Supporting Information

Visible Light-mediated NHCs and Photoredox Co-catalyzed 1,2-Sulfonylacylation of Allenes via Acyl and Allyl Radical Cross-coupling

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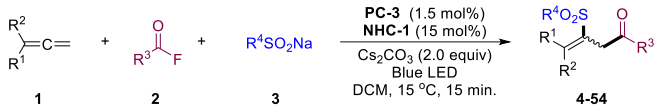
I. General Information

All reactions were carried out under a nitrogen atmosphere. Reagents were purchased from commercial sources and used without further purification unless otherwise noted. All of the solvents were anhydrous according to distillation. The reactions were monitored with the aid of thin-layer chromatography (TLC) on 0.25 mm precoated silica gel plates. Melting points were measured on Büchi B-540 apparatus. **^{1}H NMR** spectra were recorded at 25 ºC on a Bruker 600 or 500, Varian 500 MHz, **^{13}C NMR** spectra were recorded at 25 ºC on a Bruker 151, 126 MHz, respectively in $CDCl_3$ by using TMS as an internal standard. **^{19}F NMR** spectra were recorded at 25 ºC on a Bruker 565 MHz. **^{1}H** and **^{13}C NMR** spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm for ^{1}H NMR) and $CHCl_3$ (77.0 ppm for ^{13}C NMR), respectively. Letters m, s, d, t and q stand for multiplet, singlet, doublet, triplet, and quartet, respectively. High-resolution mass spectra (**HRMS**) were recorded on Bruck microtof. We use RLH-18 8-position Photo Reaction System, which is manufactured by Beijing Rogertech Co.ltd based in Beijing PRC. This Photo reactor we used has equipped with eight blue light 10 W LED. This blue light 10 W LED's energy peak wavelength is 453.5 nm, and peak width at half-height is 20.4 nm. The irradiation vessel is a borosilicate glass test tube; LED irradiates through a high-reflection channel to the test tube; the path length is 2 cm, and no filter between LED and test tube.

II. General Procedure for the Synthesis of Tetrasubstituted Olefins



Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (9.5 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol), sulfinate (0.4 mmol) and DCM (6.0 mL). Then **1** (0.2 mmol) and **2** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at 15 ℃ for 15 min. After the reaction was finished that monitored by TLC, the reaction mixture was quenched by water. The mixture was extracted with DCM (3 x 5.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was evaporated under a vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1) to give the corresponding products.

III. Preparation of the Starting Materials

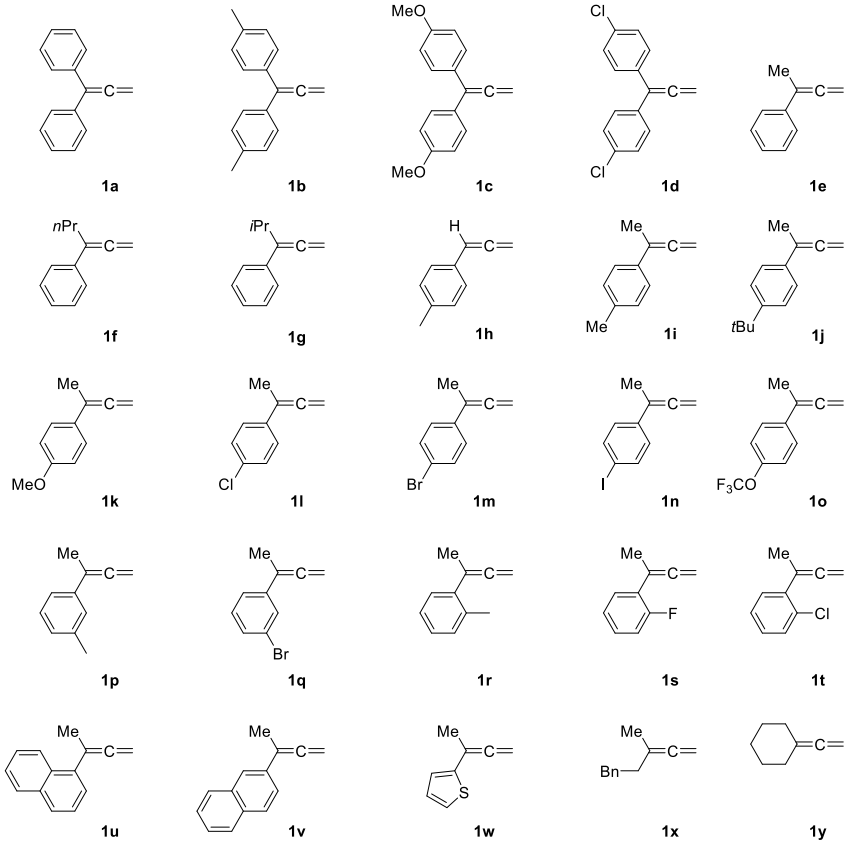
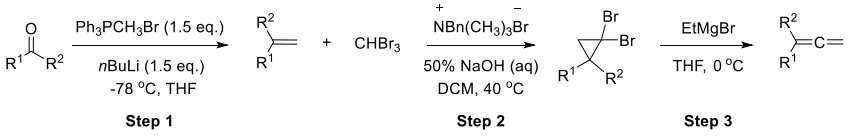


Table **S1**. The Substrates for Allenes Derivetives

Method A:

General Procedure for Preparation of Styrene **1a-1x**



Step 1: A 250.0 mL round-bottomed flask equipped with a magnetic stir bar was charged with methyltriphenylphosphonium bromide (45.0 mmol, 1.5 equiv) and 60.0 mL of THF. The solution was cooled to -78 °C, and *n*BuLi (2.5 M in THF, 45.0 mmol, 1.5 equiv) was added. The resulting solution was stirred for 30 minutes at room temperature and then cooled to -78 °C again. Ketone (30.0 mmol, 1.0 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature and monitored by TLC for completion. On completion, the reaction was quenched with saturated aqueous NH_4Cl (60.0 mL). The aqueous layer was extracted with DCM. The combined organic layers were washed with brine (50.0 mL), dried over Na_2SO_4, and filtered. All volatiles were removed under reduced pressure, and the crude mixture was purified by column chromatography to obtain the title alkene.

Step 2: The resulting alkene (20.0 mmol) was dissolved in DCM (20 mL) and poured into a 100.0 mL round-bottomed flask equipped with a magnetic stir bar, then Bromoform (20 mmol, 1.4 eq) was added with vigorous stirring. Phase transfer catalyst (2 mmol, 0.1 equiv) and 50% aq. NaOH (25 mL) was subsequently added to the reaction. The mixture was stirred at 40 °C for one day, then quenched with 10% aq. HCl and extracted with DCM. The combined organic layers were washed with water and brine, then dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Flash chromatography of the

resulting residue on silica gel gave the dibromocyclopropane products.

Step 3: Ethylmagnesium bromide in THF (3.4 M, 2.0 mmol, 2.0 equiv.) was added to a stirred solution of dibromocyclopropane (10.0 mmol) in dry THF (20 ml) under nitrogen at 0 ℃. Stirring was continued for 30 min at room temperature when water (10 ml) was added. The aqueous layer was extracted with DCM, and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography to yield the allenes.[1]

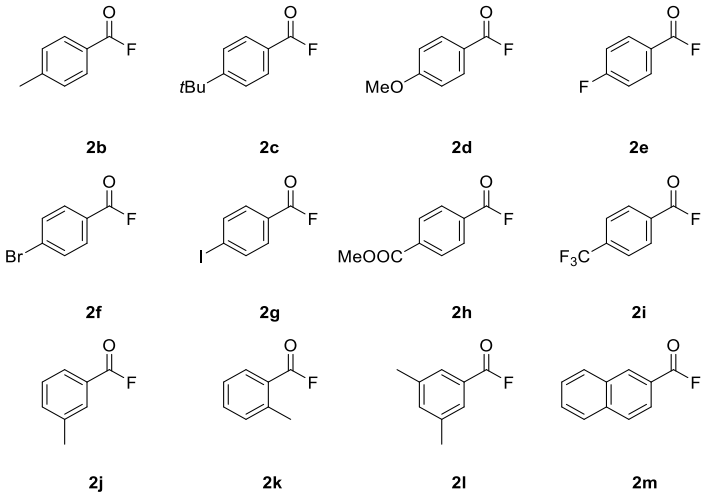
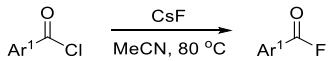


Table **S2**. The Substrates for Acyl Fluorides

Method B:

General Procedure for Preparation of Acyl Fluorides **2b–2m**



A 25.0 mL round-bottomed flask equipped with a magnetic stir bar was charged with benzoyl chloride (5.0 mmol) and anhydrous acetonitrile (10.0 mL). Cesium fluoride (1.1 g, 7.5 mmol, 1.5 equiv) was added, and the mixture was stirred for 2-4 h (monitored by TLC) at 80° C under a nitrogen atmosphere. After completion, the reaction mixture was filtered, the filtration residue washed with *n*-pentane (3 × 5 mL), and the combined organic solutions were concentrated under a vacuum. The resulting crude product was purified by column chromatography to yield the acyl fluorides.[2]

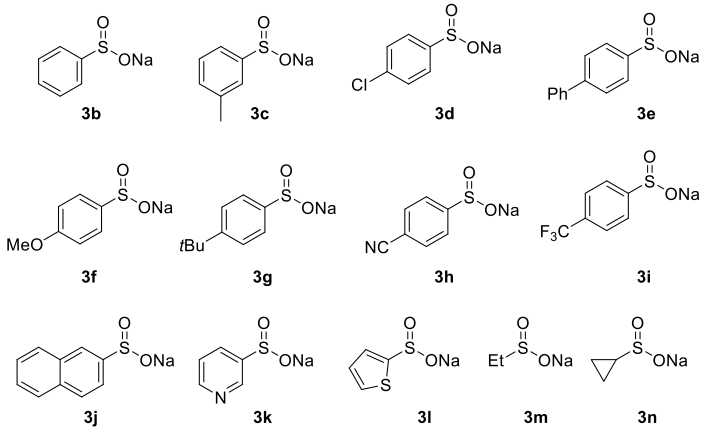
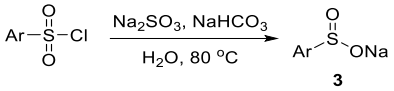


Table **S3**. The Substrates for Sulfinates

Method C:

General Procedure for Preparation of Sulfinates **3c–3l**.



A 25.0 mL round bottom flask with a magnetic stirring bar was added sodium sulfite (2.5 g, 2.0 eq.), sodium bicarbonate (1.7 g, 2.0 eq.), the corresponding aryl sulfonyl chloride (10.0 mmol), and water (10.0 mL). The reaction mixture was stirred for 4 h at 80 °C. After cooling to room temperature, the volatiles was removed in vacuo. The resultant solids were repeatedly washed with ethanol. The combined ethanol was evaporated under reduced pressure to yield the sulfinates.[3]

IV. Procedure for Large-Scale Synthesis

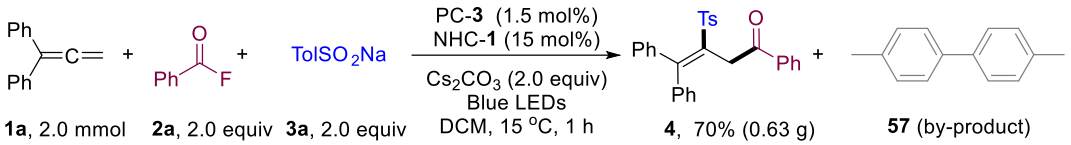
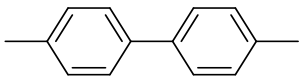


Figure **S1.** Lagre-Scale Synthesis of **4**

Into a nitrogen-filled glove box, a round-bottom flask (250.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (95.0 mg, 0.3 mmol), Cs_2CO_3 (1303.0 mg, 4.0 mmol), PC-3 (27.0 mg, 0.03 mmol) sulfinate **3a** (713.0 mg, 4.0 mmol) and DCM (150.0 mL). Then **1a** (2.0 mmol) and **2a** (4.0 mmol) were added. The round-bottom flask was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED (Kessil, PR160-456 nm) at 15 ℃ for 1 h. After the reaction was finished that monitored by TLC, the reaction mixture was quenched by water. The mixture was extracted with DCM (3 × 50.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was evaporated under a vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10 : 1) to give the corresponding product **4** (70%). In the gram-scale synthesis of **4**, we also separated 4,4'-dimethyl-1,1'-biphenyl (**57**), which undergo SO_2 fragments of sulfonyl radical produced aryl radicals, then homocoupling affording biaryl.

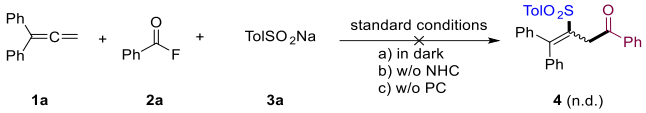


4,4'-dimethyl-1,1'-biphenyl (57)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 4H), 7.07 (d, *J* = 7.9 Hz, 4H), 2.28 (s, 6H).[4]

V. Mechanistic Studies

The Control Experiment

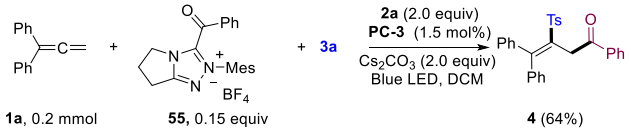


Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (9.5 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) **3a** (71.3 mg, 0.4 mmol) and DCM (6.0 mL). Then **1a** (0.2 mmol) and **2a** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was stirred in the dark for 24 hours at 15 ℃. Afterward, the reaction mixture was quenched by water. The mixture was extracted with DCM (3 × 5.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered off, and concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR and product **4** was not detected.

Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) **3a** (71.3 mg, 0.4 mmol) and DCM (6.0 mL). Then **1a** (0.2 mmol) and **2a** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at 15 ℃ for 24 hours. Afterward, the reaction mixture was quenched by water. The mixture was extracted with DCM (3 × 5.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered off, and concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR and product **4** was not detected.

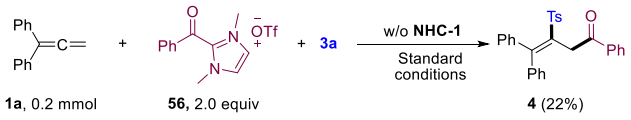
Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (9.5 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **3a** (71.3 mg, 0.4 mmol) and DCM (6.0 mL). Then **1a** (0.2 mmol) and **2a** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at 15 ℃ for 24 hours. Afterward, the reaction mixture was quenched by water. The mixture was extracted with DCM (3 × 5.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered off, and concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR and product **4** was not detected.

The Catalytic Activity of 55



Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol), **55** (15 mol%) **3a** (71.3 mg, 0.4 mmol) and DCM (6.0 mL). Then **1a** (0.2 mmol) and **2a** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at 15 ℃. After the reaction finished that monitored by TLC, the reaction mixture was quenched by water. The mixture was extracted with DCM (3 × 5.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered off, and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1) to give the corresponding product **4** (64%).

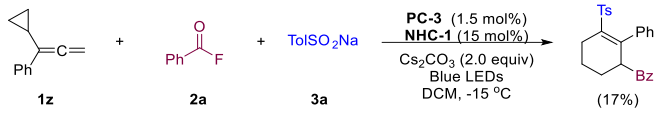
The Stoichiometric Transformation of 56



Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with

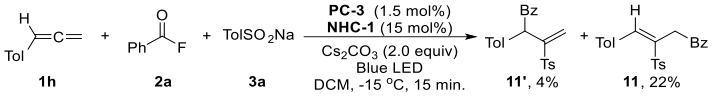
Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) **3a** (71.3 mg, 0.4 mmol) and DCM (6.0 mL). Then **1a** (0.2 mmol) and **56** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at 15 ℃. After the reaction finished that monitored by TLC, the reaction mixture was quenched by water. The mixture was extracted with DCM (3 × 5.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered off, and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1) to give the corresponding product **4** (22%).

The Radical Clock Experiment



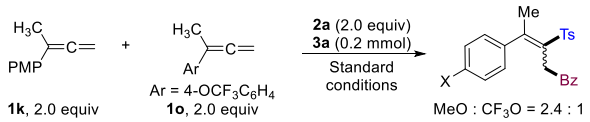
Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (9.5 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol), **3a** (71.3 mg, 0.4 mmol) and DCM (6.0 mL). Then allene **1z** (0.2 mmol) and **2a** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at -15 ℃ for 24 hours. Afterward, the reaction mixture was quenched by water. The mixture was extracted with DCM (3 × 5.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1) to give the corresponding product**.**

The Evidence for the Delocalized Nature of Allyl Radical

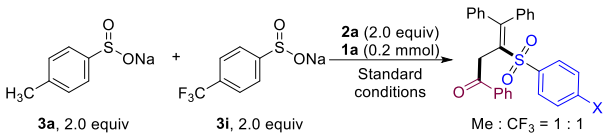


Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (9.5 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol), **3a** (71.3 mg, 0.4 mmol) and DCM (6.0 mL). Then allene **1h** (0.2 mmol) and **2a** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at -15 ℃ for 15 minutes. Afterward, the reaction mixture was quenched by water. The mixture was extracted with DCM (3 × 5.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 30:1) to give the corresponding product **11** and **11'**.

The Competing Experiment

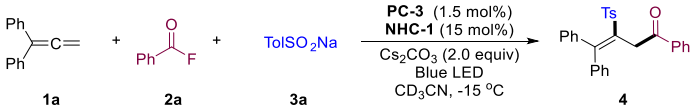


Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (9.5 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol), **3a** (71.3 mg, 0.2 mmol) and DCM (6.0 mL). Then **1k** (0.4 mmol), **1o** (0.4 mmol) and **2a** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at 15 ℃ for 15 minutes. Afterward, the reaction mixture was quenched by water. The mixture was extracted with DCM (3 × 5.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was evaporated under a vacuum. The residue was analyzed by ^1H NMR, and the products **14**:**18** = 2.4:1.



Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (9.5 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol), **3a** (0.4 mmol), **3i** (0.4 mmol) and DCM (6.0 mL). Then **1a** (0.2 mmol) and **2a** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at 15 ℃ for 15 minutes. Afterward, the reaction mixture was quenched by water. The mixture was extracted with DCM (3 × 5.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The residue was analyzed by ^{1}H NMR, and the products **14**:**37** = 1:1.

The Light on-off Experiment in CD_3CN



Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (9.5 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol), sodium benzenesulfinate **3a** (0.4 mmol) and CD_3CN (6.0 mL). Then **1a** (0.2 mmol), **2a** (0.6 mmol) and mesitylene (27.8 μl, 0.2 mmol) were added. The vial was removed from the glovebox and then the reaction mixture was irradiated with Blue LED and kept in the dark in 30 s intervals at -15 ℃. Yields of the **4** were determined by ^{1}H NMR monitors with mesitylene as the internal standard. The reaction proceeded well under the irradiation of visible light, but no further transformation was observed without the light irradiation, indicating that continuous irradiation of visible light is essential for this catalytic reaction.

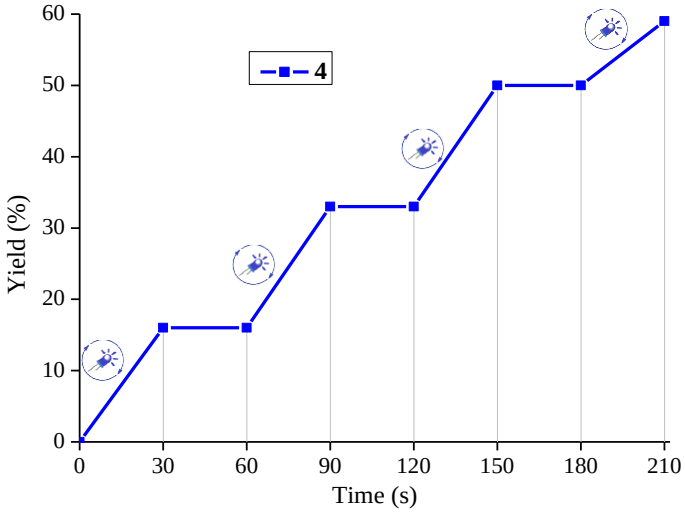
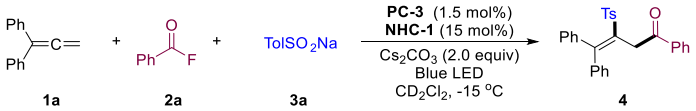


Figure **S2.** Light on-off Experiment in CD_3CN

The Light on-off Experiment in CD_2Cl_2



Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (9.5 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol), sodium

benzenesulfinate **3a** (0.4 mmol) and CD_2Cl_2 (6.0 mL). Then **1a** (0.2 mmol), **2a** (0.6 mmol) and 1,3,5-trimethoxybenzene (33.64 mg, 0.2 mmol) were added. The vial was removed from the glovebox and then the reaction mixture was irradiated with Blue LED and kept in the dark in 40 s intervals at -15 °C. Yields of the **4** were determined by ^{1}H NMR monitors with 1,3,5-trimethoxybenzene as the internal standard. The reaction proceeded well under the irradiation of visible light, but no further transformation was observed without the light irradiation, indicating that continuous irradiation of visible light is essential for this catalytic reaction.

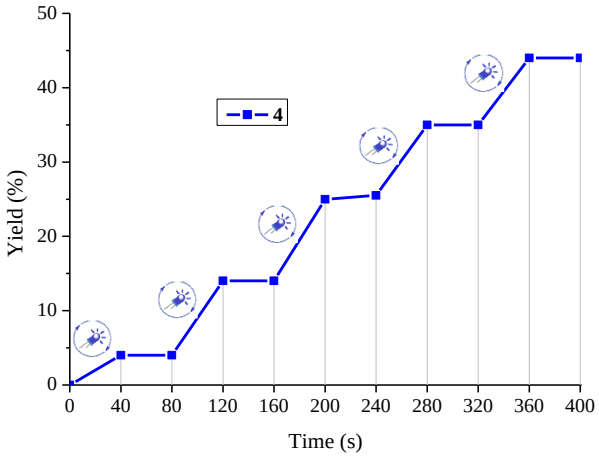
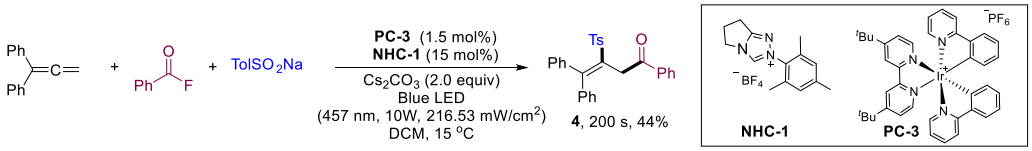


Figure **S3.** Light on-off Experiment in CD_2Cl_2

Determination of the reaction quantum yield



Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (9.5 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol), sodium benzenesulfinate **3a** (0.4 mmol) and DCM (6.0 mL). Then **1a** (0.2 mmol) and **2a** (0.6 mmol) were added. The reaction was carried out under Blue LED irradiation for 200 s and product **4** was obtained in 44% yields in 0.2 mmol scale. The reaction apparent quantum yield (AQY) was determined using eq. 1[5,6] where the N_e represents the number of electrons available, N_p represents the number of incident photons, n is amount of reactive substances (8.8×10^{-5} mol), N_A is the Avogadro constant (6.02×10^{23} mol^{-1}), K is the number of transferred electrons, h is the Planck constant (6.62×10^{-34} J·s), c is the velocity of light (3.0×10^{8} $m\cdot s^{-1}$). I is the light intensity (216.53 $mW\cdot cm^{-2}$), λ is the wavelength of incident light (457 nm) and A is actual irradiation area (4.0 cm^2), t is the reaction time (200 s).

$$\mathbf{AQY_{457\ nm}} = Ne/Np\times100\ \% = (n\cdot K\cdot N_A)/[(I\times A\times\lambda\times t)/(h\cdot c)]\times100\ \% \qquad \text{(eq. 1)}$$

$$= (0.44\times0.2\times10^{-3}\times1\times6.02\times10^{23})/[(2165\times4\times10^{-4}\times457\times10^{-9}\times200)/(6.62\times10^{-34}\times3.0\times10^{8})]\times100\ \%$$

$$= (5.298\times10^{19})/[(7.915\times10^{-5})/(1.986\times10^{-25})]\times100\ \%$$

$$= 13.3\%$$

LED test report

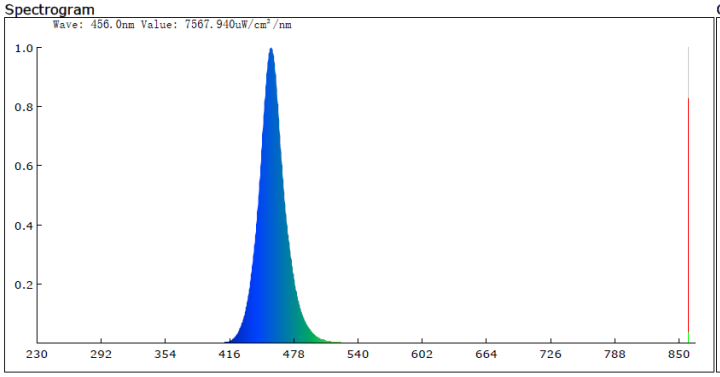
Product Mark

Model: 455nm LED | Manufacture: Rogertech
Temperature: 23°C | Humidity: 20%
Tester: WU | Test Date: 2022-06-21,15:37:36

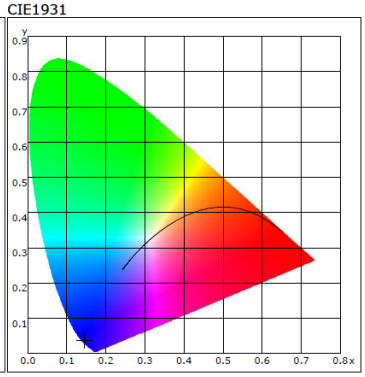
Parameter

Name	Value	Name	Value	Name	Value	Name	Value
ESuv(mW/cm²)	0.0000	CIE u,v	0.1844,0.0685	CIE1931 Y	144632.844		
Euvc(mW/cm²)	0.0000	CIE u',v'	0.1844,0.1027	CIE1931 Z	3306363.000		
Euvb(mW/cm²)	0.0000	SDCM	100.00	TLCI-2012	1		
Euva(mW/cm²)	0.0000	Ra	-64.3	Integral Time(ms)	0.1		
Euv(mW/cm²)	0.00	Ee(mW/cm²)	216.53220	Peak Signal	54246		
Eb(mW/cm²)	215.04	S/P	20.352	Dark Signal	2232		
Eg(mW/cm²)	1.67	Dominant(nm)	461.20	Compensate level	2878		
Er(mW/cm²)	0.00	Purity(%)	98.6				
Eir(mW/cm²)	0.00	HalfWidth(nm)	24.1				
E(lx)	98784.23	Peak(nm)	456.7				
Candle E(fc)	9177.28	Center(nm)	457.0				
CCT(K)	100000	Centroid(nm)	458.5				
Duv	-0.05259	Color Ratio(RGB)	0.0,11.2,88.8				
CIE x,y	0.1448,0.0358	CIE1931 X	584238.875				

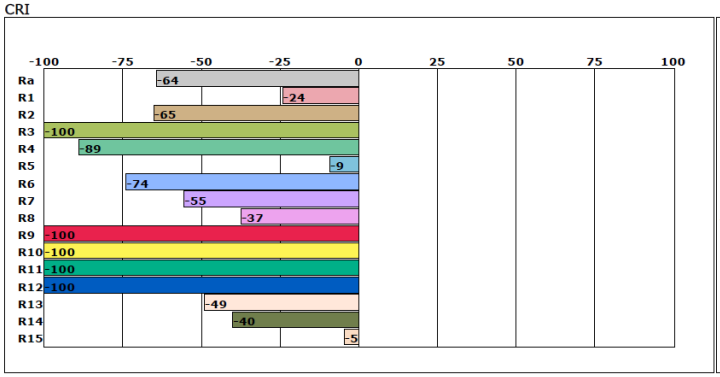
Spectrogram

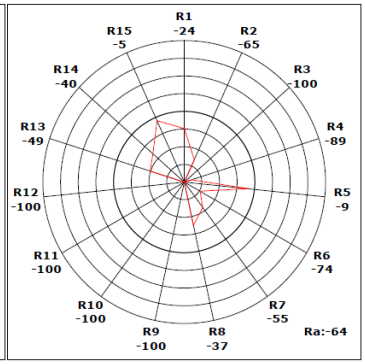


CIE1931



CRI





Instrument Status

Type: OHSP-350UV | SN: 0 | Scan Range: 230-850nm
Integral Time: 0.067ms | VPeak: 54246 | VDark: 2232

Remark: Test @ 10W sample position

Figure **S4.** LED Test Report

The Emission Quenching Experiment

Emission intensities were recorded using spectrofluorometer (Edinburgh FS5) at ambient temperature. All $[Ir(dtbbpy)(ppy)_2]PF_6$ solutions were excited at 390 nm, and the emission intensity at 470-750 nm was recorded. Firstly, the emission spectrum of a 5×10^{-5} M solution of $[Ir(dtbbpy)(ppy)_2]PF_6$ in CH_3CN was collected. Then, an appropriate amount of quencher was added to the measured solution, and the

emission spectrum of the sample was collected. The Stern-Volmer emission quenching studies tell that the acyl azolium ion **55** and **56** are easier than sodium benzenesulfinate (**3a**), allenes (**1a**), benzoyl fluoride (**2a**) to quench the excited photosensitizer.[7]

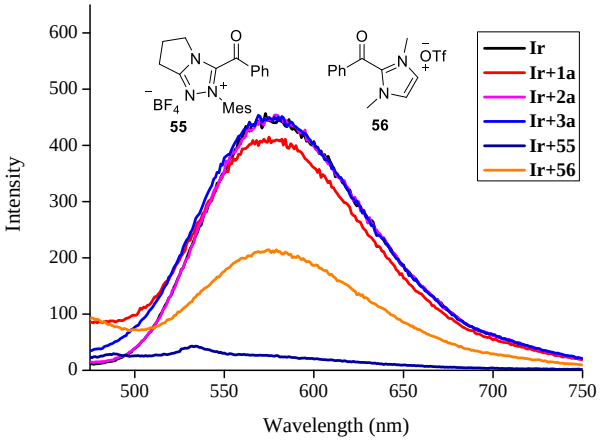


Figure **S5** Luminescence Spectrum of $[Ir(dtbbpy)(ppy)_2]PF_6$ as a Function of Concentration of Allene (**1a**) and Benzoyl Fluoride (**2a**), $TolSO_2Na$ (**3a**), Acylazolium (**55**) and Acylazolium (**56**) in CH_3CN with Excitation at 390 nm, $[[Ir(dtbbpy)(ppy)_2]PF_6] = 5.0 \times 10^{-5}$ M, [**1a**] = 3.0×10^{-2} M, [**2a**] = 3.0×10^{-2} M. [**3a**] = 3.0×10^{-2} M, [**55**] = 3.0×10^{-2} M, [**56**] = 3.0×10^{-2} M.

