Transition Metal-Free Decarboxylative Olefination of Carboxylic Acid Salts

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Supporting Information

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1. General considerations

All air and moisture-sensitive reactions were carried out with the standard Schlenk technique or in an Argon-filled glove box. All phenylacetic acids are commercially available and were used without further purification. 2−bromo−2−nitro propane is commercially available from Combi Blocks and was used without further purification. Photocatalysts 9-mesityl-2,7-dimethyl-phenylacridinium tetrafluoroborate was purchased from Sigma-Aldrich. Other chemicals were obtained from Sigma-Aldrich, Combi-Blocks, Acros, Oakwood, TCI, and Alfa-Aesar. Unless otherwise stated, all reagents were commercially available and used as received without purification. Anhydrous solvents were purchased from Acros or Alfa-Aesar. Final decarboxylative elimination reactions were run in a screw-threaded tube from Chemglass (CLS-4208).

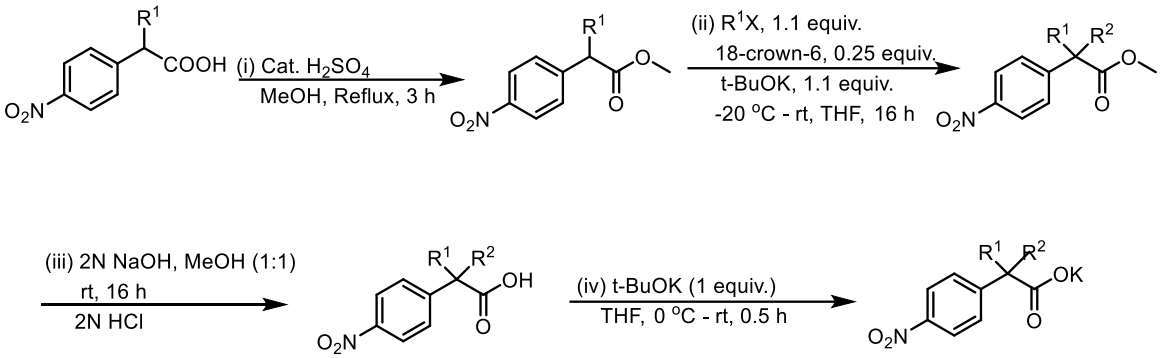
Purification was accomplished with column chromatography using silica gel (60 Å porosity, 230 x 400 mesh, standard grade) which was purchased from Sorbent Technologies (catalog # 30930M-25). TLC analysis was performed (fluorescence quenching and potassium permanganate acid stain) with silica gel HL TLC plates with UV254 purchased from Sorbent Technologies. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ADVANCE 500 DRX equipped with a QNP cryoprobe. These spectra were referenced to residual protio solvent signals. Microwave irradiation reaction was run with the Biotage Initiator EXP US, 400W. Two Kessil PR160 Blue LED grow light was used to set up photoredox decarboxylative elimination reaction, which provided 40 W and 456 nm light (no filters were used). HRMS data was obtained on an ESI LC-TOF Micromass LCT (Waters). HRMS data was collected using ESI mass spectrometry. GC/MS data was acquired on Shimadzu GCMS-QP2010 SE.

2. Experimental Procedures

2.1 General procedure for the synthesis of 4-Nitro phenylacetic acid salts

2.1.1

Method A



Step 1: Solid 4-nitrophenylcarboxylic acid (5 mmol) was added to a round bottom flask and stirred in methanol (20 mL). Sulfuric acid (0.5 mL) was added dropwise to the stirring solution, and the mixture was heated to reflux for 3 hr. The reaction mixture was allowed to cool to room temperature, and the reaction volume was decreased by evaporating off the solvent. The remaining solution was then transferred dropwise into a stirring solution of saturated sodium bicarbonate (20 mL), crushed ice, and ethyl acetate (20 mL). The bicarbonate layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude ester was then purified *via* flash chromatography on silica gel in 1:20 EtOAc: Hexanes.

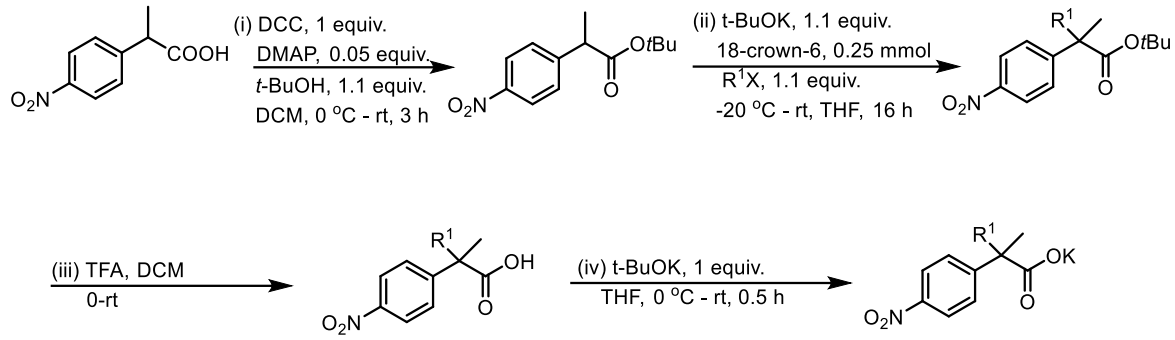
Step 2: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added the methyl ester (1 equiv.), 18-crown-6 (0.25 equiv.), and anhydrous THF (0.2 M). The reaction solution was cooled to -20 °C, and *t*-BuOK (1.1 mmol) was added. Upon adding *t*-BuOK, the reaction mixture was allowed to warm to room temperature and stirred at room temperature for 1 hour. After this time, the reaction mixture was cooled to -20 °C, and alkyl halide (1.1 mmol) was added. The reaction mixture was then warmed to room temperature and stirred overnight. Upon completion, the reaction was cooled to 0 °C and quenched with a saturated NH_4Cl solution (20 mL). After warming the solution to room temperature, it was extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with H_2O (1 x 10 mL) and brine (1 x 10 mL). The organic layers were combined and dried over $MgSO_4$, filtered, and concentrated. The residue was purified *via* silica flash chromatography in 1:20 EtOAc: Hexanes.

Step 3: The hydrolysis of the methyl ester was carried out according to a modified literature procedure.[1] To a solution of the substituted methyl ester (3 mmol) in methanol (15 mL, 0.2 M), was added 2N NaOH solution (15 mL). The resulting suspension was stirred at room temperature for 16 hours. After this time, the resulting mixture was cooled to room temperature, and the reaction volume was decreased by evaporating off the solvent. The aqueous solution was then extracted with Et_2O (2 x 10 mL), and the organic extracts were discarded. The resulting aqueous solution was then acidified to pH 1-2 with 2N HCl, and extracted with EtOAc (3 x 10 mL). The organic extracts were combined, washed with saturated NaCl solution (1 x 10 mL), dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure to afford the acid as a crystalline white solid.

Step 4: The potassium salt of the substituted 4-nitrophenylacetic acids were prepared by the neutralization of the acid. A flame-dried Schlenk flask with a stir bar under N_2 was charged with the acid (2 mmol) and THF (10 mL). The solution was cooled to 0 °C and *t*-BuOK (2 mmol) was added in one portion. The resulting

suspension was warmed to room temperature, stirred for 30 minutes, and then concentrated in *vacuo*. The resulting powder was washed with diethyl ether, decanted, and dried under vacuum to afford the potassium salts as solids.

Method B



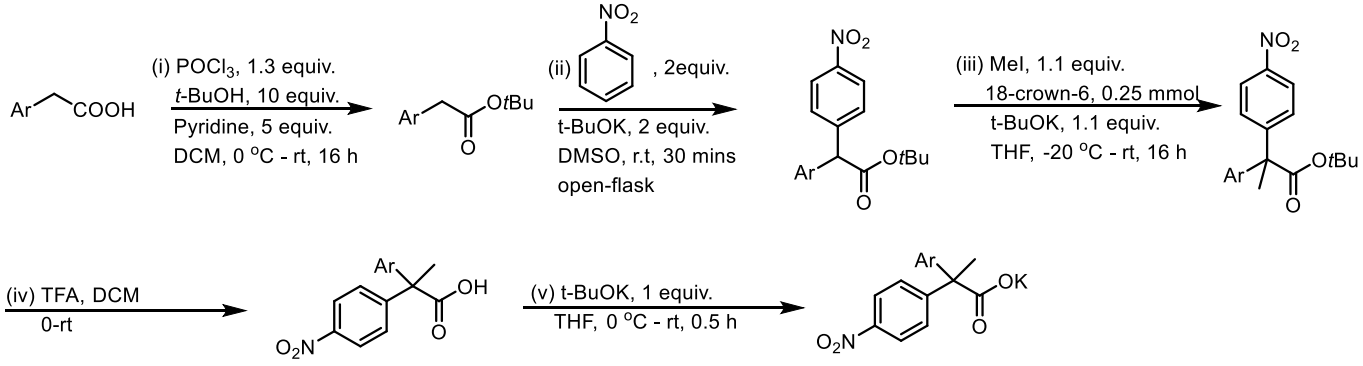
Step 1: The *t*-butyl esters were prepared by the DCC coupling of the carboxylic acids.[2] To a flame-dried Schlenk flask with a magnetic stir bar under N_2 were added the commercially available 4-nitrophenylacetic acids (1 equiv.), and dry DCM (0.2 M). The solution was cooled to 0 °C and *t*-BuOH (1.1 equiv.), DCC (1 equiv.) and DMAP (0.05 equiv.) were added. The reactions were then warmed to room temperature and allowed to stir for 16 hours. Upon completion, the reaction mixture was filtered through a bed of Celite, and the resulting filtrate was evaporated under reduced pressure to afford the crude reaction mixture, which was purified *via* flash silica column chromatography.

Step 2: Followed the same alkylating procedure as in **2.1.1, Method A**, Step 2**.**

Step 3: The hydrolysis of the ester was performed according to a modified literature procedure.[3] To a solution of *t*-butyl ester (3 mmol) in DCM (15 mL, 0.2 M), was added TFA (5 equiv.) at 0 °C. The resulting solution was stirred at room temperature until completion. After this time, the resulting mixture was concentrated and purified *via* flash column chromatography to afford the acids as crystalline solids. Alternatively, the resulting carboxylic acids can be purified using acid-base extractions. The crude acid was dissolved in DCM (10 mL) and washed with saturated $NaHCO_3$ solution (3 x 15 mL). The resulting aqueous solution was then acidified to pH 1-2 with 2N HCl and extracted with EtOAc (3 x 10 mL). The organic extracts were combined, washed with saturated NaCl solution (1 x 10 mL), dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to afford the carboxylic acids as crystalline solids.

Step 4: The potassium salt of the substituted 4-nitrophenylacetic acids were prepared following the procedure outlined in **2.1.1**, **Method A,** Step 4.

Method C



Step 1: The *t*-butyl ester of various substituted phenylacetic acids was prepared following a literature procedure.[4] Solid phenylacetic acid (5 mmol) was added to a flame-dried Schlenk flask under an atmosphere of N_2 and stirred in dry DCM (20 mL) at 0 °C. *t*-BuOH (10 equiv.) and pyridine (5 equiv.) were then added to this stirring mixture. $POCl_3$ (1.3 equiv.) was then added dropwise to this solution over a period of 15 minutes. After the addition was completed, the mixture was warmed to room temperature, and stirred for another 2-4 hours. After this time, the reaction mixture was diluted using DCM (20 mL) and quenched by adding 1N HCl (10 mL). The organic layers were then separated and washed successively with $NaHCO_3$ (2 x 10 mL), brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude esters were used for the next step without further purification.

Step 2: The alpha arylation of the esters was performed according to a modified literature procedure.[5] *t*-BuOK (2.0 equiv.) was added in one portion to a flame-dried round bottom flask containing a solution of ester (1.0 mmol) and nitrobenzene (2.0 equiv.) in dry DMSO (5 mL) at room temperature. Upon addition of the base, the mixture was stirred in an open flask at room temperature for 30 minutes. The reaction was quenched by adding saturated NH_4Cl solution (5 mL). The resulting mixture was extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude mixture was purified using silica flash chromatography.

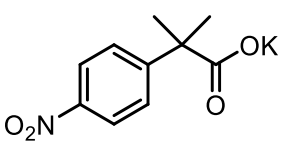
Step 3: The procedure followed in **2.1.1, Method A**, Step 2 was adapted to furnish the methylated α,α–disubstituted *t*-butyl esters which was purified via silica gel flash chromatography in Hexanes: EtOAc.

Step 4: The hydrolysis of the *t*-butyl esters was performed following the procedure outlined in **2.1.1, Method B**, Step 3**.**

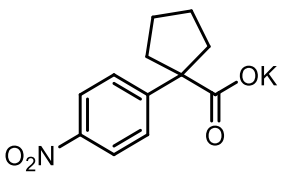
Step 5: The potassium salt of the substituted 4-nitrophenylacetic acids were prepared following the procedure outlined in **2.1.1, Method A**, step 4.

General Note: Most of these carboxylic acid salts are hygroscopic and hence shouldn't be exposed out open for longer periods. Additionally, they decompose over time and hence should be stored in the refrigerator.*

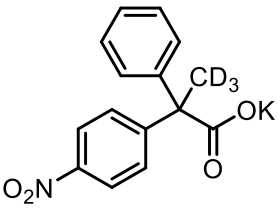
***The residual solvent (diethyl ether) after the ether washes in Step 4, **2.1.1**, **Method A**, was challenging to be removed completely. Thus, the residual solvent peaks can be seen in the NMR spectra for some of the salts.*



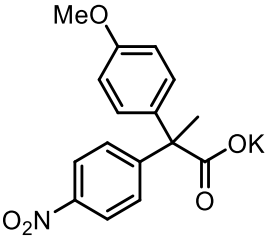
potassium 2-methyl-2-(4-nitrophenyl)propanoate (**1a**). General procedure **2.1.1**, **Method A** provided the title compound using MeI as the alkylating agent in 73% yield (20 mmol scale, over 4 steps); white solid. The product matched the previously reported literature specification.[1b] **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.17 – 8.10 (m, 2H), 7.66 – 7.60 (m, 2H), 1.54 (s, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 183.6, 157.9, 147.3, 128.4, 123.9, 50.1, 28.1.



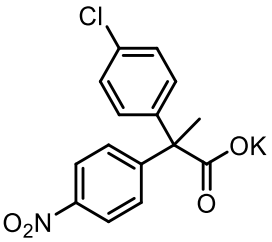
potassium 1-(4-nitrophenyl)cyclopentane-1-carboxylate (**1b**). General procedure **2.1.1**, **Method B** provided the title compound using 1,4-dibromobutane as the alkylating agent starting from 4-nitrophenylacetic acid in 27% yield (4 mmol scale, over 4 steps); white solid. The product matched the previously reported literature specification.[6] **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.16 – 8.08 (m, 2H), 7.68 – 7.57 (m, 2H), 2.73 – 2.65 (m, 2H), 1.89 – 1.63 (m, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.1, 156.4, 147.3, 129.1, 123.8, 63.2, 38.0, 24.8.



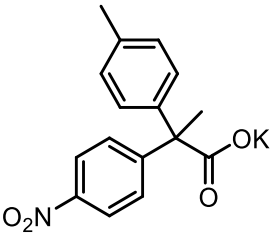
potassium 2-(4-nitrophenyl)-2-phenylpropanoate-3,3,3-d_3 (**1d-*d_3***). General procedure **2.1.1**, **Method C** provided the title compound using CD_3I as alkylating agent, starting from phenyl acetic acid in in 37% yield (4 mmol scale, over 5 steps); yellow solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.12 – 8.03 (m, 2H), 7.52 – 7.40 (m, 2H), 7.40 – 7.33 (m, 2H), 7.37 – 7.26 (m, 2H), 7.30 – 7.12 (m, 1H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 181.1, 157.8, 147.8, 147.2, 130.7, 129.3, 129.0, 127.2, 123.5, 60.2.



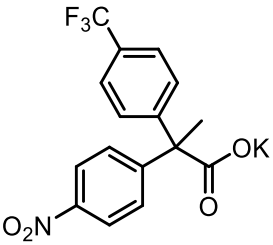
potassium 2-methyl-2-(4-nitrophenyl)-4-phenylbutanoate (**1e**). General procedure **2.1.1**, **Method C** provided the title compound using 4-methoxyphenylacetic acid in 28% yield (7 mmol scale, over 5 steps); pale yellow solid. **^{1}H NMR** (500 MHz, Methanol-d_4) δ 8.08 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H), 1.86 (s, 3H).**^{13}C NMR** (126 MHz, Methanol-d_4) δ 181.4, 159.5, 158.3, 147.2, 139.7, 130.6, 130.4, 123.4, 114.3, 59.7, 55.6, 28.7.



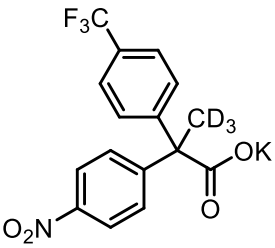
potassium 2-(4-chlorophenyl)-2-(4-nitrophenyl)propanoate (**1f**). General procedure **2.1.1**, **Method C** provided the title compound using 4-chlorophenylacetic acid in 37% yield (6 mmol scale, over 5 steps); pale yellow solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.17 – 8.00 (m, 2H), 7.48 (dd, *J* = 8.9, 2.1 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.27 (dd, *J* = 8.6, 1.7 Hz, 2H), 1.89 (d, *J* = 2.0 Hz, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 180.5, 157.2, 147.3, 146.8, 133.0, 131.1, 128.9, 130.6, 123.6, 60.0, 28.5.



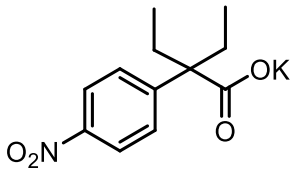
potassium 2-(4-nitrophenyl)-2-(p-tolyl)propanoate (**1g**). General procedure **2.1.1**, **Method C** provided the title compound using 4-methylphenylacetic acid in 33% yield (7 mmol scale, over 5 steps); pale yellow solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.08 (d, *J* = 9.2 Hz, 2H), 7.46 (d, *J* = 9.0 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.14 – 7.07 (m, 2H), 2.31 (s, 3H), 1.87 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 181.3, 158.1, 147.2, 144.7, 136.8, 130.7, 129.6, 129.2, 123.4, 60.0, 28.6, 21.0.



potassium 2-(4-nitrophenyl)-2-(4-(trifluoromethyl)phenyl)propanoate (**1h**). General procedure **2.1.1**, **Method C** provided the title compound using 4-trifluoromethylphenylacetic acid in 29% yield (7 mmol scale, over 5 steps); pale yellow solid. **^{1}H NMR** (500 MHz, Methanol-d_4) δ 8.13 (d, *J* = 9.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.48 (m, 4H), 1.92 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 180.1, 156.6, 152.7, 147.5, 130.7, 130.1, 129.3 (q, *J* = 32.1 Hz), 125.8 (q, *J* = 270.8), 125.7, (q, *J* = 3.7 Hz), 123.7, 60.5, 28.4. **^{19}F NMR** (376 MHz, Methanol-d_4) δ -63.87.

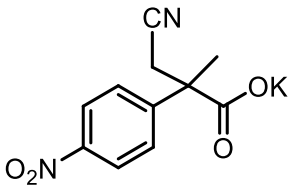


potassium 2-(4-nitrophenyl)-2-(4-(trifluoromethyl)phenyl)propanoate-3,3,3-d_3 (**1h-*d_3***). General procedure **2.1.1**, **Method C** provided the title compound using CD_3I as the alkylating agent in 27% yield (4 mmol scale, over 5 steps); yellow solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.13 (app d, *J* = 9.0 Hz, 2H), 7.58 (app d, *J* = 8.3 Hz, 2H), 7.54 – 7.47 (m, 4H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 180.1, 156.6, 152.7, 147.5, 130.7, 130.1, 129.3 (q, *J* = 32.1 Hz), 125.8 (q, *J* = 270.8), 125.7, (q, *J* = 3.7 Hz), 123.7, 60.3. **^{19}F NMR** (376 MHz, Methanol-d4) δ -62.70.

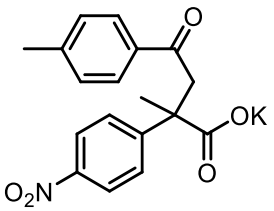


potassium 2-ethyl-2-(4-nitrophenyl)butanoate (**1i**). General procedure **2.1.1**, **Method B** provided the title compound using ethyl bromide as the alkylating agent starting from 4-nitrophenylbutyric acid in 61% yield (2 mmol scale, over 4 steps); white solid. The product matched the previously reported literature specification.[6] **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.18 – 8.09 (m, 2H), 7.62 – 7.54 (m, 2H), 2.25 –

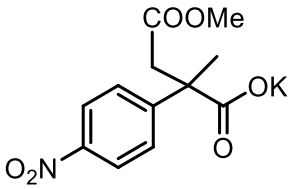
2.04 (m, 2H), 1.99 (dt, *J* = 13.9, 7.4 Hz, 2H), 0.74 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.4, 156.2, 147.2, 129.5, 123.7, 58.4, 28.4, 9.3.



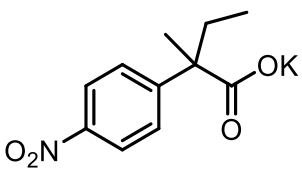
potassium 3-cyano-2-methyl-2-(4-nitrophenyl)propanoate (**1j**). General procedure **2.1.1**, **Method A** provided the title compound using bromoacetonitrile as the alkylating agent in 54% yield (4 mmol scale, over 4 steps); dark green solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.20 (d, *J* = 9.0 Hz, 2H), 7.69 (d, *J* = 9.2 Hz, 2H), 3.06 (d, *J* = 1.7 Hz, 2H), 1.75 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 177.8, 151.6, 146.7, 127.5, 122.9, 118.6, 50.3, 28.5, 22.5.



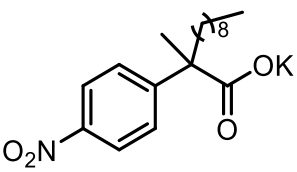
potassium 2-methyl-2-(4-nitrophenyl)-4-oxo-4-(p-tolyl)butanoate (**1k**). General procedure **2.1.1**, **Method B** provided the title compound using 2-Bromo-4'-methylacetophenone as the alkylating agent in 65% yield (4 mmol scale, over 4 steps); dark green solid. The product matched the previously reported literature specification.[6] **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.17 – 8.09 (m, 2H), 7.89 – 7.82 (m, 2H), 7.79 – 7.69 (m, 2H), 7.29 – 7.22 (m, 2H), 3.78 (dd, *J* = 17.4, 8.0 Hz, 2H), 2.38 (s, 3H), 1.73 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 200.3, 181.9, 156.3, 147.4, 145.0, 136.8, 130.1, 129.2, 128.9, 123.9, 52.1, 31.1, 25.0, 21.5.



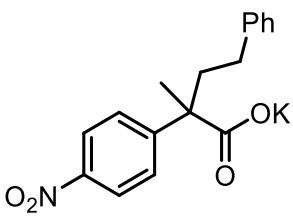
potassium 4-methoxy-2-methyl-2-(4-nitrophenyl)-4-oxobutanoate (**1l**). General procedure **2.1.1**, **Method B** provided the title compound using bromomethyl acetate as the alkylating agent in 53% yield (2 mmol scale, over 4 steps); brown solid. The product matched the previously reported literature specification.[6] **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.20 – 8.05 (m, 2H), 7.73 – 7.62 (m, 2H), 3.53 (s, 3H), 3.07 (d, *J* = 15.6 Hz, 1H), 2.99 (d, *J* = 15.7 Hz, 1H), 1.70 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 181.3, 174.0, 155.4, 147.6, 128.9, 123.9, 51.7, 45.5, 31.1, 24.6.



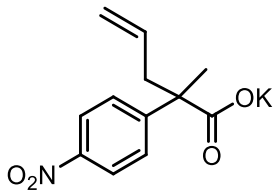
potassium 2-methyl-2-(4-nitrophenyl)butanoate (**1m**). General procedure **2.1.1, Method A** provided the title compound using bromoethane as the alkylating agent in 59% yield (5 mmol scale, over 4 steps); white solid. The product matched the previously reported literature specification.[6] **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.13 (dd, *J* = 9.6, 2.1 Hz, 2H), 7.62 (dd, *J* = 9.2, 2.3 Hz, 2H), 2.08 (qd, *J* = 7.5, 5.9 Hz, 1H), 2.01 – 1.87 (m, 1H), 1.49 (s, 3H), 0.84 (td, *J* = 7.3, 1.6 Hz, 3H).**^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.8, 157.1, 147.3, 129.0, 123.9, 54.3, 33.6, 24.0, 10.0.



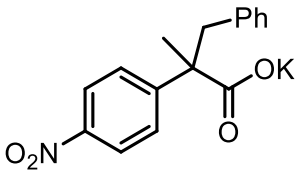
potassium 2-methyl-2-(4-nitrophenyl)undecanoate (**1n**). General procedure **2.1.1, Method B** provided the title compound using bromononane as the alkylating agent in 37% yield (3 mmol scale, over 4 steps); green solid. The product matched the previously reported literature specification.[6] **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.17 – 8.09 (m, 2H), 7.65 – 7.57 (m, 2H), 2.03 (td, *J* = 13.4, 10.1, 3.5 Hz, 1H), 1.90 (td, *J* = 13.0, 12.2, 4.3 Hz, 1H), 1.49 (s, 3H), 1.40 – 1.08 (m, 19H), 0.92 – 0.84 (m, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 183.0, 157.5, 147.2, 128.9, 123.8, 54.0, 41.2, 33.0, 31.5, 30.7, 30.4, 26.3, 24.7, 23.7, 14.4.



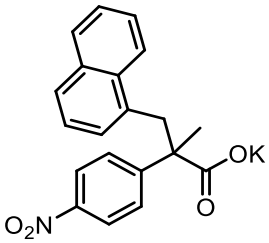
potassium 2-methyl-2-(4-nitrophenyl)-4-phenylbutanoate (**1o**). General procedure **2.1.1**, **Method A** provided the title compound using (2-bromoethyl)benzene as the alkylating agent in 43% yield (4 mmol scale, over 4 steps); pale-yellow solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.20 – 8.11 (m, 2H), 7.70 – 7.62 (m, 2H), 7.26 – 7.07 (m, 5H), 2.59 (td, *J* = 12.7, 4.6 Hz, 1H), 2.46 (td, *J* = 12.7, 4.6 Hz, 1H), 2.33 (td, *J* = 12.7, 4.6 Hz, 1H), 2.18 (td, *J* = 12.8, 4.6 Hz, 1H), 1.61 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.6, 157.1, 147.3, 144.3, 129.4, 129.3, 128.9, 126.6, 124.0, 54.1, 43.7, 32.9, 24.8.



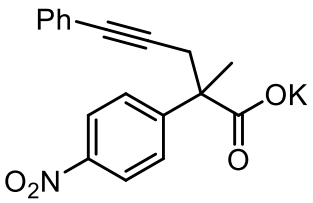
potassium 2-methyl-2-(4-nitrophenyl)pent-4-enoate (**1p**). General procedure **2.1.1**, **Method B** provided the title compound using allyl bromide as the alkylating agent in 57% yield (4 mmol scale, over 4 steps); brown solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.14 (d, *J* = 9.0 Hz, 2H), 7.62 (d, *J* = 9.2 Hz, 2H), 5.74 – 5.59 (m, 1H), 5.05 – 4.92 (m, 2H), 2.80 (ddt, *J* = 13.6, 6.8, 1.3 Hz, 1H), 2.66 (ddt, *J* = 13.6, 7.6, 1.2 Hz, 1H), 1.49 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.3, 156.5, 147.4, 136.8, 129.0, 123.9, 117.7, 53.4, 46.0, 24.3.



potassium 2-methyl-2-(4-nitrophenyl)-3-phenylpropanoate (**1q**). General procedure **2.1.1**, **Method A** provided the title compound using benzylbromide as the alkylating agent in 61% yield (4 mmol scale, over 4 steps); pale-yellow powder. The product matched the previously reported literature specification.[7] **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.13 – 8.06 (m, 2H), 7.57 – 7.48 (m, 2H), 7.16 – 7.05 (m, 3H), 6.98 – 6.85 (m, 2H), 3.38 (d, *J* = 13.2 Hz, 1H), 3.23 (d, *J* = 13.2 Hz, 1H), 1.44 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.6, 156.4, 147.4, 140.0, 131.6, 129.4, 128.6, 127.0, 123.7, 54.9, 47.5, 23.6.

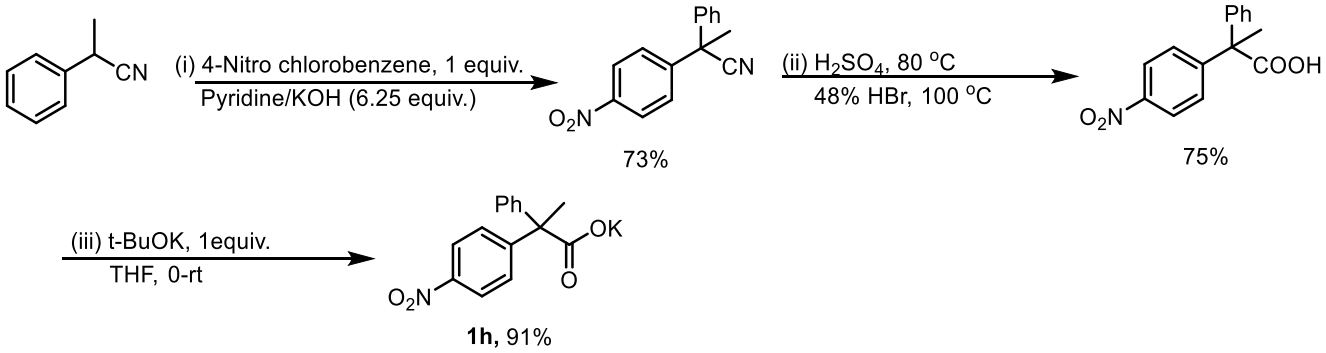


potassium 2-methyl-3-(naphthalen-1-yl)-2-(4-nitrophenyl)propanoate (**1r**). General procedure **2.1.1, Method A** provided the title compound using naphthyl bromide as the alkylating agent in 38% yield (4 mmol scale, over 4 steps); pale yellow powder. The product matched the previously reported literature specification.[6] **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.12 (dd, *J* = 9.2, 2.3 Hz, 2H), 7.76 – 7.69 (m, 1H), 7.68 – 7.61 (m, 1H), 7.61 – 7.54 (m, 3H), 7.42 (s, 1H), 7.37 (td, *J* = 6.1, 5.5, 3.2 Hz, 2H), 7.02 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.57 (d, *J* = 13.1 Hz, 1H), 3.39 (d, *J* = 13.2 Hz, 1H), 1.49 (s, 3H).**^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.5, 156.4, 147.4, 137.6, 134.6, 133.6, 130.2, 130.1, 129.4, 128.5, 128.4, 127.8, 126.6, 126.1, 123.7, 55.1, 47.6, 23.7.



potassium 2-methyl-2-(4-nitrophenyl)-5-phenylpent-4-ynoate (**1s**). General procedure **2.1**, **Method A** provided the title compound using propargyl bromide as the alkylating agent in 38% yield (4 mmol scale, over 4 steps); pale yellow solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.17 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 9.2 Hz, 2H), 7.23 (s, 5H), 3.12 (d, *J* = 16.9 Hz, 1H), 3.03 (d, *J* = 16.9 Hz, 1H), 1.76 (s, 3H).**^{13}C NMR** (126 MHz, Methanol-d_4) δ 181.5, 155.1, 147.6, 132.4, 129.2, 129.1, 128.6, 125.3, 123.8, 88.9, 83.5, 53.5, 32.2, 24.1.

2.1.2 *Potassium 2-(4-nitrophenyl)-2-phenylpropanoate* (**1h**)



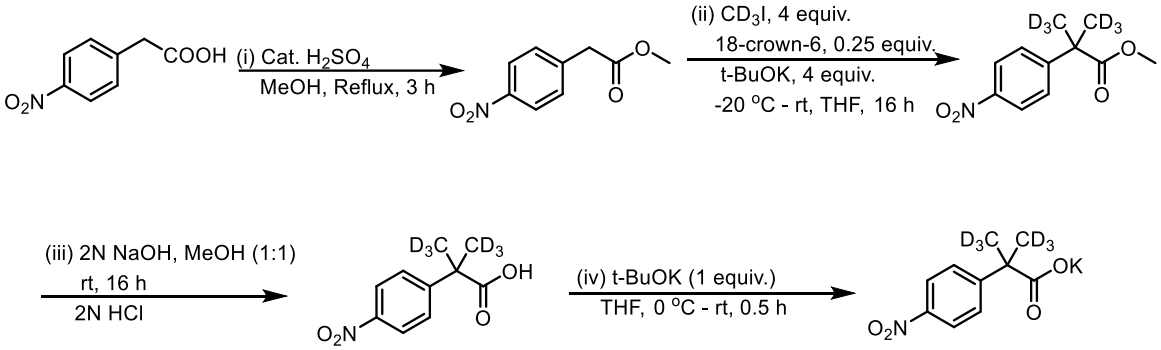
The synthesis of potassium potassium 2-(4-nitrophenyl)-2-phenylpropanoate was carried out according to a modified literature procedure.[8]

Step 1: A solution of 4-chloronitrobenzene (3.15 g, 20 mmol) in pyridine (10 mL) was added dropwise to a vigorously stirred suspension of KOH (fine powder, 7 g) and a-methylbenzyl cyanide (2.62 g, 20 mmol) in pyridine (15 mL), with the reaction temperature being maintained at 0 °C. The reaction mixture was stirred for 24 h at 25 °C and poured onto an excess of HCl-ice mixture. The acidic aqueous mixture was extracted with DCM, the organic phase washed with brine and dried (Na_2SO_4), and the solvent evaporated under vacuum. The residue was the purified via column chromatography in Hex: EtOAc, 10: to afford 2-(4-nitrophenyl)-2-phenylpropanenitrile as a white solid in 73% yield.

Step 2: 2-(4-nitrophenyl)-2-phenylpropanenitrile (1 g, 4 mmol) was dissolved in concentrated H_2SO_4 (4 mL) and the mixture heated to 80 °C for 2 h. The pale-yellow solution was then poured onto ice and extracted with ethyl acetate (2 x 20 mL). The organic solvent was evaporated under reduced pressure, and 48% HBr solution (20 mL) was added to the remaining viscous residue. After refluxing for 8 h, the viscous oil turned to a white crystalline material. The aqueous acidic phase was then removed by decantation, and the crystalline material was washed and recrystallized with H_2O to give 2-(4-nitrophenyl)-2-phenylpropanoic acid as a white solid in 75% yield.

Step 3: The potassium salt of the 2-(4-nitrophenyl)-2-phenylpropanoic acid was prepared following the procedure outlined in **2.1.1**, **Method A,** Step 4**. ^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.09 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.48 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.35 (dt, *J* = 8.3, 1.2 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.24 – 7.16 (m, 1H), 1.90 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 181.1, 157.8, 147.9, 147.2, 130.7, 129.4, 129.0, 127.2, 123.4, 60.4, 28.6.

2.1.3 *potassium 2-(methyl-d3)-2-(4-nitrophenyl)propanoate-3,3,3-d_3* (**1a-d_6**).



Step 1: Solid 4-nitrophenylacetic acid (905 mg, 5 mmol) was added to a round bottom flask and stirred in methanol (20 mL). Sulfuric acid (0.5 mL) was added dropwise to the stirring solution, and the mixture was heated to reflux for 3 hr. The reaction mixture was allowed to cool to r.t, and the reaction volume was decreased by evaporating off the solvent. The remaining solution was then transferred dropwise into a stirring solution of saturated sodium bicarbonate (20 mL), crushed ice, and ethyl acetate (20 mL). The bicarbonate layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude ester was used without purification.

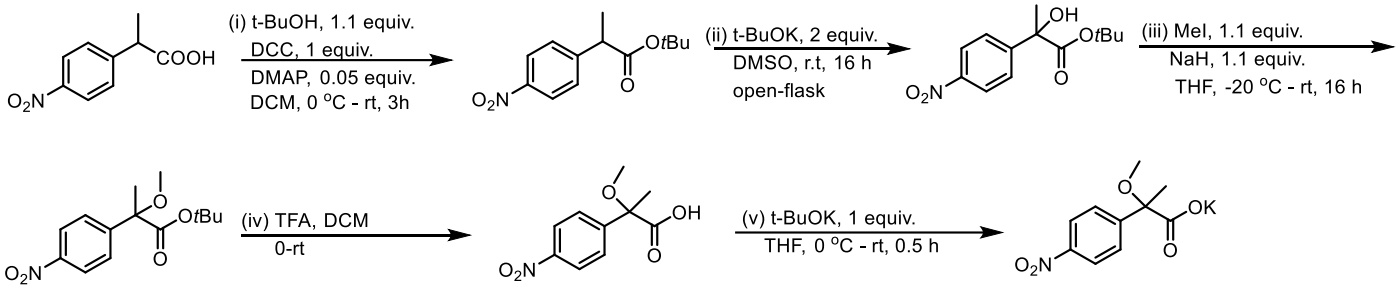
Step 2: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added the methyl ester (1 equiv.), 18-crown-6 (0.25 equiv.), CD_3I (4 equiv.), and anhydrous THF (0.2 M). The reaction solution was cooled to -20 °C and then *t*-BuOK (4 equiv.) was added. Upon adding *t*-BuOK, the reaction mixture was allowed to warm to room temperature and stirred at room temperature for overnight. Upon completion, the reaction was cooled to 0 °C and quenched with a saturated NH_4Cl solution (20 mL). After warming the solution to room temperature, it was extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with H_2O (1 x 10 mL) and brine (1 x 10 mL). The organic layers were combined and

dried over $MgSO_4$, filtered, and concentrated. The residue was purified *via* silica flash chromatography in 1:20 EtOAc: Hexanes.

Step 3: The hydrolysis of the methyl ester was done according to the procedure outlined in **2.1.1**, **Method A**, Step 3.

Step 4: The potassium salt of the substituted 4-nitrophenylacetic acid was prepared by neutralizing the acid using the procedure detailed in **2.1.1**, **Method A**, Step 4. 53% yield; white solid. **^{1}H NMR** (500 MHz, Methanol-d_4) δ 8.14 (d, J = 9.0 Hz, 2H), 7.63 (d, J = 9.0 Hz, 2H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 183.6, 157.8, 147.3, 128.4, 124.0, 49.7.

2.1.4 *Potassium 2-(4-nitrophenyl)-2-phenylpropanoate* (**1c**)



Step 1: Followed the same procedure as in **2.1.1**, **Method B**, Step 1**.**

Step 2: The benzylic oxidation of the ester was performed according to a modified literature procedure.[5] *t*-BuOK (2.0 equiv.) was added in one portion to a flame-dried round bottom flask containing a solution of ester (1.0 mmol) in dry DMSO (5 mL) at room temperature. Upon addition of the base, the mixture was stirred in an open flask at room temperature for 16 hours. The reaction was quenched via the addition of saturated NH_4Cl solution (5 mL). The resulting mixture was extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude mixture was purified using silica flash chromatography.

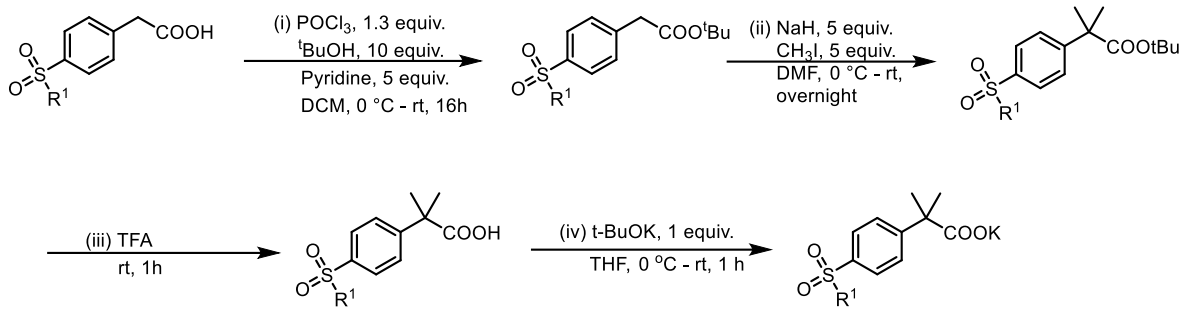
Step 3: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added the *t*-butyl ester (1 equiv.), MeI (1.2 equiv.), and anhydrous THF (0.2 M). The reaction solution was cooled to -20 °C and then NaH (1.2 equiv.) was added. Upon adding sodium hydride, the reaction mixture was allowed to warm to room temperature and stirred for 16 hours. Upon completion, the reaction was quenched by adding saturated NH_4Cl solution (20 mL) and extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with H_2O (1 x 10 mL) and brine (1 x 10 mL). The organic layers were combined and dried over $MgSO_4$, filtered, and concentrated. The residue was purified *via* silica flash chromatography in 1:20 EtOAc: Hexanes.

Step 4: The hydrolysis of the *t*-butyl esters was performed following the procedure outlined in **2.1.1**, **Method B**, Step 3**.**

Step 5: The potassium salt of the substituted 4-nitrophenylacetic acid was prepared following the procedure outlined in **2.1.1**, **Method A**, Step 4. Yield 39% (over 5 steps); light beige solid**. ^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.16 (app d, J = 9.0 Hz, 2H), 7.79 (app d, J = 9.0 Hz, 2H), 3.28 (s, 3H), 1.73 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 178.7, 153.7, 148.1, 128.3, 123.8, 84.4, 52.1, 23.0.

2.2 General procedure for the synthesis 4-Sulfono phenylacetic acid salts

Method A



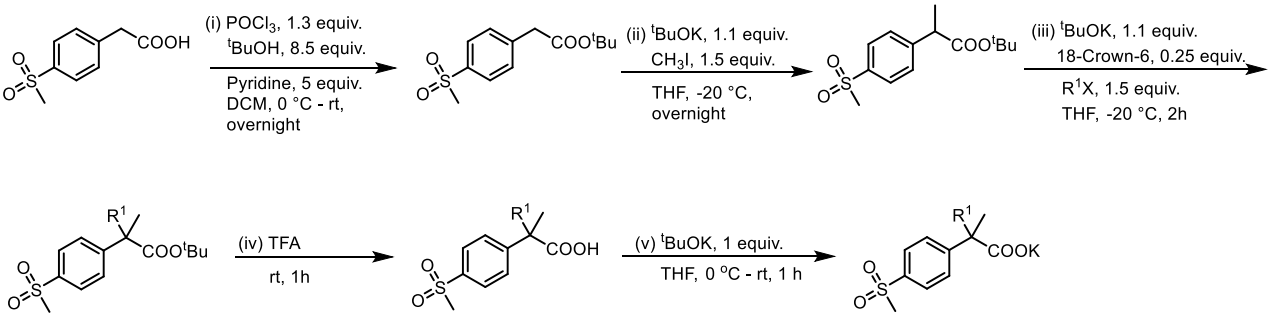
Step 1: The *t*-butyl ester of various substituted phenylacetic acids was prepared following a literature procedure.[4] Solid phenylacetic acid (5 mmol) was added to a flame-dried Schlenk flask under an atmosphere of N_2 and stirred in dry DCM (20 mL) at 0 °C. *t*-BuOH (10 equiv.) and pyridine (5 equiv.) were then added to this stirring mixture. $POCl_3$ (1.3 equiv.) was then added dropwise to this solution over a period of 15 minutes. After the addition was completed, the mixture was warmed to room temperature and stirred for another 16 hours. After this time, the reaction mixture was diluted using DCM (20 mL) and quenched by adding 2N HCl (10 mL). The organic layers were then separated and washed successively with $NaHCO_3$ (2 x 10 mL), brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude esters were used for the next step without further purification.

Step 2: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added the *t*-butyl ester (1 equiv.) and anhydrous DMF (0.4 M). The reaction solution was cooled to 0 °C and then methyl iodide (5 equiv.) was added. After stirring for 15 minutes at 0 °C, sodium hydride (5 equiv.) was added. The reaction mixture was then warmed to room temperature and stirred overnight. Upon completion, the reaction mixture was cooled to 0 °C and quenched with a saturated NH_4Cl solution (20 mL). After warming the solution to room temperature, it was extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with H_2O (2 x 30 mL), brine (1 x 30 mL). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated. The residue was purified *via* silica flash chromatography in EtOAc/Hexanes solvent system.

Step 3: The hydrolysis of the ester was carried out according to a modified literature procedure.[1a] To a solution of *t*-butyl ester (1 equiv.) was added TFA (1 mL) at 0 °C. The resulting solution was stirred at room temperature until completion. After this time, the resulting mixture was dissolved in DCM and purged with air to remove TFA, concentrated and purified *via* flash column chromatography to afford the acids as crystalline solids.

Step 4: The potassium salt of the substituted phenylacetic acids were prepared following the procedure outlined in **2.1.1**, **Method A**, step 4.

Method B



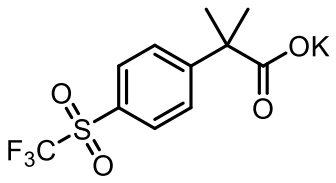
Step 1: Followed the same esterification procedure as in **2.2**, **Method A,** Step 1**.**

Step 2: The mono-alkylation was done using the modified literature procedure.[9] To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added the *t*-butyl ester (2.58 mmol, 1 equiv.), and anhydrous THF (0.1 M). The reaction solution was cooled to -20 °C and then *t*-BuOK (1M, THF, 3 mL, 2.84 mmol, 1.1 equiv.) was added dropwise. After stirring for 20 minutes at -20 °C, methyl iodide (3.88 mmol ,1.5 equiv.) was added. The reaction mixture was then stirred at -20 °C for 2h. Upon completion, the reaction mixture was quenched with a saturated NH_4Cl solution (20 mL). After warming the solution to room temperature, it was extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with brine (1 x 60 mL). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated. The residue was purified *via* silica flash chromatography in EtOAc/Hexanes solvent system.

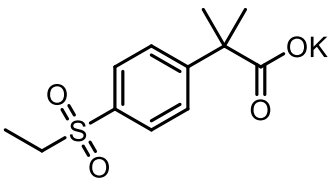
Step 3: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added the *t*-butyl ester (1 equiv.), 18-Crown-6 (0.25 equiv.) and anhydrous THF (0.25 M). The reaction solution was cooled to 0 °C and then the corresponding alkyl halide (1.1 equiv.) was added. After stirring for 15 minutes at 0 °C, solid *t*-BuOK (1.1 equiv.) was added in one portion. The reaction mixture was then warmed to room temperature and stirred overnight. Upon completion, the reaction mixture was cooled to 0 °C and quenched with a saturated NH_4Cl solution (20 mL). After warming the solution to room temperature, it was extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with brine (1 x 20 mL). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated. The residue was purified *via* silica flash chromatography in EtOAc/Hexanes solvent system.

Step 4: The hydrolysis of the *t*-butyl esters was performed following the procedure outlined in **2.1.1**, **Method B**, Step 3**.**

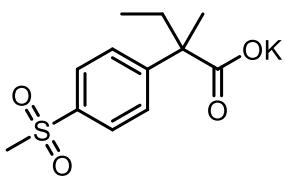
Step 5: The potassium salt of the substituted phenylacetic acids were prepared following the procedure outlined in **2.1.1**, **Method A**, step 4.



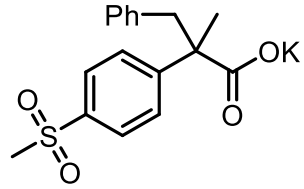
potassium 2-methyl-2-(4-((trifluoromethyl)sulfonyl)phenyl)propanoate (**1t**). General procedure 2.2, **Method A** provided the title compound in 56% yield (4 mmol scale, over 4 steps); off-white solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.97 (app d, *J* = 8.7 Hz, 2H), 7.81 (app d, *J* = 8.7 Hz, 2H), 1.55 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 183.2, 160.7, 143.4, 131.5, 129.3, 121.3 (q, J= 324.6 Hz), 50.5, 28.0. **^{19}F NMR** (376 MHz, Methanol-d4) δ -80.83.



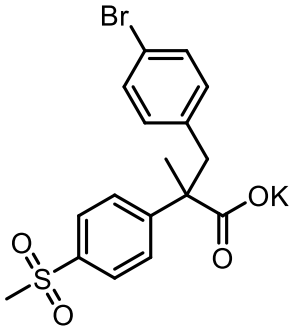
potassium 2-(4-(ethylsulfonyl)phenyl)-2-methylpropanoate (**1u**). General procedure 2.2, **Method A** provided the title compound in 62% yield (3 mmol scale, over 4 steps); white solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 3.17 (q, *J* = 7.4 Hz, 2H), 1.53 (s, 6H), 1.20 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 183.7, 156.7, 136.7, 128.8, 128.3, 51.3, 50.0, 28.1, 7.6.



potassium 2-methyl-2-(4-(methylsulfonyl)phenyl)butanoate (**1v**). General procedure 2.2, **Method B** provided the title compound in 43% yield (4 mmol scale, over 5 steps); off-white solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 3.09 (s, 3H), 2.09 (dq, *J* = 13.3, 7.4 Hz, 1H), 1.94 (dq, *J* = 13.3, 7.4 Hz, 1H), 1.49 (s, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.7, 155.6, 139.0, 128.8, 127.9, 54.0, 44.5, 33.5, 24.0, 9.9.



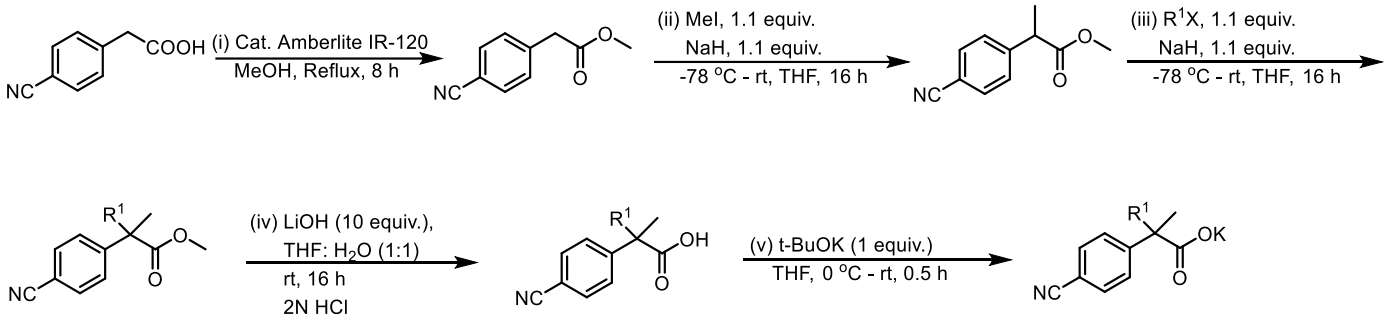
potassium 2-methyl-2-(4-(methylsulfonyl)phenyl)-3 phenylpropanoate (**1w**). General procedure 2.2, **Method B** provided the title compound in 39% yield (2 mmol scale, over 5 steps); off-white solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.16 – 7.07 (m, 3H), 6.96 – 6.89 (m, 2H), 3.40 (d, *J* = 13.0 Hz, 1H), 3.22 (d, *J* = 13.0 Hz, 1H), 3.10 (s, 3H), 1.44 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 181.8, 154.3, 139.7, 139.3, 131.6, 129.2, 128.6, 127.8, 127.1, 54.4, 47.1, 44.5, 23.5.



potassium 3-(4-bromophenyl)-2-methyl-2-(4-(methylsulfonyl)phenyl)propanoate (**1x**). General procedure 2.2, **Method B** provided the title compound in 37% yield (2 mmol scale, over 4 steps); off-white solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 3.37 (d, *J* = 13.1 Hz, 1H), 3.17 (d, *J* = 13.1 Hz, 1H), 3.10 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.0, 154.5, 139.3, 139.2, 133.5, 131.6, 129.2, 127.8, 120.9, 54.5, 46.5, 44.5, 23.6.

2.3 General procedure for the synthesis of 4-Cyano phenylacetic acid salts

Method A:



The preparation of 4-CN phenylacetic acids were carried out following a modified literature procedure.[10]

Step 1: Solid 4-cyanophenylpropionic acid (805 mg, 5 mmol) was added to a round bottom flask and stirred in methanol (20 mL). Amberlite IR-120 resin (0.5 g) was added to the stirring solution, and the mixture was heated to reflux for 8 hours. The reaction mixture was allowed to cool to room temperature, and the reaction volume was decreased by evaporating off the solvent. The remaining solution was then transferred into an ice-cold solution of saturated sodium bicarbonate (20 mL), and ethyl acetate (20 mL). The bicarbonate layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude ester was used without further purification.

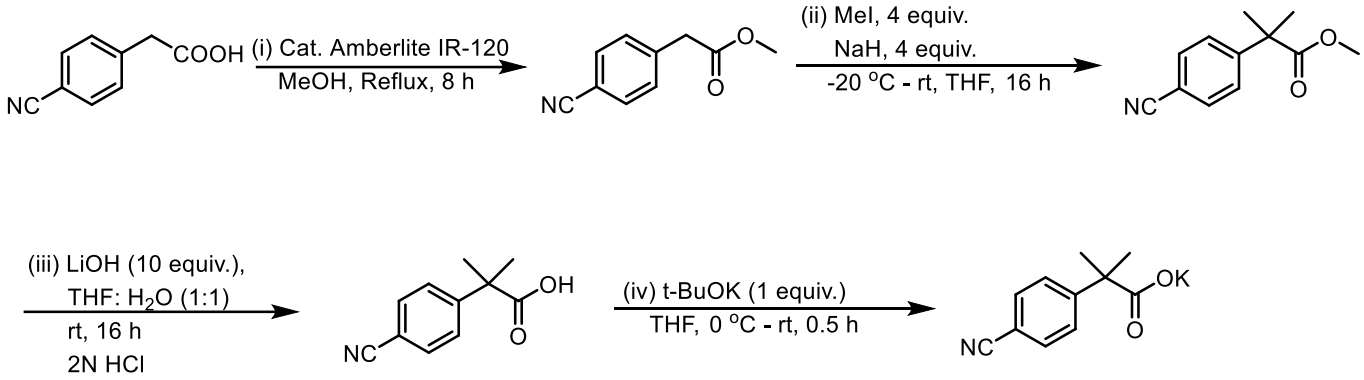
Step 2: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added the methyl ester (1 equiv.), MeI (1.1 equiv.), and anhydrous THF (0.2 M). The reaction solution was cooled to -78 °C and then NaH (1.1 equiv.) was added. Upon adding sodium hydride, the reaction mixture was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was cooled to 0 °C and quenched with a saturated NH_4Cl solution (20 mL). After warming the solution to room temperature, it was extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with H_2O (1 x 10 mL) and brine (1 x 10 mL). The organic layers were combined and dried over $MgSO_4$, filtered, and concentrated. The residue was purified *via* silica flash chromatography in 1:20 EtOAc: Hexanes.

Step 3: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added the methyl ester (1 equiv.) and anhydrous THF (0.2 M). The reaction solution was cooled to -78 °C and then NaH (1.1 equiv.) was added. Upon adding sodium hydride, the reaction mixture was allowed to warm to room temperature and stirred at room temperature for 1 hour. After this time, the reaction mixture was cooled to -78 °C, and the corresponding alkyl halide (1.1 equiv.) was added. The reaction mixture was then warmed to room temperature and stirred overnight. The workup and purification were done according to the above step.

Step 4: The hydrolysis of the ester was done according to a modified literature procedure.[10] To a solution of the substituted methyl ester (1 mmol) in a THF: H_2O mixture (1:1, 10 mL), was added LiOH (10 equiv.). The resulting suspension was stirred at room temperature for 16 hours. After this time, the resulting mixture was cooled to room temperature, and the reaction volume was decreased by evaporating off the solvent. The aqueous solution was extracted with Et_2O (2 x 10 mL), and the organic extracts were discarded. The resulting aqueous solution was acidified to pH 1-2 with 2N HCl and extracted with EtOAc (3 x 10 mL). The organic extracts were combined, washed with saturated NaCl solution (1 x 10 mL), dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure to afford the acid as a crystalline white solid.

Step 5: The potassium salt of the substituted 4-cyanophenylacetic acids was prepared by neutralizing the acid following the procedure outlined in **2.1.1**, **Method A**, step 4.

METHOD B:

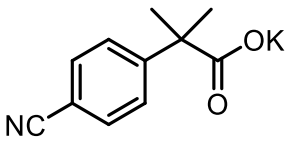


Step 1: Followed the same procedure as in 2.3, **Method A**, Step 1.

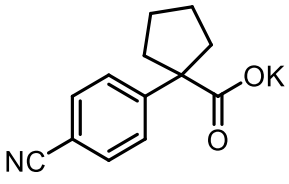
Step 2: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added the methyl ester (1 equiv.), MeI (4 equiv.) and anhydrous THF (0.2 M). The reaction solution was cooled to -20 °C and then NaH (4 equiv.) was added in portions over a period of 5 minutes. Upon adding sodium hydride, the reaction mixture was allowed to warm to room temperature and stirred and stirred overnight. Upon completion, the reaction was cooled to 0 °C and quenched with a saturated NH_4Cl solution (20 mL). After warming the solution to room temperature, it was extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with H_2O (1 x 10 mL) and brine (1 x 10 mL). The organic layers were combined and dried over $MgSO_4$, filtered, and concentrated. The residue was purified *via* silica flash chromatography in 1:20 EtOAc: Hexanes.

Step 4: The hydrolysis of the ester was done according to the procedure detailed in **2.3, Method A**, Step 4

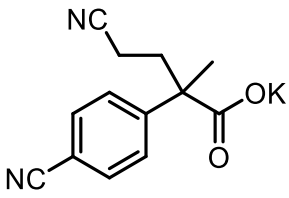
Step 5: The potassium salt of the substituted 4-cyanophenylacetic acid was prepared by neutralizing the acid following the procedure outlined in **2.1.1**, **Method A**, step 4.



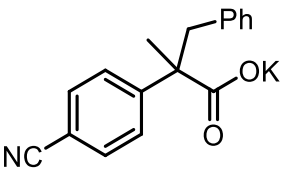
potassium 2-(4-cyanophenyl)-2-methylpropanoate (**1y**). General procedure **2.3**, **Method B**, provided the title compound using MeI as the alkylating agent in 62% yield (3 mmol scale, over 4 steps); white solid. Product matched the previously reported literature specification.[10] **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.65 – 7.60 (m, 2H), 7.60 – 7.56 (m, 2H), 1.50 (s, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 183.9, 156.0, 132.8, 128.4, 120.1, 110.1, 50.1, 28.1.



potassium 1-(4-cyanophenyl)cyclopentane-1-carboxylate (**1z**). General procedure **2.3**, **Method B**, provided the title compound using 1,4-diiodobutane *(Note: 1.1 equiv. instead of 4 equiv.)* as the alkylating agent in 32% yield (3 mmol scale, over 4 steps); white solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.59 (s, 4H), 2.65 (dddd, *J* = 7.6, 5.9, 4.0, 2.4 Hz, 2H), 1.84 – 1.60 (m, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.5, 154.5, 132.6, 129.1, 120.2, 110.0, 63.3, 38.1, 24.8.

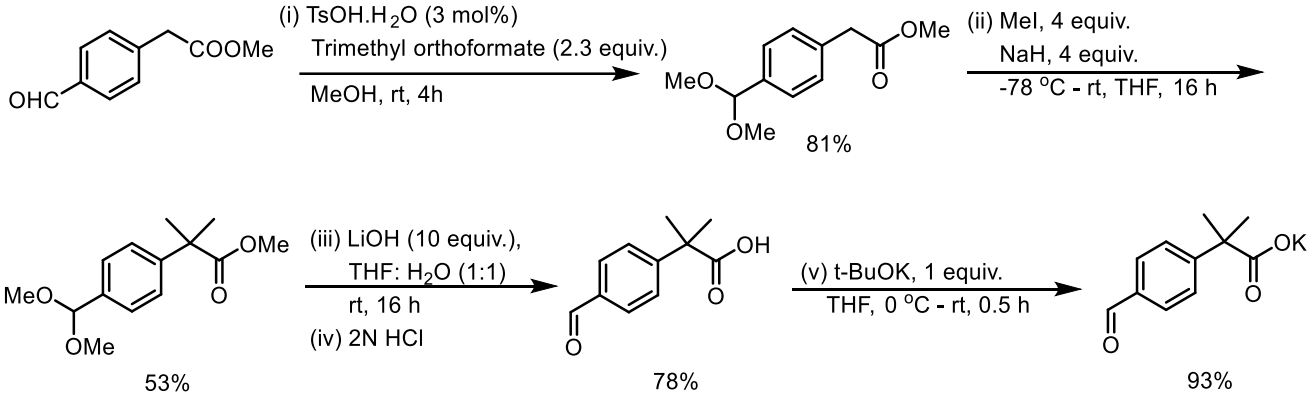


potassium 4-cyano-2-(4-cyanophenyl)-2-methylbutanoate (**1aa**). General procedure **2.3**, **Method A**, provided the title compound provided the title compound using 3-bromopropionitrile as the alkylating agent in 43% yield (4 mmol scale, over 5 steps); white solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.69 – 7.63 (m, 2H), 7.61 – 7.54 (m, 2H), 2.44 – 2.33 (m, 2H), 2.37 – 2.20 (m, 1H), 2.23 – 2.14 (m, 1H), 1.53 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 181.0, 153.1, 133.1, 128.8, 121.5, 119.9, 110.9, 53.3, 37.3, 23.9, 14.0.



potassium 2-(4-cyanophenyl)-2-methyl-3-phenylpropanoate (**1ab**). General procedure **2.3**, **Method A**, provided the title compound using benzylbromide as the alkylating agent in 49% yield (4 mmol scale, over 5 steps); pale yellow solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.59 (dd, *J* = 8.6, 2.0 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.09 (dq, *J* = 6.0, 3.8, 2.9 Hz, 3H), 6.88 (dt, *J* = 6.2, 2.0 Hz, 2H), 3.35 (d, *J* = 13.1 Hz, 1H), 3.19 (d, *J* = 13.1 Hz, 1H), 1.40 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.7, 154.3, 140.1, 132.5, 131.6, 129.4, 128.5, 127.0, 120.1, 110.2, 54.8, 47.4, 23.4.

2.4 General procedure for the synthesis of potassium 2-(4-formylphenyl)-2-methylpropanoate (**1ac**)



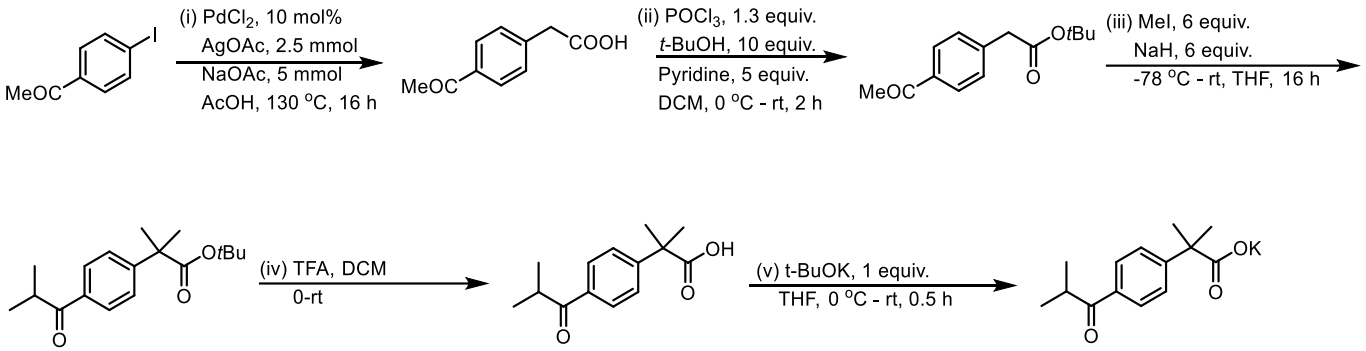
Step 1: The acetal protection of the aldehyde was carried out following a literature procedure.[11] To a solution of aldehyde (500 mg, 2.8 mmol) and trimethyl orthoformate (0.68 g, 6.44 mmol) in methanol (10 mL) was added $TsOH{\cdot}H_2O$ (16 mg, 0.084 mmol). The reaction mixture was stirred at room temperature for 4 hours. After this, the reaction was quenched by adding saturated $NaHCO_3$ solution and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4. The organic solvent was evaporated under the reduced pressure and the residue was purified by rapid column chromatography on silica gel [Hex:EtOAc (1% Et_3N) = 4/1] to afford the product as a pale yellow oil.

Step 2: The global methylation of the methyl ester was carried out following the procedure detailed in Step 2, general procedure **2.3, Method B**.

Step 3 & 4: The hydrolysis of the ester was done according to the procedure detailed in **2.3, Method A**, Step 4. During the acidification, the reaction mixture was stirred in 2N HCl for 2 hours for acetal deprotection.

Step 5: The potassium salt of the substituted 4-formylphenylacetic acid was prepared by neutralizing the acid following the procedure outlined in **2.1.1**, **Method A**, step 4. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 9.93 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 1.53 (s, 7H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 194.1, 184.1, 157.7, 135.6, 130.5, 128.1, 28.2.

2.5 General procedure for the synthesis of potassium 2-(4-isobutyrylphenyl)-2-methylpropanoate (**1ad**)



Step 1: Preparation of 2-(4-acetylphenyl)acetic acid was performed following a literature procedure.[12] To a flame-dried Schlenk tube, equipped with a stirring bar, under an atmosphere of N_2 were added 1-(4-iodophenyl)ethan-1-one (980 mg, 4 mmol), $PdCl_2$ (10 mol %, 0.4 mmol), AgOAc (6 mmol, 1.5 equiv.), and NaOAc (20 mmol, 5 equiv.). The tube was evacuated under vacuum and backfilled with N_2 thrice. Then, AcOH (12 mL) was added using a syringe and heated at 130 °C for 16 hours. Upon completion, the reaction mixture diluted using EtOAc (10 mL) and ran through a plug of silica. The resulting mixture was then poured into 2 N HCl (20 mL) and then extracted with EtOAc (3 × 20 mL). The combined organic layer was then washed with $NaHCO_3$ (2 x 10 mL). The organic layer was discarded, and the resulting aqueous solution was acidified to pH 1-2 with 2N HCl and extracted with EtOAc (3 x 10 mL). The organic extracts were combined, washed with saturated NaCl solution (1 x 10 mL), dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure to afford the acid as a crystalline yellow solid.

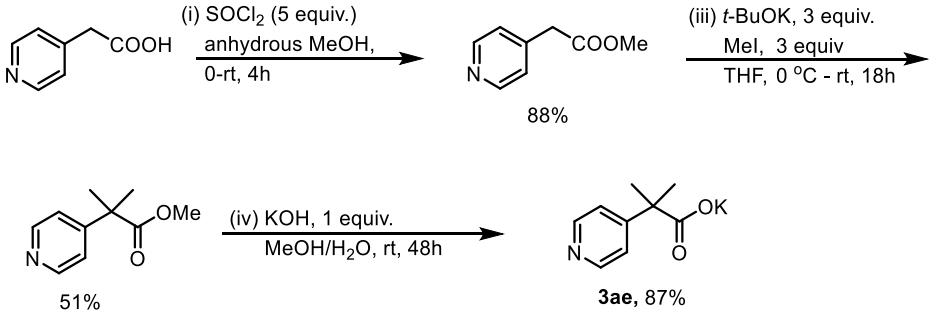
Step 2: The preparation of the *t*-butyl ester was carried out following the procedure detailed in Step 1, **2.1.1**, **Method C**

Step 2: The global methylation of the *t*-butyl ester was carried out following the procedure detailed in Step 2, general procedure **2.3, Method B***. (6 equiv. of MeI and NaH were used instead of 4 equiv.)*

Step 3: The hydrolysis of the *t*-butyl esters was performed following the procedure outlined in **2.1.1**, **Method B**, Step 3**.**

Step 4: The potassium salt of the substituted 2-(4-isobutyrylphenyl)-2-methylpropanoic acid was prepared following the procedure outlined in 2.1.1, **Method A**, Step 4. Yield: 49%; white solid. **^{1}H NMR** (500 MHz, Methanol-d_4) δ 7.95 – 7.86 (m, 2H), 7.59 – 7.50 (m, 2H), 3.65 (hept, *J* = 6.7 Hz, 1H), 1.52 (s, 6H), 1.17 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 206.8, 184.4, 155.9, 134.8, 129.2, 127.7, 50.0, 36.3, 28.3, 19.6.

2.6 General procedure for the synthesis of potassium 2-methyl-2-(pyridin-4-yl)propanoate (**1ae**)

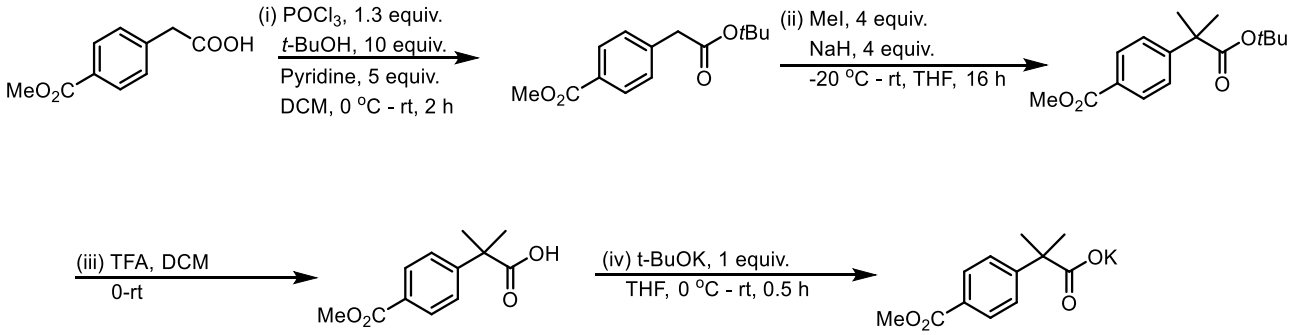


Step 1: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added 2-(pyridin-4-yl)acetic acid (5 mmol, 685 mg) and anhydrous MeOH (30 ml). The reaction mixture was cooled to 0 °C and thionyl chloride (5 equiv.) was added over a period of 20 minutes. Upon completing the addition, the reaction mixture was warmed to room temperature and stirred for 4 hours. After this time, the solvent was evaporated, and the resulting solid mixture was suspended in DCM (10 mL). To this suspension was added saturated $NaHCO_3$ solution (20 mL) and the aqueous layer was extracted with 2 more portions of DCM. The organic extracts were then combined and washed with brine (1 x 10 mL), dried over $MgSO_4$, filtered, and concentrated. The resulting crude material was used for the next step without purification.

Step 2: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added methyl 2-(pyridin-4-yl)acetate (558 mg, 3.7 mmol, 1 equiv.), MeI (0.68 ml, 11.1 mmol, 3 equiv.), and anhydrous THF (0.2 M). The reaction solution was cooled to 0 °C and then *t*-BuOK (1.24 g, 11.1 mmol, 3equiv.) was added. The reaction mixture was then warmed to room temperature and stirred overnight. Upon completion, the reaction was cooled to 0 °C, and quenched with a saturated NH_4Cl solution (20 mL). The reaction mixture was extracted with Et_2O (3 x 30 mL) and the combined organic extracts were then washed with H_2O (1 x 10 mL) and brine (1 x 10 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was then purified *via* silica flash chromatography in 1:5 EtOAc:Hexanes to afford methyl 2-methyl-2-(pyridin-4-yl)propanoate as a pale yellow oil in 51% yield.

Step 3: The preparation of the potassium salt was carried out following a literature procedure.[13] To a solution of methyl 2-methyl-2-(pyridin-4-yl)propanoate (179 mg, 1 mmol) in MeOH (5 ml) was added KOH (56 mg, 1 mmol) in water (1 ml). The reaction mixture was stirred at room temperature for 48 hours. After this time, the solvent was evaporated under reduced pressure to afford a yellow solid which was washed several times with diethyl ether and dried under vacuum to afford the title salt as a white solid in 87% yield. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.42 – 8.36 (m, 2H), 7.49 – 7.43 (m, 2H), 1.51 (s, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 183.2, 160.5, 149.4, 123.5, 49.7, 27.6.

2.7 General procedure for the synthesis of potassium 2-(4-(methoxycarbonyl)phenyl)-2-methylpropanoate (**1af**)



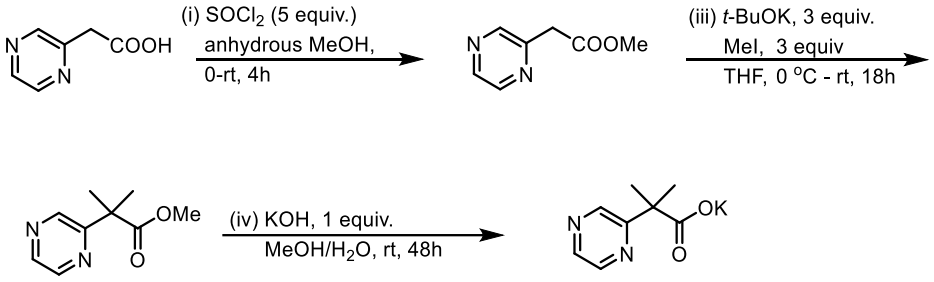
Step 1: Preparation of the *t*-butyl ester of 2-(4-(methoxycarbonyl)phenyl)acetic acid was carried out following a literature procedure.[4] Solid 2-(4-(methoxycarbonyl)phenyl)acetic acid (485 mg, 2.5 mmol) was added to a flame-dried Schlenk flask under an atmosphere of N_2 and stirred in dry DCM (10 mL) at 0 °C. *t*-BuOH (25 mmol, 10 equiv.) and pyridine (12.5 mmol, 5 equiv.) were then added to this stirring mixture. $POCl_3$ (3.25 mmol, 1.3 equiv.) was then added drop wise to this solution over a period of 15 minutes. After the addition was completed, the mixture was warmed to room temperature and stirred for another 2 hours. After this time, the reaction mixture was diluted using DCM (10 mL) and quenched by adding 2N HCl (10 mL). The organic layers were then separated and washed successively with $NaHCO_3$ (10 mL), brine (10 mL) and dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude ester was use without further purification.

Step 2: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added the *t*-butyl ester (1 equiv.), MeI (4 equiv.), and anhydrous THF (0.2 M). The reaction solution was cooled to -20 °C and then NaH (4 equiv.) was added. Upon adding sodium hydride, the reaction mixture was allowed to warm to room temperature and stirred for 16 hours. Upon completion, the reaction was cooled to 0 °C and quenched with a saturated NH_4Cl solution (20 mL). After warming the solution to room temperature, it was extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with H_2O (1 x 10 mL) and brine (1 x 10 mL). The organic layers were combined and dried over $MgSO_4$, filtered, and concentrated. The residue was purified *via* silica flash chromatography in 1:20 EtOAc: Hexanes.

Step 3: The hydrolysis of the *t*-butyl esters was performed following the procedure outlined in 2.1.1, **Method B**, Step 3**.**

Step 4: The potassium salt of the substituted 2-(4-(methoxycarbonyl)phenyl)acetic acid was prepared following the procedure outlined in 2.1.1, **Method A**, Step 4. Yield: 62%; white solid. **^{1}H NMR** (500 MHz, Methanol-d_4) δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 1.51 (s, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 184.4, 168.8, 155.9, 130.2, 128.5, 127.5, 52.4, 48.6, 28.3.

2.8 General procedure for the synthesis of potassium 2-methyl-2-(pyrazin-2-yl)propanoate (**1ag**)



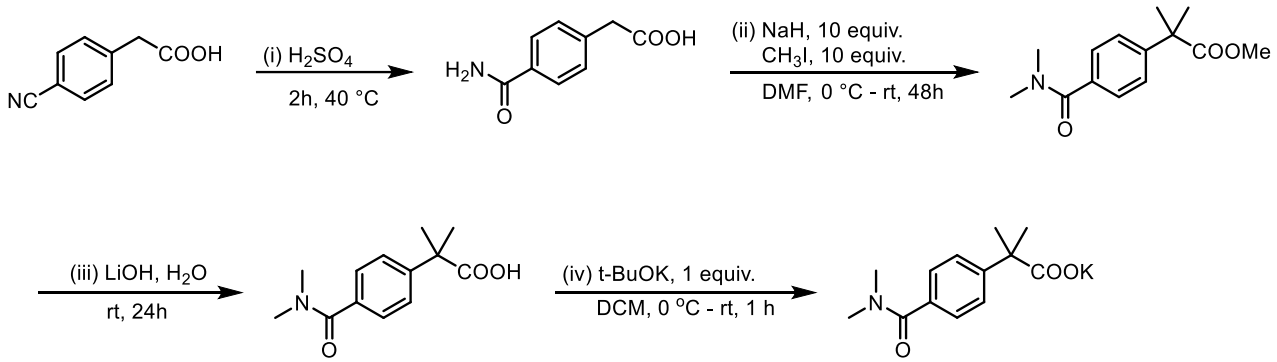
Step 1: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added 22-(pyrazin-2-yl)acetic acid (5 mmol, 690 mg) and anhydrous MeOH (30 ml). The reaction mixture was cooled to 0 °C and thionyl chloride (5 equiv.) was added over a period of 20 minutes. Upon completing the addition, the reaction mixture was warmed to room temperature and stirred for 4 hours. After this time, the solvent was evaporated, and the resulting solid mixture was suspended in DCM (10 mL). To this suspension was added saturated $NaHCO_3$ solution (20 mL) and the aqueous layer was extracted with 2 more portions of DCM. The organic extracts were then combined and washed with brine (1 x 15 mL), dried over $MgSO_4$, filtered, and concentrated. The resulting crude material was used for the next step without purification.

Step 2: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added methyl 2-(pyrazin-2-yl)acetate (456 mg, 3.0 mmol), MeI (0.56 ml, 9 mmol, 3 equiv.), and anhydrous THF (0.2 M). The reaction solution was cooled to 0 °C and then *t*-BuOK (1.00 g, 9 mmol, 3equiv.) was added. The reaction

mixture was then warmed to room temperature and stirred overnight. Upon completion, the reaction was cooled to 0 °C, and quenched with a saturated NH_4Cl solution (20 mL). The reaction mixture was extracted with Et_2O (3 x 30 mL) and the combined organic extracts were then washed with H_2O (1 x 5 mL) and brine (1 x 5 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was then purified *via* silica flash chromatography in 1:5 EtOAc:Hexanes to afford methyl 2-methyl-2-(pyrazin-2-yl)propanoate as a pale yellow oil in 51% yield.

Step 3: The preparation of the potassium salt was carried out following a literature procedure.[13] To a solution of methyl 2-methyl-2-(pyrazin-2-yl)propanoate (180 mg, 1 mmol) in MeOH (5 ml) was added KOH (56 mg, 1 mmol) in water (1 ml). The reaction mixture was stirred at room temperature for 48 hours. After this time, the solvent was evaporated under reduced pressure to afford a yellow solid which was washed several times with diethyl ether and dried under vacuum to afford the title salt as a white solid in 87% yield. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.66 (d, *J* = 1.6 Hz, 1H), 8.50 (dd, *J* = 2.6, 1.6 Hz, 1H), 8.35 (d, *J* = 2.6 Hz, 1H), 1.57 (s, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 183.3, 164.4, 144.5, 144.4, 142.1, 51.3, 26.9.

2.9 General procedure for the synthesis of potassium 2-(4-(dimethylcarbamoyl)phenyl)-2-methylpropanoate (**1ah**)



Step 1: The partial hydrolysis of the nitrile to amide was done using the modified literature procedure.[14] To a round bottom flask equipped with stir bar was added the nitrile (2 mmol, 1 equiv.) and 98% H_2SO_4 (3 mL) sequentially. The reaction mixture was warmed to 40 °C and stirred for 2 hours. Thereafter, the crushed ice was added to the reaction vessel to induce precipitation of solids. The resulting suspension was filtered and dried to yield the product as a white solid, which was used as such without further purification.

Step 2*: To a flame-dried Schlenk flask equipped with a stir bar under an atmosphere of N_2 was added the amide (1.4 mmol, 1 equiv.) and anhydrous DMF (0.14 M). The reaction solution was cooled to 0 °C and then methyl iodide (10 equiv.) was added. After stirring for 15 minutes at 0 °C, sodium hydride (10 equiv.) was added. The reaction mixture was then warmed to room temperature and stirred for 48 hours. Upon completion, the reaction mixture was cooled to 0 °C and quenched with a saturated NH_4Cl solution (20 mL). After warming the solution to room temperature, it was extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with brine (1 x 30 mL). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated. The residue was purified *via* silica flash chromatography in EtOAc/Hexanes solvent system.

Step 3: The methyl ester hydrolysis was done using the modified literature procedure.[15] To a round bottom flask charged with a stir bar were added the methyl ester (1.1 mol, 1 equiv.), methanol (4 mL), and H_2O (1.5 mL). Thereafter, solid lithium hydroxide monohydrate was added in a single portion and the reaction mixture was allowed to stir for 24 hours at room temperature. After the completion of the reaction (analyzed by

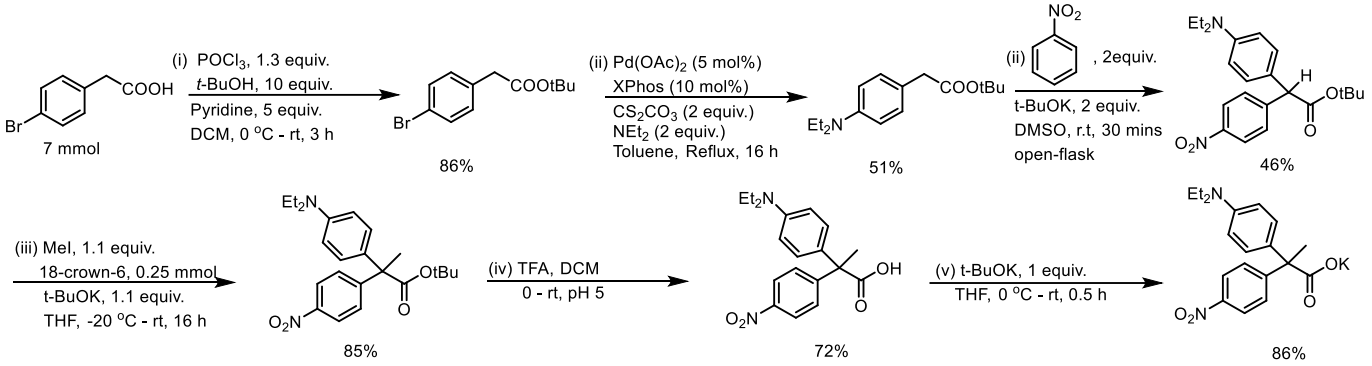
TLC), the volatiles were removed under vacuum, and the reaction mixture was acidified to pH 4 using 2N HCl. The resulting precipitates were collected using vacuum filtration and dried to afford the product, which was used without any further purification.

Step 4:** The potassium salt of the substituted phenylacetic acids were prepared following the procedure outlined in 2.1.1, **Method A**, step 4, substituting DCM as the solvent, with 75% yield; off-white solid. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.50 (app d, *J* = 8.4 Hz, 2H), 7.35 (app d, *J* = 8.4 Hz, 2H), 3.09 (s, 3H), 3.01 (s, 3H), 1.52 (s, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 183.8, 174.1, 151.6, 134.5, 127.8, 127.3, 49.3, 40.1, 35.7, 28.1.

***** This step may be hazardous at a larger scale due to danger of runaway exotherm of high equivalency of NaH in DMF.[16]

****** This step involves use of DCM with a strong base that could lead to formation of the chlorocarbene. However, we did not see its formation under our reaction conditions.

2.10 General procedure for the synthesis of potassium 2-(4-(diethylamino)phenyl)-2-(4-nitrophenyl)propanoate (**1ai**)



Step 1: The *t*-butyl ester of was prepared following a literature procedure.[4] Solid 4-Bromophenylacetic acid (7 mmol) was added to a flame-dried Schlenk flask under an atmosphere of N_2 and stirred in dry DCM (20 mL) at 0 °C. *t*-BuOH (10 equiv.) and pyridine (5 equiv.) were then added followed by $POCl_3$ (1.3 equiv.,dropwise to this solution over a period of 15 minutes). After the addition was completed, the mixture was warmed to room temperature, and stirred for another 4 hours. After this time, the reaction mixture was diluted using DCM (20 mL) and quenched by adding 1N HCl (10 mL). The organic layers were then separated and washed successively with $NaHCO_3$ (2 x 10 mL), brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude esters were used for the next step without further purification.

Step 2: The Buchwald-Hartwig amination was carried out following a literature procedure.[17] To a 50 mL Schlenk flask was added $Pd(OAc)_2$ (61.6 mg, 5 mol%), XPhos (261 mg, 10 mol%), Cs_2CO_3 (2.68 g, 1.5 equiv. 8.25 mmol) and toluene (25 mL) under N_2 atmosphere. To the mixture were added benzyl 4-bromophenylacetate (1.67 g, 5.5 mmol) and diethylamine (1.13 mL, 11 mmol). The reaction flask was stirred at 100 °C for 12 h. After filtration with hexane as eluent and concentration under reduced pressure, the crude residue was purified by flash silica column chromatography with hexane:ethyl acetate – 10:1 to give benzyl 2-(4-(diethylamino)phenyl)acetate (833 mg, 2.8 mmol) as a yellow oil.

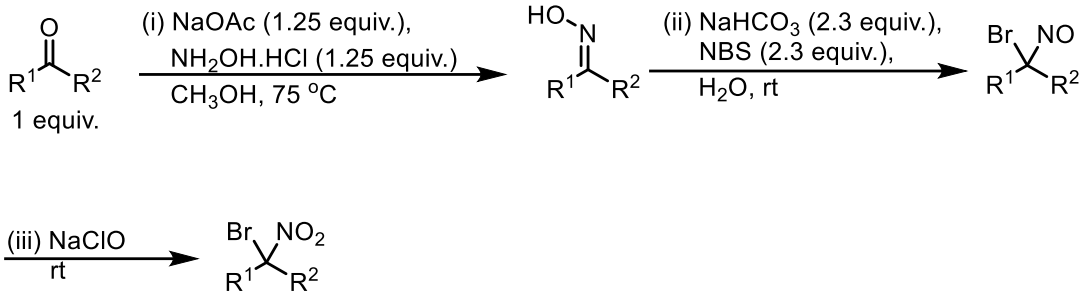
Step 3: The alpha arylation of the esters was performed following the procedure mentioned in **2.1.1**, **Method B**, Step 2.

Step 3: The procedure followed in **2.1.1, Method A**, Step 2 was adapted to furnish the methylated α,α–disubstituted Benzyl esters which was purified via silica gel flash chromatography in Hexanes: EtOAc.

Step 4: The hydrolysis of the *t*-butyl esters was performed following the procedure outlined in **2.1.1, Method B**, Step 3**.**

Step 5: The potassium salt of the substituted 4-nitrophenylacetic acids were prepared following the procedure outlined in **2.1.1, Method A**, step 4. **^{1}H NMR** (500 MHz, Methanol-d_4) δ 8.10 – 8.04 (m, 2H), 7.49 – 7.42 (m, 2H), 7.22 – 7.15 (m, 2H), 6.70 – 6.64 (m, 2H), 3.35 (q, *J* = 7.0 Hz, 3H), 1.84 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 182.0, 159.0, 147.6, 147.0, 134.6, 130.7, 130.0, 123.3, 113.4, 59.4, 45.5, 28.6, 12.9

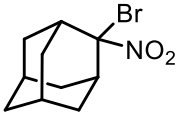
2.11 Procedure for the synthesis of gem-bromonitroalkanes



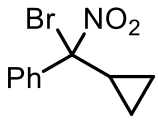
Prepared following modified literature procedure.[18]

Step 1: In a round-bottom flask, the ketone (1 equiv.) was dissolved in CH_3OH (0.2 M) under N_2 atmosphere. Sodium acetate (1.25 equiv.) and hydroxylamine hydrochloride (1.25 equiv.) were then added to this solution. The reaction mixture was then heated at 75 °C to reflux and stirred overnight. After cooling to room temperature, methanol was evaporated, and H_2O (20 mL) was added followed by EtOAc (50 mL). Then the organic layer was washed with saturated brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated to give a white solid which was used without further purification.

