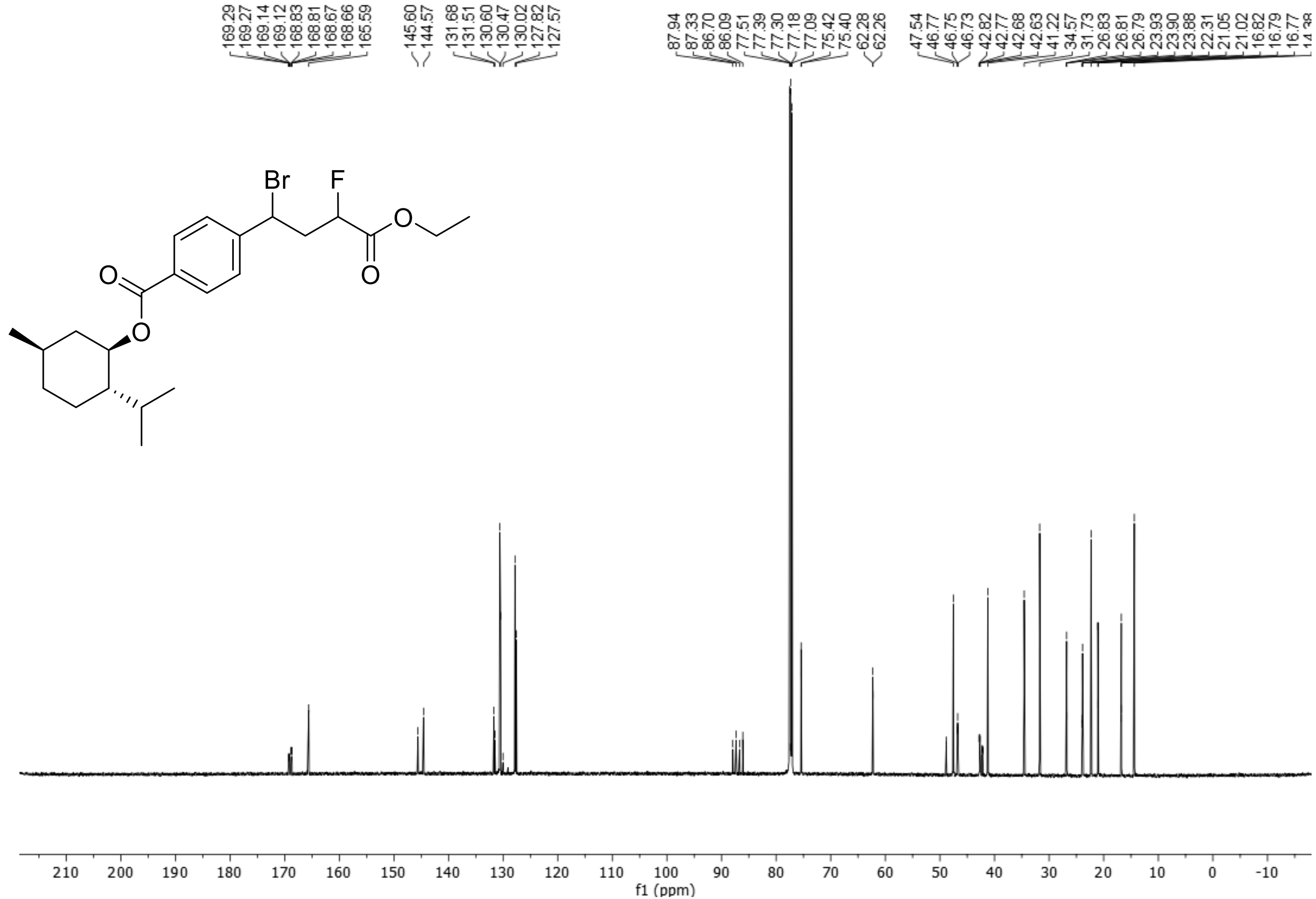
^{13}C NMR (151 MHz, CDCl$_3$) of compound **5d.**



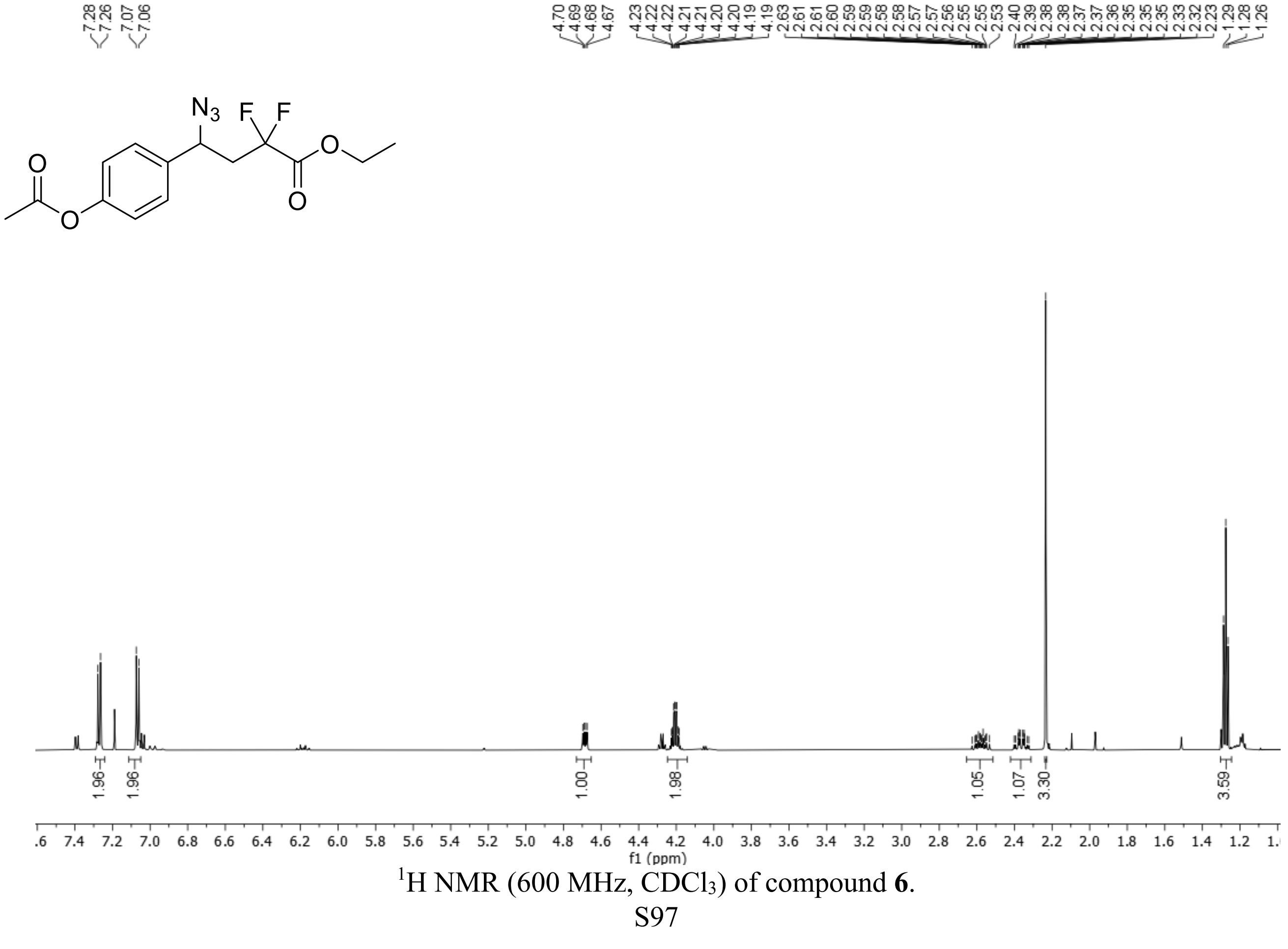
^{1}H NMR (600 MHz, CDCl$_3$) of compound **5e**.



