Supporting Information

# Rh-catalyzed chemodivergent [4+1]-annulation/allylation of sulfoxonium ylides with α-methylene-β-lactones: access to α-indanonyl/α-benzyl acrylates

## Table of Contents

**General Information.** $[Cp^*RhCl_2]_2$ (97%), $AgSbF_6$ (98%), $Cu(OAc)_2$ (98%), $Zn(OAc)_2$ (>98%), AgOAc (≥99.99%), CsOAc (98%), NaOAc (>98%), PivOH (>98%), $MesCO_2H$ (>98%), 1-$AdCO_2H$ (>98%), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) (>99%), trifluoroethanol (TFE) (>99%) and carboxylic acids of Sigma-Aldrich, BLD Pharm and TCI chemicals used as received, while $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ was prepared according reported procedure.[1] Acetonitrile ($CH_3CN$), toluene, methanol (MeOH), tetrahydrofuran (THF), 1,2-dichloroethane $(CH_2Cl)_2$ and dichloromethane ($CH_2Cl_2$) were dried prior to use as per the standard procedure. Silica gel-G/GF254 plates (Merck) used for TLC analysis with a mixture of EtOAc and n-hexane as the eluent. Column chromatography was carried out using Rankem silica gel (60-120 mesh). Bruker Avance III 400, 500 and 600 MHz NMR spectrometers used to record ($^1H$, $^{13}C$ and $^{19}F$) spectra using $CDCl_3$ and DMSO-$d_6$ as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) reported in parts per million and hertz (Hz), respectively, and to describe peak patterns following abbreviations used when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets and m = multiplet. Melting point of the products was measured on Büchi melting point apparatus, MPB-540. Mestre nova software was used for the spectral analysis. Q-Tof ESI-MS instrument (model HAB273) was used for recording HRMS. Infrared spectra recorded on Perkin Elmer FT-IR instrument. Single crystal *X*-ray data collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/-K$\alpha$ radiation and the structures solved by direct method using SHELXL-18 and SHELXL-19 (Göttingen, Germany).

**Sample Preparation for Crystal Growth.** The compounds **5ae** and **5ia** were dissolved in a 1:1 mixture of $CH_2Cl_2$ and n-hexane (1 mL) and kept at room temperature for slow evaporation (2 days). Needle and block shaped crystals were formed, which were subjected to X-ray diffraction.

**Crystal Structure and Data of 5ae.**

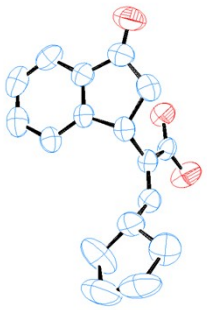


**Figure S1.** ORTEP diagram of **5ae** (CCDC No 2420493) with 50% ellipsoid. H-Atoms are omitted for clarity.

| | |
|---|---|
| CCDC No. | 2420493 |
| Identification code | **5ae** |
| Empirical formula | $C_{17}H_{18}O_3$ |
| Formula weight | 270.31 |
| Crystal habit, colour | Needle, Colourless |
| Temperature, *T*/K | 295K |
| Wavelength, λ/Å | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P -1 |
| Unit cell dimensions | a = 8.4589(6) Å<br>b = 9.2758(6) Å<br>c = 9.7016(6) Å<br>α= 93.006(2)<br>β=108.3900(10)<br>γ = 93.186(2) |
| Volume, *V*/Å$^3$ | 719.26(8) Å$^3$ |
| *Z* | 2 |
| Calculated density, Mg·m$^{-3}$ | 1.248 |
| Absorption coefficient, $\mu$/mm$^{-1}$ | 0.085 |
| *F* (000) | 288 |
| $\theta$ range for data collection | 2.205 to 25.340 |
| Limiting indices | -10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -11≤ l ≤ 11 |
| Reflection collected / unique | 2611/2136 |
| Completeness to $\theta$ | 99.2 % |
| Absorption correction | Multi-scan |
| Refinement method | 'SHELXL 2019/1 (Sheldrick, 2015)' |
| Data / restraints / parameters | 2611/ 0 / 182 |
| Goodness-of-fit on $F^2$ | 0.1479 |
| Final *R* indices [*I* >2sigma(*I*)] | R1 = 0.0612, *w*R2 = 0.1479 |
| R indices (all data) | R1 = 0.0754, *w*R2 = 0.1587 |

**Crystal Structure and Data of 5ia.**

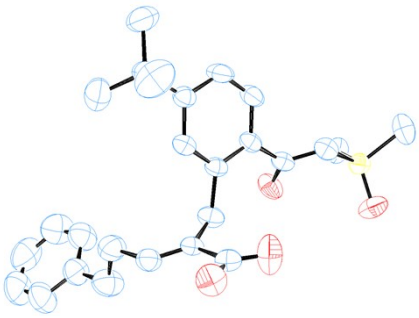
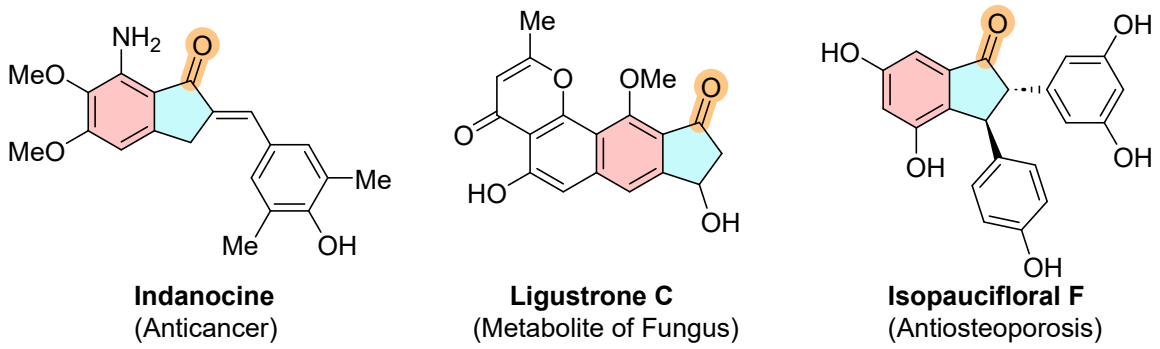


**Figure S2.** ORTEP diagram of **5ia** (CCDC No 2420491) with 50% ellipsoid. H-Atoms are omitted for clarity.

| | |
|---|---|
| CCDC No. | 2420491 |
| Identification code | **5ia** |
| Empirical formula | $C_{26}H_{32}O_4S$ |
| Formula weight | 440.57 |
| Crystal habit, colour | Block, Light yellow |
| Temperature, *T*/K | 295K |
| Wavelength, λ/Å | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P 21/c |
| Unit cell dimensions | a = 21.4284(15) Å<br>b = 10.2324(7) Å<br>c = 11.5649(8) Å<br>α= 90<br>β=105.207(2)<br>γ = 90 |
| Volume, *V*/Å$^3$ | 2447.0(3) Å$^3$ |
| *Z* | 4 |
| Calculated density, Mg·m$^{-3}$ | 1.196 |
| Absorption coefficient, $\mu$/mm$^{-1}$ | 0.160 |
| *F* (000) | 944 |
| $\theta$ range for data collection | 1.970 to 24.999 |
| Limiting indices | -25 ≤ h ≤ 25, -12 ≤ k ≤ 12, -13≤ l ≤ 13 |
| Reflection collected / unique | 4301/2704 |
| Completeness to $\theta$ | 99.9 % |

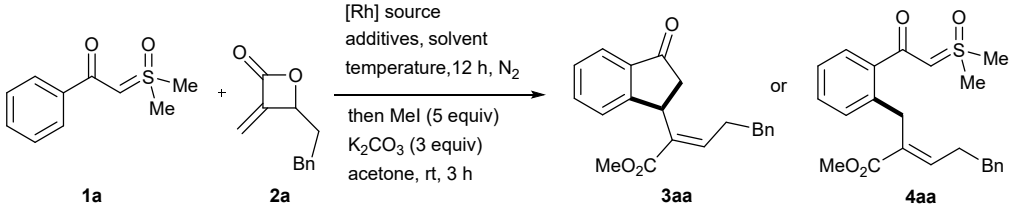
| | |
|---|---|
| Absorption correction | Multi-scan |
| Refinement method | 'SHELXL 2018/3 (Sheldrick, 2015)' |
| Data / restraints / parameters | 4301/ 0 / 286 |
| Goodness-of-fit on $F^2$ | 0.1257 |
| Final $R$ indices [$I$ >2sigma($I$)] | R1 = 0.0774, $w$R2 = 0.1257 |
| R indices (all data) | R1 = 0.1380, $w$R2 = 0.1575 |




**Indanocine** (Anticancer) **Ligustrone C** (Metabolite of Fungus) **Isopaucifloral F** (Antiosteoporosis)

**Figure S3. Examples of Biologically Important Indanonyl Motifs**

**Table S1. Optimization of the Reaction Conditions**[a]

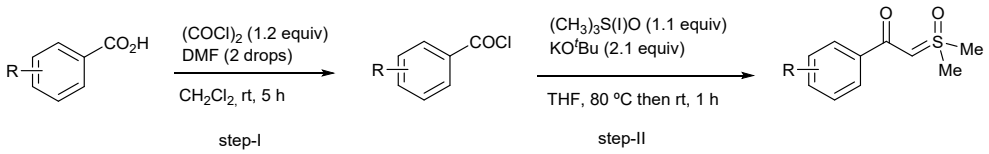



| entry | [Rh] source | additive I | additive II | solvent | yield (%)[b] | |
|---|---|---|---|---|---|---|
| | | | | | **3aa** | **4aa** |
| 1 | $[Cp^*RhCl_2]_2$ | $Cu(OAc)_2$ | $AgSbF_6$ | $(CH_2Cl)_2$ | 17 | n.d. |
| 2 | $[Cp^*RhCl_2]_2$ | $Zn(OAc)_2$ | $AgSbF_6$ | $(CH_2Cl)_2$ | 25 | n.d. |
| 3 | $[Cp^*RhCl_2]_2$ | AgOAc | $AgSbF_6$ | $(CH_2Cl)_2$ | 20 | n.d. |
| 4 | $[Cp^*RhCl_2]_2$ | CsOAc | $AgSbF_6$ | $(CH_2Cl)_2$ | trace | n.d. |
| 5 | $[Cp^*RhCl_2]_2$ | NaOAc | $AgSbF_6$ | $(CH_2Cl)_2$ | trace | n.d. |
| 6 | $[Cp^*RhCl_2]_2$ | $Zn(OAc)_2$ | $AgNTf_2$ | $(CH_2Cl)_2$ | 21 | n.d. |
| 7 | $[Cp^*RhCl_2]_2$ | $Zn(OAc)_2$ | $AgBF_4$ | $(CH_2Cl)_2$ | trace | n.d. |
| 8 | $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ | $Zn(OAc)_2$ | - | $(CH_2Cl)_2$ | 45 | n.d. |

| | | | | | | |
|---|---|---|---|---|---|---|
| 9 | $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ | $Zn(OAc)_2$ | - | $CH_2Cl_2$ | 23 | n.d. |
| 10 | $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ | $Zn(OAc)_2$ | - | THF | trace | n.d. |
| 11 | $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ | $Zn(OAc)_2$ | - | toluene | trace | n.d. |
| 12 | $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ | $Zn(OAc)_2$ | - | $CH_3CN$ | 18 | n.d. |
| 13 | $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ | $Zn(OAc)_2$ | - | MeOH | n.d. | n.d. |
| 14 | $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ | $Zn(OAc)_2$ | - | HFIP | 23 | n.d. |
| **15** | **$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$** | **$Zn(OAc)_2$** | - | **TFE** | **75** | **n.d.** |
| 16[c] | $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ | $Zn(OAc)_2$ | - | TFE | 65 | n.d. |
| 17[d] | $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ | $Zn(OAc)_2$ | - | TFE | 25 | n.d. |
| 18[e] | $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ | $Zn(OAc)_2$ | - | TFE | trace | n.d. |
| 19 | $Rh_2(OAc)_4$ | $Zn(OAc)_2$ | - | TFE | trace | n.d. |
| 20[f] | $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ | $Zn(OAc)_2$ | PivOH | TFE | n.d. | 52 |
| **21[f]** | **$[Cp^*RhCl_2]_2$** | **$Zn(OAc)_2$** | **PivOH** | **TFE** | **n.d.** | **80** |
| 22[f] | $[Cp^*RhCl_2]_2$ | $Zn(OAc)_2$ | $MesCO_2H$ | TFE | n.d. | 64 |
| 23[f] | $[Cp^*RhCl_2]_2$ | $Zn(OAc)_2$ | 1-$AdCO_2H$ | TFE | n.d. | 53 |
| 24[f,g] | $[Cp^*RhCl_2]_2$ | $Zn(OAc)_2$ | PivOH | TFE | n.d. | 74 |
| 25 | $[Cp^*RhCl_2]_2$ | $Zn(OAc)_2$ | $AgSbF_6$ | TFE | n.d. | 10 |
| 26[f] | $[Cp^*RhCl_2]_2$ | - | PivOH | TFE | n.d. | 40 |
| 27[f] | $[Cp^*RhCl_2]_2$ | $Zn(OAc)_2$ | PivOH | $(CH_2Cl)_2$ | n.d. | trace |
| 28[f] | $[Cp^*RhCl_2]_2$ | $Zn(OAc)_2$ | PivOH | $CH_3CN$ | n.d. | n.d. |
| 29[f] | $[Cp^*RhCl_2]_2$ | $Zn(OAc)_2$ | PivOH | HFIP | n.d. | trace |
| 30[f] | - | $Zn(OAc)_2$ | PivOH | TFE | n.d. | n.d. |

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), [Rh] (2.5 mol %), additive I (1 equiv), additive II (20 mol %), solvent (1 mL), 80 °C, 12 h, $N_2$ atmosphere, then MeI (5 equiv), $K_2CO_3$ (3 equiv), acetone (2 mL), rt, 3 h. [b]Isolated yield. [c]At 100 °C. [d]At room temperature. [e]Under air. [f]Additive II (1 equiv), [g]$AgSbF_6$ (20 mol %). n.d. = not detected. TFE = 2,2,2-trifluoroethanol. HFIP = 1,1,1,3,3,3-hexafluoroisopropanol.

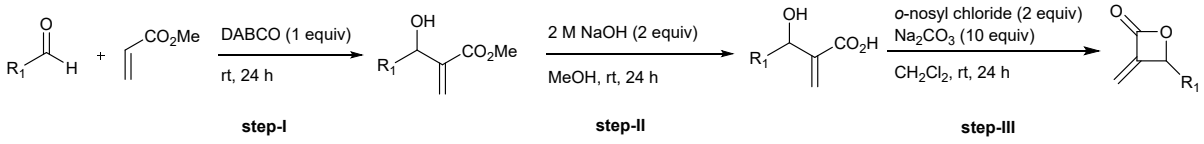
**General Procedure for the Preparation of Sulfoxonium Ylides 1.**[2]




**Step-I:** To a stirred solution of carboxylic acid (5 mmol, 1.0 equiv) in $CH_2Cl_2$ (10 mL), DMF (2 drops) was added followed by the dropwise addition of $(COCl)_2$ (6 mmol, 0.51 mL, 1.2 equiv). The reaction was allowed to stir at room temperature for 5 h. Evaporation of the solvent gave a residue, which was dissolved in THF (5 mL). The resulting solution was used as acid chloride solution in subsequent reactions.

**Step-II**: To a stirred solution of potassium *tert*-butoxide (10.5 mmol, 1.1 g, 2.1 equiv) in THF (10 mL), trimethylsulfoxonium iodide (5.5 mmol, 1.2 g, 1.1 equiv) was added under $N_2$ atmosphere and it was allowed to stir at 80 ºC for 30 minutes. The reaction mixture was then cooled to 0 °C and acid chloride solution (obtained by **step-I**) was added dropwise. The reaction mixture was allowed to stir at room temperature for an additional 1 h. After completion (monitored by TLC), the solvent was evaporated and the residue was treated with water (10 mL). The resultant solution was extracted using EtOAc (3 x 10 mL) and washed with water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography (EtOAc : MeOH = 20:1) to afford the sulfoxonium ylides **1a**-**r**.

**General Procedure for the Preparation of $\alpha$-Methylene-$\beta$-lactones 2.**[3b-d]



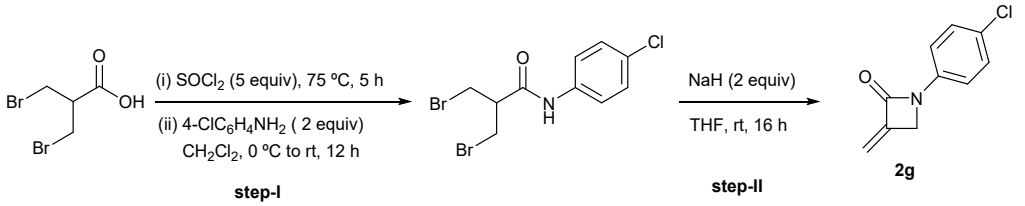

**Step-I.** Aldehyde (20 mmol, 1.0 equiv), methyl acrylate (60 mmol, 5.4 mL, 3.0 equiv) and DABCO (20 mmol, 2.24 mg, 1.0 equiv) were stirred at room temperature for 24 h. After completion (monitored by TLC), the reaction mixture was diluted with EtOAc (10 mL) and washed with saturated $NaHCO_3$ (5 mL). The residue was extracted with EtOAc (3 x 10 mL). The combined organic part was washed with water (10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave MBH adduct, which was used for the next step without further purification.

**Step-II.** To a stirred solution of MBH adduct (obtained by **step-I**) (20 mmol, 1.0 equiv) in MeOH (10 mL), 2 M NaOH (20 mL, 2 equiv) was added dropwise and the resultant mixture was allowed to stir at room temperature for 24 h. After completion (monitored by TLC), the solvent was evaporated and the resulting residue was acidified using 1 N HCl until pH = 1 and extracted using EtOAc (3 x 10 mL). The combined organic part was washed with water (10

mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography (EtOAc : n-hexane = 1:1) to afford $\alpha$-methylene-$\beta$-hydroxyacids.

**Step-III.** To a stirred solution of the acid (obtained by **step-II**) (10 mmol, 1.0 equiv) in $CH_2Cl_2$ (50 mL), $Na_2CO_3$ (100 mmol, 10.6 g, 10 equiv) was added and allowed to stir at room temperature. After 0.5 h, *o*-nosyl chloride (20 mmol, 4.42 g, 2 equiv) was added and the stirring was continued for an additional 24 h. After completion (monitored by TLC), the reaction mixture was treated with $CH_2Cl_2$ (20 mL) and water (10 mL), and stirred for 15 mins. The organic layer was separated and the aqueous solution was extracted using $CH_2Cl_2$ (3 x 20 mL). The combined organic part was washed with water (10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue, which was purified using silica gel column chromatography (EtOAc : n-hexane = 1:9) to afford $\alpha$-methylene-$\beta$-lactones **2a-f.**

**General Procedure for the Preparation of Methylene-$\beta$-lactam 2g.**[3a]

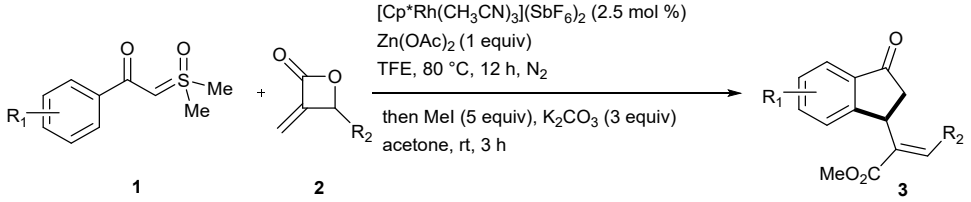



**Step-I.** 3-Bromo-2-bromomethylpropanoic acid (2 mmol, 500 mg, 1.0 equiv) was allowed to stir in $SOCl_2$ (10 mmol, 1 mL, 5 equiv) at 75 ºC for 5 h. The resultant mixture was cooled to room temperature and the volatiles were evaporated. The residue was dissolved in $CH_2Cl_2$ (5 mL) and the solution of 4-chloroaniline (4 mmol, 510 mg, 2.0 equiv) was added dropwise at 0 ºC. The resultant mixture was allowed to stir at room temperature for 12 h. After completion (monitored by TLC), the reaction mixture was diluted with $CH_2Cl_2$ (10 mL) and washed with 2 N HCl (2 mL). The residue was extracted with $CH_2Cl_2$ (3 x 10 mL). The combined organic part was washed with water (10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue, which was purified using silica gel column chromatography (EtOAc: n-hexane = 1:4) to afford 3-bromo-2-bromomethylpropionamide in 55% (410 mg) yield.

**Step-II.** To a stirred solution of 3-bromo-2-(bromomethyl)-*N*-(4-chlorophenyl)propanamide (1.1 mmol, 400 mg, 1.0 equiv) in THF (5 mL), NaH (2.2 mmol, 88 mg, 60% dispersion in mineral oil, 2.0 equiv) was added portion wise at room temperature. The resultant mixture was allowed to stir for 16 h. After completion (monitored by TLC), the reaction mixture was quenched with saturated $NH_4Cl$ (3 mL). The solvent was evaporated and the residue was extracted with EtOAc (3 x 10 mL). The combined organic part was washed with water (10 mL)

and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified using silica gel column chromatography (EtOAc : n-hexane = 1:9) to afford **2g** in 57% (124 mg) yield.

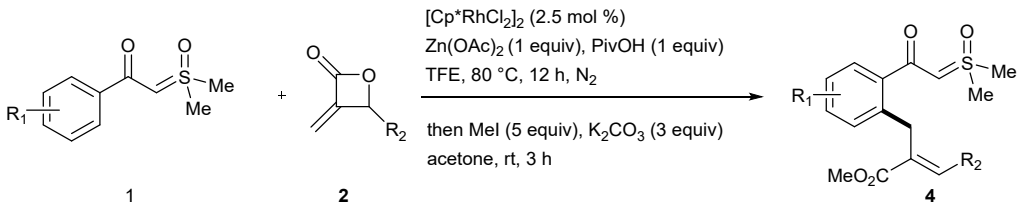
**General Procedure for the Rh-Catalyzed C-H Annulation of Sulfoxonium Ylides with $\alpha$-Methylene-$\beta$-lactones.**




Sulfoxonium ylide **1** (0.1 mmol, 1.0 equiv), $\alpha$-methylene-$\beta$-lactones **2** (0.15 mmol, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (0.0025 mmol, 2.1 mg, 0.025 equiv) and $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv) were stirred in TFE (1 mL) at 80 °C for 12 h under $N_2$ atmosphere. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was treated with EtOAc (10 mL) and was washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (0.3 mmol, 41 mg, 3.0 equiv) and MeI (0.5 mmol, 33 µL, 5.0 equiv) in acetone (2 mL) at room temperature for 3 h. After completion (monitored by TLC), the solvent was evaporated and the residue was extracted using EtOAc (2 x 10 mL). The combined organic part was washed with water (10 mL). Drying ($Na_2SO_4$) and evaporated to give a residue that was purified on silica gel column chromatography (EtOAc : n-hexane = 1:9) to afford the annulated **3**.

**Scale-up Synthesis of 3aa**. 2-(Dimethyl(oxo)-l6-sulfaneylidene)-1-phenylethan-1-one **1a** (2 mmol, 392 mg, 1.0 equiv), 3-methylene-4-phenethyloxetan-2-one **2a** (3 mmol, 564 mg, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (0.05 mmol, 42 mg, 0.025 equiv) and $Zn(OAc)_2$ (2 mmol, 366 mg, 1 equiv) were stirred in TFE (15 mL) at 80 °C for 12 h under $N_2$ atmosphere. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was treated with EtOAc (50 mL) and was washed with water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (6 mmol, 828 mg, 3.0 equiv) and MeI (10 mmol, 0.6 mL, 5.0 equiv) in acetone (30 mL) at room temperature for 3 h. The purification was carried out as described in the above general procedure to furnish **3aa** in 69% (441 mg) yield.

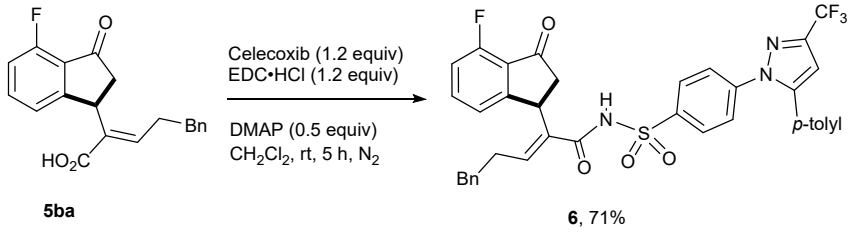
**General Procedure for the Rh-Catalyzed C-H Allylation of Sulfoxonium Ylides with $\alpha$-Methylene-$\beta$-lactones.**




Sulfoxonium ylide **1** (0.1 mmol, 1.0 equiv), $\alpha$-methylene-$\beta$-lactones **2** (0.15 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (0.0025 mmol, 1.5 mg, 0.025 equiv), $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv) and PivOH (0.1 mmol, 10 mg, 1 equiv) were stirred in TFE (1 mL) at 80 ˚C for 12 h under $N_2$ atmosphere. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was treated with EtOAc (10 mL) and was washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (0.3 mmol, 41 mg, 3.0 equiv) and MeI (0.5 mmol, 33 μL, 5.0 equiv) in acetone (2 mL) at room temperature for 3 h. After completion (monitored by TLC), the solvent was evaporated and the residue was extracted using EtOAc (2 x 10 mL). The combined organic was washed with water (10 mL), dried ($Na_2SO_4$) and evaporated to give a residue that was purified on silica gel column chromatography (EtOAc : n-hexane = 3:1) to afford the allylated **4**.

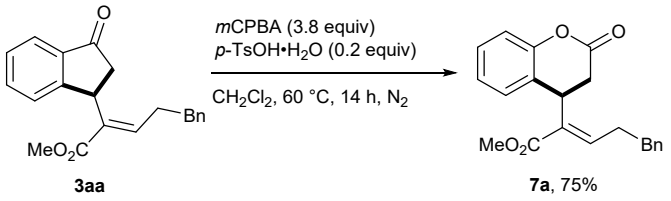
**Scale-up Synthesis of 4aa**. 2-(Dimethyl(oxo)-l6-sulfaneylidene)-1-phenylethan-1-one **1a** (2 mmol, 392 mg, 1.0 equiv), 3-methylene-4-phenethyloxetan-2-one **2a** (3 mmol, 564 mg, 1.5 equiv), $[Cp^*RhCl_2]_2$ (0.05 mmol, 31 mg, 0.025 equiv), $Zn(OAc)_2$ (2 mmol, 366 mg, 1 equiv) and PivOH (2 mmol, 204 mg, 1 equiv) were stirred in TFE (15 mL) at 80 ˚C for 12 h under $N_2$ atmosphere. Evaporation of the solvent gave a residue was treated with EtOAc (50 mL) and washed with water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (6 mmol, 828 mg, 3.0 equiv) and MeI (10 mmol, 0.6 mL, 5.0 equiv) in acetone (30 mL) at room temperature for 3 h. The purification was performed as described in the above general procedure to furnish **4aa** in 73% (581 mg) yield.

**Synthesis of 6.**[4b]



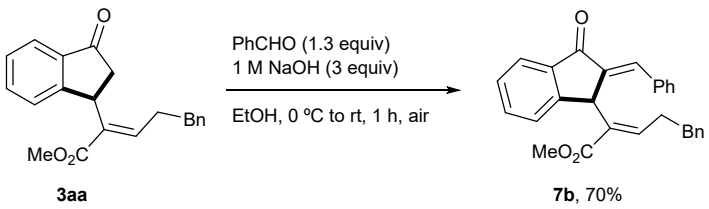

To a stirred solution of **5ba** (0.1 mmol, 33 mg, 1 equiv) in $CH_2Cl_2$ (1.5 mL) under $N_2$ atmosphere, celecoxib (0.12 mmol, 46 mg, 1.2 equiv), EDC·HCl (0.12 mmol, 23 mg, 1.2 equiv) and DMAP (0.05 mmol, 6 mg, 0.5 equiv) were added and the stirring was continued for 5 h at room temperature. After completion (monitored by TLC), the reaction mixture was quenched with 1 N HCl (1 mL). The organic layer was separated and the aqueous solution was extracted using EtOAc (2 x 10 mL). The combined organic solution was washed with saturated $NaHCO_3$ (5 mL) and water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography (EtOAc : n-hexane = 4:1) to afford **6** in 71% (48 mg) yield.

**Synthesis of 7a.**[4c]



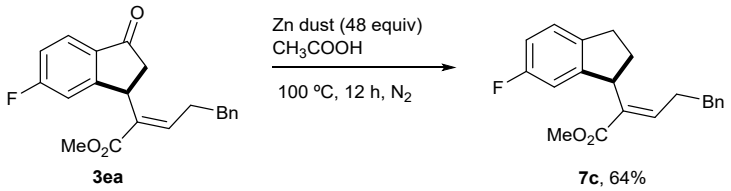

Compound **3aa** (0.1 mmol, 32 mg, 1 equiv), *m*CPBA (0.38 mmol, 65 mg, 3.8 equiv) and *p*-TsOH·$H_2O$ (0.02 mmol, 4 mg, 0.2 equiv) in $CH_2Cl_2$ (1.5 mL) were stirred at 60 ºC for 12 h under $N_2$ atmosphere. After completion (monitored by TLC), the reaction mixture was quenched using saturated $NaHCO_3$ (1 mL) and saturated $Na_2S_2O_3$ (1 mL). The residue was extracted with $CH_2Cl_2$ (2 x 10 mL). The combined organic part was washed with water (5 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified using silica gel column chromatography (EtOAc : n-hexane = 1:9) to afford **7a** in 75% (25 mg) yield.

**Synthesis of 7b.**[4c]



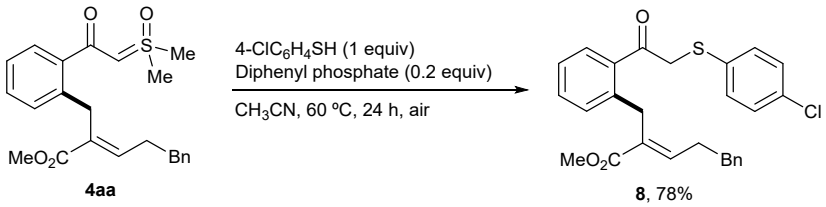
To a stirred solution of 1 M NaOH (0.3 mmol, 20 µL, 3 equiv) and EtOH (1 mL), **3aa** (0.1 mmol, 32 mg, 1 equiv) and benzaldehyde (0.13 mmol, 14 mg, 1.3 equiv) were added at 0 ˚C and the resultant mixture was stirred for 1 h at room temperature under air. After completion (monitored by TLC), evaporation of the solvent gave a residue that was extracted using EtOAc (2 x 10 mL). The combined organic solution was washed with water (5 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue that was purified using silica gel column chromatography (EtOAc : n-hexane = 1:9) to afford **7b** in 70% (29 mg) yield.

**Synthesis of 7c.**[4c]



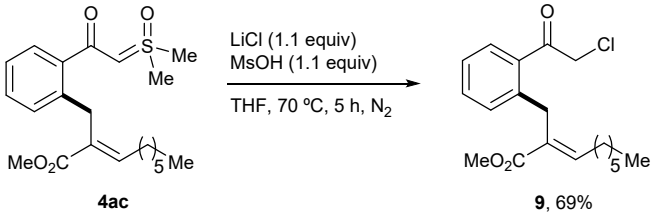

Compound **3ea** (0.1 mmol, 34 mg, 1 equiv), Zn dust (4.8 mmol, 314 mg, 48 equiv) and $CH_3COOH$ (0.5 mL), were stirred at 100 ºC for 12 h under $N_2$ atmosphere. After completion (monitored by TLC), the resultant mixture was cooled to room temperature and diluted with EtOAc (10 mL), and passed through a short pad of celite. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography (EtOAc : n-hexane = 1:9) to afford **7c** in 64% (21 mg) yield.

**Synthesis of 8.**[4d]



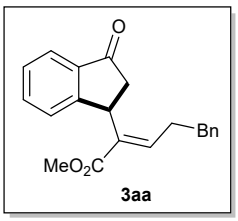

To a stirred solution of **4aa** (0.1 mmol, 40 mg, 1 equiv) in $CH_3CN$ (1.5 mL), 4-chlorothiophenol (0.1 mmol, 14 mg, 1 equiv) and diphenyl phosphate (0.02 mmol, 5 mg, 0.2 equiv) were added and the resultant mixture was allowed to stir at 60 ºC for 24 h under air. After completion (monitored by TLC), the reaction mixture was allowed to cool to room temperature, diluted with EtOAc (10 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified using silica gel column chromatography (EtOAc : n-hexane = 1:7) to afford **8** in 78% (36 mg) yield.

**Synthesis of 9.**[4a]

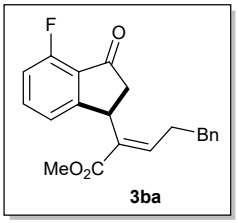



To a stirred solution of **4ac** (0.1 mmol, 38 mg, 1 equiv) in THF (1.5 mL), LiCl (0.11 mmol, 6 mg, 1.1 equiv) and MsOH (0.11 mmol, 11 mg, 1.1 equiv) were added at 0 ºC under $N_2$ atmosphere. The resultant mixture was allowed to stir at 70 ºC for 5 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was extracted using EtOAc (2 x 10 mL) and the combined organic part was washed with water (5 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue, which was purified using silica gel column chromatography (EtOAc : n-hexane = 1:7) to afford **9** in 69% (23 mg) yield.

**Characterization Data of the Products**

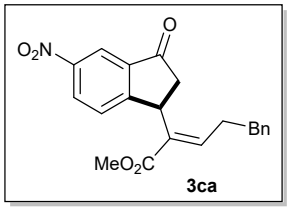



**Methyl (*E*)-2-(3-oxo-2,3-dihydro-1H-inden-1-yl)-5-phenylpent-2-enoate 3aa.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.40; colorless liquid; yield 75% (25 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.50-7.46 (m, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.32-7.28 (m, 2H), 7.25-7.21 (m, 1H), 7.17 (d, *J* = 6.8 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 4.44-4.41 (m, 1H), 3.50 (s, 3H), 2.88-2.79 (m, 2H), 2.73-2.62 (m, 3H), 2.59 (dd, *J* = 19.2, 4.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 205.9, 166.7, 156.7, 144.2, 140.6, 137.0, 134.7, 132.9, 128.7, 128.6, 127.6, 126.5, 125.0, 123.6, 51.7, 42.8, 36.7, 35.1, 30.8; FT-IR (neat) 1743, 1721, 1373, 1236, 1045 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{21}O_3$: 321.1485; Found 321.1488.

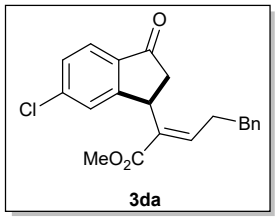



**Methyl (*E*)-2-(4-fluoro-3-oxo-2,3-dihydro-1H-inden-1-yl)-5-phenyl-pent-2-enoate 3ba.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.42; yellow liquid; yield 81% (28 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45-7.40 (m, 1H), 7.30 (t, *J* = 7.6

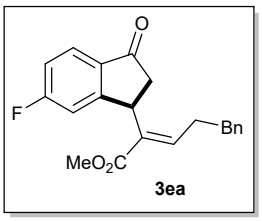
Hz, 2H), 7.25-7.21 (m, 1H), 7.18 (d, $J$ = 7.2 Hz, 2H), 7.06 (t, $J$ = 8.0 Hz, 1H), 6.95 (t, $J$ = 8.8 Hz, 1H), 6.68 (d, $J$ = 7.6 Hz, 1H), 4.39-4.36 (m, 1H), 3.52 (s, 3H), 2.89-2.81 (m, 2H), 2.71-2.62 (m, 3H), 2.61 (dd, $J$ = 13.6, 4.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.0, 166.4, 160.2($J_{C-F}$ = 242.9 Hz), 159.0 ($J_{C-F}$ = 2.3 Hz), 144.6, 140.6, 136.6 ($J_{C-F}$ = 8.2 Hz), 132.3, 128.8, 128.6, 126.6, 124.7 ($J_{C-F}$ = 12.9 Hz), 120.8 ($J_{C-F}$ = 4.1 Hz), 114.7 ($J_{C-F}$ = 19.3 Hz), 51.8, 43.2, 36.7, 35.0, 30.8; $^{19}$F NMR (470 MHz, $CDCl_3$) δ -115.1; FT-IR (neat) 1765, 1745, 1342, 1232, 1029 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{20}FO_3$: 339.1391; Found 339.1376.



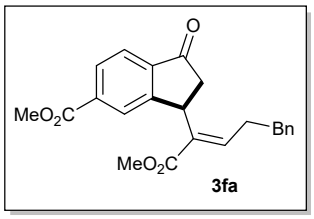

**Methyl (*E*)-2-(5-nitro-3-oxo-2,3-dihydro-1H-inden-1-yl)-5-phenyl-pent-2-enoate 3ca.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.38; colorless liquid; yield 77% (29 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.27 (d, $J$ = 8.4 Hz, 1H), 7.34-7.27 (m, 3H), 7.20 (d, $J$ = 7.2 Hz, 2H), 7.12 (t, $J$ = 7.6 Hz, 1H), 6.84 (d, $J$ = 8.4 Hz, 1H), 4.42-4.38 (m, 1H), 3.51 (s, 3H), 2.91 (t, $J$ = 6.8 Hz, 2H), 2.77-2.70 (m, 3H), 2.64 (dd, $J$ = 19.2, 4.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 203.4, 166.0, 162.3, 148.0, 145.3, 140.5, 138.0, 131.6, 128.9, 128.8, 126.8, 126.0, 119.0, 51.9, 43.1, 37.0, 35.0, 31.1; FT-IR (neat) 1766, 1747, 1369, 1226, 1040 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{20}NO_5$: 366.1336; Found 366.1316.



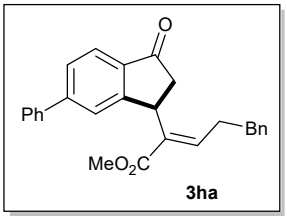

**Methyl (*E*)-2-(6-chloro-3-oxo-2,3-dihydro-1H-inden-1-yl)-5-phenyl-pent-2-enoate 3da.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.40; colorless liquid; yield 70% (25 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, $J$ = 8.0 Hz, 1H), 7.33-7.30 (m, 3H), 7.27-7.25 (m, 1H), 7.18 (d, $J$ = 7.2 Hz, 2H), 7.07 (t, $J$ = 8.0 Hz, 1H), 6.86 (s, 1H), 4.34-4.31 (m, 1H), 3.52 (s, 3H), 2.86 (t, $J$ = 8.0 Hz, 2H), 2.70-2.63 (m, 3H), 2.57 (dd, $J$ = 19.2, 4.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 204.4, 166.3, 158.2, 144.8, 141.2, 140.5, 135.5, 132.2, 128.8, 128.6, 128.4, 126.8, 125.2, 124.7, 51.8, 42.8, 36.5, 35.0, 30.9; FT-IR (neat) 1778, 1745, 1368, 1230, 1029 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{20}ClO_3$: 355.1095; Found 355.1080.




**Methyl (*E*)-2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-yl)-5-phenyl-pent-2-enoate 3ea.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.40; yellow sticky liquid; yield 68% (23 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 1H), 7.31 (t, *J* = 6.8 Hz, 2H), 7.24-7.22 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.02-6.99 (m, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 4.35-4.32 (m, 1H), 3.52 (s, 3H), 2.85 (t, *J* = 6.8 Hz, 2H), 2.72-2.67 (m, 2H), 2.63-2.55 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 204.0, 168.2($J_{C\text{-}F}$ = 203.7 Hz), 166.4, 159.8 ($J_{C\text{-}F}$ = 7.5 Hz), 144.7, 140.5, 133.3, 132.2, 128.8, 128.6, 126.8, 125.9 ($J_{C\text{-}F}$ = 8.3 Hz), 115.89 ($J_{C\text{-}F}$ = 18.9 Hz), 111.8 ($J_{C\text{-}F}$ = 17.8 Hz), 51.8, 43.0, 36.6, 35.0, 30.9; $^{19}$F NMR (470 MHz, $CDCl_3$) δ -102.9; FT-IR (neat) 1784, 1744, 1362, 1239, 1039 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{20}FO_3$: 339.1391; Found 339.1382.

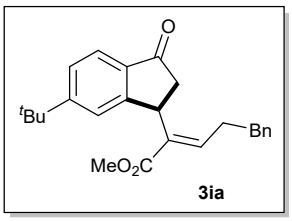



**Methyl (*E*)-3-(1-methoxy-1-oxo-5-phenylpent-2-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-5-carboxylate 3fa.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.43; yellow liquid; yield 73% (27 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.80-7.78 (m, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.24-7.20 (m, 1H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 4.43-4.41 (m, 1H), 3.94 (s, 3H), 3.49 (s, 3H), 2.95-2.88 (m, 1H), 2.84-2.77 (m, 1H), 2.72-2.64 (m, 3H), 2.59 (dd, *J* = 18.8, 4.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 205.2, 166.5, 166.4, 156.5, 144.7, 140.5, 140.3, 135.6, 132.4, 129.0, 128.8, 128.6, 126.6, 126.4, 123.6, 52.6, 51.7, 43.1, 36.8, 35.0, 30.8; FT-IR (neat) 1782, 1741, 1753, 1372, 1231, 1038 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{23}O_5$: 379.1540; Found 379.1521.

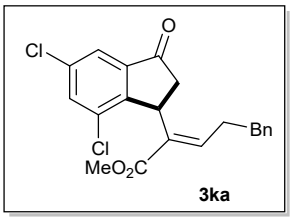



**Methyl (*E*)-2-(3-oxo-6-phenyl-2,3-dihydro-1H-inden-1-yl)-5-phenylpent-2-enoate 3ha.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.35; yellow liquid; yield 69% (27 mg); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.57-7.56 (m, 1H), 7.54-7.52 (m, 2H), 7.43 (t, *J* = 7.0 Hz, 2H), 7.40-7.36 (m, 1H), 7.24-7.23

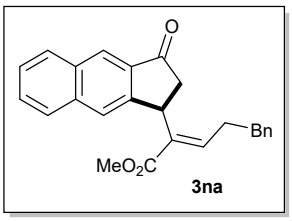
(m, 3H), 7.14-7.13 (m, 3H), 7.04 (t, $J$ = 7.5 H z, 1H), 4.46-4.44 (m, 1H), 3.50 (s, 3H), 2.86-2.78 (m, 2H), 2.74-2.69 (m, 1H), 2.65-2.56 (m, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 205.4, 166.7, 157.5, 147.8, 144.3, 140.6, 140.2, 135.9, 132.9, 129.0, 128.7, 128.5, 128.4, 127.7, 127.1, 126.6, 124.0, 123.4, 51.7, 43.2, 36.8, 35.0, 30.8; FT-IR (neat) 1784, 1738, 1365, 1236, 1042 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{27}H_{25}O_3$: 397.1798; Found 397.1780.



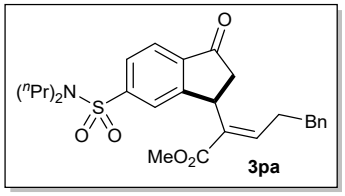

**Methyl (*E*)-2-(6-(*tert*-butyl)-3-oxo-2,3-dihydro-1H-inden-1-yl)-5-phenylpent-2-enoate 3ia.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.42; colorless liquid; yield 63% (24 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, $J$ = 8.0 Hz, 1H), 7.43 (d, $J$ = 8.0 Hz, 1H), 7.29 (t, $J$ = 6.8 Hz, 2H), 7.23-7.19 (m, 1H), 7.17 (s, 1H), 7.13 (d, $J$ = 7.2 Hz, 2H), 7.03 (t, $J$ = 8.0 Hz, 1H), 4.46-4.43 (m, 1H), 3.52 (s, 3H), 2.86-2.79 (m, 1H), 2.77-2.69 (m, 2H), 2.59-2.50 (m, 3H), 1.30 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 205.5, 167.1, 159.1, 157.1, 144.1, 140.7, 134.7, 133.2, 128.7, 128.5, 126.6, 125.4, 123.4, 121.5, 51.7, 43.5, 36.9, 35.6, 35.1, 31.4, 30.8; FT-IR (neat) 1781, 1742, 1365, 1239, 1041 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{25}H_{29}O_3$: 377.2111; Found 377.2092.



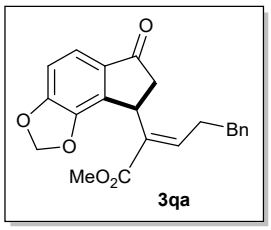

**Methyl (*E*)-2-(5,7-dichloro-3-oxo-2,3-dihydro-1H-inden-1-yl)-5-phenylpent-2-enoate 3ka.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.45; yellow liquid; yield 80% (32 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.64-7.63 (m, 1H), 7.54-7.53 (m, 1H), 7.28 (s, 1H), 7.24 (s, 1H), 7.20-7.17 (m, 1H), 7.13 (d, $J$ = 6.8 Hz, 2H), 5.89 (t, $J$ = 7.2 Hz, 1H), 4.36-4.33 (m, 1H), 3.64 (s, 3H), 3.04 (dd, $J$ = 20.0, 8.4 Hz, 1H), 2.85-2.79 (m, 2H), 2.73-2.69 (m, 2H), 2.62 (dd, $J$ = 19.2, 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 203.2, 166.7, 150.5, 144.7, 141.0, 140.7, 135.4, 134.8, 134.0, 131.5, 128.6, 128.5, 126.2, 122.1, 51.6, 45.5, 42.4, 35.2, 31.4; FT-IR (neat) 1764, 1726, 1365, 1232, 1055 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{19}Cl_2O_3$: 389.0706; Found 389.0684.




**Methyl (*E*)-2-(3-oxo-2,3-dihydro-1H-cyclopenta[*b*]naphthalen-1-yl)-5-phenylpent-2-enoate 3na.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.35; colorless liquid; yield 60% (23 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.58-7.53 (m 1H), 7.50-7.46 (m, 1H), 7.34-7.30 (m, 4H), 7.20 (d, *J* = 7.2 Hz, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 4.59-4.56 (m, 1H), 3.45 (s, 3H), 2.92-2.87 (m, 2H), 2.83-2.72 (m, 3H), 2.70 (dd, *J* = 18.8, 4.4 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 206.3, 166.7, 149.9, 143.8, 140.7, 137.2, 134.8, 133.6, 132.6, 130.6, 128.8, 128.7, 128.6, 128.0, 126.6, 126.3, 124.3, 123.4, 51.7, 43.4, 36.3, 35.2, 30.9; FT-IR (neat) 1772, 1735, 1361, 1234, 1041 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{25}H_{23}O_3$: 371.1642; Found 371.1620.

