Supporting Information

for

Modular Synthesis of α-Arylated Carboxylic Acids, Esters and Amides via Photocatalyzed Triple C−F Bond Cleavage of Methyltrifluorides

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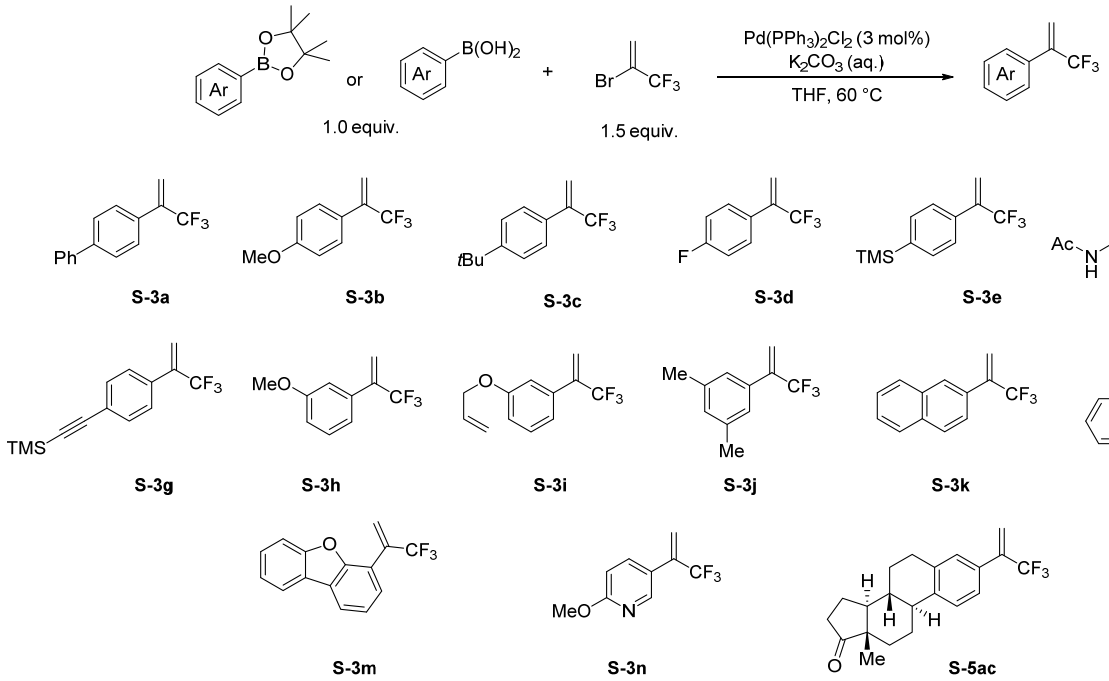
1. General Information

NMR spectra were recorded on 400 MHz or 600 MHz Bruker spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual ^{1}H and ^{13}C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (br). High-resolution electrospray ionization and electronic impact mass spectrometry was performed on a a Thermo Scientific Q Exactive mass spectrometer (mass analyzer type: Orbitrap). A mass accuracy ⩽ 2 ppm was obtained in the peak matching acquisition mode by using a solution containing 2 <l PEG200, 2 <l PPG450, and 1.5 mg NaOAc (all obtained from Sigma-Aldrich, CH-Buchs) dissolved in 100 mL MeOH (HPLC Supra grade, Scharlau, E-Barcelona) as internal standard.

Materials and Methods: Unless otherwise stated, starting materials were used as purchased. Solvents were purchased in HPLC quality, degassed by purging with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). Conversion was monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254. Compounds were visualized by UV light at 254 nm and by dipping the plates in an ethanolic vanillin/sulfuric acid solution or an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (230-400 mesh).

2. General Procedures

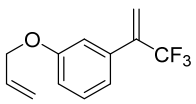
2.1 General procedure A for the synthesis of *α*-trifluoromethyl alkenes



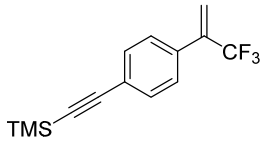
α-Trifluoromethyl alkenes used in this research were prepared according to literature reports.[1] To a Schlenk flask equipped with stir bar was added $ArB(OH)_2$ or ArBpin (1.0 equiv., 5.0 mmol) and $Pd(PPh_3)_2Cl_2$ (105 mg, 3 mol%, 0.15 mmol). The flask was evacuated and filled with N_2 (three times), then degassed aqueous solution of K_2CO_3 (2764 mg, 4.0 equiv. in 10 mL H_2O) and THF (15 mL) were added. After addition of 2-bromo-3,3,3-trifluoro-1-propene (1312 mg, 1.5 equiv., 7.5 mmol,), the solution was stirred at 60 °C in an oil-bath for 12 h (TLC tracking detection). Upon completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the corresponding *α*-trifluoromethyl alkene (hexane/EtOAc).

The experimental data are in accordance with the literature reports: **S-3a**,[1] **S-3b**,[1] **S-3c**,[1] **S-3d**,[2] **S-3e**,[3] **S-3f**,[4] **S-3h**,[2] **S-3j**,[5] **S-3k**,[3] **S-3l**,[2] **S-3m**,[5] **S-3n**,[6] **S-5ac**.[7]

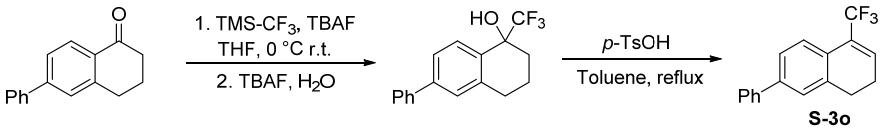
1-(Allyloxy)-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (S-3i): Following the general procedure, purification by flash column chromatography (Hexane), the product as pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 1H), 7.09 – 7.02 (m, 2H), 6.98 – 6.93 (m, 1H), 6.08 (ddt, J = 17.3, 10.6, 5.3 Hz, 1H), 5.97 (q, J = 1.4 Hz, 1H), 5.78 (q, J = 1.7 Hz, 1H), 5.48 – 5.41 (m, 1H), 5.35 – 5.29 (m, 1H), 4.59 – 4.55 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) 158.7, 138.9 (q, $^2J_{C\text{-}F}$ = 30.2 Hz), 135.1, 133.2, 129.7, 123.4 (q, $^1J_{C\text{-}F}$ = 275.0 Hz), 120.7 (q, $^3J_{C\text{-}F}$ = 5.8 Hz), 120.1, 118.0, 115.2, 114.3, 69.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.73 (s, 3F). HRMS ESI $[M+H]^+$ calculated for ($C_{12}H_{12}OF_3$) 229.0835, found 229.0832.



Trimethyl((4-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)ethynyl)silane (S-3g): Following the general procedure, purification by flash column chromatography (Hexane), the product as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.43 – 7.37 (m, 2H), 5.97 (q, J = 1.4 Hz, 1H), 5.79 (q, J = 1.7 Hz, 1H), 0.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5 (q, $^2J_{C\text{-}F}$ = 30.4 Hz), 133.6, 132.2 (2C), 127.3 (2C), 124.1, 123.3 (q, $^1J_{C\text{-}F}$ = 275.1 Hz), 120.9 (q, $^3J_{C\text{-}F}$ = 5.8 Hz), 104.4, 96.0, 0.1 (3C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.63 (s, 3F). HRMS ESI $[M+H]^+$ calculated for ($C_{14}H_{16}F_3Si$) 269.0968, found 269.0965.



2.1.1 Preparation of 7-phenyl-4-(trifluoromethyl)-1,2-dihydronaphthalene (S-3o)[8]:



S-3o

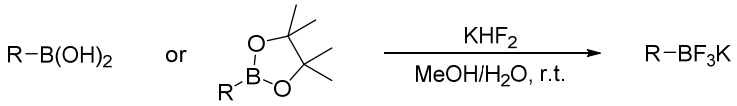
To a 250 mL Schlenk flask equipped with a stir bar was added ketone (1333 mg, 6.0 mmol, 1 equiv.), THF (60 mL), and $TMSCF_3$ (1109 mg, 7.8 mmol, 1.3 equiv.) under N_2. The reaction mixture was cooled to 0 °C in an ice-water bath. After stirring for approximately 10 min, TBAF (0.6 mL, 1 M in THF, 0.6 mmol, 0.1 equiv.) was added dropwise via a syringe. After stirring for 10 min, the ice-bath was removed, and the solution was allowed to stir overnight.

To cleave the silyl ether formed by the reaction, H_2O (~ 5.5 equiv.) was added followed by TBAF (0.6 mL, 1 M in THF, 0.1 equiv.). When the cleavage was judged to be completed by TLC, the contents of the flask were transferred to a separatory funnel. H_2O and Et_2O were added, and the layers were partitioned. The aqueous layer was extracted with Et_2O. The organic layers were combined, then washed with H_2O and brine. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the alcohol.

To a 250 mL Schlenk flask equipped with a stir bar and fitted with a reflux condenser was added alcohol, *p*-TsOH•H_2O (0.5 equiv.), and toluene. The flask was heated in an oil-bath to reflux for 24 h. When the reaction was judged to be complete, the reaction mixture was cooled to room temperature and quenched with sat. aq. $NaHCO_3$. The reaction mixture was diluted with EtOAc and the layers were separated. The combined organic layers were washed with brine (150 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure and the residue was purified by column chromatography (eluent: hexane) to afford the trifluoromethylalkene **S-3o**.

S-3o. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.55 – 7.50 (m, 2H), 7.50 – 7.45 (m, 3H), 7.42 – 7.37 (m, 1H), 6.78 – 6.74 (m, 1H), 2.91 (t, J = 8.1 Hz, 2H), 2.51 – 2.45 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 140.6, 136.5, 132.3 (q, $^3J_{C\text{-}F}$ = 6.3 Hz), 129.0 (2C), 128.6 (q, $^2J_{C\text{-}F}$ = 29.6 Hz), 127.7, 127.6, 127.1 (2C), 126.9, 125.6, 125.3 (q, $^1J_{C\text{-}F}$ = 273.0 Hz), 124.7, 27.6, 22.7; ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.87 (s, 3F). HRMS ESI $[M-H]^-$ calculated for ($C_{17}H_{12}F_3$) 273.0897, found 273.0891.

2.2 General procedure B for the synthesis of alkyltrifluoroborate compounds



Following the literature procedure,[9] to the solution of alkyl boronic acid or pinacol ester (5 mmol, 1.0 equiv.) in 20 mL methanol was added saturated aqueous KHF_2 (8 mL, 30 mmol, 6.0 equiv.). The resulting suspension was stirred for 5 h and then concentrated to dryness. The residue was extracted with hot acetone, and the combined filtered extracts were concentrated to approximately 5 mL. Ether (or CH_2Cl_2) was added and the resultant precipitate was collected and dried to afford the potassium alkyltrifluoroborate as a white solid.

2.3 General procedure C for the multicomponent formation of *α*-arylated carboxylic acids

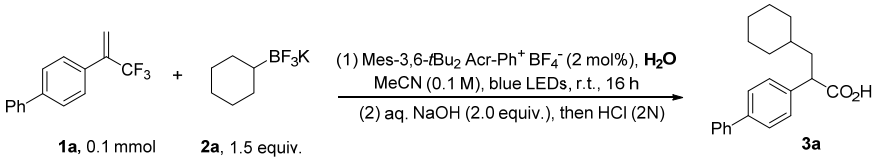
A 10-mL Schlenk tube equipped with a magnetic stir bar was charged with *α*-trifluoromethyl alkene (0.1 mmol, 1.0 equiv., if solid), alkyltrifluoroborate (0.15 mmol, 1.5 equiv.), Mes-3,6-*t*Bu_2 Acr-$Ph^+BF_4^-$ (1.2~3.0 mg, 0.002~0.005 mmol, 2~5 mol%). The flask was evacuated and backfilled with N_2 3 times. MeCN (1.0 mL) or a solution of *α*-trifluoromethyl alkene (0.1 mmol) in MeCN (1.0 mL) was then added via syringe followed by the addition of H_2O (30~100 μL) under N_2. The reaction mixture was then vigorously stirred under blue LED light (30 W) at room temperature (two fans were used to cool down the reaction mixture) for 16-48 h. After the reaction was completed, 1.0 mL of aq. NaOH (0.2 M) was added to the reaction mixture at room temperature, the resulting solution was stirred for 2 min at room temperature before acidified by HCl solution (2 N). The reaction mixture was then diluted with ethyl acetate, poured into a separatory funnel, before being washed with brine. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product.

2.4 General procedure D for the multicomponent formation of *α*-arylated amides and esters

A 10-mL Schlenk tube equipped with a magnetic stir bar was charged with *α*-trifluoromethyl alkene (0.1 mmol, 1.0 equiv., if solid), alkyltrifluoroborate (0.15 mmol, 1.5 equiv.), N-nucleophile (0.15 mmol, 1.5 equiv., if solid, 0.2 mmol for NH_4OAc, 0.5 mmol for alcohol), Mes-3,6-*t*Bu_2 Acr-$Ph^+BF_4^-$ (1.2~3.0 mg, 0.002~0.005 mmol, 2~5 mol%). The flask was evacuated and backfilled with N_2 3 times. MeCN (1.0 mL) or a solution of *α*-trifluoromethylalkene (0.1 mmol) in MeCN (1.0 mL) was then added via syringe followed by the addition of N-nucleophile (if liquid) and H_2O (100 μL, 10 μL for the synthesis of esters) under N_2. The reaction mixture was then vigorously stirred under blue LED light (30 W) at room temperature (two fans were used to cool down the reaction mixture) for 48 h. After the reaction was completed, the reaction mixture was diluted with ethyl acetate and poured into a separatory funnel, washed with brine. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product.

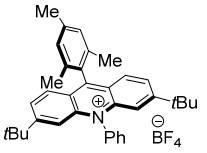
3. Reaction Optimization

3.1 Reaction optimization of the multicomponent formation of *α*-arylated carboxylic acids



1a, 0.1 mmol **2a**, 1.5 equiv. **3a**

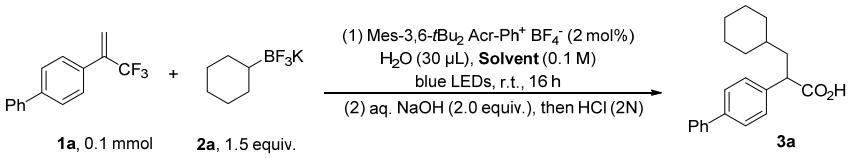
entry	H_2O (μL)	yield*
1	10	56%
2	30	88% (80%)
3	50	86%
4	70	84%
5	100	76%
6	150	60%



Mes-3,6-tBu$_2$ Acr-Ph$^+$ BF$_4^-$

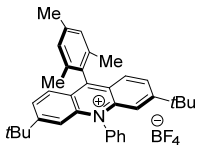
* Yields were determined by ^{1}H NMR spectroscopy of the crude reaction mixture with mesitylene as internal standard; isolated yield was shown in parentheses.

Figure S1 Evaluation of H_2O loading



1a, 0.1 mmol **2a**, 1.5 equiv. **3a**

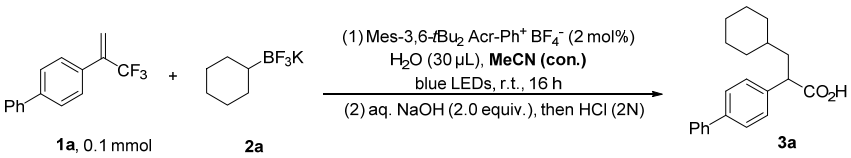
entry	solvent	yield*
1	MeCN	88% (80%)
2	CH_2Cl_2	43%
3	Et_2O	37%
4	1,4-Dioxane	n.d.
5	Toluene	47%
6	DMF	n.d.



Mes-3,6-tBu$_2$ Acr-Ph$^+$ BF$_4^-$

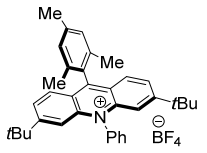
* Yields were determined by ^{1}H NMR spectroscopy of the crude reaction mixture with mesitylene as internal standard; isolated yield was shown in parentheses.

Figure S2 Evaluation of solvents



1a, 0.1 mmol **2a** **3a**

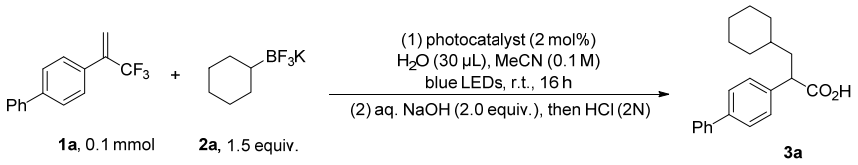
entry	**2a** (equiv.)	MeCN	yield*
1	1.5	0.20 M	73%
2	1.5	0.10 M	88% (80%)
3	1.5	0.05 M	58%
4	1.2	0.10 M	86%



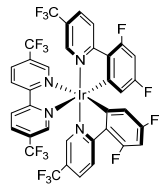
Mes-3,6-tBu$_2$ Acr-Ph$^+$ BF$_4^-$

* Yields were determined by ^{1}H NMR spectroscopy of the crude reaction mixture with mesitylene as internal standard; isolated yield was shown in parentheses.

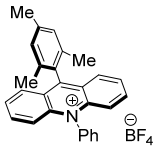
Figure S3 Evaluation of solvent concentration and equivalents of **2a**



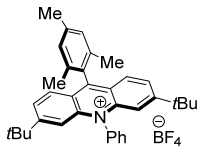
1a, 0.1 mmol **2a**, 1.5 equiv. **3a**



16%



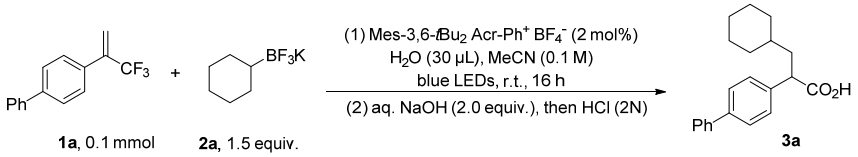
44%



88% (80%)

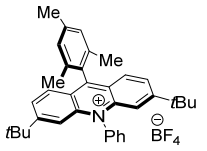
* Yields were determined by ^{1}H NMR spectroscopy of the crude reaction mixture with mesitylene as internal standard; isolated yield was shown in parentheses.

Figure S4 Evaluation of photocatalyst



1a, 0.1 mmol **2a**, 1.5 equiv. **3a**

entry	variations	yield*
1	none	88% (80%)
2	without H_2O	n.d.
3	without photocatalyst	n.d.
4	without step (2)	53%

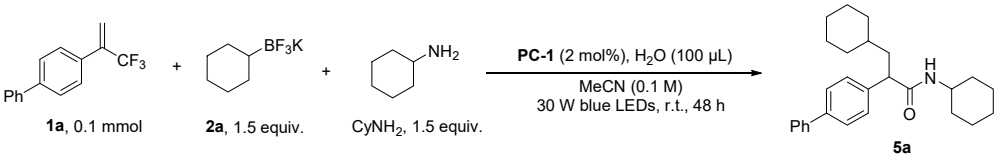


Mes-3,6-*t*Bu$_2$ Acr-Ph$^+$ BF$_4^-$

* Yields were determined by ^{1}H NMR spectroscopy of the crude reaction mixture with mesitylene as internal standard; isolated yield was shown in parentheses.

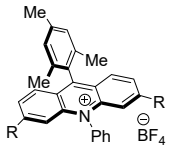
Figure S5 Control experiments

3.2 Reaction optimization of the multicomponent formation of *α*-arylated amides

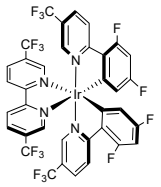


1a, 0.1 mmol **2a**, 1.5 equiv. $CyNH_2$, 1.5 equiv. **5a**

entry	variations	yield*
1	none	80% (72%)
2	**PC-2** instead of **PC-1**	16%
3	**PC-3** instead of **PC-1**	trace
4	DCM instead of MeCN	26%
5	DCE instead of MeCN	35%
6	THF instead of MeCN	0%
7	Toluene instead of MeCN	0%
8	50 µL of H_2O	59%
9	150 µL of H_2O	79%
10	200 µL of H_2O	73%
11	without H_2O	0%
12	1.2 equiv. of **2a**	71%



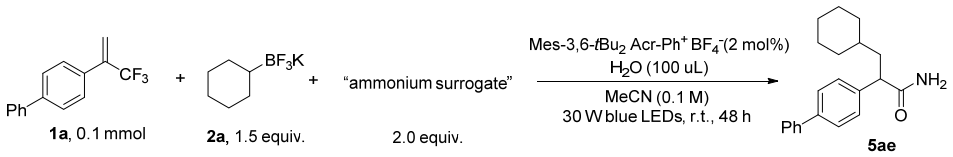
PC-1: R = *t*-Bu
PC-2: R = H



PC-3

* Yields were determined by ^{1}H NMR spectroscopy of the crude reaction mixture with mesitylene as internal standard; isolated yield was shown in parentheses.

Figure S6 Optimization summary



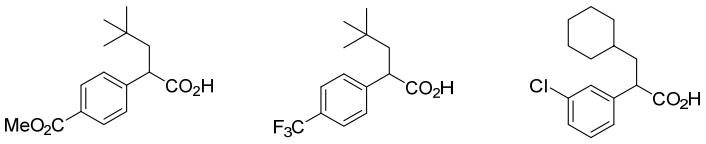
1a, 0.1 mmol **2a**, 1.5 equiv. 2.0 equiv. **5ae**

entry	"ammonium surrogate"	yield*
1	NH_4OAc	78% (70%)
2	$(NH_4)_2CO_3$	65%
3	$(NH_4)PF_6$	54%
4	$(NH_4)HCO_3$	75%
5	$(NH_4)CO_2H$	35%
6	NH_4Cl	n.d.

* Yields were determined by ^{1}H NMR of the crude reaction mixture with mesitylene as internal standard; isolated yield was shown in parentheses.

Figure S7 Screening of different ammonium surrogates

3.3 Unsuccessful substrates



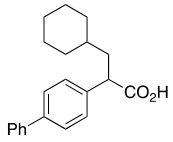
n.d. (52%) n.d. (66%) n.d. (80%)

* Yields in parentheses are corresponding *gem*-difluoroalkenes.

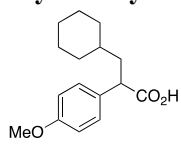
Several α-trifluoromethyl-α-(hetero)aryl alkenes with electron-deficient arenes have been tried, but only lead to the formation of corresponding *gem*-difluoroalkenes, probably due to the inefficient single-electron oxidation of *gem*-difluoroalkenes by the excited photocatalyst in the second catalytic cycle.

4. Product Characterization

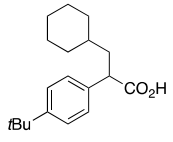
2-([1,1'-Biphenyl]-4-yl)-3-cyclohexylpropanoic acid (3a): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (24.7 mg) was obtained in 80% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.46 – 7.37 (m, 4H), 7.37 – 7.31 (m, 1H), 3.76 (t, J = 7.8 Hz, 1H), 2.02 (dt, J = 13.7, 7.8 Hz, 1H), 1.83 – 1.71 (m, 3H), 1.71 – 1.57 (m, 3H), 1.30 – 1.10 (m, 4H), 0.99 – 0.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 140.9, 140.5, 138.0, 128.9 (2C), 128.6 (2C), 127.5 (2C), 127.4, 127.2 (2C), 48.4, 40.8, 35.3, 33.4, 33.1, 26.6, 26.21, 26.18. HRMS ESI [M-H]$^-$ calculated for ($C_{21}H_{23}O_3$) 307.1698, found 307.1695.



3-Cyclohexyl-2-(4-methoxyphenyl)propanoic acid (3b): Following the general procedure **C** using 50 μL of H_2O, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (21.8 mg) was obtained in 84% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H), 3.64 (t, J = 7.8 Hz, 1H), 1.93 (dt, J = 13.7, 7.8 Hz, 1H), 1.76 – 1.68 (m, 2H), 1.68 – 1.57 (m, 4H), 1.21 – 1.09 (m, 4H), 0.95 – 0.85 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.8, 159.0, 130.9, 129.2 (2C), 114.2 (2C), 55.4, 47.9, 40.7, 35.2, 33.5, 33.0, 26.6, 26.22, 26.17. HRMS ESI [M-H]$^-$ calculated for ($C_{16}H_{21}O_3$) 261.1496, found 261.1488.



2-(4-(*Tert*-butyl)phenyl)-3-cyclohexylpropanoic acid (3c): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 10:100:2), the product (24.1 mg) was obtained in 84% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 3.70 (dd, J = 8.5, 6.9 Hz, 1H), 2.01 (ddd, J = 13.8, 8.5, 6.7 Hz, 1H), 1.81 – 1.73 (m, 2H), 1.73 – 1.63 (m, 4H), 1.34 (s, 9H), 1.27 – 1.15 (m, 4H), 0.99 – 0.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.8, 150.3, 135.9, 127.8 (2C), 125.7 (2C), 48.4, 40.81, 35.3, 34.6, 33.3, 33.2, 31.5 (3C), 26.6, 26.19, 26.17. HRMS ESI [M-H]$^-$ calculated for ($C_{19}H_{27}O_2$) 287.2017, found 287.2008.



3-Cyclohexyl-2-(4-fluorophenyl)propanoic acid (3d): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 10:100:2), the product (15.1 mg) was obtained in 60% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.03 – 6.95 (m, 2H), 3.66 (t, *J* = 7.8 Hz, 1H), 1.92 (dt, *J* = 13.8, 7.8 Hz, 1H), 1.74 – 1.56 (m, 6H), 1.17 – 1.05 (m, 4H), 0.97 – 0.79 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.4, 162.3 (d, $^1J_{C\text{-}F}$ = 246.4 Hz), 134.5 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 129.8 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, 2C), 115.6 (d, $^2J_{C\text{-}F}$= 22.2 Hz, 2C), 48.0, 40.8, 35.2, 33.4, 33.0, 26.6, 26.20, 26.15; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.16 – -115.25 (m, 1F). HRMS ESI $[M\text{-}H]^-$ calculated for ($C_{15}H_{18}O_2F$) 249.1296, found 249.1286.

3-Cyclohexyl-2-(4-(trimethylsilyl)phenyl)propanoic acid (3e): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 12:100:2), the product (15.6 mg) was obtained in 51% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0, 2H), 3.68 (dd, *J* = 8.3, 7.2 Hz, 1H), 1.98 (ddd, *J* = 13.8, 8.3, 6.9 Hz, 1H), 1.79 – 1.70 (m, 2H), 1.70 – 1.58 (m, 4H), 1.25 – 1.12 (m, 4H), 0.99 – 0.82 (m, 2H), 0.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.3, 139.6, 139.5, 133.8 (2C), 127.6 (2C), 48.8, 40.7, 35.3, 33.3, 33.2, 26.6, 26.19, 26.16, -1.0 (3C). HRMS ESI $[M+Na]^+$ calculated for ($C_{18}H_{27}O_2SiNa$) 327.1751, found 327.1745.

2-(4-Acetamidophenyl)-3-cyclohexylpropanoic acid (3f): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 30:100:2), the product (14.2 mg) was obtained in 49% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (br s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.65 (t, *J* = 7.8 Hz, 1H), 2.12 (s, 3H), 1.92 (dt, *J* = 14.4, 7.8 Hz, 1H), 1.75 – 1.60 (m, 6H), 1.17 – 1.10 (m, 4H), 0.93 – 0.85 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.4, 169.2, 137.0, 135.1, 128.7 (2C), 120.5 (2C), 48.3, 40.6, 35.2, 33.4, 33.0, 26.6, 26.20, 26.16, 24.5. HRMS ESI $[M+H]^+$ calculated for ($C_{17}H_{24}O_3N$) 290.1751, found 290.1747.

3-Cyclohexyl-2-(4-ethynylphenyl)propanoic acid (3g): Following the general procedure **C** using 5 mol% of photocatalyst and 50 μL of H_2O, purification by flash column chromatography (EtOAc:Hexane:AcOH = 12:100:2), the desilylation product (17.3 mg) was obtained in 68% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 3.69 (t, *J* = 7.8 Hz, 1H), 3.06 (s, 1H), 1.95 (dt, *J* = 13.7, 7.8 Hz, 1H), 1.74 – 1.58 (m, 6H), 1.20 – 1.09 (m, 4H), 0.94 – 0.85 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.6, 139.6, 132.6 (2C), 128.3 (2C), 121.4, 83.5, 77.5, 48.7, 40.6, 35.2, 33.4, 33.0, 26.6, 26.2, 26.1. HRMS ESI $[M+Na]^+$ calculated for ($C_{17}H_{20}O_2Na$) 279.1356, found 279.1351.

3-Cyclohexyl-2-(3-methoxyphenyl)propanoic acid (3h): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (18.5 mg) was obtained in 71% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.89 – 6.87 (m, 1H), 6.81 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.80 (s, 3H), 3.67 (t, *J* = 7.7 Hz, 1H), 1.95 (dt, *J* = 13.3, 7.7 Hz, 1H), 1.77 – 1.71

(m, 2H), 1.68 – 1.63 (m, 3H), 1.64 – 1.58 (m, 1H), 1.22 – 1.13 (m, 4H), 0.94 – 0.87 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.4, 159.9, 140.4, 129.7, 120.6, 114.0, 112.8, 55.4, 48.8, 40.7, 35.2, 33.4, 33.1, 26.6, 26.20, 26.16. HRMS ESI $[M-H]^-$ calculated for ($C_{16}H_{21}O_3$) 261.1496, found 261.1487.

2-(3-(Allyloxy)phenyl)-3-cyclohexylpropanoic acid (3i): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 12:100:2), the product (14.7 mg) was obtained in 54% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 1H), 6.93 – 6.87 (m, 2H), 6.84 – 6.79 (m, 1H), 6.05 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 5.45 – 5.37 (m, 1H), 5.31 – 5.25 (m, 1H), 4.55 – 4.51 (m, 2H), 3.66 (t, *J* = 7.8 Hz, 1H), 1.94 (dt, *J* = 13.7, 7.8 Hz, 1H), 1.77 – 1.57 (m, 6H), 1.23 – 1.07 (m, 4H), 0.96 – 0.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.8, 158.9, 140.4, 133.4, 129.7, 120.8, 117.9, 114.8, 113.6, 68.9, 48.7, 40.7, 35.2, 33.4, 33.1, 26.6, 26.20, 26.17. HRMS ESI $[M+H]^+$ calculated for ($C_{18}H_{25}O_3$) 289.1798, found 289.1792.

3-Cyclohexyl-2-(3,5-dimethylphenyl)propanoic acid (3j): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 12:100:2), the product (16.2 mg) was obtained in 62% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.93 (s, 2H), 6.91 (s, 1H), 3.62 (t, *J* = 7.7 Hz, 1H), 2.30 (s, 6H), 1.97 (dt, *J* = 13.1, 7.7 Hz, 1H), 1.78 – 1.70 (m, 2H), 1.69 – 1.65 (m, 2H), 1.63 – 1.58 (m, 2H), 1.24 – 1.09 (m, 4H), 0.95 – 0.86 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.6, 138.9, 138.3 (2C), 129.2, 125.9 (2C), 48.7, 40.7, 35.3, 33.3, 33.2, 26.6, 26.20, 26.19, 21.4 (2C). HRMS ESI $[M-H]^-$ calculated for ($C_{17}H_{23}O_2$) 259.1704, found 259.1695.

3-Cyclohexyl-2-(naphthalen-2-yl)propanoic acid (3k): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 12:100:2), the product (23.5 mg) was obtained in 83% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (br s, 1H), 7.83 – 7.71 (m, 4H), 7.47 – 7.43 (m, 3H), 3.83 (t, *J* = 7.7 Hz, 1H), 2.01 (dt, *J* = 14.5, 7.7 Hz, 1H), 1.83 – 1.73 (m, 2H), 1.72 – 1.57 (m, 4H), 1.24 – 1.03 (m, 4H), 0.97 – 0.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.5, 136.6, 133.5, 132.8, 128.4, 128.0, 127.7, 127.2, 126.21, 126.17, 125.9, 49.2, 40.7, 35.2, 33.6, 32.9, 26.6, 26.2, 26.1. HRMS ESI $[M-H]^-$ calculated for ($C_{19}H_{21}O_2$) 281.1547, found 281.1538.

2-(Benzo[*b*]thiophen-2-yl)-3-cyclohexylpropanoic acid (3l): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (17.6 mg) was obtained in 61% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.71 (dd, *J* = 7.7, 1.5Hz, 1H), 7.36 – 7.27 (m, 2H), 7.21 (s, 1H), 4.08 (t, *J* = 7.8 Hz, 1H), 2.02 (dt, *J* = 14.5, 7.8 Hz, 1H), 1.87 – 1.83 (m, 1H), 1.80 – 1.72 (m, 2H), 1.71 – 1.65 (m, 2H), 1.65 – 1.56 (m, 1H), 1.35 – 1.25 (m, 1H), 1.20 – 1.10 (m, 3H), 1.01 – 0.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.2, 142.0, 139.63, 139.55, 124.4, 124.3, 123.5, 122.6, 122.4, 44.9, 41.4, 35.2, 33.4, 32.9, 26.5, 26.2, 26.1. HRMS ESI $[M-H]^-$ calculated for ($C_{17}H_{10}O_2S$) 287.1111, found 287.1102.

3-Cyclohexyl-2-(dibenzo[*b*,*d*]furan-4-yl)propanoic acid (3m): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 12:100:2), the product (28.9 mg) was obtained in 90% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.86 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.38 – 7.29 (m, 2H), 4.48 (t, *J* = 7.7 Hz, 1H), 2.17 – 2.06 (m, 1H), 1.97 – 1.83 (m, 2H), 1.82 – 1.71 (m, 1H), 1.71 – 1.63 (m, 2H), 1.63 – 1.55 (m, 1H), 1.31 – 1.18 (m, 2H), 1.16 – 1.12 (m, 2H), 1.02 – 0.92 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.1, 156.2, 154.4, 127.3, 126.1, 124.5, 124.4, 123.2, 123.0, 122.9, 120.8, 119.7, 112.0, 42.2, 39.9, 35.4, 33.9, 33.0, 26.6, 26.2, 26.1. HRMS ESI $[M+Na]^+$ calculated for ($C_{21}H_{22}O_3Na$) 345.1461, found 345.1458.

3-Cyclohexyl-2-(6-methoxypyridin-3-yl)propanoic acid (3n): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 25:100:2), the product (10.5 mg) was obtained in 40% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.5 Hz, 1H), 7.60 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 3.92 (s, 3H), 3.65 (t, *J* = 7.8 Hz, 1H), 1.93 (dt, *J* = 13.8, 7.8 Hz, 1H), 1.72 – 1.58 (m, 6H), 1.17 – 1.09 (m, 4H), 0.96 – 0.85 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.0, 163.6, 146.3, 138.5, 127.5, 111.1, 53.8, 45.4, 40.6, 35.1, 33.5, 32.8, 26.6, 26.2, 26.1. HRMS ESI $[M+H]^+$ calculated for ($C_{15}H_{22}O_3N$) 264.1594, found 264.1591.

2-(Methoxymethyl)-6-phenyl-1,2,3,4-tetrahydronaphthalene-1-carboxylic acid (3o): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:1), the product was obtained in 57% yield as white solid, dr = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (br s, 2H), 7.61 – 7.55 (m, 4H), 7.47 – 7.41 (m, 4H), 7.39 (s, 2H), 7.38 – 7.32 (m, 6H), 4.02 (d, *J* = 5.4 Hz, 1H), 3.78 (d, *J* = 7.5 Hz, 1H), 3.62 – 3.56 (m, 1H), 3.55 – 3.46 (m, 2H), 3.45 – 3.43 (m, 1H), 3.40 (s, 3H), 3.38 (s, 3H), 3.08 – 2.98 (m, 1H), 2.97 – 2.82 (m, 3H), 2.66 – 2.57 (m, 1H), 2.36 – 2.27 (m, 1H), 2.19 – 2.06 (m, 2H), 1.89 – 1.81 (m, 1H), 1.64 – 1.53 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.8, 179.1, 141.0, 140.9, 140.4, 140.1, 137.6, 137. 5, 132.1, 131.4, 130.1, 129.5, 128.8, 128.3, 128.0, 127.3, 127.19, 127.17, 125.2, 124.9, 75.8, 75.0, 59.07, 59.05, 48.1, 45.9, 37.4, 37.2, 28.8, 28.1, 24.1, 21.6. HRMS ESI $[M+Na]^+$ calculated for ($C_{19}H_{20}O_3Na$) 319.1305, found 319.1300.

2-([1,1'-Biphenyl]-4-yl)-3-cyclopentylpropanoic acid (3p): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (21.5 mg) was obtained in 73% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.46 – 7.40 (m, 4H), 7.37 – 7.32 (m, 1H), 3.67 (t, *J* = 7.7 Hz, 1H), 2.13 (dt, *J* = 13.4, 7.7 Hz, 1H), 1.88 (ddd, *J* = 13.4, 7.8, 6.8 Hz, 1H), 1.84 – 1.76 (m, 2H), 1.73 (ddd, *J* = 13.4, 7.8, 6.8 Hz, 1H), 1.65 – 1.57 (m, 2H), 1.54 – 1.45 (m, 2H), 1.17 – 1.08 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.5, 140.9, 140.5, 137.8, 128.9 (2C), 128.7 (2C), 127.5 (2C), 127.4,

127.2 (2C), 50.6, 39.6, 37.9, 32.8, 32.5, 25.22, 25.20. HRMS ESI [M-H]$^-$ calculated for ($C_{20}H_{21}O_2$) 293.1547, found 293.1539.

2-([1,1'-Biphenyl]-4-yl)-3-cycloheptylpropanoic acid (3q): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (18.3 mg) was obtained in 57% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.32 (m, 1H), 3.73 (t, *J* = 7.7 Hz, 1H), 2.05 (dt, *J* = 14.5, 7.7 Hz, 1H), 1.79 – 1.70 (m, 3H), 1.65 – 1.57 (m, 2H), 1.58 – 1.51 (m, *J* = 5.6 Hz, 2H), 1.48 – 1.43 (m, 3H), 1.43 – 1.35 (m, 2H), 1.30 – 1.19 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.5, 140.8, 140.5, 137.9, 128.9 (2C), 128.7 (2C), 127.5 (2C), 127.4, 127.2 (2C), 49.1, 41.2, 36.7, 34.6, 34.2, 28.7 (2C), 26.2, 26.1. HRMS ESI [M-H]$^-$ calculated for ($C_{22}H_{25}O_2$) 321.1860, found 321.1850.

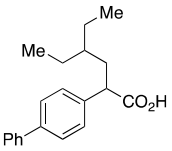
2-([1,1'-Biphenyl]-4-yl)-3-(4,4-difluorocyclohexyl)propanoic acid (3r): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (27.5 mg) was obtained in 80% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.46 – 7.42 (m, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.37 – 7.33 (m, 1H), 3.72 (t, *J* = 7.8 Hz, 1H), 2.11 – 2.00 (m, 3H), 1.85 – 1.75 (m, 3H), 1.69 – 1.57 (m, 2H), 1.35 – 1.25 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.6, 140.8, 140.6, 137.2, 129.0 (2C), 128.5 (2C), 127.7 (2C), 127.6, 127.2 (2C), 123.6 (t, $^1J_{C\text{-}F}$ = 239.9 Hz), 48.7, 39.0 (d, $^4J_{C\text{-}F}$ = 1.2 Hz), 33.43, 33.40 (t, $^2J_{C\text{-}F}$ = 22.8 Hz), 33.39 (t, $^2J_{C\text{-}F}$ = 22.8 Hz), 29.1 (d, $^3J_{C\text{-}F}$ = 9.4 Hz), 28.8 (d, $^3J_{C\text{-}F}$ = 9.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.81 (d, *J* = 233.6 Hz), -101.98 (d, *J* = 267.8 Hz). HRMS ESI [M+Na]$^+$ calculated for ($C_{21}H_{22}F_2O_2Na$) 367.1480, found 367.1477.

2-([1,1'-Biphenyl]-4-yl)-3-(1-(*tert*-butoxycarbonyl)piperidin-4-yl)propanoic acid (3s): Following the general procedure **C** using 100 μL of H_2O, purification by flash column chromatography (EtOAc:Hexane:AcOH = 20:100:2), the product (17.4 mg) was obtained in 43% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 4H), 7.45 – 7.41 (m, 2H), 7.41 – 7.38 (m, 2H), 7.37 – 7.32 (m, 1H), 4.09 – 4.02 (m, 2H), 3.74 (t, *J* = 7.7 Hz, 1H), 2.68 – 2.58 (m, 2H), 2.06 (dd, *J* = 14.4, 7.3 Hz, 1H), 1.77 (dt, *J* = 14.4, 7.3 Hz, 1H), 1.69 (t, *J* = 14.4 Hz, 2H), 1.45 (s, 9H), 1.42 – 1.38 (m, 1H), 1.18 – 1.09 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.4, 155.0, 140.7, 140.6, 137.5, 128.9 (2C), 128.5 (2C), 127.6 (2C), 127.5, 127.2 (2C), 79.6, 48.3, 43.9, 39.8, 33.7, 32.2, 31.9, 28.6 (3C), 20.9. HRMS ESI [M-H]$^-$ calculated for ($C_{25}H_{30}O_4N$) 408.2180, found 408.2166.

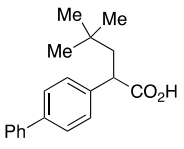
2-([1,1'-Biphenyl]-4-yl)-3-(tetrahydro-2H-pyran-4-yl)propanoic acid (3t): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (25.7 mg) was obtained in 83% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.47 – 7.41 (m, 2H), 7.41 – 7.38 (m, 2H), 7.38 – 7.32 (m, 1H), 3.99 – 3.91 (m, 2H), 3.75 (t, *J* = 7.8 Hz, 1H), 3.38 – 3.27 (m, 2H), 2.12 – 2.02 (m, 1H), 1.84 – 1.74 (m, 1H), 1.70 – 1.58 (m, 2H), 1.57 – 1.43 (m, 1H), 1.39 – 1.28 (m, 2H); ^{13}C NMR (101

MHz, $CDCl_3$) δ 179.5, 140.7, 137.5, 128.9 (2C), 128.6 (2C), 127.6 (2C), 127.5, 127.2 (2C), 67.89, 67.85, 48.0, 40.1, 33.0, 32.8, 32.6. HRMS ESI $[M-H]^-$ calculated for ($C_{20}H_{21}O_3$) 309.1496, found 309.1487.

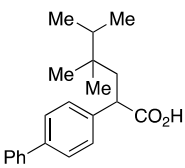
2-([1,1'-Biphenyl]-4-yl)-4-ethylhexanoic acid (3u): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (22.5 mg) was obtained in 78% yield as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 4H), 7.48 – 7.40 (m, 4H), 7.39 – 7.32 (m, 1H), 3.73 (t, J = 7.8 Hz, 1H), 2.11 – 2.02 (m, 1H), 1.84 – 1.74 (m, 1H), 1.42 – 1.29 (m, 4H), 1.24 – 1.16 (m, 1H), 0.87 (t, J = 7.4, 3H), 0.84 (t, J = 7.4, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.6, 140.8, 140.5, 137.9, 128.9 (2C), 128.7 (2C), 127.5 (2C), 127.4, 127.2 (2C), 49.1, 37.8, 36.6, 25.2, 25.0, 10.6, 10.4. HRMS ESI $[M+Na]^+$ calculated for ($C_{20}H_{24}O_2Na$) 319.1669, found 319.1663.



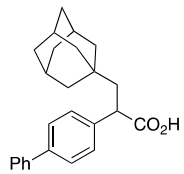
2-([1,1'-Biphenyl]-4-yl)-4,4-dimethylpentanoic acid (3v): Following the general procedure **C** using 50 μL of H_2O and 5 mol% of photocatalyst, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (21.1 mg) was obtained in 75% yield as white solid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.56 – 7.53 (m, 2H), 7.45 – 7.40 (m, 4H), 7.37 – 7.32 (m, 1H), 3.72 (dd, J = 8.7, 4.2 Hz, 1H), 2.32 (dd, J = 14.0, 8.7 Hz, 1H), 1.68 (dd, J = 14.0, 4.3 Hz, 1H), 0.94 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.0, 140.8, 140.4, 139.4, 128.9 (2C), 128.5 (2C), 127.6 (2C), 127.4, 127.2 (2C), 47.9, 47.0, 31.3, 29.6 (3C). HRMS ESI $[M-H]^-$ calculated for ($C_{19}H_{21}O_2$) 281.1547, found 281.1546.



2-([1,1'-Biphenyl]-4-yl)-4,4,5-trimethylhexanoic acid (3w): Following the general procedure **C** using 50 μL of H_2O and 5 mol% of photocatalyst, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (25.3 mg) was obtained in 82% yield as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 4H), 7.46 – 7.40 (m, 4H), 7.38 – 7.31 (m, 1H), 3.73 (dd, J = 8.6, 4.0 Hz, 1H), 2.34 (dd, J = 14.2, 8.6 Hz, 1H), 1.70 (dd, J = 14.2, 4.0 Hz, 1H), 1.56 (p, J = 6.8 Hz, 1H), 0.88 (d, J = 6.8 Hz, 3H), 0.86 – 0.80 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.1, 140.8, 140.4, 139.7, 128.9 (2C), 128.5 (2C), 127.5 (2C), 127.4, 127.2 (2C), 47.3, 43.3, 36.2, 36.0, 24.4, 23.9, 17.60, 17.55. HRMS ESI $[M+Na]^+$ calculated for ($C_{21}H_{26}O_2Na$) 333.1825, found 333.1819.



2-([1,1'-Biphenyl]-4-yl)-3-(adamantan-1-yl)propanoic acid (3x): Following the general procedure **C** using 50 μL of H_2O and 5 mol% of photocatalyst, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (21.1 mg) was obtained in 68% yield as white solid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.45 – 7.39 (m, 4H), 7.36 – 7.32 (m, 2H), 3.78 (dd, J = 8.8, 4.0 Hz, 1H), 2.19 (dd, J = 14.1, 8.8 Hz, 1H), 1.94 (s, 3H), 1.69 (d, J = 12.4 Hz, 3H), 1.62 (d, J = 12.4 Hz, 3H), 1.57 – 1.50 (m, 4H), 1.47 (d, J = 12.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.9, 140.8, 140.3, 139.7, 128.9 (2C), 128.5 (2C), 127.5 (2C), 127.4, 127.2 (2C), 47.8, 45.9, 42.4 (2C), 37.1 (2C), 33.1, 28.7 (3C). HRMS ESI $[M-H]^-$ calculated for ($C_{25}H_{27}O_2$) 359.2017, found 359.2004.



2-([1,1'-Biphenyl]-4-yl)-4,4-dimethyl-6-oxoheptanoic acid (3y): Following the general procedure **C** using 50 μL of H_2O and 5 mol% of photocatalyst, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (20.4 mg) was obtained in 63% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 4H), 7.45 – 7.37 (m, 4H), 7.37 – 7.30 (m, 1H), 3.71 (dd, *J* = 8.0, 5.0 Hz, 1H), 2.39 – 2.35 (m, 1H), 2.33 (q, *J* = 2.6 Hz, 2H), 2.02 (s, 3H), 1.94 (dd, *J* = 14.2, 5.0 Hz, 1H), 1.04 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4, 179.9, 140.9, 140.6, 138.9, 128.9 (2C), 128.6 (2C), 127.6 (2C), 127.5, 127.2 (2C), 53.8, 47.5, 44.6, 34.0, 32.3, 27.6, 27.5. HRMS ESI $[M+Na]^+$ calculated for ($C_{21}H_{24}O_3Na$) 347.1618, found 347.1611.

2-([1,1'-Biphenyl]-4-yl)-4-methoxybutanoic acid (3z): Following the general procedure **C**, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (14.2 mg) was obtained in 57% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 4H), 7.45 – 7.41 (m, 2H), 7.41 – 7.38 (m, 2H), 7.37 – 7.32 (m, 1H), 3.85 (t, *J* = 7.6 Hz, 1H), 3.44 – 3.39 (m, 1H), 3.34 – 3.29 (m, 1H), 3.31 (s, 3H), 2.46 – 2.37 (m, 1H), 2.07 – 2.00 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.4, 140.8, 140.6, 137.3, 128.9 (2C), 128.7 (2C), 127.6 (2C), 127.5, 127.2 (2C), 70.0, 58.8, 47.7, 33.0. HRMS ESI $[M-H]^-$ calculated for ($C_{17}H_{17}O_3$) 269.1183, found 269.1174.

2-([1,1'-Biphenyl]-4-yl)-4-((3-methylbut-3-en-1-yl)oxy)butanoic acid (3aa): Following the general procedure **C,** purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (17.1 mg) was obtained in 53% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 4H), 7.46 – 7.42 (m, 2H), 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 1H), 4.78 (s, 1H), 4.72 (s, 1H), 3.86 (t, *J* = 7.6 Hz, 1H), 3.54 – 3.43 (m, 3H), 3.37 – 3.32 (m, 1H), 2.51 – 2.34 (m, 1H), 2.28 (t, *J* = 6.9 Hz, 2H), 2.07 – 1.96 (m, 1H), 1.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 142.9, 140.8, 140.6, 137.3, 128.9 (2C), 128.7 (2C), 127.6 (2C), 127.5, 127.2 (2C), 111.7, 69.5, 68.0, 47.8, 37.8, 33.0, 22.9. HRMS ESI $[M+Na]^+$ calculated for ($C_{21}H_{24}O_3Na$) 347.1618, found 347.1611.

2-([1,1'-Biphenyl]-4-yl)-4-(((1*R*,2*S*,5*R*)-2-*iso*propyl-5-methylcyclohexyl)oxy)butanoic acid (3ab): Following the general procedure **C** using 50 μL of H_2O and 5 mol% of photocatalyst, purification by flash column chromatography (EtOAc:Hexane:AcOH = 15:100:2), the product (24.2 mg) was obtained in 61% yield as colourless oil (d.r. = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 8H), 7.47 – 7.37 (m, 8H), 7.36 – 7.32 (m, 2H), 3.90 (t, *J* = 7.5 Hz, 2H), 3.64 (dt, *J* = 10.2, 5.9 Hz, 1H), 3.62 – 3.55 (m, 1H), 3.32 (ddd, *J* = 9.5, 6.7, 5.0 Hz, 1H), 3.18 (td, *J* = 8.7, 4.8 Hz, 1H), 3.04 – 2.91 (m, 2H), 2.46 – 2.33 (m, 2H), 2.30 – 2.18 (m, 2H), 2.14 – 1.97 (m, 4H), 1.67 – 1.56 (m, 4H), 1.38 – 1.14 (m, 4H), 1.02 – 0.86 (m, 15H), 0.86 – 0.80 (m, 3H), 0.76 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 140.8, 140.5, 137.5, 128.9 (2C), 128.8, 128.7, 127.5 (2C), 127.4, 127.2 (2C), 79.5,

65.6, 48.4, 47.8, 40.5, 34.7, 33.6, 31.6, 25.8, 23.5, 22.5, 21.2, 16.4. HRMS ESI $[M+Na]^+$ calculated for ($C_{26}H_{34}O_3Na$) 417.2400, found 417.2393.

2-([1,1'-Biphenyl]-4-yl)-*N*,3-dicyclohexylpropanamide (5a): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 15:100:2), the product (28.0 mg) was obtained in 72% yield as white foam. ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.41 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 5.33 (d, *J* = 8.2 Hz, 1H), 3.75 (m, 1H), 3.46 (t, *J* = 7.7 Hz, 1H), 2.06 (dt, *J* = 14.4, 7.7 Hz, 1H), 1.89 (m, 1H), 1.78 (m, 3H), 1.74 – 1.64 (m, 4H), 1.60 (m, 3H), 1.40 – 1.24 (m, 2H), 1.24 – 1.13 (m, 4H), 1.13 – 1.05 (m, 2H), 0.97 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8, 140.8, 139.9, 139.9, 128.9 (2C), 128.4 (2C), 127.5 (2C), 127.4, 127.1 (2C), 50.4, 48.3, 41.1, 35.4, 33.7, 33.2, 33.1, 33.0, 26.7, 26.3, 26.2, 25.6, 24.91, 24.86. HRMS ESI $[M+H]^+$ calculated for ($C_{27}H_{36}ON$) 390.2791, found 390.2786.

2-([1,1'-Biphenyl]-4-yl)-*N*-butyl-3-cyclohexylpropanamide (5b): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 15:100:2), the product (26.9 mg) was obtained in 74% yield as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.57 – 7.53 (m, 2H), 7.46 – 7.40 (m, 2H), 7.40 – 7.31 (m, 3H), 5.52 (t, *J* = 5.8 Hz, 1H), 3.51 (t, *J* = 7.7 Hz, 1H), 3.30 – 3.20 (m, 1H), 3.20 – 3.11 (m, 1H), 2.08 (dt, *J* = 14.4, 7.7 Hz, 1H), 1.85 – 1.58 (m, 7H), 1.46 – 1.35 (m, 2H), 1.31 – 1.21 (m, 2H), 1.19 – 1.09 (m, 3H), 1.01 – 0.90 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 140.8, 140.0, 139.7, 128.9 (2C), 128.5 (2C), 127.5 (2C), 127.4, 127.1 (2C), 50.3, 40.91, 39.5, 35.2, 33.7, 33.0, 31.7, 26.7, 26.3, 26.2, 20.1, 13.8. HRMS ESI $[M+H]^+$ calculated for ($C_{25}H_{34}ON$) 364.2635, found 364.2630.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-*N*-isobutylpropanamide (5c): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 15:100:2), the product (23.8 mg) was obtained in 65% yield as white solid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.36 – 7.32 (m, 1H), 5.53 (t, *J* = 6.1 Hz, 1H), 3.53 (t, *J* = 7.7 Hz, 1H), 3.09 – 2.98 (m, 2H), 2.12 – 2.06 (m, 1H), 1.81 – 1.59 (m, 7H), 1.24 – 1.10 (m, 4H), 1.00 – 0.89 (m, 2H), 0.82 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.8, 140.8, 140.1, 139.7, 128.9 (2C), 128.5 (2C), 127.6 (2C), 127.4, 127.1 (2C), 50.4, 47.0, 40.9, 35.3, 33.7, 33.0, 28.6, 26.7, 26.3, 26.2, 20.1 (2C). HRMS ESI $[M+H]^+$ calculated for ($C_{25}H_{34}ON$) 364.2635, found 364.2630.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-*N*-neopentylpropanamide (5d): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 15:100:2), the product (28.6 mg) was obtained in 75% yield as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 4H), 7.46 – 7.41 (m, 2H), 7.41 – 7.37 (m, 2H), 7.37 – 7.31 (m, 1H), 5.51 (t, *J* = 6.4 Hz, 1H), 3.56 (t, *J* = 7.8 Hz, 1H), 3.01 (dd, *J* = 6.4, 1.8

Hz, 2H), 2.10 (dt, *J* = 13.7, 7.8 Hz, 1H), 1.78 – 1.64 (m, 5H), 1.64 – 1.57 (m, 1H), 1.25 – 1.09 (m, 4H), 1.03 – 0.89 (m, 2H), 0.80 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 140.7, 140.1, 139.7, 128.9 (2C), 128.5 (2C), 127.6 (2C), 127.4, 127.1 (2C), 50.6, 50.5, 40.7, 35.3, 33.7, 33.0, 32.1, 27.2 (3C), 26.7, 26.3, 26.2. HRMS ESI $[M+H]^+$ calculated for ($C_{26}H_{36}ON$) 378.2791, found 378.2786.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-*N*-phenethylpropanamide (5e): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 15:100:2), the product (23.1 mg) was obtained in 56% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.47 – 7.43 (m, 2H), 7.38 – 7.34 (m, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.23 – 7.15 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 2H), 5.46 (t, *J* = 6.0 Hz, 1H), 3.54 – 2.40 (m, 3H), 2.73 (t, *J* = 6.8 Hz, 2H), 2.07 (dt, *J* = 14.2, 7.3 Hz, 1H), 1.78 – 1.59 (m, 6H), 1.22 – 1.09 (m, 4H), 1.00 – 0.86 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.8, 140.8, 140.1, 139.5, 139.0, 128.9 (2C), 128.9 (2C), 128.7 (2C), 128.5 (2C), 127.6 (2C), 127.4, 127.1 (2C), 126.5, 50.3, 40.8, 40.6, 35.7, 35.2, 33.7, 32.9, 26.7, 26.3, 26.2. HRMS ESI $[M+H]^+$ calculated for ($C_{29}H_{33}ON$) 412.2635, found 412.2630.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-*N*-(2-methylallyl)propenamide (5f): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 10:100:2), the product (20.1 mg) was obtained in 56% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.47 – 7.41 (m, 2H), 7.41 – 7.37 (m, 2H), 7.37 – 7.31 (m, 1H), 5.61 (t, *J* = 6.1 Hz, 1H), 4.77 – 4.72 (m, 1H), 4.68 – 4.64 (m, 1H), 3.84 – 3.69 (m, 2H), 3.57 (t, *J* = 7.7 Hz, 1H), 2.11 (dt, *J* = 13.7, 7.7 Hz, 1H), 1.84 – 1.54 (m, 9H), 1.27 – 1.05 (m, 4H), 1.01 – 0.86 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 142.2, 140.7, 140.1, 139.5, 128.9 (2C), 128.5 (2C), 127.6 (2C), 127.4, 127.1 (2C), 110.7, 50.3, 45.1, 40.8, 35.2, 33.7, 33.0, 26.7, 26.3, 26.2, 20.4. HRMS ESI $[M+H]^+$ calculated for ($C_{25}H_{31}ON$) 362.2478, found 362.2473.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-*N*-(prop-2-yn-1-yl)propenamide (5g): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 15:100:2), the product (18.2 mg) was obtained in 53% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.47 – 7.40 (m, 2H), 7.39 – 7.30 (m, 3H), 5.68 (t, *J* = 5.3 Hz, 1H), 4.13 – 3.88 (m, 2H), 3.54 (dd, *J* = 8.3, 7.1 Hz, 1H), 2.18 (t, *J* = 2.5 Hz, 1H), 2.13 – 2.00 (m, 1H), 1.82 – 1.57 (m, 7H), 1.23 – 1.08 (m, 4H), 1.01 – 0.86 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 140.7, 140.3, 139.0, 128.9 (2C), 128.5 (2C), 127.7 (2C), 127.5, 127.1 (2C), 79.6, 71.7, 50.0, 40.8, 35.1, 33.8, 32.9, 29.5, 26.6, 26.3, 26.2. HRMS ESI $[M+H]^+$ calculated for ($C_{24}H_{27}ON$) 346.2165, found 346.2159.

2-([1,1'-biphenyl]-4-yl)-3-cyclohexyl-*N*-(2,2,2-trifluoroethyl)propenamide (5h): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 8:100:2), the product (28.1 mg) was obtained in 72% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 4H), 7.47 – 7.41 (m, 2H), 7.40 – 7.30 (m, 3H), 5.81 (t, *J* = 6.6 Hz, 1H), 4.05 – 3.90 (m, 1H), 3.83 – 3.68 (m, 1H), 3.61 (t, *J*

= 7.7 Hz, 1H), 2.08 (dt, *J* = 13.8, 7.7 Hz, 1H), 1.81 – 1.57 (m, 6H), 1.24 – 1.09 (m, 4H), 1.03 – 0.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 140.6, 138.6, 129.0 (2C), 128.5 (2C), 127.8 (2C), 127.5, 127.1 (2C), 124.2 (q, $^{1}J_{C\text{-}F}$ = 279.7 Hz) , 50.0, 40.8, 40.8 (q, $^{2}J_{C\text{-}F}$ = 34.8 Hz), 35.1, 33.7, 32.9, 26.6, 26.24, 26.17; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.53 (t, *J* = 9.1 Hz, 3F). HRMS ESI $[M+H]^+$ calculated for ($C_{23}H_{27}ONF_3$) 390.2039, found 390.2032.

2-([1,1'-biphenyl]-4-yl)-*N*-(2-cyanoethyl)-3-cyclohexylpropanamide (5i): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 25:100:2), the product (24.0 mg) was obtained in 67% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.47 – 7.40 (m, 2H), 7.40 – 7.29 (m, 3H), 6.07 (t, *J* = 6.2 Hz, 1H), 3.57 (t, *J* = 7.7 Hz, 1H), 3.53 – 3.43 (m, 1H), 3.43 – 3.34 (m, 1H), 2.68 – 2.49 (m, 2H), 2.05 (dt, *J* = 14.3, 7.7 Hz, 1H), 1.86 – 1.64 (m, 5H), 1.64 – 1.55 (m, 1H), 1.24 – 1.04 (m, 4H), 1.01 – 0.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 140.6, 140.4, 138.8, 128.9 (2C), 128.5 (2C), 127.7 (2C), 127.5, 127.1 (2C), 118.2, 50.0, 40.7, 35.9, 35.2, 33.72, 32.9, 26.6, 26.23, 26.15, 18.4. HRMS ESI $[M+H]^+$ calculated for ($C_{24}H_{29}ON_2$) 361.2274, found 361.2267.

2-([1,1'-biphenyl]-4-yl)-3-cyclohexyl-*N*-(2-hydroxyethyl)propenamide (5j): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 25:100:2), the product (25.2 mg) was obtained in 72% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 4H), 7.46 – 7.40 (m, 2H), 7.39 – 7.30 (m, 3H), 6.14 (t, *J* = 5.7 Hz, 1H), 3.64 (t, *J* = 5.0 Hz, 2H), 3.56 (t, *J* = 7.7 Hz, 1H), 3.44 – 3.27 (m, 2H), 2.51 (br s, 1H), 2.04 (dt, *J* = 14.4, 7.7 Hz, 1H), 1.82 – 1.63 (m, 5H), 1.63 – 1.54 (m, 1H), 1.21 – 1.08 (m, 4H), 1.00 – 0.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 140.7, 140.2, 139.3, 128.9 (2C), 128.5 (2C), 127.6 (2C), 127.4, 127.1 (2C), 62.5, 50.1, 42.8, 40.9, 35.2, 33.8, 32.9, 26.6, 26.3, 26.2. HRMS ESI $[M+H]^+$ calculated for ($C_{23}H_{30}O_2N$) 352.2271, found 352.2266.

***N*,*N*'-(Ethane-1,2-diyl)bis(2-([1,1'-biphenyl]-4-yl)-3-cyclohexylpropanamide) (5k)**: Following the general procedure **D**, purification by flash column chromatography (DCM:MeOH:Et_3N = 50:1:1), the product (24.5 mg) was obtained in 75% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.46 (m, 8H), 7.46 – 7.36 (m, 4H), 7.36 – 7.24 (m, 6H), 6.32 – 6.19 (m, 2H), 3.47 (q, *J* = 7.4 Hz, 2H), 3.33 – 3.15 (m, 4H), 1.97 (dq, *J* = 14.8, 7.6 Hz, 2H), 1.80 – 1.54 (m, 14H), 1.19 – 1.02 (m, 8H), 0.99 – 0.81 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3 (2C), 140.7, 140.7, 140.11, 140.08, 139.3, 139.3, 128.91 (2C), 128.90 (2C), 128.49 (2C), 128.47 (2C), 127.58 (2C), 127.57 (2C), 127.43, 127.41, 127.09 (2C), 127.08 (2C), 50.1 (2C), 40.8, 40.6, 40.4, 40.3, 35.2, 35.1, 33.82, 33.81, 32.9, 32.8, 26.63, 26.61, 26.3 (2C), 26.18, 26.15. HRMS ESI $[M+H]^+$ calculated for ($C_{44}H_{53}O_2N_2$) 641.4102, found 641.4096.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-*N*,*N*-dimethylpropanamide (5l): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 12:100:1), the product (16.7 mg) was obtained in 50% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.55 – 7.50 (m, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.30 (m, 3H), 3.92 (dd, *J* = 8.1, 6.6 Hz, 1H), 3.00 (s, 3H), 2.96 (s, 3H), 2.06 (ddd, *J* = 13.7, 8.2, 6.6 Hz, 1H), 1.86 – 1.75 (m, 1H), 1.73 – 1.54 (m, 5H), 1.28 – 1.09 (m, 4H), 1.00 – 0.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 140.9, 139.8, 139.7, 128.9 (2C), 128.4 (2C), 127.5 (2C), 127.3, 127.1 (2C), 45.3 (2C), 42.9, 37.4, 36.1, 35.3, 33.5, 26.7, 26.31, 26.26. HRMS ESI $[M+H]^+$ calculated for ($C_{23}H_{30}ON$) 336.2322, found 336.2315.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-1-(piperidin-1-yl)propan-1-one (5m): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 10:100:1), the product (29.2 mg) was obtained in 78% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.56 – 7.50 (m, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.29 (m, 3H), 3.94 (dd, *J* = 8.1, 6.6 Hz, 1H), 3.72 – 3.60 (m, 1H), 3.54 – 3.35 (m, 3H), 2.08 (ddd, *J* = 14.2, 8.1, 6.6 Hz, 1H), 1.92 – 1.76 (m, 1H), 1.74 – 1.34 (m, 10H), 1.32 – 1.03 (m, 2H), 0.99 – 0.86 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 140.8, 140.3, 139.5, 128.8 (2C), 128.3 (2C), 127.4 (2C), 127.3, 127.1 (2C), 46.8, 44.9 (2C), 43.3, 42.8, 35.3, 33.5 (2C), 26.7, 26.30, 26.25, 25.7, 24.7. HRMS ESI $[M+H]^+$ calculated for ($C_{26}H_{34}ON$) 376.2635, found 376.2628.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-1-morpholinopropan-1-one (5n): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 10:100:1), the product (31.3 mg) was obtained in 83% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.35 – 7.29 (m, 3H), 3.88 (t, *J* = 7.3 Hz, 1H), 3.79 – 3.72 (m, 1H), 3.69 – 3.62 (m, 1H), 3.57 – 3.48 (m, 4H), 3.47 – 3.40 (m, 1H), 3.23 – 3.17 (m, 1H), 2.08 (dt, *J* = 14.2, 7.3 Hz, 1H), 1.85 – 1.78 (m, 1H), 1.72 – 1.65 (m, 3H), 1.65 – 1.58 (m, 2H), 1.30 – 1.10 (m, 4H), 0.99 – 0.88 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 140.6, 139.8, 139.6, 128.8 (2C), 128.2 (2C), 127.6 (2C), 127.4, 127.0 (2C), 66.9, 66.5, 46.2, 45.0, 42.6, 42.5, 35.2, 33.49, 33.47, 26.6, 26.24, 26.20. HRMS ESI $[M+H]^+$ calculated for ($C_{25}H_{32}O_2N$) 378.2428, found 378.2420.

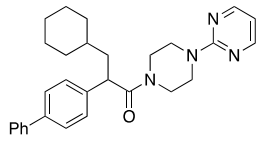
2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-1-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)propan-1-one (5o): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 15:100:1), the product (38.7 mg) was obtained in 90% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.55 – 7.50 (m, 2H), 7.44 – 7.38 (m, 2H), 7.35 – 7.28 (m, 3H), 3.97 – 3.38 (m, 6H), 3.62 – 3.48 (m, 3H), 2.12 – 2.02 (m, 1H), 1.90 – 1.74 (m, 1H), 1.72 – 1.44 (m, 8H), 1.29 – 1.07 (m, 5H), 0.98 – 0.84 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 140.7, 140.0, 139.7, 128.8 (2C), 128.2 (2C), 127.5 (2C), 127.3, 127.1 (2C), 107.1, 64.5 (2C), 45.1, 43.6, 42.7, 40.3, 35.3, 35.2, 34.8, 33.53, 33.51, 26.7, 26.3, 26.2. HRMS ESI $[M+H]^+$ calculated for ($C_{28}H_{36}ON$) 434.2690, found 434.2681.

Ethyl 1-(2-([1,1'-biphenyl]-4-yl)-3-cyclohexylpropanoyl)piperidine-4-carboxylate (5p): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 10:100:1), the product (35.7 mg) was obtained in 80% yield as white solid, d.r. = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.55 – 7.48 (m, 2H), 7.45 – 7.37 (m, 2H), 7.36 – 7.27 (m, 3H), 4.43 (dd, *J* = 58.5, 13.5 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 1H), 3.98 – 3.85 (m, 2H), 3.16 – 2.92 (m, 1H), 2.92 – 2.74 (m, 1H), 2.50 – 2.37 (m, 1H), 2.13 – 2.00 (m, 1H), 1.94 – 1.73 (m, 3H), 1.73 – 1.43 (m, 7H), 1.32 – 1.07 (m, 7H), 1.04 – 0.82 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 171.7, 140.8, 140.0, 139.7, 128.8 (2C), 128.3 (2C), 127.6 (2C), 127.3, 127.1 (2C), 60.7, 45.2, 45.0, 42.7, 41.6, 41.2, 35.3, 33.5, 28.5, 28.1, 27.7, 26.7, 26.3, 26.2, 14.3; the other isomer: ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 171.6, 140.8, 139.9, 139.7, 128.8 (2C), 128.2 (2C), 127.5 (2C), 127.3, 127.1 (2C), 60.6, 45.0, 44.9, 42.7, 41.5, 40.9, 35.2, 33.5, 28.5, 28.1, 27.7, 26.7, 26.3, 26.2, 14.2. HRMS ESI $[M+H]^+$ calculated for ($C_{29}H_{38}O_3N$) 448.2846, found 448.2838.

1-(2-([1,1'-Biphenyl]-4-yl)-3-cyclohexylpropanoyl)piperidine-4-carboxylic acid (5q): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane = 25:100), the product (26.8 mg) was obtained in 64% yield as white solid, d.r. = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.36 – 7.28 (m, 3H), 4.54 – 4.26 (m, 1H), 3.98 – 3.85 (m, 2H), 3.18 – 2.96 (m, 1H), 2.96 – 2.76 (m, 1H), 2.54 – 2.40 (m, 1H), 2.10 – 1.99 (m, 1H), 1.95 – 1.85 (m, 1H), 1.84 – 1.75 (m, 1H), 1.74 – 1.40 (m, 8H), 1.29 – 1.08 (m, 4H), 1.03 – 0.83 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.5, 171.9, 140.8, 139.9, 139.7, 128.9 (2C), 128.3 (2C), 127.6 (2C), 127.4, 127.1 (2C), 45.2, 45.0, 42.7, 41.6, 40.8, 35.3, 33.6, 33.5, 28.2, 27.9, 26.7, 26.3, 26.2; the other isomer: ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.4, 171.8, 140.8, 139.9, 139.7, 128.9 (2C), 128.2 (2C), 127.6 (2C), 127.4, 127.1 (2C), 45.0, 44.8, 42.7, 41.5, 40.6, 35.2, 33.54, 33.47, 27.8, 27.5, 26.7, 26.3, 26.2. HRMS ESI $[M+H]^+$ calculated for ($C_{27}H_{34}O_3N$) 420.2533, found 420.2525.

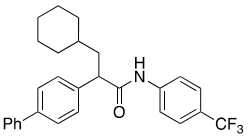
2-([1,1'-Biphenyl]-4-yl)-1-(azepan-1-yl)-3-cyclohexylpropan-1-one (5r): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 10:100:1), the product (29.0 mg) was obtained in 75% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.56 – 7.50 (m, 2H), 7.46 – 7.35 (m, 4H), 7.35 – 7.29 (m, 1H), 3.91 (dd, *J* = 8.1, 6.6 Hz, 1H), 3.73 – 3.64 (m, 1H), 3.63 – 3.55 (m, 1H), 3.41 – 3.27 (m, 2H), 2.06 (ddd, *J* = 14.2, 8.1, 6.6 Hz, 1H), 1.89 – 1.78 (m, 1H), 1.76 – 1.45 (m, 12H), 1.42 – 1.31 (m, 1H), 1.27 – 1.10 (m, 4H), 1.00 – 0.86 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 140.9, 140.3, 139.6, 128.8 (2C), 128.5 (2C), 127.4 (2C), 127.3, 127.1 (2C), 47.9, 46.6, 45.4, 43.2, 35.5, 33.63, 33.58, 29.4, 27.7, 27.1, 26.7, 26.6, 26.33, 26.28. HRMS ESI $[M+H]^+$ calculated for ($C_{27}H_{36}ON$) 390.2791, found 390.2784.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-1-(4-(pyrimidin-2-yl)piperazin-1-yl)propan-1-one (5s):



Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 10:100:1), the product (24.9 mg) was obtained in 55% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 4.8 Hz, 2H), 7.61 – 7.51 (m, 4H), 7.46 – 7.38 (m, 2H), 7.38 – 7.29 (m, 3H), 6.49 (t, *J* = 4.8 Hz, 1H), 3.99 – 3.79 (m, 4H), 3.63 – 3.50 (m, 4H), 3.28 – 3.17 (m, 1H), 2.10 (ddd, *J* = 14.3, 7.9, 6.7 Hz, 1H), 1.88 – 1.78 (m, 1H), 1.74 – 1.57 (m, 5H), 1.32 – 1.07 (m, 4H), 1.00 – 0.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 161.5, 157.8 (2C), 140.7, 139.8, 128.9 (2C), 128.3 (2C), 127.6 (2C), 127.4, 127.1 (2C), 110.4, 45.5, 45.3, 43.7 (2C), 42.7, 42.0, 35.3, 33.6, 33.5, 26.7, 26.3, 26.2. HRMS ESI $[M+H]^+$ calculated for ($C_{29}H_{35}ON_4$) 455.2805, found 455.2803.

2-([1,1'-biphenyl]-4-yl)-*N*-(4-(*tert*-butyl)phenyl)-3-cyclohexylpropanamide (5t): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 4:100:1), the product (32.9 mg) was obtained in 75% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 4H), 7.42 – 7.38 (m, 4H), 7.37 – 7.34 (m, 2H), 7.33 – 7.29 (m, 1H), 7.27 – 7.21 (m, 2H), 3.66 (t, *J* = 7.6 Hz, 1H), 2.14 (dt, *J* = 14.3, 7.6 Hz, 1H), 1.81 – 1.68 (m, 3H), 1.68 – 1.60 (m, 2H), 1.60 – 1.54 (m, 1H), 1.26 – 1.20 (m, 10H), 1.16 – 1.08 (m, 3H), 0.99 – 0.87 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 147.3, 140.7, 140.3, 139.2, 135.5, 128.9 (2C), 128.5 (2C), 127.8 (2C), 127.5, 127.1 (2C), 125.8 (2C), 119.7 (2C), 51.4, 41.0, 35.3, 34.4, 33.7, 33.0, 31.5 (3C), 26.6, 26.3, 26.2. HRMS ESI $[M+H]^+$ calculated for ($C_{31}H_{38}ON$) 440.2948, found 440.2940.



2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-*N*-(4-(trifluoromethyl)phenyl)propenamide (5u): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 4:100:1), the product (23.1 mg) was obtained in 51% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 6H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.39 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29 (br s, 1H), 3.70 (t, *J* = 7.6 Hz, 1H), 2.16 (dt, *J* = 14.4, 7.4 Hz, 1H), 1.84 – 1.76 (m, 2H), 1.76 – 1.65 (m, 3H), 1.64 – 1.60 (m, 1H), 1.30 – 1.09 (m, 4H), 1.05 – 0.86 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 141.1, 140.7, 140.5, 138.6, 129.0 (2C), 128.5 (2C), 128.0 (2C), 127.6, 127.2 (2C), 126.3 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, 2C), 124.2 (q, $^1J_{C\text{-}F}$ = 271.6 Hz), 119.4, 51.3, 40.8, 35.2, 33.8, 32.9, 26.6, 26.3, 26.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.12 (s, 3F). HRMS ESI $[M+H]^+$ calculated for ($C_{28}H_{29}ONF_3$) 452.2196, found 452.2188.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-*N*-(2,4-dimethylphenyl)propenamide (5v): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 5:100:1), the product (27.2 mg) was obtained in 66% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 5H), 7.48 – 7.41 (m, 4H), 7.39 – 7.34 (m, 1H), 7.00 – 6.88 (m, 3H), 3.75 (t, *J* = 7.8 Hz, 1H), 2.26 (s, 3H), 2.20 (dt, *J* = 14.5, 7.8 Hz, 1H), 1.95 (s, 3H), 1.87 – 1.79 (m, 2H), 1.78 – 1.74 (m, 1H), 1.73 – 1.67 (m, 2H), 1.66 – 1.60 (m, 1H), 1.35 – 1.25 (m, 1H), 1.23 – 1.13 (m, 3H), 1.05 – 0.93 (m, 2H); ^{13}C NMR (151

MHz, $CDCl_3$) δ 172.1, 140.7, 140.4, 139.3, 134.8, 133.2, 131.1, 129.0, 129.0 (2C), 128.7 (2C), 127.8 (2C), 127.5, 127.3, 127.1 (2C), 123.0, 51.0, 40.4, 35.3, 33.9, 32.9, 26.7, 26.3, 26.2, 20.9, 17.4. HRMS ESI $[M+H]^+$ calculated for ($C_{29}H_{34}ON$) 412.2635, found 412.2628.

2-([1,1'-Biphenyl]-4-yl)-*N*-butyl-4-(2-(trimethylsilyl)ethoxy)butanamide (5w): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 10:100:1), the product (19.7 mg) was obtained in 48% yield as colourless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.53 (m, 2H), 7.45 – 7.41 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.32 (m, 1H), 5.57 (br s, 1H), 3.64 – 3.59 (m, 1H), 3.46 (t, *J* = 8.0 Hz, 2H), 3.43 – 3.39 (m, 1H), 3.34 – 3.29 (m, 1H), 3.28 – 3.23 (m, 1H), 3.20 – 3.14 (m, 1H), 2.46 – 2.39 (m, 1H), 2.06 – 1.99 (m, 1H), 1.46 – 1.39 (m, 2H), 1.31 – 1.23 (m, 2H), 0.93 (t, *J* = 8.0 Hz, 2H), 0.88 (t, *J* = 7.4Hz, 3H), 0.02 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.3, 140.8, 140.2, 139.2, 128.9 (2C), 128.6 (2C), 127.5 (2C), 127.4, 127.1 (2C), 68.1, 67.7, 49.4, 39.5, 33.6, 31.8, 20.1, 18.4, 13.8, -1.2 (3C). HRMS ESI $[M+H]^+$ calculated for ($C_{25}H_{37}O_2NSi$) 412.2666, found 412.2658.

***N*-butyl-2-(dibenzo[*b*,*d*]furan-4-yl)-4,4-dimethyl-6-oxoheptanamide (5x)**: Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 10:100:1), the product (25.2 mg) was obtained in 64% yield as colourless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 (ddd, *J* = 7.7, 1.3, 0.6 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.50 – 7.45 (m, 2H), 7.38 – 7.33 (m, 1H), 7.33 – 7.30 (m, 1H), 5.86 (t, *J* = 5.8 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 1H), 3.22 – 3.16 (m, 1H), 3.16 – 3.07 (m, 1H), 2.57 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.44 – 2.29 (m, 2H), 2.03 – 1.98 (m, 4H), 1.40 – 1.29 (m, 2H), 1.20 – 1.14 (m, 2H), 1.03 (s, 3H), 1.01 (s, 3H), 0.78 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.9, 173.0, 156.0, 153.7, 127.4, 126.3, 125.7, 124.6, 124.2, 123.6, 123.1, 121.0, 119.3, 111.8, 53.8, 43.7, 42.5, 39.6, 34.1, 32.4, 31.5, 27.6, 27.5, 20.0, 13.7. HRMS ESI $[M+H]^+$ calculated for ($C_{25}H_{31}O_3N$) 394.2377, found 394.2374.

2-([1,1'-Biphenyl]-4-yl)-3-cycloheptyl-1-morpholinopropan-1-one (5y): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 10:100:1), the product (28.9 mg) was obtained in 74% yield as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 4H), 7.46 – 7.39 (m, 2H), 7.36 – 7.28 (m, 3H), 3.84 (t, *J* = 7.3 Hz, 1H), 3.79 – 3.71 (m, 1H), 3.70 – 3.61 (m, 1H), 3.60 – 3.47 (m, 4H), 3.46 – 3.38 (m, 1H), 3.26 – 3.15 (m, 1H), 2.09 (dt, *J* = 14.1, 7.3 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.72 – 1.59 (m, 3H), 1.59 – 1.46 (m, 4H), 1.46 – 1.31 (m, 4H), 1.29 – 1.16 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 140.7, 139.8, 139.6, 128.9 (2C), 128.3 (2C), 127.6 (2C), 127.4, 127.1 (2C), 67.0, 66.6, 46.2, 45.7, 43.0, 42.6, 36.6, 34.7, 34.6, 28.70, 28.69, 26.33, 26.27. HRMS ESI $[M+H]^+$ calculated for ($C_{26}H_{34}O_2N$) 392.2584, found 392.2582.

2-([1,1'-Biphenyl]-4-yl)-4,4-dimethyl-1-morpholinopentan-1-one (5z): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 10:100:1), the product (28.1 mg) was obtained in 80% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.55 – 7.50 (m, 2H), 7.46 – 7.39 (m, 2H), 7.36 – 7.30 (m, 3H), 3.86 (dd, *J* = 8.6, 3.2 Hz, 1H), 3.76 – 3.69 (m, 1H), 3.68 – 3.57 (m, 3H), 3.57 – 3.48 (m, 3H), 3.37 – 3.26 (m, 1H), 2.58 (dd, *J* = 14.0, 8.6 Hz, 1H), 1.52 (dd, *J* = 14.0, 3.2 Hz, 1H), 0.92 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 140.9, 140.7, 139.7, 128.9 (2C), 128.1 (2C), 127.7 (2C), 127.4, 127.1 (2C), 66.9, 66.6, 48.1, 46.3, 44.0, 42.7, 31.2, 29.8 (3C). HRMS ESI $[M+H]^+$ calculated for ($C_{23}H_{30}O_2N$) 352.2271, found 352.2269.

2-([1,1'-Biphenyl]-4-yl)-4,4,5-trimethyl-1-morpholinohexan-1-one (5aa): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 10:100:1), the product (32.8 mg) was obtained in 87% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.30 (m, 3H), 3.87 (dd, *J* = 8.5, 3.0 Hz, 1H), 3.76 – 3.68 (m, 1H), 3.68 – 3.47 (m, 6H), 3.34 – 3.25 (m, 1H), 2.60 (dd, *J* = 14.1, 8.5 Hz, 1H), 1.58 – 1.44 (m, 2H), 0.90 – 0.82 (m, 9H), 0.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 141.1, 140.7, 139.7, 128.9 (2C), 128.1 (2C), 127.6 (2C), 127.4, 127.1 (2C), 66.9, 66.6, 46.3, 43.9, 43.2, 42.8, 36.7, 35.9, 24.8, 23.9, 17.7, 17.6. HRMS ESI $[M+H]^+$ calculated for ($C_{25}H_{34}O_2N$) 380.2584, found 380.2582.

3-Cyclohexyl-2-(4-ethynylphenyl)-1-morpholinopropan-1-one (5ab): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 5:100:1), the desilylation product (13.9 mg) was obtained in 43% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 3.82 (t, *J* = 7.3 Hz, 1H), 3.78 – 3.70 (m, 1H), 3.69 – 3.59 (m, 1H), 3.57 – 3.30 (m, 5H), 3.20 – 3.11 (m, 1H), 3.06 (s, 1H), 2.01 (dt, *J* = 14.3, 7.3 Hz, 1H), 1.81 – 1.72 (m, 1H), 1.70 – 1.59 (m, 4H), 1.58 – 1.50 (m, 1H), 1.23 – 1.06 (m, 4H), 0.96 – 0.82 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 141.5, 132.8 (2C), 127.9 (2C), 12`0.8, 83.4, 77.5, 66.9, 66.5, 46.2, 45.3, 42.6, 42.5, 35.2, 33.5, 33.4, 26.6, 26.3, 26.2. HRMS ESI $[M+H]^+$ calculated for ($C_{21}H_{28}O_2N$) 326.2115, found 326.2112.