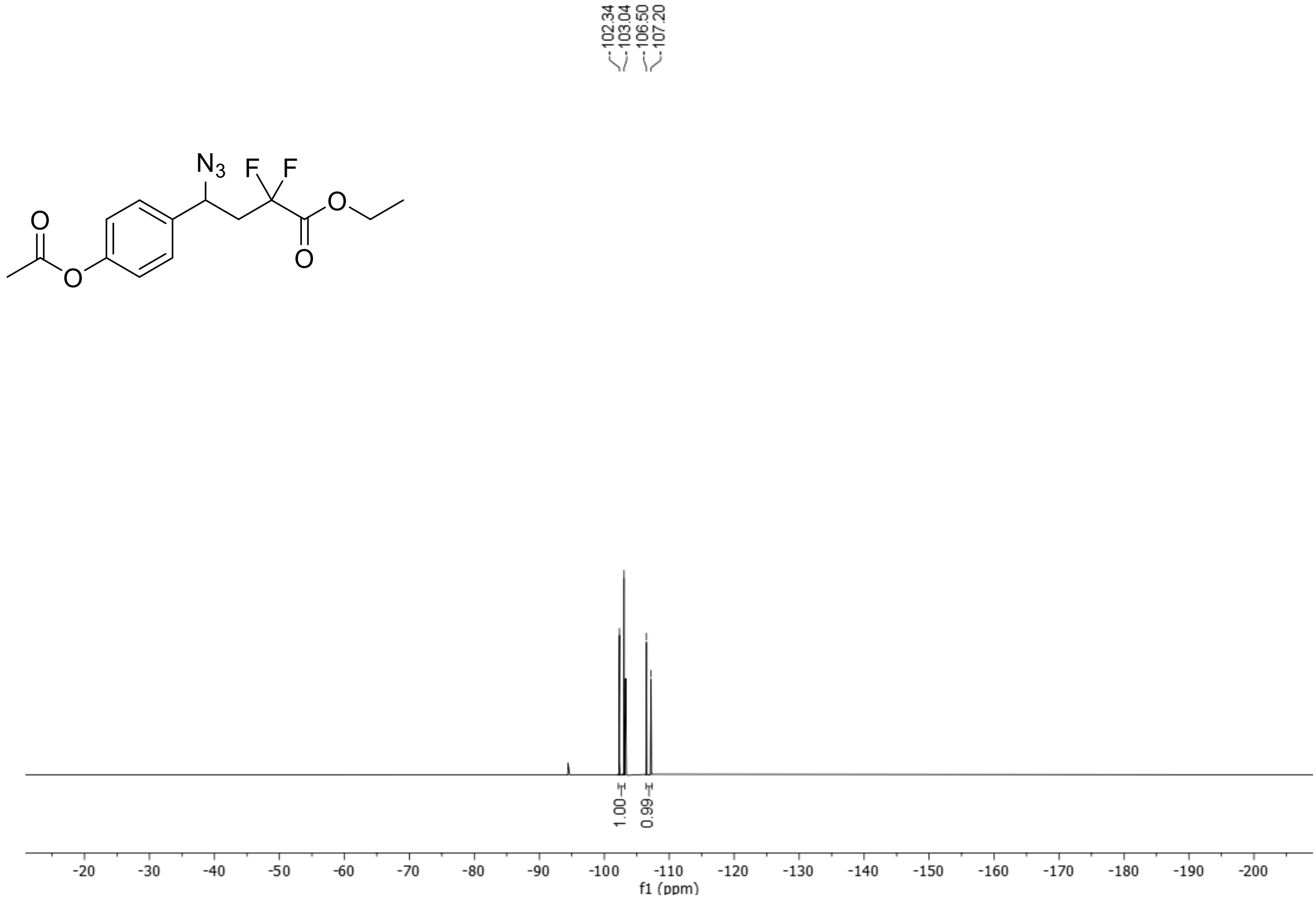
^{19}F NMR (376 MHz, CDCl$_3$) of compound **5e.**



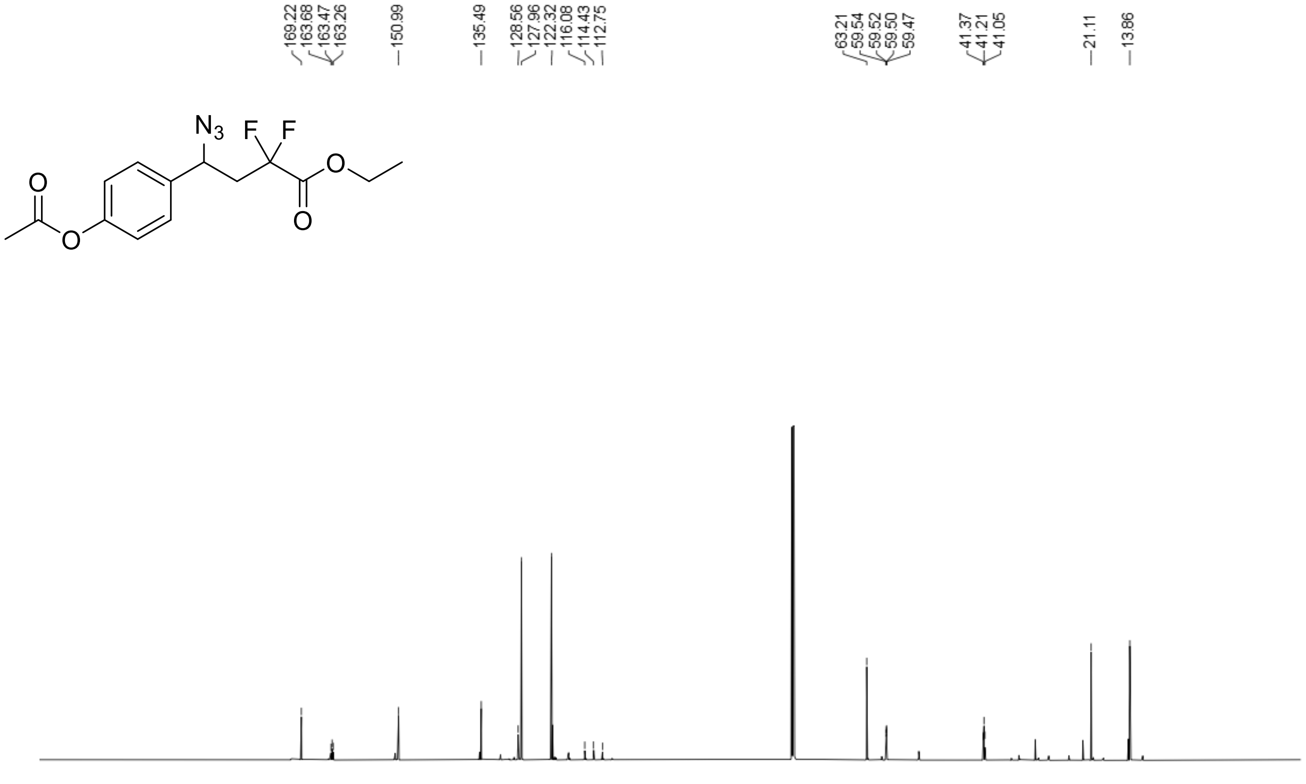
^{13}C NMR (151 MHz, CDCl$_3$) of compound **5e.**