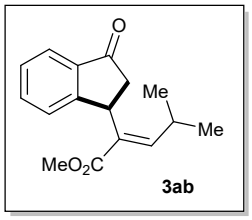



**Methyl (*E*)-2-(6-(*N*,*N*-dipropylsulfamoyl)-3-oxo-2,3-dihydro-1H-inden-1-yl)-5-phenylpent-2-enoate 3pa.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.34; yellow liquid; yield 71% (34 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86-7.84 (m, 1H), 7.81-7.79 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 2H), 6.11 (t, *J* = 7.2 Hz, 1H), 4.29-4.26 (m, 1H), 3.55 (s, 3H), 3.13-3.06 (m, 4H), 3.04-2.99 (m, 1H), 2.87-2.82 (m, 2H), 2.77-2.74 (m, 2H), 2.71(dd, *J* = 19.6, 3.6 Hz , 1H), 1.52 (q, *J* = 7.2 Hz, 4H), 0.86 (t, *J* = 7.2 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 204.4, 166.6, 156.7, 146.1, 145.1, 140.9, 139.7, 132.8, 128.6, 128.7, 126.5, 126.4, 124.9, 124.4, 51.5, 49.9, 44.5, 44.0, 35.4, 31.5, 21.9, 11.3; FT-IR (neat) 1772, 1733, 1365, 1240, 1044, 852 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{27}H_{34}NO_5S$: 484.2152; Found 484.2138.

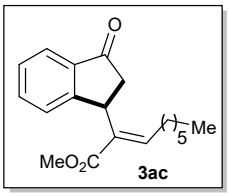



**Methyl (*E*)-2-(6-oxo-7,8-dihydro-6H-indeno[4,5-d][1,3]dioxol-8-yl)-5-phenylpent-2-enoate 3qa.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.38; colorless liquid; yield 67% (24 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.23-7.20 (m, 1H), 7.17 (d, *J* = 6.8 Hz, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.00-5.99 (m, 2H), 4.48-4.45 (m, 1H), 3.57 (s, 3H), 2.91-2.83 (m,

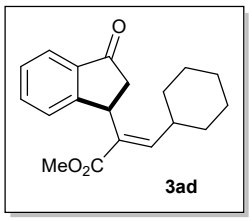
1H), 2.79-2.64 (m, 4H), 2.54 (dd, *J* = 18.8, 3.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 203.6, 166.7, 152.8, 144.3, 143.7, 140.9, 135.6, 133.1, 131.3, 128.7, 128.5, 126.5, 119.0, 108.9, 102.3, 51.8, 43.2, 34.9, 33.4, 30.7; FT-IR (neat) 1763, 1735, 1372, 1235, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{22}H_{21}O_5$: 365.1384; Found 365.1363.



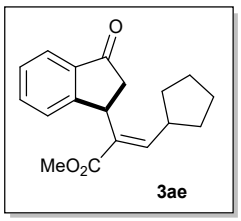

**Methyl (*E*)-4-methyl-2-(3-oxo-2,3-dihydro-1H-inden-1-yl)pent-2-enoate 3ab.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.48; colorless liquid; yield 78% (20 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.27-7.25 (m, 1H), 6.84 (d, *J* = 10.0 Hz, 1H), 4.57-4.54 (m, 1H), 3.51 (s, 3H), 2.96 (dd, *J* = 18.8, 8.0 Hz,1H), 2.77-2.73 (m, 2H), 1.18 (d, *J* = 6.4 Hz, 3H), 1.06 (d, *J* = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 206.0, 167.1, 157.0 152.2, 137.0, 134.8, 129.9, 127.7, 125.0, 123.8, 51.7, 43.3, 36.9, 28.1, 22.8, 22.4; FT-IR (neat) 1964, 1742, 1372, 1234, 1041 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{16}H_{19}O_3$: 259.1329; Found 259.1323.



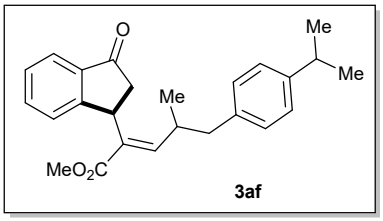

**Methyl (*E*)-2-(3-oxo-2,3-dihydro-1H-inden-1-yl)non-2-enoate 3ac.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.40; colorless liquid; yield 88% (27 mg); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.0 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.26 (s, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 4.58-4.56 (m, 1H), 3.51 (s, 3H), 2.93 (dd, *J* = 19.0, 8.0 Hz, 1H), 2.76 (d, *J* = 19.5 Hz, 1H), 2.32-2.25 (m, 2H), 1.49 (q, *J* = 7.5 Hz, 2H), 1.33-1.25 (m, 6H), 0.89 (t, *J* = 6.0 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 206.0, 166.9, 157.0, 146.0, 137.0, 134.8, 132.1, 127.7, 125.0, 123.7, 51.7, 43.1, 36.7, 31.7, 29.2, 29.0, 28.8, 22.7, 14.2; FT-IR (neat) 1738, 1719, 1370, 1246, 1054 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{25}O_3$: 301.1798; Found 301.1790.




**Methyl (*E*)-3-cyclohexyl-2-(3-oxo-2,3-dihydro-1H-inden-1-yl)acrylate 3ad.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.43; yellow liquid; yield 75% (23 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.27-7.25 (m, 1H), 6.85 (d, *J* = 10.0 Hz, 1H), 4.57-4.54 (m, 1H), 3.50 (s, 3H), 2.94 (dd, *J* = 18.8, 8.4 Hz, 1H), 2.77 (dd, *J* = 18.8, 4.0 Hz, 1H), 2.47-2.41 (m, 1H), 1.80-1.75 (m, 3H), 1.70-1.69 (m, 1H), 1.64-1.59 (m, 2H), 1.34-1.30 (m, 2H), 1.25 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 206.0, 167.1, 157.0, 150.8, 137.1, 134.7, 130.3, 127.7, 125.0, 123.7, 51.6, 43.4, 37.9, 37.0, 32.9, 32.4, 25.8, 25.6, 25.5; FT-IR (neat) 1775, 1736, 1373, 1236, 1044 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{23}O_3$: 299.1642; Found 299.1635.

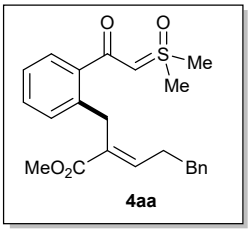



**Methyl (*E*)-3-cyclopentyl-2-(3-oxo-2,3-dihydro-1H-inden-1-yl)acrylate 3ae.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.43; colorless liquid; yield 71% (21 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 6.94 (d, *J* = 10.0 Hz, 1H), 4.61-4.58 (m, 1H), 3.51 (s, 3H), 2.94 (dd, *J* = 18.8, 8.0 Hz, 1H), 2.86-2.80 (m, 1H), 2.77 (dd, *J* = 18.8, 4.0 Hz, 1H), 1.99-1.92 (m, 1H), 1.84-1.73 (m, 3H), 1.69-1.62 (m, 2H), 1.55-1.48 (m, 1H), 1.44-1.37 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 206.1, 167.1, 157.1, 150.9, 137.0, 134.7, 130.5, 127.6, 125.1, 123.7, 51.7, 43.4, 39.4, 37.0, 34.0, 33.6, 25.8; FT-IR (neat) 1752, 1720, 1363, 1235, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{21}O_3$: 285.1485; Found 285.1478.

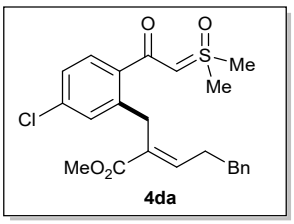



**Methyl (*E*)-5-(4-isopropylphenyl)-4-methyl-2-(3-oxo-2,3-dihydro-1H-inden-1-yl)pent-2-enoate 3af.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.41; colorless liquid; yield 73% (28 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.35-7.29 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 10.4 Hz, 1H), 6.40 (d, *J* = 7.2 Hz, 1H), 4.36-4.33 (m, 1H), 3.47 (s, 3H), 2.95-2.88 (m, 2H), 2.84-2.77 (m, 2H), 2.69-2.63 (m, 1H), 2.55-2.50 (m, 1H), 1.28-1.25 (m, 6H), 1.12 (d, *J* = 7.2

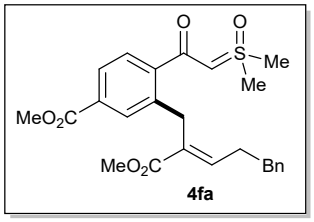
Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 206.0, 166.9, 156.8, 150.4, 147.2, 137.3, 136.9, 134.5, 131.0, 129.1, 127.5, 126.8, 125.0, 123.4, 51.6, 43.3, 43.1, 36.8, 36.4, 33.9, 24.3, 24.2, 20.9; FT-IR (neat) 1763, 1732, 1371, 1236, 1045 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{25}H_{29}O_3$: 377.2111; Found 377.2101.



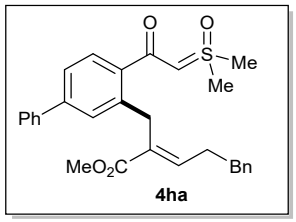

**Methyl (*E*)-2-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)benzyl) -5-phenylpent-2-enoate 4aa.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.30; yellow liquid; yield 80% (32 mg); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 1H), 7.27-7.24 (m, 2H), 7.18 (t, *J* = 6 Hz, 2H), 7.15-7.12 (m, 3H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 4.68 (s, 1H), 3.94 (s, 2H), 3.66 (s, 3H), 3.47 (s, 6H), 2.71 (t, *J* = 6.6 Hz, 2H), 2.51 (q, *J* = 7.8 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 187.0, 168.4, 143.8, 141.2, 140.9, 137.1, 131.5, 129.2, 128.6, 128.5, 128.0, 127.5, 126.2, 125.7, 71.6, 51.9, 42.4, 34.9, 30.8, 29.5; FT-IR (neat) 1755, 1737, 1372, 1234, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{27}O_4S$: 399.1625; Found 399.1625.



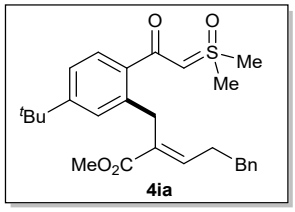

**Methyl (*E*)-2-(5-chloro-2-(2-(dimethyl(oxo)-l6-sulfaneylidene) acetyl)benzyl)-5-phenylpent-2-enoate 4da.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.38; colorless liquid; yield 72% (31 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 1H), 7.28-7.27 (m, 1H), 7.25 (s, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.14-7.11 (m, 3H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.96-6.95 (m, 1H), 4.67 (s, 1H), 3.91 (s, 2H), 3.68 (s, 3H), 3.46 (s, 6H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.50 (q, *J* = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 185.7, 168.1, 144.5, 141.0, 139.4, 139.3, 135.1, 130.8, 128.9, 128.6, 128.5, 128.1, 126.3, 125.9, 72.0, 52.0, 42.3, 34.8, 30.8, 29.4; FT-IR (neat) 1757, 1737, 1375, 1234, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{26}ClO_4S$: 433.1235; Found 433.1233.




**Methyl (*E*)-4-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-3-(2-(methoxycarbonyl)-5-phenylpent-2-en-1-yl)benzoate 4fa.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.35; yellow liquid; yield 76% (35 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.25-7.23 (m, 2H), 7.18 (d, *J* = 6.8 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 4.70 (s, 1H), 3.93 (s, 2H), 3.88 (s, 3H), 3.67 (s, 3H), 3.49 (s, 6H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.52 (q, *J* = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 185.8, 168.2, 166.9, 145.4, 144.3, 141.2, 137.5, 131.0, 130.6, 129.4, 128.6, 128.5, 127.5, 127.3, 126.3, 72.3, 52.2, 51.9, 42.5, 34.9, 30.9, 29.6; FT-IR (neat) 1765, 1736, 1723, 1372, 1234, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{25}H_{29}O_6S$: 457.1679; Found 457.1676.

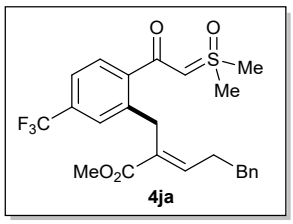



**Methyl (*E*)-2-((4-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-[1,1'-biphenyl]-3-yl)methyl)-5-phenylpent-2-enoate 4ha.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.30; yellow liquid; yield 67% (33 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.41 (t, *J* = 7.2 Hz, 3H), 7.37-7.32 (m, 2H), 7.25-7.24 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.16-7.14 (m, 1H), 7.13-7.11 (m, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 4.73 (s, 1H), 4.03 (s, 2H), 3.68 (s, 3H), 3.49 (s, 6H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.54 (q, *J* = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.7, 168.5, 143.9, 142.0, 141.2, 140.9, 139.8, 137.8, 131.5, 128.9, 128.6, 128.5, 128.3, 127.6, 127.3, 127.0, 126.2, 124.6, 71.6, 52.0, 42.5, 34.9, 30.8, 29.8; FT-IR (neat) 1771, 1737, 1373, 1234, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{29}H_{31}O_4S$: 475.1938; Found 475.1920.



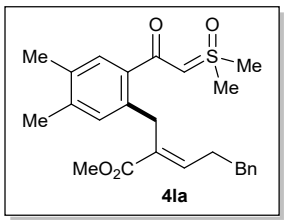

**Methyl (*E*)-2-(5-(*tert*-butyl)-2-(2-(dimethyl(oxo)-l6-sulfaneylidene) acetyl)benzyl)-5-phenylpent-2-enoate 4ia.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.32; light yellow liquid; yield 65% (29 mg); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 2H), 7.17 (t, *J* = 7.0 Hz, 2H), 7.13 (d, *J* = 9.0 Hz, 3H), 6.98 (t, *J* =

7.5 Hz, 1H), 4.69 (s, 1H), 3.98 (s, 2H), 3.68 (s, 3H), 3.45 (s, 6H), 2.69 (t, $J$ = 7.5 Hz, 2H), 2.50 (q, $J$ = 7.5 Hz, 2H), 1.25 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 187.1, 168.7, 152.3, 143.3, 141.3, 138.0, 136.9, 131.9, 128.6, 128.5, 127.6, 126.2, 125.5, 122.6, 71.3, 51.9, 42.4, 35.0, 34.8, 31.3, 30.8, 29.9; FT-IR (neat) 1770, 1735, 1372, 1236, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{27}H_{35}O_4S$: 455.2251; Found 455.2255.



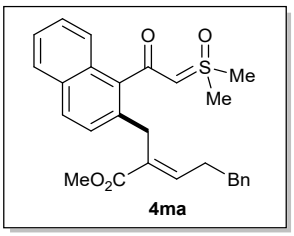
**4ja**

**Methyl (*E*)-2-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-5-(trifluoromethyl)benzyl)-5-phenylpent-2-enoate 4ja.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.30; yellow liquid; yield 80% (38 mg); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, $J$ = 7.8 Hz, 1H), 7.42 (d, $J$ = 7.8 Hz, 1H), 7.27 (s, 1H), 7.25 (s, 2H), 7.18 (t, $J$ = 7.2 Hz, 1H), 7.14 (d, $J$ = 7.8 Hz, 2H), 7.05 (t, $J$ = 7.8 Hz, 1H), 4.69 (s, 1H), 3.94 (s, 2H), 3.68 (s, 3H), 3.49 (s, 6H), 2.73 (t, $J$ = 7.8 Hz, 2H), 2.51 (q, $J$ = 7.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 185.3, 168.1, 144.6, 144.4, 141.0, 138.1, 131.2 ($J_{C\text{-}F}$ = 31.9 Hz), 130.6 ($J_{C\text{-}F}$ = 279.1 Hz), 128.6, 128.5, 126.3, 125.5, 124.9 ($J_{C\text{-}F}$ = 3.5 Hz), 122.9 ($J_{C\text{-}F}$ = 3.9 Hz), 72.3, 52.1, 42.4, 34.8, 30.9, 29.5; $^{19}$F NMR (470 MHz, $CDCl_3$) δ -62.7; FT-IR (neat) 1765, 1737, 1373, 1234, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{24}H_{26}F_3O_4S$: 467.1498; Found 467.1477.

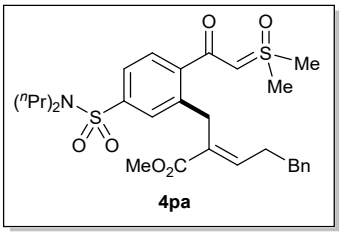


**4la**

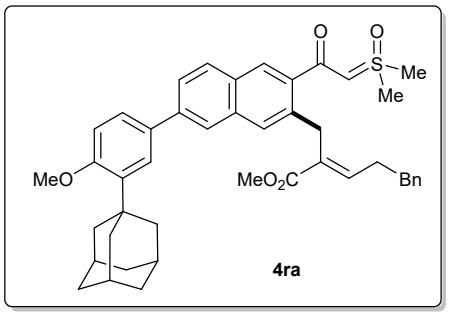
**Methyl (*E*)-2-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-4,5-dimethylbenzyl)-5-phenylpent-2-enoate 4la.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.31; colorless liquid; yield 77% (34 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.24 (s, 1H), 7.20 (s, 1H), 7.18-7.16 (m, 2H), 7.14 (d, $J$ = 7.2 Hz, 2H), 6.98 (t, $J$ = 7.2 Hz, 1H), 6.75 (s, 1H), 3.91 (s, 2H), 3.68 (s, 3H), 3.46 (s, 6H), 2.71 (t, $J$ = 7.2 Hz, 2H), 2.51 (q, $J$ = 7.6 Hz, 2H), 2.20 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 187.1, 168.6, 143.5, 141.3, 138.3, 137.7, 134.4, 133.8, 131.8, 129.4, 129.1, 128.5, 128.4, 126.2, 71.4, 51.9, 42.4, 34.9, 30.7, 29.1, 19.8, 19.3; FT-IR (neat) 1763, 1737, 1374, 1234, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{25}H_{31}O_4S$: 427.1938; Found 427.1933.



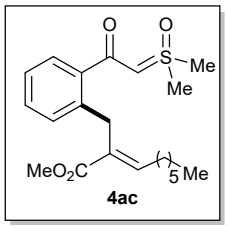

**Methyl (*E*)-2-((1-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl) naphthalen-2-yl)methyl)-5-phenylpent-2-enoate 4ma.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.30; yellow liquid; yield 81% (37 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.47-7.38 (m, 2H), 7.25-7.21 (m, 2H), 7.18-7.15 (m, 1H), 7.11 (d, *J* = 6.8 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 4.78 (s, 1H), 3.93 (s, 2H), 3.67 (s, 3H), 3.59 (s, 6H), 2.73 (t, *J* = 7.2 Hz, 2H), 2.56 (q, *J* = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.5, 168.4, 144.5, 141.1, 138.8, 132.3, 132.1, 131.2, 130.4, 128.6, 128.2, 127.9, 126.3, 126.2, 125.5, 125.3, 74.4, 52.0, 42.4, 34.8, 30.8, 29.7; FT-IR (neat) 1766, 1737, 1375, 1234, 1040 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{27}H_{29}O_4S$: 449.1781; Found 449.1776.



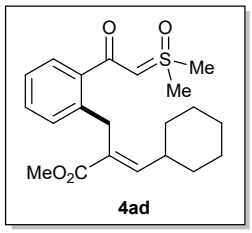

**Methyl (*E*)-2-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene) acetyl)-5-(*N*, *N*-dipropylsulfamoyl)benzyl)-5-phenylpent-2-enoate 4pa.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.28; yellow liquid; yield 69% (39 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 1H), 7.50-7.48 (m, 2H), 7.29-7.27 (m, 1H), 7.25 (s, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 4.71 (s, 1H), 3.94 (s, 2H), 3.66 (s, 3H), 3.48 (s, 6H), 2.98 (t, *J* = 7.6 Hz, 4H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.50 (q, *J* = 7.2 Hz, 2H), 1.49 (q, *J* = 7.6 Hz, 4H), 0.83 (t, *J* = 7.6 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 185.1, 167.9, 144.7, 144.6, 140.9, 140.3, 138.5, 130.5, 128.7, 128.5, 128.0, 126.6, 126.3, 124.7, 72.6, 52.0, 50.2, 42.3, 34.8, 30.9, 29.7, 22.1, 11.3; FT-IR (neat) 1768, 1733, 1372, 1231, 1045, 809 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{29}H_{40}NO_6S_2$: 562.2292; Found 562.2273.




**Methyl (*E*)-2-((7-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)-3-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)naphthalen-2-yl)methyl) -5-phenylpent-2-enoate 4ra.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.32; colorless liquid; yield 75% (52 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.2 Hz, 1H), 7.96-7.95 (m, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.72-7.69 (m, 1H), 7.59-7.58 (m, 1H), 7.54-7.51(m, 2H), 7.16 (t, *J* = 6.8 Hz, 2H), 7.12-7.09 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 6.8 Hz, 2H), 6.79 (t, *J* = 7.6 Hz, 1H), 4.65 (s, 1H), 4.46 (s, 2H), 3.90 (s, 3H), 3.71 (s, 3H), 3.48 (s, 6H), 2.36 (t, *J* = 7.2 Hz, 2H), 2.21-2.16 (m, 8H), 2.10 (s, 3H), 1.80 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 187.4, 169.0, 158.8, 142.8, 141.3, 139.1, 139.0, 138.9, 134.4, 133.6, 132.8, 131.9, 131.4, 128.4, 128.3, 127.1, 126.1, 126.0, 125.9, 125.8, 125.7, 125.63, 125.61, 112.2, 72.1, 55.3, 52.1, 42.4, 40.8, 37.34, 37.29, 34.6, 30.0, 29.3, 28.3; FT-IR (neat) 1777, 1735, 1373, 1234, 1042 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{44}H_{49}O_5S$: 689.3295; Found 689.3282.

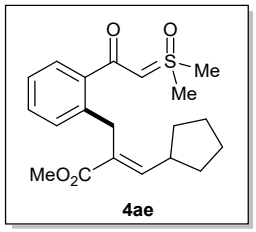



**Methyl (*E*)-2-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)benzyl)non -2-enoate 4ac.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.40; colorless liquid; yield 85% (33 mg); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 4.72 (s, 1H), 3.95 (s, 2H), 3.66 (s, 3H), 3.53 (s, 6H), 2.19 (q, *J* = 7.8 Hz, 2H), 1.43-1.38 (m, 2H), 1.30-1.22 (m, 6H), 0.86 (t, *J* = 6.6 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 187.2, 168.6, 145.4, 141.1, 137.2, 130.7, 129.2, 127.9, 127.5, 125.7, 71.5, 51.9, 42.5, 31.8, 29.6, 29.2, 29.0, 28.8, 22.7, 14.2; FT-IR (neat) 1768, 1737, 1372, 1232, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{31}O_4S$: 379.1938; Found 379.1936.



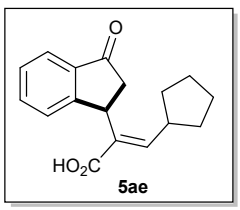
4ad

**Methyl (*E*)-3-cyclohexyl-2-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene) acetyl)benzyl)acrylate 4ad.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.37; yellow liquid; yield 74% (28 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.24-7.20 (m, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 10.0 Hz, 1H), 4.74 (s, 1H), 3.94 (s, 2H), 3.64 (s, 3H), 3.53 (s, 6H), 2.39-2.32 (m, 1H), 1.72-1.67 (m, 2H), 1.62 (t, *J* = 9.6 Hz, 3H), 1.20 (t, *J* = 6.4 Hz, 4H), 1.15-1.12 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 187.1, 168.7, 150.0, 141.0, 137.4, 129.2, 128.7, 127.7, 127.5, 125.7, 71.7, 51.9, 42.5, 37.8, 32.2, 29.8, 25.9, 25.5; FT-IR (neat) 1776, 1738, 1370, 1234, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{29}O_4S$: 377.1781; Found 377.1780.



4ae

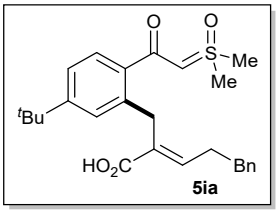
**Methyl (*E*)-3-cyclopentyl-2-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene) acetyl)benzyl)acrylate 4ae.** Analytical TLC on silica gel, 3:1 EtOAc : n-hexane $R_f$ = 0.35; yellow liquid; yield 78% (29 mg); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.14 (t, *J* = 7.0 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 10.0 Hz, 1H), 4.73 (s, 1H), 3.96 (s, 2H), 3.64 (s, 3H), 3.52 (s, 6H), 2.76-2.70 (m, 1H), 1.88 (s, 1H), 1.77-1.74 (m, 3H), 1.70-1.67 (m, 1H), 1.56-1.52 (m, 1H), 1.37-1.30 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 187.1, 168.6, 150.2, 141.0, 137.4, 129.1, 128.8, 127.7, 127.4, 125.7, 71.7, 51.8, 42.4, 39.6, 33.3, 29.6, 25.7; FT-IR (neat) 1778, 1737, 1372, 1233, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{27}O_4S$: 363.1625; Found 363.1624.



5ae

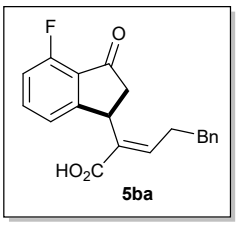
**(*E*)-3-cyclopentyl-2-(3-oxo-2,3-dihydro-1H-inden-1-yl)acrylic acid 5ae.** Analytical TLC on silica gel, 1:1 EtOAc: n-Hexane $R_f$ = 0.43; colorless solid; mp 167-168 ˚C; yield 71% (20 mg); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.25 (s, 1H), 7.03 (d, *J* = 10.2 Hz, 1H), 4.57-4.55 (m, 1H), 2.91 (dd, *J* = 19.2, 7.8 Hz, 1H), 2.82-2.74 (m, 2H), 1.96-1.90 (m, 1H), 1.77-1.72 (m, 3H), 1.64-1.58

(m, 3H), 1.50-1.47 (m, 1H), 1.39-1.35 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 206.1, 171.1, 157.0, 153.4, 136.9, 134.8, 129.7, 127.7, 125.0, 123.8, 43.2, 39.5, 36.8, 33.9, 33.5, 25.8; FT-IR (neat) 2982, 1720, 1363, 1235, 1043 cm$^{-1}$; H RMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{19}O_3$: 271.1329; Found 271.1328.



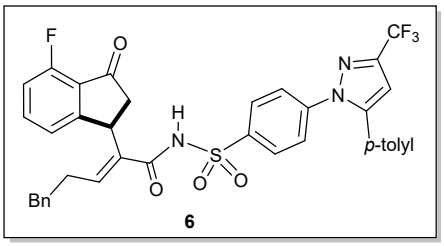
**5ia**

**(*E*)-2-(5-(*tert*-butyl)-2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl) benzyl)-5-phenylpent-2-enoic acid 5ia.** Analytical TLC on silica gel, 4:1:0.1 EtOAc: n-Hexane: AcOH $R_f$ = 0.32; light yellow solid; mp >200 ˚C; yield 65% (28 mg); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.38 (s, 1H), 7.25 (t, *J* = 7.6 Hz, 3H), 7.18-7.17 (m, 1H), 7.14 (t, *J* = 6.4 Hz, 3H), 7.03-7.02 (m, 1H), 6.85 (t, *J* = 7.2 Hz, 1H), 5.05 (s, 1H), 3.82 (s, 2H), 3.52 (s, 6H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.42 (q, *J* = 7.6 Hz, 2H), 1.20 (s, 9H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 185.1, 168.7, 150.8, 142.4, 141.0, 138.6, 136.5, 131.9, 128.3, 128.2, 126.9, 125.9, 124.4, 122.1, 75.3, 40.4, 34.3, 34.0, 31.0, 30.0, 28.9; FT-IR (neat) 2984, 1735, 1372, 1236, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{26}H_{33}O_4S$: 441.2094; Found 441.2095.



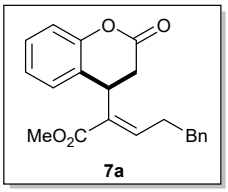
**5ba**

**(*E*)-2-(4-fluoro-3-oxo-2,3-dihydro-1H-inden-1-yl)-5-phenylpent-2-enoic acid 5ba.** Analytical TLC on silica gel, 1:1 EtOAc: n-Hexane $R_f$ = 0.42; colorless solid; mp 170-171 ˚C; yield 81% (27 mg); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.43-7.38 (m, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.15-7.12 (m, 3H), 6.94 (t, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 7.5 Hz, 1H), 4.34-4.31 (m, 1H), 2.87-2.80 (m, 2H), 2.66-2.55 (m, 4H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 202.0, 170.6, 159.9 ($J_{C\text{-}F}$ = 262.1 Hz), 158.7, 147.1, 140.4, 136.6 ($J_{C\text{-}F}$ = 8.3 Hz), 131.6, 128.8, 128.6, 126.7, 124.7 ($J_{C\text{-}F}$ = 12.9 Hz), 120.7 ($J_{C\text{-}F}$ = 3.8 Hz), 114.8 ($J_{C\text{-}F}$ = 19.3 Hz), 43.0, 36.5, 34.9, 31.0; $^{19}$F NMR (470 MHz, $CDCl_3$) δ -115.0; FT-IR (neat) 2983, 1736, 1372, 1245, 1030 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{18}FO_3$ 325.1234; Found 325.1217.



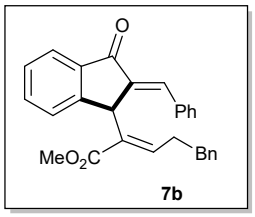
6

**(*E*)-2-(4-fluoro-3-oxo-2,3-dihydro-1H-inden-1-yl)-5-phenyl-*N*-((4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenyl)sulfonyl)pent-2-enamide 6.** Analytical TLC on silica gel, 4:1 EtOAc : n-hexane $R_f$ = 0.30; colorless solid; mp 197-198 °C; yield 71% (48 mg); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.68 (d, $J$ = 8.4 Hz, 2H), 7.49-7.44 (m, 1H), 7.40 (d, $J$ = 8.8 Hz, 2H), 7.30-7.27 (m, 2H), 7.25-7.23 (m, 2H), 7.22-7.18 (m, 4H), 7.16-7.14 (m, 2H), 6.98 (t, $J$ = 9.2 Hz, 1H), 6.76-6.72 (m, 2H), 4.42-4.39 (m, 1H), 2.82-2.73 (m, 2H), 2.67-2.54 (m, 3H), 2.35-2.29 (m, 4H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 201.5, 168.1 ($J_{C\text{-}F}$ = 7.3 Hz), 159.9, 158.9 ($J_{C\text{-}F}$ = 258.4 Hz), 145.2, 142.7, 142.4, 142.0, 141.6 ($J_{C\text{-}F}$ = 29.0 Hz), 141.1, 140.6 ($J_{C\text{-}F}$ = 7.2 Hz), 139.1, 136.7 ($J_{C\text{-}F}$ = 8.1 Hz), 135.7 ($J_{C\text{-}F}$ = 3.0 Hz), 129.4 ($J_{C\text{-}F}$ = 74.6 Hz), 128.5, 128.3, 128.2 ($J_{C\text{-}F}$ = 4.7 Hz), 128.1, 126.0, 125.4, 125.3, 123.9 ($J_{C\text{-}F}$ = 12.9 Hz), 122.7, 120.9 ($J_{C\text{-}F}$ = 3.3 Hz), 120.0, 113.8 ($J_{C\text{-}F}$ = 19.1 Hz), 106.0, 43.0, 36.6, 34.3, 30.0, 20.8; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -117.4, -60.9; FT-IR (neat) 2995, 1737, 1372, 1323, 1234, 1043 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{37}H_{30}F_4N_3O_4S$: 688.1888; Found 688.1858.

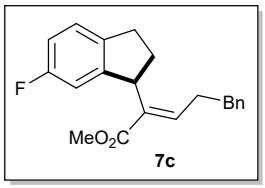


7a

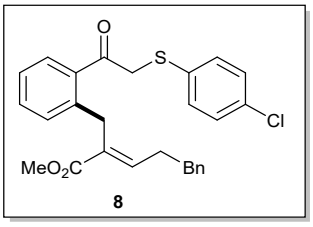
**Methyl (*E*)-2-(2-oxochroman-4-yl)-5-phenylpent-2-enoate 7a.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.52; colorless liquid; yield 75% (25 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.25-7.23 (m, 2H), 7.19 (d, $J$ = 6.8 Hz, 2H), 7.16-7.13 (m, 2H), 7.09-7.07 (m, 1H), 7.05-7.04 (m, 1H), 7.03-7.00 (m, 1H), 4.21 (t, $J$ = 6.8 Hz, 1H), 3.60 (s, 3H), 2.84-2.79 (m, 2H), 2.69-2.63 (m, 2H), 2.49 (dd, $J$ = 15.6, 7.6 Hz, 1H), 2.33 (dd, $J$ = 15.6, 6.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.0, 164.0, 150.5, 146.1, 140.5, 129.0, 128.7, 128.6, 128.1, 127.8, 126.6, 124.7, 124.5, 117.4, 51.9, 41.6, 34.6, 34.5, 30.7; FT-IR (neat) 1763, 1727, 1556, 1454, 1174, 1023 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{21}O_4$: 337.1434; Found 337.1415.




**Methyl (*E*)-2-(2-((*E*)-benzylidene)-3-oxo-2,3-dihydro-1H-inden-1-yl)-5-phenylpent-2-enoate 7b.** Analytical TLC on silica gel, 3:7 EtOAc : n-hexane $R_f$ = 0.40; colorless liquid; yield 70% (29 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.76-7.75 (m, 1H), 7.60-7.56 (m, 1H), 7.55-7.53 (m, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.41-7.36 (m, 4H), 7.20-7.13 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.03 (t, *J* = 7.2 Hz, 1H), 5.31-5.30 (m, 1H), 3.71 (s, 3H), 2.68-2.60 (m, 1H), 2.57-2.49 (m, 1H), 2.42-2.38 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 194.3, 167.6, 153.7, 143.9, 141.1, 138.0, 136.6, 135.1, 135.0, 134.5, 133.7, 131.3, 131.2, 129.8, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.1, 126.1, 125.3, 124.4, 51.8, 46.3, 35.1, 31.5; FT-IR (neat) 1738, 1718, 1552, 1370, 1245, 1054 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{28}H_{25}O_3$: 409.1798; Found 409.1798.

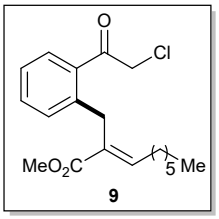



**Methyl (*E*)-2-(6-fluoro-2,3-dihydro-1H-inden-1-yl)-5-phenyl pent-2-enoate 7c.** Analytical TLC on silica gel, 1:9 EtOAc : n-hexane $R_f$ = 0.45; colorless liquid; yield 64% (21 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.29-7.27 (m, 1H), 7.26 (s, 1H), 7.22-7.18 (m, 1H), 7.13-7.09 (m, 3H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.83-6.78 (m, 1H), 6.50 (d, *J* = 8.8 Hz, 1H), 4.34 (t, *J* = 9.2 Hz, 1H), 3.63 (s, 3H), 3.01-2.95 (m, 1H), 2.88-2.80 (m, 1H), 2.76-2.72 (m, 2H), 2.48-2.42 (m, 2H), 2.29-2.21 (m, 1H), 2.13-2.03 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.7, 163.5 ($J_{C\text{-}F}$ = 241.0 Hz), 148.0 ($J_{C\text{-}F}$ = 7.5 Hz), 143.8, 141.0, 138.9 ($J_{C\text{-}F}$ = 2.3 Hz), 134.2, 128.6, 128.5, 126.4, 125.3 ($J_{C\text{-}F}$ = 8.6 Hz), 113.3 ($J_{C\text{-}F}$ = 22.3 Hz), 110.3 ($J_{C\text{-}F}$ = 22.1 Hz), 51.7, 44.0, 35.1, 32.4, 31.3, 30.8; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -117.9; FT-IR (neat) 1725, 1371, 1249, 1054 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{22}FO_2$: 325.1598; Found 325.1579.




**Methyl (*E*)-2-(2-(2-((4-chlorophenyl)thio)acetyl)benzyl)-5-phenyl pent-2-enoate 8.** Analytical TLC on silica gel, 1:7 EtOAc : n-hexane $R_f$ = 0.40; colorless liquid; yield 78% (36 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (m, 1H), 7.34-7.28 (m, 4H), 7.25-7.24 (m, 1H), 7.23-7.21 (m, 2H), 7.20-7.17 (m, 2H), 7.14-7.12 (m, 2H), 7.03 (t, *J* =

7.6 Hz, 1H), 6.99 (d, $J$ = 7.6 Hz, 1H), 4.24 (s, 2H), 3.81 (s, 2H), 3.63 (s, 3H), 2.73 (t, $J$ = 7.6 Hz, 2H), 2.46 (q, $J$ = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 198.1, 168.0, 144.4, 141.0, 139.9, 136.6, 133.7, 133.1, 131.9, 131.7, 130.7, 129.3, 128.9, 128.6, 128.5, 128.4, 126.3, 125.9, 51.9, 44.1, 34.8, 30.8, 30.1; FT-IR (neat) 1764, 1737, 1375, 1234, 1040 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{27}H_{26}ClO_3S$: 465.1286; Found 465.1277.

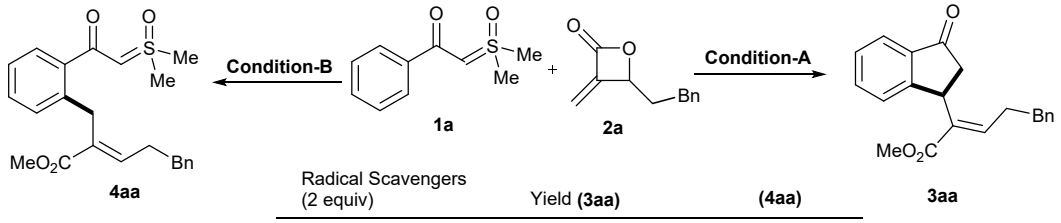


**9**

**Methyl (*E*)-2-(2-(2-chloroacetyl)benzyl)non-2-enoate 9.** Analytical TLC on silica gel, 1:7 EtOAc : n-hexane $R_f$ = 0.49; colorless liquid; yield 69% (23 mg); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.65-7.63 (m, 1H), 7.41-7.37 (m, 1H), 7.28-7.24 (m, 1H), 7.16 (d, $J$ = 7.6 Hz, 1H), 7.04 (t, $J$ = 7.2 Hz, 1H), 4.40 (s, 2H), 3.91 (s, 2H), 3.66 (s, 3H), 2.18 (q, $J$ = 7.6 Hz, 2H), 1.41 (q, $J$ = 7.6 Hz, 1H), 1.30-1.23 (m, 7H), 0.86 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.4, 168.3, 146.1, 140.6, 135.0, 132.2, 129.9, 129.0, 128.6, 126.0, 52.0, 31.8, 30.1, 29.2, 29.1, 28.7, 22.7, 14.2, 6.5; FT-IR (neat) 1769, 1737, 1373, 1234, 1041 cm$^{-1}$; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{26}ClO_3$: 337.1565; Found 337.1547.

## Mechanistic investigation

### Scheme S1. Radical Trapping Experiments



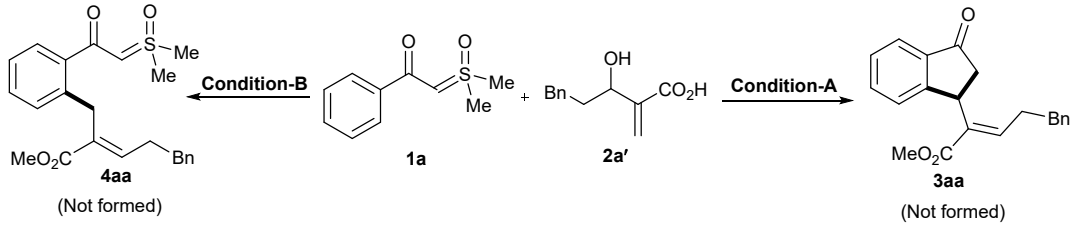

| Radical Scavengers (2 equiv) | Yield (**3aa**) | (**4aa**) |
|---|---|---|
| TEMPO | 60% (20 mg) | 65% (26 mg) |
| BHT | 66% (22 mg) | 72% (29 mg) |

**C-H Annulation.** Substrate **1a** (0.1 mmol, 20 mg, 1 equiv), **2a** (0.15 mmol, 28 mg, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (0.0025 mmol, 2.1 mg, 0.025 equiv), $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv) and TEMPO or BHT (0.2 mmol, 2 equiv) were stirred in TFE (1 mL) at 80 °C for 12 h under $N_2$ atmosphere. Evaporation of the solvent gave a residue that was extracted with EtOAc (10 mL) and washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (0.3 mmol, 41 mg, 3.0 equiv) and MeI (0.5 mmol, 33 μL, 5.0 equiv) in acetone (2 mL) at room temperature for 3 h. After completion (monitored by TLC), evaporation of the solvent provided a residue that was extracted with EtOAc (2 x 10 mL) and was washed with water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent

gave a residue that was purified on silica gel column chromatography as described in the general procedure to afford **3aa.**

**C-H Allylation.** Substrate **1a** (0.1 mmol, 20 mg, 1 equiv), **2a** (0.15 mmol, 28 mg, 1.5 equiv), $[Cp^*RhCl_2]_2$ (0.0025 mmol, 1.5 mg, 0.025 equiv), $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv), PivOH (0.1 mmol, 10 mg, 1 equiv) and TEMPO or BHT (2 equiv) were stirred in TFE (1 mL) at 80 ˚C for 12 h under $N_2$ atmosphere. Evaporation of the solvent gave a residue that was extracted with EtOAc (10 mL) and washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (0.3 mmol, 41 mg, 3.0 equiv) and MeI (0.5 mmol, 33 µL, 5.0 equiv) in acetone (2 mL) at room temperature for 3 h. After completion (monitored by TLC), evaporation of the solvent provided a residue that was extracted with EtOAc (2 x 10 mL) and was washed with water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography as described in the general procedure to afford **4aa**.

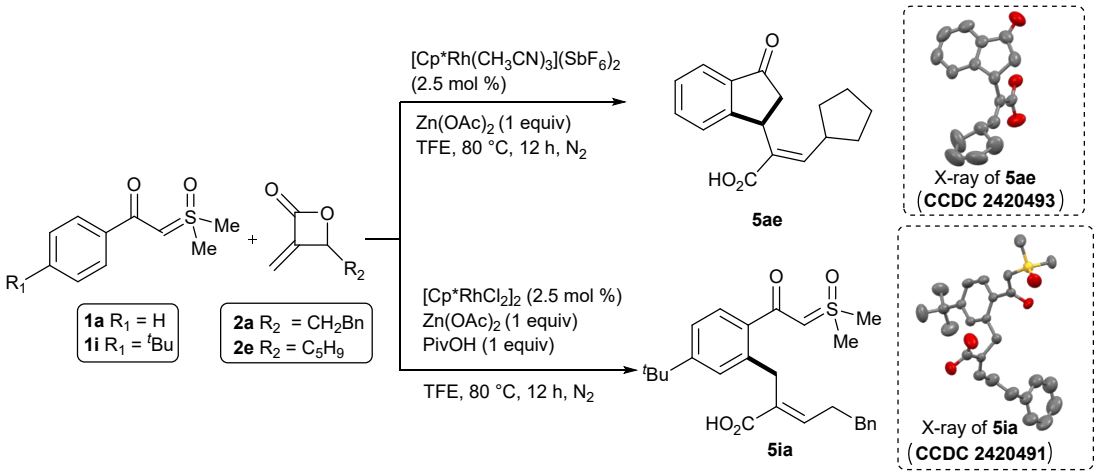
**Scheme S2. Control Experiments**




**C-H Annulation.** Substrate **1a** (0.1 mmol, 20 mg, 1 equiv), 3-hydroxy-2-methylene-5-phenylpentanoic acid **2a'** (0.15 mmol, 31 mg, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (0.0025 mmol, 2.1 mg, 0.025 equiv) and $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv) were stirred in TFE (1 mL) at 80 ˚C for 12 h under $N_2$ atmosphere. The formation of **3aa** was not observed.

**C-H Allylation.** Substrate **1a** (0.1 mmol, 20 mg, 1 equiv), **2a'** (0.15 mmol, 31 mg, 1.5 equiv), $[Cp^*RhCl_2]_2$ (0.0025 mmol, 1.5 mg, 0.025 equiv), $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv) and PivOH (0.1 mmol, 10 mg, 1 equiv) were stirred in TFE (1 mL) at 80 ˚C for 12 h under $N_2$ atmosphere. The formation of **4aa** was not observed.

**Scheme S3. Isolation of Acrylic acid derived Annulated and Allylated Products**




**C-H Annulation.** Substrate **1a** (0.1 mmol, 20 mg, 1 equiv), **2e** (0.15 mmol, 23 mg, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (0.0025 mmol, 2.1 mg, 0.025 equiv) and $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv) were stirred in TFE (1 mL) at 80 °C for 12 h under $N_2$ atmosphere. Evaporation of the solvent gave a residue that was extracted with EtOAc (10 mL) and washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography (EtOAc : n-hexane = 1:1) to afford **5ae** in 71% (20 mg) yield.

