Supporting Information

Direct α-Acylation of Alkenes via *N*-Heterocyclic Carbene, Sulfinate and Photoredox Cooperative Triple Catalysis

Kun Liu and Armido Studer*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Corrensstrasse 40, 48149 Münster (Germany)

Corresponding Author: studer@uni-muenster.de

Content

1. General information

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard *Schlenk* techniques. Acetonitrile (MeCN, 99.9%, Extra Dry over Molecular Sieves) was purchased from Acros Organics. All styrene derivatives were distilled prior to use. Otherwise noted, other commercially available reagents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros, ABCR or BLD pharm in the highest purity grade and used directly without further purification. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F-254 plates and visualized by fluorescence quenching under UV light. Column chromatography was performed on Merck or Fluka silica gel 60 (40-63 μm) using a forced flow of 0.5 bar. ^{1}H NMR (300 MHz and 400 MHz), ^{13}C NMR (75 MHz and 100 MHz) and ^{19}F NMR (282 MHz) spectra were measured on a Bruker DPX 300 and Bruker AV 400 spectrometer at 300 K. The multiplicity of all signals were described as s (singlet), d(doublet), t (triplet), q (quartet) and m (multiplet). Chemical shifts (δ in ppm) were referenced on the residual peak of $CDCl_3$ (^{1}H NMR: δ = 7.26; ^{13}C NMR: δ = 77.0). HRMS ESI (m/z) measurements were performed on a Bruker MicroTof and HRMS EI (m/z) on a Waters-Micromass QuattroMicro GC-MS. Reactions were performed with a compact fluorescent lamp (23 W, Philips). IR spectra were recorded on a Digilab 3100 FT-IR Excalibur Series spectrometer and the position of the absorption bands is given in wave numbers ν (cm^{-1}). Melting points were measured on a Stuart SMP10 and are uncorrected.

2. Substrate structures

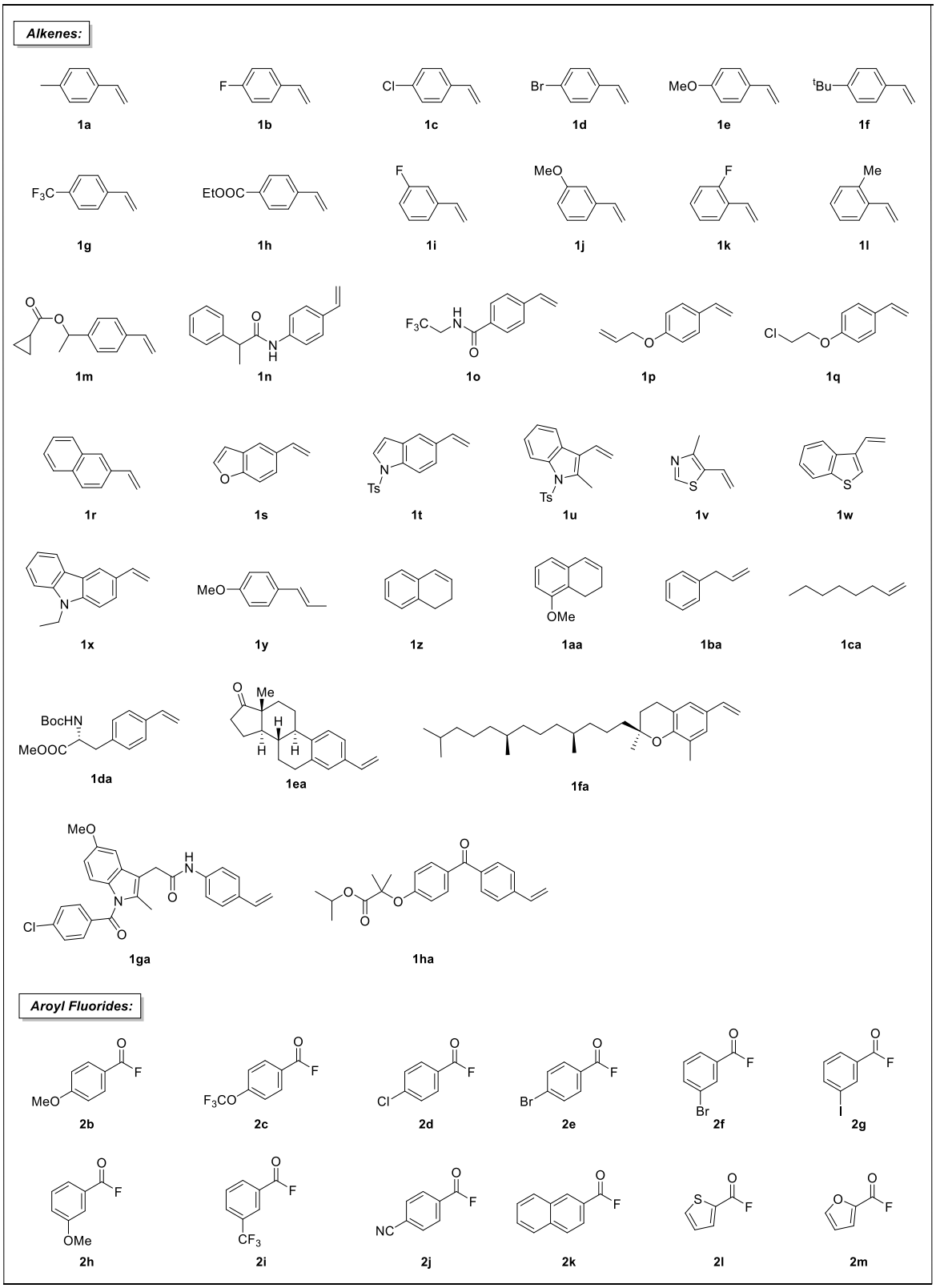
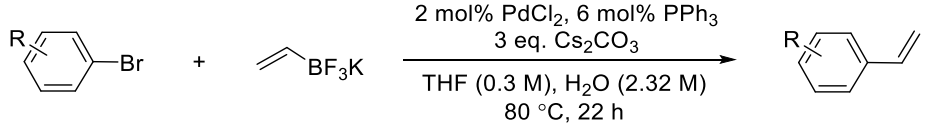


Figure S1. Substrate structures

3. Preparation of starting materials

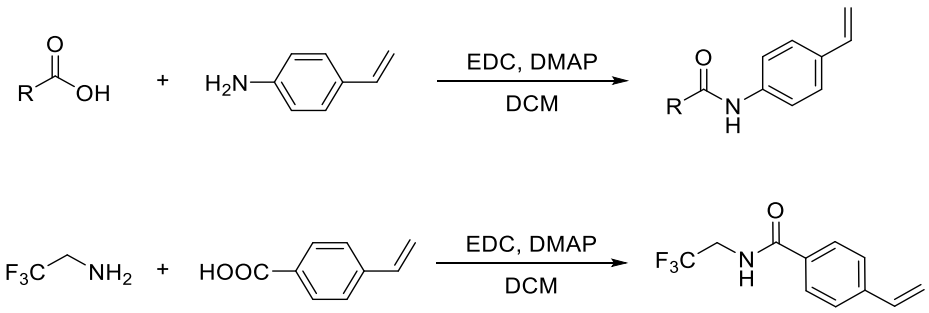
Triazolium salt **B**, 2-benzoyl-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate **8** and acyl fluorides were all synthesized according to a reported procedure[1].

Preparation of 1m, 1s, 1t and 1x:



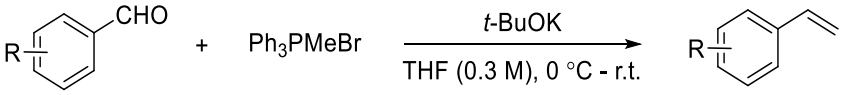
A 20 mL vial was charged with the corresponding aryl bromide (1.00 mmol, 1.00 equiv), potassium vinyltrifluoroborate (160 mg, 1.20 mmol, 1.20 equiv), $PdCl_2$ (4.00 mg, 0.0200 mmol, 2.00 mol%), PPh_3 (16.0 mg, 0.0600 mmol, 6.00 mol%) and Cs_2CO_3 (980 mg, 3.00 mmol, 3.00 equiv). The vial was capped with a septa cap and filled with nitrogen through a triple cycle of gas exchange process. Freshly distilled THF (5.50 mL) and degassed distilled water (0.400 mL) were added. The resulting mixture was then stirred at 80 ℃ for 22 h, and it was allowed to cool to 23 ℃. DCM (20.0 mL) and water (30.0 mL) were then added. The layers were separated, and the aqueous layer was extracted with DCM (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, eluting with pentane: Et_2O to afford the title compound. The ^1H NMR spectra were identical with those reported in the literature.[2]

Preparation of 1n, 1ga and 1o:



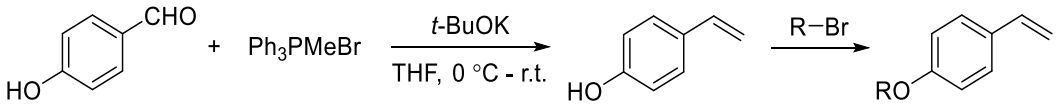
According to a previous reference,[3] a mixture of the corresponding acid (1.0 mmol), 4-vinylaniline (121.5 mg, 1.02 mmol), 1-(3- dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (287.6 mg, 1.5 mmol), and DMAP (2.5 mg, 0.02 mmol) in CH_2Cl_2 (20.0 mL) was stirred at room temperature for 2.5 h. The reaction mixture was added to H_2O and extracted with CH_2Cl_2. The organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo. Flash chromatography (EtOAc/hexane = 1:5) afforded the product. The analytical data of the alkenes are in accordance with the reported data.

Preparation of 1u and 1w:



In an oven dried flask, methyl triphenylphosphonium bromide (12.0 mmol, 1.2 eq.) and THF (30 mL) were added. The suspension was cooled to 0 ^{o}C, *t*-BuOK (12.0 mmol, 1.2 eq.) was added and the resulting yellow suspension was stirred at 0 ^{o}C for 1 hour. To this suspension, a solution of the corresponding aldehyde (10.0 mmol, 1.0 eq.) in THF (10 mL) was added slowly and the resulting mixture was warmed gradually to room temperature and stirred at room temperature for 18 hours. The reaction mixture was concentrated under reduced pressure and filtered over celite. The filtrate was concentrated under reduced pressure and purified by column chromatography to afford the desired product. The analytical data of alkenes are in accordance with the reported data.[4]

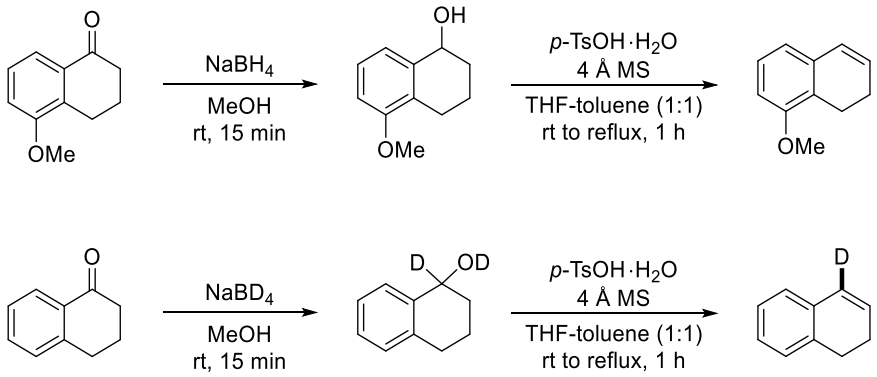
Preparation of 1p and 1q:



Step 1: In an oven dried flask, methyl triphenylphosphonium bromide (12.0 mmol, 1.2 eq.) and THF (30 mL) were added. The suspension was cooled to 0 ^{o}C, *t*-BuOK (12.0 mmol, 1.2 eq.) was added and the resulting yellow suspension was stirred at 0 ^{o}C for 1 hour. To this suspension, a solution of the corresponding aldehyde (10.0 mmol, 1.0 eq.) in THF (10 mL) was added slowly and the resulting mixture was warmed gradually to room temperature and stirred at room temperature for 18 hours. The reaction mixture was concentrated under reduced pressure and filtered over celite. The filtrate was concentrated under reduced pressure and purified by column chromatography to afford the desired product.

Step 2: To a solution of 4-vinylphenol (8.2 mmol, 1.0 equiv) in MeCN (10 mL), K_2CO_3 (3.4 g, 25 mmol, 3.0 equiv) and corresponding aliphatic bromide (12.3 mmol, 1.5 equiv) were added. The reaction mixture was heated to reflux for 10 h. After cooling to room temperature, the solution was filtered, washed with acetone and concentrated in vacuo. Purification by flash chromatography (10% EtOAc/hexanes) afforded the pure products.

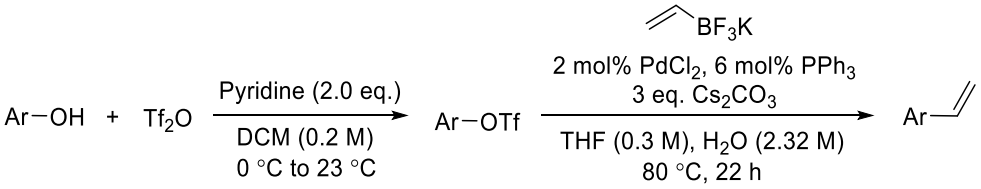
Preparation of 1aa and [D]-1z:



Step 1: To a stirred solution of 5-methoxy-3,4-dihydronaphthalen-1(2H)-one (6.8 mmol) in MeOH (6.8 mL), $NaBH_4$ (647 mg, 17.1 mmol) was added portionwise at room temperature. After the completion of the reaction, the reaction was quenched with H_2O at 0 ℃. The resulting mixture was extracted with EtOAc three times. The combined organic extracts were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was subjected to the next reaction without further purification.

Step 2: A suspension of the crude product, dried MS4Å (735 mg), and $TsOH{\cdot}H_2O$ (1.40 g, 7.35 mmol) in THF (4.9 mL) and toluene (4.9 mL) was refluxed at 110 ℃ for 1 hour. The mixture was cooled to room temperature. The reaction was quenched with saturated aqueous solution of NH_4Cl. The resulting mixture was extracted with EtOAc three times. The combined organic extracts were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (pentane) to afford the desired product. The ^1H NMR spectrum was identical with that reported in the literature.[5]

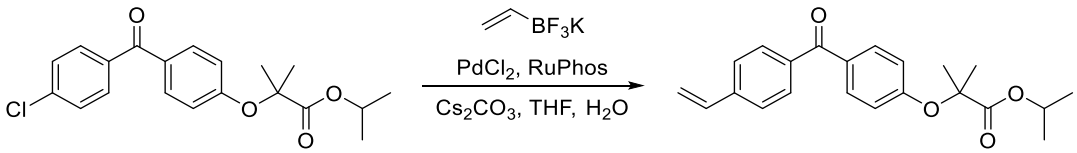
Preparation of 1ea, 1ba and 1da:



Step 1: These two alkenes were synthesized according to a reported procedure.[2] Under nitrogen atmosphere, to a 50 mL flamed dried round bottom charged with phenol (1.0 mmol, 1.0 equiv), DCM (5.0 mL, 0.20 M) and pyridine (158 mg, 0.16 mL, 2.0 mmol, 2.0 equiv) was added. The resulting mixture was cooled to 0 ℃ in an ice/water bath. Tf_2O (339 mg, 0.21 mL, 1.5 mmol, 1.5 equiv) was added dropwise over 5 minutes. The reaction mixture was warmed to room temperature and stirred for 5 hours. The resulting brown reaction mixture was then quenched by water (15 mL). The layers were separated, and the aqueous layer was extracted with DCM (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, eluting with pentane : EtOAc to afford the first-step product.

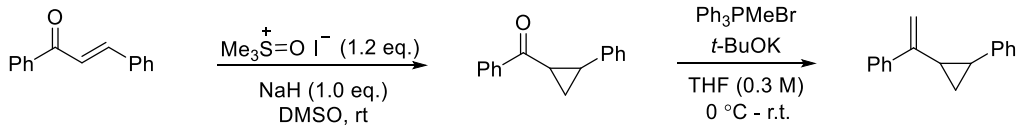
Step 2: A 20 mL vial was charged with the first-step product (0.586 mmol, 1.00 equiv), potassium vinyltrifluoroborate (94.2 mg, 0.703 mmol, 1.20 equiv), $PdCl_2$ (2.08 mg, 0.0110 mmol, 2.00 mol%), PPh_3 (9.22 mg, 0.0340 mmol, 6.00 mol%) and Cs_2CO_3 (573 mg, 1.76 mmol, 3.00 equiv). The vial was capped with a septa cap and filled with nitrogen through a triple-cycle of gas exchange process. Freshly distilled THF (2.00 mL) and degassed distilled water (0.250 mL) were added. After stirring at 80 °C for 22 h, the mixture was allowed to cool to 23 °C. DCM (15.0 mL) and water (20.0 mL) were then added. The layers were separated, and the aqueous layer was extracted with DCM (3 × 15 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel, eluting with pentanes: EtOAc to afford the title compound. The ^1H NMR spectrum was identical with that reported in the literature.[2]

Preparation of 1ha:



An oven-dried vial with a magnetic stirring bar was charged with fenofibrate (300 mg, 0.77 mmol), potassium vinyltrifluoroborate (195 mg, 1.46 mmol, 1.75 equiv), palladium(II) chloride (7.4 mg, 5 mol%), RuPhos (39 mg, 10 mol%) and cesium carbonate (813 mg, 2.49 mmol, 3 equiv) and then it was evacuated and refilled with argon three times. THF (2 mL) and distilled water (0.3 mL) (0.35 M considering both solvents) were added, the vial was sealed with the corresponding cap and the resulting dark brown mixture was stirred at 85 ºC for 20 h. More water was added and the mixture was extracted three times with Et_2O. The combined organic fractions were washed once with water, once with brine and dried over anhydrous $MgSO_4$, concentrated in vacuum, and the crude product was purified by flash column chromatography using pentane/EtOAc (9:1) to give vinyl-fenofibrate. The analytical data of this alkene are in accordance with the reported data.[6]

Preparation of 11:

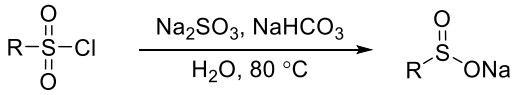


Step 1: To a two-necked round flask, sodium hydride (60% in mineral oil, 1.0 equiv.) was added. Then, dry DMSO and trimethylsulfoxonium iodide (1.2 equiv.) were added to the flask at room temperature under an Ar atmosphere. After hydrogen evolution ceased, the reaction mixture was stirred for an additional 15 mins, during which time the solution became clear. Chalcone (1.0 equiv.)

was then added in one portion to the clear solution. The reaction solution was stirred at room temperature for 5 h. After completion of the reaction (TLC), the reaction was quenched with ice cold water and the mixture was diluted with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4. The product was purified by flash silica gel column chromatography using (petroleum ether/ethyl acetate) as eluent to afford the cyclopropyl ketone product.

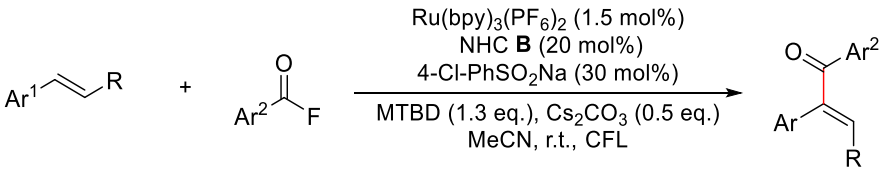
Step 2: Then, to an oven dried flask, methyl triphenylphosphonium bromide (12.0 mmol, 1.2 eq.) and THF (30 mL) were added. The suspension was cooled to 0 ^oC, *t*-BuOK (12.0 mmol, 1.2 eq.) was added and the resulting yellow suspension was stirred at 0 ^oC for 1 hour. To this suspension, a solution of the corresponding ketone (10.0 mmol, 1.0 eq.) in THF (10 mL) was added slowly and the resulting mixture was warmed gradually to room temperature and stirred at room temperature for 18 hours. The reaction mixture was concentrated under reduced pressure and filtered over celite. The filtrate was concentrated under reduced pressure and purified by column chromatography to afford the desired product. The analytical data of the alkenes are in accordance with the reported data.[7]

General procedure for the preparation of sodium sulfonates



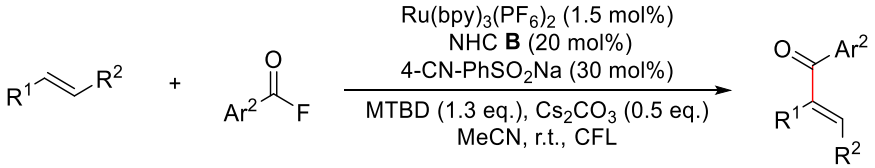
Sulfonyl chlorides (5.00 mmol) were added to a solution of sodium sulfites (10.0 mmol) and sodium bicarbonate (840 mg, 10.0 mmol) in water (5 mL, 1 M) and heated at 80 ℃ for 3 h, after cooling to room temperaturethe volatiles were removed in vacuo. The resultant solids were repeatedly washed with ethanol. The combined ethanol washes were evaporated under reduced pressure to yield the titled sulfinates as an amorphous solid

4. General procedure A for the α-acylation of aryl olefins



To a Schlenk tube, $Ru(bpy)_3(PF_6)_2$ (1.9 mg, 0.00225 mmol), carbene catalyst **B** (9.5 mg, 0.03 mmol), sodium 4-chlorobenzene sulfinate (9.0 mg, 0.045 mmol) and Cs_2CO_3 (24.5 mg, 0.075 mmol) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, styrene (0.15 mmol), 1-methyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (MTDB, 29.8 mg, 0.195 mmol), acyl fluoride (0.375 mmol, if solid, it should be added at the beginning) and MeCN (1.5 mL) were added. The resulting mixture was degassed under vacuum for two times and then the reaction mixture was irradiated with a 23 W CFL at room temperature for 24 hours. After that, the residue was purified by silica gel chromatography using a mixture of pentane/Et_2O as an eluent to get the desired product.

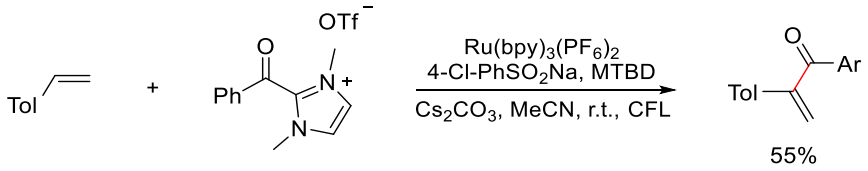
General procedure B for the α-acylation of alkenes



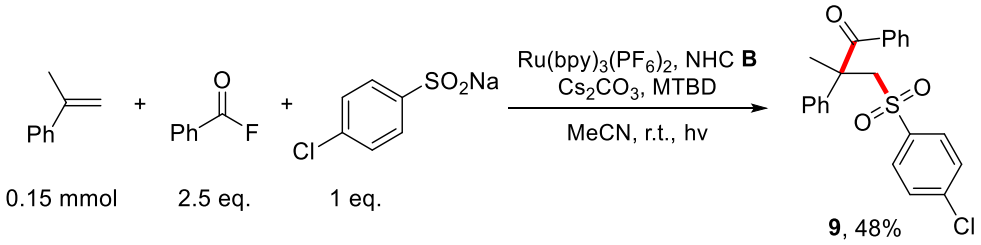
To a Schlenk tube, $Ru(bpy)_3(PF_6)_2$ (1.9 mg, 0.00225 mmol), carbene catalyst **B** (9.5 mg, 0.03 mmol), sodium 4-(cyano)benzene sulfinate (10.4 mg, 0.045 mmol) or sodium 4-(trifluoromethyl)benzene sulfinate (11.3 mg, 0.045 mmol) and Cs_2CO_3 (24.5 mg, 0.075 mmol) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, styrene (0.15 mmol), 1-methyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (MTDB, 29.8 mg, 0.195 mmol), acyl fluoride (0.375 mmol, if solid, it should be added at the beginning) and MeCN (1.5 mL) were added. The resulting mixture was degassed under vacuum for two times and then the reaction mixture was irradiated with a 23 W CFL at room temperature for 24 hours. After that, the residue was purified by silica gel chromatography using a mixture of pentane/Et_2O as an eluent to get the desired product.

5. Mechanistic studies

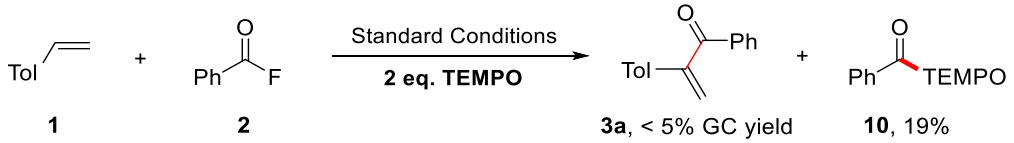
5.1 Control experiment



According to the General Procedure A, to a Schlenk tube, $Ru(bpy)_3(PF_6)_2$ (1.9 mg, 0.00225 mmol), 2-benzoyl-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate (87.5 mg , 0.25 mmol), sodium 4-chlorobenzene sulfonate (9.0 mg, 0.045 mmol) and Cs_2CO_3 (24.5 mg, 0.075 mmol) were added. Then the reaction tube was evacuated and backfilled with argon for three times. Subsequently, 4-methyl styrene (17.7 mg, 0.15 mmol), 1-methyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (MTDB, 29.8 mg, 0.195 mmol) and MeCN (1.5 mL) were added. The resulting mixture was degassed under vacuum for two times and then it was irradiated with a 23 W CFL at room temperature for 24 hours. After that, the residue was purified by silica gel chromatography using a mixture of pentane/Et_2O as an eluent to get the desired product.

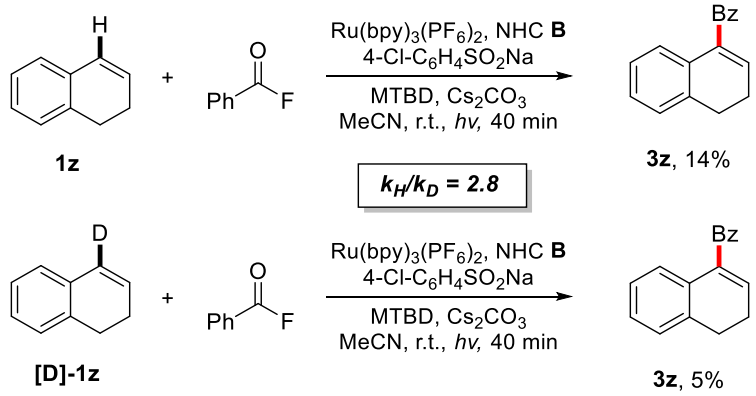


To a Schlenk tube, $Ru(bpy)_3(PF_6)_2$ (1.9 mg, 0.00225 mmol), carbene catalyst **B** (9.5 mg, 0.03 mmol), sodium 4-chlorobenzene sulfonate (9.0 mg, 0.045 mmol) and Cs_2CO_3 (24.5 mg, 0.075 mmol) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, α-methyl styrene (0.15 mmol), 1-methyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (MTDB, 29.8 mg, 0.195 mmol), benzoyl fluoride (46.5 mg, 0.375 mmol) and MeCN (1.5 mL) were added. The resulting mixture was degassed under vacuum for two times and then it was irradiated with a 23 W CFL at room temperature for 24 hours. After that, the residue was purified by silica gel chromatography using a mixture of pentane/Et_2O as an eluent to get the three-component coupling product.



To a Schlenk tube, $Ru(bpy)_3(PF_6)_2$ (1.9 mg, 0.00225 mmol), carbene catalyst **B** (9.5 mg, 0.03 mmol), sodium 4-chlorobenzene sulfonate (9.0 mg, 0.045 mmol), 2,2,6,6-tetramethyl piperidine-*N*-oxyl (TEMPO, 0.3 mmol, 2 eq.) and Cs_2CO_3 (24.5 mg, 0.075 mmol) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, 4-methyl styrene (0.15 mmol), 1-methyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (MTDB, 29.8 mg, 0.195 mmol), benzoyl fluoride (46.5 mg, 0.375 mmol) and MeCN (1.5 mL) were added. The resulting mixture was degassed under vacuum for two times and then it was irradiated with a 23 W CFL at room temperature for 24 hours. The yield of **3** was determined by GC with biphenyl as an internal standard. The reaction was suppressed upon addition of TEMPO, and less than 5% yield of **3** was obtained. Instead, the benzoyl-TEMPO adduct **10** was isolated in 19% yield.

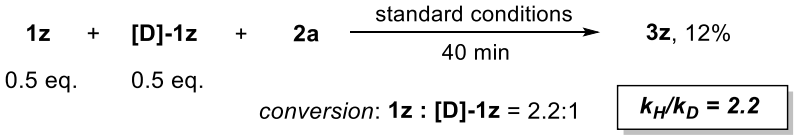
5.2 Parallel kinetic isotope effect (KIE) experiment



Procedure for kinetic isotopic effect experiments: To a Schlenk tube, $Ru(bpy)_3(PF_6)_2$ (1.9 mg, 0.00225 mmol), carbene catalyst **B** (9.5 mg, 0.03 mmol), sodium 4-chlorobenzene sulfonate (9.0 mg, 0.045 mmol) and Cs_2CO_3 (24.5 mg, 0.075 mmol) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, **1z** (0.15 mmol), 1-methyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (MTDB, 29.8 mg, 0.195 mmol), acyl fluoride (0.375 mmol, if solid, it should be added at the beginning) and MeCN (1.5 mL) were added. The resulting mixture was degassed under vacuum for two times and then it was irradiated with a 23 W CFL at room temperature for 40 min. After that, the yield of product **3z** was determined by GC with biphenyl as the internal standard.

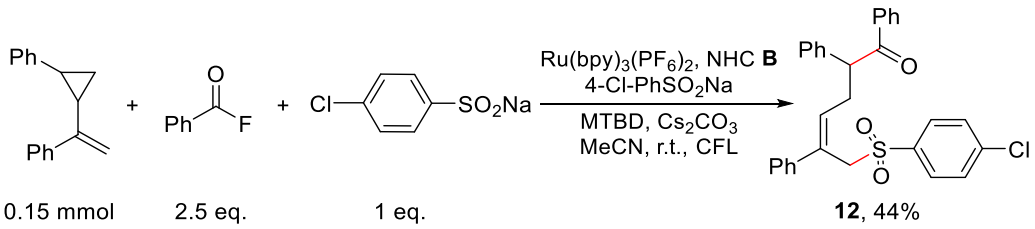
To a Schlenk tube, $Ru(bpy)_3(PF_6)_2$ (1.9 mg, 0.00225 mmol), carbene catalyst **B** (9.5 mg, 0.03 mmol), sodium 4-chlorobenzene sulfonate (9.0 mg, 0.045 mmol) and Cs_2CO_3 (24.5 mg, 0.075 mmol) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, **[D]-1z** (0.15 mmol), 1-methyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine

(MTDB, 29.8 mg, 0.195 mmol), acyl fluoride (0.375 mmol, if solid, it should be added at the beginning) and MeCN (1.5 mL) were added. The resulting mixture was degassed under vacuum for two times and then it was irradiated with a 23 W CFL at room temperature for 40 min. After that, the yield of product **3z** was determined by GC with biphenyl as the internal standard.



To a Schlenk tube, $Ru(bpy)_3(PF_6)_2$ (1.9 mg, 0.00225 mmol), carbene catalyst **B** (9.5 mg, 0.03 mmol), sodium 4-chlorobenzene sulfonate (9.0 mg, 0.045 mmol) and Cs_2CO_3 (24.5 mg, 0.075 mmol) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, **1z** (0.075 mmol) and **[D]-1z** (0.075 mmol), 1-methyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (MTDB, 29.8 mg, 0.195 mmol), acyl fluoride (0.375 mmol, if solid, it should be added at the beginning) and MeCN (1.5 mL) were added. The resulting mixture was degassed under vacuum for two times and then it was irradiated with a 23 W CFL at room temperature for 40 min. After that, the yield of product **3z** was determined by GC with biphenyl as the internal standard. The ratio for the conversion of **1z** and **[D]-1z** was determined by NMR.

5.3 Radical probe experiments



To a Schlenk tube, $Ru(bpy)_3(PF_6)_2$ (1.9 mg, 0.00225 mmol), carbene catalyst **B** (9.5 mg, 0.03 mmol), sodium 4-chlorobenzene sulfonate (29.7 mg, 0.15 mmol) and Cs_2CO_3 (24.5 mg, 0.075 mmol) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, (1-(2-phenylcyclopropyl)vinyl)benzene (0.15 mmol), 1-methyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (MTDB, 29.8 mg, 0.195 mmol), benzoyl fluoride (46.5 mg, 0.375 mmol) and MeCN (1.5 mL) were added. The resulting mixture was degassed under vacuum for two times and then it was irradiated with a 23 W CFL at room temperature for 24 hours. After that, the residue was purified by silica gel chromatography using a mixture of pentane/diethyl ether as an eluent to get the ring-opening product.

5.4 Luminescence quenching experiments

Emission intensities were recorded using a Jasco FP-8300 spectrofluorometer. All $Ru(bpy)_3PF_6$ solutions were excited at 449 nm and the emission intensity was recorded at 592 nm. In a typical experiment, to a certain amount of a solution of $Ru(bpy)_3PF_6$ in MeCN (5 mL), the appropriate amount of quencher (4-Cl-$PhSO_2Na$, 4-CN-$PhSO_2Na$, acylazolium ion **8** or MTBD) was added in a screw-top quartz cuvette. After degassing the solution by bubbling argon for 8 minutes, the emission of the sample was recorded.

Stern-Volmer fluorescence quenching experiments revealed that only sodium sulfinates were found to quench the excited state of Ru*(II), while no significant quenching was observed with acylazolium ion **8** and MTBD. These results support the proposed reductive quenching pathway.

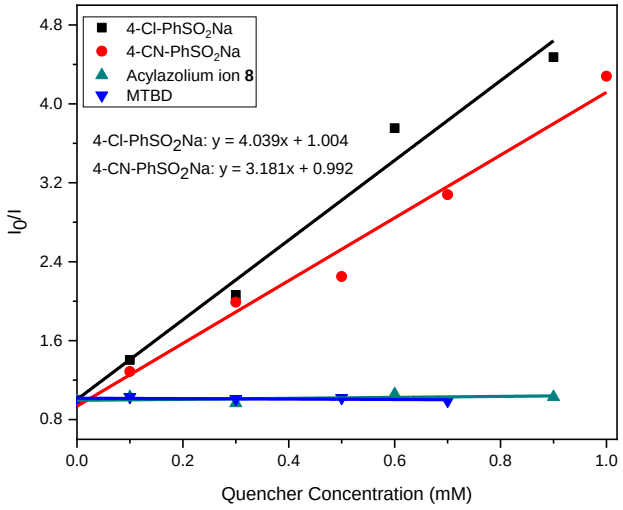
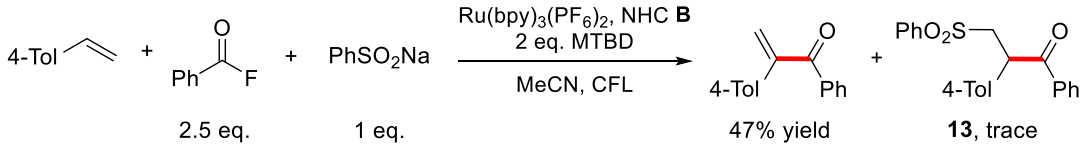


Figure S2. Stern-Volmer fluorescence quenching studies

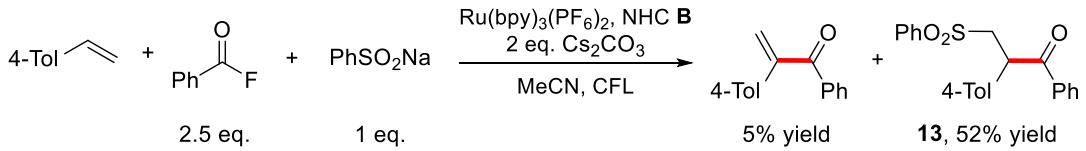
5.5 Exploration the role of MTBD and Cs_2CO_3

We have conducted the alpha-acylation reactions with a stoichiometric amount of sulfinate in the presence of different bases. With 2 eq. MTBD as the sole base, 47% yield of α-acylation product and a trace amount of the difunctionalization product **13** were obtained. On the other hand, with 2 eq. Cs_2CO_3 as the sole base, only 5% yield of the targeted α-acylation product along with 52% yield of the difunctionalization product **13** were noted. These results demonstrate that MTBD mediates the sulfinate elimination process. Cs_2CO_3 mainly played the role in facilitating radical difunctionalization of styrenes without inducing the subsequent elimination. A mixture of both bases provided the best result, as discussed in the manuscript.

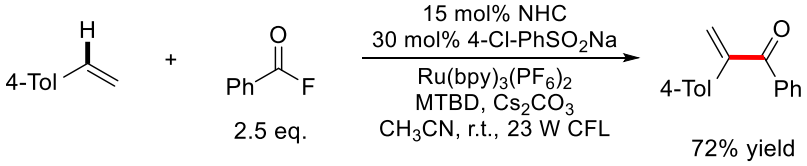
a) Only with MTBD

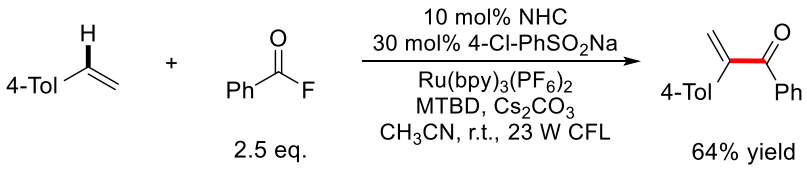


b) Only with Cs_2CO_3



5.5 Standard reactions with reduced NHC catalysis loading

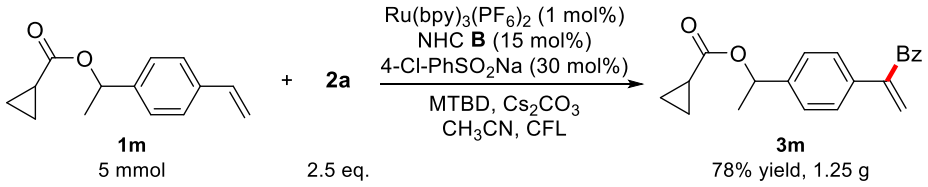




We have conducted the standard reaction with reduced NHC catalysis loading (15 mol% and 10 mol%). As a result, 72% and 64% yields were obtained, respectively.

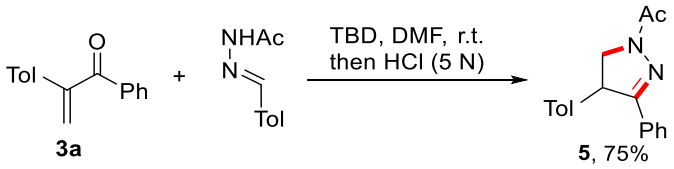
6. Synthetic transformations

6.1 Gram scale synthesis

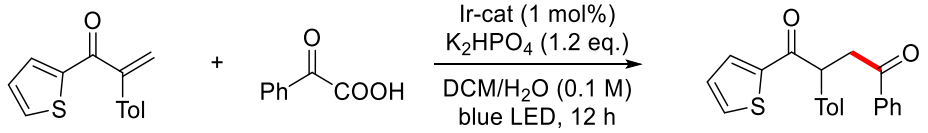


To an oven-dried Schlenk tube (100 mL), $Ru(bpy)_3(PF_6)_2$ (43.0 mg, 0.05 mmol), carbene catalyst **B** (236.3 mg, 0.75 mmol), sodium 4-chlorobenzene sulfinate (297 mg, 1.5 mmol) and Cs_2CO_3 (815.0 mg, 2.5 mmol) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, styrene (5.0 mmol), 1-methyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (MTDB, 994.5 mg, 6.5 mmol), benzoyl fluoride (1.55 g, 12.5 mmol) and MeCN (50 mL) were added. The resulting mixture was degassed under vacuum for two times and then the reaction mixture was irradiated with a 23 W CFL and a 30 W CFL at room temperature. The reaction was monitored by TLC until the full conversion of alkene. After that, the residue was purified by silica gel chromatography using a mixture of pentane/Et_2O as an eluent to get the desired product.

6.2 Synthetic transformations

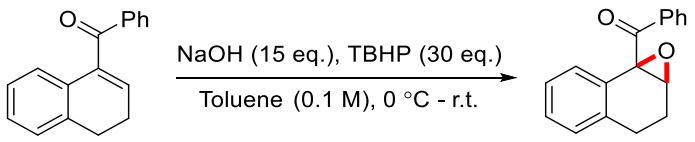


The title compound was prepared according to a literature procedure.[8] 1-Phenyl-2-(*p*-tolyl)prop-2-en-1-one **3** (0.5 mmol, 1 equiv.), *N*-acetyl hydrazone (0.75 mmol, 1.5 equiv.) and triazabicyclo[4.4.0]dec-5-ene (TBD, 0.1 mmol, 0.2 equiv.) were introduced into a Schlenk tube under atmosphere. Next, 1 mL of anhydrous acetonitrile was added and the solution was stirred at room temperature for 24 h. Then, HCl (5N, 1 mL) was added to the solution and the mixture was stirred for another 1 h. Afterwards, the reaction mixture was diluted with Et_2O and extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo and the crude material was purified by flash chromatography (pentane/Et_2O = 10:1) to afford the corresponding *N*-acetylpyrazoline **5** (104.3 mg, 75%) as a white solid.



3al (Ir-cat = $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$) **6**, 82%

According to a reported procedure,[9] α-oxocarboxylic acid (0.5 mmol), $Ir[dF(CF_3)ppy]_2(phen)PF_6$ (1 mol %, 5 mg), **3al** (0.75 mmol) and K_2HPO_4 (0.6 mmol, 104 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The solvents DCM (1 mL) and H_2O (1 mL) were added under air atmosphere. The reaction mixture was stirred under irradiation of 30 W blue LEDs at room temperature for 12 h. After that, the mixture was quenched with water and extracted with ethyl ether (3 x 10 mL). The organic layers were combined and concentrated in vacuo. The product **6** was purified by flash column chromatography on silica gel (diethyl ether: petroleum ether = 1:20).

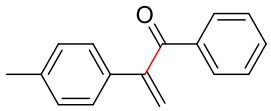


3z **7**, 71%

(2,3-Dihydronaphtho[1,2-*b*]oxiren-7b(1a*H*)-yl)(phenyl)methanone was synthesized according to a modified literature procedure.[2] A 5.00 M aqueous NaOH solution (0.400 mL, 20.0 equiv) was added dropwise at 0 °C to a stirred solution of (3,4-dihydronaphthalen-1-yl)(phenyl)methanone (0.100 mmol, 1.00 equiv) in toluene (0.100 M) and stirring was continued for 10 min. Then, TBHP (0.400 mL, 70 wt%, 30.0 equiv) was added dropwise and the mixture was stirred at r.t. until the starting material is fully consumed. After that, the reaction mixture was concentrated under reduced pressure and the resulting mixture was purified by purified by flash column chromatography on silica gel, eluting with pentane:Et_2O to afford the title compound **7** as a gummy oil (17.8 mg, 71% yield).

7. Product characterization

1-Phenyl-2-(*p*-tolyl)prop-2-en-1-one (3a)

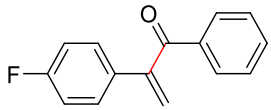


The reaction was performed according to general procedure **A** with 4-methyl styrene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3a** was obtained as a colorless oil (26.0 mg, 78% yield).

FT IR (neat) υ (cm^{-1}) = 2931, 2861, 1657, 1439, 1408, 1386, 1256, 1091, 1063, 865, 658.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 2H), 7.42 – 7.34 (m, 1H), 7.31 – 7.22 (m, 2H), 7.19 – 7.12 (m, 2H), 7.03 – 6.95 (m, 2H), 5.86 (s, 1H), 5.42 (s, 1H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.76, 148.14, 138.35, 137.10, 134.11, 133.01, 129.96, 129.30, 128.36, 126.87, 119.85, 21.17. HRMS (ESI) Calcd. for $C_{16}H_{14}NaO^+$ $[M+Na]^+$: 245.0937, found: 245.0937.

2-(4-Fluorophenyl)-1-phenylprop-2-en-1-one (3b)

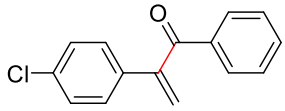


The reaction was performed according to general procedure **A** with 4-fluoro styrene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3b** was obtained as a colorless oil (24.1 mg, 71% yield).

FT IR (neat) υ (cm^{-1}) = 2928, 1678, 1666, 1660, 1510, 1450, 1226, 980, 840.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.64 – 7.52 (m, 1H), 7.50 – 7.36 (m, 4H), 7.11 – 7.00 (m, 2H), 6.05 (s, 1H), 5.65 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.34, 162.82 (d, J_{C-F} = 248.5 Hz), 147.08, 137.01, 133.17, 133.11 (d, J_{C-F} = 4.0 Hz), 129.21 (d, J_{C-F} = 111.1 Hz), 128.94 (d, J_{C-F} = 9.1 Hz), 121.40, 121.38, 115.58 (d, J_{C-F} = 21.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.22. HRMS (ESI) Calcd. for $C_{15}H_{11}FNaO^+$ $[M+Na]^+$: 249.0686, found: 249.0686.

2-(4-Chlorophenyl)-1-phenylprop-2-en-1-one (3c)



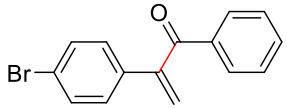
The reaction was performed according to general procedure **A** with 4-chloro styrene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3c** was obtained as a colorless oil (25.4 mg, 70% yield).

FT IR (neat) υ (cm^{-1}) = 2959, 1598, 1493, 1213, 981, 838, 718.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.61 – 7.53 (m, 1H), 7.48 – 7.41 (m, 2H), 7.40 – 7.29 (m, 4H), 6.08 (s, 1H), 5.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.12, 147.03, 136.91, 135.42, 134.43, 133.23, 129.95, 128.80, 128.47, 128.45, 121.87. HRMS (ESI) Calcd. for

$C_{15}H_{11}ClNaO^+$ $[M+Na]^+$: 265.0391, found: 265.0390.

2-(4-Bromophenyl)-1-phenylprop-2-en-1-one (3d)

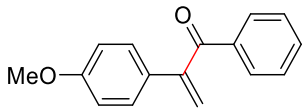


The reaction was performed according to general procedure **A** with 4-bromo styrene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3d** was obtained as a colorless oil (27.9 mg, 65% yield).

FT IR (neat) υ (cm^{-1}) = 3058, 2926, 1666, 1596, 1487, 1448, 1212, 1072, 1000, 980, 834, 715.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.61 – 7.53 (m, 1H), 7.51 – 7.41 (m, 4H), 7.36 – 7.28 (m, 2H), 6.09 (s, 1H), 5.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.03, 147.12, 136.90, 135.90, 133.23, 131.76, 129.95, 128.74, 128.48, 122.67, 121.94. HRMS (ESI) Calcd. for $C_{15}H_{11}BrNaO^+$ $[M+Na]^+$: 308.9885, found: 308.9886.

2-(4-Methoxyphenyl)-1-phenylprop-2-en-1-one (3e)

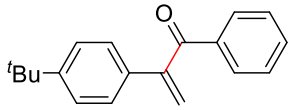


The reaction was performed according to general procedure **A** with 4-methoxy styrene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 40:1), the desired product **3e** was obtained as a colorless oil (27.5 mg, 77% yield).

FT IR (neat) υ (cm^{-1}) = 2935, 2838, 1727, 1692, 1678, 1666, 1599, 1510, 1450, 1226, 980, 840.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.86 (m, 2H), 7.61 – 7.50 (m, 1H), 7.47 – 7.33 (m, 4H), 6.93 – 6.83 (m, 2H), 5.98 (s, 1H), 5.53 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.91, 159.77, 147.64, 137.14, 133.03, 129.99, 129.47, 128.37, 128.28, 119.00, 114.01, 55.28. HRMS (ESI) Calcd. for $C_{16}H_{14}NaO_2^+$ $[M+Na]^+$: 261.0886, found: 261.0886.

2-(4-(*tert*-Butyl)phenyl)-1-phenylprop-2-en-1-one (3f)



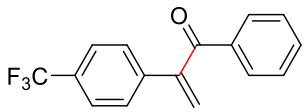
The reaction was performed according to general procedure **A** with 4-(*tert*-butyl) styrene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3f** was obtained as a colorless oil (29.7 mg, 75% yield).

FT IR (neat) υ (cm^{-1}) = 2964, 2871, 1727, 1687, 1678, 1673, 1667, 1602, 1450, 1409, 1336, 1269, 708.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.87 (m, 2H), 7.64 – 7.51 (m, 1H), 7.50 – 7.41 (m, 2H), 7.40 – 7.33 (m, 4H), 6.06 (s, 1H), 5.58 (s, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.87,

151.54, 147.93, 137.24, 134.01, 133.04, 130.01, 128.38, 126.69, 125.57, 120.09, 34.60, 31.22. HRMS (ESI) Calcd. for $C_{19}H_{20}NaO^+$ $[M+Na]^+$: 287.1406, found: 287.1406.

1-Phenyl-2-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (3g)

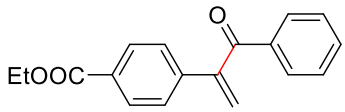


The reaction was performed according to general procedure **B** with ethyl 4-trifluoromethyl styrene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 50:1), the desired product **3g** was obtained as a colorless oil (20.7 mg, 50% yield).

FT IR (neat) υ (cm^{-1}) = 2925, 2855, 1666, 1325, 1166, 1124, 1067, 850, 694.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.67 – 7.52 (m, 5H), 7.52 – 7.43 (m, 2H), 6.18 (s, 1H), 5.79 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.76, 146.97, 140.51 (q, J_{C-F} = 1.3 Hz), 136.84, 133.34, 130.37 (q, J_{C-F} = 32.3 Hz), 129.94, 128.54, 127.55, 125.57 (q, J_{C-F} = 4.0 Hz), 123.98 (q, J_{C-F} = 273.0 Hz), 123.63. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.69. HRMS (ESI) Calcd. for $C_{16}H_{11}F_3NaO^+$ $[M+Na]^+$: 299.0654, found: 299.0655.

Ethyl 4-(3-oxo-3-phenylprop-1-en-2-yl)benzoate (3h)

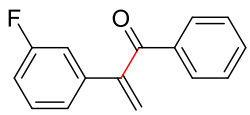


The reaction was performed according to general procedure **B** with ethyl 4-vinylbenzoate (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 20:1), the desired product **3h** was obtained as a colorless oil (21.4 mg, 51% yield).