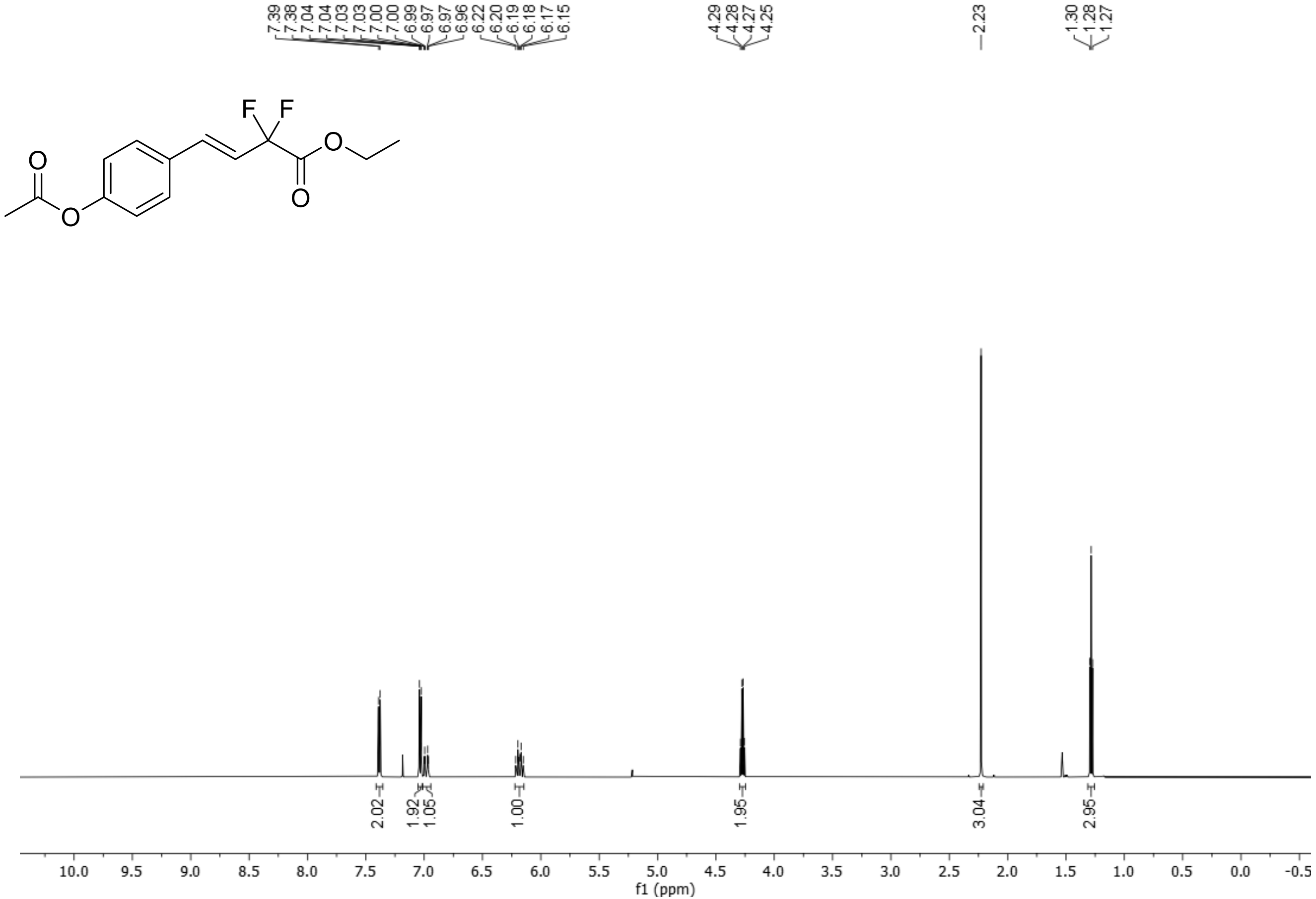
^{1}H NMR (600 MHz, CDCl$_3$) of compound **6**.



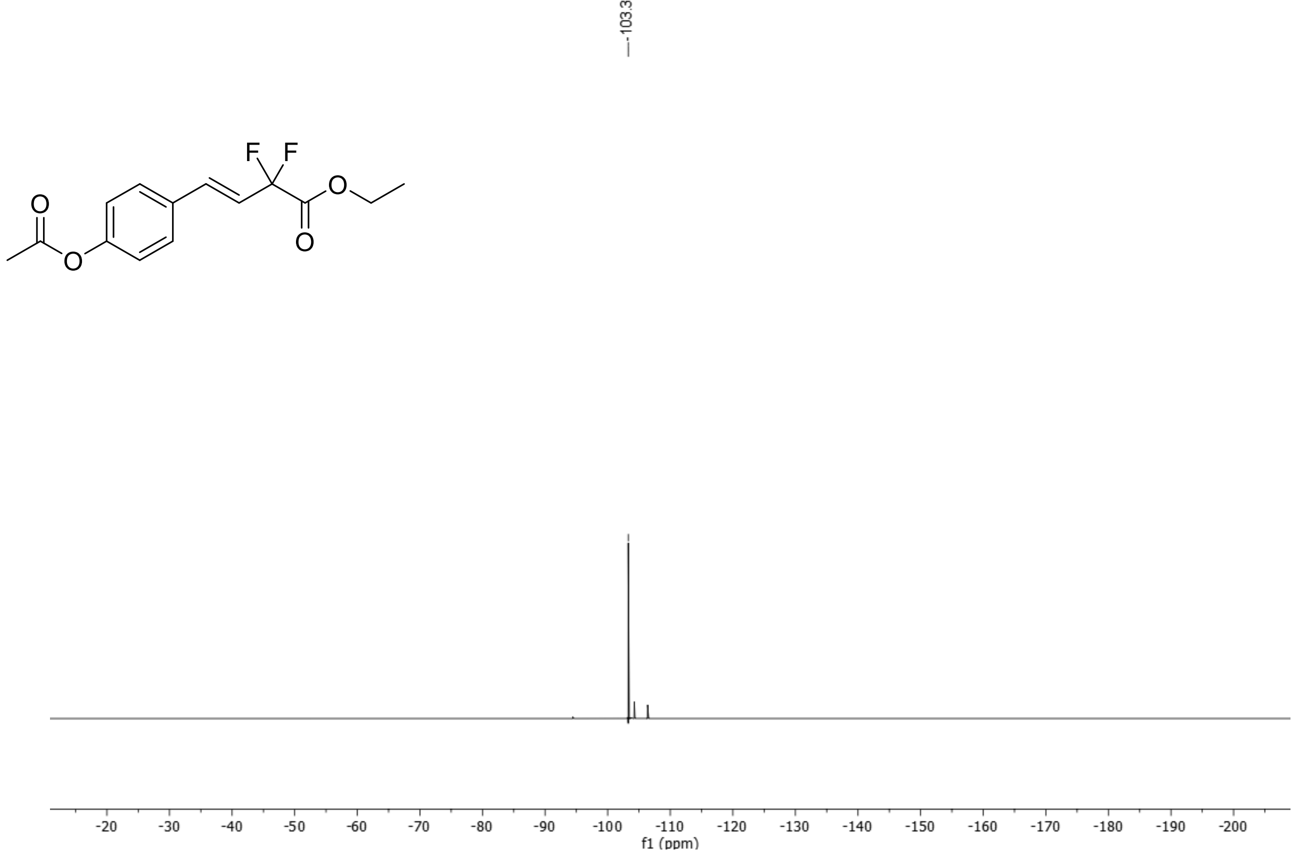
^{19}F NMR (376 MHz, CDCl$_3$) of compound **6.**