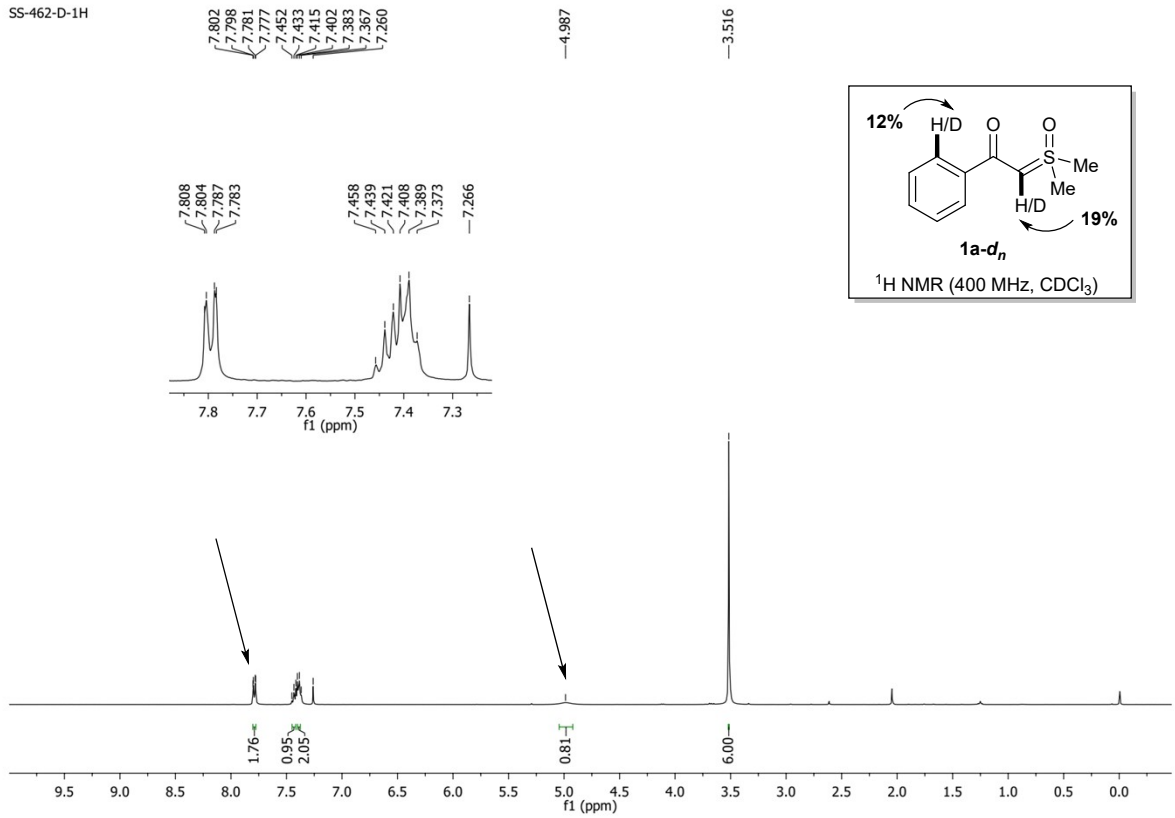
**C-H Allylation.** Substrate **1i** (0.1 mmol, 25 mg, 1 equiv), **2a** (0.15 mmol, 28 mg, 1.5 equiv), $[Cp^*RhCl_2]_2$ (0.0025 mmol, 1.5 mg, 0.025 equiv), $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv) and PivOH (0.1 mmol, 10 mg, 1 equiv) were stirred in TFE (1 mL) at 80 °C for 12 h under $N_2$ atmosphere. Evaporation of the solvent gave a residue that was extracted with EtOAc (10 mL) and washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography (EtOAc : n-hexane : AcOH = 4:1:0.1) to afford **5ia** in 65% (28 mg) yield.

## H/D Exchange Experiments

### C-H Annulation

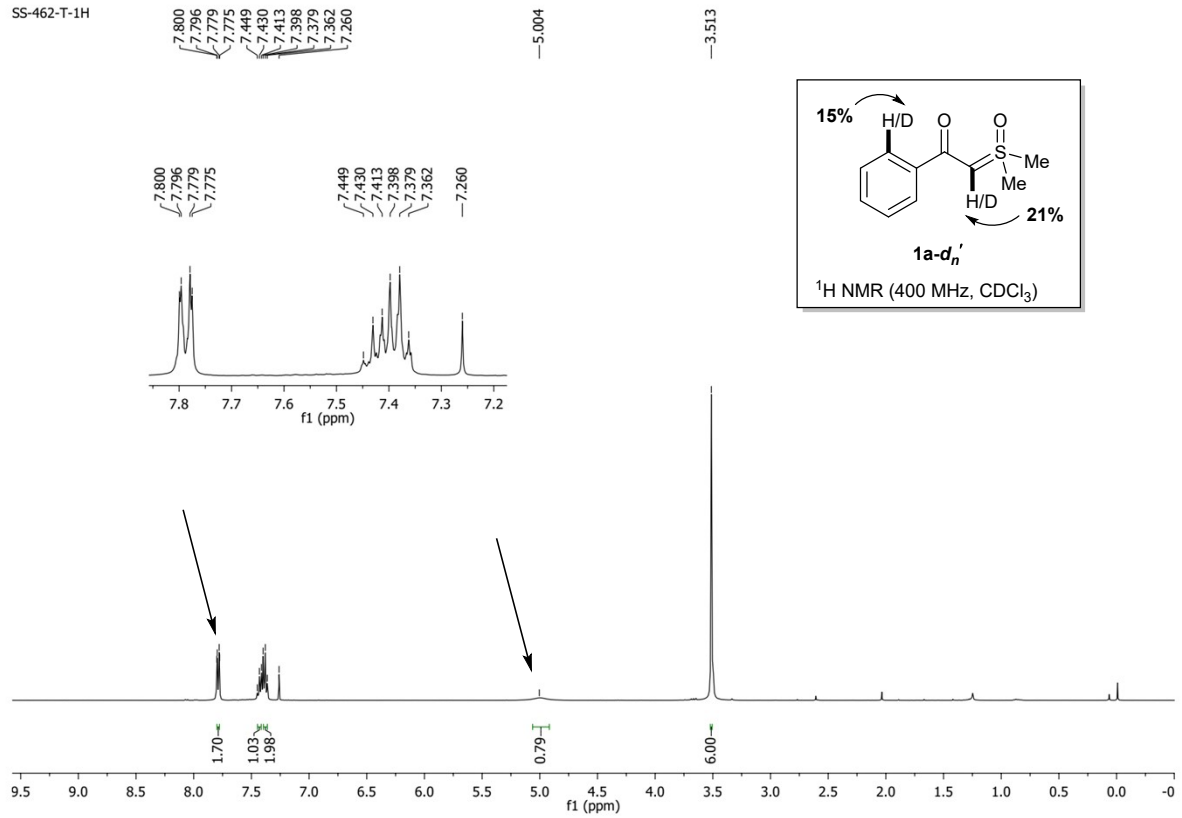
**H/D Exchange Experiment of 1a with $CD_3OD$ in Absence of 2a.** Substrate **1a** (0.1 mmol, 20 mg, 1 equiv), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (0.0025 mmol, 2.1 mg, 0.025 equiv), $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv) and $CD_3OD$ (1 mmol, 0.03 mL, 1 equiv) were stirred in TFE (1 mL) at 80 °C for 15 min under $N_2$ atmosphere. The reaction mixture was cooled to room temperature, diluted with EtOAc (10 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified using silica gel column chromatography (EtOAc : MeOH = 20:1) to afford **1a-*d*$_n$**. The deuterium incorporation was observed as 12% at C2-H

and 19% at the H of $\alpha$-carbon of carbonyl group of **1a-$d_n$** on the basis of 400 MHz $^1$H NMR. (See the following $^1$H NMR spectrum)



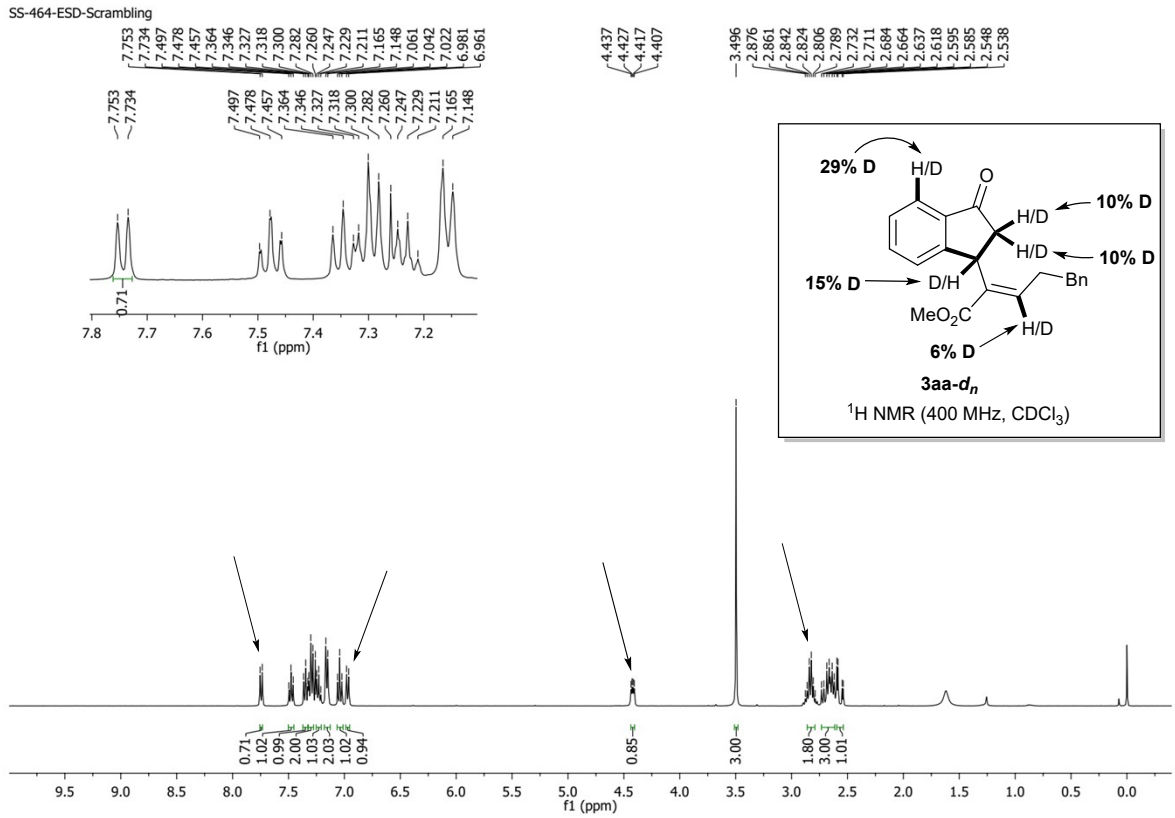

**C-H Allylation**

**H/D Exchange Experiment of 1a with $CD_3OD$ in Absence of 2a.** Substrate **1a** (0.1 mmol, 20 mg, 1 equiv), $[Cp^*RhCl_2]_2$ (0.0025 mmol, 1.5 mg, 0.025 equiv), $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv), PivOH (0.1 mmol, 10 mg, 1 equiv) and $CD_3OD$ (1 mmol, 0.03 mL, 1 equiv) were stirred in TFE (1 mL) at 80 ˚C for 15 min under $N_2$ atmosphere. The reaction mixture was cooled to room temperature, diluted with EtOAc (10 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified using silica gel chromatography (EtOAc : MeOH = 20:1) to afford **1a-$d_n$′**. The deuterium incorporation was observed as 15% at C2-H and 21% at the H of $\alpha$-carbon of carbonyl group of **1a-$d_n$′** on the basis of 400 MHz $^1$H NMR. (See the following $^1$H NMR spectrum)



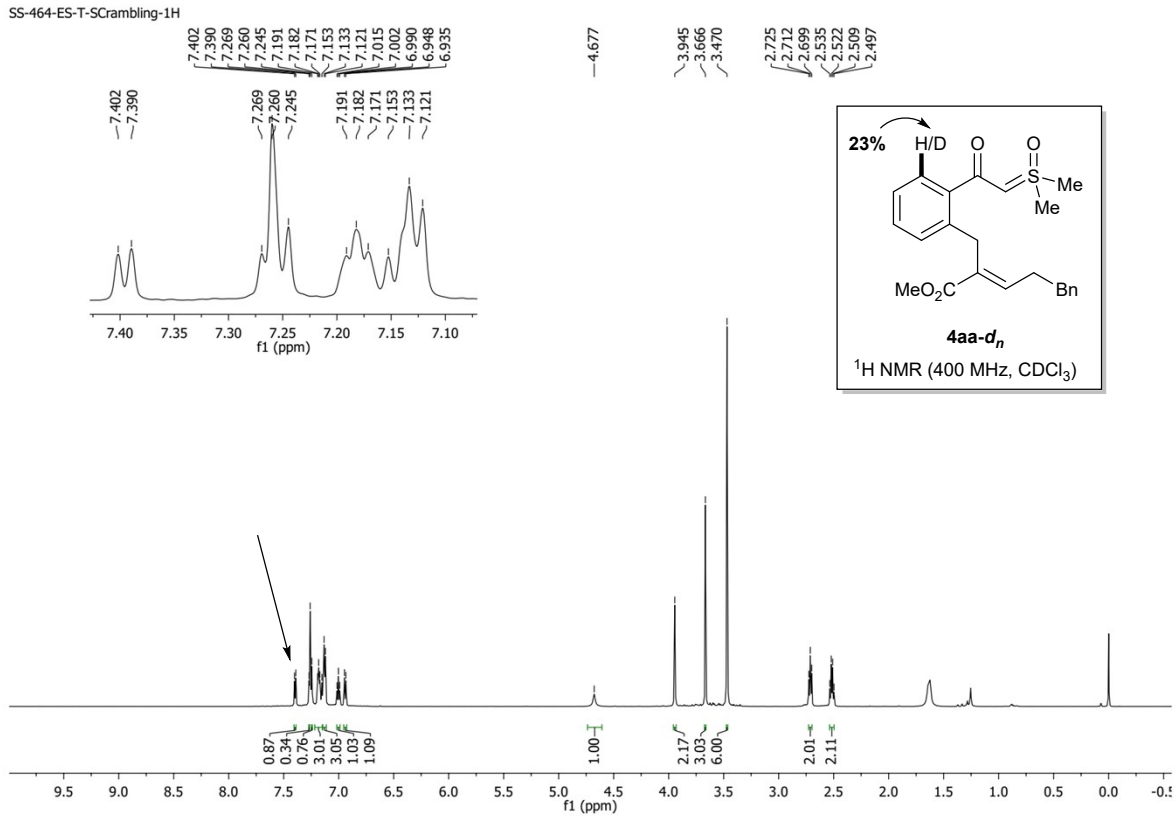

**C-H Annulation**

**H/D Exchange Experiment of 1a with $CD_3OD$ in Presence of 2a.** Substrate **1a** (0.1 mmol, 20 mg, 1 equiv), **2a** (0.15 mmol, 28 mg, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (0.0025 mmol, 2.1 mg, 0.025 equiv), $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv) and $CD_3OD$ (1 mmol, 0.03 mL, 1 equiv) were stirred in TFE (1 mL) at 80 ˚C for 12 h under $N_2$ atmosphere. After completion (monitored by TLC), the reaction mixture was cooled to room temperature. Evaporation of the solvent gave a residue that was extracted using EtOAc (10 mL) and was washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (0.3 mmol, 41 mg, 3.0 equiv) and MeI (0.5 mmol, 33 µL, 5.0 equiv) in acetone (2 mL) at room temperature for 3 h. After completion (monitored by TLC), evaporation of the solvent gave a residue that was extracted with EtOAc (2 x 10 mL) and was washed with water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography (EtOAc : n-hexane = 1:9) to afford the annulated **3aa-$d_n$**. The deuterium incorporation was observed as 29% at C2-H, 20% at the 'H' of $\alpha$-carbon of carbonyl group, 15% at the quaternary 'H' and 6% at the 'H' of unsaturated double bond of **3aa-$d_n$** on the basis of 400 MHz $^1$H NMR. (See the following $^1$H NMR spectrum)




## C-H Allylation

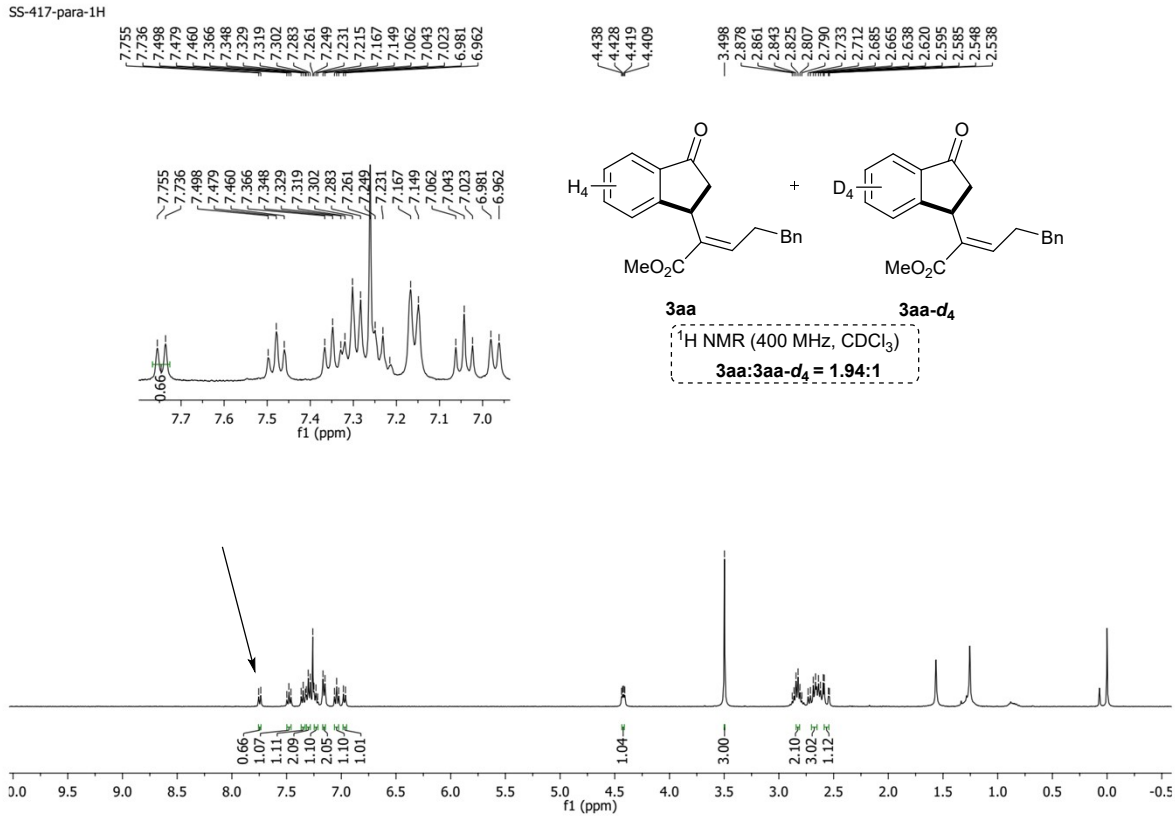
**H/D Exchange Experiment of 1a with $CD_3OD$ in Presence of 2a.** Substrate **1a** (0.1 mmol, 20 mg, 1 equiv), **2a** (0.15 mmol, 28 mg, 1.5 equiv), $[Cp^*RhCl_2]_2$ (0.0025 mmol, 1.5 mg, 0.025 equiv), $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1 equiv), PivOH (0.1 mmol, 10 mg, 1 equiv) and $CD_3OD$ (1 mmol, 0.03 mL, 1 equiv) were stirred in TFE (1 mL) at 80 ˚C for 12 h under $N_2$ atmosphere. After completion (monitored by TLC), the reaction mixture was cooled to room temperature. Evaporation of the solvent provided a residue that was extracted with EtOAc (10 mL) and was washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (0.3 mmol, 41 mg, 3.0 equiv) and MeI (0.5 mmol, 33 µL, 5.0 equiv) in acetone (2 mL) at room temperature for 3 h. After completion (monitored by TLC), evaporation of solvent yielded a residue that was extracted with EtOAc (2 x 10 mL) and was washed with water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography (EtOAc : n-hexane = 3:1) to afford the allylated **4aa-*d*$_n$**. The deuterium incorporation was observed as 23% at C2-H of **4aa-*d*$_n$** on the basis 400 MHz $^1$H NMR. (See the following $^1$H NMR spectrum)



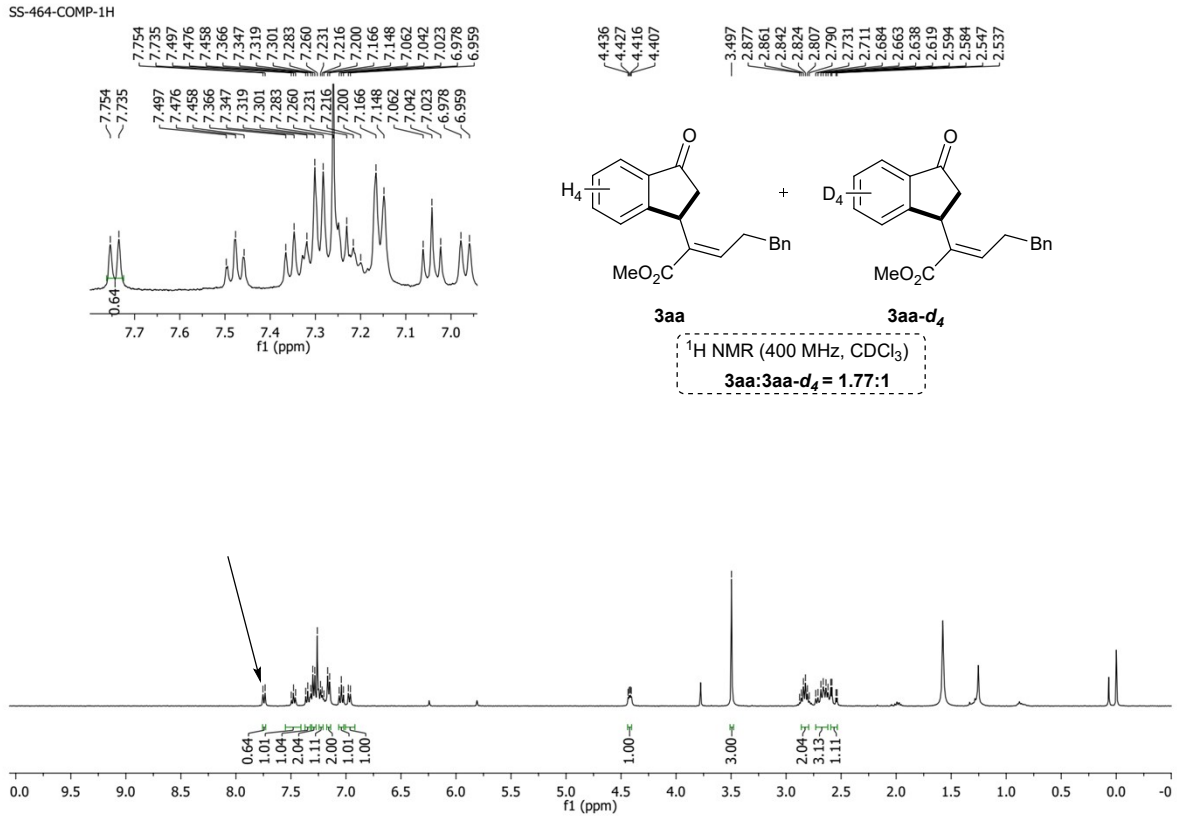

## Kinetic Isotope Effect Experiments

### C-H Annulation

**Parallel Experiment.** Two round bottom flasks were charged with **1a** (0.1 mmol, 20 mg, 1.0 equiv) or 2-(dimethyl(oxo)-l6-sulfaneylidene)-1-(phenyl-$d_5$)ethan-1-one **1a-*d*$_5$** (0.1 mmol, 21 mg, 1.0 equiv), **2a** (0.15 mmol, 28 mg, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (0.0025 mmol, 2.1 mg, 0.025 equiv), and $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1.0 equiv) were stirred in TFE (1 mL) at 80 °C for 2 h under $N_2$ atmosphere. Then both the reaction mixtures were combined. Evaporation of the solvent furnished a residue, which was extracted using EtOAc (10 mL) and washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (0.3 mmol, 41 mg, 3.0 equiv) and MeI (0.5 mmol, 33 µL, 5.0 equiv) in acetone (2 mL) at room temperature for 3 h. After completion (monitored by TLC), evaporation of the solvent provided a residue that was extracted with EtOAc (2 x 10 mL) and was washed with water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography as described in the general procedure to afford **3aa** and **3aa-*d*$_4$**. The KIE value was determined to be $k_H/k_D$ = 1.94 on the basis of $^1$H NMR analysis.

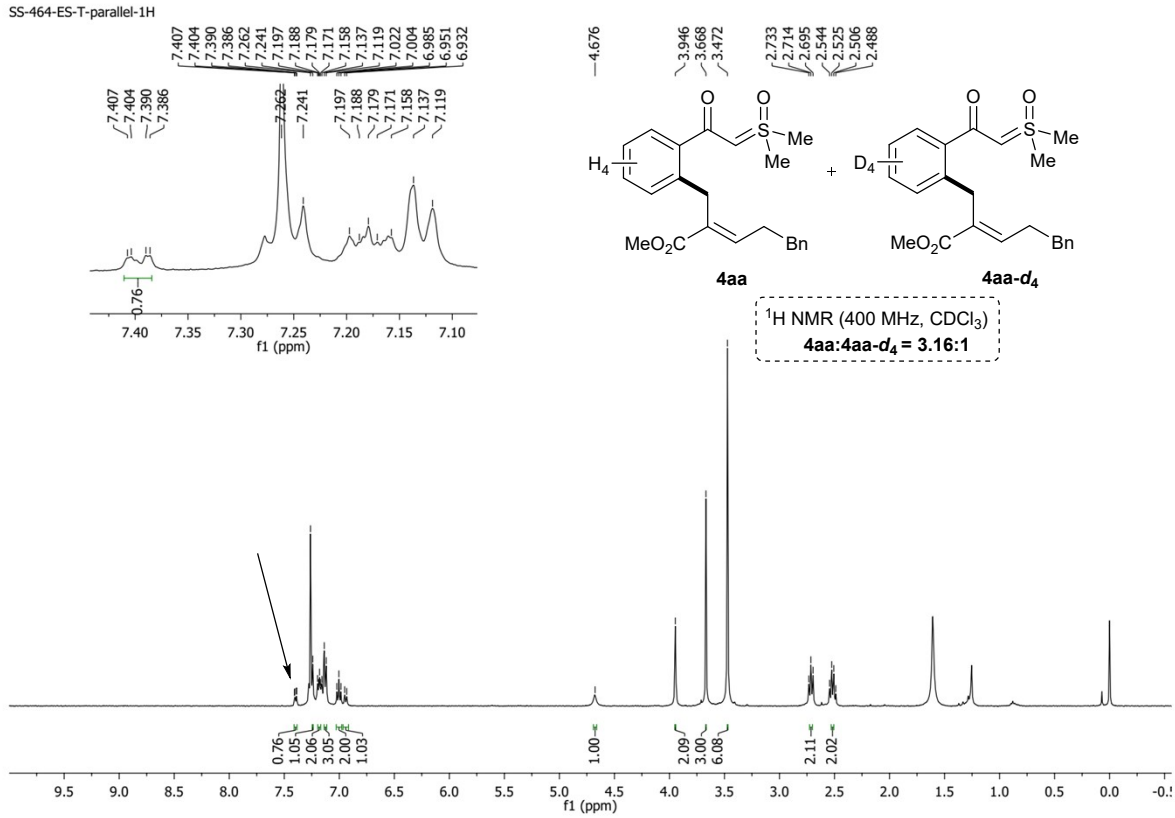



**Competitive Experiment:** A mixture of **1a** (0.1 mmol, 20 mg, 1.0 equiv), 2-(dimethyl(oxo)-l6-sulfaneylidene)-1-(phenyl-$d_5$)ethan-1-one **1a-*d*$_5$** (0.1 mmol, 21 mg, 1.0 equiv), **2a** (0.30 mmol, 56 mg, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (0.005 mmol, 4.2 mg, 0.025 equiv), and $Zn(OAc)_2$ (0.2 mmol, 36 mg, 1.0 equiv) was stirred in TFE (1.5 mL) at 80 ˚C for 2 h under $N_2$ atmosphere. Evaporation of the solvent furnished a residue, which was extracted using EtOAc (10 mL) and washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (0.6 mmol, 82 mg, 3.0 equiv) and MeI (1 mmol, 66 µL, 5.0 equiv) in acetone (4 mL) at room temperature for 3 h. After completion (monitored by TLC), evaporation of the solvent provided a residue that was extracted with EtOAc (2 x 10 mL) and was washed with water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography as described in the general procedure to afford **3aa** and **3aa-*d*$_4$**. The KIE value was determined to be $k_H/k_D$ = 1.77 on the basis of $^1$H NMR analysis.

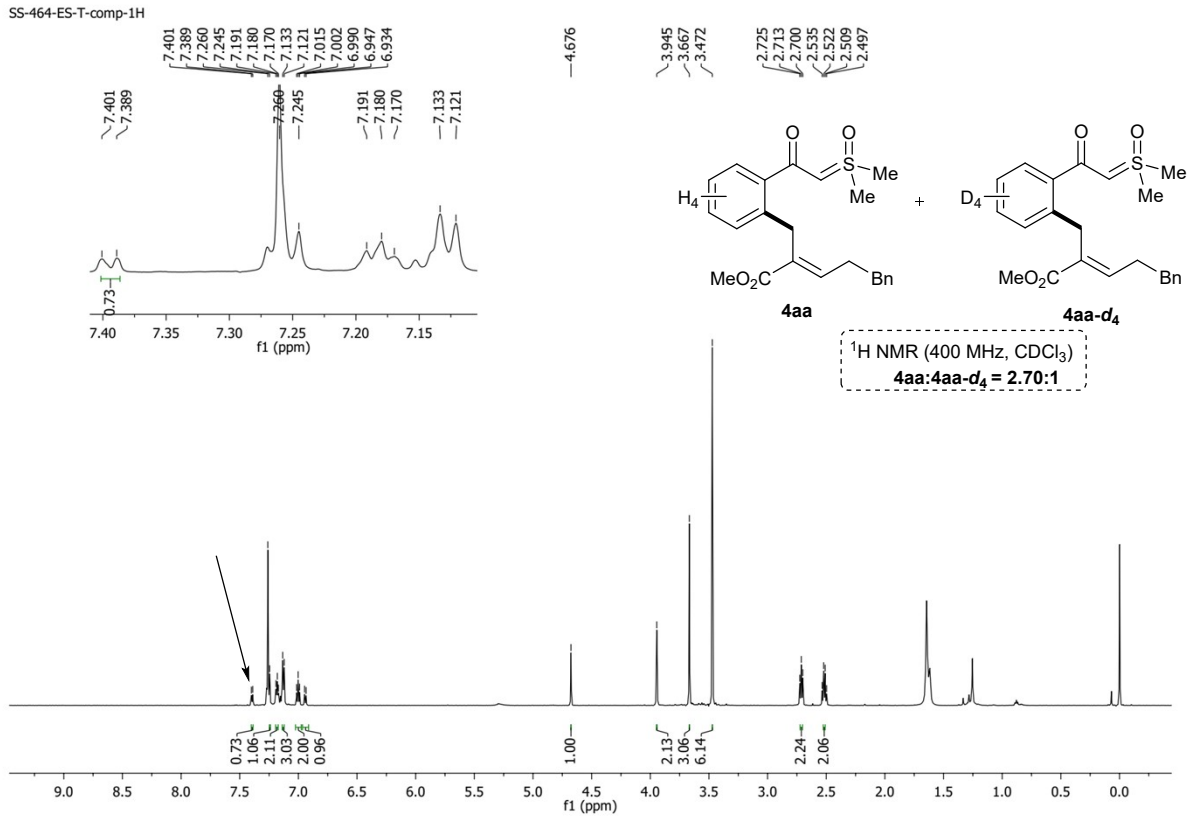



## C-H Allylation

**Parallel Experiment.** Two round bottom flasks were charged with **1a** (0.1 mmol, 20 mg, 1.0 equiv) or 2-(dimethyl(oxo)-l6-sulfaneylidene)-1-(phenyl-$d_5$)ethan-1-one **1a-*d*$_5$** (0.1 mmol, 21 mg, 1.0 equiv), **2a** (0.15 mmol, 28 mg, 1.5 equiv), $[Cp^*RhCl_2]_2$ (0.0025 mmol, 1.5 mg, 0.025 equiv), $Zn(OAc)_2$ (0.1 mmol, 18 mg, 1.0 equiv), and PivOH (0.1 mmol, 10 mg, 1.0 equiv) were stirred in TFE (1 mL) at 80 ˚C for 2 h under $N_2$ atmosphere. Then both the reaction mixtures were combined. Evaporation of the solvent furnished a residue, which was extracted using EtOAc (10 mL) and washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (0.3 mmol, 41 mg, 3.0 equiv) and MeI (0.5 mmol, 33 µL, 5.0 equiv) in acetone (2 mL) at room temperature for 3 h. After completion (monitored by TLC), evaporation of the solvent provided a residue that was extracted with EtOAc (2 x 10 mL) and was washed with water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography as described in the general procedure to afford **4aa** and **4aa-*d*$_4$**. The KIE value was determined to be $k_H/k_D$ = 3.16 on the basis of $^1$H NMR analysis.




**Competitive Experiment:** A mixture of **1a** (0.1 mmol, 20 mg, 1.0 equiv)**,** 2-(dimethyl(oxo)-l6-sulfaneylidene)-1-(phenyl-$d_5$)ethan-1-one **1a-*d*$_5$** (0.1 mmol, 21 mg, 1.0 equiv), **2a** (0.30 mmol, 56 mg, 1.5 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg, 0.025 equiv)), $Zn(OAc)_2$ (0.2 mmol, 36 mg, 1.0 equiv), and PivOH (0.2 mmol, 20 mg, 1.0 equiv) was stirred in TFE (1.5 mL) at 80 ˚C for 2 h under $N_2$ atmosphere. Evaporation of the solvent produced a resultant residue that was extracted using EtOAc (10 mL) and washed with water (5 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was stirred with $K_2CO_3$ (0.6 mmol, 82 mg, 3.0 equiv) and MeI (1.0 mmol, 66 µL, 5.0 equiv) in acetone (4 mL) at room temperature for 3 h. After completion (monitored by TLC), evaporation of the solvent provided a residue that was extracted with EtOAc (2 x 10 mL) and was washed with water (10 mL). Drying ($Na_2SO_4$) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography as described in the general procedure to afford **4aa** and **4aa-*d*$_4$**. The KIE value was determined to be $k_H/k_D$ = 2.70 on the basis of $^1$H NMR analysis.

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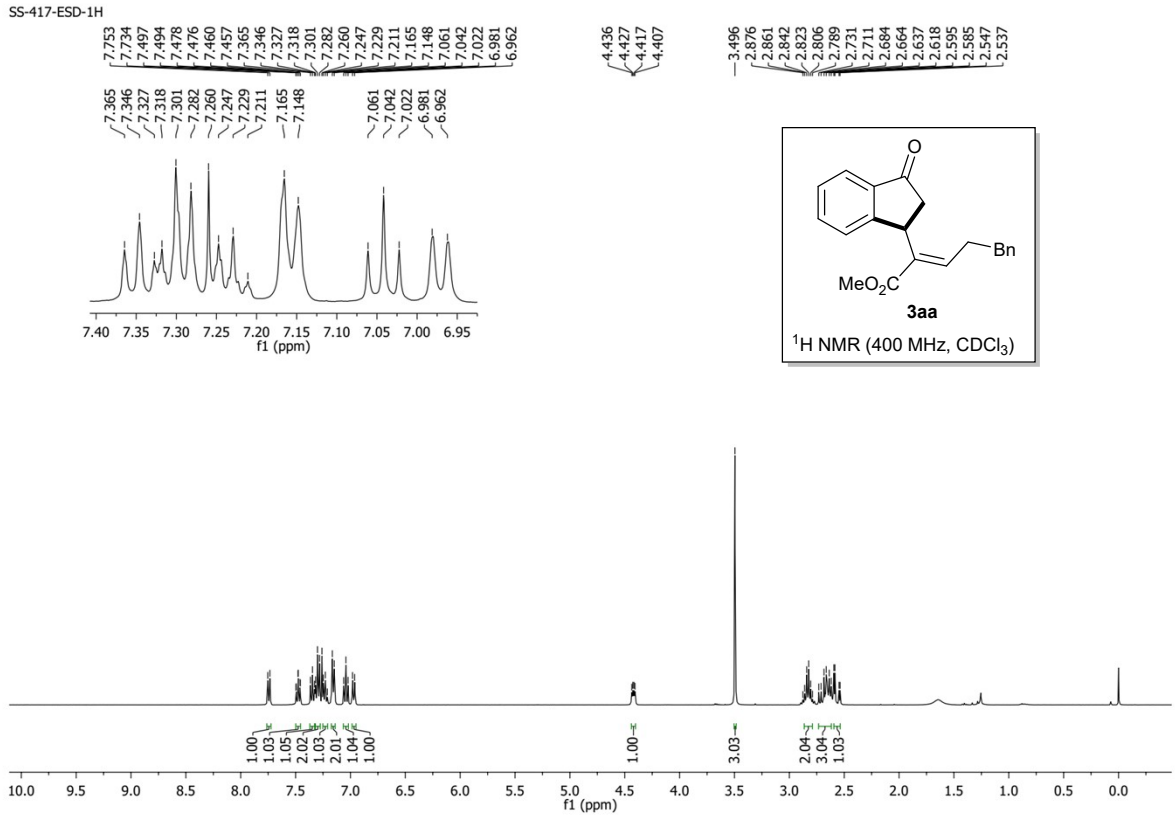
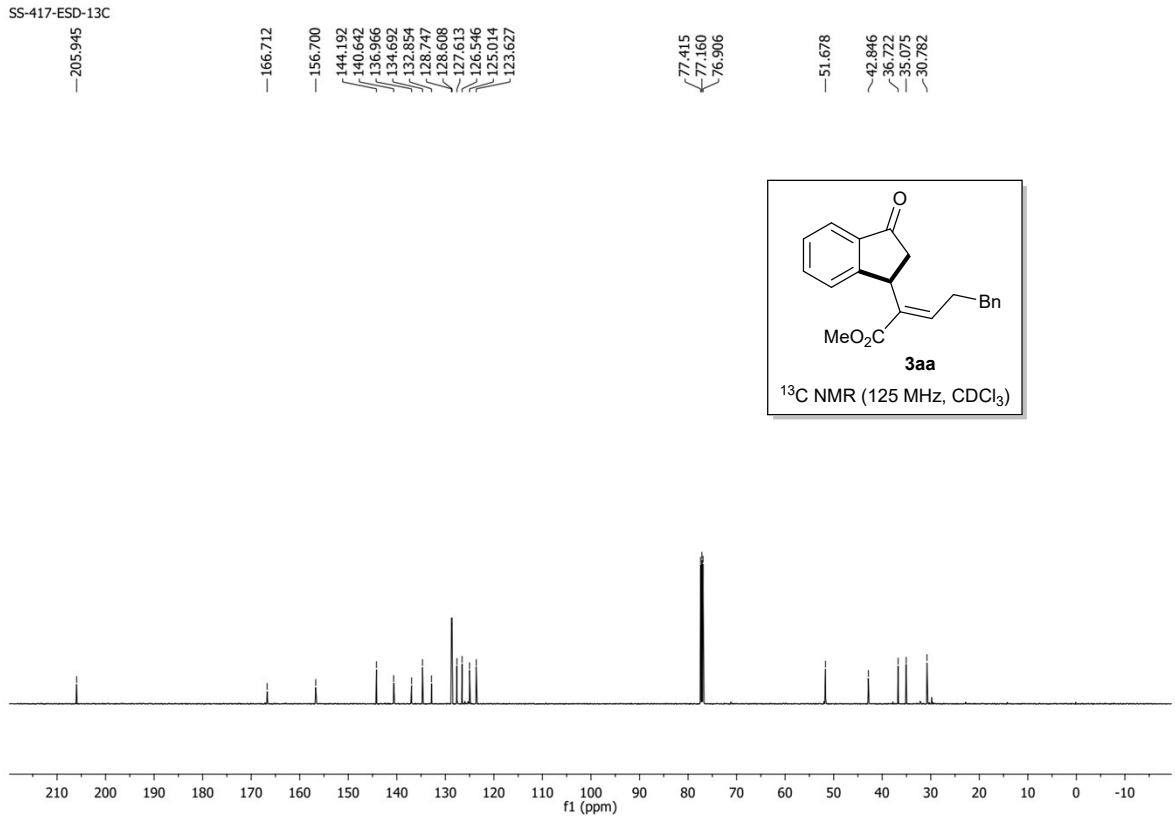
1. M. P. Huestis, L. Chan, D. R. Stuart and K. Fagnou, *Angew. Chem. Int. Ed.*, 2011, **50**, 1338.
2. For preparation of sulfoxonium ylides, see: (a) S. Kumar, S. Nunewar, T. K. Sabbi and V. Kanchupalli, *Org. Lett.*, 2022, **24**, 3395; (b) P. S. K. Prabhakar Ganesh, P. Muthuraja and P. Gopinath, *Org. Lett.*, 2023, **25**, 8361; (c) A. C. B. Burtoloso, J. H. de Souza and J. A. M. Vargas, *Synthesis*, 2024, **56**, 758.
3. For preparation of methylene-*β*-lactams, see: (a) N. Riemer, M. Riemer, M. Krüger, G. J. Clarkson, M. Shipman and B. Schmidt, *J. Org. Chem.*, 2021, **86**, 8786; For preparation of *α*-methylene-*β*-lactones, see: (b) M. Bian, K. Ma, H. Mawjuda, X. Yu, X. Li, H. Gao, Z. Zhou and W. Yi, *Org. Biomol. Chem.*, 2019, **17**, 6114; (c) R. Zhou, S. Fan, L. Fang, B. Chu and J. Zhu, *Org. Lett.*, 2023, **25**, 8688; (d) H. Bhattacharyya, S. Saha, K. Verma and T. Punniyamurthy, *Chem. Commun.*, 2025, **61**, 4200.
4. (a) D. Wang, M. D. Schwinden, L. Radesca, B. Patel, D. Kronenthal, M.-H. Huang and W. A. Nugent, *J. Org. Chem.*, 2004, **69**, 1629; (b) A. Adachi, K. Aikawa, Y. Ishibashi, K. Nozaki and T. Okazoe, *Chem. - Eur. J.*, 2021, **27**, 11919; (c) B. Yang, S.-J. Li, Y. Wang, Y. Lan and S. Zhu, *Nat. Commun.*, 2021, **12**, 5257; (d) R. Echemendía, K. T. de Oliveira and A. C. B. Burtoloso, *Org. Lett.*, 2022, **24**, 6386.

