Electronic Supplementary Information for

H-F Bond Insertions onto α-Diazo Carbonyl Compounds

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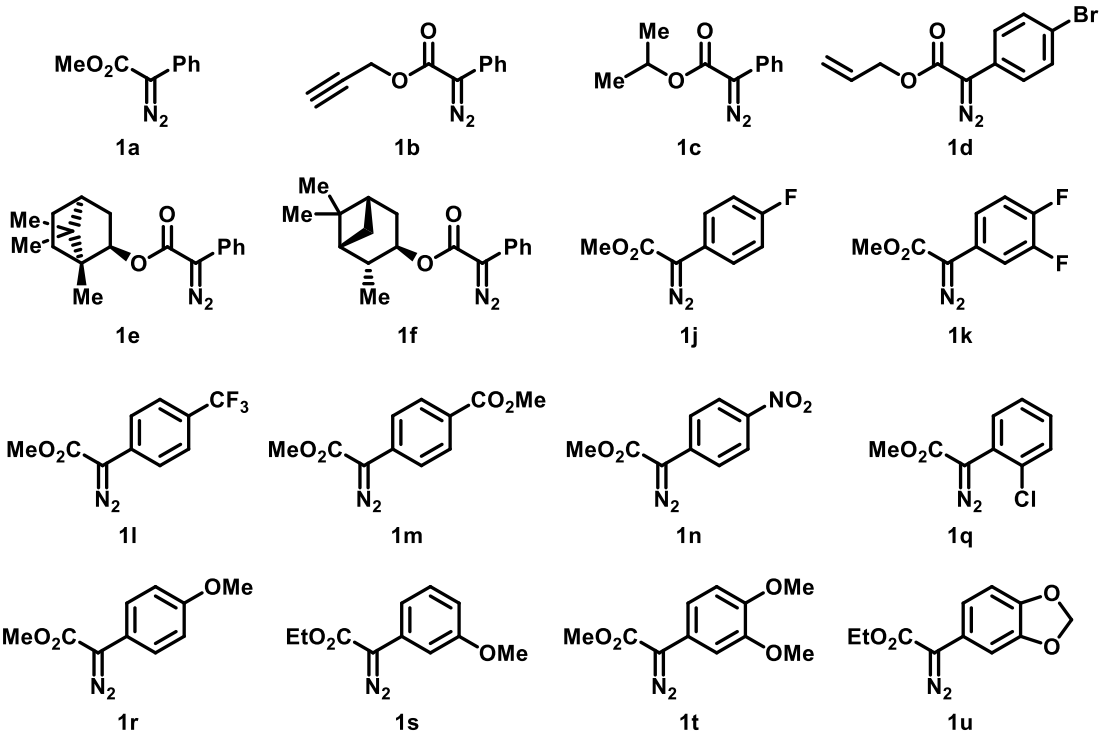
1. Materials and Methods

All reactions were carried out under air, in oven dried glassware with magnetic stirring, unless otherwise noted. All reagents employed in this work were purchased from Sigma-Aldrich/ Merck or Oakwood and used as such without further purification. All solvents employed in the reactions were distilled from appropriate drying agents prior to use. Organic solutions were concentrated under reduced pressure on a IKA rotary evaporator RV-10 Control. Reactions were monitored by thin-layer chromatography (TLC) on Silica gel 60 F_{254} aluminium plates (Merck). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using *para*-anisaldehyde or $KMnO_4$ solutions. Flash column chromatography was performed using Merck silica gel 60 (particle size 35-70µm) and purification by preparative layer chromatography was performed using Merk silica gel 60 PF_{254} containing gypsum. ^{1}H and ^{13}C NMR spectra were recorded either on Bruker AV-250, AV-400 or AV-500 spectrometers. Chemical shifts (δ) are given in parts per million, referenced to the residual peak of $CDCl_3$, δ = 7.26 (^{1}H NMR) and δ = 77.0 (^{13}C NMR) as internal references. The following abbreviations were used to designate chemical shift multiplicities: app s = apparent singlet, s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, sext. = sextet, sept. = septet, m = multiplet, br s = broad singlet. High-resolution mass spectra were recorded on Q Exactive Orbitrap spectrometer working with an electrospray ionization (ESI). Infrared spectra were performed on the Agilent Cary 630 FTIR spectrometer. Melting points were measured on Metler Toledo MP50 Melting Point System and are uncorrected.

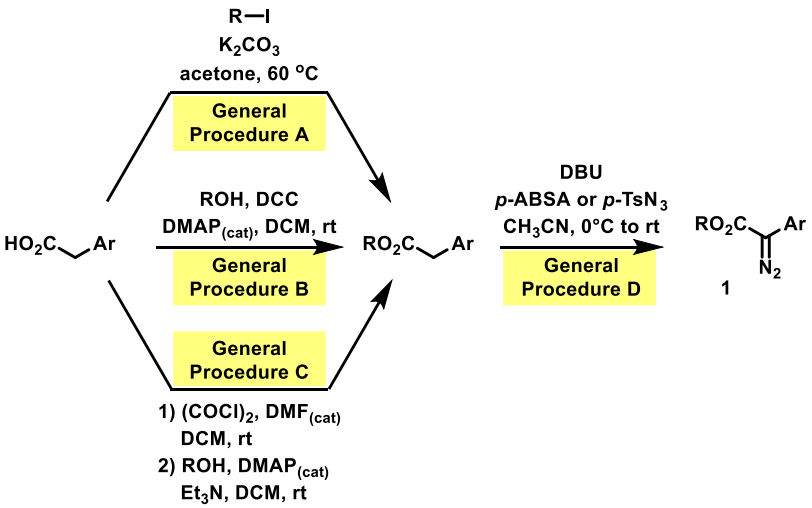
1.1. α-Diazo Esters 1a - 1u

α-Diazo esters **1** have been numbered following their order of appearance in the manuscript. The following diazo esters were prepared as previously reported in the literature: *methyl 2-diazo-2-phenylacetate* (**1a**),[1] *prop-2-yn-1-yl 2-diazo-2-phenylacetate* (**1b**),[2] *isopropyl 2-diazo-2-phenylacetate* (**1c**),[2] *allyl 2-(4-bromophenyl)-2-diazoacetate* (**1d**),[1] *(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-diazo-2-phenylacetate* (**1e**),[3] *(1R,2R,3R,5S)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl 2-diazo-2-phenylacetate* (**1f**),[2] *methyl 2-diazo-2-(4-fluorophenyl)acetate* (**1j**),[4] *methyl 2-diazo-2-(3,4-difluorophenyl)acetate* (**1k**),[1] *methyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate* (**1l**),[1] *methyl 4-(1-diazo-2-methoxy-2-oxoethyl)benzoate* (**1m**),[5] *methyl 2-diazo-2-(4-nitrophenyl)acetate* (**1n**),[6] *methyl 2-(2-chlorophenyl)-2-diazoacetate* (**1q**),[1] *methyl 2-diazo-2-(4-methoxyphenyl)acetate* (**1r**),[1] *ethyl 2-diazo-2-(3-methoxyphenyl)acetate* (**1s**),[2] *methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate* (**1t**),[4] *ethyl 2-(benzo[d][1,3]dioxol-5-yl)-2-diazoacetate* (**1u**).[2]

[1] Stivanin, M. L.; Fernandes, A. A. G.; da Silva, A. F.; Okada Jr, C. Y.; Jurberg, I. D.; *Adv. Synth. Catal.* **2020**, *362*, 1106-1111.
[2] Thurow, S.; Fernandes, A. A. G.; Quevedo-Acosta, Y.; de Oliveira, M. F.; de Oliveira, M. G.; Jurberg, I. D.; *Org. Lett.* **2019**, *21*, 6909-6913.
[3] Jana, S.; Yang, Z.; Pei, C.; Xu, X.; Koenigs, R. M.; *Chem. Sci.* **2019**, *10*, 10129-10134.
[4] Da Silva, A. F.; Afonso, M. A. S.; Cormanich, R. A.; Jurberg, I. D.; *Chem. Eur. J.* **2020**, *26*, 5648-5653.
[5] Ye, F.; Wang, C.; Zhang, Y.; Wang, J.; *Angew. Chem. Int. Ed.* **2014**, *53*, 11625-11628.
[6] Chan, W.-W.; Yeung, S.-H.; Zhou, Z.; Chan, A. S. C.; Yu, W.-Y.; *Org. Lett.* **2010**, *12*, 604-607.



α-Diazo esters **1** used in this work were either prepared according to one of the following synthetic routes shown below (Scheme S1) or by specific procedures that will be detailed later, as appropriate.



Scheme S1. General synthetic routes employed for the preparation of α-diazo esters **1**.

General Procedure A: *Alkylation of Carboxylic Acids*

Under air, a round bottomed flask is charged with the carboxylic acid (1 equiv.), acetone (0.5 M), alkyl halide (1.2 equiv.) and K_2CO_3 (1 equiv.). The reaction mixture is heated at reflux (60 ^oC) overnight. Then, the reaction is allowed to cool to room temperature and is concentrated under vacuum. The residue is dissolved in AcOEt, washed with H_2O (1x), brine (1x), dried ($MgSO_4$) and concentrated again under vacuum. Purification by flash column chromatography affords the title compounds in the stated yields.

General Procedure B: *Steglich Esterification*

To a stirred, ice cooled solution of the phenylacetic acid (1.3 g, 10 mmol, 1 equiv.), and chiral alcohol (12 mmol, 1.2 equiv.) in 20 mL DCM was added a solution of DCC (13 mmol, 1.3 equiv.) and DMAP (1 mmol, 0.1 equiv.) in 10 mL DCM at once. The solution was stirred 6 h while slowly warming up to room temperature. After finishing the reaction, the solid was filtered off and washed with Et_2O. The solvent was evaporated, and the residue was purified by flash column chromatography to afford the corresponding ester.

General Procedure C: *Acyl Chloride Synthesis/ Nucleophilic Substitution*

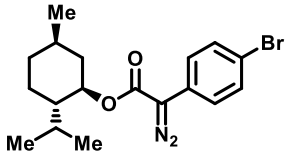
Step 1: Under nitrogen, at room temperature, a round bottomed flask is charged with the carboxylic acid (1 equiv.), dry DCM (0.2 M), oxalyl chloride (2 equiv.). Then, DMF (2 drops) is add and the reaction is allowed to stir overnight at room temperature. Then, the reaction mixture is concentrated under vacuum. The corresponding acyl chloride is generally clean and can be directly employed in the next step.

Step 2: Under nitrogen, at room temperature, a round bottomed flask is charged with dry DCM (0.2 M), ROH (1.2 equiv.), Et_3N (1.2 equiv.) and DMAP (10 mol%). Then, the temperature of the reaction mixture is cooled to 0 ^oC and the previously prepared acyl chloride (1 equiv., dissolved in a minimun amount of DCM) is added. The reaction is allowed to warm up to room temperature and to stir at this temperature overnight. Then, the reaction is quenched with a saturated aqueous solution of $NaHCO_3$, extracted with AcOEt (3x), dried ($MgSO_4$) and concentrated under vacuum. Purification by flash column chromatography affords the title compounds in the stated yields.

General Procedure D: *Regitz Diazo Transfer with p-ABSA or p-TsN_3*

Under nitrogen, a round-bottomed flask is charged with carboxylic acid (1 equiv.), dry CH_3CN (0.1 M) and *p*-ABSA (1.3 equiv.) or TsN_3 (1.1 equiv.). The solution is cooled to 0 °C and DBU (1.3 equiv.) is added slowly. The temperature is allowed to warm up to 25 °C and the reaction mixture is stirred at this temperature overnight. Then, a saturated aqueous solution of NH_4Cl is added. The resulting mixture is extracted with AcOEt (3x). The combined organic extracts are dried ($MgSO_4$) and concentrated under vacuum. Purification by flash column chromatography affords the title compounds in the stated yields.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-(4-bromophenyl)-2-diazoacetate (**1g**)



General Procedure C is employed with 4-bromophenyl)acetic acid (2.15 g, 10 mmol, 1 equiv.), oxalyl chloride (1.69 mL, 20 mmol, 2 equiv.), DMF (10 drops) and DCM (50 mL) for the preparation of the corresponding acyl chloride. Then, (−)-menthol (1.88 g, 12 mmol, 1.2 equiv.), Et_3N (1.68 mL, 12 mmol, 1.2 equiv.), DMAP (122 mg, 0.1 mmol, 0.1 equiv.) and DCM (50 mL) were used for the preparation of the corresponding ester. Purification by flash column chromatography (SiO_2, gradient: Hex - 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl-2-(4-bromophenyl)acetate as a transparent oil: 3.41 g, 96%.

Next, **General Procedure D** is employed with the previously prepared ester (2.81 g, 7.4 mmol, 1 equiv.), *p*-ABSA (3.56 g, 14.8 mmol, 1.2 equiv.), DBU (2.2 mL, 14.8 mmol, 1.2 equiv.) and MeCN (3 mL). Purification by flash column chromatography (SiO_2, gradient: Hex - 95:5 Hex:AcOEt - 9:1 Hex:AcOEt - 8:2 Hex:AcOEt) affords the title compound as an orange oil: 2.81 g, 74%.

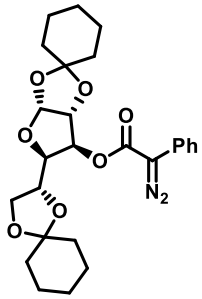
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 4.92 – 4.82 (m, 1H), 2.13 – 2.08 (m, 1H), 1.91 – 1.87 (m, 1H), 1.71 – 1.67 (m, 2H), 1.49 – 1.39 (m, 2H), 1.12 – 1.03 (m, 2H), 0.98 – 0.79 (m, 10H).

^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.1, 131.8, 125.1, 124.9, 118.9, 75.1, 63.0, 47.0, 41.1, 34.1, 31.3, 26.4, 23.5, 21.9, 20.6, 16.5.

IR (ATR, cm^{-1}): 2957, 2870, 2086, 1695, 1491, 1243, 1167, 1003.

HRMS (ESI-Orbitrap) m/z: $[M - N_2 + H]^+$ Calcd. for $C_{18}H_{24}BrO_2$: 351.0954; Found 351.0955.

(3a'R,5'R,6'S,6a'R)-5'-((R)-1,4-dioxaspiro[4.5]decan-2-yl)tetrahydrospiro[cyclohexane-1,2'-furo[2,3-d][1,3]dioxol]-6'-yl 2-diazo-2-phenylacetate (**1h**)



General Procedure B is employed with phenylacetic acid (272 mg, 2 mmol, 1 equiv.), 1,2:5,6-Di-O-cyclohexylidene-α-D-glucofuranose (817 mg, 2.4 mmol, 1.2 equiv.), DCM (5 mL), DCC (536 mg, 2.6 mmol, 1.3 equiv.) and DMAP (25 mg, 0.2 mmol, 0.1 equiv.) DCM in (1 mL) Purification by flash column chromatography (SiO_2, gradient: Hex - 99:1 Hex:AcOEt – 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords the corresponding ester as a colorless oil: 724 mg, 79%

Then, **General Procedure D** is employed with the previously prepared (3a'R,5'R,6'S,6a'R)-5'-((R)-1,4-dioxaspiro [4.5]decan-2-yl)tetrahydrospiro[cyclohexane-1,2'furo[2,3-*d*][1,3] dioxol]-6'-yl 2-phenylacetate (458 mg, 1 mmol, 1.0 equiv.), MeCN (10 mL), *p*-TsN_3 (238 mg, 1.2 mmol, 1.2 equiv.) and DBU (197 µL, 1.3 mmol, 1.3 equiv.). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords the title compound as a yellow solid: 262 mg, 54% yield.

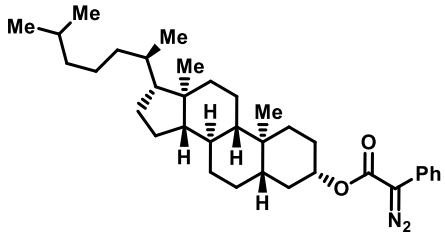
^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.50 – 7.36 (m, 4H), 7.24 – 7.17 (m, 1H), 5.91 (d, *J* = 3.7 Hz, 1H), 5.43 (d, *J* = 3.0 Hz, 1H), 4.65 (d, *J* = 3.7 Hz, 1H), 4.26 (dd, *J* = 8.0 Hz, *J* = 3.0 Hz, 1H), 4.20 – 4.07 (m, 2H), 3.98 (dd, *J* = 8.0 Hz, *J* = 4.6 Hz, 1H), 1.76 – 1.65 (m, 4H), 1.62 – 1.53 (m, 12H), 1.42 – 1.31 (m, 4H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (1C cannot be unambiguously assigned): 163.8, 129.0, 126.2, 124.9, 124.1, 113.0, 110.0, 104.7, 83.0, 80.1, 77.0, 72.2, 67.2, 36.5, 36.4, 35.7, 34.6, 25.1, 24.8, 24.0, 23.8, 23.7, 23.5.

IR (ATR, cm^{-1}): 2936, 2088, 1709, 1449, 1366, 1245, 1117, 1024.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{33}N_2O_7$ 485.2282; Found 485.2282.

(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-diazo-2-phenylacetate (**1i**)



General Procedure B is employed with phenylacetic acid (2.6 g, 20 mmol, 1 equiv.), 5α-cholestan-3β-ol (9.33 g, 24 mmol, 1.2 equiv.), DCM (40 mL), DCC (5.35 g, 26 mmol, 1.3 equiv.) and DMAP (244 mg, 2 mmol, 0.1 equiv.) DCM in (10 mL) Purification by flash column chromatography (SiO_2, gradient: 99:1 Hex:AcOEt – 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords the corresponding ester as a colorless oil: 6.89 g, 68%.

Then, **General Procedure D** is employed with (3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-phenylacetate (1.26 g, 2.5 mmol, 1.0 equiv.), MeCN (10 mL), *p*-TsN_3 (591 mg, 3 mmol, 1.2 equiv.) and DBU (485 µL, 3.25 mmol, 1.3 equiv.). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords the title compound as a yellow solid: 546 mg, 41% yield.

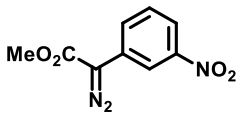
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 – 7.47 (m, 2H), 7.39 - 7.36 (m, 2H), 7.18 – 7.17 (m, 1H), 4.92 – 4.85 (m, 1H), 1.97 (dt, *J* = 12.4 Hz, *J* = 3.2 Hz, 1H), 1.94 – 1.89 (m, 1H), 1.86 – 1.79 (m, 1H), 1.76 (dt, *J* = 6.9 Hz, *J* = 3.2 Hz, 1H), 1.71 – 1.64 (m, 2H), 1.59 – 1.50 (m, 4H), 1.46 – 1.40 (m, 1H), 1.39 – 1.18 (m, 10H), 1.17 – 0.94 (m, 10H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 2.2 Hz, 3H), 0.86 (d, *J* = 2.2 Hz, 3H), 0.84 (s, 3H), 0.65 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) (1C cannot be unambiguously assigned) δ: 164.8, 128.9, 125.8, 125.6, 124.0, 74.7, 63.4, 56.4, 56.3, 54.2, 44.7, 42.6, 40.0, 39.5, 36.8, 36.2, 35.8, 35.5, 34.3, 32.0, 28.6, 28.2, 28.0, 27.8, 24.2, 23.8, 22.8, 22.6, 21.2, 18.7, 12.3, 12.1.

IR (ATR, cm^{-1}): 2937, 2860, 2089, 1711, 1501, 1462, 1247, 1152, 1097, 1028.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{35}H_{53}N_2O_2$ 533.4102; Found: 533.4212.

methyl 2-diazo-2-(3-nitrophenyl)acetate (**1o**)



General Procedure A is employed with 2-(3-nitrophenyl)acetic acid (1.81 g, 10 mmol, 1 equiv.), K_2CO_3 (1.5 g, 11 mmol), MeI (1.25 mL, 20 mmol) and acetone (32 mL) to afford methyl 2-(3-nitrophenyl)acetate as a yellow oil: 1.85 g, 95%.

Next, **General procedure D** is employed with the previously prepared ester (1.85 g, 9.5 mmol, 1 equiv.), *p*-TsN_3 (2.8 g, 14.2 mmol, 1.5 equiv.), DBU (2.12 mL, 14.2 mmol, 1.5 equiv.) and MeCN (20 mL). Purification by flash column chromatography (SiO_2, gradient: Hex - 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords the title compound as an orange solid: 1.7 g, 82%.

^{1}H (500 MHz, $CDCl_3$) δ: 8.37 – 8.35 (m, 1H), 8.01 (ddd, *J* = 8.2 Hz, *J* = 2.2 Hz, *J* = 0.8 Hz, 1H), 7.84 (ddd, *J* = 8.0 Hz, *J* = 1.8 Hz, *J* = 0.9 Hz, 1H), 7.58 – 7.51 (m, 1H), 3.91 (s, 3H).

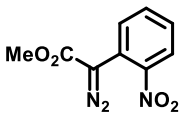
^{13}C (125 MHz, $CDCl_3$) (1C cannot be unambiguously assigned) δ: 164.6, 148.8, 129.8, 129.0, 128.4, 120.3, 118.2, 52.3.

M.P.: 54 - 56°C.

IR (ATR, cm^{-1}): 3115, 2957, 2101, 1698, 1531, 1442, 1353, 1246.

HRMS (ESI-Orbitrap) m/z: $[M - N_2 + H]^+$ Calcd. for $C_9H_8NO_4$ 194.0448; Found: 194.0449.

methyl 2-(2-nitophenyl)-2-diazoacetate (**1p**)



General Procedure A is employed with 2-(2-nitrophenyl)acetic acid (1.7 g, 10 mmol), K_2CO_3 (1.5 g, 11 mmol), MeI (1.25 mL, 20 mmol) and acetone (32 mL) to afford methyl 2-(2-nitrophenyl)acetate as a yellow oil: 1.68 g, 86%.

Then, **General Procedure D** is employed with methyl 2-(2-nitrophenyl)acetate (1.38 g, 7.5 mmol), *p*-TsN_3 (2.22 g, 11.2 mmol), DBU (1.7 mL, 11.3 mmol) and MeCN (7.5 mL). Purification by flash column chromatography (SiO_2, gradient: Hex - 95:5 Hex:AcOEt - 9:1 Hex:AcOEt – 8:2 Hex: AcOEt) affords the title compound as a yellow solid: 1.29 g, 61%.

^{1}H (250 MHz, $CDCl_3$) δ: 8.05 (dd, *J* = 8.3 Hz, *J* = 1.5 Hz, 1H), 7.68 - 7.62 (m, 1H), 7.57 - 7.44 (m, 2H), 3.82 (s, 3H).

^{13}C (250 MHz, $CDCl_3$) (1C cannot be unambiguously assigned) δ: 165.1, 147.2, 133.2, 131.1, 128.9, 125.6, 121.0, 52.5.

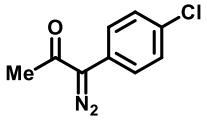
IR (ATR, cm^{-1}): 2099, 1703, 1606, 1574, 1528, 1486, 1436, 1358, 1293, 1252, 1196, 1163, 1030.

M.P.: 75 - 77°C.

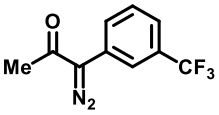
HRMS (ESI-Orbitrap) m/z: $[M - N_2 + H]^+$ Calcd. for $C_9H_8NO_4$ 194.0448; Found 194.0449.

1.2. α-Diazo Ketones 1v – 1y

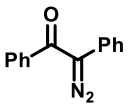
The following α-diazo ketones have been prepared as previously described in the literature, being numbered following their order of appearance in the manuscript: 1-(4-chlorophenyl)-1-diazopropan-2-one (**1v**),[7] 1-diazo-1-(3-(trifluoromethyl)phenyl)propan-2-one (**1w**),[7] *2-diazo-1,2-diphenylethan-1-one* (**1x**),[1] 2-diazo-1-(4-methoxyphenyl)-2-phenylethan-1-one (**1y**).[8,9]



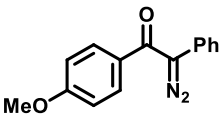
1v



1w



1x



1y

1.3. α-Diazo Amides 1z – 1ii and 1rr

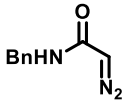
α-Diazo amides **1z** – **1ii** and **1rr** are numbered following their order of appearance in the manuscript: The following diazo amides have been prepared as previously reported in the literature:

[7] Wang, Y.; Bartlett, M. J.; Denard, C. A.; Hartwig, J. F.; Zhao, H.; *ACS Catal.* **2017**, *7*, 2548-2552.

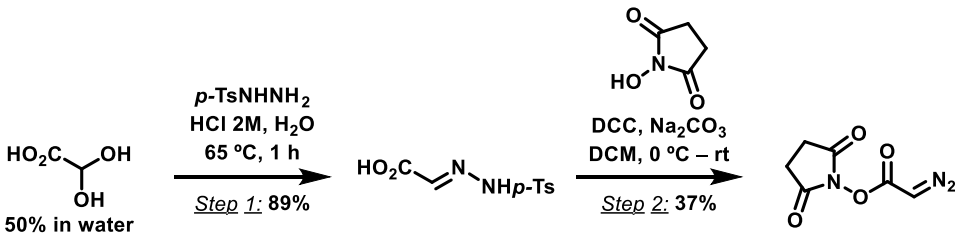
[8] For the synthesis of the ketone precursor via an acylation procedure, see: Gupton, J. T.; Shimozono, A.; Crawford, E.; Ortolani, J.; Clark, E.; Mahoney, M.; Heese, C.; Noble, J.; Mandry, C. P.; Kanters, R.; Dominey, R. N.; Goldman, E. W.; Sikorski, J. A. Fisher, D. C.; *Tetrahedron* **2018**, *74*, 2650-2663.

[9] For spectroscopic data of diazo compound, see: Xu, B.; Zhu, S.-F.; Zuo, X.-D.; Zhang, Z.-C.; Zhou, Q.-L.; *Angew. Chem. Int. Ed.* **2014**, *53*, 3913-3916.

N-benzyl-2-diazoacetamide[10] (**1z**).



1z



pre-1z

Step 1:[11] At room temperature, a round bottom flask is charged with *p*-toluenesulfonylhydrazide (2.79 g, 15 mmol, 1 equiv.), distilled water (15 mL), HCl 2M (24 mL). The reaction is allowed to stir at 65 ºC until total solubilization of the *p*-toluenesulfonylhydrazide. Then, glyoxylic acid 50% in water (3.3 mL, 30 mmol, 2 equiv.) is added and the reaction is stirred at 65 ºC for 1h. The reaction mixture is allowed to cool down to room temperature and then it is moved to the refrigerator and kept there for 1h to induce precipitation. The obtained solid is collected by vacuum filtration, washed with cold water (30 mL), then washed with DCM (to remove any trace of p-toluenesulfonylhydrazide) and dried under vacuum to afford 2-(2-tosylhydrazono)acetic acid as a white solid: 3.24 g, 13.4 mmol, 89%.

^{1}H NMR (250 MHz, $CDCl_3$) δ:[11] 8.79 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.16 (s, 1H), 2.46 (s, 3H).

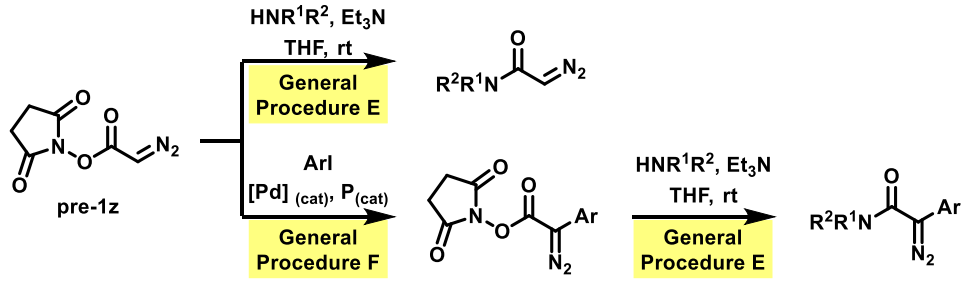
Step 2:[11] Next, at room temperature, a round bottom flask is charged with the previously prepared hydrazone (3.24 g, 13.4 mmol, 1 equiv), *N*-

[10] Adapted procedure from: Gupta, A. K.; Yin, X.; Mukherjee, M.; Desai, A. A.; Mohammadlou, A.; Jurewicz, K.; Wulff, W. D.; *Angew. Chem., Int. Ed.* **2019**, *58*, 3361-3367.
[11] Adapted procedure from: Jun, J. V.; Raines, R. T.; *Org. Lett.* **2021**, *23*, 3110-3114.

hydroxysuccinimide (1.7 g, 14.7 mmol, 1.1 equiv) and anhydrous DCM (40 mL). The resulting reaction mixture is cooled to 0 °C. Then, *N*,*N*'-dicyclohexylcarbodiimide (DCC) (3.0 g, 14.7 mmol, 1.1 equiv) is added; and the reaction mixture is stirred at 0 °C for 1 h. Then, at this temperature, Na_2CO_3 (1.6 g, 14.7 mmol, 1.1 equiv) is added and the reaction mixture is allowed to warm up to room temperature and is stirred at this temperature overnight. At this moment, the reaction is moved to the refrigerator and kept there for 1h to induce precipitation. The resulting solid (urea by-product, DCU) is filtered off and the collected solution is concentrated under reduced pressure. The reaction mixture is extracted with AcOEt (3x) and washed with a saturated aqueous solution of $NaHCO_3$ (3x), brine (1x). Then, organic layer is dried ($MgSO_4$), and filtered. The solvent is removed under reduced pressure and the resulting residue is purified by flash column chromatography (SiO_2 6:3:1 Hex:AcOEt:DCM) to afford 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** as a pale yellow crystalline solid: 907 mg, 37%.

^{1}H NMR (500 MHz, $CDCl_3$) δ:[12] 5.12 (br s, 1H), 2.83 (s, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) (1C cannot be unambiguously assigned) δ: 169.3, 45.1, 25.5.



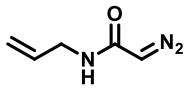
General Procedure E:[11] A round bottom flask is charged with 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** (1 equiv.) and THF (0.1M). Then, **R^1R^2NH** (or **$R^1R^2NH.HCl$**) (2 - 5 equiv) is added; accompanied by the eventual simultaneous addition of Et_3N (2 - 5 equiv.) in THF (0.1 M) in one portion. The

[12] Spectroscopic data is in good agreement with reported literature. See: Mukherjee, M.; Gupta, A. K.; Lu, Z.; Zhang, Y.; Wulff, W. D.*; J. Org. Chem.* **2010**, *75*, 5643-5660.

resulting reaction mixture is stirred at room temperature. Upon reaction completion (TLC), the solvent is removed under reduced pressure. Purification by flash column chromatography affords the corresponding α-diazo amide.

General Procedure F:[11] Under nitrogen, at room temperature, a round bottom flask is charged with aryl iodide (1.5 equiv.), tri(furan-2-yl)phosphane (10 mol%), $Pd(OAc)_2$ (5 mol%) and Ag_2CO_3 (0.7 equiv.). The resulting mixture is then evacuated and backfilled with N_2. In the sequence, a solution of 2,5-dioxopyrrolidin-1-yl 2-diazoacetate (1 equiv) and Et_3N (1.5 equiv) in dry EtOAc (0.05M in relation to diazoacetate) is added in one portion. The reaction mixture is stirred at room temperature for 16 h under N_2. The progress of the reaction is monitored by TLC. Upon completion, the reaction mixture is filtered through a Celite pad, while being washed with AcOEt. The filtrate is concentrated under reduced pressure and purified by silica gel chromatography to afford the targeted aryldiazoester in the stated yield.

N-allyl-2-diazoacetamide (**1aa**)[13]



General Procedure E is employed with 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** (92 mg, 0.5 mmol, 1 equiv.), allylamine (75 μL, 1 mmol, 2 equiv.) and THF (5 mL, 0.1M). Purification by flash column chromatography (SiO_2, 6:3:1 Hex:AcOEt:DCM) affords the title compound as an yellow oil: 61 mg, 98%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 5.88 – 5.77 (m, 1H), 5.75 (br s, 1H), 5.22 – 5.10 (m, 2H), 4.83 (s, 1H), 3.91 – 3.86 (m, 2H).

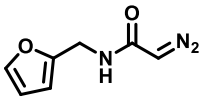
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 165.7, 134.3, 116.3, 47.0, 42.3.

IR (ATR, cm^{-1}): 3921, 2100, 1724, 1617, 1379, 1239.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_5H_8N_3O$ 126.0662; Found 126.0664.

[13] NMR data only reported in d_6-acetone: Chow, S.; Green, A. I.; Liver, S.; Arter, C.; Leggott, A.; Trask, L.; Karageorgis, G.; Warriner, S.; Nelson, A. *Synthesis* **2020**, *52*, 1695-1706.

2-diazo-N-(furan-2-ylmethyl)acetamide (**1bb**)



General Procedure E is employed with 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** (93 mg, 0.5 mmol, 1 equiv.), furfuryl amine (88 μL, 1 mmol, 2 equiv.) and THF (5 mL, 0.1M). Purification by flash column chromatography (SiO_2, 5.5:4.5:0.5 Hex:AcOEt:DCM) affords the title compound as an yellow oil: 55 mg, 66%.

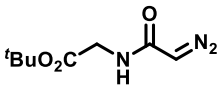
^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.33 (d, *J* = 1.0 Hz, 1H), 6.30 (dd, *J* = 3.2 Hz, *J* = 1.8 Hz, 1H), 6.21 (d, *J* = 3.2 Hz, 1H), 5.71 (br s, 1H), 4.79 (s, 1H), 4.44 (d, *J* = 5.7 Hz, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 165.7, 151.4, 142.1, 110.4, 107.3, 47.1, 36.7.

IR (ATR, cm^{-1}): 2100, 1616, 1551, 1381, 1244.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_7H_8N_3O_2$ 166.0611; Found 166.0611.

tert-butyl (2-diazoacetyl)glycinate (**1cc**)



General Procedure E is employed with 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** (92 mg, 0.5 mmol, 1 equiv.), *tert*-butyl glycinate hydrochloride (168 mg, 1 mmol, 2 equiv.), Et_3N (557 μL, 4 mmol, 4 equiv.) and THF (5 mL, 0.1M). 16h, rt. Purification by flash column chromatography (SiO_2, 6:3:1 Hex:AcOEt:DCM) affords the title compound as an yellow oil: 49 mg, 45% (isolated with the starting ester as a minor impurity).

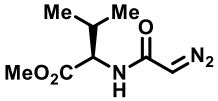
^{1}H NMR (250 MHz, $CDCl_3$) δ: 5.75 (br s, 1H), 4.83 (s, 1H), 3.97 (d, *J* = 5.2 Hz, 2H), 1.46 (s, 9H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 169.4, 165.6, 82.4, 47.3, 42.3, 28.0.

IR (ATR, cm^{-1}): 3264, 2982, 2099, 1731, 1609, 1397, 1245.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_8H_{14}N_3O_3$ 200.1030; Found 200.1031.

methyl (2-diazoacetyl)valinate (**1dd**)



General Procedure E is employed with 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** (92 mg, 0.5 mmol, 1 equiv.), methyl L-valinate hydrochloride (334 mg, 1 mmol, 4 equiv.), Et_3N (557 μL, 4 mmol, 4 equiv.) and THF (5 mL, 0.1M). Purification by flash column chromatography (SiO_2, 6:3:1 Hex:EtOAc:DCM) affords the title compound as an yellow oil: 61 mg, 57%.

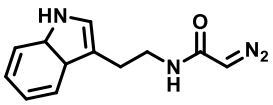
^{1}H NMR (250 MHz, $CDCl_3$) δ: 5.77 (br s, 1H), 4.84 (s, 1H), 4.64 – 4.59 (m, 1H), 3.73 (s, 3H), 2.18 – 2.08 (m, 1H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 173.0, 165.6, 57.3, 52.2, 47.4, 31.4, 18.9, 17.7.

IR (ATR, cm^{-1}): 3286, 2964, 2103, 1742, 1538, 1382, 1207.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_8H_{14}N_3O_3$ 200.1030; Found 200.1030.

2-diazo-N-(2-(3a,7a-dihydro-1H-indol-3-yl)ethyl)acetamide (**1ee**)



General Procedure E is employed with 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** (92 mg, 0.5 mmol, 1 equiv.) and tryptamine (160 mg, 1 mmol, 2 equiv.) and THF (5 mL, 0.1M). Purification by flash column chromatography (SiO_2, 98:2 DCM:MeOH) affords the title compound as an yellow solid: 105 mg, 92%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.20 (br s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.10 (m, 2H), 7.02 (d, *J* = 2.0 Hz, 1H), 5.18 (br s, 1H), 4.60 (s, 1H), 3.64 – 3.62 (m, 2H), 2.98 (t, *J* = 6.8 Hz, 2H).

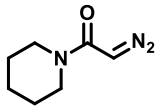
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 165.4, 136.4, 127.3, 122.2, 122.1, 119.5, 118.7, 112.8, 111.3, 47.1, 40.2, 25.6.

M.P.: 115 – 117 °C.

IR (ATR, cm^{-1}): 3405, 2917, 2104, 1609, 1365, 1094.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{12}H_{15}N_4O$ 231.1240; Found 231.1231.

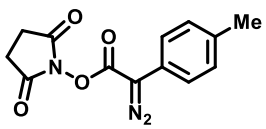
2-diazo-1-(piperidin-1-yl)ethan-1-one (**1ff**)[14]



General Procedure E is employed with 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** (92 mg, 0.5 mmol, 1 equiv.), piperidine (99 μL, 1 mmol, 2 equiv.) and THF (5 mL, 0.1M). Purification by flash column chromatography (SiO_2, 6:3:1 Hex:AcOEt:DCM) affords the title compound as an yellow oil: 68 mg, 89%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 5.01 (s, 1H), 3.31 (app s, 4H), 1.64 – 1.46 (m, 6H).
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 164.2, 46.1, 44.9, 25.7, 24.3.
IR (ATR, cm^{-1}): 2939, 2855, 2098, 1597, 1433, 1224, 1018.
HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_7H_{12}N_3O$ 154.0975; Found 154.0975.

2,5-dioxopyrrolidin-1-yl 2-diazo-2-(p-tolyl)acetate (**pre-1gg**)[11]

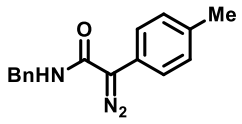


General Procedure F is employed with 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** (183 mg, 1 mmol, 1 equiv.), 1-iodo-4-methylbenzene (327 mg, 1.5 mmol, 1.5 equiv.), tri(furan-2-yl)phosphane (23 mg, 0.1 mmol, 10 mol%), $Pd(OAc)_2$ (11 mg, 0.05 mmol, 5 mol%), Ag_2CO_3 (189 mg, 0.7 mmol, 0.7 equiv.), Et_3N (210 μL, 1.5 mmol, 1.5 equiv) and dry EtOAc (20 mL, 0.05M). Purification by flash column chromatography (SiO_2, 95.5:4:0.5 Hex:AcOEt:DCM) affords the title compound as yellow oil: 84 mg, 51%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 2.86 (s, 4H), 2.34 (m, 3H).
^{13}C NMR (62.5 MHz, $CDCl_3$) (1C cannot be unambiguously assigned) δ: 169.3, 160.5, 137.1, 129.9, 124.6, 119.8, 25.5, 21.0.

[14] Spectroscopic data is in good agreement with the literature. See: Döben, N.; Yan, H.; Kischkewitz, M.; Mao, J.; Studer, A.; *Org. Lett.* **2018**, *20*, 7933-7936.

N-benzyl-2-diazo-2-(p-tolyl)acetamide (**1gg**)[15]

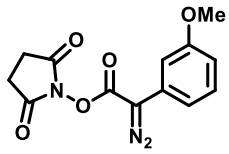


General Procedure E is employed with diazo compound **pre-1kk** (82 mg, 0.3 mmol, 1 equiv.), Et_3N (210 μL, 1.5 mmol, 5 equiv.) and dry THF (3 mL, 0.1M), followed by the addition of benzylamine (164 μL, 1.5 mmol, 5 equiv.) and Et_3N (210 μL, 1.5 mmol, 5 equiv.) in THF (3 mL, 0.1M, in relation to diazo compound **pre-1kk**). Purification by flash column chromatography (SiO_2, 8:2 Hex:AcOEt) affords the title compound as a yellow oil: 46 mg, 58%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.39 – 7.28 (m, 9H), 5.76 (br s,1H), 4.56 (d, *J* = 5.8 Hz, 2H), 2.37 (s, 3H).

^{13}C NMR (62.5 MHz, $CDCl_3$) (1C cannot be unambiguously assigned) δ: 165.0, 138.4, 138.0, 130.4, 128.7, 127.8, 127.6, 127.4, 122.9, 44.0, 21.1.

2,5-dioxopyrrolidin-1-yl 2-diazo-2-(3-methoxyphenyl)acetate (**pre-1hh**)[11]



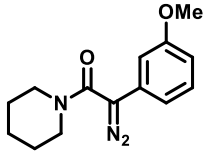
General Procedure F is employed with 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** (183 mg, 1 mmol, 1 equiv.), 1-iodo-3-methoxybenzene (179 μL, 1.5 mmol, 1.5 equiv.), tri(furan-2-yl)phosphane (23 mg, 0.1 mmol, 10 mol%), $Pd(OAc)_2$ (11 mg, 0.05 mmol, 5 mol%), Ag_2CO_3 (189 mg, 0.7 mmol, 0.7 equiv.), Et_3N (210 μL, 1.5 mmol, 1.5 equiv) and dry AcOEt (20 mL, 0.05M). Purification by flash column chromatography (SiO_2, gradient: Hex – 96:3:1 Hex:AcOEt:DCM – 5:4:1 Hex:AcOEt:DCM) affords the title compound as an yellow oil: 260 mg, 90%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.31 (t, *J* = 8.0 Hz, 1H), 7.07 – 7.05 (m, 1H), 6.94 (ddd, *J* = 8.1 Hz, *J* = 1.8 Hz, *J* = 0.7 Hz, 1H), 6.78 (ddd, *J* = 8.1 Hz, *J* = 2.4 Hz, *J* = 0.7 Hz, 1H), 3.80 (s, 3H), 2.86 (s, 4H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 169.3, 160.1 (x2), 130.1, 124.6, 116.3, 112.6, 110.0, 61.6, 55.3, 25.5.

[15] Mix, K. A.; Raines, R. T.; *Org. Lett.* **2015**, *17*, 2358-2361.

2-diazo-2-(3-methoxyphenyl)-1-(piperidin-1-yl)ethan-1-one (**1hh**)



General Procedure E is employed with diazo compound **pre-1hh** (87 mg, 0.3 mmol, 1 equiv.), Et_3N (210 μL, 1.5 mmol, 5 equiv.) and dry THF (3 mL, 0.1M), followed by the addition of piperidine (148 μL, 1.5 mmol, 5 equiv.) and Et_3N (210 μL, 1.5 mmol, 5 equiv.) in THF (3 mL, 0.1M, in relation to diazo compound **pre-1hh**). Purification by flash column chromatography (SiO_2, Hex - 96.5:3.5:0.5 Hex:AcOEt:DCM) affords the title compound as an yellow oil: 24 mg, 30%.

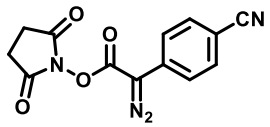
^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.27 (t, *J* = 8.3 Hz, 1H), 6.78 – 6.75 (m, 2H), 6.72 – 6.68 (m, 1H), 3.80 (s, 3H), 3.42 – 3.38 (m, 4H), 1.65 – 1.55 (m, 6H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 164.9, 160.2, 130.0, 129.5, 116.6, 111.1, 109.9, 63.0, 55.3, 46.6, 25.8, 24.5.

IR (ATR, cm^{-1}): 2937, 2854, 2060, 1627, 1415, 1264, 1037.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{18}N_3O_2$ 260.1394; Found 260.1394.

2,5-dioxopyrrolidin-1-yl 2-(4-cyanophenyl)-2-diazoacetate (**pre-1ii**)



General Procedure F is employed with 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** (183 mg, 1 mmol, 1 equiv.), 4-iodobenzonitrile (229 mg, 1.5 mmol, 1.5 equiv.), tri(furan-2-yl)phosphane (23 mg, 0.1 mmol, 10 mol%), $Pd(OAc)_2$ (11 mg, 0.05 mmol, 5 mol%), Ag_2CO_3 (189 mg, 0.7 mmol, 0.7 equiv.), Et_3N (210 μL, 1.5 mmol, 1.5 equiv) and dry AcOEt (20 mL, 0.05M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95.5:4.5 Hex:AcOEt - 4:6 Hex:AcOEt) affords the title compound as an yellow oil: 160 mg, 56%.

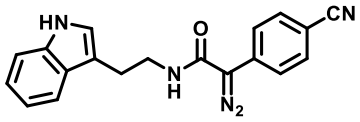
^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 2.89 (s, 4H).

^{13}C NMR (62.5 MHz, $CDCl_3$) (1C cannot be unambiguously assigned) δ: 169.0, 159.2, 132.8, 129.2, 123.7, 118.3, 110.0, 25.5.

IR (ATR, cm^{-1}): 2916, 2228, 2111, 1737, 1511, 1201, 1072.

HRMS (ESI-Orbitrap) m/z: [M - N_2+ H]$^+$ Calcd. for $C_{13}H_9N_2O_4$ 257.0557; Found 257.0555.

2-(4-cyanophenyl)-2-diazo-N-(2-(3a,7a-dihydro-1H-indol-3-yl)ethyl)acetamide (**1ii**)



General Procedure E is employed with diazo compound **pre-1ii** (85 mg, 0.3 mmol, 1 equiv.), Et_3N (210 μL, 1.5 mmol, 5 equiv.) and dry THF (3 mL, 0.1M), followed by the addition of tryptamine (240 mg, 1.5 mmol, 5 equiv.) in THF (3 mL, 0.1M, in relation to diazo compound **pre-1ii**). Purification by flash column chromatography (SiO_2, 8:2 Hex:AcOEt) affords the title compound as an yellow oil: 46 mg, 58%.

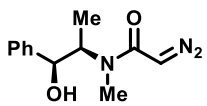
^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.15 (br s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.23 (m, 3H), 7.18 – 7.12 (m, 1H), 7.08 (d, *J* = 2.3 Hz, 1H), 5.53 (t, *J* = 5.0 Hz, 1H), 3.81 – 3.73 (m, 2H), 3.09 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) (2C cannot be unambiguously assigned) δ: 162.7, 136.4, 132.8, 132.2, 127.2, 125.2, 122.5, 122.1, 119.8, 118.6, 112.6, 111.4, 109.2, 40.6, 25.1.

IR (ATR, cm^{-1}): 2925, 2853, 2067, 1636, 1507, 1262, 1096, 1018.

HRMS (ESI-Orbitrap) m/z: [M + H]$^+$ Calcd. for $C_{19}H_{16}N_5O$ 330.1349; Found 330.1349.

2-diazo-N-(1-hydroxy-1-phenylpropan-2-yl)-N-methylacetamide (**1rr**)



General Procedure E is employed with 2,5-dioxopyrrolidin-1-yl 2-diazoacetate **pre-1z** (92 mg, 0.5 mmol, 1 equiv.) and (*1S,2R*)-(+)-ephedrine hemihydrate (174 mg, 1 mmol, 2 equiv.), Et_3N (557 μL, 4 mmol, 4 equiv.) and THF (5 mL, 0.1M). Purification by flash column chromatography (SiO_2, 5:4:1 Hex:AcOEt:DCM) affords the title compound as an yellow oil: 98 mg, 84%.

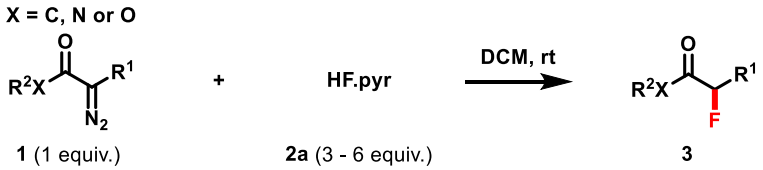
^{1}H NMR (250 MHz, $CDCl_3$) (1H cannot be unambiguously assigned) δ: 7.34 – 7.24 (m, 5H), 4.89 (s, 1H), 4.79 (br s, 1H), 4.46 (br s, 1H), 2.57 (app s, 3H), 1.18 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (62.5 MHz, $CDCl_3$) (1C cannot be unambiguously assigned) δ: 167.4, 141.6, 128.1, 127.4, 126.2, 57.9, 46.9, 32.0, 12.3.

IR (ATR, cm^{-1}): 3364, 2927, 2005, 1590, 1407, 1172.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{12}H_{16}N_3O_2$ 234.1237; Found 234.1236.

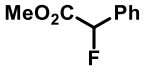
1.4 α-Fluorinated Carbonyl Compounds 3a – 3ii



1 (1 equiv.) **2a** (3 - 6 equiv.) **3**

General Procedure G: Under air, a plastic vessel (an Eppendorf for ~0.1 mmol scale; or a falcon tube for ~0.2 mmol or higher scale) is added the α-diazo carbonyl compound **1** (1 equiv.) and DCM (0.1M). Then, at 0 ºC or rt, the Olah's reagent HF.pyr **2a**, (3 - 6 equiv., 70% HF/ 30% pyridine) is carefully added. The reaction mixture is typically stirred for 1h at room temperature. Upon reaction completion (TLC), silica (SiO_2, 20 mg/ 0.1 mmol of the diazo compound **1**) is added. The resulting mixture is filtrated using a pipette while washing with DCM. Then, the solvent is removed under reduced pressure. Purification by flash column chromatography affords the target α-fluorinated carbonyl compound **3** in the stated yield.

methyl 2-fluoro-2-phenylacetate (**3a**)[16]

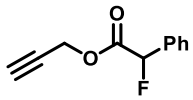


General Procedure G is employed with methyl 2-diazo-2-phenylacetate **1a** (18 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration using SiO_2 affords the title compound as transparent oil: 17 mg, 99%.

This reaction has been also carried out in a preparative scale using methyl 2-diazo-2-phenylacetate **1a** (528 mg, 3 mmol, 1 equiv.), HF·pyr **2a** (480 μL, 18 mmol, 6 equiv.) and DCM (25 mL). Filtration using SiO_2 affords the title compound as transparent oil: 428 mg, 85%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.45 – 7.40 (m, 5H), 5.80 (d, *J* = 48.2 Hz, 1H), 3.78 (s, 3H).
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 169.0 (d, *J* = 27.5 Hz), 134.1 (d, *J* = 20.0 Hz), 129.6 (d, *J* = 2.5 Hz), 128.8, 126.6 (d, *J* = 6.9 Hz), 89.4 (d, *J* = 184.4 Hz), 52.6 (d, *J* = 1.3 Hz).
^{19}F (235 MHz, $CDCl_3$) δ: -179.91 (d, *J* = 47.8 Hz).

prop-2-yn-1-yl 2-fluoro-2-phenylacetate (**3b**)



General Procedure G is employed with methyl 2-diazo-2-(4-fluorophenyl)acetate **1b** (19 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration using SiO_2 affords the title compound as transparent oil: 19 mg, 99%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.50 – 7.40 (m, 5H), 5.83 (d, *J* = 47.4 Hz, 1H), 4.82 (dd, *J* = 15.4 Hz, *J* = 2.4 Hz, 1H) 4.72 (dd, *J* = 15.4 Hz, *J* = 2.4 Hz, 1H), 2.49 (t, *J* = 2.4Hz, 1H).

[16] Spectroscopic data is in good agreement with reported literature. See: Gray, E. E.; Nielsen, M. K., Choquette, K. A.; Kalow, J. A.; Graham, T. J. A.; Diyle, A. G.; *J. Am. Chem. Soc.* **2016**, *138*, 10802-10805.

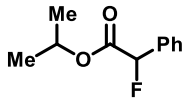
^{13}C NMR (62.5 MHz, $CDCl_3$) (1C cannot be unambiguously assigned) δ: 167.8 (d, *J* = 27.5 Hz), 133.7 (d, *J* = 20.6 Hz), 129.8 (d, *J* = 2.5 Hz), 128.9, 126.8 (d, *J* = 5.6 Hz), 89.2 (d, *J* = 185.0 Hz), 75.8, 53.1 (d, *J* = 1.3 Hz).

^{19}F (235 MHz, $CDCl_3$) δ: -179.62 (d, *J* = 47.2 Hz).

IR (ATR, cm^{-1}): 3298, 2924, 1770, 1457, 1182, 1058.

HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. for $C_{11}H_9O_2$ 173.0597; Found 173.0598.

isopropyl 2-fluoro-2-phenylacetate (**3c**)



General Procedure G is employed with isopropyl 2-diazo-2-phenylacetate **1c** (20 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration through SiO_2 affords the title compound as transparent oil: 18 mg, 92%

^{1}H NMR (250 MHz, $CDCl_3$) *δ*: 7.47-7.38 (m, 5H), 5.74 (d, *J* = 47.7 Hz, 1H), 5.12 (sept, *J* = 6.3 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.20 (d, *J* = 6.3 Hz, 3H).

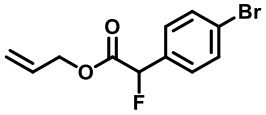
^{13}C NMR (62.5 MHz, $CDCl_3$) *δ*: 168.1 (d, *J* = 27.5 Hz), 134.4 (d, *J* = 20.0 Hz), 129.5 (d, *J* = 2.5 Hz), 128.7, 126.6 (d, *J* = 6.3 Hz), 89.4 (d, *J* = 184.4 Hz), 69.7, 21.7, 21.5.

^{19}F NMR (235 MHz, $CDCl_3$): - 179.76 (d, *J* = 47.7 Hz).

IR (ATR, cm^{-1}): 2983, 2937, 1754, 1737, 1218.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{11}H_{14}FO_2$ 197.0972; Found 192.0972.

allyl 2-(4-bromophenyl)-2-fluoroacetate (**3d**)



General Procedure G is employed with allyl 2-(4-bromophenyl)-2-diazoacetate **1d** (21 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex - 95:5 Hex:AcOEt) affords the title compound as transparent oil: 27 mg, 99%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.92 – 5.81 (m, 1H), 5.76 (d, *J* = 47.5 Hz, 1H), 5.30 – 5.22 (m, 2H), 4.74 – 4.60 (m, 2H).

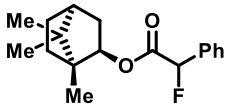
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 167.7 (d, *J* = 27.2 Hz), 133.1 (d, *J* = 21.0 Hz), 132.0, 130.9, 128.2 (d, *J* = 6.3 Hz), 123.9 (d, *J* = 2.7 Hz), 119.3, 88.6 (d, *J* = 187.8 Hz), 66.3.

^{19}F (235 MHz, $CDCl_3$) δ: −181.31 (d, *J* = 47.6 Hz).

IR (ATR, cm^{-1}): 2911, 1762, 1489, 1208, 1072.

HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. for $C_{11}H_{10}BrO_2$ 252.9859; Found 252.9858.

(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-fluoro-2-phenylacetate (**3e**)



General Procedure G is employed with (1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-diazo-2-phenylacetate **1e** (30 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration using SiO_2 affords the title compound as a transparent oil: 29 mg, 99%, 1:1 dr.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.47 – 7.40 (m, 5H), 5.80 (d, *J* = 47.7 Hz, 1H), 5.01 – 4.94 (m, 1H), 2.40 – 2.24 (m, 2H), 1.88 – 1.74 (m, 1H), 1.69 – 1.60 (m, 1H), 1.33 – 1.16 (m, 2H), 1.05 – 0.98 (m, 1H), 0.88 – 0.63 (m, 10H)

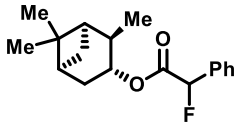
^{13}C NMR (62.5 MHz, $CDCl_3$) (5C cannot be unambiguously assigned) δ: 168.8 (d, *J* = 28.1 Hz), 168.7 (d, *J* = 27.5 Hz), 134.8 (d, *J* = 10.0 Hz), 134.4 (d, *J* = 10.6 Hz), 129.5 (d, *J* = 2.5 Hz), 129.4 (d, *J* = 2.5 Hz), 128.7, 126.5 (d, *J* = 6.9 Hz), 126.4 (d, *J* = 5.6 Hz), 89.4 (d, *J* = 184.4 Hz), 89.3 (d, *J* = 184.4 Hz), 81.6, 81.4, 49.0, 48.8, 47.9, 44.8, 44.7, 36.4, 27.9, 27.8, 27.0, 26.8, 19.6, 18.8, 13.4, 13.2.

^{19}F (235 MHz, $CDCl_3$) δ: −180.35 (d, *J* = 48.6 Hz), −181.30 (d, *J* = 49.3 Hz).

IR (ATR, cm^{-1}): 2957, 1759, 1455, 1251, 1060.

HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. for $C_{18}H_{23}O_2$ 271.1693; Found 271.1698.

(*1R,2R,3R,5S)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl 2-fluoro-2-phenylacetate* (**3f**)



General Procedure G is employed with (1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl2-diazo-2-phenylacetate **1f** (30 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration using SiO_2 affords the title compound as a transparent oil: 27 mg, 93%, 1:1 dr.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.48 – 7.40 (m, 5H), 5.78 (d, *J* = 47.7 Hz, 1H), 5.19 – 5.09 (m, 1H), 2.64 – 2.45 (m, 1H), 2.40 – 2.29 (m, 1H), 2.18 – 1.75 (m, 4H), 1.69 – 1.44 (m, 1H), 1.26 - 0.93 (m, 9H).

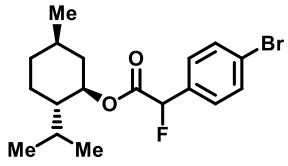
^{13}C NMR (62.5 MHz, $CDCl_3$) (4C cannot be unambiguously assigned) δ: 168.5 (d, *J* = 27.8 Hz), 168.4 (d, *J* = 27.5 Hz), 134.6 (d, *J* = 7.4 Hz), 134.3 (d, *J* = 7.3 Hz), 129.5, 128.7, 126.6 (d, *J* = 6.1 Hz), 126.5 (d, *J* = 6.0 Hz), 89.4 (d, *J* = 186.5 Hz, x2), 75.9, 75.8, 47.4, 47.3, 43.5, 41.1, 41.0, 38.2, 38.1, 35.5, 35.3, 33.4, 33.3, 27.4, 27.3, 23.7, 20.4, 20.3.

^{19}F (235 MHz, $CDCl_3$) δ: −179.97 (d, *J* = 49.1 Hz), −180.17 (d, *J* = 49.1 Hz).

IR (ATR, cm^{-1}): 2913, 1756, 1455, 1212, 1057.

HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. for $C_{18}H_{23}O_2$ 271.1693; Found 271.1692.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-(4-bromophenyl)-2-fluoroacetate (**3g**)



General Procedure G is employed with (2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 2-(4-bromophenyl)-2-diazoacetate **1g** (38 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration using SiO_2 affords the title compound as a transparent oil: 37 mg, 99%, 1.5:1 dr.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 5.72 (d, *J* = 47.9 Hz, 0.4H), 5.68 (d, *J* = 47.9 Hz, 0.6H), 4.83 – 4.66 (m, 1H), 2.04 – 1.95 (m, 0.6 H), 1.85 – 1.76 (m, 1H), 1.72 – 1.59 (m, 2.4 H), 1.54 – 1.25 (m,

3H), 1.12 – 0.94 (m, 2H), 0.91 – 0.85 (m, 4.2H), 0.74 – 0.70 (m, 3H), 0.53 (d, *J* = 7.0 Hz, 1.8 H).

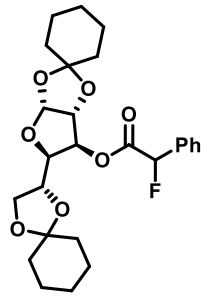
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 167.7 (d, *J* = 27.5 Hz), 167.6 (d, *J* = 26.9 Hz), 133.6 (d, *J* = 6.9 Hz), 133.3 (d, *J* = 6.9 Hz), 131.9, 131.8, 128.3 (d, *J* = 5.6 Hz), 128.1 (d, *J* = 6.3 Hz), 123.8 (d, *J* = 3.1 Hz), 123.7 (d, *J* = 1.9 Hz), 88.7 (d, *J* = 185.6 Hz), 88.6 (d, *J* = 185.6 Hz), 76.3 (x2), 46.9, 46.8, 40.6, 40.2, 34.0 (x2), 31.4, 31.3, 26.2, 25.8, 23.3, 23.1, 21.9 (x2), 20.6, 20.5, 16.2, 15.8.

^{19}F (235 MHz, $CDCl_3$) δ: −179.91 (d, *J* = 48.3 Hz), −181.08 (d, *J* = 45.8 Hz).

IR (ATR, cm^{-1}): 2957, 2871, 1756, 1488, 1214, 1072, 1012.

HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. for $C_{18}H_{24}BrO_2$ 351.0954; Found 351.0954.

(3a'R,5'R,6'S,6a'R)-5'-((R)-1,4-dioxaspiro[4.5]decan-2-yl)tetrahydrospiro [cyclohexane-1,2'-furo[2,3-d][1,3]dioxol]-6'-yl-2-fluoro-2-phenylacetate (**3h**)



General Procedure G is employed with (3a'*R*,5'*R*,6'*S*,6a'*R*)-5'-((*R*)-1,4-dioxaspiro[4.5]decan-2-yl)tetrahydrospiro[cyclohexane-1,2'-furo[2,3-*d*][1,3]dioxol]-6'-yl 2-diazo-2-phenylacetate **1h** (48 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration using SiO_2 affords the title compound as a transparent oil: 47 mg, 99%, 1:1 dr.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.48 – 7.38 (m, 5H), 5.91 – 5.87 (m, 1H), 5.72 – 5.69 (m, 1H), 5.45 – 5.42 (m, 1H), 4.37 (d, *J* = 55.8 Hz, 0.5 H), 4.36 (d, *J* = 55.8 Hz, 0.5H), 4.17 – 4.05 (m, 2H), 3.99 – 3.94 (m, 0.5H), 3.88 – 3.84 (m, 1H), 3.73 – 3.65 (m, 0.5H), 2.34 (t, *J* = 6.3 Hz, 0.5H), 1.91 – 1.81 (m, 1H), 1.73 – 1.63 (m, 5H), 1.53 – 1.34 (m, 13H), 0.89 - 0.83 (m, 0.5H).

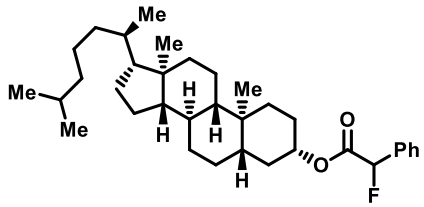
^{13}C NMR (62.5 MHz, $CDCl_3$) (2C cannot be unambiguously assigned) δ: 167.1 (d, *J* = 28.1 Hz), 166.9 (d, *J* = 27.5 Hz), 133.9 (d, *J* = 6.3 Hz), 133.6 (d, *J* = 6.3 Hz), 129.8 (x2), 128.8 (x2), 126.8 (d, *J* = 5.6 Hz), 126.6 (d, *J* = 5.6 Hz), 113.2 (x2), 110.0, 109.9, 104.8, 104.7, 89.2 (d, *J* = 185.0 Hz), 89.1 (d, *J* = 186.9 Hz), 82.7, 82.5, 80.2, 80.0, 77.2, 77.1, 72.0, 71.5, 67.2, 67.0, 42.0, 36.6, 36.5, 36.3 (x2), 35.6, 34.7, 34.5, 27.0, 25.1, 25.0, 24.8 (x2), 23.9 (x2), 23.8, 23.7, 23.5.

^{19}F (235 MHz, $CDCl_3$) δ: −178.63 (d, *J* = 46.8 Hz), −180.05 (d, *J* = 47.8 Hz).

IR (ATR, cm^{-1}): 2937, 2863, 1770, 1449, 1207, 1093.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{34}FO_7$ 477.2283; Found 477.2283.

(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-fluoro-2-phenylacetate (**3i**)



General Procedure G is employed with (3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-diazo-2-phenylacetate **1i** (53 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration using SiO_2 affords the title compound as a transparent oil: 52 mg, 99%, 1:1 dr.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.46 – 7.38 (m, 5H), 5.73 (d, *J* = 48.0 Hz, 1H), 4.87 – 4.74 (m, 1H), 1.98 – 1.42 (m, 12H), 1.39 – 0.96 (m, 17H), 0.91 – 0.85 (m, 9H), 0.80 (s, 3H), 0.68 – 0.55 (m, 5H).

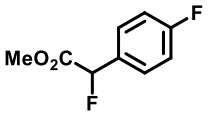
^{13}C NMR (62.5 MHz, $CDCl_3$) (28C cannot be unambiguously assigned) δ: 168.1 (d, *J* = 26.9 Hz), 134.5 (d, *J* = 20.7 Hz), 129.4 (d, *J* = 2.2 Hz), 128.7, 126.6 (d, *J* = 6.0 Hz), 89.4 (d, *J* = 185.8 Hz), 75.5, 63.4, 56.4, 56.2, 54.1, 44.6 (x2), 42.6, 39.9, 39.5, 36.6 (x2), 36.1, 35.8, 35.4 (x2), 33.8, 33.5, 31.9, 28.5 (x2), 28.2, 28.0, 27.3, 27.1, 24.2, 23.8, 22.5, 21.2, 18.6, 12.2, 12.0.

^{19}F (235 MHz, $CDCl_3$) δ: −179.27 (d, *J* = 41.1 Hz), −179.47 (d, *J* = 41.1 Hz).

IR (ATR, cm^{-1}): 2945, 2868, 1757, 1468, 1213, 1002.

HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. for $C_{35}H_{53}O_2$ 505.4040; Found: 505.4030

methyl 2-fluoro-2-(4-fluorophenyl)acetate (**3j**)[16]



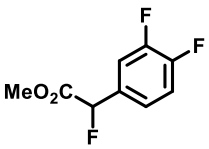
General Procedure G is employed with methyl 2-diazo-2-(4-fluorophenyl)acetate **1j** (19 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration using SiO_2 affords the title compound as transparent oil: 17 mg, 91%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.45 (dd, *J* = 8.2 Hz, *J* = 5.5 Hz, 2H), 7.10 (t, *J* = 8.2 Hz, 2H), 5.78 (d, *J* = 47.5 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 168.8 (d, *J* = 27.5 Hz), 163.4 (dd, *J* = 248.1 Hz, *J* = 2.5 Hz), 130.0 (dd, *J* = 20.6 Hz, *J* = 3.1 Hz), 128.7 (dd, *J* = 8.8 Hz, *J* = 6.3 Hz), 115.9 (d, *J* = 21.9 Hz), 88.7 (d, *J* = 185.0 Hz), 52.7 (d, *J* = 0.6 Hz).

^{19}F (235 MHz, $CDCl_3$) δ: −111.24 (app oct, *J* = 4.7 Hz), −178.49 (dd, *J* = 47.0 Hz, *J* = 2.4 Hz).

methyl 2-(3,4-difluorophenyl)-2-fluoroacetate (**3k**)



General Procedure G is employed with methyl 2-diazo-2-(3,4-difluorophenyl)acetate **1k** (21 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration through SiO_2 affords the title compound as transparent oil: 20 mg, 98%

^{1}H NMR (250 MHz, $CDCl_3$) *δ:* 7.35 - 7.27 (m, 1H), 7.26 - 7.18 (m, 2H), 5.75 (d, *J* = 47.5 Hz, 1H), 3.80 (s, 3H).

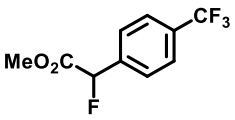
^{13}C NMR (62.5 MHz, $CDCl_3$) *δ:* 168.4 (d, *J* = 11.3 Hz), 151.1 (ddd, *J* = 251.9 Hz, *J* = 14.4 Hz, *J* = 1.9 Hz), 150.4 (dd, *J* = 250.6 Hz, *J* = 15.0 Hz), 131.0 (ddd, *J* = 21.3 Hz, *J* = 5.6 Hz, *J* = 3.8 Hz), 122.9 (td, *J* = 6.3 Hz, *J* = 3.8 Hz), 117.8 (dd, *J* = *J* = 16.9 Hz, *J* = 1.3 Hz), 115.9 (ddd, *J* = 18.1 Hz, *J* = 6.9 Hz, *J* = 1.9 Hz), 88.0 (dd, *J* = 186.3 Hz, *J* = 0.9 Hz), 52.9 (d, *J* = 0.6 Hz).

^{19}F NMR (235 MHz, $CDCl_3$) *δ*: -135.88 (dm), -180.82 (dd, *J* = 47.0 Hz, *J* = 4.7 Hz).

IR (ATR, cm^{-1}): 2963, 1763, 1521, 1439, 1281.

HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. for $C_9H_7F_2O_2$ 185.0409; Found 185.0409.

methyl 2-fluoro-2-(4-(trifluoromethyl)phenyl)acetate (**3l**)[16]



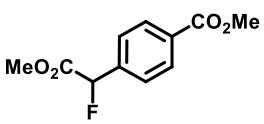
General Procedure G is employed with methyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate **1l** (49 mg, 0.2 mmol, 1 equiv.), HF·pyr **2a** (32 μL, 1.2 mmol, 6 equiv.) and DCM (2 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex - 95:5 Hex:AcOEt) affords the title compound as transparent oil: 42 mg, 89%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 5.86 (*d*, J = 47.5 Hz, 1H), 3.80 (s, 3H),

^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 168.2 (d, *J* = 26.3 Hz), 137.9 (dq, *J* = 20.6 Hz, J = 1.3 Hz), 131.7 (qd, *J* = 32.5 Hz, *J* = 1.3 Hz), 126.7 (d, *J* = 6.9 Hz), 125.8 (q, *J* = 3.1 Hz), 123.7(q, *J* = 270.6 Hz), 88.5 (d, *J* = 186.3 Hz), 52.9 (d, *J* = 1.3 Hz).

^{19}F (235 MHz, $CDCl_3$) δ: −62.89 (s), −184.31 (d, *J* = 47.0 Hz).

methyl 4-(1-fluoro-2-methoxy-2-oxoethyl)benzoate (**3m**)



General Procedure G is employed with methyl 4-(1-diazo-2-methoxy-2-oxoethyl)benzoate **1m** (48 mg, 0.2 mmol, 1.0 equiv.), HF·pyr **2a** (32 μL, 1.2 mmol, 6 equiv.) and DCM (2 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a yellow solid: 43 mg, 95%.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 5.86 (d, *J* = 47.3 Hz, 1H), 3.92 (s, 3H), 3.79 (s, 3H).

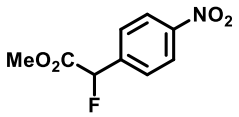
^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.3 (d, *J* = 27.5 Hz), 166.4, 138.7 (d, *J* = 21.3 Hz), 131.2, 130.0, 126.3 (d, *J* = 7.5 Hz), 88.7 (d, *J* = 186.3 Hz), 52.8, 52.3.

^{19}F NMR (235 MHz, $CDCl_3$) δ: -183.92 (d, *J* = 47.0 Hz).

IR (ATR, cm^{-1}): 3004, 2955, 1765, 1721, 1439, 1279, 1113.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{11}H_{12}FO_4$ 227.0714; Found 227.0715.

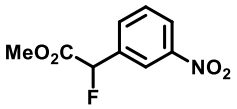
methyl 2-fluoro-2-(4-nitrophenyl)acetate (**3n**)[16]



General Procedure G is employed with methyl 2-diazo-2-(4-nitrophenyl)acetate **1n** (22 mg, 0.2 mmol, 1 equiv.), HF·pyr **2a** (32 μL, 1.2 mmol, 6 equiv.) and DCM (2 mL, 0.1M). Filtration using SiO_2 affords the title compound as a transparent oil: 42 mg, 99%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.28 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 5.92 (d, *J* = 47.5 Hz, 1H), 3.81 (s, 3H).
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 167.7 (d, *J* = 25.6 Hz), 148.6, 140.7 (d, *J* = 20.6 Hz), 127.1 (d, *J* = 6.9 Hz), 124.0, 88.1 (d, *J* = 188.1 Hz), 53.1.
^{19}F (235 MHz, $CDCl_3$) δ: −185.95 (d, *J* = 47.0 Hz).

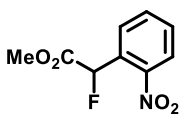
methyl 2-fluoro-2-(3-nitrophenyl)acetate (**3o**)[16]



General Procedure G is employed with methyl 2-diazo-2-(3-nitrophenyl)acetate **1o** (22 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration using SiO_2 affords the title compound as a transparent oil: 19 mg, 89%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.35 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 5.92 (d, *J* = 47.0 Hz, 1H), 3.82 (s, 3H).
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 167.8 (d, *J* = 26.3 Hz), 148.4, 136.1 (d, *J* = 21.9 Hz), 132.1 (d, *J* = 6.3 Hz), 129.9, 124.4 (d, *J* = 1.3 Hz), 121.5 (d, *J* = 6.9 Hz), 88.0 (d, *J* = 187.5 Hz), 53.1.
^{19}F (235 MHz, $CDCl_3$) δ: −184.40 (d, *J* = 47.0 Hz).

methyl 2-fluoro-2-(2-nitrophenyl)acetate (**3p**)[17]



General Procedure G is employed with methyl 2-diazo-2-(2-nitrophenyl)acetate **1p** (22 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration using SiO_2 affords the title compound as a transparent oil: 21 mg, 99%.

[17] Zhu, F.; Xu, P.-W.; Zhou, F.; Wang, C.-H.; Zhou, J.; *Org. Lett.* **2015**, *17*, 972-975.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.16 (d, *J* = 8.3 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.63 – 7.56 (m, 1H), 6.62 (d, *J* = 46.8 Hz, 1H), 3.79 (s, 3H).

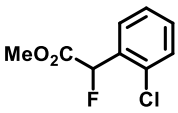
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 167.1 (d, *J* = 25.0 Hz), 146.8, 134.1 (d, *J* = 1.0 Hz), 130.3 (d, *J* = 21.0 Hz), 130.0, 127.7 (d, *J* = 14.0 Hz), 125.2, 86.5 (d, *J* = 183.0 Hz), 53.1.

^{19}F (235 MHz, $CDCl_3$) δ: −187.22 (d, *J* = 47.0 Hz).

IR (ATR, cm^{-1}): 2959, 2924, 1754, 1533, 1351, 1221, 1024.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_9H_9FNO_4$ 214.0510; Found 214.0510.

methyl 2-(2-chlorophenyl)-2-fluoroacetate (**3q**)



General Procedure G is employed with methyl 2-(2-chlorophenyl)-2-diazoacetate **1q** (21 mg, 0.2 mmol, 1 equiv.), HF·pyr **2a** (32 μL, 1.2 mmol, 6 equiv.) and DCM (2 mL, 0.1M). Filtration using SiO_2 affords the title compound as transparent oil: 40 mg, 99%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.52 – 7.47 (m, 1H), 7.45 – 7.38 (m, 1H), 7.36 - 7.30 (m, 2H), 6.24 (d, *J* = 46.5 Hz, 1H), 3.80 (s, 3H).

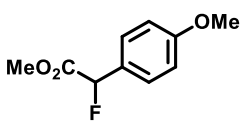
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 168.4 (d, *J* = 27.5 Hz), 133.5 (d, *J* = 4.4 Hz), 132.2 (d, *J* = 20.6 Hz), 131.0 (d, *J* = 1.9), 129.9, 128.7 (d, *J* = 5.6 Hz), 127.3, 86.2 (d, *J* = 183.1 Hz), 52.7 (d, *J* = 0.6 Hz).

^{19}F (235 MHz, $CDCl_3$) δ: −180.66 (d, *J* = 47.0 Hz).

IR (ATR, cm^{-1}): 2956, 1763, 1438, 1222, 1070.

HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. for $C_9H_8ClO_2$ 183.0207; Found 183.0207.

methyl 2-fluoro-2-(4-methoxyphenyl)acetate (**3r**)[16]

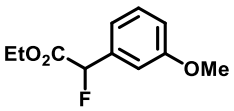


General Procedure G is employed with methyl 2-diazo-2-(4-dimethoxyphenyl)acetate **1r** (21 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M).

Purification by flash column chromatography (SiO_2, gradient: Hex - 95:5 Hex:AcOEt) affords the title compound as transparent oil: 13 mg, 66%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.38 (dd, *J* = 8.8 Hz, *J* = 1.5 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.74 (d, *J* = 47.8 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H).
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 169.2 (d, *J* = 28.1 Hz), 160.7 (d, *J* = 1.9 Hz), 128.5 (d, *J* = 5.6 Hz), 126.2 (d, *J* = 20.6 Hz), 114.2, 89.1 (d, *J* = 183.1 Hz), 55.3, 52.5 (d, *J* = 0.6 Hz).
^{19}F (235 MHz, $CDCl_3$) δ: −174.71 (d, *J* = 47.0 Hz).

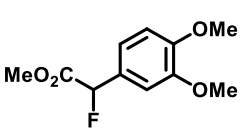
ethyl 2-fluoro-2-(3-methoxyphenyl)acetate (**3s**)[18]



General Procedure G is employed with ethyl 2-diazo-2-(3-methoxyphenyl)acetate **1s** (22 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Filtration using SiO_2 affords the title compound as a transparent oil: 21 mg, 99%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.32 (t, *J* = 7.8 Hz, 1H), 7.06 – 6.92 (m, 3H), 5.74 (d, *J* = 47.8 Hz, 1H), 4.35 – 4.14 (m, 2H), 3.82 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 168.4 (d, *J* = 27.5 Hz), 159.8, 135.6 (d, *J* = 20.6 Hz), 129.8, 118.9 (d, *J* = 6.3 Hz), 115.4 (d, *J* = 1.9 Hz), 111.7 (d, *J* = 6.3 Hz), 89.2 (d, *J* = 185.0 Hz), 61.8, 55.3, 14.0.
^{19}F (235 MHz, $CDCl_3$) δ: −180.25 (d, *J* = 49.4 Hz).
IR (ATR, cm^{-1}): 2926, 1759, 1603, 1491, 1265, 1044.
HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{11}H_{14}FO_3$ 213.0921; Found 213.0918.

methyl 2-(3,4-dimethoxyphenyl)-2-fluoroacetate (**3t**)



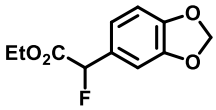
General Procedure G is employed with methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate **1t** (24 mg, 0.1 mmol, 1 equiv.),

[18] Xia, T.; He, L.; Liu, Y. A.; Hartwig, J. F.; Liao, X.; *Org. Lett.* **2017**, *19*, 2610-2613.

HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords the title compound as transparent oil: 9 mg, 40%.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.03 – 6.97 (m, 2H), 6.89 – 6.86 (m, 1H), 5.72 (d, *J* = 47.5 Hz, 1H), 3.90 (s, 6H), 3.79 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.2 (d, *J* = 28.8.4 Hz), 150.2 (d, *J* = 3.8 Hz), 149.3, 126.5 (d, *J* = 21.3 Hz), 120.0 (d, *J* = 6.3 Hz), 111.0, 109.5 (d, *J* = 6.3 Hz), 89.3 (d, *J* = 185.0 Hz), 56.0, 55.9, 52.6.
^{19}F (235 MHz, $CDCl_3$) δ: −175.35 (d, *J* = 49.4 Hz).
IR (ATR, cm^{-1}): 2926, 1759, 1603, 1491, 1265, 1044.
HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{11}H_{14}FO_4$ 229.0871; Found 229.0873.

ethyl 2-(benzo[d][1,3]dioxol-5-yl)-2-fluoroacetate (**3u**)[19]

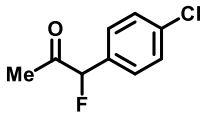


General Procedure G is employed with methyl ethyl 2-(benzo[*d*][1,3]dioxol-5-yl)-2-diazoacetate **1u** (22 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords the title compound as transparent oil: 10 mg, 44%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 6.95 – 6.92 (m, 2H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.99 (s, 2H), 5.65 (d, *J* = 47.8 Hz, 1H), 4.35 – 4.14 (m, 2H), 1.27 (t, *J* = 6.7 Hz, 3H).
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 168.6 (d, *J* = 29.1 Hz), 148.8 (d, *J* = 2.2 Hz), 148.0, 127.9 (d, *J* = 21.0 Hz), 121.3 (d, *J* = 6.5 Hz), 108.4, 107.2 (d, *J* = 5.2 Hz), 101.4, 89.2 (d, *J* = 183.9 Hz), 61.8, 14.0.
^{19}F (235 MHz, $CDCl_3$) δ: −174.87 (d, *J* = 49.4 Hz).
IR (ATR, cm^{-1}): 2959, 2918, 1749, 1615, 1491, 1270, 1067.
HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. for $C_{11}H_{11}O_4$ 207.0652; Found 207.0653.

[19] Guo, C.; Yue, X.; Qing, F.-L. *Synthesis* **2010**, *11*, 1837-1844.

1-(4-chlorophenyl)-1-fluoropropan-2-one (**3v**)



General Procedure G is employed with 1-(4-chlorophenyl)-1-diazopropan-2-one **1v** (58 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords the title compound as an yellowish oil: 11 mg, 59%.

^{1}H NMR (250 MHz, $CDCl_3$) *δ:* 7.40 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 5.65 (d, *J* = 48.5 Hz, 1H) 2.24 (d, *J* = 4.3 Hz, 3H).

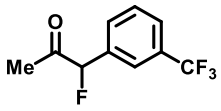
^{13}C NMR (62.5 MHz, $CDCl_3$) *δ*: 204.3 (d, *J* = 26.3 Hz), 135.4 (d, *J* = 1.9 Hz), 132.4 (d, *J* = 21.3 Hz), 129.1, 127.2 (d, *J* = 6.9 Hz), 95.1 (d, *J* = 187.5 Hz), 25.1.

^{19}F NMR (235 MHz, $CDCl_3$) *δ*: – 183.78 (dq, *J* = 47.0 Hz, *J* = 4.7 Hz).

IR (ATR, cm^{-1}): 2926, 1732, 1493, 1359, 1093, 1016.

HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. for C_9H_8ClO 167.0258; Found 167.0259.

1-fluoro-1-(3-(trifluoromethyl)phenyl)propan-2-one (**3w**)



General Procedure G is employed with 1-diazo-1-(4-(trifluoromethyl)phenyl)propan-2-one **1w** (115 mg, 0.5 mmol, 1 equiv.), HF·pyr **2a** (80 μL, 3.0 mmol, 6 equiv.) and DCM (5 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords the title compound as an yellowish oil: 55 mg, 50%

^{1}H NMR (250 MHz, $CDCl_3$) *δ:* 7.69-7.51 (m, 4H), 5.73 (d, *J* = 48.5 Hz, 1H), 2.28 (d, *J* = 4.5 Hz, 3H).

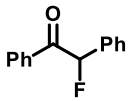
^{13}C NMR (62.5 MHz, $CDCl_3$) *δ:* 204.2 (d, *J* = 26.9 Hz), 135.0 (d, *J* = 20.6 Hz), 131.4 (q, *J* = 32.5 Hz), 129.4, 129.0 (dq, *J* = 6.9 Hz, *J* = 0.6 Hz), 126.0 (qd, *J* = 3.8 Hz, *J* = 1.3 Hz), 123.7 (q, *J* = 270.6 Hz), 122.5 (qd, *J* = 8.8 Hz, *J* = 3.8 Hz), 95.0 (d, *J* = 188.1 Hz), 25.2.

^{19}F NMR (235 MHz, $CDCl_3$) *δ:* – 62.80 (s), - 185.81 (dq, *J* = 49.4 Hz, *J* = 4.7 Hz).

IR (ATR, cm^{-1}): 1728, 1329, 1167, 1076, 1124.

HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. For $C_{10}H_8F_3O$ 201.0522; Found 201.0522.

2-fluoro-1,2-diphenylethanone (**3x**)[20]



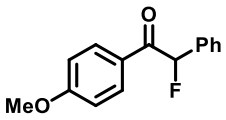
General Procedure G is employed with 2-diazo-1,2-diphenylethan-1-one **1x** (22 mg, 0.1 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 6 equiv.) and DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords the title compound as white solid: 13 mg, 61%.

^{1}H NMR (250 MHz, $CDCl_3$) *δ:* 7.96 - 7.92 (m, 2H), 7.55 - 7.38 (m, 8H), 6.51 (d, *J* = 48.8 Hz, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) *δ:* 194.2 (d, *J* = 21.3 Hz), 134.2 (d, *J* = 24.4 Hz), 134.0, 133.8, 129.6 (d, *J* = 2.5 Hz), 129.1, 129.0, 128.7, 127.4 (d, *J* = 5.6 Hz), 94.0 (d, *J* = 185.0 Hz).

^{19}F NMR (235 MHz, $CDCl_3$) *δ:* - 175.87 (d, *J* = 49.4 MHz).

2-fluoro-1-(4-methoxyphenyl)-2-phenylethan-1-one (**3y**)[20]



General Procedure G is employed with 2-diazo-1-(4-methoxyphenyl)-2-phenylethan-1-one **1y** (15 mg, 0.06 mmol, 1 equiv.), HF·pyr **2a** (10 μL, 0.36 mmol, 6 equiv.) and DCM (600 μL, 0.1M). Filtration using SiO_2 affords the title compound as a transparent oil: 14 mg, 96%.

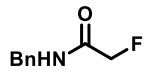
^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 8.8 Hz, 2H), 7.50 – 7.37 (m, 5H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 48.8 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 192.7 (d, *J* = 20.6 Hz), 163.9, 134.7 (d, *J* = 20.0 Hz), 131.5 (d, *J* = 3.1 Hz), 129.4 (d, *J* = 2.5 Hz), 129.0, 127.2 (d, *J* = 5.0 Hz), 126.9, 113.9, 94.0 (d, *J* = 184.4 Hz), 55.5.

^{19}F (235 MHz, $CDCl_3$) δ: −175.59 (d, *J* = 47.0 Hz).

[20] Liang, J.; Han, J.; Wu, J.; Wu, P.; Hu, J.; Hu, F.; Wu, F. *Org. Lett.* **2019**, *21*, 6844-6849.

N-benzyl-2-diazoacetamide (**3z**)[16]



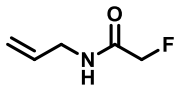
General Procedure G is employed with *N*-benzyl-2-diazoacetamide **1z** (53 mg, 0.3 mmol, 1 equiv.) HF·pyr **2a** (24 μL, 0.9 mmol, 3 equiv.) and DCM (3 mL, 0.1M). The addition of HF.pyr **2a** is made at 0 ºC. Purification by flash column chromatography (SiO_2, - 99:1 DCM:MeOH) affords the title compound as transparent oil: 22 mg, 44%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.36 – 7.29 (m, 5H), 6.57 (br s, 1H), 4.86 (d, *J* = 47.3 Hz, 2H), 4.53 (d, *J* = 5.8 Hz, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 167.4 (d, *J* = 16.3 Hz), 137.3, 128.8, 127.9 (d, *J* = 3.8 Hz), 127.8, 80.4 (d, *J* = 185.0 Hz), 43.0.

^{19}F (235 MHz, $CDCl_3$) δ: −224.85 (td, *J* = 47.0 Hz, *J* = 2.4 Hz).

N-allyl-2-diazoacetamide (**3aa**)



General Procedure G is employed with *N*-allyl-2-diazoacetamide **1aa** (38 mg, 0.3 mmol, 1 equiv.) HF·pyr **2a** (24 μL, 0.9 mmol, 3 equiv.) and DCM (3 mL, 0.1M). The addition of HF.pyr **2a** is made at 0 ºC. Purification by flash column chromatography (SiO_2, Hex - 6:3.5:0.5 Hex:AcOEt:DCM) affords the title compound as transparent oil (volatile): 10 mg, 29%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 6.38 (br s, 1H), 5.91 – 5.80 (m, 1H), 5.27 – 5.17 (m, 2H), 4.82 (d, *J* = 47.5 Hz, 2H), 3.97 (t, *J* = 5.8 Hz, 2H).

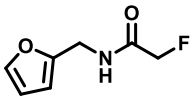
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 167.4 (d, *J* = 16.9 Hz), 133.3, 117.1, 80.3 (d, *J* = 184.4 Hz), 41.2.

^{19}F (235 MHz, $CDCl_3$) δ: −224.91 (td, *J* = 47.0 Hz, *J* = 2.4 Hz).

IR (ATR, cm^{-1}): 2450, 1676, 1079.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for C_5H_9FNO 118.0663; Found 118.0665.

2-diazo-N-(furan-2-ylmethyl)acetamide (**3bb**)



General Procedure G is employed with 2-diazo-N-(furan-2-ylmethyl)acetamide **1bb** (38 mg, 0.3 mmol, 1 equiv.) HF·pyr **2a** (24 μL, 0.9 mmol, 3 equiv.) and DCM (3 mL, 0.1M). The addition of HF.pyr **2a** is made at 0 ºC. Purification by flash column chromatography (SiO_2, Hex - 6:3.5:0.5 Hex:AcOEt:DCM) affords the title compound as transparent oil (volatile): 10 mg, 21%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.37 (dd, *J* = 1.8, *J* = 0.8, 1H), 6.61 (br s, 1H), 6.33 (dd, *J* = 3.3 Hz, *J* = 1.9 Hz, 1H), 6.26 (dd, *J* = 3.0 Hz, *J* = 0.5 Hz, 1H), 4.82 (d, *J* = 47.5 Hz, 2H), 4.52 (d, *J* = 5.8 Hz, 2H).

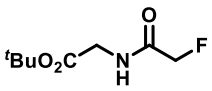
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 165.3 (d, *J* = 17.5 Hz), 150.3, 142.5, 110.5, 107.9, 80.2 (d, *J* = 185.0 Hz), 35.7.

^{19}F (235 MHz, $CDCl_3$) δ: −225.23 (td, *J* = 47.0 Hz, *J* = 4.7 Hz).

IR (ATR, cm^{-1}): 3304, 2957, 1668, 1544, 1046.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ $C_7H_9FNO_2$ 158.0612; Found 158.0612.

tert-butyl (2-fluoroacetyl)glycinate (**3cc**)



General Procedure G is employed with tert-butyl (2-diazoacetyl)glycinate **1cc** (40 mg, 0.2 mmol, 1 equiv.) HF·pyr **2a** (32 μL, 1.2 mmol, 6 equiv.) and DCM (2 mL, 0.1M). The addition of HF.pyr **2a** is made at 0 ºC. Purification by flash column chromatography (SiO_2, - 6:3:1 Hex:AcOEt:DCM) affords the title compound as transparent oil (volatile): 17 mg, 45%.

^{1}H NMR (250 MHz, CDCl3) δ: 6.78 (br s, 1H), 4.84 (d, *J* = 47.5 Hz, 2H), 4.01 (d, *J* = 5.3 Hz, 2H), 1.48 (s, 9H).

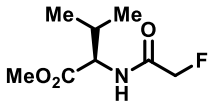
^{13}C NMR (62.5 MHz, CDCl3) δ: 168.3, 165.7 (d, *J* = 16.9 Hz), 82.7, 80.1 (d, *J* = 185.0 Hz), 41.3, 28.0.

^{19}F (235 MHz, $CDCl_3$) δ: −225.50 (td, *J* = 47.0 Hz, *J* = 2.4 Hz).

IR (ATR, cm^{-1}): 3264, 2982, 2099, 1731, 1609, 1397, 1245.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_8H_{15}FNO_3$ 192.1030; Found 192.1028.

methyl (2-fluoroacetyl)valinate (**3dd**)



General Procedure G is employed with methyl (2-diazoacetyl)valinate **1dd** (40 mg, 0.2 mmol, 1 equiv.) HF·pyr **2a** (32 μL, 1.2 mmol, 6 equiv.) and DCM (2 mL, 0.1M). The addition of HF.pyr **2a** is made at 0 ºC. Purification by flash column chromatography (SiO_2, - 6:3:1 Hex:AcOEt:DCM) affords the title compound as transparent oil: 14 mg, 37%.

^{1}H NMR (250 MHz, CDCl3) δ: 6.75 (br s, 1H), 4.84 (dd, *J* = 47.3 Hz, *J* = 1.3 Hz, 2H), 4.61 (ddd, *J* = 9.0 Hz, *J* = 5.0 Hz, *J* = 1.3 Hz, 1H), 3.76 (s, 3H), 2.28 – 2.13 (m, 1H), 0.95 (d, *J* = 7.1 Hz, 6H).

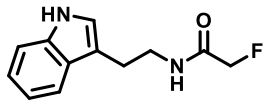
^{13}C NMR (62.5 MHz, CDCl3) δ: 171.8, 167.5 (d, *J* = 17.5 Hz), 80.2 (d, *J* = 185.0 Hz), 56.5, 52.3, 31.3, 18.9, 17.7.

^{19}F (235 MHz, $CDCl_3$) δ: −225.00 (tdd, *J* = 47.2 Hz, *J* = 3.3 Hz, *J* = 1.2 Hz).

IR (ATR, cm^{-1}): 2959, 2923, 1751, 1685, 1464, 11260, 1044.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_8H_{15}FNO_3$ 192.1030; Found 192.1030.

2-diazo-N-(2-(3a,7a-dihydro-1H-indol-3-yl)ethyl)acetamide (**3ee**)[21]



General Procedure G is employed with 2-diazo-N-(2-(3a,7a-dihydro-1H-indol-3-yl)ethyl)acetamide **1ee** (46 mg, 0.2 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 3 equiv.) and DCM (2 mL, 0.1M). The addition of HF.pyr **2a** is made at 0 ºC. Purification by flash column chromatography (SiO_2, DCM - 98:2 DCM:MeOH) affords the title compound as transparent oil: 16 mg, 36%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.09 (br s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.23 – 7.14 (m, 2H), 7.07 (s, 1H), 6.40 (br s, 1H), 4.76 (d, *J* = 47.5 Hz, 2H), 3.69 (td, *J* = 6.7 Hz, *J* = 6.3 Hz, 2H), 3.03 (t, *J* = 6.7 Hz, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 167.5 (d, *J* = 16.9 Hz), 136.4, 127.2, 122.3, 122.0, 119.6, 118.6, 112.6, 111.3, 80.3 (d, *J* = 185.0 Hz), 39.0, 25.3.

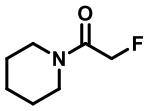
[21] Zheng, W.; Scheibner, K. A.; Ho, A. K.; Cole, P. A.; *Chem. Biol.* **2001**, *8*, 379-389.

^{19}F (235 MHz, $CDCl_3$) δ: −224.63 (td, *J* = 47.0 Hz, *J* = 4.7 Hz).

IR (ATR, cm^{-1}): 3409, 2928, 1664, 1546, 1262, 1093.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{12}H_{14}FN_2O$ 221.1085; Found 221.1086.

2-fluoro-1-(piperidin-1-yl)ethan-1-one (**3ff**)



General Procedure G is employed with 2-diazo-1-(piperidin-1-yl)ethan-1-one **1ff** (46 mg, 0.3 mmol, 1 equiv.), HF·pyr **2a** (48 μL, 1.8 mmol, 6 equiv.) and DCM (3 mL, 0.1M). The addition of HF.pyr **2a** is made at 0 ºC. Purification by flash column chromatography (SiO_2, 98:2 DCM:MeOH) affords the title compound as transparent oil (volatile): 19 mg, 44%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 4.97 (d, *J* = 47.3 Hz, 2H), 3.58 – 3.56 (m, 2H), 3.34 – 3.32 (m, 2H), 1.68 – 1.56 (m, 6H).

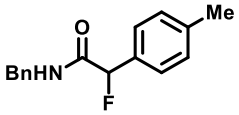
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 165.0 (d, *J* = 17.5 Hz), 80.0 (d, *J* = 178.1 Hz), 45.6, 43.0, 26.4, 25.4, 24.4.

^{19}F (235 MHz, $CDCl_3$) δ: −224.56 (t, *J* = 47.0 Hz).

IR (ATR, cm^{-1}): 2939, 2853, 1773, 1647, 1446, 1256.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_7H_{13}FNO$ 146.0976; Found 146.0976.

N-benzyl-2-fluoro-2-(p-tolyl)acetamide (**3gg**)



General Procedure G is employed with *N*-benzyl-2-diazo-2-(p-tolyl)acetamide **1gg** (40 mg, 0.15 mmol, 1 equiv.), HF·pyr **2a** (12 μL, 0.45 mmol, 6 equiv.) and DCM (1.5 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex - 95:5 Hex:AcOEt - 9:1 Hex:AcOEt - 8:2 Hex:AcOEt - 7:3 Hex:AcOEt) affords the title compound as transparent oil: 25 mg, 65%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.37 – 7.29 (m, 7H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.79 (br s,1H), 5.80 (d, *J* = 48.5 Hz, 1H), 4.53 (d, *J* = 6.0 Hz, 2H), 2.36 (s, 3H).

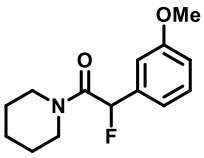
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 168.6 (d, *J* = 21.9 Hz), 139.5 (d, *J* = 3.1 Hz), 137.5, 131.8 (d, *J* = 18.8 Hz), 129.4, 128.8, 127.9, 127.8, 126.7 (d, *J* = 6.3 Hz), 91.9 (d, *J* = 185.6 Hz), 43.2, 21.3.

^{19}F (235 MHz, $CDCl_3$) δ: −175.42 (t, *J* = 49.4 Hz).

IR (ATR, cm^{-1}): 2939, 2853, 1773, 1647, 1446, 1256.

HRMS (ESI-Orbitrap) m/z: $[M - F]^+$ Calcd. for $C_{16}H_{16}NO$ 238.1226; Found 238.1228.

2-fluoro-2-(3-methoxyphenyl)-1-(piperidin-1-yl)ethan-1-one (**3hh**)



General Procedure G is employed with 2-diazo-2-(3-methoxyphenyl)-1-(piperidin-1-yl)ethan-1-one **1hh** (20 mg, 0.078 mmol, 1 equiv.), HF·pyr **2a** (13 μL, 0.47 mmol, 6 equiv.) and DCM (780 μL, 0.1M). Filtration using SiO_2 affords the title compound as a transparent oil: 14 mg, 72%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.32 (t, *J* = 7.8 Hz, 1H), 7.03 – 6.90 (m, 3H), 6.04 (d, *J* = 49.0 Hz, 1H), 3.82 (s, 3H), 3.69 – 3.64 (m, 1H), 3.54 – 3.48 (m, 1H), 3.37 – 3.23 (m, 2H), 1.63 – 1.49 (m, 4H), 1.33 – 1.23 (m, 2/H).

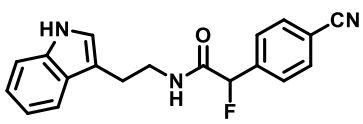
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 165.8 (d, *J* = 21.9 Hz), 160.0, 136.2 (d, *J* = 20.0 Hz), 129.9, 118.8 (d, *J* = 5.6 Hz), 115.1 (d, *J* = 2.5 Hz), 111.7 (d, *J* = 6.3 Hz), 90.8 (d, *J* = 183.1 Hz), 55.4, 46.1, 43.5, 25.8, 25.5, 24.3.

^{19}F (235 MHz, $CDCl_3$) δ: −173.77 (d, *J* = 49.4 Hz).

IR (ATR, cm^{-1}): 2940, 2856, 1655, 1601, 1455, 1262, 1044, 1007.

HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{19}FNO_2$ 252.1394; Found 252.1393.

N-(2-(1H-indol-3-yl)ethyl)-2-(4-cyanophenyl)-2-fluoroacetamide (**3ii**)

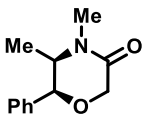


General Procedure G is employed with *N*-(2-(1*H*-indol-3-yl)ethyl)-2-(4-cyanophenyl)-2-diazoacetamide **1ii** (82 mg, 0.25 mmol, 1 equiv.), HF·pyr **2a** (40 μL, 1.5 mmol, 6 equiv.) and DCM (2.5 mL, 0.1 M). Purification by

preparative TLC (SiO_2, DCM - 98:2 DCM:MeOH) affords the title compound as transparent oil: 70 mg, 87%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.07 (br s, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 1.8 Hz, 1H), 6.54 (br s, 1H), 5.78 (d, *J* = 48.0 Hz, 1H), 3.67 (dt, *J* = 6.5 Hz, *J* = 6.3 Hz, 2H), 3.02 (t, *J* = 6.8 Hz, 2H).
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 167.2 (d, *J* = 20.6 Hz), 139.7 (d, *J* = 19.4 Hz), 136.4, 132.3, 127.2, 126.6 (d, *J* = 7.5 Hz), 122.4, 122.0, 119.7, 188.6, 118.3, 113.0 (d, *J* = 1.9 Hz), 112.4, 111.3, 90.5 (d, *J* = 190.6 Hz), 39.4, 25.1.
^{19}F (235 MHz, $CDCl_3$) δ: −184.66 (dd, *J* = 47.0 Hz, *J* = 3.5 Hz).
IR (ATR, cm^{-1}): 3390, 2927, 2230, 1670, 1458, 1264.
HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{19}H_{17}FN_3O$ 322.1350; Found 322.1350.

(5R,6S)-4,5-dimethyl-6-phenylmorpholin-3-one (**4**)



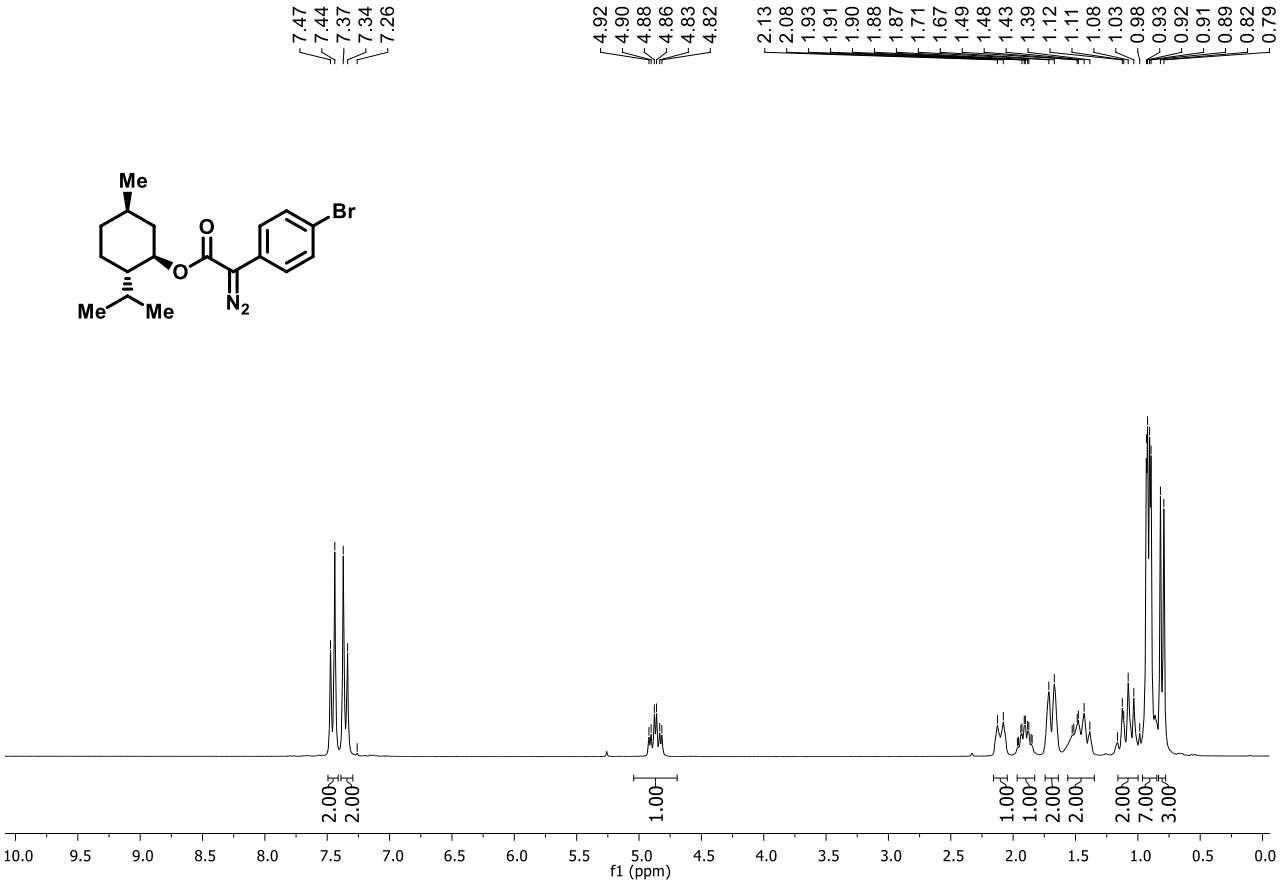
General Procedure G is employed with 2-diazo-*N*-(1-hydroxy-1-phenylpropan-2-yl)-*N*-methylacetamide **1rr** (47 mg, 0.2 mmol, 1 equiv.), HF·pyr **2a** (16 μL, 0.6 mmol, 3 equiv.) and DCM (2 mL, 0.1M). The addition of HF.pyr **2a** is made at 0 ºC. Purification by flash column chromatography (SiO_2, DCM - 98:2 DCM:MeOH) affords the title compound as transparent oil: 32 mg, 78%.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.40 – 7.27 (m, 5H), 4.96 (d, *J* = 2.8 Hz, 1H), 4.44 (d, *J* = 17.0 Hz, 1H), 4.32 (d, *J* = 17.0 Hz, 1H), 3.49 (qd, *J* = 6.5 Hz, *J* = 2.8 Hz, 1H), 3.03 (s, 3H), 0.97 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 166.8, 137.5, 128.4, 127.7, 125.4, 77.4, 68.1, 58.3, 33.1, 12.5.
IR (ATR, cm^{-1}): 2925, 1653, 1452, 1253, 1149.
HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ Calcd. for $C_{12}H_{16}NO_2$ 206.1176; Found 206.1176.

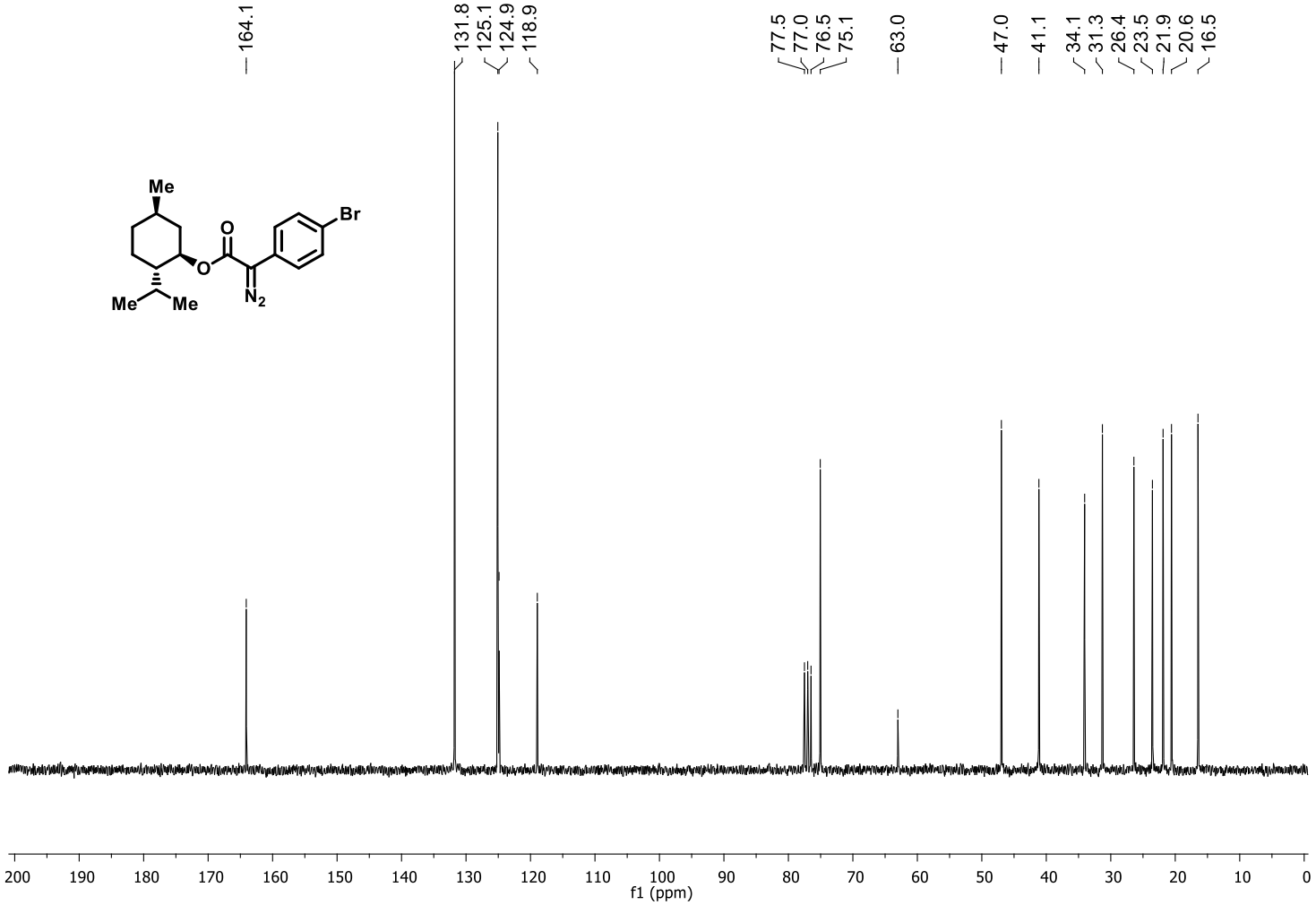
2. NMR Spectra

2.1. NMR Spectra of α-Diazo Carbonyl Compounds 1

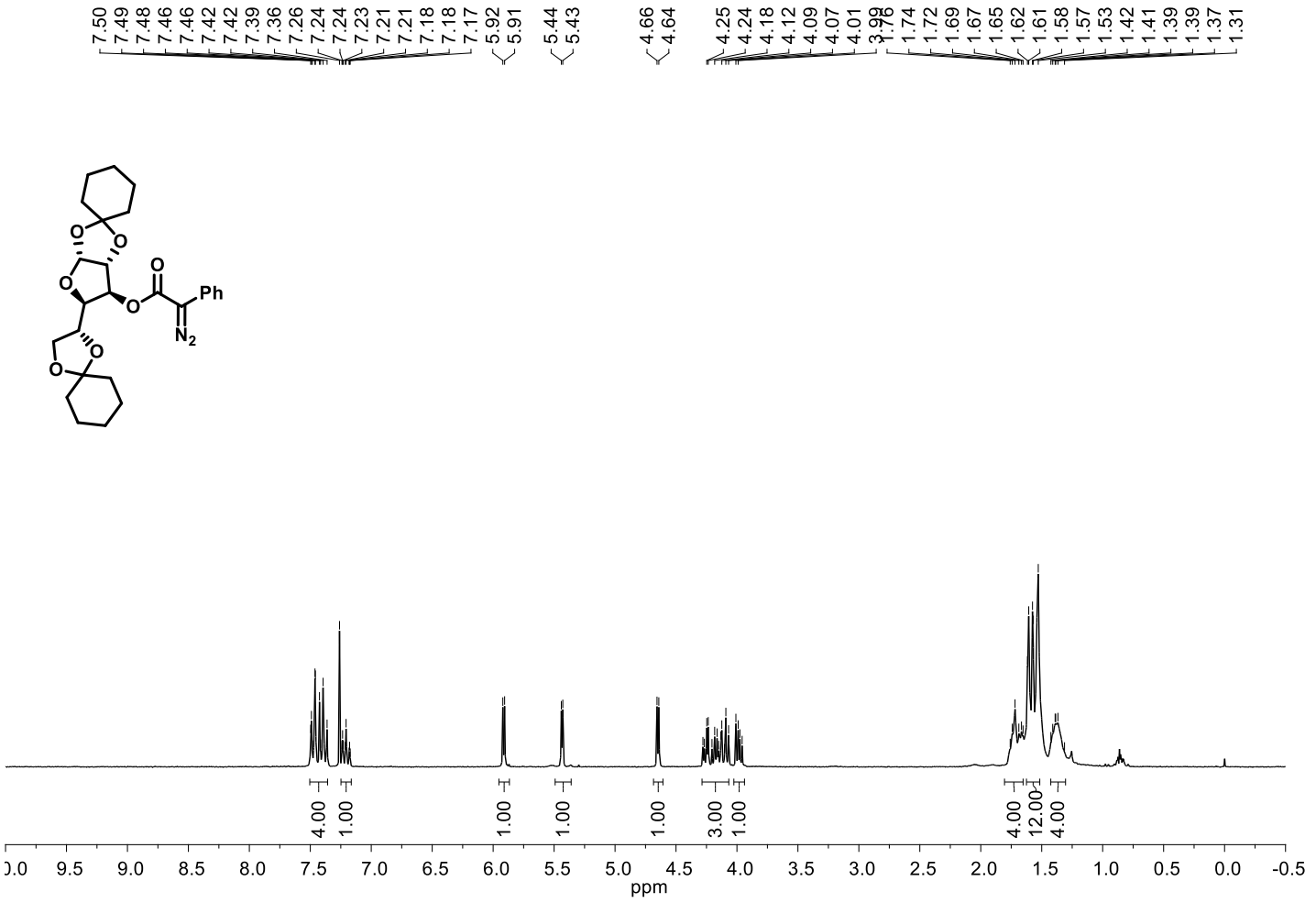
1g - ^{1}H NMR (250 MHz, $CDCl_3$)



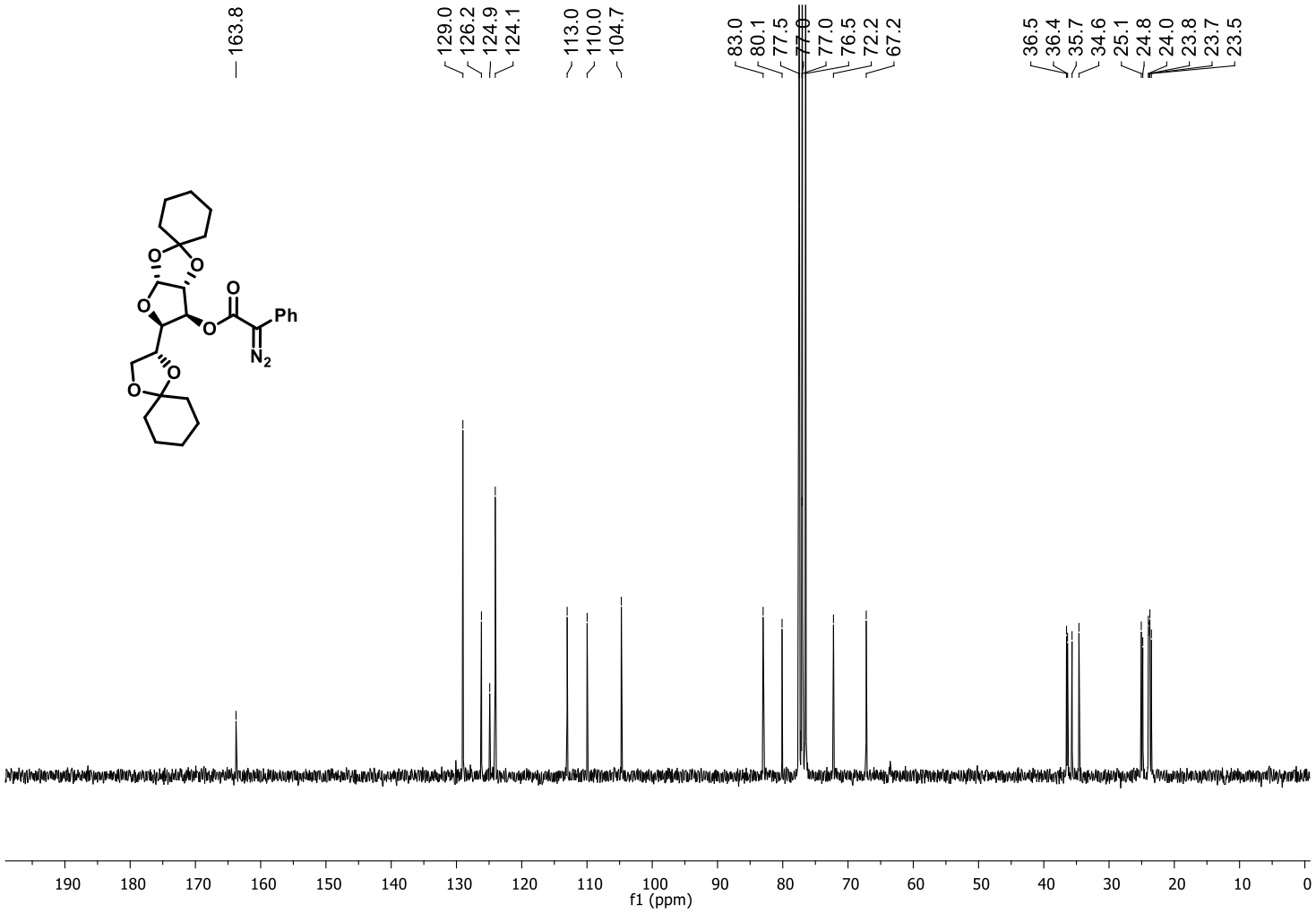
1g - ^{13}C NMR (62.5 MHz, $CDCl_3$)



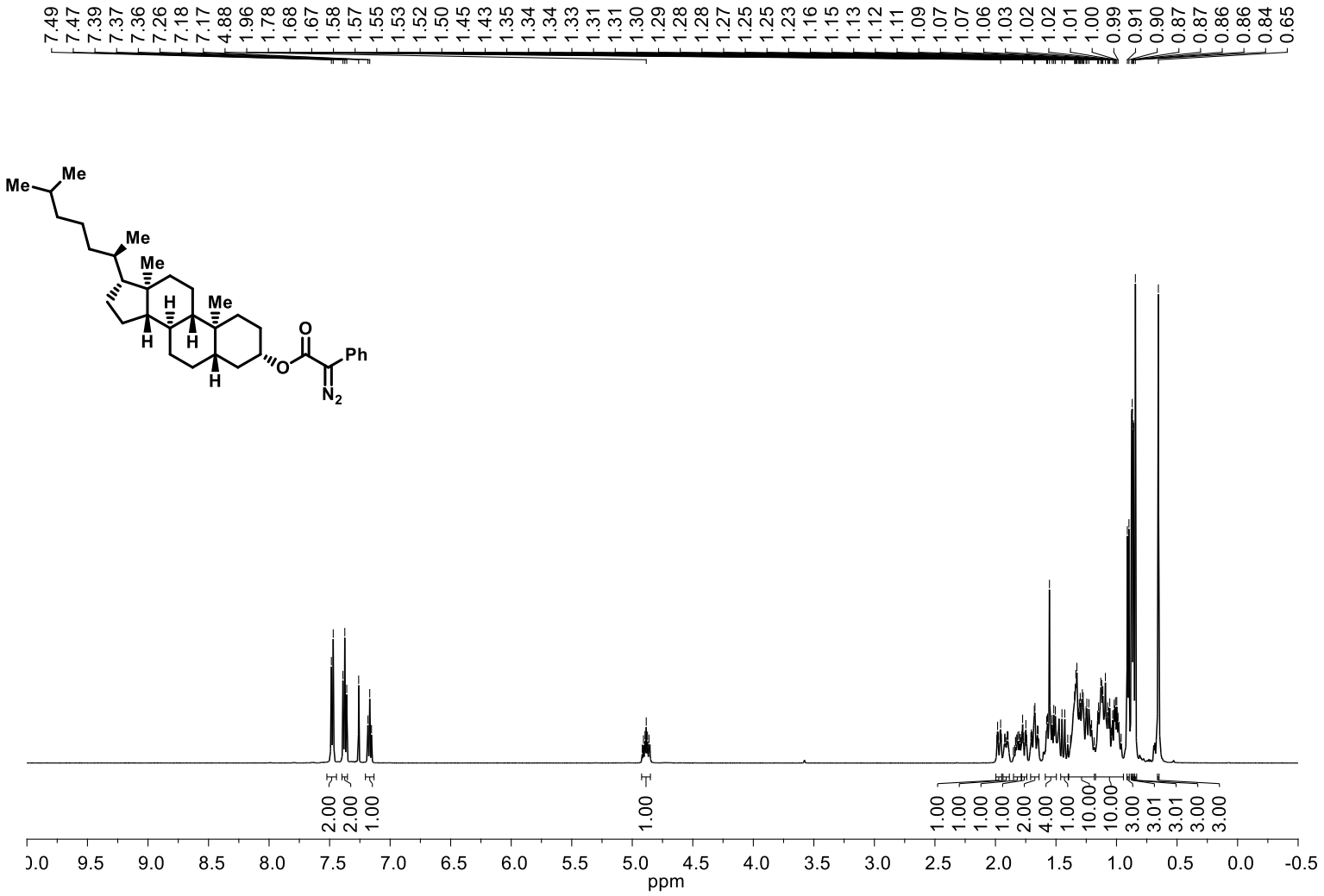
1h - ^{1}H NMR (250 MHz, $CDCl_3$)



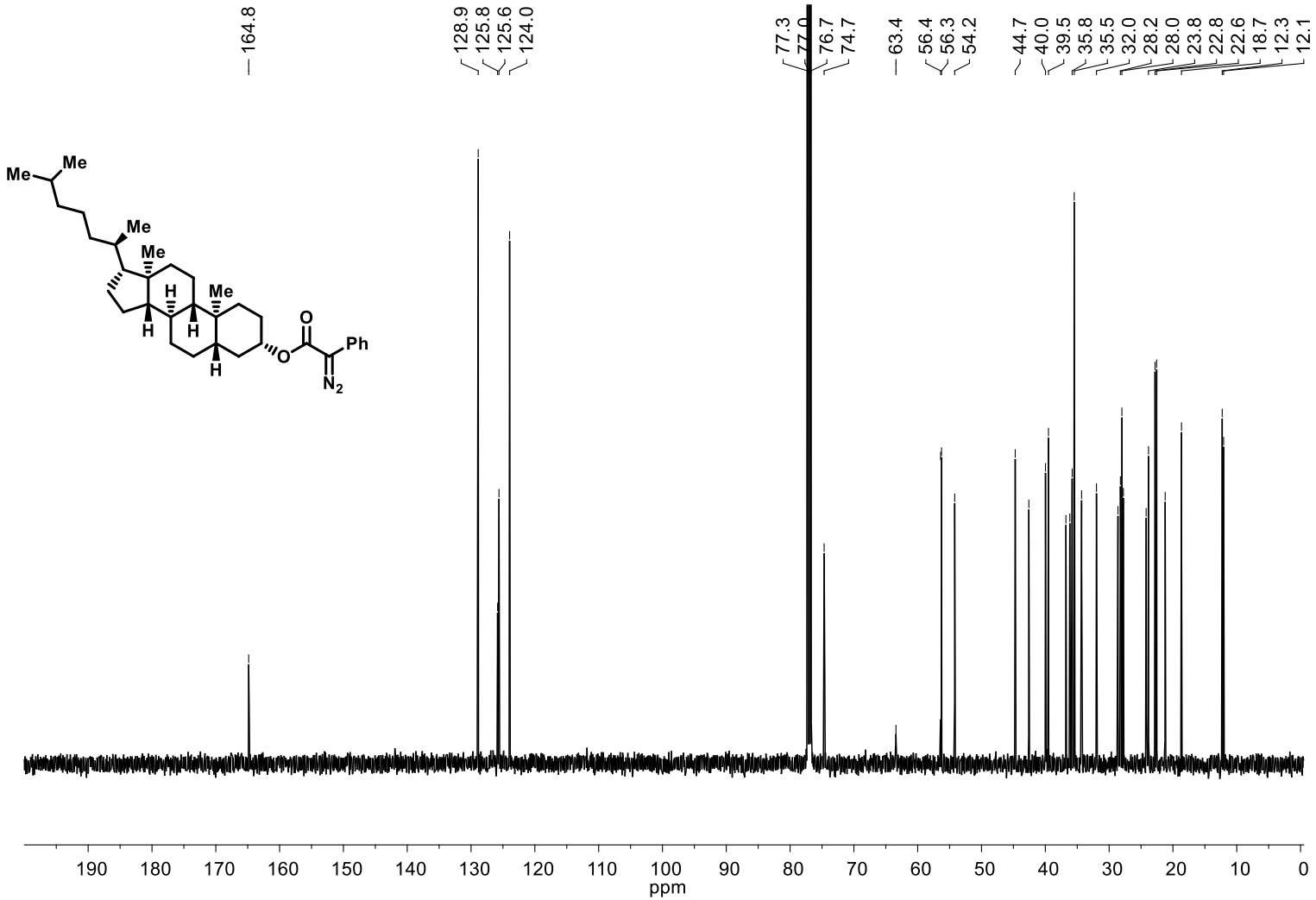
1h - ^{13}C NMR (62.5 MHz, $CDCl_3$)



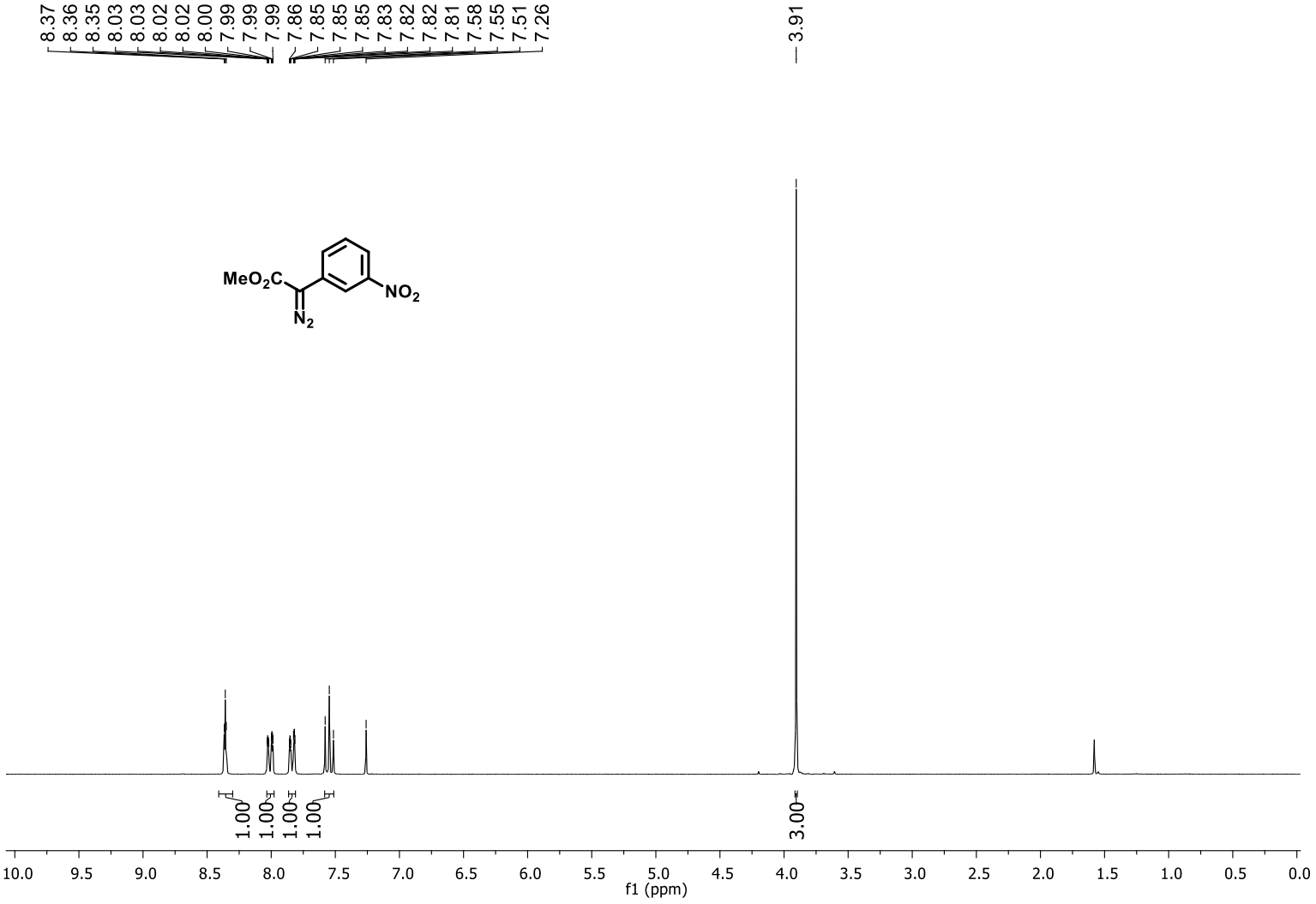
1i - ^{1}H NMR (500 MHz, $CDCl_3$)



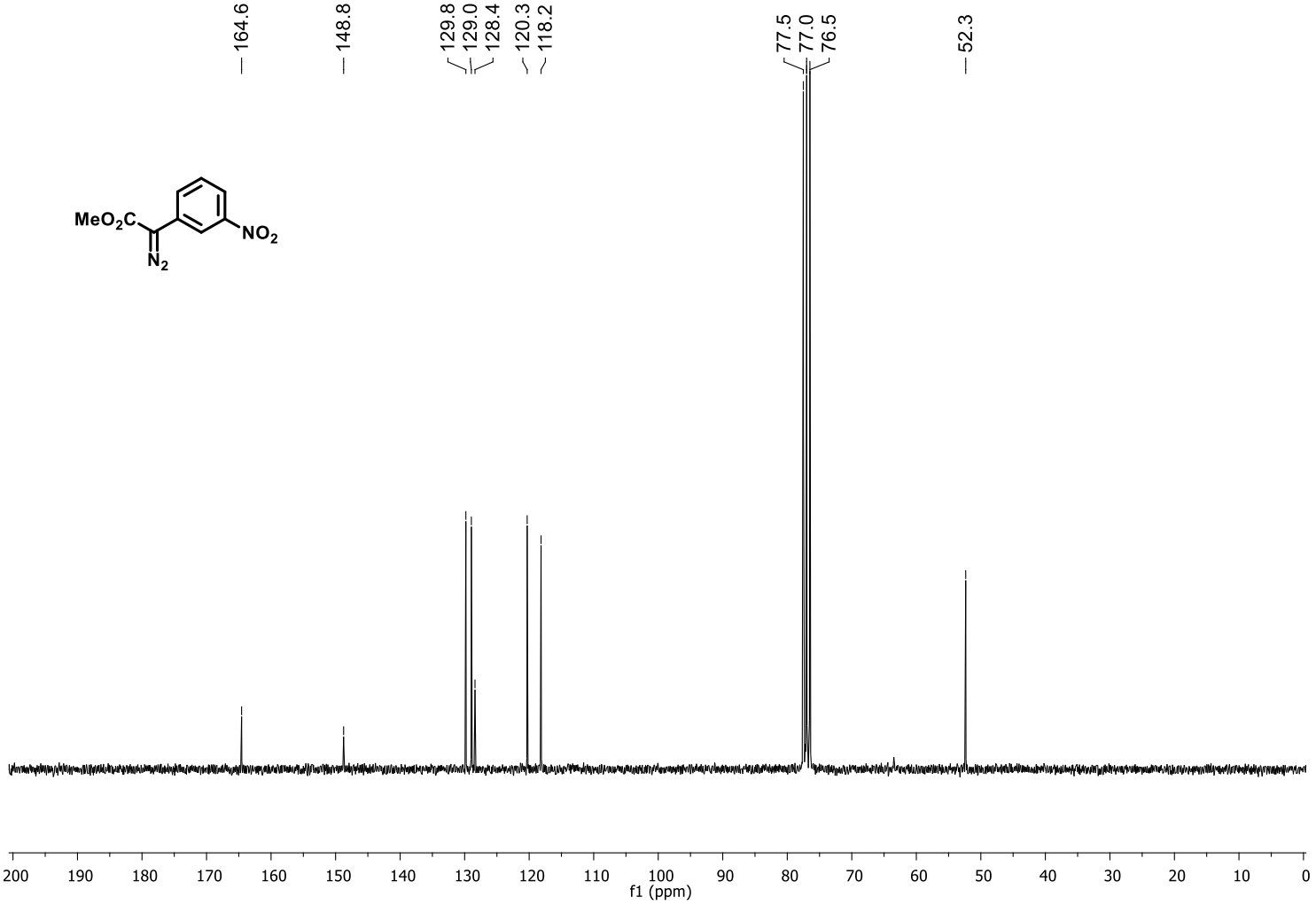
1i - ^{13}C NMR (125MHz, $CDCl_3$)



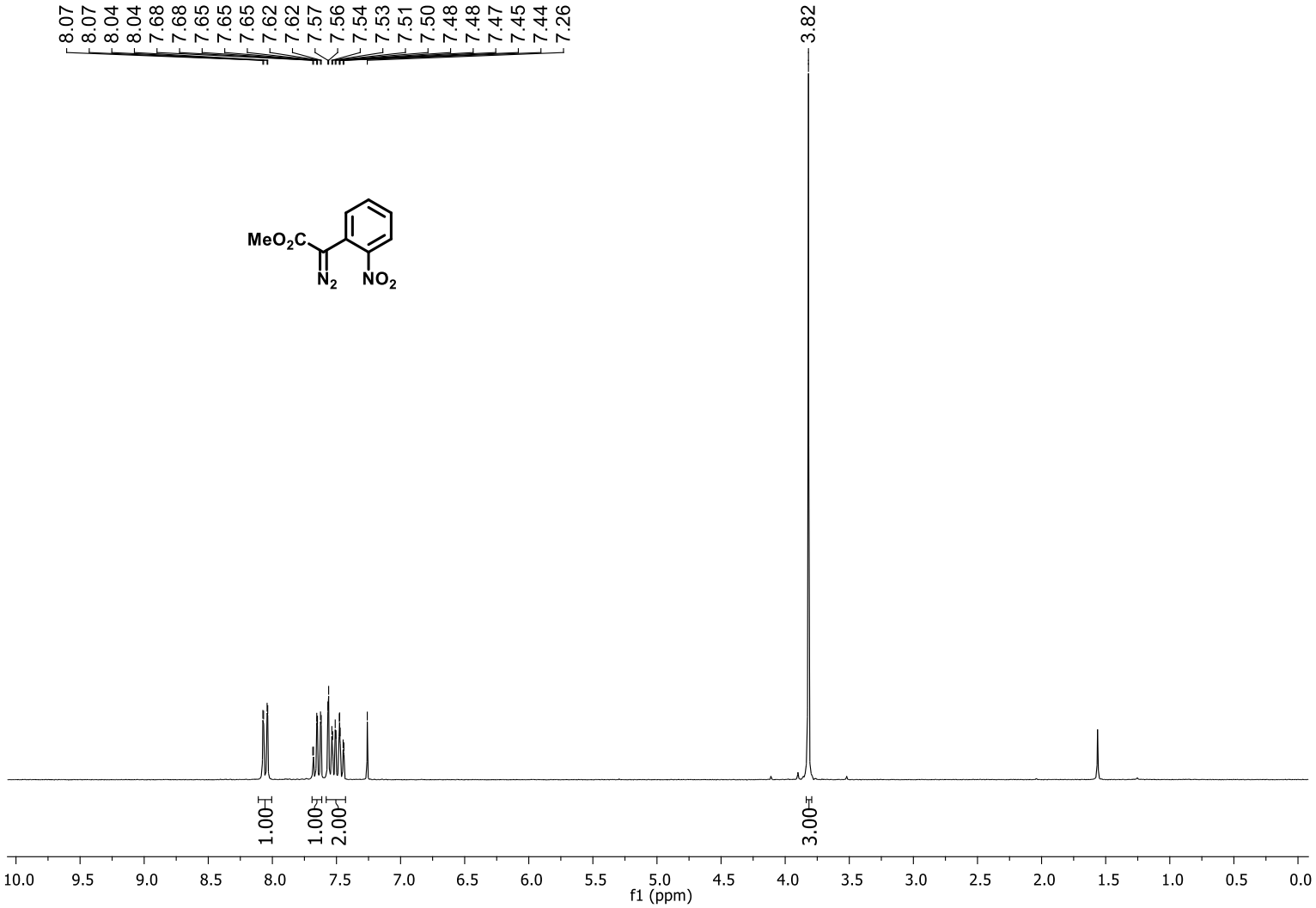
1o - ^{1}H NMR (250 MHz, $CDCl_3$)



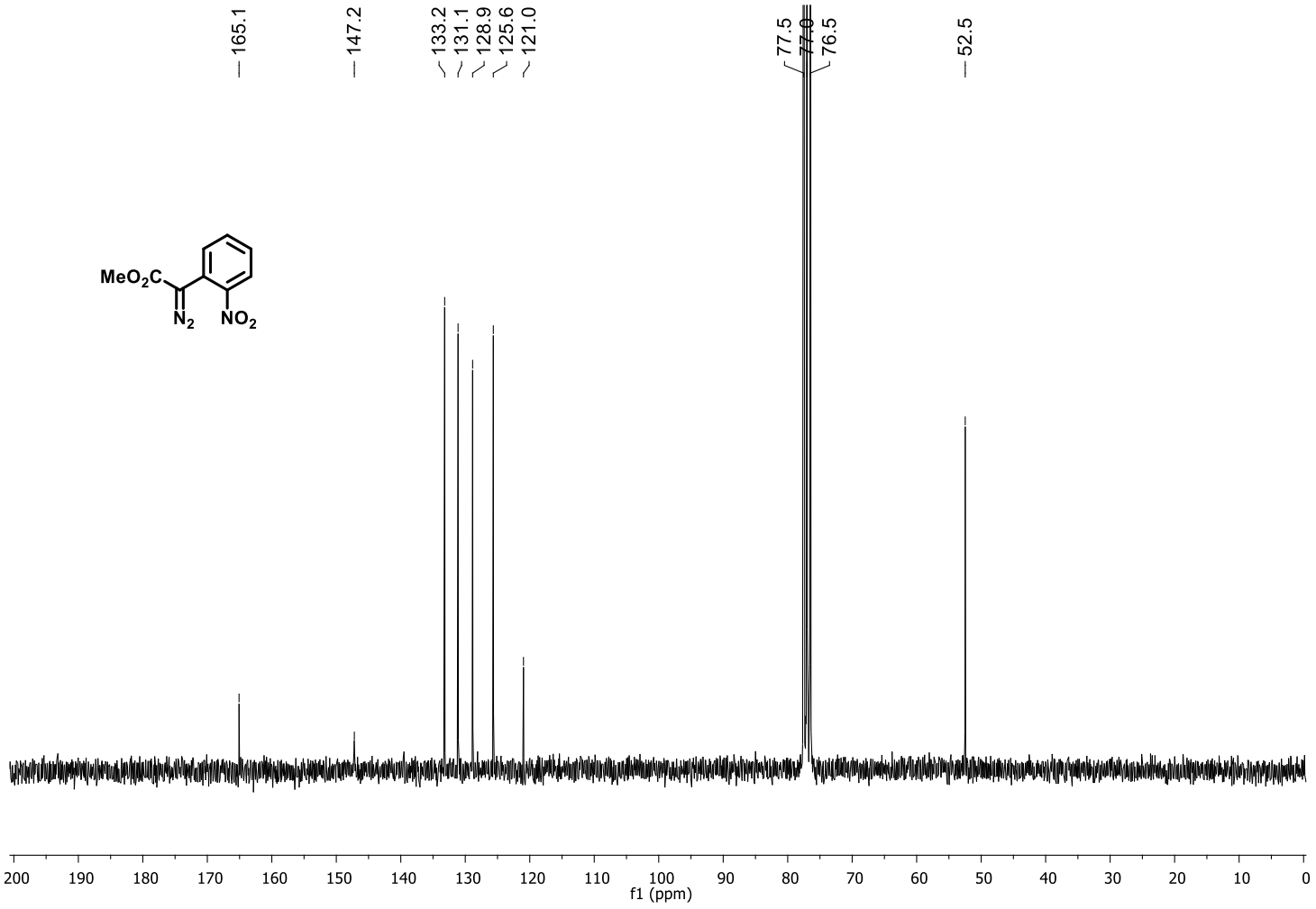
1o -^{13}C NMR (62.5 MHz, $CDCl_3$)



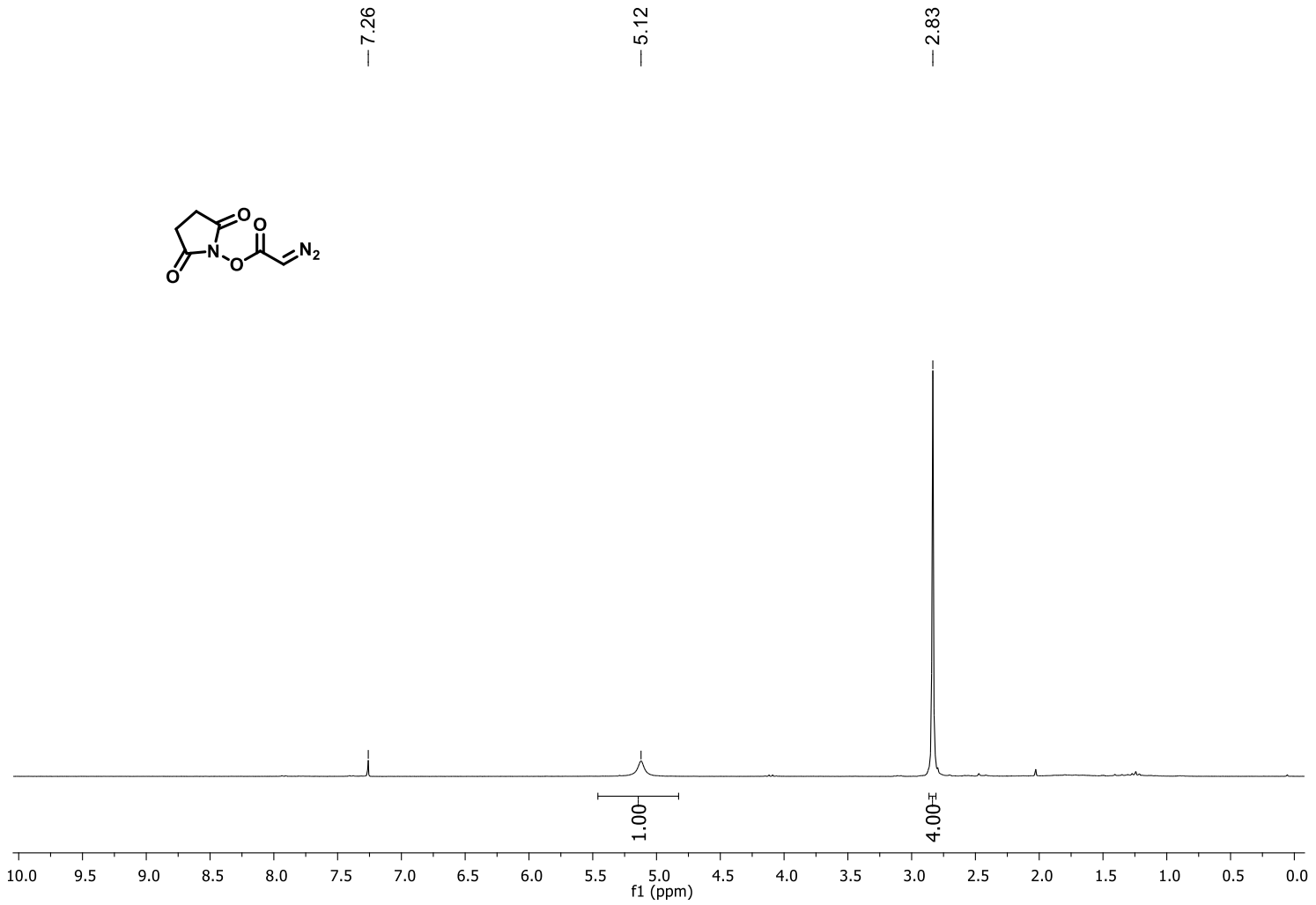
1p - ^{1}H NMR (250 MHz, $CDCl_3$)



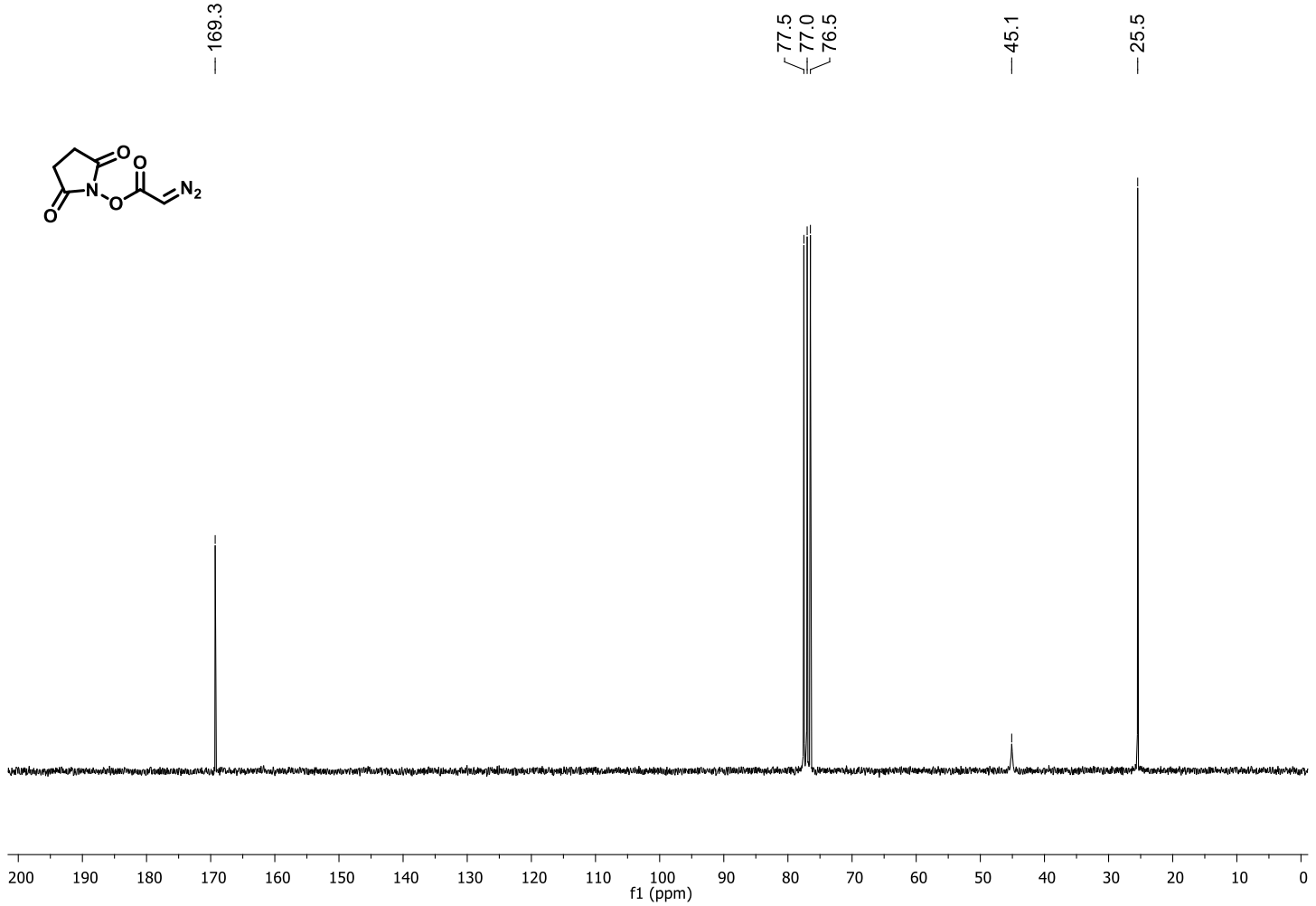
1p - ^{13}C NMR (62.5 MHz, $CDCl_3$)



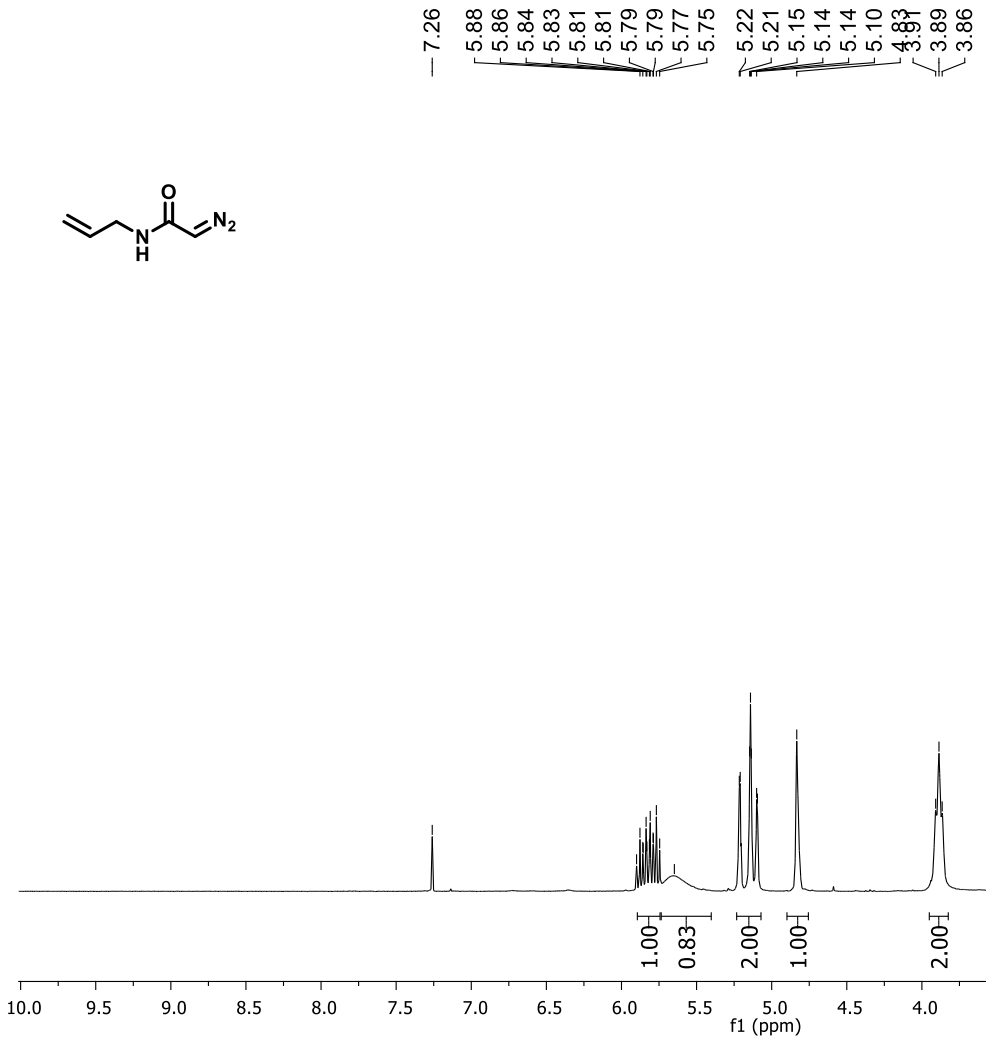
pre-1z - ^{1}H NMR (250 MHz, $CDCl_3$)



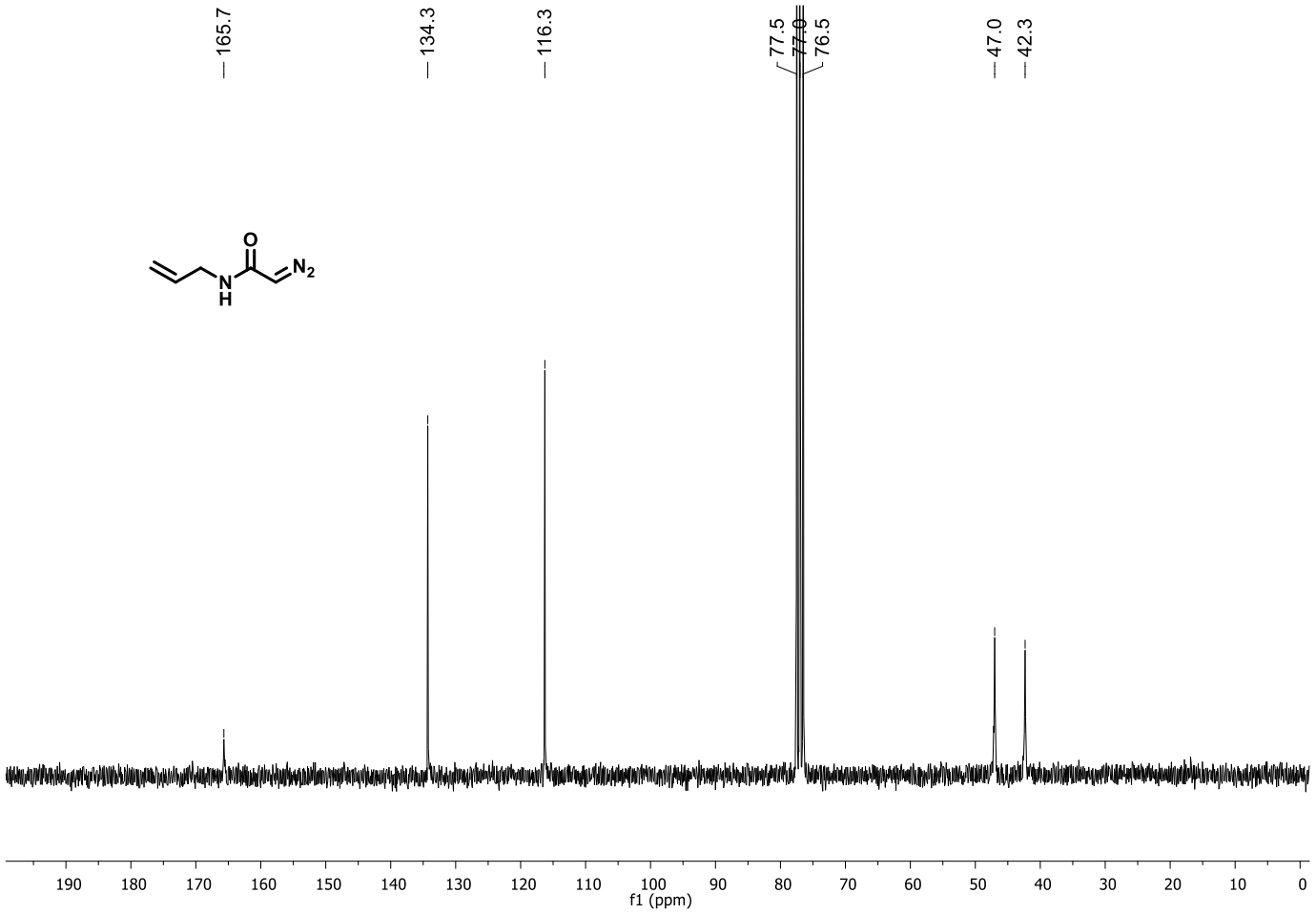
pre-1z - ^{13}C NMR (62.5 MHz, $CDCl_3$)



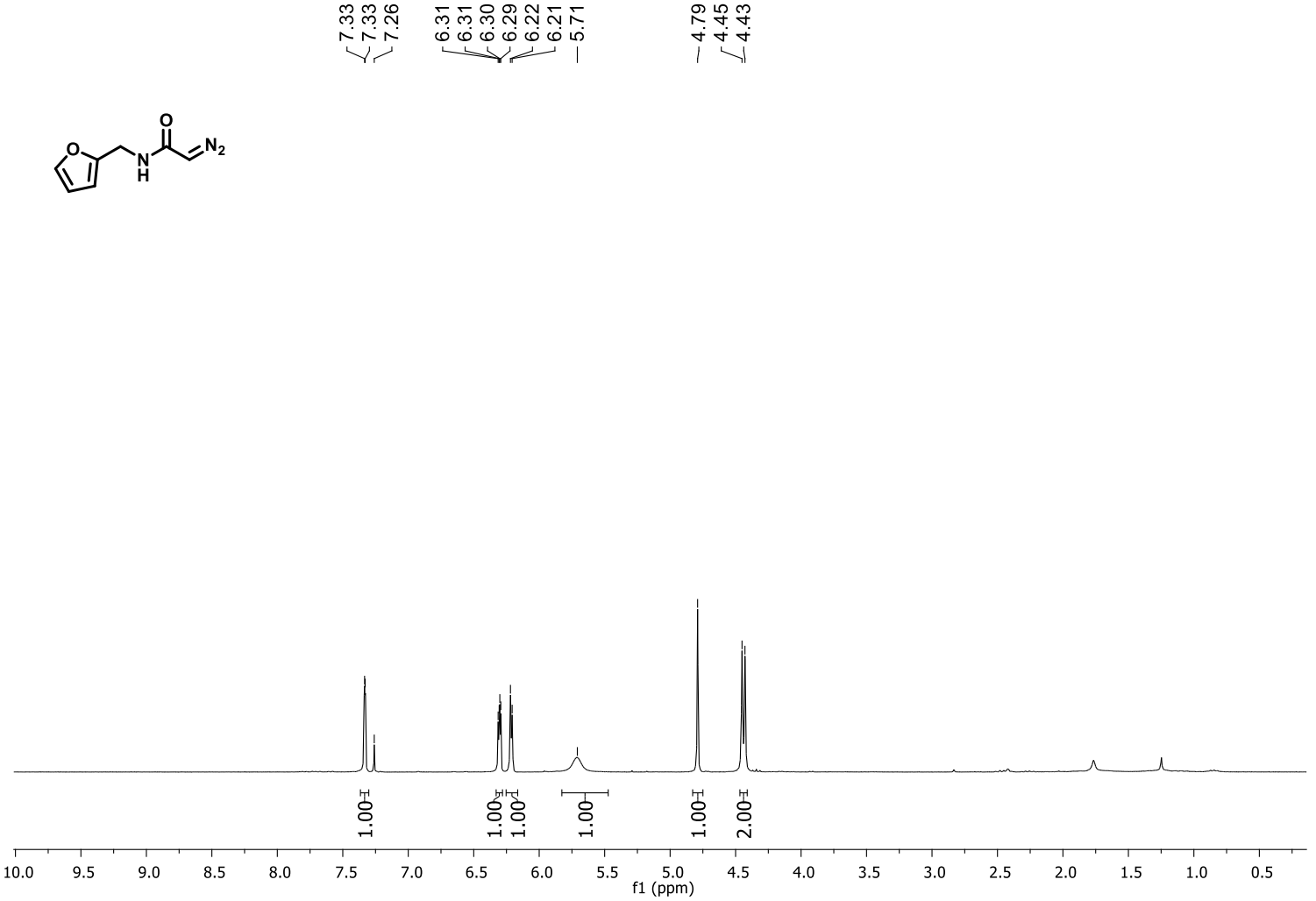
1aa - ^{1}H NMR (250 MHz, $CDCl_3$)