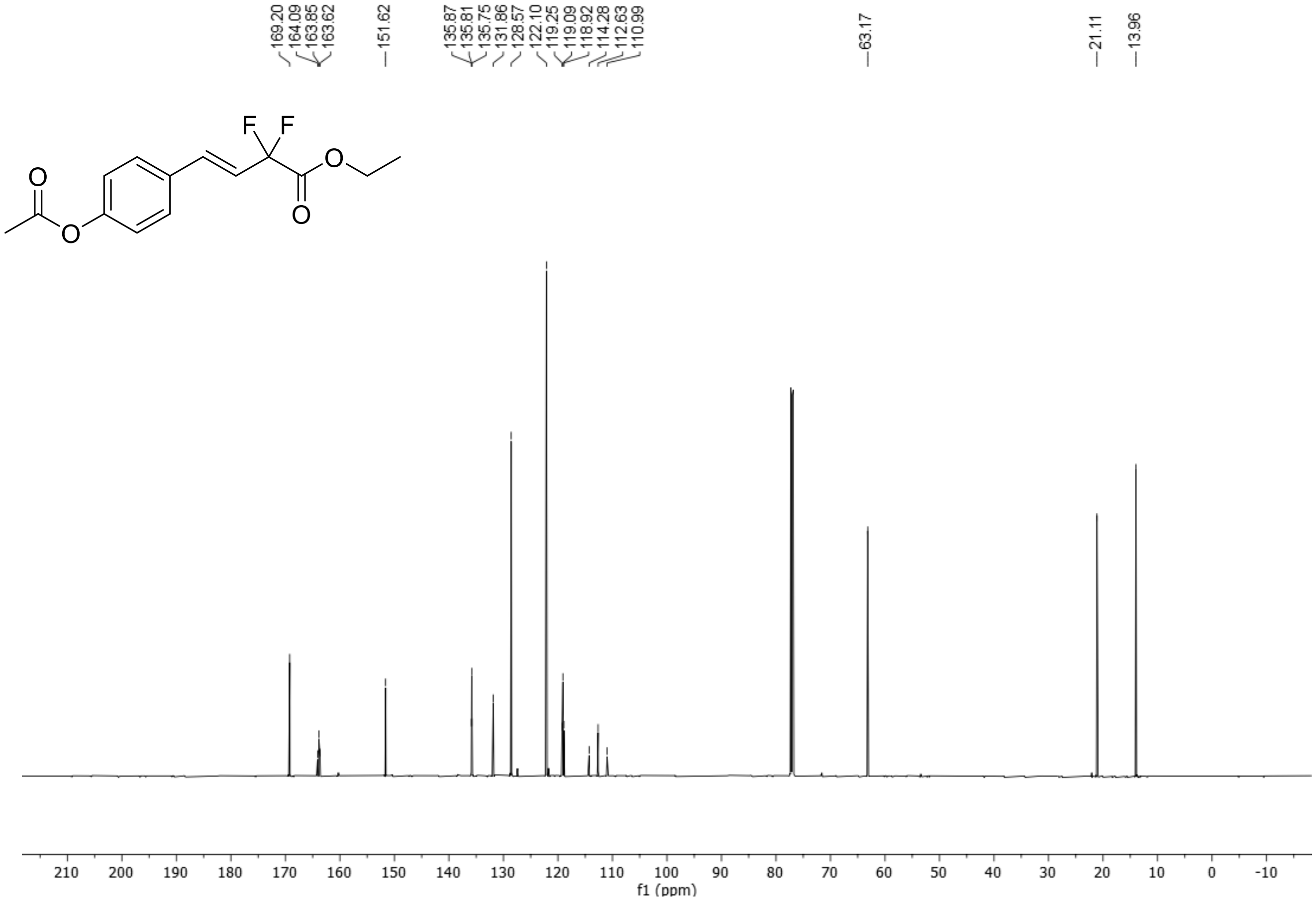
^{13}C NMR (151 MHz, CDCl$_3$) of compound **6.**



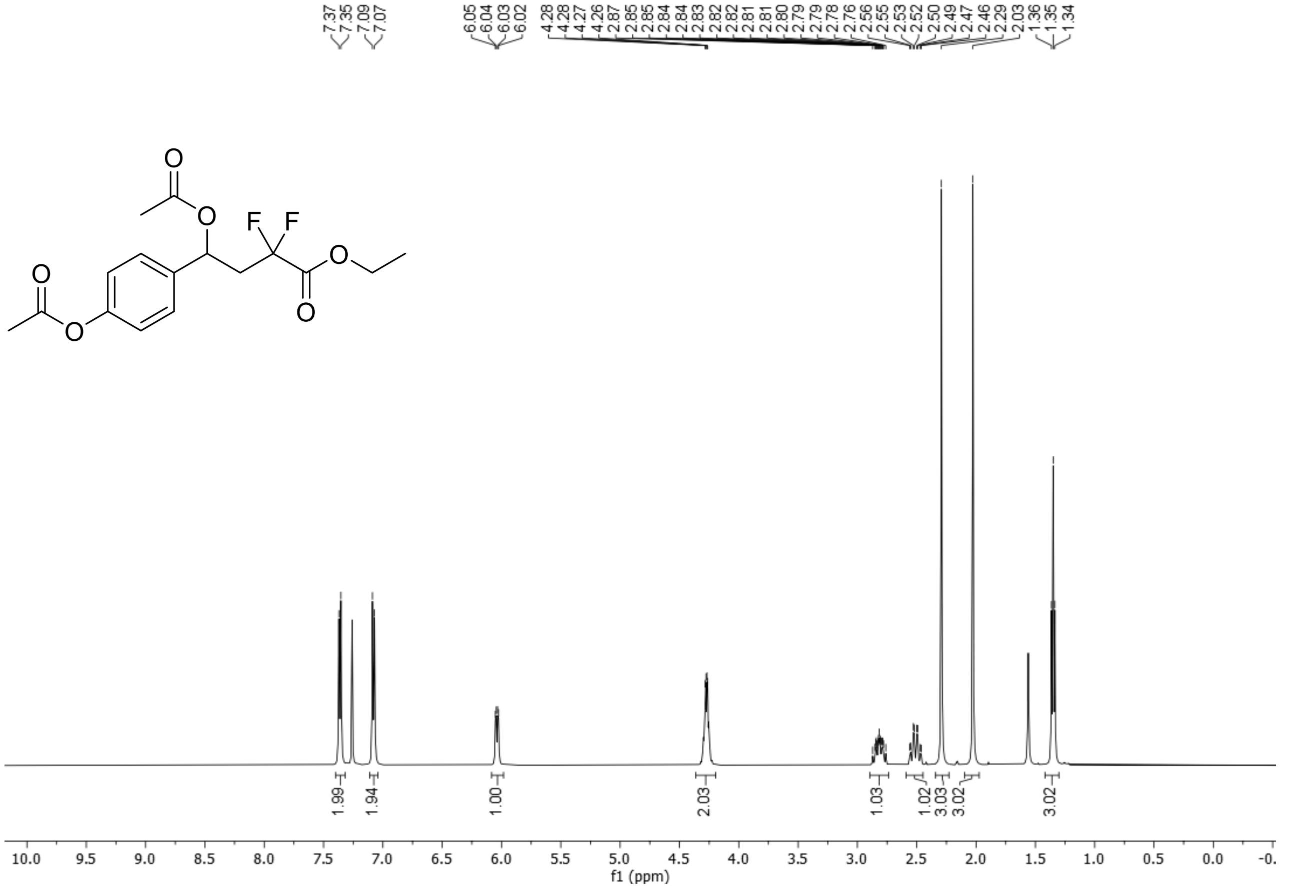
^{1}H NMR (600 MHz, CDCl$_3$) of compound **7**.