VI. References

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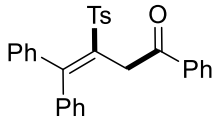
VII. Characterization Data of New Compounds



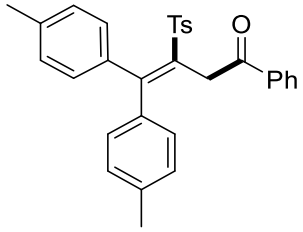
1,4,4-triphenyl-3-tosylbut-3-en-1-one (4)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a white solid (yield 69.7 mg, 77%), mp 102 – 103 ºC.

^{1}H NMR (600 MHz, CD_3Cl) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.1 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.20 (s, 5H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 4.33 (s, 2H), 2.32 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.33, 154.54, 142.89, 140.56, 138.32, 137.51, 136.57, 133.26, 129.46, 128.65, 128.61, 128.52, 128.48, 128.30, 128.06, 127.70, 127.48, 127.38, 40.85, 21.48.

HRMS (ESI) (m/z): calcd for $C_{29}H_{24}NaO_3S$ ([M + Na] $^{+}$), 475.1338; found 475.1342.



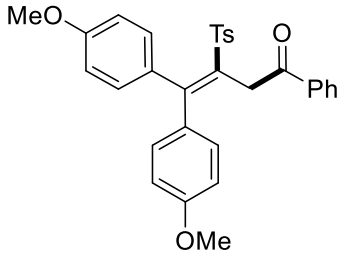
1-phenyl-4,4-di-p-tolyl-3-tosylbut-3-en-1-one (5)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 76.9 mg, 80%).

^{1}H NMR (500 MHz, CD_3Cl) δ 8.01 (d, *J* = 7.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.00 – 6.97 (m, 4H), 6.86 – 6.81 (m, 4H), 4.33 (s, 2H), 2.32 (s, 3H), 2.28 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.49, 154.82, 142.79, 138.51, 137.88, 137.66, 137.62, 137.59, 136.65, 135.74, 133.19, 129.45, 129.10, 128.58, 128.41, 128.31, 128.11, 128.04, 127.42, 40.94, 21.51, 21.23, 21.13.

HRMS (ESI) (m/z): calcd for $C_{31}H_{28}NaO_3S$ ([M + Na] $^{+}$), 503.1651; found 503.1656.



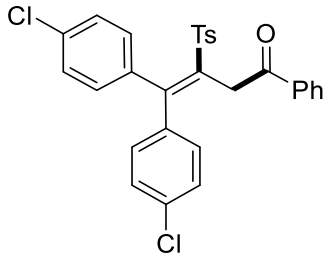
4,4-bis(4-methoxyphenyl)-1-phenyl-3-tosylbut-3-en-1-one (6)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) affords the title compound as a white solid (yield 68.7 mg, 67%), mp 88 – 89 ºC.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.1 Hz, 1H), 7.51 – 7.43 (m, 4H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 4.36 (s, 2H), 3.78 (s, 3H), 3.71 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.83, 159.88, 159.39, 154.32, 142.71, 137.79, 137.11, 136.71, 133.21, 131.28, 131.19, 129.32, 128.60, 128.50, 128.33, 127.95, 55.26, 55.17, 41.12, 21.48.

HRMS (ESI) (m/z): calcd for $C_{31}H_{28}NaO_5S$ ([M + Na] $^+$), 535.1550; found 535.1547.



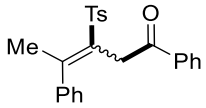
4,4-bis(4-chlorophenyl)-1-phenyl-3-tosylbut-3-en-1-one (7)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 89.7 mg, 86%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 6.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.04 (t, *J* = 8.5 Hz, 4H), 6.87 (d, *J* = 8.0 Hz, 2H), 4.31 (s, 2H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.11, 151.73, 143.49, 139.71, 138.32, 137.10, 136.33, 136.25, 135.02, 134.31, 133.51, 130.87, 128.91, 128.86, 128.73, 128.68, 128.31, 128.03, 127.77, 40.75, 21.52.

HRMS (ESI) (m/z): calcd for $C_{29}H_{22}Cl_2NaO_3S$ ([M + Na] $^+$), 543.0559; found 543.0559.



1,4-diphenyl-3-tosylpent-3-en-1-one (8)

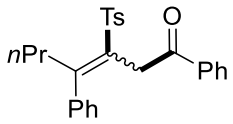
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 54.7 mg, 70%).

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 9:1 mixture based on the peak at δ 4.51 and at δ 4.11.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 2H), 7.85 (d, *J* = 7.1 Hz, 1.79H), 7.62 (t, *J* = 7.4 Hz, 0.1H), 7.55 – 7.48 (m, 1.13H), 7.40 (t, *J* = 7.8 Hz, 1.81H), 7.36 (d, *J* = 8.0 Hz, 1.85H), 7.30 – 7.20 (m, 3.12H), 7.17 (d, *J* = 6.3 Hz, 1.90H), 7.10 (t, *J* = 7.5 Hz, 0.21H), 6.95 (t, *J* = 8.6 Hz, 0.41H), 4.51 (s, 0.2H), 4.11 (s, 1.8H), 2.44 (s, 2.69H), 2.30 (s, 0.32H), 2.28 (s, 2.66H), 2.02 (s, 0.30H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.76, 194.88, 153.27, 152.32, 143.86, 142.75, 142.03, 139.87, 138.97, 138.09, 136.40, 136.35, 134.87, 134.81, 133.44, 133.12, 129.50, 128.71, 128.64, 128.60, 128.46, 128.28, 128.16, 128.08, 127.98, 127.89, 127.77, 127.55, 127.41, 126.08, 40.94, 38.79, 25.49, 23.10, 21.56, 21.41.

HRMS (ESI) (m/z): calcd for $C_{24}H_{22}NaO_3S$ ([M + Na] $^+$), 413.1182; found 413.1199.



1,4-diphenyl-3-tosylhept-3-en-1-one (9)

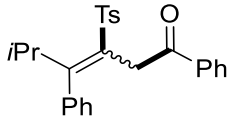
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 63.6 mg, 76%).

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 4.5:1 mixture based on the peak at δ 4.5 and at δ 4.06.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.09 (m, 2H), 7.84 (d, *J* = 6.9 Hz, 1.66H), 7.63 (t, *J* = 7.4 Hz, 0.18H), 7.56 – 7.51 (m, 1.21H), 7.44 – 7.34 (m, 3.37H), 7.26 – 7.21 (m, 2.85H), 7.18 – 7.11 (m, 1.84H), 7.07 (t, *J* = 7.6 Hz, 0.41H), 6.94 (d, *J* = 8.0 Hz, 0.37H), 6.88 (d, *J* = 7.1 Hz, 0.37H), 4.50 (s, 0.36H), 4.06 (s, 1.63H), 2.77 – 2.70 (m, 1.61H), 2.45 (s, 2.44H), 2.31 (s, 0.57H), 2.27 – 2.22 (m, 2.38H), 1.27 – 1.20 (m, 0.41H), 0.85 – 0.79 (m, 2.12H), 0.57 (t, *J* = 7.3 Hz, 2.29H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.93, 195.37, 157.61, 143.92, 142.64, 140.20, 139.66, 136.46, 135.22, 134.91, 133.47, 133.13, 129.50, 128.82, 128.76, 128.64, 128.49, 128.47, 128.38, 128.10, 127.76, 127.41, 127.35, 126.58, 40.88, 40.21, 38.27, 37.36, 21.61, 21.46, 20.34, 20.16, 13.77, 13.73.

HRMS (ESI) (m/z): calcd for $C_{26}H_{26}NaO_3S$ ([M + Na] $^+$), 441.1495; found 441.1489.



5-methyl-1,4-diphenyl-3-tosylhex-3-en-1-one (10)

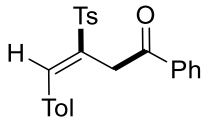
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 41.9 mg, 50%).

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 3.1:1 mixture based on the peak at δ 4.48 and at δ 3.86.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1.5H), 7.52 (t, *J* = 7.3 Hz, 0.25H), 7.40 (dt, *J* = 20.9, 7.5 Hz, 1.32H), 7.27 (d, *J* = 8.0 Hz, 3H), 7.17 – 7.04 (m, 3.25H), 6.95 (t, *J* = 7.4 Hz, 0.53H), 6.90 (d, *J* = 7.5 Hz, 2H), 6.64 (d, *J* = 7.5 Hz, 0.47H), 4.48 (s, 0.48H), 3.86 (s, 1.49H), 3.65 (p, *J* = 6.8 Hz, 0.73H), 2.74 – 2.62 (m, 0.23H), 2.35 (s, 2.3H), 2.24 (s, 0.78H), 0.75 (d, *J* = 6.8 Hz, 1.59H), 0.63 (d, *J* = 6.8 Hz, 4.37H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.40, 195.30, 161.95, 159.95, 143.78, 142.81, 140.06, 138.73, 136.52, 136.47, 136.43, 134.70, 134.67, 133.98, 133.42, 132.99, 129.74, 129.48, 128.85, 128.71, 128.39, 128.29, 127.94, 127.90, 127.75, 127.65, 127.62, 127.58, 126.97, 126.70, 40.53, 37.82, 33.67, 31.14, 21.59, 21.47, 20.31, 19.78.

HRMS (ESI) (m/z): calcd for $C_{26}H_{26}NaO_3S$ ([M + Na] $^+$), 441.1495; found 441.1494.



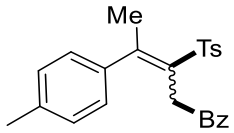
(*E*)-1-phenyl-4-(p-tolyl)-3-tosylbut-3-en-1-one (11)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 17.2 mg, 22%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.80 (d, *J* = 6.8 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.19 (m, 4H), 7.13 (d, *J* = 7.9 Hz, 2H), 4.28 (s, 2H), 2.39 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.18, 144.24, 141.57, 140.15, 136.18, 136.16, 135.06, 133.49, 130.47, 129.69, 129.52, 128.90, 128.63, 128.47, 128.10, 37.16, 21.59, 21.35.

HRMS (ESI) (m/z): calcd for $C_{24}H_{22}NaO_3S$ ([M + Na] $^+$), 413.1182; found 413.1180.



1-phenyl-4-(p-tolyl)-3-tosylpent-3-en-1-one (12)

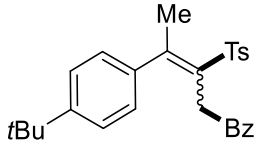
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 67.2 mg, 83 %).

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 8.9:1 mixture based on the peak at δ 4.49 and at δ 4.13.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 2H), 7.87 (d, *J* = 7.0 Hz, 1.74H), 7.61 (t, *J* = 7.4 Hz, 0.13H), 7.52 (t, *J* = 7.3 Hz, 1.15H), 7.41 (t, *J* = 7.8 Hz, 1.87H), 7.35 (d, *J* = 8.1 Hz, 1.77H), 7.28 (d, *J* = 8.2 Hz, 0.25H), 7.06 (s, 3.56H), 6.96 (d, *J* = 7.9 Hz, 0.24H), 6.91 (d, *J* = 7.8 Hz, 0.22H), 6.83 (d, *J* = 7.8 Hz, 0.21H), 4.49 (s, 0.2H), 4.13 (s, 1.77H), 2.44 (s, 2.77H), 2.31 (s, 0.82H), 2.26 (s, 5.39H), 2.00 (s, 0.32H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.93, 194.91, 153.41, 152.46, 143.79, 142.73, 139.10, 139.05, 138.12, 137.29, 136.99, 136.44, 134.69, 134.54, 133.42, 133.11, 129.49, 129.23, 128.70, 128.46, 128.28, 128.16, 128.13, 127.91, 127.88, 127.84, 126.06, 41.05, 38.80, 25.48, 23.14, 21.58, 21.46, 21.18, 21.08.

HRMS (ESI) (m/z): calcd for $C_{25}H_{24}NaO_3S$ ([M + Na] $^+$), 427.1338; found 427.1332.



4-(4-(tert-butyl)phenyl)-1-phenyl-3-tosylpent-3-en-1-one (13)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 65.2 mg, 73%).

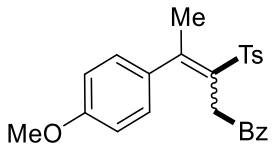
The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 5.8:1 mixture based on the peak at δ 4.52 and at δ 4.15.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.03 (m, 2H), 7.87 (d, *J* = 7.0 Hz, 1.68H), 7.62 (t, *J* = 7.4 Hz, 0.15H), 7.52 (t, *J* = 7.2 Hz, 1.16H), 7.41 (t, *J* = 7.7 Hz, 1.74H), 7.35 (d, *J* = 8.1 Hz, 1.73H), 7.26 (d, *J* = 8.4 Hz 2H), 7.11 (d, *J* = 8.4 Hz, 1.71H), 7.07 (d, *J* = 8.3 Hz, 0.29H), 6.92 (d, *J* = 8.0 Hz, 0.30H), 6.84 (d, *J* = 8.3 Hz, 0.29H), 4.52 (s, 0.29H), 4.15 (s, 1.68H), 2.44 (s, 2.61H), 2.29 (s, 0.50H), 2.26 (s, 2.51H), 2.02 (s, 0.45H), 1.27 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.13, 195.15, 153.40, 152.28, 151.29, 150.49, 143.76, 142.35, 139.08, 138.97, 138.19, 136.75, 136.57, 136.40, 135.02, 134.62, 133.43, 133.07, 129.48, 128.72, 128.51, 128.45,

128.33, 128.16, 127.86, 127.81, 127.72, 125.94, 125.47, 124.41, 40.94, 38.69, 34.52, 34.41, 31.31, 31.13, 25.28, 23.10, 21.59, 21.40.

HRMS (ESI) (m/z): calcd for $C_{28}H_{30}NaO_3S$ ([M + Na] $^+$), 469.1808; found 469.1795.



4-(4-methoxyphenyl)-1-phenyl-3-tosylpent-3-en-1-one (14)

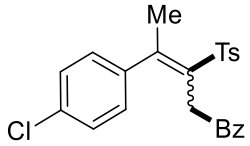
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1, v/v) affords the title compound as a white solid (yield 57.2 mg, 68%), mp 87 – 88 °C.

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 9.4:1 mixture based on the peak at δ 4.50 and at δ 4.16.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H), 7.89 (d, *J* = 7.2 Hz, 1.79H), 7.62 (t, *J* = 7.3 Hz, 0.10H), 7.55 – 7.51(m, 1.14H), 7.42 (t, *J* = 7.6 Hz, 1.80H), 7.36 (d, *J* = 8.0 Hz, 1.79H), 7.30 (d, *J* = 8.0 Hz, 0.22H), 7.13 (d, *J* = 8.6 Hz, 1.78H), 6.98 (d, *J* = 8.0 Hz, 0.21H), 6.87 (d, *J* = 8.4 Hz, 0.20H), 6.78 (d, *J* = 8.6 Hz, 1.78H), 6.62 (d, *J* = 8.4 Hz, 0.21H), 4.50 (s, 0.19H), 4.16 (s, 1.79H), 3.79 (s, 0.32H), 3.73 (s, 2.69H), 2.44 (s, 2.70H), 2.31 (s, 0.32H), 2.25 (s, 2.67H), 2.00 (s, 0.29H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.13, 195.04, 159.48, 159.11, 153.08, 152.20, 143.78, 142.64, 139.04, 138.26, 136.45, 134.91, 134.49, 134.21, 133.44, 133.15, 132.11, 129.48, 129.45, 128.72, 128.52, 128.49, 128.31, 128.15, 127.89, 127.71, 127.64, 113.91, 112.99, 55.26, 55.18, 41.16, 38.83, 25.43, 23.16, 21.59, 21.45.

HRMS (ESI) (m/z): calcd for $C_{25}H_{24}NaO_4S$ ([M + Na] $^+$), 443.1288; found 443.1269.



4-(4-chlorophenyl)-1-phenyl-3-tosylpent-3-en-1-one (15)

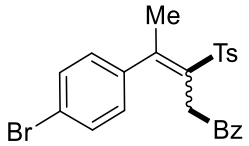
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 63.7 mg, 75%).

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 6.9:1 mixture based on the peak at δ 4.50 and at δ 4.09.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.01(m, 2H), 7.86 (d, *J* = 7.8 Hz, 1.72H), 7.62 (t, *J* = 7.2 Hz, 0.14H), 7.56 – 7.51 (m, 1.15H), 7.42 (t, *J* = 7.6 Hz, 1.72H), 7.36 (d, *J* = 8.0 Hz, 1.71H), 7.30 (d, *J* = 8.0 Hz, 0.35H), 7.24 (d, *J* = 8.2 Hz, 1.75H), 7.13 (d, *J* = 8.1 Hz, 1.70H), 7.07 (d, *J* = 8.1 Hz, 0.28H), 7.03 (d, *J* = 8.0 Hz, 0.26H), 6.88 (d, *J* = 8.0 Hz, 0.26H), 4.50 (s, 0.25H), 4.09 (s, 1.72H), 2.44 (s, 2.59H), 2.34 (s, 0.42H), 2.26 (s, 2.54H), 2.00 (s, 0.39H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.59, 194.66, 151.88, 150.79, 144.03, 143.21, 140.34, 138.64, 138.22, 137.90, 136.19, 135.75, 135.41, 134.23, 133.61, 133.53, 133.32, 129.55, 129.41, 128.86, 128.74, 128.70, 128.54, 128.28, 128.11, 127.92, 127.77, 127.72, 127.65, 40.90, 38.71, 25.22, 22.98, 21.58, 21.48.

HRMS (ESI) (m/z): calcd for $C_{24}H_{21}ClNaO_3S$ ([M + Na] $^+$), 447.0792; found 447.0791.



4-(4-bromophenyl)-1-phenyl-3-tosylpent-3-en-1-one (16)

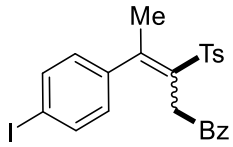
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a colorless oil (yield 87.3 mg, 93%).

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 3.9:1 mixture based on the peak at δ 4.49 and at δ 4.09.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 2H), 7.86 (d, *J* = 7.0 Hz, 1.57H), 7.62 (t, *J* = 7.4 Hz, 0.22H), 7.55 – 7.51 (m, 1.24H), 7.43 – 7.35 (m, 3.22H), 7.35 (d, *J* = 8.0 Hz, 1.53H), 7.30 (d, *J* = 8.2 Hz, 0.42H), 7.22 (d, *J* = 8.3 Hz, 0.42H), 7.06 (d, *J* = 8.4 Hz, 1.55H), 7.03 (d, *J* = 8.0 Hz, 0.39H), 6.82 (d, *J* = 8.3 Hz, 0.39H), 4.49 (s, 0.41H), 4.09 (s, 1.59H), 2.43 (s, 2.38H), 2.34 (s, 0.62H), 2.26 (s, 2.34H), 1.99 (s, 0.60H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.55, 194.63, 151.85, 150.69, 144.04, 143.23, 140.83, 138.71, 138.62, 137.86, 136.21, 136.18, 135.76, 135.39, 133.53, 133.32, 131.81, 130.68, 129.69, 129.55, 128.73, 128.72, 128.54, 128.27, 128.12, 127.92, 127.78, 122.40, 121.79, 40.89, 38.69, 25.14, 22.92, 21.58, 21.49.

HRMS (ESI) (m/z): calcd for $C_{24}H_{21}BrNaO_3S$ ([M + Na] $^+$), 491.0287; found 491.0285.



4-(4-iodophenyl)-1-phenyl-3-tosylpent-3-en-1-one (17)

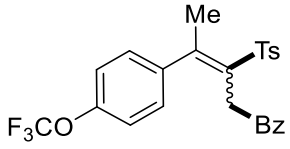
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a white solid (yield 87.8 mg, 85%), mp 79 – 80 °C.

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 4.1:1 mixture based on the peak at δ 4.11 and at δ 4.09.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.87 – 7.84 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 0.4H), 7.55 – 7.51 (m, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.35 (m, 2H), 7.28 – 7.23 (m, 2H), 7.19 – 7.15 (m, 1.63H), 6.93 (d, *J* = 8.4 Hz, 0.43H), 4.11 (s, 1.64H), 4.09 (s, 0.40H), 2.44 (s, 3H), 2.28 (s, 2.41H), 2.25 (s, 0.61H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.80, 196.60, 153.28, 151.94, 144.06, 143.87, 142.03, 141.46, 138.96, 138.63, 137.77, 136.40, 136.20, 135.36, 134.82, 133.34, 133.15, 129.57, 129.52, 128.62, 128.56, 128.48, 128.19, 128.15, 128.11, 128.07, 127.95, 127.92, 126.10, 40.96, 40.91, 23.12, 22.90, 21.61 (overlapping).

HRMS (ESI) (m/z): calcd for $C_{24}H_{21}INaO_3S$ ([M + Na] $^+$), 539.0148; found 539.0147.



1-phenyl-3-tosyl-4-(4-(trifluoromethoxy)phenyl)pent-3-en-1-one (18)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 83.4 mg, 88%).

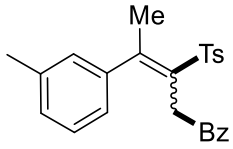
The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 6.7:1 mixture based on the peak at δ 8.10 and at δ 8.01.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 0.25H), 8.01 (d, *J* = 8.1 Hz, 1.68H), 7.86 (d, *J* = 8.0 Hz, 1.72H), 7.63 (t, *J* = 7.3 Hz, 0.12H), 7.55 – 7.53 (m, 1H), 7.42 (t, *J* = 7.7 Hz, 1.75H), 7.37 – 7.30 (m, 2H), 7.23 (d, *J* = 8.7 Hz, 1.72H), 7.12 (d, *J* = 8.3 Hz, 1.70H), 7.00 (d, *J* = 8.0 Hz, 0.27H), 6.97 (d, *J* = 8.6 Hz, 0.24H), 6.93 (d, *J* = 8.5 Hz, 0.25H), 4.53 (s, 0.24H), 4.09 (s, 1.71H), 2.44 (s, 2.59H), 2.31 (s, 0.39H), 2.28 (s, 2.55H), 2.02 (s, 0.37H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.65, 194.80, 151.67, 150.48, 148.91, 144.10, 143.22, 140.50, 138.60, 138.45, 137.93, 136.23, 135.70, 133.59, 133.34, 129.69, 129.58, 128.77, 128.75, 128.56, 128.33, 128.12, 127.94, 127.91, 127.64, 121.05, 120.66 (q, *J* = 257.8), 120.20, 40.82, 38.67, 25.23, 23.06, 21.59, 21.36.

^{19}F NMR (565 MHz, $CDCl_3$) δ -57.84.

HRMS (ESI) (m/z): calcd for $C_{25}H_{21}F_3NaO_4S$ ([M + Na] $^+$), 497.1005; found 497.1005.



1-phenyl-4-(m-tolyl)-3-tosylpent-3-en-1-one (19)

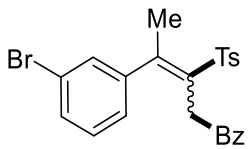
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 72.7 mg, 90%).

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 9.3:1 mixture based on the peak at δ 4.51 and at δ 4.11.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.05(m, 2H), 7.85 (d, *J* = 7.0 Hz, 1.76H), 7.62 (t, *J* = 7.4 Hz, 0.12H), 7.55 – 7.49 (m, 1.13H), 7.40 (t, *J* = 7.8 Hz, 1.79H), 7.36 (d, *J* = 8.0 Hz, 1.78H), 7.27 (s, 0.12H), 7.16 – 7.13 (m, 0.9H), 7.05 – 7.02 (m, 0.96H), 6.96 (s, 2.11H), 6.87 (d, *J* = 7.5 Hz, 0.12H), 6.53 (s, 0.11H), 4.51 (s, 0.19H), 4.11 (s, 1.77H), 2.44 (s, 2.67H), 2.32 (s, 0.37H), 2.26 (s, 2.68H), 2.23 (s, 2.61H), 2.13 (s, 0.36H), 2.00 (s, 0.35H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.87, 194.97, 153.44, 152.43, 143.80, 142.56, 142.02, 139.71, 139.04, 138.33, 138.20, 137.19, 136.46, 136.36, 134.86, 134.63, 133.07, 129.48, 128.88, 128.71, 128.52, 128.48, 128.44, 128.30, 128.16, 128.10, 128.05, 127.89, 127.84, 127.48, 126.62, 125.40, 123.06, 40.97, 38.66, 25.38, 23.08, 21.57, 21.38, 21.24, 21.08.

HRMS (ESI) (m/z): calcd for $C_{25}H_{24}NaO_3S$ ([M + Na] $^+$), 427.1338; found 427.1325.



4-(3-bromophenyl)-1-phenyl-3-tosylpent-3-en-1-one (20)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 57.3 mg, 61%).

The ^{1}H NMR spectrum of the product showed a 5.0:1 mixture based on the peak at δ 4.51 and at δ 4.09. **20** can be further purified by silica gel chromatography.

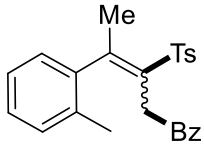
For **20** NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.37 – 7.36 (m, 3H), 7.32 (s, 1H), 7.15 – 7.11 (m, 2H), 4.09 (s, 2H), 2.45 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.50, 151.45, 144.12, 143.95, 138.62, 136.30, 135.75, 133.29, 131.30, 130.29, 129.60, 129.14, 128.55, 128.13, 127.98, 124.86, 122.67, 40.89, 22.96, 21.62.

For **20'** NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.0 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 3H), 7.11 – 7.07 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.76 (s, 1H), 4.51 (s, 2H), 2.38 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.69, 150.29, 143.57, 141.70, 137.79, 136.28, 136.23, 133.60, 130.44, 130.34, 129.25, 128.95, 128.80, 128.36, 127.76, 127.26, 121.91, 38.62, 25.19, 21.63.

HRMS (ESI) (m/z): calcd for $C_{24}H_{21}BrNaO_3S$ ([M + Na] $^{+}$), 491.0287; found 491.0287.



1-phenyl-4-(o-tolyl)-3-tosylpent-3-en-1-one (21)

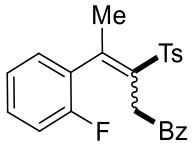
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 50.2 mg, 62%).

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 3.0:1 mixture based on the peak at δ 4.74 and at δ 4.23.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 2H), 7.77 (d, *J* = 6.9 Hz, 1.49H), 7.62 (t, *J* = 7.4 Hz, 0.28H), 7.53 (t, *J* = 7.7 Hz, 0.56H), 7.51 – 7.47 (m, 0.76H), 7.38 – 7.36 (m, 3H), 7.19 (d, *J* = 8.1 Hz, 0.54H), 7.15 – 7.09 (m, 1.81H), 7.07 – 7.05 (m, 1H), 7.00 – 6.96 (m, 1.44H), 6.89 (d, *J* = 7.5 Hz, 0.25H), 4.74 (d, *J* = 18.1 Hz, 0.25H), 4.31 (d, *J* = 18.1 Hz, 0.27H), 4.23 (d, *J* = 17.6 Hz 0.74H), 3.75 (d, *J* = 17.6 Hz, 0.75H), 2.45 (s, 2.28H), 2.34 (s, 0.8H), 2.20 (s, 2.29H), 2.17 (s, 2.20H), 1.96 (s, 0.73H), 1.90 (s, 0.72H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.94, 194.91, 153.59, 152.32, 143.89, 143.11, 141.38, 139.15, 139.04, 137.57, 136.46, 136.38, 135.38, 134.99, 134.88, 133.48, 133.23, 133.02, 130.54, 129.66, 129.52, 128.74, 128.68, 128.57, 128.41, 128.28, 128.11, 128.00, 127.92, 127.83, 127.78, 126.11, 126.09, 125.06, 40.30, 38.73, 24.32, 22.20, 21.62, 21.48, 19.25, 18.79.

HRMS (ESI) (m/z): calcd for $C_{25}H_{24}NaO_3S$ ([M + Na] $^{+}$), 427.1338; found 427.1322.



4-(2-fluorophenyl)-1-phenyl-3-tosylpent-3-en-1-one (22)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 52.3 mg, 64%).

The ^{1}H NMR spectrum of the product showed a 1.9:1 mixture based on the peak at δ 4.63 and at δ 4.36. **22** can be further purified by silica gel chromatography.

For **22** NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.17 – 7.13(m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.98 – 6.90 (m, 2H), 4.36 (s, 1H), 3.65 (s, 1H), 2.37 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.85, 157.9 (d, *J* = 247.5 Hz), 148.28, 144.01, 138.81, 136.57, 136.28, 133.18, 130.14 (d, *J* = 8.0 Hz), 129.58, 129.19 (d, *J* = 16.2 Hz), 128.60 (d, *J* = 3.0 Hz), 128.48, 128.08, 127.77, 124.36 (d, *J* = 3.6 Hz), 116.03 (d, *J* = 20.9 Hz), 40.84, 22.09, 22.07, 21.61.

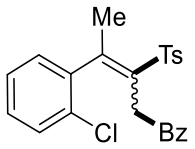
^{19}F NMR (565 MHz, $CDCl_3$) δ -114.86 – -114.89.

For**22'** NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.0 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.17(m, 2H), 7.09 – 6.99 (m, 3H), 6.70 (t, *J* = 9.0 Hz, 1H), 4.63 (d, *J* = 18.0 Hz, 1H), 4.36 (d, *J* = 18.0 Hz, 1H), 2.34 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.23, 158.28 (d, *J* = 247.8 Hz) 146.86, 143.19, 137.40, 136.55, 136.29, 133.50, 130.89 (d, *J* = 3.3 Hz), 129.88 (d, *J* = 8.0 Hz), 128.86, 128.75, 128.31, 127.66, 127.39 (d, *J* = 16.2 Hz), 123.39 (d, *J* = 3.2 Hz), 114.95 (d, *J* = 21.1 Hz), 38.66, 23.92, 21.51.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.33 – -112.36.

HRMS (ESI) (m/z): calcd for $C_{24}H_{21}FNaO_3S$ ([M + Na] $^+$), 431.1088; found 431.1088.



4-(2-chlorophenyl)-1-phenyl-3-tosylpent-3-en-1-one (23)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 56.1 mg, 66%).

The ^{1}H NMR spectrum of the product showed a 1.7:1 mixture based on the peak at δ 4.61 and at δ 4.42. **23** can be further purified by silica gel chromatography.