Step 2 & 3: The corresponding oxime (1 equiv.) was added to a solution of sodium bicarbonate (2.3 equiv.) in water (0.15 M) followed by N-bromosuccinimide (2.3 equiv.). The reaction mixture was stirred at room temperature overnight and extracted with EtOAc, and the organic layers were washed with brine and dried over Na_2SO_4. After evaporation of solvents, the residue of bromonitrosoalkane was diluted with DCM (0.25 M). To this solution were added tetrabutylammonium hydrogensulfate (0.5 equiv.) and sodium hypochlorite solution (ca. 1.3 M, 3.12 equiv.) in portions. Stirring was continued until blue or green color of the reaction mixture faded (roughly 30 minutes). After separation/extraction and concentration of the organic phase, the crude product was purified by flash column chromatography on silica gel (Hexanes).



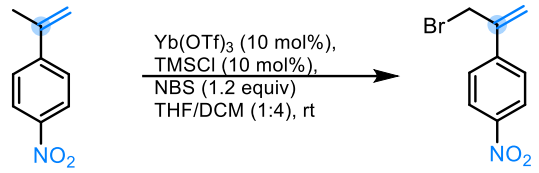
(1r,3r,5r,7r)-2-bromo-2-nitroadamantane (**2b**): General procedure **2.10**, provided the title compound starting with (1r,3r,5r,7r)-adamantan-2-one in 82% yield (33.3 mmol scale, over 3 steps); white solid. Product matched with previous literature specification.[18] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 2.90 (s, 2H), 2.37 (d, *J* = 12.6 Hz, 2H), 2.07 – 1.72 (m, 8H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 102.6, 38.5, 37.7, 35.1, 26.2, 25.7.



(bromo(cyclopropyl)(nitro)methyl)benzene (**2c**): General procedure **2.10**, provided the title compound starting with cyclopropyl(phenyl)methanone in 21% yield (7.2 mmol scale, over 3 steps); white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 – 7.50 (m, 2H), 7.45 – 7.34 (m,

3H), 2.04 (tt, *J* = 8.1, 5.3 Hz, 1H), 1.13 – 1.00 (m, 1H), 0.88 (dtd, *J* = 5.3, 4.0, 2.9 Hz, 2H), 0.84 – 0.75 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 139.2, 130.3, 128.8, 126.8, 107.6, 21.1, 7.5, 4.2.

2.12 Procedure for the synthesis of 1-(3-bromoprop-1-en-2-yl)-4-nitrobenzene (**4b**)

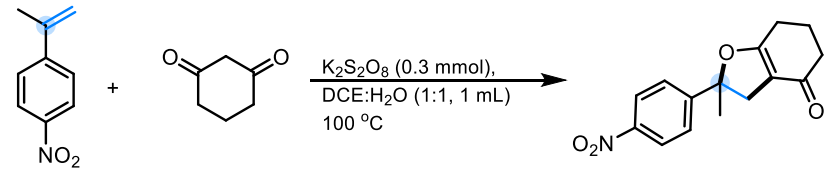


0.3 mmol
3a

4b; 42%

The allylic bromination of **3a** was carried out following a modified literature procedure.[19] A Schlenk flask was charged with the α-(methyl)styrene **3a** (1.0 equiv.), and a 4:1 mixture of dry DCM and dry THF (0.3 M). The resulting mixture was stirred at room temperature, while adding TMSCl (10 mol%), followed by NBS (1.2 equiv.) and $Yb(OTf)_3$ (10 mol%). After stirring for 1 hour at room temperature, the solvent was removed under reduced pressure. The crude mixture was purified by silica gel flash column chromatography in 1:10 EtOAc:Hexane to afford the title compound as a colorless liquid. Yield; 42%. Product matched with previously reported literature specification.[19] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.9 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 5.69 (s, 1H), 5.68 (s, 1H), 4.39 – 4.38 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.73, 144.20, 142.89, 127.20, 124.00, 120.55, 33.18.

2.13 Procedure for the synthesis of 2-methyl-2-(4-nitrophenyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (**4c**)



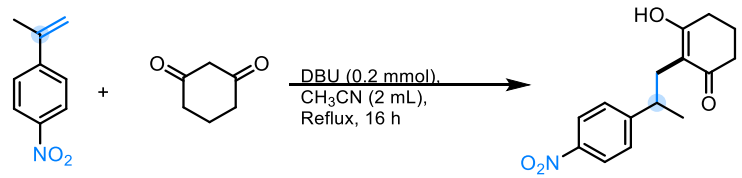
0.2 mmol,
3a

0.3 mmol

4c; 61%

The oxidative cyclisation of **3a** was carried out following a modified literature procedure.[20] An oven-dried, Schlenk-tube was charged with the cyclohexane-1,3-dione **1** (0.3 mmol, 1.5 equiv.) and $K_2S_2O_8$ (0.2 mmol, 1.0 equiv.). The tube was evacuated and backfilled with N_2 thrice. After this, a solution of α-(methyl)styrene **3a** (0.2 mmol, 1.0 equiv) in DCE–H_2O (1:1; 1 mL) was added via a syringe into the Schelnk-tube. The tube was then sealed, and the mixture was stirred for 24 h at 100 °C. The resulting mixture was then diluted with EtOAc (10 mL), and the organic phase was washed successively with H_2O (2 × 10 mL) and brine (10 mL), dried using anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel flash column chromatography EtOAc:Hexane; 3:2. White solid; 61%. Product matched with previously reported literature specification.[20] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 2H), 3.06 (dt, *J* = 5.3, 1.8 Hz, 2H), 2.56 (tt, *J* = 6.4, 1.8 Hz, 2H), 2.43 – 2.31 (m, 2H), 2.19 – 1.97 (m, 2H), 1.74 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 195.60, 175.53, 152.91, 147.36, 125.50, 124.04, 112.60, 91.78, 40.78, 36.55, 29.91, 24.11, 21.81.

2.14 Procedure for the synthesis of 2-(2-(4-nitrophenyl)propyl)cyclohexane-1,3-dione (**4d**)



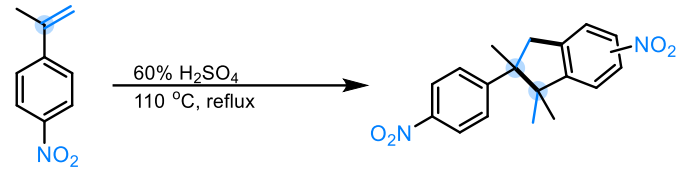
0.2 mmol,
3a

0.3 mmol

4d; 67%

The nucleophilic addition to **3a** was carried out following a modified literature procedure.[21] To an oven-dried, Schlenk-tube was added cyclohexane-1,3-dione (1.0 mmol), acetonitrile (10 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.67 mmol) and α-(methyl)styrene **3a** (0.7 mmol). The tube was sealed, and the solution was stirred and heated to reflux for 6 h. After this, the reaction vessel was cooled to room temperature and concentrated under vacuum. The resulting crude product was purified by silica flash column chromatography, Hex:EtOAc – 1:1. White solid; 67%. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.11 (d, *J* = 8.7 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 2H), 3.10 (h, *J* = 7.2 Hz, 1H), 2.60 – 2.47 (m, 2H), 2.36 – 2.30 (m, 6H), 1.86 (p, *J* = 6.4 Hz, 2H), 1.25 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ 198.66, 177.13, 156.99, 147.63, 129.38, 124.03, 114.91, 40.03, 31.32, 21.97, 21.18. **IR** (film): 3110, 3078, 2955, 1716, 1598, 1517, 1347, 1152, 855 cm^{-1}. **HRMS** Calcd for $C_{15}H_{17}NO_4$ (M+Na) = 298.1055, found 2298.1065.

2.15 Procedure for the synthesis of 5(6)-Nitro-1-(4-nitrophenyl)-1,3,3-trimethylindane (**4e**)

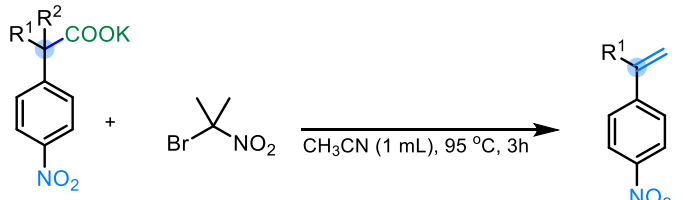


0.2 mmol, **3a**

4e; 50%

The dimerization of **3a** was achieved following a modified literature procedure.[22] 60% sulfuric acid (3 mL) was added dropwise into **3a**. The reaction mixture was then refluxed at 110 °C for 16 hours. After this, the reaction mixture was diluted by adding dichloromethane (5 mL) and the aqueous solution was extracted with additional portions of DCM (3 x 5 mL). The organic layers were combined, dried and, concentrated under vacuum. The resulting crude product was purified by silica flash column chromatography, Hex:EtOAc – 1:1. Pale yellow solid; 50%. Product matched with previously reported literature specification.[22] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 2.2 Hz, 1H), 8.22 – 8.16 (m, 2H), 8.16 – 8.10 (m, 2H), 7.96 (d, *J* = 2.1 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.27 (m, 2H), 2.50 (d, *J* = 13.4 Hz, 1H), 2.35 (d, *J* = 13.4 Hz, 1H), 1.78 (s, 3H), 1.58 (s, 3H), 1.41 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.7, 157.7, 157.0, 150.6, 149.3, 148.0, 146.5, 141.0, 137.3, 136.1, 128.9, 127.5, 127.3, 127.1, 126.6, 124.0, 123.9, 123.9, 123.8, 123.8, 123.3, 123.2, 120.4, 59.0, 51.2, 43.6, 41.0, 31.2, 31.2, 30.7, 30.4, 30.2, 17.5.

2.16 Procedure for the Decarboxylative Olefination of Potassium 4-nitrophenylacetates



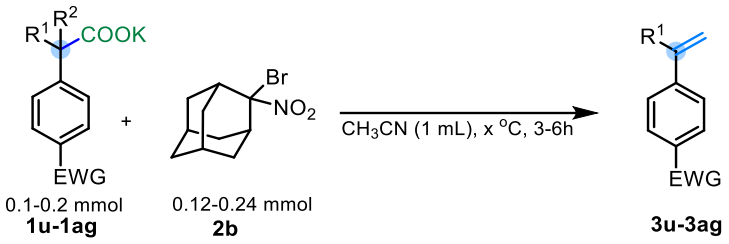
0.2 mmol **1a-s**

0.24 mmol **2a**

3a-s

In an argon atmosphere glove box, a 10 mL screw-threaded glass tube equipped with stir bar was charged with the carboxylate salt (0.2 mmol), **2a** (0.04g, 0.025 mL, 0.24 mmol) and degassed MeCN (2 mL). The reaction vessel was sealed and removed from the glovebox. The reaction was stirred at 95 °C for 3 hours. After this time, the reaction was removed from the heating source and the solvent was removed under reduced pressure. The resulting styrene was purified via silica gel flash chromatography in 1:5-1:40 EtOAc:Hexanes. *Note:* These reactions can be performed outside the glovebox using normal Schlenk techniques without any significant reduction in the yields. The anhydrous nature of the solvent is important in these cases.

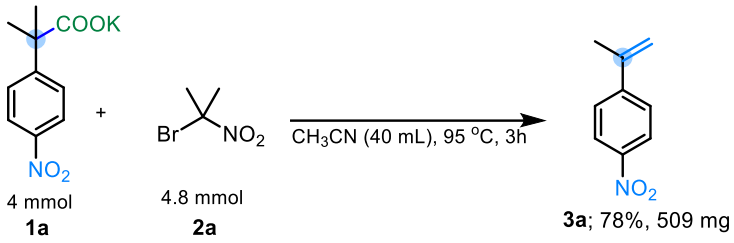
2.17 Procedure for the Decarboxylative Olefination of Other carboxylate salts



In an argon atmosphere glove box, a 10 mL screw-threaded glass tube equipped with stir bar was charged with the carboxylate salt (0.1-0.2 mmol), **2b** (0.12- 0.24 mmol) and degassed MeCN (1-2 mL). The reaction vessel was sealed and removed from the glovebox. The reaction was stirred at specified temperature for various 4-substituted aryl carboxylates for 3-6 hours. After this time, the reaction was removed from the heating source and the solvent was removed under reduced pressure. The resulting styrene was purified via silica gel flash chromatography in 1:5-1:40 EtOAc:Hexanes.

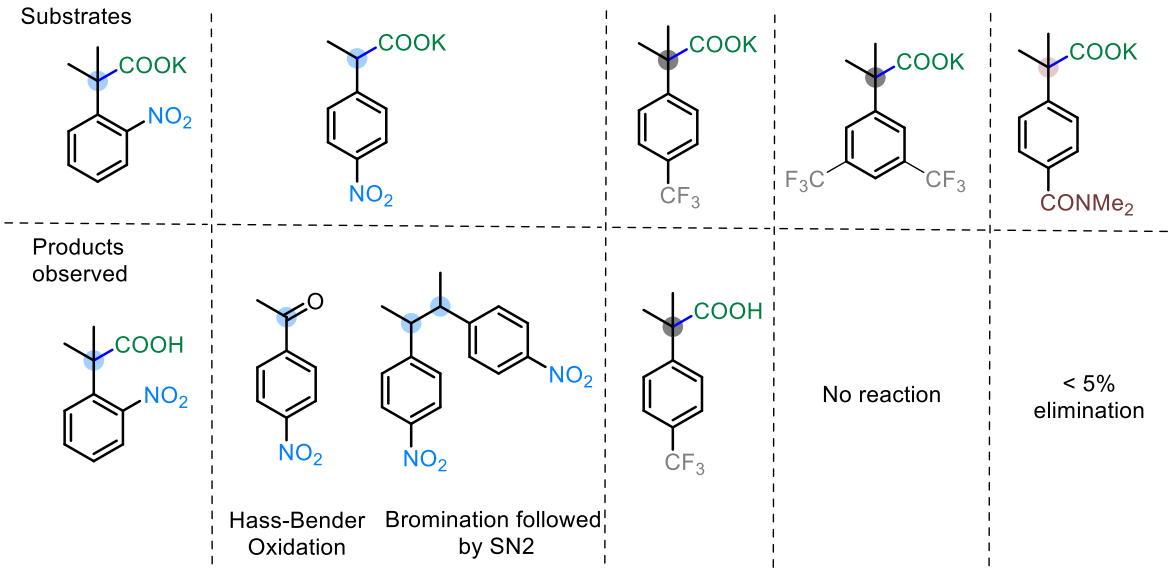
Cautionary Note*: At elevated temperatures, pressure buildup can occur.

2.18 Procedure for Large Scale Decarboxylative Olefination



To a flame-dried Schlenk tube, equipped with a stirring bar, under an atmosphere of nitrogen was added potassium 2-methyl-2-(4-nitrophenyl)propanoate (998 mg, 4 mmol), **2a** (801 mg, 0.506 mL, 4.8 mmol) and degassed MeCN (40 mL). The reaction tube was sealed heated at 95 °C for 3 hours. After this time, the reaction was removed from the heating source and the solvent was removed under reduced pressure. The resulting styrene was purified via silica gel flash chromatography in 1:40 EtOAc:Hexanes.

Unsuccessful Substrates:



3. Additional Reaction Optimization Tables

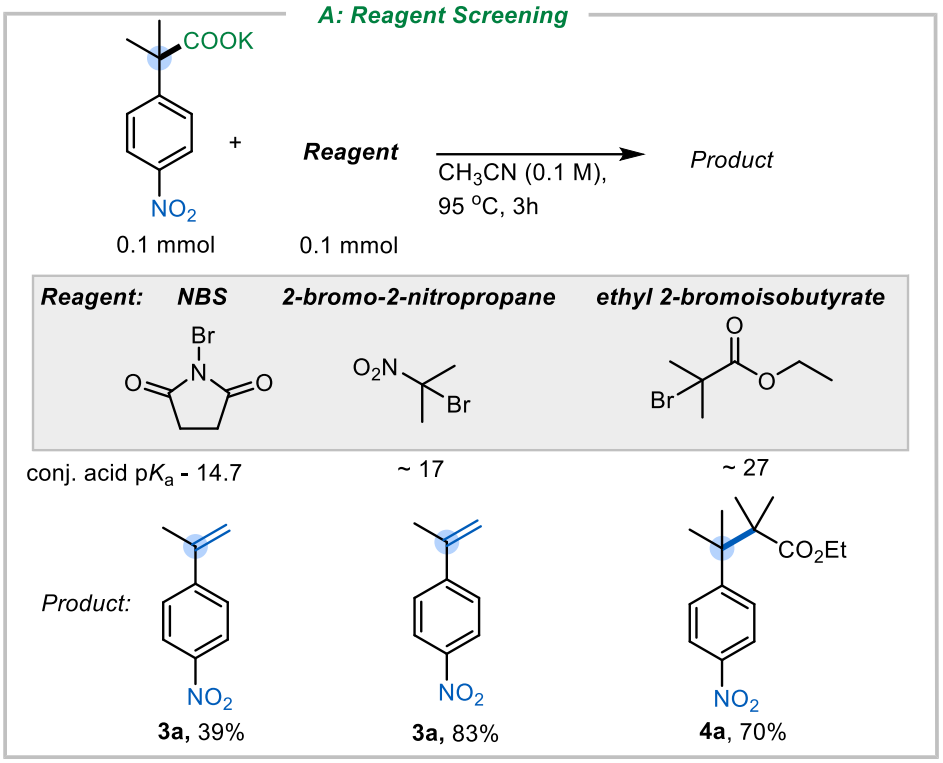
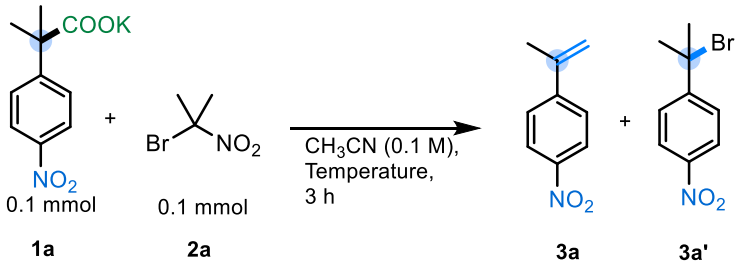
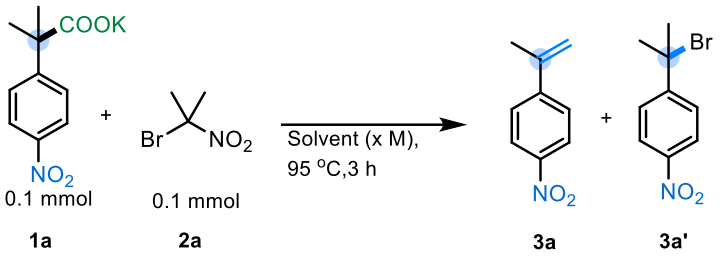


Table S1: Reagents screening. [a] Yields determined by quantitative ^{1}H NMR analysis using anisole as an internal standard.



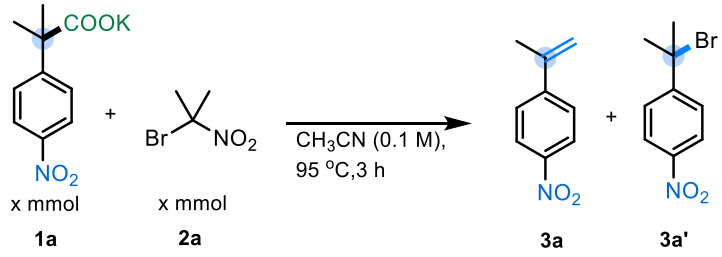
Entry	Temperature (x °C)	% Yield (3a/3a')[a]
1	60	38/25
2	70	47/27
3	80	65/14
4	95	77/-
5	110	69/-

Table S2: Temperature screening. [a] Yields determined by quantitative ^{1}H NMR analysis using anisole as an internal standard.



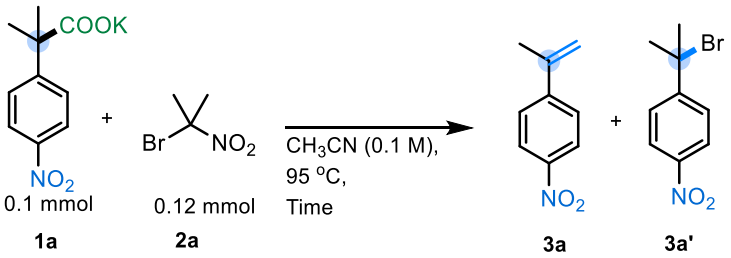
Entry	Solvent	Concentration (x M)	% Yield (3a/3a')[a]
1	CH_3CN	0.1	77/-
2	DMF	0.1	36/-
3	THF	0.1	-
4	Et_2O	0.1	-
5	DCM	0.1	-
7	CH_3CN (wet)	0.1	60/-
8	CH_3CN	0.05	39/-

Table S3: Solvent and concentration screening. [a] Yields determined by quantitative ^{1}H NMR analysis using anisole as an internal standard.



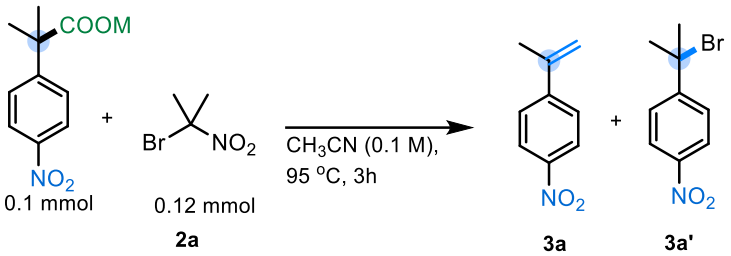
Entry	1a (x mmol)	2a (x mmol)	% Yield (3a/3a')[a]
1	1	1	77/-
2	1	1.2	88/-
3	1	1.5	80/-
4	1	2	67/-
5	1.2	1	91/-
6	1.5	1	41/-

Table S4: Reagents loading screening. [a] Yields determined by quantitative ^{1}H NMR analysis using anisole as an internal standard.



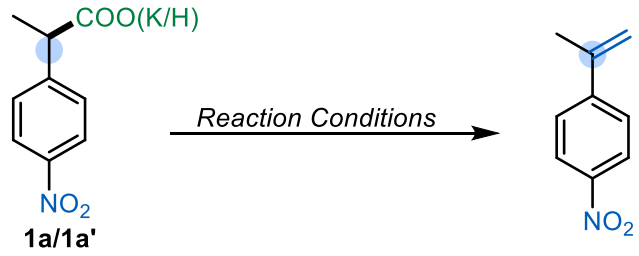
Entry	Time (x h)	% Yield (3a/3a')[a]
1	1.5	73/10
2	3	88/-
3	4.5	84/-
4	6	84/-

Table S5: Time screening. [a] Yields determined by quantitative ^{1}H NMR analysis using anisole as an internal standard.



Entry	Cation (M)	% Yield (3a/3a')[a]
1	Li^+	5/2
2	Na^+	63/-
3	K^+	88/-
4	Cs^+	81/-

Table S6: Cation screening. [a] Yields determined by quantitative ^{1}H NMR analysis using anisole as an internal standard.



B: State-of-the-Art Conditions

Entry	Reaction Conditions	% Yield (**3a**)[a]
1	**2a** (1.2 equiv.), CH_3CN, 95 °C, 3h, 0.2 mmol scale	88
2	[Co] (3 mol%), [Acr] (5 mol%), STAB (1 mol%), Na_2CO_3 (1 mol%), H_2O (7.5 mol%), MeOH, blue LED, rt, 18h, 0.2 mmol scale.	6
3	PIFA (1.2 equiv.), CH_3CN, μW 120 °C, 20 mins, 0.2 mmol scale.	-
4	[Cu] (20 mol%), [bpy] (20 mol%), MnO_2 (2 equiv.), LiOAc (2 equiv.), DMA, 120 °C, 24h, 0.2 mmol scale.	89

Table S7: Comparison against the current available literature conditions. [a] Yields determined by quantitative ^{1}H NMR analysis using anisole as an internal standard.

Entry 1: Standard conditions as optimized above.

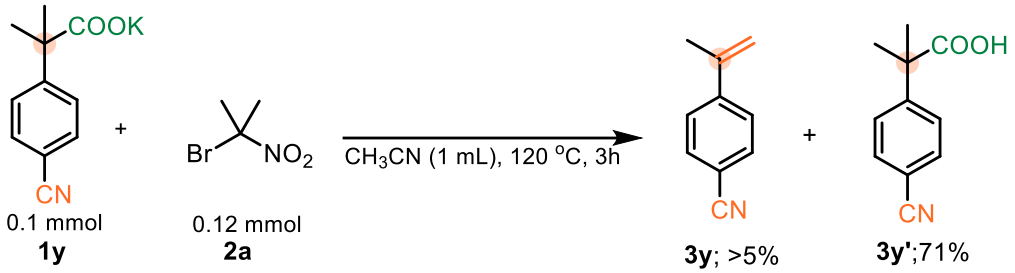
Entry 2: Co/Acr photoredox dual catalytic decarboxylative elimination conditions.[23] Reaction was ran using 9-Mes-2,7-Me_2-Acr-10-$Ph^+BF_4^-$ and $Co(dmgH)_2ClNMI$ on a 0.2 mmol scale starting from **1a'**.

Entry 3: Microwave assisted decarboxylative elimination conditions.[24] Reaction was ran on a 0.2 mmol scale starting from **1a'**.

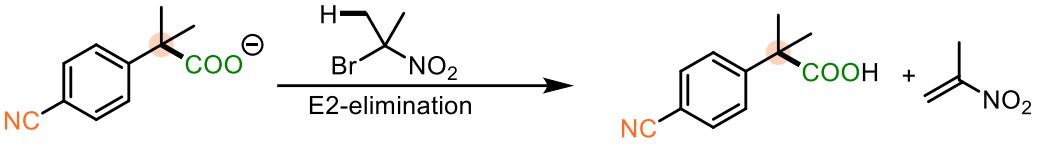
Entry 4: Copper-catalyzed decarboxylative elimination conditions.[25] Yields were directly taken from the literature.

4. Conceptual framework for the development of 2b

*(a) Attempted Elimination of **1y***



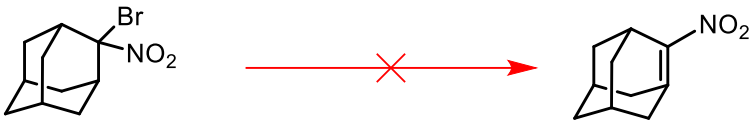
(b) Proposed pathway for the formation of the carboxylic acid byproduct



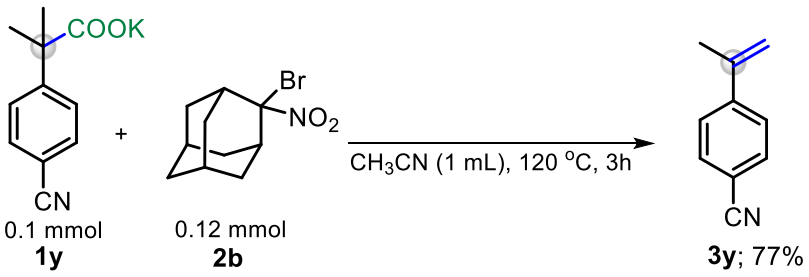
Scheme S1: Attempted Elimination of **1y** using **2a.**

These findings necessitated the creation of a novel reagent for elimination reactions that would not be susceptible to E2-elimination itself. Thus, an adamantane derived *gem*-bromonitro alkane was identified as the ideal candidate for this decarboxylative elimination reaction as these bromonitro alkane as less prone to undergo an E2-elimination itself.

(a) Adamantane derived gem-bromonitro alkane

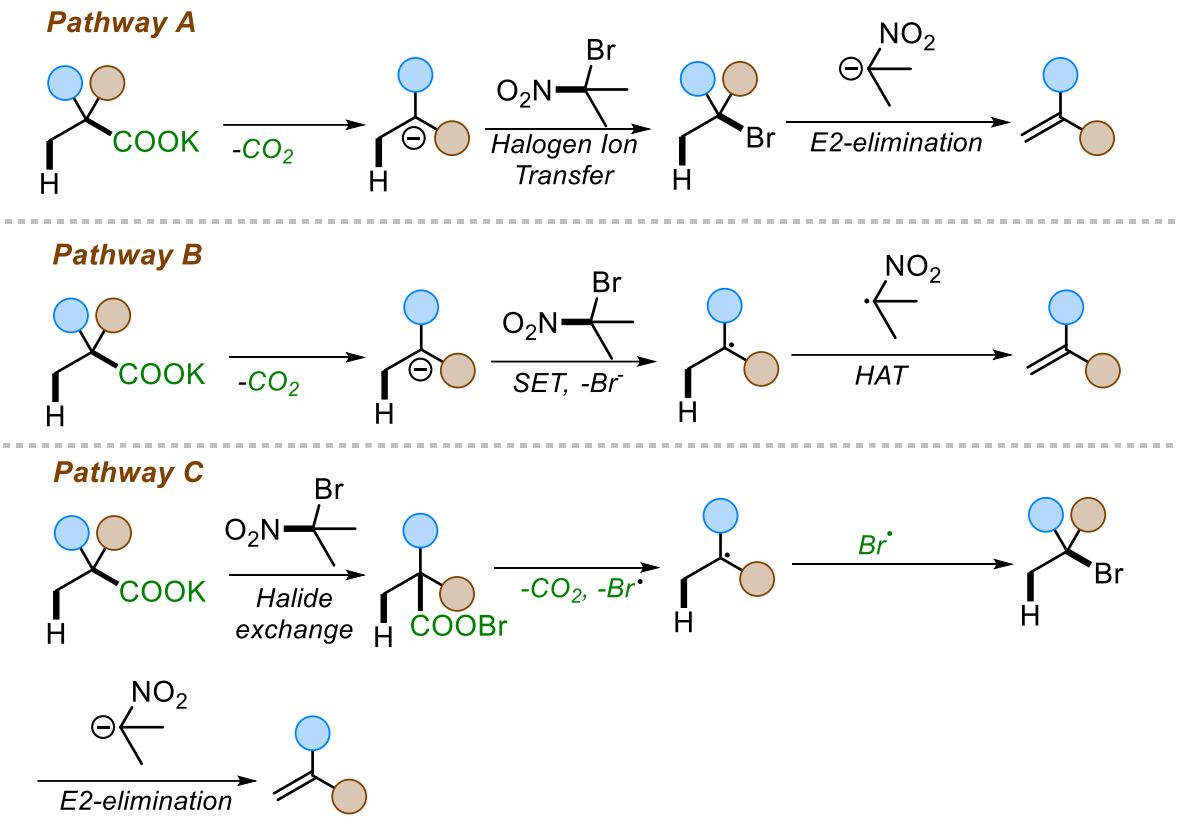


*(b) Decarboxylative elimination using **2b***



Scheme S2: Elimination of **1y** using **2b.**

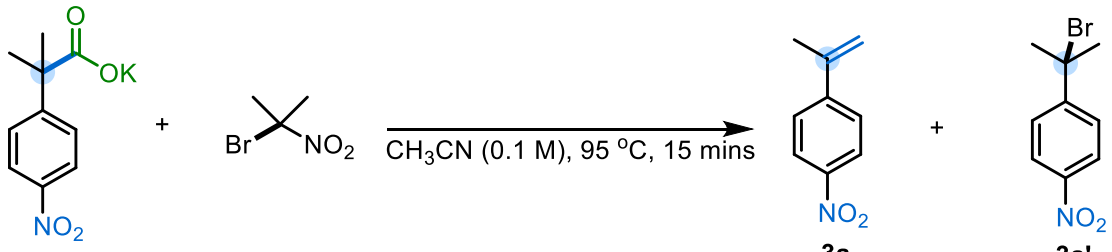
5. Possible Mechanistic Pathways



Scheme S3: Mechanistic Pathways

6. Mechanistic Studies

6.1 Intermediate Analysis

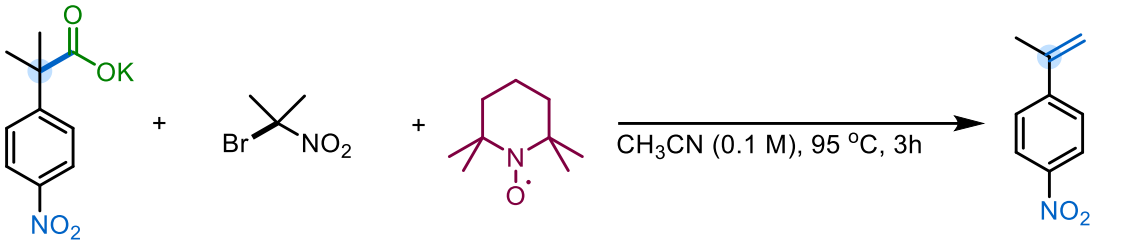


In an argon atmosphere glove box, a 10 mL screw-threaded glass tube equipped with stir bar was charged with **1a** (24.7 mg, 0.1 mmol), **2a** (17.6 mg, 0.12 mmol), and degassed MeCN (1 mL). The reaction vessel was sealed, removed from the glovebox, and stirred at 95 °C for 10 miniutes. After this time, the reaction was removed from the heating source and the solvent was removed under reduced pressure. GC-MS analysis of the crude reaction mixture showed styrene **3a** and the Bromo-intermediate **3a'** in a ratio of 72:28. The crude mixture was purified via silica gel flash chromatography in 1:40 EtOAc:Hexanes to isolate the intermediate **3a'**. Product matched with previous literature specification.[26] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 9.2 Hz, 2H), 7.78 (d, *J* = 9.0 Hz, 2H), 2.21 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 153.7, 147.2, 127.0, 123.7, 61.0, 35.3.

6.2 Experiments Probing for Radical Evidence

6.2.1 TEMPO Trapping

In an argon atmosphere glove box, a 10 mL screw-threaded glass tube equipped with stir bar was charged with **1a** (24.7 mg, 0.1 mmol), **2a** (17.6 mg, 0.12 mmol), TEMPO (15.6 mg, 0.1 mmol), and degassed MeCN (1 mL). The reaction vessel was sealed, removed from the glovebox, and stirred at 95 °C for 3 hours. After this time, the reaction was removed from the heating source and the solvent was removed under reduced pressure. Anisole (0.1 mmol) was added to the crude reaction mixture and the yields were determined using ^{1}H NMR experiment.

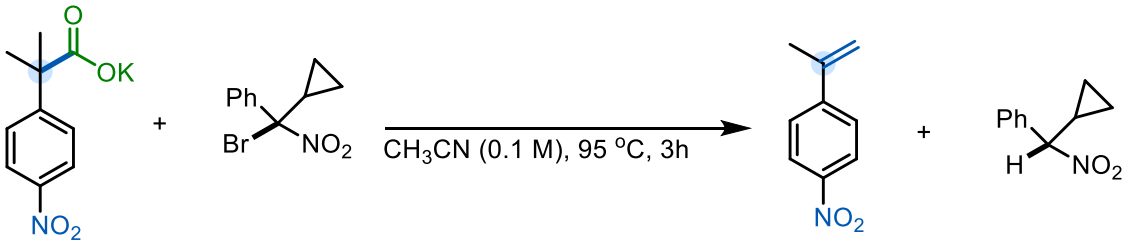


0.1 mmol **1a** + 0.1 mmol **2a** + 0.1 mmol **4f** → **3a**, 90 %

The results of this experiment showed that there wasn't any TEMPO trapped product and TEMPO did not inhibit the reaction suggesting the absence of radical intermediates in the process.

6.2.2 Radical Clock Experiments

In an argon atmosphere glove box, a 10 mL screw-threaded glass tube equipped with stir bar was charged with **1a** (24.7 mg, 0.1 mmol), **2c** (25.4 mg, 0.1 mmol), and degassed MeCN (1 mL). The reaction vessel was sealed, removed from the glovebox, and stirred at 95 °C for 3 hours. After this time, the reaction was removed from the heating source and the solvent was removed under reduced pressure. Anisole (0.1 mmol) was added to the crude reaction mixture and the yields were determined using ^{1}H NMR experiment.



0.1 mmol **1a** + 0.1 mmol **2c** → **3a**, 71 % + **2c'**, 70 %

This experiment demonstrated that there wasn't any ring opened products, again suggesting no radical intermediates involved in the process.

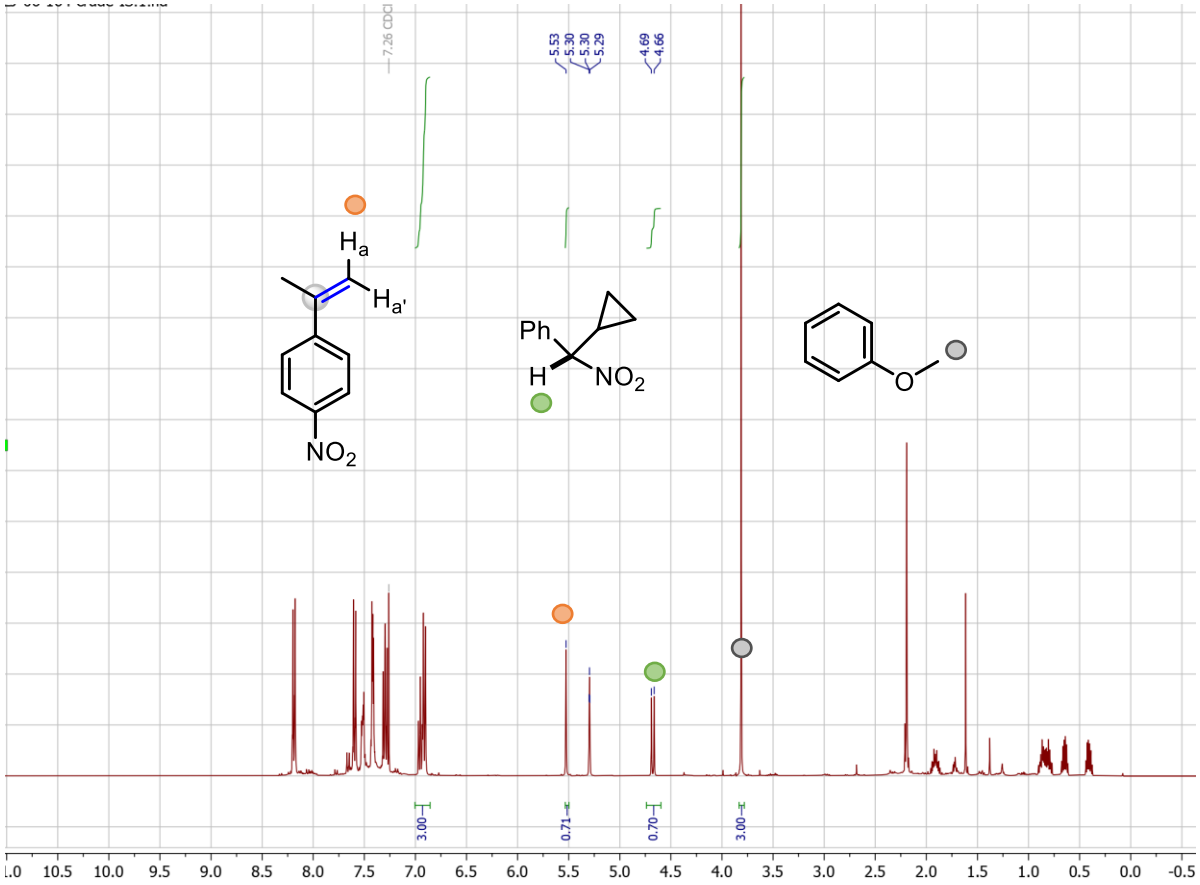
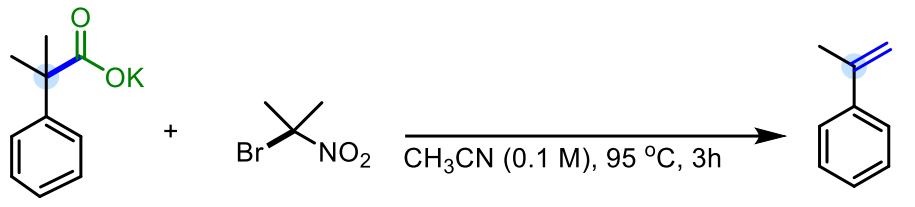


Figure S1: Crude ^{1}H NMR analysis of radical clock experiment

6.2.3 Radical Decarboxylation

In an argon atmosphere glove box, a 10 mL screw-threaded glass tube equipped with stir bar was charged with **1aj** (20.2 mg, 0.1 mmol), **2a** (17.6 mg, 0.12 mmol), and degassed MeCN (1 mL). The reaction vessel was sealed, removed from the glovebox, and stirred at 95 °C for 3 hours. After this time, the reaction was removed from the heating source and the solvent was removed under reduced pressure. Anisole (0.1 mmol) was added to the crude reaction mixture and the yields were determined using ^{1}H NMR experiment.

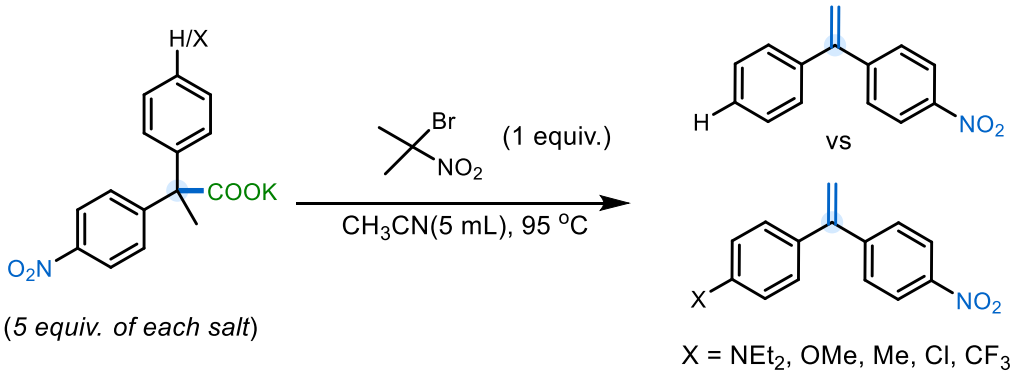


0.1 mmol **1aj** | 0.1 mmol **2a** | **3aj**, 0%

The result of this experiment demonstrated that Hunsdeicker type decarboxylative halogenation was not occurring in this reaction.

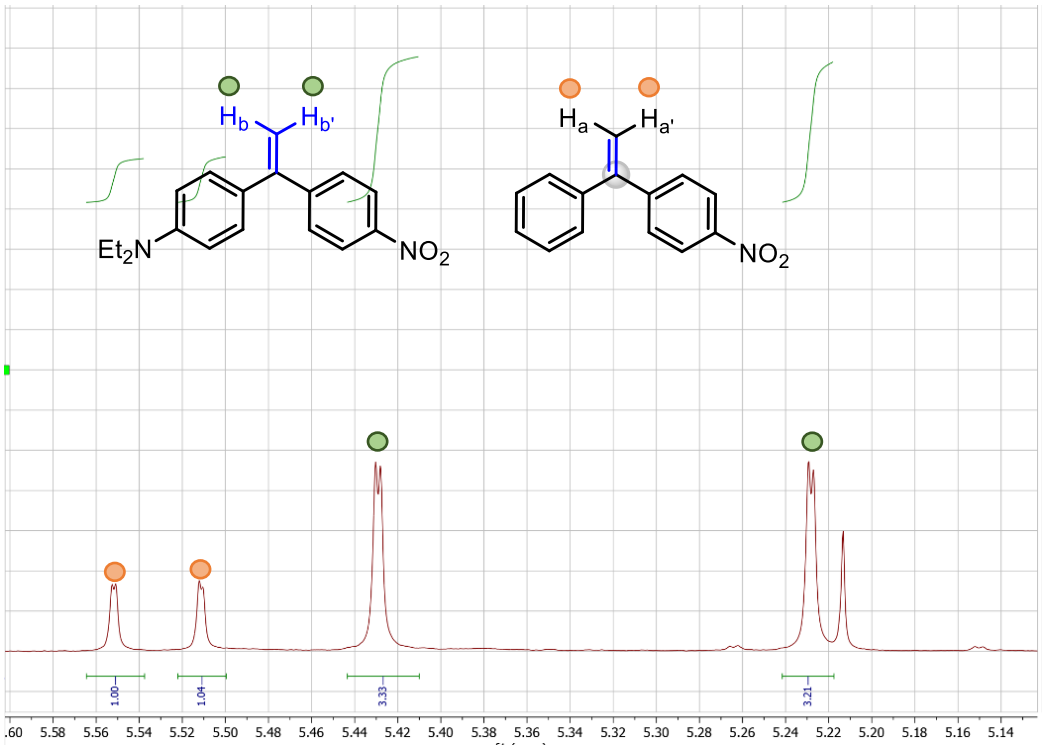
6.3 Hammett Analysis

6.3.1 Product Selectivity



(*5 equiv. of each salt*)

Competition studies for Hammett analysis were carried out by following general procedure 2.16, except 5 equivalents of both potassium 2-(4-nitrophenyl)-2-phenylpropanoate and the competing 4-substituted carboxylate were added. The ratios between the two potential products (P_X/P_H) were determined by ^{1}H NMR analysis of the crude material, using the alkene H's as reference (indicated on the example below). Log(P_X/P_H) values were then plotted against the appropriate σ_p^- value for that substrate. 2 trials of each competition study were carried out and an average product ratio was taken across the two experiments.



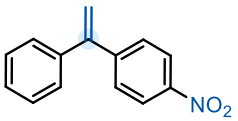
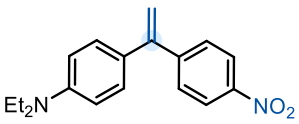
Product	Relative Product Ratios
	1.00
	3.33

Figure S2: Ratio Calculation (4-H vs 4-NEt$_2$)

	X = NEt_2	X = OMe	X = Me	X = H	X = Cl	X = CF_3
(P_X/P_H) Trail 1	3.33	2.66	1.55	1.00	0.36	0.065
(P_X/P_H) Trail 2	3.40	2.55	1.70	1.00	0.42	0.069
(P_X/P_H) Average	3.36	2.44	1.62	1.00	0.39	0.067
σ_p^- value	-0.43	-0.268	-0.170	0.00	0.19	0.650
$\log(P_X/P_H)$	0.527	0.406	0.211	0.00	-0.408	-1.173

Table S8: *Hammett Analysis Data*. [a] All reactions were performed on 0.1 mmol scale with respect to **2a** and 5 equivalents of both the carboxylate substrates. [b] Relative product ratios determined by ^{1}H NMR analysis of the crude material as shown in **Figure S2**.

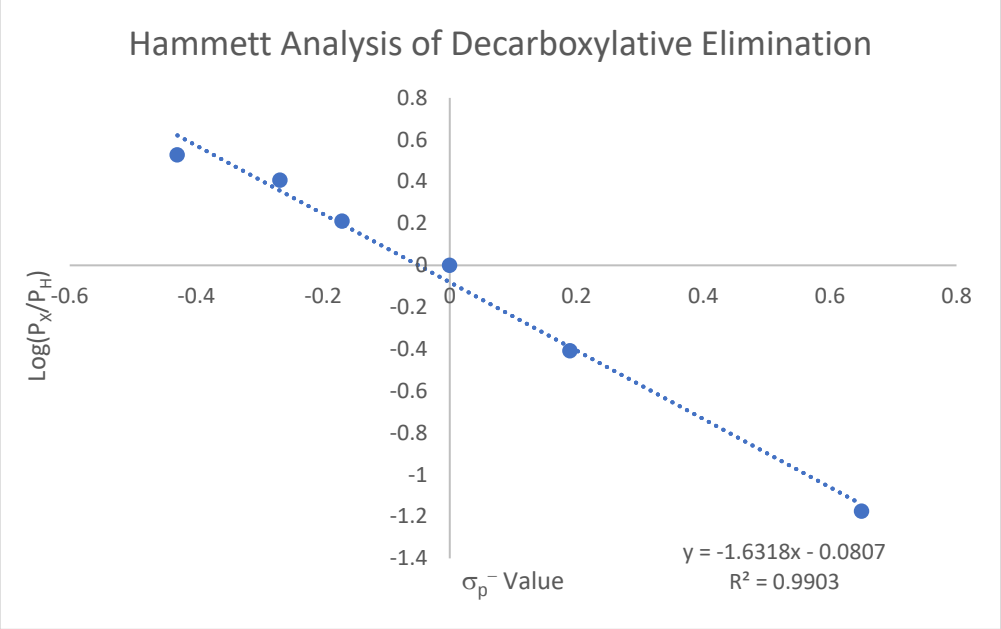


Figure S3: Hammett Plot fit to σ_p^-

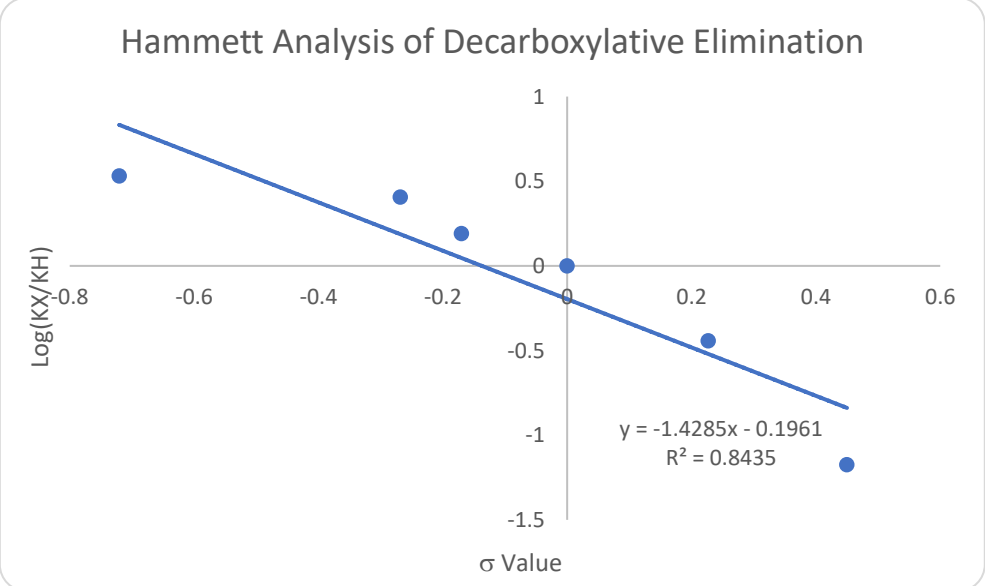
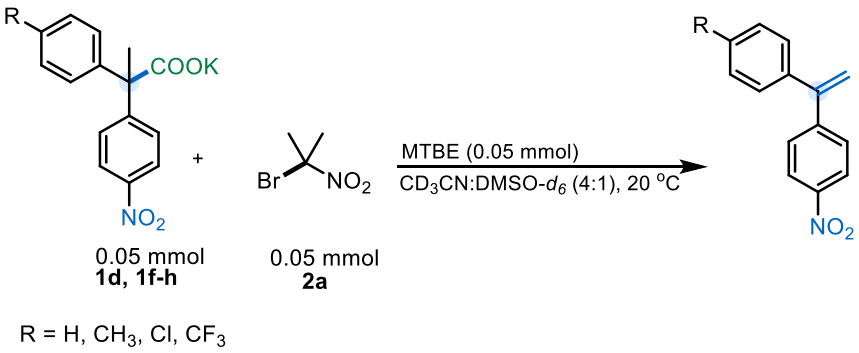


Figure S4: Hammett Plot fit to σ_p

6.3.2 Independent Rate Studies



In an argon atmosphere glove box, a glass NMR tube was charged with the carboxylate salt (0.05 mmol), **10a** (0.05 mmol), and t-butyl methyl ether (0.05 mmol, internal standard). The NMR tube was sealed with a septum, covered with a parafilm, and removed from the glovebox. CD_3CN (0.4 mL), and DMSO-d_6 (0.1 mL) was added to the NMR tube and shaken well for uniform mixing. The NMR spectra were taken at designated time points for each substrates.

Data Analysis: The yield of the product was calculated from the integration values of the methyl peak of methyl *t*-butyl ether and the alkene peaks of product at each time point. The concentration was calculated by diving the moles of product with the reaction volume. The E2-elimination was assumed to be the Rate Determining Step (R.D.S) based on the KIE data (See below). Thus, the second order rate kinetics can be determined using the integrated rate law, $1/[A]_t = kt + 1/[A]_o$, where $[A]_t$ is the concentration of R-Br at time 't'. A plot of $[A]_t$ vs time should yield a straight line where the slope *k* is the second order rate constant.

The results of this study demonstrate a decrease in rate from substrate **1g** (4–CH_3) to **1h** (4–CF_3). This correlates with a negative slope in the Hammett study and confirmed that the Rate Determining Step (R.D.S) and the Product Determining Step (P.D.S) was the E2-elimination.

*Rate Kinetics of **1d***

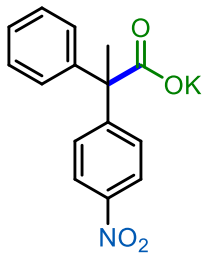
Starting Carboxylic Salts	Time (mins)	[**3d**] [M][a]	Rate constant ($M^{-1}.h^{-1}$)
 **1d**	0	0	138.02
	6	0.0395	
	8	0.05	
	10	0.0585	
	12	0.64	
	14	0.07	
	16	0.075	
	18	0.08	
	20	0.083	
	25	0.084	

Table S9: *Rate kinetics of substrate **1d**. [a] Concentration of **3d** at time 't'.*

*Rate Kinetics of **1f***

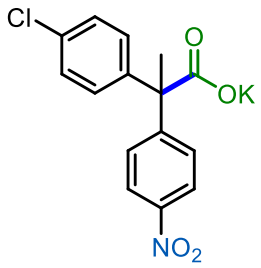
Starting Carboxylic Salts	Time (mins)	[**3f**] [M][a]	Rate constant ($M^{-1}.h^{-1}$)
 **1f**	0	0	11.42
	6	0.0085	
	8	0.013	
	10	0.017	
	12	0.0195	
	15	0.022	
	20	0.027	
	25	0.034	
	30	0.039	
	45	0.0425	
	60	0.046	
	75	0.05	

Table S10: *Rate kinetics of substrate **1f**. [a] Concentration of **3f** at time 't'.*

*Rate Kinetics of **1g***

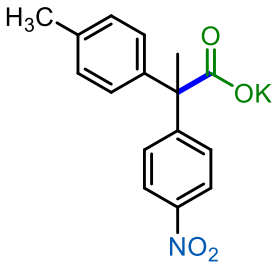
Starting Carboxylic Salts	Time (mins)	[**3g**] [M][a]	Rate constant ($M^{-1}.h^{-1}$)
 **1g**	0	0	398.43
	6	0.076	
	8	0.0845	
	10	0.086	
	12	0.0895	
	14	0.09	
	16	0.091	
	21	0.093	
	25	0.0935	
	35	0.0935	

Table S11: *Rate kinetics of substrate **1g**. [a] Concentration of **3g** at time 't'.*

*Rate Kinetics of **1h***

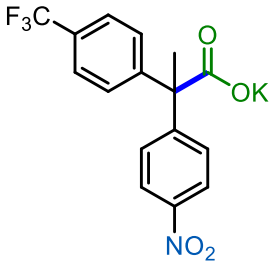
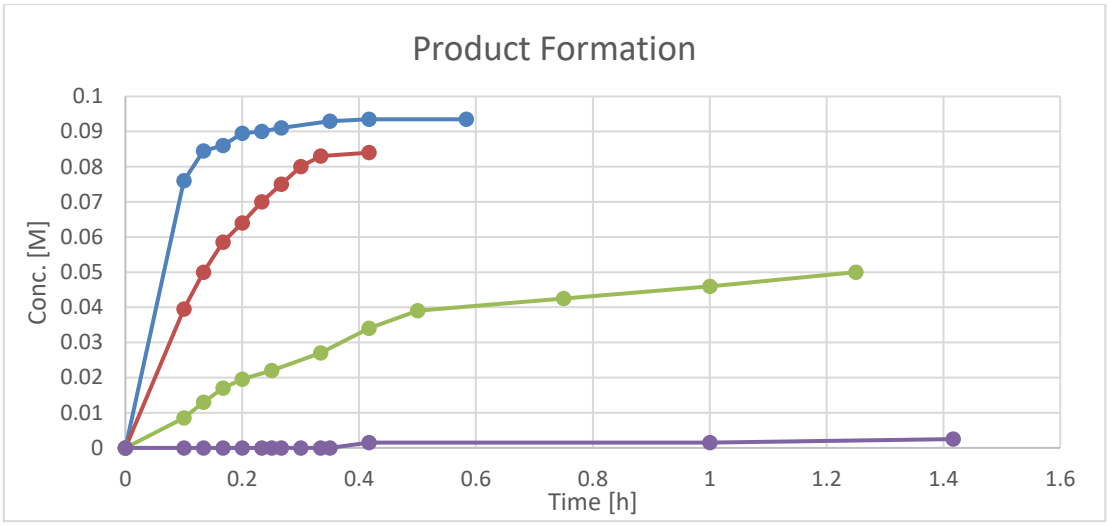
Starting Carboxylic Salts	Time (mins)	[**3h**] [M][a]	Rate constant ($M^{-1}.h^{-1}$)
 **1h**	0	0	0.2256
	6	0	
	8	0	
	15	0	
	20	0	
	25	0.0005	
	55	0.0015	
	85	0.0025	
	105	0.003	
	150	0.005	

Table S12: *Rate kinetics of substrate **1h**. [a] Concentration of **3h** at time 't'.*



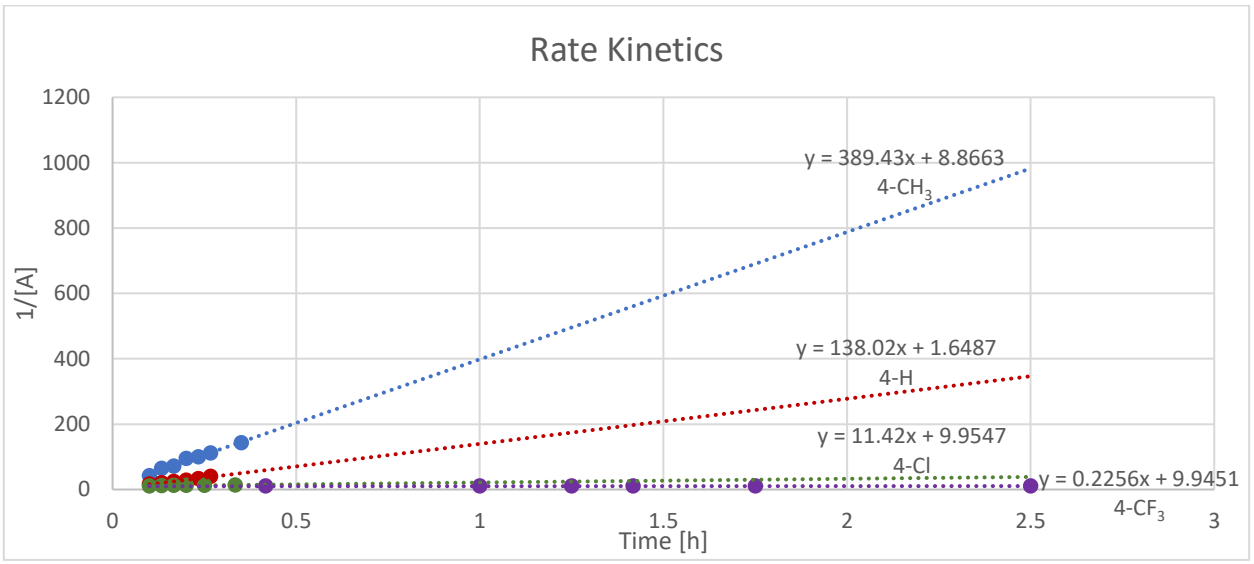
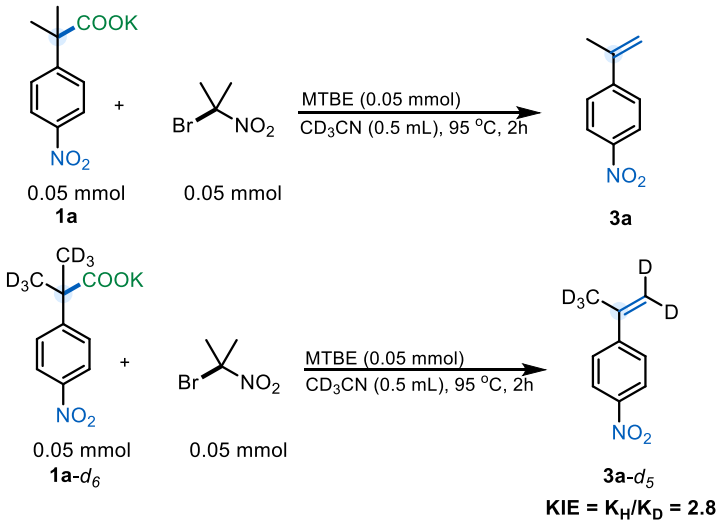


Figure S5: *Rate of decarboxylative elimination for substrates **1d, 1f-h**. The blue trace is the plot for the rate of decarboxylative elimination of **1g**. The red trace is for substrate **1hd**. The green trace is for substrate **1f**. The purple trace is for substrate **1h**.*

6.4 KIE Studies

A: Potassium 2-methyl-2-(4-nitrophenyl)propanoate (Parallel Reactions)



In an argon atmosphere glove box, a glass NMR tube was charged with the carboxylate salt (0.05 mmol), **2a** (0.05 mmol), t-butyl methyl ether (0.05 mmol, internal standard) and CD_3CN (0.5 mL). The NMR tube was

sealed with a septum, covered with a parafilm, and removed from the glovebox. The tube was shaken well for uniform mixing and was placed in a preheated oil bath at 85 °C. NMR spectra were taken at designated time points (10, 20, 30, 45, 60 and 90 mins). The process was repeated for the deuterated substrate **1a**-d_6. *NOTE:* The reaction tube was cooled down immediately after taken out of the oil bath and the time was halted, presuming not reaction to be happening at room temperature.

Data Analysis: The concentration of the product was calculated from the integration values of the methyl peak of methyl *t*-butyl ether and the alkene peaks of product **3a** at each time points. For product **3a**-d_5, the aromatic peaks were used for integration. The initial rates were determined from the first three time points. The KIE was determined by dividing the initial rates for the product formation of **3a** with **3a**-d_5 to give a KIE of 2.8.

Starting Carboxylic Salts	Time (mins)	Trail 1 [**3a**] or [**3a**-d_5] [M]	Trail 2 [**3a**] or [**3a**-d_5] [M]	Avg. [**3a**] or [**3a**-d_5] [M]	Initial Rate (M/h)
1a	0	0	0	0	0.1027
	10	0.025	0.024	0.0245	
	20	0.038	0.044	0.041	
	30	0.05	0.053	0.0515	
	45	0.06	0.063	0.0615	
	60	0.07	0.075	0.0725	
	90	0.08	0.083	0.08155	
1a-d_6	0	0	0	0	0.0366
	10	0.008	0.009	0.0085	
	20	0.013	0.015	0.014	
	30	0.018	0.017	0.0185	
	45	0.025	0.023	0.024	
	60	0.032	0.033	0.0315	
	90	0.04	0.041	0.040	

Table S13: *Initial rate study of substrate **1a** and **1a**-d_6.* All reactions were performed on 0.05 mmol scale with respect to **2a** and 1 equivalent of both the carboxylate substrates. [b] Relative concentration was determined by ^{1}H NMR analysis of the crude material from an average of 2 trails. [a] Initial rates were determined from the linear fit of the first three time points.

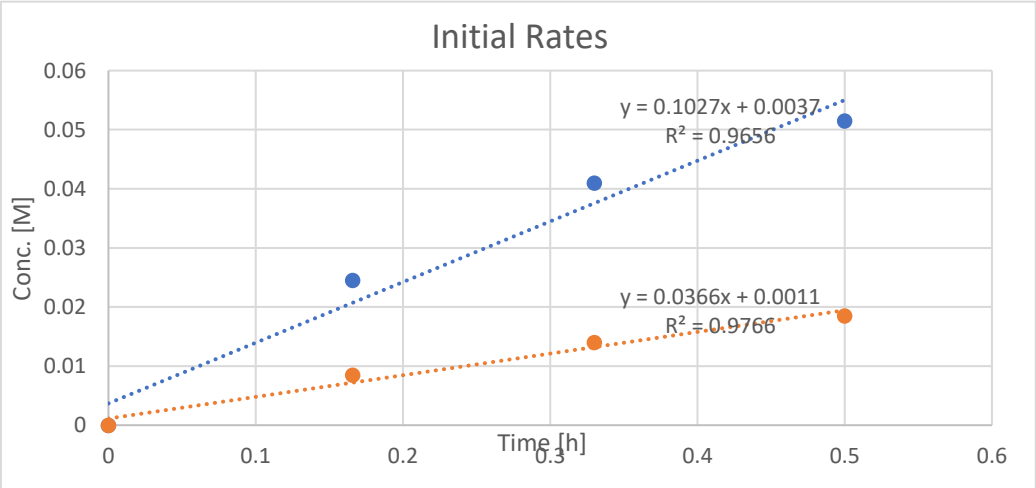


Figure S6: Initial Rate Kinetics. Blue trace represents the initial rate of substrate **1a** for the decarboxylative elimination reaction. Orange trace represents the initial rate of substrate ***1a***-d_6 for the decarboxylative elimination reaction.

The same experiment can be used to track the formation and consumption of the Bromo-intermediate **3a'**.

Time (mins)	% yield [**3a**]	% yield [**3a'**]
10	28	44
20	40	31
30	50	23.5
45	60	14
60	70	7
90	80	3

Table S14: Yield of **3a** and **3a'** monitored over time.

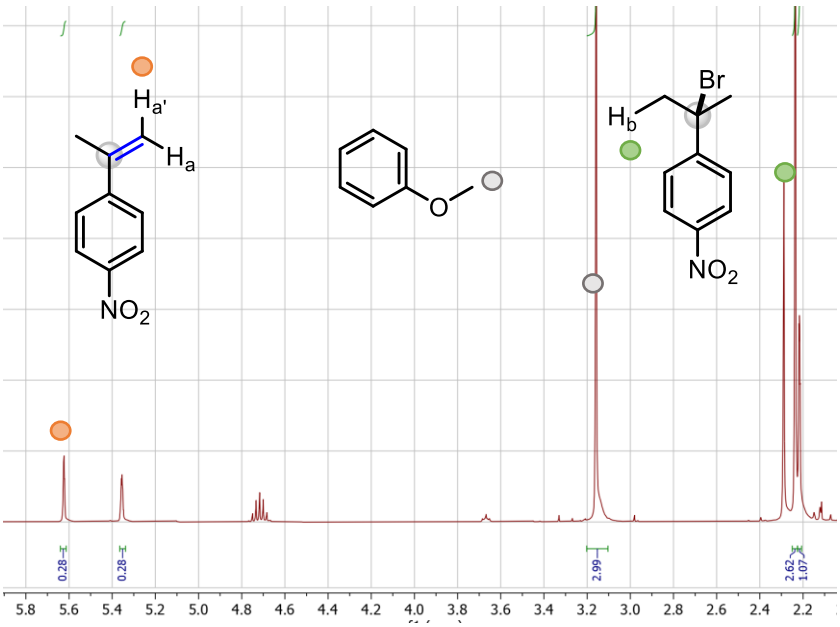


Figure S7: ^{1}H NMR analysis of reaction progressing.

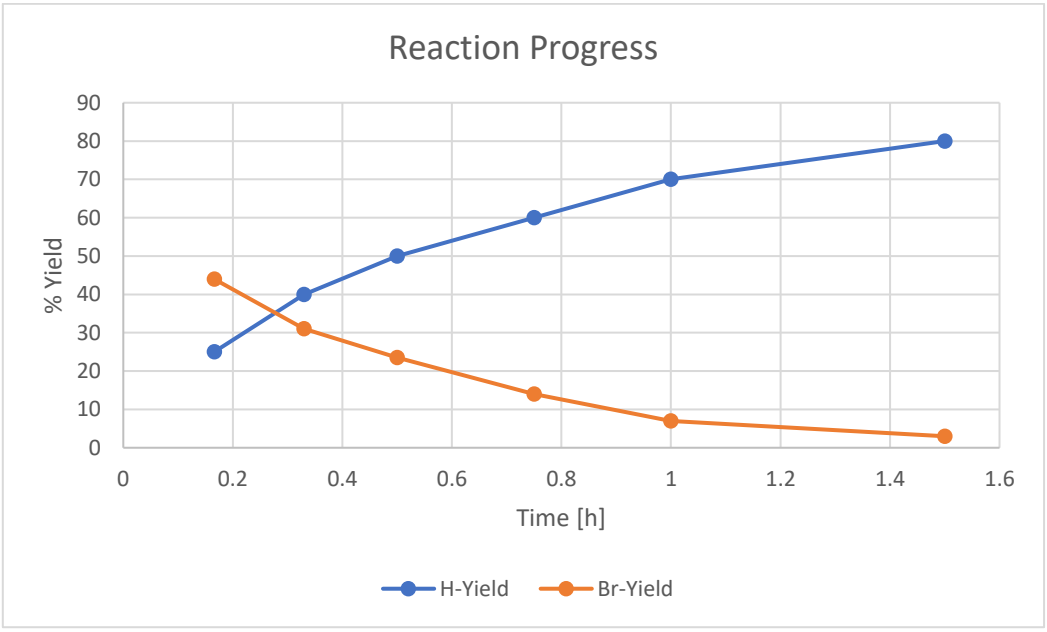
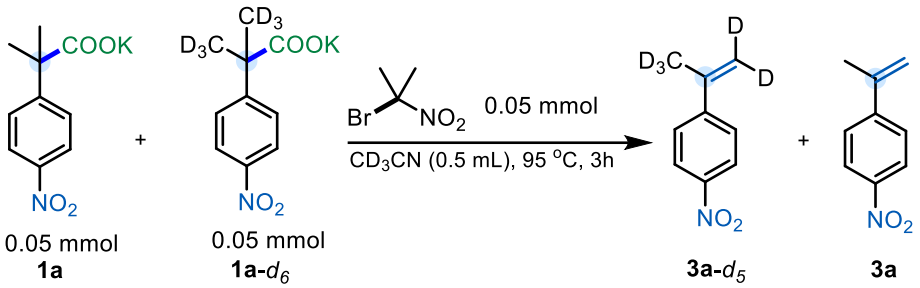


Figure S8: Decarboxylative Elimination monitored over time.

Potassium 2-methyl-2-(4-nitrophenyl)propanoate (Intermolecular Competition Reactions)



In an argon atmosphere glove box, a 10 mL screw-threaded glass tube equipped with stir bar was charged with **1a** (0.05 mmol), **1a**-d_6 (0.05 mmol), **2a** (0.05 mmol), and CD_3CN (0.5 mL). The reaction vessel was sealed, covered with a parafilm, and removed from the glovebox. The tube was then placed in a preheated oil bath at 95 °C for 3 hours. After this time, the solvent was removed under reduced pressure and anisole (0.1 mmol) was added to the crude reaction mixture as the internal standard to determine the yields using ^{1}H NMR experiment.

Data Analysis: The product ratios were calculated from the integration values of the alkene peaks of substrate **3a** and the aromatic Hydrogens of substrate **3a**-d_5. The KIE was determined by dividing the integration values of **3a** with **3a**-d_5 to give a KIE of 2.0.

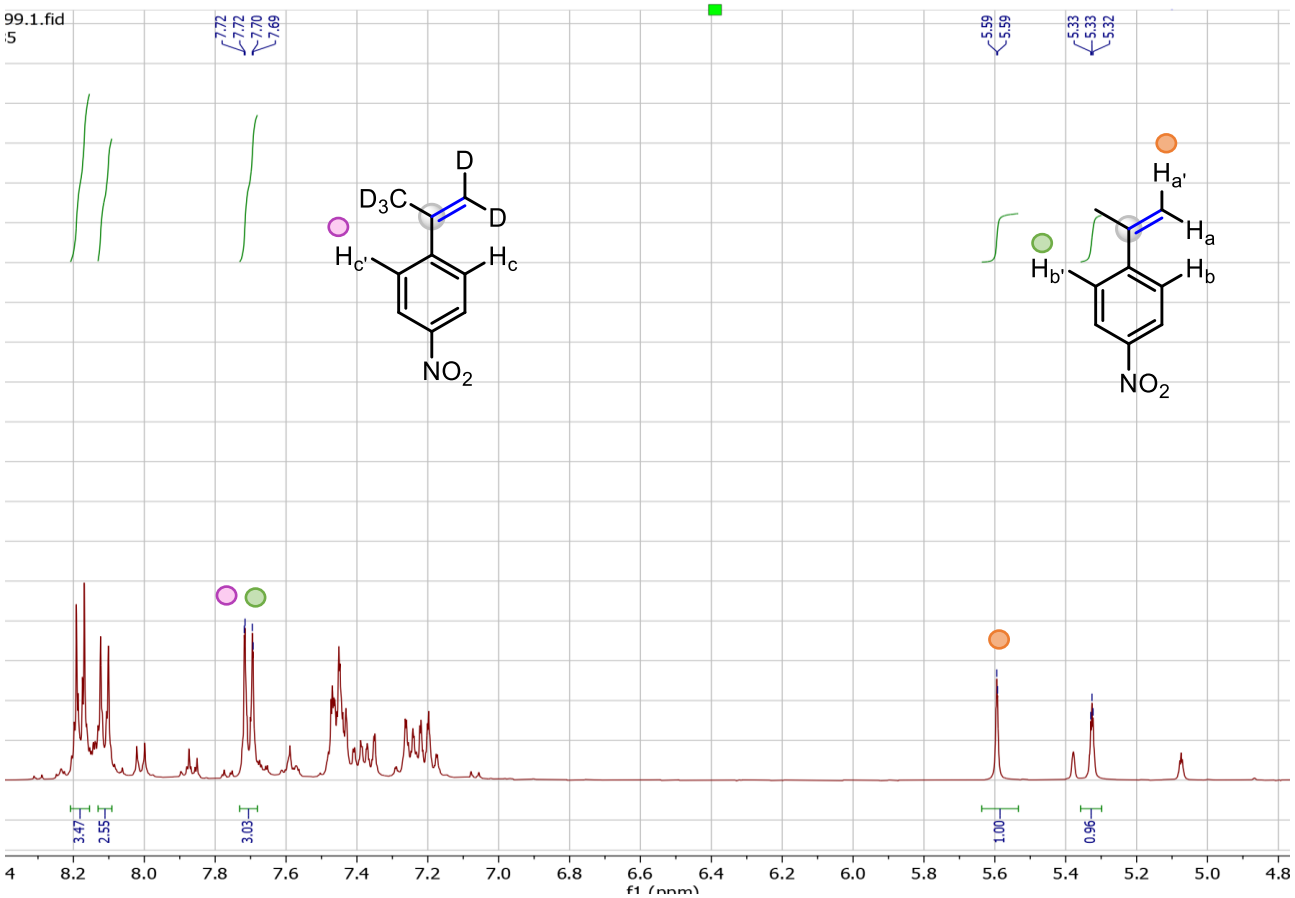
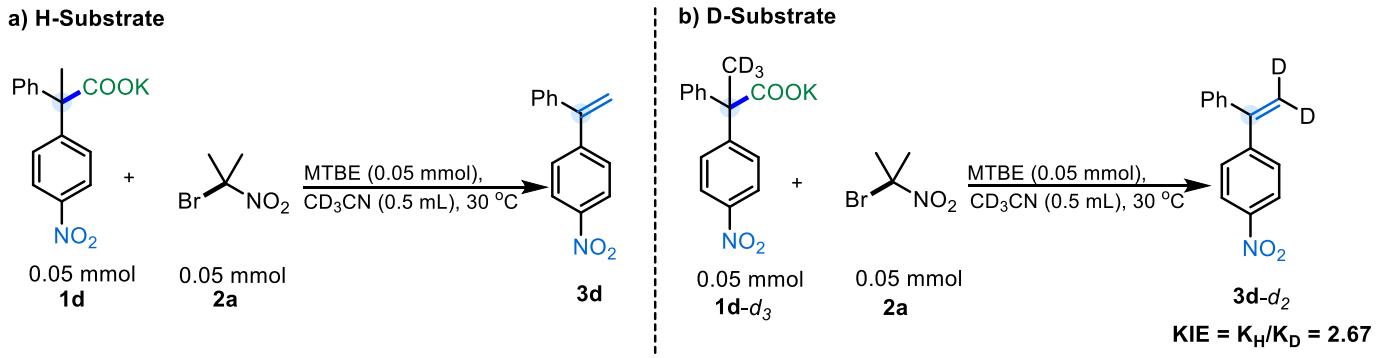


Figure S9: Ratio determination for the competitive experiment.

B: Potassium 2-(4-nitrophenyl)-2-phenylpropanoate (Parallel Reactions)



In an argon atmosphere glove box, a glass NMR tube was charged with the carboxylate salt **1d** (0.05 mmol), **2a** (0.05 mmol), t-butyl methyl ether (0.05 mmol, internal standard) and CD_3CN (0.5 mL). The NMR tube was sealed with a septum, covered with a parafilm, and removed from the glovebox. The reaction tube was shaken well for uniform mixing and the NMR spectra were taken at designated time points (7, 15, 21, 27, and 34 mins). The process was repeated for the deuterated substrate **1d**-d_3. *NOTE:* As the reaction proceeded at room temperature, the experiment was run inside the NMR and data points were taken at various time points.

Data Analysis: The concentration of the product was calculated from the integration values of the methyl peak of methyl *t*-butyl ether and the alkene peaks of product **3d** at each time points. For substrate **3d**-d_2, the aromatic peaks were used for integration. The initial rates were determined from the first three time points. The KIE was determined by dividing the initial rates for the product formation of **3d** with **3d**-d_2 to give a KIE of 2.67.

Starting Carboxylic Salts	Time (mins)	[**3d**] or [**3d**-d_2] [M]	Initial Rate (M/h)[a]
1d	0	0	0.1083
	7	0.0085	
	15	0.022	
	21	0.0385	
	27	0.052	
	35	0.66	
1d-d_5	0	0	0.0405
	7	0.003	
	15	0.009	
	21	0.014	
	27	0.0175	
	35	0.0225	

Table S15: *Initial rate study of substrate **1d** and **1d**-d_6.* [a]All reactions were performed on 0.05 mmol scale with respect to **2a** and 1 equivalent of both the carboxylate substrates. [a] Initial rates were determined from the linear fit of the first three time points.

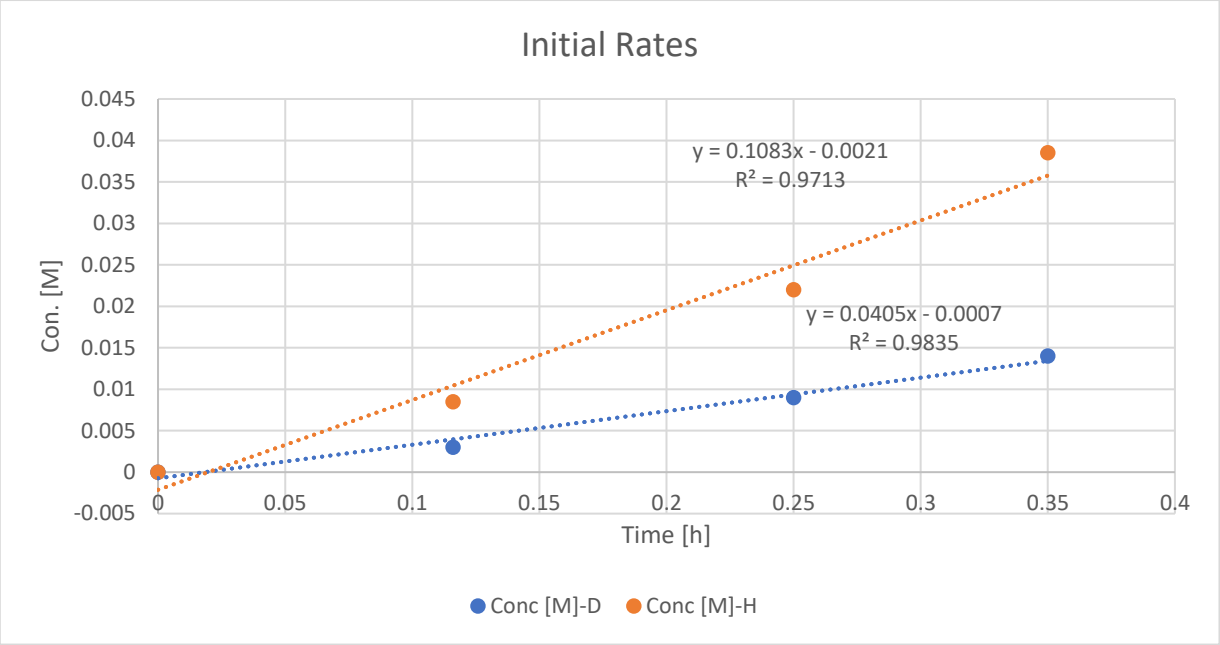
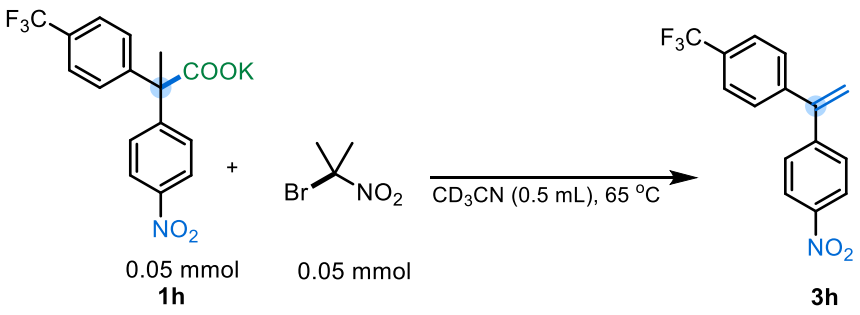


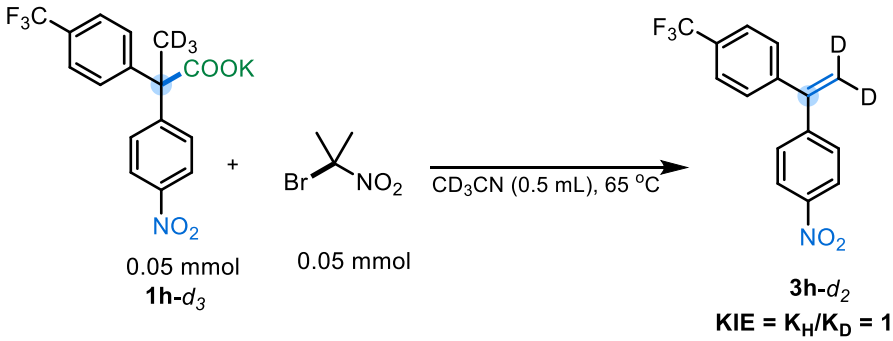
Figure S10: Initial Rate Kinetics of substrate ***1d*** *and* ***1d***-d_6. Orange trace represents the initial rate of substrate ***1h*** for the decarboxylative elimination reaction. Blue trace represents the initial rate of substrate **1d**-d_6 for the decarboxylative elimination reaction.

C: potassium 2-(4-nitrophenyl)-2-(4-(trifluoromethyl)phenyl)propanoate (Parallel Reactions)

a) H-Substrate



b) D-Substrate



In an argon atmosphere glove box, a glass NMR tube was charged with the carboxylate salt **1h** (0.05 mmol), **2a** (0.05 mmol), t-butyl methyl ether (0.05 mmol, internal standard) and degassed MeCN (0.5 mL). The NMR tube was sealed with a septum, covered with a parafilm, and removed from the glovebox. The reaction tube was shaken well for uniform mixing and the NMR spectra were taken at designated time points (7, 15, 21, 27, and 34 mins). The process was repeated for the deuterated substrate **1h**-d_3. *NOTE:* The reaction was run

inside the NMR at 65 °C using variable temperature NMR experiments and data points were taken at various time points.

Data Analysis: The concentration of the product was calculated from the integration values of the methyl peak of *t*-butyl ether and the alkene peaks of product **3h** at each time points. For substrate **3h**-d_2, the aromatic peaks were used for integration. The initial rates were determined from the first four time points. The KIE was determined by dividing the initial rates for the product formation of **3h** with **3h**-d_2 to give a KIE of 1.84.

Starting Carboxylic Salts	Time (mins)	[**3h**] or [**3h**-d_2] [M]	Initial Rate (M/h)[a]
1h	0	0	0.028
	14	0.00975	
	24	0.01375	
	34	0.0175	
	44	0.021	
	54	0.0235	
	64	0.0257	
1h-d_3	0	0	0.0152
	14	0.00475	
	24	0.007	
	34	0.00875	
	44	0.0115	
	54	0.01275	
	64	0.01475	

Table S16: *Initial rate study of substrate **1h** and **1h**-d_6.* [a]All reactions were performed on 0.05 mmol scale with respect to **2a** and 1 equivalent of both the carboxylate substrates. [a] Initial rates were determined from the linear fit of the first four time points.

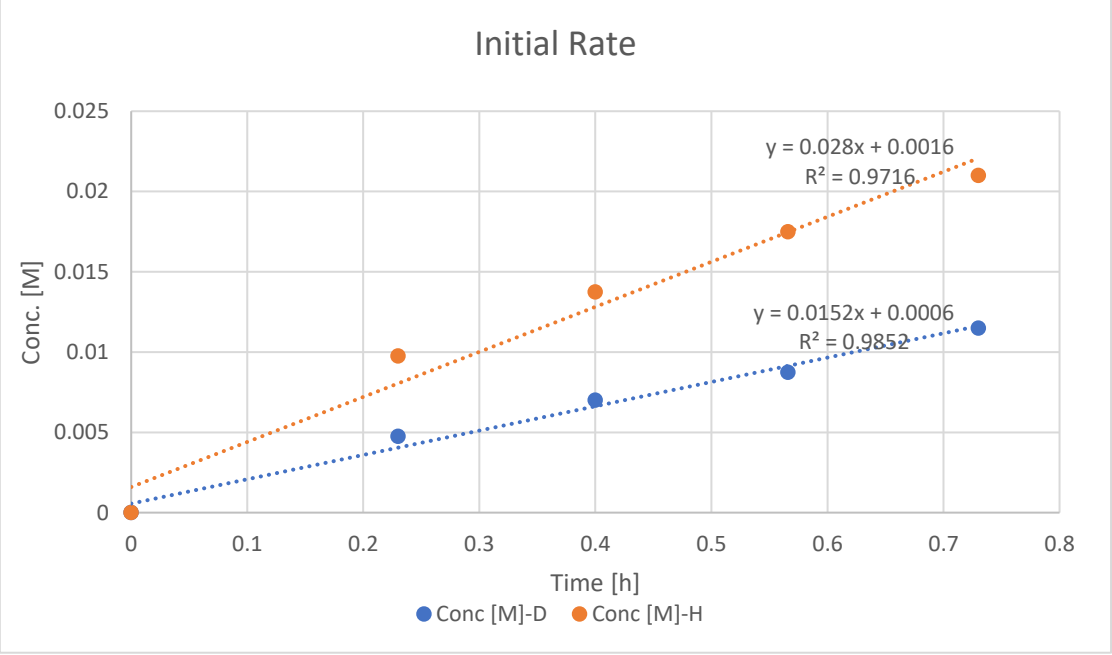
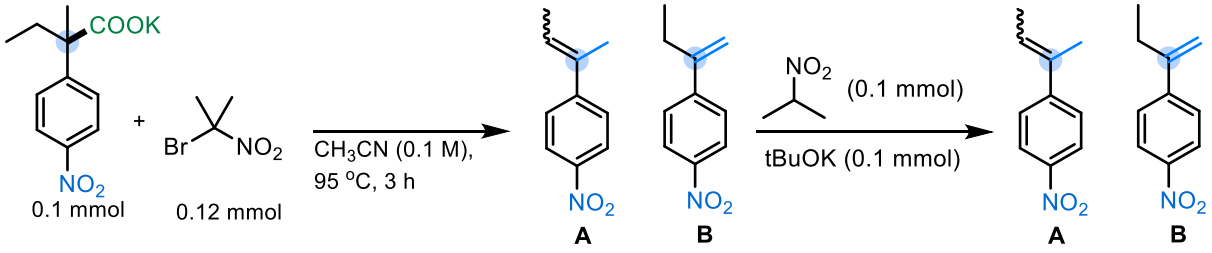


Figure S11: Initial Rate Kinetics of substrate ***1h*** *and* ***1h***-d_6. Orange trace represents the initial rate of substrate ***1l*** for the decarboxylative elimination reaction. Blue trace represents the initial rate of substrate **1h**-d_6 for the decarboxylative elimination reaction.