***N*-butyl-3-cyclohexyl-2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)propenamide (5ac)**: Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 15:100:1), the product (31.2 mg) was obtained in 67% yield as colourless oil, d.r. = 1:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 1H), 7.07 – 7.02 (m, 1H), 7.01 (d, *J* = 4.3 Hz, 1H), 5.43 (t, *J* = 5.9 Hz, 1H), 3.38 (t, *J* = 7.7 Hz, 1H), 3.22 (dq, *J* = 13.6, 6.9 Hz, 1H), 3.12 (dp, *J* = 15.1, 8.0, 7.4 Hz, 1H), 2.89 (dd, *J* = 9.5, 4.1 Hz, 2H), 2.50 (dd, *J* = 19.0, 8.8 Hz, 1H), 2.40 (dd, *J* = 12.9, 4.2 Hz, 1H), 2.28 (td, *J* = 11.1, 3.9 Hz, 1H), 2.14 (dt, *J* = 18.5, 8.9 Hz, 1H), 2.09 – 2.04 (m, 0H), 2.04 (s, 1H), 1.96 (d, *J* = 11.9 Hz, 1H), 1.84 (s, 1H), 1.74 (d, *J* = 12.9 Hz, 1H), 1.69 (d, *J* = 13.4 Hz, 0H), 1.67 – 1.63 (m, 1H), 1.59 (dt, *J* = 14.1, 7.8

Hz, 2H), 1.51 (qd, *J* = 13.3, 5.7 Hz, 3H), 1.47 – 1.43 (m, 1H), 1.40 (p, *J* = 7.1 Hz, 3H), 1.25 (h, *J* = 7.5 Hz, 3H), 1.19 – 1.09 (m, 4H), 0.93 (t, *J* = 6.5 Hz, 1H), 0.91 (s, 4H), 0.87 (t, *J* = 7.4 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.0, 173.9, 138.6, 138.2, 137.0, 128.5, 125.8, 125.4, 50.7, 50.1, 48.1, 46.0, 44.5, 41.0, 39.4, 38.2, 36.0, 35.3, 33.6, 33.1, 31.7, 29.5, 26.7, 26.6, 26.3, 25.8, 21.7, 20.1, 14.0, 13.9, 8.8. HRMS ESI $[M+H]^+$ calculated for ($C_{31}H_{46}O_2N$) 464.3523, found 464.3521.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexyl-N-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)propanamide (5ad): Following the general procedure **D**, using MeCN : DCE (3:1, 1.5 mL) as solvent, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 12:100:1), the product (36.5 mg) was obtained in 62% yield as colourless oil, d.r. = 1:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.32 (q, *J* = 7.5 Hz, 2H), 7.26 (q, *J* = 9.7, 8.9 Hz, 2H), 7.04 (dd, *J* = 30.6, 8.1 Hz, 1H), 6.90 (dd, *J* = 21.5, 8.3 Hz, 1H), 6.83 (d, *J* = 7.3 Hz, 1H), 5.42 (dt, *J* = 13.8, 6.7 Hz, 1H), 3.49 (dt, *J* = 14.5, 7.9 Hz, 1H), 3.27 (td, *J* = 14.9, 6.7 Hz, 1H), 2.92 – 2.62 (m, 4H), 2.16 (dd, *J* = 30.6, 12.8 Hz, 1H), 2.10 – 2.02 (m, 1H), 1.86 – 1.77 (m, 1H), 1.76 – 1.59 (m, 7H), 1.59 – 1.46 (m, 3H), 1.26 – 1.15 (m, 10H), 1.13 (d, *J* = 11.8 Hz, 3H), 1.11 – 0.95 (m, 6H), 0.92 – 0.86 (m, 2H), 0.83 (d, *J* = 10.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.7, 147.2, 145.6, 140.8, 140.2, 139.8, 134.9, 128.8 (2C), 128.3 (2C), 127.6 (2C), 127.4, 127.2 (2C), 127.0, 124.3, 123.8, 50.6, 49.7, 44.9, 40.6, 38.5, 37.5, 36.2, 35.3, 33.7, 33.5, 33.1, 30.4, 26.7, 26.2, 26.1, 25.4, 24.2, 24.1 (2C), 19.1, 19.0, 18.7. HRMS ESI $[M+H]^+$ calculated for ($C_{41}H_{54}ON$) 576.4200, found 576.4192.

2-([1,1'-Biphenyl]-4-yl)-3-cyclohexylpropanamide (5ae): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 30:70:1), the product (21.3 mg) was obtained in 70% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 10.5, 7.8 Hz, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 5.71 (s, 1H), 5.49 (s, 1H), 3.59 (t, *J* = 7.7 Hz, 1H), 2.05 (dt, *J* = 14.4, 7.4 Hz, 1H), 1.82 – 1.59 (m, 6H), 1.25 – 1.10 (m, 4H), 1.00 – 0.87 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 140.7, 140.3, 139.3, 128.9 (2C), 128.5 (2C), 127.7 (2C), 127.5, 127.1 (2C), 49.6, 40.6, 35.1, 33.8, 32.9, 26.6, 26.3, 26.2. HRMS ESI $[M+H]^+$ calculated for ($C_{21}H_{26}ON$) 308.2009, found 308.2005.

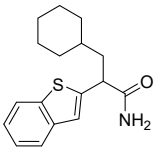
2-([1,1'-Biphenyl]-4-yl)-3-(adamantan-1-yl)propanamide (5af): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 30:70:1), the product (21.3 mg) was obtained in 73% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.46 – 7.41 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.31 (m, 1H), 5.52 (br s, 2H), 3.59 (dd, *J* = 7.3, 5.1 Hz, 1H), 2.26 (dd, *J* = 14.2, 7.3 Hz, 1H), 1.93 (q, *J* = 3.6 Hz, 4H), 1.68 (d, *J* = 12.4 Hz, 3H), 1.60 (d, *J* = 12.4 Hz, 3H), 1.56 – 1.43 (m, 7H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 141.3, 140.7, 140.1, 128.9 (2C), 128.3 (2C), 127.7 (2C), 127.4, 127.1 (2C), 47.4, 47.2, 42.6 (2C), 37.1 (2C), 33.1, 28.7 (2C). HRMS ESI $[M+H]^+$ calculated for ($C_{25}H_{30}ON$) 360.2322, found 360.2319.

2-([1,1'-Biphenyl]-4-yl)-4-((3-methylbut-3-en-1-yl)oxy)butanamide (5ag): Following the general procedure **D**, purification by flash column chromatography (EtOAc:Hexane:Et_3N = 30:70:1), the product (16.0 mg) was obtained in 53% yield as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 4H), 7.46 – 7.41 (m, 2H), 7.41 – 7.37 (m, 2H), 7.37 – 7.31 (m, 1H), 5.66 (br s, 2H), 4.82 – 4.78 (m, 1H), 4.78 – 4.67 (m, 1H), 3.72 (t, *J* = 7.5 Hz, 1H), 3.55 – 3.44 (m, 3H), 3.39 – 3.30 (m, 1H), 2.48 – 2.38 (m, 1H), 2.29 (t, *J* = 6.8 Hz, 2H), 2.13 – 1.89 (m, 1H), 1.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 143.1, 140.7, 140.4, 138.7, 128.9 (2C), 128.6 (2C), 127.6 (2C), 127.5, 127.1 (2C), 111.6, 69.3, 68.1, 48.6, 37.9, 33.2, 22.9. HRMS ESI $[M+H]^+$ calculated for ($C_{21}H_{26}O_2N$) 324.1958, found 324.1956.

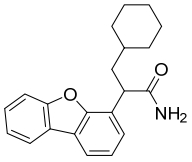
2-([1,1'-Biphenyl]-4-yl)-4,4-dimethyl-6-oxoheptanamide (5ah): Following the general procedure **D**, purification by flash column chromatography (EtOAc : Hexane : Et_3N = 30:70:1), the product (24.2 mg) was obtained in 75% yield as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 4H), 7.45 – 7.40 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.31 (m, 1H), 5.79 (br s, 1H), 5.72 (br s, 1H), 3.59 (t, *J* = 6.4 Hz, 1H), 2.41 (dd, *J* = 14.3, 6.0 Hz, 1H), 2.40 – 2.27 (m, 2H), 2.03 (s, 3H), 1.90 (dd, *J* = 14.3, 6.0 Hz, 1H), 1.01 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1, 176.5, 140.7, 140.4, 140.3 128.9 (2C), 128.5 (2C), 127.7 (2C), 127.5, 127.1 (2C), 53.8, 48.7, 44.4, 34.1, 32.4, 27.9, 27.8. HRMS ESI $[M+H]^+$ calculated for ($C_{21}H_{26}O_2N$) 324.1958, found 324.1956.

3-Cyclohexyl-2-(naphthalen-2-yl)propanamide (5ai): Following the general procedure **D**, purification by flash column chromatography (EtOAc : Hexane : Et_3N = 30:70:1), the product (19.4 mg) was obtained in 69% yield as white solid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 3H), 7.74 (s, 1H), 7.51 – 7.45 (m, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 5.64 (br s, 1H), 5.46 (br s, 1H), 3.71 (t, *J* = 7.7 Hz, 1H), 2.09 (dt, *J* = 14.4, 7.7 Hz, 1H), 1.85 – 1.77 (m, 2H), 1.70 – 1.62 (m, 3H), 1.61 – 1.56 (m, 1H), 1.21 – 1.05 (m, 4H), 1.00 – 0.87 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.4, 137.7, 133.6, 132.8, 128.9, 127.9, 127.8, 127.0, 126.4, 126.1, 126.0, 50.0, 40.4, 35.1, 33.9, 32.8, 26.6, 26.3, 26.2. HRMS ESI $[M+H]^+$ calculated for ($C_{19}H_{24}ON$) 282.1852, found 282.1849.

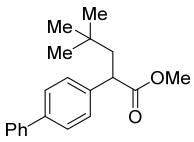
2-(4-(*Tert*-butyl)phenyl)-3-cyclopentylpropanamide (5aj): Following the general procedure **D**, purification by flash column chromatography (EtOAc : Hexane : Et_3N = 30:70:1), the product (17.1 mg) was obtained in 62% yield as white solid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.25 – 7.20 (m, 2H), 5.58 (br s, 1H), 5.39 (br s, 1H), 3.41 (t, *J* = 7.7 Hz, 1H), 2.11 (dt, *J* = 14.1, 7.7 Hz, 1H), 1.87 – 1.80 (m, 1H), 1.78 – 1.72 (m, 1H), 1.71 – 1.63 (m, 1H), 1.61 – 1.55 (m, 1H), 1.50 – 1.41 (m, 1H), 1.31 (s, 9H), 1.16 – 1.08 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 150.3, 137.1, 127.7 (2C), 125.9 (2C), 51.6, 39.3, 37.7, 34.6, 33.0, 32.3, 31.5 (3C), 25.3, 25.2. HRMS ESI $[M+H]^+$ calculated for ($C_{18}H_{28}ON$) 274.2165, found 274.2161.

2-(Benzo[b]thiophen-2-yl)-3-cyclohexylpropanamide (5ak): Following the general procedure **D**, 

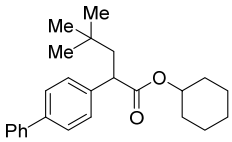
purification by flash column chromatography (EtOAc:Hexane:Et_3N = 30:70:1), the product (14.9 mg) was obtained in 52% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 1H), 7.71 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.19 (s, 1H), 5.83 (br s, 1H), 5.73 (br s, 1H), 3.92 (dd, *J* = 9.2, 6.3 Hz, 1H), 2.10 – 2.01 (m, 1H), 1.88 – 1.77 (m, 2H), 1.75 – 1.56 (m, 4H), 1.33 – 1.22 (m, 1H), 1.22 – 1.06 (m, 3H), 1.03 – 0.86 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 143.8, 139.7, 139.6, 124.6, 124.4, 123.4, 122.4 (2C), 46.0, 41.3, 35.1, 33.7, 32.6, 26.6, 26.2, 26.1. HRMS ESI $[M+H]^+$ calculated for ($C_{17}H_{22}ONS$) 288.1417, found 288.1414.

3-Cyclohexyl-2-(dibenzo[*b*,*d*]furan-4-yl)propanamide (5al): Following the general procedure **D**, 

purification by flash column chromatography (EtOAc : Hexane : Et_3N = 30:70:1), the product (23.6 mg) was obtained in 73% yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.38 – 7.31 (m, 2H), 5.75 (d, *J* = 8.9 Hz, 2H), 4.28 (t, *J* = 7.7 Hz, 1H), 2.19 (dt, *J* = 14.4, 7.7 Hz, 1H), 1.91 (dt, *J* = 14.4, 7.2 Hz, 1H), 1.83 (d, *J* = 12.9 Hz, 1H), 1.75 (d, *J* = 12.9 Hz, 1H), 1.68 – 1.62 (m, 2H), 1.61 – 1.56 (m, 1H), 1.28 – 1.19 (m, 1H), 1.18 – 1.06 (m, 3H), 1.02 – 0.91 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 156.0, 154.2, 127.4, 126.0, 124.6, 124.3, 124.2, 123.6, 123.1, 120.9, 119.6, 111.9, 43.3, 38.9, 35.4, 33.7, 33.0, 26.6, 26.3, 26.2 HRMS ESI $[M+H]^+$ calculated for ($C_{21}H_{24}O_2N$) 322.1802, found 322.1797.

Methyl 2-([1,1'-biphenyl]-4-yl)-4,4-dimethylpentanoate (5am): Following the general procedure **D**, 

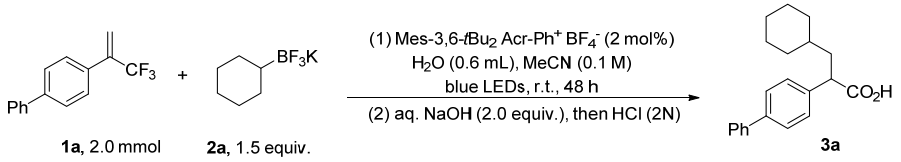
purification by flash column chromatography (EtOAc : Hexane = 5:95), the product (18.1 mg) was obtained in 61% yield as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.31 (m, 1H), 3.72 (dd, *J* = 9.3, 3.8 Hz, 1H), 3.67 (s, 3H), 2.36 (dd, *J* = 14.0, 9.3 Hz, 1H), 1.63 (dd, *J* = 14.0, 3.8 Hz, 1H), 0.93 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 140.9, 140.14, 140.08, 128.9 (2C), 128.3 (2C), 127.5 (2C), 127.4, 127.2 (2C), 52.2, 47.9, 47.6, 31.2, 29.5 (3C). HRMS ESI $[M+H]^+$ calculated for ($C_{20}H_{25}O_2$) 297.1849, found 297.1843.

Cyclohexyl 2-([1,1'-biphenyl]-4-yl)-4,4-dimethylpentanoate (5an): Following the general procedure 

D, purification by flash column chromatography (EtOAc : Hexane = 5:95), the product (21.2 mg) was obtained in 58% yield as colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.45 – 7.39 (m, 4H), 7.36 – 7.31 (m, 1H), 4.79 – 4.70 (m, 1H), 3.68 (d, *J* = 9.1 Hz, 1H), 2.37 (dd, *J* = 14.0, 9.1 Hz, 1H), 1.85 (dd, *J* = 14.0, 5.3 Hz, 1H), 1.75 – 1.69 (m, 2H), 1.68 – 1.57 (m, 2H), 1.55 – 1.48 (m, 1H), 1.48 – 1.40 (m, 1H), 1.39 – 1.24 (m, 4H), 0.95 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 141.0, 140.6, 139.9, 128.9 (2C), 128.3 (2C), 127.4 (2C), 127.3, 127.2 (2C), 73.0, 48.4, 47.4, 31.52, 31.45, 31.2, 29.6 (3C), 25.5, 23.82, 23.75. HRMS ESI $[M+H]^+$ calculated for ($C_{25}H_{33}O_2$) 365.2475, found 365.2475.

5. Synthetic Applications

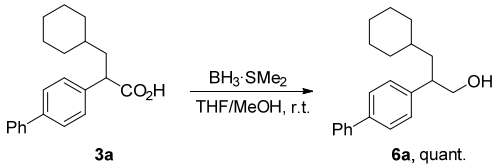
(1)



1a, 2.0 mmol **2a**, 1.5 equiv. **3a**

A 100 mL Schlenk tube equipped with a magnetic stir bar was charged with α-trifluoromethyl alkene **1a** (496.5 mg, 2.0 mmol, 1.0 equiv.), alkyltrifluoroborate (570.2 mg, 3.0 mmol, 1.5 equiv.), Mes-3,6-tBu$_2$ Acr-Ph$^+$BF$_4^-$ (23 mg, 2 mol%). The flask was evacuated and backfilled with N_2 3 times. MeCN (20 mL) and H_2O (0.6 mL) were then added via syringe under N_2. The reaction mixture was then vigorously stirred under blue LED light (30 W) at room temperature (two fans were used to cool down the reaction mixture) for 48 h. After the reaction was completed, 8.0 mL of aq. NaOH (0.5 M) was added to the reaction mixture at room temperature, the resulting solution was stirred for 5 min at room temperature before acidified by HCl solution (2 N). The reaction mixture was then diluted with ethyl acetate, poured into a separatory funnel, before being washed with brine. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford **3a** as a white solid (506 mg, 82%).

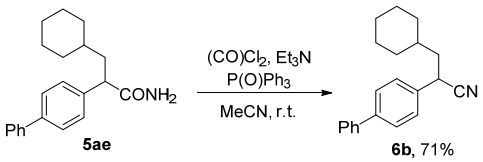
(2)



3a **6a**, quant.

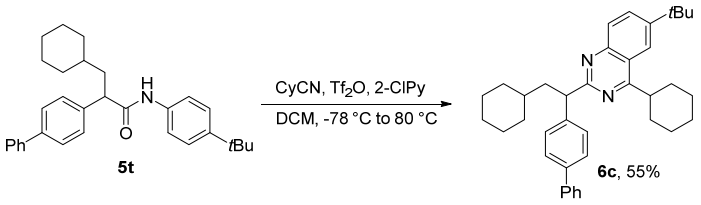
To a solution of **3a** (61.7 mg, 0.2 mmol, 1.0 equiv.) in of THF (2.0 mL) was slowly added $BH_3{\cdot}SMe_2$ (0.2 mL, 10 M, 2.0 mmol) at 0 ℃ under N_2. The solution was stirred at 0 ℃ for 3 h and then at room temperature overnight. Then the reaction solution was cooled to 0 ℃ and of H_2O (4 mL) was slowly added. The organic layer was extracted with of EtOAc for three times and washed with brine. The organic layers were dried over Na_2SO_4, filtered and evaporated. The crude reaction mixture was purified by flash chromatography (EtOAc:Hexane = 1:10) to give the reduced product **6a** as a white solid (60.0 mg, quant.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 2H), 7.58 (d, J = 7.7 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.38 – 7.33 (m, 1H), 7.30 (d, J = 7.7 Hz, 2H), 3.78 – 3.74 (m, 1H), 3.73 – 3.68 (m, 1H), 3.03 – 2.95 (m, 1H), 1.87 – 1.81 (m, 1H), 1.72 – 1.61 (m, 4H), 1.60 – 1.48 (m, 3H), 1.23 – 1.10 (m, 4H), 0.99 – 0.85 (m, 2H); 13C NMR (151 MHz, CDCl3) δ 141.9, 141.0, 139.6, 128.9 (2C), 128.6 (2C), 127.4 (2C), 127.2, 127.1 (2C), 68.1, 45.3, 39.9 34.8, 34.3, 32.9, 26.7, 26.3, 26.2. HRMS ESI $[M+Na]^+$ calculated for ($C_{21}H_{26}ONa$) 317.1876, found 317.1870.

(3)



Following a literature procedure,[10] Ph_3PO (0.5 mg, 0.0018 mmol, 1.8 mol%) and amide **5ae** (30.7 mg, 0.1 mmol, 1.0 equiv.) were dissolved in 0.5 mL of anhydrous acetonitrile in a 5 mL vial equipped with a magnetic stirring bar, followed by addition of Et_3N (30.4 mg, 0.3 mmol, 3.0 equiv.). The resulting solution was treated dropwise with oxalyl chloride (25.4 mg, 0.2 n mmol, 2.0 equiv.), the reaction mixture was stirred for 10 min at room temperature. After the reaction was complete, the solution was concentrated and purified by flash chromatography (EtOAc:Hexane = 1:10), **6b** was obtained as a yellow solid (20.6 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.48 – 7.42 (m, 2H), 7.42 – 7.33 (m, 3H), 3.89 (dd, *J* = 10.0, 6.2 Hz, 1H), 1.97 – 1.89 (m, 1H), 1.89 – 1.81 (m, 1H), 1.80 – 1.62 (m, 5H), 1.63 – 1.50 (m, 1H), 1.35 – 1.25 (m, 2H), 1.25 – 1.12 (m, 1H), 1.05 – 0.89 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 140.4, 135.6, 129.0 (2C), 127.9 (2C), 127.8 (2C), 127.7, 127.2 (2C), 121.2, 43.8, 35.5, 34.6, 33.4, 32.5, 26.5, 26.1, 26.0. HRMS ESI $[M+Na]^+$ calculated for ($C_{21}H_{23}NNa$) 312.1723, found 312.1717.

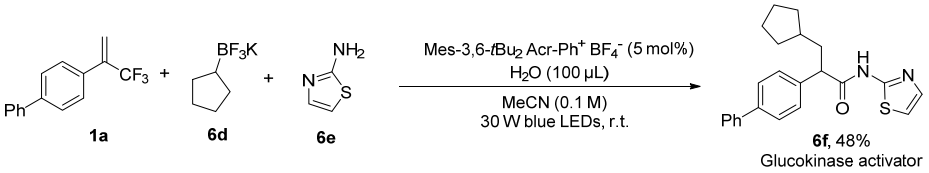
(4)



Following a modified literature procedure,[11] trifluoromethanesulfonic anhydride (31.0 mg, 0.11 mmol, 1.1 equiv.) was added via syringe over 1 min to a stirred mixture of amide **50** (44 mg, 0.1 mmol, 1.0 equiv.) and 2-chloropyridine (13.6 mg, 0.12 mmol, 1.2 equiv.) in dichloromethane (0.5 mL) at –78 ºC. After 5 min, the reaction vessel was placed in an ice-water bath and allowed to warm to 0 ºC, beforecyclohexanecarbonitrile (12.1 mg, 0.11 mmol, 1.1 equiv.) was added via syringe. The resulting solution was allowed to warm to room temperature for 5 minutes before the reaction vessel was heated to 80 ºC. After 16 h, the reaction vessel was allowed to cool to room temperature. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), dried over Na_2SO_4, filtered and evaporated. The residue was purified by flash column chromatography (EtOAc : hexanes = 1:15) to give the product **6c** as colourless oil (29.2 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.1 Hz, 1H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.92 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.60 – 7.56 (m, 2H), 7.55 – 7.50 (m, 2H), 7.45 – 7.38 (m, 2H), 7.35 – 7.27 (m, 1H), 4.53 (dd, *J* = 9.0, 6.5 Hz, 1H), 3.55 (tt, *J* = 11.0, 3.5 Hz, 1H), 2.48 (ddd, *J* = 13.5, 9.0, 6.5 Hz, 1H), 2.08 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.04 – 1.84 (m, 9H), 1.78 (d, *J* = 13.0 Hz, 1H), 1.72 – 1.51 (m,

4H), 1.45 (s, 9H), 1.22 – 0.96 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.6, 167.2, 149.4, 149.0, 143.3, 141.3, 139.1, 131.9, 128.9 (2C), 128.8 (2C), 128.6, 127.1 (2C), 127.0, 127.0 (2C), 121.1, 118.7, 52.5, 43.6, 41.5, 35.8, 35.2, 33.8, 33.5, 32.3, 32.1, 31.3 (3C), 29.6, 26.8, 26.7, 26.6, 26.4, 26.3. HRMS ESI $[M+H]^+$ calculated for ($C_{38}H_{47}N_2$) 531.3734, found 531.3726.

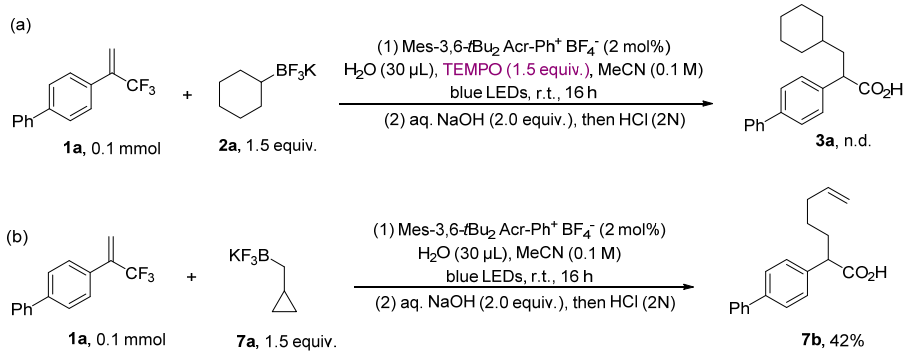
(5)



Following General procedure **D** using **1a** (24.8 mg, 0.1 mmol, 1.0 equiv.), **6d** (26.4 mg, 0.15 mmol, 1.5 equiv.), **6e** (15.0 mg, 0.15 mmol, 1.5 equiv.). afforded the glucokinase activator **6f** obtained as white solid (18.1 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.37 (m, 6H), 7.37 – 7.29 (m, 4H), 7.28 – 7.22 (m, 1H), 6.96 (d, J = 3.6 Hz, 1H), 3.71 (t, J = 7.6 Hz, 1H), 2.22 (dt, J = 13.9, 7.6 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.76 – 1.60 (m, 3H), 1.56 – 1.50 (m, 2H), 1.44 – 1.38 (m, 2H), 1.12 – 1.00 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 159.9, 140.73, 140.65, 137.7, 135.9, 128.9 (2C), 128.4 (2C), 127.8 (2C), 127.5, 127.2 (2C), 114.0, 52.0, 39.8, 37.9, 32.9, 32.6, 25.3, 25.2. HRMS ESI $[M+H]^+$ calculated for ($C_{23}H_{25}N_2OS$) 377.1682, found 377.1680.

6. Mechanistic Studies

6.1 Radical trapping experiments



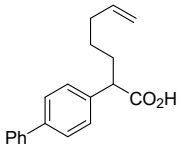
(a) **Reaction procedure**: A 10-mL Schlenk tube equipped with a magnetic stir bar was charged with *α*-trifluoromethyl alkene **1a** (24.8 mg, 0.1 mmol, 1.0 equiv.), cyclohexyltrifluoroborate **2a** (28.5 mg, 1.5 equiv.), Mes-3,6-*t*Bu$_2$ Acr-Ph$^+$BF$_4^-$ (1.2 mg, 2 mol%) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (23.4 mg, 1.5 equiv.). The flask was evacuated and backfilled with N_2 3 times. MeCN (1.0 mL) was then added via syringe followed by the addition of H_2O (30 μL) under N_2. The reaction mixture was then vigorously stirred under blue LED light (30 W) at room temperature (two fans were used to cool down the reaction mixture) for 16 h. After the reaction was completed, 1.0 mL of aq. NaOH (0.2 M) was added to the reaction mixture at room temperature, the resulting solution was stirred for 2 min at room temperature before acidified by HCl solution (2 N). The reaction mixture was then diluted with ethyl acetate, poured into a separatory funnel, before being washed with brine. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration, the crude reaction mixture was analyzed by ^{1}H NMR spectroscopy.

Results: The present reaction was completely inhibited by the addition of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).

(b) **Reaction procedure**: A 10-mL Schlenk tube equipped with a magnetic stir bar was charged with *α*-trifluoromethyl alkene **1a** (24.8 mg, 0.1 mmol, 1.0 equiv.), alkyltrifluoroborate **7a** (24.3 mg, 1.5 equiv.), Mes-3,6-*t*Bu$_2$ Acr-Ph$^+$BF$_4^-$ (1.2 mg, 2 mol%). The flask was evacuated and backfilled with N_2 3 times. MeCN (1.0 mL) was then added via syringe followed by the addition of H_2O (30 μL) under N_2. The reaction mixture was then vigorously stirred under blue LED light (30 W) at room temperature (two fans were used to cool down the reaction mixture) for 16 h. After the reaction was completed, 1.0 mL of aq. NaOH (0.2 M) was added to the reaction mixture at room temperature, the resulting solution was stirred for 2 min at room temperature before acidified by HCl solution (2 N). The reaction mixture was then diluted with ethyl acetate, poured into a separatory funnel, before being washed with brine. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration, The crude product was purified by flash chromatography on silica gel to afford the **7b**.

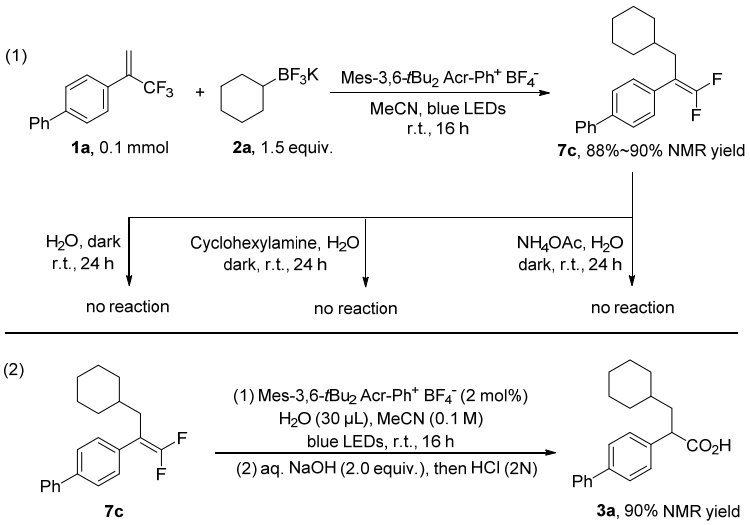
Results: The ring-opened product **7b** was obtained in 42% yield (11.8 mg) when the cyclopropylmethylenetrifluoroborate **7a** was used in the reaction. These observations suggest free radicals were generated in the reactions.

2-([1,1'-Biphenyl]-4-yl)hept-6-enoic acid (7b): purification by flash column chromatography (EtOAc: Hexane : AcOH = 20:80:2), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 4H), 7.46 – 7.40 (m, 2H), 7.40 – 7.37 (m, 2H), 7.37 – 7.30 (m, 1H), 5.77 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03 – 4.98 (m, 1H), 4.97 – 4.93 (m, 1H), 3.61 (t, *J* = 7.7 Hz, 1H), 2.17 – 2.02 (m, 3H), 1.92 – 1.77 (m, 1H), 1.50 – 1.36 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.8, 140.8, 140.6, 138.3, 137.6, 128.9 (2C), 128.6 (2C), 127.6 (2C), 127.5, 127.2 (2C), 115.1, 51.2, 33.6, 32.6, 26.9. HRMS ESI $[M+H]^+$ calculated for ($C_{19}H_{21}O_2$) 281.1542, found 281.1532.



6.2 Control experiments

(a) *gem*-Difluoroalkene as an intermediate in the catalytic system



(1) **Reaction procedure**: A 10-mL Schlenk tube equipped with a magnetic stir bar was charged with *α*-trifluoromethyl alkene **1a** (24.8 mg, 0.1 mmol, 1.0 equiv.), cyclohexyltrifluoroborate **2a** (28.5 mg, 1.5 equiv.), Mes-3,6-*t*Bu$_2$ Acr-Ph$^+$BF$_4^-$ (1.2 mg, 2 mol%). The flask was evacuated and backfilled with N_2 3 times. MeCN (1.0 mL) was then added via syringe under N_2. The reaction mixture was then vigorously stirred under blue LED light (30 W) at room temperature (two fans were used to cool down the reaction mixture) for 16 h. After the reaction was completed, the crude reaction mixture was analyzed by ^{1}H NMR spectroscopy.

Results: The *gem*-difluoroalkene **7c** was obtained in 88%~90% yield. In addition, *in-situ* treated the crude reaction mixture with H_2O and nucleophiles (H_2O, cyclohexylamine) or ammonium surrogate NH_4OAc in the dark did not yield the desired *a*-arylated carboxylic acid or amide products, thus exclude the possibility of direct nucleophilic substitution of *gem*-difluoroalkene.[12]

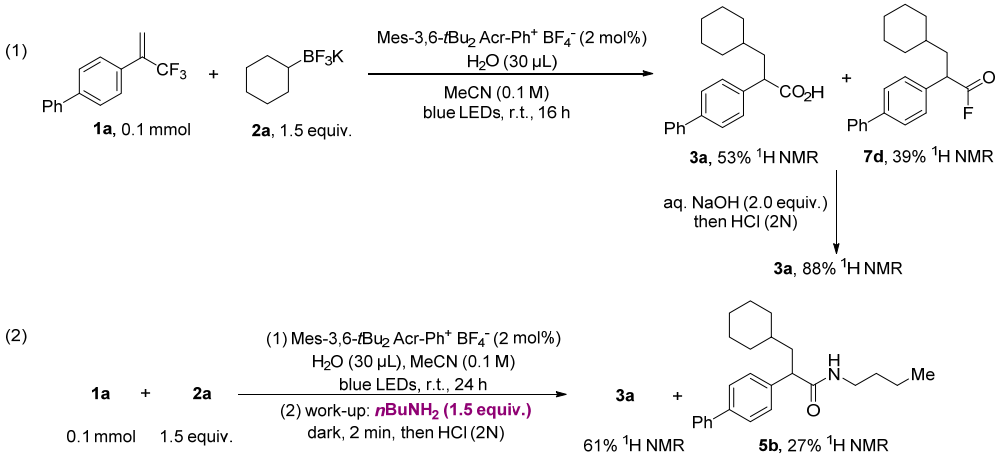
4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (7c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.55 (m, 4H), 7.49 – 7.43 (m, 2H), 7.43 – 7.39 (m, 2H), 7.39 – 7.34 (m, 1H), 2.37 – 2.30 (m, 2H),

1.76 – 1.60 (m, 5H), 1.40 – 1.26 (m, 1H), 1.22 – 1.09 (m, 3H), 1.03 – 0.85 (m, 2H). The spectral data are in accordance with the literature report.[13]

(2) **Reaction procedure**: A 10-mL Schlenk tube equipped with a magnetic stir bar was charged with *gem*-difluoroalkene **7c** (31.2 mg, 0.1 mmol, 1.0 equiv.), Mes-3,6-*t*Bu$_2$ Acr-Ph$^+$BF$_4^-$ (1.3 mg, 2 mol%). The flask was evacuated and backfilled with N_2 3 times. MeCN (1.0 mL) was then added via syringe followed by the addition of H_2O (30 uL) under N_2. The reaction mixture was then vigorously stirred under blue LED light (30 W) at room temperature (two fans were used to cool down the reaction mixture) for 16 h. After the reaction was completed, 1.0 mL of aq. NaOH (0.2 M) was added to the reaction mixture at room temperature, the resulting solution was stirred for 2 min at room temperature before acidified by HCl solution (2 N). The reaction mixture was then diluted with ethyl acetate, poured into a separatory funnel, before being washed with brine. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration, the crude reaction mixture was analyzed by ^{1}H NMR spectroscopy.

Results: The desired product **3a** was obtained in a similar yield (90%) when **7c** was used as starting material under standard conditions, all these results suggest *gem*-difluoroalkene is an intermediate in this reaction.

(b) Acyl fluoride species is a possible intermediate in the reaction



Reaction procedure: A 10-mL Schlenk tube equipped with a magnetic stir bar was charged with *α*-trifluoromethyl alkene **1a** (24.8 mg, 0.1 mmol, 1.0 equiv.), cyclohexyltrifluoroborate **2a** (28.5 mg, 1.5 equiv.), Mes-3,6-*t*Bu$_2$ Acr-Ph$^+$BF$_4^-$ (1.2 mg, 2 mol%). The flask was evacuated and backfilled with N_2 3 times. MeCN (1.0 mL) was then added via syringe followed by the addition of H_2O (30 μL) under N_2. The reaction mixture was then vigorously stirred under blue LED light (30 W) at room temperature (two fans were used to cool down the reaction mixture) for 16 h. After the reaction was completed, the reaction mixture was then diluted with ethyl acetate, poured into a separatory funnel, before being washed with brine. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration, the crude reaction mixture was analyzed by ^{1}H NMR spectroscopy.

Results: 53% of the product **3a** was obtained when the reaction was carried out under standard conditions but without base-acid work-up procedure, about 39% yield of compound **7d** was detected according to the ^{1}H NMR, ^{19}F NMR spectroscopy (Figure S8, S10) and HRMS-ESI ([M-H$^-$] calculated for ($C_{21}H_{22}FO$) 309.1660, found 309.1658. Compound **7d** transformed into product **3a** after the treatment of the crude reaction mixture with aq. NaOH and then acidified with HCl (2N) (Figure S8). Additionally, when replacing aq. NaOH with 1.5 equiv. of *n*-butyl amine during the work-up procedure (2), 27% of product **5b** was obtained, indicated *n*-butyl amine acted as a nucleophile during the work-up procedure to trap electrophilic species **7d**. Based on these observations, compound **7d** was an acyl fluoride intermediate.

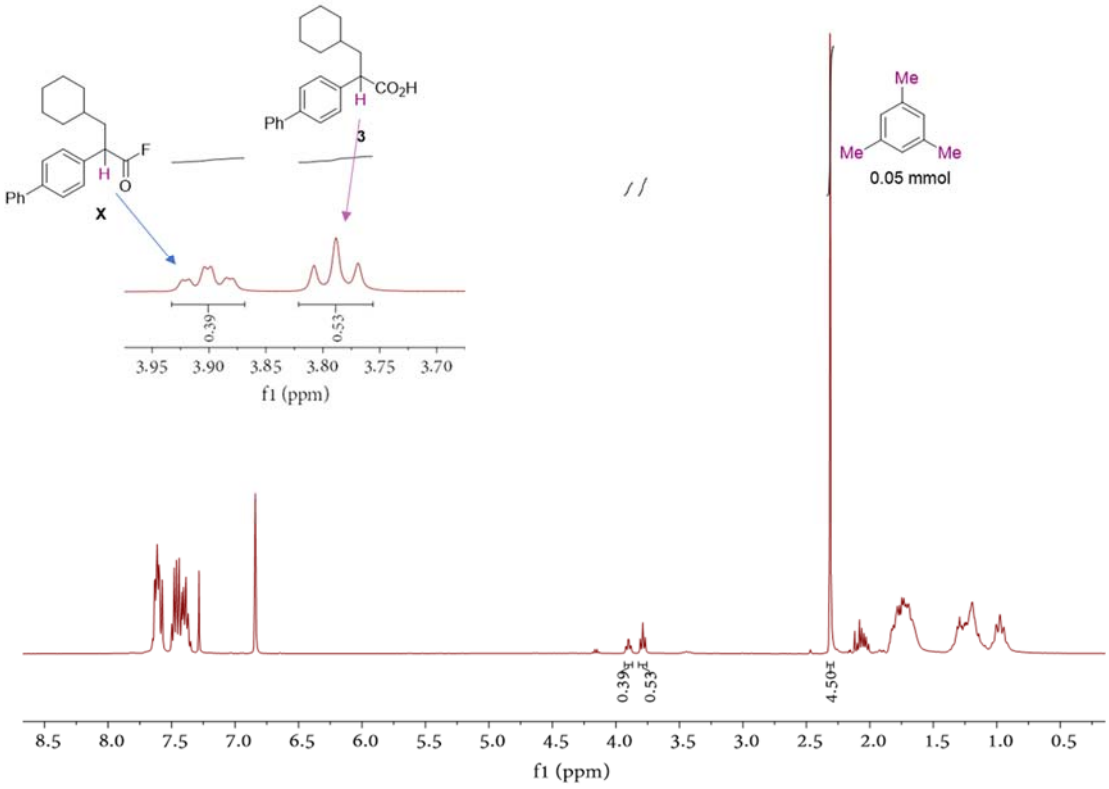


Figure S8 ^{1}H NMR spectroscopy of the crude reaction mixture without work-up procedure (mesitylene as IS)

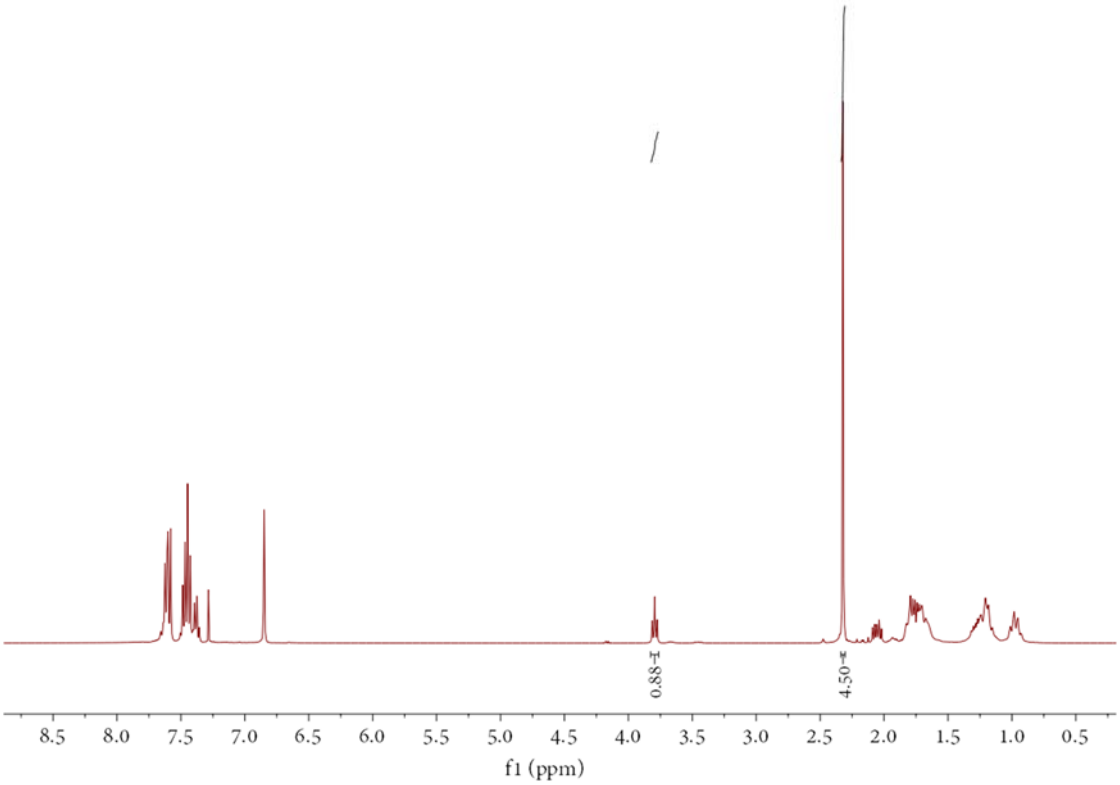


Figure S9 [1]H NMR spectroscopy of the crude reaction mixture after work-up procedure (mesitylene as IS)

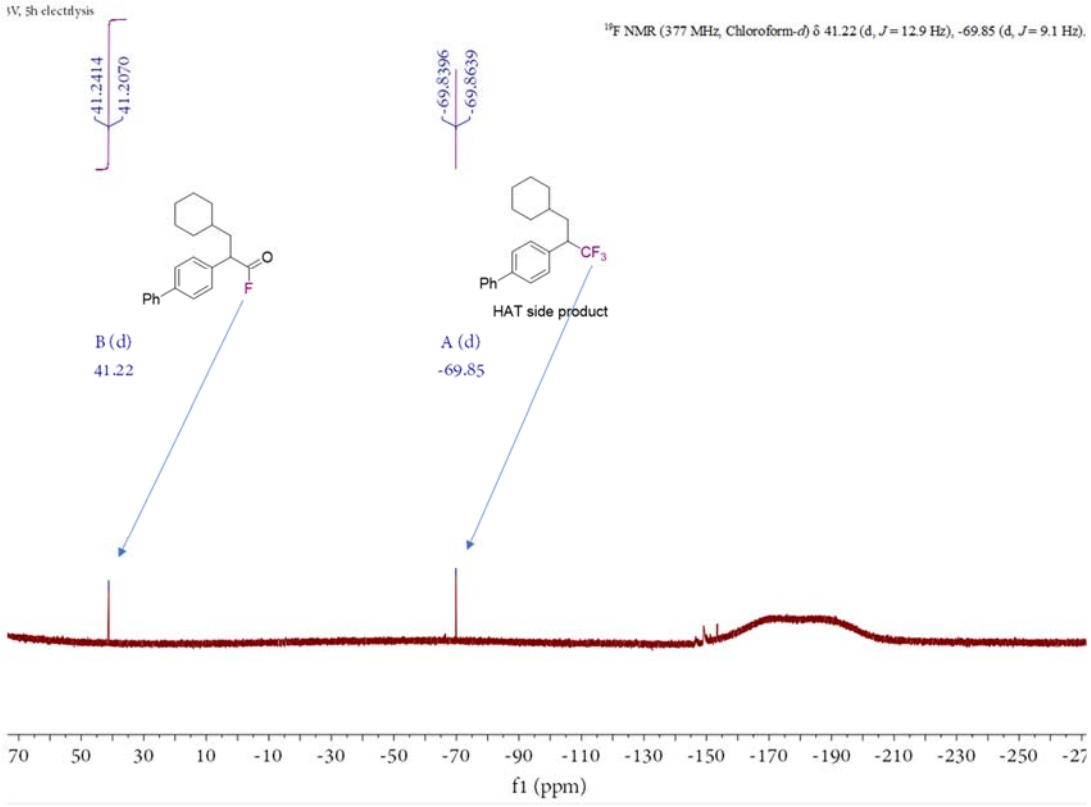


Figure S10 [19]F NMR spectroscopy of the crude reaction mixture without work-up procedure

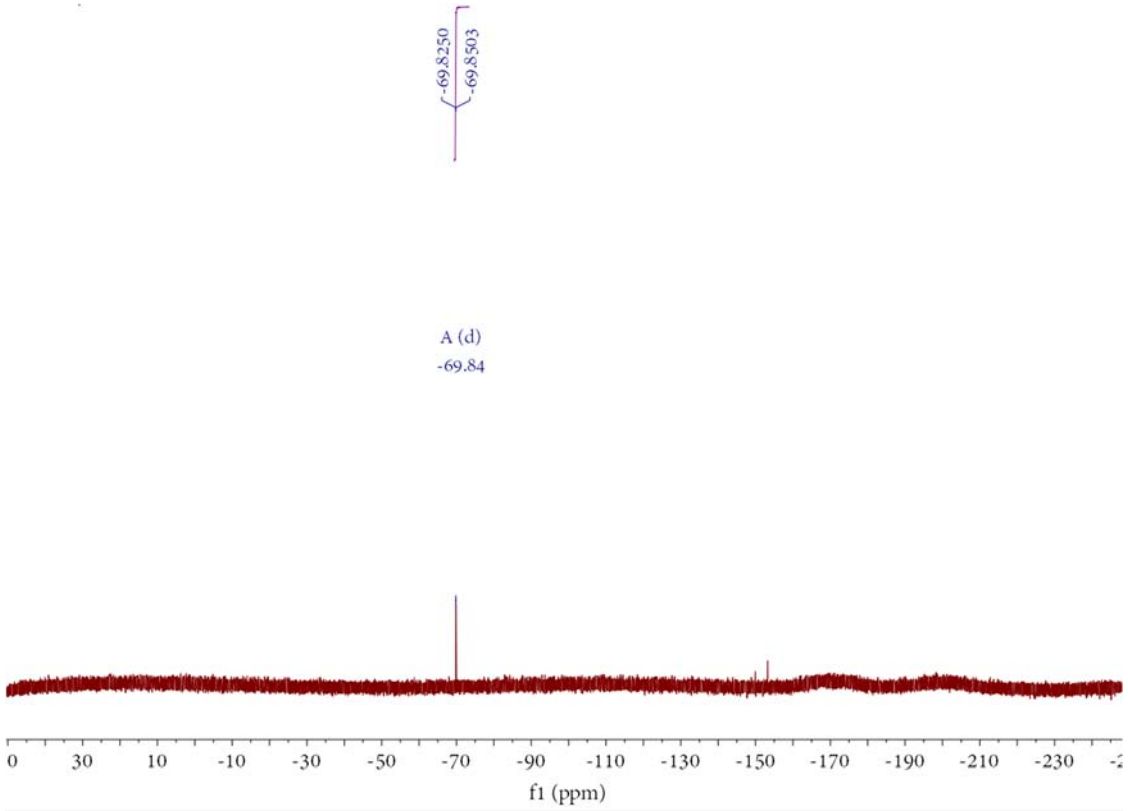
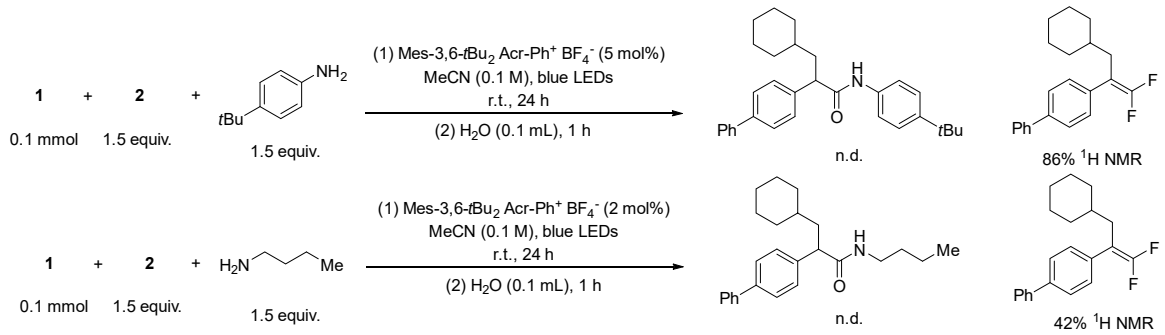


Figure S11 ^{19}F NMR spectroscopy of the crude reaction mixture after work-up procedure

(c)



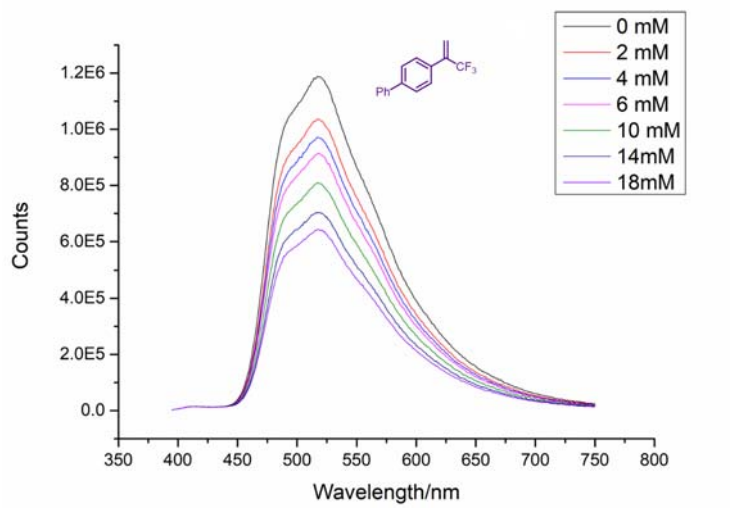
Reaction procedure: A 10-mL Schlenk tube equipped with a magnetic stir bar was charged with *α*-trifluoromethyl alkene **1a** (24.8 mg, 0.1 mmol, 1.0 equiv.), cyclohexyltrifluoroborate **2a** (28.5 mg, 1.5 equiv.), Mes-3,6-*t*Bu$_2$ Acr-Ph$^+$BF$_4^-$ (1.2~2.9 mg, 2~5 mol%). The flask was evacuated and backfilled with N_2 3 times. MeCN (1.0 mL) was then added via syringe followed by the addition of N-nucleophile (4-(*tert*-butyl)aniline or butyl amine) under N_2. The reaction mixture was then vigorously stirred under blue LED light (30 W) at room temperature (two fans were used to cool down the reaction mixture) for 24 h. After that, H_2O (100 uL) was added, and the reaction mixture was stirred for another hour in the dark. After the reaction was completed, the reaction mixture was diluted with ethyl acetate and poured into a separatory funnel, washed with brine. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. the crude reaction mixture was analyzed by ^1H NMR spectroscopy.

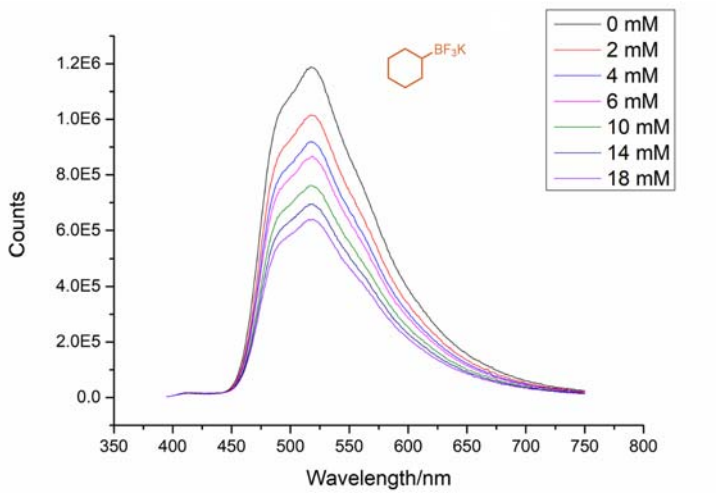
Results: The desired products were not formed in the absence of H_2O during the photocatalytic systems, considerable amount of *gem*-difluoroalkene were obtained instead. These results indicated that aniline, alkyl amine could not react with *gem*-difluoroalkene under the given reaction conditions to yield the products.

6.3 Stern-Volmer quenching studies

The photocatalyst, potential quenchers and MeCN/H_2O (10:1) were weighed into vials inside a glovebox under nitrogen. Prior to fluorescence experiments, 3,6-di-*tert*-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluroborate ($2.5* 10^{-5}$ M) in 2.0 ml of MeCN/H_2O (10:1) was recorded in 1 cm path quartz cuvettes using a Thermo Nanodrop 2000c UV/Vis spectrometer. The emission spectra were recorded using an Edinburgh FLS980 spectrometer.

3,6-Di-*tert*-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluroborate was excited at 375 nm and the emission intensity was collected at 519 nm. In a typical experiment, to a $2.5*10^{-5}$ M solution of 3,6-di-*tert*-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluroborate in MeCN/H_2O (10:1) was added the appropriate amount of trifluoromethyl alkene, potassium cyclohexyl trifluoroborate, *gem*-difluoroalkene, cyclohexyl amine or ammonium acetate in a screw-top quartz cuvette, the emission of the sample was collected.

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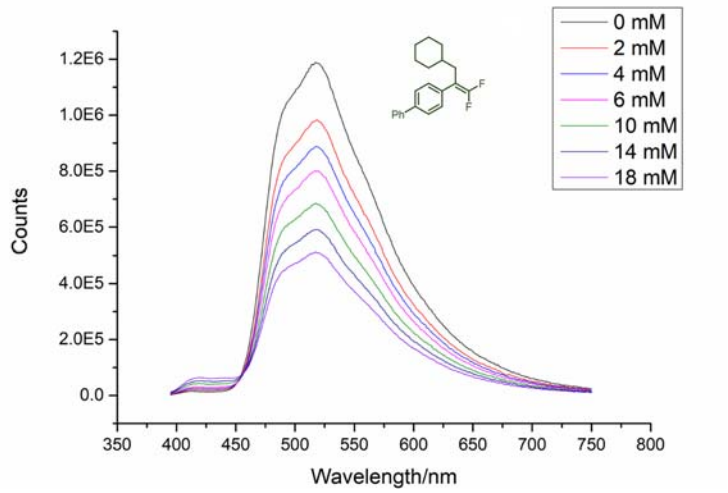
4 mM
6 mM
10 mM
14 mM
18 mM
BF3K
Counts
Wavelength/nm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10 mM
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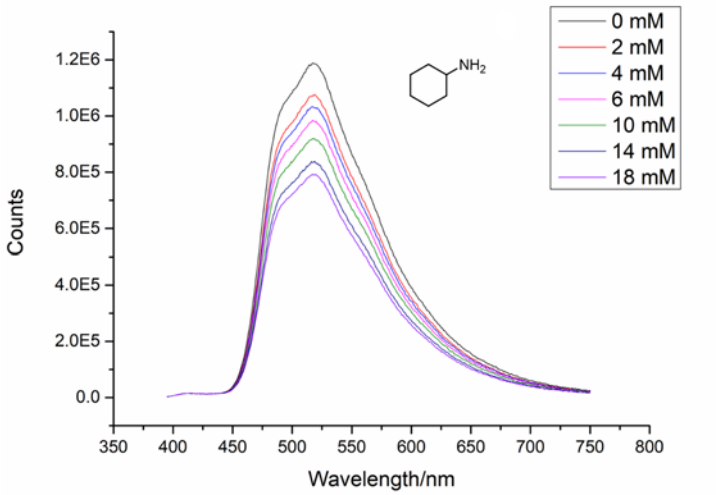
18 mM
Ph
F
F
Counts
Wavelength/nm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NH2
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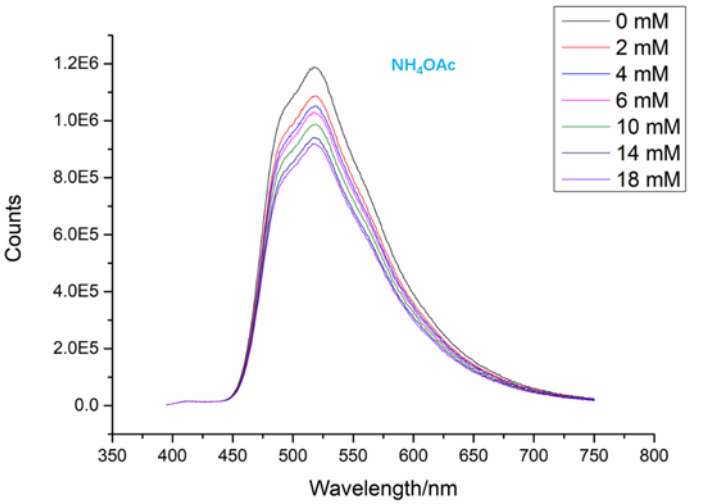
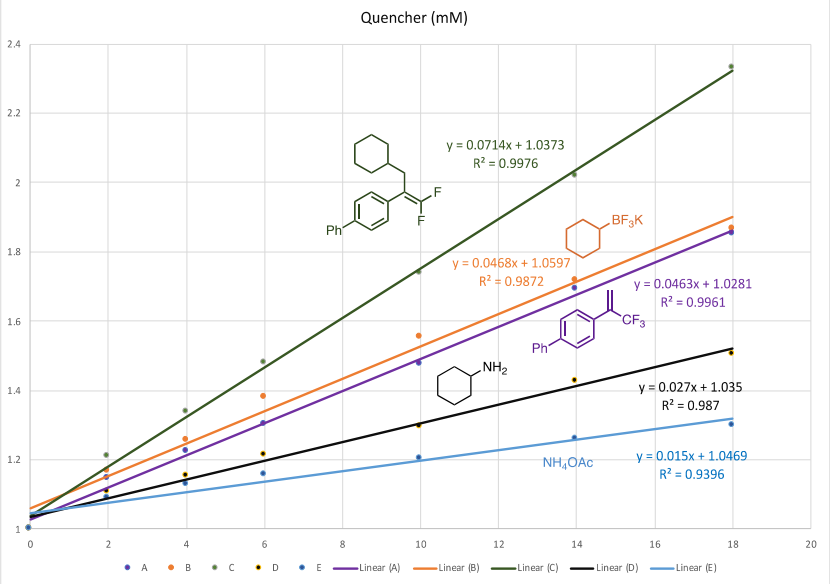
Wavelength/nm


0 mM
2 mM
4 mM
6 mM
10 mM
14 mM
18 mM
NH4OAc
Counts
Wavelength/nm


Quencher (mM)
y = 0.0714x + 1.0373
R² = 0.9976
y = 0.0468x + 1.0597
R² = 0.9872
y = 0.0463x + 1.0281
R² = 0.9961
y = 0.027x + 1.035
R² = 0.987
y = 0.015x + 1.0469
R² = 0.9396
NH4OAc
Linear (A)
Linear (B)
Linear (C)
Linear (D)
Linear (E)

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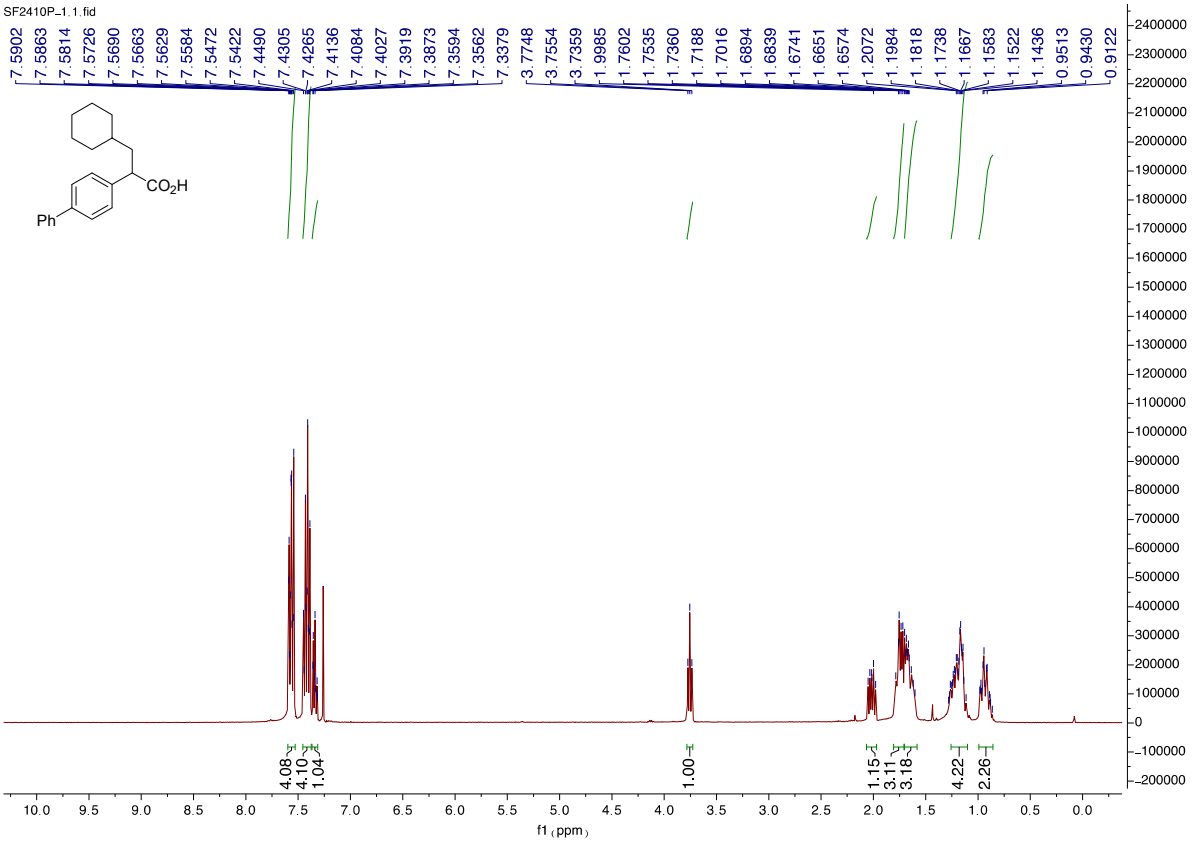
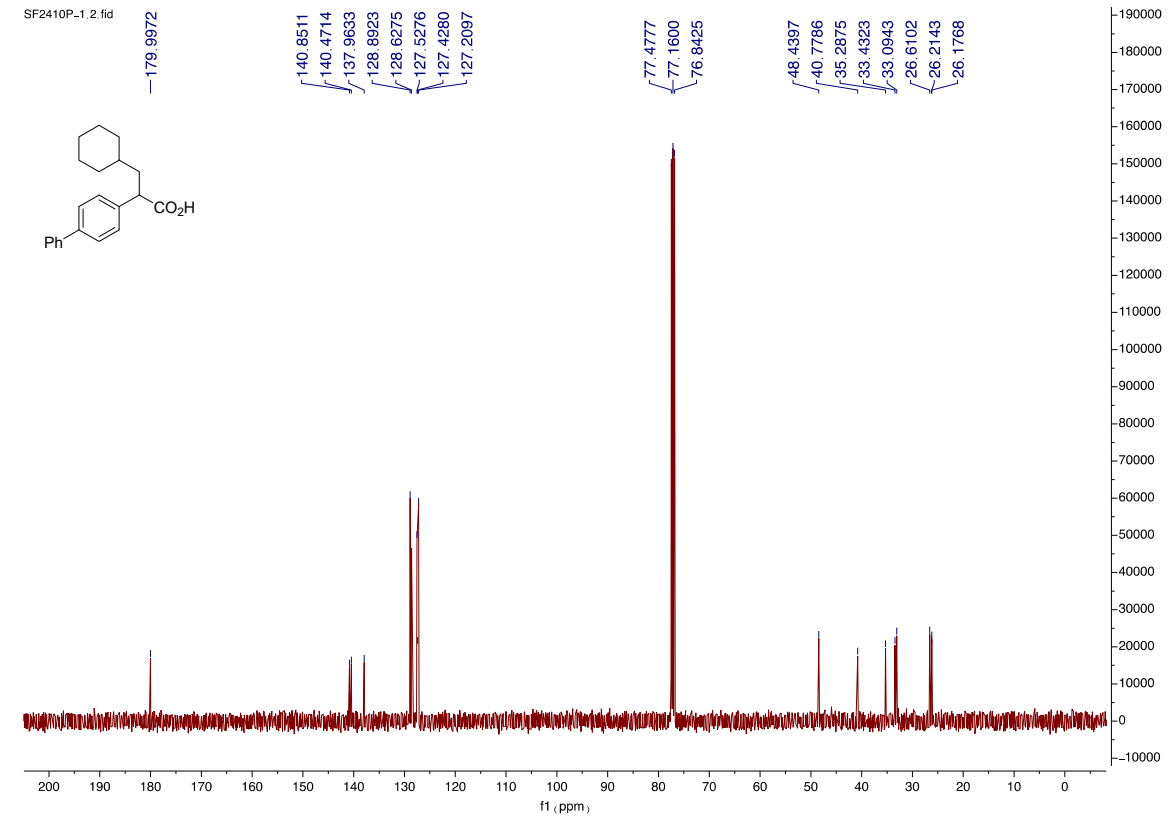
8. Spectral Data



3a ^{1}H NMR (400 MHz, $CDCl_3$)



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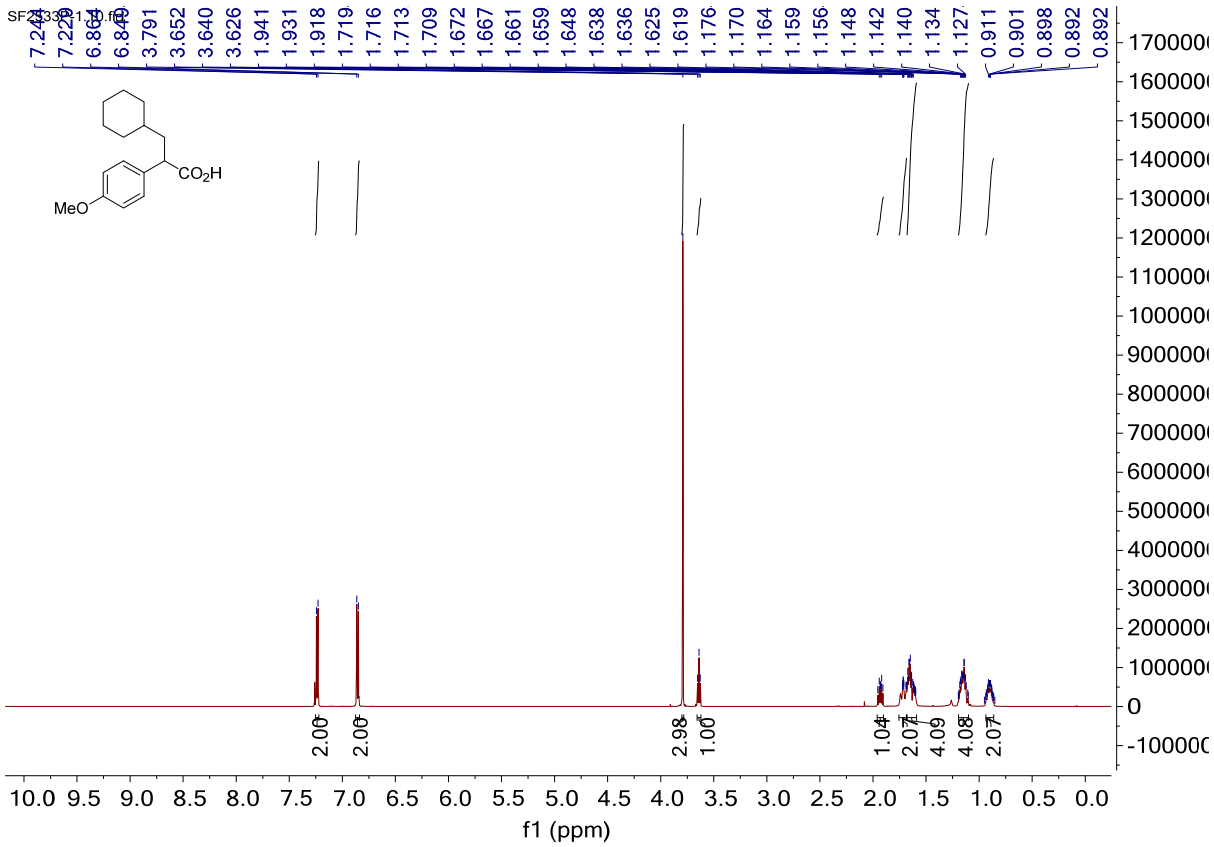

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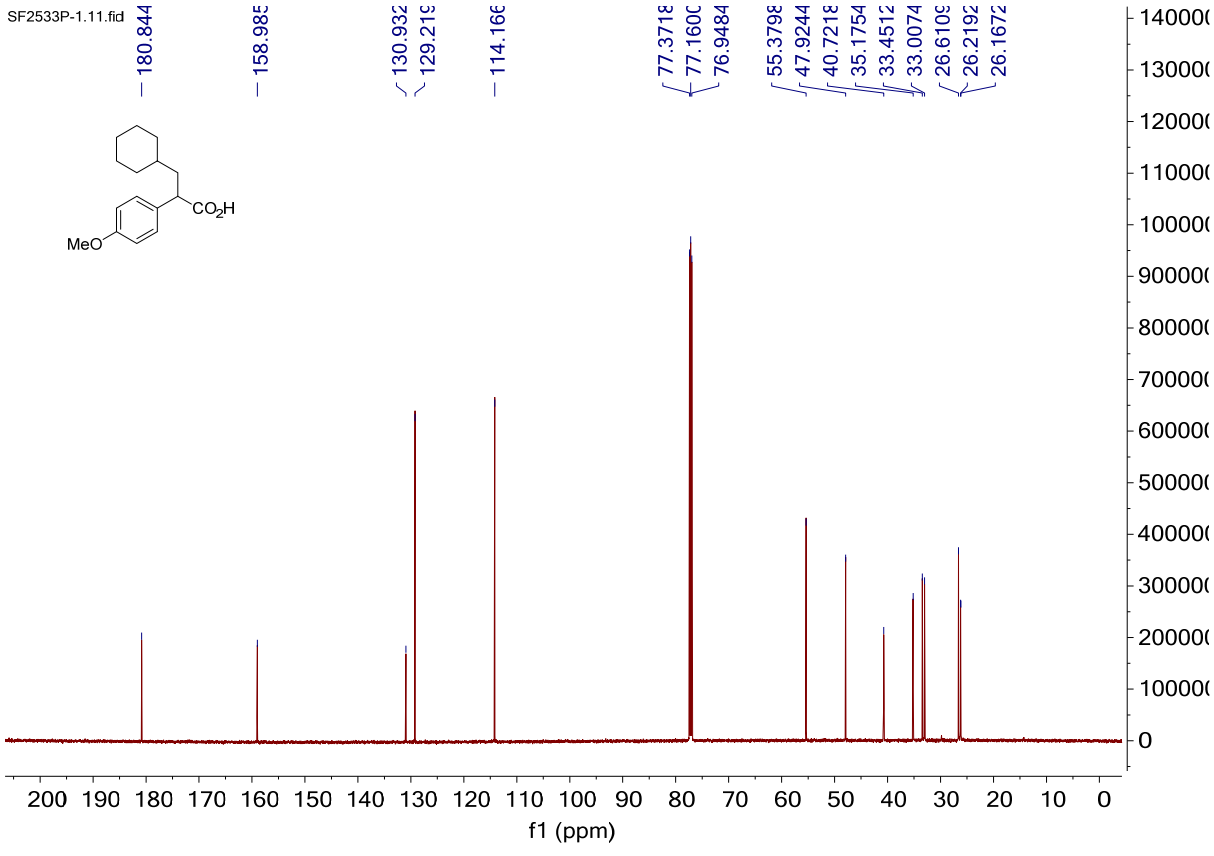

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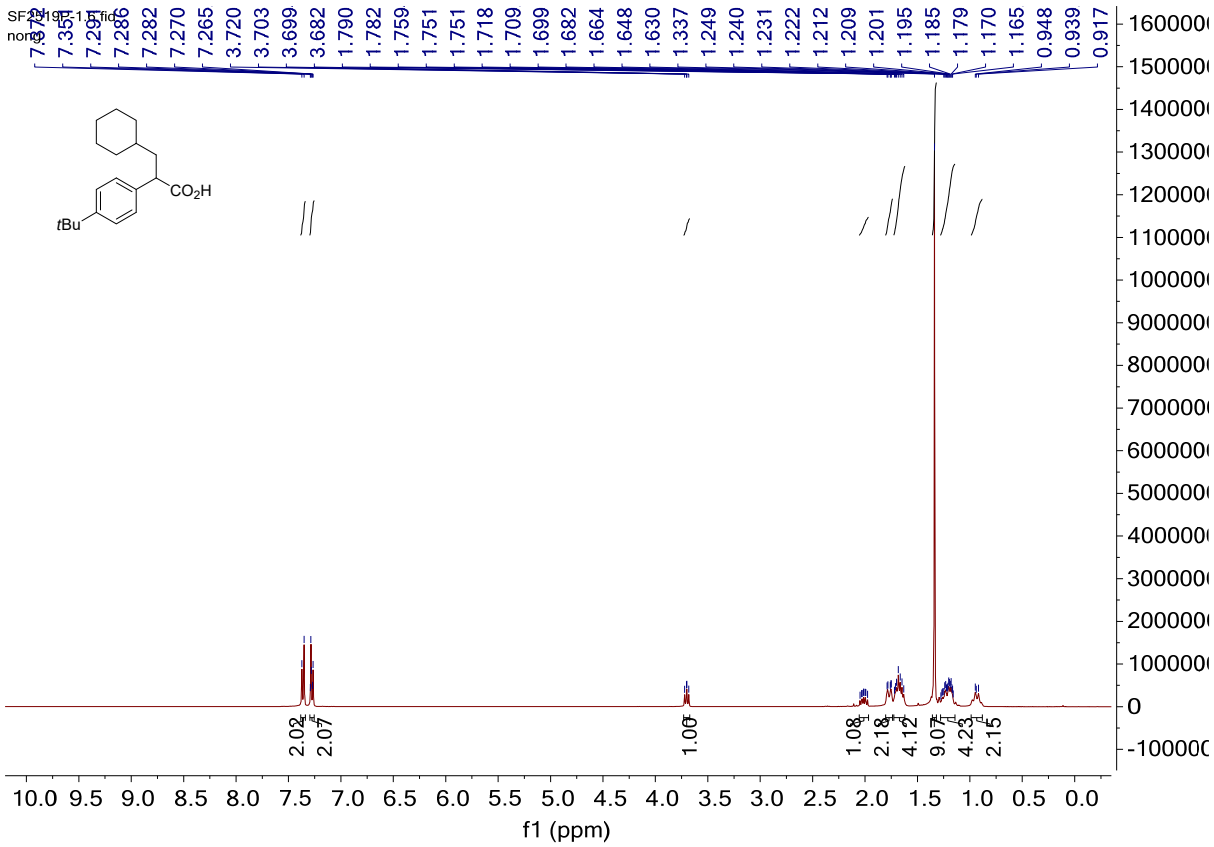

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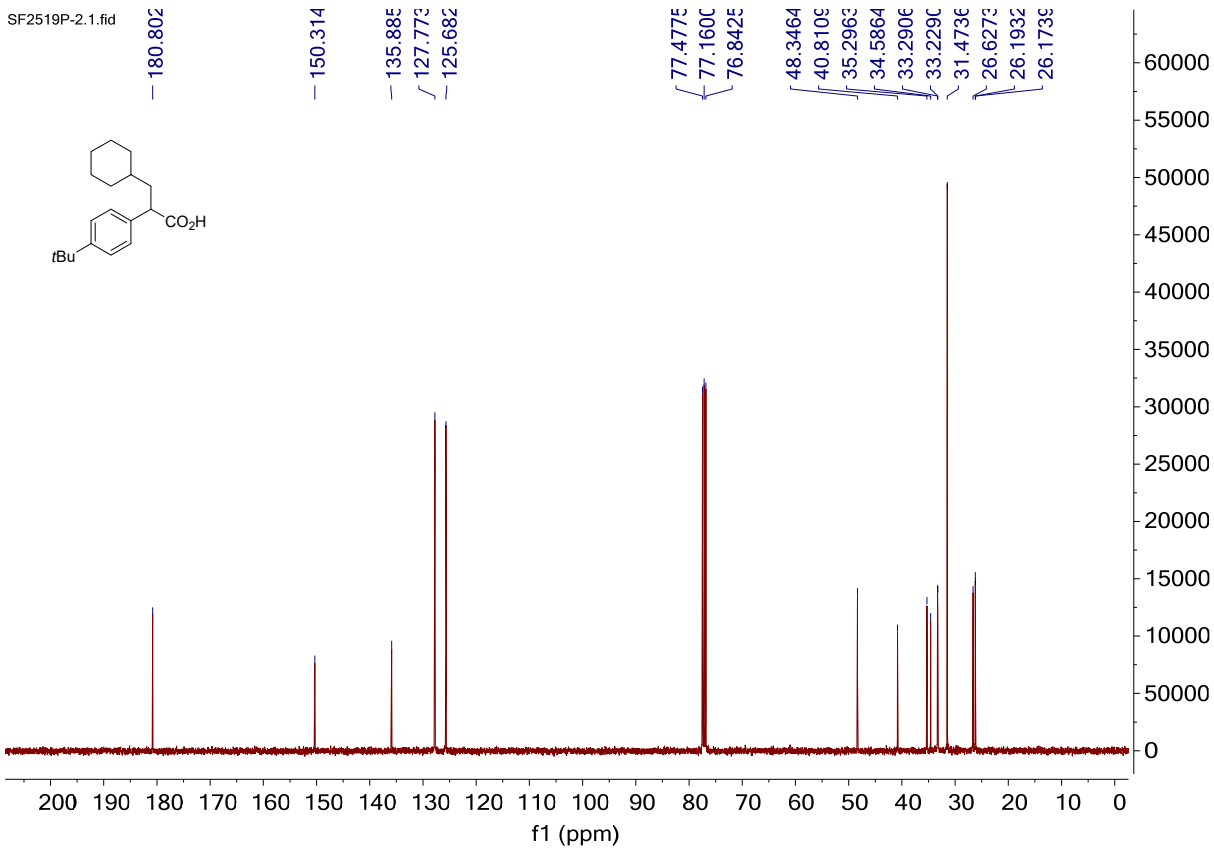

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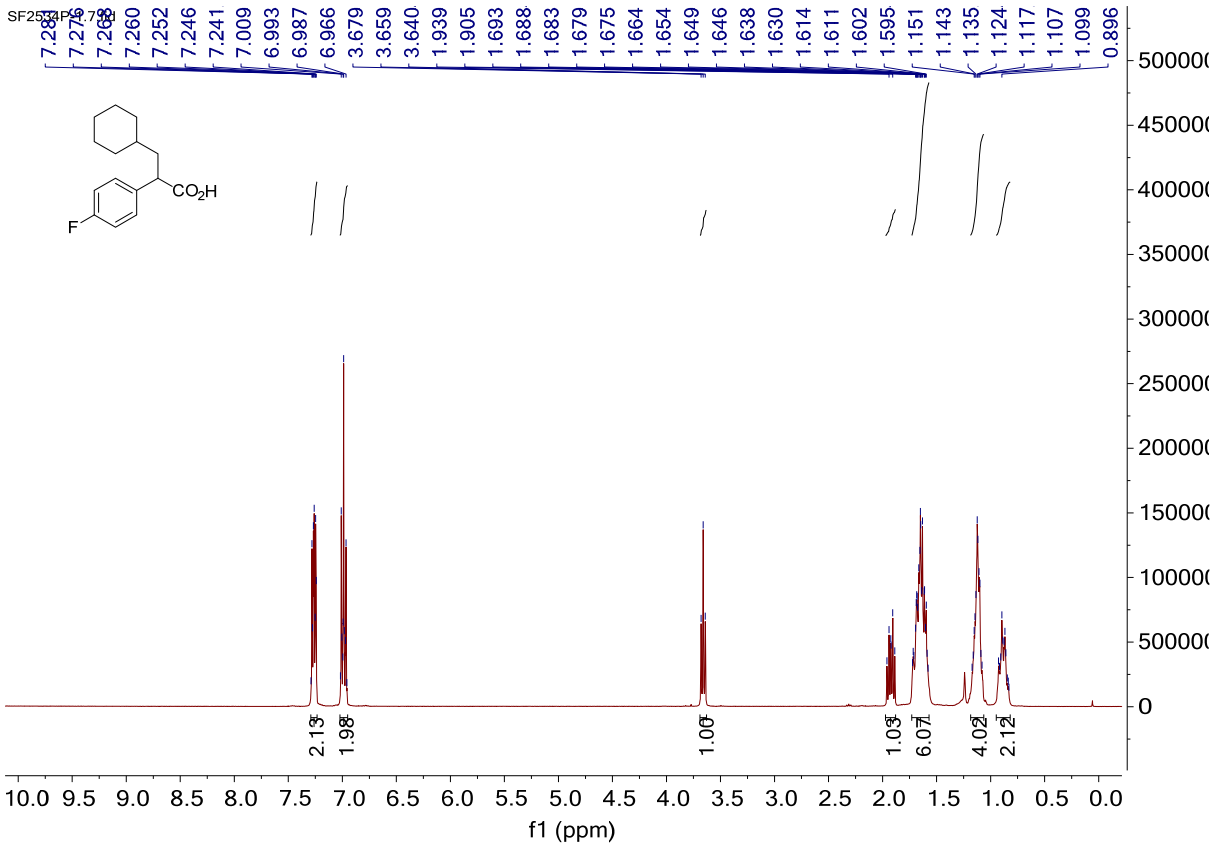

