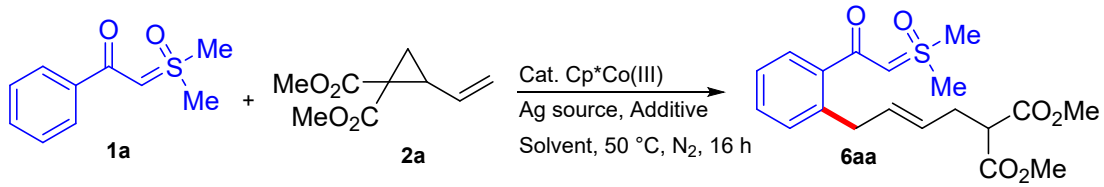
Supporting Information

Expedient C-H allylation of sulfoxonium ylides: merging C-H and C-C/C-het bond activation

Table of Contents

General Information. $Co_2(CO)_8$ (≥90%), $AgSbF_6$ (98%), NaOPiv (98%), CsOPiv (>98%), NaOAc (99%), CsOAc (>98%), Cu_2O (≥99.99%), AgOAc (≥99.99%), Cs_2CO_3 (>98%), CH_3COOH (>98%), PivOH (>98%), 1-AdCOOH (>98%), MesCOOH (>98%), 2,2,2-trifluoroethanol (TFE) and carboxylic acids were purchased from Aldrich and TCI chemicals and used as received. Acetonitrile (CH_3CN), tetrahydrofuran (THF), MeOH and 1,2-DCE (1,2-dichloroethane) were dried prior as per the standard procedure. Silica gel-G/GF254 plates (Merck) were used for TLC analysis with a mixture of hexane and ethyl acetate 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 were used to record (^1H, ^{13}C, ^{19}F and NOESY) spectra using $CDCl_3$ and DMSO-d_6 as the solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in parts per million and hertz (Hz), respectively, and to describe peak patterns following abbreviations were used when appropriate: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Melting point of the products was measured on Büchi melting point apparatus, MPB-540. Open capillary tubes were used for the measurements and are uncorrected. Mestre nova software was used throughout the spectral analysis. Q-Tof ESI-MS instrument was used for recording HRMS data. Infrared spectra were recorded on Perkin Elmer FT-IR instrument. HPLC analysis was carried out using Waters 515 system bearing C18 column with iso-propanol and hexane as an eluent.

Table S1. Optimization of Reaction Conditions[a]



entry	catalyst	Ag source	additive	solvent	yield (%)[b]	*E*/*Z*[c]
1	[Cp*Co(CO)I_2]	$AgSbF_6$	CH_3COOH	1,2-DCE	n.d.	-
2	[Cp*Co(CO)I_2]	$AgSbF_6$	PivOH	1,2-DCE	22	9:1
3	**[Cp*Co(CO)I_2]**	**$AgSbF_6$**	**-**	1,2-DCE	**88**	**21:1**
4	[Cp*Co(CO)I_2]	$AgBF_4$	-	1,2-DCE	n.d.	-
5	[Cp*Co(CO)I_2]	AgOTf	-	1,2-DCE	trace	-
6	[Cp*Co(CO)I_2]	AgOAc	-	1,2-DCE	24	6:1
7	[Cp*Co(CO)I_2]	$AgSbF_6$	-	THF	trace	-

8	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	-	MeOH	n.d.	-
9	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	-	TFE	n.d.	-
10	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	-	CH_3CN	trace	-
11[d]	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	-	1,2-DCE	68	16:1
12[e]	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	-	1,2-DCE	22	17:1
13[f]	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	-	1,2-DCE	trace	-
14[g]	$[Cp^*Co(CO)I_2]$	$AgSbF_6$	-	1,2-DCE	34	16:1
15	$[Cp^*RhCl_2]_2$	$AgSbF_6$	-	1,2-DCE	trace	-
16	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$	-	1,2-DCE	trace	-
17	$Pd(OAc)_2$	$AgSbF_6$	-	1,2-DCE	n.d	-
18	$Ir(ppy)_3$	$AgSbF_6$	-	1,2-DCE	n.d	-

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Catalyst (10 mol %), Ag source (20 mol %), additive (20 mol %), solvent (2 mL), 50 °C, 16 h, N_2 atmosphere. [b]Isolated yield. [c]Determined by ^1H NMR. [d]At 80 °C. [e]Room temperature. [f]Under air. [g]At 120 °C. n.d. = not detected. TFE = 2,2,2-trifluoroethanol.

Plausible Reaction Pathway for Other Strain Rings

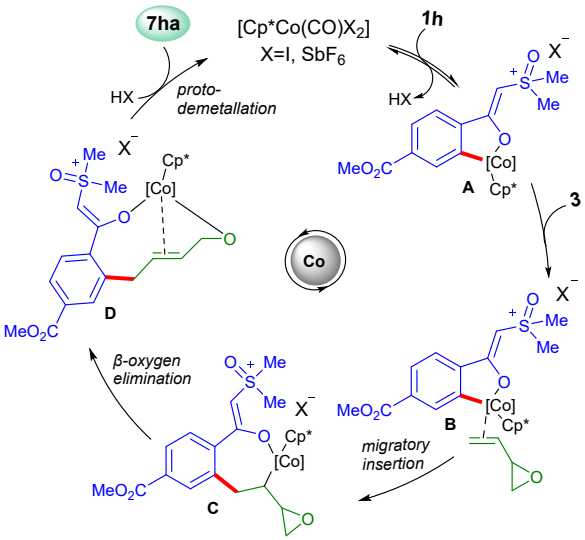


Figure 1. Mechanism when vinyl epoxide used as a coupling partner

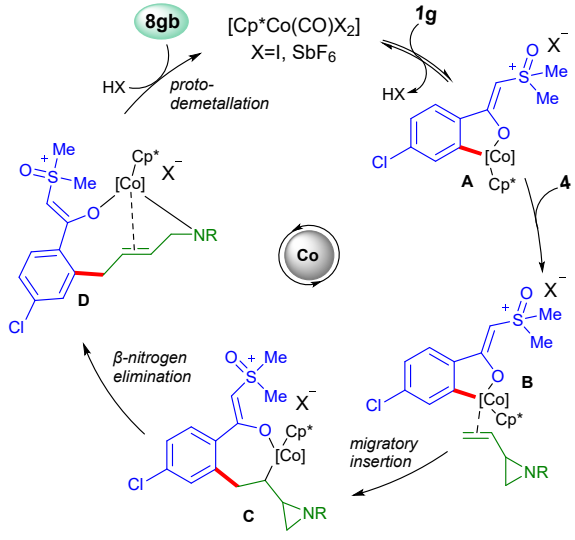


Figure 2. Mechanism when vinyl aziridine used as a coupling partner

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

Step-I: To a stirred solution of a carboxylic acid (5 mmol) and DMF (2 drops) in CH_2Cl_2 (15 mL), $(COCl)_2$ (6.5 mmol, 0.56 mL) was added dropwise. The solution was allowed to stir at

room temperature for 12 h and the resulting solution was concentrated in vacuo and dissolved in THF (10 mL). The resultant solution was used in subsequent reactions.

Step-II: To a stirred solution of potassium *tert*-butoxide (6.9 mmol, 774 mg) in THF (10 mL), trimethylsulfoxonium iodide (6.9 mmol, 1.5 g) was added at room temperature and the reaction was allowed to reflux for 2 h. The solution was then cooled to 0 °C followed by the dropwise addition of acid chloride (obtained in **Step-I**). The reaction was allowed to stir at room temperature for additional 3 h. After completion, 10 mL of water was added to the reaction mixture and the organic part was extracted with ethyl acetate (3 x 25 mL). The combined organic layer was washed with brine (10 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 (ethyl acetate/methanol = 9:1) to afford sulfoxonium ylides **1a-t**.

General Procedure for the Preparation of Vinyl cyclopropanes 2.

Synthesis of 2a.[2f] To a round bottom flask containing MeOH (7 mL) portion wise Na metal (10.3 mmol, 250 mg) was added at room temperature and the solution was allowed to stir till Na metal gets dissolved. The resulting solution was added dropwise to a stirred solution of (*E*)-1,4-dibromobut-2-ene (4.7 mmol, 1 g) and dimethyl malonate (5.1 mmol, 0.59 mL) in MeOH (5 mL) at room temperature under N_2 atmosphere. The reaction was allowed to stir for 16 h. After completion, water (20 mL) was added and the reaction mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine (10 mL) and water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue, which was purified using silica gel column chromatography (hexane:ethyl acetate = 9:1) to afford vinyl cyclopropane **2a**.

Synthesis of 2b-h.[2c] To a stirred solution of the malonate (2.1 mmol) and (*E*)-1,4-dibromobut-2-ene (2.3 mmol, 492 mg) in THF (6 mL) was added cesium carbonate (4.2 mmol, 580 mg). The reaction was allowed to reflux for 16 h. After completion, the reaction mixture was cooled to room temperature and passed through a short pad of celite. The organic part was washed with saturated aq. NH_4Cl (20 mL), extracted with ethyl acetate (3 x 15 mL) and dried over Na_2SO_4. Then all the volatiles were removed under reduced pressure to get a residue, which was purified using silica gel column chromatography (hexane: ethyl acetate = 4:1) to afford vinyl cyclopropanes **2b-h**.

General Procedure for the Preparation of Vinyl Aziridines 4.[2i]

Step-I: To a stirred solution of sulfonamide (20 mmol, 3.42 g) and potassium hydroxide (50 mmol, 2.8 g) in MeOH (80 mL), (diacetoxyiodo)benzene (20 mmol, 6.44 g) was added portion wise at 0 °C. The resulting mixture was stirred at room temperature for 3 h and poured into

water (200 mL). The solution was kept in refrigerator overnight to precipitate a yellow solid, which was recrystallized to afford PhI=NR.

Step-II: To a stirred solution of PhI=NR (10 mmol, 3.37 g) and $Cu(OTf)_2$ (1 mmol, 0.36 g) in MeCN (20 mL), 1,3-butadiene (10 mmol, 0.84 mL) was added at 0 °C under N_2 atmosphere. The reaction was stirred at room temperature for 3 h. After completion, the residue was poured into 1M NaOH (100 mL) and extracted with ethyl acetate (2 x 100 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography (hexane/ethyl acetate 10:1) to afford the vinyl aziridines **4**.

General Procedure of Cobalt-Catalyzed Ring opening of Strain Rings *via* Sulfoxonium Ylide 6/7/8/9. Sulfoxonium ylide **1** (0.2 mmol), vinyl cyclopropane **2** (0.3 mmol/2-vinyloxirane **3** (0.3 mmol)/2-vinylaziridines **4** (0.3 mmol)/4-vinyl-1,3-dioxolan-2-one **5** (0.3 mmol), [Cp*Co(CO)I_2] (10 mol %, 0.02 mmol, 10 mg) and $AgSbF_6$ (20 mol %, 0.04 mmol, 13 mg) were stirred in 1,2-DCE (2 mL) at 50 °C under N_2 atmosphere in a preheated oil bath for 16 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and filtered through a short pad of celite. Evaporation of the solvent gave a residue, which was purified using silica gel chromatography (hexane: ethyl acetate =1:4) to afford the ring opening allylated products **6/7/8/9**.

Scale-up Synthesis of 6aa. 2-(Dimethyl(oxo)-l6-sulfaneylidene)-1-phenylethan-1-one **1a** (5 mmol, 1 g), 1-dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **2a** (7.5 mmol, 1.4 g), [Cp*Co(CO)I_2] (10 mol %, 0.5 mmol, 242 mg) and $AgSbF_6$ (20 mol %, 1 mmol, 350 mg) were stirred in 1,2-DCE (100 mL) at 50 °C under N_2 atmosphere in a preheated oil bath for 16 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with ethyl acetate (60 mL) and filtered through a celite pad. Evaporation of the solvent gave a residue, which was purified using silica gel chromatography (hexane: ethyl acetate =2:8) to afford the ring opening allylated product **6aa** in 72% (1.4 g) yield.

Procedures for the Post-Synthetic Modifications

Synthesis of 10.[3a] To a stirred solution of CS_2 (2.5 M in THF, 0.3 mmol, 0.12 mL) and benzyl amine (0.2 mmol, 22.5 mg) in water (0.7 mL), dimethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)phenyl)but-2-en-1-yl)malonate **6aa** (0.1 mmol, 40 mg) was added and the reaction mixture was stirred at room temperature for 10 h. After completion (monitored by TLC), it was extracted with ethyl acetate (3 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue, which was purified using silica gel chromatography (hexane/ethyl acetate = 9:1) to afford **10** in 57% (19 mg) yield.

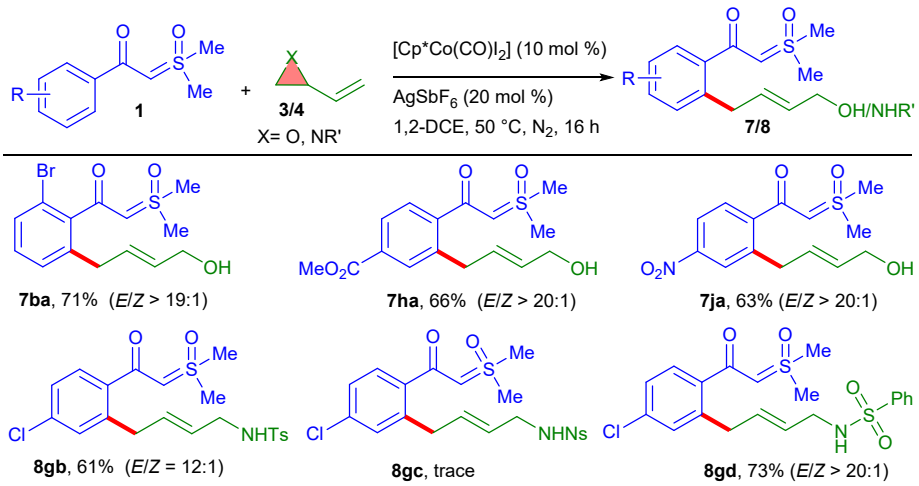
Synthesis of 11.[3b] To a stirred solution of **6da** (0.1 mmol, 50 mg) in MeOH (2 mL) was added MeONa (0.3 mmol, 17.5 mg) and $PhI(OAc)_2$ (0.1 mmol, 32.5 mg) and the mixture was stirred at 80 °C for 12 h under N_2 atmosphere. After completion (monitored by TLC), all the volatiles were evaporated using rotary evaporator to give a residue, which was purified using silica gel chromatography (hexane/ethyl acetate = 7:3) to afford **11** in 82% (40 mg) yield.

Synthesis of 13.[3c] To a stirred solution of **6ab** (0.1 mmol, 50 mg) in HFIP (2 mL), [Ru(*p*-cymene)Cl_2]$_2$ (0.03 mmol, 4 mg) and cyclopropanol **12** (0.12 mmol, 25 mg) were added and the reaction was allowed to stir at room temperature for 16 h. After completion (monitored by TLC), all the volatiles were evaporated using rotary evaporator. The resulting residue was purified using silica gel chromatography (hexane/ethyl acetate = 9:1) to afford **13** in 81% (26 mg) yield.

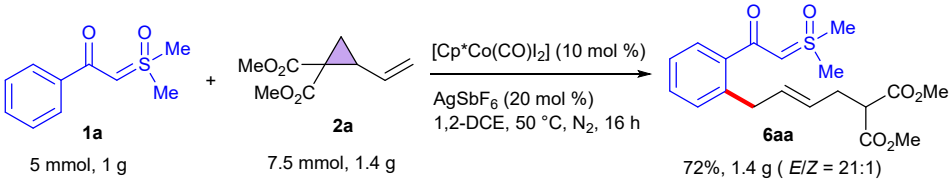
Synthesis of 14. To a stirred solution of **11** (0.1 mmol, 35 mg) in MeOH (1 mL) was added 2M NaOH solution (0.25 mmol, 0.15 mL) at 0 °C and the mixture was stirred at room temperature for 4 h. After completion (monitored by TLC), all the volatiles were evaporated using rotary evaporator. The resulting residue was added 1M HCl solution and white solid compound was formed, which was filtered through sintered funnel and the filtrate was washed with water (10 mL) to afford **14** in 80% (35 mg) yield.

Synthesis of 15. Compound **11** (0.1 mmol, 35 mg) and LiCl (0.5 mmol, 21 mg) were stirred in DMSO (1 mL) and H_2O (0.5 mmol, 10 µL) for 12 h at 150 °C under N_2 atmosphere. After completion (monitored by TLC), it was extracted with ethyl acetate (3 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue, which was purified using silica gel chromatography (hexane/ethyl acetate = 9:1) to afford **15** as a sticky liquid in 85% (17 mg) yield.

Synthesis of 16. Compound **11** (0.1 mmol, 35 mg) and Pd/C (10 mol%, 12 mg) were stirred in MeOH (1 mL) under H_2 balloon for 2 h at room temperature. After completion (monitored by TLC), the reaction mixture was passed through a short Celite pad using ethyl acetate (10 mL). The volatile was evaporated using rotary evaporator and the resulting residue was purified using silica gel chromatography (hexane/ethyl acetate = 9:1) to afford **16** as a colorless liquid in 90% (15 mg) yield.

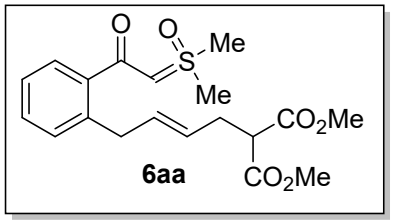


Scheme S1 Scope of sulfoxonium ylides, 2-vinyloxirane and 2-vinylaziridines.[a,b] [a]Reaction conditions: **1** (0.2 mmol), **3/4** (0.3 mmol), [Cp*Co(CO)I_2] (10 mol %), $AgSbF_6$ (20 mol %), 1,2-dichloroethane (2 mL), N_2, 50 °C, 16 h. [b]Isolated yield.

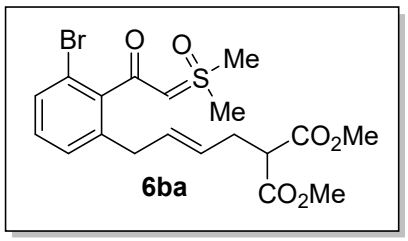


Scheme S2. Scale-up synthesis.

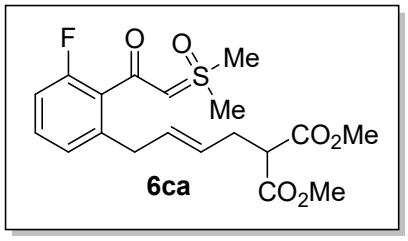
Characterization Data of the Products



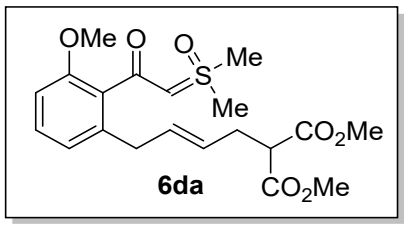
Dimethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)-acetyl)phenyl)but-2-en-1-yl)malonate 6aa. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.28; brown liquid; yield 88% (89 mg); major diastereomer (*E*/*Z* > 21:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.29-7.26 (m, 1H), 7.19-7.16 (m, 2H), 5.71-5.66 (m, 1H), 5.41-5.36 (m, 1H), 4.67 (bs, 1H), 3.72 (s, 6H), 3.67 (s, 0.29H, minor), 3.65-3.63 (m, 2H), 3.53 (s, 6H), 3.45 (t, *J* = 7.8 Hz, 1H), 2.75 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.8, 169.6, 132.2, 129.9, 129.4, 127.7, 126.0, 125.2, 71.8, 52.7, 51.7, 42.3, 31.0, 27.0; FT-IR (neat) 3025, 1723, 1542, 1382, 1328, 1255, 1121 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{25}O_6S$: 381.1366; Found 381.1373.



Dimethyl (*E*)-2-(4-(3-bromo-2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)phenyl)but-2-en-1-yl)malonate 6ba. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.25; brown liquid; yield 84% (70 mg); major diastereomer (*E*/*Z* > 21:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.5 Hz, 1H), 7.13-7.07 (m, 2H), 5.71-5.66 (m, 1H), 5.44-5.39 (m, 1H), 4.55 (s, 1H), 3.72 (s, 6H), 3.65 (s, 0.18H, minor), 3.57 (s, 6H), 3.52 (d, *J* = 7.0 Hz, 2H), 3.44 (t, *J* = 7.5 Hz, 1H), 2.74 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.2, 169.5, 142.8, 139.1, 131.3, 130.4, 129.3, 127.9, 125.9, 120.0, 72.7, 52.7, 51.6, 42.2, 31.1, 27.1; FT-IR (neat) 3009, 1720, 1536, 1375, 1321, 1240, 1128 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{24}BrO_6S$: 459.0471; Found 459.0464.

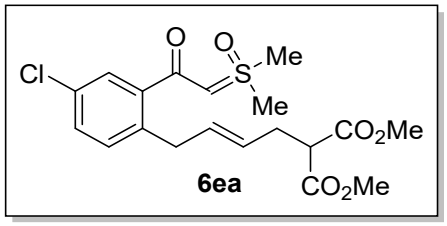


Dimethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-3-fluorophenyl)but-2-en-1-yl)malonate 6ca. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.26; brown sticky liquid; yield 86% (80 mg); major diastereomer (*E*/*Z* = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.16 (m, 1H), 6.96-6.93 (m, 1H), 6.88 (t, *J* = 8.5 Hz, 1H), 5.71-5.66 (m, 1H), 5.43-5.38 (m, 1H), 4.64 (s, 1H), 3.72 (s, 6H), 3.68 (s, 0.40H, minor), 3.55-3.53 (m, 8H), 3.44 (t, *J* = 7.5 Hz, 1H), 2.74 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.8, 169.6, 159.9 (J_{C-F} = 244.1 Hz), 140.2 (J_{C-F} = 3.3 Hz), 131.4, 130.0 (J_{C-F} = 18.2 Hz), 129.5 (J_{C-F} = 8.6 Hz), 125.7, 124.7 (J_{C-F} = 2.9 Hz), 113.4 (J_{C-F} = 22.5 Hz), 73.9, 52.7, 51.6, 42.4, 30.5, 27.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ -116.97; FT-IR (neat) 3007, 1722, 1574, 1436, 1252, 1150, 1128 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{25}FO_6S$: 399.1272; Found 399.1275.

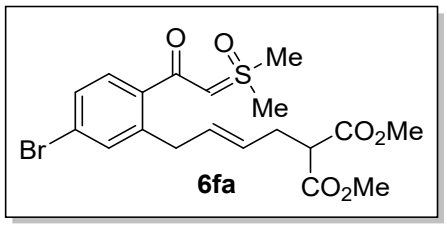


Dimethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)-acetyl)-3-methoxyphenyl)but-2-en-1-yl)malonate 6da. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.27; yellow sticky liquid; yield 83% (75 mg); major diastereomer

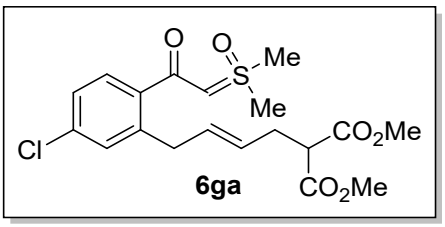
(*E*/*Z* = 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 8.0 Hz, 1H), 6.78-6.72 (m, 2H), 5.74-5.67 (m, 1H), 5.42-5.35 (m, 1H), 4.57 (bs, 1H), 3.79 (s, 3H), 3.72 (s, 6H), 3.69 (s, 0.40H, minor), 3.55-3.53 (m, 6H), 3.48-3.46 (m, 2H), 3.44-3.42 (m, 1H), 2.74 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.6, 169.6, 156.1, 138.4, 132.0, 131.9, 128.9, 125.2, 121.2, 108.9, 72.9, 56.0, 52.7, 51.7, 42.5, 30.5, 27.1; FT-IR (neat) 2957, 1731, 1673, 1438, 1345, 1283, 1257, 1153, 1022 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{27}O_7S$: 411.1472; Found 411.1476.



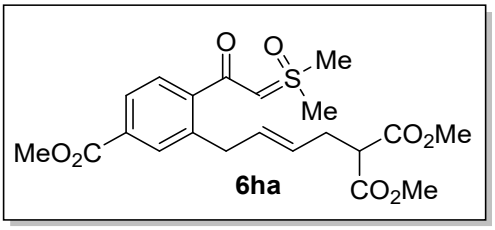
Dimethyl (*E*)-2-(4-(4-chloro-2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)phenyl)but-2-en-1-yl)malonate 6ea. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.27; yellow sticky liquid; yield 72% (65 mg); major diastereomer (*E*/*Z* > 21:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.24-7.22 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 5.66-5.62 (m, 1H), 5.41-5.37 (m, 1H), 4.65 (bs, 1H), 3.72 (s, 6H), 3.69 (s, 0.30H, minor), 3.58 (d, *J* = 7.8 Hz, 2H), 3.53 (s, 6H), 3.44 (t, *J* = 7.8 Hz, 1H), 2.73 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.0, 169.6, 137.6, 136.7, 131.7, 131.6, 131.2, 129.2, 127.6, 125.6, 72.2, 52.7, 51.7, 42.3, 30.4, 27.1; FT-IR (neat) 2973, 1718, 1573, 1385, 1283, 1121, 1084 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{24}ClO_6S$: 415.0977; Found 415.0978.



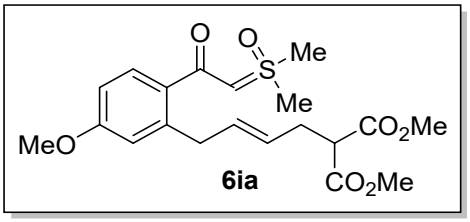
Dimethyl (*E*)-2-(4-(5-bromo-2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)phenyl)but-2-en-1-yl)malonate 6fa. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.27; brown sticky liquid; yield 83% (75 mg); major diastereomer (*E*/*Z* > 23:1);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.27-7.25 (m, 1H), 5.66-5.62 (m, 1H), 5.44-5.40 (m, 1H), 4.64 (s, 1H), 3.73 (s, 6H), 3.69 (s, 0.20H, minor), 3.60 (d, *J* = 7.2 Hz, 2H), 3.53 (s, 6H), 3.45 (t, *J* = 7.8 Hz, 1H), 2.74 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.5, 169.6, 140.5, 139.9, 132.6, 131.3, 129.2, 129.0, 125.9, 123.3, 72.1, 52.8, 51.6, 42.2, 30.7, 27.0; FT-IR (neat) 3013, 1729, 1543, 1385, 1328, 1256, 1165, 1023 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{24}BrO_6S$: 459.0471; Found 459.0470.



Dimethyl (*E*)-2-(4-(5-chloro-2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)phenyl)but-2-en-1-yl)malonate 6ga. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.27; yellow sticky liquid; yield 79% (80 mg); major diastereomer (*E*/*Z* > 23:1) mixture of diastereomers; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 1H), 7.16-7.14 (m, 2H), 5.68-5.63 (m, 1H), 5.45-5.40 (m, 1H), 4.63 (bs, 1H), 3.73 (s, 6H), 3.70 (s, 0.27H, minor), 3.62 (d, *J* = 7.5 Hz, 2H), 3.52-3.51 (m, 6H), 3.47-3.44 (m, 1H), 2.74 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.6, 169.6, 140.3, 139.5, 135.0, 131.4, 129.8, 129.0, 126.0, 125.9, 72.1, 52.7, 51.6, 42.4, 30.8, 27.0; FT-IR (neat) 2953, 1722, 1673, 1438, 1345, 1283, 1257, 1159, 1067 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{24}ClO_6S$: 415.0977; Found 415.0967.

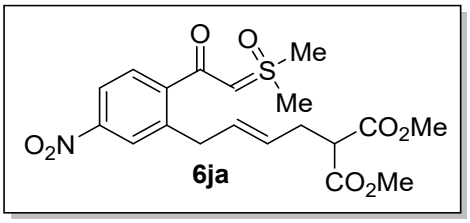


Dimethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-5-(methoxycarbonyl)phenyl)but-2-en-1-yl)malonate 6ha. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.27; yellow sticky liquid; yield 87% (75 mg); major diastereomer (*E*/*Z* > 23:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85-7.83 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 5.71-5.66 (m, 1H), 5.45-5.40 (m, 1H), 4.67 (bs, 1H), 3.90 (s, 3H), 3.73 (s, 6H), 3.68-3.66 (m, 2H), 3.55 (s, 6H), 3.46 (t, *J* = 7.5 Hz, 1H), 2.76 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.7, 169.6, 166.9, 145.5, 138.5, 131.6, 131.0, 130.6, 127.6, 127.3, 125.8, 72.3, 52.7, 52.3, 51.7, 42.4, 30.8, 27.1; FT-IR (neat) 3012, 1733, 1728, 1381, 1243, 1221, 1159, 1033 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{27}O_8S$: 439.1421; Found 439.1419.

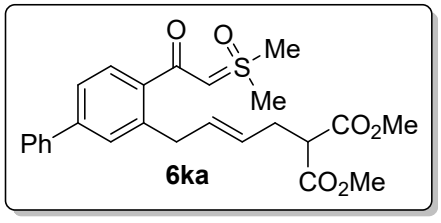


Dimethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-5-methoxyphenyl)but-2-en-1-yl)malonate 6ia. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.27; brown liquid; yield 82% (73 mg); major diastereomer (*E*/*Z*

> 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 1H), 6.73-6.72 (m, 1H), 6.70-6.67 (m, 1H), 5.71-5.64 (m, 1H), 5.42-5.36 (m, 1H), 4.63 (bs, 1H), 3.80 (s, 3H), 3.72 (s, 6H), 3.68-3.66 (m, 2H), 3.50 (s, 6H), 3.45 (t, *J* = 8.0 Hz, 1H), 2.75 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.5, 169.6, 160.4, 140.6, 133.6, 132.2, 129.5, 125.2, 115.5, 110.9, 71.0, 55.4, 52.7, 51.8, 42.5, 31.3, 27.0; FT-IR (neat) 2956, 1733, 1431, 1345, 1270, 1257, 1153, 1012 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{27}O_7S$: 411.1472; Found 411.1476.

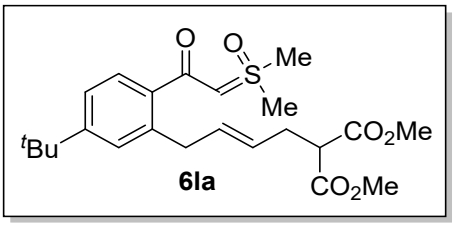


Dimethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-5-nitrophenyl)but-2-en-1-yl)malonate 6ja. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.27; yellow sticky liquid; yield 78% (75 mg); major diastereomer (*E*/*Z* = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.02 (m, 2H, major + minor), 7.54-7.50 (m, 1H, major + minor), 5.72-5.65 (m, 1H, major + minor), 5.53-5.46 (m, 1H, major + minor), 4.68-4.67 (m, 1H, major + minor), 3.74 (m, 6H, major), 3.73 (m, 1H, minor), 3.71-3.70 (m, 2H, major + minor), 3.56 (s, 6H, major), 3.55 (s, 1H, minor), 3.47 (t, *J* = 7.6 Hz, 1H, major + minor), 2.75 (t, *J* = 7.2 Hz, 2H, major + minor); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1 (major + minor), 171.7 (minor) 169.5 (major), 148.1 (major + minor), 147.2 (major + minor), 140.2 (major + minor), 130.6 (minor), 130.5 (major), 129.9 (minor), 128.5 (minor), 128.3 (major), 126.9 (major), 125.0 (minor), 124.7 (major), 121.5 (minor), 121.2 (major), 73.0 (minor), 72.9 (major), 53.0 (minor), 52.8 (major), 51.5 (major + minor), 42.3 (major), 42.2 (minor), 30.7 (major + minor), 27.1 (major + minor); FT-IR (neat) 2980, 1722, 1675, 1438, 1330, 1283, 1252, 1160, 1068 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{19}H_{24}NO_8S$: 426.1217; Found 426.1223.

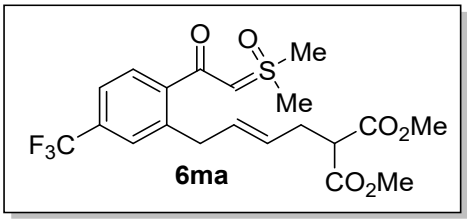


Dimethyl (*E*)-2-(4-(4-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-[1,1'-biphenyl]-3-yl)but-2-en-1-yl)malonate 6ka. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.32; brown sticky liquid; yield 84% (70 mg); major diastereomer (*E*/*Z* = 17:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.44-7.40 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 1H), 5.76-5.71 (m, 1H), 5.43-5.39 (m, 1H), 4.71 (s, 1H), 3.73-3.70 (m, 8H), 3.63 (s, 0.36H, minor), 3.55 (s, 6H), 3.46 (t, *J* = 7.8 Hz, 1H), 2.79 (t, *J* =

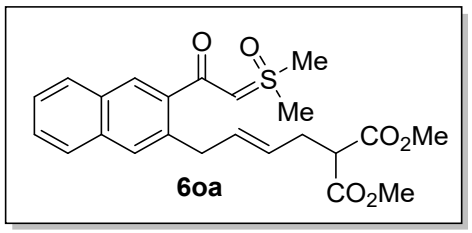
7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.5, 169.6, 142.1, 140.7, 139.8, 138.8, 132.3, 128.9, 128.7, 128.2, 127.6, 127.3, 125.2, 124.6, 71.7, 52.7, 51.7, 42.3, 31.1, 27.0; FT-IR (neat) 3031, 1730, 1438, 1345, 1281, 1260, 1155, 1020 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{25}H_{29}O_6S$: 457.1679; Found 457.1671.



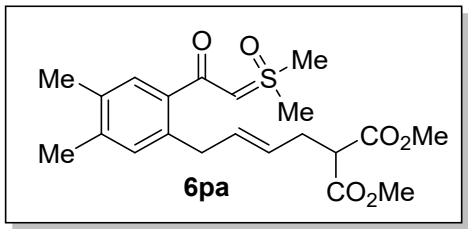
Dimethyl (*E*)-2-(4-(5-(*tert*-butyl)-2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)phenyl)but-2-en-1-yl)malonate 6la. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.27; yellow sticky liquid; yield 88% (79 mg); major diastereomer (*E*/*Z* > 22:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.5 Hz, 1H), 7.20-7.18 (m, 2H), 5.72-5.67 (m, 1H), 5.40-5.35 (m, 1H), 4.64 (bs, 1H), 3.73 (s, 6H), 3.65 (d, *J* = 7.5 Hz, 2H), 3.53-3.51 (m, 6H), 3.47-3.44 (m, 1H), 2.77 (t, *J* = 7.0 Hz, 2H), 1.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.9, 169.6, 152.5, 138.2, 137.9, 132.7, 127.6, 127.0, 124.8, 122.8, 71.2, 52.7, 51.8, 42.4, 34.8, 31.4, 31.2, 27.1; FT-IR (neat) 2956, 1733, 1673, 1438, 1283, 1257, 1153, 1022 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{33}O_6S$: 437.1992; Found 437.1995.



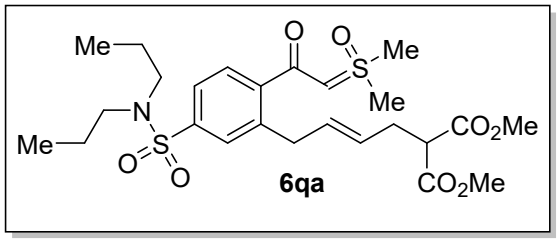
Dimethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-5-(trifluoromethyl)phenyl)but-2-en-1-yl)malonate 6ma. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.27; yellow liquid; yield 81% (73 mg); major diastereomer (*E*/*Z* > 17:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.8 Hz, 1H), 7.45-7.43 (m, 2H), 5.70-5.65 (m, 1H), 5.47-5.42 (m, 1H), 4.65 (s, 1H), 3.73 (s, 6H), 3.72 (s, 0.26H, minor), 3.67 (d, *J* = 7.8 Hz, 2H), 3.55 (s, 6H), 3.45 (t, *J* = 7.2 Hz, 1H), 2.75 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.2, 169.6, 144.6, 139.1, 131.2, 131.1 ($J_{C\text{-}F}$ = 35.3 Hz), 127.83 ($J_{C\text{-}F}$ = 245.1 Hz), 127.81, 126.6 ($J_{C\text{-}F}$ = 3.8 Hz), 126.2, 122.9 ($J_{C\text{-}F}$ = 3.9 Hz), 72.3, 52.7, 51.6, 42.4, 30.8, 27.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.62; FT-IR (neat) 2957, 1722, 1437, 1280, 1240, 1152, 1029 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{24}F_3O_6S$: 449.1240; Found 449.1233.



Dimethyl (*E*)-2-(4-(3-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)naphthalen-2-yl)but-2-en-1-yl)malonate 6oa. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.27; yellow sticky liquid; yield 86% (76 mg); major diastereomer (*E*/*Z* > 23:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.80-7.74 (m, 2H), 7.62 (s, 1H), 7.48-7.40 (m, 2H), 5.81-5.75 (m, 1H), 5.49-5.42 (m, 1H), 4.81 (bs, 1H), 3.79 (d, *J* = 7.2 Hz, 2H), 3.72 (s, 6H), 3.56 (s, 6H), 3.47 (t, *J* = 8.0 Hz, 1H), 2.80 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.8, 169.6, 136.0, 133.9, 132.1, 131.6, 128.1, 128.0, 127.3, 127.2, 126.83, 126.82, 125.9, 125.5, 71.9, 52.7, 51.8, 42.4, 31.2, 27.1; FT-IR (neat) 2953, 1727, 1438, 1351, 1288, 1259, 1187, 1067 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{27}O_6S$: 431.1523; Found 431.1516.

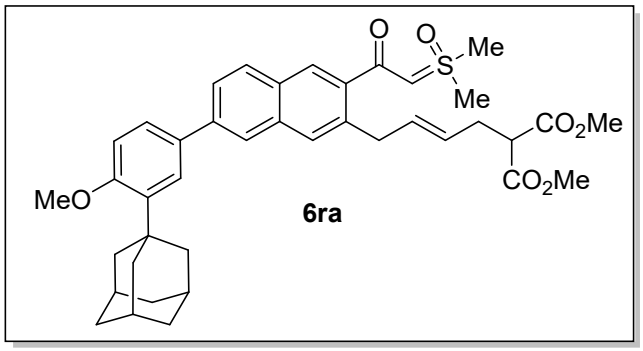


Dimethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-4,5-dimethylphenyl)but-2-en-1-yl)malonate 6pa. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.27; brown sticky liquid; yield 84% (80 mg); major diastereomer (*E*/*Z* = 19:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (s, 1H), 6.94 (s, 1H), 5.69-5.64 (m, 1H), 5.38-5.33 (m, 1H), 4.62 (bs, 1H), 3.73 (s, 6H), 3.69 (s, 0.31H, minor), 3.58 (d, *J* = 7.5 Hz, 2H), 3.51 (s, 6H), 3.45 (t, *J* = 7.5 Hz, 1H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.21 (d, *J* = 5.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.0, 169.6, 138.6, 137.9, 135.5, 134.0, 132.8, 131.2, 129.0, 124.7, 71.1, 52.6, 51.8, 42.4, 30.6, 27.0, 19.7, 19.3; FT-IR (neat) 2987, 1731, 1441, 1355, 1285, 1237, 1153, 1065 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{29}O_6S$: 409.1679; Found 409.1679.

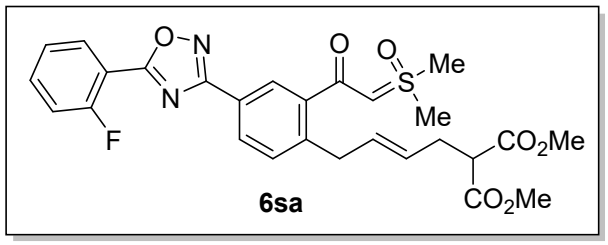


Dimethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-5-(*N*,*N*-dipropylsulfamoyl)phenyl)but-2-en-1-yl)malonate 6qa. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.28; brown liquid; yield 80% (63 mg); major diastereomer (*E*/*Z* > 21:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 2H), 7.47

(d, *J* = 8.0 Hz, 1H), 5.68-5.62 (m, 1H), 5.46-5.40 (m, 1H), 4.68 (s, 1H), 3.74 (s, 6H), 3.69-3.67 (m, 2H), 3.55 (s, 6H), 3.45 (t, *J* = 7.6 Hz, 1H), 3.07-3.03 (m, 4H), 2.73 (t, *J* = 7.2 Hz, 2H), 1.59-1.49 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 169.6, 144.9, 140.4, 139.5, 131.1, 128.2, 128.1, 126.3, 124.7, 72.6, 52.8, 51.5, 50.2, 42.3, 30.8, 29.8, 27.1, 22.2, 11.3; FT-IR (neat) 2954, 1722, 1625, 1462, 1438, 1364, 1285, 1252,1165, 1088, 1023 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{25}H_{38}NO_8S_2$: 544.2033; Found 544.2043.

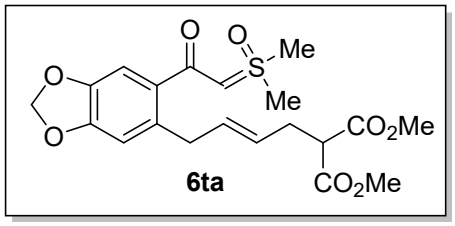


Dimethyl 2-((*E*)-4-(7-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-3-(2-(dimethyl(oxo)-l6 sulfaneylidene)acetyl)naphthalen-2-yl)but-2-en-1-yl)malonate 6ra. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.31; brown sticky liquid; yield 68% (40 mg); major diastereomer (*E*/*Z* > 23:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 5.2 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.69-7.66 (m, 2H), 7.59-7.58 (m, 1H), 7.53-7.51 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.84-5.78 (m, 1H), 5.50-5.44 (m, 1H), 4.81 (bs, 1H), 3.90 (s, 3H), 3.81 (d, *J* = 7.2 Hz, 2H), 3.73 (s, 6H), 3.68 (s, 0.26H, minor), 3.57 (s, 6H), 3.48 (t, *J* = 8.4 Hz, 1H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.18 (s, 6H), 2.10 (s, 3H), 1.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 169.7, 158.8, 139.0, 136.3, 134.3, 133.2, 133.1, 132.2, 131.7, 130.4, 129.6, 128.4, 128.1, 126.0, 125.7, 125.5, 124.8, 124.4, 124.2, 112.3, 77.4, 55.3, 52.7, 51.8, 47.9, 42.5, 40.8, 40.2, 37.3, 31.2, 29.3, 27.1; FT-IR (neat) 2903, 1721, 1643, 1495, 1255, 1202, 1143, 1034 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{40}H_{47}O_7S$: 671.3037; Found: 671.3030.

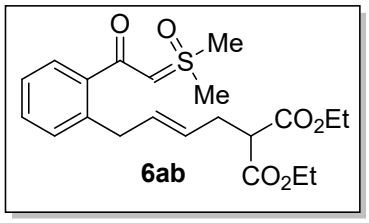


Dimethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-4-(5-(2-fluorophenyl)-1,2,4-oxadiazol-3-yl)phenyl)but-2-en-1-yl)-malonate 6sa. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.25; yellow sticky liquid; yield 79% (60 mg); major diastereomer (*E*/*Z* > 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24-8.19 (m, 2H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.62-7.58 (m, 1H), 7.35-7.33 (m, 2H), 7.28 (d, *J*

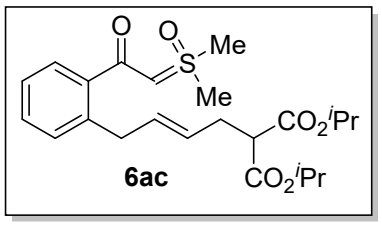
= 9.5 Hz, 1H), 5.73-5.68 (m, 1H), 5.46-5.41 (m, 1H), 4.81 (bs, 1H), 3.73-3.68 (m, 8H), 3.58 (s, 6H), 3.46 (t, J = 7.5 Hz, 1H), 2.77 (t, J = 7.0 Hz, 2H), 2.61 (0.11H, minor); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 169.6, 168.4, 161.8, 160.0, 134.8 ($J_{C\text{-}F}$ = 8.6 Hz), 131.3, 131.2, 130.7, 130.6, 130.5, 126.9, 126.0, 124.9, 124.8 ($J_{C\text{-}F}$ = 3.6 Hz), 124.6, 117.3 ($J_{C\text{-}F}$ = 20.7 Hz), 113.0 ($J_{C\text{-}F}$ = 11.6 Hz), 67.6, 52.7, 51.7, 42.2, 31.1, 27.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.34; FT-IR (neat) 3012, 1720, 1252, 1226, 1067, 757 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{27}H_{28}FN_2O_7S$: 543.1596; Found 543.1578.



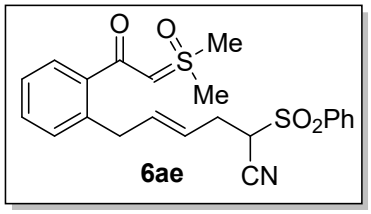
Dimethyl (*E*)-2-(4-(6-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)benzo[d][1,3]dioxol-5-yl)but-2-en-1-yl)malonate 6ta. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.28; yellow sticky liquid; yield 85% (75 mg); major diastereomer (*E*/*Z* > 23:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, J = 8.0 Hz, 1H), 6.61 (d, J = 8.0 Hz, 1H), 5.96 (s, 2H), 5.70-5.65 (m, 1H), 5.35-5.29 (m, 1H), 4.62 (bs, 1H), 3.72 (s, 6H), 3.66 (s, 0.20H, minor), 3.60 (d, J = 7.0 Hz, 2H), 3.50 (s, 6H), 3.45 (t, J = 7.5 Hz, 1H), 2.77 (t, J = 7.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.7, 169.7, 147.9, 146.5, 135.4, 131.0, 125.0, 122.2, 120.7, 105.8, 101.2, 70.9, 52.6, 51.8, 42.4, 27.0, 25.2; FT-IR (neat) 2959, 1722, 1670, 1462, 1438, 1364, 1255, 1243 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{25}O_8S$: 425.1265; Found 425.1273.



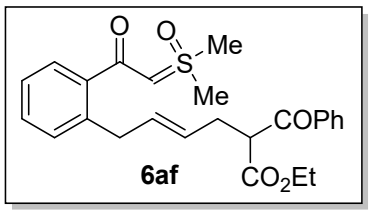
Diethyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)phenyl)but-2-en-1-yl)malonate 6ab. Analytical TLC on silica gel, 7:3 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 87% (95 mg); major diastereomer (*E*/*Z* > 21:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.5 Hz, 1H), 7.27-7.24 (m, 1H), 7.19-7.14 (m, 2H), 5.70-5.65 (m, 1H), 5.41-5.36 (m, 1H), 4.65 (bs, 1H), 4.18 (q, J = 7.0 Hz, 4H), 3.63 (d, J = 7.5 Hz, 2H), 3.52 (s, 6H), 3.39 (t, J = 7.5 Hz, 1H), 2.74 (t, J = 7.5 Hz, 2H), 2.60-2.56 (m, 0.09H, minor), 1.25 (t, J = 7.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.8, 169.2, 141.1, 138.1, 132.0, 129.8, 129.2, 127.5, 125.9, 125.3, 71.9, 61.5, 52.0, 42.3, 31.0, 26.9, 14.2; FT-IR (neat) 2981, 1726, 1336, 1277, 1296, 1212, 1067 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{29}O_6S$: 409.1679; Found 409.1689.