## NMR ($^{1}$H, $^{13}$C and $^{19}$F) Spectra









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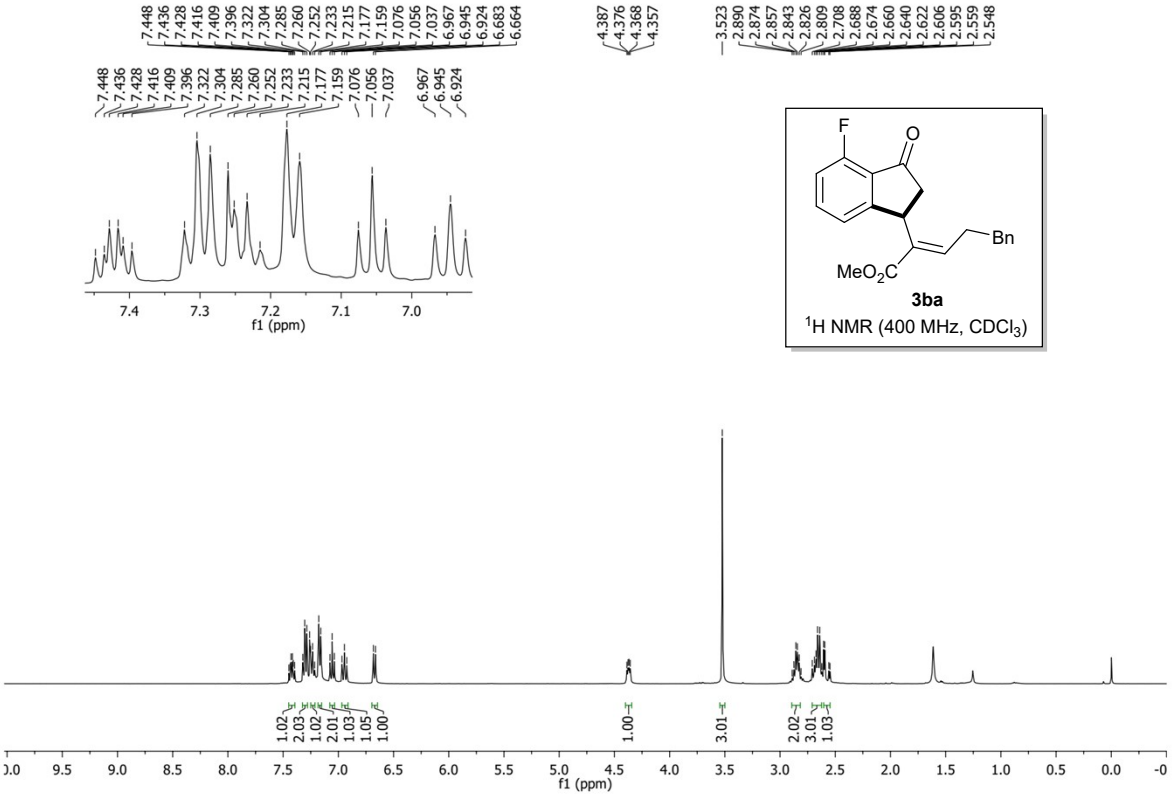


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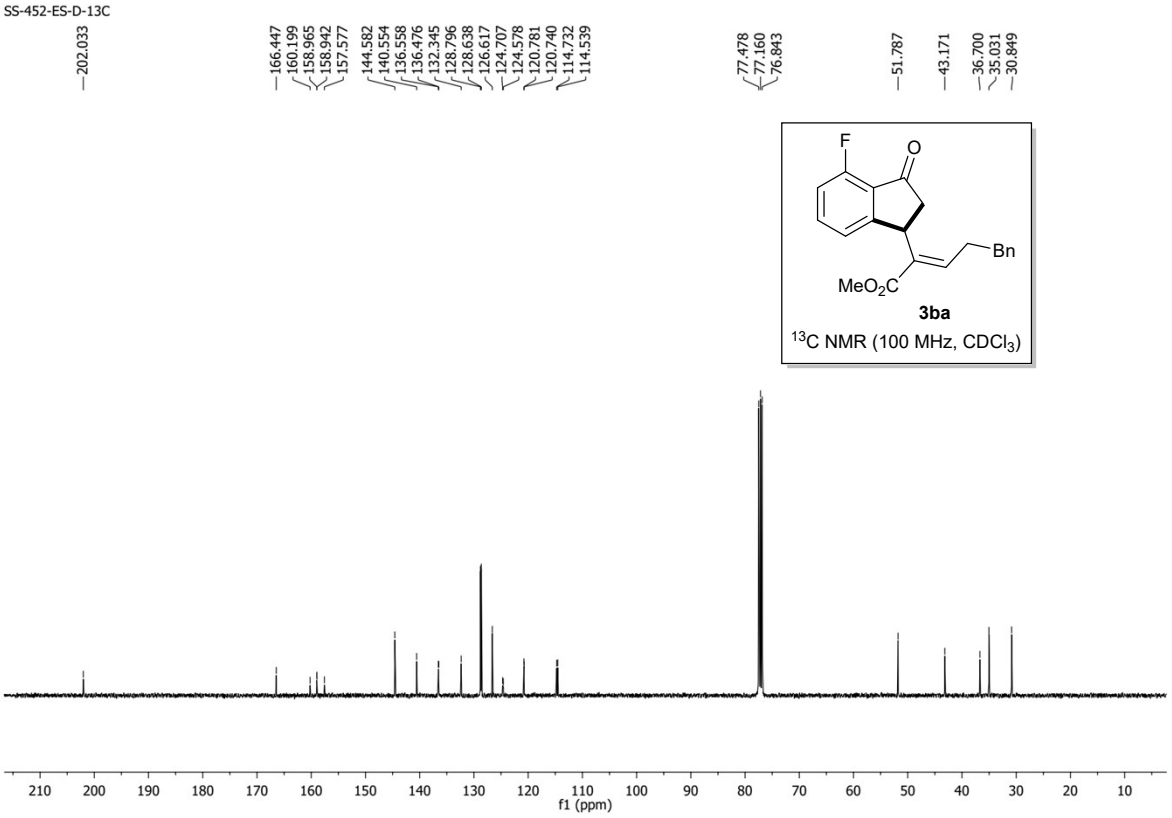

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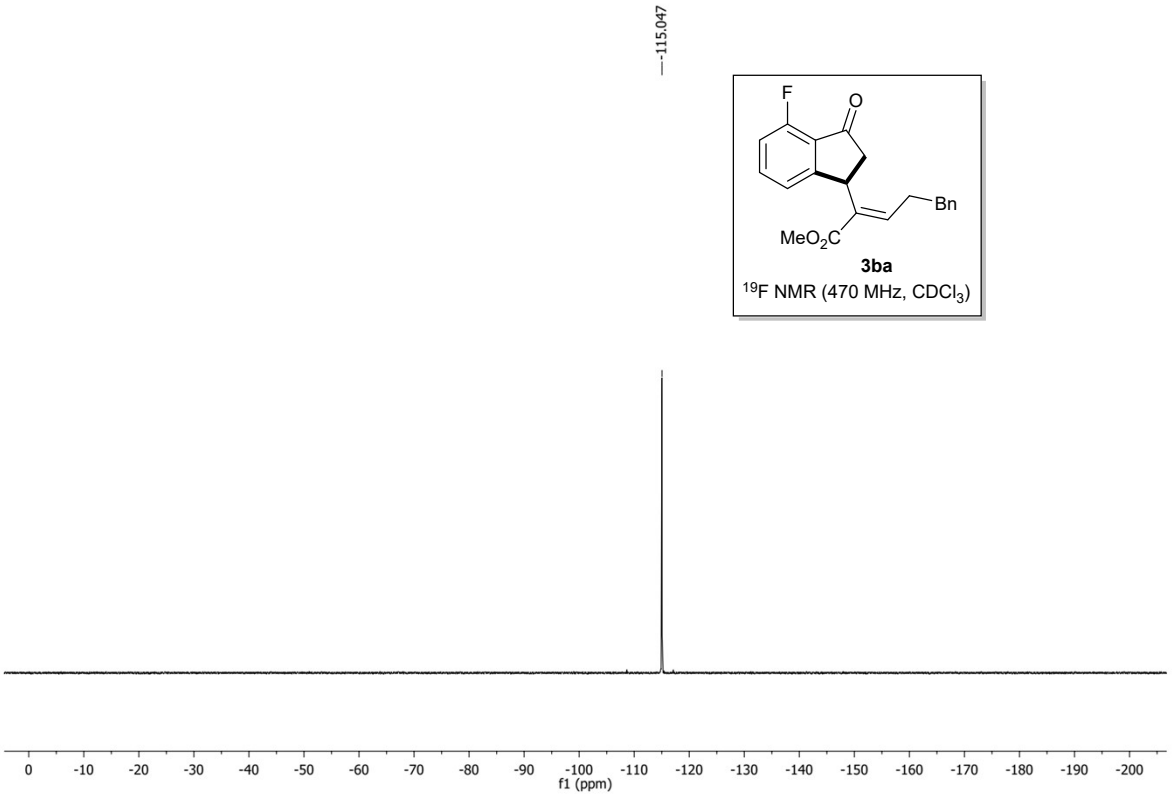


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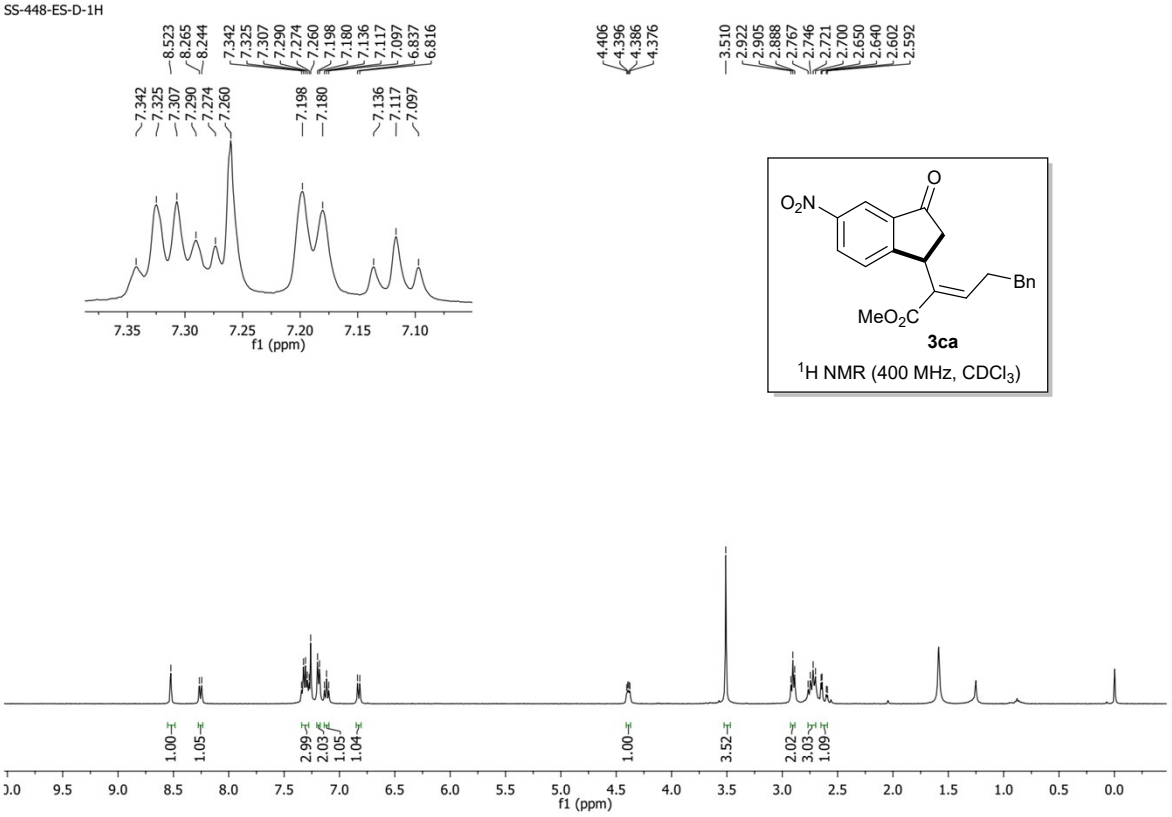

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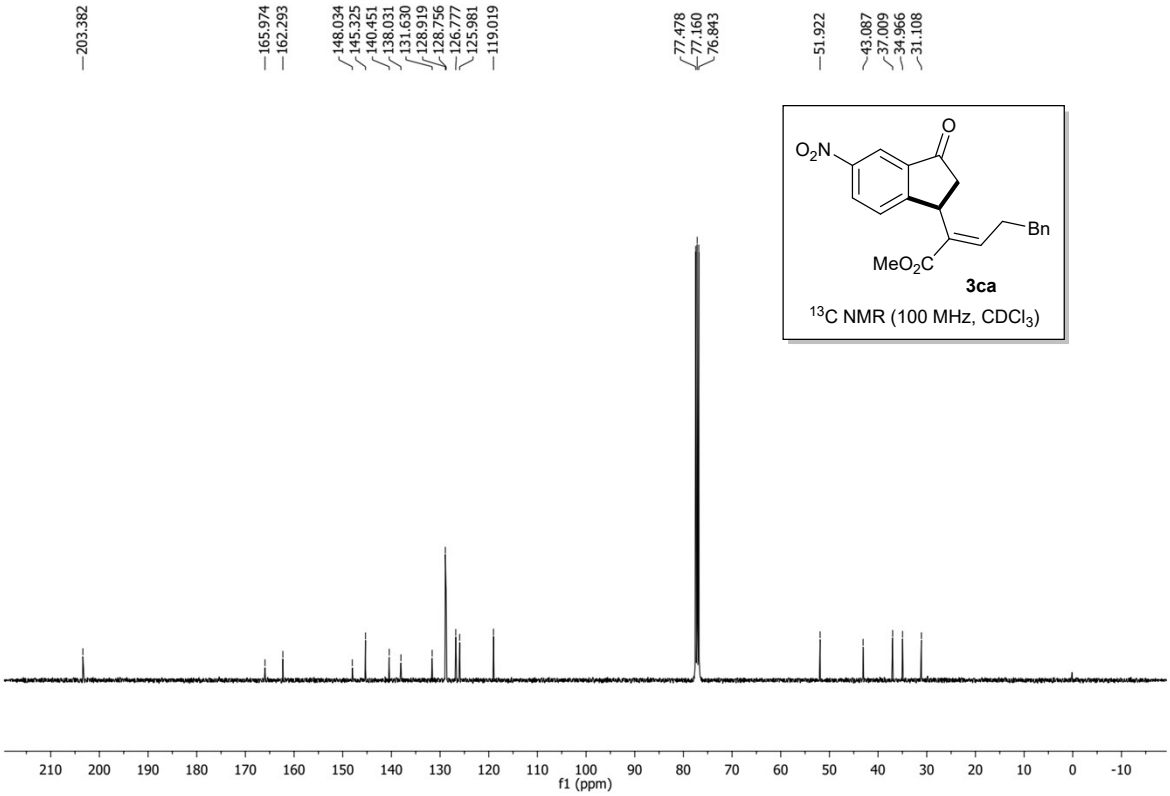





**3ca**

$^{13}$C NMR (100 MHz, $CDCl_3$)

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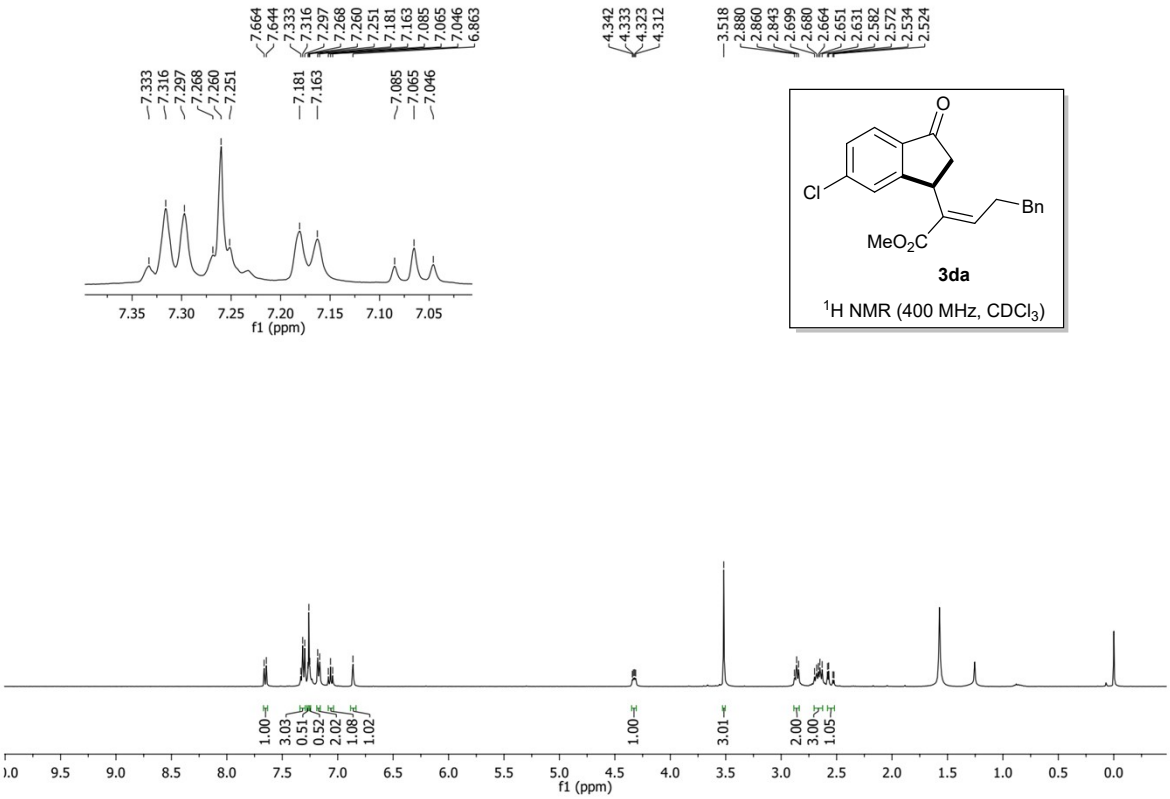





**3da**

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

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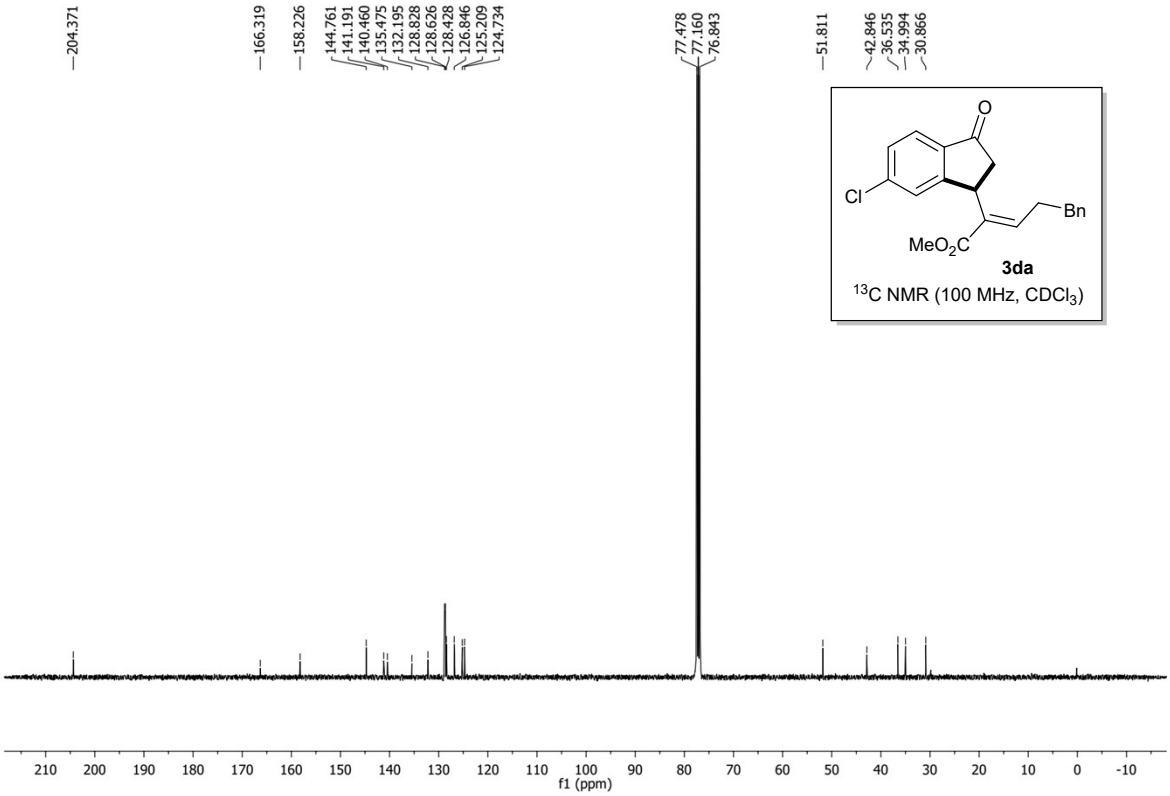





**3da**

$^{13}$C NMR (100 MHz, $CDCl_3$)

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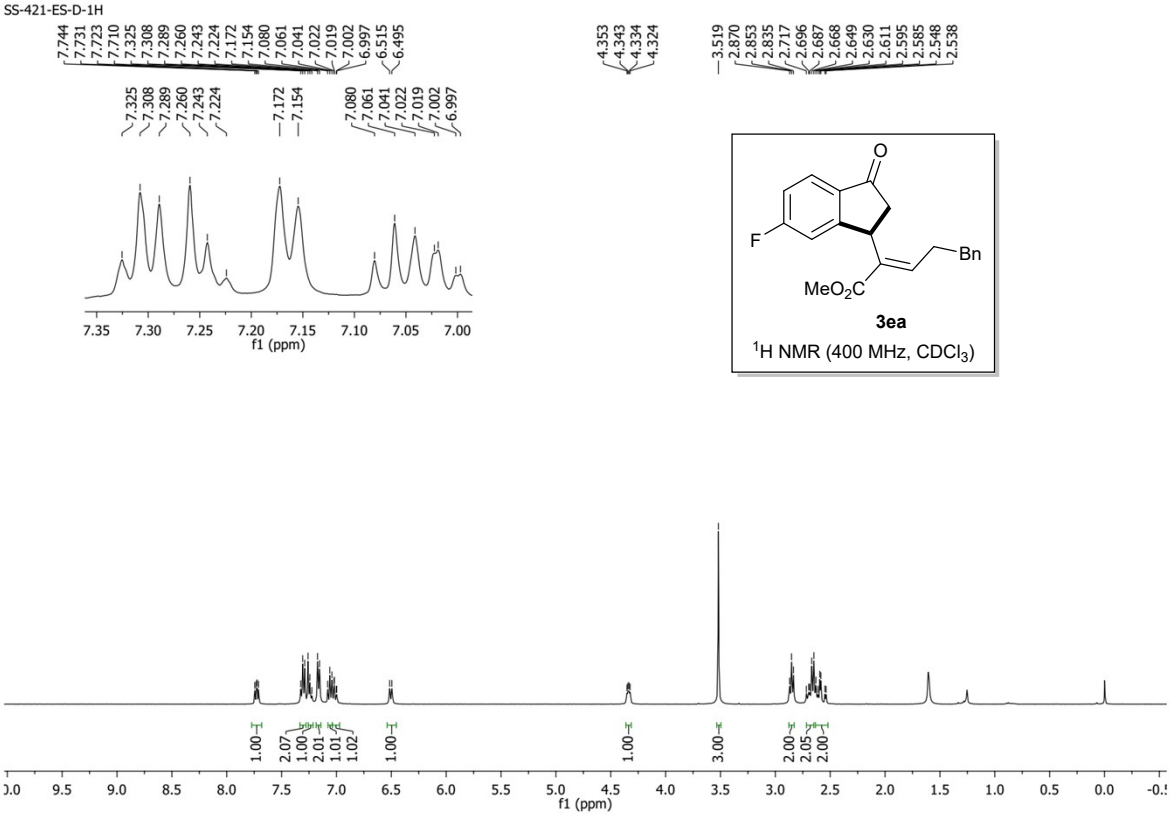


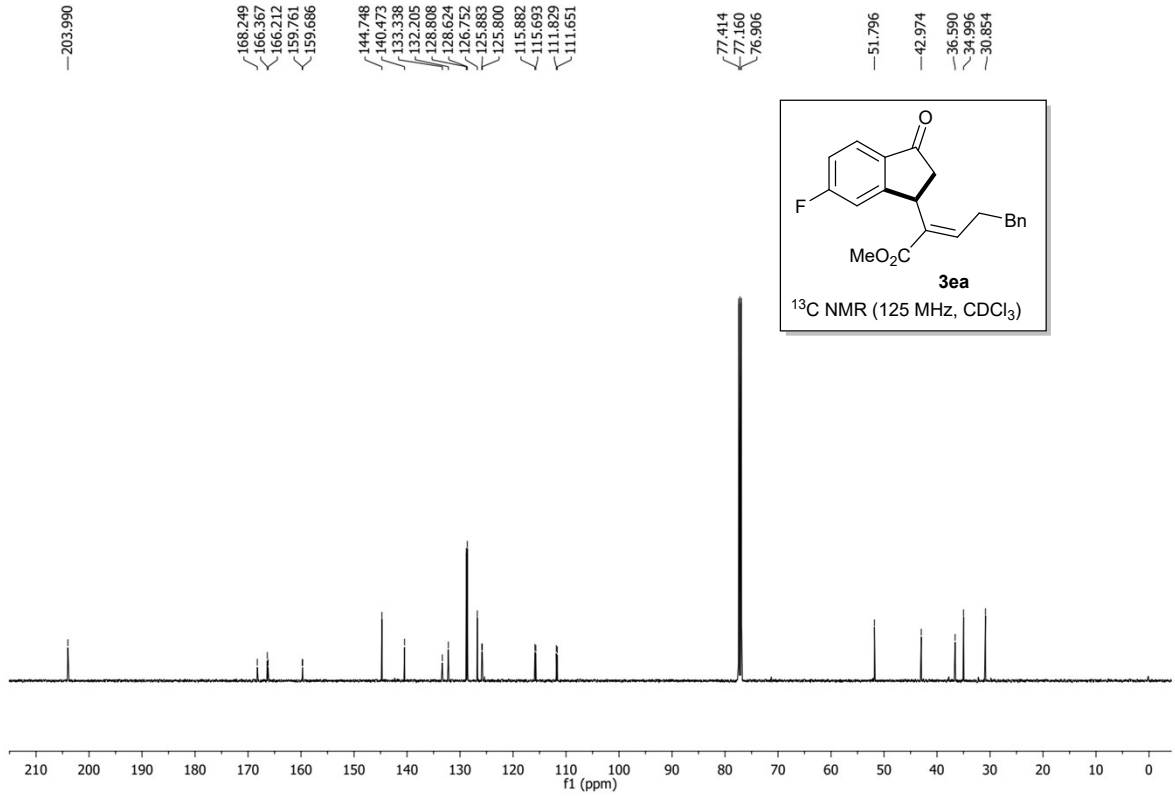




**3ea**

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

SS-421-ES-D-13C

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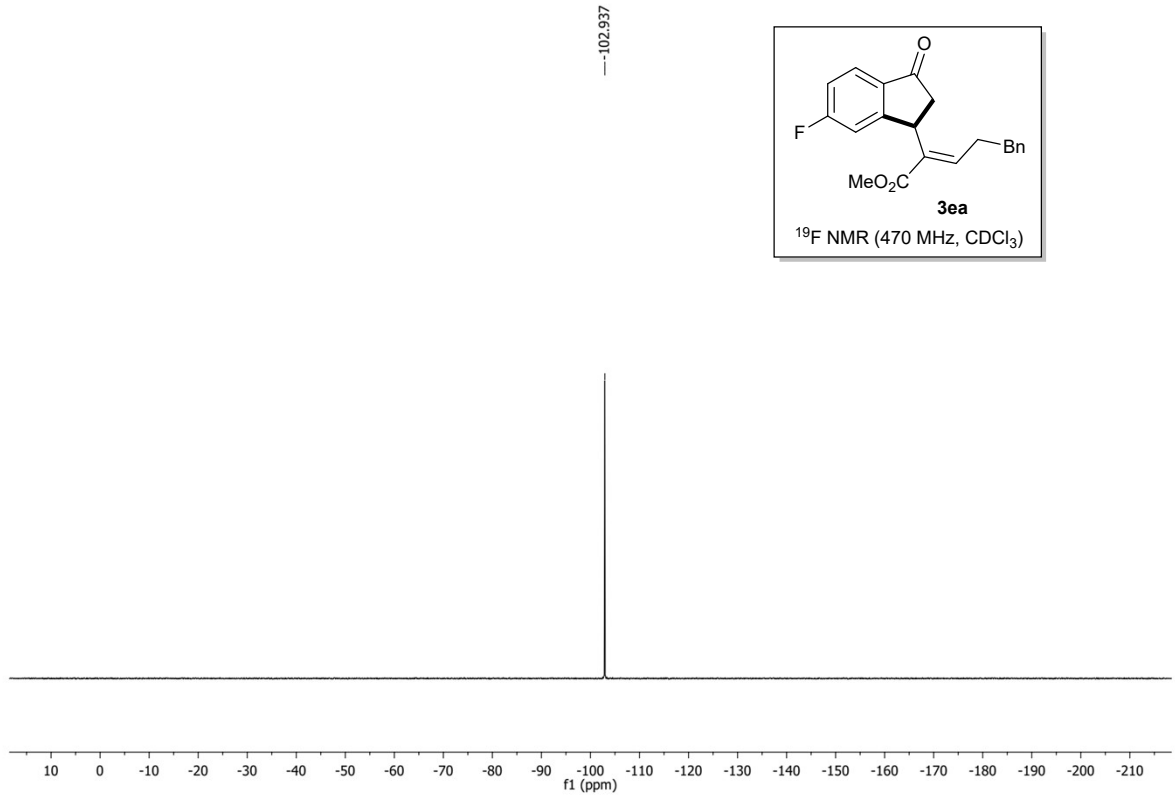

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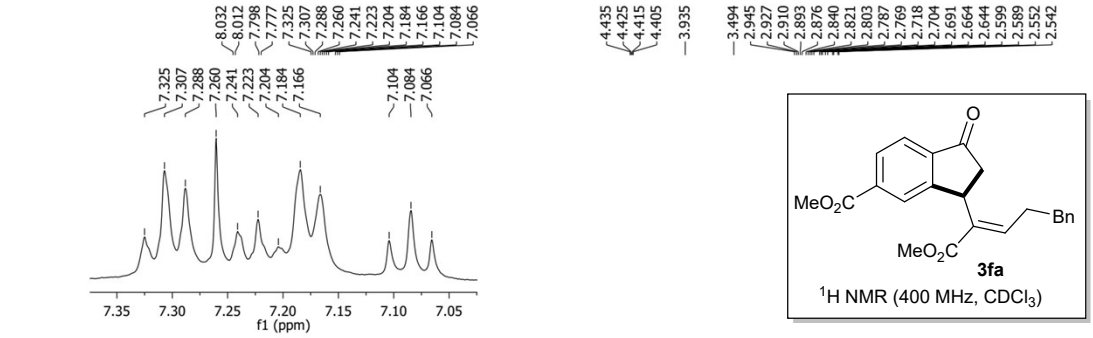
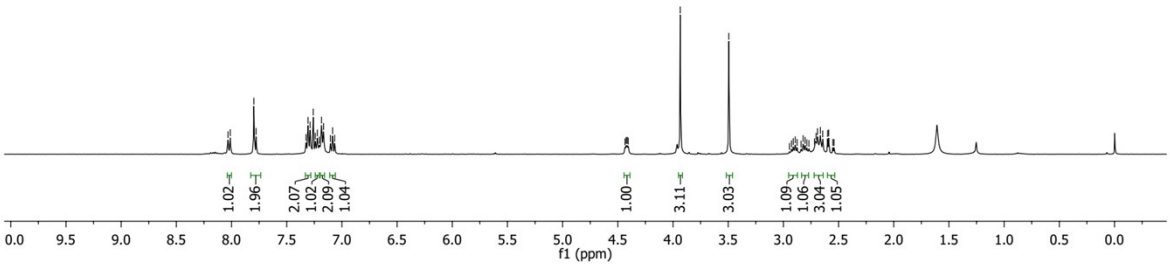






**3fa**

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

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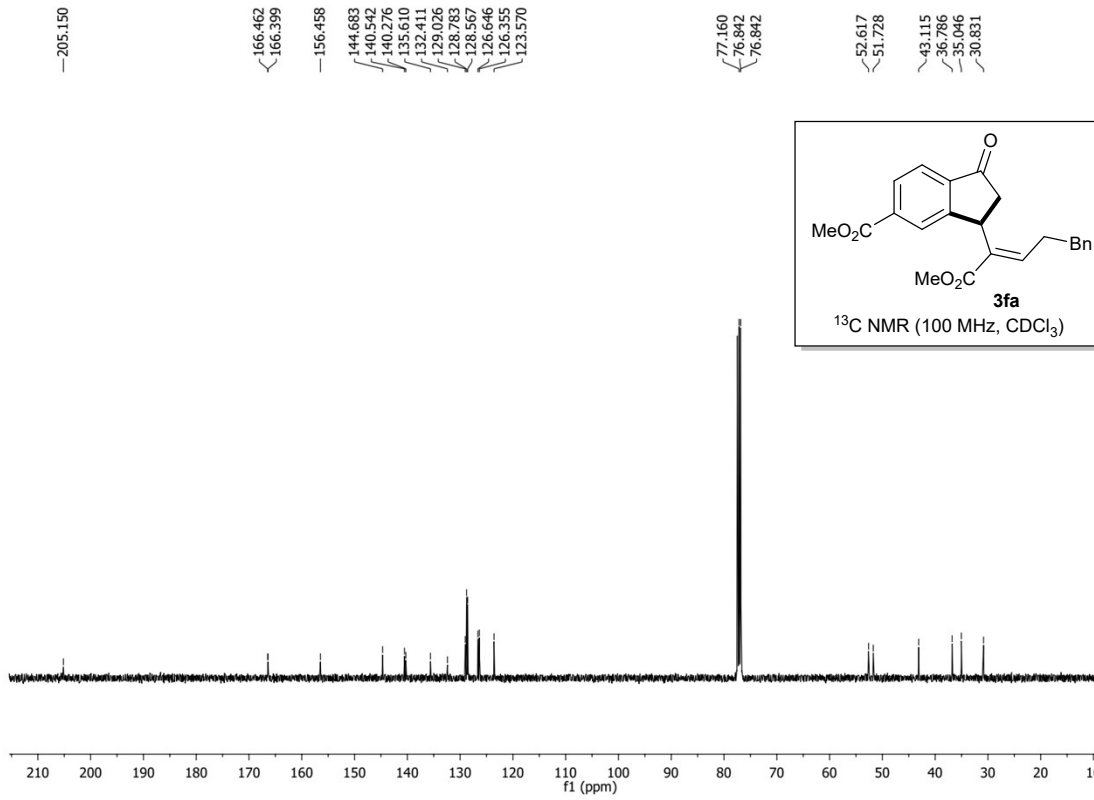


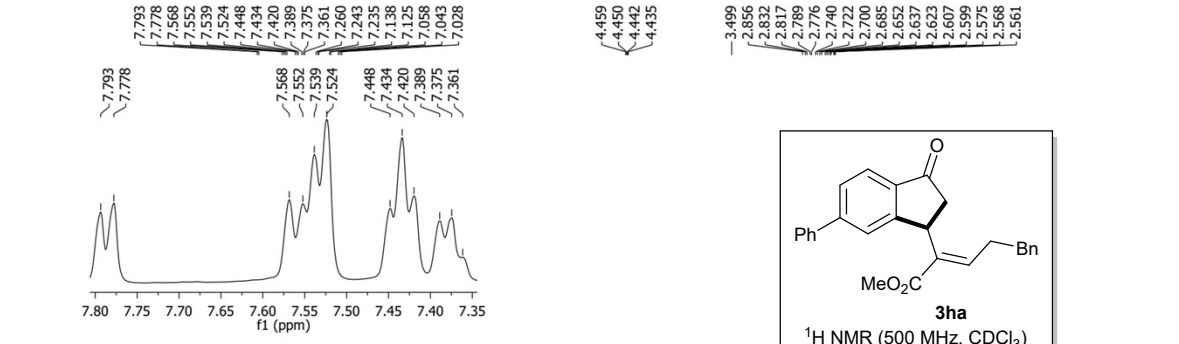




**3fa**

$^{13}$C NMR (100 MHz, $CDCl_3$)

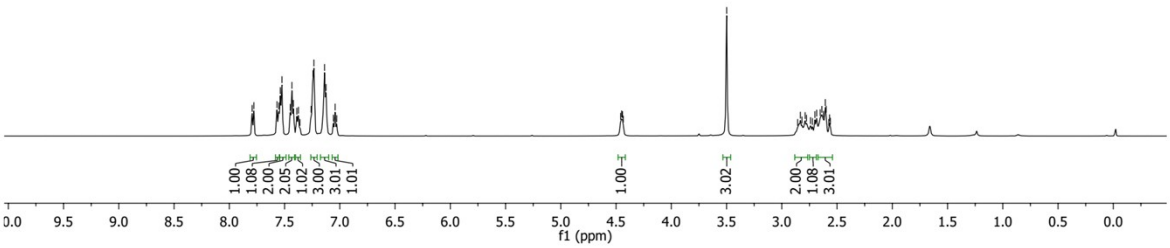
SS-420-ES-D-1H






**3ha**

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



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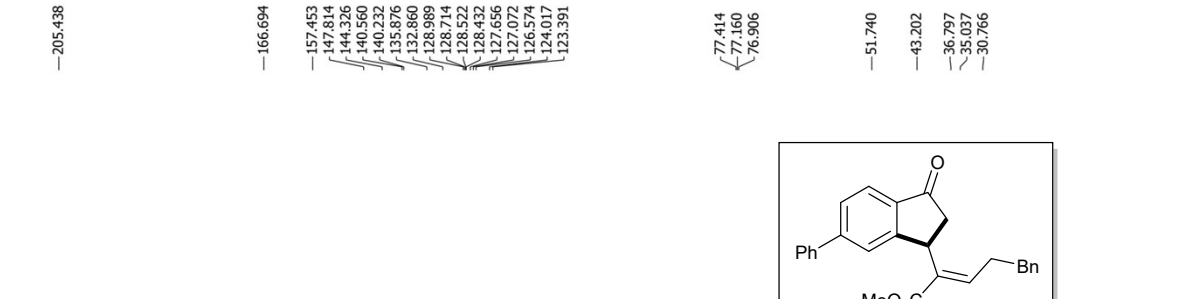
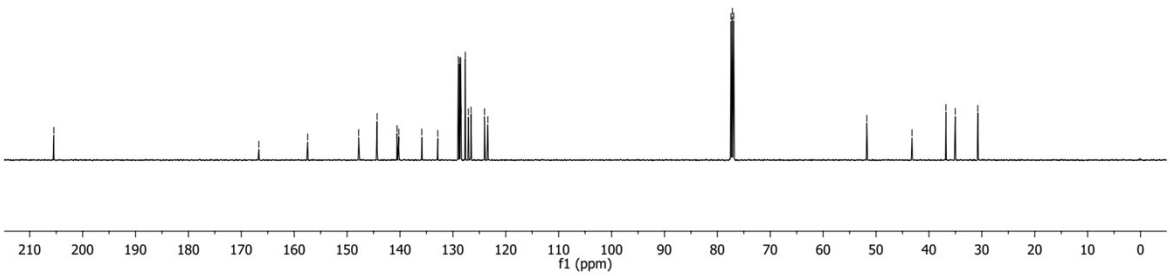





**3ha**

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



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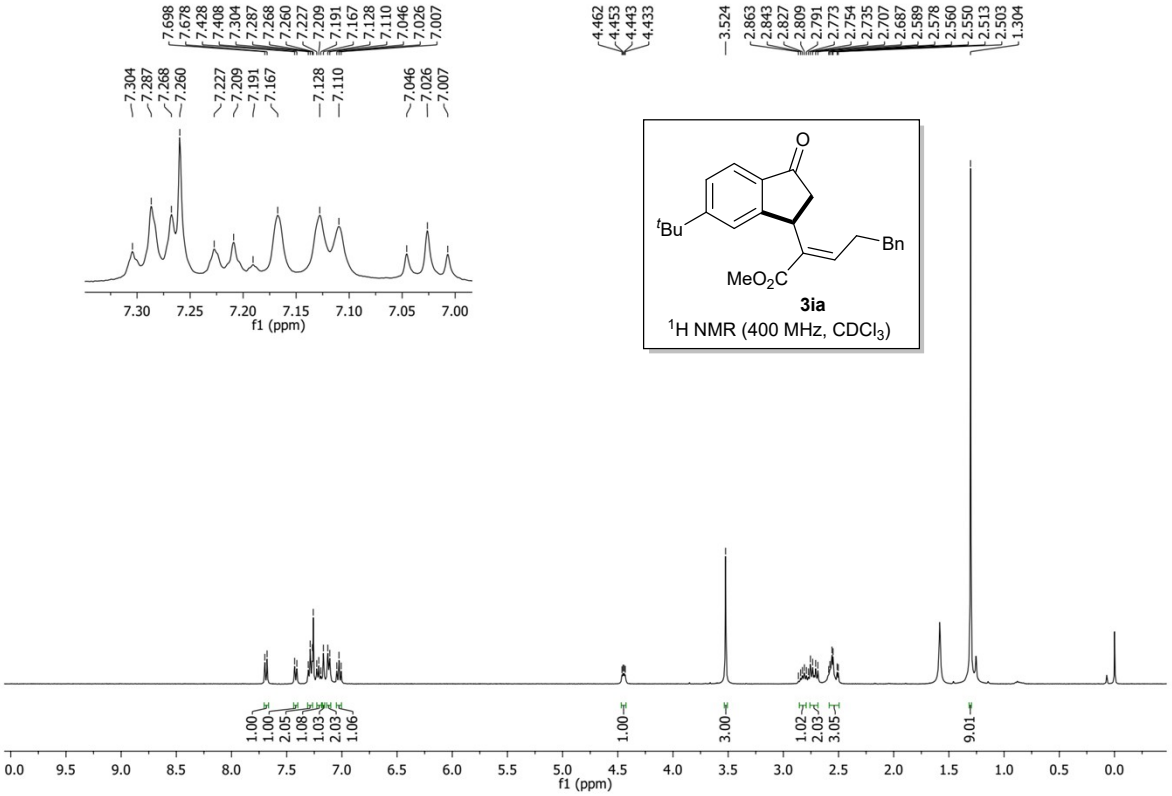


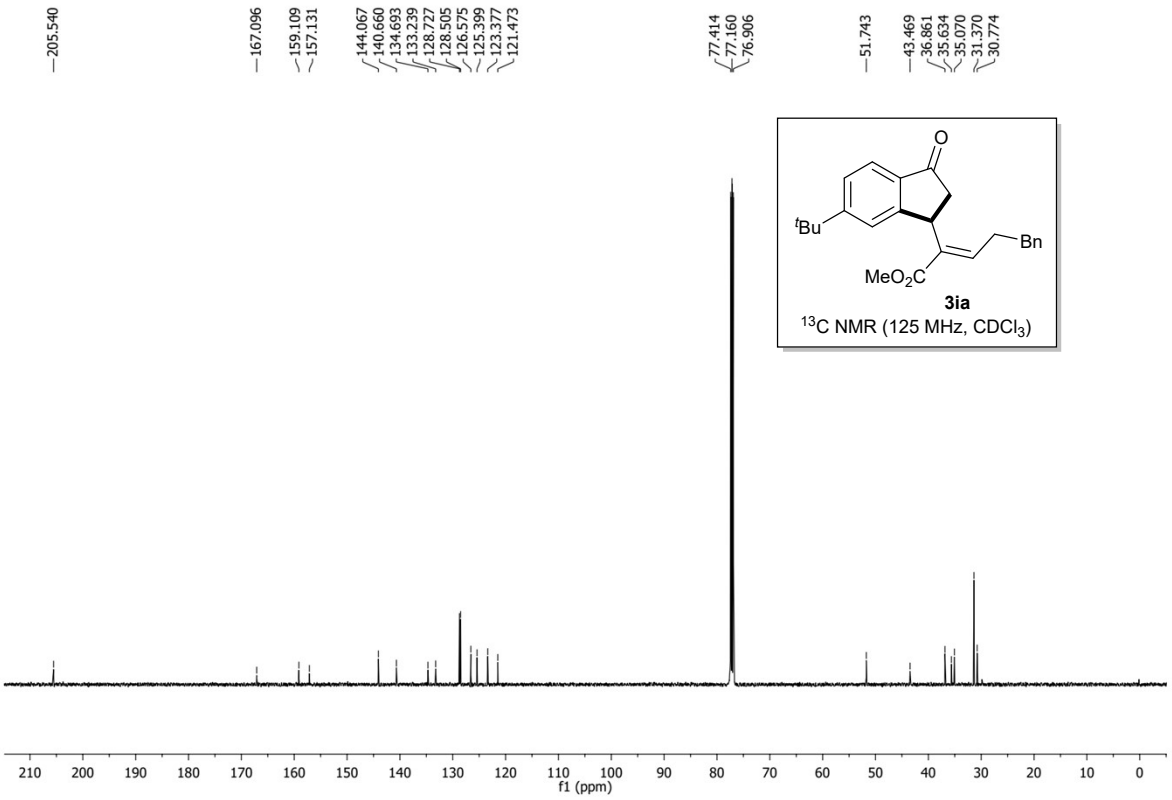




**3ia**

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

SS-427-ES-D-13C



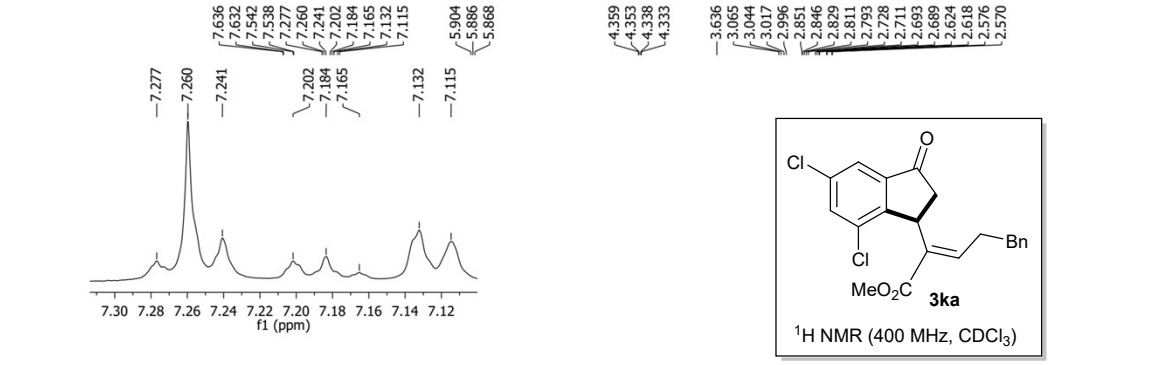




**3ia**

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

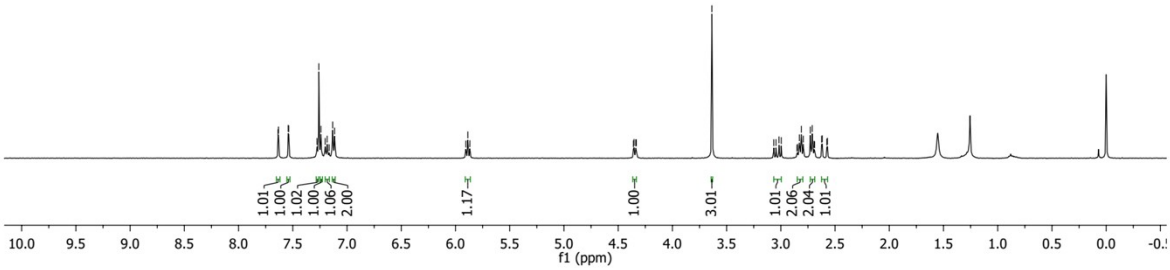
SS-442-ES-D-1H







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

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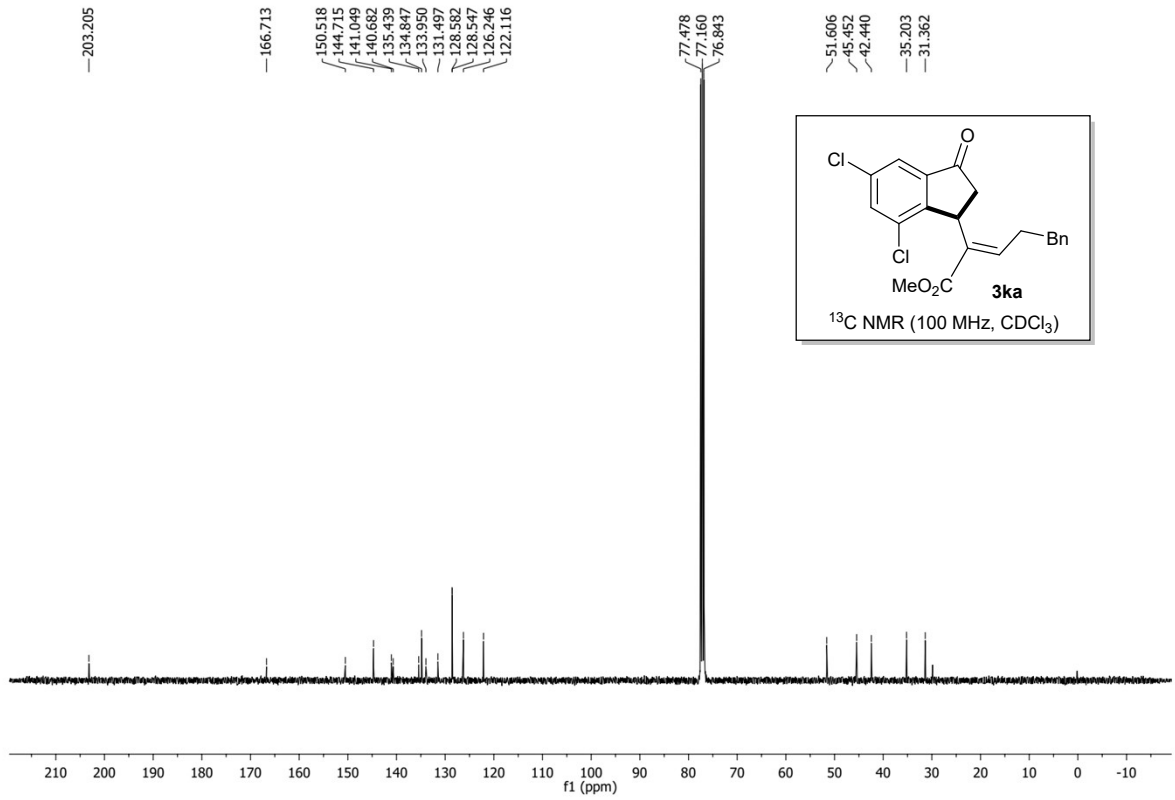
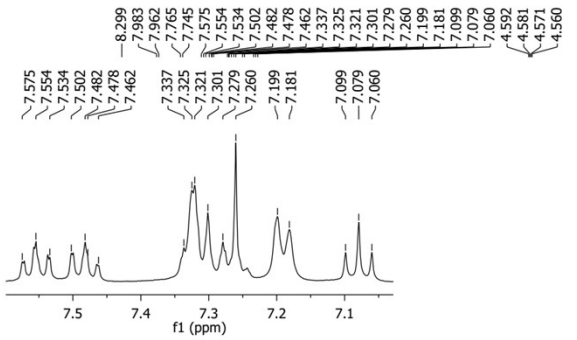