6.4 E/Z vs Internal External Alkene Isomerization Study.

In an argon atmosphere glove box, a 10 mL screw-threaded glass tube equipped with a stir bar was charged with carboxylates (0.1 mmol), **2a** (0.12 mmol), and MeCN (1 mL). The reaction vessel was sealed, covered with a parafilm, and removed from the glovebox. The tube was then placed in a preheated oil bath at 95 °C for 3 hours. After this time, the solvent was removed under reduced pressure, and the ^{1}H NMR of the crude reaction mixture was taken to determine the ratios of the isomers. To another 10 mL screw-threaded glass tube was added 2-nitropropane (0.1 mmol), t-BuOK (0.1 mmol), and MeCN (1 mL) and stirred at room temperature for 30 mins. After this, the alkene mixture was dissolved in MeCN (1 mL) and added to this stirring mixture. The reaction mixture was then stirred at 95 °C and the NMR spectra of the aliquots were taken at designated time points.

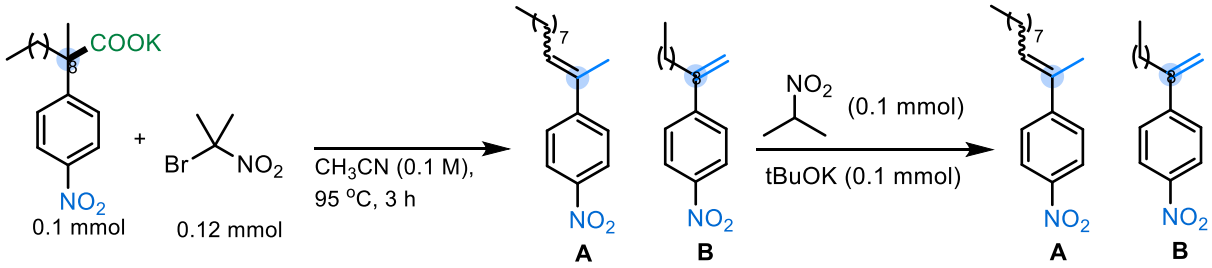
Experiment 1



A:B, 70:30
E:Z, 95:5

Entry	Time (x h)	(A/B)	(E/Z)
1	3	72:28	95:5
2	16	78:22	95:5
3	24	74:26	95:3
4	40	75:25	95:5

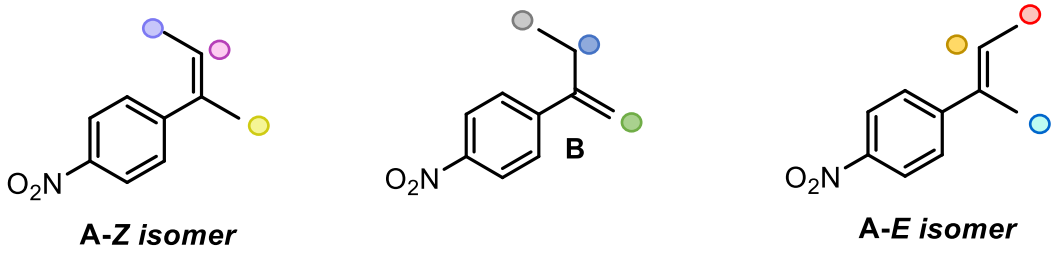
Experiment 2



A:B, 45:55
E:Z, 92:8

Entry	Time (x h)	(A/B)	(E/Z)
1	3	56:44	93:7
2	16	50:50	93:7

7. Product Analysis



A-*Z* isomer **A-*E* isomer**

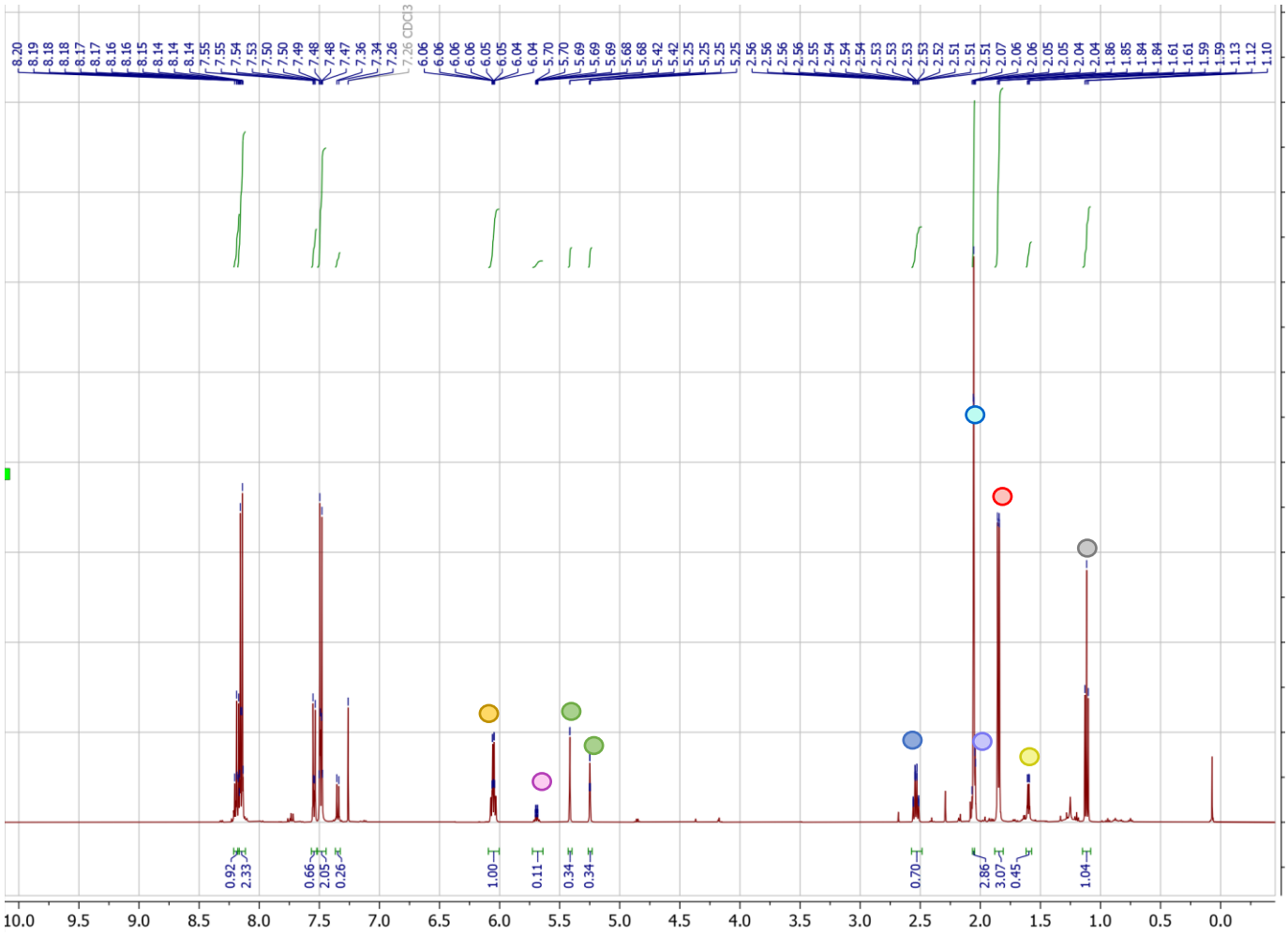


Figure S12: ^{1}H NMR spectrum of **3m**

Ratio of isomers:

E isomer = (.11/1.11) * 100 = 10

E:Z = 10:90

Internal alkene = (1.11/1.45) * 100 = 76

Internal:Terminal = 76:24

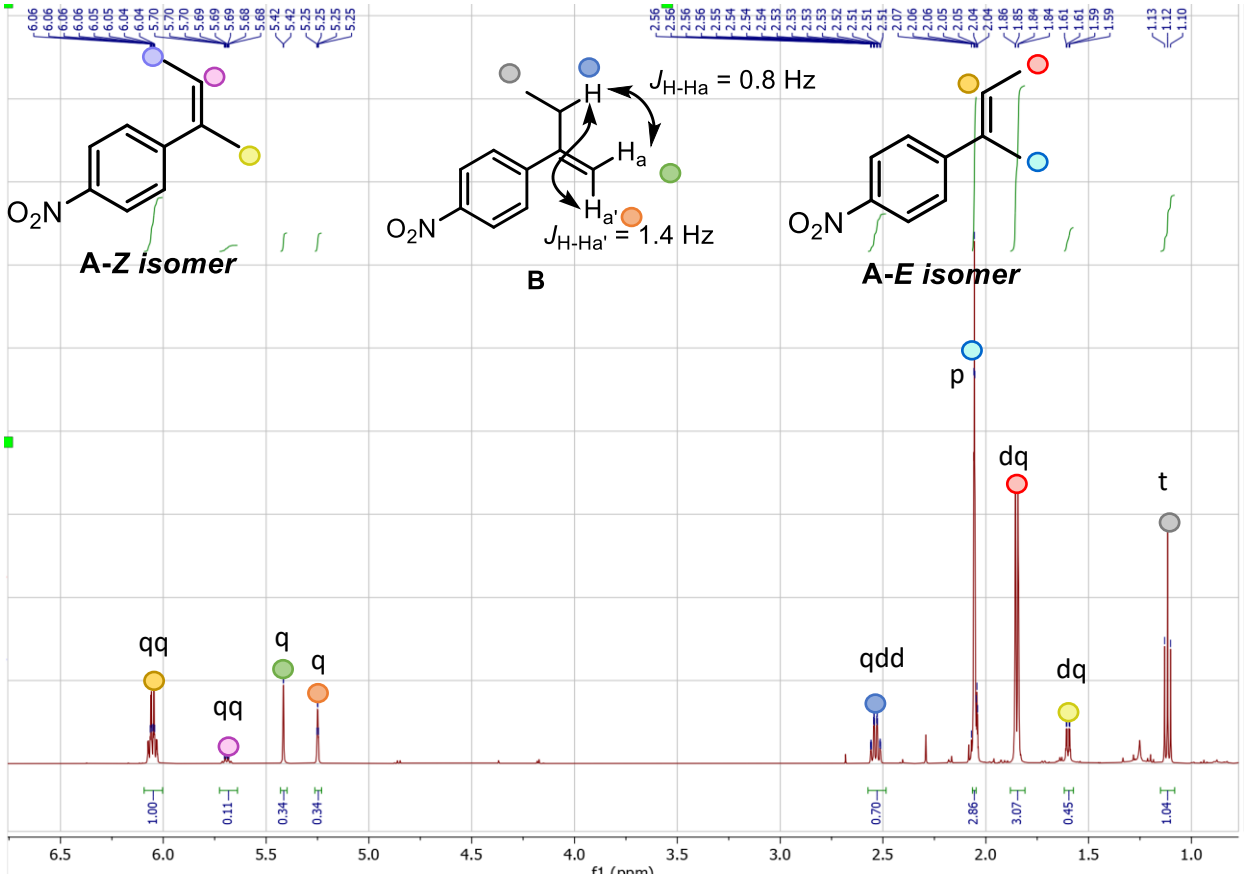


Figure S13: Zoomed in ^{1}H NMR spectrum of **3m**

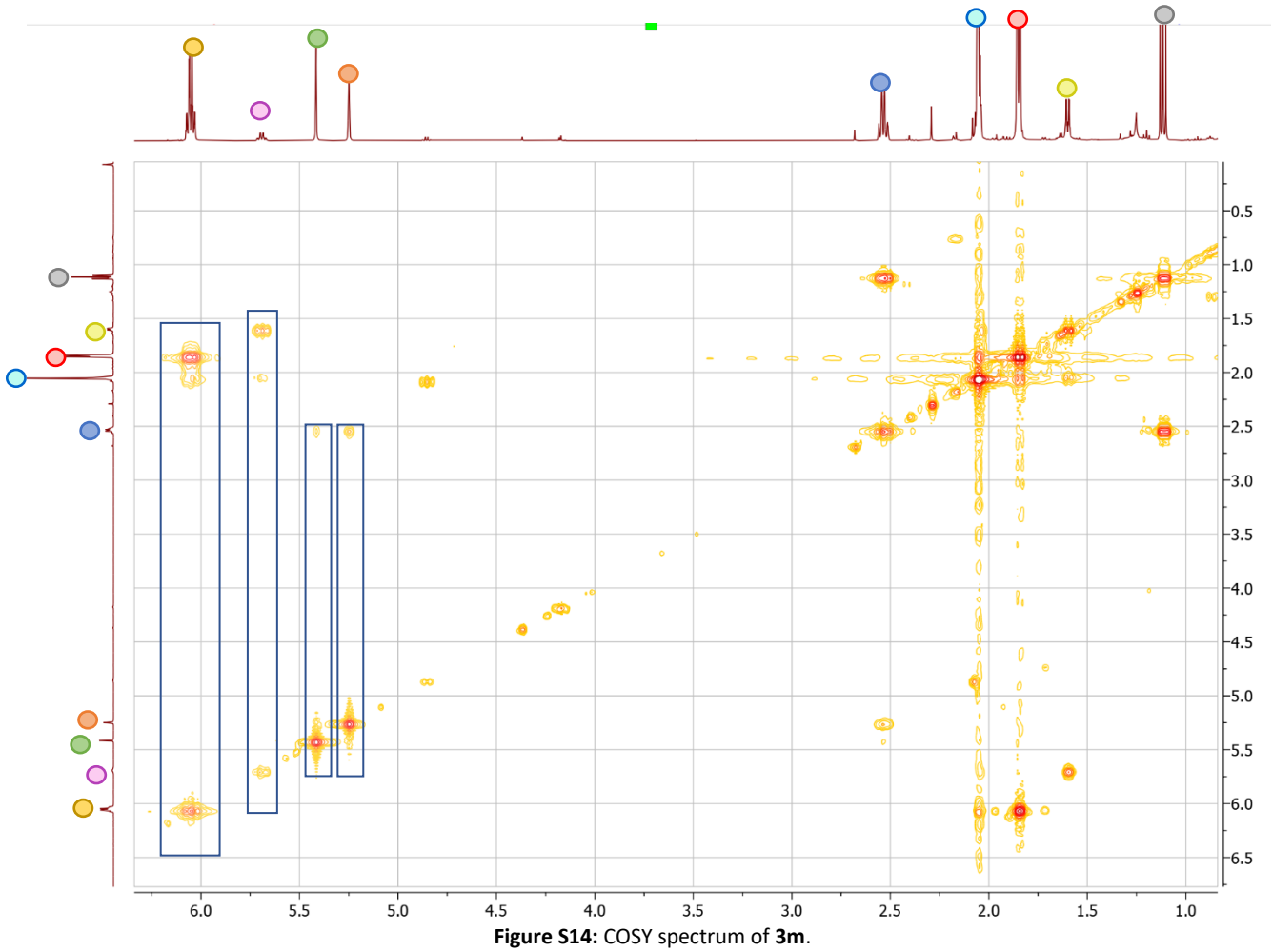
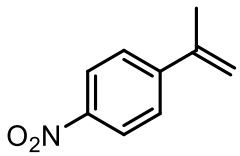


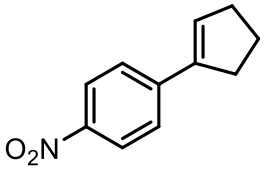
Figure S14: COSY spectrum of **3m**.

8. Compound Characterization

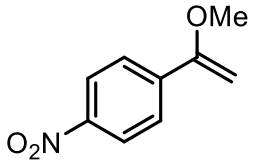
5.1 Styrenes synthesized by procedures.



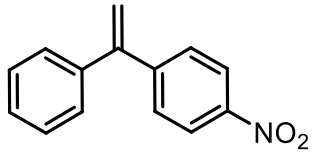
1-nitro-4-(prop-1-en-2-yl)benzene (**3a**). General procedure 2.16 provided the styrene as a white solid in 83% yield (27 mg, Hex:EtOAc – 20:1). Product matched with previous reported literature specification.[25] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.22 – 8.14 (m, 2H), 7.63 – 7.55 (m, 2H), 5.55 – 5.50 (m, –CC*H*, 1H), 5.32 – 5.26 (m, –CC*H*, 1H), 2.19 (dd, *J* = 1.4, 0.8 Hz, –CC*H*$_3$, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.79, 147.13, 141.72, 126.37, 123.74, 116.53, 21.72.



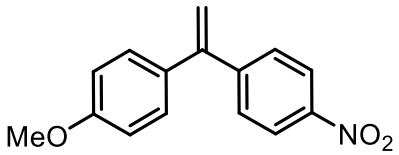
1-(cyclopent-1-en-1-yl)-4-nitrobenzene (**3b**). General procedure 2.16 provided the styrene as a white solid in 83% yield (31.4 mg, Hex:EtOAc – 20:1). Product matched with previous reported literature specification.[27] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.24 – 8.10 (m, 2H), 7.59 – 7.50 (m, 2H), 6.42 (ddd, *J* = 4.6, 2.7, 1.9 Hz, 1H), 2.73 (dtd, *J* = 8.4, 4.5, 2.2 Hz, 2H), 2.59 (ddq, *J* = 10.3, 5.1, 2.6 Hz, 2H), 2.15 – 2.01 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.46, 143.32, 141.16, 131.92, 126.15, 123.86, 33.86, 33.20, 23.39.



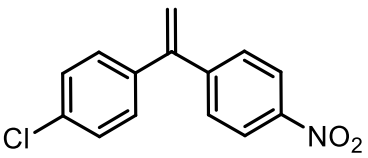
1-(1-methoxyvinyl)-4-nitrobenzene (**3c**). General procedure 2.16 provided the styrene as a yellow solid in 68% yield (24.3 mg, Hex:EtOAc – 10:1). Product matched the previously reported literature specification.[28] **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.19 (d, *J* = 9.0 Hz, 2H), 7.77 (d, *J* = 9.0 Hz, 2H), 4.84 (d, *J* = 3.4 Hz, 1H), 4.42 (d, *J* = 3.4 Hz, 1H), 3.78 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 158.81, 147.80, 142.54, 126.15, 123.60, 85.43, 55.69.



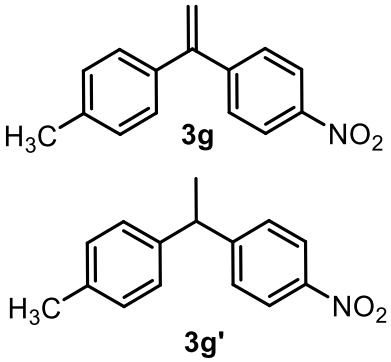
1-nitro-4-(1-phenylvinyl)benzene (**3d**). General procedure 2.16 provided the styrene as a pale-yellow solid in 80% yield (36 mg, Hex:EtOAc – 20:1). Product matched with previous reported literature specification.[25] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.24 – 8.16 (m, 2H), 7.55 – 7.45 (m, 2H), 7.43 – 7.35 (m, 3H), 7.33 – 7.24 (m, 2H), 5.63 (d, *J* = 0.6 Hz, 1H), 5.59 (d, *J* = 0.6 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.55, 148.20, 147.47, 140.28, 129.14, 128.66, 128.49, 128.29, 123.70, 117.38.



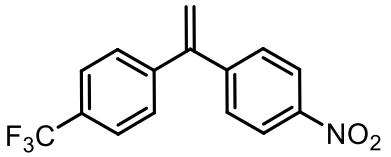
1-methoxy-4-(1-(4-nitrophenyl)vinyl)benzene (**3e**). General procedure 2.16 provided the styrene as a pale-yellow solid in 81% yield (41.3 mg, Hex:EtOAc – 10:1). Product matched with previous reported literature specification.[25] **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.14 – 8.09 (m, 2H), 7.45 – 7.39 (m, 2H), 7.17 – 7.09 (m, 2H), 6.88 – 6.75 (m, 2H), 5.48 (s, 1H), 5.40 (s, 1H), 3.76 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.90, 148.61, 148.01, 147.43, 132.72, 129.47, 129.18, 123.65, 115.98, 113.99, 55.48.



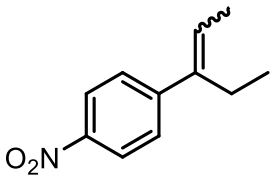
1-chloro-4-(1-(4-nitrophenyl)vinyl)benzene (**3f**). General procedure 2.16 provided the styrene as a white solid in 90% yield (46.6 mg, Hex:EtOAc – 15:1). Product matched with previous reported literature specification.[25] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 5.62 (s, 1H), 5.60 (s, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.65, 147.59, 147.46, 138.70, 134.49, 129.57, 129.08, 128.88, 123.80, 117.80.



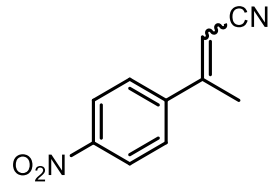
1-methyl-4-(1-(4-nitrophenyl)vinyl)benzene (**3g**). General procedure 2.16 provided the styrene as a pale-yellow solid in 82% yield along with 9% of the protonated pdt **3g'** (39.2 mg, Hex:EtOAc – 20:1). Product matched with previous reported literature specification.[25] **^{1}H NMR** (400 MHz, Chloroform-*d*) **3g**: δ 8.25 – 8.12 (m, 2H), 7.58 – 7.43 (m, 2H), 7.18 (s, 4H), 5.60 (d, *J* = 0.7 Hz, 1H), 5.53 (d, *J* = 0.7 Hz, 1H), 2.39 (s, 3H). **3g'**: δ 8.16 – 8.08 (m, 2H), 7.41 – 7.32 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ (126 MHz, $CDCl_3$) δ 154.5, 148.5, 148.4, 147.4, 141.7, 138.4, 137.4, 136.4, 129.5, 129.3, 129.1, 128.5, 128.2, 127.5, 123.8, 123.6, 116.7, 44.5, 21.7, 21.3.



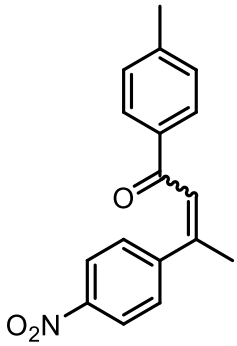
1-nitro-4-(1-(4-(trifluoromethyl)phenyl)vinyl)benzene (**3h**). General procedure 2.16 provided the styrene as a white solid in 85% yield (49.8 mg, Hex:EtOAc – 15:1). Product matched with previous reported literature specification.[25] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.26 – 8.18 (m, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.44 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 5.70 (s, 1H), 5.70 (s, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.71, 147.42, 147.20, 143.82, 130.58 (q, *J* = 32.2, 31.8 Hz), 129.08, 128.63, 125.70 (q, *J* = 3.6 Hz), 123.90, 124.1 (q, *J* = 271.6 Hz), 119.02. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.62.



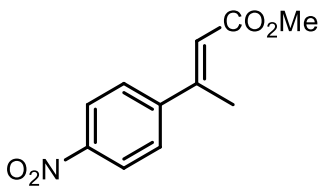
(E,Z)-1-nitro-4-(pent-2-en-3-yl)benzene (**3i**). General procedure 2.16 provided the styrene as a mixture geometric isomers (E:Z; 72:28) in 91% yield (Colorless oil, 34.7 mg, Hex:EtOAc – 100:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) E isomer: δ 8.18 – 8.12 (m, 2H), 7.53 – 7.43 (m, 2H), 5.91 (q, *J* = 7.0 Hz, –CC*H*CH_3, 1H), 2.55 (q, *J* = 7.5 Hz, –C*C*H_2CH_3, 2H), 1.85 (d, *J* = 7.0 Hz, –CCHCH_3, 3H), 0.97 (t, *J* = 7.6 Hz, –CCH_2CH_3, 3H). Z isomer: δ 8.23 – 8.18 (m, 2H), 7.38 – 7.28 (m, 2H), 5.64 (qt, *J* = 7.0, 1.3 Hz, –CC*H*CH_3, 1H), 2.42 – 2.34 (m, –C*C*H_2CH_3, 2H), 1.55 (dt, *J* = 7.0, 1.3 Hz, –CCHCH_3, 3H), 0.96 (t, *J* = 7.0 Hz, –CCH_2CH_3, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.3, 149.9, 148.8, 146.6, 146.5, 141.7, 141.1, 129.5, 129.1, 128.6, 126.8, 126.4, 123.7, 123.5, 123.4, 122.3, 37.4, 31.7, 22.5, 14.8, 14.4, 13.2, 13.1, 10.4. **IR** (film): 3077, 2968, 1607, 1514, 1344, 1108, 852 cm^{-1}. **HRMS** Calcd for $C_{11}H_{14}NO_2$ (M+H) = 192.1025, found 192.1025.



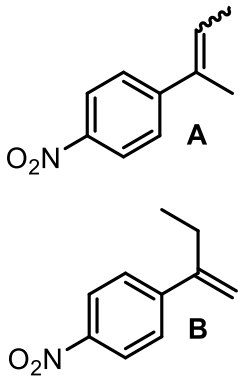
(E,Z)-3-(4-nitrophenyl)but-2-enenitrile (**3j**). General procedure 2.16 provided the styrene as a mixture geometric isomers (E:Z; 82:18) in 91% yield (White solid, 34.2 mg, Hex:EtOAc – 3:1). Product matched with previous reported literature specification.[29] **^{1}H NMR** (400 MHz, Chloroform-*d*) E isomer: (400 MHz, Chloroform-*d*) δ 8.33 – 8.23 (m, 2H), 7.62 (d, *J* = 8.9 Hz, 2H), 5.73 (q, *J* = 1.1 Hz, –CC*H*CN, 1H), 2.52 (d, *J* = 1.1 Hz, –CCH_3, 3H). Z isomer: (400 MHz, Chloroform-*d*) δ 8.34 – 8.26 (m, 2H), 7.73 – 7.65 (m, 2H), 5.56 (q, *J* = 1.6 Hz, –CC*H*CN, 1H), 2.33 (d, *J* = 1.6 Hz, –CCH_3, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 157.54, 148.78, 144.42, 127.08, 124.04, 116.67, 99.32, 20.48.



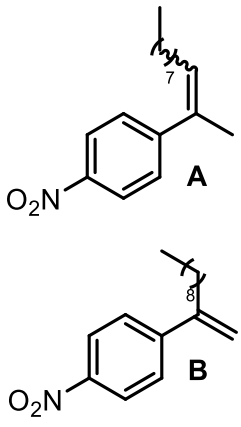
(E,Z)-3-(4-nitrophenyl)-1-(p-tolyl)but-2-en-1-one (**3k**). General procedure 2.16 provided the styrene as a mixture geometric isomers (E:Z; 94:6) in 71% yield (White solid, 39.9 mg, Hex:EtOAc – 5:1). Product matched with previous reported literature specification.[30] **^{1}H NMR** (400 MHz, Chloroform-*d*) E isomer: δ 8.31 – 8.23 (m, 2H), 7.93 – 7.84 (m, 2H), 7.74 – 7.66 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.16 (q, *J* = 1.3 Hz, –CC*H*CO–, 1H), 2.55 (d, *J* = 1.3 Hz, –CC*H*$_3$, 3H), 2.43 (s, Ar-C*H*$_3$, 3H). Z isomer: δ 8.20 – 8.10 (m, 2H), 7.80 (dd, *J* = 11.0, 8.3 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.90 (q, *J* = 1.5 Hz, –CC*H*CO–, 1H), 2.39 (s, Ar-C*H*$_3$, 3H), 2.31 (d, *J* = 1.5 Hz, –CC*H*$_3$, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 191.4, 191.1, 151.0, 150.4, 149.3, 148.3, 148.0, 144.2, 144.1, 136.2, 135.2, 129.6, 129.4, 128.9, 128.7, 128.6, 128.3, 128.2, 128.0, 127.5, 125.5, 125.2, 124.0, 123.9, 123.7, 77.4, 77.2, 76.9, 26.6, 23.2, 21.8, 18.8. **HRMS** Calcd for $C_{17}H_{15}NO_3$ (M+Na) = 302.0950, found 304.0936.



methyl (E)-3-(4-nitrophenyl)but-2-enoate (**3l**). General procedure 2.16 provided the styrene as white solid in 76% yield (33.6 mg, Hex:EtOAc – 20:1). Product matched with previous reported literature specification.[31] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.27 – 8.19 (m, 2H), 7.65 – 7.57 (m, 2H), 6.18 (q, *J* = 1.3 Hz, –CC*H*CO$_2$CH$_3$, 1H), 3.78 (s, –CCHCO$_2$C*H*$_3$, 3H), 2.59 (d, *J* = 1.3 Hz, –CC*H*$_3$, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.65, 153.22, 148.64, 148.10, 127.39, 123.96, 119.80, 51.60, 18.11.

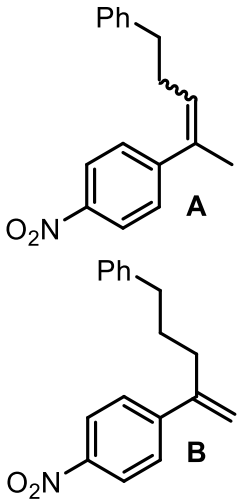


(E,Z)-1-(but-2-en-2-yl)-4-nitrobenzene & 1-(but-1-en-2-yl)-4-nitrobenzene (**3m**). General procedure 2.16 provided the styrene as a mixture of regioisomers (**A**:**B**; 76:24) and geometric isomers (E:Z; 90:10) in 88% yield (Colorless oil, 31.1 mg, Hex:EtOAc – 20:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) Regioisomer **A** - E:Z mixture: δ [8.18 – 8.08 (m, maj. & min.), Σ2H], [7.52 – 7.42 (m, maj.), 7.35 (d, *J* = 8.9 Hz, min.), Σ2H], [6.06 (qq, *J* = 6.8, 1.3 Hz, maj.), 5.69 (qq, *J* = 7.0, 1.5 Hz, min.), –CC*H*CH$_3$, Σ1H], [2.06 (dt, *J* = 2.4, 1.3 Hz, maj. & min.), –CC*H*$_3$, Σ3H], [1.85 (dq, *J* = 7.0, 1.1 Hz, maj.), 1.60 (dq, *J* = 7.0, 1.5 Hz, min.), –CCH*CH*$_3$, Σ3H]. Regiosomer **B**: δ 8.19 (d, *J* = 9.0 Hz, 2H), 7.60 – 7.53 (m, 2H), 5.42 (q, *J* = 0.9 Hz, –CC*H*$_2$, 1H), 5.31 – 5.20 (m, –CC*H*$_2$, 1H), 2.54 (qdd, *J* = 7.3, 1.4, 0.7 Hz, –CC*H*$_2$CH$_3$, 2H), 1.12 (t, *J* = 7.4 Hz, –CCH$_2$C*H*$_3$, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.5, 149.1, 148.4, 148.3, 147.1, 146.4, 135.1, 134.3, 129.1, 128.5, 128.5, 127.9, 127.0, 126.9, 126.1, 124.4, 123.7, 123.7, 123.6, 114.7, 77.4, 77.2, 76.9, 28.0, 25.0, 24.7, 23.1, 15.4, 15.1, 14.8, 12.9. **IR** (film): 3077, 2922, 1648, 1520, 1345, 1182, 853 cm^{-1}. **HRMS** Calcd for $C_{10}H_{12}NO_2$ (M+H) = 178.0868, found 178.0875.

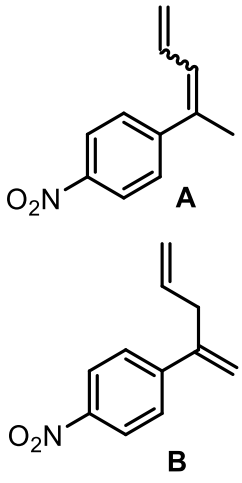


*(E,Z)-1-nitro-4-(undec-2-en-2-yl)benzene & 1-nitro-4-(undec-1-en-2-yl)benzene (***3n**). General procedure 2.16 provided the styrene as a mixture of regioisomers (**A**:**B**; 52:48) and geometric isomers (E:Z; 81:19) in 66% yield (Colorless oil, 36.3 mg, Hexane). **^{1}H NMR** (400 MHz, Chloroform-*d*) Regioisomer **A** - E:Z mixture: δ [8.23 – 8.17 (m, maj. & min.), Σ2H], [7.58 – 7.52 (m, maj.), 7.33 (d, *J* = 8.8 Hz, min.), Σ2H], [5.97 (td, *J* = 7.2, 1.2 Hz, maj.), 5.58 (td, *J* = 7.5, 1.4 Hz, min.), –CC*H*CH$_2$–, Σ1H], [2.23 (q, *J* = 7.2 Hz), –CHC*H*$_2$CH$_2$–, Σ2H], 2.05 (dd, *J* = 5.3, 1.2 Hz, –CC*H*$_3$, Σ3H), 1.97 – 1.89 (m, maj. & min.), Σ2H), 1.33 – 1.23 (m, maj. & min.), Σ8H], [0.92 – 0.81 (m, maj. & min.), –CH$_2$CH$_2$C*H*$_3$, Σ3H]. Regiosomer **B**: (400 MHz, Chloroform-*d*) δ 8.17 – 8.12 (m, 2H), 7.52 – 7.45 (m, 2H), 5.39 (s, –CC*H*, 1H), 5.24 (d, *J* = 1.2 Hz, –CC*H*, 1H), 2.55 – 2.47 (m, –CC*H*$_2$CH$_2$–, 2H), 1.56 – 1.38 (m, 2H), 1.33 – 1.23 (m, 10H), 0.92 – 0.81 (m, –CCH$_2$C*H*$_3$, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.7, 150.6, 149.5, 148.3, 147.2, 147.1, 146.4, 146.2, 134.2, 133.3, 133.2, 130.7, 129.0, 127.0, 126.2, 123.8, 123.7, 123.6, 115.7, 35.2, 32.0, 32.0, 30.7, 30.0, 29.9, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4,

29.4, 29.3, 29.2, 28.2, 25.2, 22.8, 15.7, 14.2. **IR** (film): 3080, 2953, 1594, 1515, 1343, 779 cm^{-1}. **HRMS** Calcd for $C_{18}H_{28}NO_2$ (M+H) = 290.2120, found 290.2104.

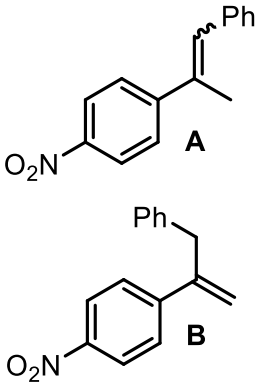


(E,Z)-1-nitro-4-(5-phenylpent-2-en-2-yl)benzene & 1-nitro-4-(5-phenylpent-1-en-2-yl)benzene (**3o**). General procedure 2.16 provided the styrene as a mixture of regioisomers (**A**:**B**; 1:1) and geometric isomers (E:Z; 92:8) in 91% yield (Pale yellow solid, 48.6 mg, Hex:EtOAc – 20:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) Regioisomer **A** - E:Z mixture: (400 MHz, Chloroform-*d*) δ [8.16 – 8.12 (m, maj. & min.), Σ2H], [7.52 – 7.48 (m, maj. & min.), Σ2H], [7.36 – 7.28 (m, maj. & min.), Σ3H)], [7.24 – 7.18 (m, maj. & min], Σ2H], [5.98 (qt, *J* = 7.2, 1.3 Hz, maj.), 5.61 (qt, *J* = 7.5, 1.3 Hz, min.), –CC*H*CH_2–, Σ1H], [2.57 (q, *J* = 7.5 Hz, maj.), 2.31 – 2.20 (m, min.), –CHC*H_2CH_2*Ph–, Σ4H), [2.02 (d, *J* = 1.3 Hz, min.), 1.99 (d, *J* = 1.2 Hz, maj.), –CC*H_3*, Σ3H). Regiosiomer **B**: δ 8.18 (d, *J* = 7.3 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.34 – 7.27 (m, 3H), 7.21 (dd, *J* = 9.4, 7.2 Hz, 2H), 5.43 (s, –CC*H*, 1H), 5.26 (q, *J* = 1.1 Hz, –CC*H*, 1H), 2.80 (t, *J* = 7.7 Hz,–CCH_2CH_2C*H_2*–, 2H), 2.65 (t, *J* = 7.6 Hz,–CC*H_2*CH_2–, 2H), 1.78 (ddd, *J* = 15.2, 8.3, 6.9 Hz,–CCH_2C*H_2*CH_2–, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.6, 149.4, 147.4, 147.2, 146.9, 145.4, 138.5, 137.4, 136.8, 136.4, 135.6, 131.3, 129.5, 129.3, 129.3, 129.1, 128.9, 128.7, 128.5, 128.4, 128.3, 127.5, 127.1, 127.0, 126.8, 126.7, 123.9, 123.8, 123.7, 118.3, 77.4, 77.2, 76.9, 41.6, 26.4, 17.5. **IR** (film): 3083, 2933, 1595, 1514, 1452, 1154, 855 cm^{-1}. **HRMS** Calcd for $C_{17}H_{17}NO_2$ (M+) = 267.1259, found 267.1257.



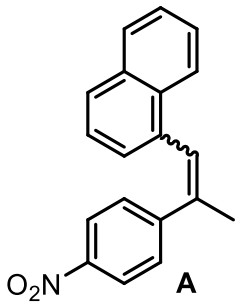
3p

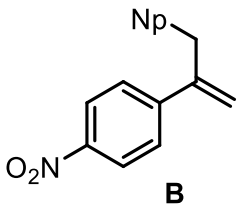
(E,Z)-1-nitro-4-(penta-2,4-dien-2-yl)benzene & 1-nitro-4-(penta-1,4-dien-2-yl)benzene (**3p**). General procedure 2.16 provided the styrene as a mixture of regioisomers (**A**:**B**; 87:13) and geometric isomers (E:Z; 87:13) in 67% yield (Yellow oil, 25.3 mg, Hex:EtOAc – 20:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) Regioisomer **A** - E:Z mixture: (400 MHz, Chloroform-*d*) δ [8.16 – 8.12 (m, maj. & min.), Σ2H], [7.52 – 7.48 (m, maj. & min.), Σ2H], [6.77 (ddd, *J* = 16.6, 10.9, 10.1 Hz, maj. & min.), Σ1H], [6.62 – 6.55 (m, maj. & min), Σ1H], [5.52 – 5.32 (m, maj. & min.), Σ2H], [2.22 – 2.19 (m, maj.), 1.80 (dd, *J* = 6.7, 1.7 Hz, min.), Σ3H). Regiosiomer **B**: δ 8.18 (d, *J* = 7.3 Hz, 2H), 7.48 – 7.42 (m, 2H), δ 6.36 – 6.21 (m, 1H), 5.87 (ddt, *J* = 16.8, 10.1, 6.4 Hz, 1H), 5.79 – 5.57 (m, 1H), 5.18 – 5.10 (m, 2H), 3.31 – 3.24 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.6, 148.5, 147.7, 147.6, 146.8, 144.7, 136.8, 135.3, 134.7, 133.4, 133.1, 133.0, 131.9, 131.2, 130.3, 130.2, 129.3, 129.2, 127.8, 126.9, 126.4, 123.8, 123.8, 123.6, 123.6, 123.6, 120.6, 120.1, 118.5, 117.4, 117.1, 116.4, 77.4, 77.2, 76.9, 51.5, 39.4, 31.5, 29.9, 25.0, 18.5, 16.0. **IR** (film): 3061, 2922, 1648, 1591, 1510, 1340, 1151, 898, 854 cm^{-1}. **HRMS** Calcd for $C_{11}H_{11}NO_2$ (M+) = 189.0790, found 189.0788.



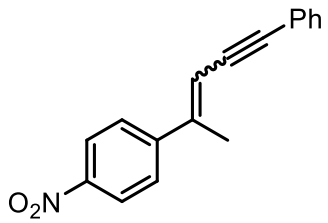
(E,Z)-1-nitro-4-(1-phenylprop-1-en-2-yl)benzene & 1-nitro-4-(3-phenylprop-1-en-2-yl)benzene (**3q**). General procedure 2.16 provided the styrene as a mixture of regioisomers (**A**:**B**; 83:17) and geometric isomers (E:Z; 88:12) in 83% yield (White solid, 39.7 mg, Hex:EtOAc – 20:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) Regioisomer **A** - E:Z mixture: δ [8.27 – 8.19 (m, maj.), 8.19 – 8.08 (m, min.), Σ2H], [7.70 – 7.62 (m, maj. & min.) Σ2H], [7.44 – 7.32 (m, maj. & min.), Σ3H], [7.35 – 7.25 (m, maj. & min.), Σ2H], [6.98 (s, maj.), 6.65 – 6.61 (m, min.), –CC*H*Ph, Σ1H], [2.32 (d, *J* = 1.3 Hz, maj.), 2.24 (d, *J* = 1.6 Hz, min.), –CC*H_3*, Σ3H]. Regiosiomer **B**: δ 8.16 – 8.07 (m, 2H), 7.58 – 7.49 (m, 2H), 7.35 – 7.25 (m, 3H), 7.20 (dt, *J* = 7.3, 2.4 Hz, 2H), 5.63 (s, –CC*H*, 1H), 5.27 (d, *J* = 1.0 Hz, –CC*H*, 1H), 3.87 (s, –CC*H_2*Ph, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.6, 149.4, 147.4, 147.2, 146.9, 145.4, 138.5, 137.4, 136.8, 136.4, 135.6, 131.3, 129.5, 129.3, 129.3, 129.1, 128.9, 128.7, 128.5, 128.4, 128.3, 127.5, 127.1, 127.0, 126.8, 126.7, 123.9, 123.8,

123.7, 118.3, 77.4, 77.2, 76.9, 41.6, 26.4, 17.5. **IR** (film): 3075, 2985, 1589, 1513, 1341, 1151, 885 cm^{-1}. **HRMS** Calcd for $C_{15}H_{13}NO_2$ (M+) = 239.0946, found 239.0953.

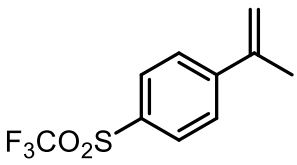




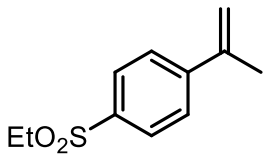
(E,Z)-1-(2-(4-nitrophenyl)prop-1-en-1-yl)naphthalene & 1-(2-(4-nitrophenyl)allyl)naphthalene (**3r**). General procedure 2.16 provided the styrene as a mixture of regioisomers (**A**:**B**; 81:19) and geometric isomers (E:Z; 89:11) in 75% yield (Yellow solid, 25.3 mg, Hex:EtOAc – 20:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) Regioisomer **A** - E:Z mixture: δ [8.29 – 8.21 (m, maj.& min.), Σ2H), [7.93 – 7.84 (m, maj. & min.), Σ4H], [7.73 – 7.67 (m, maj. & min.), Σ2H], [7.67 – 7.31 (m, maj & min), Σ3H], [7.13 (s, maj.), 6.80 (s, min.), –CC*H*C–, Σ1H], [2.40 (d, *J* = 1.3 Hz, maj.), 2.30 (d, *J* = 1.6 Hz, min), –CCH_3, Σ3H]. Regiosomer **B**: δ 8.12 (d, *J* = 9.0, 2H), 7.93 – 7.84 (m, 4H), 7.65 (s, 1H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.48 – 7.39 (m, 2H), 5.68 (s, –CC*H*, 1H), 5.32 (d, *J* = 1.0 Hz, –CC*H*, 1H), 4.03 (s, –CCH_3, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.5, 146.9, 145.3, 136.0, 136.0, 134.9, 133.7, 133.4, 132.6, 131.3, 129.6, 129.4, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.4, 127.3, 127.2, 127.1, 127.0, 126.8, 126.5, 126.4, 126.3, 126.3, 126.1, 125.7, 123.9, 123.9, 123.7, 123.3, 118.5, 77.4, 77.2, 76.9, 54.1, 41.7, 26.4, 17.6. **IR** (film): 3061, 2922, 1648, 1591, 1510, 1340, 1151, 898, 854 cm^{-1}.**HRMS** Calcd for $C_{19}H_{15}NO_2$ (M+Na) = 312.1000, found 312.0996.



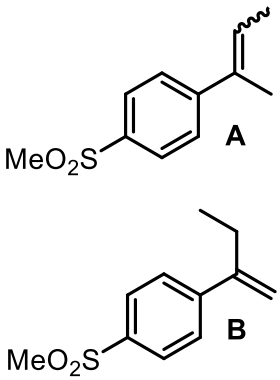
(E,Z)-1-nitro-4-(5-phenylpent-2-en-4-yn-2-yl)benzene (**3s**). General procedure 2.16 provided the styrene as a mixture of geometric isomers (E:Z; 89:11) in 75% yield (39.4 mg, Hex:EtOAc – 20:1). Yellow solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) E isomer: δ 8.26 – 8.16 (m, 2H), 7.66 – 7.58 (m, 2H), 7.56 – 7.43 (m, 2H), 7.36 – 7.25 (m, 3H), 6.26 (q, *J* = 1.1 Hz, –CC*H*CC–, 1H), 2.43 (d, *J* = 1.2 Hz, –CCH_3, 3H). Z isomer: δ 8.30 – 8.23 (m, 2H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.33 – 7.28 (m, 5H), 6.00 (q, *J* = 1.6 Hz, –CC*H*CC–, 1H), 2.28 (d, *J* = 1.5 Hz, –CCH_3, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.4, 147.3, 145.9, 145.5, 131.7, 131.5, 128.7, 128.6, 128.6, 126.2, 124.0, 123.4, 123.3, 123.2, 110.7, 109.7, 97.9, 93.4, 87.7, 87.5, 77.4, 77.2, 76.9, 24.0, 18.7. **IR** (film): 3072, 2923, 1590, 1511, 1488, 1151, 855 cm^{-1}. **HRMS** Calcd for $C_{17}H_{13}NO_2$ (M+Na) = 286.0844, found 286.0843.



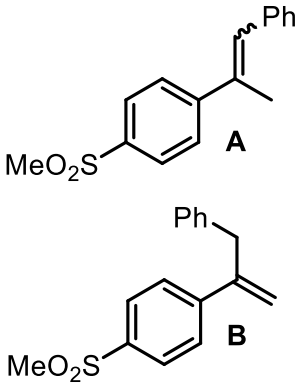
1-(prop-1-en-2-yl)-4-((trifluoromethyl)sulfonyl)benzene (**3t**). General procedure 2.16 provided the styrene as a colorless oil in 79% yield (39.5 mg, Hex:EtOAc – 8:2). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.99 (app d, *J* = 8.5 Hz, 2H), 7.72 (app d, *J* = 8.5 Hz, 2H), 5.57 (app p, *J* = 0.8 Hz, –CC*H*, 1H), 5.38 – 5.32 (m, –CC*H*, 1H), 2.20 (dd, *J* = 1.5, 0.9 Hz, –CCH_3, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 149.8, 141.6, 131.0, 129.6, 127.0, 119.9 (q, *J* = 325.9), 117.5, 21.6. **^{19}F NMR** (376 MHz, Chloroform-d) δ -78.49. **IR** (film): 2979, 1592, 1558, 1367, 1205, 1149, 764 cm^{-1} **HRMS** Calcd for $C_{10}H_9F_3O_2S$ (M+) = 250.0275, found 250.0280.



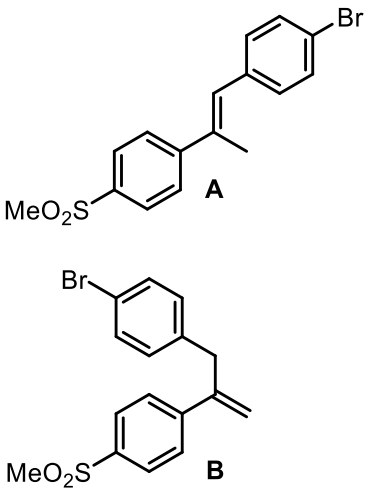
4-(prop-1-en-2-yl)benzonitrile (**3u**). General procedure 2.17 provided the styrene as a colorless oil in 65% yield (27.3 mg, Hex:EtOAc – 85:15); Temperature - 130 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.65 – 7.59 (m, 2H), 5.49 (s, –CC*H*, 1H), 5.28 – 5.24 (m, –CC*H*, 1H), 3.11 (q, *J* = 7.5 Hz, –$SO_2CH_2$$CH_3$, 2H), 2.20 – 2.16 (m, –CCH_3, 3H), 1.28 (t, *J* = 7.4 Hz, –$SO_2CH_2CH_3$, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.8, 142.0, 137.1, 128.4, 126.4, 115.9, 50.8, 21.7, 7.6. **IR** (film): 3087, 2974, 1593, 1540, 1146, 780 cm^{-1}. **HRMS** Calcd for $C_{11}H_{14}O_2S$ (M+Na) = 233.0612, found 233.0617.



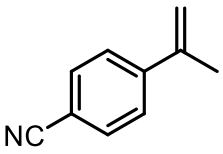
(E,Z)-1-(but-2-en-2-yl)-4-(methylsulfonyl)benzene and *1-(but-1-en-2-yl)-4-(methylsulfonyl)benzene* (**3v**). General procedure 2.17 provided the styrene as a mixture of regioisomers (**A**:**B**; 63:37) and geometric isomers (E:Z; 91:9) in 71% yield (Colorless oil, 29.8 mg, Hex:EtOAc – 85:15); Temperature - 130 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) Regioisomer **A** – E:Z mixture: [7.85 (app d, *J* = 8.6 Hz, maj.), 7.91 – 7.90 (m, min.) Σ2H], [7.52 (app d, *J* = 8.6 Hz, maj.), 7.62 (app d, *J* = 8.6 Hz, min.), Σ2H], [6.00 (qq, *J* = 6.9, 1.4 Hz, maj.), 5.71 – 5.61 (m, min.), –CC*H*CH$_3$, Σ1H], [3.04 (s, maj.), 3.05 (s, min.), –SO$_2$C*H$_3$*, Σ3H], [2.07 – 2.03 (m, maj.), 2.19 – 2.16 (m, min.), –CCHC*H$_3$*, Σ3H], [1.83 (dd, *J* = 6.9, 1.2 Hz, maj.), 2.03 – 2.01 (m, min.), –CC*H$_3$*, Σ3H]. Regioisomer **B** - δ 7.88 (app d, *J* = 8.6 Hz, 2H), 7.57 (app d, *J* = 8.5 Hz, 2H), 5.37 (d, *J* = 1.0 Hz, –CC*H*, 1H), 5.21 (d, *J* = 1.1 Hz, –CC*H*, 1H), 3.05 (s, –SO$_2$C*H$_3$*, 3H), 2.52 (qdd, *J* = 7.3, 1.6, 0.8 Hz, –CC*H$_2$*CH$_3$, 2H), 1.10 (t, *J* = 7.4 Hz, –CCH$_2$C*H$_3$*, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 149.6, 148.7, 147.4, 139.1, 138.2, 134.4, 127.6, 127.5, 127.1, 126.4, 126.4, 114.3, 77.2, 44.8, 44.7, 28.0, 15.5, 14.7, 12.9. **IR** (film): 3018, 2964, 1592, 1309, 1206, 1150, 779 cm^{-1}. **HRMS** Calcd for C$_{11}$H$_{14}$O$_2$S (M+Na) = 233.0612, found 233.0616.



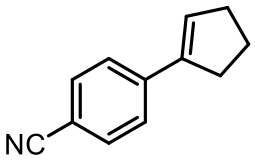
(E,Z)-1-(methylsulfonyl)-4-(1-phenylprop-1-en-2-yl)benzene & 1-(methylsulfonyl)-4-(3-phenylprop-1-en-2-yl)benzene (**3w**). General procedure 2.17 provided the styrene as a mixture of regioisomers (**A**:**B**; 83:17) and geometric isomers (E:Z; 92:8) in 75% yield (40.8 mg, Hex:EtOAc – 85:15); Temperature - 130 °C. Product matched the previously reported literature specification.[32] White solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) Regioisomer **A** - E:Z mixture: δ [7.98 – 7.89 (m, maj.), 7.84 (d, *J* = 8.6, min.), Σ2H], [7.74 – 7.66 (m, maj. & min.), Σ2H], [7.41 – 7.37 (m, maj.), 7.33 – 7.27 (m, min), Σ3H], [7.26 – 7.17 (m, maj.), 7.15 – 7.05 (m, min.), Σ2H], [6.93 (s, maj.), 6.61 (s, min), –CC*H*Ph, Σ1H], [3.08 (s, maj.), 3.06 (s, min), –SO$_2$C*H$_3$*, Σ3H], [2.31 (d, *J* = 1.3 Hz, maj.), 2.22 (d, *J* = 1.5 Hz, min.), –CC*H$_3$*, Σ3H]. Regiosiomer **B**: δ [7.84 (d, *J* = 8.6, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.41 – 7.26 (m, 3H), 7.21 – 7.08 (m, 2H), 5.60 (s, –CC*H*, 1H), 5.23 (d, *J* = 1.1 Hz, –CC*H*, 1H), 3.86 (s, SO$_2$C*H$_3$*, 3H), 3.03 (s, –CC*H$_2$*Ph, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 149.7, 146.4, 145.6, 139.3, 138.9, 138.9, 138.6, 137.5, 136.8, 135.9, 130.8, 129.5, 129.3, 129.2, 129.1, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 127.7, 127.6, 127.6, 127.6, 127.5, 127.3, 127.2, 127.1, 127.0, 126.9, 126.6, 126.3, 117.9, 77.4, 77.2, 76.9, 44.7, 44.7, 44.6, 42.1, 41.6, 29.8, 26.6, 21.2, 17.5. **IR** cm^{-1}.



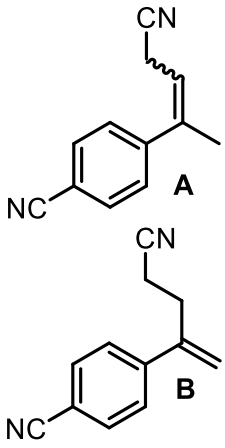
(E)-1-bromo-4-(2-(4-(methylsulfonyl)phenyl)prop-1-en-1-yl)benzene and *1-bromo-4-(2-(4-(methylsulfonyl)phenyl)allyl)benzene (***3x**). General procedure 2.17 provided the styrene as a mixture of regioisomers (**A**:**B**; 94:6) and geometric isomers (E:Z; > 95%) in 72% yield (White solid, 50.4 mg, Hex:EtOAc – 85:15); Temperature - 130 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) Regioisomer **A** - δ 7.93 (app d, *J* = 8.5 Hz, 2H), 7.68 (app d, *J* = 8.5 Hz, 2H), 7.52 (app d, *J* = 8.5 Hz, 2H), 7.24 (app d, *J* = 8.5 Hz, 2H), 6.83 (s, –CC*H*Ph, 1H), 3.08 (s, –SO$_2$C*H$_3$*, 3H), 2.28 (d, *J* = 1.4 Hz, –CC*H$_3$*, 3H). Regioisomer **B** - δ 7.87 – 7.85 (m, 2H), 7.39 (app d, *J* = 8.4 Hz, 2H), 7.07 (app d, *J* = 8.4 Hz, 2H), 6.90 (app d, *J* = 8.4 Hz, 2H), 5.60 (s, –CC*H*, 1H), 5.25 – 5.14 (m, –CC*H*, 1H), 3.80 (s, –CC*H$_2$*, 2H), 3.07 (s, –SO$_2$C*H$_3$*, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) Regioisomer **A** - δ 149.3, 139.1, 136.7, 136.4, 131.6, 130.9, 129.5, 127.7, 127.0, 121.3, 44.7, 17.6. Regioisomer **B** - δ 138.7, 131.5, 130.6, 128.2, 127.1, 118.1, 44.7, 44.0. **IR** (film): 3016, 2918, 1559, 1484, 1302, 1142, 763 cm^{-1}. **HRMS** Calcd for C$_{16}$H$_{15}$BrO$_2$SNa (M+Na) = 372.9874, found 372.9870.



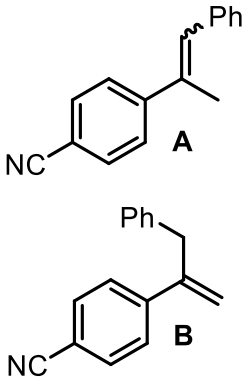
4-(prop-1-en-2-yl)benzonitrile (**3y**). General procedure 2.17 provided the styrene as a colorless oil in 77% NMR yield. Product matched the previously reported literature specification.[33] The product was volatile, and the isolated yield was 67% (0.2 mmol scale, 4 hours, 19.2 mg, Pentane:Et_2O – 20:1); Temperature - 110 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 – 7.59 (m, 2H), 7.59 – 7.51 (m, 2H), 5.47 (s, –CC*H*, 1H), 5.27 – 5.22 (m, –CC*H*, 1H), 2.18 – 2.13 (m, –CCH_3, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 145.81, 141.95, 132.24, 126.26, 119.11, 115.78, 110.99, 21.57.



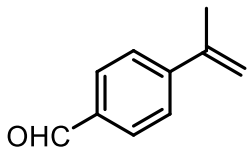
4-(cyclopent-1-en-1-yl)benzonitrile (**3z**). General procedure 2.17 provided the styrene as a white solid 70% yield (0.1 mmol scale, 6 hours, 12 mg, Pentane:Et_2O – 20:1); Temperature - 110 °C. Product matched the previously reported literature specification.[34] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 2H), 7.54 – 7.46 (m, 2H), 6.36 (ddd, *J* = 4.6, 2.7, 1.9 Hz, –CC*H*CH_2–, 1H), 2.70 (ddt, *J* = 8.4, 4.4, 2.2 Hz, –CC$H_2$$CH_2$–, 2H), 2.57 (ddt, *J* = 7.7, 5.1, 2.6 Hz, –CCHCH_2– 2H), 2.05 (p, *J* = 7.1 Hz, –$CCH_2$$CH_2$–, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.38, 141.32, 132.28, 130.80, 126.17, 119.36, 110.08, 33.74, 33.06, 23.37.



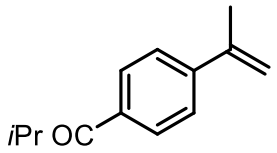
4-(4-cyanobut-2-en-2-yl)benzonitrile & 4-(4-cyanobut-1-en-2-yl)benzonitrile (**3aa**). General procedure 2.17 provided the styrene as a mixture of regioisomers (**A**:**B**; 77:23) and geometric isomers (E:Z; 87:13) in 61% yield (0.1 mmol scale, 4 hours, yellow oil, 11.1 mg, Hex:EtOAc – 3:2); Temperature - 110 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) Regioisomer **A** - E:Z mixture: δ [7.66 – 7.60 (m, maj. & min.), Σ2H], [7.48 – 7.43 (m, maj. & min.), Σ2H], [5.85 – 5.77 (m, maj.), 5.59 (td, *J* = 7.4, 1.5 Hz, min.), –CC*H*CH_2CN, Σ1H), [3.32 – 3.25 (m, maj.), 2.95 – 2.90 (m, min), –CCHCH_2CN, Σ2H], [2.15 – 2.08 (s, maj. & min.), –CCH_3, Σ3H]. Regiosomer **B**: δ 7.73 – 7.61 (m, 2H), 7.51 – 7.43 (m, 2H), 5.53 (s, –CC*H*, 1H), 5.37 (s, –CC*H*, 1H), 2.87 (t, *J* = 7.0 Hz, –CCH_2CH_2CN, 2H), 2.49 (t, *J* = 7.3 Hz, –CC$H_2$$CH_2$CN, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.6, 138.6, 137.5, 135.9, 132.4, 132.3, 132.3, 130.6, 129.3, 129.3, 129.1, 128.9, 128.8, 128.7, 128.5, 128.3, 127.3, 127.0, 126.9, 126.7, 126.6, 119.2, 117.7, 110.7, 77.4, 77.2, 76.9, 41.5, 26.4, 17.3. **IR** (film): 3060, 2925, 2249, 2226, 1684, 1605, 1504, 1406, 1154, 846 cm^{-1}. **HRMS** Calcd for $C_{12}H_{11}N_2$ (M+H) = 183.0922, found 183.0933.



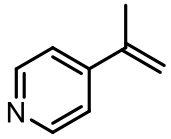
4-(1-phenylprop-1-en-2-yl)benzonitrile & 4-(3-phenylprop-1-en-2-yl)benzonitrile (**3ab**). General procedure 2.17 provided the styrene as a mixture of regioisomers (**A**:**B**; 88:12) and geometric isomers (E:Z; 94:6) in 82% yield (0.1 mmol scale, 6 hours, white solid, 18 mg, Hex:EtOAc – 20:1); Temperature - 110 °C. Product matched the previously reported literature specification.[35] **^{1}H NMR** (400 MHz, Chloroform-*d*) Regioisomer **A** - E:Z mixture: δ [7.63 – 7.56 (m, maj. & min.), Σ2H], [7.56 – 7.52 (m, maj. & min.), Σ2H], [7.36 – 7.26 (m, maj. & min.), Σ4H), [7.25 – 7.19 (m, maj. & min.), Σ1H], [6.85 (s, maj.), 6.51 (s, min.), –CC*H*Ph–, Σ1H], [2.21 (d, *J* = 1.3 Hz, maj.), 2.13 (d, *J* = 1.6 Hz, min.), –CCH_3, Σ3H]. Regiosomer **B**: δ 7.49 – 7.45 (m, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.17 – 7.08 (m, 3H), 7.07 – 7.02 (m, 2H), 5.51 (s, –CC*H*, 1H), 5.14 (d, *J* = 1.1 Hz, –CC*H*, 1H), 3.76 (s, –CCH_2Ph, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.6, 138.6, 137.5, 135.9, 132.4, 132.3, 132.3, 130.6, 129.3, 129.3, 129.1, 128.9, 128.8, 128.7, 128.5, 128.3, 127.3, 127.0, 126.9, 126.7, 126.6, 119.2, 117.7, 110.7, 77.4, 77.2, 76.9, 41.5, 26.4, 17.3.



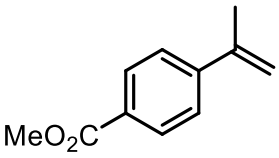
4-(prop-1-en-2-yl)benzaldehyde (**3ac**). General procedure 2.17 provided the styrene as a colorless liquid in 61% NMR yield. The product was volatile, and the isolated yield was 47% (0.2 mmol scale, 4 hours, 14 mg, Pentane:Et_2O – 10:1); Temperature - 115 °C. Product matched the previously reported literature specification.[36] **^{1}H NMR** (400 MHz, Acetonitrile-d_3) δ 9.98 (s, –C*HO*, 1H), 7.90 – 7.81 (m, 2H), 7.74 – 7.64 (m, 2H), 5.59 – 5.54 (m, –CC*H*, 1H), 5.30 – 5.24 (m, –CC*H*, 1H), 2.19 (dd, *J* = 1.4, 0.8 Hz, –CCH_3, 3H). **^{13}C NMR** (126 MHz, CD_3CN) δ 193.1, 147.8, 143.6, 136.6, 130.5, 127.1, 115.9, 21.7.



2-methyl-1-(4-(prop-1-en-2-yl)phenyl)propan-1-one (**3ad**). General procedure 2.17 provided the styrene as a colorless oil in 62% yield (0.15 mmol scale, 6 hours, 17.5 mg, Pentane:DCM – 4:1); Temperature - 140 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.99 – 7.86 (m, 2H), 7.61 – 7.51 (m, 2H), 5.49 – 5.46 (m, –CC*H*, 1H), 5.22 – 5.18 (m, –CC*H*, 1H), 3.55 (p, *J* = 6.9 Hz, –COC*H*$(CH_3)_2$, 1H), 2.18 (dd, *J* = 1.4, 0.8 Hz, –CCH_3, 3H), 1.22 (d, *J* = 6.9 Hz, –COCH(CH_3)$_2$, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 204.2, 145.7, 142.6, 135.1, 128.6, 125.8, 114.7, 35.5, 21.8, 19.3. **IR** (film): 3056, 2969, 1717, 1682, 1405, 1355, 1151, 868 cm^{-1}. **HRMS** Calcd for $C_{13}H_{17}O$ (M+H) = 189.1279, found 189.1276.

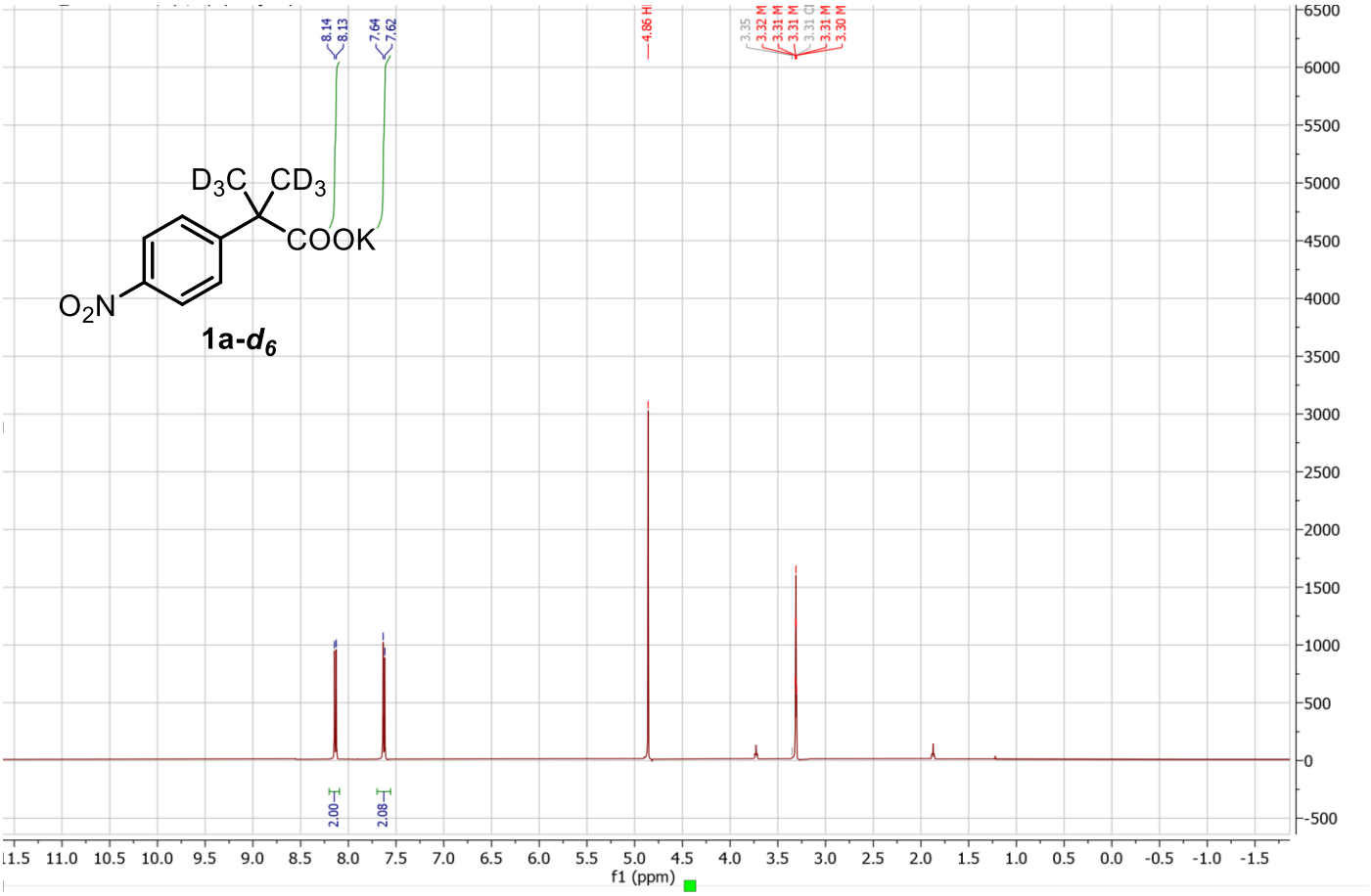


4-(prop-1-en-2-yl)pyridine (**3ae**). General procedure 2.17 provided the styrene as an yellow oil in 70% NMR yield. The product was volatile, and the isolated yield was 59% (0.1 mmol scale, 4 hours, 7 mg, Pentane:Et_2O – 1:1); Temperature - 140 °C. Product matched with previous reported literature specification.[25] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 5.9 Hz, 2H), 7.36 – 7.30 (m, 2H), 5.59 – 5.54 (m, –CC*H*, 1H), 5.26 (q, *J* = 1.4 Hz, –CC*H*, 1H), 2.14 (dd, *J* = 1.5, 0.7 Hz, –CCH_3, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.1, 148.4, 141.2, 120.3, 116.0, 21.0.

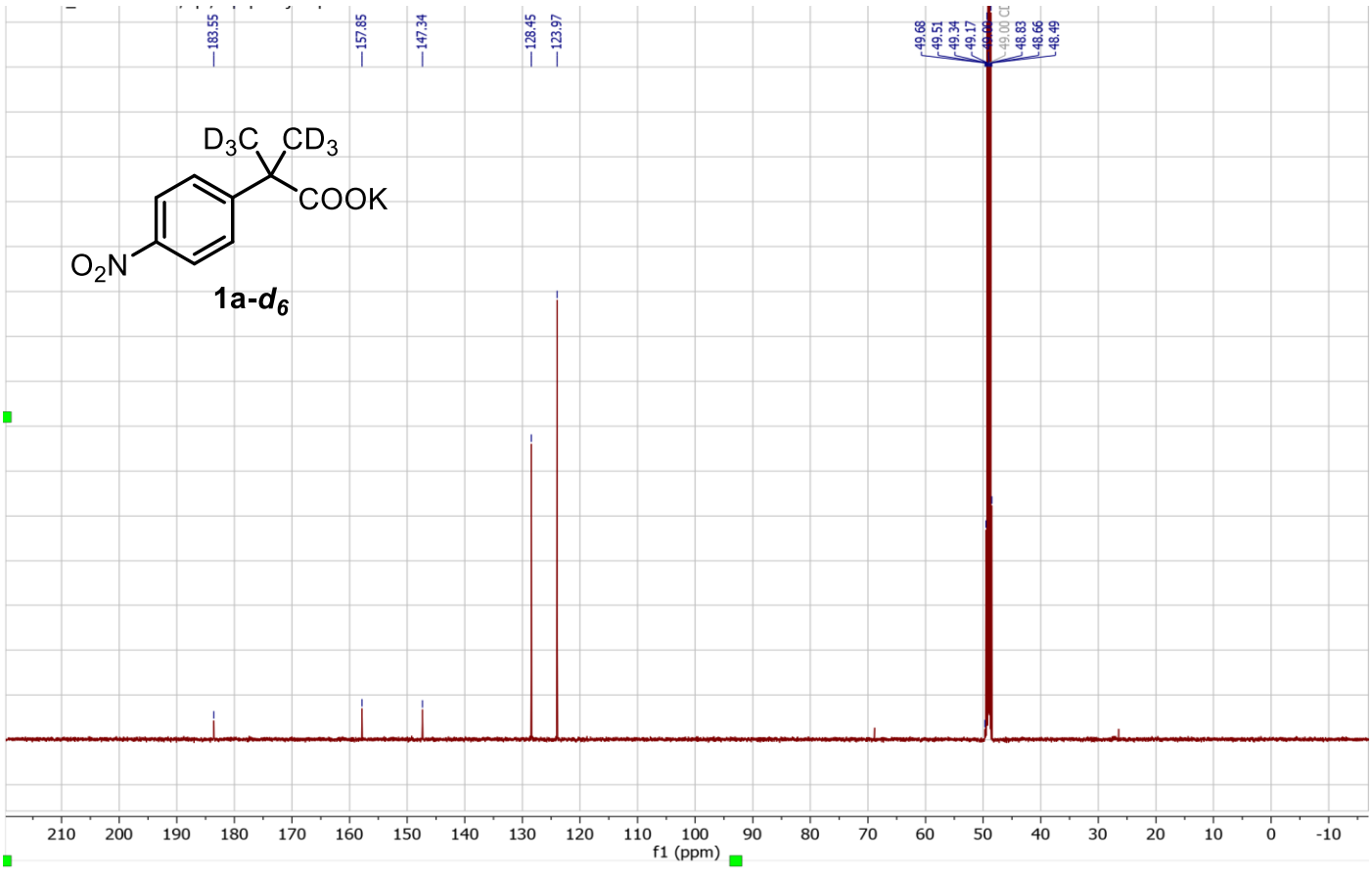


methyl 4-(prop-1-en-2-yl)benzoate (**3af**). General procedure 2.17 provided the styrene as a white solid in 72% NMR yield (0.15 mmol scale, 6 hours, 19 mg, Hex: EtOAc – 10:1); Temperature - 150 °C. Product matched with previous reported literature specification.[37] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 – 7.93 (m, 2H), 7.56 – 7.48 (m, 2H), 5.49 – 5.45 (m, –CC*H*, 1H), 5.22 – 5.17 (m, –CC*H*, 1H), 3.92 (s, –CO_2CH_3, 3H), 2.17 (dd, *J* = 1.4, 0.8 Hz, –CCH_3, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 145.8, 142.6, 129.7, 129.1, 125.6, 114.7, 52.2, 21.8.

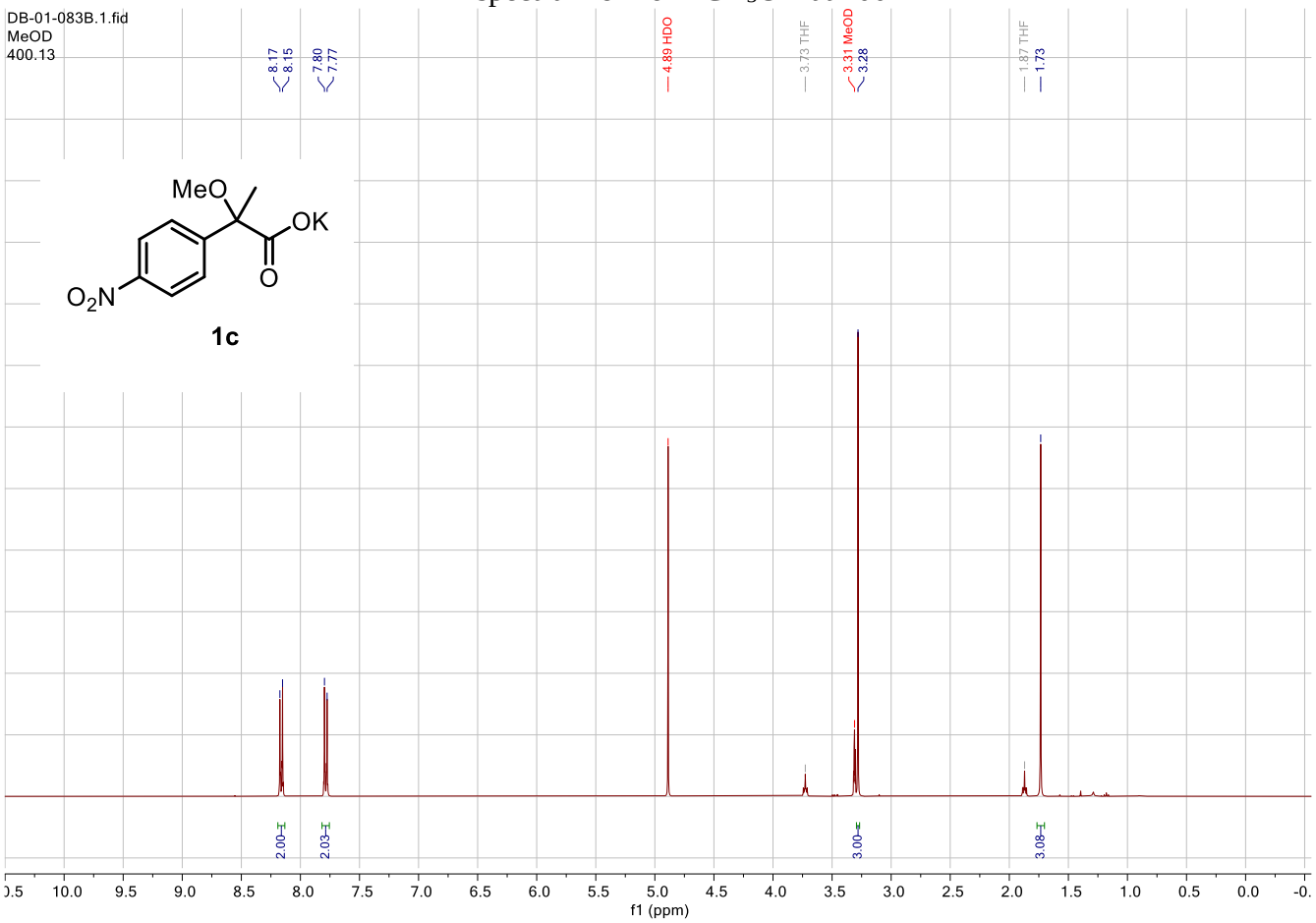
^{1}H NMR spectrum of **1a-*d*$_6$** in CD_3OD at 500 MHz



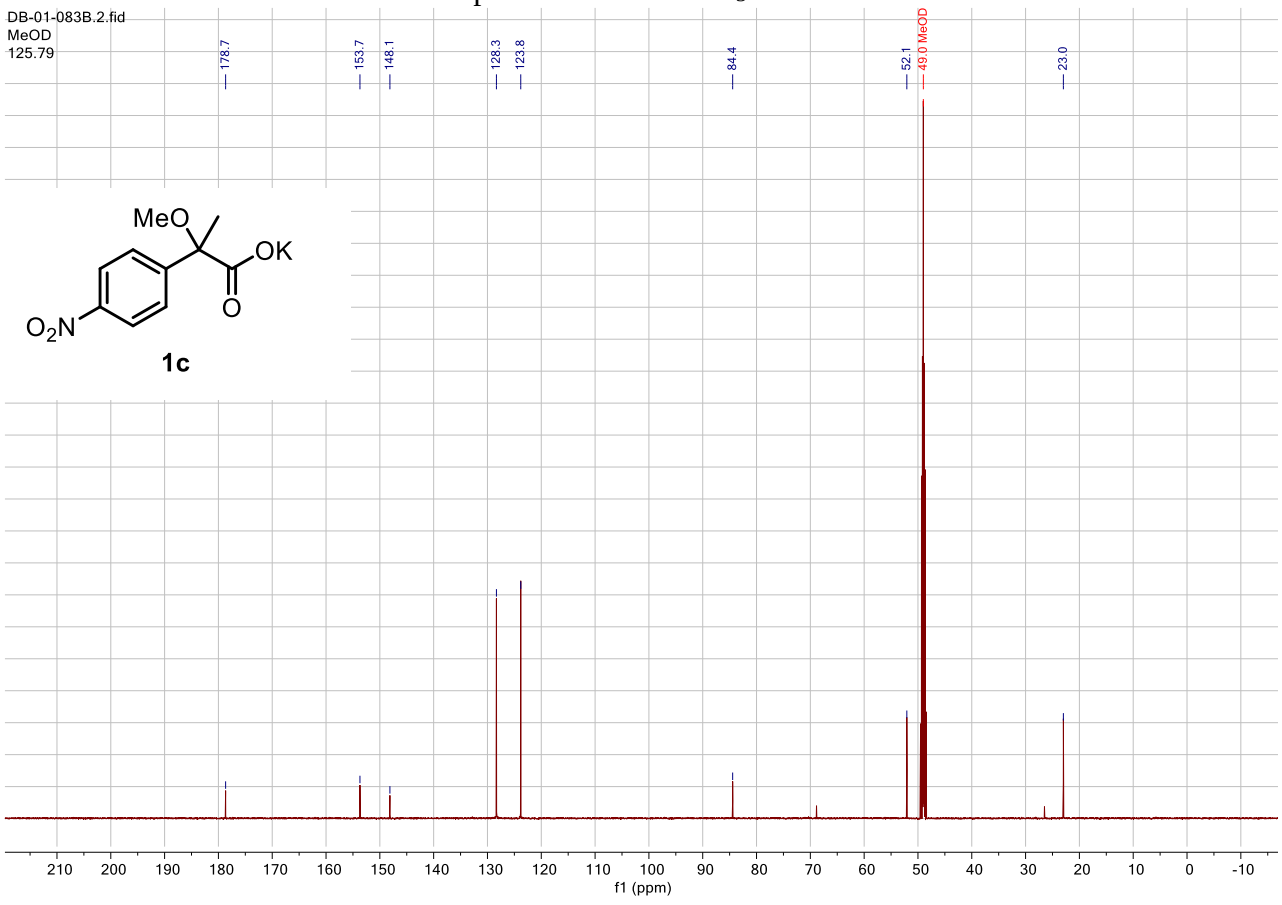
^{13}C NMR spectrum of **1a-*d*$_6$** in CD_3OD at 126 MHz



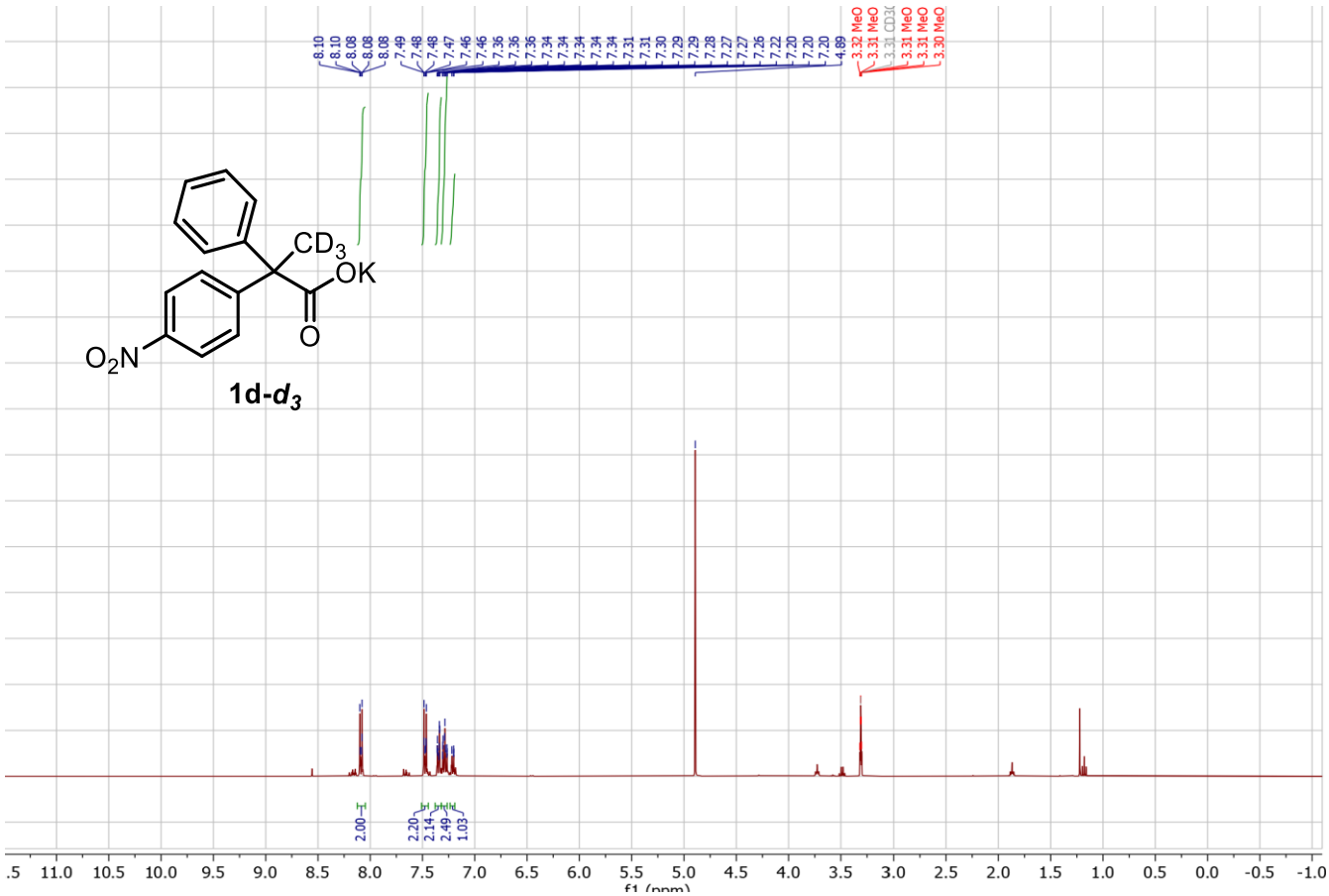
^{1}H NMR spectrum of **1c** in CD_3OD at 400 MHz



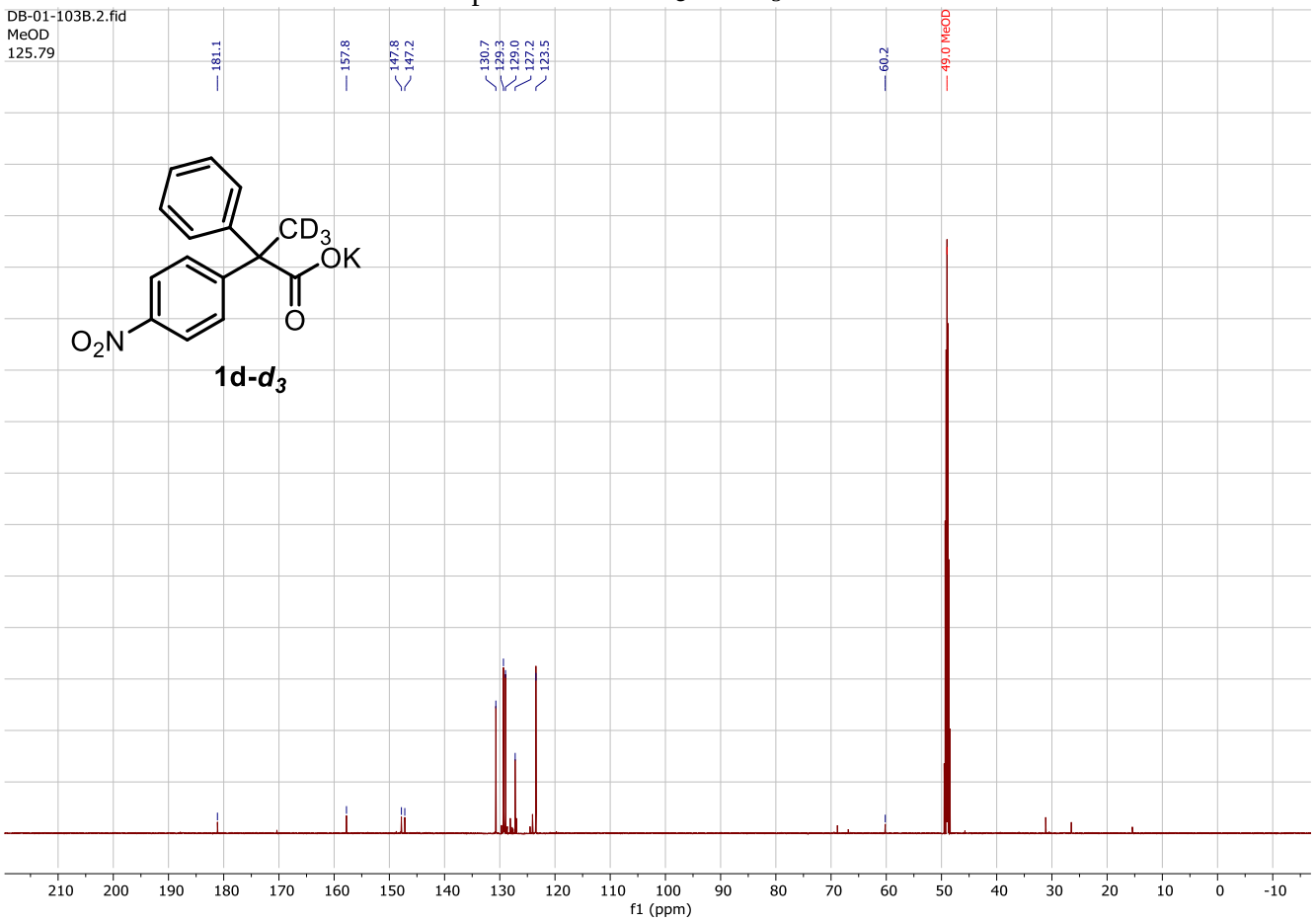
^{13}C NMR spectrum of **1c** in CD_3OD at 126 MHz