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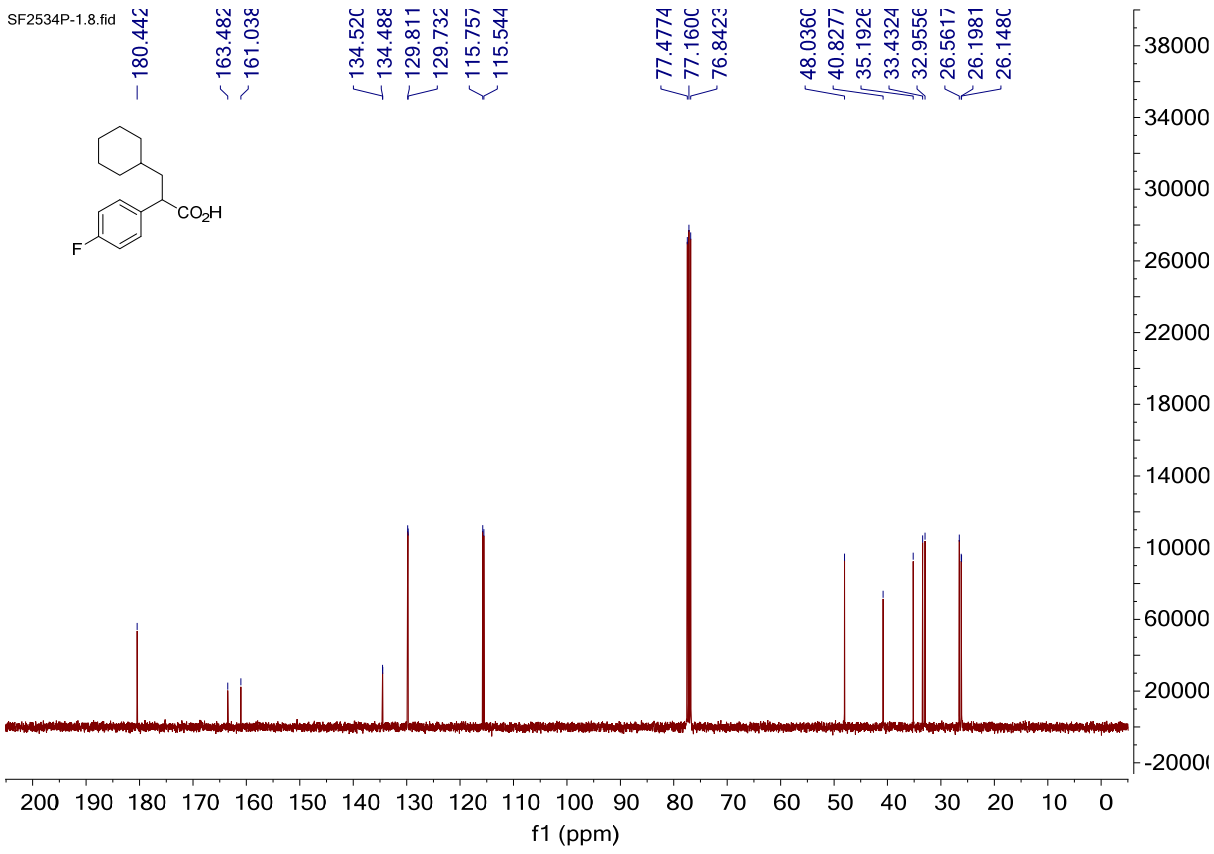

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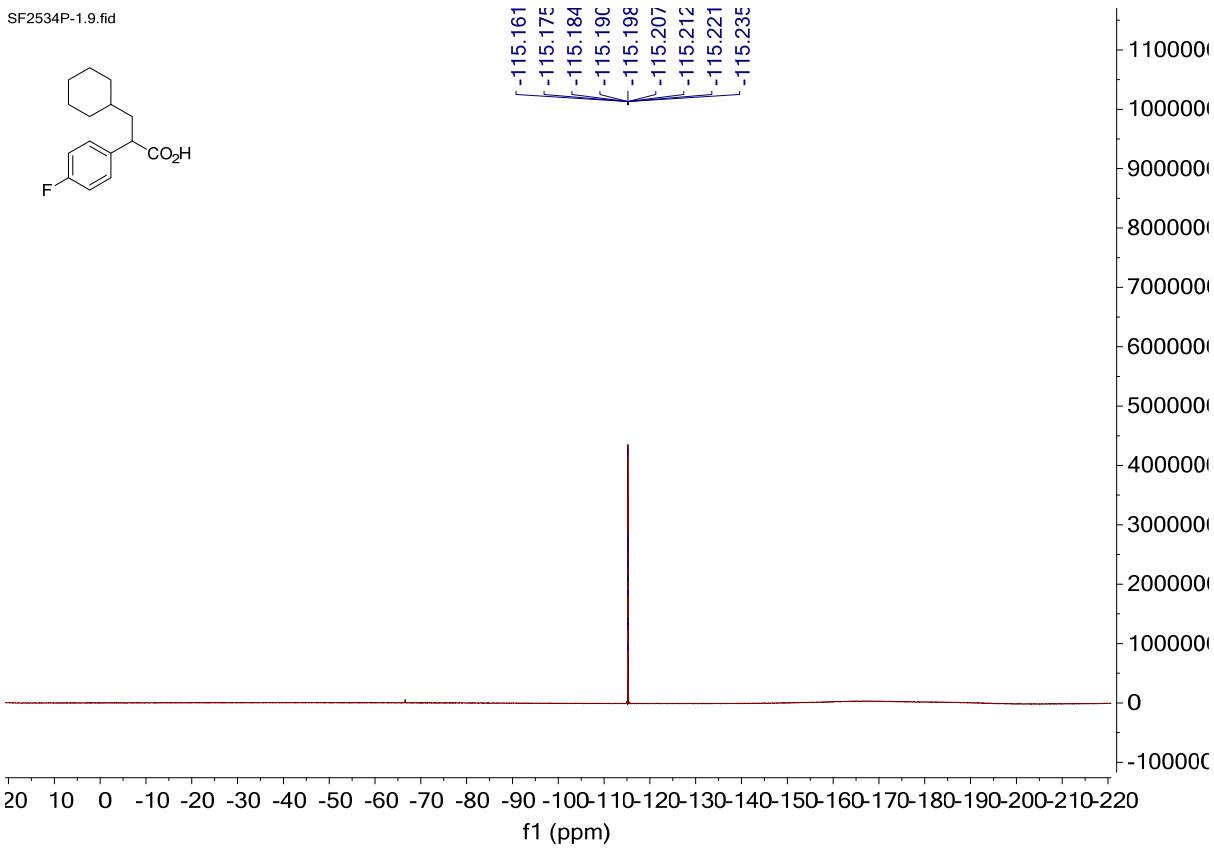

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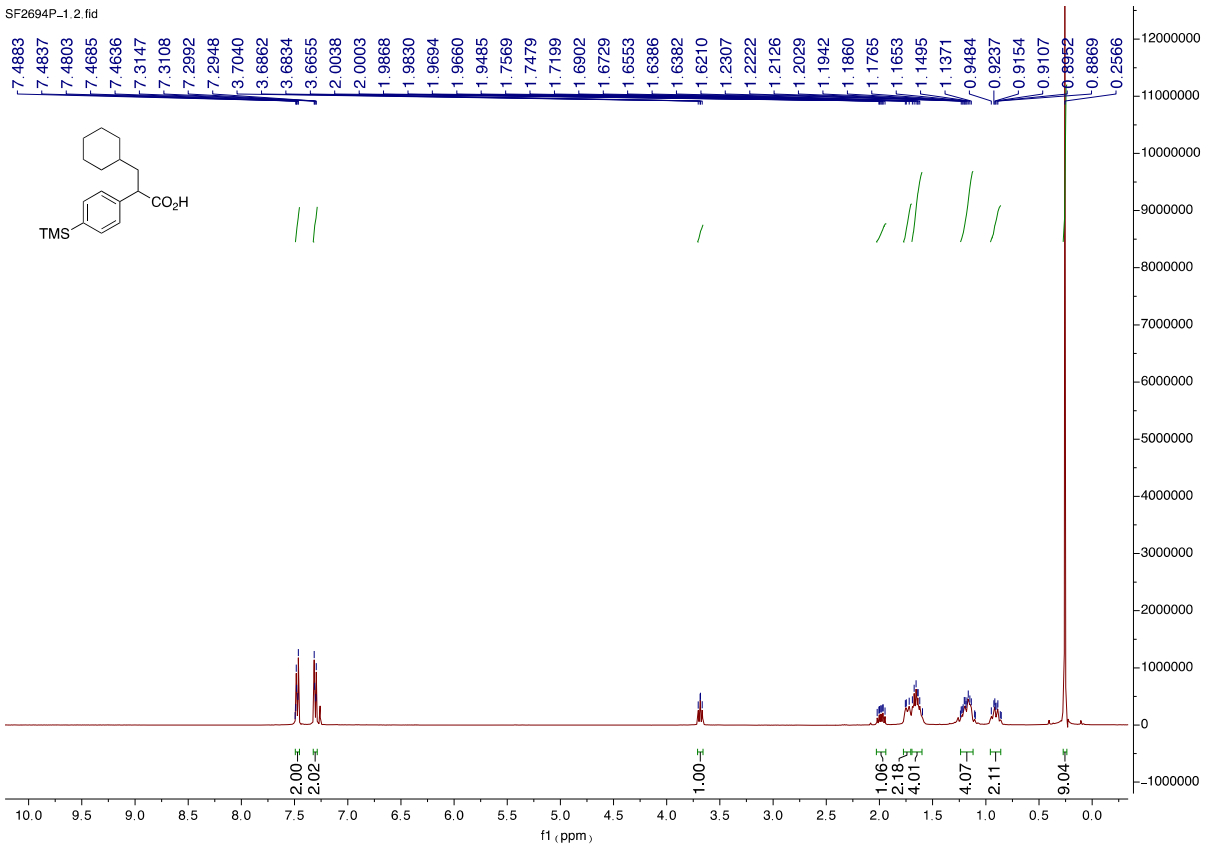

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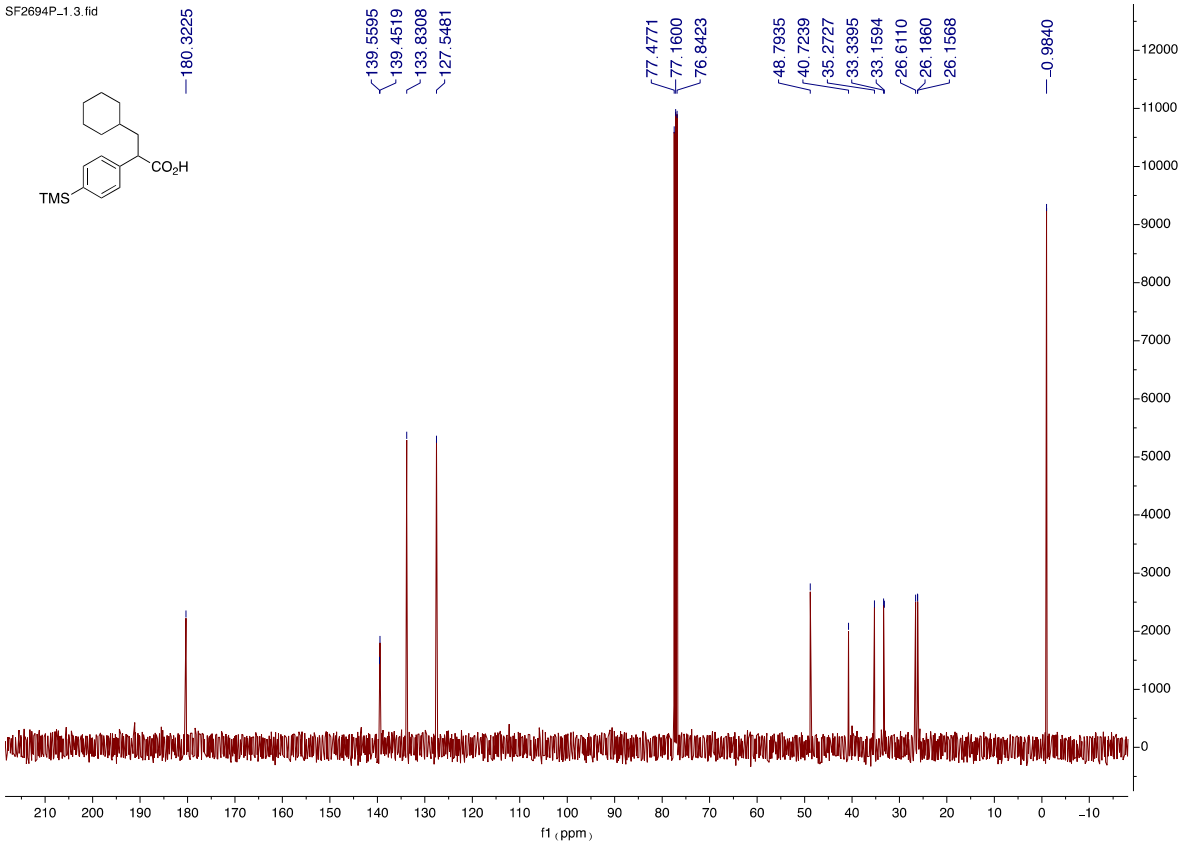

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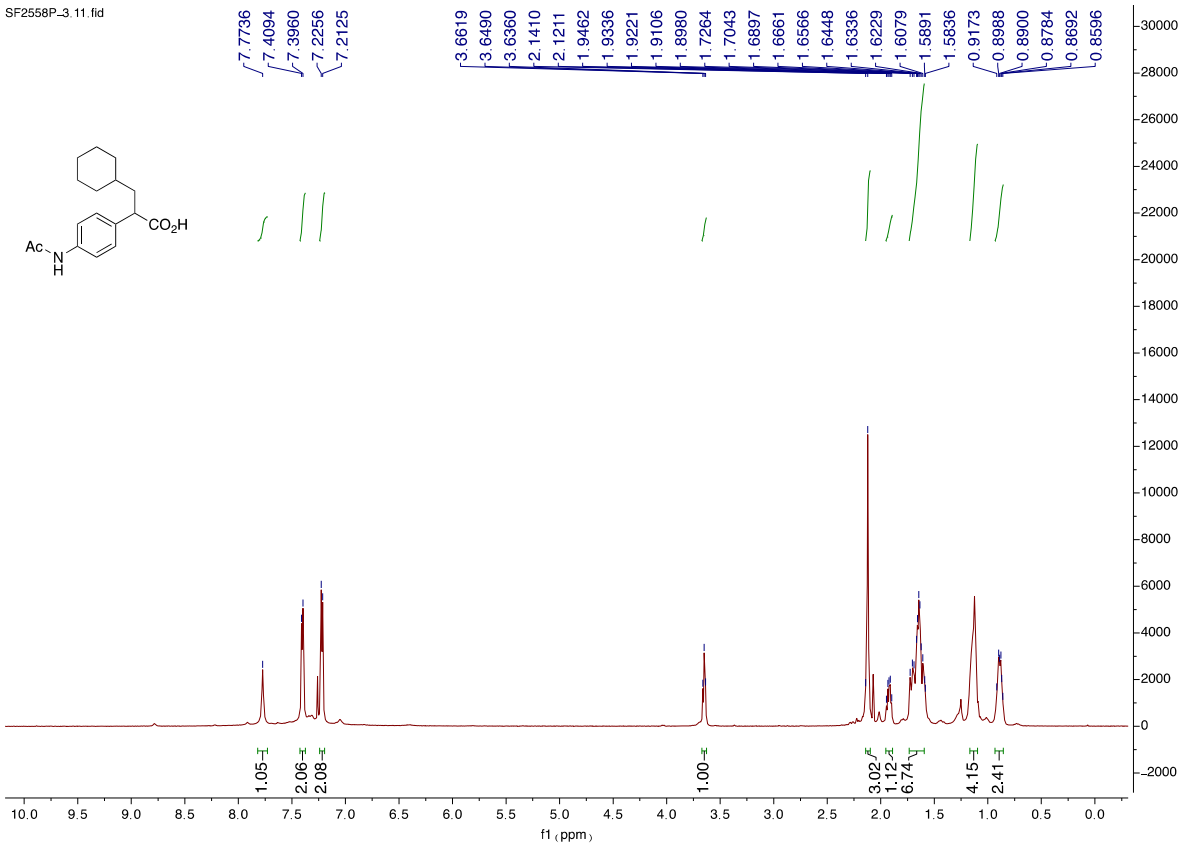

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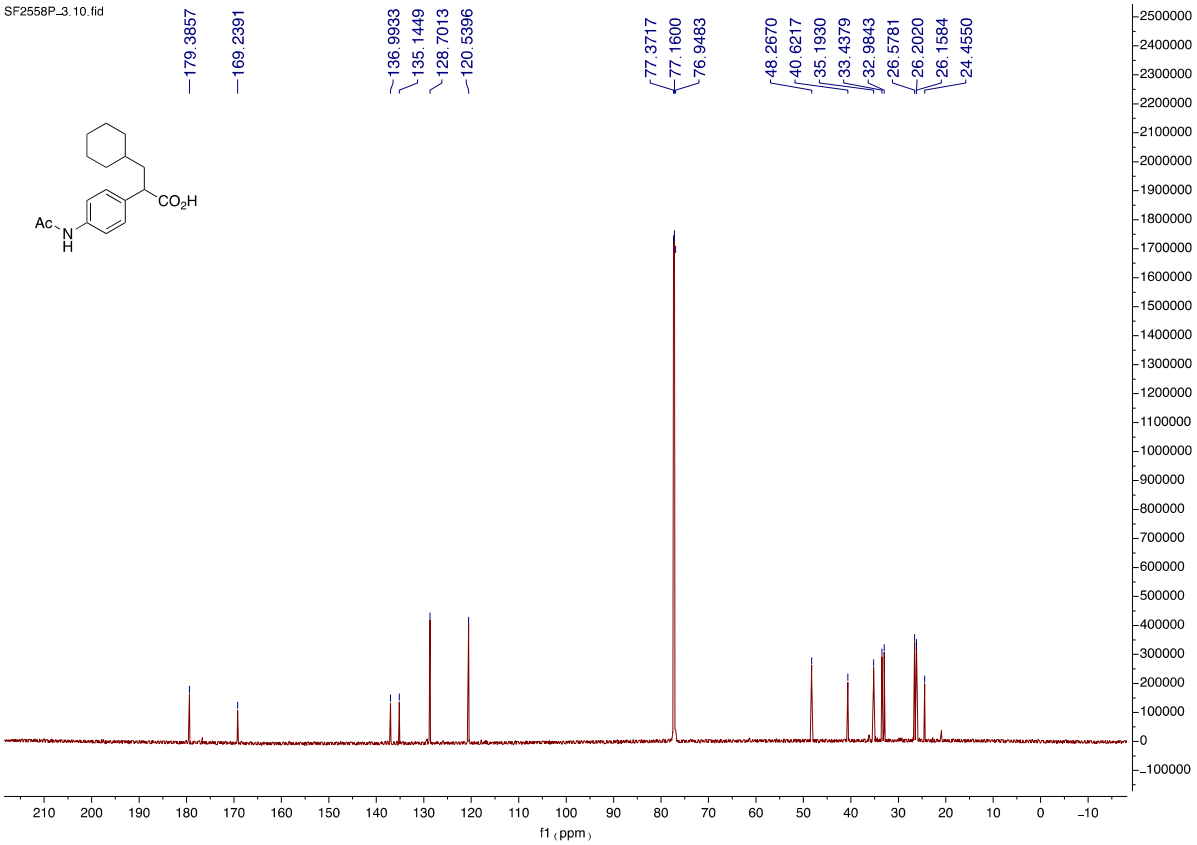

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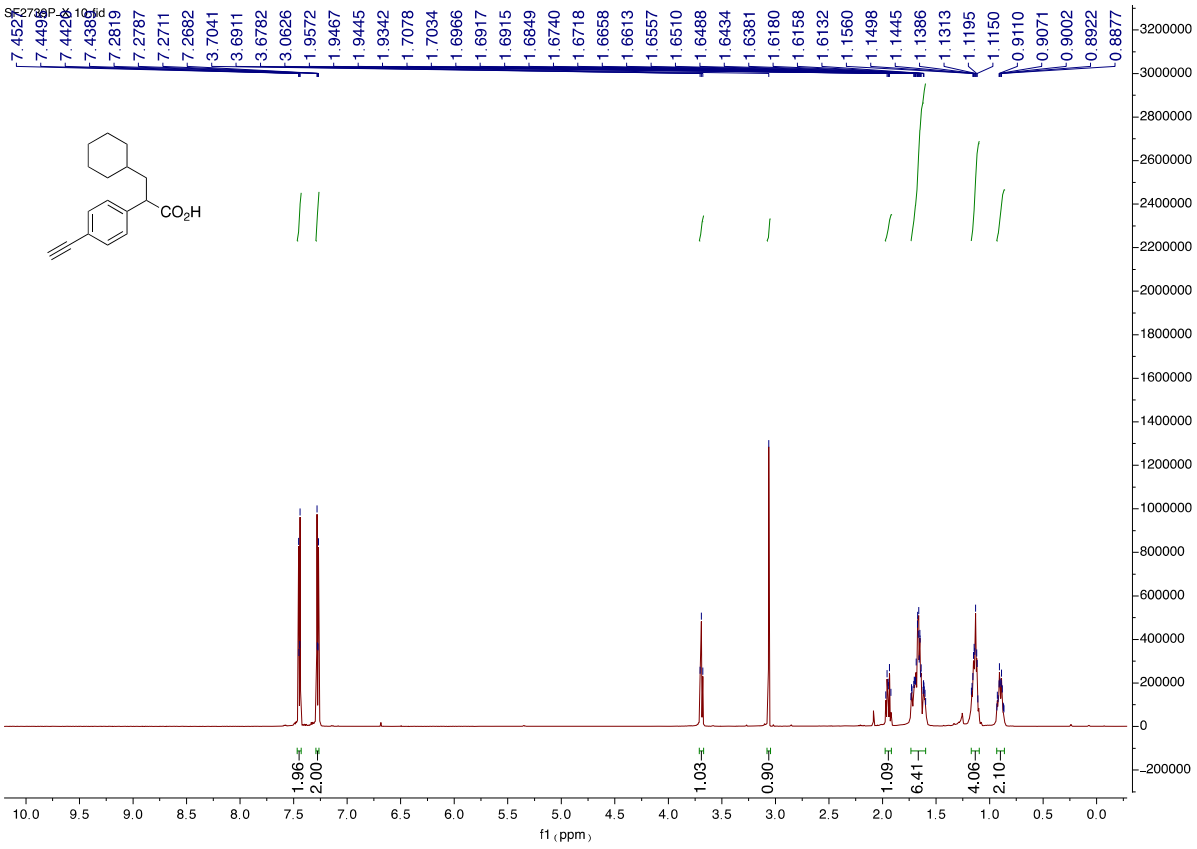

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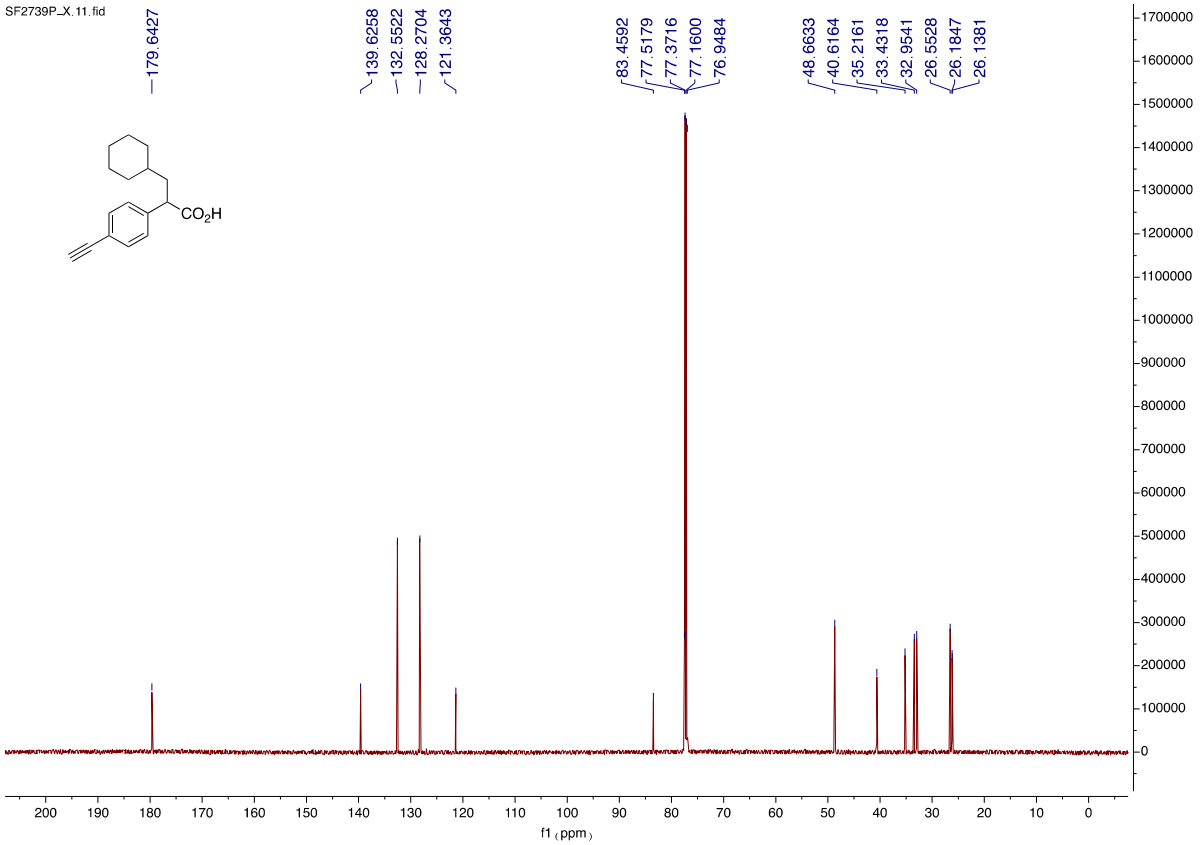

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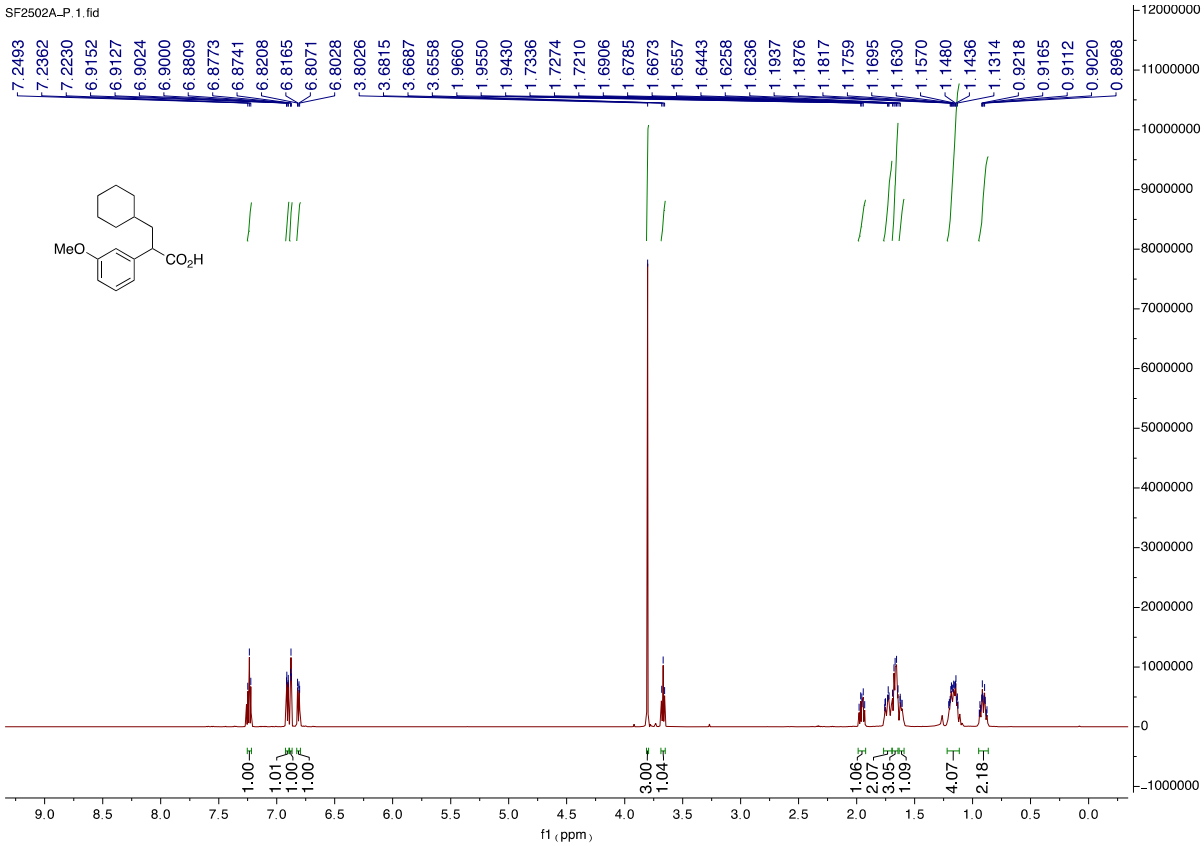

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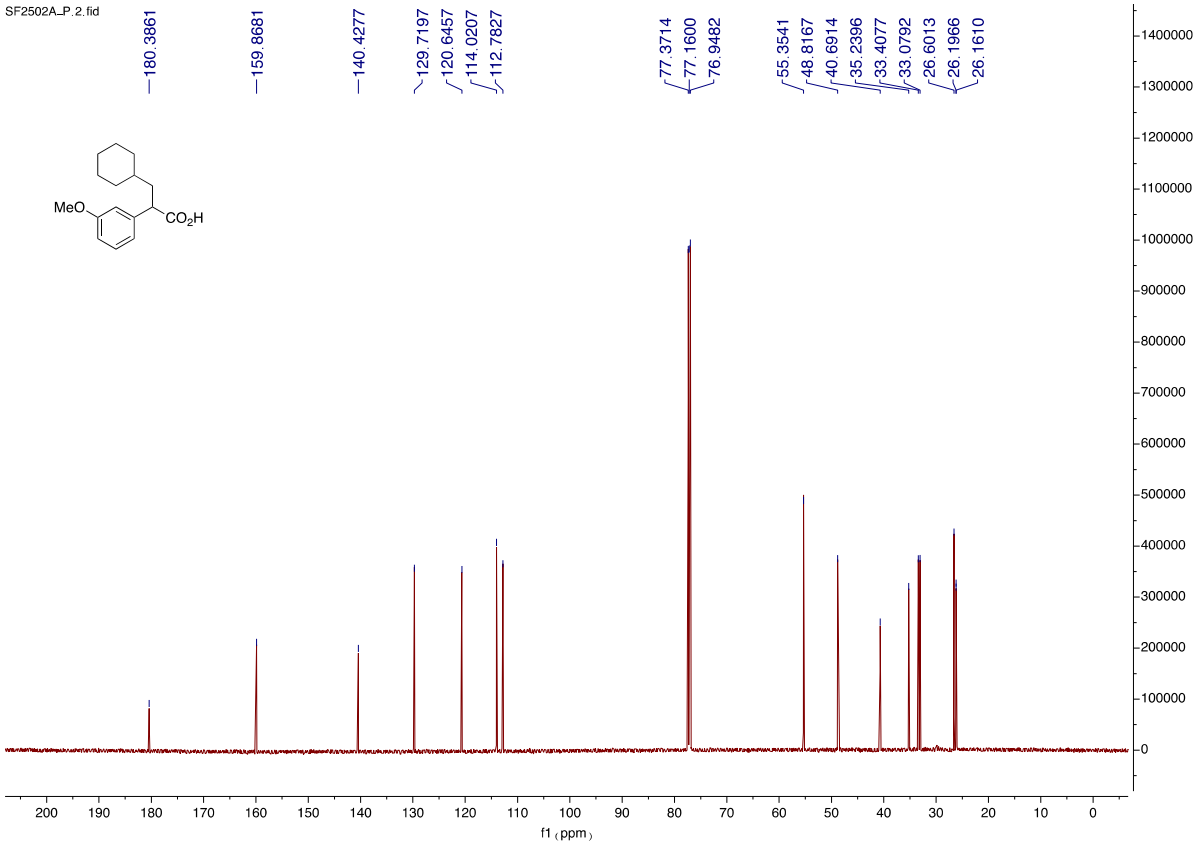

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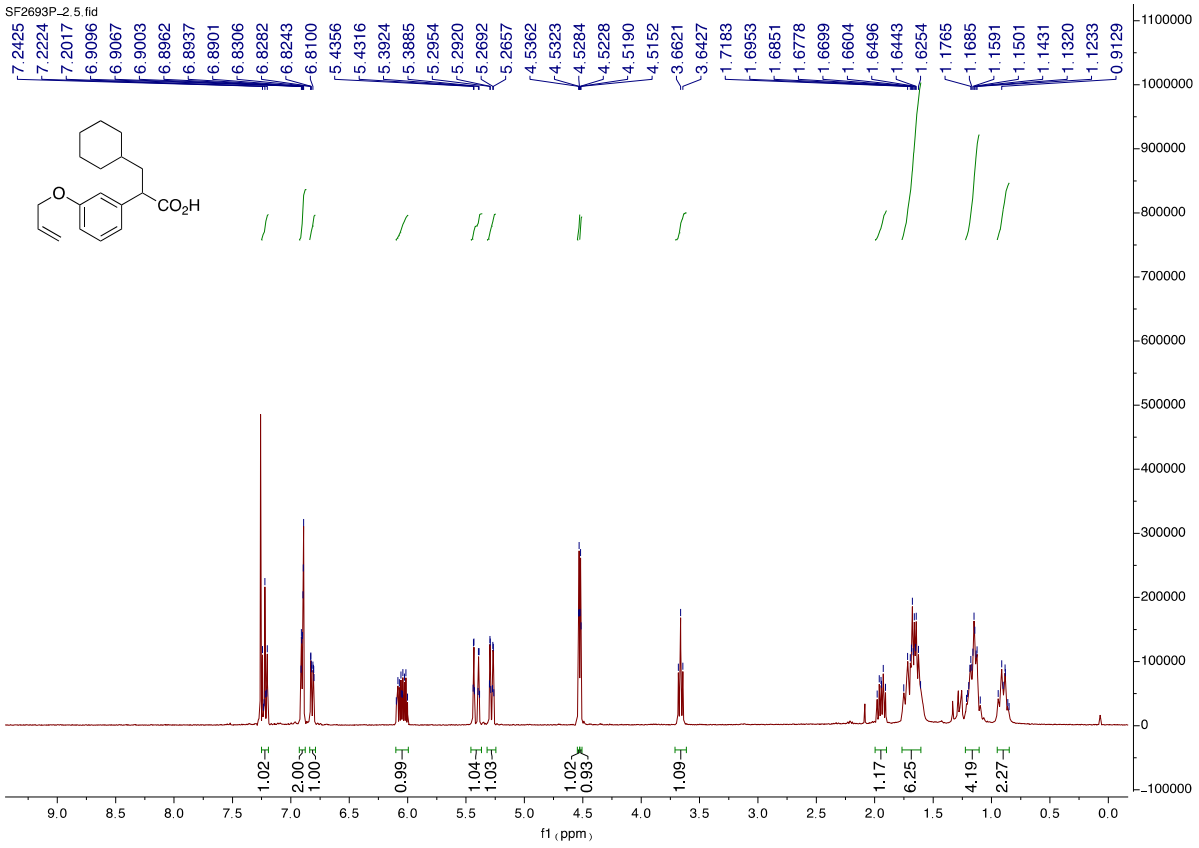

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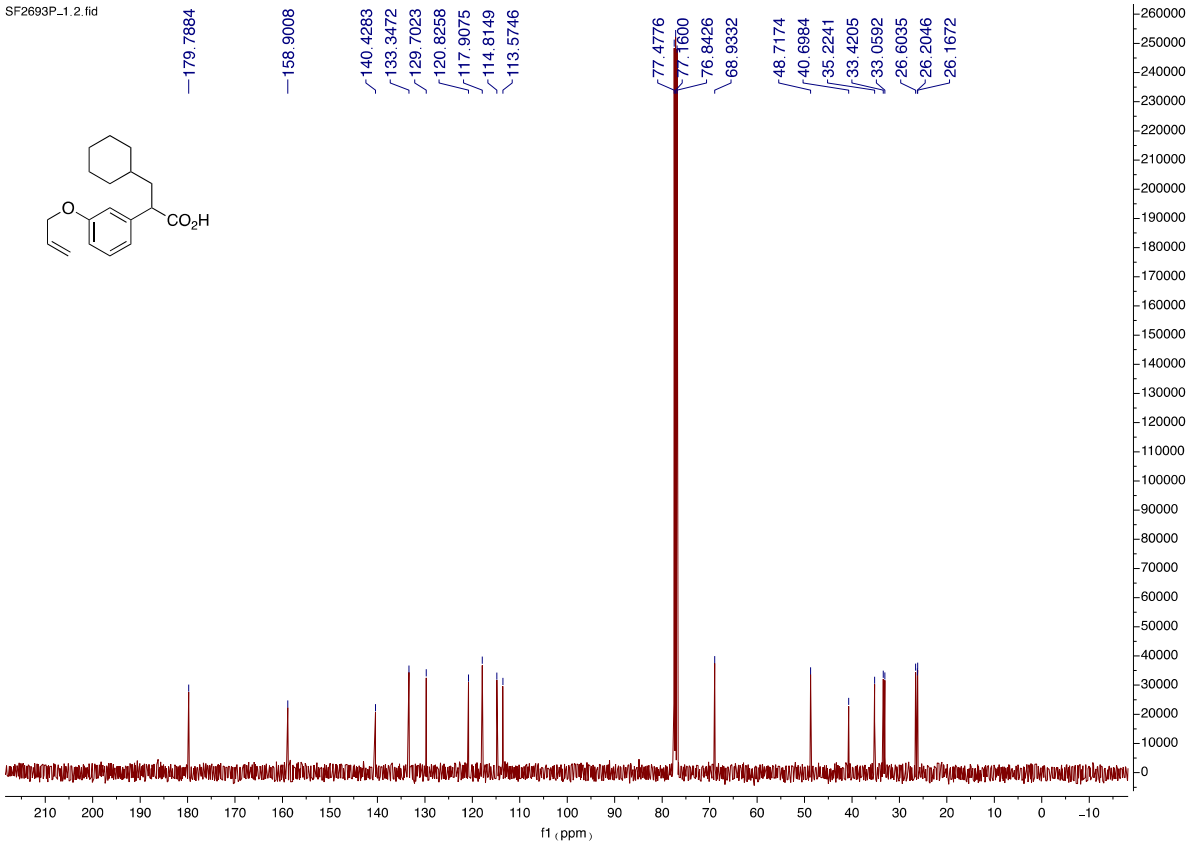

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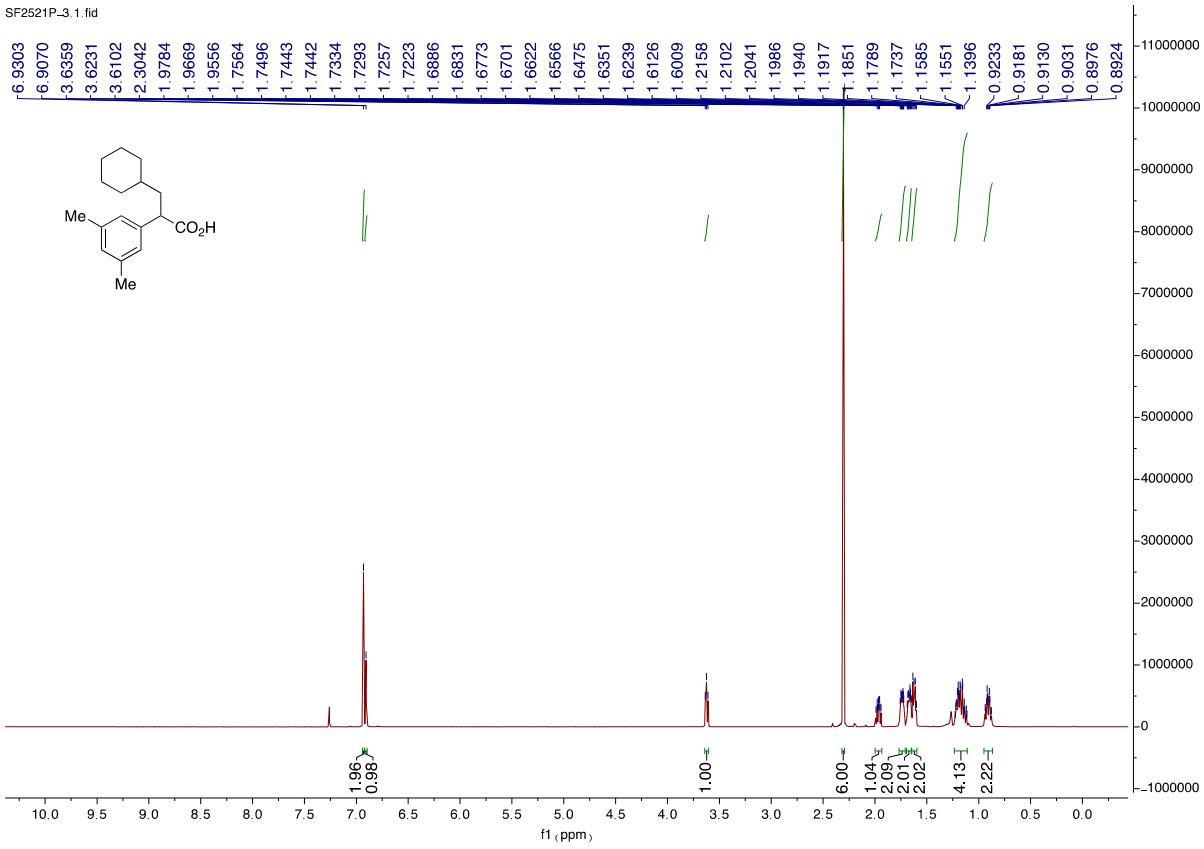

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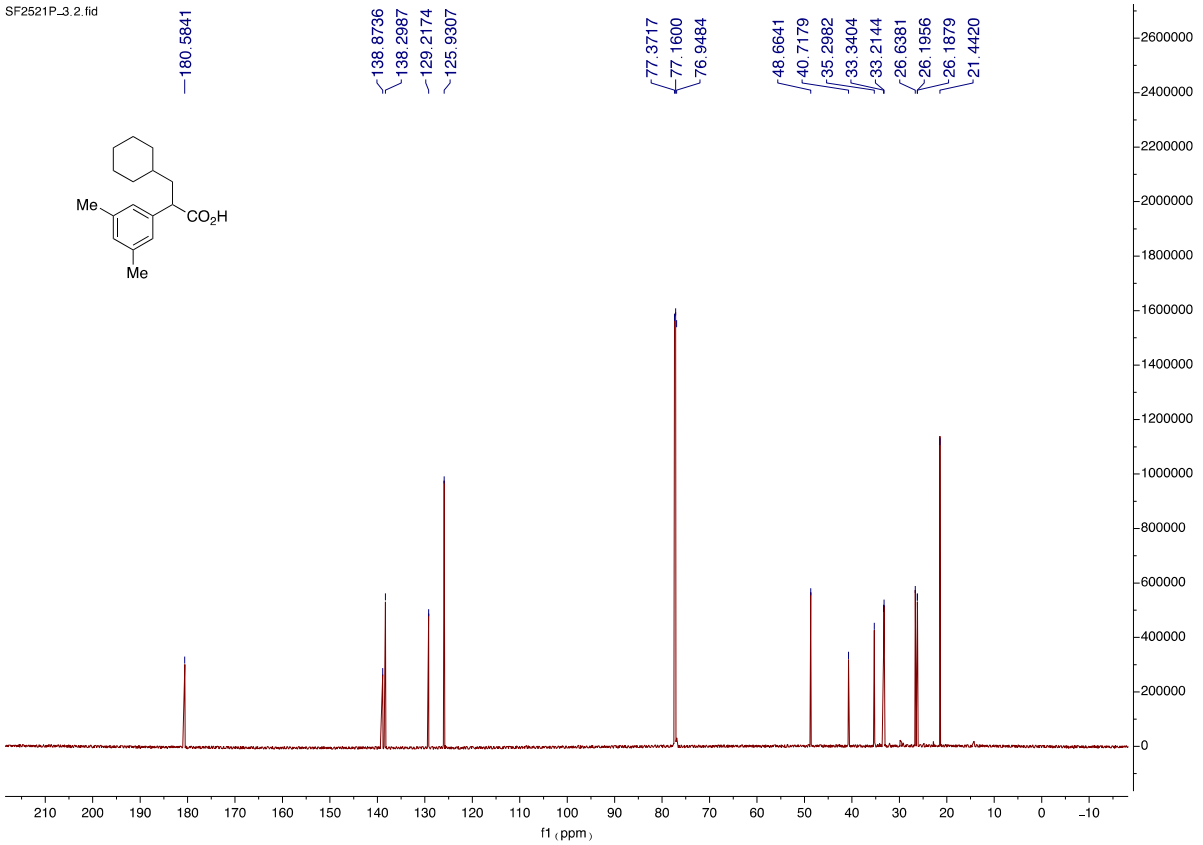

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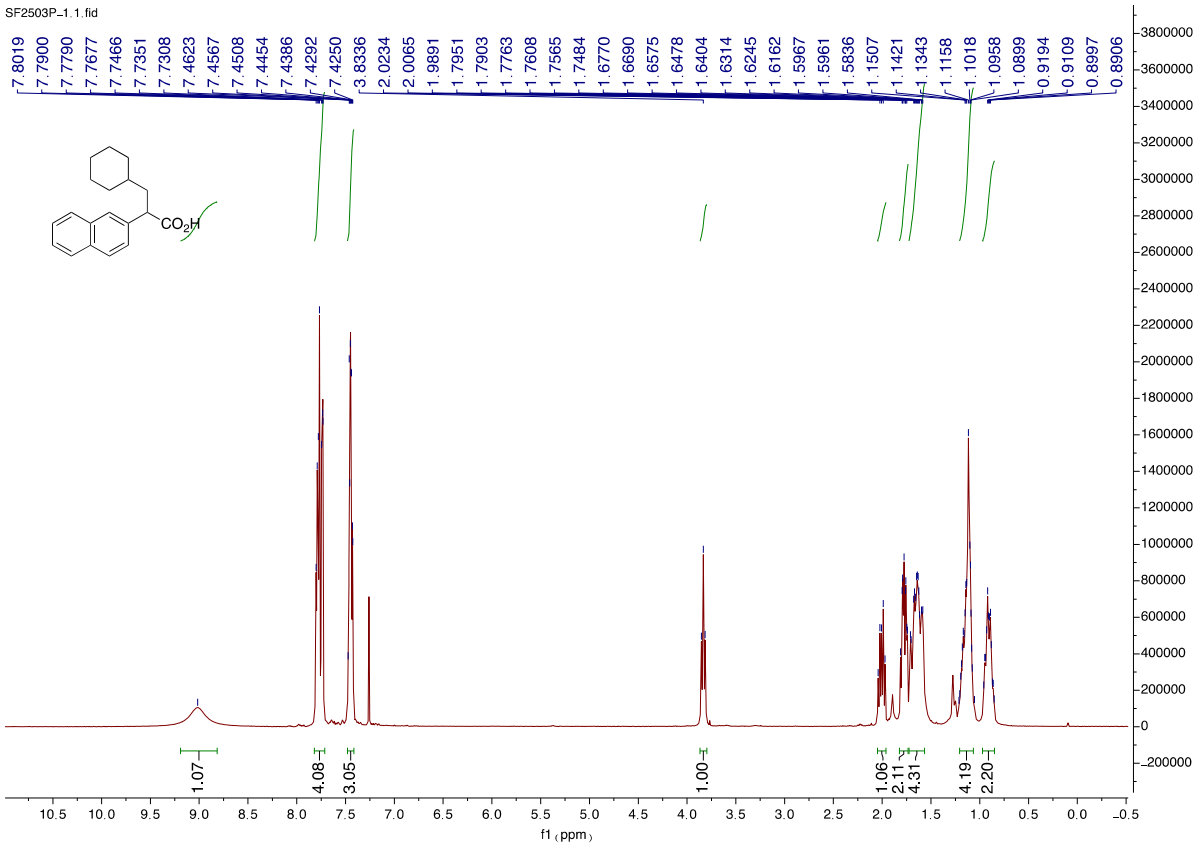
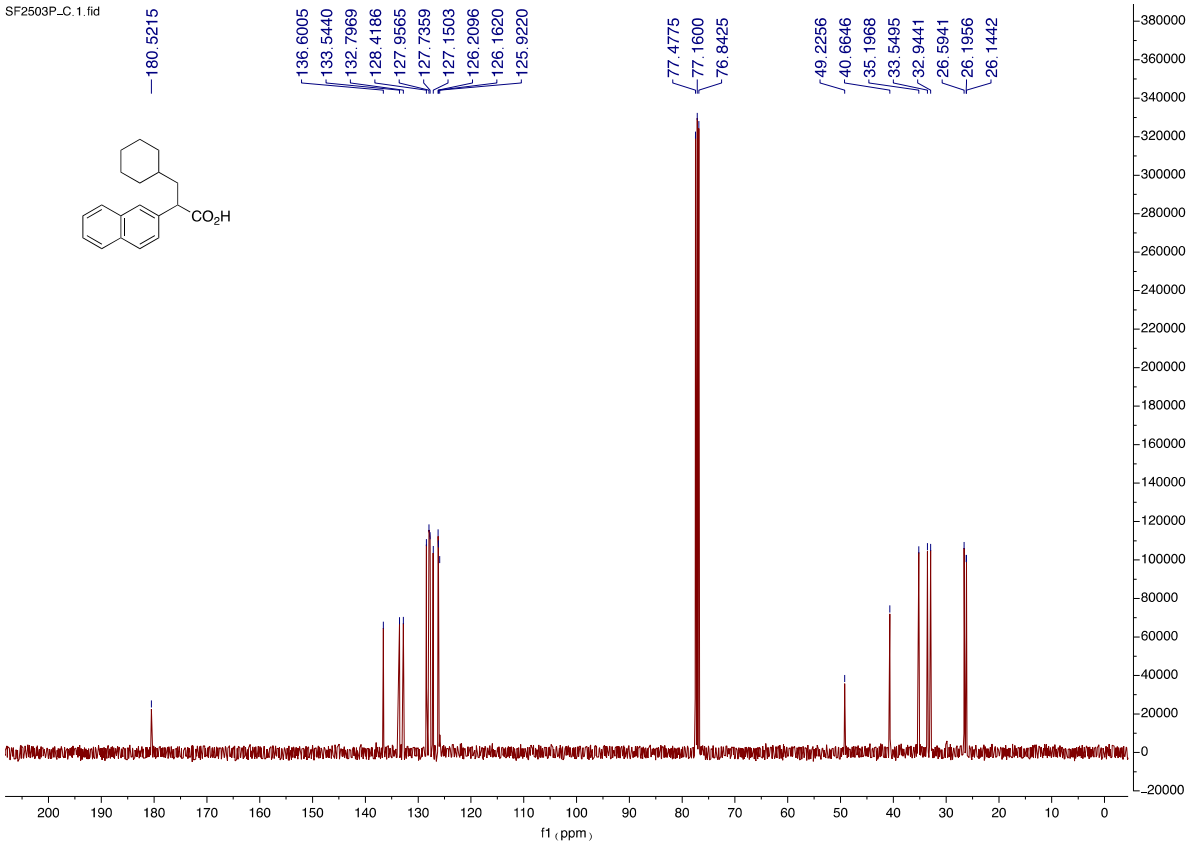
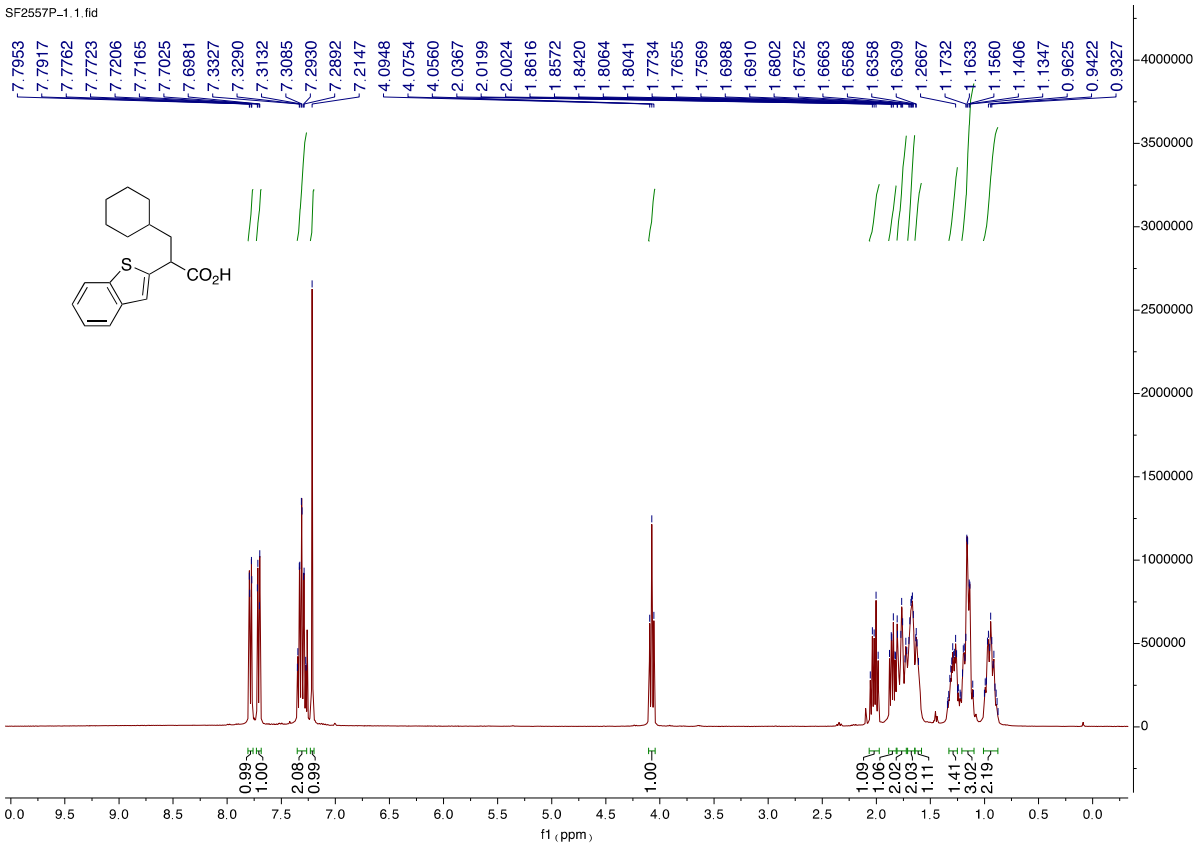


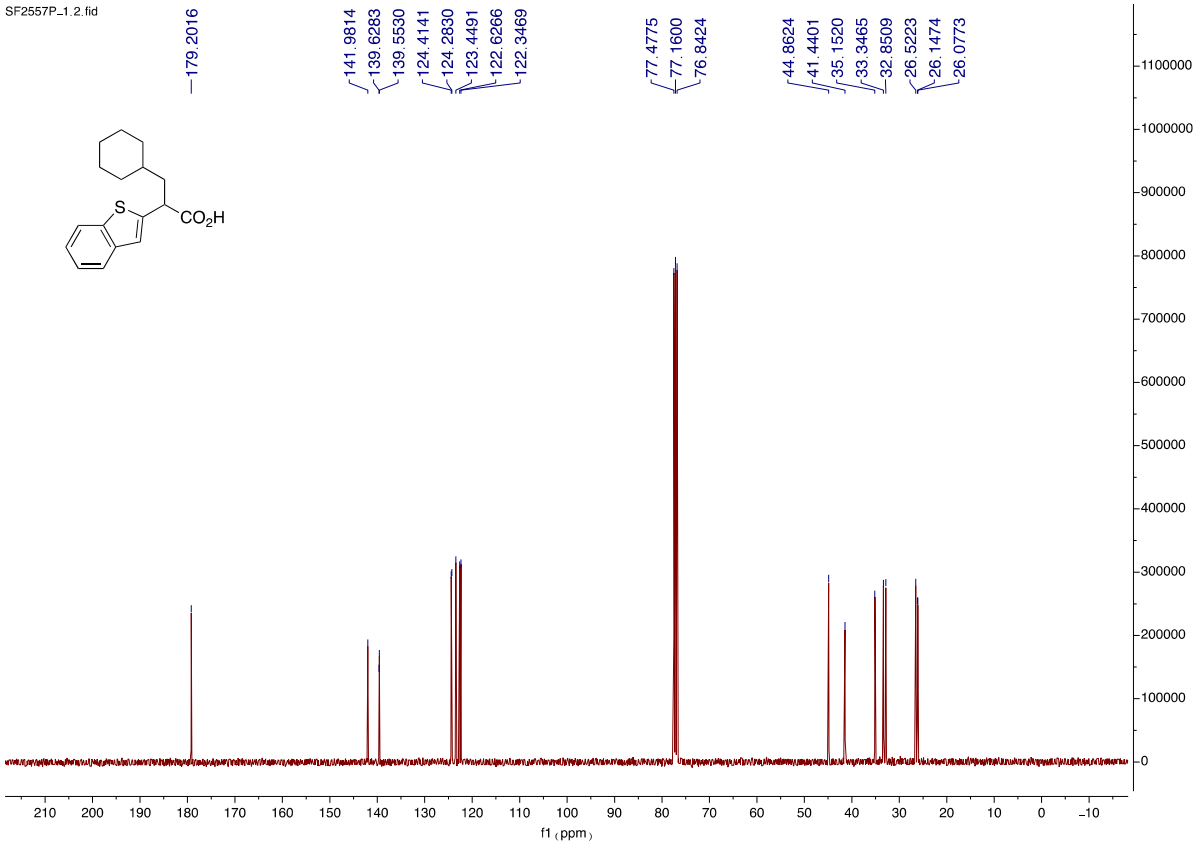
3k ^{1}H NMR (400 MHz, $CDCl_3$)



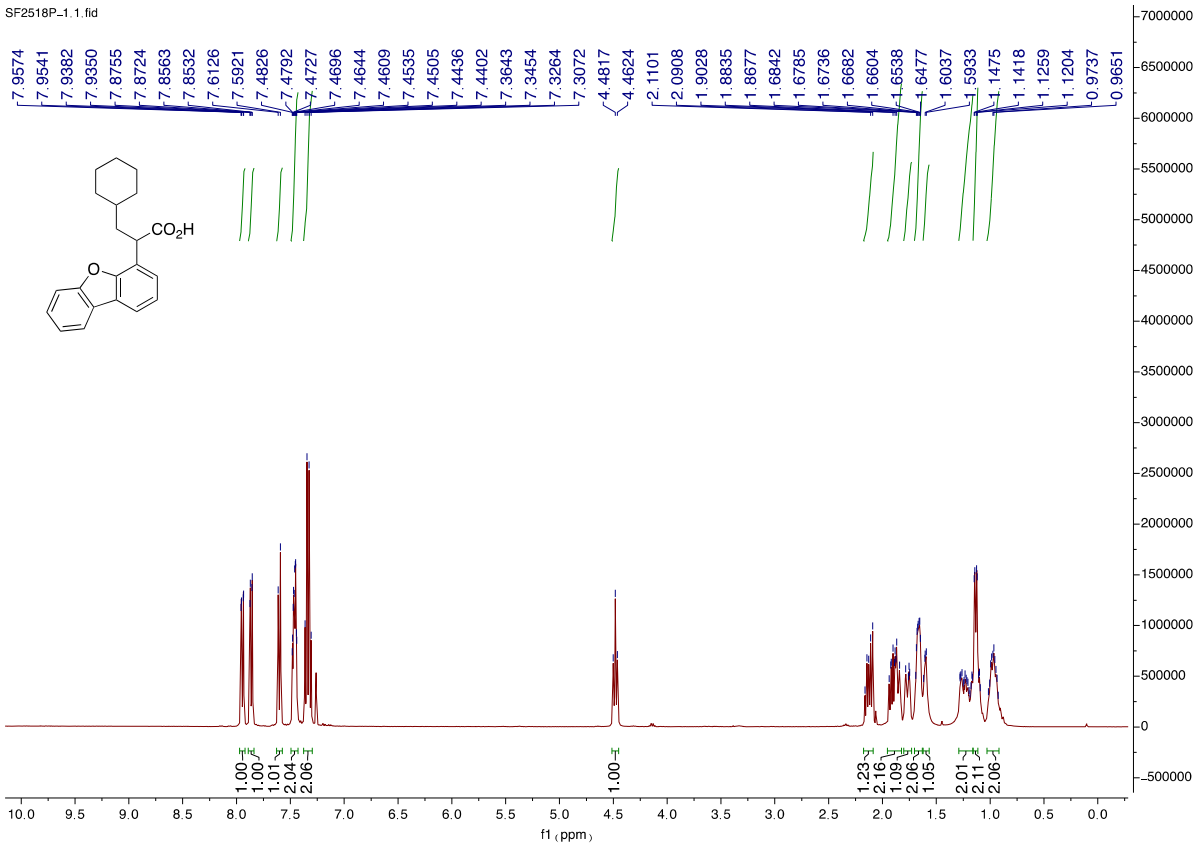
3k ^{13}C NMR (101 MHz, $CDCl_3$)



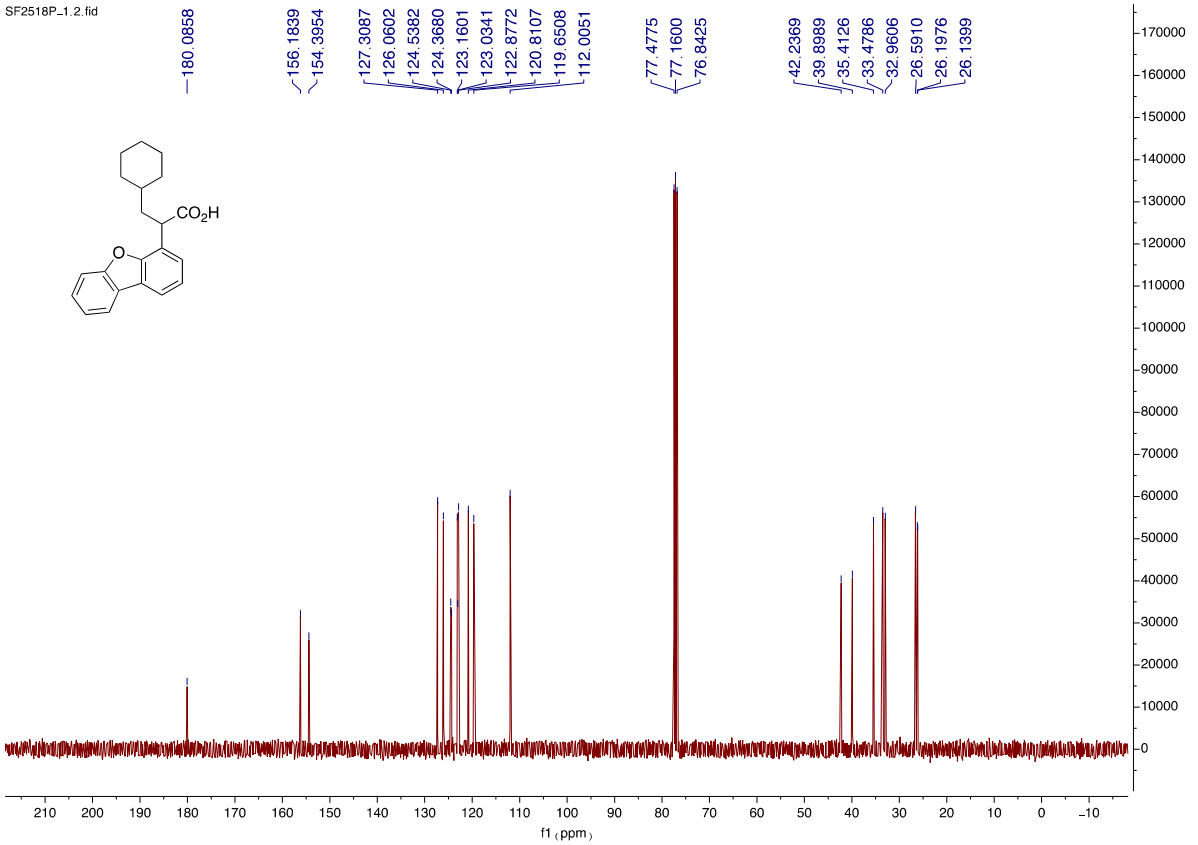
3l ^{1}H NMR (400 MHz, $CDCl_3$)



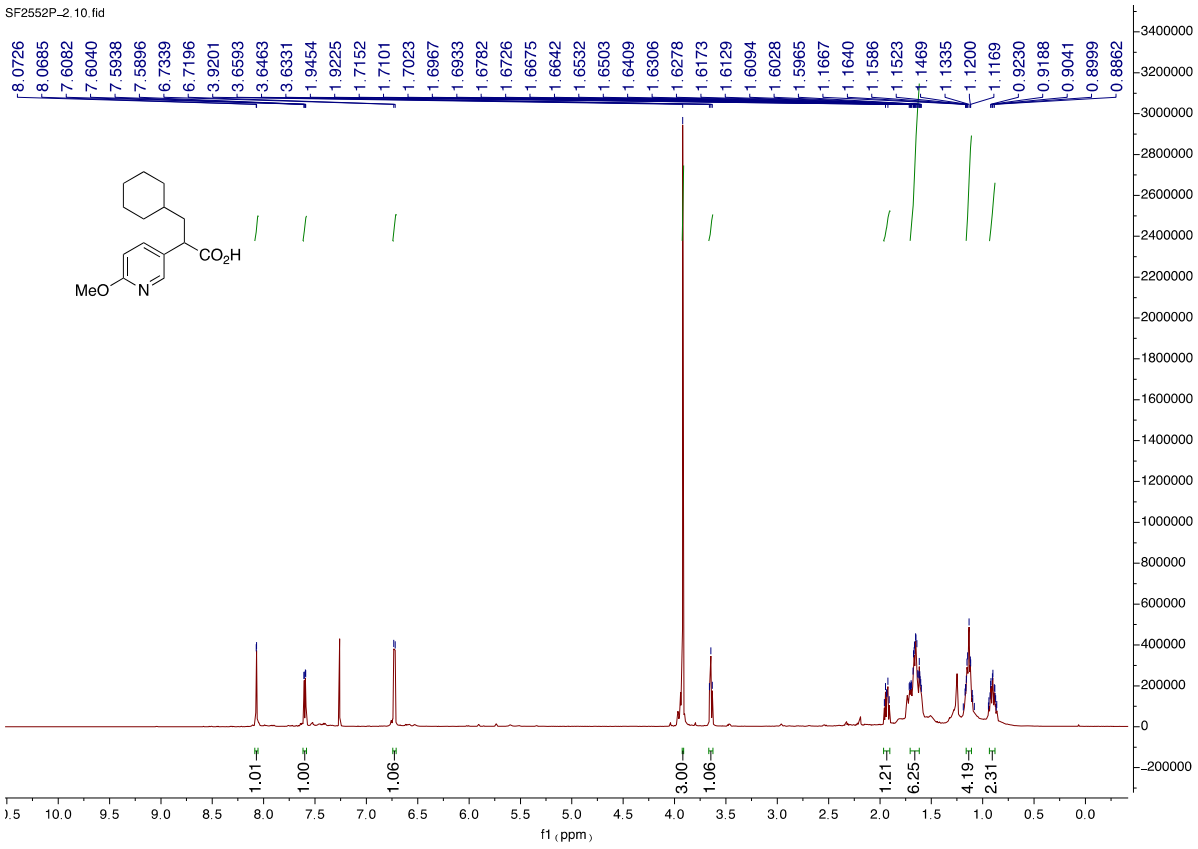
3l ^{13}C NMR (101 MHz, $CDCl_3$)



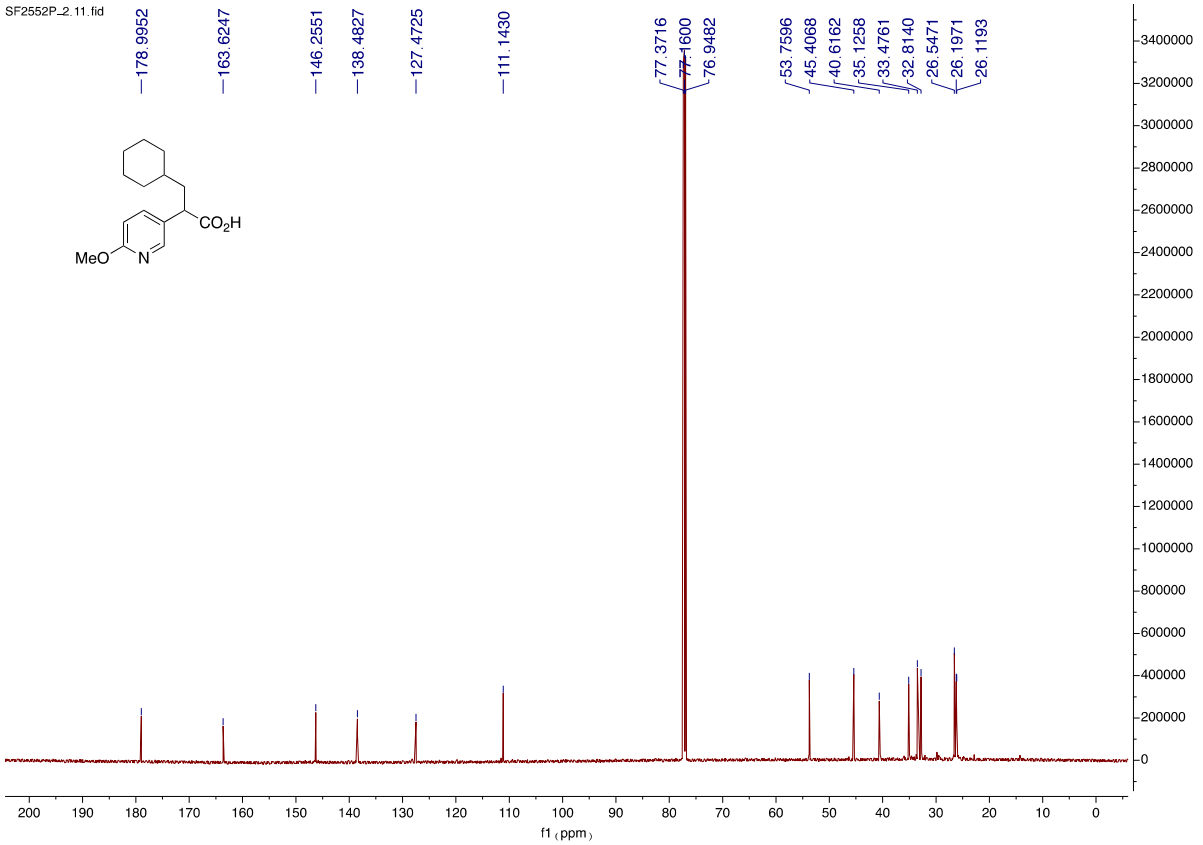
3m ^{1}H NMR (400 MHz, $CDCl_3$)



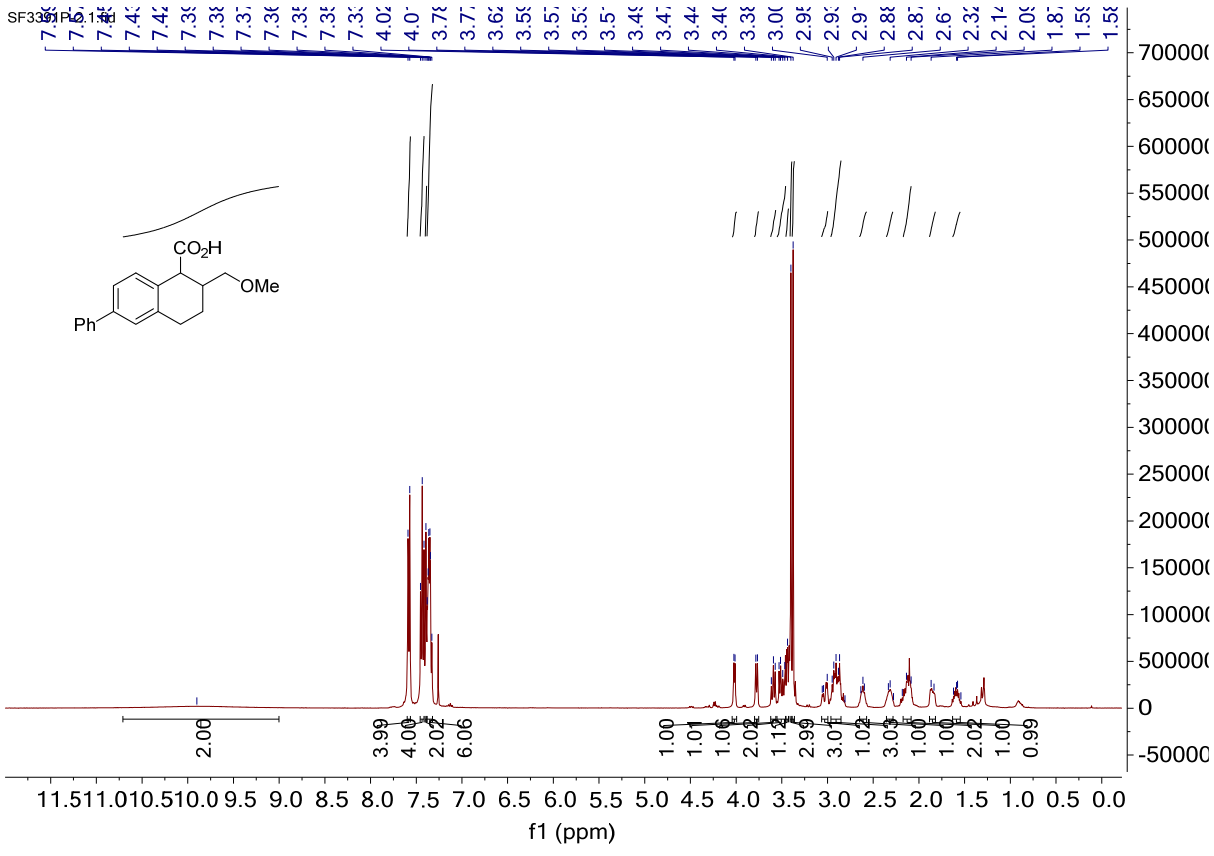
3m ^{13}C NMR (101 MHz, $CDCl_3$)



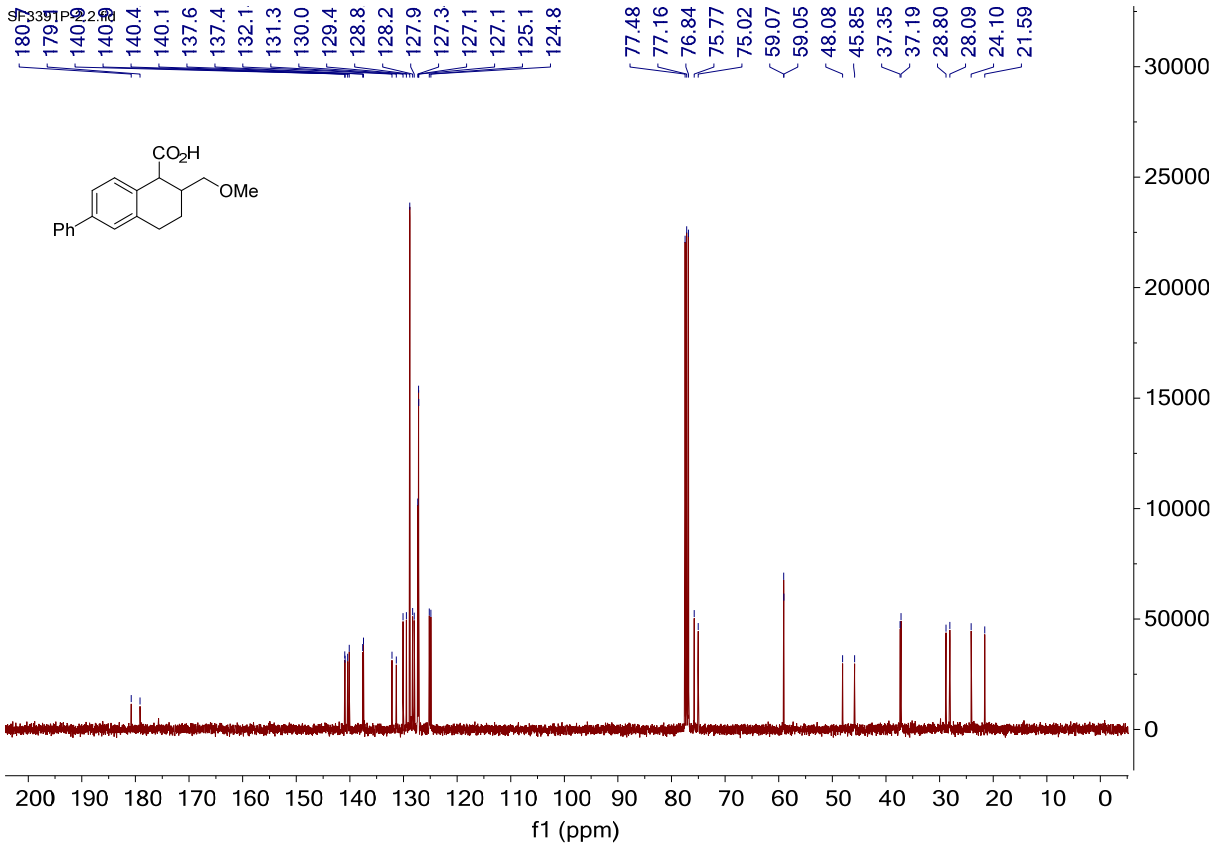
3n ^{1}H NMR (600 MHz, $CDCl_3$)



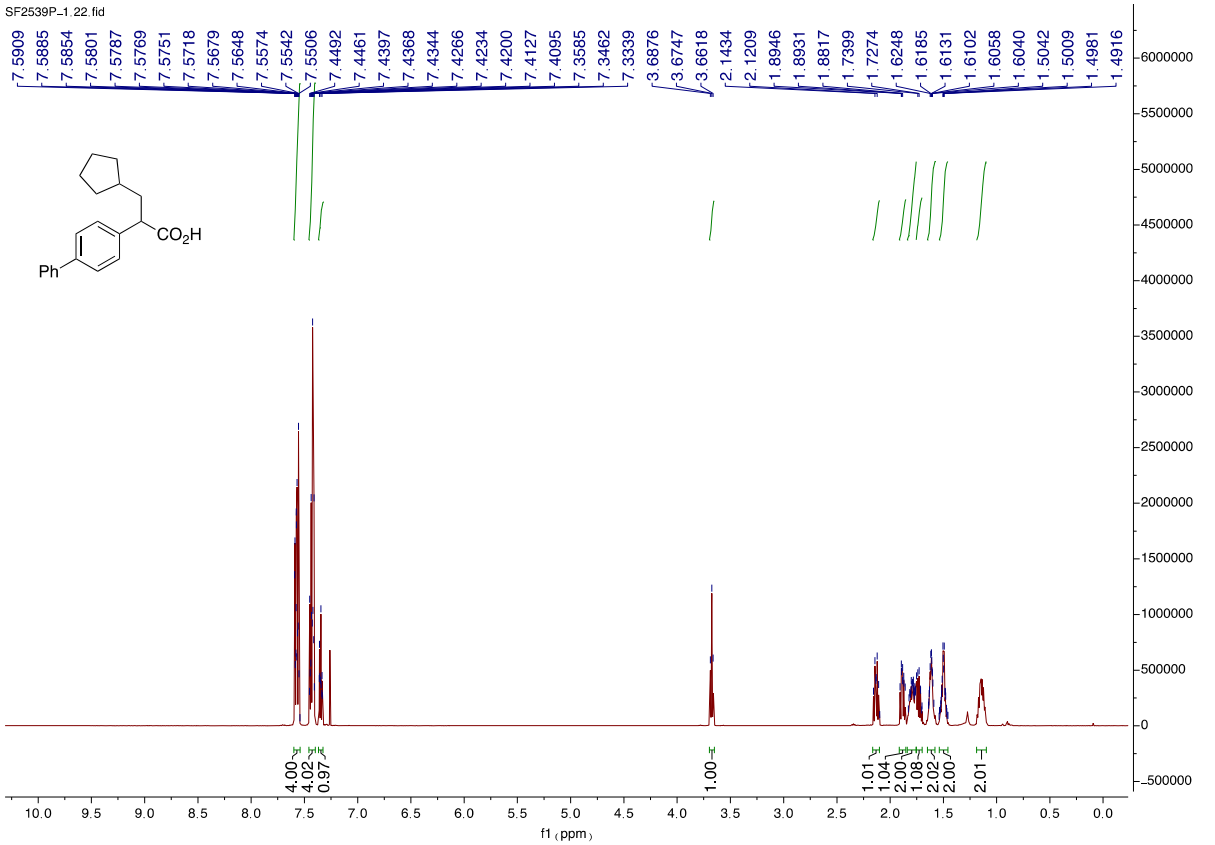
3n ^{13}C NMR (151 MHz, $CDCl_3$)



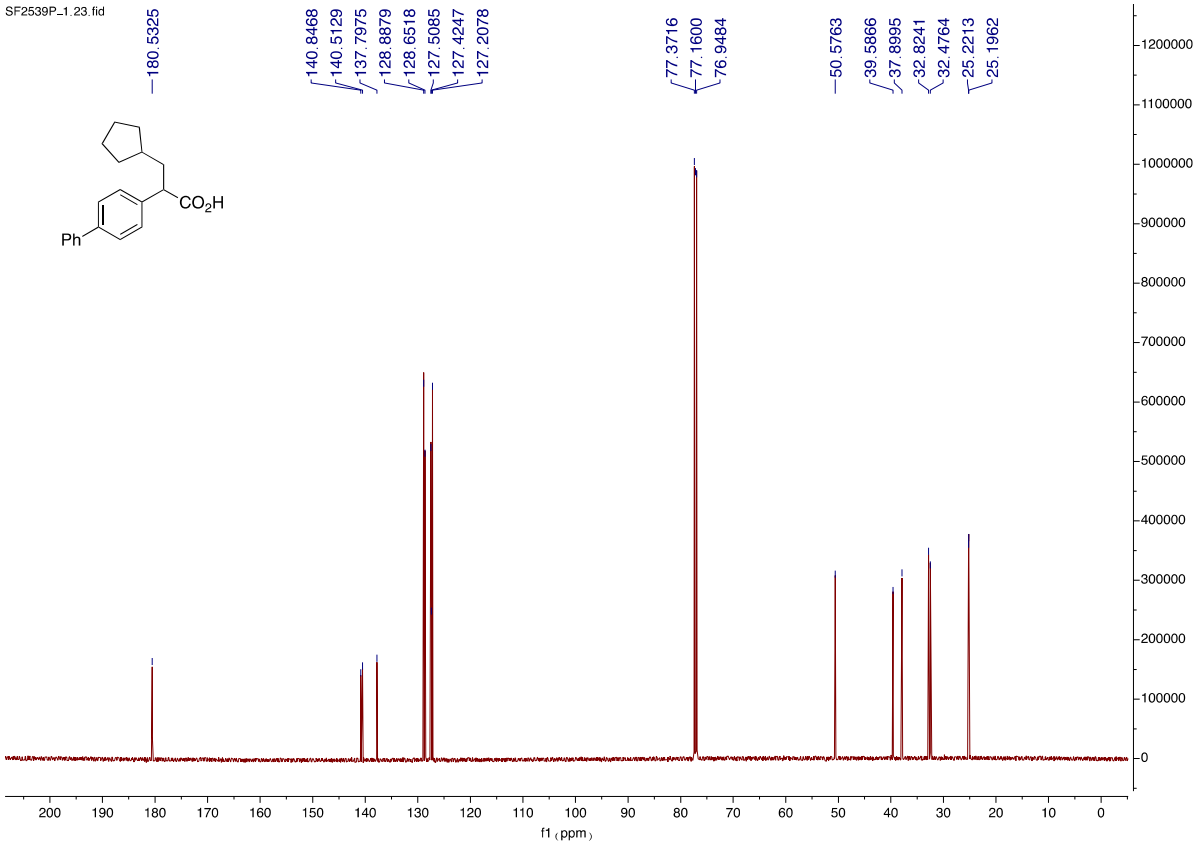
3o ^{1}H NMR (400 MHz, $CDCl_3$)