FT IR (neat) υ (cm^{-1}) = 2982, 2941, 1721, 1713, 1682, 1276, 1106, 1019, 716.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.97 (m, 2H), 7.97 – 7.80 (m, 2H), 7.60 – 7.53 (m, 1H), 7.55 – 7.35 (m, 4H), 6.17 (s, 1H), 5.77 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.93, 166.18, 147.47, 141.25, 136.83, 133.28, 130.27, 129.96, 129.85, 128.50, 127.06, 122.95, 61.06, 14.30. HRMS (ESI) Calcd. for $C_{18}H_{16}NaO_3^+$ $[M+Na]^+$: 303.0992, found: 303.0993.

2-(3-Fluorophenyl)-1-phenylprop-2-en-1-one (3i)

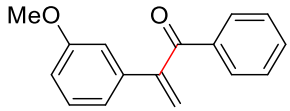


The reaction was performed according to general procedure **A** with 3-fluoro styrene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3i** was obtained as a colorless oil (24.7 mg, 73% yield).

FT IR (neat) υ (cm^{-1}) = 2931, 2923, 1666, 1580, 1446, 1333, 1233, 980, 918, 790.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.68 – 7.52 (m, 1H), 7.51 – 7.40 (m, 2H), 7.38 – 7.28 (m, 1H), 7.26 – 7.14 (m, 2H), 7.09 – 6.98 (m, 1H), 6.10 (s, 1H), 5.70 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.90, 162.85 (d, J_{C-F} = 244.5 Hz), 147.10, 139.07 (d, J_{C-F} = 7.5 Hz), 136.90, 133.26, 130.12 (d, J_{C-F} = 8.3 Hz), 129.97, 128.49, 122.89 (d, J_{C-F} = 3.0 Hz), 122.15, 115.35 (d, J_{C-F} = 21.0 Hz), 114.06 (d, J_{C-F} = 22.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.67. HRMS (ESI) Calcd. for $C_{15}H_{11}FNaO^+$ $[M+Na]^+$: 249.0686, found: 249.0687.

2-(3-Methoxyphenyl)-1-phenylprop-2-en-1-one (3j)

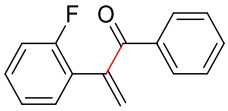


The reaction was performed according to general procedure **A** with 3-methoxy styrene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 40:1), the desired product **3j** was obtained as a colorless oil (22.8 mg, 64% yield).

FT IR (neat) υ (cm^{-1}) = 3060, 2939, 2836, 1726, 1637, 1597, 1580, 1486, 1450, 1287, 1244, 1048, 980, 697.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 2H), 7.65 – 7.51 (m, 1H), 7.47 – 7.40 (m, 2H), 7.31 – 7.23 (m, 1H), 7.05 – 6.96 (m, 2H), 6.90 – 6.84 (m, 1H), 6.06 (s, 1H), 5.64 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.43, 159.67, 148.18, 138.34, 137.01, 133.11, 129.98, 129.63, 128.40, 121.01, 119.58, 113.99, 112.59, 55.25. HRMS (ESI) Calcd. for $C_{16}H_{14}NaO_2^+$ $[M+Na]^+$: 261.0886, found: 261.0885.

2-(2-Fluorophenyl)-1-phenylprop-2-en-1-one (3k)

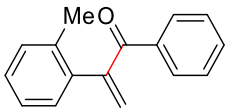


The reaction was performed according to general procedure **A** with 2-fluoro styrene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3k** was obtained as a colorless oil (22.0 mg, 65% yield).

FT IR (neat) υ (cm^{-1}) = 3076, 3037, 1738, 1269, 1598, 1450, 1263, 1050, 1022, 762, 712.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.62 – 7.53 (m, 1H), 7.49 – 7.38 (m, 3H), 7.37 – 7.30 (m, 1H), 7.17 (td, *J* = 7.6, 1.2 Hz, 1H), 7.09 – 7.00 (m, 1H), 6.15 (s, 1H), 5.90 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.14, 159.61 (d, J_{C-F} = 249.67 Hz), 143.61, 136.85, 132.81, 130.29 (d, J_{C-F} = 9.1 Hz), 130.20 (d, J_{C-F} = 3.0 Hz), 129.83, 128.31, 126.23 (d, J_{C-F} = 2.0 Hz), 125.99 (d, J_{C-F} = 14.1 Hz), 124.38 (d, J_{C-F} = 4.0 Hz), 115.79 (d, J_{C-F} = 22.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.52. HRMS (ESI) Calcd. for $C_{15}H_{11}FNaO^+$ $[M+Na]^+$: 249.0686, found: 249.0685.

1-Phenyl-2-(*m*-tolyl)prop-2-en-1-one (3l)

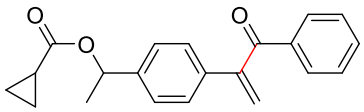


The reaction was performed according to general procedure **A** with 2-methyl styrene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3l** was obtained as a colorless oil (19.9 mg, 60% yield).

FT IR (neat) υ (cm^{-1}) = 3060, 2964, 2929, 1658, 1597, 1447, 1332, 1219, 980, 731, 702.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 2H), 7.61 – 7.53 (m, 1H), 7.50 – 7.42 (m, 2H), 7.34 – 7.22 (m, 3H), 7.21 – 7.15 (m, 1H), 6.04 (d, *J* = 1.2 Hz, 1H), 6.01 (d, *J* = 1.2 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.45, 149.18, 138.28, 137.26, 135.58, 132.53, 130.22, 129.72, 128.34, 128.27, 127.98, 126.05, 20.46. HRMS (ESI) Calcd. for $C_{16}H_{14}NaO^+$ $[M+Na]^+$: 245.0937, found: 245.0936.

1-(4-(3-Oxo-3-phenylprop-1-en-2-yl)phenyl)ethyl cyclopropanecarboxylate (3m)

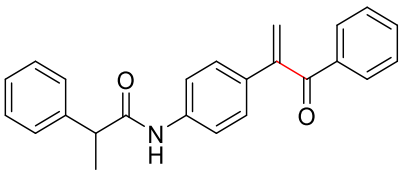


The reaction was performed according to general procedure **A** with 1-(4-vinylphenyl)ethyl cyclopropanecarboxylate (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 20:1), the desired product **3m** was obtained as a colorless oil (40.8 mg, 85% yield).

FT IR (neat) υ (cm^{-1}) = 2930, 1726, 1679, 1392, 1175, 1066.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.60 – 7.52 (m, 1H), 7.50 – 7.38 (m, 4H), 7.37 – 7.32 (m, 2H), 6.08 (s, 1H), 5.88 (q, *J* = 6.5 Hz, 1H), 5.63 (s, 1H), 1.69 – 1.58 (m, 1H), 1.52 (d, *J* = 6.6 Hz, 3H), 1.07 – 0.92 (m, 2H), 0.92 – 0.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.54, 174.07, 147.73, 142.08, 137.09, 136.42, 133.12, 129.99, 128.42, 127.21, 126.29, 121.16, 71.79, 22.18, 13.11, 8.47, 8.46. HRMS (ESI) Calcd. for $C_{21}H_{20}NaO_3^+$ $[M+Na]^+$: 343.1305, found: 343.1306.

***N*-(4-(3-Oxo-3-phenylprop-1-en-2-yl)phenyl)-2-phenylpropanamide (3n)**

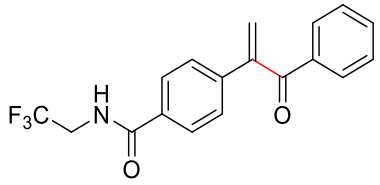


The reaction was performed according to general procedure **A** with 2-phenyl-*N*-(4-vinylphenyl)propanamide (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 5:1), the desired product **3n** was obtained as a colorless oil (36.2 mg, 68% yield).

FT IR (neat) υ (cm^{-1}) = 3310, 2977, 2934, 1665, 1596, 1515, 1407, 1177, 842, 698.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 2H), 7.49 – 7.42 (m, 1H), 7.38 – 7.17 (m, 11H), 7.14 (brs, 1H), 5.91 (s, 1H), 5.49 (s, 1H), 3.62 (q, *J* = 7.1 Hz, 1H), 1.49 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.68, 172.30, 147.50, 140.75, 138.04, 136.95, 133.12, 132.71, 129.95, 129.13, 128.39, 127.63, 127.60, 127.58, 120.22, 119.56, 48.06, 18.54. HRMS (ESI) Calcd. for $C_{24}H_{21}NNaO_2^+$ $[M+Na]^+$: 378.1465, found: 378.1463.

4-(3-Oxo-3-phenylprop-1-en-2-yl)-*N*-(2,2,2-trifluoroethyl)benzamide (3o)

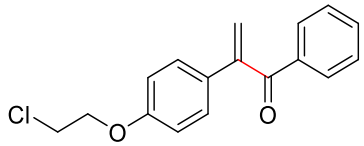


The reaction was performed according to general procedure **A** with *N*-(2,2,2-trifluoroethyl)-4-vinylbenzamide (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 10:1), the desired product **3o** was obtained as a colorless oil (27.9 mg, 56% yield).

FT IR (neat) υ (cm^{-1}) = 3347, 2349, 1725, 1674, 1660, 1261, 1159, 713.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 2H), 7.81 – 7.74 (m, 2H), 7.63 – 7.54 (m, 1H), 7.53 – 7.41 (m, 4H), 6.63 – 6.47 (m, 1H), 6.17 (s, 1H), 5.78 (s, 1H), 4.17 – 4.03 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.95, 166.91, 147.15, 140.81, 136.82, 133.36, 132.88, 129.95, 128.54, 127.81 (q, J_{C-F} = 276.6 Hz), 127.52, 127.48, 123.34, 41.07 (q, J_{C-F} = 34.7 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -72.26. HRMS (ESI) Calcd. for $C_{18}H_{14}F_3NNaO_2^+$ $[M+Na]^+$: 356.0869, found: 356.0868.

2-(4-(2-Chloroethoxy)phenyl)-1-phenylprop-2-en-1-one (3p)

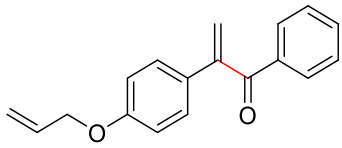


The reaction was performed according to general procedure **A** with 1-(2-chloroethoxy)-4-vinylbenzene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 20:1), the desired product **3p** was obtained as a colorless oil (32.6 mg, 76% yield).

FT IR (neat) υ (cm^{-1}) = 2349, 1600, 1512, 1301, 1242, 1178, 783, 716.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.59 – 7.52 (m, 1H), 7.47 – 7.40 (m, 2H), 7.40 – 7.33 (m, 2H), 6.93 – 6.86 (m, 2H), 6.00 (s, 1H), 5.55 (s, 1H), 4.23 (t, *J* = 5.9 Hz, 2H), 3.81 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.75, 158.37, 147.50, 137.12, 133.06, 130.23, 129.97, 128.42, 128.39, 119.47, 114.77, 68.00, 41.76. HRMS (ESI) Calcd. for $C_{17}H_{15}ClNaO_2^+$ $[M+Na]^+$: 309.0653, found: 309.0653.

2-(4-(Allyloxy)phenyl)-1-phenylprop-2-en-1-one (3q)

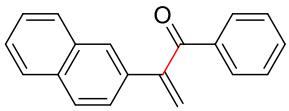


The reaction was performed according to general procedure **A** with 1-(allyloxy)-4-vinylbenzene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 30:1), the desired product **3q** was obtained as a colorless oil (28.9 mg, 73% yield).

FT IR (neat) υ (cm^{-1}) = 2350, 1669, 1666, 1606, 1511, 1248, 1216, 1176, 980, 837.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 2H), 7.59 – 7.51 (m, 1H), 7.47 – 7.39 (m, 2H), 7.39 – 7.32 (m, 2H), 7.04 – 6.83 (m, 2H), 6.12 – 5.99 (m, 1H), 5.98 (s, 1H), 5.53 (s, 1H), 5.41 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.29 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.54 (dt, *J* = 5.3, 1.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.86, 158.81, 147.63, 137.16, 133.03, 129.99, 129.62, 128.37, 128.26, 118.99, 117.79, 114.81, 68.80. HRMS (ESI) Calcd. for $C_{18}H_{16}NaO_2^+$ $[M+Na]^+$: 287.1043, found: 287.1040.

2-(Naphthalen-2-yl)-1-phenylprop-2-en-1-one (3r)

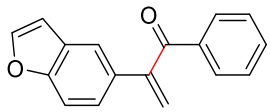


The reaction was performed according to general procedure **A** with 2-vinyl naphthalene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3r** was obtained as a colorless oil (27.8 mg, 72% yield).

FT IR (neat) υ (cm^{-1}) = 3059, 2931, 1666, 1595, 1448, 1321, 1216, 1193, 980, 820, 751.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.87 – 7.75 (m, 4H), 7.63 – 7.52 (m, 2H), 7.51 – 7.40 (m, 4H), 6.20 (s, 1H), 5.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.69, 148.26, 137.01, 134.20, 133.23, 133.20, 133.10, 130.06, 128.46, 128.37, 128.36, 127.58, 126.56, 126.46, 126.37, 124.41, 120.80. HRMS (ESI) Calcd. for $C_{19}H_{14}NaO^+$ $[M+Na]^+$: 281.0937, found: 281.0937.

2-(Benzofuran-5-yl)-1-phenylprop-2-en-1-one (3s)



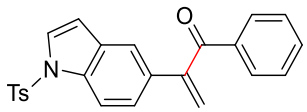
The reaction was performed according to general procedure **A** with 5-vinylbenzofuran (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 50:1), the desired product **3s** was obtained as a colorless oil (26.7 mg, 72% yield).

FT IR (neat) υ (cm^{-1}) = 1742, 1681, 1600, 1451, 1282, 1262, 1051, 1022, 976, 712.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.43 – 7.33 (m, 3H), 7.31 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.67 (dd, *J* = 2.2, 1.0 Hz, 1H), 5.99 (s, 1H), 5.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.85, 154.88, 148.45, 145.67, 137.10, 133.07, 132.08, 130.03, 128.41, 127.73, 123.56, 120.38, 120.05, 111.54, 106.79. HRMS

(ESI) Calcd. for $C_{17}H_{12}NaO_2^+$ $[M+Na]^+$: 271.0730, found: 271.0731.

1-Phenyl-2-(1-tosyl-1H-indol-5-yl)prop-2-en-1-one (3t)

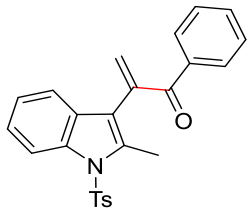


The reaction was performed according to general procedure **A** with 1-tosyl-5-vinyl-1H-indole (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 50:1), the desired product **3t** was obtained as a colorless oil (34.3 mg, 57% yield).

FT IR (neat) υ (cm^{-1}) = 1666, 1595, 1461, 1372, 1257, 1173, 1132, 670, 583.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 1H), 7.94 – 7.89 (m, 2H), 7.79 – 7.73 (m, 2H), 7.60 – 7.53 (m, 3H), 7.48 – 7.37 (m, 3H), 7.24 – 7.20 (m, 2H), 6.62 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.07 (s, 1H), 5.62 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.79, 148.05, 145.08, 137.09, 135.13, 134.65, 133.14, 132.37, 130.96, 130.02, 129.93, 128.42, 126.99, 126.80, 123.69, 120.74, 120.20, 113.64, 109.18, 21.55. HRMS (ESI) Calcd. for $C_{24}H_{19}NNaO_3S^+$ $[M+Na]^+$: 424.0978, found: 424.0973.

2-(2-Methyl-1-tosyl-1H-indol-3-yl)-1-phenylprop-2-en-1-one (3u)



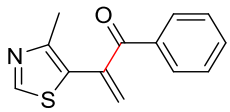
The reaction was performed according to general procedure **A** with 2-methyl-1-tosyl-3-vinyl-1H-indole (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 50:1), the desired product **3u** was obtained as a white solid (47.3 mg, 76% yield).

MP: 95-97 °C.

FT IR (neat) υ (cm^{-1}) = 1665, 1660, 1598, 1453, 1366, 1174, 1099, 966, 746, 705, 577.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.62 – 7.57 (m, 2H), 7.54 – 7.48 (m, 1H), 7.44 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 1H), 7.26 – 7.20 (m, 1H), 7.20 – 7.15 (m, 2H), 6.22 (d, *J* = 1.3 Hz, 1H), 6.03 (d, *J* = 1.3 Hz, 1H), 2.47 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.28, 144.76, 140.63, 136.91, 136.30, 136.14, 134.75, 132.67, 129.90, 129.42, 129.01, 128.93, 128.30, 126.29, 124.38, 123.74, 119.03, 118.86, 114.62, 21.56, 13.92. HRMS (ESI) Calcd. for $C_{25}H_{21}NNaO_3S^+$ $[M+Na]^+$: 438.1134, found: 438.1129.

2-(4-Methylthiazol-5-yl)-1-phenylprop-2-en-1-one (3v)

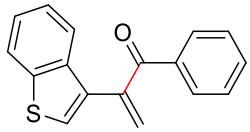


The reaction was performed according to general procedure **A** with 4-methyl-5-vinylthiazole (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 5:1), the desired product **3v** was obtained as a colorless oil (18.8 mg, 55% yield).

FT IR (neat) υ (cm^{-1}) = 2962, 2923, 2855, 1687, 1666, 1597, 1446, 1413, 1139, 950, 696.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.91 – 7.86 (m, 2H), 7.66 – 7.56 (m, 1H), 7.52 – 7.44 (m, 2H), 6.12 (s, 1H), 5.98 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.35, 151.81, 150.76, 139.52, 136.31, 133.26, 129.91, 128.53, 127.72, 126.82, 16.76. HRMS (ESI) Calcd. for $C_{13}H_{11}NNaOS^{+}$ $[M+Na]^{+}$: 252.0454, found: 252.0453.

2-(Benzo[b]thiophen-3-yl)-1-phenylprop-2-en-1-one (3w)

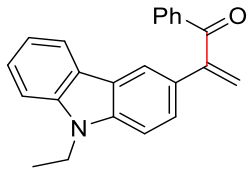


The reaction was performed according to general procedure **A** with 3-vinylbenzo[b]thiophene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 60:1), the desired product **3w** was obtained as a colorless oil (27.7 mg, 70% yield).

FT IR (neat) υ (cm^{-1}) = 2961, 2922, 1666, 1598, 1197, 978, 762, 736.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.91 – 7.85 (m, 1H), 7.83 – 7.79 (m, 1H), 7.62 – 7.53 (m, 2H), 7.49 – 7.41 (m, 2H), 7.41 – 7.34 (m, 2H), 6.23 (d, *J* = 0.9 Hz, 1H), 5.98 (d, *J* = 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.40, 142.74, 140.30, 137.24, 136.94, 133.16, 133.03, 129.90, 128.44, 125.90, 125.25, 124.49, 124.48, 122.96, 122.61. HRMS (ESI) Calcd. for $C_{17}H_{12}NaOS^{+}$ $[M+Na]^{+}$: 287.0501, found: 287.0502.

2-(9-Ethyl-9H-carbazol-3-yl)-1-phenylprop-2-en-1-one (3x)

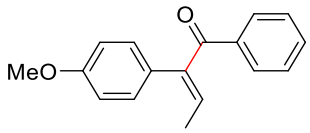


The reaction was performed according to general procedure **A** with 9-ethyl-3-vinyl-9H-carbazole (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 50:1), the desired product **3x** was obtained as a colorless oil (31.7 mg, 65% yield).

FT IR (neat) υ (cm^{-1}) = 2929, 1666, 1598, 1493, 1470, 1233, 980, 749.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 1.8, 0.6 Hz, 1H), 8.09 – 8.04 (m, 1H), 8.02 – 7.97 (m, 2H), 7.59 – 7.49 (m, 2H), 7.48 – 7.34 (m, 5H), 7.26 – 7.19 (m, 1H), 6.11 (s, 1H), 5.61 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.37, 149.01, 140.32, 139.90, 137.26, 133.00, 130.12, 128.38, 127.92, 125.93, 124.80, 123.12, 122.90, 120.56, 119.15, 119.09, 118.52, 108.60, 108.52, 37.62, 13.81. HRMS (ESI) Calcd. for $C_{23}H_{19}NNaO^+$ $[M+Na]^+$: 348.1359, found: 348.1360.

2-(4-Methoxyphenyl)-1-phenylbut-2-en-1-one (3y)



The reaction was performed according to general procedure **B** with *trans*-anethole (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 40:1), the desired product **3y** was obtained as a colorless oil (22.3 mg, 59% yield, two separate E/Z isomer (6.7:1)).

(Z)-2-(4-Methoxyphenyl)-1-phenylbut-2-en-1-one:

FT IR (neat) υ (cm^{-1}) = 2932, 2839, 1667, 1607, 1511, 1450, 1288, 1249, 1219, 1175, 1035, 824, 720.

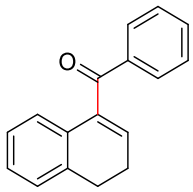
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.57 – 7.50 (m, 1H), 7.46 – 7.39 (m, 2H), 7.28 – 7.21 (m, 2H), 6.85 – 6.78 (m, 2H), 6.24 (q, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 1.74 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.01, 159.16, 141.24, 136.75, 133.44, 130.07, 129.65, 128.71, 127.11, 124.98, 114.10, 55.24, 15.48. HRMS (ESI) Calcd. for $C_{17}H_{16}O_2Na^+$ $[M+Na]^+$: 275.1042, found: 275.1040.

(E)-2-(4-Methoxyphenyl)-1-phenylbut-2-en-1-one:

FT IR (neat) υ (cm^{-1}) = 2935, 2839, 1667, 1607, 1511, 1451, 1288, 1249, 1175, 1035, 824, 730.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.54 – 7.46 (m, 1H), 7.45 – 7.37 (m, 2H), 7.22 – 7.16 (m, 2H), 6.95 – 6.89 (m, 2H), 6.54 (q, *J* = 7.1 Hz, 1H), 3.82 (s, 3H), 1.90 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.61, 158.85, 142.36, 139.08, 138.50, 131.81, 130.79, 129.60, 128.09, 128.01, 113.71, 55.22, 15.61. HRMS (ESI) Calcd. for $C_{17}H_{16}O_2Na^+$ $[M+Na]^+$: 275.1042, found: 275.1041.

(3,4-Dihydronaphthalen-1-yl)(phenyl)methanone (3z)



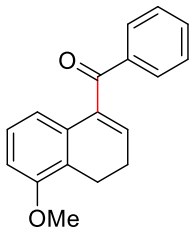
The reaction was performed according to general procedure **A** with 1,2-dihydronaphthalene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-

pentane/diethyl ether = 70:1), the desired product **3z** was obtained as a colorless oil (26.6 mg, 76% yield).

FT IR (neat) υ (cm^{-1}) = 3058, 2935, 1657, 1448, 1268, 1176, 912, 764, 712.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.62 – 7.53 (m, 1H), 7.48 – 7.39 (m, 2H), 7.30 – 7.24 (m, 1H), 7.23 – 7.10 (m, 3H), 6.49 (t, *J* = 4.8 Hz, 1H), 2.89 (t, *J* = 8.1 Hz, 2H), 2.55 – 2.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.09, 138.71, 137.91, 136.45, 135.75, 132.82, 131.95, 129.90, 128.32, 127.81, 127.78, 126.64, 125.72, 27.52, 23.28. HRMS (ESI) Calcd. for $C_{17}H_{14}NaO^+$ $[M+Na]^+$: 257.0937, found: 257.0936.

(5-Methoxy-3,4-dihydronaphthalen-1-yl)(phenyl)methanone (3aa)

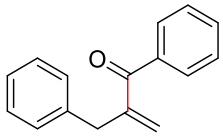


The reaction was performed according to general procedure **A** with 8-methoxy-1,2-dihydronaphthalene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 40:1), the desired product **3aa** was obtained as a colorless oil (32.0 mg, 81% yield).

FT IR (neat) υ (cm^{-1}) = 2836, 1659, 1469, 1439, 1262, 1232, 1132, 943, 748, 715.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.60 – 7.51 (m, 1H), 7.47 – 7.38 (m, 2H), 7.11 (t, *J* = 8.4 Hz, 1H), 6.89 – 6.79 (m, 2H), 6.48 (t, *J* = 4.5 Hz, 1H), 3.86 (s, 3H), 2.89 (t, *J* = 8.1 Hz, 2H), 2.52 – 2.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.18, 156.04, 138.73, 137.87, 136.35, 132.90, 132.82, 129.92, 128.30, 126.72, 123.71, 118.52, 110.30, 55.55, 22.72, 19.30. HRMS (ESI) Calcd. for $C_{18}H_{16}NaO_2^+$ $[M+Na]^+$: 287.1043, found: 287.1043.

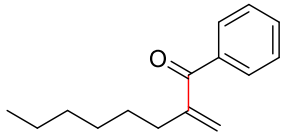
2-Benzyl-1-phenylprop-2-en-1-one (3ba)



The reaction was performed according to general procedure **B** with allylbenzene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3ba** was obtained as a colorless oil (11.7 mg, 35% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.57 – 7.49 (m, 1H), 7.45 – 7.38 (m, 2H), 7.34 – 7.18 (m, 5H), 5.76 (d, *J* = 0.9 Hz, 1H), 5.69 (d, *J* = 0.9 Hz, 1H), 3.81 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.65, 147.61, 138.66, 137.68, 132.19, 129.49, 129.16, 128.51, 128.16, 126.97, 126.35, 38.32. Spectroscopic data are in accordance with those described in literature.[10]

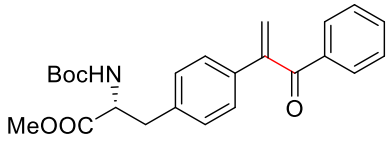
2-Methylene-1-phenyloctan-1-one (3ca)



The reaction was performed according to general procedure **B** with oct-1-ene (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3ca** was obtained as a colorless oil (10.4 mg, 32% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 2H), 7.59 – 7.47 (m, 1H), 7.49 – 7.37 (m, 2H), 5.81 (d, *J* = 1.2 Hz, 1H), 5.56 (d, *J* = 1.2 Hz, 1H), 2.47 (t, *J* = 8.4 Hz, 2H), 1.60 – 1.42 (m, 2H), 1.42 – 1.21 (m, 6H), 0.95 – 0.82 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.44, 148.49, 137.90, 132.10, 129.48, 128.11, 125.04, 32.30, 31.60, 28.98, 28.10, 22.54, 14.03. Spectroscopic data are in accordance with those described in literature.[10]

Methyl 2-((tert-butoxycarbonyl)amino)-3-(4-(3-oxo-3-phenylprop-1-en-2-yl)phenyl)propanoate (3da)

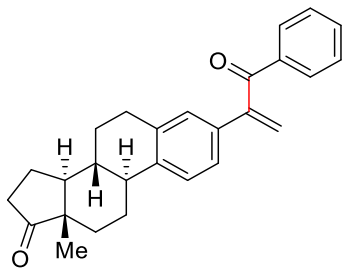


The reaction was performed according to general procedure **A** with methyl (*R*)-2-((tert-butoxycarbonyl)amino)-3-(4-vinylphenyl)propanoate (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3da** was obtained as a colorless oil (43.5 mg, 71% yield).

FT IR (neat) υ (cm^{-1}) = 2975, 1746, 1712, 1596, 1503, 1450, 1336, 1216, 1169, 1058.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.59 – 7.52 (m, 1H), 7.48 – 7.39 (m, 2H), 7.38 – 7.34 (m, 2H), 7.16 – 7.05 (m, 2H), 6.06 (s, 1H), 5.61 (s, 1H), 5.07 – 4.77 (m, 1H), 4.64 – 4.50 (m, 1H), 3.70 (s, 3H), 3.20 – 2.94 (m, 2H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.58, 172.18, 155.02, 147.69, 137.04, 136.40, 135.65, 133.13, 129.98, 129.56, 128.40, 127.18, 120.74, 79.97, 54.25, 52.25, 37.97, 28.25. HRMS (ESI) Calcd. for $C_{24}H_{27}NNaO_5^+$ $[M+Na]^+$: 432.1781, found: 432.1778.

(8R,9S,13S,14S)-13-Methyl-3-(3-oxo-3-phenylprop-1-en-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3ea)



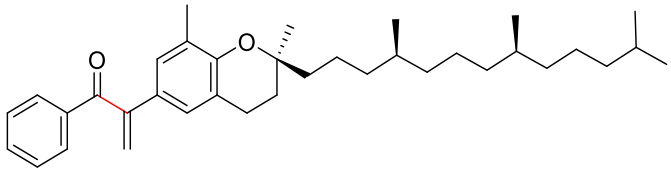
The reaction was performed according to general procedure **A** with (*8R,9S,13S,14S*)-13-Methyl-3-

vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3ea** was obtained as a colorless oil (42.0 mg, 73% yield).

FT IR (neat) υ (cm^{-1}) = 2931, 2859, 1737, 1732, 1666, 1450, 1220, 980, 825.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.40 (m, 2H), 7.32 – 7.19 (m, 2H), 7.18 – 7.13 (m, 1H), 6.05 (s, 1H), 5.57 (s, 1H), 2.90 (dd, *J* = 9.0, 4.2 Hz, 1H), 2.58 – 2.37 (m, 2H), 2.37 – 2.24 (m, 1H), 2.22 – 1.91 (m, 4H), 1.71 – 1.38 (m, 7H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.81, 197.85, 147.95, 140.24, 137.19, 136.76, 134.50, 133.07, 130.01, 128.39, 127.56, 125.67, 124.42, 120.17, 50.47, 47.94, 44.38, 38.01, 35.83, 31.54, 29.36, 26.40, 25.61, 21.56, 13.81. HRMS (ESI) Calcd. for $C_{27}H_{28}NaO_2^+$ $[M+Na]^+$: 407.1982, found: 407.1981.

2-((S)-2,8-Dimethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)-1-phenylprop-2-en-1-one (3fa)

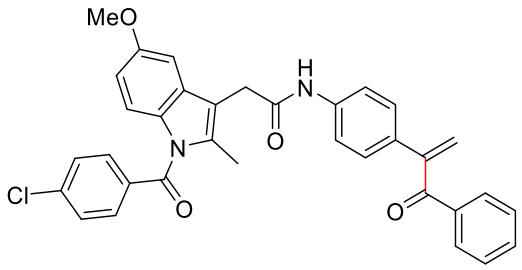


The reaction was performed according to general procedure **A** with (S)-2,8-Dimethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)-6-vinylchromane (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 200:1), the desired product **3fa** was obtained as a colorless oil (64.2 mg, 83% yield).

FT IR (neat) υ (cm^{-1}) = 2950, 2926, 2868, 1667, 1667, 1480, 1449, 1377, 1268, 1227, 1171, 1153, 718.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.60 – 7.52 (m, 1H), 7.47 – 7.40 (m, 2H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 5.93 (s, 1H), 5.40 (s, 1H), 2.76 – 2.64 (m, 2H), 2.14 (s, 3H), 1.85 – 1.68 (m, 2H), 1.63 – 1.27 (m, 12H), 1.26 – 0.99 (m, 11H), 0.92 – 0.79 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.42, 152.74, 148.05, 137.32, 132.99, 130.08, 128.33, 127.46, 126.83, 126.53, 125.72, 120.42, 117.46, 76.44, 40.18, 39.35, 37.43, 37.41, 37.27, 32.78, 32.68, 31.08, 27.97, 24.79, 24.43, 24.27, 22.71, 22.62, 22.28, 20.95, 19.74, 19.63, 16.13. HRMS (ESI) Calcd. for $C_{36}H_{52}NaO_2^+$ $[M+Na]^+$: 539.3860, found: 539.3858.

2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-N-(4-(3-oxo-3-phenylprop-1-en-2-yl)phenyl)acetamide (3ga)



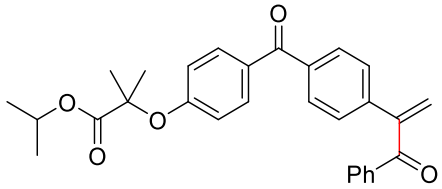
The reaction was performed according to general procedure **A** with 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-N-(4-vinylphenyl)acetamide (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3ga** was obtained as a white solid (58.1 mg, 69% yield).

MP: 115-116 °C.

FT IR (neat) υ (cm^{-1}) = 1678, 1666, 1595, 1530, 1479, 1323, 1219, 1116, 844, 755.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.70 – 7.64 (m, 2H), 7.57 – 7.51 (m, 1H), 7.51 - 7.46 (m, 2H), 7.45 – 7.36 (m, 5H), 7.35 – 7.29 (m, 2H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.86 (d, *J* = 9.2 Hz, 1H), 6.70 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.00 (s, 1H), 5.59 (s, 1H), 3.82 – 3.77 (m, 5H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.53, 168.28, 168.19, 156.36, 147.42, 139.63, 137.56, 136.93, 136.65, 133.43, 133.12, 131.19, 130.90, 130.07, 129.93, 129.22, 128.85, 128.39, 127.66, 120.44, 120.00, 115.20, 112.41, 112.18, 100.68, 55.73, 33.31, 13.32. HRMS (ESI) Calcd. for $C_{34}H_{27}ClN_2NaO_4^+$ $[M+Na]^+$: 585.1552, found: 585.1551.

Isopropyl 2-methyl-2-(4-(4-(3-oxo-3-phenylprop-1-en-2-yl)benzoyl)phenoxy)propanoate (3ha)

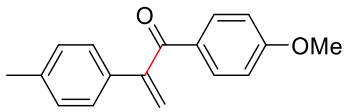


The reaction was performed according to general procedure **B** with isopropyl 2-methyl-2-(4-(4-vinylbenzoyl)phenoxy)propanoate (0.15 mmol) and benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3ha** was obtained as a colorless oil (30.7 mg, 45% yield).

FT IR (neat) υ (cm^{-1}) = 1715, 1728, 1659, 1598, 1288, 1177, 1149, 1103, 930, 695.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.82 – 7.70 (m, 4H), 7.62 – 7.39 (m, 5H), 6.94 – 6.79 (m, 2H), 6.20 (s, 1H), 5.77 (s, 1H), 5.17 – 5.00 (m, 1H), 1.66 (s, 6H), 1.20 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.02, 194.86, 173.12, 159.61, 147.41, 140.43, 137.85, 136.88, 133.31, 132.01, 130.41, 130.09, 129.99, 128.52, 126.95, 122.85, 117.15, 79.36, 69.31, 25.35, 21.50. HRMS (ESI) Calcd. for $C_{29}H_{28}NaO_5^+$ $[M+Na]^+$: 479.1829, found: 479.1825.

1-(4-Methoxyphenyl)-2-(*p*-tolyl)prop-2-en-1-one (3ab)

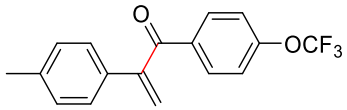


The reaction was performed according to general procedure **A** with 4-methyl styrene (0.15 mmol) and 4-methoxybenzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 40:1), the desired product **3ab** was obtained as a colorless oil (28.3 mg, 75% yield).

FT IR (neat) υ (cm^{-1}) = 1665, 1659, 1598, 1573, 1511, 1308, 1261, 1221, 1161, 1029, 980, 826.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.35 – 7.29 (m, 2H), 7.18 – 7.11 (m, 2H), 6.94 – 6.87 (m, 2H), 5.95 (s, 1H), 5.50 (s, 1H), 3.85 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.57, 163.62, 148.32, 138.28, 134.26, 132.41, 129.84, 129.31, 126.65, 117.93, 113.62, 55.46, 21.18. HRMS (ESI) Calcd. for $C_{17}H_{16}NaO_2^+$ $[M+Na]^+$: 275.1043, found: 275.1042.

2-(*p*-Tolyl)-1-(4-(trifluoromethoxy)phenyl)prop-2-en-1-one (3ac)

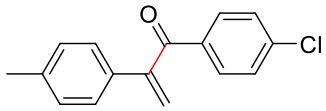


The reaction was performed according to general procedure **A** with 4-methyl styrene (0.15 mmol) and 4-(trifluoromethoxy)benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 80:1), the desired product **3ac** was obtained as a colorless oil (28.4 mg, 62% yield).

FT IR (neat) υ (cm^{-1}) = 2924, 2852, 1600, 1503, 1307, 1258, 1212, 1166, 982, 825.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.32 – 7.21 (m, 4H), 7.20 – 7.12 (m, 2H), 6.01 (s, 1H), 5.57 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.04, 152.52 (q, J_{C-F} = 1.7 Hz), 147.88, 138.60, 135.27, 133.77, 131.91, 129.39, 126.81, 120.25 (q, J_{C-F} = 260.7 Hz), 120.14, 120.09, 21.12. ^{19}F NMR (282 MHz, $CDCl_3$) δ -57.59. HRMS (ESI) Calcd. for $C_{17}H_{13}F_3NaO_2^+$ $[M+Na]^+$: 329.0760, found: 329.0760.

1-(4-Chlorophenyl)-2-(*p*-tolyl)prop-2-en-1-one (3ad)



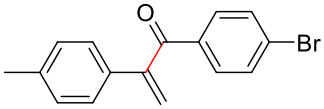
The reaction was performed according to general procedure **A** with 4-methyl styrene (0.15 mmol) and 4-chlorobenzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3ad** was obtained as a colorless oil (27.2 mg, 71% yield).

FT IR (neat) υ (cm^{-1}) = 2922, 2854, 1687, 1666, 1586, 1486, 1401, 1210, 1092, 1014, 830, 814.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 2H), 7.41 – 7.32 (m, 2H), 7.28 – 7.21 (m, 2H), 7.17 – 7.08 (m, 2H), 6.01 (s, 1H), 5.58 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.25, 147.80, 139.36, 138.43, 135.30, 133.76, 131.23, 129.30, 128.62, 126.73, 119.89, 21.08. HRMS (ESI) Calcd. for

$C_{16}H_{13}ClNaO^+$ $[M+Na]^+$: 279.0547, found: 279.0547.

1-(4-Bromophenyl)-2-(*p*-tolyl)prop-2-en-1-one (3ae)

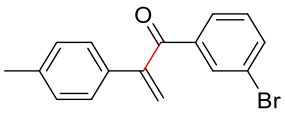


The reaction was performed according to general procedure **A** with 4-methyl styrene (0.15 mmol) and 4-bromobenzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3ae** was obtained as a colorless oil (32.8 mg, 73% yield).

FT IR (neat) υ (cm^{-1}) = 1678, 1666, 1659, 1584, 1209, 1172, 1070, 980, 824.

^1H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.70 (m, 2H), 7.59 – 7.52 (m, 2H), 7.33 – 7.23 (m, 2H), 7.18 – 7.12 (m, 2H), 6.02 (s, 1H), 5.58 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.53, 147.85, 138.52, 135.78, 133.79, 131.68, 131.40, 129.36, 128.19, 126.80, 120.08, 21.15. HRMS (ESI) Calcd. for $C_{16}H_{13}BrNaO^+$ $[M+Na]^+$: 323.0042, found: 323.0042.

1-(3-Bromophenyl)-2-(*p*-tolyl)prop-2-en-1-one (3af)

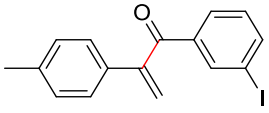


The reaction was performed according to general procedure **A** with 4-methyl styrene (0.15 mmol) and 4-bromobenzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3af** was obtained as a colorless oil (30.5 mg, 68% yield).

FT IR (neat) υ (cm^{-1}) = 2961, 2923, 1678, 1666, 1567, 1326, 1309, 1204, 1188, 1002, 993, 825.

^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (t, *J* = 1.8 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.70 – 7.64 (m, 1H), 7.35 – 7.27 (m, 3H), 7.20 – 7.13 (m, 2H), 6.06 (s, 1H), 5.60 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.24, 147.64, 139.01, 138.63, 135.84, 133.69, 132.67, 129.96, 129.40, 128.56, 126.91, 122.70, 120.81, 21.21. HRMS (ESI) Calcd. for $C_{16}H_{13}BrNaO^+$ $[M+Na]^+$: 323.0042, found: 323.0044.

1-(3-Iodophenyl)-2-(*p*-tolyl)prop-2-en-1-one (3ag)

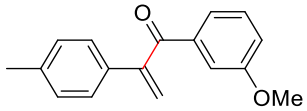


The reaction was performed according to general procedure **A** with 4-methyl styrene (0.15 mmol) and 3-iodobenzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3ag** was obtained as a colorless oil (32.7 mg, 63% yield).

FT IR (neat) υ (cm^{-1}) = 2922, 2854, 1687, 1667, 1562, 1552, 1514, 1468, 1408, 1328, 1203, 1186, 1143, 999, 815, 784.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (t, *J* = 1.5 Hz, 1H), 7.90 – 7.77 (m, 2H), 7.32 – 7.27 (m, 2H), 7.20 - 7.12 (m, 3H), 6.06 (s, 1H), 5.59 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.17, 147.59, 141.71, 139.02, 138.61, 138.53, 133.70, 130.05, 129.39, 129.17, 126.91, 120.82, 94.15, 21.21. HRMS (ESI) Calcd. for $C_{16}H_{13}INaO^+$ $[M+Na]^+$: 370.9903, found: 370.9902.

1-(3-Methoxyphenyl)-2-(*p*-tolyl)prop-2-en-1-one (3ah)

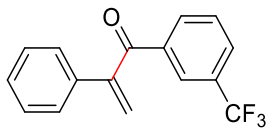


The reaction was performed according to general procedure **A** with 4-methyl styrene (0.15 mmol) and 3-methoxybenzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 50:1), the desired product **3ah** was obtained as a colorless oil (26.8 mg, 71% yield).

FT IR (neat) υ (cm^{-1}) = 2963, 2921, 1666, 1596, 1583, 1485, 1258, 1197, 1002, 826, 624.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.33 – 7.25 (m, 3H), 7.16 – 7.10 (m, 2H), 7.09 – 7.03 (m, 1H), 5.99 (s, 1H), 5.56 (s, 1H), 3.79 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.35, 159.50, 148.04, 138.30, 138.20, 134.03, 129.23, 129.19, 126.71, 122.81, 119.54, 119.52, 113.70, 55.21, 21.04. HRMS (ESI) Calcd. for $C_{17}H_{16}NaO_2^+$ $[M+Na]^+$: 275.1043, found: 275.1043.

2-Phenyl-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one (3ai)

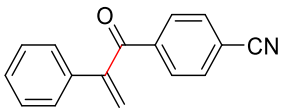


The reaction was performed according to general procedure **A** with styrene (0.15 mmol) and 3-(trifluoromethyl)benzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 50:1), the desired product **3ai** was obtained as a colorless oil (21.1 mg, 51% yield).

FT IR (neat) υ (cm^{-1}) = 3060, 1693, 1641, 1611, 1485, 1443, 1332, 1169, 1127, 1074, 1005, 761, 697.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 – 8.14 (m, 1H), 8.08 – 8.02 (m, 1H), 7.84 – 7.77 (m, 1H), 7.62 – 7.53 (m, 1H), 7.45 – 7.33 (m, 5H), 6.14 (s, 1H), 5.70 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.97, 147.74, 137.72, 136.51, 133.11 (q, J_{C-F} = 0.9 Hz), 131.1 (q, J_{C-F} = 33.4 Hz), 129.42 (q, J_{C-F} = 3.0 Hz), 129.08, 128.74, 128.71, 127.12, 126.60 (q, J_{C-F} = 3.8 Hz), 123.60 (q, J_{C-F} = 274.4 Hz), 122.29. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.83. HRMS (ESI) Calcd. for $C_{16}H_{11}F_3NaO^+$ $[M+Na]^+$: 299.0654, found: 299.0655.

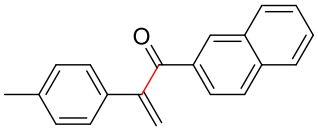
4-(2-Phenylacryloyl)benzonitrile (3aj)



The reaction was performed according to general procedure **A** with styrene (0.15 mmol) and 4-cyanobenzoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 10:1), the desired product **3aj** was obtained as a colorless oil (17.9 mg, 57% yield).

FT IR (neat) υ (cm^{-1}) = 3060, 2921, 2232, 1666, 1651, 1605, 1407, 1333, 1211, 981, 860, 777, 700. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.76 – 7.69 (m, 2H), 7.42 – 7.33 (m, 5H), 6.15 (s, 1H), 5.72 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.75, 147.68, 140.45, 136.28, 132.26, 130.16, 128.81, 128.78, 127.16, 123.14, 117.91, 116.15. HRMS (EI) Calcd. for $C_{16}H_{11}NO^{+}$ $[M]^{+}$: 233.0835, found: 233.0835.

1-(Naphthalen-2-yl)-2-(*p*-tolyl)prop-2-en-1-one (3ak)

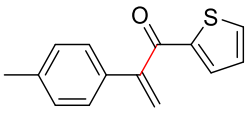


The reaction was performed according to general procedure **A** with 4-methyl styrene (0.15 mmol) and 2-naphthoyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 100:1), the desired product **3ak** was obtained as a colorless oil (28.5 mg, 70% yield).

FT IR (neat) υ (cm^{-1}) = 1693, 1632, 1503, 1468, 1441, 1329, 1287, 1206, 824.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.1 Hz, 1H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.95 – 7.85 (m, 3H), 7.64 – 7.50 (m, 2H), 7.45 – 7.37 (m, 2H), 7.23 – 7.15 (m, 2H), 6.12 (s, 1H), 5.66 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.90, 148.24, 138.46, 135.63, 134.49, 134.21, 132.39, 132.37, 129.67, 129.40, 128.58, 128.36, 127.80, 126.90, 126.74, 125.18, 119.55, 21.23. HRMS (ESI) Calcd. for $C_{20}H_{16}NaO^{+}$ $[M+Na]^{+}$: 295.1093, found: 295.1095.

1-(Thiophen-2-yl)-2-(*p*-tolyl)prop-2-en-1-one (3al)



The reaction was performed according to general procedure **B** with 4-methyl styrene (0.15 mmol) and thiophene-2-carbonyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 50:1), the desired product **3al** was obtained as a white solid (15.9 mg, 52% yield).

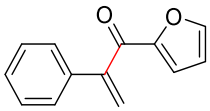
MP: 47-48 °C.

FT IR (neat) υ (cm^{-1}) =3102, 3027, 2922, 1657, 1644, 1606, 1513, 1410, 1354, 1231, 1179, 1054, 820, 725.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.60 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.39 –

7.33 (m, 2H), 7.20 – 7.14 (m, 2H), 7.08 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.97 (s, 1H), 5.72 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.51, 147.96, 144.09, 138.50, 134.96, 134.73, 133.88, 129.27, 128.03, 126.93, 119.15, 21.18. HRMS (ESI) Calcd. for $C_{14}H_{12}OS^+$ $[M]^+$: 228.0603, found: 228.0603.

1-(Furan-2-yl)-2-phenylprop-2-en-1-one (3am)

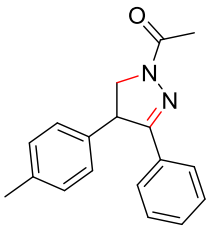


The reaction was performed according to general procedure **A** with 4-methyl styrene (0.15 mmol) and furan-2-carbonyl fluoride (0.375 mmol). After purification by flash chromatography (*n*-pentane/diethyl ether = 50:1), the desired product **3am** was obtained as a colorless oil (16.3 mg, 55% yield).

FT IR (neat) υ (cm^{-1}) = 3136, 3034, 1650, 1607, 1567, 1462, 1391, 1243, 1162, 1025, 985, 910, 766, 698, 594.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.47 – 7.31 (m, 5H), 7.02 (dd, *J* = 3.6, 0.6 Hz, 1H), 6.50 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.00 (d, *J* = 0.3 Hz, 1H), 5.89 (d, *J* = 0.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.83, 152.21, 147.59, 147.55, 136.81, 128.53, 128.51, 127.27, 121.58, 121.11, 112.11. HRMS (ESI) Calcd. for $C_{13}H_{10}NaO_2^+$ $[M+Na]^+$: 221.0573, found: 221.0572.

1-(3-Phenyl-4-(*p*-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5)



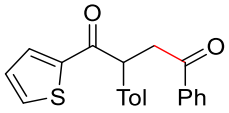
After purification by flash chromatography (*n*-pentane/diethyl ether = 10:1), the desired product **5** was obtained as a white solid (104.2 mg, 75% yield).

MP: 111-113 °C.

FT IR (neat) υ (cm^{-1}) = 1665, 1660, 1461, 1440, 1415, 1360, 1305, 1155, 955, 865, 816, 772, 692.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.60 (m, 2H), 7.34 – 7.23 (m, 3H), 7.14 – 7.00 (m, 4H), 4.67 (dd, *J* = 11.4, 5.4 Hz, 1H), 4.36 (t, *J* = 12.0 Hz, 1H), 4.00 (dd, *J* = 12.0, 5.4 Hz, 1H), 2.47 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.39, 156.95, 137.32, 137.27, 130.78, 129.93, 129.82, 128.47, 127.17, 127.09, 54.21, 50.36, 21.58, 21.03. HRMS (ESI) Calcd. for $C_{18}H_{18}N_2NaO^+$ $[M+Na]^+$: 301.1311, found: 301.1306.

4-Phenyl-1-(thiophen-2-yl)-2-(*p*-tolyl)butane-1,4-dione (6)

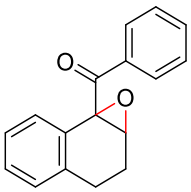


After purification by flash chromatography (*n*-pentane/diethyl ether = 70:1), the desired product **6** was obtained as a yellow oil (136.9 mg, 82% yield).

FT IR (neat) υ (cm^{-1}) = 2921, 1682, 1659, 1513, 1449, 1414, 1353, 1235, 1199, 725, 714, 689.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.81 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.49 – 7.40 (m, 2H), 7.32 – 7.27 (m, 2H), 7.18 – 7.10 (m, 2H), 7.07 (dd, *J* = 4.8, 3.6 Hz, 1H), 5.11 (dd, *J* = 9.9, 3.9 Hz, 1H), 4.17 (dd, *J* = 18.0, 9.9 Hz, 1H), 3.28 (dd, *J* = 18.0, 3.9 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.93, 191.75, 143.38, 137.22, 136.41, 135.68, 133.53, 133.22, 132.75, 129.82, 128.54, 128.14, 128.05, 128.03, 49.71, 43.35, 21.02. HRMS (ESI) Calcd. for $C_{21}H_{18}O_2SNa^+$ $[M+Na]^+$: 357.0919, found: 357.0915.

(2,3-Dihydronaphtho[1,2-b]oxiren-7b(1aH)-yl)(phenyl)methanone (7)

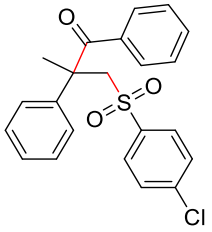


After purification by flash chromatography (*n*-pentane/diethyl ether = 70:1), the desired product **7** was obtained as a colorless oil (17.8 mg, 71% yield).