Diisopropyl (*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)phenyl)but-2-en-1-yl)malonate 6ac. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.32; yellow sticky liquid; yield 85% (50 mg); major diastereomer (*E*/*Z* > 21:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.5 Hz, 1H), 7.28-7.25 (m, 1H), 7.20-7.14 (m, 2H), 5.69-5.64 (m, 1H), 5.42-5.37 (m, 1H), 5.06-5.01 (m, 2H), 3.63 (d, *J* = 7.0 Hz, 2H), 3.53 (s, 6H), 3.32 (t, *J* = 7.5 Hz, 1H), 2.71 (t, *J* = 7.0 Hz, 2H), 2.57 (t, *J* = 7.0 Hz, 0.09H, minor), 1.24-1.22 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.8, 168.8, 141.1, 138.2, 131.8, 129.8, 129.3, 127.6, 125.9, 125.5, 69.0, 52.4, 42.3, 31.1, 26.8, 21.8, 21.7; FT-IR (neat) 2971, 1720, 1574, 1442, 1258, 1144 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{33}O_6S$: 437.1992; Found 437.1992.

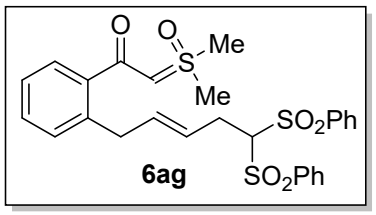


(*E*)-6-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)phenyl) -2-(phenylsulfonyl)hex-4-enenitrile 6ae. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 83% (48 mg); major diastereomer (*E*/*Z* > 21:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.28-7.26 (m, 1H), 7.19-7.14 (m, 2H), 5.93-5.88 (m, 1H), 5.39-5.34 (m, 1H), 4.72 (s, 1H), 4.03-4.00 (m, 1H), 3.79-3.78 (m, 0.05H, minor), 3.70-3.67 (m, 1H), 3.54 (s, 4H), 3.45 (s, 3H), 2.90-2.88 (m, 1H), 2.58-2.52 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.1, 141.0, 136.9, 136.8, 135.6, 135.4, 130.4, 129.7, 129.4, 127.7, 126.3, 122.0, 114.2, 72.4, 57.7, 42.2, 42.0, 36.2, 30.2; FT-IR (neat) 3012, 1725, 1339, 1289, 1253, 1218, 1052 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{22}H_{24}NO_4S_2$: 430.1141; Found 430.1141.

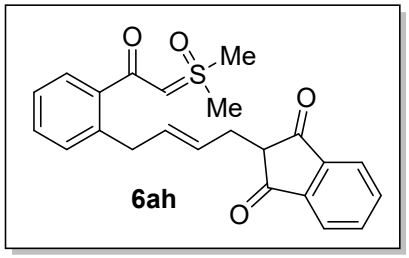


Ethyl (*E*)-2-benzoyl-6-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)phenyl)hex-4-enoate 6af. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 87% (51 mg); major diastereomer (*E*/*Z* > 23:1); ^{1}H NMR

(600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 7.20-7.17 (m, 2H), 5.71-5.67 (m, 1H), 5.47-5.43 (m, 1H), 4.67 (bs, 1H), 4.40 (t, *J* = 7.2 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.67 (s, 2H), 3.52 (d, *J* = 6.0 Hz, 6H), 2.92-2.83 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.1, 186.9, 169.7, 141.2, 138.2, 136.4, 133.7, 132.0, 129.8, 129.2, 128.9, 128.8, 127.5, 125.9, 125.7, 71.8, 61.6, 54.2, 42.3, 31.0, 27.2, 14.1; FT-IR (neat) 2987, 1723, 1673, 1323, 1272, 1221, 1210, 1053 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{25}H_{29}O_5S$: 441.1730; Found 441.1728.

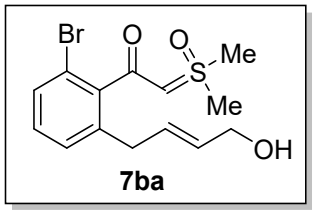


(*E*)-1-(2-(5,5-bis(phenylsulfonyl)pent-2-en-1-yl)phenyl)-2-(dimethyl(oxo)-l6-sulfaneylidene)ethan-1-one 6ag. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 85% (60 mg); major diastereomer (*E*/*Z* > 23:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.5 Hz, 4H), 7.66 (t, *J* = 7.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 4H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.30-7.28 (m, 1H), 7.22-7.19 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 5.63-5.57 (m, 1H), 5.46-5.41 (m, 1H), 4.50 (t, *J* = 5.0 Hz, 1H), 3.53 (s, 8H), 2.85 (t, *J* = 5.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.9, 141.2, 137.8, 137.3, 134.8, 134.6, 130.3, 129.8, 129.3, 129.2, 127.7, 126.2, 124.6, 83.7, 72.3, 42.2, 36.2, 29.0; FT-IR (neat) 3010, 1723, 1673, 1340, 1290, 1253, 1220, 1067 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{27}H_{29}O_6S_3$: 545.1121; Found 545.1127.



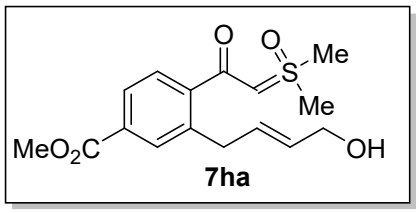
(*E*)-2-(4-(2-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-phenyl)but-2-en-1-yl)-1H-indene-1,3(2H)-dione 6ah. Analytical TLC on silica gel, 7:3 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 79% (89 mg); major diastereomer (*E*/*Z* > 23:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.84-7.82 (m, 2H), 7.43-7.37 (m, 1H), 7.34-7.32 (m, 1H), 7.14-7.10 (m, 1H), 6.92-6.90 (m, 1H), 6.70-6.68 (m, 0.04H, minor), 5.74-5.67 (m, 1H), 5.38-5.30 (m, 1H), 4.58 (bs, 1H), 3.51 (s, 6H), 3.42 (d, *J* = 6.8 Hz, 2H), 3.06 (t, *J* = 5.6 Hz, 1H), 2.71 (t, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 186.8, 142.8, 140.9, 137.7, 135.8, 133.8, 130.9, 129.8, 129.1, 128.3, 127.5, 126.7, 125.8, 125.5, 123.2, 71.5,

53.8, 42.7, 42.4, 36.0, 30.0; FT-IR (neat) 2980, 1723, 1681, 1339, 1276, 1253, 1250, 1061 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{23}H_{23}O_4S$: 351.1203; Found 351.1211.



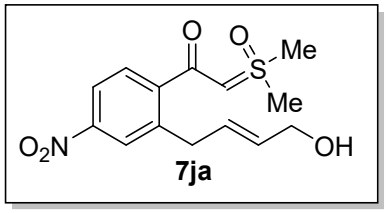
7ba

(*E*)-1-(2-bromo-6-(4-hydroxybut-2-en-1-yl)phenyl)-2-(dimethyl-(oxo)-l6-sulfaneylidene)ethan-1-one 7ba. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.35; yellow sticky liquid; yield 71% (45 mg); major diastereomer (*E*/*Z* > 19:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.14-7.07 (m, 2H), 5.86-5.79 (m, 1H), 5.72-5.65 (m, 1H), 4.54 (s, 1H), 4.08 (d, *J* = 5.6 Hz, 2H), 3.58 (s, 0.20H, minor), 3.55 (s, 6H), 3.48 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.1, 142.8, 138.6, 131.3, 130.9, 130.6, 129.4, 128.6, 120.2, 72.9, 63.6, 42.3, 36.6; FT-IR (neat) 3020, 2920, 1732, 1549, 1382, 1162, 1094 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{14}H_{18}BrO_3S$: 345.0155; Found 345.0175.



7ha

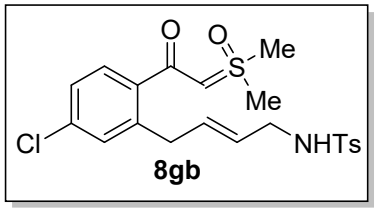
Methyl (*E*)-4-(2-(dimethyl(oxo)-l6-sulfaneylidene)acetyl)-3-(4-hydroxybut-2-en-1-yl)benzoate 7ha. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 66% (42 mg); major diastereomer (*E*/*Z* > 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87-7.85 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 5.89-5.82 (m, 1H), 5.70-5.63 (m, 1H), 4.68 (bs, 1H), 4.21 (d, *J* = 6.0 Hz, 0.07H, minor), 4.09 (d, *J* = 6.0 Hz, 2H), 3.91 (s, 3H), 3.64 (d, *J* = 6.0 Hz, 2H), 3.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 166.9, 145.4, 138.0, 131.6, 131.4, 130.7, 127.7, 127.5, 72.5, 64.4, 63.8, 52.3, 42.4, 41.1, 36.1; FT-IR (neat) 3015, 2903, 1725, 1567, 1370, 1162, 1093 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{16}H_{21}O_5S$: 325.1104; Found 325.1105.



7ja

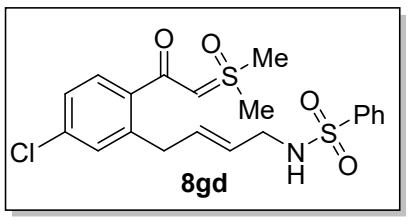
(*E*)-2-(dimethyl(oxo)-l6-sulfaneylidene)-1-(2-(4-hydroxy-but-2-en-1-yl)-4-nitrophenyl)ethan-1-one 7ja. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 63% (41 mg); major diastereomer (*E*/*Z* >

20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.03 (m, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 5.88-5.81 (m, 1H), 5.74-5.67 (m, 1H), 4.69 (s, 1H), 4.12 (d, *J* = 5.6 Hz, 2H), 3.68 (d, *J* = 6.0 Hz, 2H), 3.56-3.55 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.2, 148.1, 147.1, 139.8, 131.6, 130.1, 128.5, 125.2, 121.4, 73.0, 63.5, 42.3, 36.0; FT-IR (neat) 3036, 2915, 1732, 1550, 1381, 1161, 1093 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{14}H_{18}NO_5S$: 312.0900; Found 312.0916.



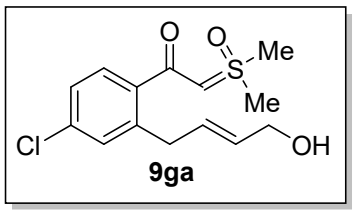
8gb

(*E*)-*N*-(4-(5-chloro-2-(2-(dimethyl(oxo)-l6-sulfaneylidene)-acetyl)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide 8gb. Analytical TLC on silica gel, 8:2 ethyl acetate/hexane R_f = 0.32; brown sticky liquid; yield 61% (30 mg); major diastereomer (*E*/*Z* = 12:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74-7.68 (m, 2H, major + minor), 7.34 (d, *J* = 8.5 Hz, 0.2H, minor), 7.30 (d, *J* = 8.0 Hz, 1H), 7.26-7.25 (m, 2H, major + minor), 7.17-7.15 (m, 1H), 7.12-7.11 (m, 0.2H, minor), 7.08-7.07 (m, 1H, major), 5.73-5.67 (m, 1H, major), 5.35-5.29 (m, 1H, major), 5.05 (t, *J* = 5.5 Hz, 1H, major), 4.79 (bs, 1H, major), 3.61 (m, 0.51H, minor), 3.54-3.51 (m, 8H, major + minor), 3.45 (t, *J* = 6.0 Hz, 2H, major), 2.40 (s, 3H, major + minor); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.4, 143.5, 139.4, 137.1, 135.0, 133.0, 130.5, 129.8, 129.1, 128.5, 128.1, 127.2, 127.1, 126.3, 126.1, 73.2, 45.4, 42.1, 35.9, 21.6; FT-IR (neat) 3392, 2963, 1734, 1605, 1520, 1385, 1182 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{21}H_{25}ClNO_4S_2$: 454.0908; Found 454.0912.



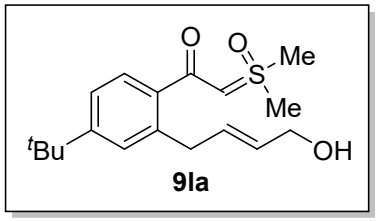
8gd

(*E*)-*N*-(4-(5-chloro-2-(2-(dimethyl(oxo)-l6-sulfaneylidene)-acetyl)phenyl)but-2-en-1-yl)benzenesulfonamide 8gd. Analytical TLC on silica gel, 7:3 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 72% (30 mg); major diastereomer (*E*/*Z* > 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 0.09H, minor), 7.55 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.18-7.15 (m, 2H), 7.04 (t, *J* = 5.5 Hz, 1H), 5.54-5.49 (m, 1H), 5.47-5.42 (m, 1H), 4.74 (bs, 1H), 3.58 (s, 6H), 3.56-3.51 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.8, 140.4, 140.3, 138.4, 135.5, 133.9, 132.6, 131.0, 130.0, 129.2, 127.2, 126.5, 123.7, 73.9, 43.1, 39.4, 32.3; FT-IR (neat) 3373, 2941, 1737, 1592, 1512, 1343, 1080 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{20}H_{22}ClNO_4S_2$: 440.0752; Found 440.0754.



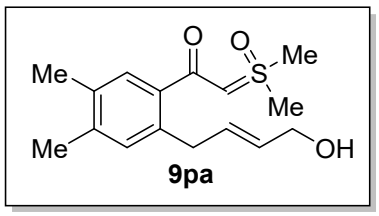
9ga

(*E*)-1-(4-chloro-2-(4-hydroxybut-2-en-1-yl)phenyl)-2-(dimethyl(oxo)-l6-sulfaneylidene)ethan-1-one 9ga. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 67% (46 mg); major diastereomer (*E*/*Z* > 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.8 Hz, 1H), 7.17-7.16 (m, 2H), 5.85-5.80 (m, 1H), 5.69-5.64 (m, 1H), 4.65 (bs, 1H), 4.19 (d, *J* = 7.2 Hz, 0.10H, minor), 4.10 (d, *J* = 6.0 Hz, 2H), 3.59 (d, *J* = 6.6 Hz, 2H), 3.51 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.8, 139.9, 139.5, 131.2, 130.8, 130.3, 129.1, 126.2, 72.1, 63.7, 42.4, 36.0; FT-IR (neat) 3010, 2920, 1731, 1539, 1383, 1154, 1087 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{14}H_{18}ClO_3S$: 301.0660; Found 301.0664.



9la

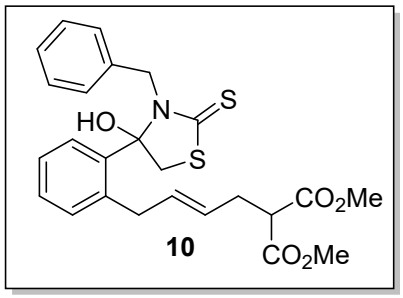
(*E*)-1-(4-(*tert*-butyl)-2-(4-hydroxybut-2-en-1-yl)phenyl)-2-(dimethyl(oxo)-l6-sulfaneylidene)ethan-1-one 9la. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 74% (24 mg); major diastereomer (*E*/*Z* > 19:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 1H), 7.22-7.18 (m, 2H), 5.90-5.83 (m, 1H), 5.69-5.64 (m, 1H), 4.67 (bs, 1H), 4.07 (d, *J* = 5.6 Hz, 2H), 3.63 (d, *J* = 6.0 Hz, 2H), 3.52 (s, 1H), 3.50 (s, 6H), 1.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.2, 141.8, 138.3, 137.4, 132.7, 129.8, 127.7, 127.6, 123.1, 71.4, 63.9, 42.4, 41.2, 36.7, 34.8, 31.4; FT-IR (neat) 3023, 2921, 1730, 1543, 1375, 1160, 1076 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{18}H_{27}O_3S$: 323.1675; Found 323.1690.



9pa

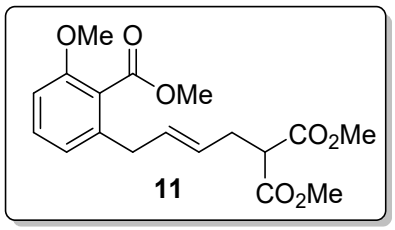
(*E*)-2-(dimethyl(oxo)-l6-sulfaneylidene)-1-(2-(4-hydroxybut-2-en-1-yl)-4,5-dimethylphenyl)ethan-1-one 9pa. Analytical TLC on silica gel, 9:1 ethyl acetate/hexane R_f = 0.35; brown sticky liquid; yield 72% (22 mg); major diastereomer (*E*/*Z* > 21:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 6.94 (s, 1H), 5.88-5.81 (m, 1H), 5.67-5.61 (m, 1H), 4.66 (bs, 1H), 4.06 (d, *J* = 5.6 Hz, 2H), 3.55 (d, *J* = 6.4 Hz, 2H), 3.51 (s, 6H), 2.22 (d, *J* = 4.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.2, 138.5, 138.0, 135.0, 134.3, 132.8, 131.8,

129.7, 129.1, 71.5, 64.4, 63.9, 42.4, 35.9, 19.7, 19.3; FT-IR (neat) 3054, 2923, 1718, 1539, 1389, 1140, 1091 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{16}H_{23}O_3S$: 295.1362; Found 295.1382.



10

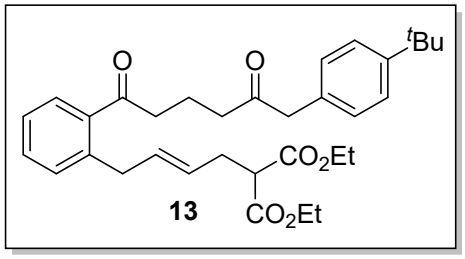
Dimethyl (*E*)-2-(4-(2-(3-benzyl-4-hydroxy-2-thioxothiazolidin-4-yl)phenyl)but-2-en-1-yl)malonate 10. Analytical TLC on silica gel, 2:8 ethyl acetate/hexane R_f = 0.30; colorless sticky liquid; yield 57% (19 mg); major diastereomer (*E*/*Z* = 8:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H, major + minor), 7.68 (bs, 1H, major + minor), 7.45 (t, *J* = 7.2 Hz, 1H, major + minor), 7.37-7.30 (m, 7H, major + minor), 7.22 (s, 1H, major + minor), 5.66-5.60 (m, 1H, major + minor), 5.44-5.38 (m, 2H, major + minor), 4.90 (d, *J* = 5.2 Hz, 1H, major + minor), 4.67 (s, 1H, major + minor), 4.27 (d, *J* = 14.4 Hz, 1H, major + minor), 3.74 (s, 1H, minor), 3.72-3.69 (m, 6H, major), 3.66-3.62 (m, 2H, major + minor), 3.45-3.42 (m, 1H, major + minor), 2.74 (t, *J* = 7.6 Hz, 2H, major + minor); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5 (major), 196.09 (minor), 169.6 (major), 169.5 (minor), 141.2 (major + minor), 136.6 (major), 136.4 (minor), 136.0 (major + minor), 132.3 (major + minor), 131.3 (major + minor), 131.0 (major + minor), 130.0 (major + minor), 129.1 (major + minor), 128.9 (major + minor), 128.7 (major + minor), 128.5 (major + minor), 128.3 (major + minor), 126.7 (major + minor), 126.3 (major + minor), 126.0 (major + minor), 52.8 (major + minor), 52.7 (major + minor), 51.8 (minor), 51.7 (major), 51.5 (major + minor), 45.2 (major + minor), 31.6 (major + minor), 27.1(minor), 27.0 (major); FT-IR (neat) 3015, 2936, 1750, 1532, 1361, 1156, 1182 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{25}H_{27}NO_5S_2Na$: 508.1223; Found 508.1222.



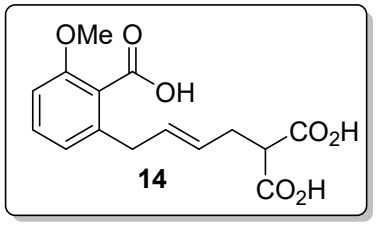
11

Dimethyl (*E*)-2-(4-(3-methoxy-2-(methoxycarbonyl)-phenyl)but-2-en-1-yl)malonate 11. Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.25; colorless sticky liquid; yield 82% (40 mg); major diastereomer (*E*/*Z* = 8:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 1H, major + minor), 6.79-6.76 (m, 2H, major + minor), 5.66-5.59 (m, 1H, major + minor), 5.48-5.41 (m, 1H, major + minor), 3.90 (s, 0.4H, minor)

3.89 (s, 3H, major), 3.81 (s, 3H, major + minor), 3.74 (s, 0.8H, minor), 3.71 (s, 6H, major), 3.42 (t, J = 7.6 Hz, 1H, major + minor), 3.36 (d, J = 7.2 Hz, 0.35H, minor), 3.26 (d, J = 6.8 Hz, 2H, major), 2.73 (t, J = 7.2 Hz, 0.39H, minor), 2.60 (t, J = 7.2 Hz, 2H, major); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5 (major + minor), 168.7 (major + minor), 156.6 (major + minor), 139.1(minor), 138.9 (major), 131.5 (major), 130.72 (minor), 130.67 (minor), 130.62 (major) 127.4 (major), 126.0 (minor), 123.5 (major + minor), 121.6 (major), 121.5 (major + minor), 109.1(major + minor), 56.1 (major + minor), 52.7 (minor), 52.6 (major), 52.4 (minor), 52.3 (major), 51.9 (major), 51.7 (minor), 36.5 (major), 31.9 (major), 31.2 (minor), 26.9 (minor); FT-IR (neat) 2979, 2932, 1715, 1600, 1575, 1454, 1432, 1259, 1102 cm^{-1}; HRMS (ESI-TOF) *m/z* [M+Na]$^+$ calcd for $C_{18}H_{22}O_7Na$: 373.1258; Found 373.1258.

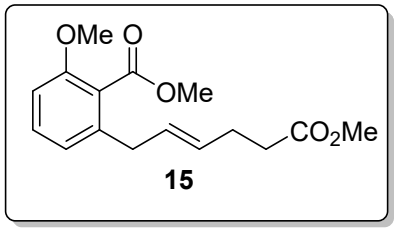


Diethyl (*E*)-2-(4-(2-(6-(4-(*tert*-butyl)phenyl)-5-oxohexanoyl)phenyl)but-2-en-1-yl)malonate 13. Analytical TLC on silica gel, 2:8 ethyl acetate/hexane R_f = 0.30; colorless sticky liquid; yield 81% (26 mg); major diastereomer (*E*/*Z* > 21:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 1H), 7.40-7.32 (m, 3H), 7.27 (s, 1H), 7.24-7.22 (m, 1H), 7.12 (d, J = 8.4 Hz, 2H), 5.61-5.54 (m, 1H), 5.44-5.38 (m, 1H), 4.20 (q, J = 7.2 Hz, 4H), 3.66 (s, 2H), 3.60 (d, J = 7.2 Hz, 2H), 3.40 (t, J = 7.6 Hz, 1H), 2.86 (t, J = 7.2 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H), 1.99-1.92 (m, 2H), 1.30 (s, 9H), 1.26 (t, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 204.2, 169.2, 150.0, 140.3, 138.2, 131.5, 131.4, 131.2, 131.0, 129.2, 128.5, 126.2, 125.9, 125.8, 61.6, 52.1, 49.8, 41.0, 40.7, 34.6, 31.7, 31.5, 26.9, 18.4, 14.2; FT-IR (neat) 3070, 1738, 1671, 1599, 1437, 1166, 1085 cm^{-1}; HRMS (ESI-TOF) *m/z* [M+Na]$^+$ calcd for $C_{33}H_{42}O_6Na$: 557.2874; Found 557.2874.

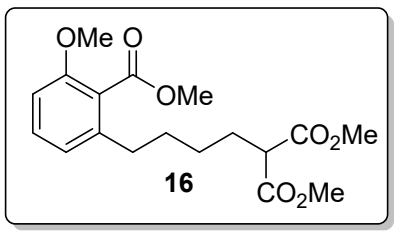


(*E*)-2-(4-(2-carboxy-3-methoxyphenyl)but-2-en-1-yl)malonic acid 14. Analytical TLC on silica gel, 1:9 methanol/ethyl acetate R_f = 0.22; colorless solid; mp 115-116 °C; yield 80% (35 mg); major diastereomer (*E*/*Z* > 20:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.27 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 5.58-5.51 (m, 1H), 5.48-5.40 (m, 1H), 3.73 (s, 3H), 3.25-3.23 (m, 1H), 3.19 (d, J = 6.4 Hz, 2H), 2.39 (t, J =

6.8 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.9, 169.2, 155.7, 137.7, 130.4, 130.3, 128.5, 125.0, 121.4, 109.5, 56.0, 51.9, 35.9, 31.7; FT-IR (neat) 3476, 3006, 1731, 1665, 1603, 1435, 1338, 1286 cm^{-1}; HRMS (ESI-TOF) *m/z* [M+Na]$^+$ calcd for $C_{15}H_{16}O_7Na$: 331.0788; Found 331.0790.



Methyl (*E*)-2-methoxy-6-(6-methoxy-6-oxohex-2-en-1-yl)-benzoate 15. Analytical TLC on silica gel, 2:8 ethyl acetate /hexane R_f = 0.30; colorless sticky liquid; yield 85% (17 mg); major diastereomer (*E*/*Z* > 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 1H, major + minor), 6.82-6.77 (m, 2H, major + minor), 5.60-5.44 (m, 2H, major + minor), 3.90-3.89 (m, 3H, major + minor), 3.82 (bs, 3H, major + minor), 3.67-3.65 (m, 3H, major + minor), 3.38 (d, *J* = 6.8 Hz, 0.31H, minor) 3.28 (d, *J* = 6.4 Hz, 2H, major), 2.45-2.30 (m, 5H, major + minor); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.7 (major), 173.6 (minor), 168.83 (minor), 168.76 (major), 156.6 (major + minor), 139.4 (minor), 139.3 (major), 130.7 (minor), 130.6 (major), 130.2 (major), 129.3 (major), 129.0 (minor), 128.8 (minor), 123.5 (major + minor), 121.7 (major), 121.5 (minor), 109.0 (major + minor), 56.08 (minor), 56.06 (major), 52.4 (minor), 52.3 (major), 51.73 (minor), 51.67(major), 36.6 (major), 34.0 (minor), 33.9 (major), 31.1 (minor), 27.9 (major), 22.9 (minor); FT-IR (neat) 1728, 1725, 1612, 1439, 1357, 1280 cm^{-1}; HRMS (ESI-TOF) *m/z* [M+Na]$^+$ calcd for $C_{16}H_{21}O_5Na$: 315.1203; Found 315.1203.



Dimethyl 2-(4-(3-methoxy-2-(methoxycarbonyl)-phenyl)-butyl)malonate 16. Analytical TLC on silica gel, 2:8 ethyl acetate /hexane R_f = 0.32; colorless sticky liquid; yield 90% (15 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 1H), 6.80-6.75 (m, 2H), 3.90 (s, 3H), 3.81 (s, 3H), 3.73 (s, 6H), 3.37-3.31 (m, 1H), 2.56-2.52 (m, 2H), 1.94-1.88 (m, 2H), 1.65-1.59 (m, 2H), 1.38-1.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 169.0, 156.5, 140.8, 130.5, 123.7, 121.6, 108.7, 56.0, 52.6, 52.3, 51.7, 33.2, 30.7, 28.7, 27.2; FT-IR (neat) 1732, 1722, 1665, 1555, 1338, 956 cm^{-1}; HRMS (ESI-TOF) *m/z* [M+Na]$^+$ calcd for $C_{18}H_{24}O_7Na$: 375.1414; Found 375.1419.

Mechanistic Investigation

H/D Exchange Experiment of 1a with D_2O in Absence of 2a. To a stirred solution of 2-(dimethyl(oxo)-l6-sulfaneylidene)-1-phenylethan-1-one **1a** (0.2 mmol, 50 mg), [Cp*Co(CO)I_2] (10 mol %, 0.02 mmol, 10 mg) and $AgSbF_6$ (20 mol %, 0.04 mmol, 13 mg) in 1,2-DCE (5 mL), D_2O (2 mmol, 0.05 mL) was added and the resultant mixture was stirred at 50 °C in an oil bath for 20 minutes under N_2 atmosphere. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and passed through a short pad of celite. Substrate **1a** was recovered using silica gel chromatography (ethyl acetate: methanol = 9:1) to afford [D_n]-**1a**. The deuterium incorporation was observed as 23% at C2-H, 16% at the H of *α*-C of carbonyl group of [D_n]-**1a** based on 400 MHz ^{1}H NMR.

Preparation of 2-(Dimethyl(oxo)-l6-sulfaneylidene)-1-(4-methoxyphenyl-2,6-d2)ethan-1-one 1i-*d_2*.

Step-I: 4-Methoxybenzoic acid (0.50 mmol, 76 mg), [Ru(O_2CAd)$_2$(*p*-cymene)] (5 mol %, 14.9 mg) and D_2O (10 mmol, 0.18 mL) were stirred in 1,4-dioxane (1 mL) at 100 °C for 16 h under N_2 atmosphere. After cooling to room temperature, the residue was diluted with ethyl acetate (8 mL) and filtered through a short pad of celite. Evaporation of the solvent gave a residue that was purified using silica gel column chromatography (hexane: ethyl acetate: acetic acid= 8:1:0.1) to afford [D]-**1i**.

Step-II: To a stirred solution of [D]-**1i** (0.6 mmol, 100 mg) and DMF (1 drop) in CH_2Cl_2 (2 mL), $(COCl)_2$ (0.8 mmol, 0.07 mL) was added dropwise. The reaction mixture was allowed to stir at room temperature for 12 h. Then the solvent was evaporated under reduced pressure and the residue having [D]-**1i** acid chloride was used in the subsequent step.

Step-III: To a stirred solution of potassium *tert*-butoxide (2.4 mmol, 266 mg) in THF (4 mL), trimethylsulfoxonium iodide (2.4 mmol, 522 mg) was added at room temperature. The solution was allowed to reflux for 3 h. The reaction mixture was then cooled to 0 °C, followed by the slow addition of the solution of the [D]-**1i** acid chloride obtained by the above procedure (**Step II**). The reaction was allowed to warm to room temperature and stirred for 3 h. After completion, the reaction mixture was concentrated under vacuum and water (10 mL) was added to the residue and extracted with ethyl acetate (3 x 10 mL) and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified using silica gel chromatography (ethyl acetate/methanol = 9:1) to afford **1i-*d_2*** with 93% deuteriation.

Kinetic Isotope Effect Experiments

Parallel Reactions. [Cp*Co(CO)I_2] (10 mol %, 0.02 mmol, 10 mg), 2-(dimethyl(oxo)-l6-sulfaneylidene)-1-(4 methoxyphenyl)ethan-1-one (**1i** or **1i-*d_2***, 0.2 mmol, 50 mg), dimethyl 2-

vinylcyclopropane-1,1-dicarboxylate **2a** (0.3 mmol, 61 mg) and 1,2-DCE (5 mL) were subjected to the standard conditions for 1 h. The reaction was then cooled to room temperature, diluted with ethyl acetate (10 mL) and filtered through a short pad of celite. The solvent was removed under vacuum and purification was performed as described in the general procedure to afford **6ia** and **6ia-*d***. The KIE value was determined to be P_H/P_D = 1.63 on the basis of ^{1}H NMR analysis (See Scheme 6b).

Competitive Reactions

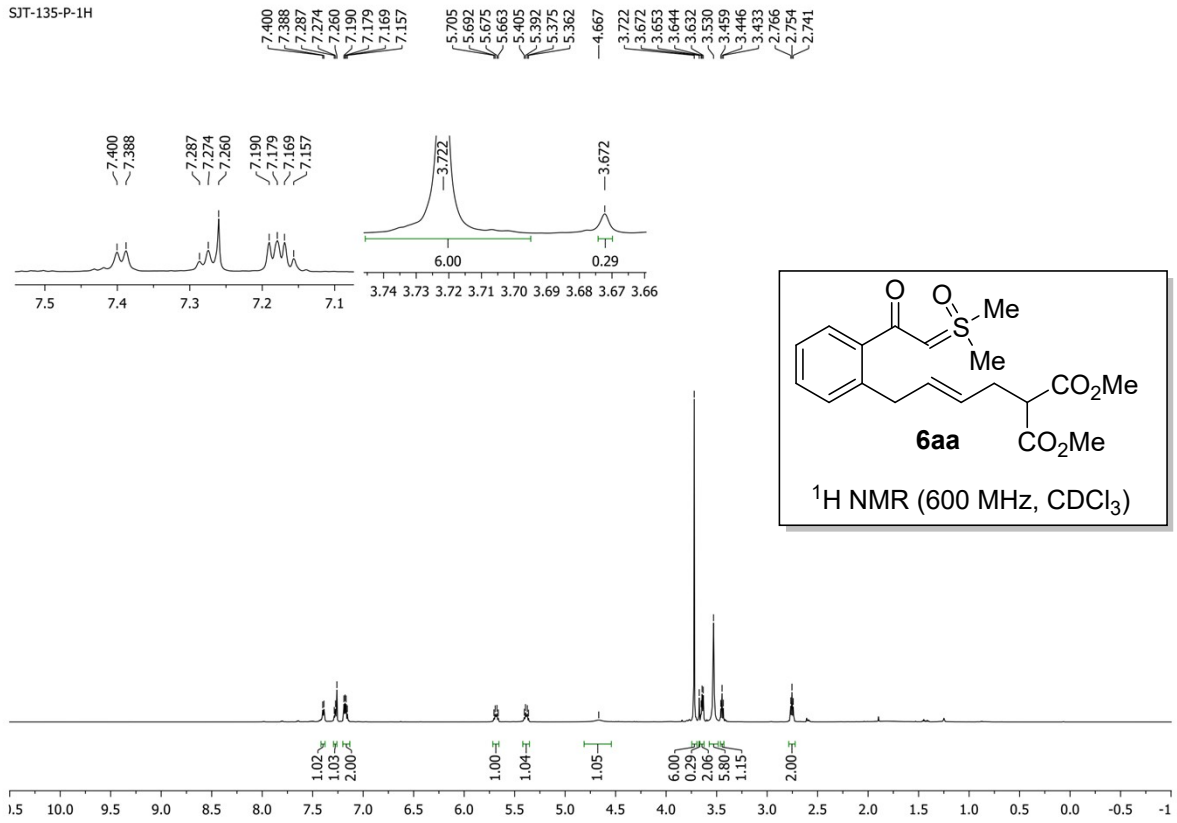
A mixture of 2-(dimethyl(oxo)-l6-sulfaneylidene)-1-(4 methoxyphenyl)ethan-1-one **1i** (0.25 mmol, 46 mg) and 2-(dimethyl(oxo)-l6 sulfaneylidene)-1-(4-methoxyphenyl-2,6-d2)ethan-1-one **1i-*d*$_2$** (0.3 mmol, 48 mg) [93% D] was reacted with dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **2a** (0.3 mmol, 165 mg) in 1,2-DCE (8 mL) for 1 h at standard reaction conditions. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (15 mL) and passed through a short pad of celite. Then the solvent was removed under vacuum and the purification was performed as described in the general procedure to afford mixture of **6ia/ 6ia-*d*** in 32% yield and the KIE value was determined to be P_H/P_D = 1.5, based on ^{1}H NMR analysis (See Scheme 6b).

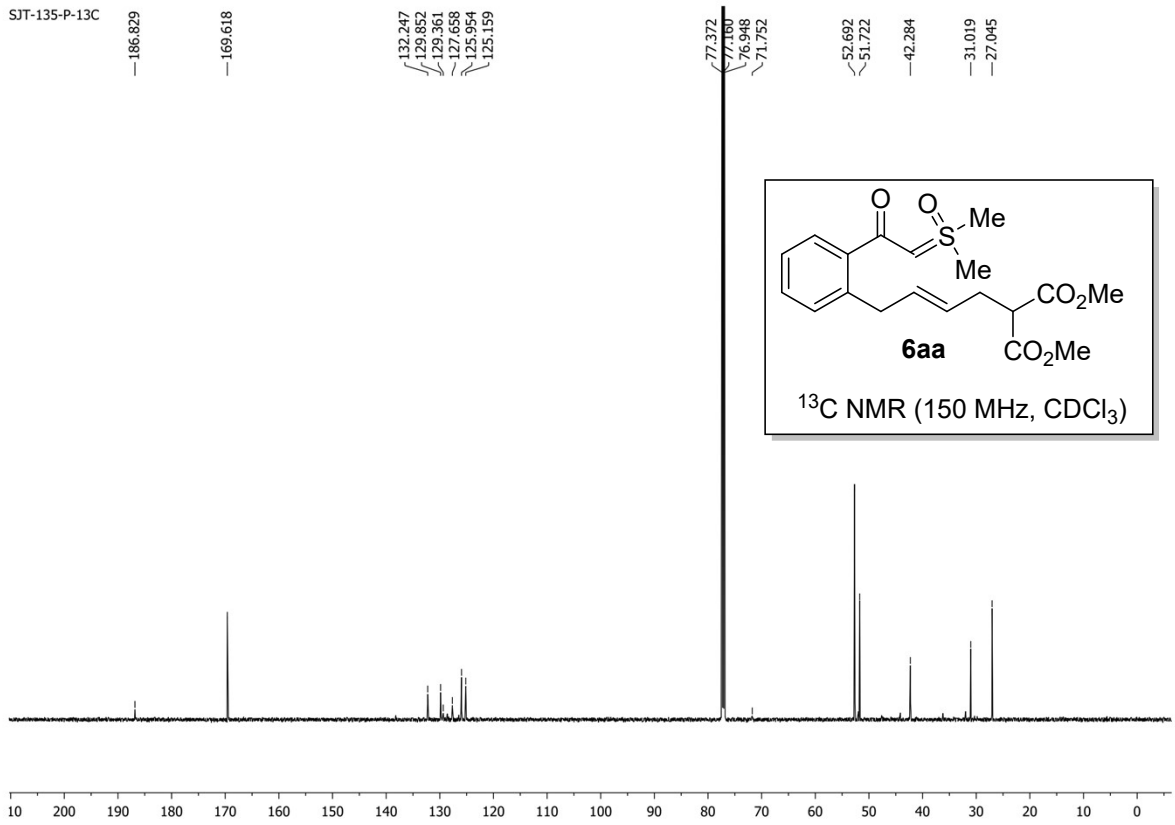
References

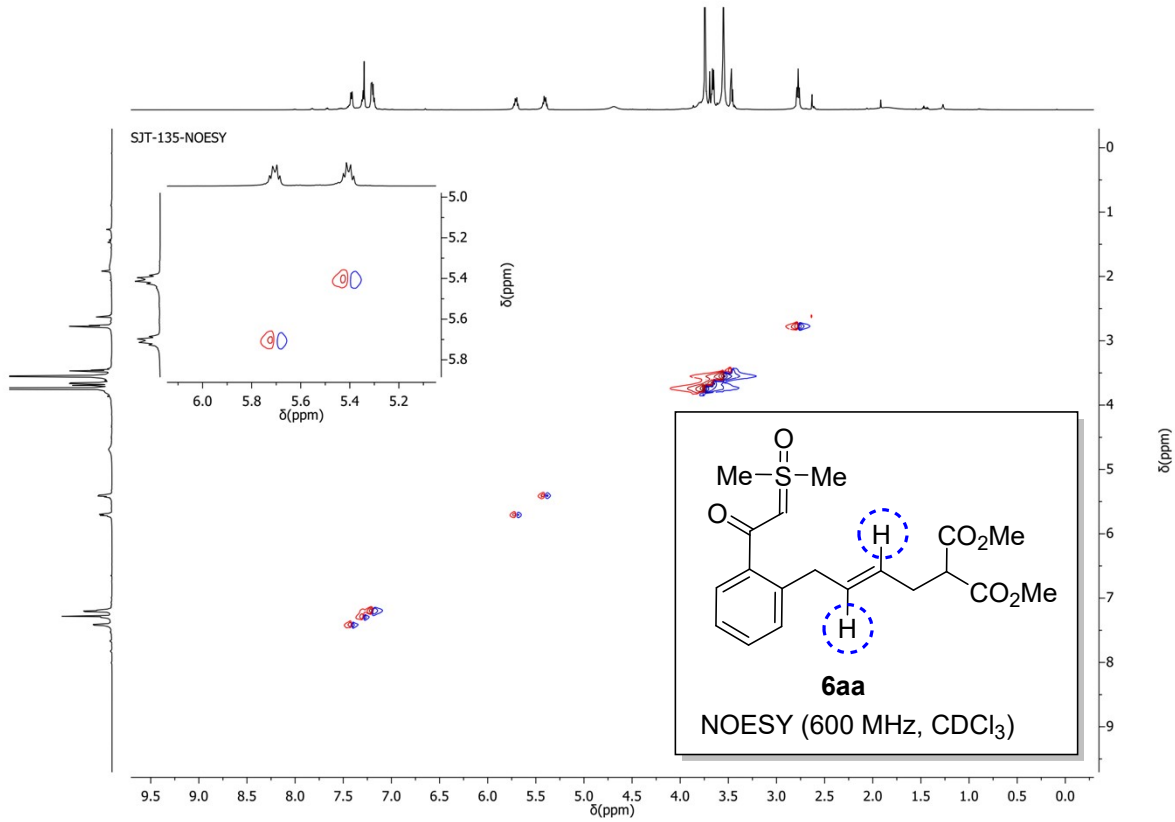
1. For preparation of sulfoxonium ylides, see: (*a*) P. Wang, Y. Xu, J. Sun and X. Li, *Org. Lett.*, 2019, **21**, 8459; (*b*) J. Lou, Q. Wang, Y.-G. Zhou and Z. Yu, *Org. Lett.*, 2019, **21**, 9217; (*c*) Y. Kommagalla, S. Ando and N. Chatani, *Org. Lett.*, 2020, **22**, 1375; (*d*) S. Kumar, S. Nunewar, T. K. Sabbi and V. Kanchupalli, *Org. Lett.*, 2022, **24**, 3395.
2. For preparation of VCPs and vinyl aziridines, see: (*a*) A. T. Parsons, M. J. Campbell and J. S. Johnson, *Org. Lett.*, 2008, **10**, 2541; (*b*) P. D. Pohlhaus, S. D. Sanders, A. T. Parsons, W. Li and J. S. Johnson, *J. Am. Chem. Soc.*, 2008, **130**, 8642; (*c*) A. P. Dieskau, M. S. Holzwarth and B. Plietker, *J. Am. Chem. Soc.*, 2012, **134**, 5048; (*d*) T. H. Meyer, W. Liu, M. Feldt, A. Wuttke, R. A. Mata and L. Ackermann, *Chem.-Eur. J.*, 2017, **23**, 5443; (*e*) Q. Lu, F. J. R. Klauck and F. Glorius, *Chem. Sci.*, 2017, **8**, 3379; (*f*) M. M. Littleson, C. M. Baker, A. J. Dalençon, E. C. Frye, C. Jamieson, A. R. Kennedy, K. B. Ling, M. M. McLachlan, M. G. Montgomery, C. J. Russell and A. J. B. Watson, *Nat. Commun.,* 2018, **9***,* 1105; (*g*) Q. Wang, C.-L. Zhi, P.-P. Lu, S. Liu, X. Zhu, X.-Q. Hao and M.-P. Song, *Adv. Synth. Catal.*, 2019, **361**, 1253; (*h*) F. Wei, C.-L. Ren, D. Wang and L. Liu, *Chem.-Eur. J.*, 2015, **21**, 2335; (*i*) L. Kong, B. Biletskyi, D. Nuel and H. Clavier, *Org. Chem. Front.*, 2018, **5**, 1600.
3. For post synthetic modifications, see: (*a*) N. Kumar, A. Sharma, U. Kumar and S. K. Pandey, *J. Org. Chem.*, 2023, **88**, 6120; (*b*) Q. Jia, L. Kong and X. Li, *Org. Chem. Front.*,

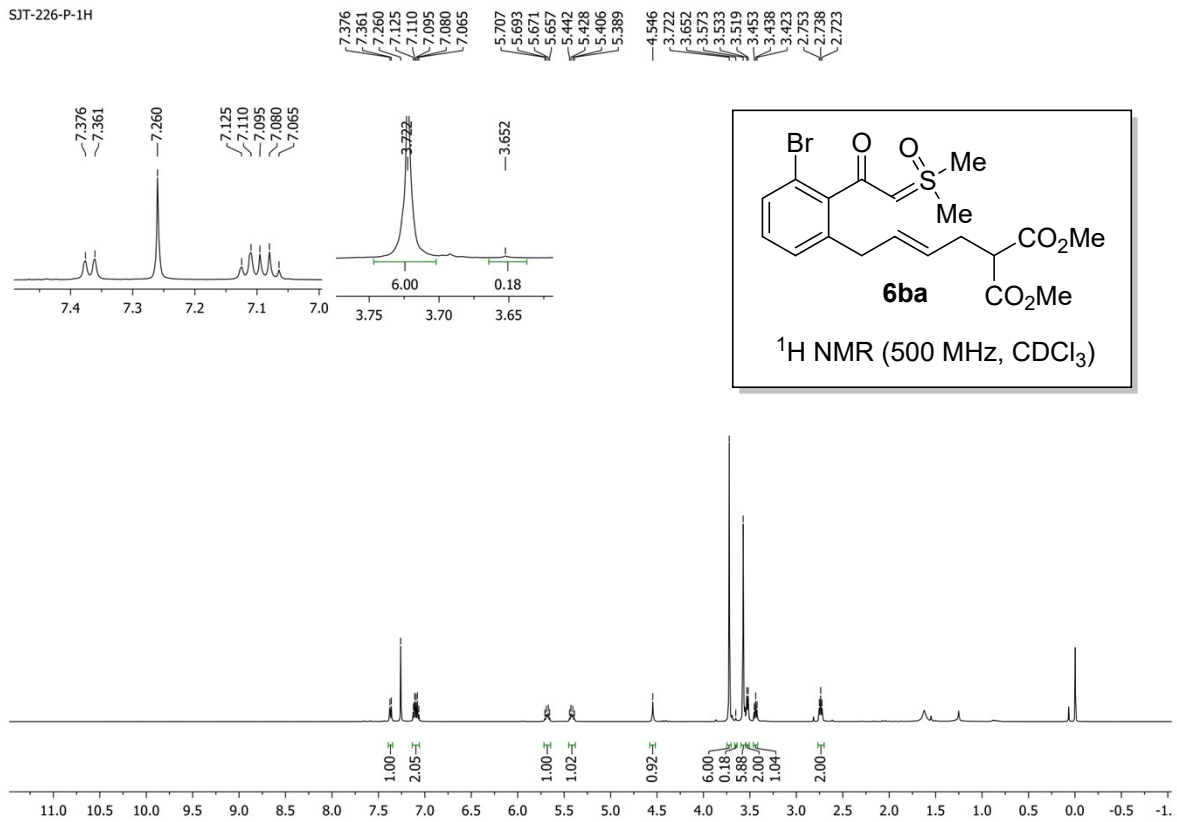
2019, **6**, 741; (*c*) L. Fang, S. Fan, W. Wu, T. Li and J. Zhu, *Chem. Commun.*, 2021, **57**, 7386.