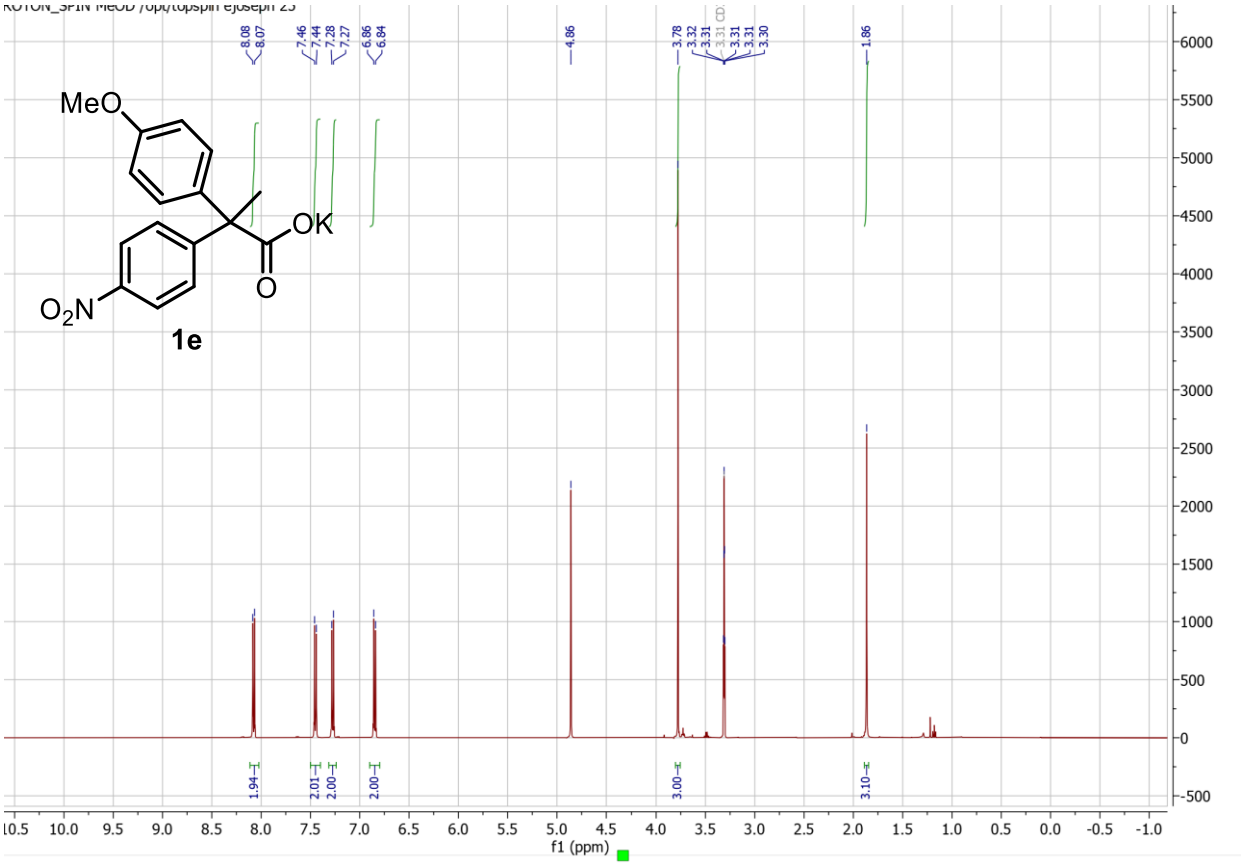
^{1}H NMR spectrum of **1d-*d*$_3$** in CD_3OD at 500 MHz



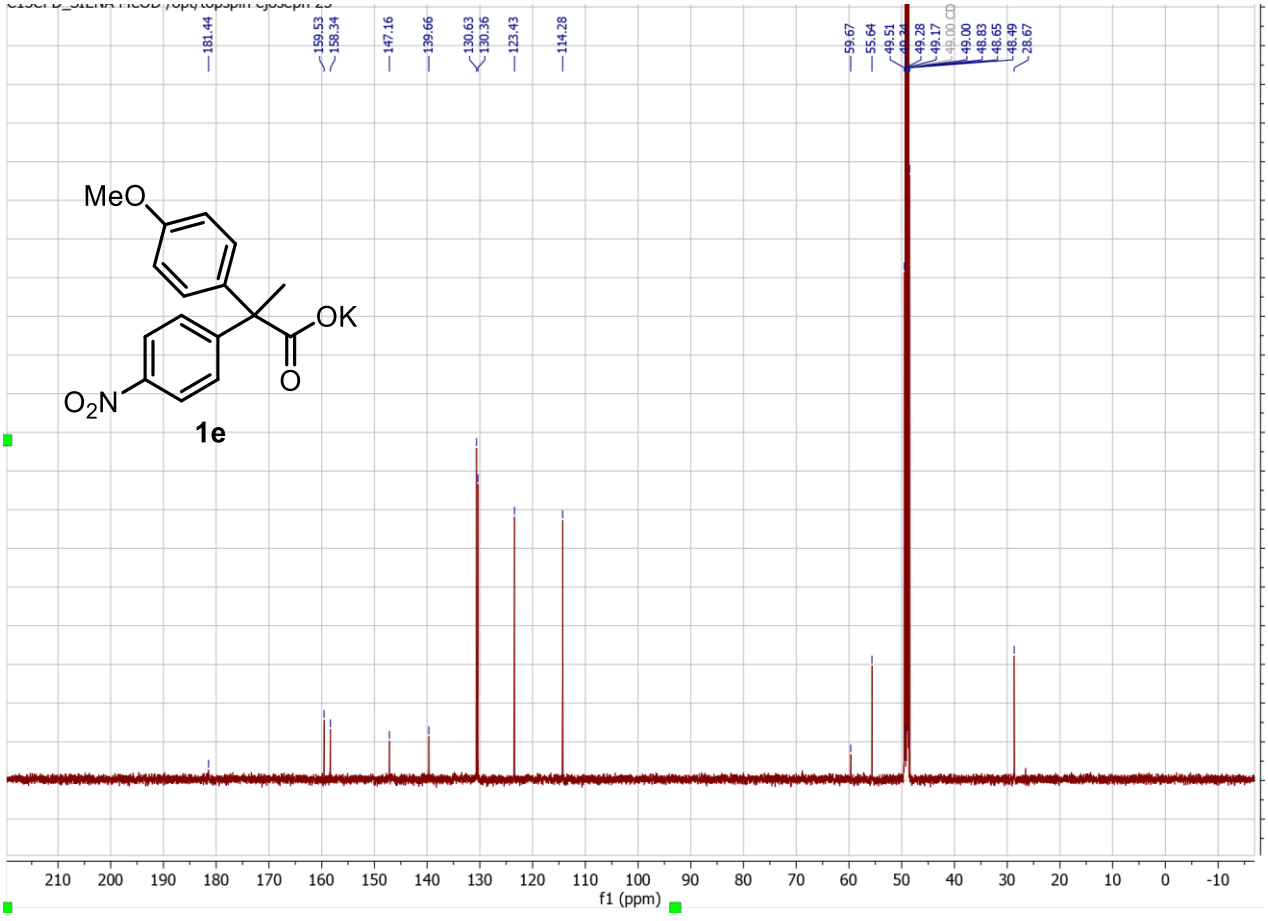
^{13}C NMR spectrum of **1d-*d*$_3$** in CD_3OD at 126 MHz



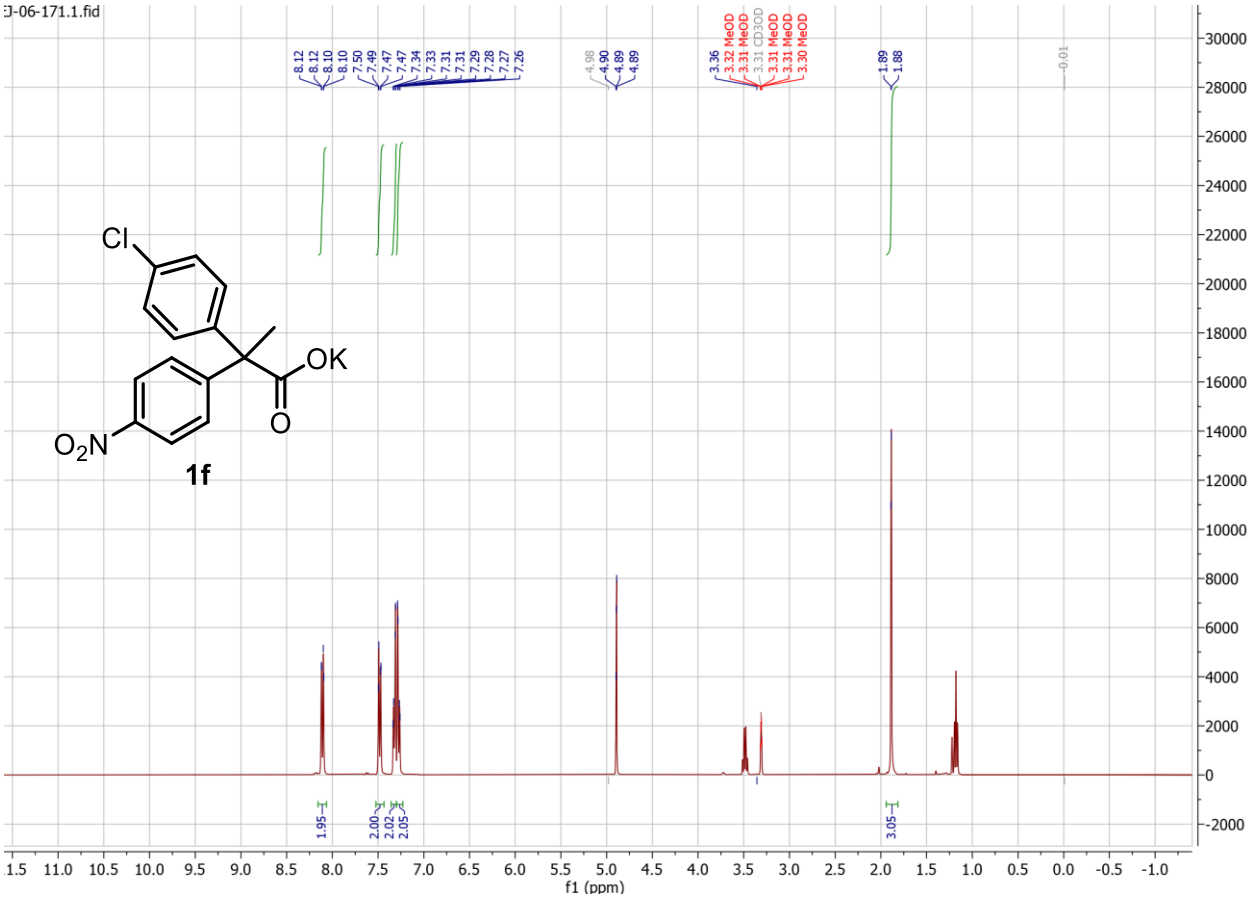
^{1}H NMR spectrum of **1e** in CD_3OD at 500 MHz



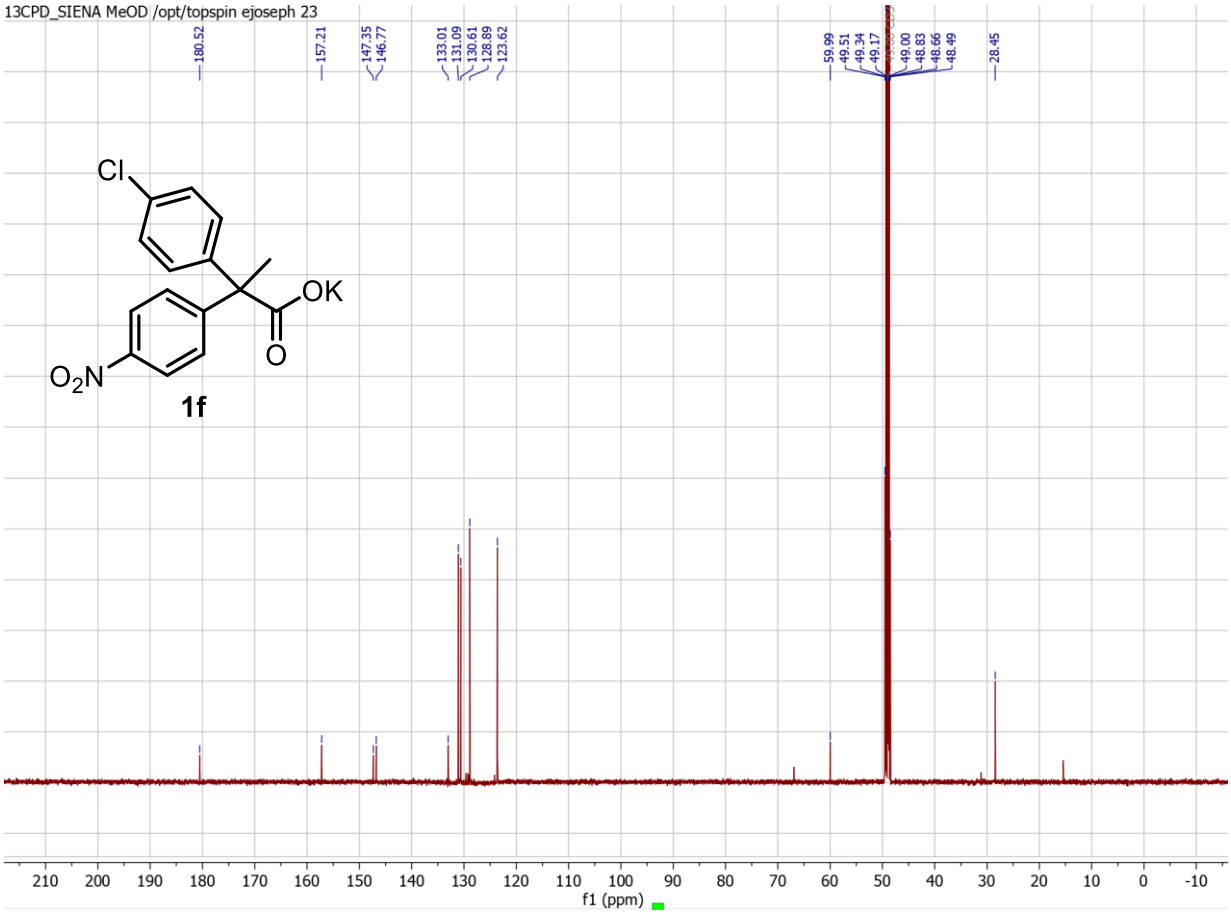
^{13}C NMR spectrum of **1e** in CD_3OD at 126 MHz



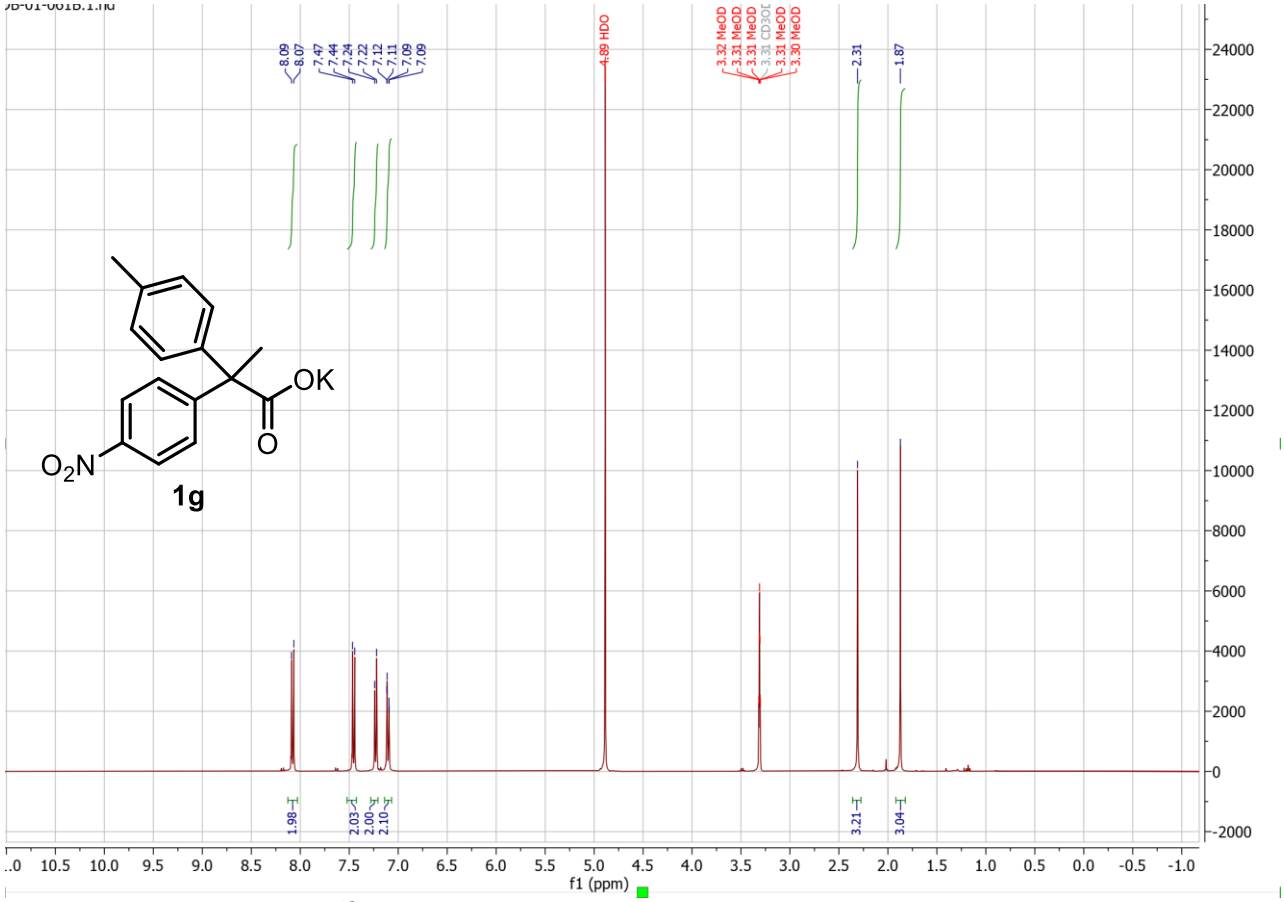
^{1}H NMR spectrum of **1f** in CD_3OD at 400 MHz



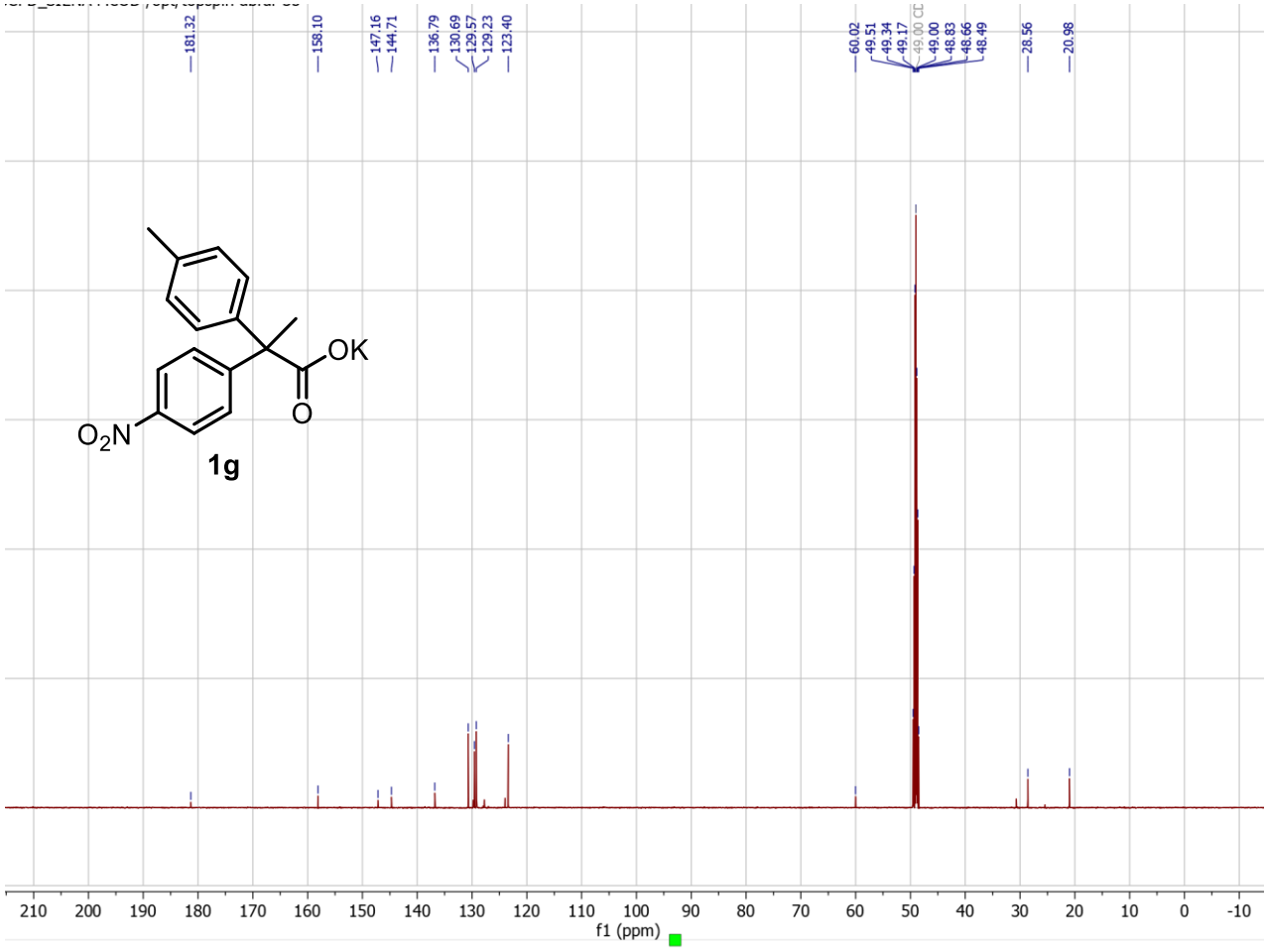
^{13}C NMR spectrum of **1f** in CD_3OD at 126 MHz



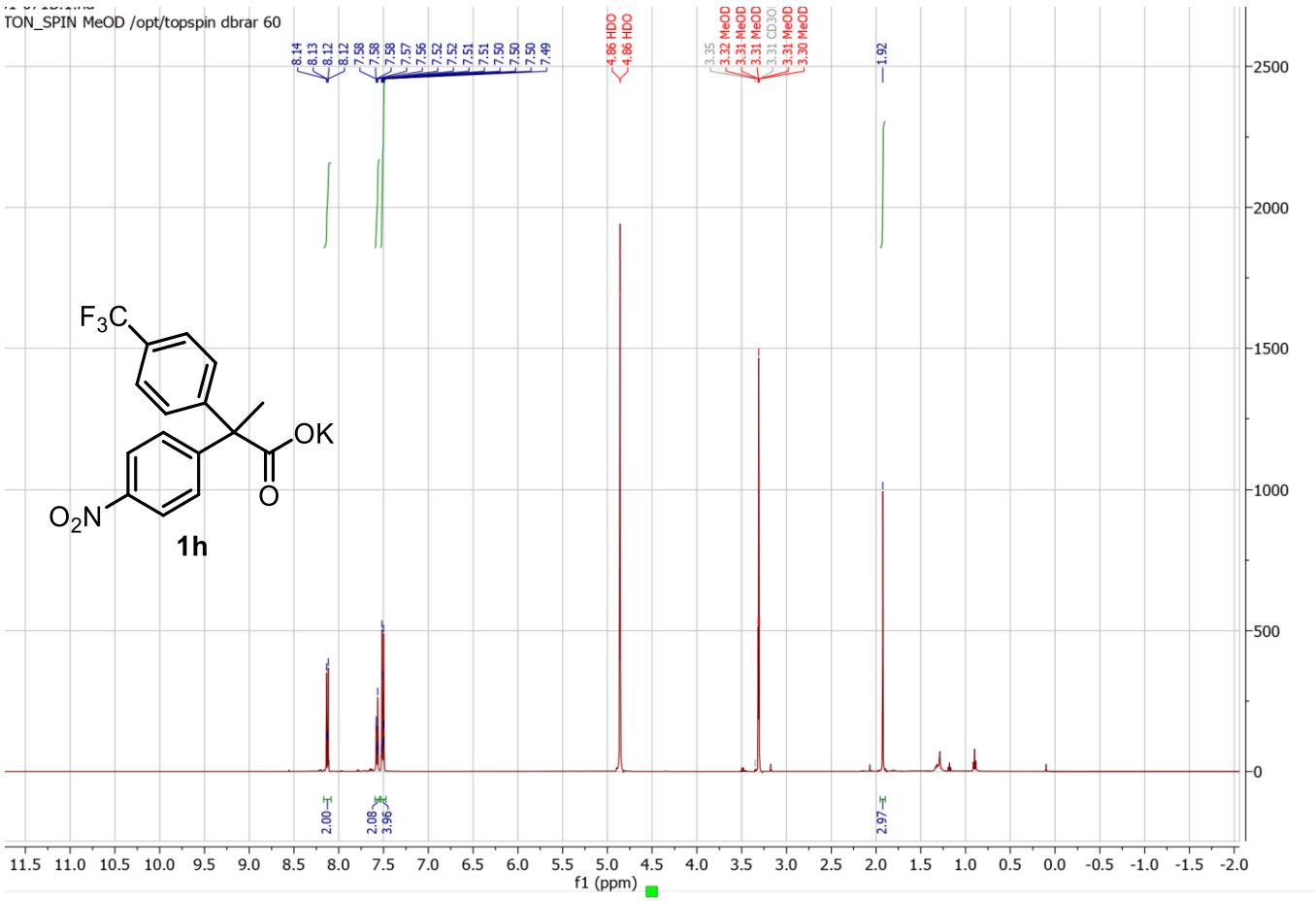
^{1}H NMR spectrum of **1g** in CD_3OD at 400 MHz



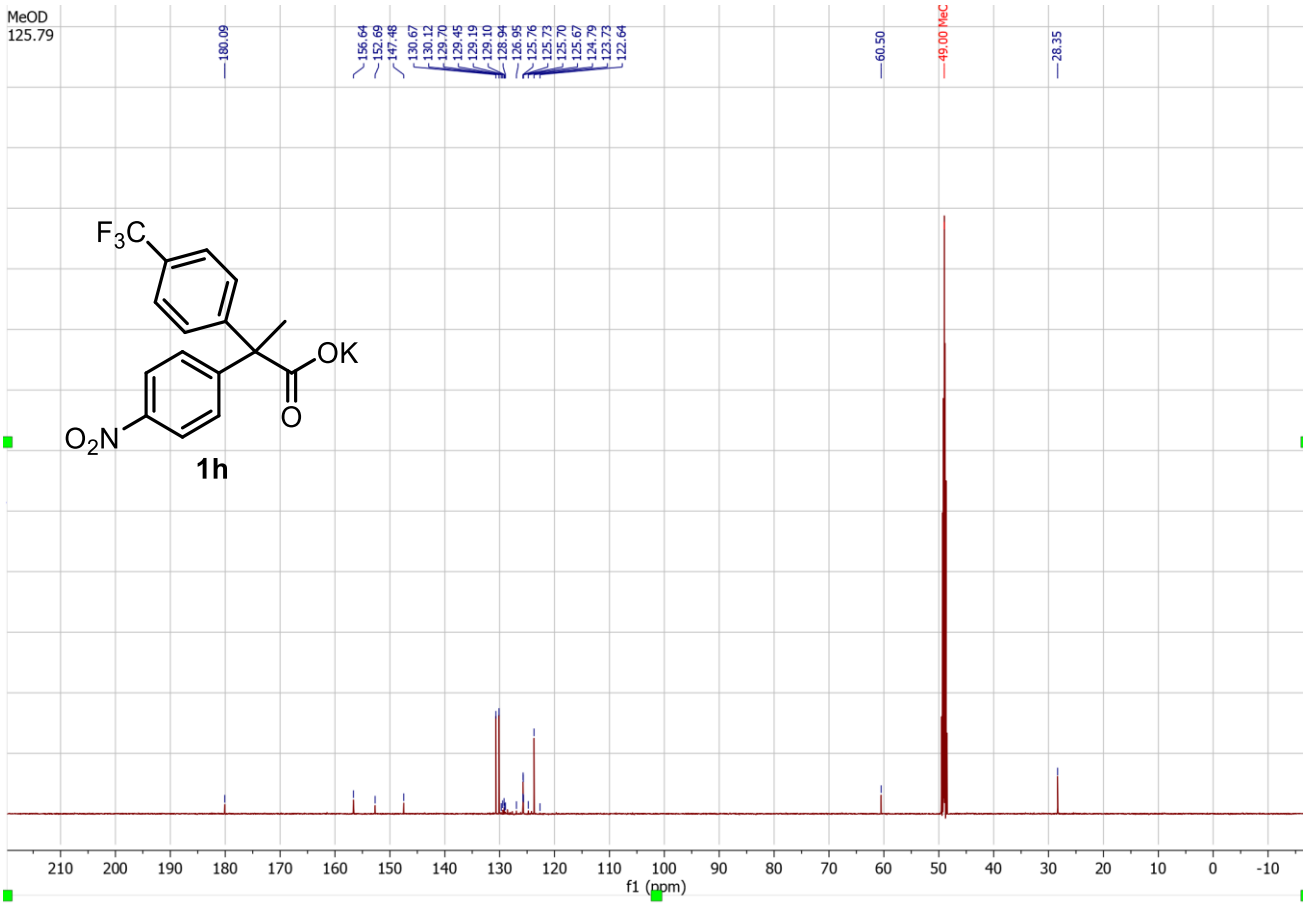
^{13}C NMR spectrum of **1g** in CD_3OD at 126 MHz



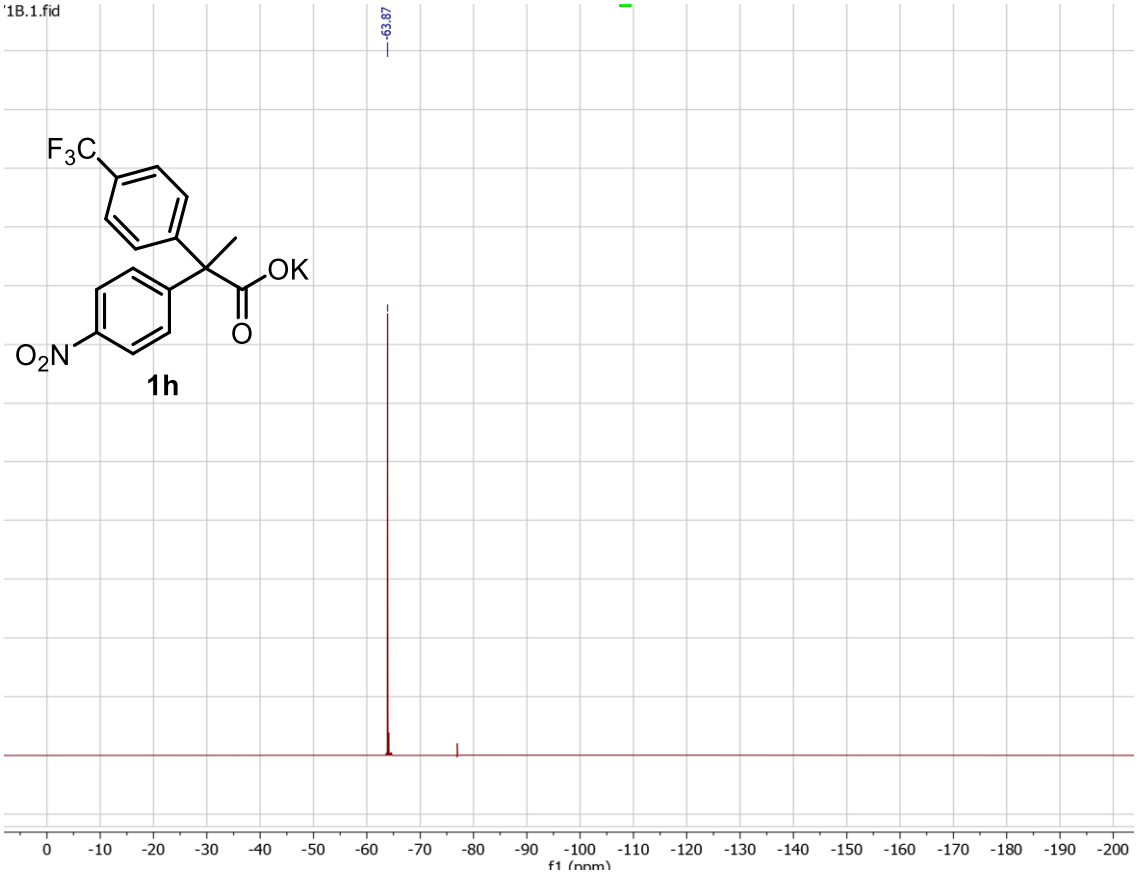
^{1}H NMR spectrum of **1h** in CD_3OD at 500 MHz



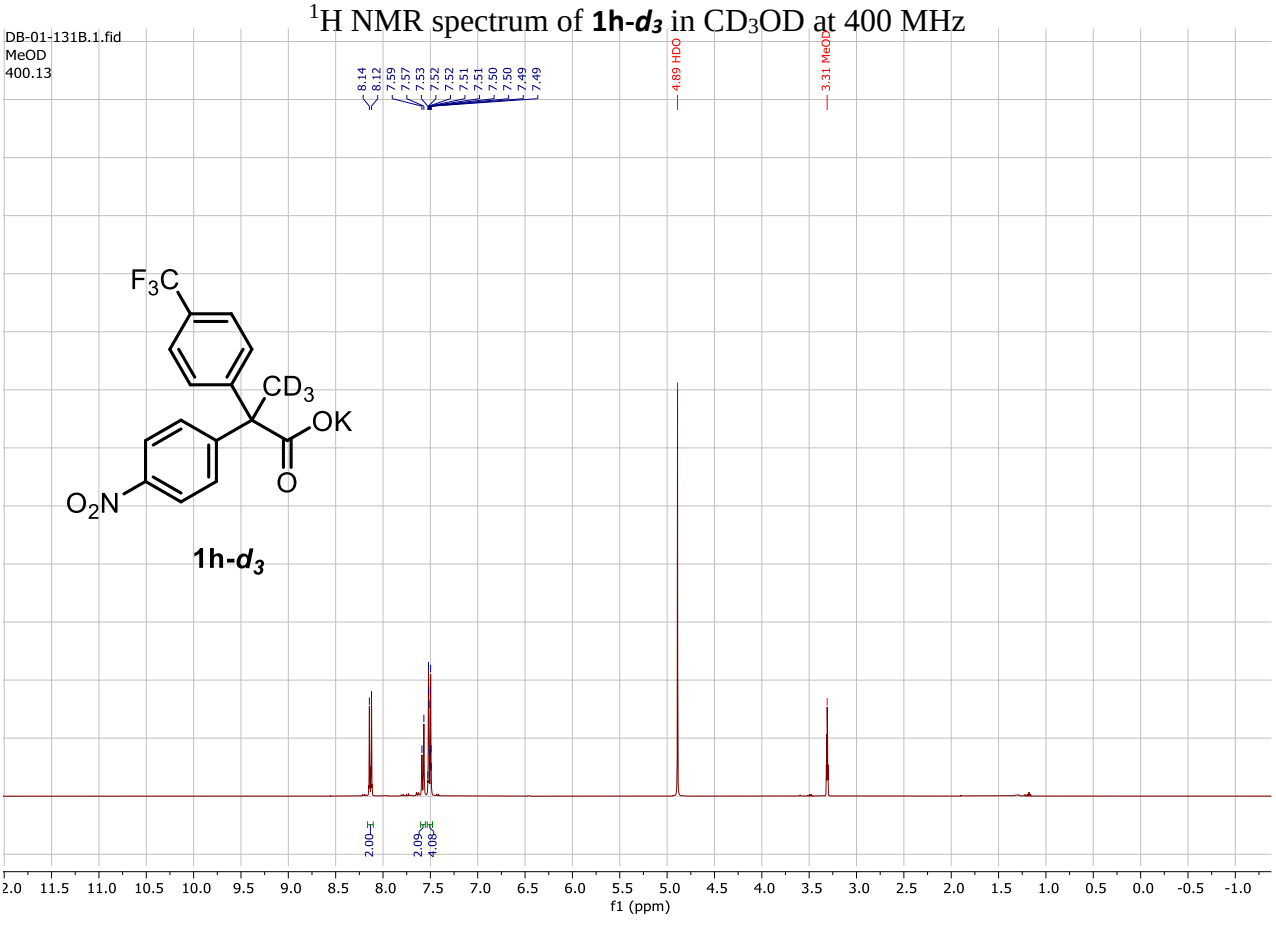
^{13}C NMR spectrum of **1h** in CD_3OD at 126 MHz



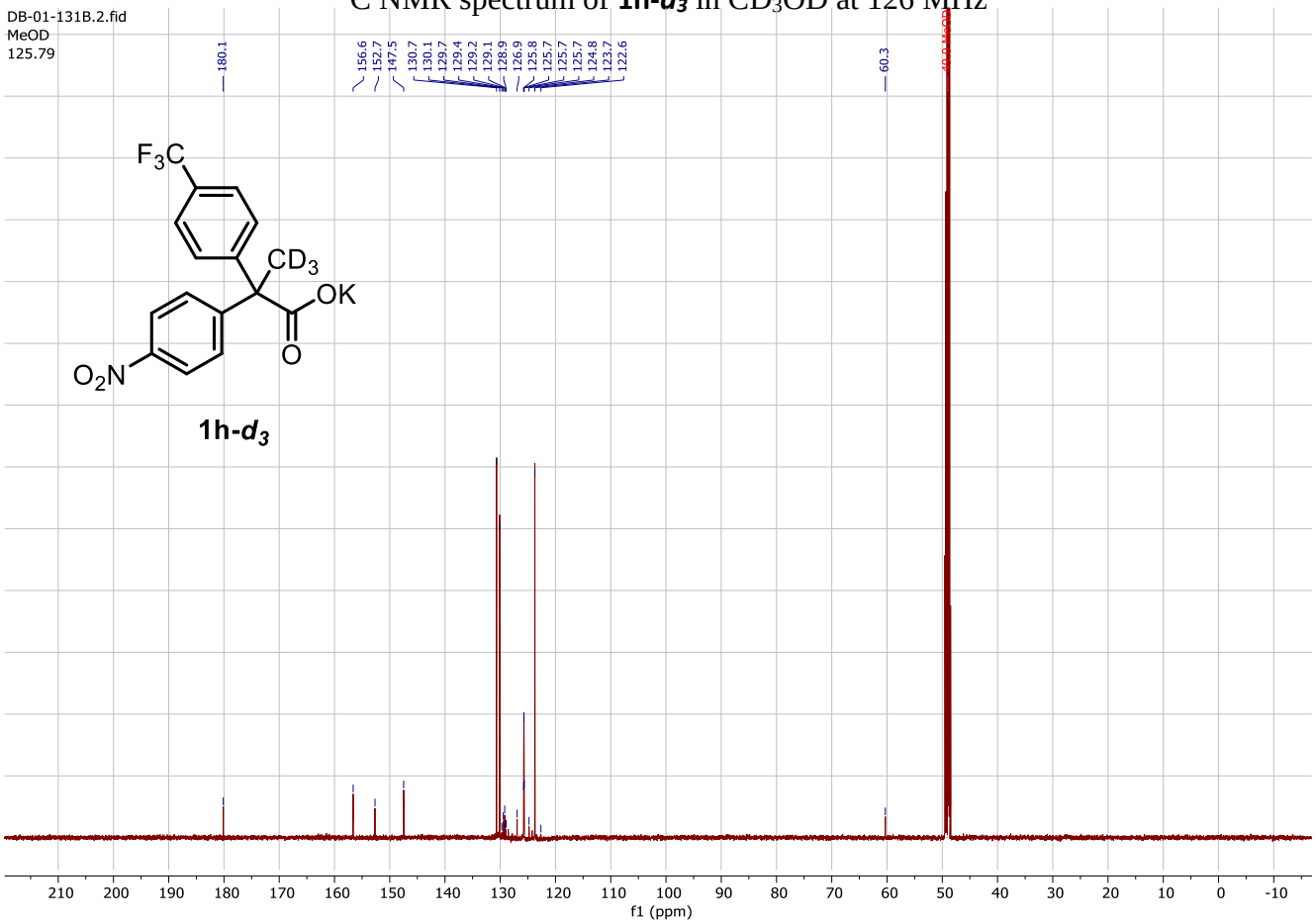
^{19}F NMR spectrum of **1h** in CD_3OD at 376 MHz



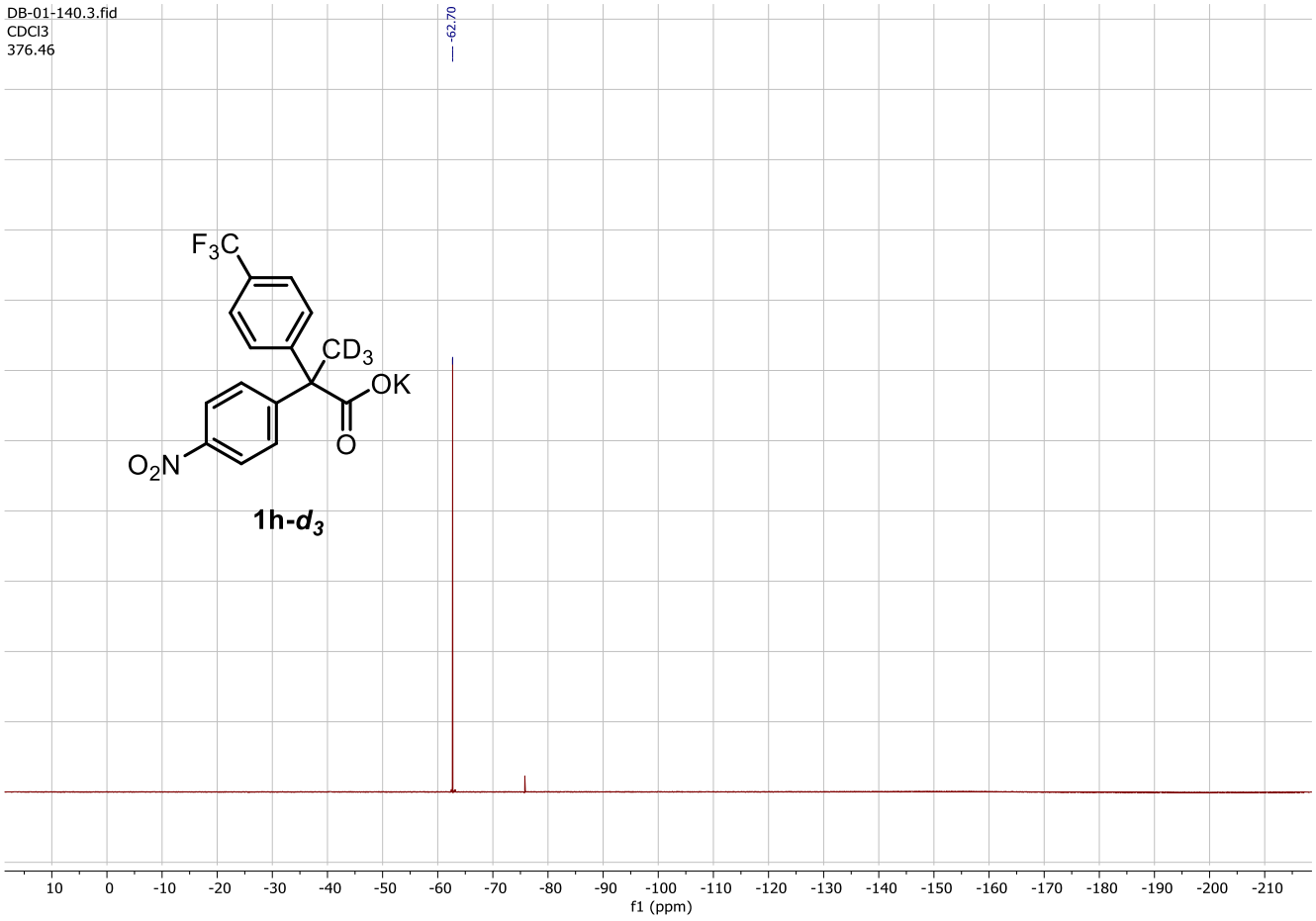
^{1}H NMR spectrum of **1h-*d*$_3$** in CD_3OD at 400 MHz



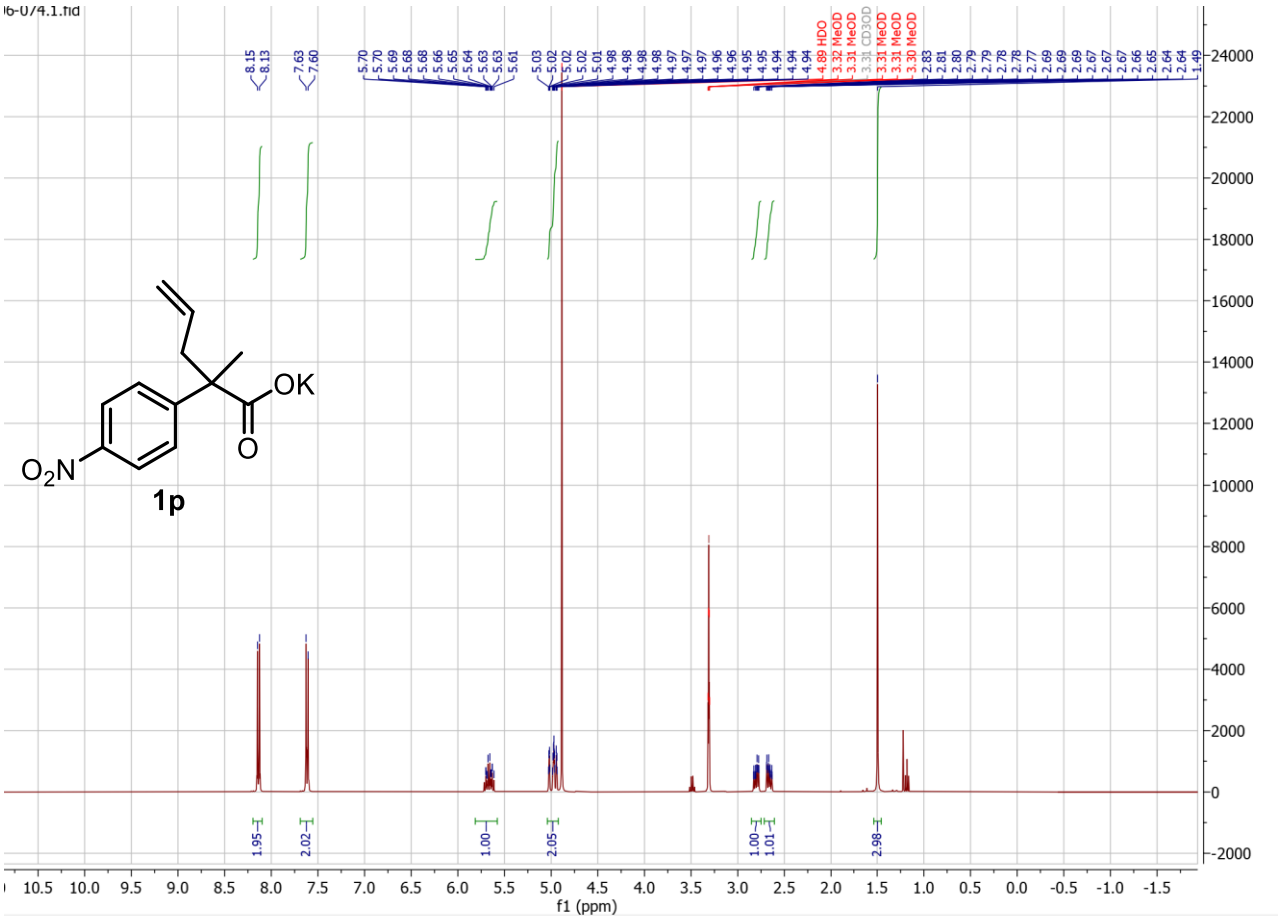
^{13}C NMR spectrum of **1h-*d*$_3$** in CD_3OD at 126 MHz



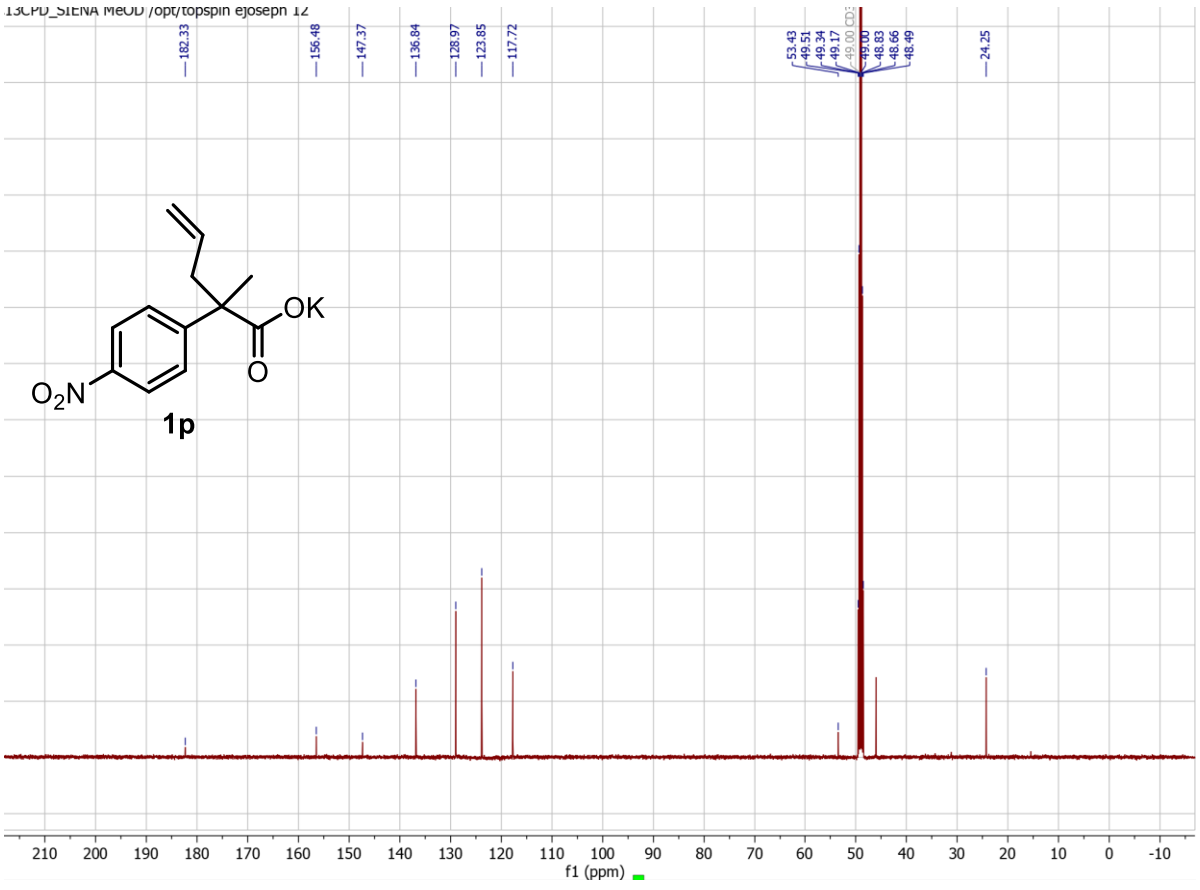
^{19}F NMR spectrum of **1h-*d*$_3$** in CD_3OD at 376 MHz



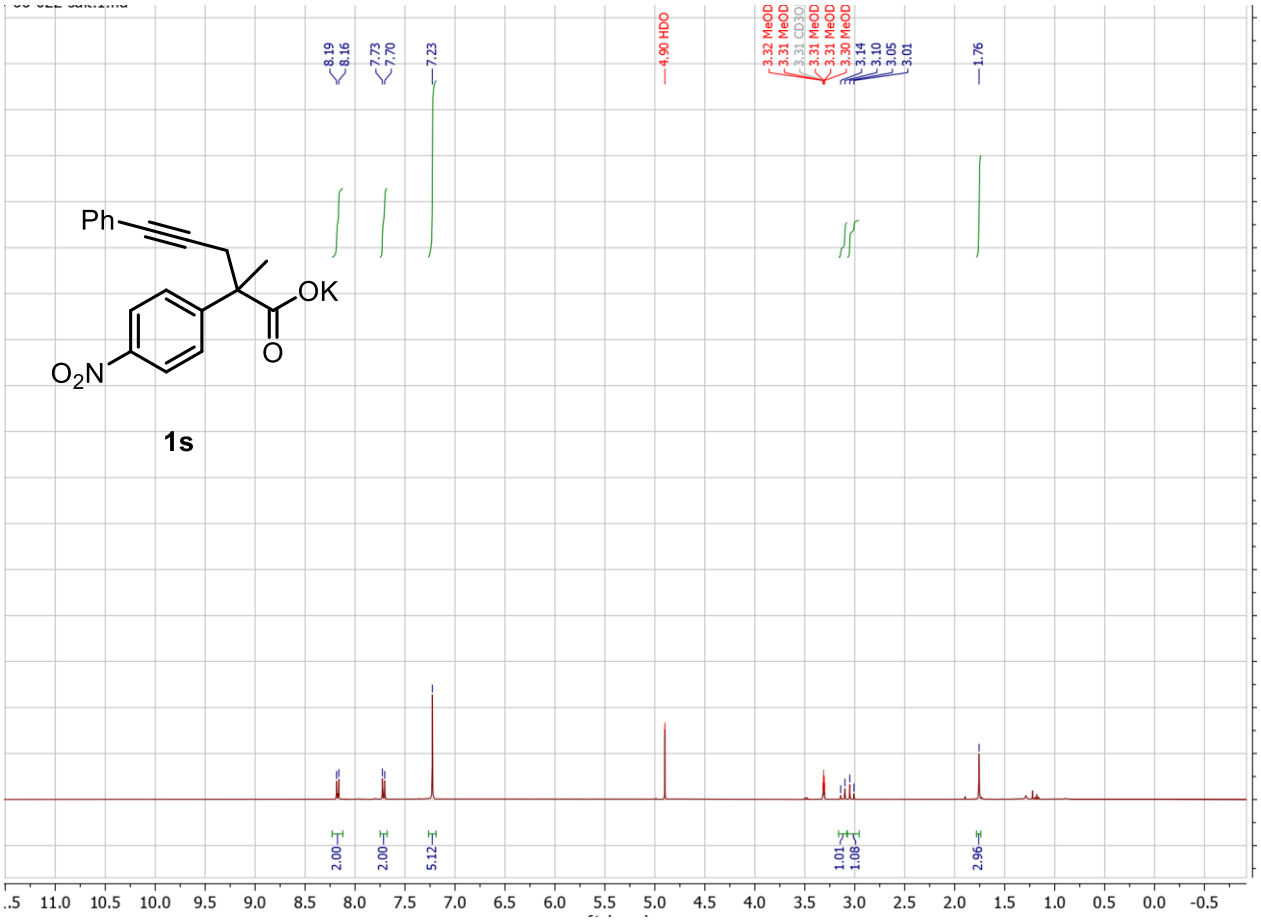
^{1}H NMR spectrum of **1p** in CD_3OD at 400 MHz



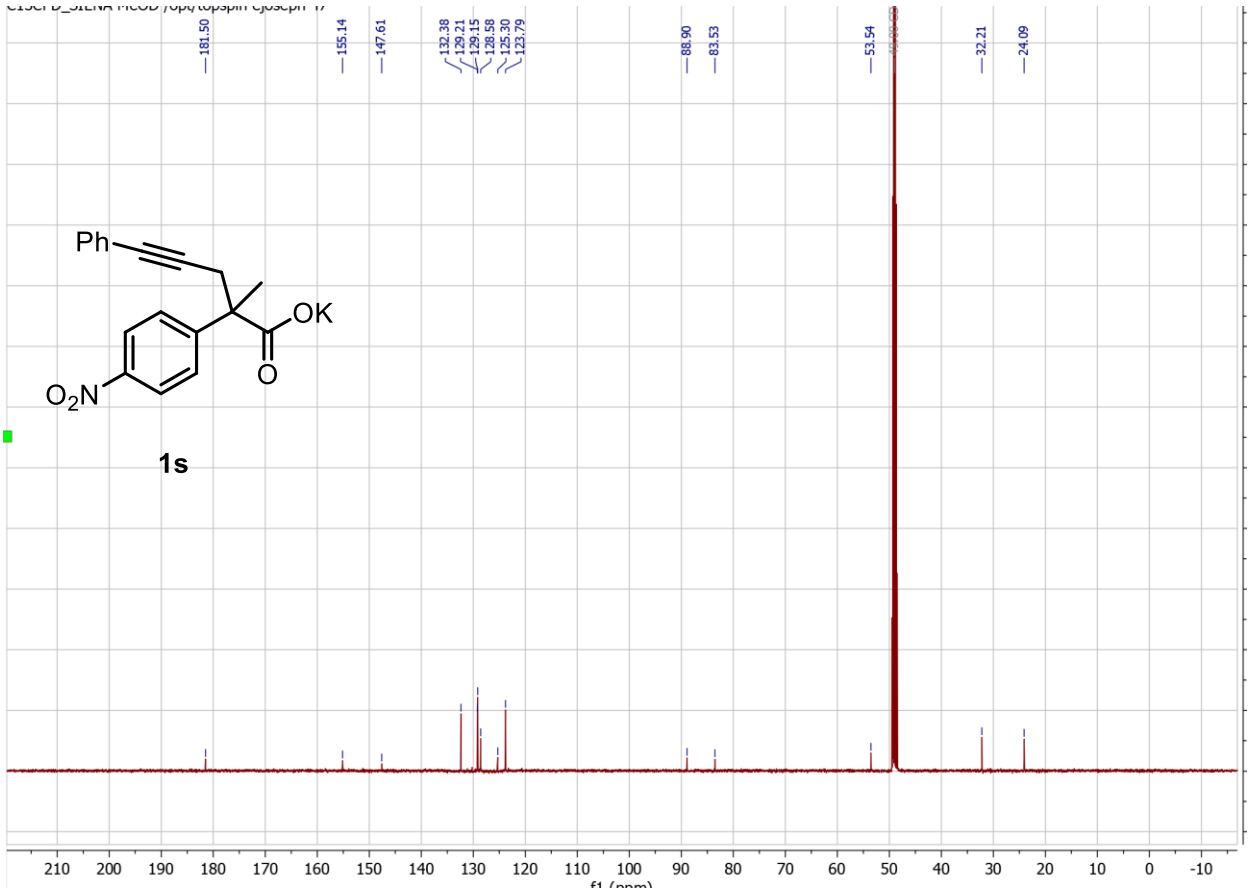
^{13}C NMR spectrum of **1p** in CD_3OD at 126 MHz



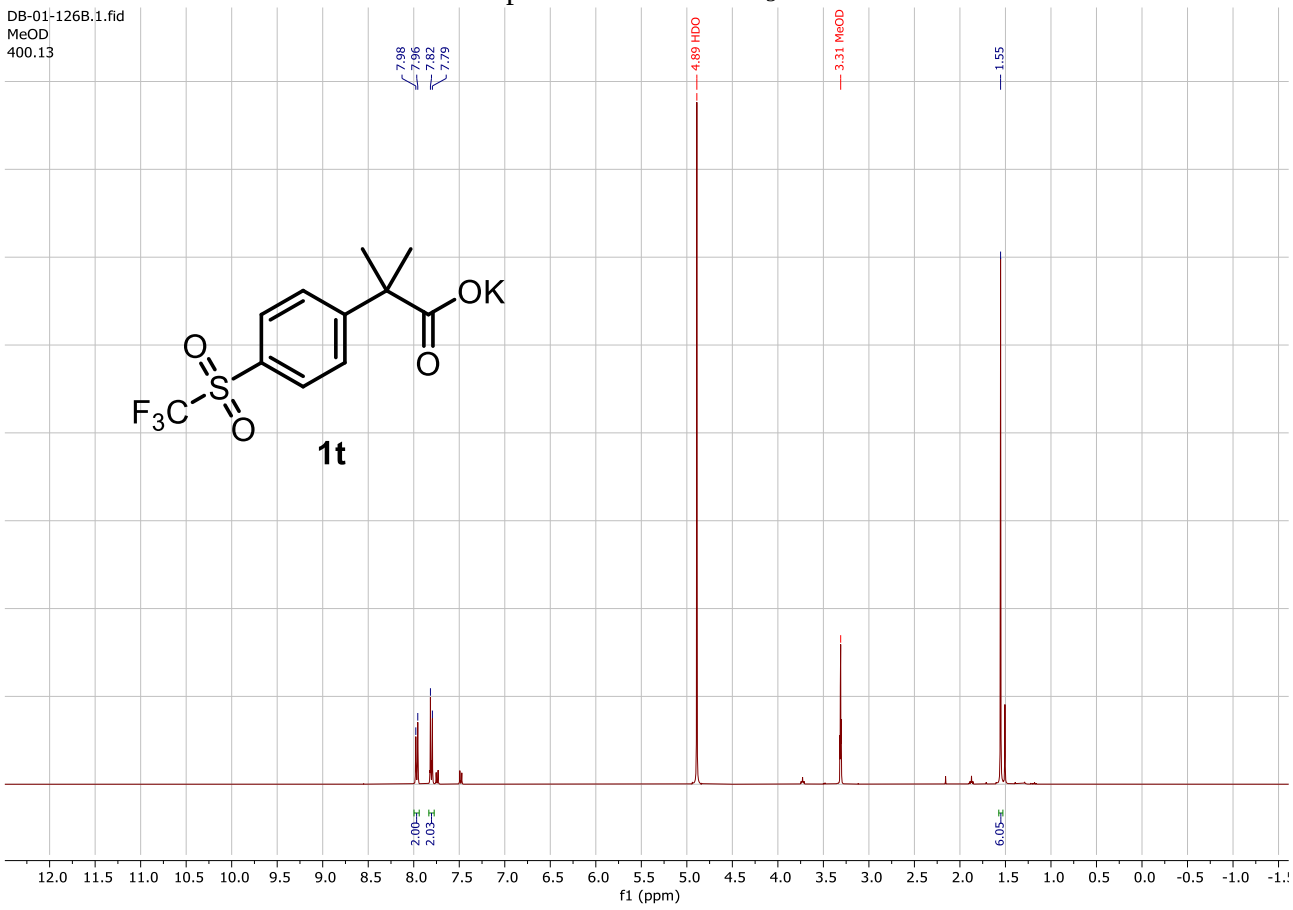
^{1}H NMR spectrum of **1s** in CD_3OD at 400 MHz



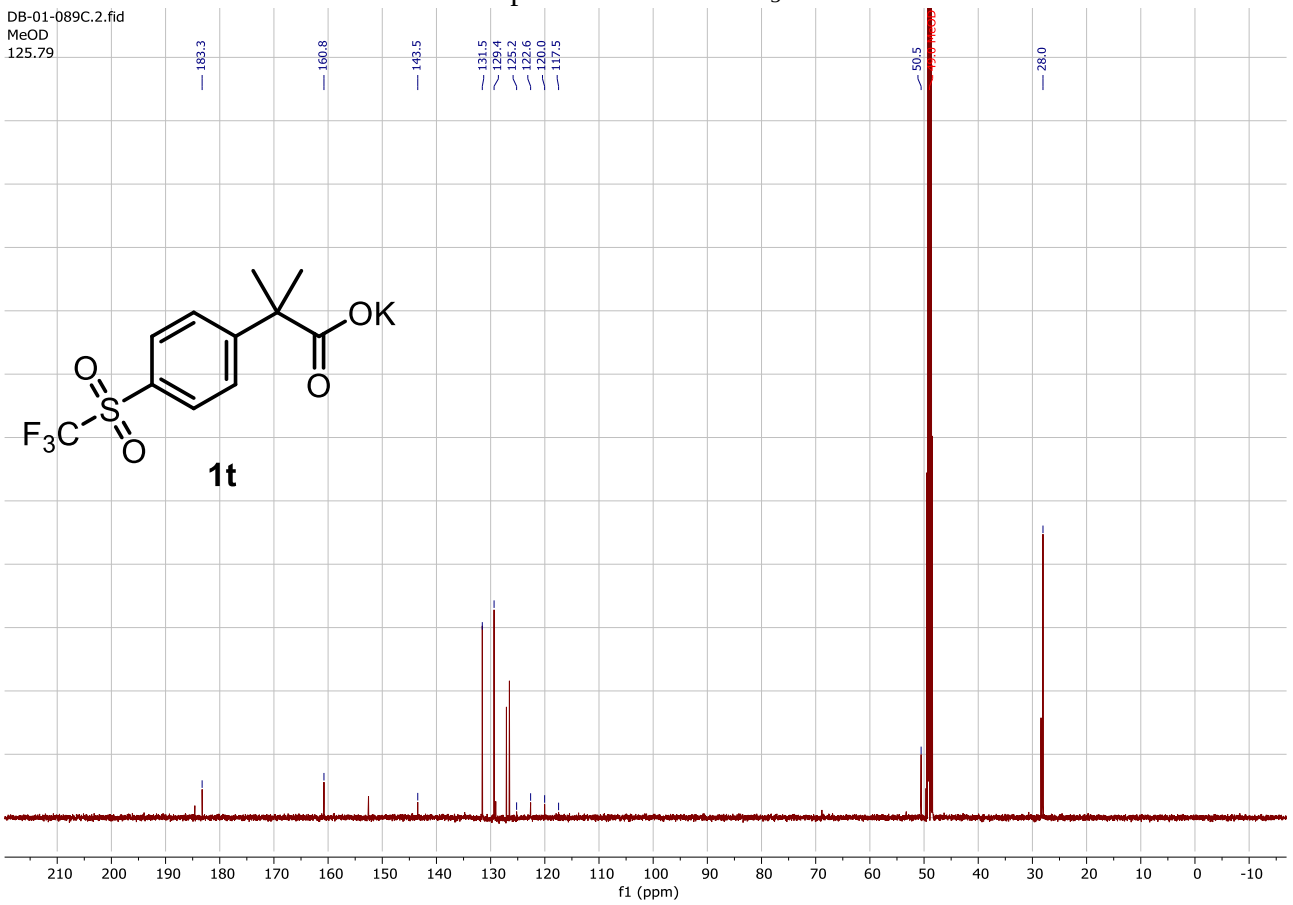
^{13}C NMR spectrum of **1s** in CD_3OD at 126 MHz



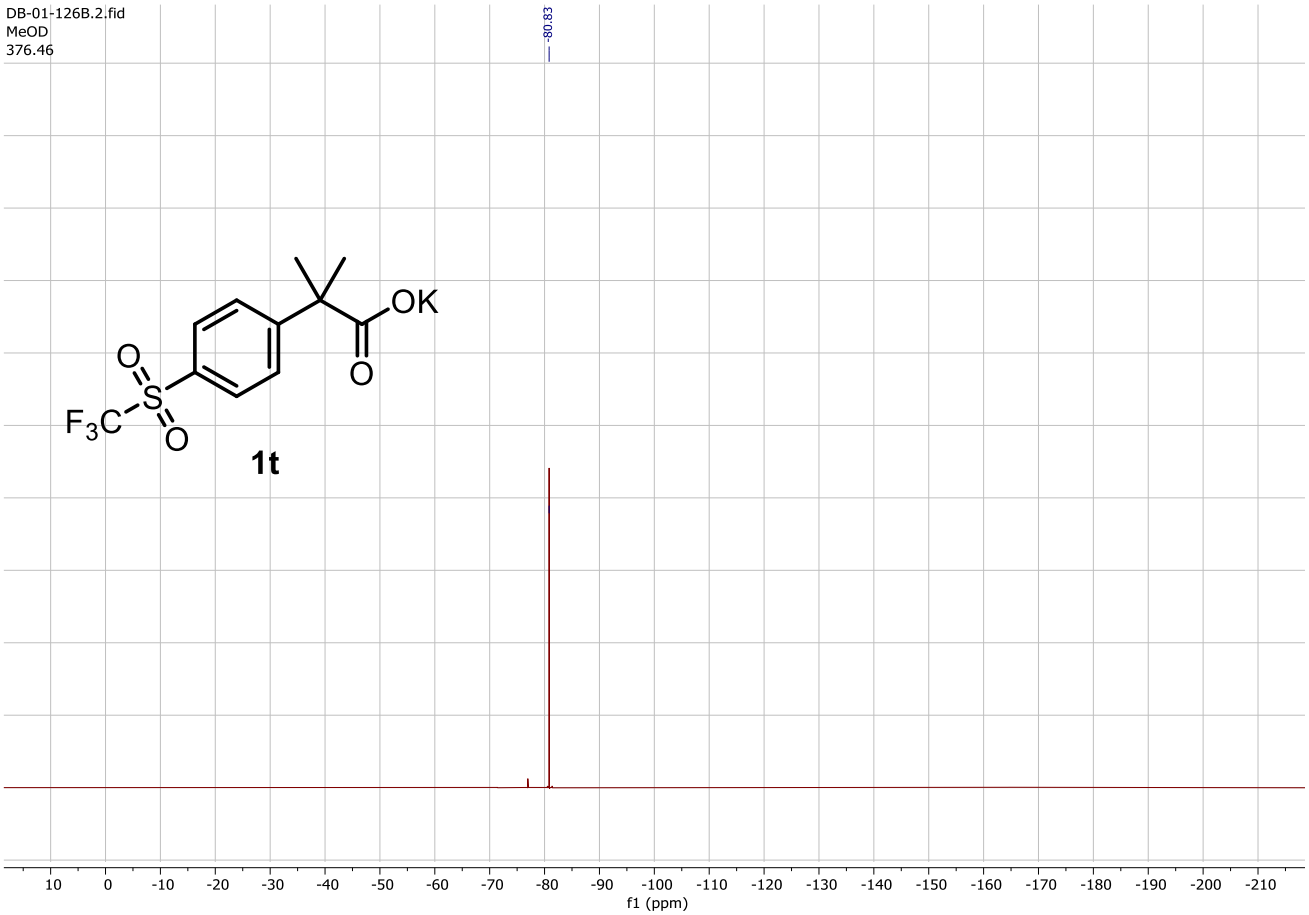
^{1}H NMR spectrum of **1t** in CD_3OD at 400 MHz



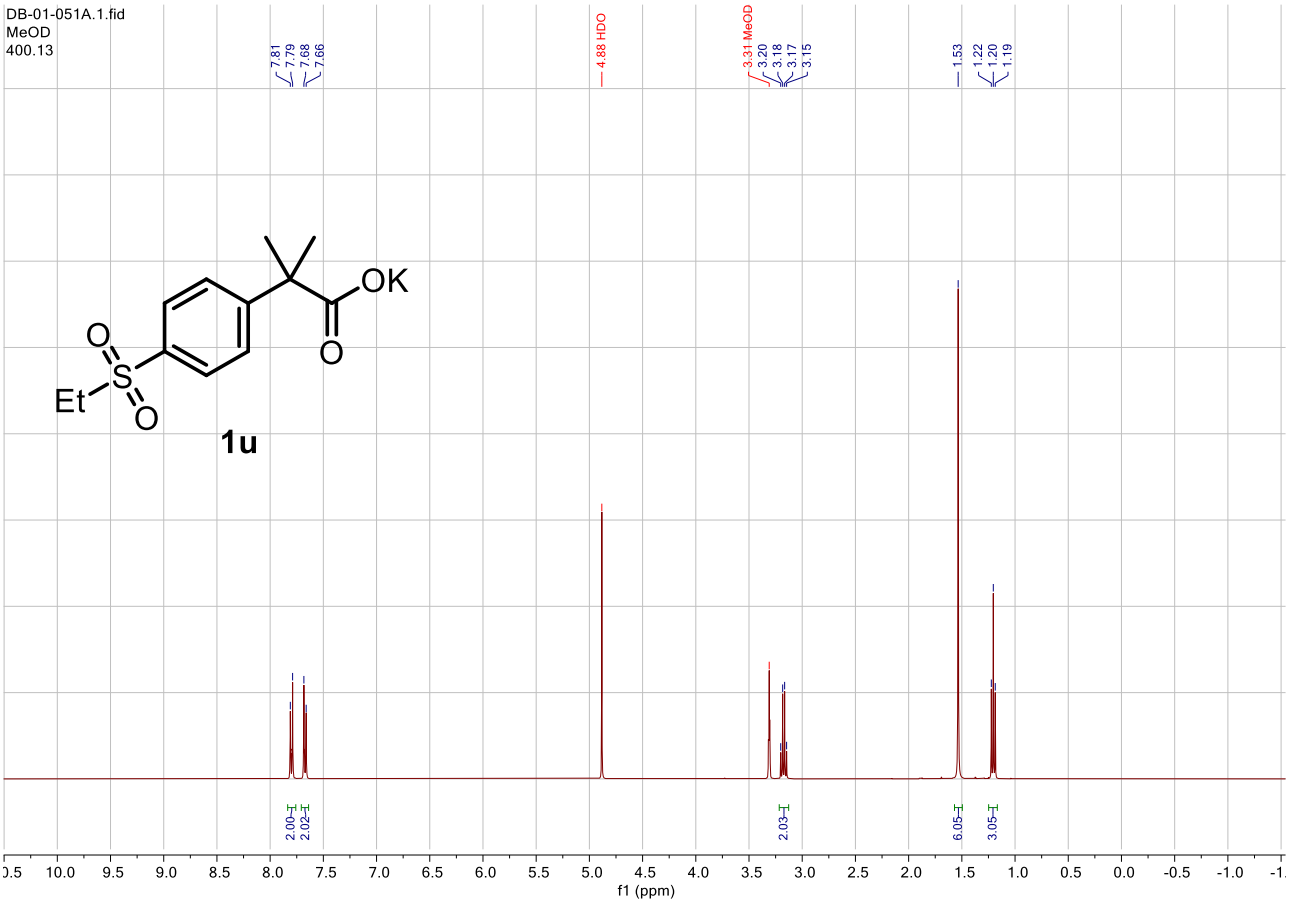
^{13}C NMR spectrum of **1t** in CD_3OD at 126 MHz



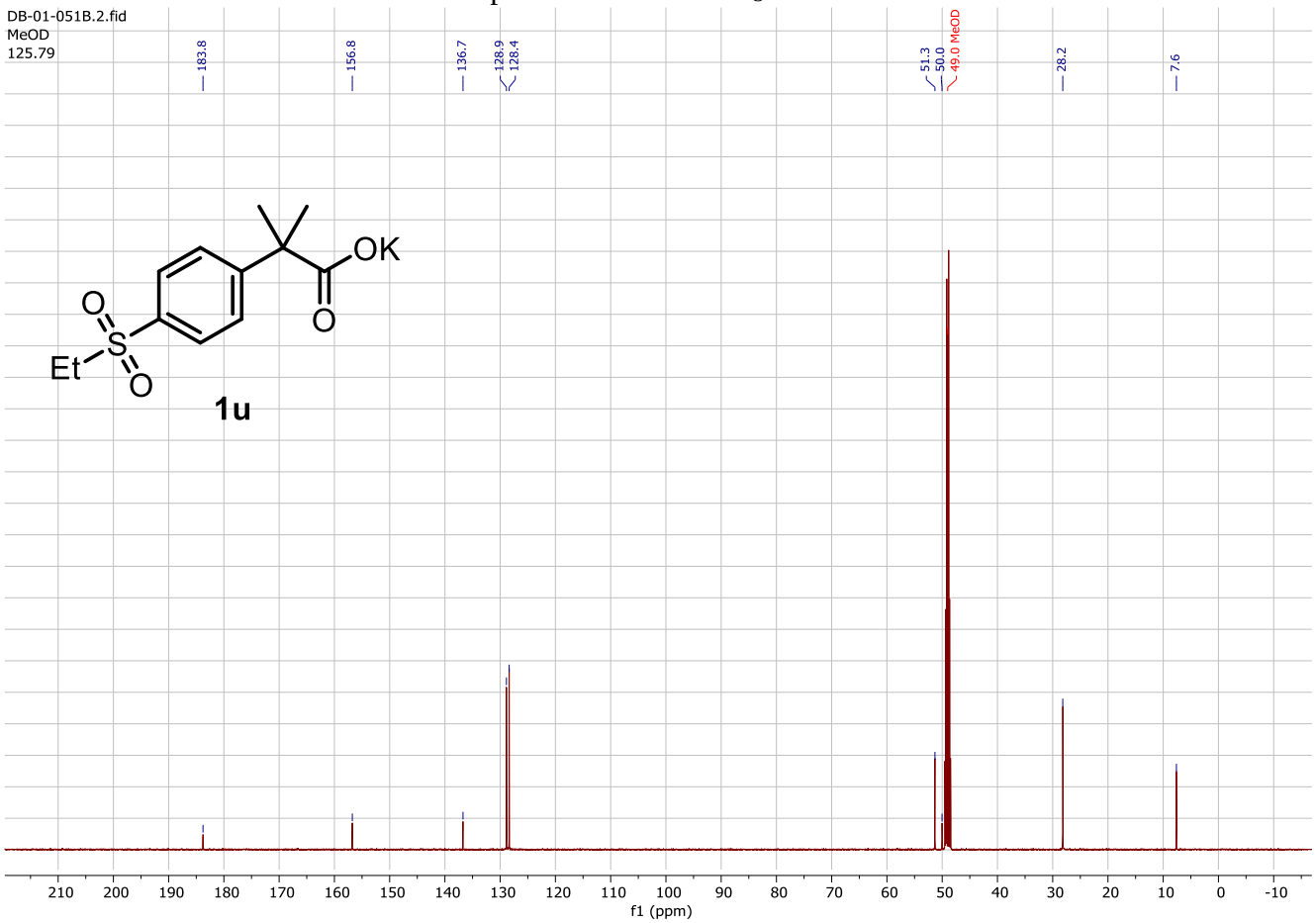
^{19}F NMR spectrum of **1t** in CD_3OD at 376 MHz



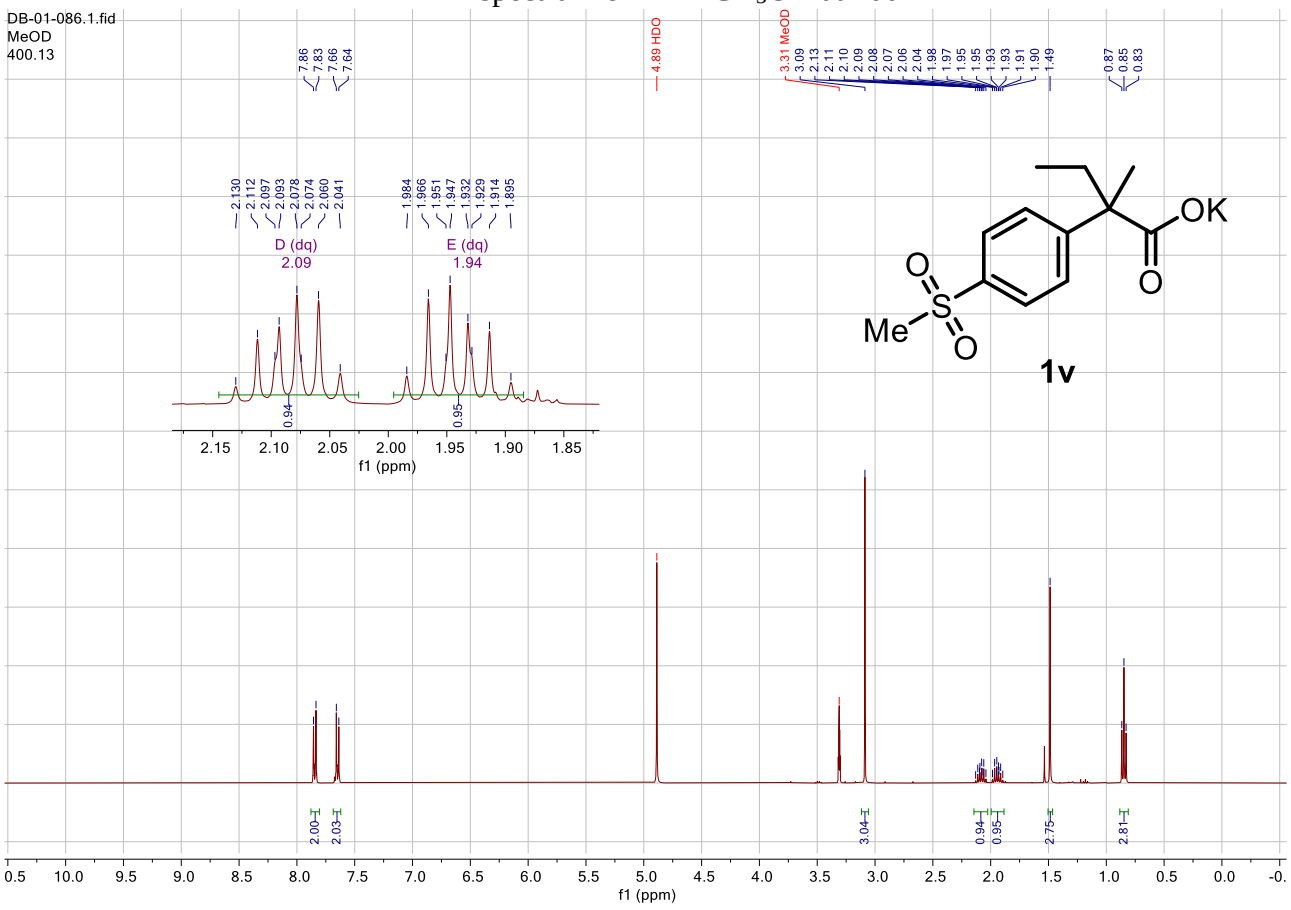
^{1}H NMR spectrum of **1u** in CD_3OD at 400 MHz



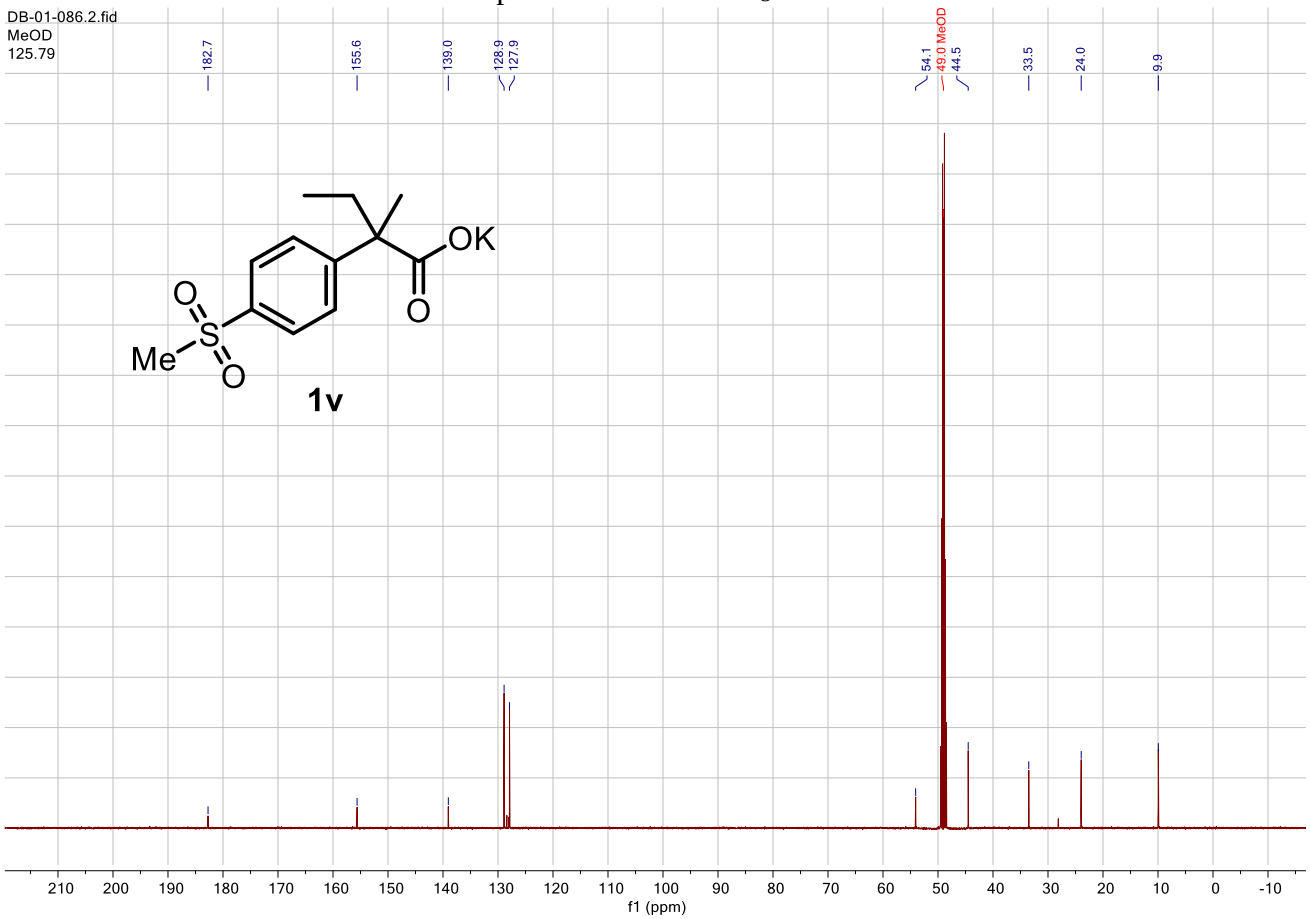
^{13}C NMR spectrum of **1u** in CD_3OD at 126 MHz



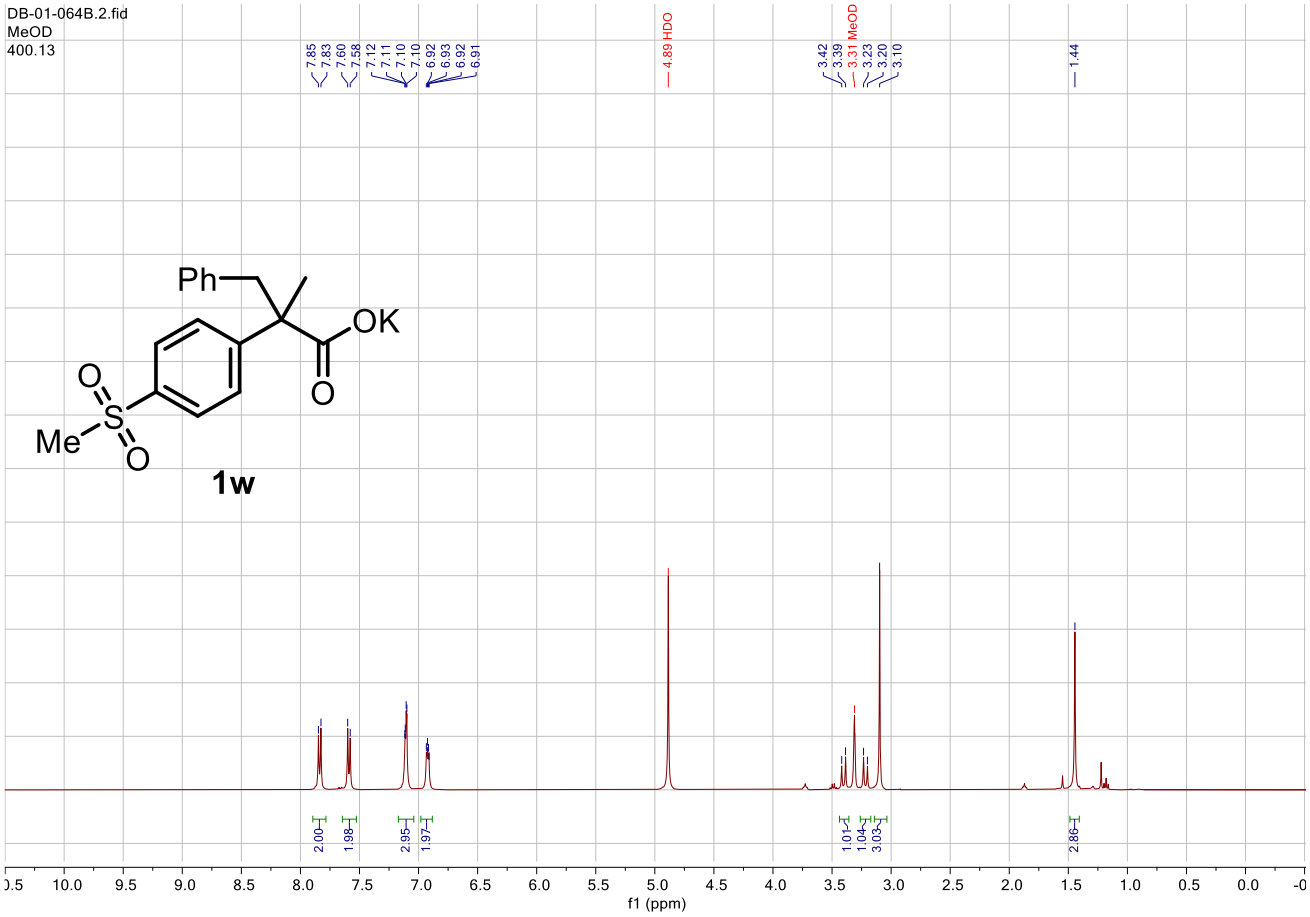
^{1}H NMR spectrum of **1v** in CD_3OD at 400 MHz