FT IR (neat) υ (cm^{-1}) = 2931, 2922, 1692, 1681, 1598, 1540, 1274, 1208, 1176, 759, 702, 624.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.62 – 7.55 (m, 1H), 7.49 – 7.41 (m, 2H), 7.30 – 7.23 (m, 1H), 7.21 – 7.15 (m, 1H), 7.11 – 7.04 (m, 2H), 3.84 – 3.79 (m, 1H), 3.01 - 2.86 (m, 1H), 2.78 – 2.66 (m, 1H), 2.59 – 2.47 (m, 1H), 2.13 – 1.97 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.99, 136.53, 135.19, 133.81, 131.26, 129.72, 129.44, 128.90, 128.77, 128.61, 126.28, 61.97, 60.01, 24.75, 21.52. HRMS (ESI) Calcd. for $C_{17}H_{14}NaO_2^+$ $[M+Na]^+$: 273.0886, found: 273.0884.

3-((4-Chlorophenyl)sulfonyl)-2-methyl-1,2-diphenylpropan-1-one (9)

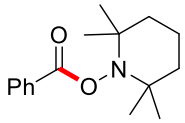


After purification by flash chromatography (*n*-pentane/diethyl ether = 20:1), the desired product **9** was obtained as a colorless oil (28.6 mg, 48% yield).

FT IR (neat) υ (cm^{-1}) = 3090, 2931, 1687, 1678, 1582, 1477, 1446, 1317, 1277, 1149, 1087, 968, 772, 700, 577.

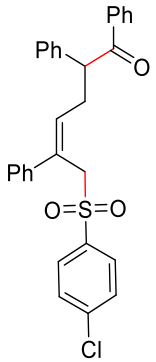
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.42 – 7.30 (m, 5H), 7.29 – 7.18 (m, 7H), 4.03 (d, *J* = 14.8 Hz, 1H), 3.87 (d, *J* = 14.7 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.92, 139.82, 139.71, 138.86, 135.82, 131.97, 129.27, 129.25, 129.20, 128.99, 128.11, 128.09, 126.71, 65.70, 53.63, 21.95. HRMS (ESI) Calcd. for $C_{22}H_{19}ClNaO_3S^+$ $[M+Na]^+$: 421.0636, found: 421.0629.

2,2,6,6-Tetramethylpiperidin-1-yl benzoate (10)



After purification by flash chromatography (*n*-pentane/diethyl ether = 30:1), the desired product **10** was obtained as a white solid (10.1 mg, 19% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 – 8.03 (m, 2H), 7.64 – 7.52 (m, 1H), 7.52 – 7.42 (dd, *J* = 8.2, 6.8 Hz, 2H), 1.87 – 1.54 (m, 5H), 1.52 – 1.42 (m, 1H), 1.28 (s, 6H), 1.12 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.35, 132.81, 129.70, 129.54, 128.41, 60.37, 39.03, 31.95, 20.82, 16.98. Spectroscopic data are in accordance with those described in literature.[11]

6-((4-Chlorophenyl)sulfonyl)-1,2,5-triphenylhex-4-en-1-one (12)

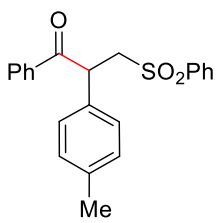


After purification by flash chromatography (*n*-pentane/diethyl ether = 20:1), the desired product **12** was obtained as a colorless oil (33.0 mg, 44% yield).

FT IR (neat) υ (cm^{-1}) = 3030, 2964, 2927, 1687, 1678, 1673, 1582, 1446, 1321, 1137, 1088, 759, 698.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.58 – 7.53 (m, 2H), 7.46 – 7.39 (m, 1H), 7.35 – 7.29 (m, 2H), 7.27 (d, *J* = 2.9 Hz, 2H), 7.24 – 7.16 (m, 5H), 7.12 – 7.05 (m, 3H), 6.99 – 6.93 (m, 2H), 5.91 (t, *J* = 8.0 Hz, 1H), 4.71 (dd, *J* = 8.0, 6.4 Hz, 1H), 4.42 (d, *J* = 14.4 Hz, 1H), 4.23 (d, *J* = 14.4 Hz, 1H), 3.03 – 2.93 (m, 1H), 2.64 - 2.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.90, 140.45, 140.24, 138.76, 137.49, 136.31, 135.71, 133.05, 129.84, 129.43, 129.15, 129.09, 128.80, 128.56, 128.29, 128.15, 127.39, 127.31, 126.38, 57.72, 53.36, 33.89. HRMS (ESI) Calcd. for $C_{30}H_{25}ClNaO_3S^+$ $[M+Na]^+$: 523.1105, found: 523.1101.

1-Phenyl-3-(phenylsulfonyl)-2-(p-tolyl)propan-1-one (13)



After purification by flash chromatography (*n*-pentane/diethyl ether = 20:1), the desired product **13** was obtained as a colorless oil.

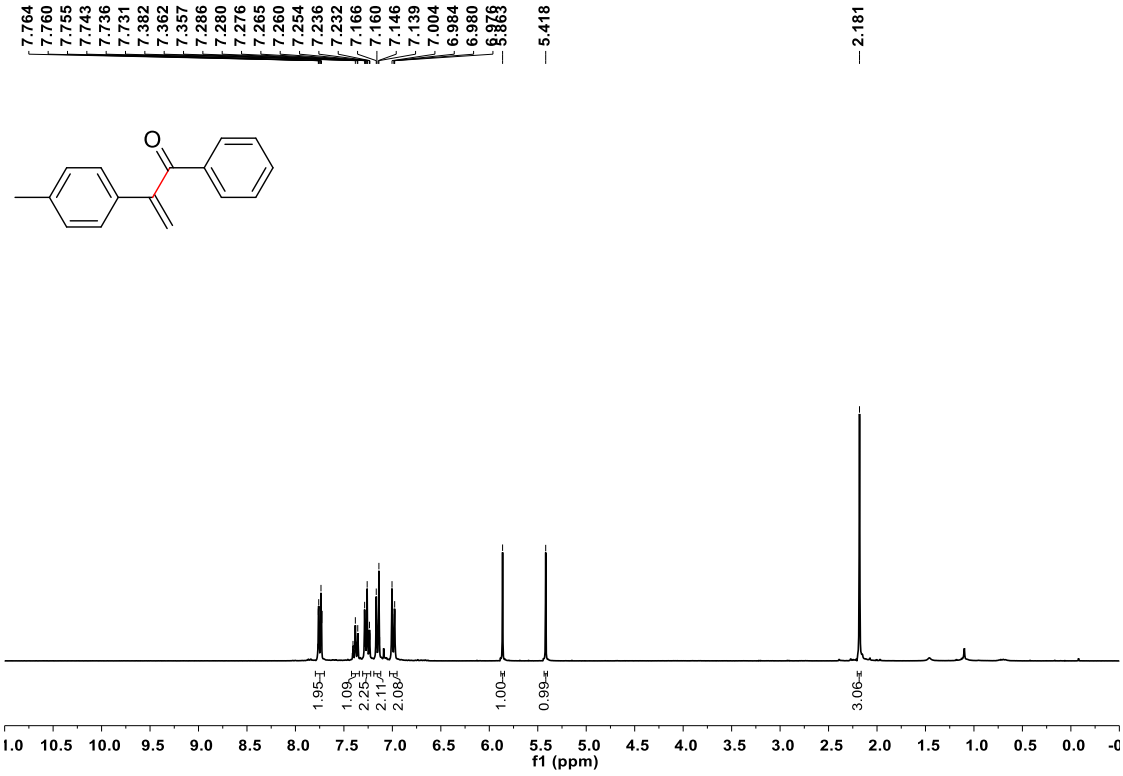
FT IR (neat) υ (cm^{-1}) = 2394, 1682, 1447, 1306, 1229, 1152, 1086, 742, 688, 584.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.87 (m, 2H), 7.85 – 7.79 (m, 2H), 7.62 – 7.54 (m, 1H), 7.53 – 7.34 (m, 5H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 5.26 (dd, *J* = 8.7, 3.9 Hz, 1H), 4.40 (dd, *J* = 14.2, 8.7 Hz, 1H), 3.44 (dd, *J* = 14.2, 3.9 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.85, 139.42, 137.83, 135.40, 133.60, 133.36, 133.29, 130.05, 129.13, 128.86, 128.57, 128.00, 127.98, 59.18, 47.11, 20.99. HRMS (ESI) Calcd. for $C_{22}H_{20}NaO_3S^+$ $[M+Na]^+$: 387.1025, found: 387.1022.