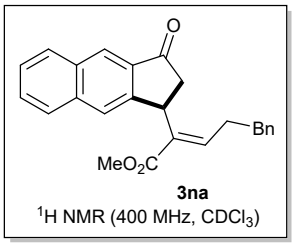




$^{13}$C NMR (100 MHz, $CDCl_3$)

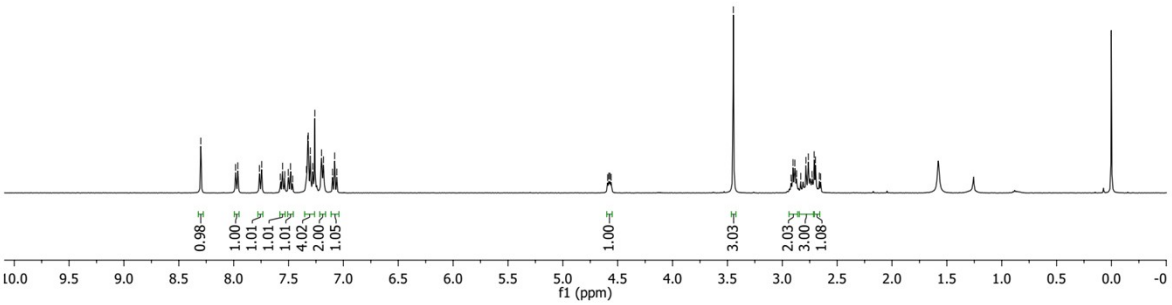
SS-428-ES-D-1H




**3na**

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

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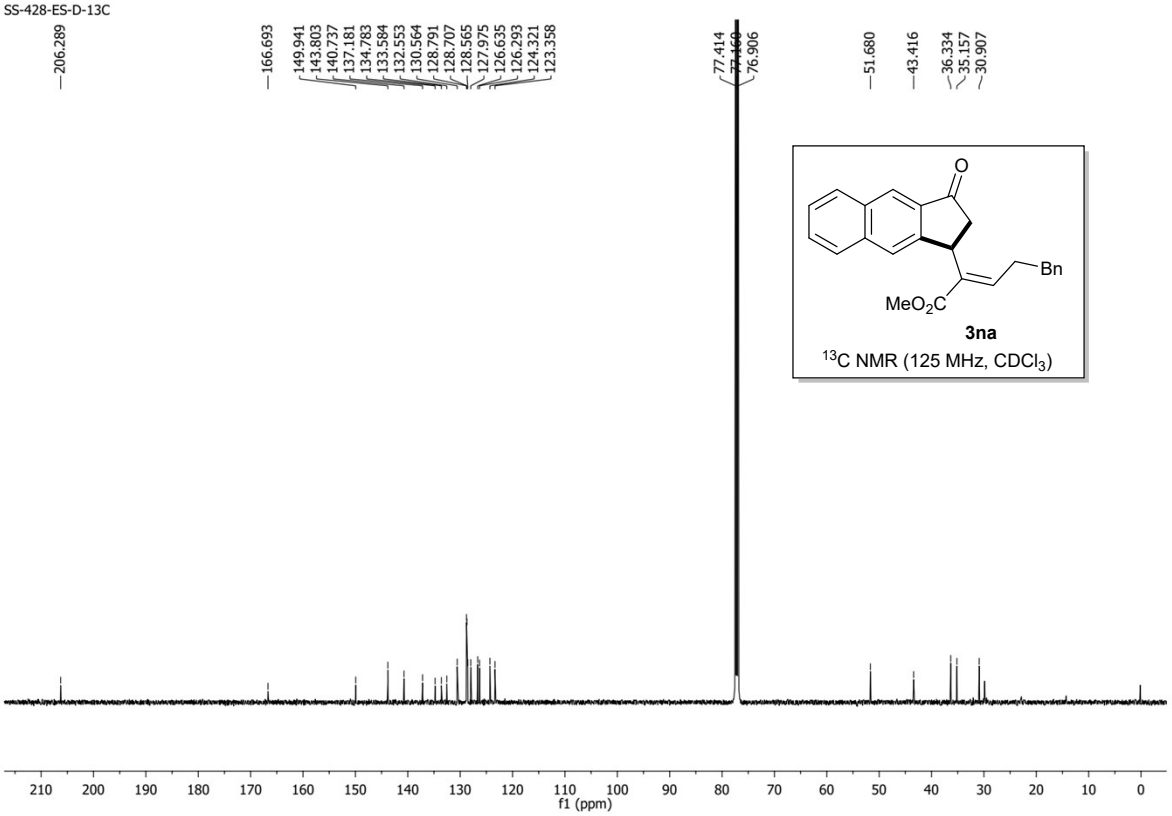


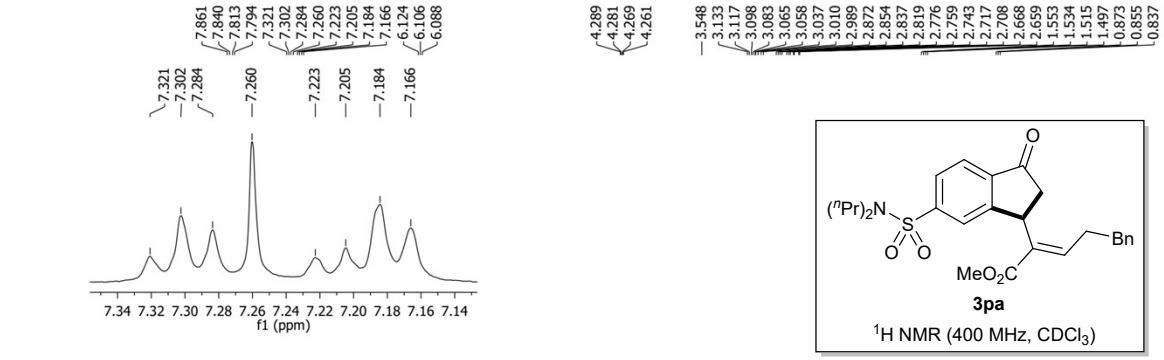




**3na**

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

SS-445-ES-D-1H

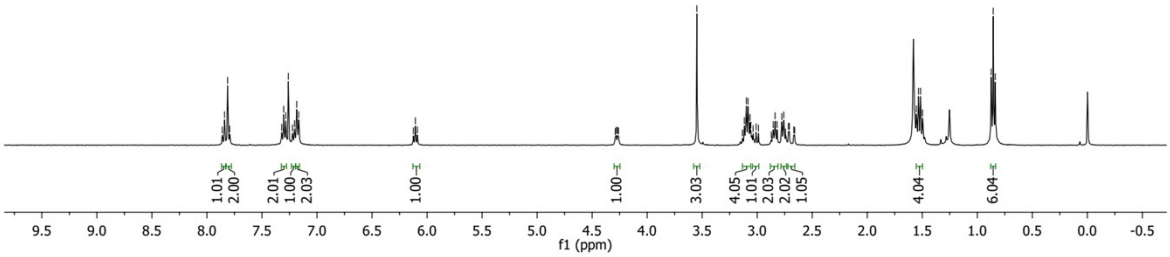






**3pa**

$^1$H NMR (400 MHz, $CDCl_3$)

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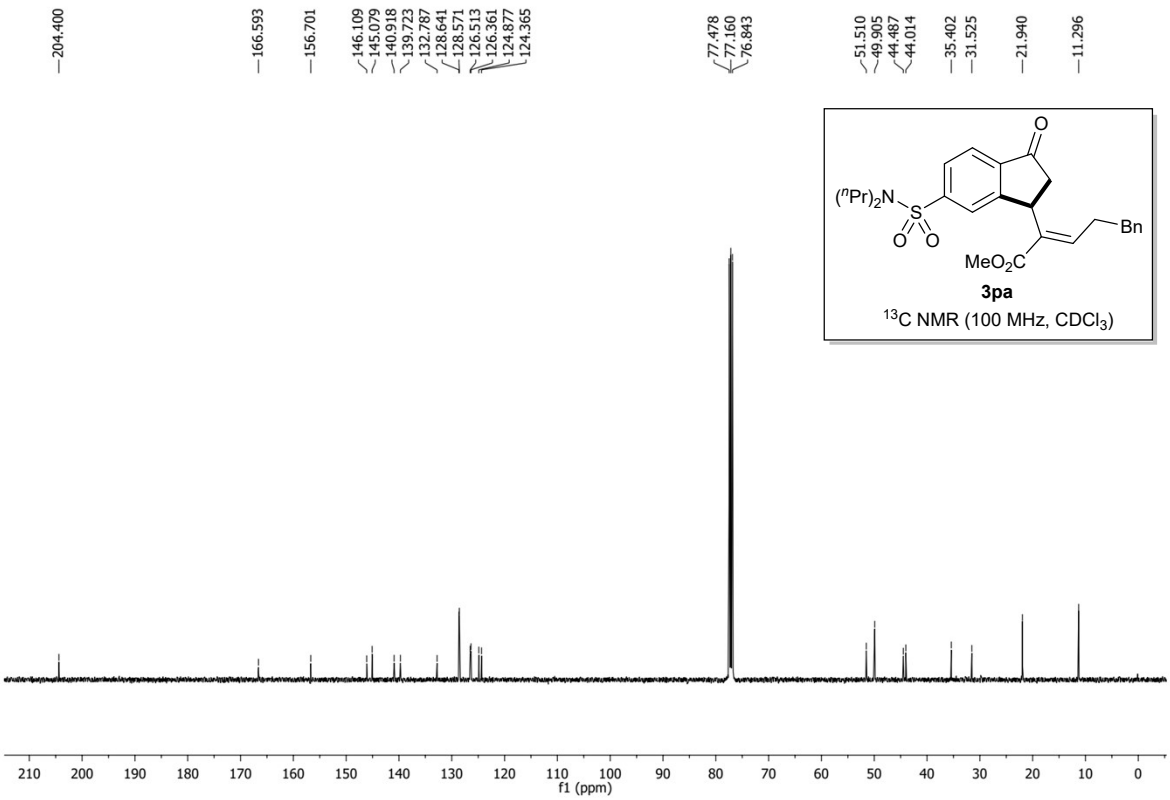


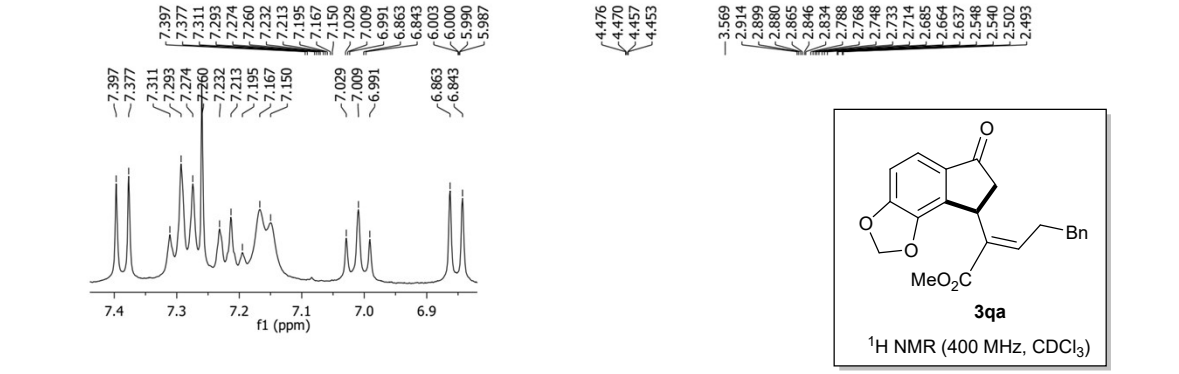




**3pa**

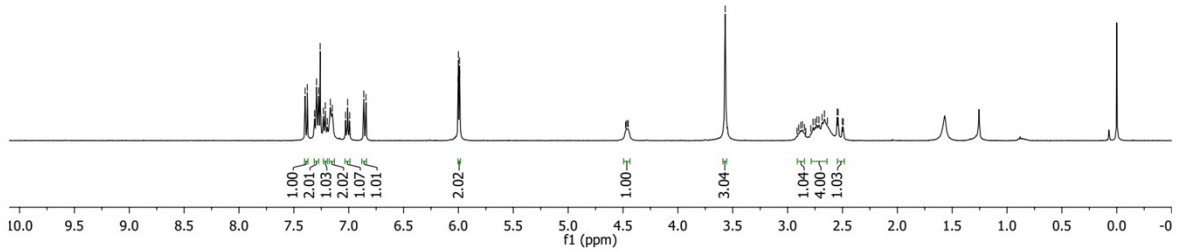
$^{13}$C NMR (100 MHz, $CDCl_3$)

SS-443-ES-D-1H



**3qa**

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



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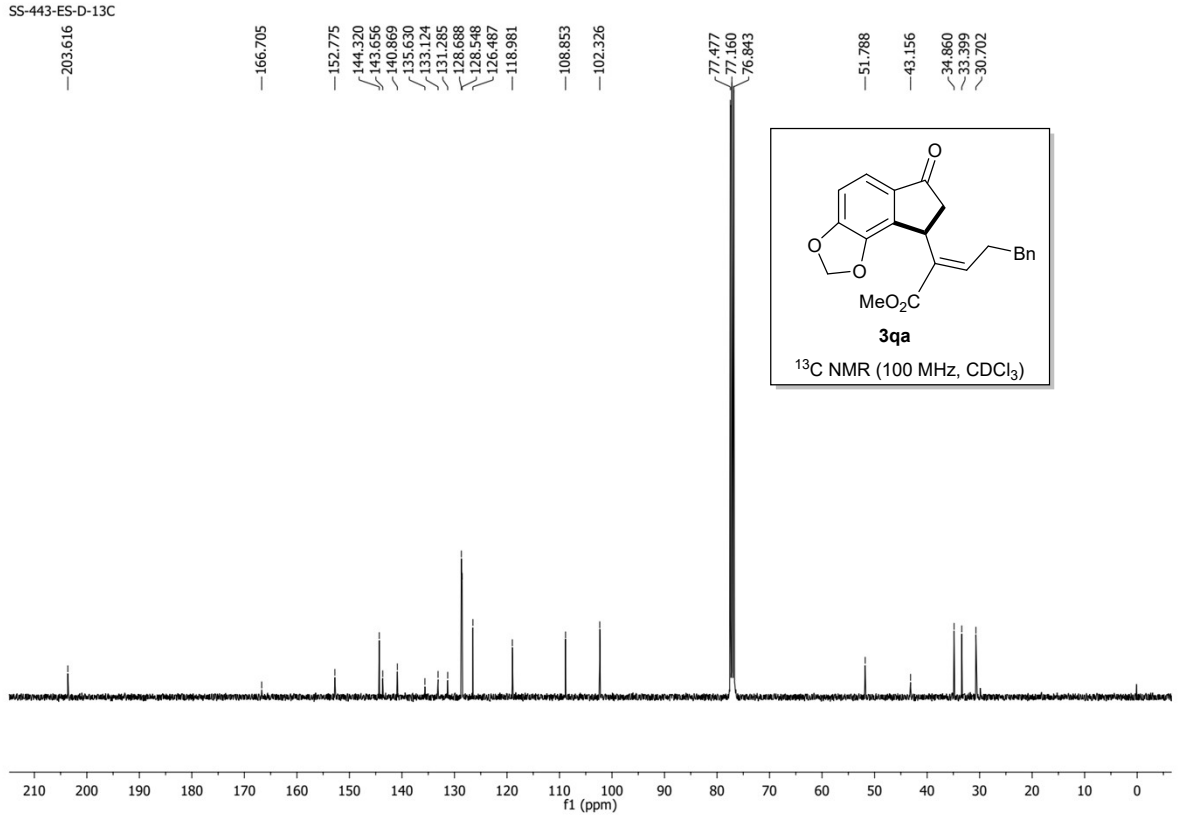
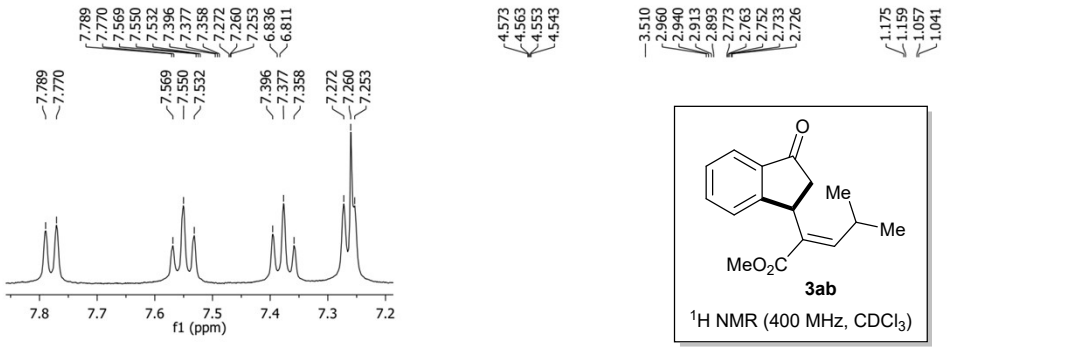


**3qa**

$^{13}$C NMR (100 MHz, $CDCl_3$)

SS-436-ES-D-1H

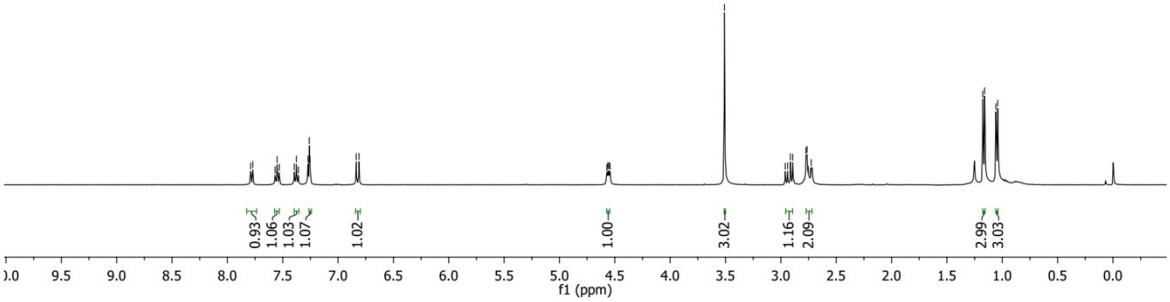






**3ab**

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

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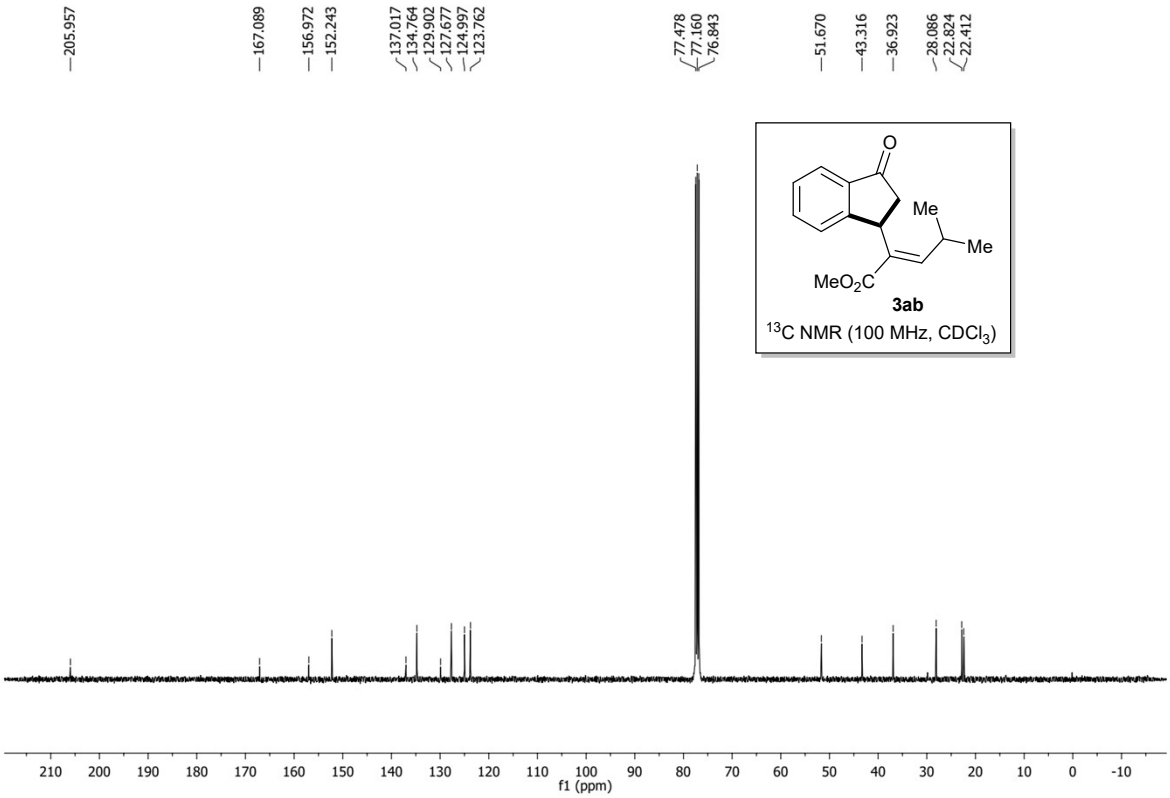


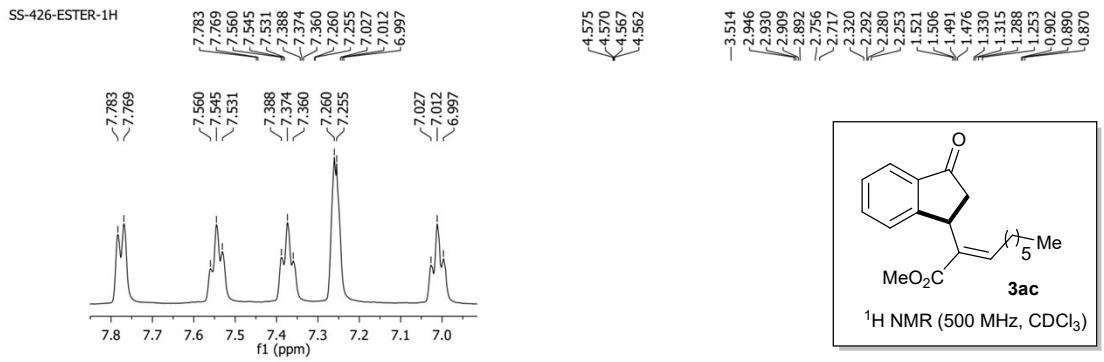




**3ab**

$^{13}$C NMR (100 MHz, $CDCl_3$)

SS-426-ESTER-1H

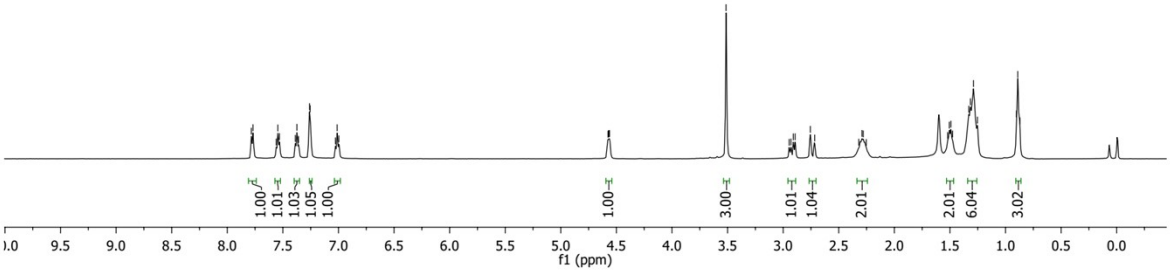






**3ac**

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

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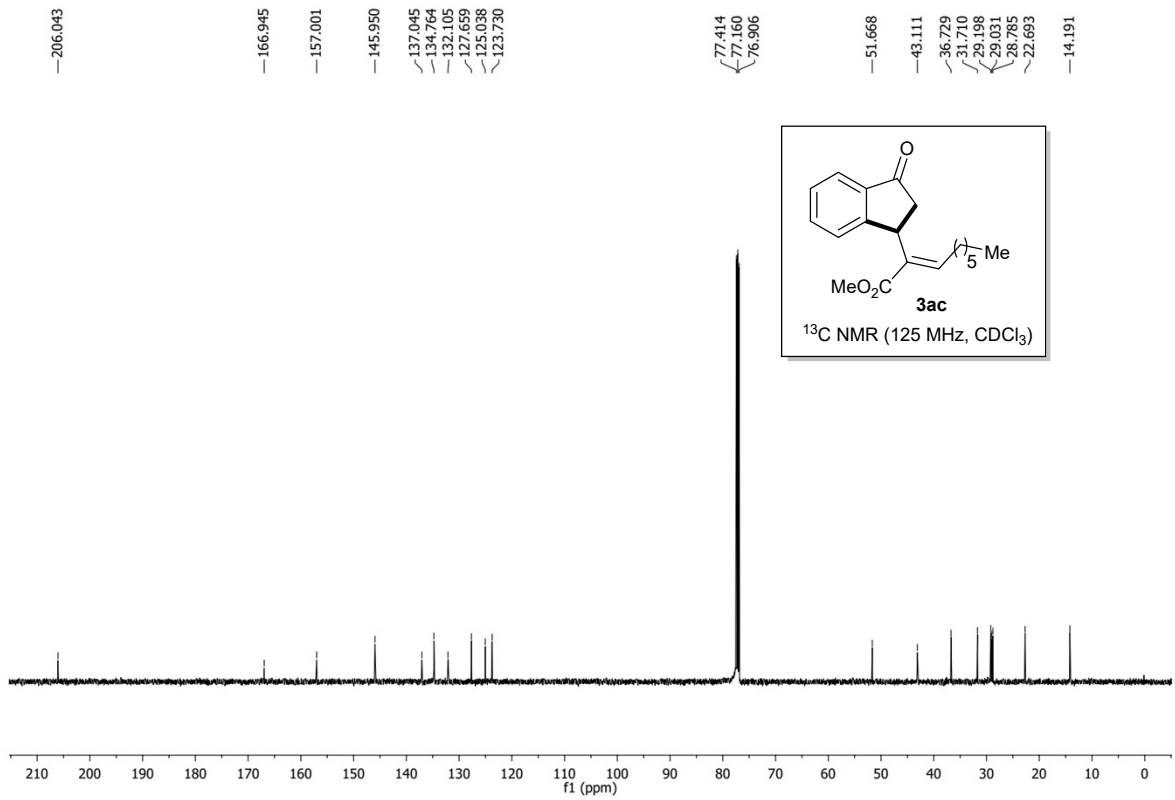


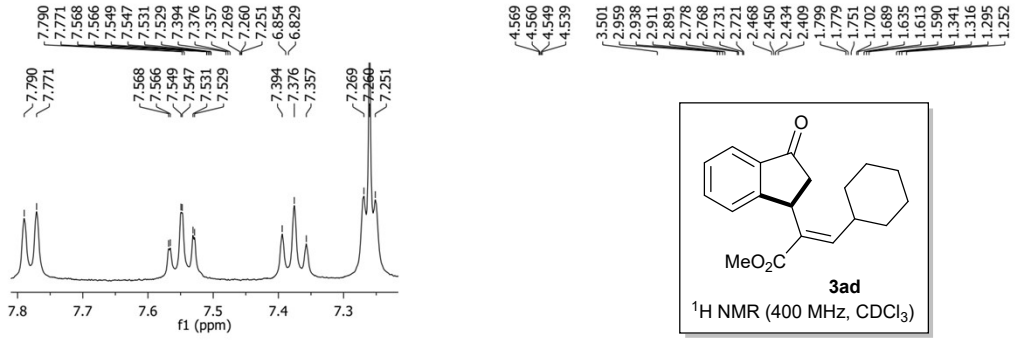




**3ac**

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

SS-429-ES-D-1H

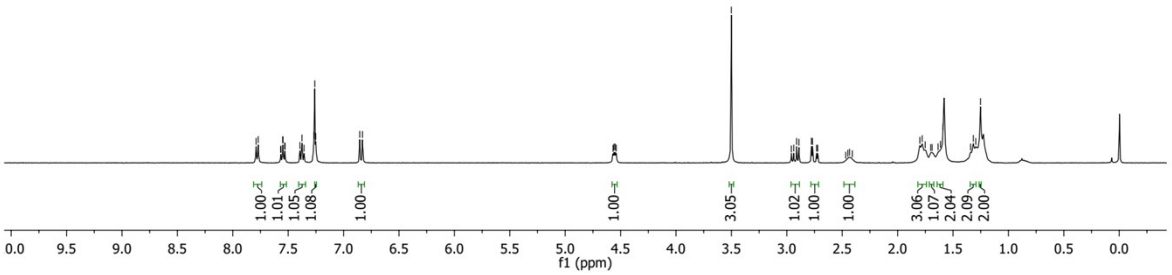




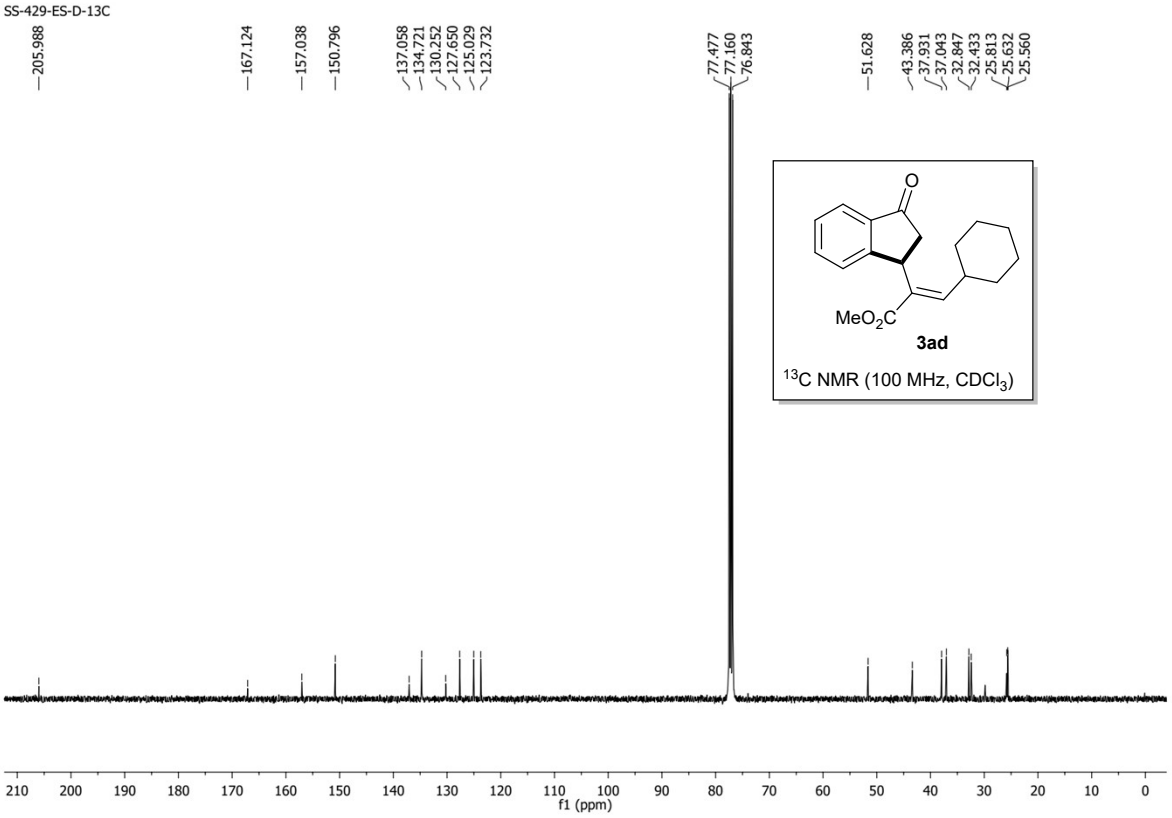


**3ad**

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




SS-429-ES-D-13C



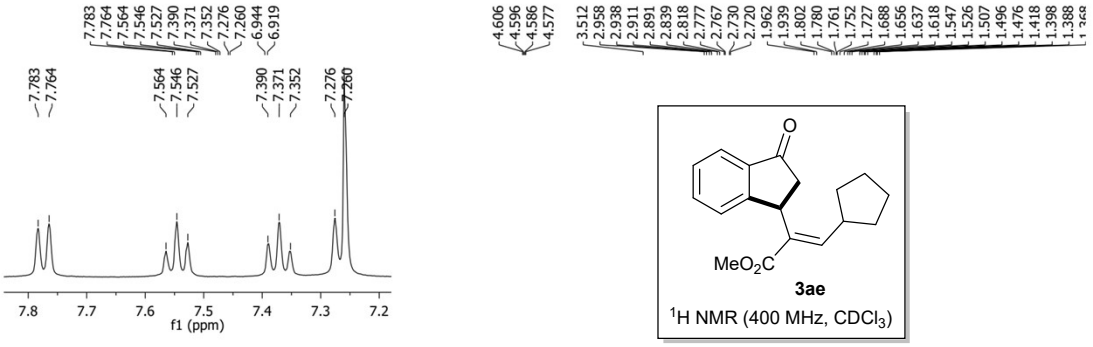




**3ad**

$^{13}$C NMR (100 MHz, $CDCl_3$)

SS-450-ES-D-1H

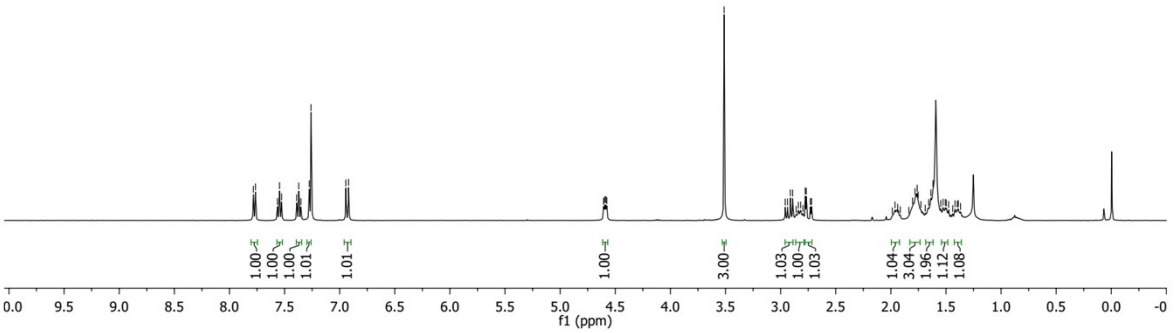




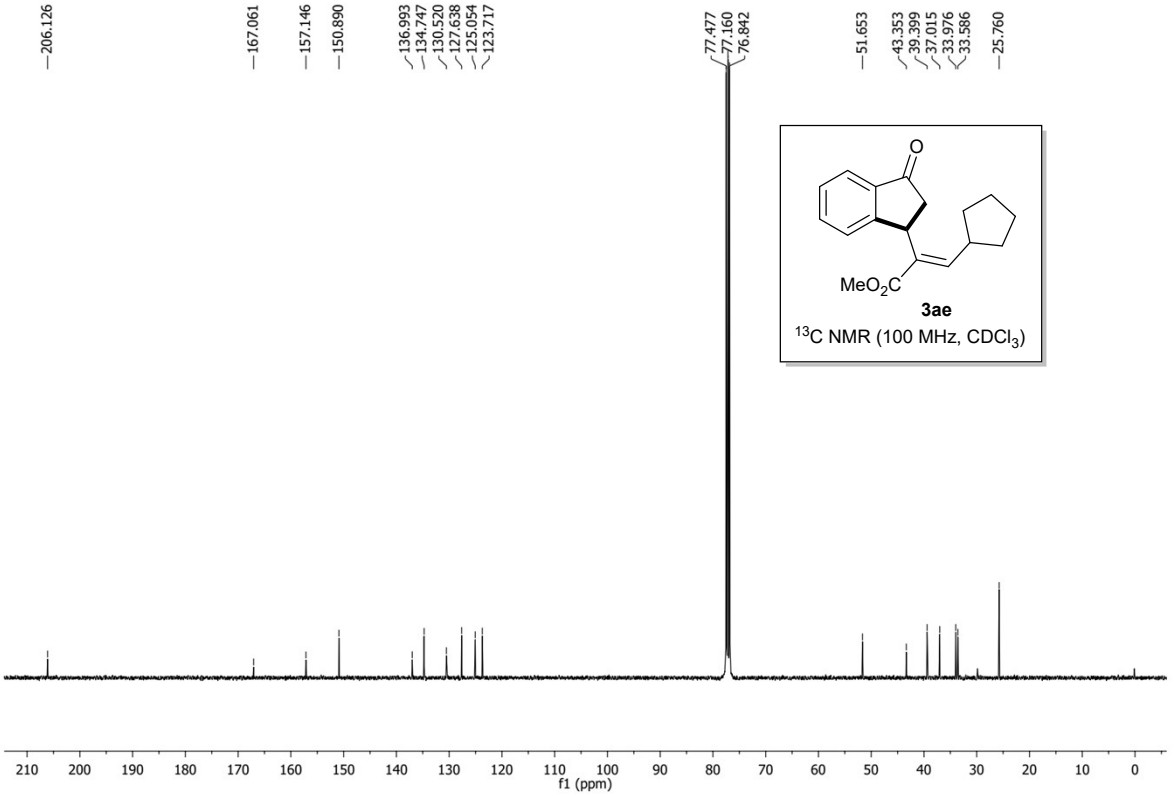


**3ae**

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




SS-450-ES-D-13C



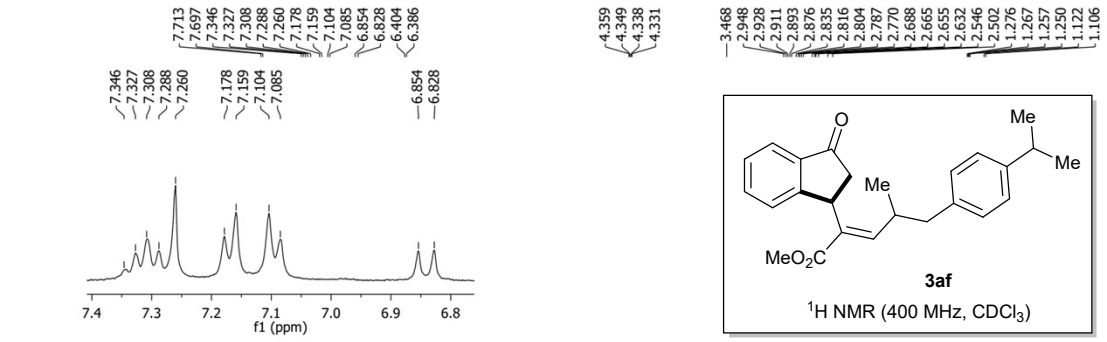


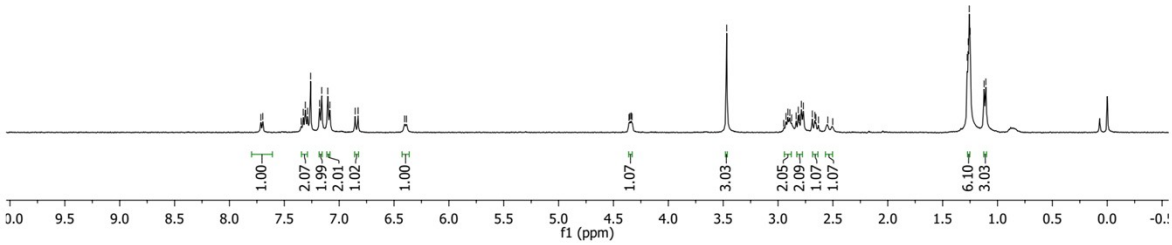


**3ae**

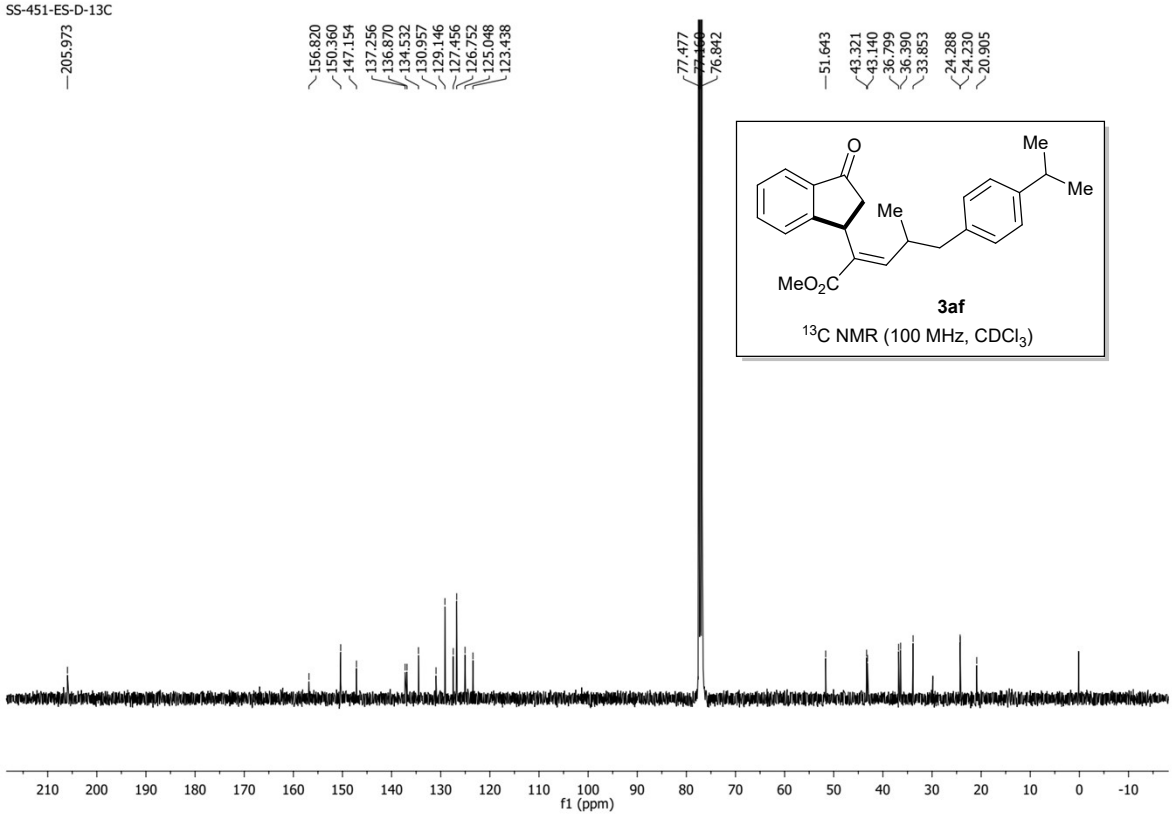
$^{13}$C NMR (100 MHz, $CDCl_3$)