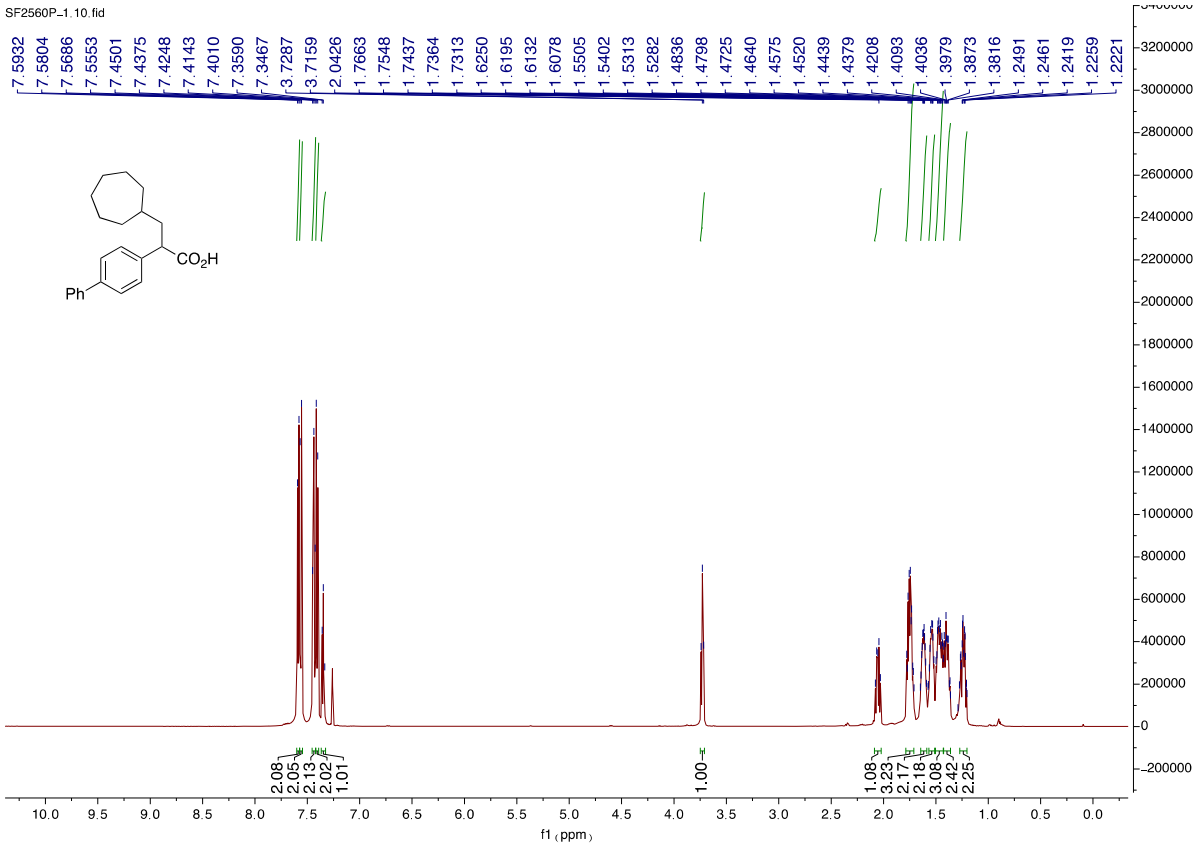
3o ^{13}C NMR (101 MHz, $CDCl_3$)



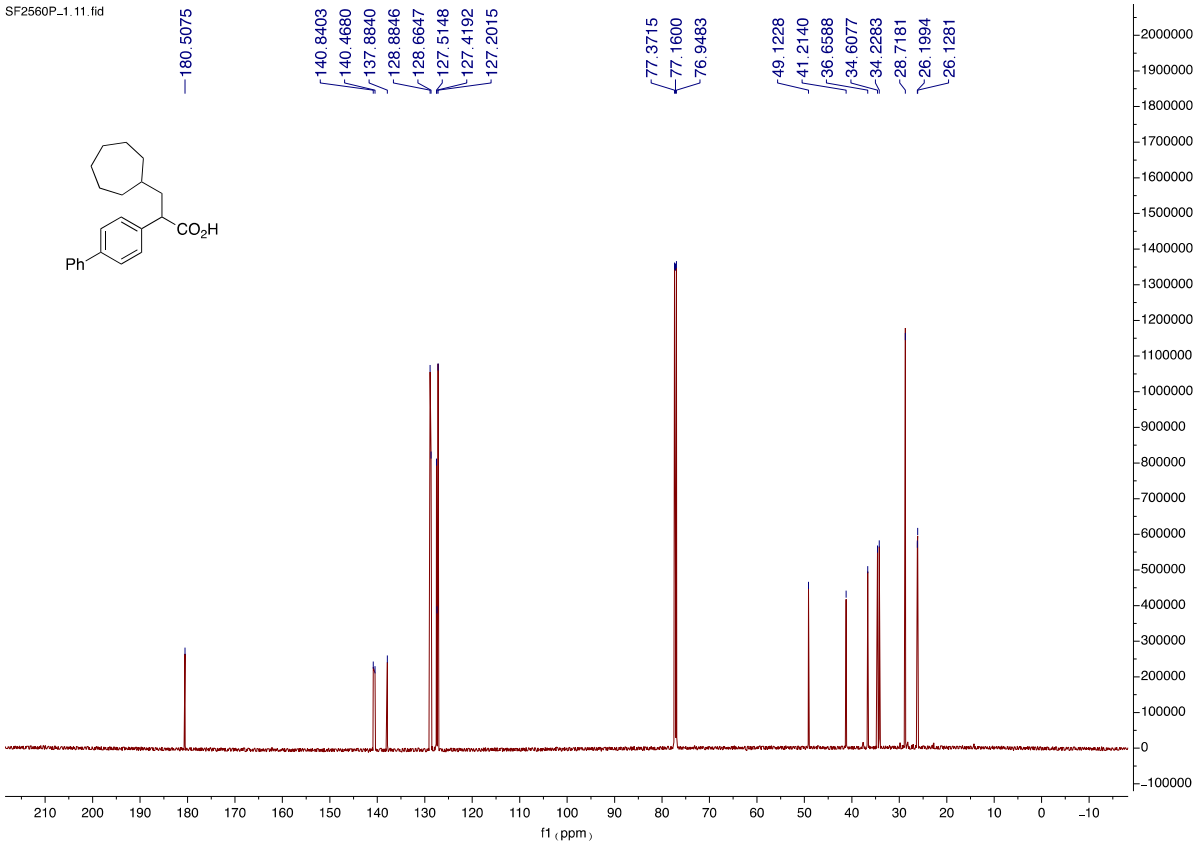
3p ^{1}H NMR (600 MHz, $CDCl_3$)



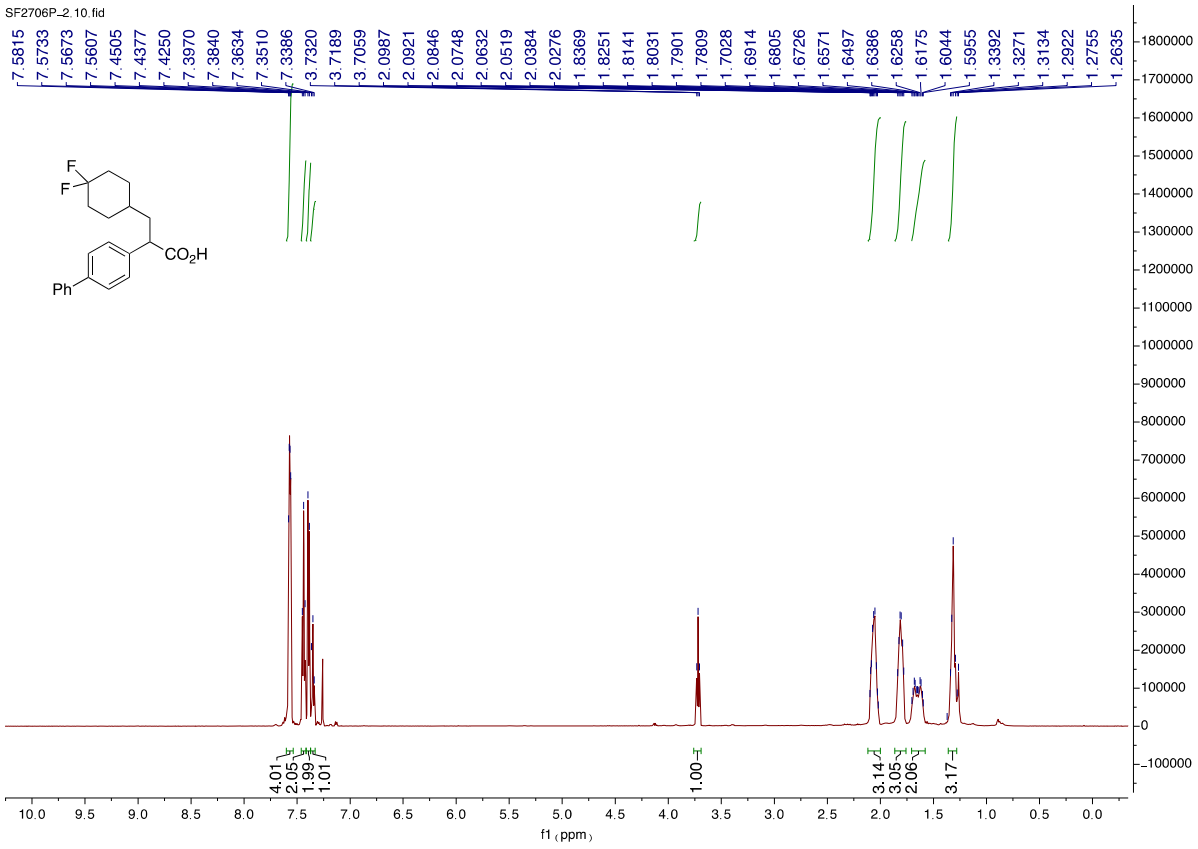
3p ^{13}C NMR (151 MHz, $CDCl_3$)



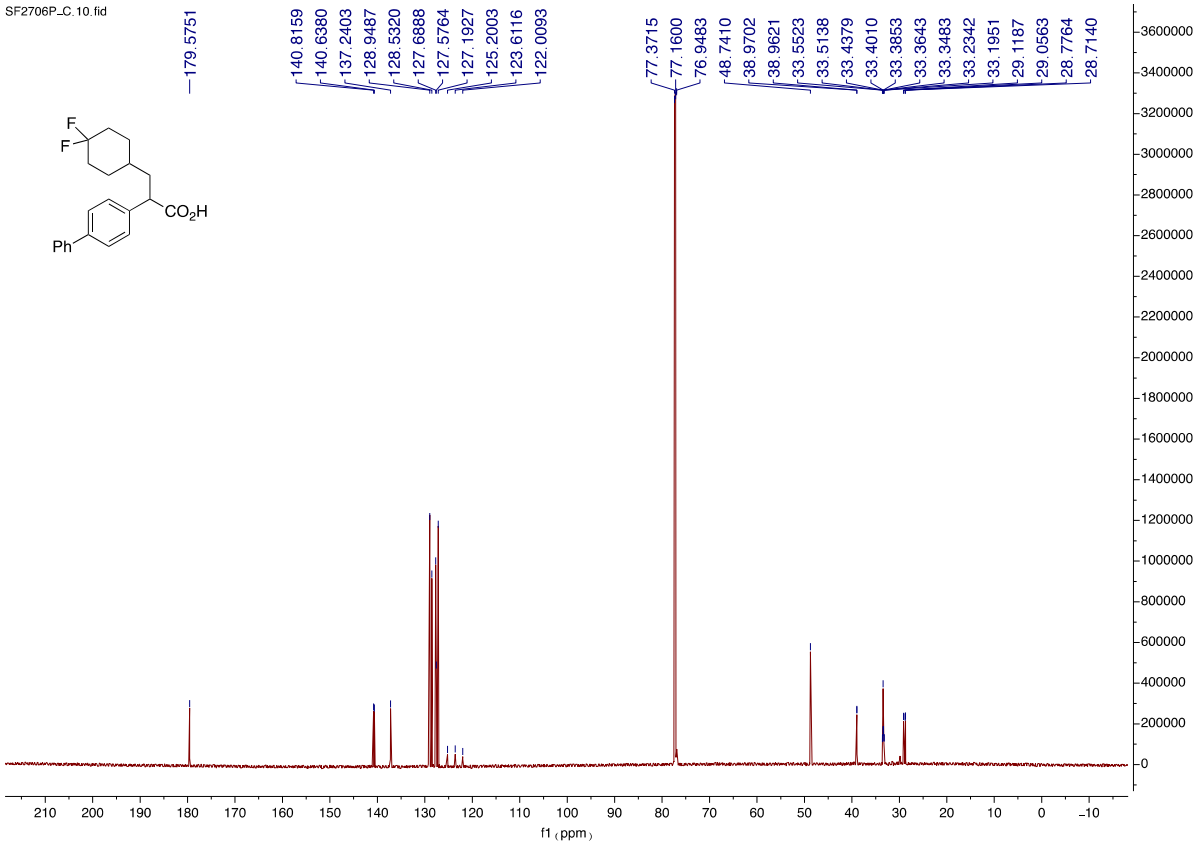
3q ^{1}H NMR (600 MHz, $CDCl_3$)



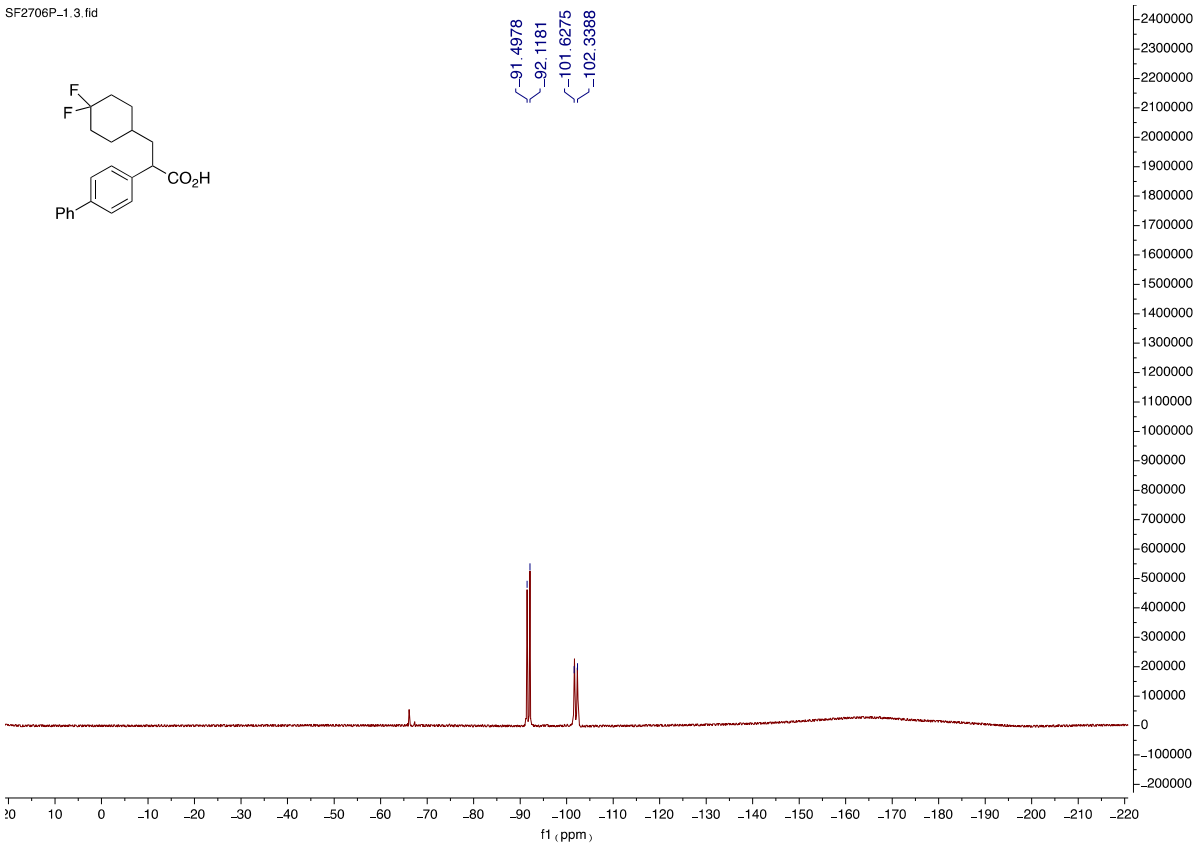
3q ^{13}C NMR (151 MHz, $CDCl_3$)



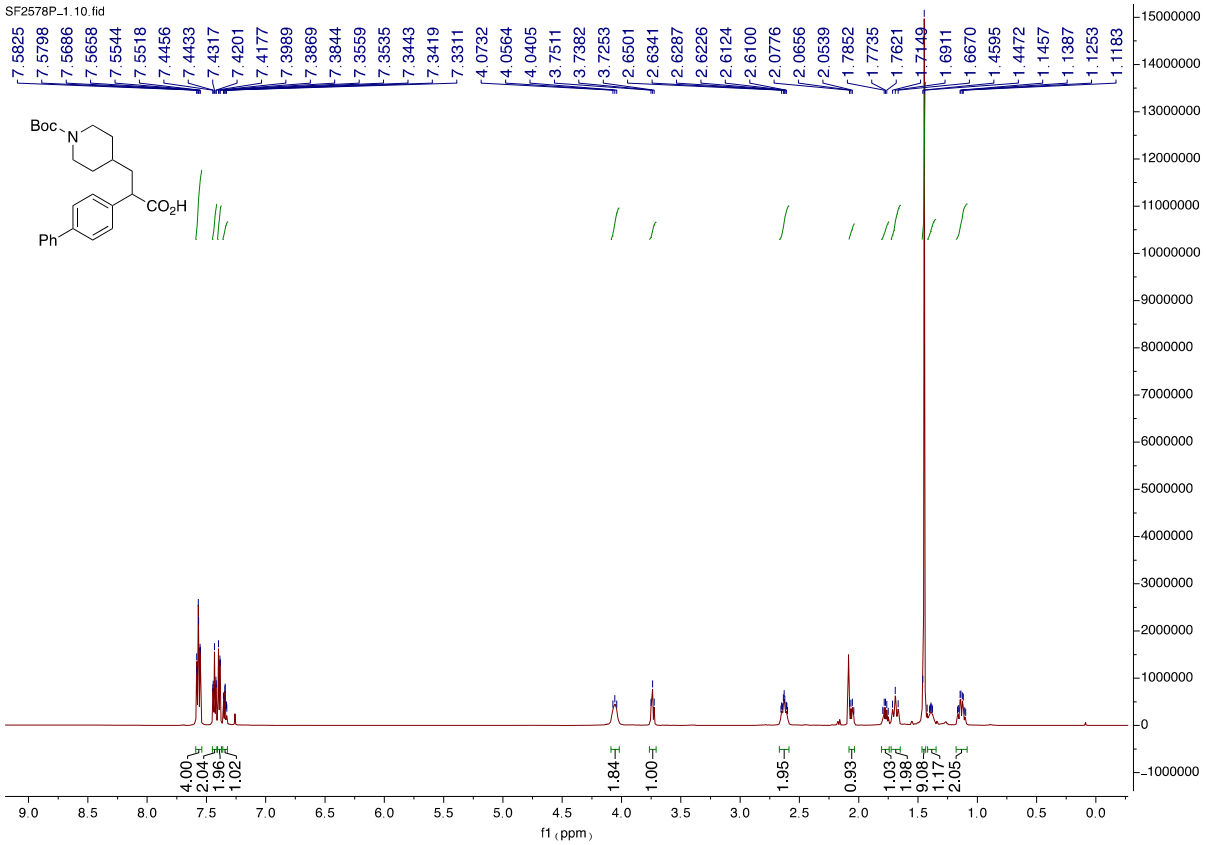
3r ^{1}H NMR (600 MHz, $CDCl_3$)



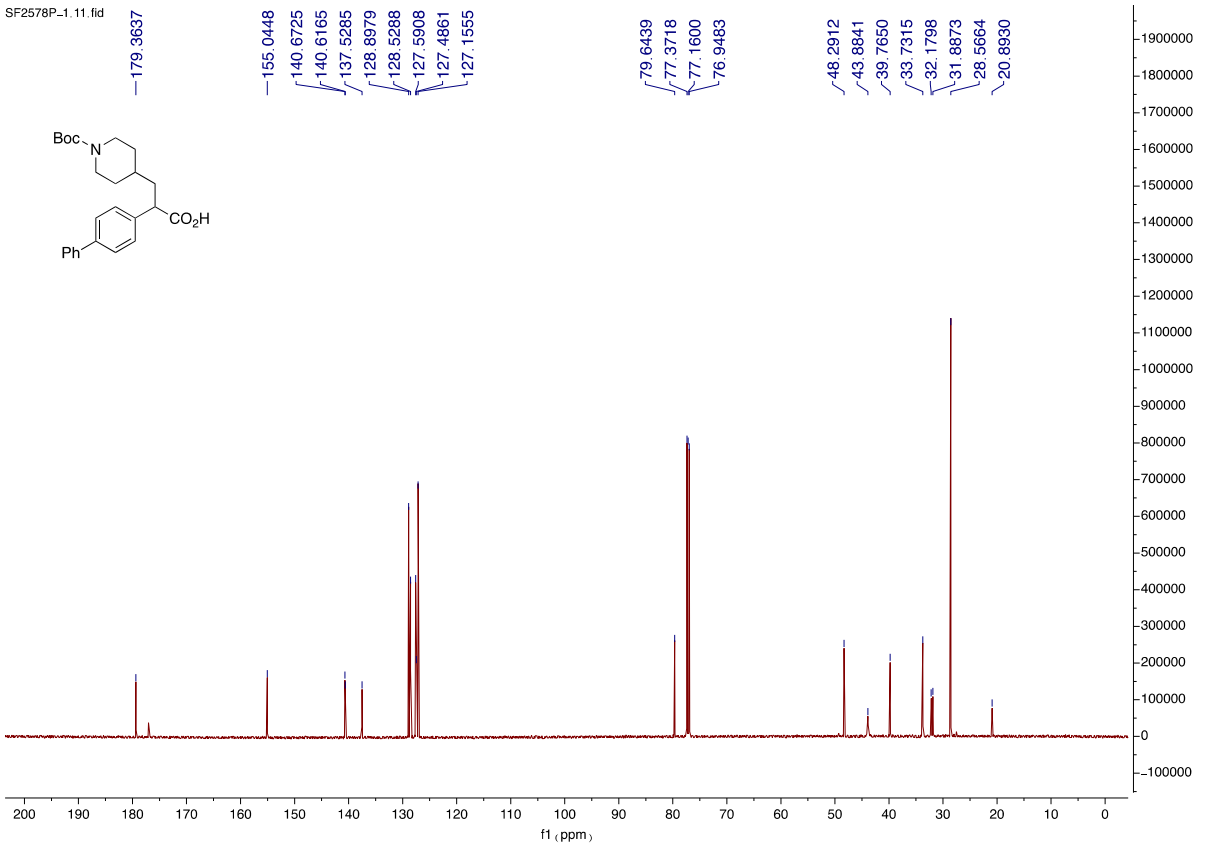
3r ^{13}C NMR (151 MHz, $CDCl_3$)



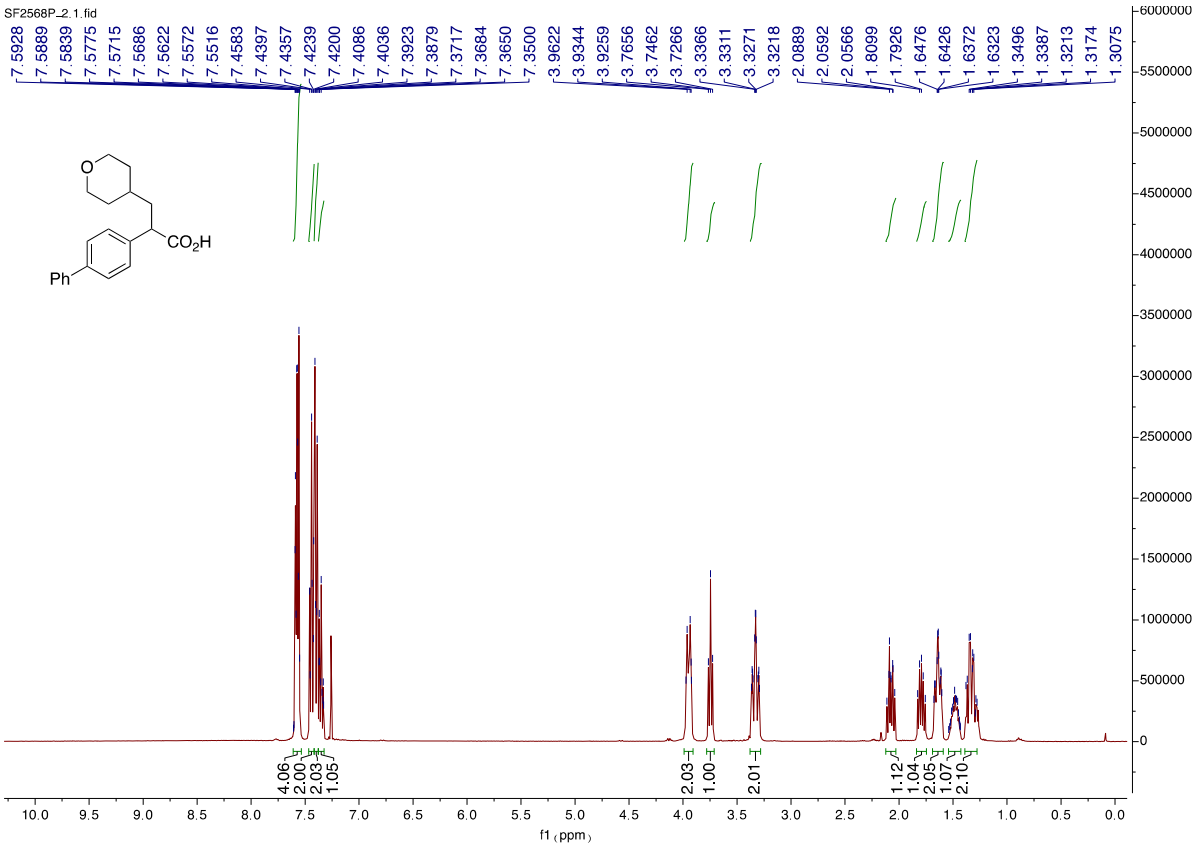
3r ^{19}F NMR (376 MHz, $CDCl_3$)



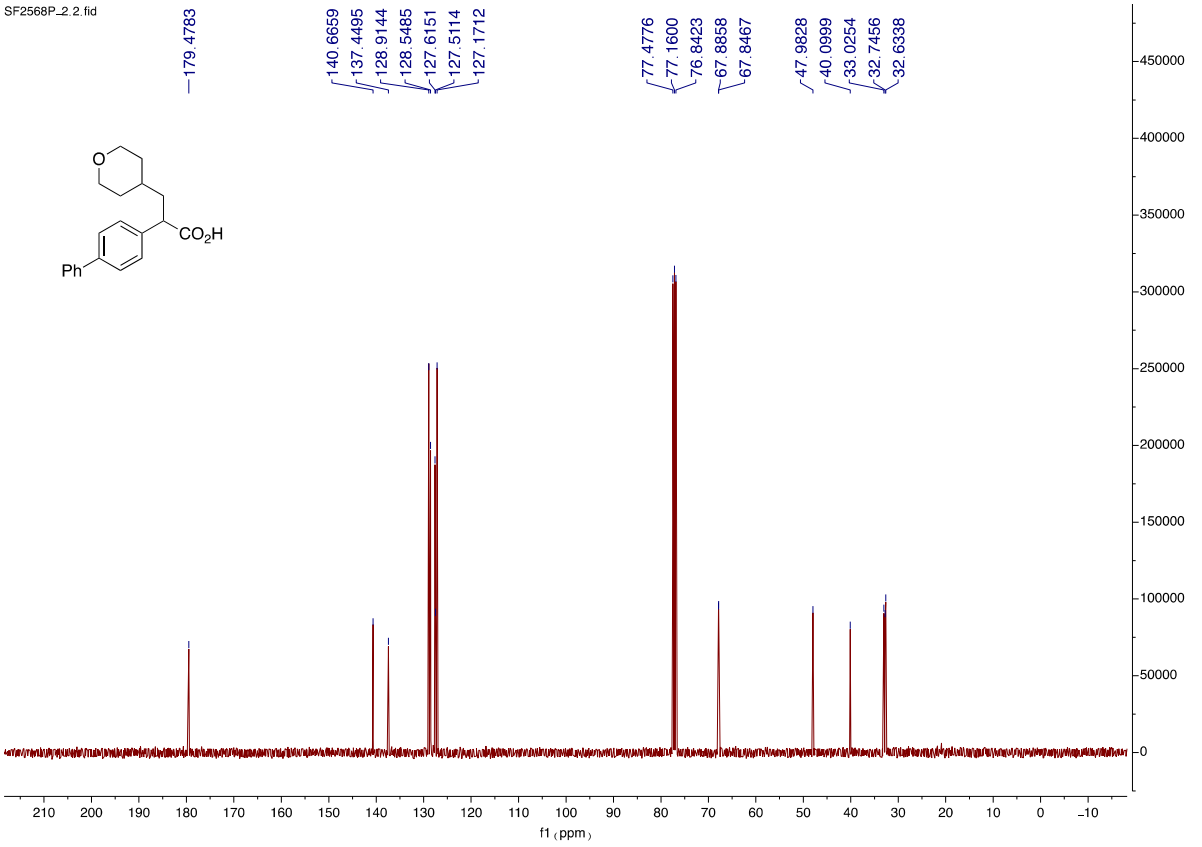
3s ^{1}H NMR (600 MHz, $CDCl_3$)



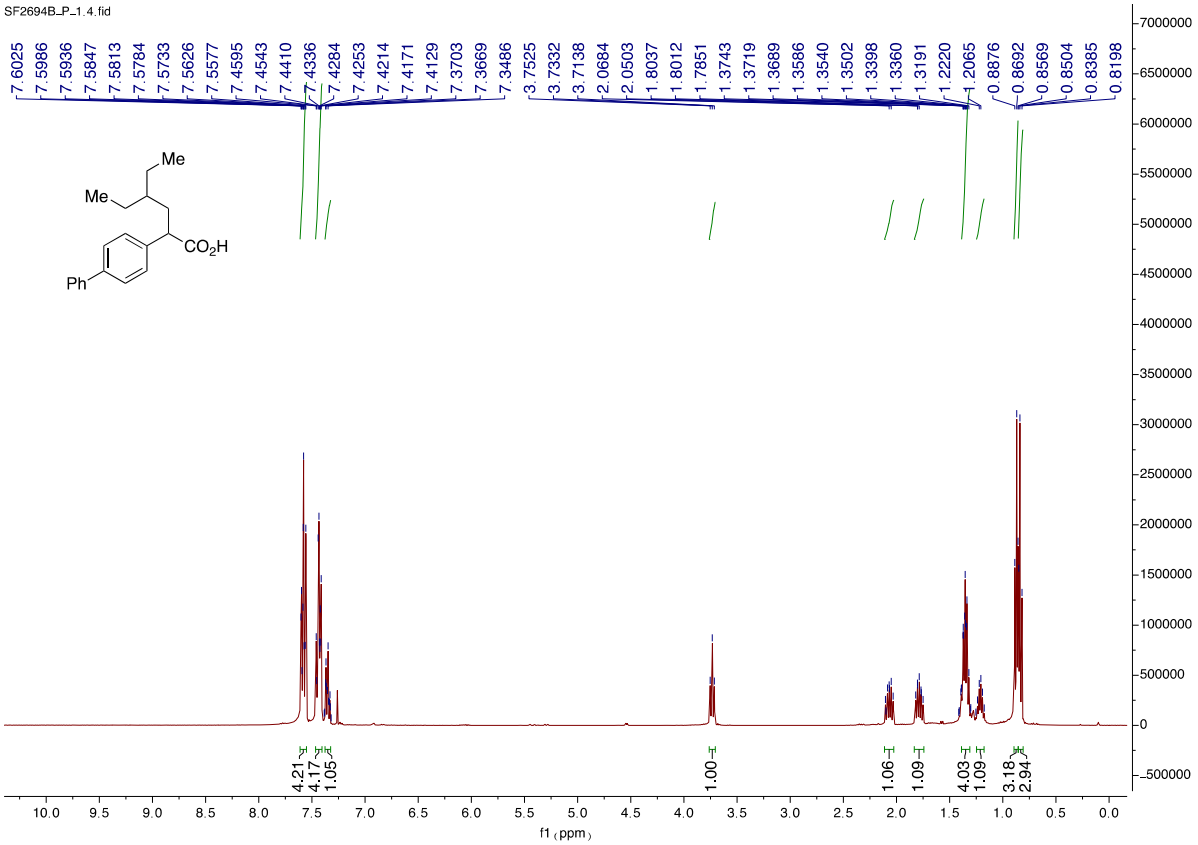
3s ^{13}C NMR (151 MHz, $CDCl_3$)



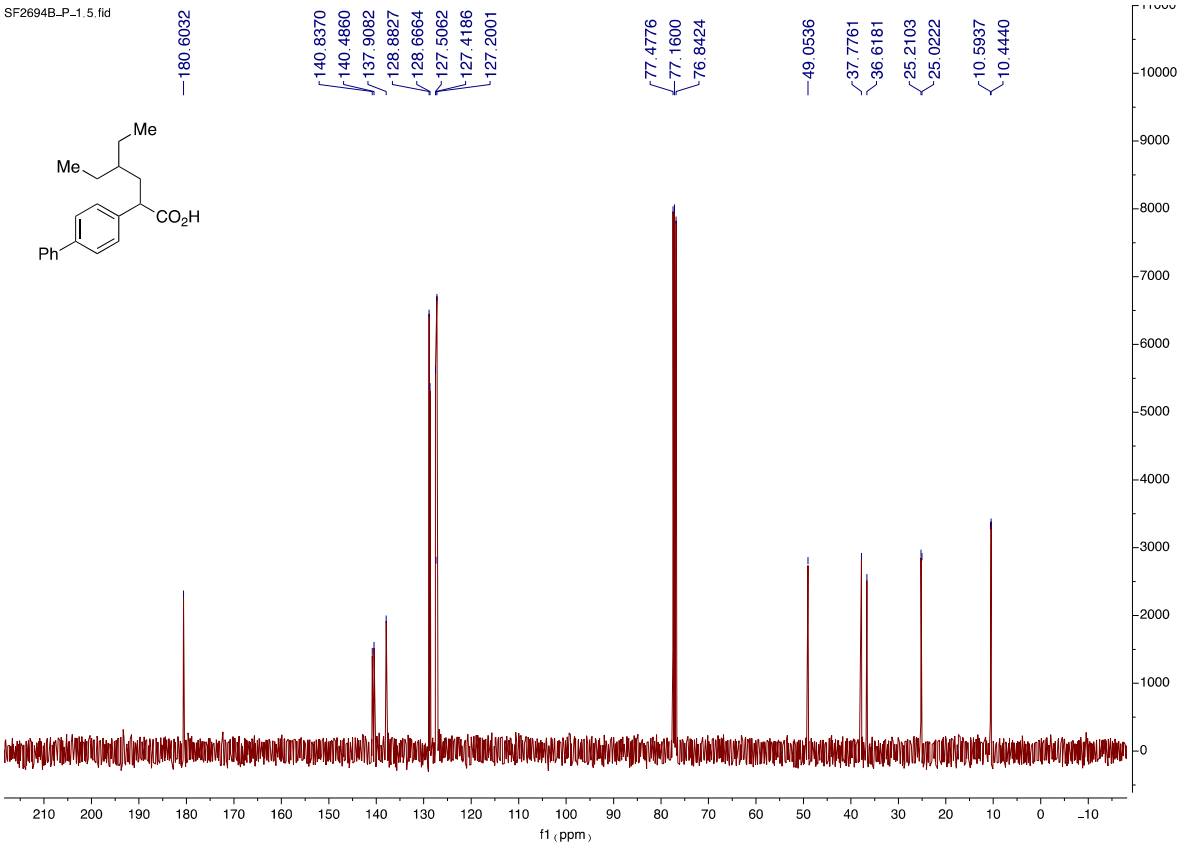
3t ^{1}H NMR (400 MHz, $CDCl_3$)



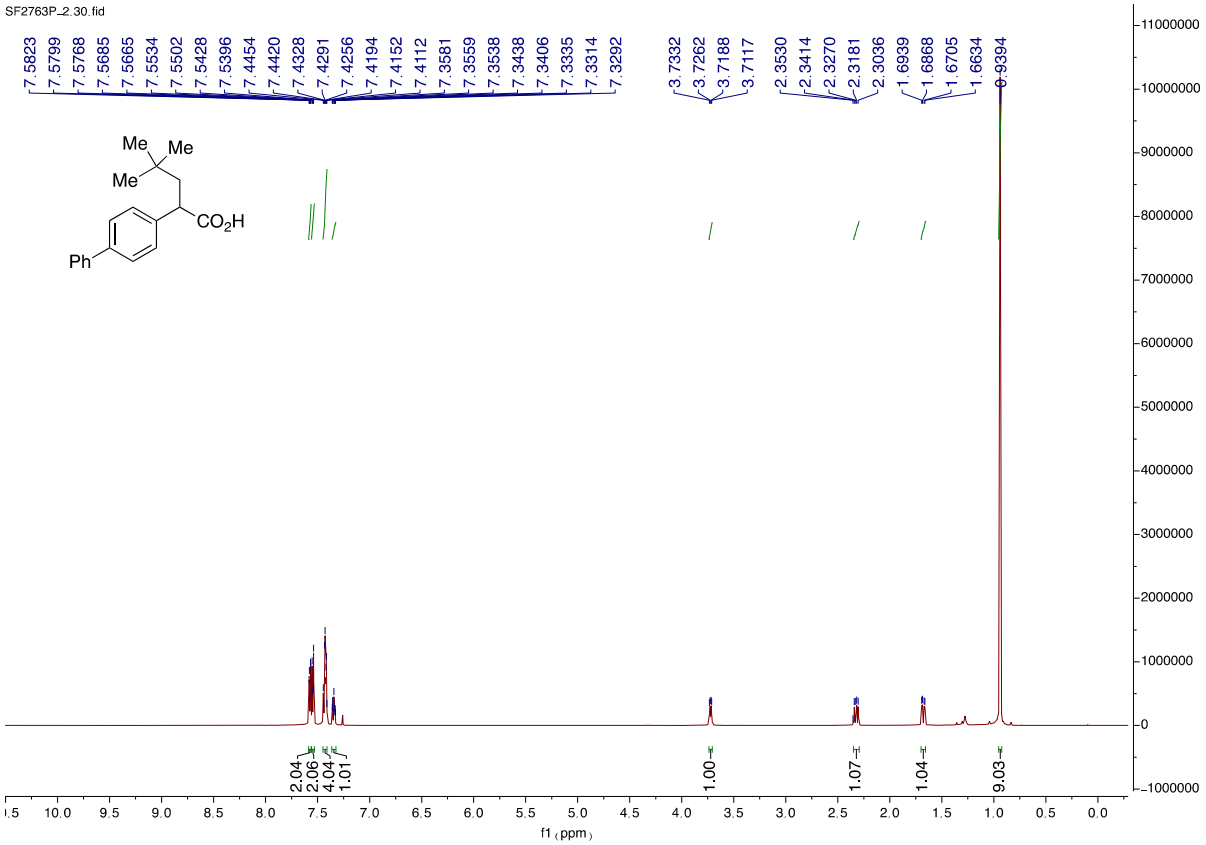
3t ^{13}C NMR (101 MHz, $CDCl_3$)



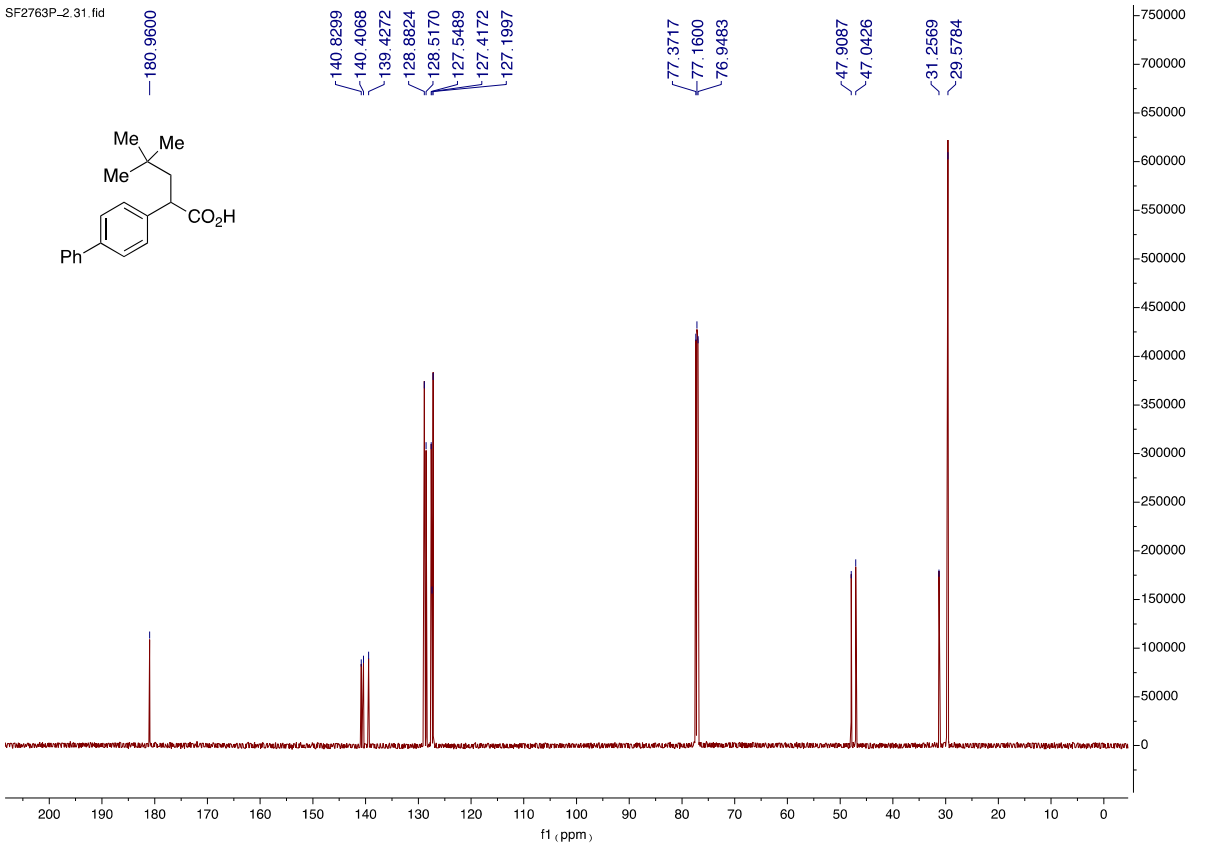
3u ^{1}H NMR (400 MHz, $CDCl_3$)



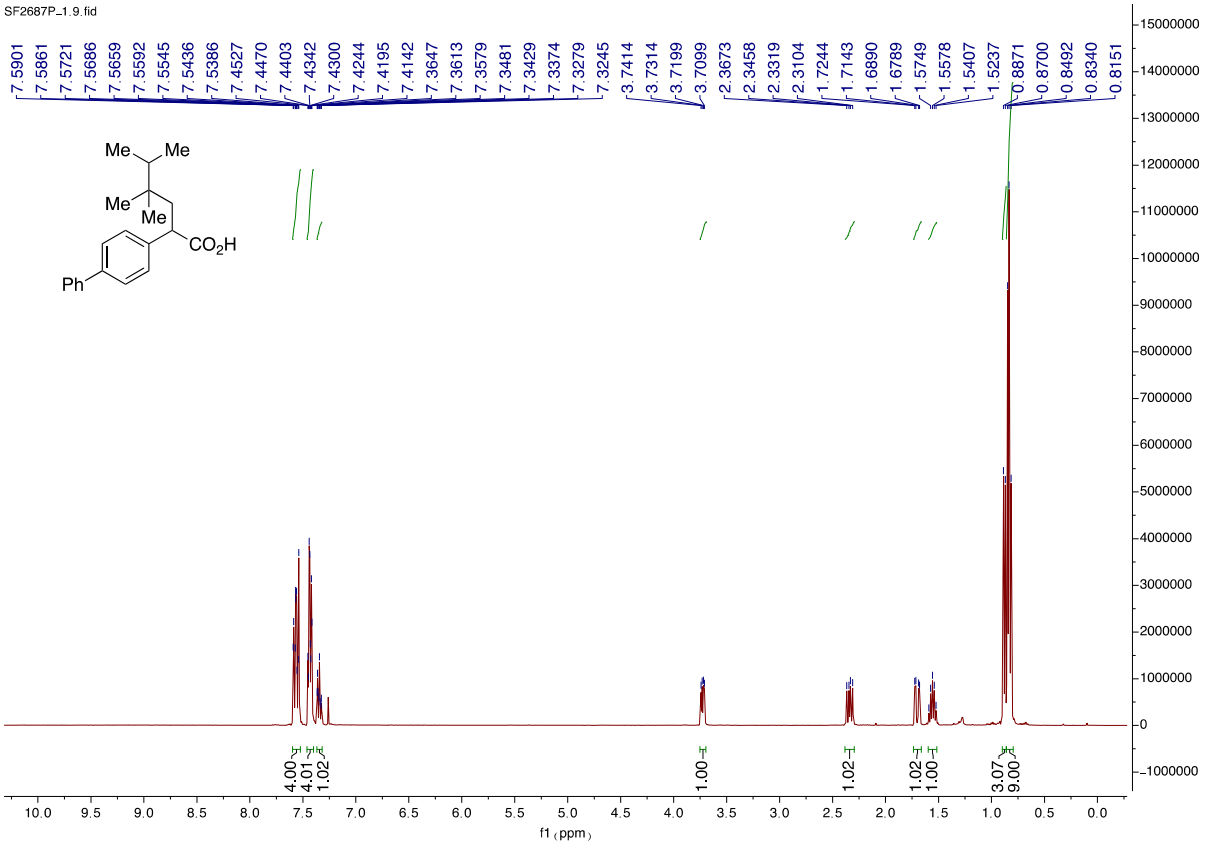
3u ^{13}C NMR (101 MHz, $CDCl_3$)



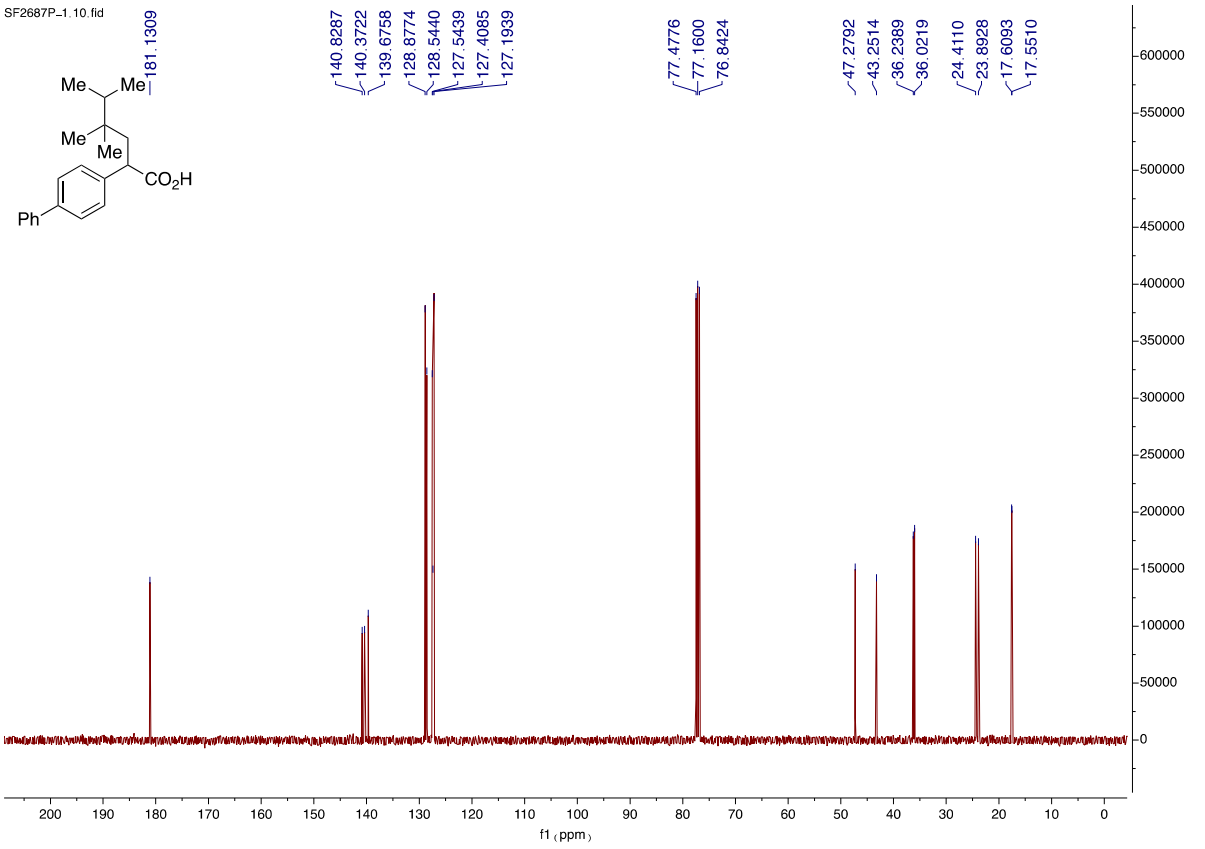
3v ^{1}H NMR (600 MHz, $CDCl_3$)



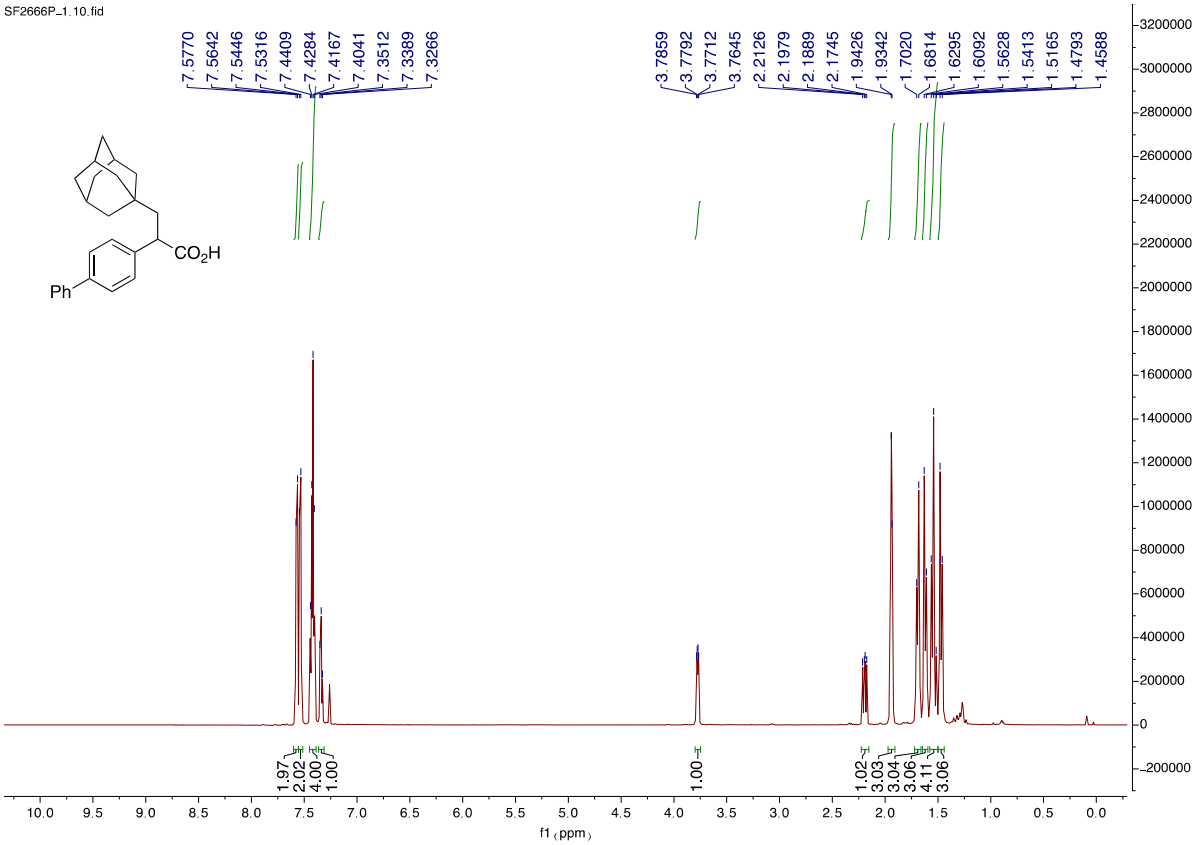
3v ^{13}C NMR (151 MHz, $CDCl_3$)



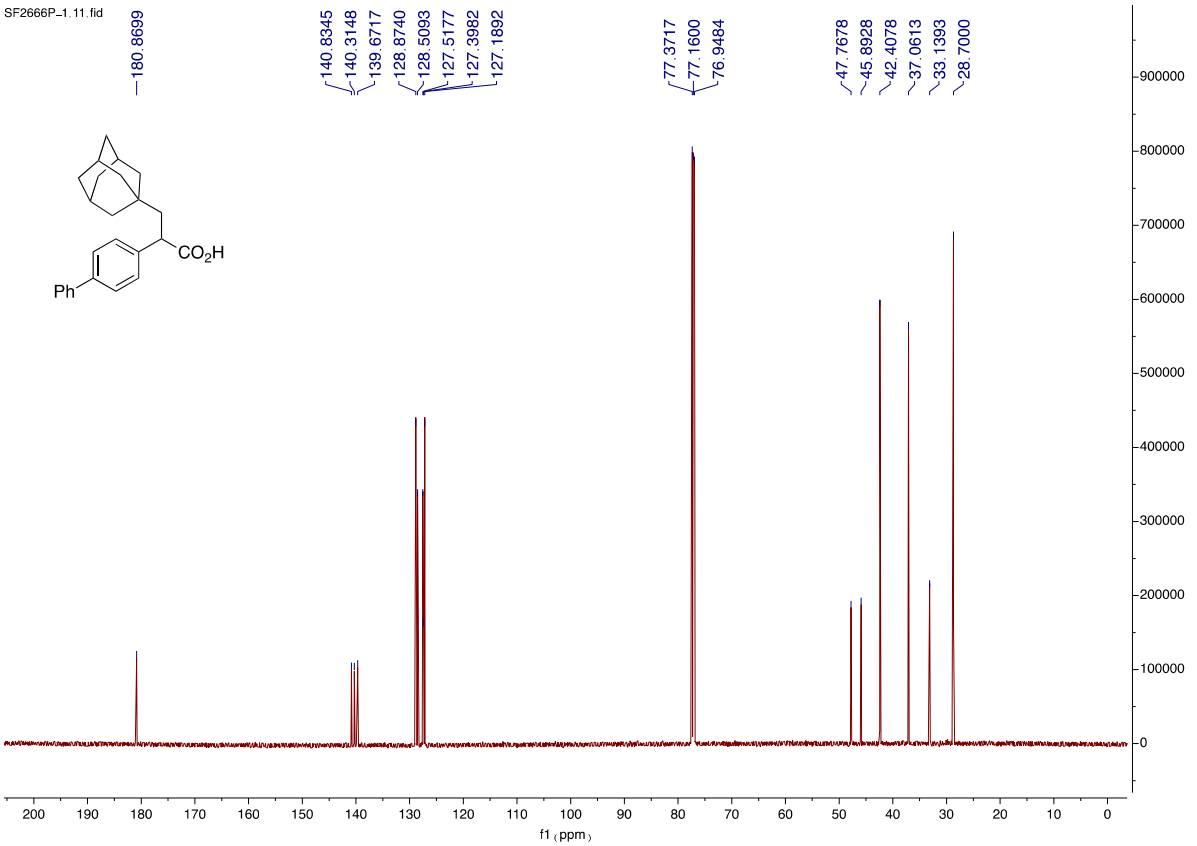
3w ^{1}H NMR (400 MHz, $CDCl_3$)



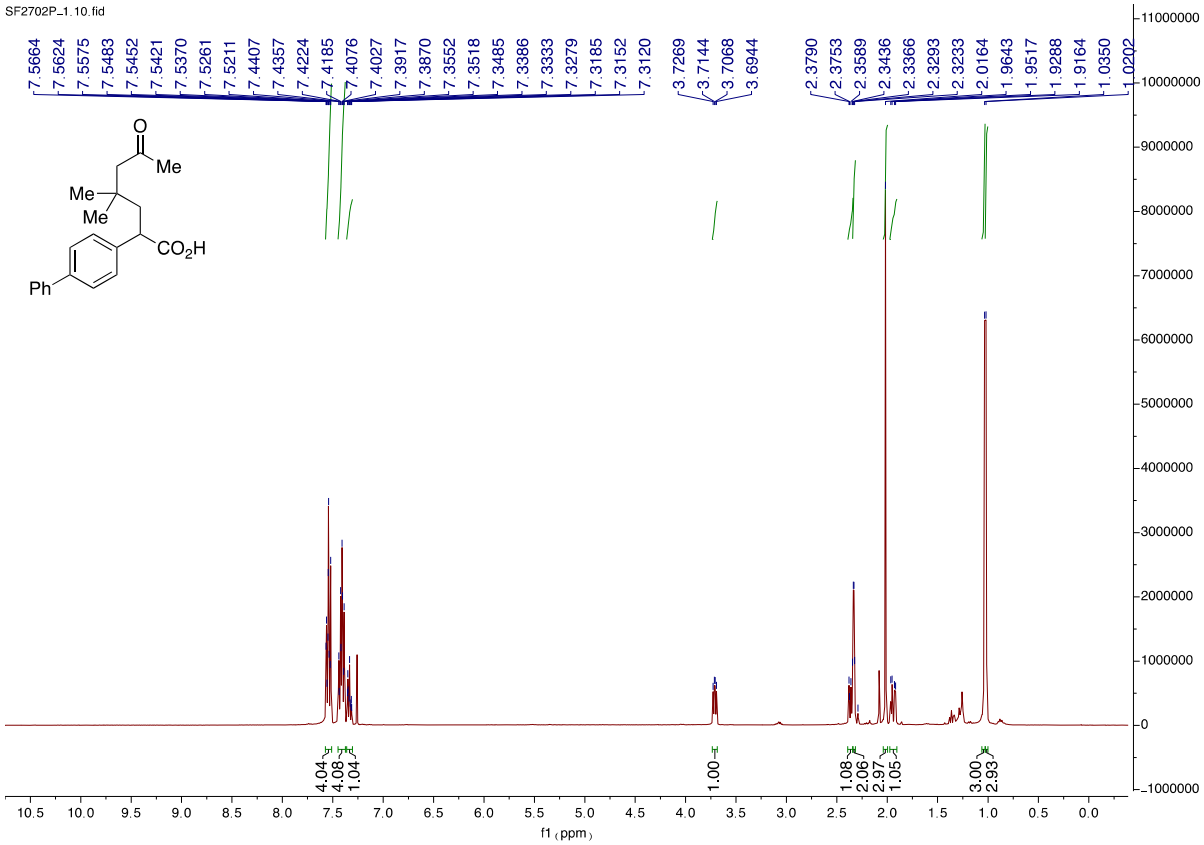
3w ^{13}C NMR (101 MHz, $CDCl_3$)



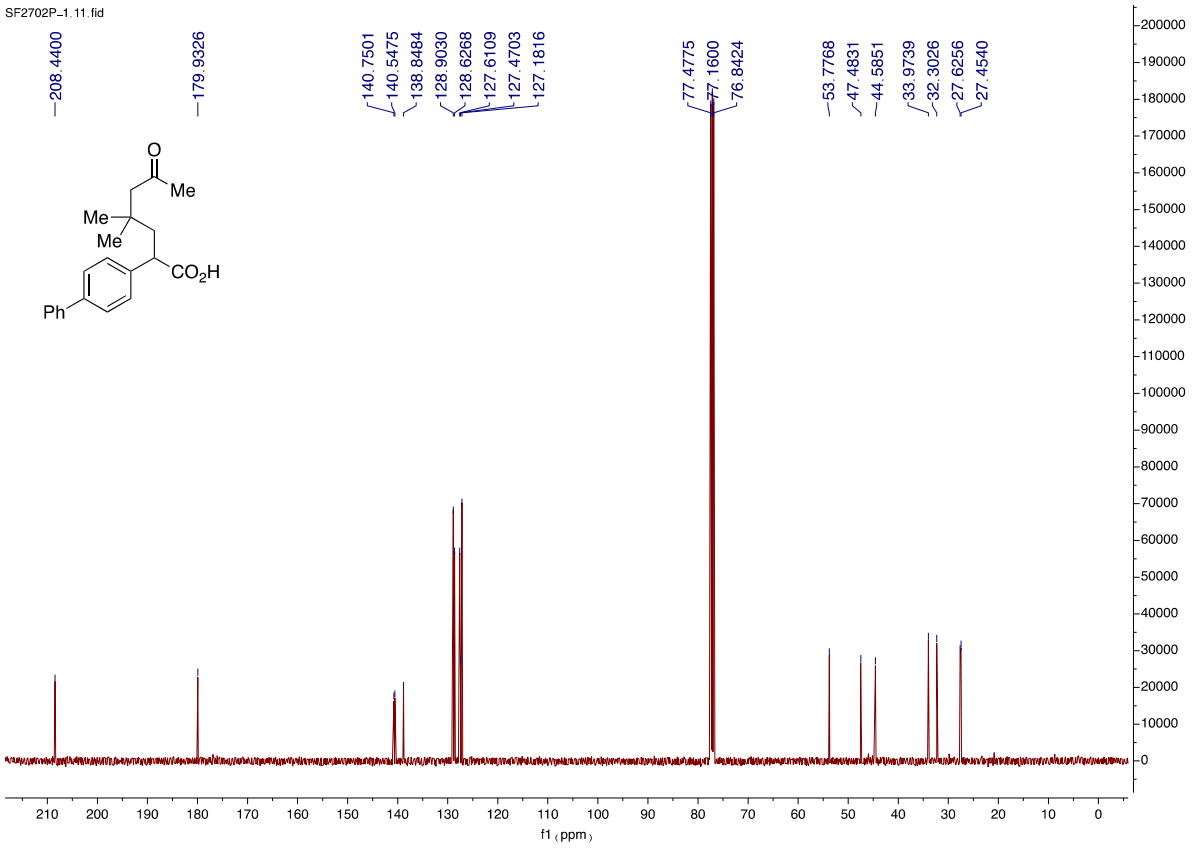
3x ^{1}H NMR (600 MHz, $CDCl_3$)



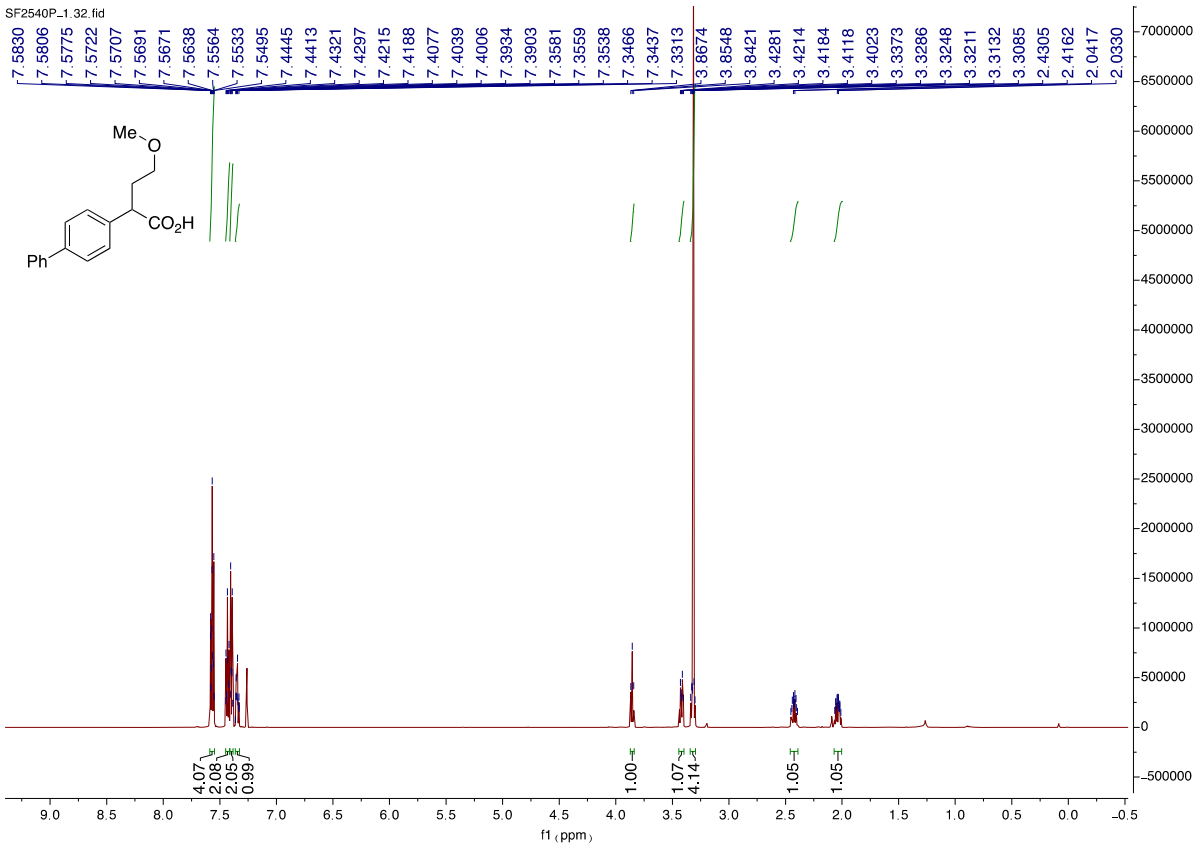
3x ^{13}C NMR (151 MHz, $CDCl_3$)



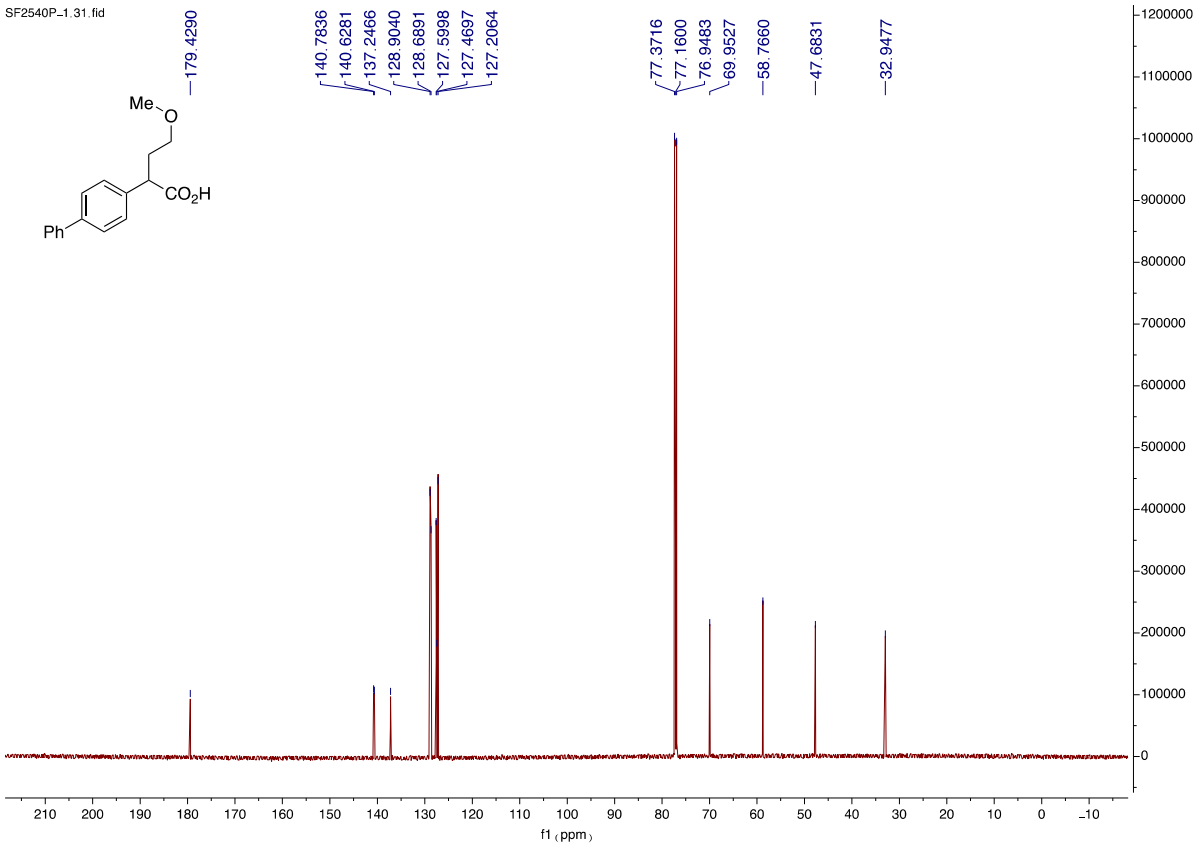
3y ^{1}H NMR (400 MHz, $CDCl_3$)



3y ^{13}C NMR (101 MHz, $CDCl_3$)



3z ^{1}H NMR (600 MHz, $CDCl_3$)



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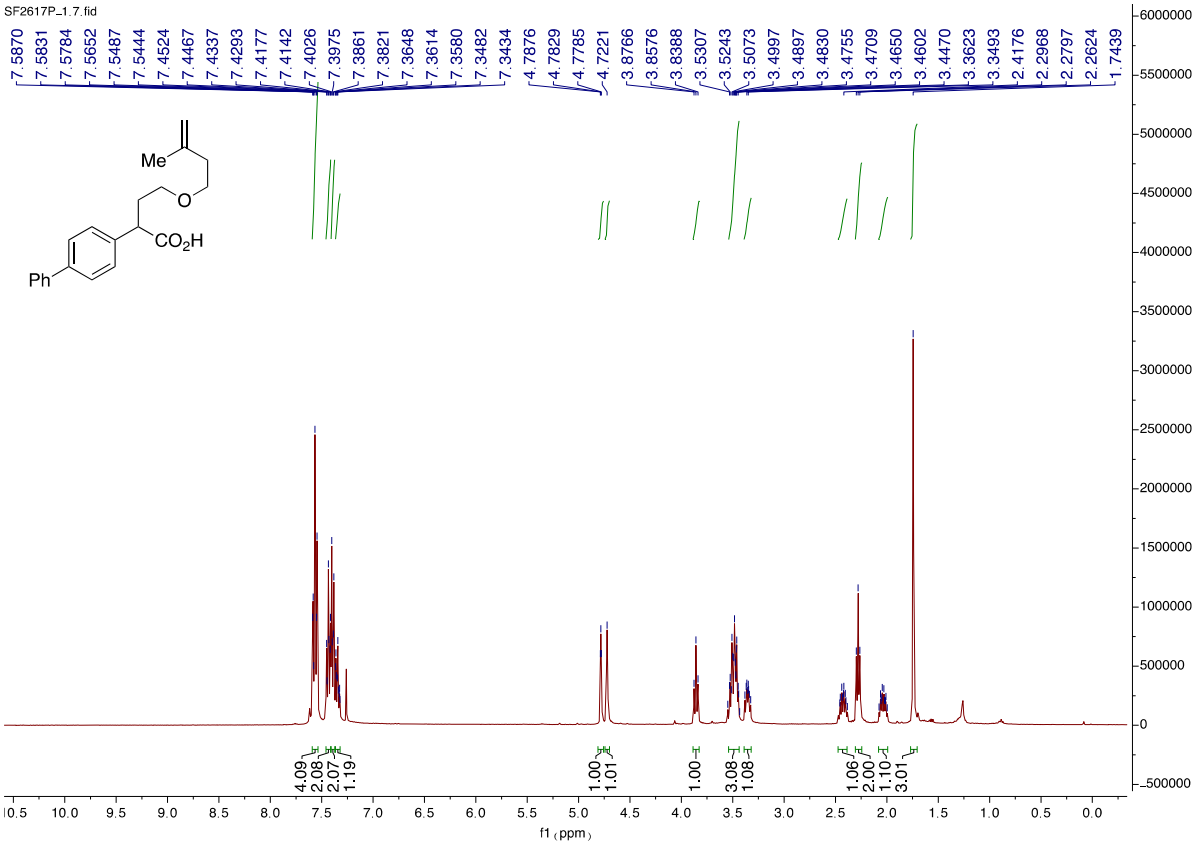
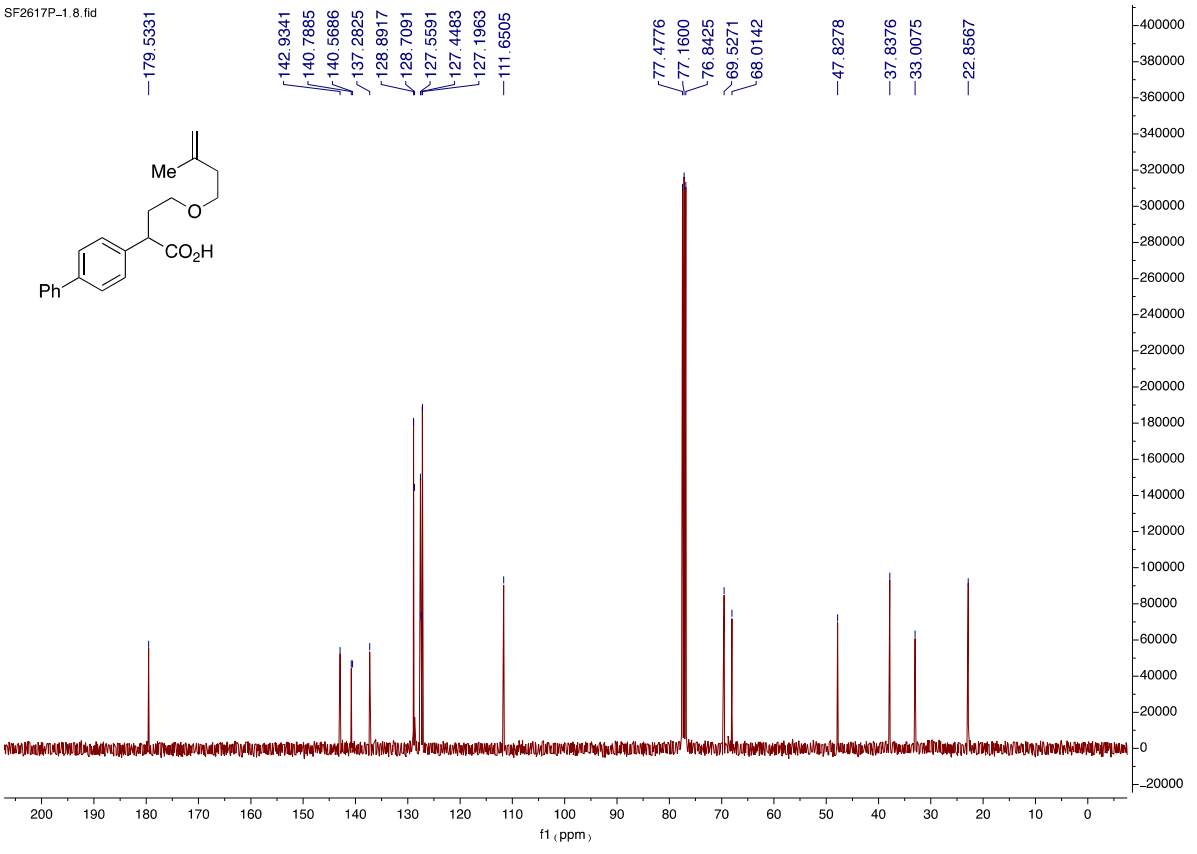
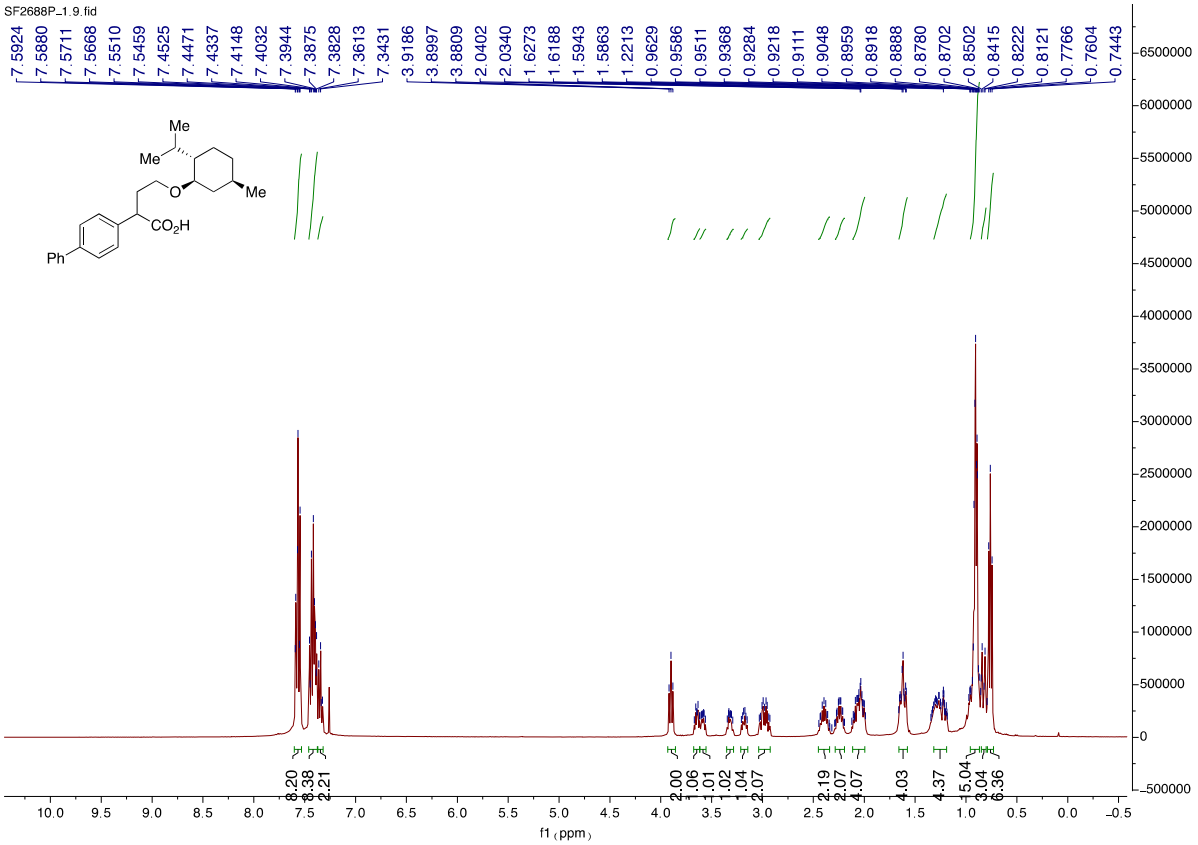


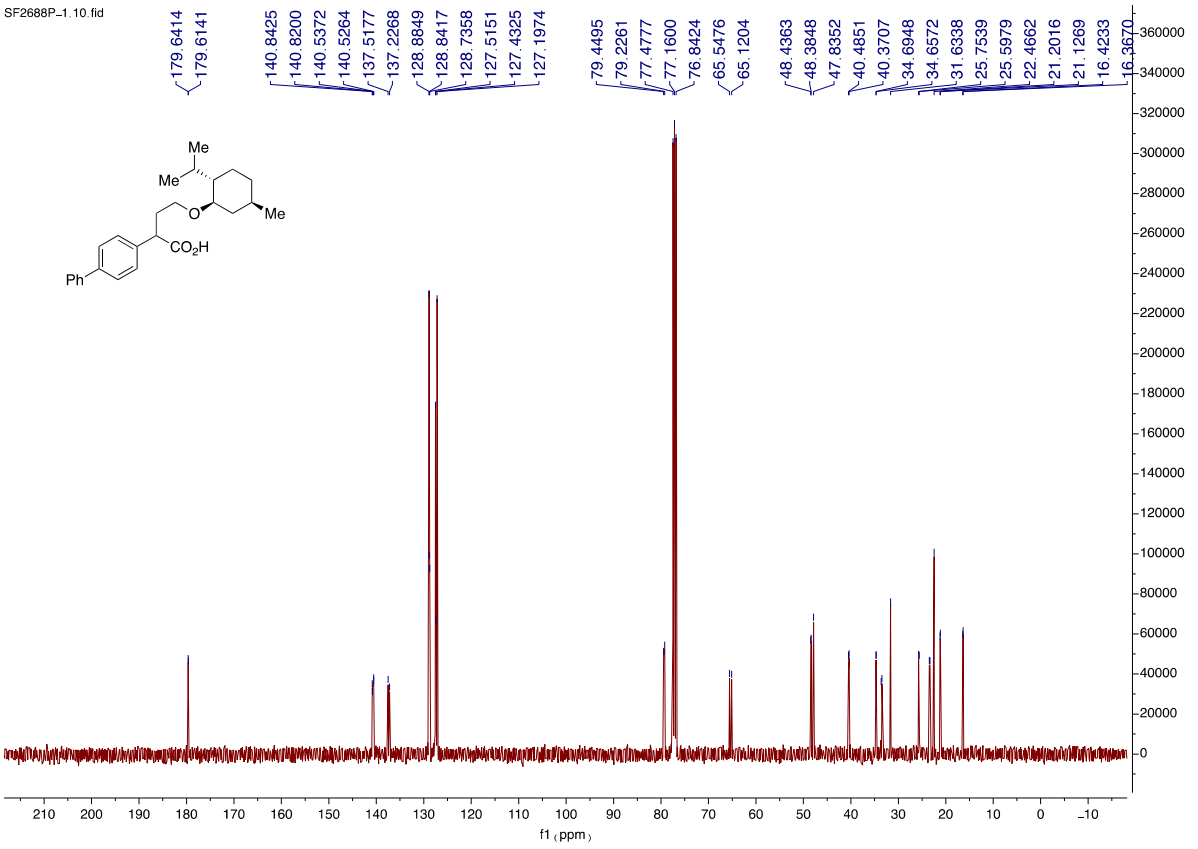
3aa ^{1}H NMR (400 MHz, $CDCl_3$)



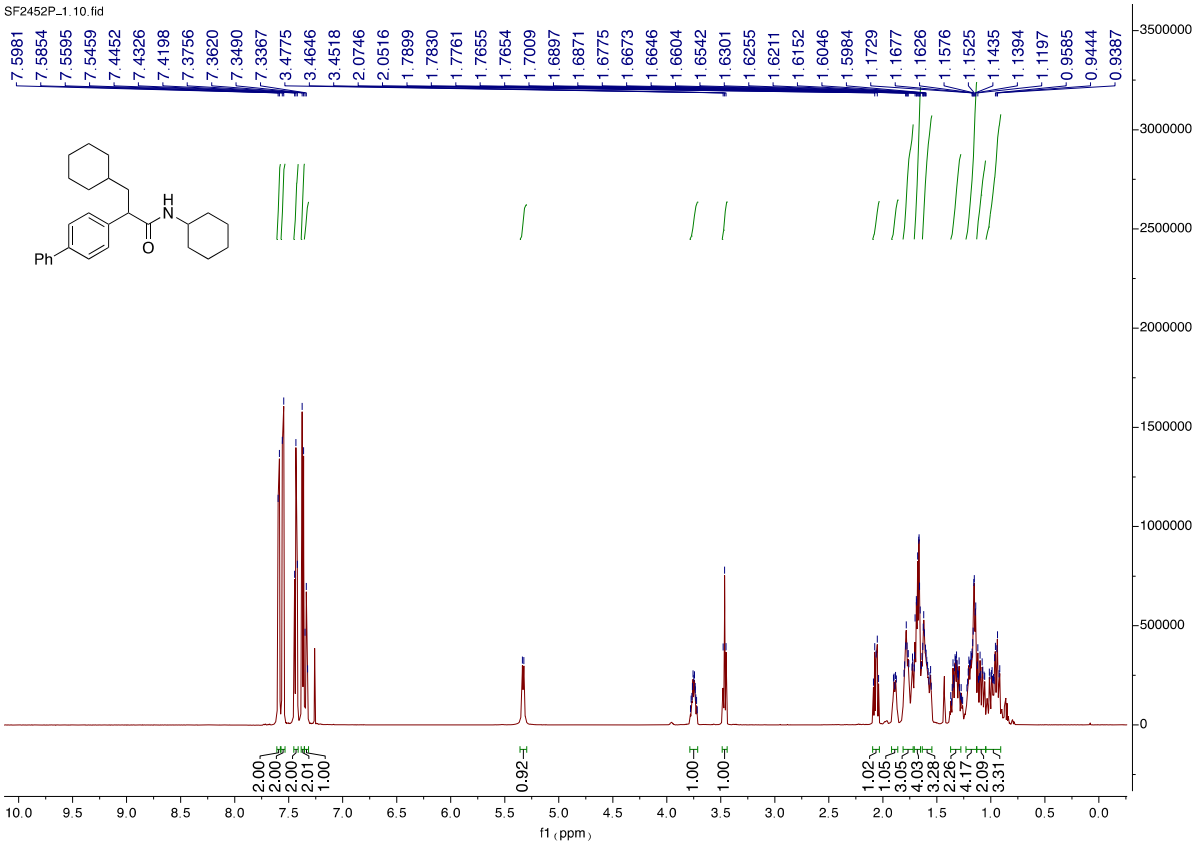
3aa ^{13}C NMR (101 MHz, $CDCl_3$)