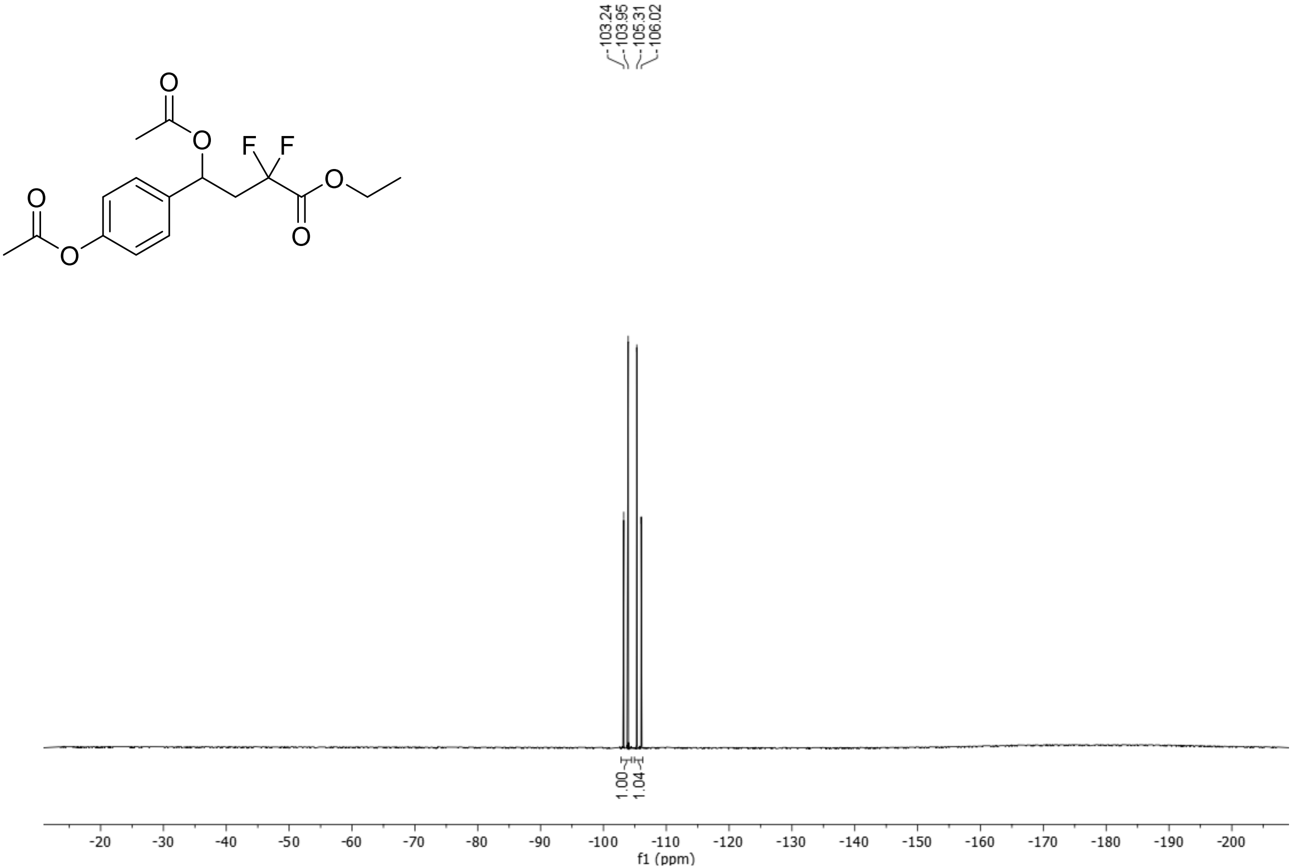
^{19}F NMR (376 MHz, CDCl$_3$) of compound **7.**



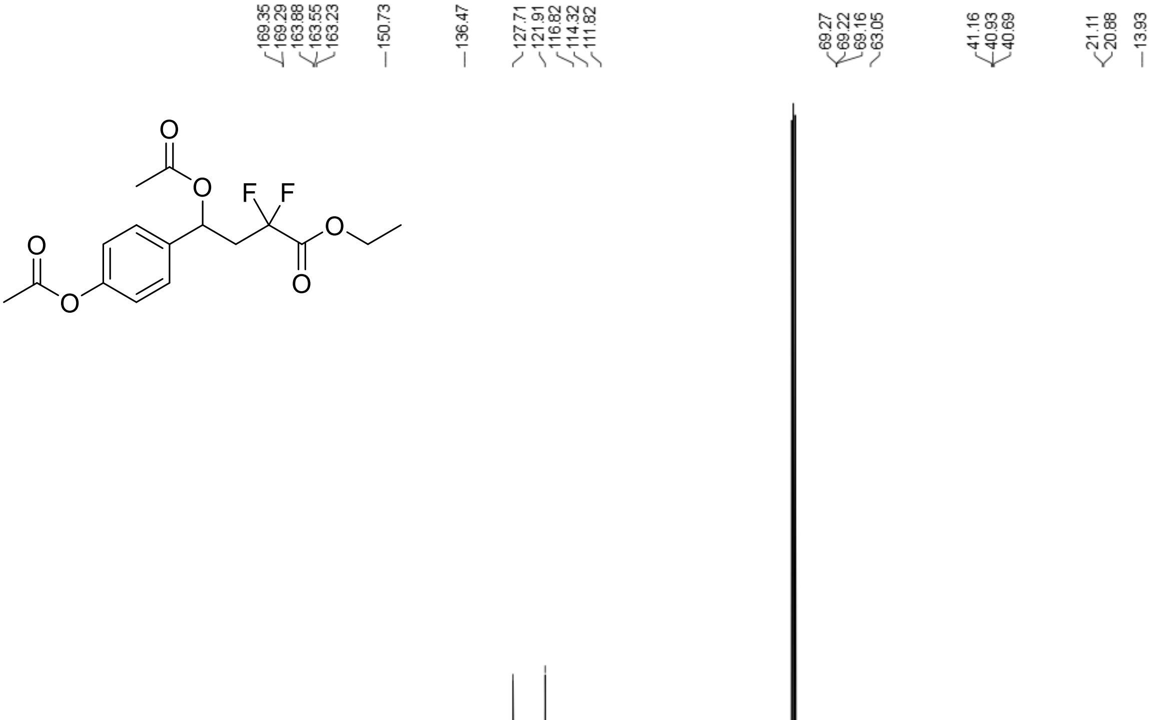
^{13}C NMR (151 MHz, CDCl$_3$) of compound **7.**