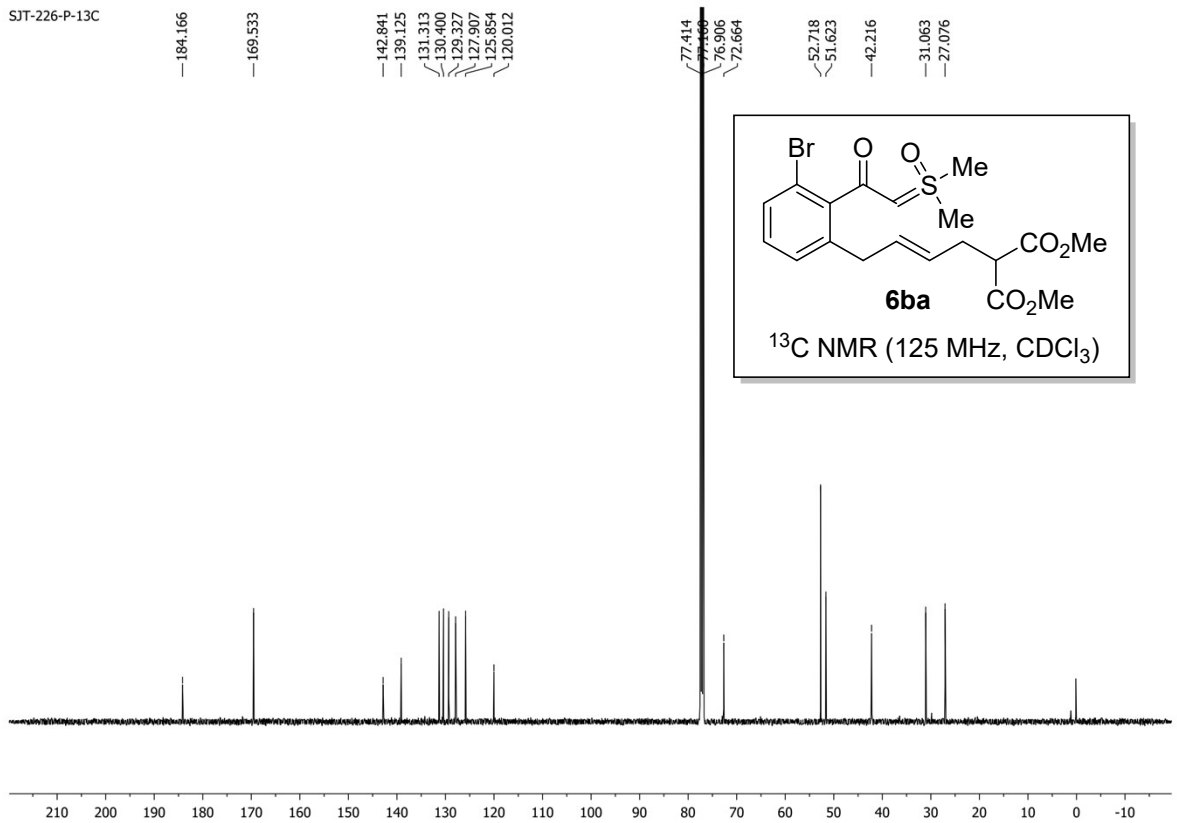
NMR (^{1}H, ^{13}C, ^{19}F and NOESY) and HPLC Spectra

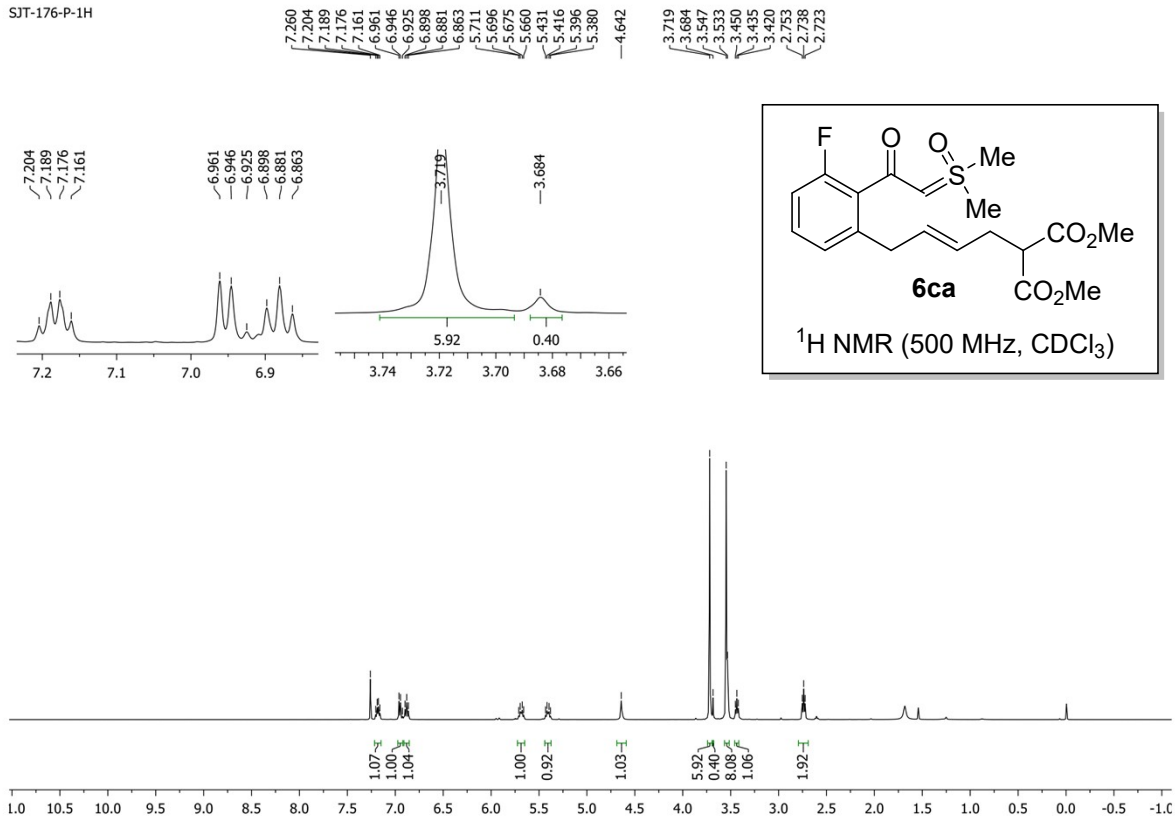


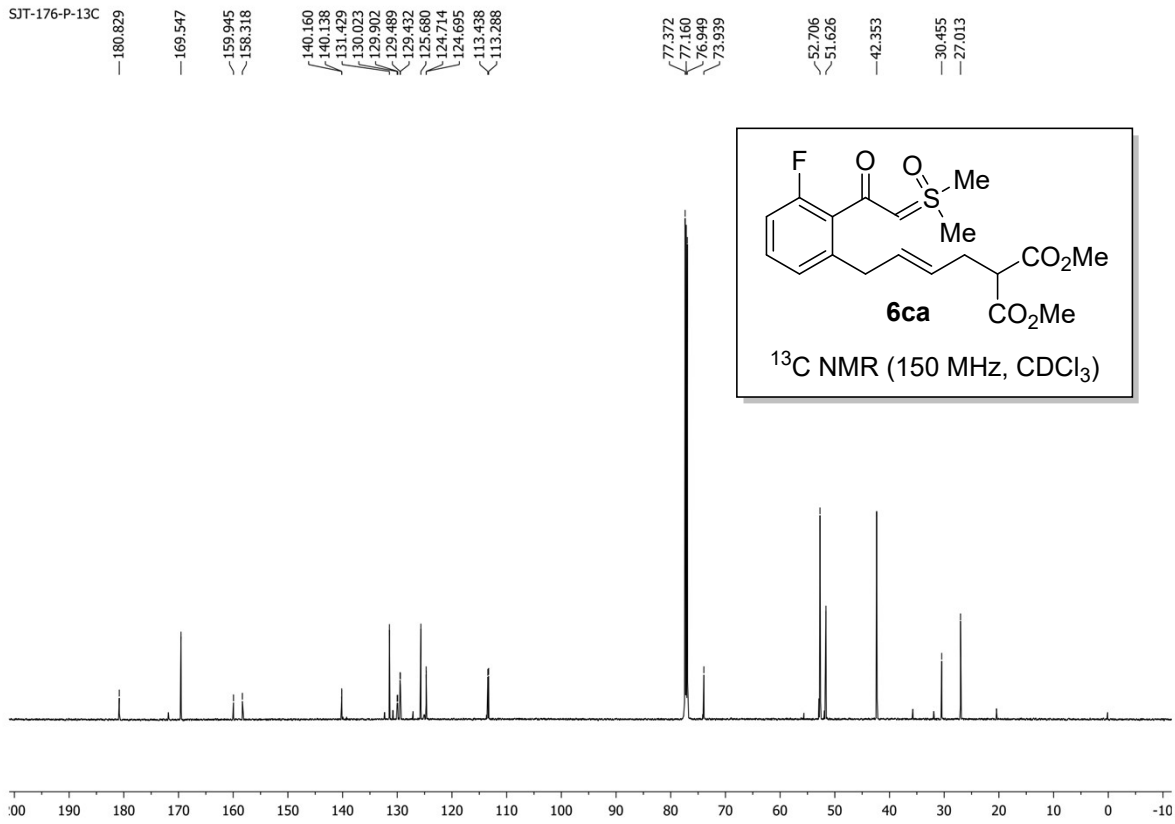

SJT-135-P-13C
186.829
169.618
132.247
129.852
129.361
127.658
125.954
125.159
77.372
77.160
76.948
71.752
52.692
51.722
42.284
31.019
27.045
O
O
S
Me
Me
CO2Me
CO2Me
6aa
13C NMR (150 MHz, CDCl3)


SJT-135-NOESY
δ(ppm)
Me−S−Me
O
O
H
H
CO2Me
CO2Me
6aa
NOESY (600 MHz, CDCl3)

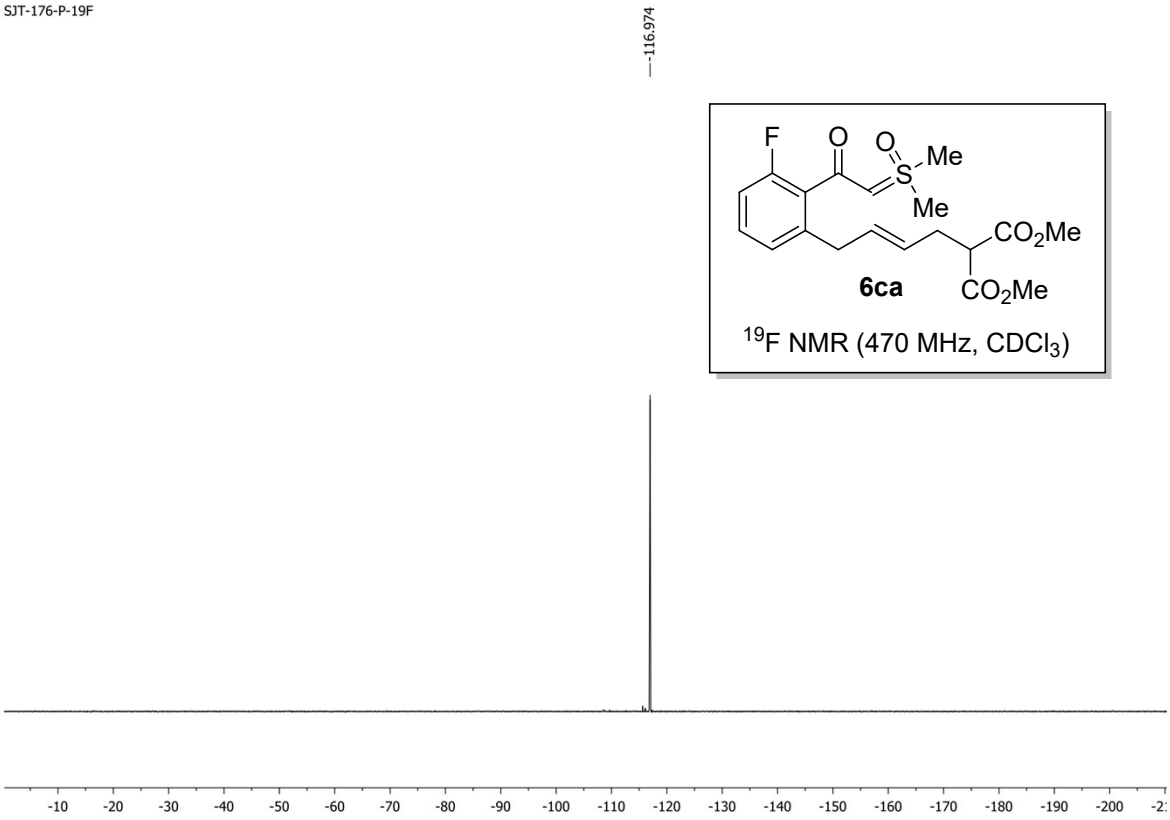

SJT-226-P-1H
7.376
7.361
7.260
7.125
7.110
7.095
7.080
7.065
5.707
5.693
5.671
5.657
5.442
5.428
5.406
5.389
4.546
3.722
3.652
3.573
3.533
3.519
3.453
3.438
3.423
2.753
2.738
2.723
6.00
0.18
Br
O
O
S
Me
Me
CO2Me
CO2Me
6ba
1H NMR (500 MHz, CDCl3)
1.00
2.05
1.00
1.02
0.92
6.00
0.18
5.88
2.00
1.04
2.00


SJT-226-P-13C
184.166
169.533
142.841
139.125
131.313
130.400
129.327
127.907
125.854
120.012
77.414
77.166
76.906
72.664
52.718
51.623
42.216
31.063
27.076
Br
O
O
S
Me
Me
CO2Me
CO2Me
6ba
13C NMR (125 MHz, CDCl3)


SJT-176-P-1H
7.260
7.204
7.189
7.176
7.161
6.961
6.946
6.925
6.898
6.881
6.863
5.711
5.696
5.675
5.660
5.431
5.416
5.396
5.380
4.642
3.719
3.684
3.547
3.533
3.450
3.435
3.420
2.753
2.738
2.723
5.92
0.40
F
O
O
Me
S
Me
CO2Me
6ca
CO2Me
1H NMR (500 MHz, CDCl3)

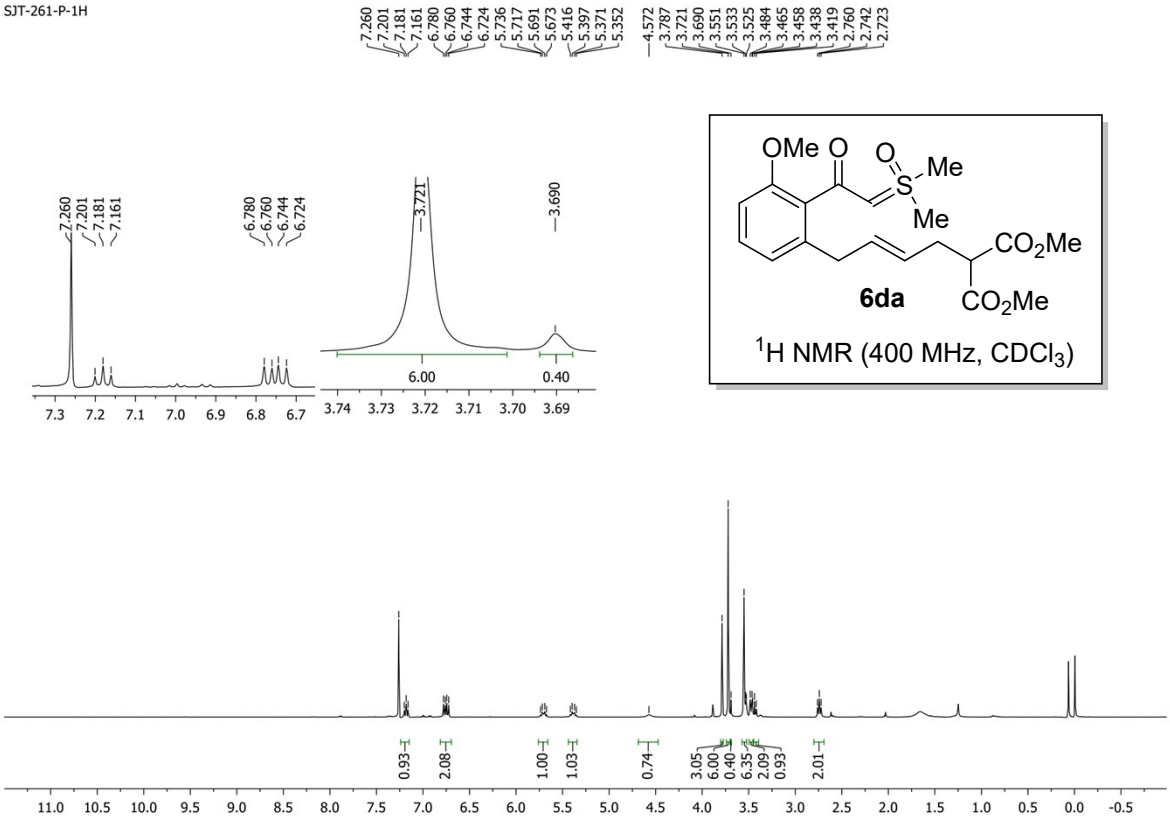

SJT-176-P-13C
180.829
169.547
159.945
158.318
140.160
140.138
131.429
130.023
129.902
129.489
129.432
125.680
124.714
124.695
113.438
113.288
77.372
77.160
76.949
73.939
52.706
51.626
42.353
30.455
27.013
F
O
O
Me
S
Me
CO2Me
6ca
CO2Me
13C NMR (150 MHz, CDCl3)

SJT-176-P-19F

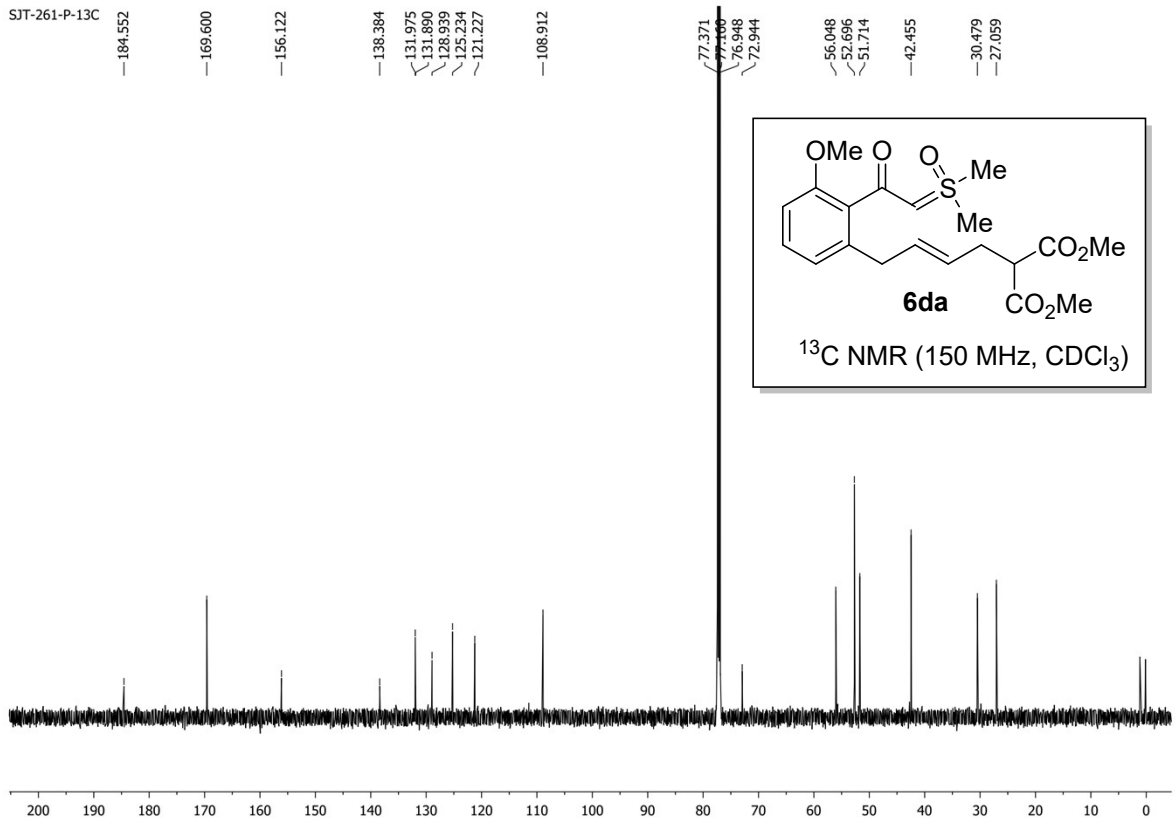


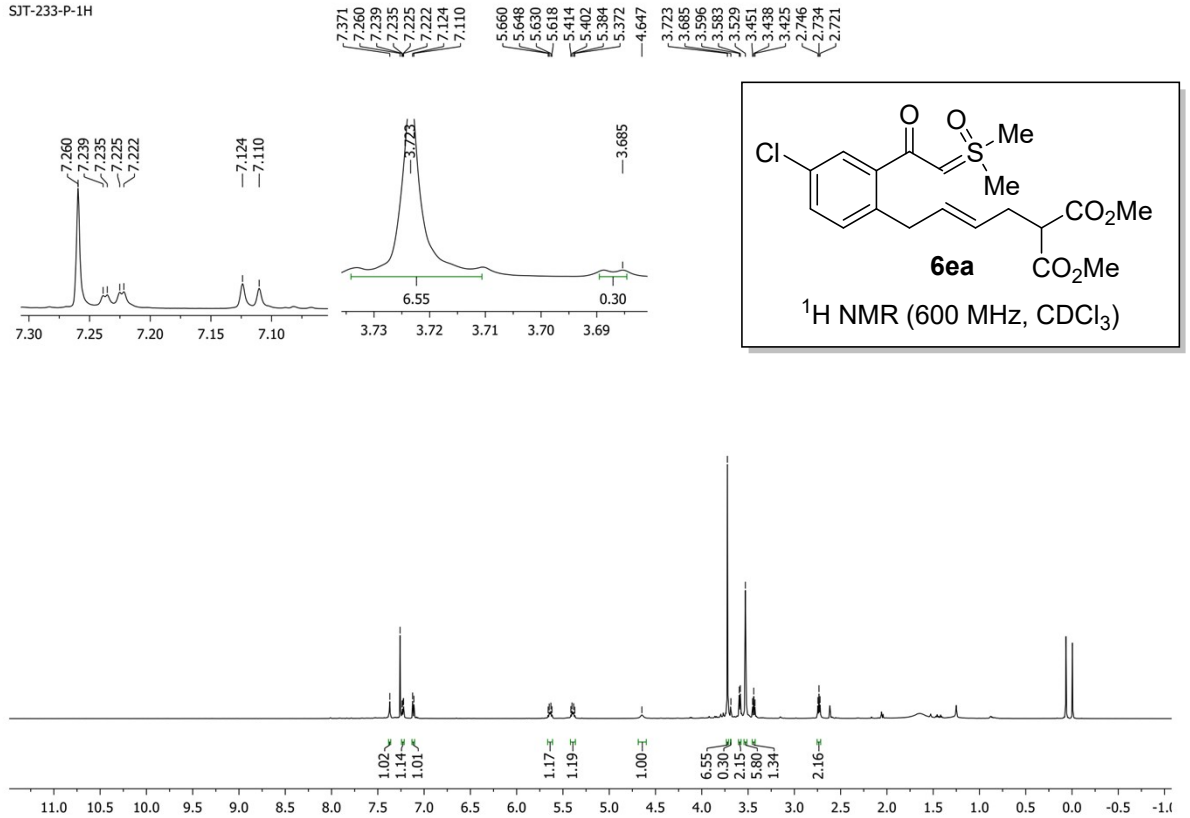
^{19}F NMR (470 MHz, $CDCl_3$)

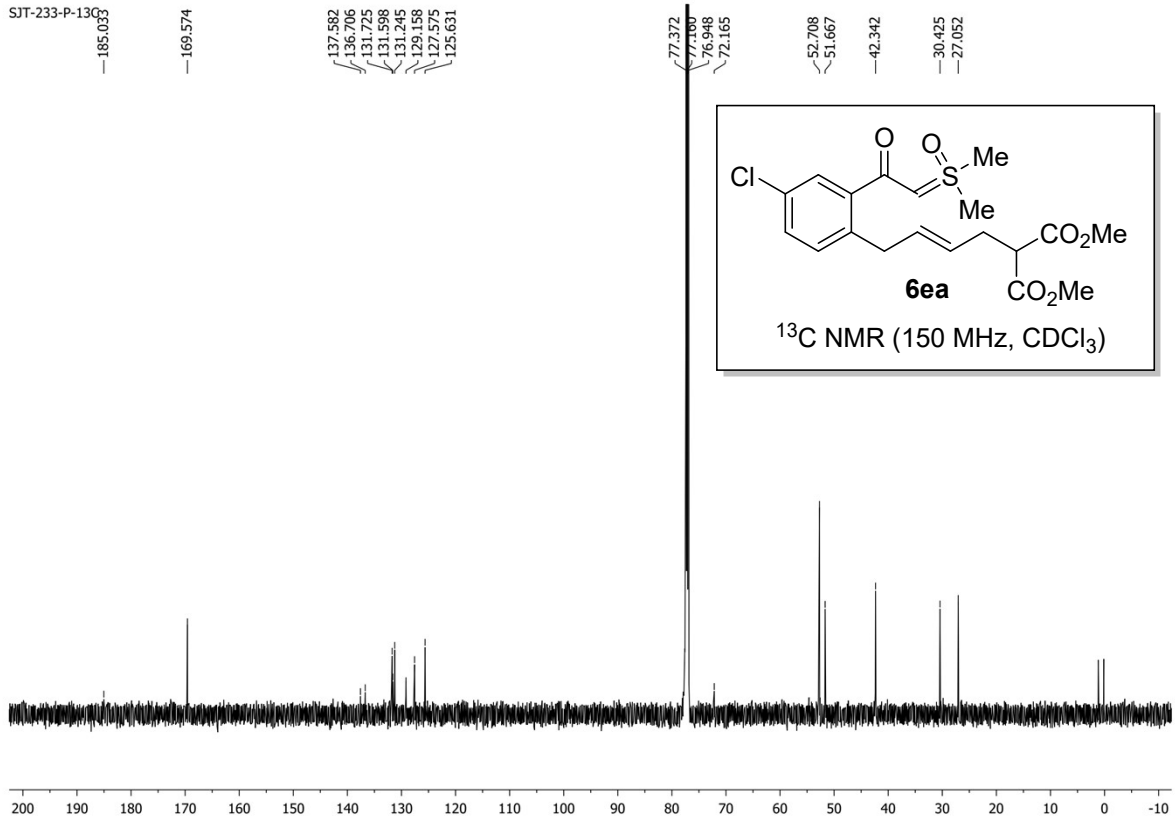
SJT-261-P-1H

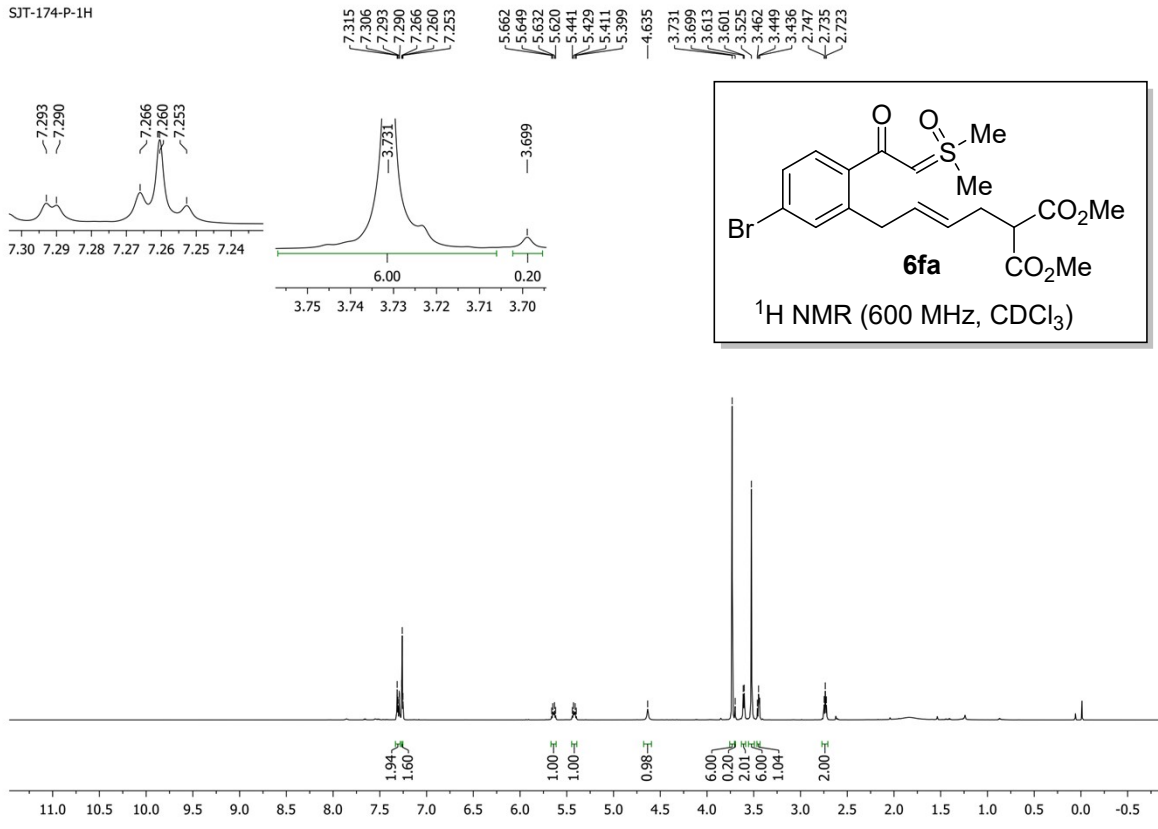


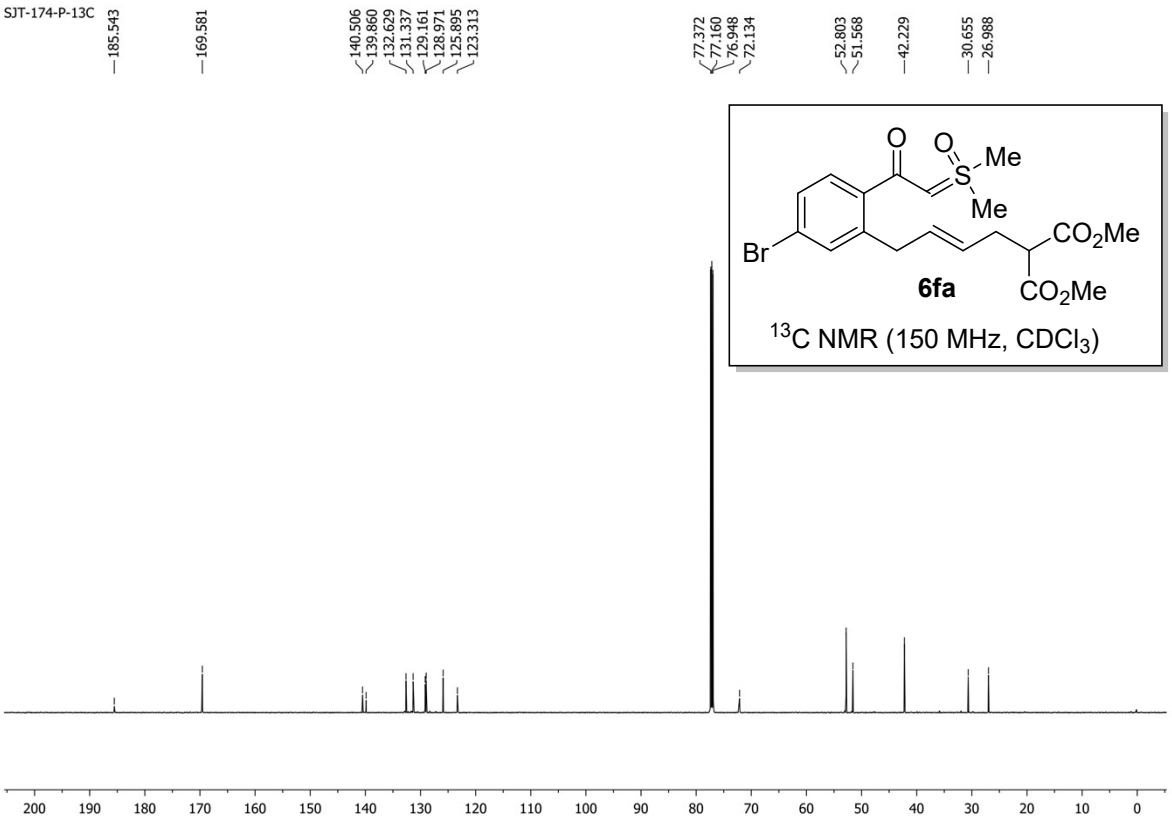
^{1}H NMR (400 MHz, $CDCl_3$)

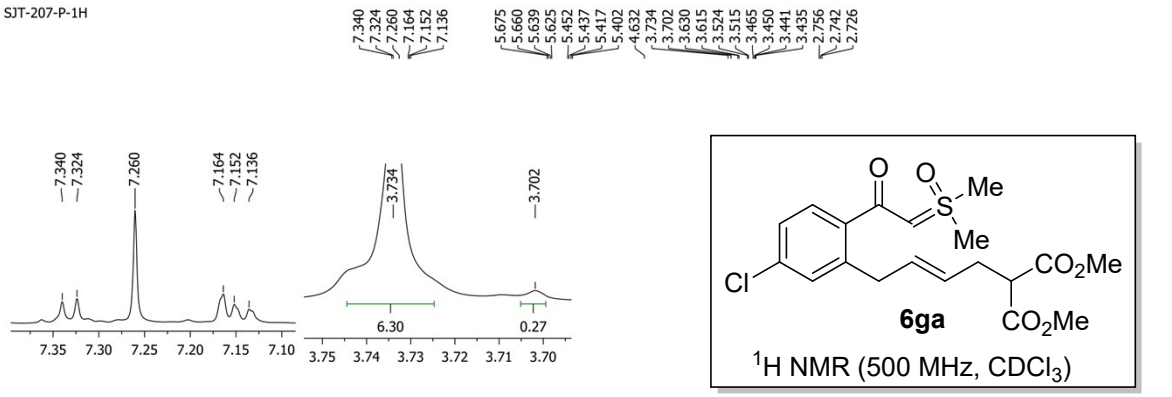

SJT-261-P-13C
184.552
169.600
156.122
138.384
131.975
131.890
128.939
125.234
121.227
108.912
77.371
77.160
76.948
72.944
56.048
52.696
51.714
42.455
30.479
27.059
OMe
O
O
S
Me
Me
CO2Me
CO2Me
6da
13C NMR (150 MHz, CDCl3)

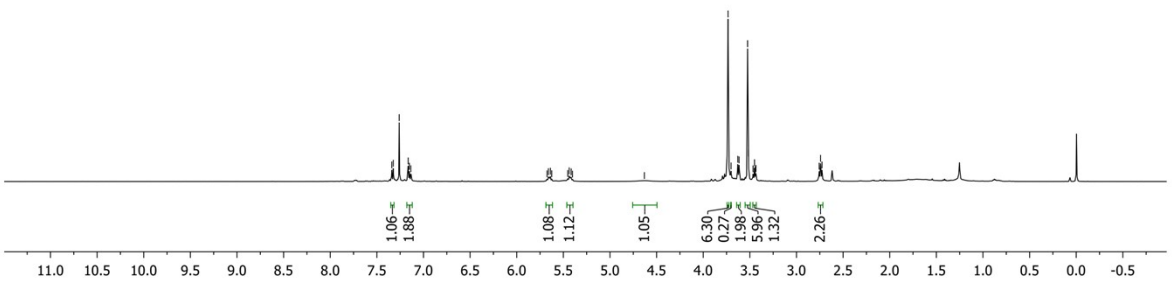

SJT-233-P-1H
7.371
7.260
7.239
7.235
7.225
7.222
7.124
7.110
5.660
5.648
5.630
5.618
5.414
5.402
5.384
5.372
4.647
3.723
3.685
3.596
3.583
3.529
3.451
3.438
3.425
2.746
2.734
2.721
6.55
0.30
1.02
1.14
1.01
1.17
1.19
1.00
6.55
0.30
2.15
5.80
1.34
2.16
Cl
O
O
S
Me
Me
CO2Me
CO2Me
6ea
1H NMR (600 MHz, CDCl3)

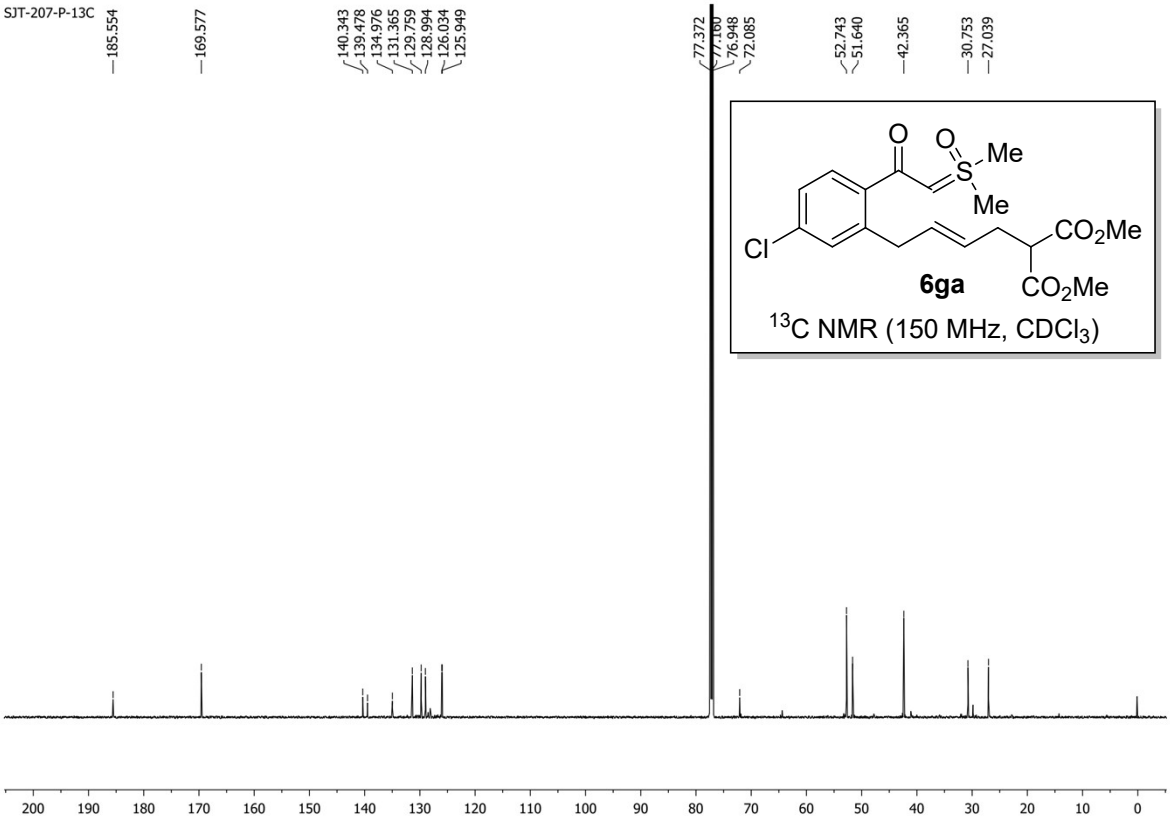

SJT-233-P-13C
185.033
169.574
137.582
136.706
131.725
131.598
131.245
129.158
127.575
125.631
77.372
77.160
76.948
72.165
52.708
51.667
42.342
30.425
27.052
O
O
S
Me
Me
Cl
CO2Me
CO2Me
6ea
13C NMR (150 MHz, CDCl3)

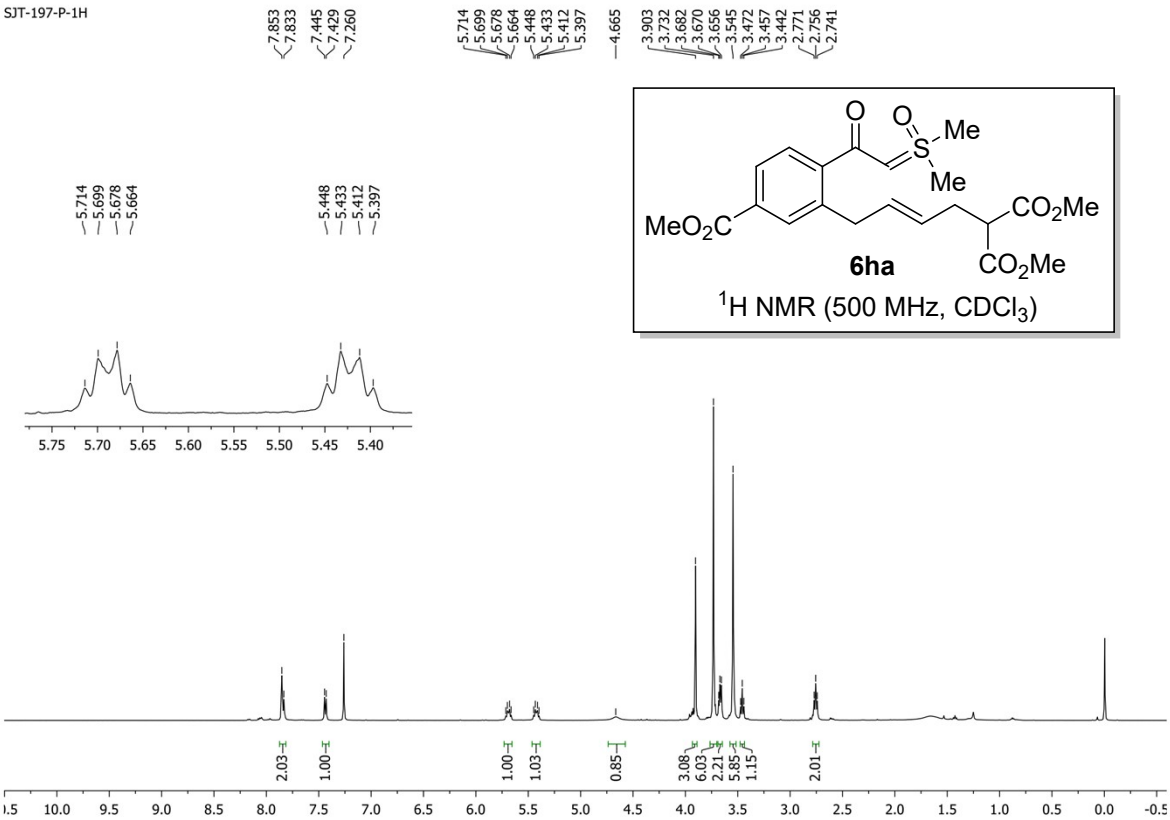

SJT-174-P-1H
7.315
7.306
7.293
7.290
7.266
7.260
7.253
5.662
5.649
5.632
5.620
5.441
5.429
5.411
5.399
4.635
3.731
3.699
3.613
3.601
3.525
3.462
3.449
3.436
2.747
2.735
2.723
7.293
7.290
7.266
7.260
7.253
3.731
3.699
6.00
0.20
O
O
S
Me
Me
Br
CO2Me
CO2Me
6fa
1H NMR (600 MHz, CDCl3)
1.94
1.60
1.00
1.00
0.98
6.00
0.20
2.01
6.00
1.04
2.00

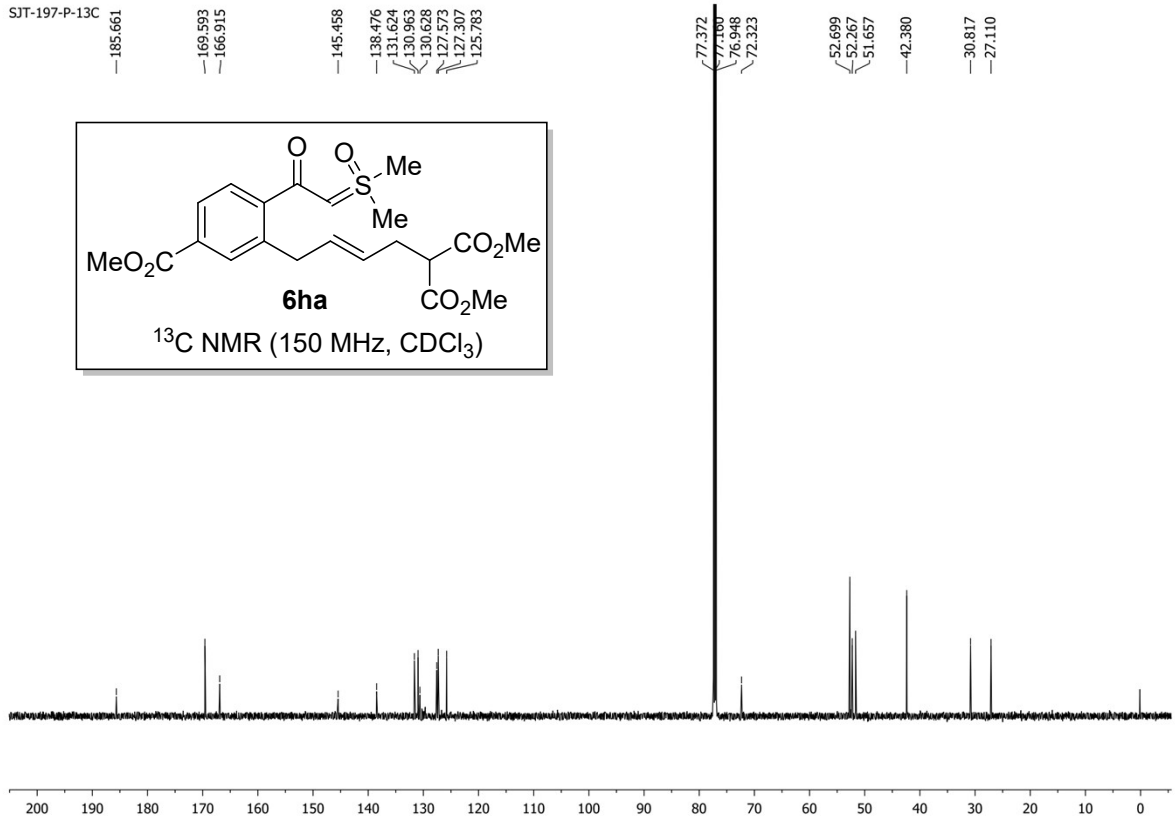

SJT-174-P-13C
185.543
169.581
140.506
139.860
132.629
131.337
129.161
128.971
125.895
123.313
77.372
77.160
76.948
72.134
52.803
51.568
42.229
30.655
26.988
O
O
S
Me
Me
Br
CO2Me
CO2Me
6fa
13C NMR (150 MHz, CDCl3)

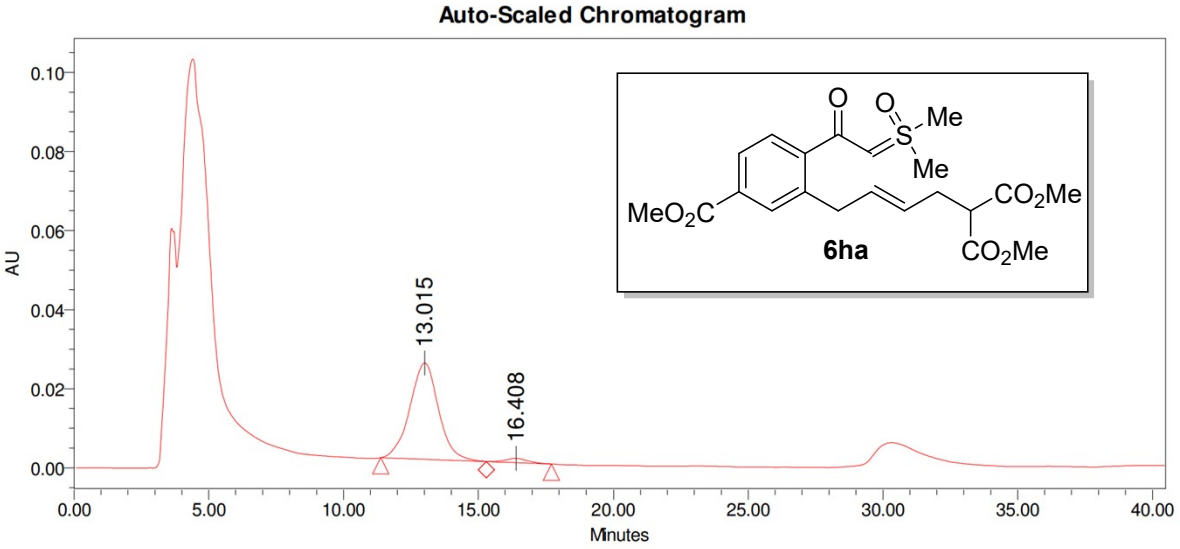

SJT-207-P-1H
7.340
7.324
7.260
7.164
7.152
7.136
5.675
5.660
5.639
5.625
5.452
5.437
5.417
5.402
4.632
3.734
3.702
3.630
3.615
3.524
3.515
3.465
3.450
3.441
3.435
2.756
2.742
2.726
6.30
0.27
O
O
S
Me
Me
Cl
CO2Me
CO2Me
6ga
1H NMR (500 MHz, CDCl3)