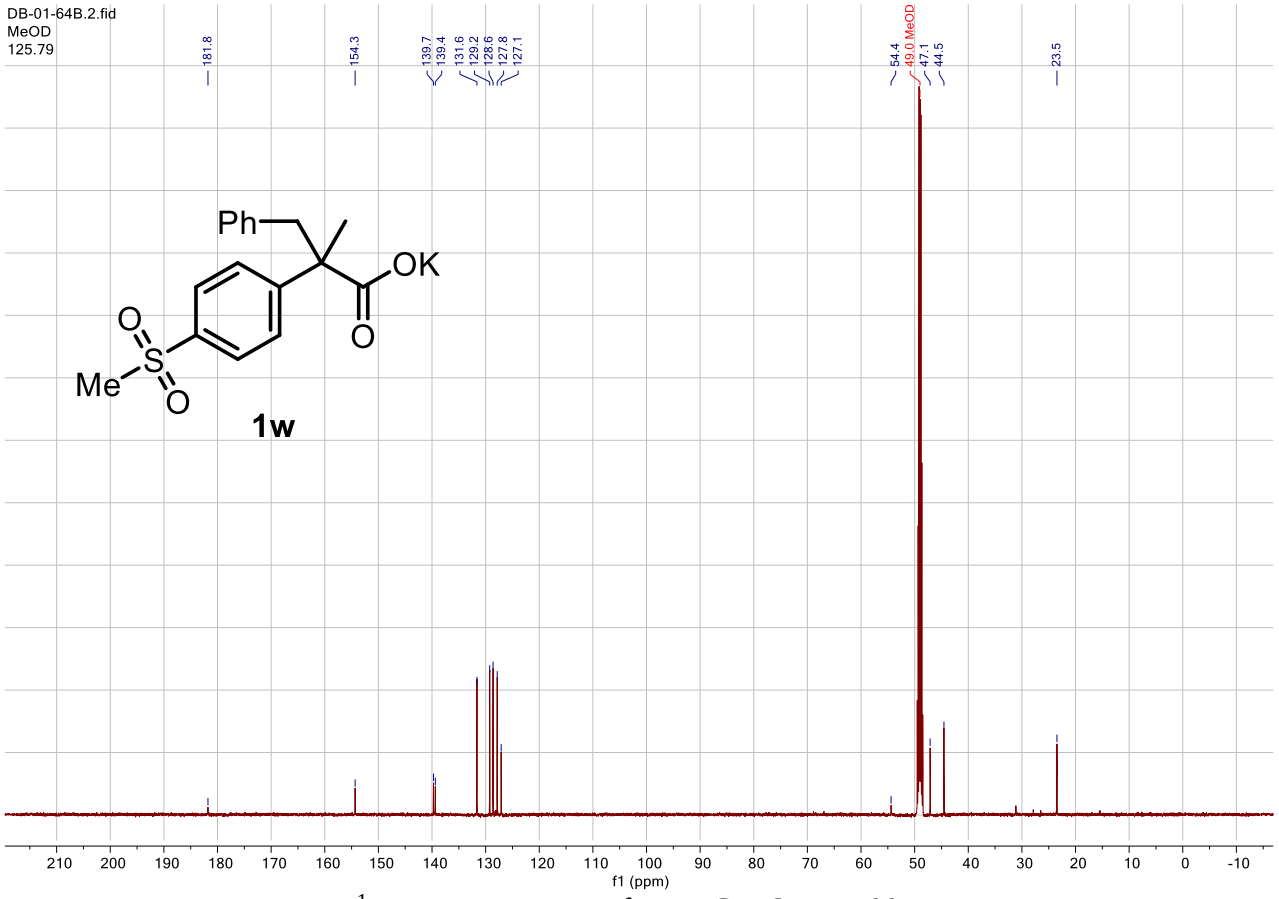
^{13}C NMR spectrum of **1v** in CD_3OD at 126 MHz



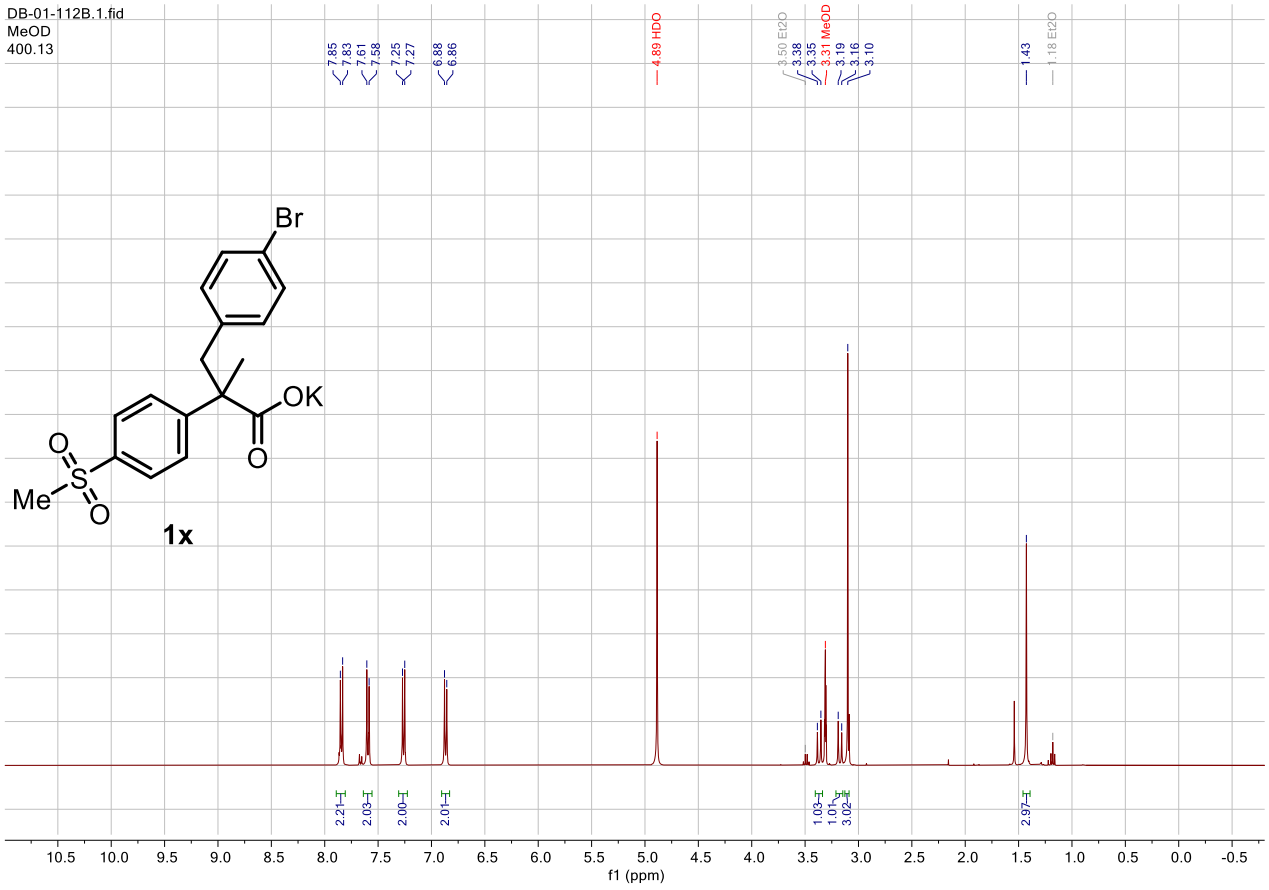
^{1}H NMR spectrum of **1w** in CD_3OD at 400 MHz



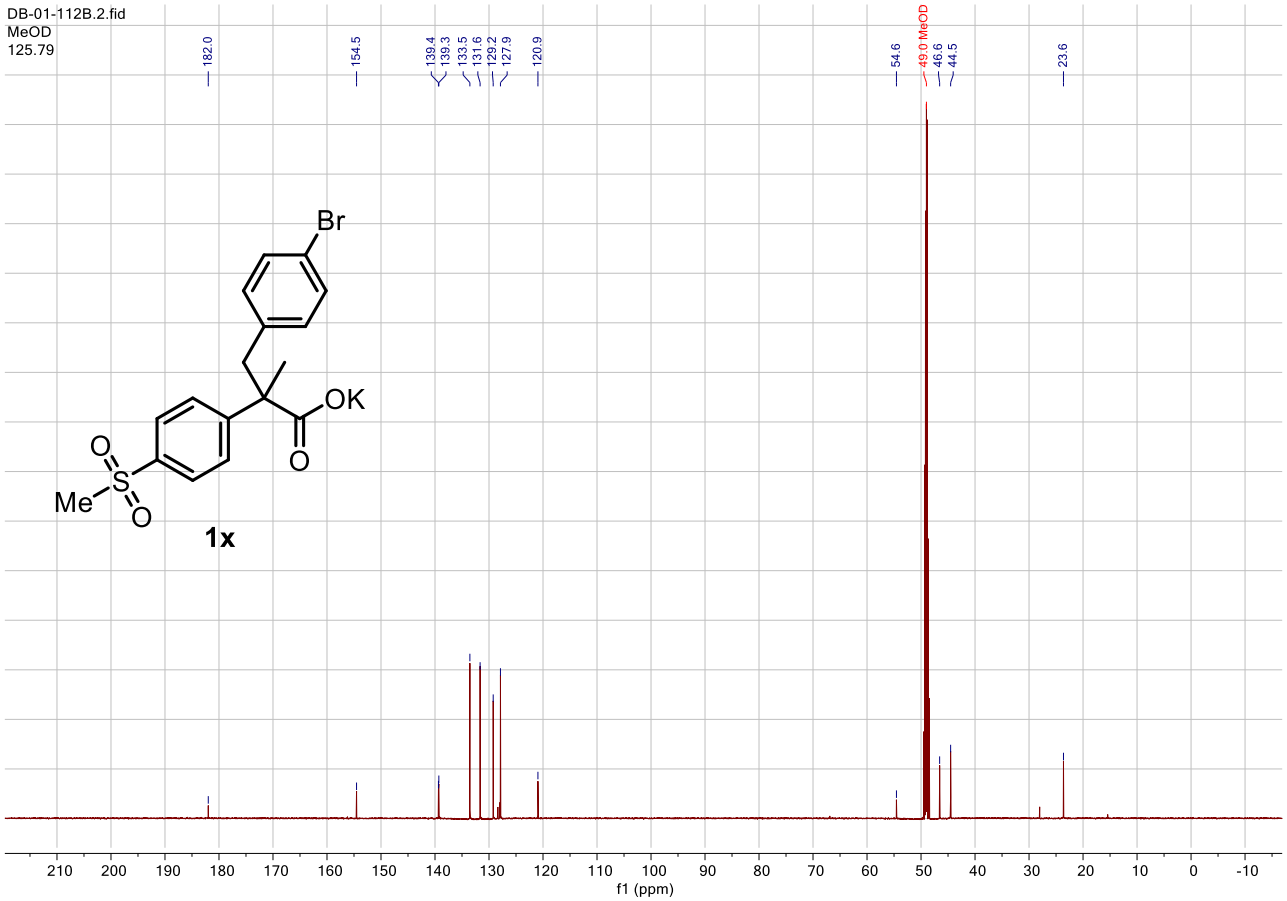
^{13}C NMR spectrum of **1w** in CD_3OD at 126 MHz



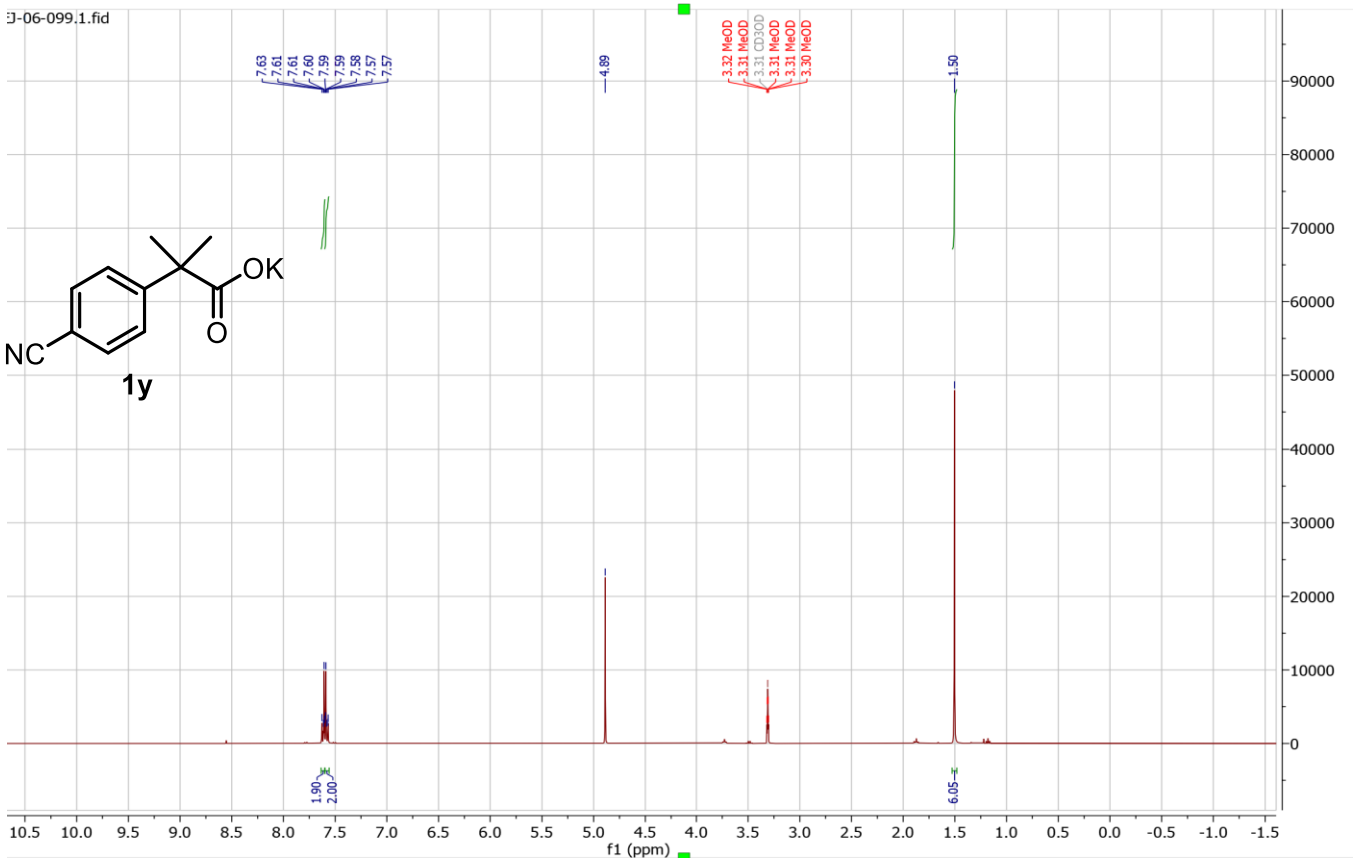
^{1}H NMR spectrum of **1x** in CD_3OD at 400 MHz



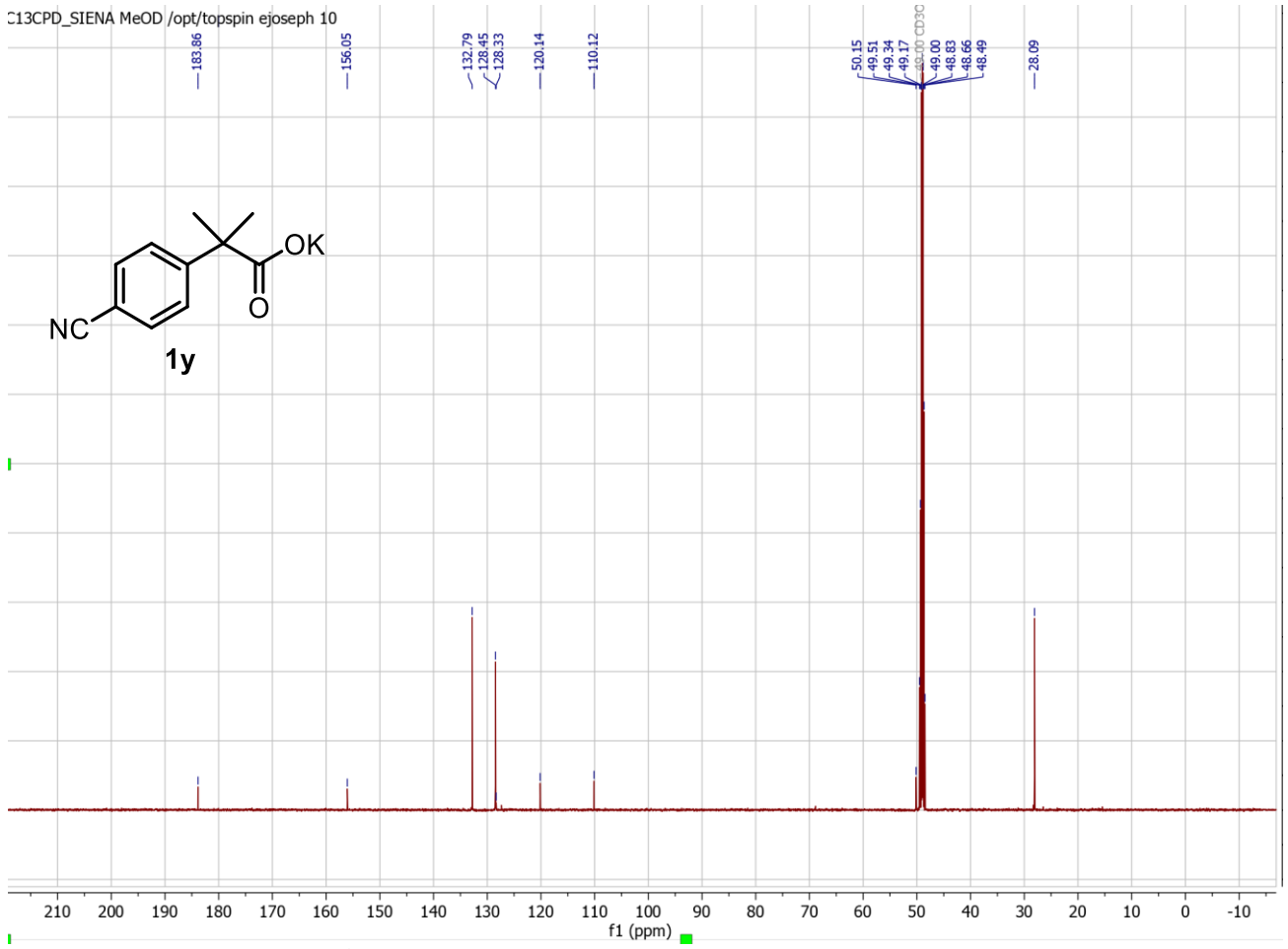
^{13}C NMR spectrum of **1x** in CD_3OD at 126 MHz



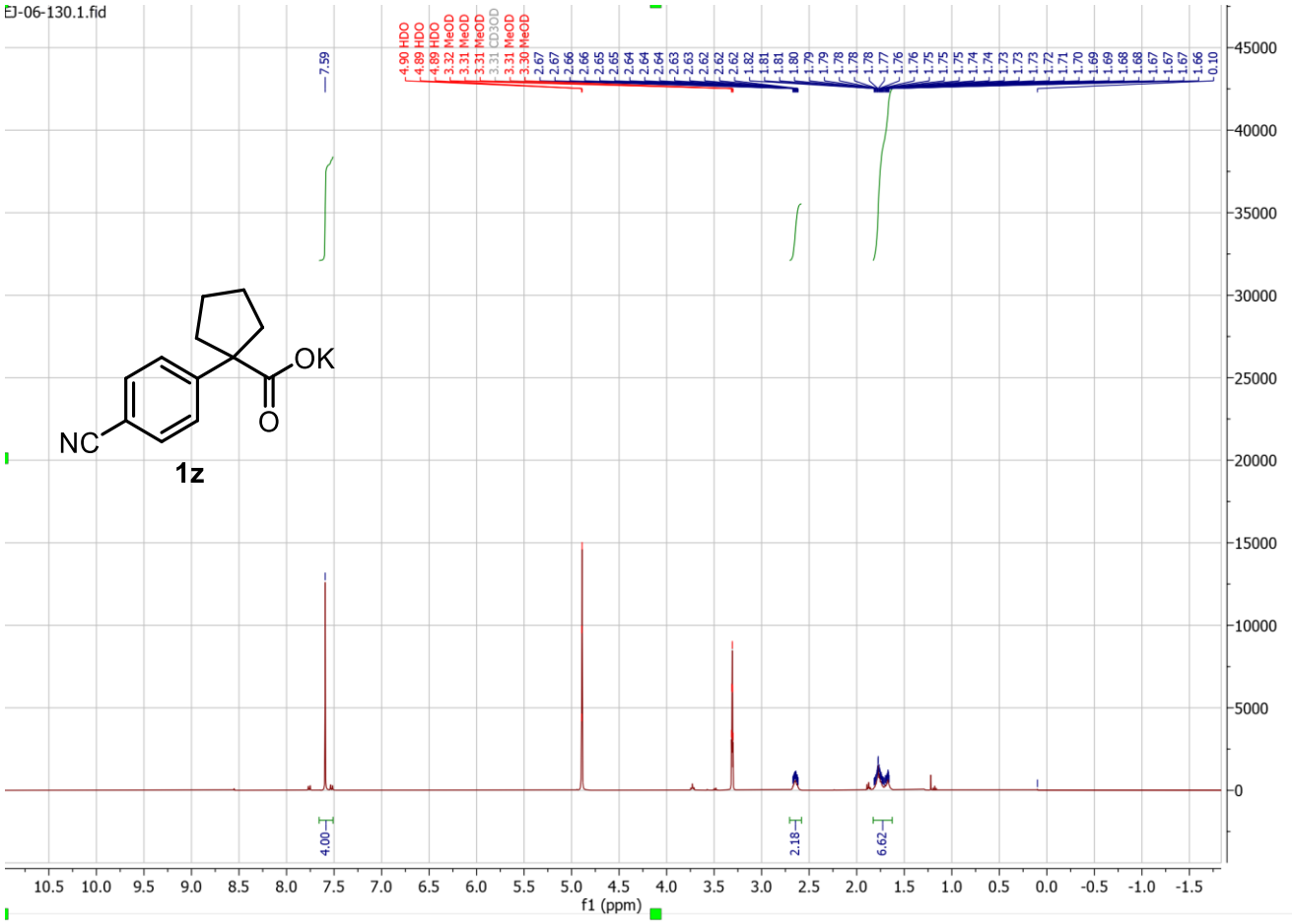
^{1}H NMR spectrum of **1y** in CD_3OD at 400 MHz



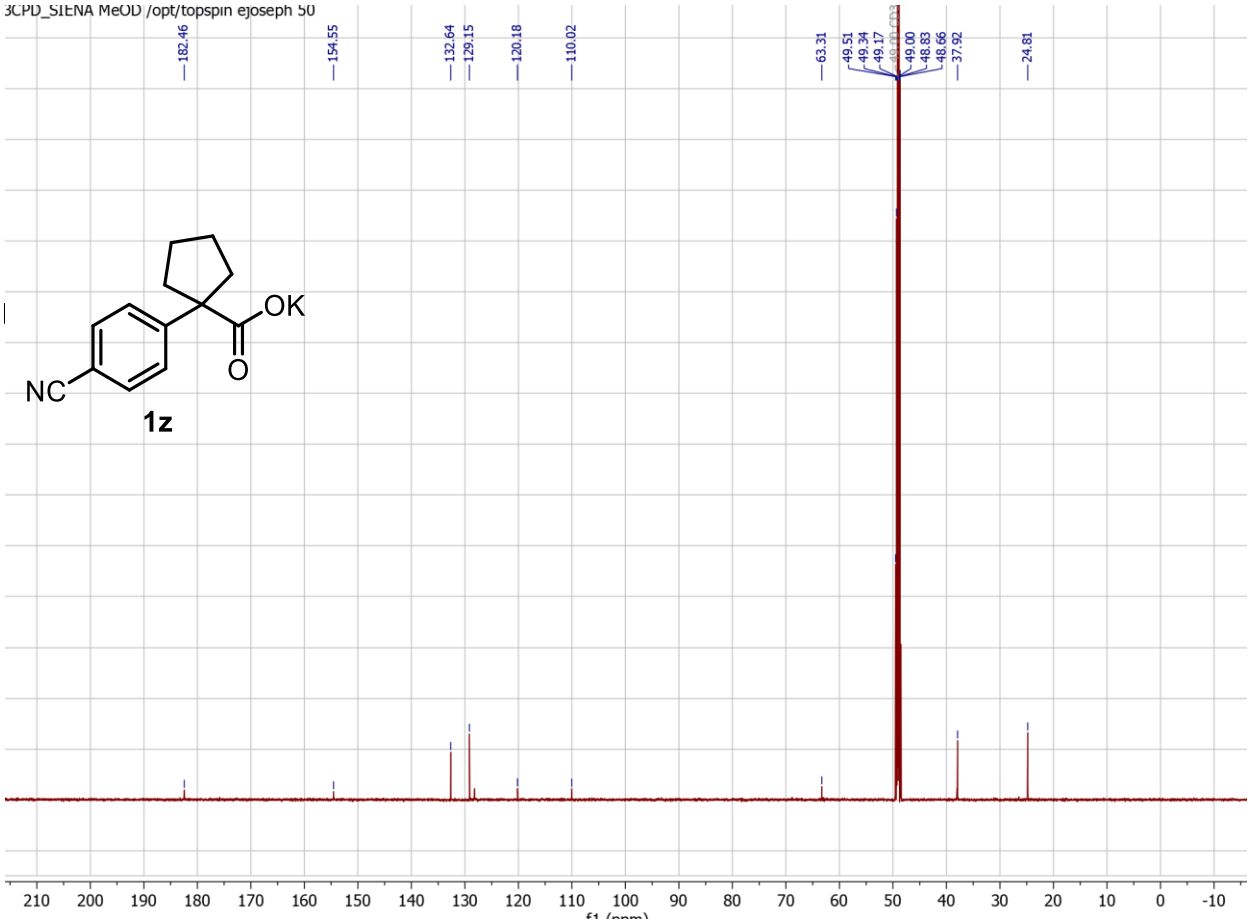
^{13}C NMR spectrum of **1y** in CD_3OD at 126 MHz



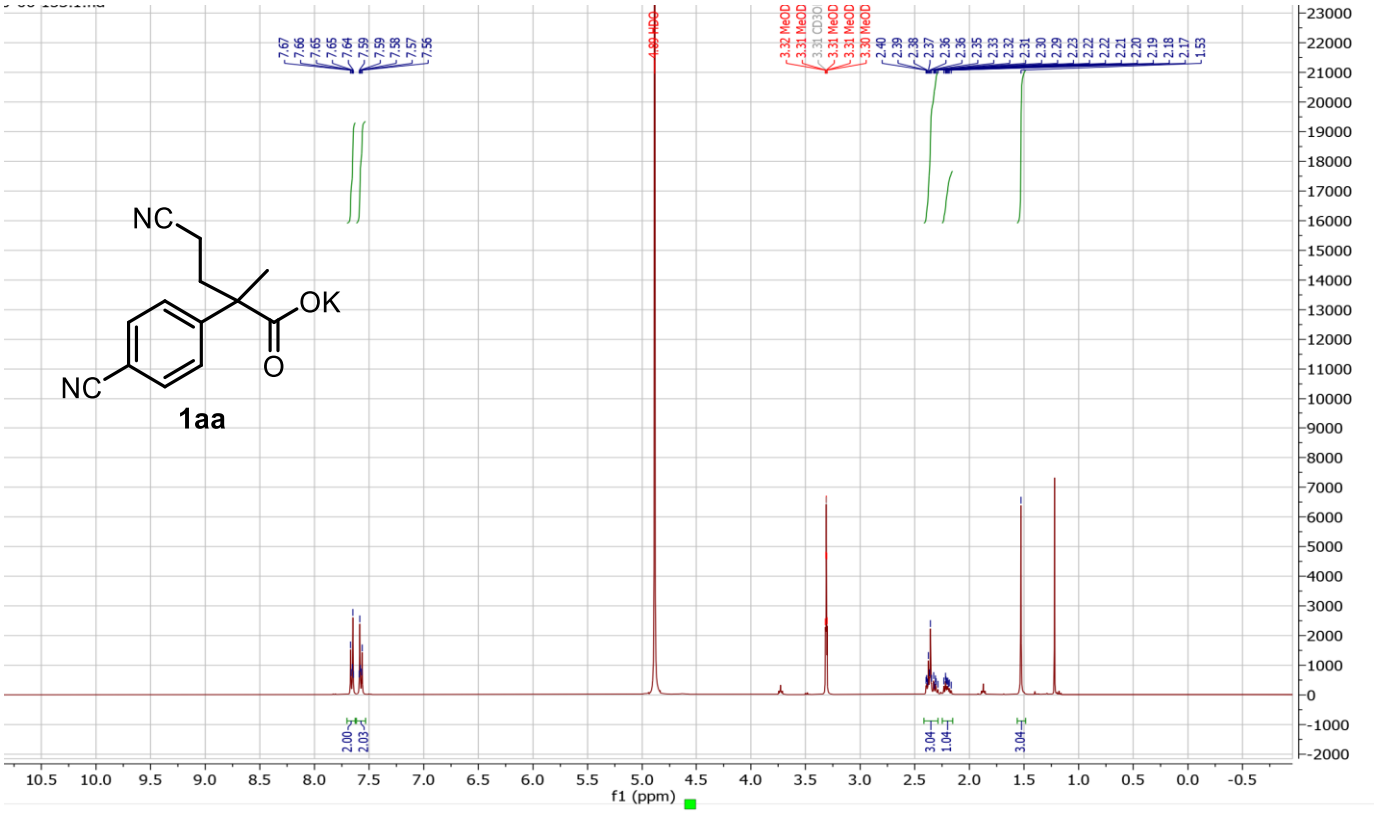
^{1}H NMR spectrum of **1z** in CD_3OD at 400 MHz



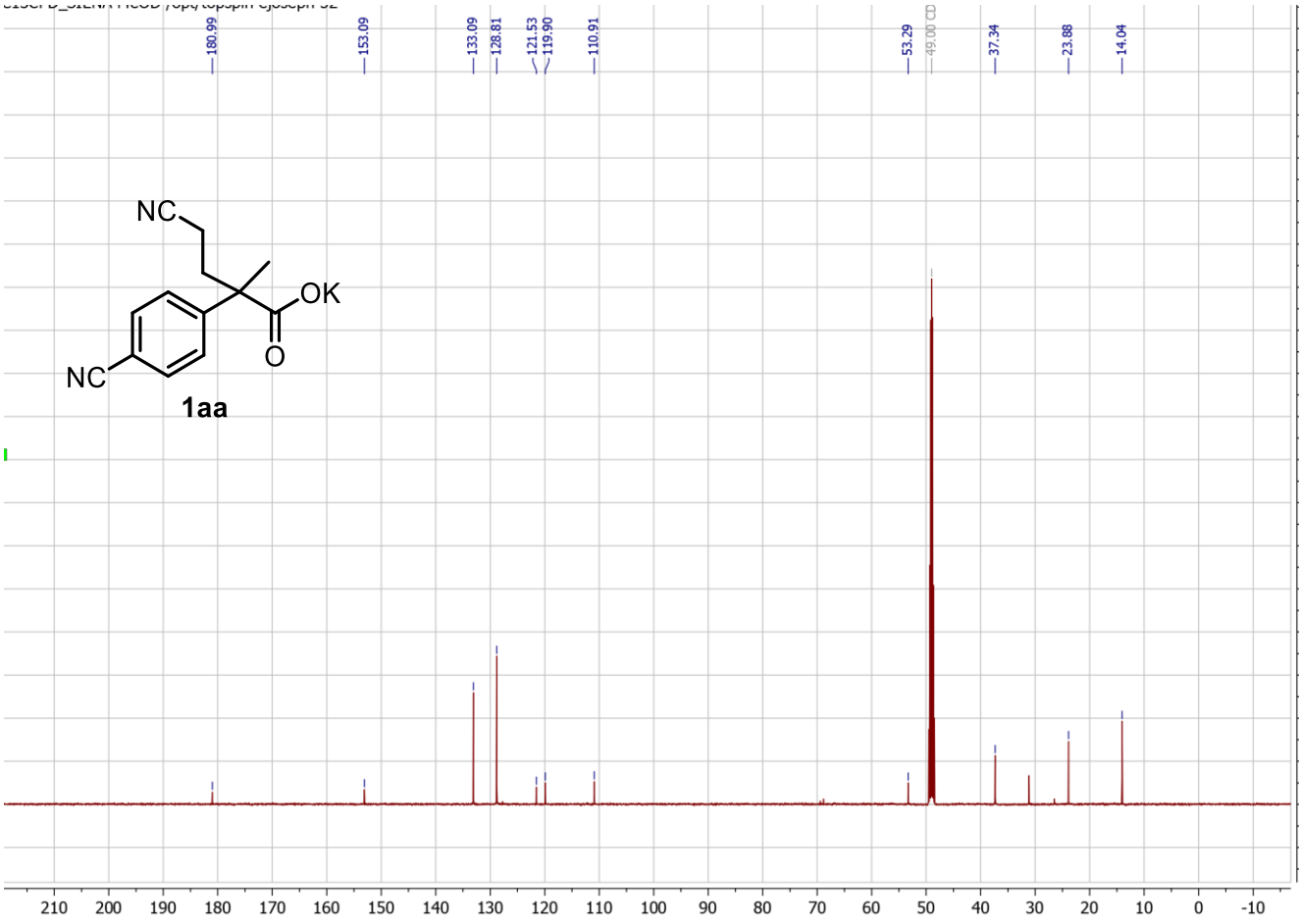
^{13}C NMR spectrum of **1z** in CD_3OD at 126 MHz



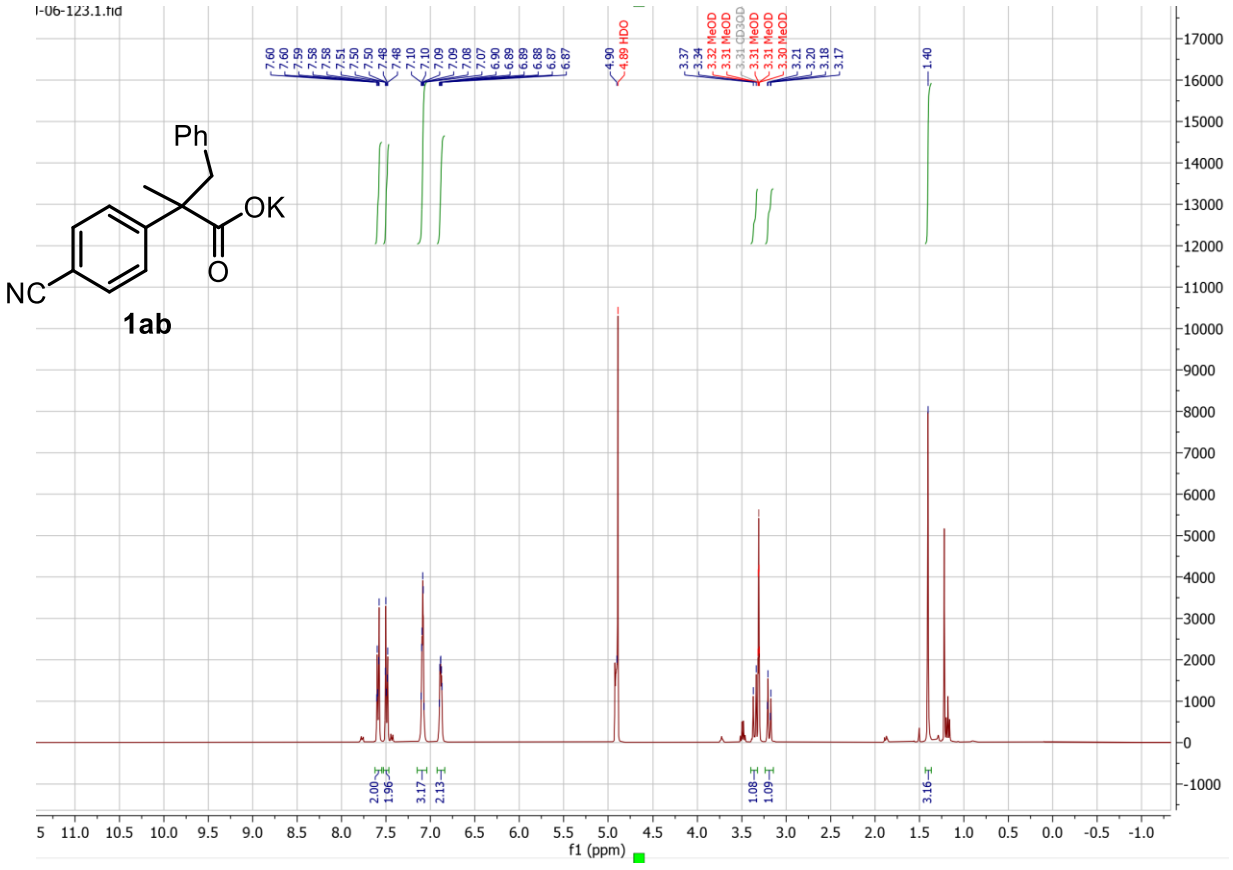
^{1}H NMR spectrum of **1aa** in CD_3OD at 400 MHz



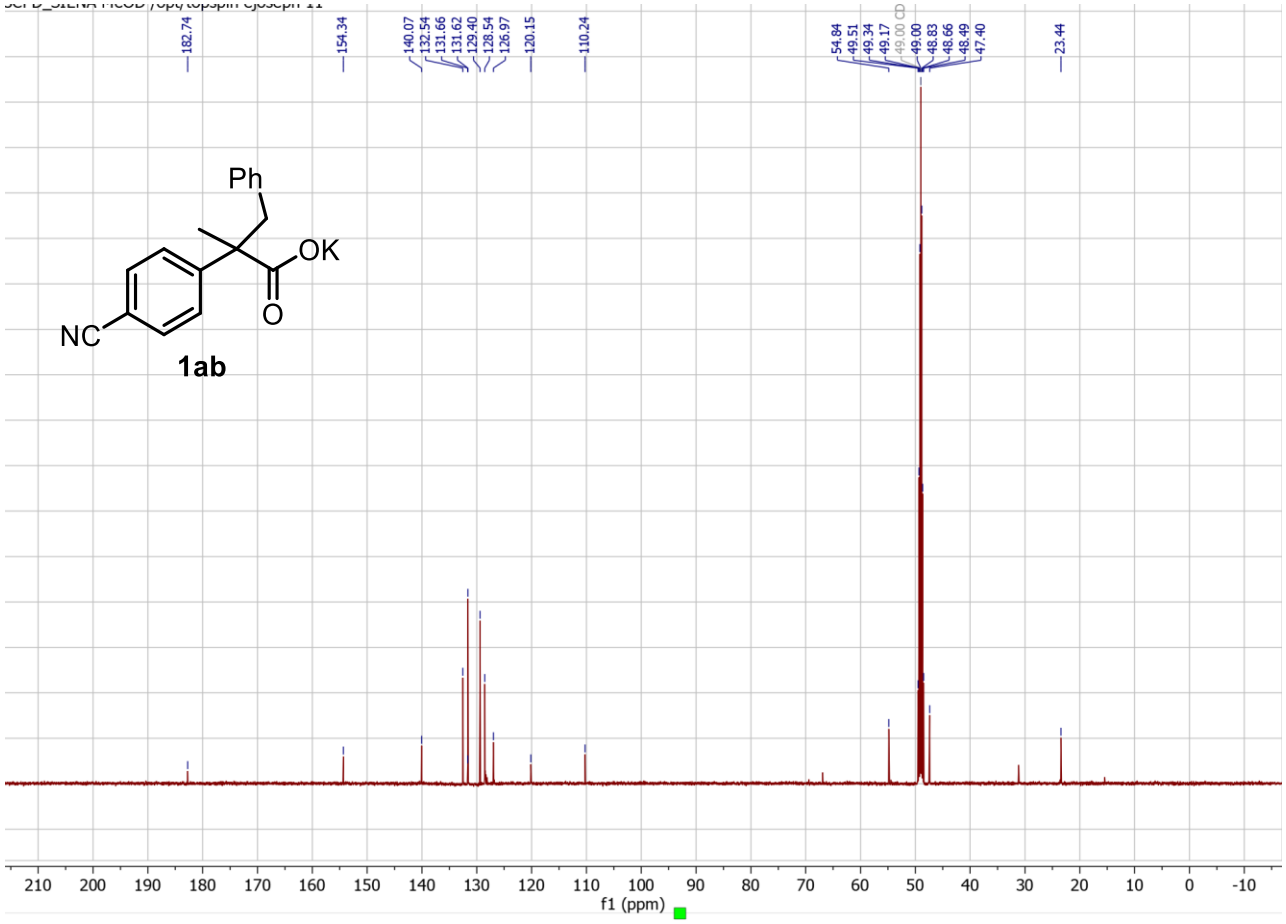
^{13}C NMR spectrum of **1aa** in CD_3OD at 126 MHz



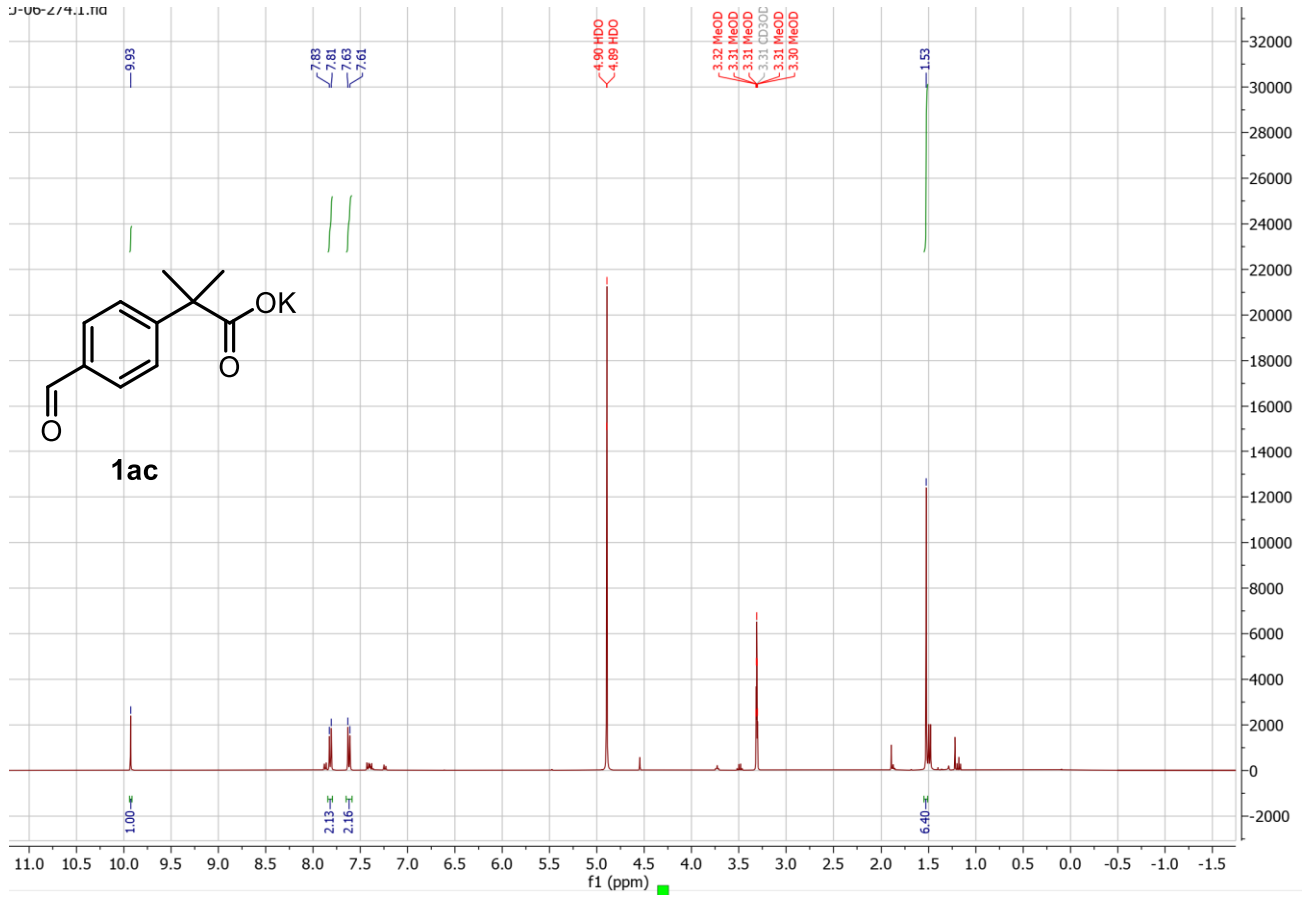
^{1}H NMR spectrum of **1ab** in CD_3OD at 400 MHz



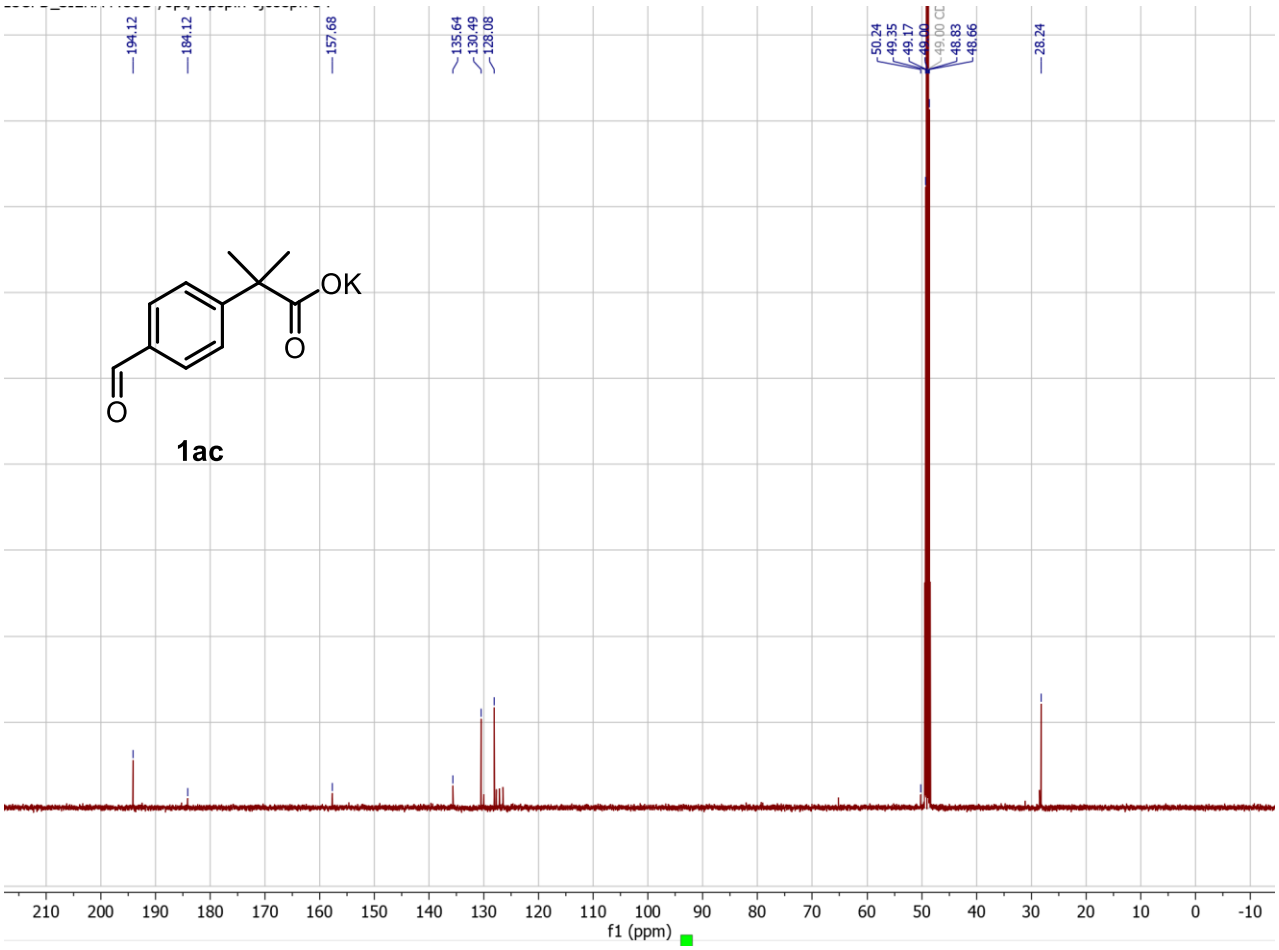
^{13}C NMR spectrum of **1ab** in CD_3OD at 126 MHz



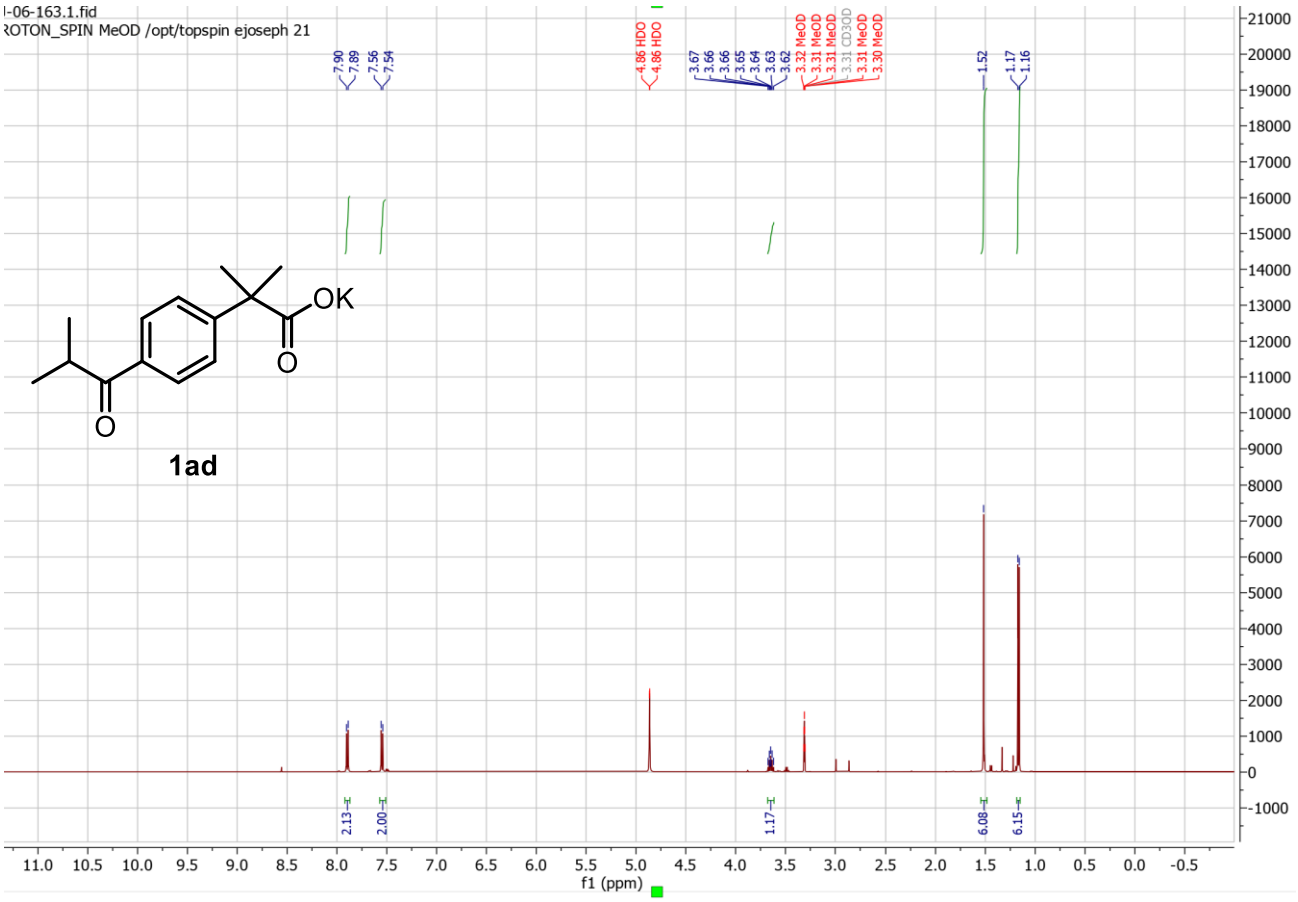
^{1}H NMR spectrum of **1ac** in CD_3OD at 400 MHz



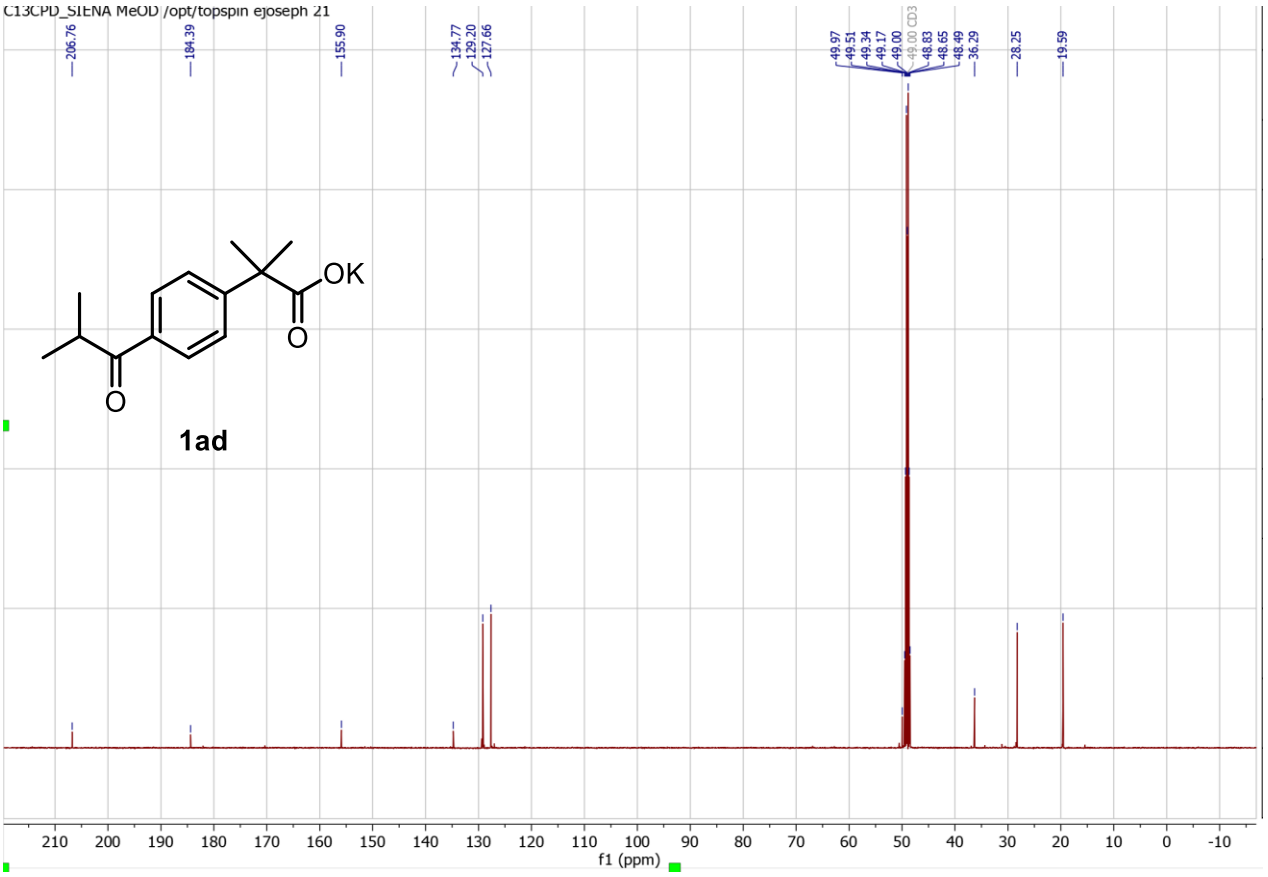
^{13}C NMR spectrum of **1ac** in CD_3OD at 126 MHz



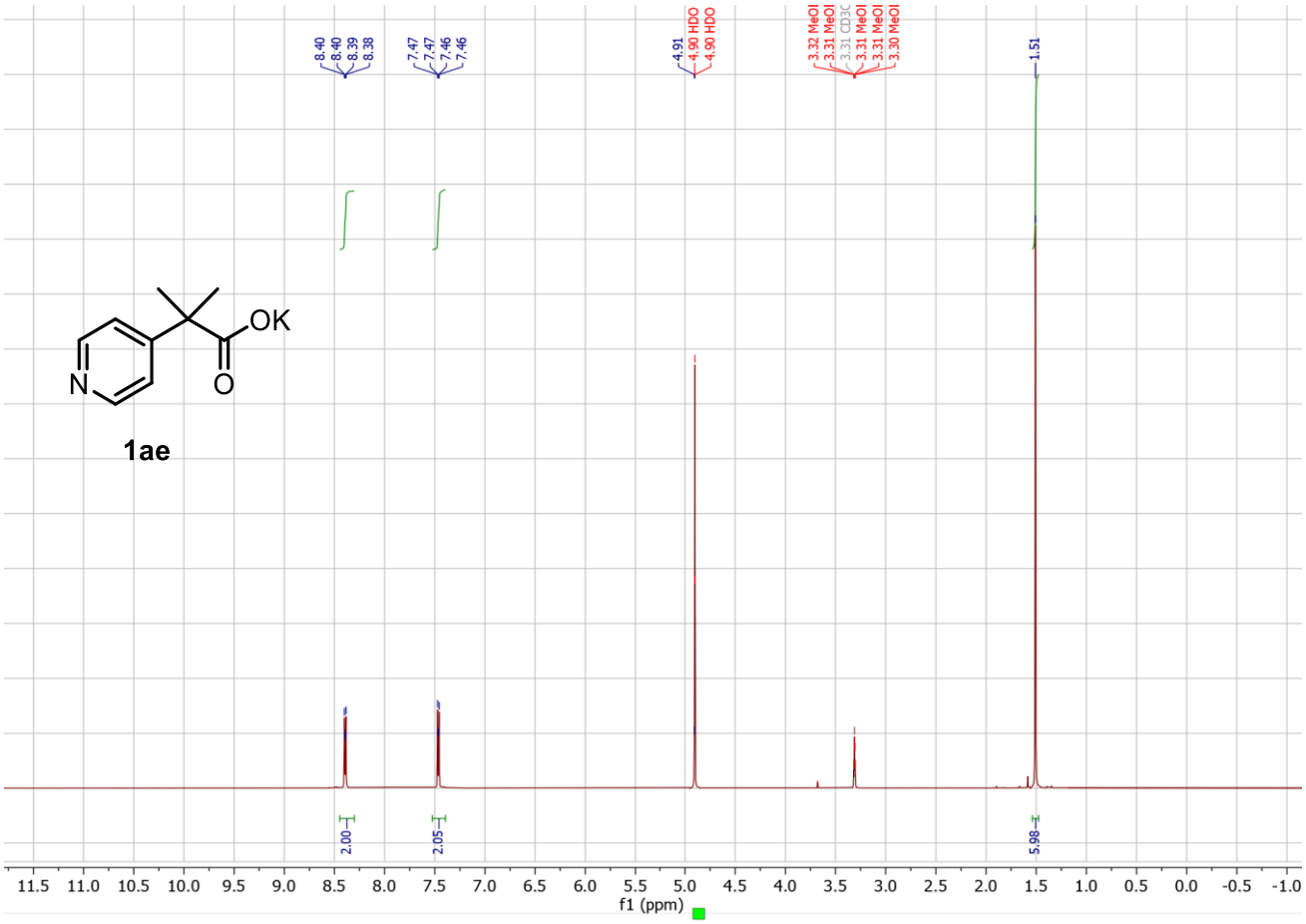
^{1}H NMR spectrum of **1ad** in CD_3OD at 500 MHz



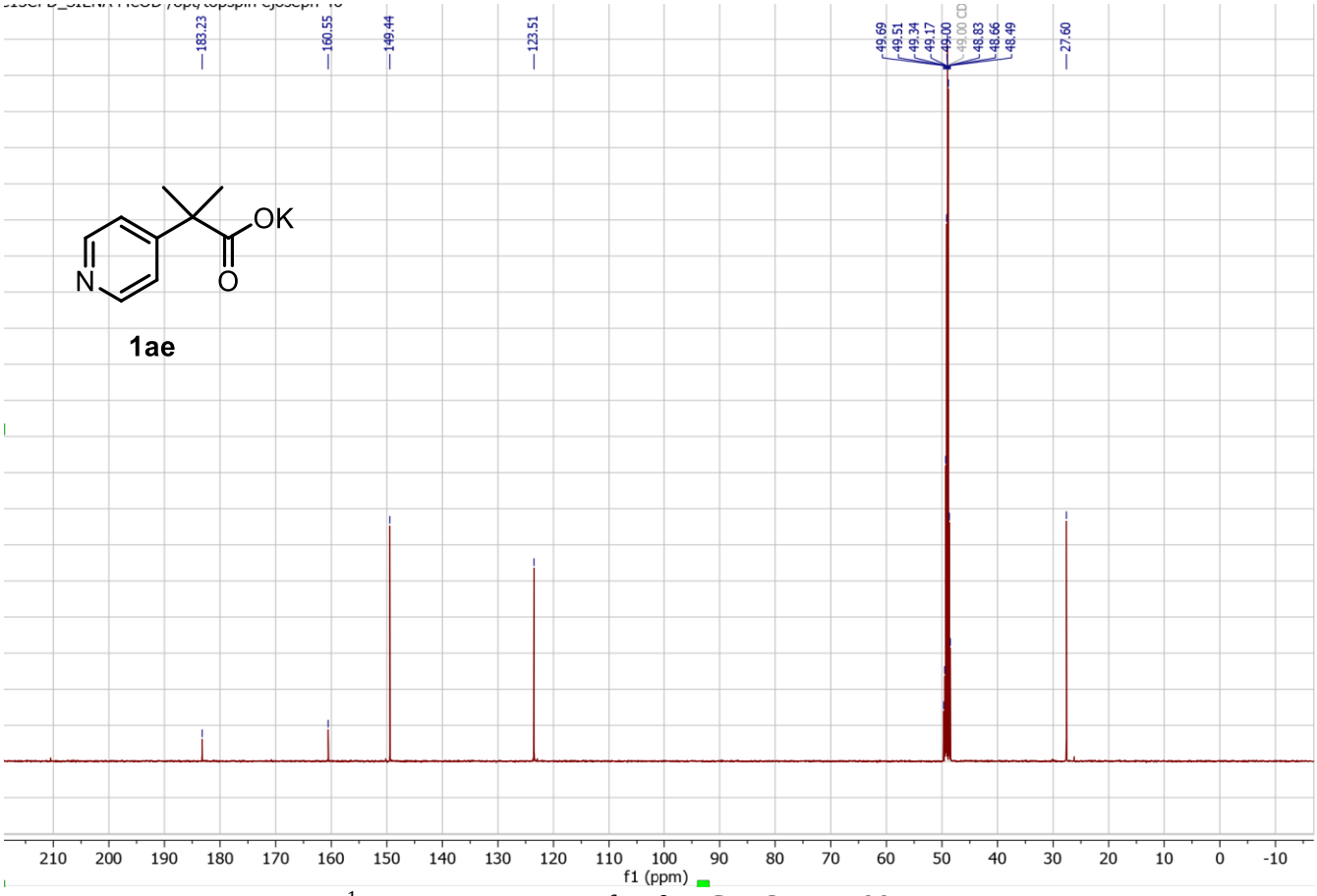
^{13}C NMR spectrum of **1ad** in CD_3OD at 126 MHz



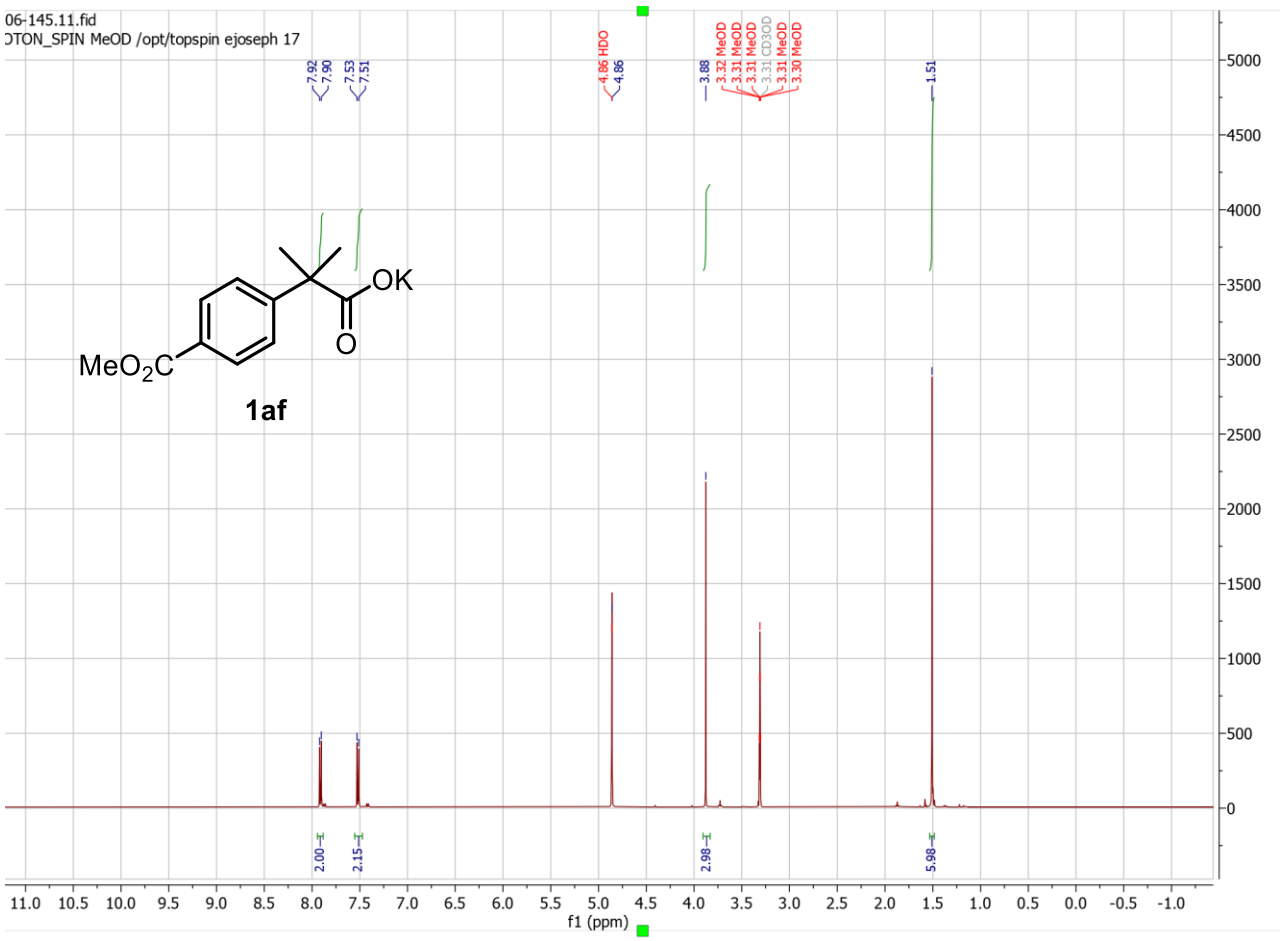
^{1}H NMR spectrum of **1ae** in CD_3OD at 400 MHz



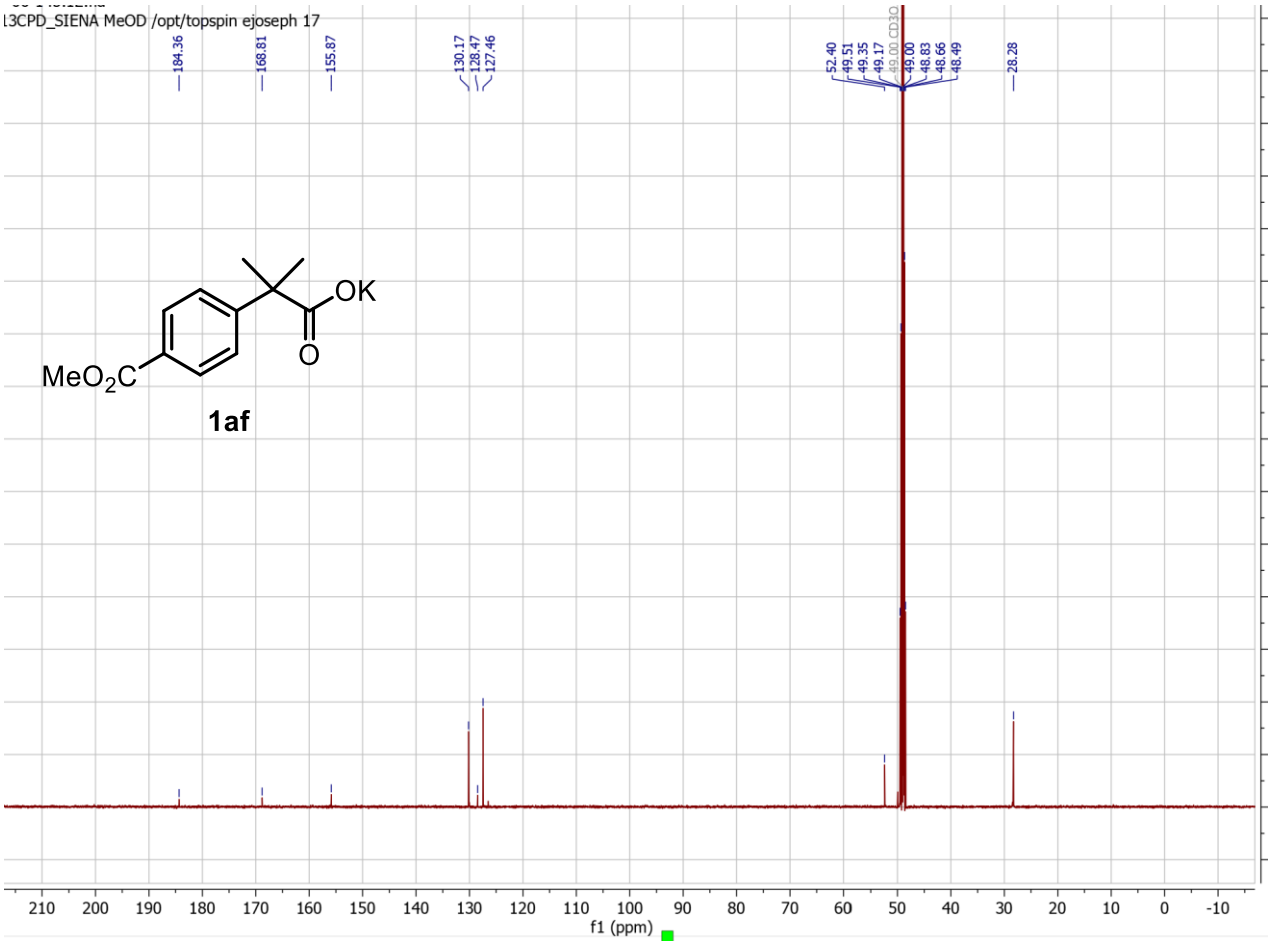
^{13}C NMR spectrum of **1ae** in CD_3OD at 126 MHz



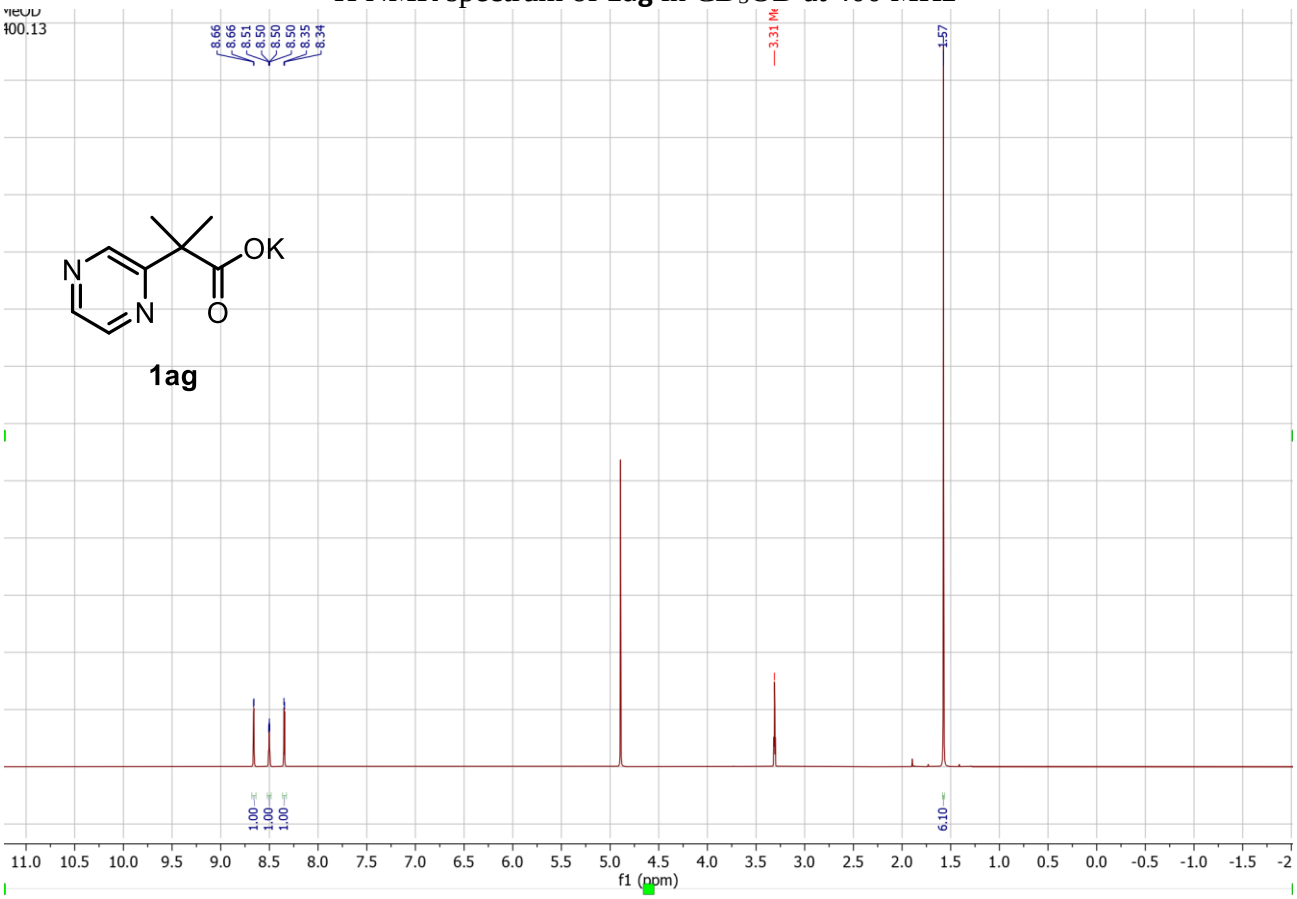
^{1}H NMR spectrum of **1af** in CD_3OD at 400 MHz



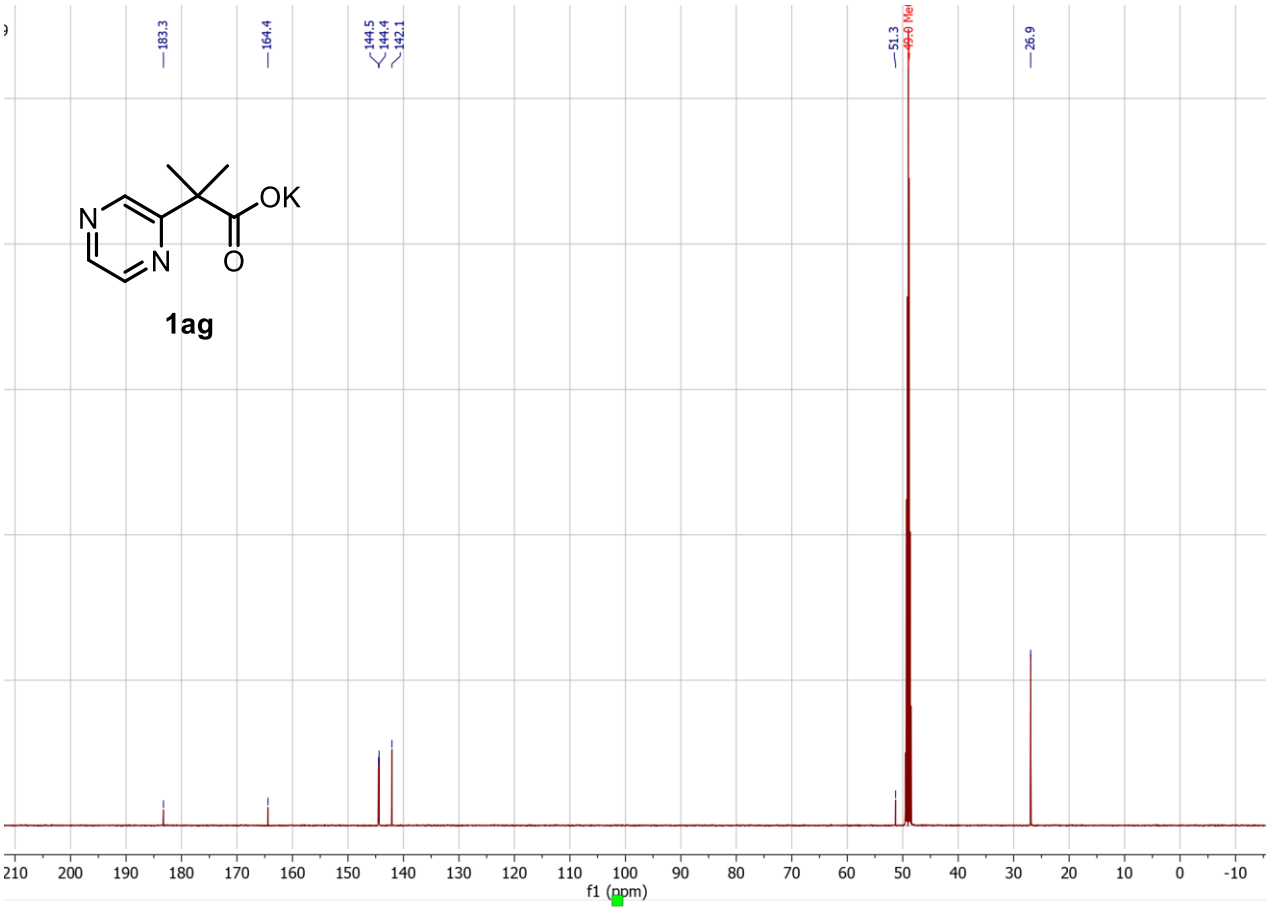
^{13}C NMR spectrum of **1af** in CD_3OD at 126 MHz



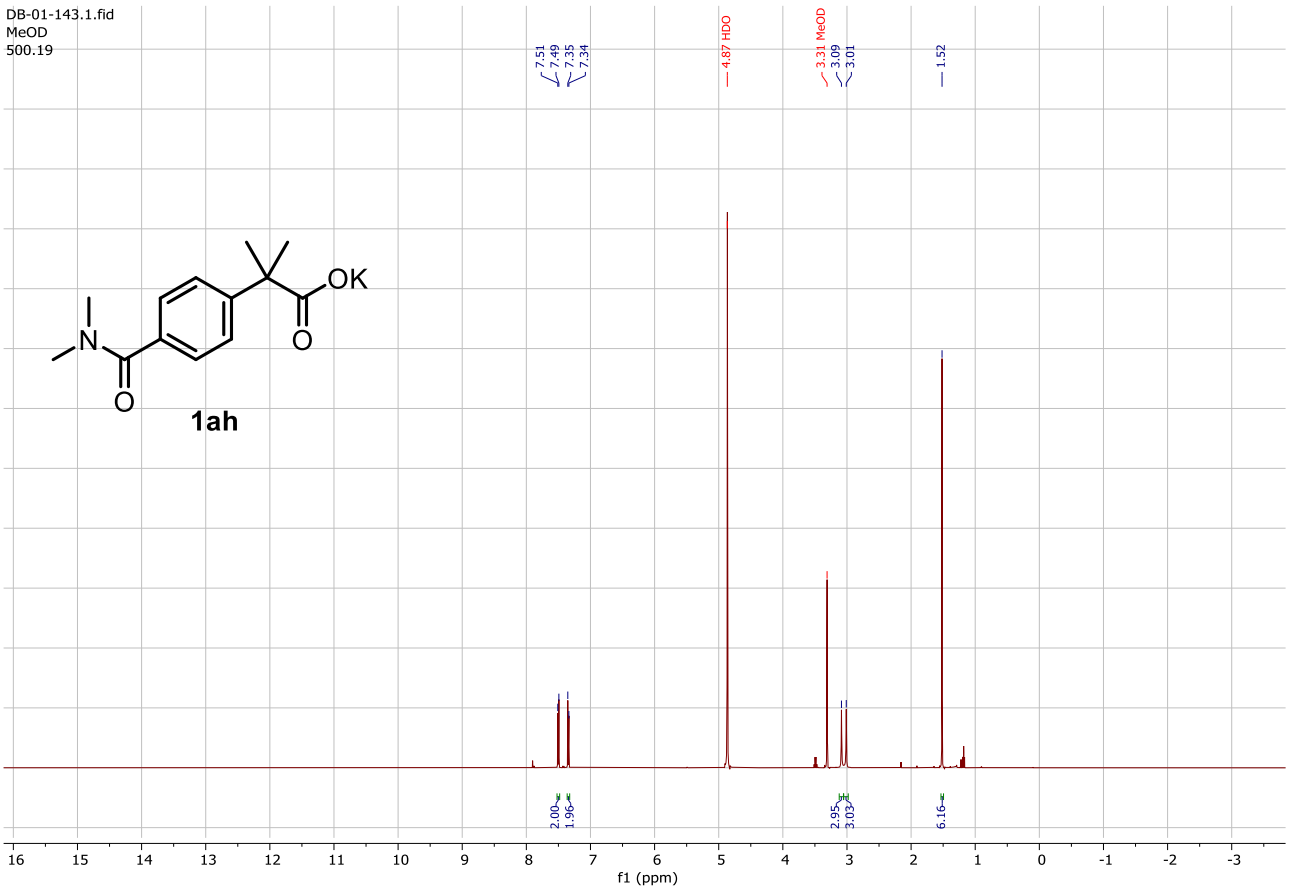
^{1}H NMR spectrum of **1ag** in CD_3OD at 400 MHz



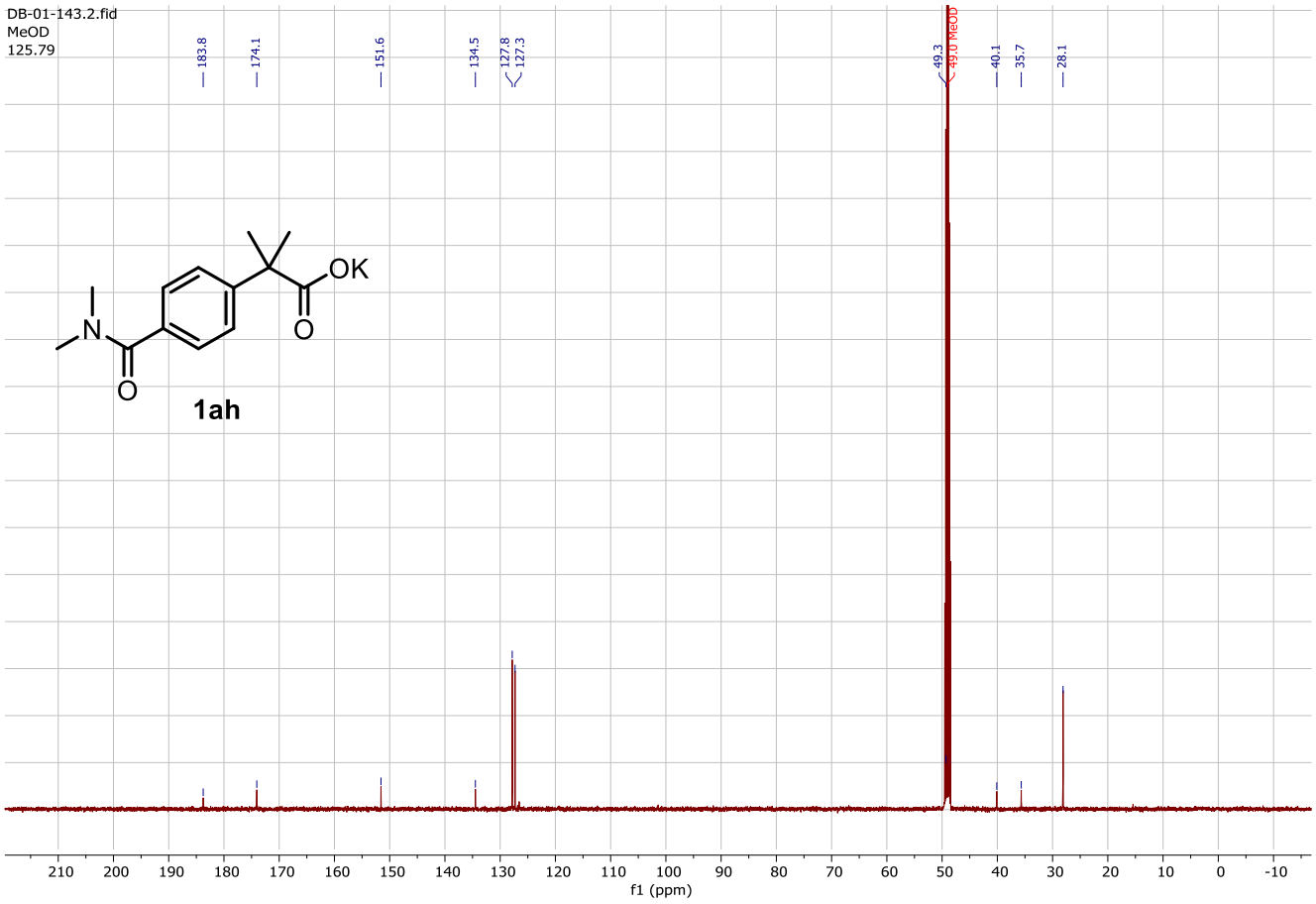
^{13}C NMR spectrum of **1ag** in CD_3OD at 126 MHz