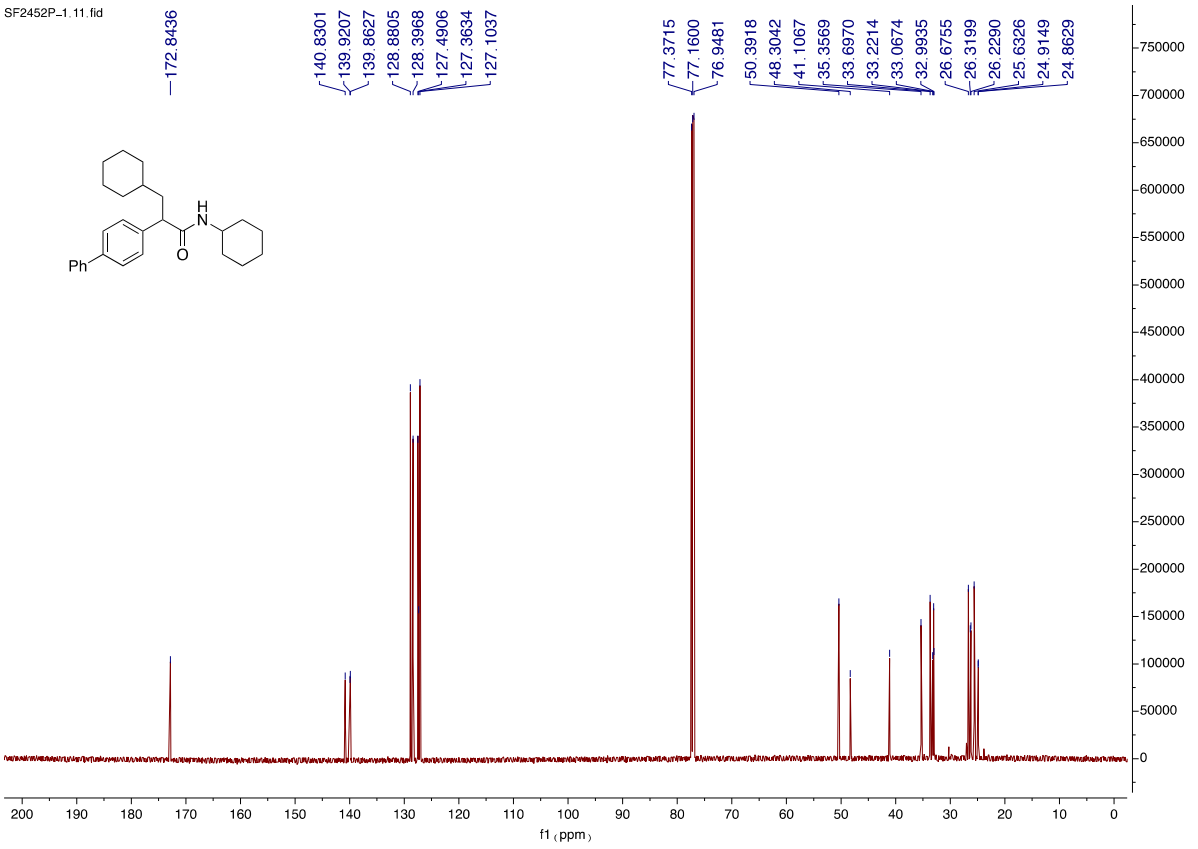
3ab ^{1}H NMR (400 MHz, $CDCl_3$)



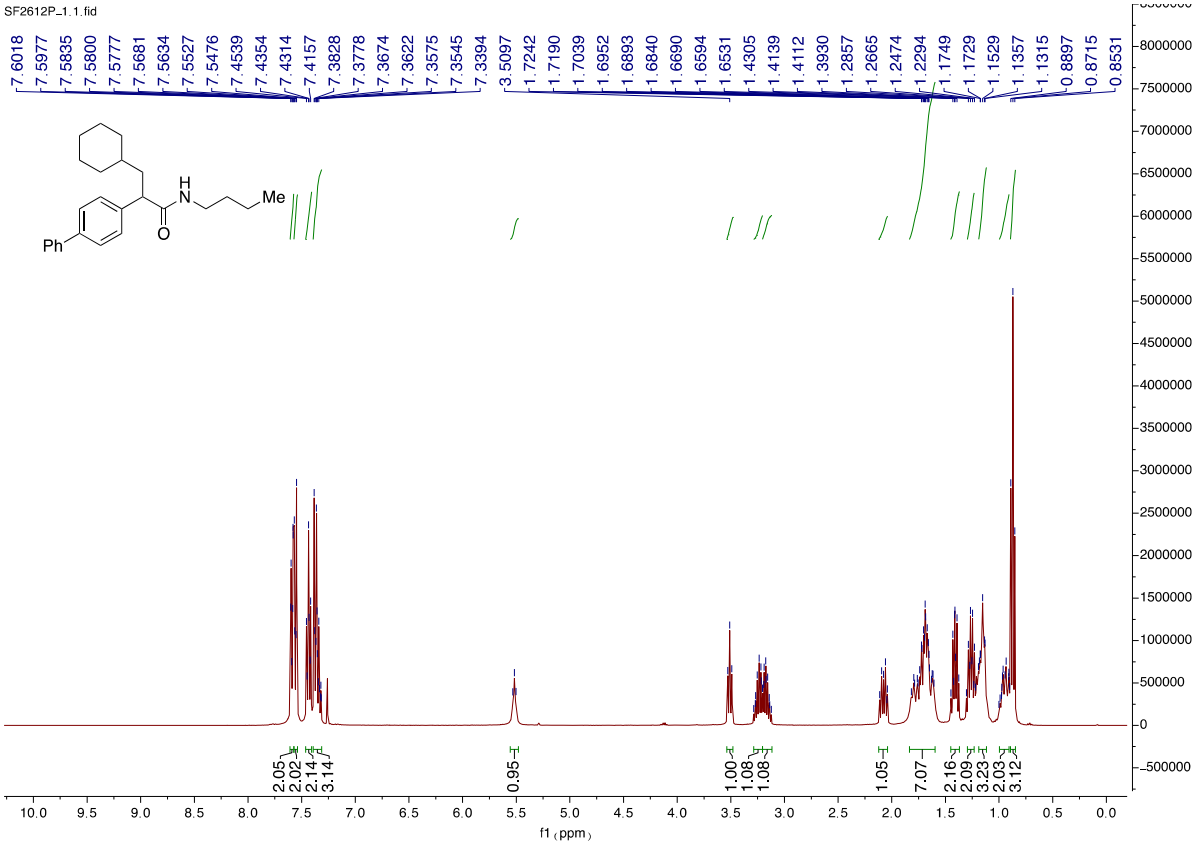
3ab ^{13}C NMR (101 MHz, $CDCl_3$)



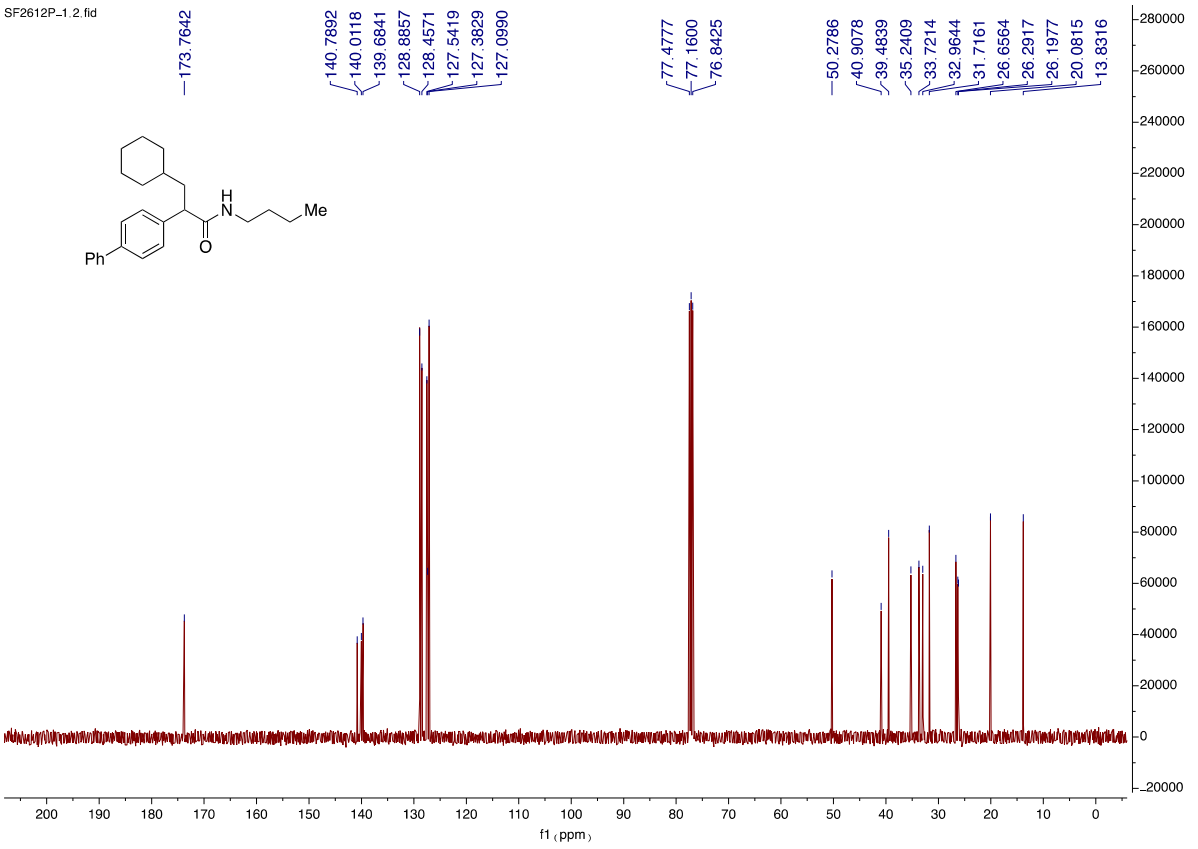
5a ^{1}H NMR (600 MHz, $CDCl_3$)



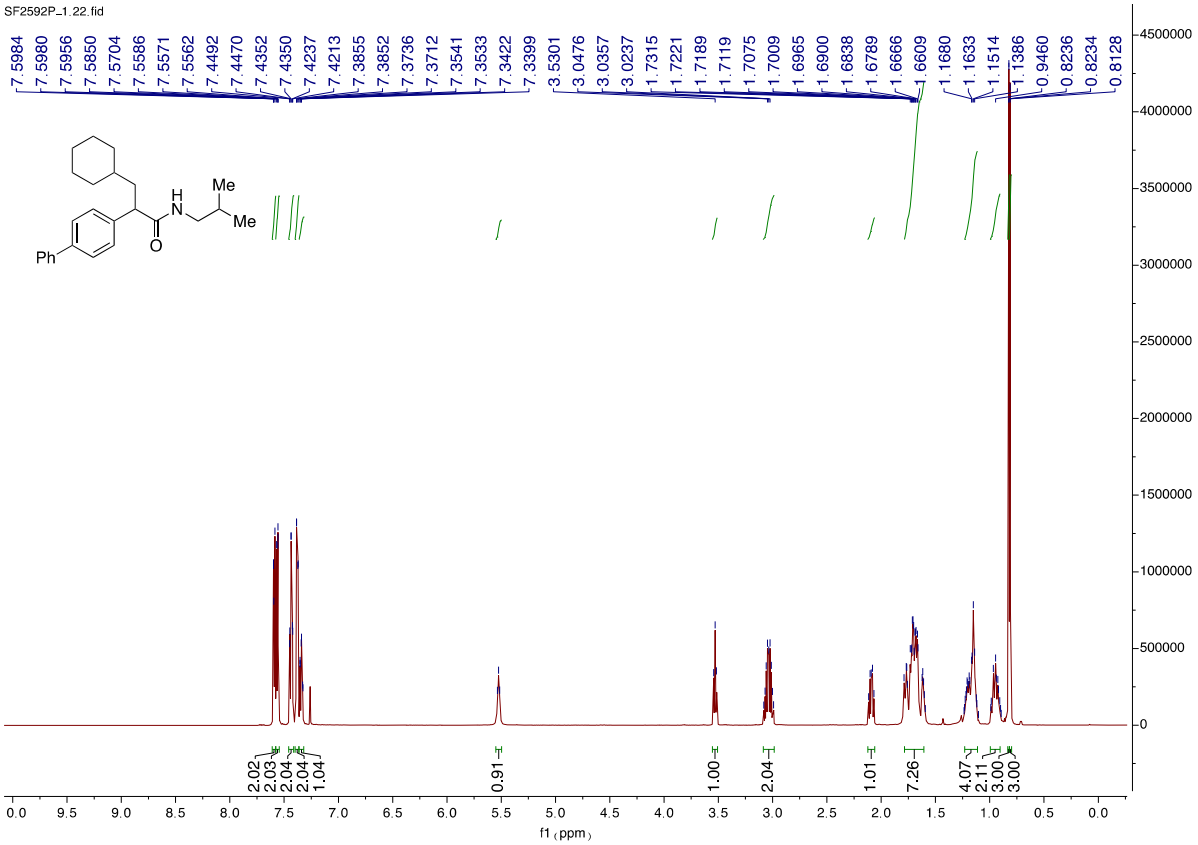
5a ^{13}C NMR (151 MHz, $CDCl_3$)



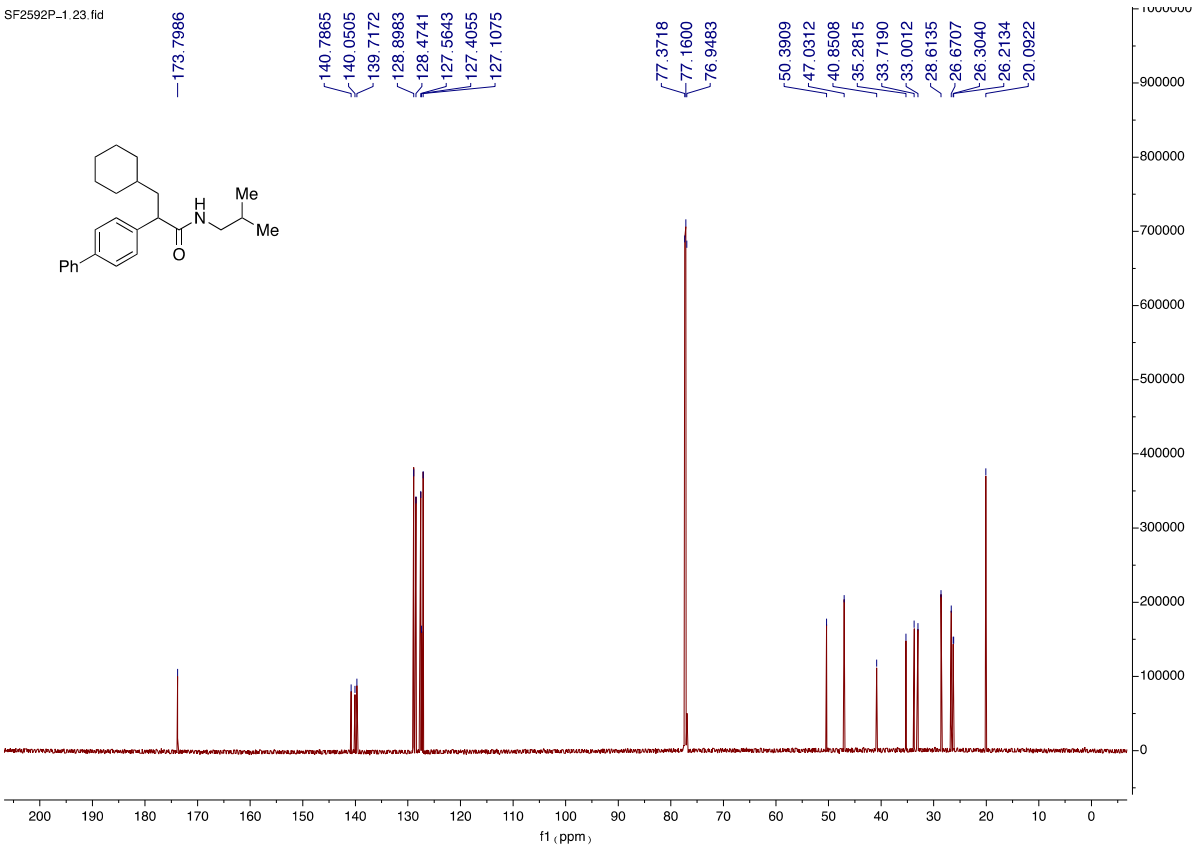
5b ^{1}H NMR (400 MHz, $CDCl_3$)



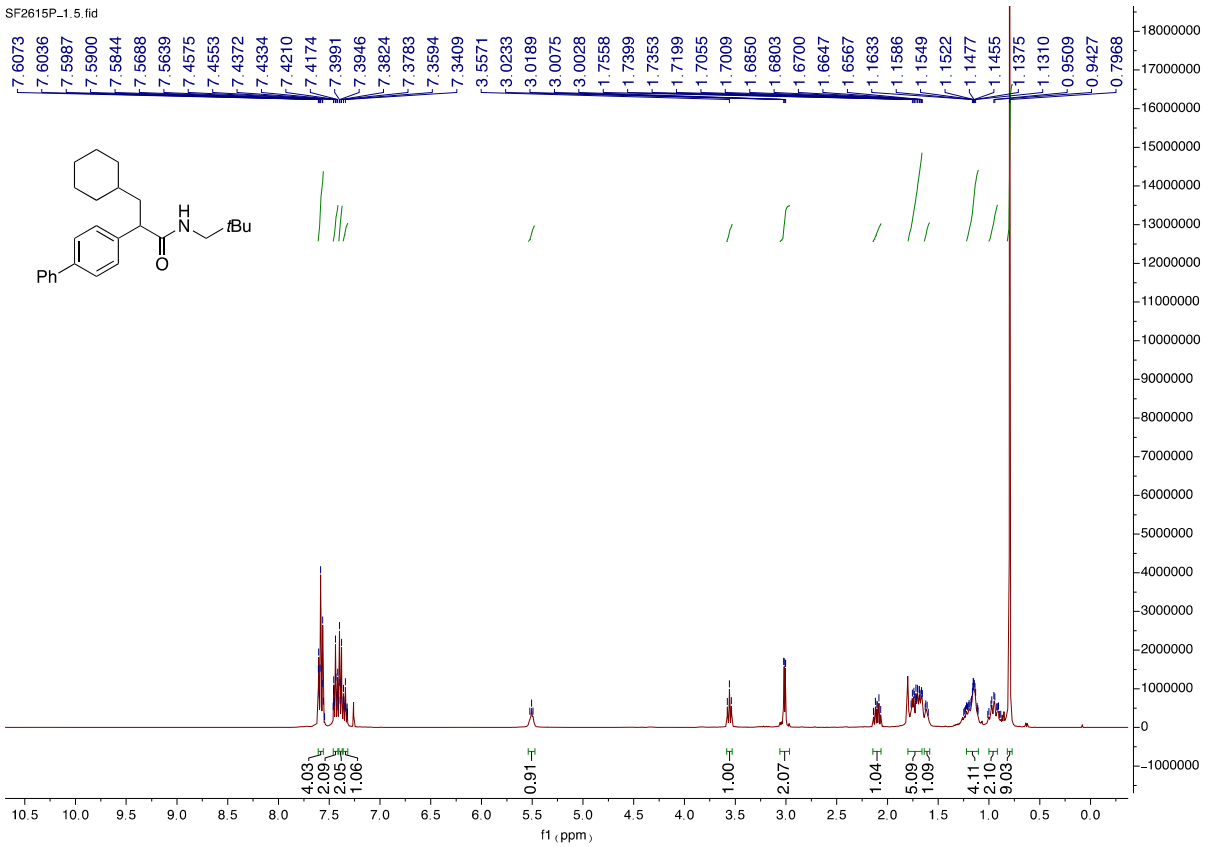
5b ^{13}C NMR (101 MHz, $CDCl_3$)



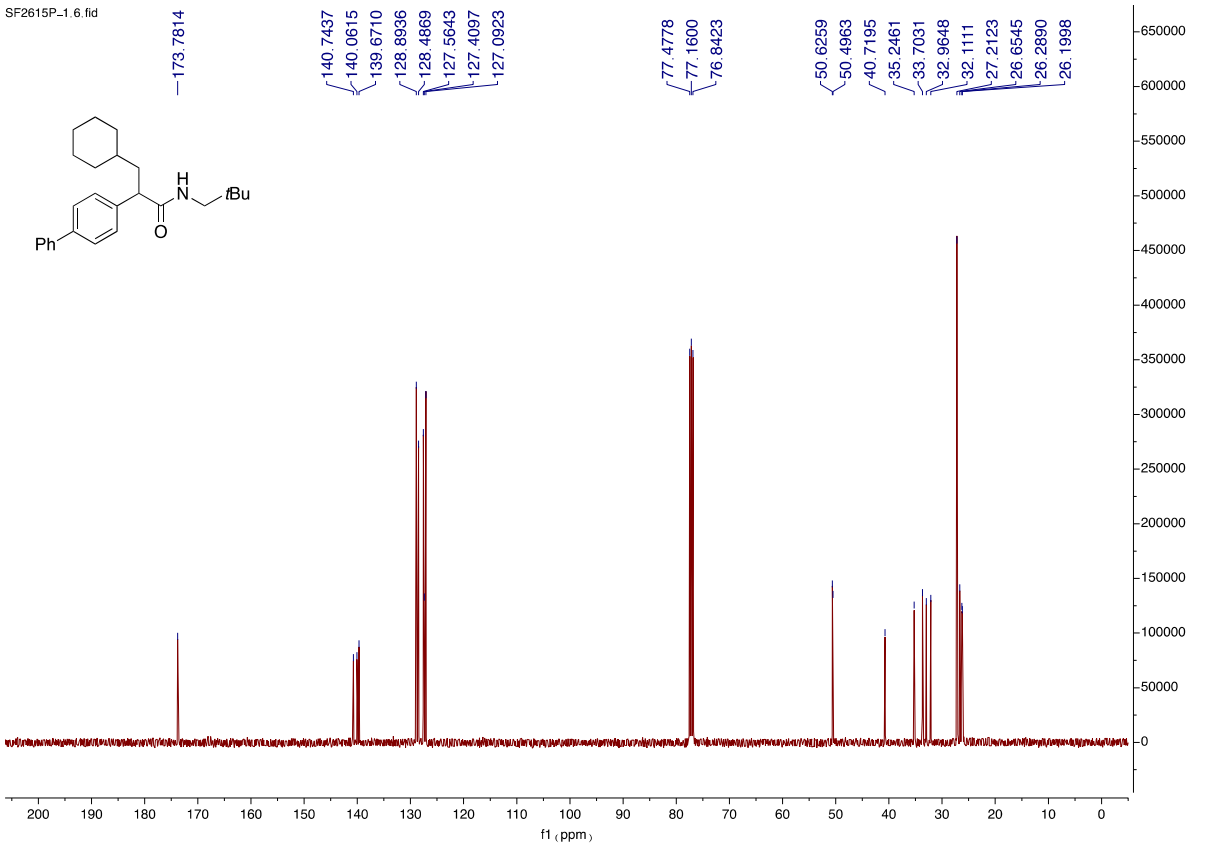
5c ^{1}H NMR (600 MHz, $CDCl_3$)



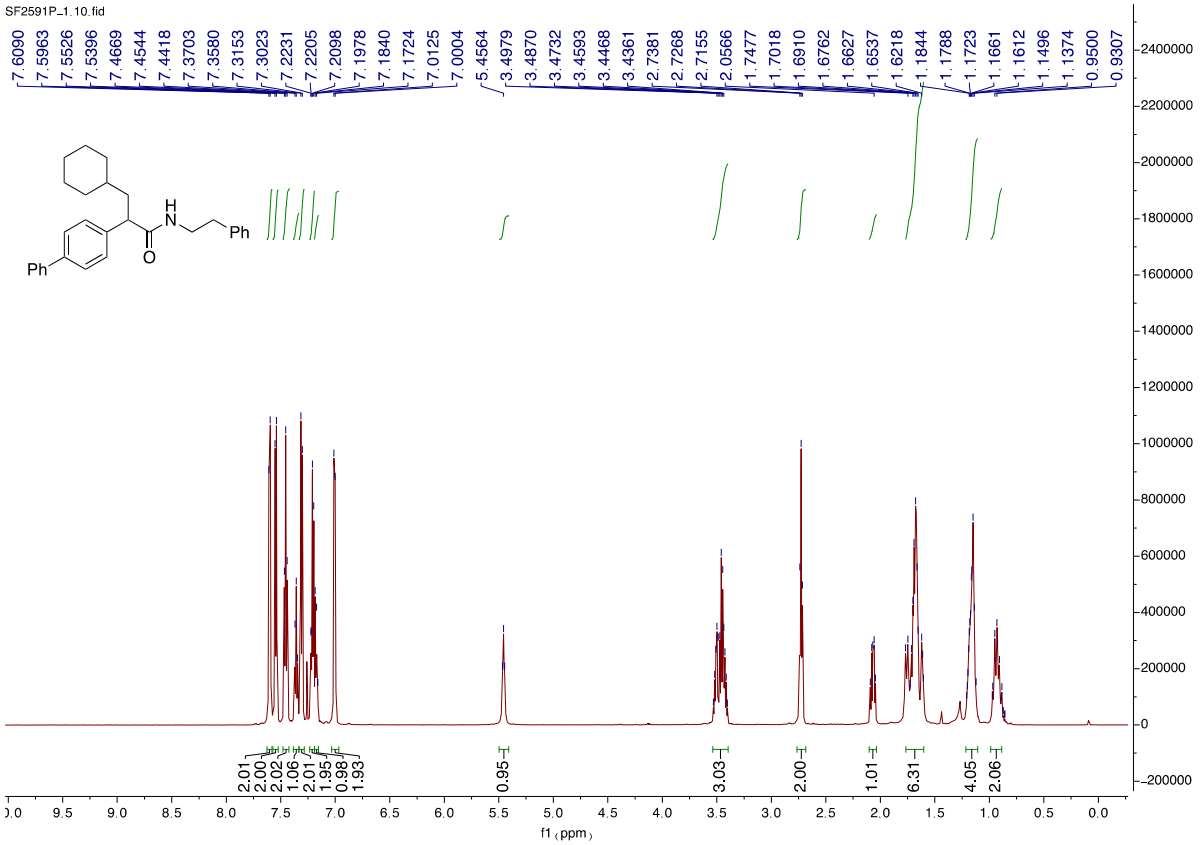
5c ^{13}C NMR (151 MHz, $CDCl_3$)



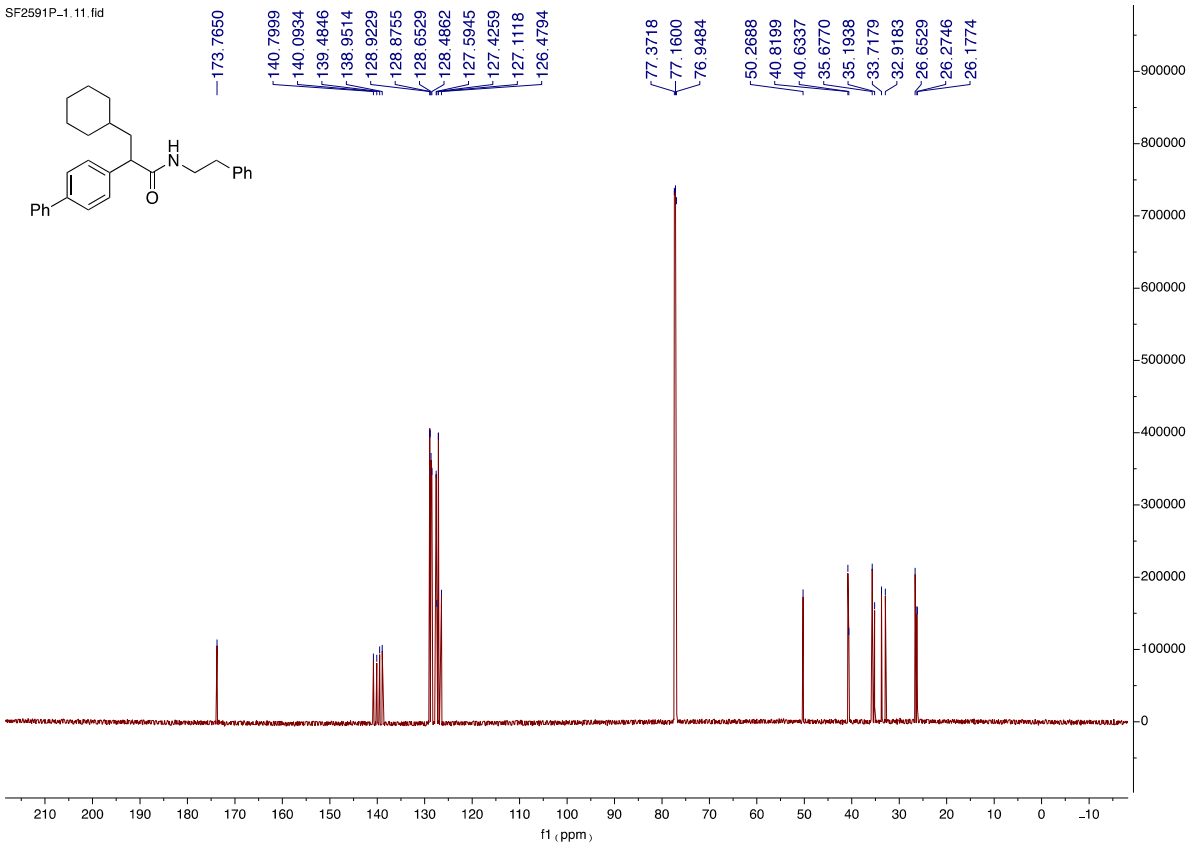
5d ^{1}H NMR (400 MHz, $CDCl_3$)



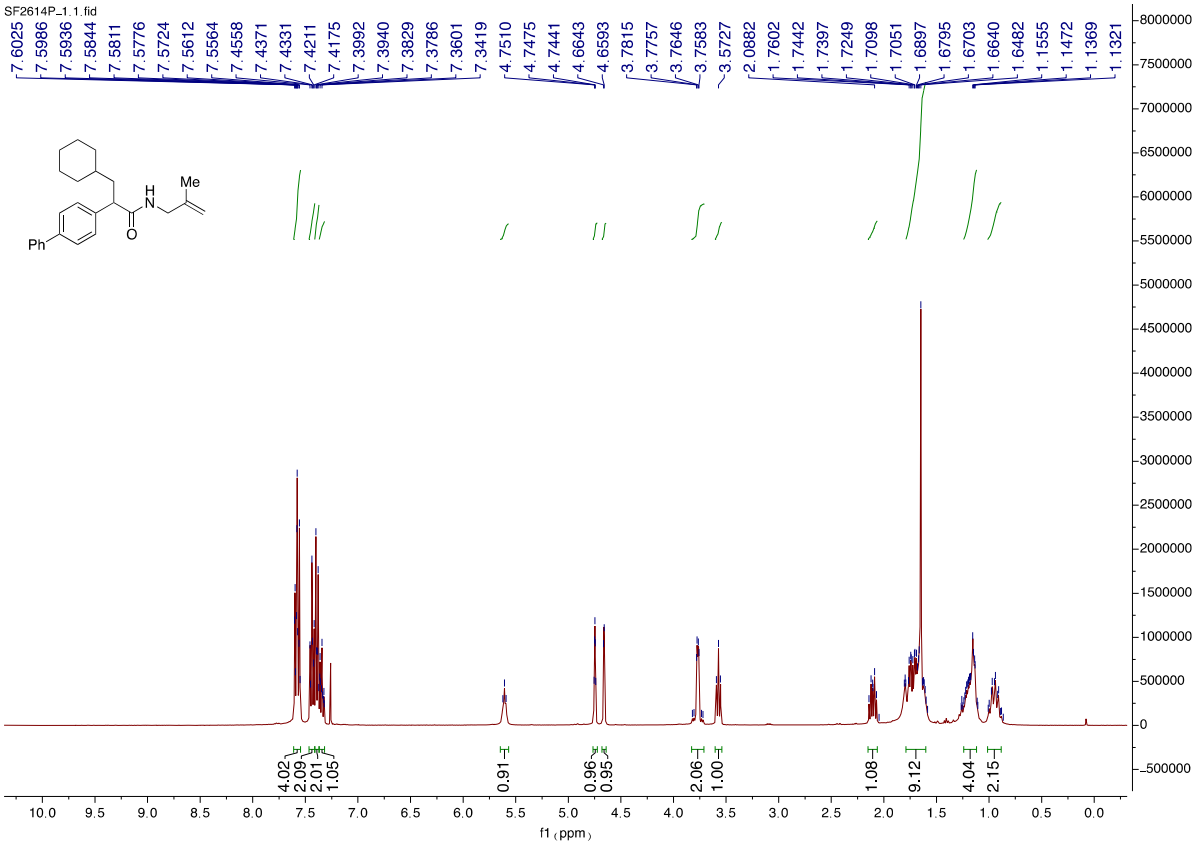
5d ^{13}C NMR (101 MHz, $CDCl_3$)



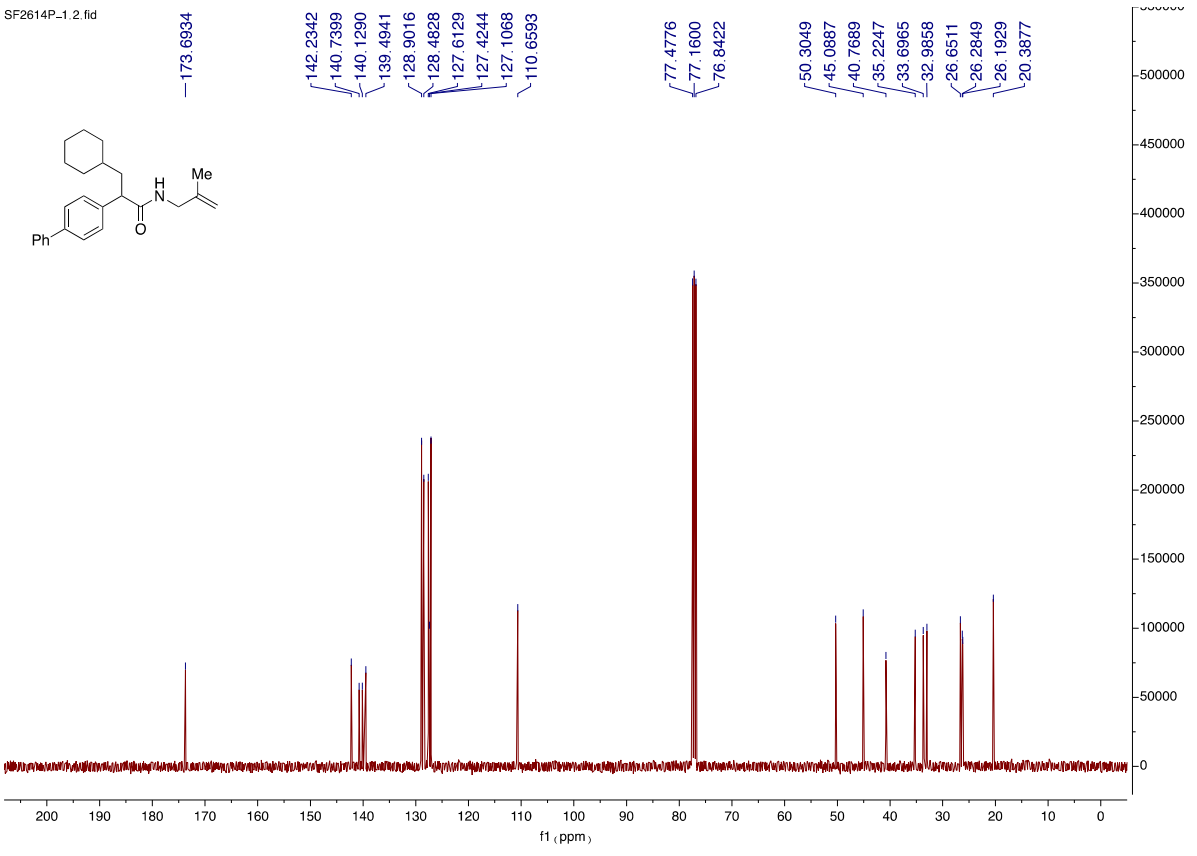
5e ^{1}H NMR (600 MHz, $CDCl_3$)



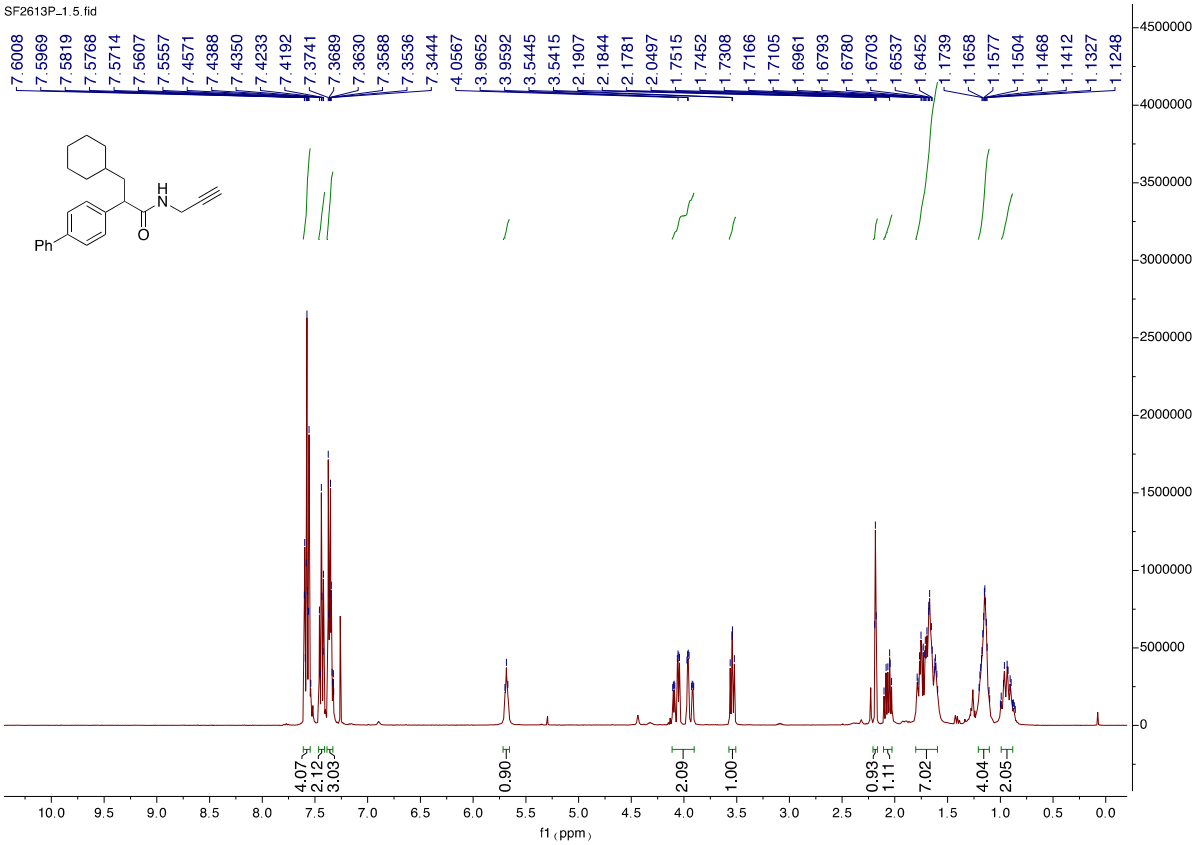
5e ^{13}C NMR (151 MHz, $CDCl_3$)



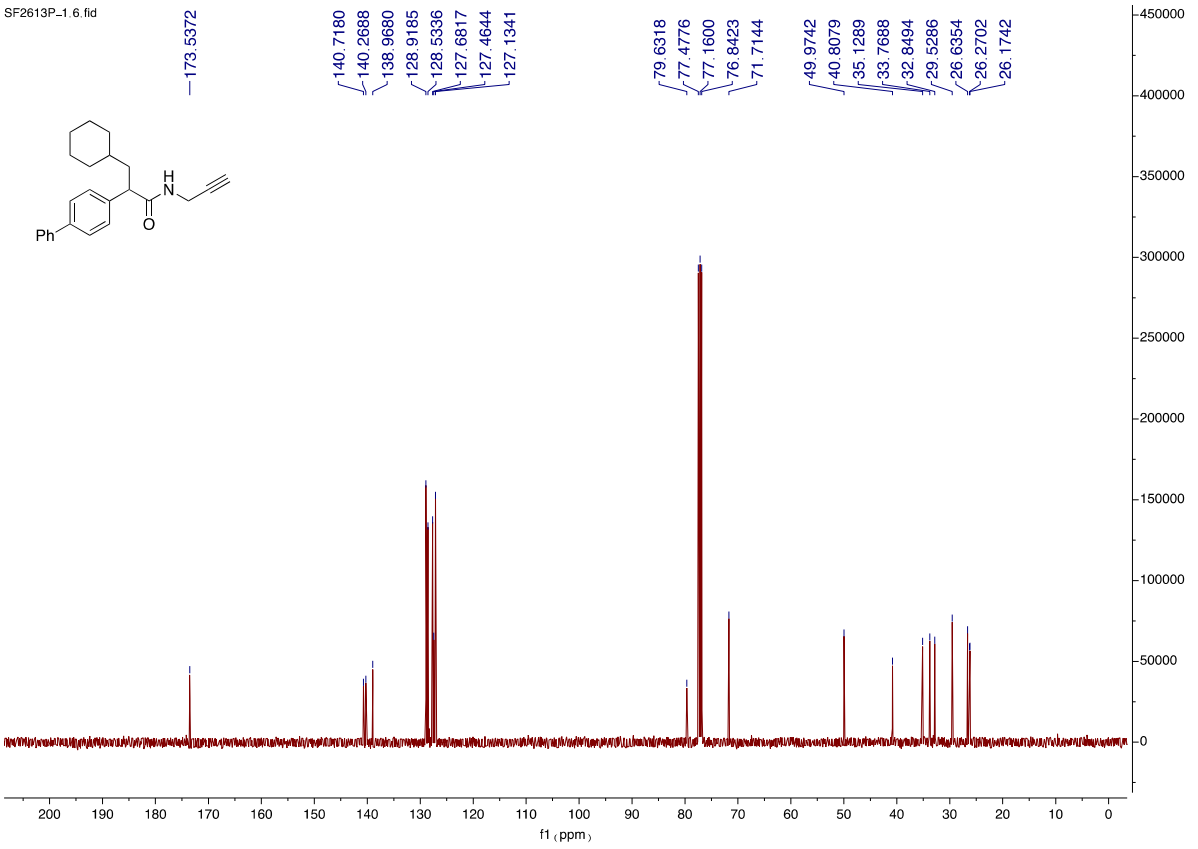
5f ^{1}H NMR (400 MHz, $CDCl_3$)



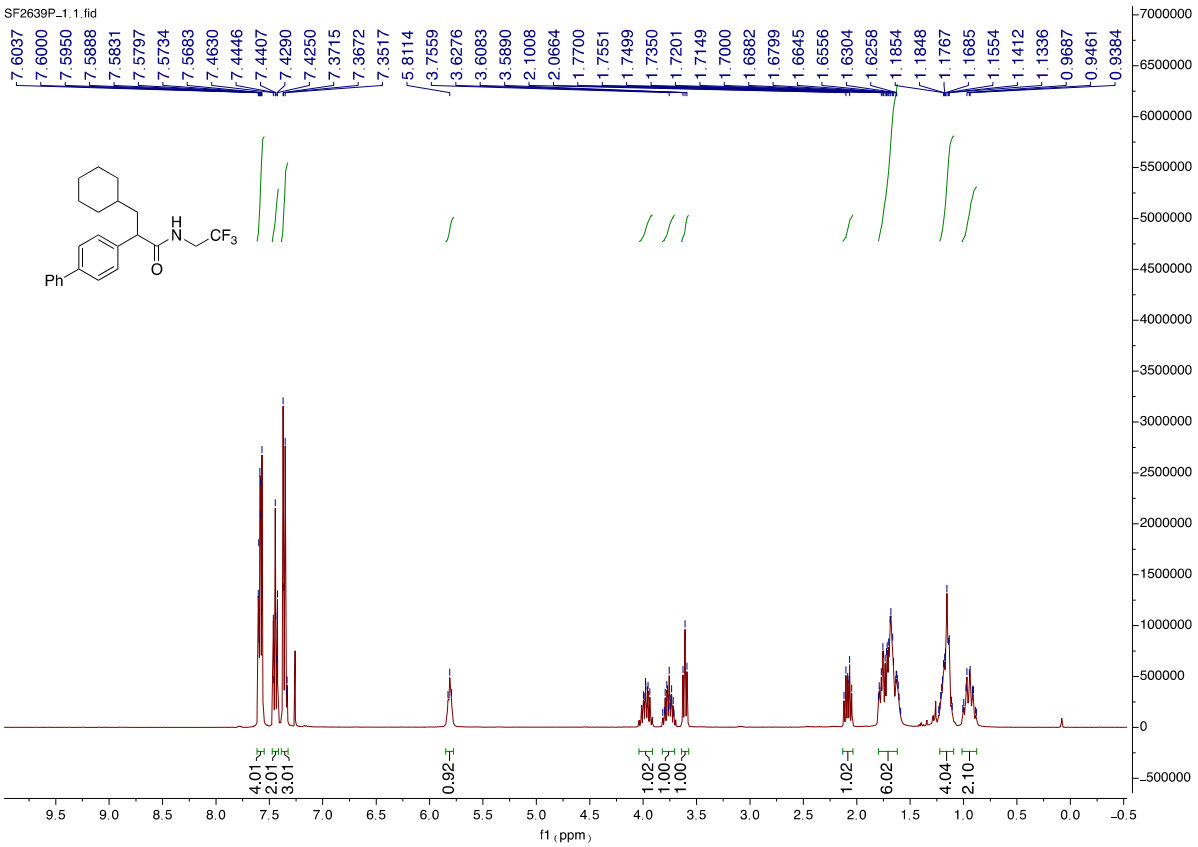
5f ^{13}C NMR (101 MHz, $CDCl_3$)



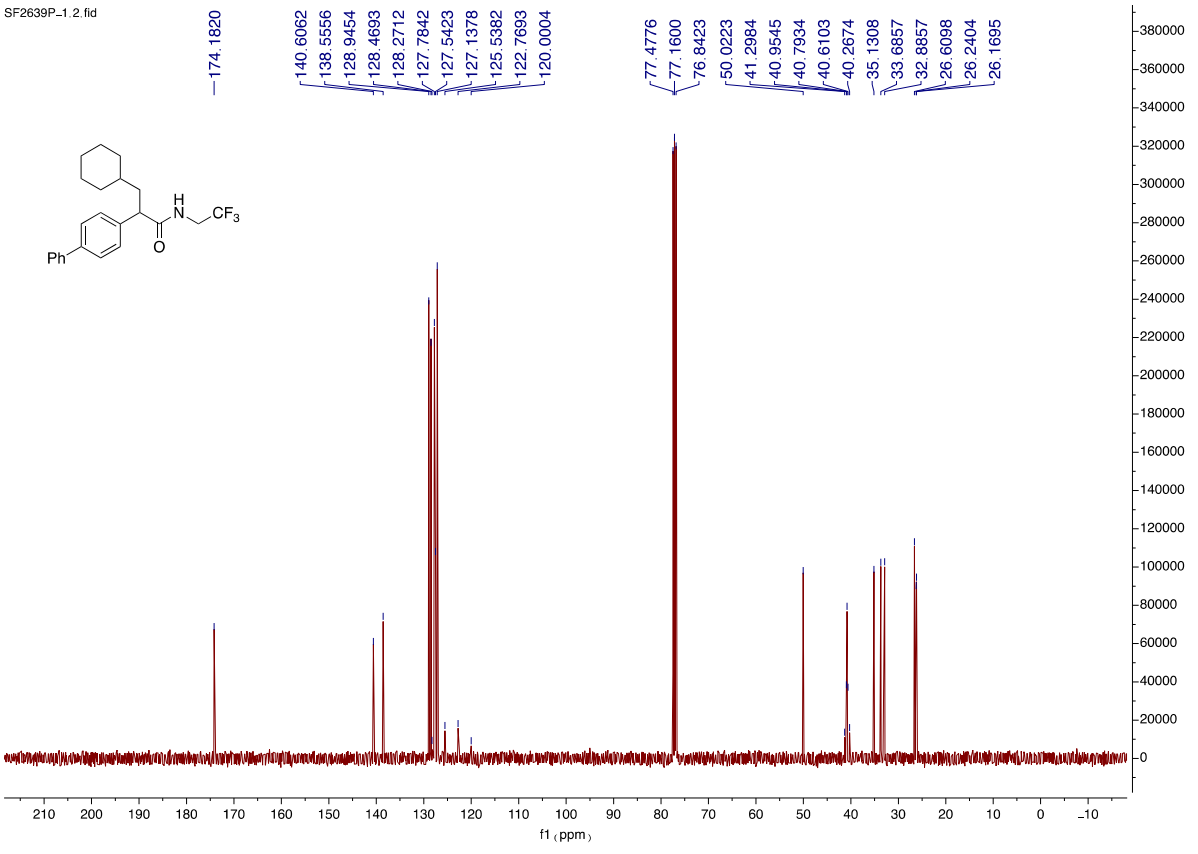
5g ^{1}H NMR (400 MHz, $CDCl_3$)



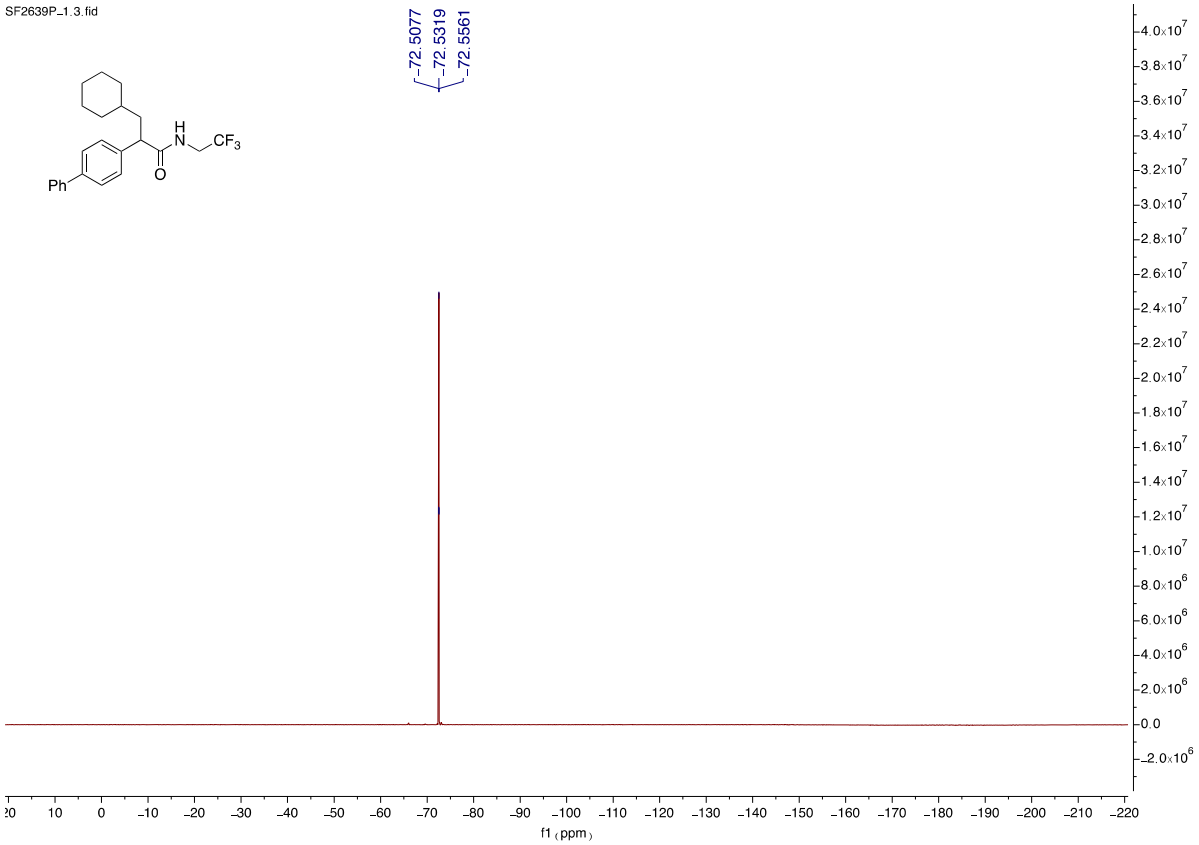
5g ^{13}C NMR (101 MHz, $CDCl_3$)



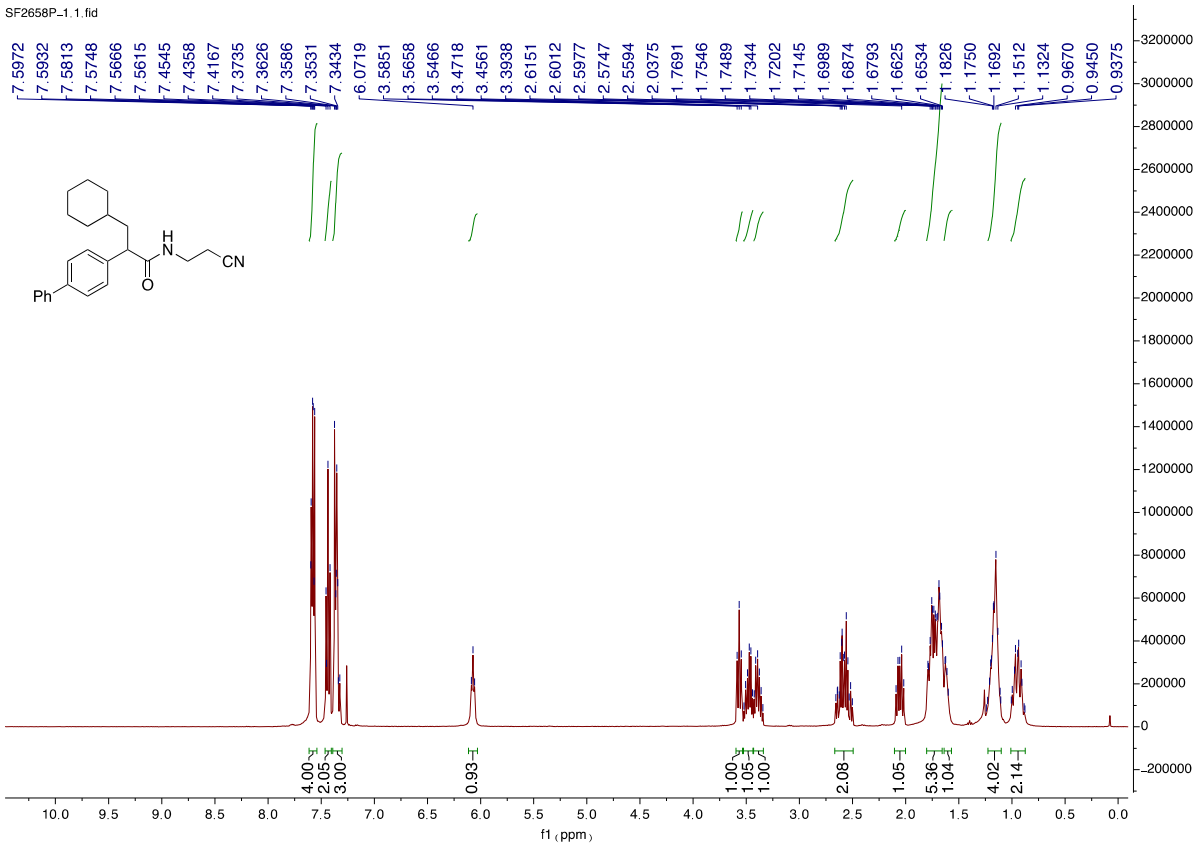
5h ^{1}H NMR (400 MHz, $CDCl_3$)



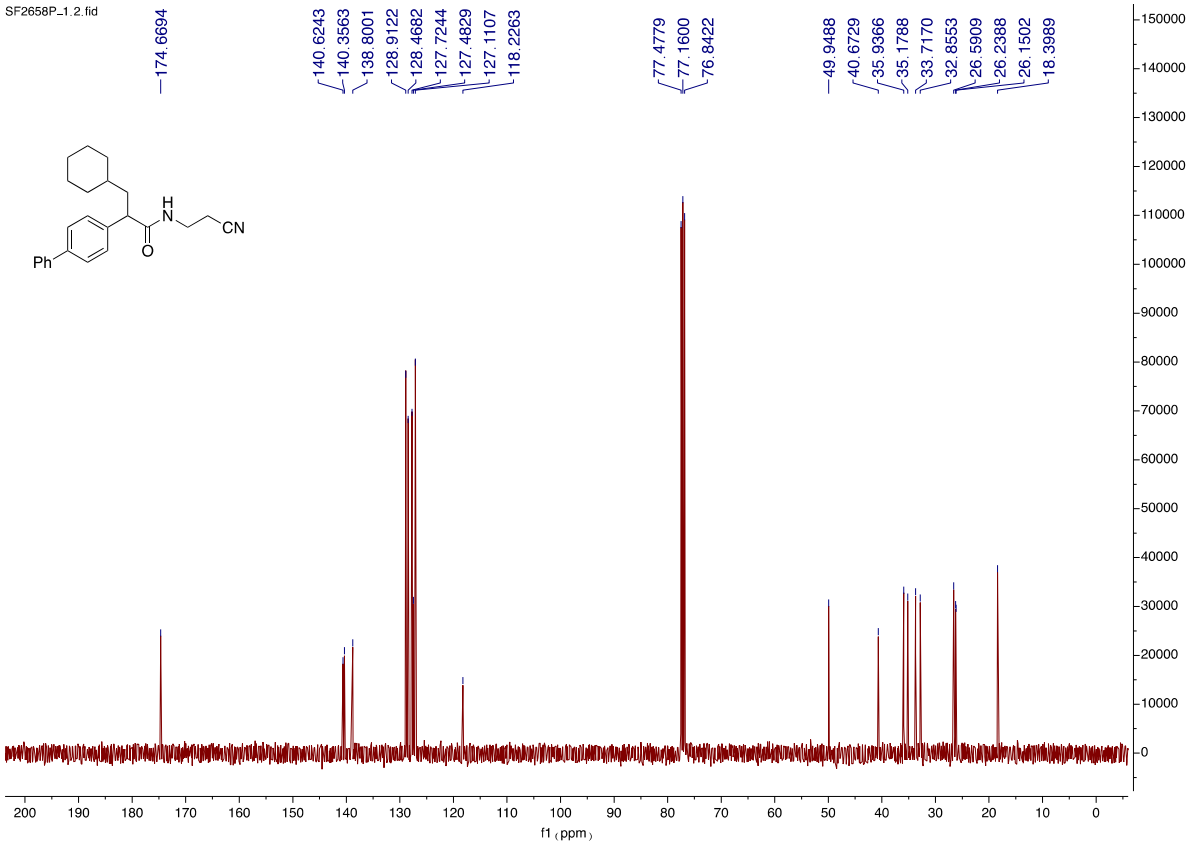
5h ^{13}C NMR (101 MHz, $CDCl_3$)



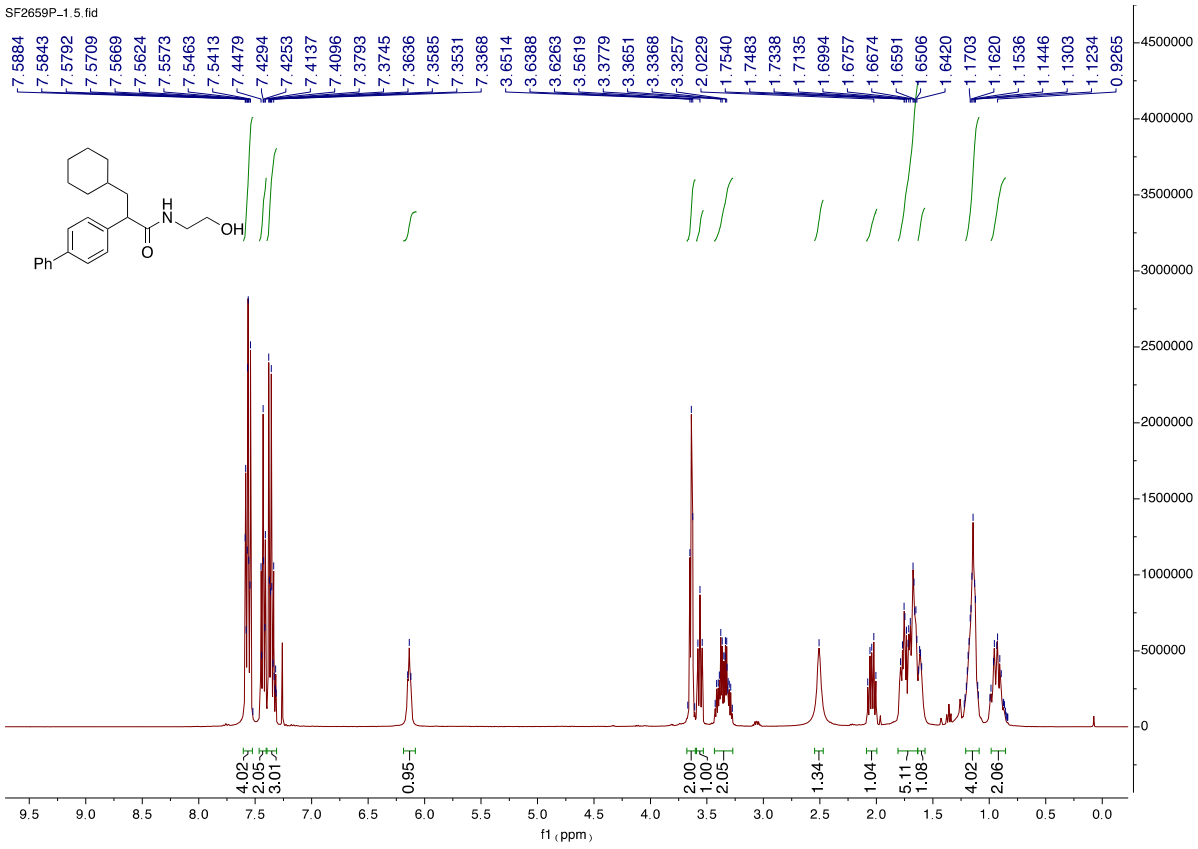
5h ^{19}F NMR (376 MHz, $CDCl_3$)



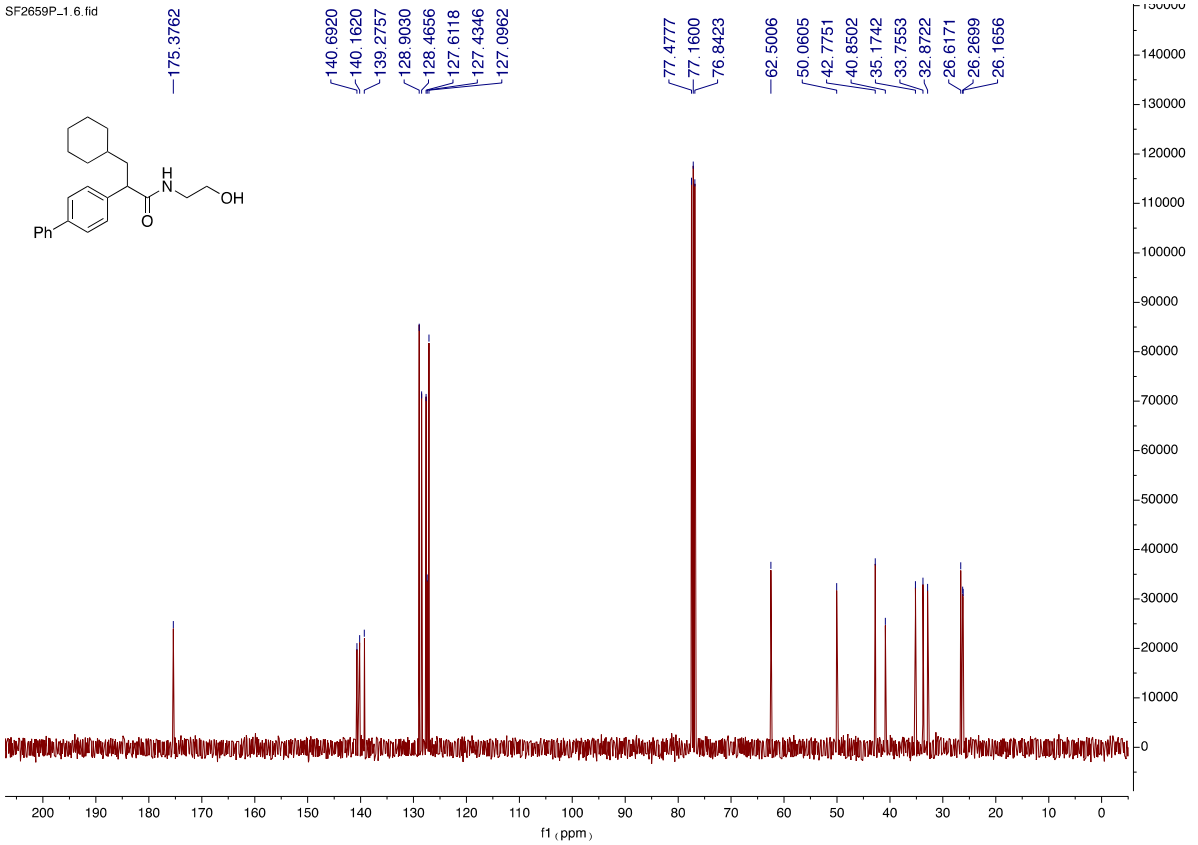
5i ^{1}H NMR (400 MHz, $CDCl_3$)



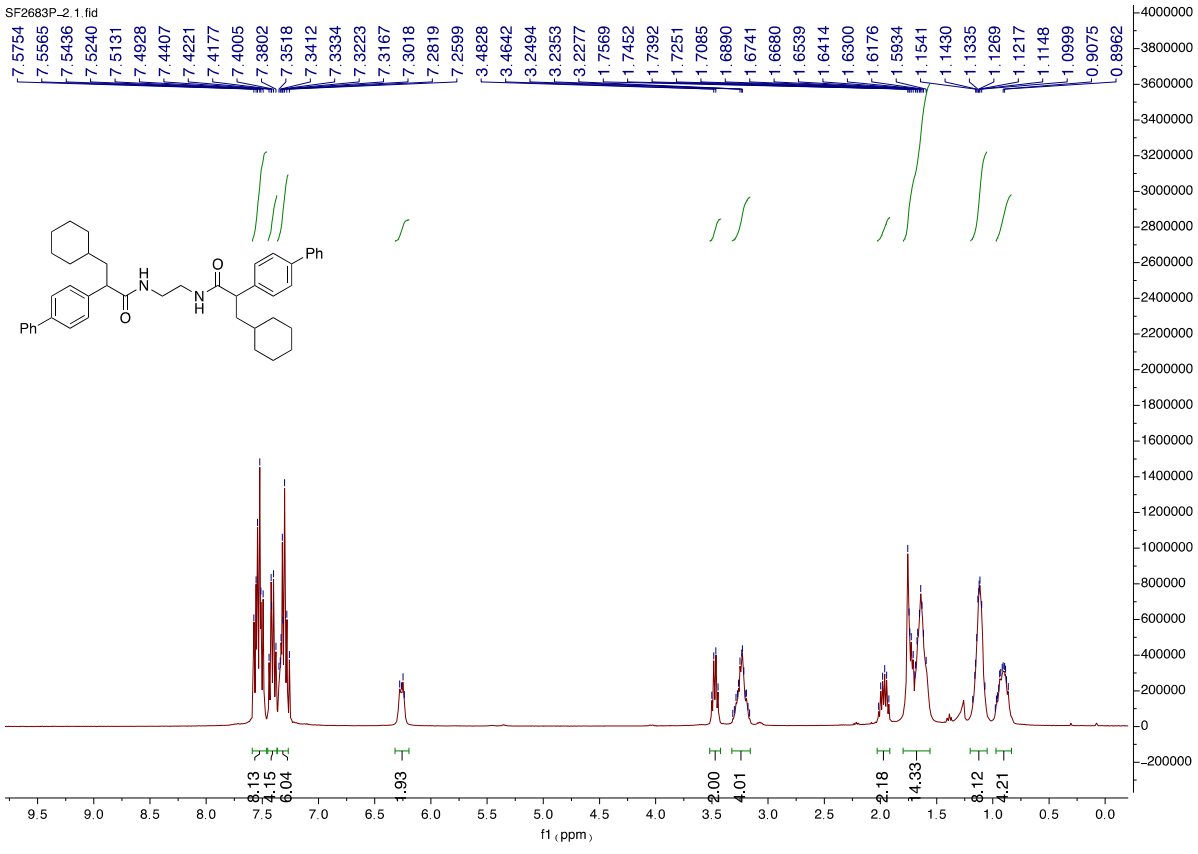
5i ^{13}C NMR (101 MHz, $CDCl_3$)



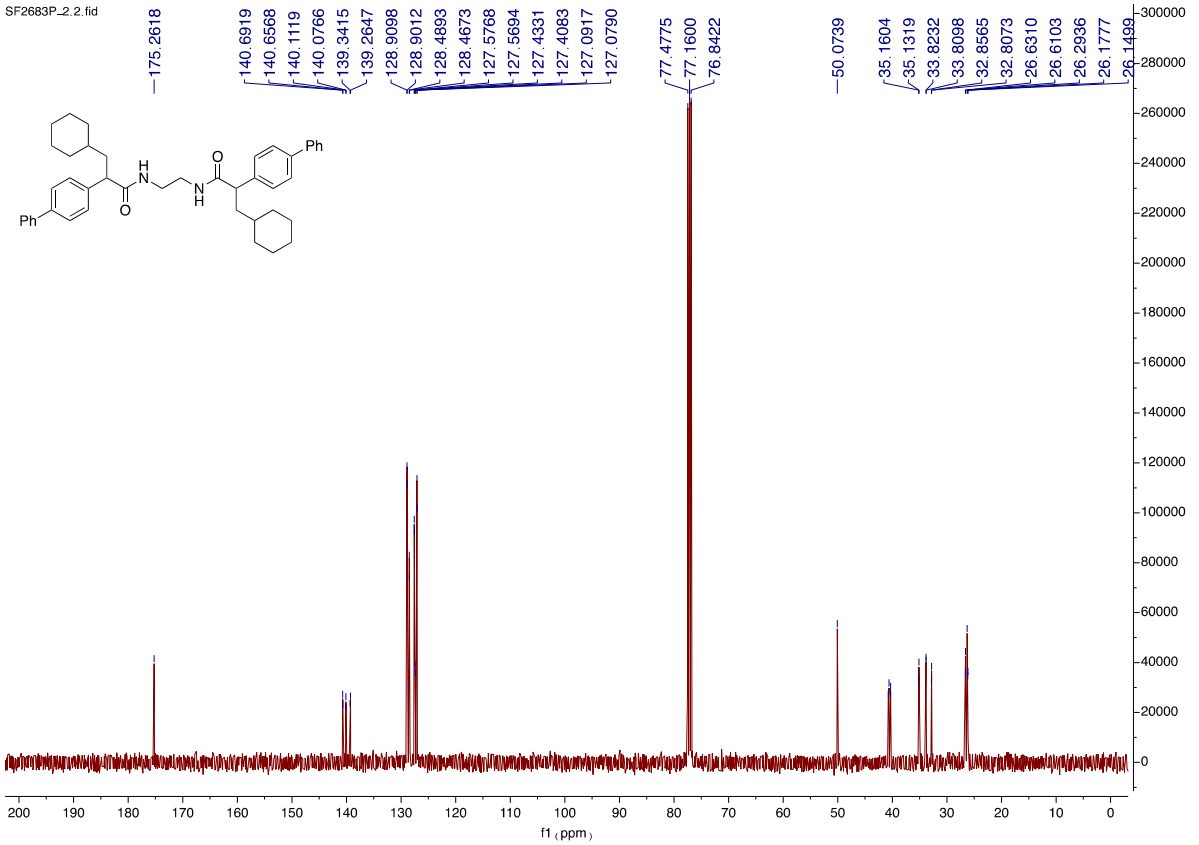
5j ^{1}H NMR (400 MHz, $CDCl_3$)



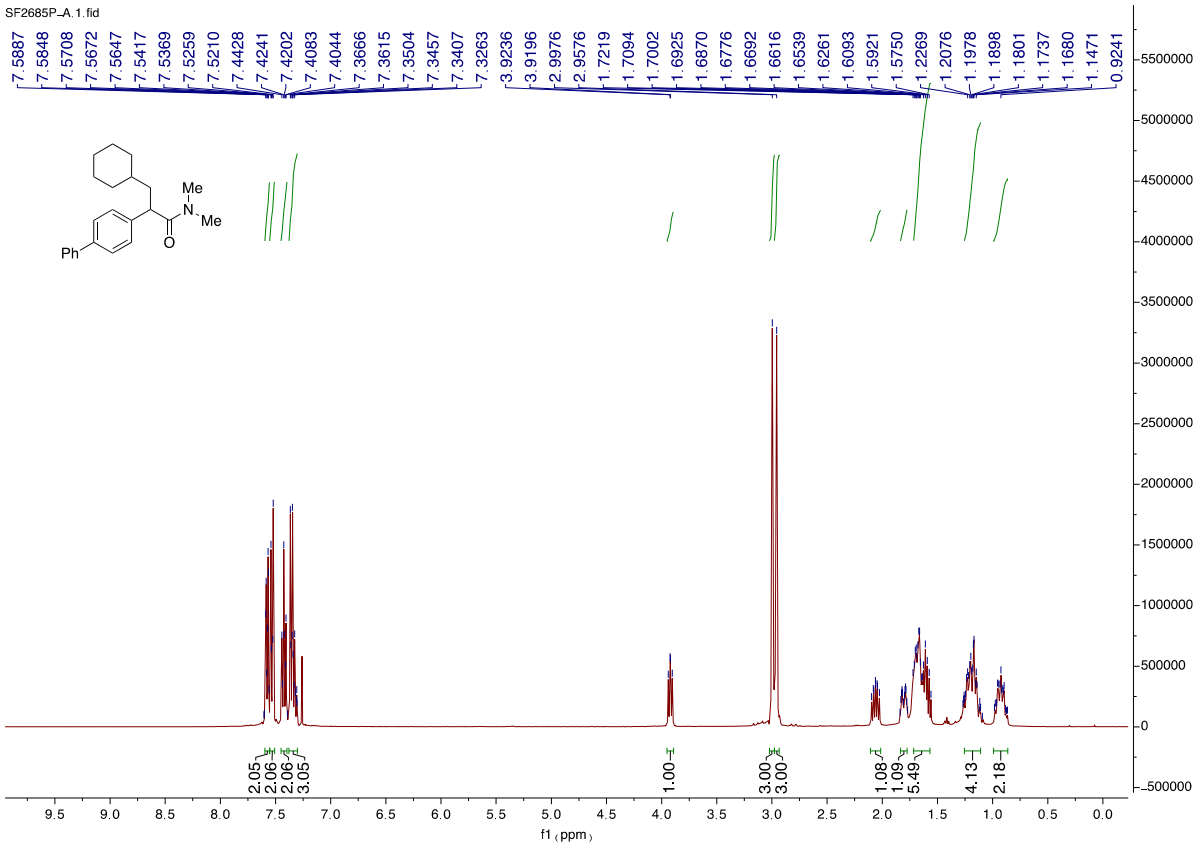
5j ^{13}C NMR (101 MHz, $CDCl_3$)



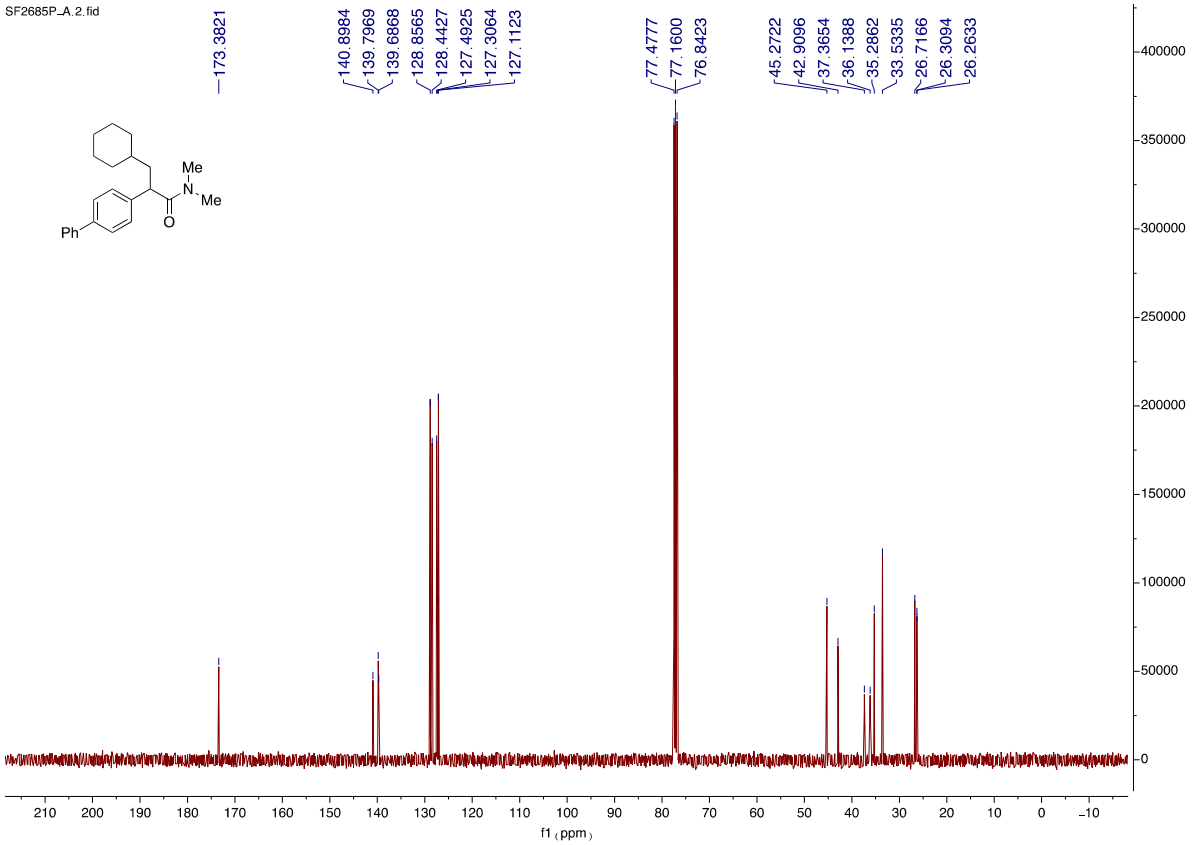
5k ^{1}H NMR (400 MHz, $CDCl_3$)



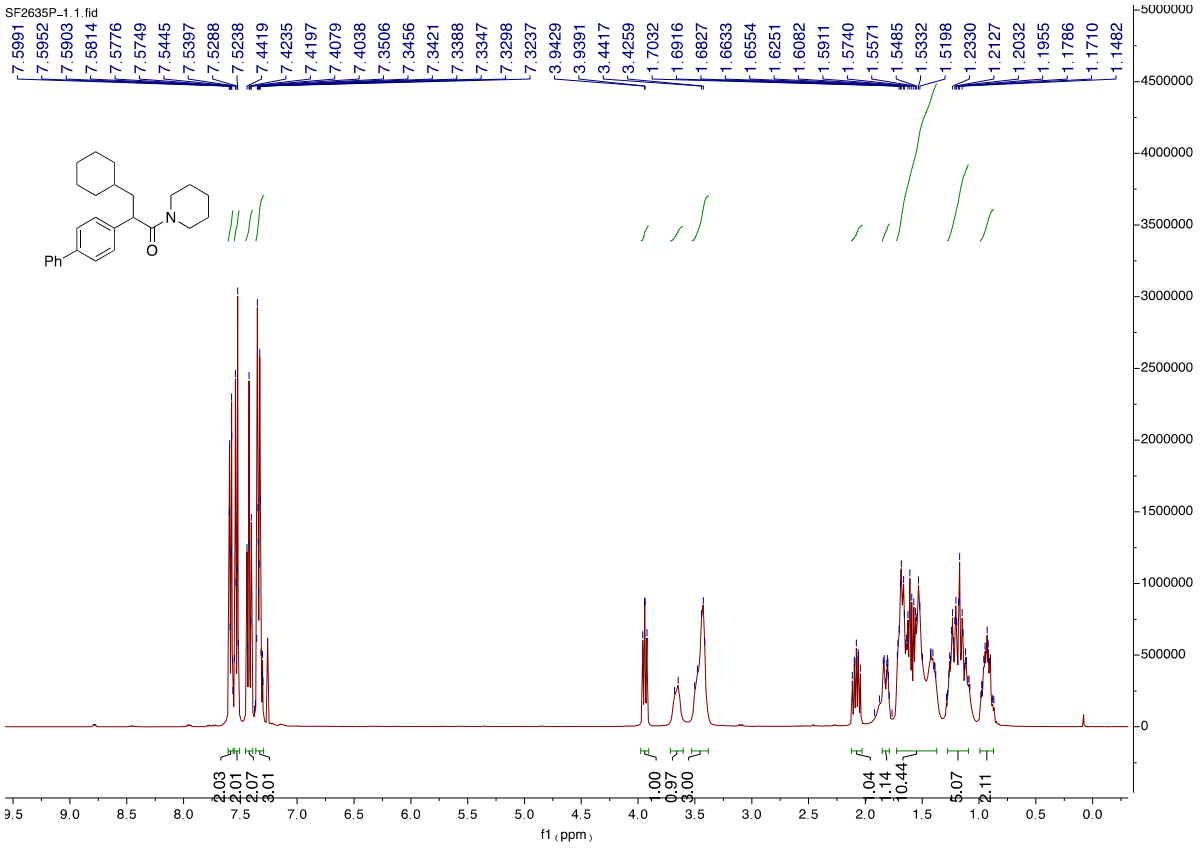
5k ^{13}C NMR (101 MHz, $CDCl_3$)