1.06
1.88
1.08
1.12
1.05
6.30
0.27
1.98
5.96
1.32
2.26


SJT-207-P-13C
185.554
169.577
140.343
139.478
134.976
131.365
129.759
128.994
126.034
125.949
77.372
77.100
76.948
72.085
52.743
51.640
42.365
30.753
27.039
O
O
S
Me
Me
Cl
CO2Me
CO2Me
6ga
13C NMR (150 MHz, CDCl3)

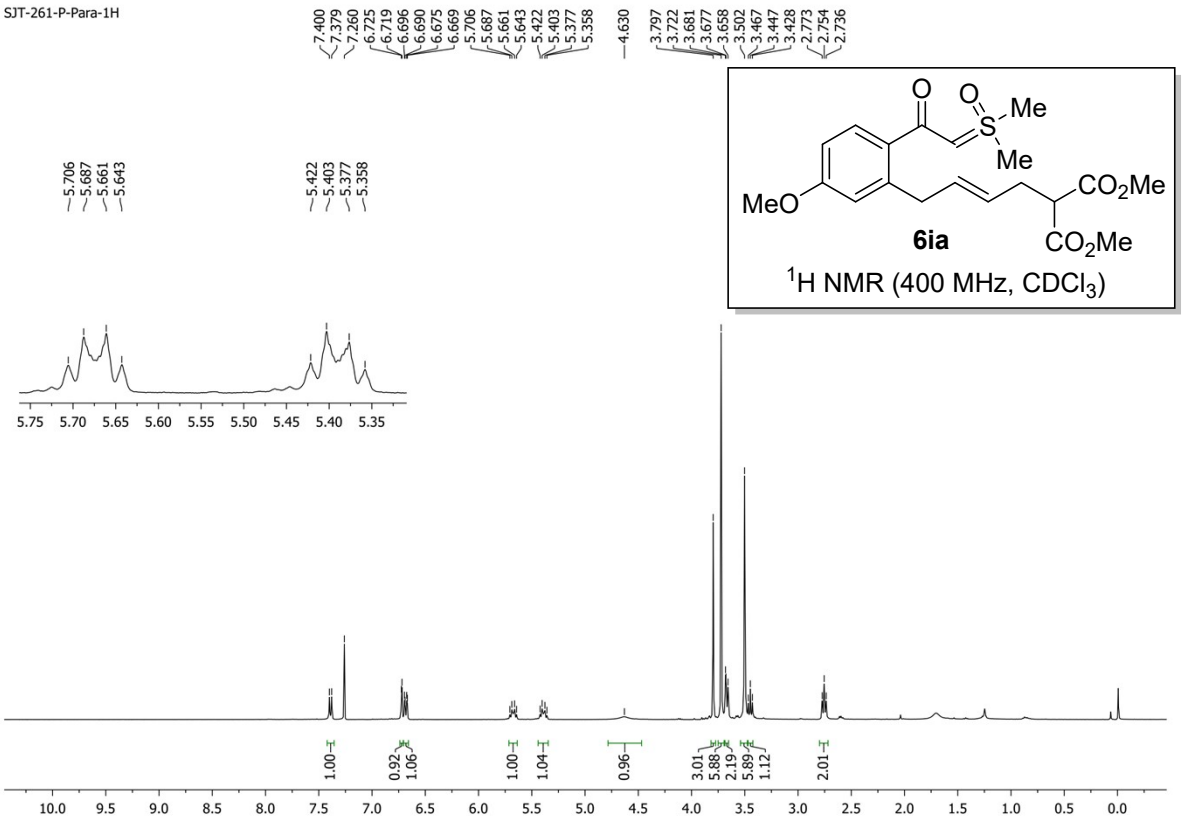

SJT-197-P-1H
7.853
7.833
7.445
7.429
7.260
5.714
5.699
5.678
5.664
5.448
5.433
5.412
5.397
4.665
3.903
3.732
3.682
3.670
3.656
3.545
3.472
3.457
3.442
2.771
2.756
2.741
O
O
S
Me
Me
MeO2C
CO2Me
CO2Me
6ha
1H NMR (500 MHz, CDCl3)
2.03
1.00
1.00
1.03
0.85
3.08
6.03
2.21
5.85
1.15
2.01

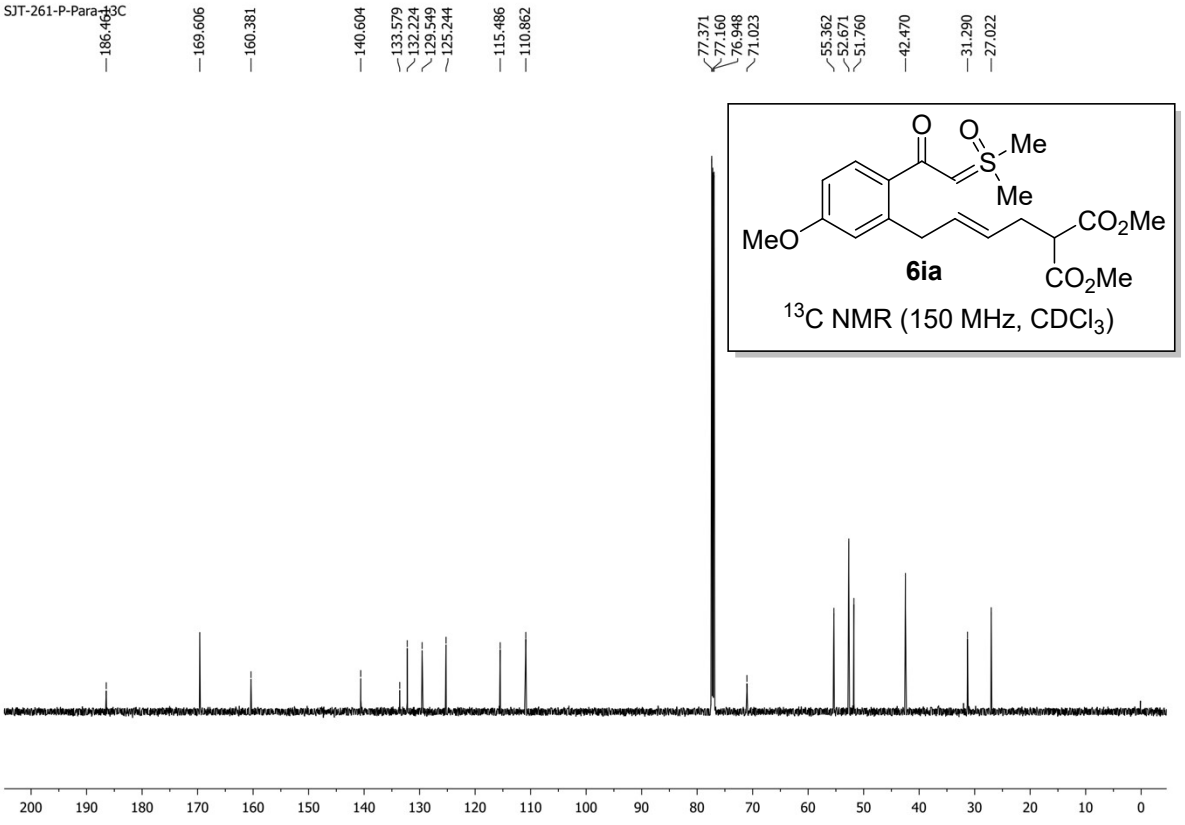


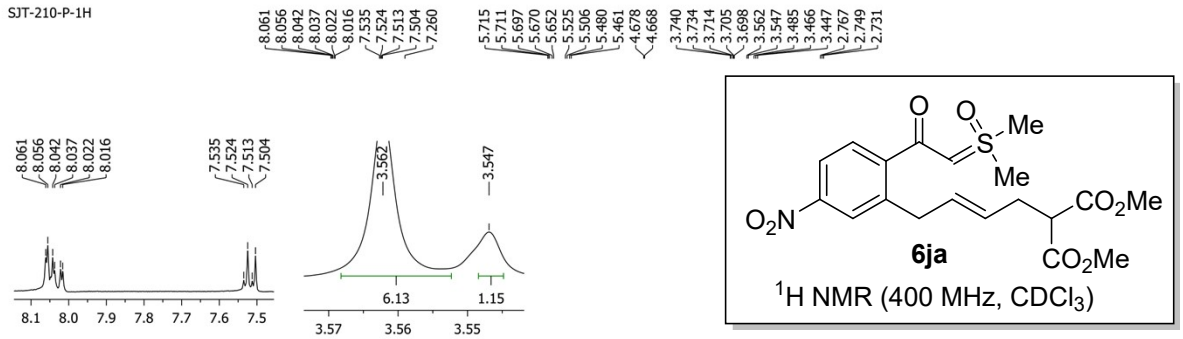


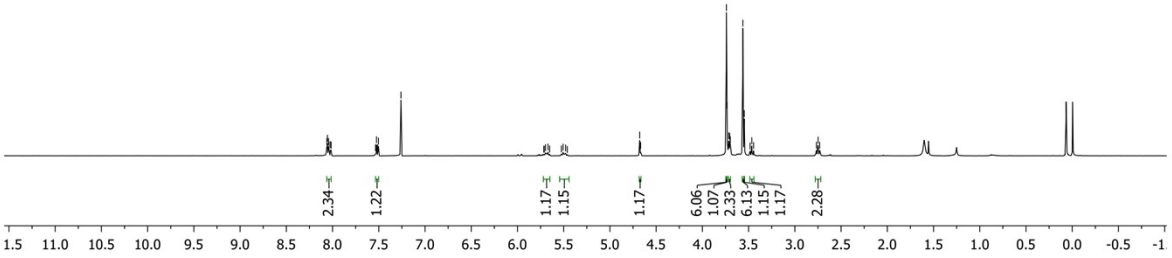
Peak Results

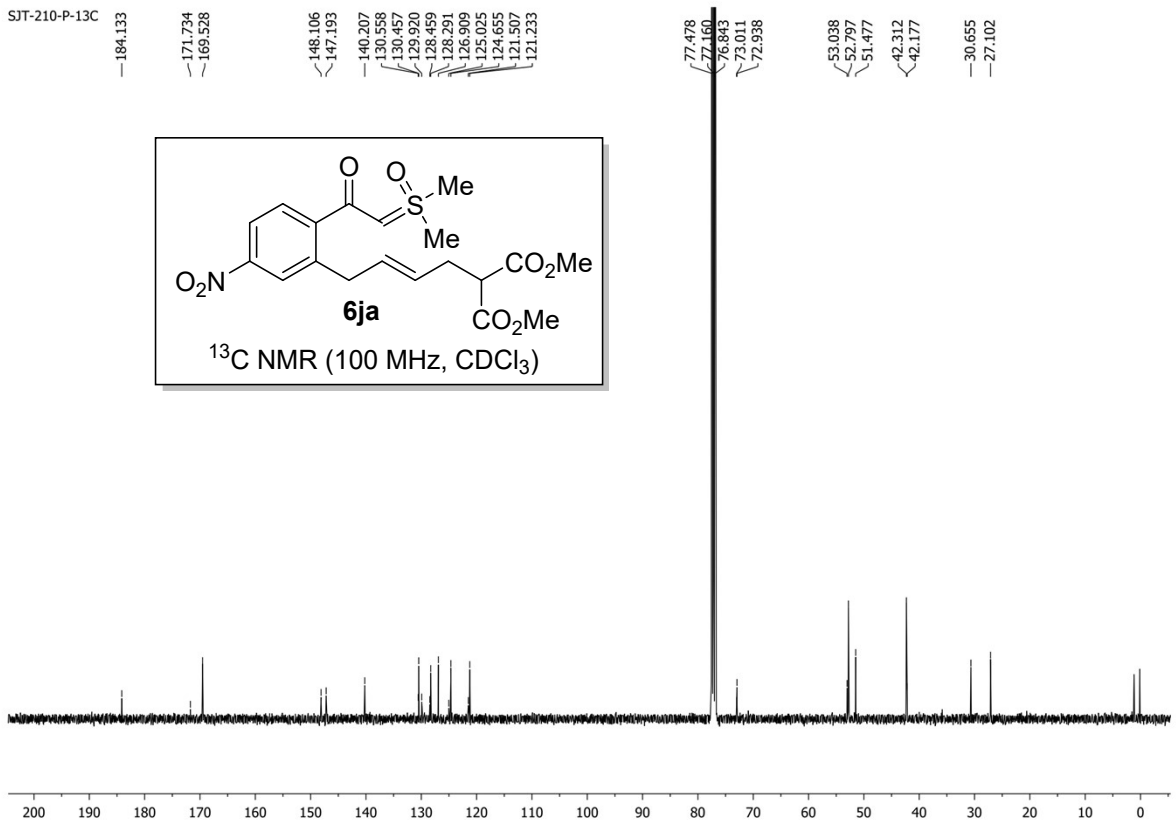
	Start Time (min)	End Time (min)	RT	Height (μV)	% Area
1	11.383	15.300	13.015	24339	96.56
2	15.300	17.717	16.408	1110	3.44

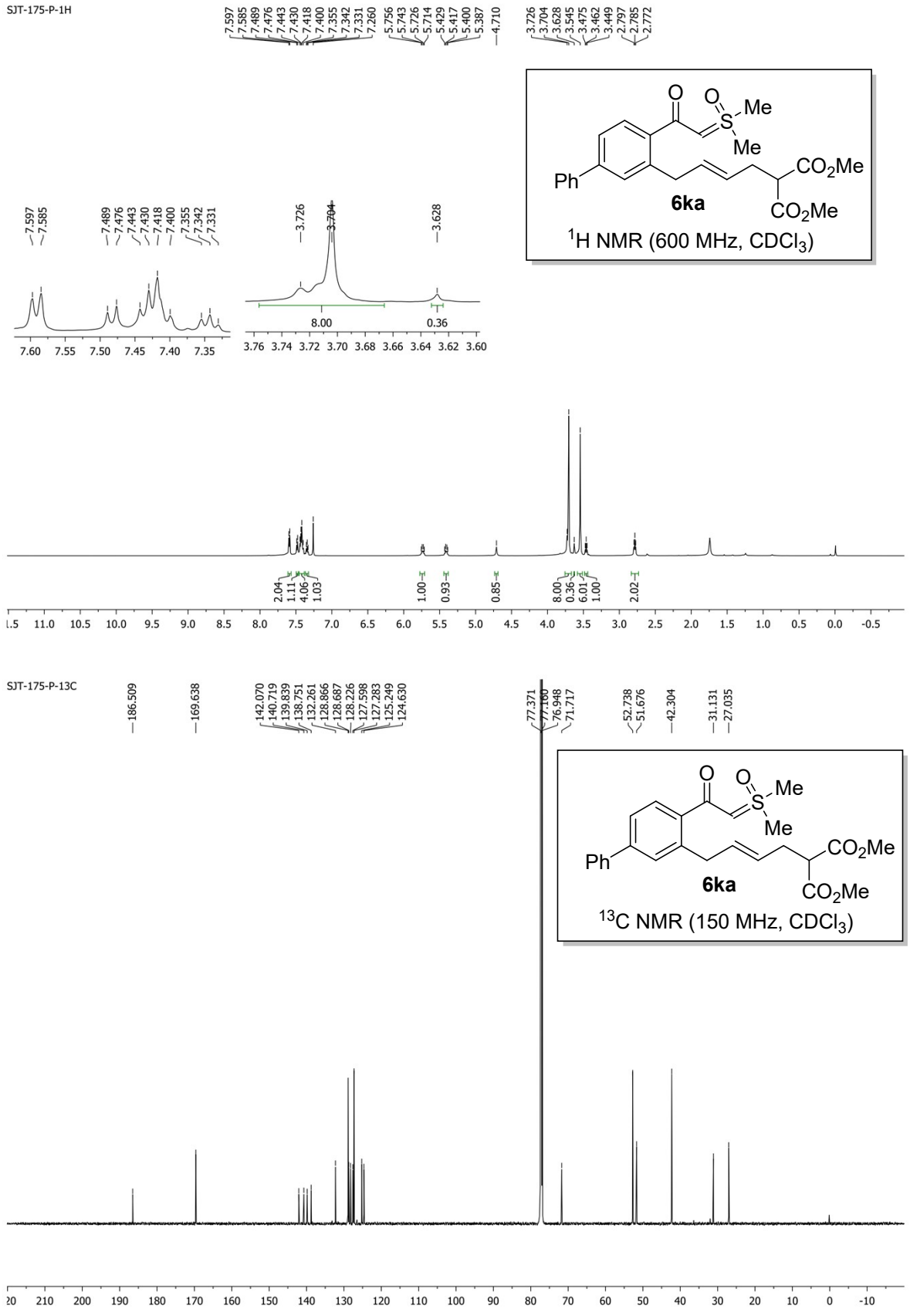

SJT-261-P-Para-1H
7.400
7.379
7.260
6.725
6.719
6.696
6.690
6.675
6.669
5.706
5.687
5.661
5.643
5.422
5.403
5.377
5.358
4.630
3.797
3.722
3.681
3.677
3.658
3.502
3.467
3.447
3.428
2.773
2.754
2.736
O
O
S
Me
Me
MeO
CO2Me
CO2Me
6ia
1H NMR (400 MHz, CDCl3)
1.00
0.92
1.06
1.00
1.04
0.96
3.01
5.88
2.19
5.89
1.12
2.01

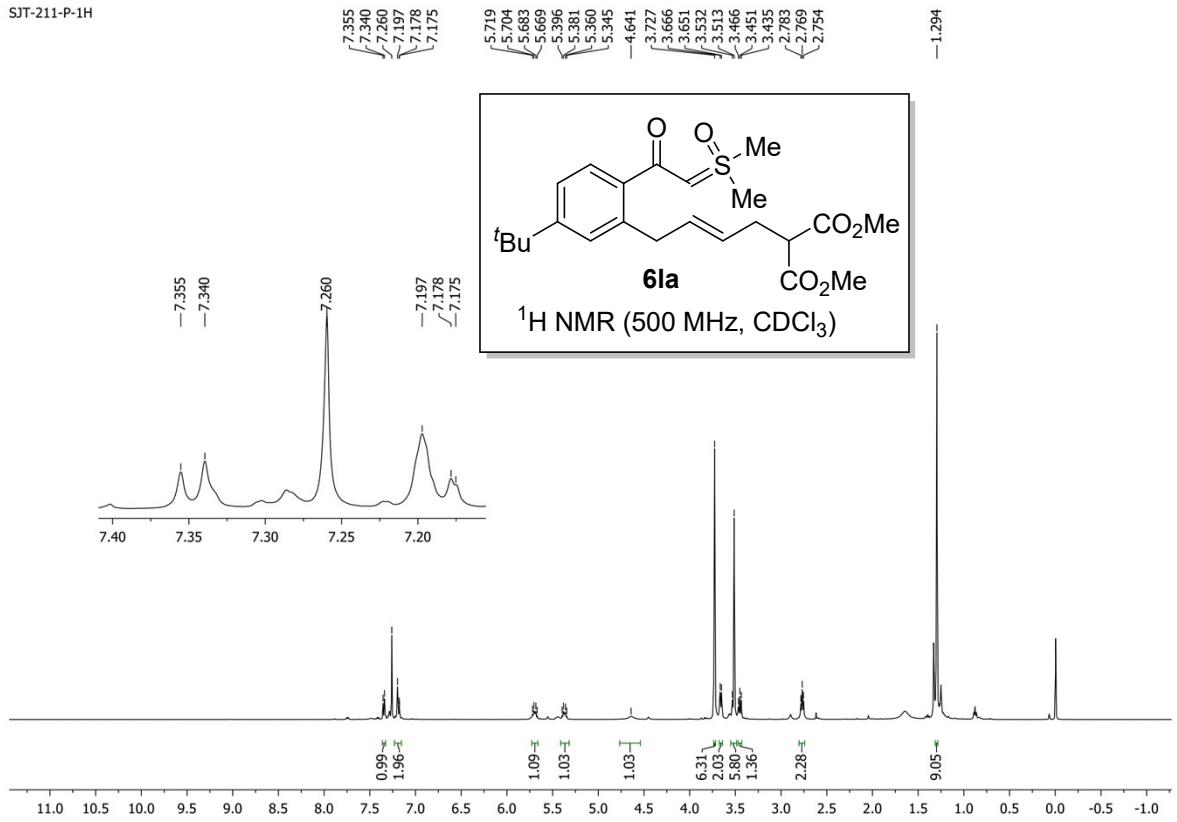

SJT-261-P-Para-13C
186.462
169.606
160.381
140.604
133.579
132.224
129.549
125.244
115.486
110.862
77.371
77.160
76.948
71.023
55.362
52.671
51.760
42.470
31.290
27.022
O
O
S
Me
Me
MeO
CO2Me
CO2Me
6ia
13C NMR (150 MHz, CDCl3)

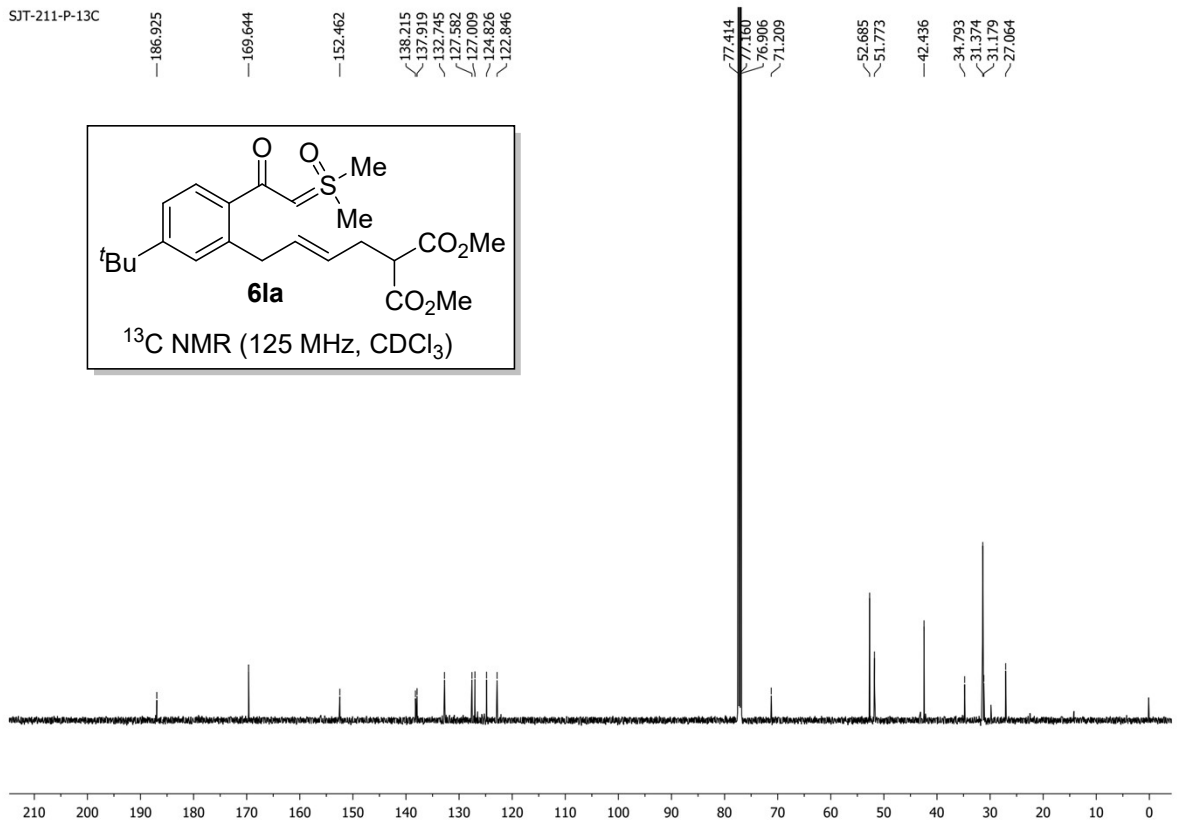

SJT-210-P-1H
8.061
8.056
8.042
8.037
8.022
8.016
7.535
7.524
7.513
7.504
7.260
5.715
5.711
5.697
5.670
5.652
5.525
5.506
5.480
5.461
4.678
4.668
3.740
3.734
3.714
3.705
3.698
3.562
3.547
3.485
3.466
3.447
2.767
2.749
2.731
3.562
3.547
6.13
1.15
8.1 8.0 7.9 7.8 7.7 7.6 7.5
3.57 3.56 3.55
O
O
S
Me
Me
O2N
CO2Me
CO2Me
6ja
1H NMR (400 MHz, CDCl3)

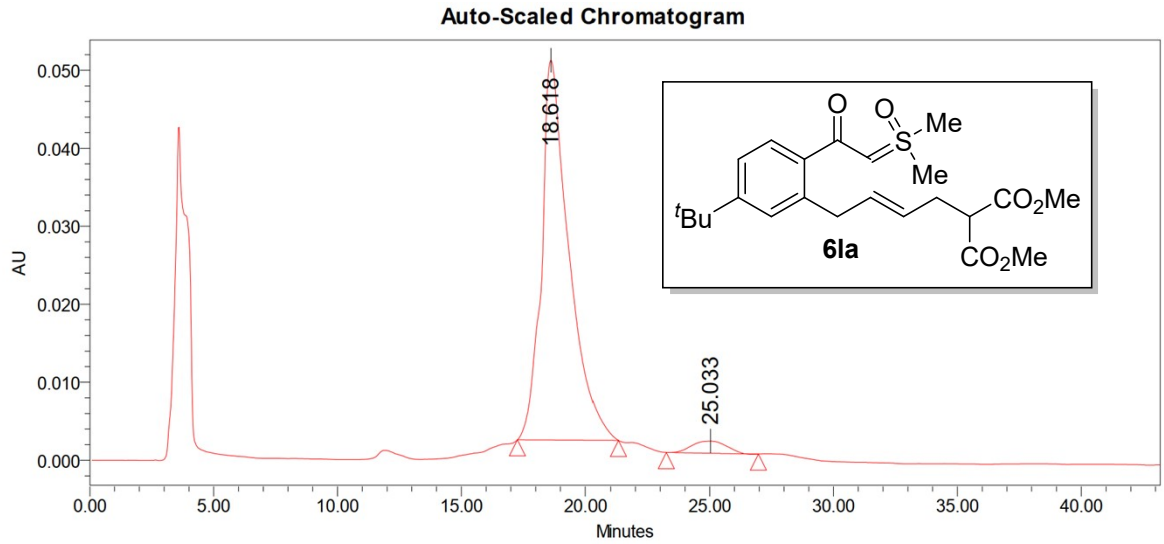

2.34
1.22
1.17
1.15
1.17
6.06
1.07
2.33
6.13
1.15
1.17
2.28
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


SJT-210-P-13C
184.133
171.734
169.528
148.106
147.193
140.207
130.558
130.457
129.920
128.459
128.291
126.909
125.025
124.655
121.507
121.233
77.478
77.160
76.843
73.011
72.938
53.038
52.797
51.477
42.312
42.177
30.655
27.102
O
O
S
Me
Me
O2N
CO2Me
CO2Me
6ja
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


SJT-175-P-1H
7.597
7.585
7.489
7.476
7.443
7.430
7.418
7.400
7.355
7.342
7.331
7.260
5.756
5.743
5.726
5.714
5.429
5.417
5.400
5.387
4.710
3.726
3.704
3.628
3.545
3.475
3.462
3.449
2.797
2.785
2.772
O
O
Me
S
Me
Ph
CO2Me
CO2Me
6ka
1H NMR (600 MHz, CDCl3)
8.00
0.36
2.04
1.11
4.06
1.03
1.00
0.93
0.85
8.00
0.36
6.01
1.00
2.02
SJT-175-P-13C
186.509
169.638
142.070
140.719
139.839
138.751
132.261
128.866
128.687
128.226
127.598
127.283
125.249
124.630
77.371
77.160
76.948
71.717
52.738
51.676
42.304
31.131
27.035
13C NMR (150 MHz, CDCl3)

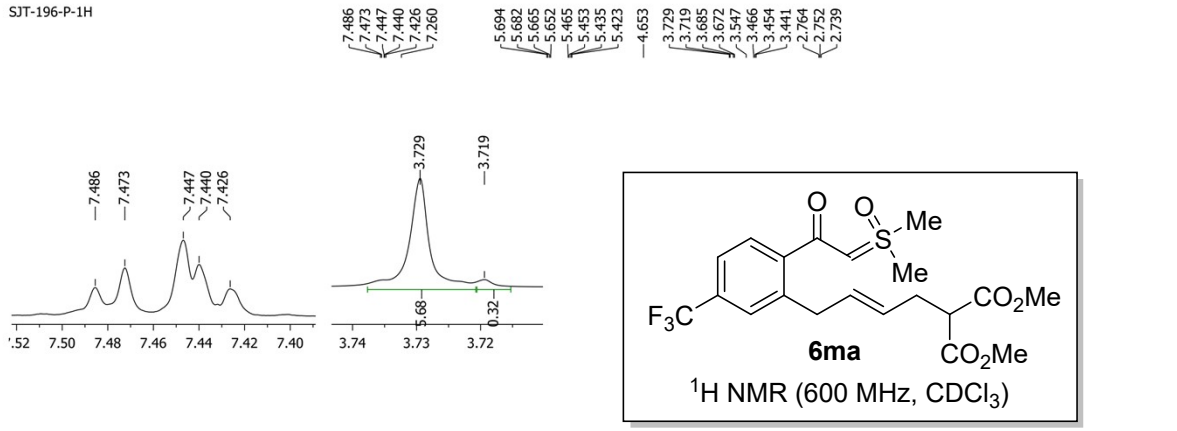

SJT-211-P-1H
7.355
7.340
7.260
7.197
7.178
7.175
5.719
5.704
5.683
5.669
5.396
5.381
5.360
5.345
4.641
3.727
3.666
3.651
3.532
3.513
3.466
3.451
3.435
2.783
2.769
2.754
1.294
O
O
Me
S
Me
tBu
CO2Me
CO2Me
6la
1H NMR (500 MHz, CDCl3)
0.99
1.96
1.09
1.03
1.03
6.31
2.03
5.80
1.36
2.28
9.05

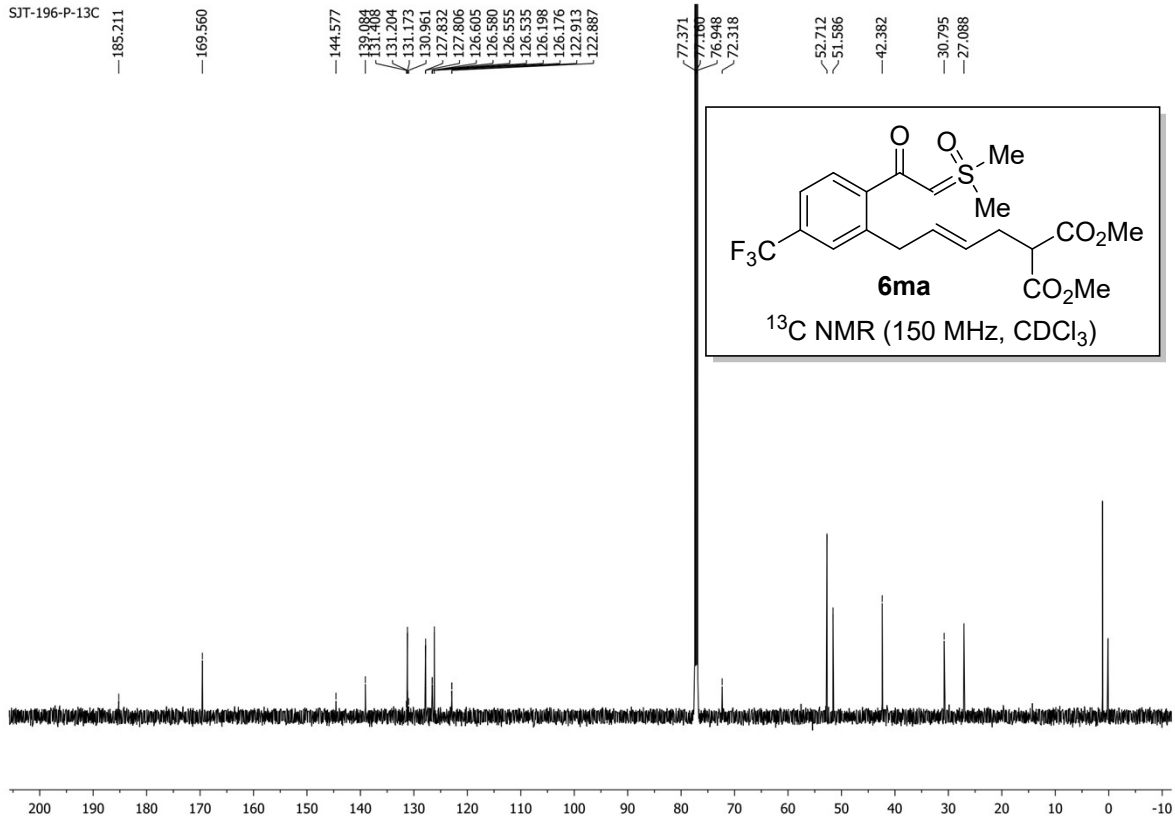

SJT-211-P-13C
186.925
169.644
152.462
138.215
137.919
132.745
127.582
127.009
124.826
122.846
77.414
77.160
76.906
71.209
52.685
51.773
42.436
34.793
31.374
31.179
27.064
O
O
Me
S
Me
tBu
CO2Me
CO2Me
6la
13C NMR (125 MHz, CDCl3)

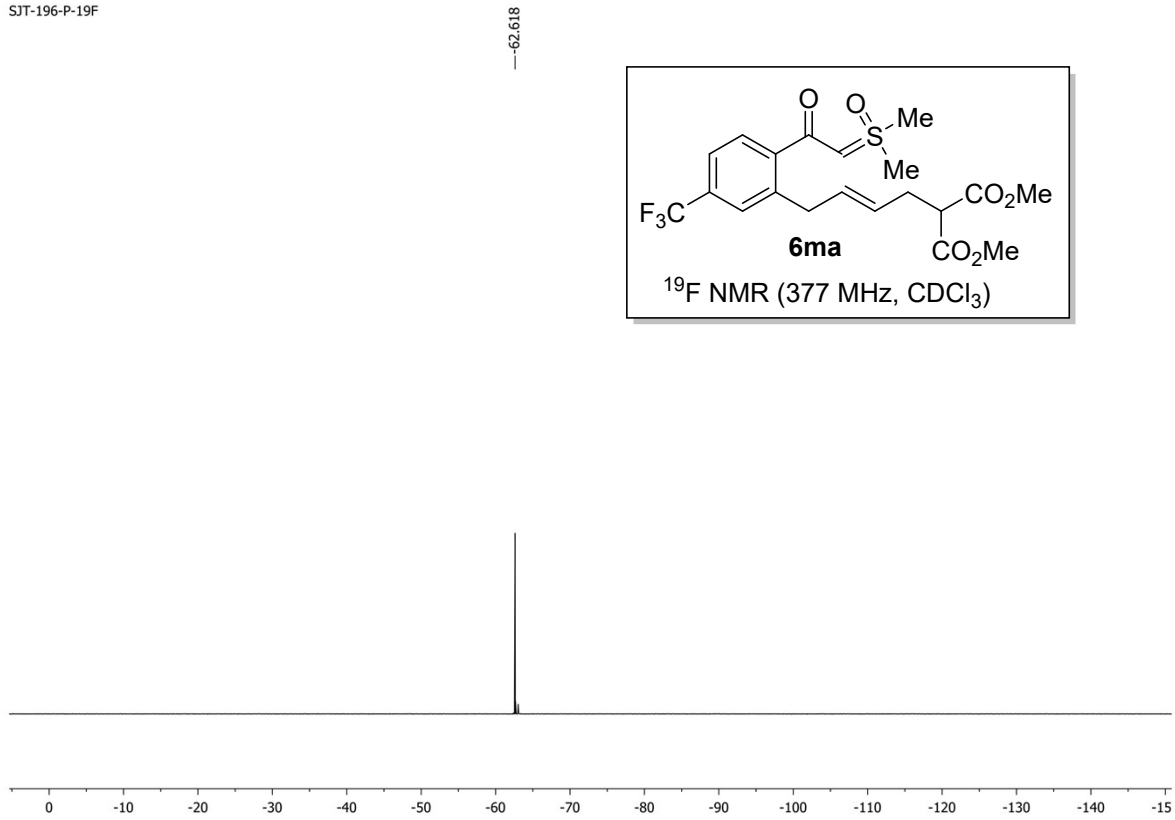


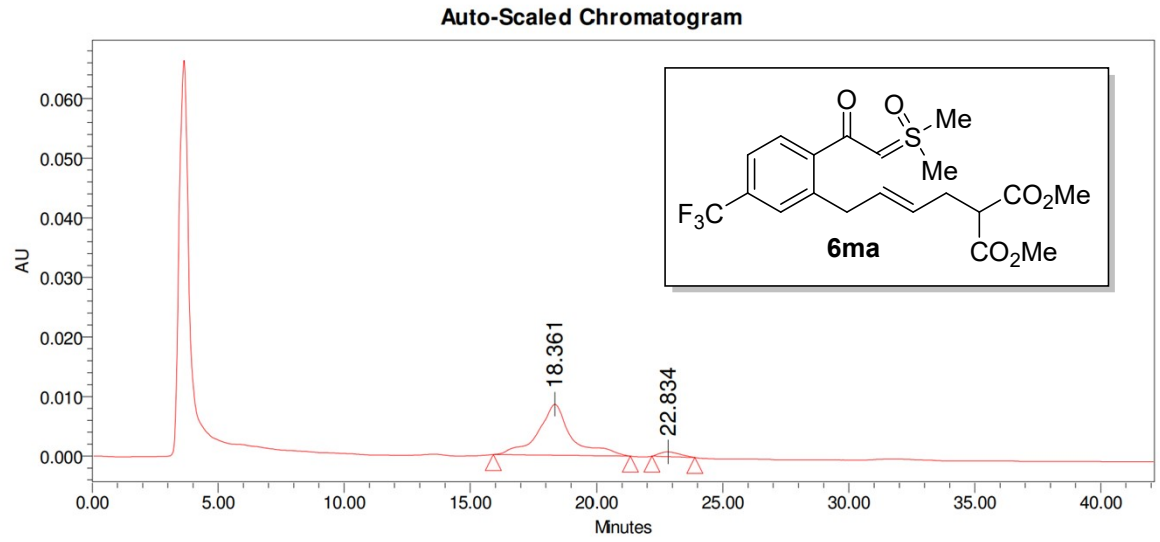
Peak Results

	Start Time (min)	End Time (min)	RT	Height (μV)	% Area
1	17.267	21.317	18.618	48679	96.13
2	23.250	26.967	25.033	1558	3.87



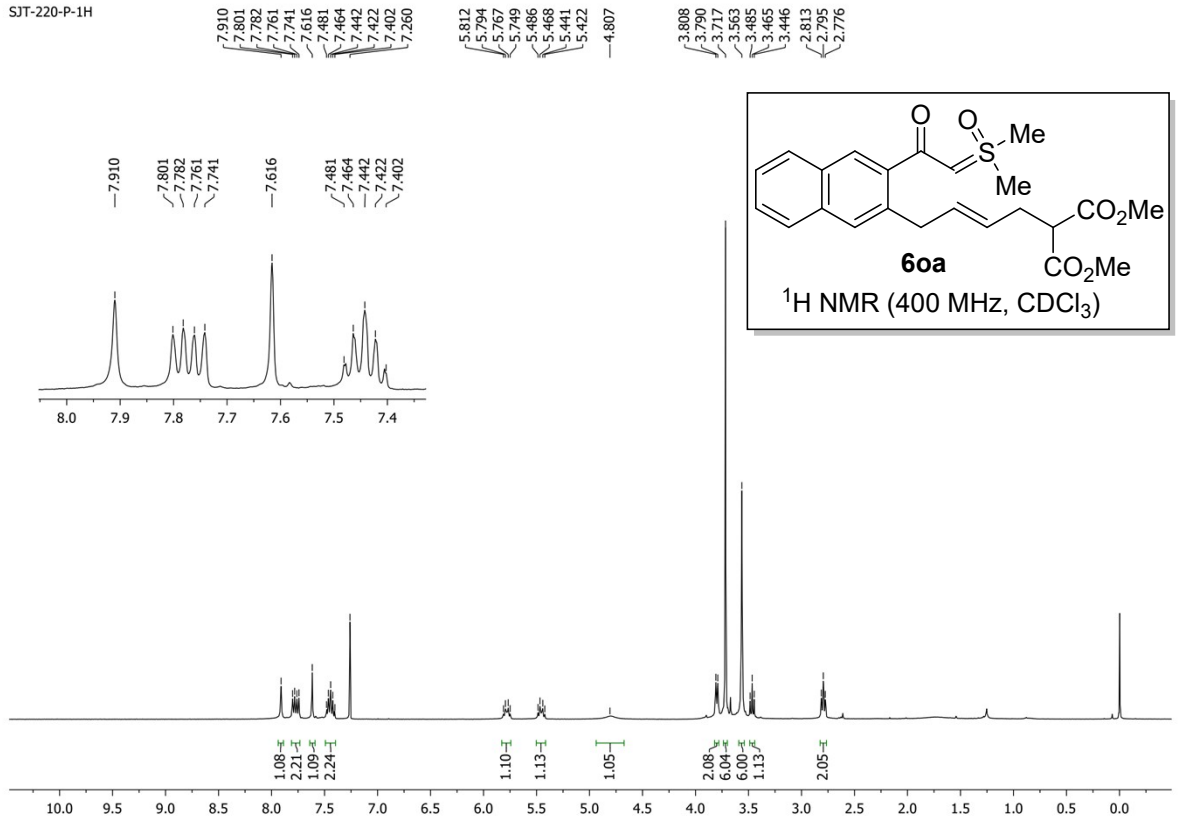

SJT-196-P-13C
185.211
169.560
144.577
139.084
131.408
131.204
131.173
130.961
127.832
127.806
126.605
126.580
126.555
126.535
126.198
126.176
122.913
122.887
77.371
77.160
76.948
72.318
52.712
51.586
42.382
30.795
27.088
O
O
Me
S
Me
F3C
CO2Me
CO2Me
6ma
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

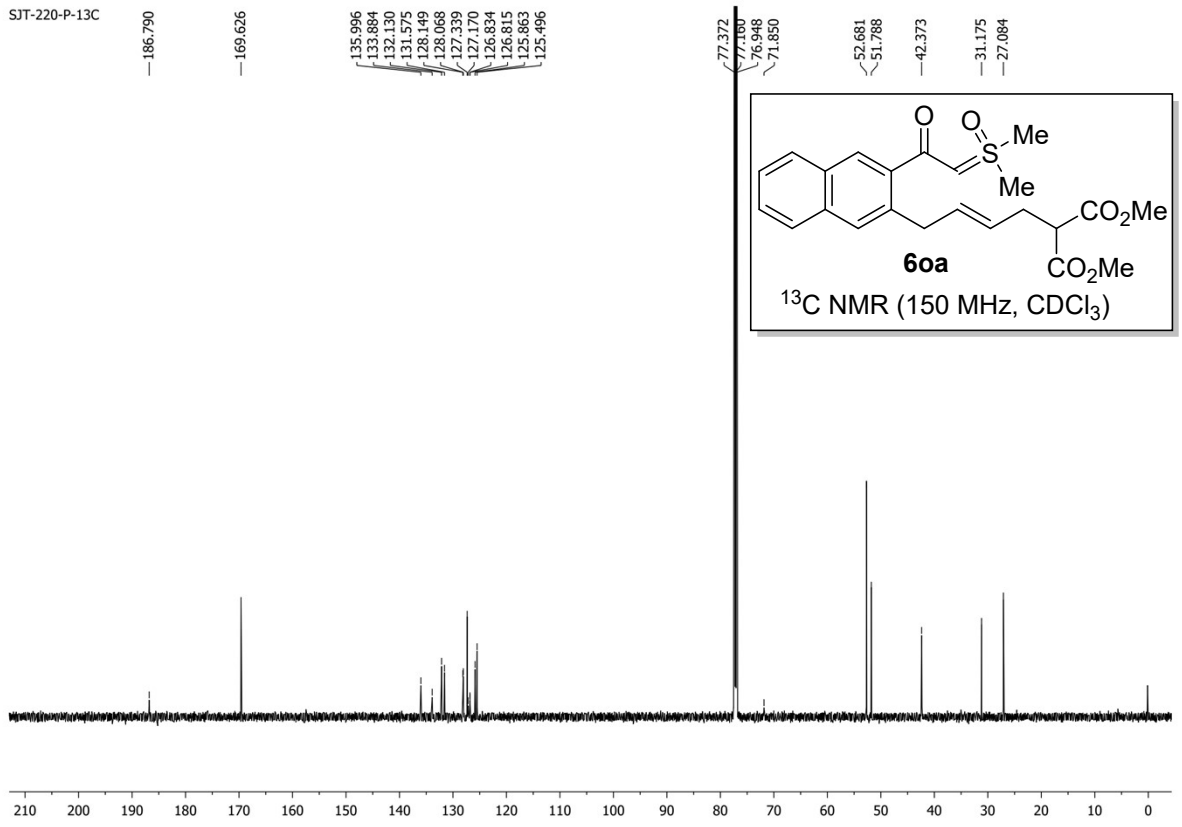

SJT-196-P-19F
62.618
O
O
Me
S
Me
F3C
CO2Me
CO2Me
6ma
19F NMR (377 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -15

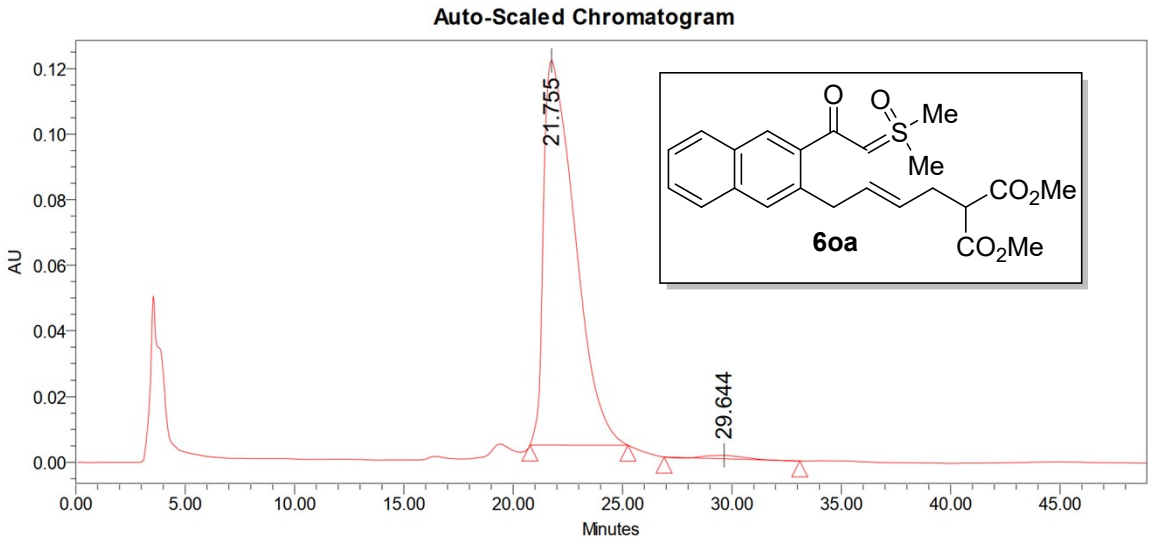


Peak Results

	Start Time (min)	End Time (min)	RT	Height (μV)	% Area
1	15.917	21.333	18.361	8547	94.58
2	22.183	23.883	22.834	794	5.42