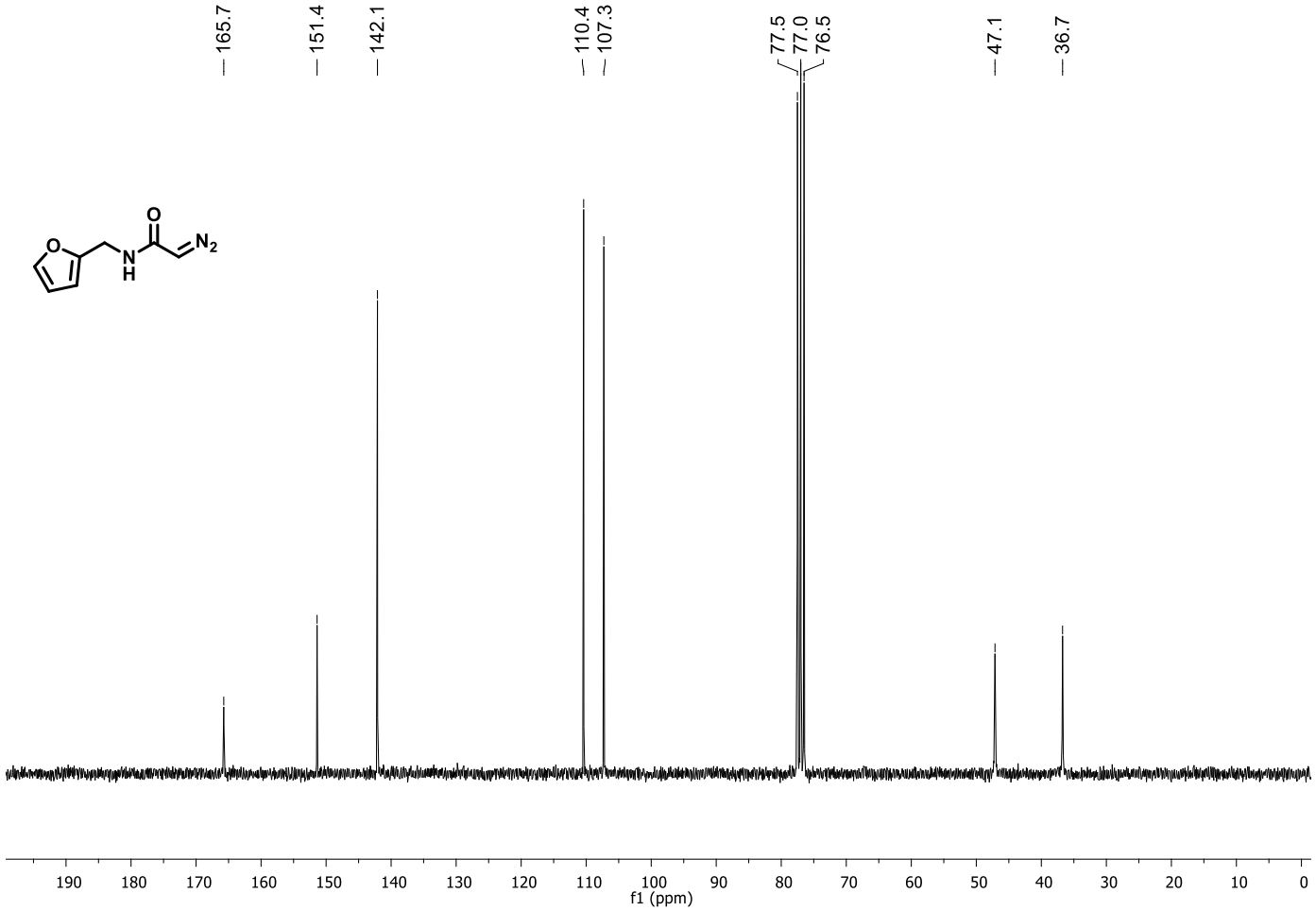
1aa - ^{13}C NMR (62.5 MHz, $CDCl_3$)



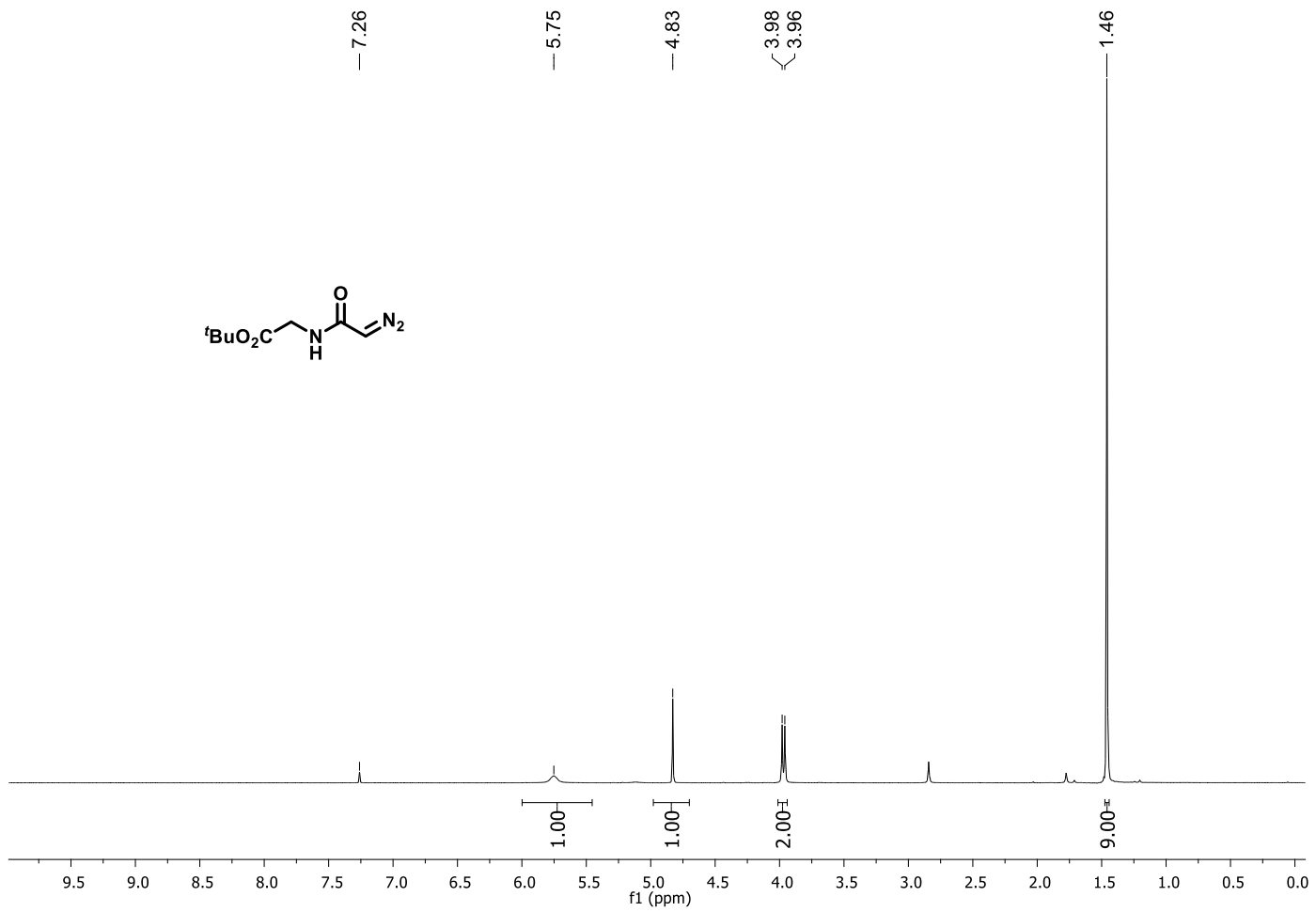
1bb - ^{1}H NMR (250 MHz, $CDCl_3$)



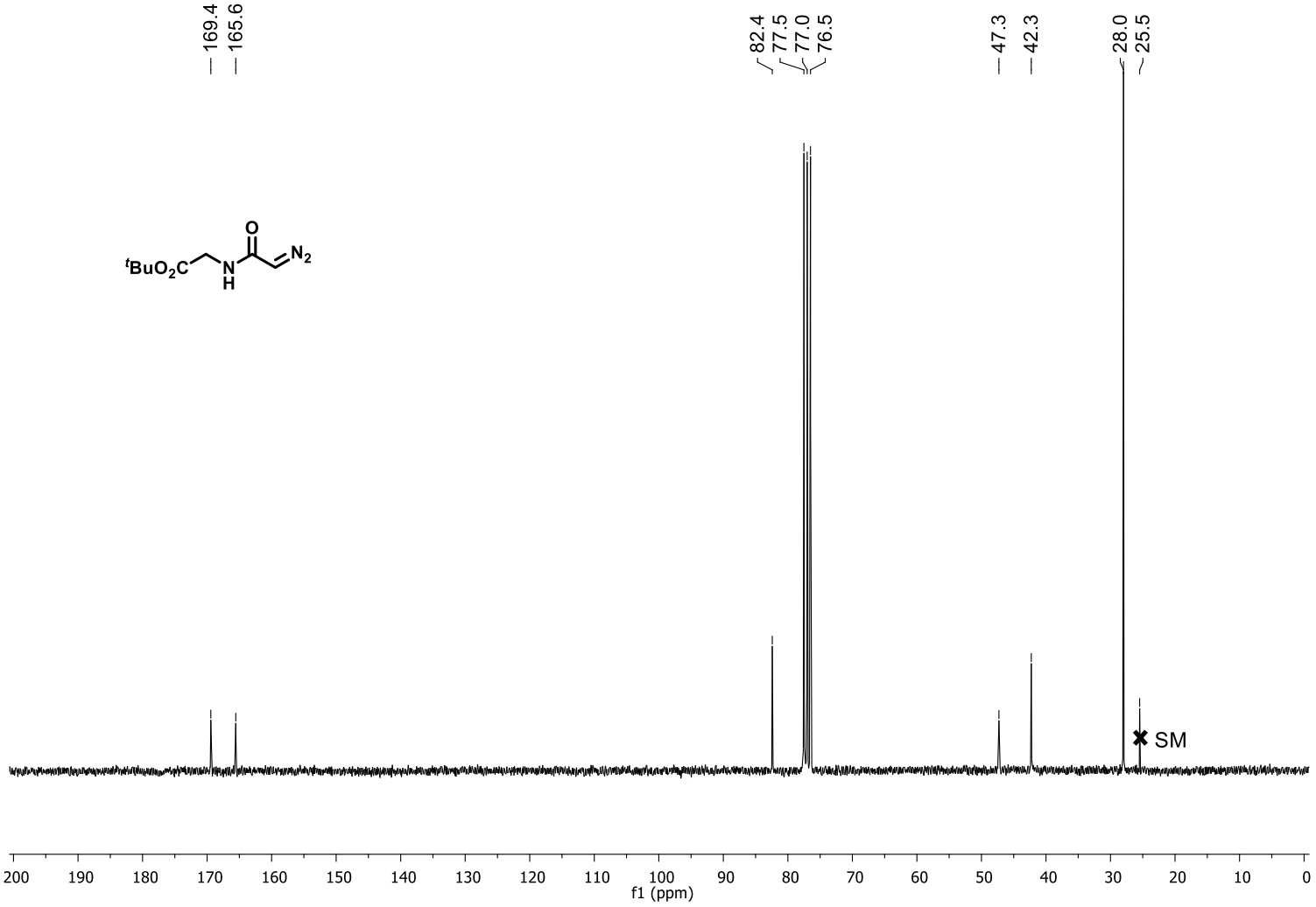
1bb - ^{13}C NMR (62.5 MHz, $CDCl_3$)



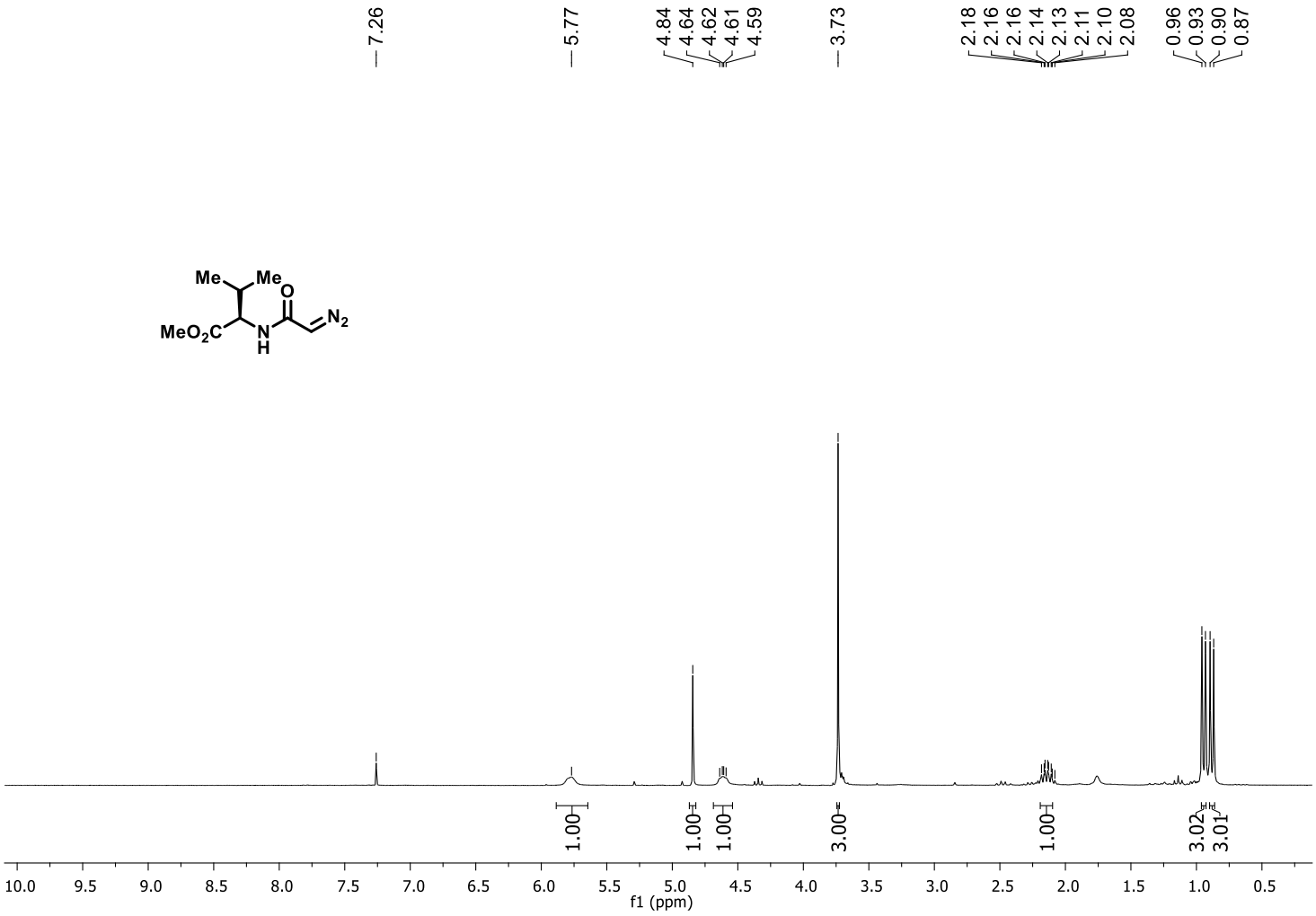
1cc - ^{1}H NMR (250 MHz, $CDCl_3$)



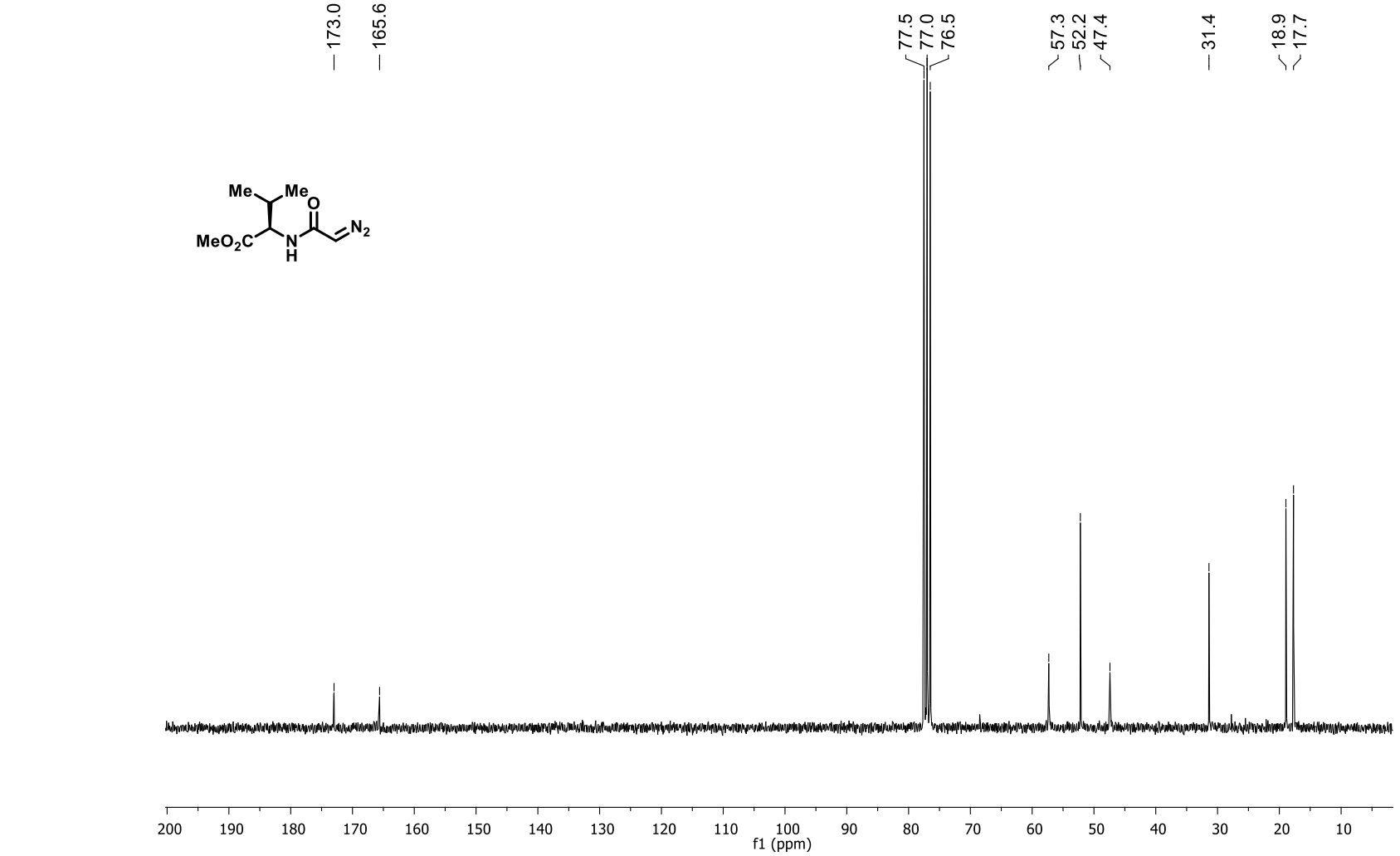
1cc - ^{13}C NMR (62.5 MHz, $CDCl_3$)



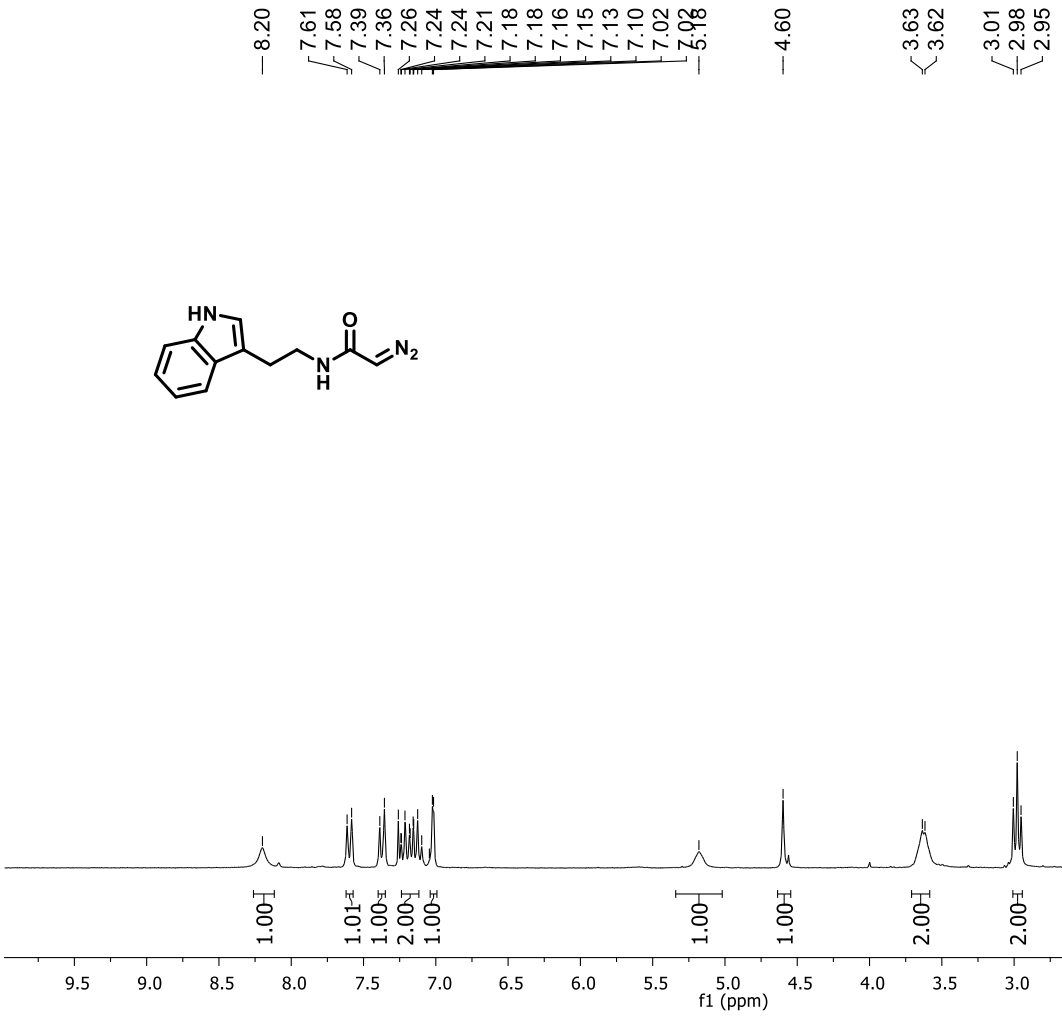
1dd - ^{1}H NMR (250 MHz, $CDCl_3$)



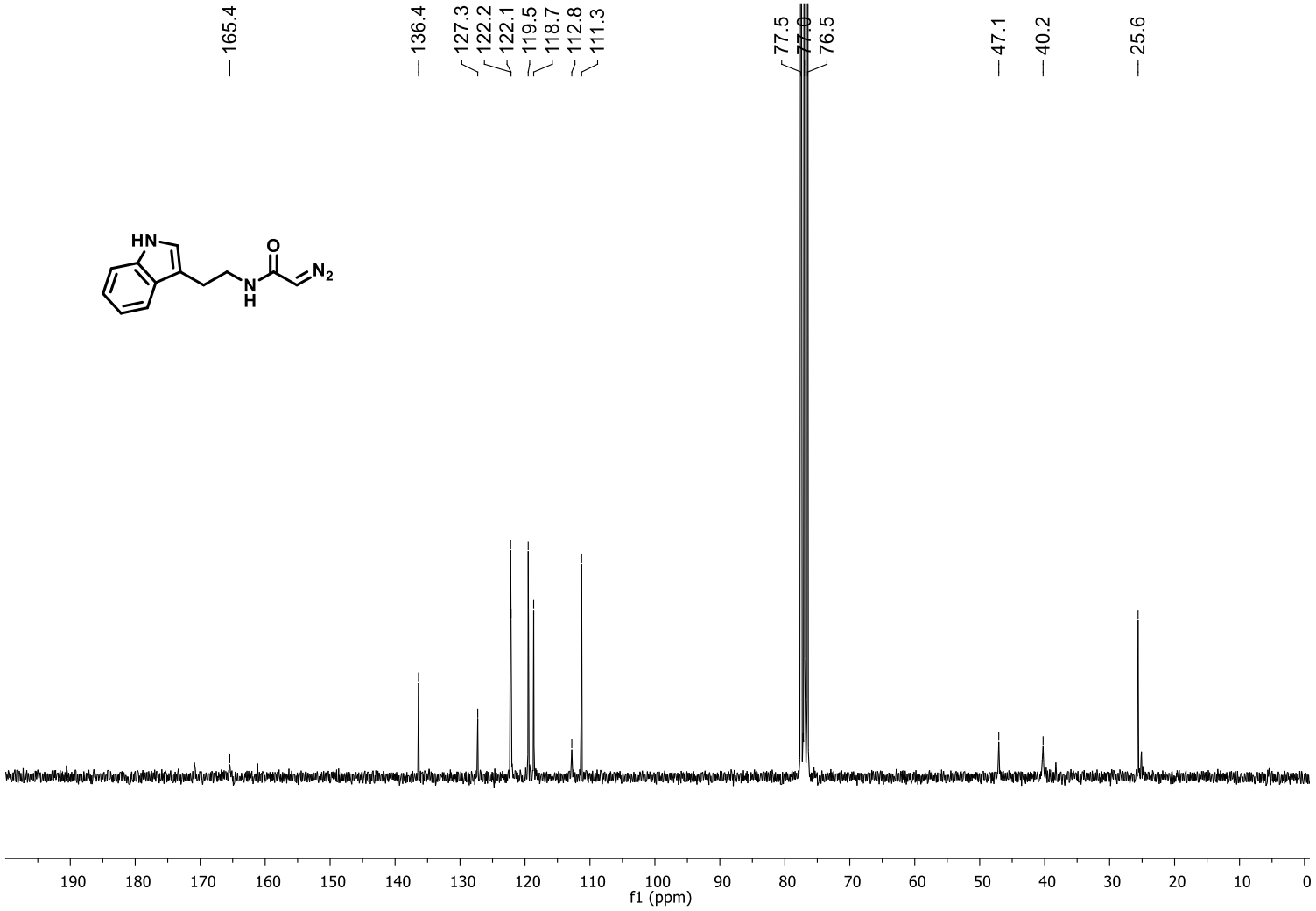
1dd - ^{13}C NMR (62.5 MHz, $CDCl_3$)



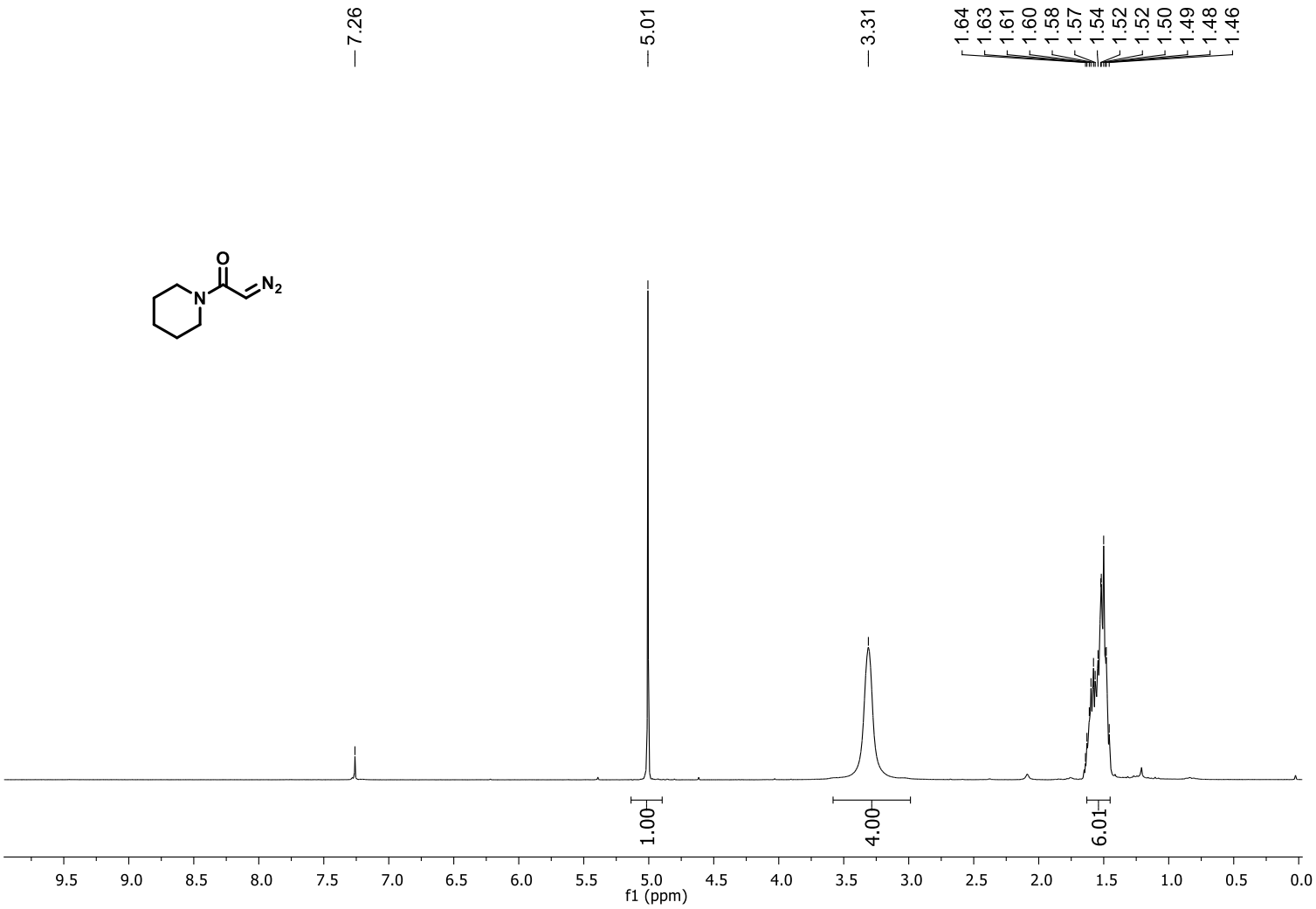
1ee - ^{1}H NMR (250 MHz, $CDCl_3$)



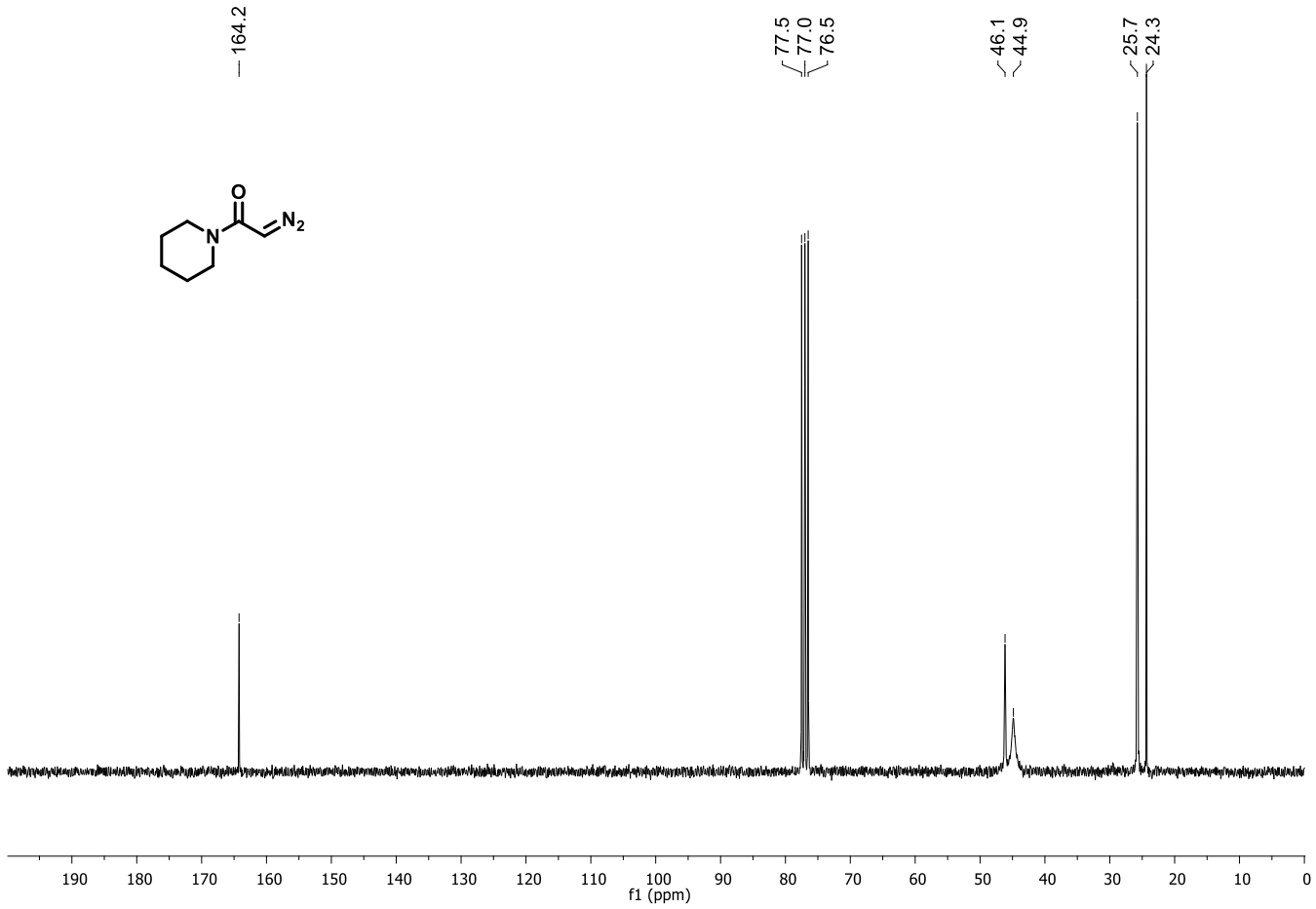
1ee - ^{13}C NMR (62.5 MHz, $CDCl_3$)



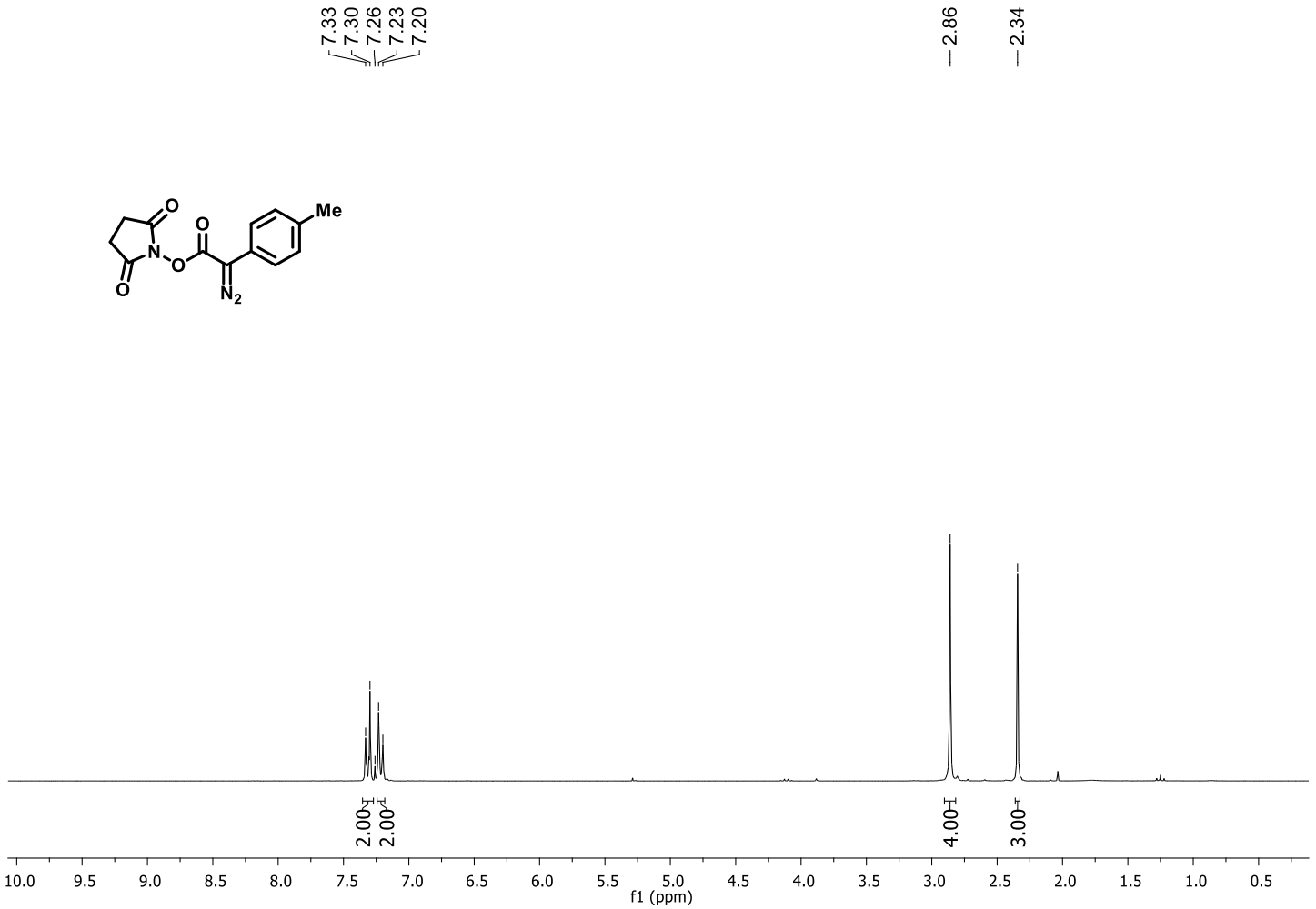
1ff - ^{1}H NMR (250 MHz, $CDCl_3$)



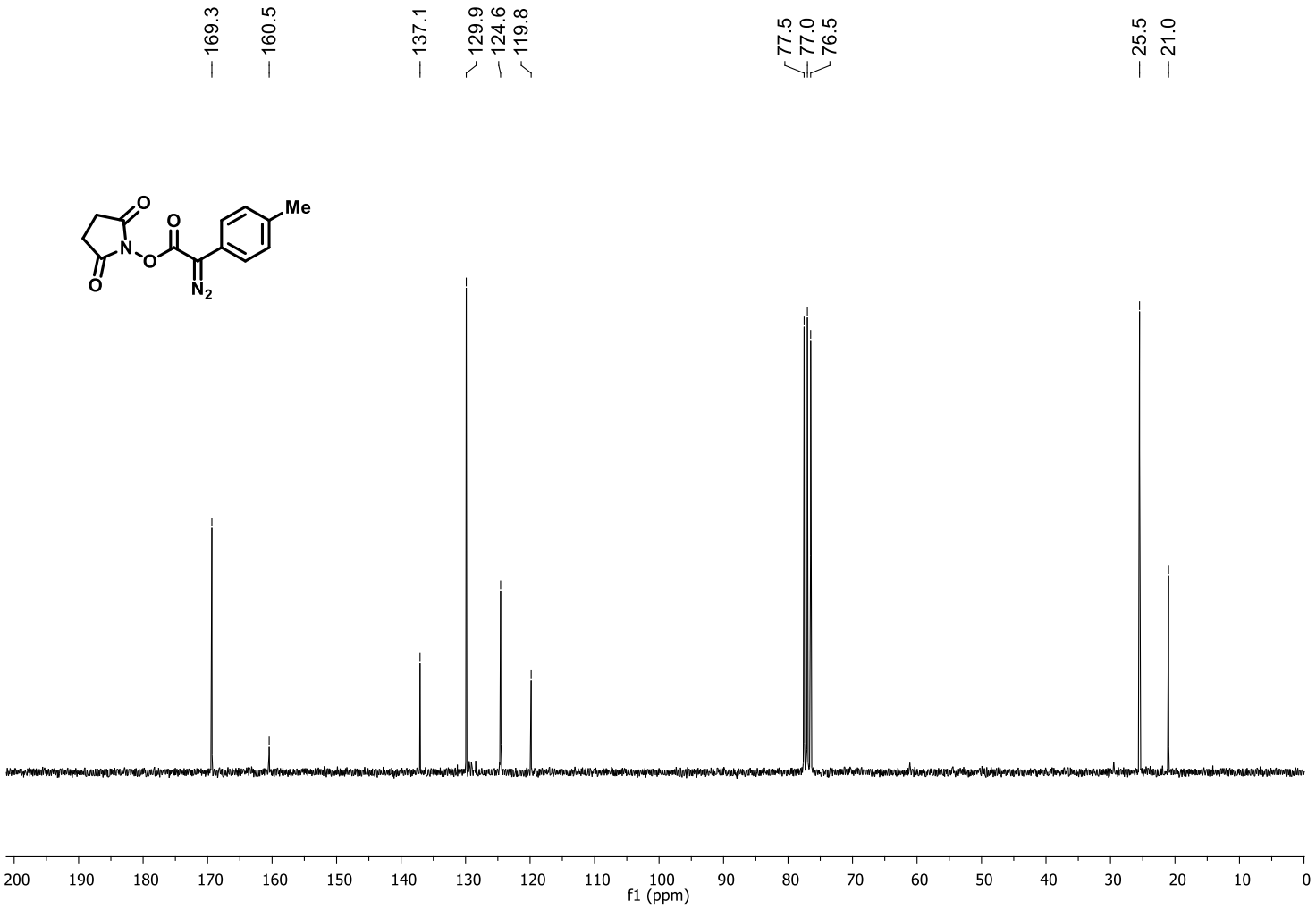
1ff - ^{13}C NMR (62.5 MHz, $CDCl_3$)



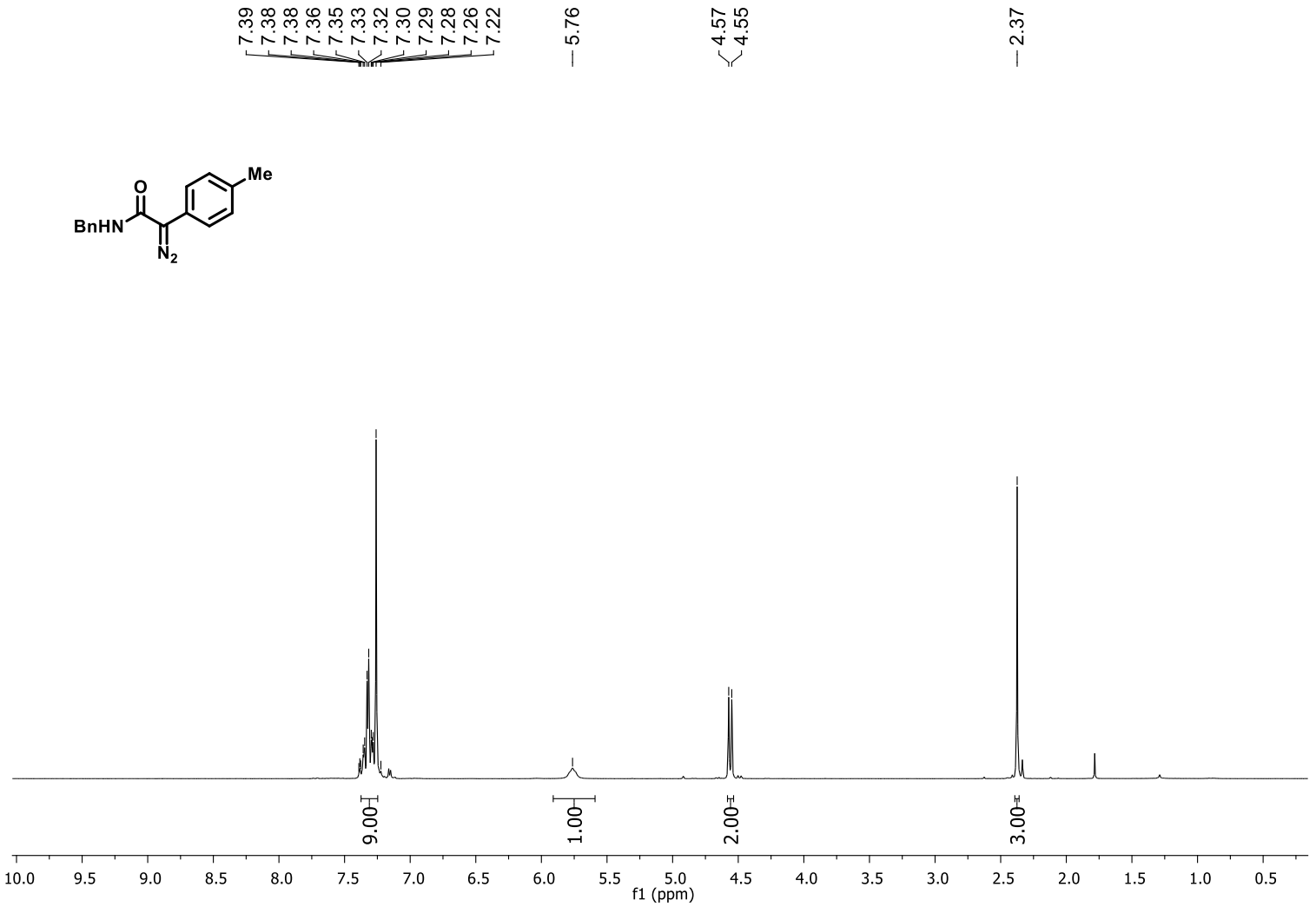
Pre-1gg - ^{1}H NMR (250 MHz, $CDCl_3$)



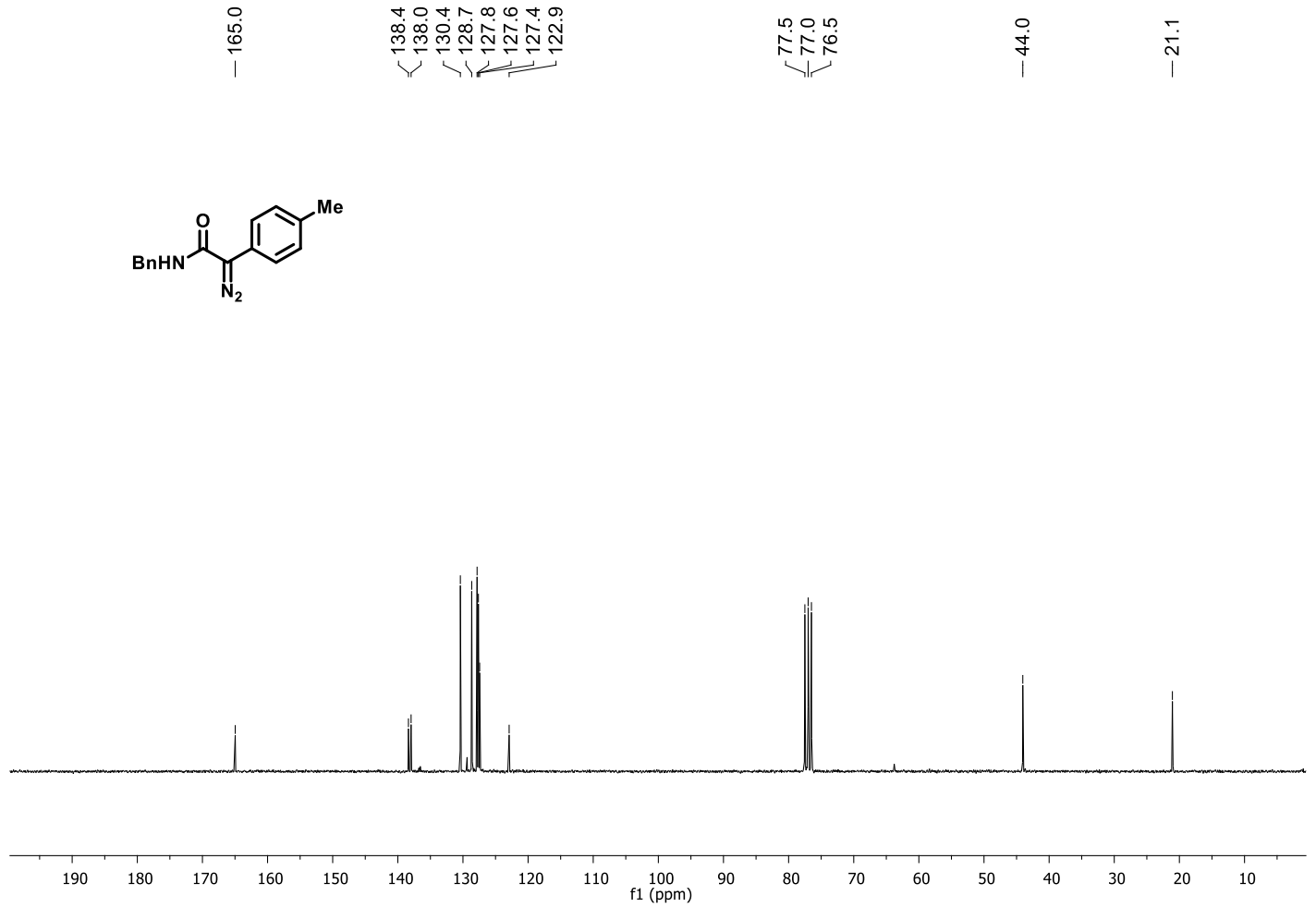
Pre-1gg - ^{13}C NMR (62.5 MHz, $CDCl_3$)



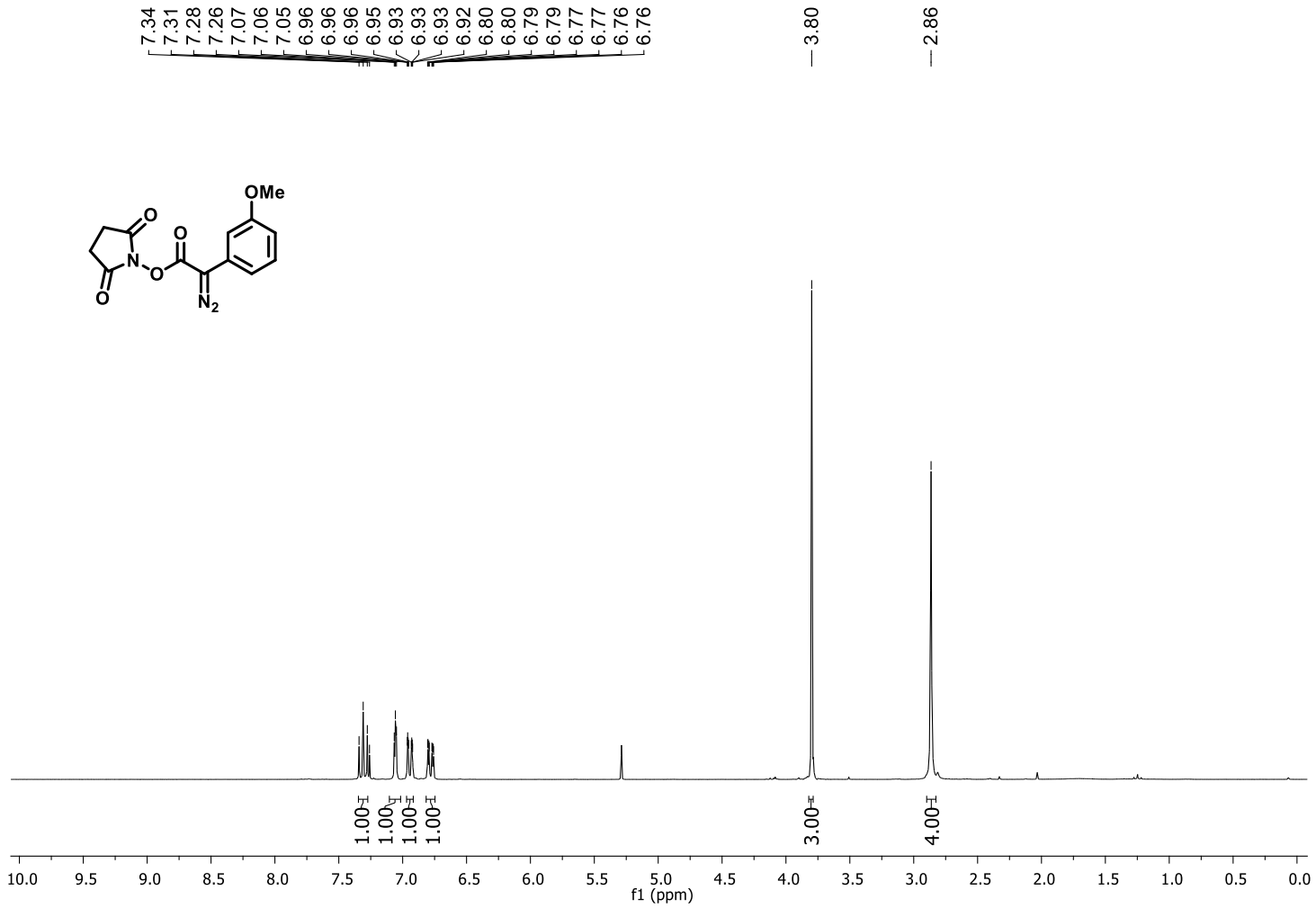
1gg - ^{1}H NMR (250 MHz, $CDCl_3$)



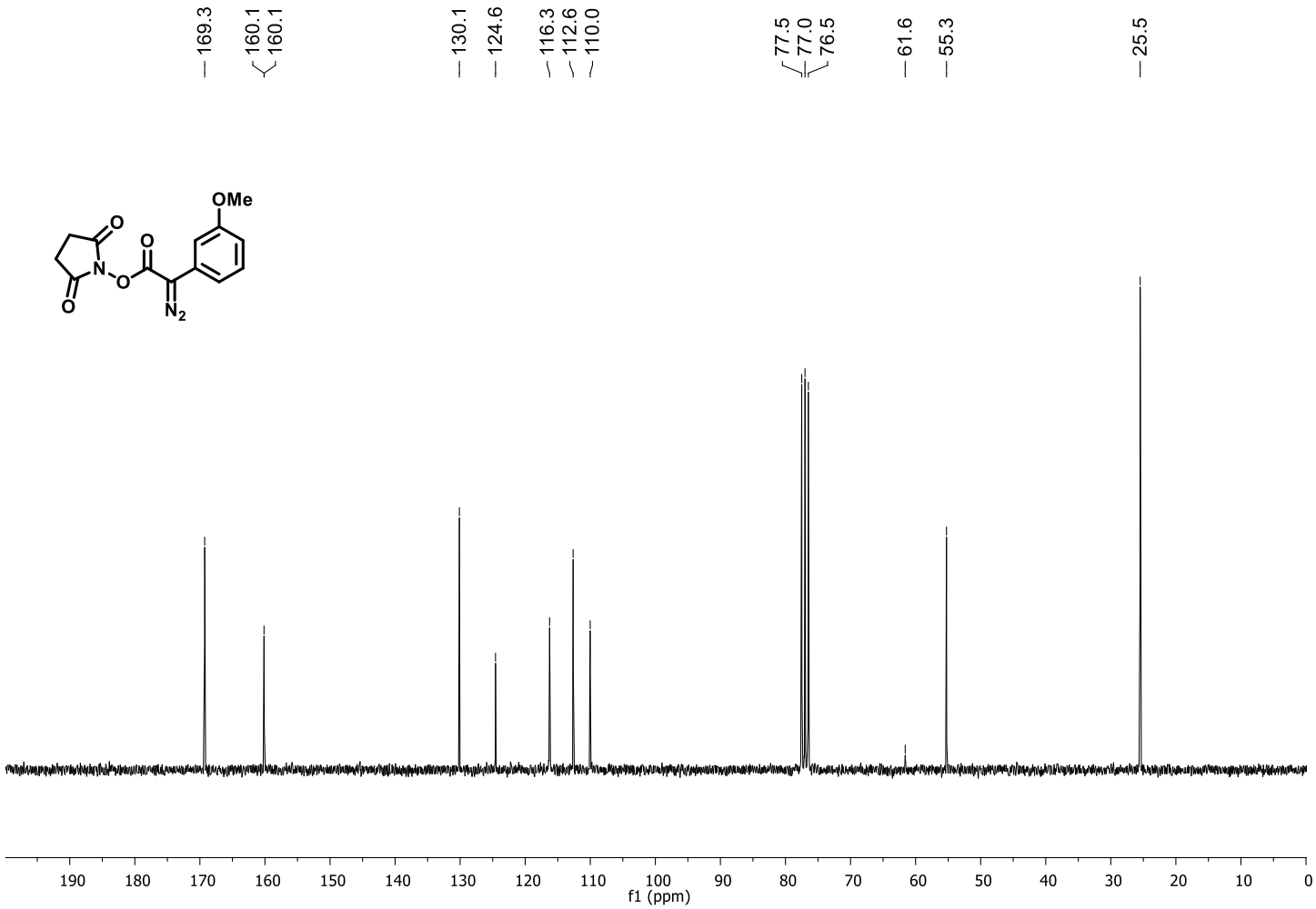
1gg - ^{13}C NMR (62.5 MHz, $CDCl_3$)



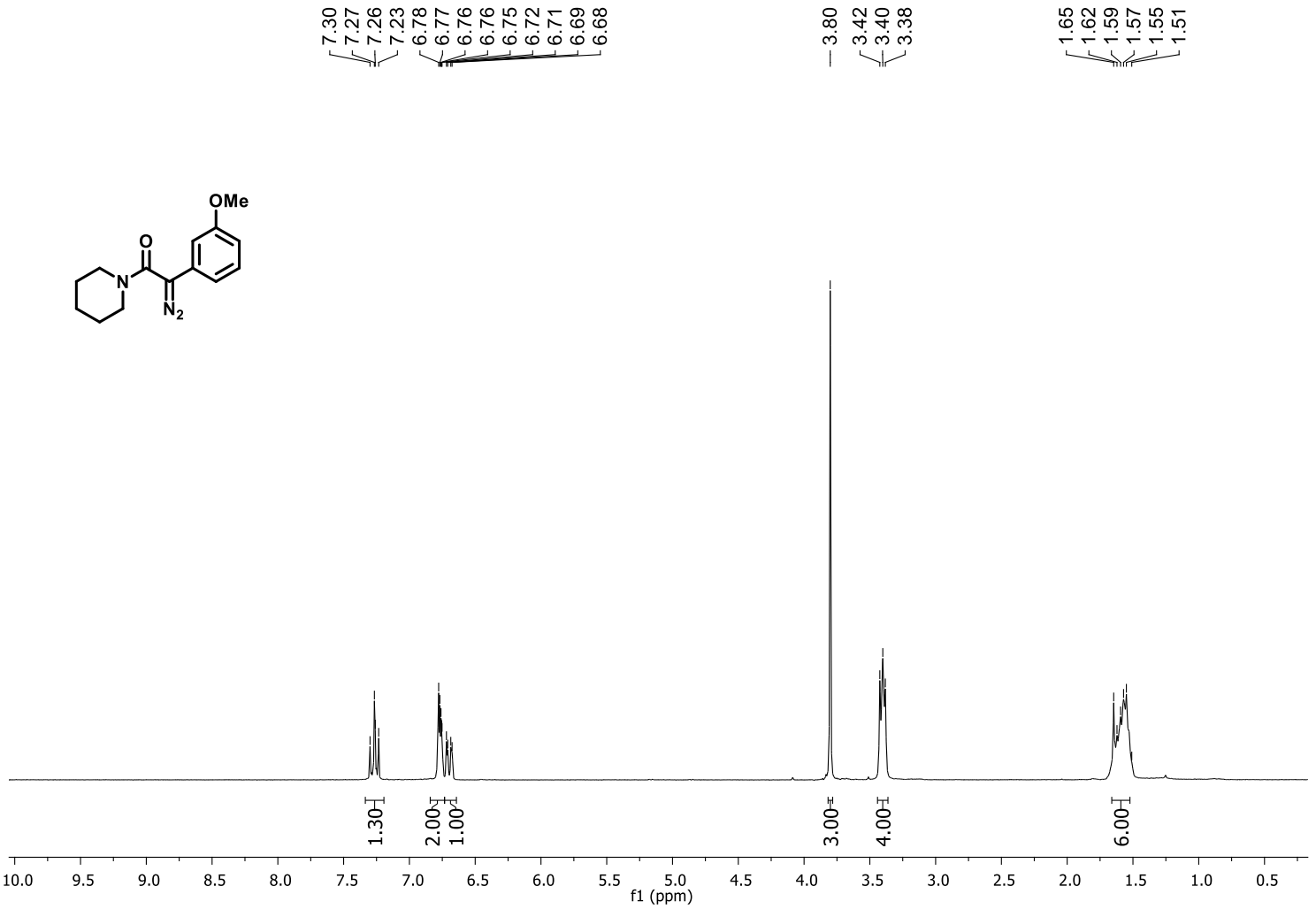
pre-1hh - ^{1}H NMR (250 MHz, $CDCl_3$)



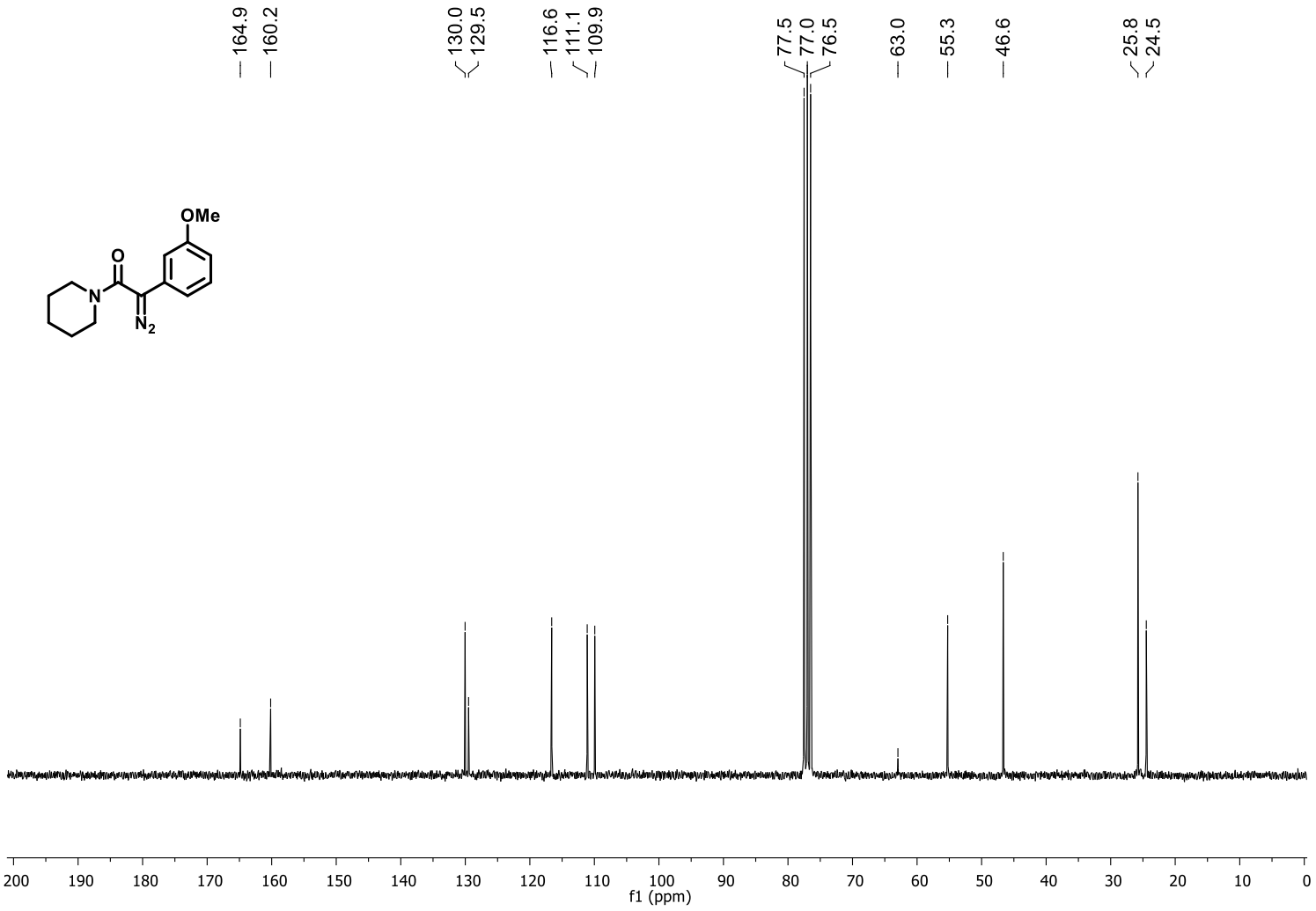
pre-1hh - ^{13}C NMR (62.5 MHz, $CDCl_3$)



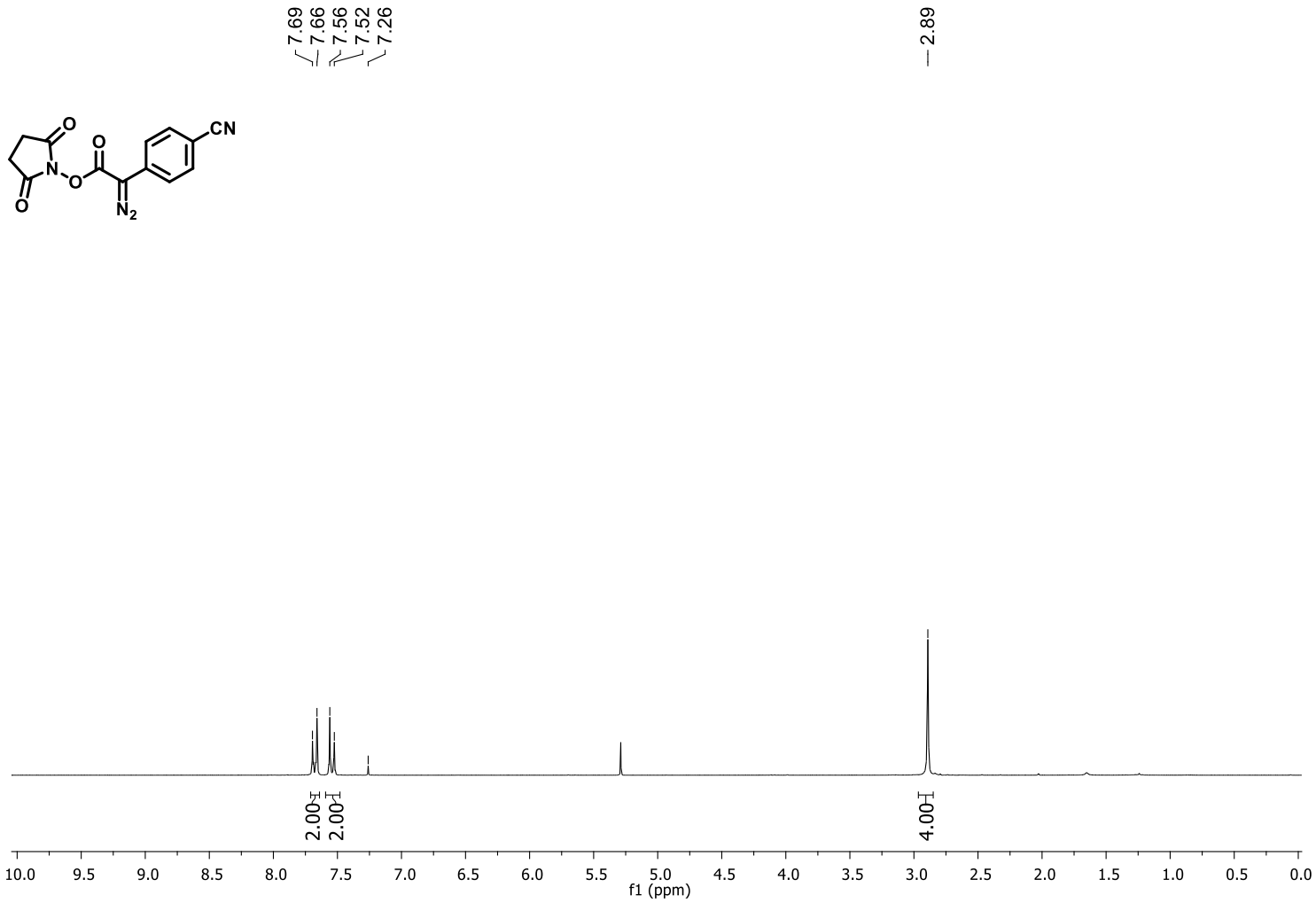
1hh - ^{1}H NMR (250 MHz, $CDCl_3$)



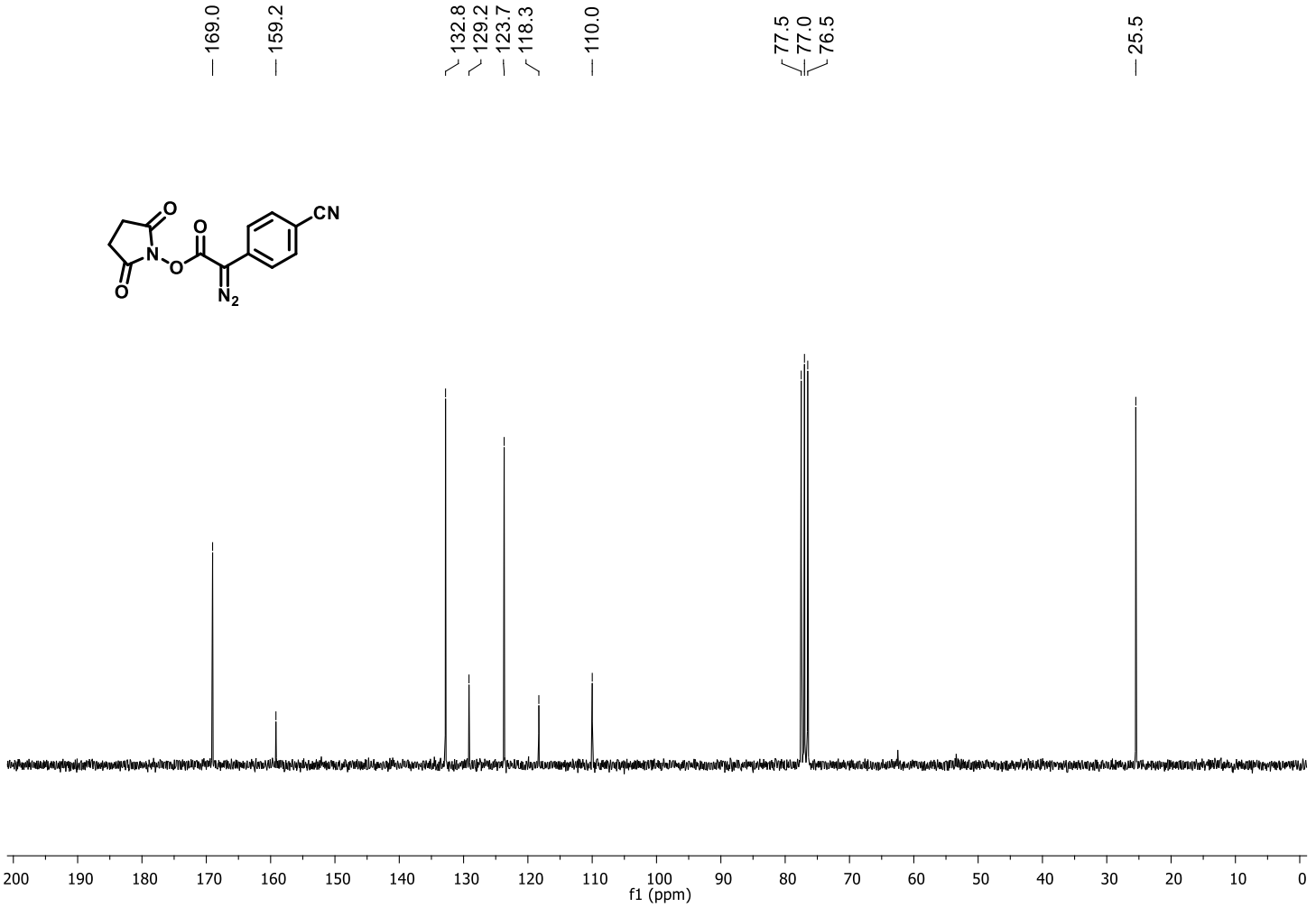
1hh - ^{13}C NMR (62.5 MHz, $CDCl_3$)



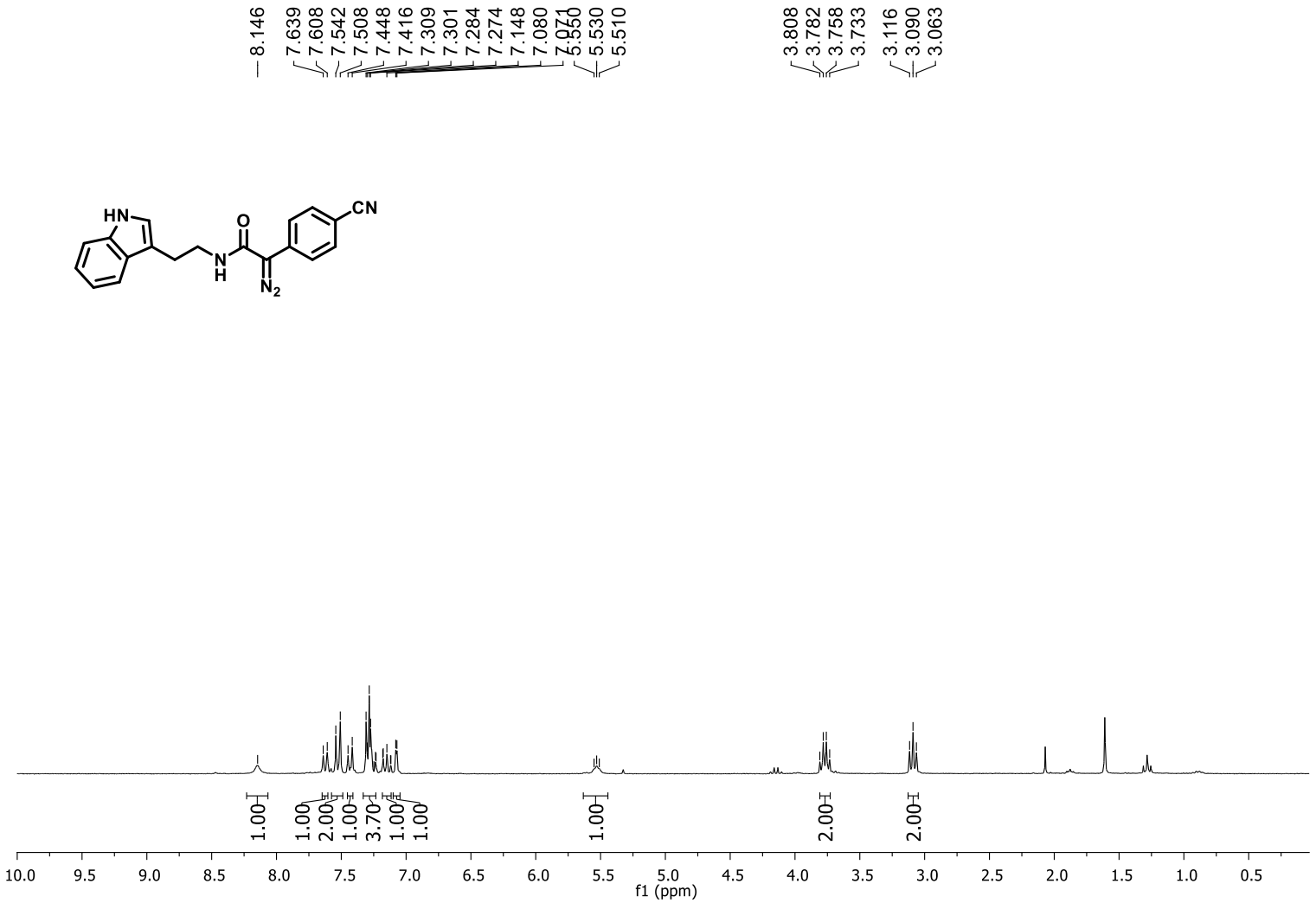
pre-1ii - ^{1}H NMR (250 MHz, $CDCl_3$)



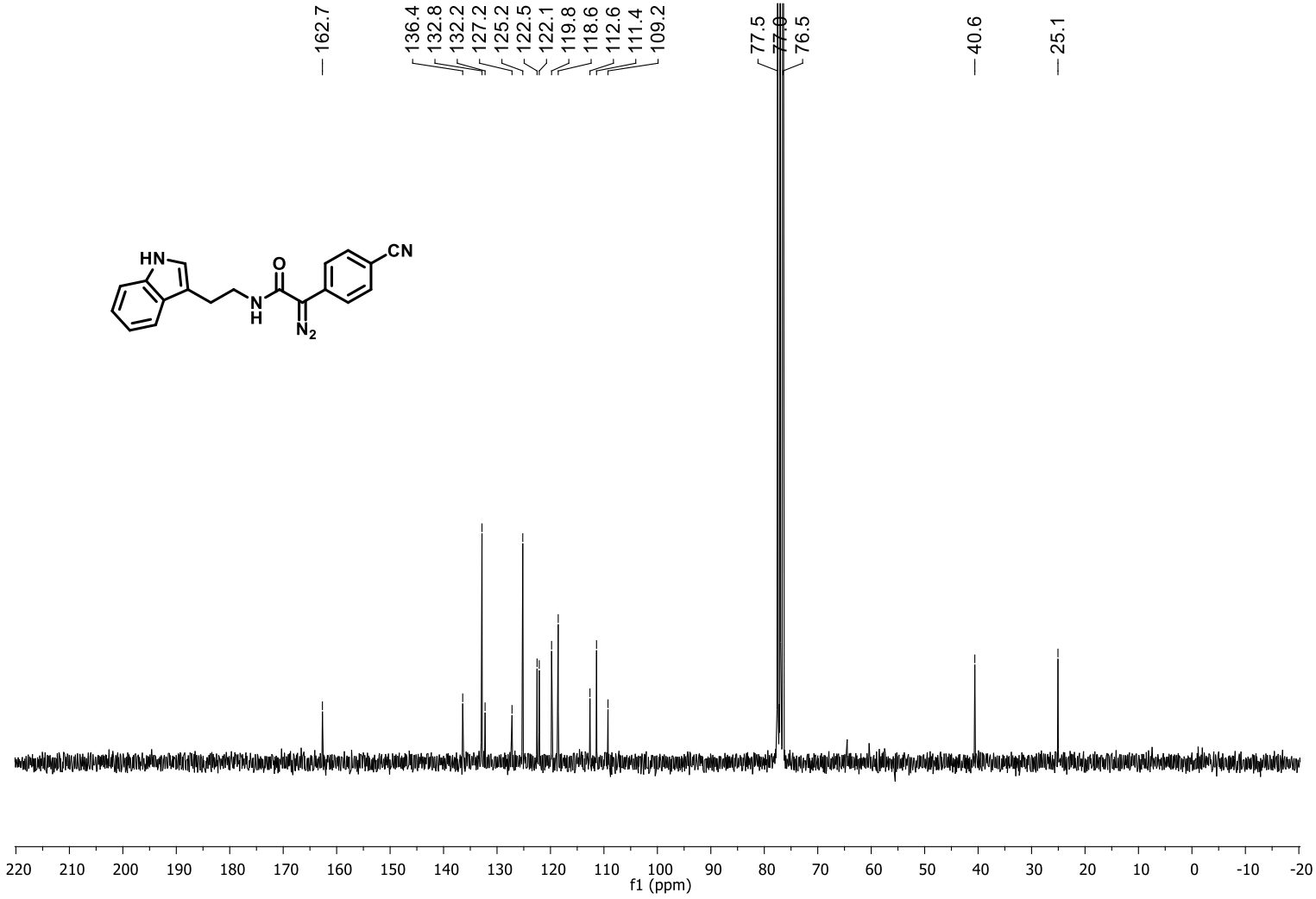
pre-1ii - ^{13}C NMR (62.5 MHz, $CDCl_3$)