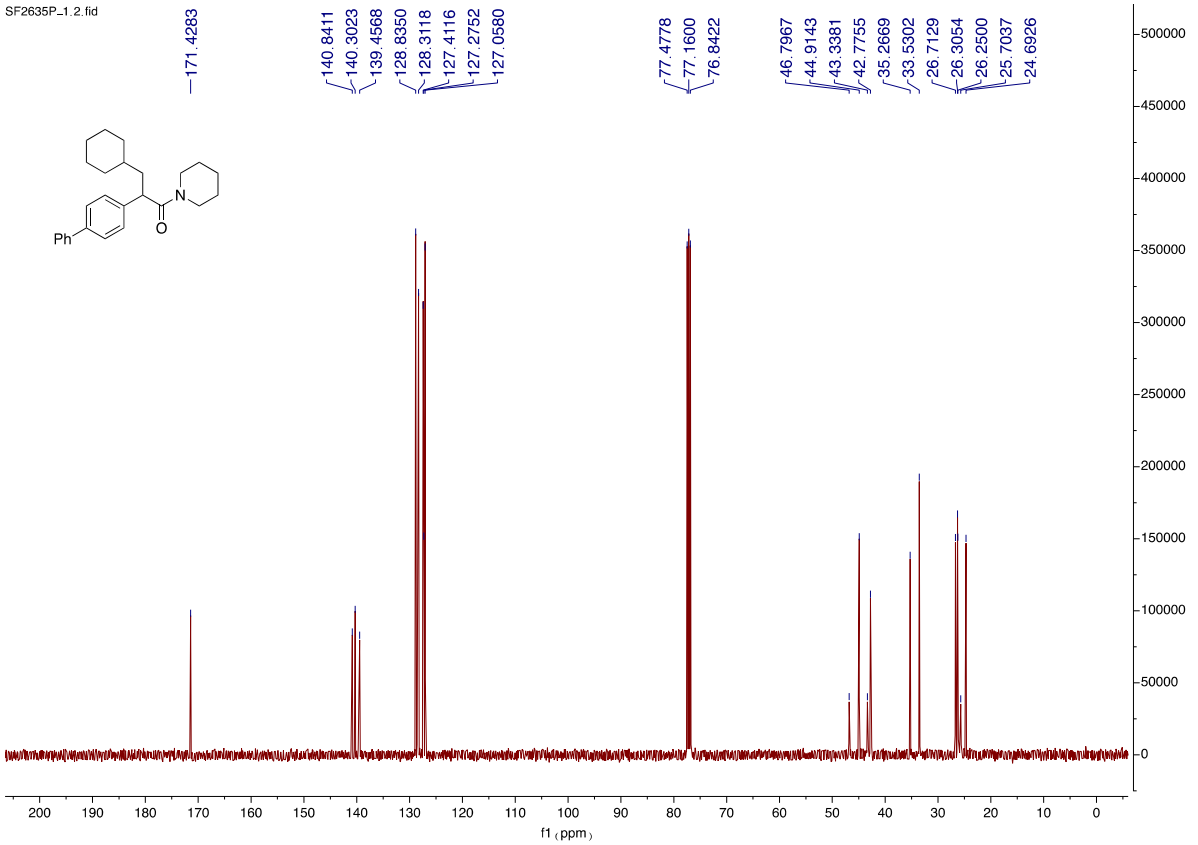
5l ^{1}H NMR (400 MHz, $CDCl_3$)



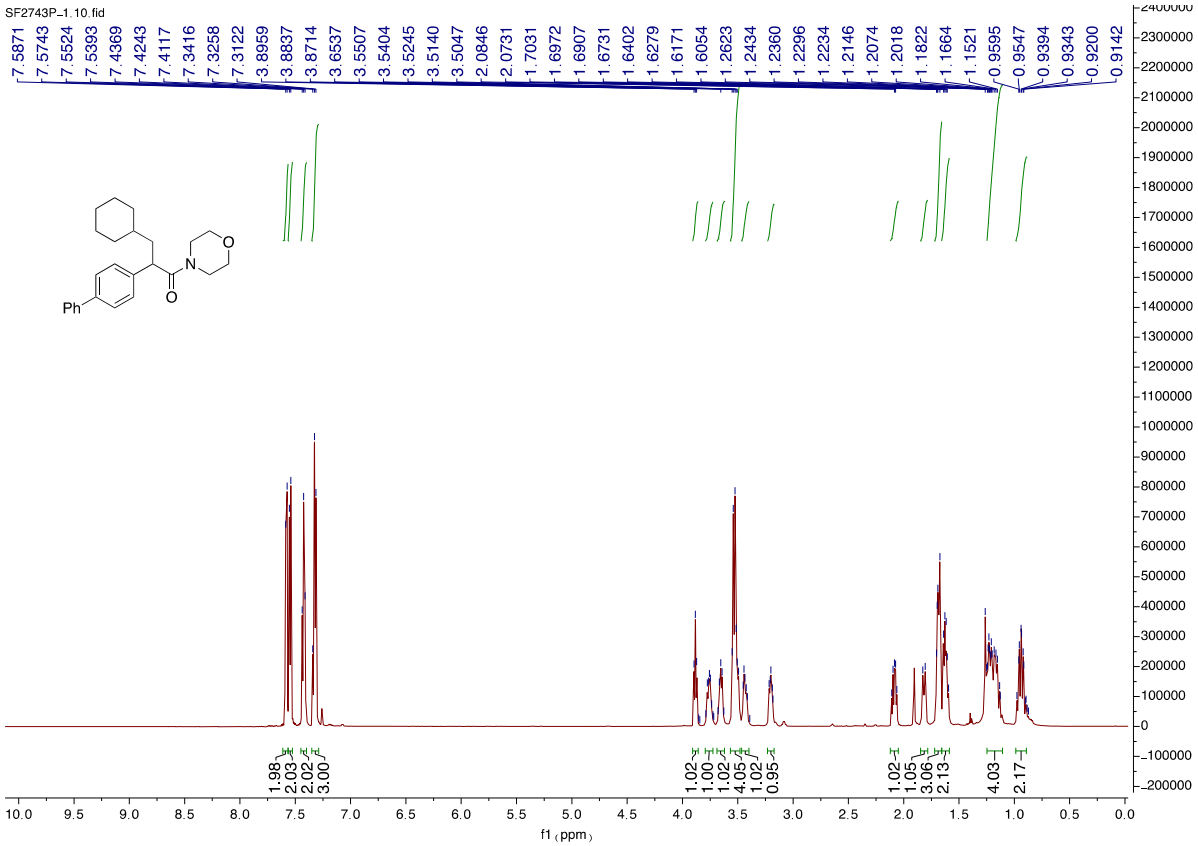
5l ^{13}C NMR (101 MHz, $CDCl_3$)



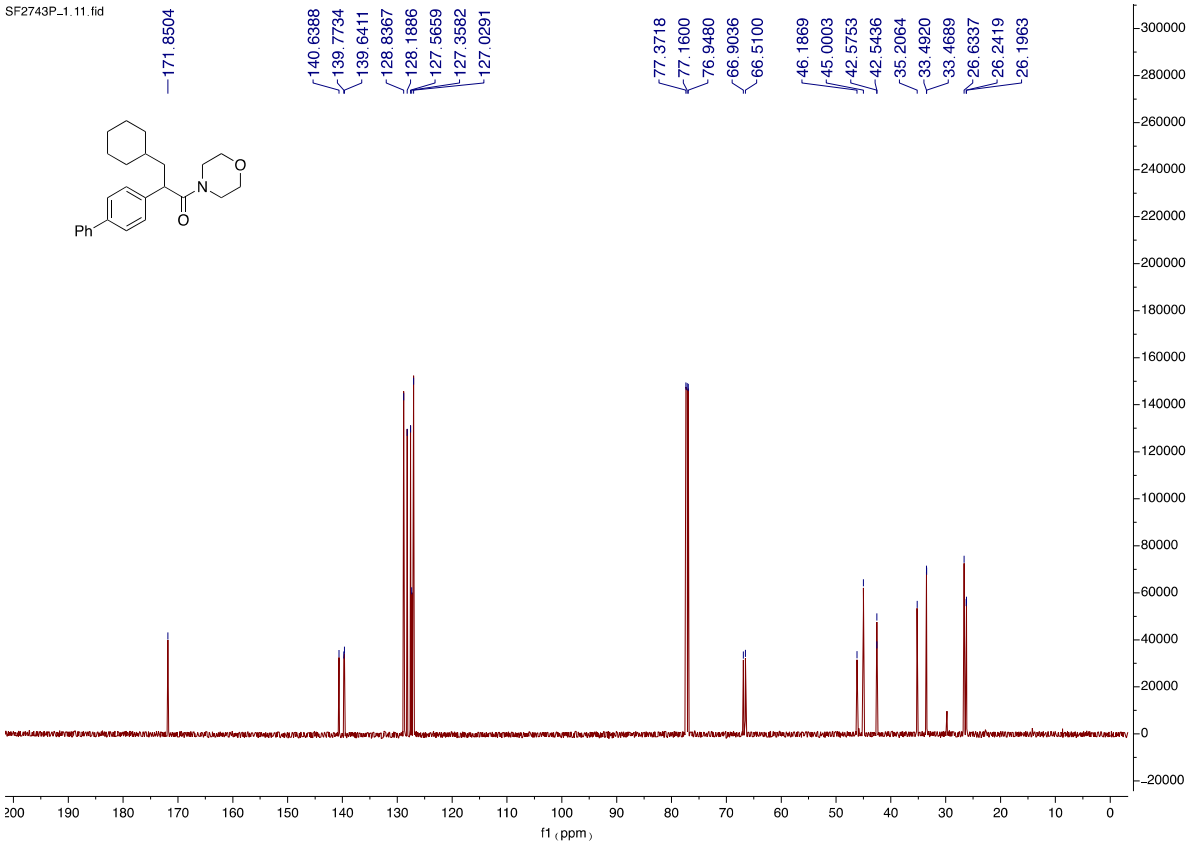
5m ^{1}H NMR (400 MHz, $CDCl_3$)



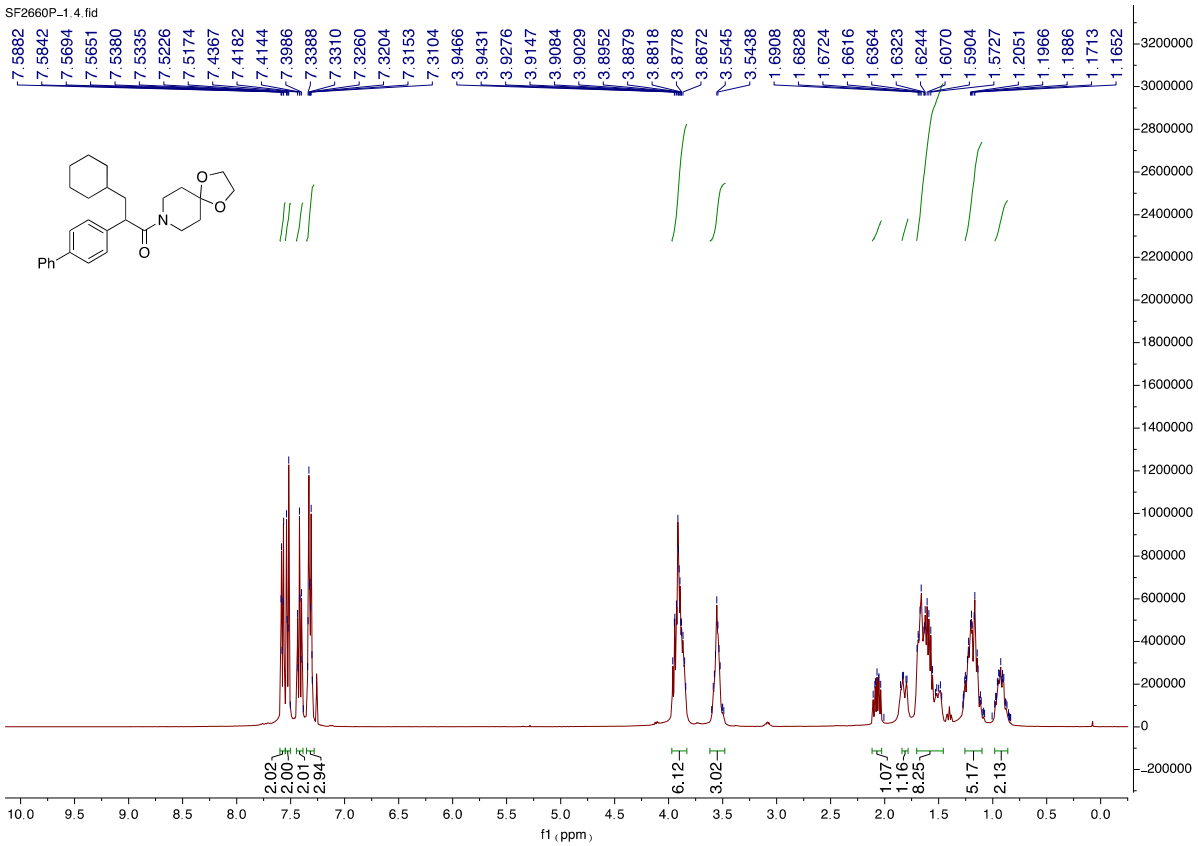
5m ^{13}C NMR (101 MHz, $CDCl_3$)



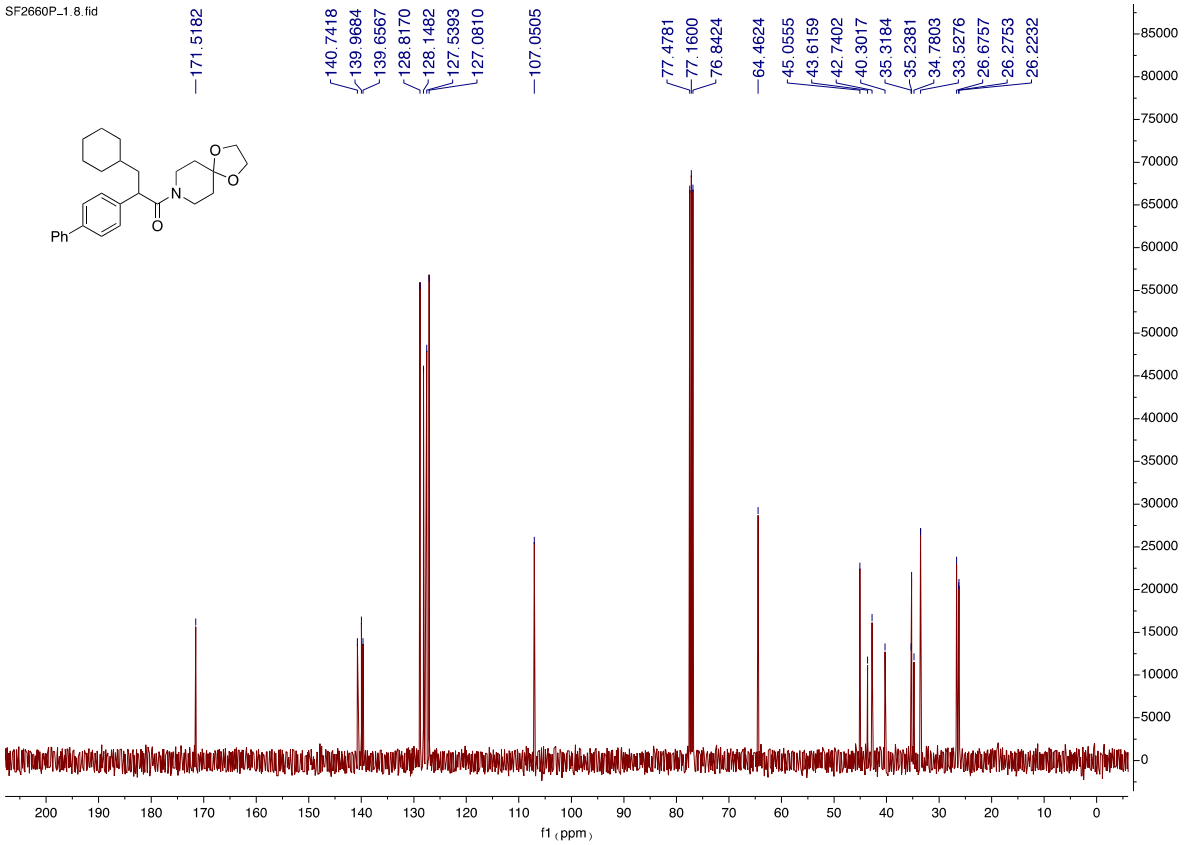
5n ^{1}H NMR (600 MHz, $CDCl_3$)



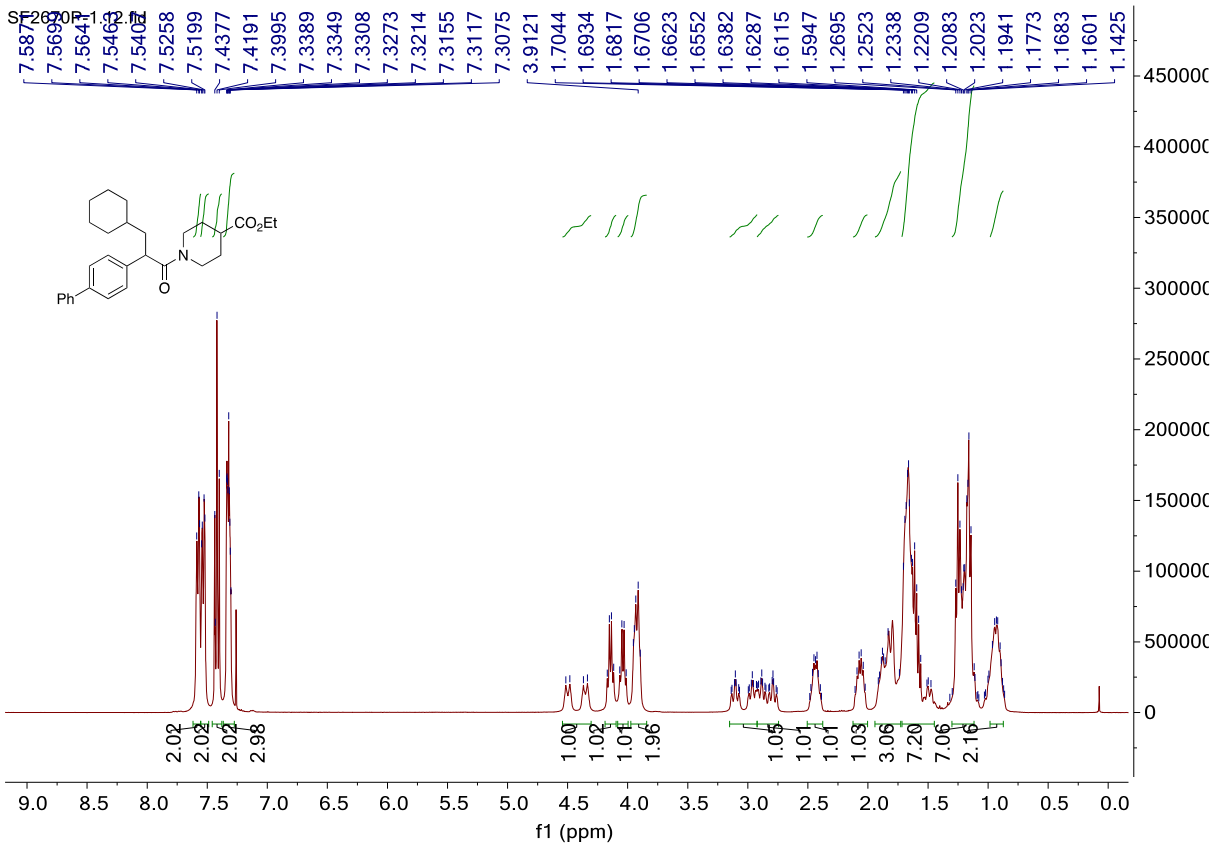
5n ^{13}C NMR (151 MHz, $CDCl_3$)



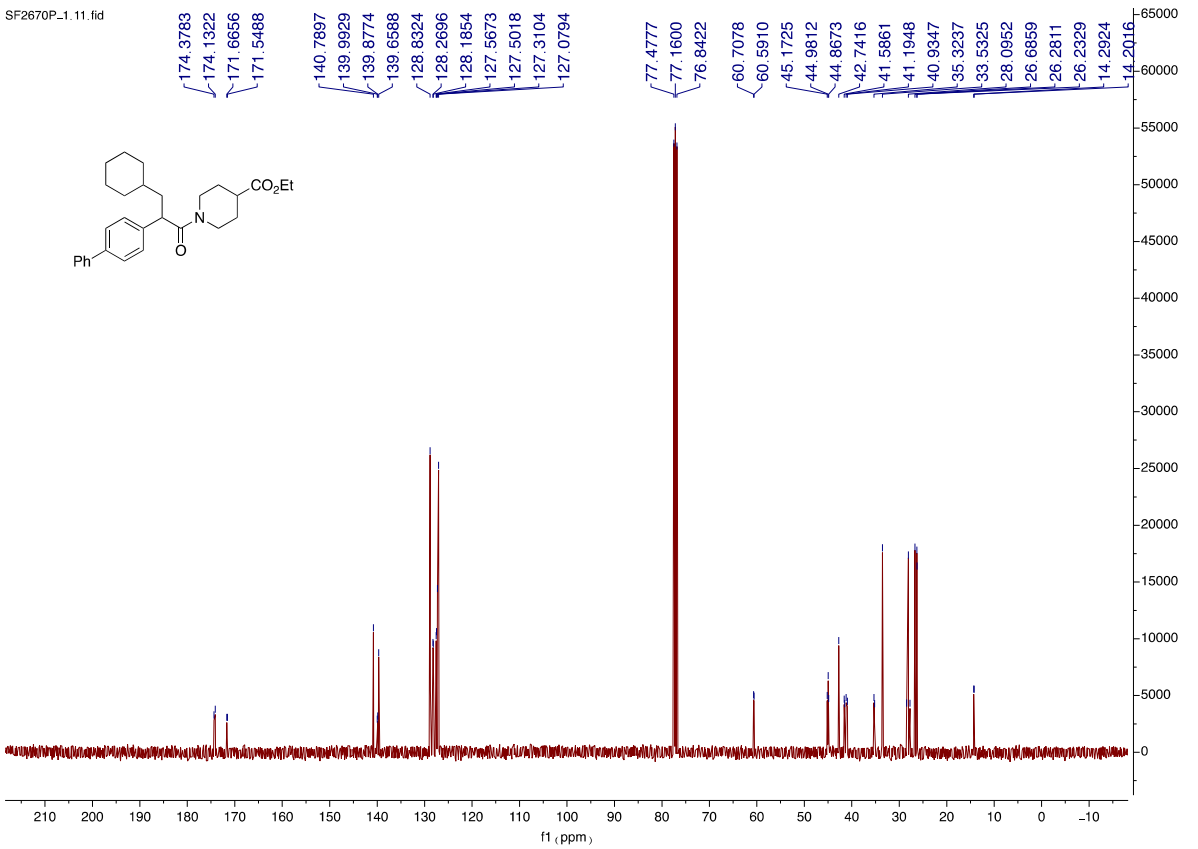
5o ^{1}H NMR (400 MHz, $CDCl_3$)



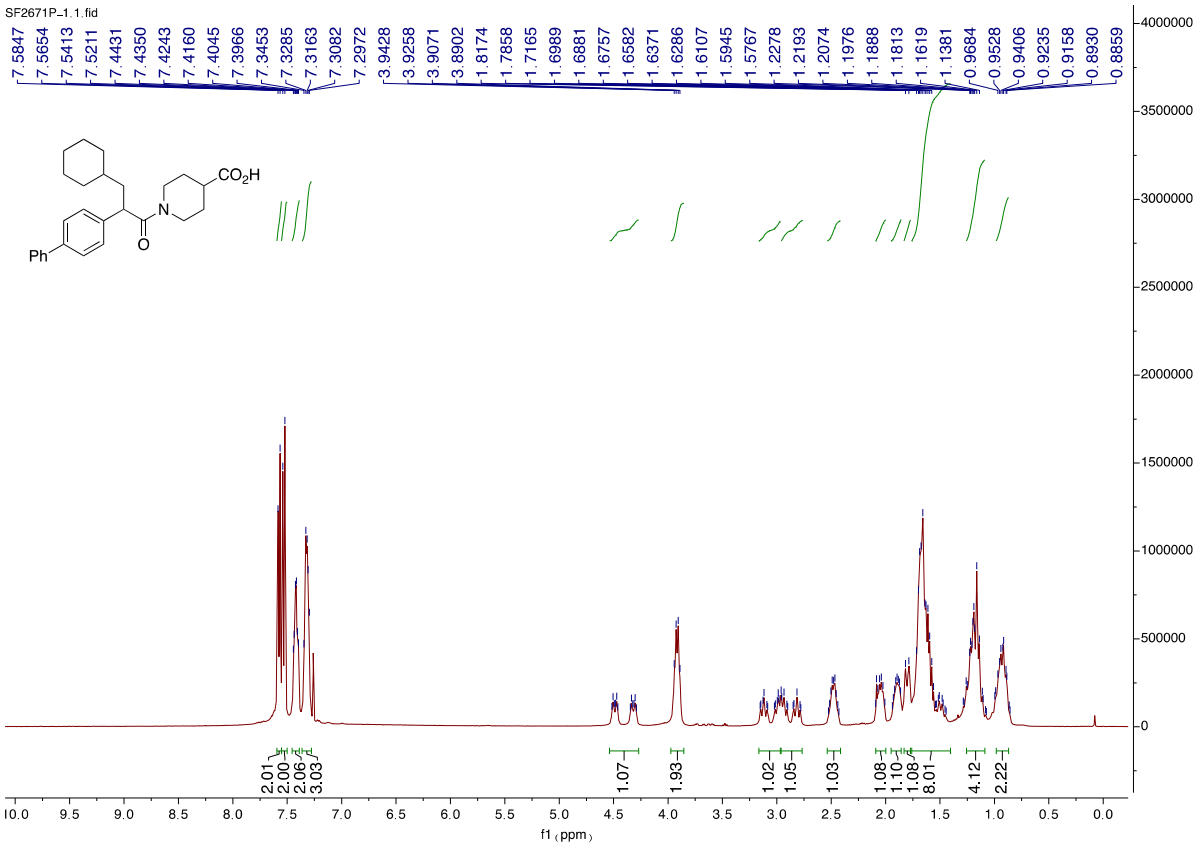
5o ^{13}C NMR (101 MHz, $CDCl_3$)



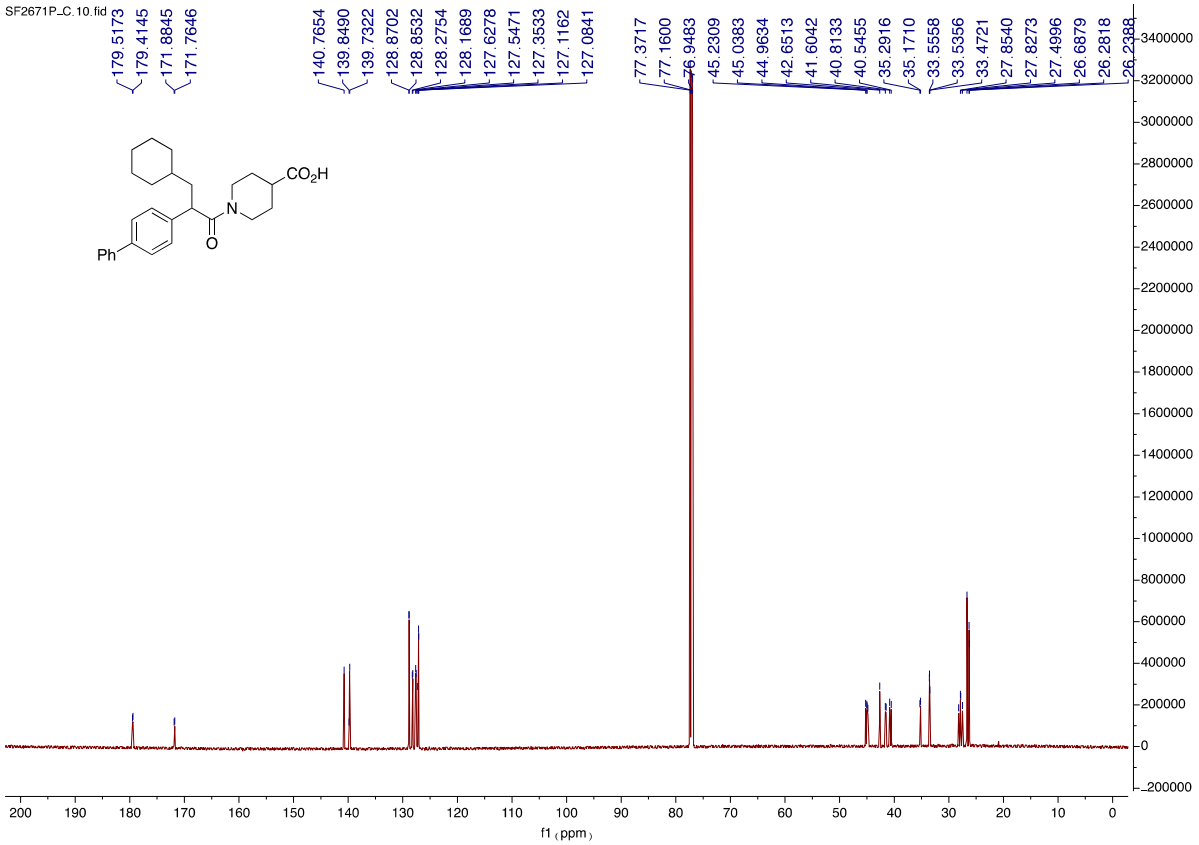
5p ^{1}H NMR (400 MHz, $CDCl_3$)



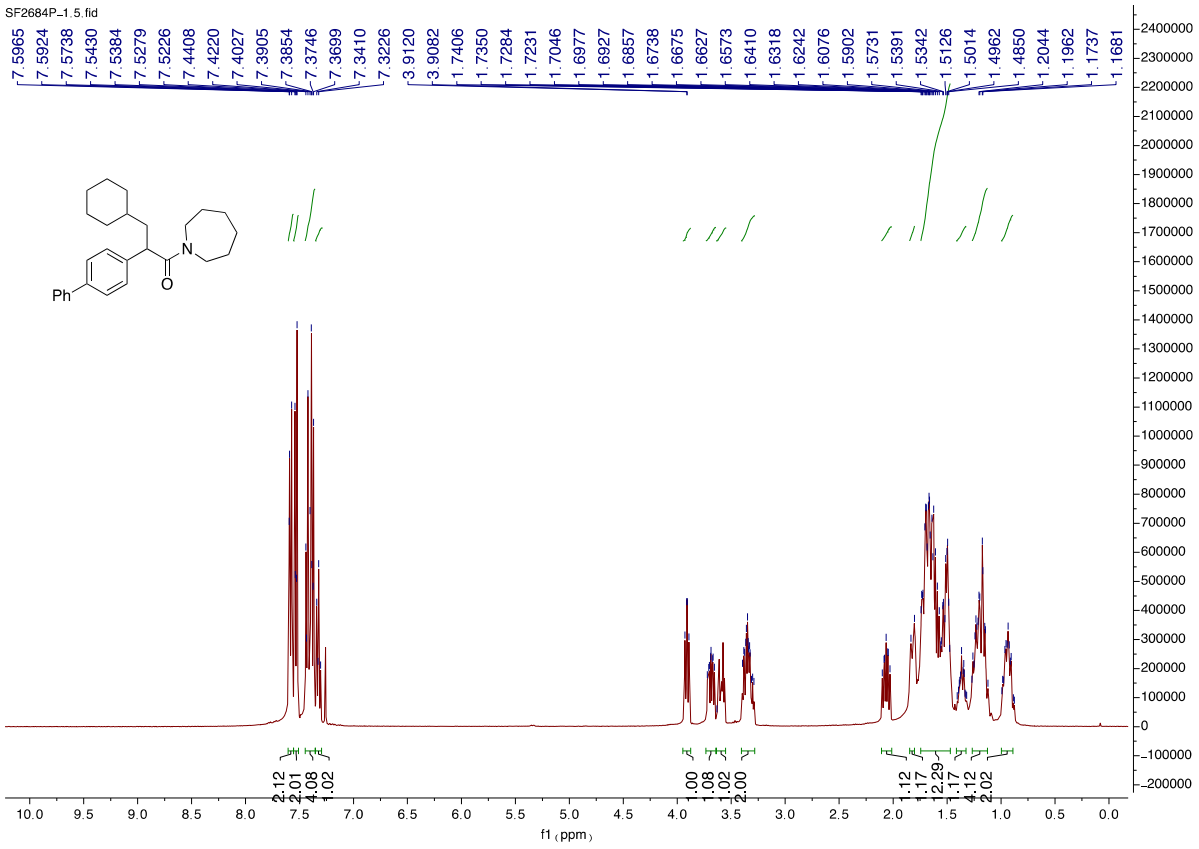
5p ^{13}C NMR (101 MHz, $CDCl_3$)



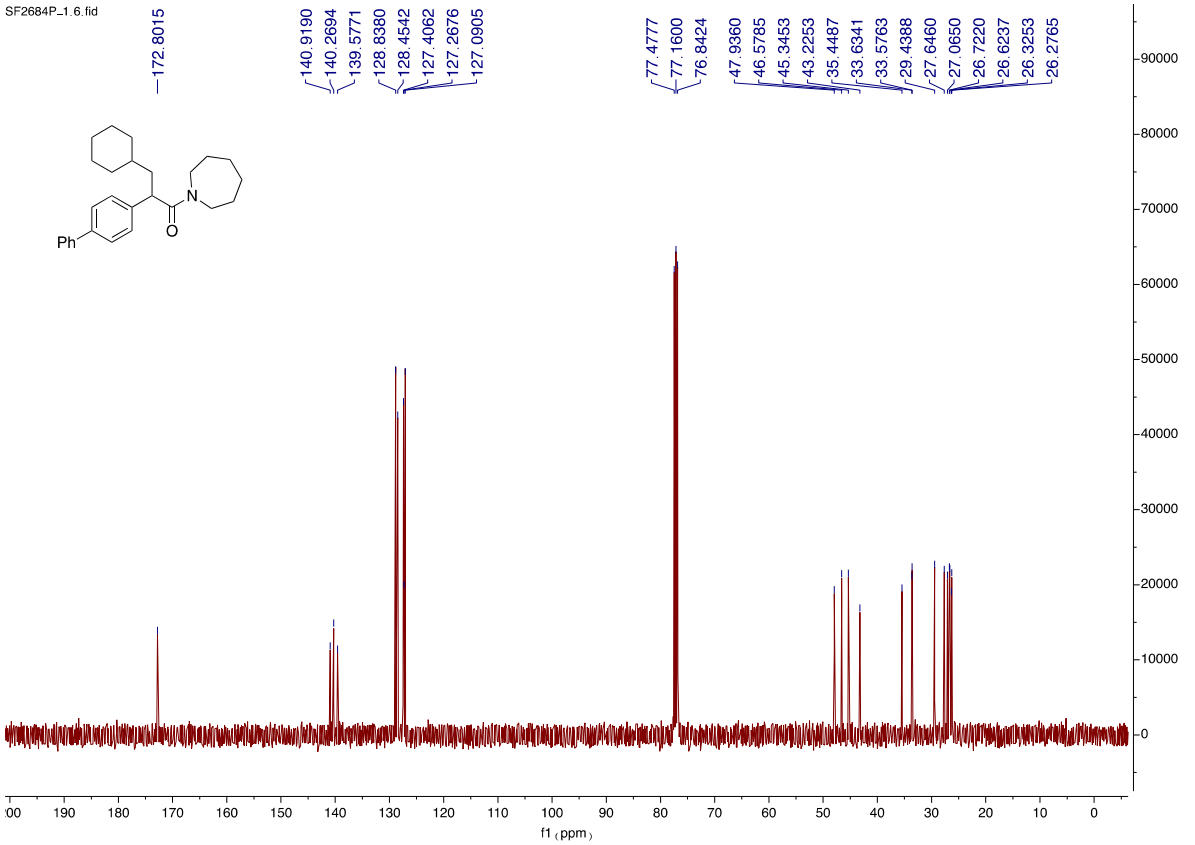
5q ^{1}H NMR (400 MHz, $CDCl_3$)



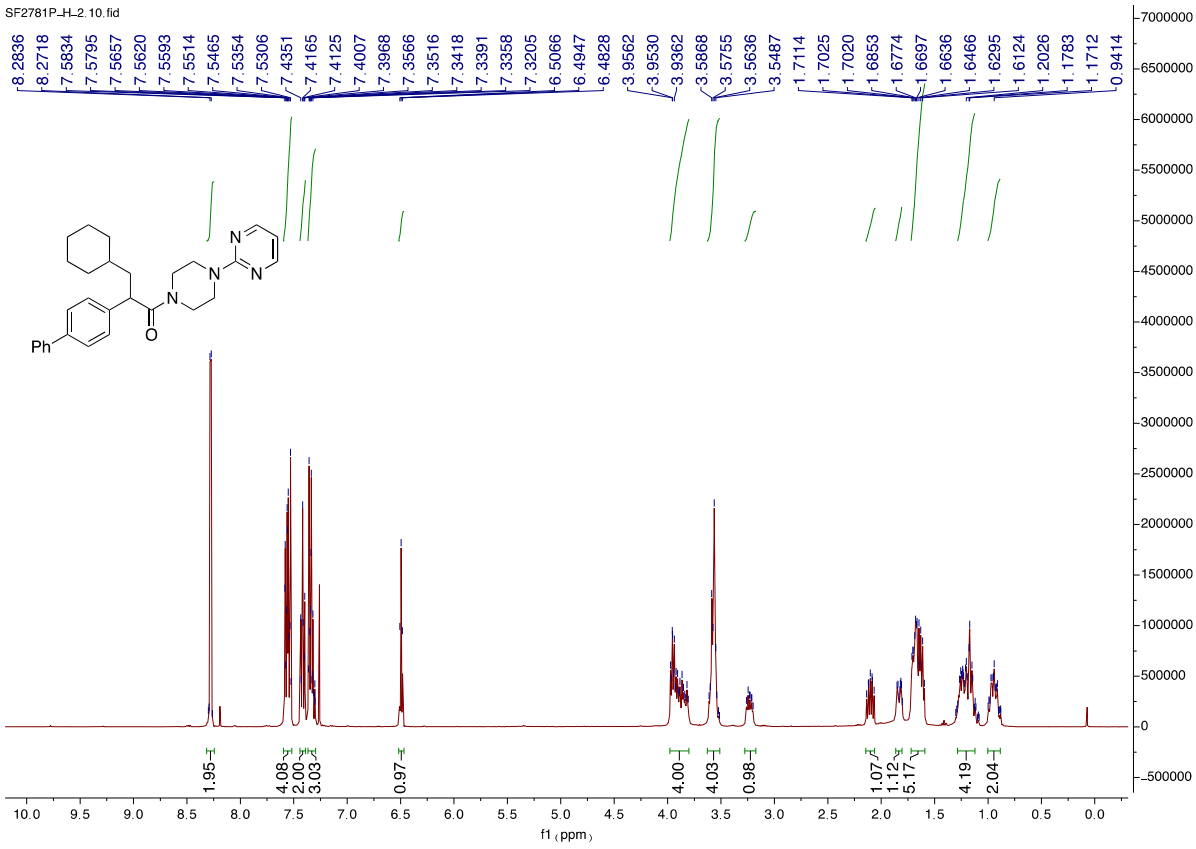
5q ^{13}C NMR (151 MHz, $CDCl_3$)



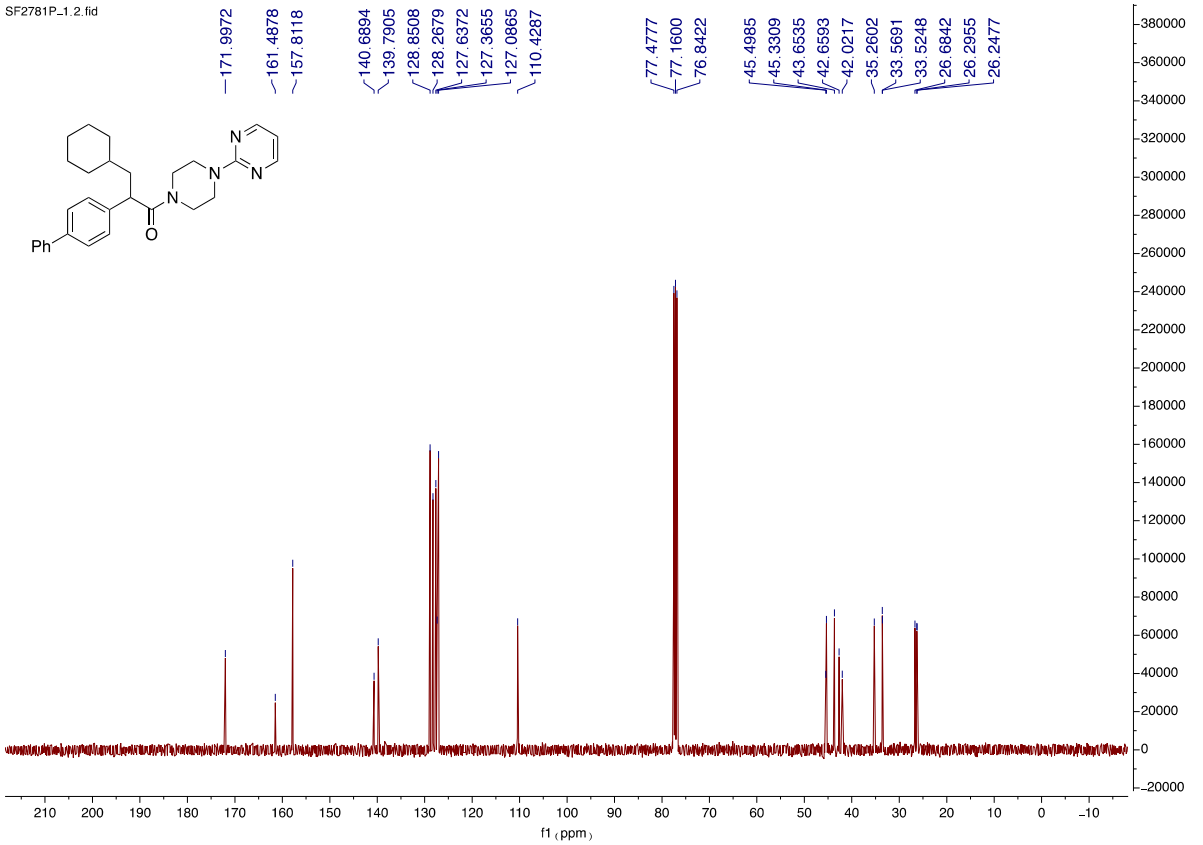
5r ^{1}H NMR (400 MHz, $CDCl_3$)



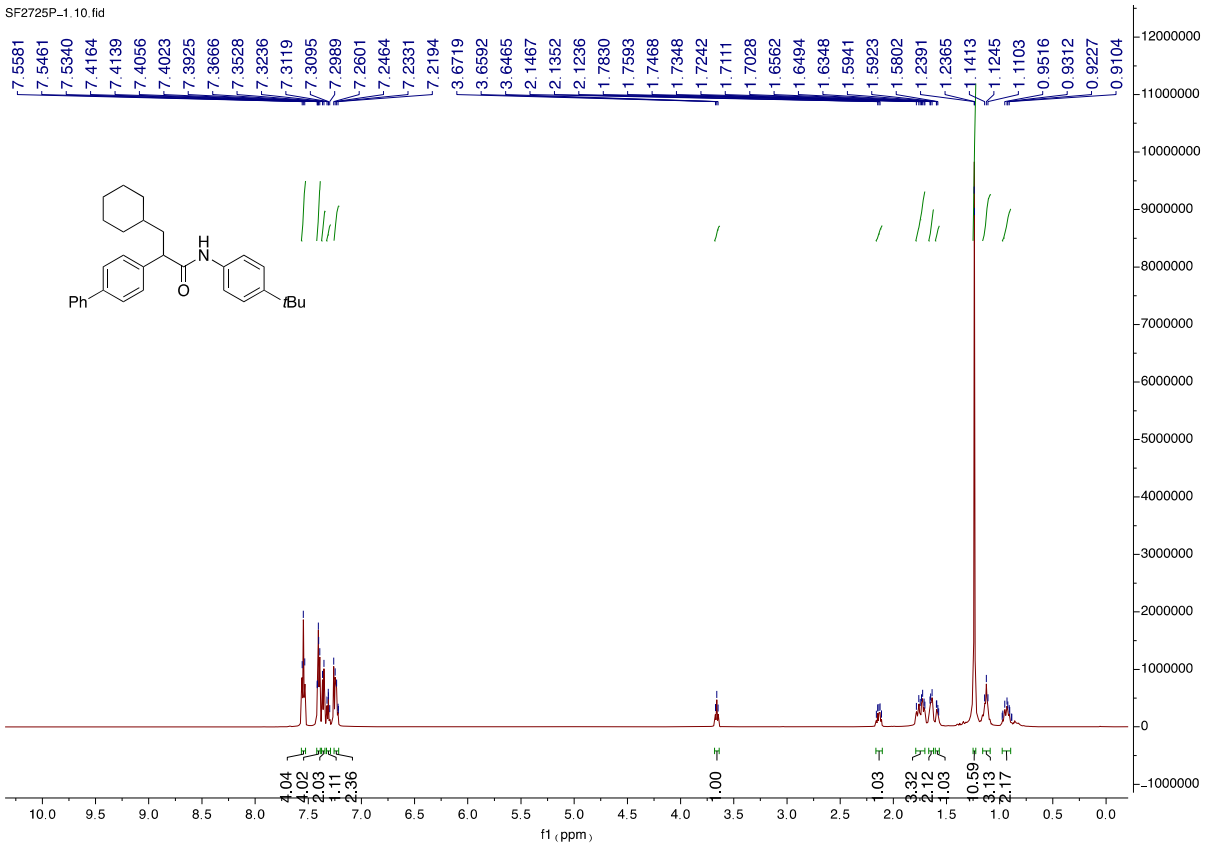
5r ^{13}C NMR (101 MHz, $CDCl_3$)



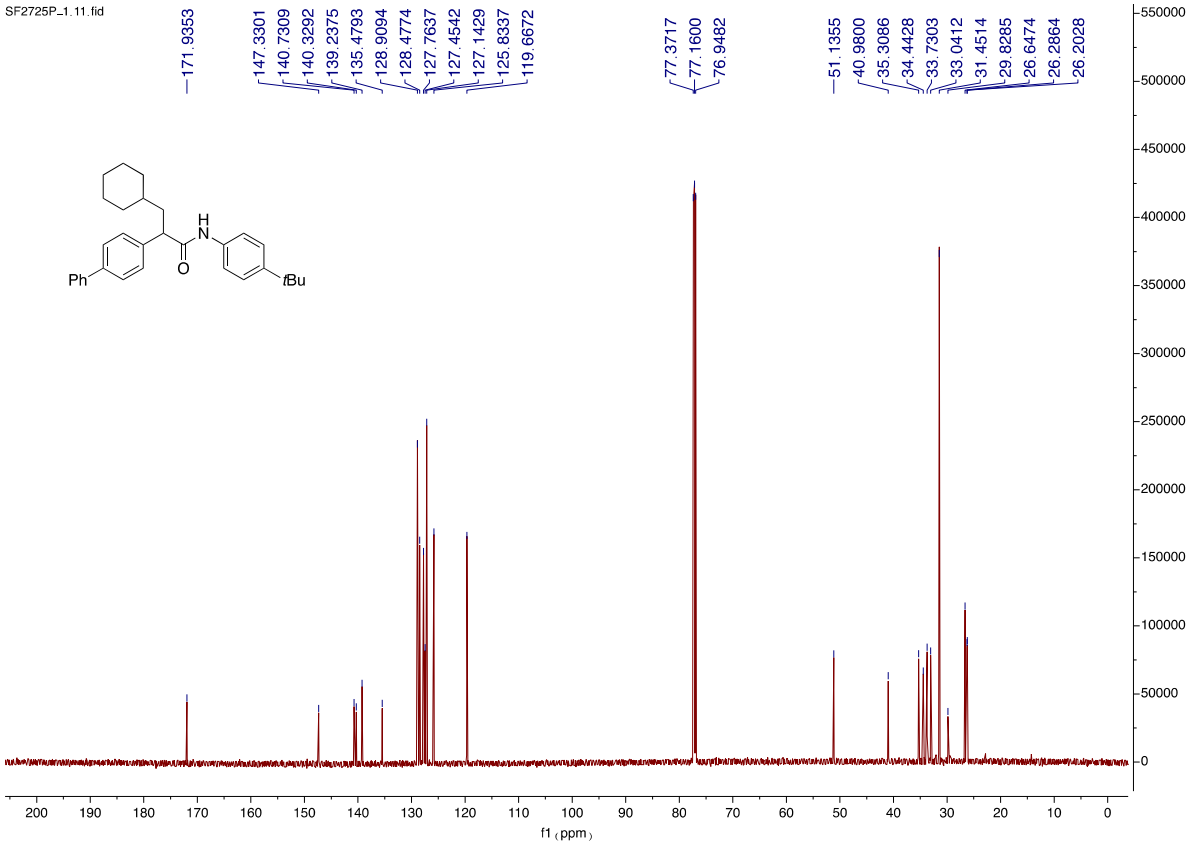
5s ^{1}H NMR (400 MHz, $CDCl_3$)



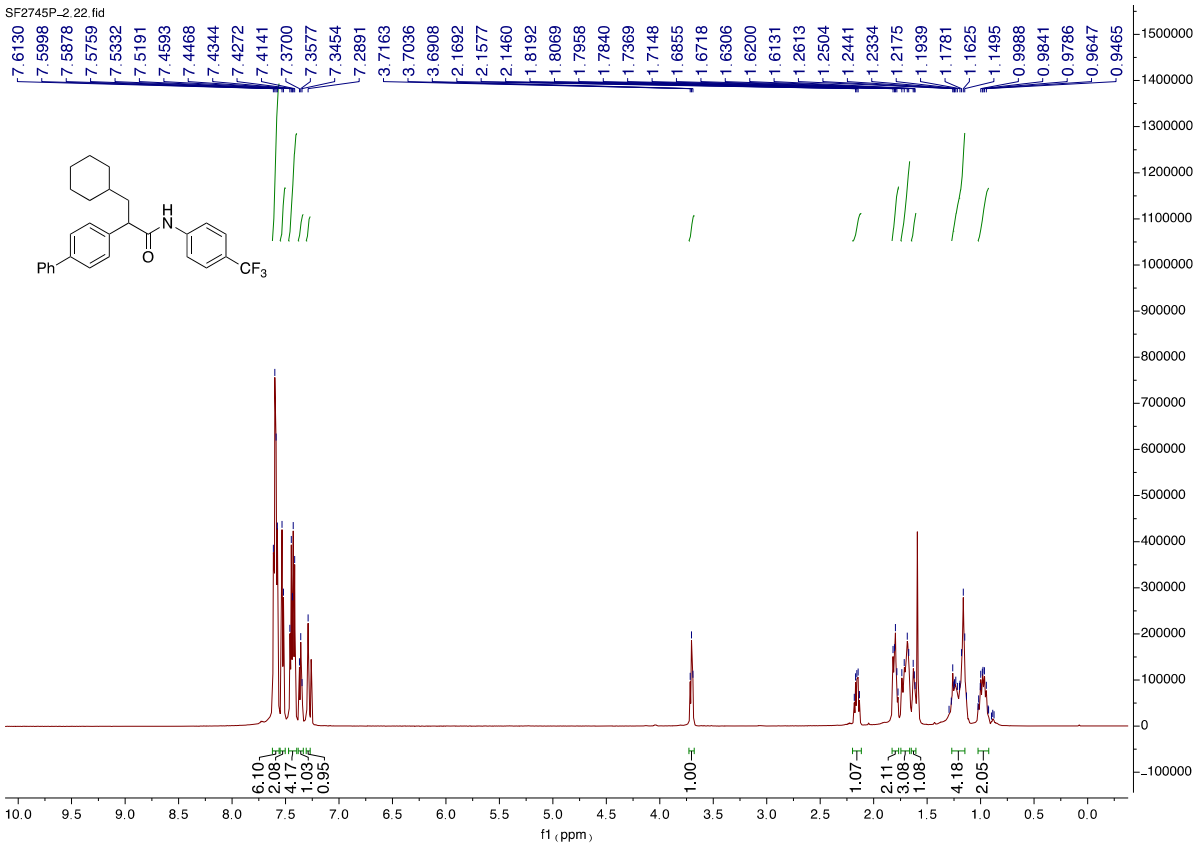
5s ^{13}C NMR (101 MHz, $CDCl_3$)



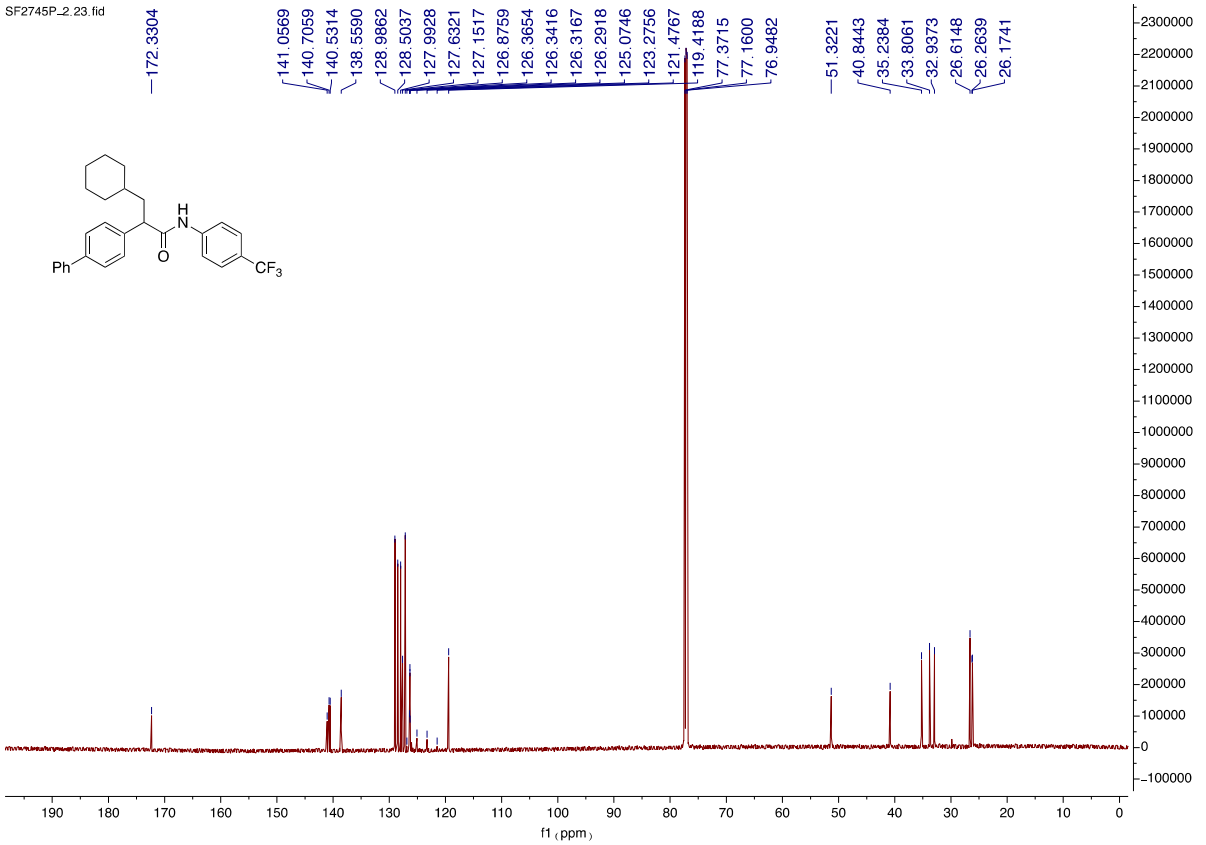
5t ^{1}H NMR (600 MHz, $CDCl_3$)



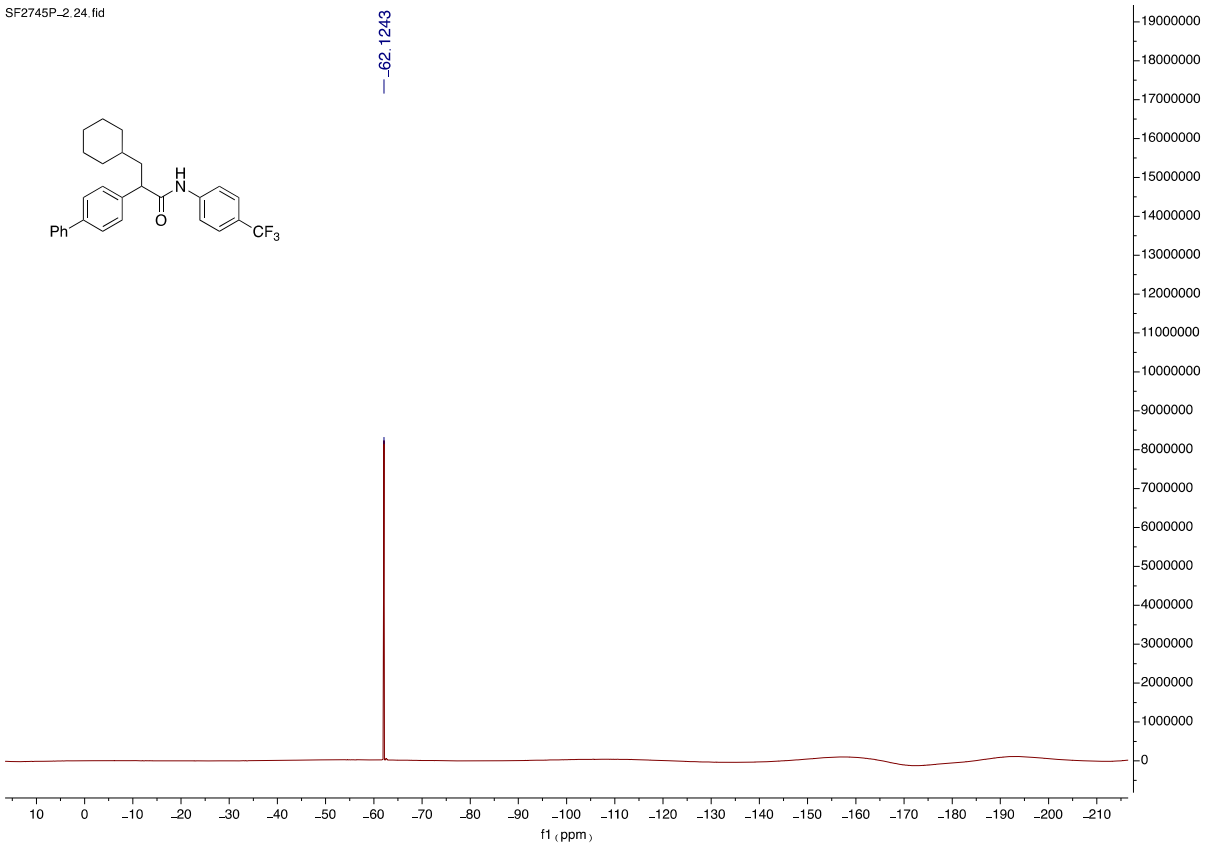
5t ^{13}C NMR (151 MHz, $CDCl_3$)



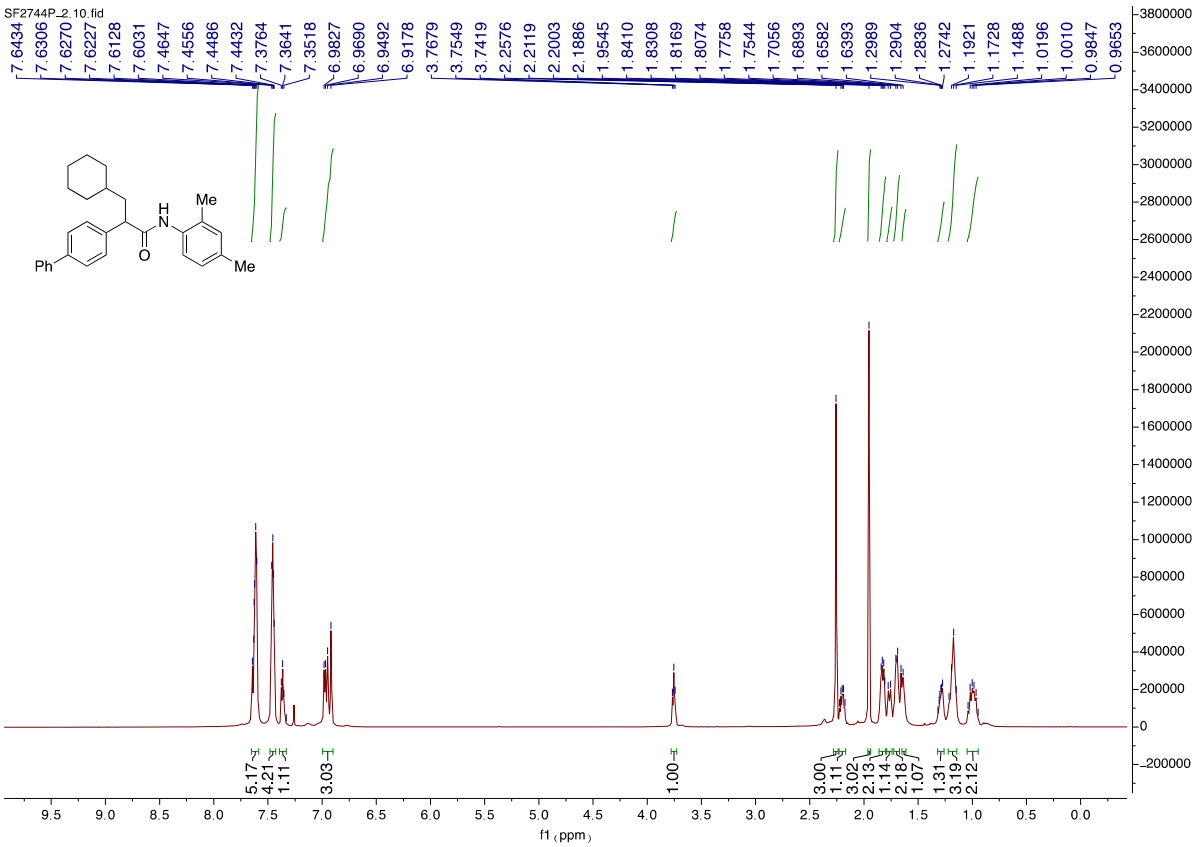
5u ^{1}H NMR (600 MHz, $CDCl_3$)



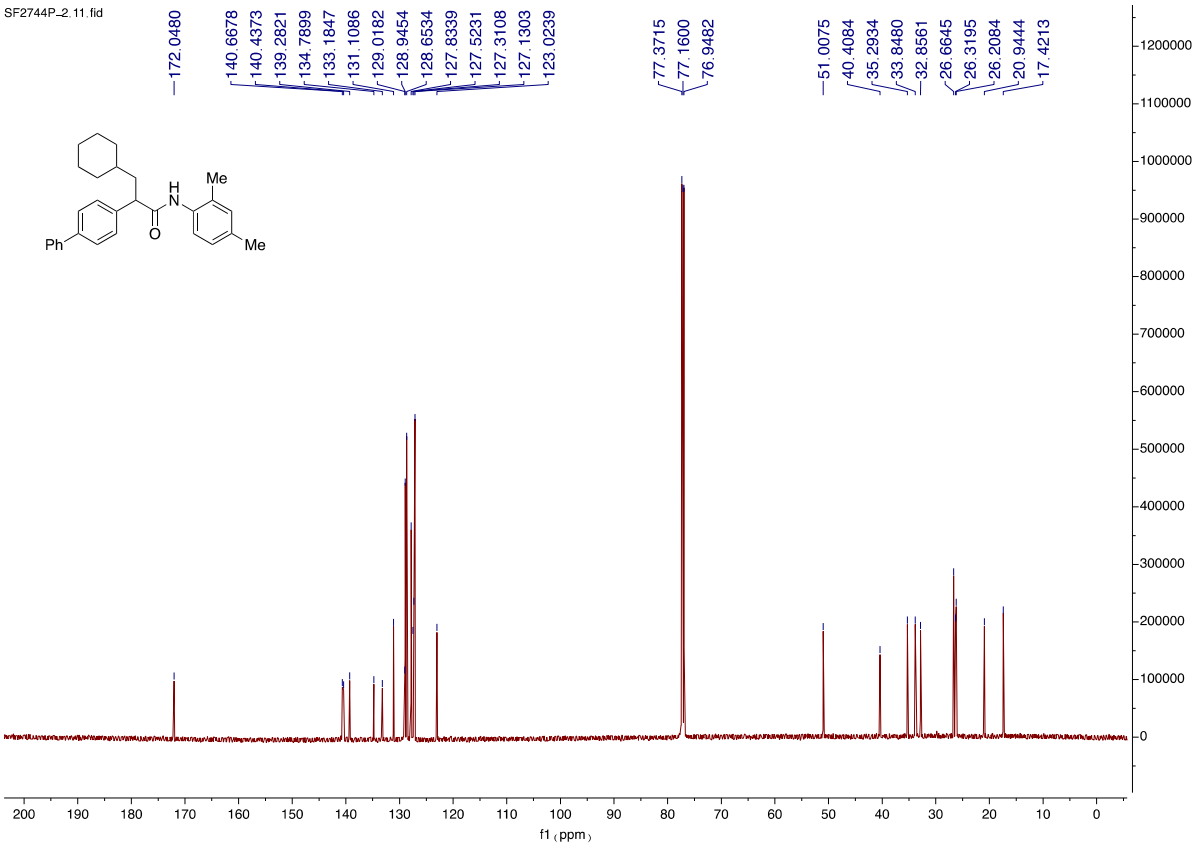
5u ^{13}C NMR (151 MHz, $CDCl_3$)



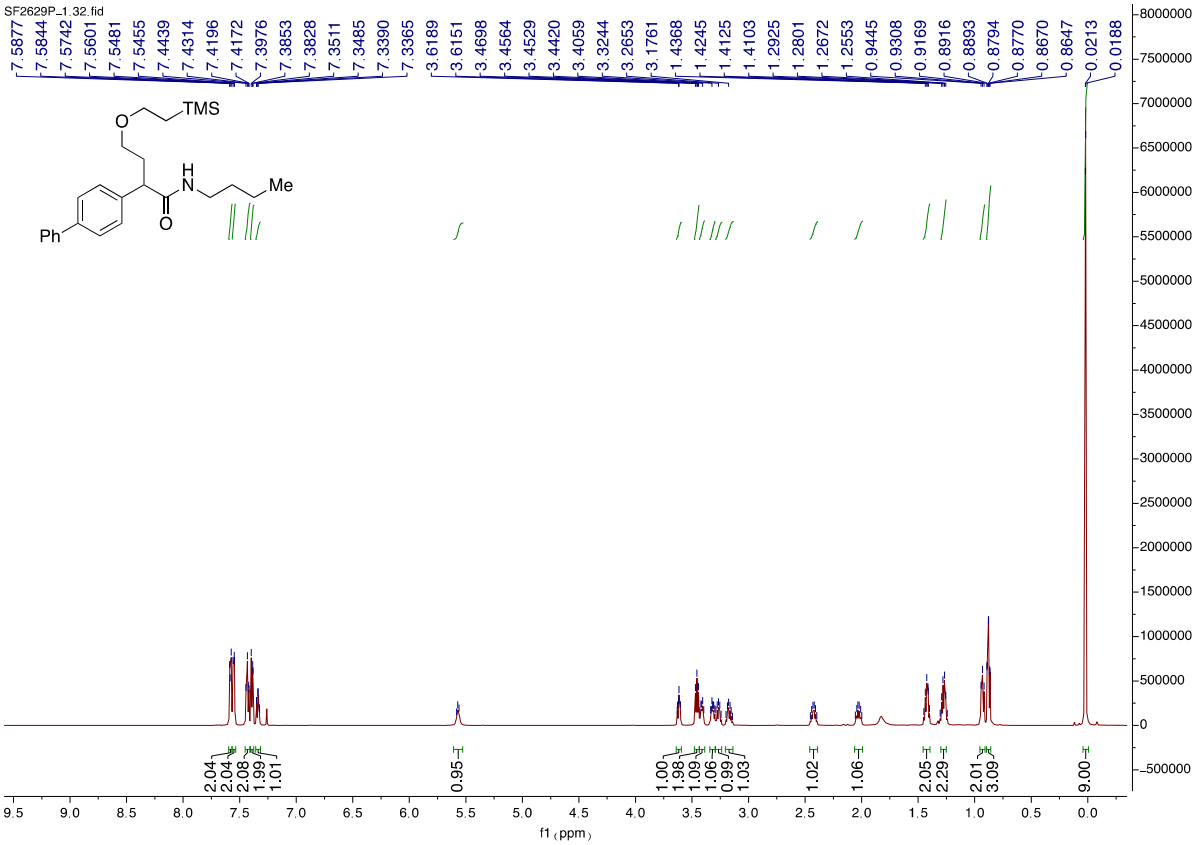
5u ^{19}F NMR (565 MHz, $CDCl_3$)



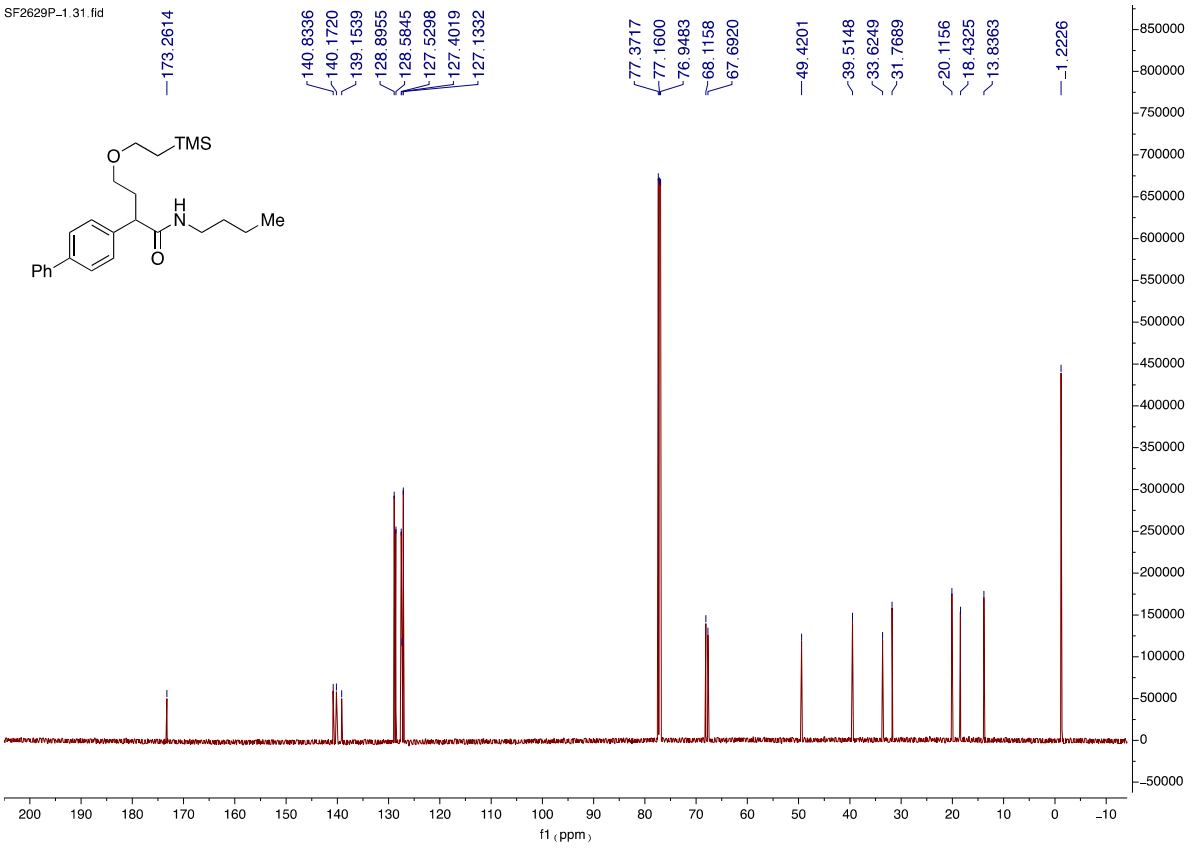
5v ^{1}H NMR (600 MHz, $CDCl_3$)



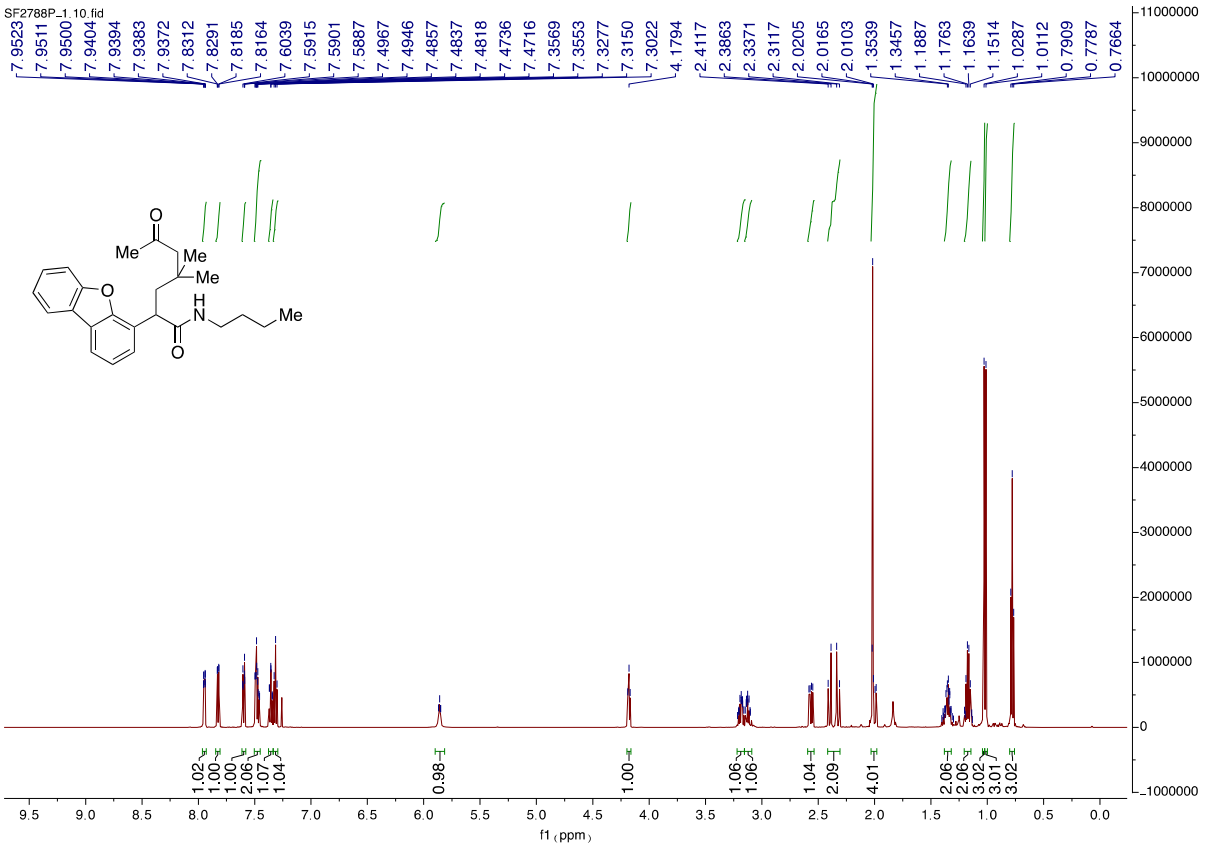
5v ^{13}C NMR (151 MHz, $CDCl_3$)



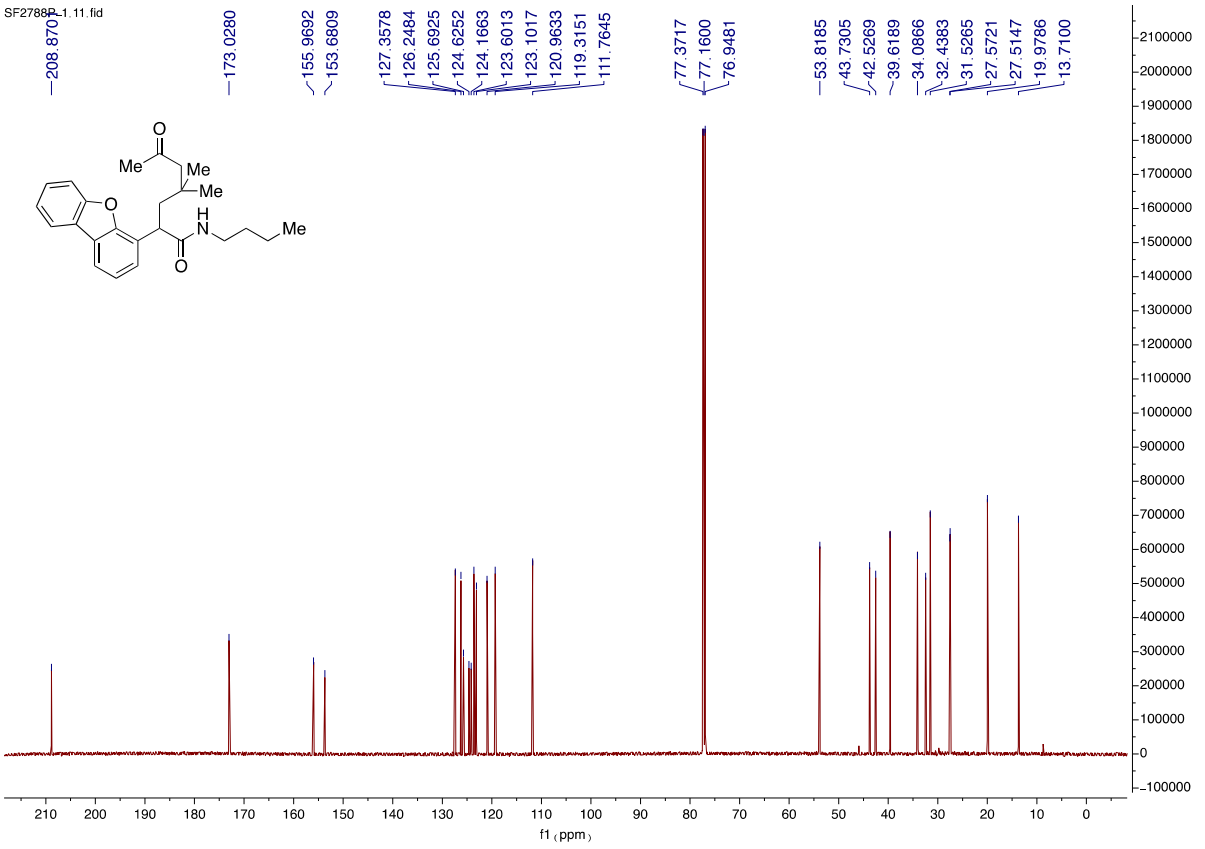
5w ^{1}H NMR (600 MHz, $CDCl_3$)



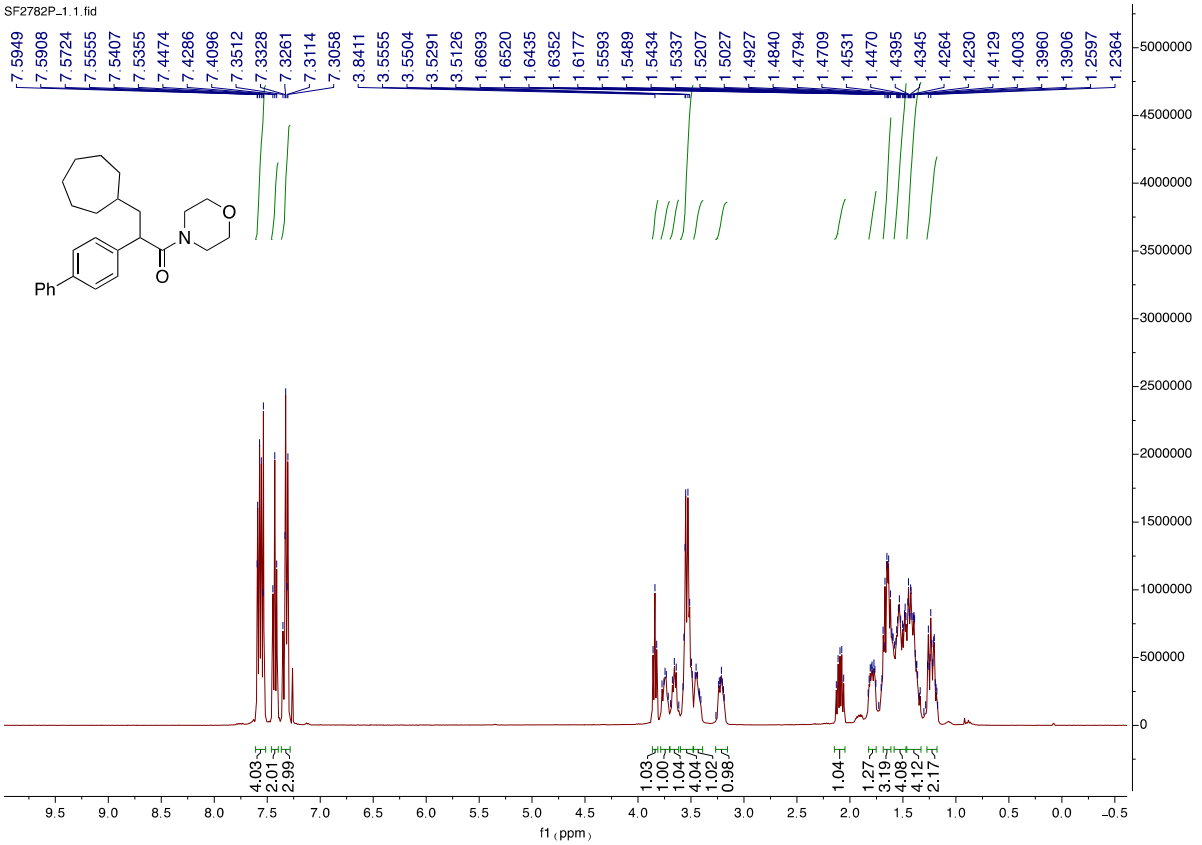
5w ^{13}C NMR (151 MHz, $CDCl_3$)



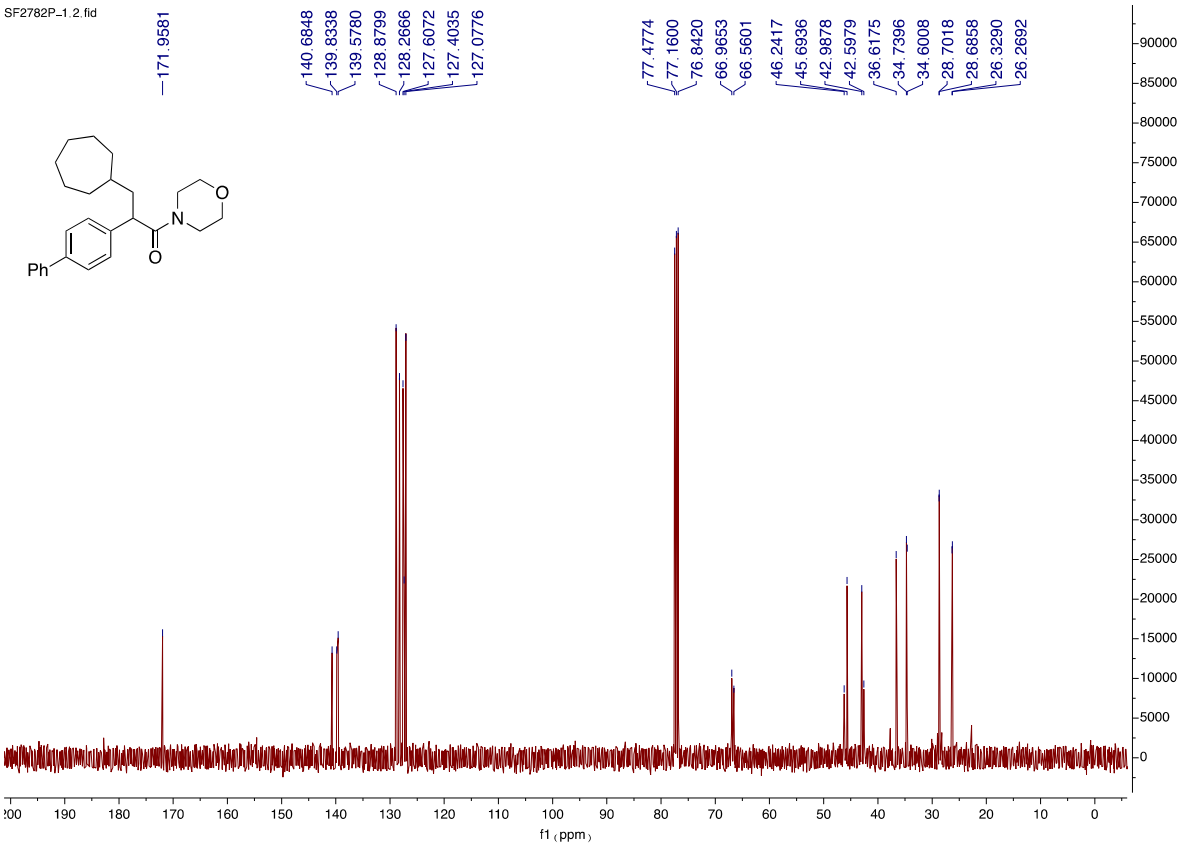
5x ^{1}H NMR (600 MHz, $CDCl_3$)