SS-451-ES-D-1H

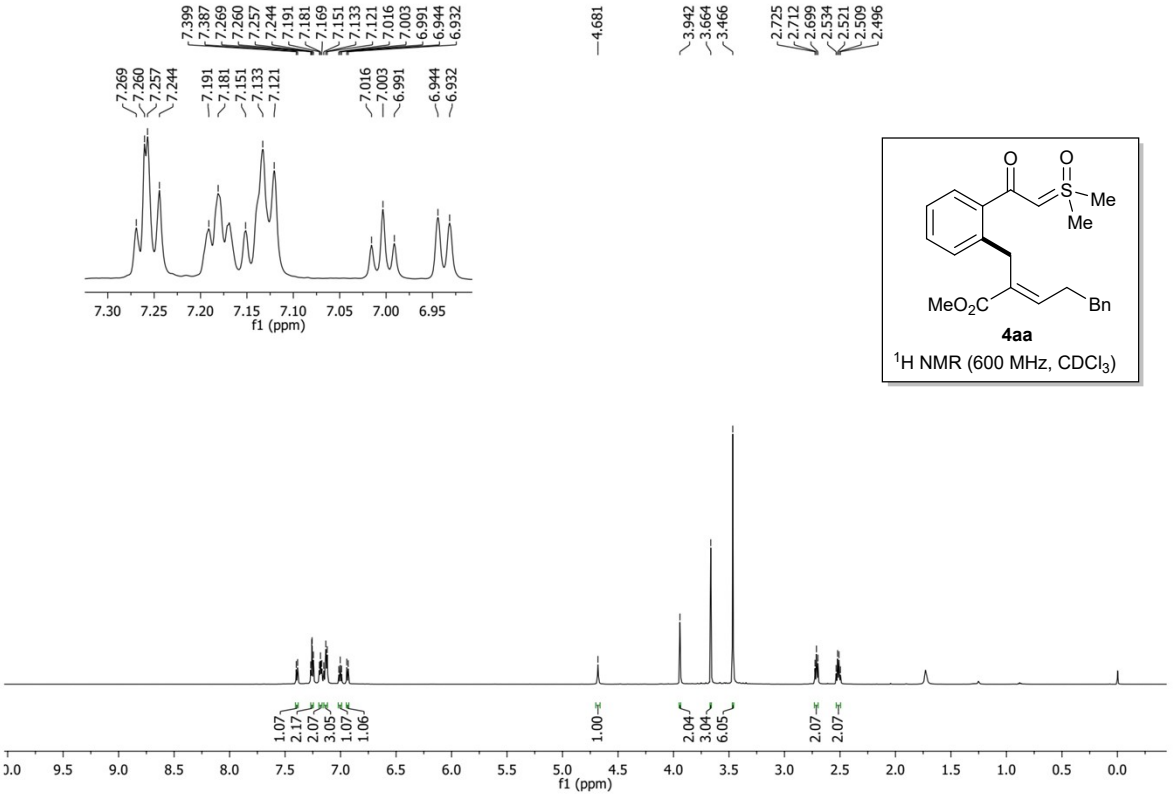



SS-451-ES-D-13C



SS-417-ES-T-1H



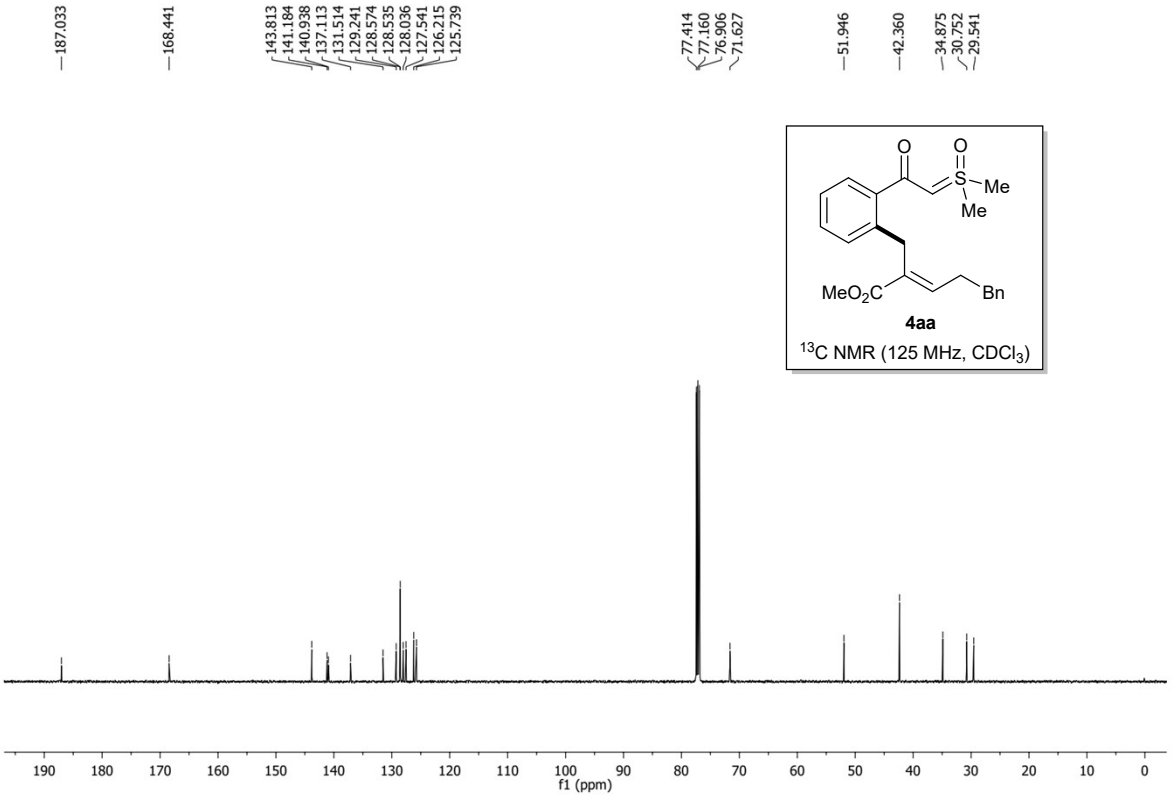




**4aa**

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

SS-417-ES-T-13C



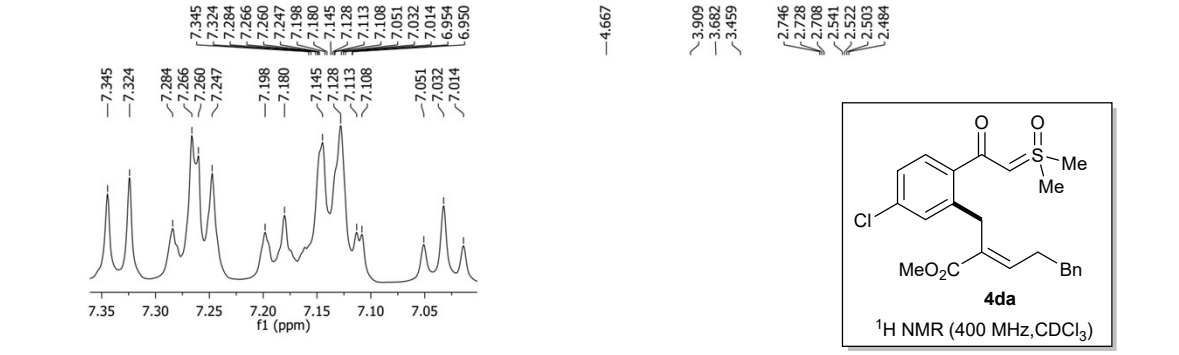




**4aa**

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

SS-425-ES-T-1H

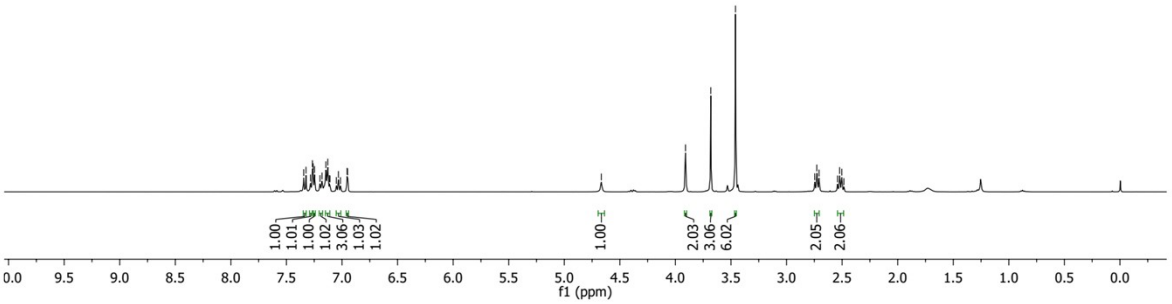




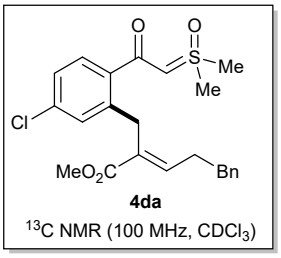


**4da**

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

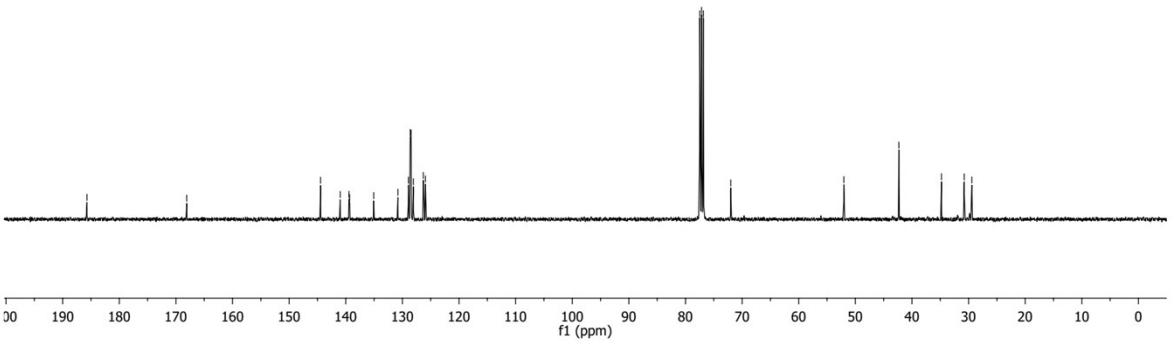



SS-425-ES-T-13C

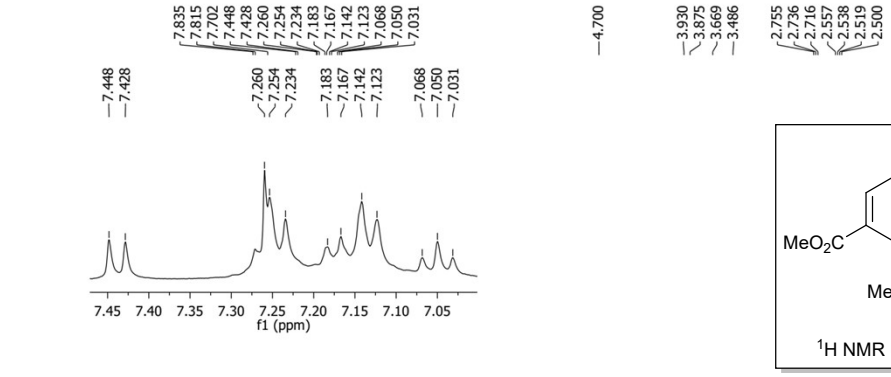



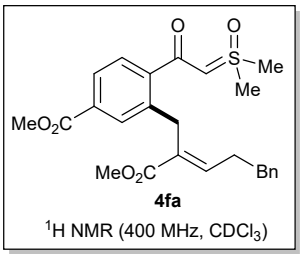

**4da**

$^{13}$C NMR (100 MHz, $CDCl_3$)



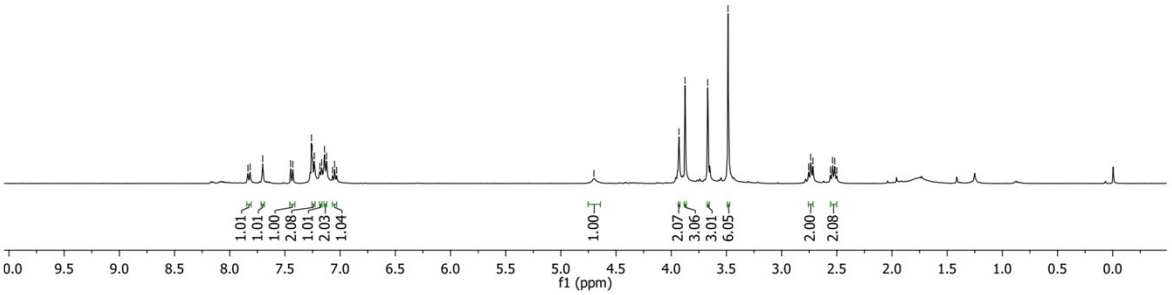
SS-418-ES-T-1H



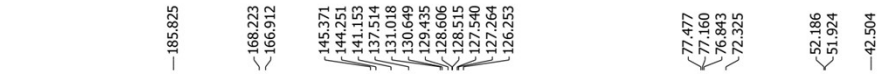



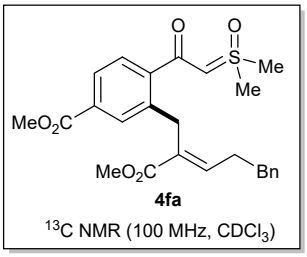

**4fa**

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



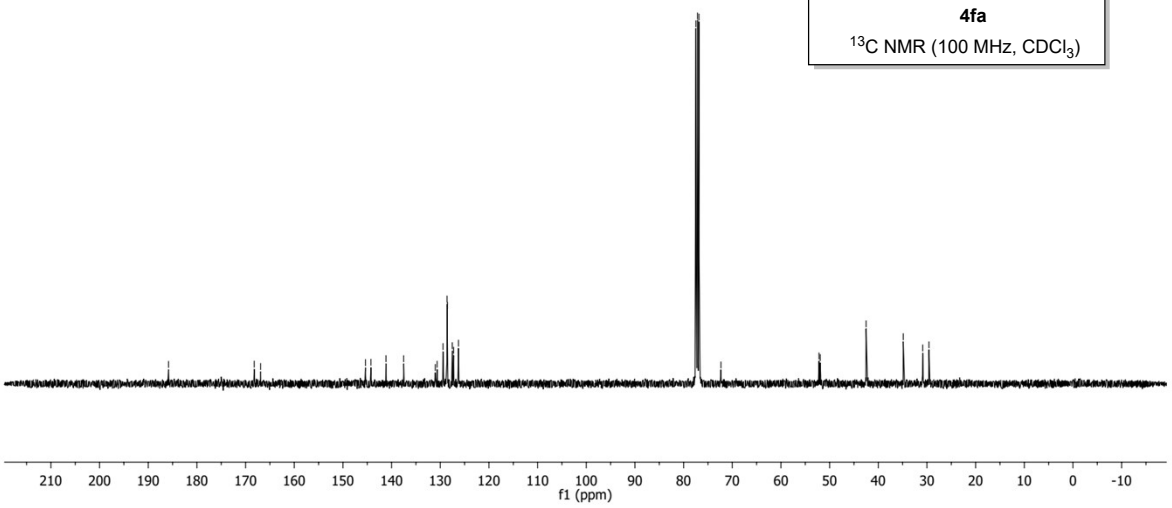

SS-418-ES-T-13C



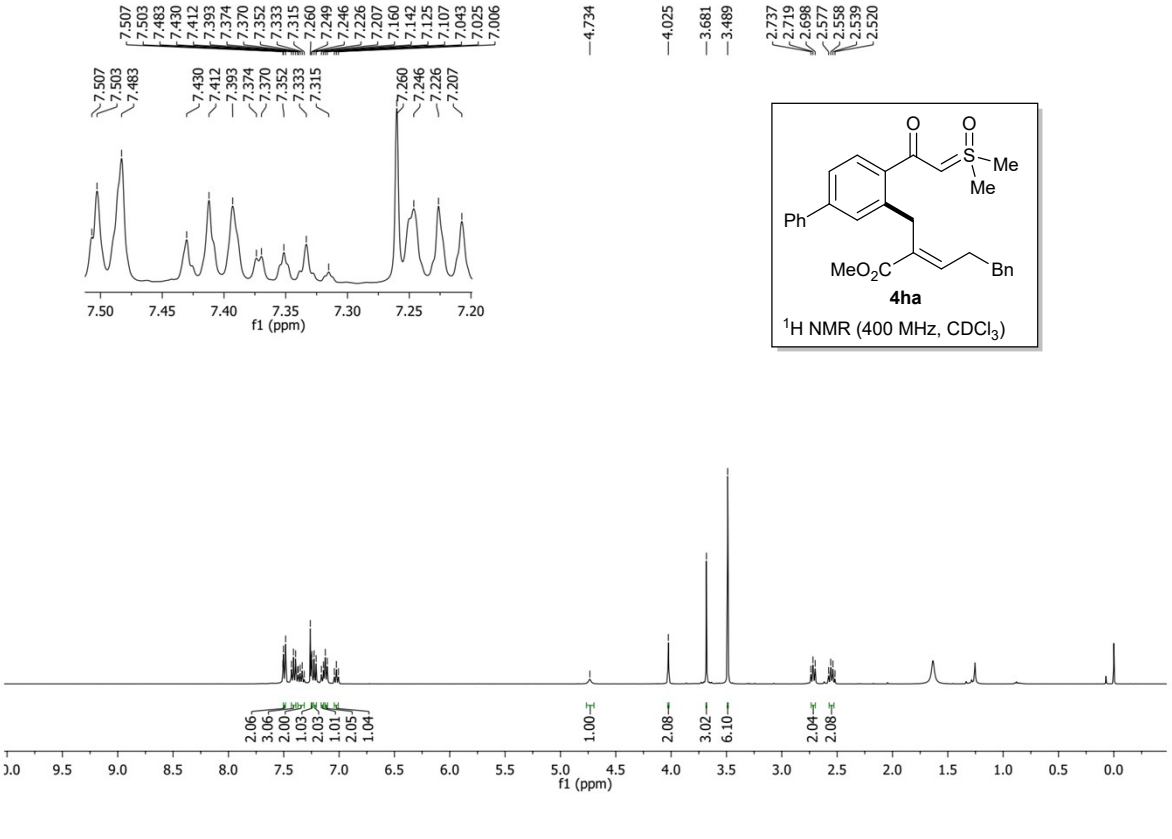




**4fa**

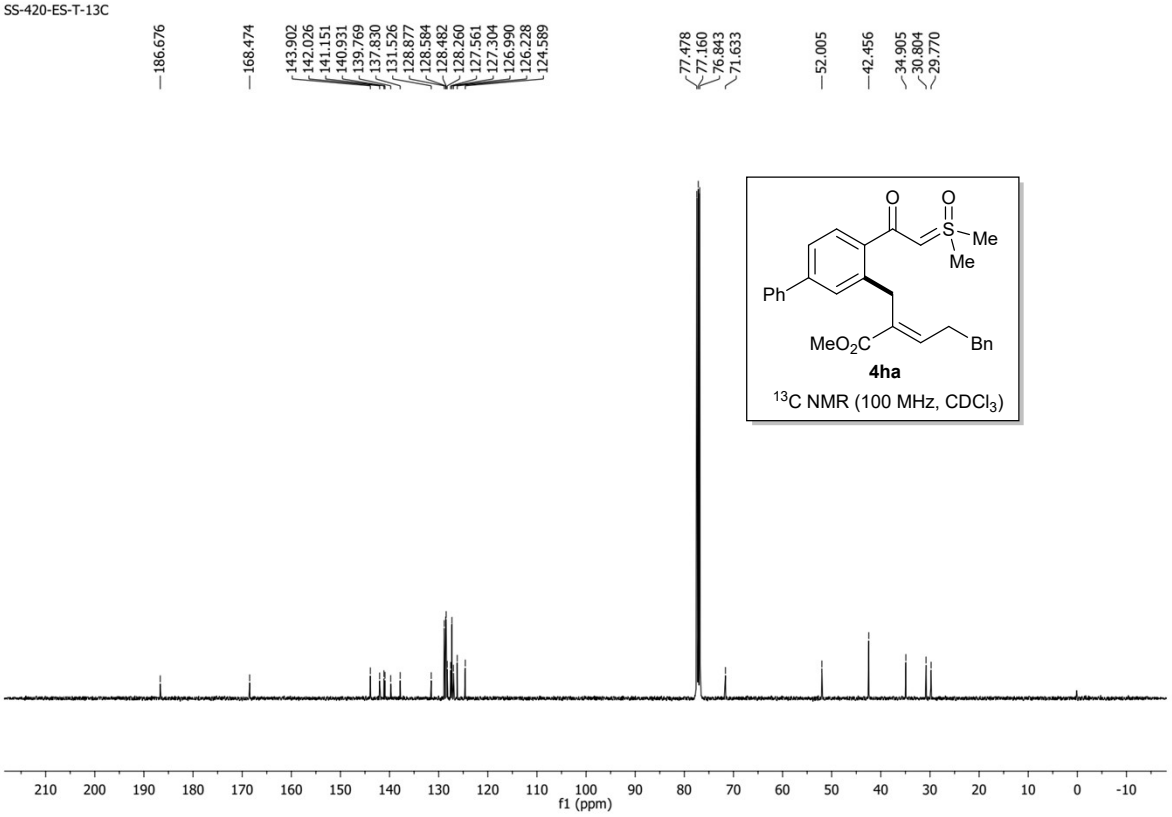
$^{13}$C NMR (100 MHz, $CDCl_3$)



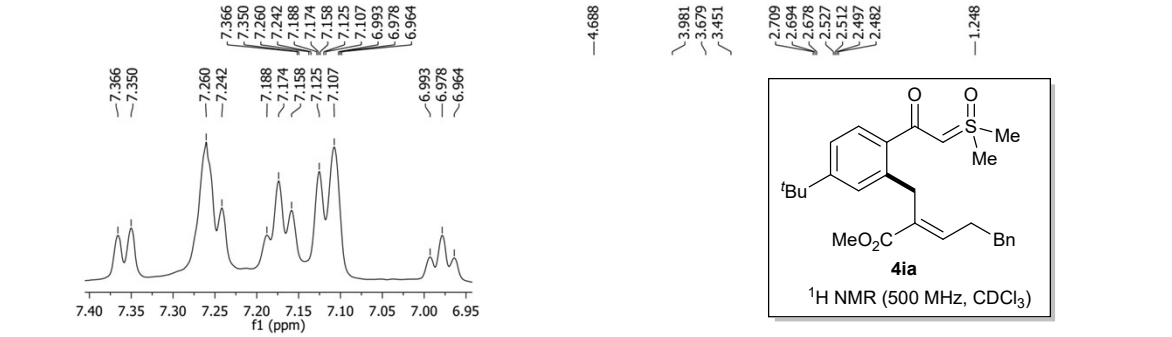
SS-420-ES-T-1H

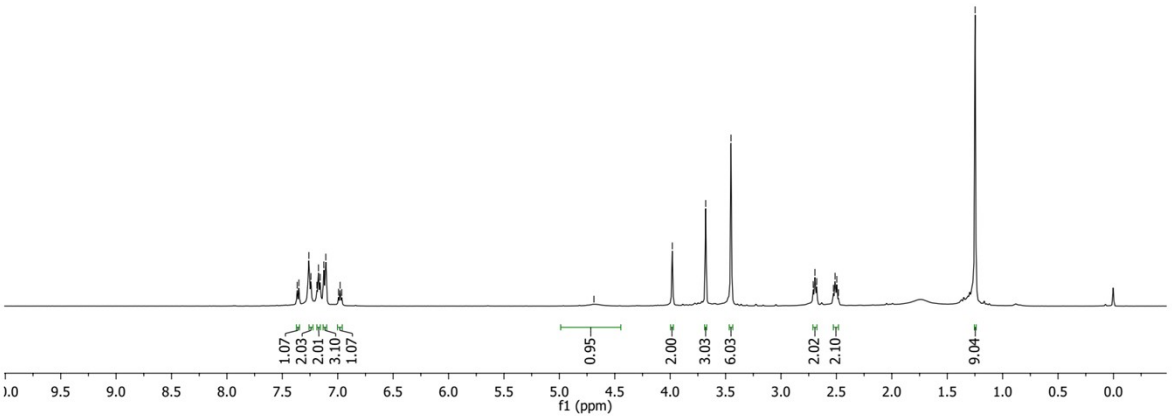



SS-420-ES-T-13C

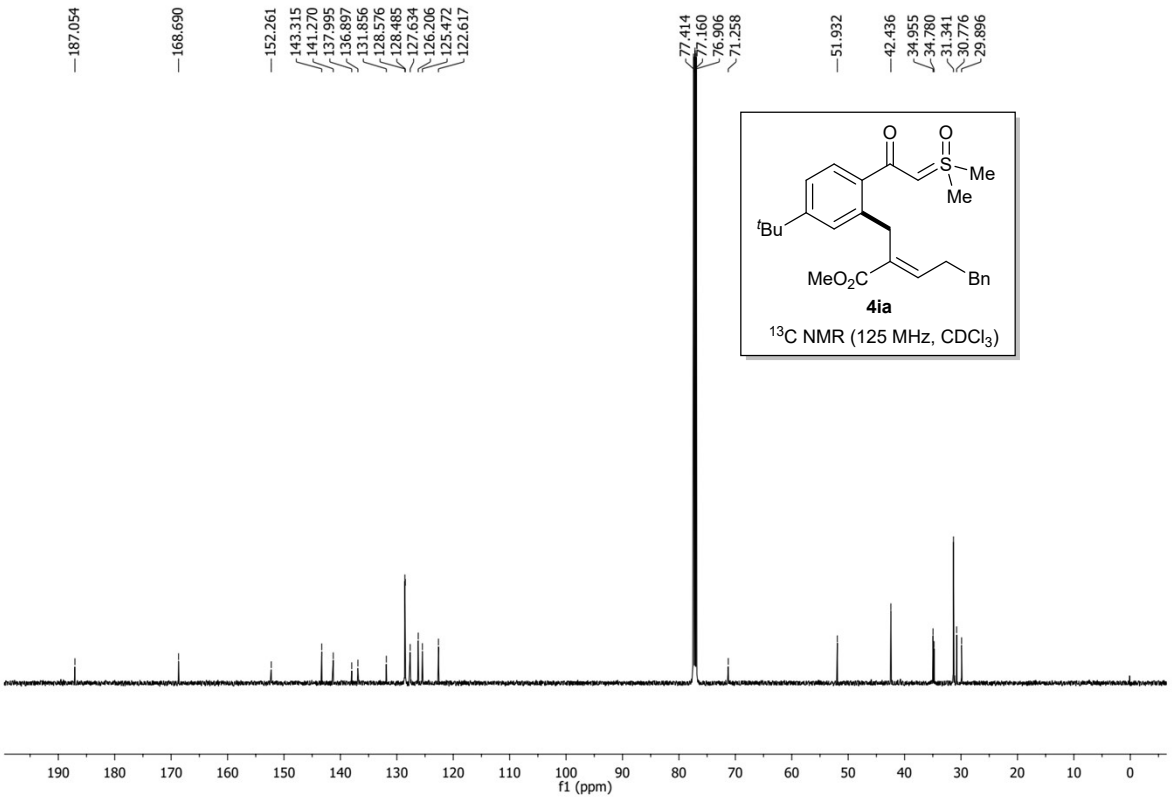


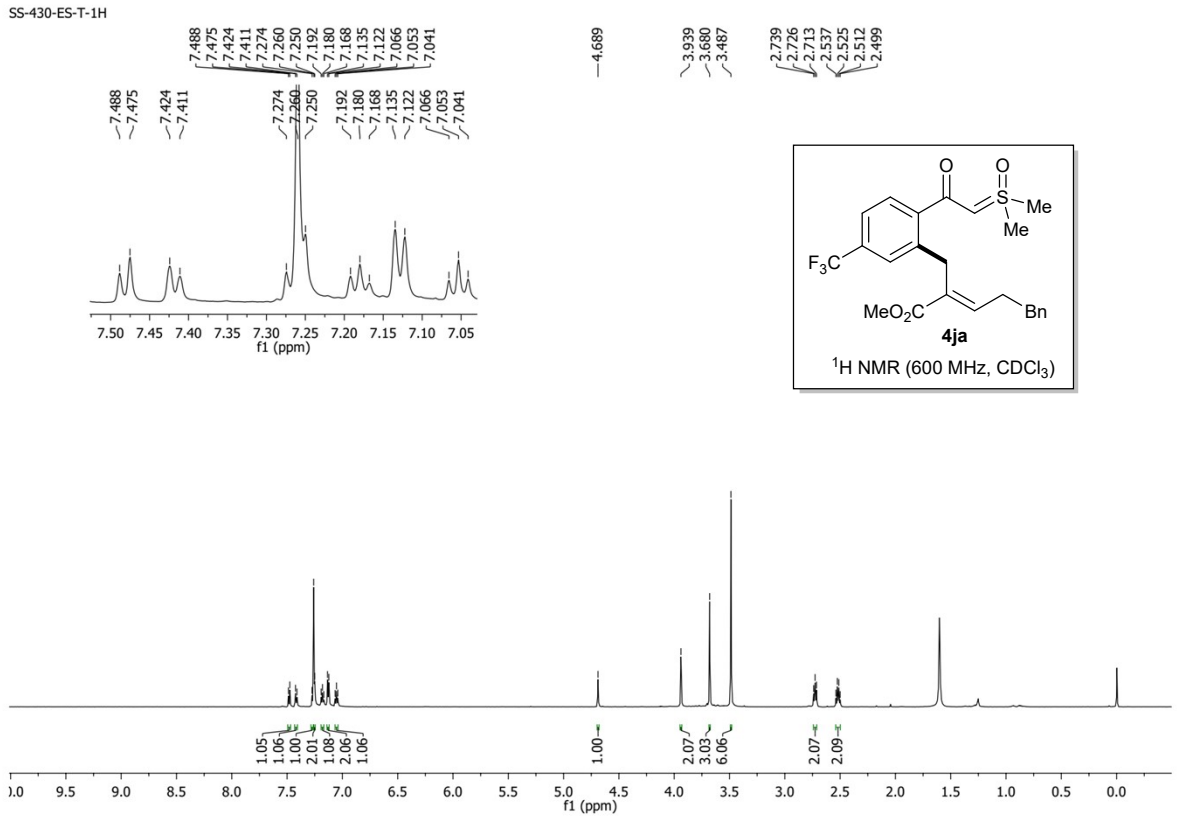
SS-427-ES-T-1H

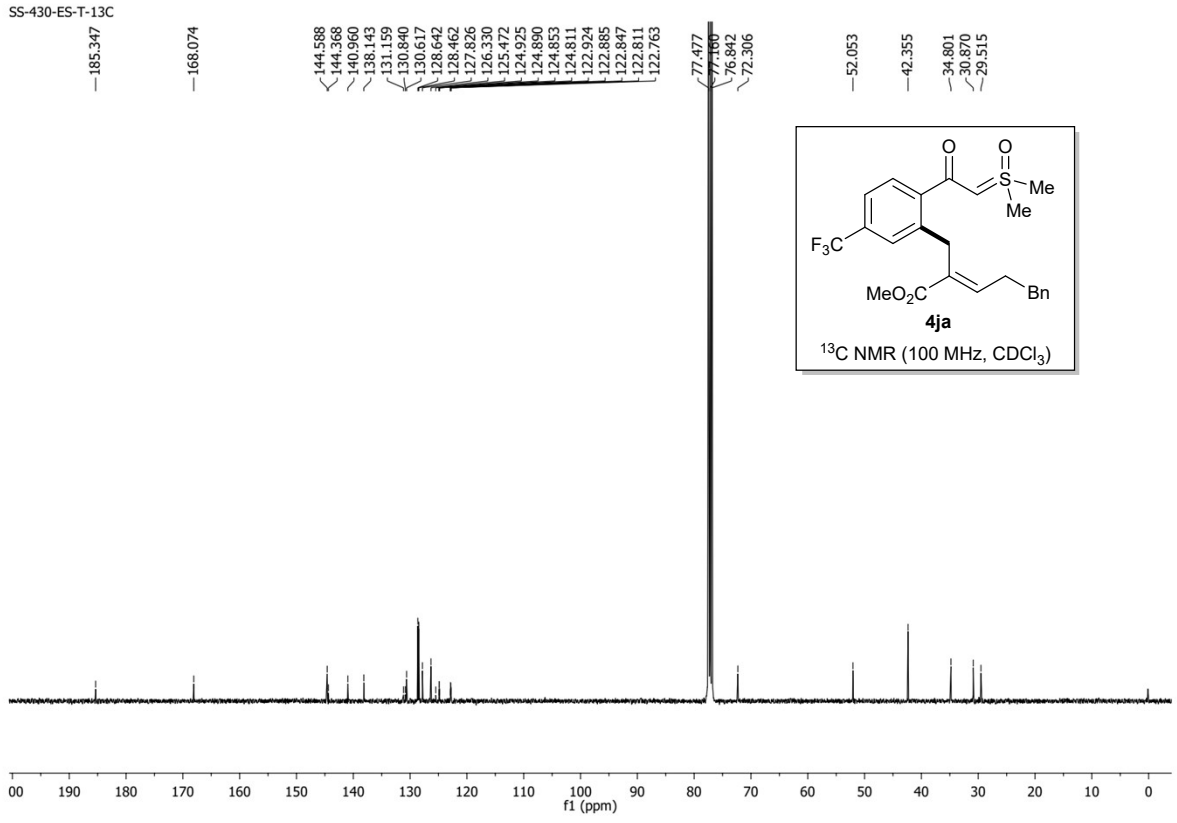


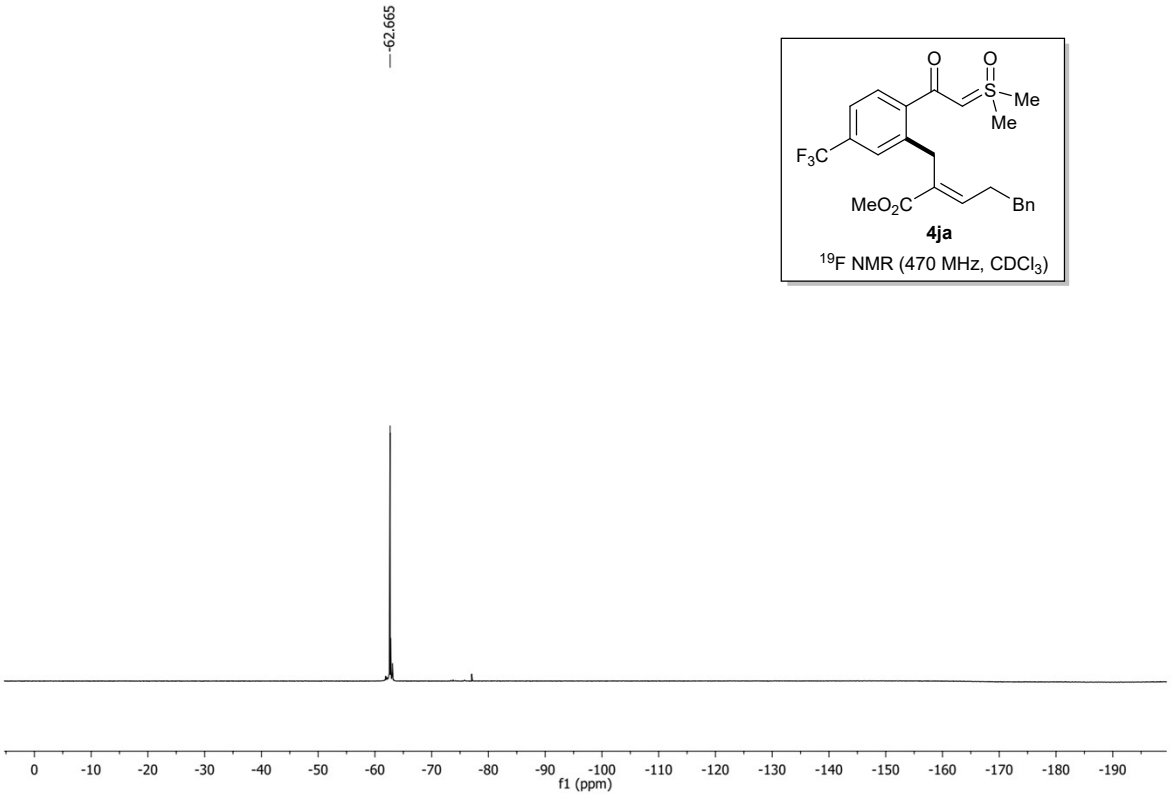

SS-427-ES-T-13C




SS-430-ES-T-1H
7.488
7.475
7.424
7.411
7.274
7.260
7.250
7.192
7.180
7.168
7.135
7.122
7.066
7.053
7.041
4.689
3.939
3.680
3.487
2.739
2.726
2.713
2.537
2.525
2.512
2.499
f1 (ppm)
1.05
1.06
1.00
2.01
1.08
2.06
1.06
1.00
2.07
3.03
6.06
2.07
2.09
f1 (ppm)
O
O
S
Me
Me
F3C
MeO2C
Bn
4ja
1H NMR (600 MHz, CDCl3)


SS-430-ES-T-13C
185.347
168.074
144.588
144.368
140.960
138.143
131.159
130.840
130.617
128.642
128.462
127.826
126.330
125.472
124.925
124.890
124.853
124.811
122.924
122.885
122.847
122.811
122.763
77.477
77.160
76.842
72.306
52.053
42.355
34.801
30.870
29.515
f1 (ppm)
O
O
S
Me
Me
F3C
MeO2C
Bn
4ja
13C NMR (100 MHz, CDCl3)

SS-430-ES-T-19F



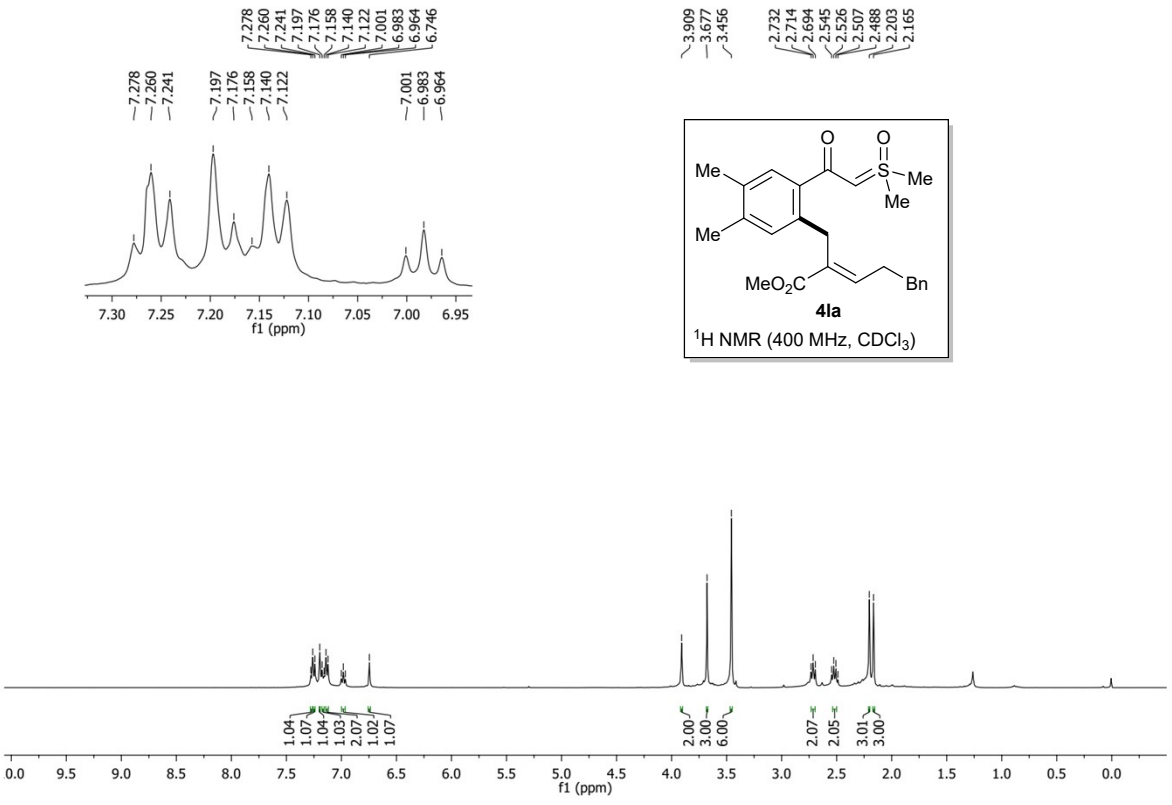




**4ja**

$^{19}$F NMR (470 MHz, $CDCl_3$)

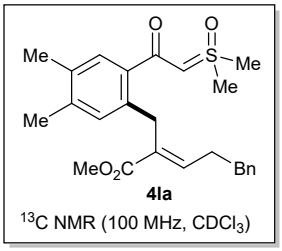
SS-419-ES-T-1H




**4la**

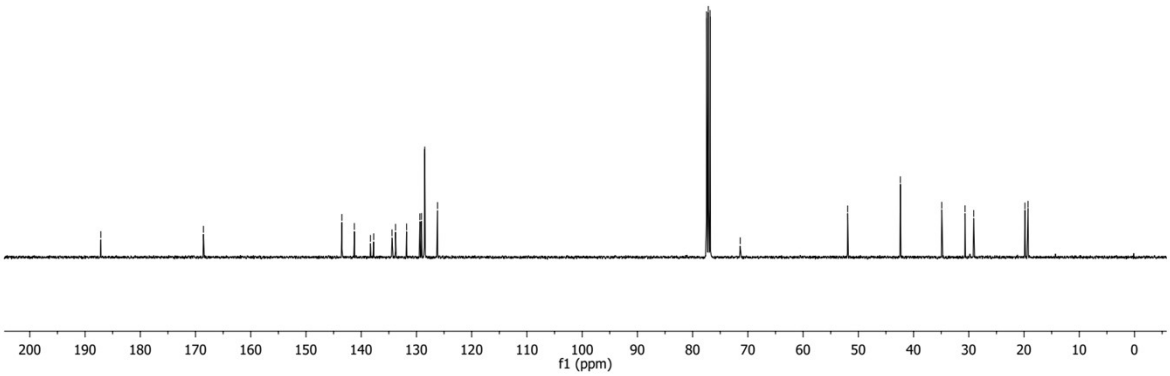
$^{1}$H NMR (400 MHz, $CDCl_3$)

SS-419-ES-T-13C

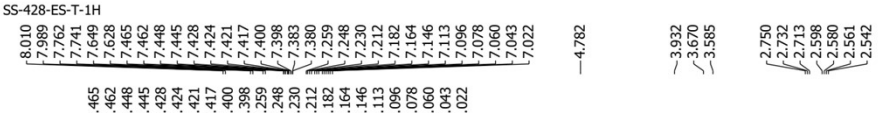



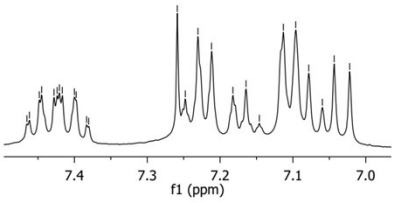

**4la**

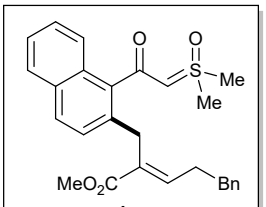
$^{13}$C NMR (100 MHz, $CDCl_3$)




SS-428-ES-T-1H

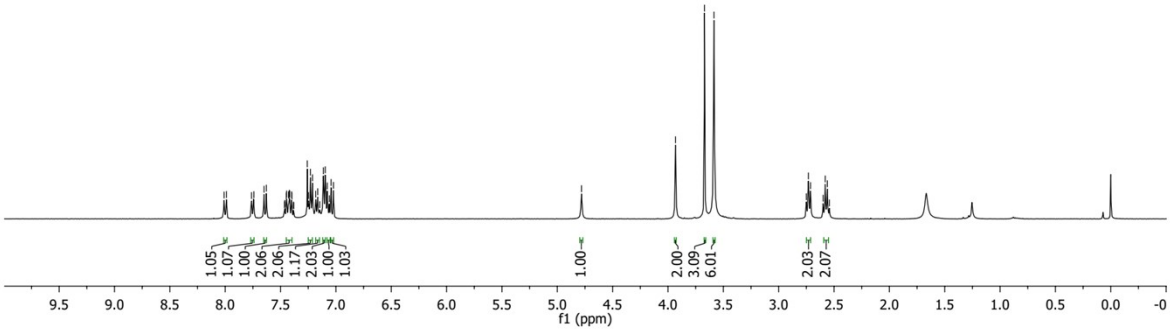


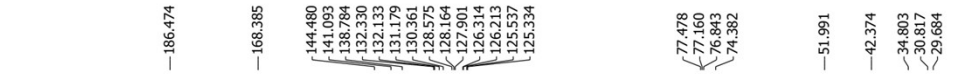



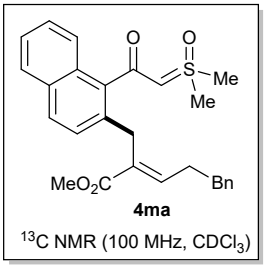

**4ma**

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



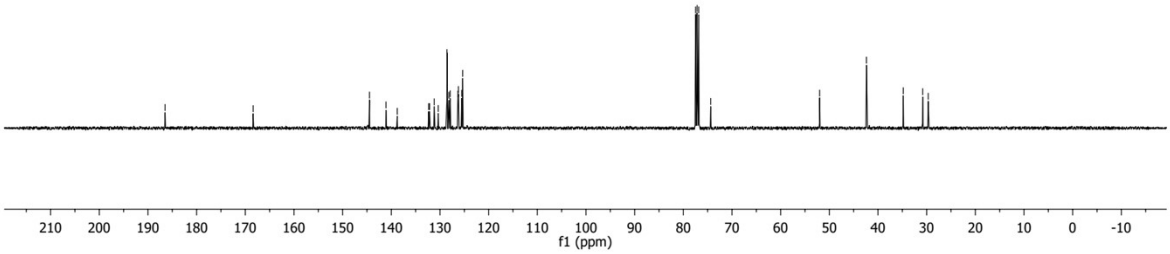
SS-428-ES-T-13C



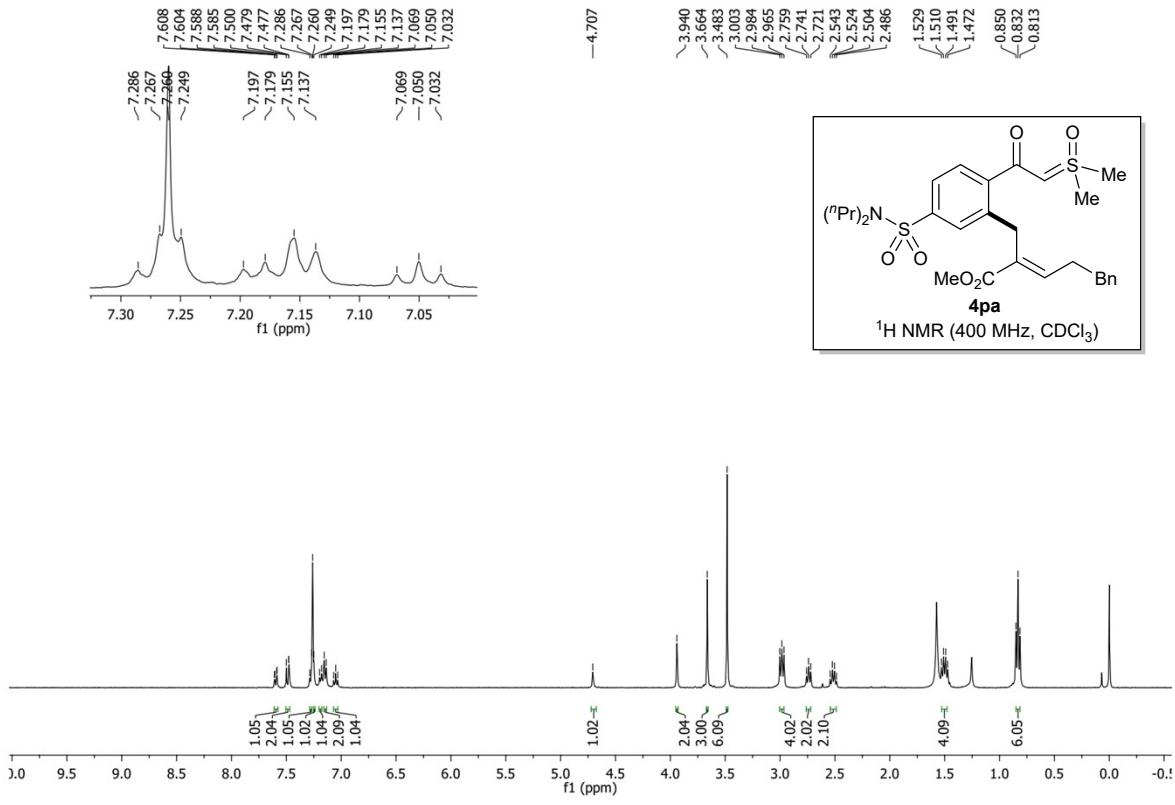




**4ma**

$^{13}$C NMR (100 MHz, $CDCl_3$)