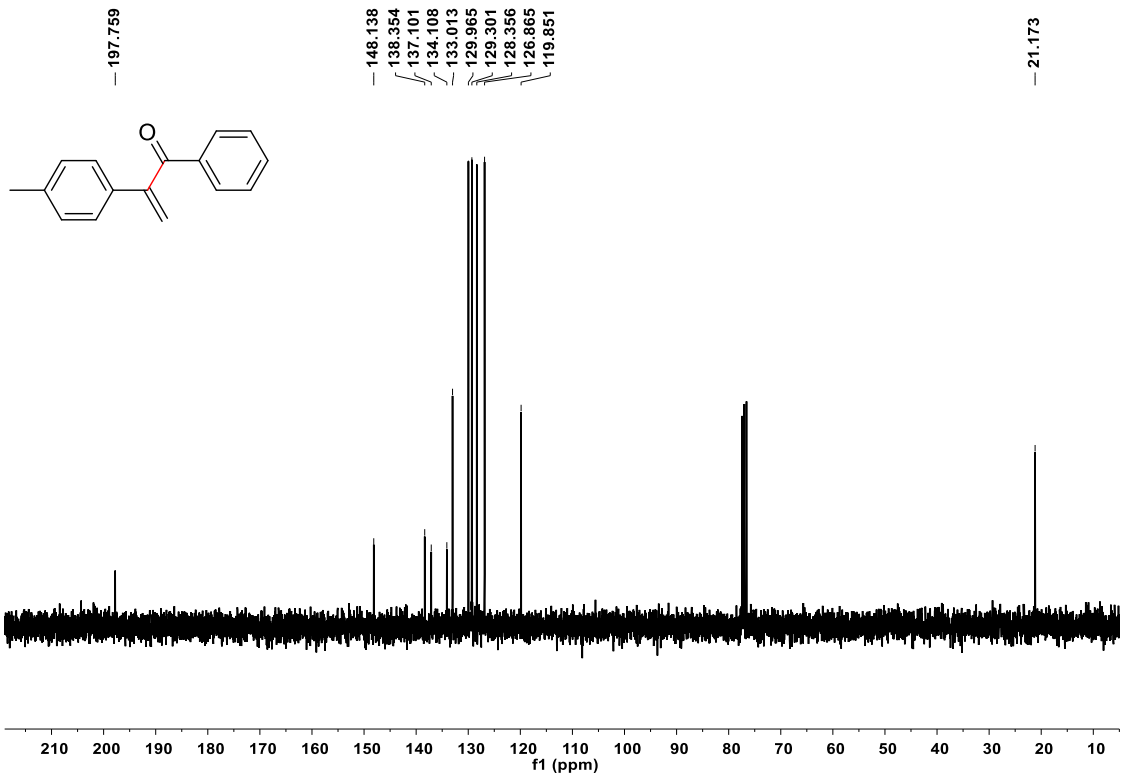
8. Copies of product NMR Spectra

3a

^{1}H NMR

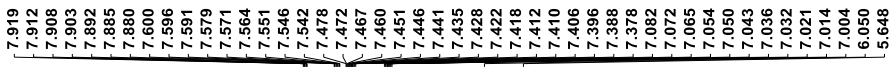


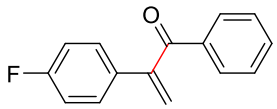
^{13}C NMR

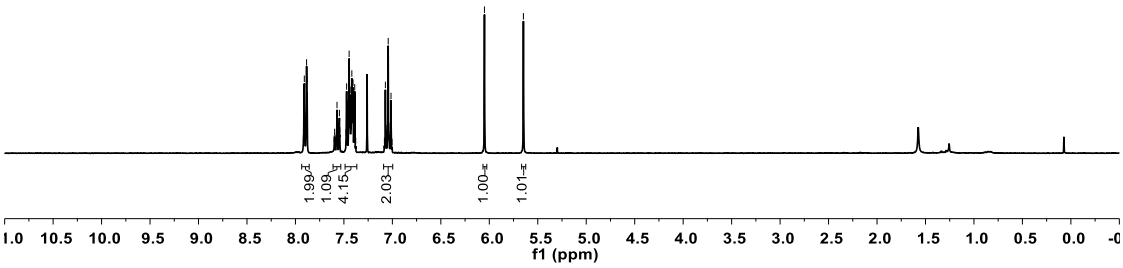


3b

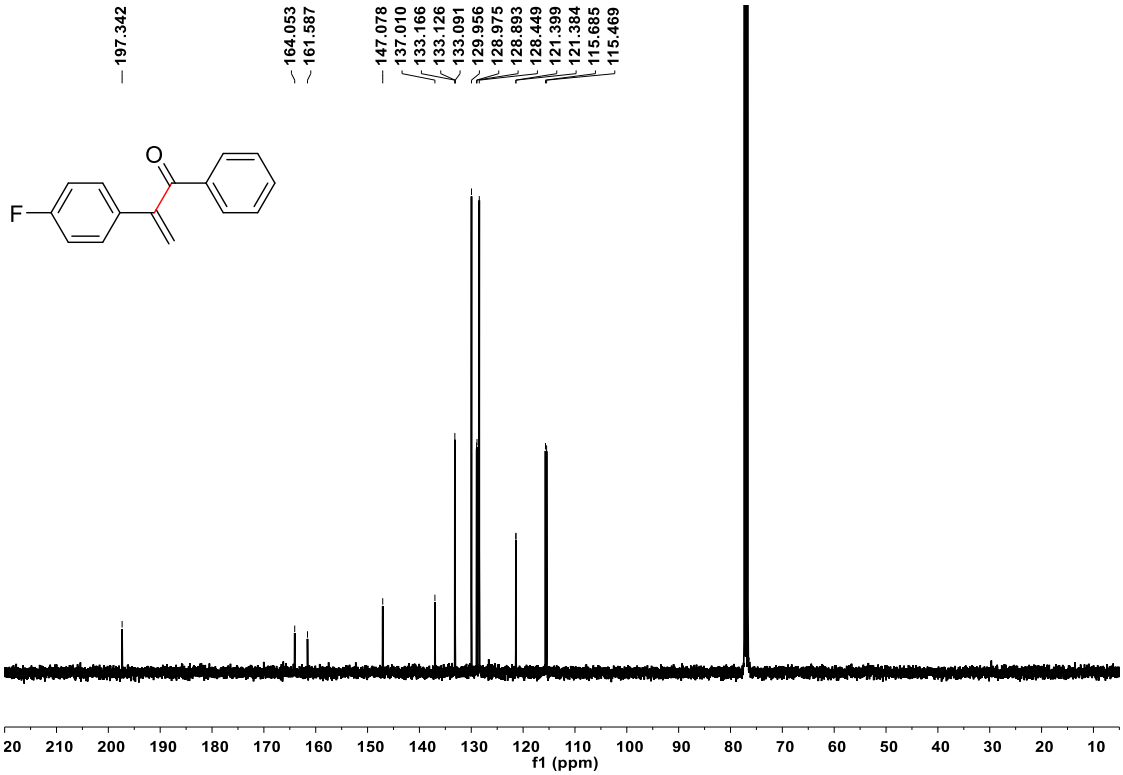
^{1}H NMR



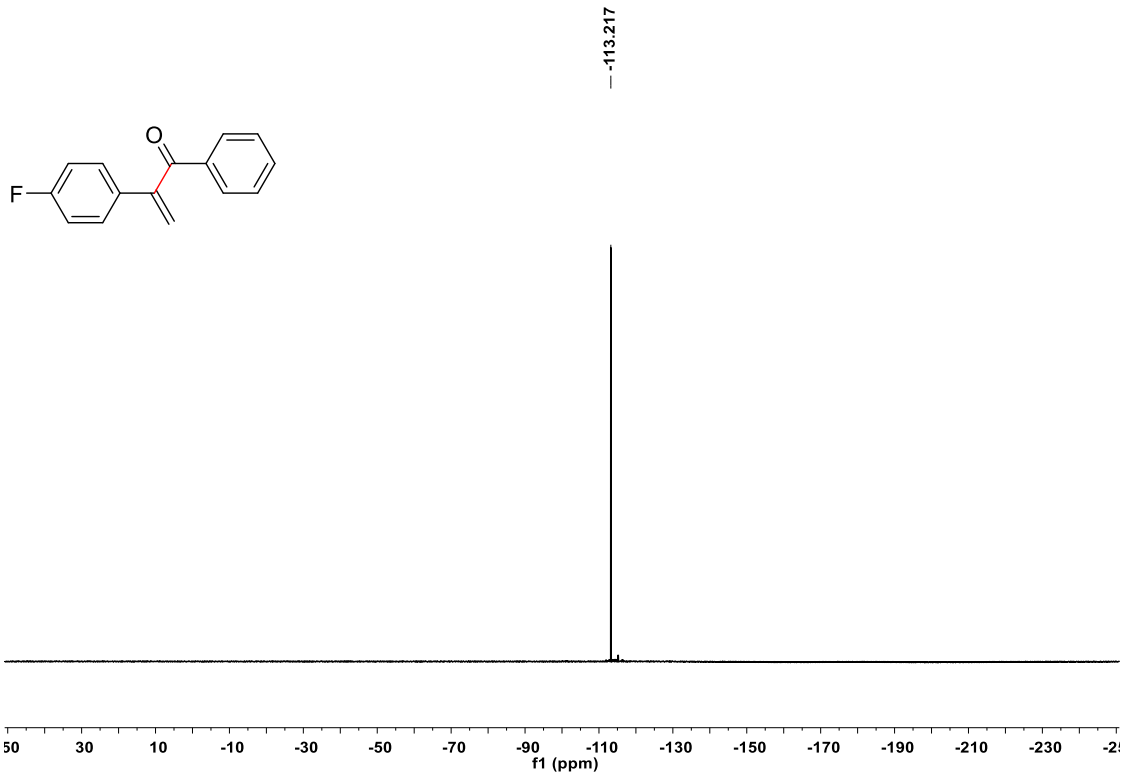




^{13}C NMR

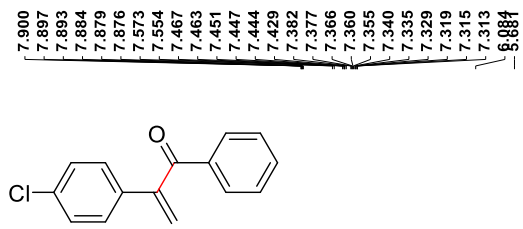


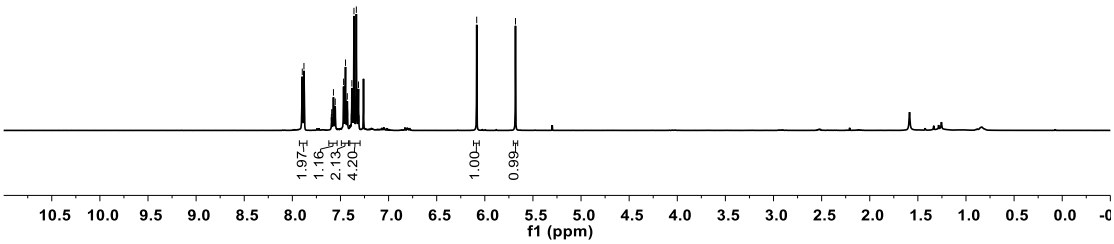
^{19}F NMR


-113.217
O
F
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

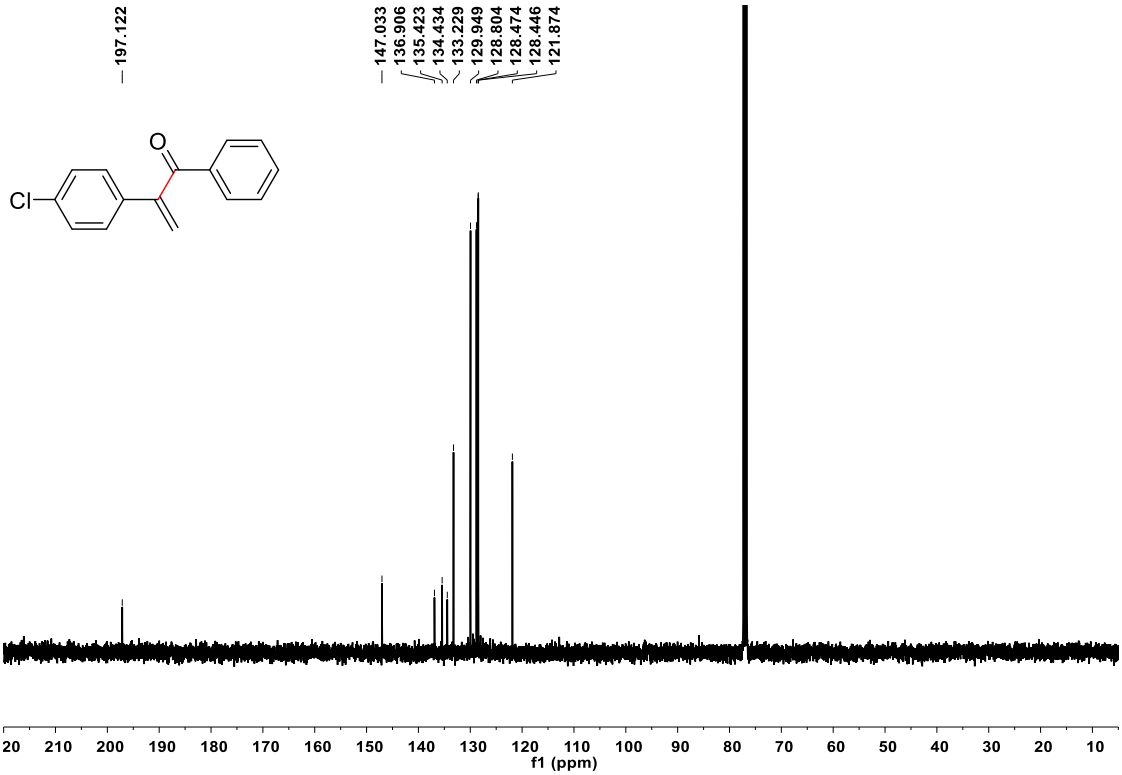
3c

^{1}H NMR



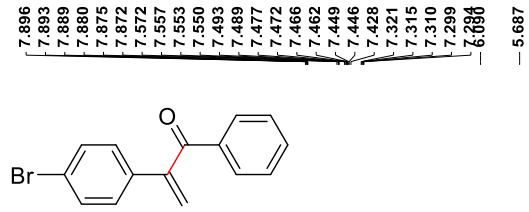


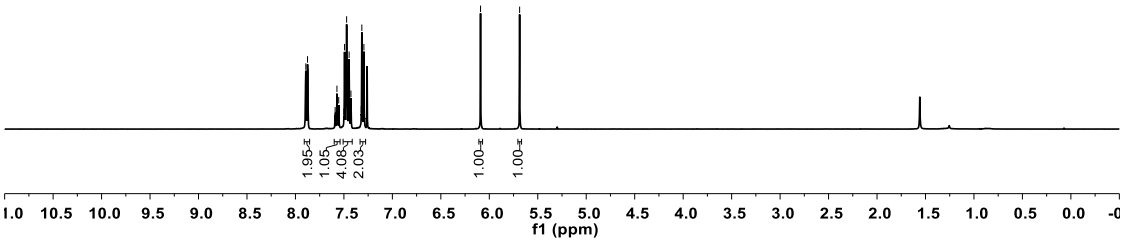
^{13}C NMR



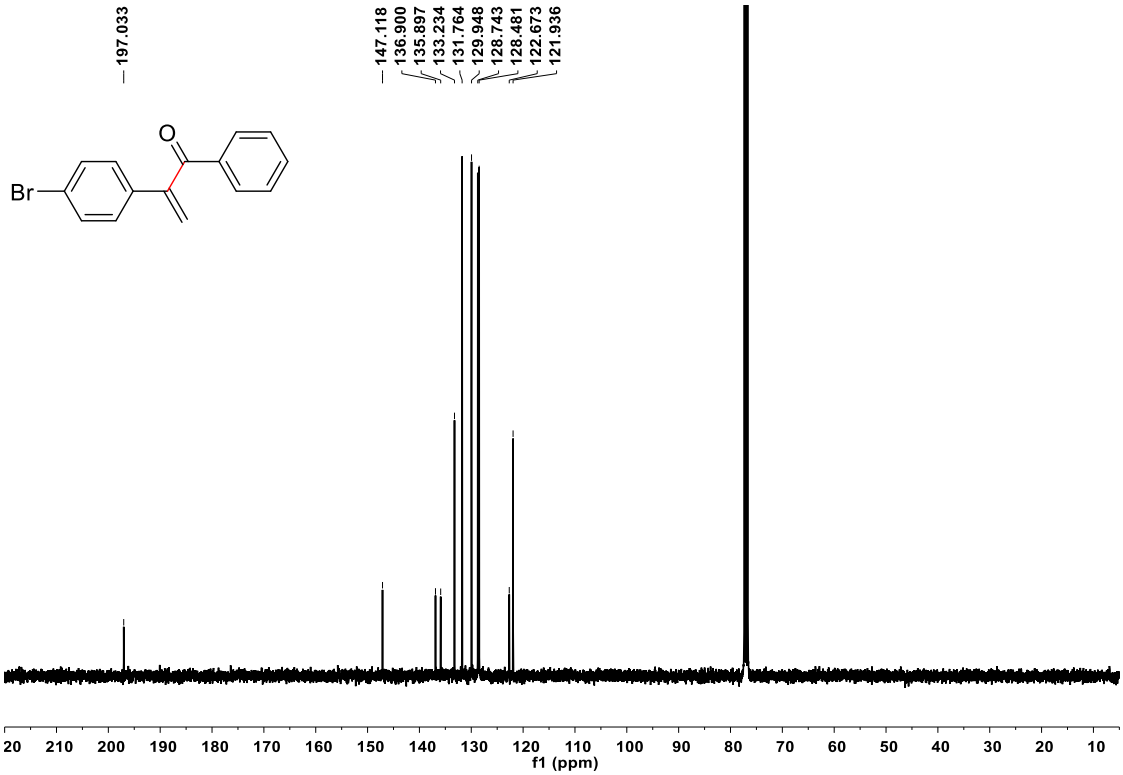
3d

^{1}H NMR



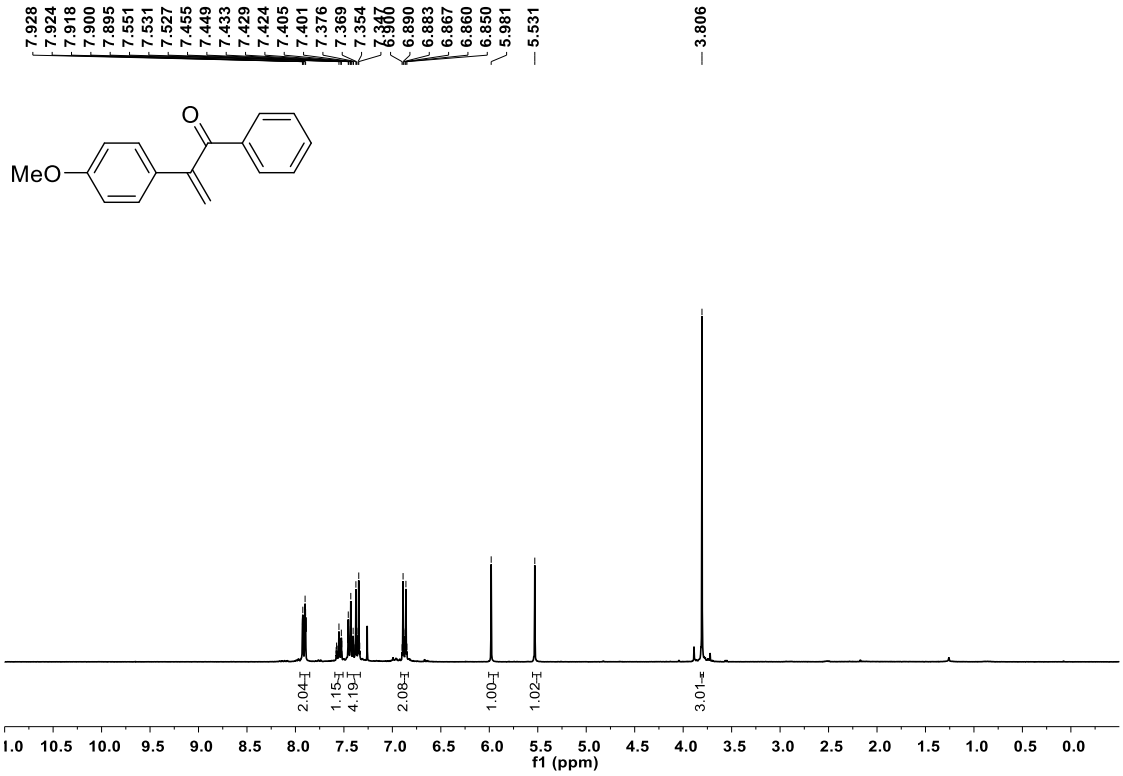


^{13}C NMR

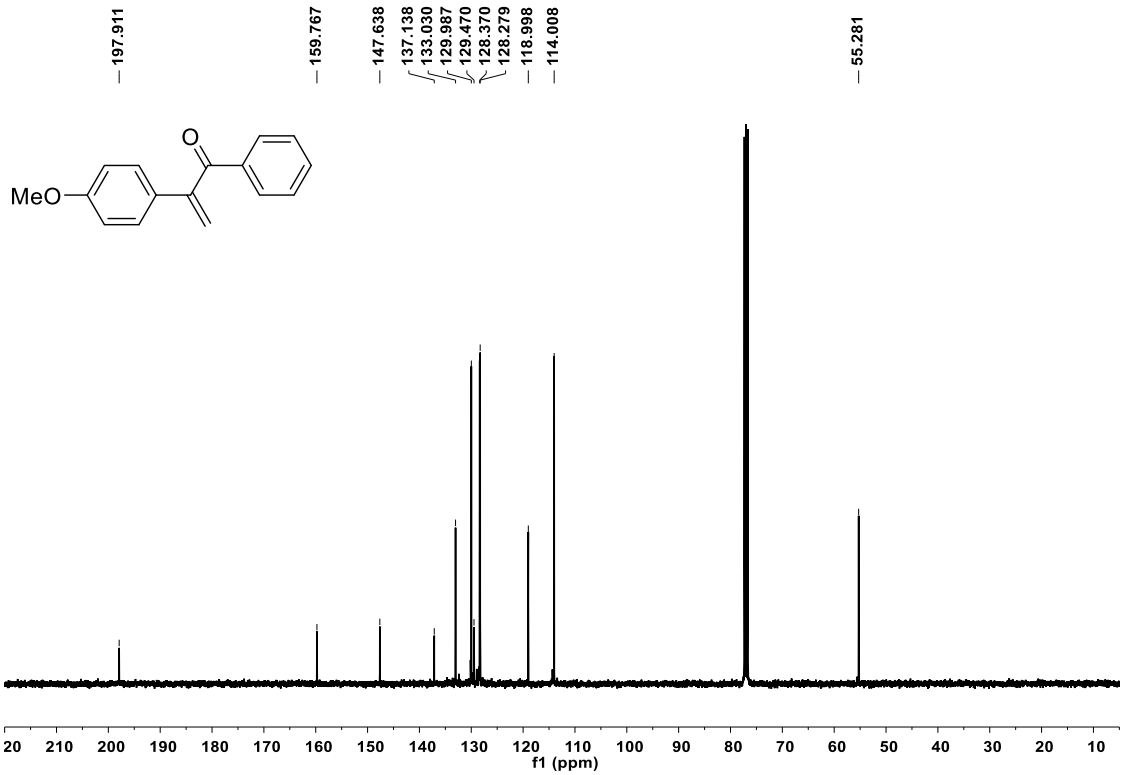


3e

^{1}H NMR

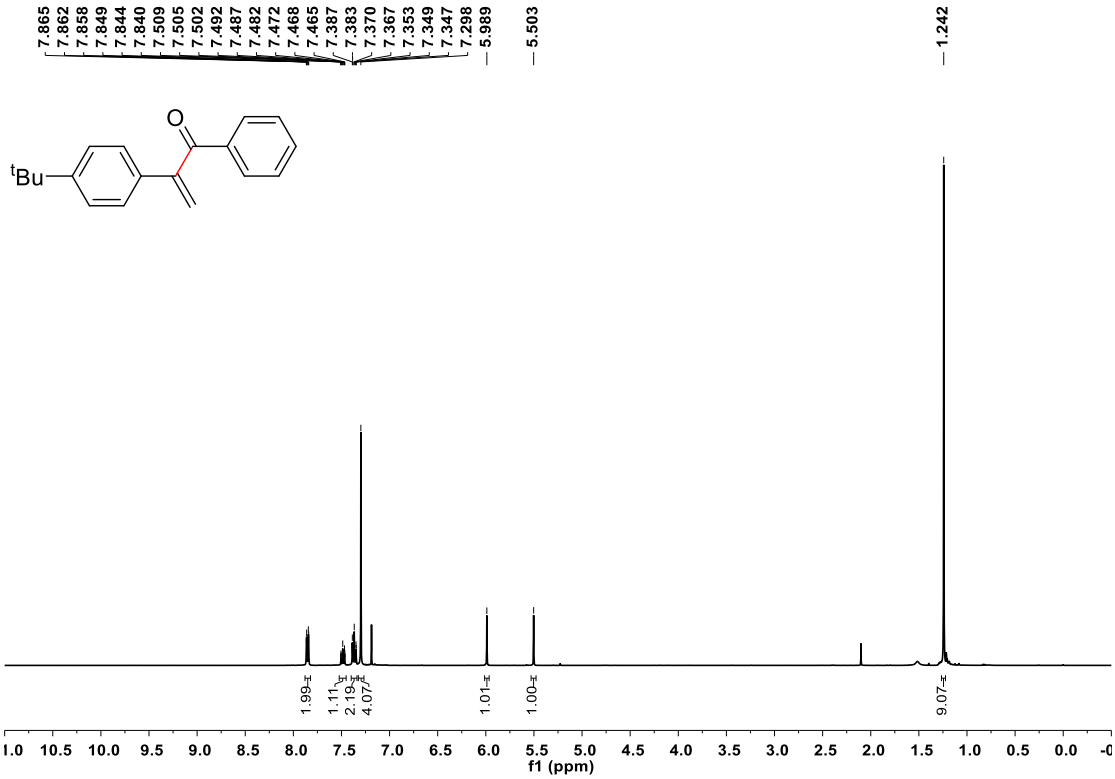


^{13}C NMR

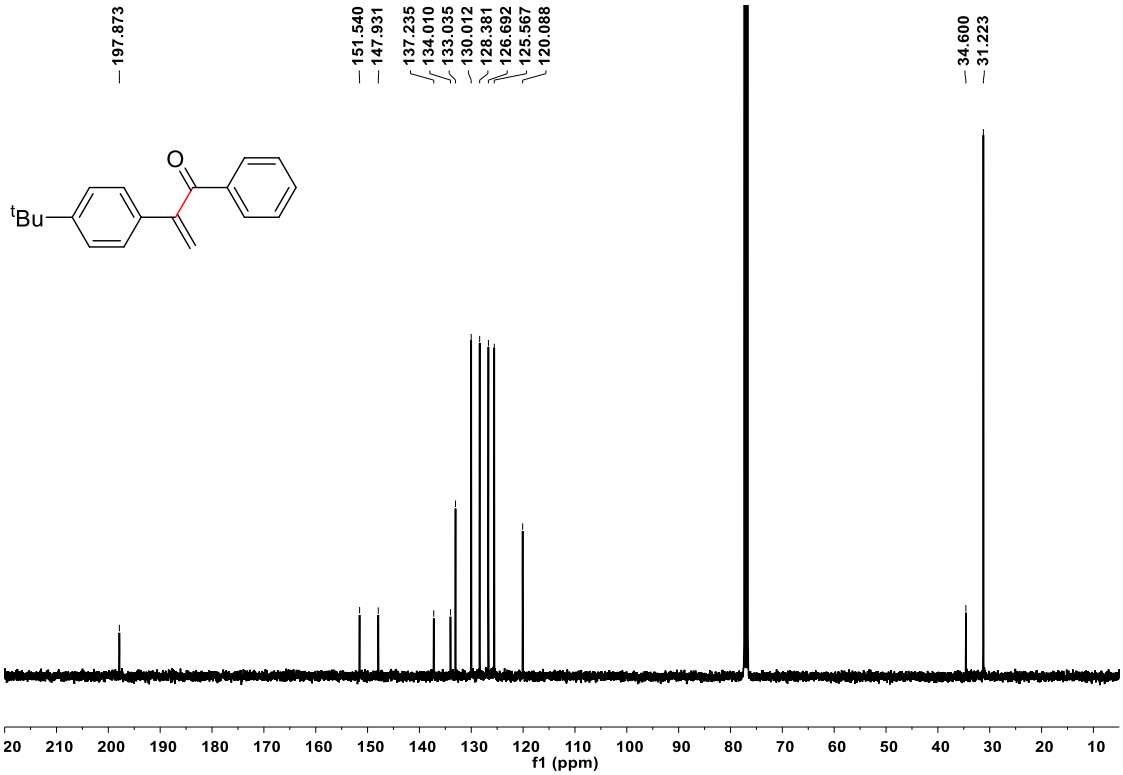


3f

^{1}H NMR

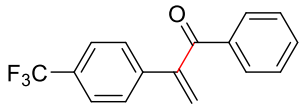


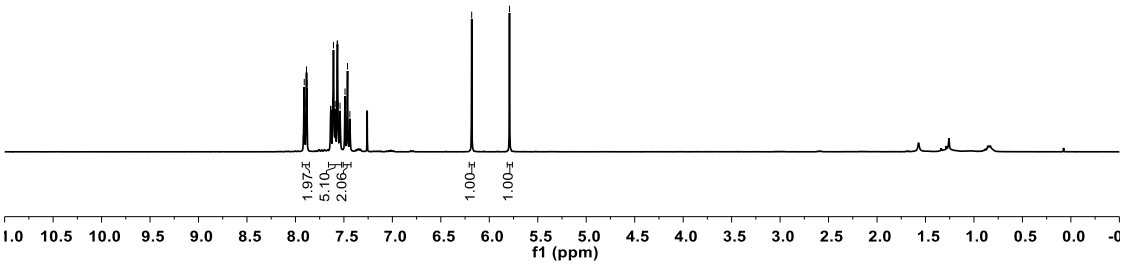
^{13}C NMR



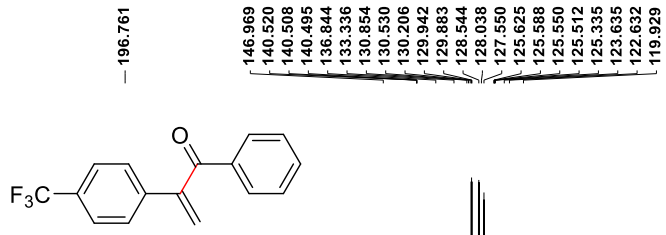
3g

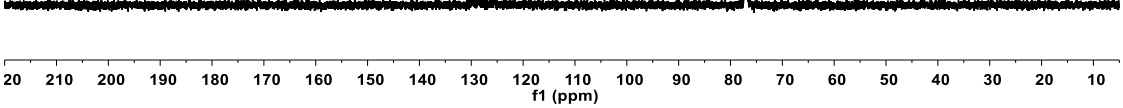
^{1}H NMR



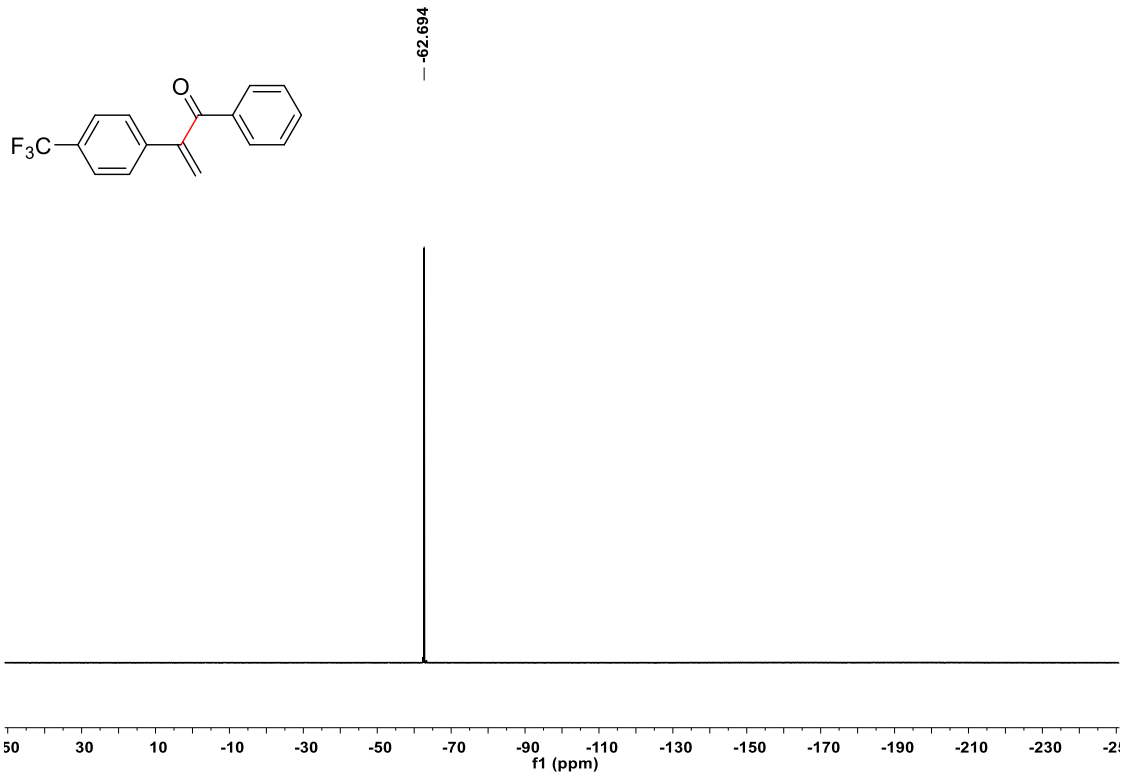


^{13}C NMR



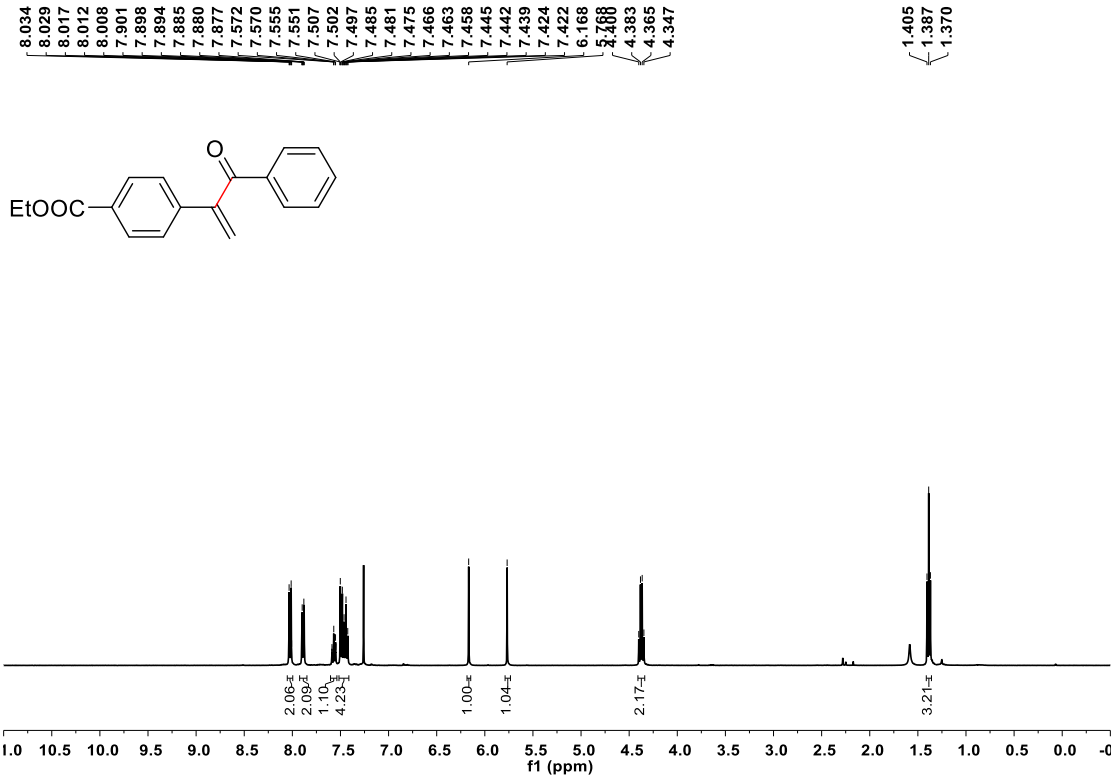


^{19}F NMR

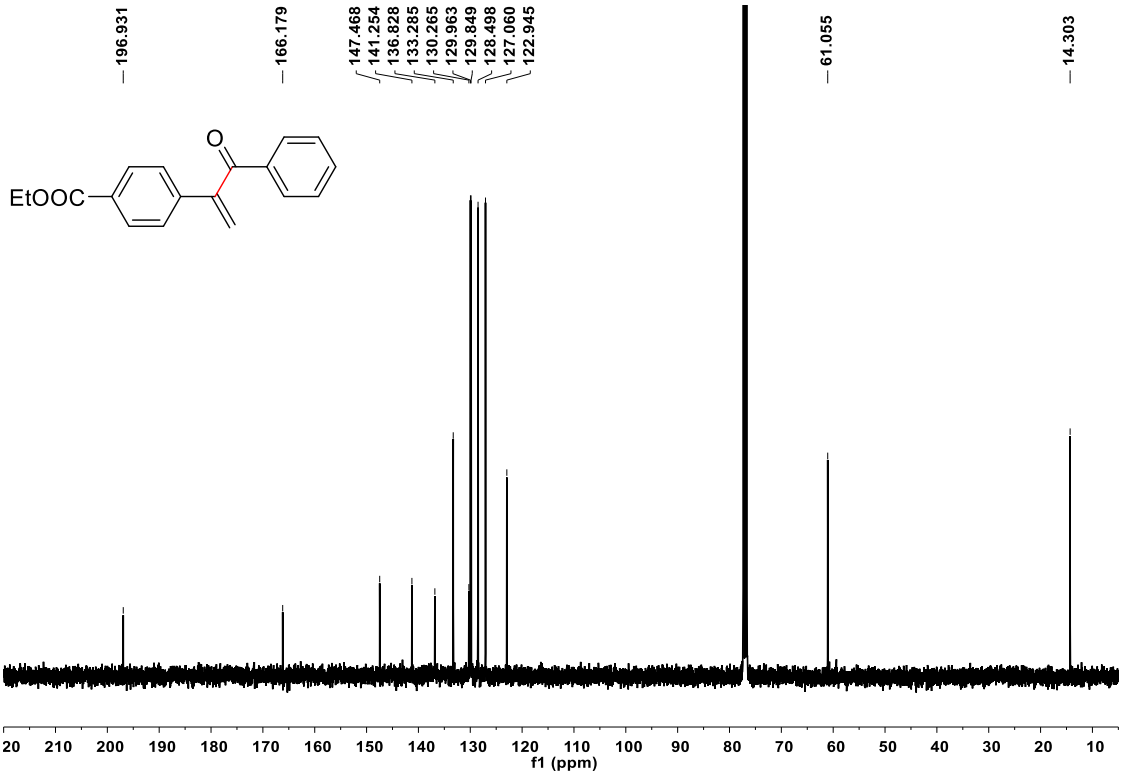

-62.694
O
F3C
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

3h

^{1}H NMR

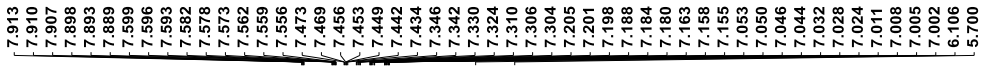


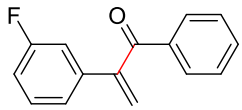
^{13}C NMR

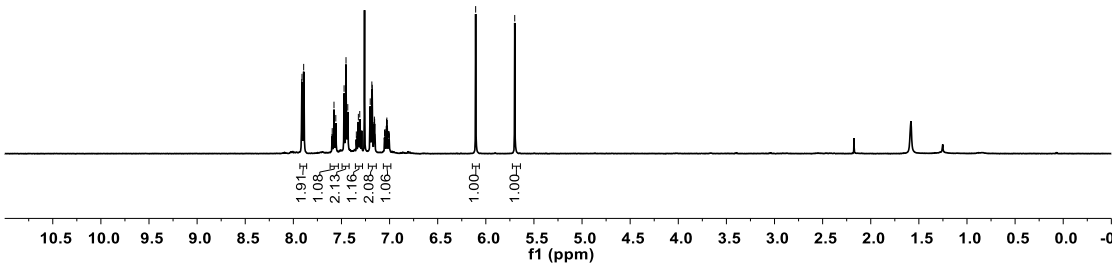


3i

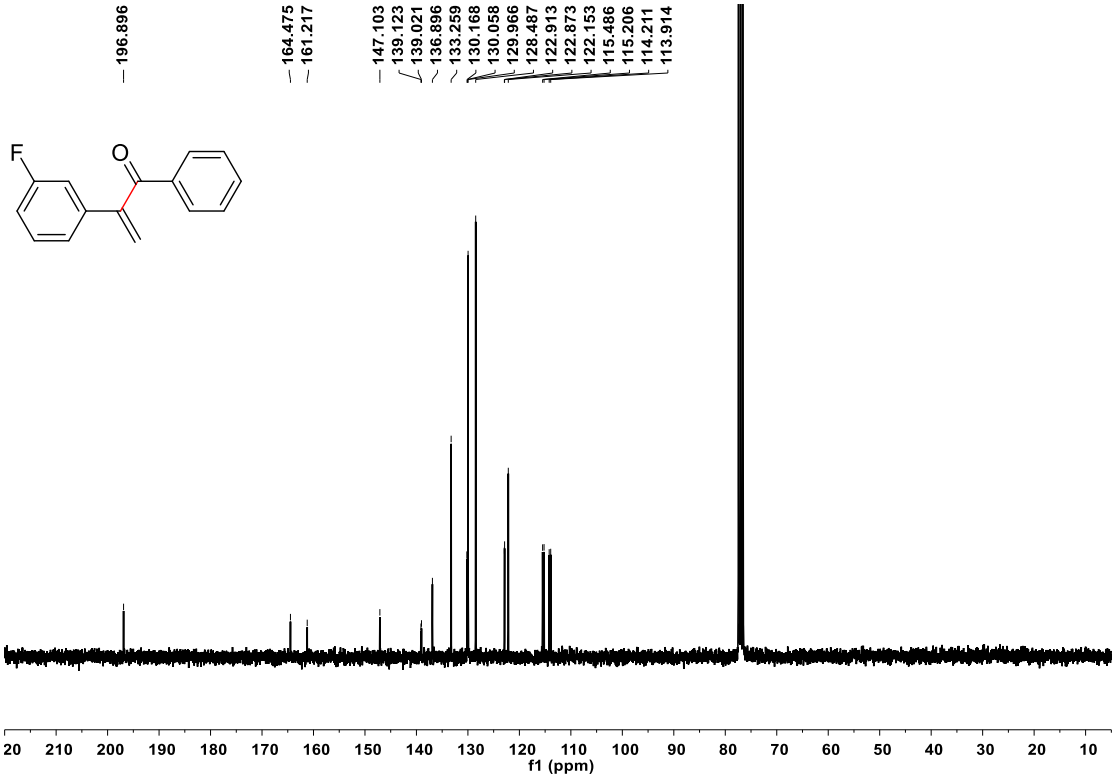
^{1}H NMR



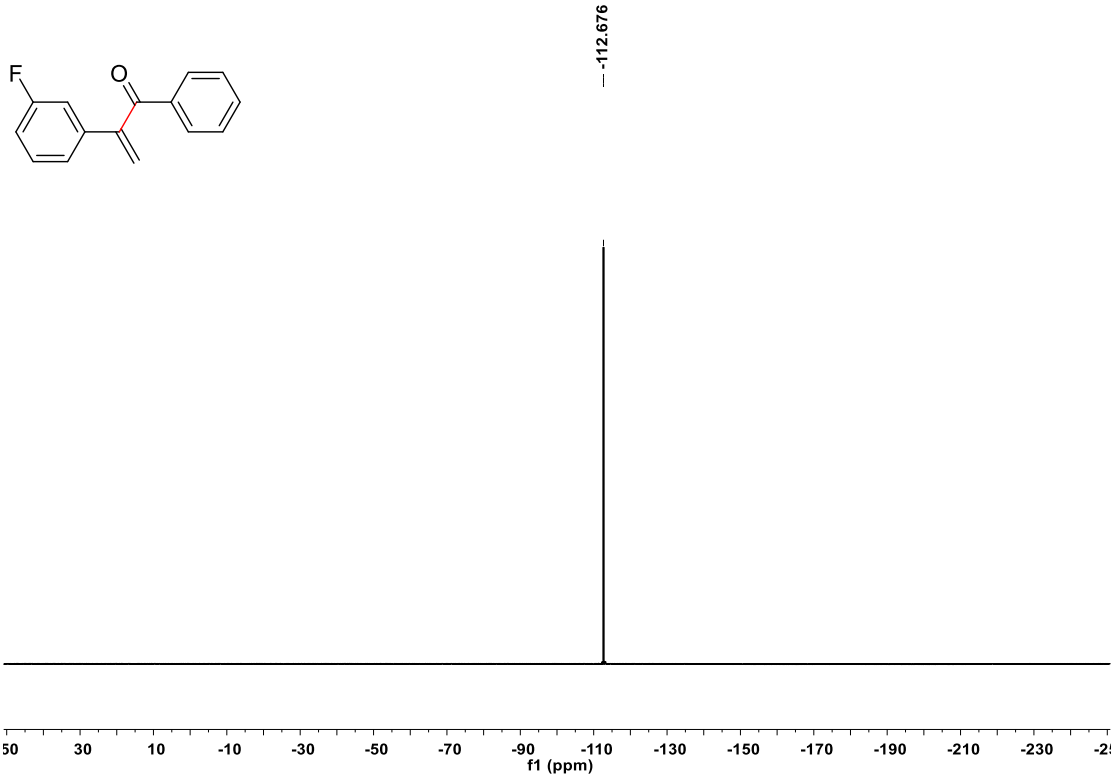




^{13}C NMR

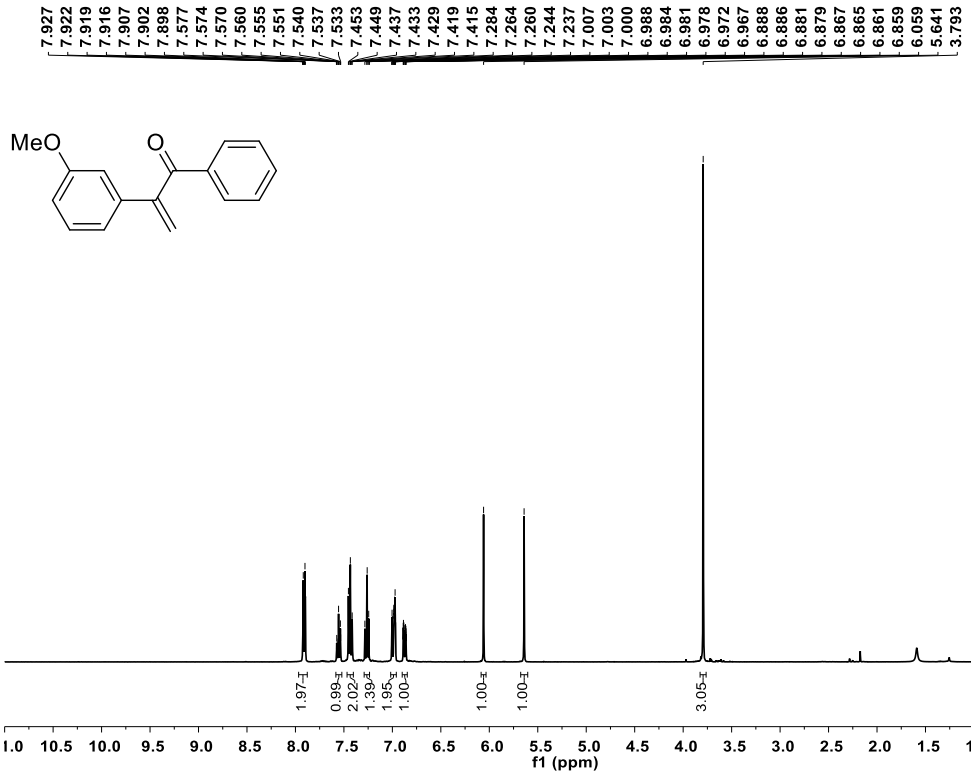


^{19}F NMR

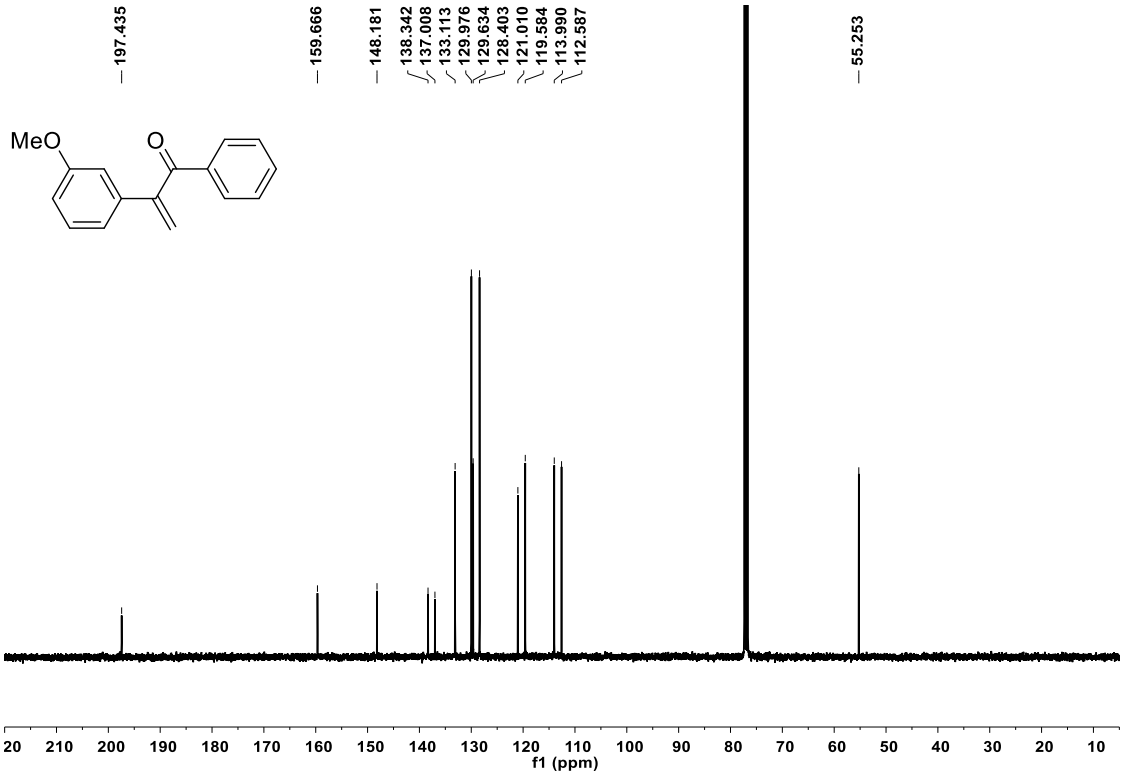

F
O
-112.676
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

3j

^{1}H NMR

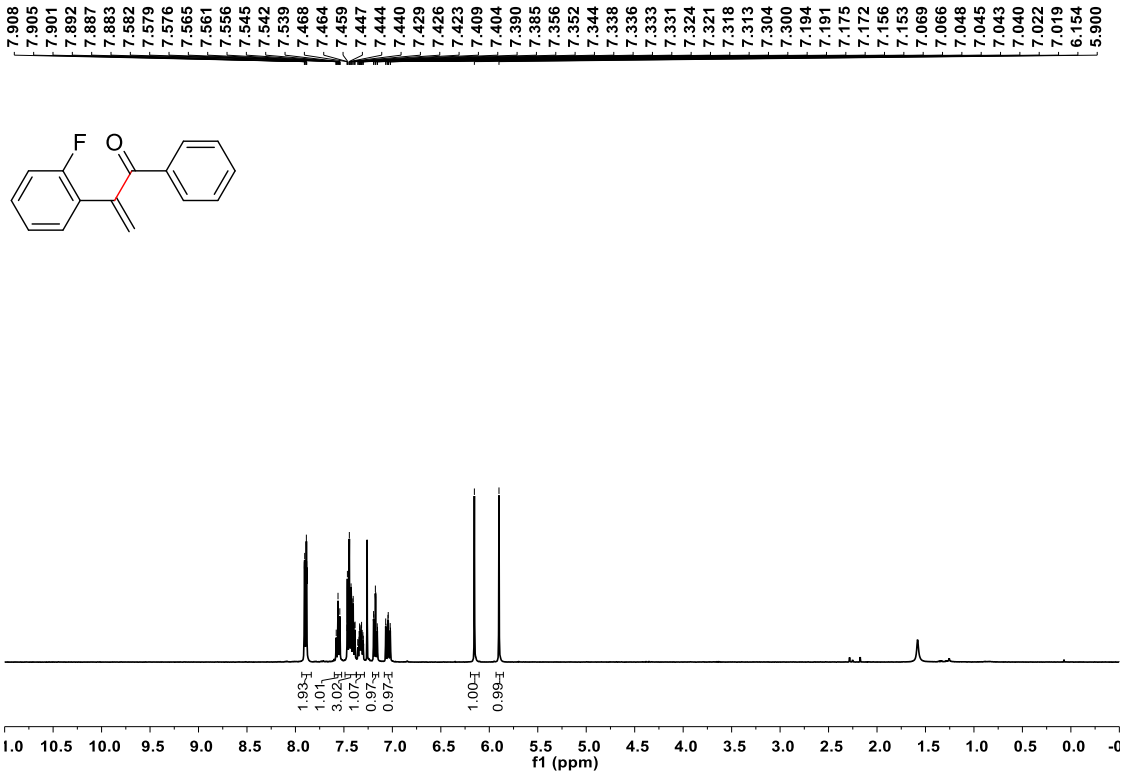


^{13}C NMR

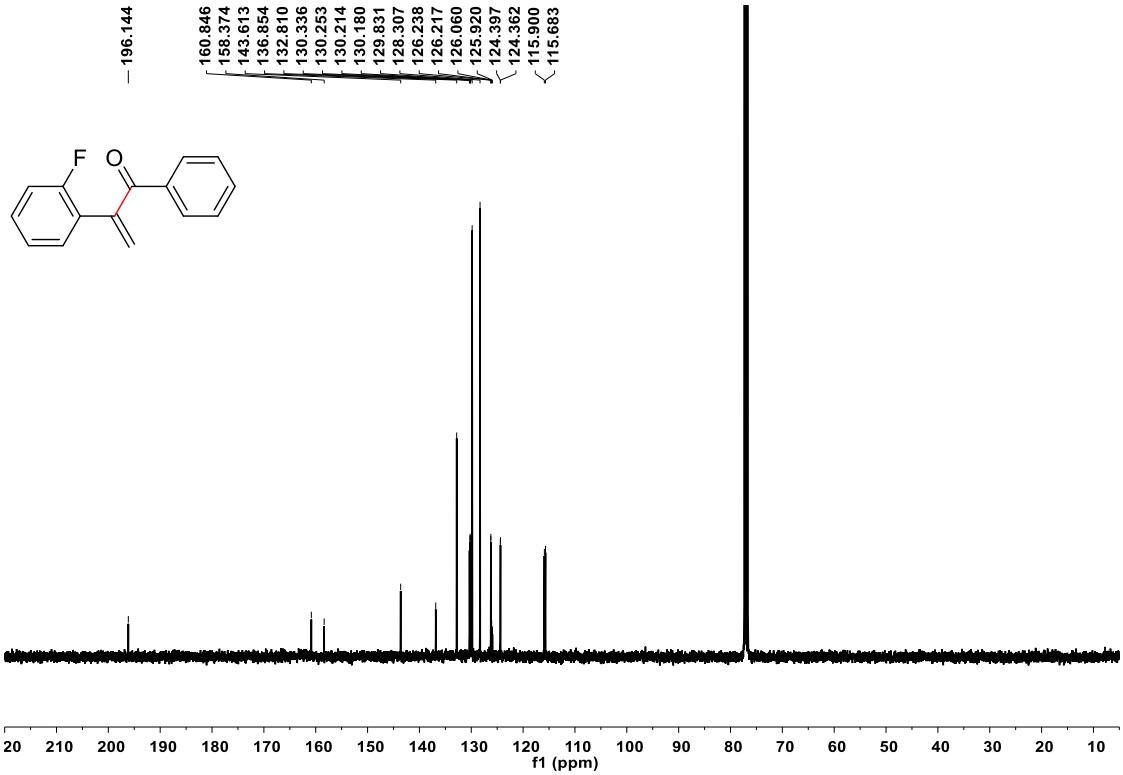


3k

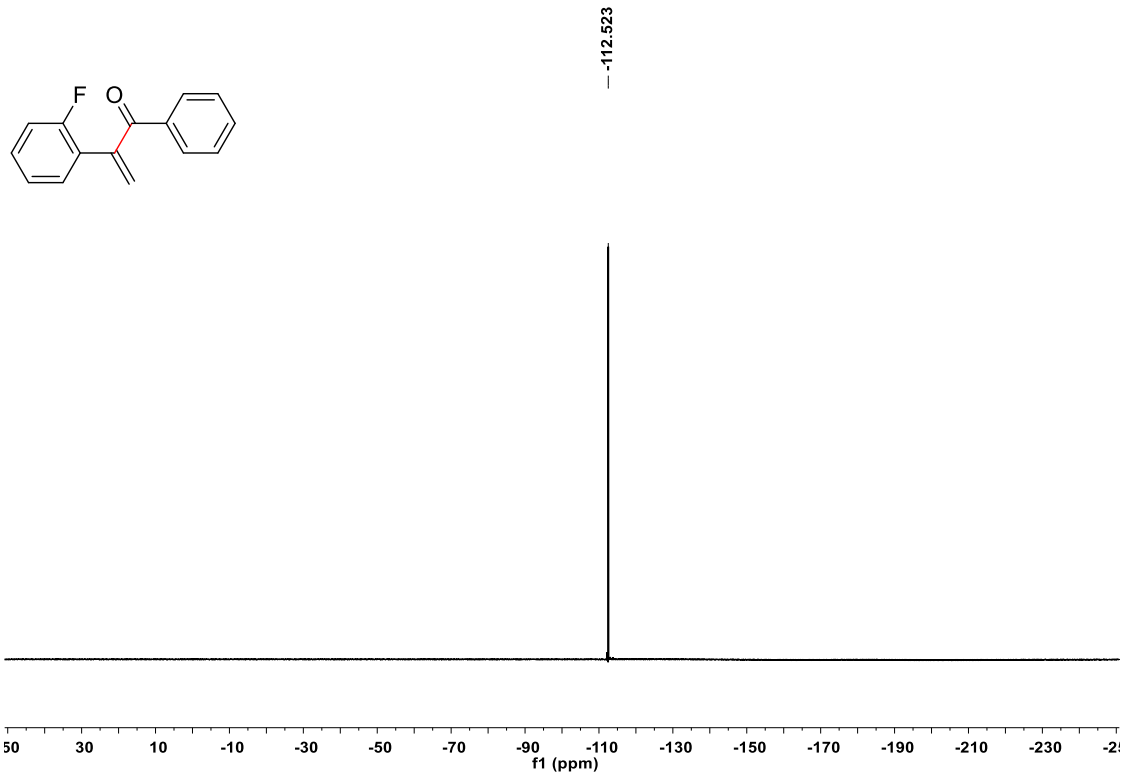
^{1}H NMR



^{13}C NMR

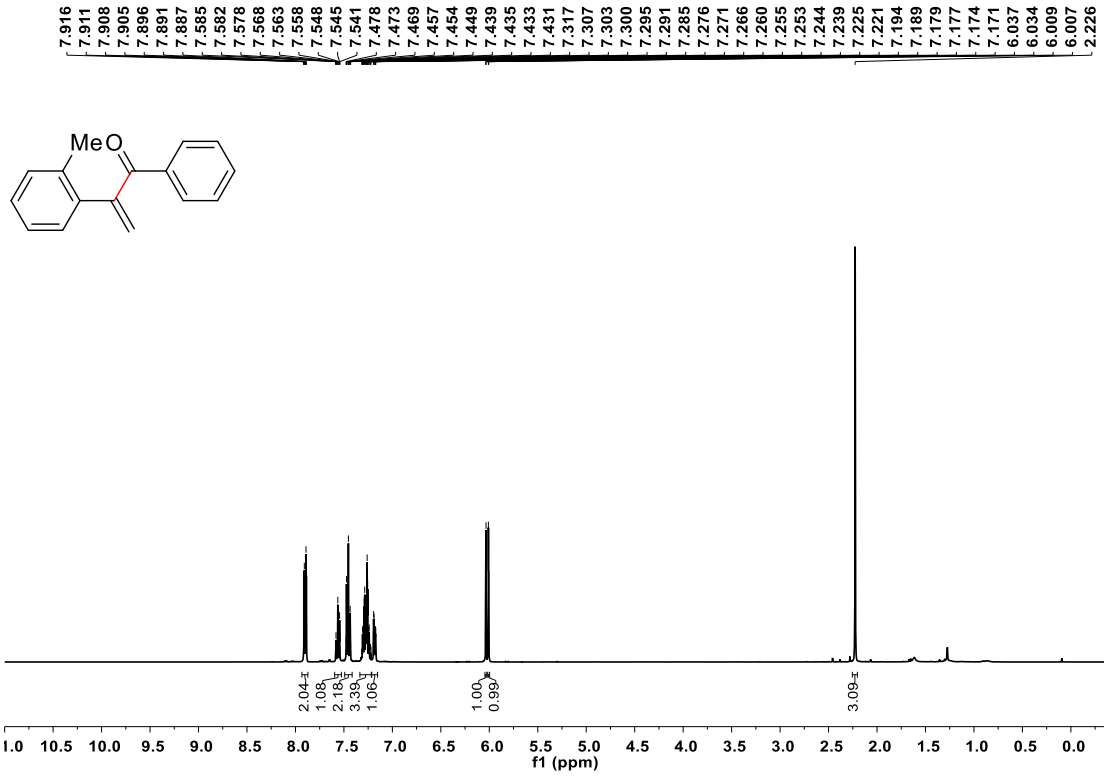


^{19}F NMR

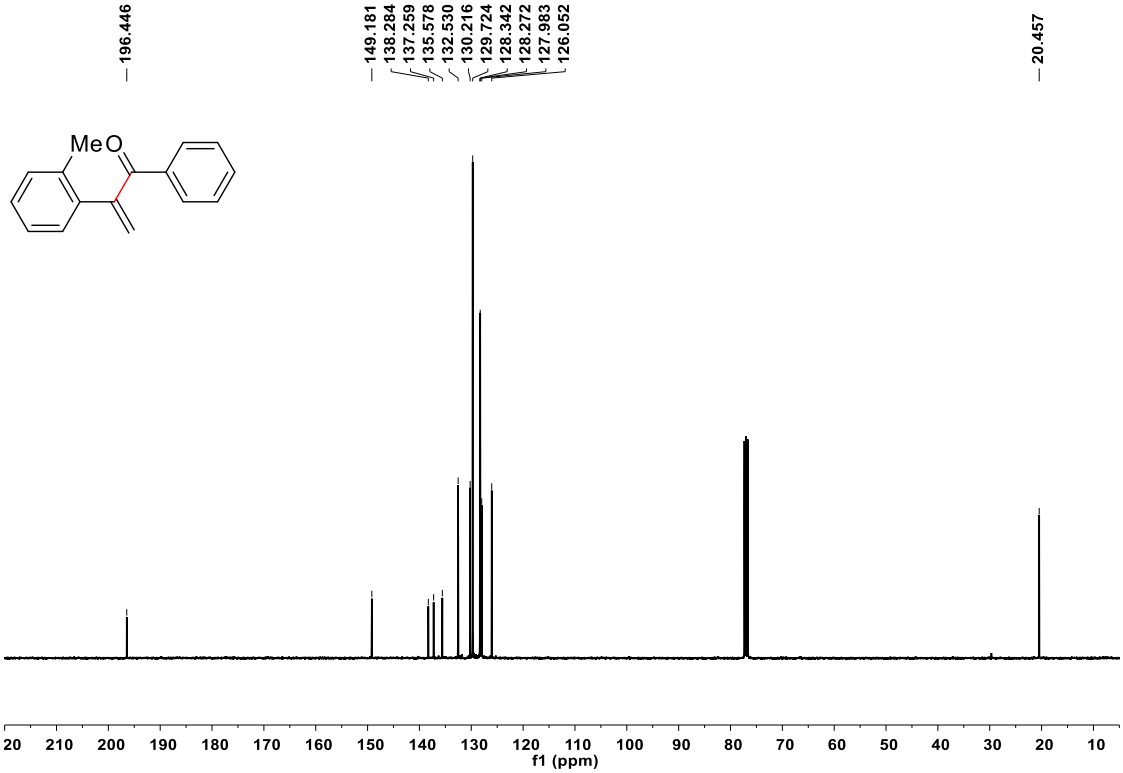

F
O
-112.523
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

3l