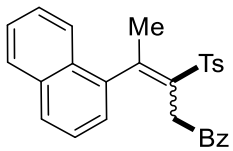
For **23** NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.40 – 7.33 (m, *J* = 16.4, 7.6 Hz, 5H), 7.18 – 7.12 (m, 3H), 4.42 (d, *J* = 17.7 Hz, 1H), 3.51 (d, *J* = 17.7 Hz, 1H), 2.45 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.54, 151.03, 144.01, 140.33, 138.86, 136.30, 136.00, 133.15, 130.47, 129.77, 129.56, 129.36, 128.47, 128.37, 128.07, 127.73, 127.15, 40.59, 21.78, 21.64.

For **23'** NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 2H), 4.61 (d, *J* = 18.0 Hz, 1H), 4.34 (d, *J* = 18.0 Hz, 1H), 2.34 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.17, 149.43, 143.46, 138.44, 136.95, 136.32, 135.67, 133.47, 131.80, 130.76, 129.12, 129.10, 128.94, 128.73, 128.26, 128.08, 126.13, 38.67, 23.58, 21.53.

HRMS (ESI) (m/z): calcd for $C_{24}H_{21}ClNaO_3S$ ([M + Na] $^+$), 447.0792; found 447.0775.



4-(naphthalen-1-yl)-1-phenyl-3-tosylpent-3-en-1-one (24)

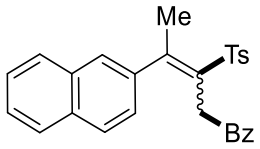
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 59.9 mg, 68%).

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 3.3:1 mixture based on the peak at δ 5.03 and at δ 4.38.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.11 (m, 2H), 7.84 – 7.78 (m, 0.26H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.65 (m, 1.25H), 7.65 – 7.61 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 1.54H), 7.51 – 7.48 (m, 1.37H), 7.45 – 7.38 (m, 2.24H), 7.35 – 7.28 (m, 1.48H), 7.25 – 7.19 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1.49H), 6.49 (d, *J* = 8.0 Hz, 1.51H), 5.03 (d, *J* = 18.0 Hz, 0.75H), 4.38 (d, *J* = 17.8 Hz, 0.23H), 4.26 (d, *J* = 18.0 Hz, 0.75H), 3.56 (d, *J* = 17.8 Hz, 0.23H), 2.48 (s, 0.69H), 2.35 (s, 0.70H), 2.13 (s, 2.26H), 1.96 (s, 2.23H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.12, 195.17, 152.40, 150.71, 144.05, 142.35, 139.16, 139.11, 137.23, 136.94, 136.80, 136.45, 136.31, 136.22, 133.64, 133.57, 133.19, 133.02, 129.62, 129.42, 128.82, 128.51, 128.44, 128.41, 128.36, 128.22, 128.17, 128.04, 127.98, 127.78, 127.75, 126.84, 126.83, 126.29, 125.85, 125.78, 125.40, 125.36, 124.86, 124.48, 123.72, 40.76, 38.62, 24.64, 23.02, 21.67, 21.07.

HRMS (ESI) (m/z): calcd for $C_{28}H_{24}NaO_3S$ ([M + Na] $^+$), 463.1338; found 463.1331.



4-(naphthalen-2-yl)-1-phenyl-3-tosylpent-3-en-1-one (25)

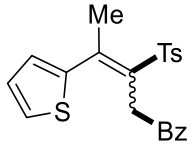
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 59.0 mg, 67%).

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 6.4:1 mixture based on the peak at δ 4.56 and at δ 4.15.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 2H), 7.82 (d, *J* = 7.0 Hz, 1.71H), 7.76 (d, *J* = 8.6 Hz, 1.85H), 7.74 – 7.71 (m, 0.86H), 7.66 (s, 0.86H), 7.65 – 7.61 (m, 0.32H), 7.56 – 7.52 (m, 0.46H), 7.49 – 7.45 (m, 1.27H), 7.45 – 7.42 (m, 1.65H), 7.41 – 7.33 (m, 3.61H), 7.28 (dd, *J* = 8.5, 1.8 Hz, 0.87H), 7.14 (d, *J* = 8.3 Hz, 0.29H), 7.01 (dd, *J* = 8.4, 1.8 Hz, 0.14H), 6.67 (d, *J* = 7.8 Hz, 0.29H), 4.56 (s, 0.27H), 4.15 (s, 1.73H), 2.45 (s, 2.58H), 2.37 (s, 2.55H), 2.15 (s, 0.45H), 2.10 (s, 0.44H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.87, 194.95, 153.20, 152.02, 143.94, 142.86, 139.44, 138.97, 137.98, 137.22, 136.40, 135.64, 135.20, 133.50, 133.12, 132.90, 132.72, 132.51, 132.36, 129.56, 128.76, 128.54, 128.44, 128.39, 128.35, 128.08, 128.02, 127.99, 127.75, 127.60, 127.44, 127.36, 127.21, 126.55, 126.51, 126.28, 126.02, 125.59, 125.14, 124.12, 41.09, 38.73, 25.29, 23.16, 21.61, 21.29.

HRMS (ESI) (m/z): calcd for $C_{28}H_{24}NaO_3S$ ([M + Na] $^+$), 463.1338; found 463.1331.



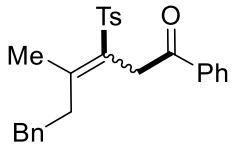
1-phenyl-4-(thiophen-2-yl)-3-tosylpent-3-en-1-one (26)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 28.5 mg, 36%).The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 4.4:1 mixture based on the peak at δ 8.10 and at δ 8.03.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.9 Hz, 1.63H), 8.03 (d, *J* = 8.1 Hz, 0.37H), 8.00 – 7.95 (m, 0.35H), 7.63 (t, *J* = 7.3 Hz, 0.82H), 7.58 (t, *J* = 7.4 Hz, 0.23H), 7.53 (t, *J* = 7.6 Hz, 1.63H), 7.47 (t, *J* = 7.7 Hz, 0.4H), 7.42 (d, *J* = 8.2 Hz, 1.6H), 7.35 (d, *J* = 8.1 Hz, 0.41H), 7.30 (d, *J* = 4.4 Hz, 0.19H), 7.21 – 7.18 (m, 1.62H), 7.03 (d, *J* = 7.8 Hz, 1.80H), 6.91 – 6.87 (m, 0.18H), 6.86 – 6.84 (m, 0.8H), 4.48 (s, 2H), 2.43 (s, 0.57H), 2.34 (s, 0.54H), 2.32 (s, 2.42H), 2.07 (s, 2.41H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.89, 194.85, 145.43, 144.60, 143.95, 142.83, 140.15, 138.81, 137.42, 137.27, 136.30, 135.54, 133.53, 133.35, 130.53, 129.55, 128.76, 128.62, 128.37, 128.32, 128.03, 127.94, 127.25, 127.15, 127.06, 126.13, 41.77, 39.25, 26.08, 23.79, 21.61, 21.51.

HRMS (ESI) (m/z): calcd for $C_{22}H_{20}NaO_3S_2$ ([M + Na] $^+$), 419.0746; found 419.0746.



4-methyl-1,6-diphenyl-3-tosylhex-3-en-1-one (27)

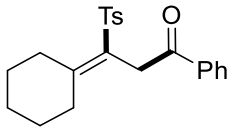
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 64.5 mg, 77%).

The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 1.2:1 mixture based on the peak at δ 4.35 and at δ 4.07.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.84 (t, *J* = 8.0 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.50 – 7.45 (m, 2H), 7.32 – 7.27 (m, 1.74H), 7.26 – 7.22 (m, 2H), 7.21 – 7.17 (m, 1.54H), 7.13 (d, *J* = 7.0 Hz, 1.12H), 7.04 (d, *J* = 5.7 Hz, 0.91H), 4.35 (s, 1.08H), 4.07 (s, 0.91H), 2.87 – 2.81 (m, 1H), 2.73 (t, *J* = 7.7 Hz, 1H), 2.67 – 2.61 (m, 1H), 2.42 (s, 1.45H), 2.38 (s, 1.61H), 2.33 (t, *J* = 7.8 Hz, 0.92H), 2.08 (s, 1.46H), 1.84 (s, 1.59H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.46, 194.67, 154.72, 153.11, 143.70, 143.60, 141.16, 140.43, 139.43, 139.16, 136.30, 133.41, 133.35, 132.63, 131.57, 129.55, 129.41, 128.66, 128.62, 128.49, 128.35, 128.33, 128.31, 128.18, 128.14, 127.56, 127.41, 126.33, 126.03, 40.04, 39.32, 38.53, 37.85, 34.12, 33.39, 22.42, 21.56, 21.52, 20.32.

HRMS (ESI) (m/z): calcd for $C_{26}H_{26}NaO_3S$ ([M + Na] $^+$), 441.1495; found 441.1495.



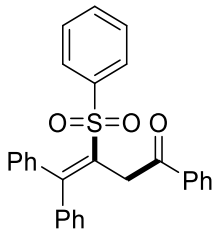
3-cyclohexylidene-1-phenyl-3-tosylpropan-1-one (28)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 54.5 mg, 74%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.41 (s, 2H), 2.62 – 2.55 (m, 2H), 2.41 (s, 3H), 2.14 – 2.06 (m, 2H), 1.64 – 1.61(m, 2H), 1.51 – 1.47 (m, 2H), 1.36 – 1.31 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.40, 158.75, 143.34, 140.29, 136.36, 133.36, 129.38, 128.66, 128.32, 128.21, 127.22, 38.28, 34.37, 32.31, 27.88, 27.01, 25.70, 21.54.

HRMS (ESI) (m/z): calcd for $C_{22}H_{24}NaO_3S$ ([M + Na] $^+$), 391.1338; found 391.1332.



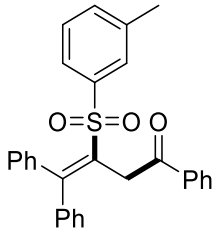
1,4,4-triphenyl-3-(phenylsulfonyl)but-3-en-1-one (30)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a white solid (yield 68.4 mg, 78%), mp 90 – 91 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.9 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 3H), 7.47 (t, *J* = 7.6 Hz 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.17 (m, 7H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 2H), 4.35 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.35, 154.83, 140.48, 140.40, 138.15, 138.10, 136.49, 133.30, 132.11, 129.47, 128.61, 128.59, 128.48, 128.29, 128.03, 127.92, 127.73, 127.58, 127.36, 40.75.

HRMS (ESI) (m/z): calcd for $C_{28}H_{22}NaO_3S$ ([M + Na] $^+$), 461.1182; found 461.1161.



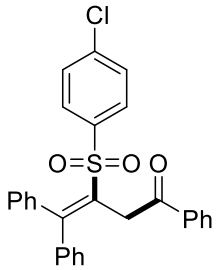
1,4,4-triphenyl-3-(m-tolylsulfonyl)but-3-en-1-one (31)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 65.2 mg, 72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.57 (dd, *J* = 19.3, 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.11 (m, 9H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 7.1 Hz, 2H), 4.33 (s, 2H), 2.18 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.21, 154.58, 140.39, 140.19, 138.30, 138.13, 137.72, 136.50, 133.24, 133.00, 129.46, 128.59, 128.57, 128.54, 128.45, 128.26, 128.17, 127.55, 127.41, 127.35, 125.21, 40.71, 20.88.

HRMS (ESI) (m/z): calcd for $C_{29}H_{24}NaO_3S$ ([M + Na] $^+$), 475.1338; found 475.1338.



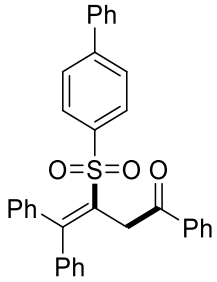
3-((4-chlorophenyl)sulfonyl)-1,4,4-triphenylbut-3-en-1-one (32)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a colorless oil (yield 69.1 mg, 73%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.45 (m, 4H), 7.24 – 7.14 (m, 8H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 7.4 Hz, 2H), 4.34 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.42, 155.09, 140.17, 139.00, 138.76, 138.10, 137.98, 136.35, 133.41, 129.50, 129.44, 128.73, 128.65, 128.54, 128.28, 128.23, 127.99, 127.63, 127.29, 40.77.

HRMS (ESI) (m/z): calcd for $C_{28}H_{21}ClNaO_3S$ ([M + Na] $^+$), 495.0792; found 495.0792.



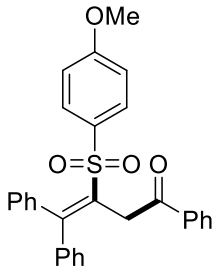
3-([1,1'-biphenyl]-4-ylsulfonyl)-1,4,4-triphenylbut-3-en-1-one (33)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a colorless oil (yield 51.5 mg, 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.50 – 7.45 (m, 4H), 7.42 – 7.38 (m, 3H), 7.24 – 7.19 (m, 5H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 7.4 Hz, 2H), 4.37 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.38, 154.70, 144.95, 140.41, 139.73, 139.04, 138.34, 138.33, 136.53, 133.32, 129.50, 128.94, 128.64, 128.60, 128.51, 128.48, 128.32, 128.26, 127.76, 127.57, 127.37, 127.25, 126.72, 40.77.

HRMS (ESI) (m/z): calcd for $C_{34}H_{26}NaO_3S$ ([M + Na] $^+$), 537.1495; found 537.1477.



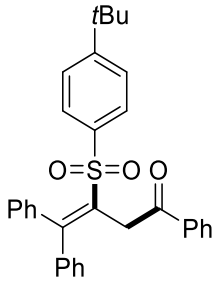
3-((4-methoxyphenyl)sulfonyl)-1,4,4-triphenylbut-3-en-1-one (34)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a colorless oil (yield 44.0 mg, 47%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.51 – 7.44 (m, 4H), 7.23 – 7.19 (m, 5H), 7.18 (t, *J* = 7.2 Hz 1H), 7.09 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 4.33 (s, 2H), 3.79 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.43, 162.58, 154.31, 140.61, 138.54, 138.41, 136.57, 133.26, 132.07, 130.22, 129.44, 128.61, 128.50, 128.48, 128.30, 127.74, 127.58, 127.38, 113.33, 55.49, 40.97.

HRMS (ESI) (m/z): calcd for $C_{29}H_{24}NaO_4S$ ([M + Na] $^+$), 491.1288; found 491.1271.



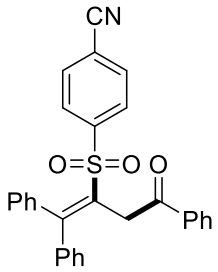
3-((4-(tert-butyl)phenyl)sulfonyl)-1,4,4-triphenylbut-3-en-1-one (35)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow solid (yield 61.3 mg, 62%), mp 83 – 84 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.43 (m, 4H), 7.22 – 7.18 (m, 7H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 7.4 Hz, 2H), 4.33 (s, 2H), 1.27 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.26, 155.74, 154.36, 140.50, 138.38, 138.35, 137.24, 136.56, 133.24, 129.40, 128.59, 128.50, 128.45, 128.29, 127.78, 127.56, 127.50, 127.38, 125.03, 40.69, 34.90, 30.98.

HRMS (ESI) (m/z): calcd for $C_{32}H_{30}NaO_3S$ ([M + Na] $^+$), 517.1808; found 517.1813.



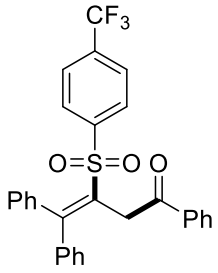
4-((4-oxo-1,1,4-triphenylbut-1-en-2-yl)sulfonyl)benzonitrile (36)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a white solid (yield 65.8 mg, 71%), mp 96 – 97 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.8 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 4H), 7.24 – 7.22 (m, 3H), 7.20 – 7.17(m, 3H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.93 (d, *J* = 7.1 Hz, 2H), 4.37 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.46, 155.82, 144.90, 139.81, 137.86, 137.46, 136.19, 133.61, 131.69, 129.69, 129.00, 128.74, 128.64, 128.55, 128.31, 128.24, 127.76, 127.27, 117.54, 115.58, 40.68.

HRMS (ESI) (m/z): calcd for $C_{29}H_{21}NNaO_3S$ ([M + Na] $^+$), 486.1134; found 486.1156.



1,4,4-triphenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)but-3-en-1-one (37)

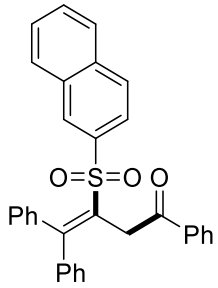
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 12:1, v/v) affords the title compound as a yellow oil (yield 75.0 mg, 74%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.9 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.18 (m, 5H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 4.37 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.38, 155.48, 144.07, 139.97, 137.97, 137.76, 136.30, 133.65 (q, *J* = 32.6 Hz), 133.51, 129.55, 128.87, 128.70, 128.59, 128.48, 128.31, 128.05, 127.68, 127.29, 125.02 (q, *J* = 3.6 Hz), 124.16 (q, *J* = 273.0 Hz), 40.64.

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.27, -63.28.

HRMS (ESI) (m/z): calcd for $C_{29}H_{21}F_3NaO_3S$ ([M + Na] $^+$), 529.1056; found 529.1049.



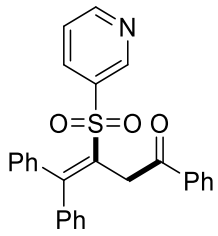
3-(naphthalen-2-ylsulfonyl)-1,4,4-triphenylbut-3-en-1-one (38)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 44.0 mg, 45%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.8 Hz, 2H), 7.91 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.76 (s, 1H), 7.68 – 7.62 (m, 1H), 7.60 – 7.53 (m, 2H), 7.50 – 7.45 (m, 3H), 7.22 – 7.19 (m, *J* = 7.4, 6.9, 3.9 Hz, 5H), 6.95 – 6.86 (m, 3H), 6.82 (t, *J* = 7.5 Hz, 2H), 4.39 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.33, 154.95, 140.36, 138.04, 137.96, 136.97, 136.57, 134.57, 133.31, 131.59, 130.21, 129.32, 129.29, 128.64, 128.60, 128.55, 128.49, 128.41, 128.33, 128.04, 127.57, 127.39, 127.30, 126.73, 122.99, 40.78.

HRMS (ESI) (m/z): calcd for $C_{32}H_{24}NaO_3S$ ([M + Na] $^+$), 511.1338; found 511.1334.



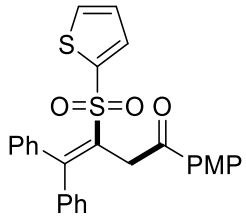
1,4,4-triphenyl-3-(pyridin-3-ylsulfonyl)but-3-en-1-one (39)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1, v/v) affords the title compound as a white solid (yield 63.3 mg, 72%), mp 92 – 93 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 – 8.43 (m, 2H), 7.96 – 7.88 (m, 3H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.15 – 7.06 (m, 7H), 7.01 (t, *J* = 7.6 Hz, 2H), 6.87 (d, *J* = 7.3 Hz, 2H), 4.27 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.28, 155.70, 152.30, 148.68, 139.98, 137.78, 137.68, 136.28, 135.80, 133.52, 129.60, 128.90, 128.71, 128.62, 128.51, 128.32, 127.86, 127.32, 122.94, 40.83.

HRMS (ESI) (m/z): calcd for $C_{27}H_{21}NNaO_3S$ ([M + Na] $^+$), 462.1134; found 462.1136.



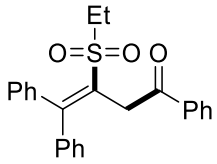
1-(4-methoxyphenyl)-4,4-diphenyl-3-(thiophen-2-ylsulfonyl)but-3-en-1-one (40)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1, v/v) affords the title compound as a white solid (yield 50.3 mg, 53%), mp 90 – 91 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 4.9 Hz, 1H), 7.23 – 7.12 (m, 9H), 7.09 (d, *J* = 7.1 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.76 (t, *J* = 4.5 Hz, 1H), 4.29 (s, 2H), 3.86 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.19, 163.70, 155.42, 141.90, 140.72, 138.51, 138.43, 134.55, 133.47, 130.57, 129.38, 129.32, 128.51, 127.84, 127.65, 127.35, 126.48, 113.79, 55.47, 41.11.

HRMS (ESI) (m/z): calcd for $C_{27}H_{22}NaO_4S_2$ ([M + Na] $^+$), 497.0852; found 497.0849.



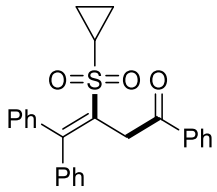
3-(ethylsulfonyl)-1,4,4-triphenylbut-3-en-1-one (41)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 57.4 mg, 71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.0 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.31 – 7.25 (m, 3H), 7.16 (s, 5H), 4.12 (s, 2H), 2.60 (q, *J* = 7.4 Hz, 2H), 1.12 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.05, 154.24, 140.73, 138.47, 136.27, 135.86, 133.29, 129.39, 128.70, 128.64, 128.57, 128.19, 128.12, 127.29, 48.78, 40.99, 6.18.

HRMS (ESI) (m/z): calcd for $C_{24}H_{22}NaO_3S$ ([M + Na] $^+$), 413.1182; found 413.1165.



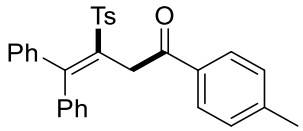
3-(cyclopropylsulfonyl)-1,4,4-triphenylbut-3-en-1-one (42)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 52.3 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 6.4 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.28 – 7.23 (m, 5H), 4.19 (s, 2H), 1.88 – 1.82 (m, 1H), 1.09 – 1.06 (m, 2H), 0.75 – 0.70 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.03, 153.54, 140.74, 139.18, 137.37, 136.39, 133.28, 129.77, 128.63, 128.61, 128.59, 128.52, 128.21, 128.04, 127.43, 41.04, 31.86, 6.09.

HRMS (ESI) (m/z): calcd for $C_{25}H_{22}NaO_3S$ ([M + Na] $^+$), 413.1182; found 413.1178.



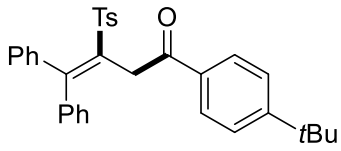
4,4-diphenyl-1-(p-tolyl)-3-tosylbut-3-en-1-one (43)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a white solid (yield 69.1 mg, 74%), mp 93 – 94 ºC.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.19 (s, 5H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.97 (d, 7.7 Hz, 2H), 6.95 (d, 7.2 Hz, 2H), 4.31 (s, 2H), 2.40 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.86, 154.38, 144.09, 142.83, 140.56, 138.39, 138.35, 137.55, 134.01, 129.45, 129.26, 128.62, 128.44, 128.40, 128.04, 127.65, 127.44, 127.39, 40.71, 21.63, 21.47.

HRMS (ESI) (m/z): calcd for $C_{30}H_{26}NaO_3S$ ([M + Na] $^+$), 489.1495; found 489.1501.



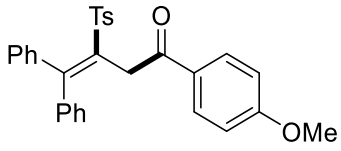
1-(4-(tert-butyl)phenyl)-4,4-diphenyl-3-tosylbut-3-en-1-one (44)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a white solid (yield 87.5 mg, 86%), mp 100 – 101 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.18 (m, 5H), 7.15 – 7.11 (m, 1H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.98 – 6.94 (m, 4H), 4.32 (s, 2H), 2.30 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.87, 157.01, 154.40, 142.81, 140.56, 138.42, 138.36, 137.53, 133.91, 129.46, 128.61, 128.46, 128.44, 128.27, 128.03, 127.64, 127.44, 127.39, 125.56, 40.71, 35.08, 31.03, 21.46.

HRMS (ESI) (m/z): calcd for $C_{33}H_{32}NaO_3S$ ([M + Na] $^+$), 531.1964; found 4 531.1966.



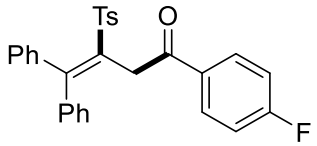
1-(4-methoxyphenyl)-4,4-diphenyl-3-tosylbut-3-en-1-one (45)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1, v/v) affords the title compound as a colorless oil (yield 85.9 mg, 89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.20 (s, 5H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.95 – 6.93 (m, 4H), 4.29 (s, 2H), 3.86 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.65, 163.63, 154.33, 142.82, 140.59, 138.47, 138.39, 137.59, 130.60, 129.50, 129.47, 128.62, 128.44, 128.43, 128.04, 127.63, 127.44, 113.75, 55.48, 40.45, 21.48.

HRMS (ESI) (m/z): calcd for $C_{30}H_{26}NaO_4S$ ([M + Na] $^+$), 505.1444; found 505.1439.



1-(4-fluorophenyl)-4,4-diphenyl-3-tosylbut-3-en-1-one (46)

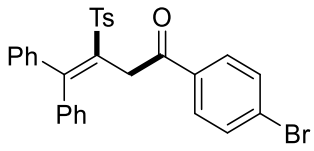
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a white solid (yield 80.9 mg, 86%), mp 79 – 80 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.17 (m, 5H), 7.14 (t, *J* = 8.5 Hz, 3H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 2H), 4.29 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.79, 165.844 (d, *J* = 255.2 Hz), 154.66, 142.95, 140.49, 138.19 (d, *J* = 8.2 Hz), 137.38, 132.96 (d, *J* = 2.9 Hz), 131.01, 130.95, 129.44, 128.67, 128.58, 128.50, 128.00, 127.76, 127.49, 127.38, 115.73 (d, *J* = 21.7 Hz) 40.68, 21.49.

^{19}F NMR (565 MHz, $CDCl_3$) δ -104.81.

HRMS (ESI) (m/z): calcd for $C_{29}H_{23}FNaO_3S$ ([M + Na] $^+$), 493.1244; found 493.1239.



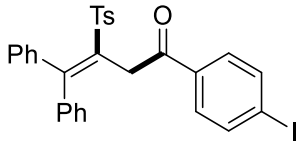
1-(4-bromophenyl)-4,4-diphenyl-3-tosylbut-3-en-1-one (47)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 79.7 mg, 75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.12 – 7.09(m, 5H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 7.2 Hz, 2H), 4.18 (s, 2H), 2.21 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.43, 154.73, 142.97, 140.44, 138.16, 138.04, 137.32, 135.28, 131.90, 129.81, 129.42, 128.66, 128.61, 128.51, 128.45, 127.98, 127.78, 127.49, 127.34, 40.69, 21.47.

HRMS (ESI) (m/z): calcd for $C_{29}H_{23}BrNaO_3S$ ([M + Na] $^+$), 553.0443; found 555.0418.



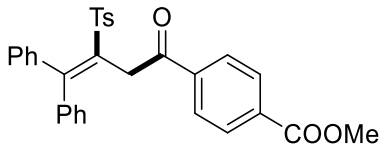
1-(4-iodophenyl)-4,4-diphenyl-3-tosylbut-3-en-1-one (48)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a white solid (yield 74.0 mg, 64%), mp 100 – 101 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.13 – 7.07 (m, 5H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 4.16 (s, 2H), 2.21 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.75, 154.74, 142.97, 140.45, 138.17, 138.04, 137.91, 137.34, 135.83, 129.68, 129.42, 128.67, 128.62, 128.52, 127.99, 127.78, 127.50, 127.34, 101.26, 40.64, 21.48.

HRMS (ESI) (m/z): calcd for $C_{29}H_{23}INaO_3S$ ([M + Na] $^+$), 601.0305; found 601.0303.



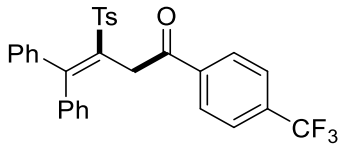
methyl 4-(4,4-diphenyl-3-tosylbut-3-enoyl)benzoate (49)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 75.6 mg, 74%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.3 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.13(m, 5H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 7.3 Hz, 2H), 4.33 (s, 2H), 3.94 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.06, 166.11, 154.82, 142.99, 140.45, 139.88, 138.15, 138.03, 137.31, 133.95, 129.81, 129.41, 128.68, 128.63, 128.52, 128.20, 127.99, 127.80, 127.50, 127.32, 52.43, 41.11, 21.47.

HRMS (ESI) (m/z): calcd for $C_{31}H_{26}NaO_5S$ ([M + Na] $^+$), 533.1393; found 533.1402.



4,4-diphenyl-3-tosyl-1-(4-(trifluoromethyl)phenyl)but-3-en-1-one (50)

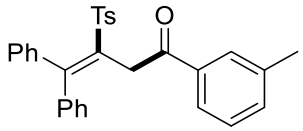
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 12:1, v/v) affords the title compound as a yellow solid (yield 58.3 mg, 56%), mp 81 – 82 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.15 (m, 5H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 7.4 Hz, 2H), 4.28 (s, 2H), 2.27 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.70, 154.95, 143.06, 140.40, 139.33, 138.08, 137.92, 137.20, 134.49 (q, *J* = 32.9 Hz,), 129.42, 128.71, 128.65, 128.56, 127.97, 127.86, 127.53, 127.33, 125.70 (q, *J* = 272.6 Hz,) 125.27 (q, *J* = 3.8 Hz,) 41.02, 21.49.

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.11.

HRMS (ESI) (m/z): calcd for $C_{30}H_{23}F_3NaO_3S$ ([M + Na] $^+$), 543.1212; found 543.1211.



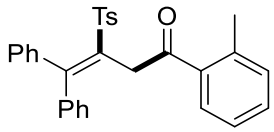
4,4-diphenyl-1-(m-tolyl)-3-tosylbut-3-en-1-one (51)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 58.8 mg, 63%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.39 –7.34 (m, 2H), 7.20 (s, 5H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.4 Hz, 2H), 4.32 (s, 2H), 2.41 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.53, 154.45, 142.85, 140.55, 138.39, 138.37, 138.33, 137.49, 136.53, 134.04, 129.47, 128.85, 128.63, 128.50, 128.49, 128.47, 128.04, 127.68, 127.46, 127.39, 125.51, 40.90, 21.49, 21.34.

HRMS (ESI) (m/z): calcd for $C_{30}H_{26}NaO_3S$ ([M + Na] $^+$), 489.1495; found 489.1478.



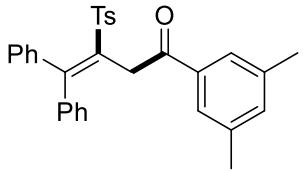
4,4-diphenyl-1-(o-tolyl)-3-tosylbut-3-en-1-one (52)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow solid (yield 42.0 mg, 45%), mp 90 – 91 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.26 – 7.22 (m, 7H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 7.3 Hz, 2H), 4.22 (s, 2H), 2.54 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 201.53, 154.50, 142.89, 140.58, 138.33, 138.24, 138.22, 137.57, 137.47, 131.62, 131.18, 129.46, 128.68, 128.64, 128.45, 128.22, 128.01, 127.74, 127.49, 127.40, 125.65, 44.12, 21.49, 20.70.

HRMS (ESI) (m/z): calcd for $C_{30}H_{26}NaO_3S$ ([M + Na] $^+$), 489.1495; found 489.1486.