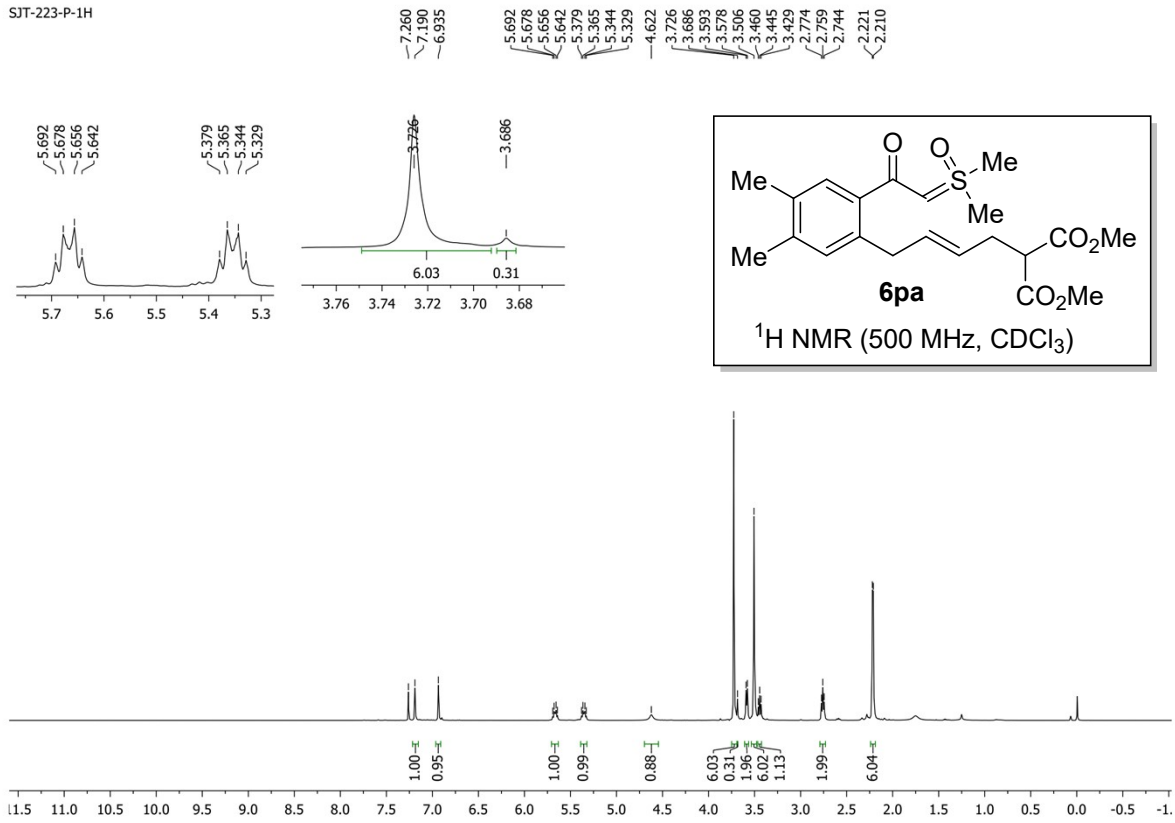


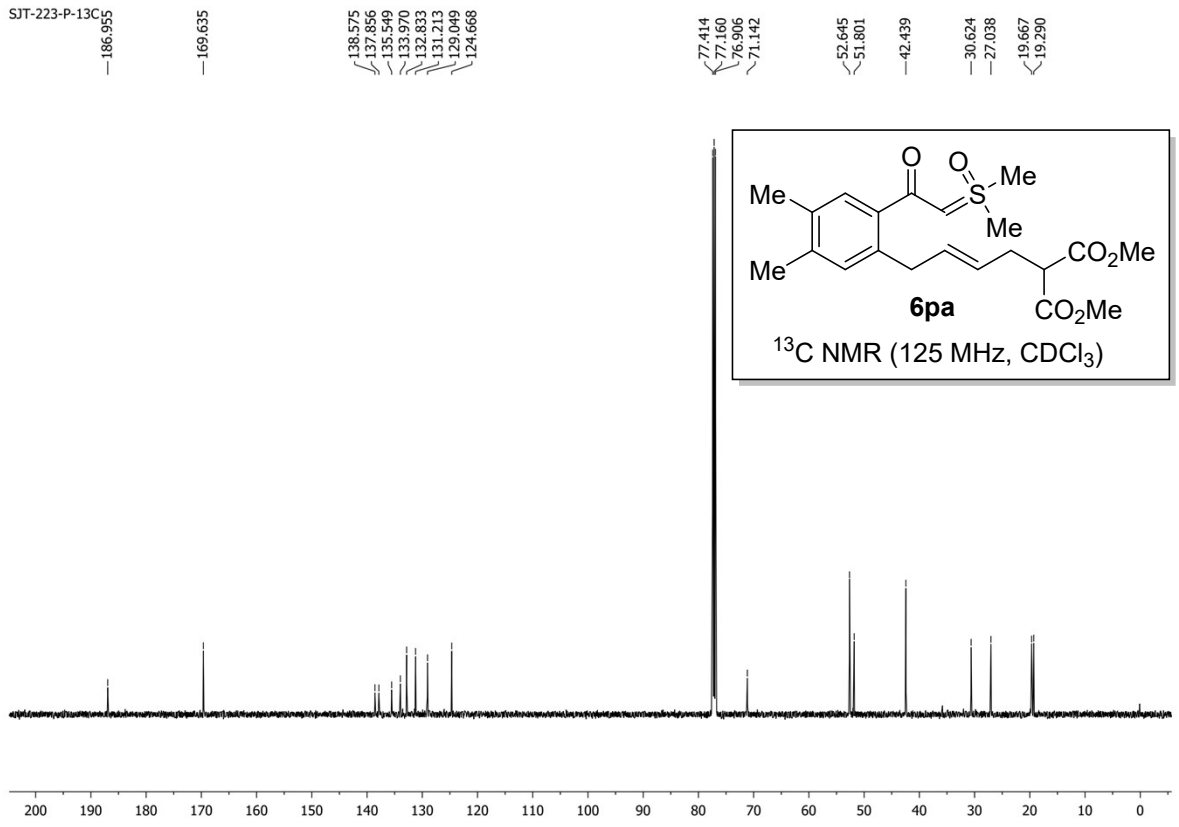


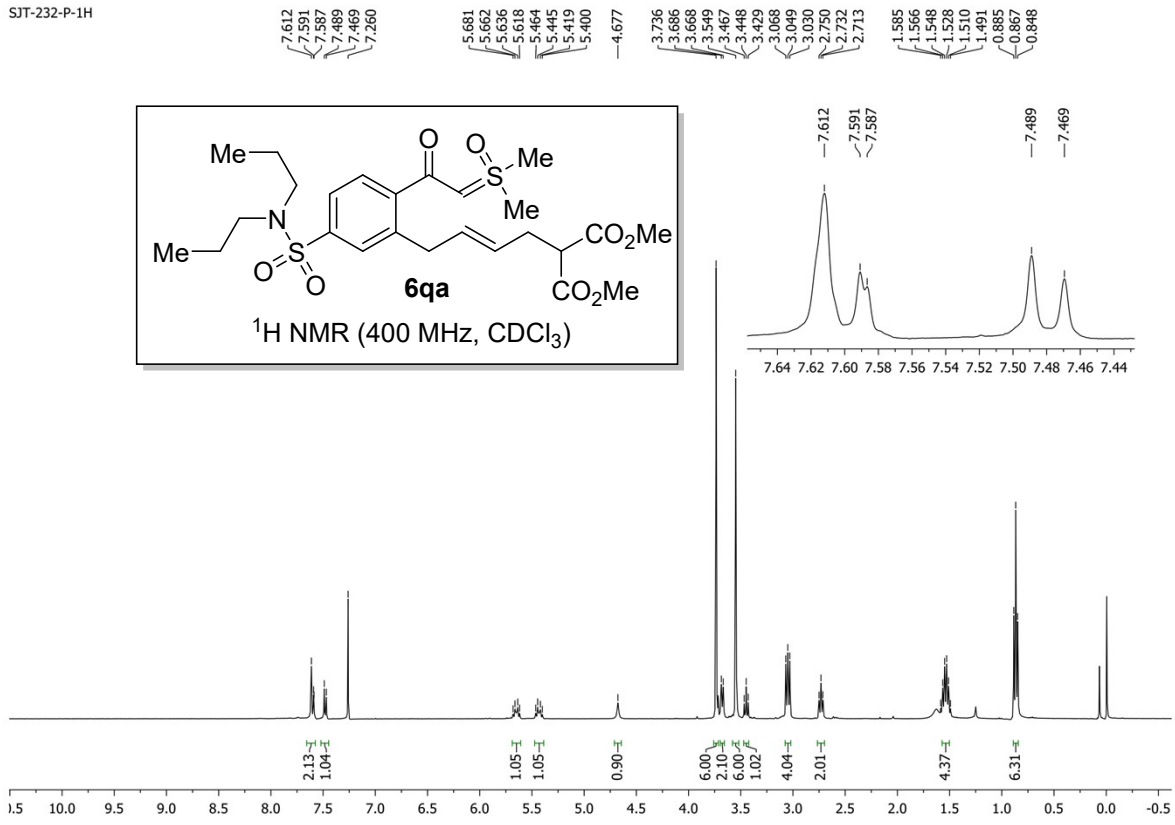


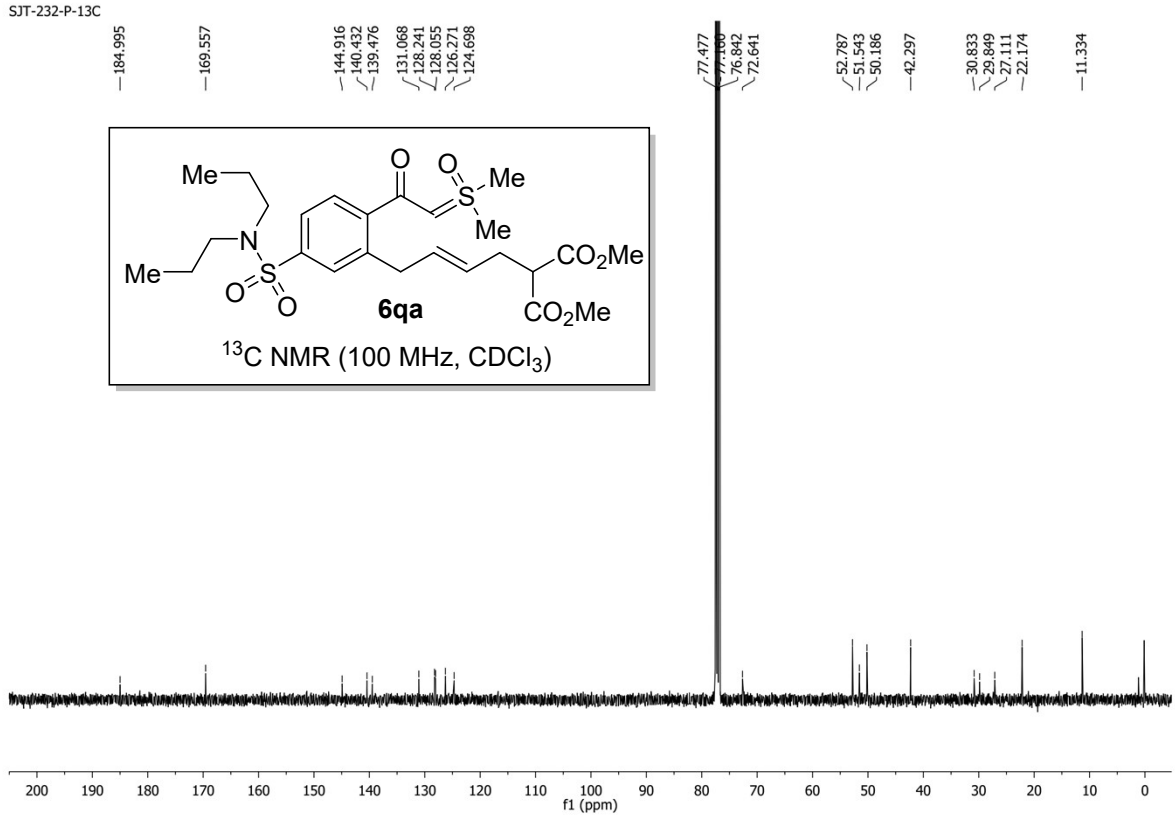
Peak Results

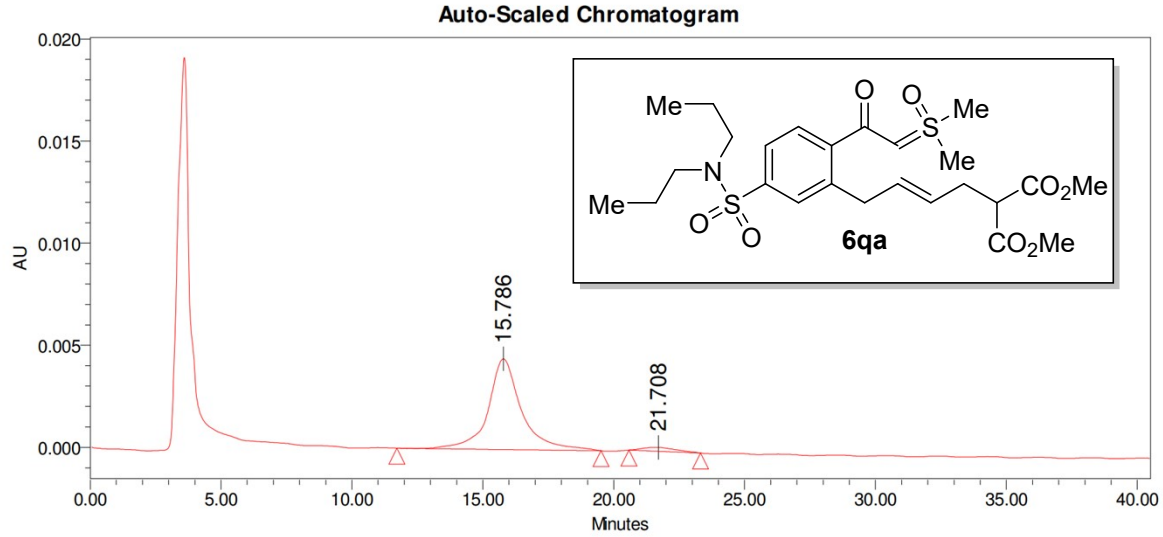
	Start Time (min)	End Time (min)	RT	Height (μV)	% Area
1	20.767	25.250	21.755	117230	98.86
2	26.900	33.100	29.644	1059	1.14


SJT-223-P-1H
7.260
7.190
6.935
5.692
5.678
5.656
5.642
5.379
5.365
5.344
5.329
4.622
3.726
3.686
3.593
3.578
3.506
3.460
3.445
3.429
2.774
2.759
2.744
2.221
2.210
6.03
0.31
Me
Me
Me
O
O
S
CO2Me
CO2Me
6pa
1H NMR (500 MHz, CDCl3)
1.00
0.95
1.00
0.99
0.88
6.03
0.31
1.96
6.02
1.13
1.99
6.04


SJT-223-P-13C
186.955
169.635
138.575
137.856
135.549
133.970
132.833
131.213
129.049
124.668
77.414
77.160
76.906
71.142
52.645
51.801
42.439
30.624
27.038
19.667
19.290
Me
Me
Me
O
O
S
CO2Me
CO2Me
6pa
13C NMR (125 MHz, CDCl3)

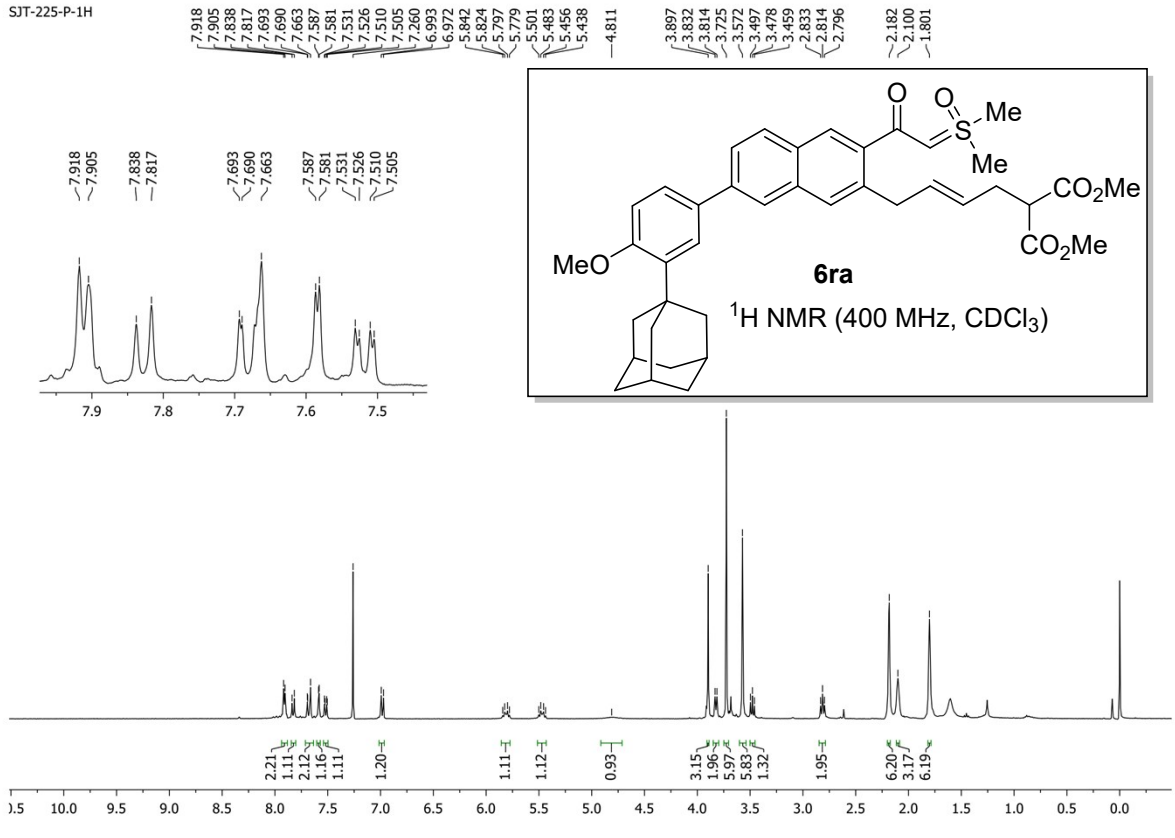

SJT-232-P-1H
7.612
7.591
7.587
7.489
7.469
7.260
5.681
5.662
5.636
5.618
5.464
5.445
5.419
5.400
4.677
3.736
3.686
3.668
3.549
3.467
3.448
3.429
3.068
3.049
3.030
2.750
2.732
2.713
1.585
1.566
1.548
1.528
1.510
1.491
0.885
0.867
0.848
Me
N
Me
S
O
O
O
O
Me
S
Me
CO2Me
CO2Me
6qa
1H NMR (400 MHz, CDCl3)
7.64 7.62 7.60 7.58 7.56 7.54 7.52 7.50 7.48 7.46 7.44
2.13
1.04
1.05
1.05
0.90
6.00
2.10
6.00
1.02
4.04
2.01
4.37
6.31

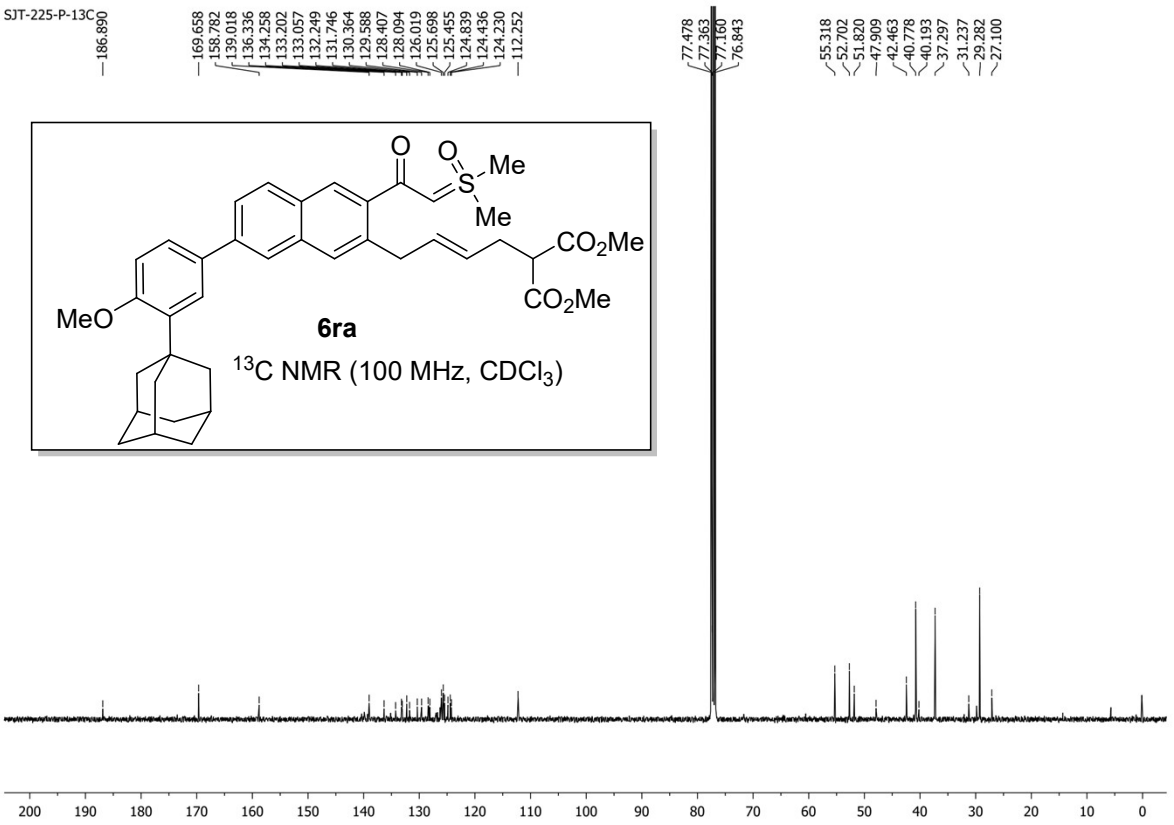

SJT-232-P-13C
184.995
169.557
144.916
140.432
139.476
131.068
128.241
128.055
126.271
124.698
77.477
77.160
76.842
72.641
52.787
51.543
50.186
42.297
30.833
29.849
27.111
22.174
11.334
Me
N
Me
S
O
O
O
O
Me
S
Me
CO2Me
CO2Me
6qa
13C NMR (100 MHz, CDCl3)
f1 (ppm)

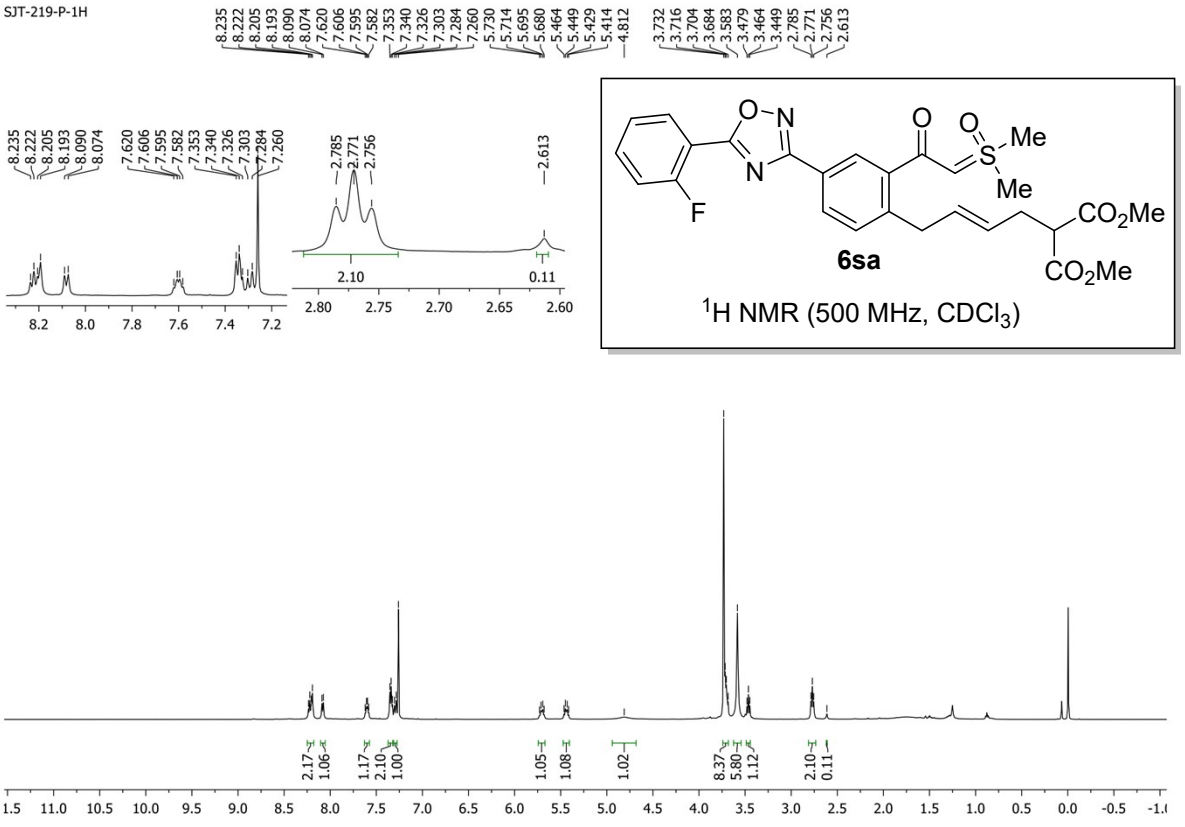


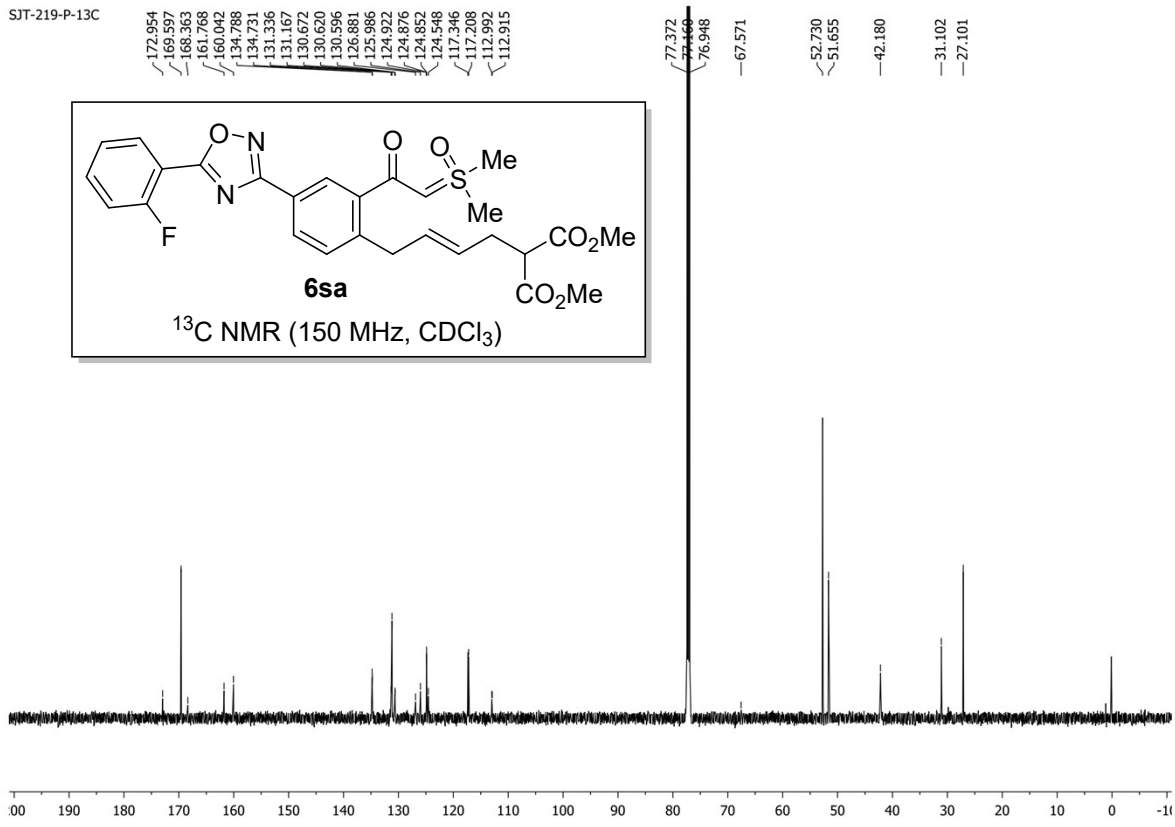
Peak Results

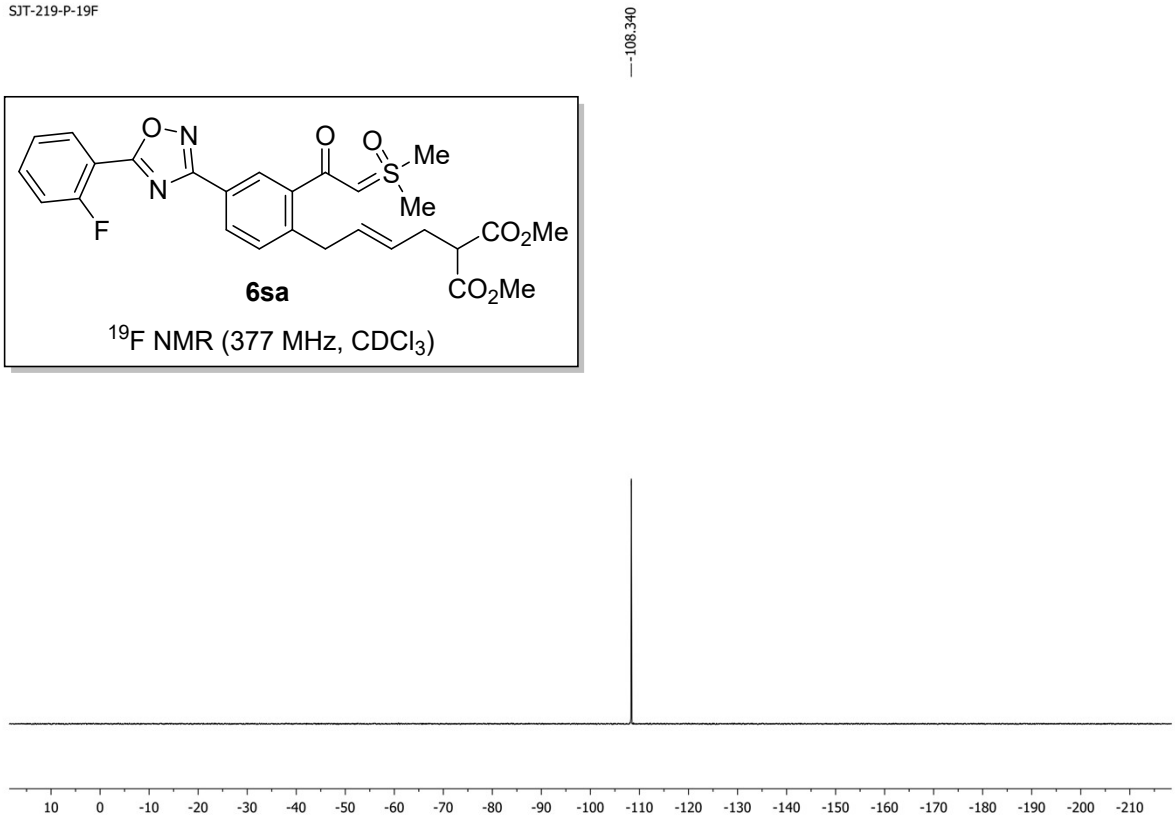
	Start Time (min)	End Time (min)	RT	Height (μV)	% Area
1	11.717	19.517	15.786	4441	95.88
2	20.583	23.317	21.708	192	4.12

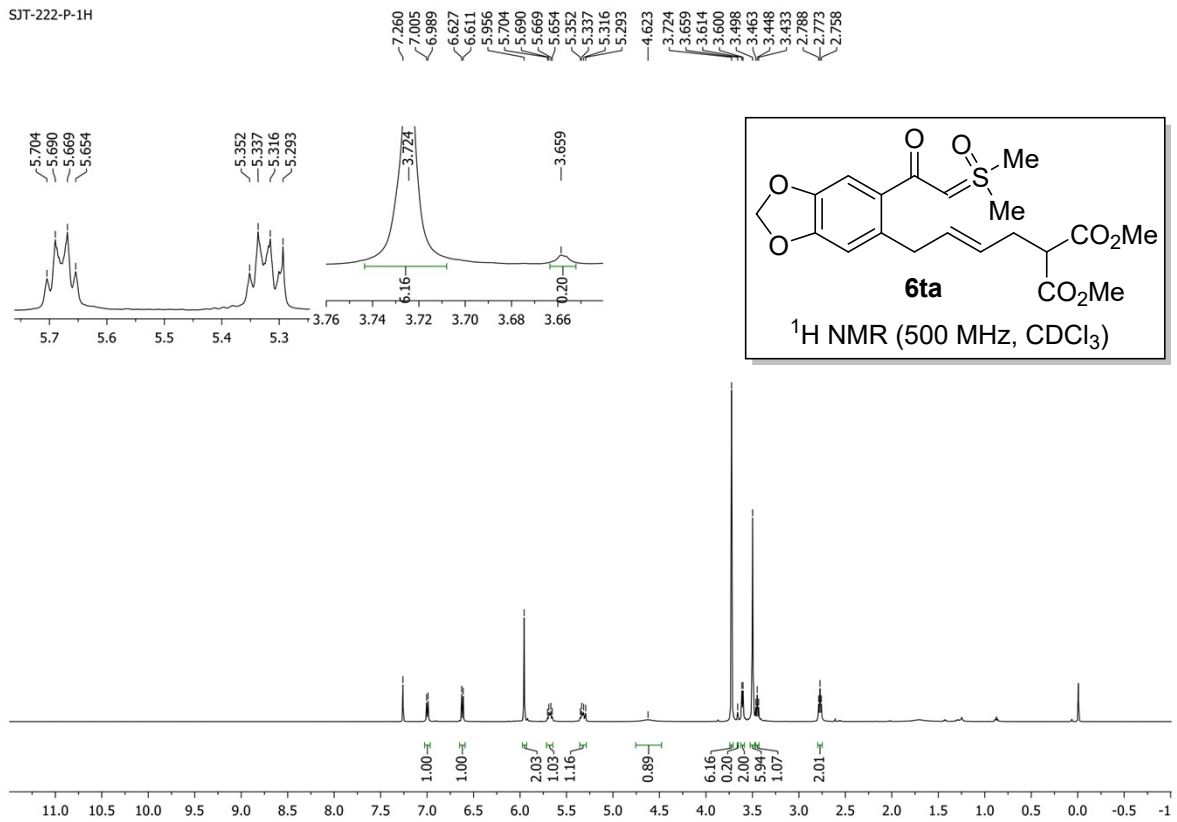


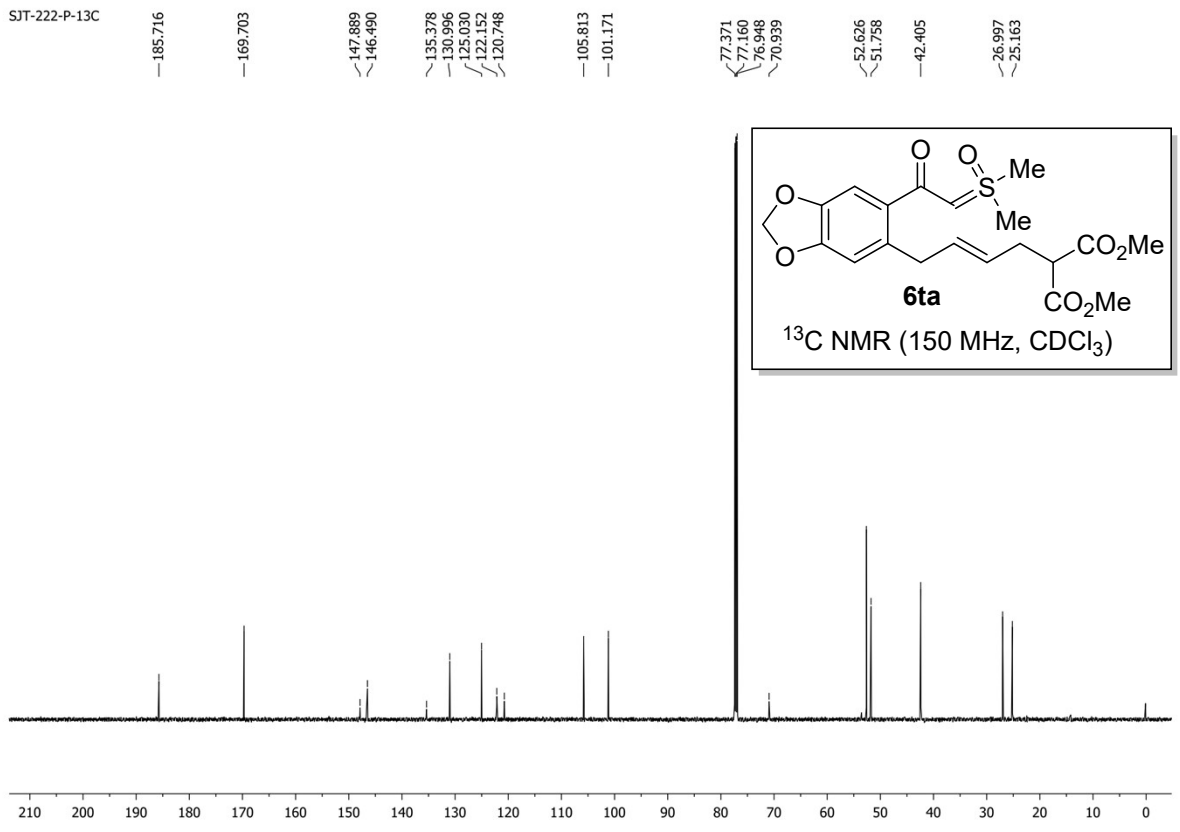

SJT-225-P-13C
186.890
169.658
158.782
139.018
136.336
134.258
133.202
133.057
132.249
131.746
130.364
129.588
128.407
128.094
126.019
125.698
125.455
124.839
124.436
124.230
112.252
77.478
77.363
77.160
76.843
55.318
52.702
51.820
47.909
42.463
40.778
40.193
37.297
31.237
29.282
27.100
O
O
S
Me
Me
CO2Me
CO2Me
MeO
6ra
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

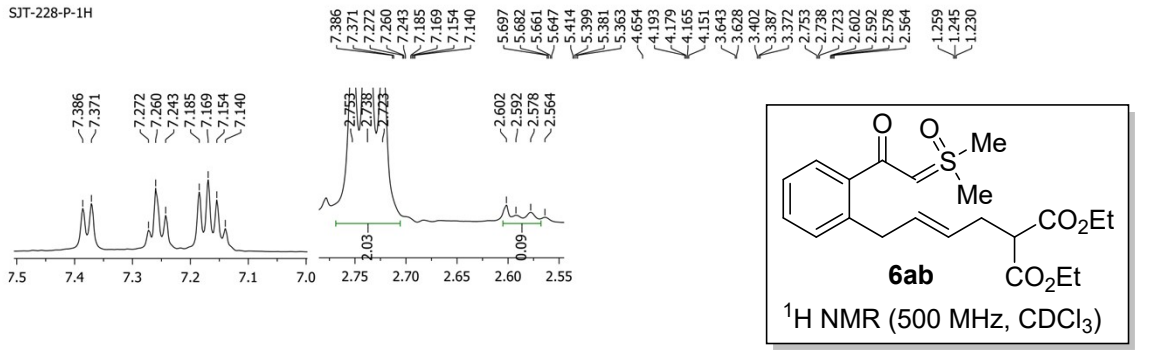

SJT-219-P-1H
8.235
8.222
8.205
8.193
8.090
8.074
7.620
7.606
7.595
7.582
7.353
7.340
7.326
7.303
7.284
7.260
5.730
5.714
5.695
5.680
5.464
5.449
5.429
5.414
4.812
3.732
3.716
3.704
3.684
3.583
3.479
3.464
3.449
2.785
2.771
2.756
2.613
2.10
0.11
8.2
8.0
7.8
7.6
7.4
7.2
2.80
2.75
2.70
2.65
2.60
O
N
N
F
O
O
S
Me
Me
CO2Me
CO2Me
6sa
1H NMR (500 MHz, CDCl3)
2.17
1.06
1.17
2.10
1.00
1.05
1.08
1.02
8.37
5.80
1.12
2.10
0.11
1.5
11.0
10.5
10.0
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
-0.5

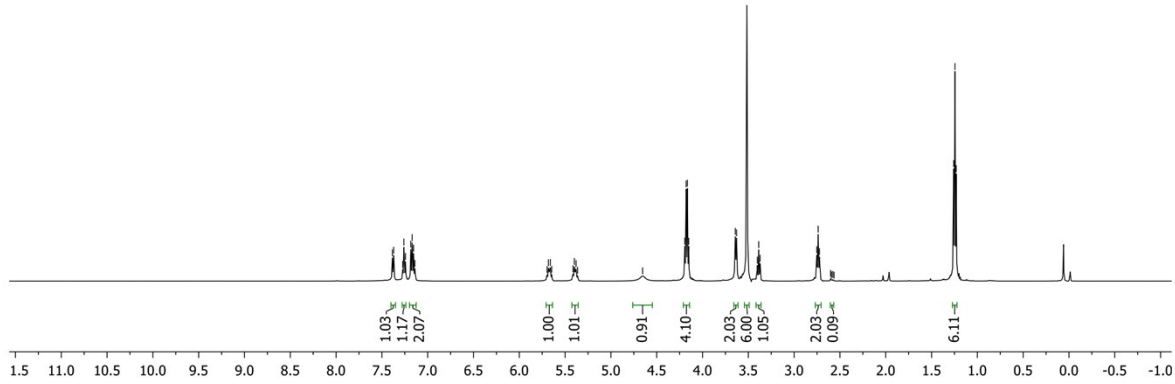

SJT-219-P-13C
172.954
169.597
168.363
161.768
160.042
134.788
134.731
131.336
131.167
130.672
130.620
130.596
126.881
125.986
124.922
124.876
124.852
124.548
117.346
117.208
112.992
112.915
77.372
77.160
76.948
67.571
52.730
51.655
42.180
31.102
27.101
6sa
13C NMR (150 MHz, CDCl3)

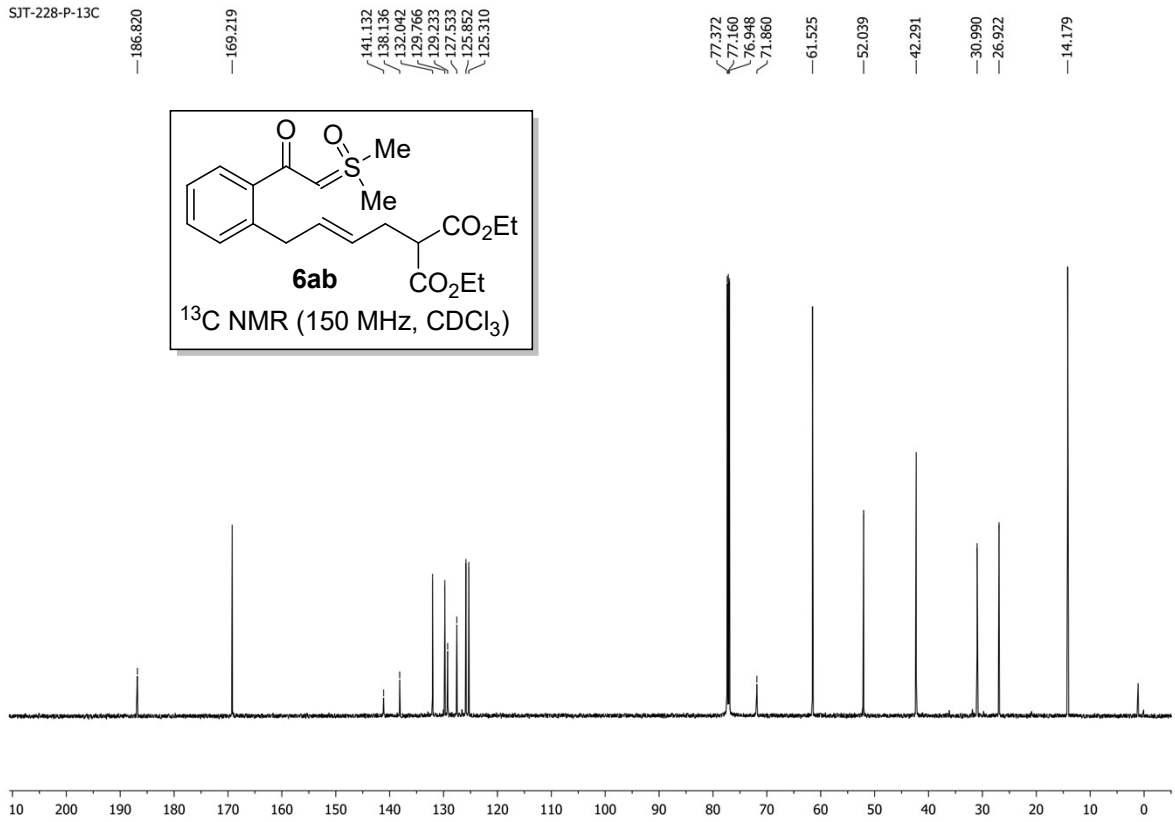

SJT-219-P-19F
-108.340
6sa
19F NMR (377 MHz, CDCl3)

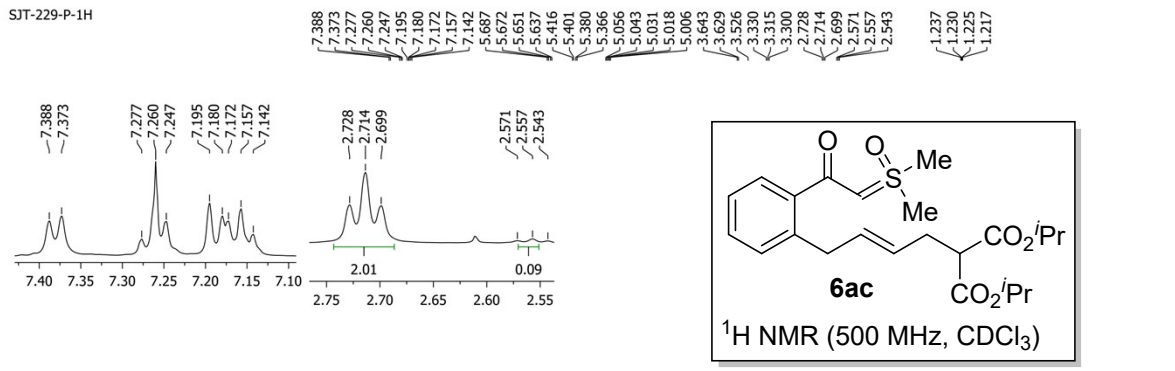

SJT-222-P-1H
7.260
7.005
6.989
6.627
6.611
5.956
5.704
5.690
5.669
5.654
5.352
5.337
5.316
5.293
4.623
3.724
3.659
3.614
3.600
3.498
3.463
3.448
3.433
2.788
2.773
2.758
6.16
0.20
O
O
Me
S
Me
O
O
CO2Me
CO2Me
6ta
1H NMR (500 MHz, CDCl3)
1.00
1.00
2.03
1.03
1.16
0.89
6.16
0.20
2.00
5.94
1.07
2.01