^{1}H NMR

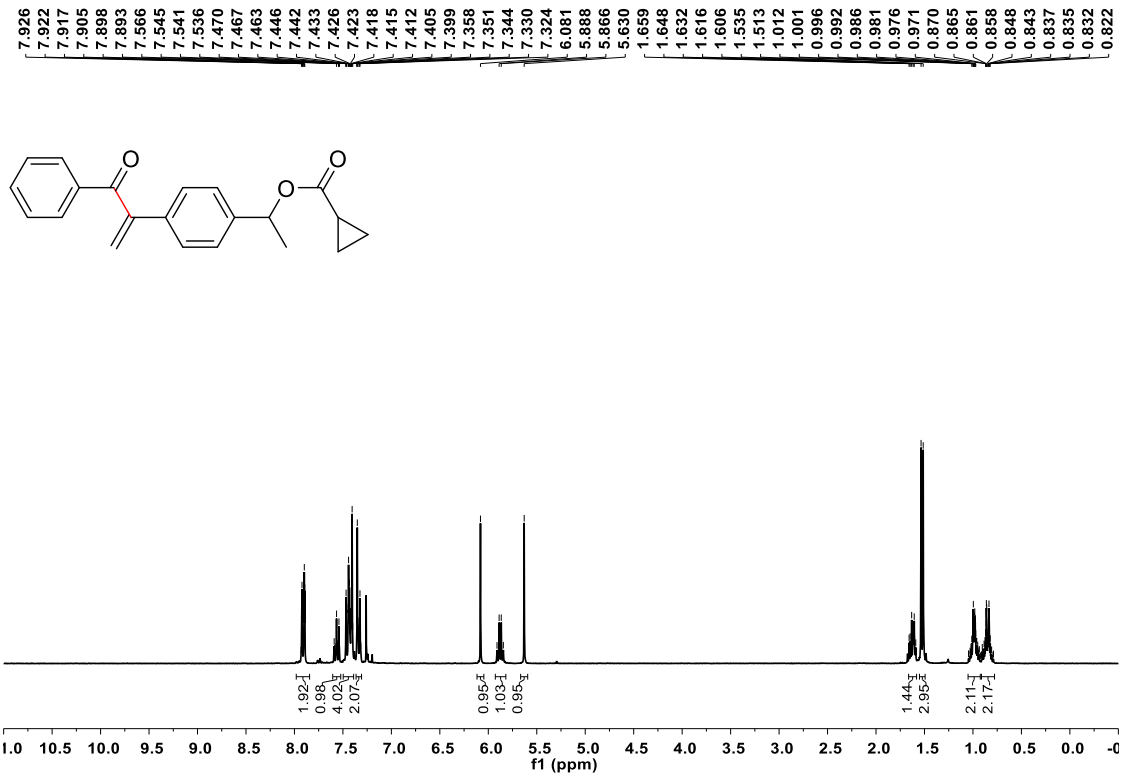


^{13}C NMR

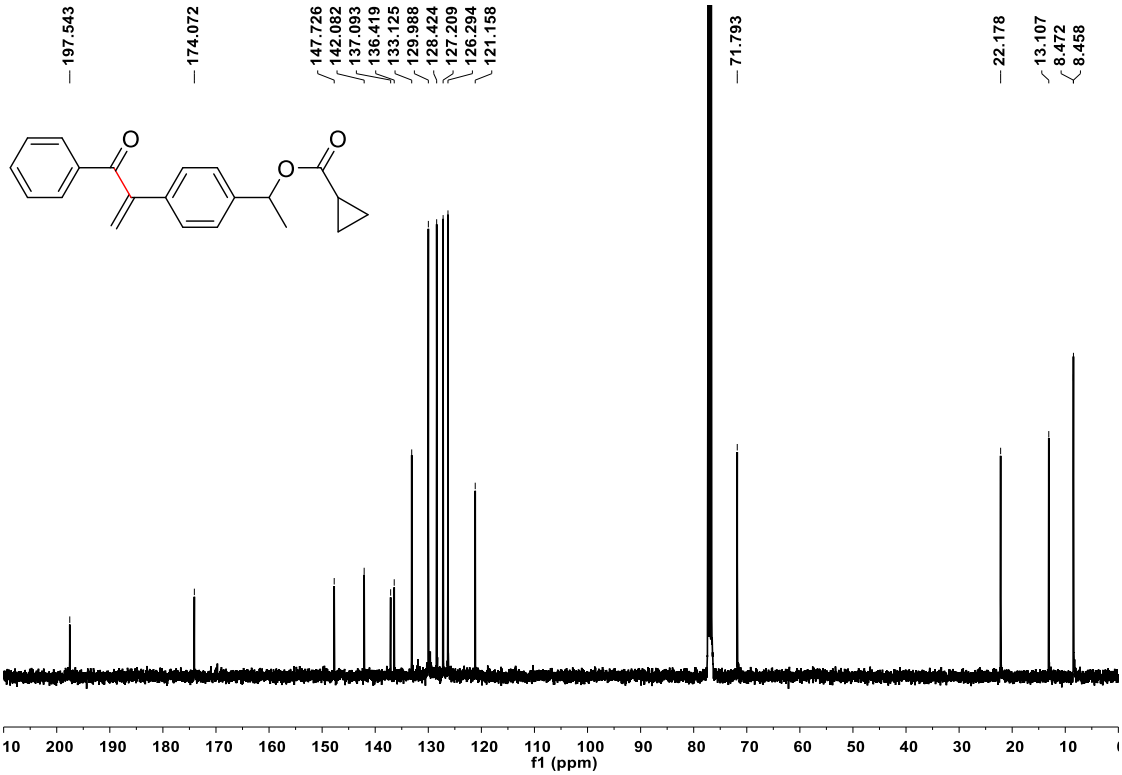


3m

^{1}H NMR

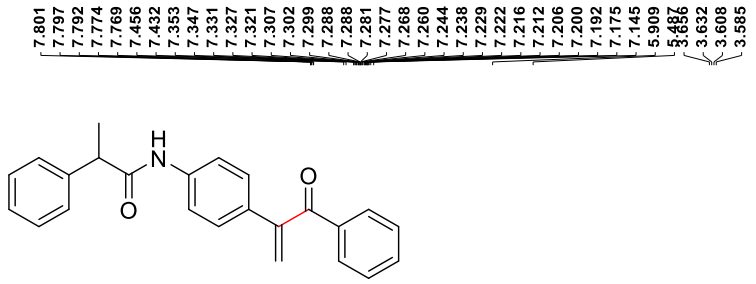


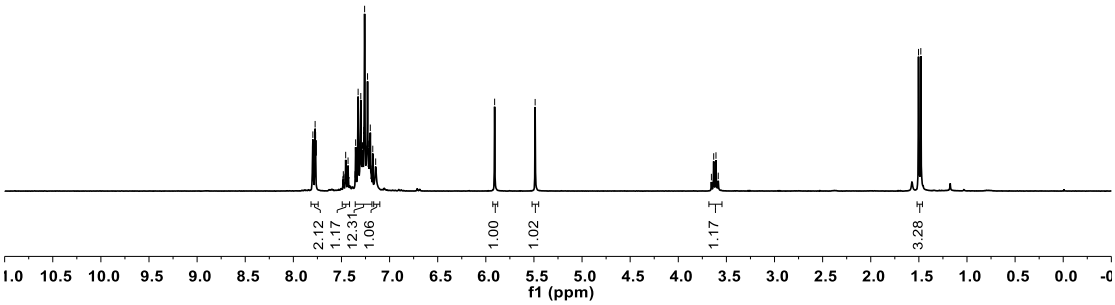
^{13}C NMR



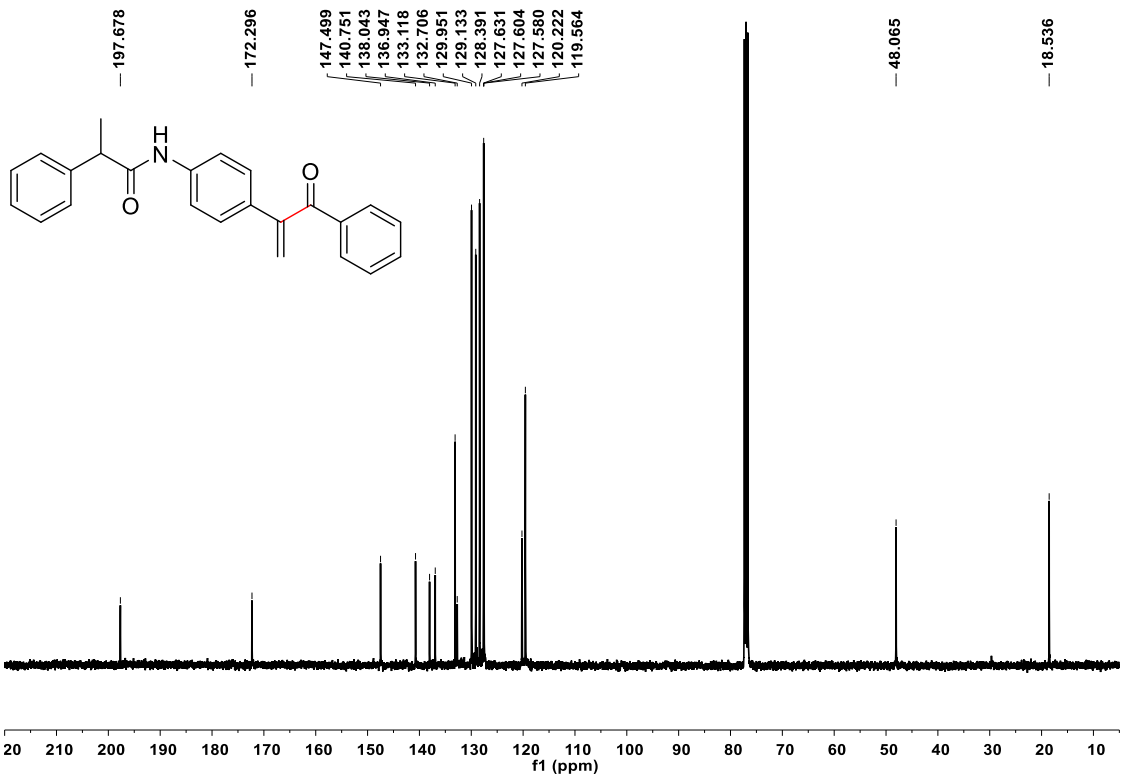
3n

^{1}H NMR



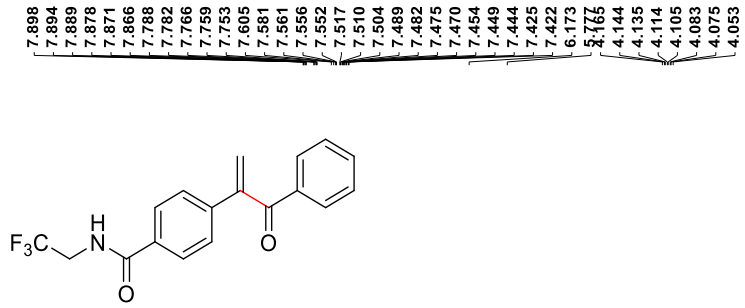


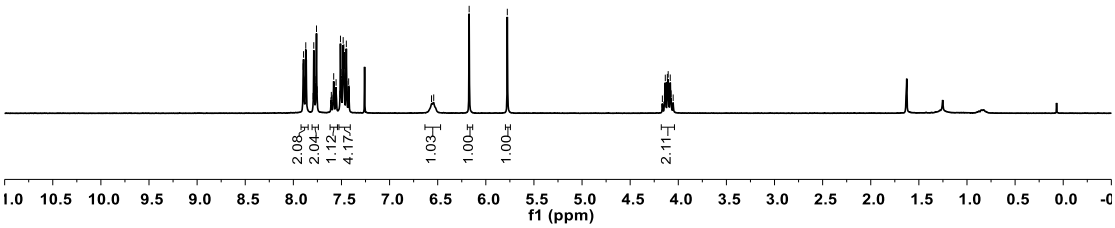
^{13}C NMR



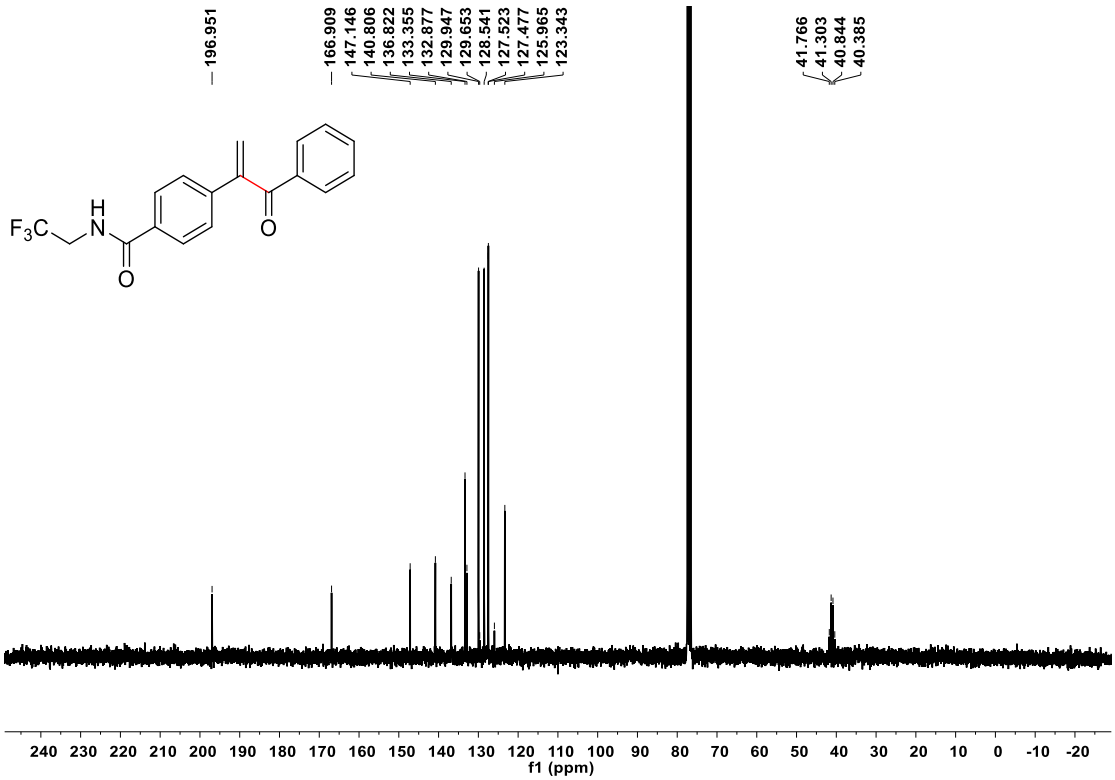
3o

^{1}H NMR

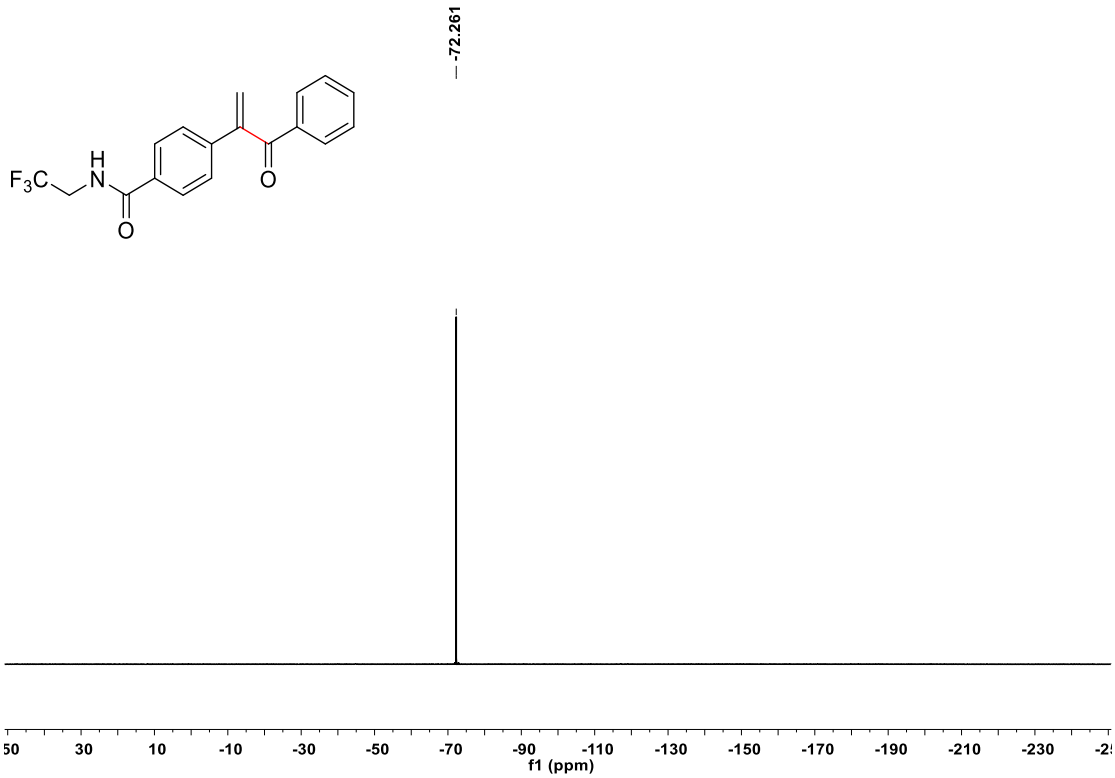




^{13}C NMR

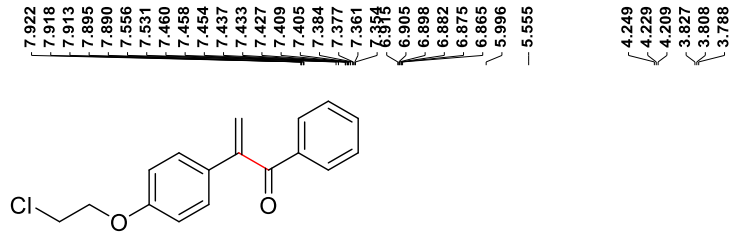


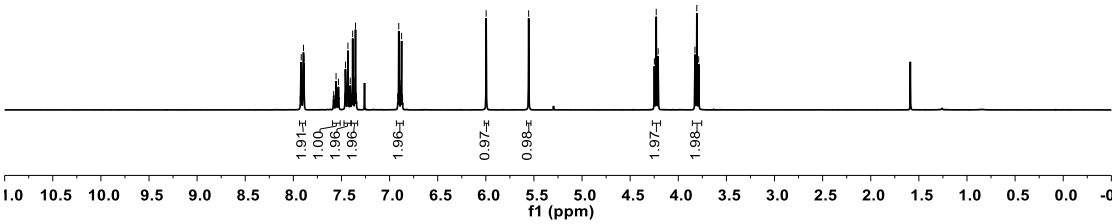
^{19}F NMR


-72.261
F3C
H
N
O
O
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

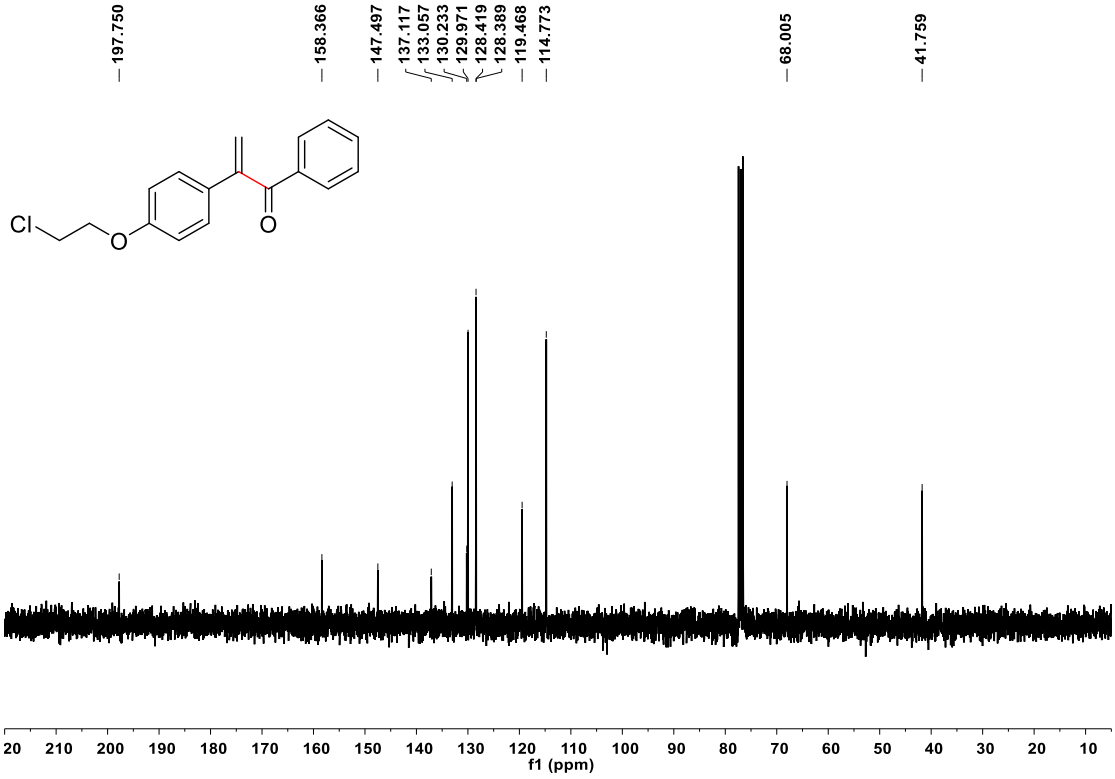
3p

^{1}H NMR



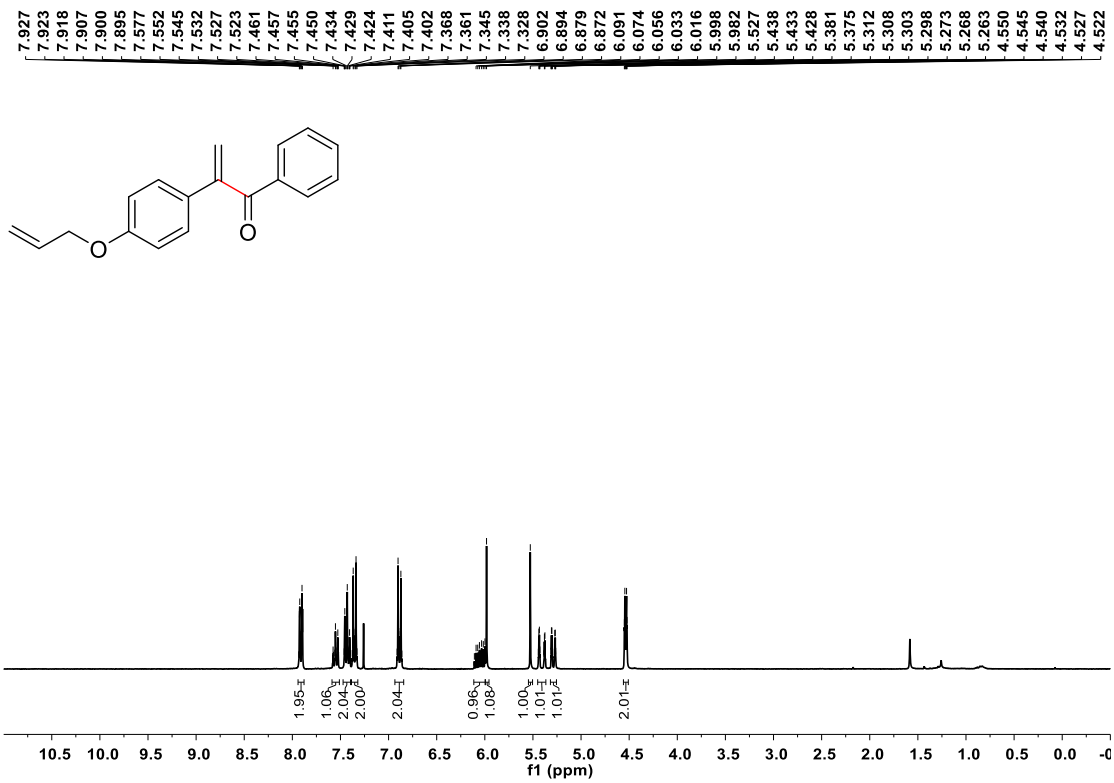


^{13}C NMR

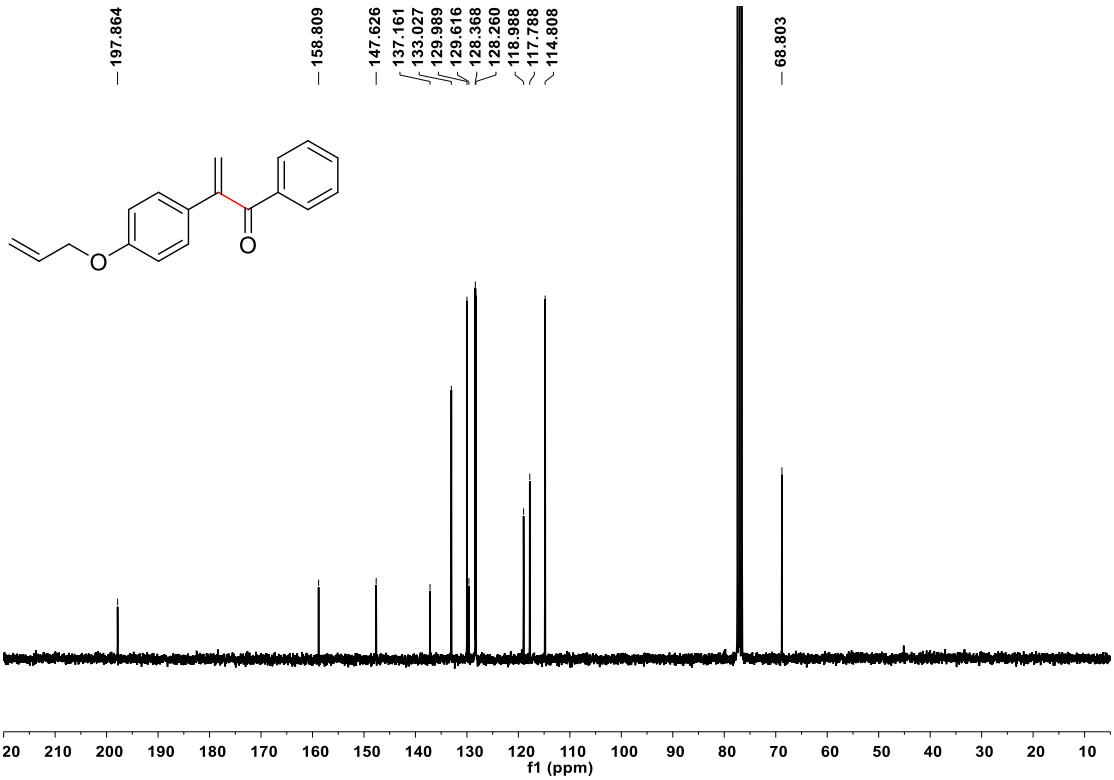


3q

^{1}H NMR

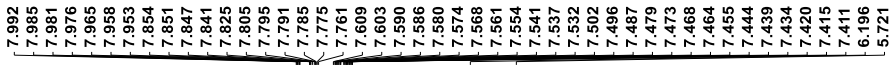


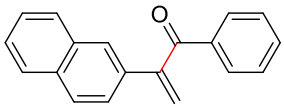
^{13}C NMR

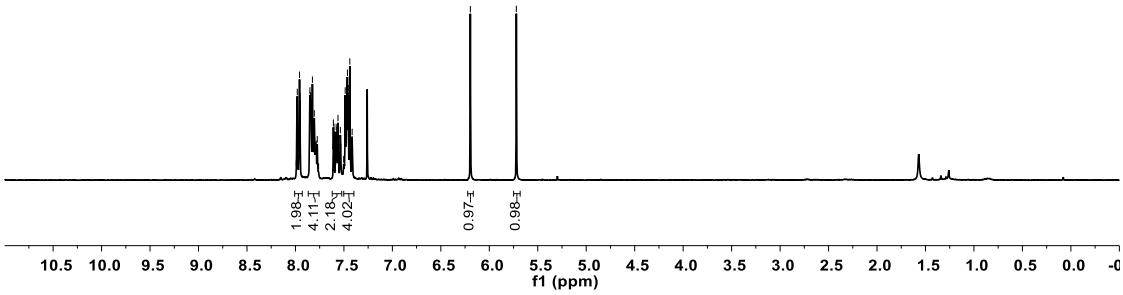


3r

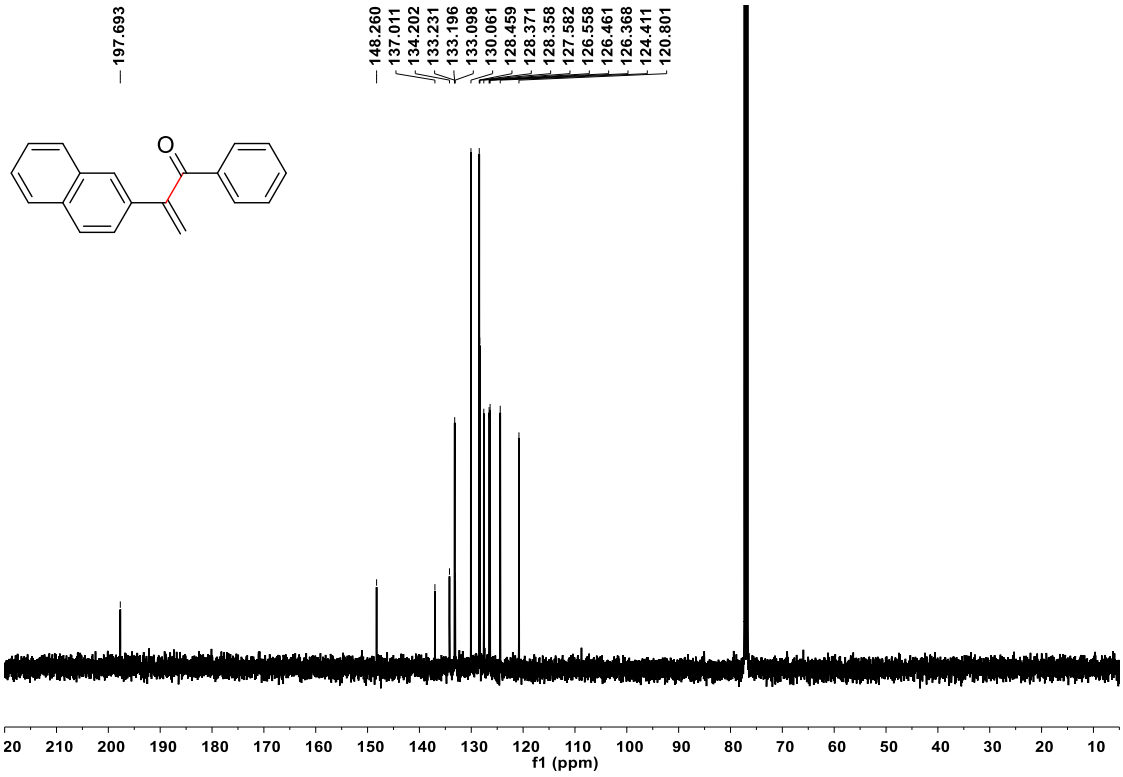
^{1}H NMR





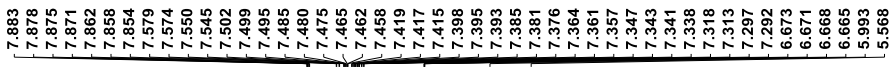


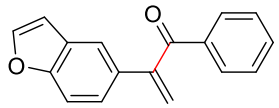
^{13}C NMR

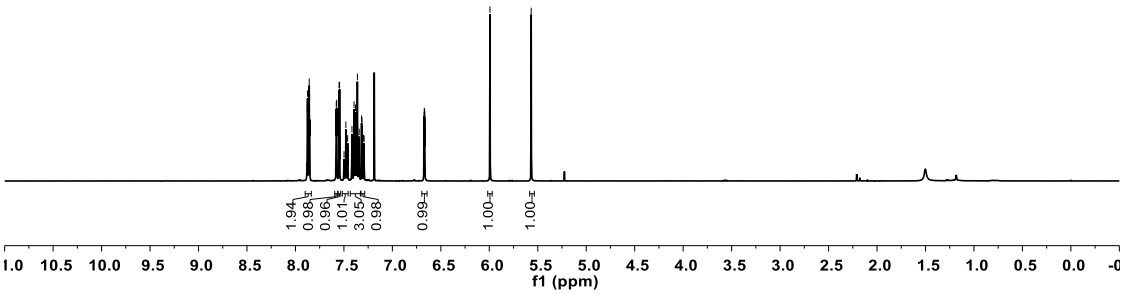


3s

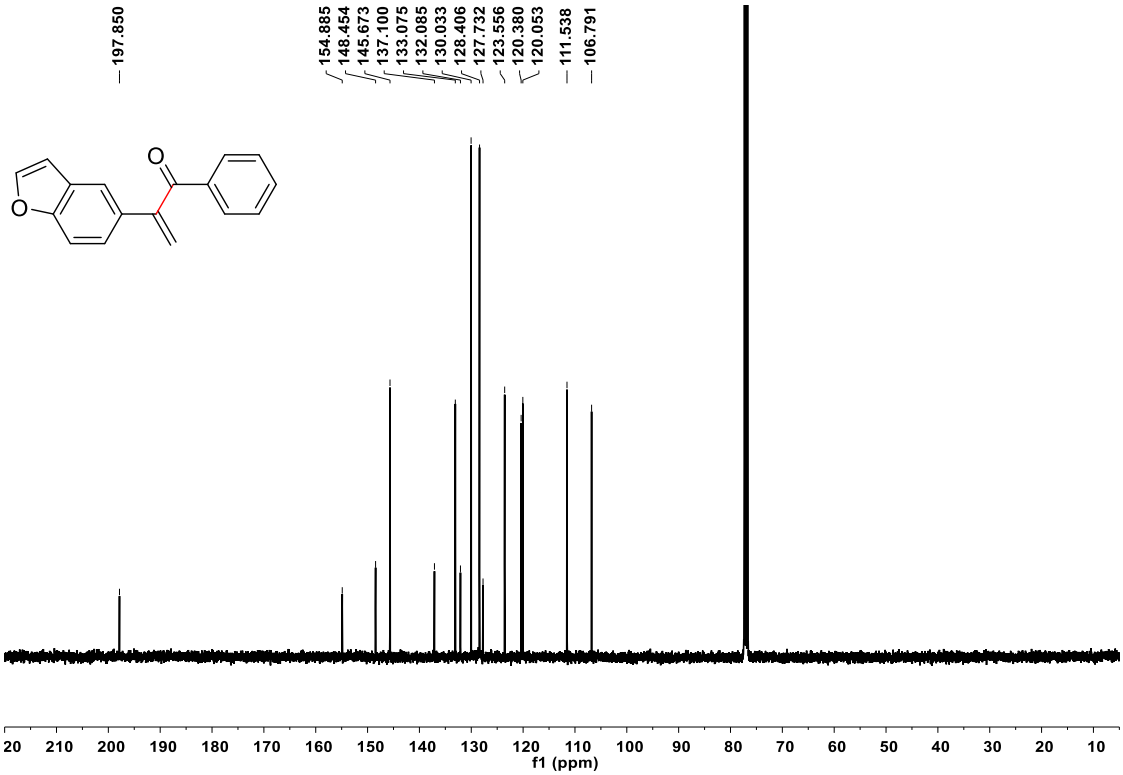
^{1}H NMR





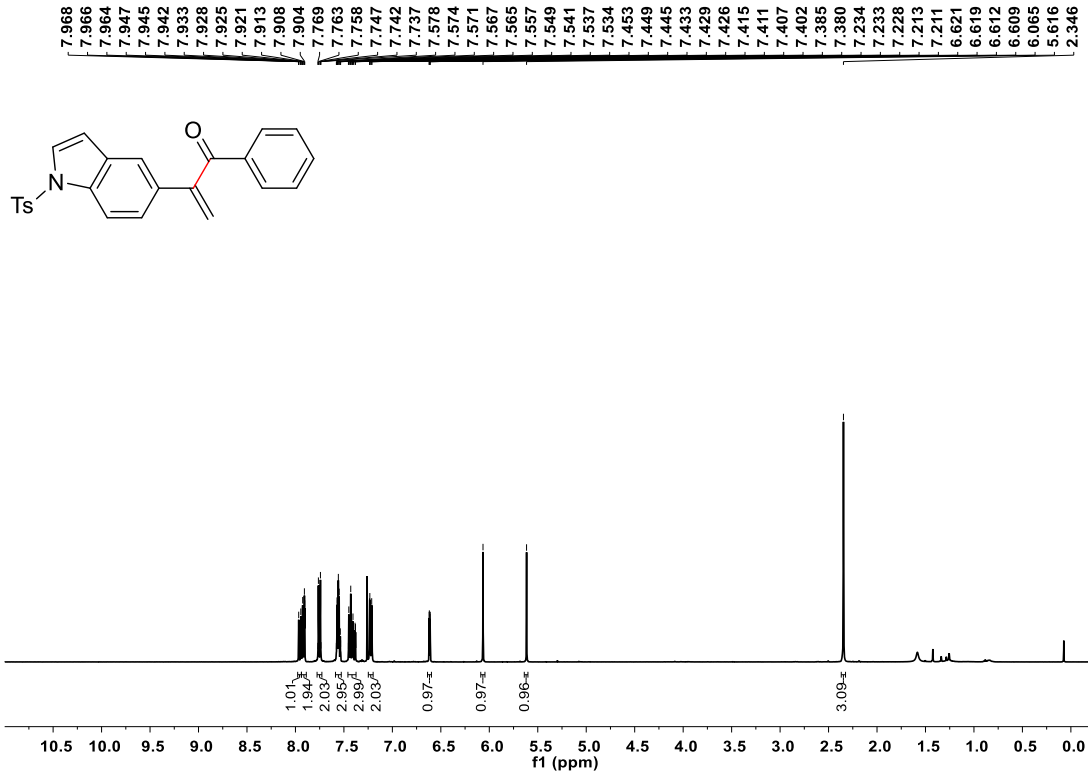


^{13}C NMR

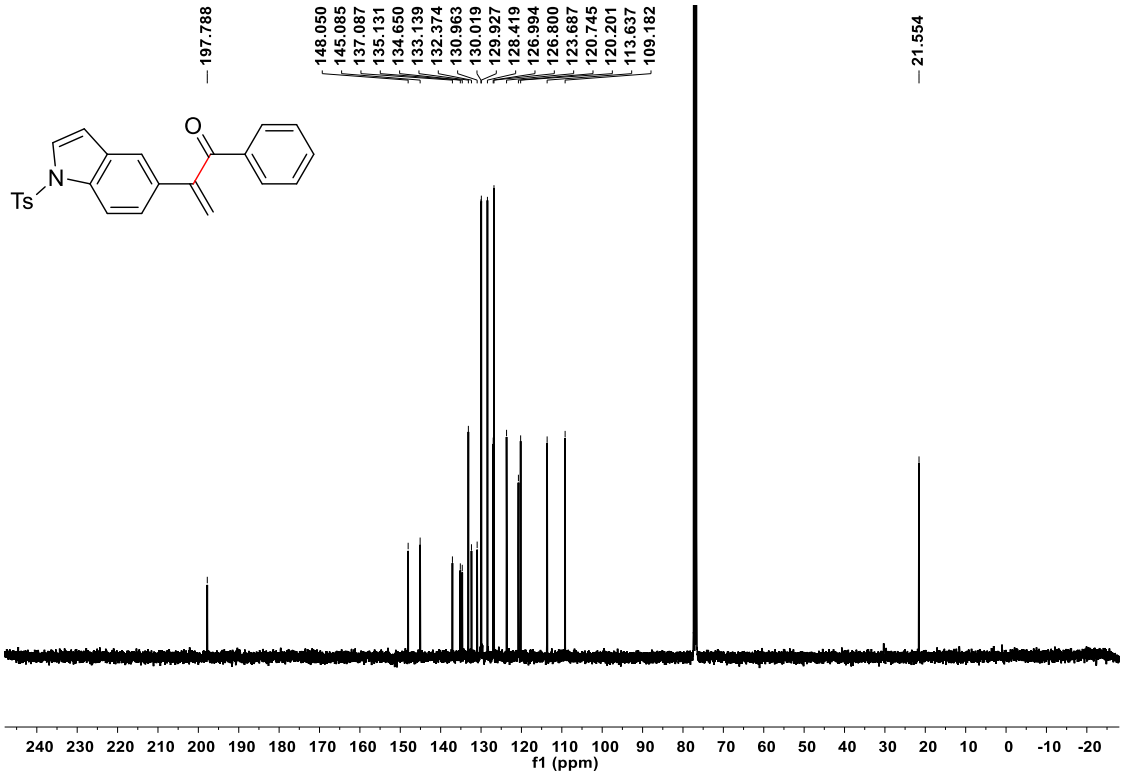


3t

^{1}H NMR

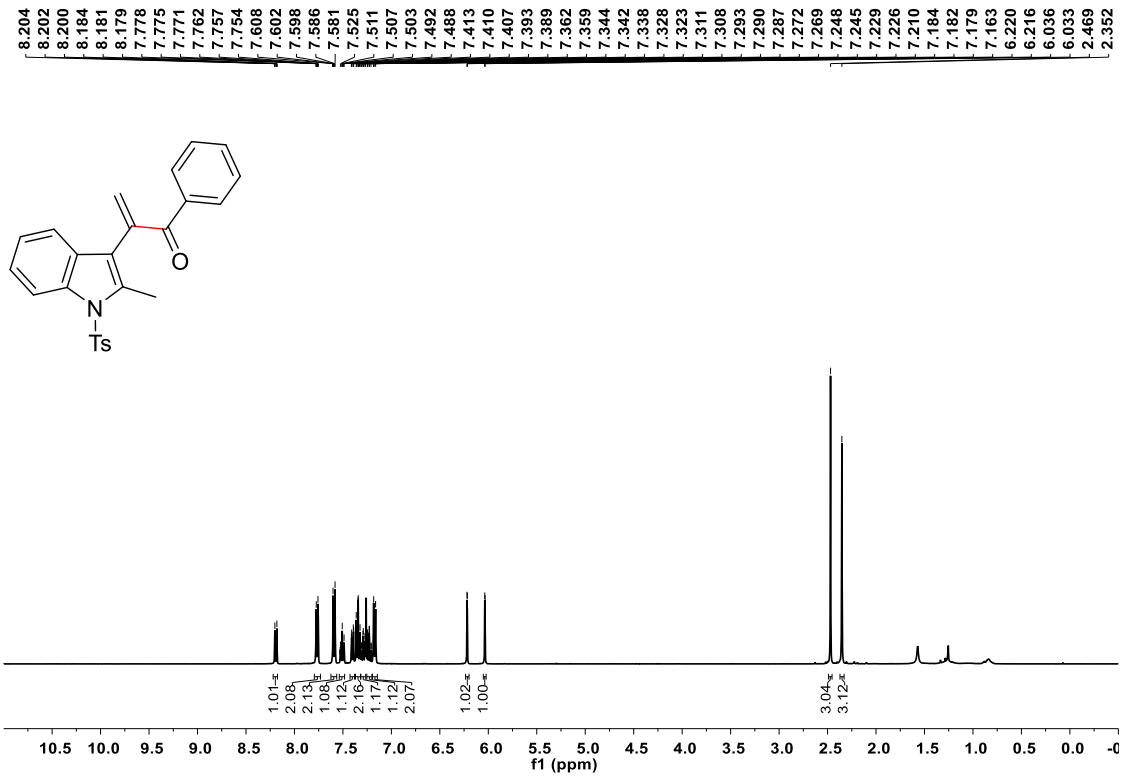


^{13}C NMR

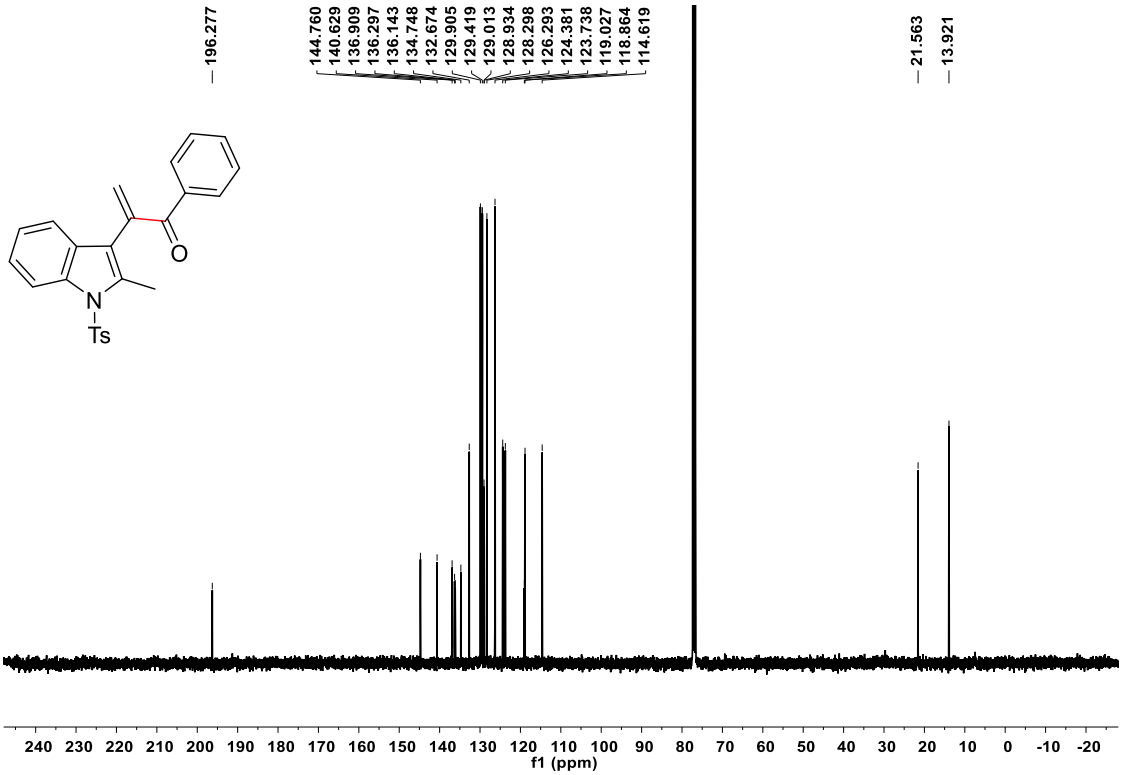


3u

^{1}H NMR

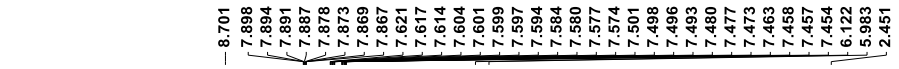


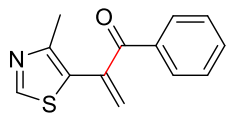
^{13}C NMR

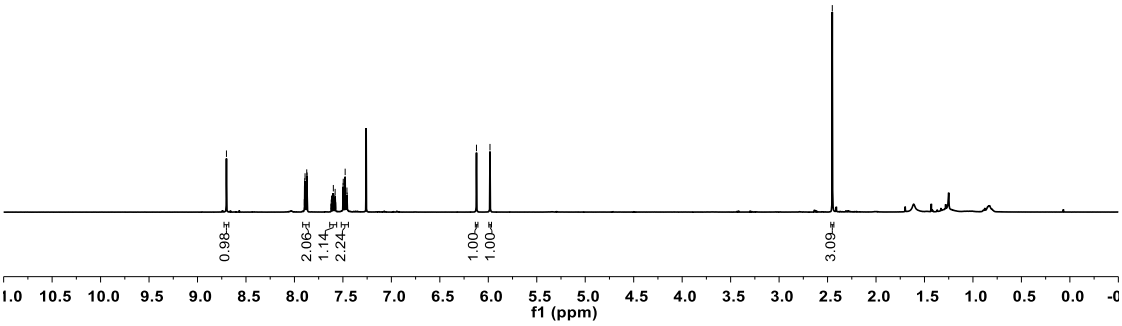


3v

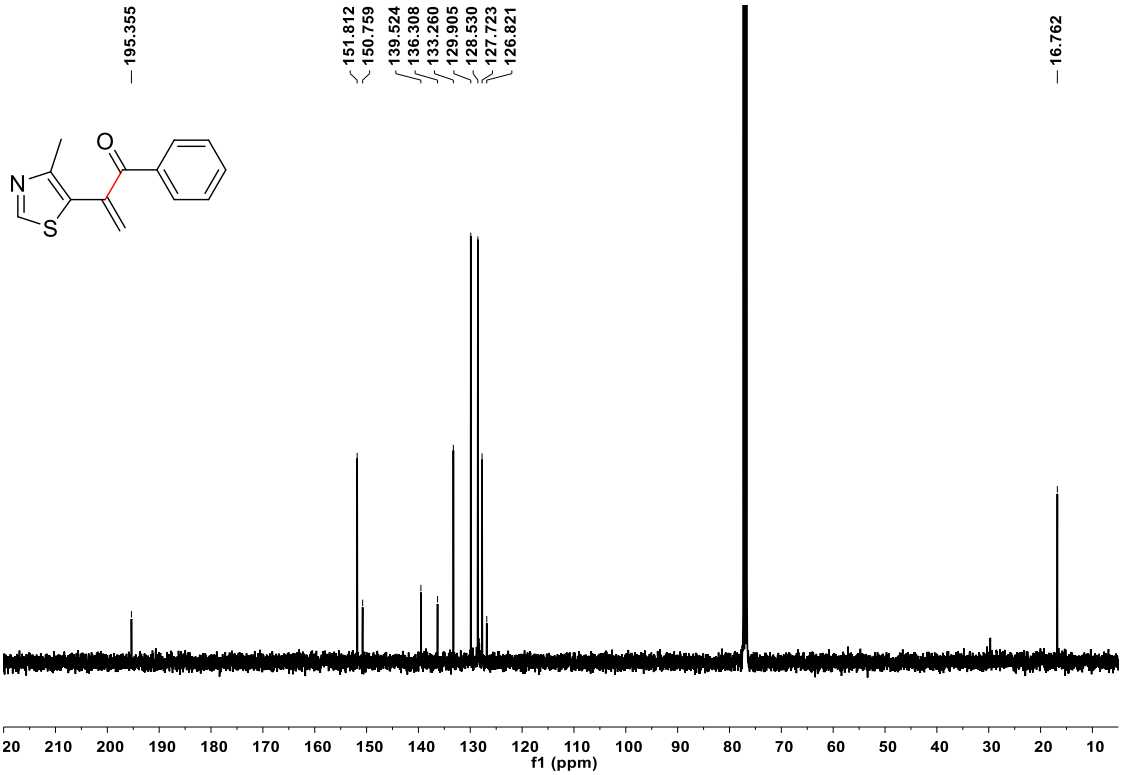
^{1}H NMR





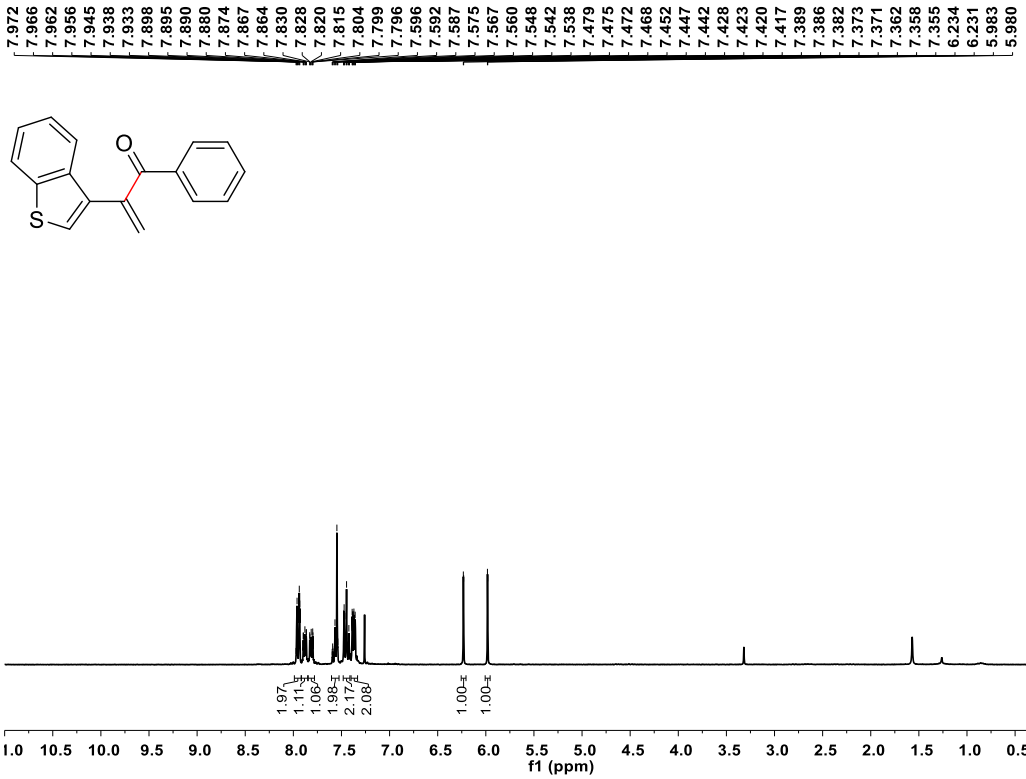


^{13}C NMR

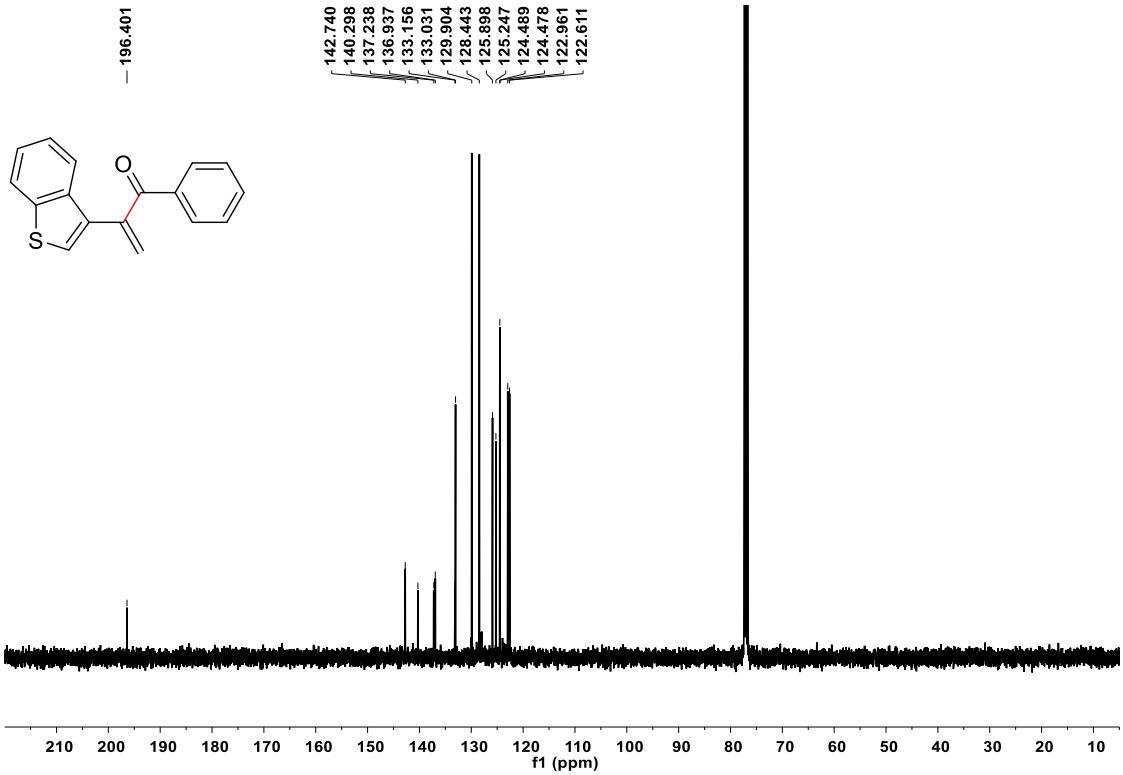


3w

^{1}H NMR

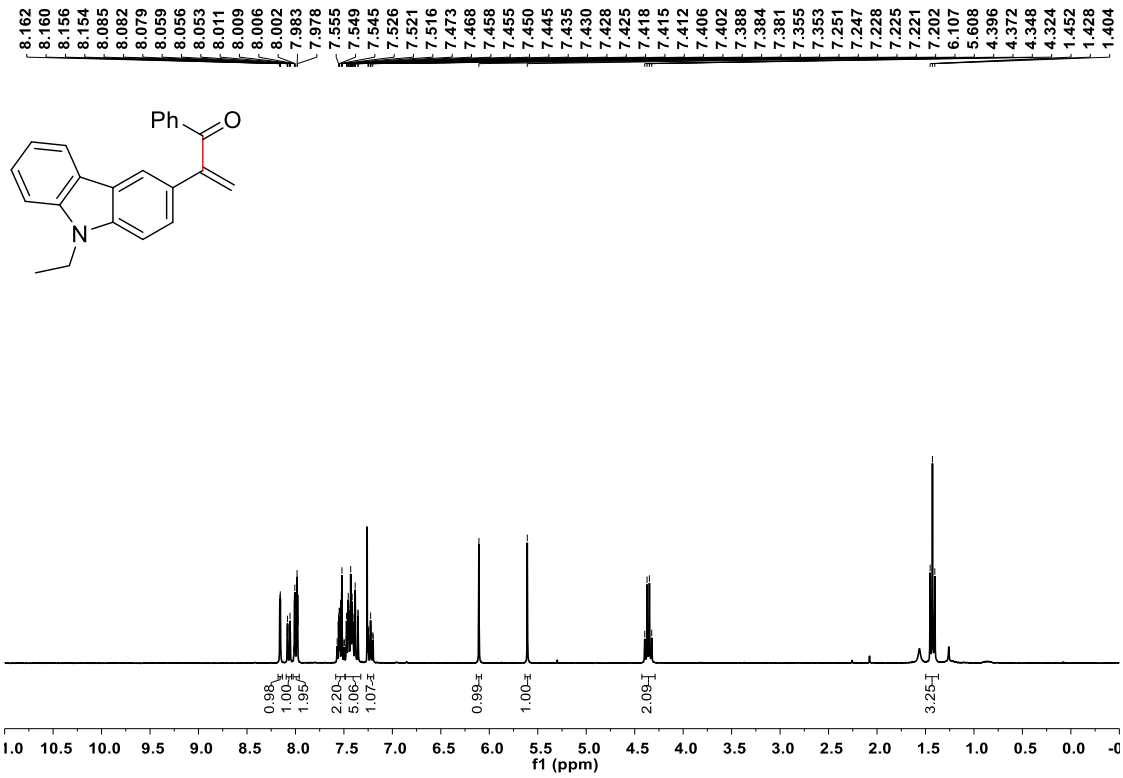


^{13}C NMR

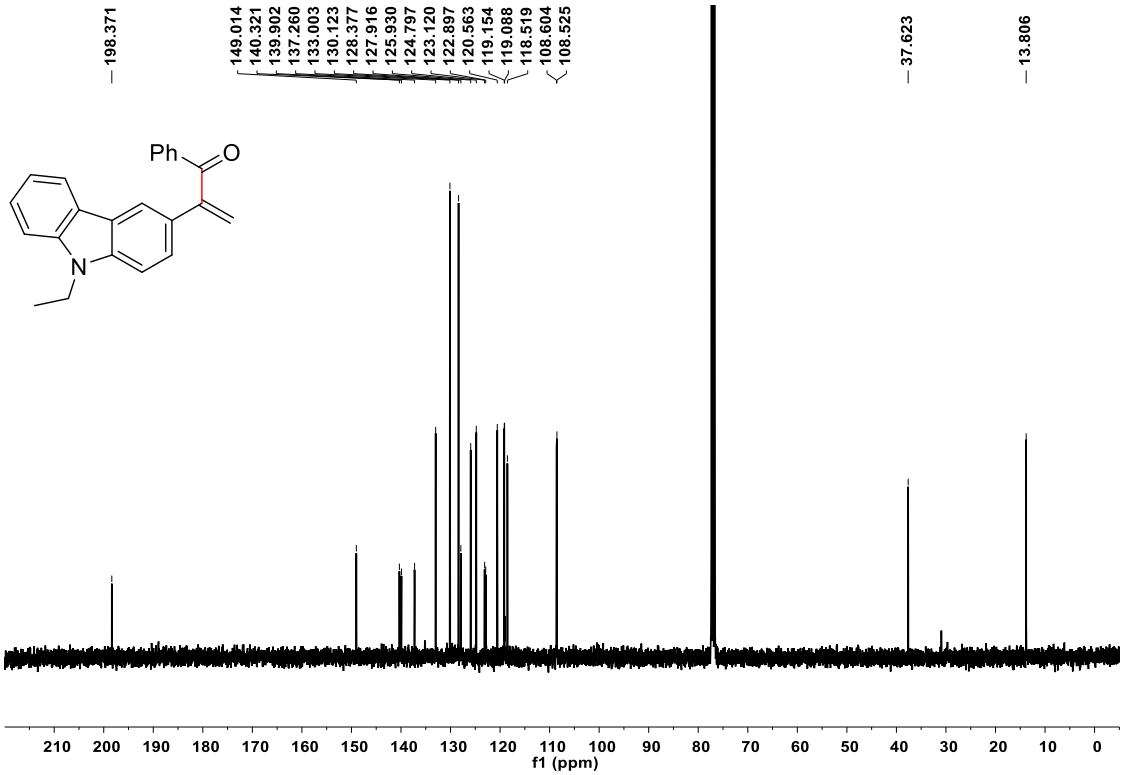


3x

^{1}H NMR

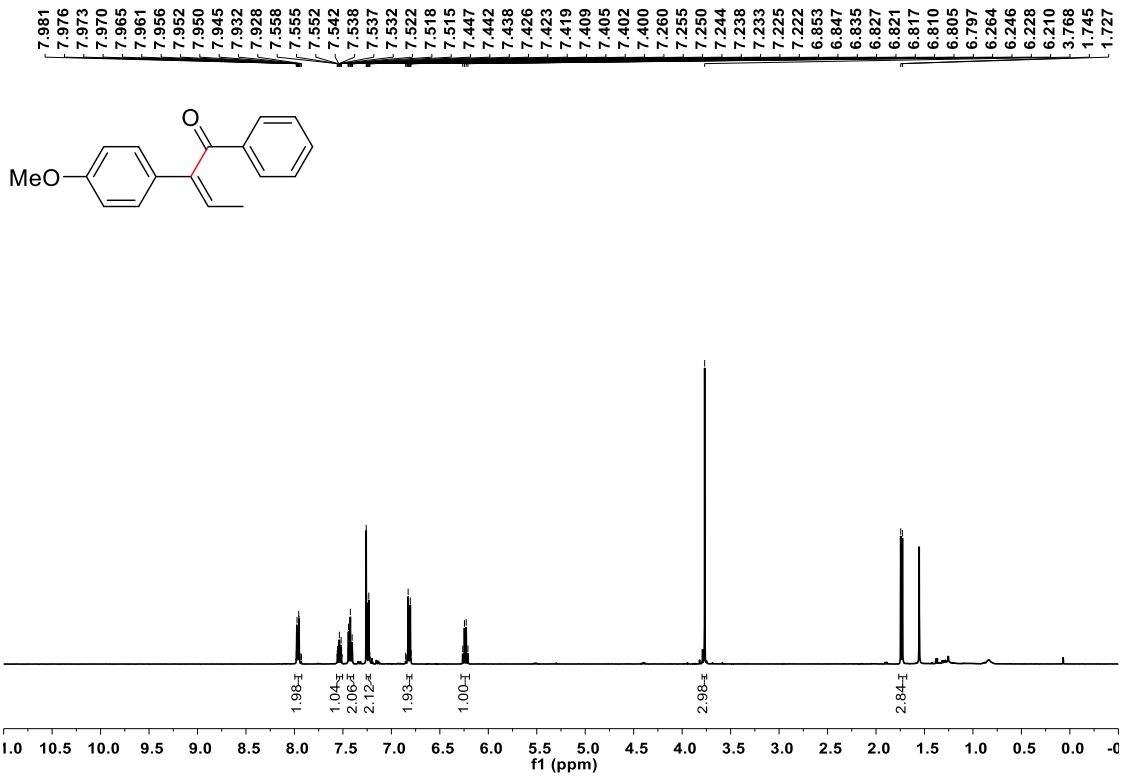


^{13}C NMR

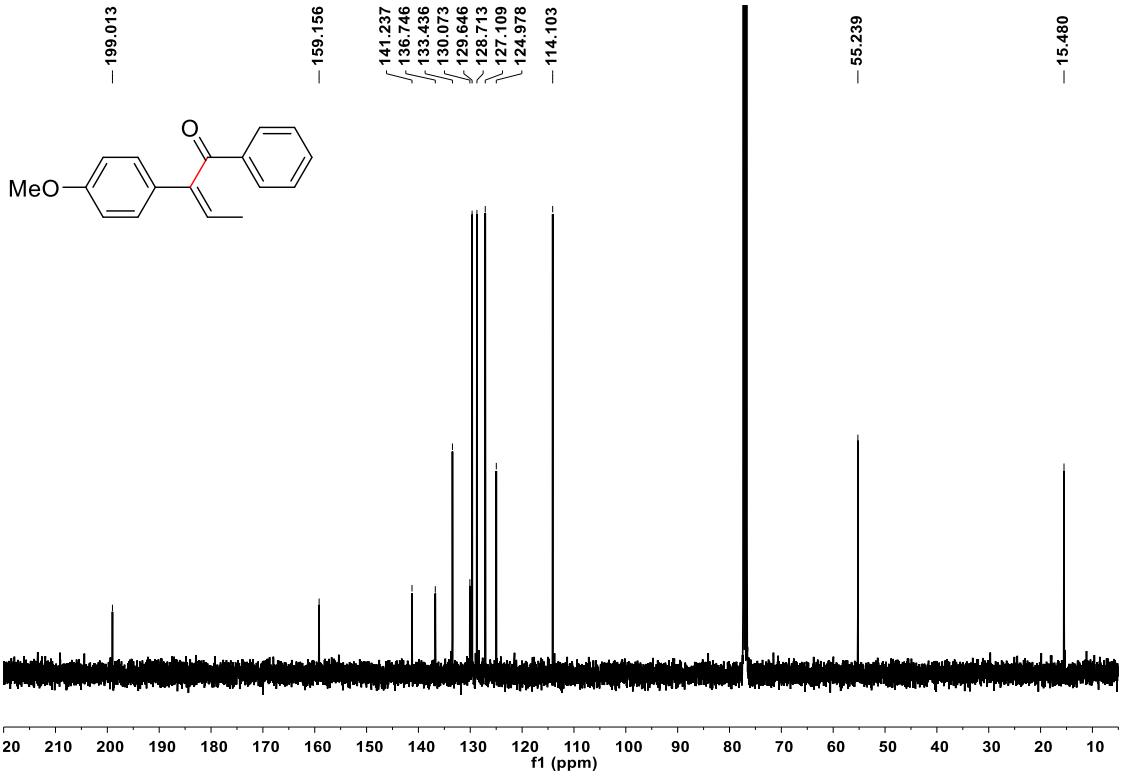


3y (Z isomer)

^{1}H NMR

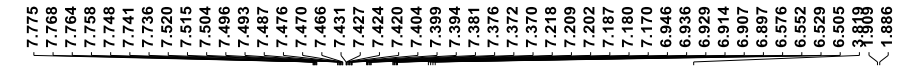


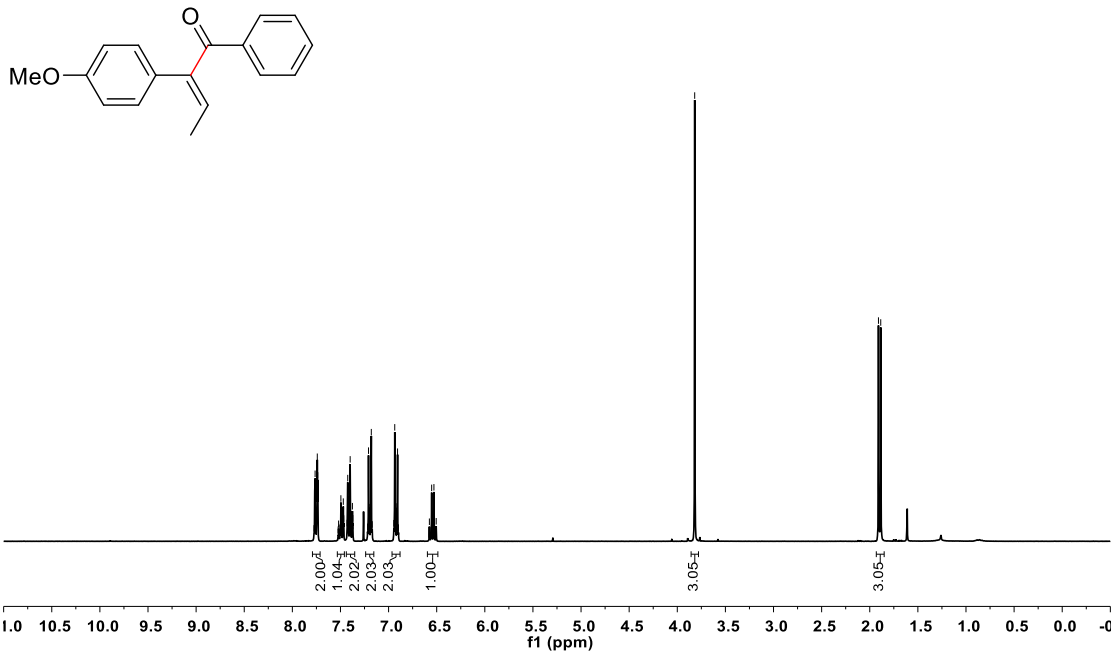
^{13}C NMR



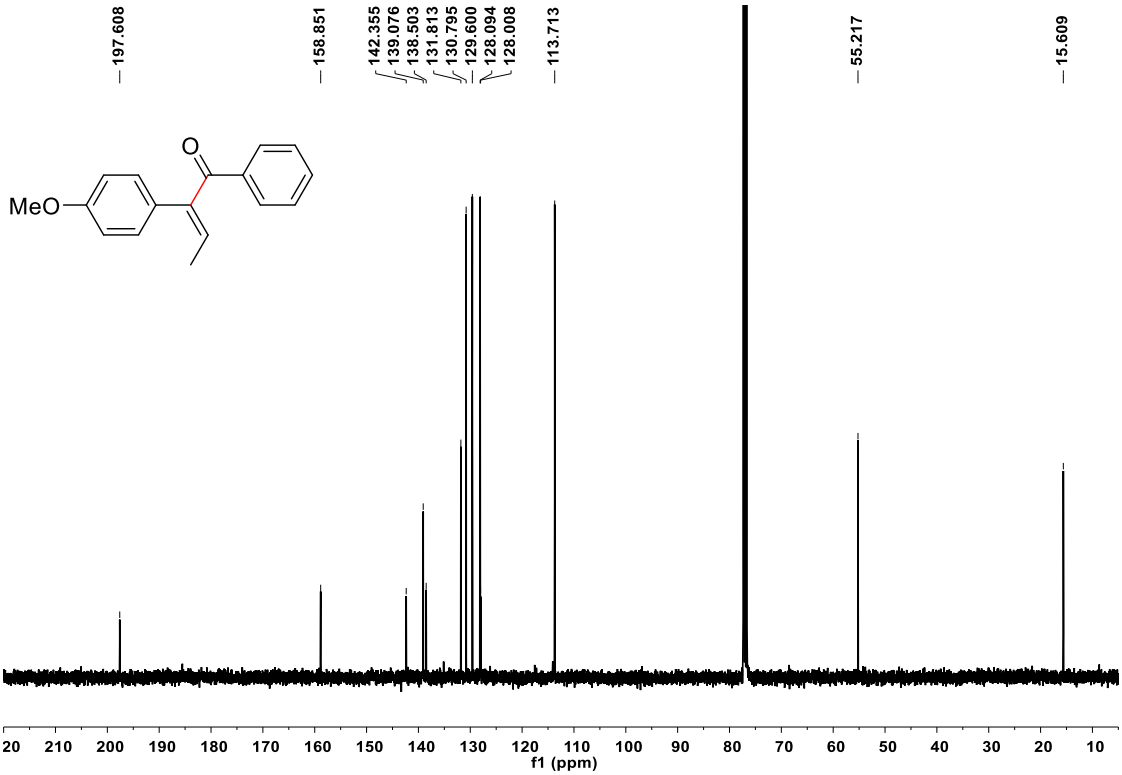
3y (E isomer)