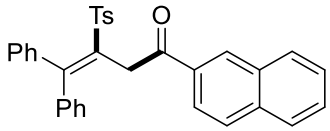
1-(3,5-dimethylphenyl)-4,4-diphenyl-3-tosylbut-3-en-1-one (53)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 73.1 mg, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.16 (s, 6H), 7.12 – 7.07 (m, 1H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.94 – 6.90 (m, 4H), 4.27 (s, 2H), 2.32 (s, 6H), 2.27 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.69, 154.36, 142.81, 140.56, 138.44, 138.34, 138.23, 137.50, 136.55, 134.92, 129.47, 128.61, 128.47, 128.45, 128.03, 127.65, 127.44, 127.40, 126.11, 40.95, 21.48, 21.21.

HRMS (ESI) (m/z): calcd for $C_{31}H_{28}NaO_3S$ ([M + Na] $^+$), 503.1651; found 503.1653.



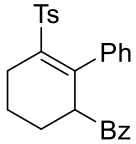
1-(naphthalen-2-yl)-4,4-diphenyl-3-tosylbut-3-en-1-one (54)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 81.4 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.92 (dd, *J* = 17.6, 8.4 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.11 (m, 6H), 7.05 (t, *J* = 7.3 Hz, 2H), 6.99 – 6.97 (m, 4H), 4.47 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.20, 154.59, 142.91, 140.61, 138.38, 138.37, 137.56, 135.65, 133.84, 132.45, 130.06, 129.59, 129.48, 128.67, 128.53, 128.51, 128.49, 128.45, 128.09, 127.71, 127.49, 127.42, 126.76, 123.97, 40.96, 21.47.

HRMS (ESI) (m/z): calcd for $C_{33}H_{26}NaO_3S$ ([M + Na] $^+$), 525.1495; found 525.1510.



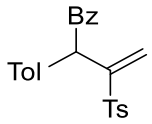
phenyl(6-tosyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)methanone (58)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1, v/v) affords the title compound as a yellow oil (yield 14.2 mg, 17%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.07 (m, 3H), 6.98 (d, *J* = 7.3 Hz, 2H), 4.47 (t, *J* = 5.0 Hz, 1H), 2.75 (dt, *J* = 18.2, 4.4 Hz, 1H), 2.63 – 2.57 (m, 1H), 2.39 (s, 3H), 1.99 – 1.97 (m, 2H), 1.83 – 1.78 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.11, 146.12, 143.39, 141.06, 139.10, 138.39, 135.85, 133.14, 129.21, 128.60, 128.28, 127.64, 127.49, 127.36, 51.86, 26.12, 25.85, 21.54, 18.61.

HRMS (ESI) (m/z): calcd for $C_{26}H_{24}NaO_3S$ ([M + Na] $^+$), 439.1338; found 439.1337.



1-phenyl-2-(p-tolyl)-3-tosylbut-3-en-1-one (11')

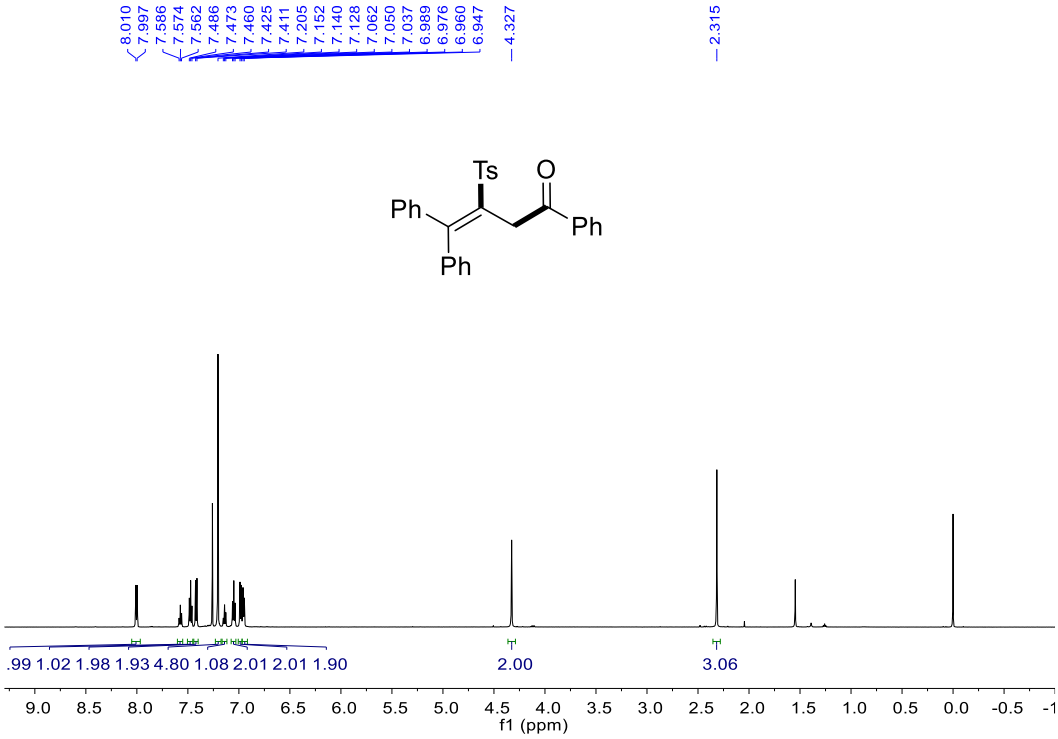
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1, v/v) affords the title compound as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 6.9 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.59 (s, 1H), 5.87 (s, 1H), 5.80 (s, 1H), 2.36 (s, 3H), 2.27 (s, 3H).

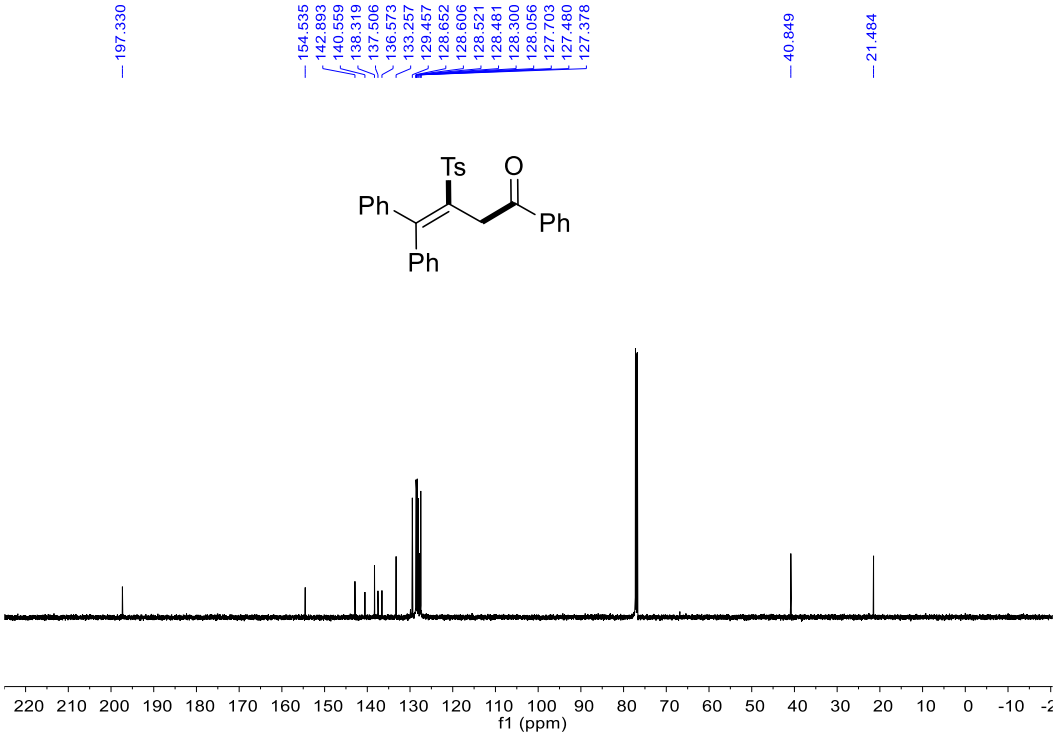
HRMS (ESI) (m/z): calcd for $C_{24}H_{22}NaO_3S$ ($[M + Na]^+$), 413.1182; found 413.1177.

Obtained the product was not enough for ^{13}C NMR analysis, so we characterized it with ^{1}H NMR and HRMS.

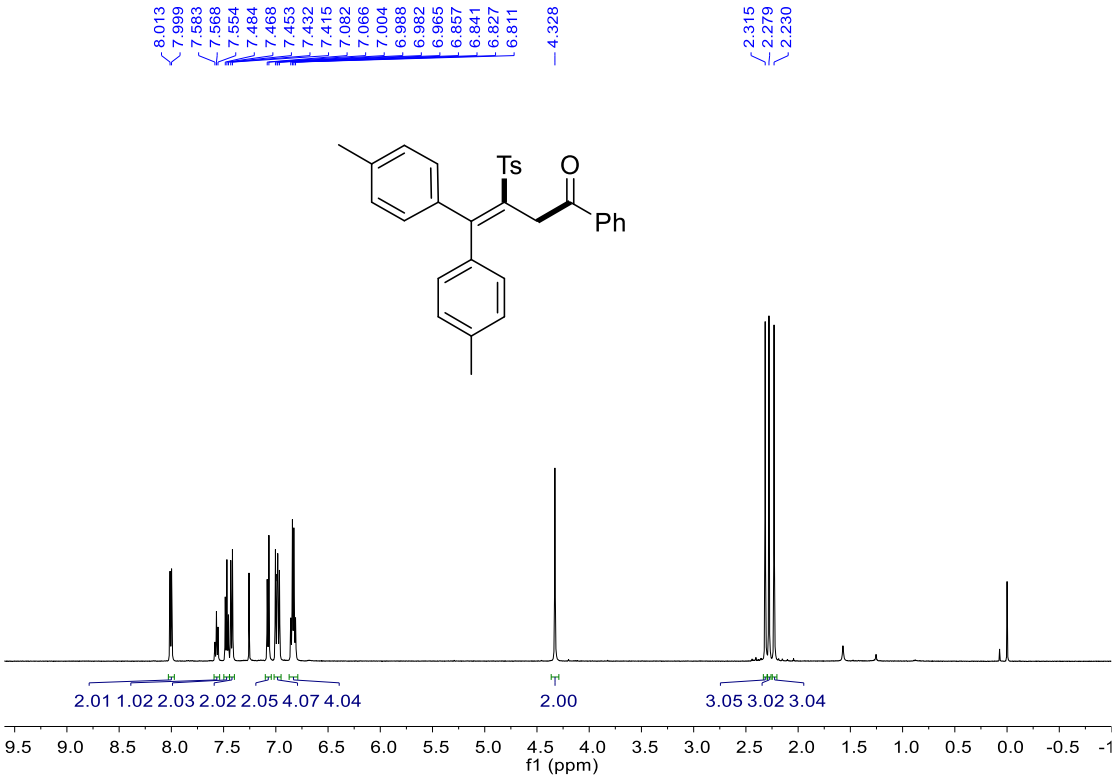
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **4**



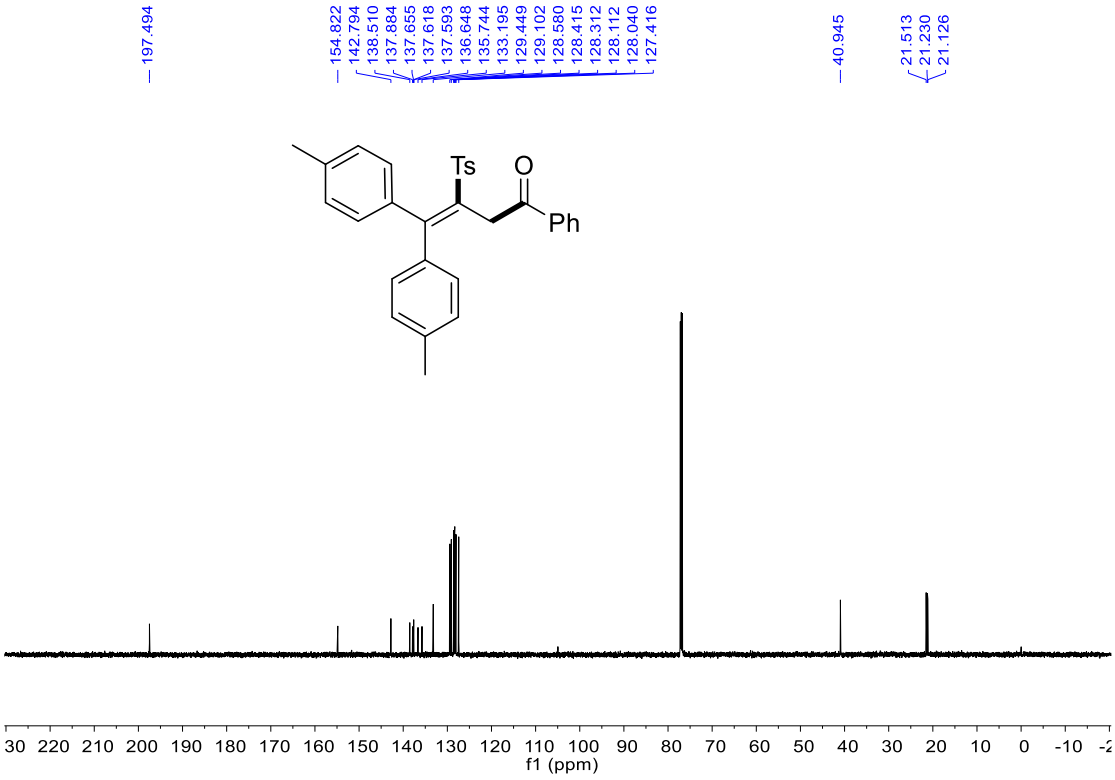
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4**



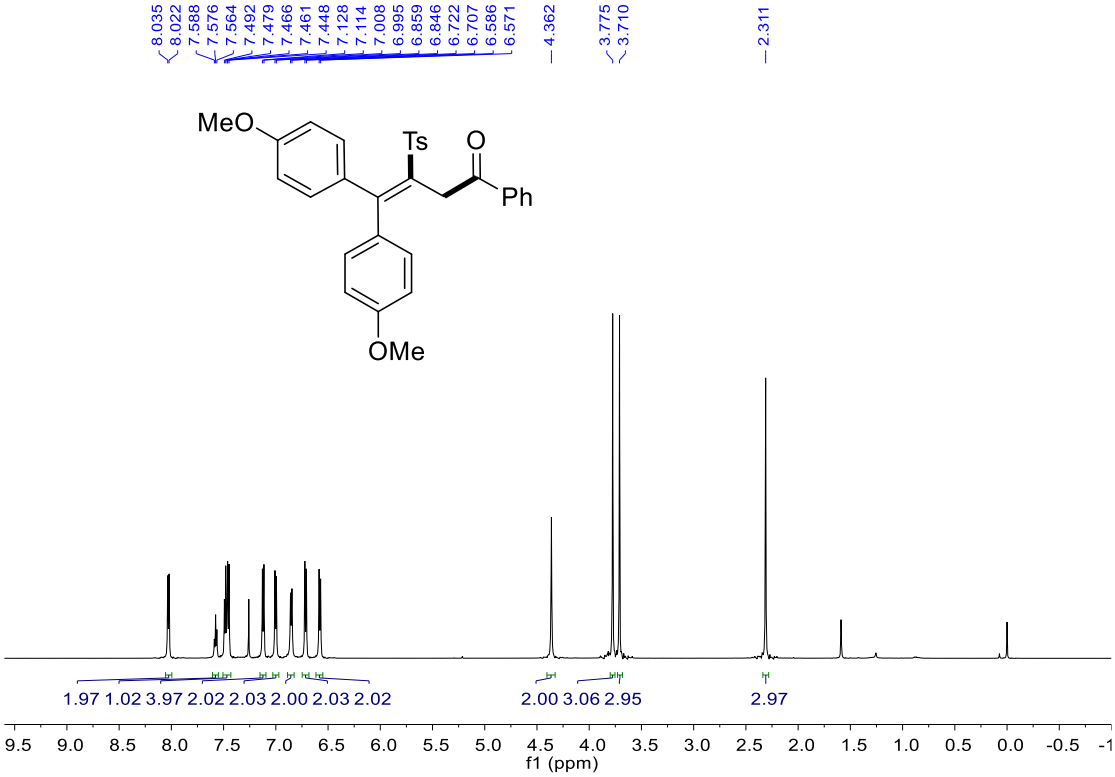
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5**



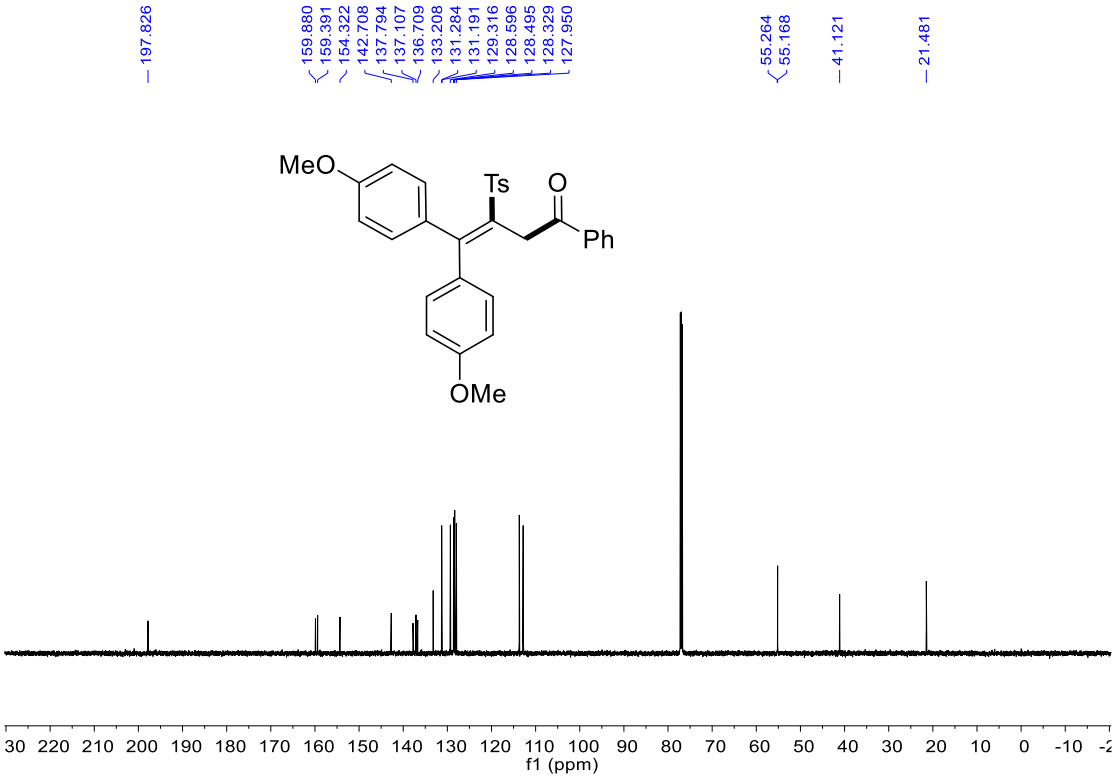
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **5**



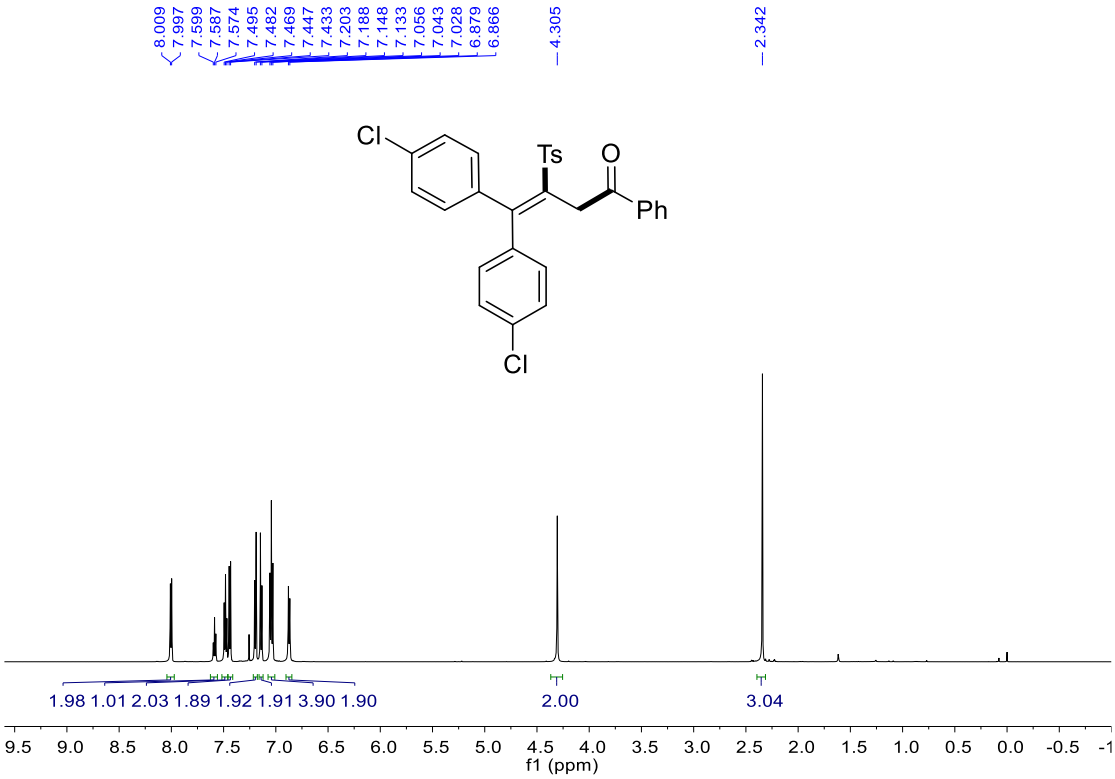
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **6**



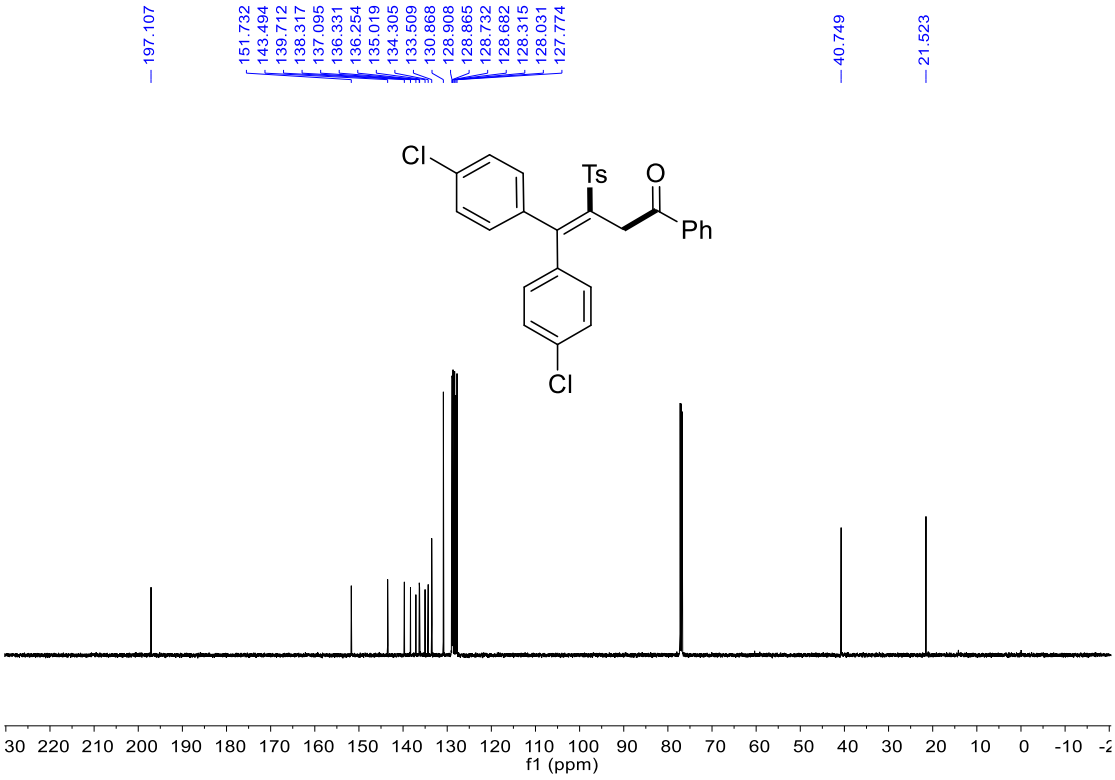
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **6**



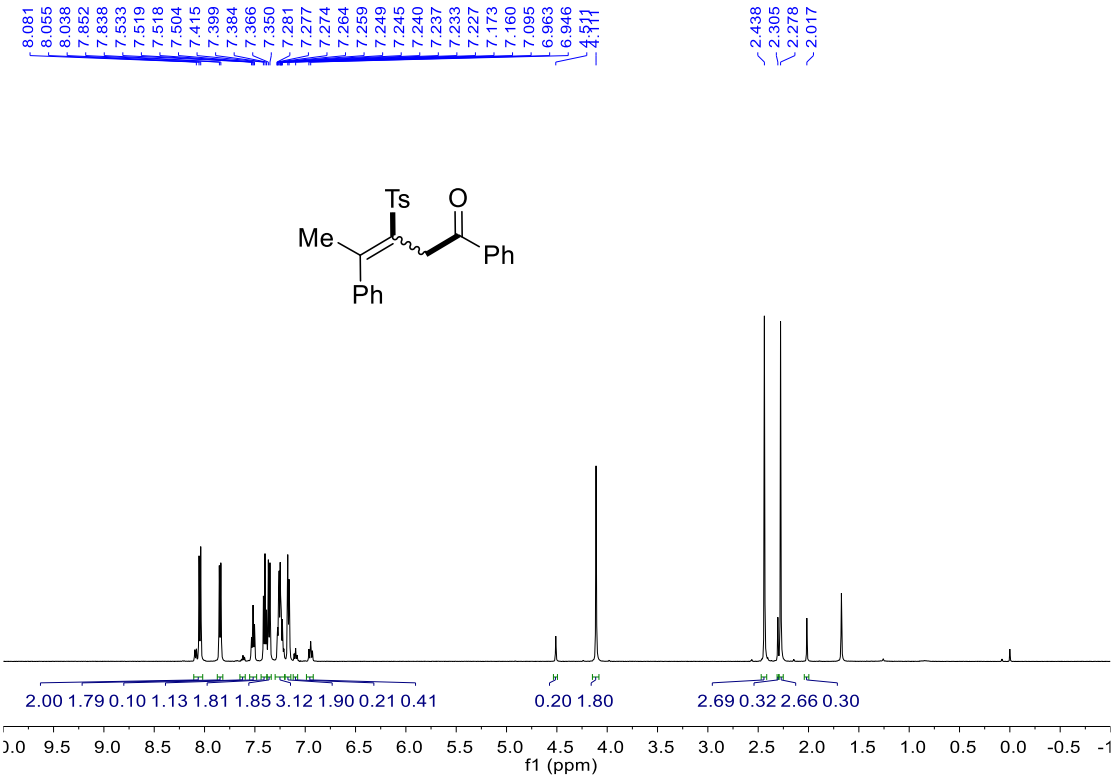
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **7**



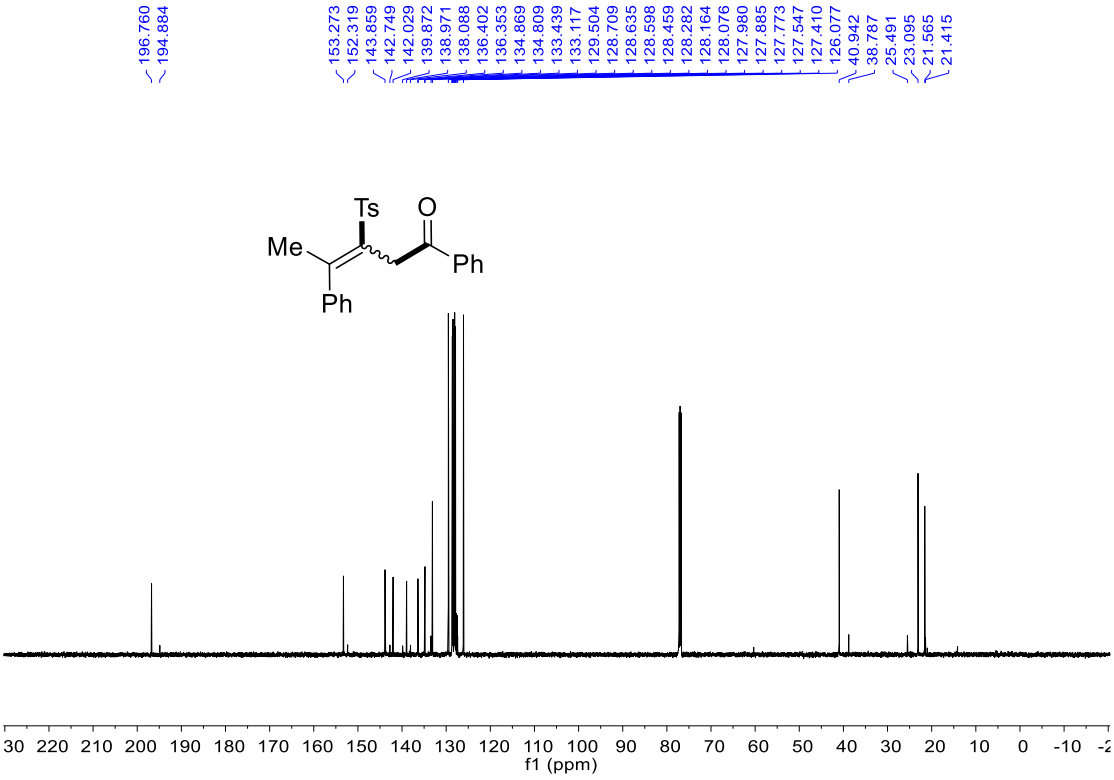
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **7**