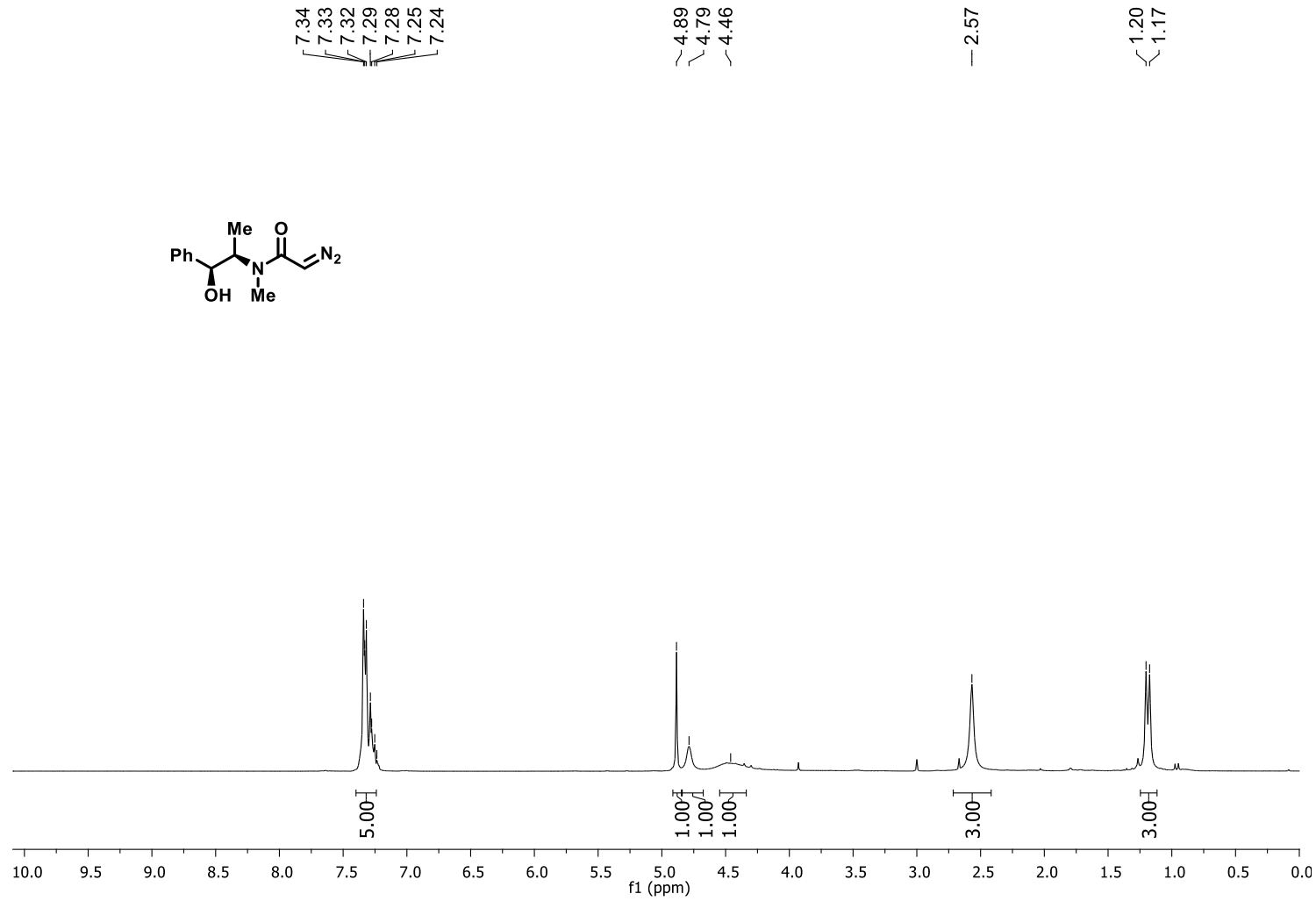
1ii - ^{1}H NMR (250 MHz, $CDCl_3$)



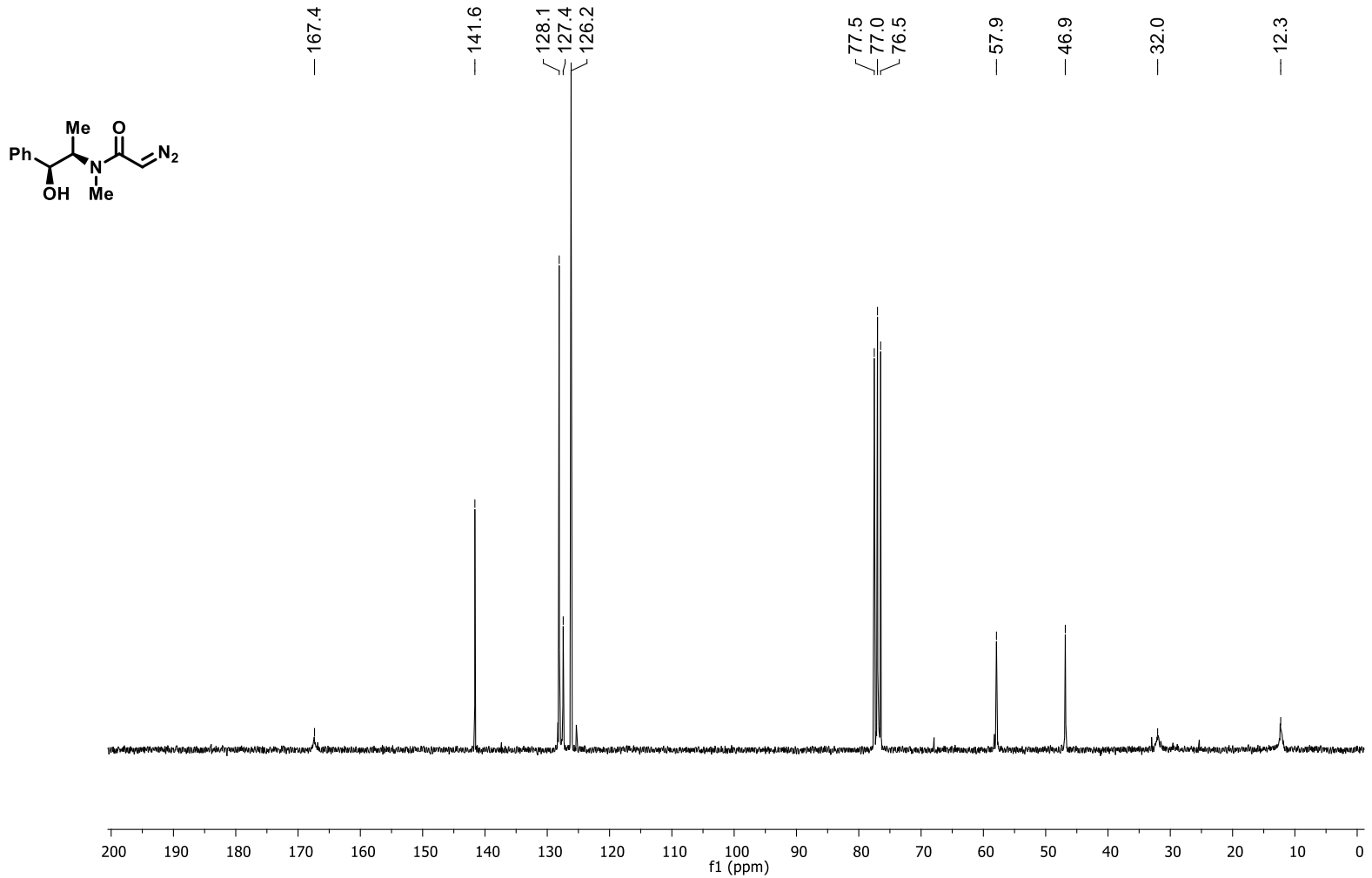
1ii - ^{13}C NMR (62.5 MHz, $CDCl_3$)



1rr - ^{1}H NMR (250 MHz, $CDCl_3$)

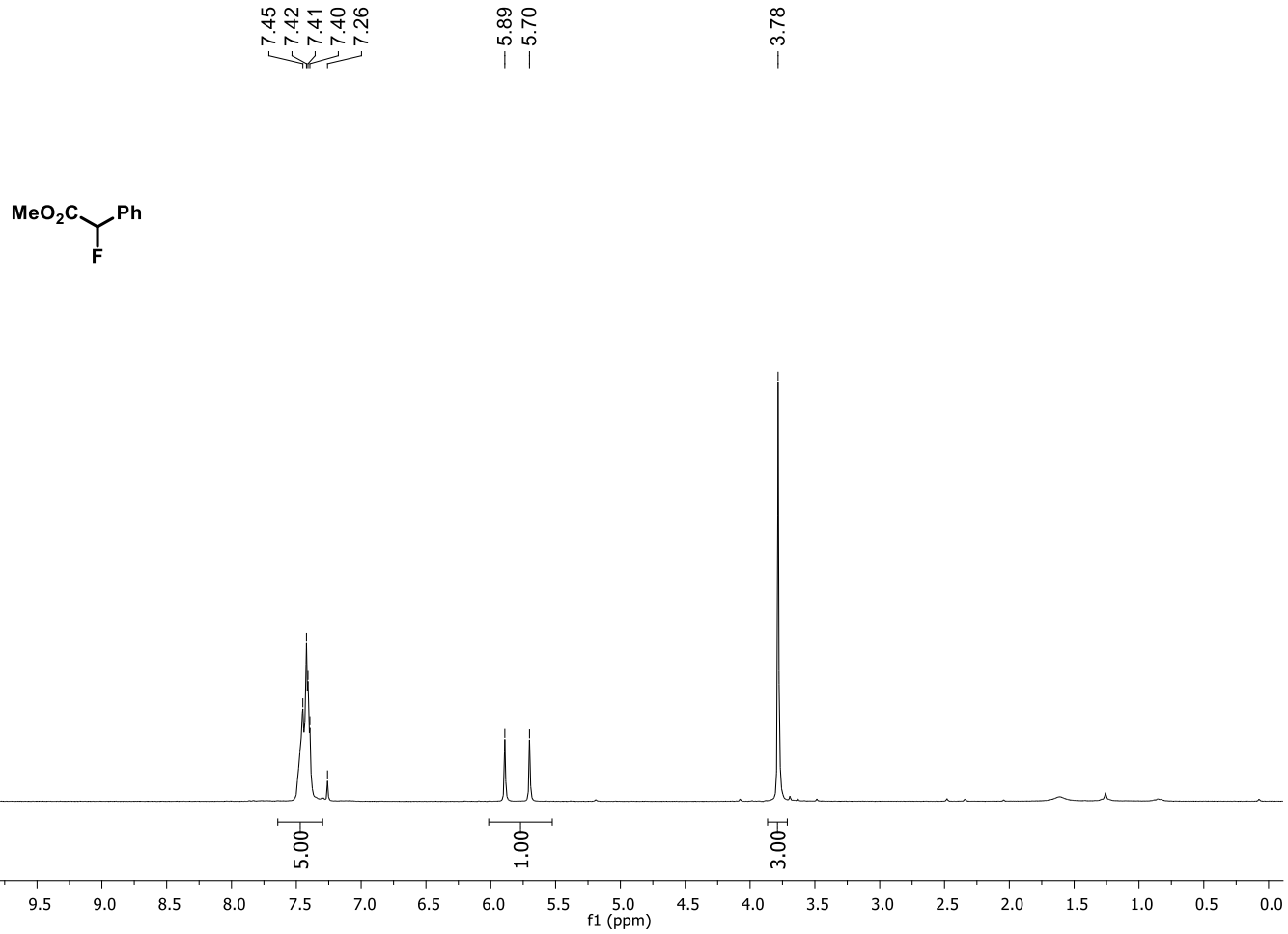


1rr - ^{13}C NMR (62.5 MHz, $CDCl_3$)

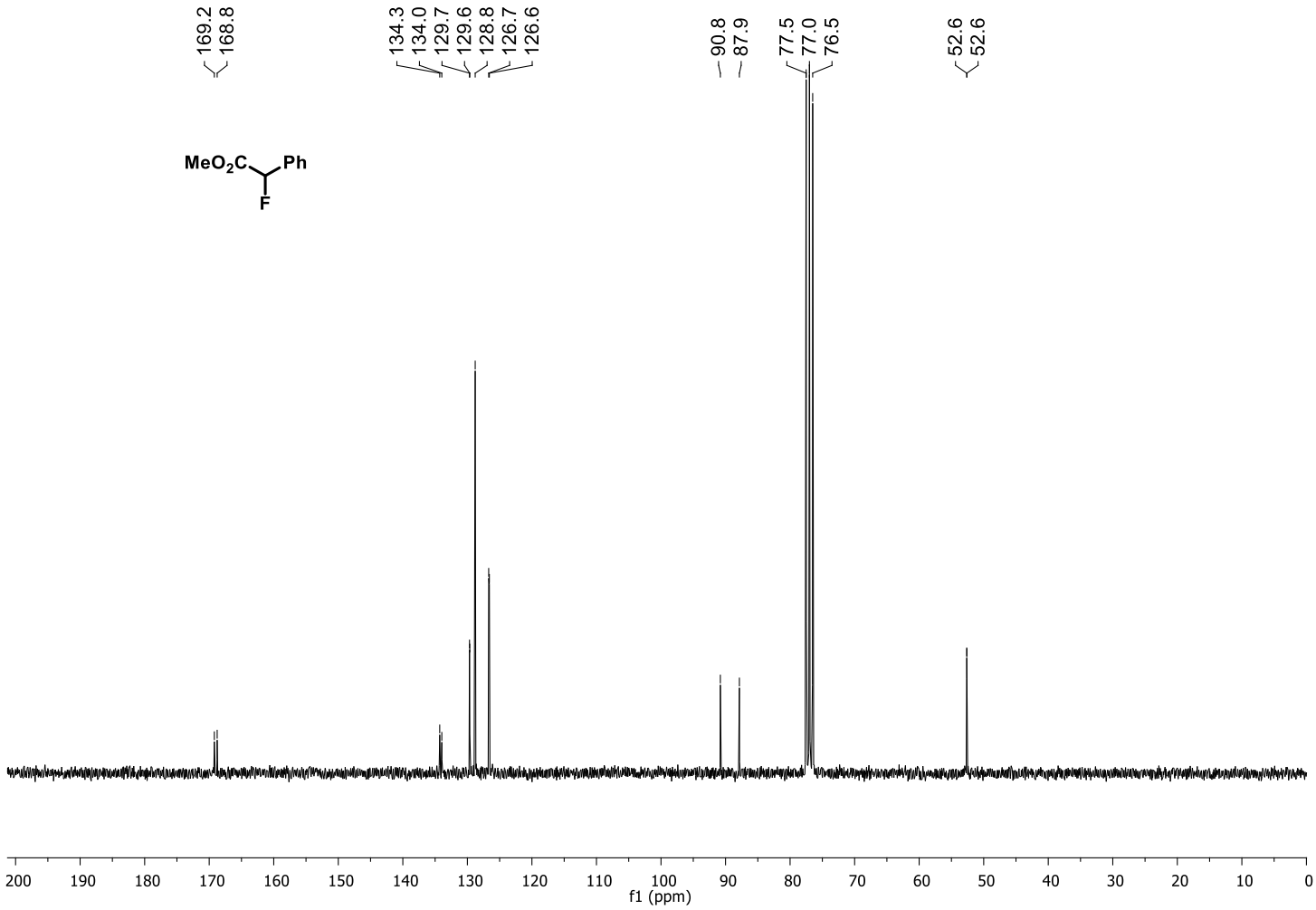


2.2. NMR of α-Fluorinated Carbonyl Compounds 3

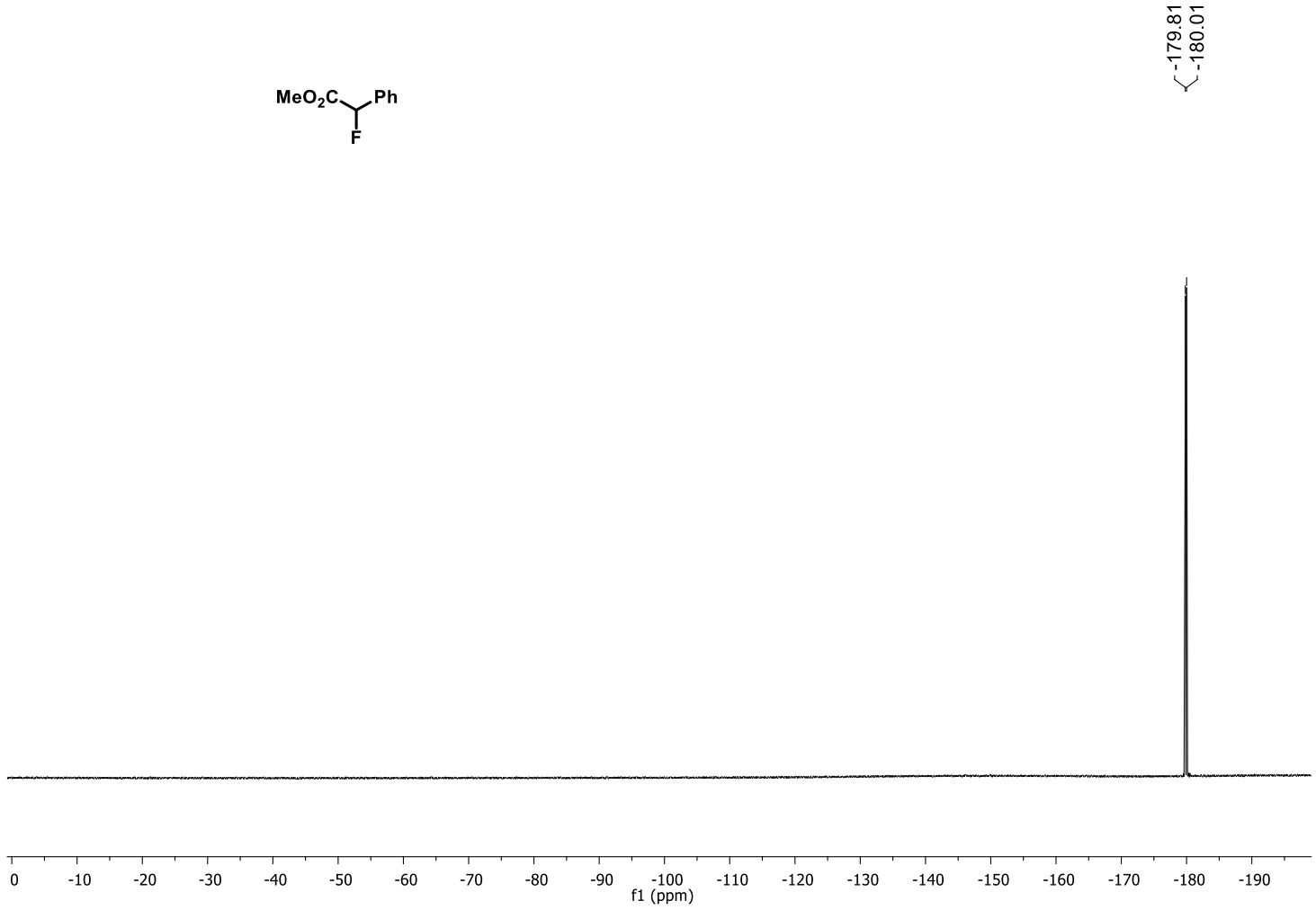
3a - ^{1}H NMR (250 MHz, $CDCl_3$)



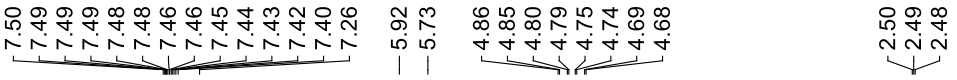
3a - ^{13}C NMR (62.5 MHz, $CDCl_3$)

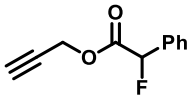


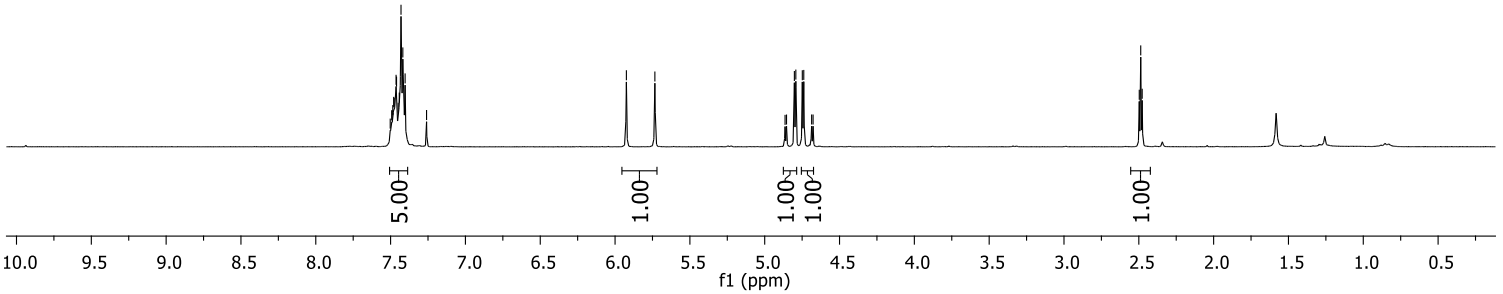
3a - ^{19}F NMR (235 MHz, $CDCl_3$)



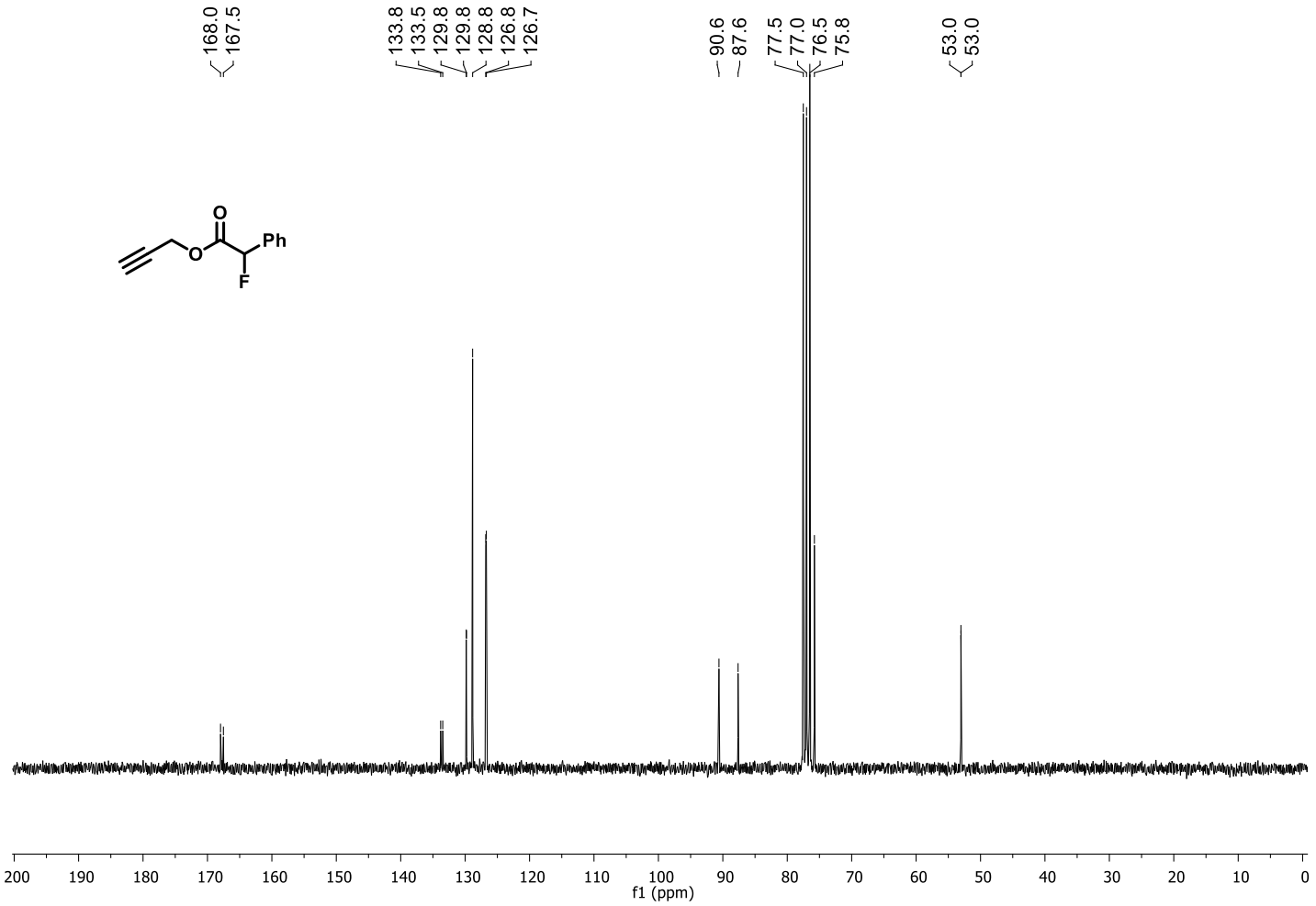
3b - ^{1}H NMR (250 MHz, $CDCl_3$)



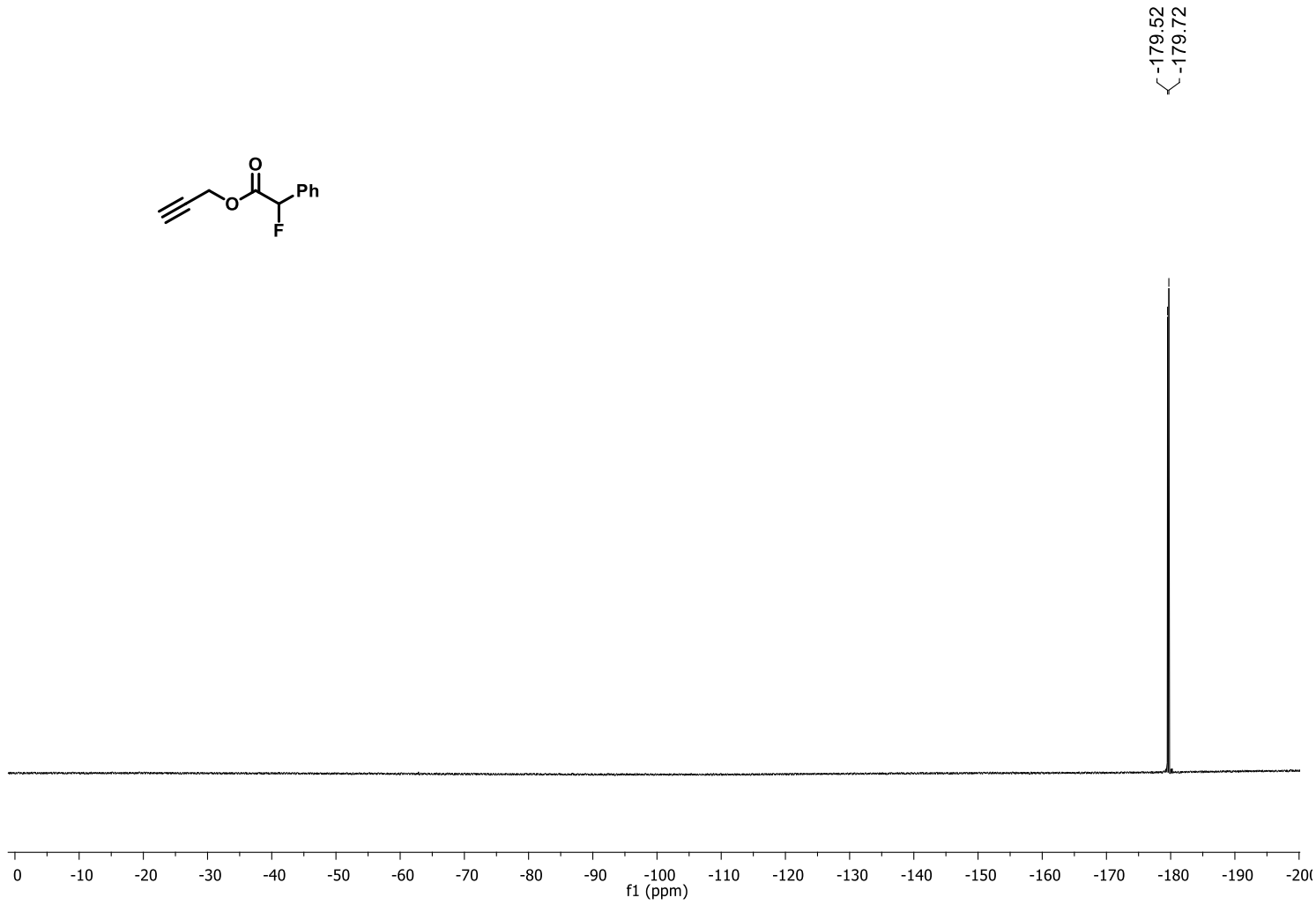




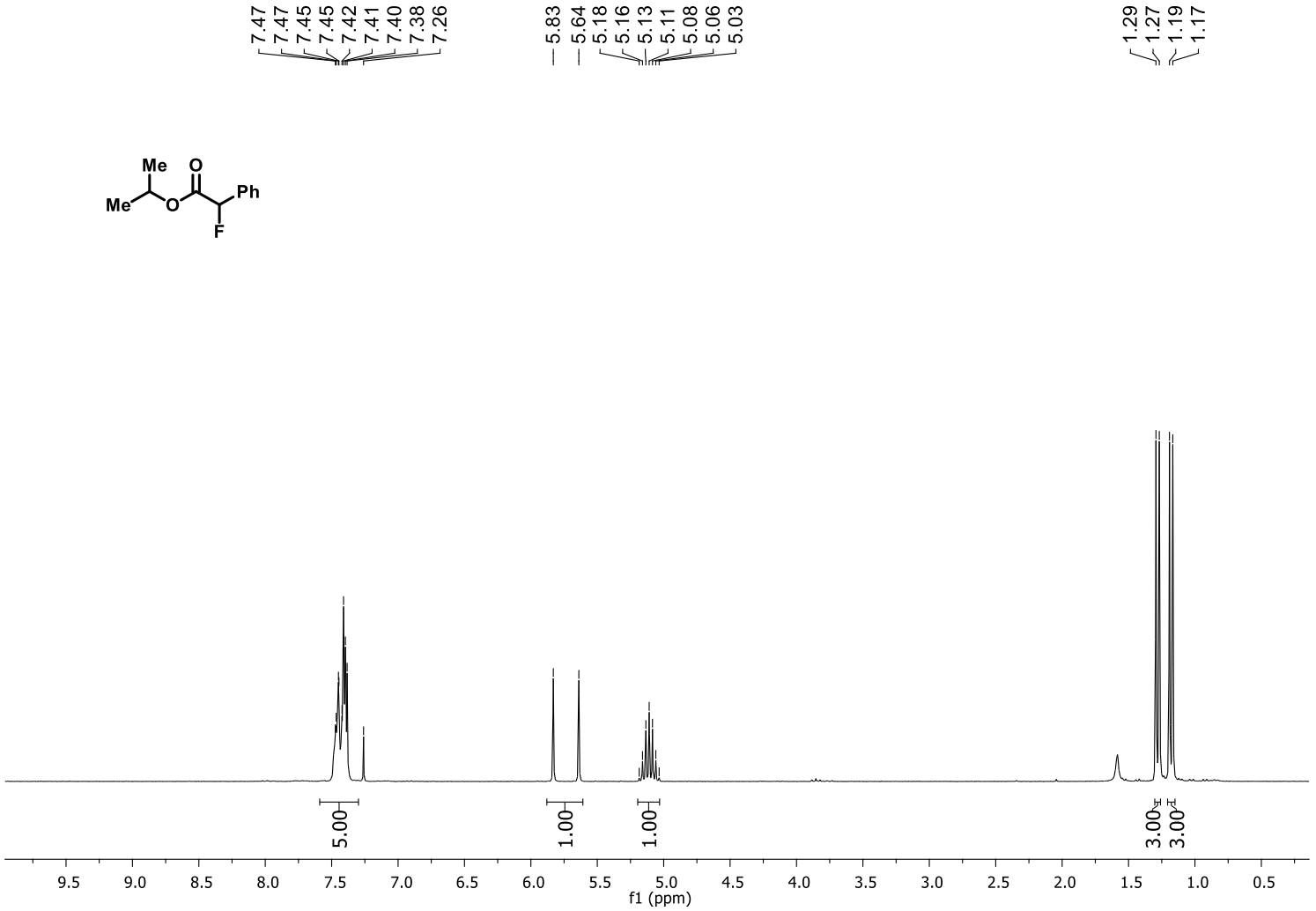
3b - ^{13}C NMR (62.5 MHz, $CDCl_3$)



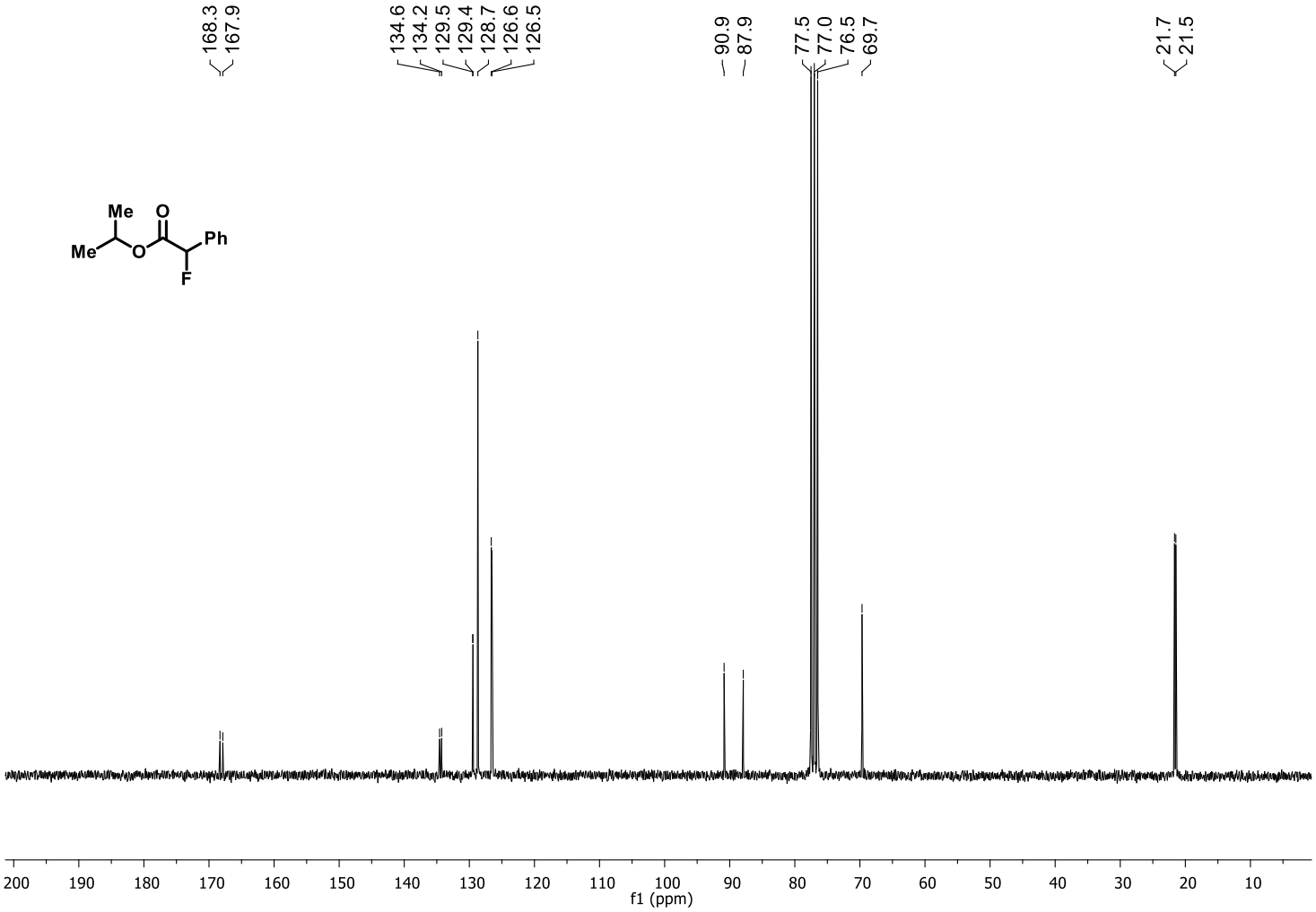
3b - ^{19}F NMR (235 MHz, $CDCl_3$)



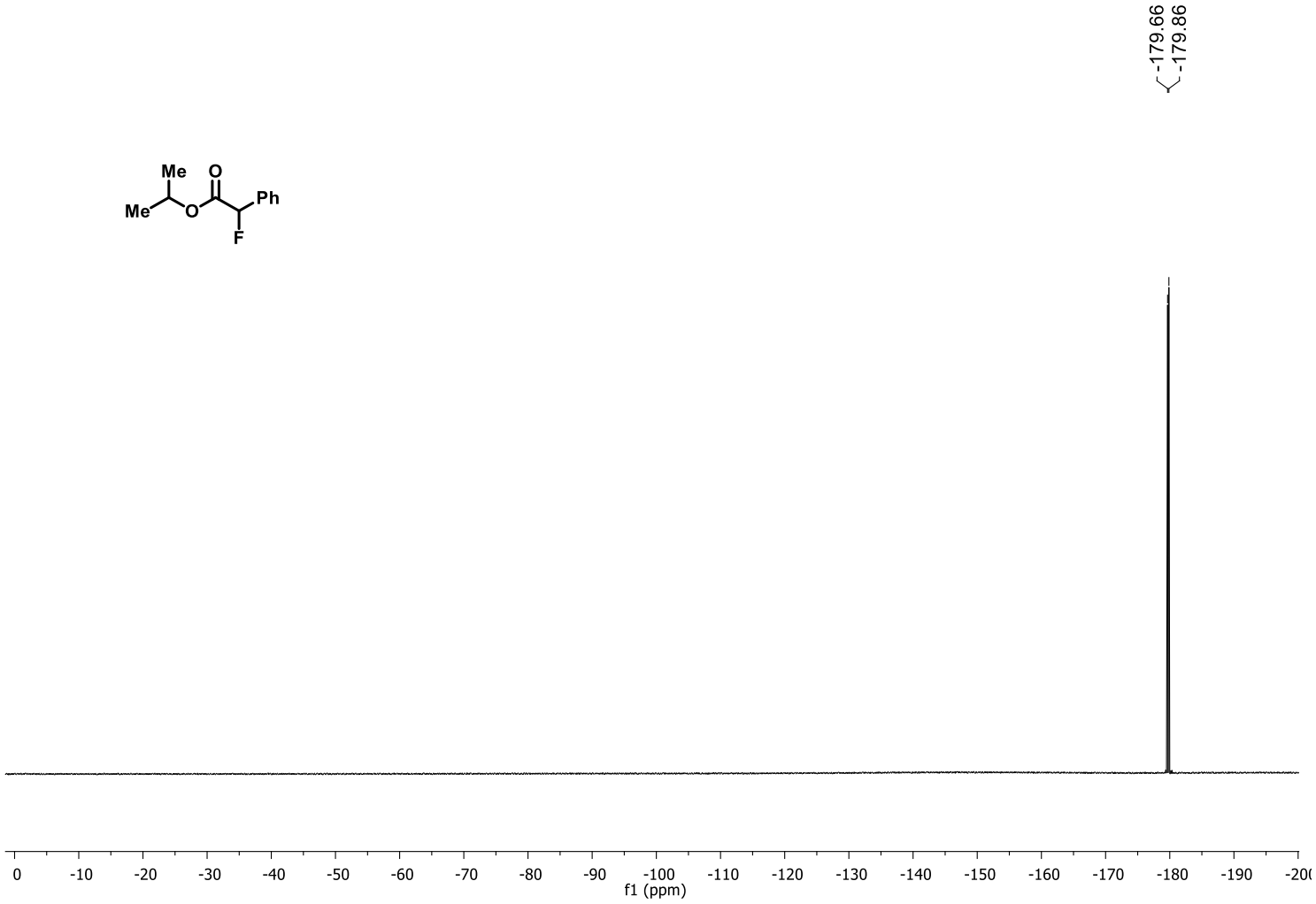
3c - ^{1}H NMR (250 MHz, $CDCl_3$)



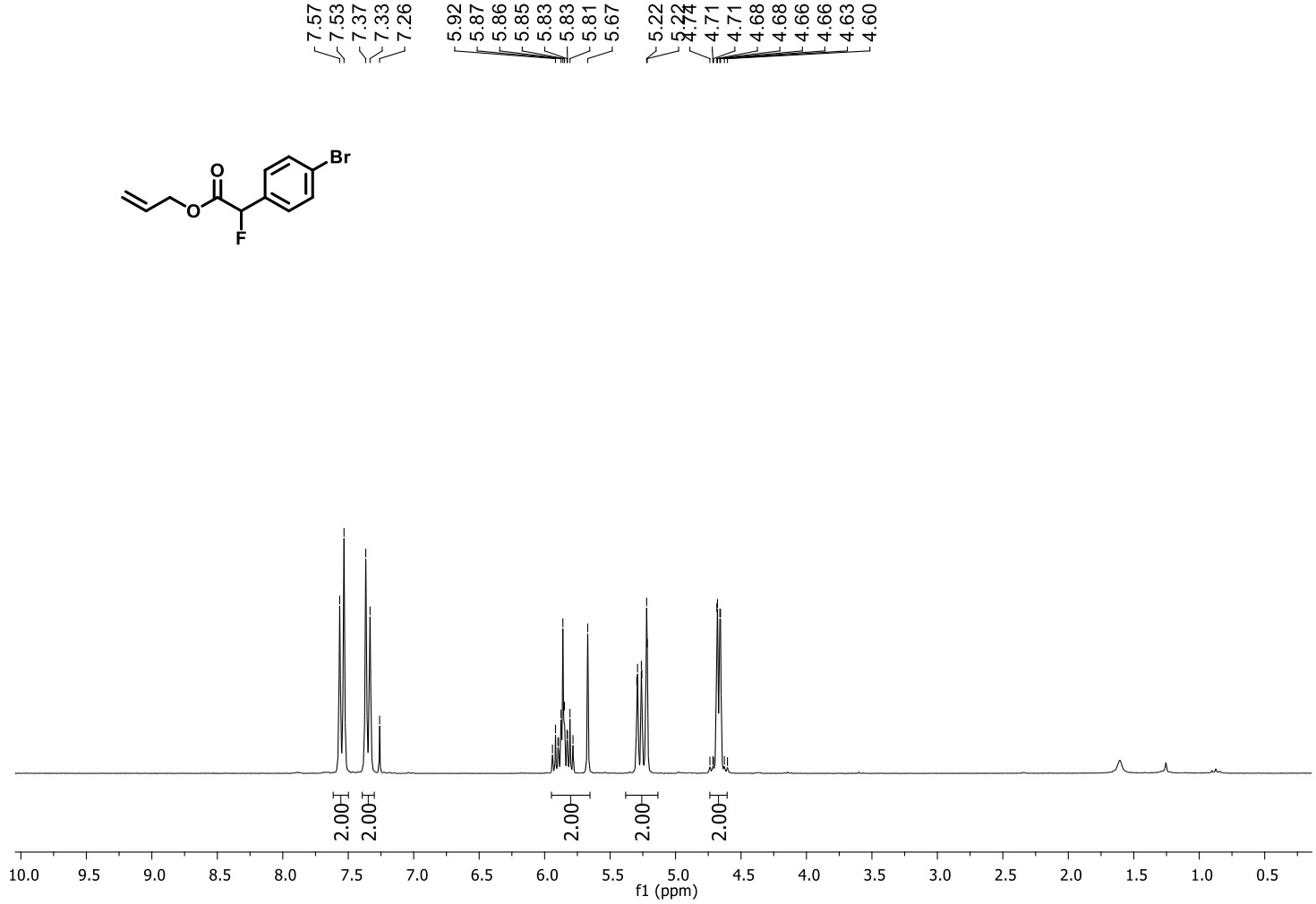
3c – ^{13}C NMR (62.5 MHz, $CDCl_3$)



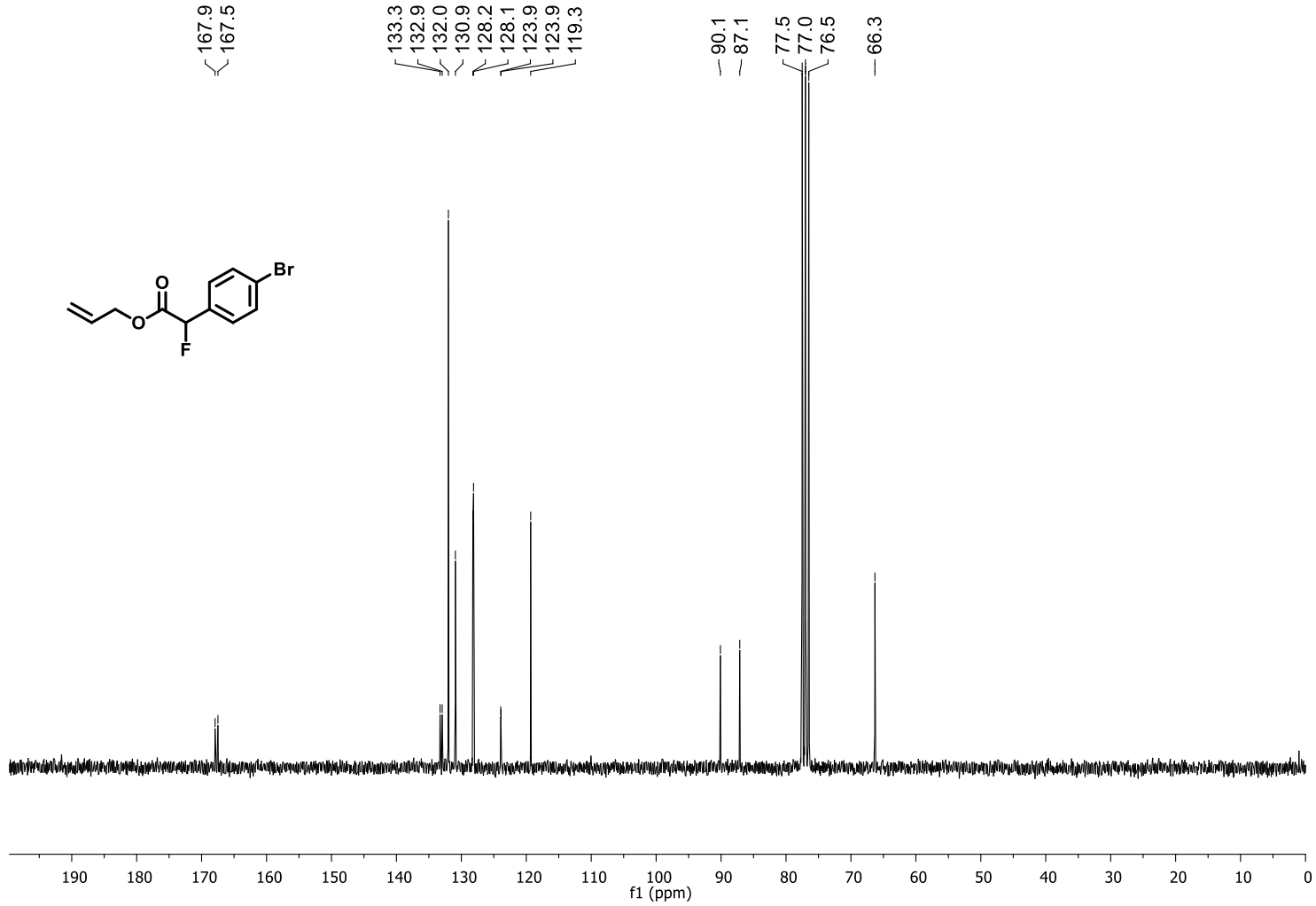
3c – ^{19}F NMR (235 MHz, $CDCl_3$)



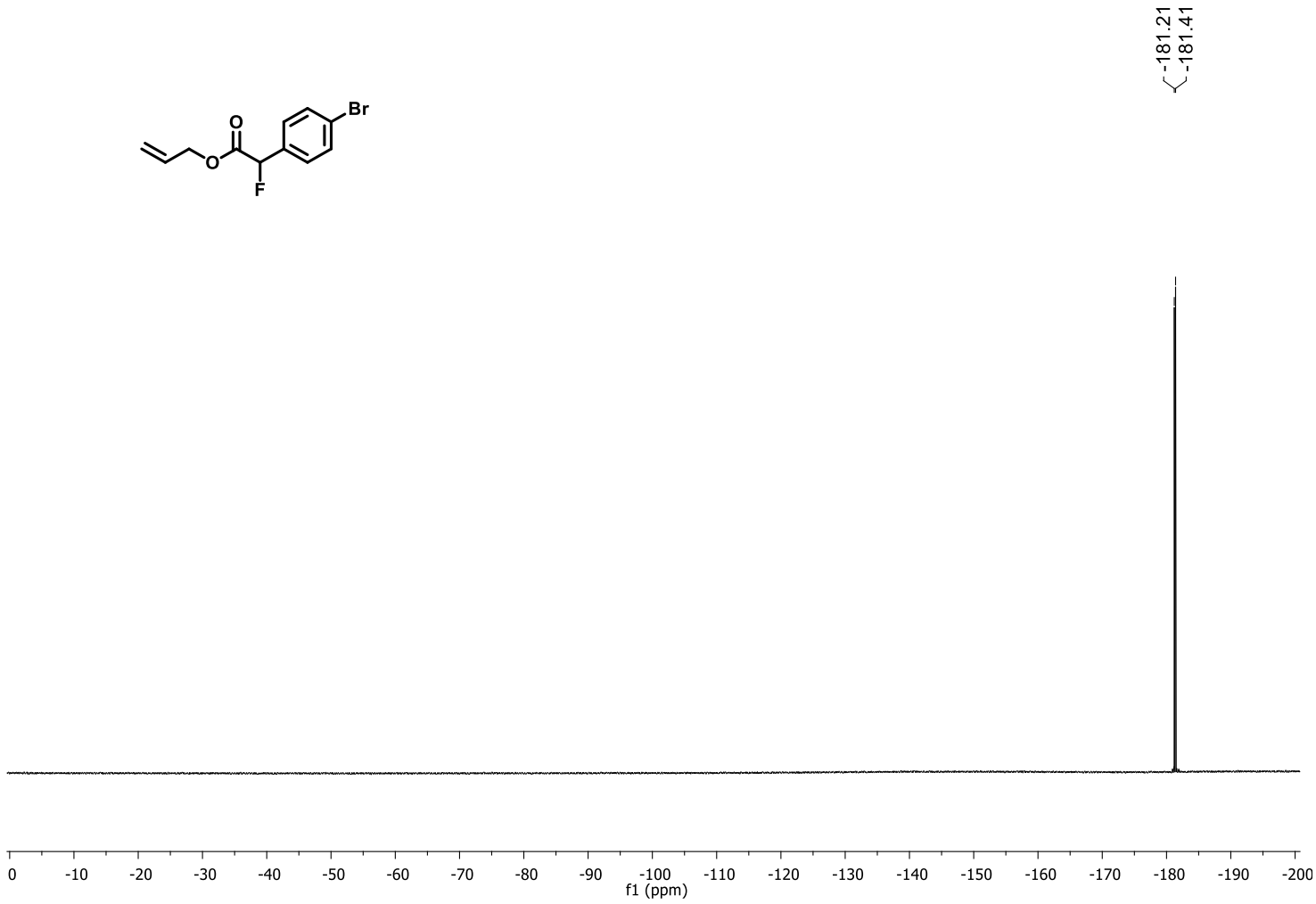
3d - ^{1}H NMR (250 MHz, $CDCl_3$)



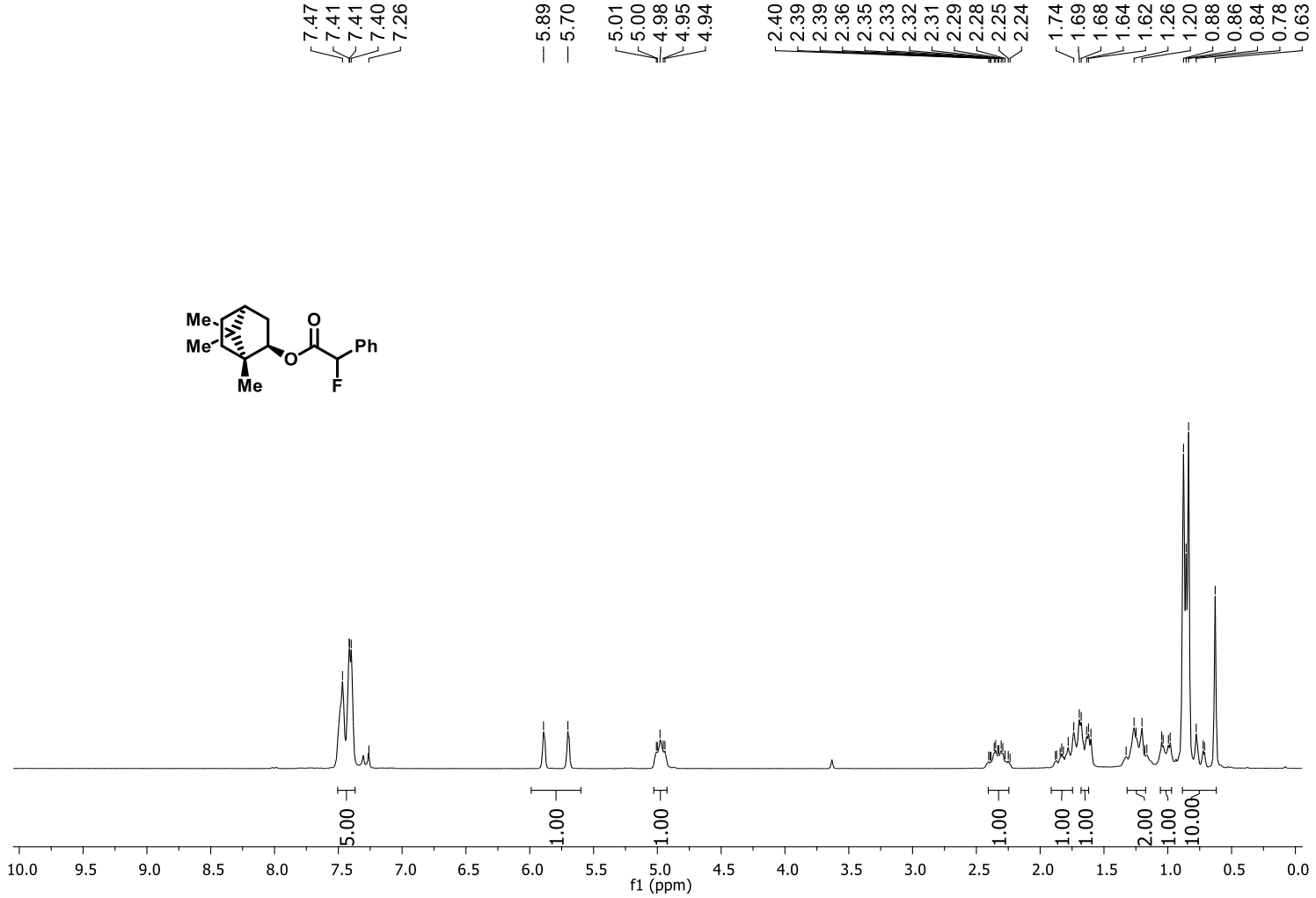
3d - ^{13}C NMR (62.5 MHz, $CDCl_3$)



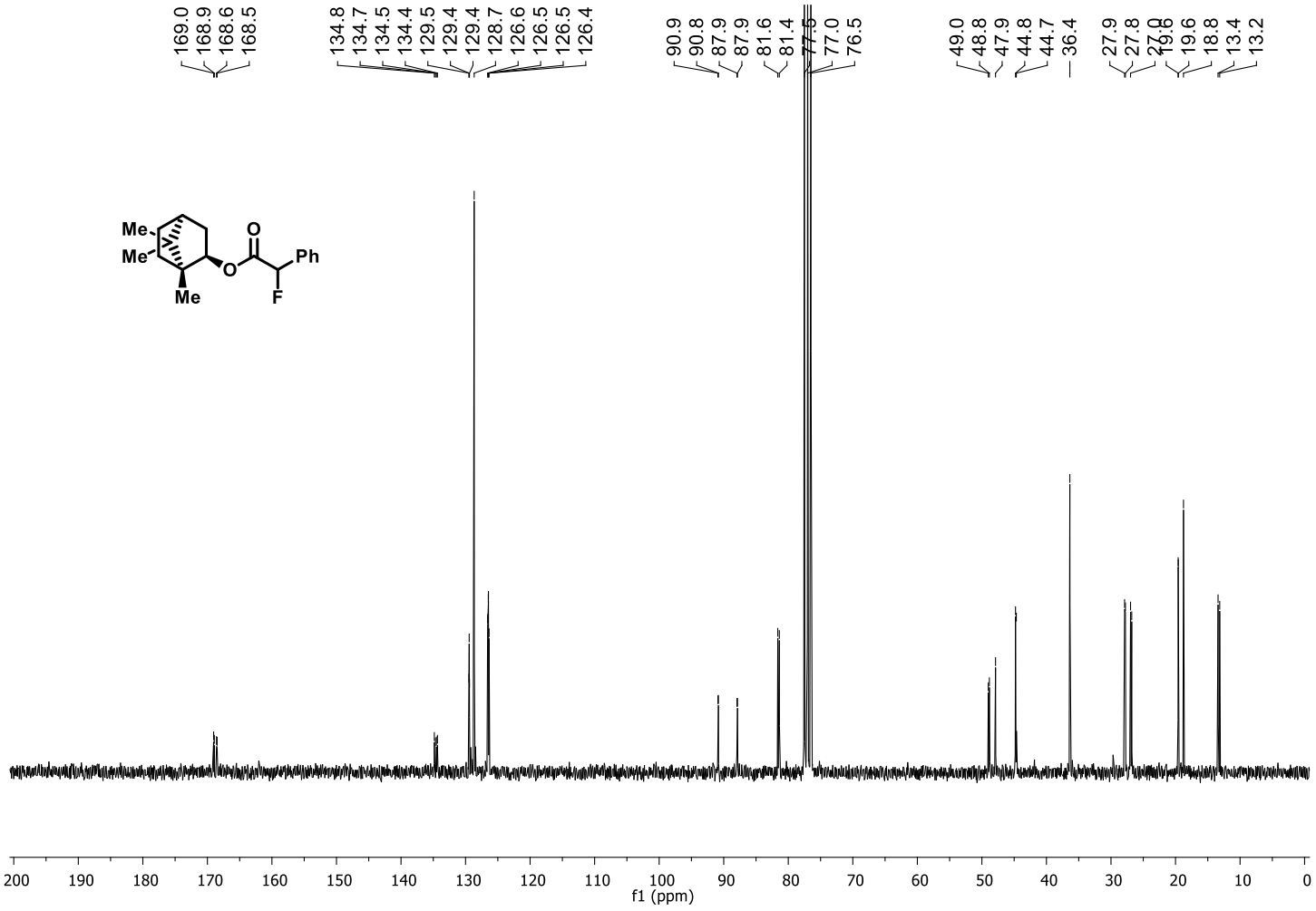
3d - ^{19}F NMR (235 MHz, $CDCl_3$)



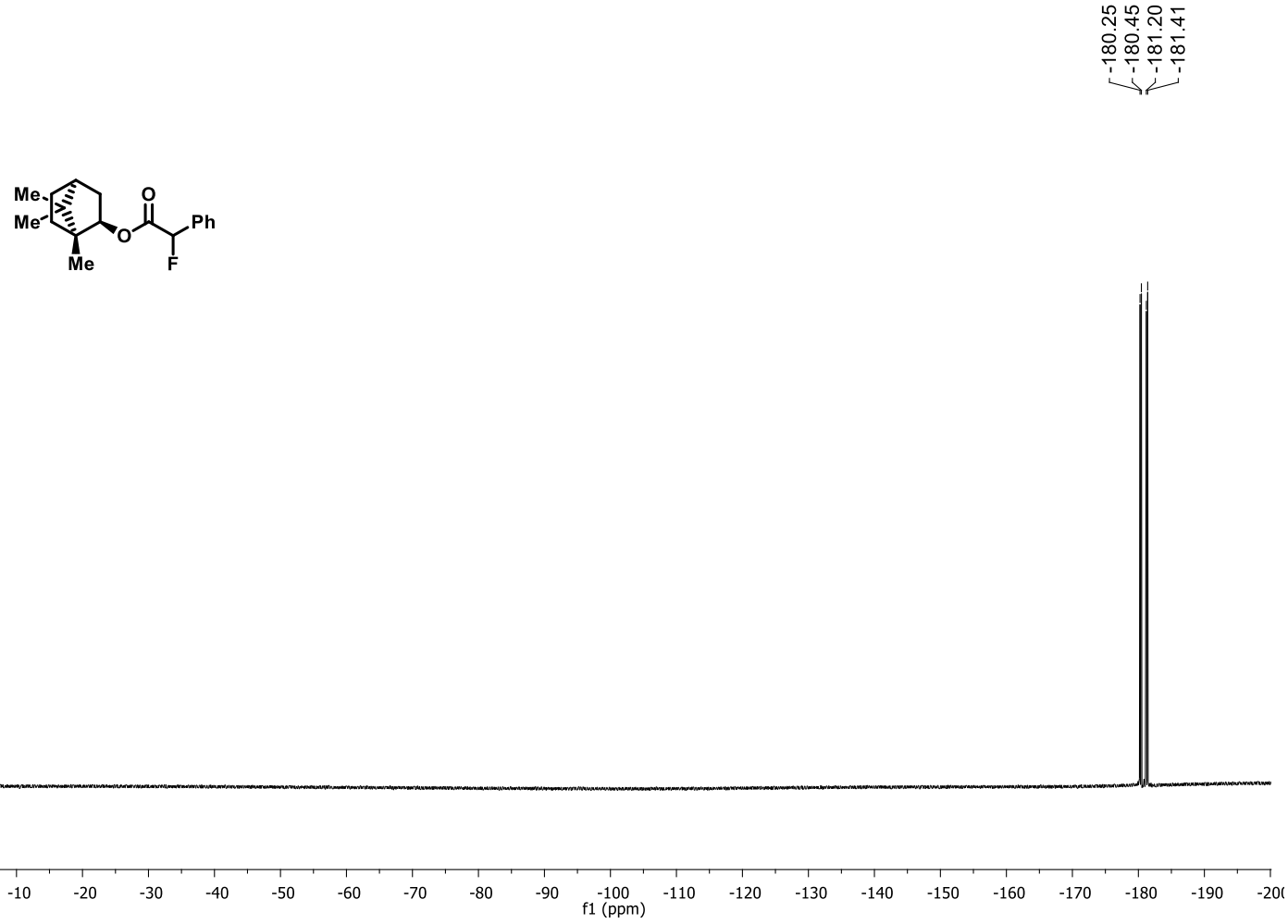
3e - ^{1}H NMR (250 MHz, $CDCl_3$)



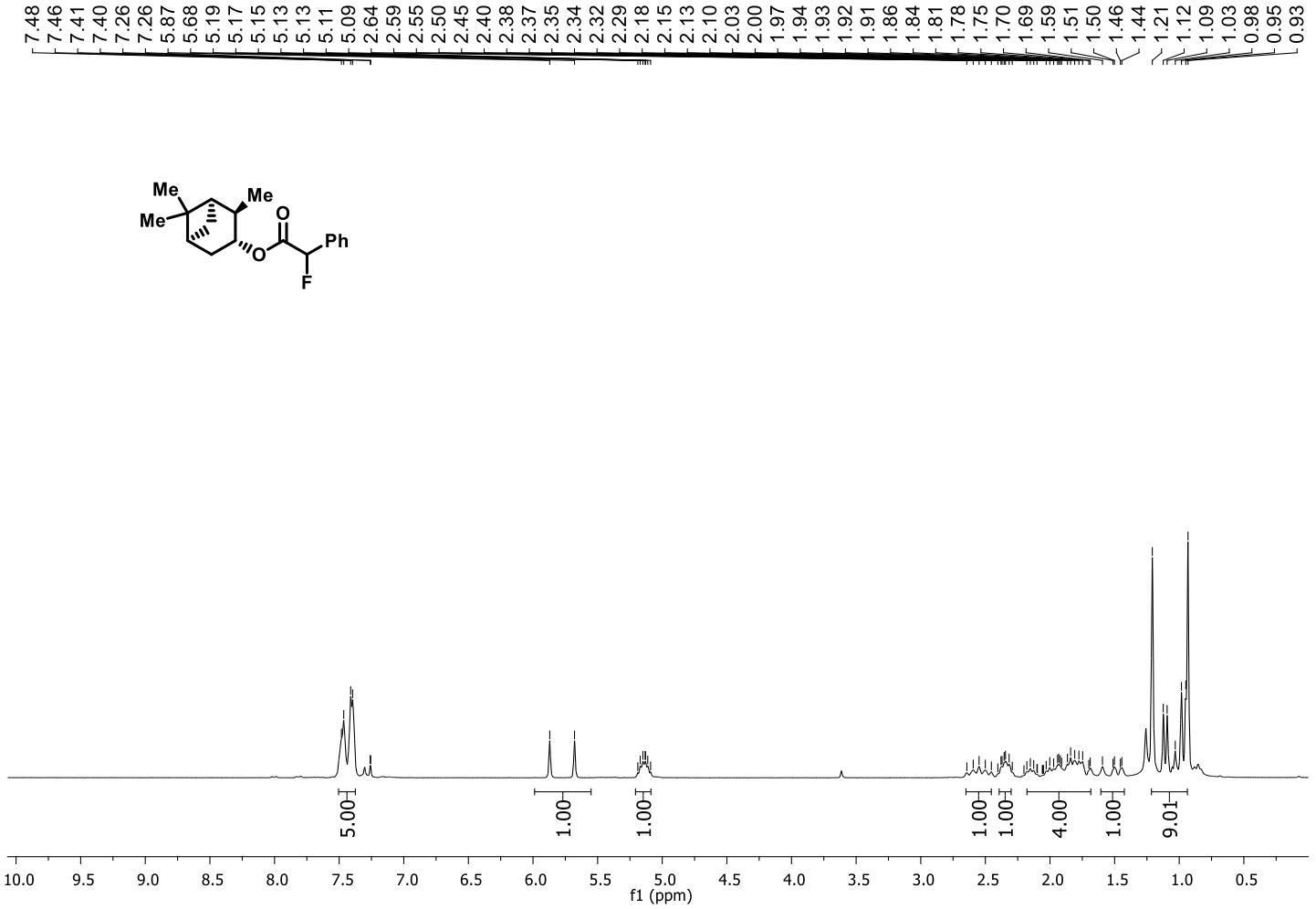
3e - ^{13}C NMR (62.5 MHz, $CDCl_3$)



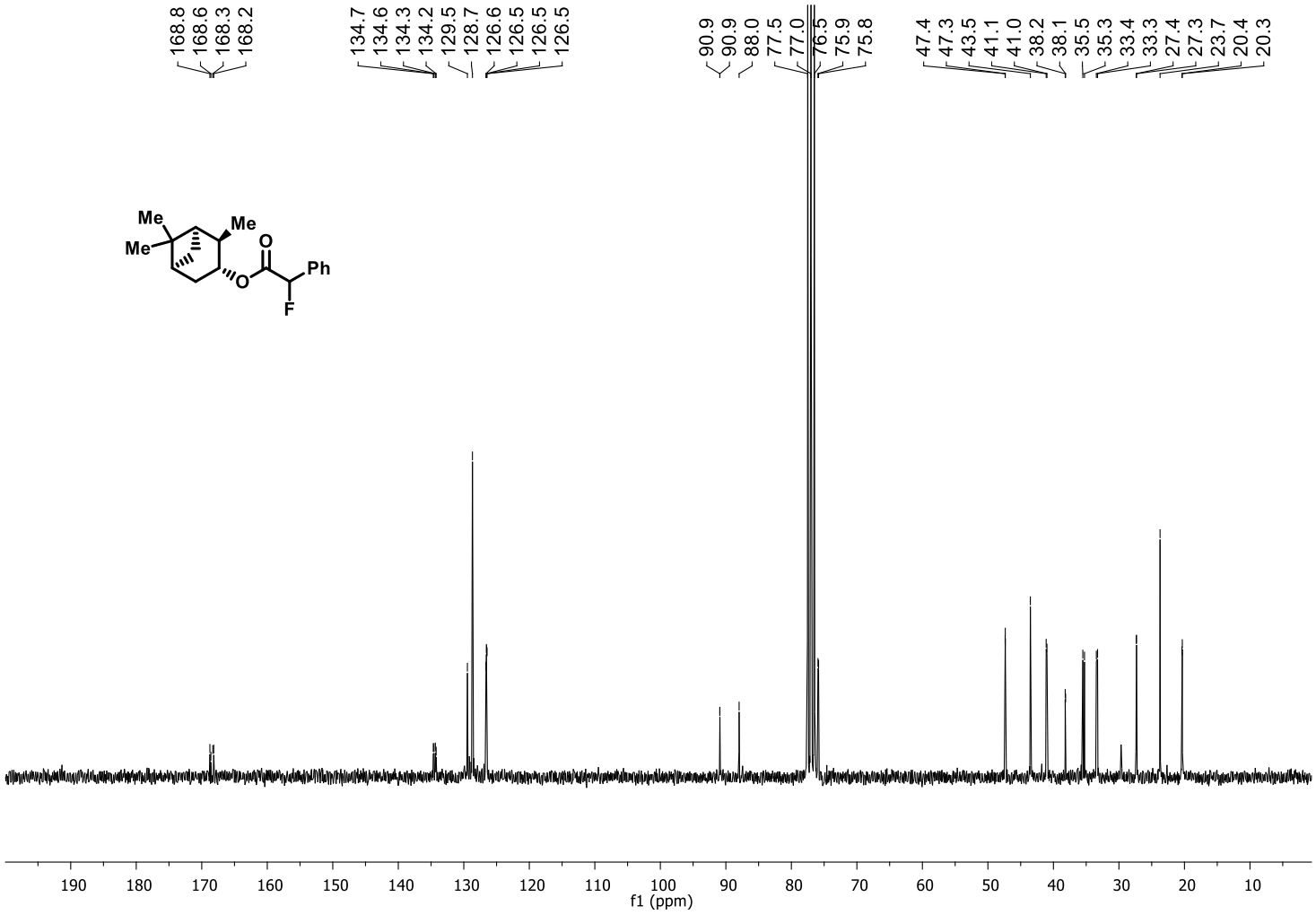
3e - ^{19}F NMR (235 MHz, $CDCl_3$)



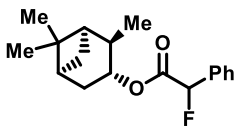
3f - ^{1}H NMR (250 MHz, $CDCl_3$)



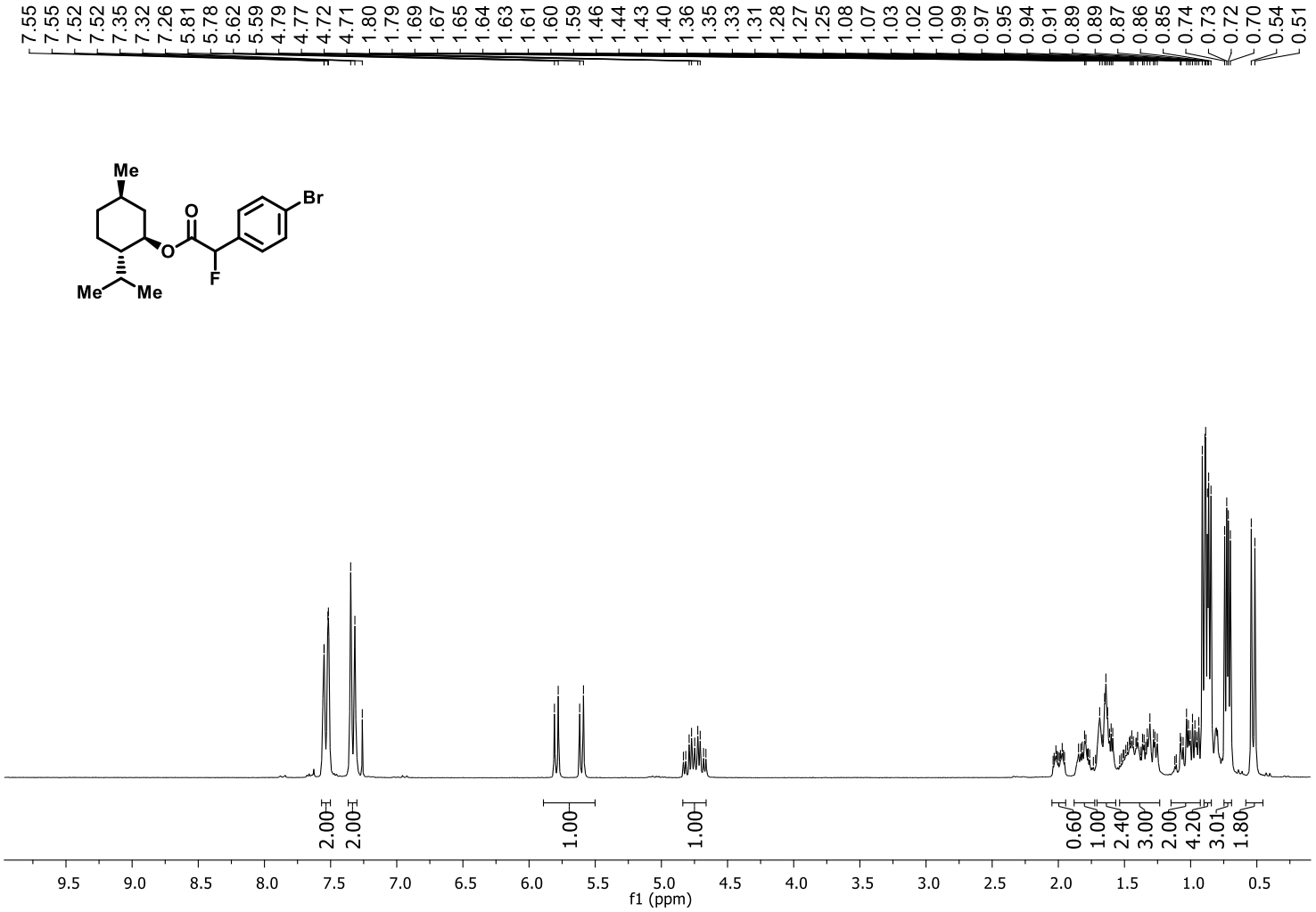
3f - ^{13}C NMR (62.5 MHz, $CDCl_3$)



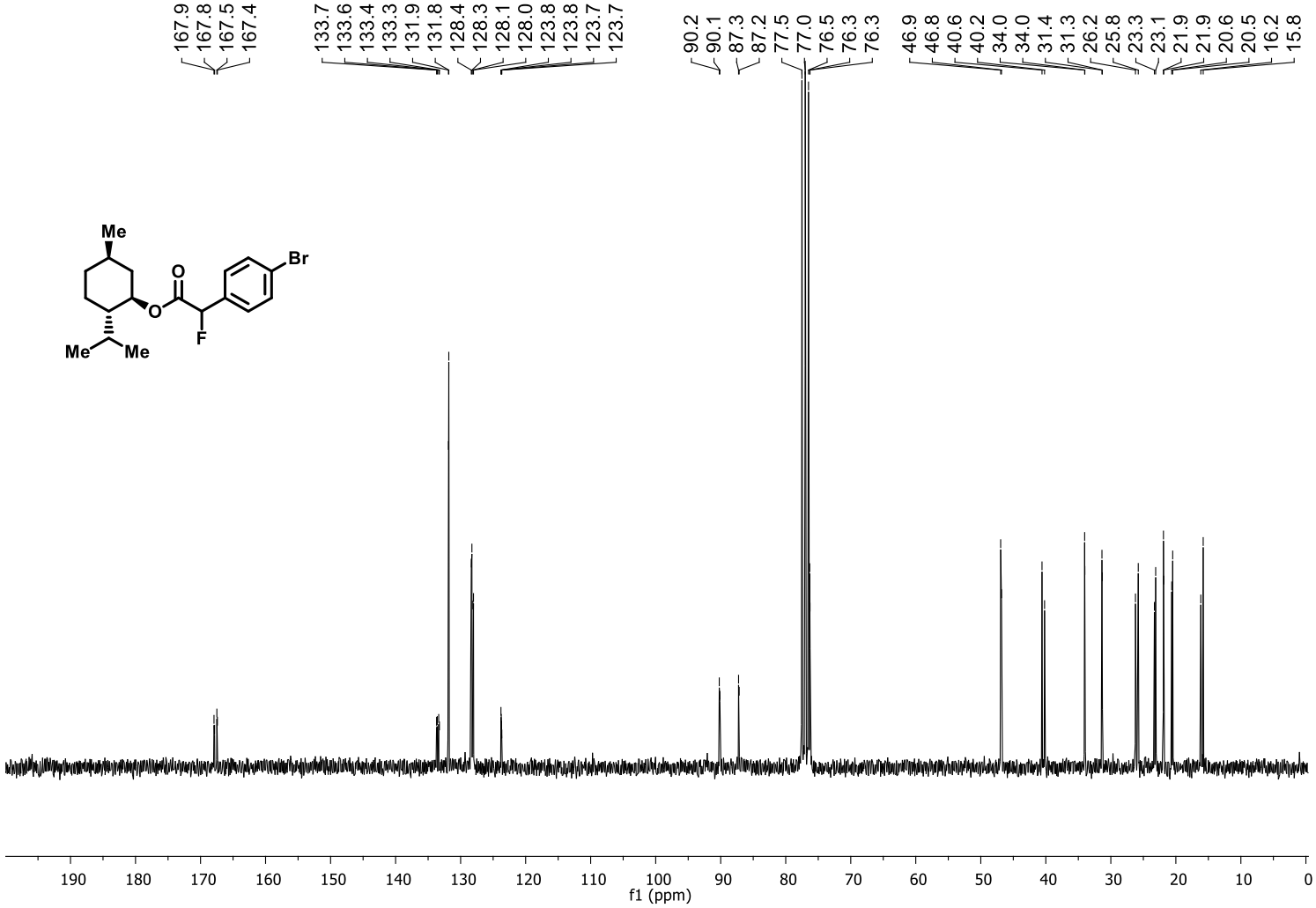
3f - ^{19}F NMR (235 MHz, $CDCl_3$)