^{1}H NMR



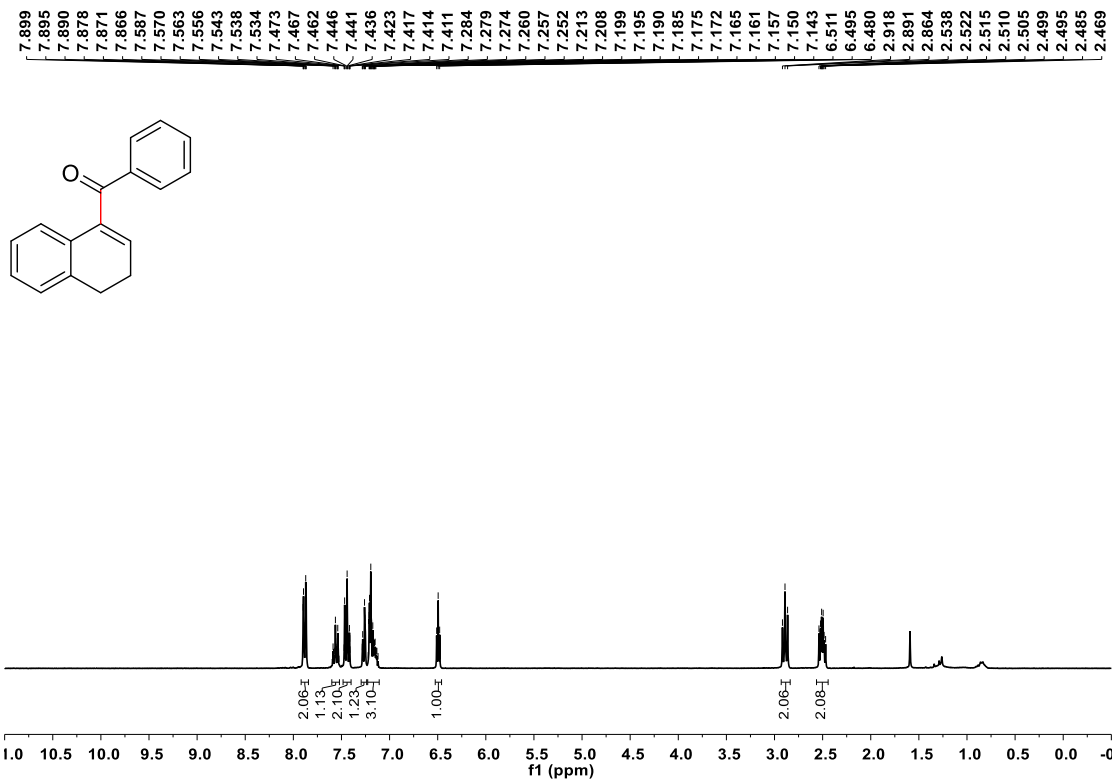


^{13}C NMR

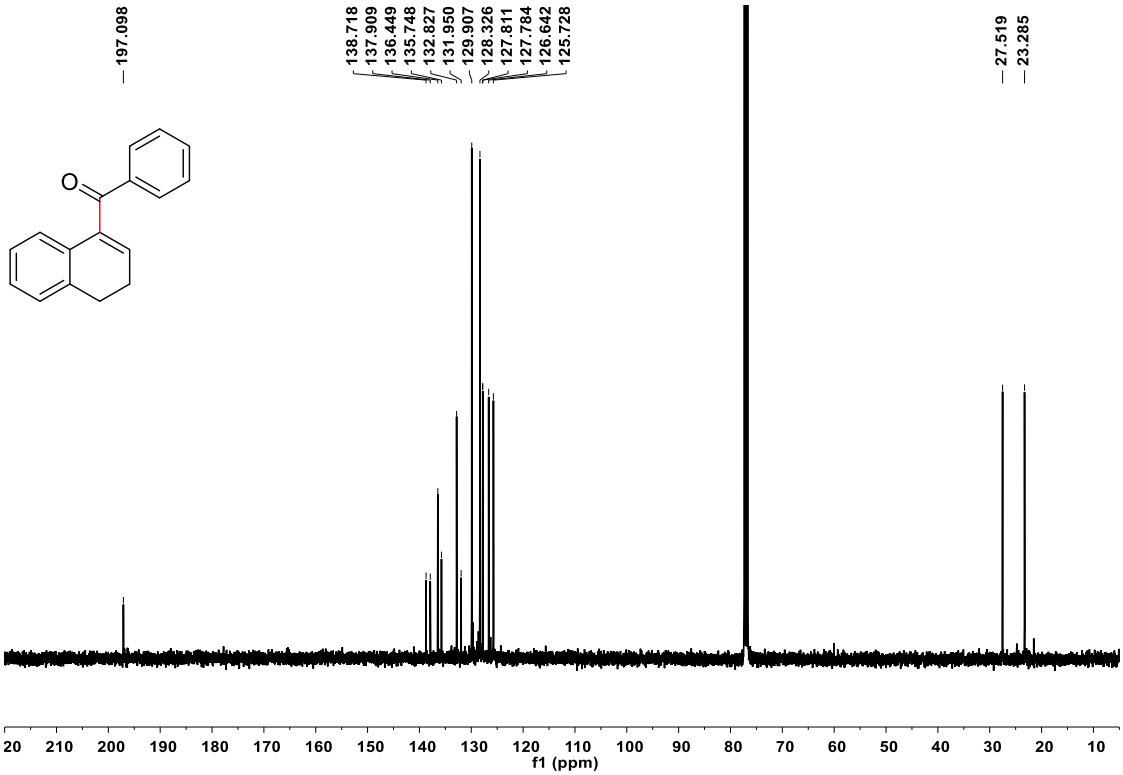


3z

^{1}H NMR

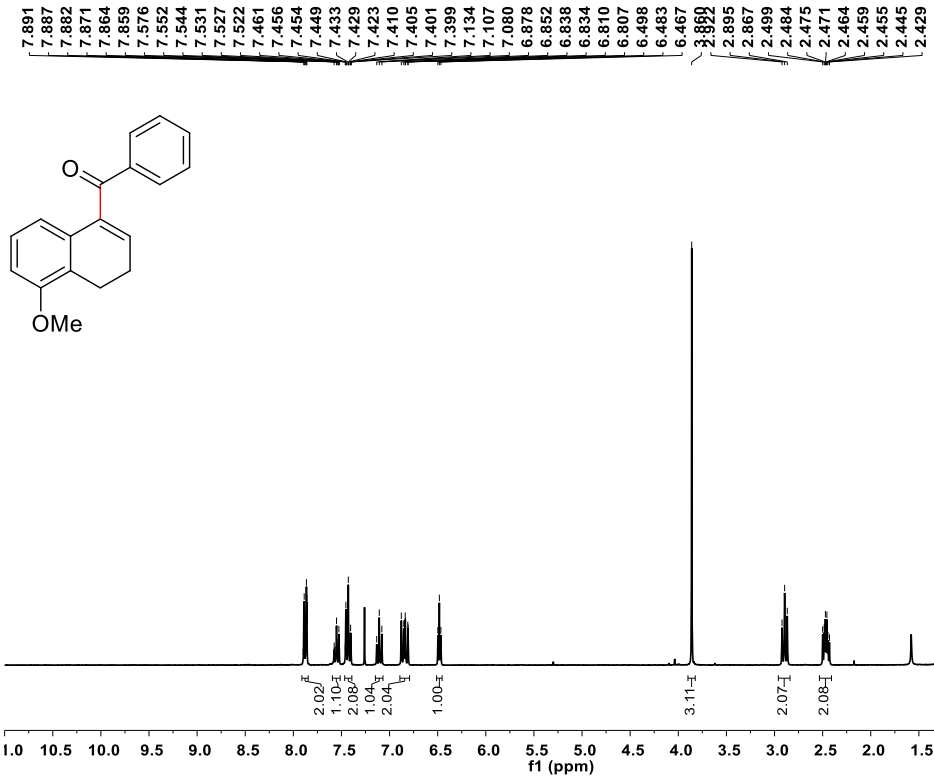


^{13}C NMR

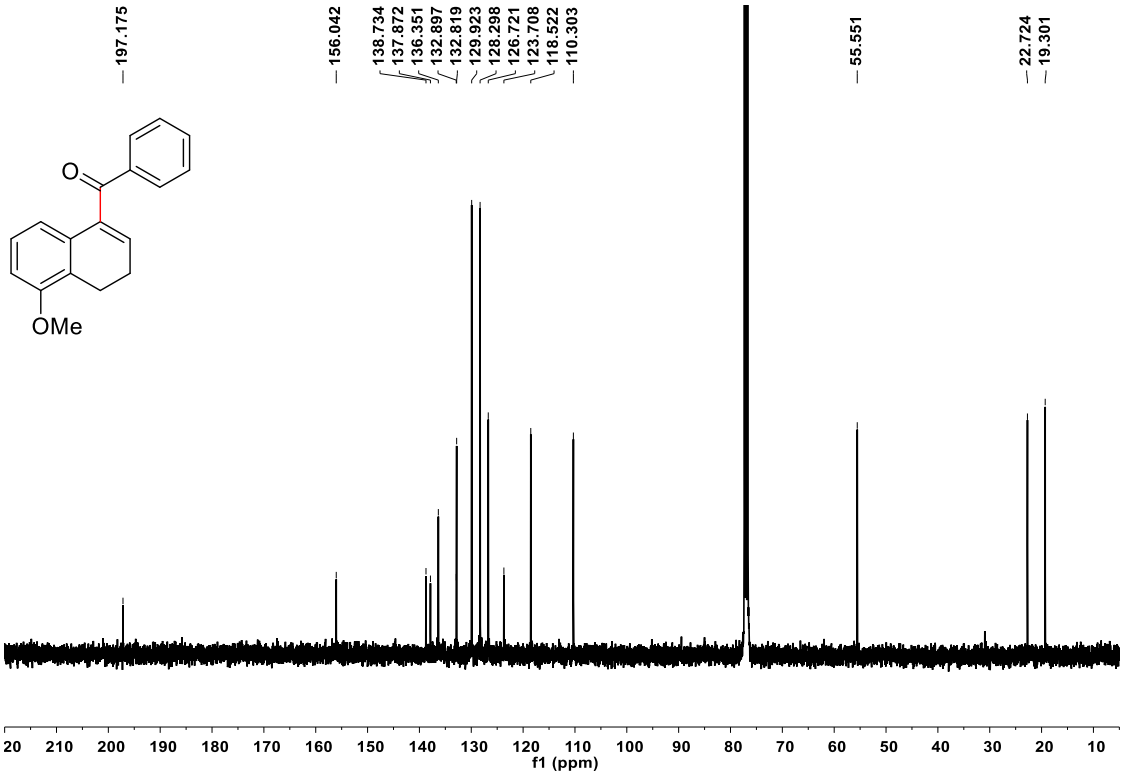


3aa

^{1}H NMR

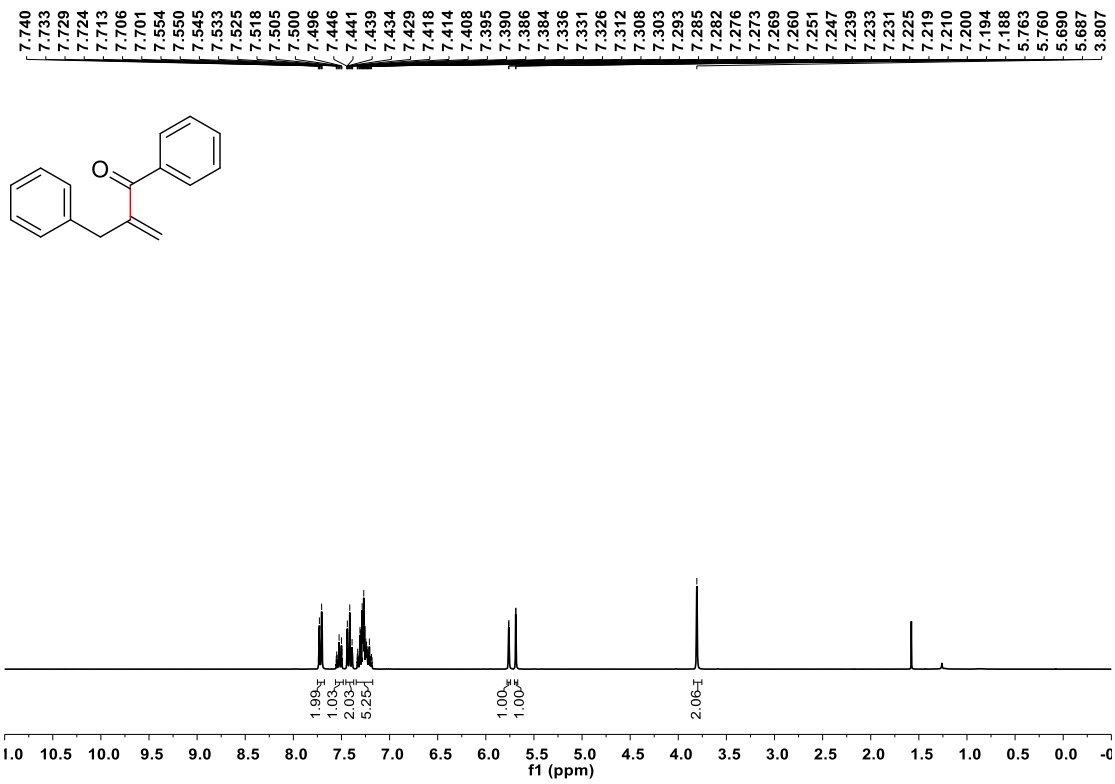


^{13}C NMR

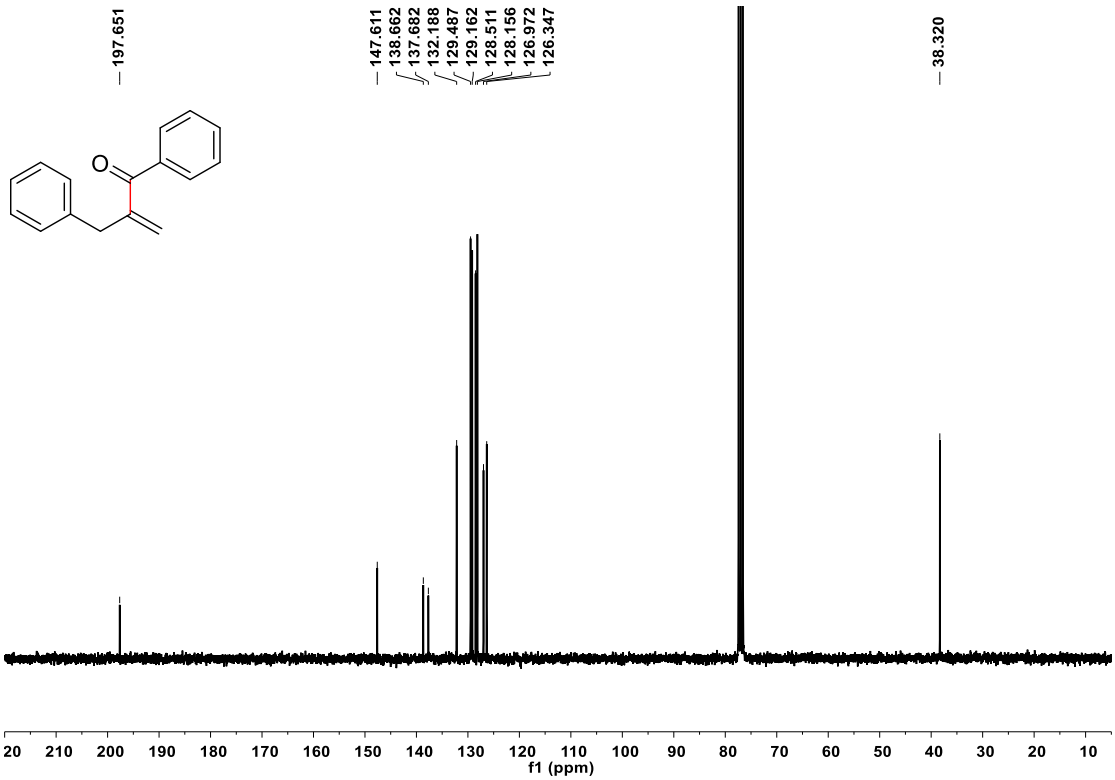


3ba

^{1}H NMR

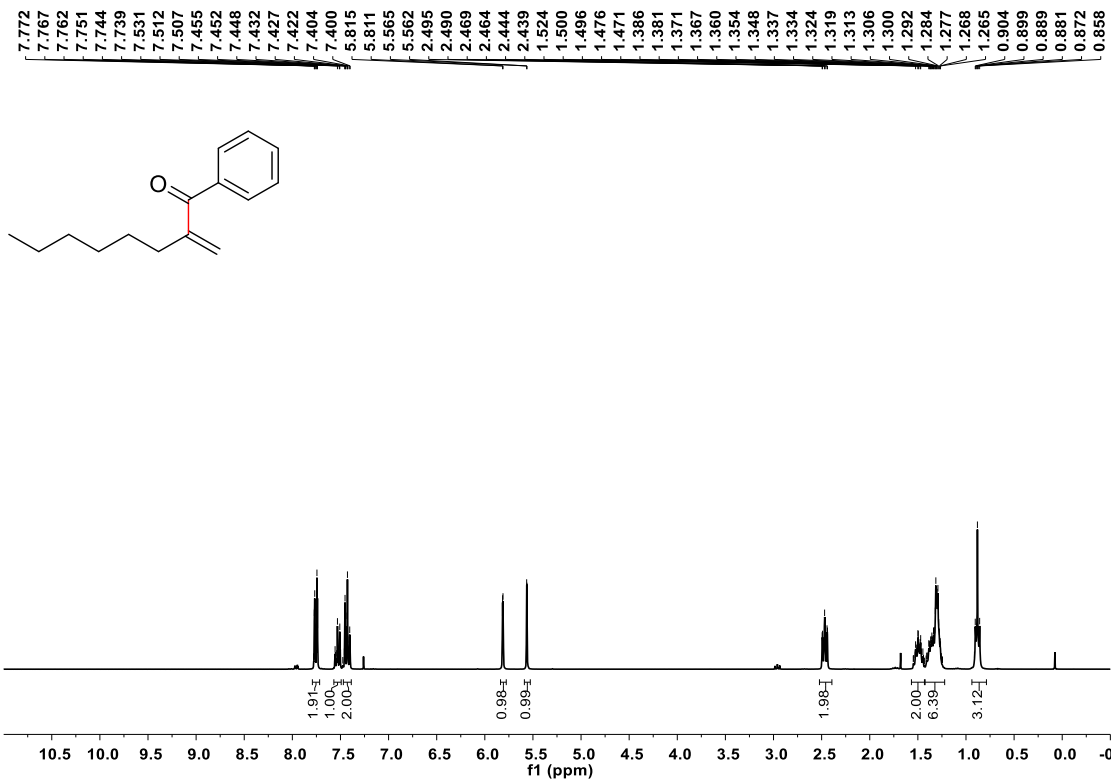


^{13}C NMR

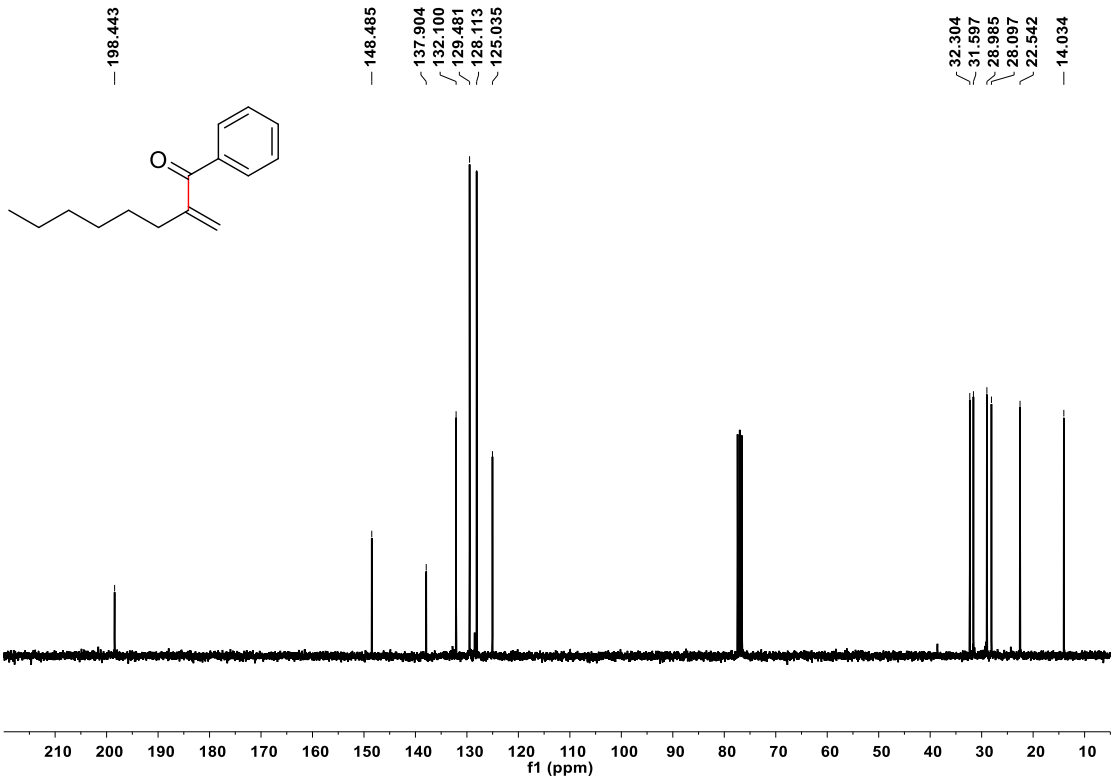


3ca

^{1}H NMR

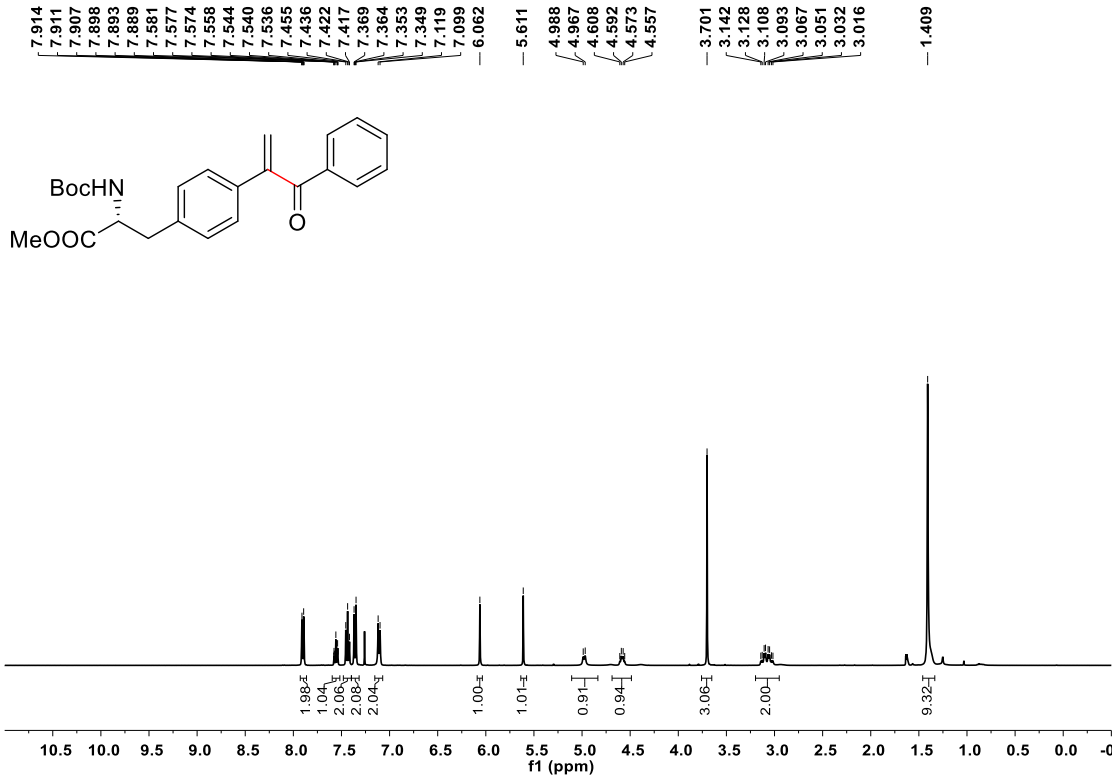


^{13}C NMR

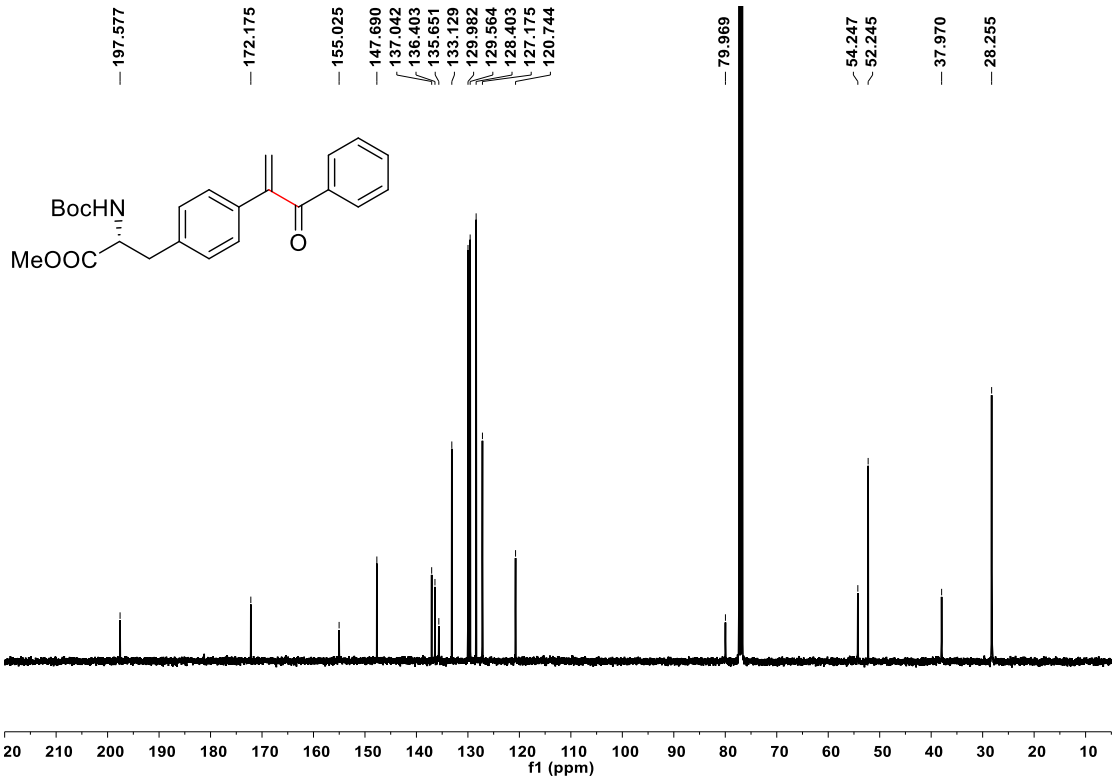


3da

^{1}H NMR

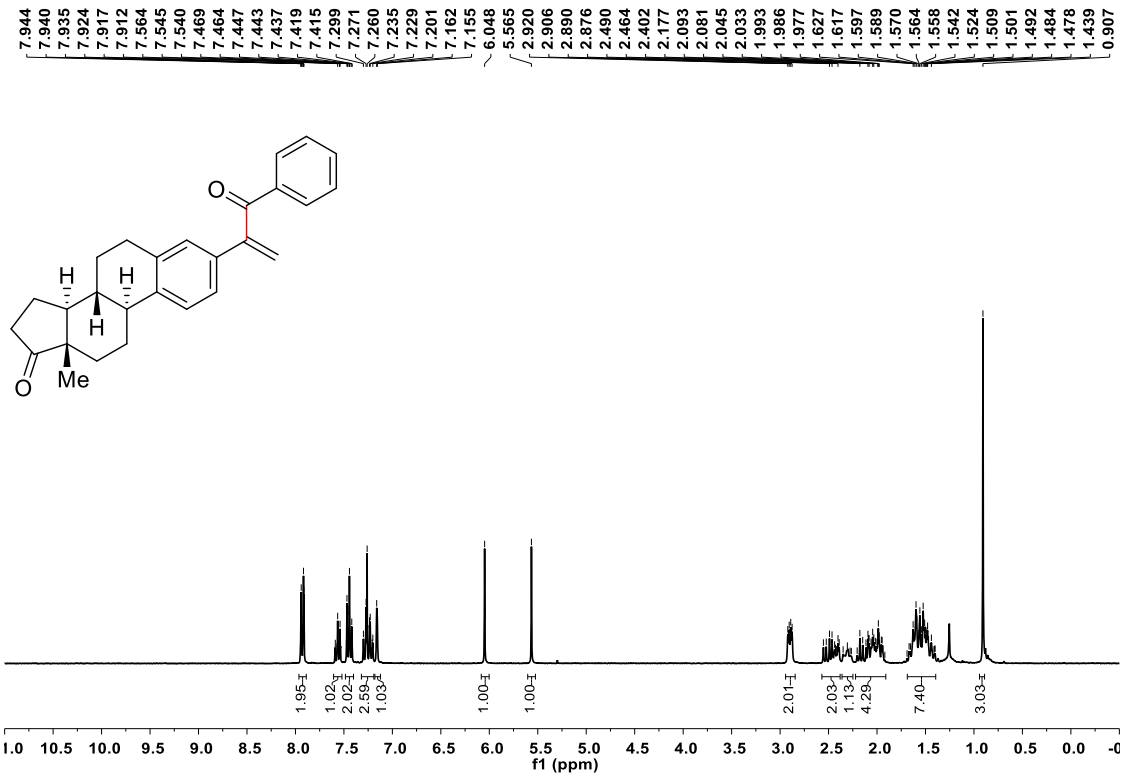


^{13}C NMR

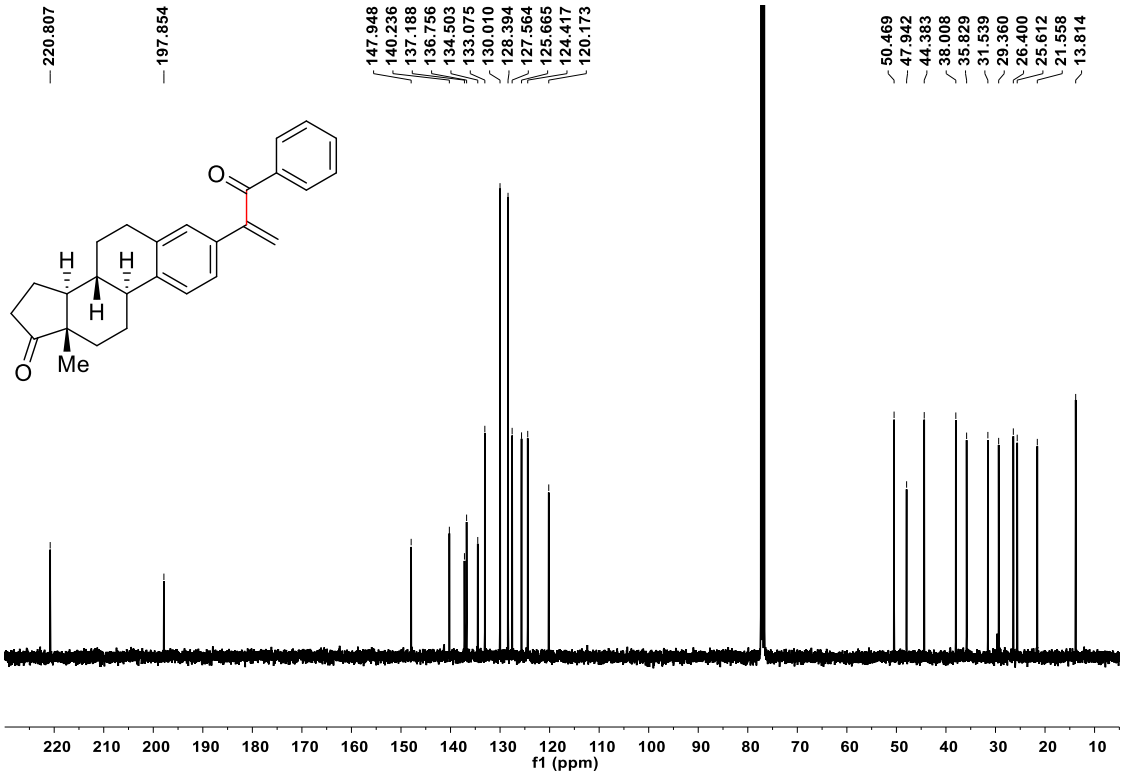


3ea

^{1}H NMR

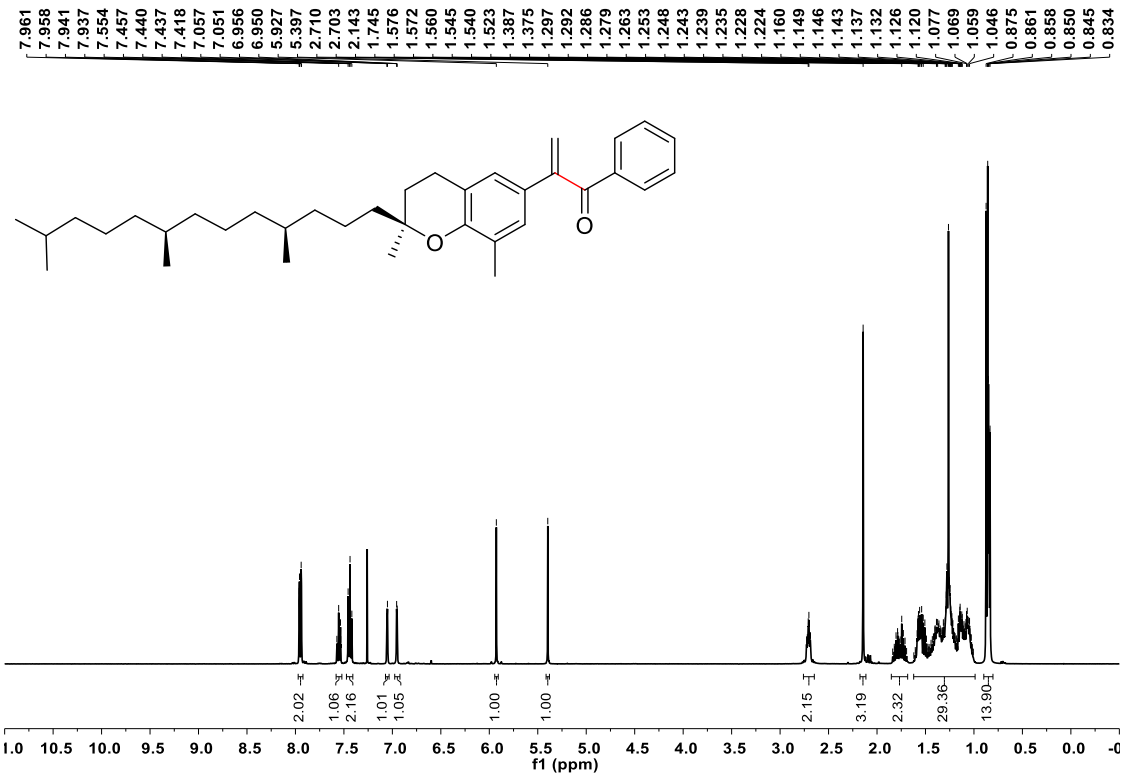


^{13}C NMR

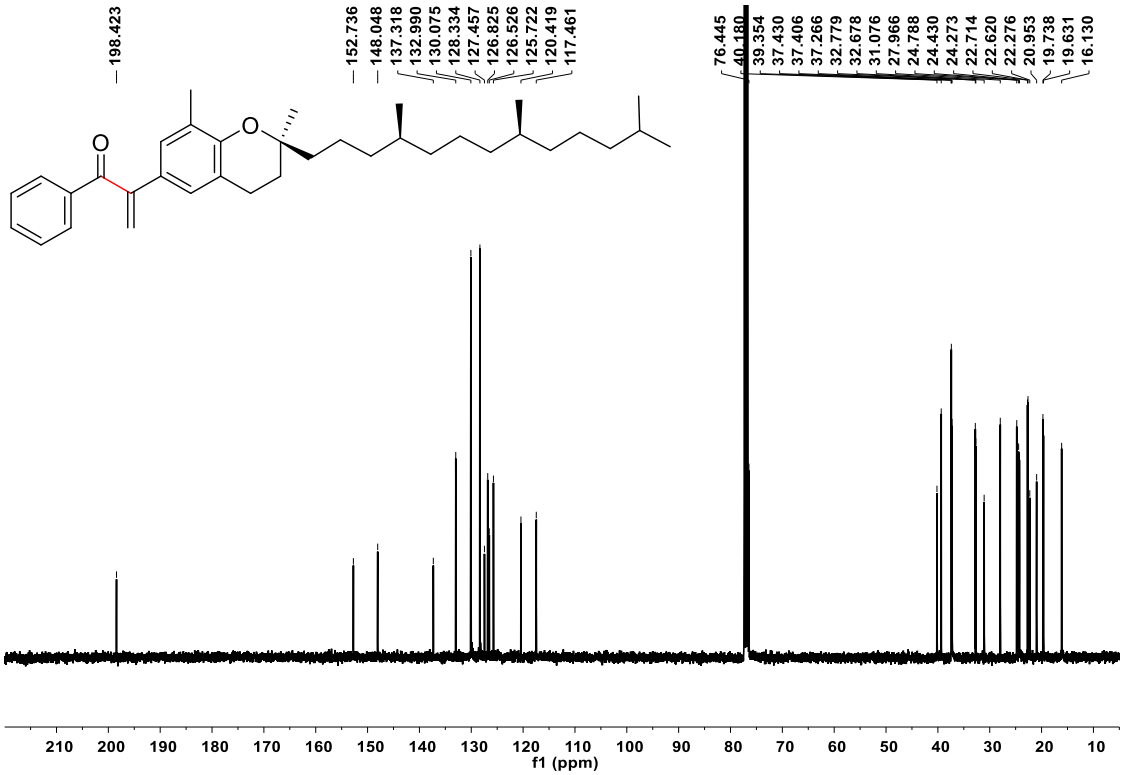


3fa

^{1}H NMR

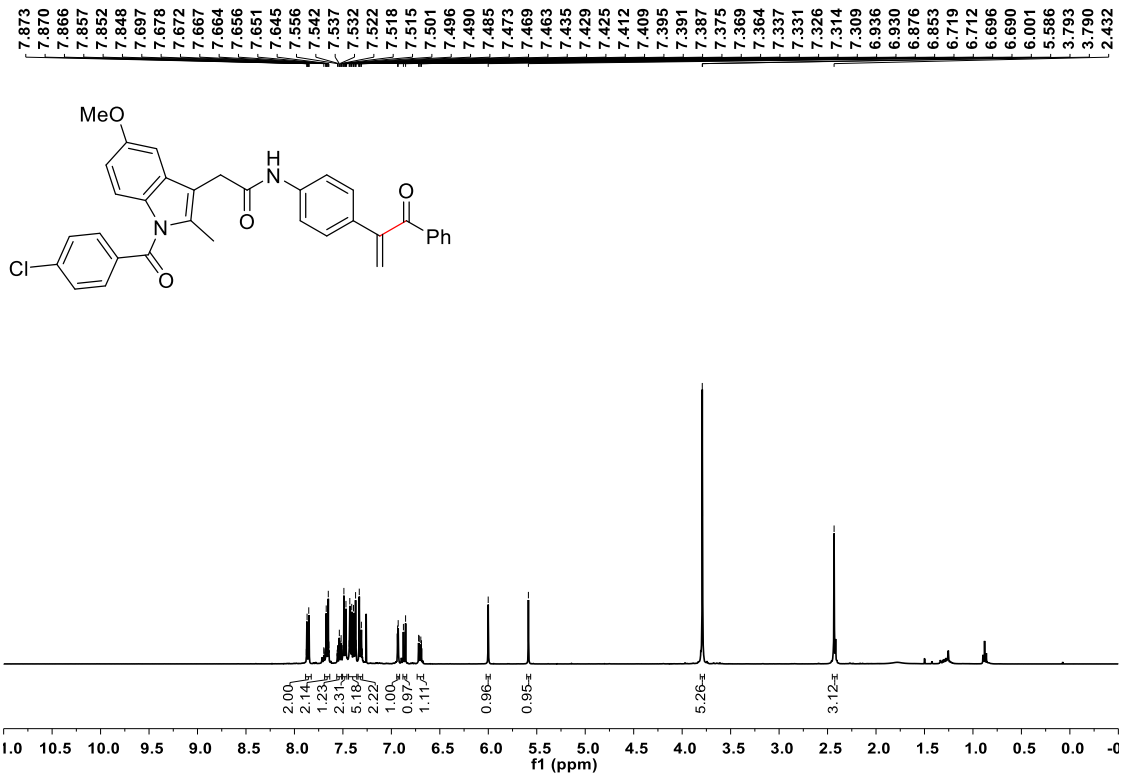


^{13}C NMR

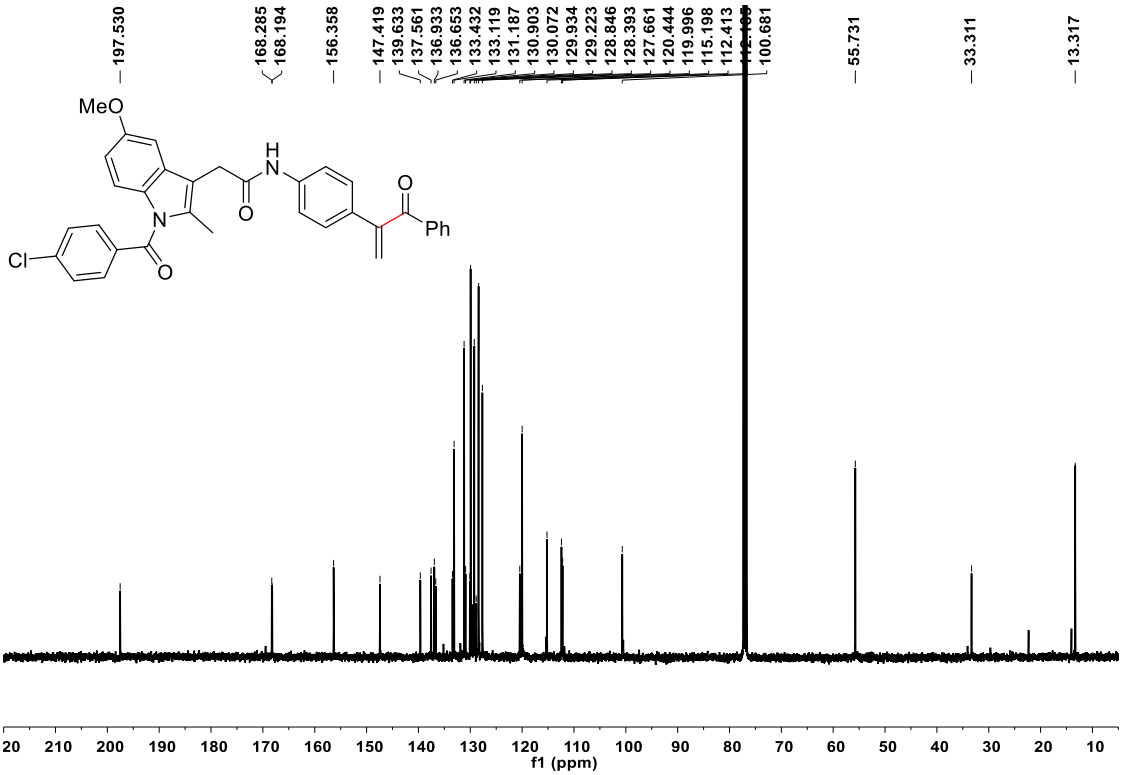


3ga

^{1}H NMR

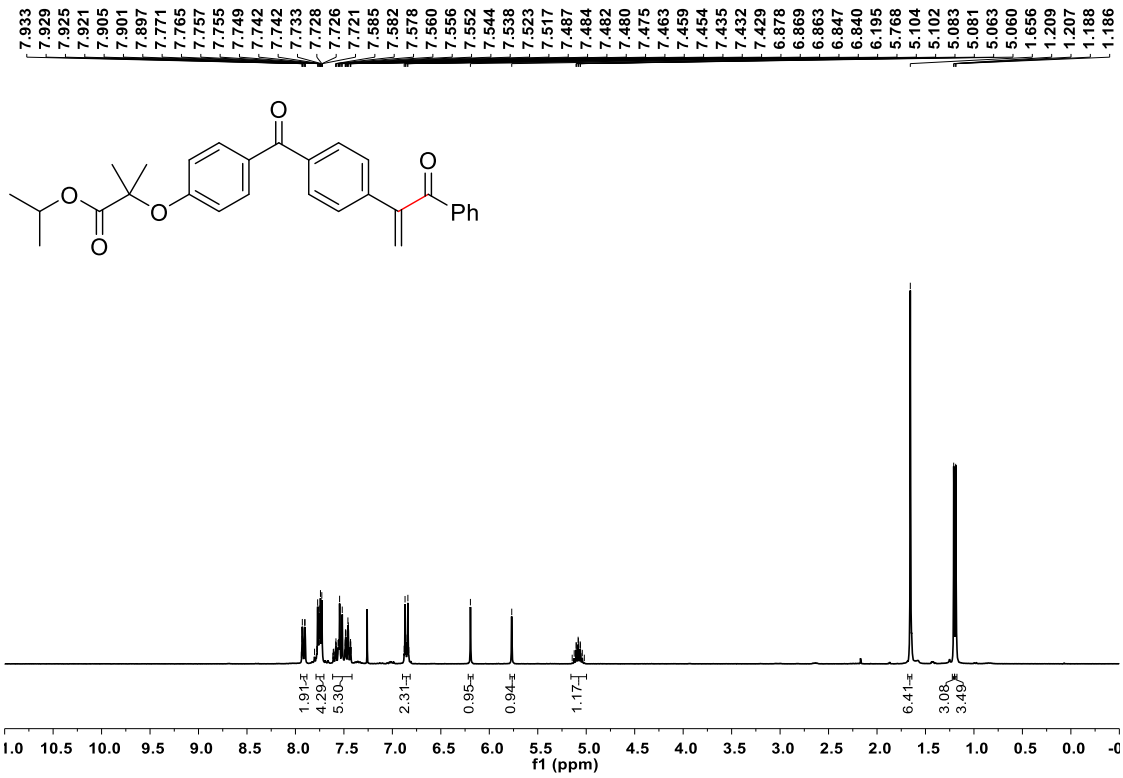


^{13}C NMR

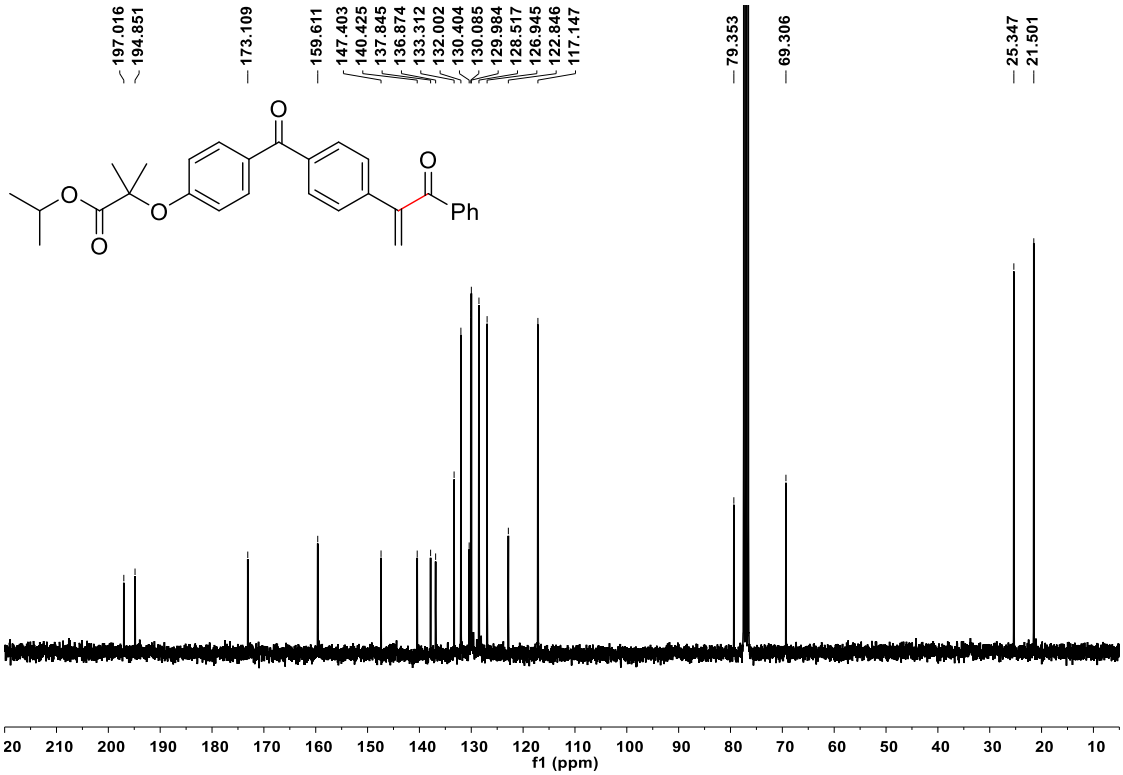


3ha

^{1}H NMR

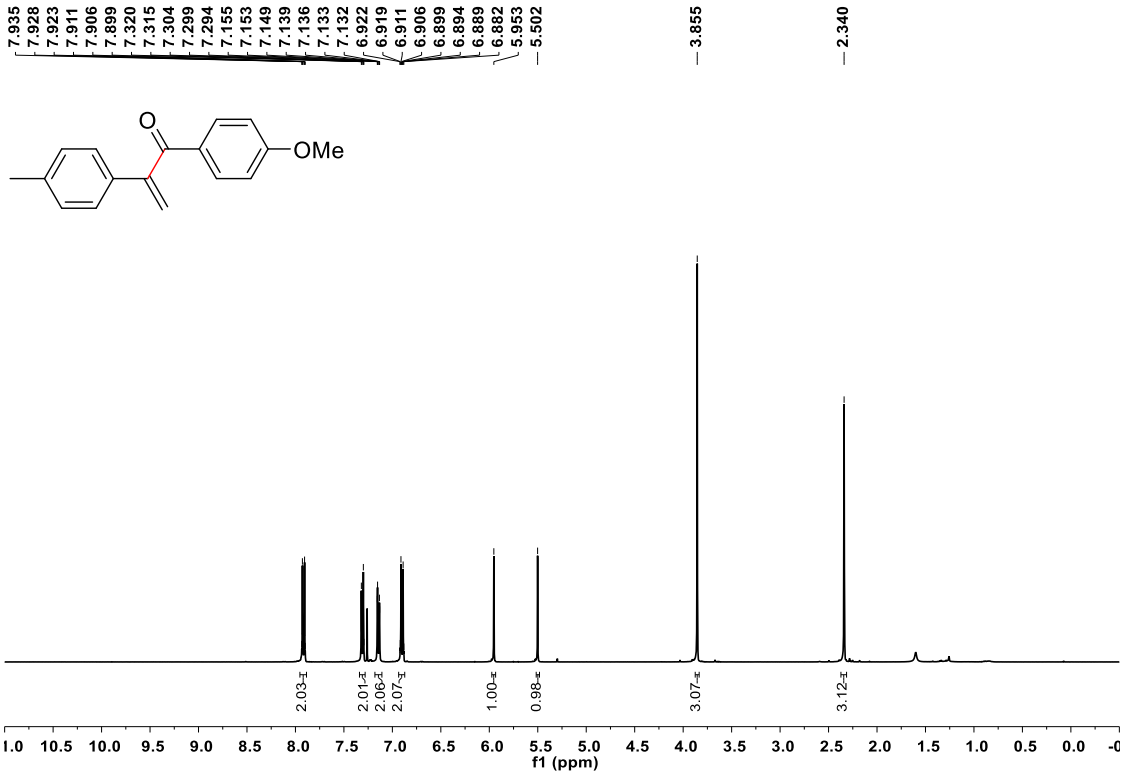


^{13}C NMR

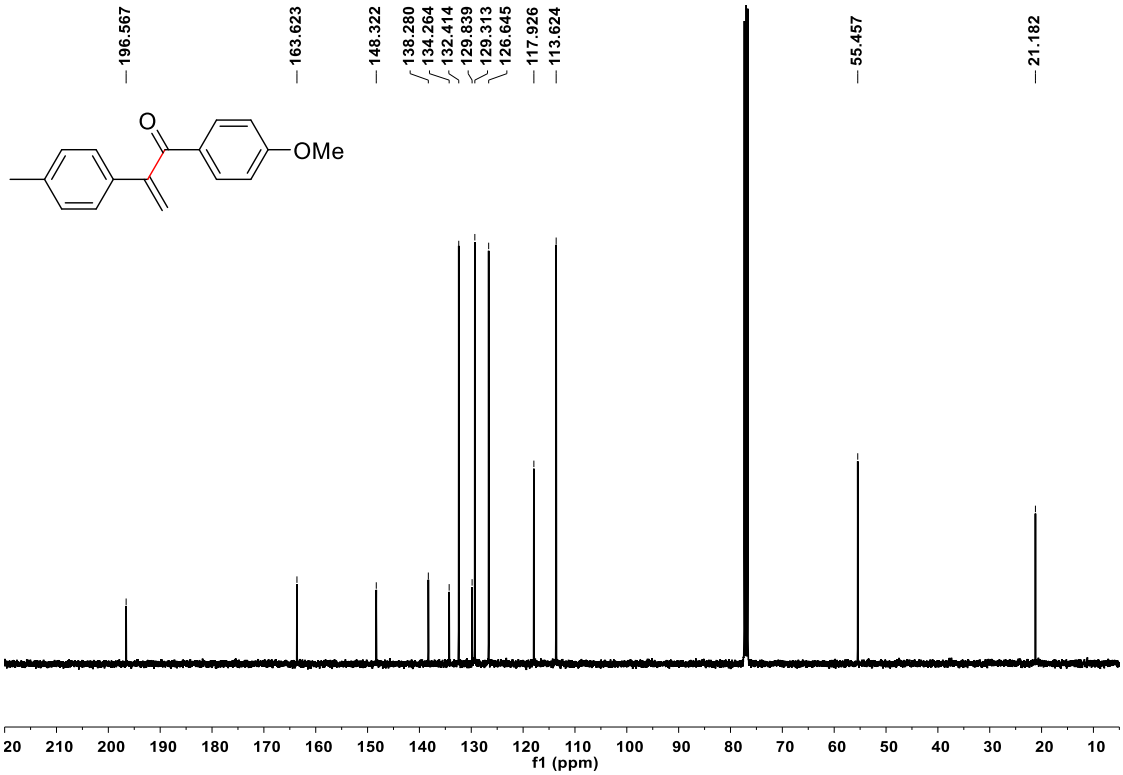


3ab

^{1}H NMR

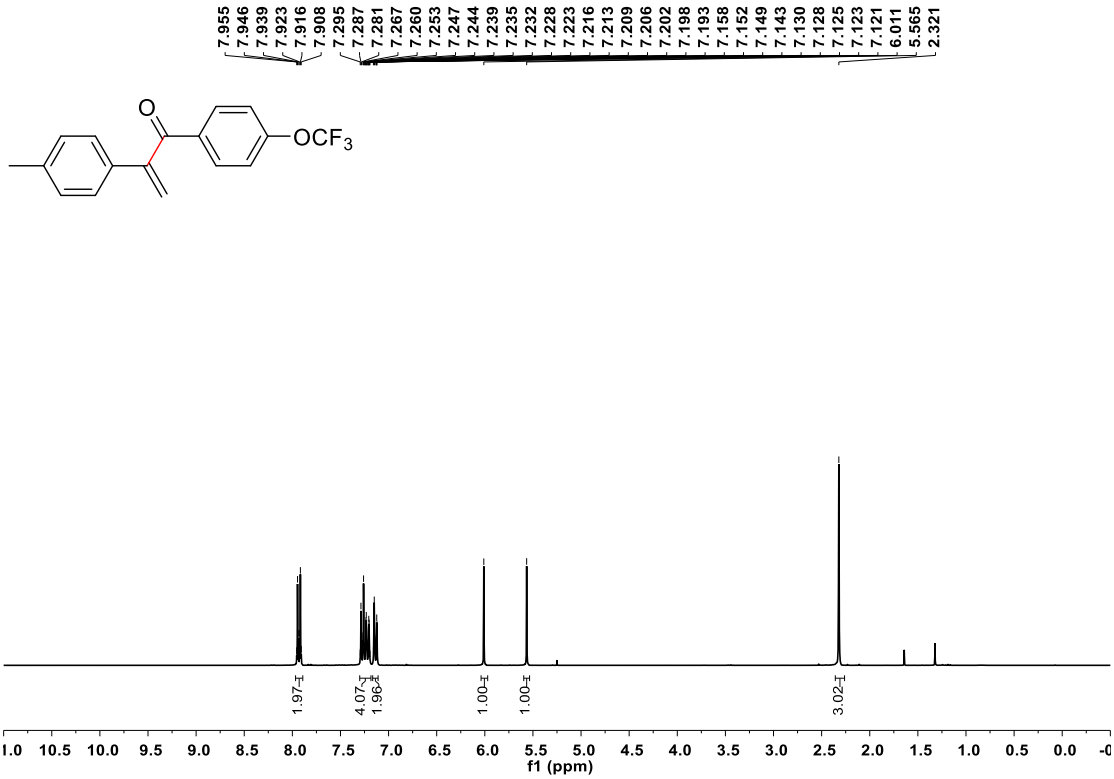


^{13}C NMR

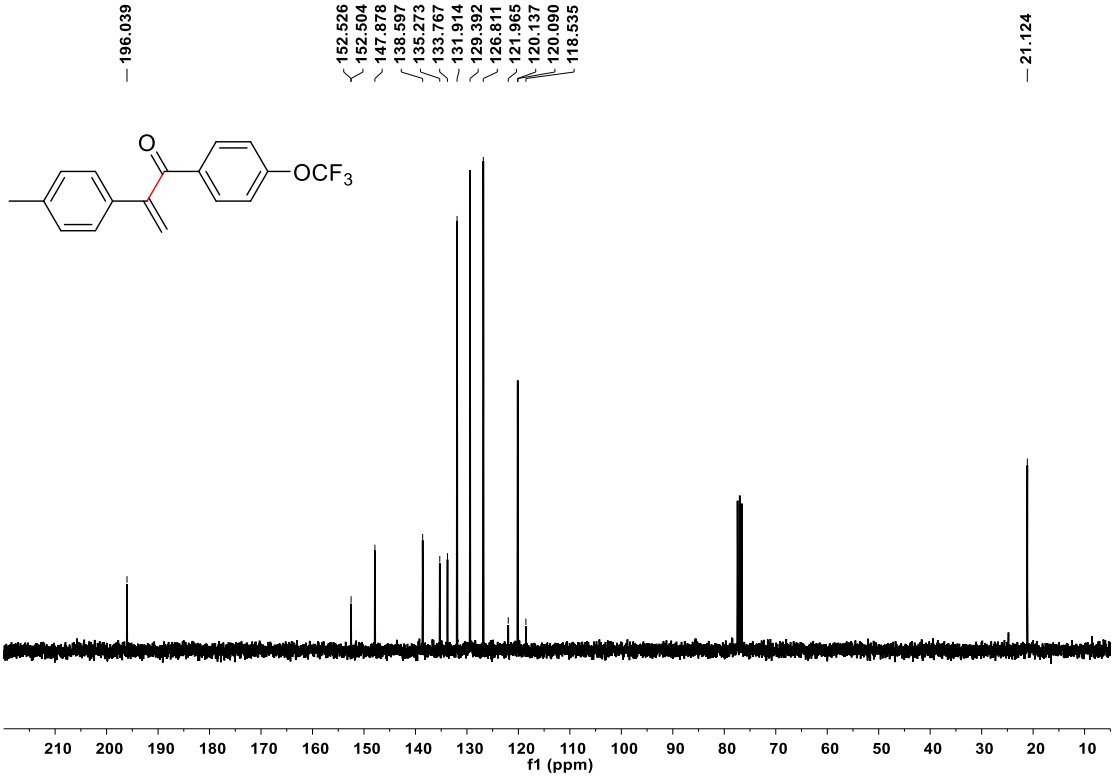


3ac

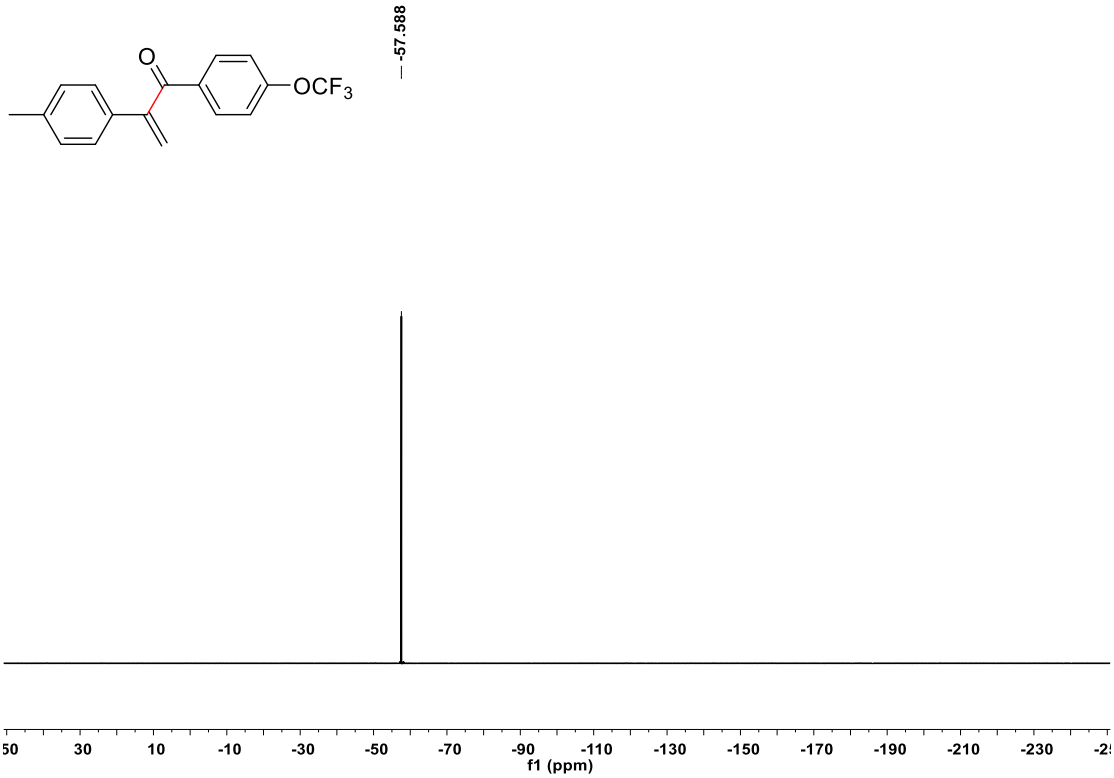
^{1}H NMR



^{13}C NMR

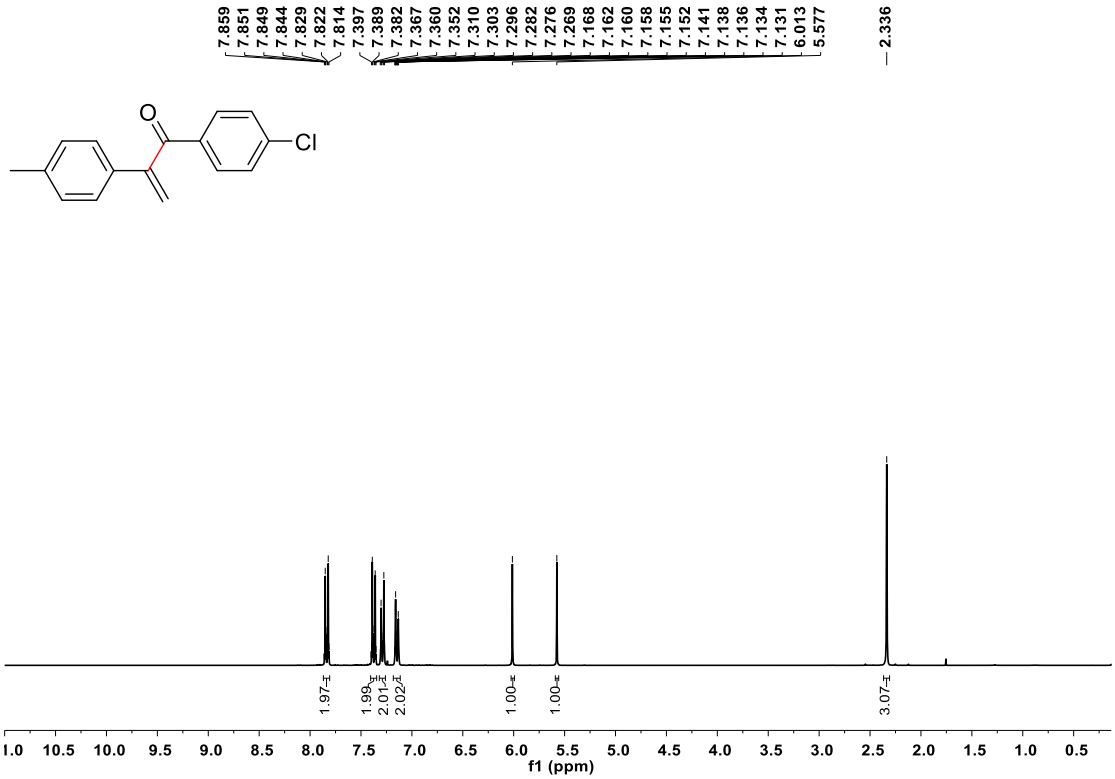


^{19}F NMR

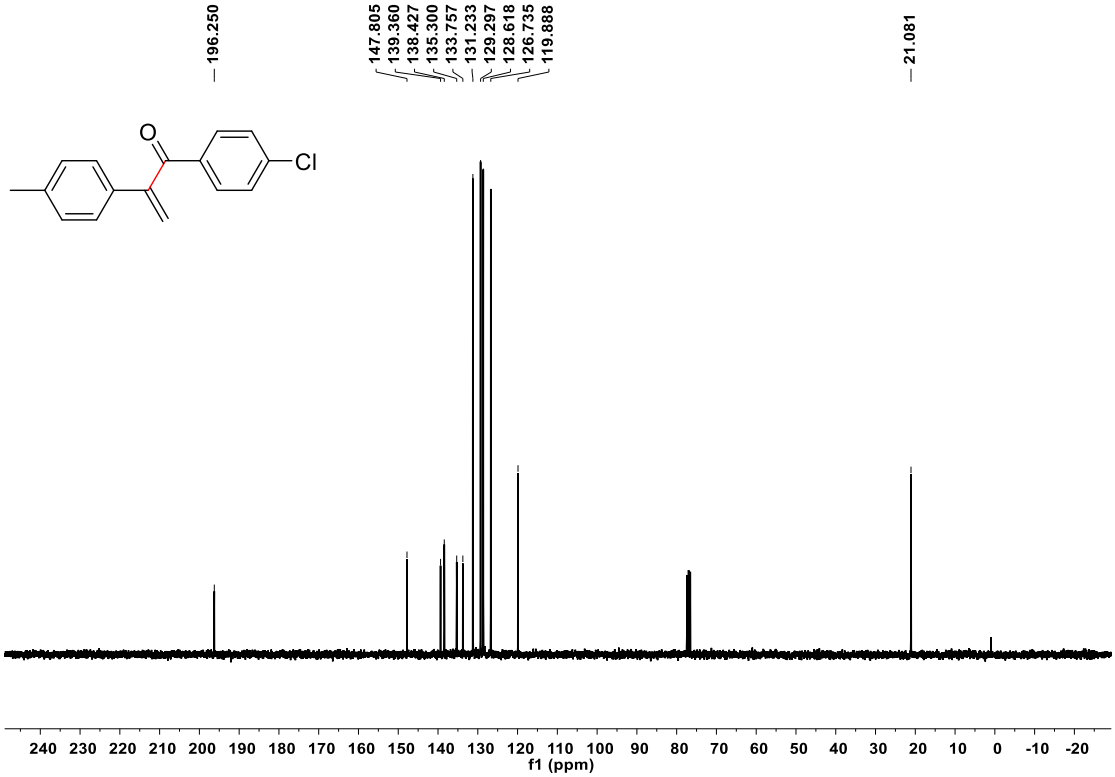

O
OCF3
-57.588
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

3ad

^{1}H NMR

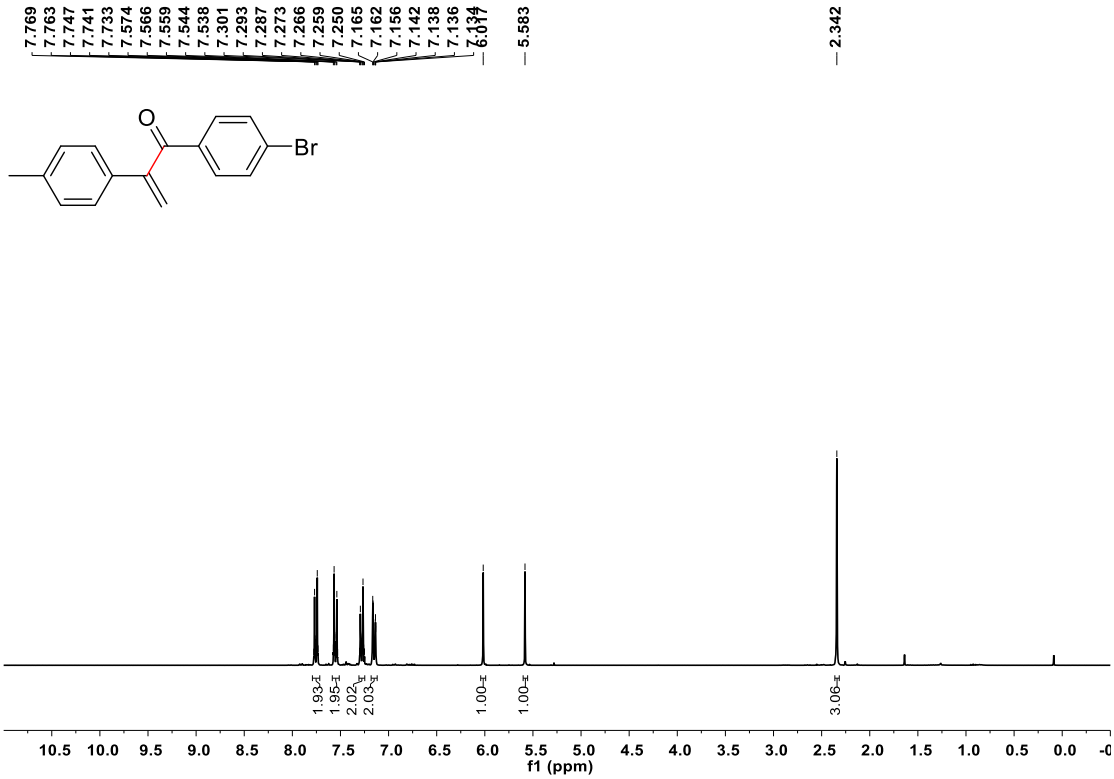


^{13}C NMR

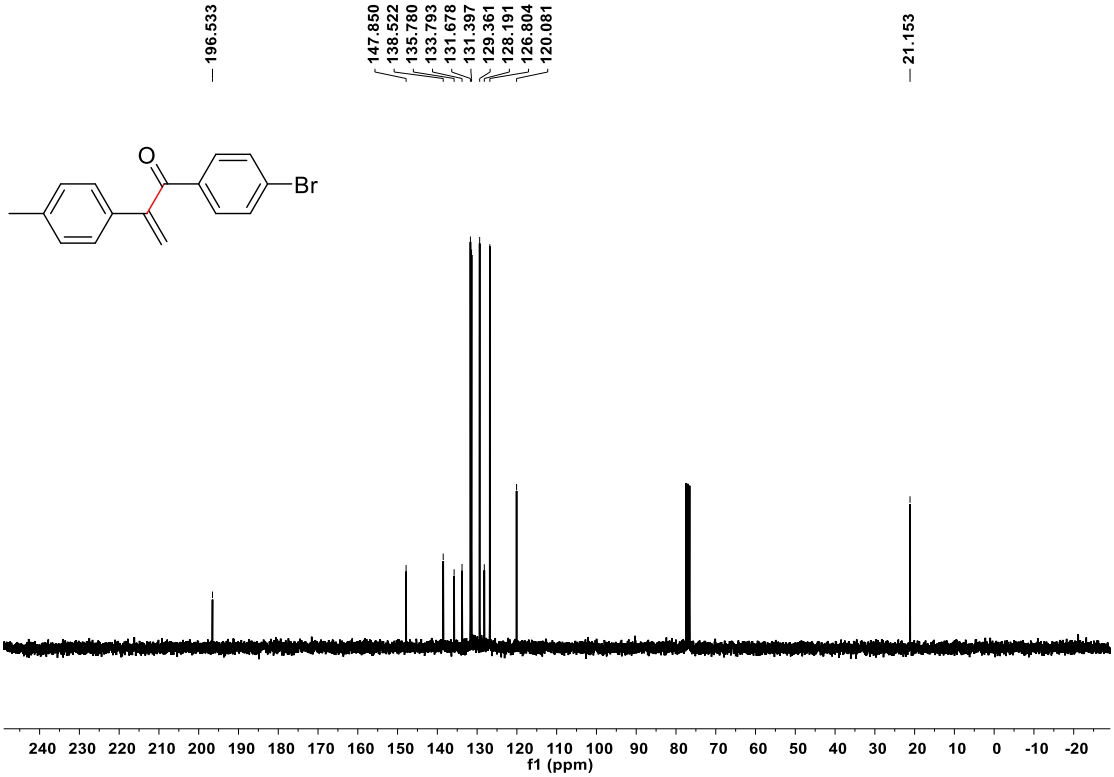


3ae

^{1}H NMR

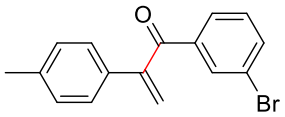


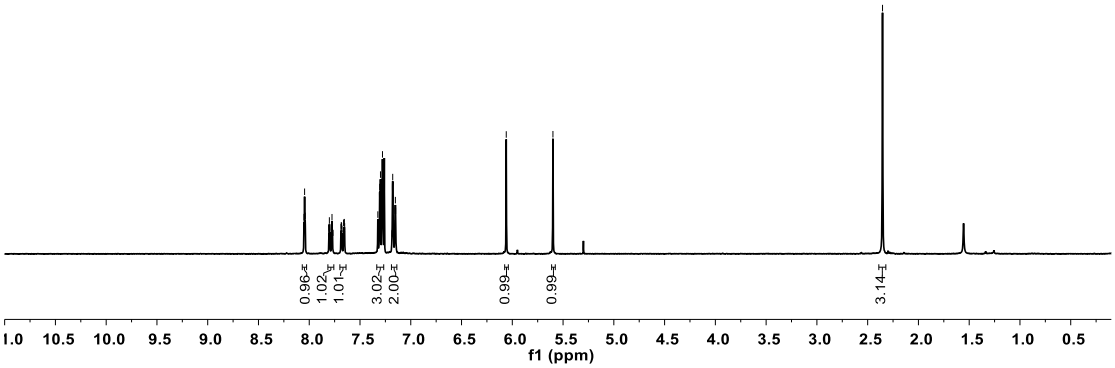
^{13}C NMR



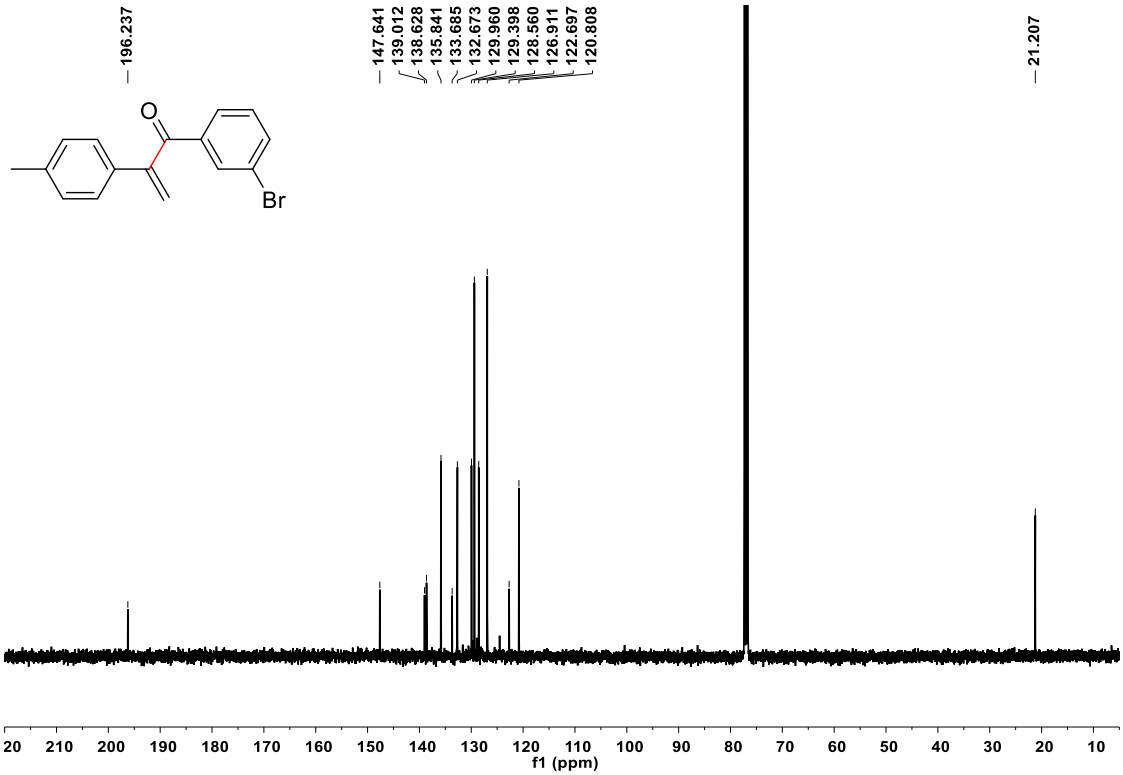
3af

^{1}H NMR



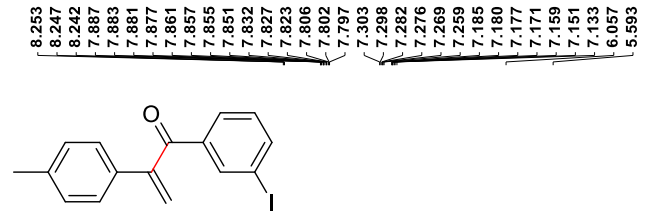


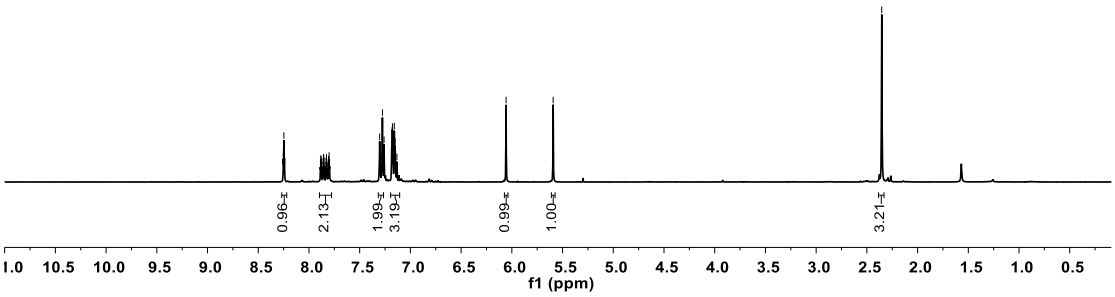
^{13}C NMR



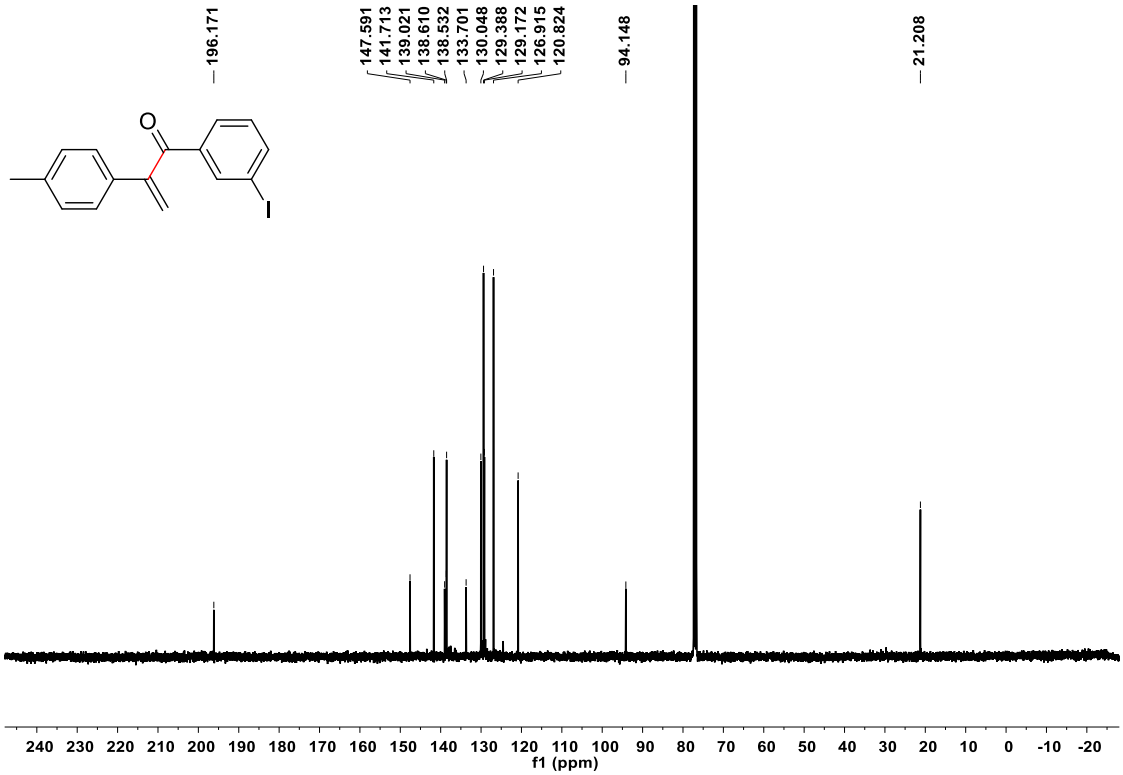
3ag

^{1}H NMR



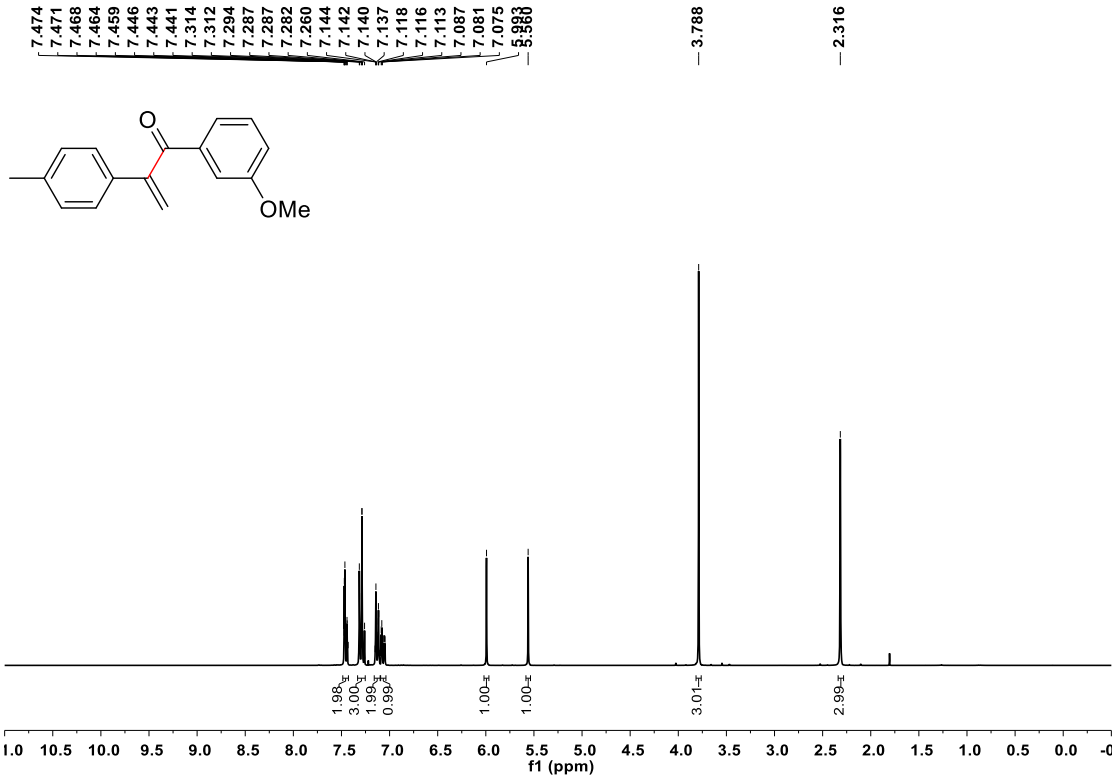