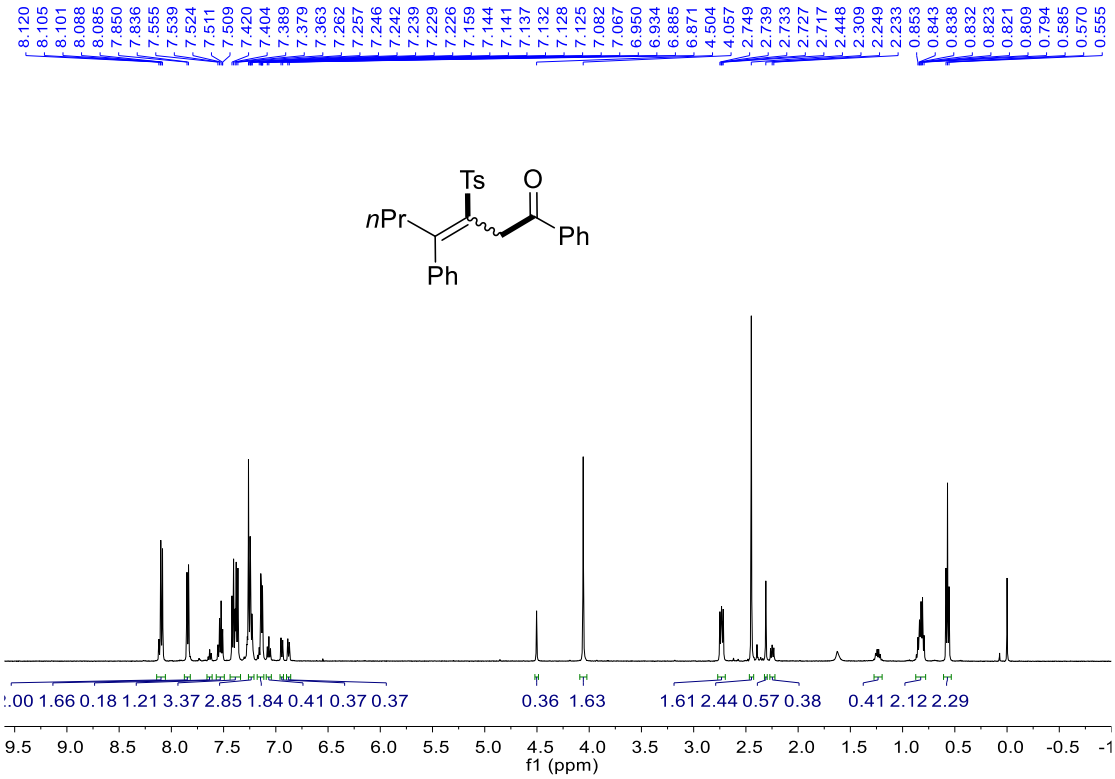
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **8**



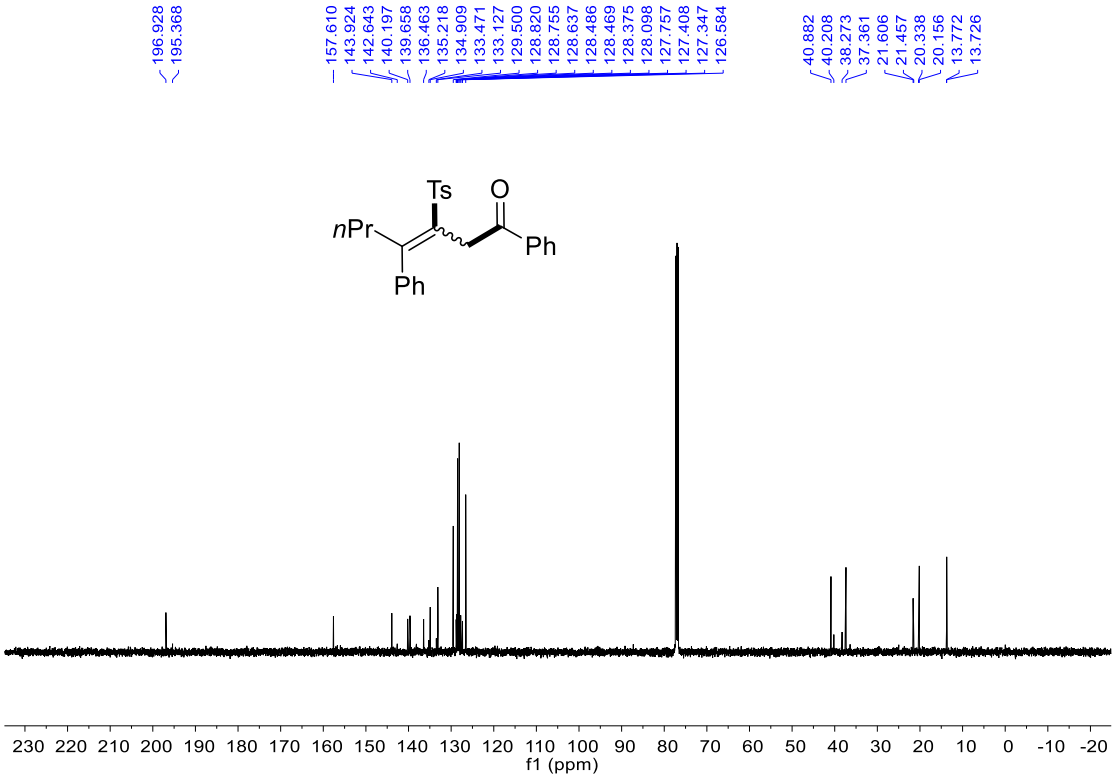
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **8**



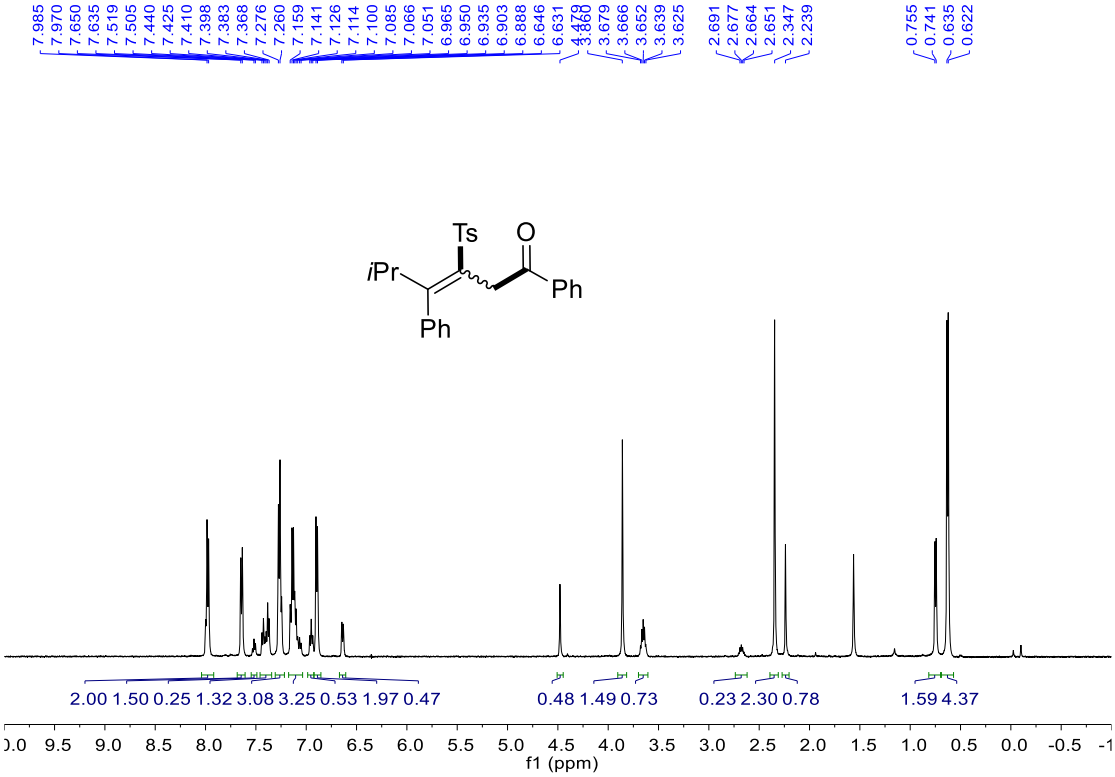
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **9**



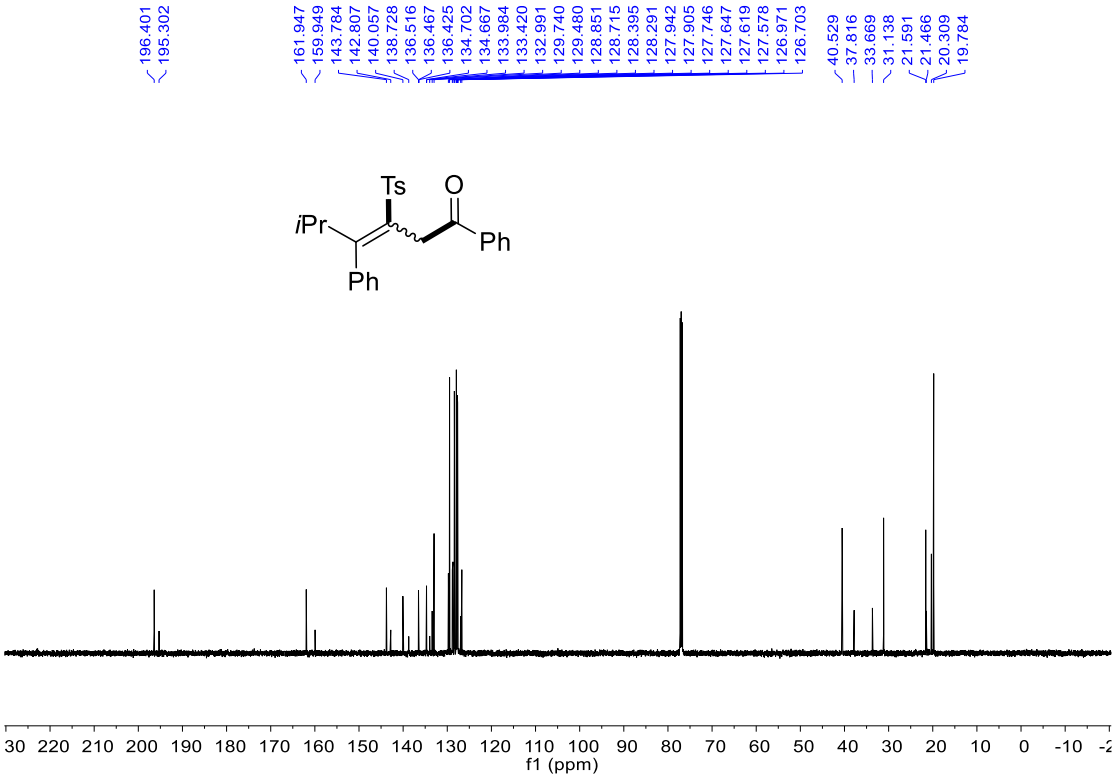
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **9**



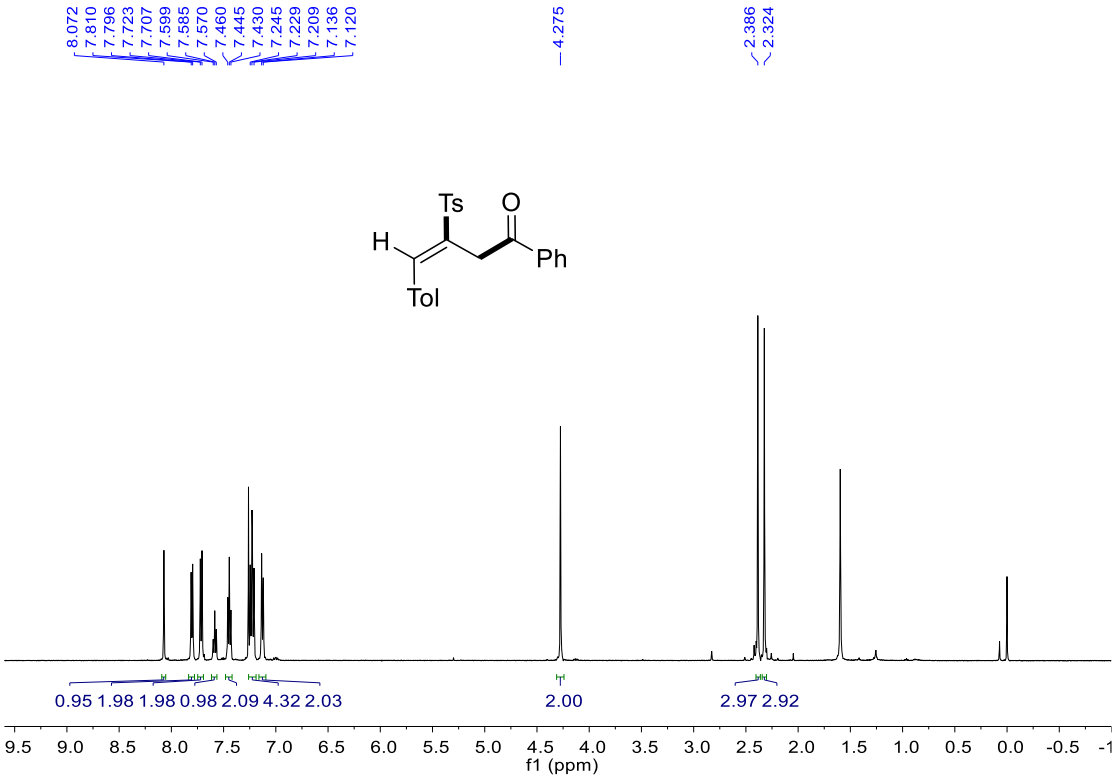
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **10**



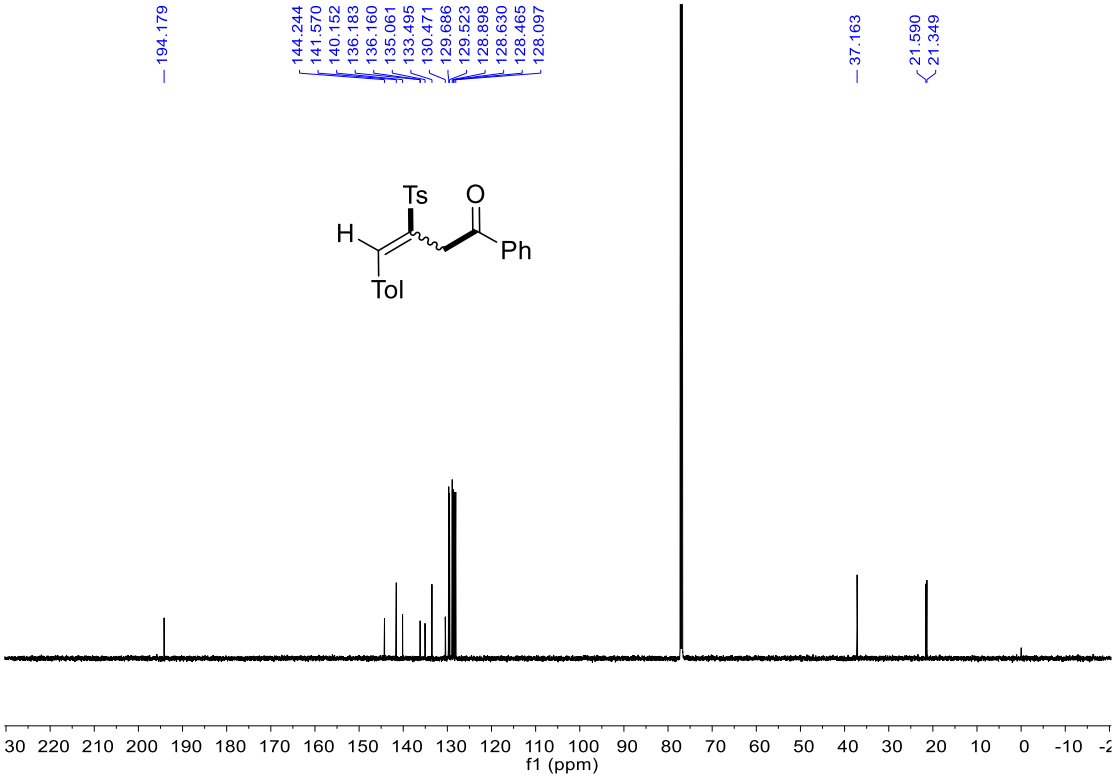
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **10**



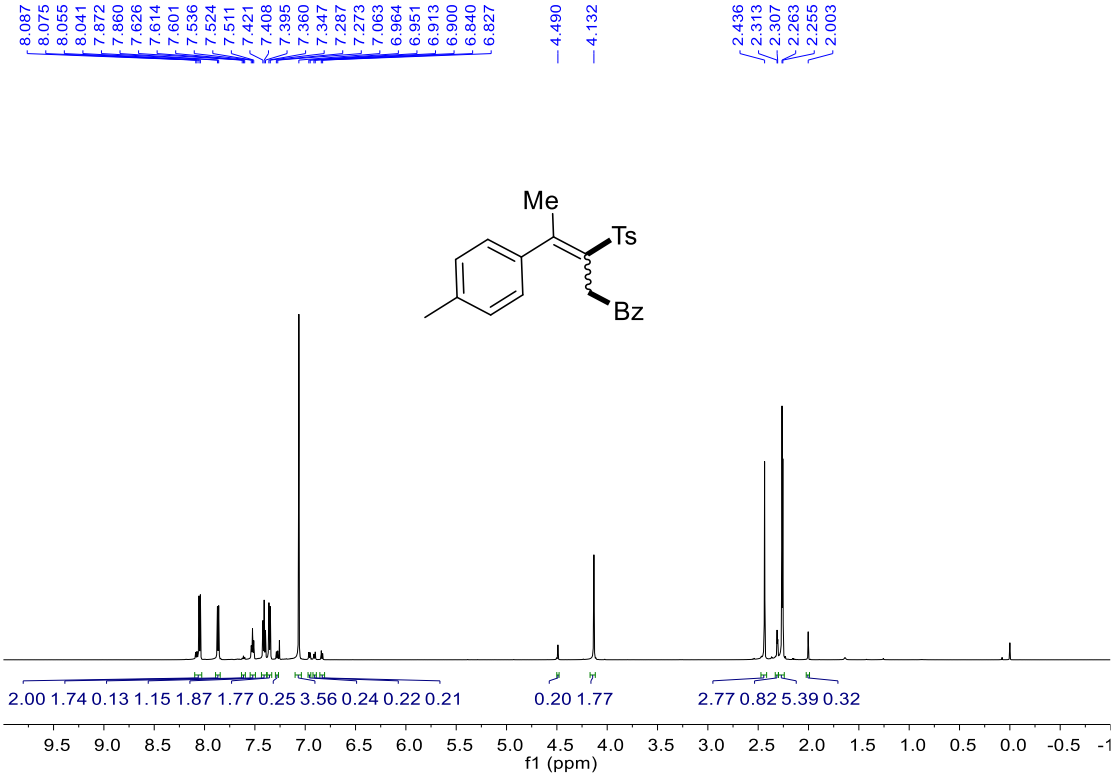
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **11**



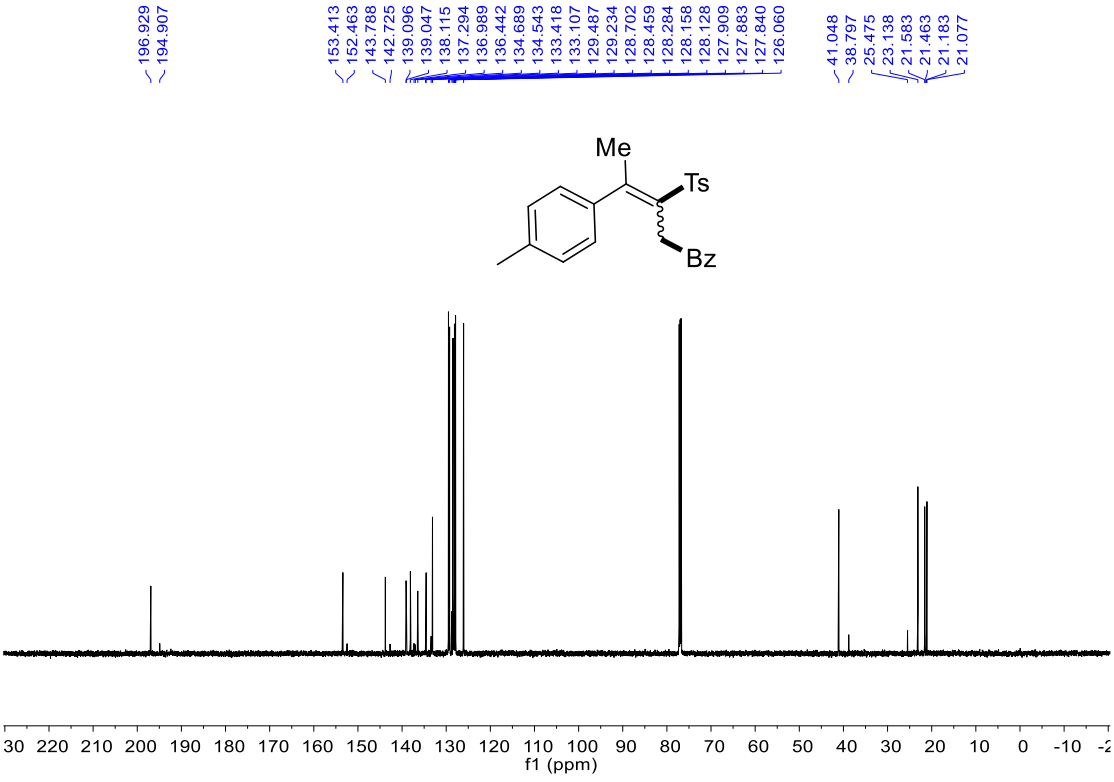
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **11**



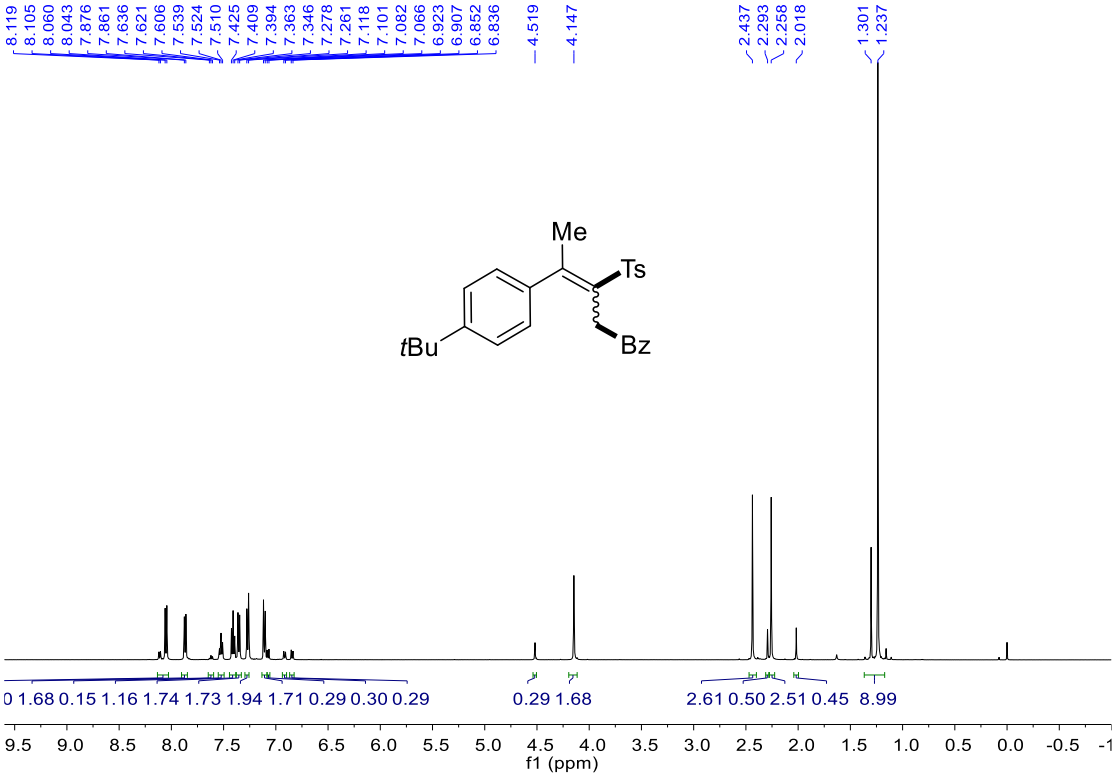
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **12**



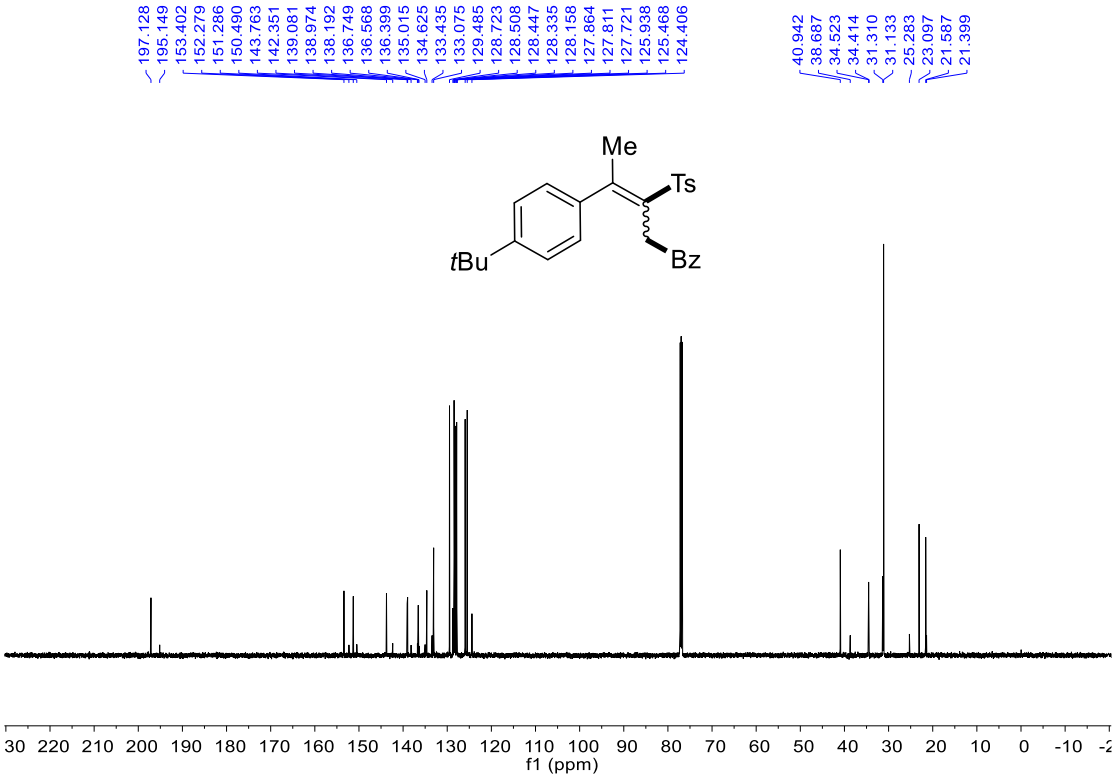
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **12**



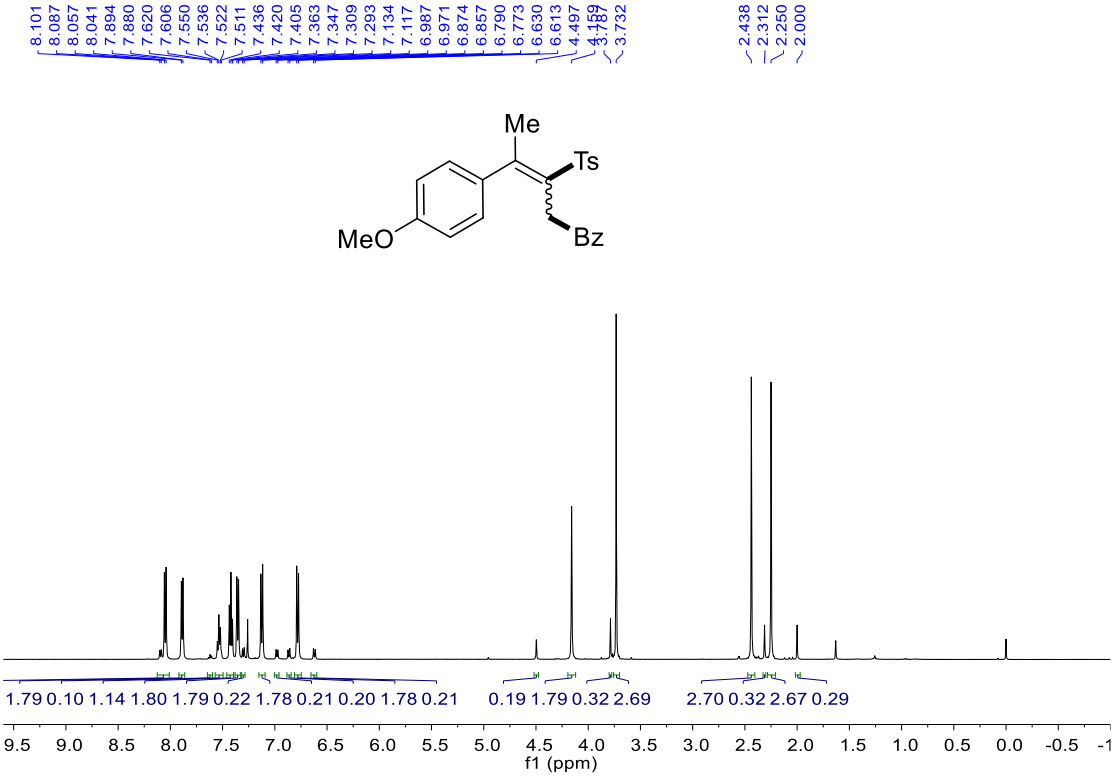
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **13**



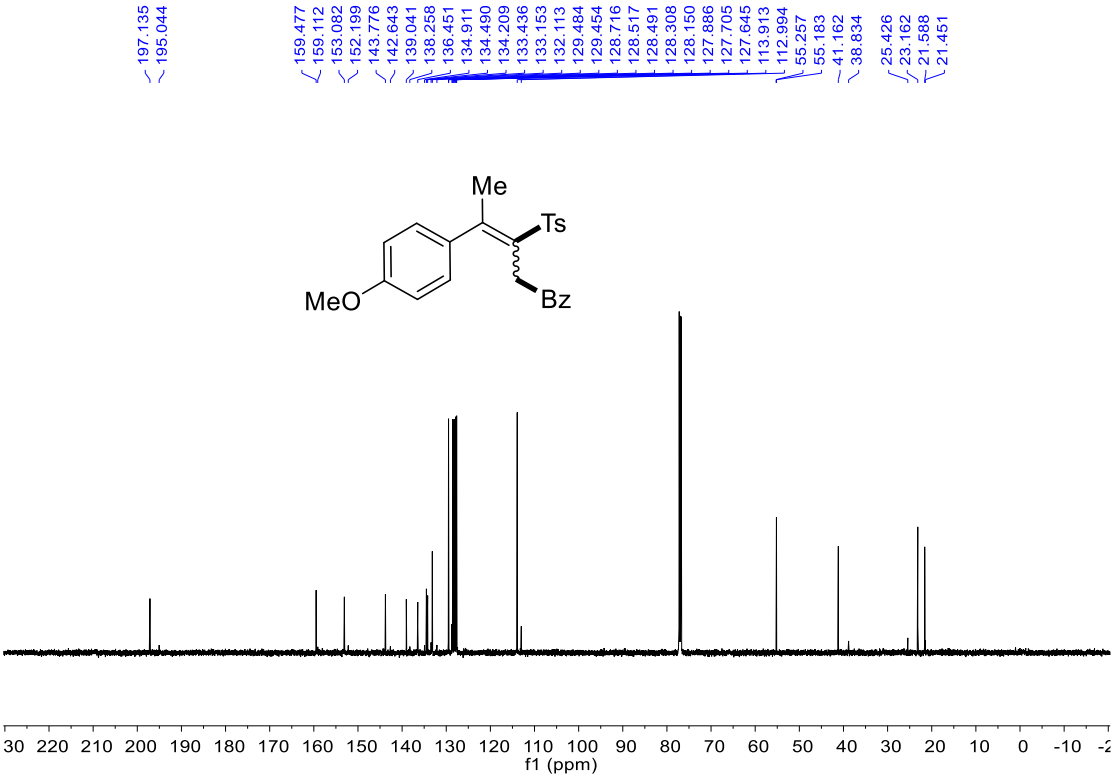
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **13**