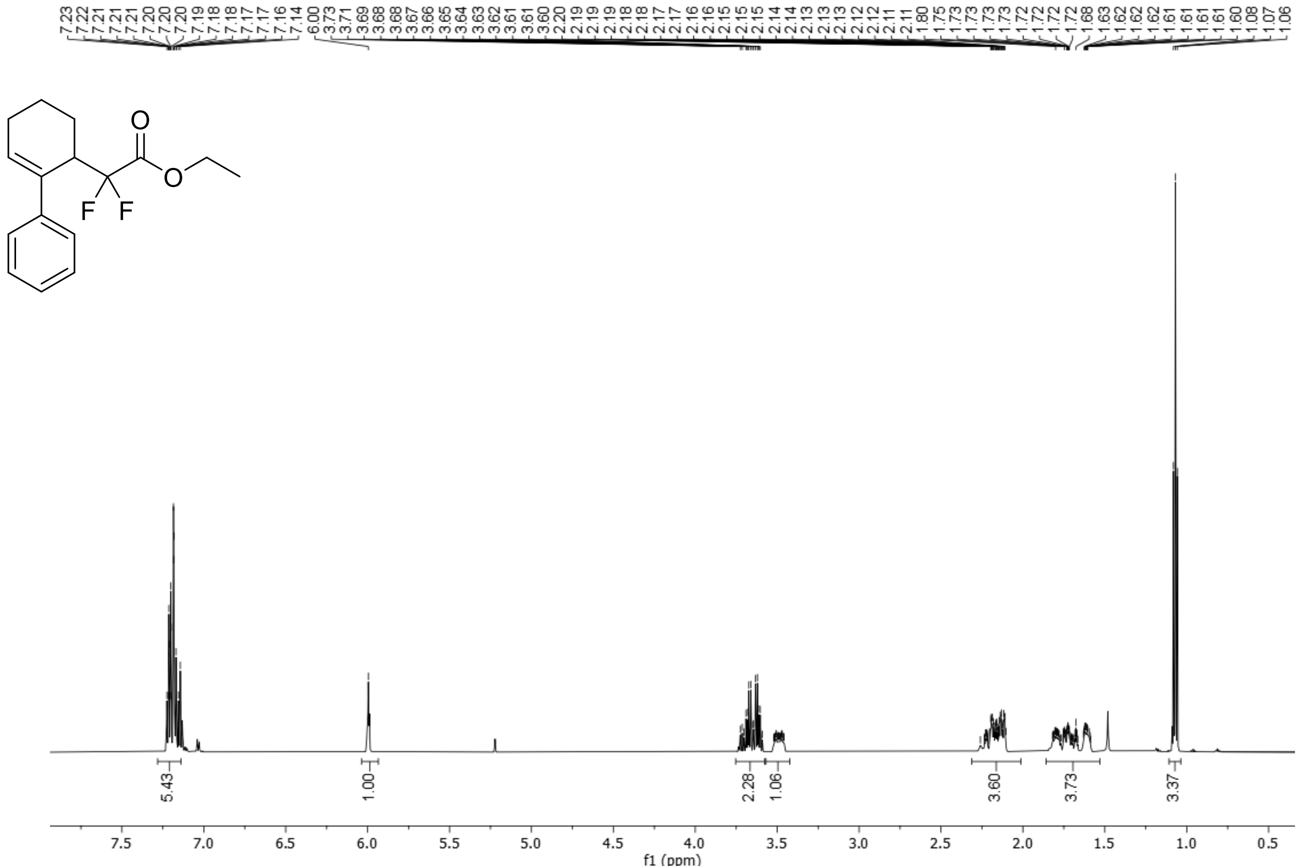
^{1}H NMR (500 MHz, CDCl$_3$) of compound **8**.



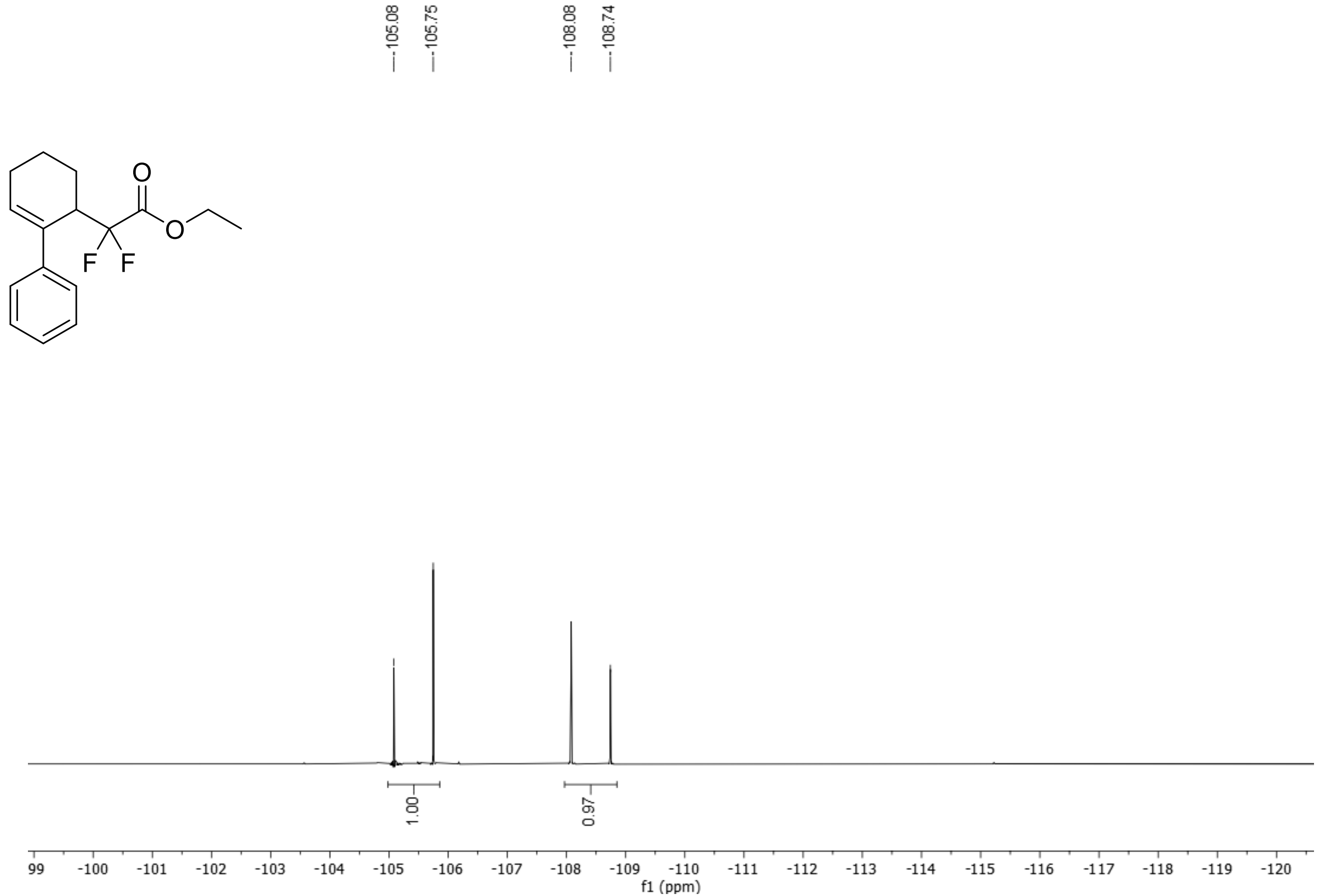
^{19}F NMR (376 MHz, CDCl$_3$) of compound **8.**