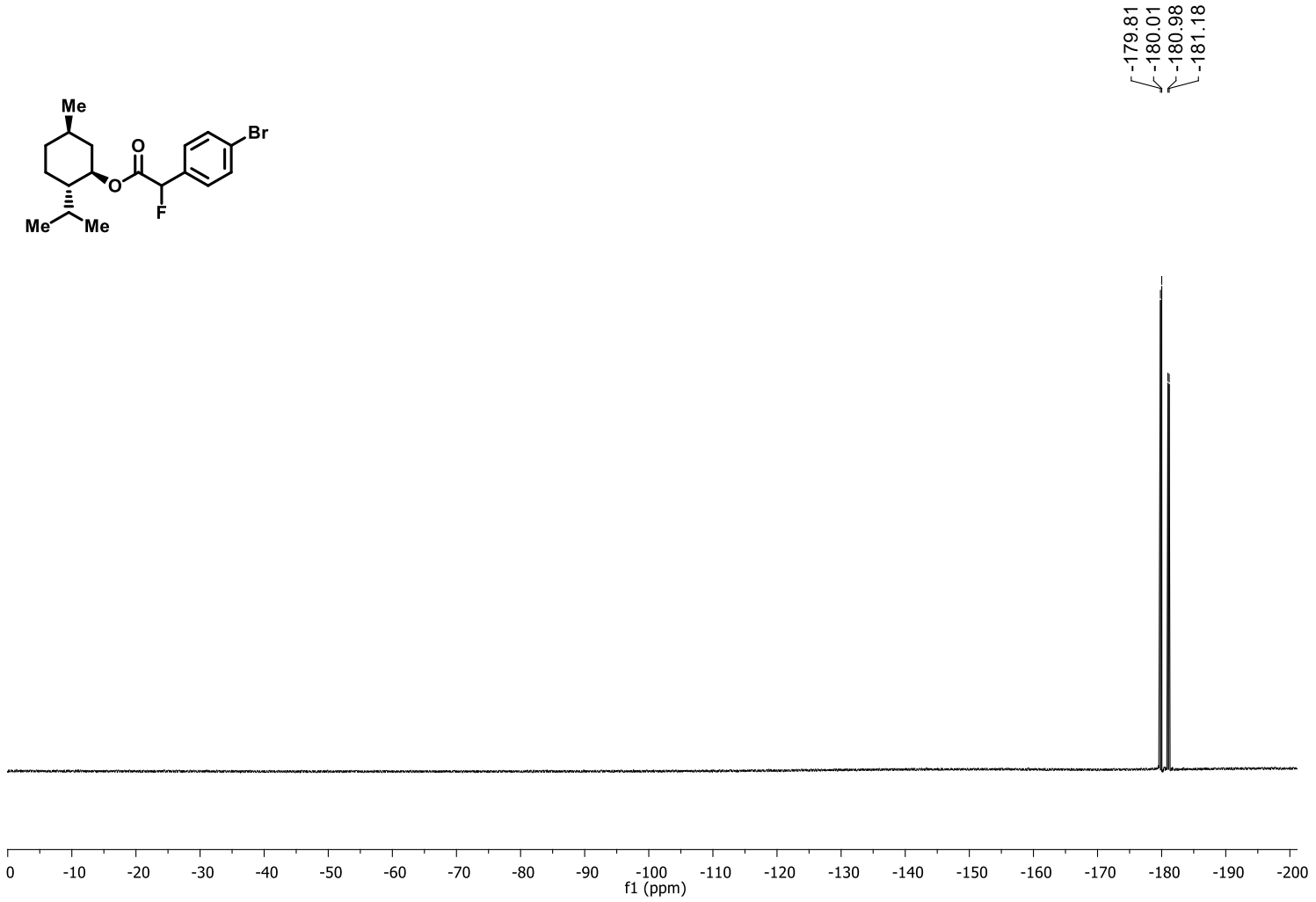
3g - ^{1}H NMR (250 MHz, $CDCl_3$)



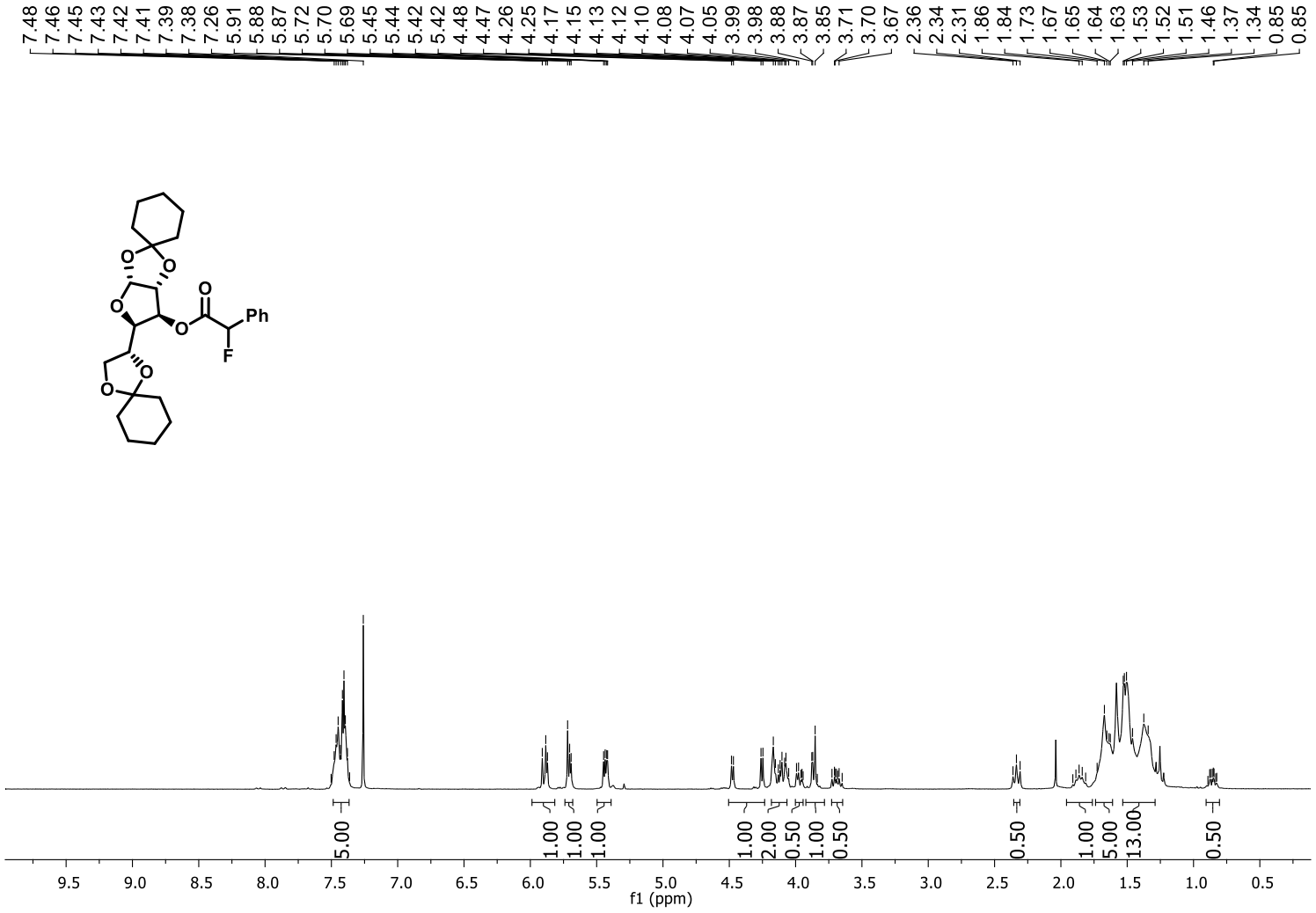
3g - ^{13}C NMR (62.5 MHz, $CDCl_3$)



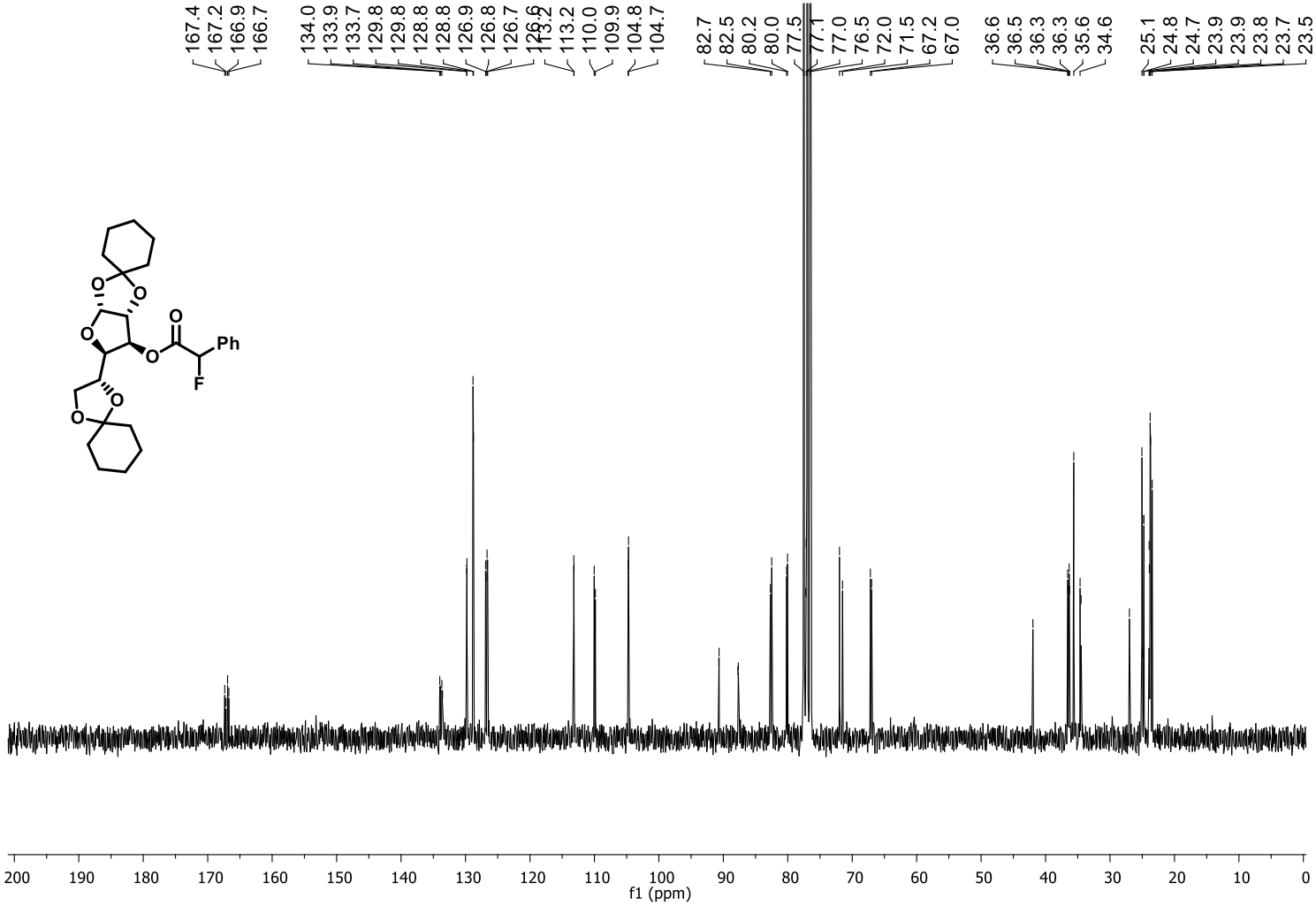
3g - ^{19}F NMR (235 MHz, $CDCl_3$)



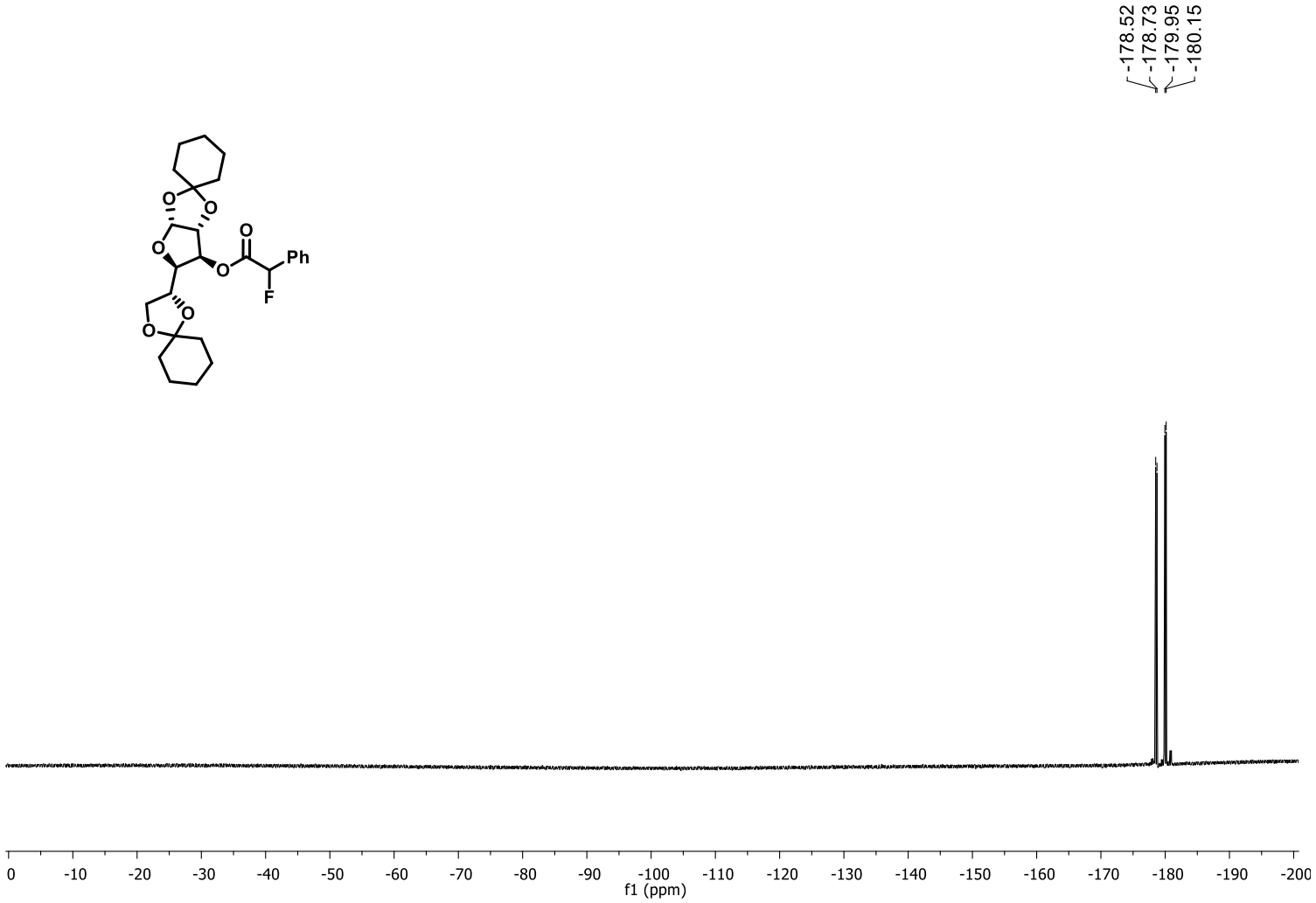
3h - ^{1}H NMR (250 MHz, $CDCl_3$)



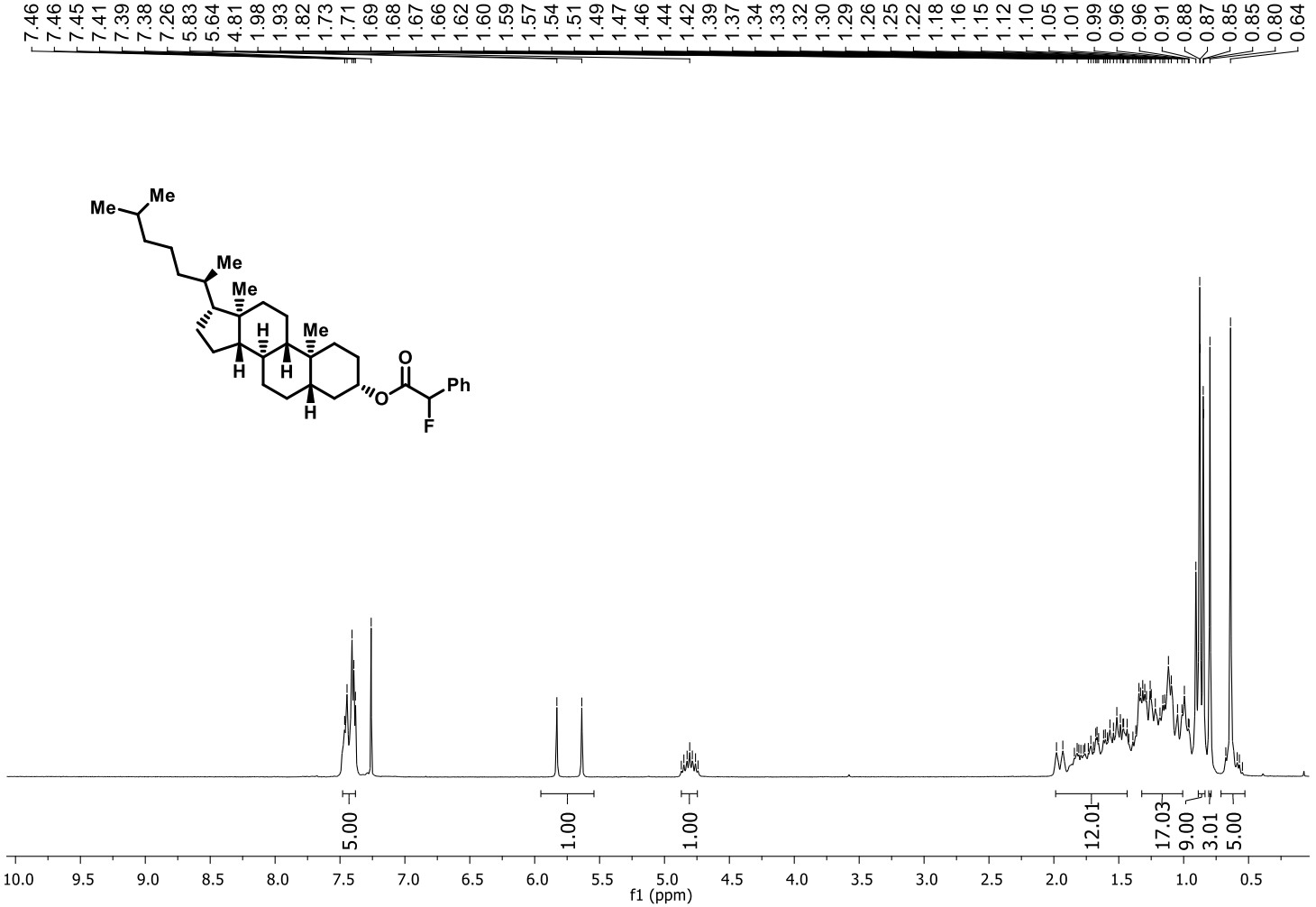
3h - ^{13}C NMR (62.5 MHz, $CDCl_3$)



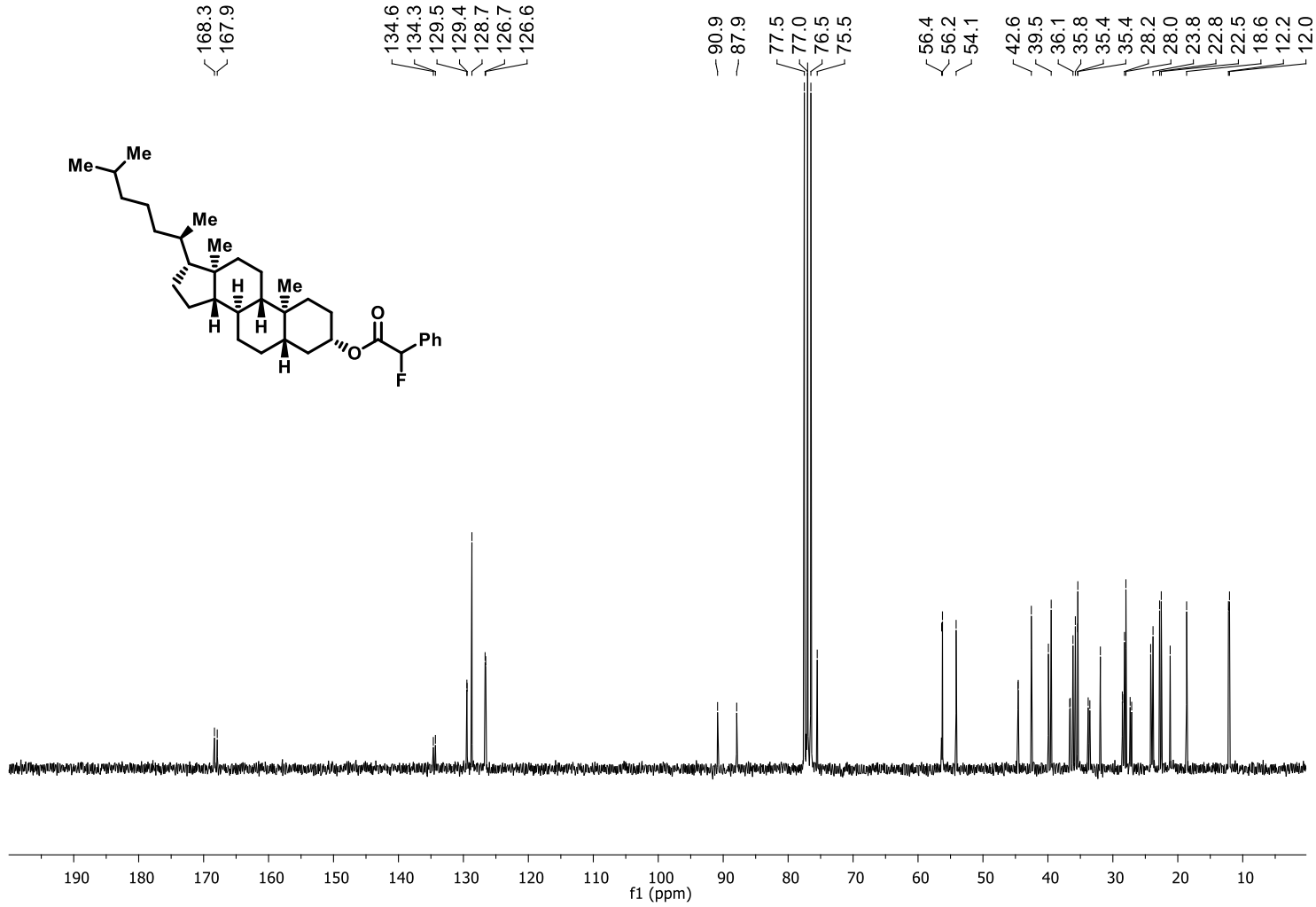
3h - ^{19}F NMR (235 MHz, $CDCl_3$)



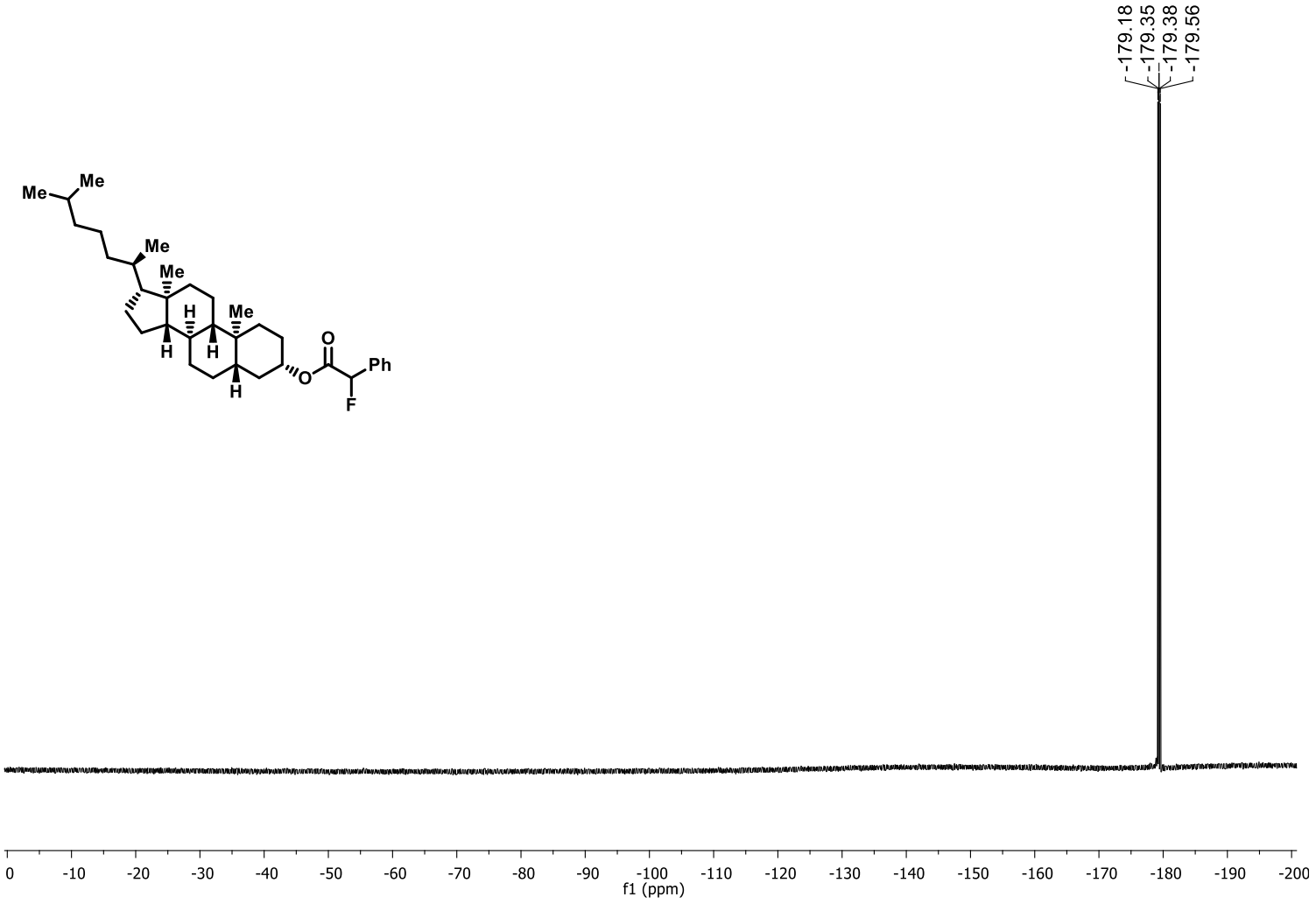
3i - ^{1}H NMR (250 MHz, $CDCl_3$)



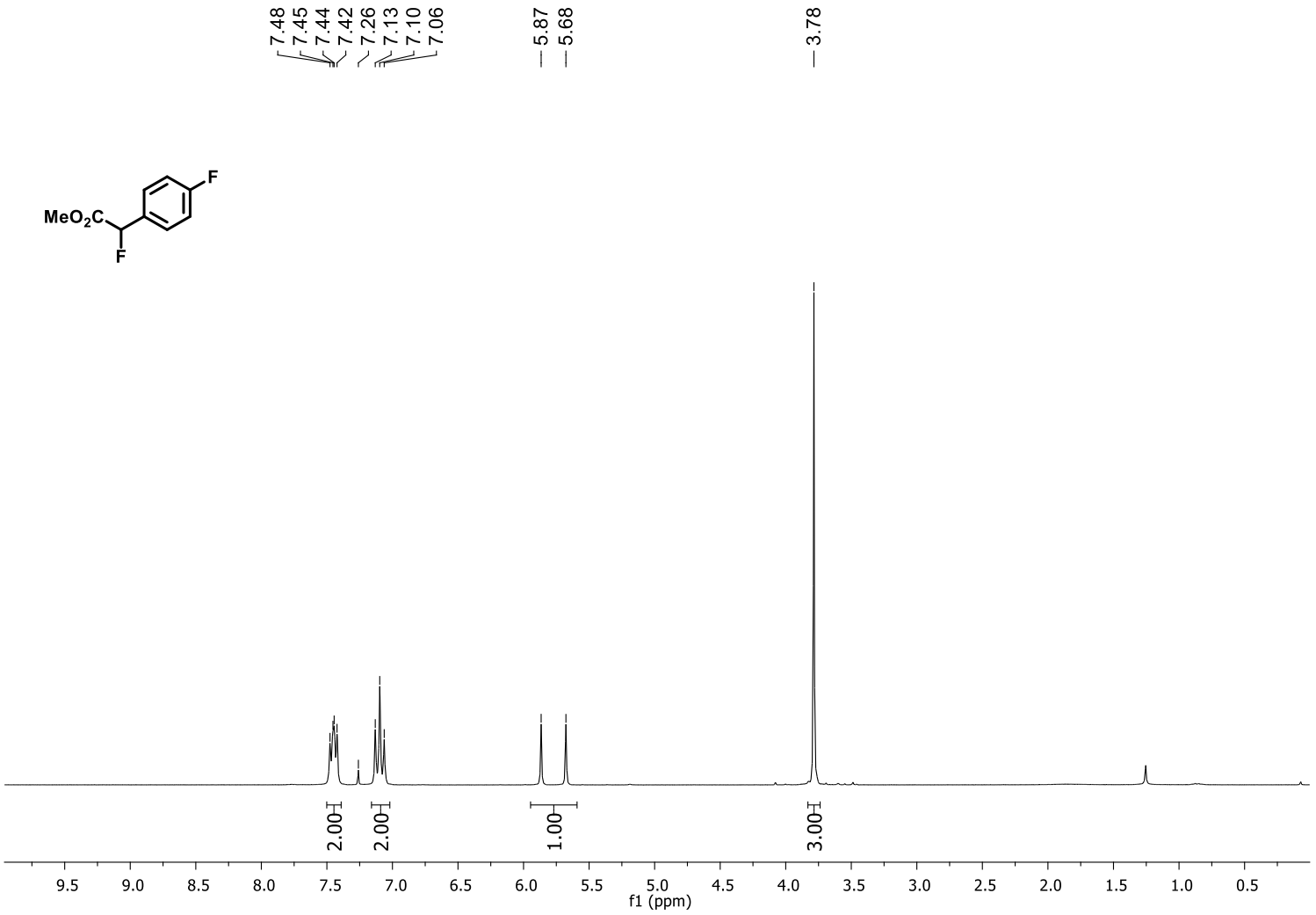
3i - ^{13}C NMR (62.5 MHz, $CDCl_3$)



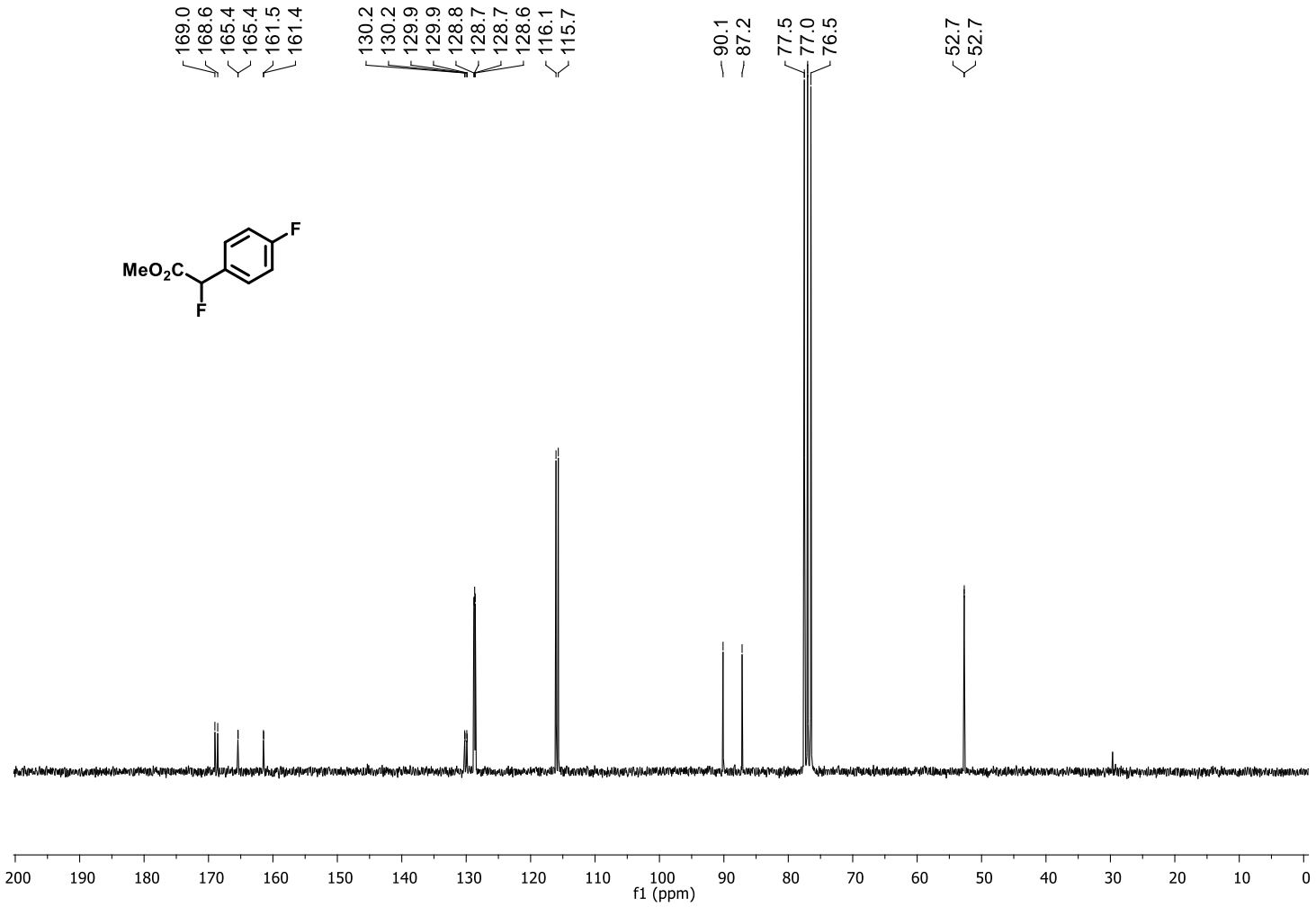
3i - ^{19}F NMR (235 MHz, $CDCl_3$)



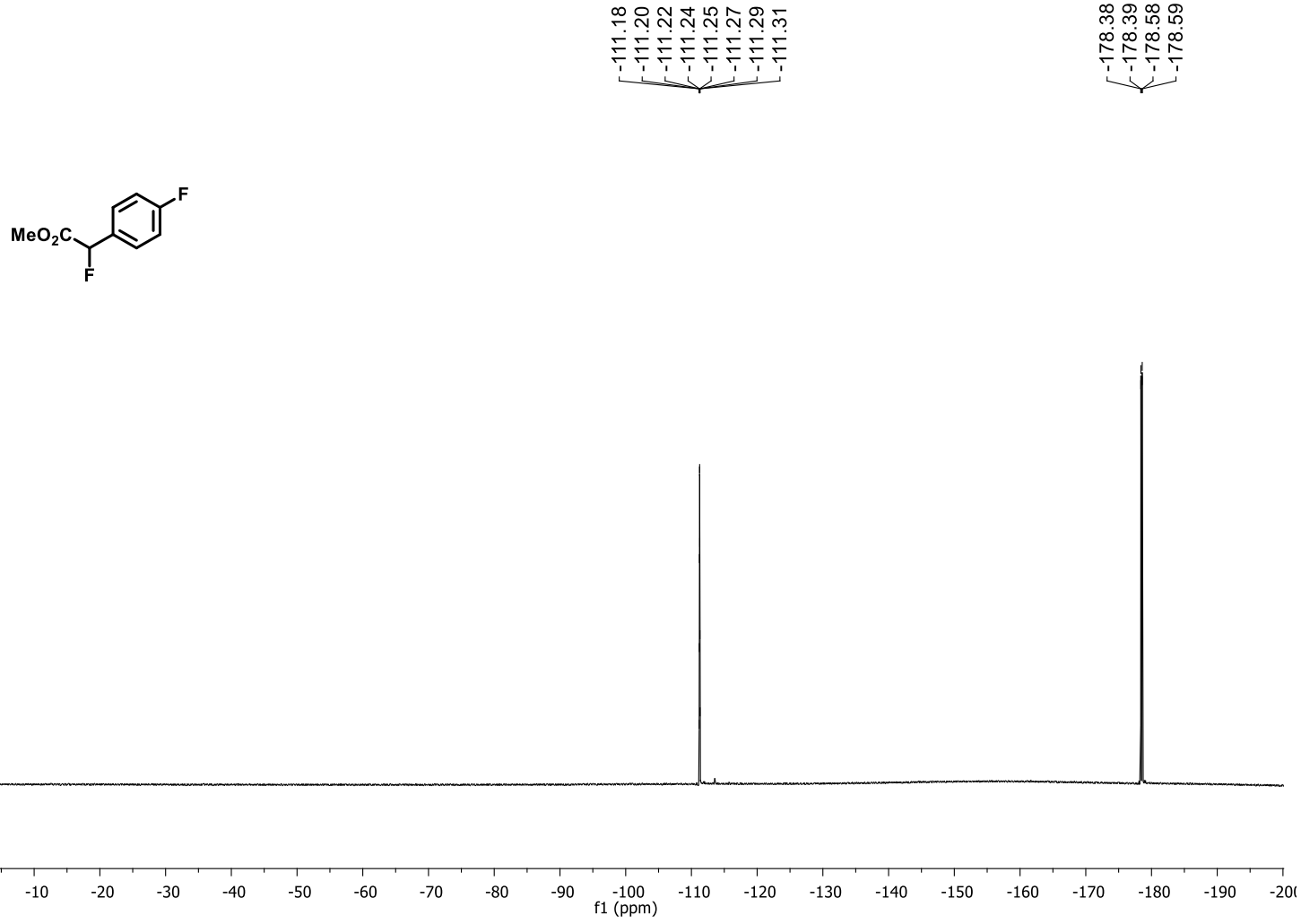
3j - ^{1}H NMR (250 MHz, $CDCl_3$)



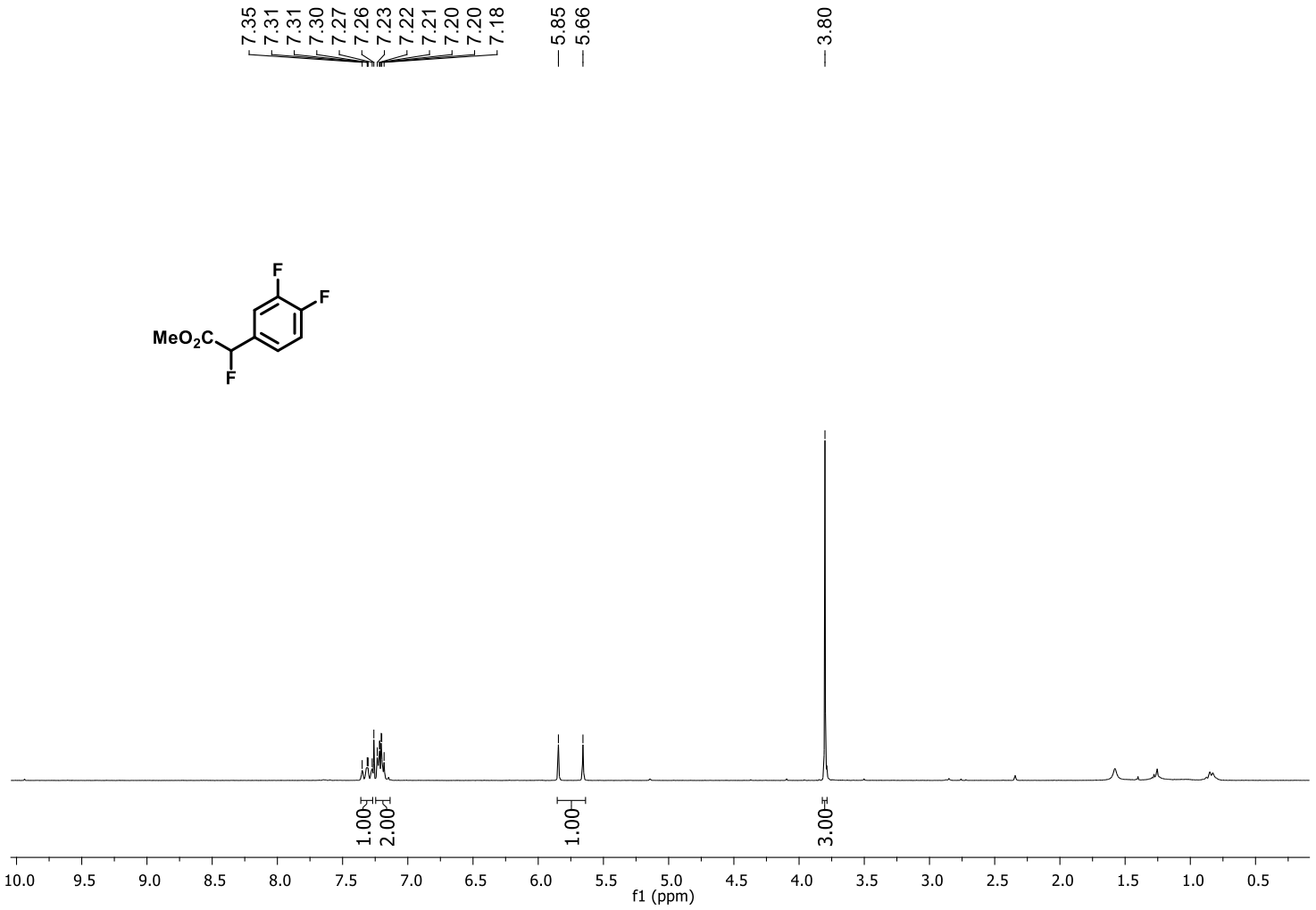
3j - ^{13}C NMR (62.5 MHz, $CDCl_3$)



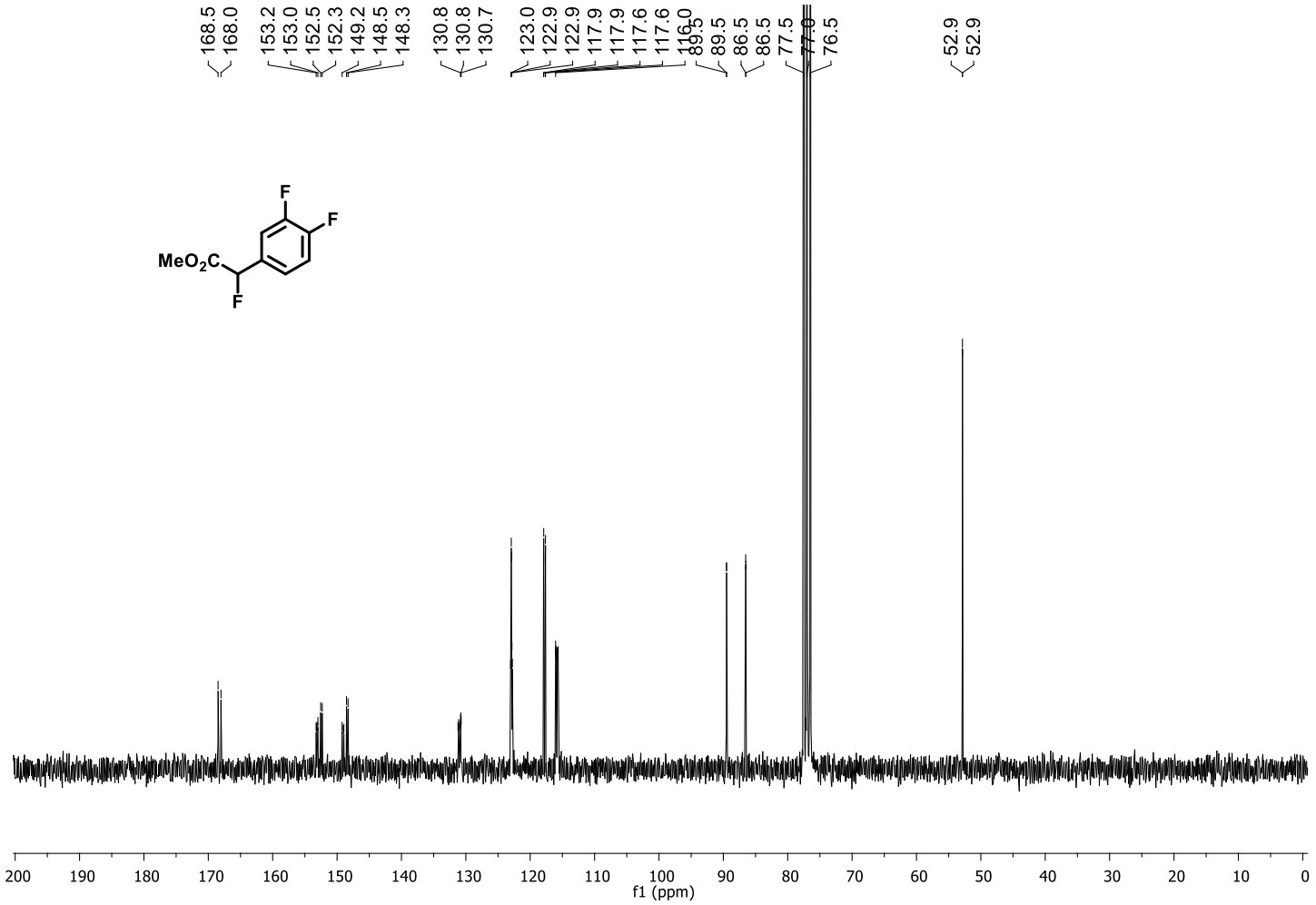
3j - ^{19}F NMR (235 MHz, $CDCl_3$)



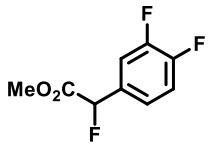
3k - ^{1}H NMR (250 MHz, $CDCl_3$)



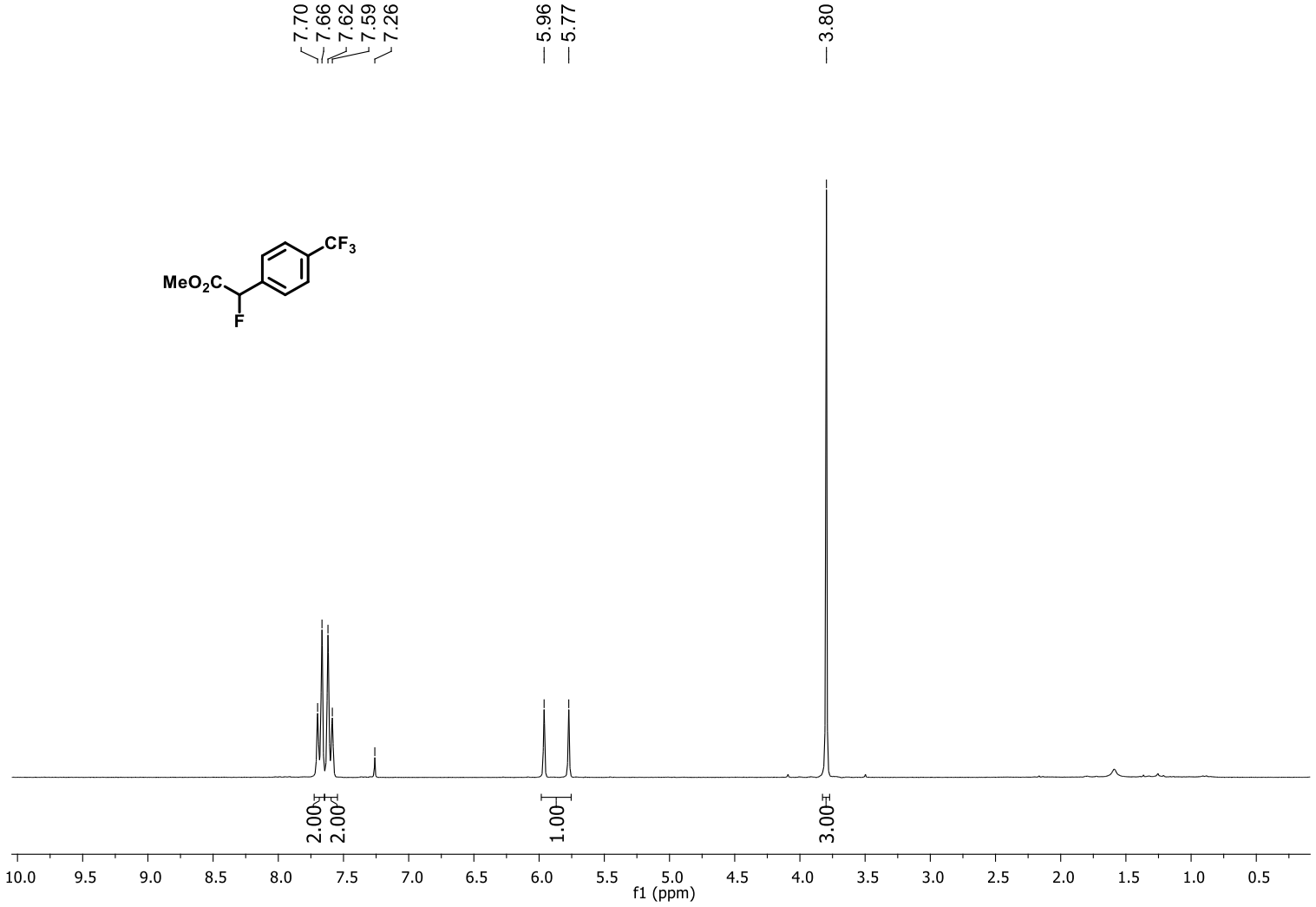
3k – ^{13}C NMR (62.5 MHz, $CDCl_3$)



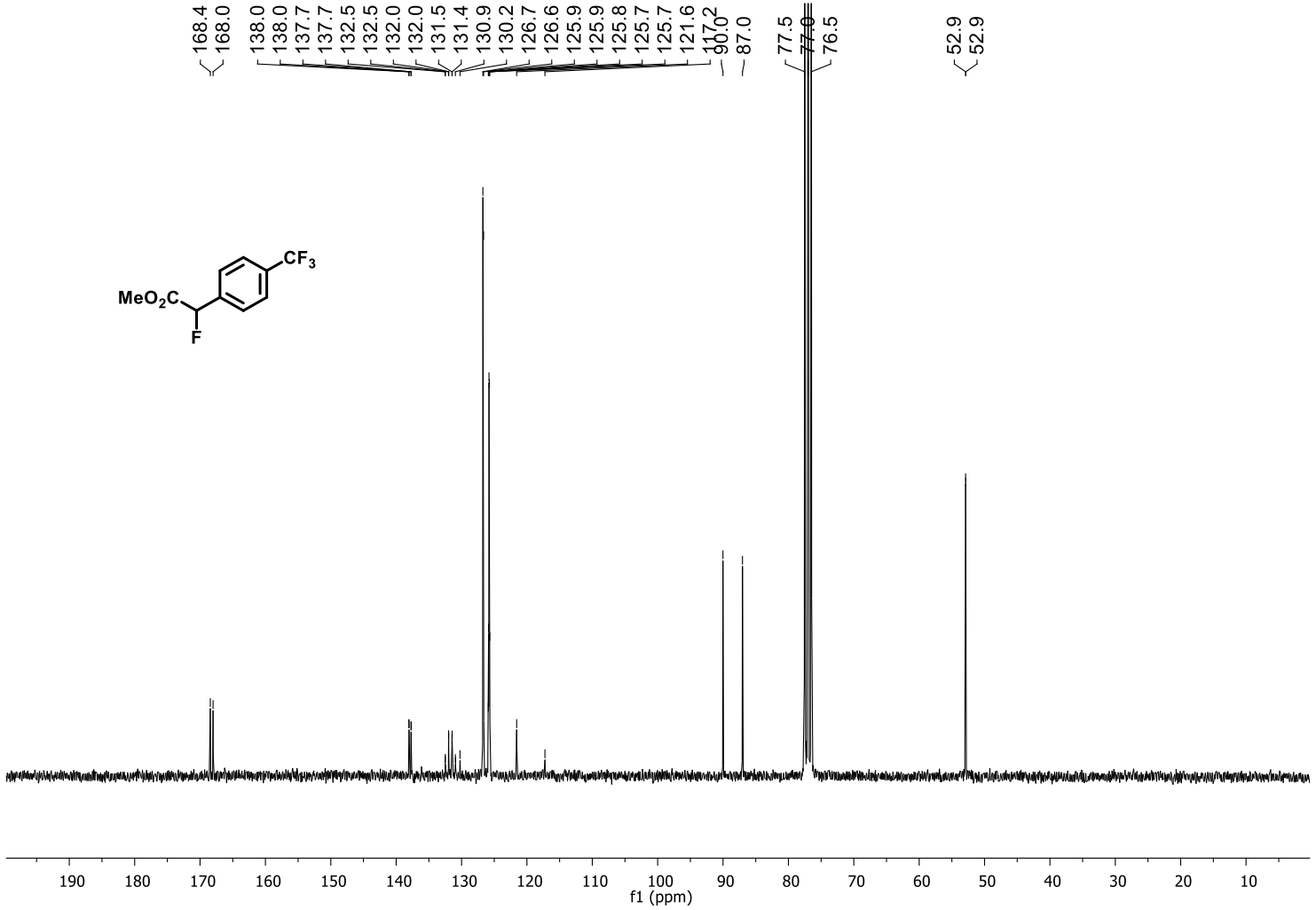
3k – ^{19}F NMR (235 MHz, $CDCl_3$)



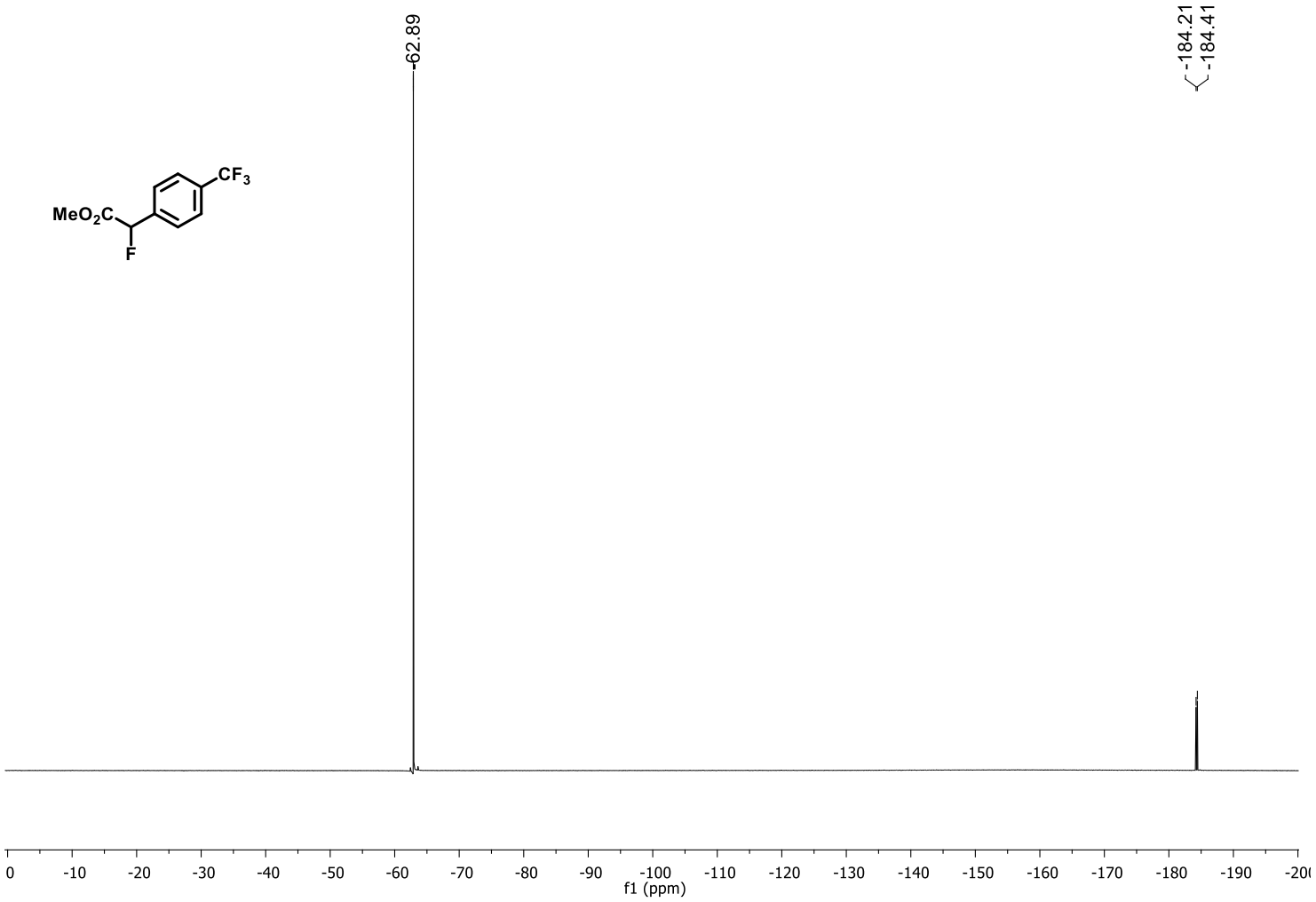
3l - ^{1}H NMR (250 MHz, $CDCl_3$)



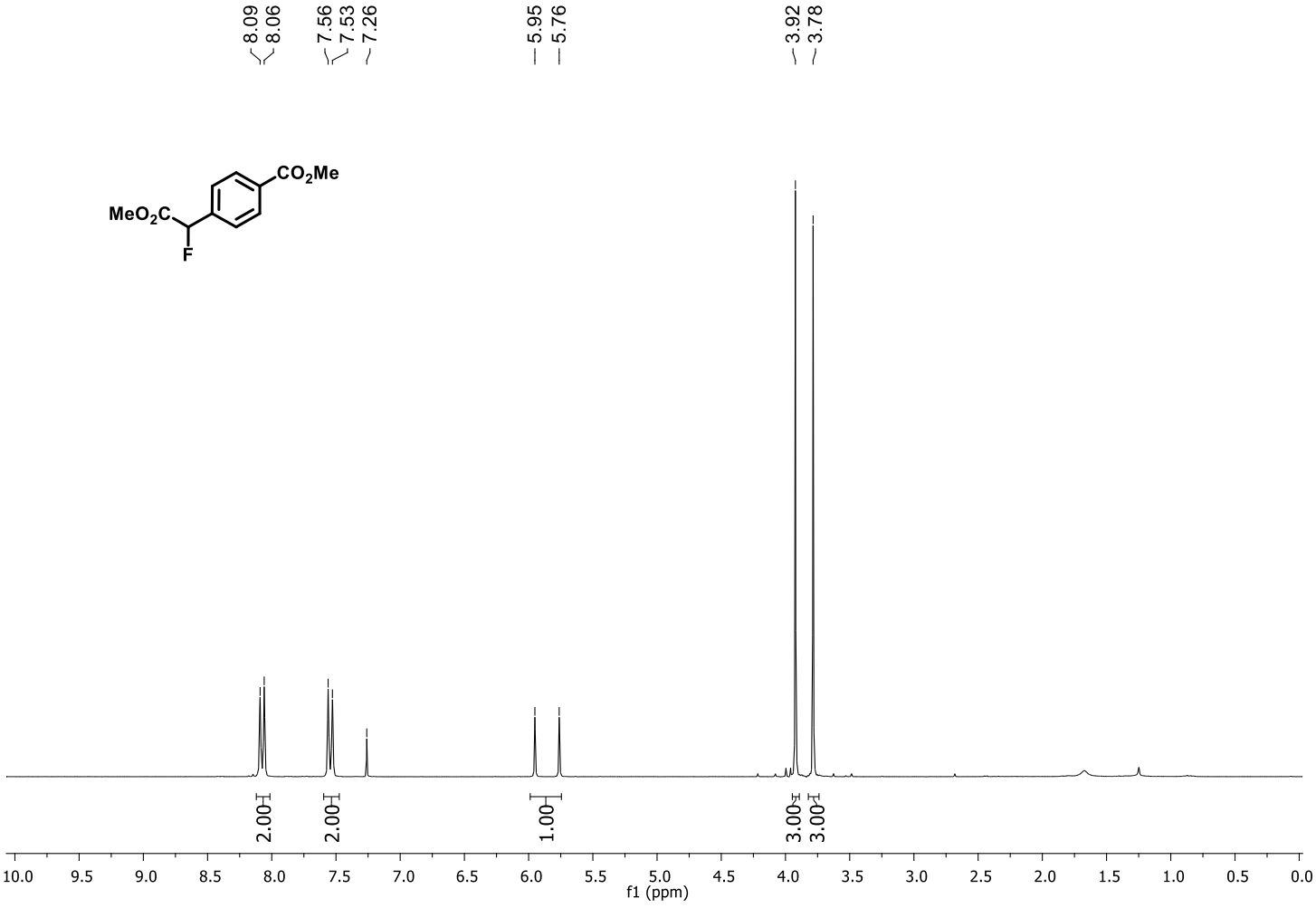
3l - ^{13}C NMR (62.5 MHz, $CDCl_3$)



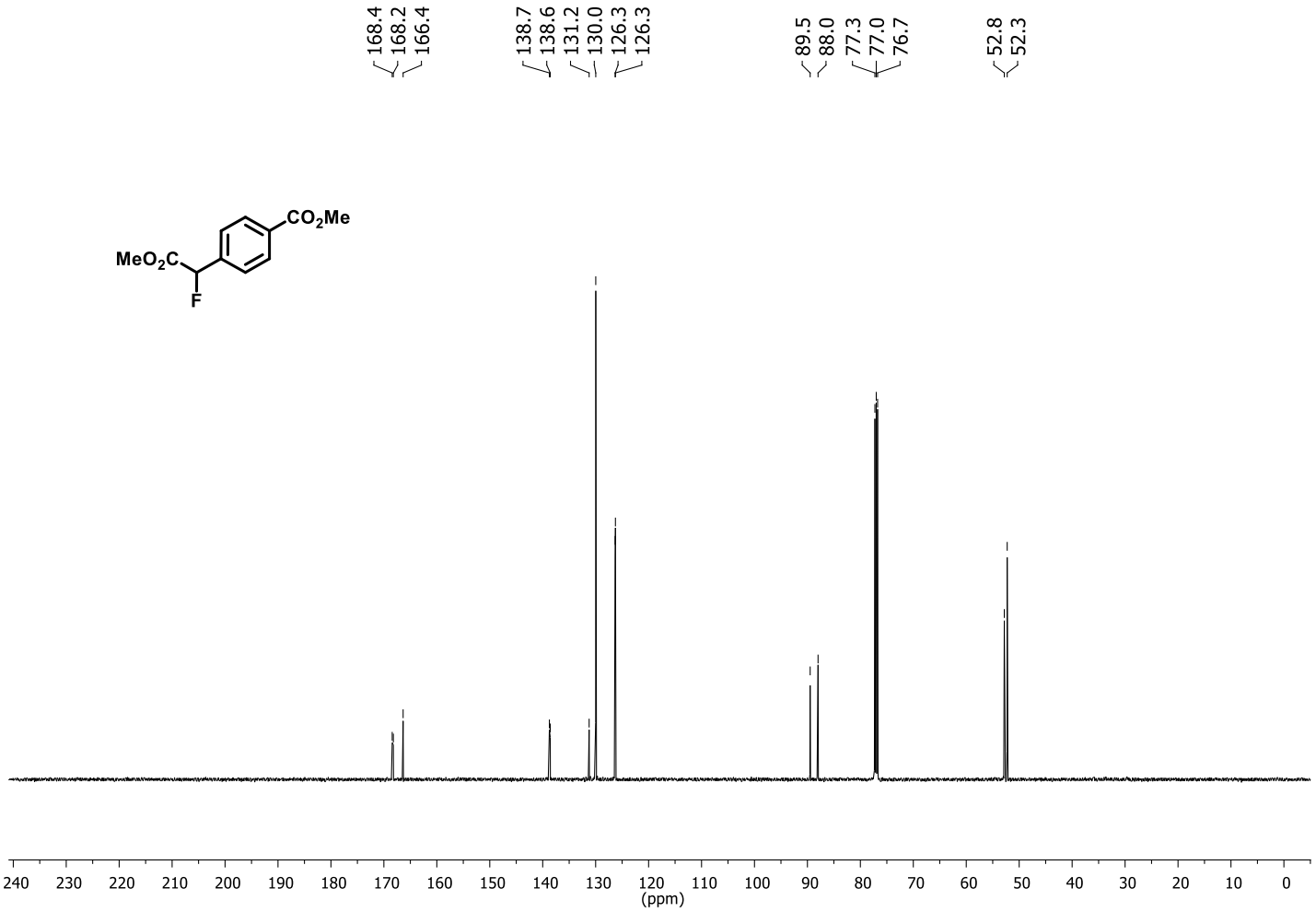
3l - ^{19}F NMR (235 MHz, $CDCl_3$)



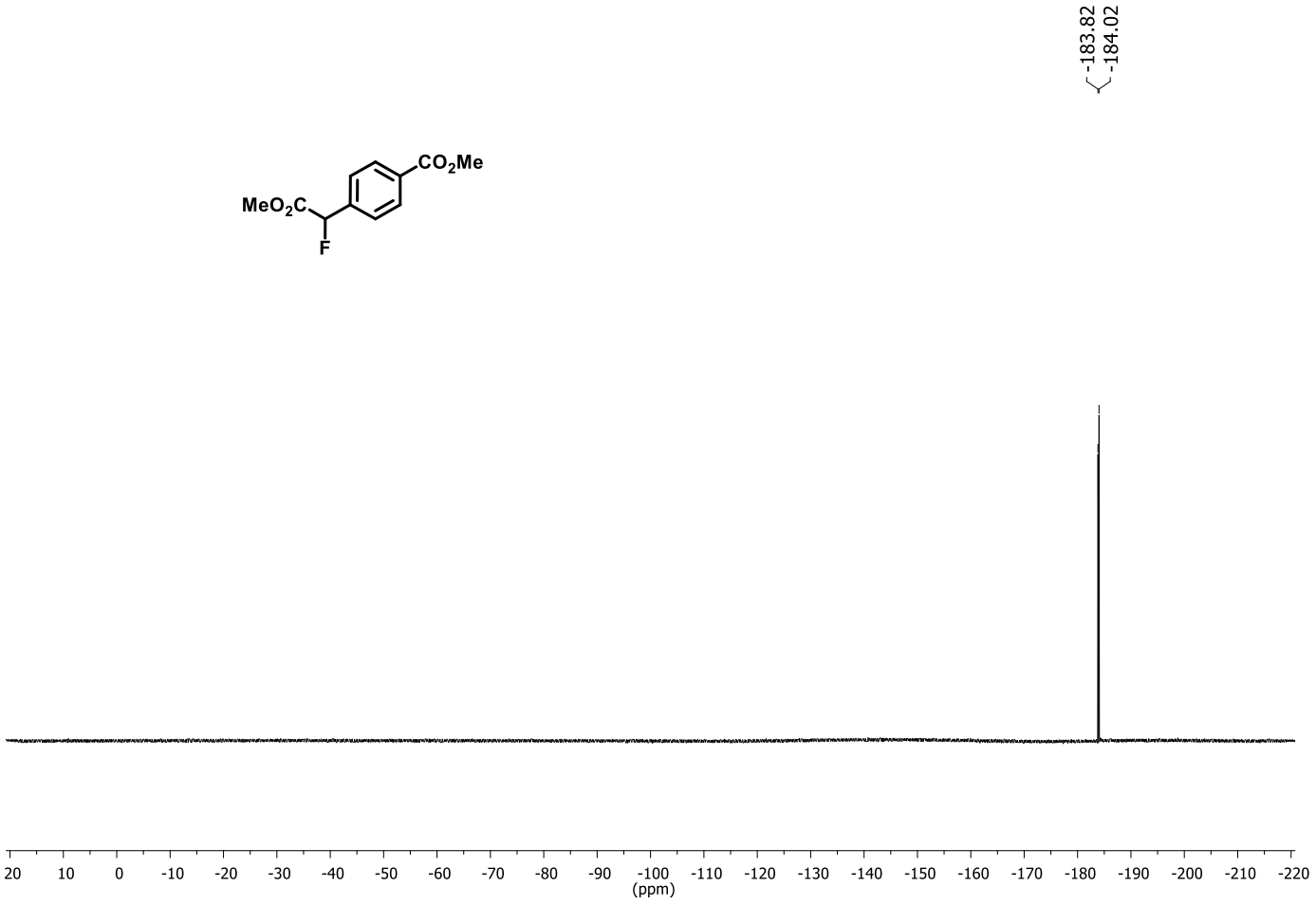
3m – ^{1}H NMR (250 MHz, $CDCl_3$)



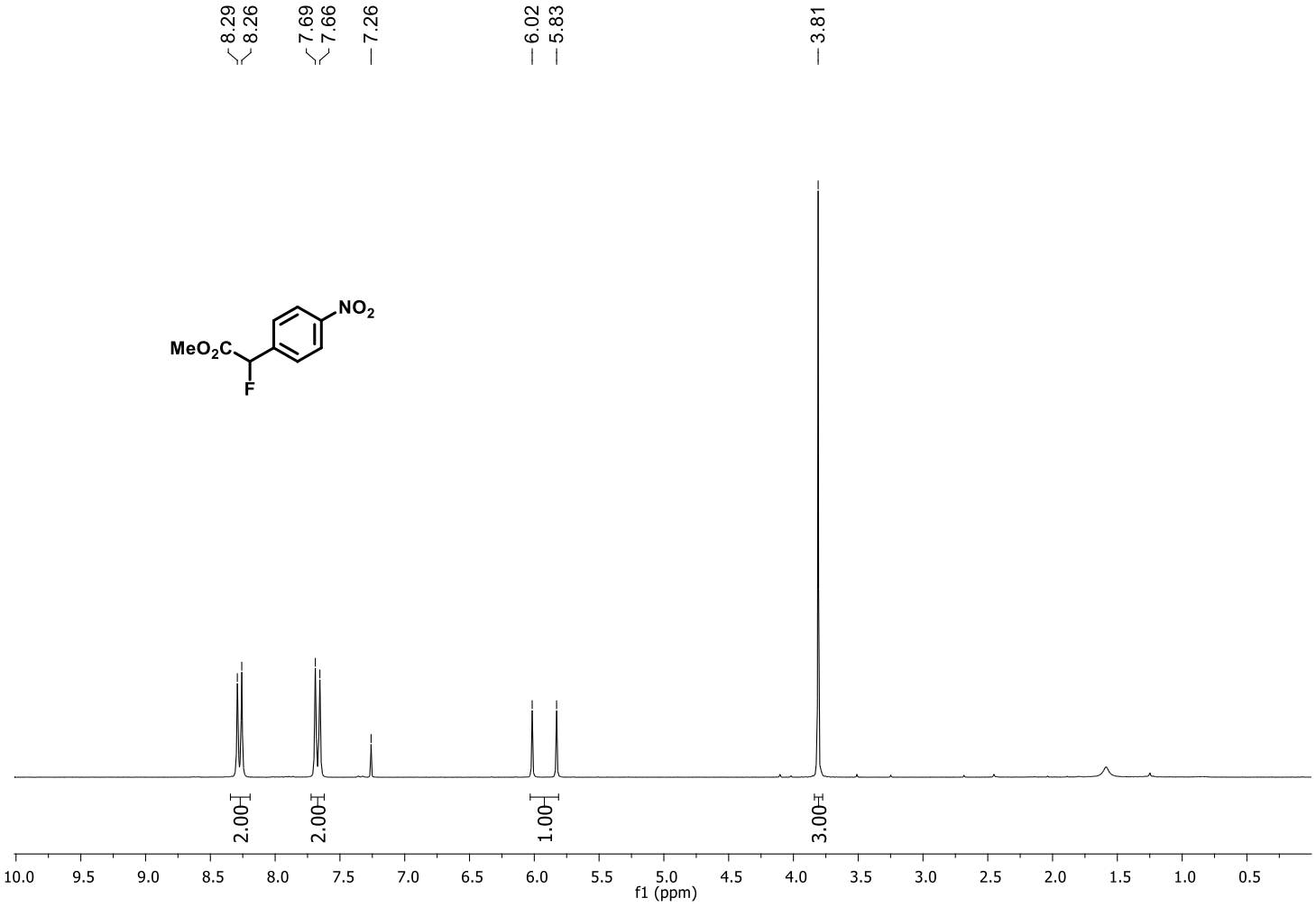
3m - ^{13}C NMR (125 MHz, $CDCl_3$)



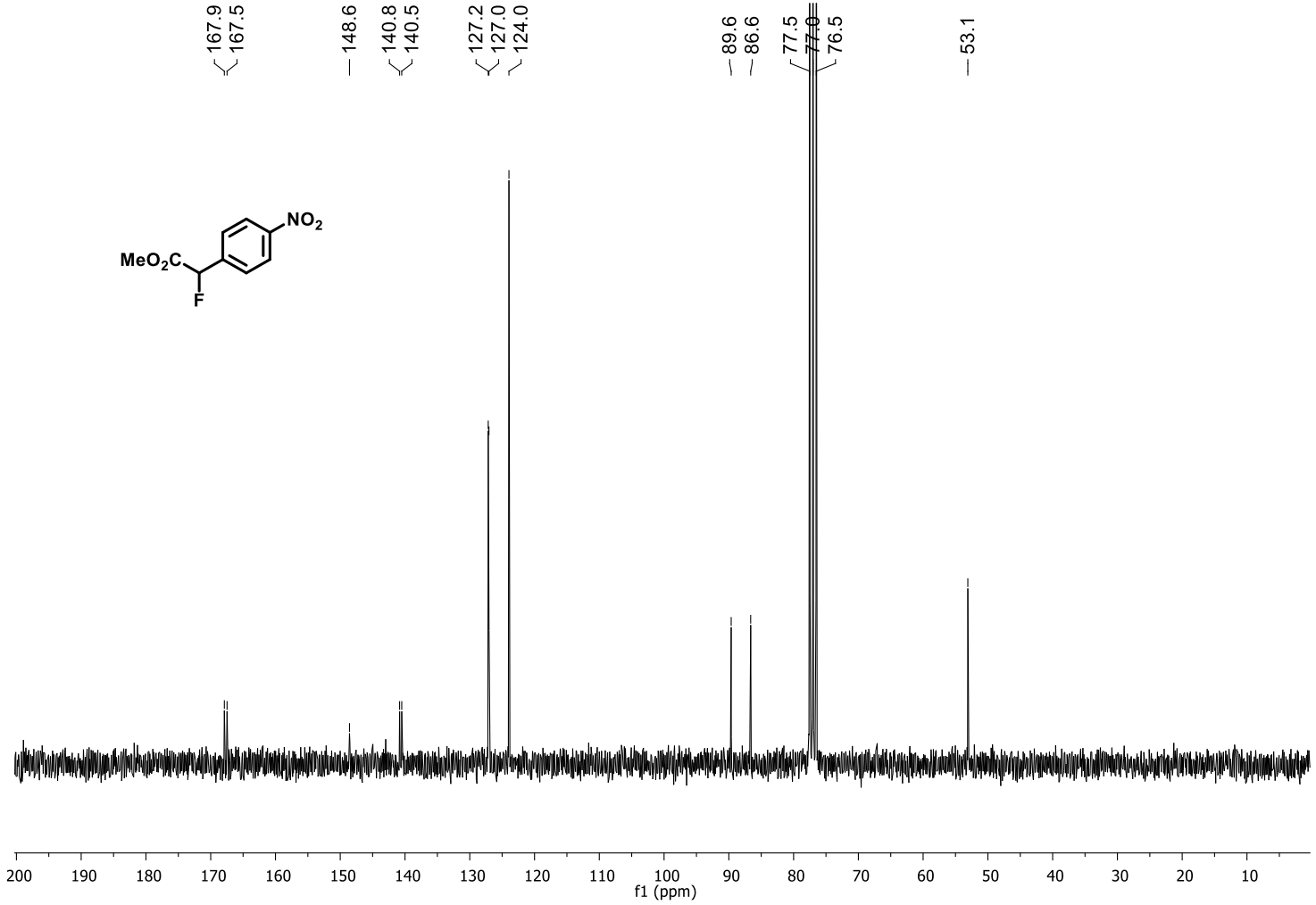
3m - ^{19}F NMR (235 MHz, $CDCl_3$)



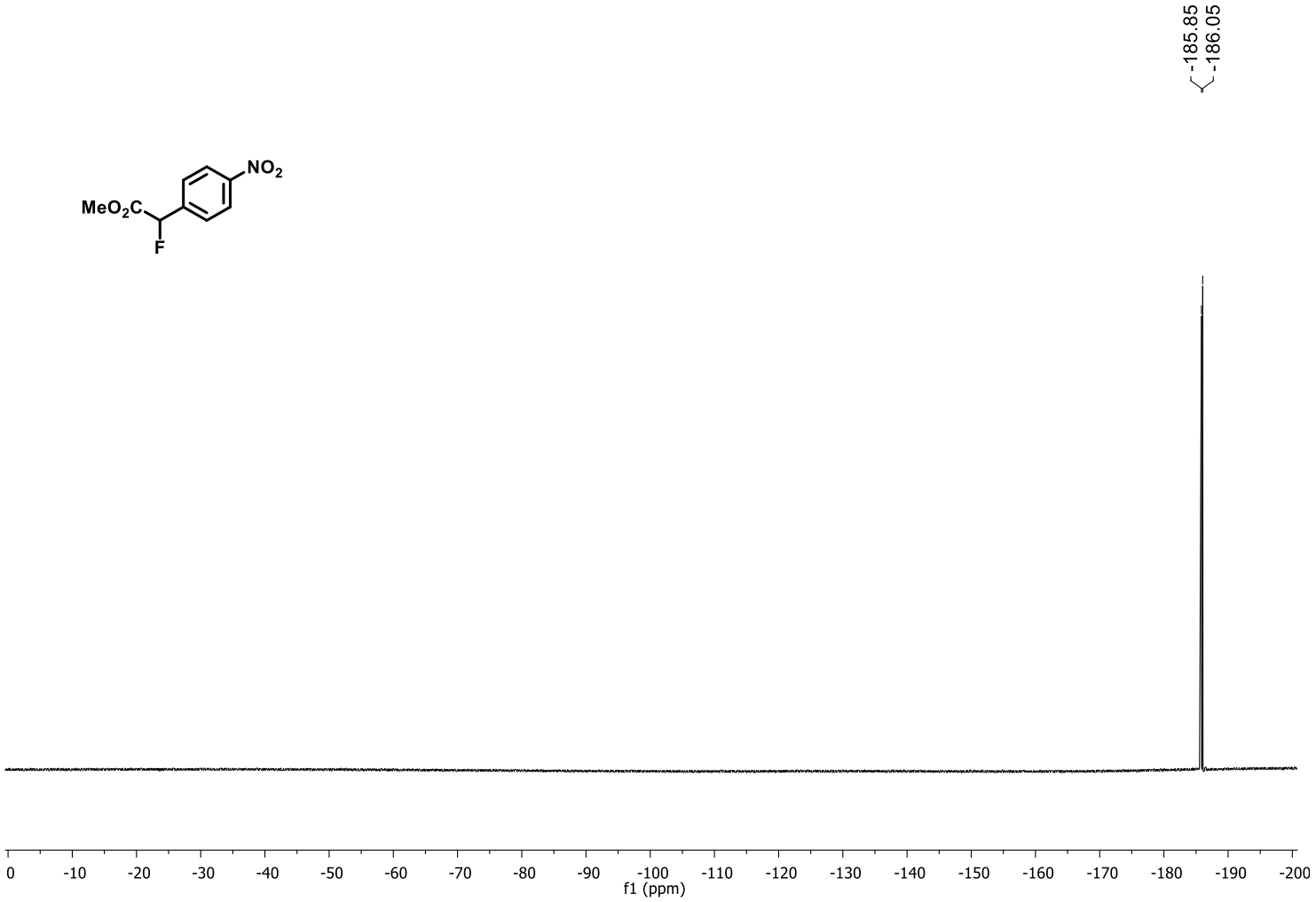
3n - ^{1}H NMR (250 MHz, $CDCl_3$)