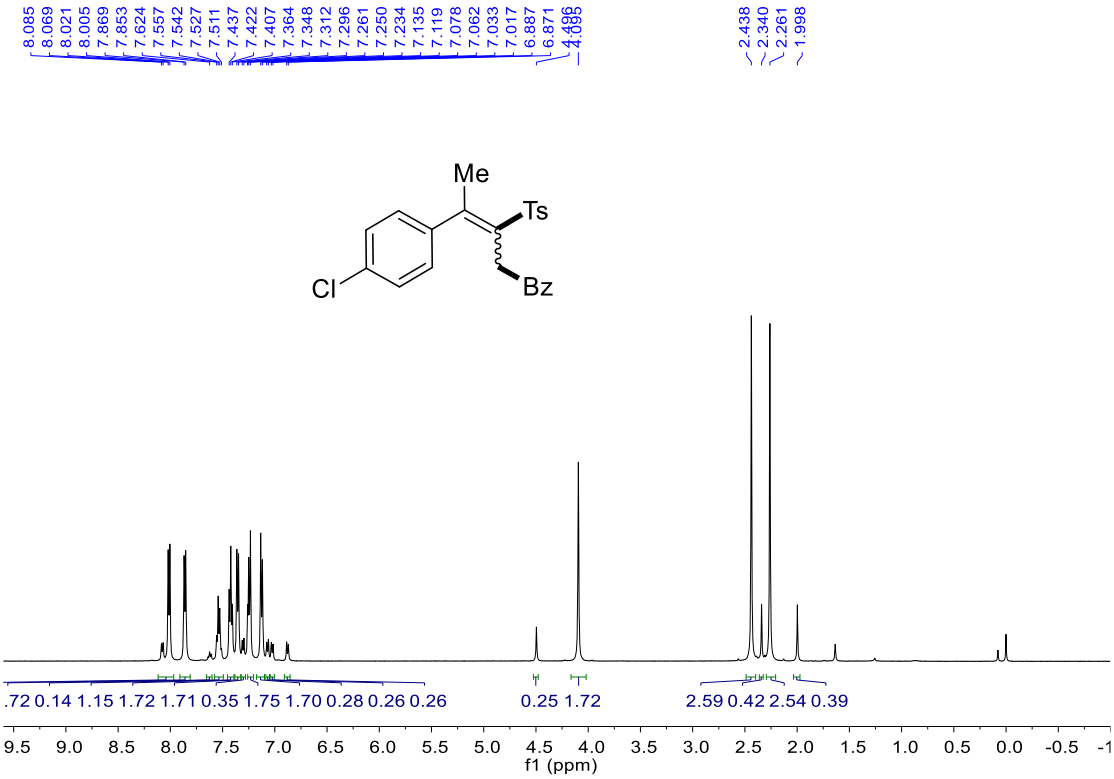
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **14**



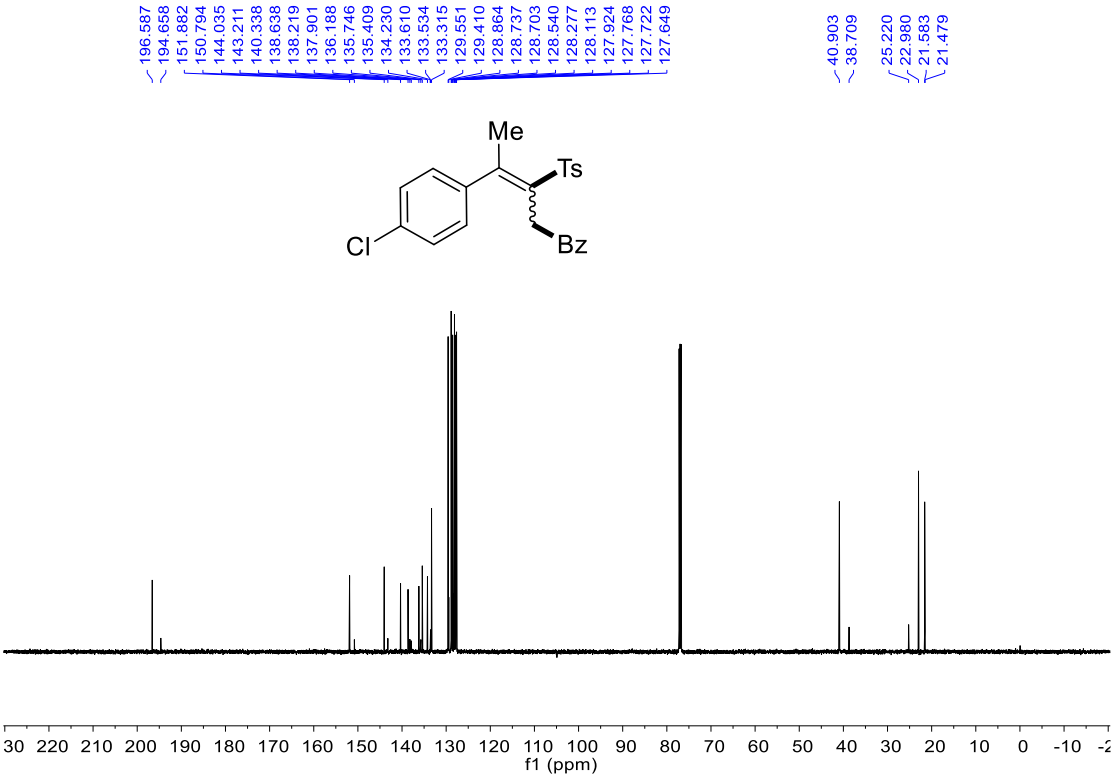
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **14**



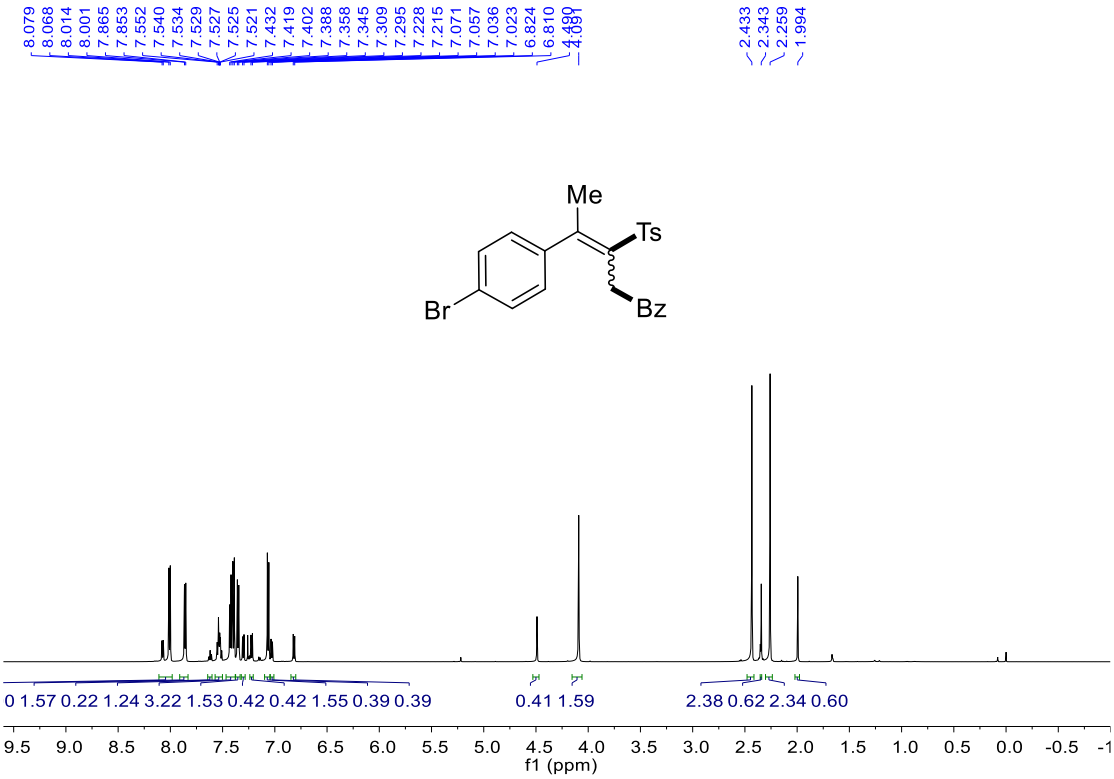
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **15**



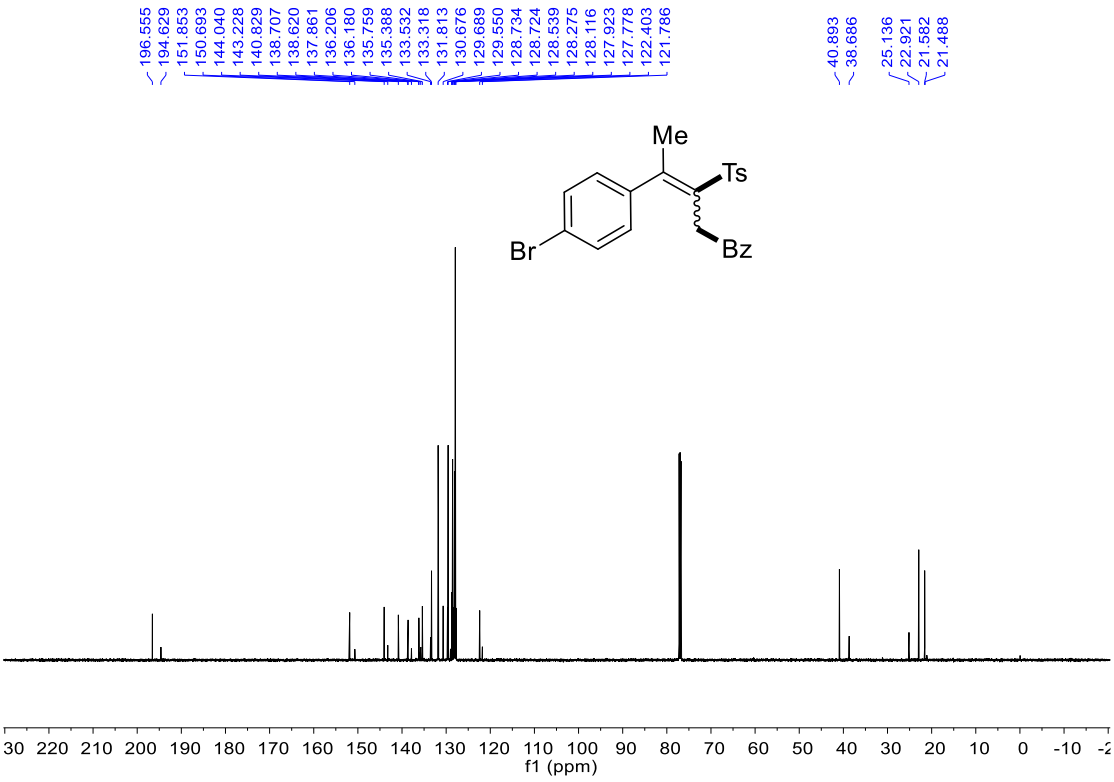
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **15**



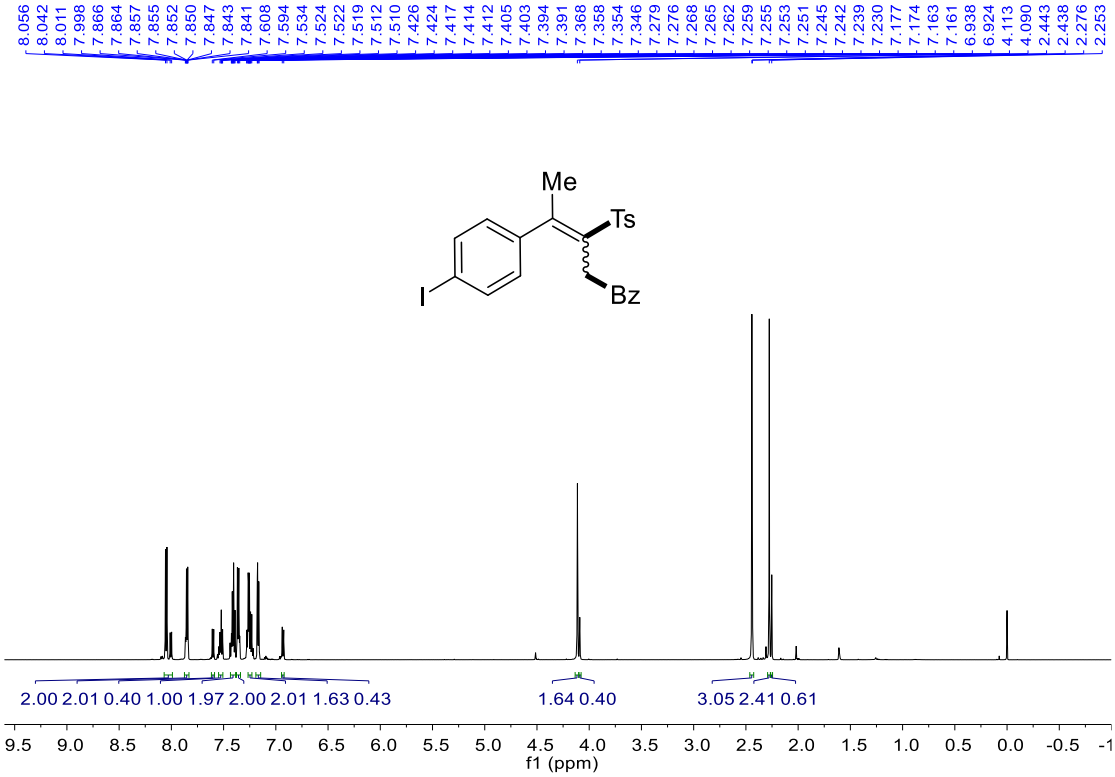
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **16**



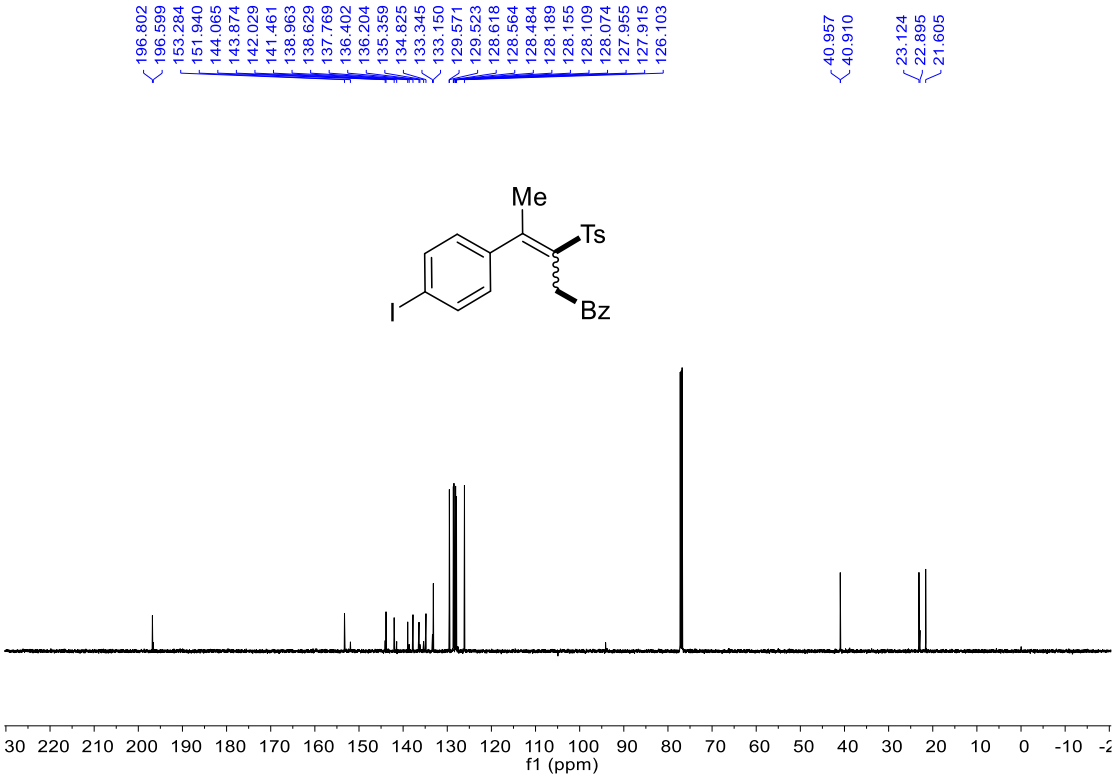
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **16**



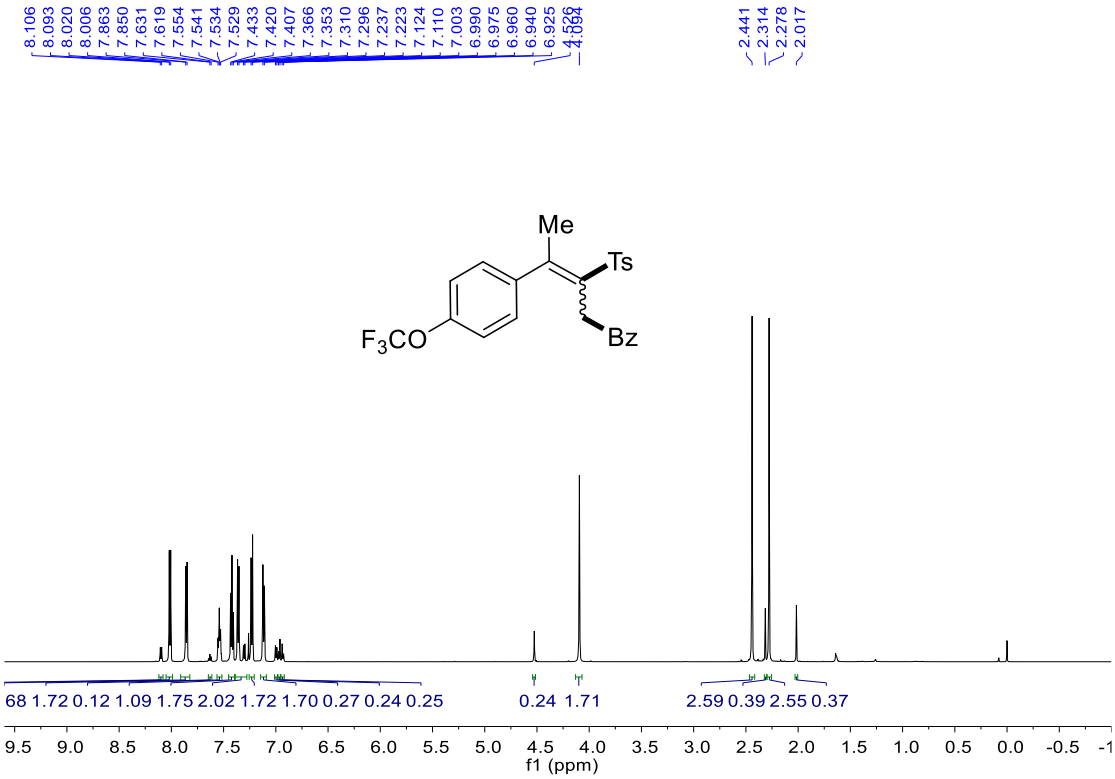
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **17**



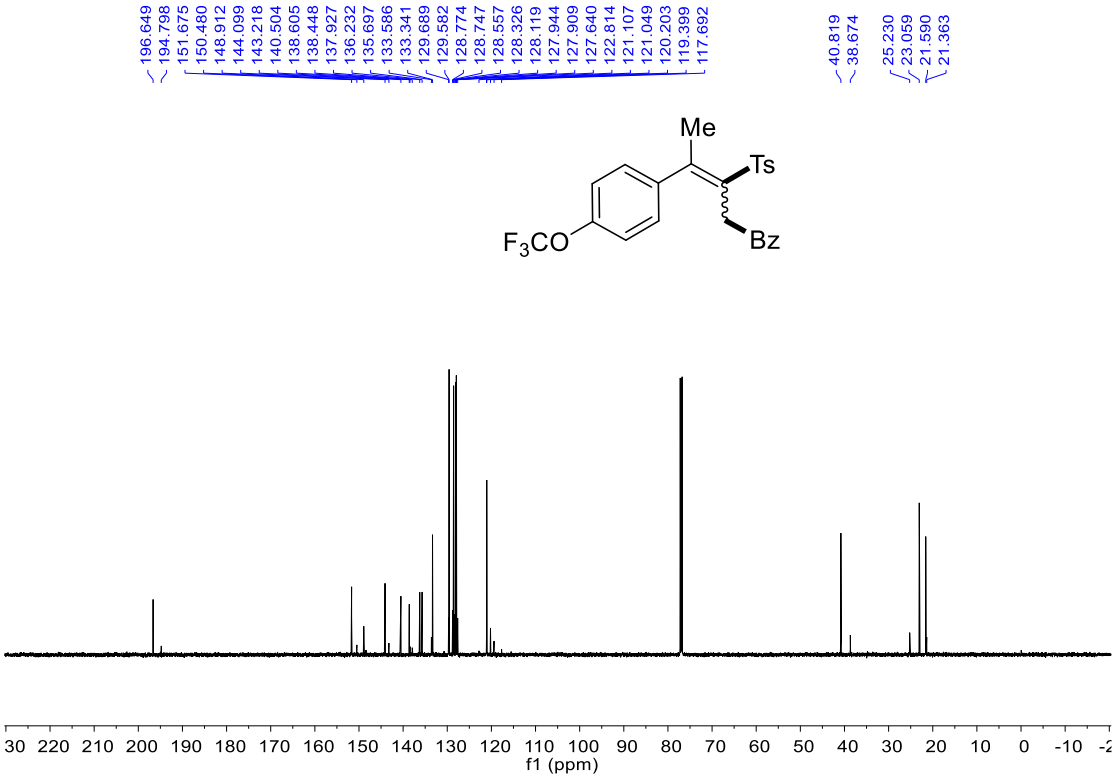
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **17**



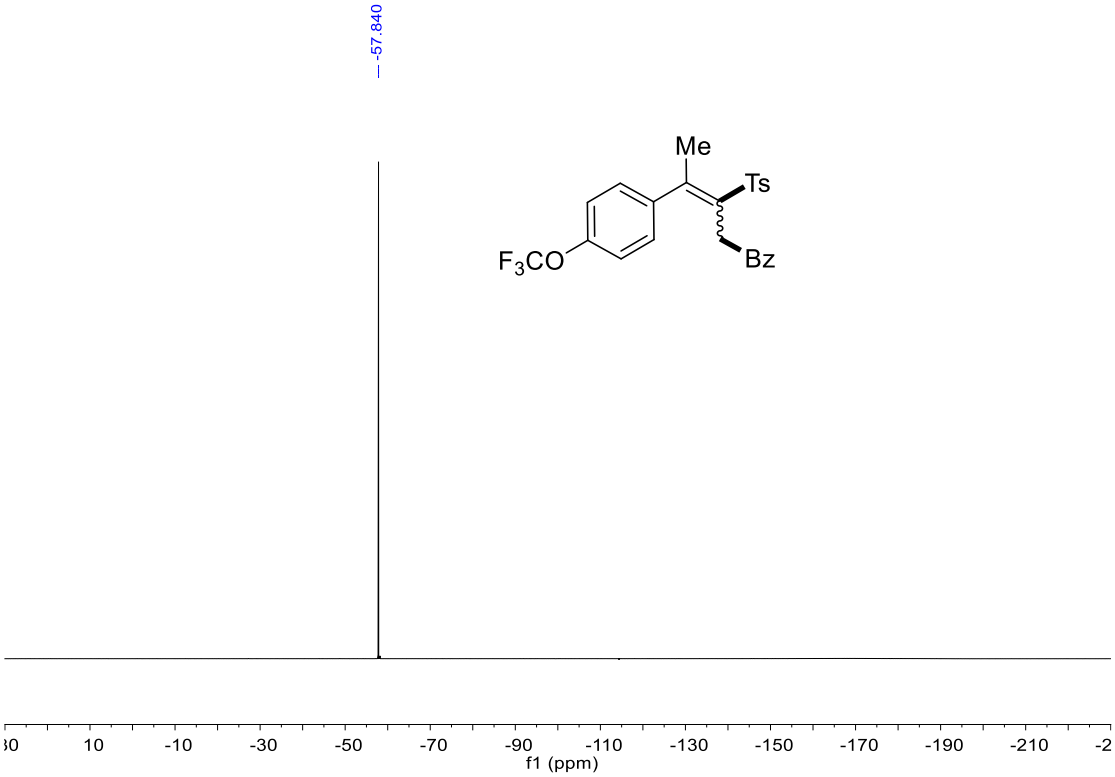
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **18**



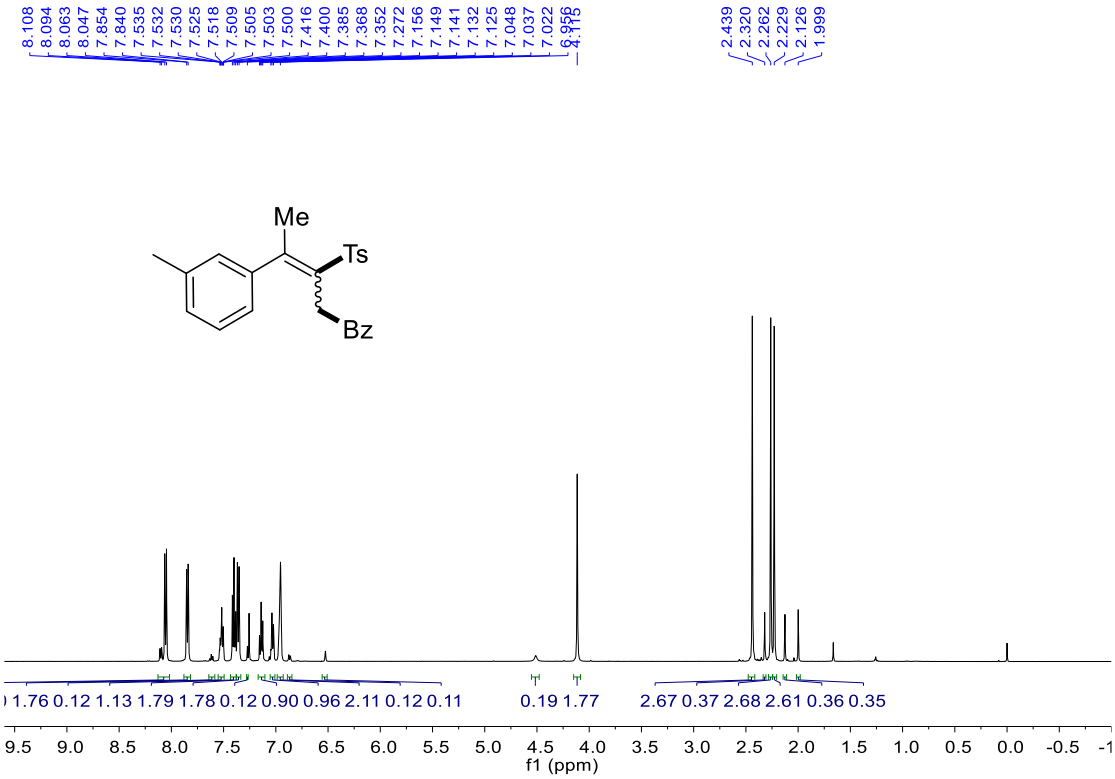
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **18**



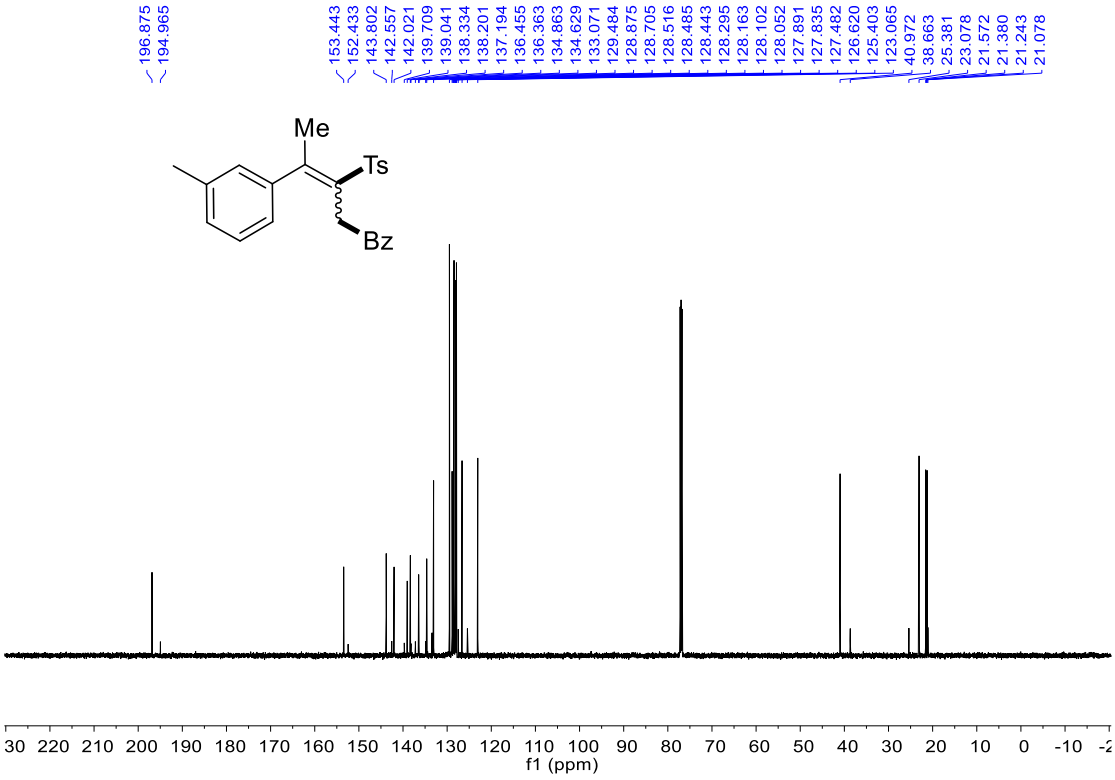
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **18**