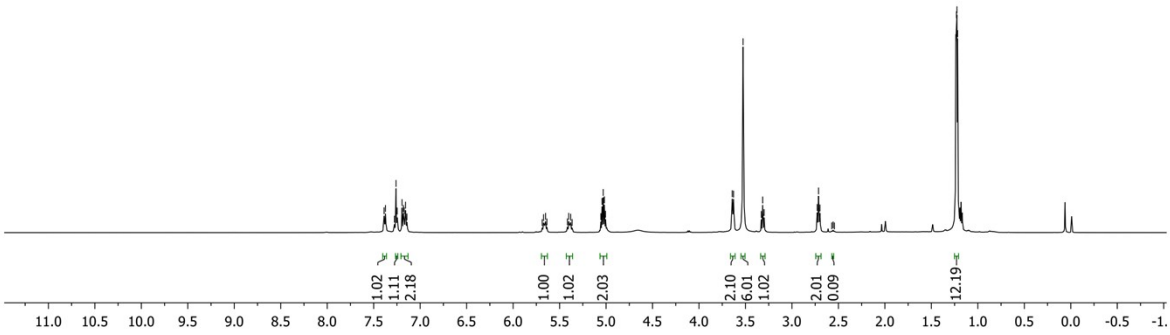

SJT-222-P-13C
185.716
169.703
147.889
146.490
135.378
130.996
125.030
122.152
120.748
105.813
101.171
77.371
77.160
76.948
70.939
52.626
51.758
42.405
26.997
25.163
O
O
Me
S
Me
O
O
CO2Me
CO2Me
6ta
13C NMR (150 MHz, CDCl3)

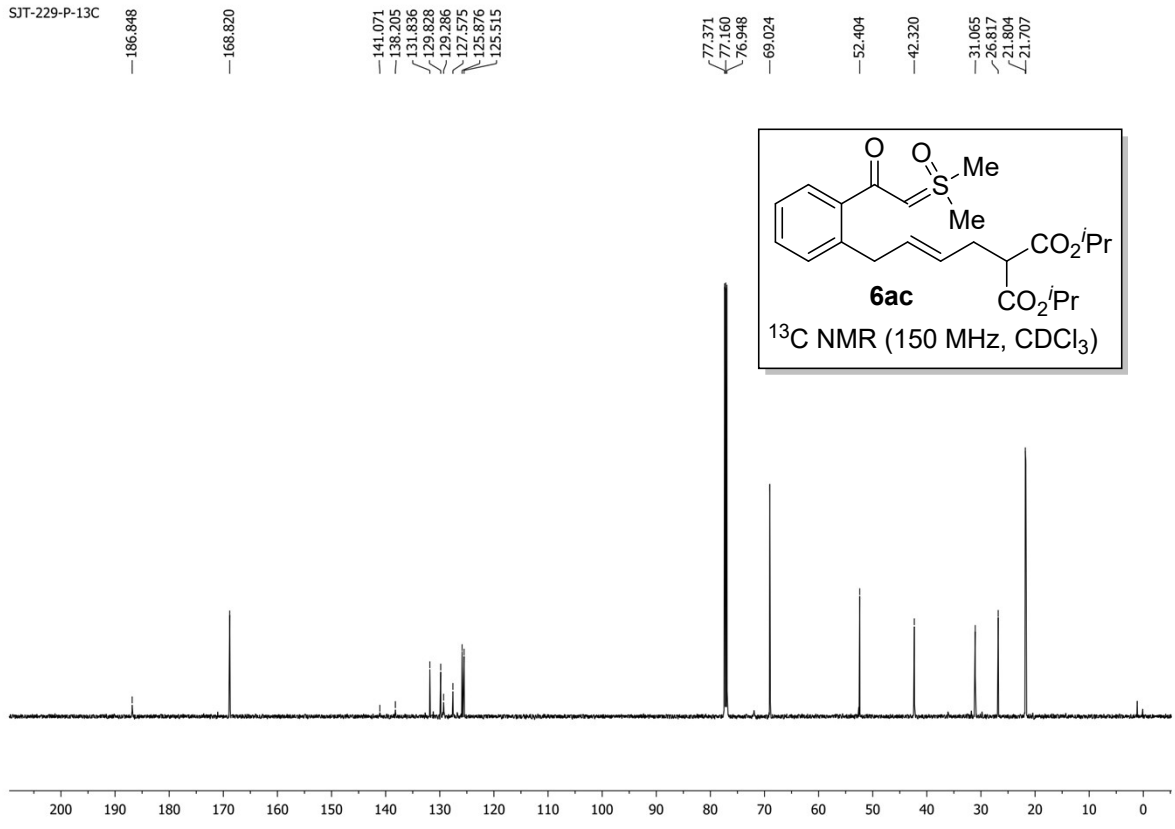

SJT-228-P-1H
7.386
7.371
7.272
7.260
7.243
7.185
7.169
7.154
7.140
5.697
5.682
5.661
5.647
5.414
5.399
5.381
5.363
4.654
4.193
4.179
4.165
4.151
3.643
3.628
3.402
3.387
3.372
2.753
2.738
2.723
2.602
2.592
2.578
2.564
1.259
1.245
1.230
2.03
0.09
O
O
Me
S
Me
CO2Et
6ab
CO2Et
1H NMR (500 MHz, CDCl3)

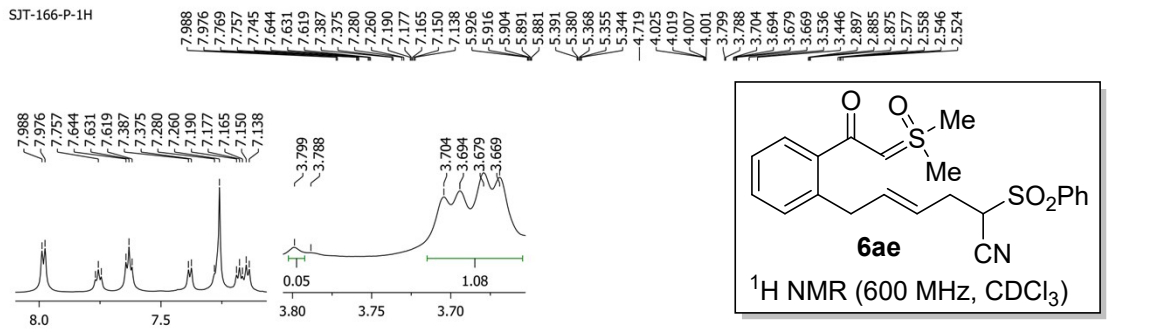

1.03
1.17
2.07
1.00
1.01
0.91
4.10
2.03
6.00
1.05
2.03
0.09
6.11


SJT-228-P-13C
186.820
169.219
141.132
138.136
132.042
129.766
129.233
127.533
125.852
125.310
77.372
77.160
76.948
71.860
61.525
52.039
42.291
30.990
26.922
14.179
O
O
Me
S
Me
CO2Et
6ab
CO2Et
13C NMR (150 MHz, CDCl3)

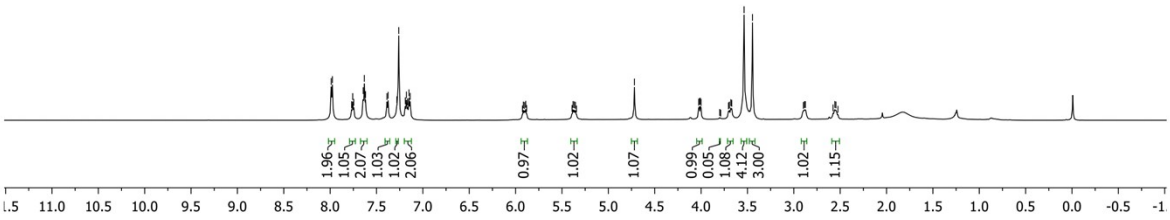

SJT-229-P-1H
7.388
7.373
7.277
7.260
7.247
7.195
7.180
7.172
7.157
7.142
5.687
5.672
5.651
5.637
5.416
5.401
5.380
5.366
5.056
5.043
5.031
5.018
5.006
3.643
3.629
3.326
3.330
3.315
3.300
2.728
2.714
2.699
2.571
2.557
2.543
1.237
1.230
1.225
1.217
2.01
0.09
O
O
S
Me
Me
CO2iPr
CO2iPr
6ac
1H NMR (500 MHz, CDCl3)

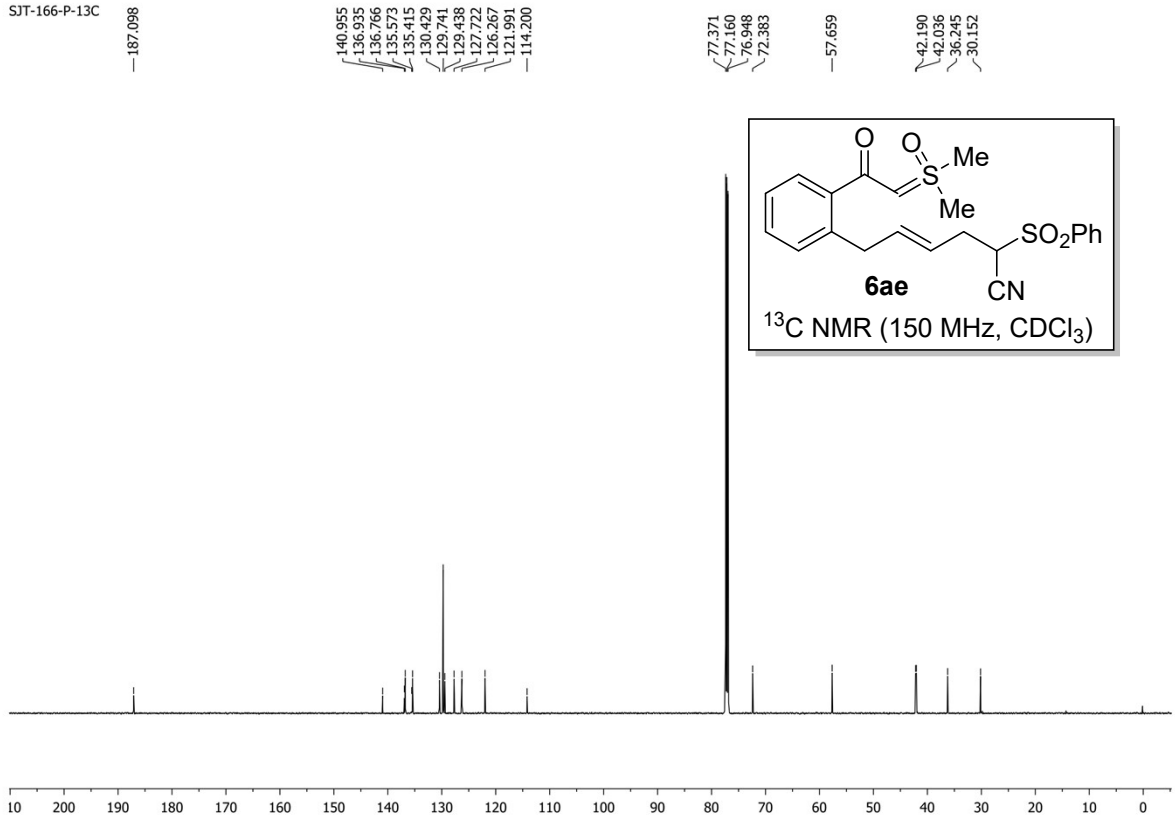

1.02
1.11
2.18
1.00
1.02
2.03
2.10
6.01
1.02
2.01
0.09
12.19


SJT-229-P-13C
186.848
168.820
141.071
138.205
131.836
129.828
129.286
127.575
125.876
125.515
77.371
77.160
76.948
69.024
52.404
42.320
31.065
26.817
21.804
21.707
O
O
S
Me
Me
CO2iPr
CO2iPr
6ac
13C NMR (150 MHz, CDCl3)



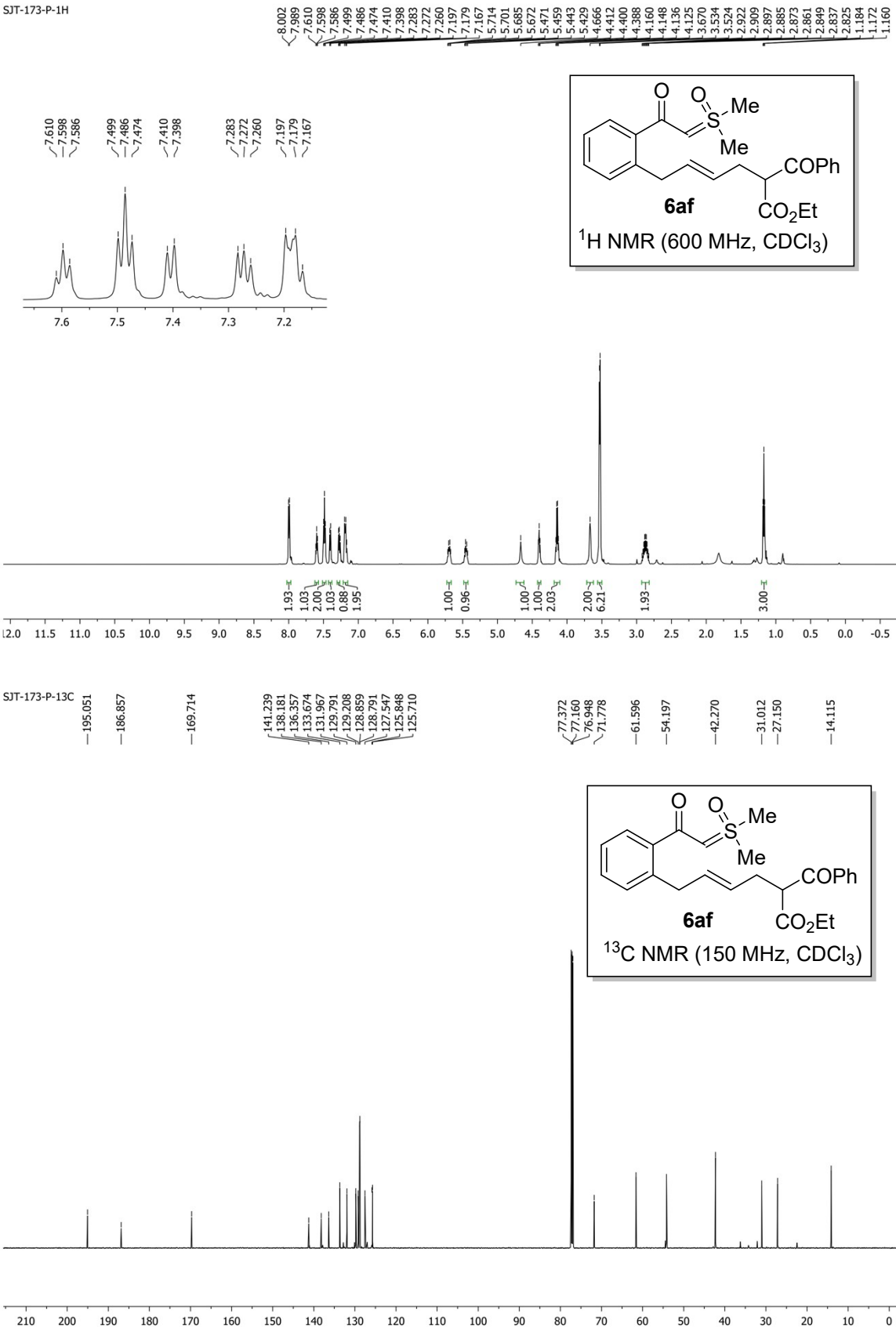
^{1}H NMR (600 MHz, $CDCl_3$)



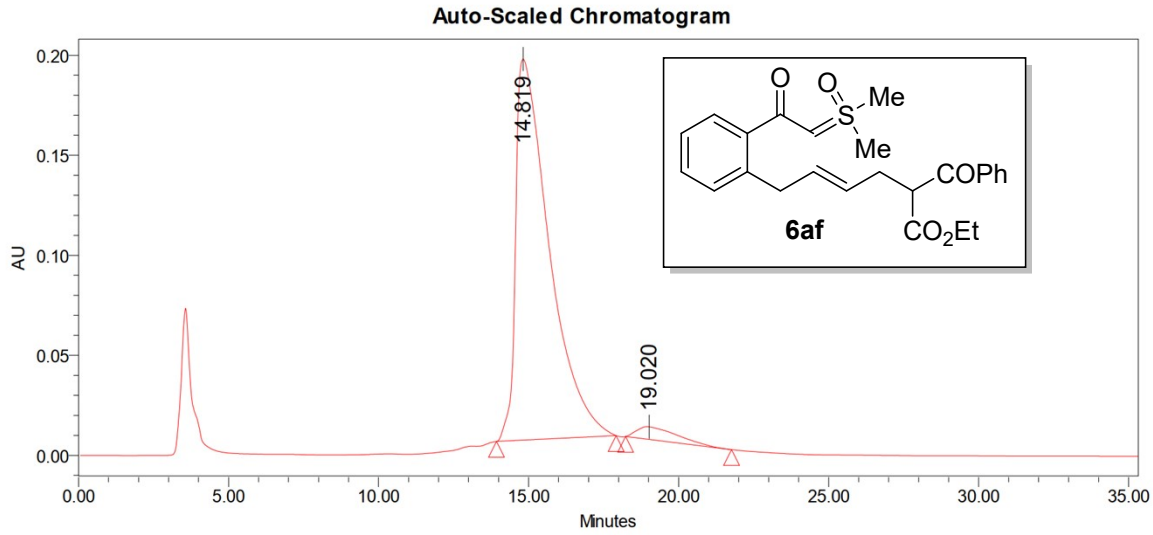


^{13}C NMR (150 MHz, $CDCl_3$)

SJT-173-P-1H

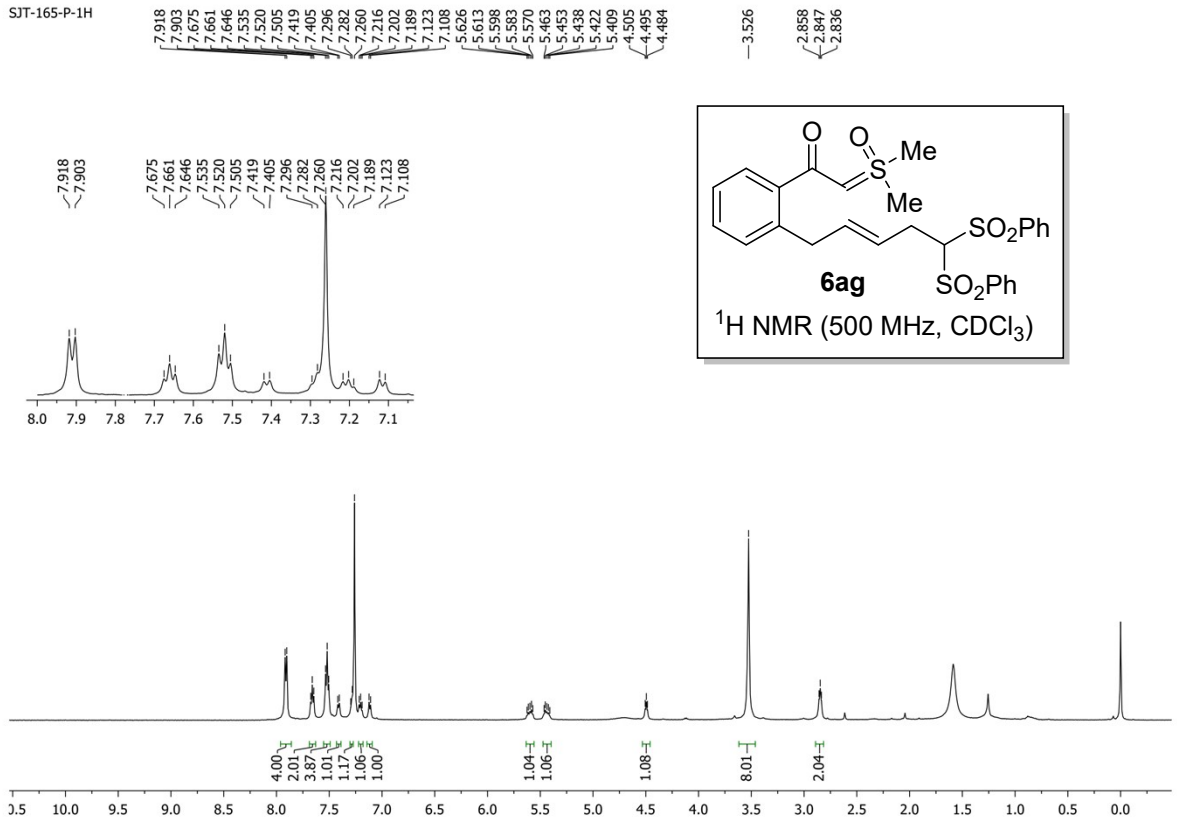


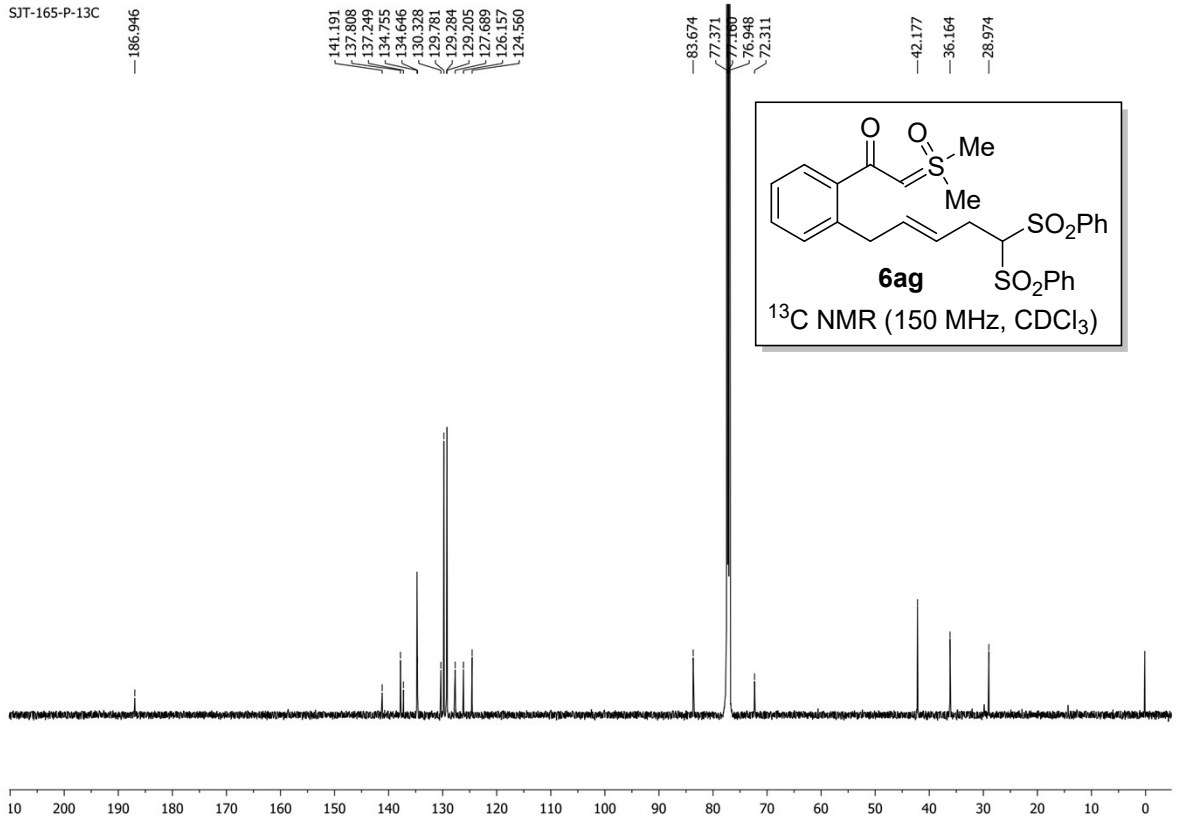
SJT-173-P-13C

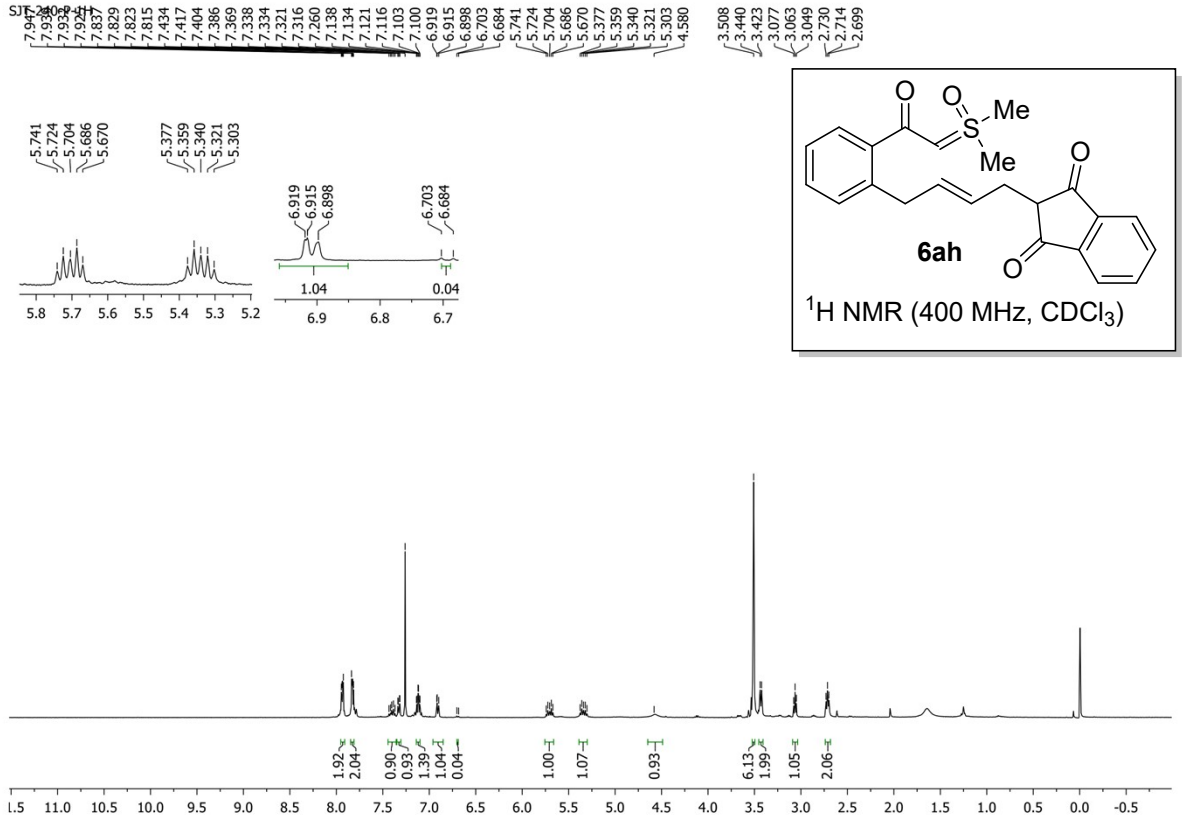


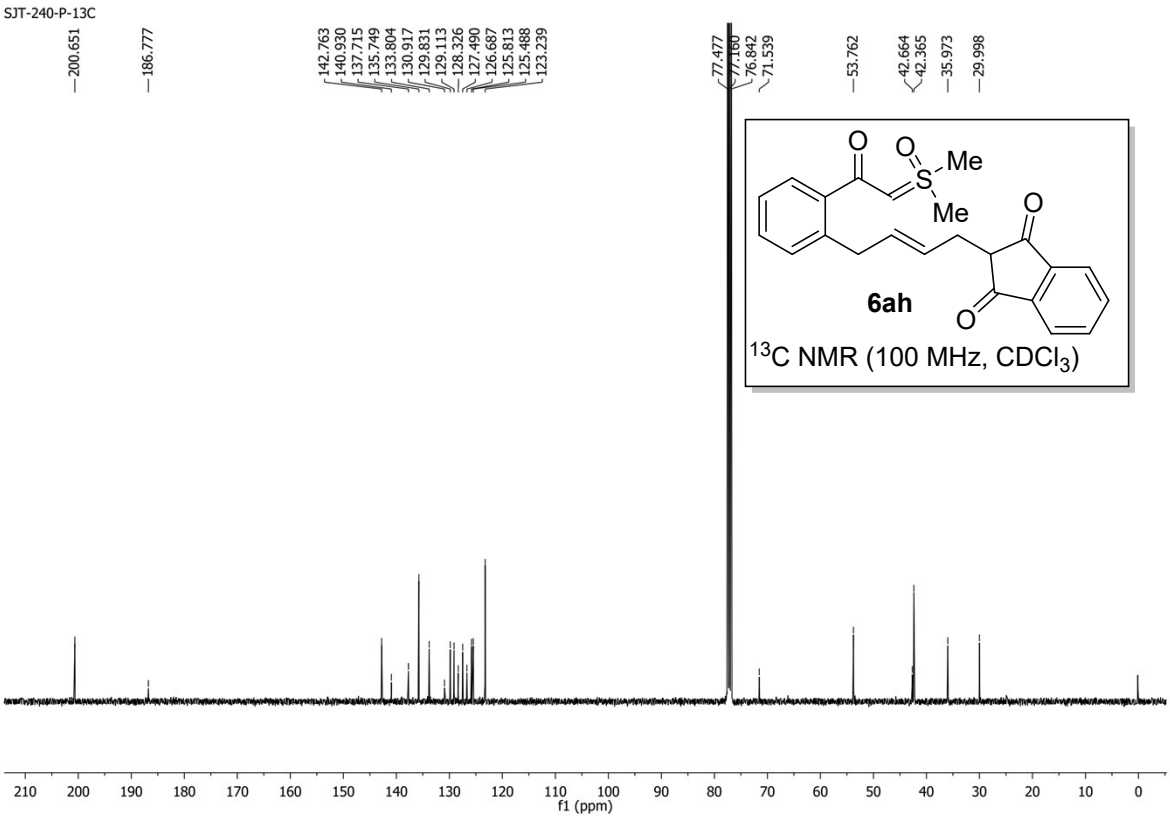
Peak Results

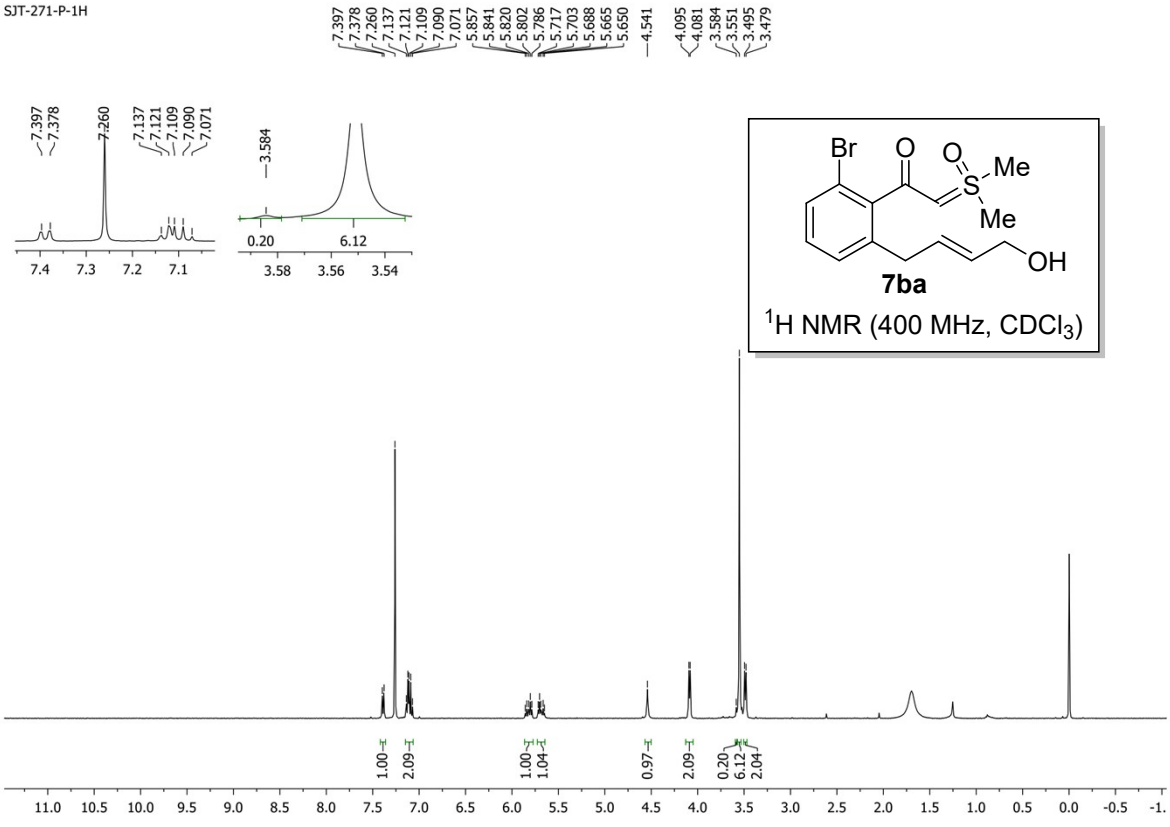
	Start Time (min)	End Time (min)	RT	Height (μV)	% Area
1	13.933	17.917	14.819	190429	96.04
2	18.233	21.767	19.020	6289	3.96

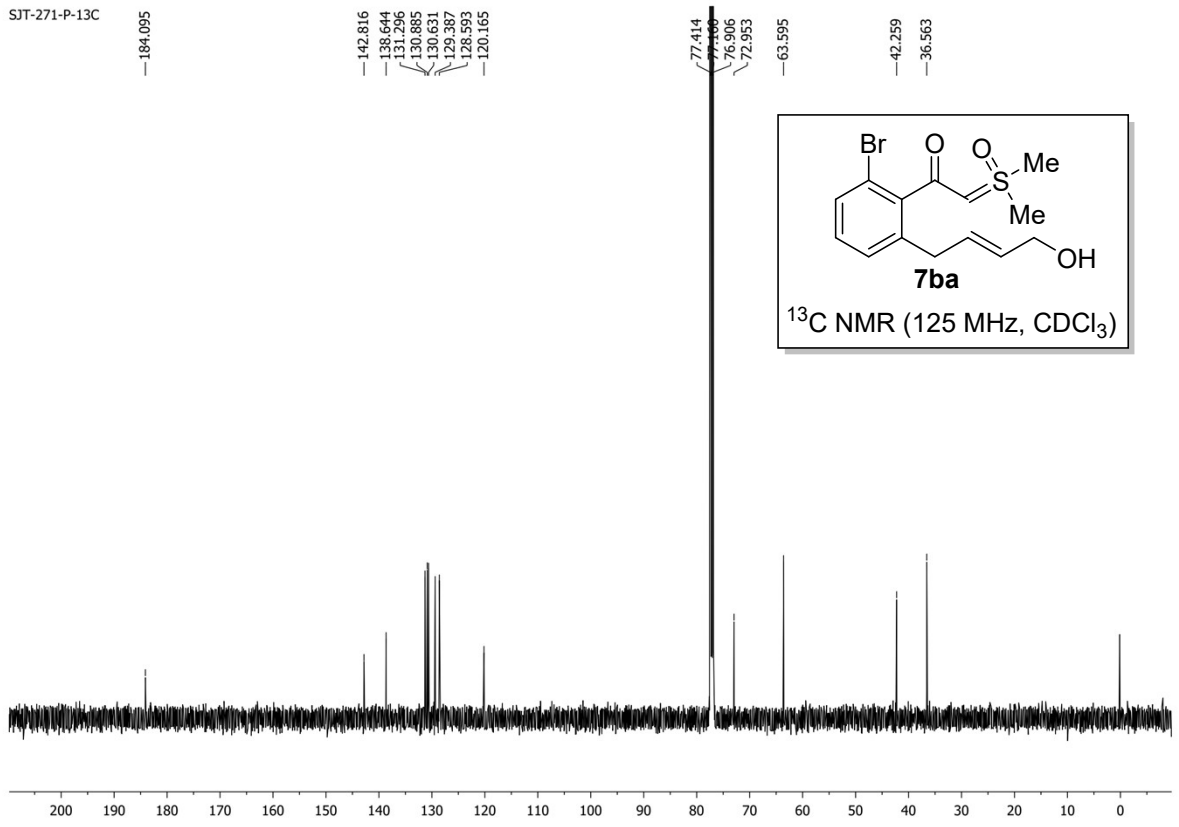


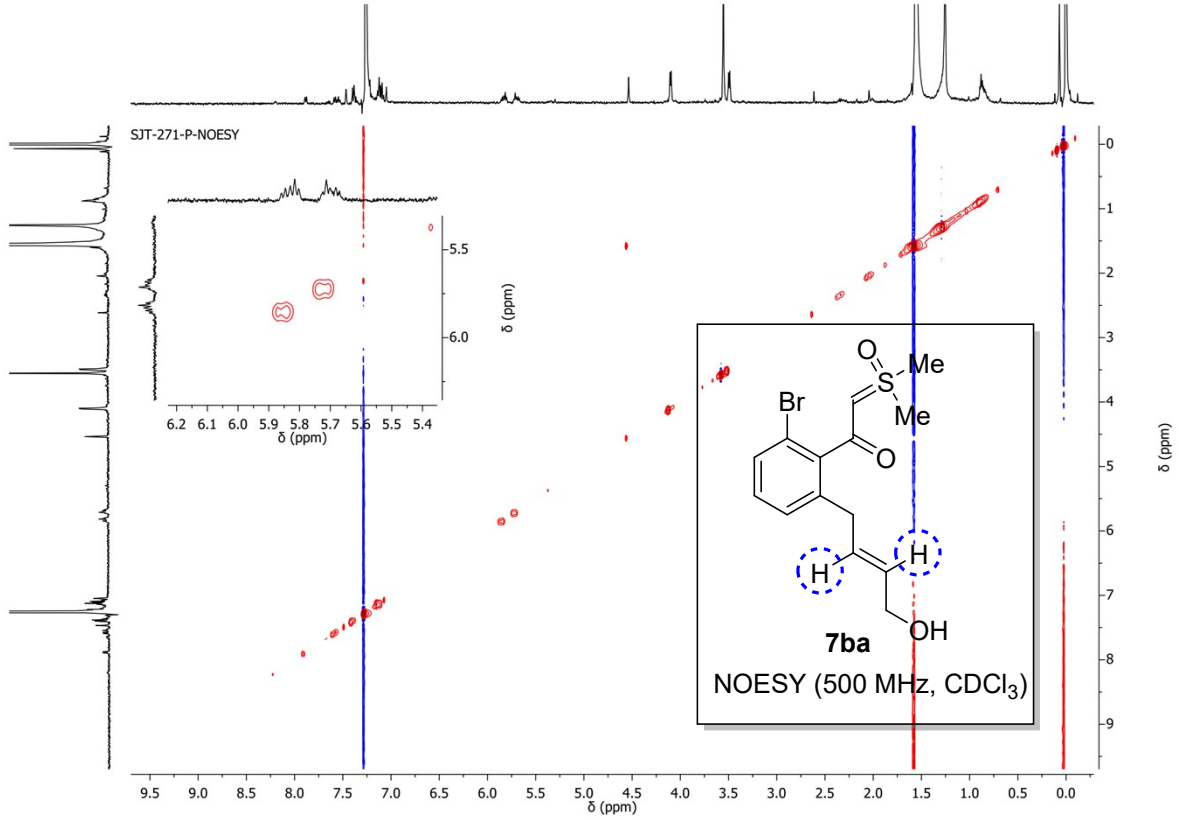

SJT-165-P-13C
186.946
141.191
137.808
137.249
134.755
134.646
130.328
129.781
129.284
129.205
127.689
126.157
124.560
83.674
77.371
77.160
76.948
72.311
42.177
36.164
28.974
O
O
S
Me
Me
SO2Ph
SO2Ph
6ag
13C NMR (150 MHz, CDCl3)

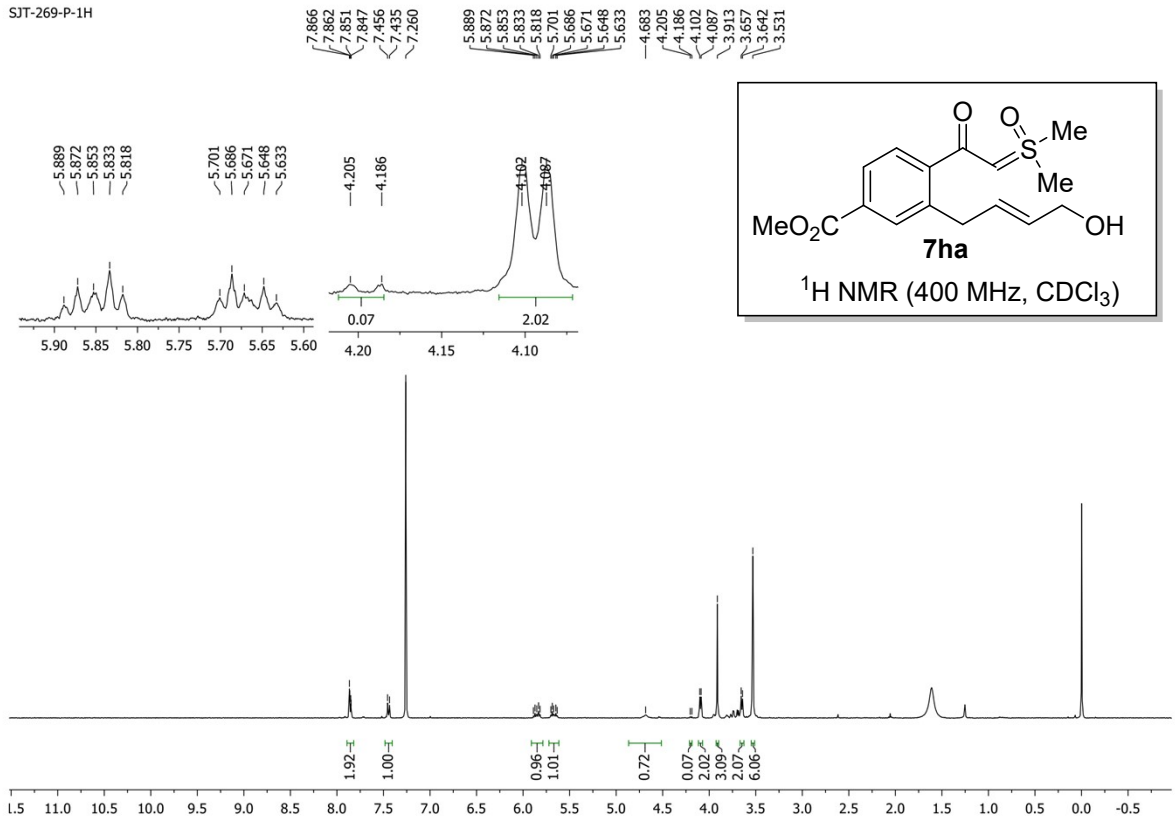

7.947
7.938
7.932
7.927
7.837
7.829
7.823
7.815
7.434
7.417
7.404
7.386
7.369
7.338
7.334
7.321
7.316
7.260
7.138
7.134
7.121
7.116
7.103
7.100
6.919
6.915
6.898
6.703
6.684
5.741
5.724
5.704
5.686
5.670
5.377
5.359
5.340
5.321
5.303
4.580
3.508
3.440
3.423
3.077
3.063
3.049
2.730
2.714
2.699
1.04
0.04
O
O
S
Me
Me
O
O
6ah
1H NMR (400 MHz, CDCl3)
1.92
2.04
0.90
0.93
1.39
1.04
0.04
1.00
1.07
0.93
6.13
1.99
1.05
2.06

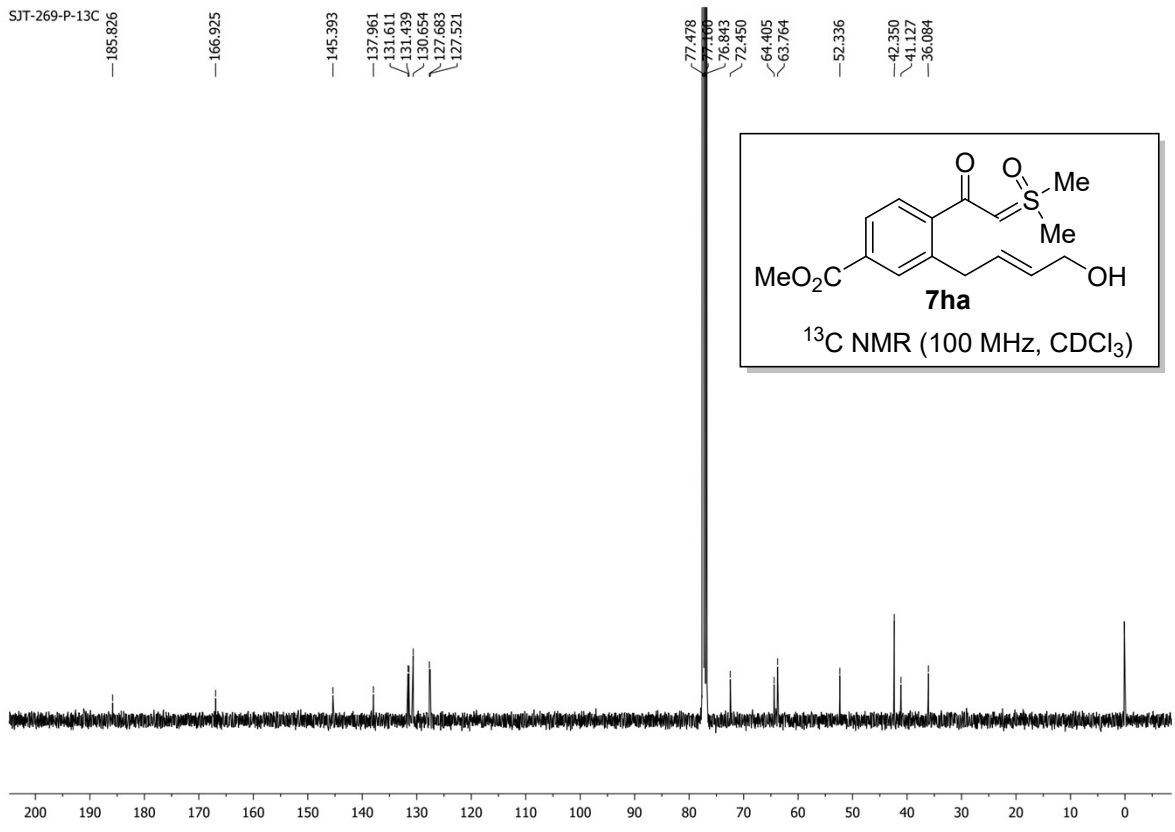

SJT-240-P-13C
200.651
186.777
142.763
140.930
137.715
135.749
133.804
130.917
129.831
129.113
128.326
127.490
126.687
125.813
125.488
123.239
77.477
77.160
76.842
71.539
53.762
42.664
42.365
35.973
29.998
O
O
S
Me
Me
O
O
6ah
13C NMR (100 MHz, CDCl3)
f1 (ppm)