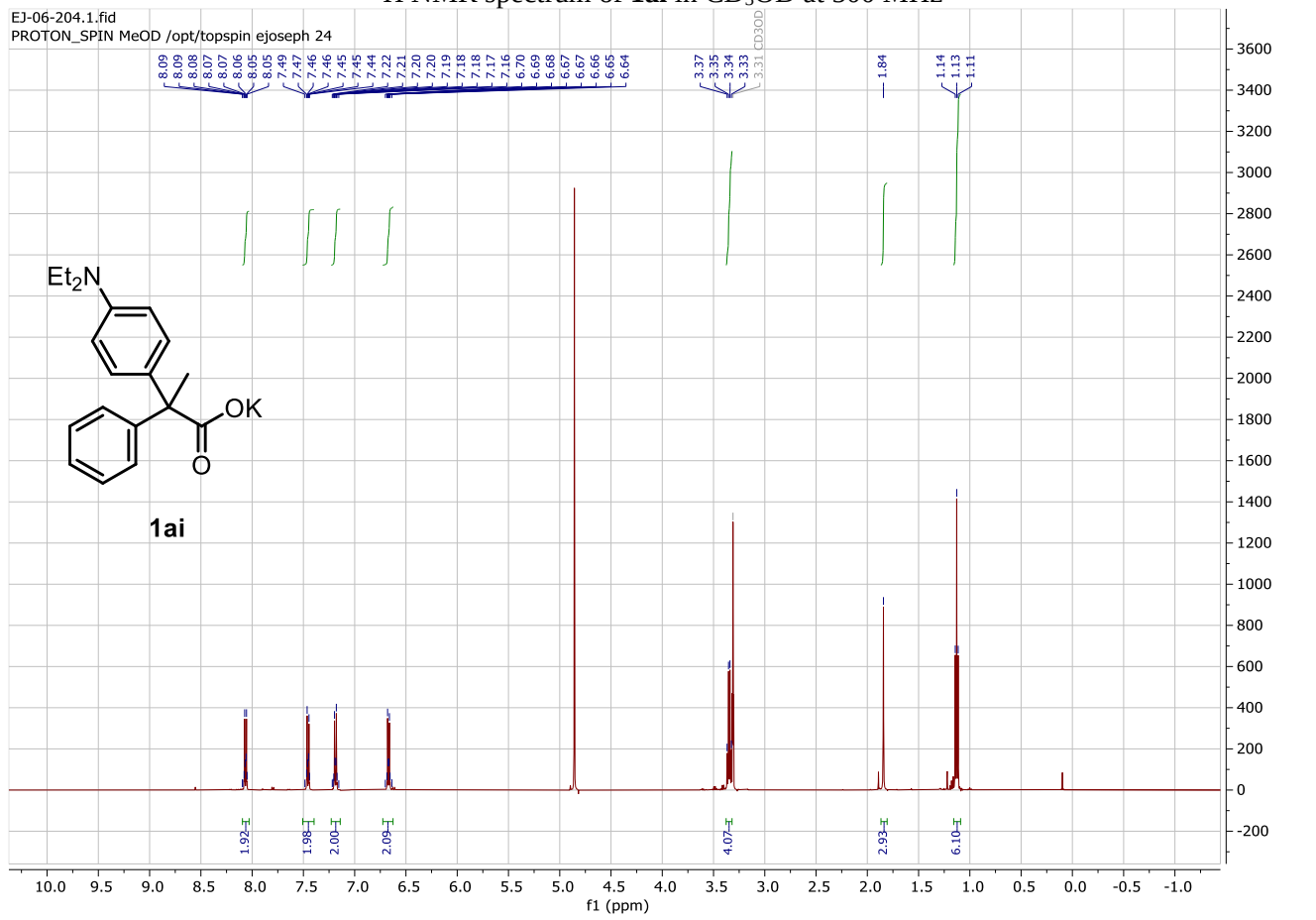
^{1}H NMR spectrum of **1ah** in CD_3OD at 400 MHz



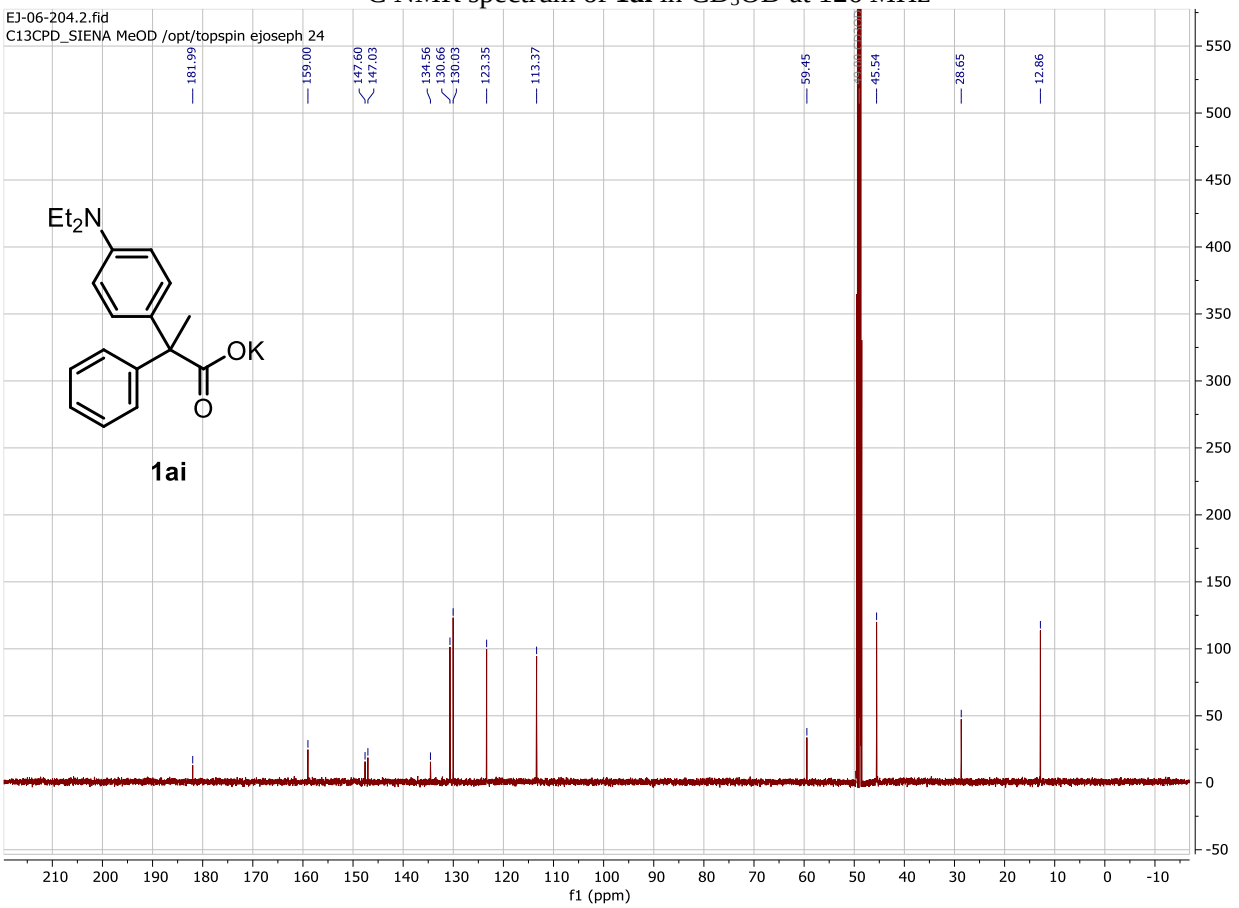
^{13}C NMR spectrum of **1ah** in CD_3OD at 126 MHz



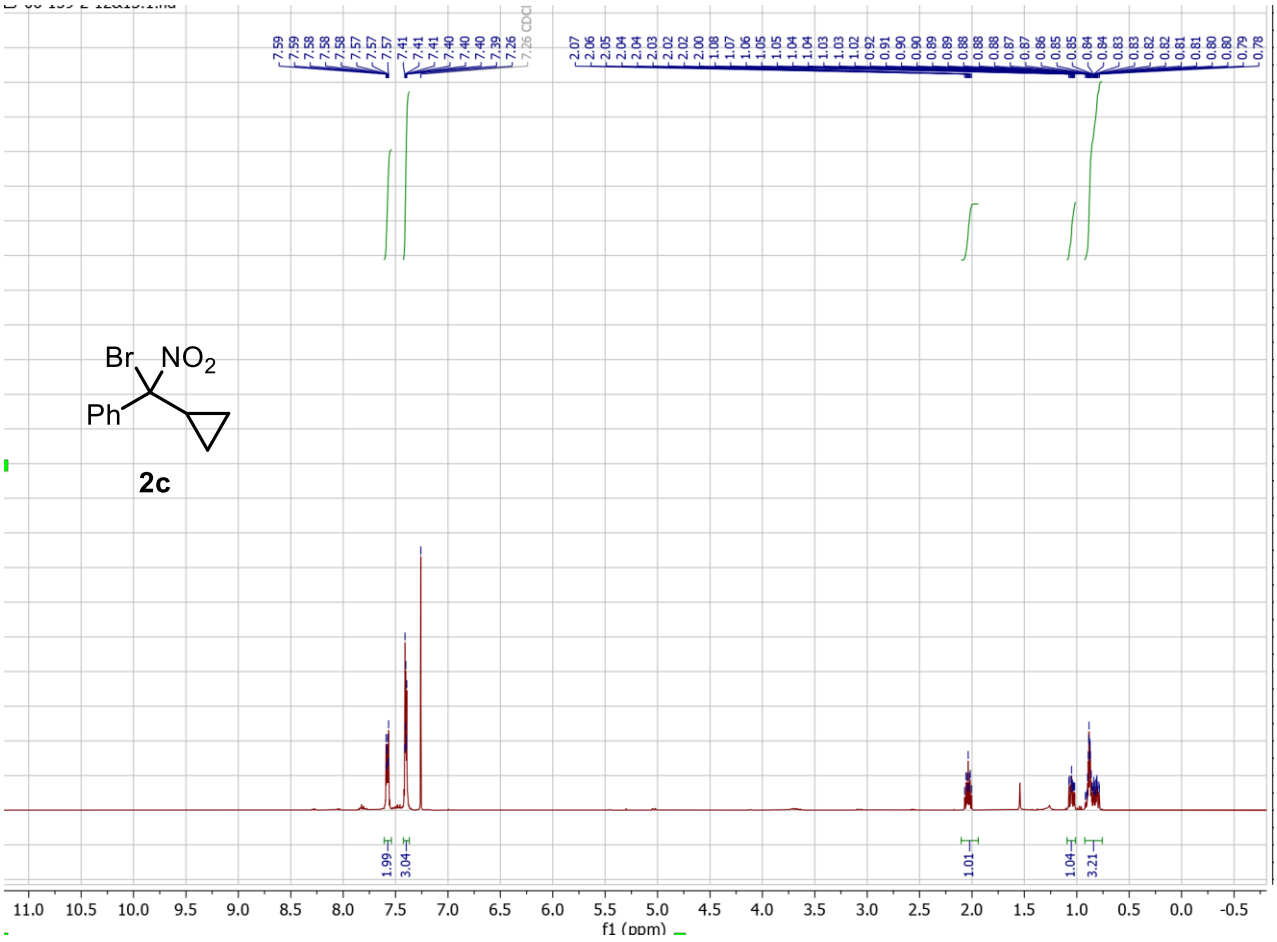
^{1}H NMR spectrum of **1ai** in CD_3OD at 500 MHz



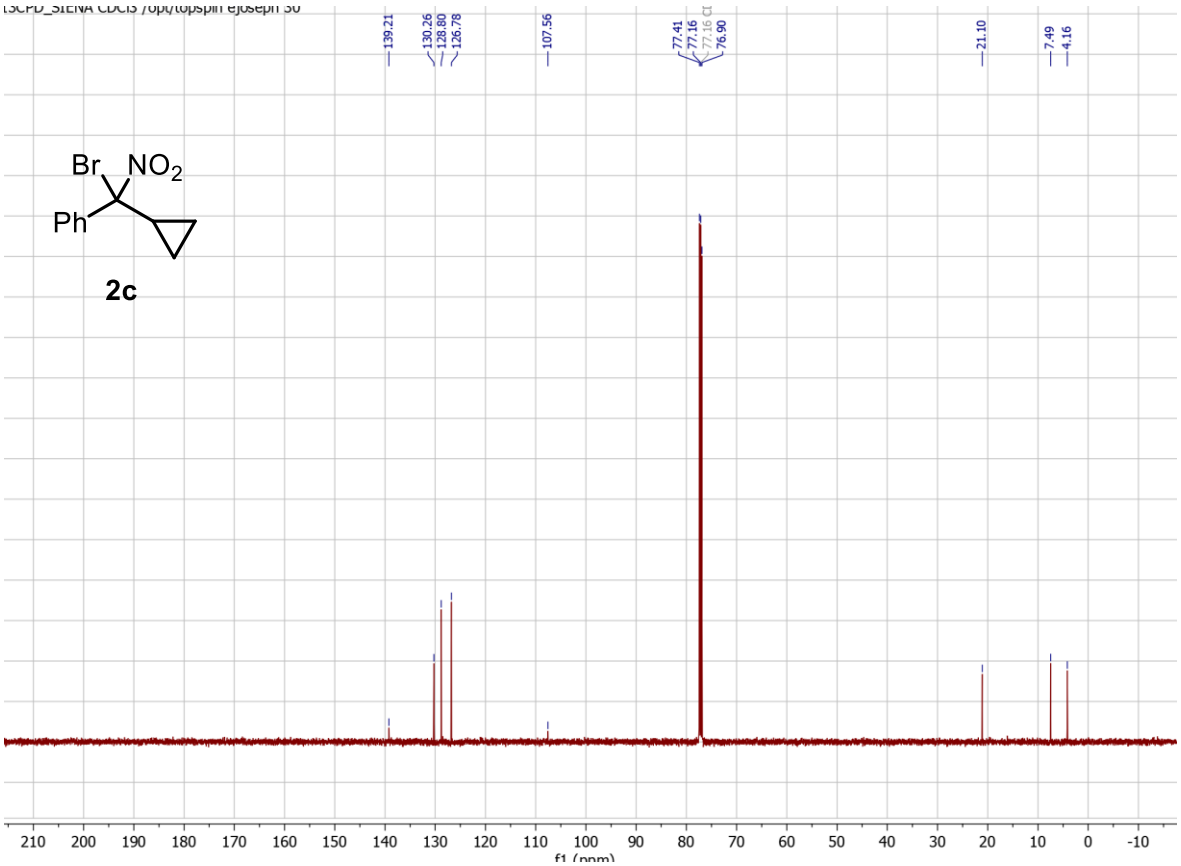
^{13}C NMR spectrum of **1ai** in CD_3OD at 126 MHz



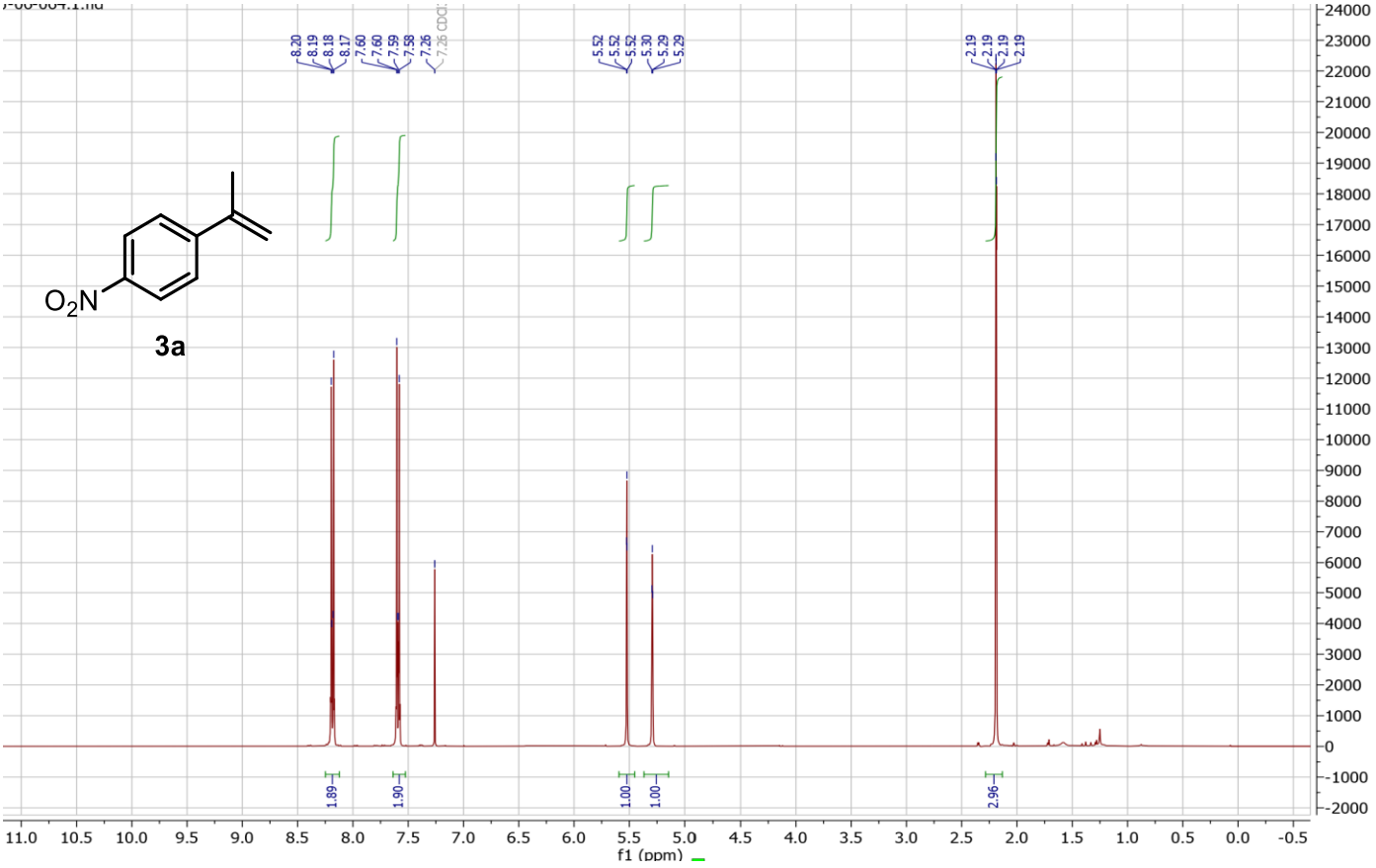
^{1}H NMR spectrum of **2c** in $CDCl_3$ at 400 MHz



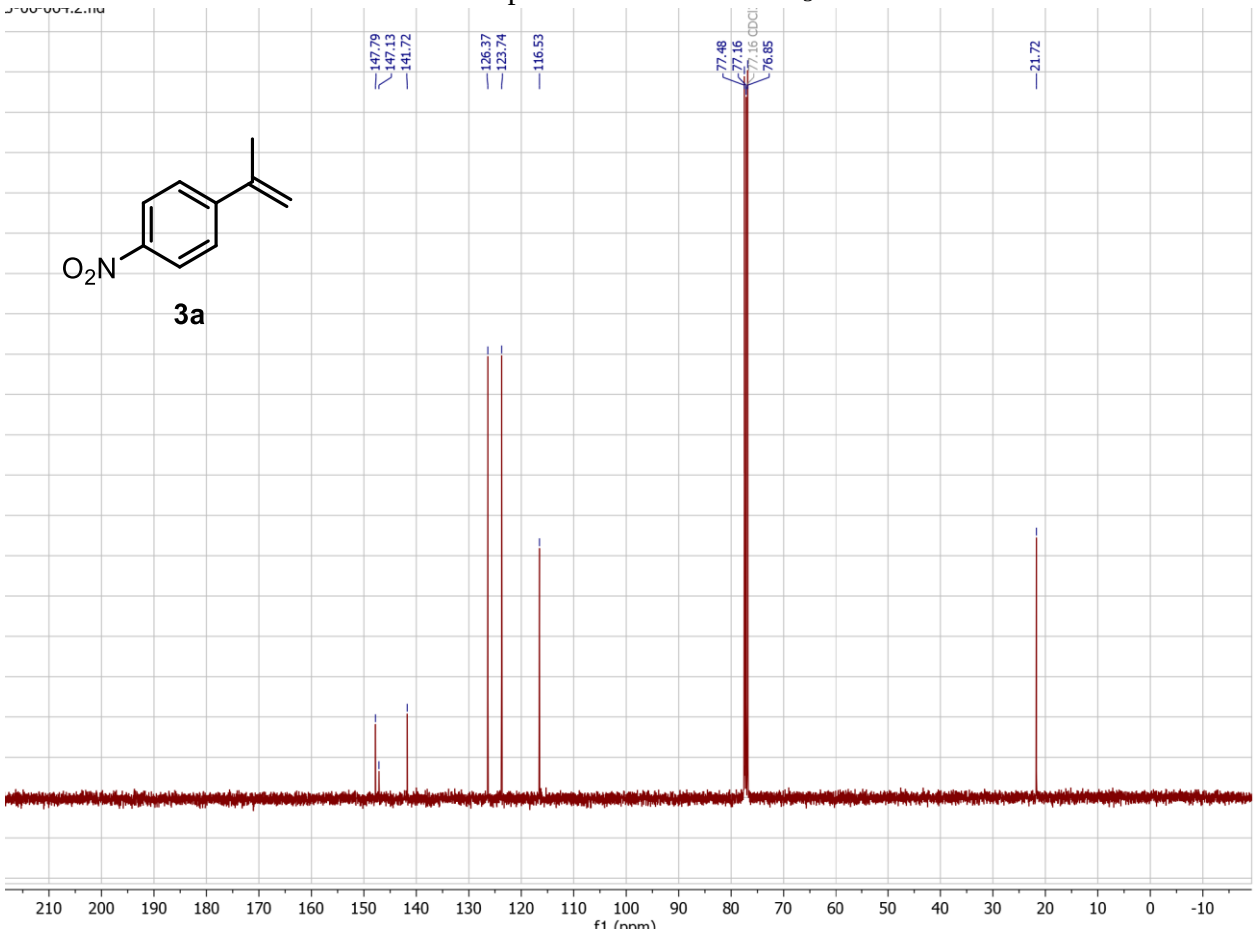
^{13}C NMR spectrum of **2c** in $CDCl_3$ at 126 MHz



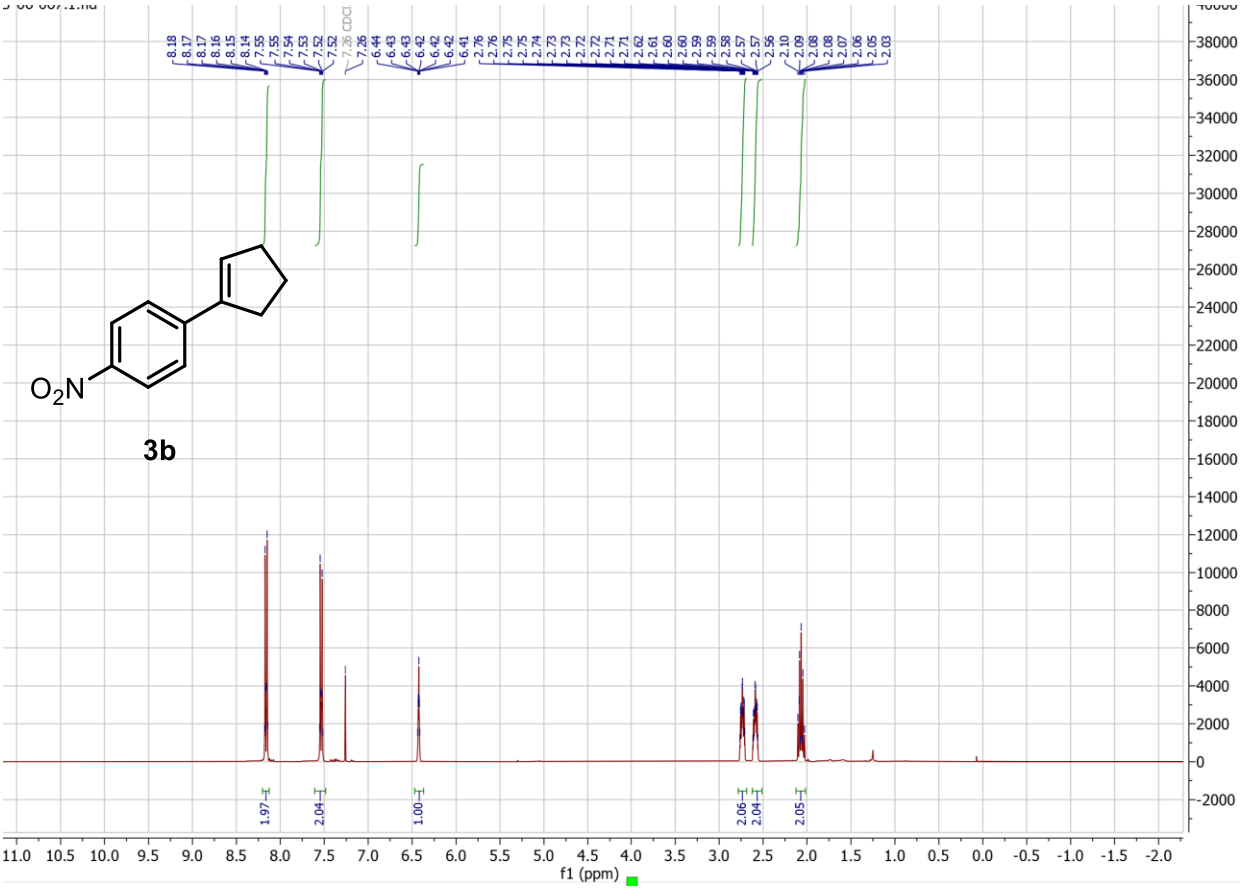
^{1}H NMR spectrum of **3a** in $CDCl_3$ at 400 MHz



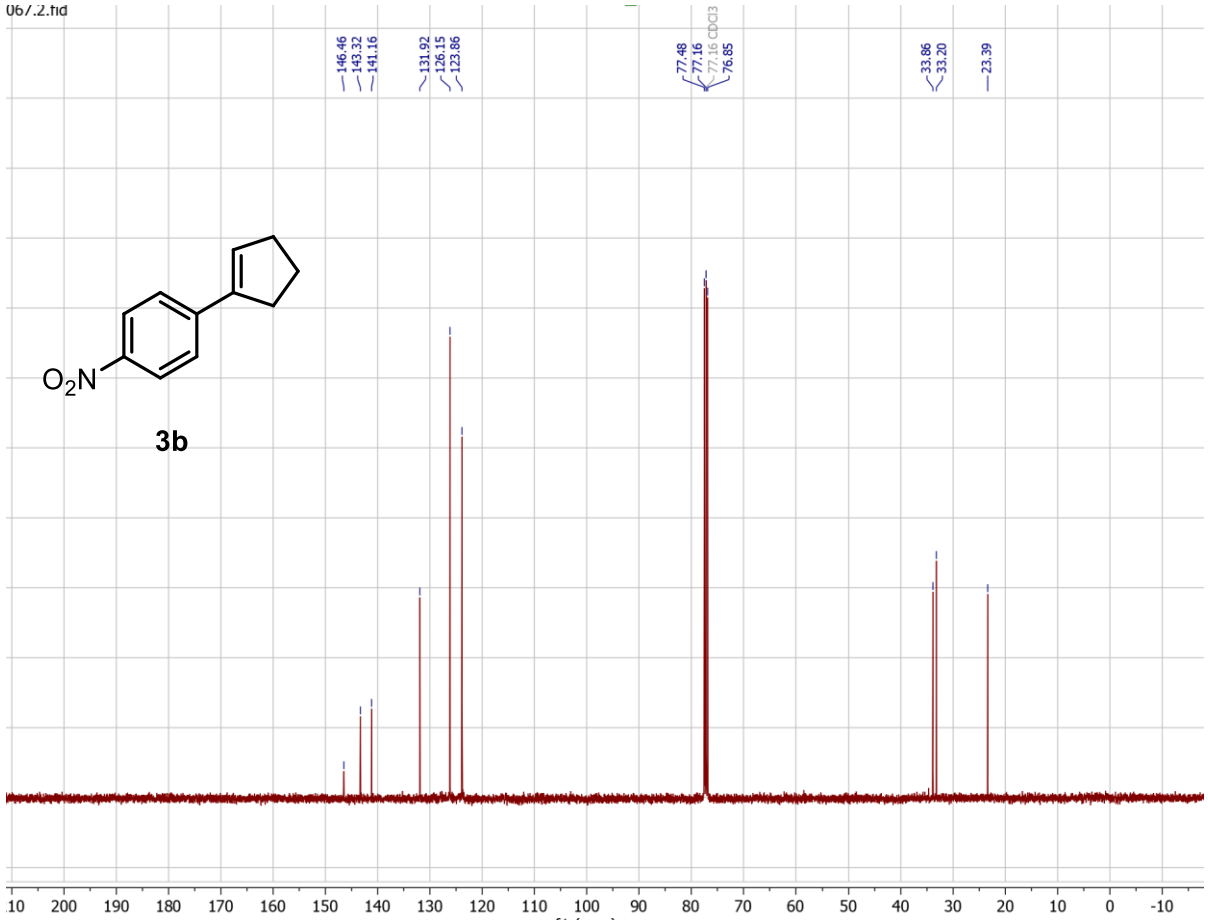
^{13}C NMR spectrum of **3a** in $CDCl_3$ at 101 MHz



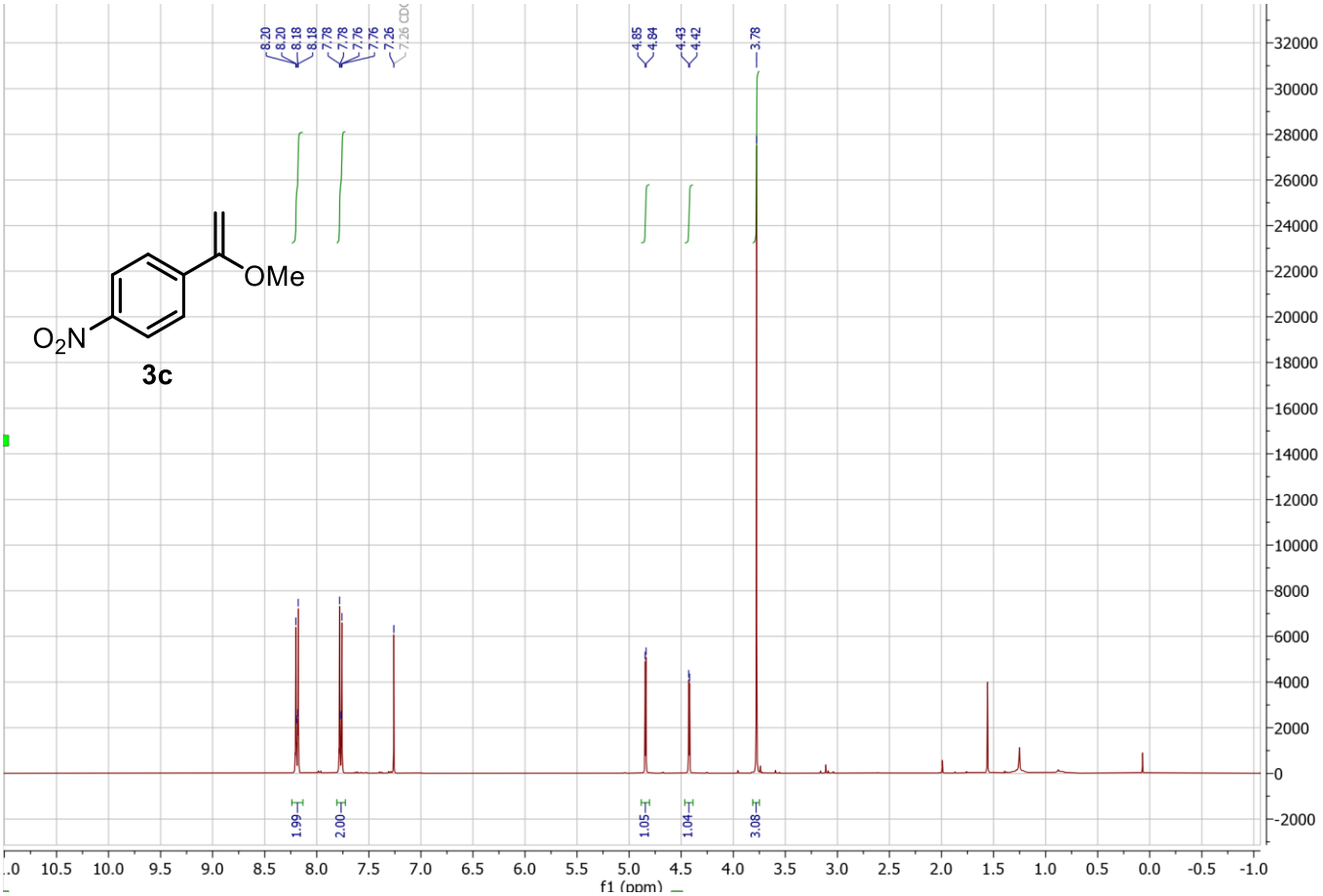
^{1}H NMR spectrum of **3b** in $CDCl_3$ at 400 MHz



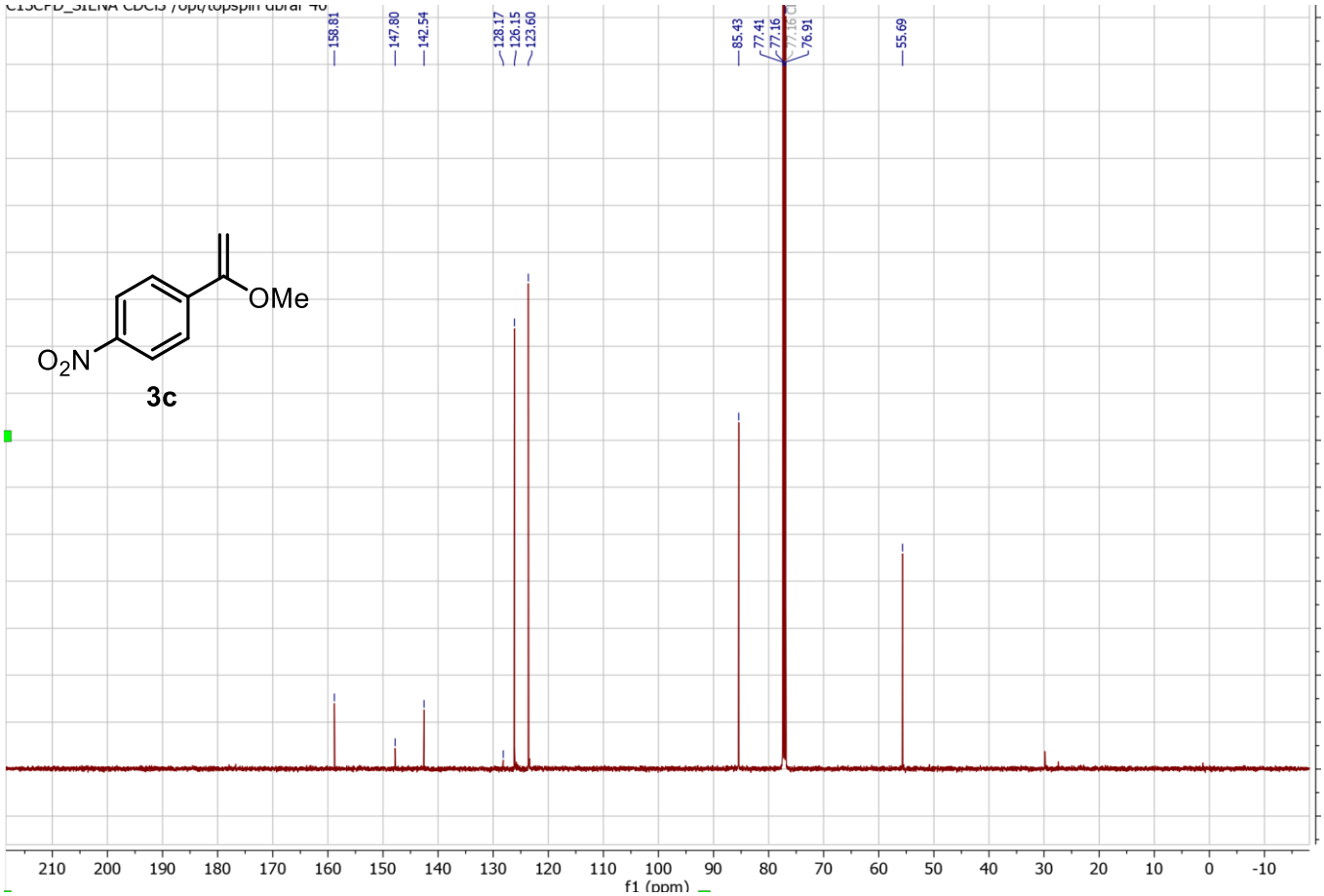
^{13}C NMR spectrum of **3b** in $CDCl_3$ at 101 MHz



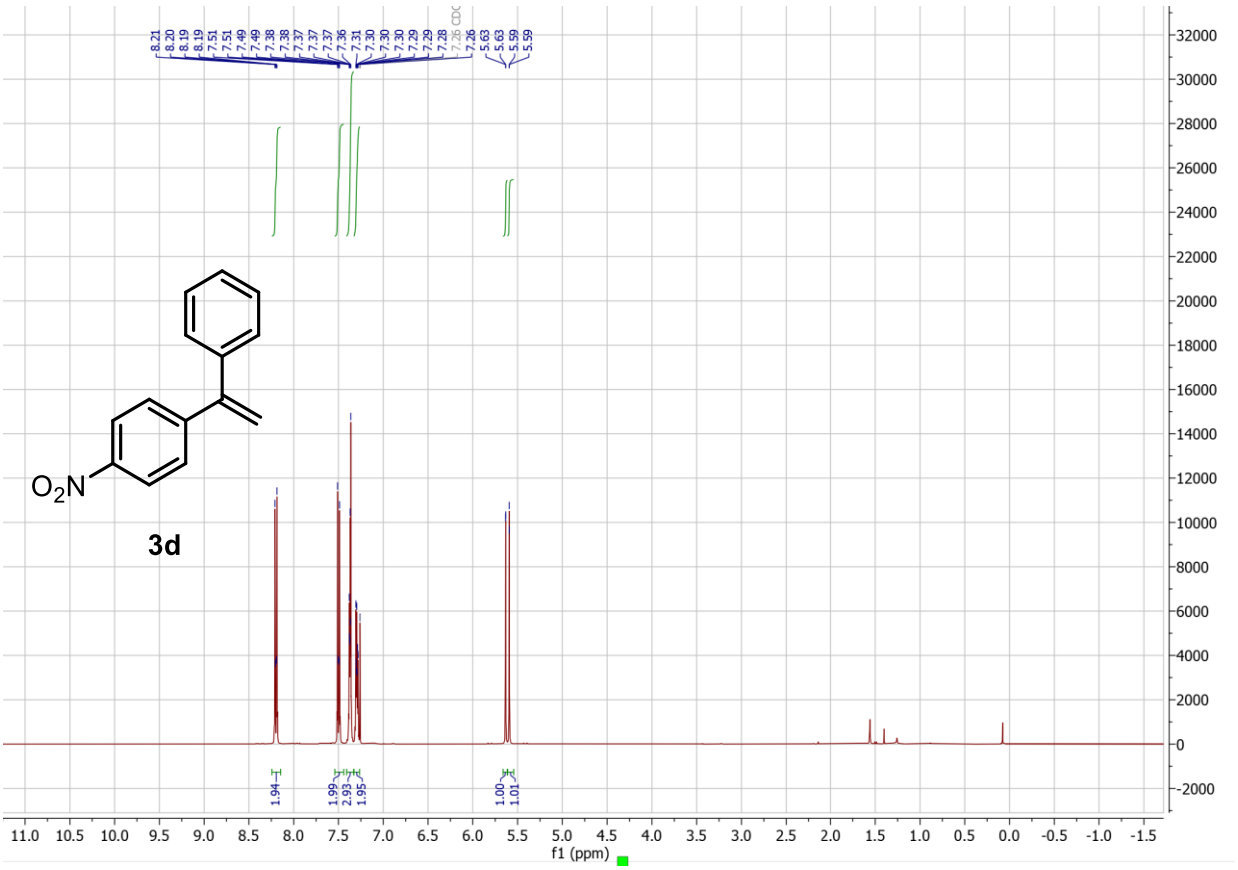
^{1}H NMR spectrum of **3c** in $CDCl_3$ at 400 MHz



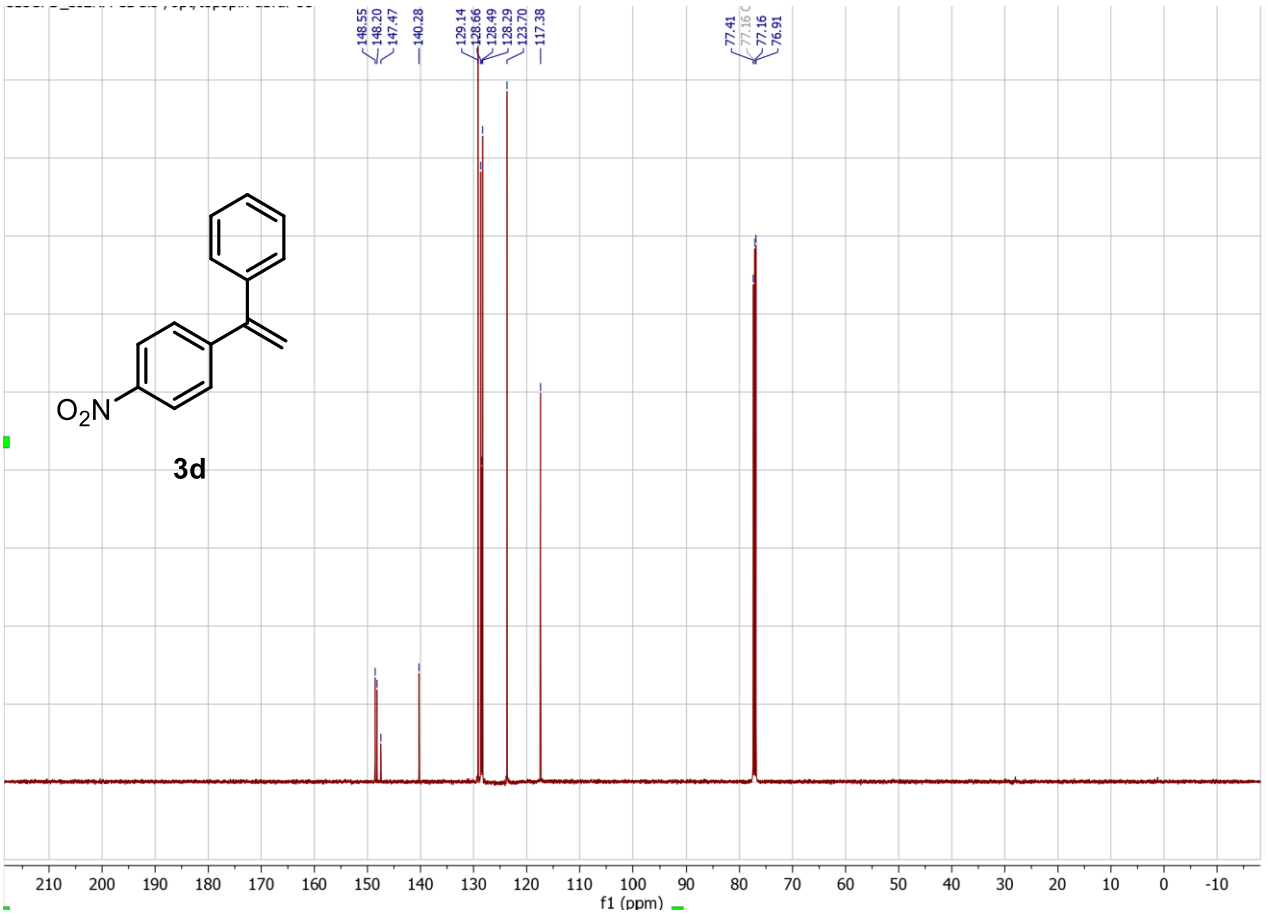
^{13}C NMR spectrum of **3c** in $CDCl_3$ at 126 MHz



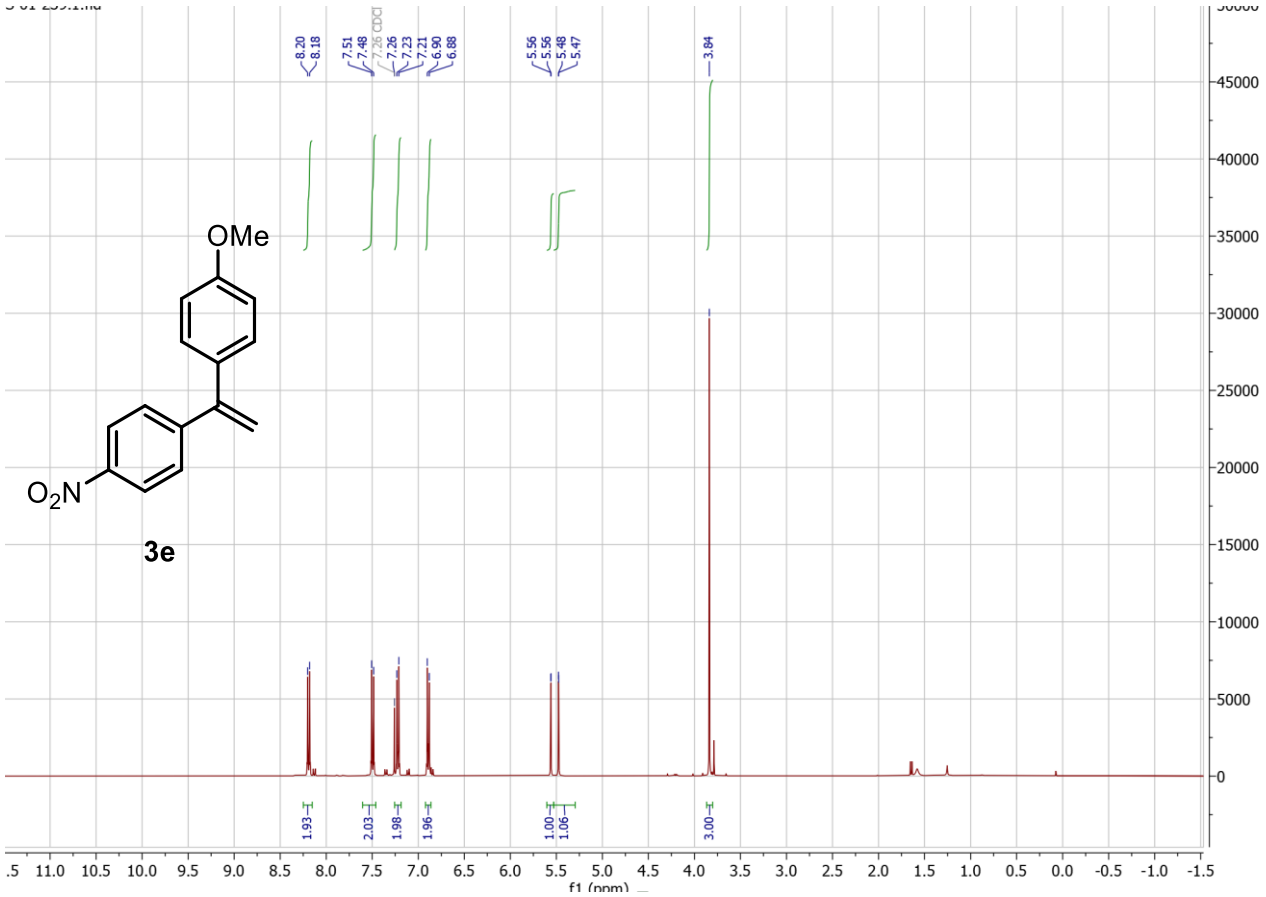
^{1}H NMR spectrum of **3d** in $CDCl_3$ at 400 MHz



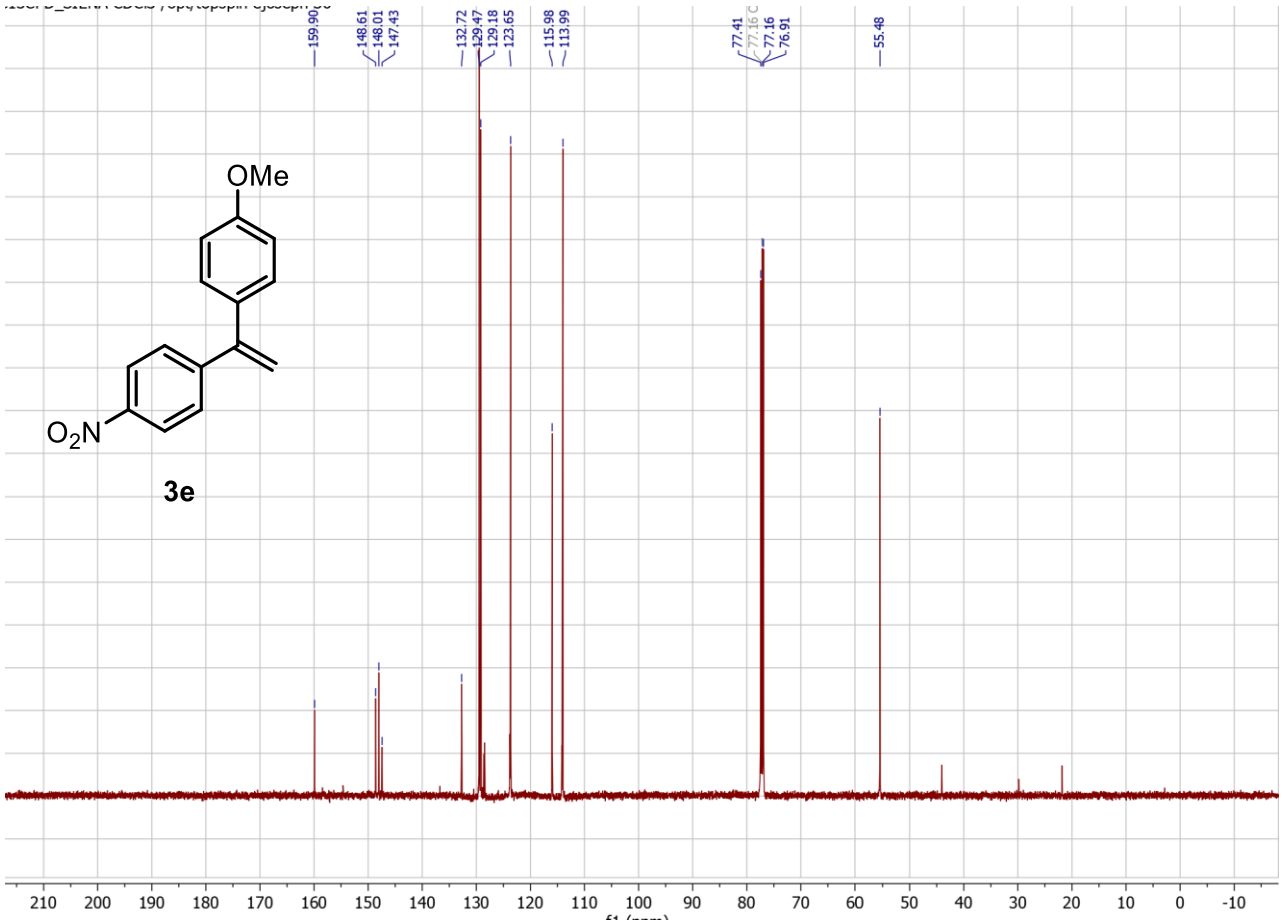
^{13}C NMR spectrum of **3d** in $CDCl_3$ at 126 MHz



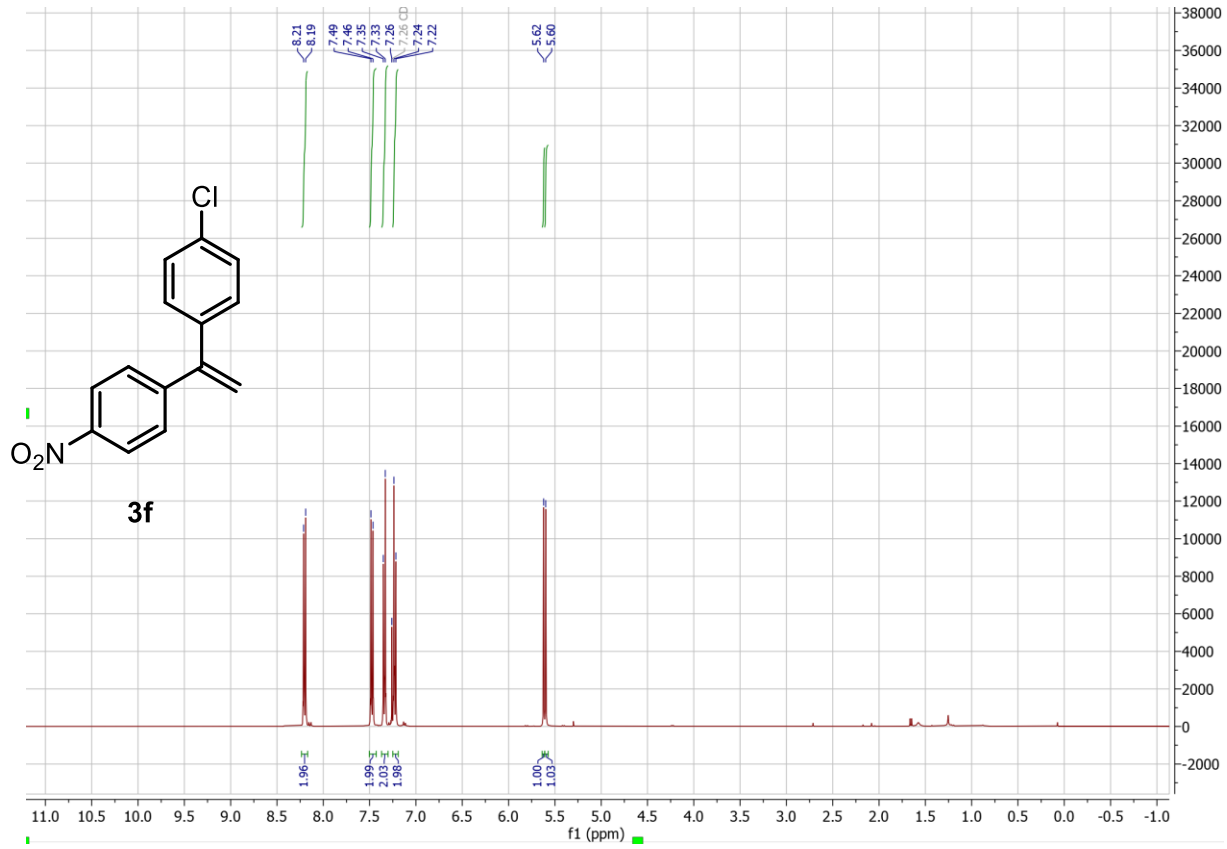
^{1}H NMR spectrum of **3e** in $CDCl_3$ at 500 MHz



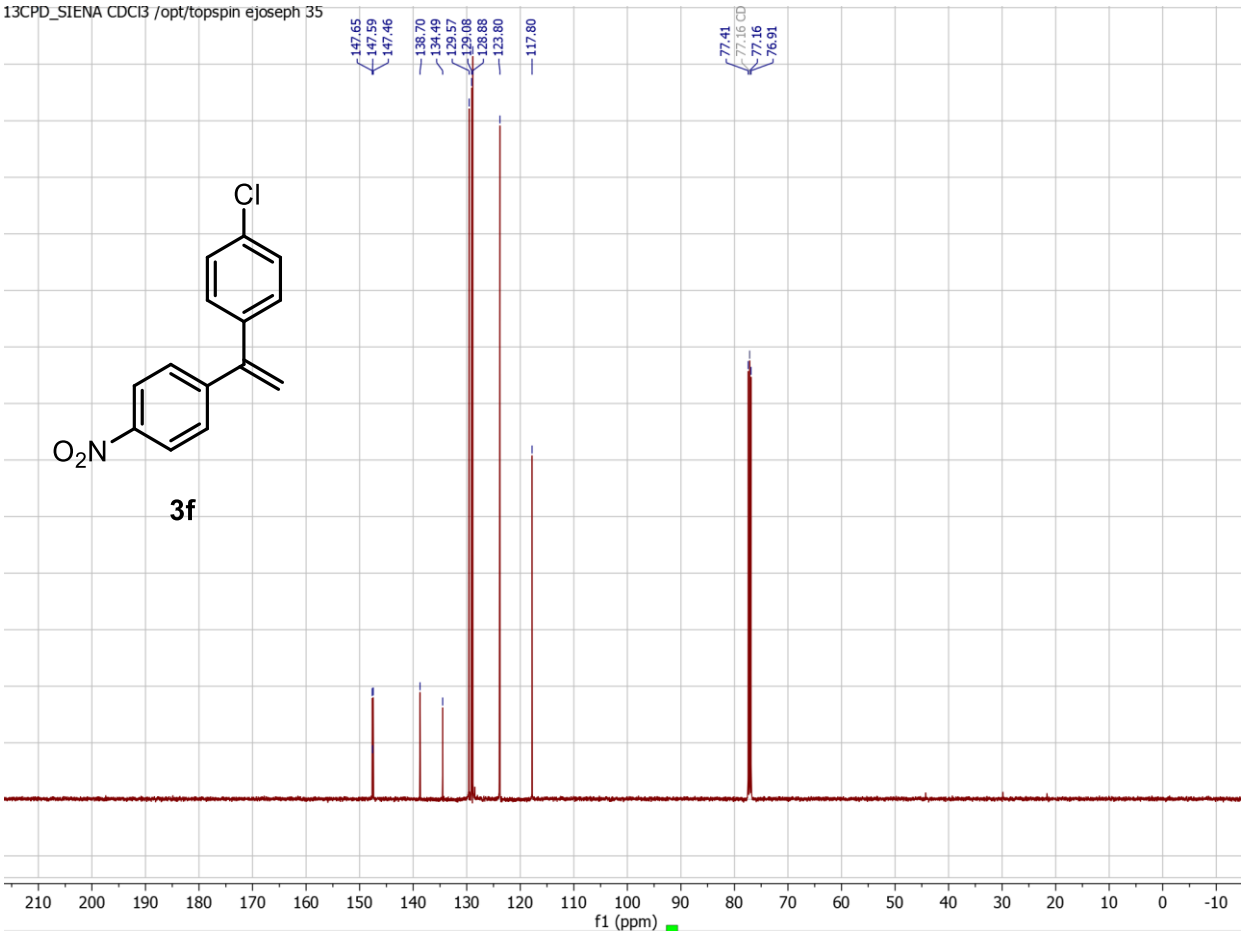
^{13}C NMR spectrum of **3e** in $CDCl_3$ at 126 MHz



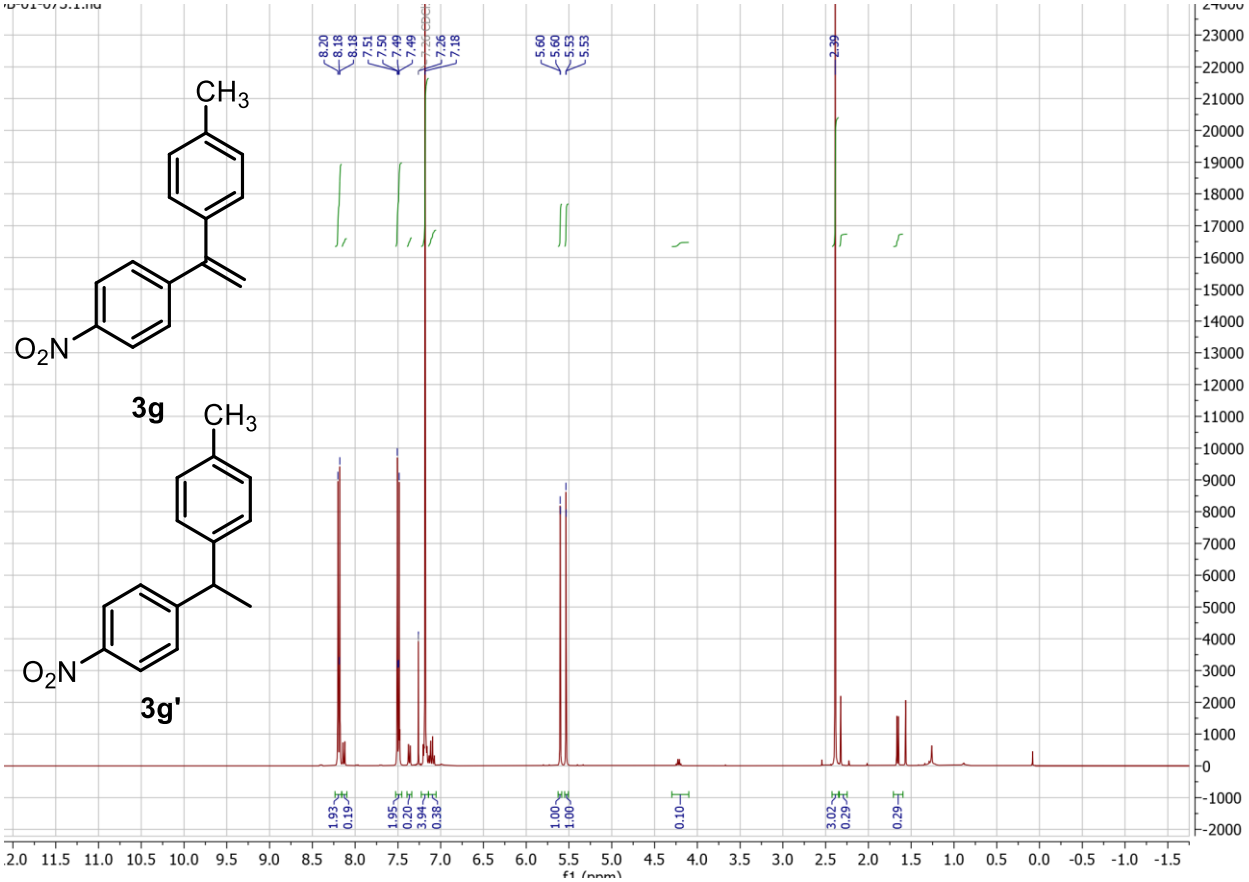
^{1}H NMR spectrum of **3f** in $CDCl_3$ at 400 MHz



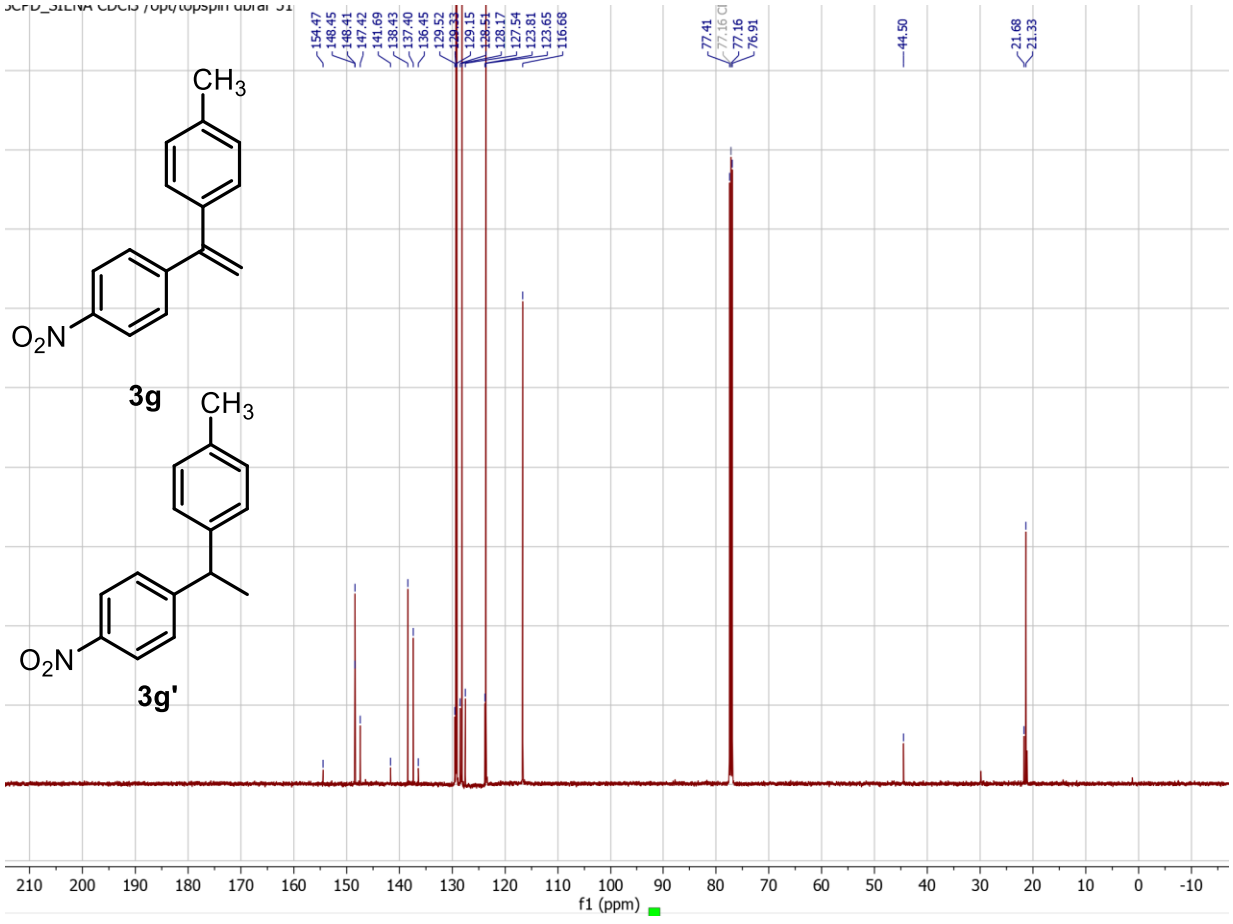
^{13}C NMR spectrum of **3f** in $CDCl_3$ at 126 MHz



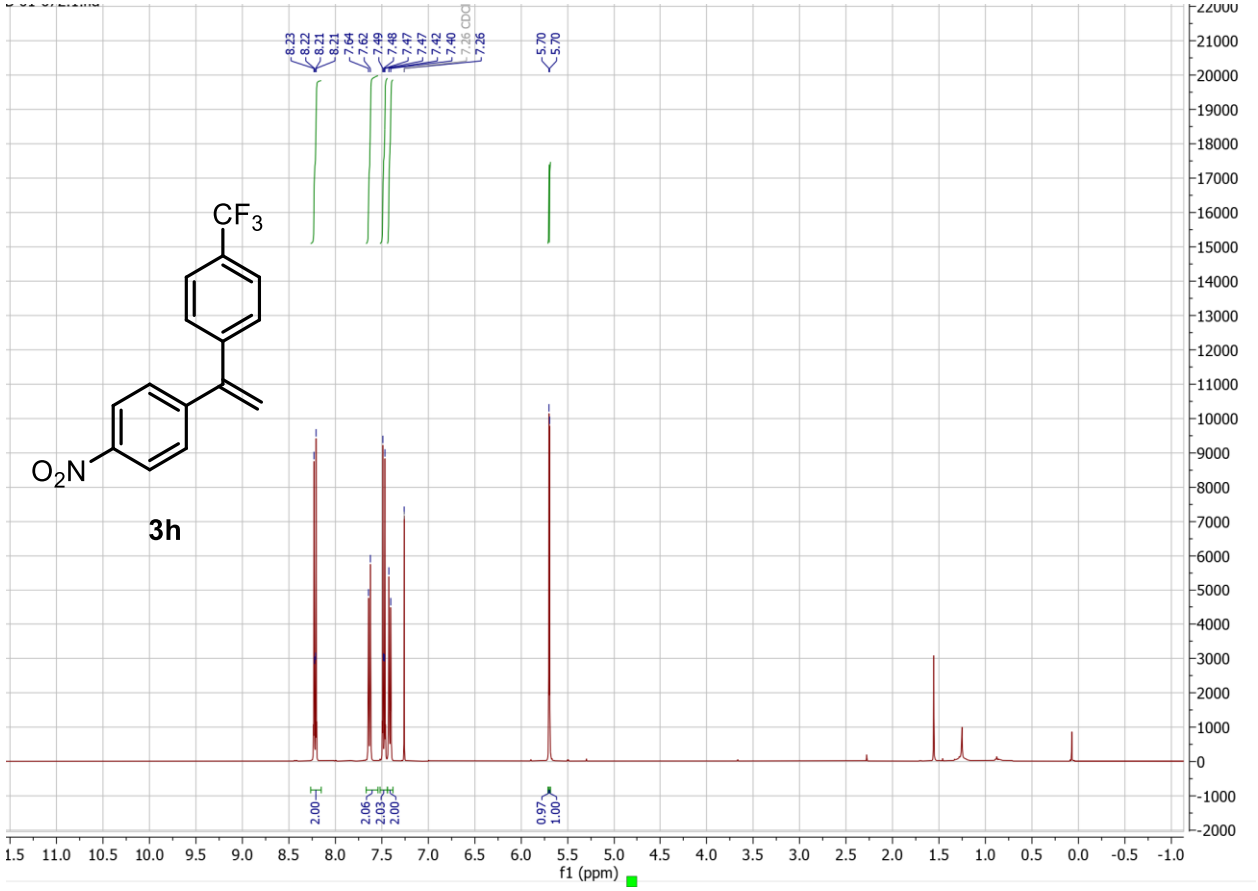
^{1}H NMR spectrum of **3g** & **3g'** in $CDCl_3$ at 400 MHz



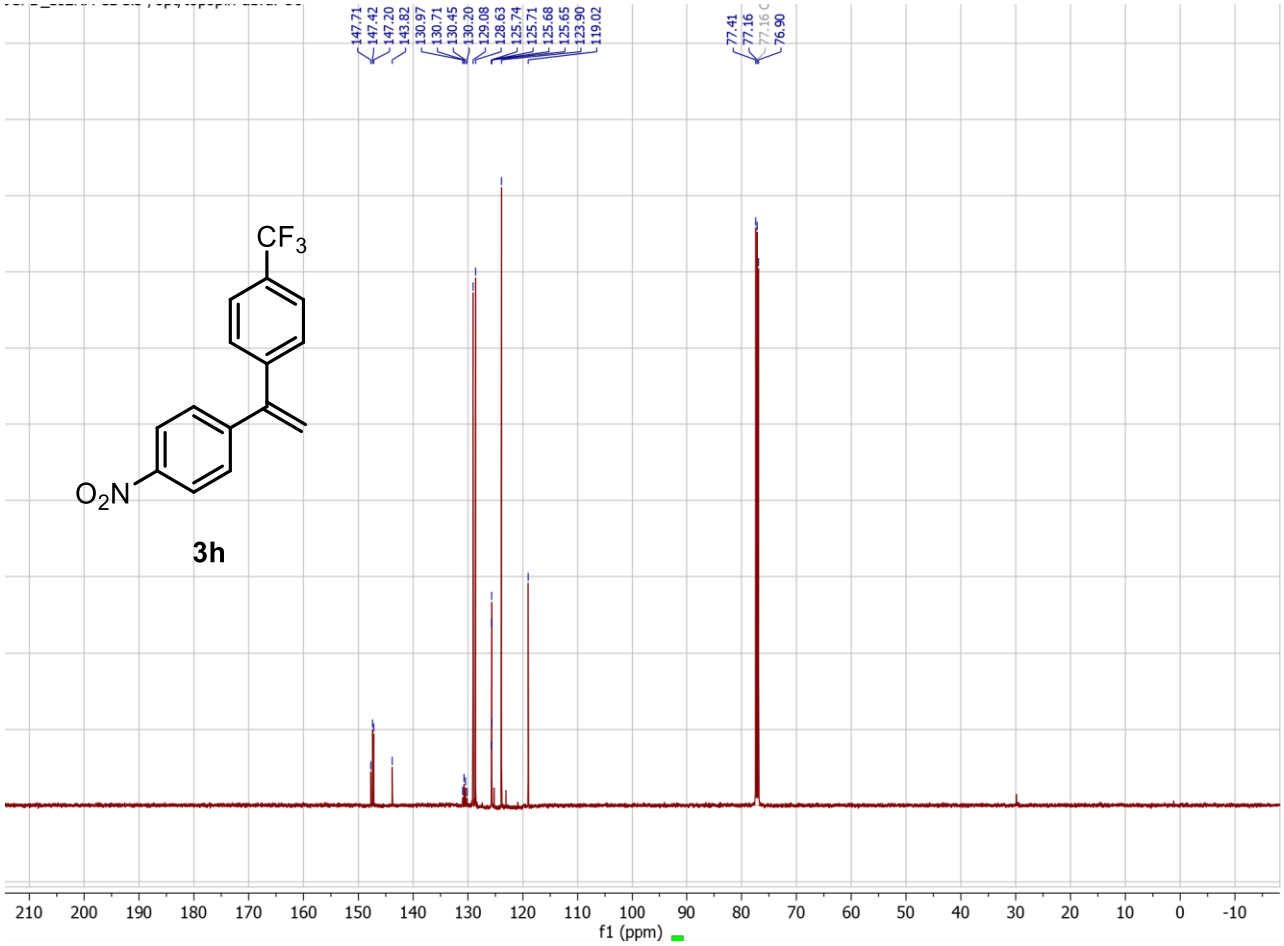
^{13}C NMR spectrum of **3g** & **3g'** in $CDCl_3$ at 400 MHz



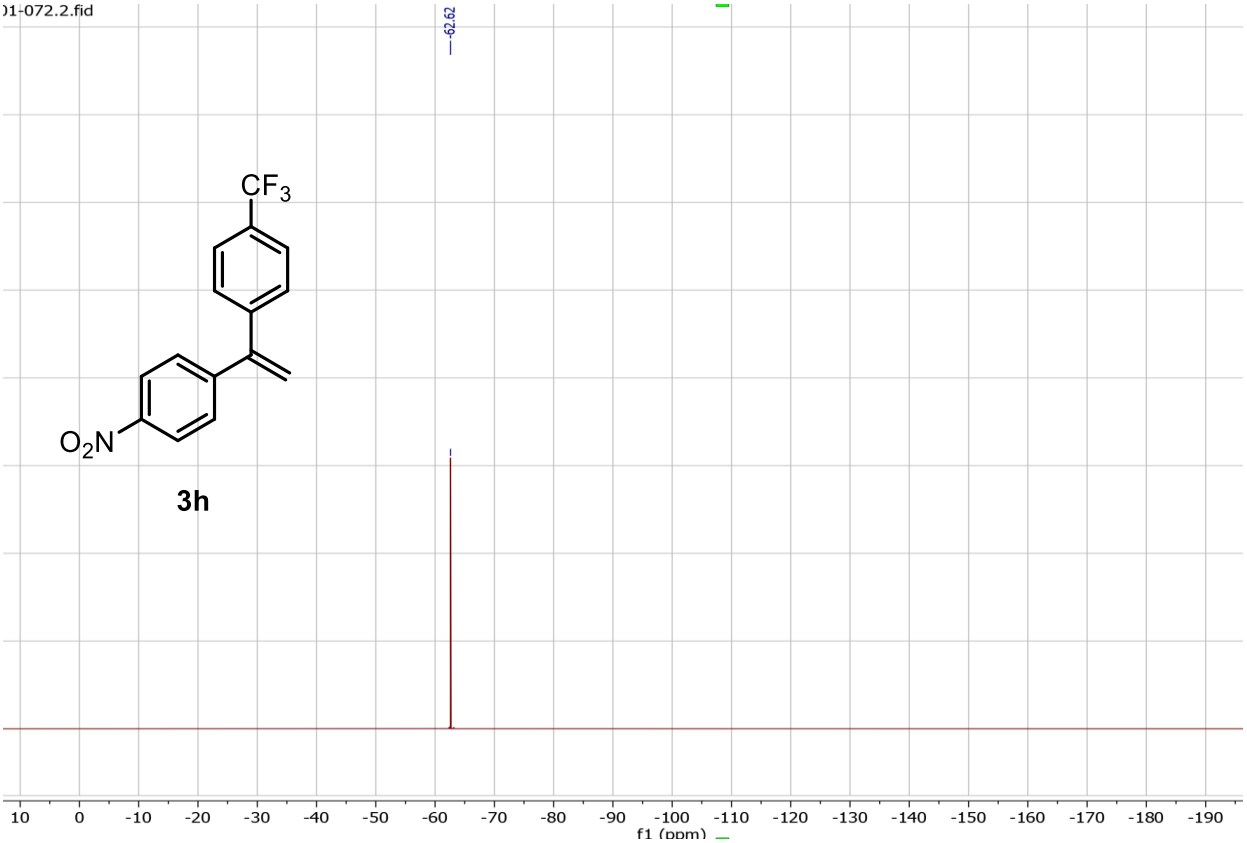
^{1}H NMR spectrum of **3h** in $CDCl_3$ at 400 MHz



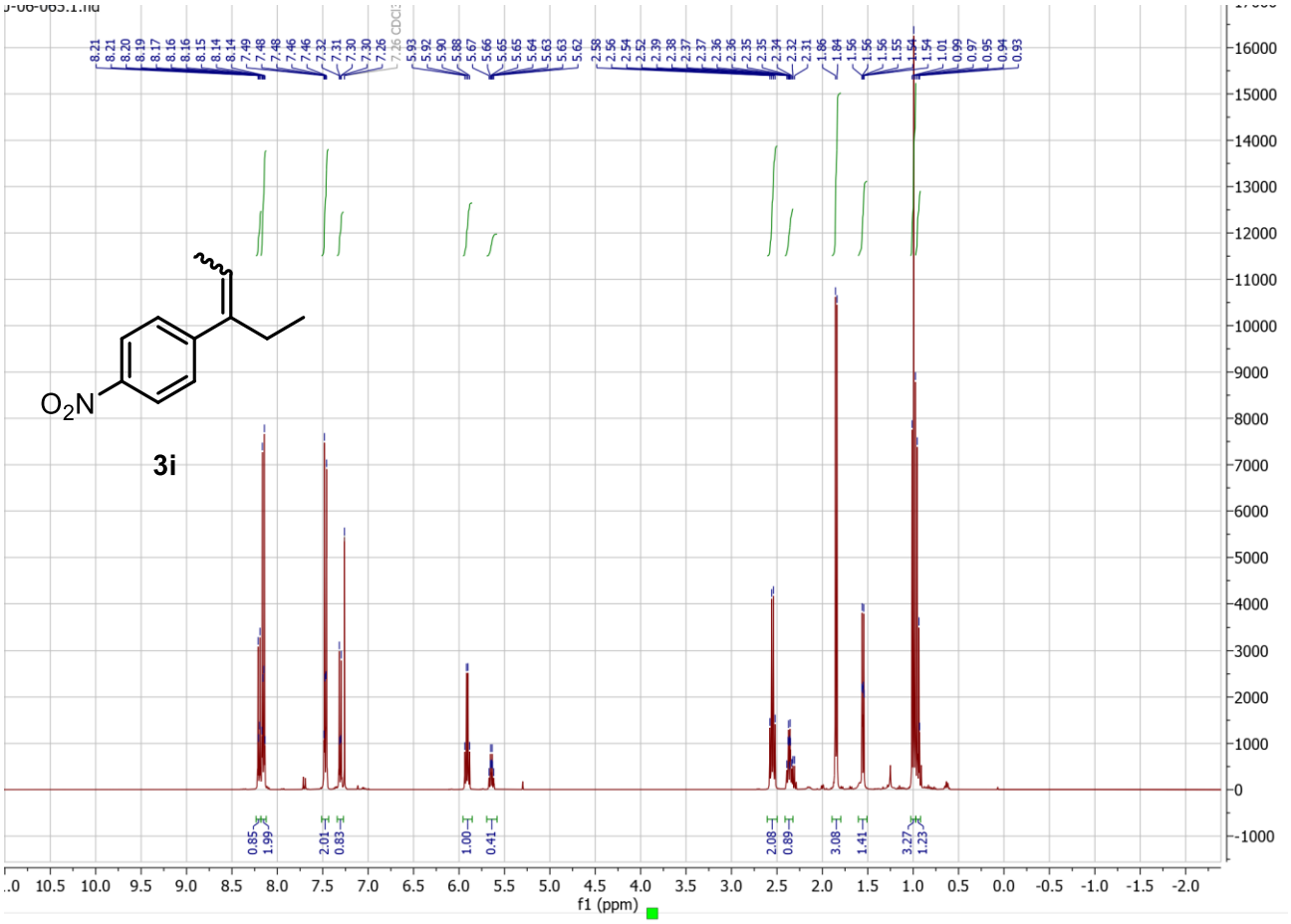
^{13}C NMR spectrum of **3h** in $CDCl_3$ at 126 MHz



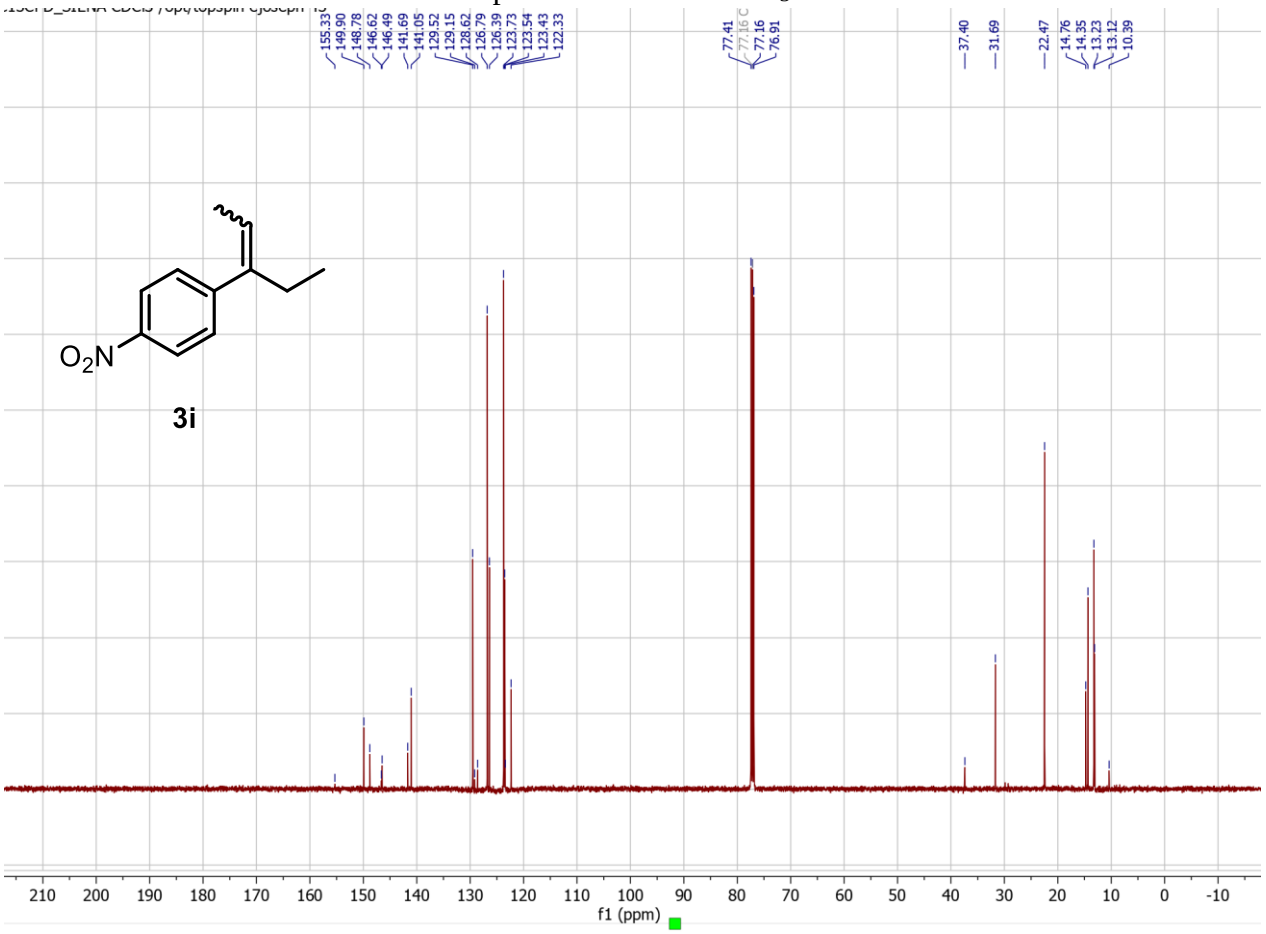
^{19}F NMR spectrum of **3h** in $CDCl_3$ at 376 MHz



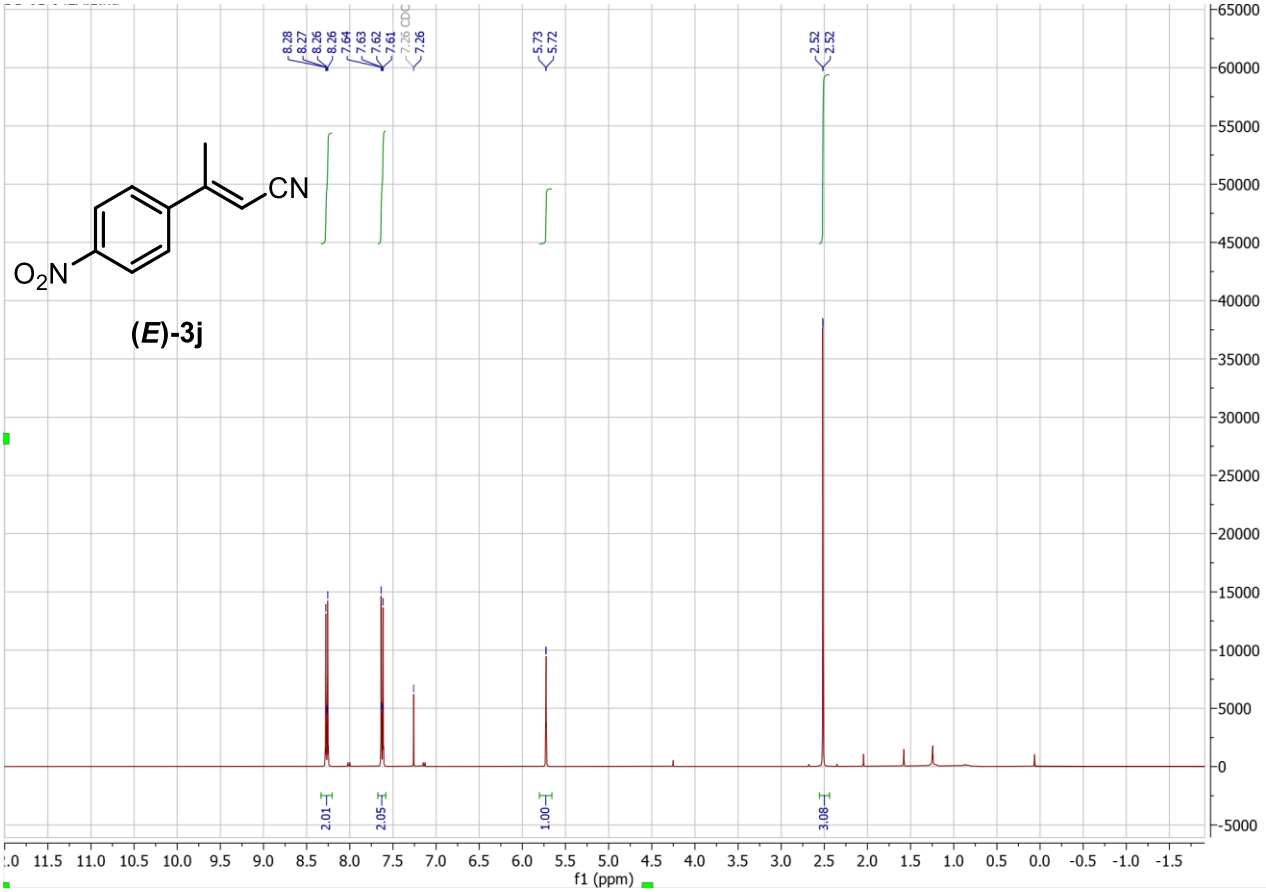
^{1}H NMR spectrum of **3i** in $CDCl_3$ at 400 MHz