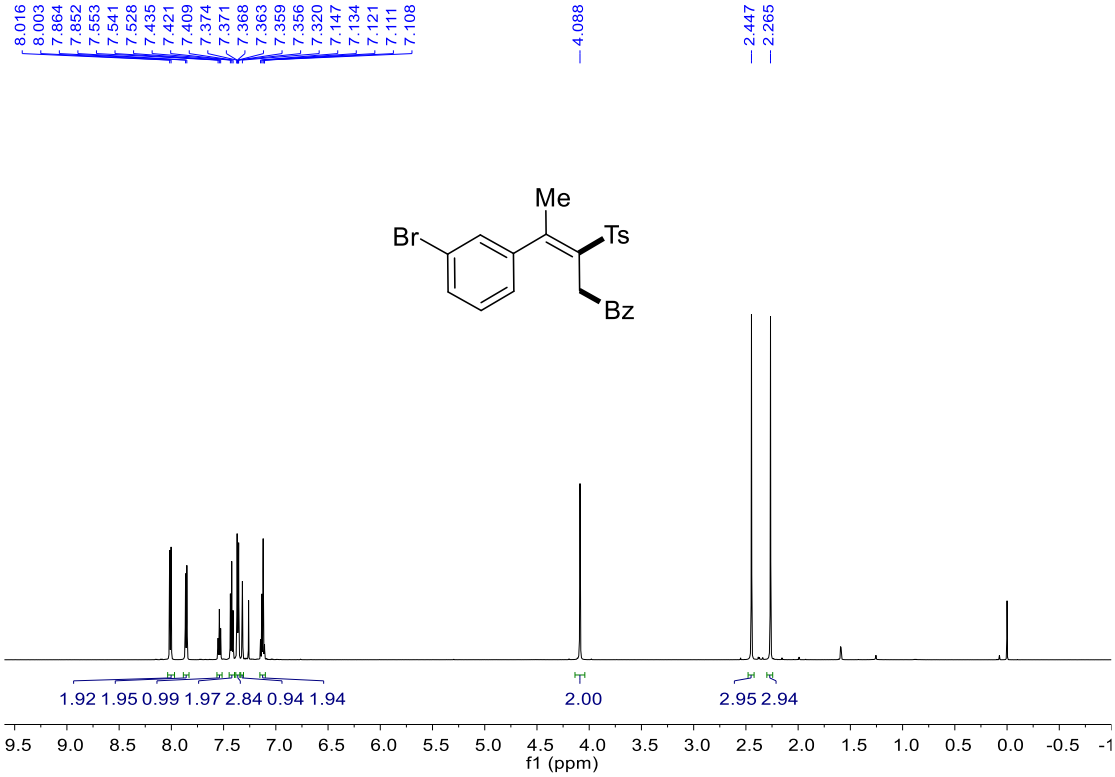
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **19**



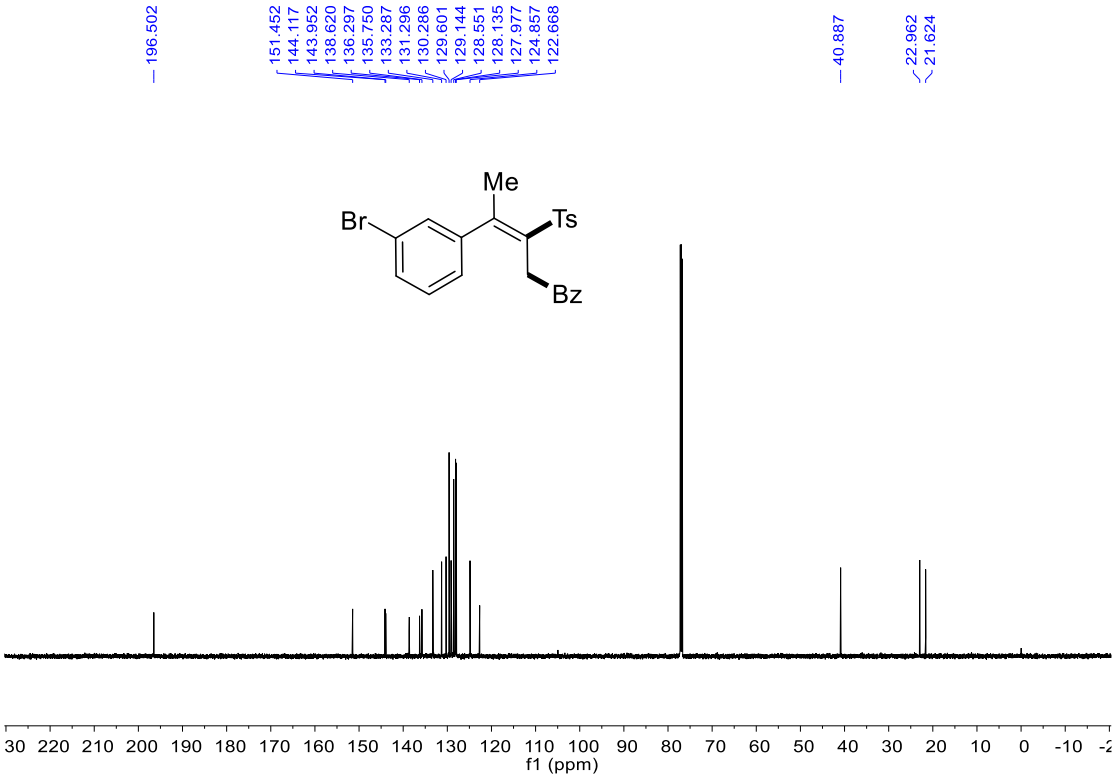
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **19**



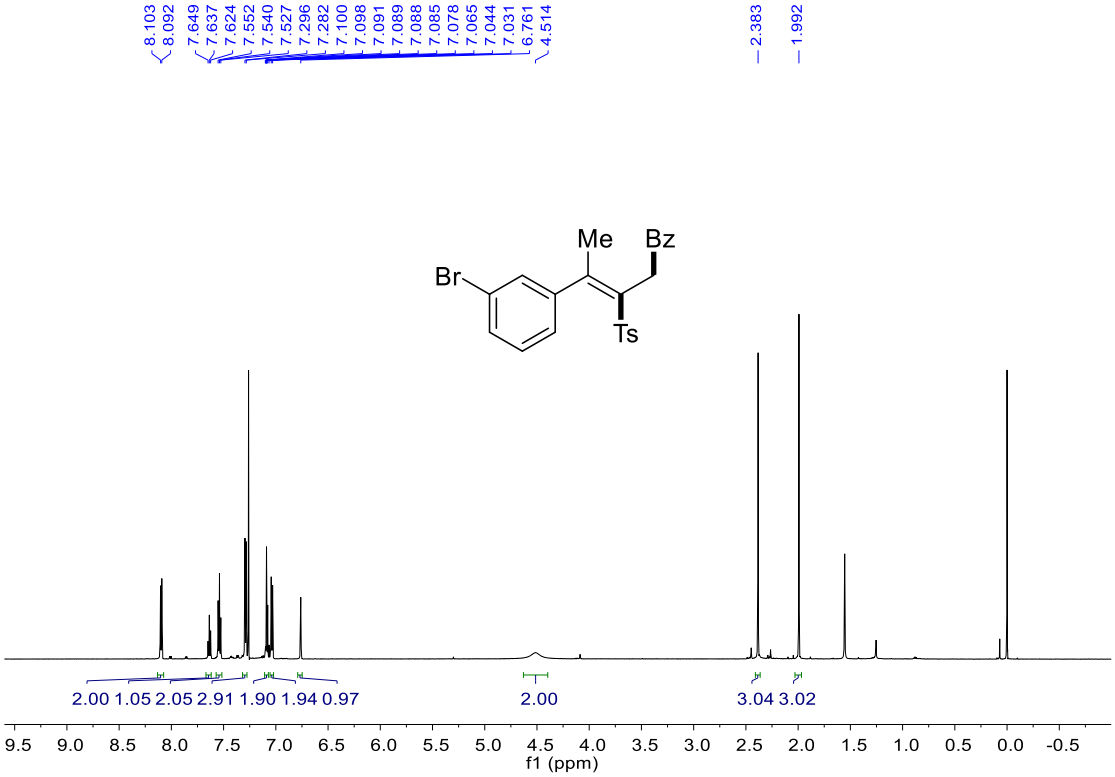
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **20**



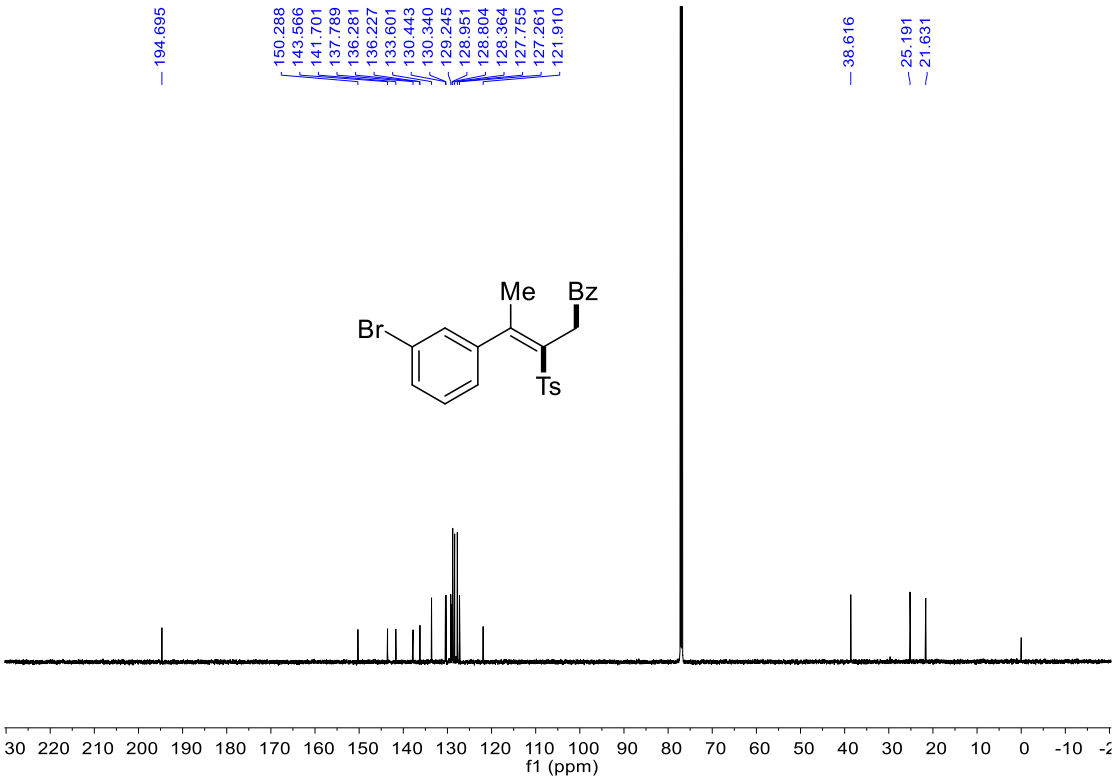
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **20**



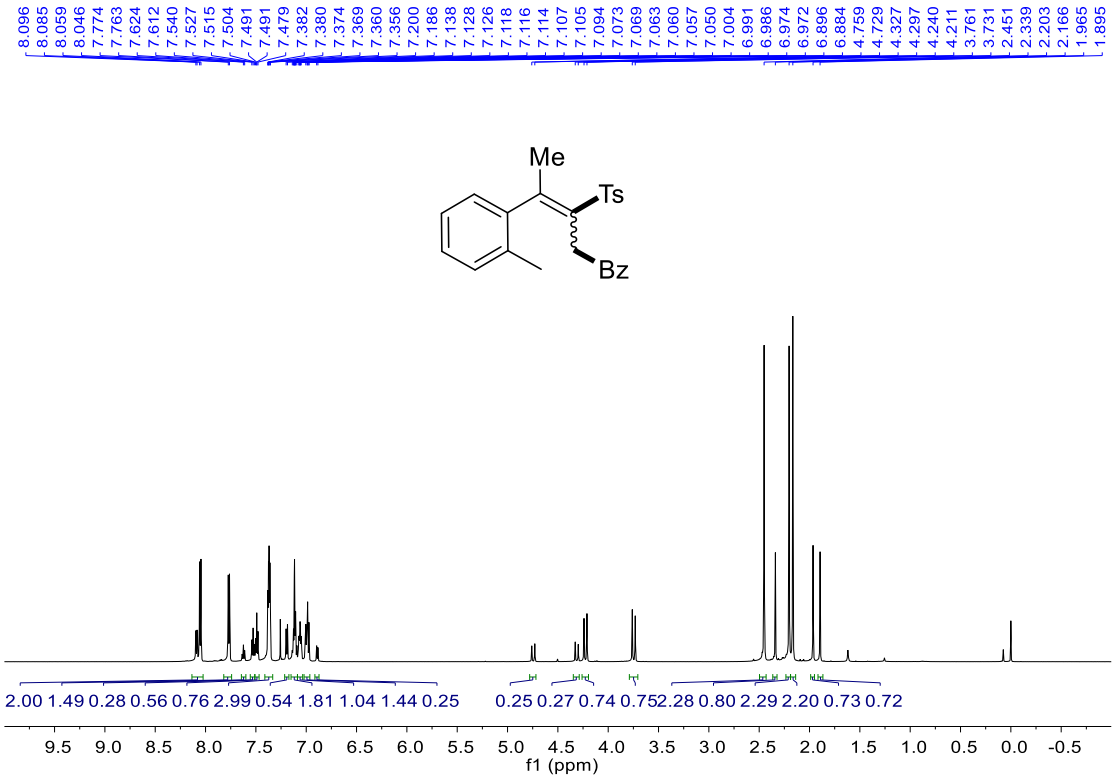
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **20'**



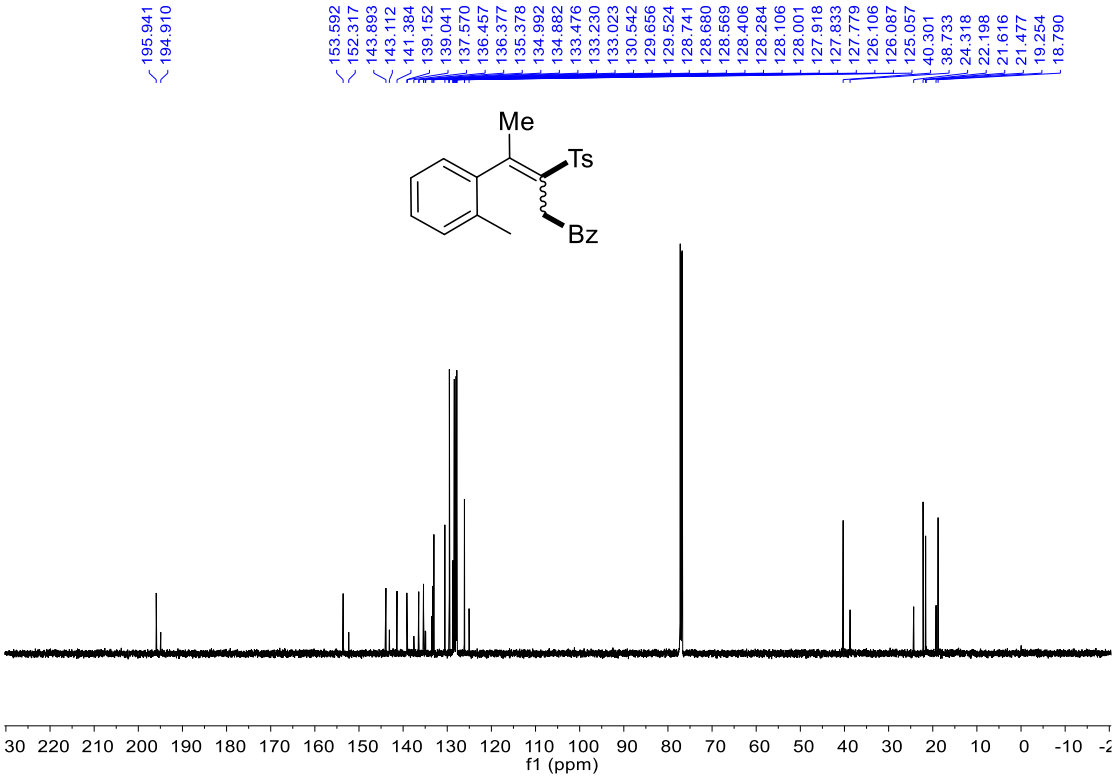
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **20'**



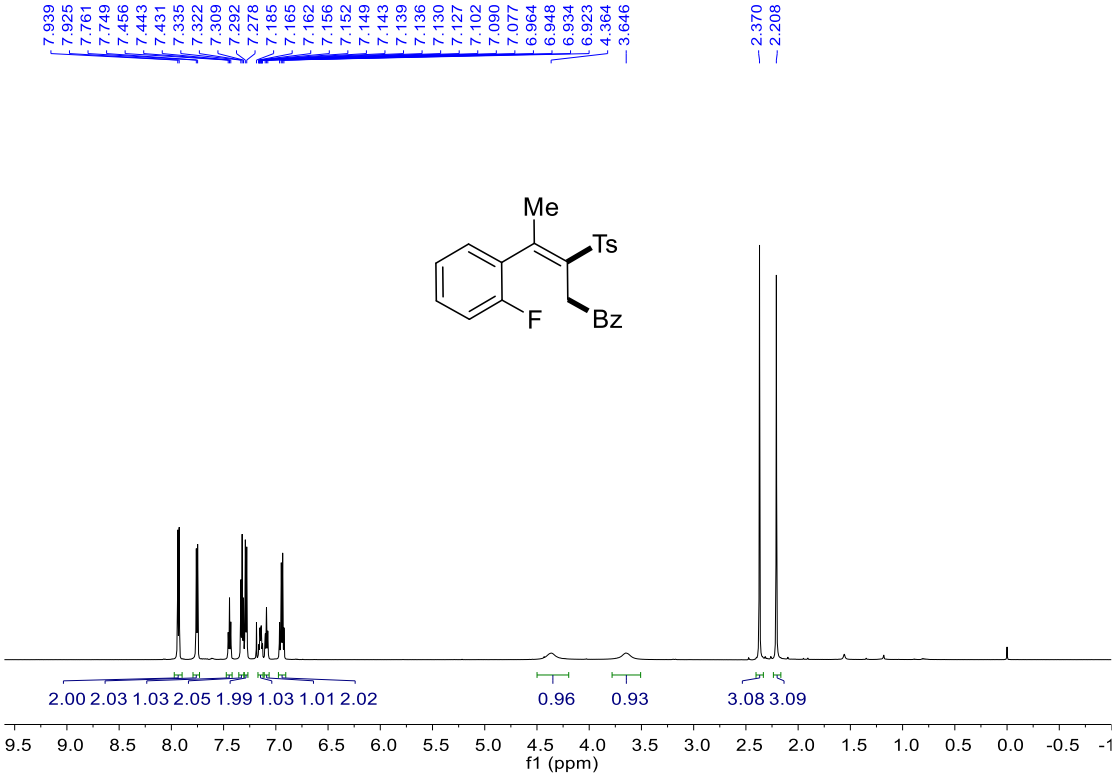
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **21**



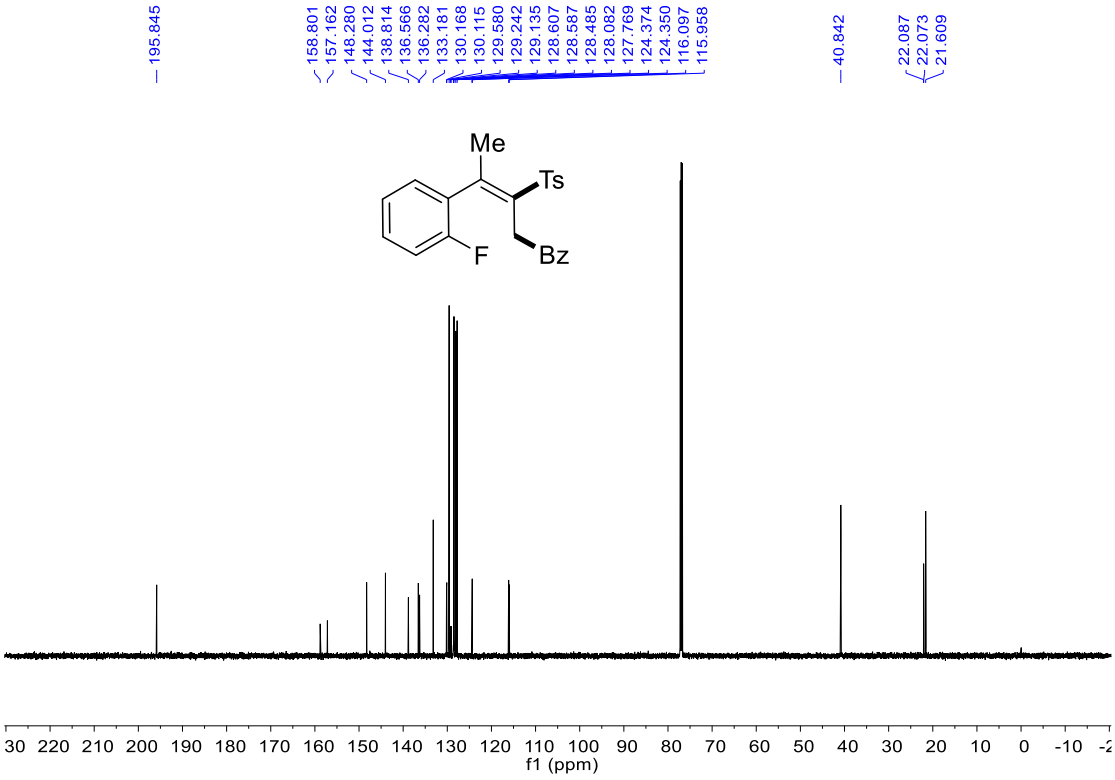
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **21**



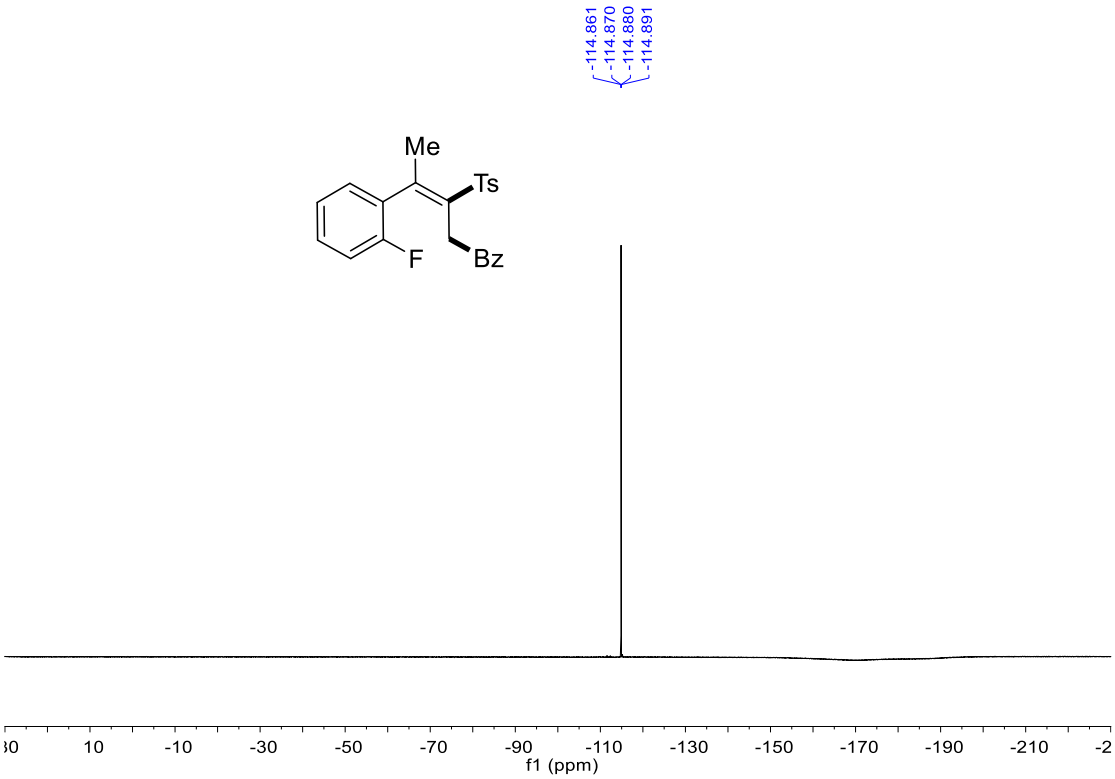
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **22**



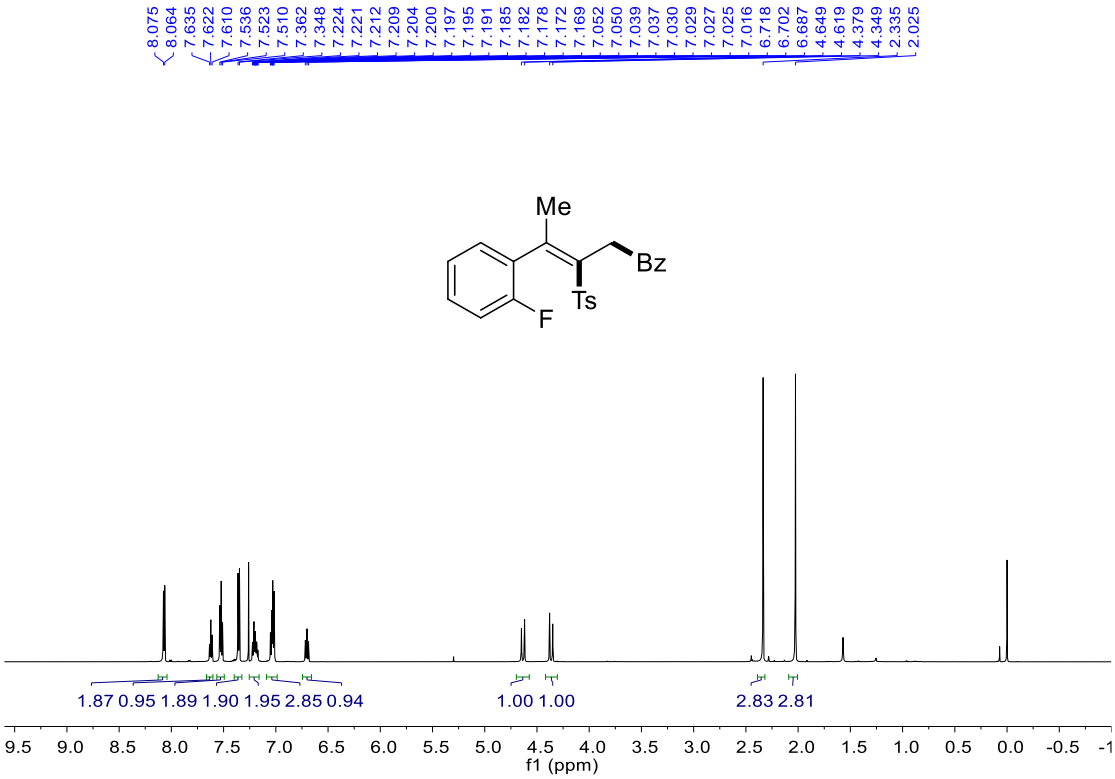
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **22**



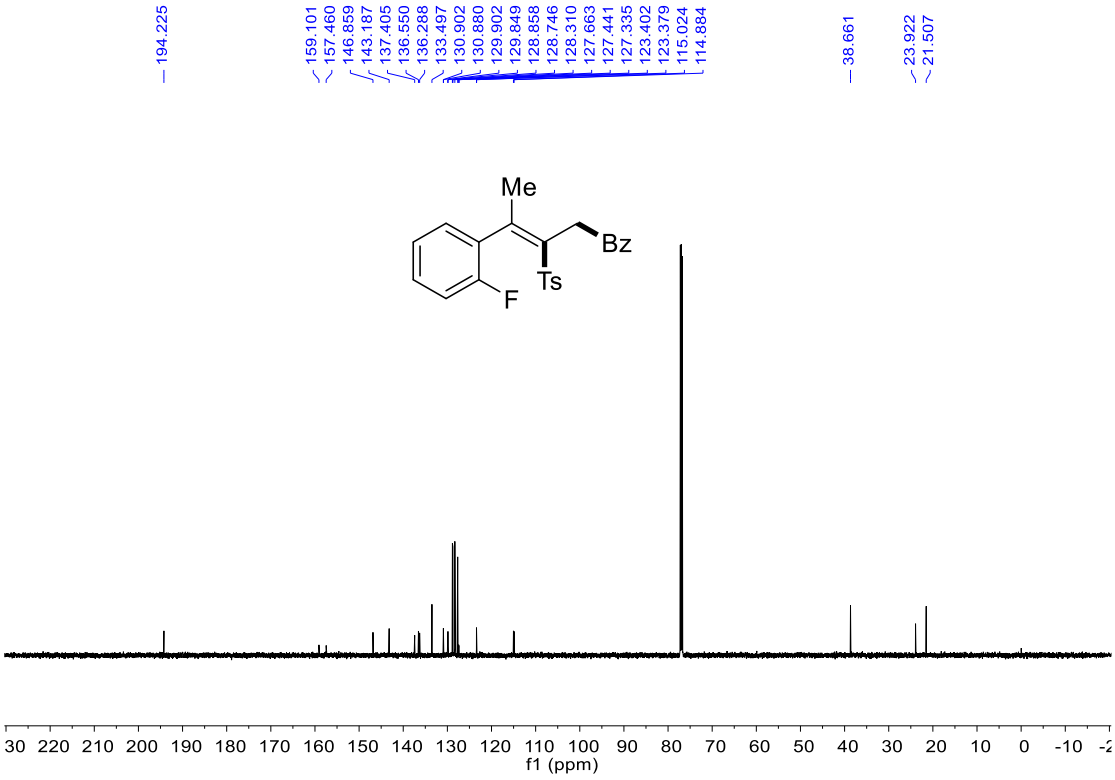
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **22**