^{13}C NMR

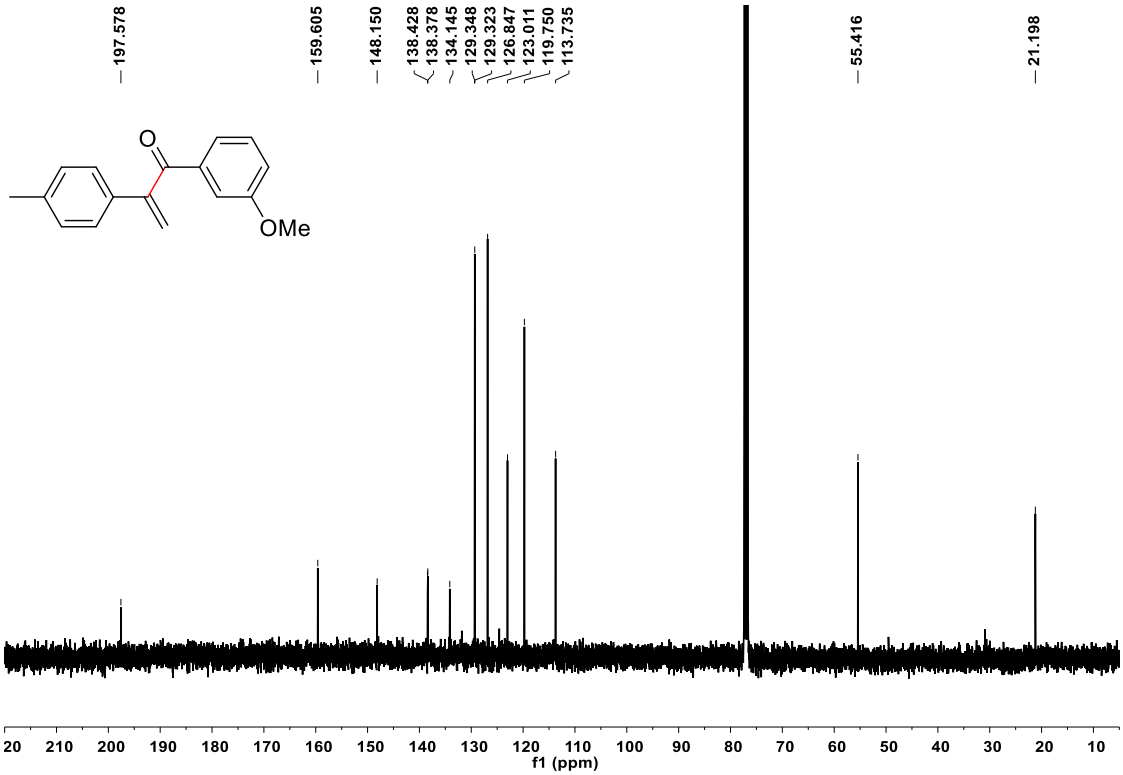


3ah

^{1}H NMR

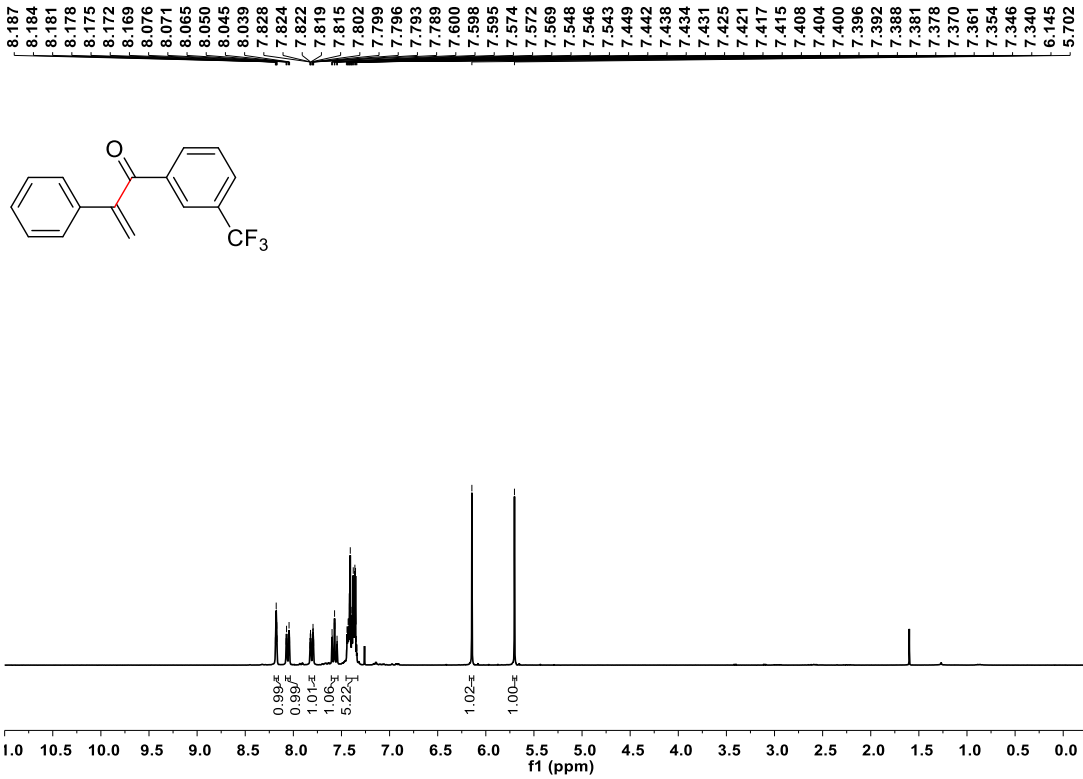


^{13}C NMR

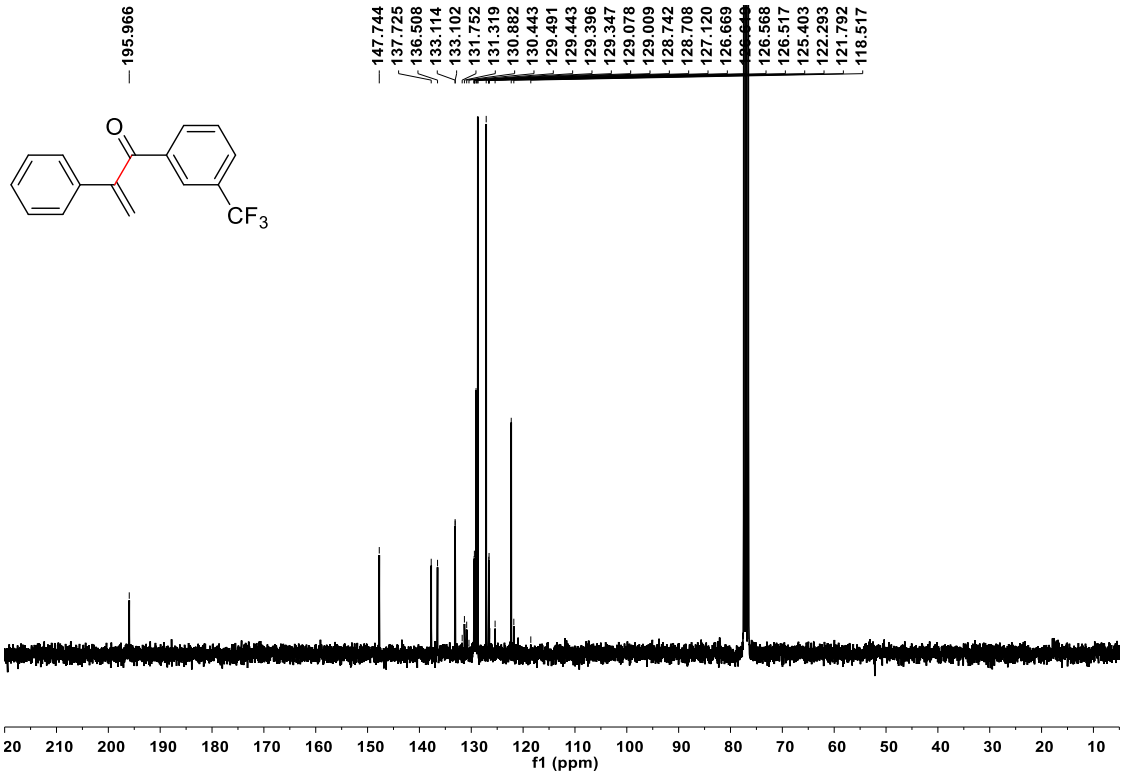


3ai

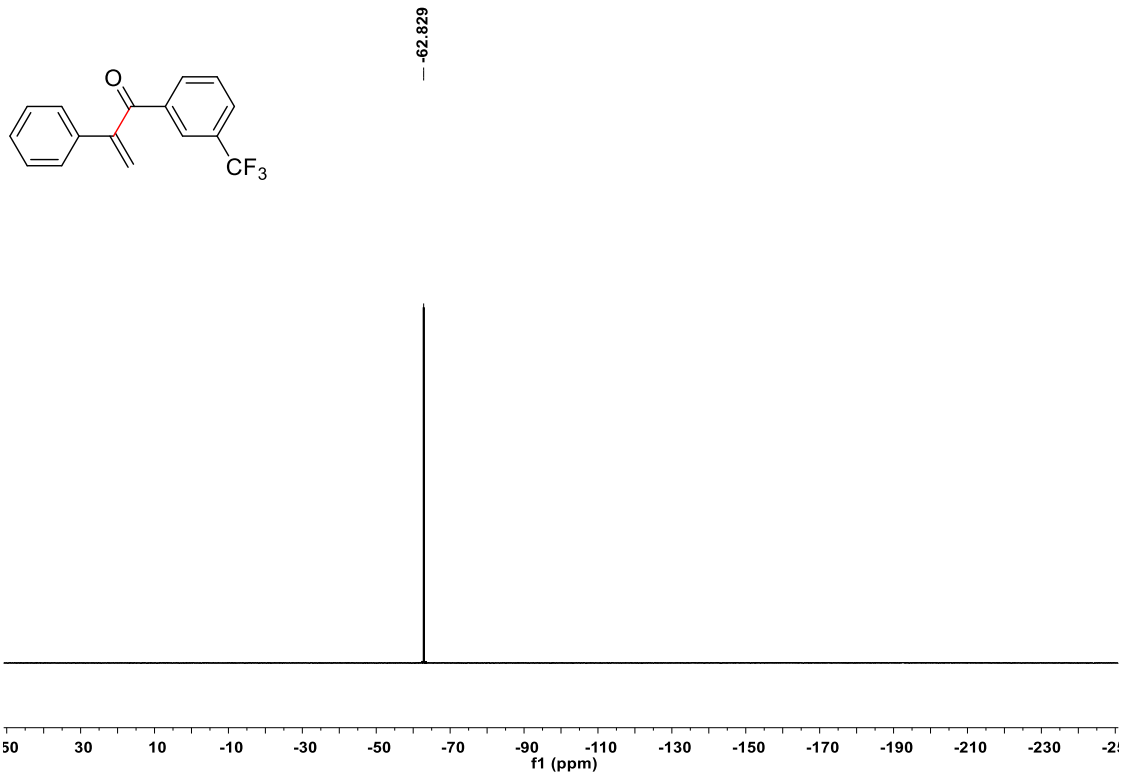
^{1}H NMR



^{13}C NMR

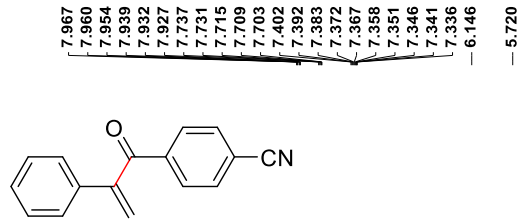


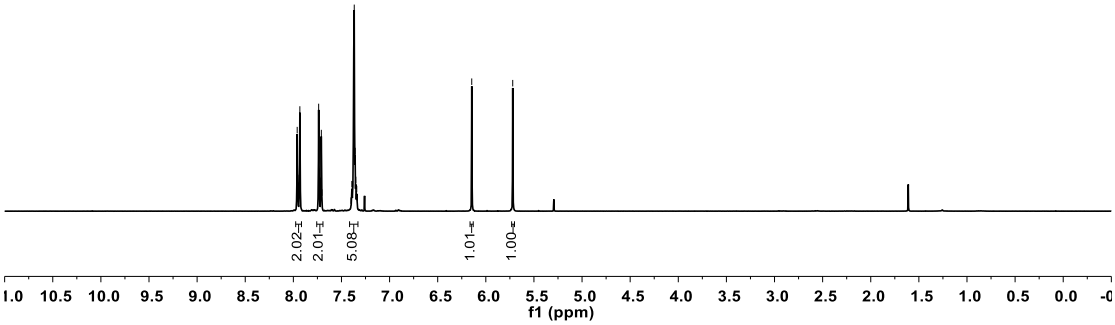
^{19}F NMR


-62.829
O
CF3
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

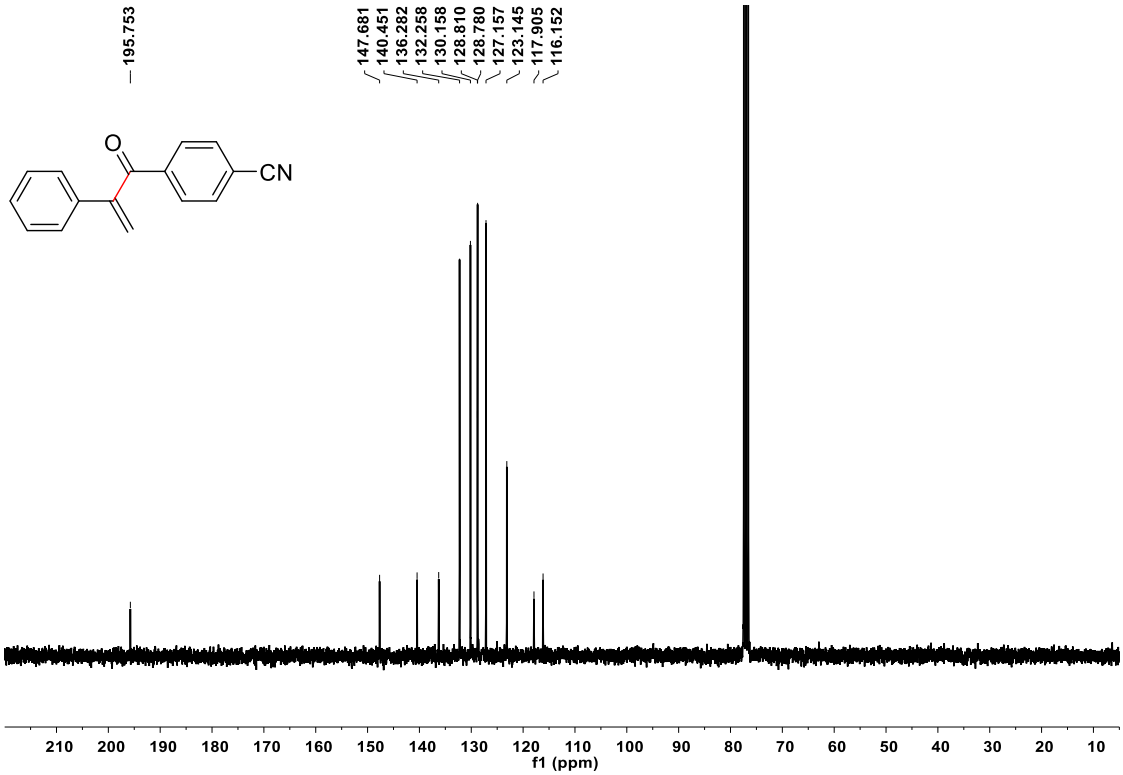
3aj

^{1}H NMR



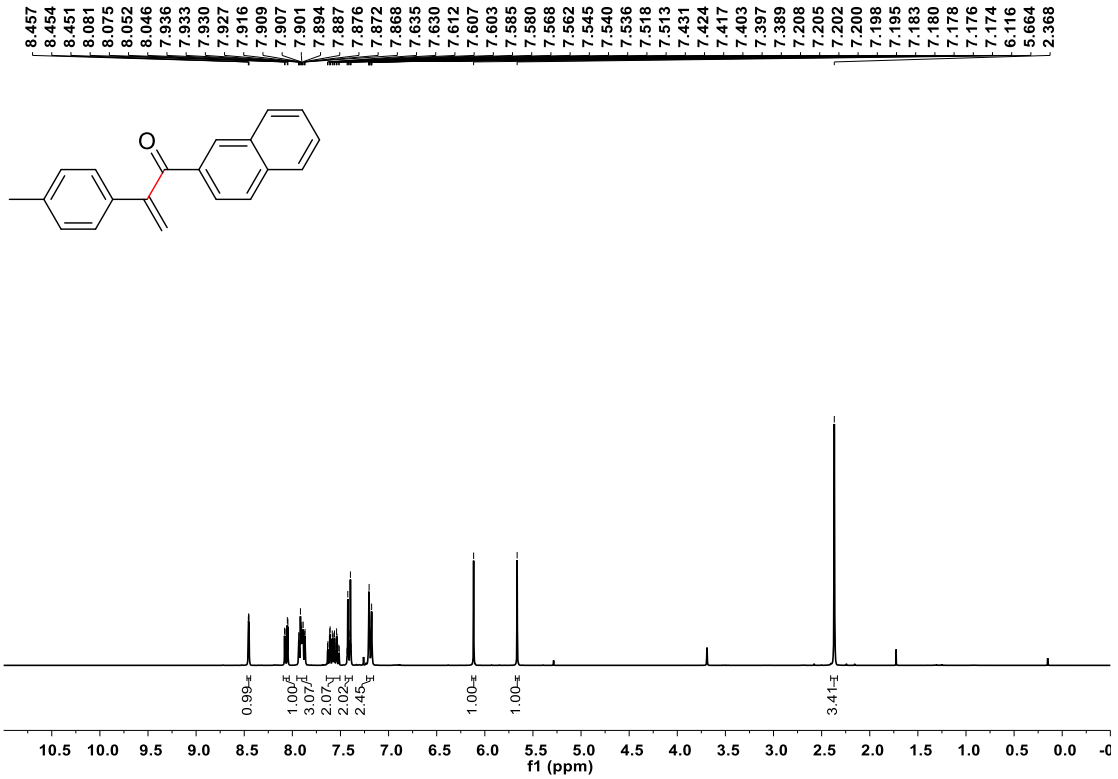


^{13}C NMR

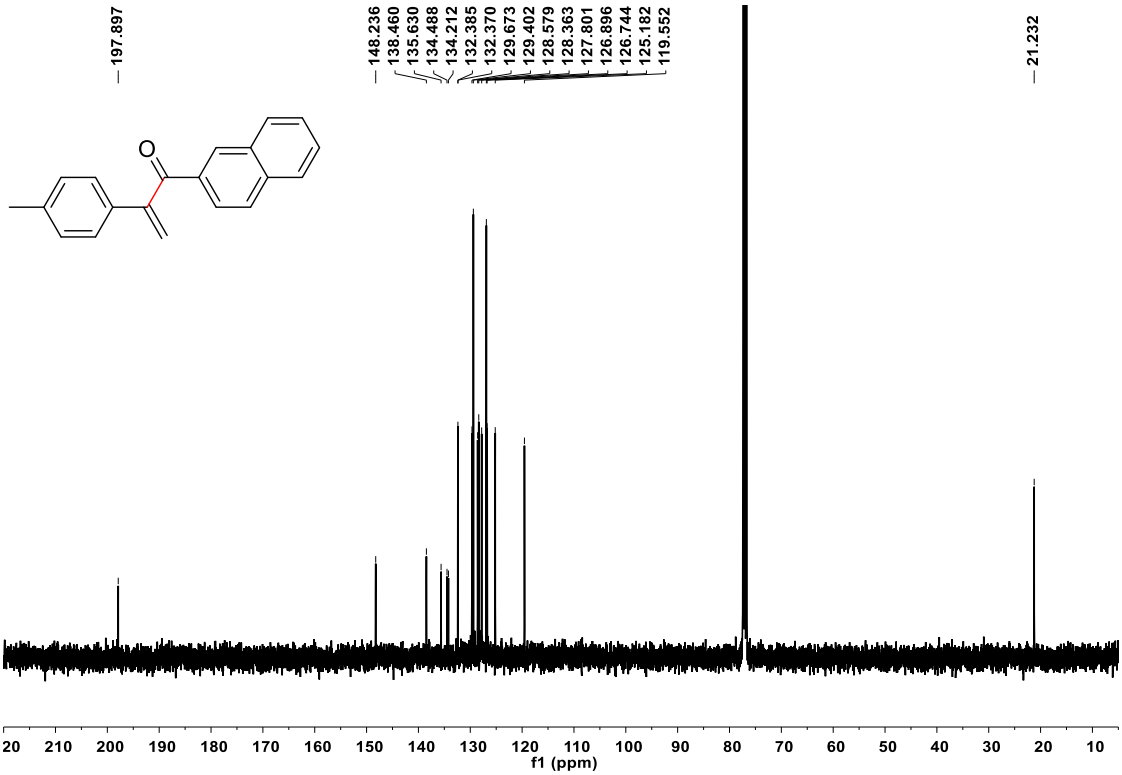


3ak

^{1}H NMR

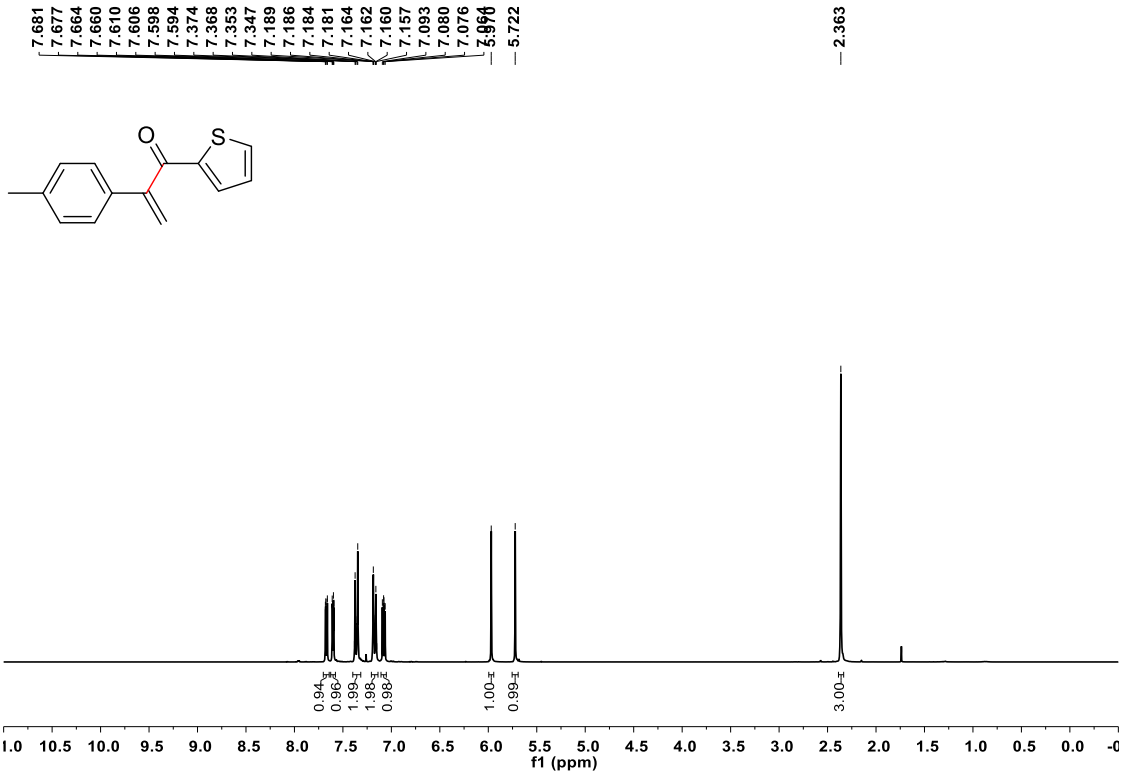


^{13}C NMR

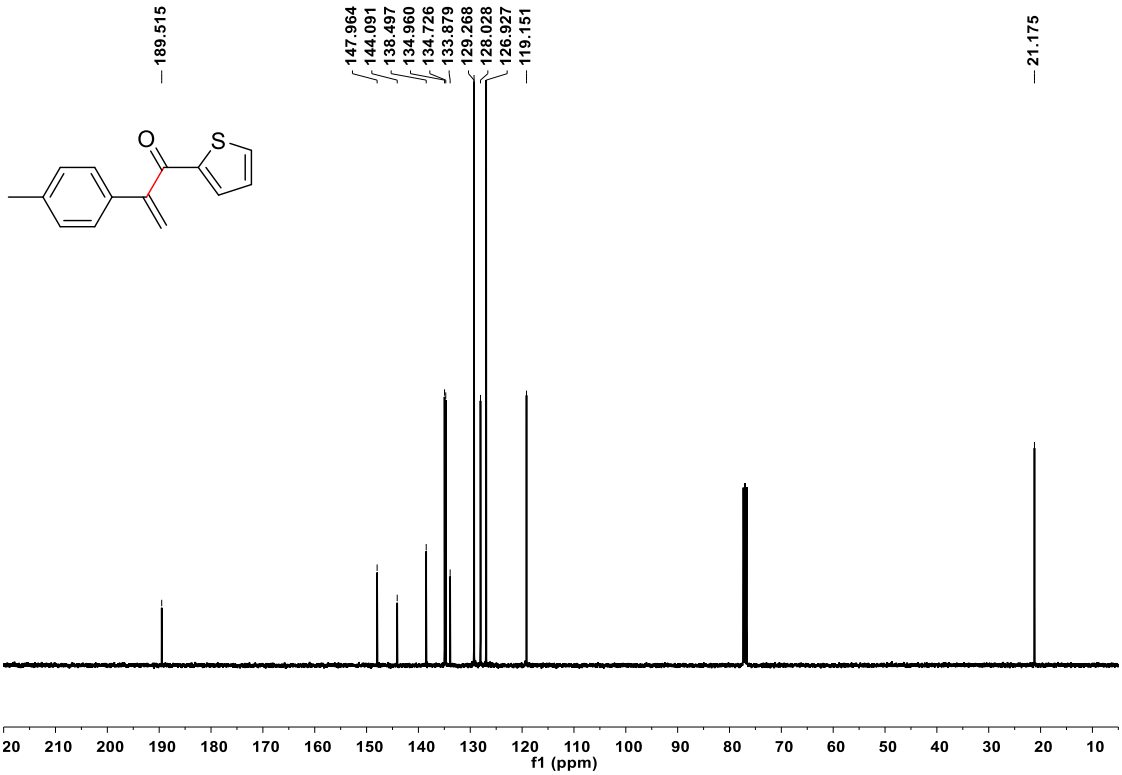


3al

^{1}H NMR

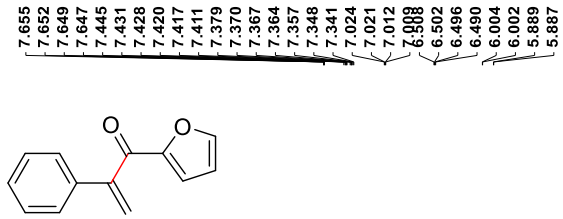


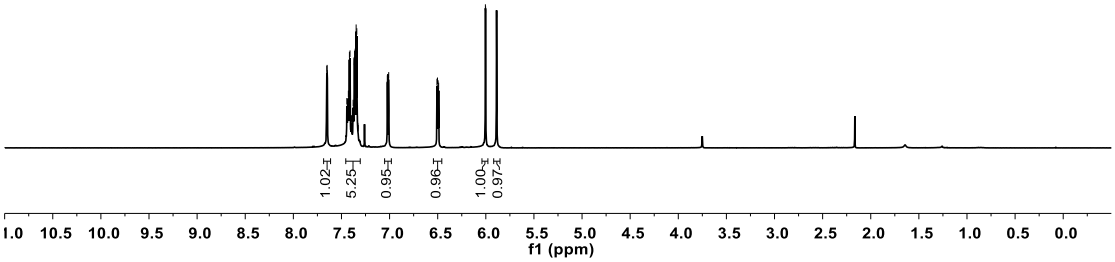
^{13}C NMR



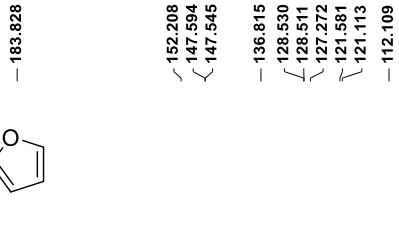
3am

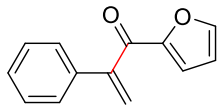
^{1}H NMR

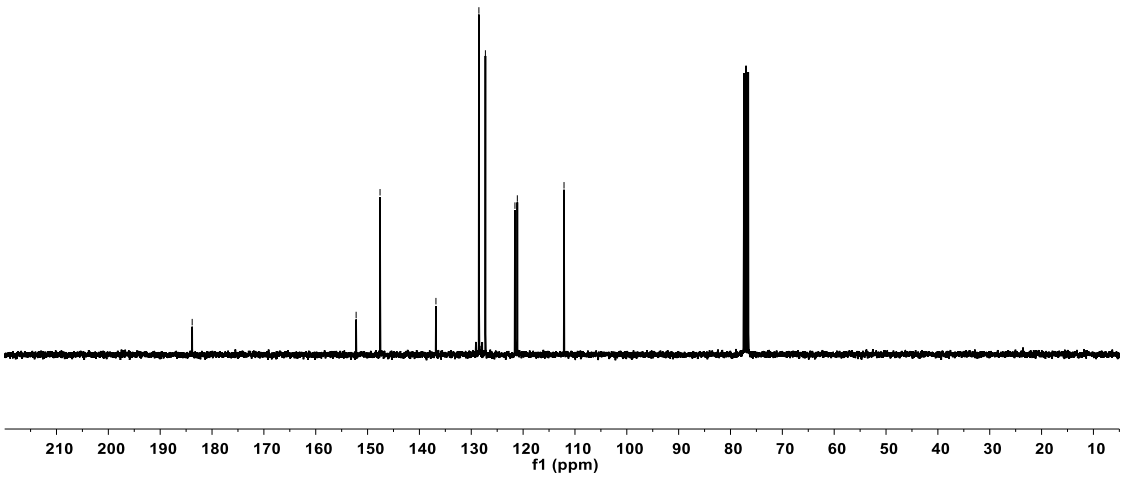




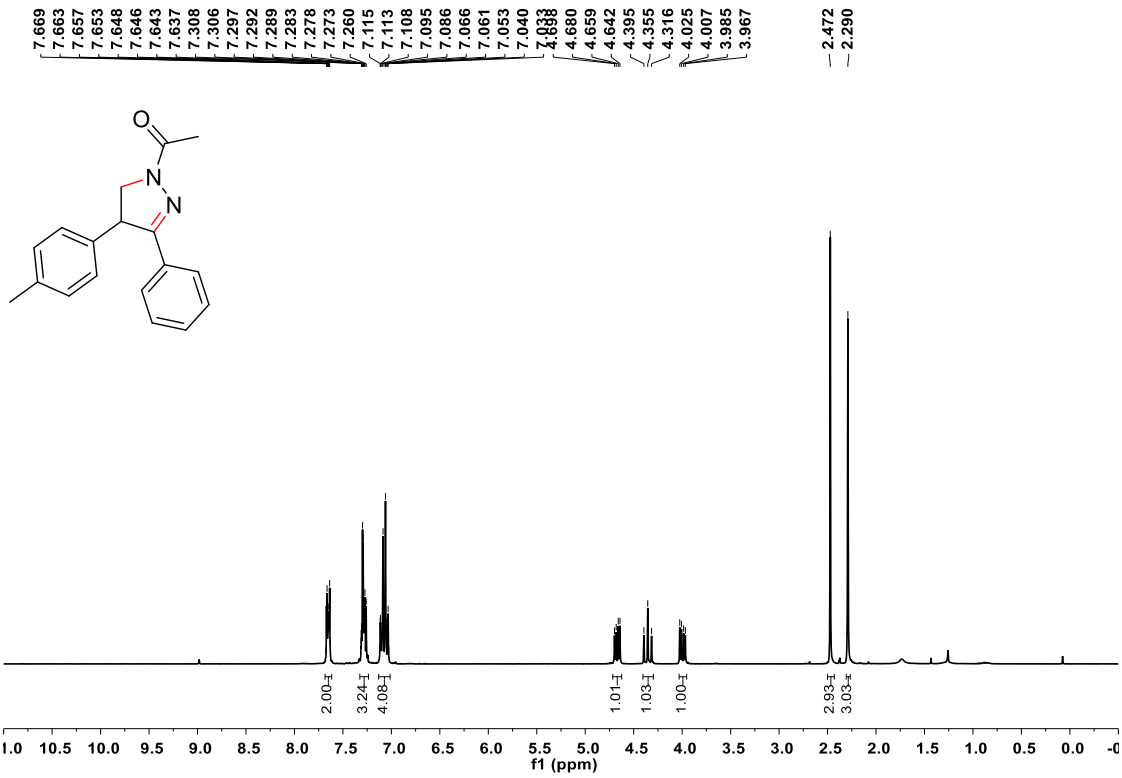
^{13}C NMR



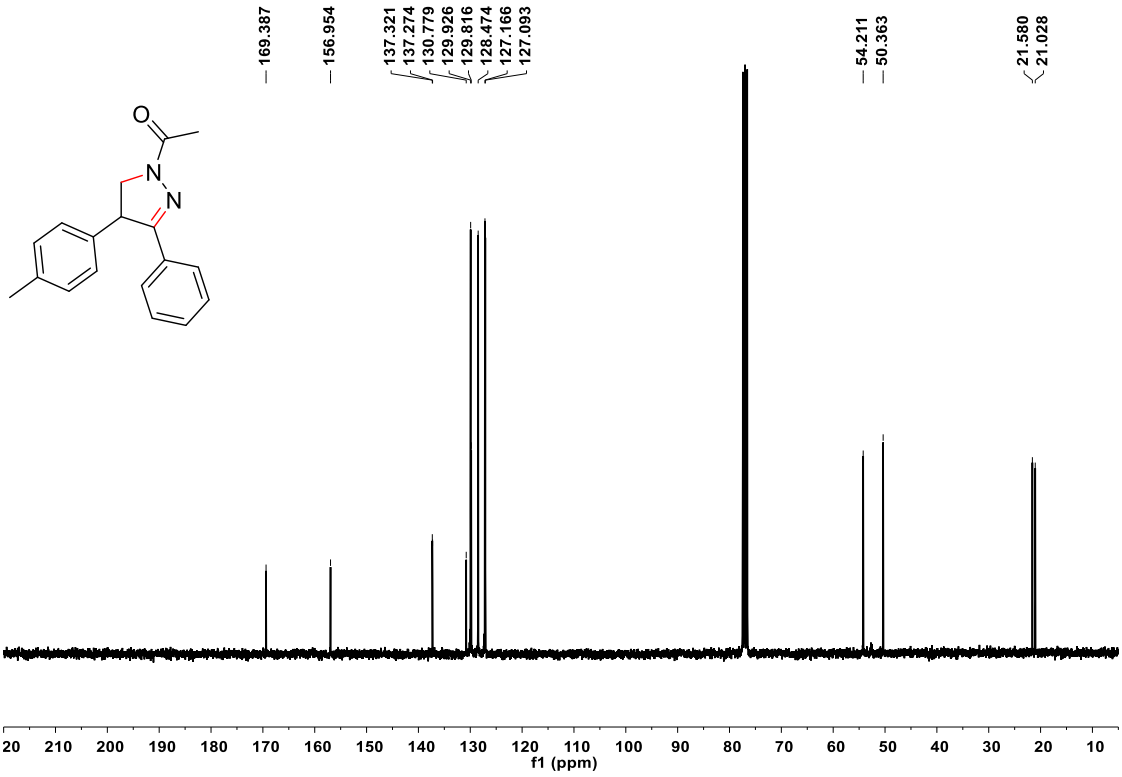




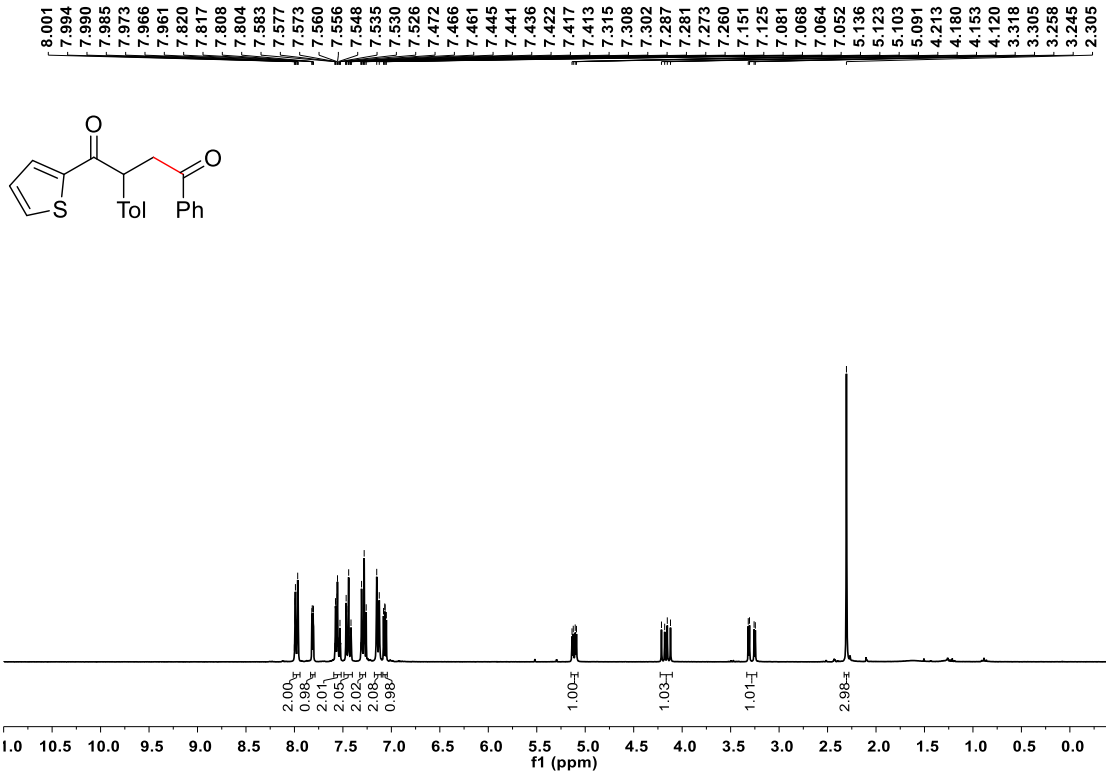
^{1}H NMR



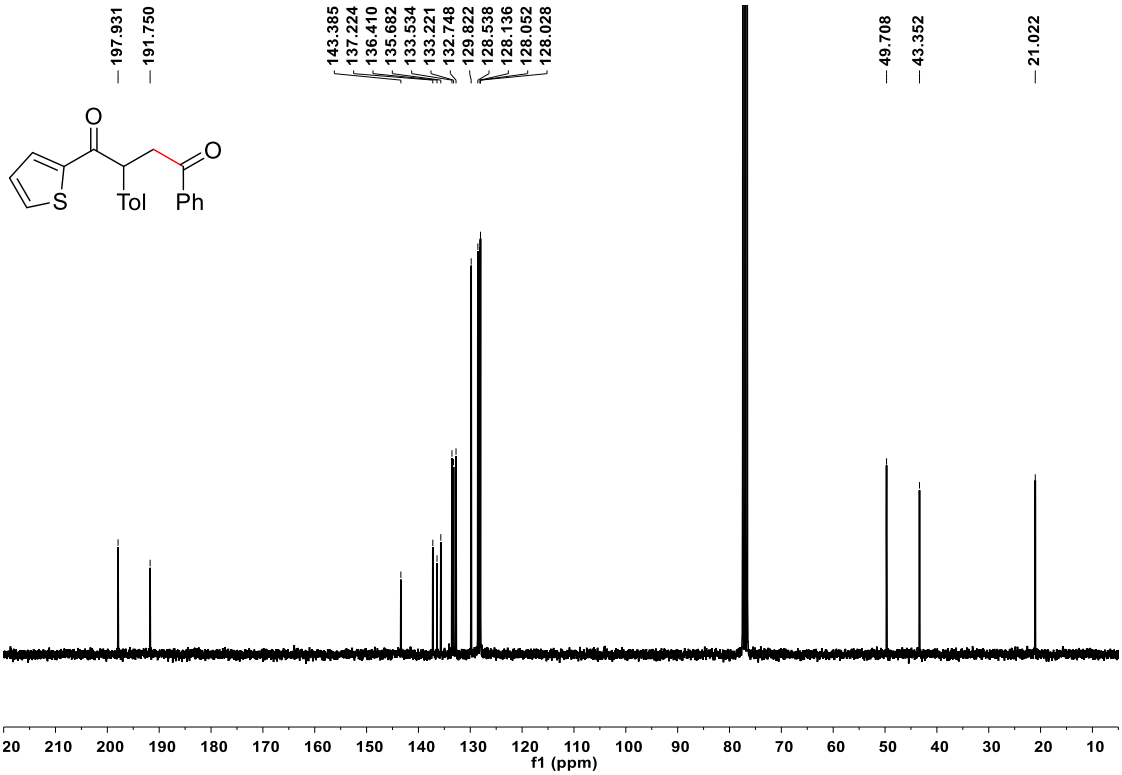
^{13}C NMR



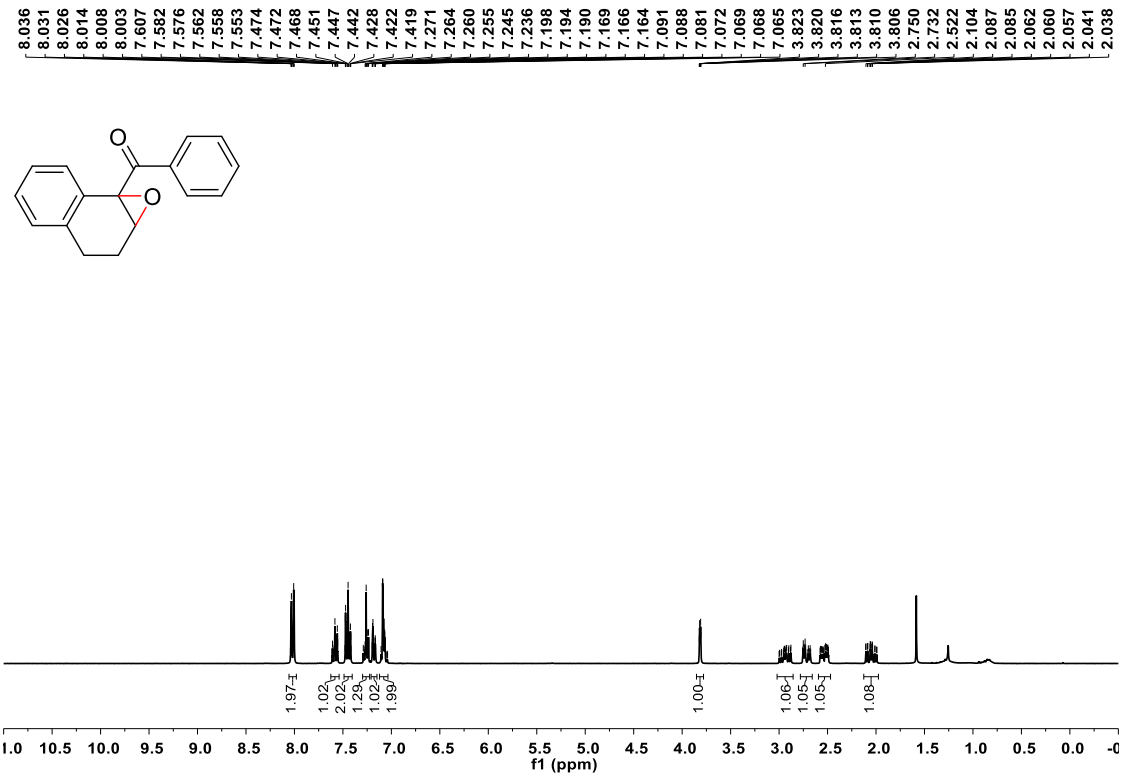
^{1}H NMR



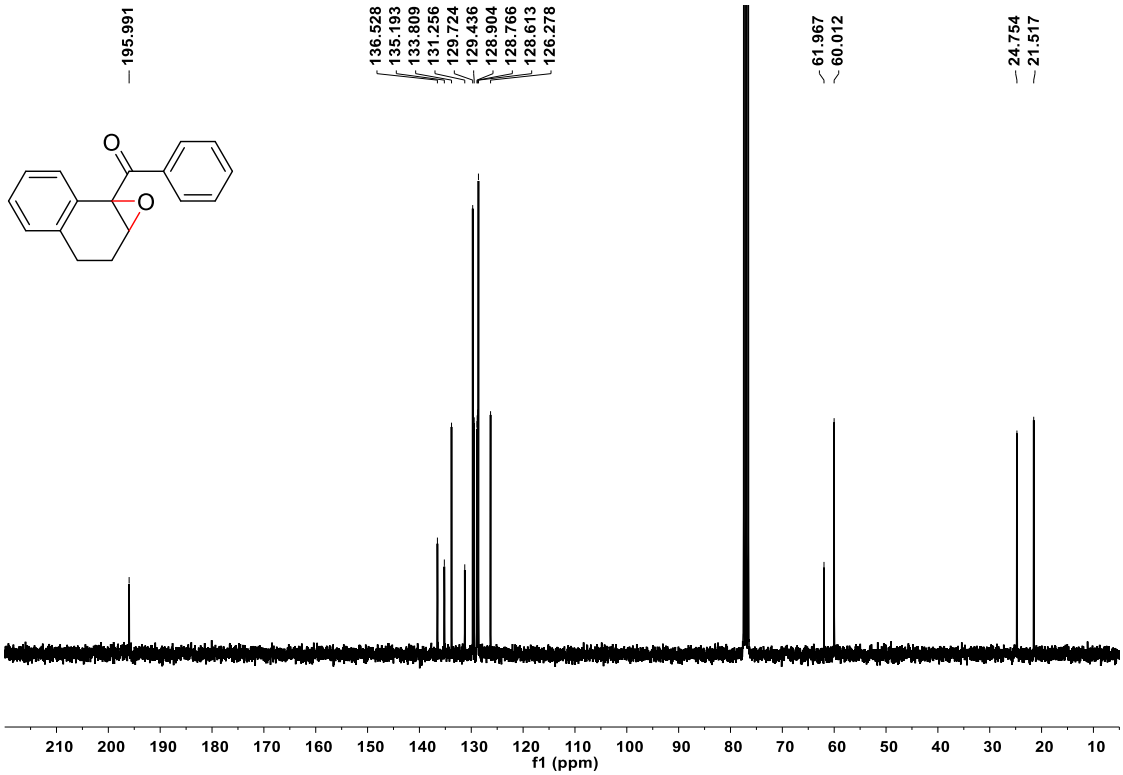
^{13}C NMR



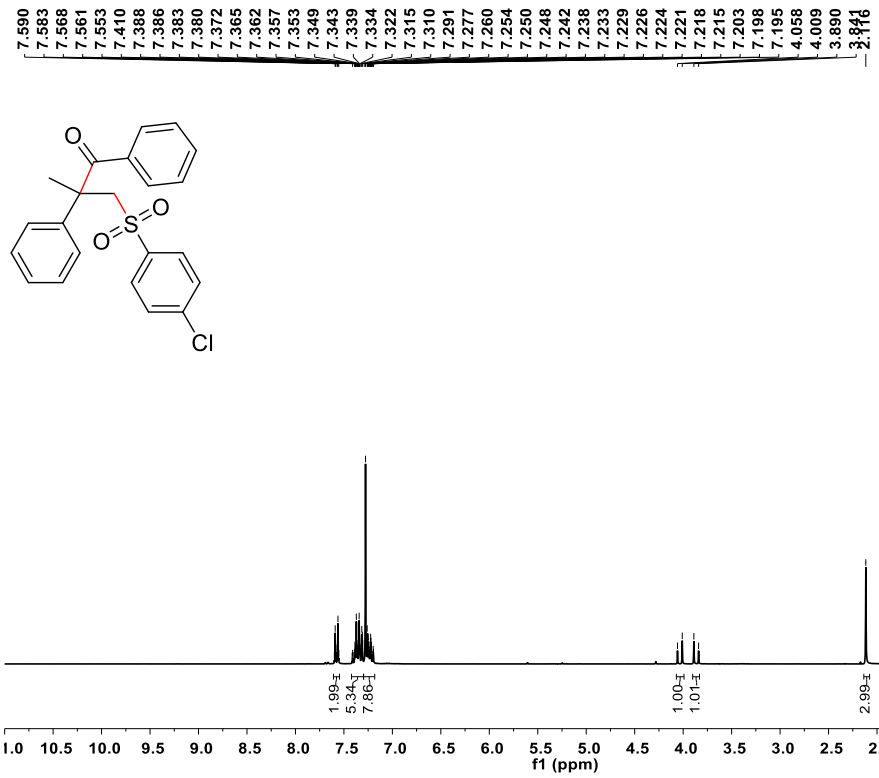
^{1}H NMR



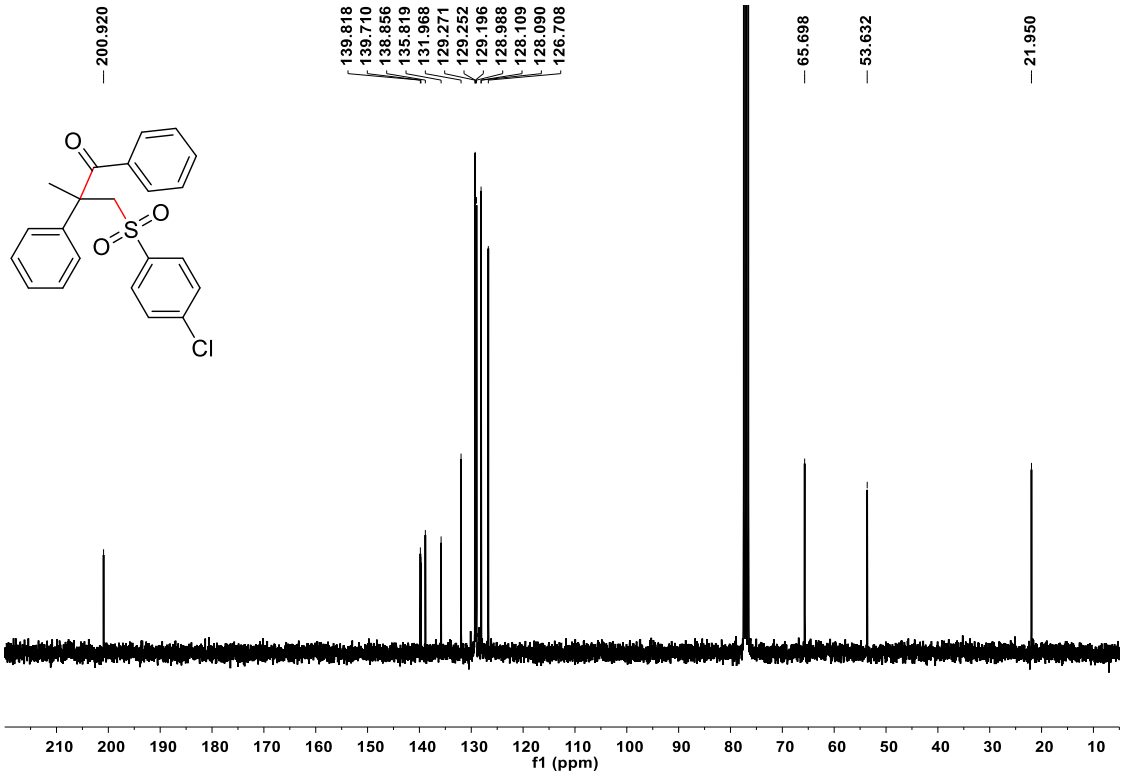
^{13}C NMR



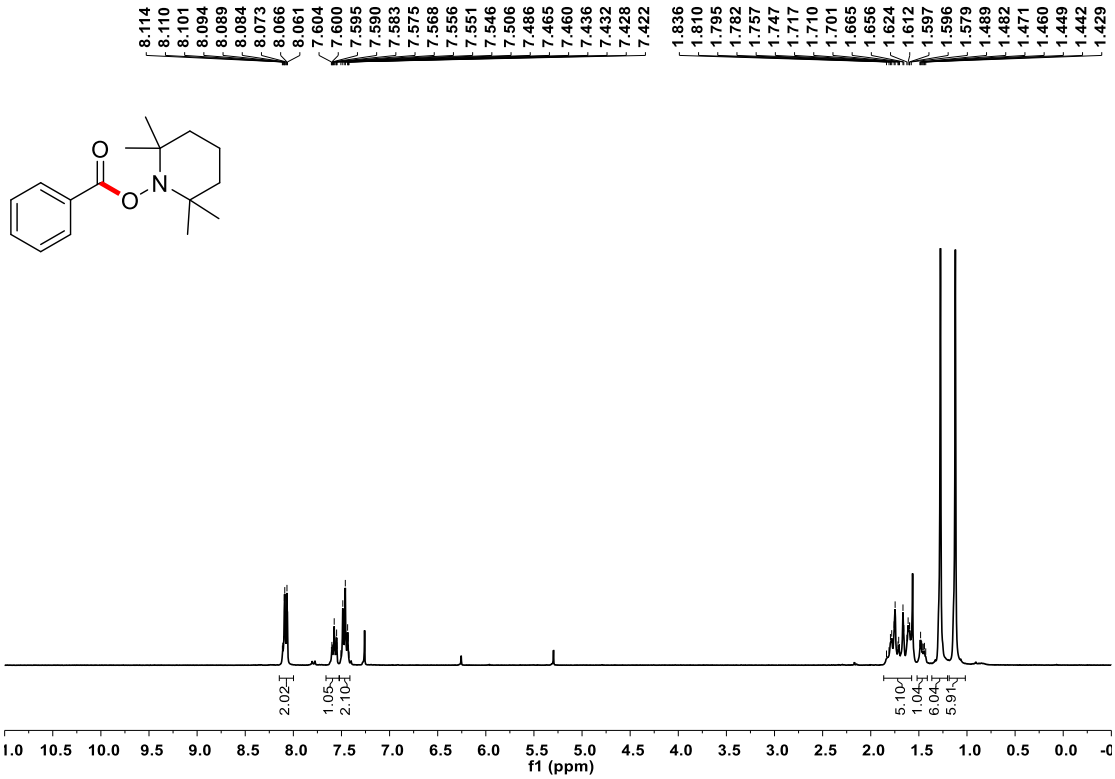
^{1}H NMR



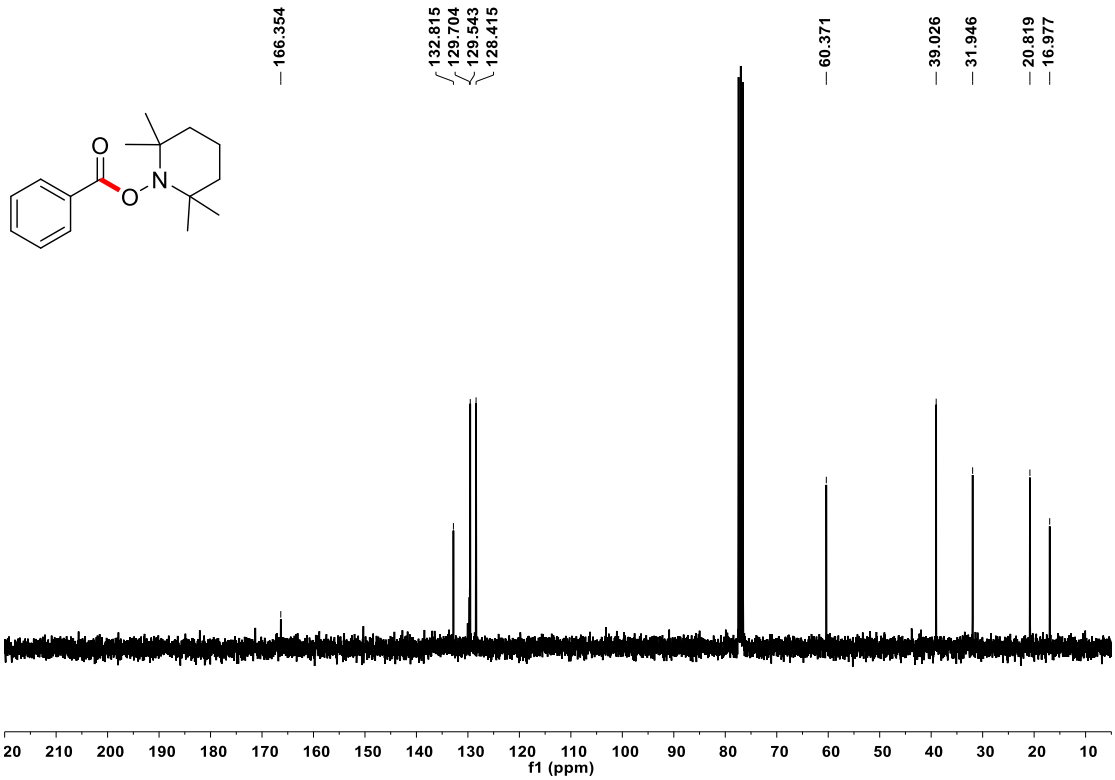
^{13}C NMR



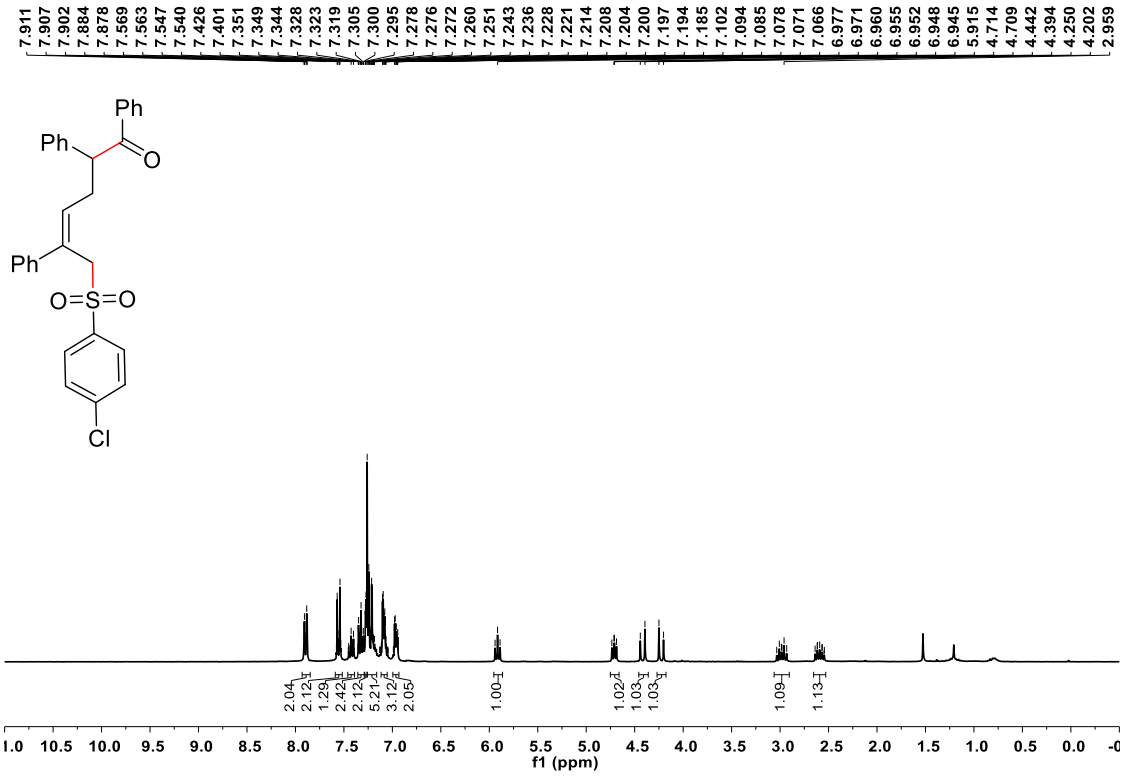
^{1}H NMR



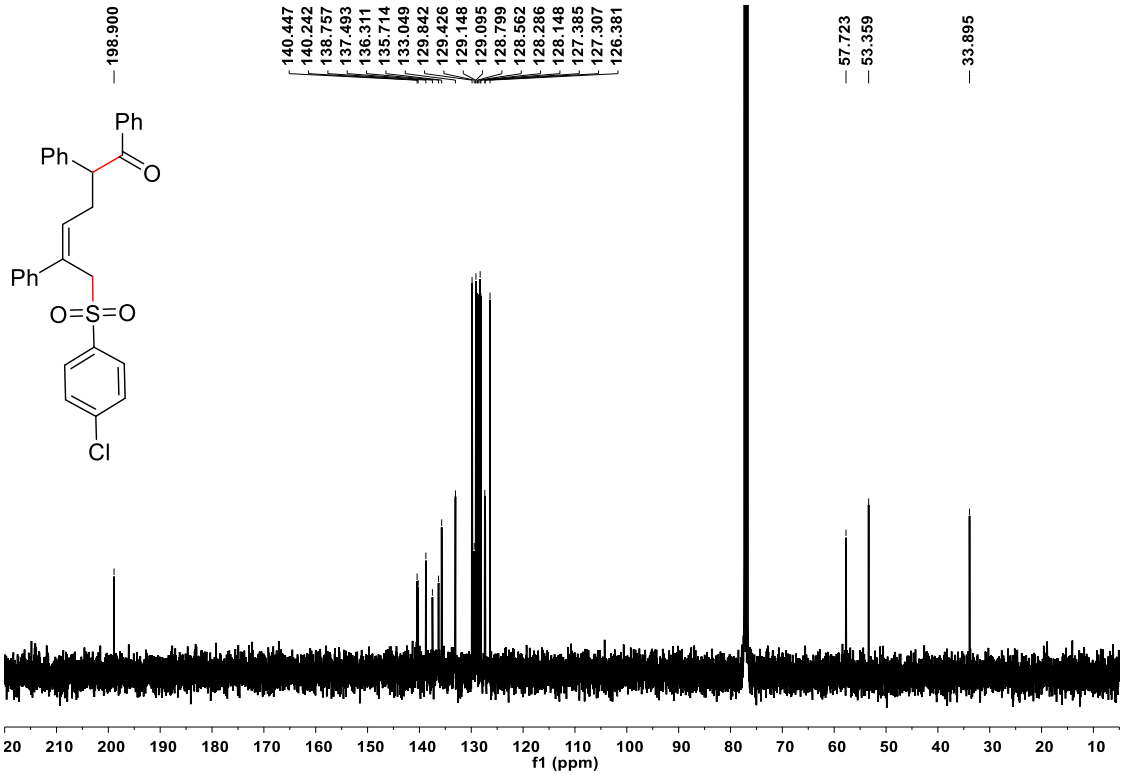
^{13}C NMR



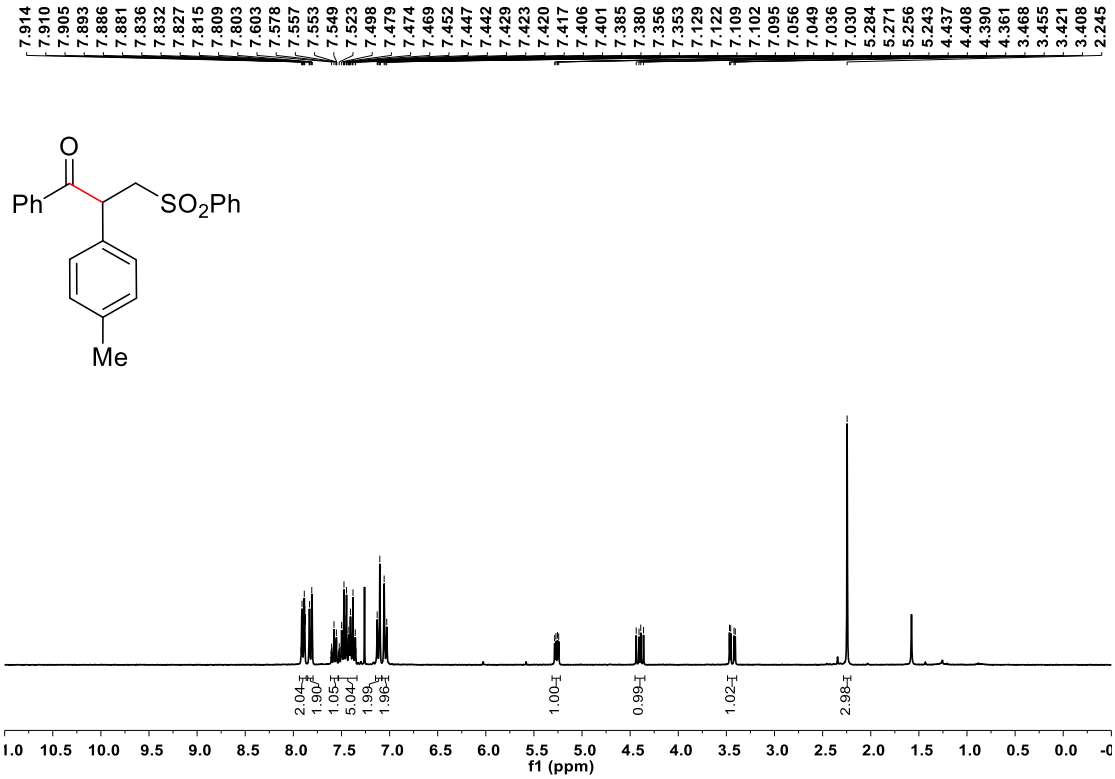
^{1}H NMR



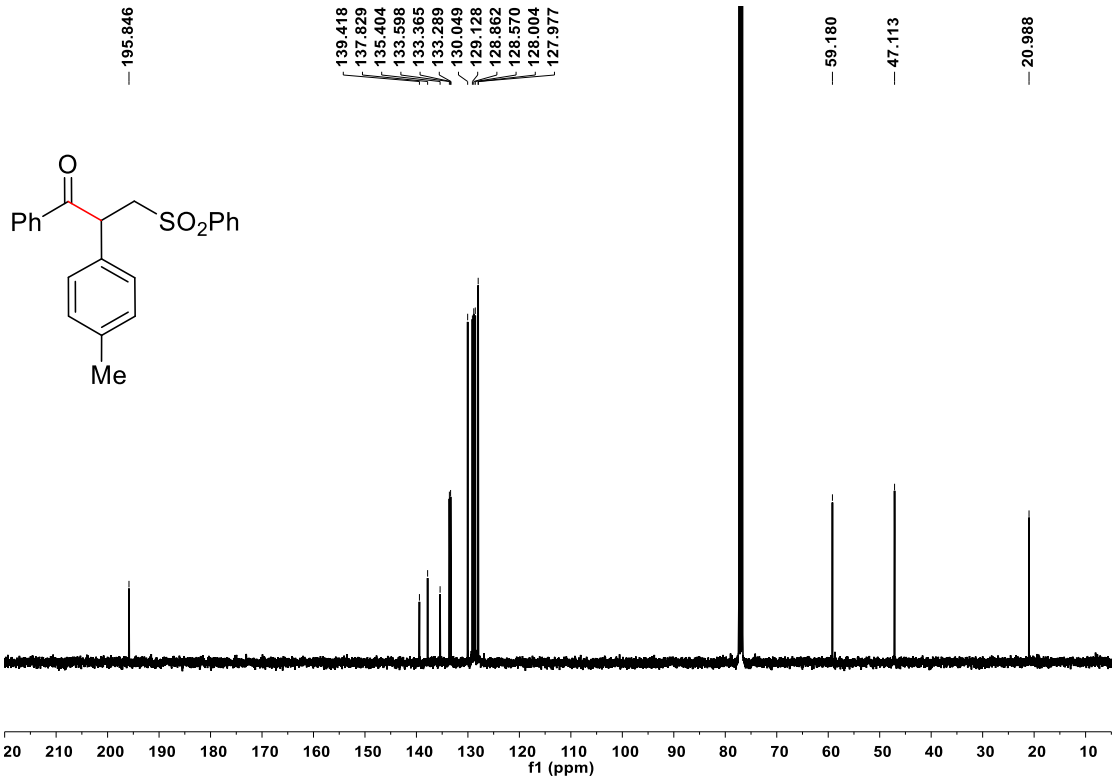
^{13}C NMR



^{1}H NMR



^{13}C NMR



9. References

(1) Meng, Q.-Y.; Döben, N.; Studer, A. Cooperative NHC and Photoredox Catalysis for the Synthesis of β-Trifluoromethylated Alkyl Aryl Ketones. *Angew. Chem., Int. Ed*. **2020**, *59*, 19956-19960.