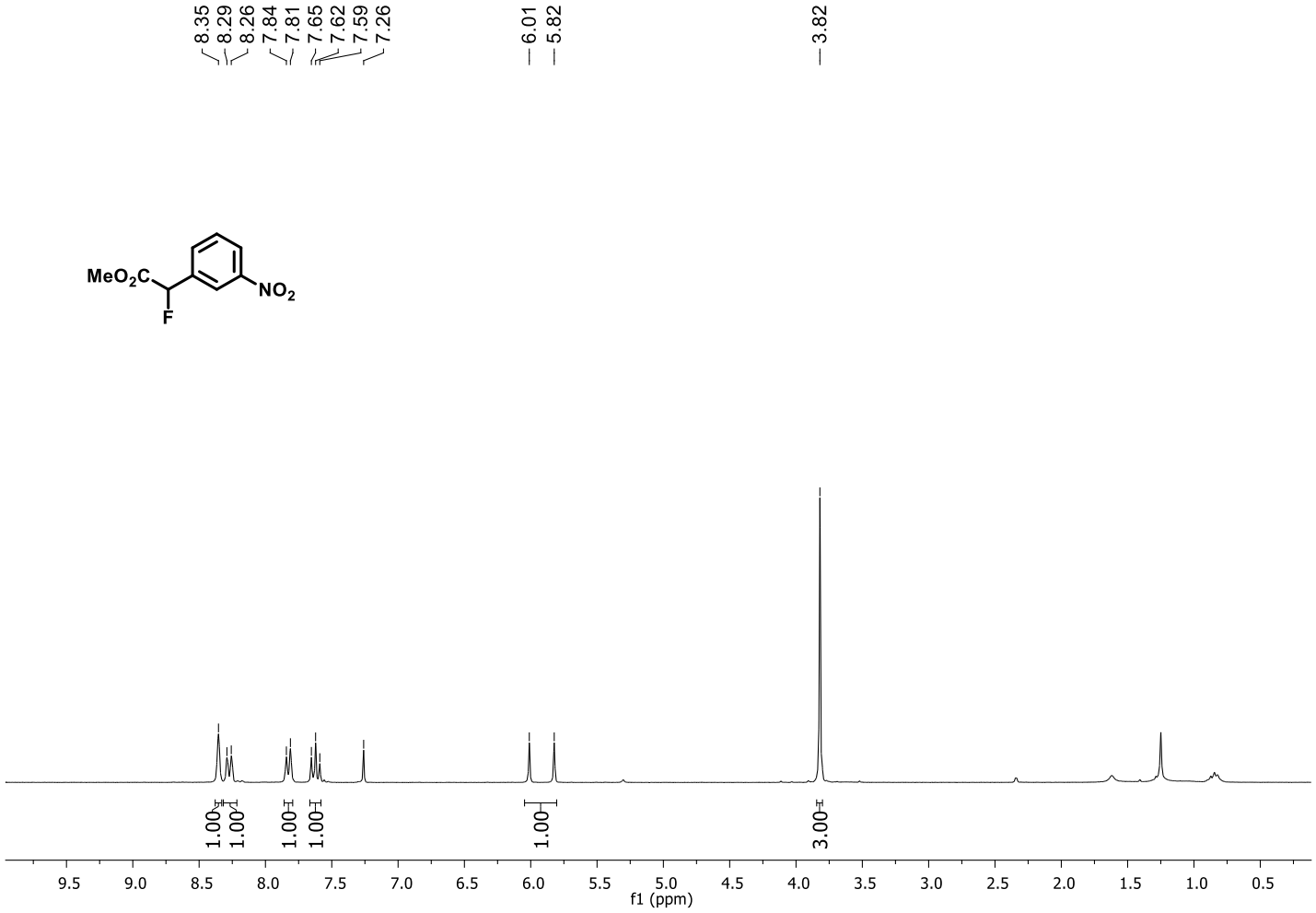
3n - ^{13}C NMR (62.5 MHz, $CDCl_3$)



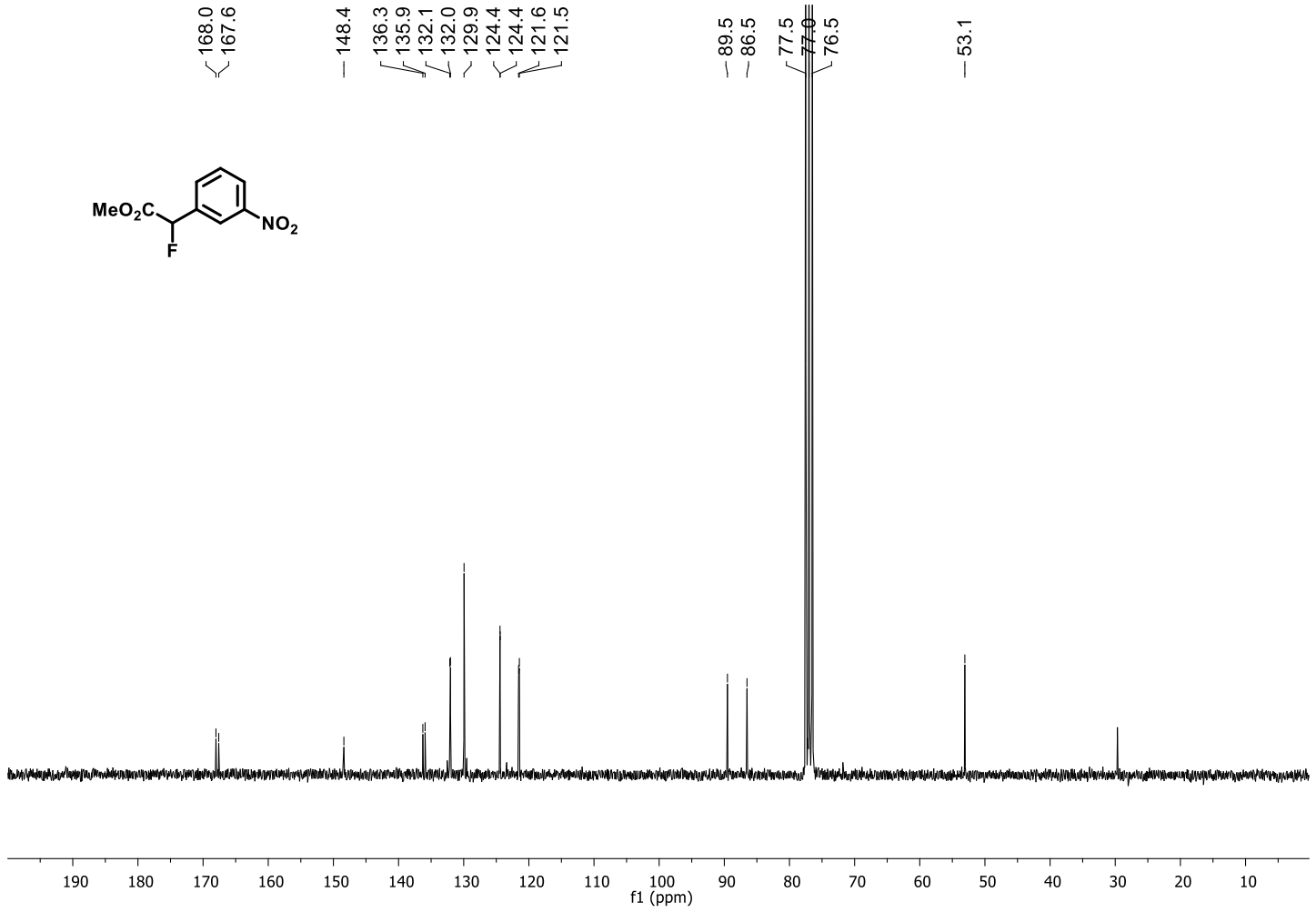
3n - ^{19}F NMR (235 MHz, $CDCl_3$)



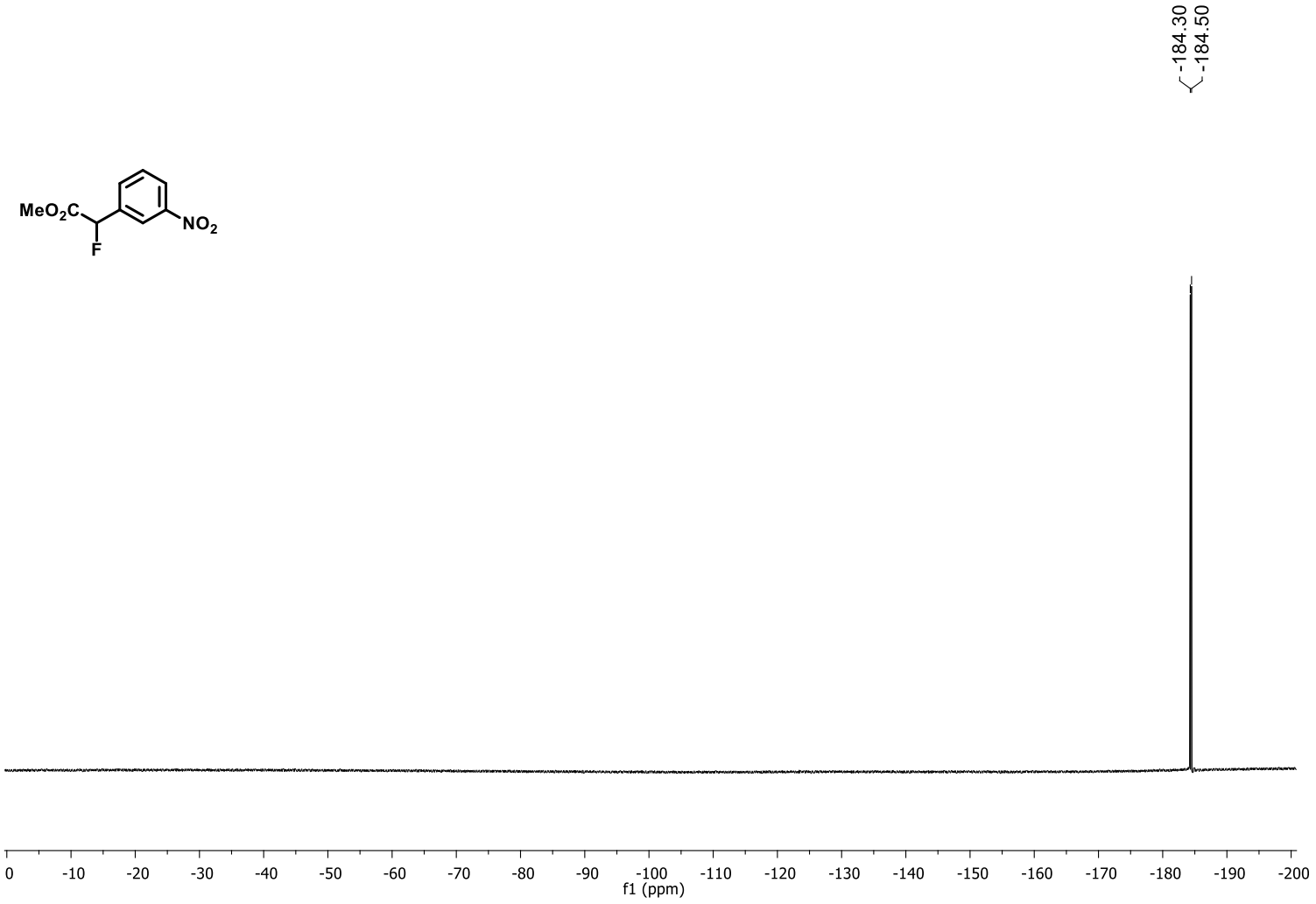
3o - ^{1}H NMR (250 MHz, $CDCl_3$)



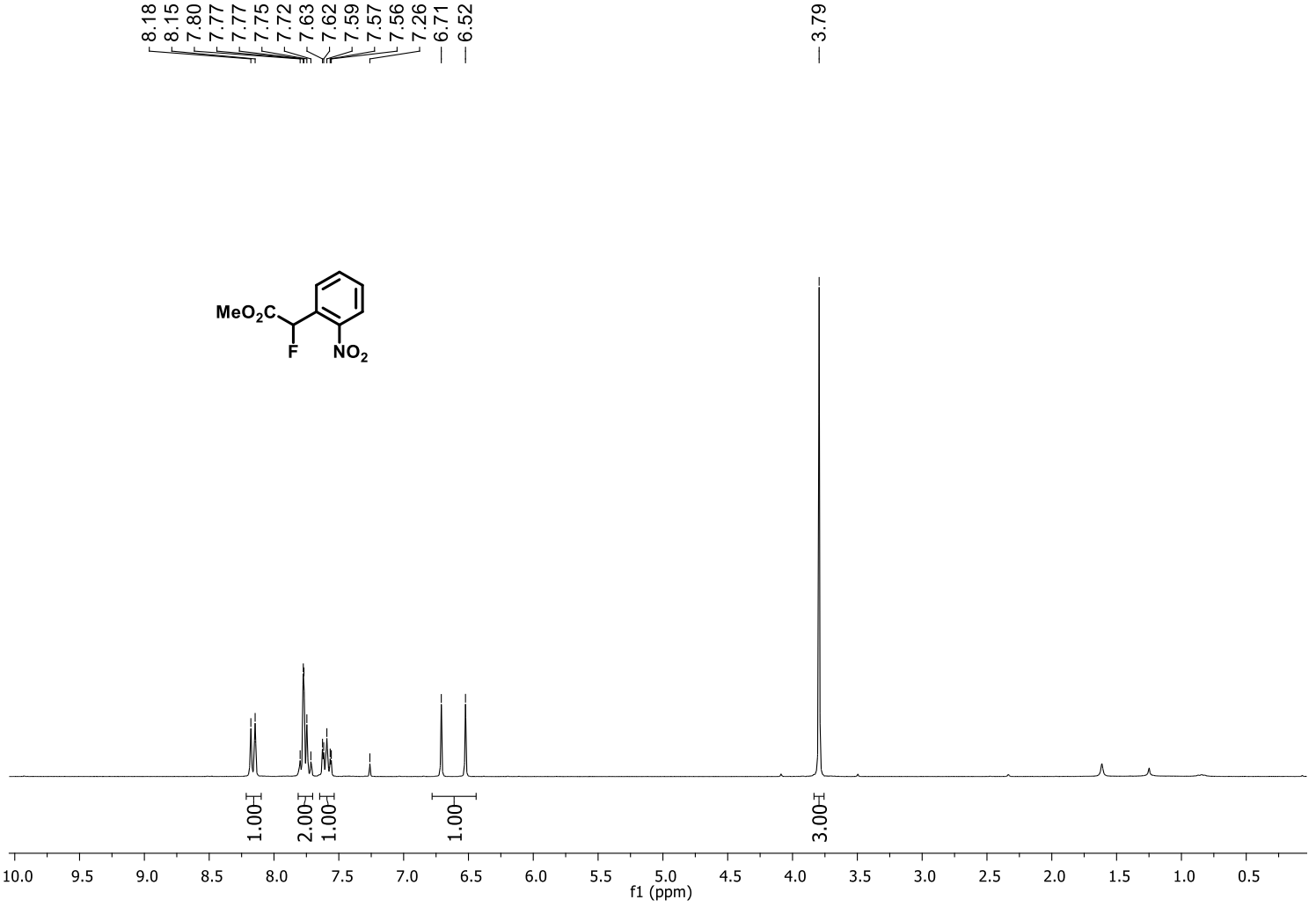
3o - ^{13}C NMR (62.5 MHz, $CDCl_3$)



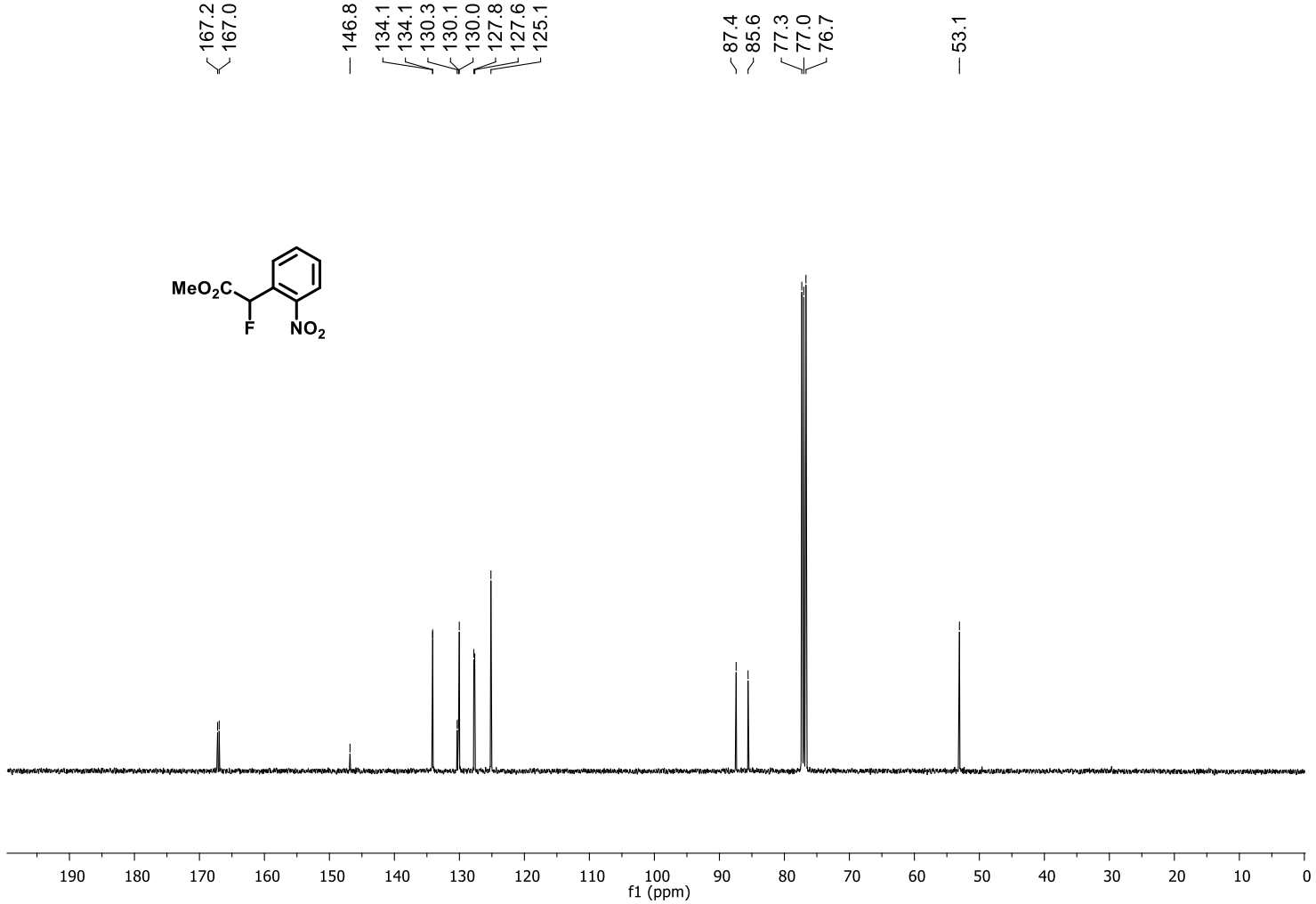
3o - ^{19}F NMR (235 MHz, $CDCl_3$)



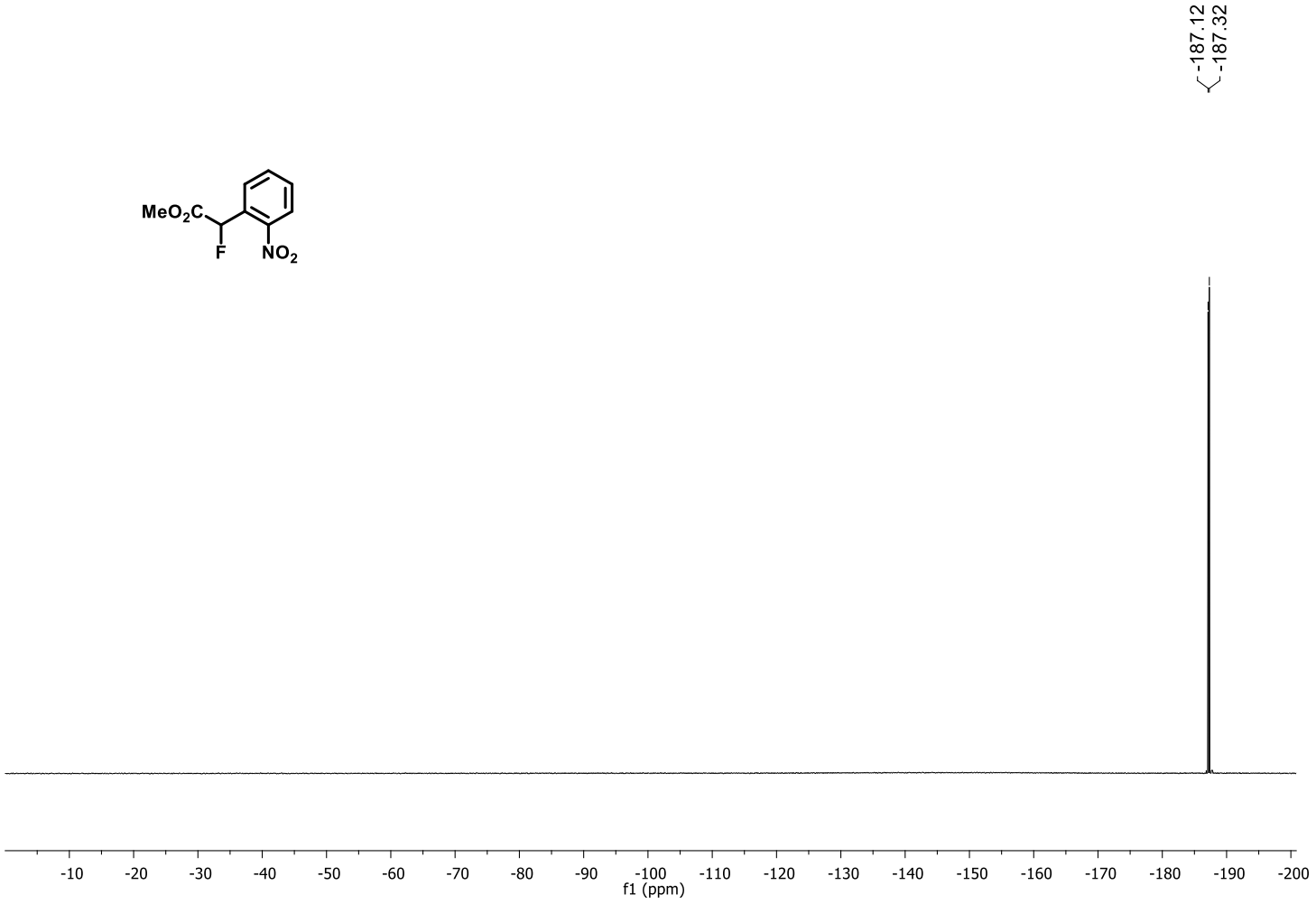
3p - ^{1}H NMR (250 MHz, $CDCl_3$)



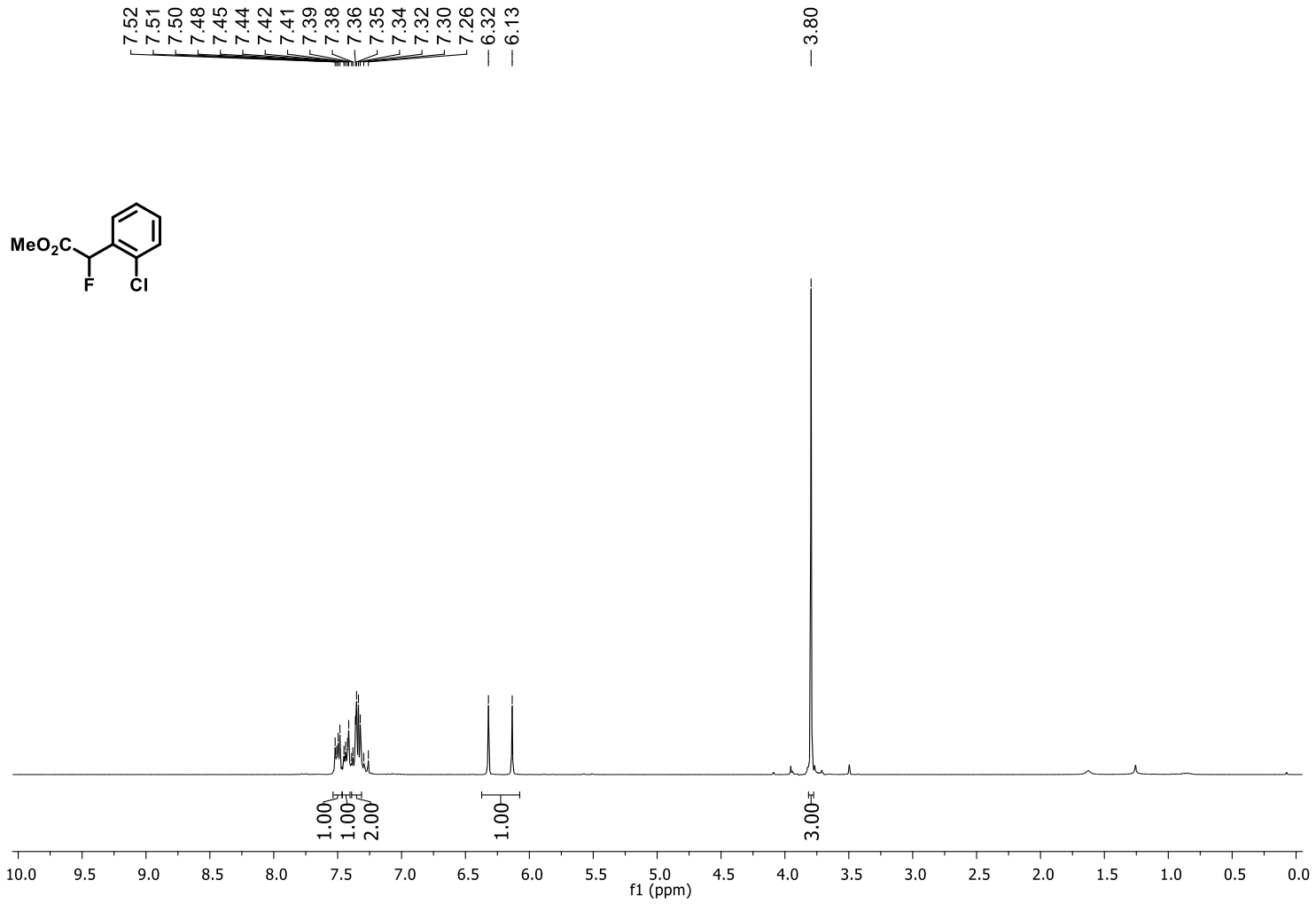
3p - ^{13}C NMR (62.5 MHz, $CDCl_3$)



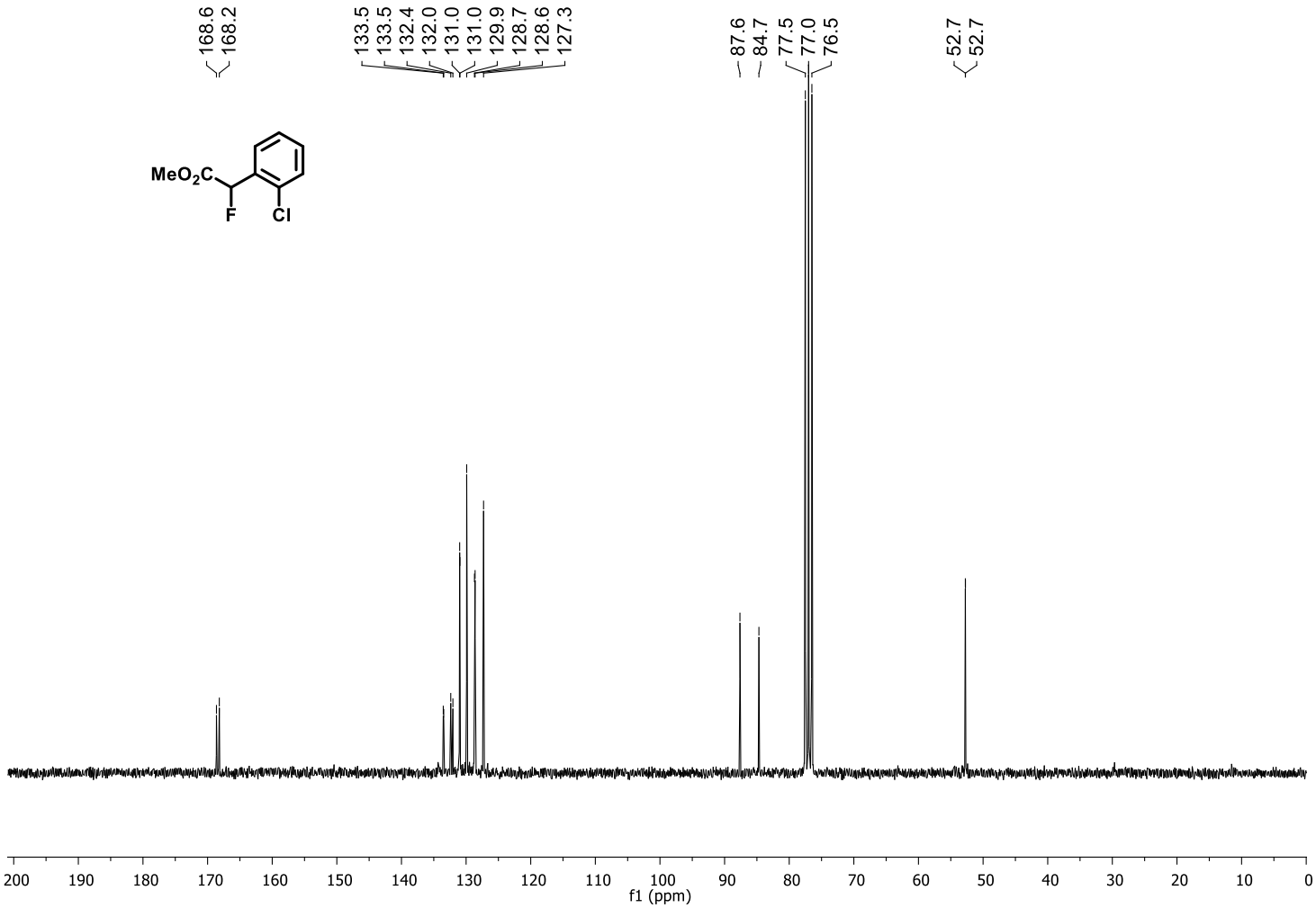
3p - ^{19}F NMR (235 MHz, $CDCl_3$)



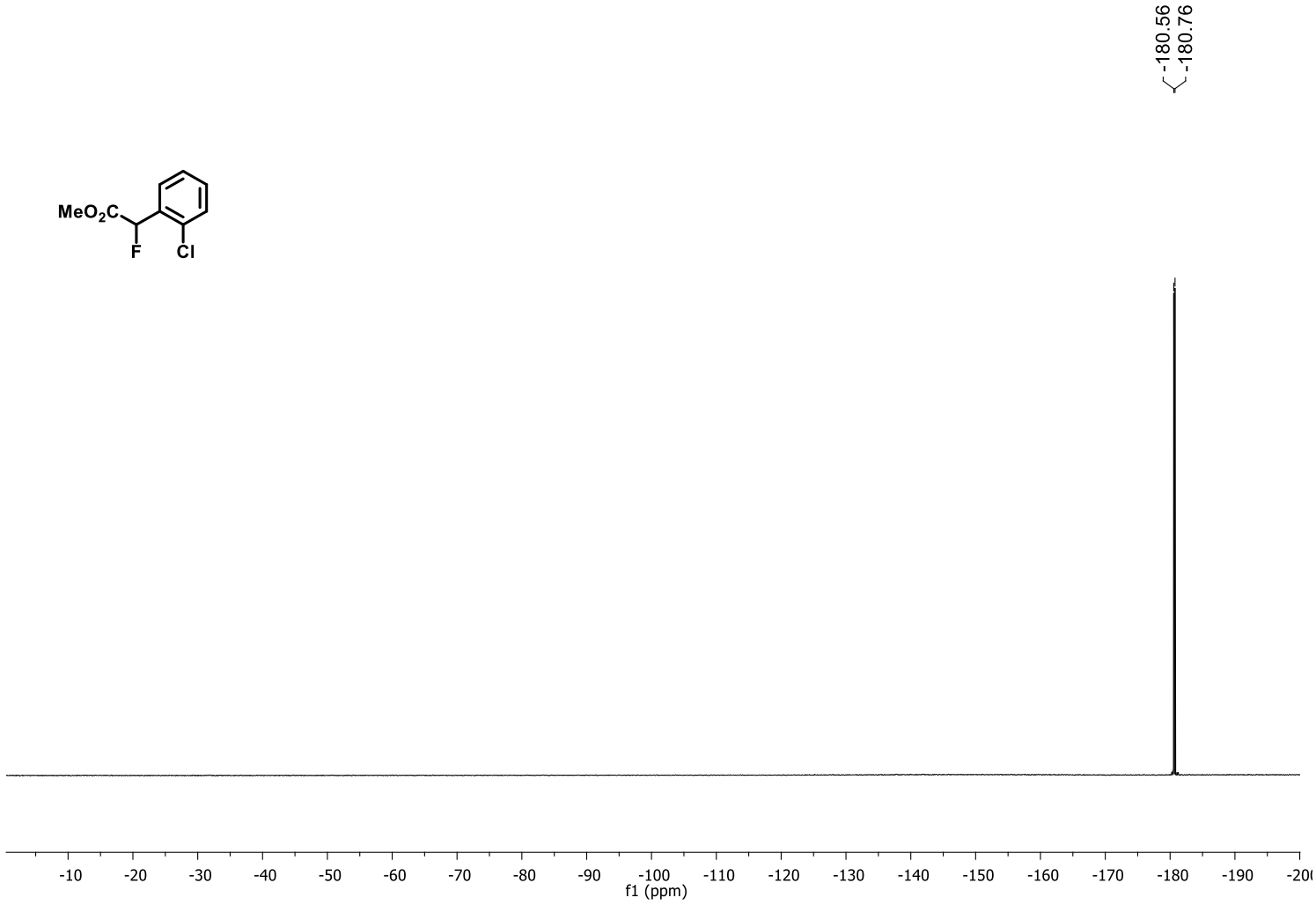
3q - ^{1}H NMR (250 MHz, $CDCl_3$)



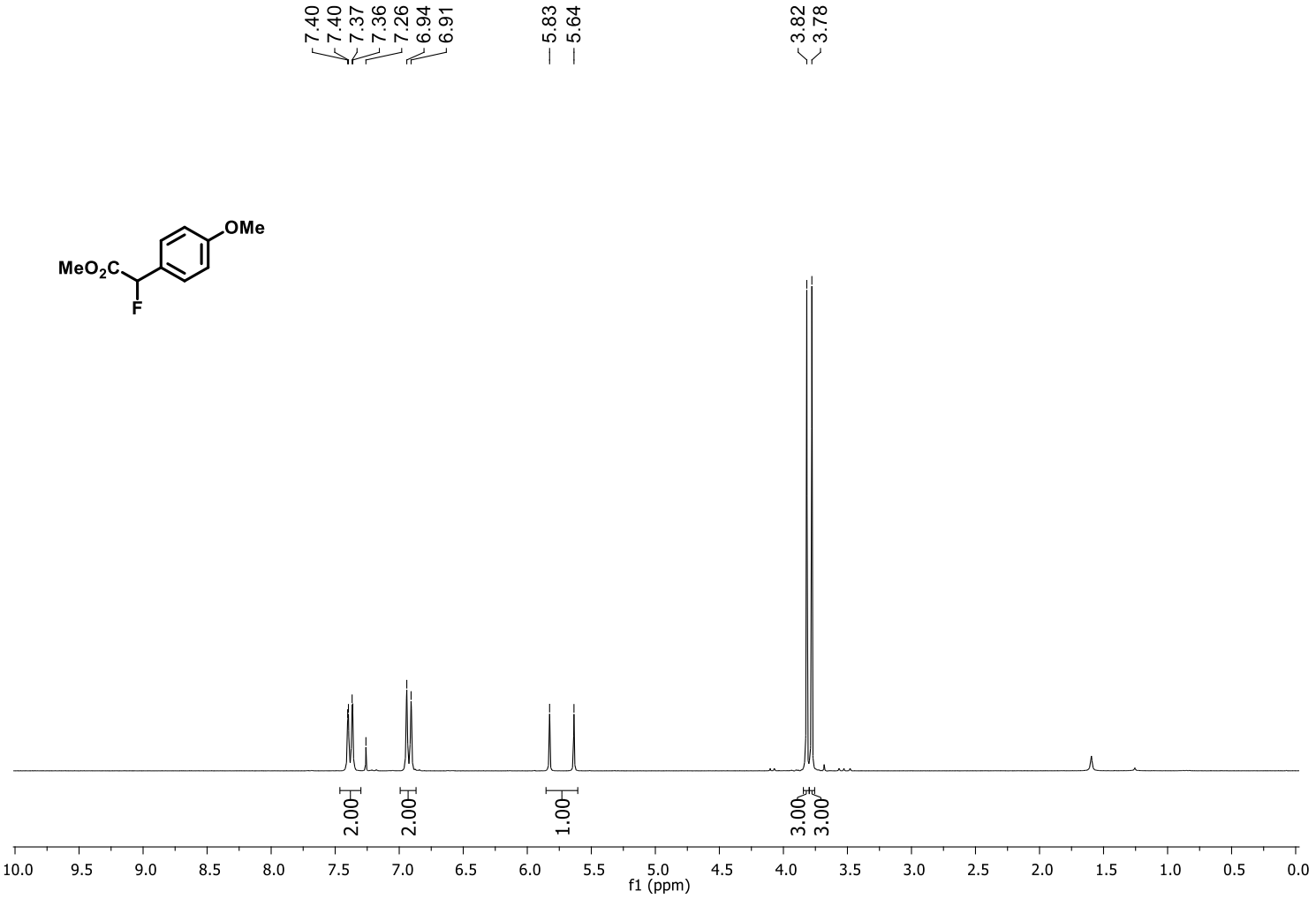
3q - ^{13}C NMR (62.5 MHz, $CDCl_3$)



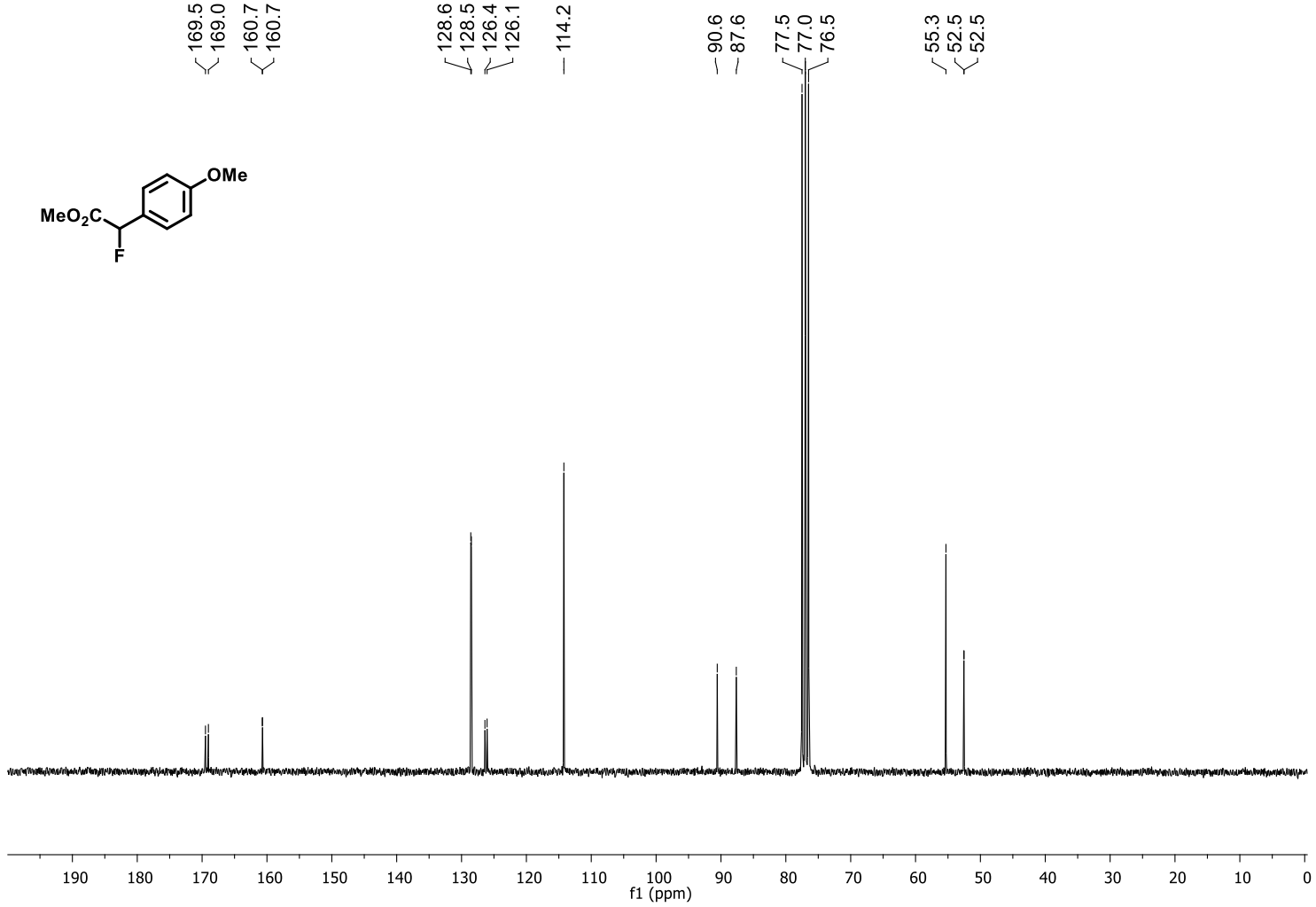
3q - ^{19}F NMR (235 MHz, $CDCl_3$)



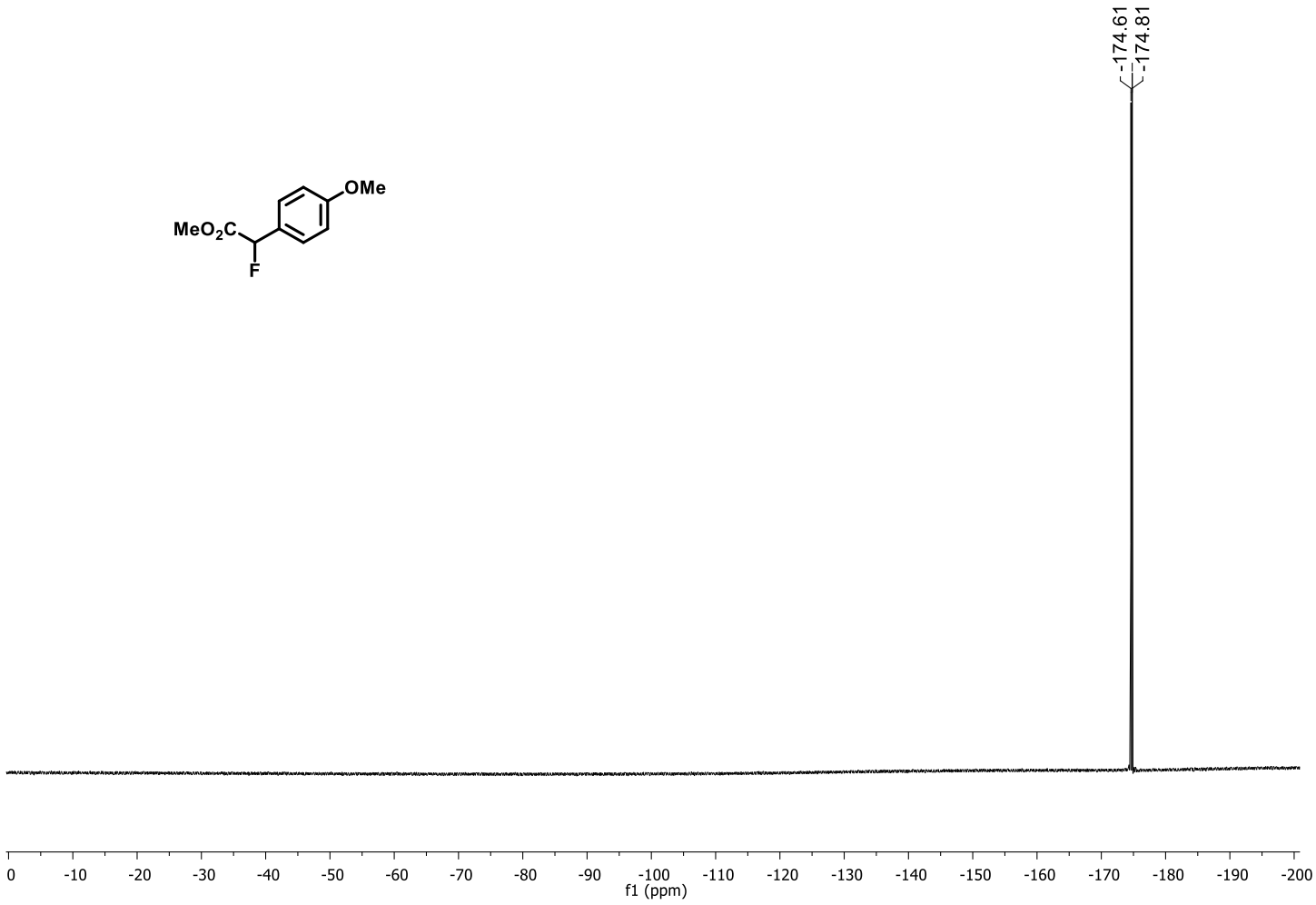
3r - ^{1}H NMR (250 MHz, $CDCl_3$)



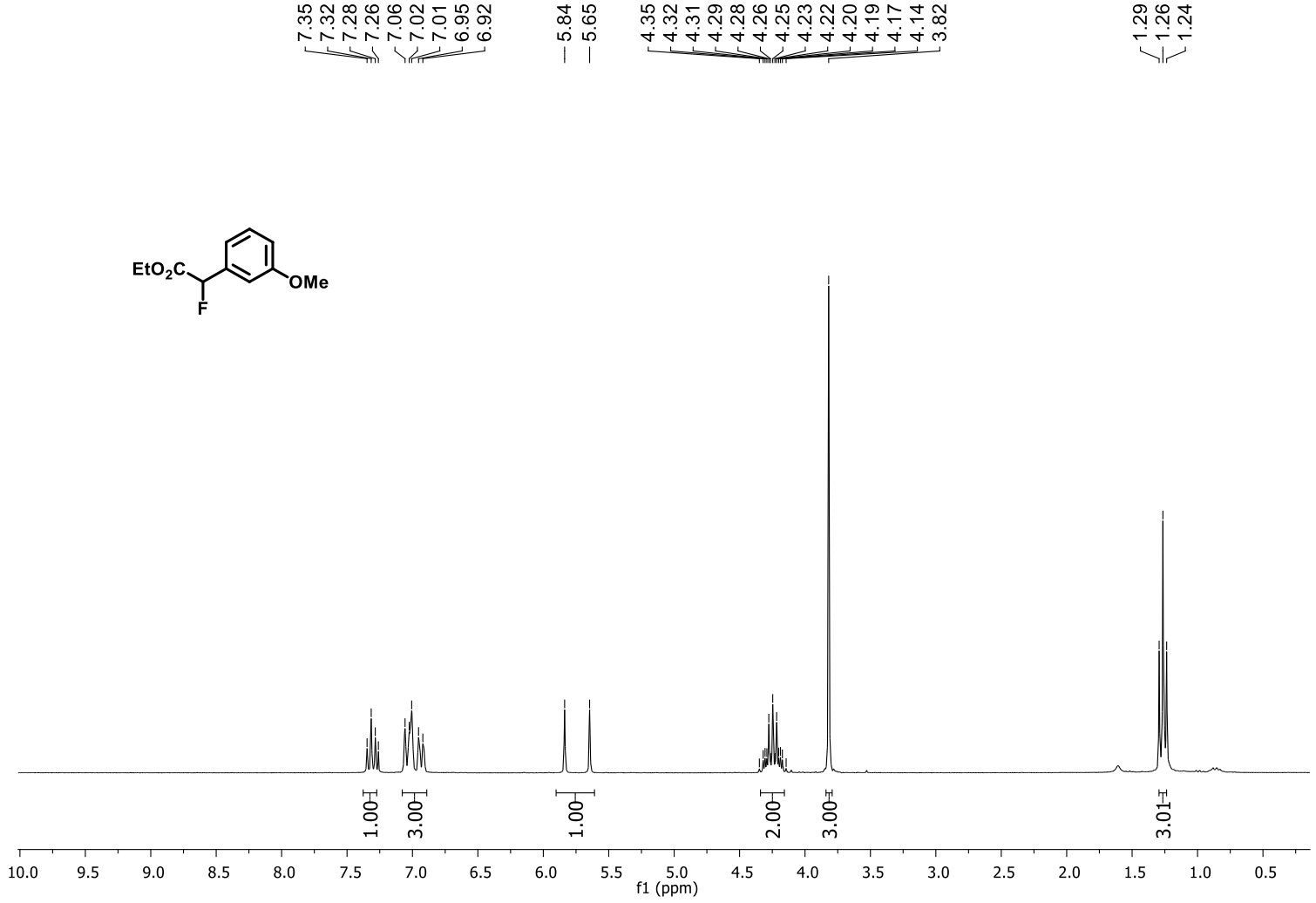
3r - ^{13}C NMR (62.5 MHz, $CDCl_3$)



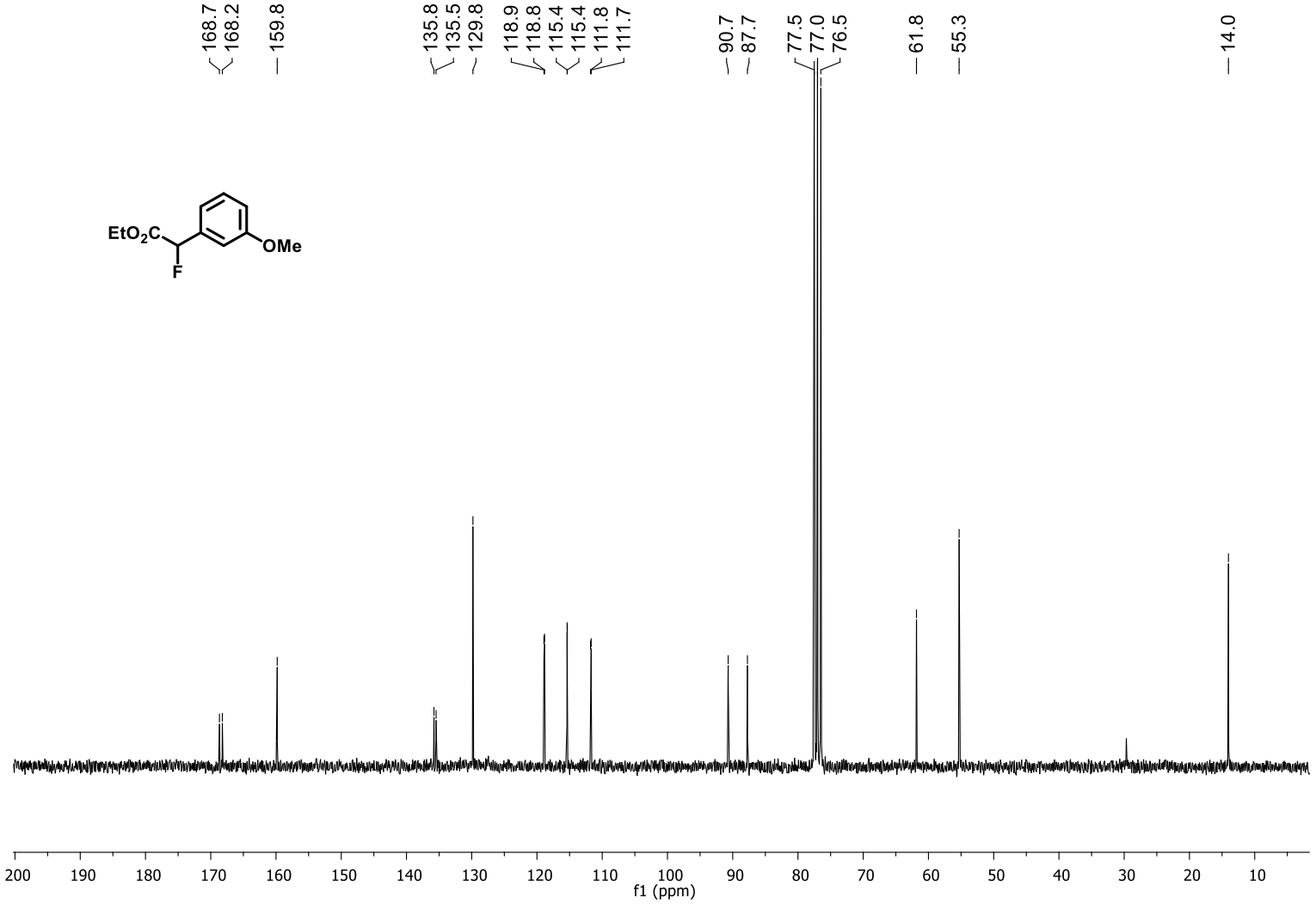
3r - ^{19}F NMR (235 MHz, $CDCl_3$)



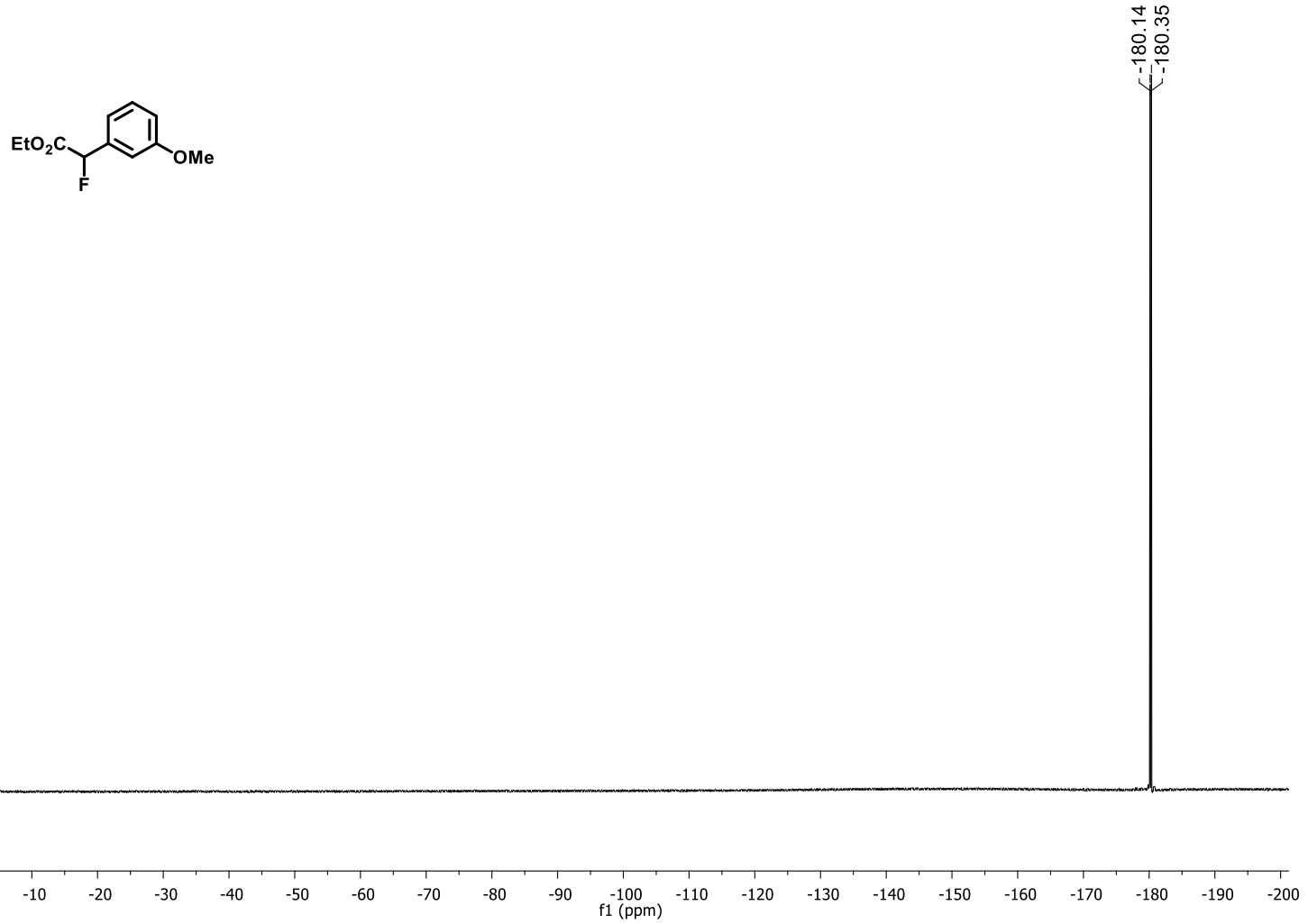
3s - ^{1}H NMR (250 MHz, $CDCl_3$)



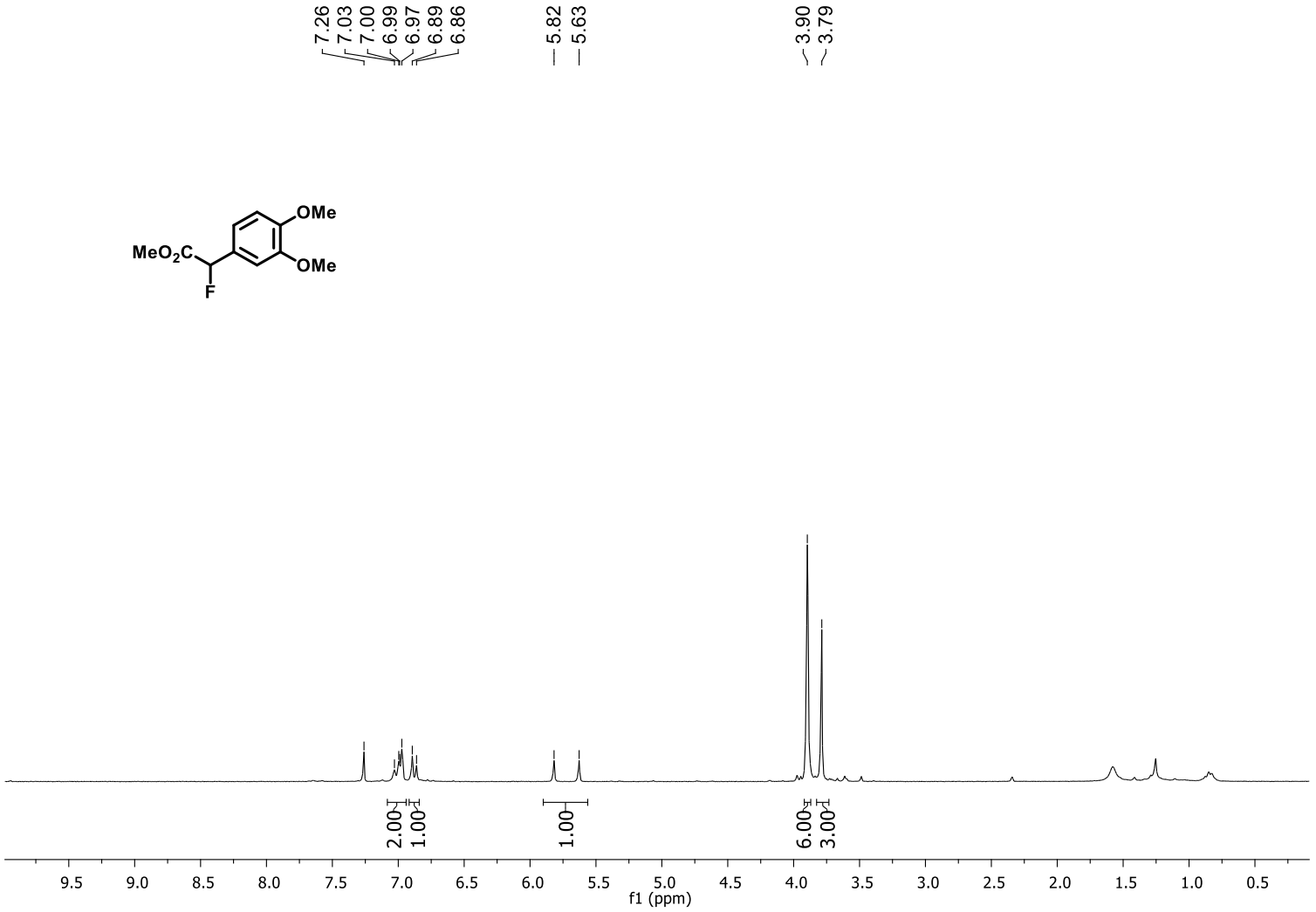
3s - ^{13}C NMR (62.5 MHz, $CDCl_3$)



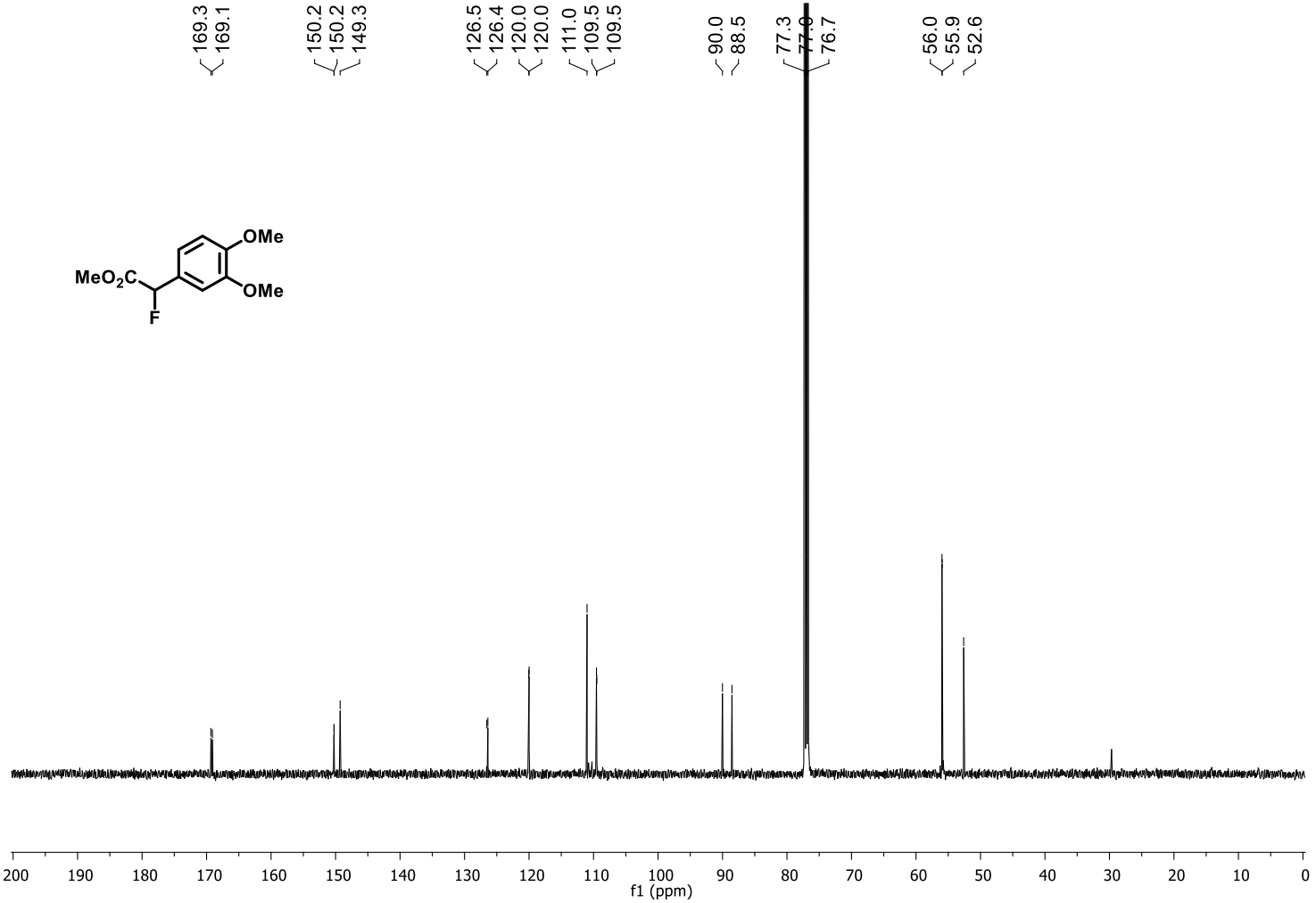
3s - ^{19}F NMR (235 MHz, $CDCl_3$)



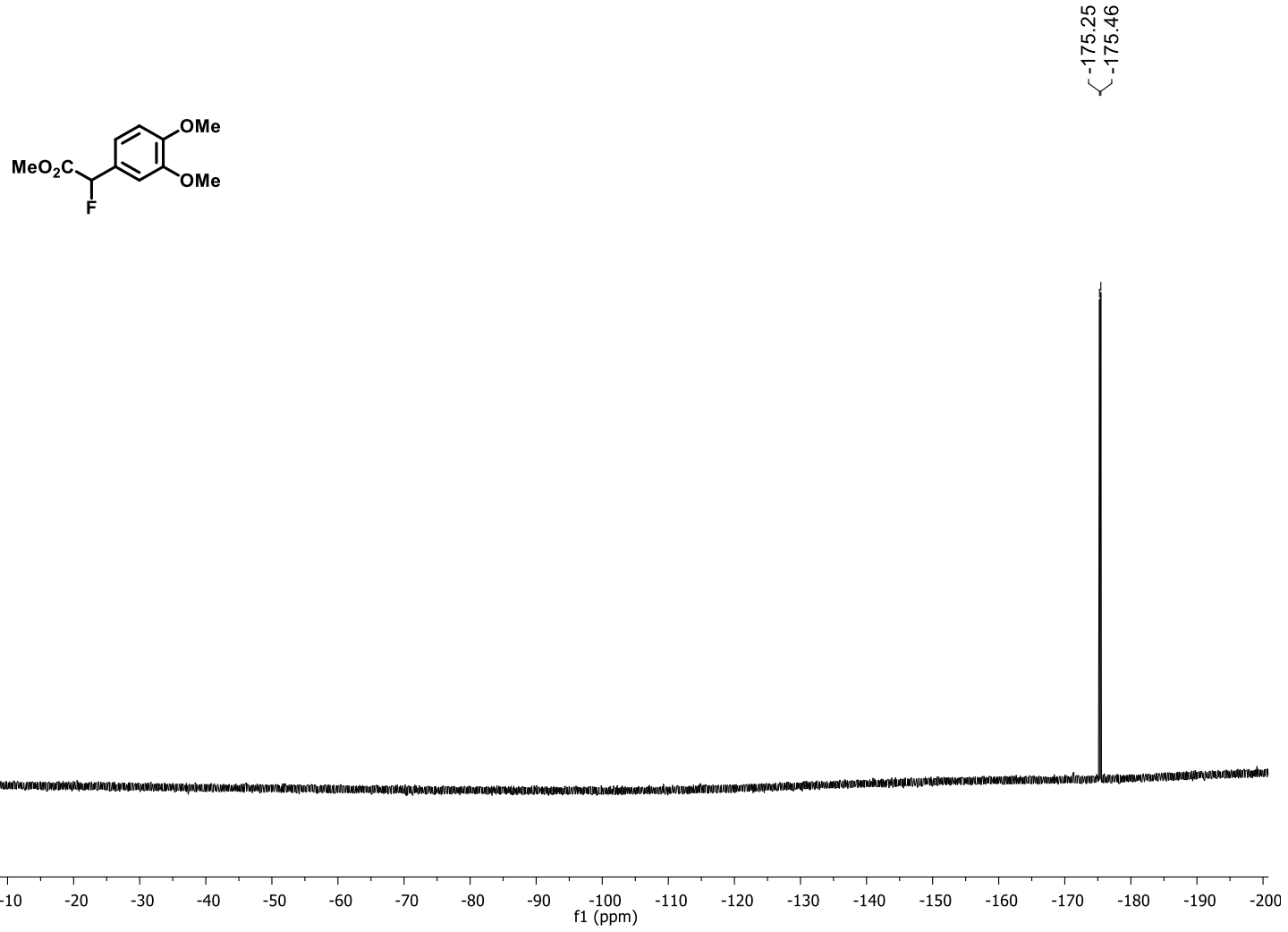
3t -^{1}H NMR (250 MHz, $CDCl_3$)



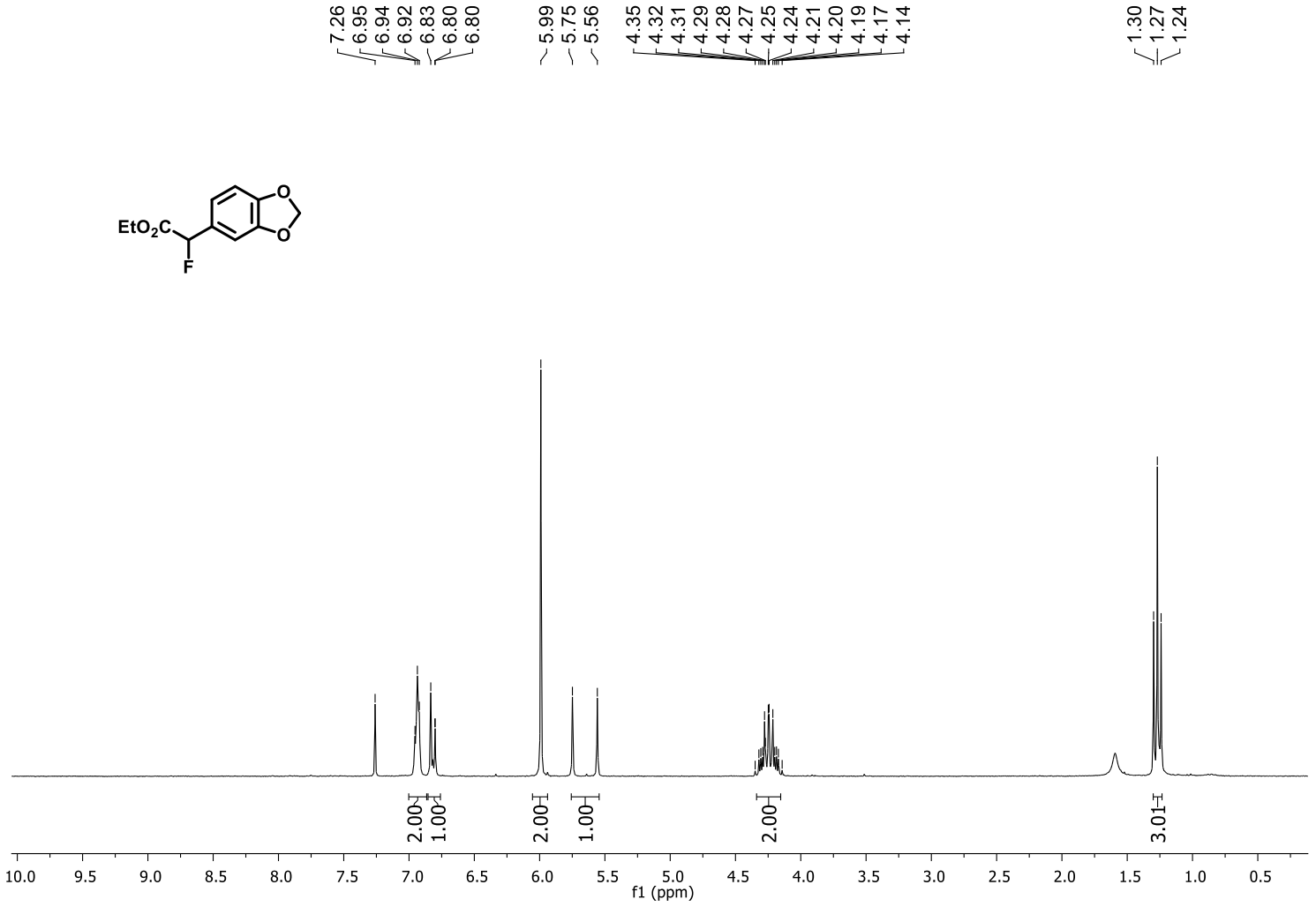
3t - ^{13}C NMR (62.5 MHz, $CDCl_3$)



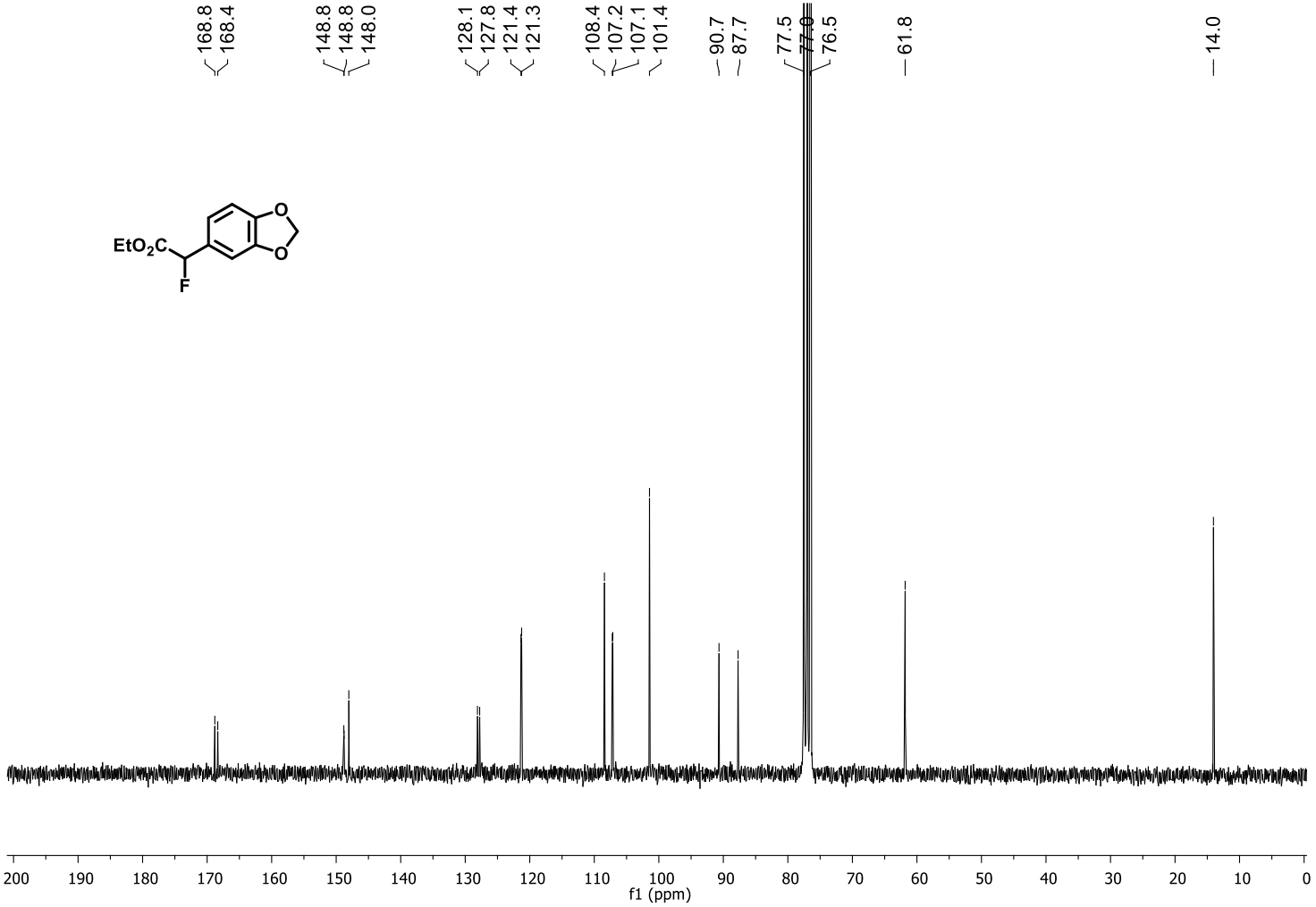
3t - ^{19}F NMR (235 MHz, $CDCl_3$)



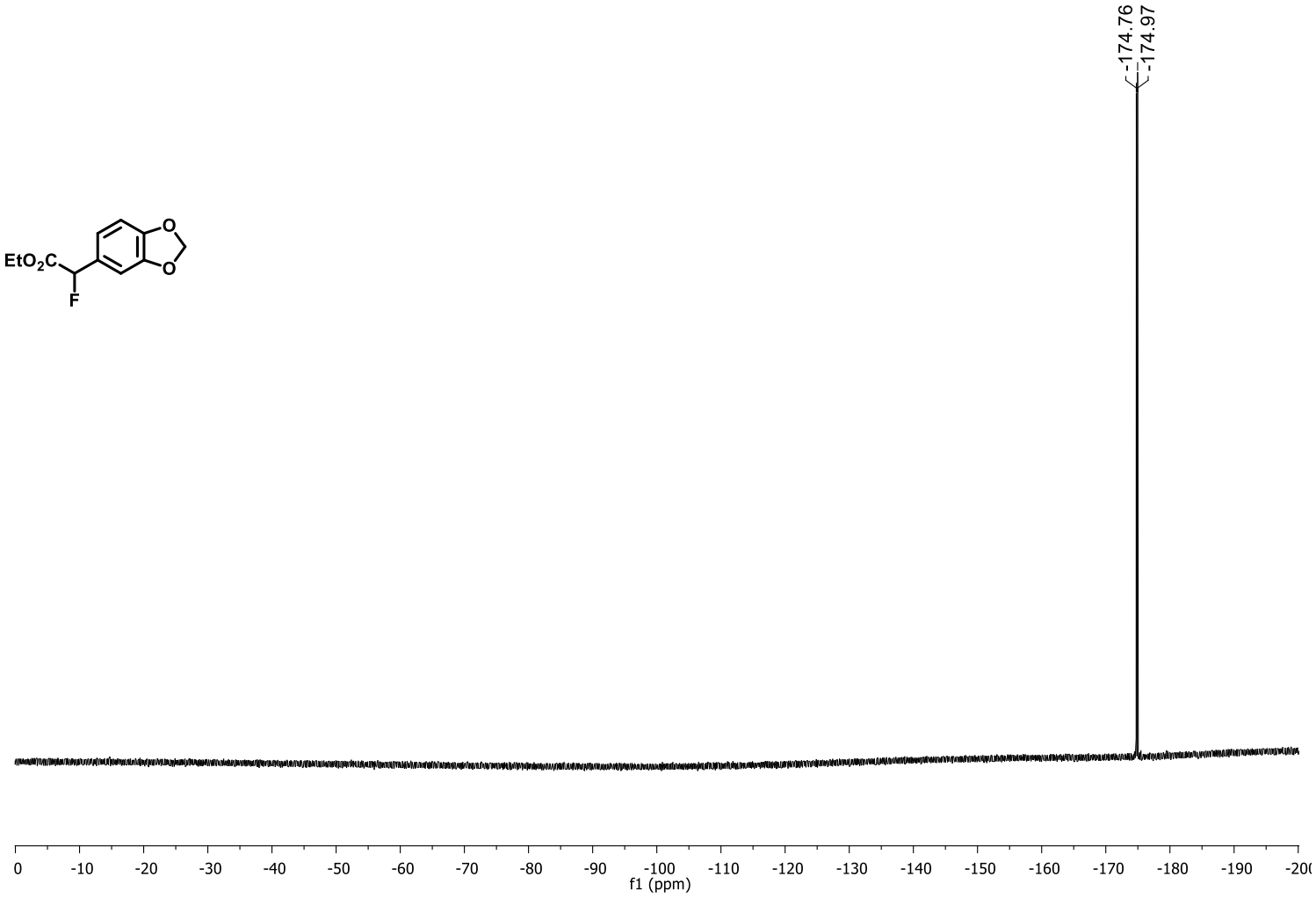
3u - ^{1}H NMR (250 MHz, $CDCl_3$)