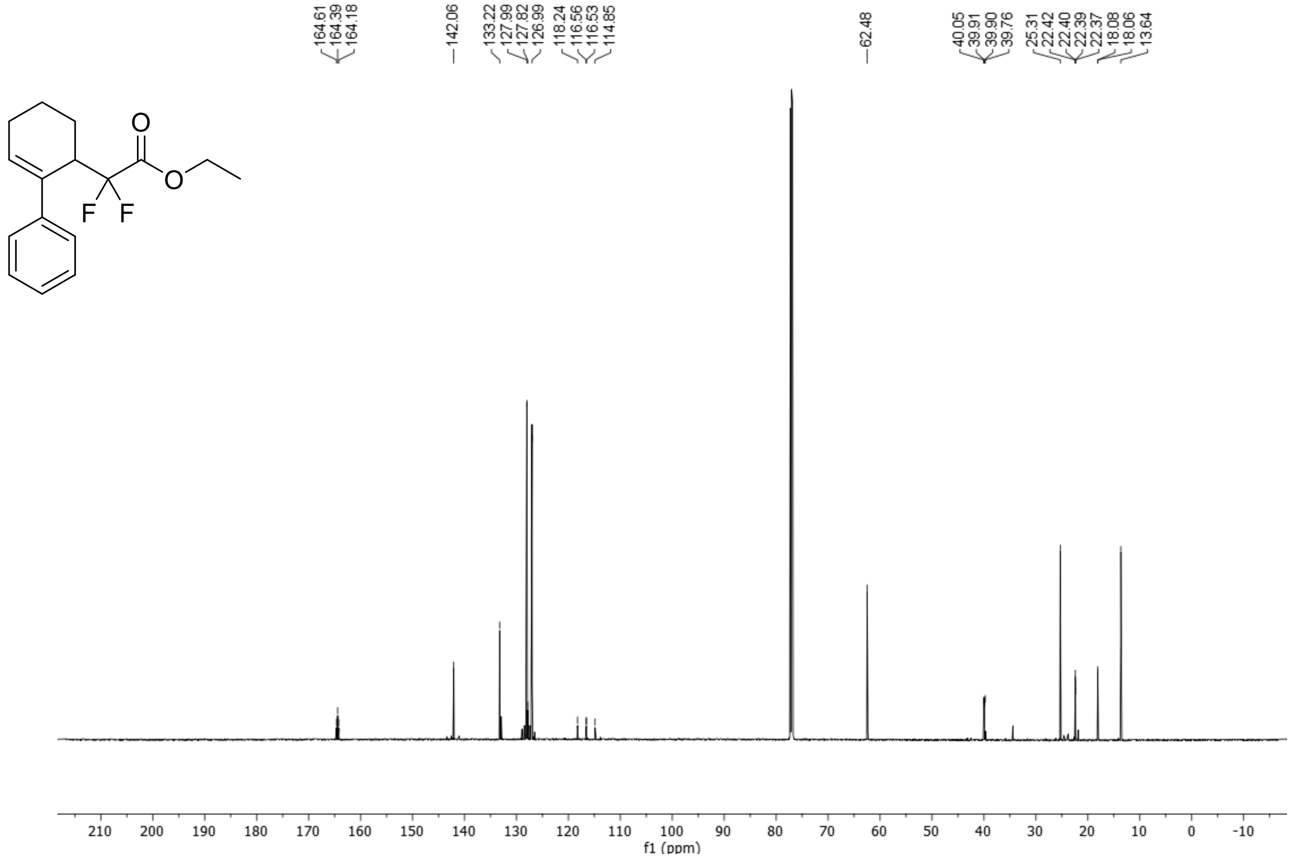
^{13}C NMR (101 MHz, CDCl$_3$) of compound **8.**



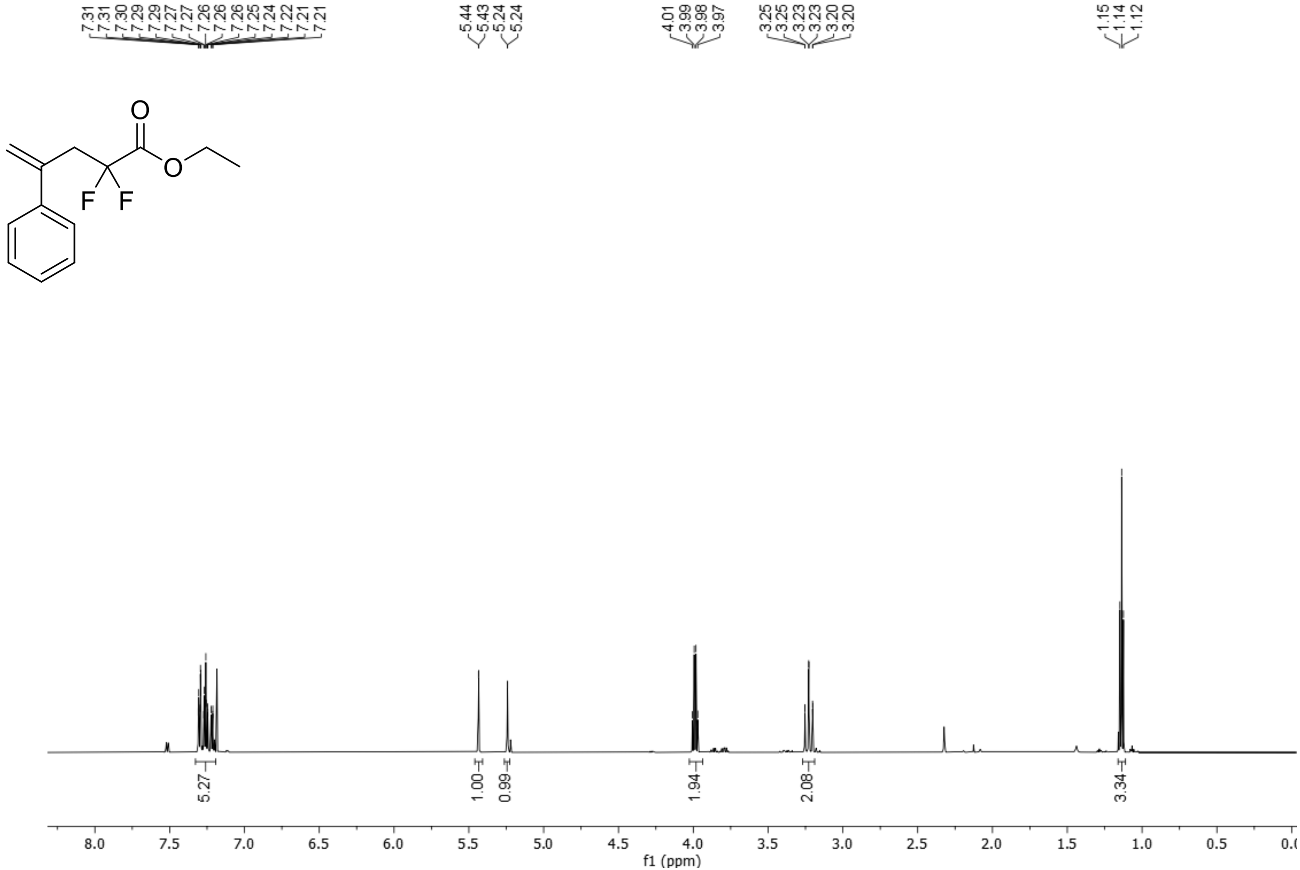
^{1}H NMR (600 MHz, CDCl$_3$) of compound **9**.