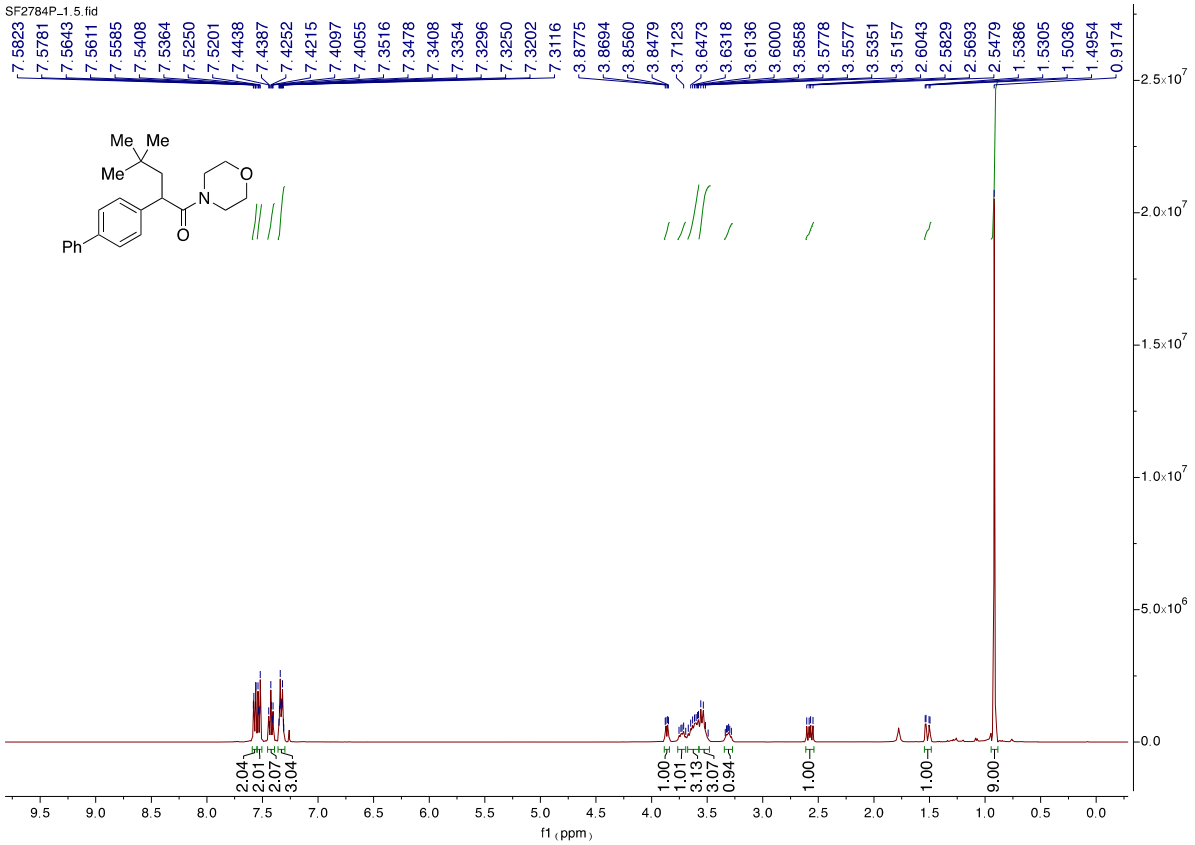
5x ^{13}C NMR (151 MHz, $CDCl_3$)



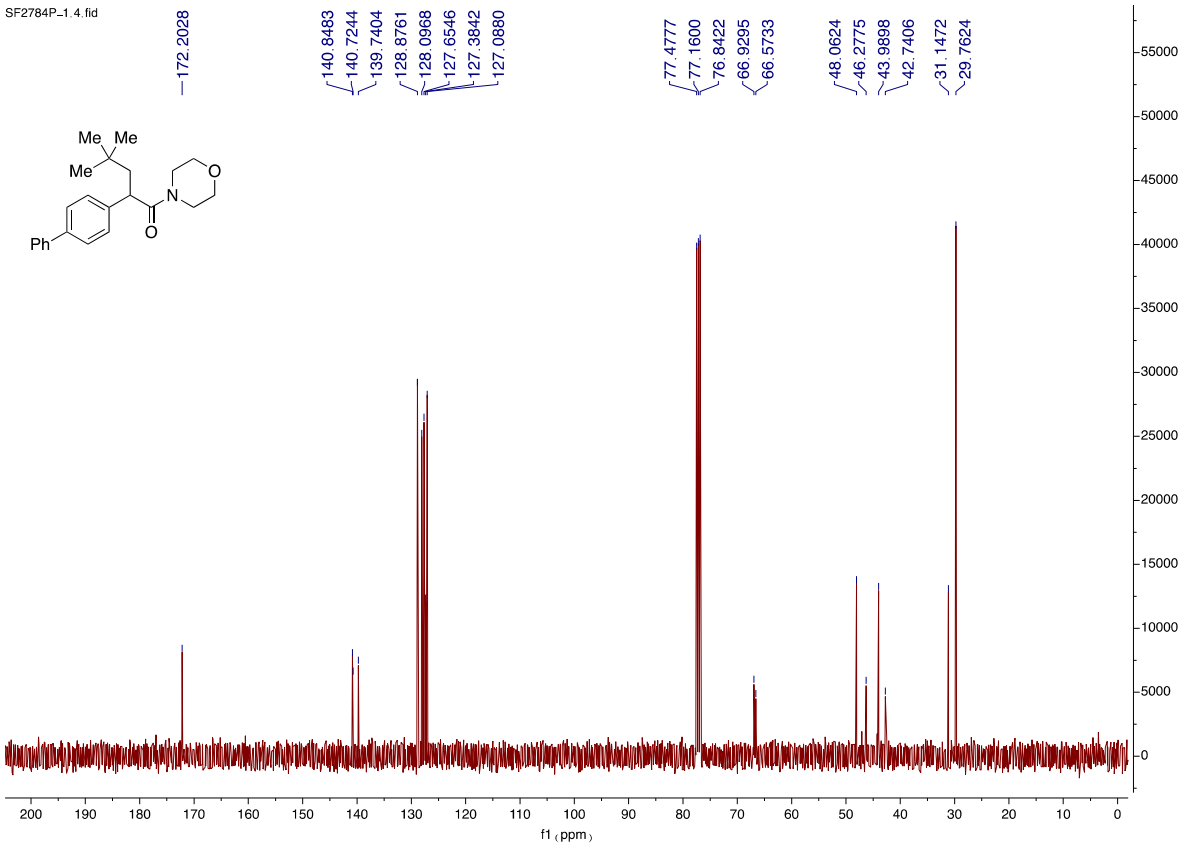
5y ^{1}H NMR (400 MHz, $CDCl_3$)



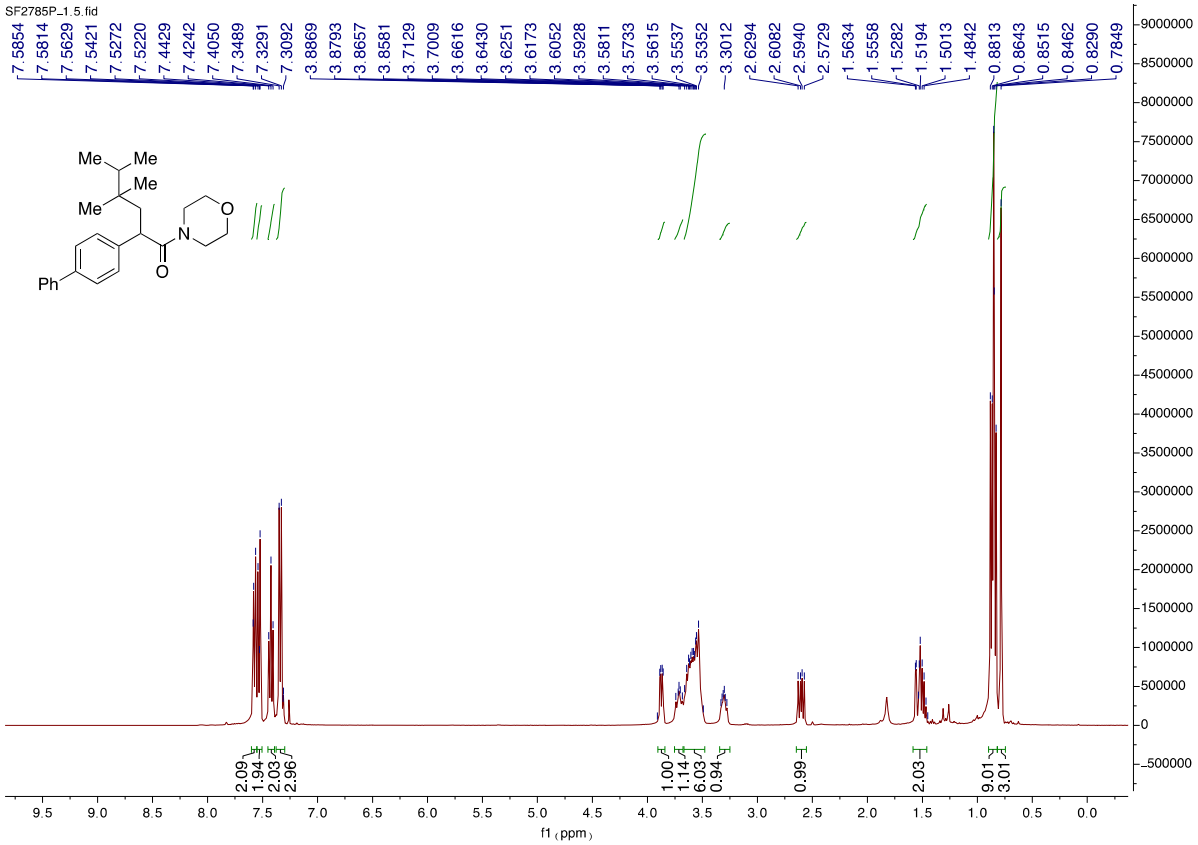
5y ^{13}C NMR (101 MHz, $CDCl_3$)



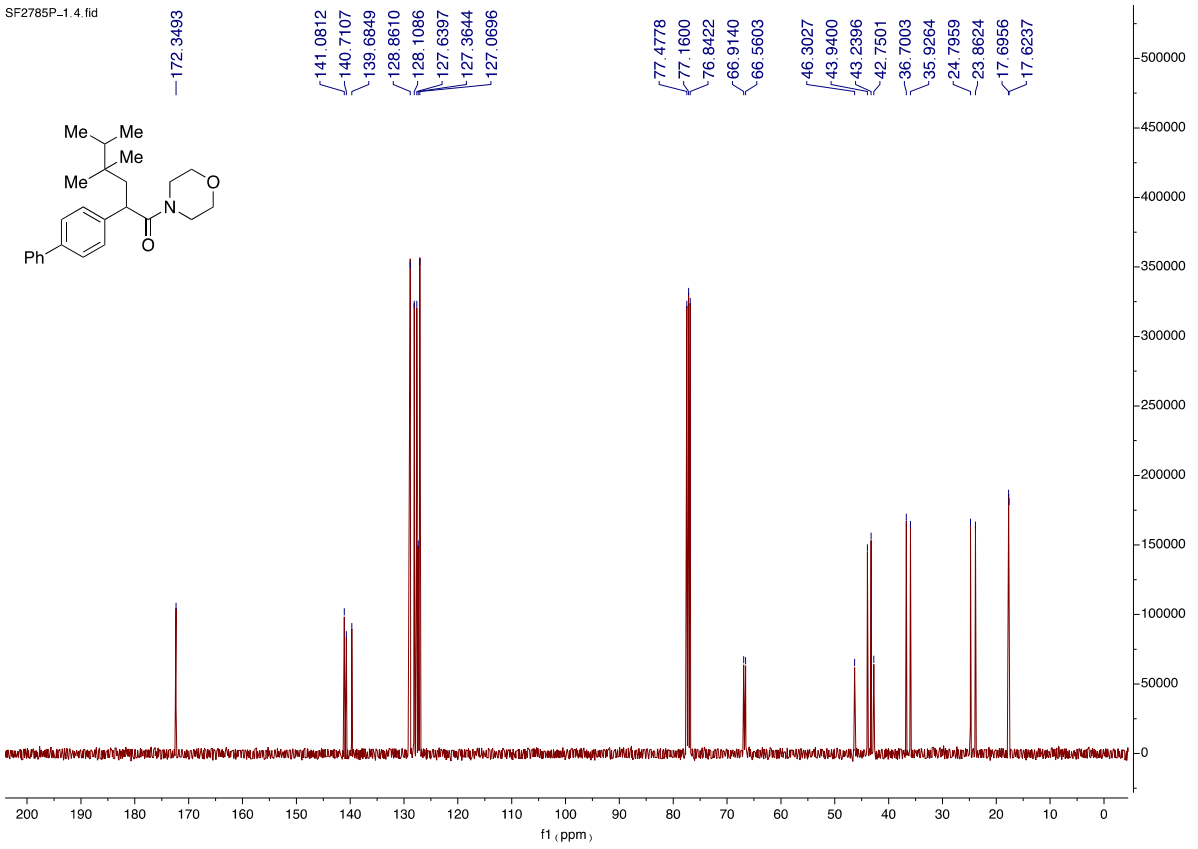
5z ^{1}H NMR (400 MHz, $CDCl_3$)



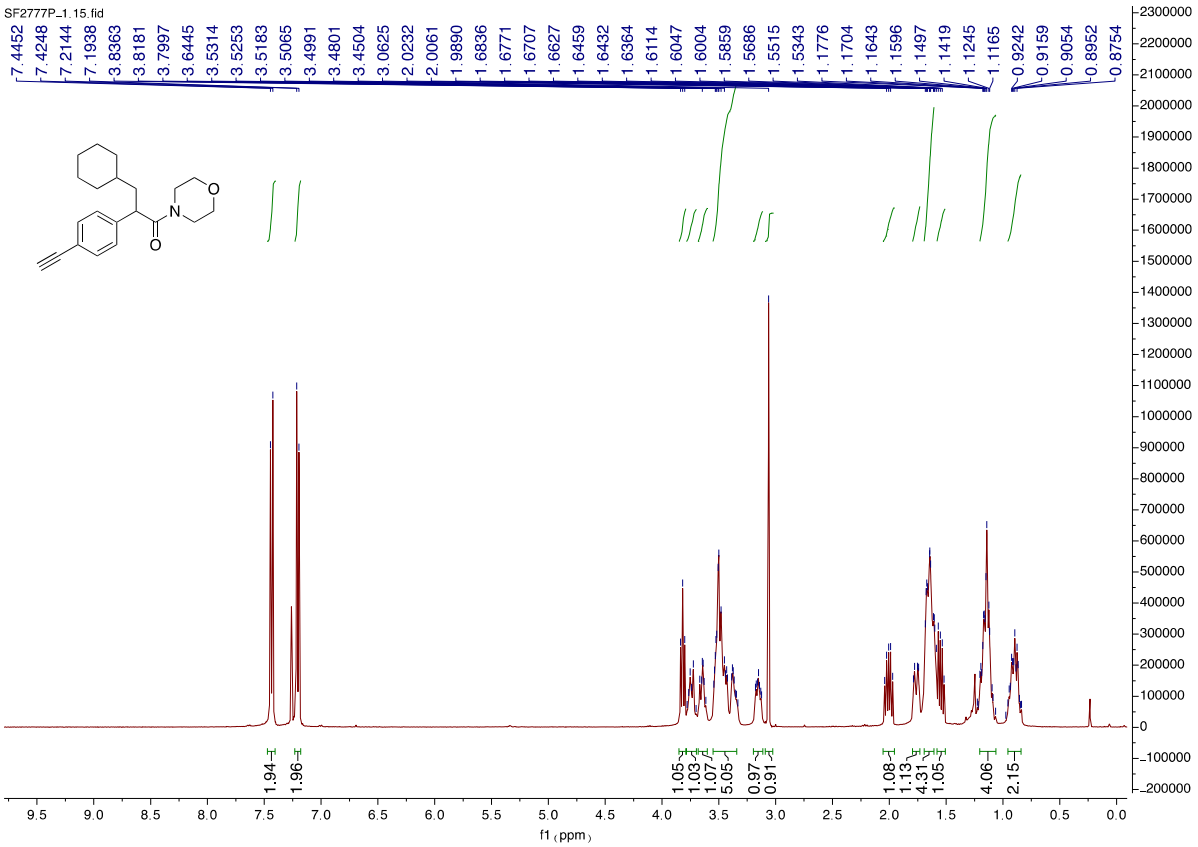
5z ^{13}C NMR (101 MHz, $CDCl_3$)



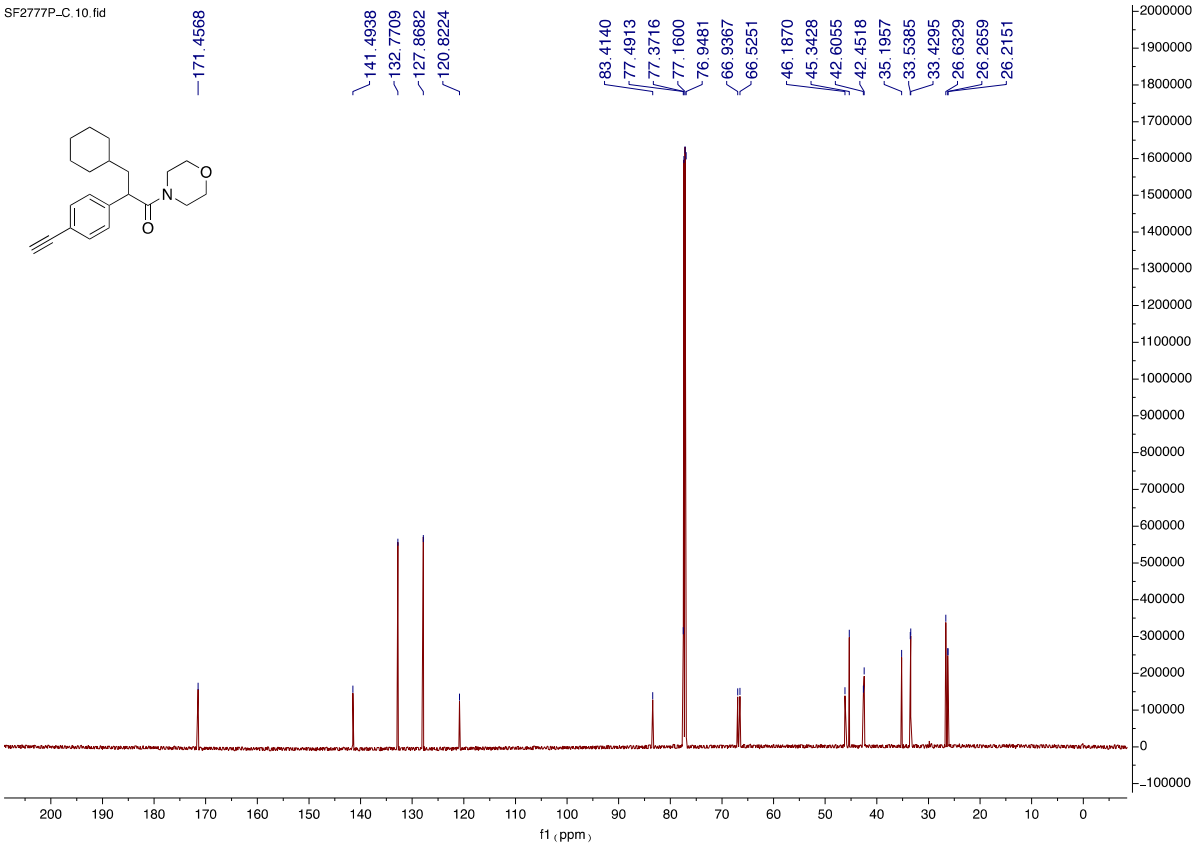
5aa ^{1}H NMR (400 MHz, $CDCl_3$)



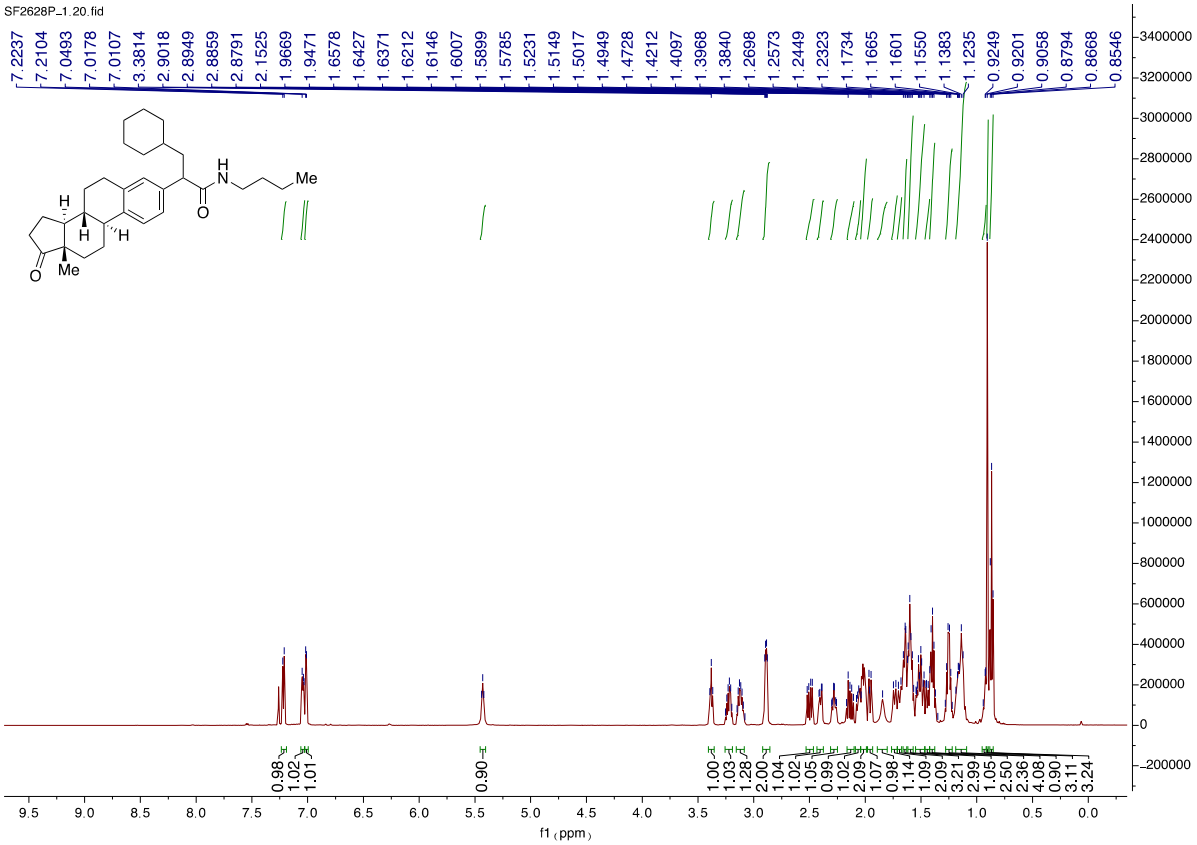
5aa ^{13}C NMR (101 MHz, $CDCl_3$)



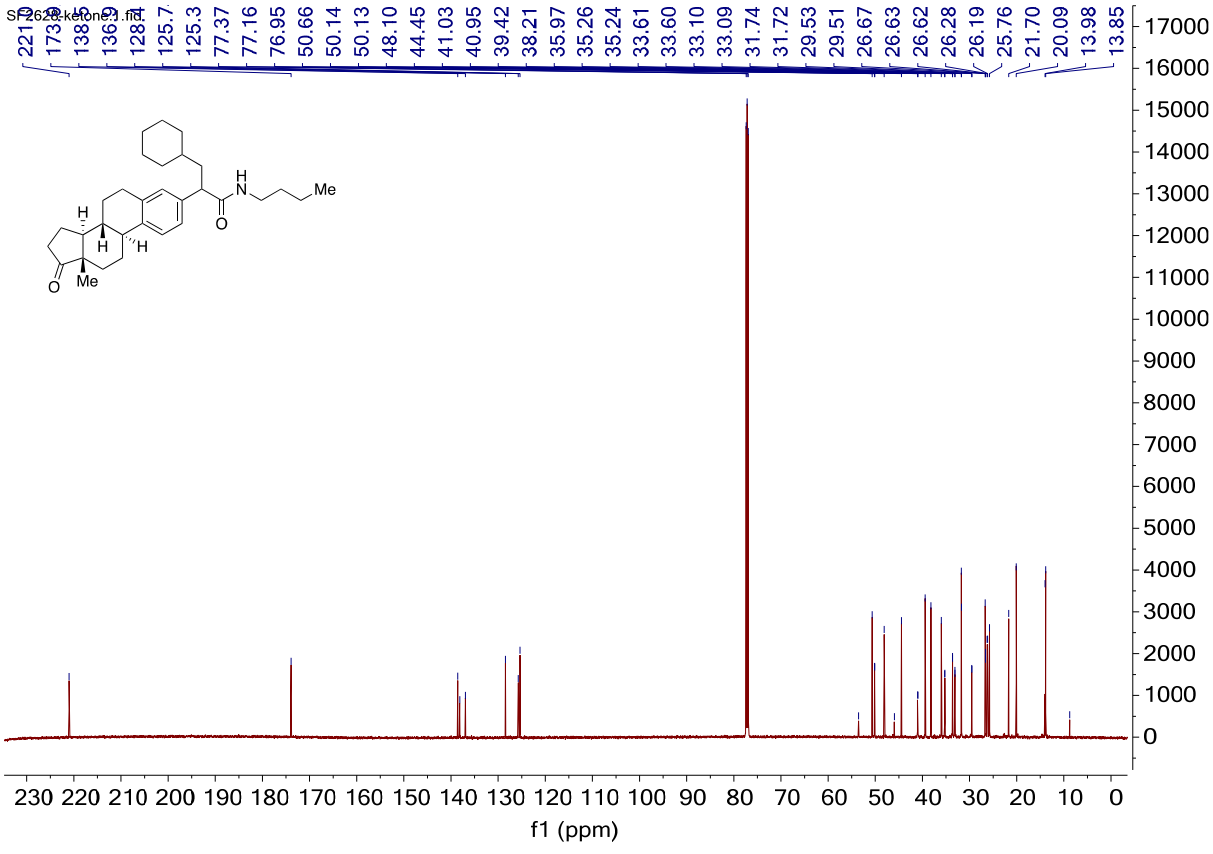
5ab ^{1}H NMR (400 MHz, $CDCl_3$)



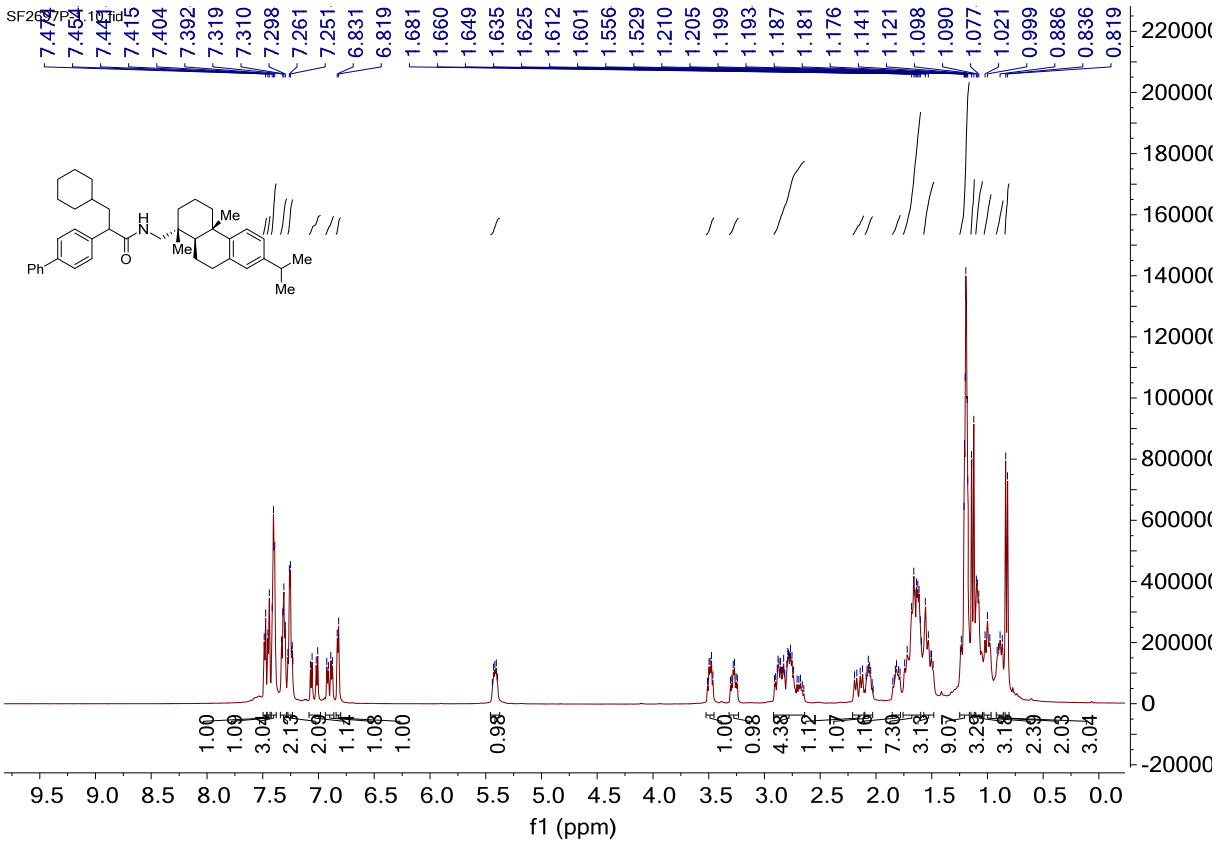
5ab ^{13}C NMR (151 MHz, $CDCl_3$)



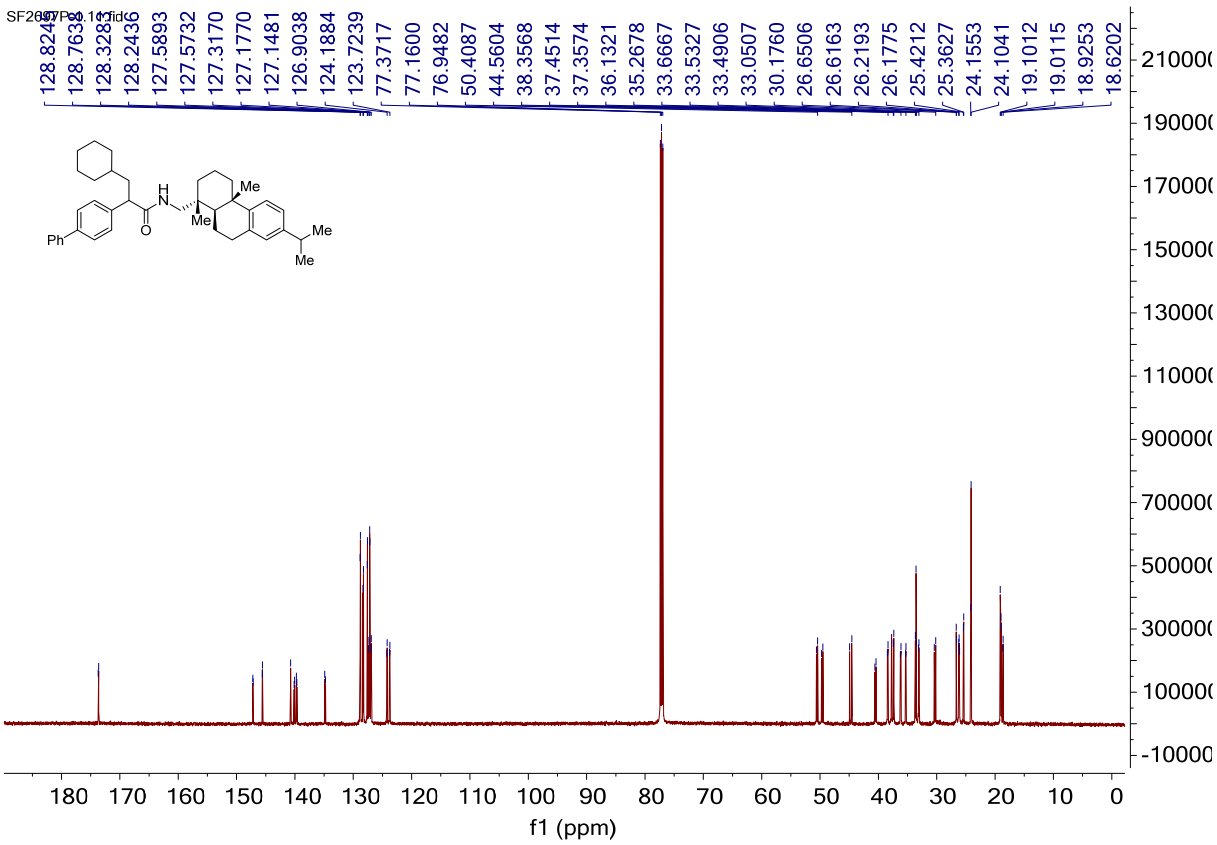
5ac ^{1}H NMR (600 MHz, $CDCl_3$)



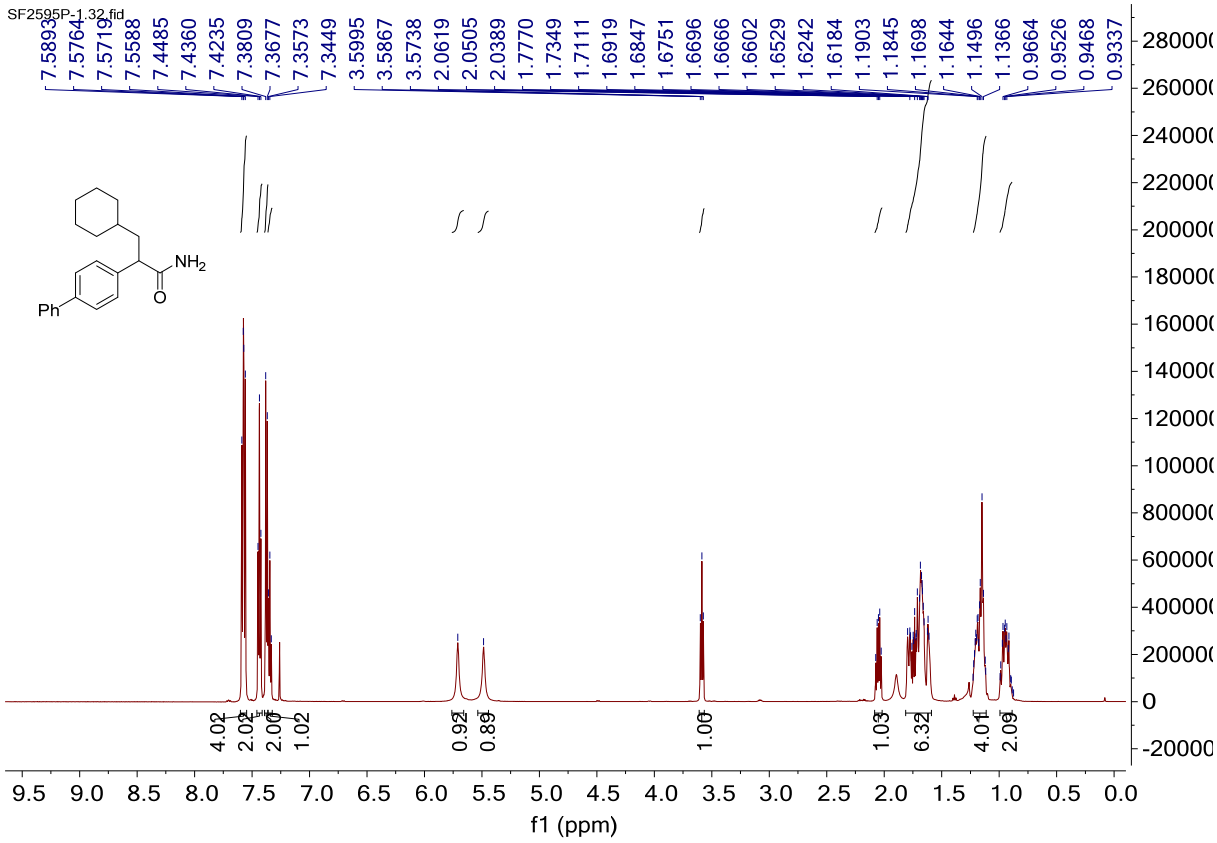
5ac ^{13}C NMR (151 MHz, $CDCl_3$)



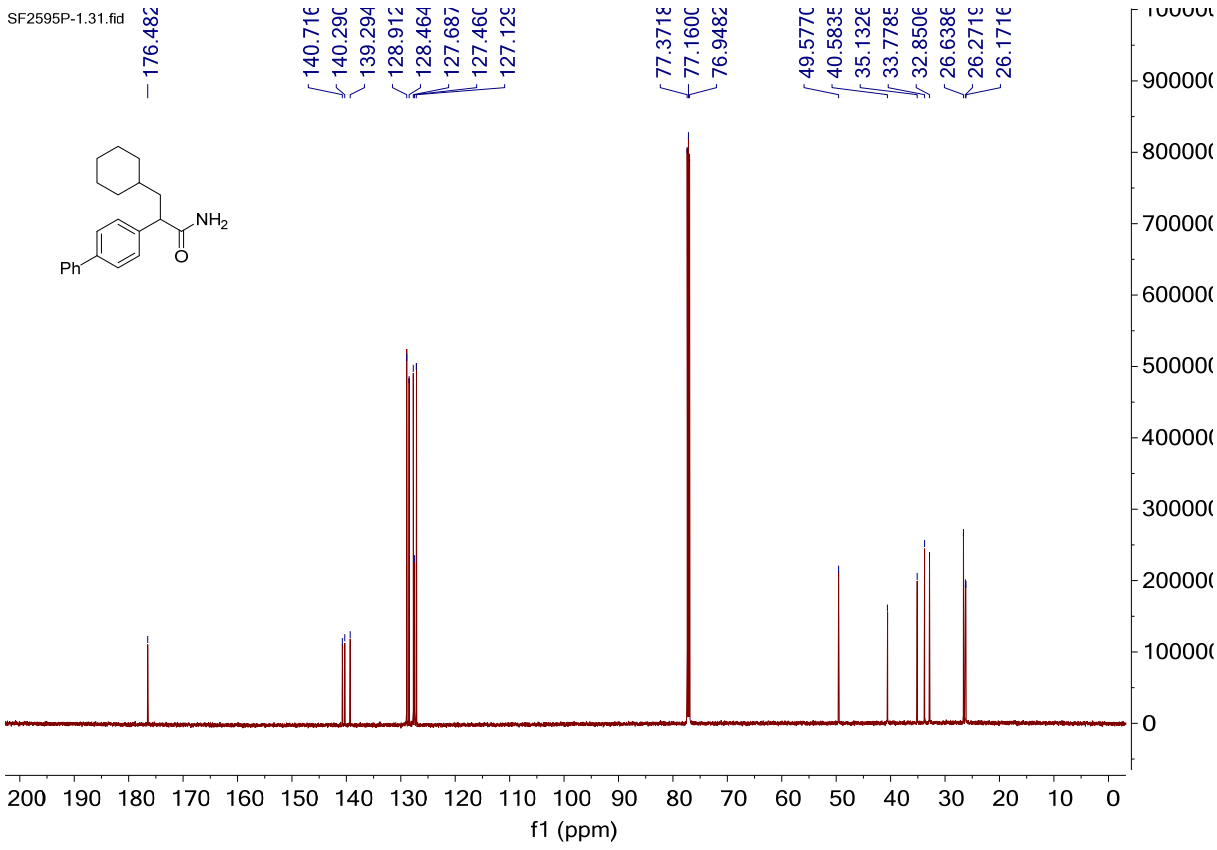
5ad ^{1}H NMR (600 MHz, $CDCl_3$)



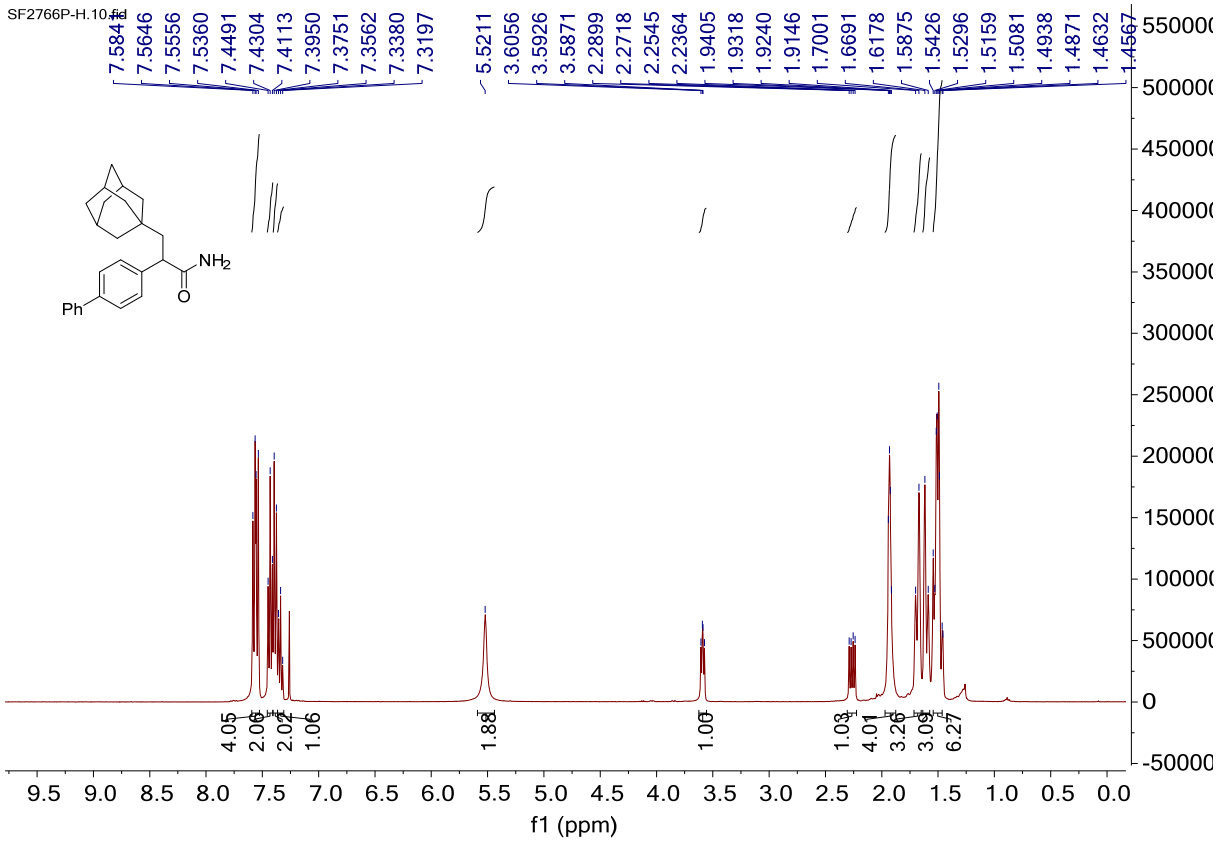
5ad ^{13}C NMR (151 MHz, $CDCl_3$)



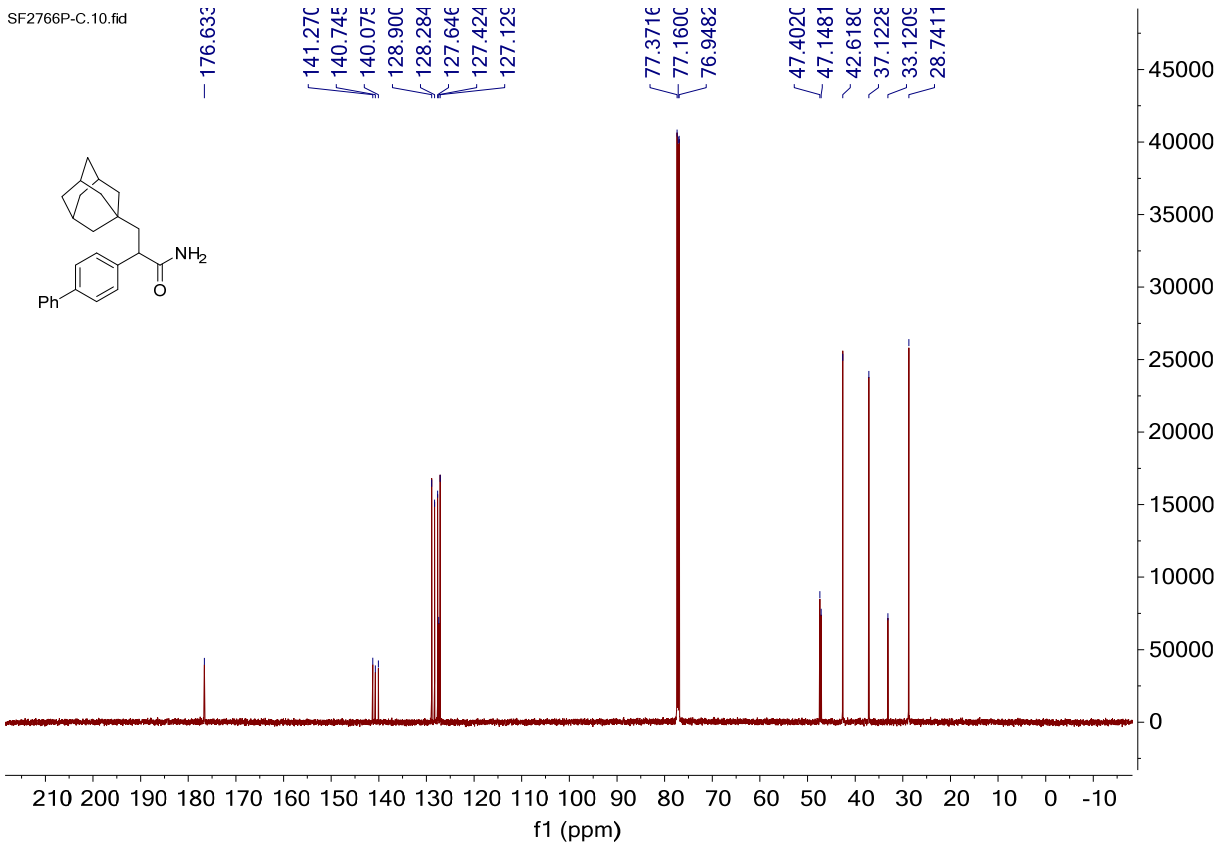
5ae ^{1}H NMR (600 MHz, $CDCl_3$)



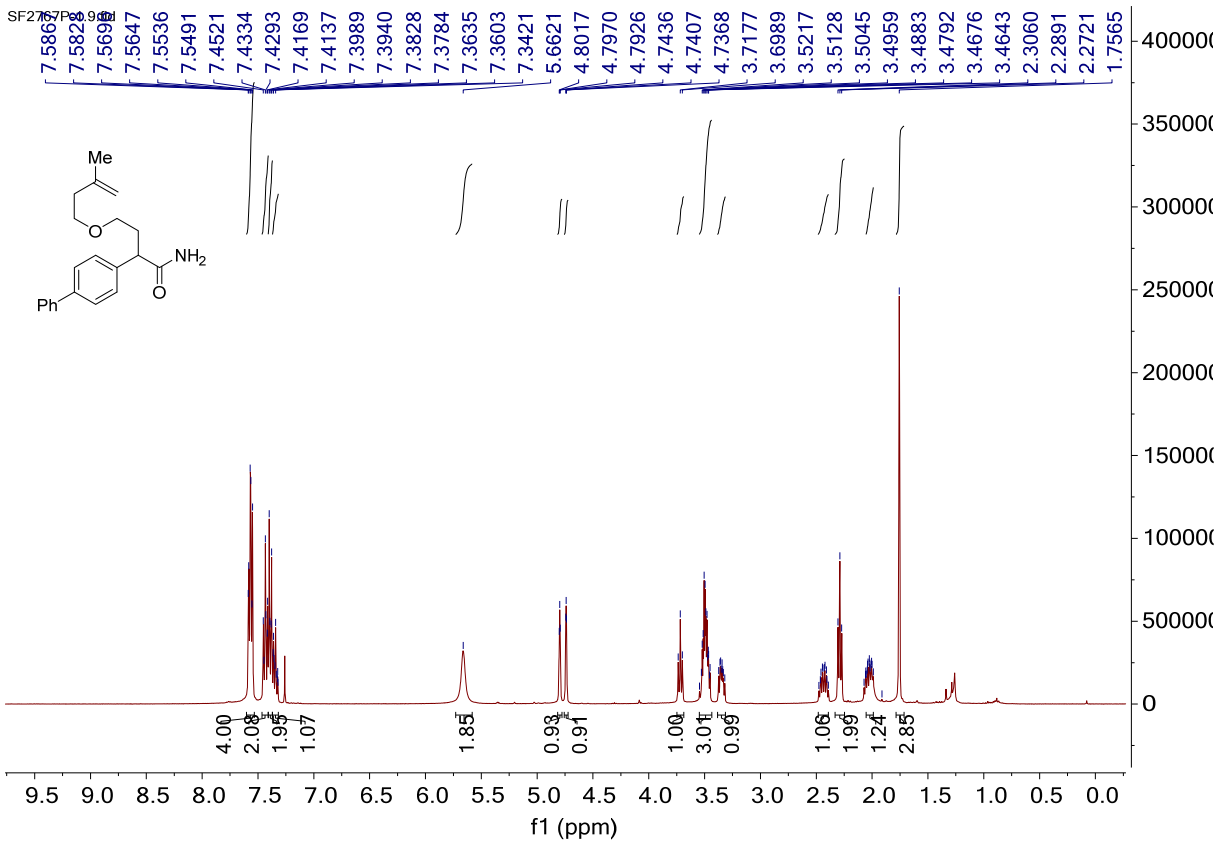
5ae ^{13}C NMR (151 MHz, $CDCl_3$)



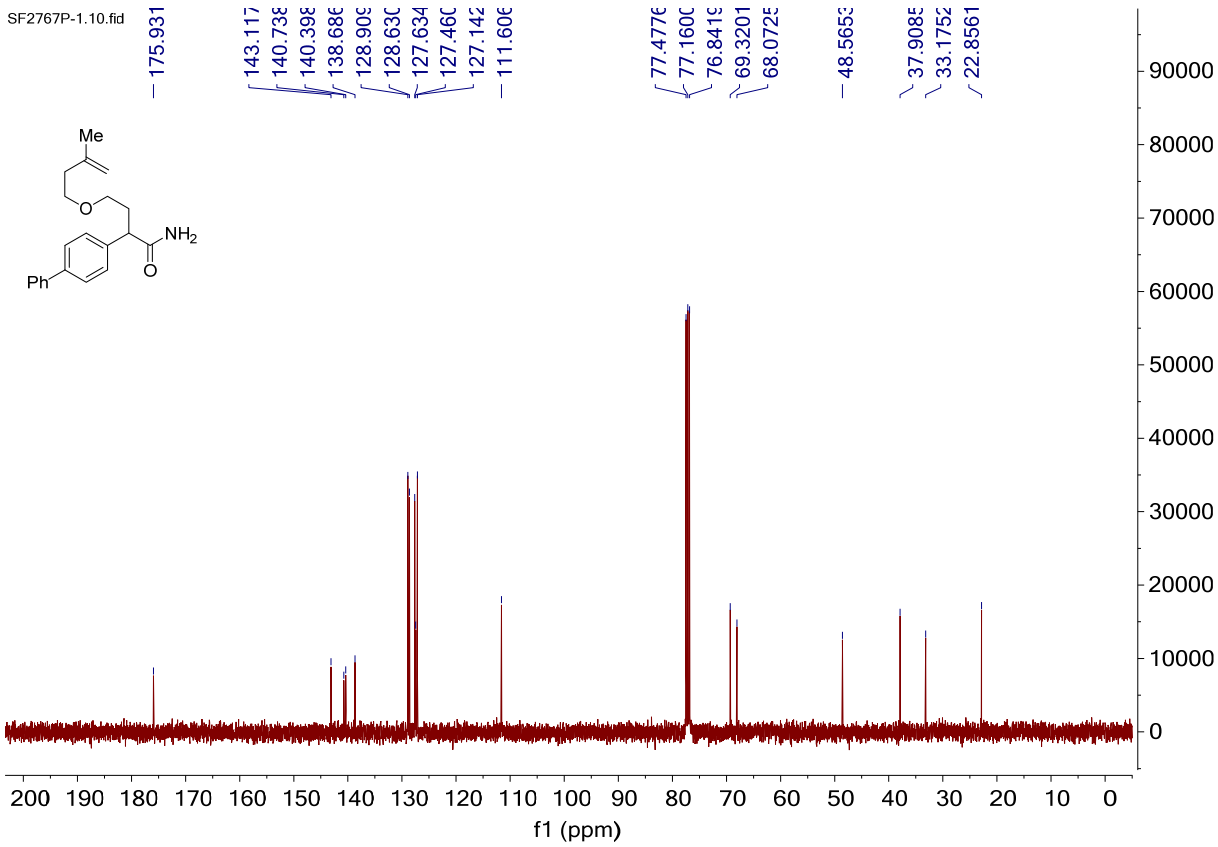
5af ^{1}H NMR (400 MHz, $CDCl_3$)



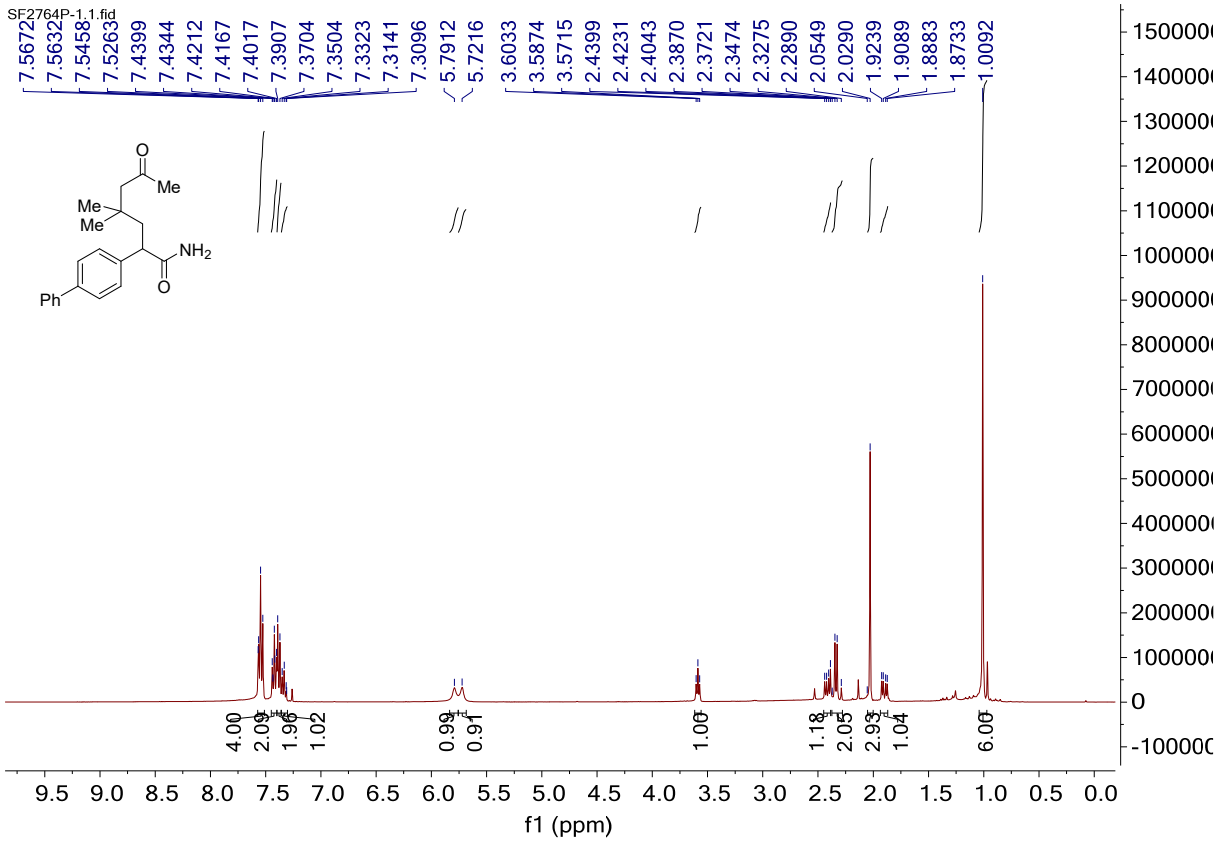
5af ^{13}C NMR (151 MHz, $CDCl_3$)



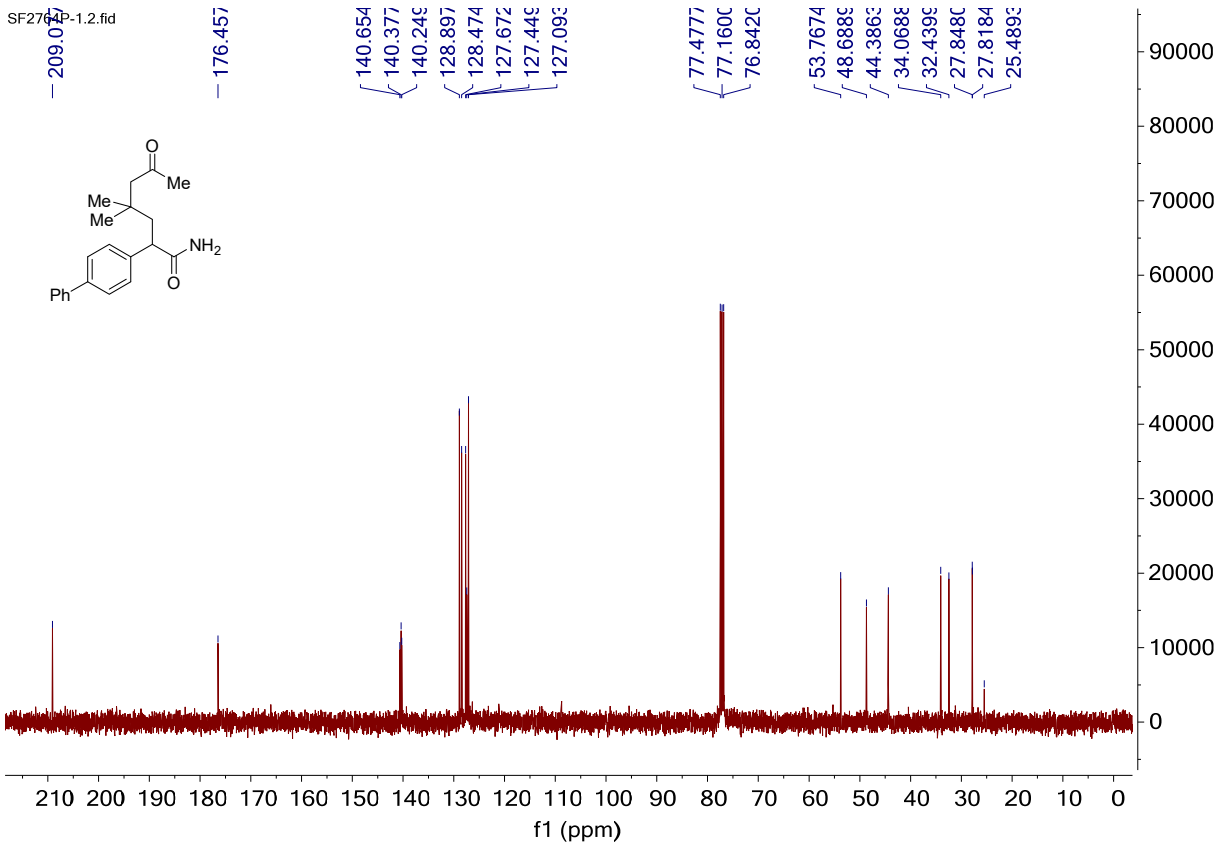
5ag ^{1}H NMR (400 MHz, $CDCl_3$)



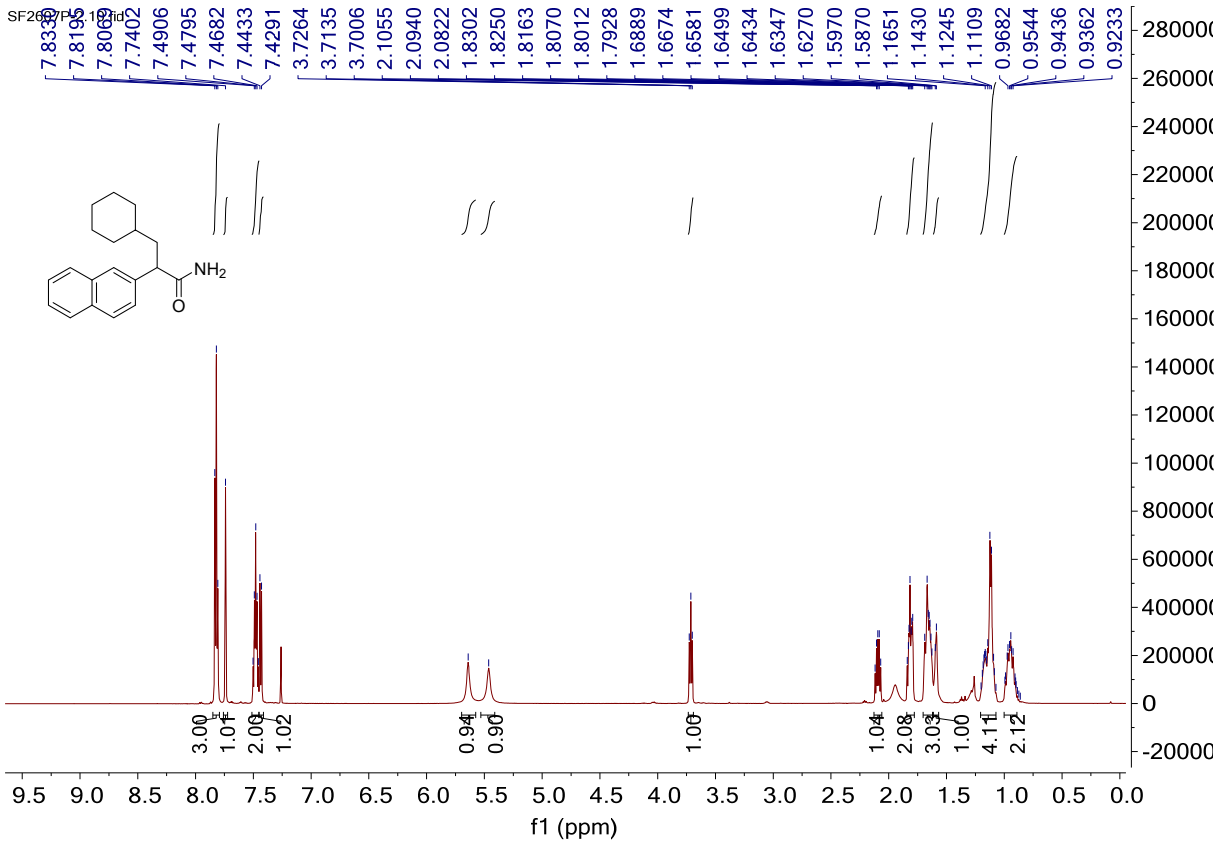
5ag ^{13}C NMR (101 MHz, $CDCl_3$)



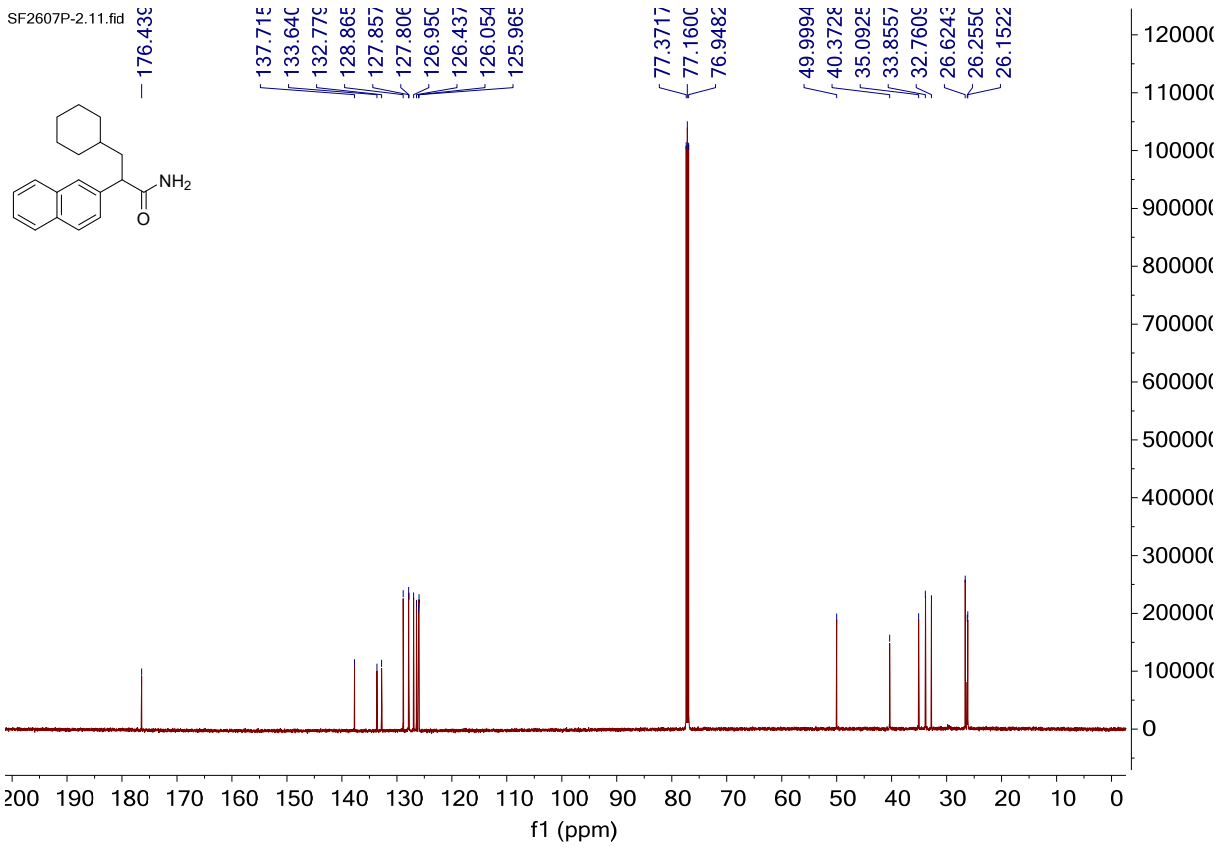
5ah ^{1}H NMR (400 MHz, $CDCl_3$)



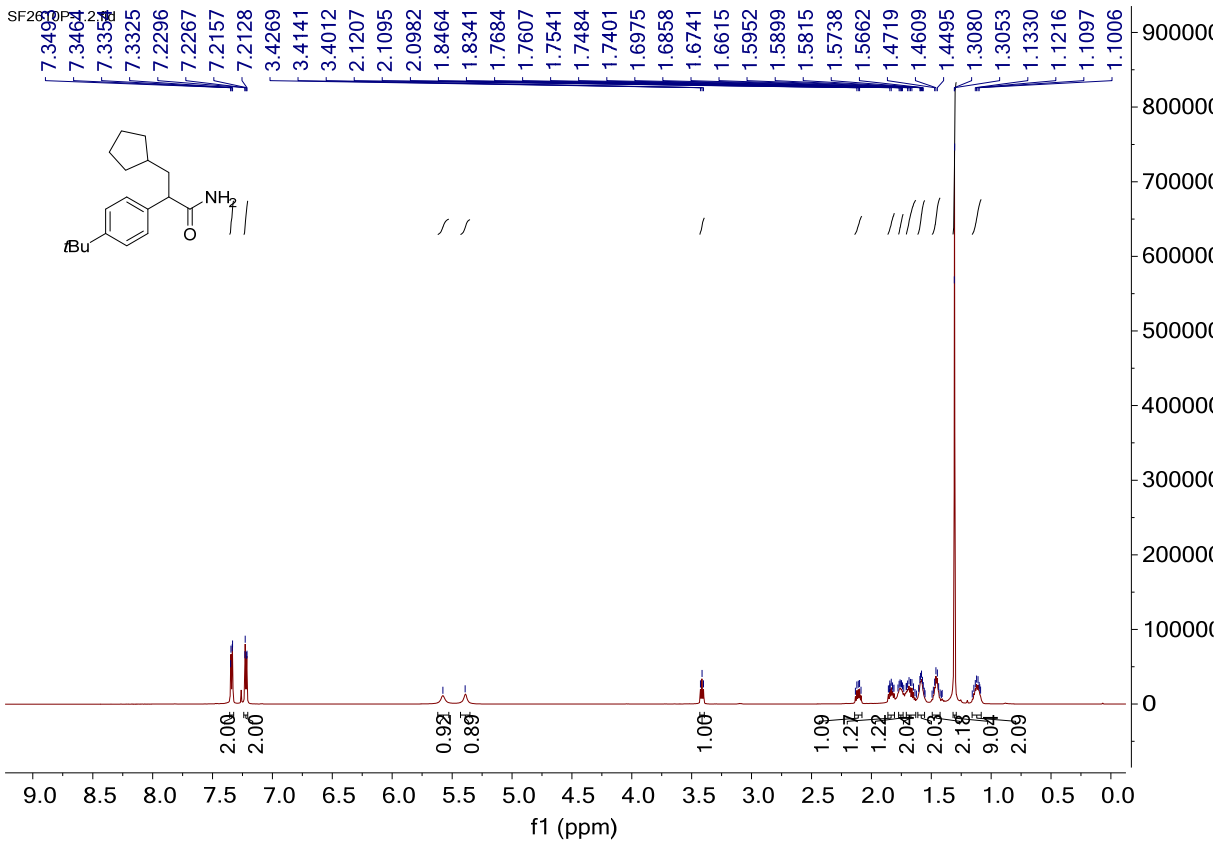
5ah ^{13}C NMR (101 MHz, $CDCl_3$)



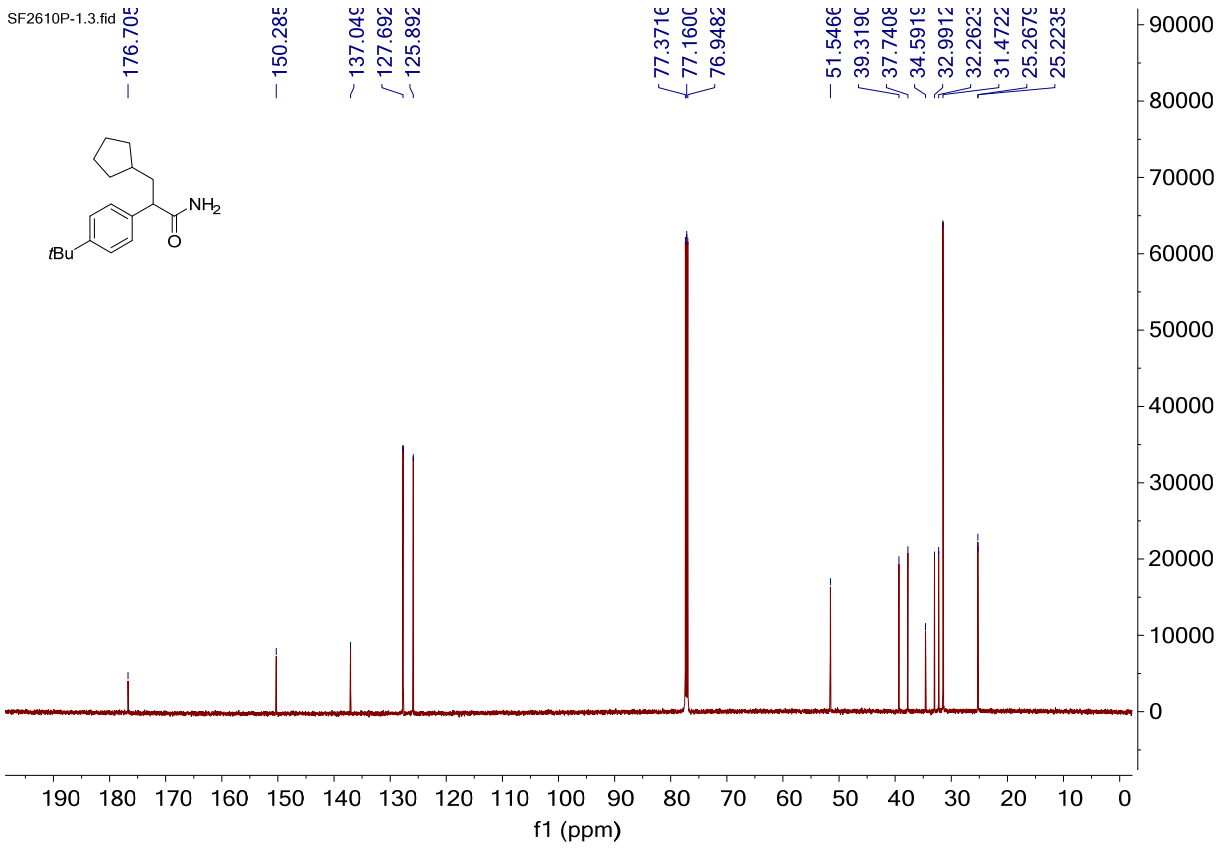
5ai ^{1}H NMR (600 MHz, $CDCl_3$)



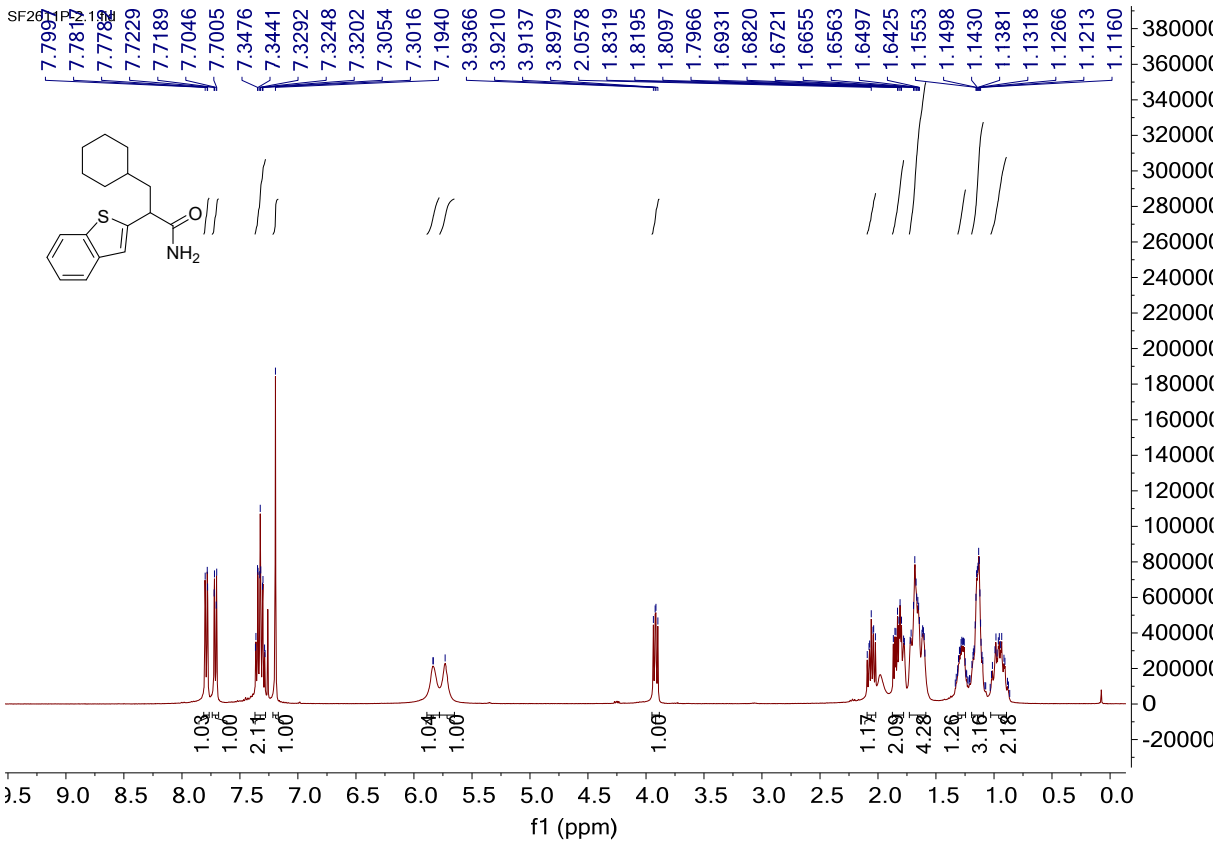
5ai ^{13}C NMR (151 MHz, $CDCl_3$)



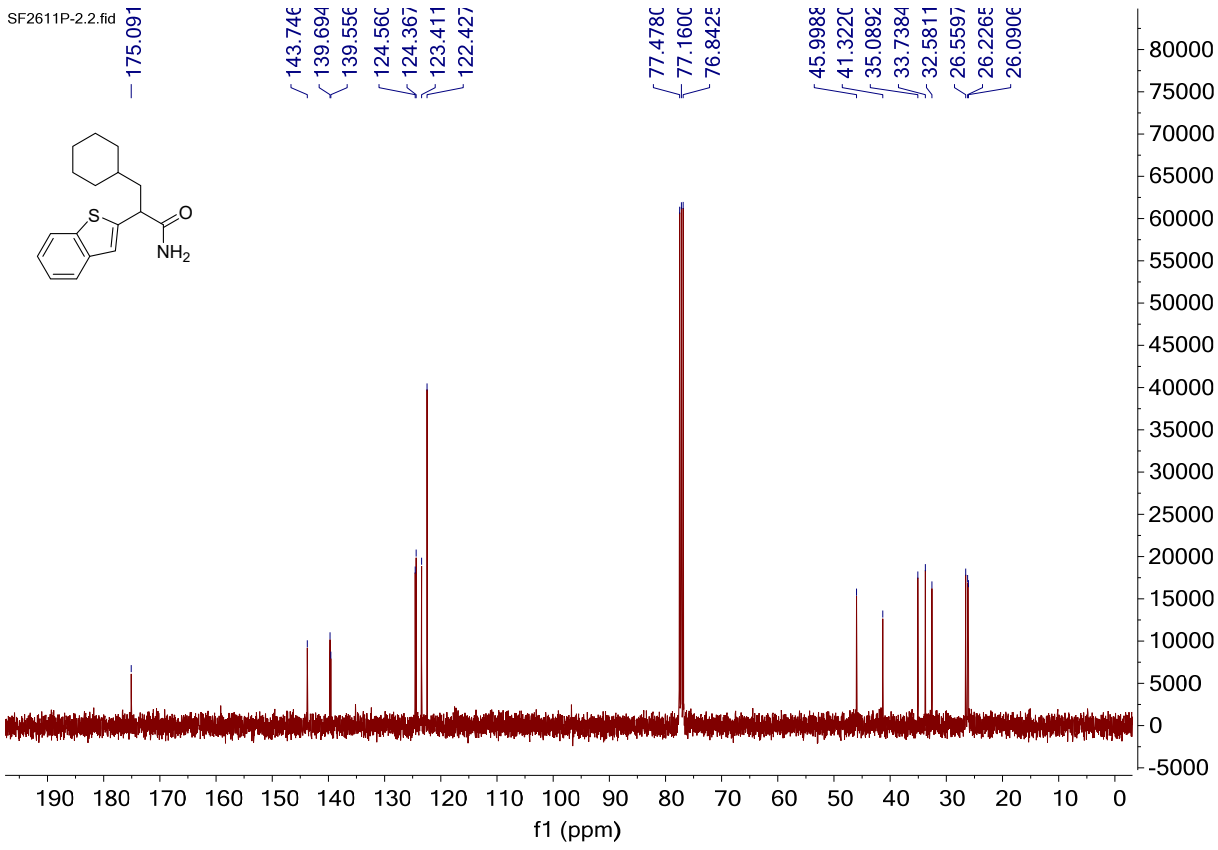
5aj ^{1}H NMR (600 MHz, $CDCl_3$)



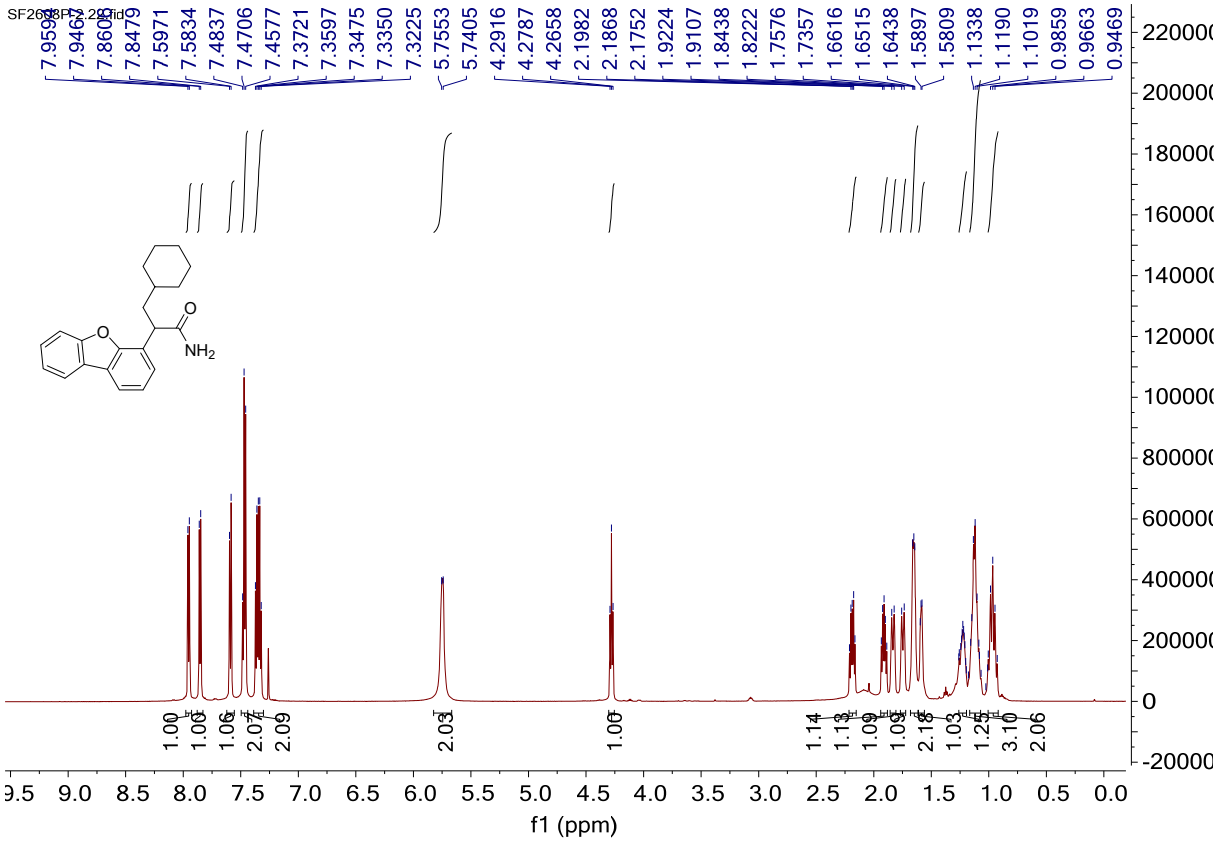
5aj ^{13}C NMR (151 MHz, $CDCl_3$)