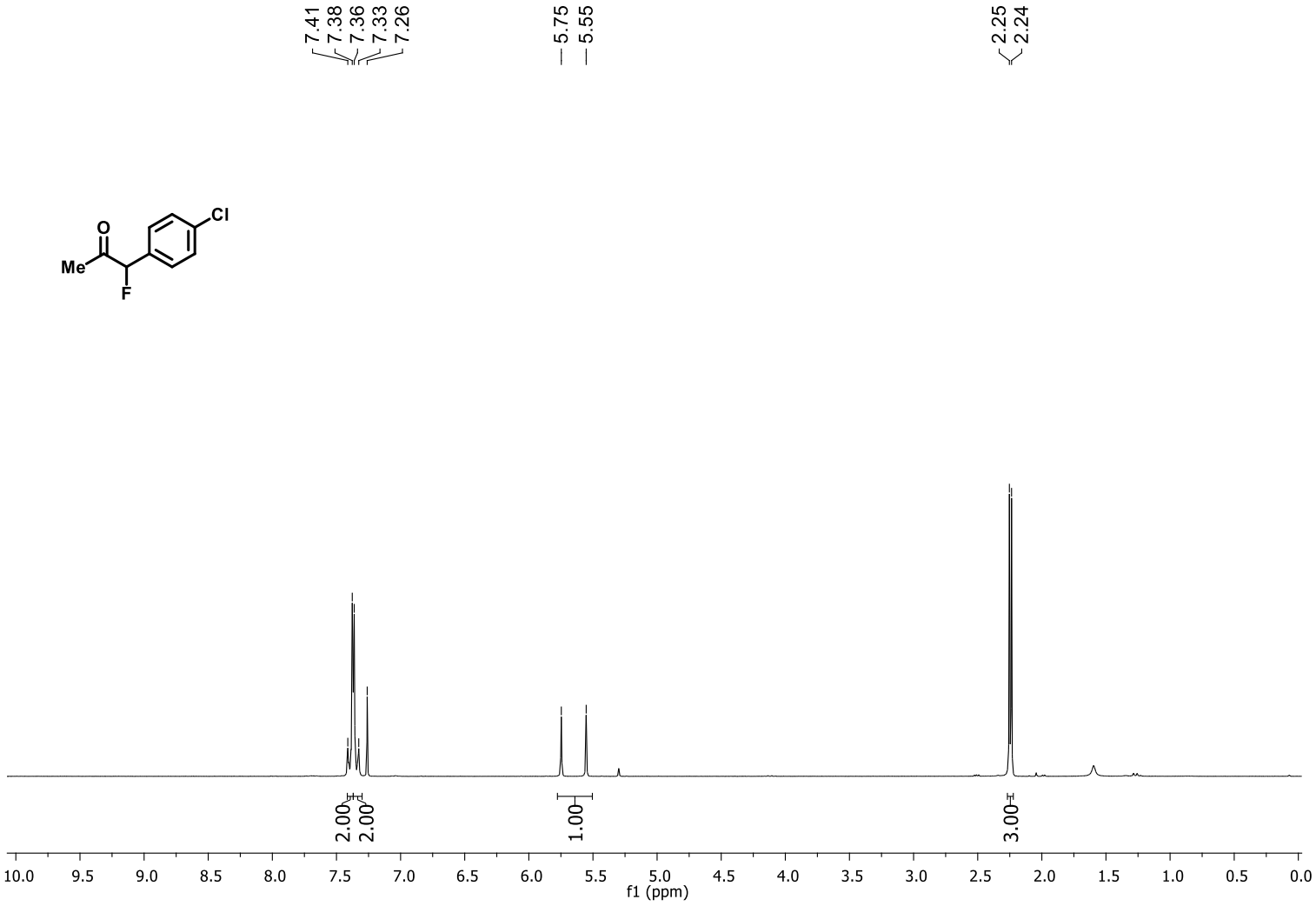
3u - ^{13}C NMR (62.5 MHz, $CDCl_3$)



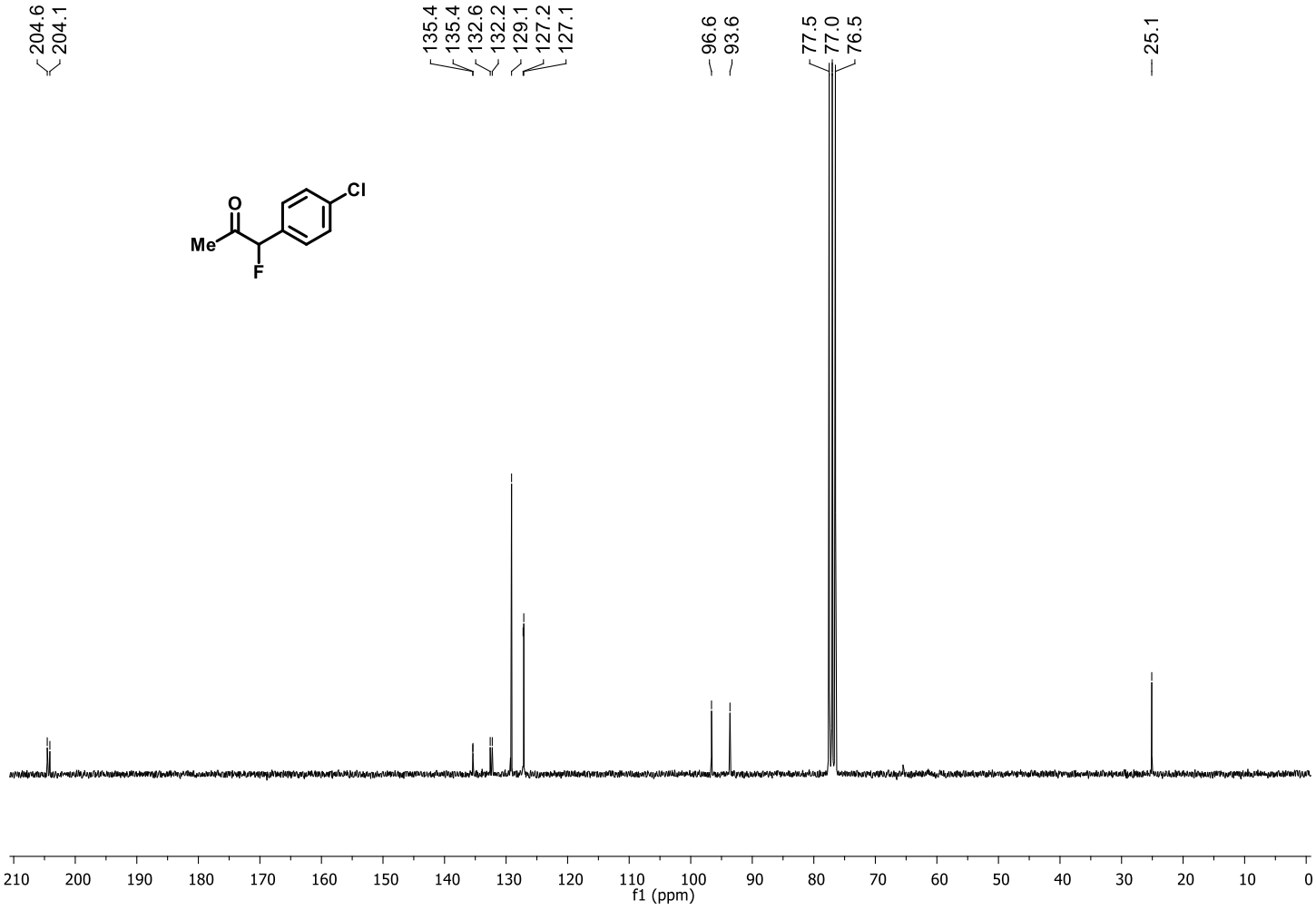
3u - ^{19}F NMR (235 MHz, $CDCl_3$)



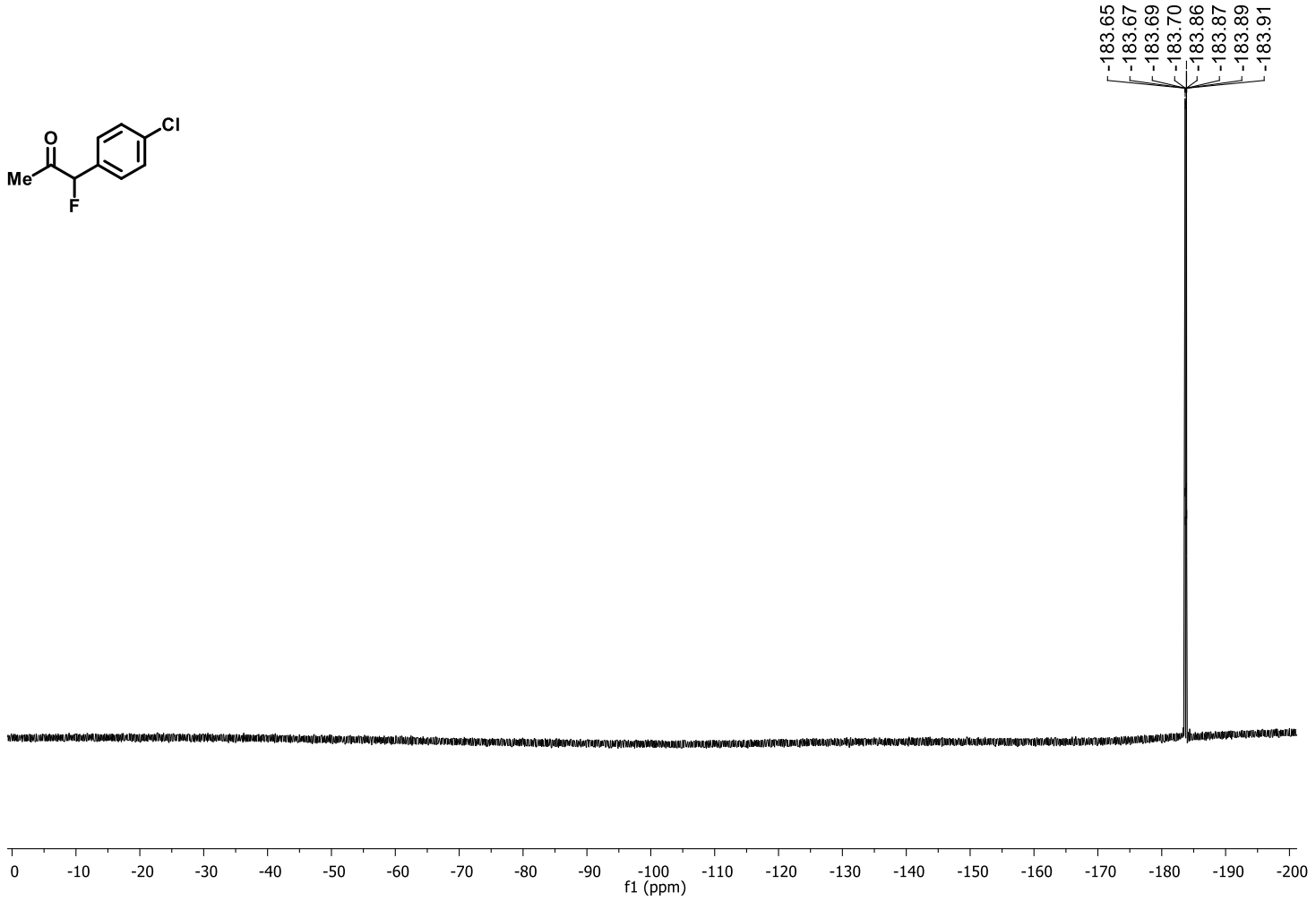
3v - ^{1}H NMR (250 MHz, $CDCl_3$)



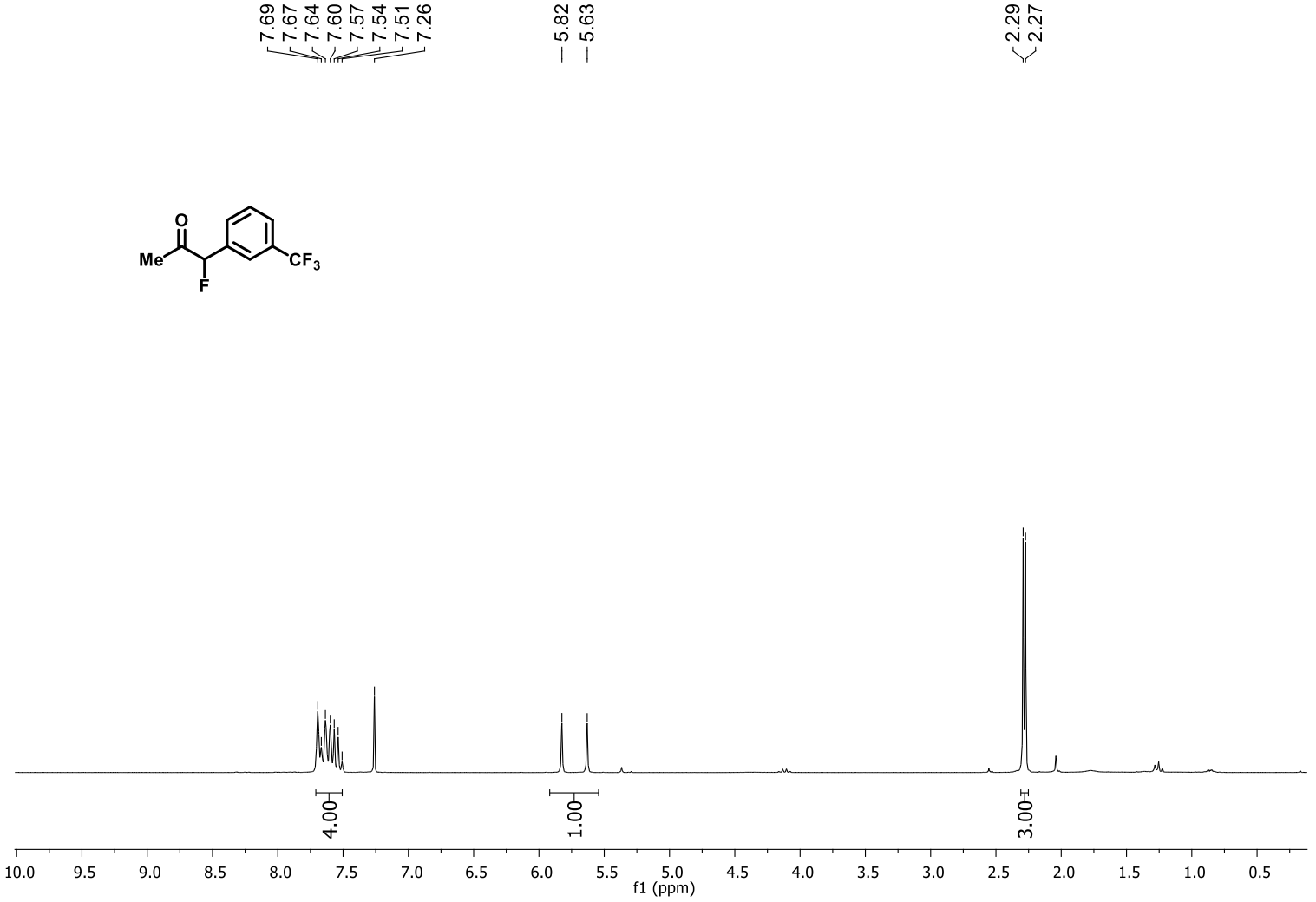
3v - ^{13}C NMR (62.5 MHz, $CDCl_3$)



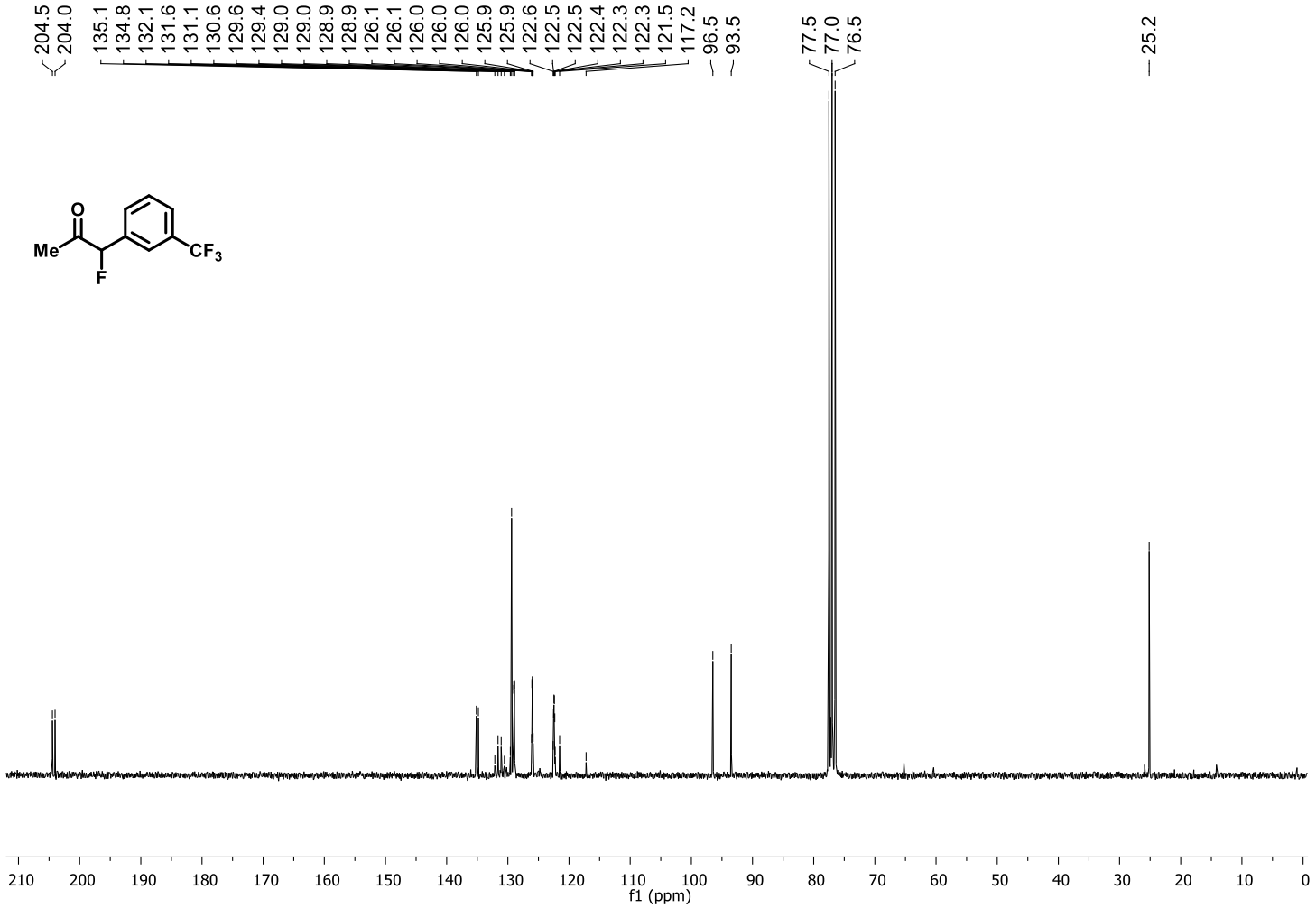
3v – ^{19}F NMR (235 MHz, $CDCl_3$)



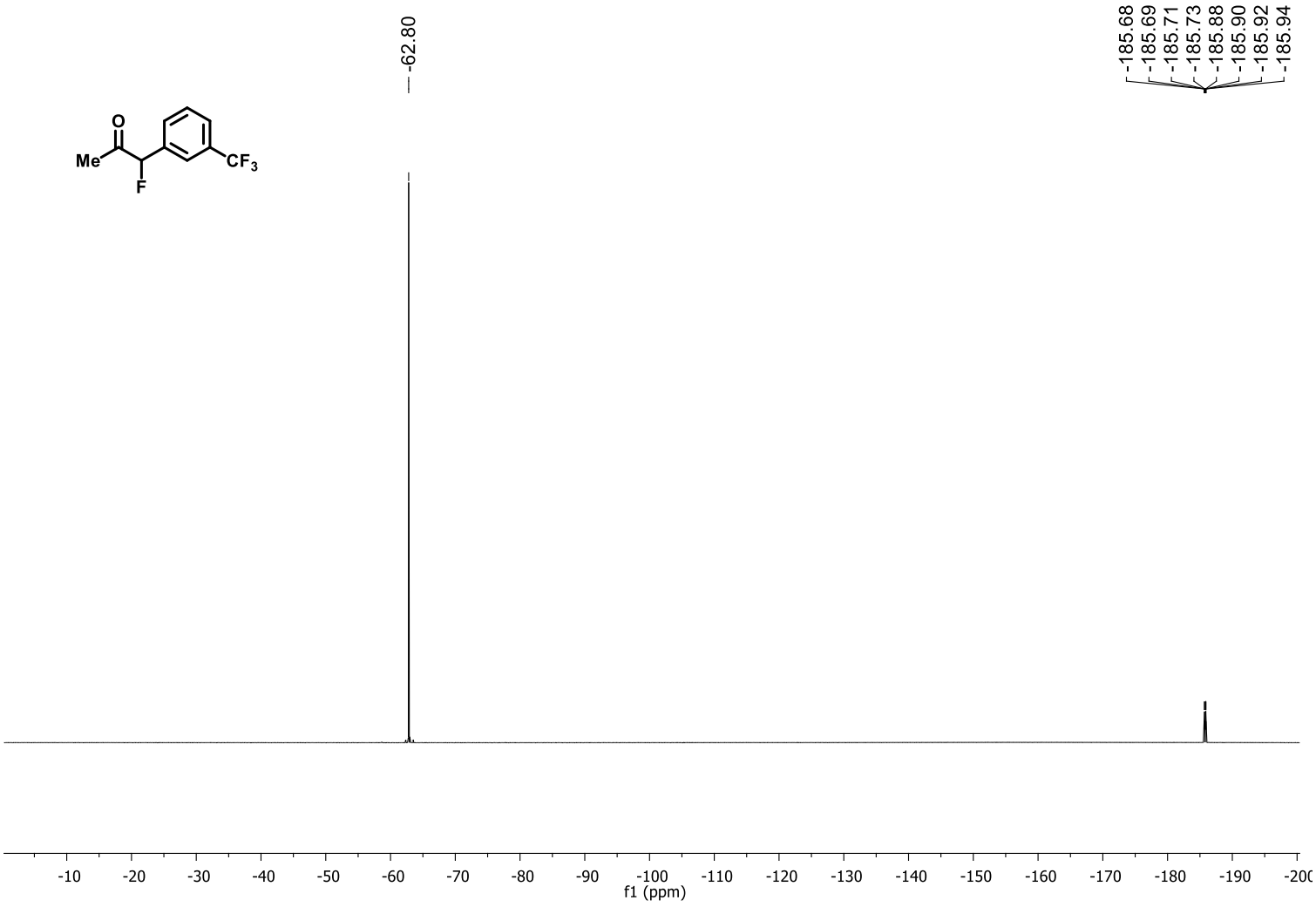
3w - ^{1}H NMR (250 MHz, $CDCl_3$)



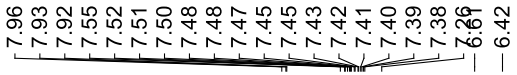
3w - ^{13}C NMR (62.5 MHz, $CDCl_3$)

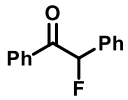


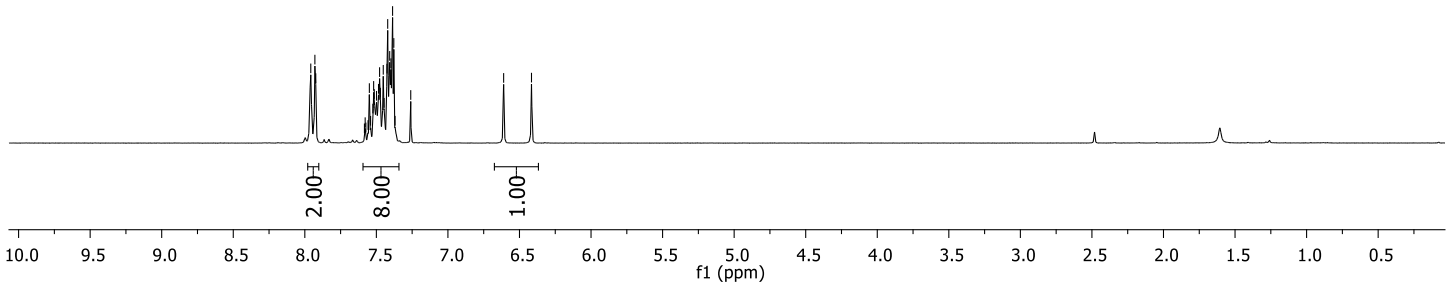
3w – ^{19}F NMR (235 MHz, $CDCl_3$)



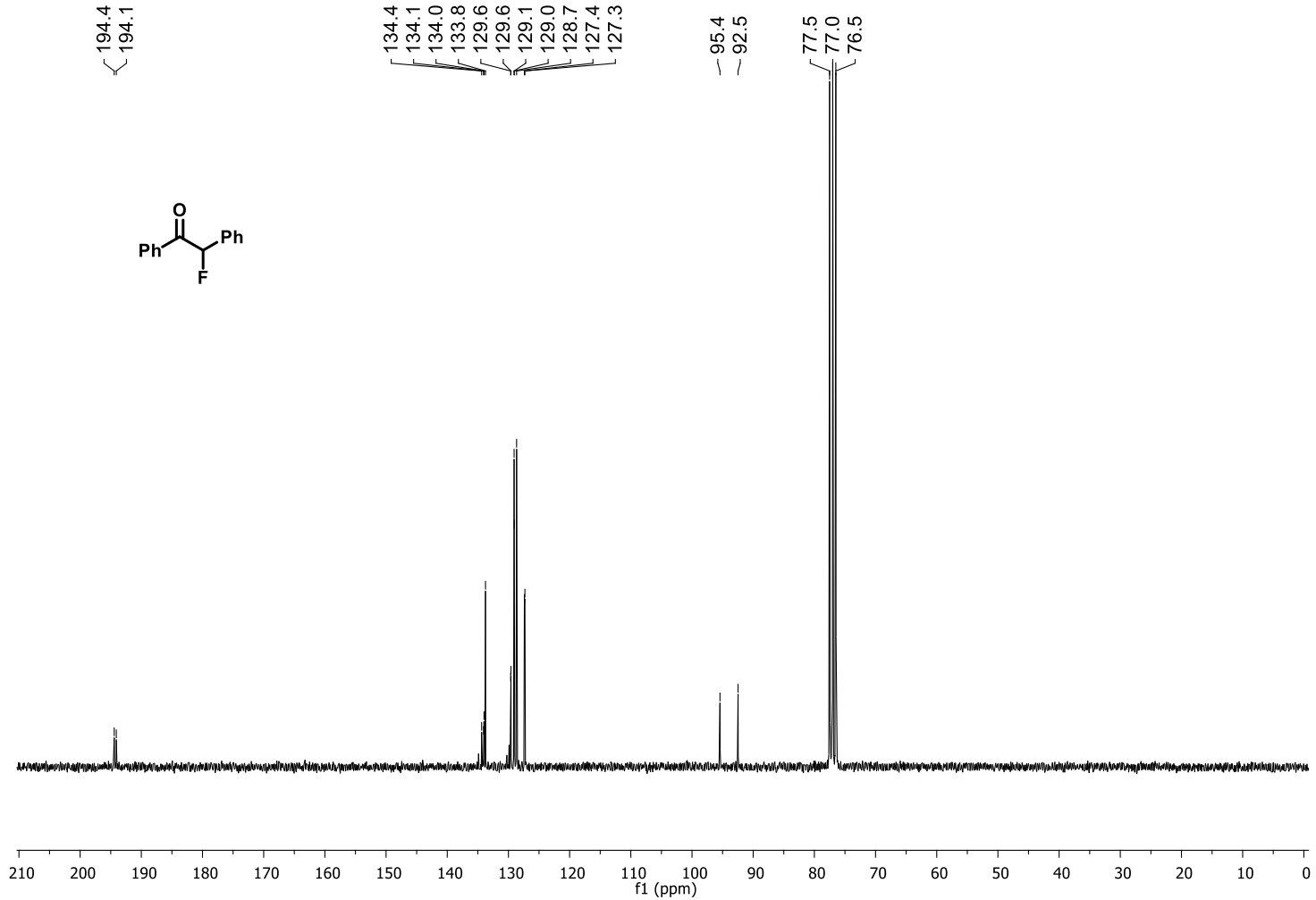
3x - ^{1}H NMR (250 MHz, $CDCl_3$)



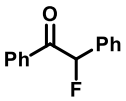




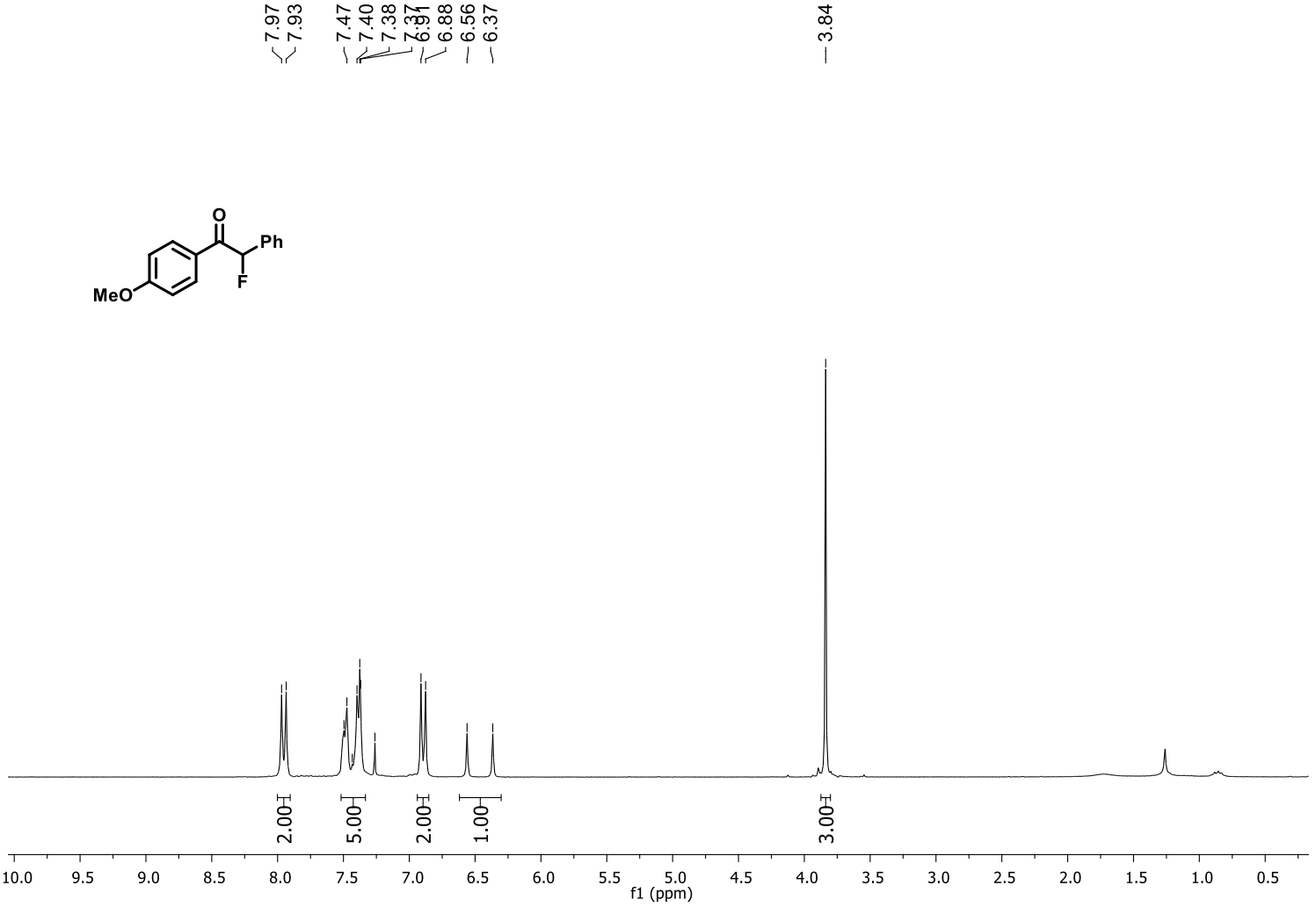
3x – ^{13}C NMR (62.5 MHz, $CDCl_3$)



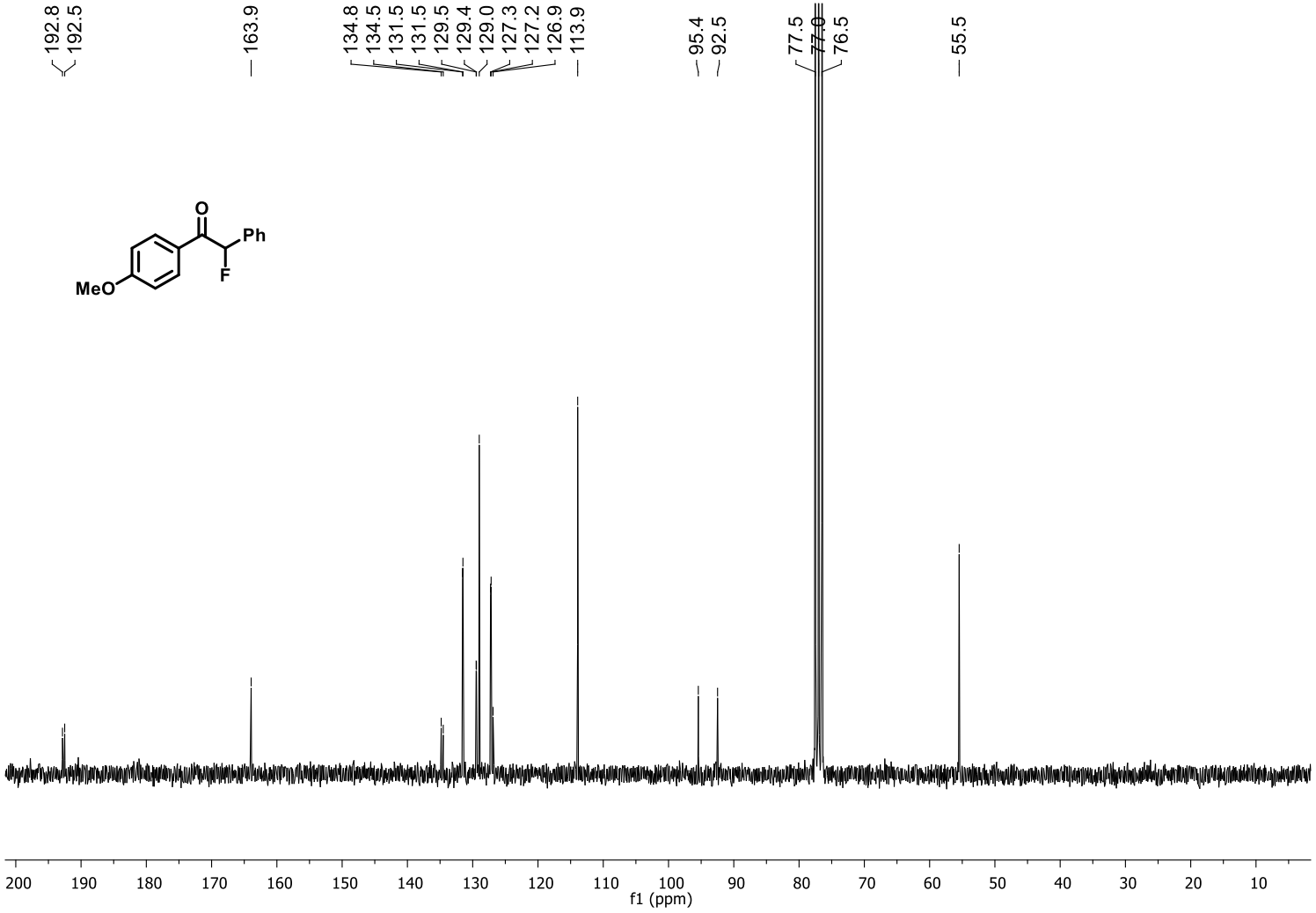
3x – ^{19}F NMR (235 MHz, $CDCl_3$)



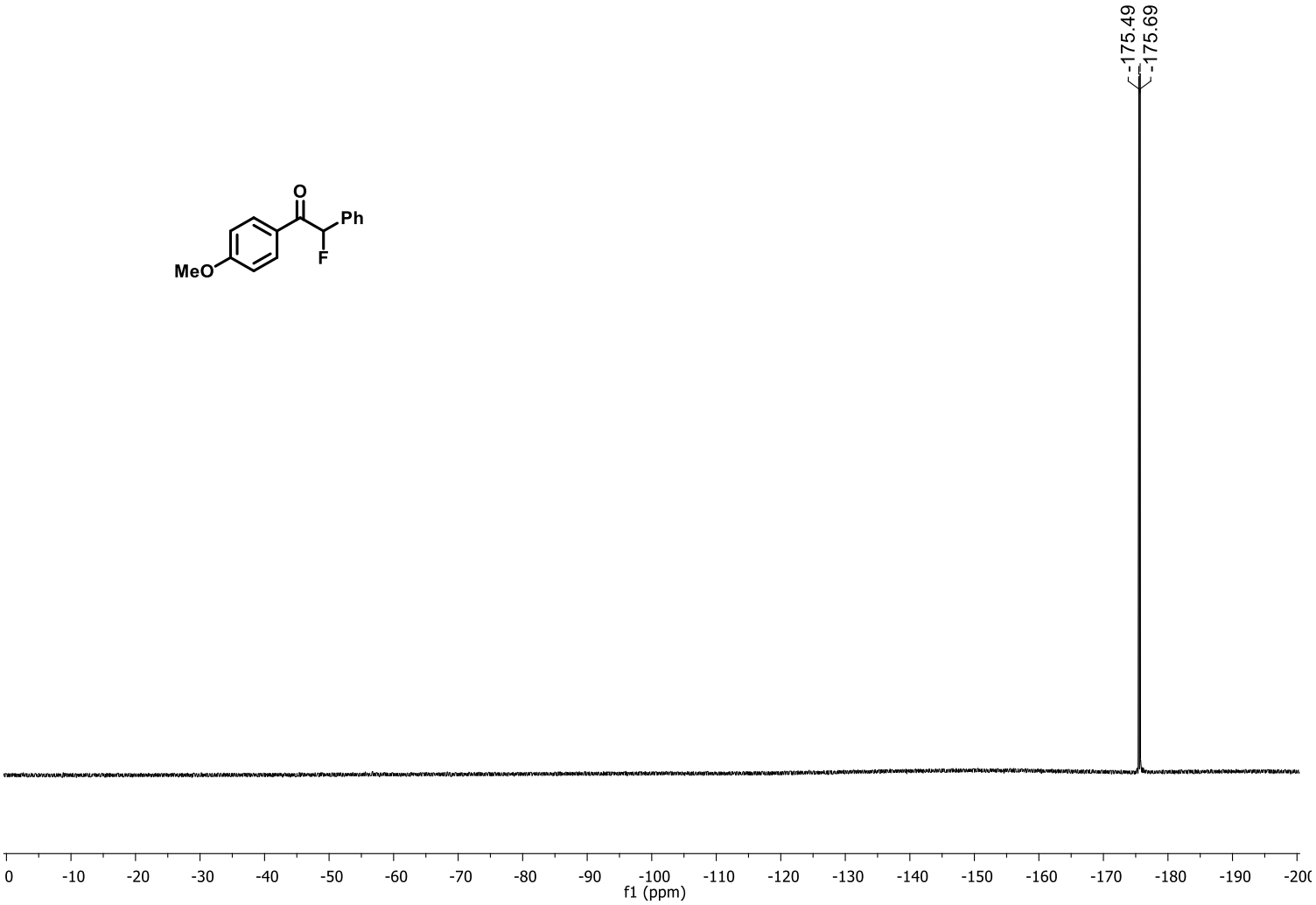
3y - ^{1}H NMR (250 MHz, $CDCl_3$)



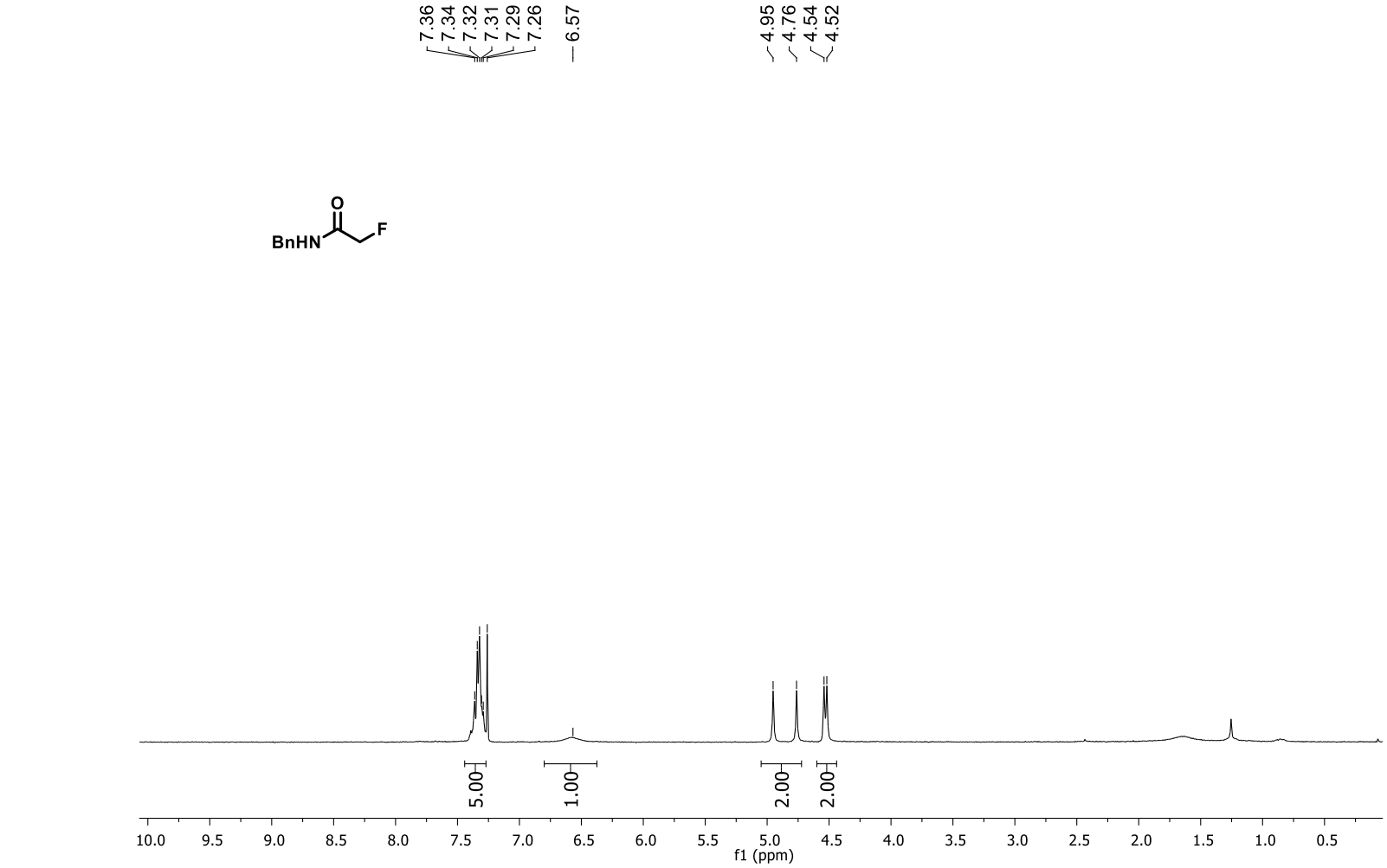
3y - ^{13}C NMR (62.5 MHz, $CDCl_3$)



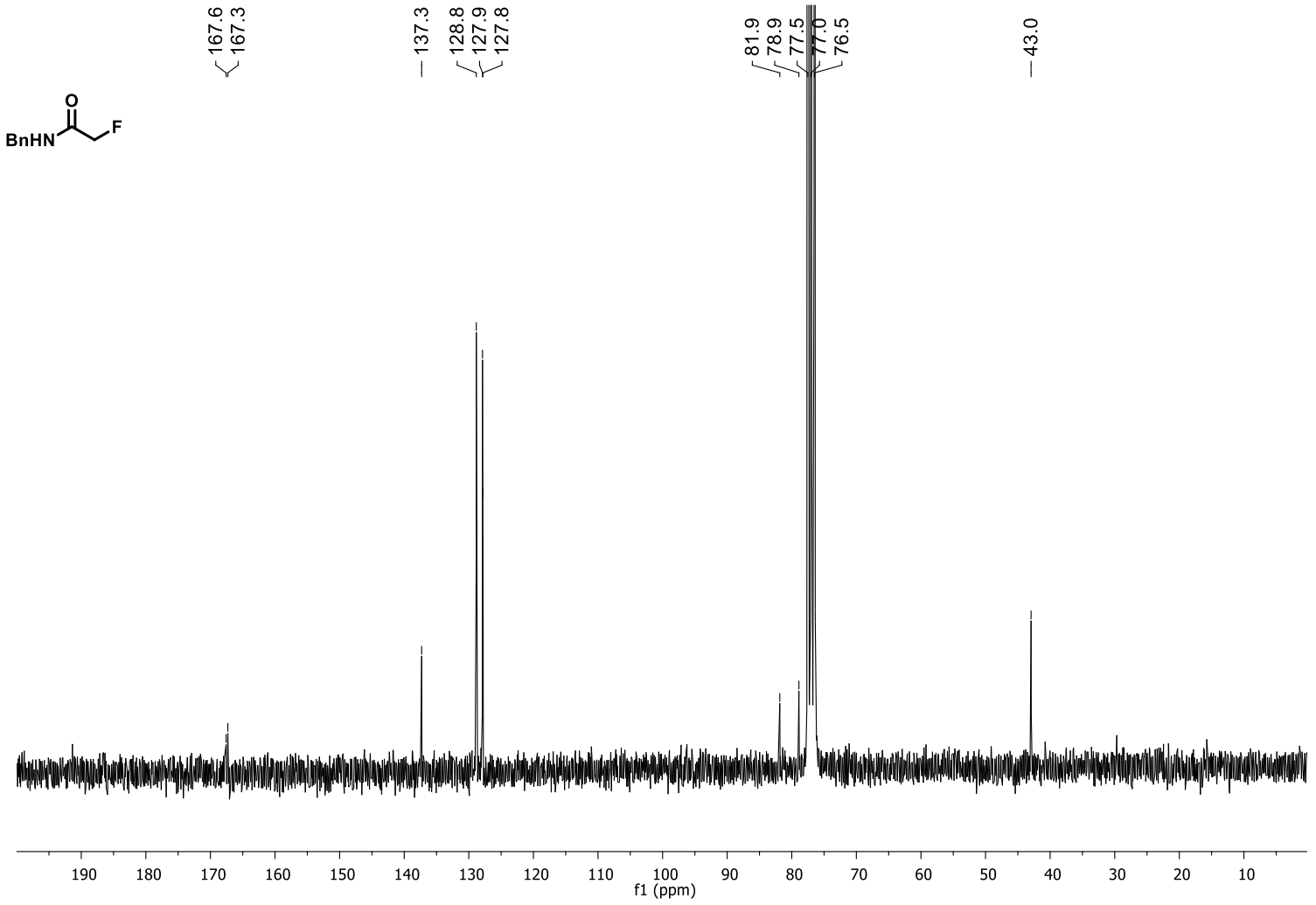
3y - ^{19}F NMR (235 MHz, $CDCl_3$)



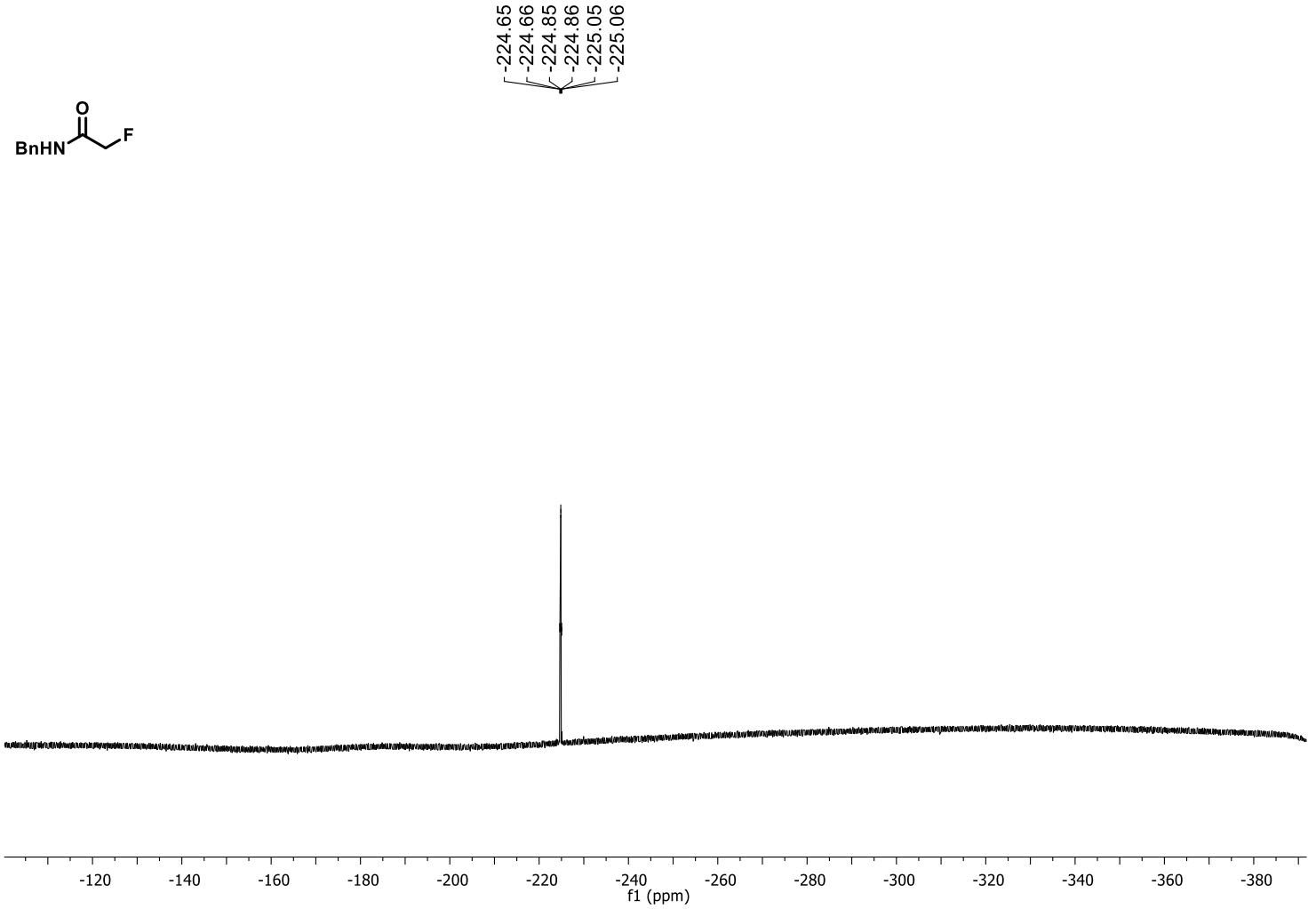
3z - ^{1}H NMR (250 MHz, $CDCl_3$)



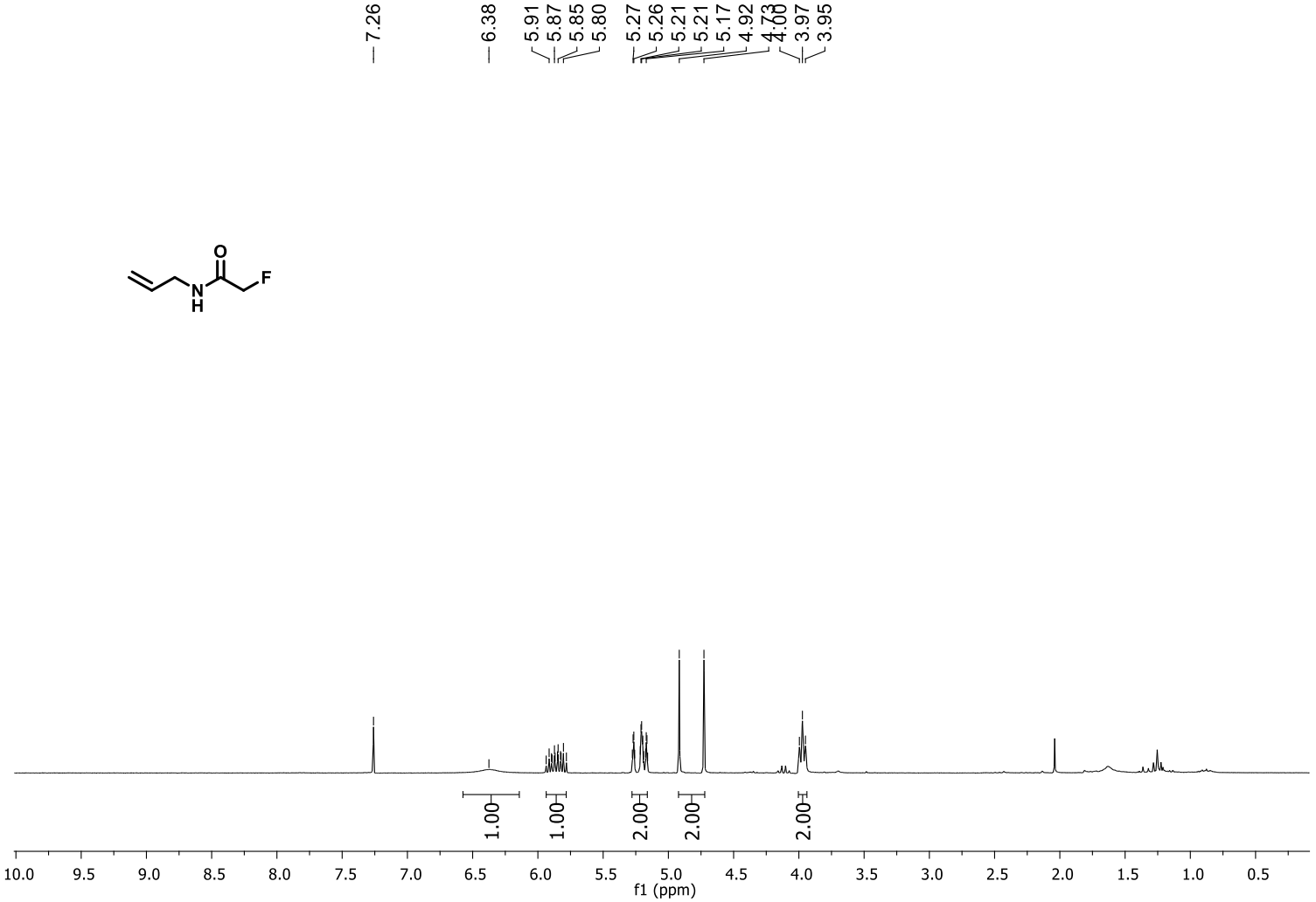
3z - ^{13}C NMR (62.5 MHz, $CDCl_3$)



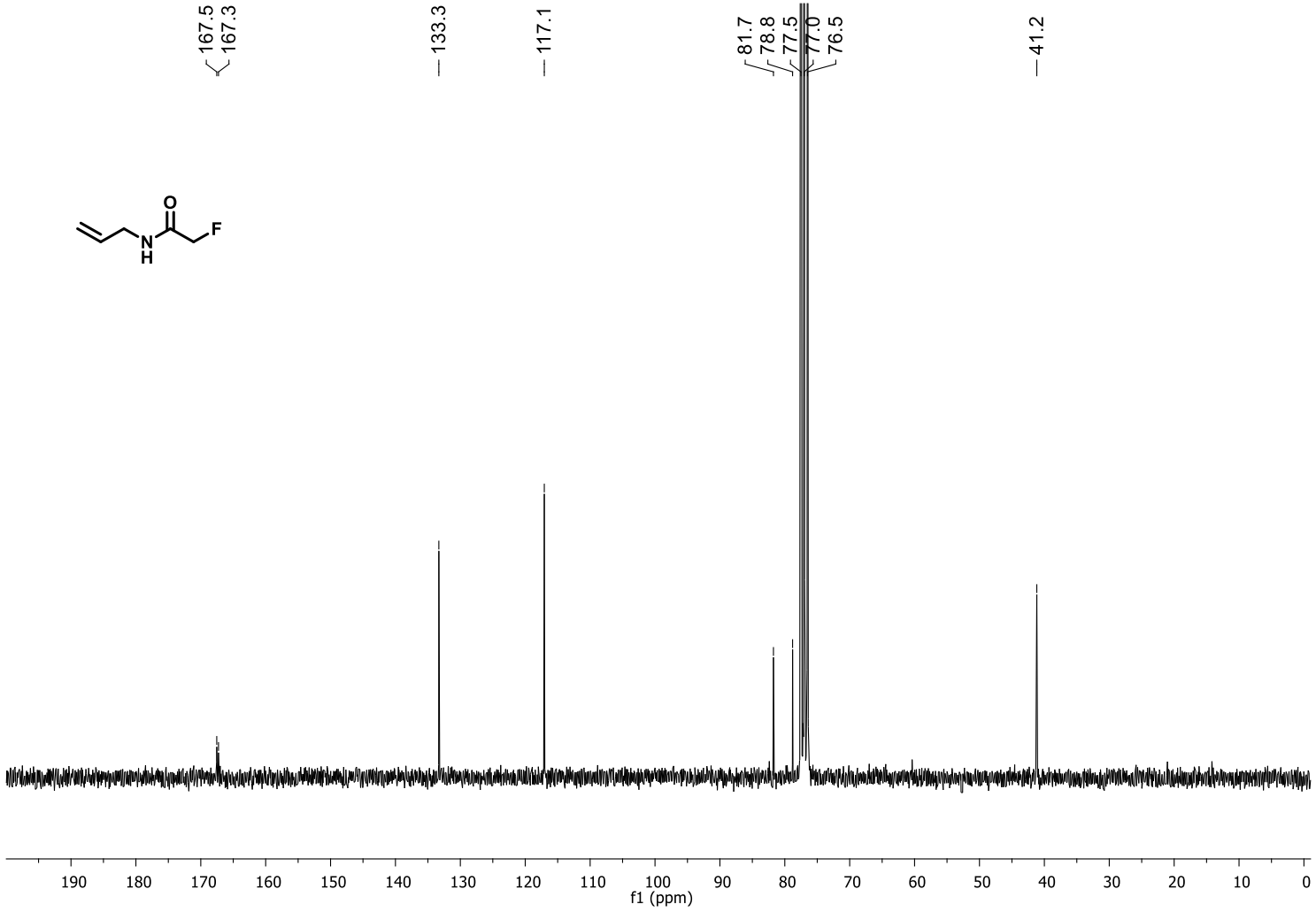
3z - ^{19}F NMR (235 MHz, $CDCl_3$)



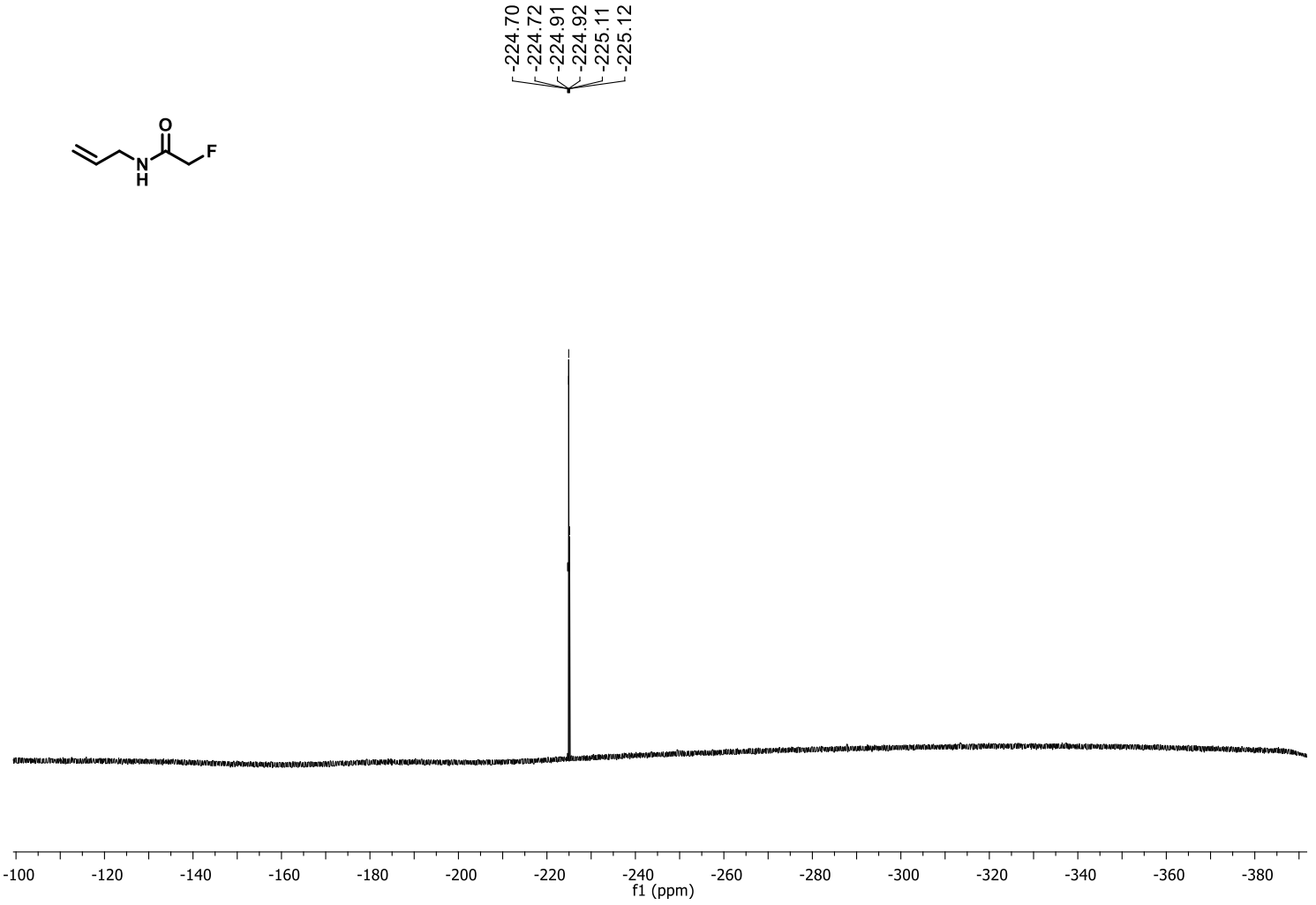
3aa - ^{1}H NMR (250 MHz, $CDCl_3$)



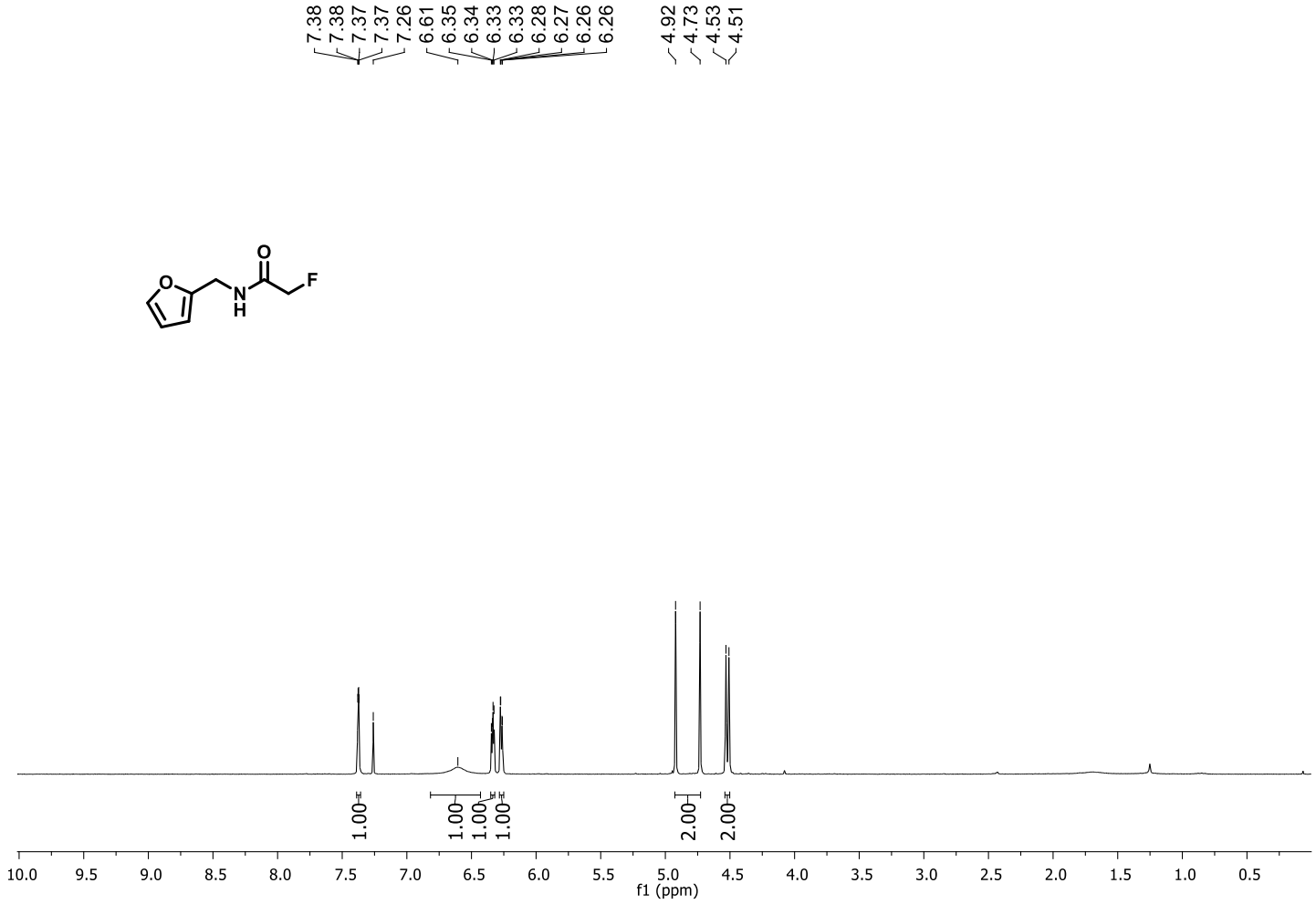
3aa - ^{13}C NMR (62.5 MHz, $CDCl_3$)



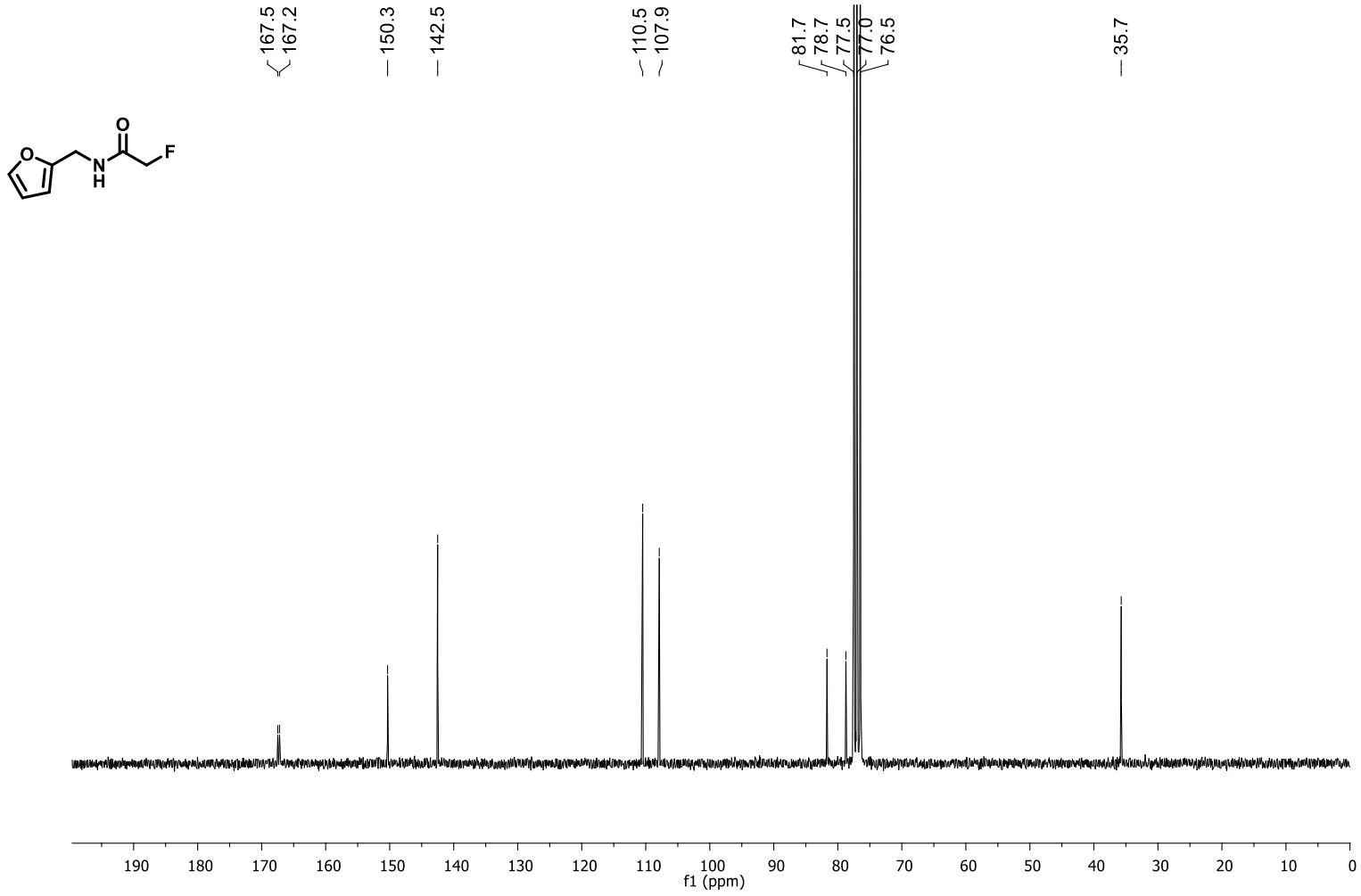
3aa - ^{19}F NMR (235 MHz, $CDCl_3$)



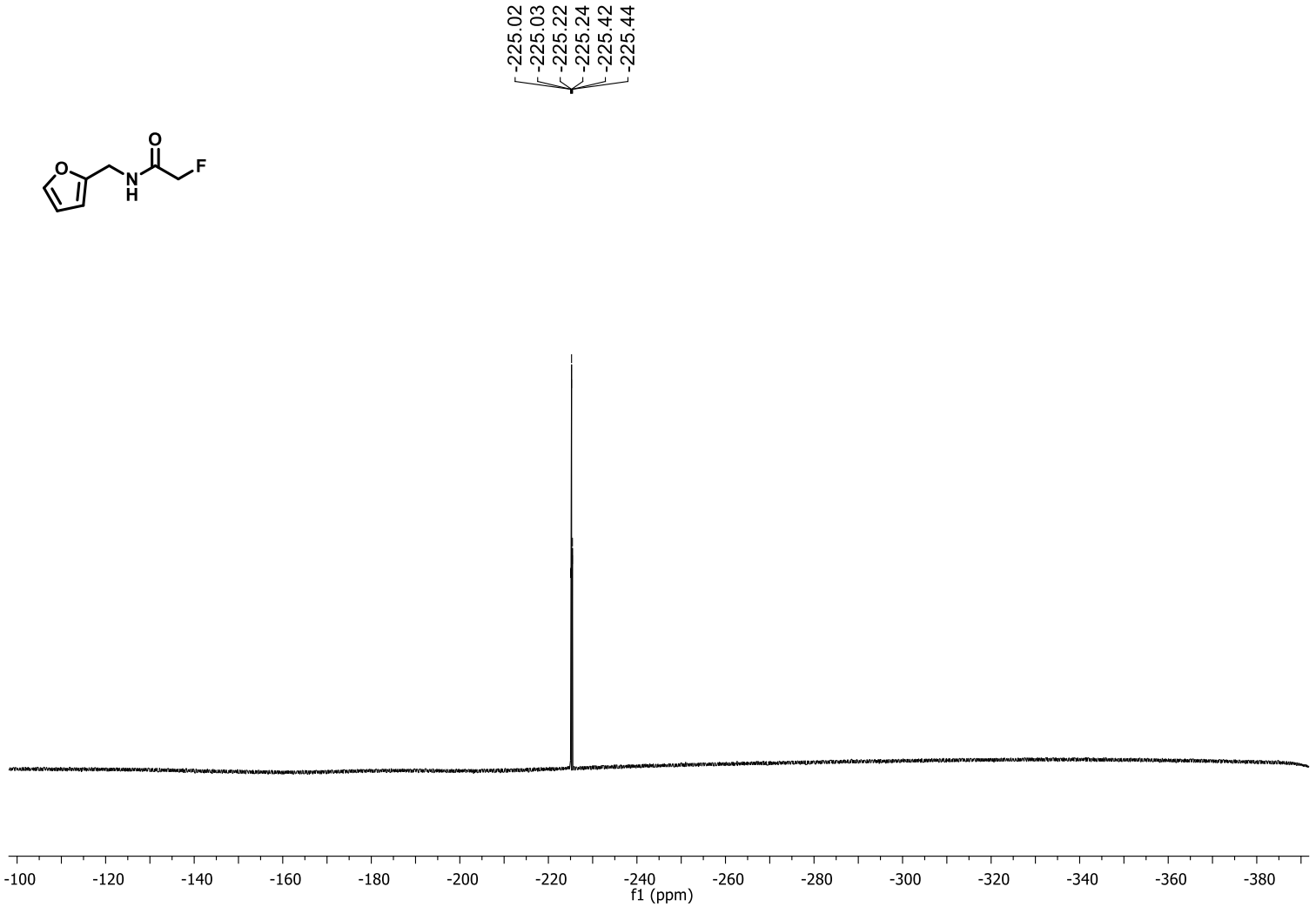
3bb - ^{1}H NMR (250 MHz, $CDCl_3$)



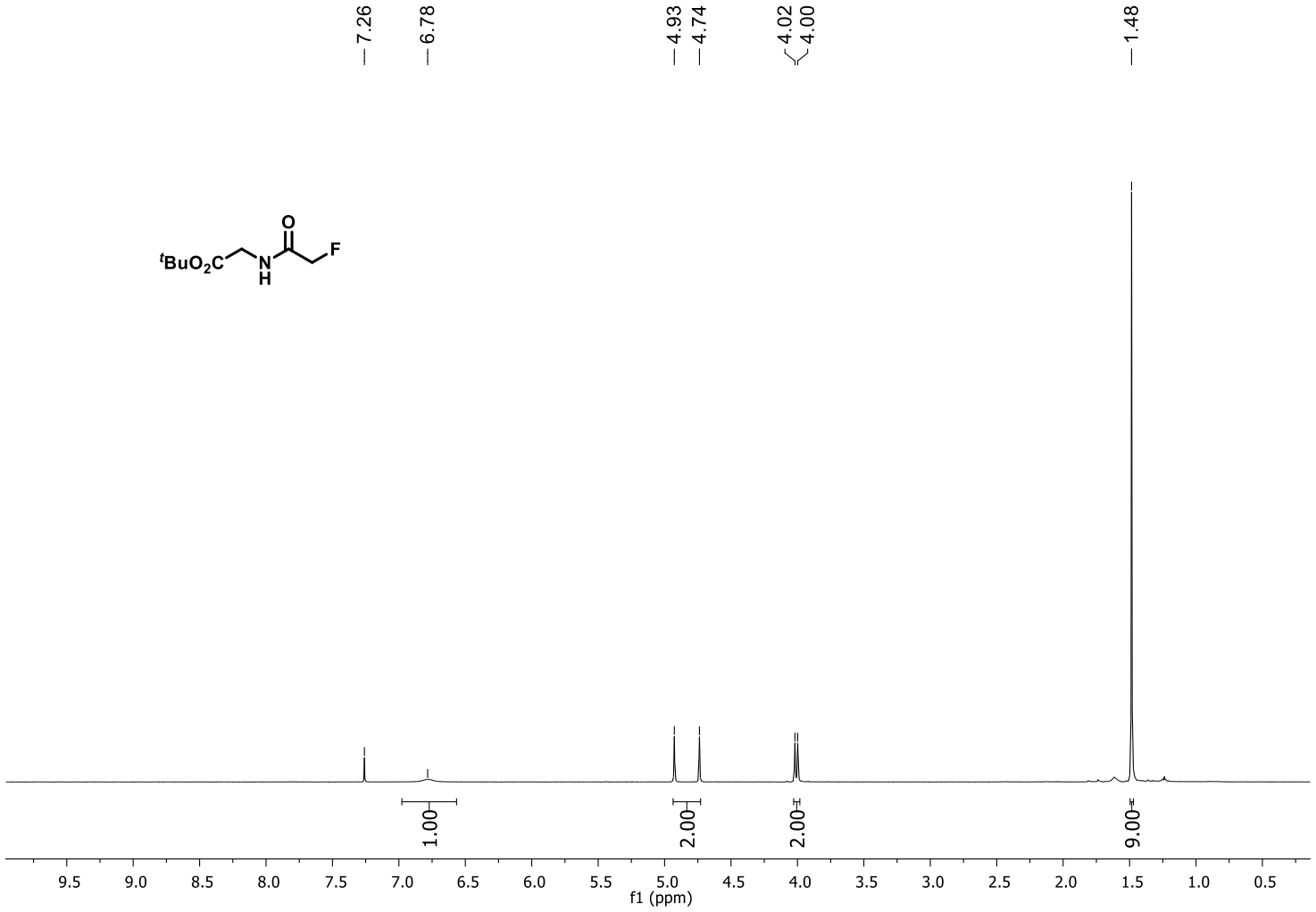
3bb - ^{13}C NMR (62.5 MHz, $CDCl_3$)