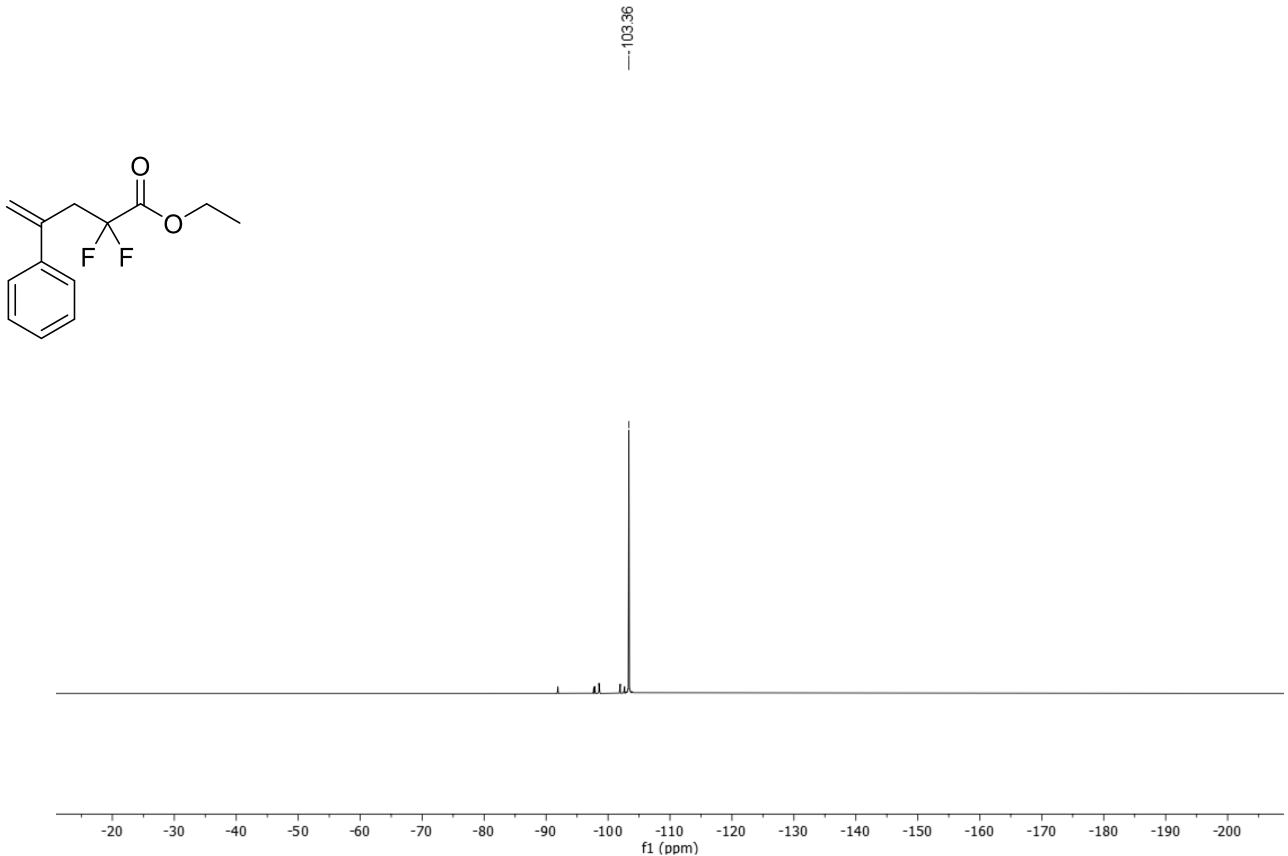
^{19}F NMR (376 MHz, CDCl$_3$) of compound **9.**



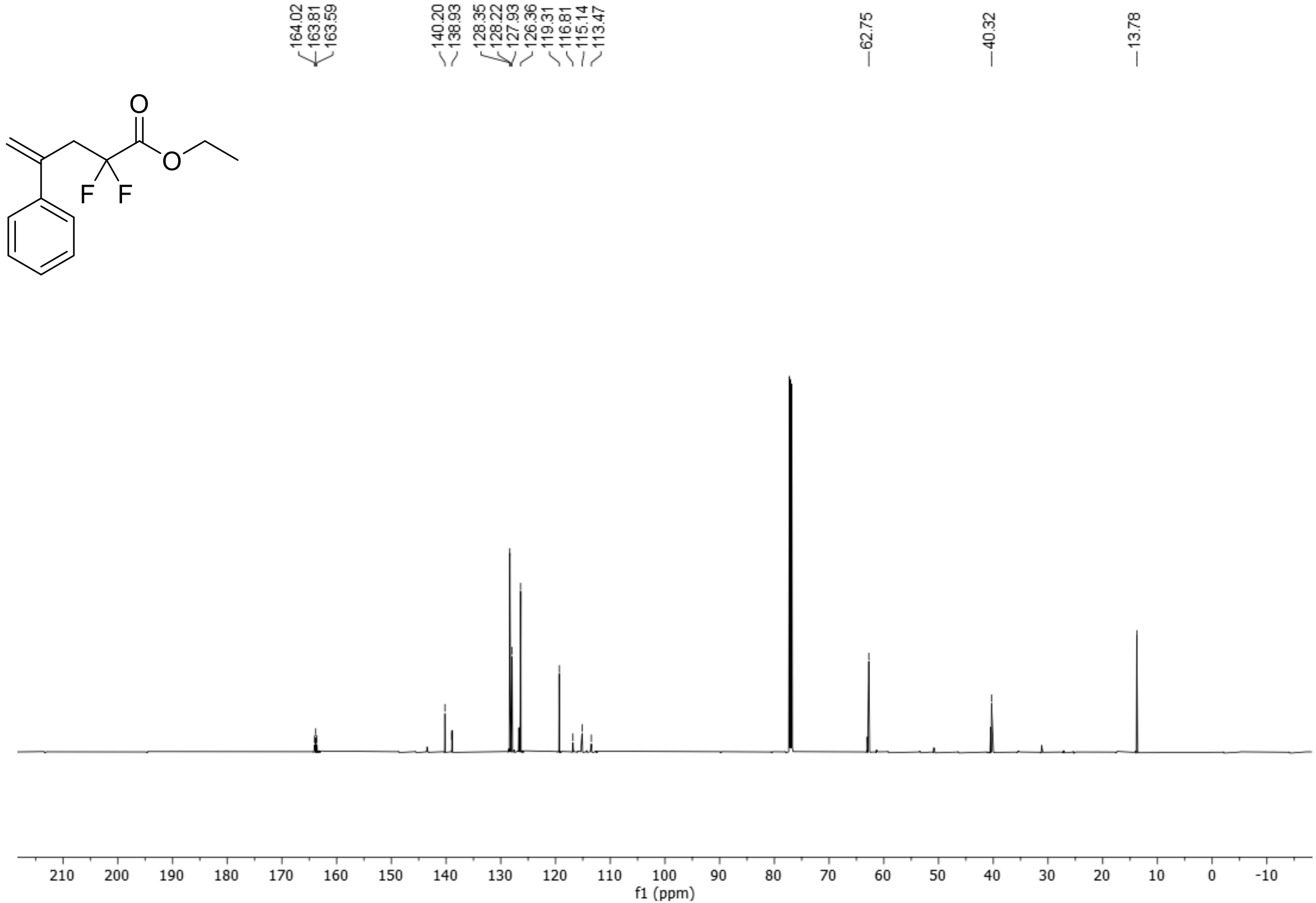
^{13}C NMR (151 MHz, $CDCl_3$) of compound **9.**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **10**.



^{19}F NMR (376 MHz, $CDCl_3$) of compound **10.**



^{13}C NMR (151 MHz, $CDCl_3$) of compound **10.**