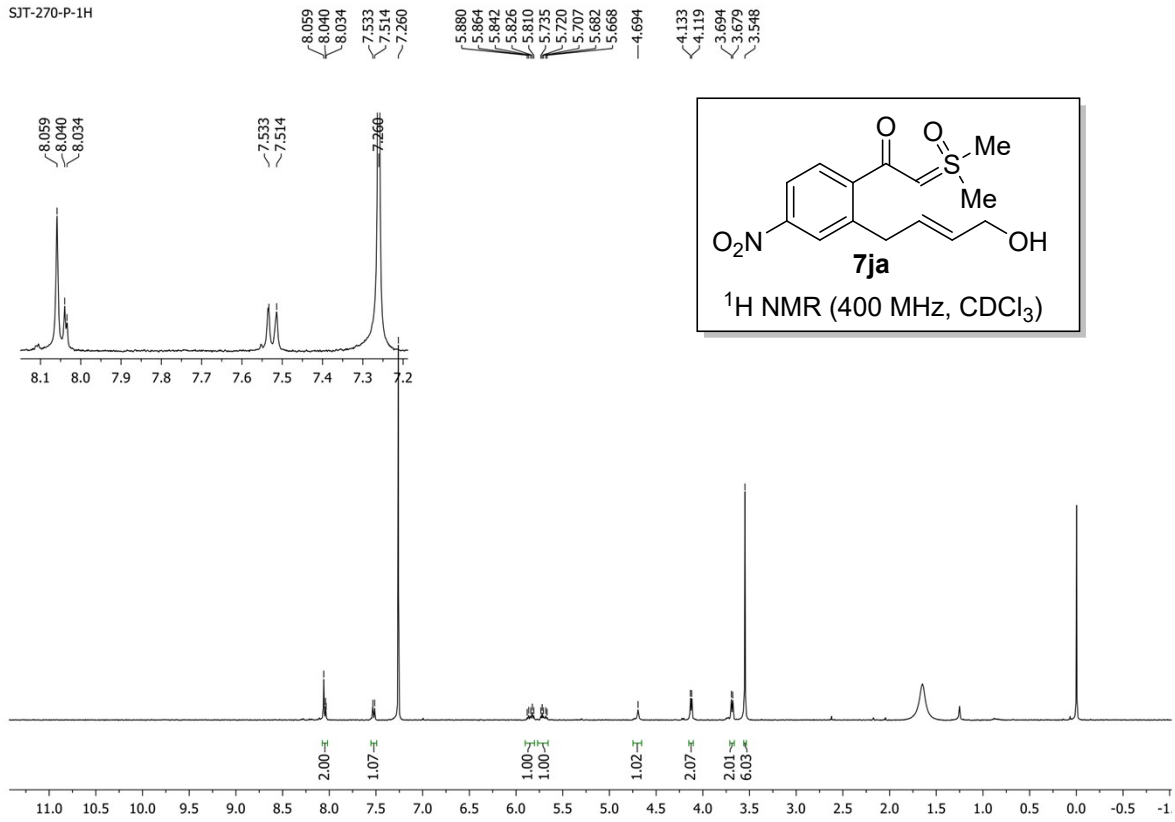

SJT-271-P-1H
7.397
7.378
7.260
7.137
7.121
7.109
7.090
7.071
5.857
5.841
5.820
5.802
5.786
5.717
5.703
5.688
5.665
5.650
4.541
4.095
4.081
3.584
3.551
3.495
3.479
3.584
0.20
6.12
Br
O
O
S
Me
Me
OH
7ba
1H NMR (400 MHz, CDCl3)
1.00
2.09
1.00
1.04
0.97
2.09
0.20
6.12
2.04

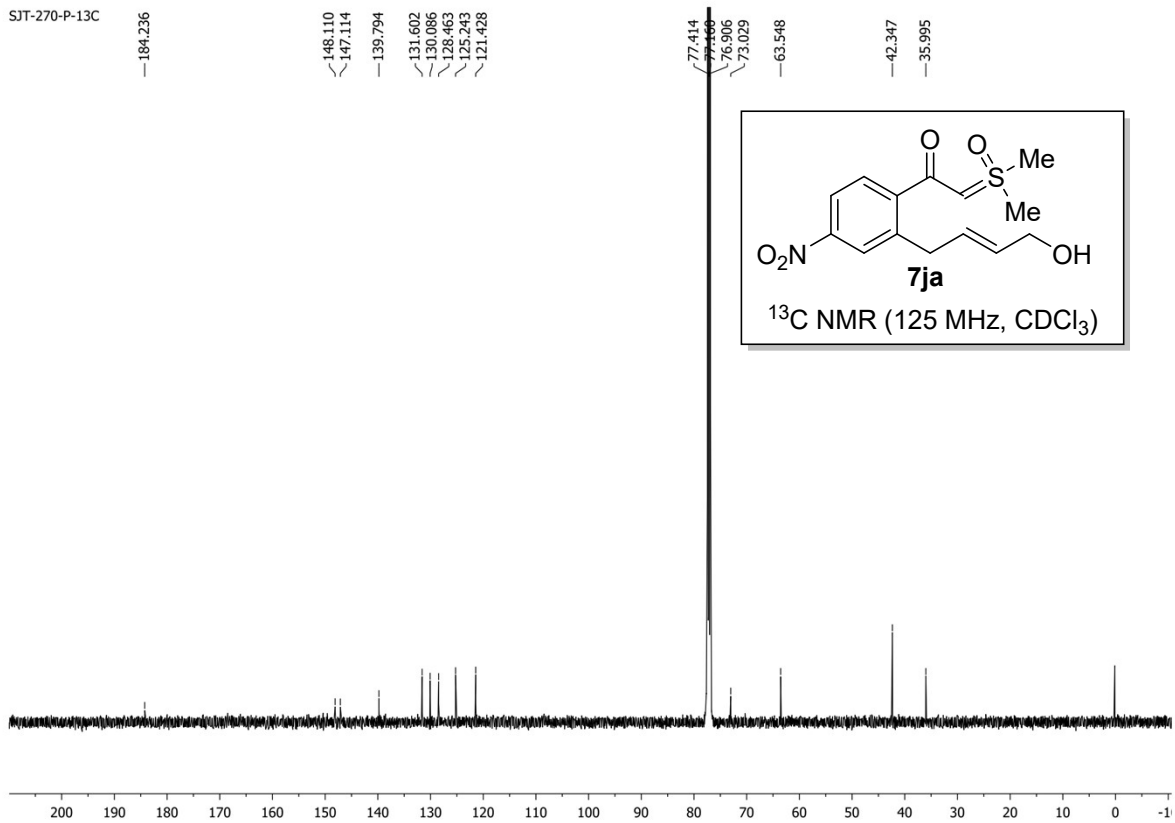

SJT-271-P-13C
184.095
142.816
138.644
131.296
130.885
130.631
129.387
128.593
120.165
77.414
76.906
72.953
63.595
42.259
36.563
Br
O
O
S
Me
Me
OH
7ba
13C NMR (125 MHz, CDCl3)

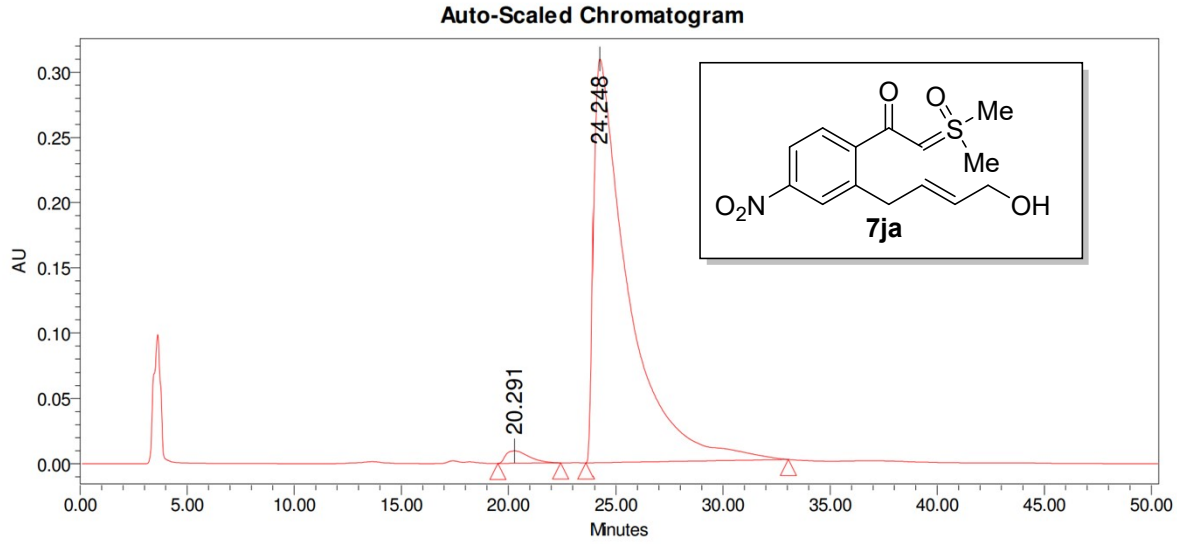

SJT-271-P-NOESY
δ (ppm)
O
S
Me
Me
Br
O
H
H
OH
7ba
NOESY (500 MHz, CDCl3)


SJT-269-P-1H
7.866
7.862
7.851
7.847
7.456
7.435
7.260
5.889
5.872
5.853
5.833
5.818
5.701
5.686
5.671
5.648
5.633
4.683
4.205
4.186
4.102
4.087
3.913
3.657
3.642
3.531
0.07
2.02
1.92
1.00
0.96
1.01
0.72
0.07
2.02
3.09
2.07
6.06
7ha
1H NMR (400 MHz, CDCl3)


SJT-269-P-13C
185.826
166.925
145.393
137.961
131.611
131.439
130.654
127.683
127.521
77.478
77.160
76.843
72.450
64.405
63.764
52.336
42.350
41.127
36.084
7ha
13C NMR (100 MHz, CDCl3)

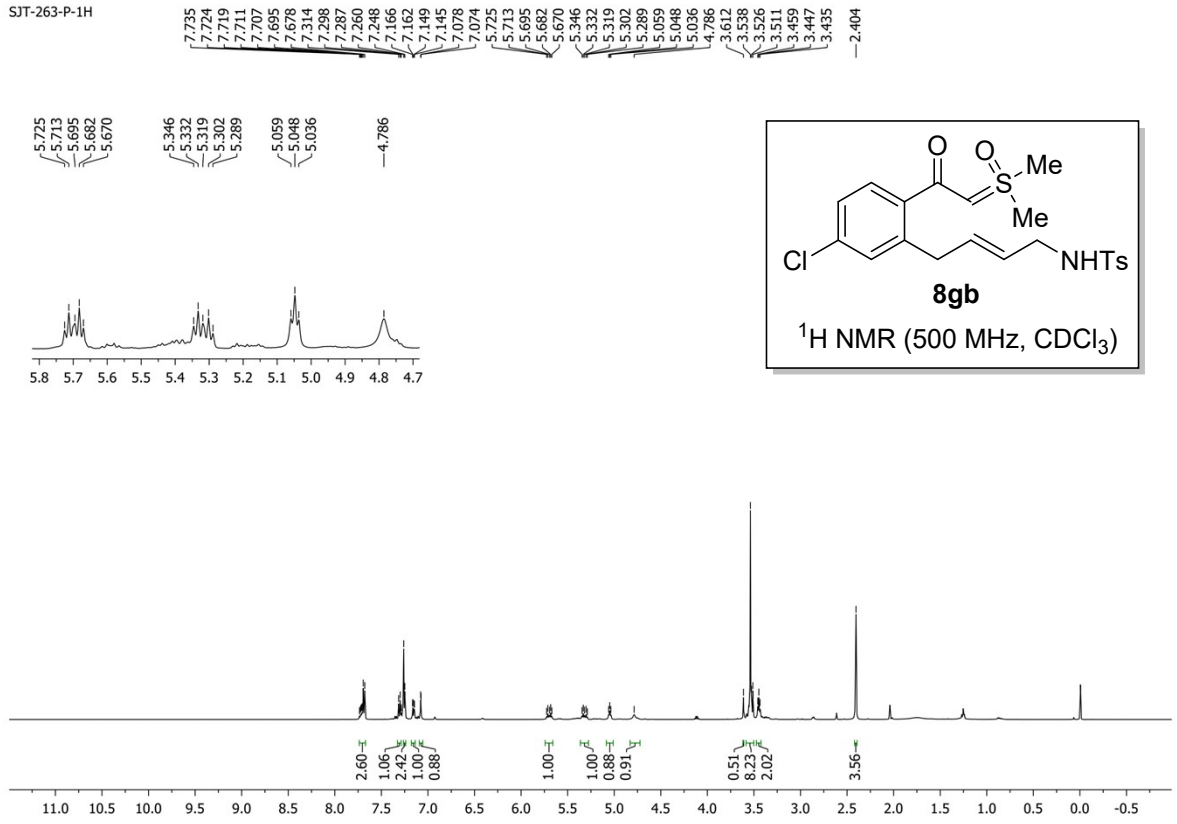

SJT-270-P-1H
8.059
8.040
8.034
7.533
7.514
7.260
5.880
5.864
5.842
5.826
5.810
5.735
5.720
5.707
5.682
5.668
4.694
4.133
4.119
3.694
3.679
3.548
O
O
S
Me
Me
O2N
OH
7ja
1H NMR (400 MHz, CDCl3)
2.00
1.07
1.00
1.00
1.02
2.07
2.01
6.03

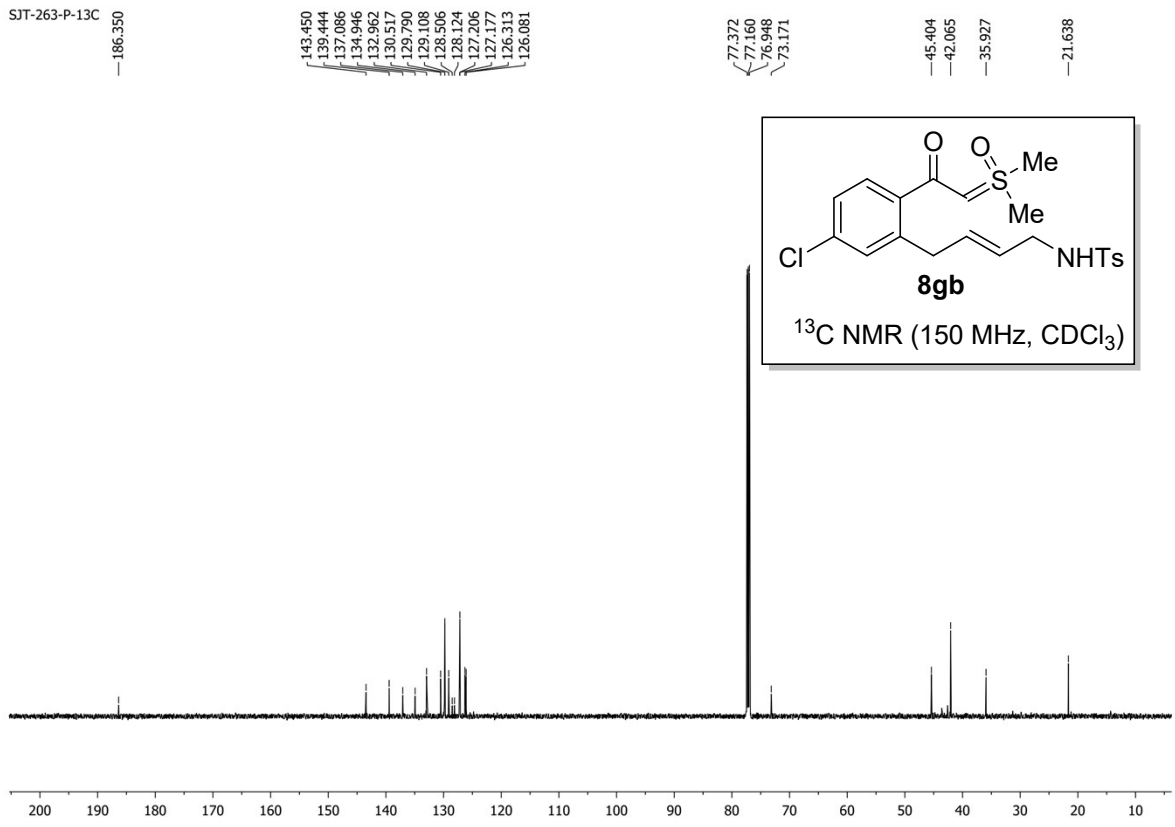

SJT-270-P-13C
184.236
148.110
147.114
139.794
131.602
130.086
128.463
125.243
121.428
77.414
76.906
73.029
63.548
42.347
35.995
O
O
S
Me
Me
O2N
OH
7ja
13C NMR (125 MHz, CDCl3)

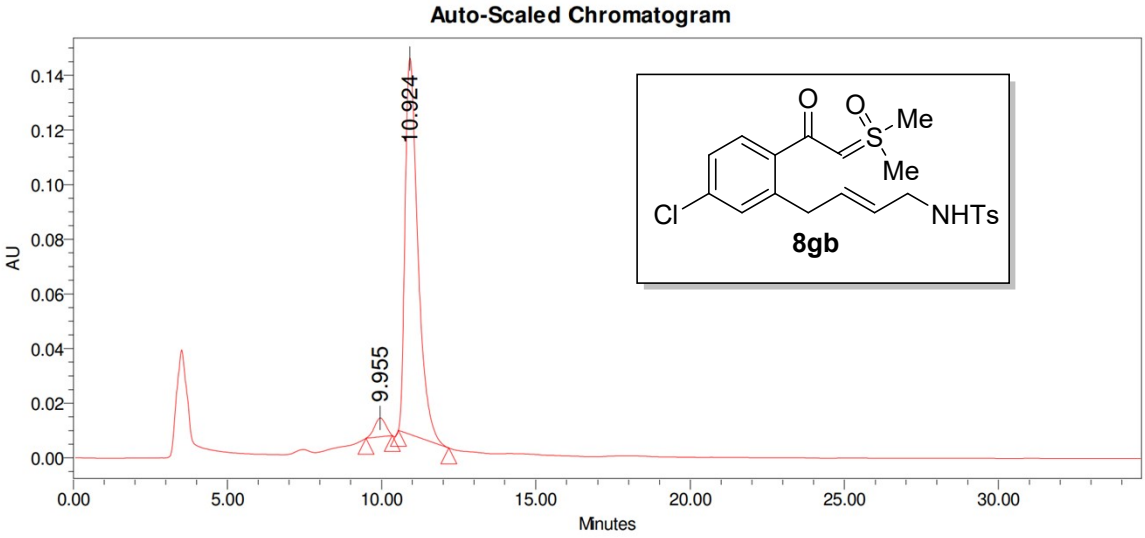


Peak Results

	Start Time (min)	End Time (min)	RT	Height (μV)	% Area
1	19.517	22.450	20.291	9432	2.03
2	23.617	33.050	24.248	309406	97.97

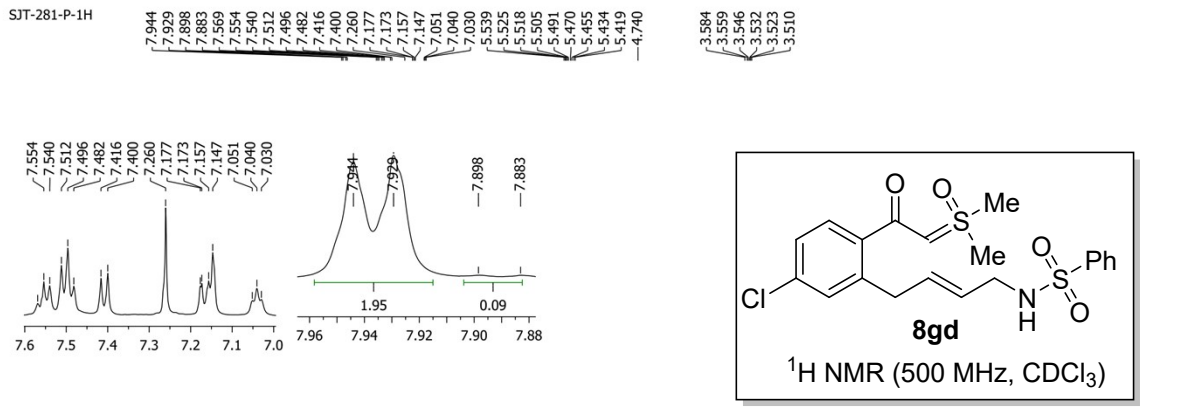


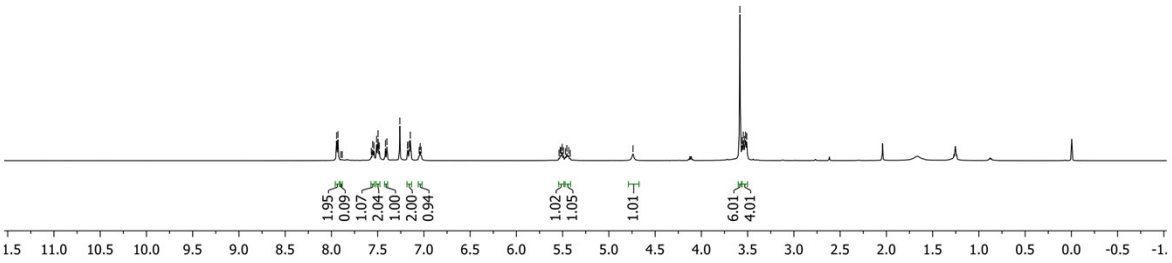


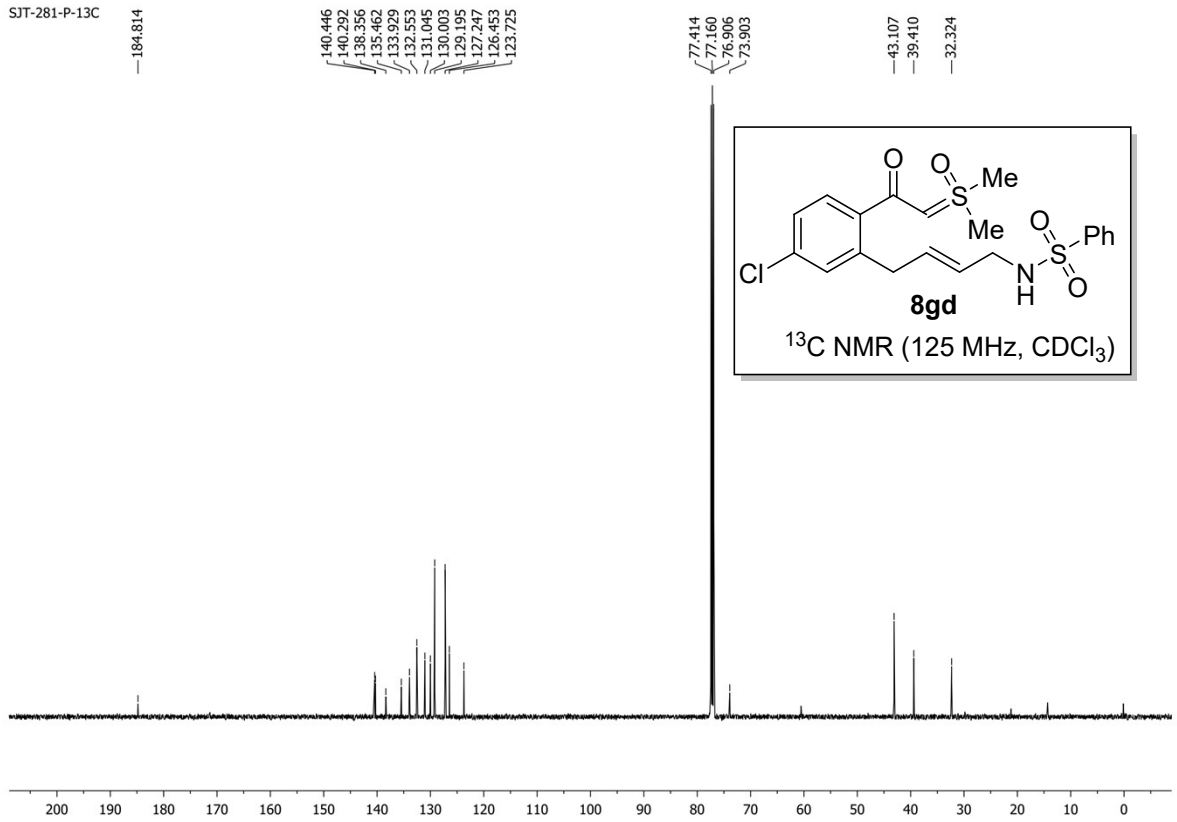


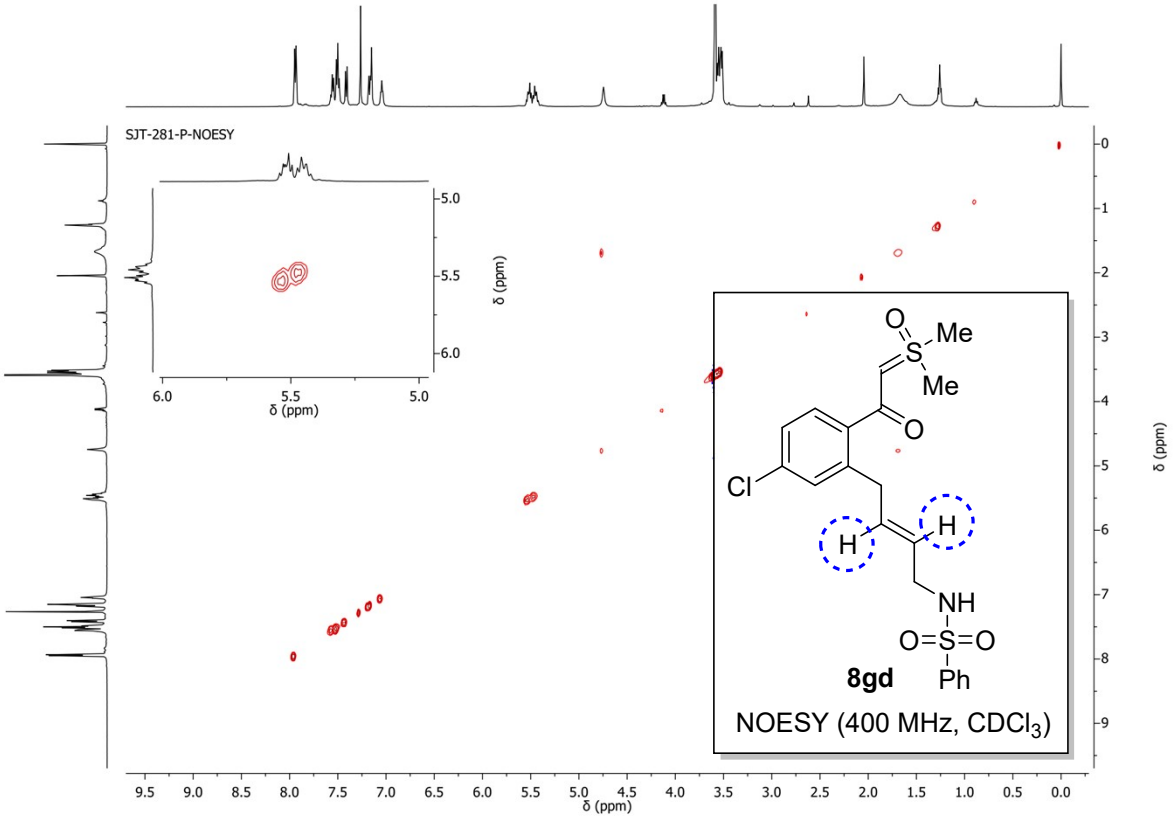
Peak Results

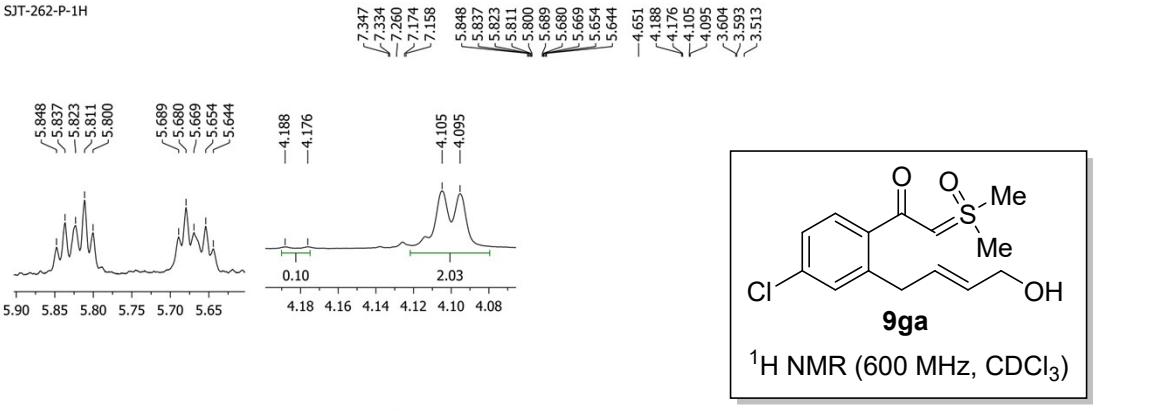
	Start Time (min)	End Time (min)	RT	Height (µV)	% Area
1	9.500	10.350	9.955	6882	4.20
2	10.550	12.183	10.924	137738	95.80

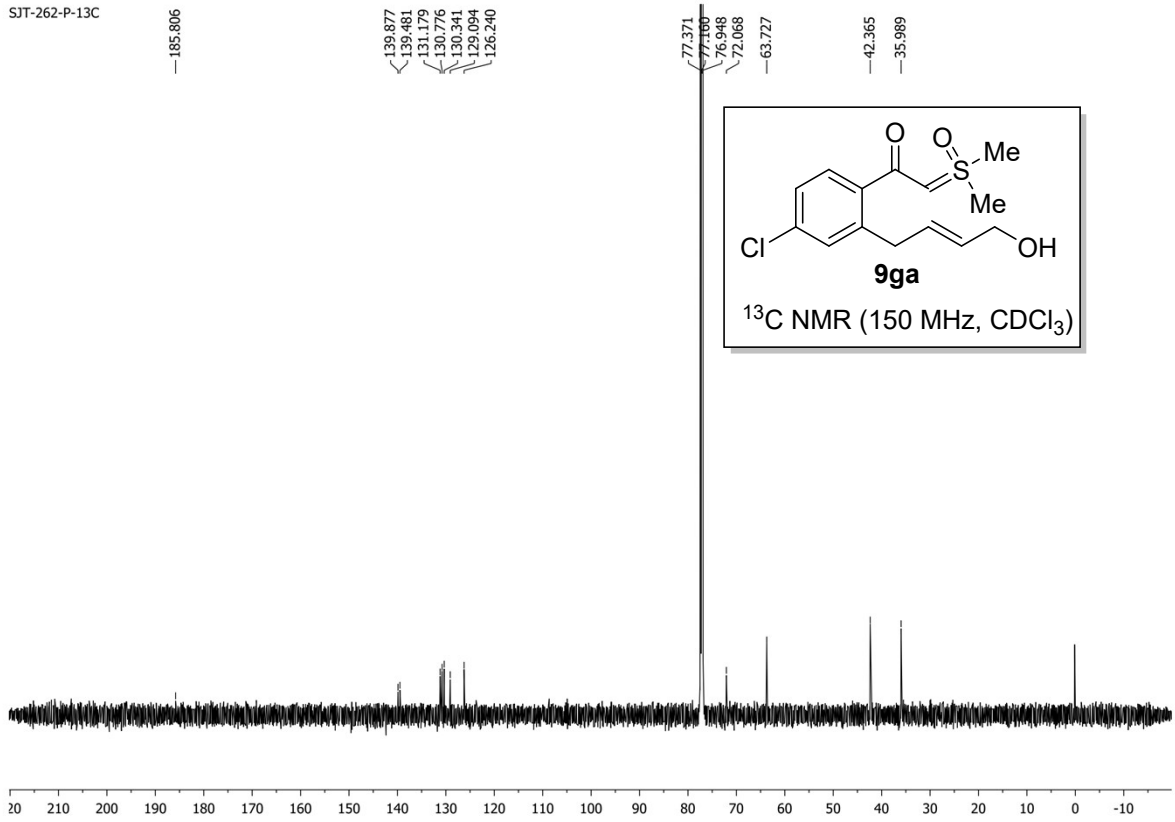

SJT-281-P-1H
7.944
7.929
7.898
7.883
7.569
7.554
7.540
7.512
7.496
7.482
7.416
7.400
7.260
7.177
7.173
7.157
7.147
7.051
7.040
7.030
5.539
5.525
5.518
5.505
5.491
5.470
5.455
5.434
5.419
4.740
3.584
3.559
3.546
3.532
3.523
3.510
1.95
0.09
8gd
1H NMR (500 MHz, CDCl3)

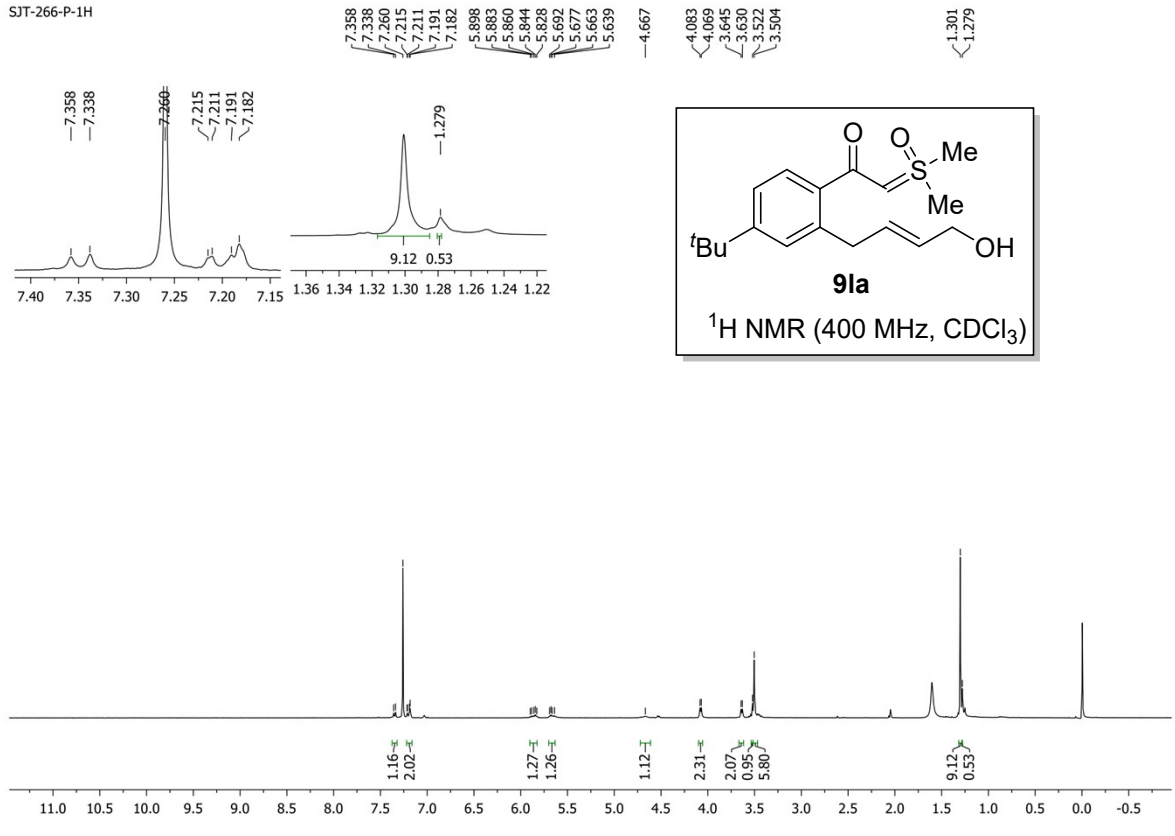

1.95
0.09
1.07
2.04
1.00
2.00
0.94
1.02
1.05
1.01
6.01
4.01

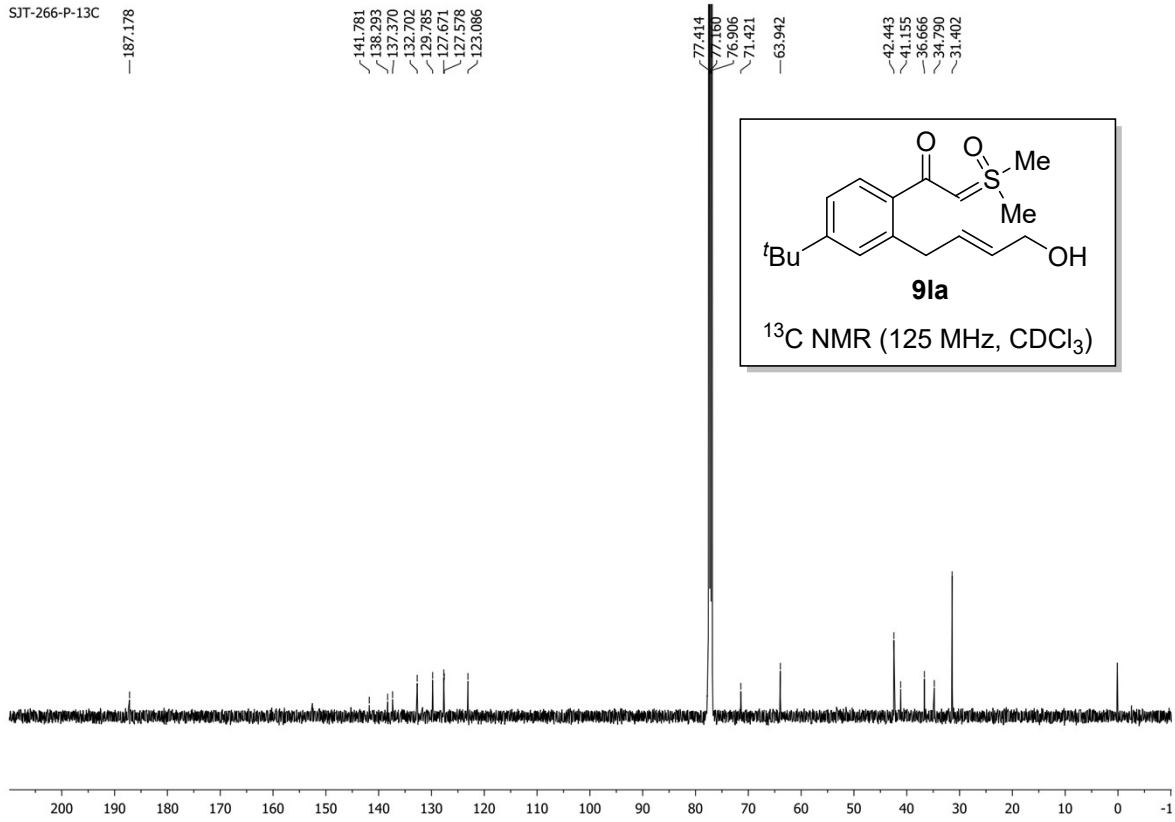

SJT-281-P-13C
184.814
140.446
140.292
138.356
135.462
133.929
132.553
131.045
130.003
129.195
127.247
126.453
123.725
77.414
77.160
76.906
73.903
43.107
39.410
32.324
8gd
13C NMR (125 MHz, CDCl3)

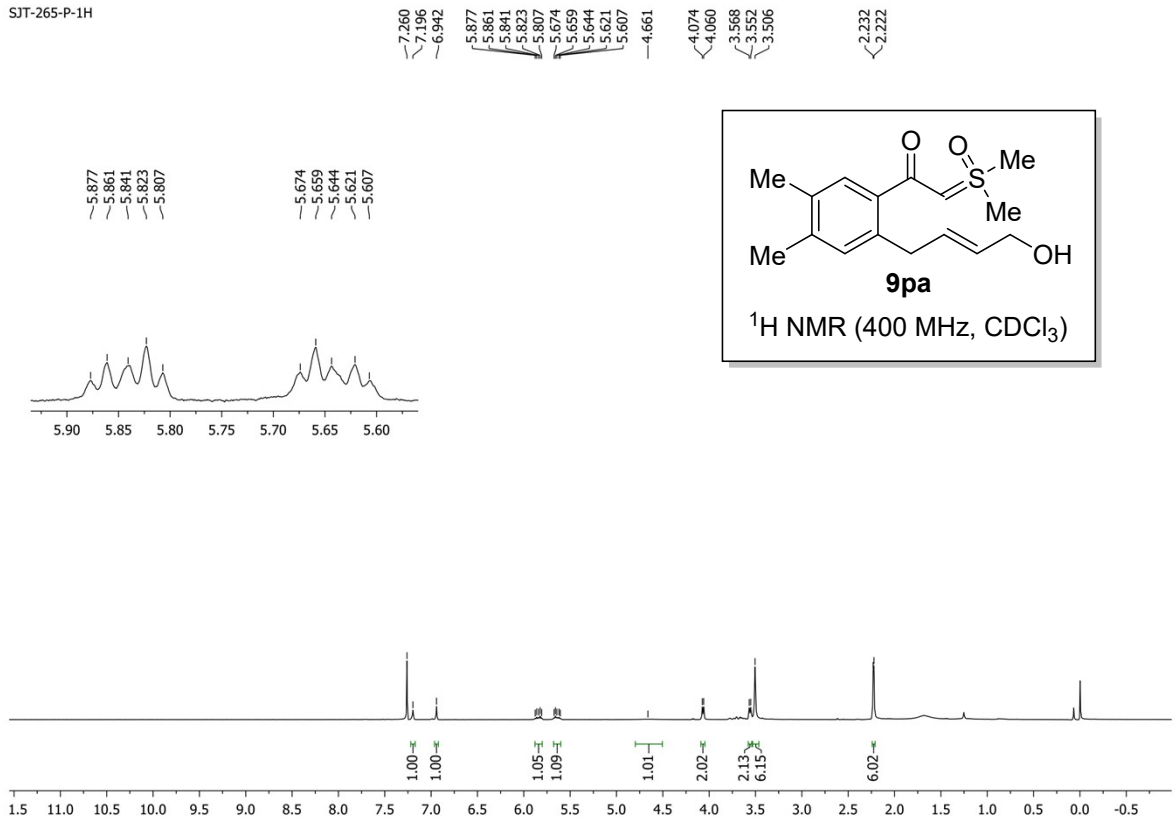

SJT-281-P-NOESY
δ (ppm)
δ (ppm)
δ (ppm)
δ (ppm)
Cl
H
H
NH
O=S=O
Ph
8gd
NOESY (400 MHz, CDCl3)

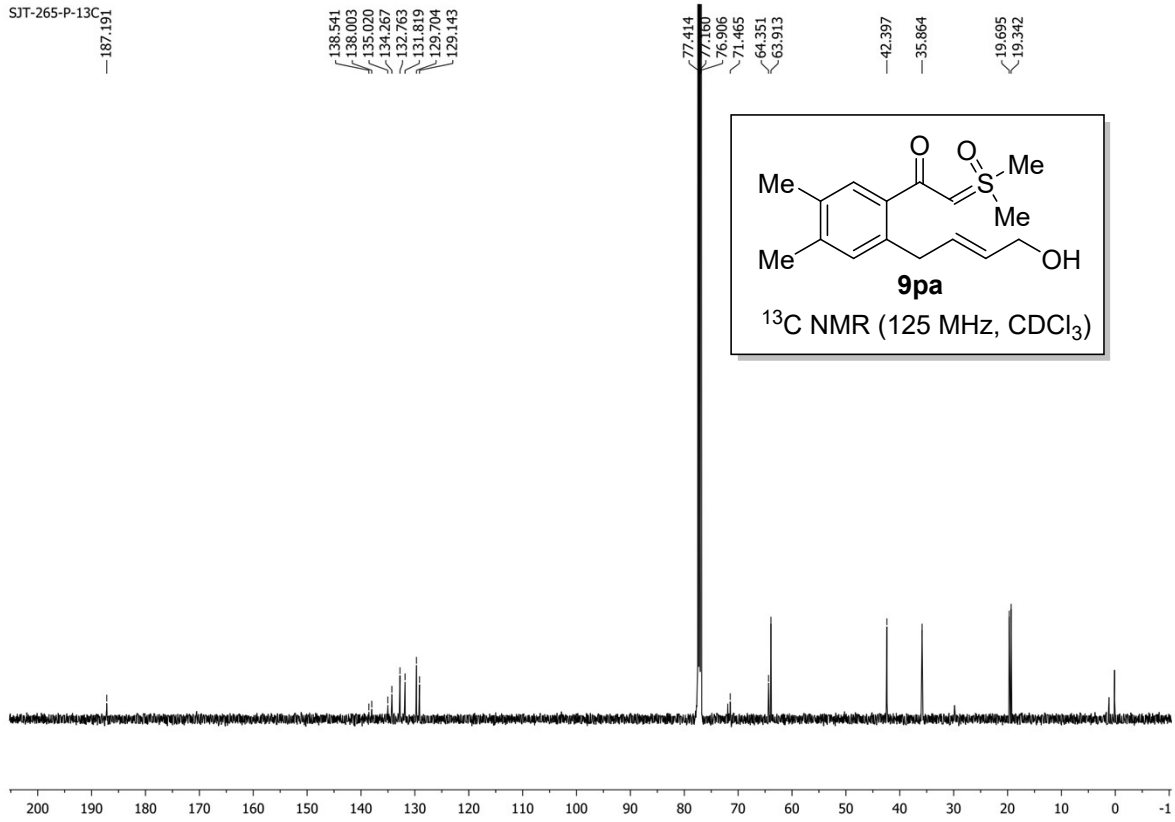

SJT-262-P-1H
0.10
2.03
Cl
OH
9ga
1H NMR (600 MHz, CDCl3)

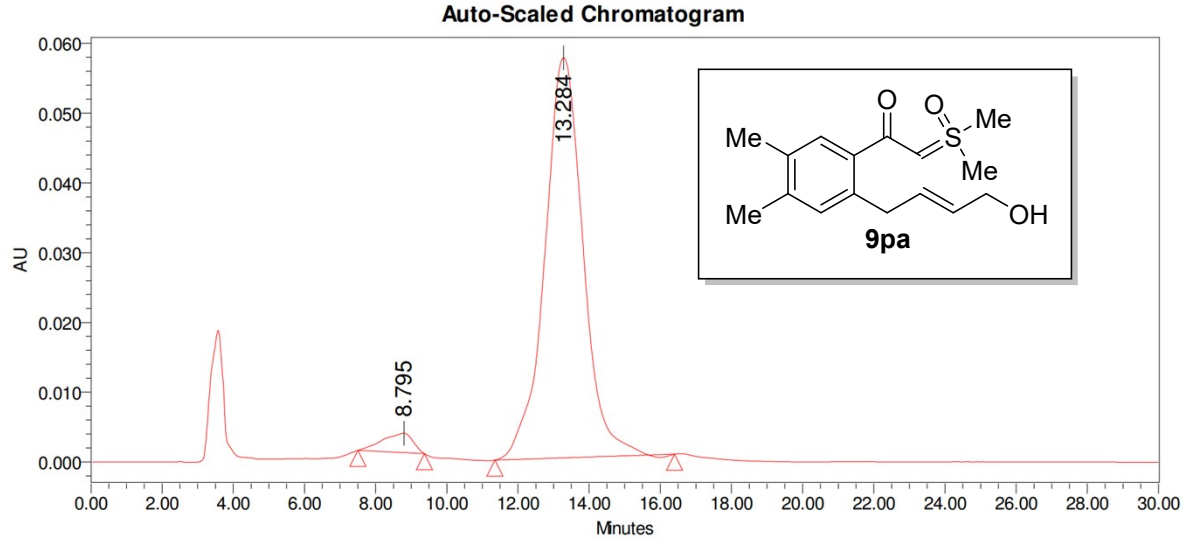

SJT-262-P-13C
185.806
139.877
139.481
131.179
130.776
130.341
129.094
126.240
77.371
77.160
76.948
72.068
63.727
42.365
35.989
O
O
S
Me
Me
Cl
OH
9ga
13C NMR (150 MHz, CDCl3)