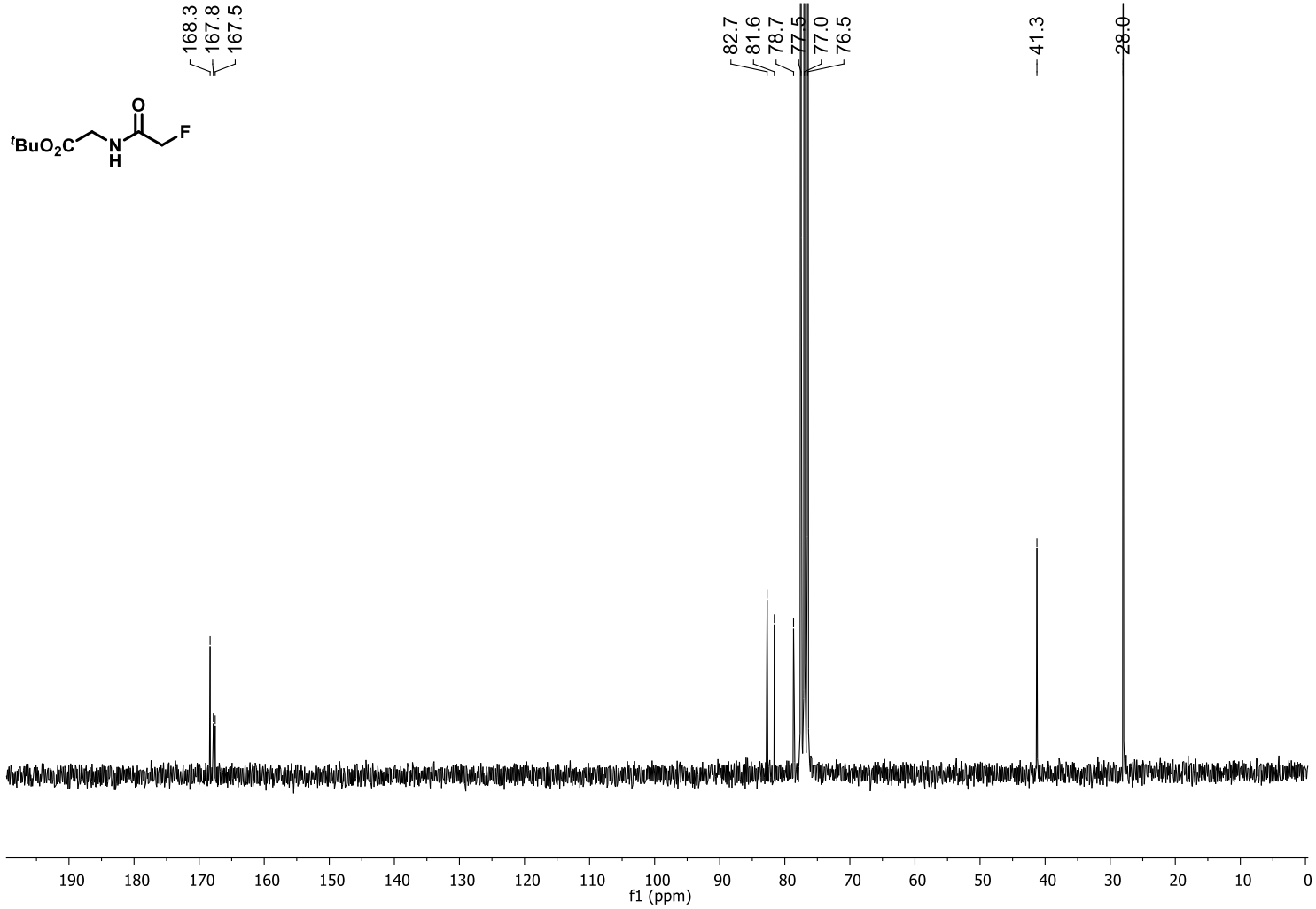
3bb - ^{19}F NMR (235 MHz, $CDCl_3$)



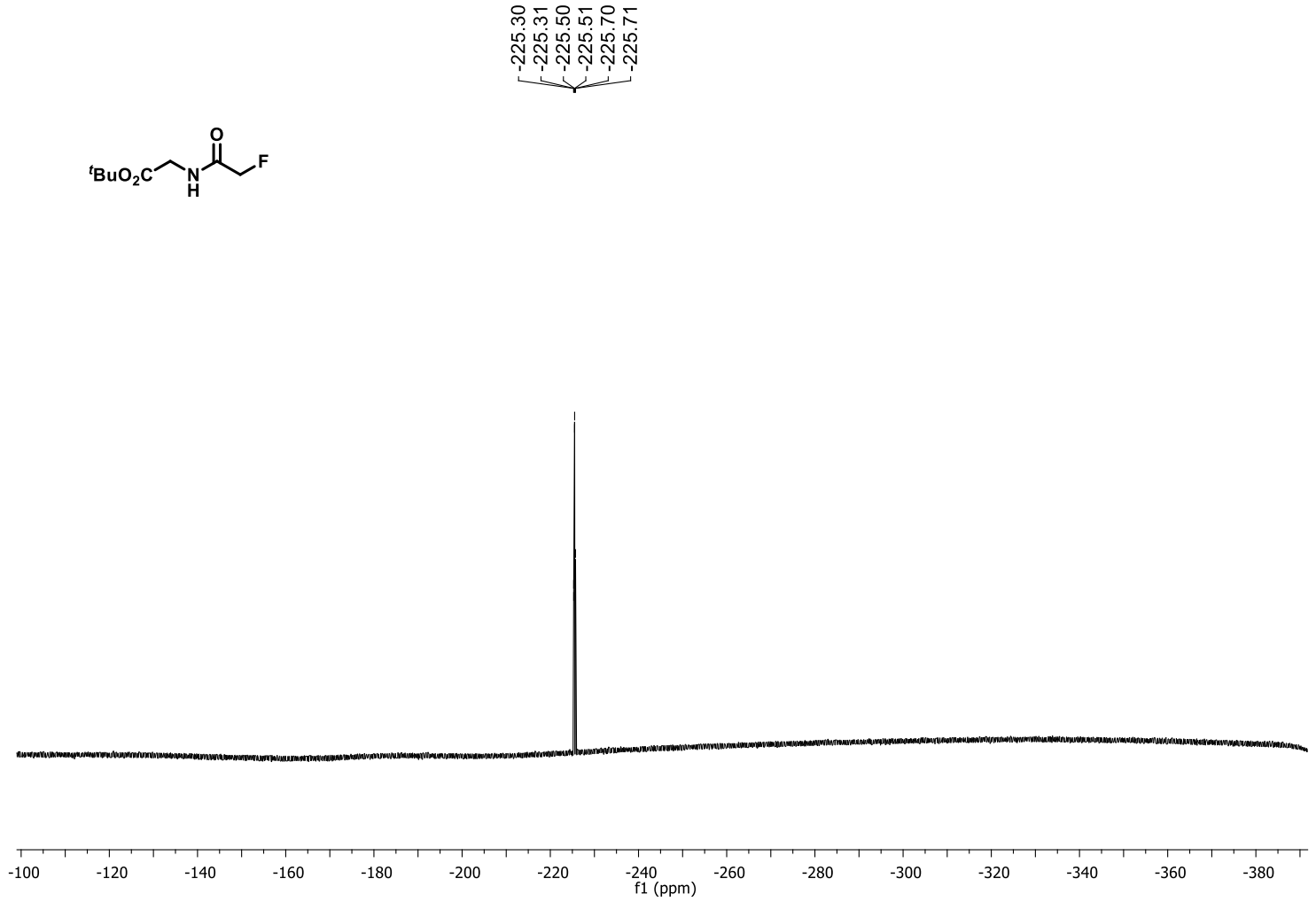
3cc - ^{1}H NMR (250 MHz, $CDCl_3$)



3cc - ^{13}C NMR (62.5 MHz, $CDCl_3$)



3cc - ^{19}F NMR (235 MHz, $CDCl_3$)



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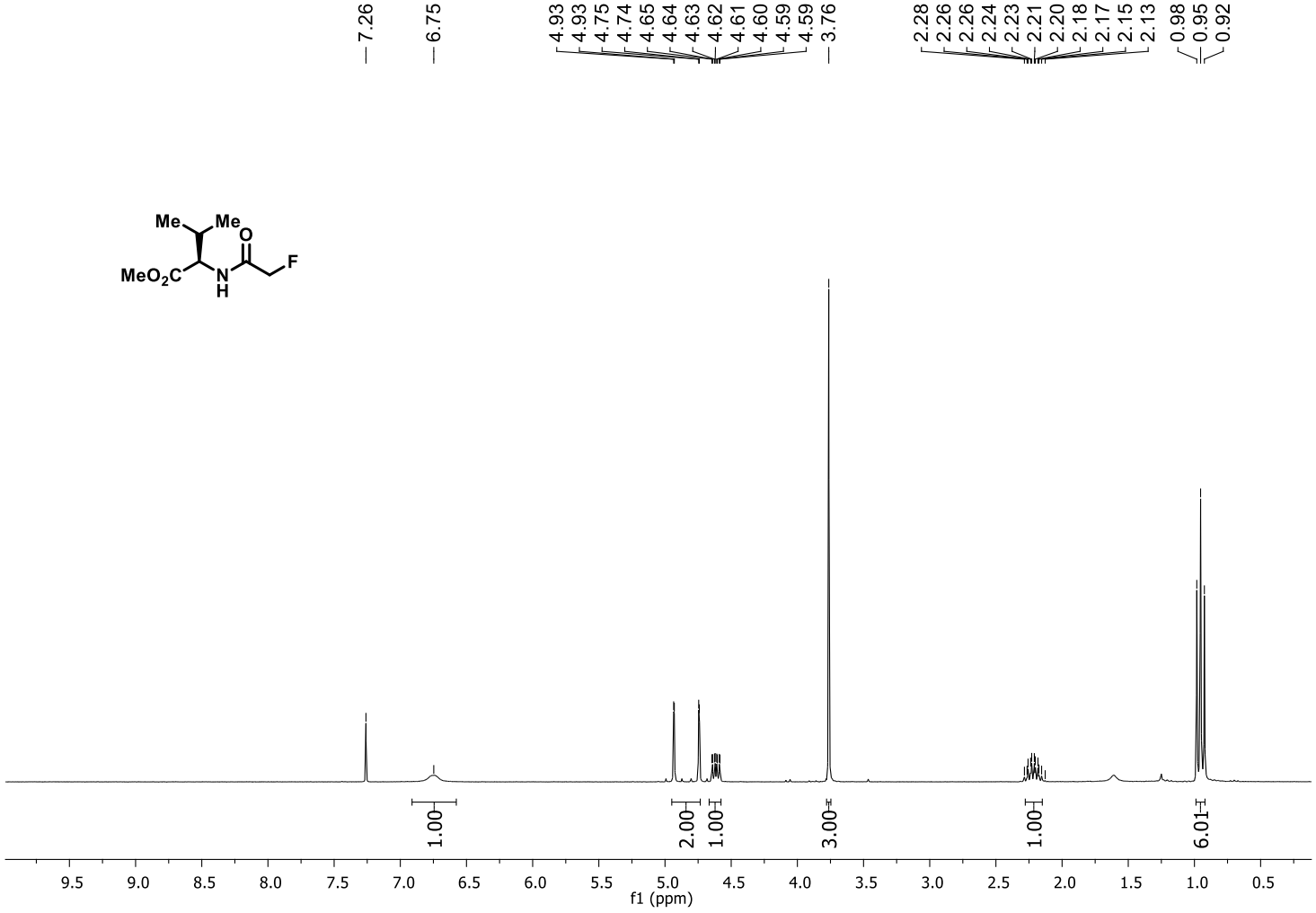
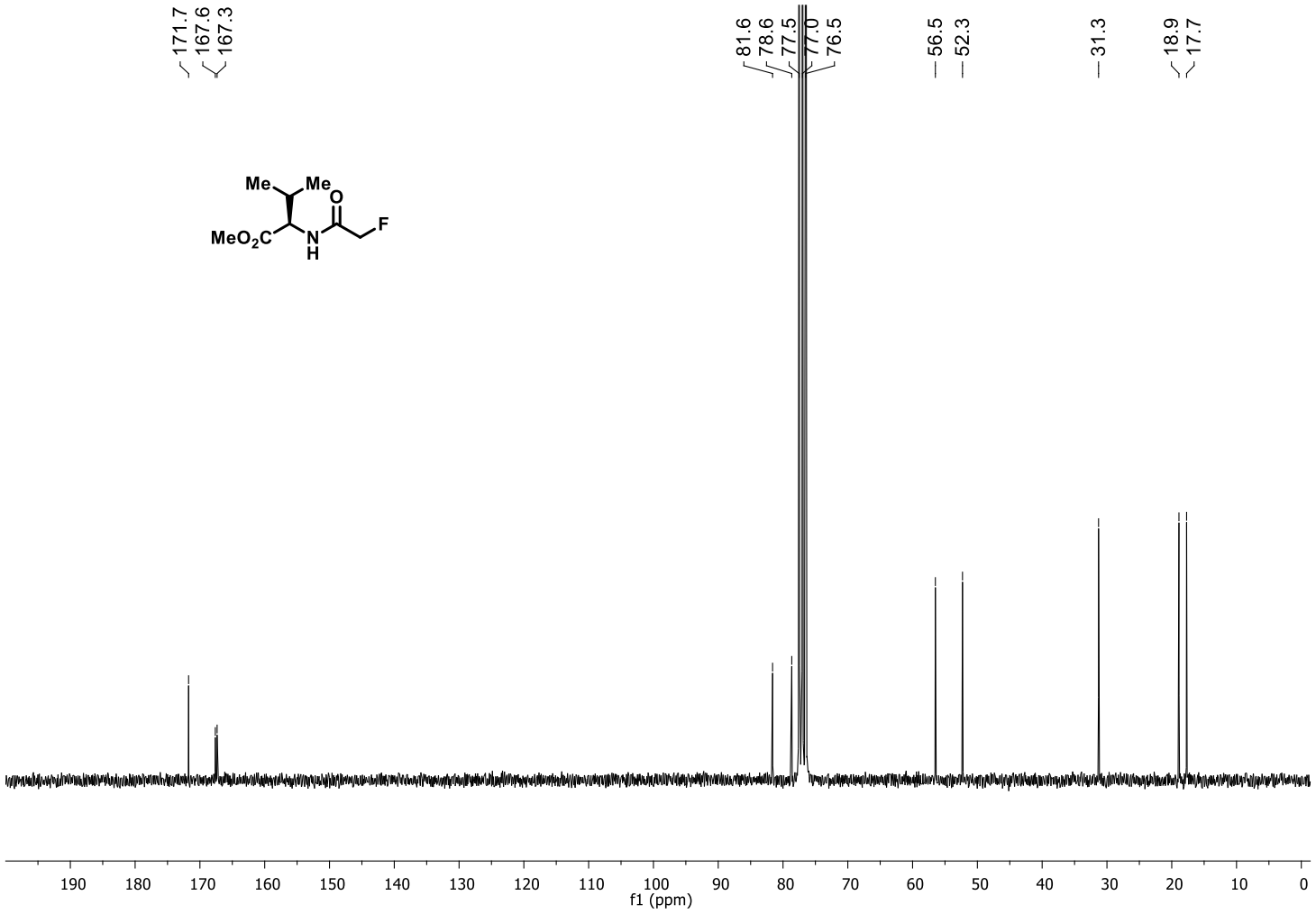
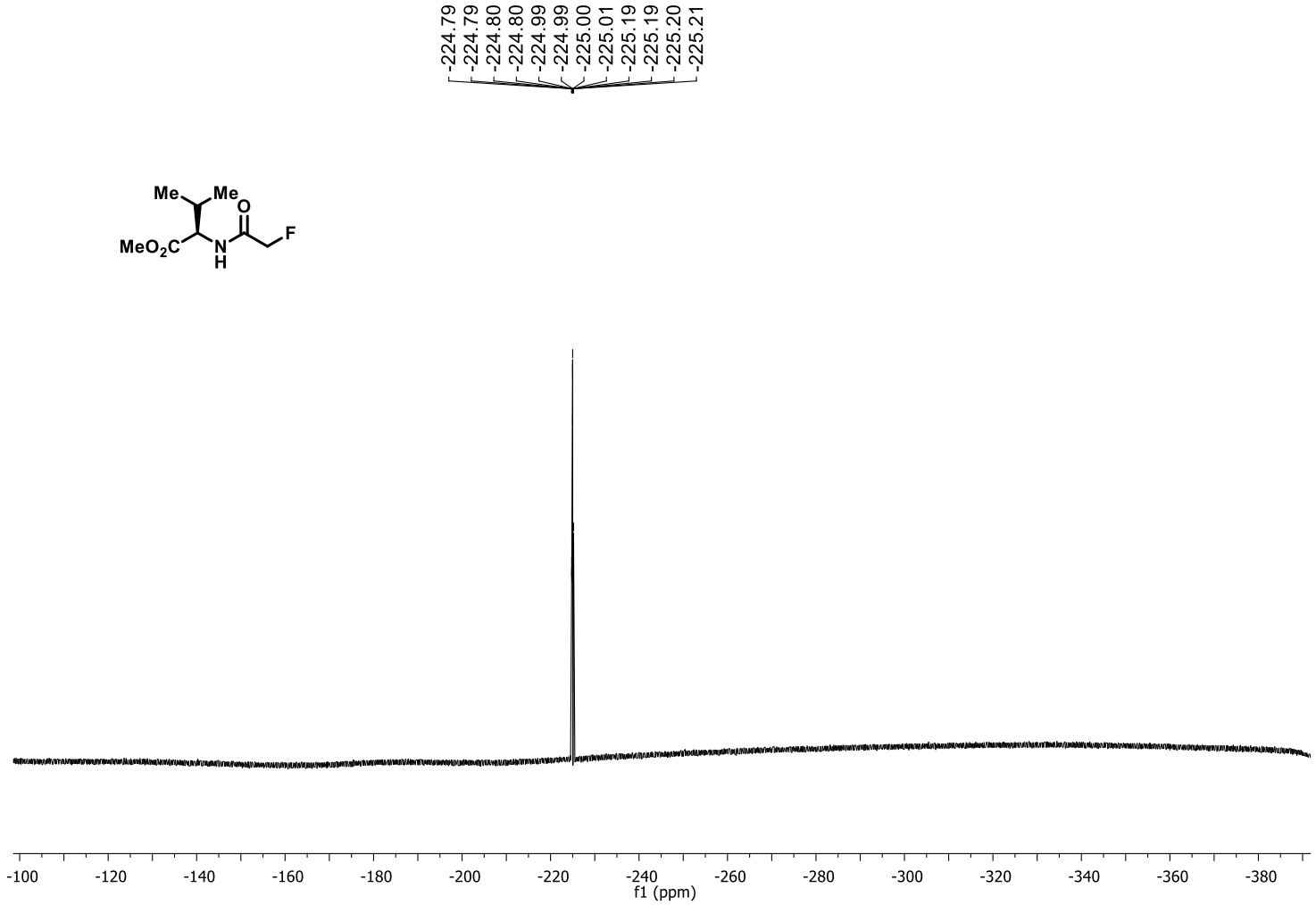


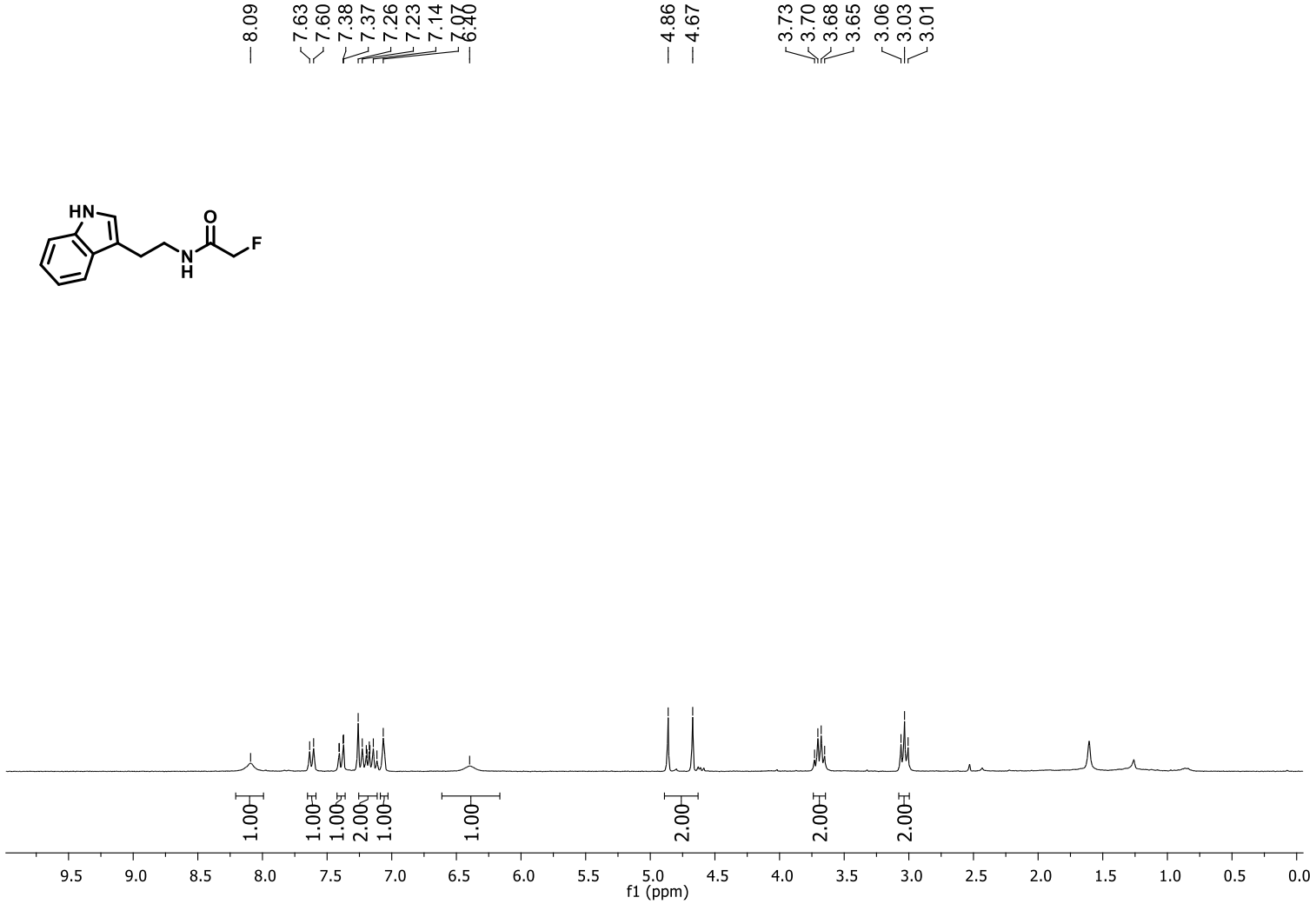
3dd - ^{13}C NMR (62.5 MHz, $CDCl_3$)



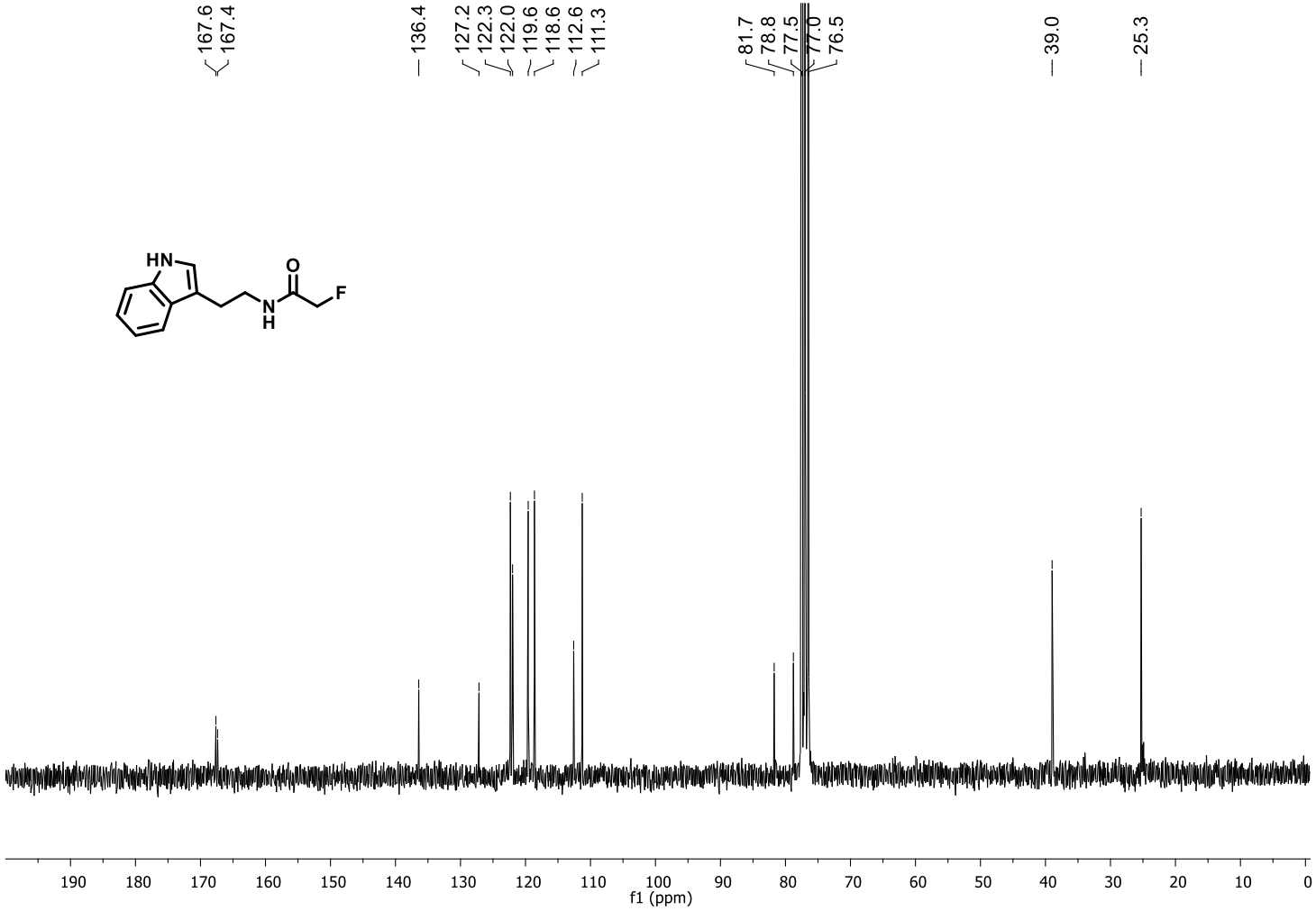
3dd - ^{19}F NMR (235 MHz, $CDCl_3$)



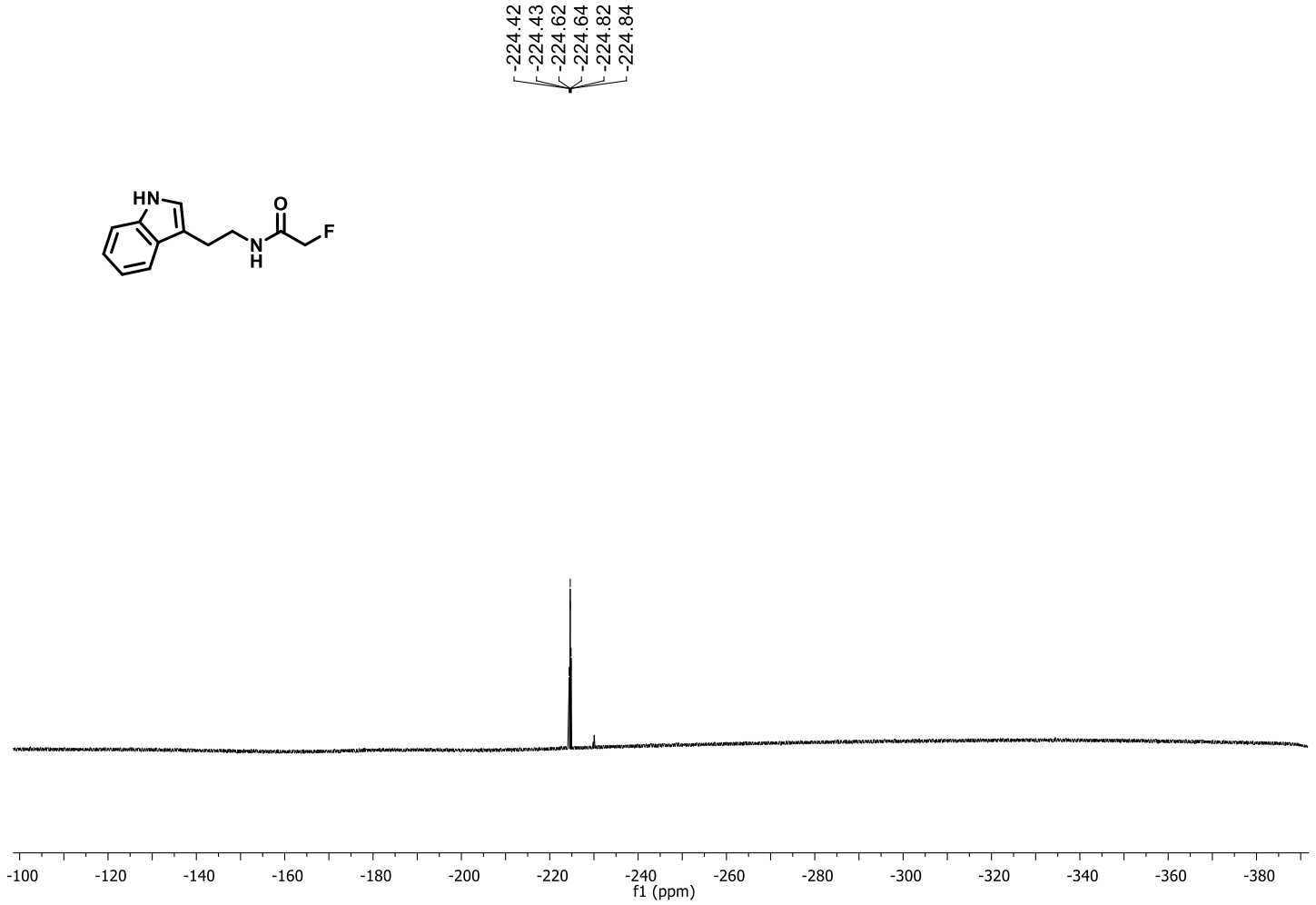
3ee - ^{1}H NMR (250 MHz, $CDCl_3$)



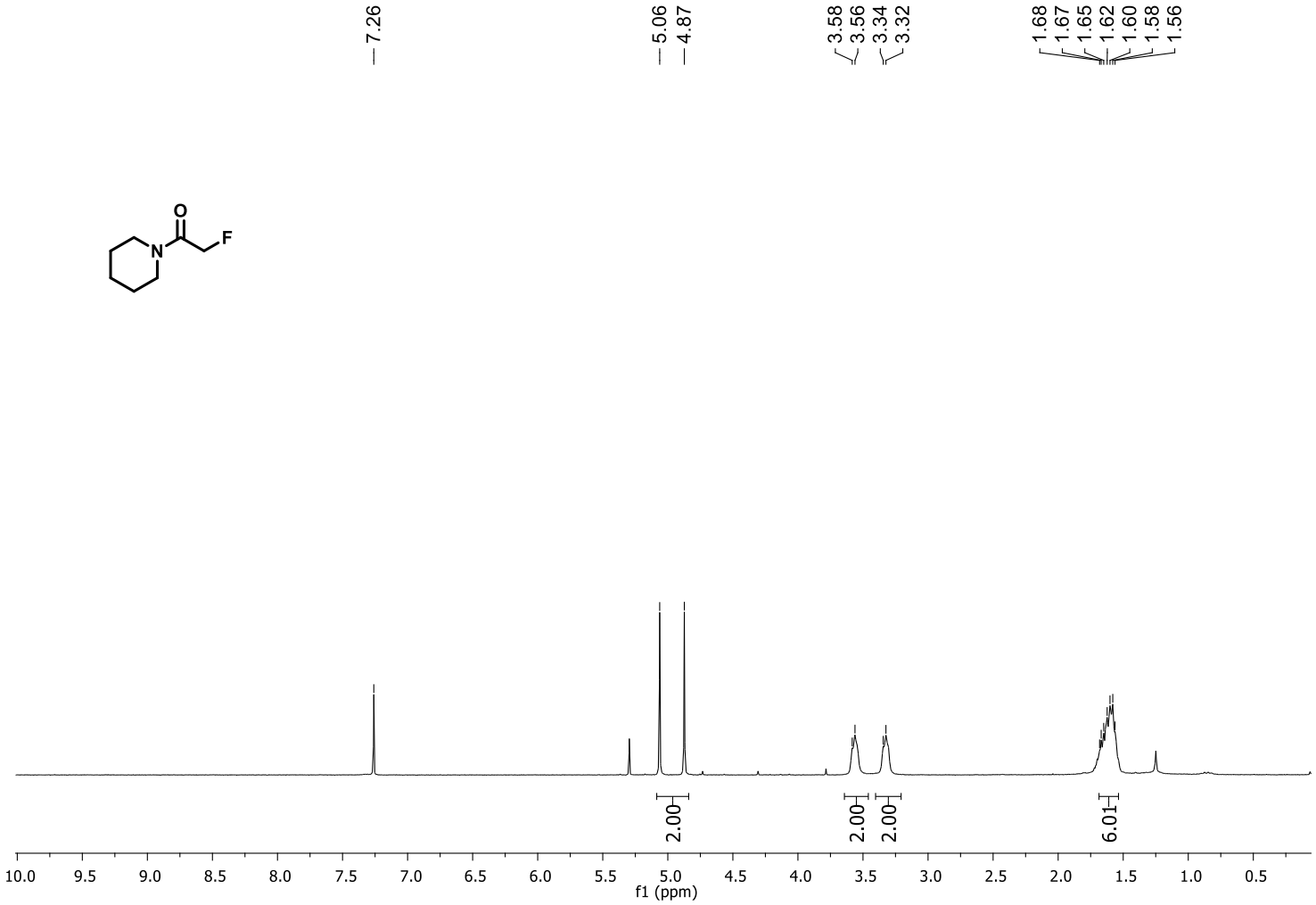
3ee - ^{13}C NMR (62.5 MHz, $CDCl_3$)



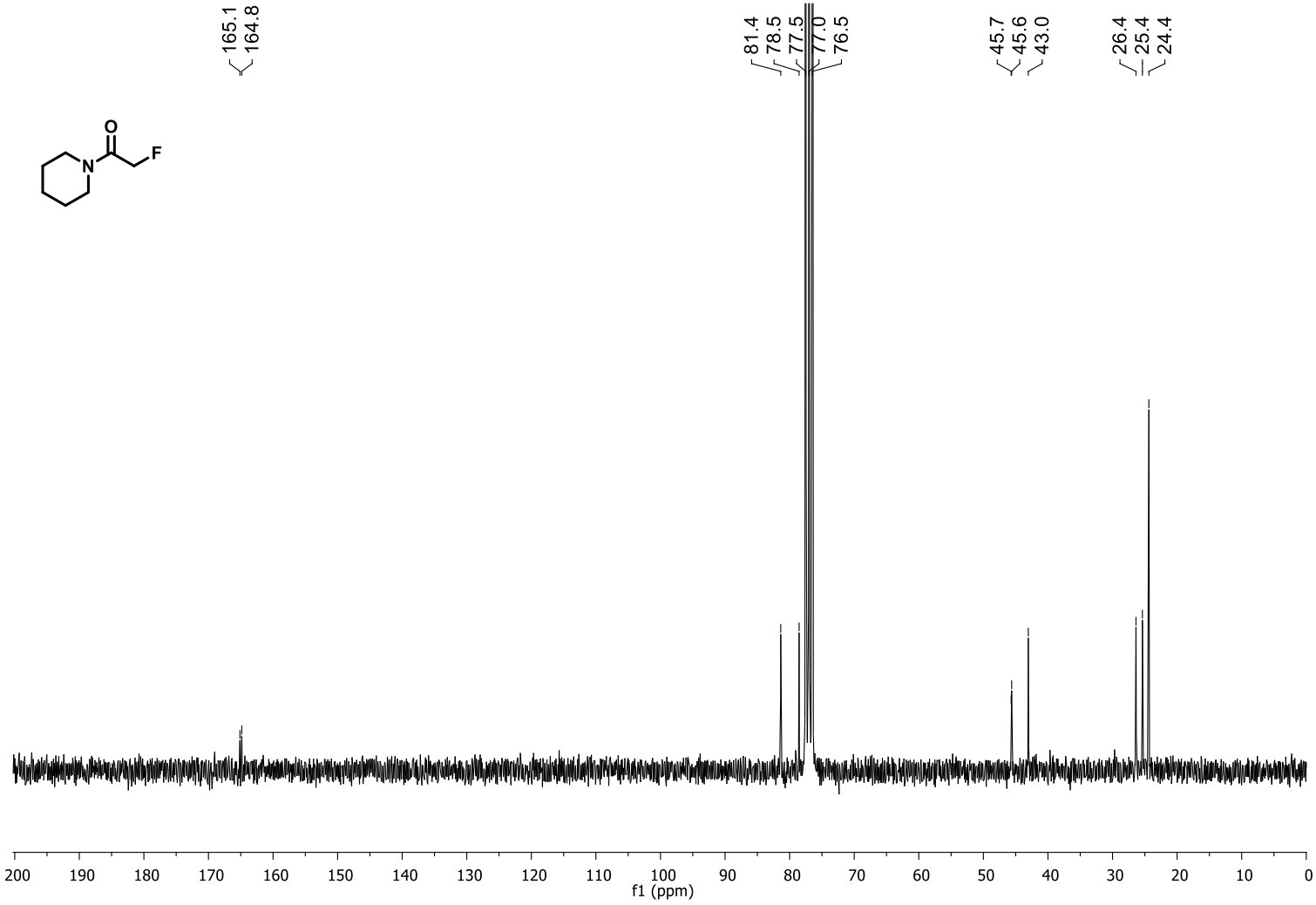
3ee - ^{19}F NMR (235 MHz, $CDCl_3$)



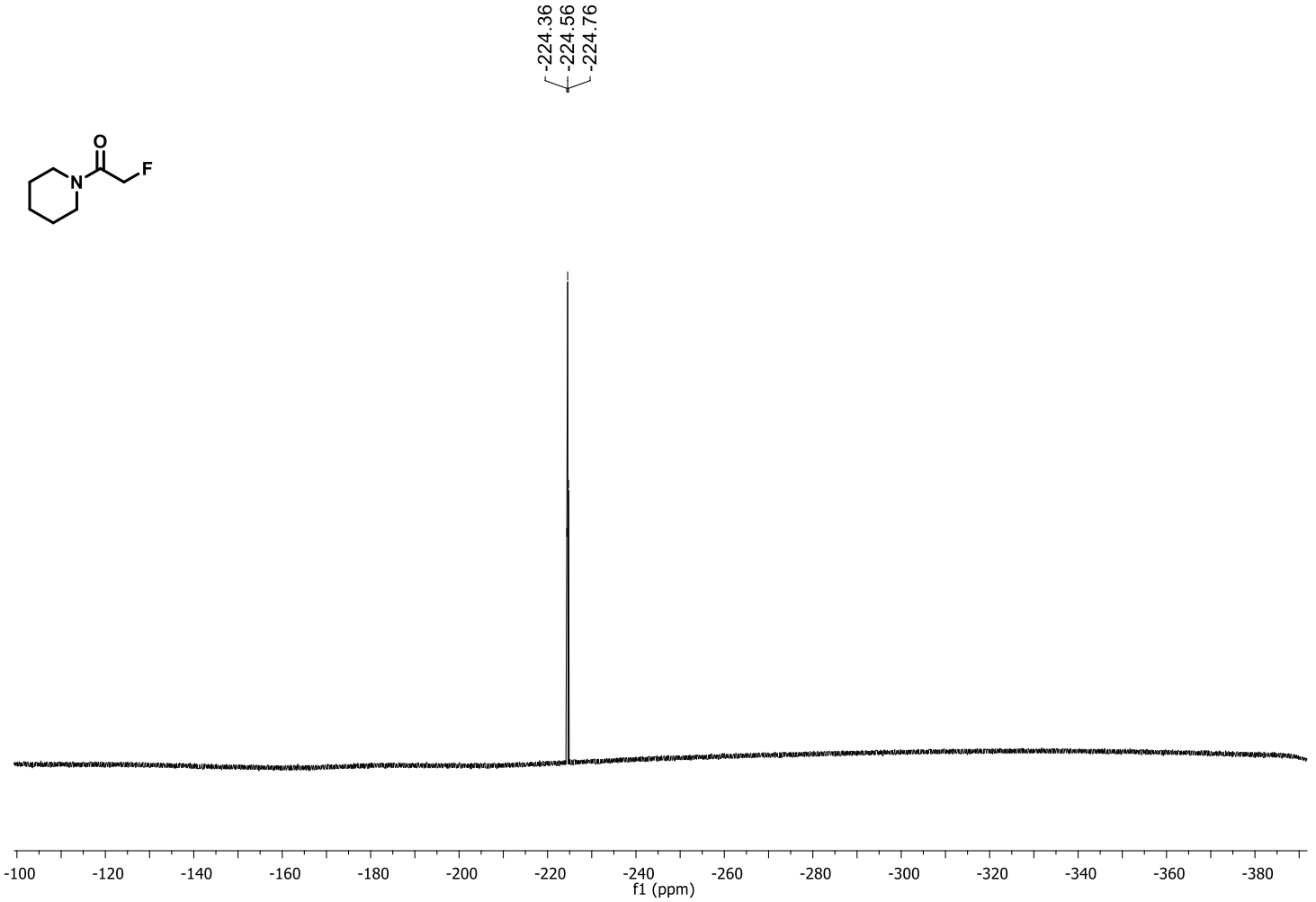
3ff - ^{1}H NMR (250 MHz, $CDCl_3$)



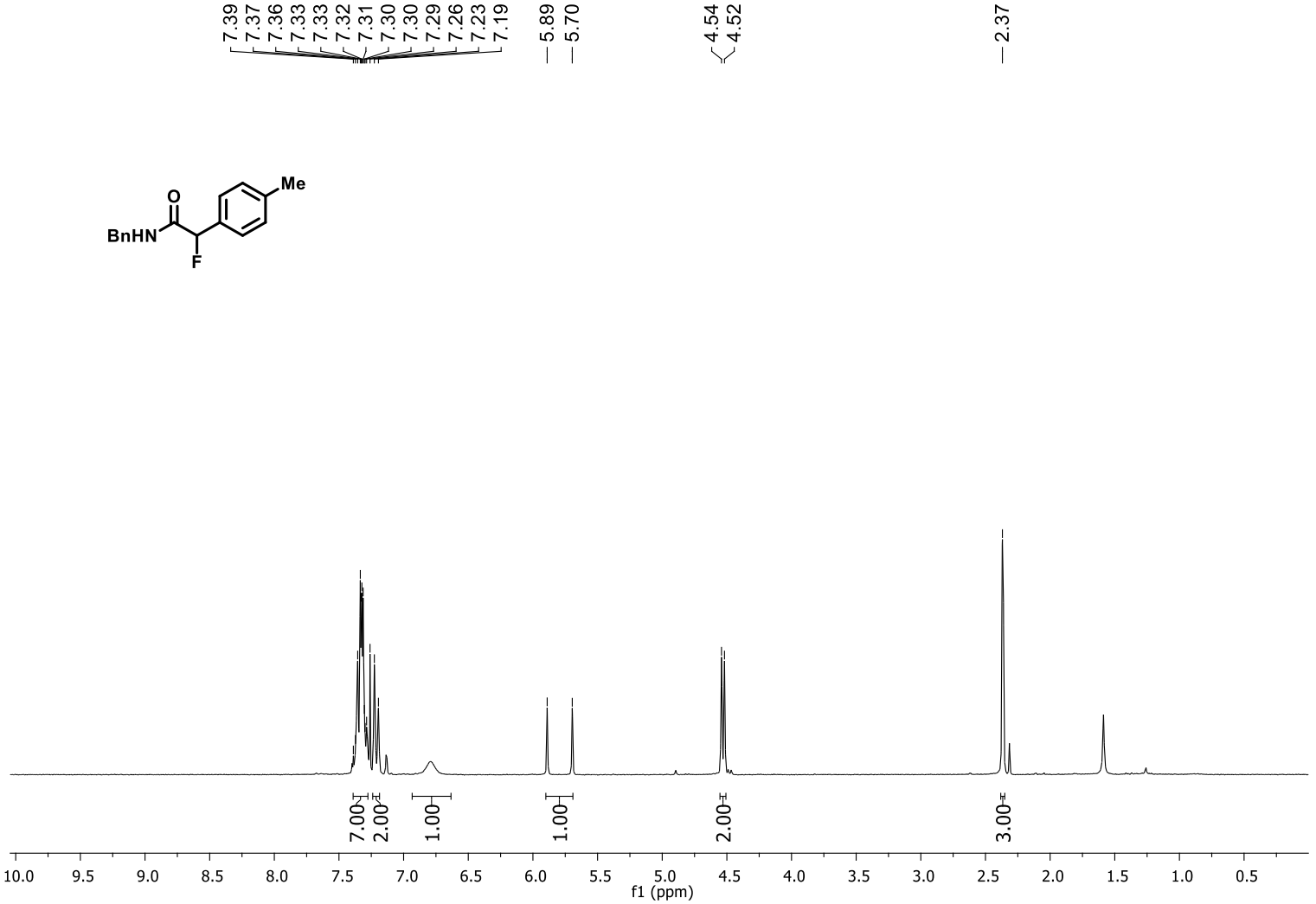
3ff - ^{13}C NMR (62.5 MHz, $CDCl_3$)



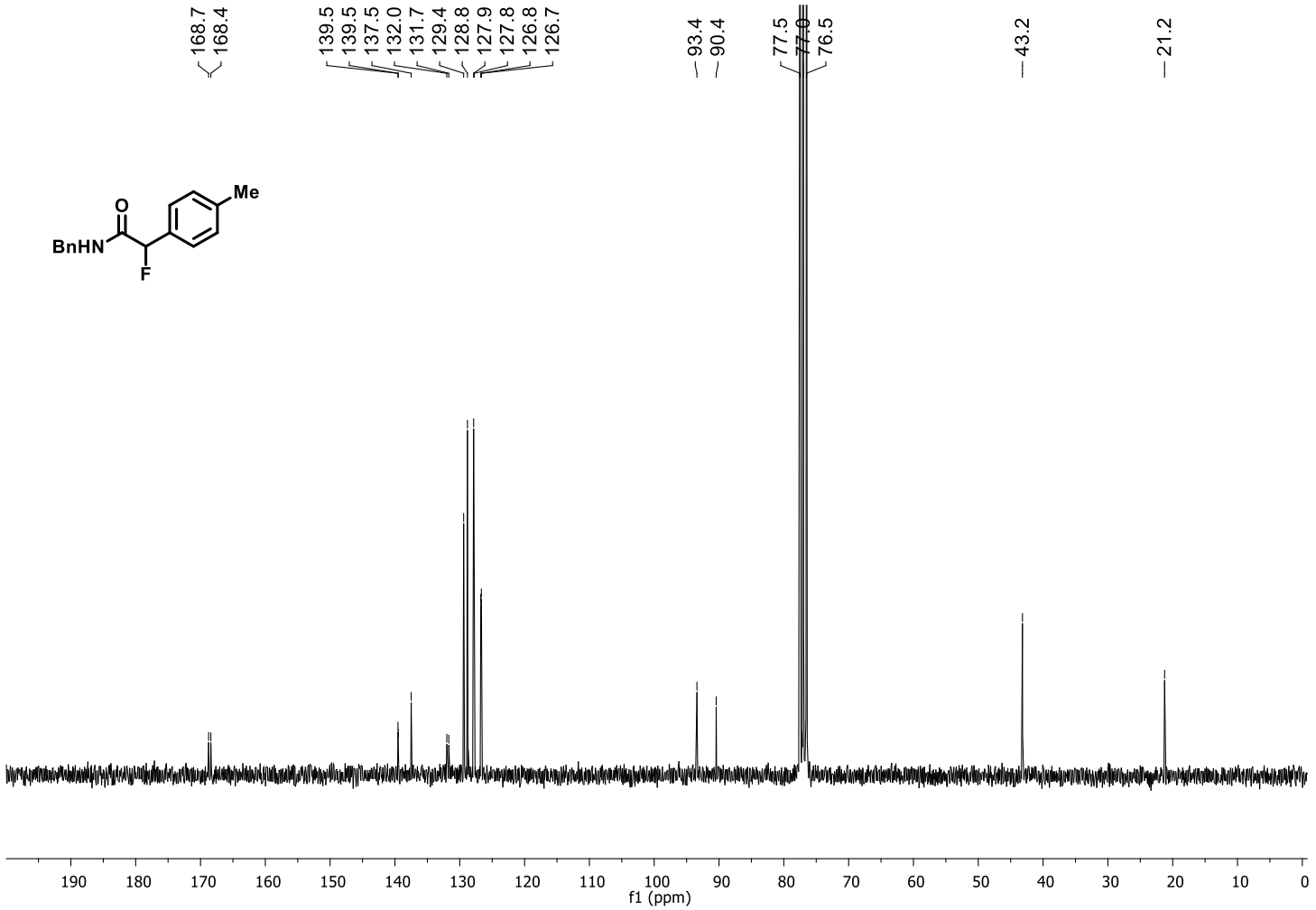
3ff - ^{19}F NMR (235 MHz, $CDCl_3$)



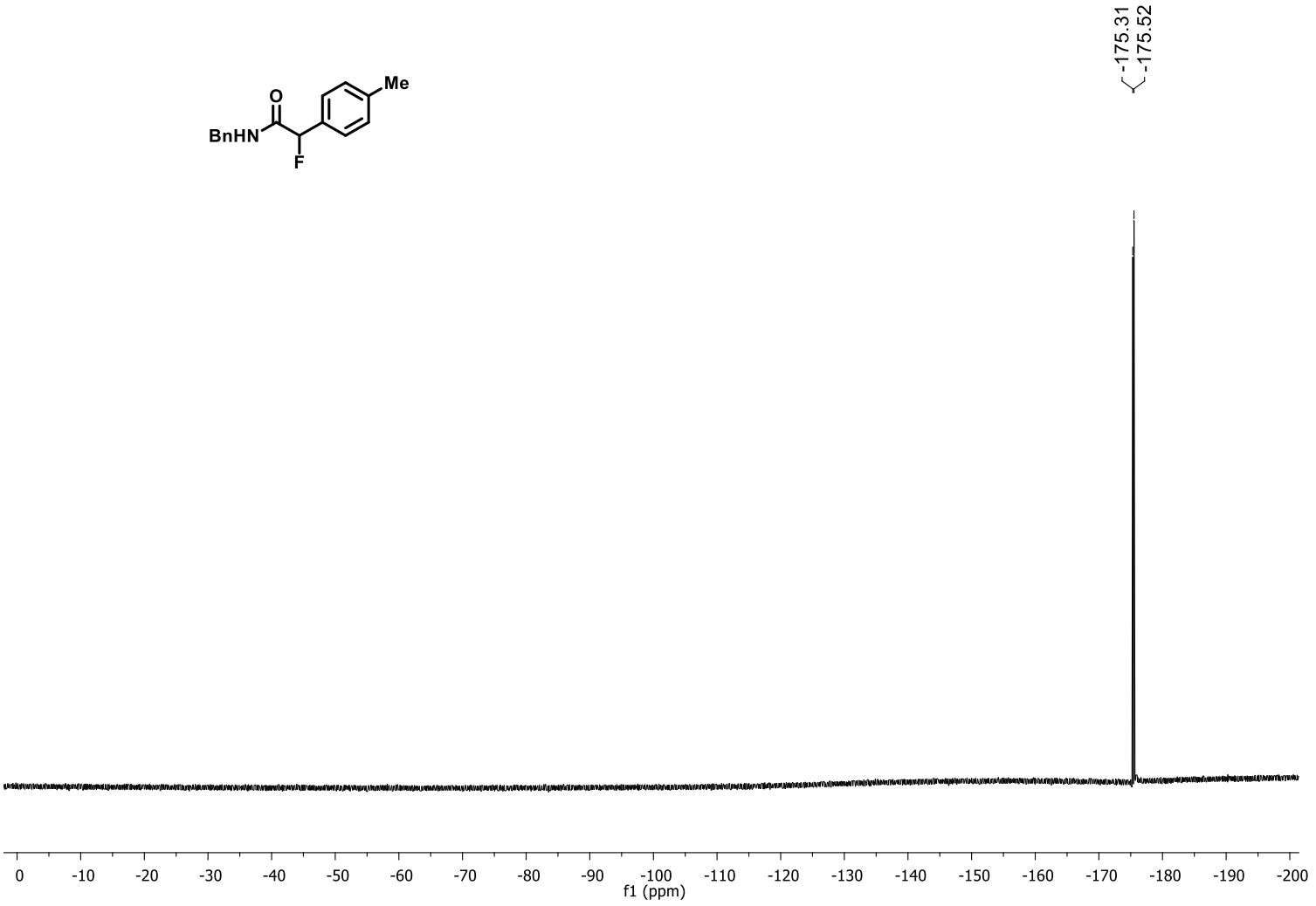
3gg - ^{1}H NMR (250 MHz, $CDCl_3$)



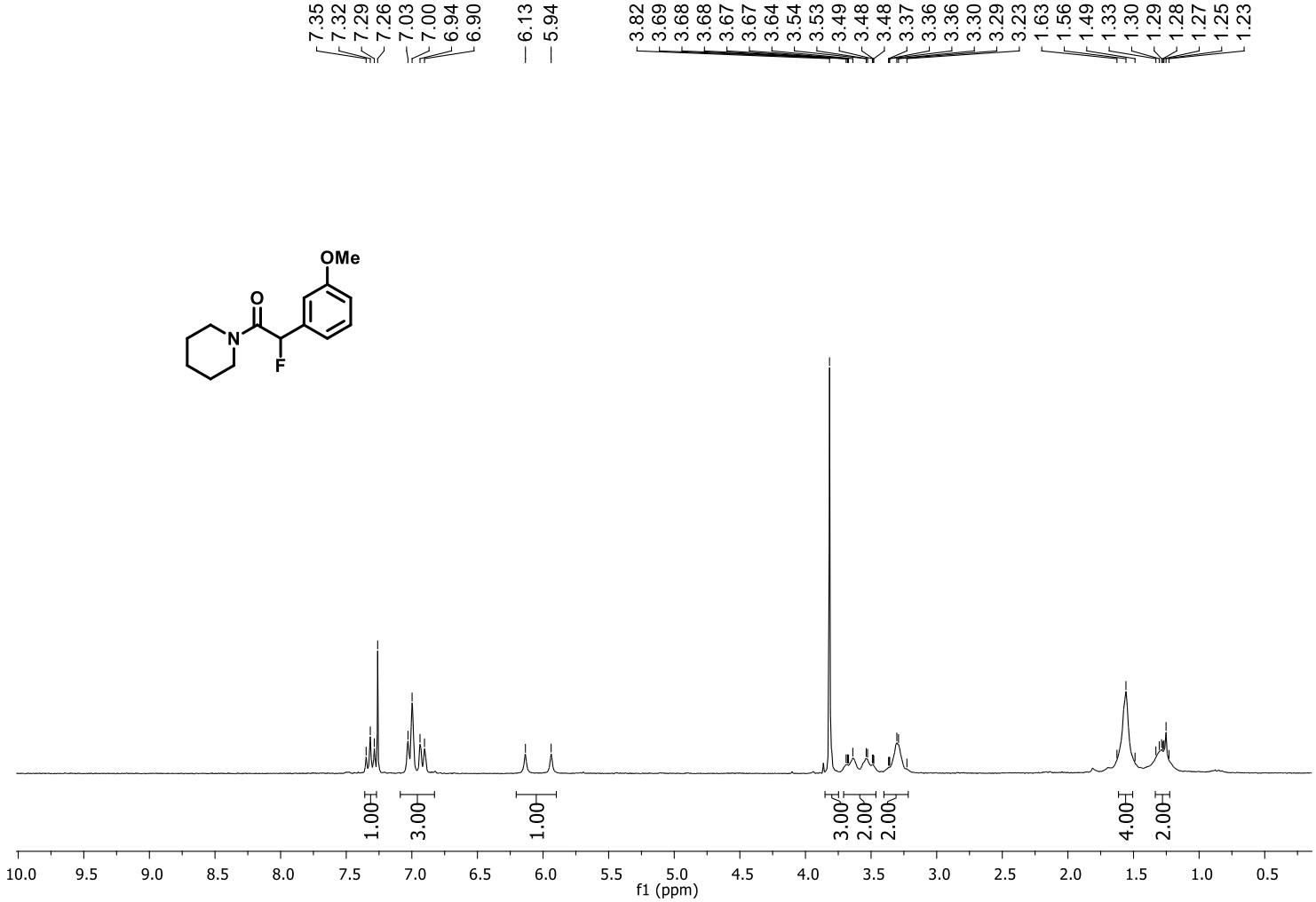
3gg - ^{13}C NMR (62.5 MHz, $CDCl_3$)



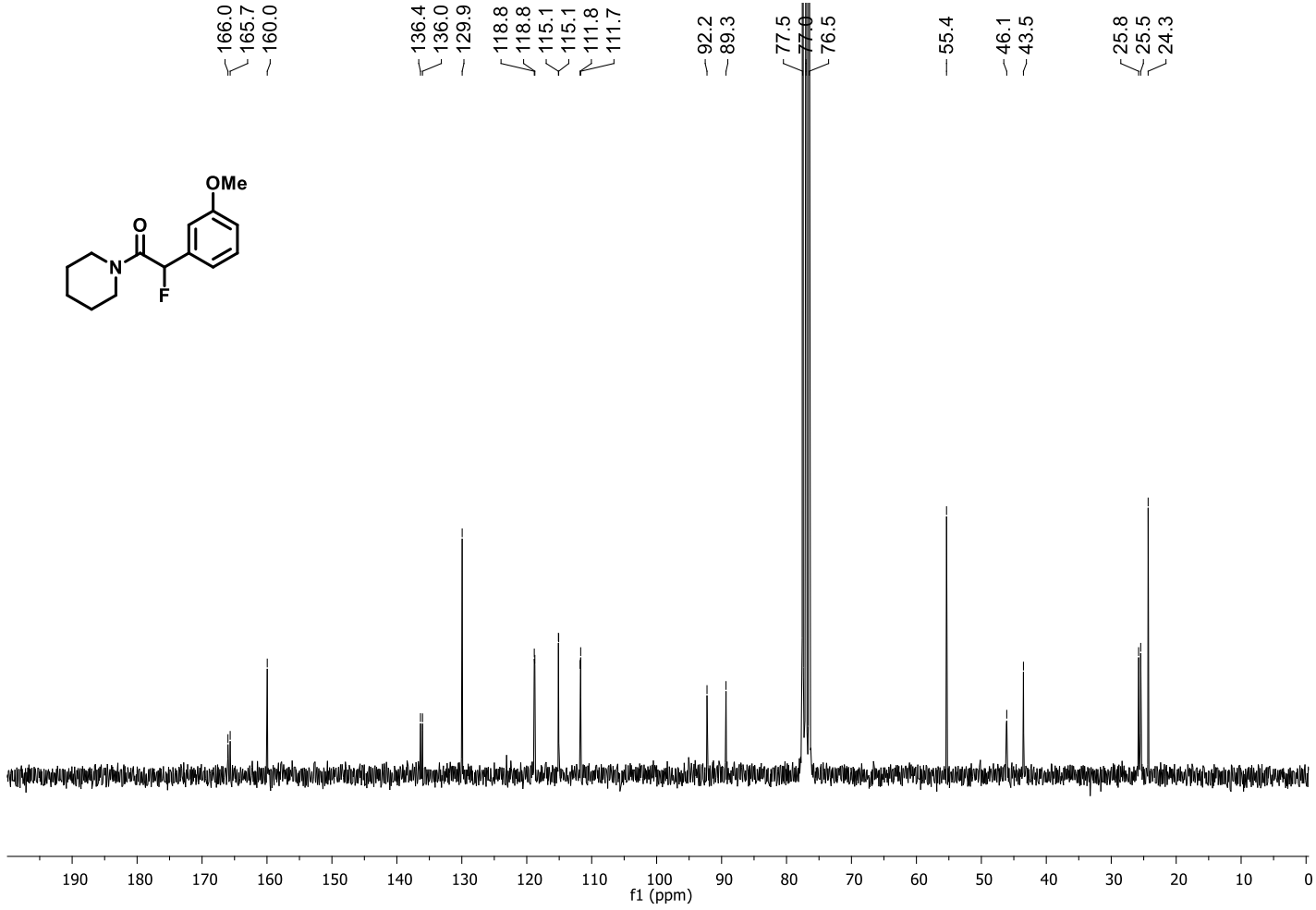
3gg - ^{19}F NMR (235 MHz, $CDCl_3$)



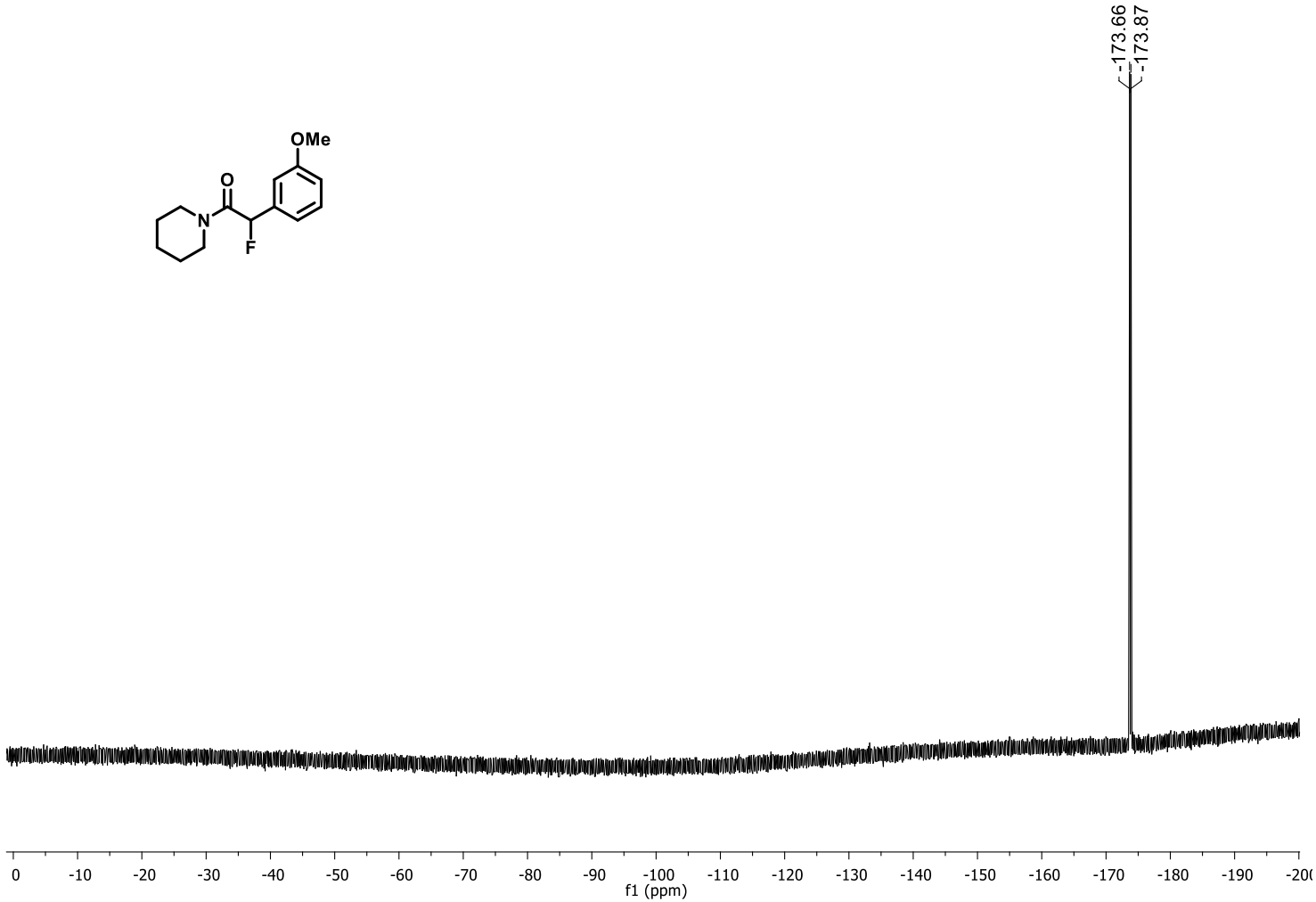
3hh - ^{1}H NMR (250 MHz, $CDCl_3$)



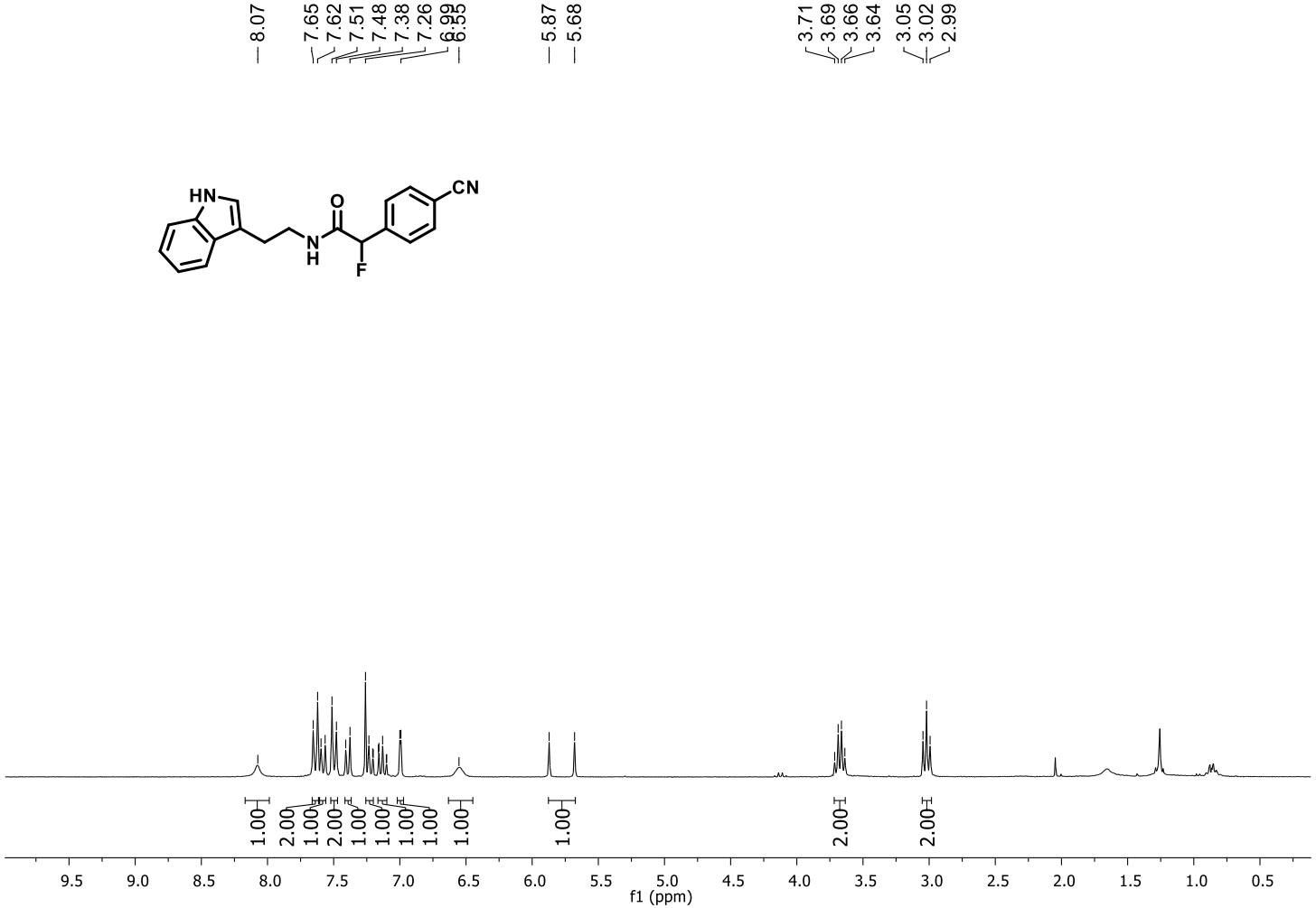
3hh - ^{13}C NMR (62.5 MHz, $CDCl_3$)



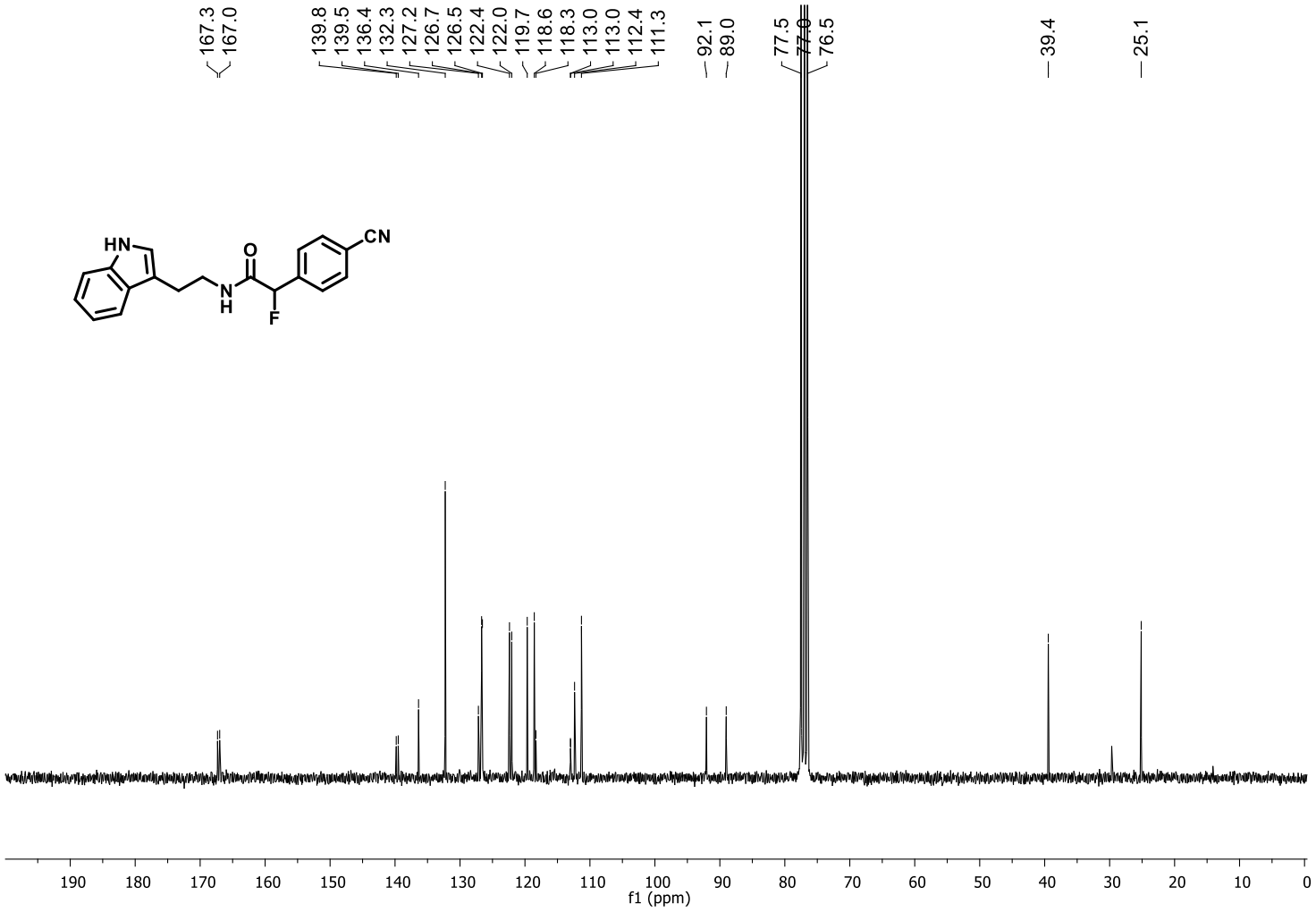
3hh - ^{19}F NMR (235 MHz, $CDCl_3$)



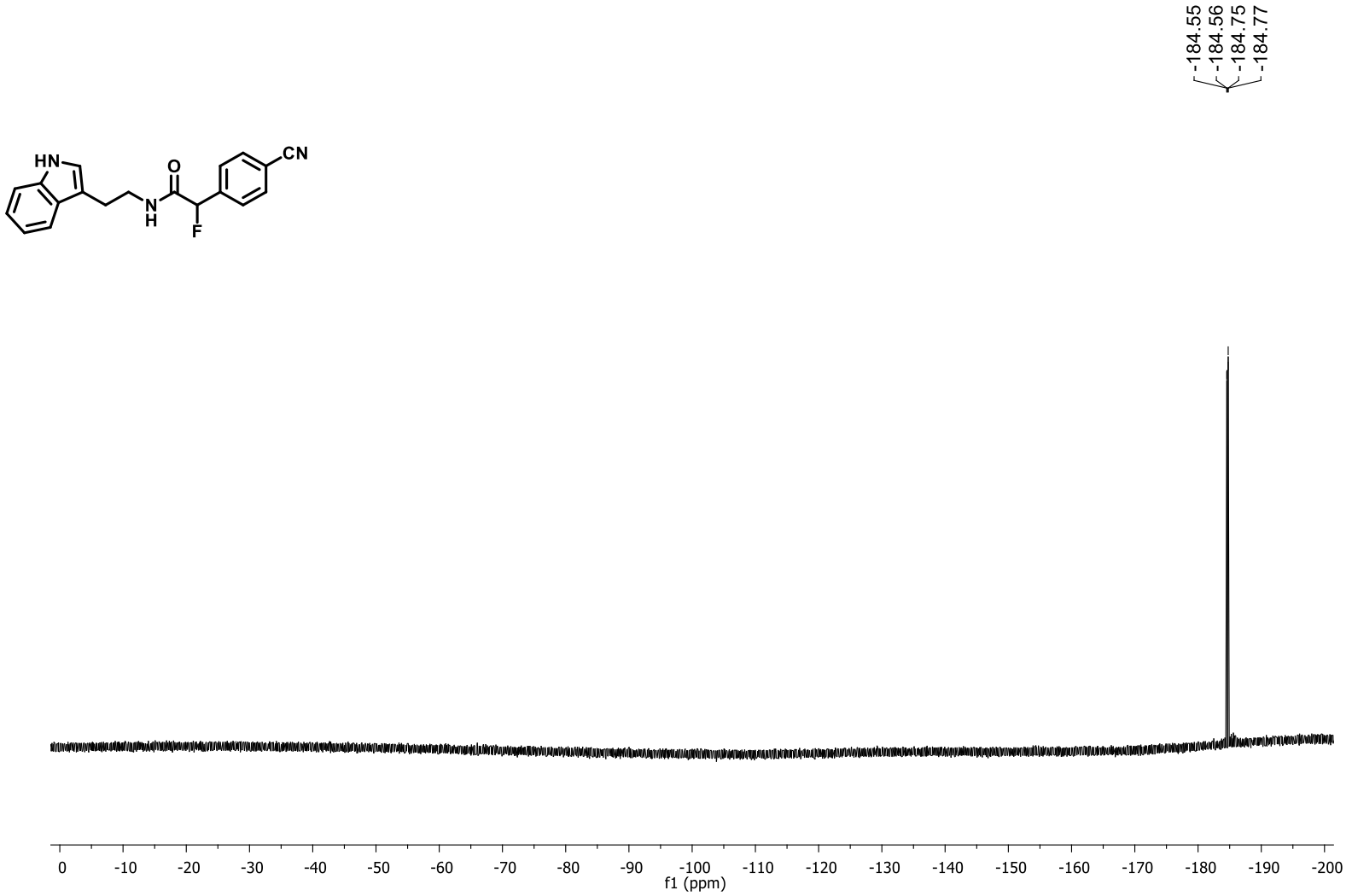
3ii - ^{1}H NMR (250 MHz, $CDCl_3$)



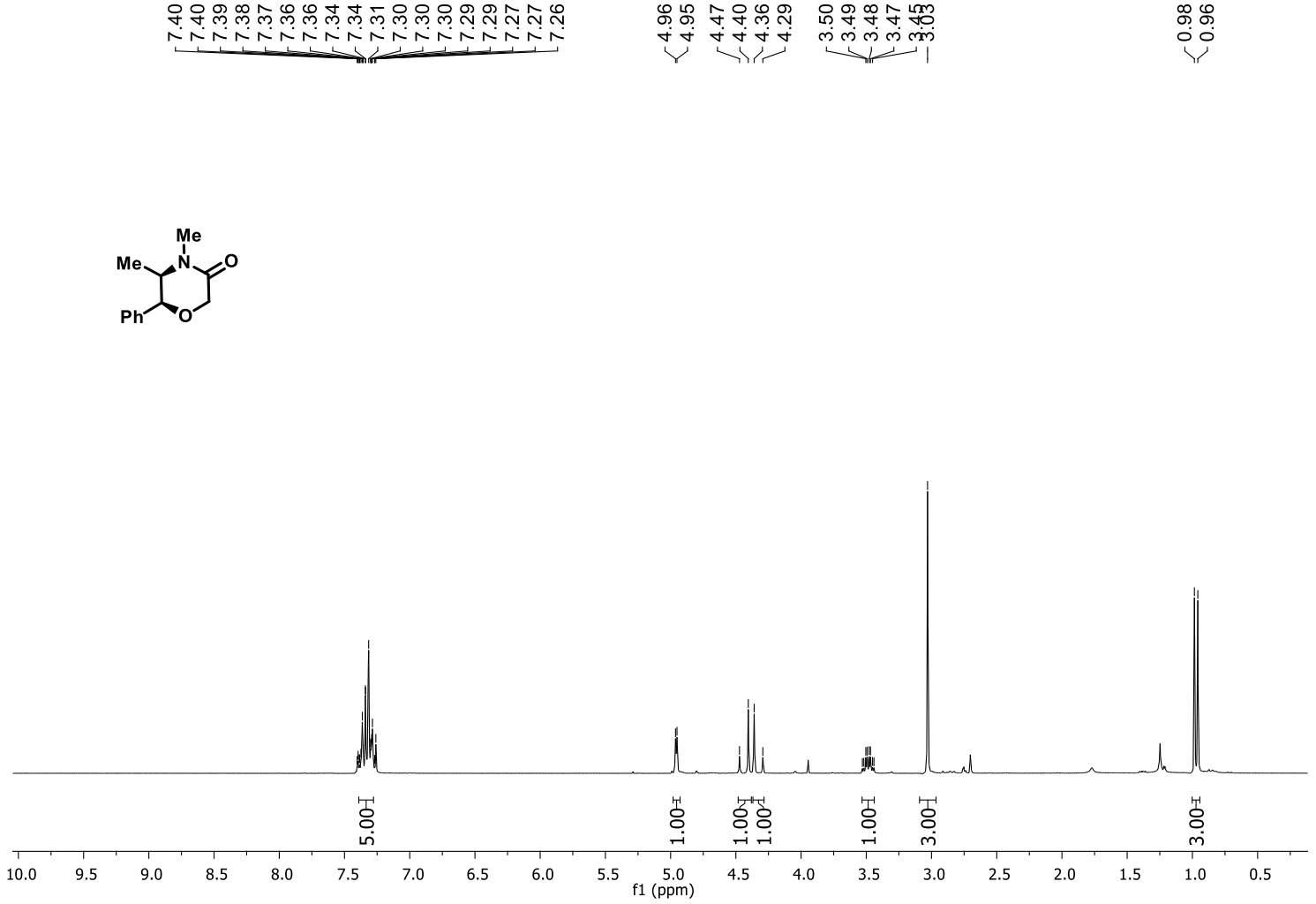
3ii - ^{13}C NMR (62.5 MHz, $CDCl_3$)



3ii - ^{19}F NMR (235 MHz, $CDCl_3$)



4 - ^{1}H NMR (250 MHz, $CDCl_3$)



4 - ^{13}C NMR (62.5 MHz, $CDCl_3$)