SS-445-ES-T-1H

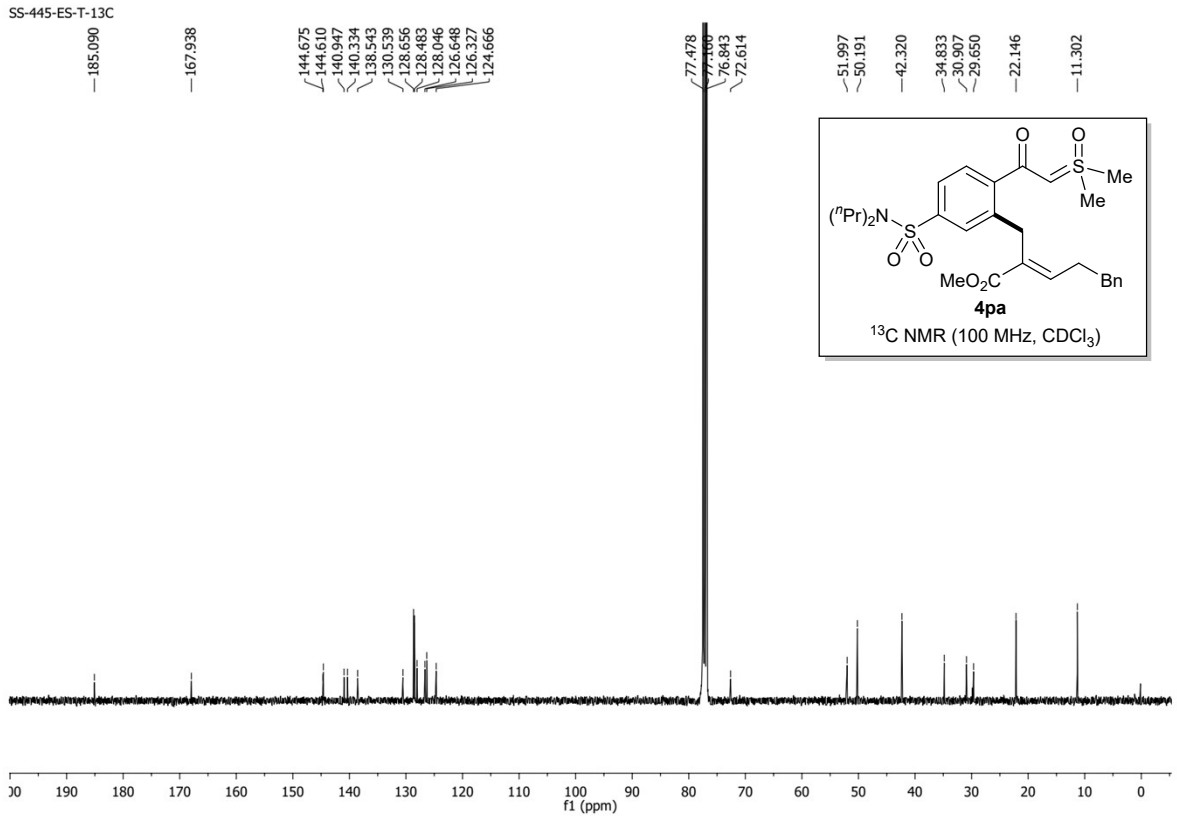


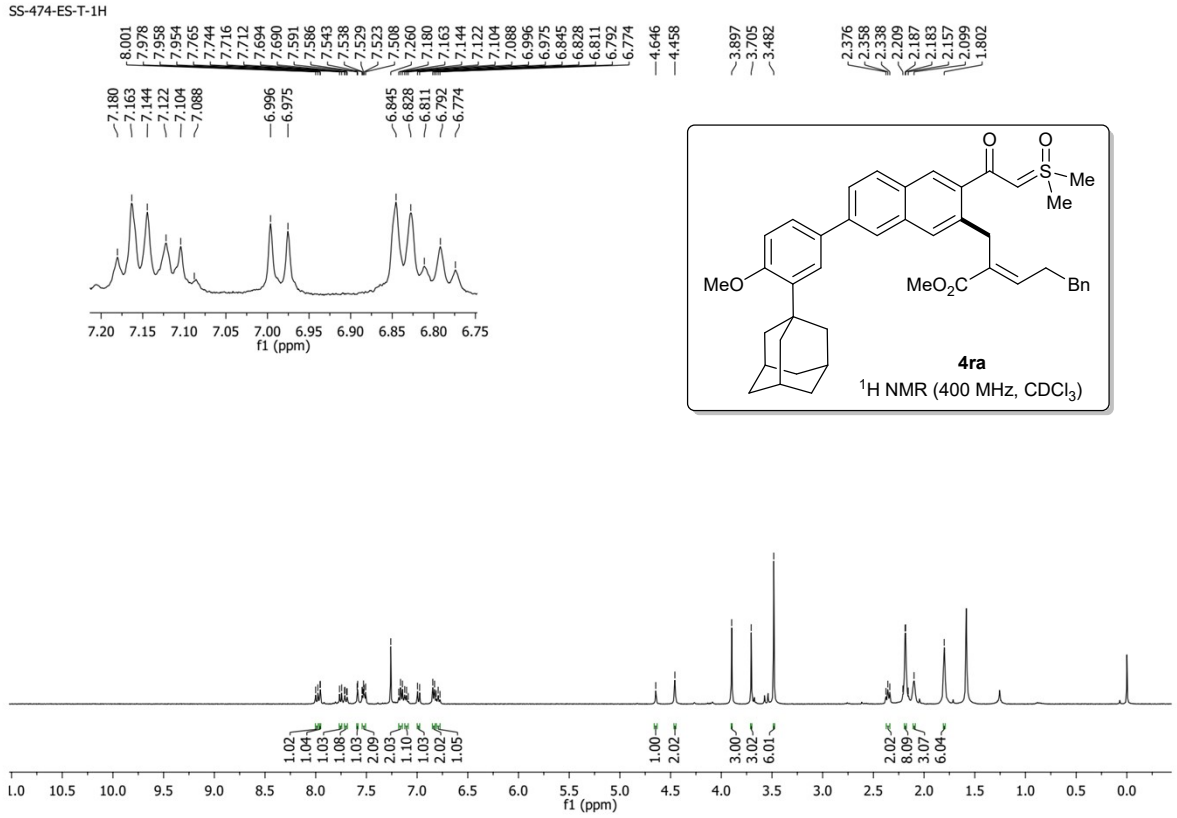




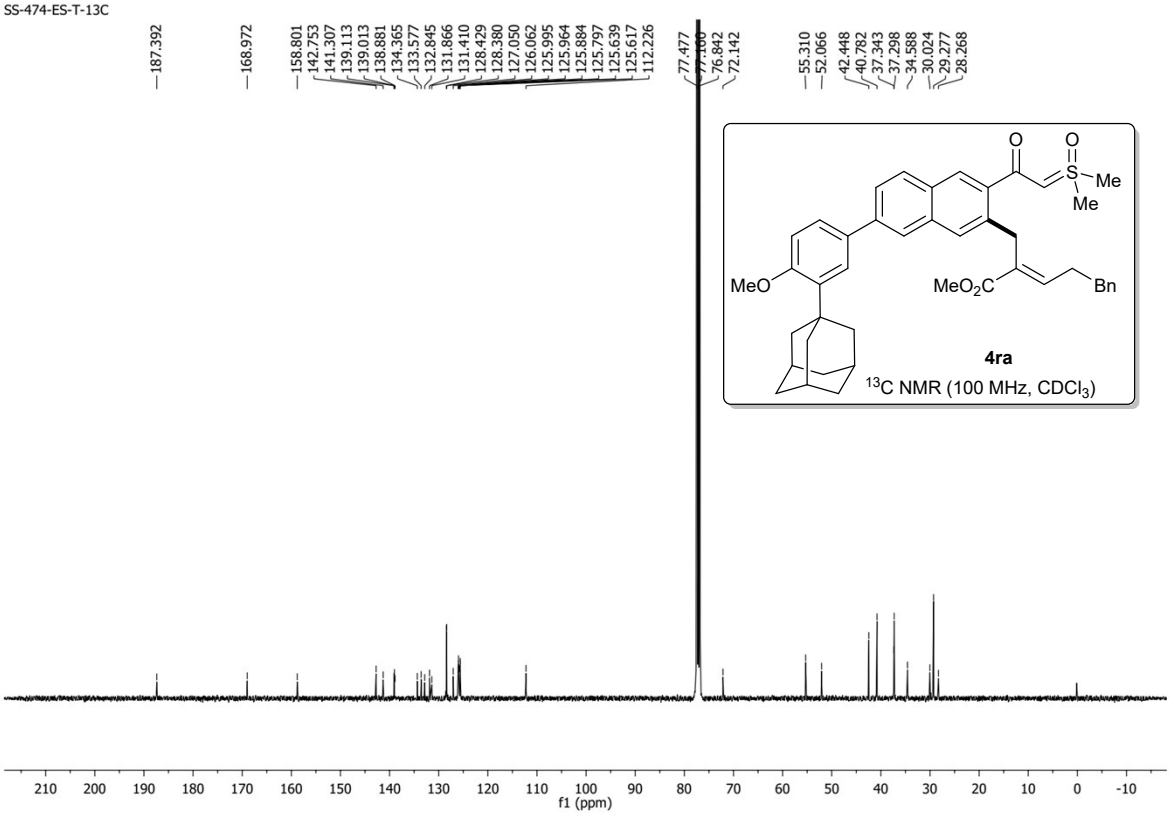
**4pa**

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


SS-445-ES-T-13C
185.090
167.938
144.675
144.610
140.947
140.334
138.543
130.539
128.656
128.483
128.046
126.648
126.327
124.666
77.478
77.160
76.843
72.614
51.997
50.191
42.320
34.833
30.907
29.650
22.146
11.302
f1 (ppm)
4pa
13C NMR (100 MHz, CDCl3)


SS-474-ES-T-1H
8.001
7.978
7.958
7.954
7.765
7.744
7.716
7.712
7.694
7.690
7.591
7.586
7.543
7.538
7.529
7.523
7.508
7.260
7.180
7.163
7.144
7.122
7.104
7.088
6.996
6.975
6.845
6.828
6.811
6.792
6.774
4.646
4.458
3.897
3.705
3.482
2.376
2.358
2.338
2.209
2.187
2.183
2.157
2.099
1.802
f1 (ppm)
4ra
1H NMR (400 MHz, CDCl3)

SS-474-ES-T-13C



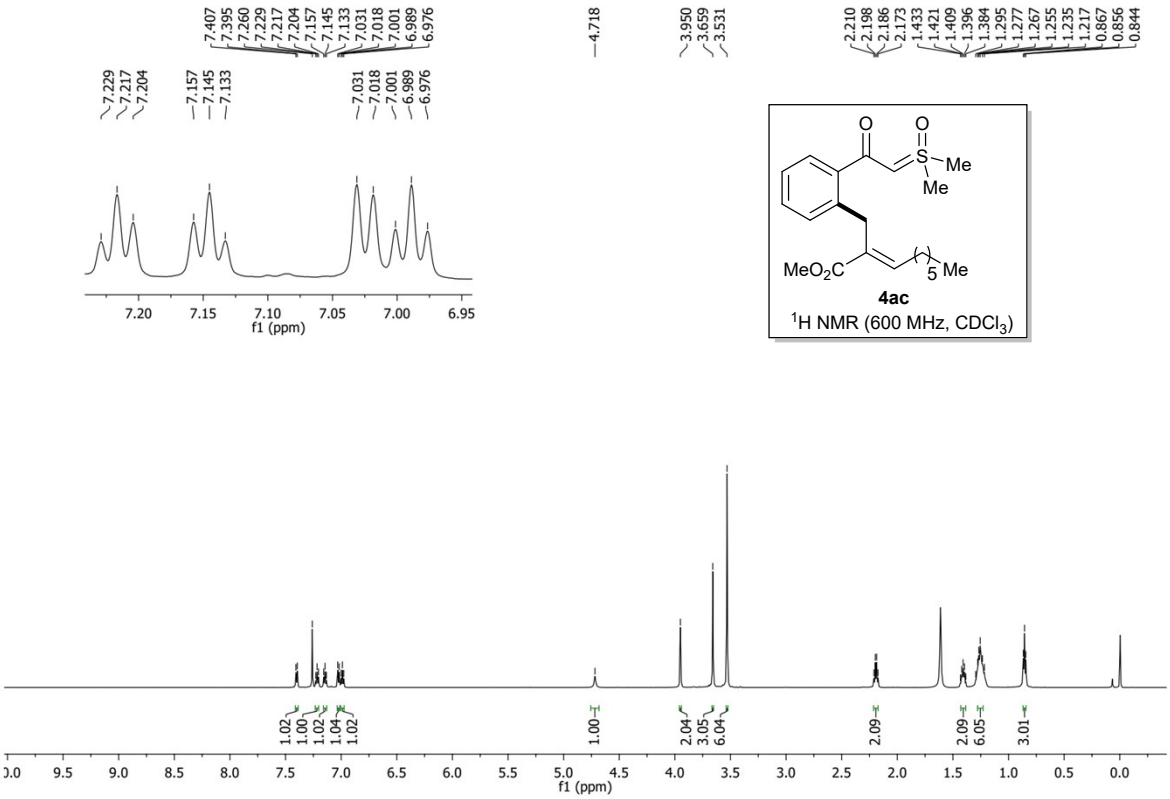




**4ra**

$^{13}$C NMR (100 MHz, $CDCl_3$)

SS-426-ES-T-1H

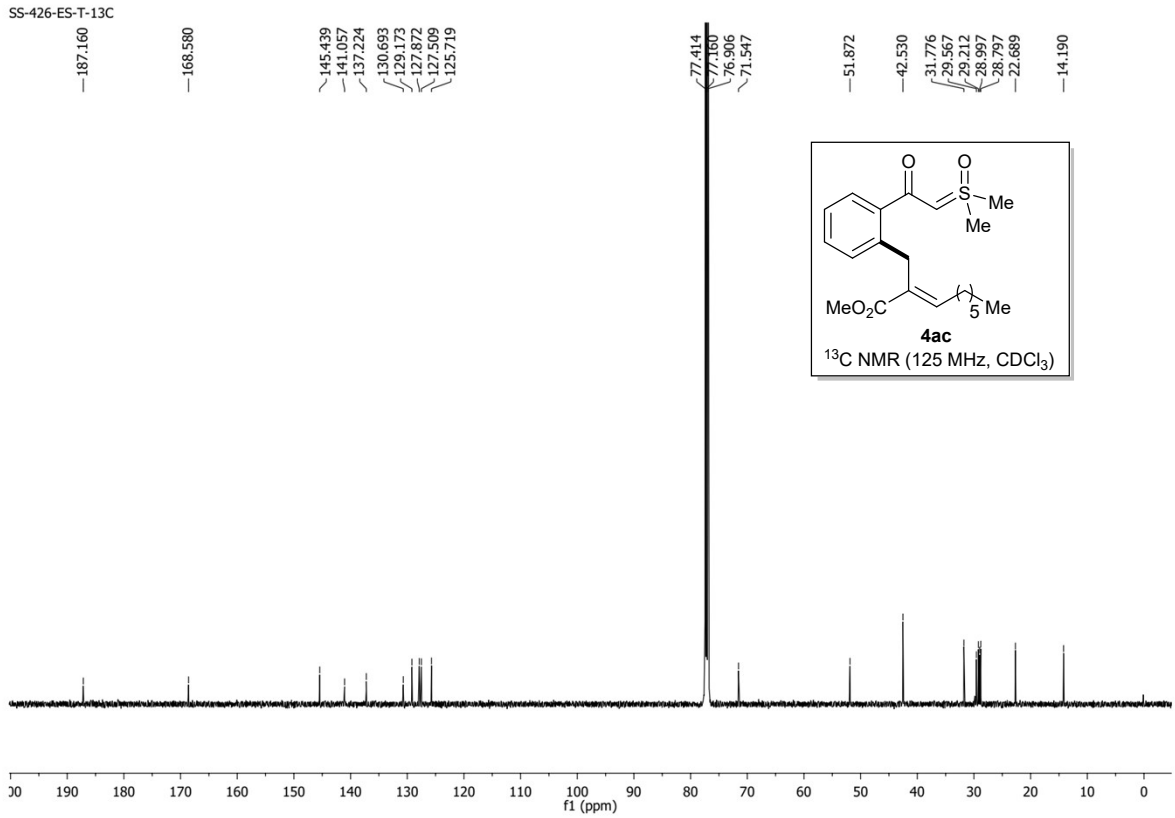


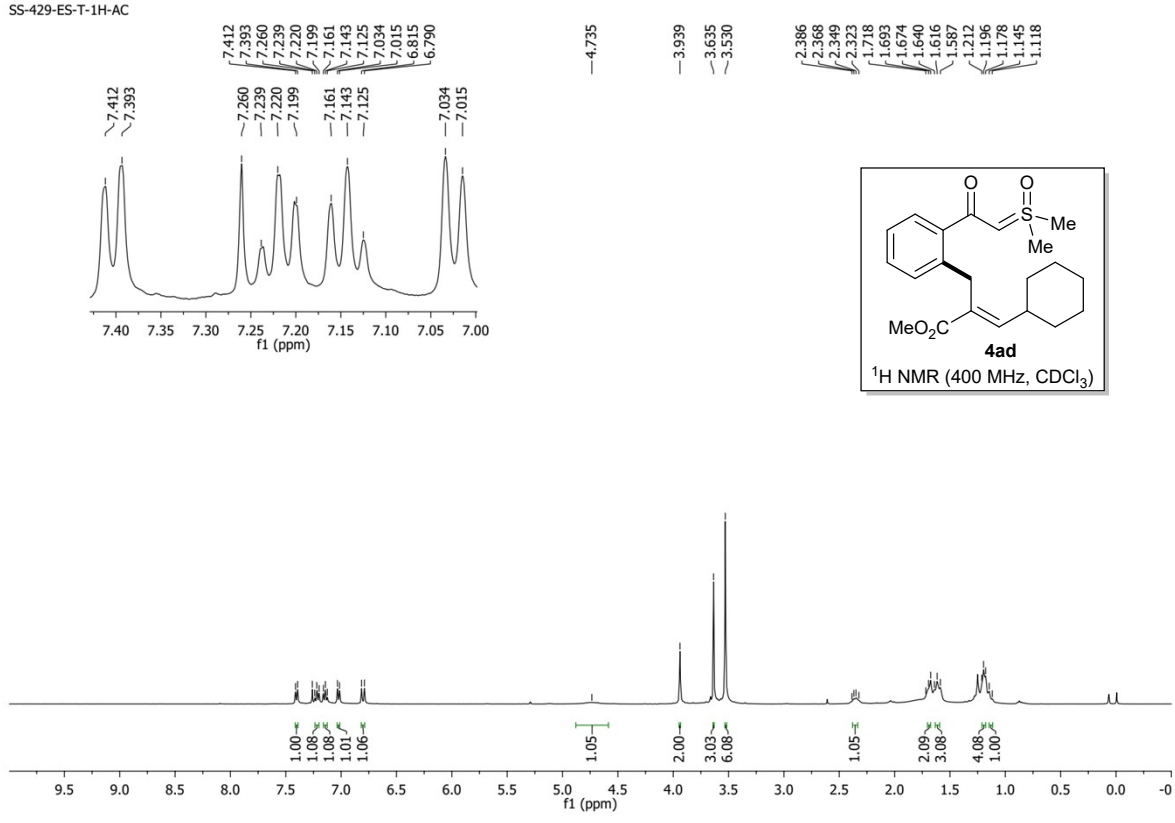




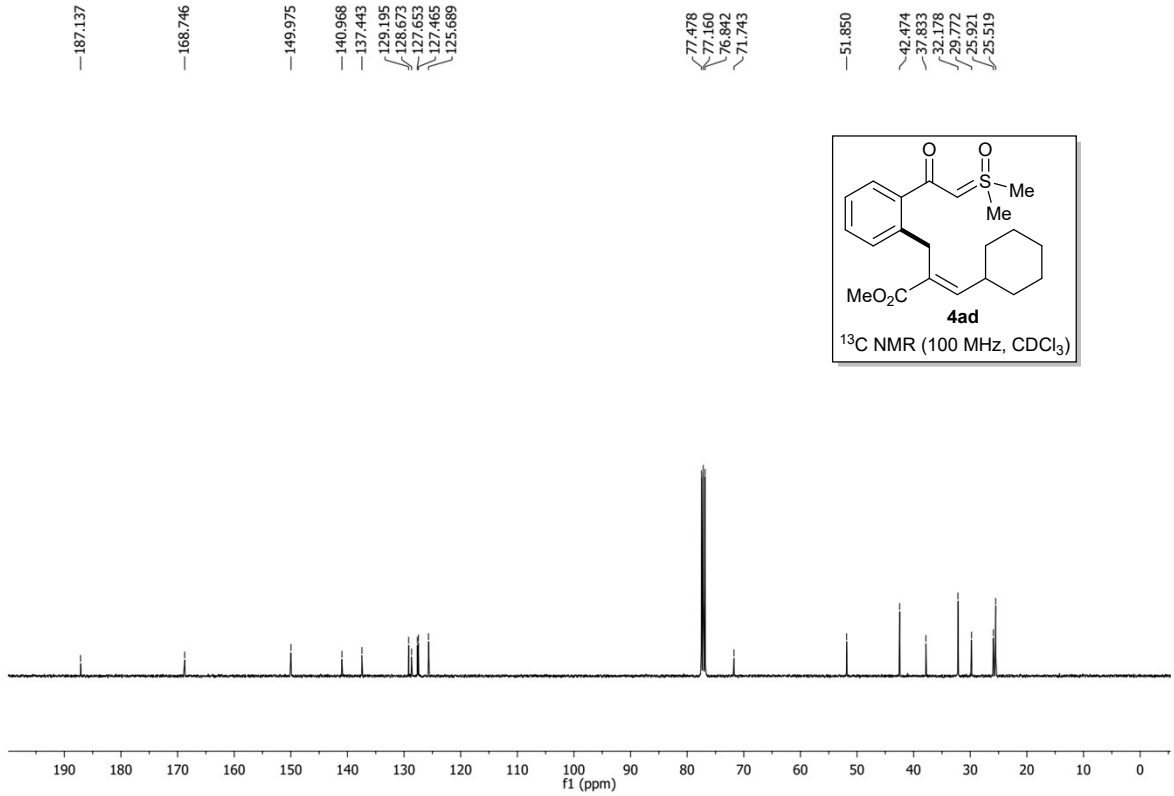
**4ac**

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

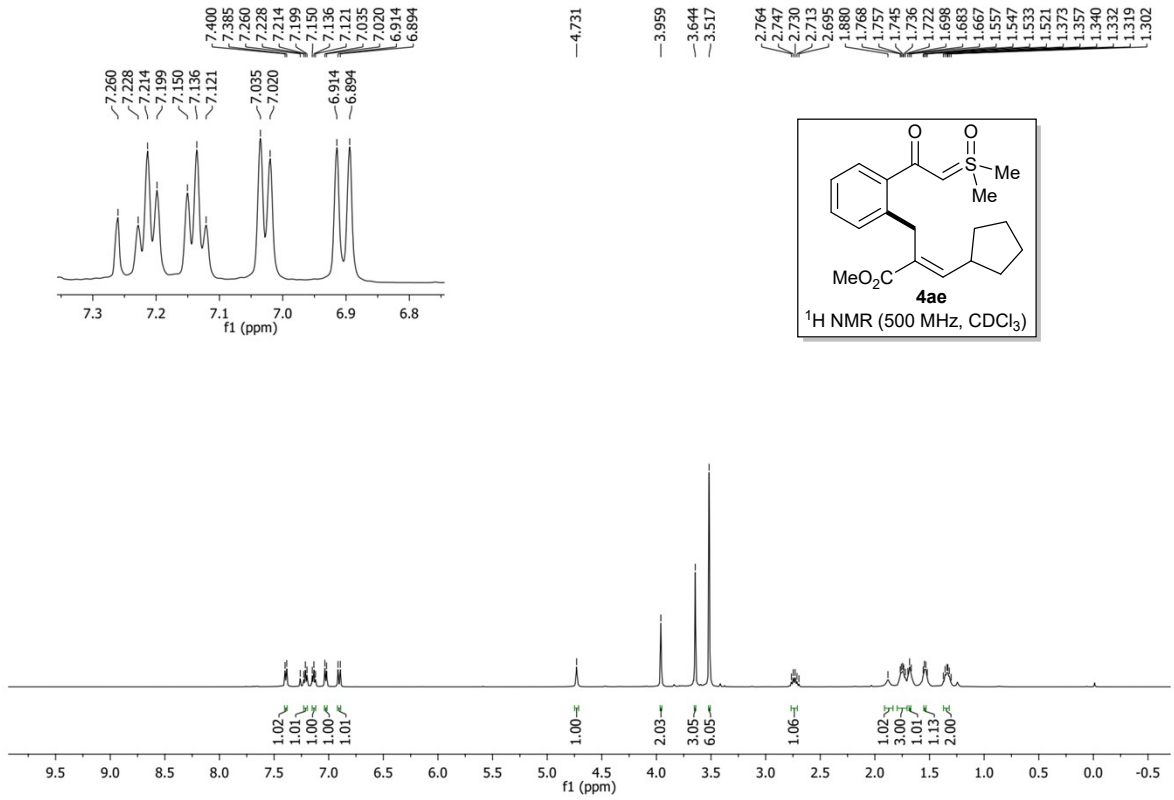

SS-426-ES-T-13C
187.160
168.580
145.439
141.057
137.224
130.693
129.173
127.872
127.509
125.719
77.414
77.160
76.906
71.547
51.872
42.530
31.776
29.567
29.212
28.997
28.797
22.689
14.190
O
O
S
Me
Me
MeO2C
5
Me
4ac
13C NMR (125 MHz, CDCl3)
f1 (ppm)


SS-429-ES-T-1H-AC
7.412
7.393
7.260
7.239
7.220
7.199
7.161
7.143
7.125
7.034
7.015
6.815
6.790
4.735
3.939
3.635
3.530
2.386
2.368
2.349
2.323
1.718
1.693
1.674
1.640
1.616
1.587
1.212
1.196
1.178
1.145
1.118
O
O
S
Me
Me
MeO2C
4ad
1H NMR (400 MHz, CDCl3)
1.00
1.08
1.08
1.01
1.06
1.05
2.00
3.03
6.08
1.05
2.09
3.08
4.08
1.00
f1 (ppm)

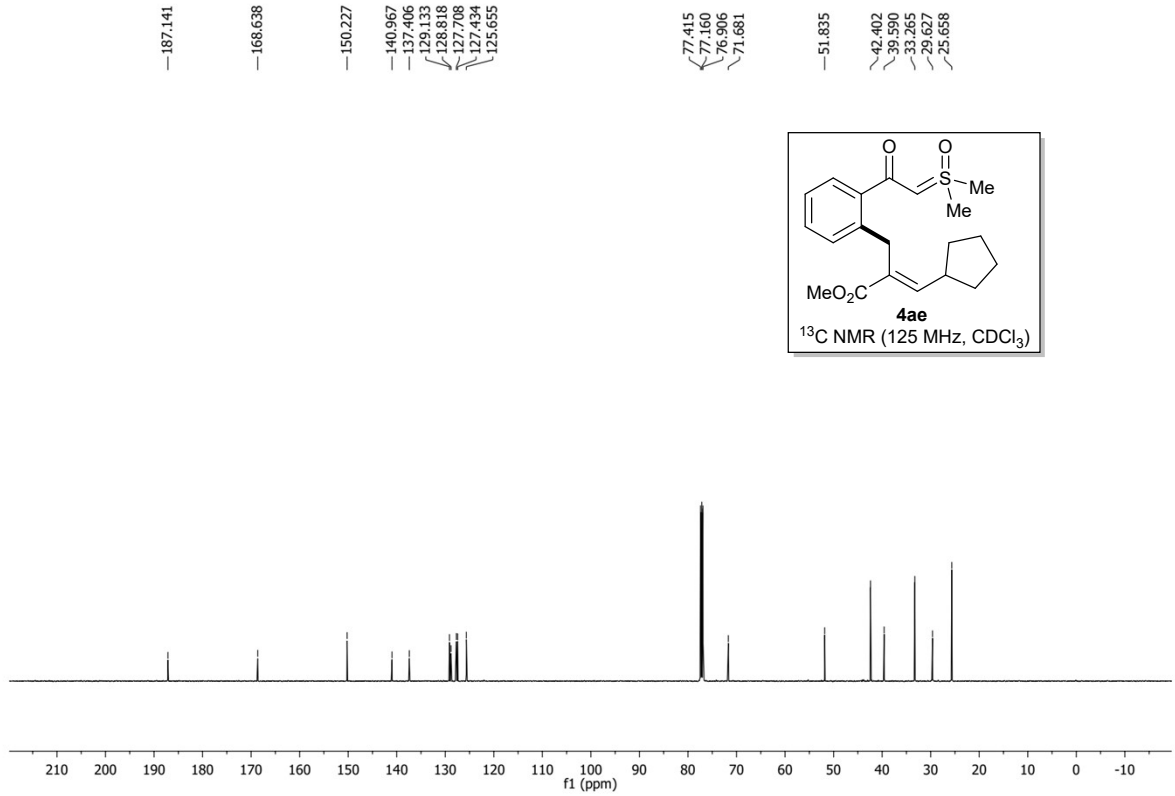
SS-429-ES-T-13C




SS-450-ES-T-1H



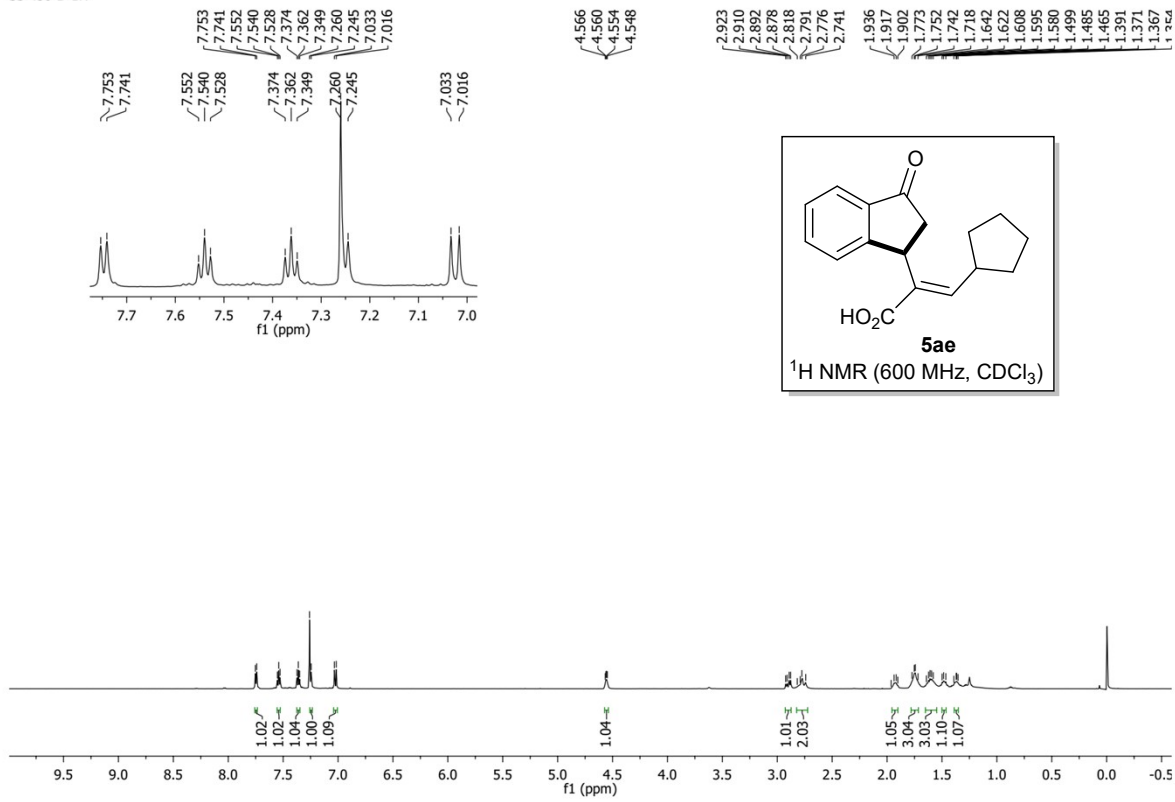
SS-450-ES-T-13C




**4ae**

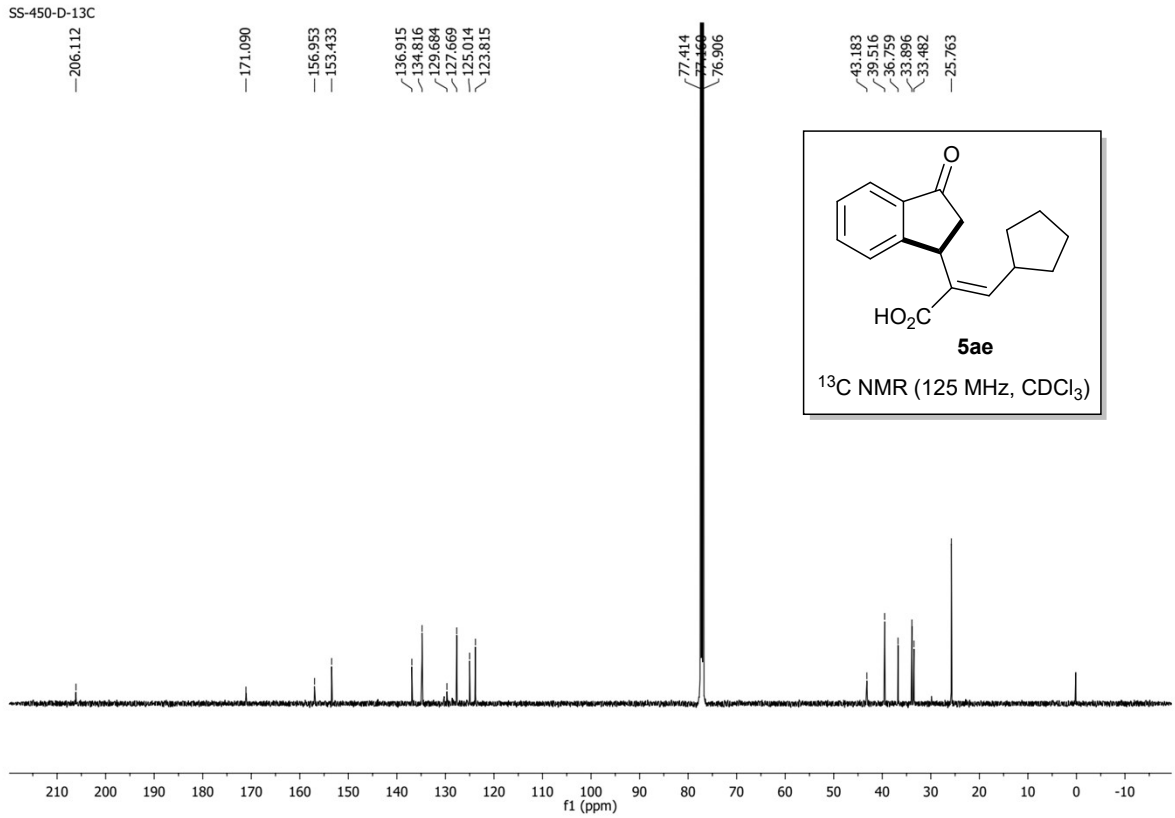
$^{13}$C NMR (125 MHz, $CDCl_3$)

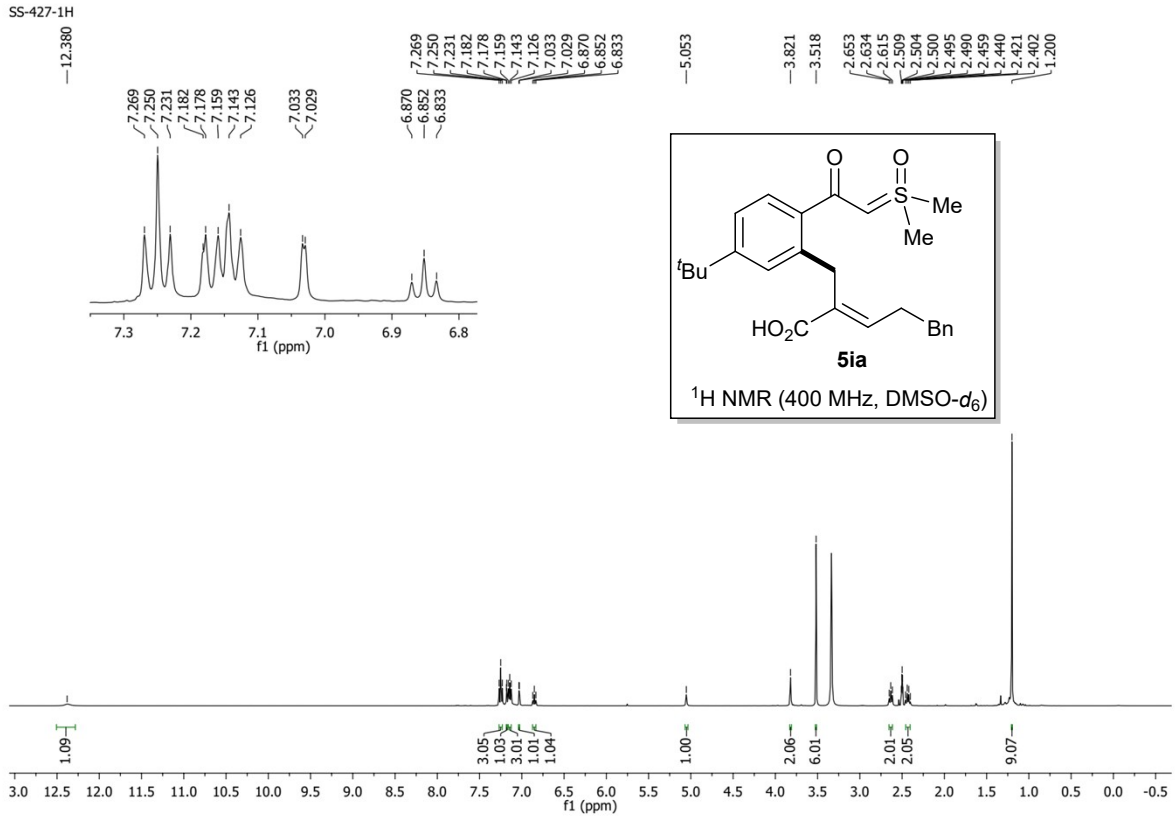
SS-450-D-1H

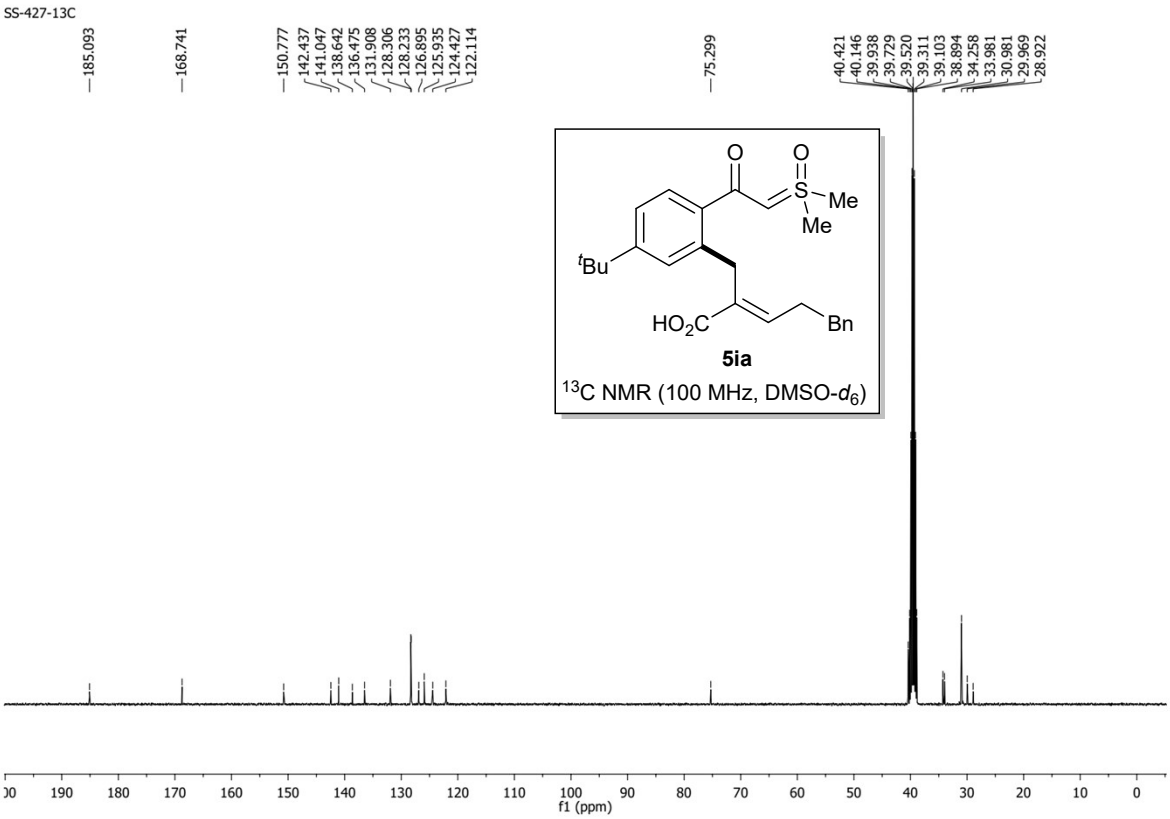



**5ae**

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


SS-450-D-13C
206.112
171.090
156.953
153.433
136.915
134.816
129.684
127.669
125.014
123.815
77.414
77.160
76.906
43.183
39.516
36.759
33.896
33.482
25.763
O
HO2C
5ae
13C NMR (125 MHz, CDCl3)
f1 (ppm)


SS-427-1H
12.380
7.269
7.250
7.231
7.182
7.178
7.159
7.143
7.126
7.033
7.029
6.870
6.852
6.833
5.053
3.821
3.518
2.653
2.634
2.615
2.509
2.504
2.500
2.495
2.490
2.459
2.440
2.421
2.402
1.200
O
O
S
Me
Me
tBu
HO2C
Bn
5ia
1H NMR (400 MHz, DMSO-d6)
1.09
3.05
1.03
3.01
1.01
1.04
1.00
2.06
6.01
2.01
2.05
9.07
f1 (ppm)

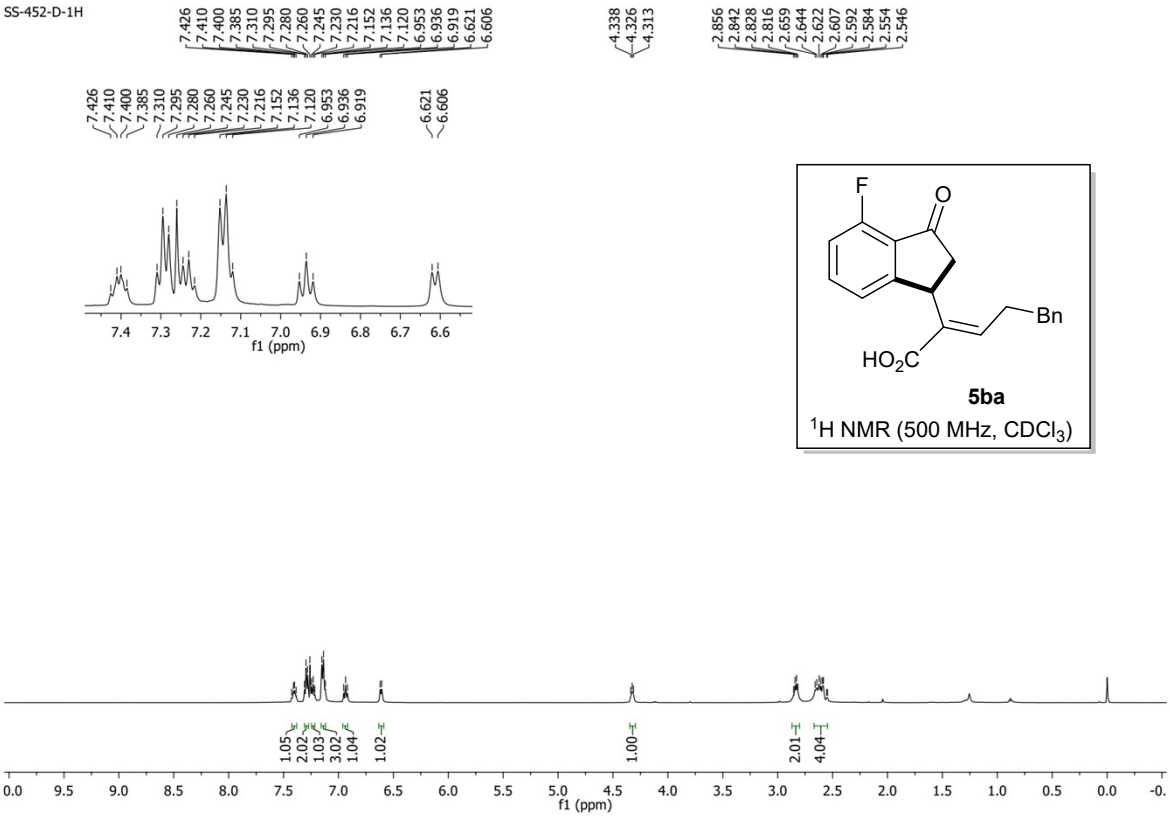






**5ia**

$^{13}$C NMR (100 MHz, DMSO-$d_6$)