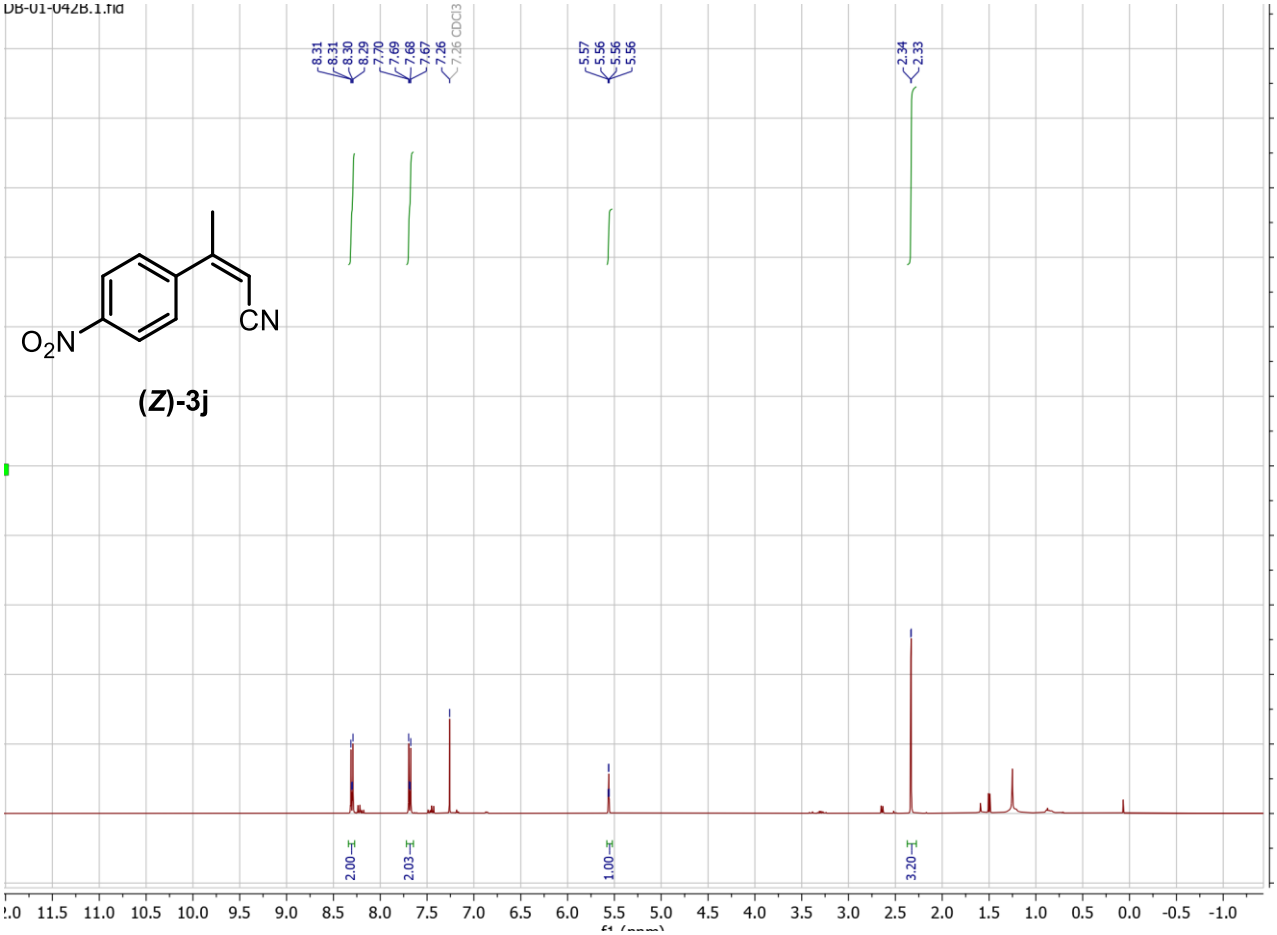
^{13}C NMR spectrum of **3i** in $CDCl_3$ at 126 MHz



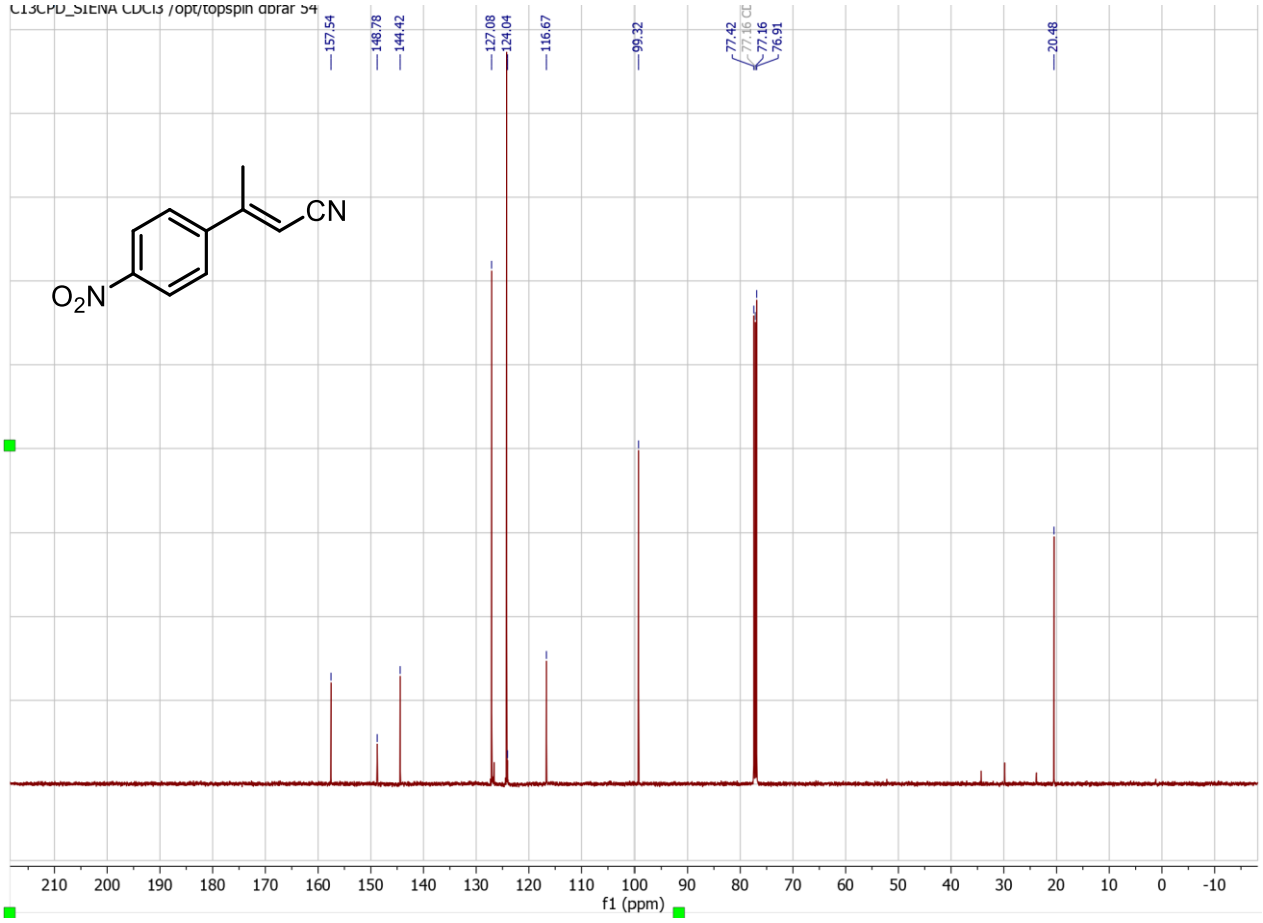
^{1}H NMR spectrum of **(*E*)-3j** in $CDCl_3$ at 400 MHz



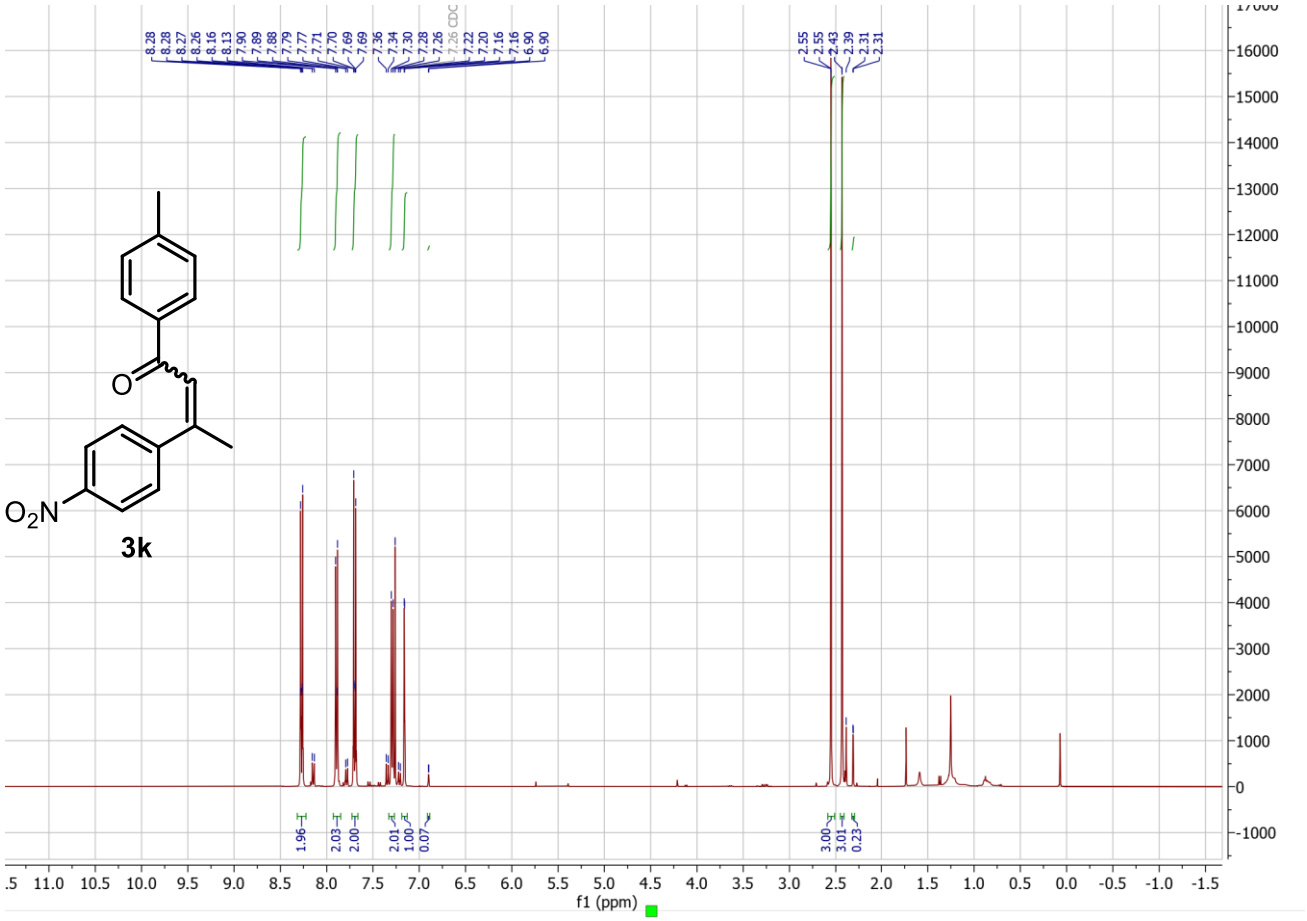
^{1}H NMR spectrum of **(*Z*)-3j** in $CDCl_3$ at 400 MHz



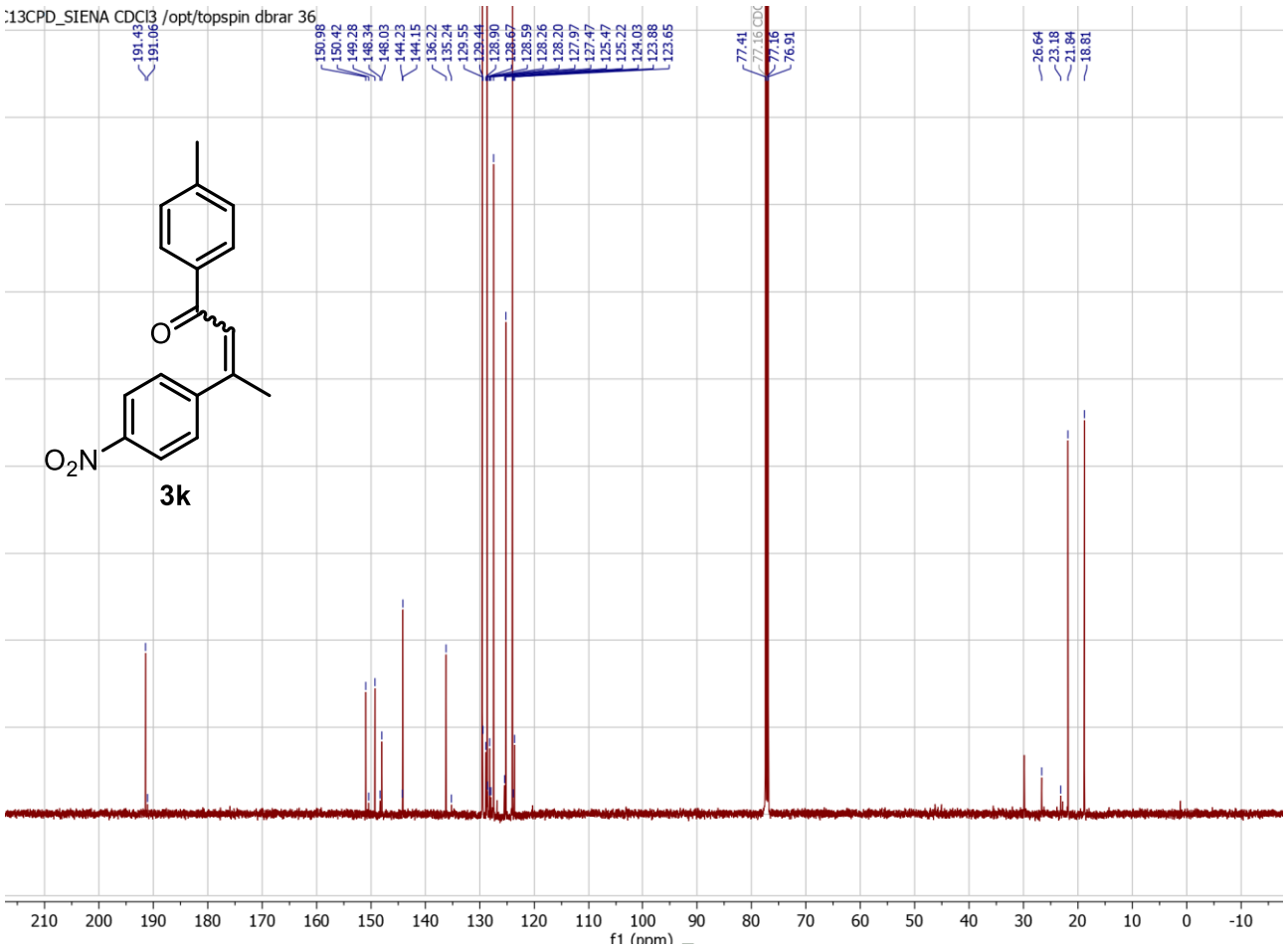
^{13}C NMR spectrum of **(*E*)-3j** in $CDCl_3$ at 126 MHz



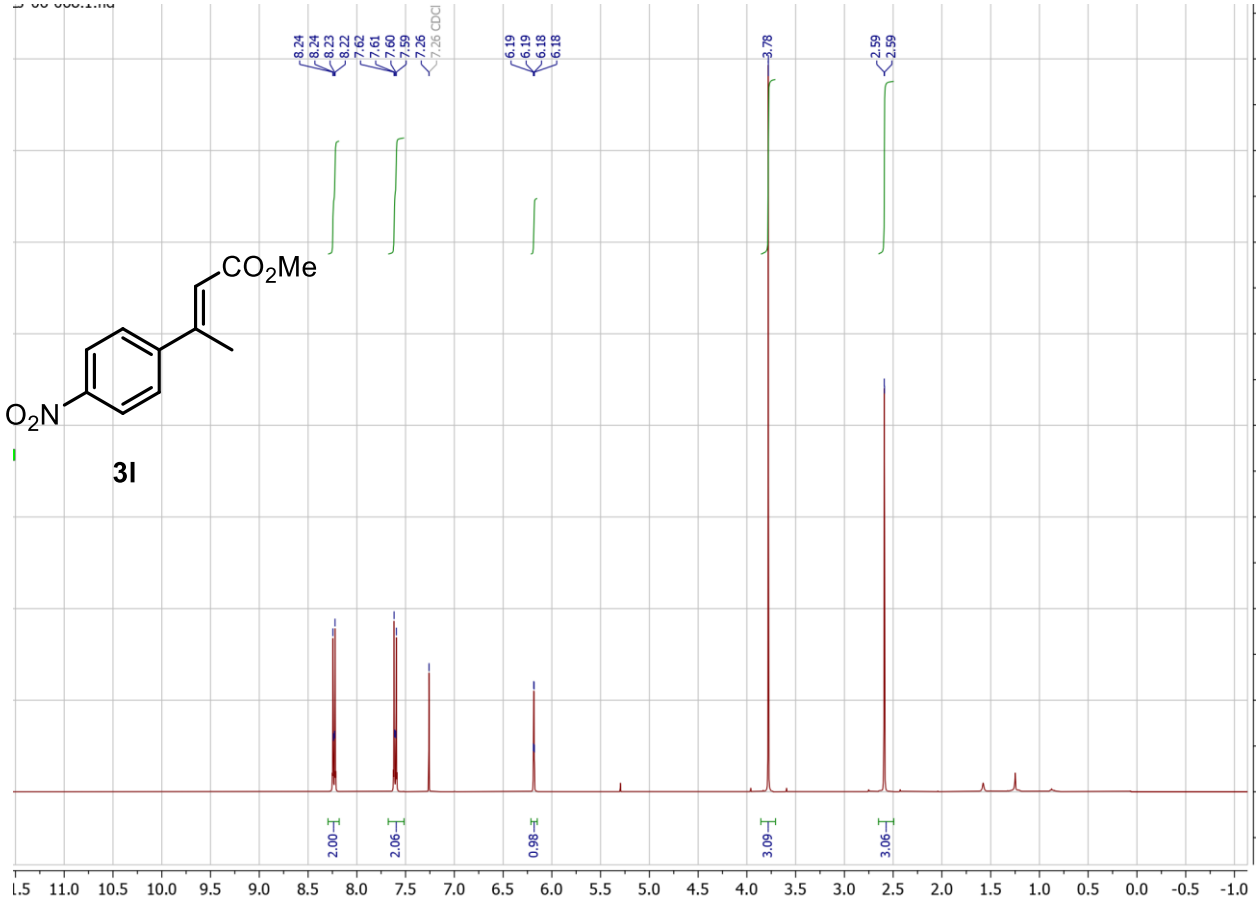
^{1}H NMR spectrum of **3k** in $CDCl_3$ at 400 MHz



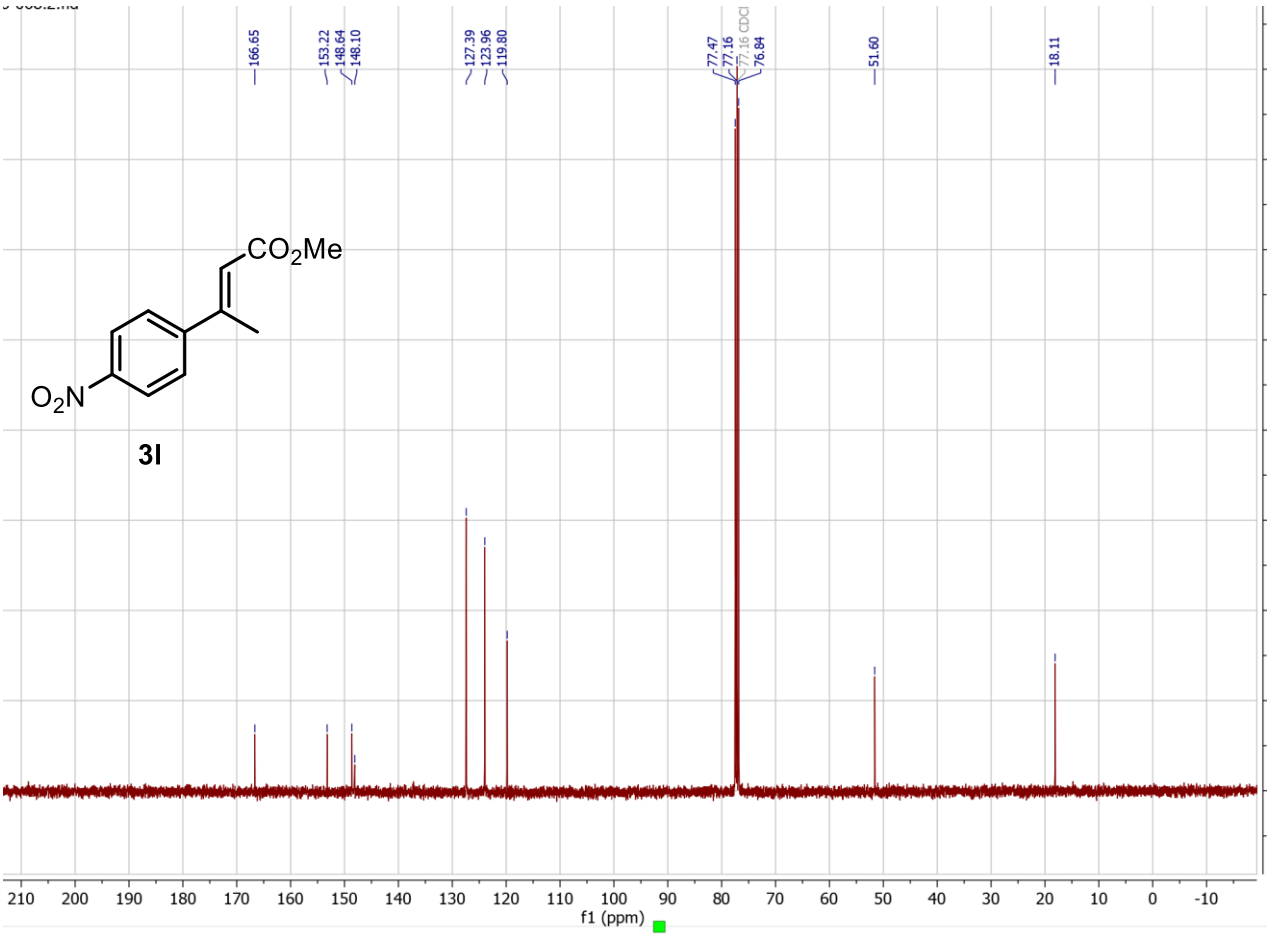
^{13}C NMR spectrum of **3k** in $CDCl_3$ at 126 MHz



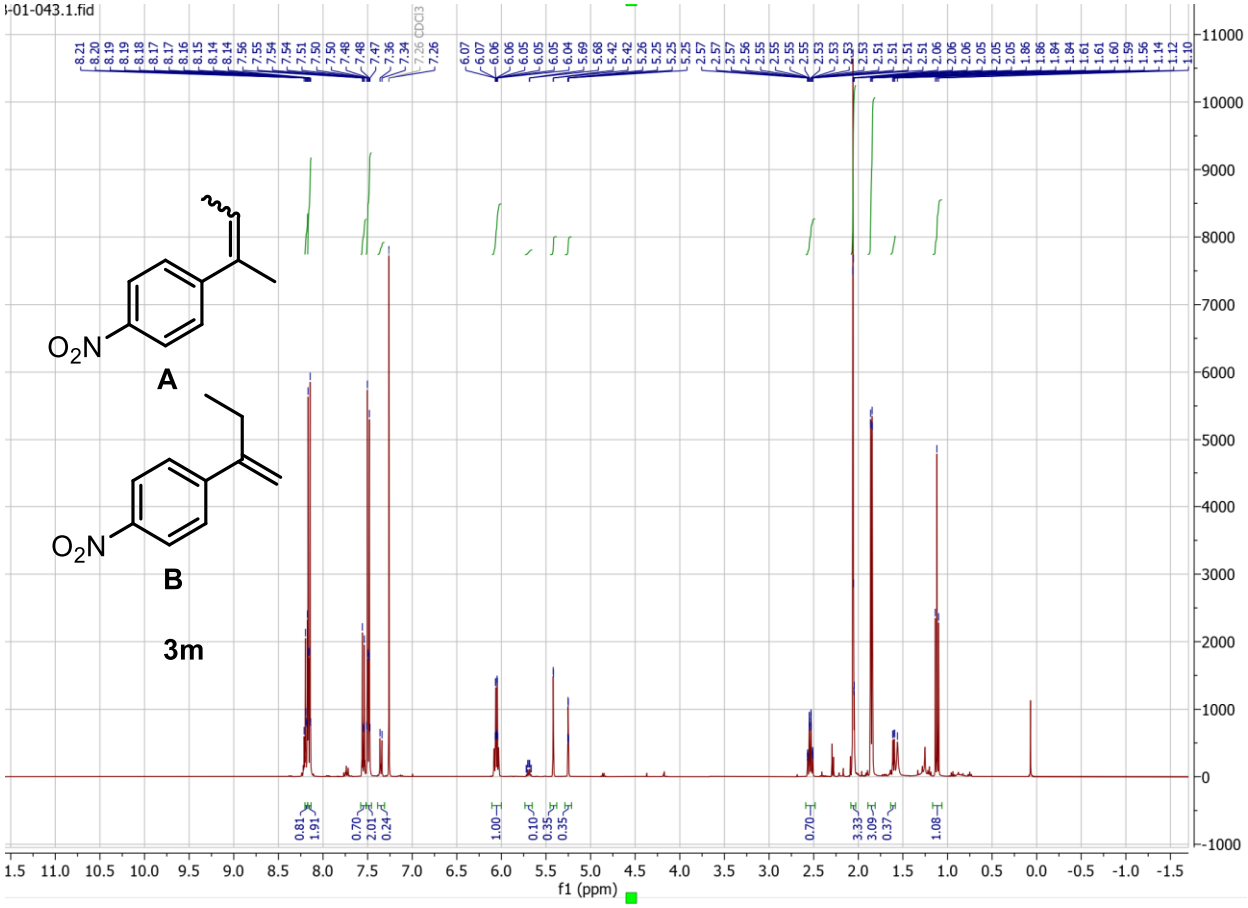
^{1}H NMR spectrum of **3l** in $CDCl_3$ at 400 MHz



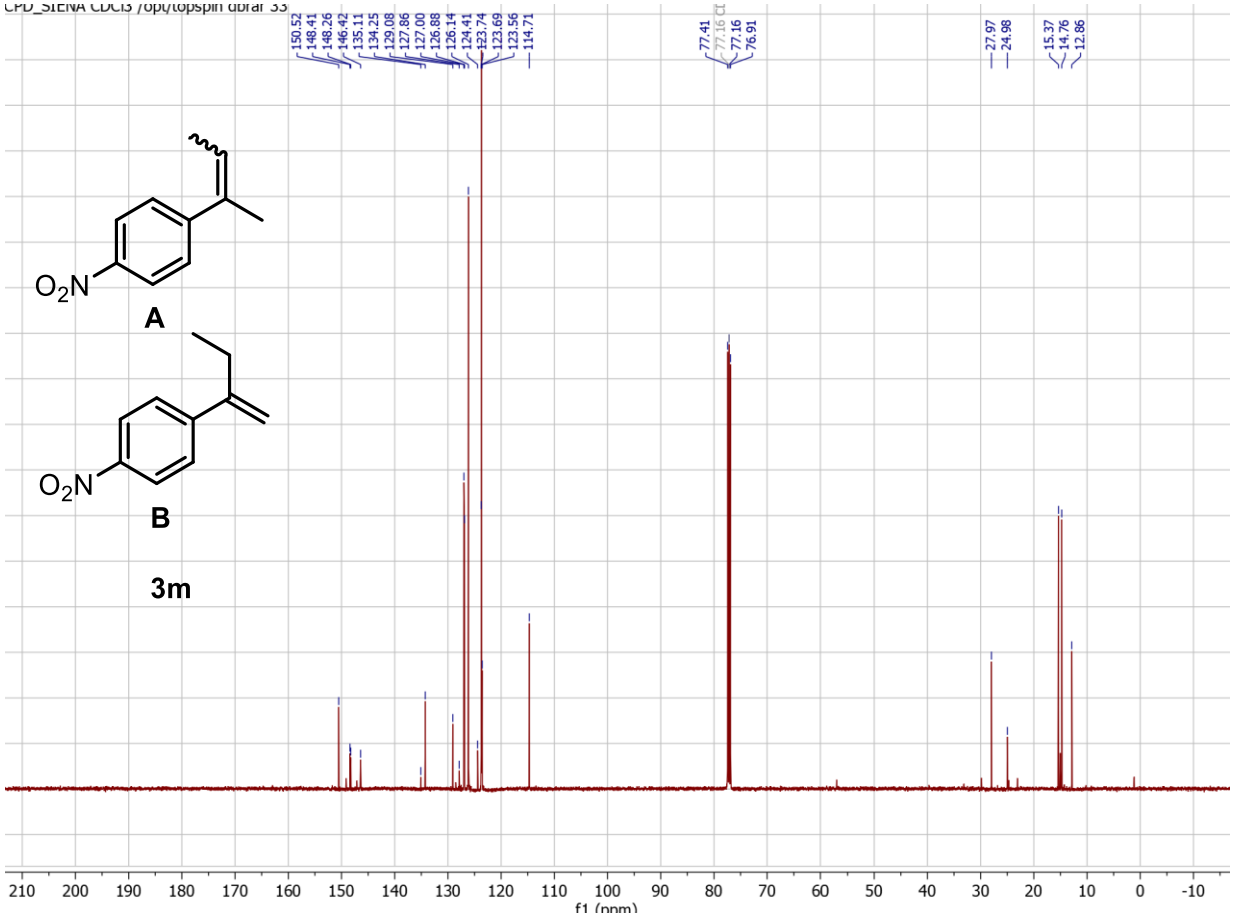
^{13}C NMR spectrum of **3l** in $CDCl_3$ at 101 MHz



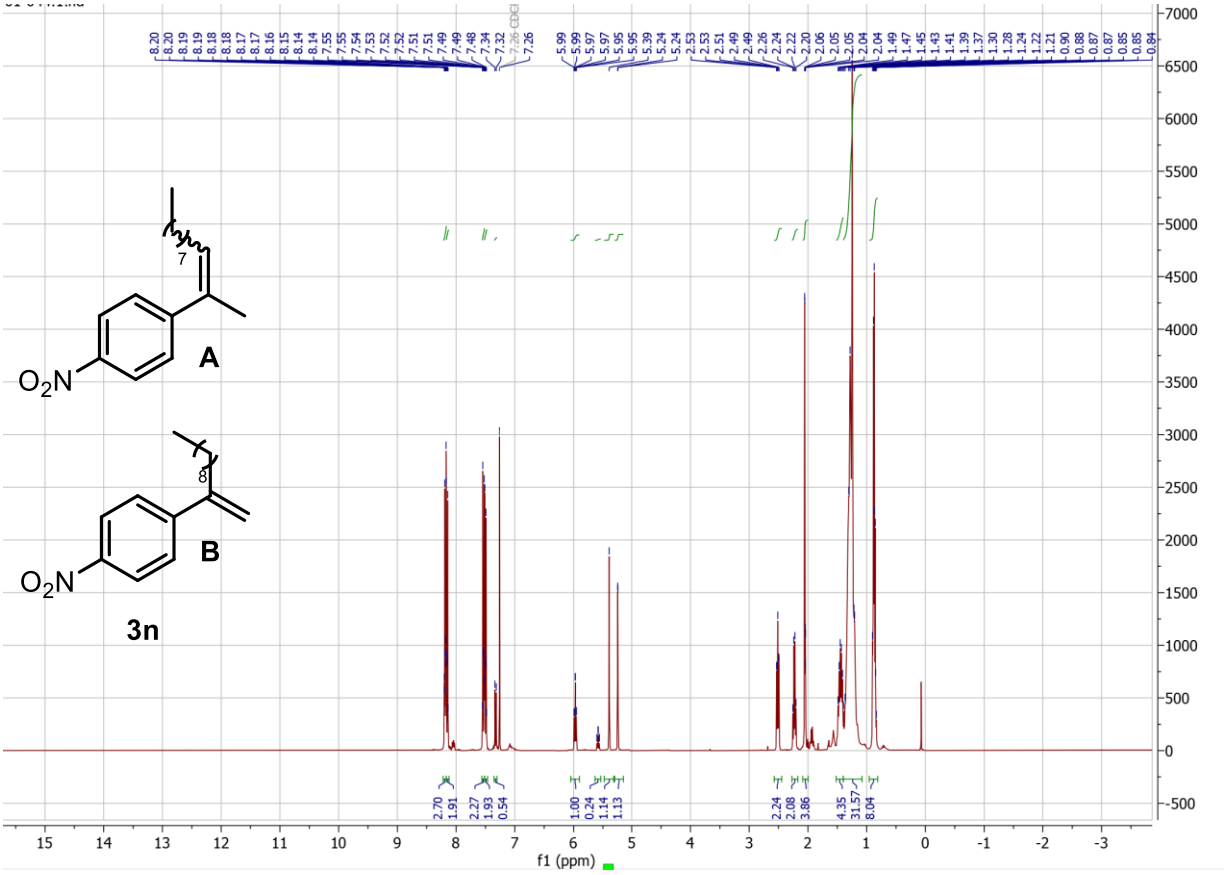
^{1}H NMR spectrum of **3m** in $CDCl_3$ at 400 MHz



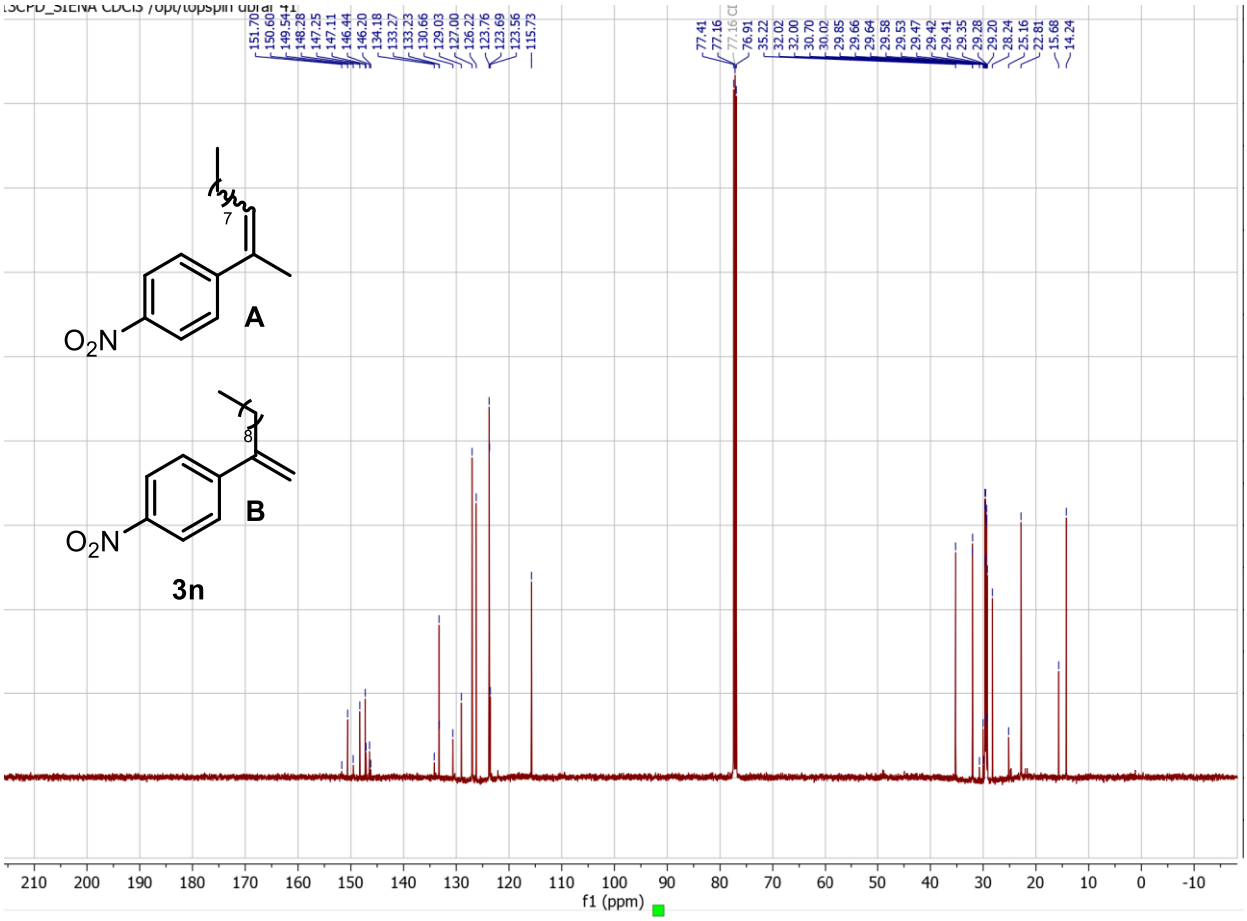
^{13}C NMR spectrum of **3m** in $CDCl_3$ at 126 MHz



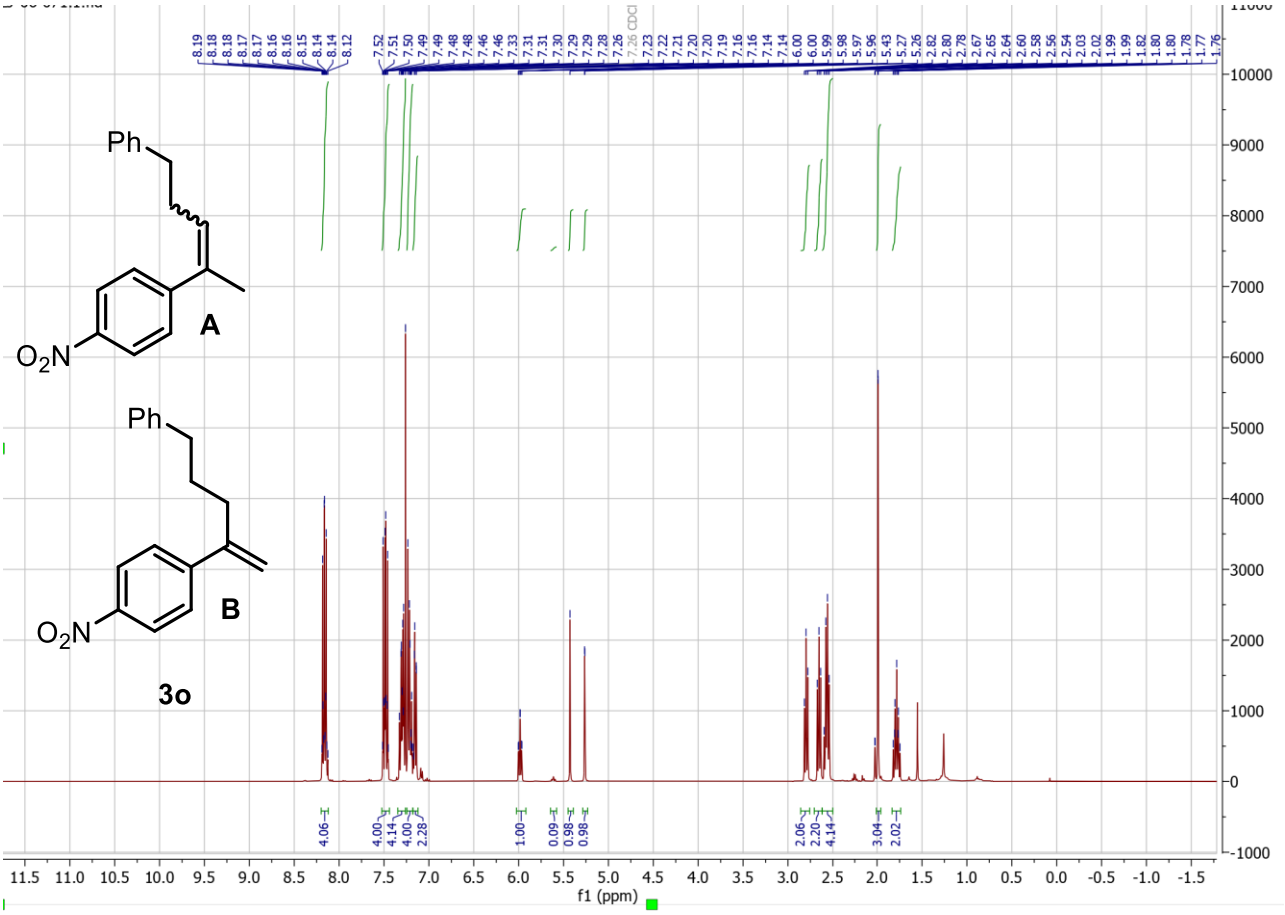
^{1}H NMR spectrum of **3n** in $CDCl_3$ at 400 MHz



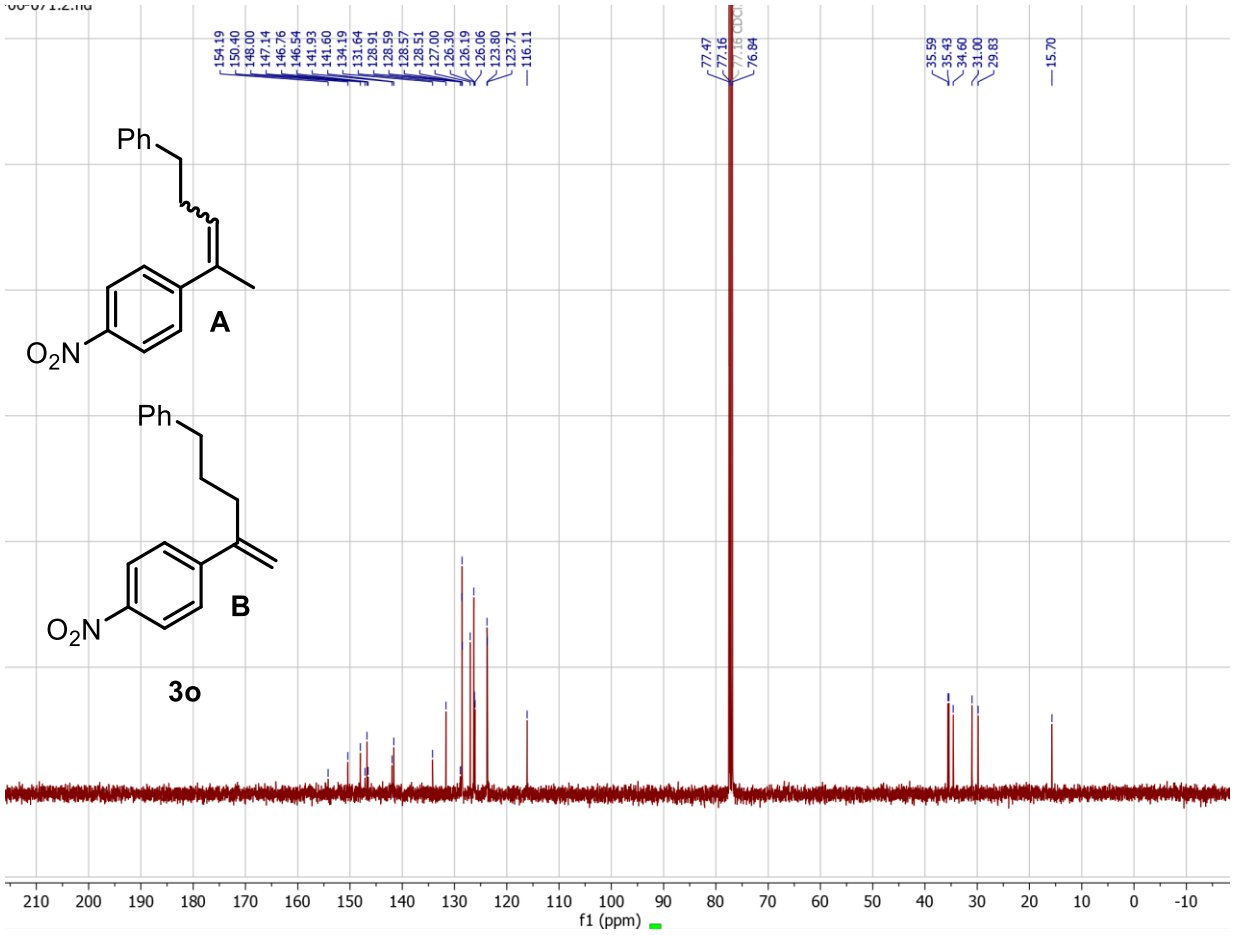
^{13}C NMR spectrum of **3n** in $CDCl_3$ at 126 MHz



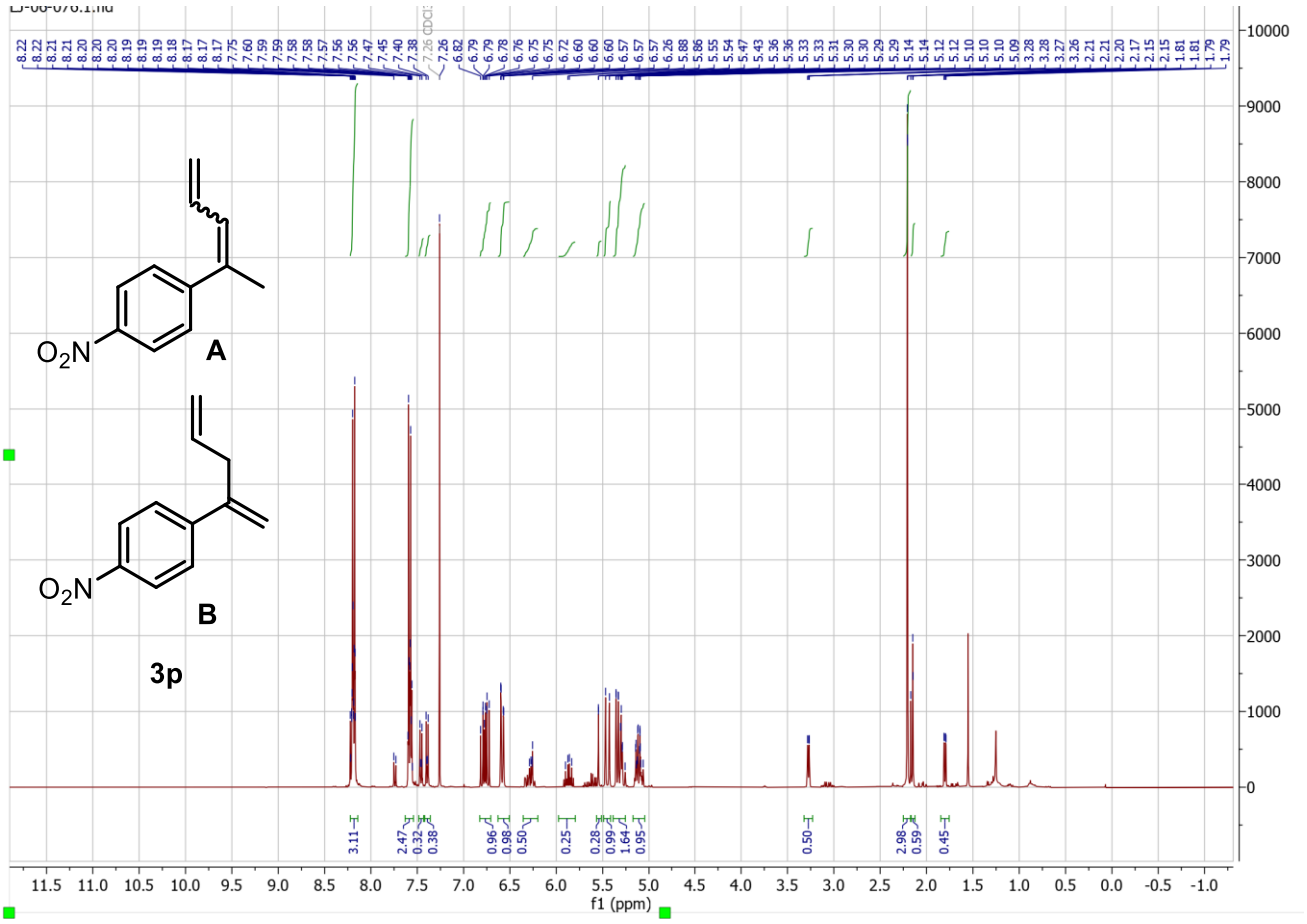
^{1}H NMR spectrum of **3o** in $CDCl_3$ at 400 MHz



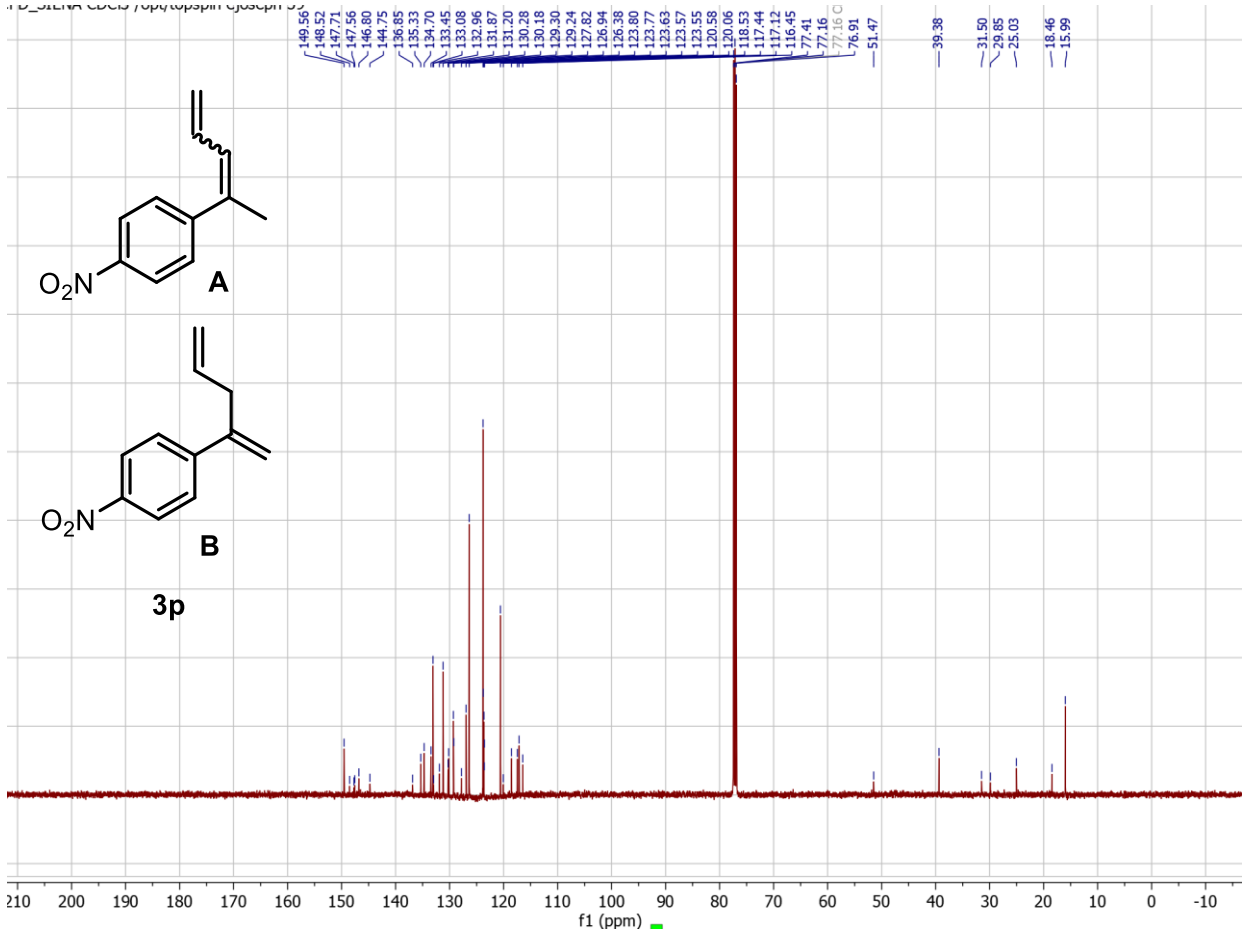
^{13}C NMR spectrum of **3o** in $CDCl_3$ at 126 MHz



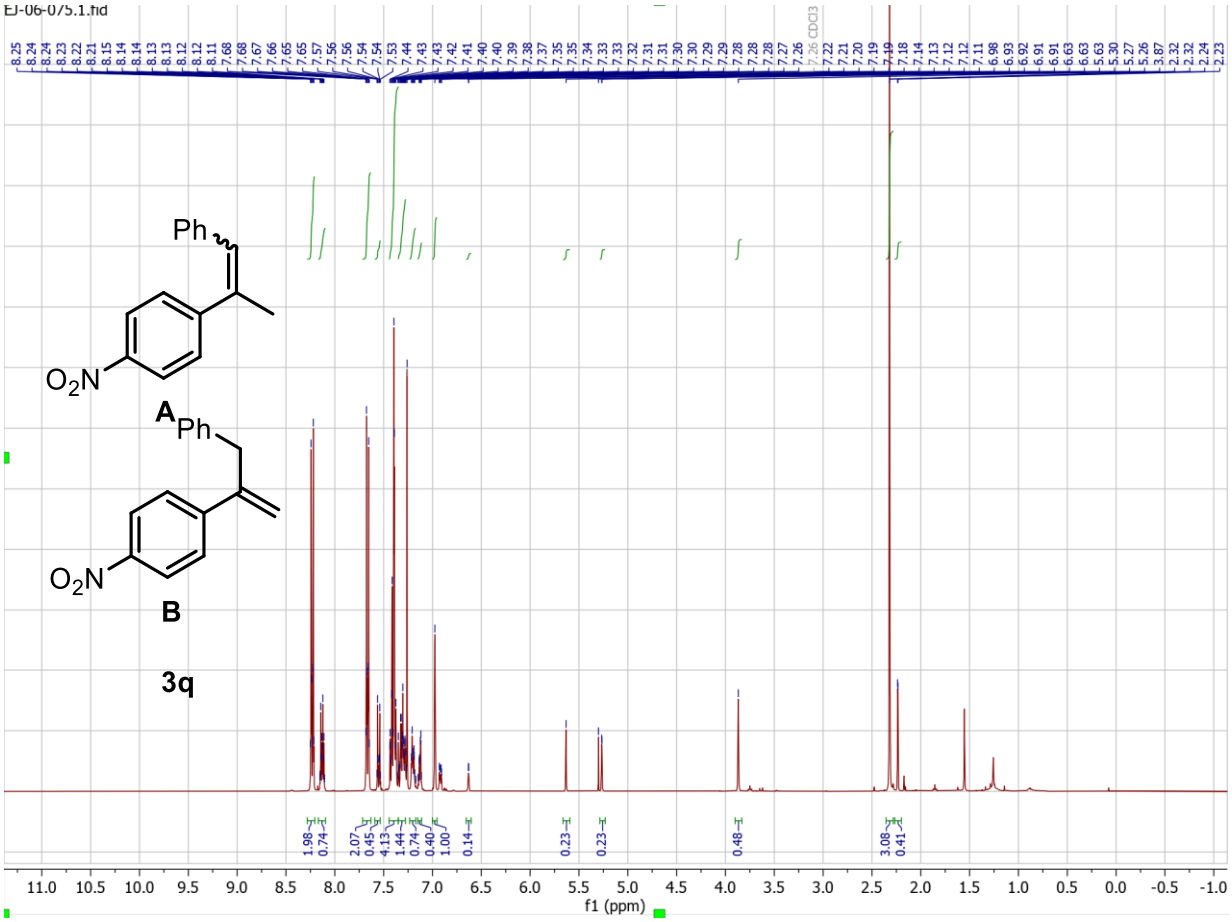
^{1}H NMR spectrum of **3p** in $CDCl_3$ at 400 MHz



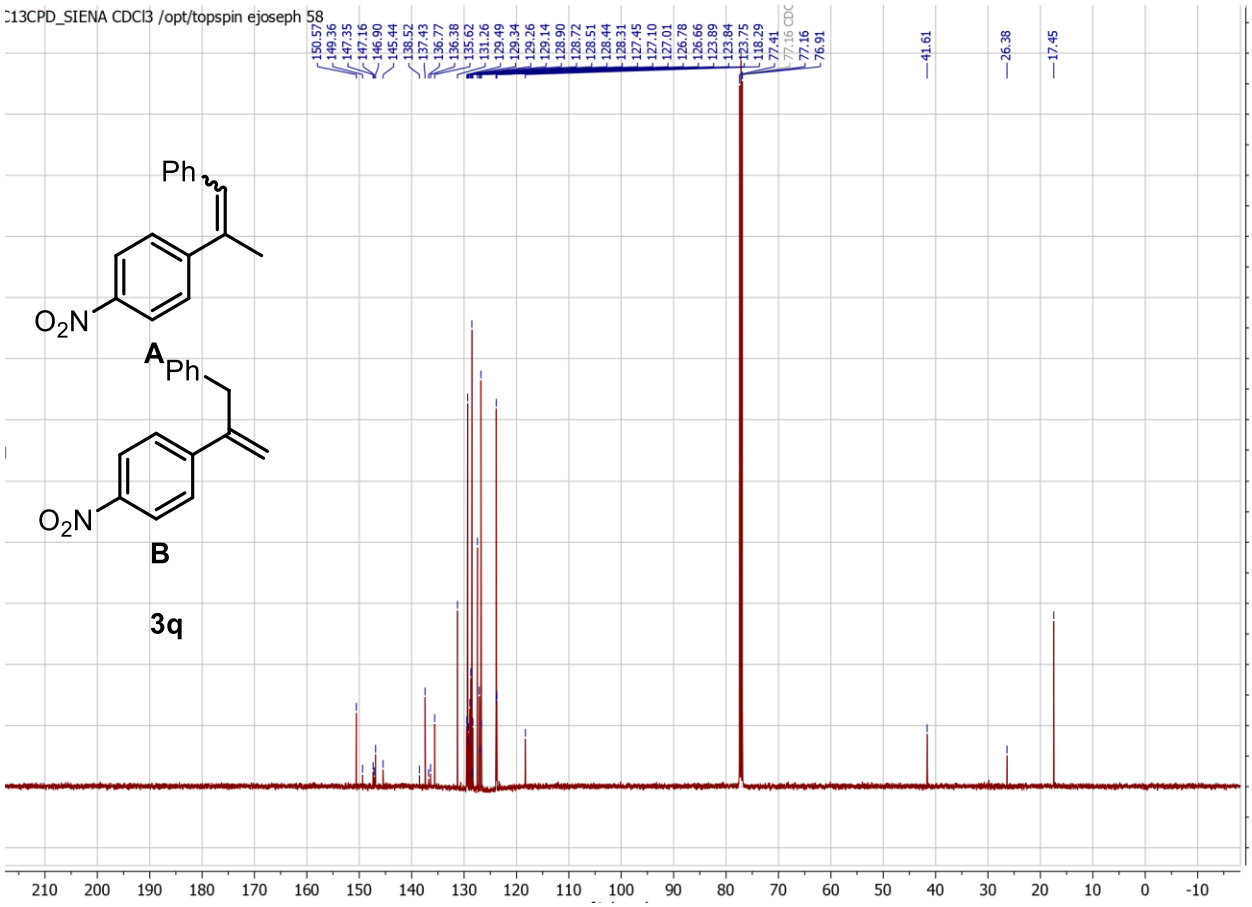
^{13}C NMR spectrum of **3p** in $CDCl_3$ at 126 MHz



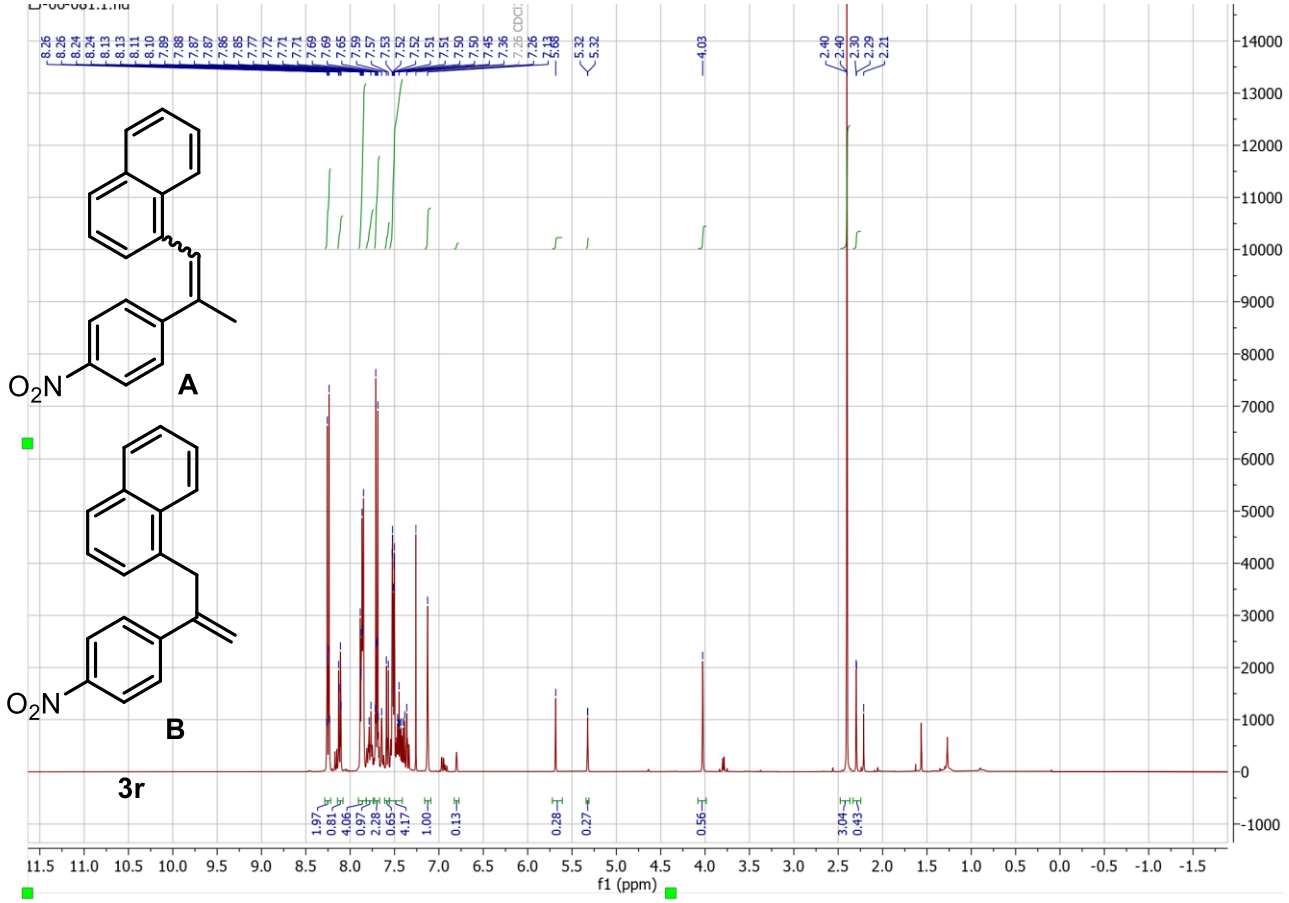
^{1}H NMR spectrum of **3q** in $CDCl_3$ at 400 MHz



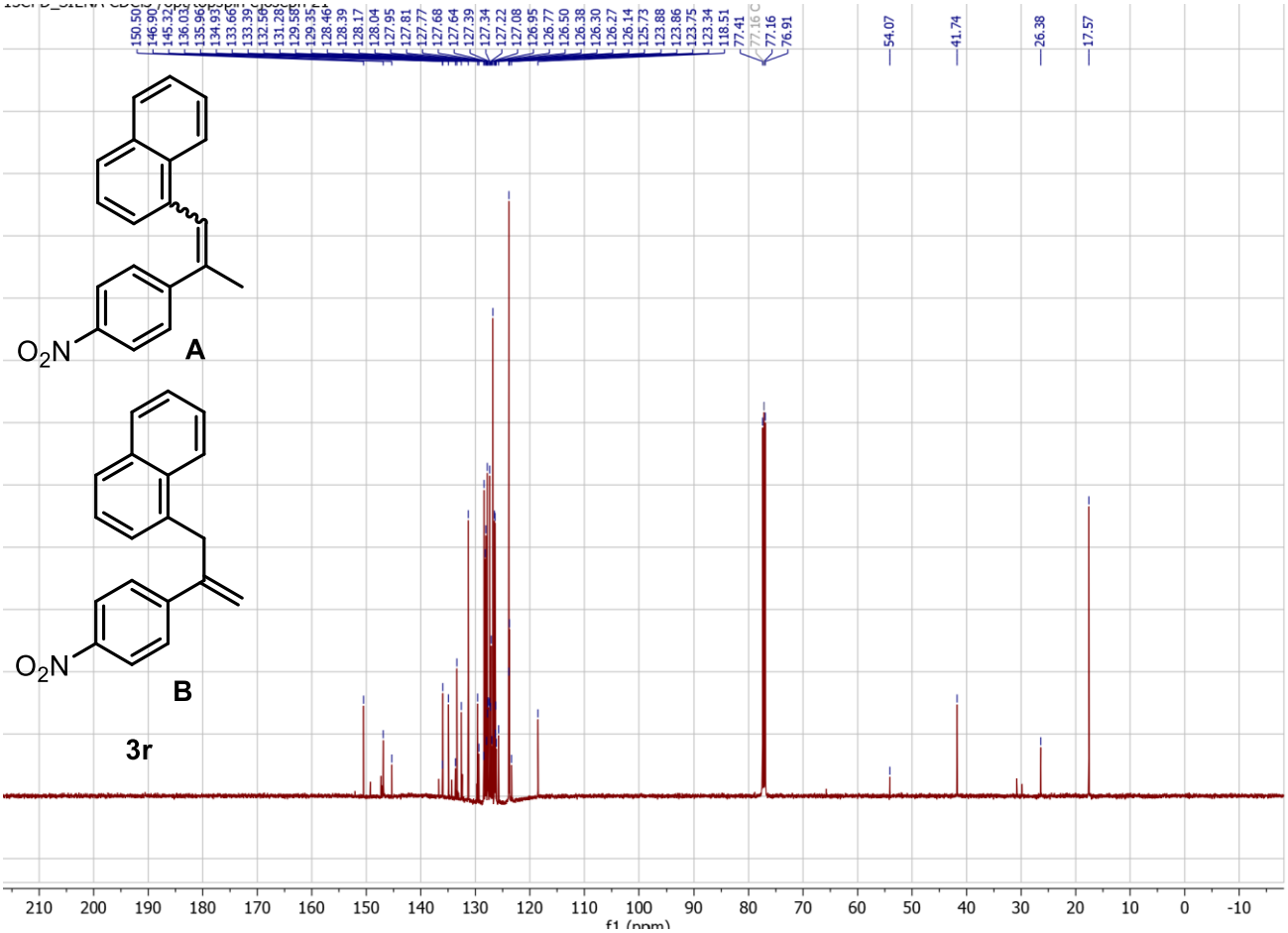
^{13}C NMR spectrum of **3q** in $CDCl_3$ at 126 MHz



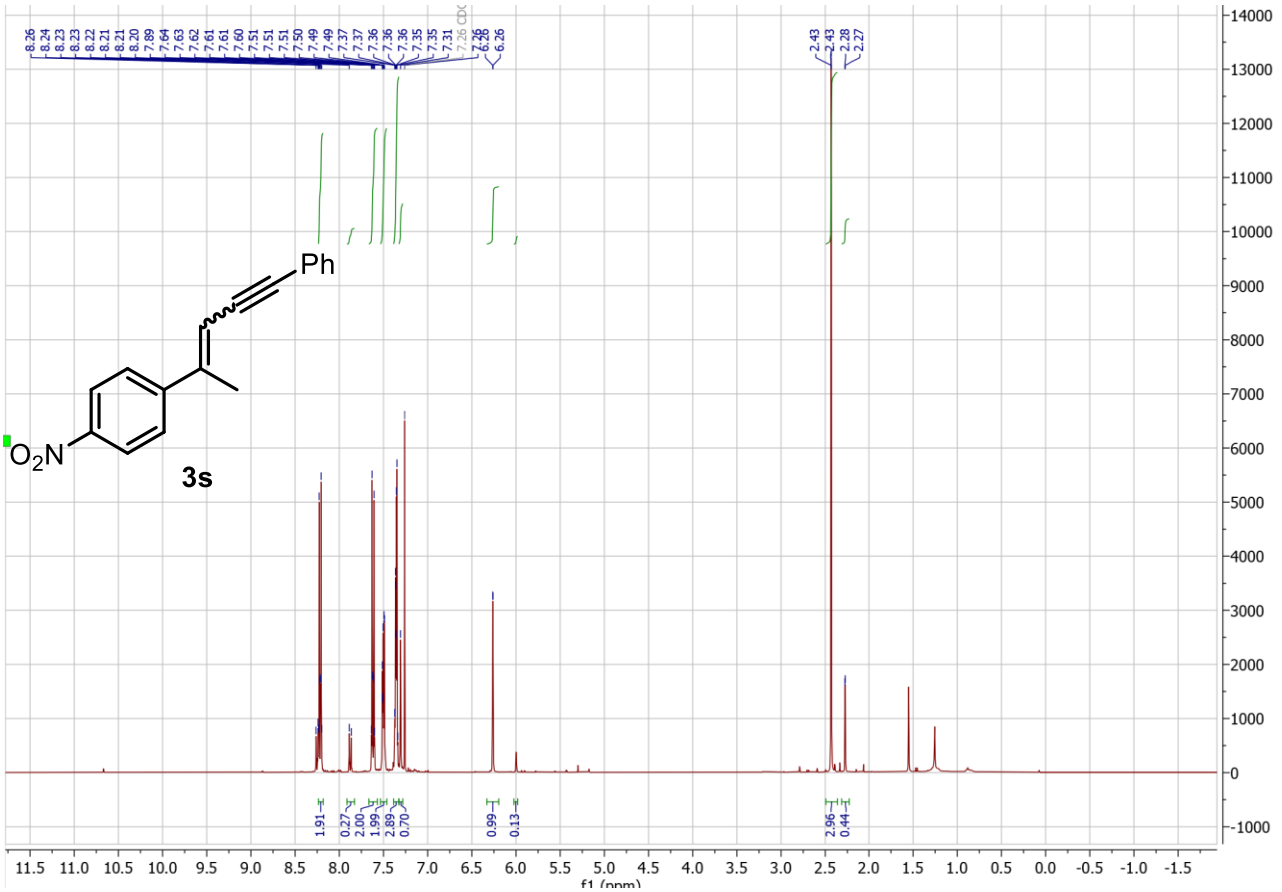
^{1}H NMR spectrum of **3r** in $CDCl_3$ at 400 MHz



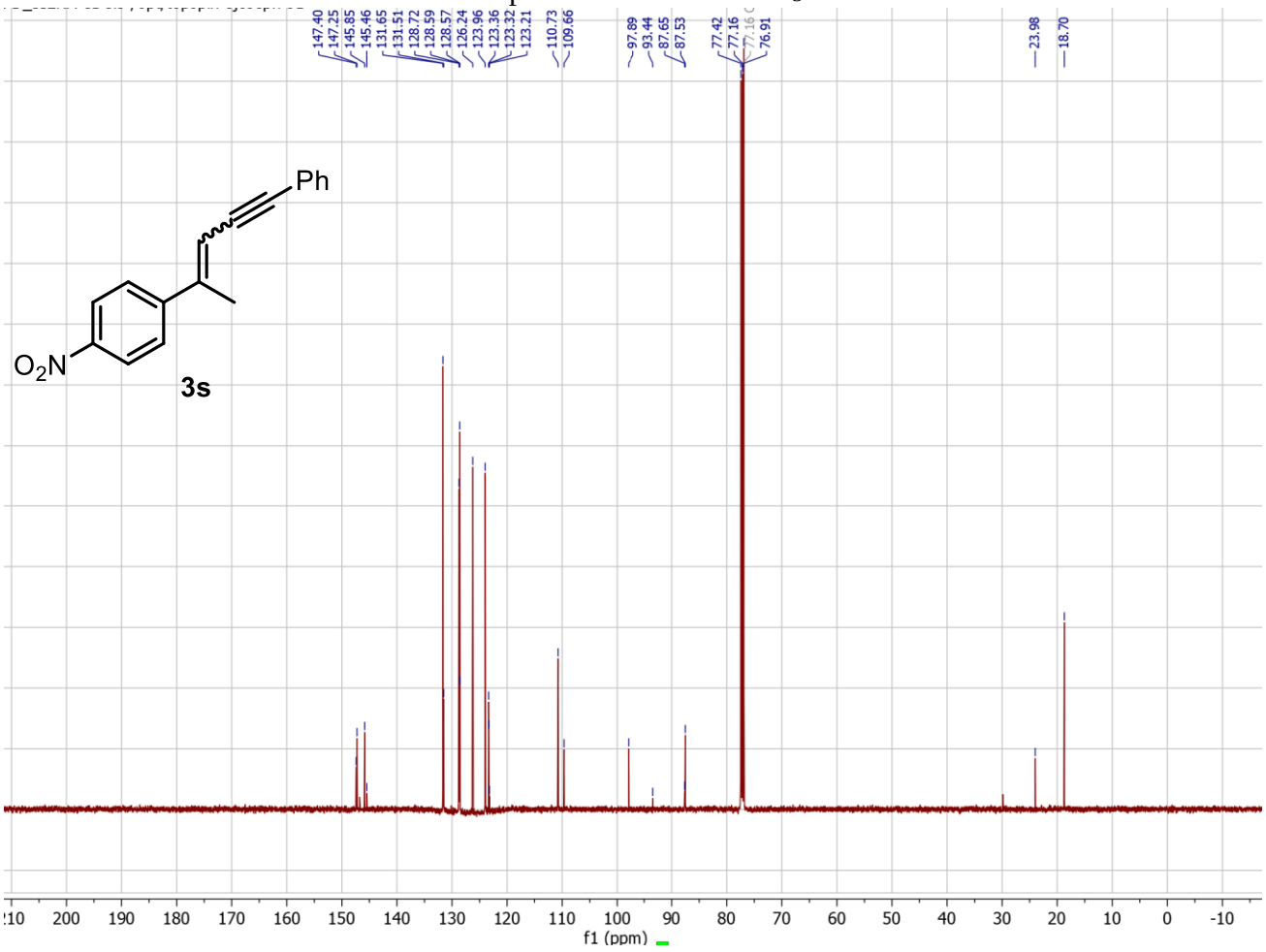
^{13}C NMR spectrum of **3r** in $CDCl_3$ at 126 MHz



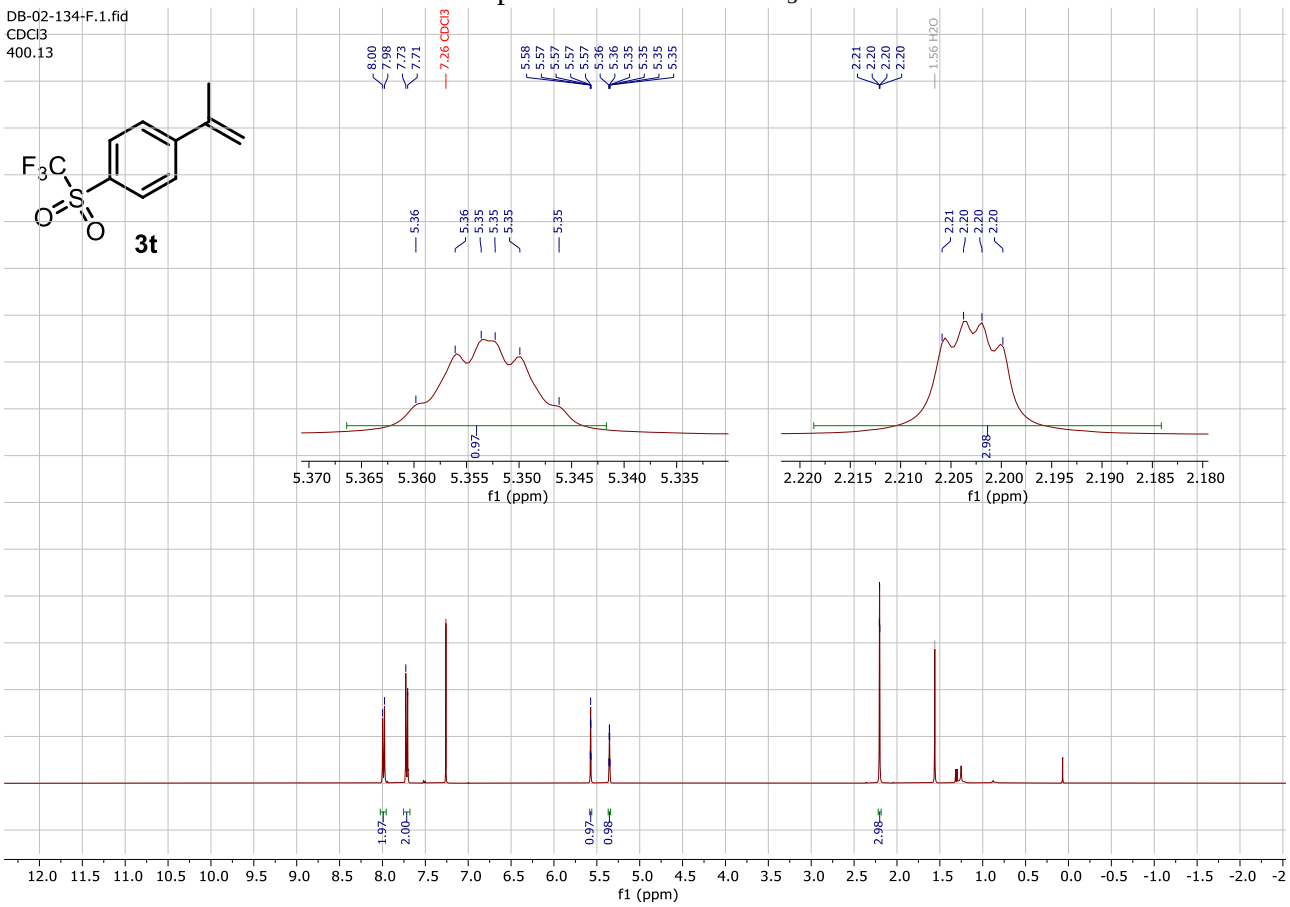
^{1}H NMR spectrum of **3s** in $CDCl_3$ at 400 MHz



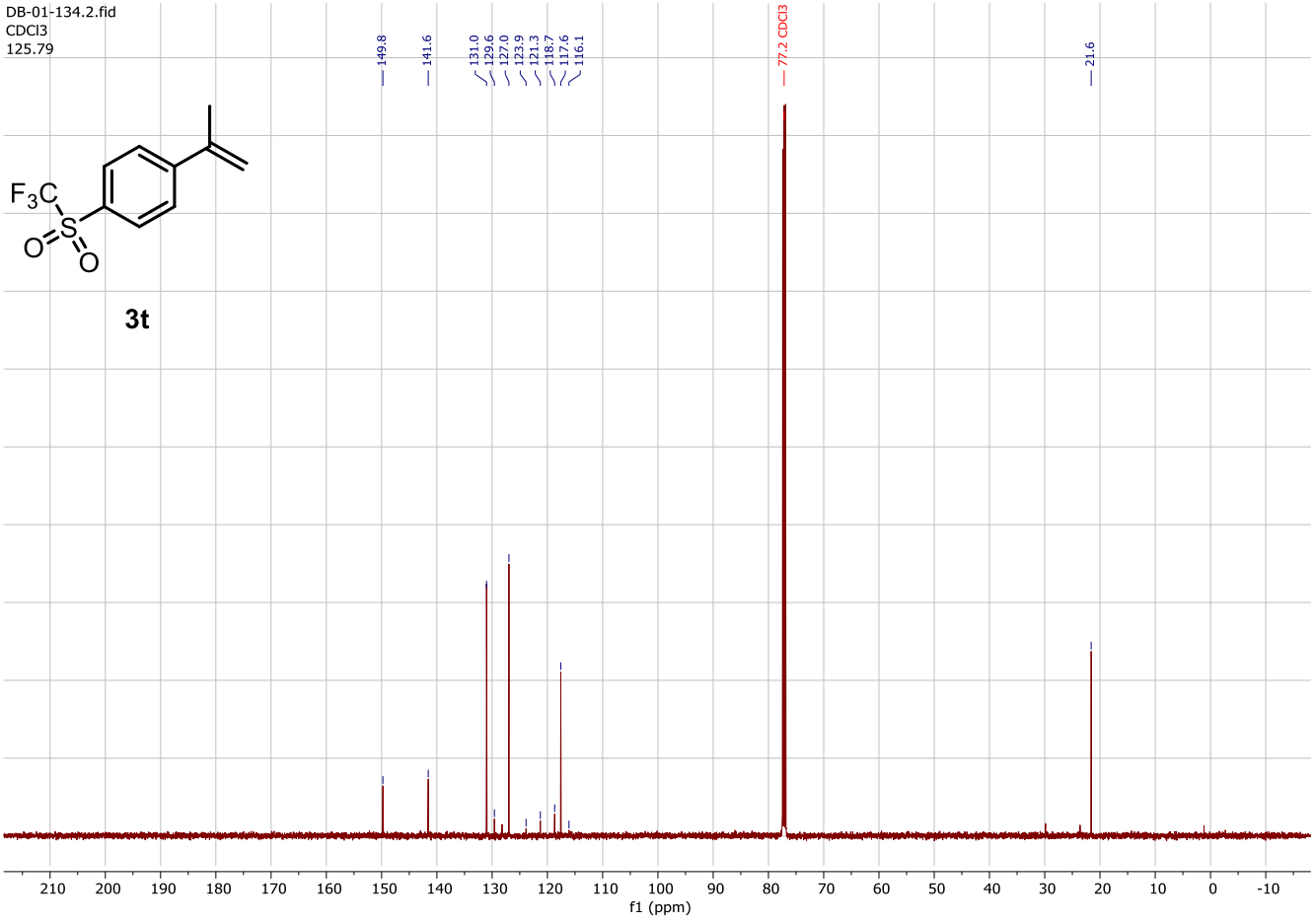
^{13}C NMR spectrum of **3s** in $CDCl_3$ at 126 MHz



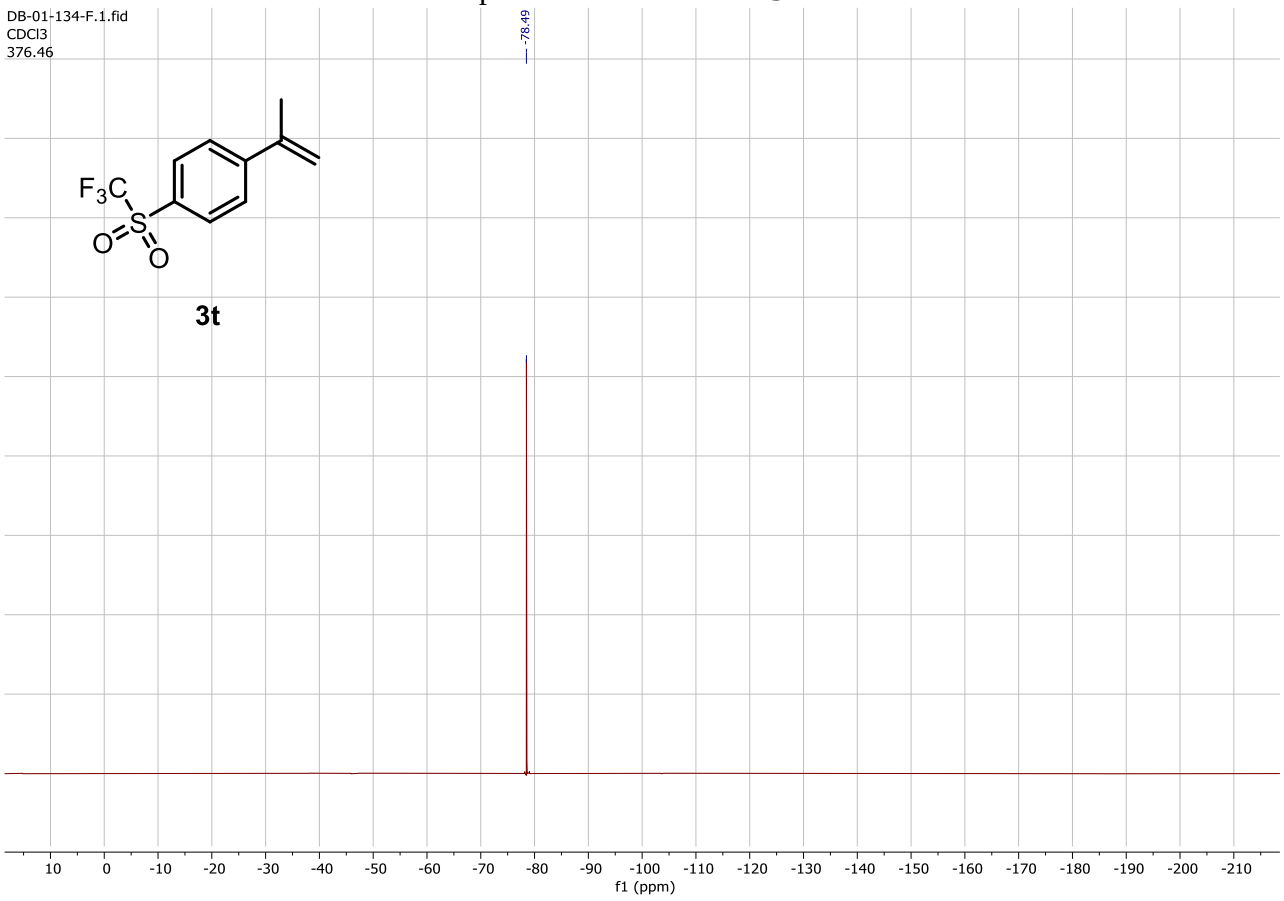
^{1}H NMR spectrum of **3t** in $CDCl_3$ at 400 MHz



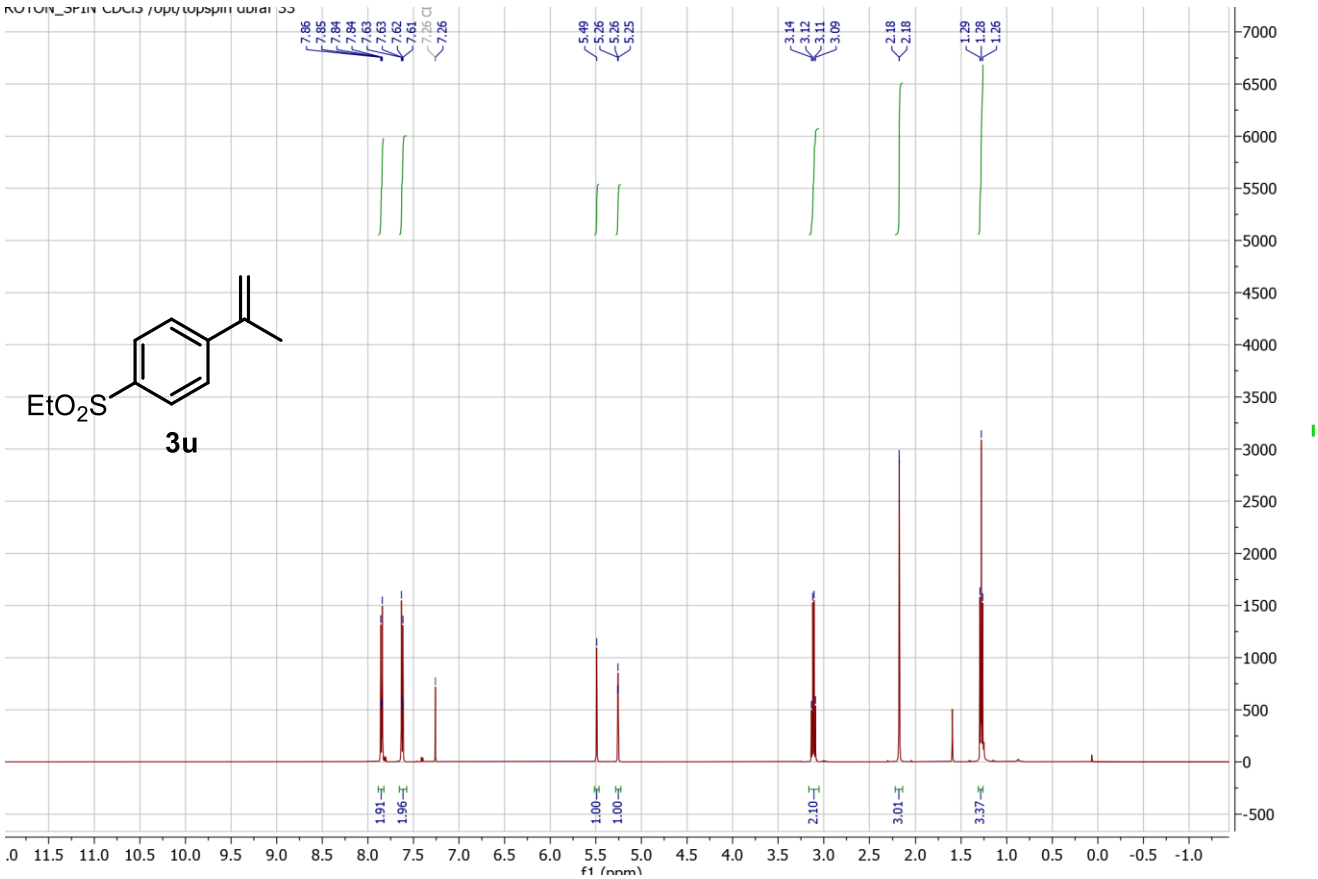
^{13}C NMR spectrum of **3t** in $CDCl_3$ at 126 MHz