SJT-266-P-1H
7.358
7.338
7.260
7.215
7.211
7.191
7.182
5.898
5.883
5.860
5.844
5.828
5.692
5.677
5.663
5.639
4.667
4.083
4.069
3.645
3.630
3.522
3.504
1.301
1.279
9.12
0.53
O
O
S
Me
Me
tBu
OH
9la
1H NMR (400 MHz, CDCl3)
1.16
2.02
1.27
1.26
1.12
2.31
2.07
0.95
5.80
9.12
0.53


SJT-266-P-13C
187.178
141.781
138.293
137.370
132.702
129.785
127.671
127.578
123.086
77.414
77.160
76.906
71.421
63.942
42.443
41.155
36.666
34.790
31.402
O
O
S
Me
Me
tBu
OH
9la
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

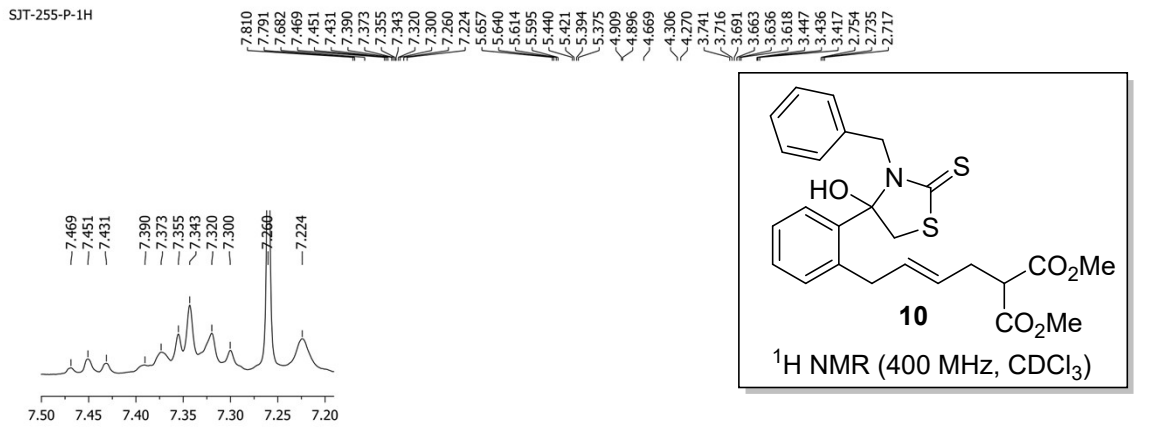

SJT-265-P-1H
7.260
7.196
6.942
5.877
5.861
5.841
5.823
5.807
5.674
5.659
5.644
5.621
5.607
4.661
4.074
4.060
3.568
3.552
3.506
2.232
2.222
5.877
5.861
5.841
5.823
5.807
5.674
5.659
5.644
5.621
5.607
5.90 5.85 5.80 5.75 5.70 5.65 5.60
O
O
S
Me
Me
Me
Me
OH
9pa
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.05
1.09
1.01
2.02
2.13
6.15
6.02
1.5 11.0 10.5 10.0 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 -0.5

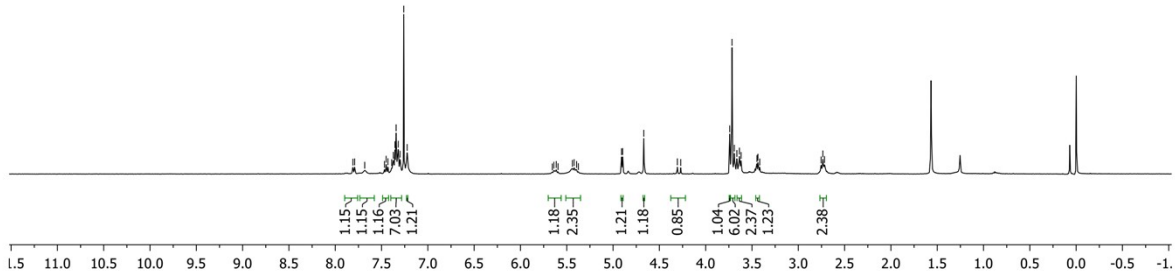


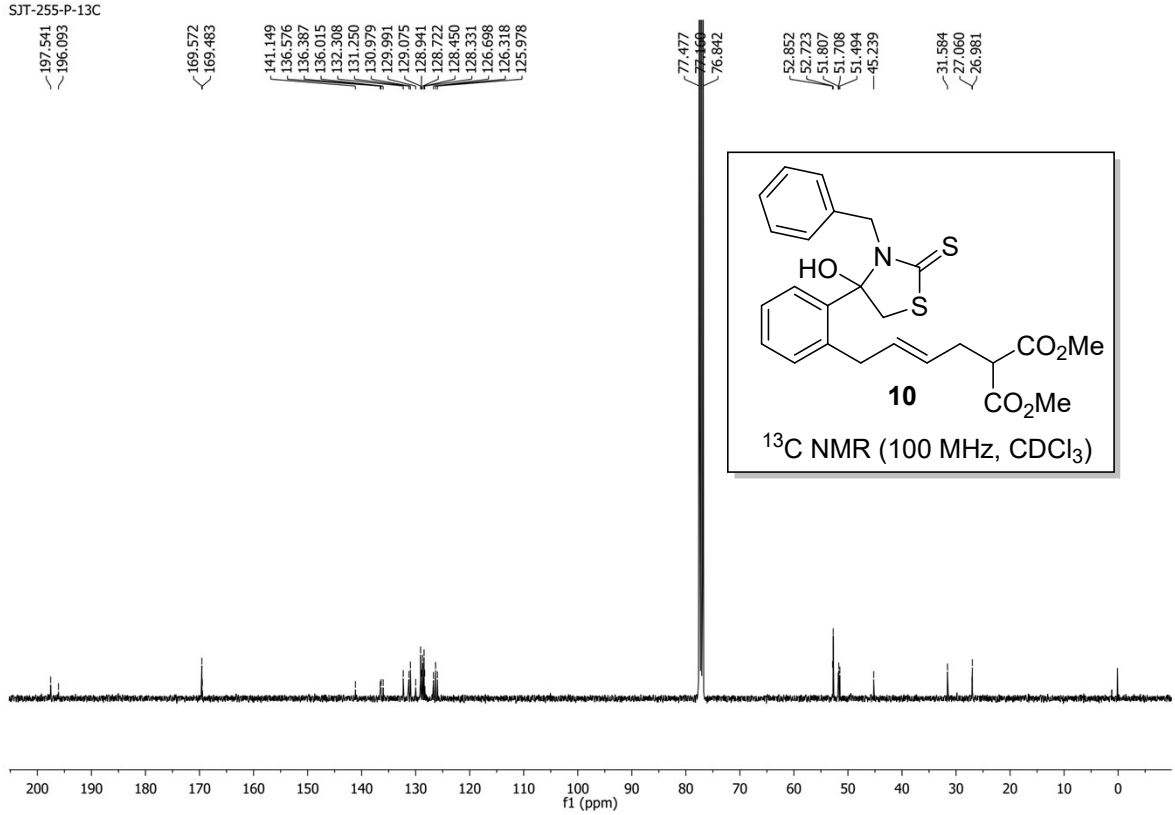


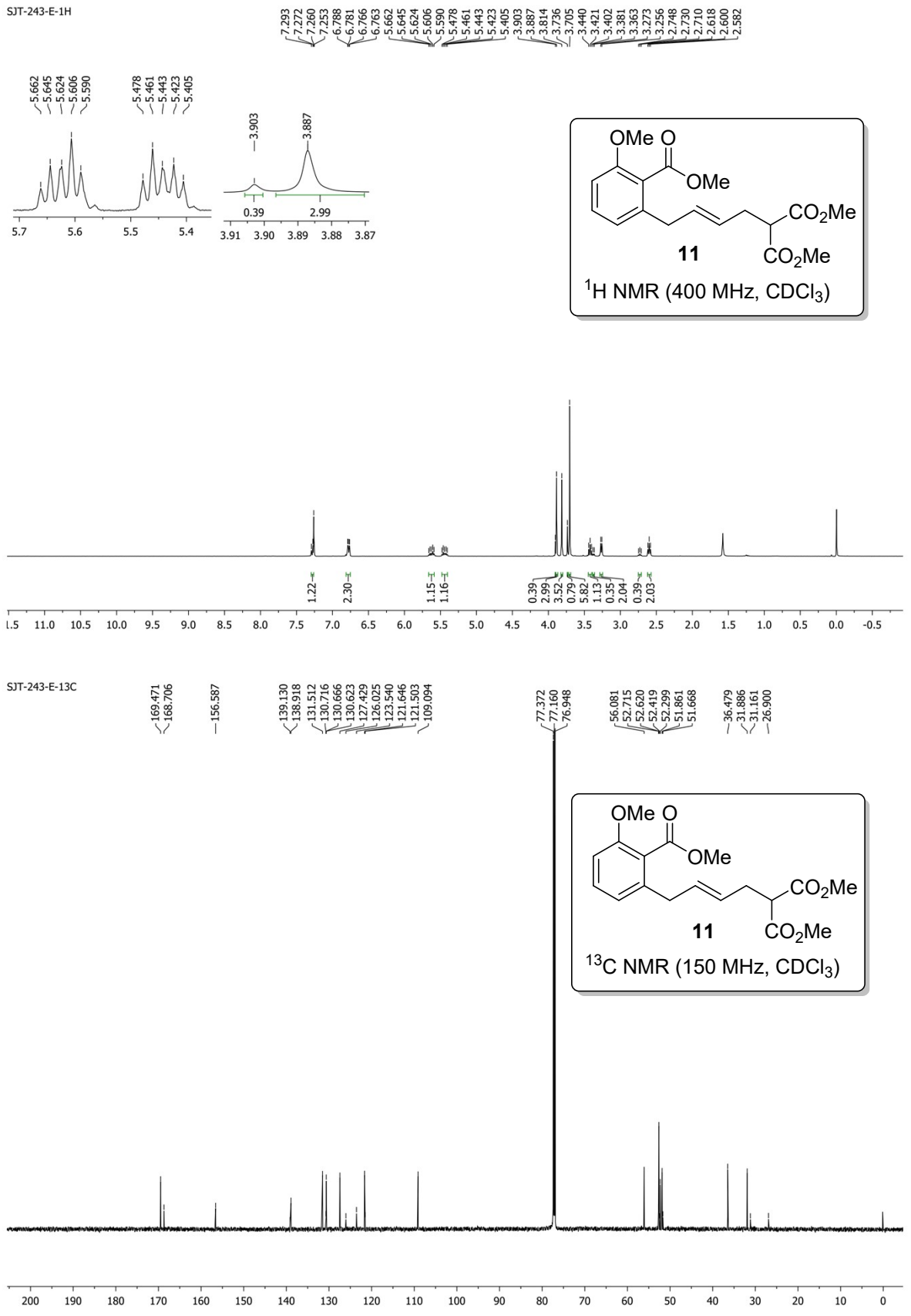
Peak Results

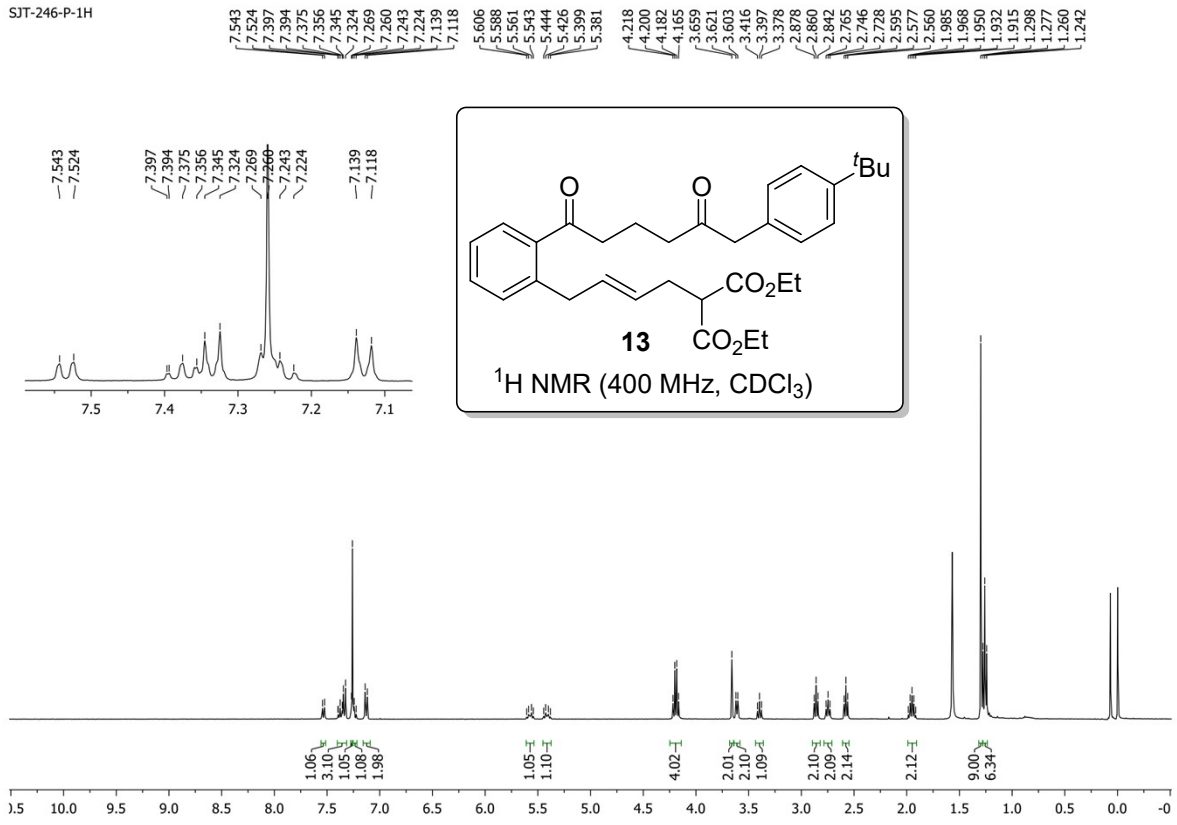
	Start Time (min)	End Time (min)	RT	Height (μV)	% Area
1	7.500	9.367	8.795	2777	3.67
2	11.350	16.400	13.284	57356	96.33

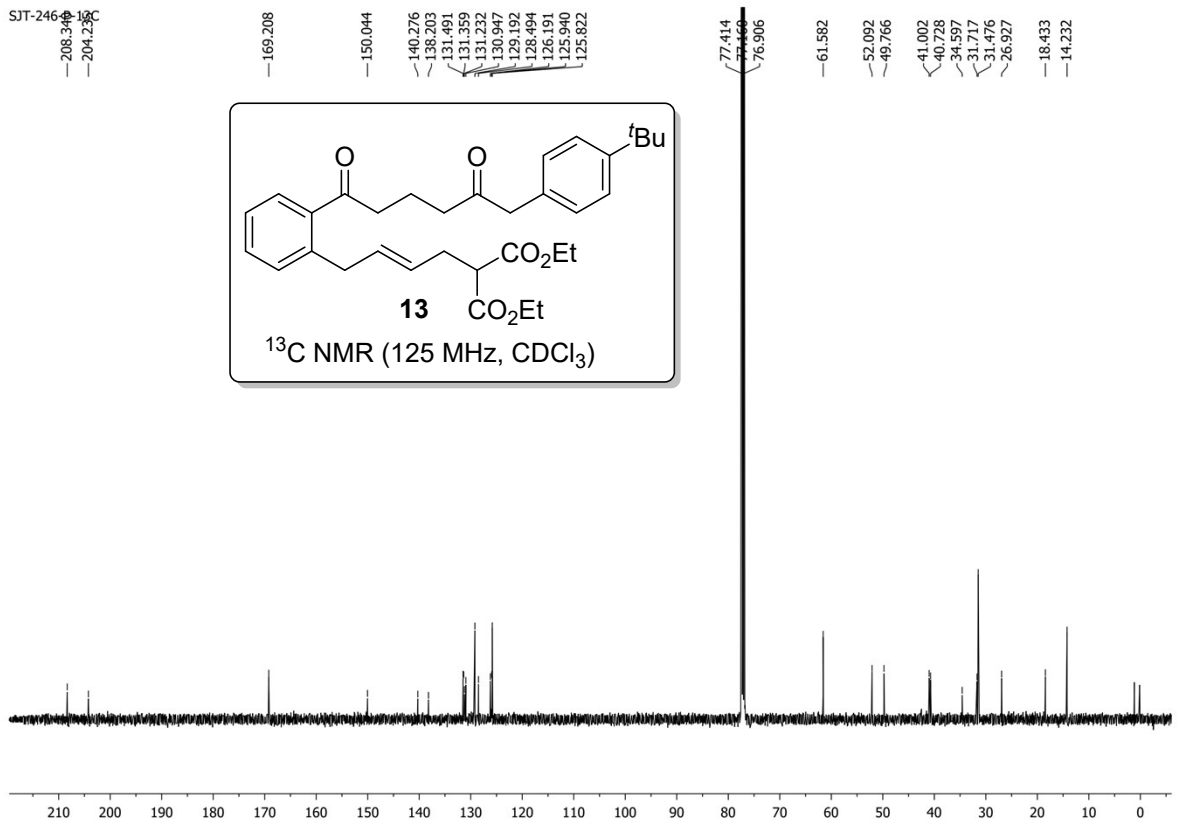

SJT-255-P-1H
7.810
7.791
7.682
7.469
7.451
7.431
7.390
7.373
7.355
7.343
7.320
7.300
7.260
7.224
5.657
5.640
5.614
5.595
5.440
5.421
5.394
5.375
4.909
4.896
4.669
4.306
4.270
3.741
3.716
3.691
3.663
3.636
3.618
3.447
3.436
3.417
2.754
2.735
2.717
7.469
7.451
7.431
7.390
7.373
7.355
7.343
7.320
7.300
7.260
7.224
7.50 7.45 7.40 7.35 7.30 7.25 7.20
HO
N
S
S
CO2Me
CO2Me
10
1H NMR (400 MHz, CDCl3)


1.15
1.15
1.16
7.03
1.21
1.18
2.35
1.21
1.18
0.85
1.04
6.02
2.37
1.23
2.38
11.0 10.5 10.0 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 -0.5

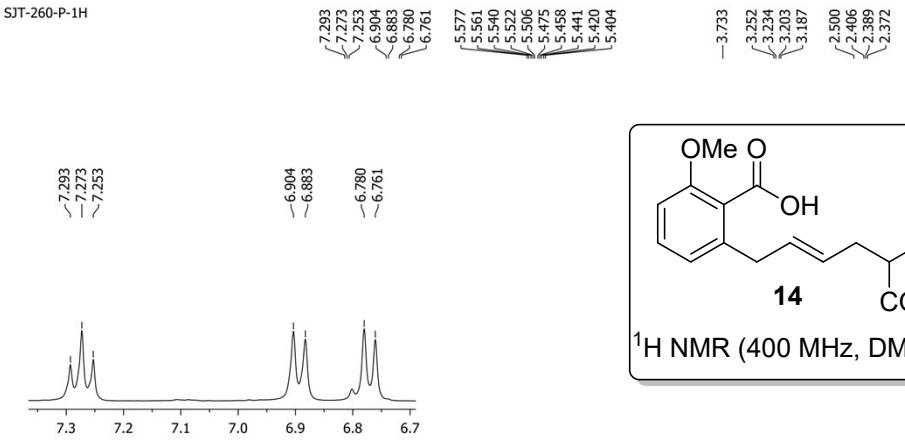

SJT-255-P-13C
197.541
196.093
169.572
169.483
141.149
136.576
136.387
136.015
132.308
131.250
130.979
129.991
129.075
128.941
128.722
128.450
128.331
126.698
126.318
125.978
77.477
77.160
76.842
52.852
52.723
51.807
51.708
51.494
45.239
31.584
27.060
26.981
HO
N
S
S
CO2Me
CO2Me
10
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


SJT-243-E-1H
7.293
7.272
7.260
7.253
6.788
6.781
6.766
6.763
5.662
5.645
5.624
5.606
5.590
5.478
5.461
5.443
5.423
5.405
3.903
3.887
3.814
3.736
3.705
3.440
3.421
3.402
3.381
3.363
3.273
3.256
2.748
2.730
2.710
2.618
2.600
2.582
0.39
2.99
OMe O
OMe
CO2Me
11
CO2Me
1H NMR (400 MHz, CDCl3)
1.22
2.30
1.15
1.16
0.39
2.99
3.52
0.79
5.82
1.13
0.35
2.04
0.39
2.03
SJT-243-E-13C
169.471
168.706
156.587
139.130
138.918
131.512
130.716
130.666
130.623
127.429
126.025
123.540
121.646
121.503
109.094
77.372
77.160
76.948
56.081
52.715
52.620
52.419
52.299
51.861
51.668
36.479
31.886
31.161
26.900
OMe O
OMe
CO2Me
11
CO2Me
13C NMR (150 MHz, CDCl3)

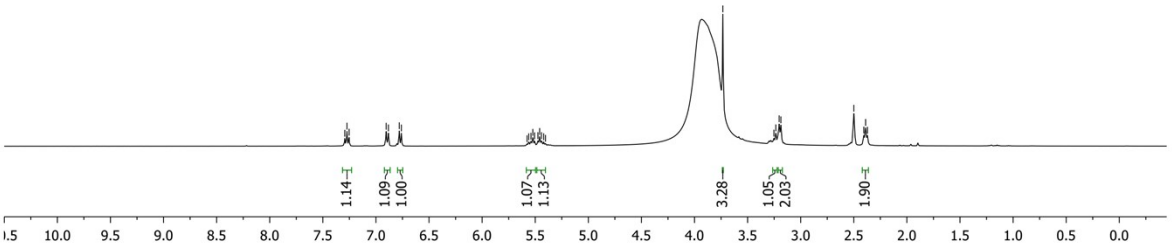

SJT-246-P-1H
13
^{1}H NMR (400 MHz, CDCl$_3$)


SJT-246-P-13C
13
^{13}C NMR (125 MHz, CDCl$_3$)

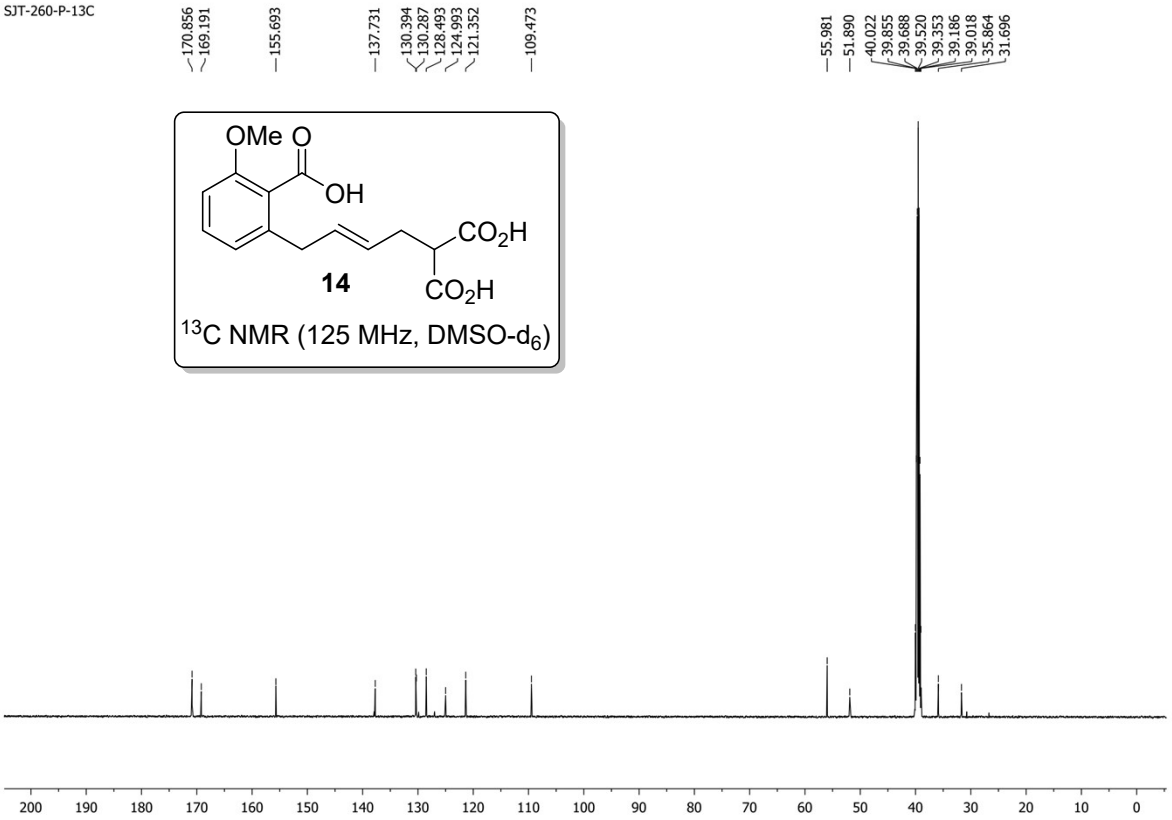
SJT-260-P-1H



^{1}H NMR (400 MHz, DMSO-d_6)

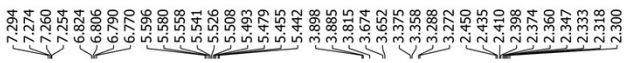


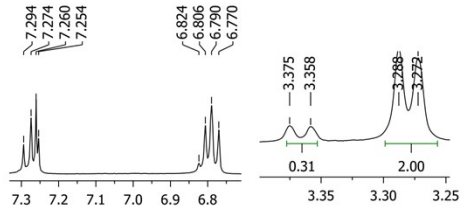
SJT-260-P-13C

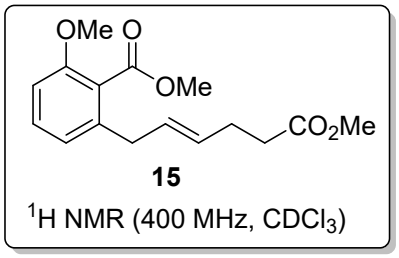


^{13}C NMR (125 MHz, DMSO-d_6)

SJT-338-P-1H

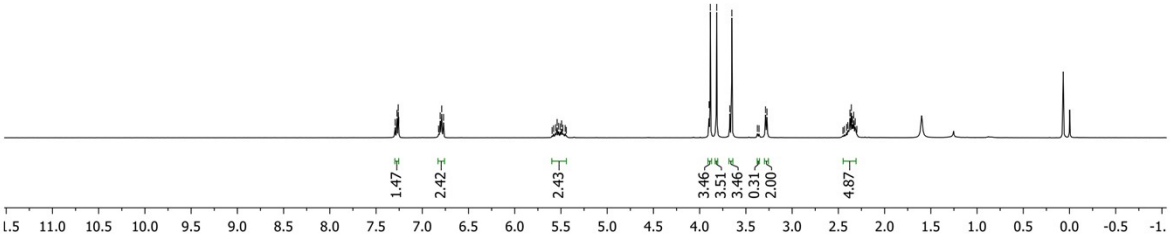




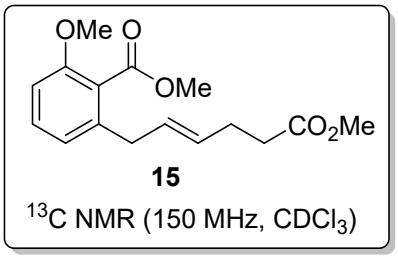


15

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

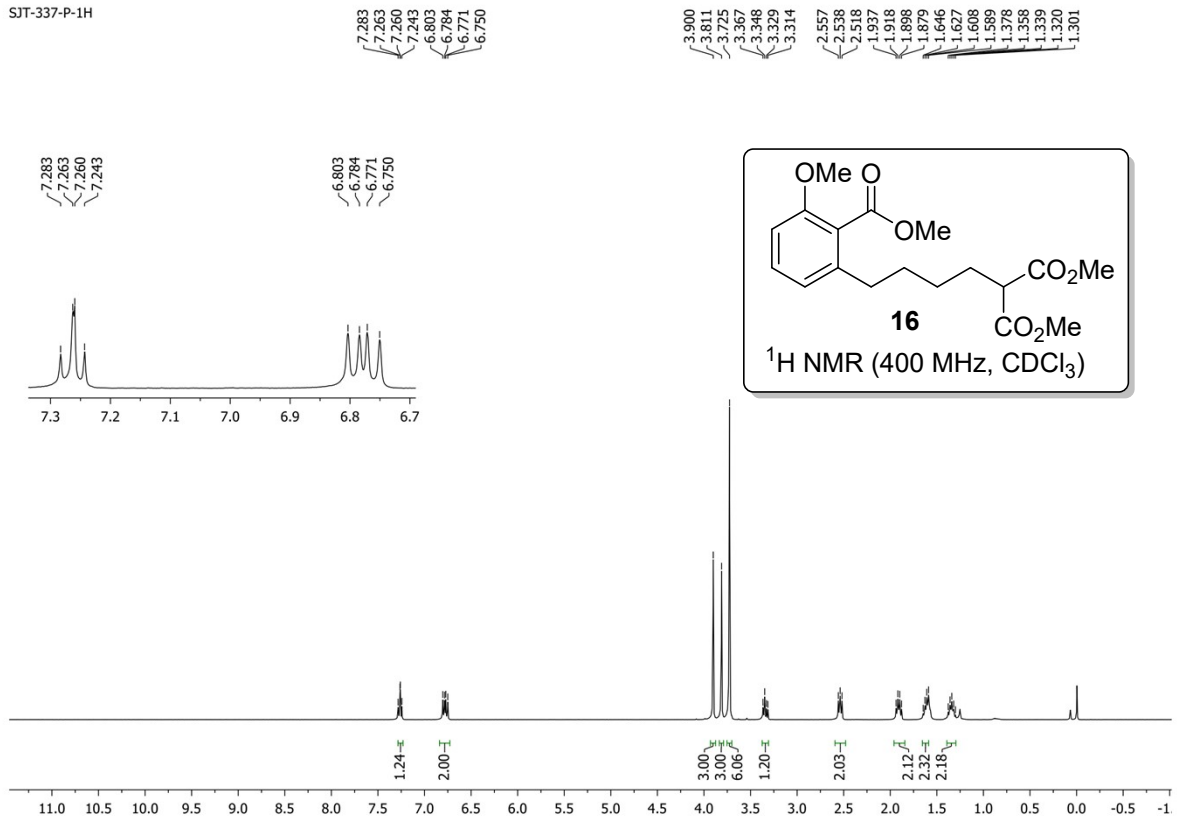


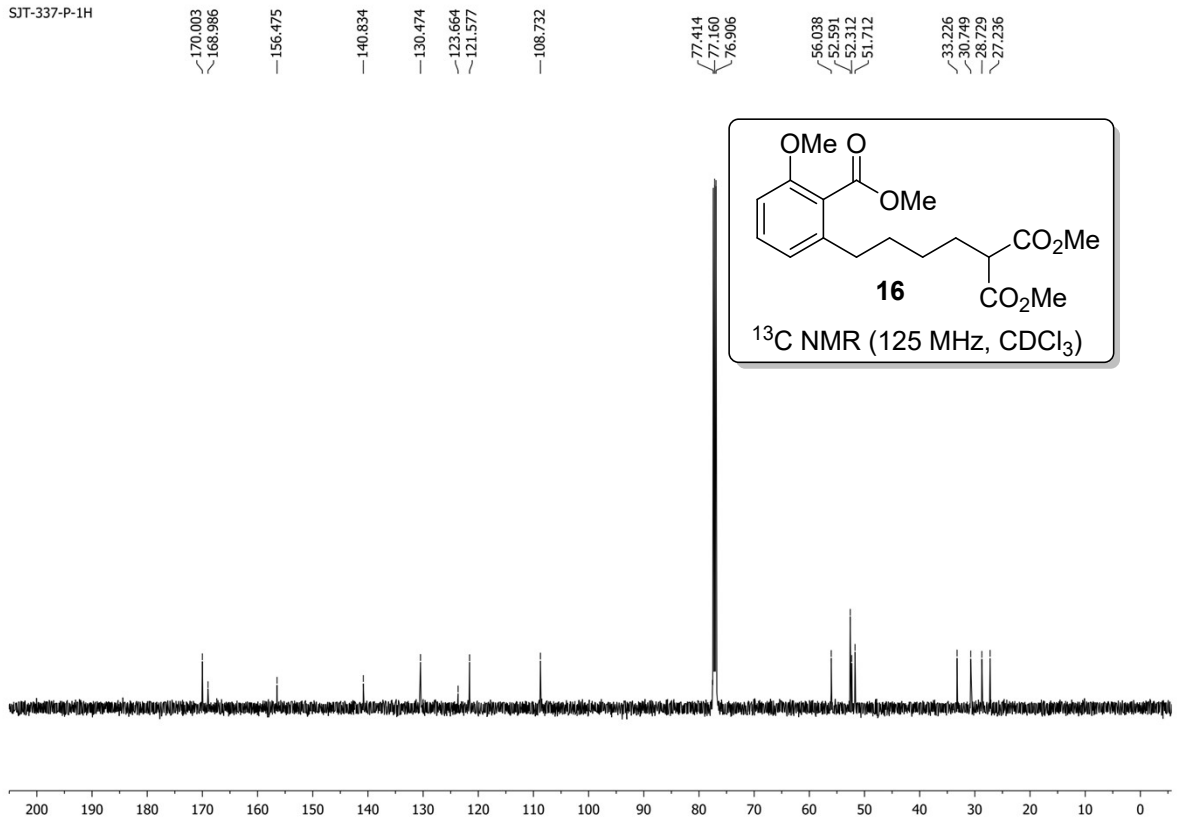
SJT-338-P-13C

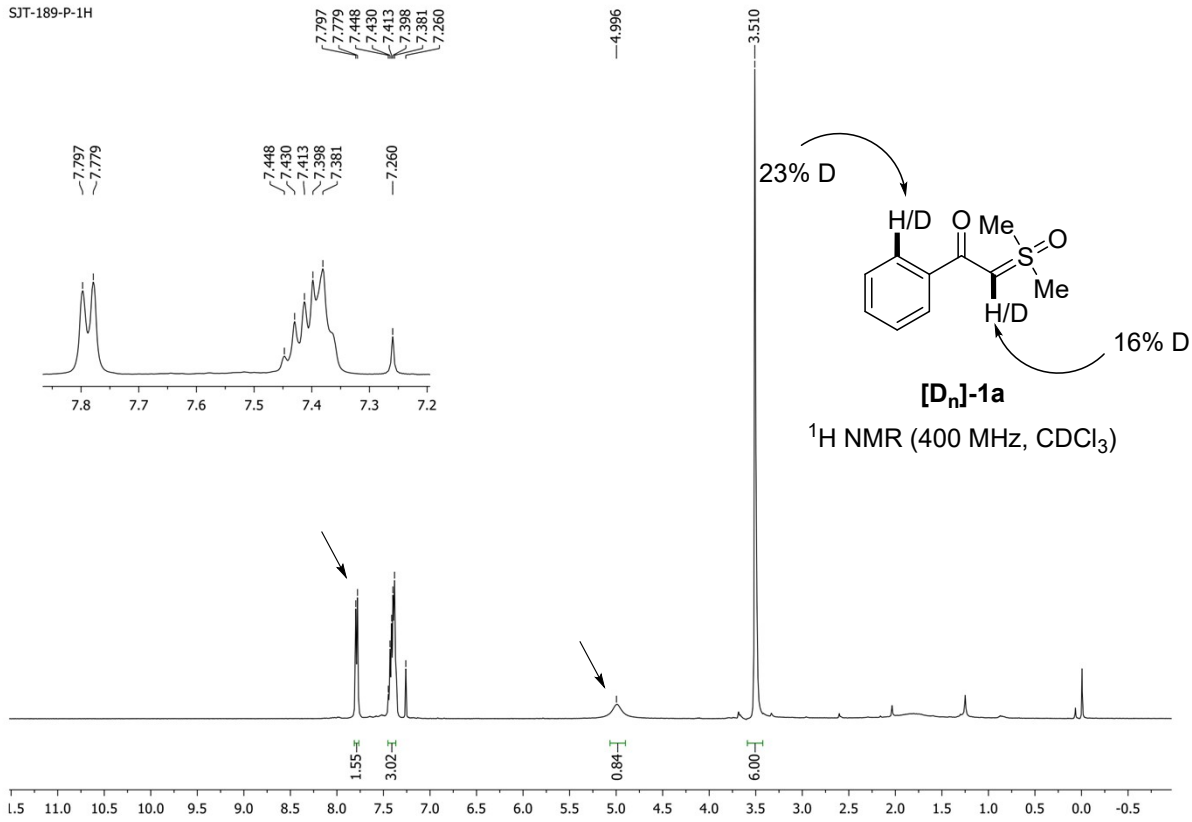


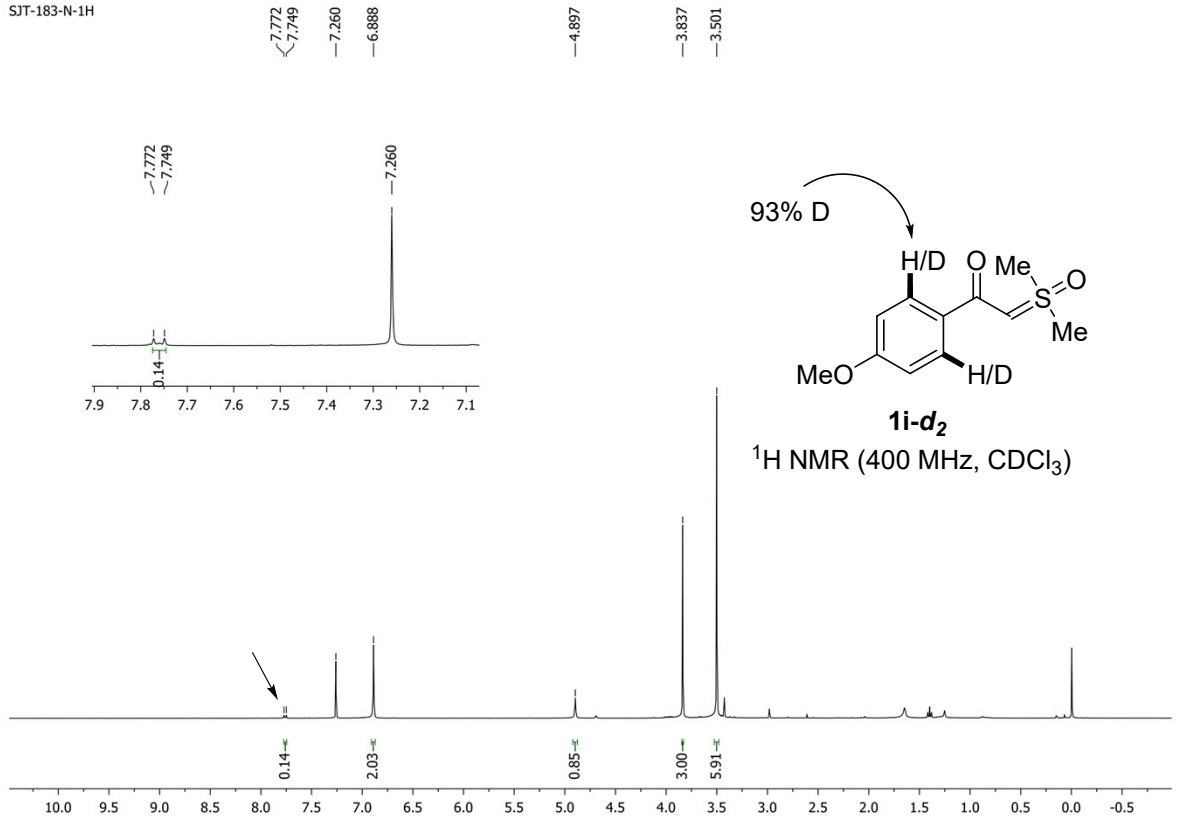
15

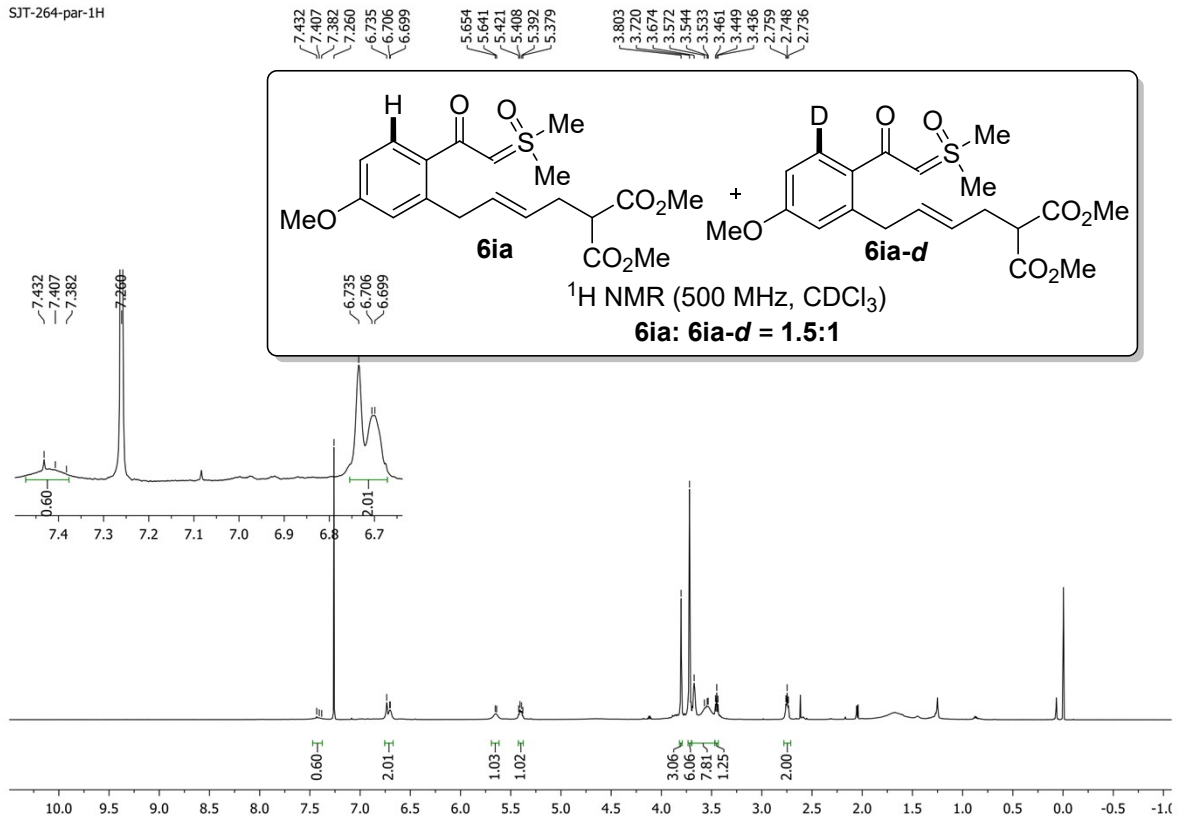
^{13}C NMR (150 MHz, $CDCl_3$)

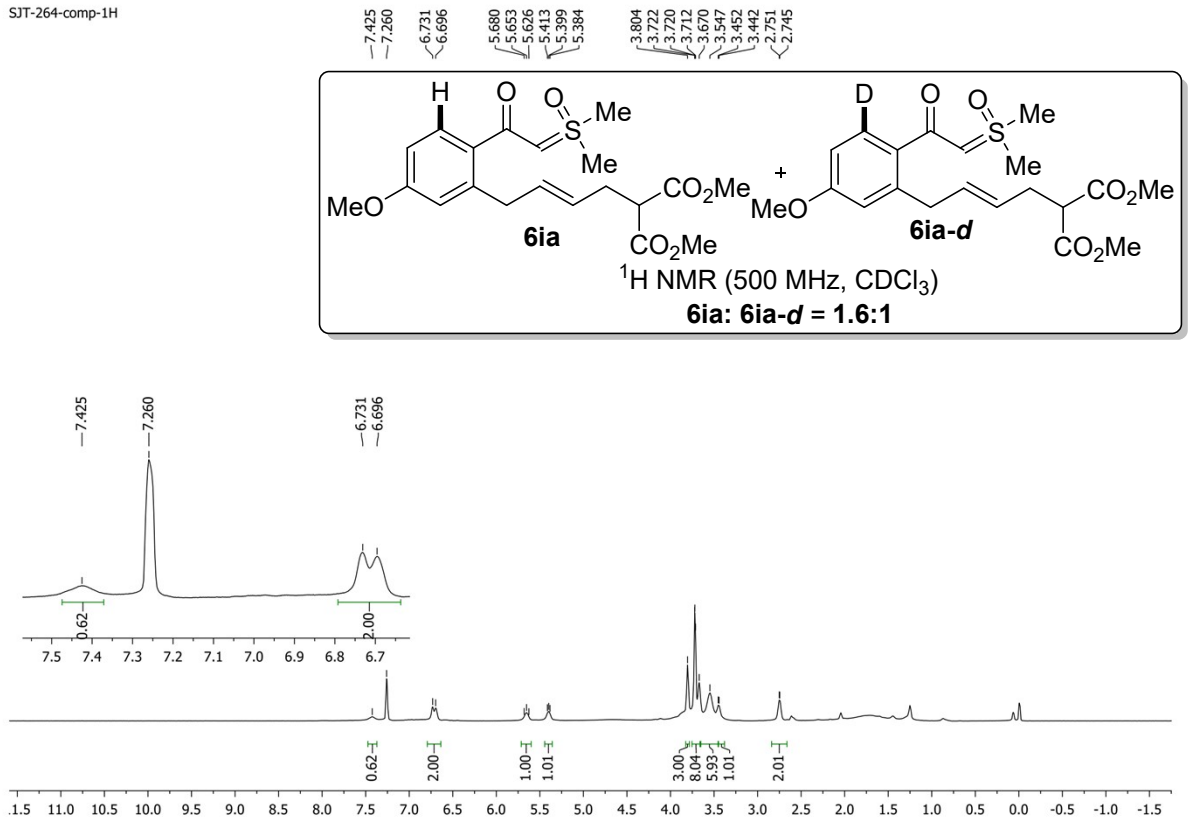

SJT-337-P-1H
7.283
7.263
7.260
7.243
6.803
6.784
6.771
6.750
3.900
3.811
3.725
3.367
3.348
3.329
3.314
2.557
2.538
2.518
1.937
1.918
1.898
1.879
1.646
1.627
1.608
1.589
1.378
1.358
1.339
1.320
1.301
OMe O
OMe
CO2Me
CO2Me
16
1H NMR (400 MHz, CDCl3)
1.24
2.00
3.00
3.00
6.06
1.20
2.03
2.12
2.32
2.18


SJT-337-P-1H
170.003
168.986
156.475
140.834
130.474
123.664
121.577
108.732
77.414
77.160
76.906
56.038
52.591
52.312
51.712
33.226
30.749
28.729
27.236
OMe O
OMe
CO2Me
CO2Me
16
13C NMR (125 MHz, CDCl3)


SJT-189-P-1H
7.797
7.779
7.448
7.430
7.413
7.398
7.381
7.260
4.996
3.510
23% D
H/D
O
Me
S
O
Me
H/D
16% D
[Dn]-1a
1H NMR (400 MHz, CDCl3)
1.55
3.02
0.84
6.00


SJT-183-N-1H
7.772
7.749
7.260
6.888
4.897
3.837
3.501
93% D
H/D
O
Me
S
O
Me
MeO
H/D
1i-d2
1H NMR (400 MHz, CDCl3)
0.14
2.03
0.85
3.00
5.91


SJT-264-par-1H
6ia
6ia-d
1H NMR (500 MHz, CDCl3)
6ia: 6ia-d = 1.5:1


SJT-264-comp-1H
6ia
6ia-d
1H NMR (500 MHz, CDCl3)
6ia: 6ia-d = 1.6:1