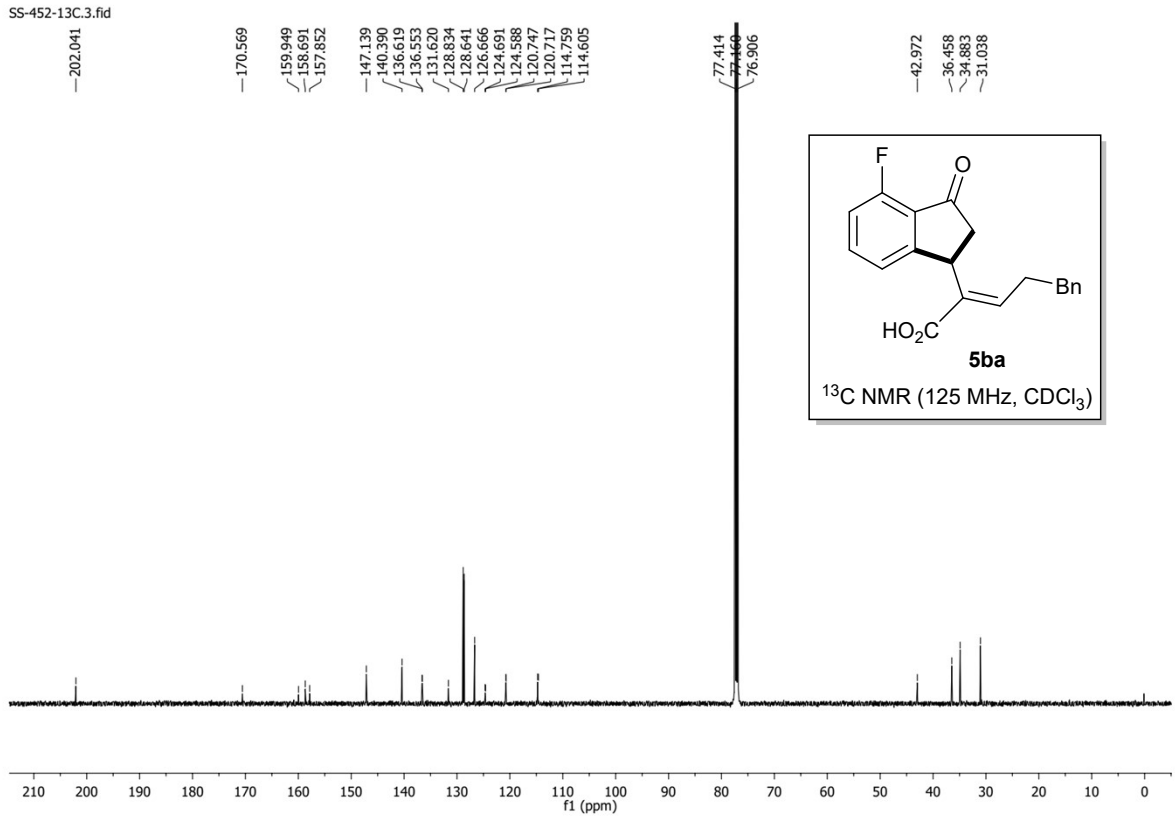


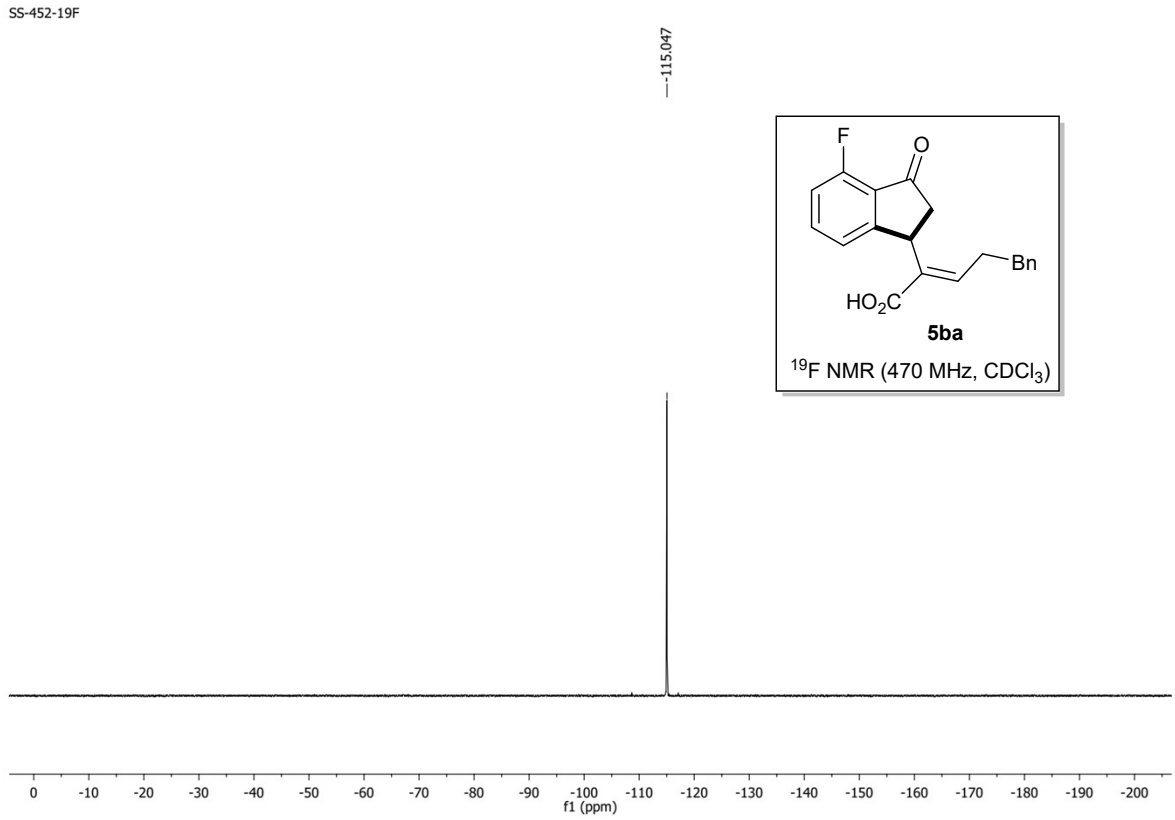


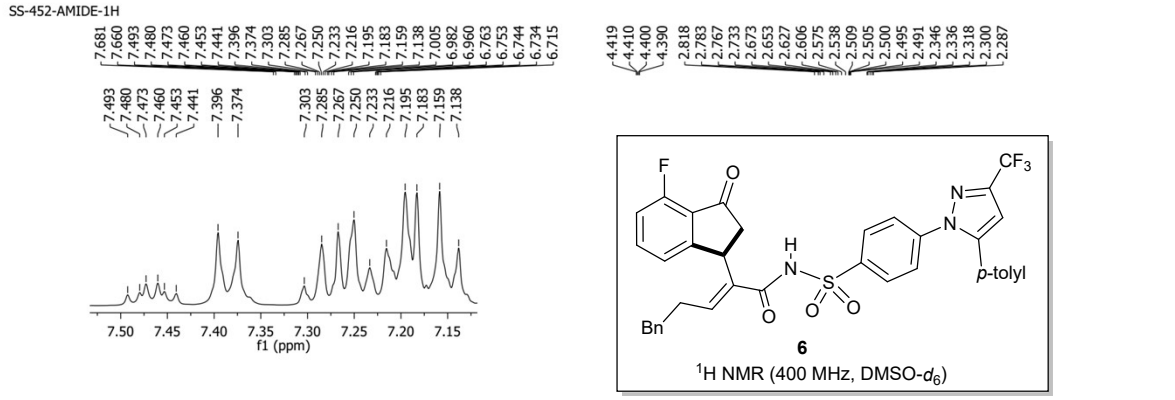


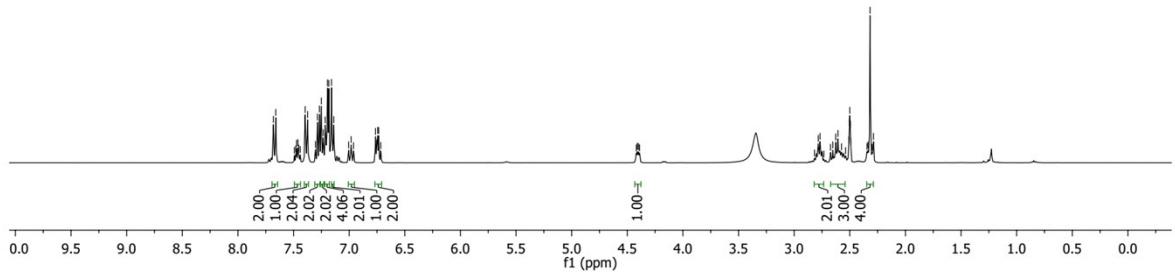
**5ba**

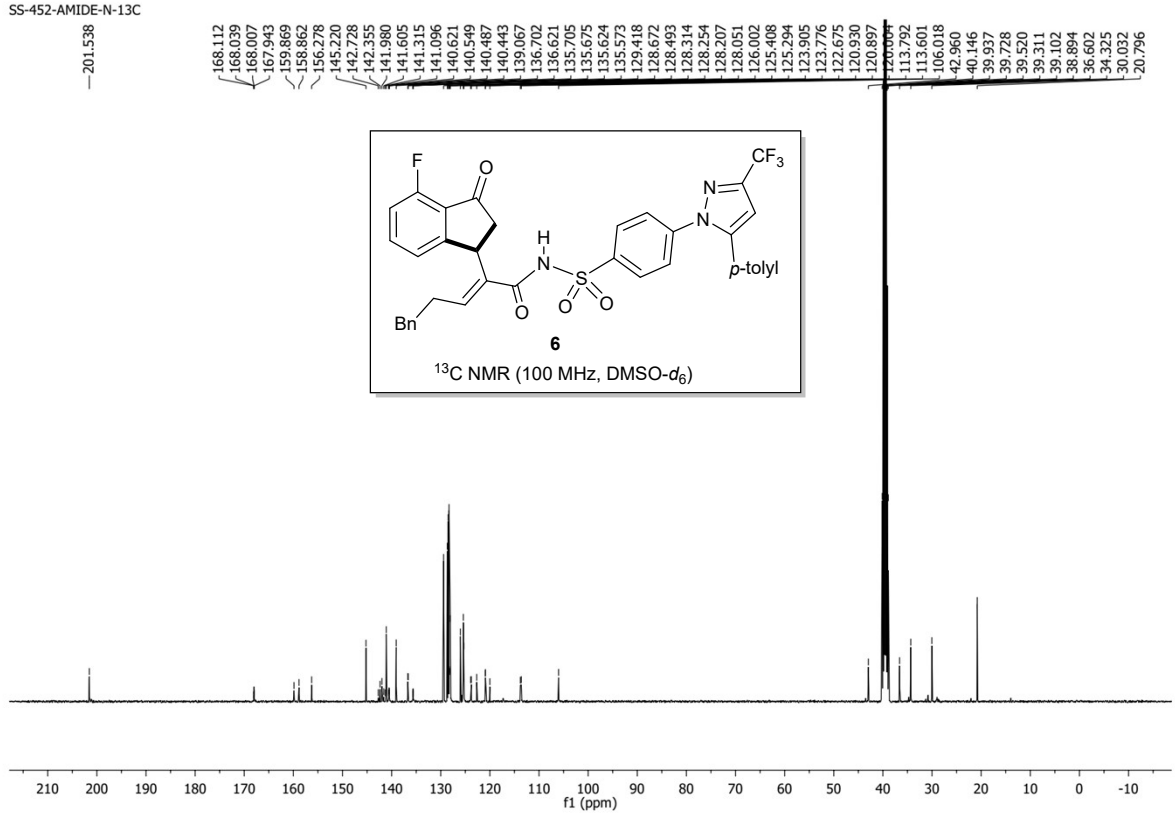
$^{1}$H NMR (500 MHz, $CDCl_3$)


SS-452-13C.3.fid
202.041
170.569
159.949
158.691
157.852
147.139
140.390
136.619
136.553
131.620
128.834
128.641
126.666
124.691
124.588
120.747
120.717
114.759
114.605
77.414
77.160
76.906
42.972
36.458
34.883
31.038
F
O
Bn
HO2C
5ba
13C NMR (125 MHz, CDCl3)
f1 (ppm)

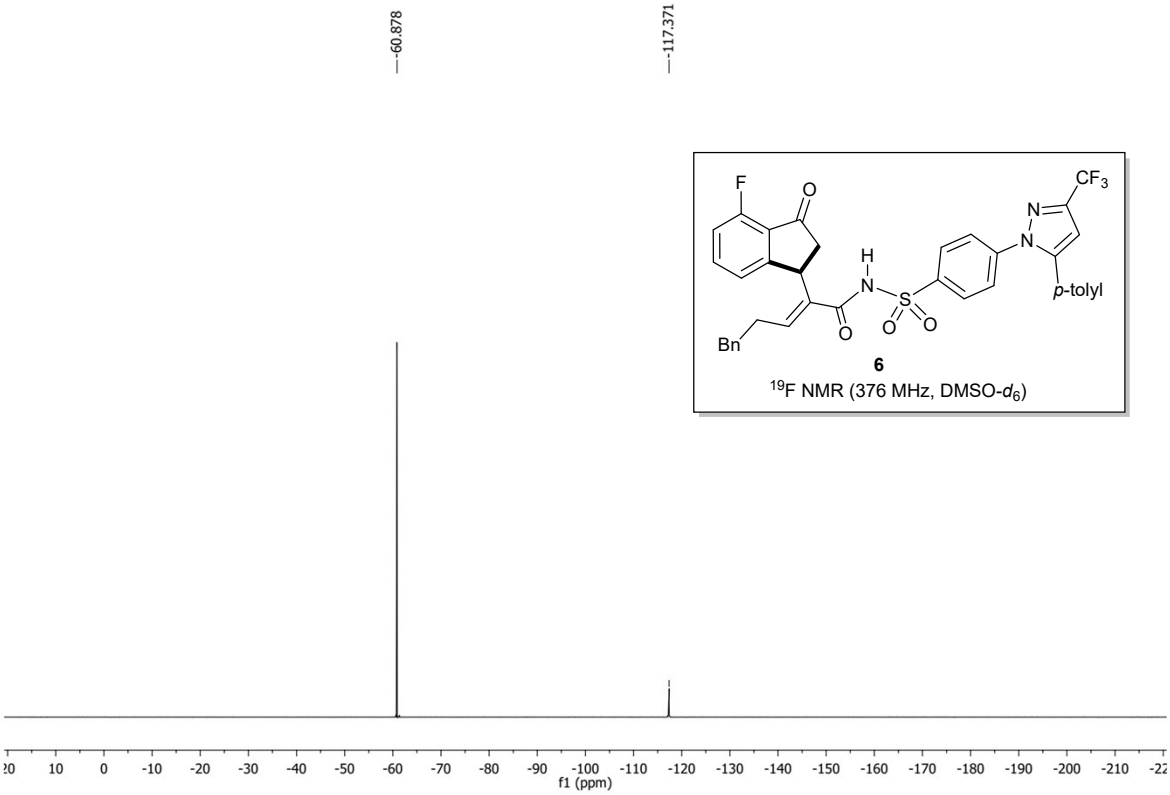

SS-452-19F
-115.047
F
O
Bn
HO2C
5ba
19F NMR (470 MHz, CDCl3)
f1 (ppm)


SS-452-AMIDE-1H
7.681 7.660 7.493 7.480 7.473 7.460 7.453 7.441 7.396 7.374 7.303 7.285 7.267 7.250 7.233 7.216 7.195 7.183 7.159 7.138 7.005 6.982 6.960 6.763 6.753 6.744 6.734 6.715
4.419 4.410 4.400 4.390 2.818 2.783 2.767 2.733 2.673 2.653 2.627 2.606 2.575 2.538 2.509 2.505 2.500 2.495 2.491 2.346 2.336 2.318 2.300 2.287
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
F
O
CF3
N
N
H
N
S
O
O
O
p-tolyl
Bn
6
1H NMR (400 MHz, DMSO-d6)


2.00 1.00 2.04 2.02 2.02 4.06 2.01 1.00 2.00
1.00
2.01 3.00 4.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


SS-452-AMIDE-N-13C
201.538
168.112 168.039 168.007 167.943 159.869 158.862 156.278 145.220 142.728 142.355 141.980 141.605 141.315 141.096 140.621 140.549 140.487 140.443 139.067 136.702 136.621 135.705 135.675 135.624 135.573 129.418 128.672 128.493 128.314 128.254 128.207 128.051 126.002 125.408 125.294 123.905 123.776 122.675 120.930 120.897 113.792 113.601 106.018 42.960 40.146 39.937 39.728 39.520 39.311 39.102 38.894 36.602 34.325 30.032 20.796
F
O
CF3
N
N
H
N
S
O
O
O
p-tolyl
Bn
6
13C NMR (100 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

SS-452-AMIDE-N-19F



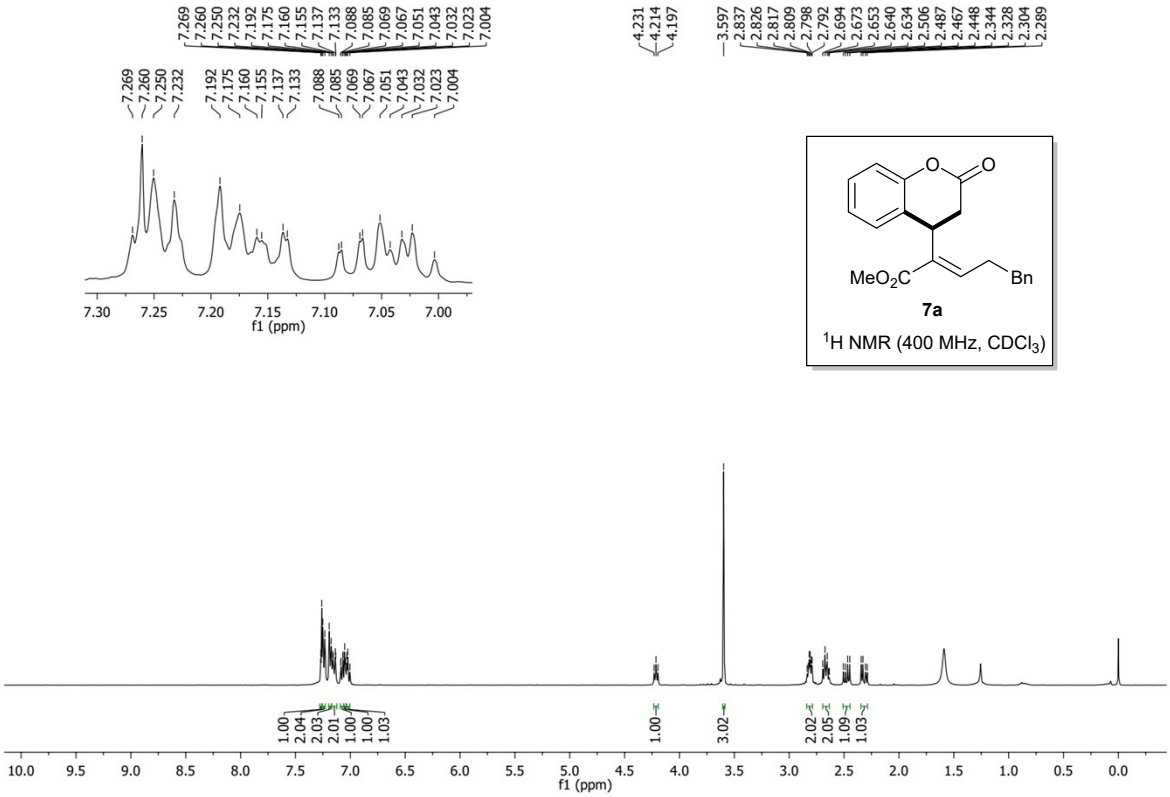




**6**

$^{19}$F NMR (376 MHz, DMSO-$d_6$)

SS-473-BV-1H



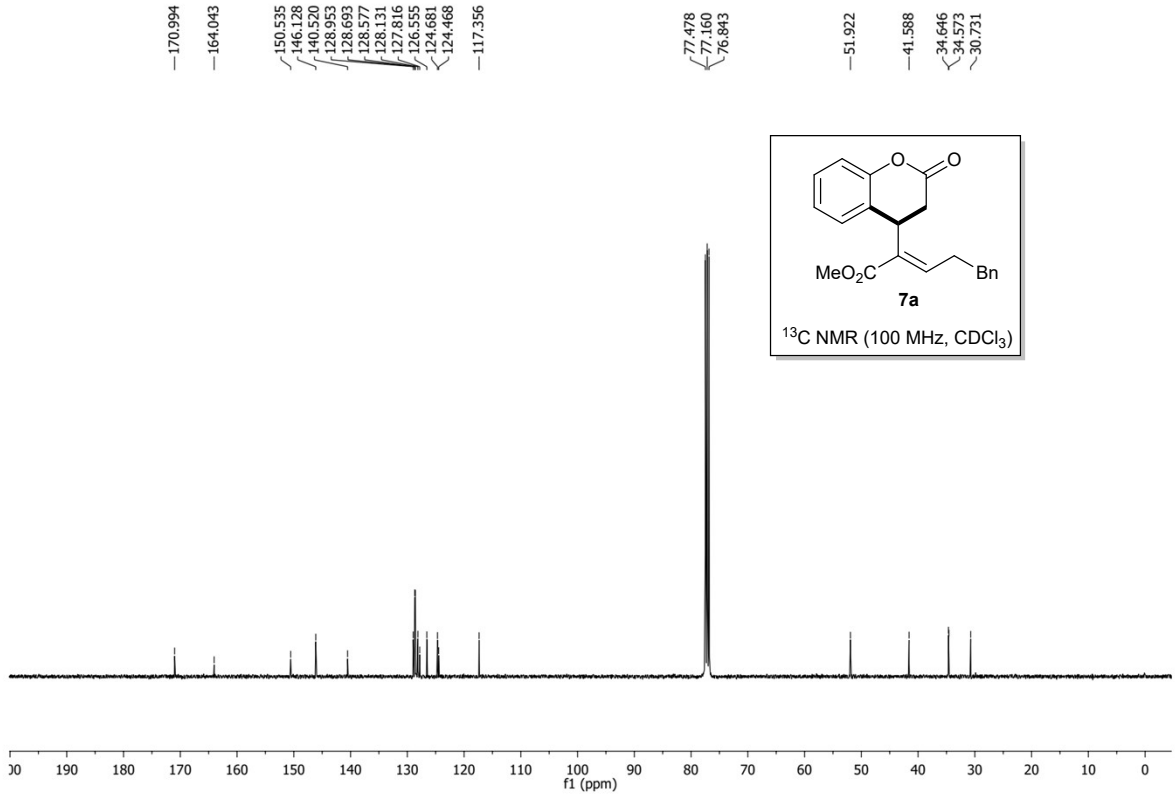




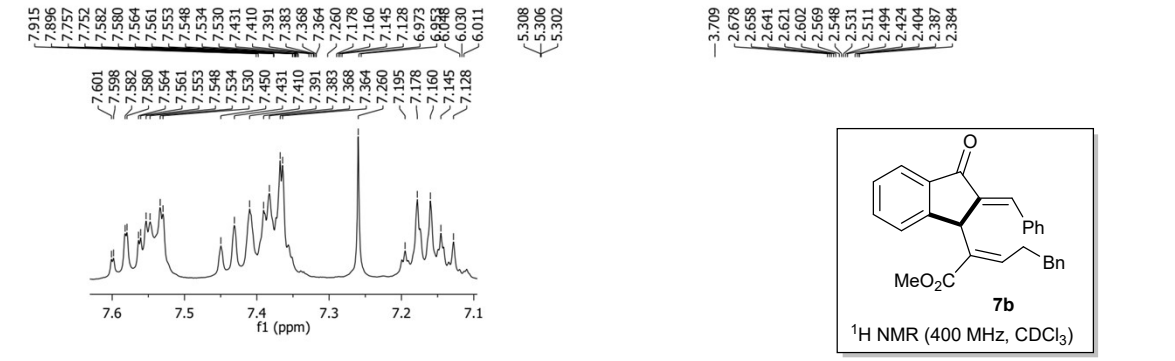
**7a**

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

SS-473-BV-13C


170.994
164.043
150.535
146.128
140.520
128.953
128.693
128.577
128.131
127.816
126.555
124.681
124.468
117.356
77.478
77.160
76.843
51.922
41.588
34.646
34.573
30.731
O
O
MeO2C
Bn
7a
13C NMR (100 MHz, CDCl3)
f1 (ppm)

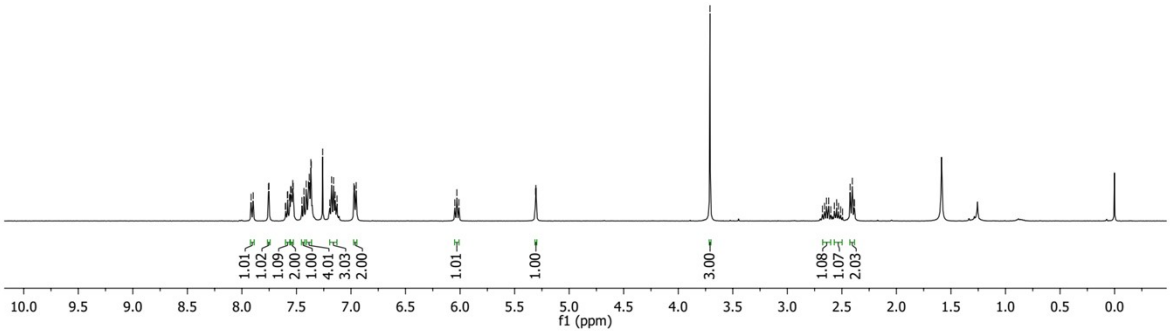
SS-417-ALD-1H



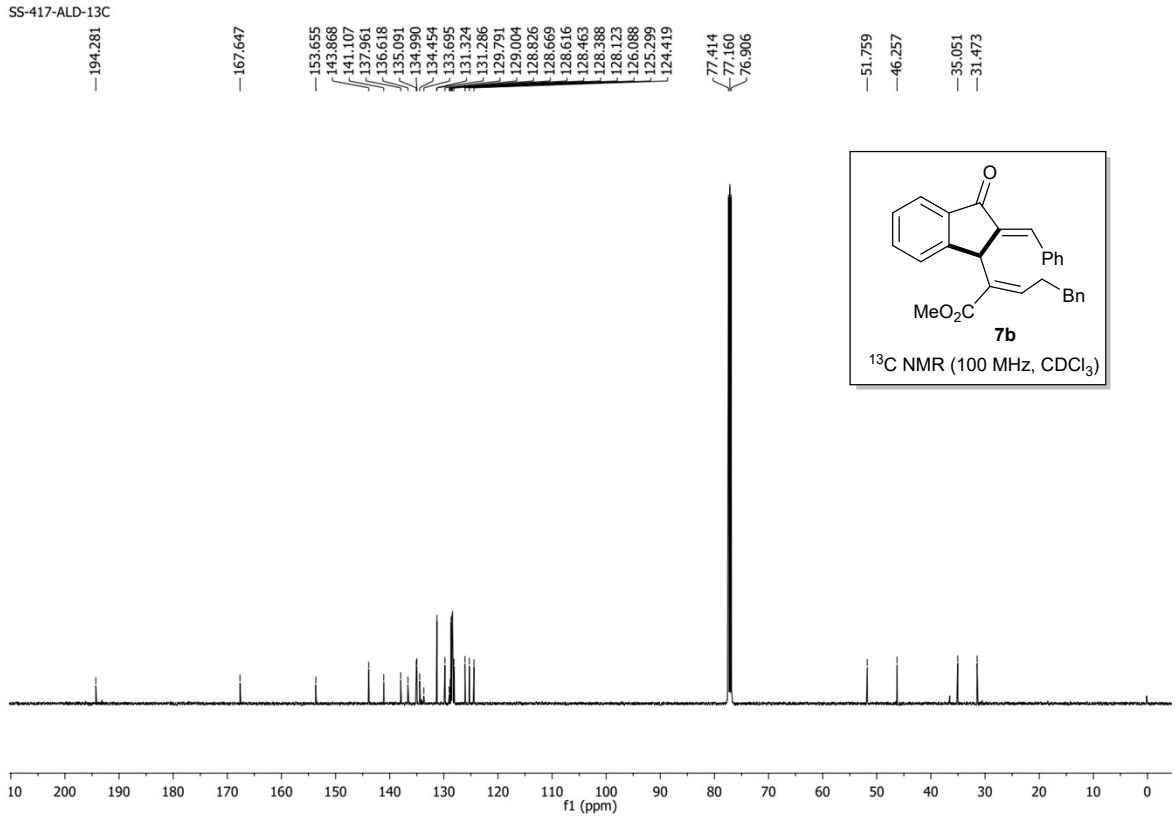



**7b**

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



SS-417-ALD-13C

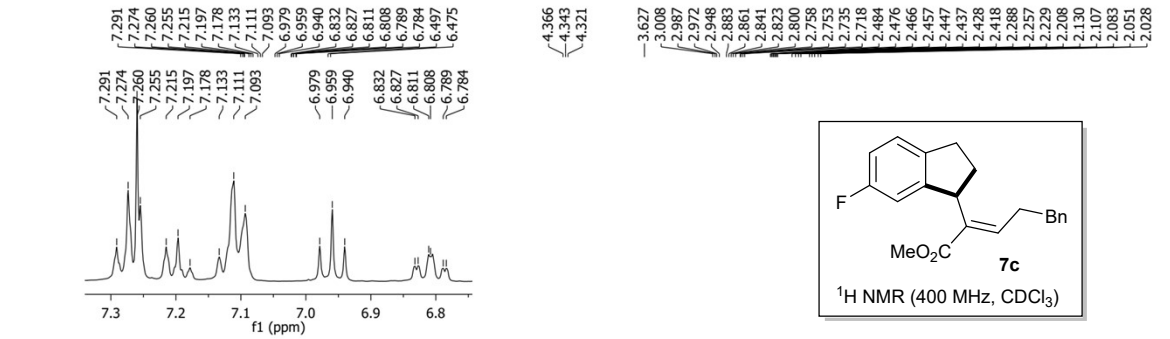





**7b**

$^{13}$C NMR (100 MHz, $CDCl_3$)

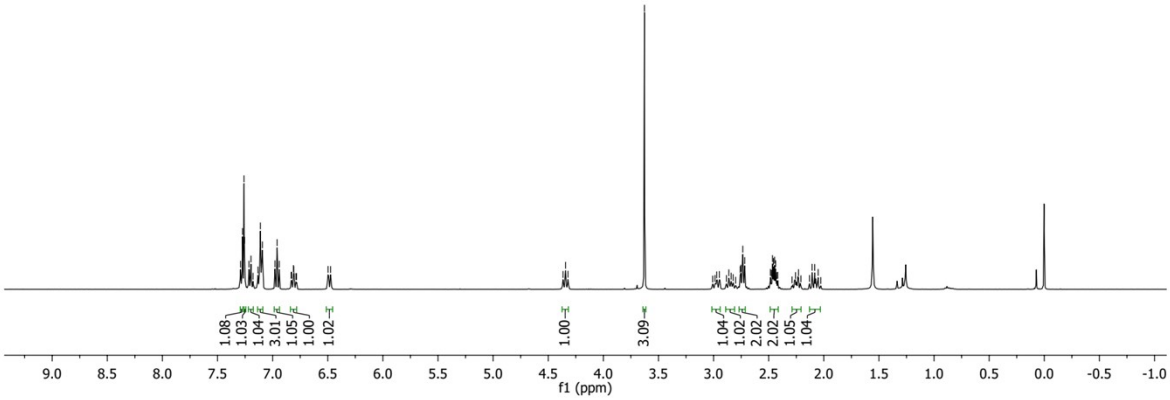
SS-421-ZN-1H

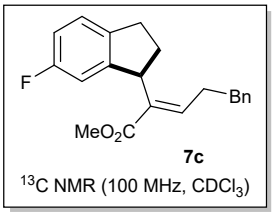





**7c**

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

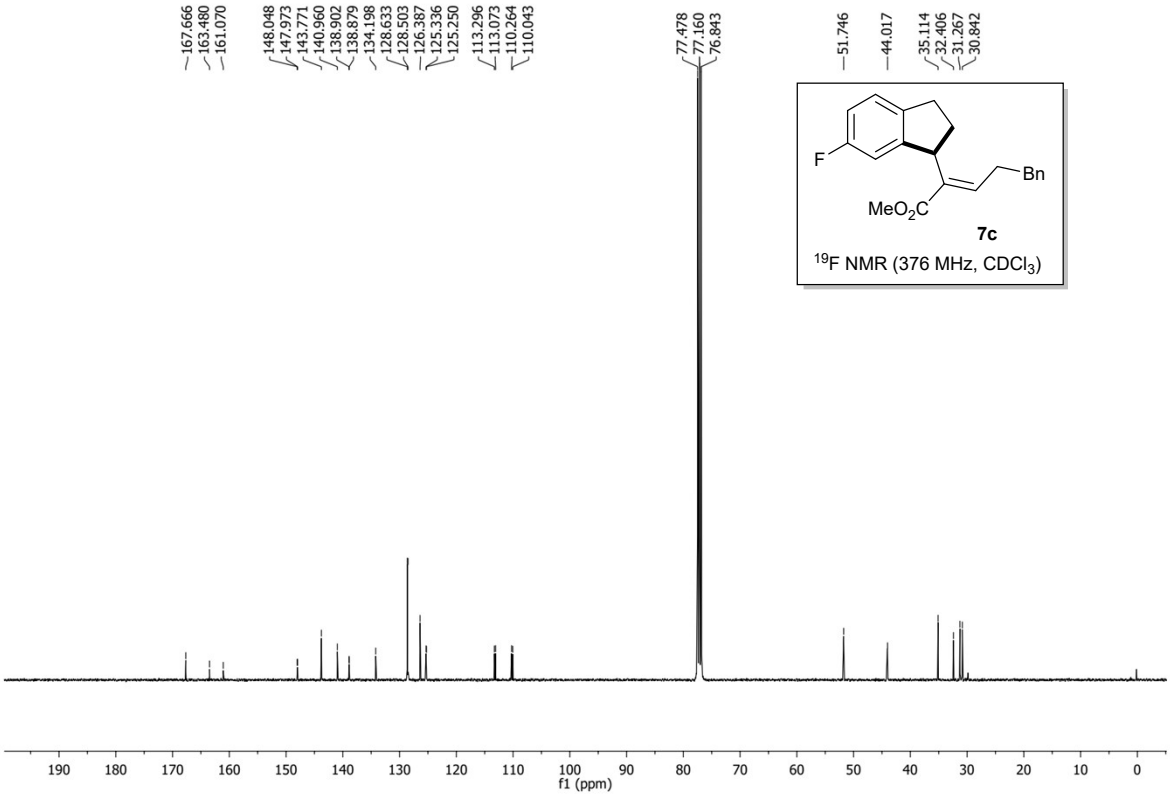




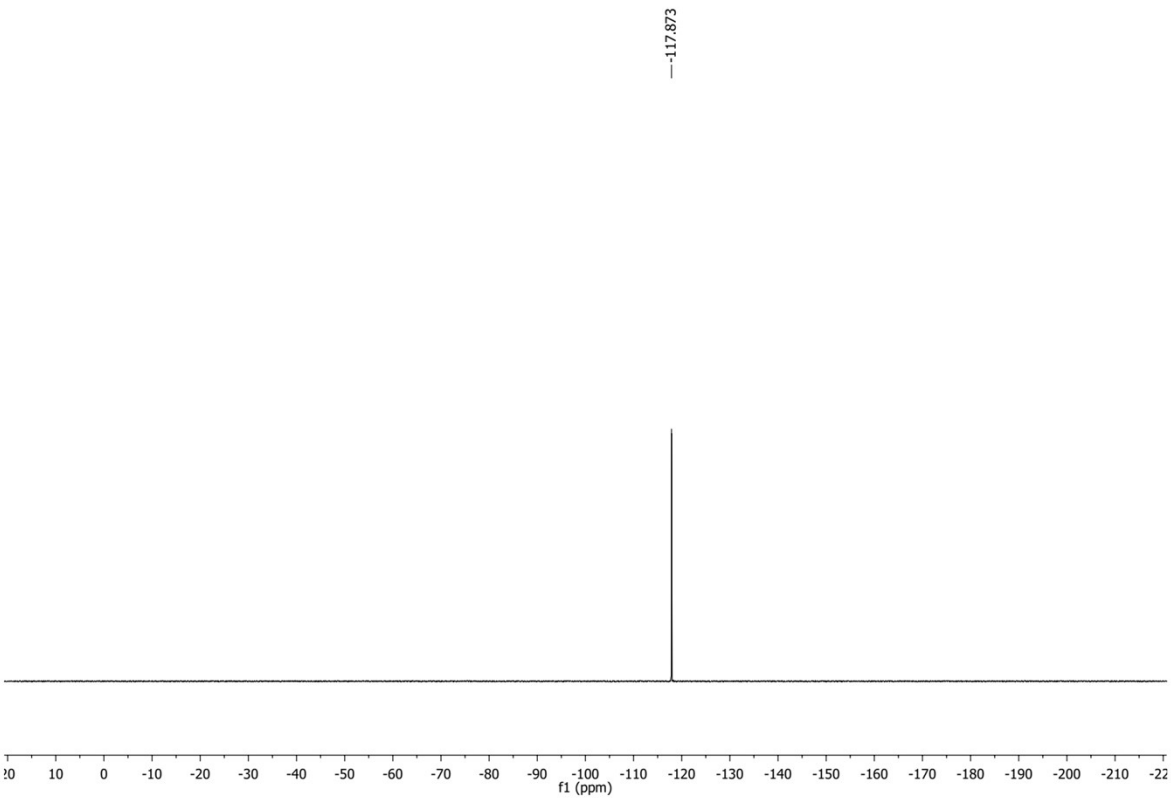

**7c**

$^{13}$C NMR (100 MHz, $CDCl_3$)

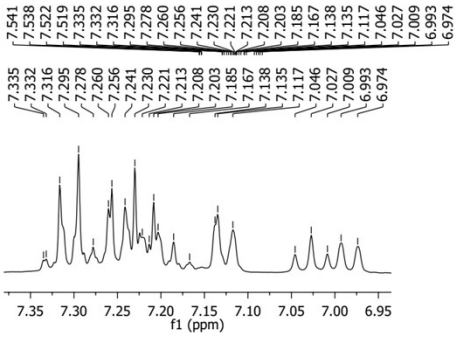
SS-421-ZN-13C

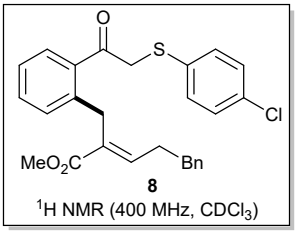



SS-421-ZN-19F



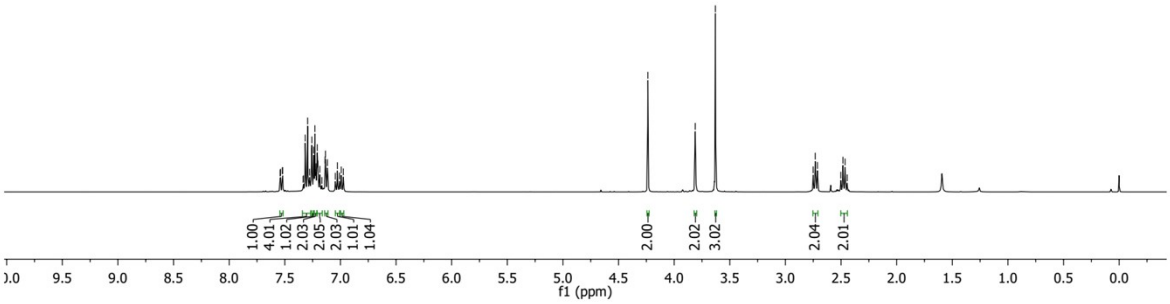
SS-417-SH-1H



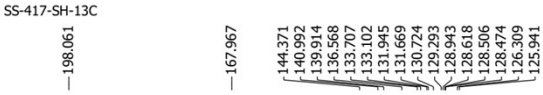


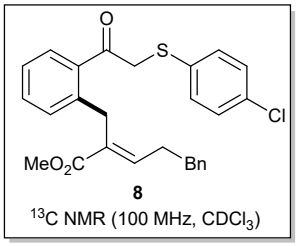
**8**

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



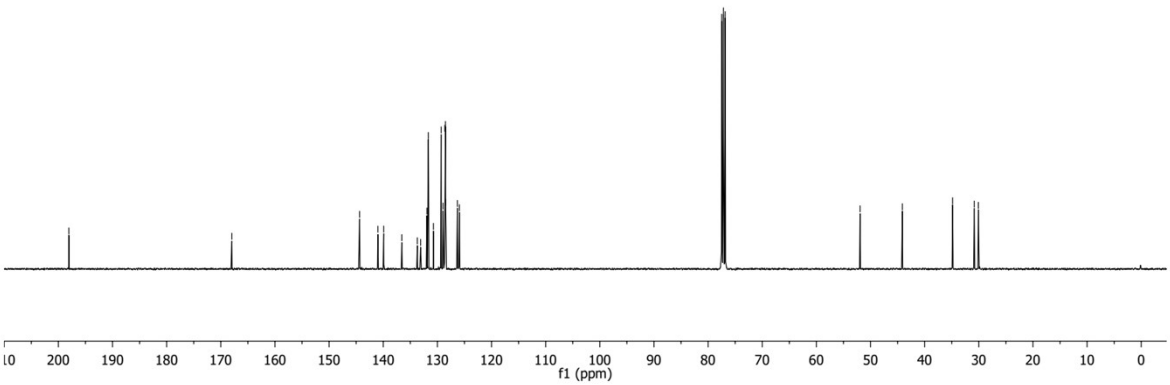
SS-417-SH-13C



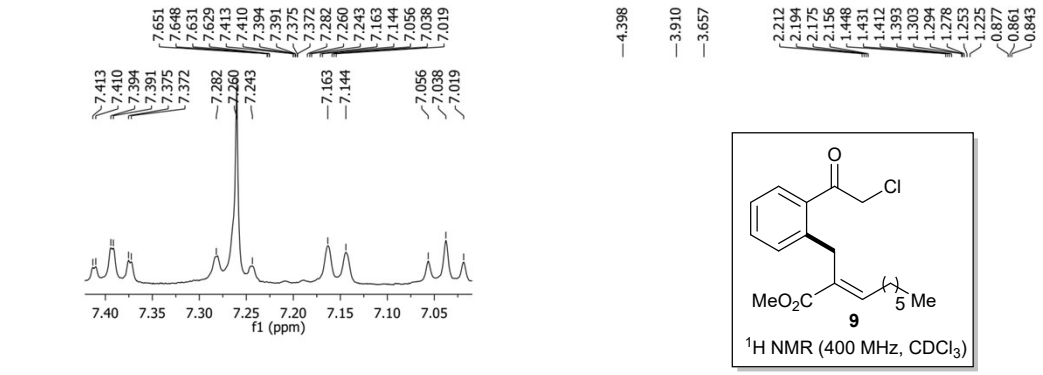


**8**

$^{13}$C NMR (100 MHz, $CDCl_3$)



SS-455-ES-1H

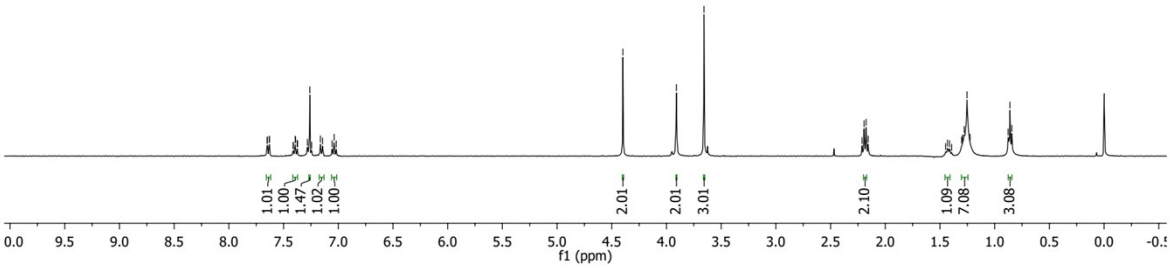




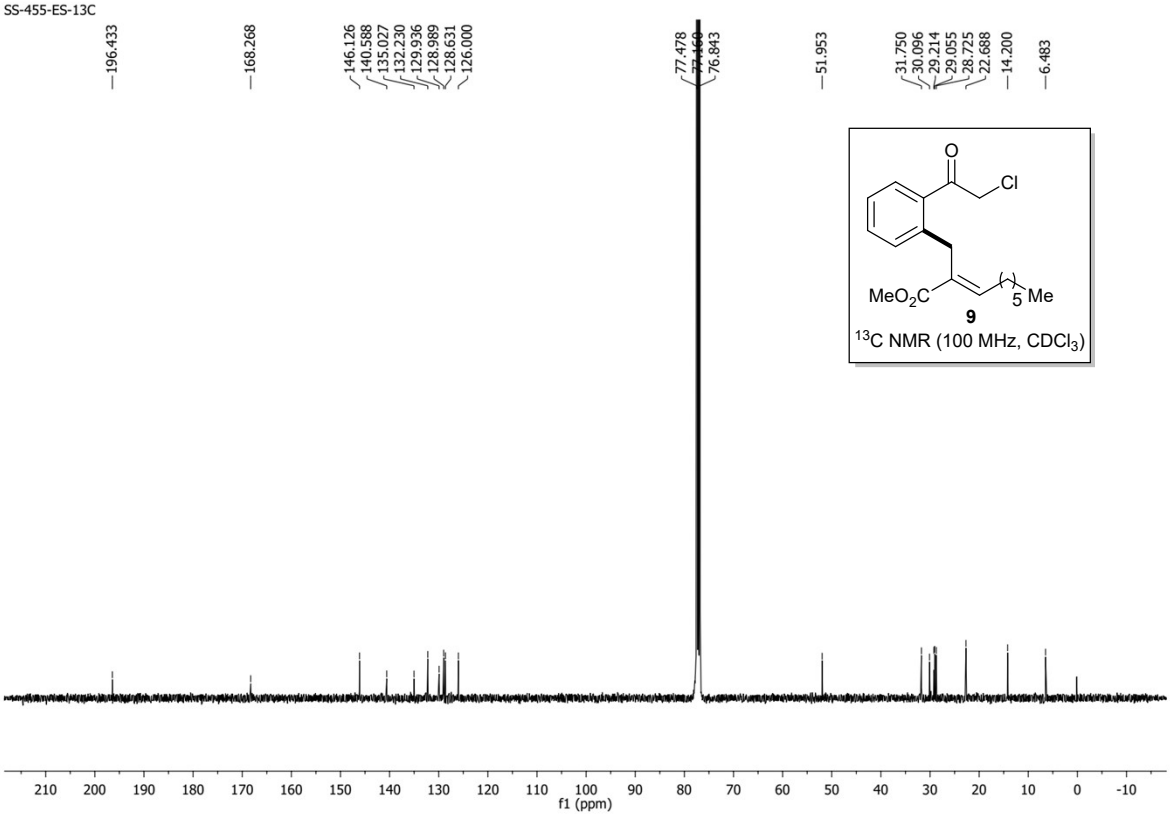


**9**

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




SS-455-ES-13C







**9**

$^{13}$C NMR (100 MHz, $CDCl_3$)