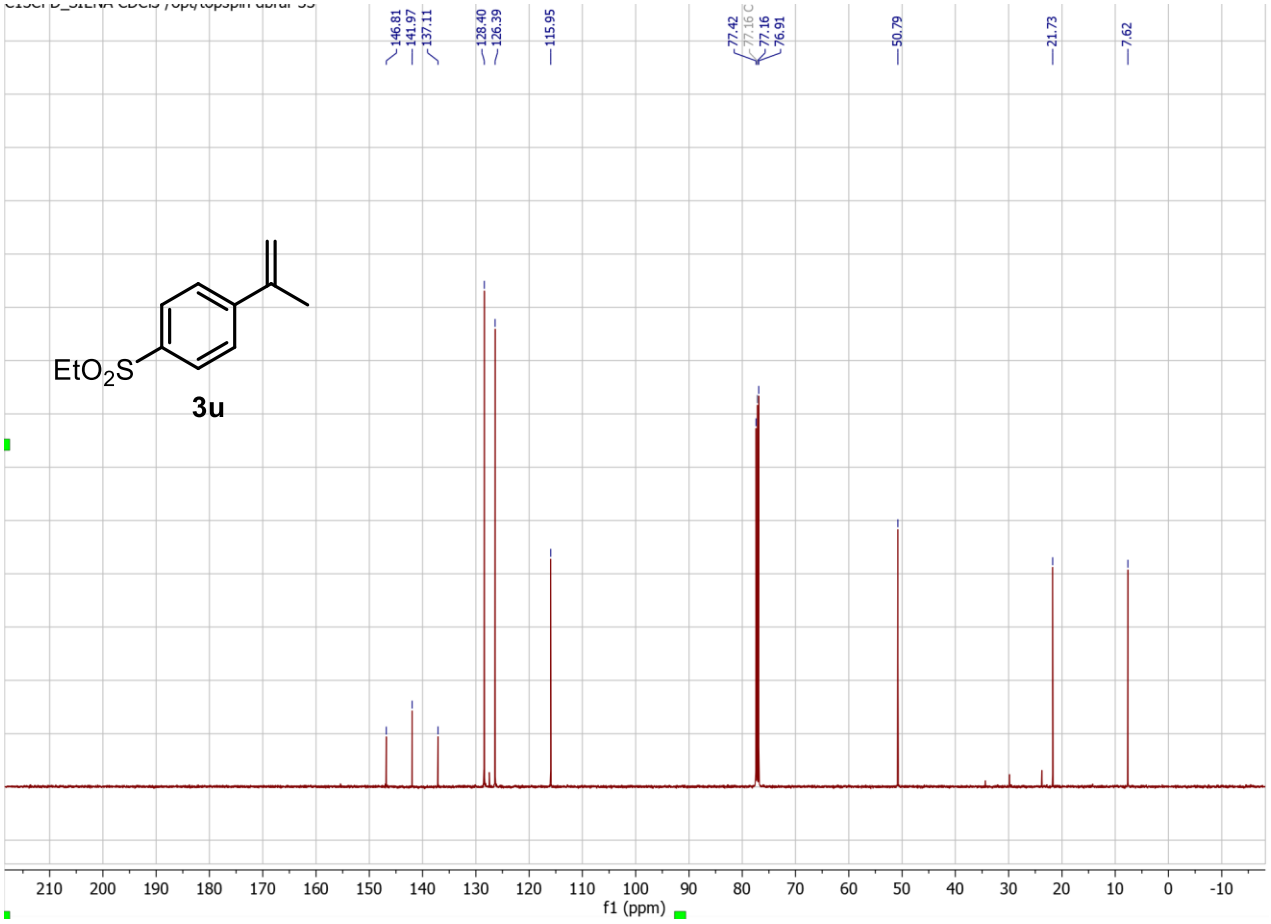
^{19}F NMR spectrum of **3t** in $CDCl_3$ at 376 MHz



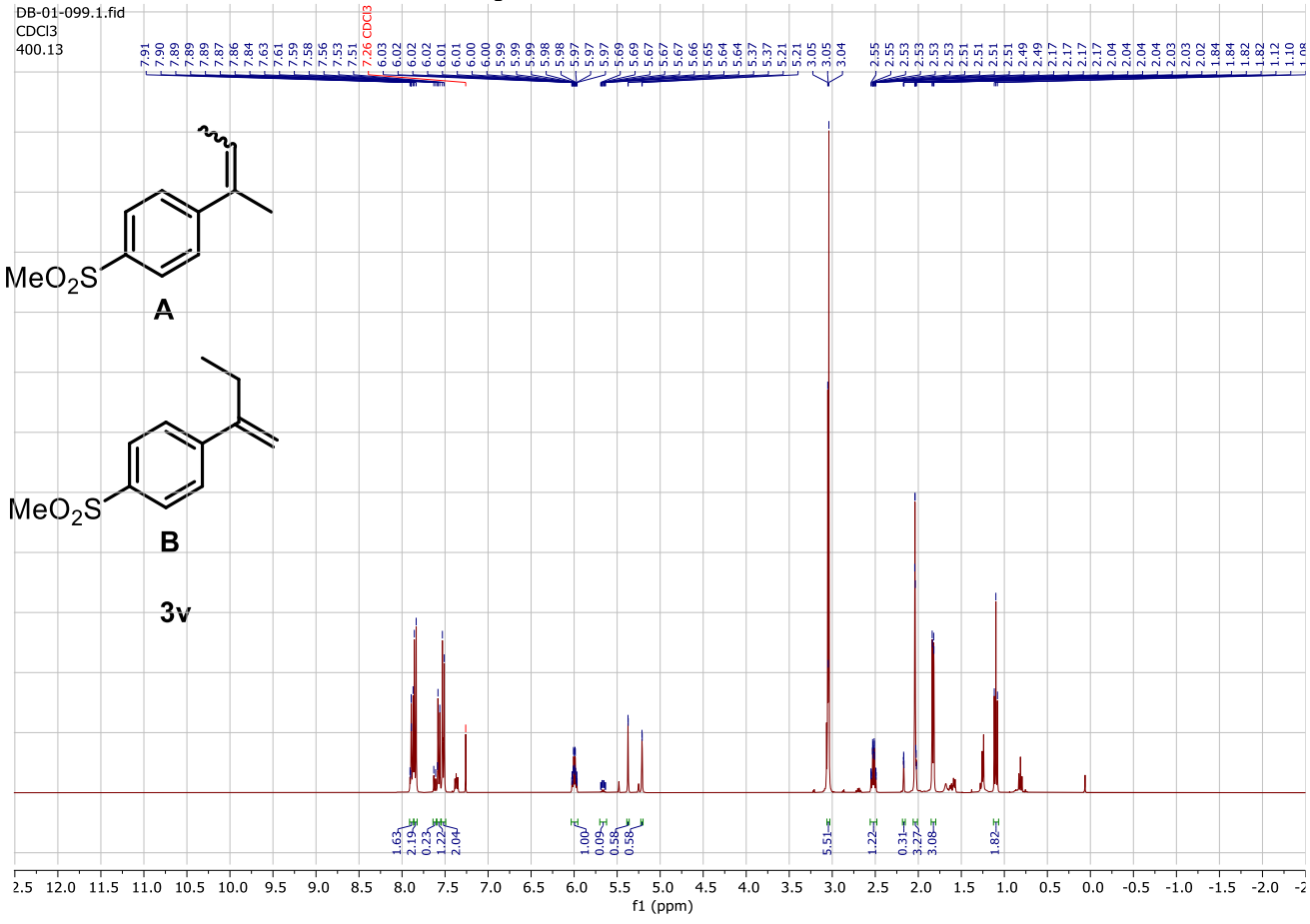
^{1}H NMR spectrum of **3u** in $CDCl_3$ at 500 MHz



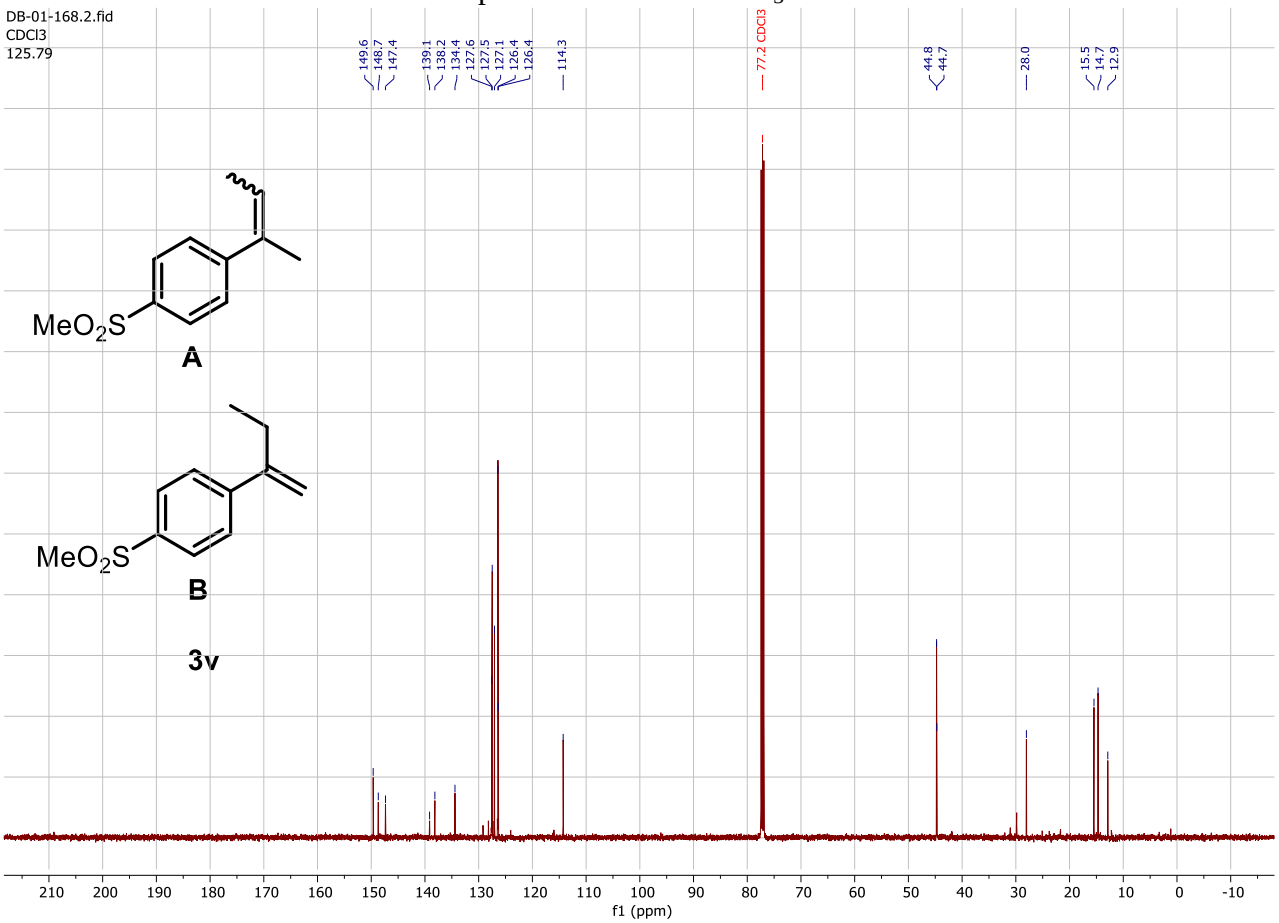
^{13}C NMR spectrum of **3u** in $CDCl_3$ at 126 MHz



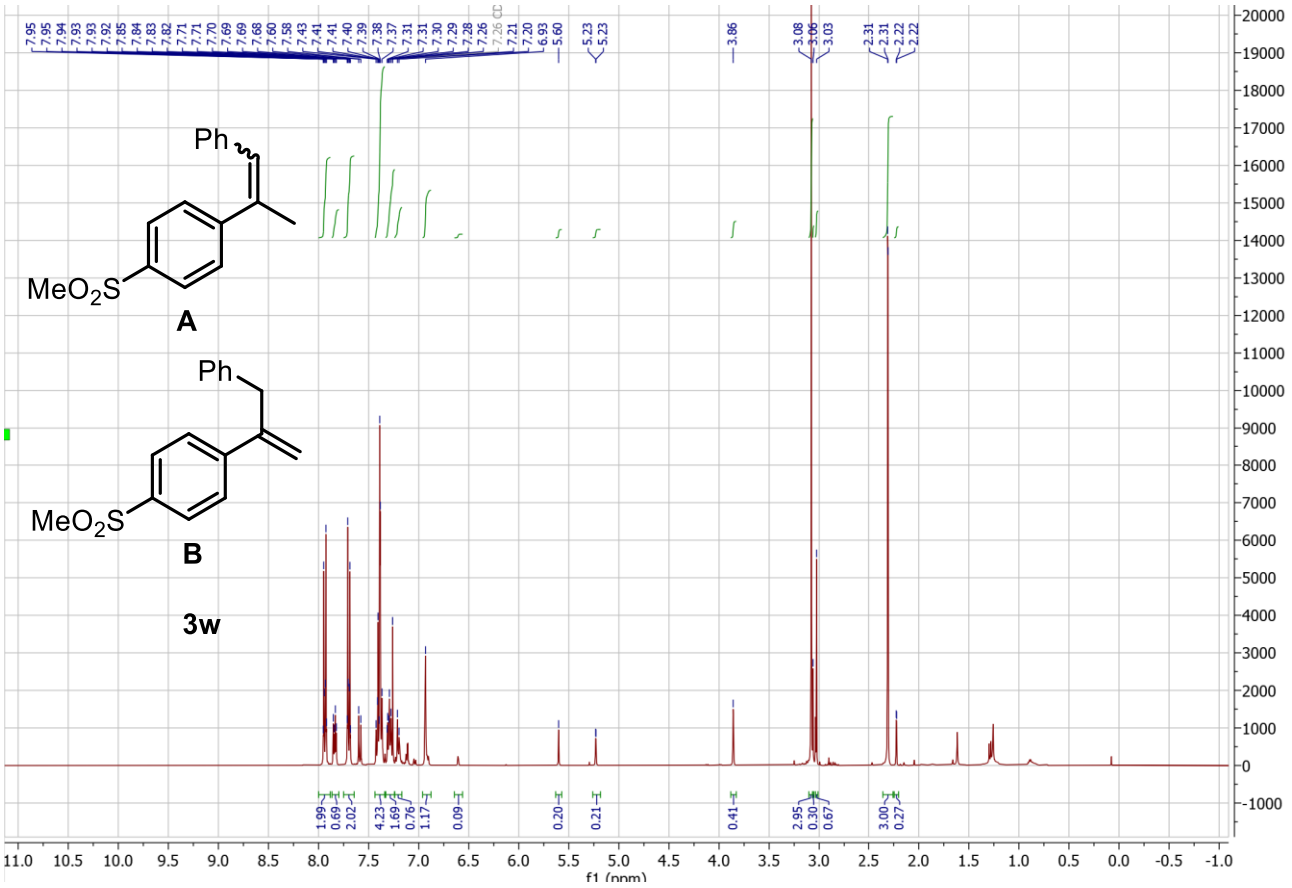
^{1}H NMR spectrum of **3v** in $CDCl_3$ at 400 MHz



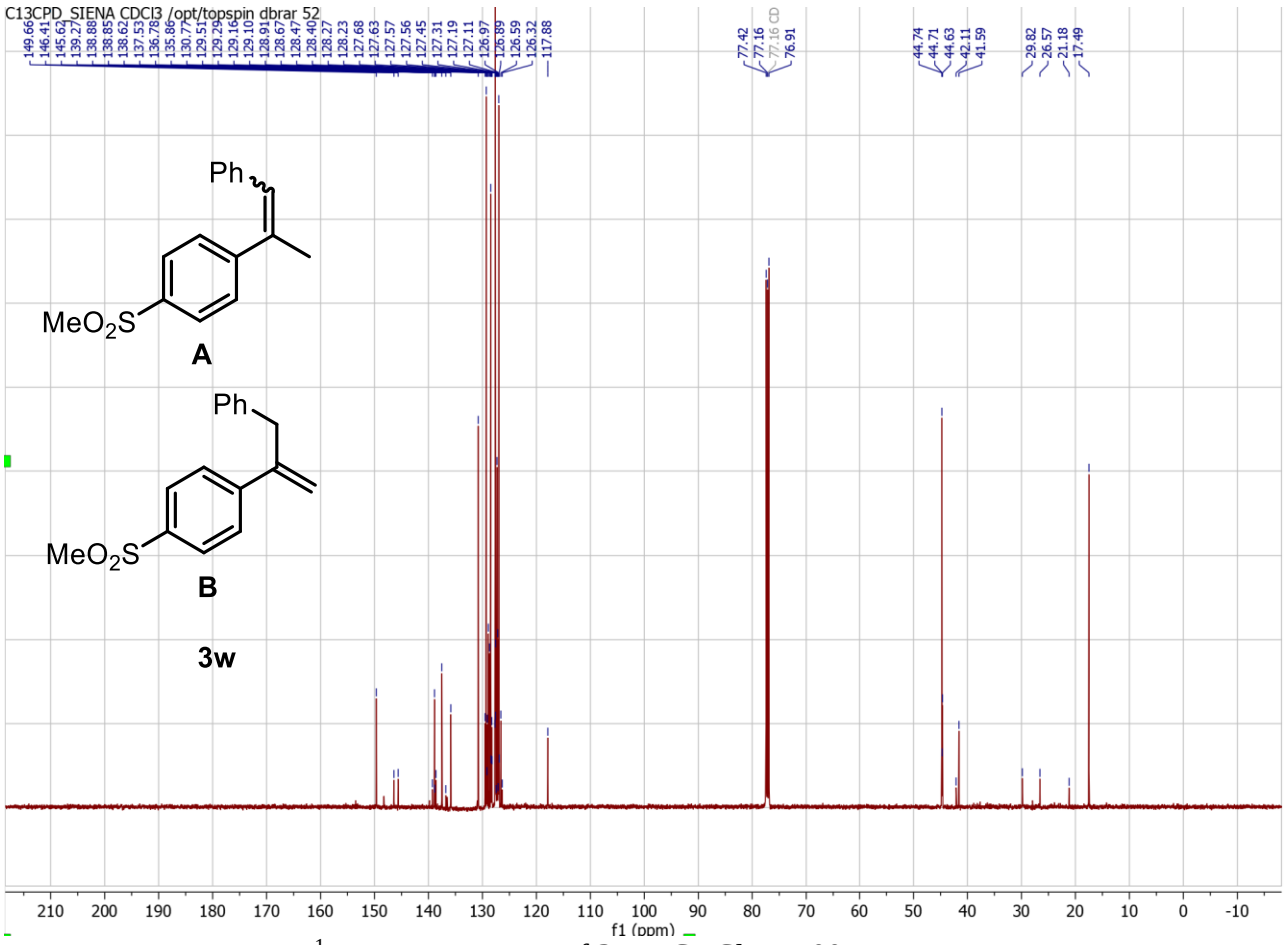
^{13}C NMR spectrum of **3v** in $CDCl_3$ at 126 MHz



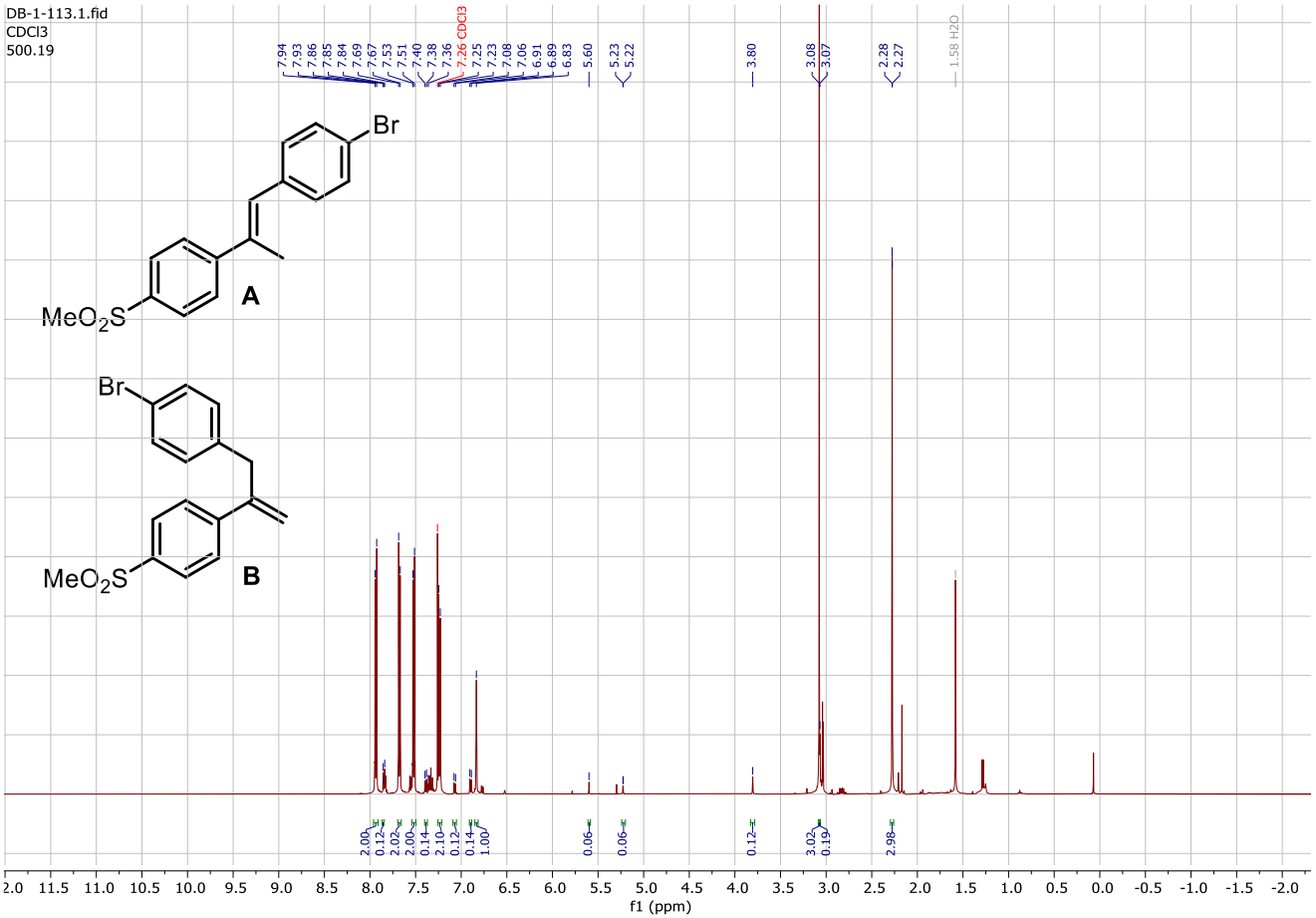
^{1}H NMR spectrum of **3w** in $CDCl_3$ at 400 MHz



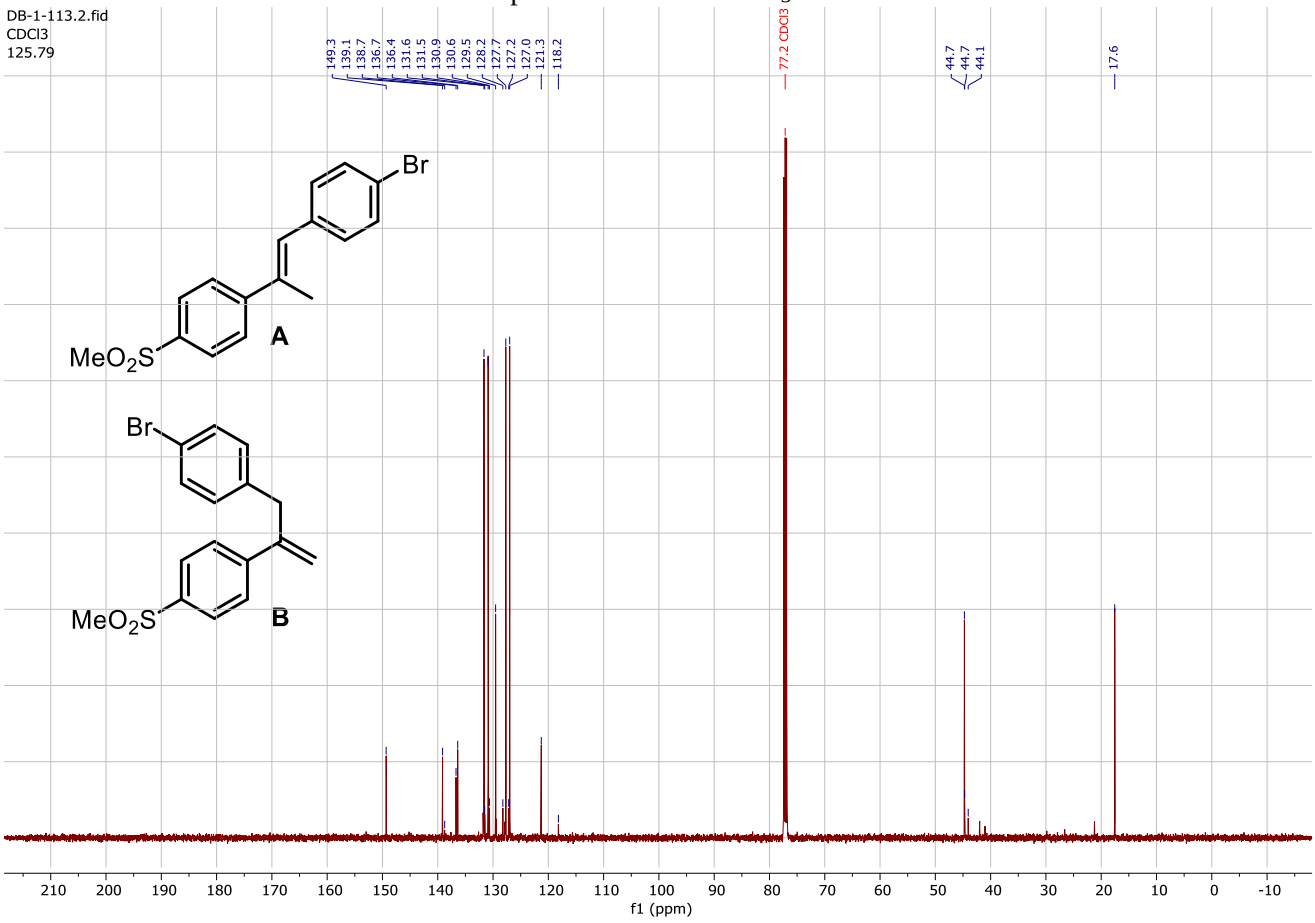
^{13}C NMR spectrum of **3w** in $CDCl_3$ at 126 MHz



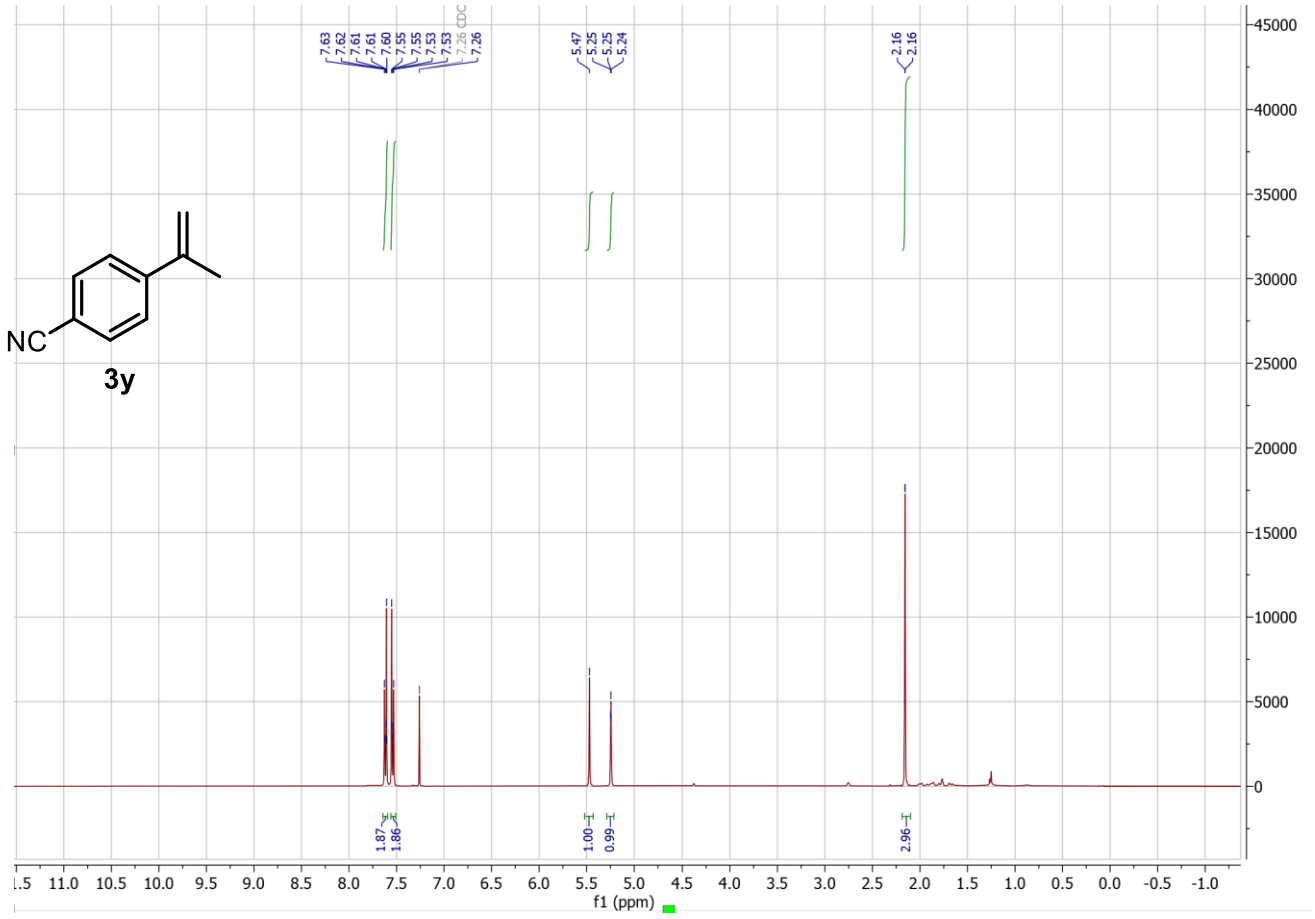
^{1}H NMR spectrum of **3x** in $CDCl_3$ at 500 MHz



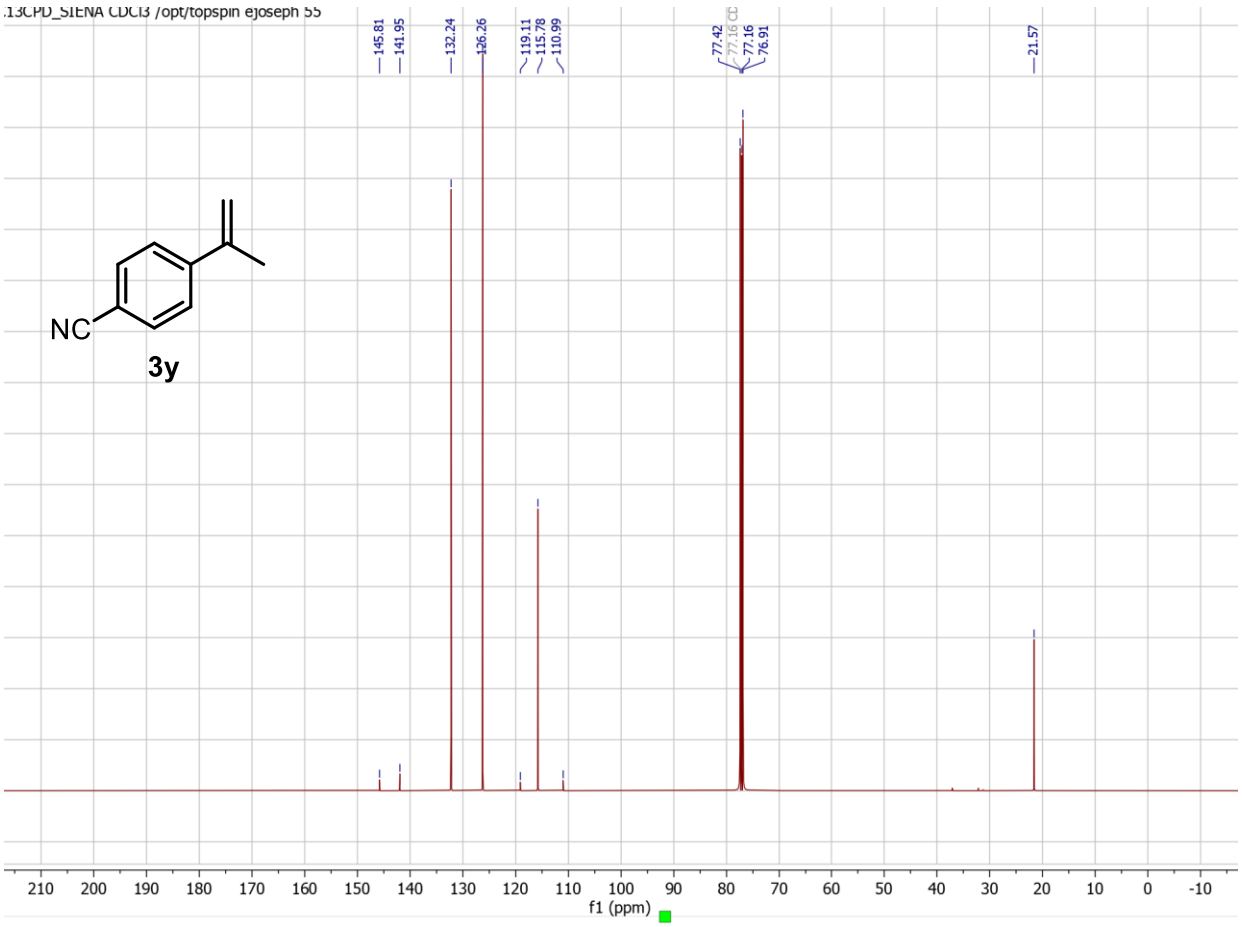
^{13}C NMR spectrum of **3x** in $CDCl_3$ at 126 MHz



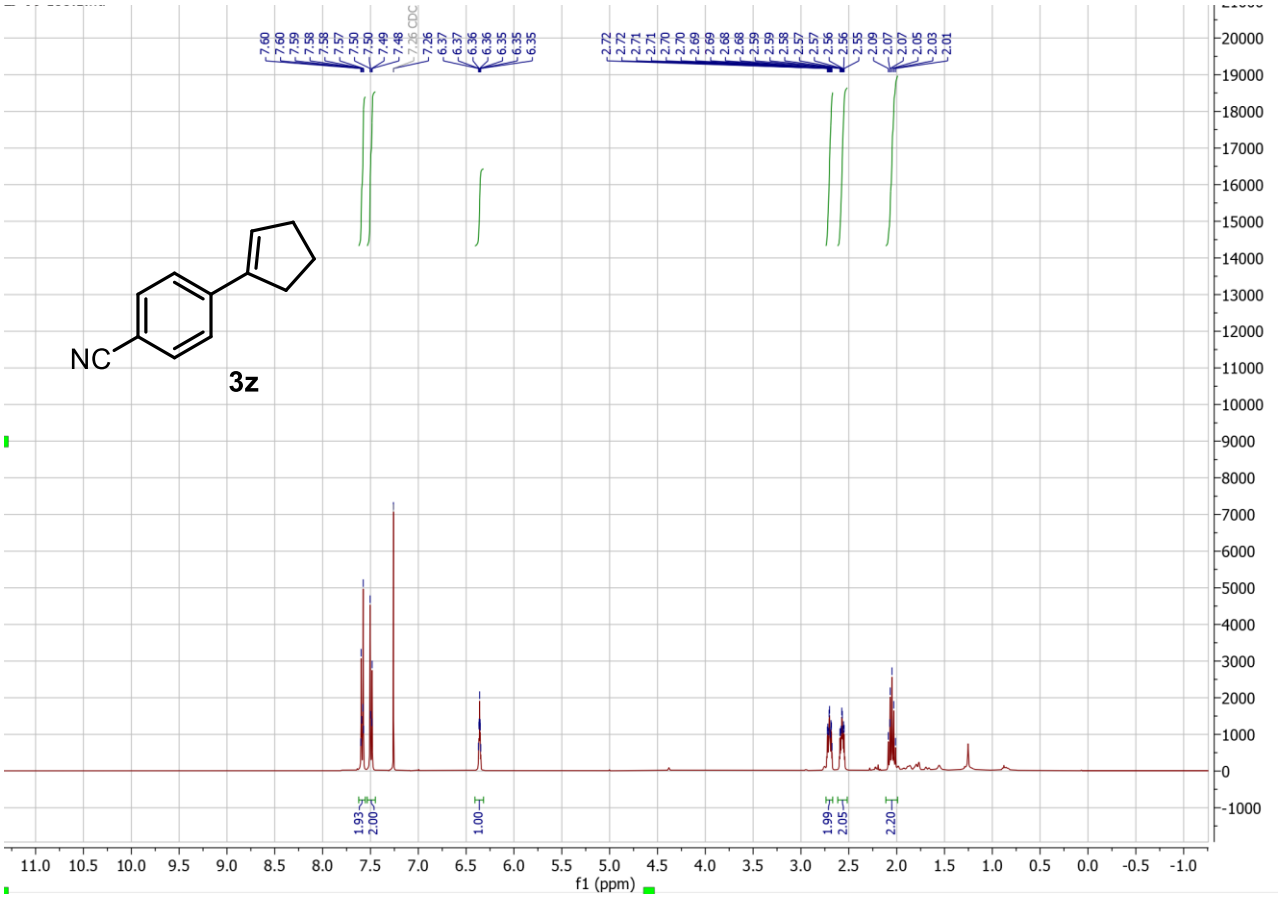
^{1}H NMR spectrum of **3y** in $CDCl_3$ at 400 MHz



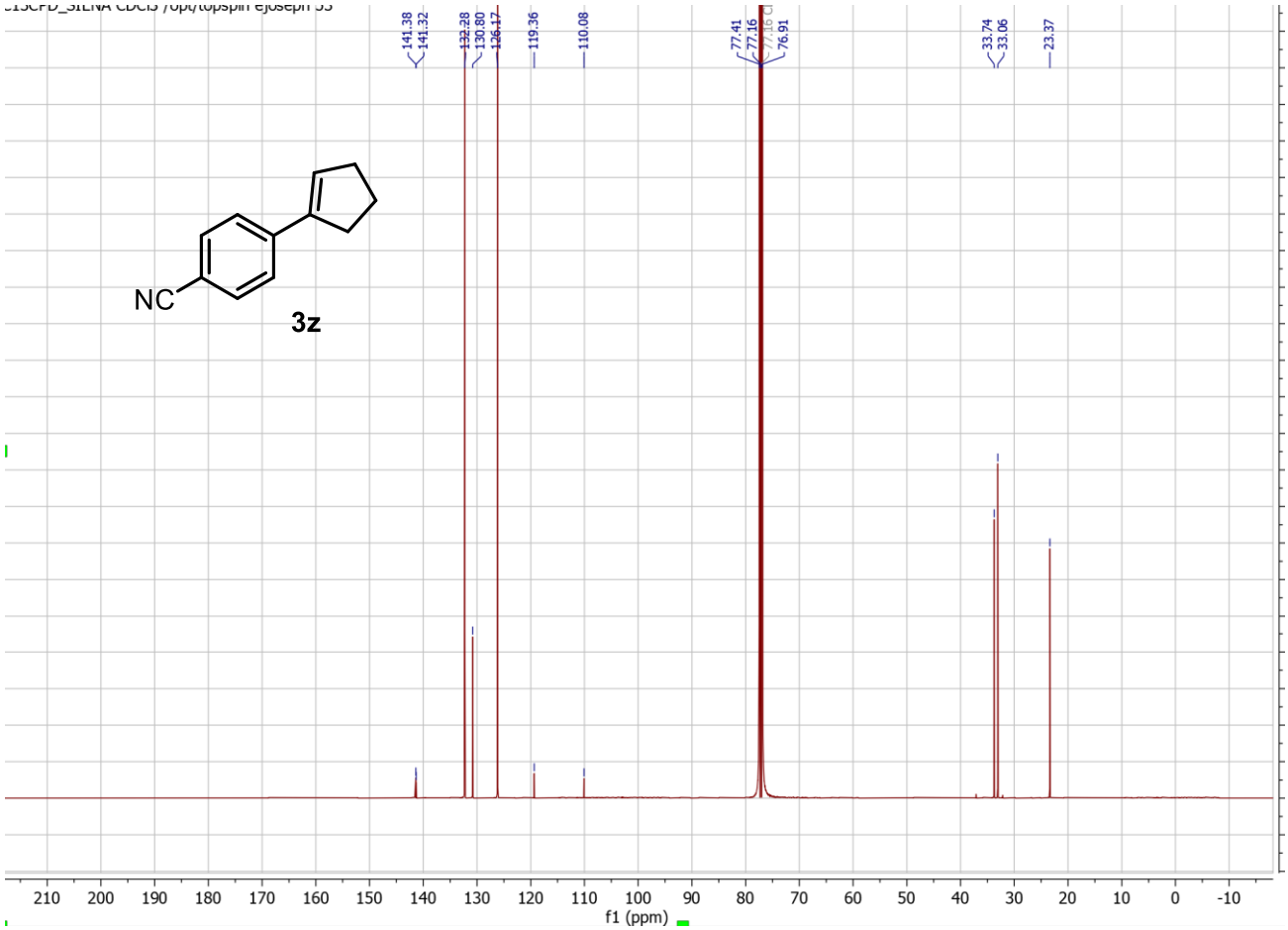
^{13}C NMR spectrum of **3y** in $CDCl_3$ at 126 MHz



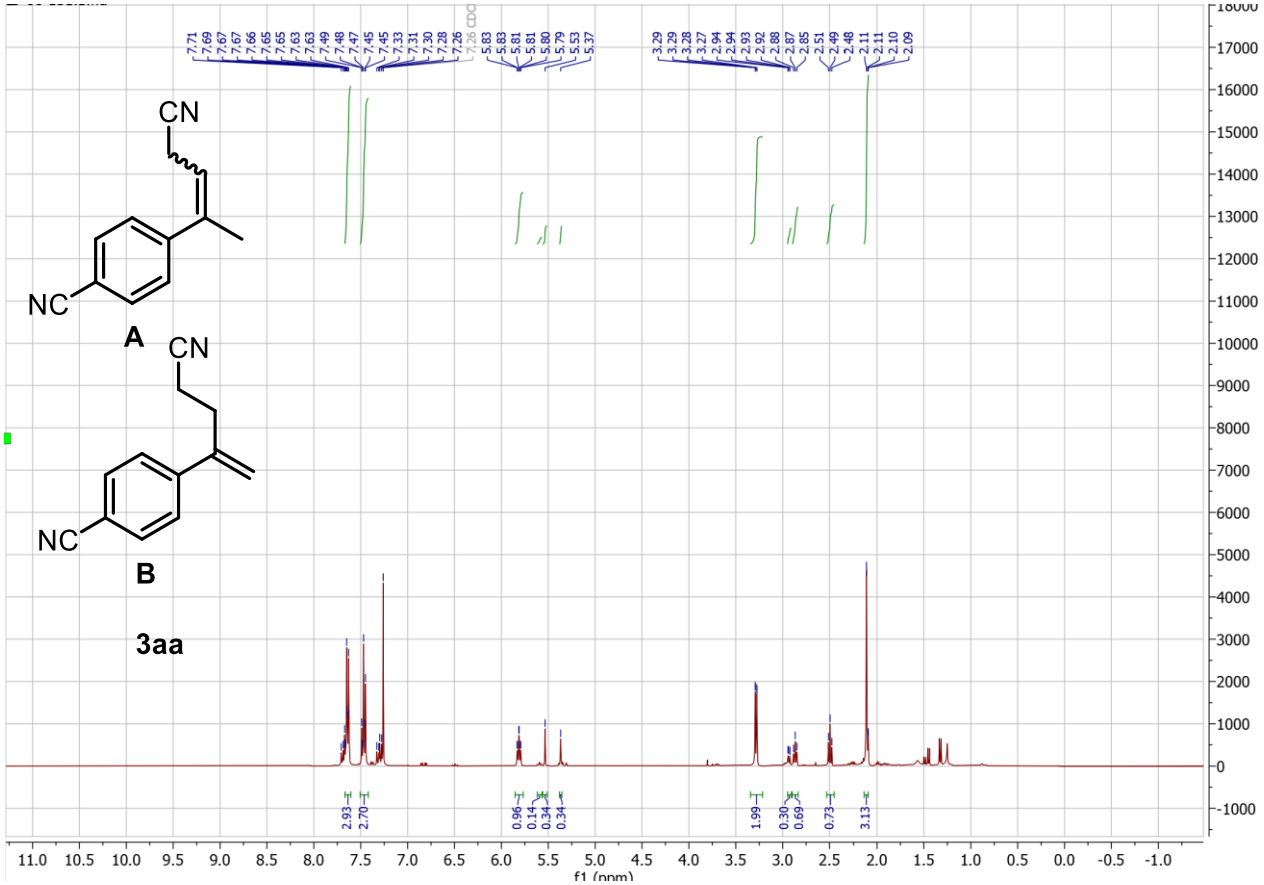
^{1}H NMR spectrum of **3z** in $CDCl_3$ at 400 MHz



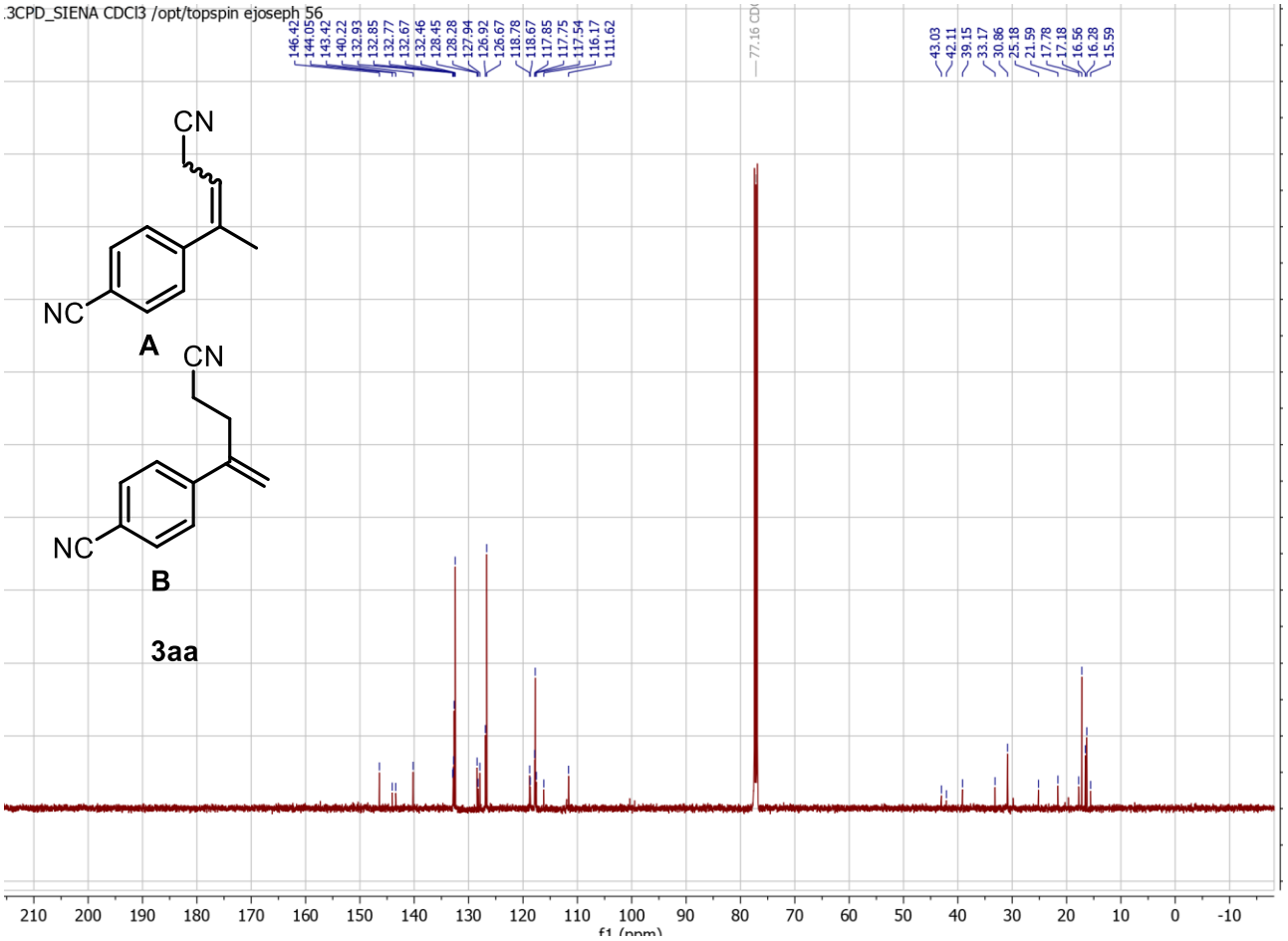
^{13}C NMR spectrum of **3z** in $CDCl_3$ at 126 MHz



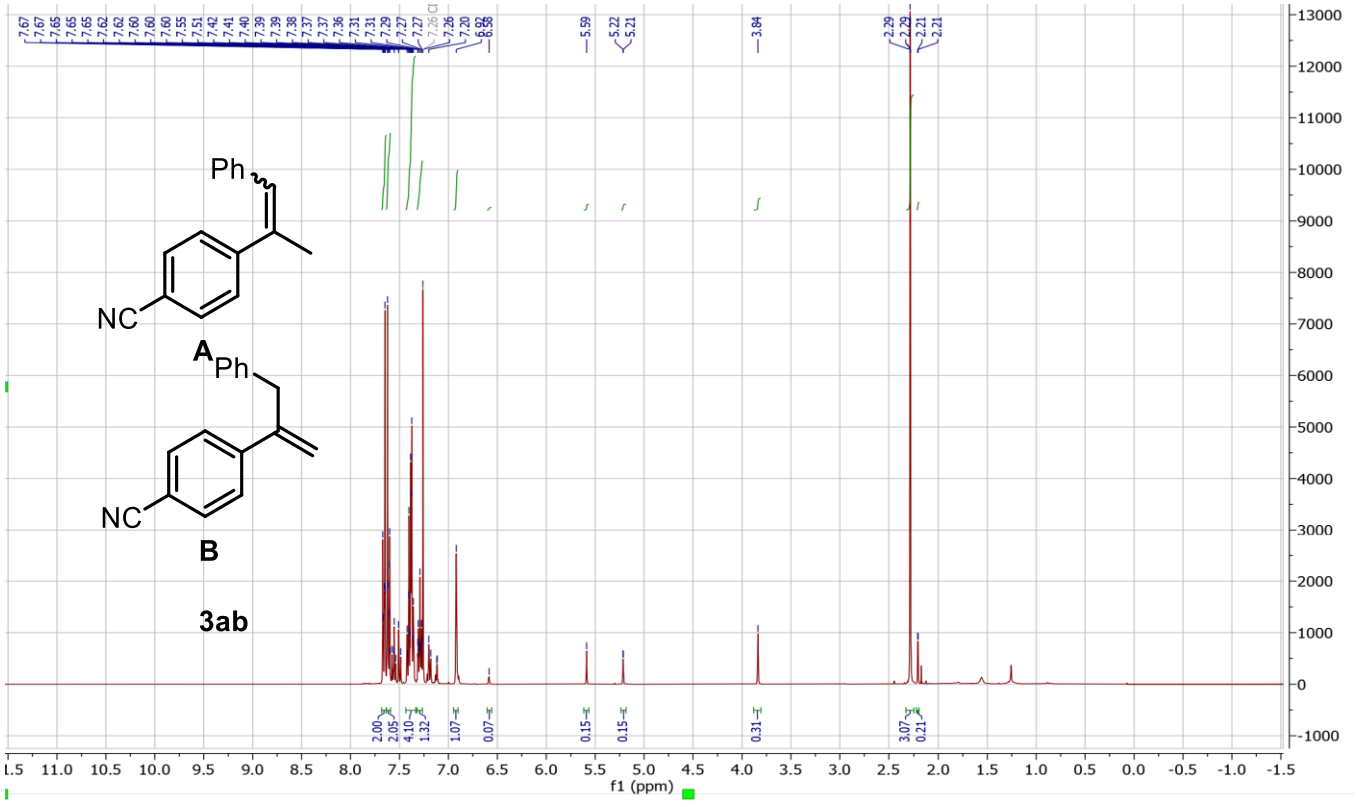
^{1}H NMR spectrum of **3aa** in $CDCl_3$ at 400 MHz



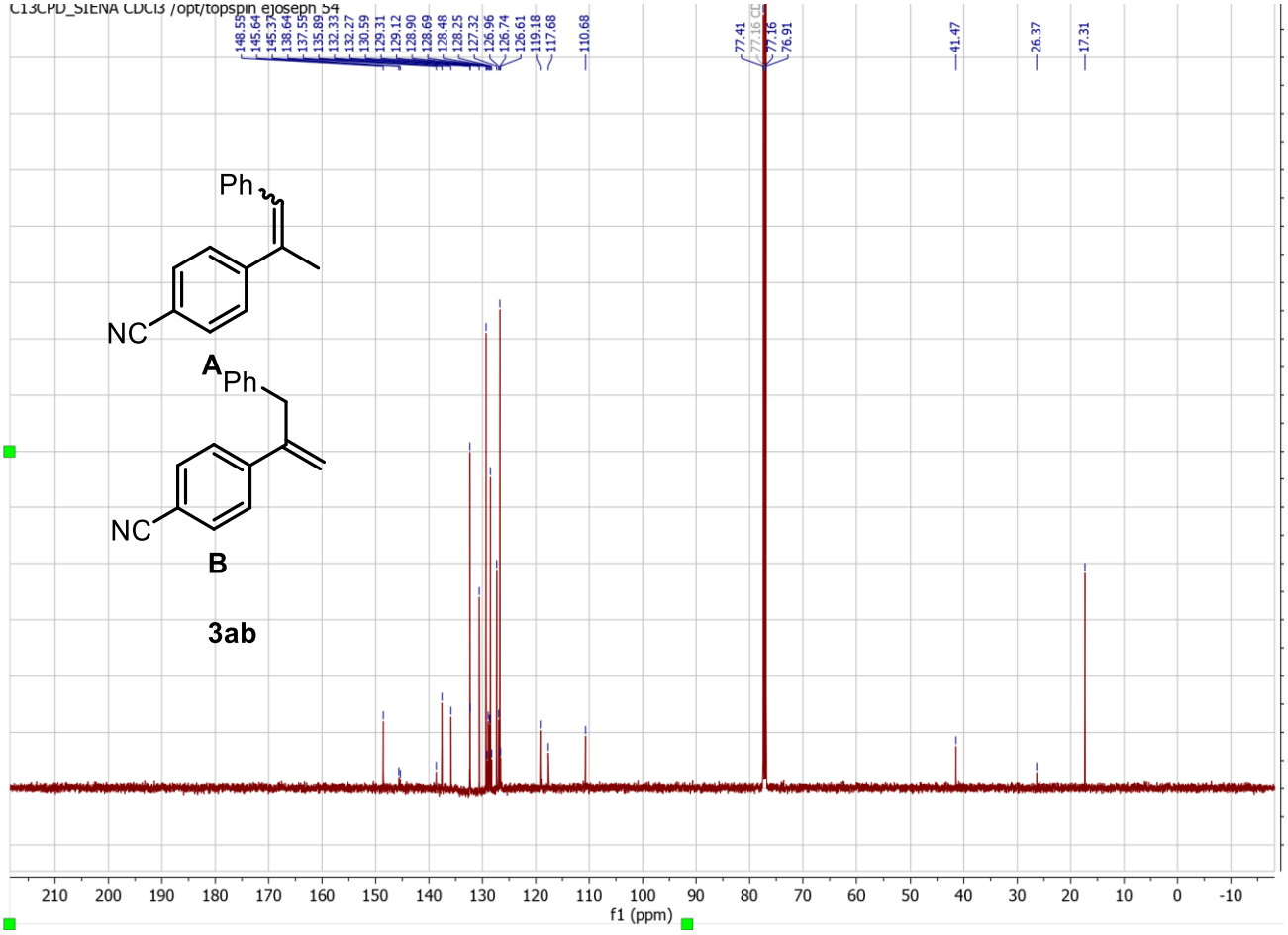
^{13}C NMR spectrum of **3aa** in $CDCl_3$ at 126 MHz



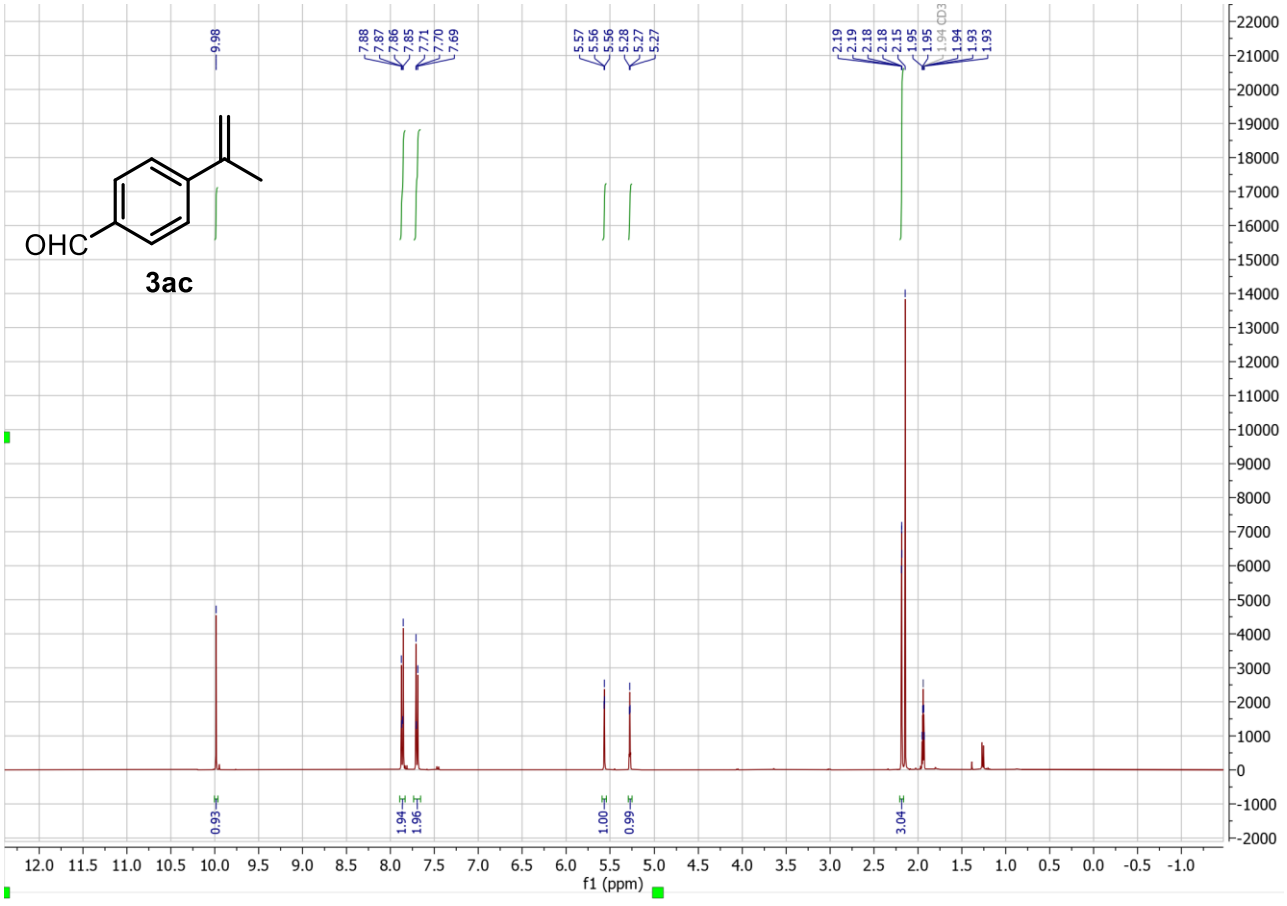
^{1}H NMR spectrum of **3ab** in $CDCl_3$ at 400 MHz



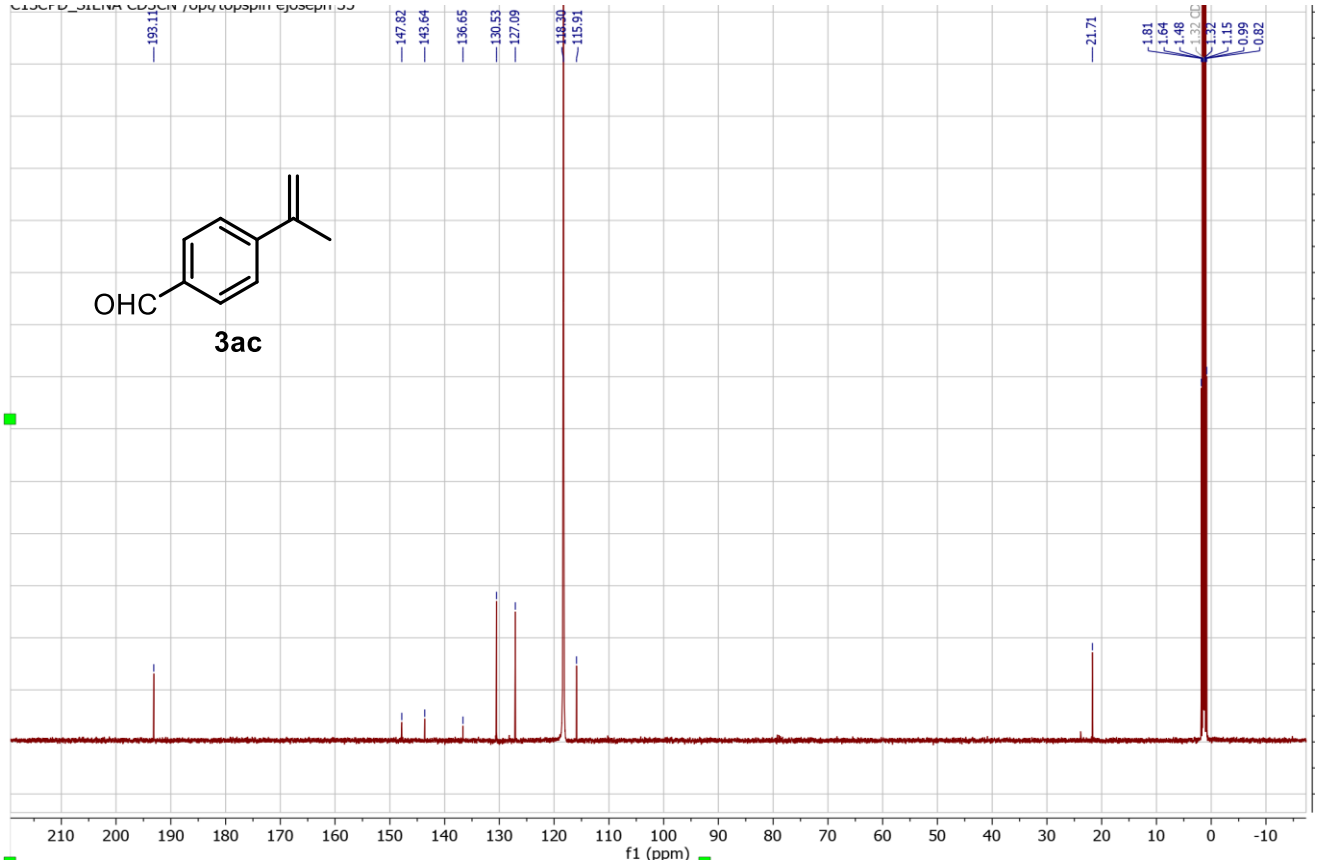
^{13}C NMR spectrum of **3ab** in $CDCl_3$ at 126 MHz



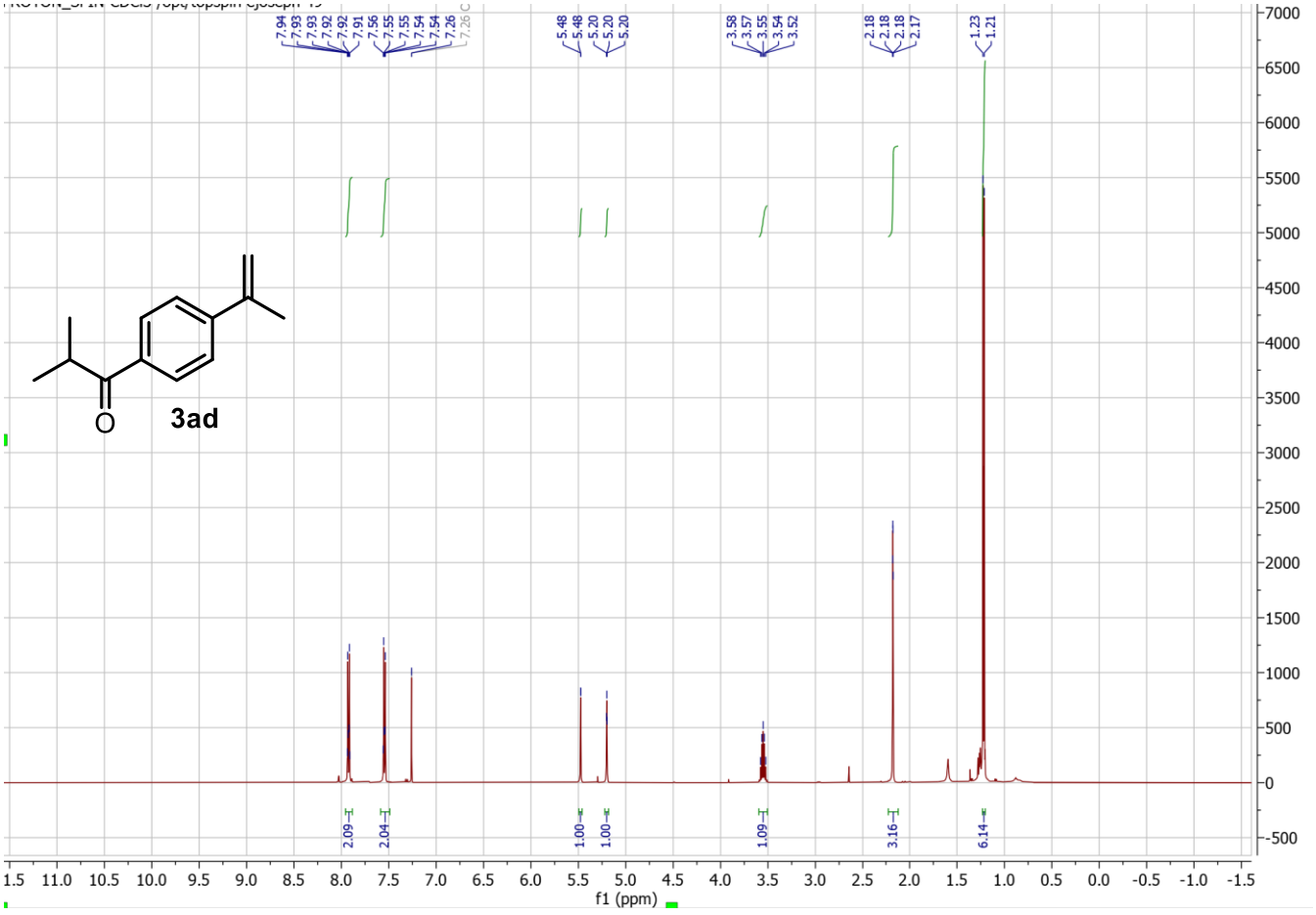
^{1}H NMR spectrum of **3ac** in CD_3CN at 400 MHz



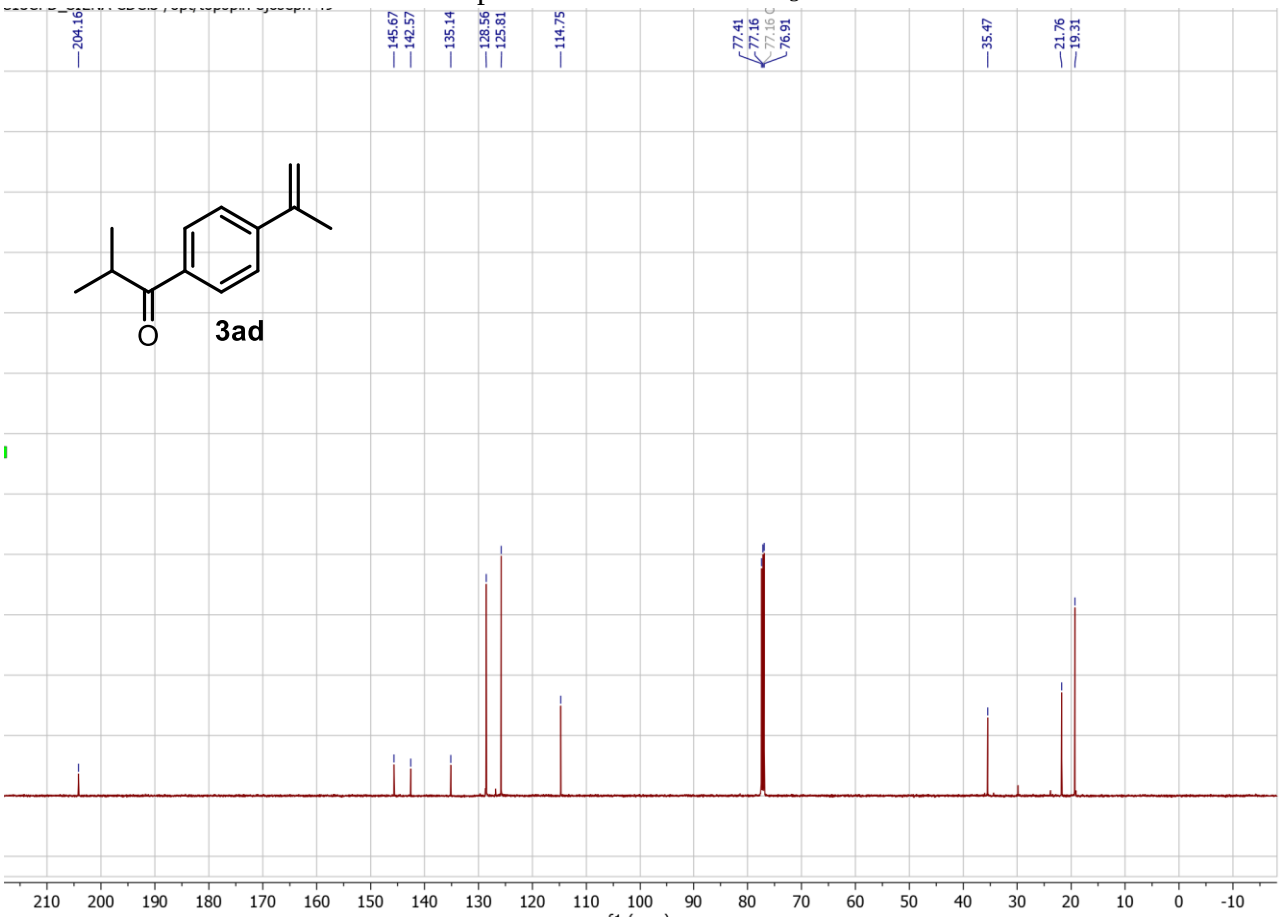
^{13}C NMR spectrum of **3ac** in CD_3CN at 126 MHz



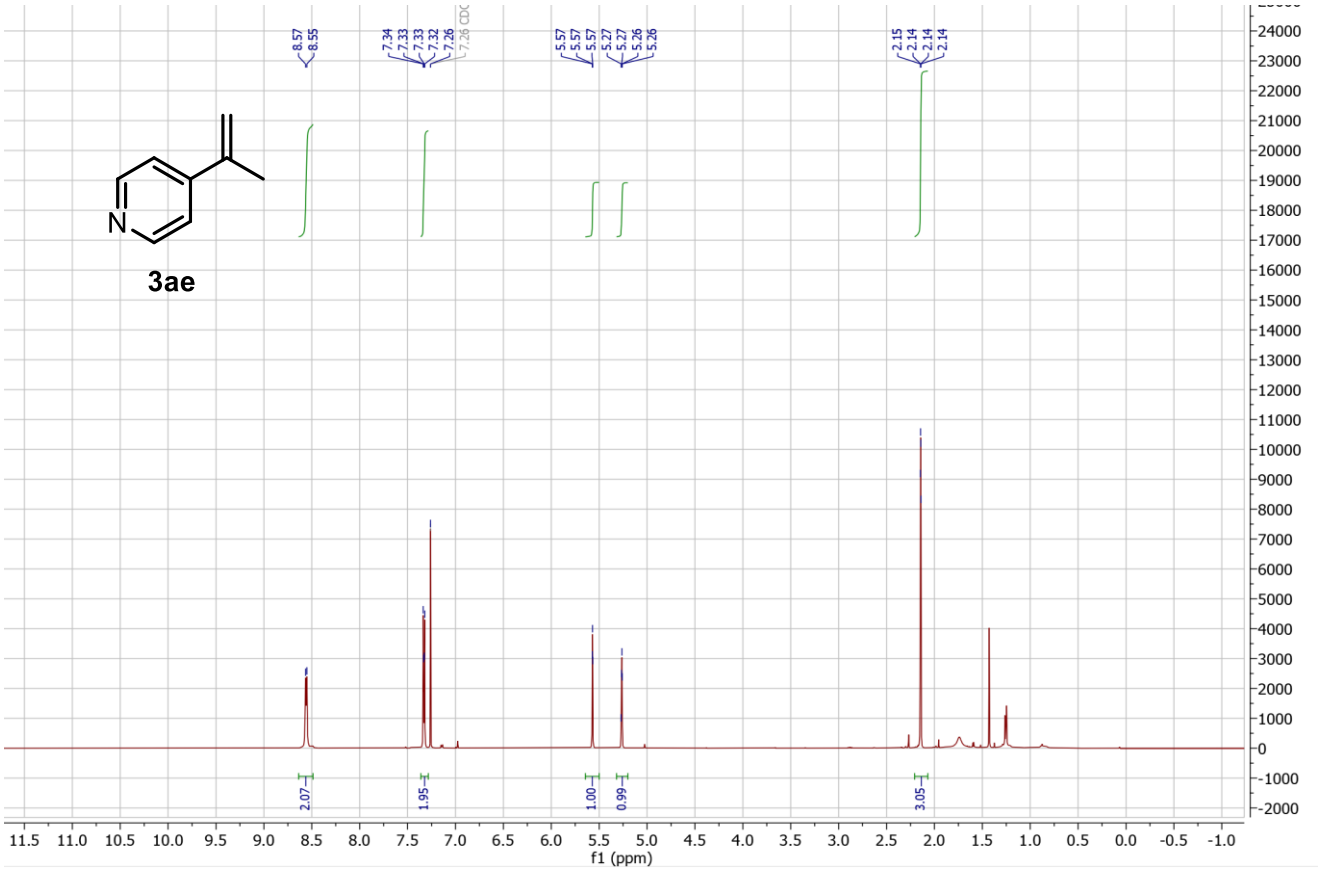
^{1}H NMR spectrum of **3ad** in $CDCl_3$ at 500 MHz



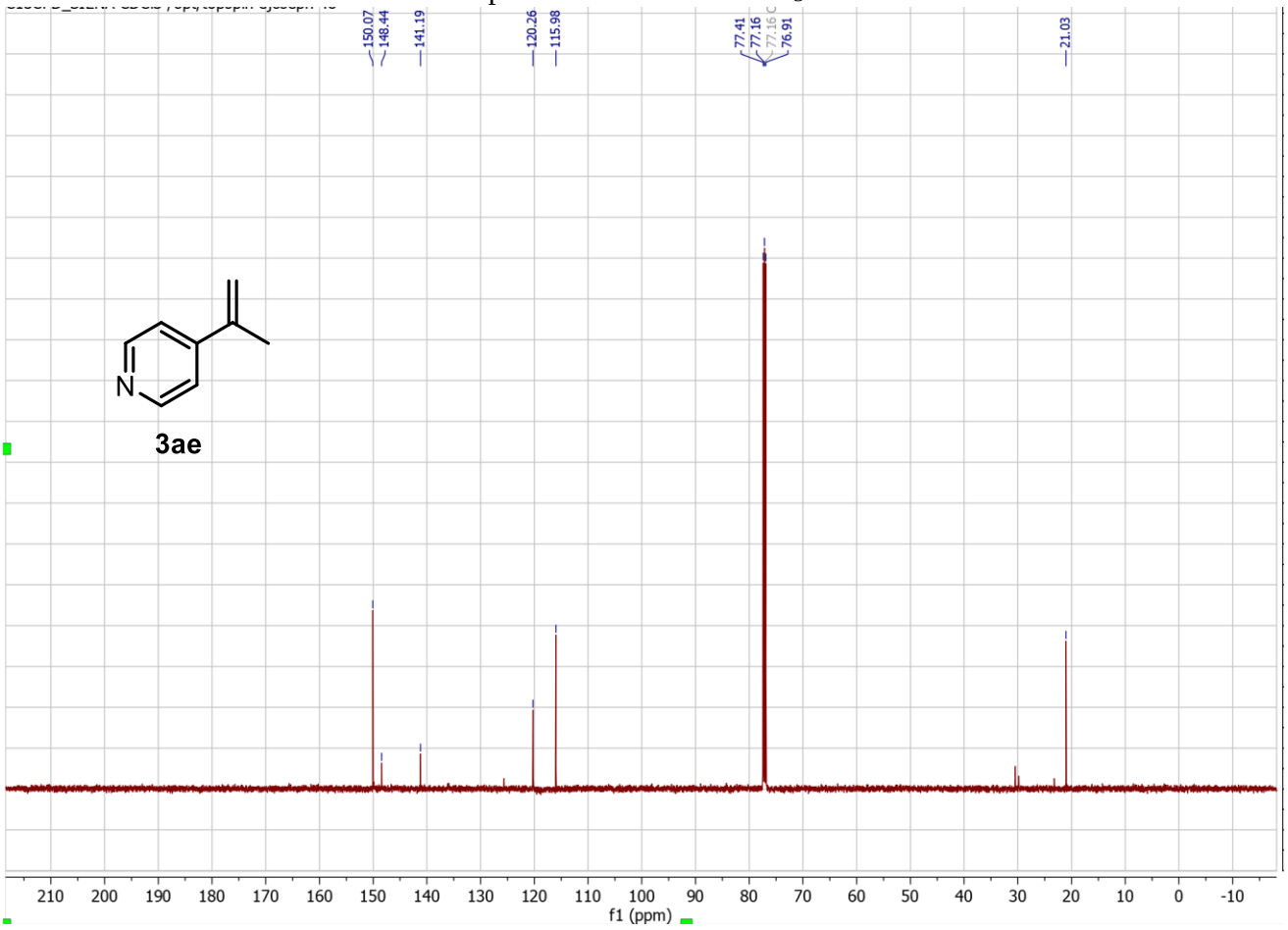
^{13}C NMR spectrum of **3ad** in $CDCl_3$ at 126 MHz



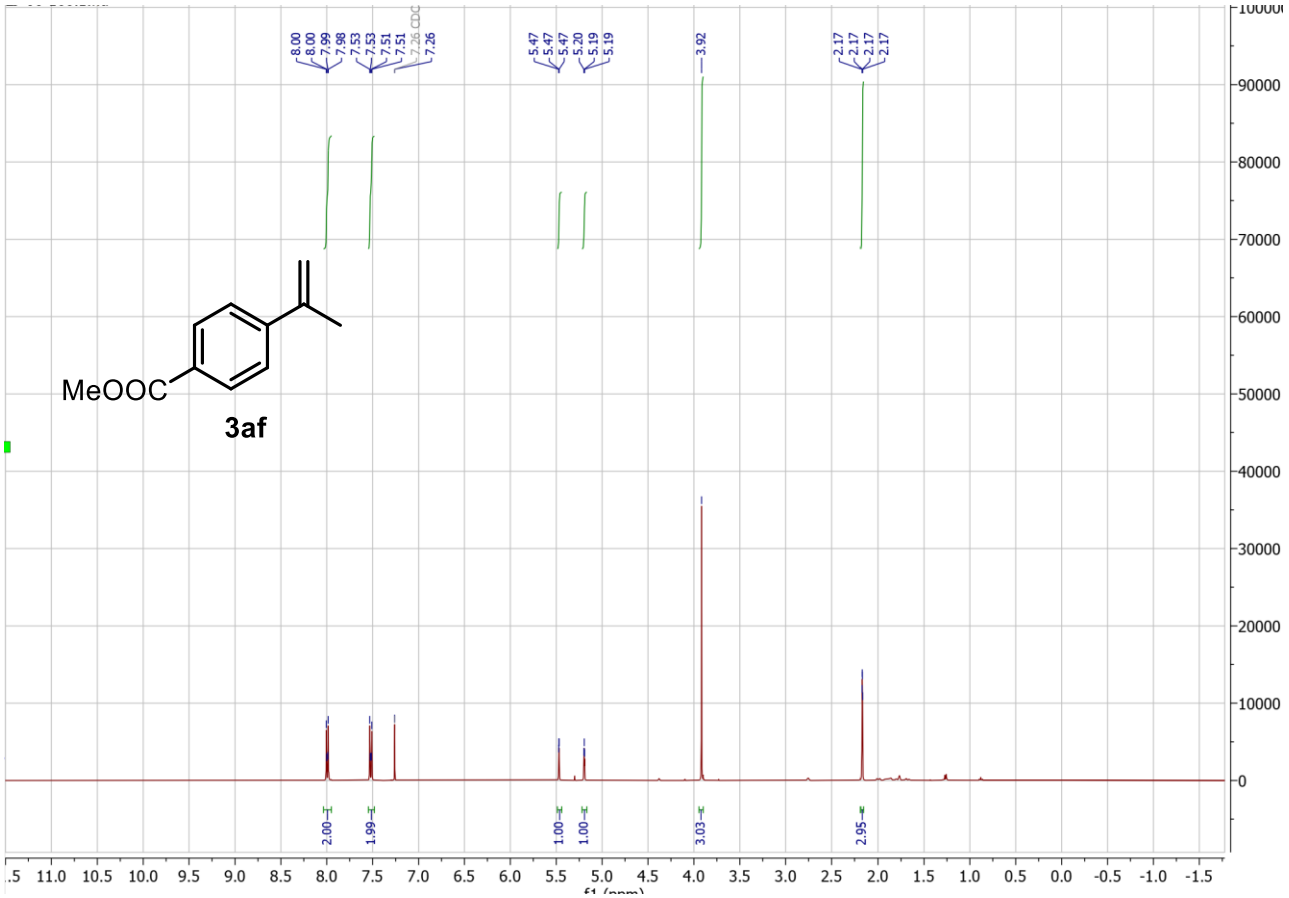
^{1}H NMR spectrum of **3ae** in $CDCl_3$ at 400 MHz



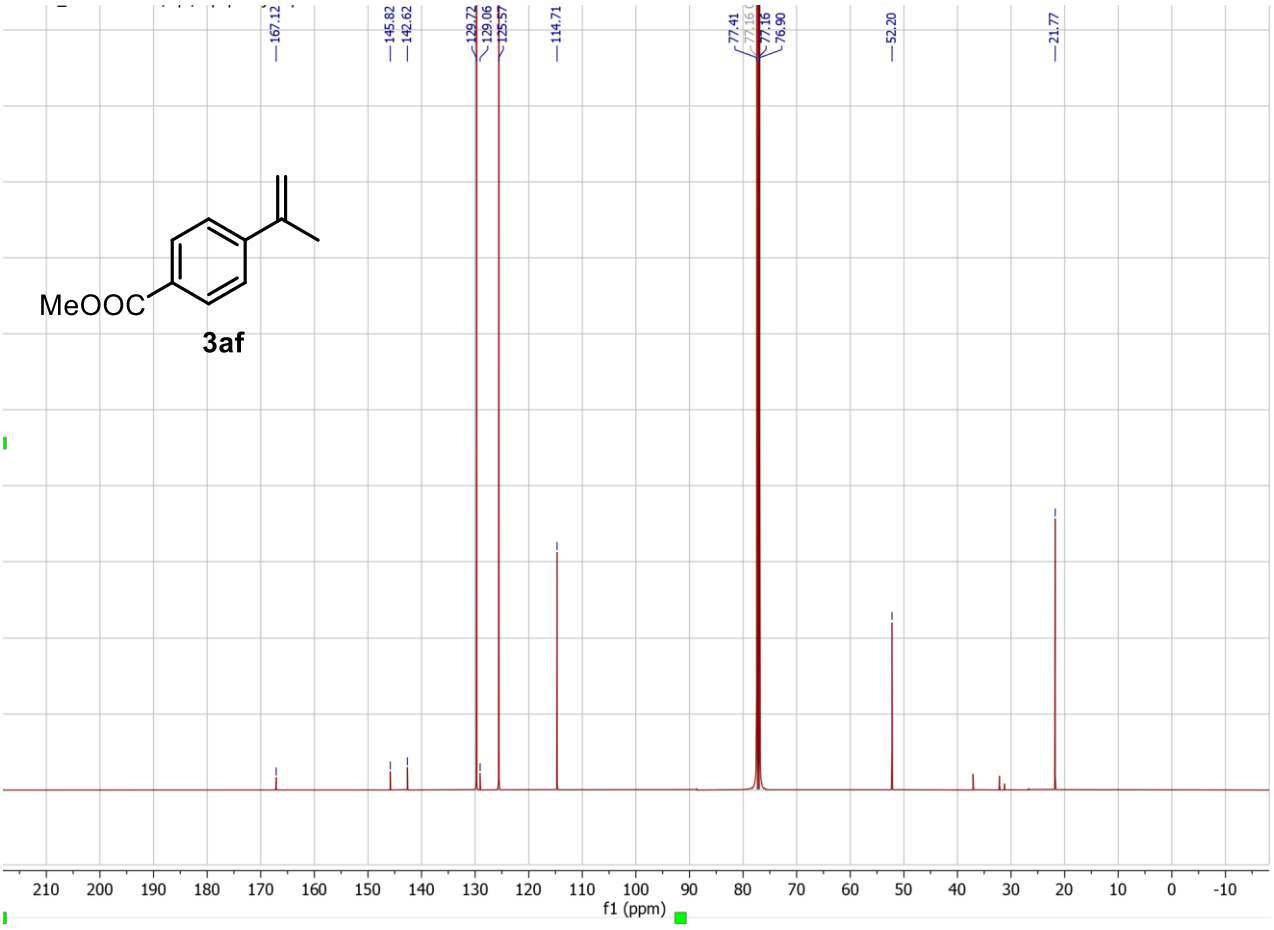
^{13}C NMR spectrum of **3ae** in $CDCl_3$ at 126 MHz



^{1}H NMR spectrum of **3af** in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **3af** in $CDCl_3$ at 126 MHz



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