(2) Lei, Z.; Banerjee, A.; Kusevska, E.; Rizzo, E.; Liu, P.; Ngai, M.-Y. β-Selective Aroylation of Activated Alkenes by Photoredox Catalysis. *Angew. Chem., Int. Ed*. **2019**, *58*, 7318-7323.

(3) Tanaka, F.; Mase, N.; Barbas, C. F. Design and Use of Fluorogenic Aldehydes for Monitoring the Progress of Aldehyde Transformations. *J. Am. Chem. Soc.* **2004**, *126*, 3692-3693.

(4) Hu, N.; Jung, H.; Zheng, Y.; Lee, J.; Zhang, L.; Ullah, Z.; Xie, X.; Harms, K.; Baik, M.-H.; Meggers, E. Catalytic Asymmetric Dearomatization by Visible-Light-Activated [2+2] Photocycloaddition. *Angew. Chem., Int. Ed*. **2018**, *57*, 6242-6246.

(5) Kawauchi, D.; Ueda, H.; Tokuyama, H. Double Functionalization of Styrenes by Cu-Mediated Assisted Tandem Catalysis. *Eur. J. Org. Chem.* **2019**, *2019*, 2056-2060.

(6) Mato, M.; Herlé, B.; Echavarren, A. M. Cyclopropanation by Gold- or Zinc-Catalyzed Retro-Buchner Reaction at Room Temperature. *Org. Lett.* **2018**, *20*, 4341-4345.

(7) Liu, J.; Liu, X.-P.; Wu, H.; Wei, Y.; Lu, F.-D.; Guo, K.-R.; Cheng, Y.; Xiao, W.-J. Visible-light-induced triple catalysis for a ring-opening cyanation of cyclopropyl ketones. *Chem. Commun.* **2020**, *56*, 11508-11511.

(8) Gembus, V.; Bonnet, J.-J.; Janin, F.; Bohn, P.; Levacher, V.; Brière, J.-F. Synthesis of pyrazolines by a site isolated resin-bound reagents methodology. *Organic & Biomolecular Chemistry* **2010**, *8*, 3287-3293.

(9) Wang, G.-Z.; Shang, R.; Cheng, W.-M.; Fu, Y. Decarboxylative 1,4-Addition of α-Oxocarboxylic Acids with Michael Acceptors Enabled by Photoredox Catalysis. *Org. Lett.* **2015**, *17*, 4830-4833.

(10) Jun, C.-H.; Lee, H.; Hong, J.-B.; Kwon, B.-I. Efficient and Selective Hydroacylation of 1-Alkynes with Aldehydes by a Chelation-Assisted Catalytic System. *Angew. Chem., Int. Ed*. **2002**, *41*, 2146-2147.

(11) Guin, J.; De Sarkar, S.; Grimme, S.; Studer, A. Biomimetic Carbene-Catalyzed Oxidations of Aldehydes Using TEMPO. *Angew. Chem., Int. Ed*. **2008**, *47*, 8727-8730.