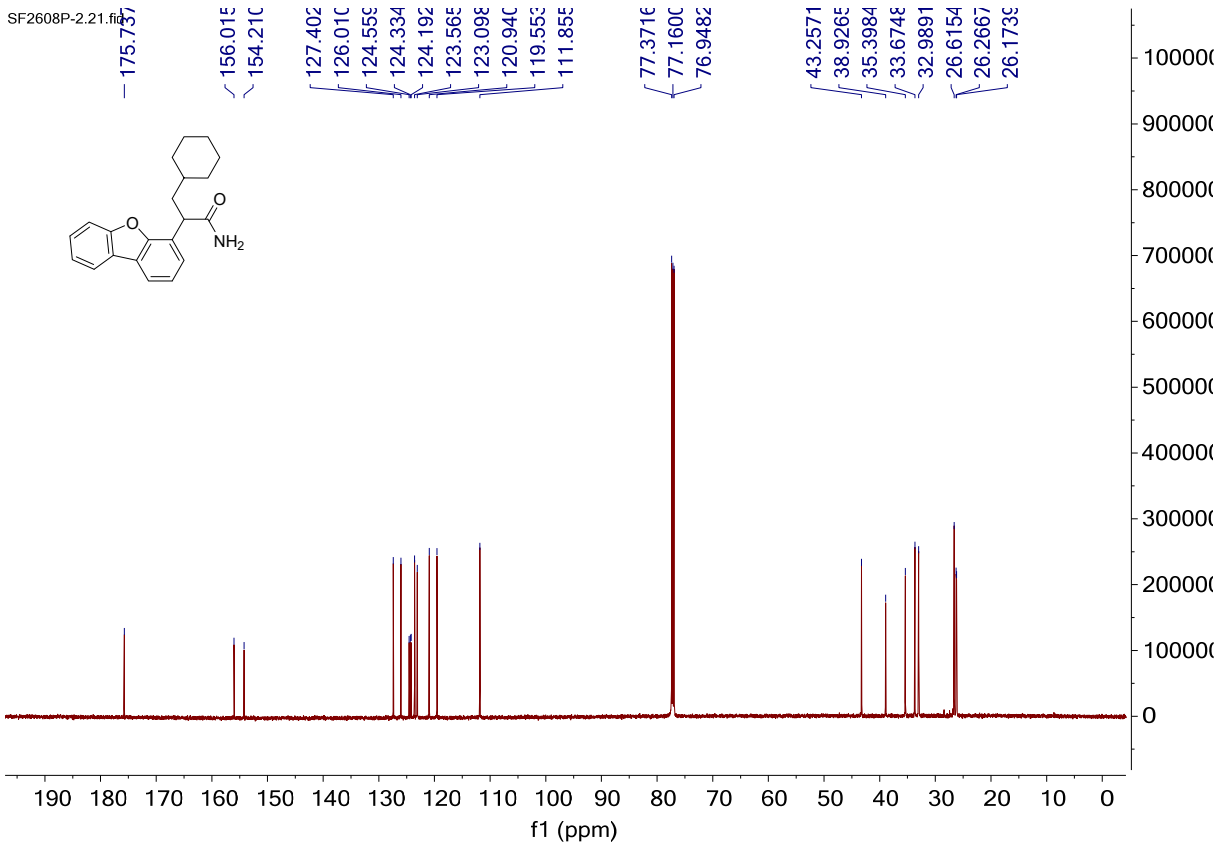
5ak ^{1}H NMR (400 MHz, $CDCl_3$)



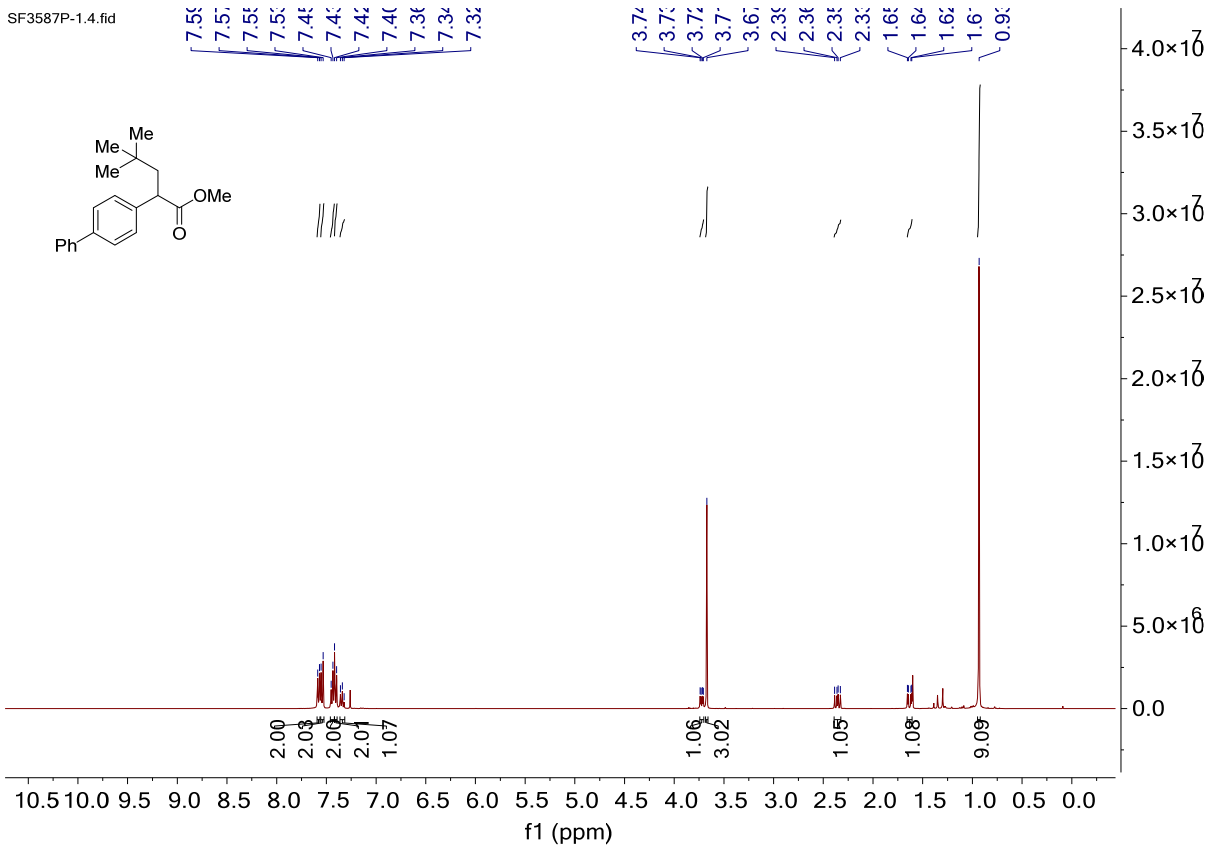
5ak ^{13}C NMR (101 MHz, $CDCl_3$)



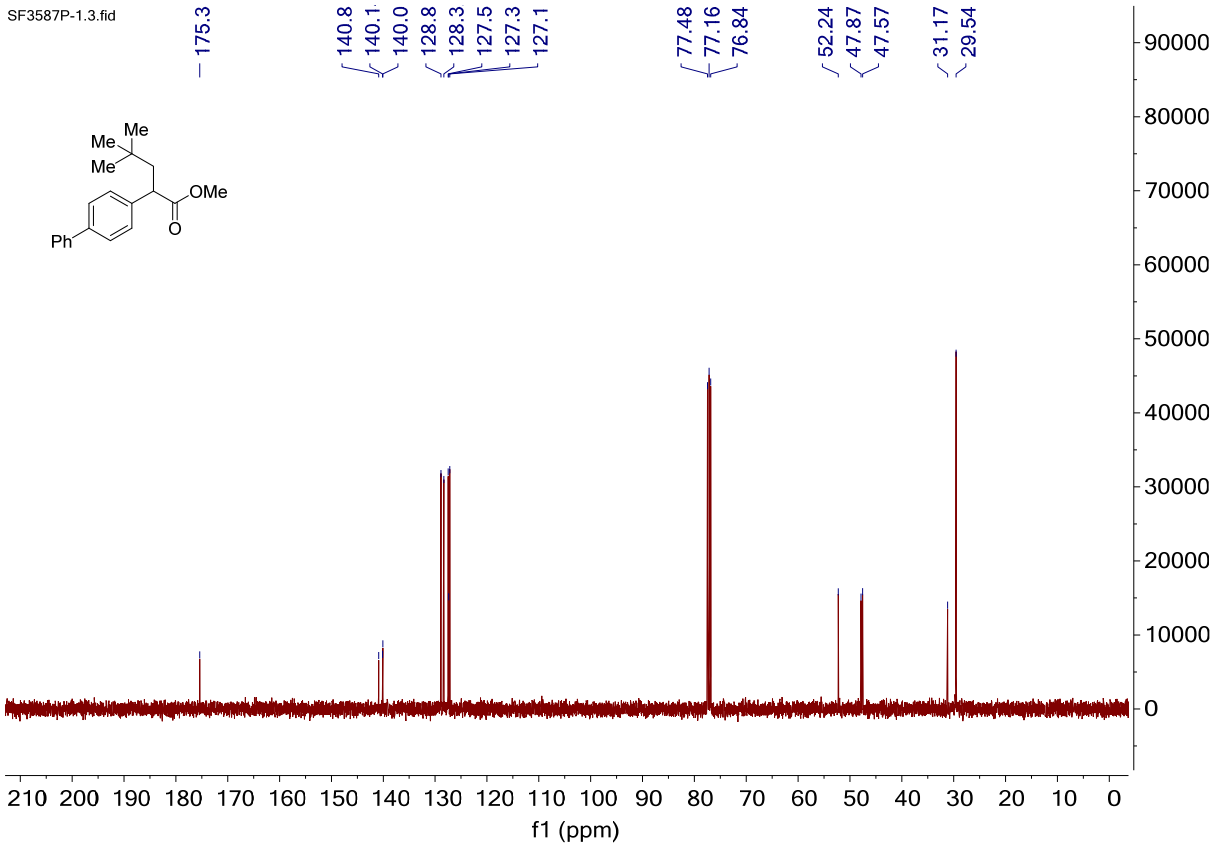
5al ^{1}H NMR (600 MHz, $CDCl_3$)



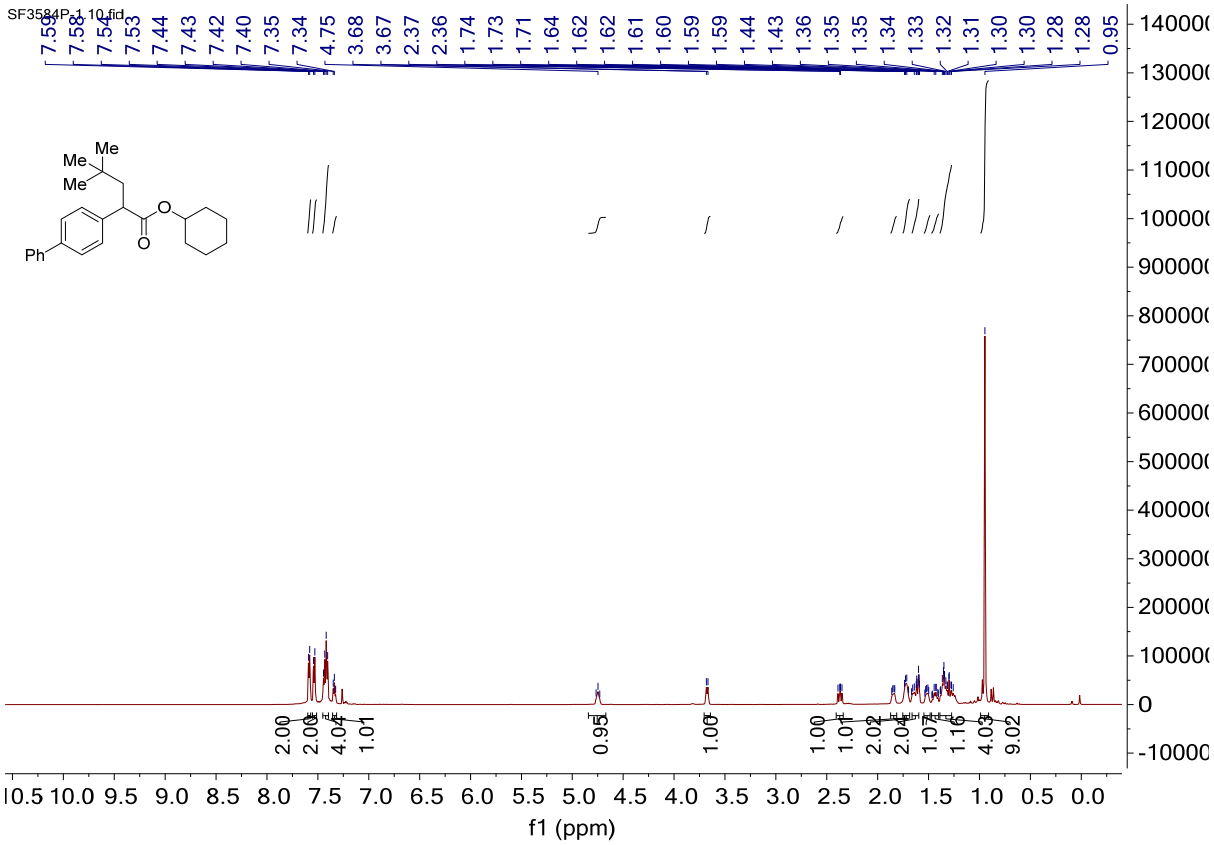
5al ^{13}C NMR (101 MHz, $CDCl_3$)



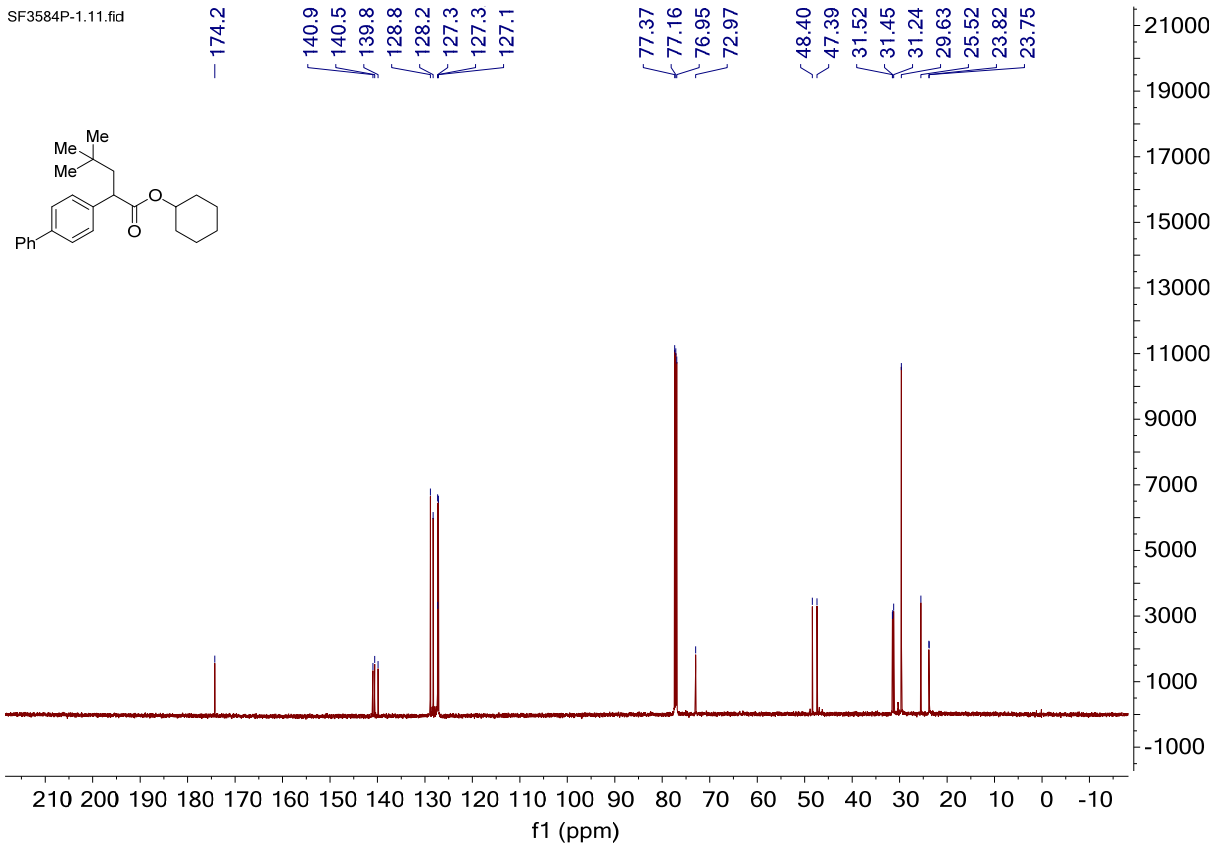
5am ^{1}H NMR (400 MHz, $CDCl_3$)



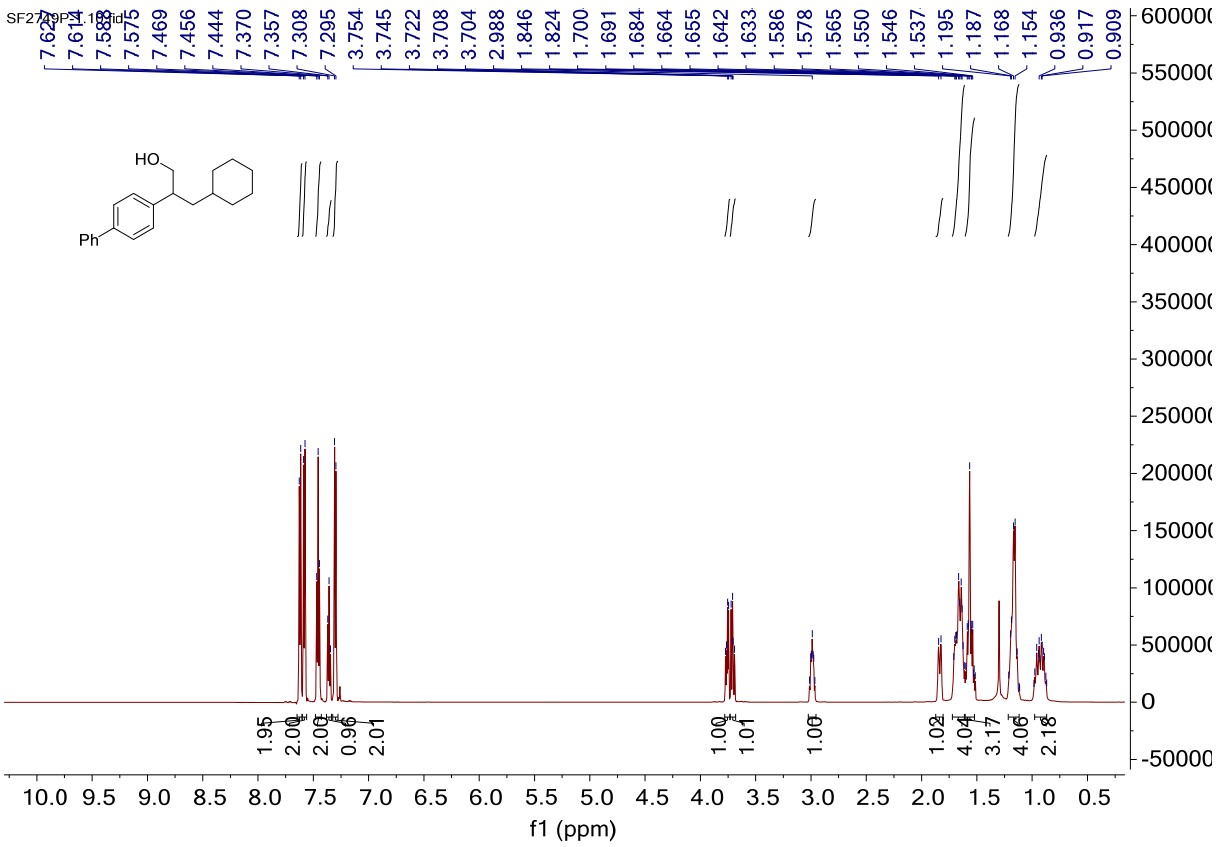
5am ^{13}C NMR (101 MHz, $CDCl_3$)



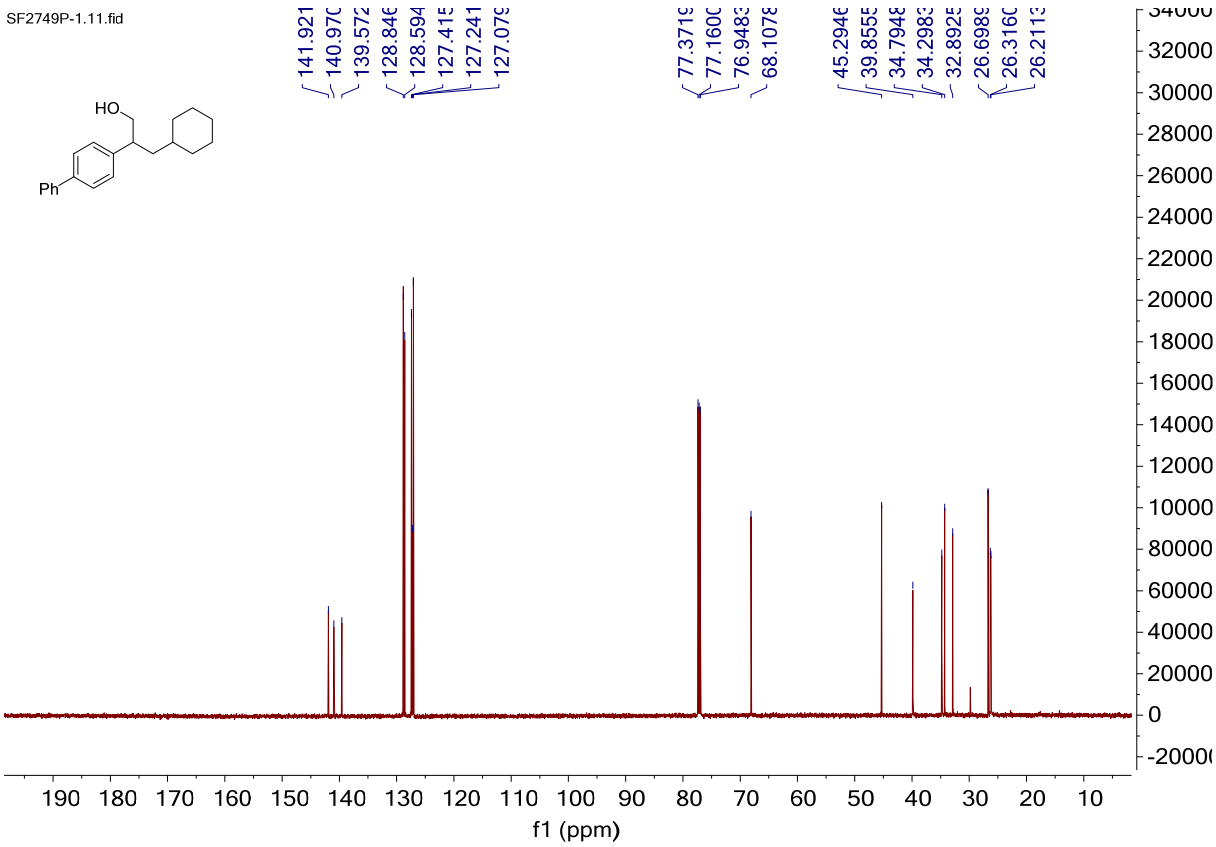
5an ^{1}H NMR (600 MHz, $CDCl_3$)



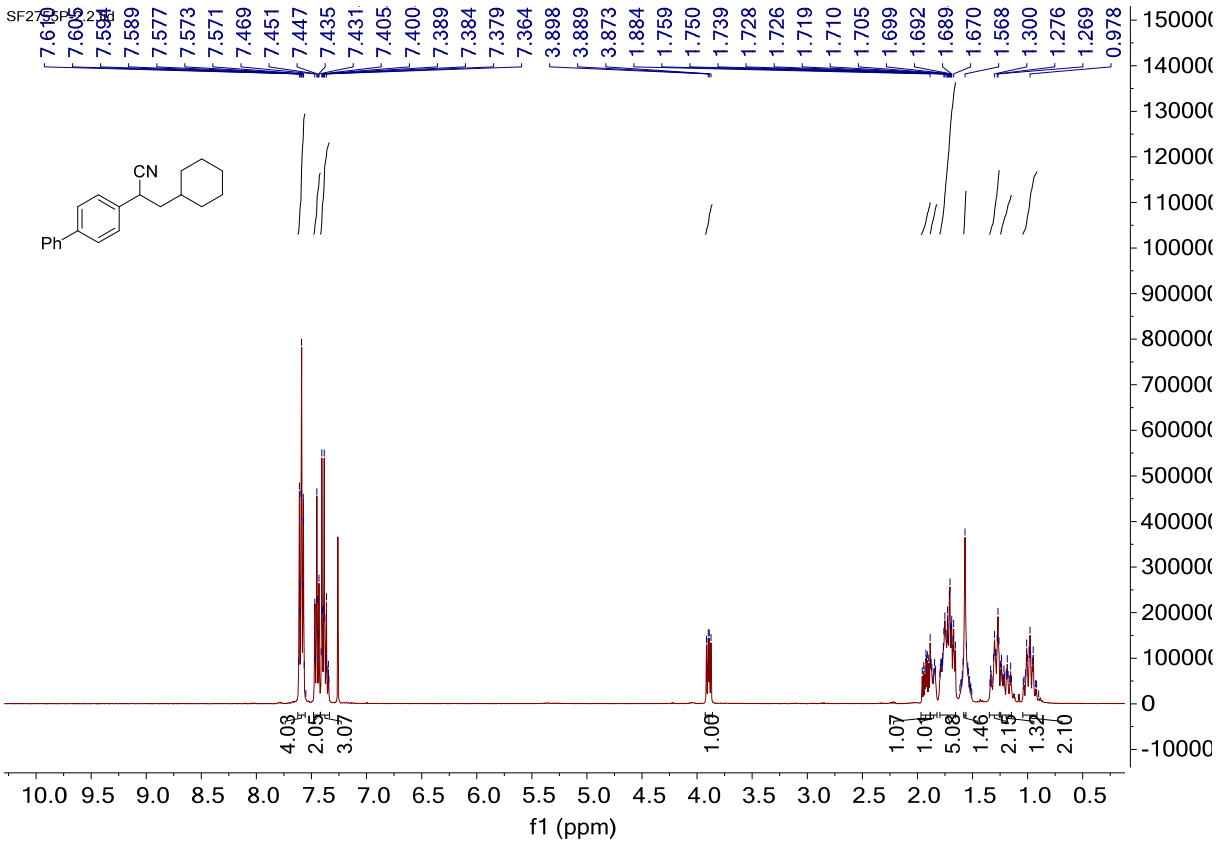
5an ^{13}C NMR (151 MHz, $CDCl_3$)



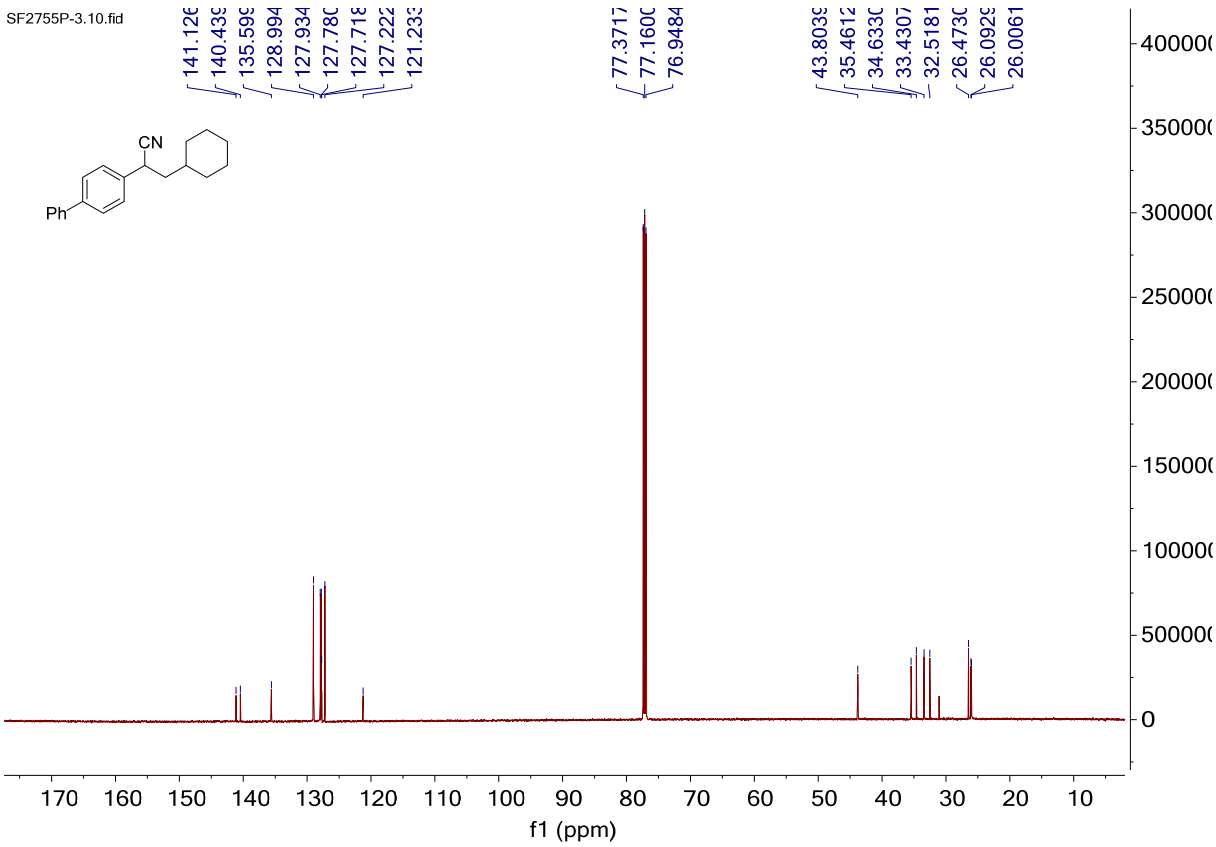
6a ^{1}H NMR (600 MHz, $CDCl_3$)



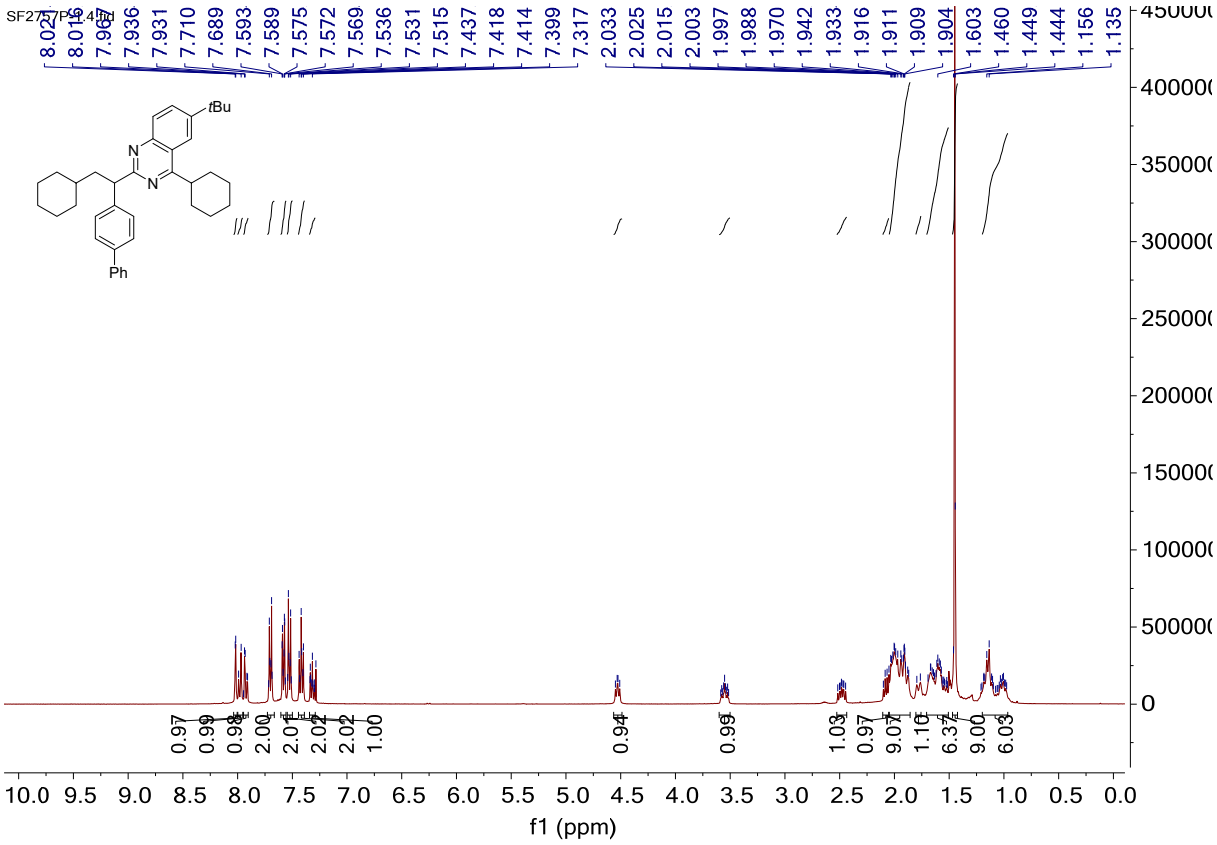
6a ^{13}C NMR (151 MHz, $CDCl_3$)



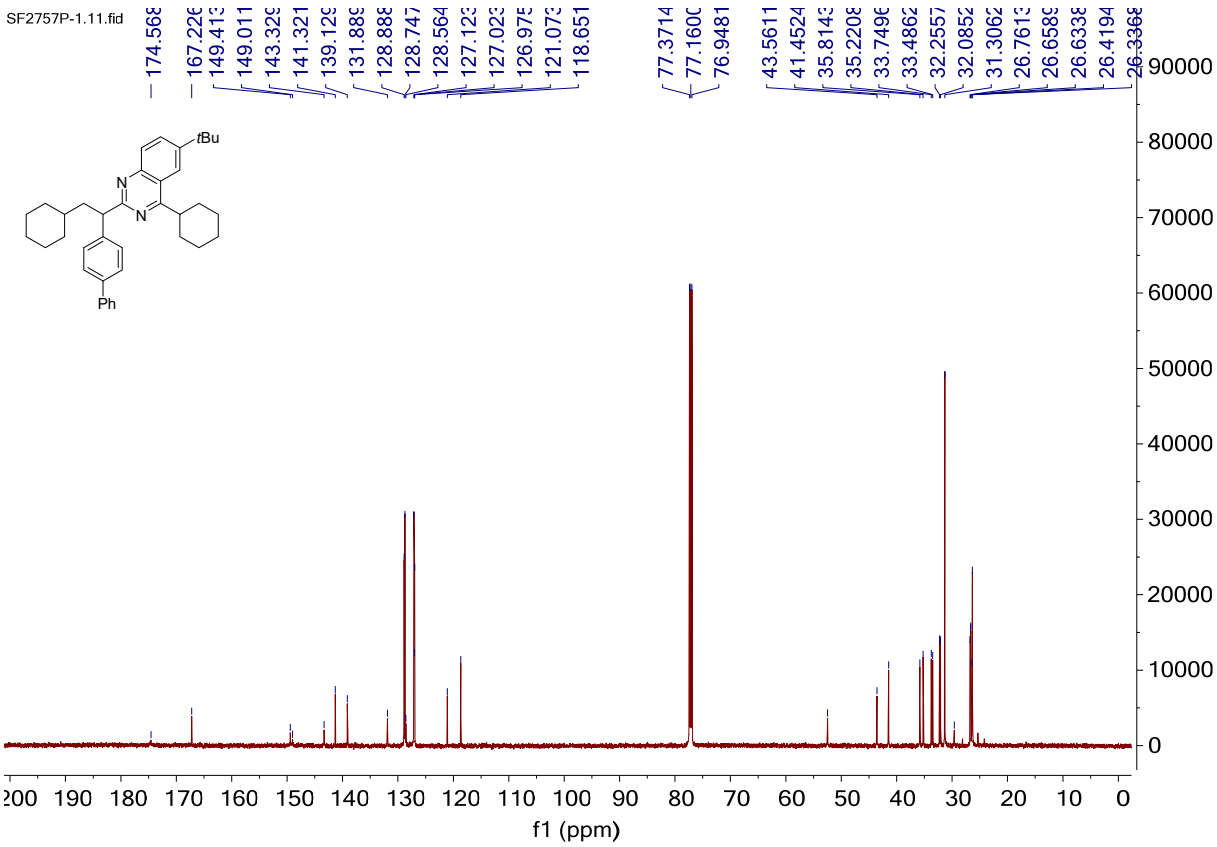
6b ^{1}H NMR (400 MHz, $CDCl_3$)



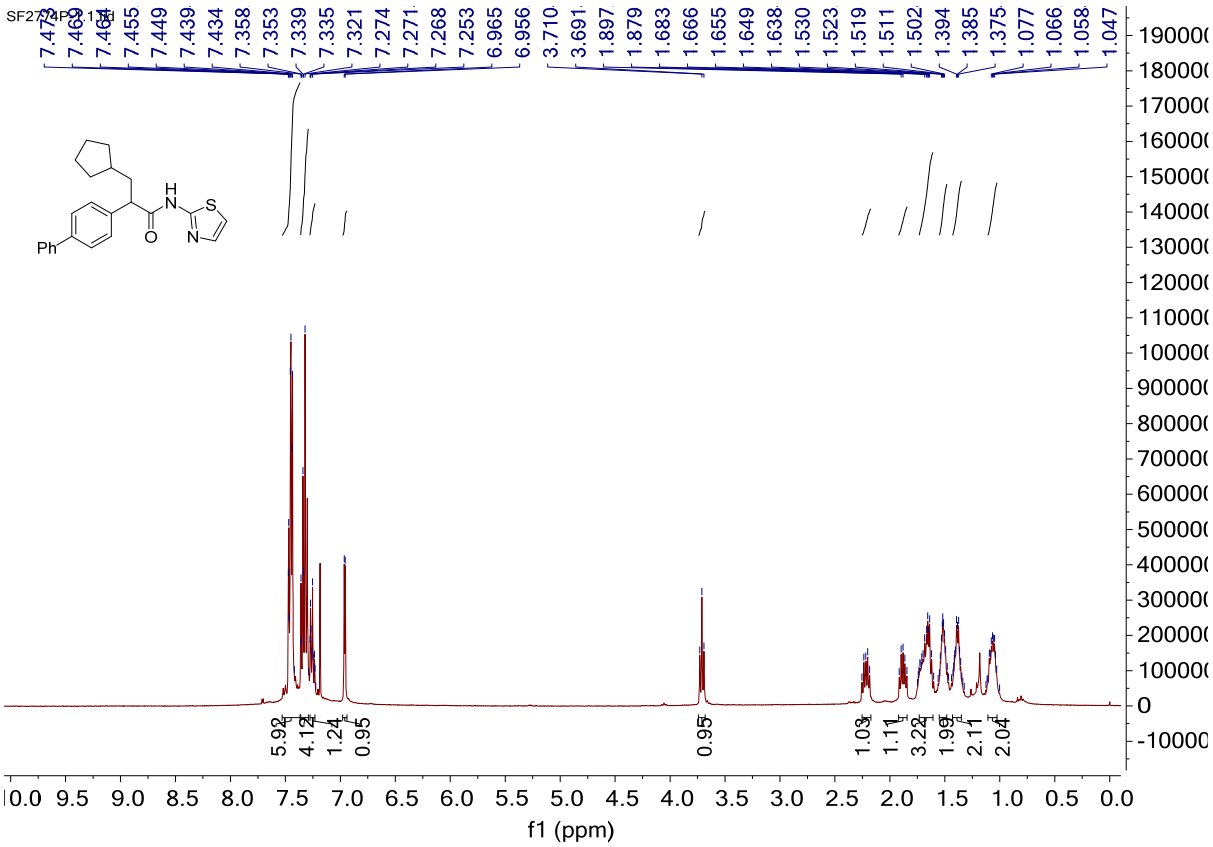
6b ^{13}C NMR (151 MHz, $CDCl_3$)



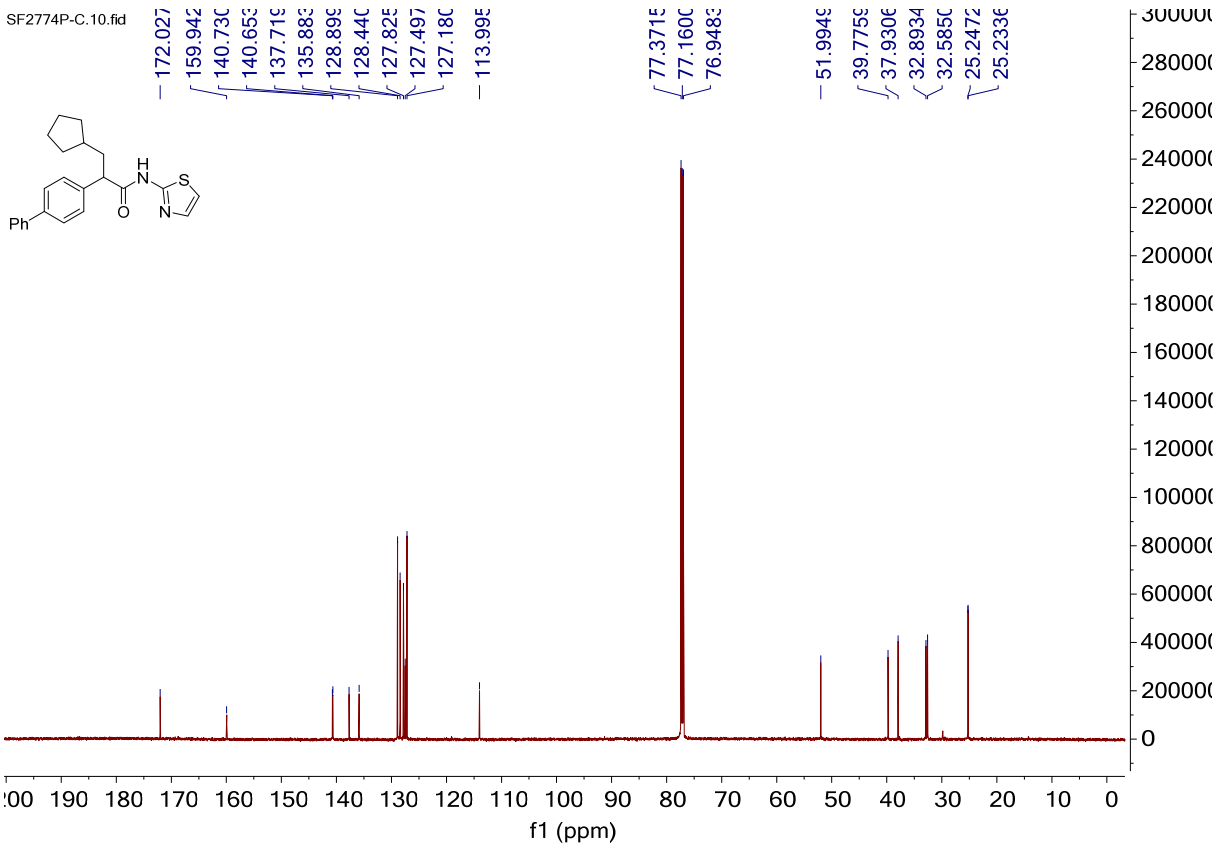
6c ^{1}H NMR (400 MHz, $CDCl_3$)



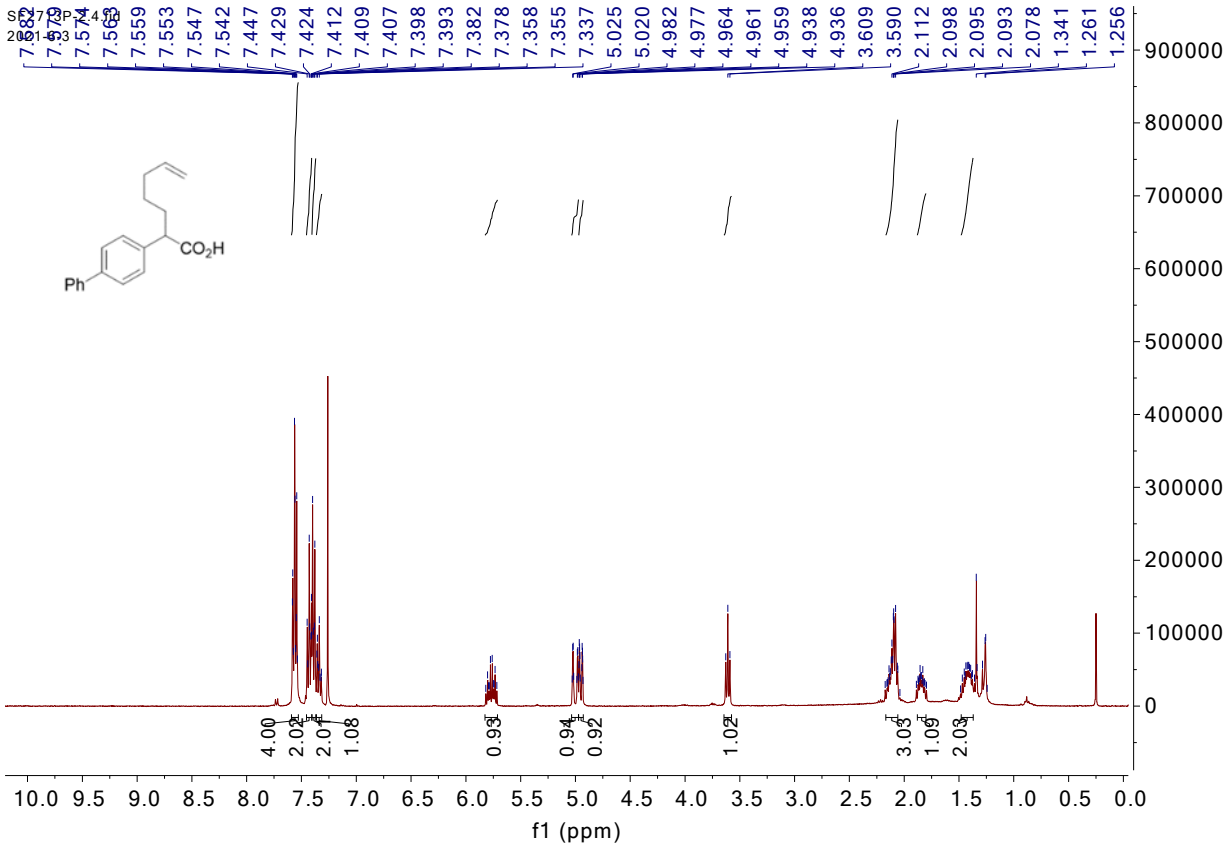
6c ^{13}C NMR (151 MHz, $CDCl_3$)



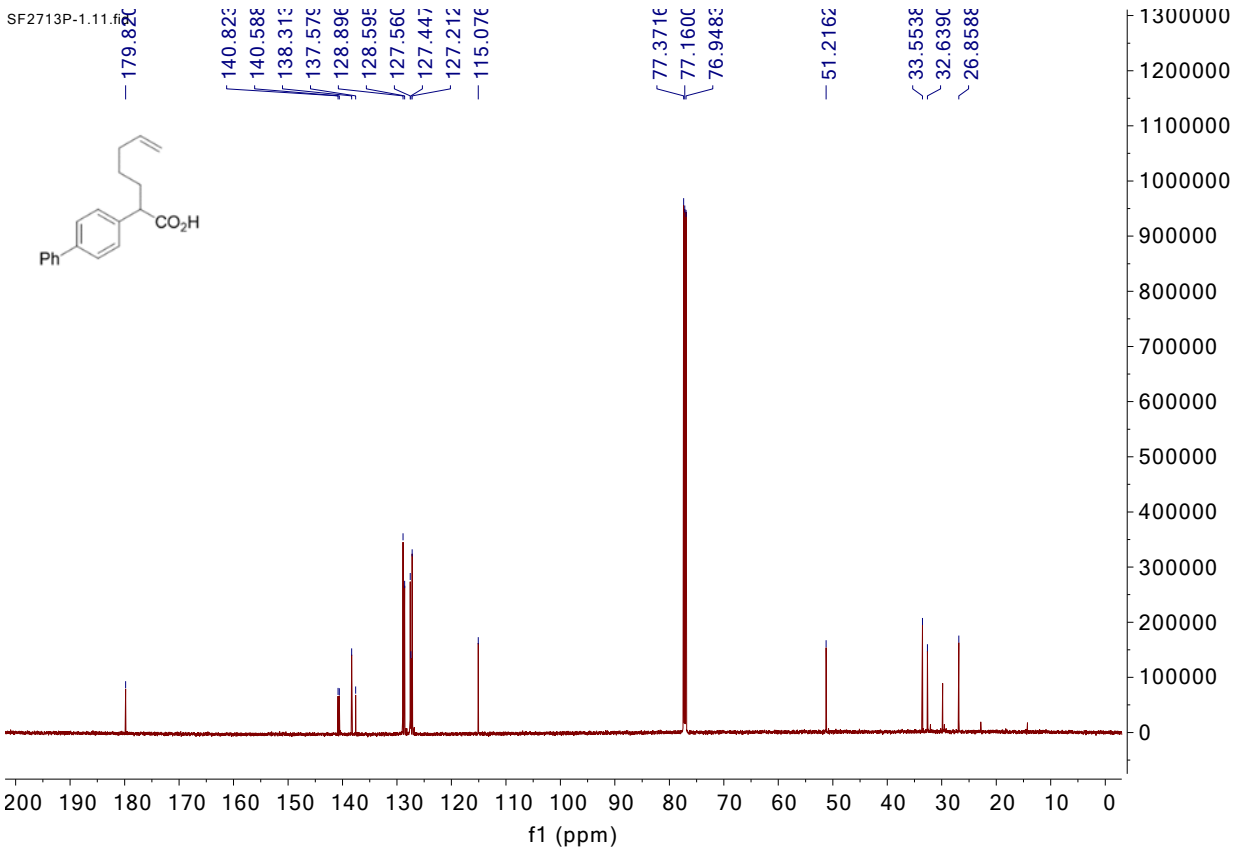
6f ^{1}H NMR (400 MHz, $CDCl_3$)



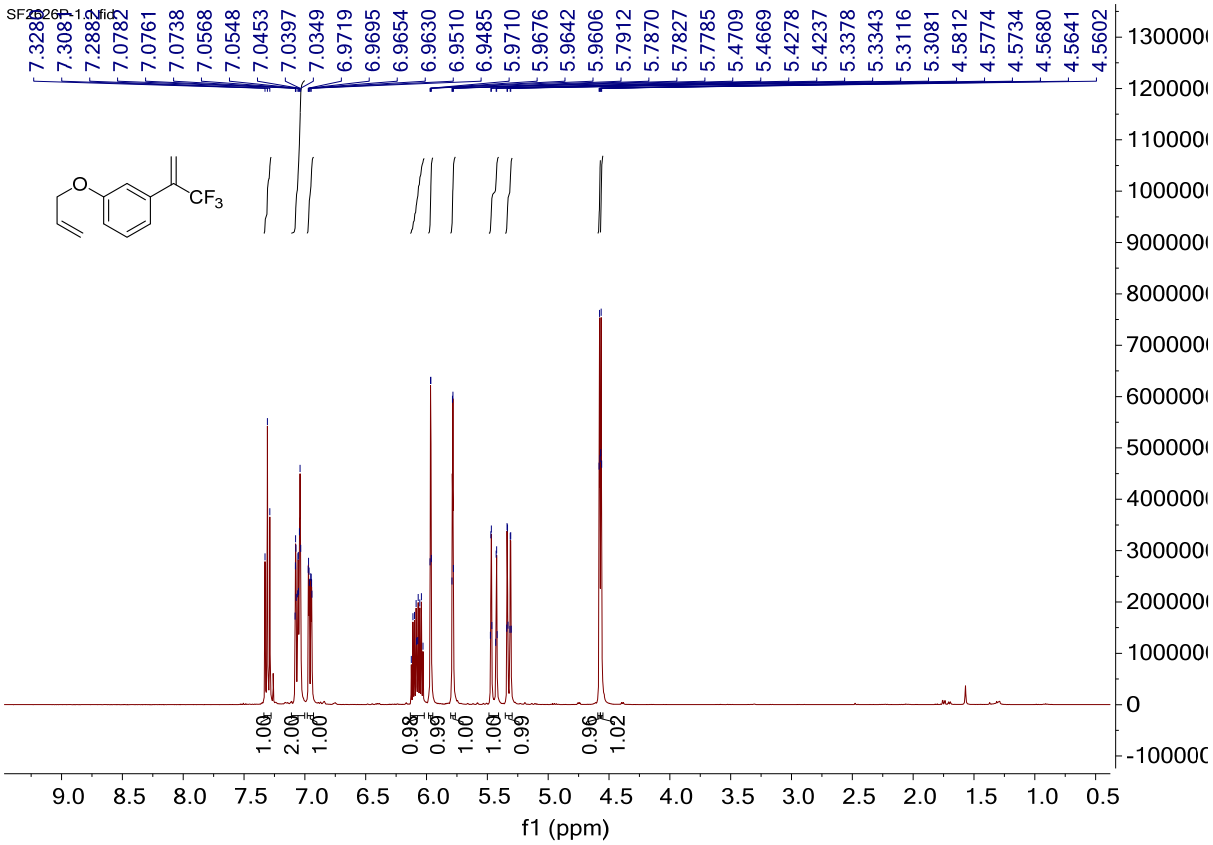
6f ^{13}C NMR (151 MHz, $CDCl_3$)



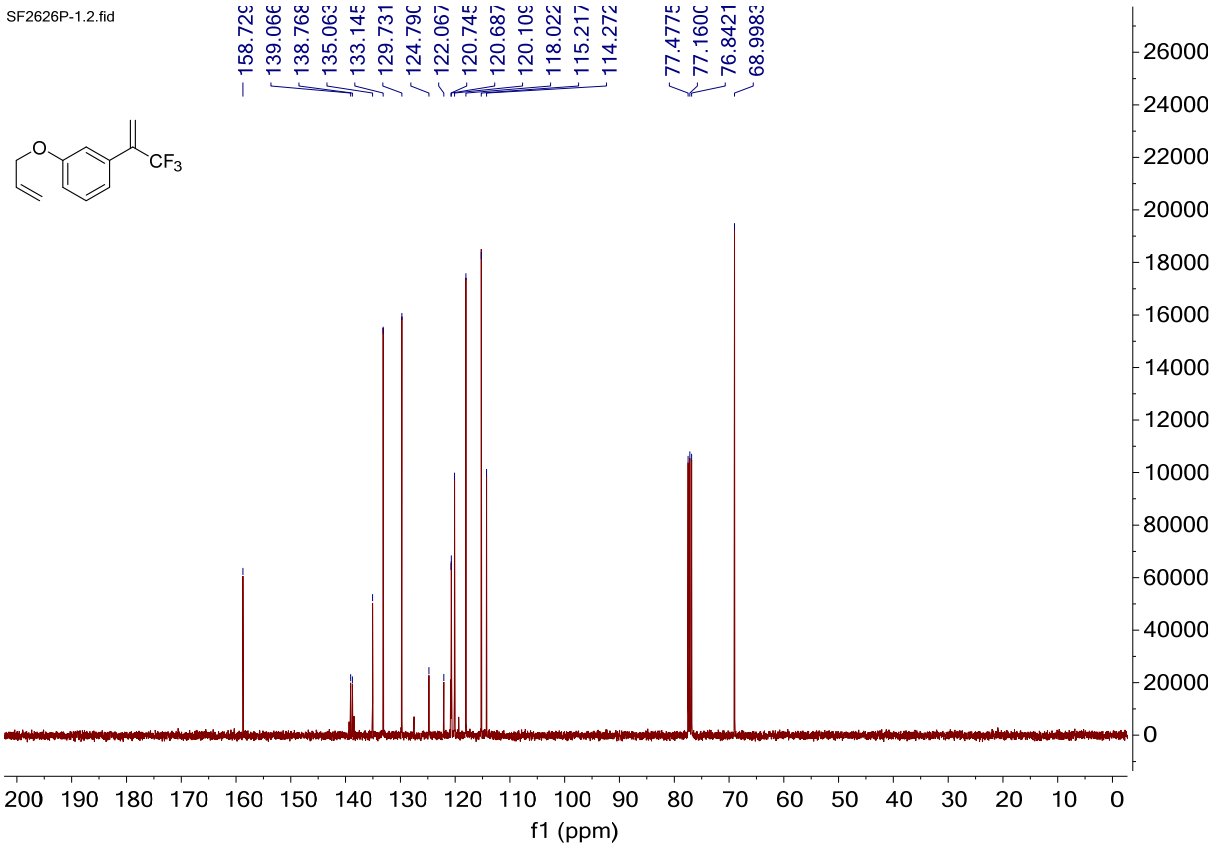
7b ^{1}H NMR (400 MHz, $CDCl_3$)



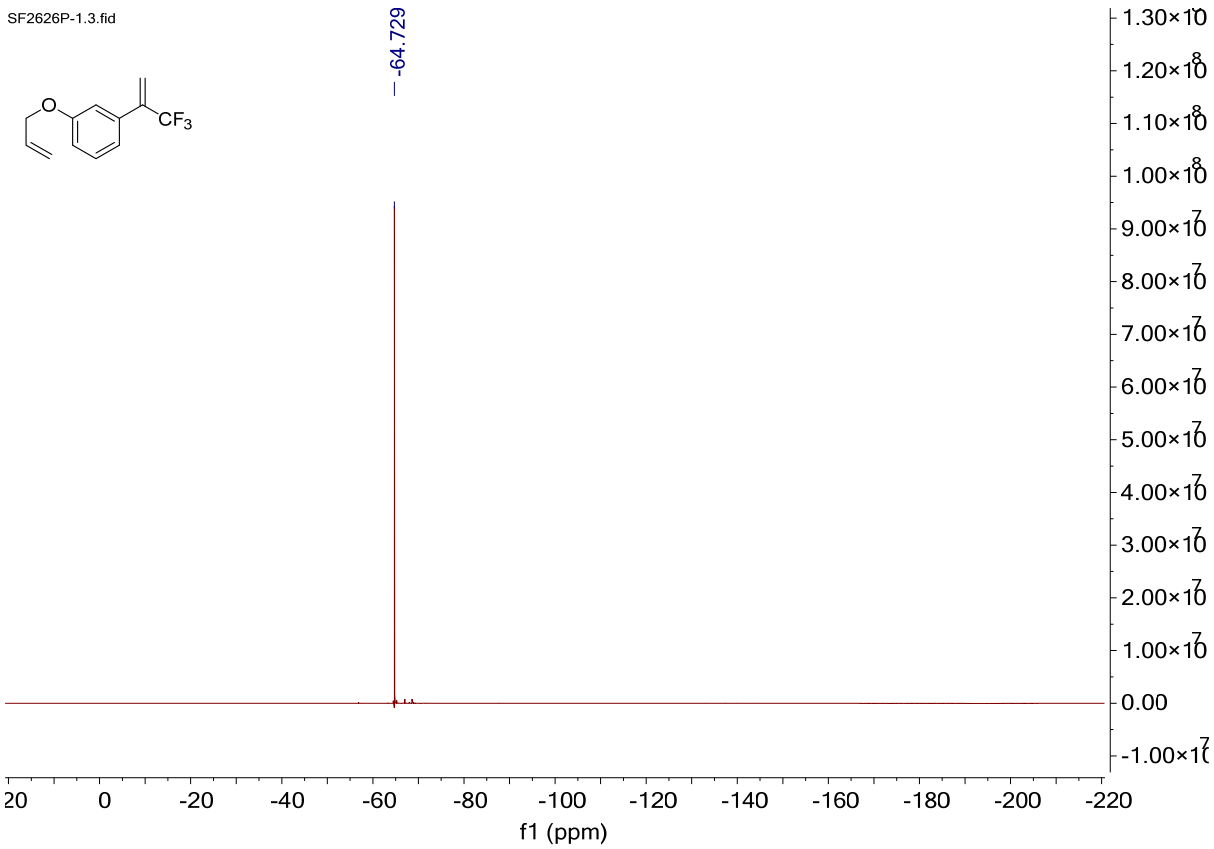
7b ^{13}C NMR (151 MHz, $CDCl_3$)



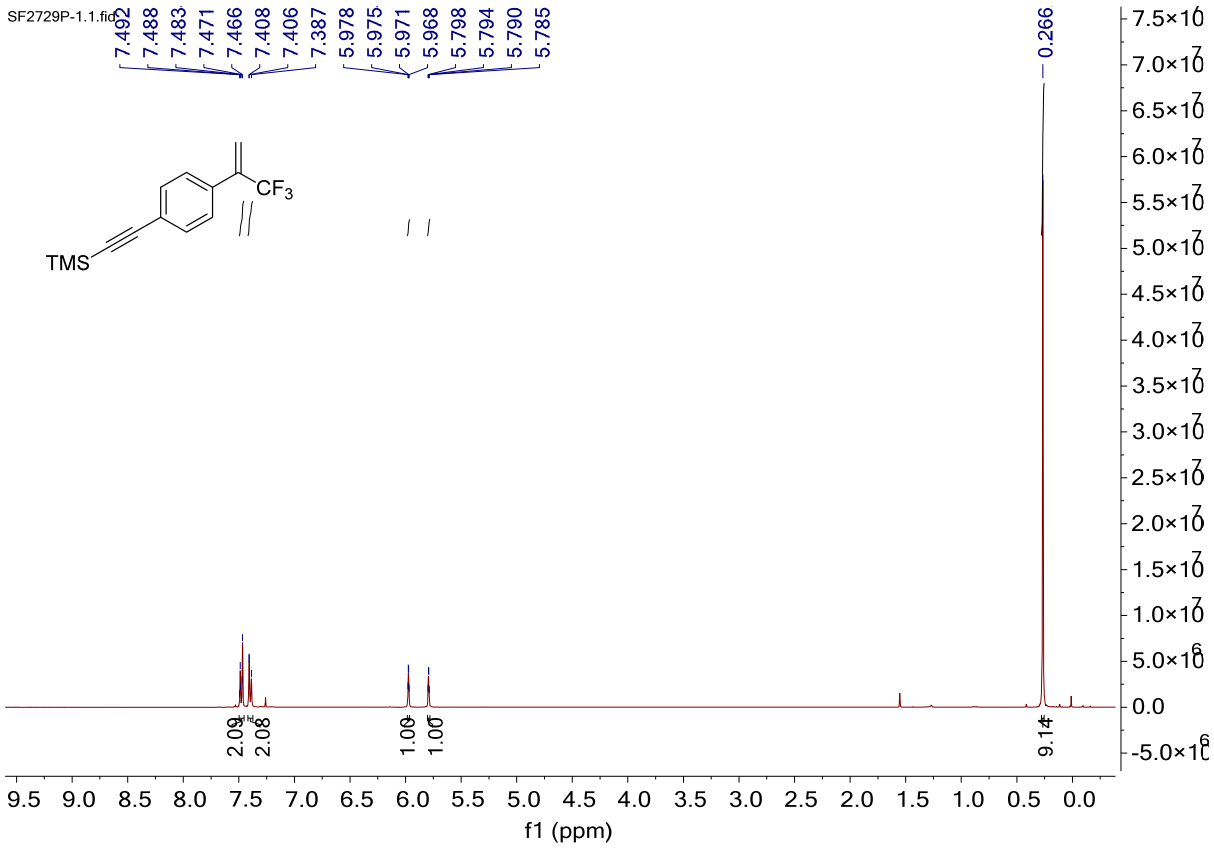
S-3i ^{1}H NMR (400 MHz, $CDCl_3$)



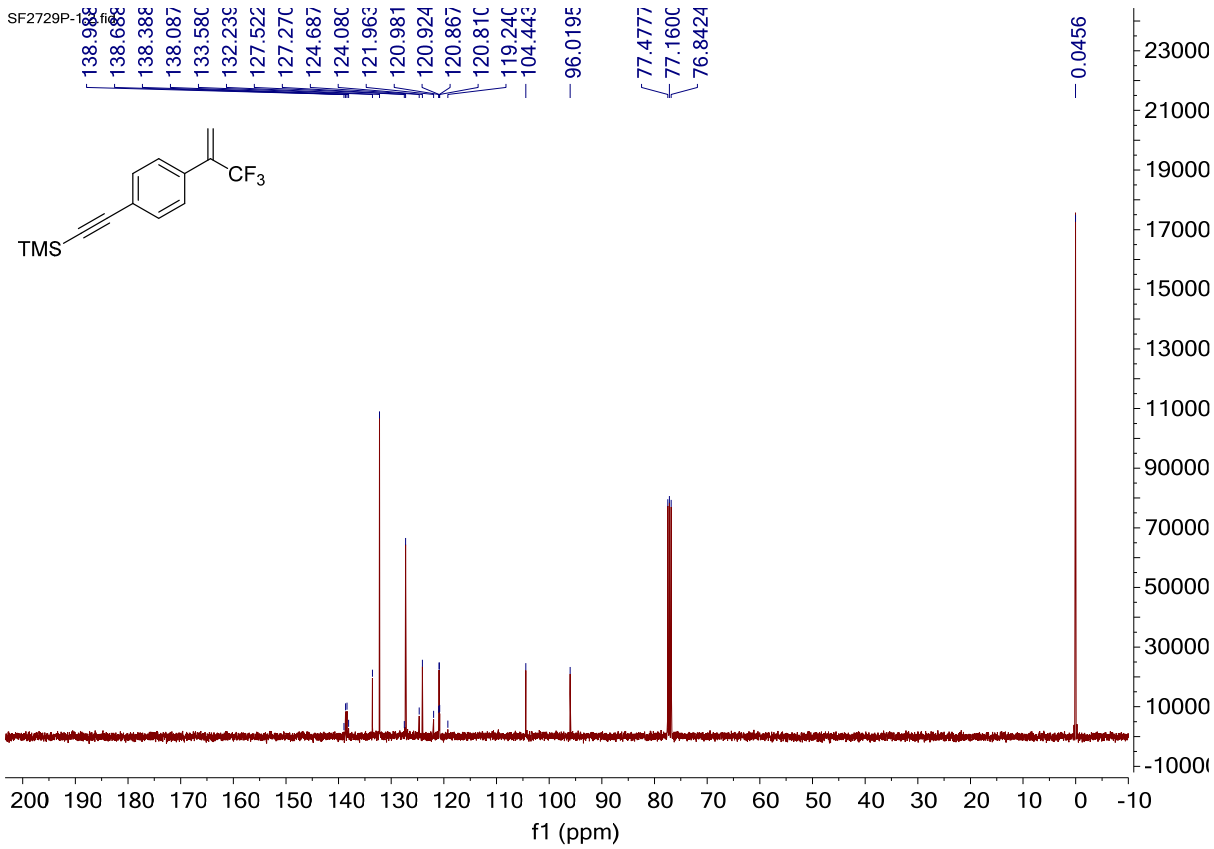
S-3i ^{13}C NMR (101 MHz, $CDCl_3$)



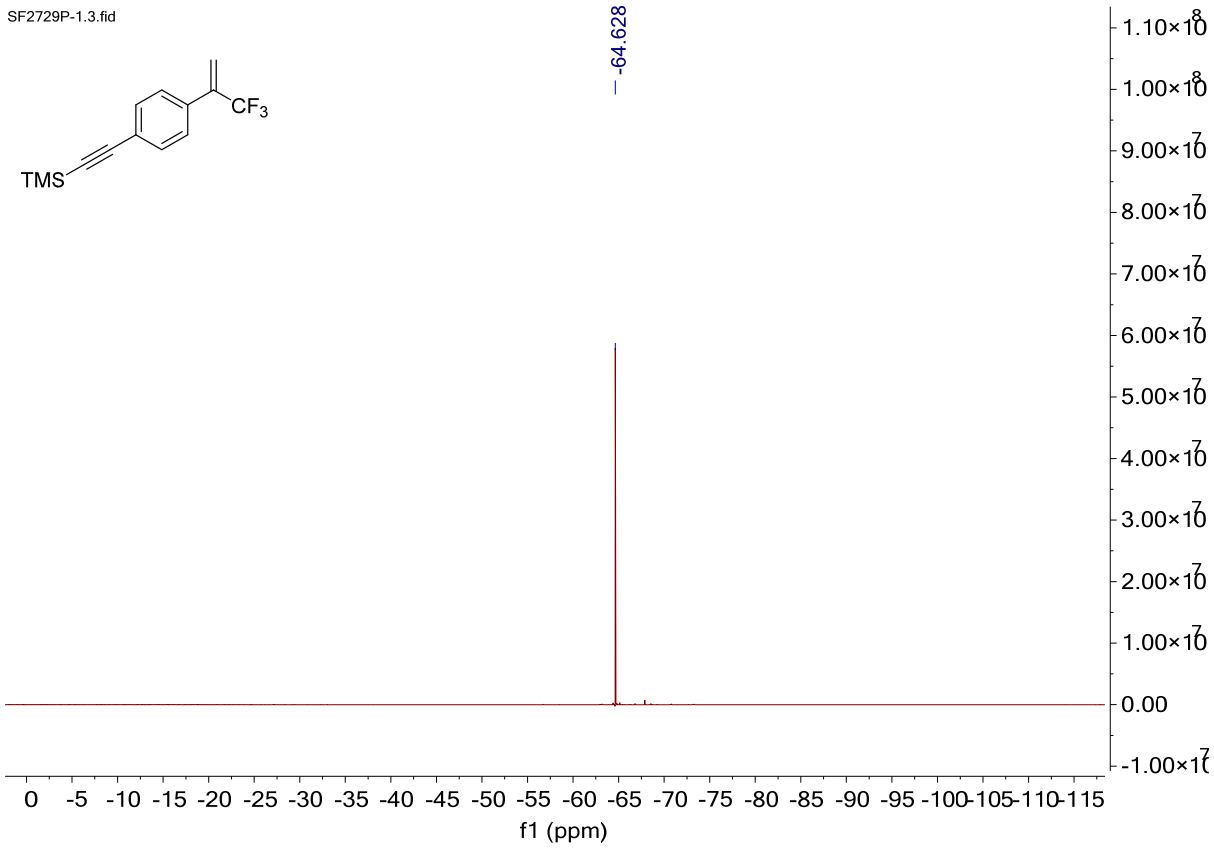
S-3i ^{19}F NMR (376 MHz, $CDCl_3$)



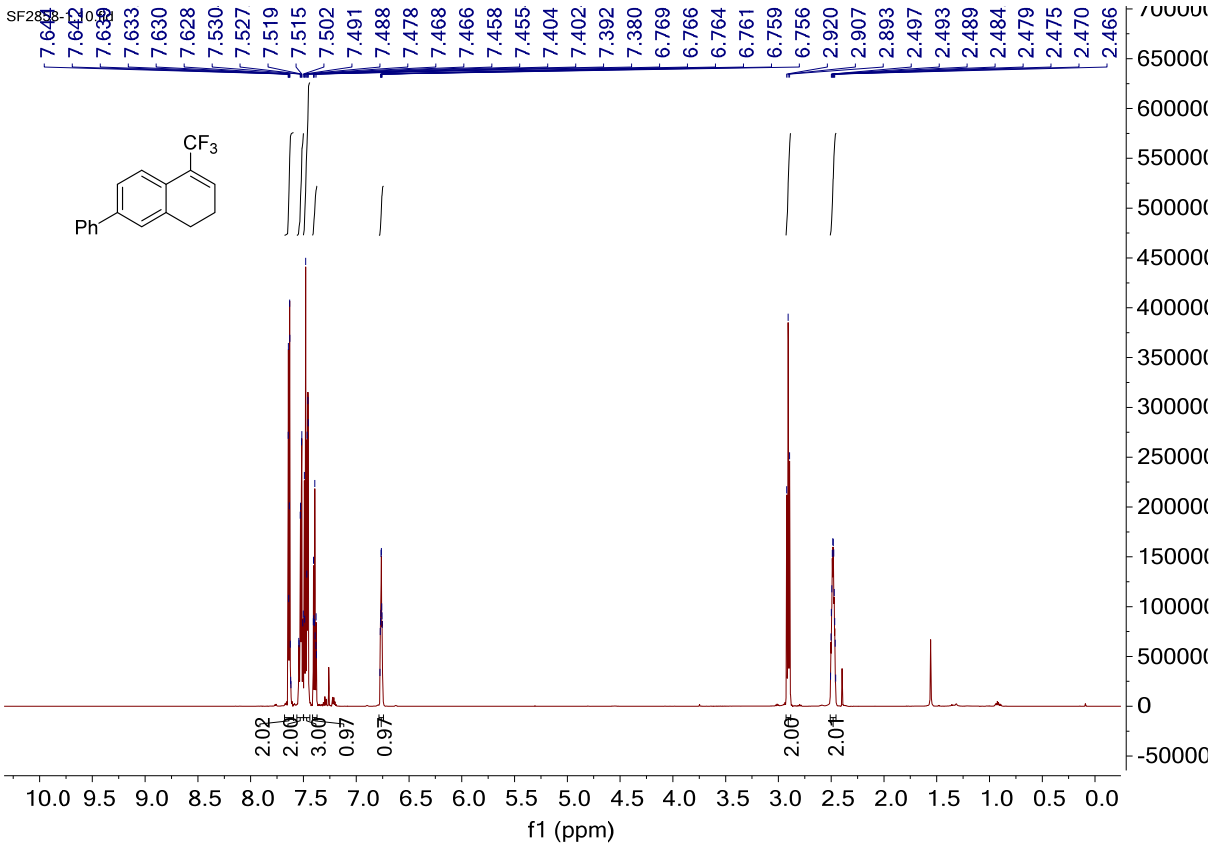
S-3g ^{1}H NMR (400 MHz, $CDCl_3$)



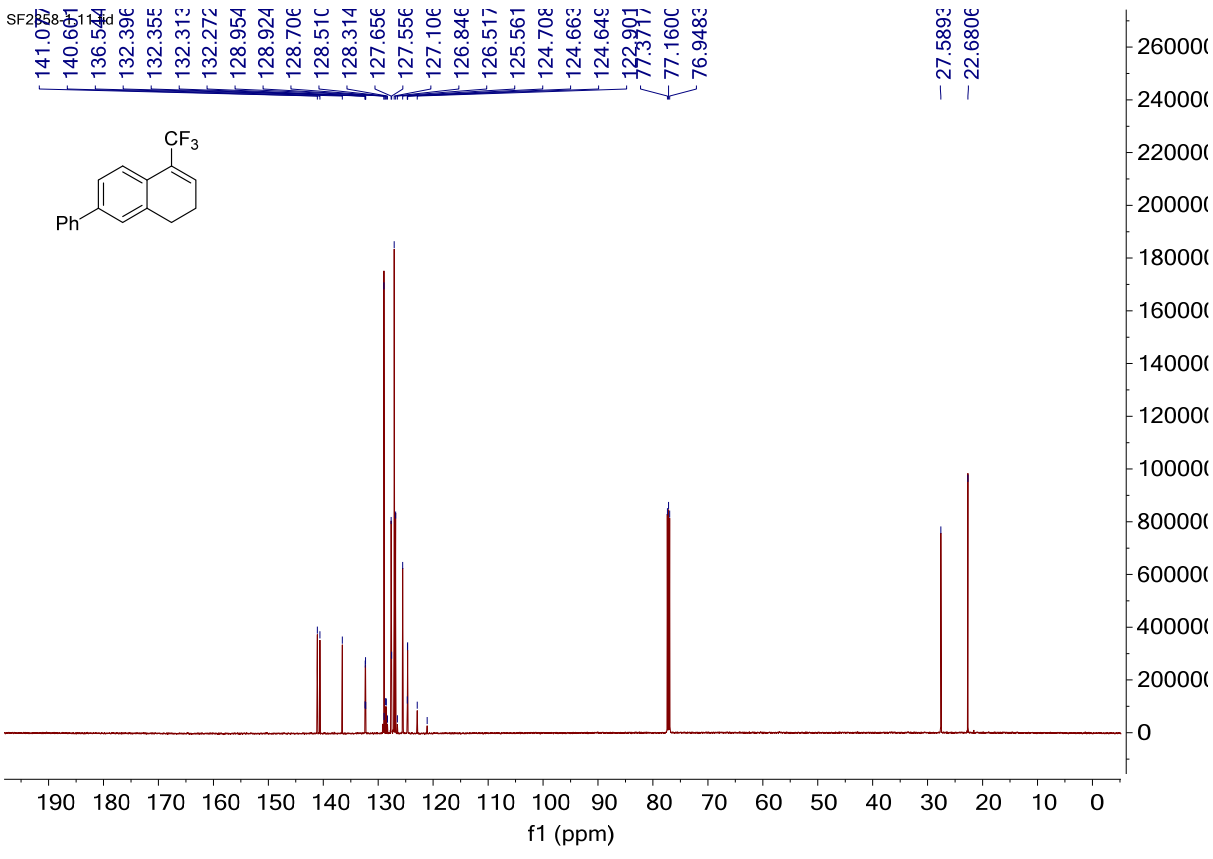
S-3g ^{13}C NMR (101 MHz, $CDCl_3$)



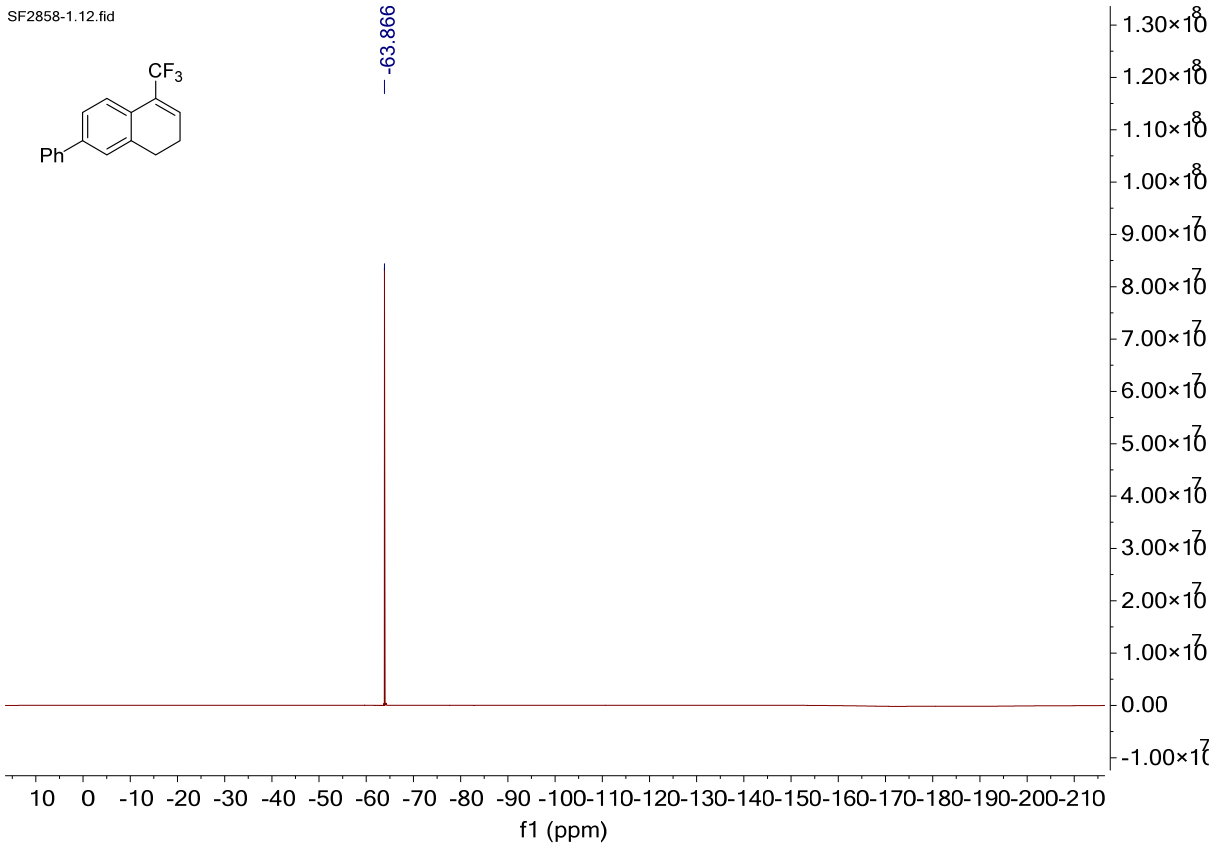
S-3g ^{19}F NMR (376 MHz, $CDCl_3$)



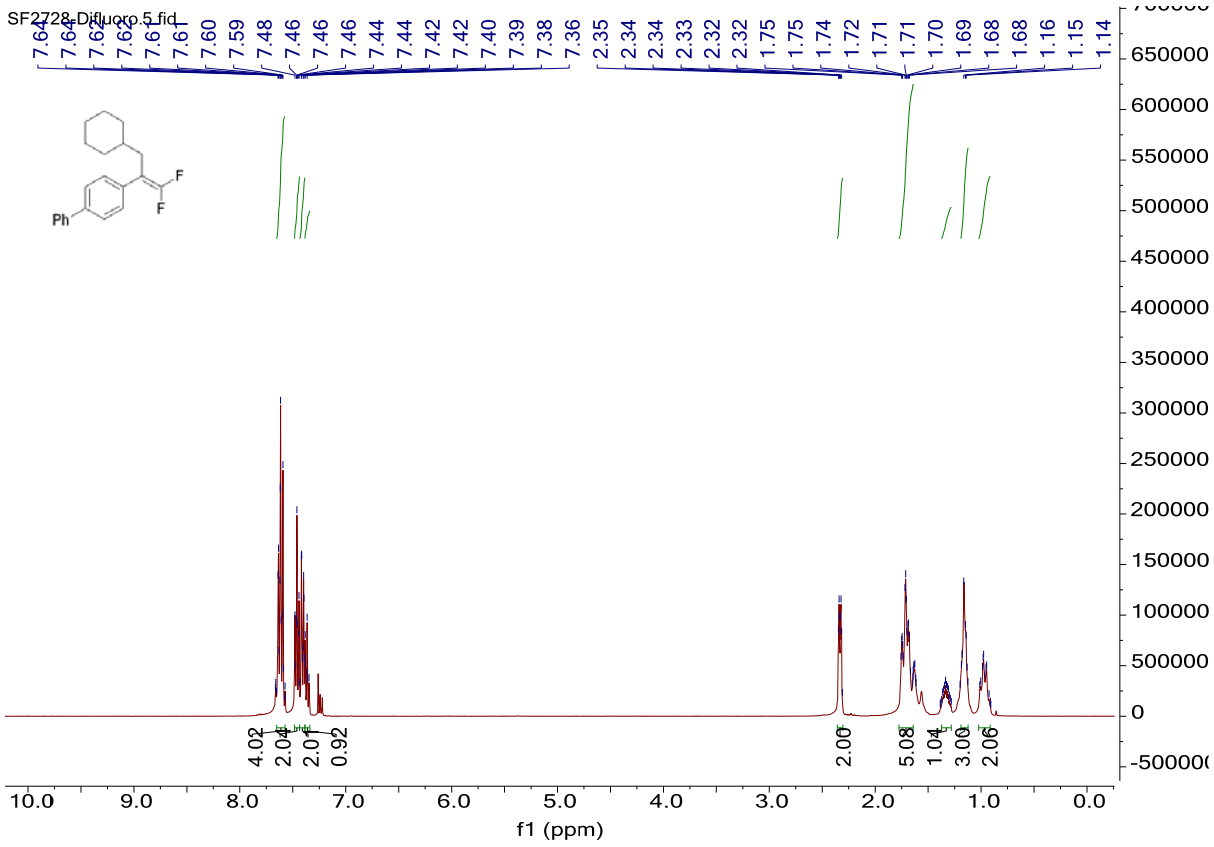
S-3o ^{1}H NMR (600 MHz, $CDCl_3$)



S-3o ^{13}C NMR (151 MHz, $CDCl_3$)



S-3o ^{19}F NMR (3565 MHz, $CDCl_3$)



7c ^{1}H NMR (400 MHz, $CDCl_3$)