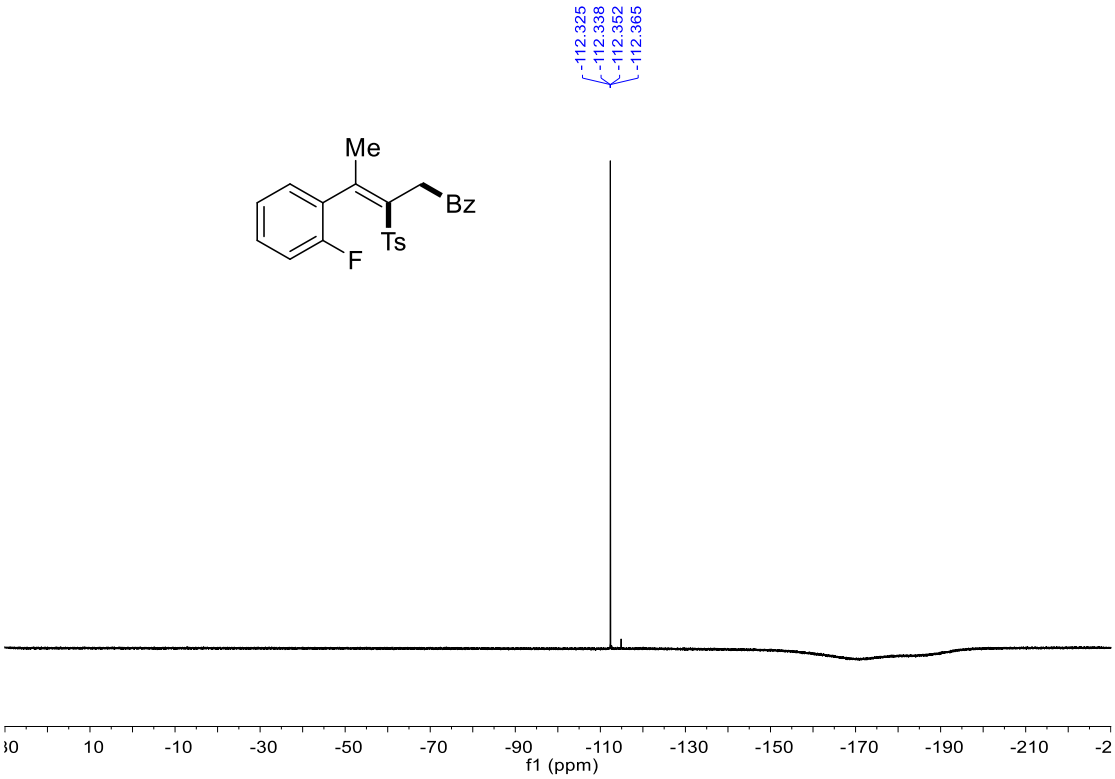
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **22'**



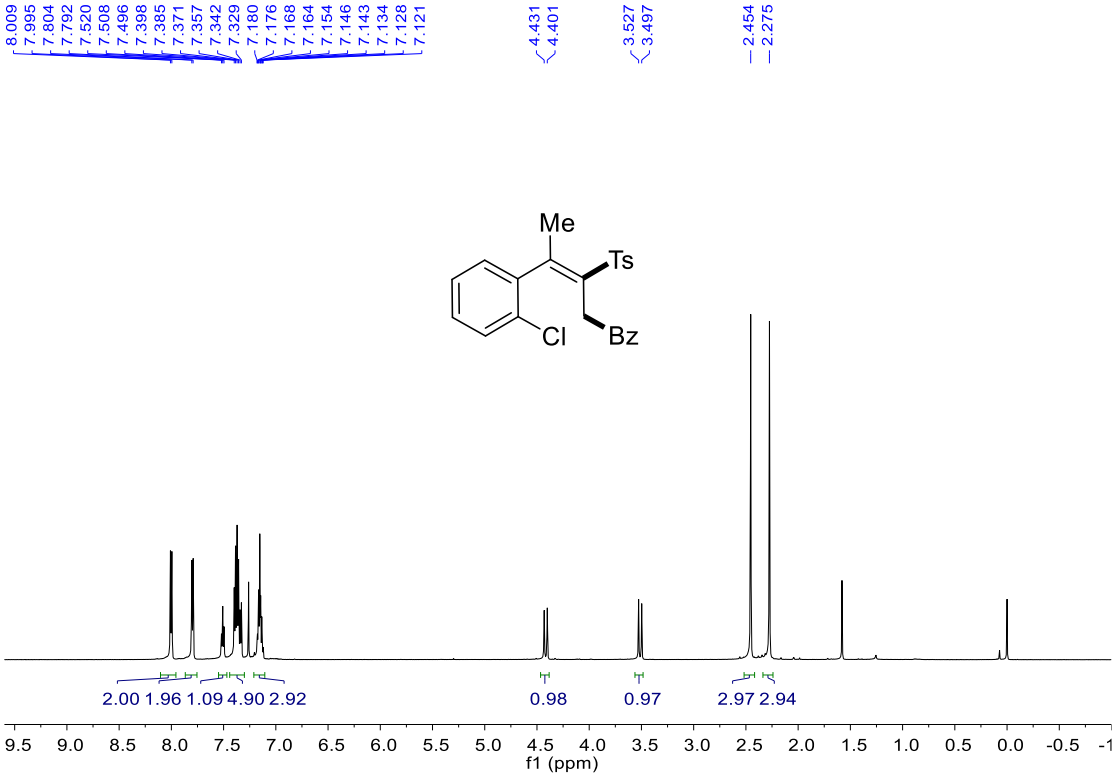
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **22'**



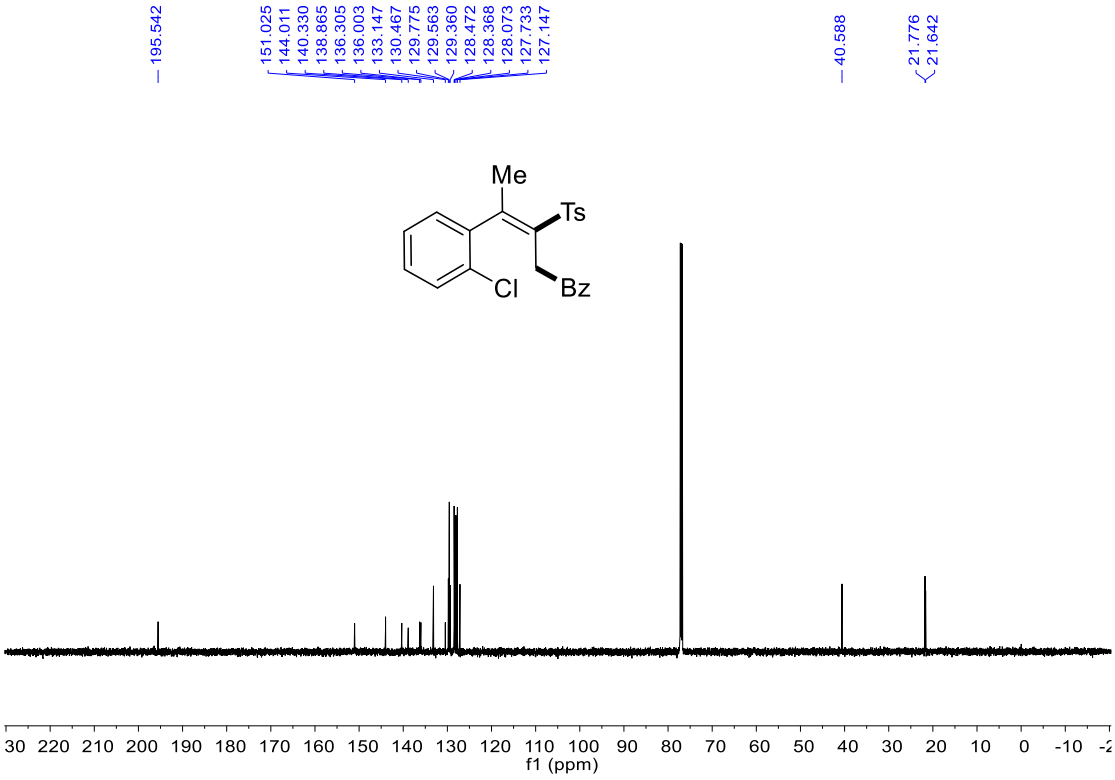
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **22'**



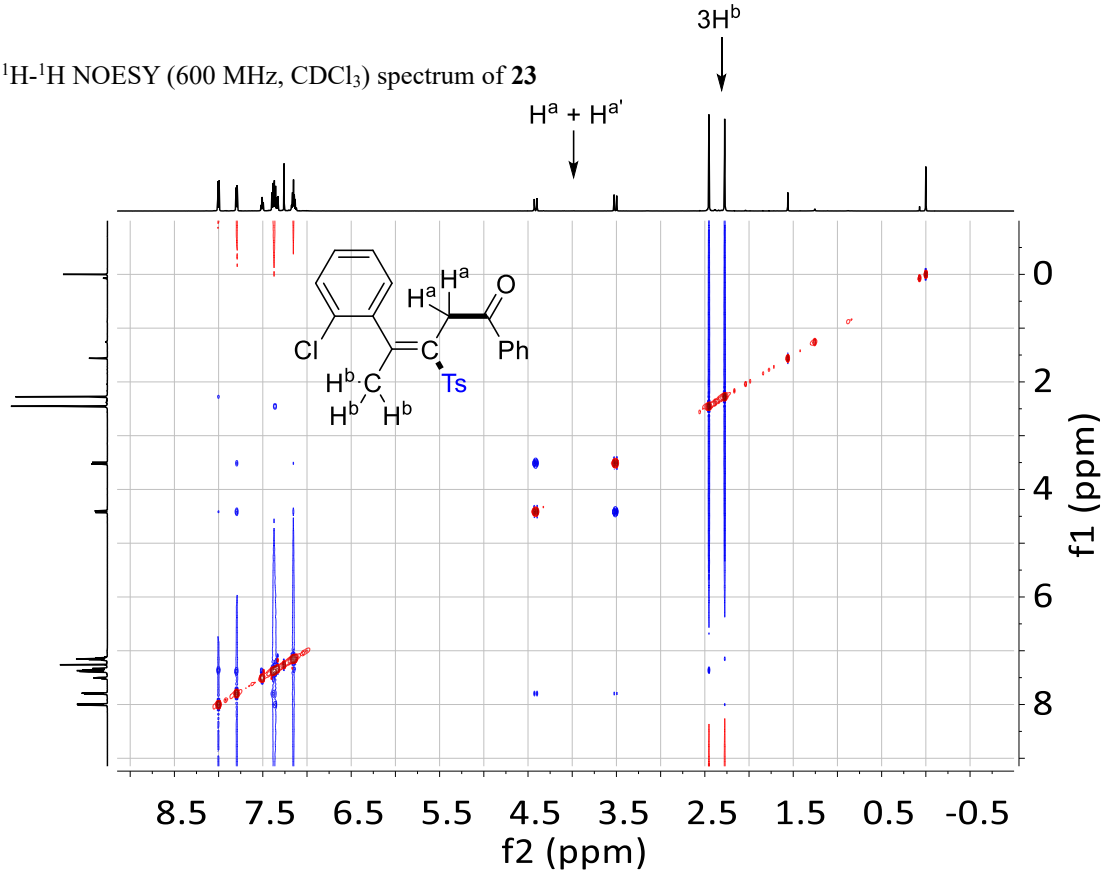
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **23**



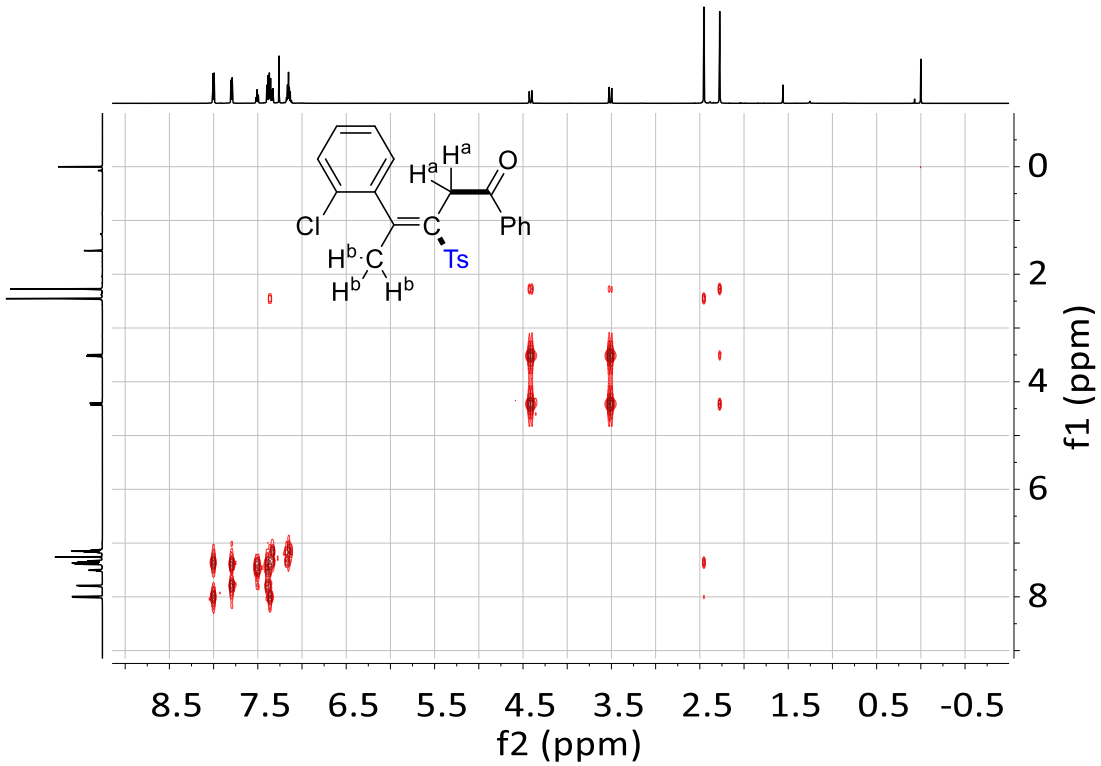
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **23**



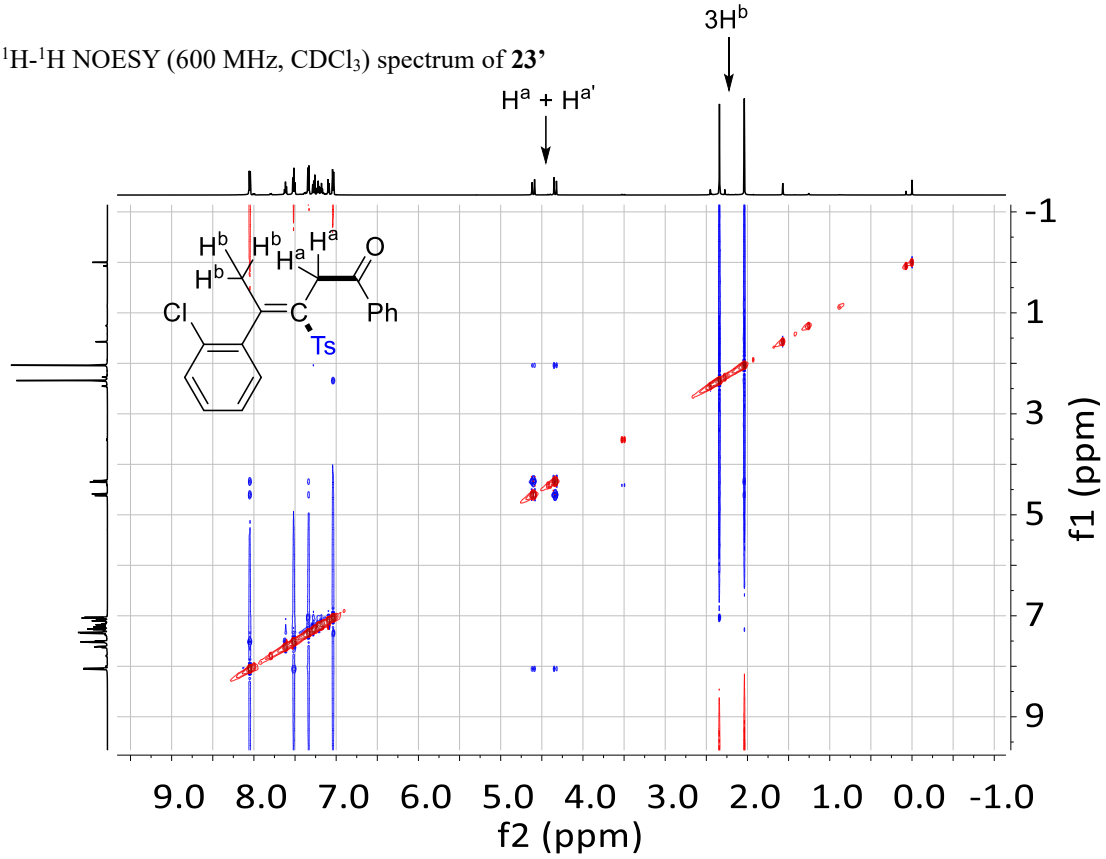
^{1}H-^{1}H NOESY (600 MHz, $CDCl_3$) spectrum of **23**



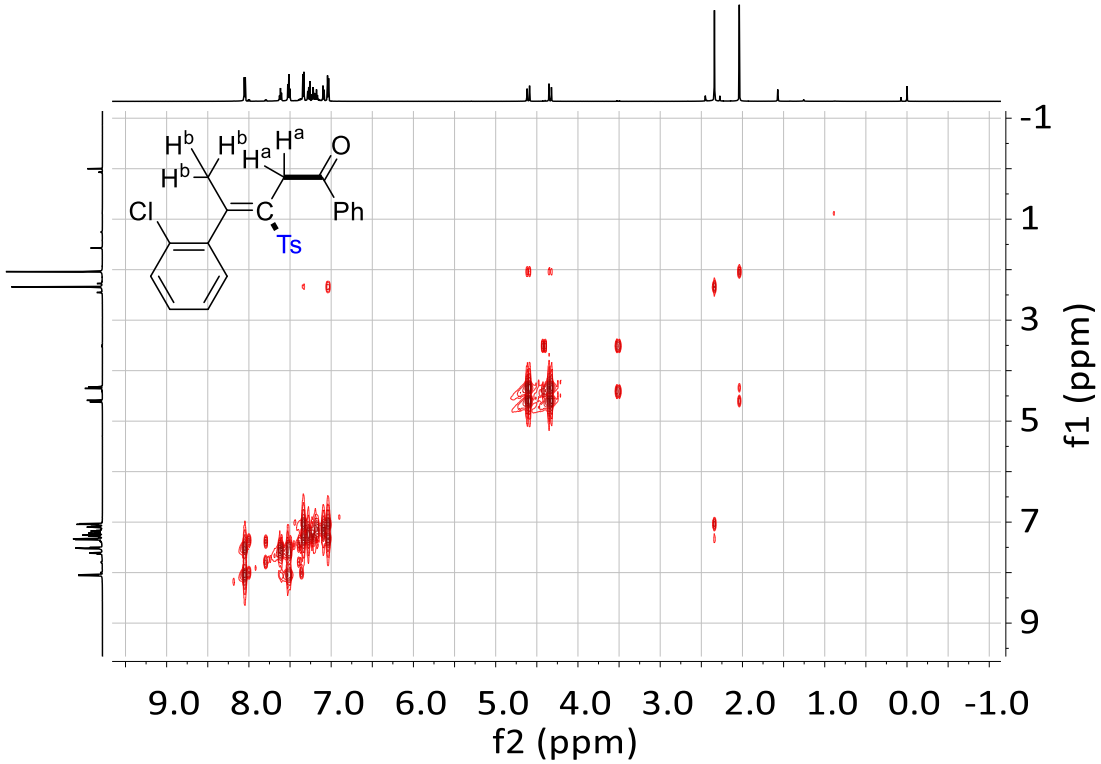
^{1}H-^{1}H COSY NMR (600 MHz, $CDCl_3$) spectrum of **23**



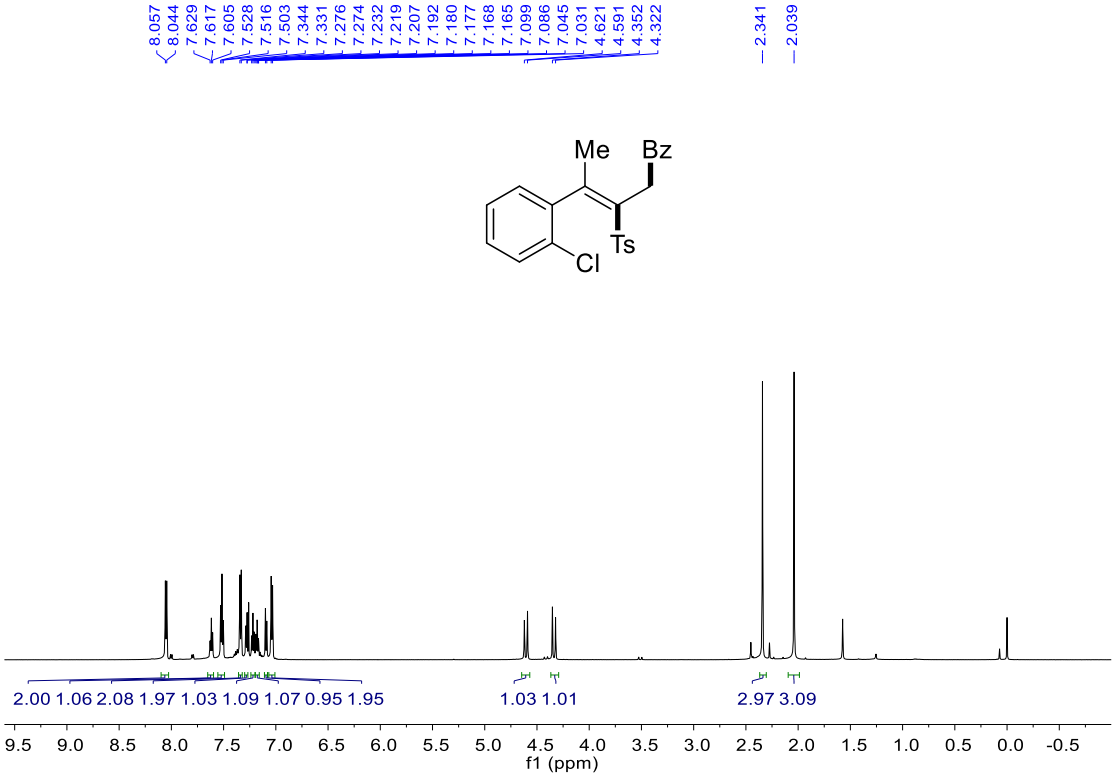
^{1}H-^{1}H NOESY (600 MHz, $CDCl_3$) spectrum of **23'**



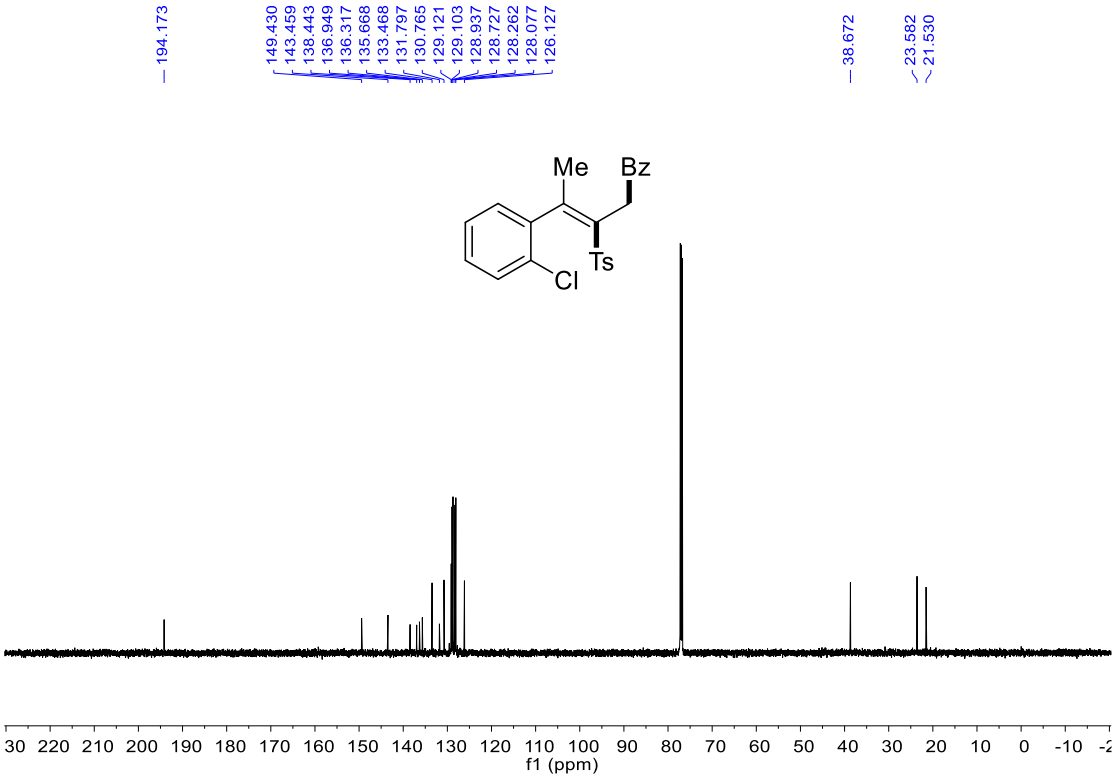
^{1}H-^{1}H COESY (600 MHz, $CDCl_3$) spectrum of **23'**



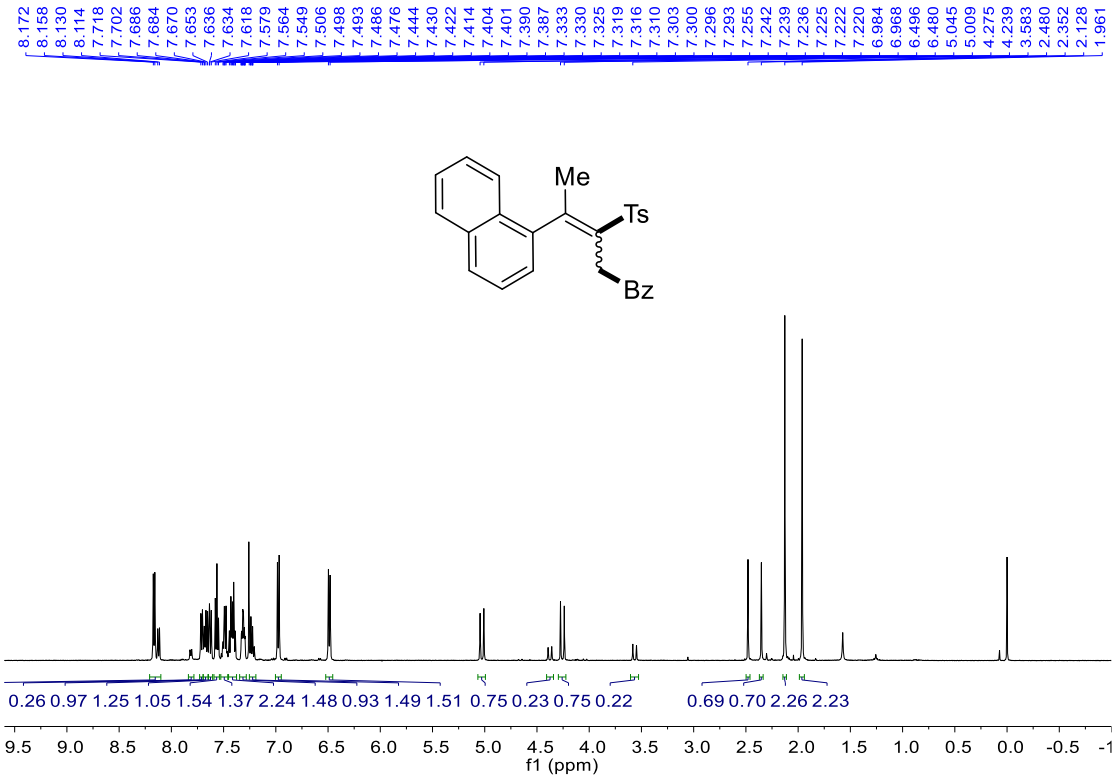
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **23'**



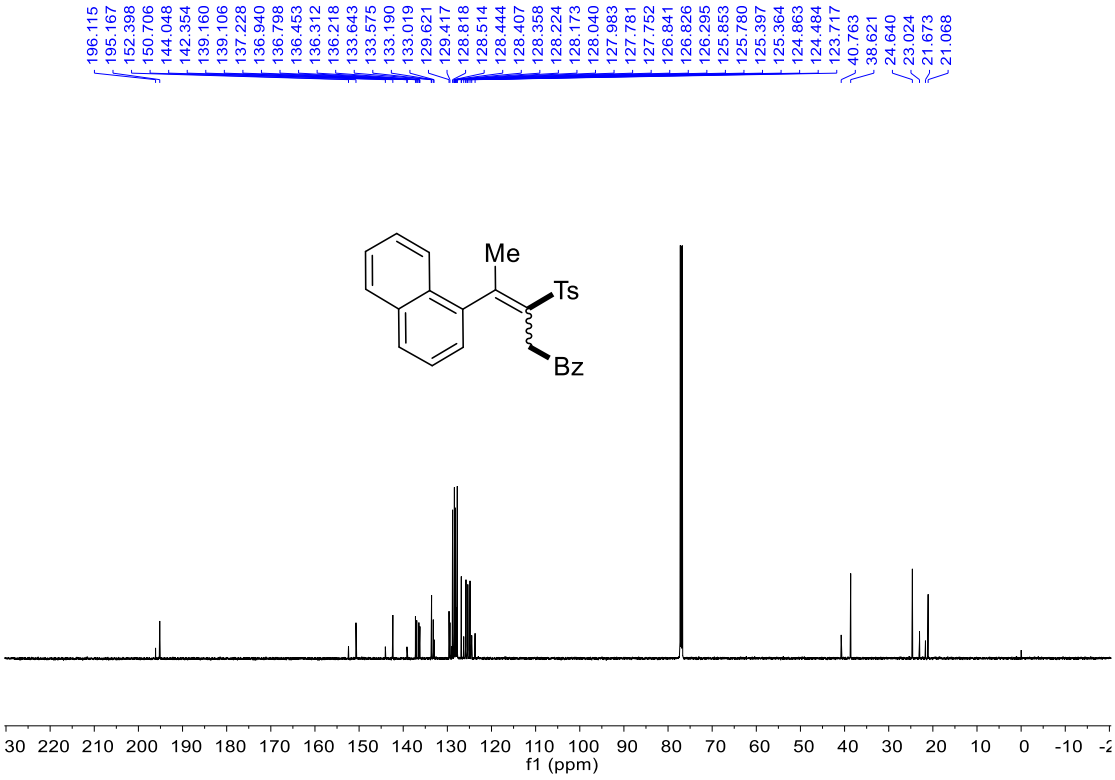
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **23'**



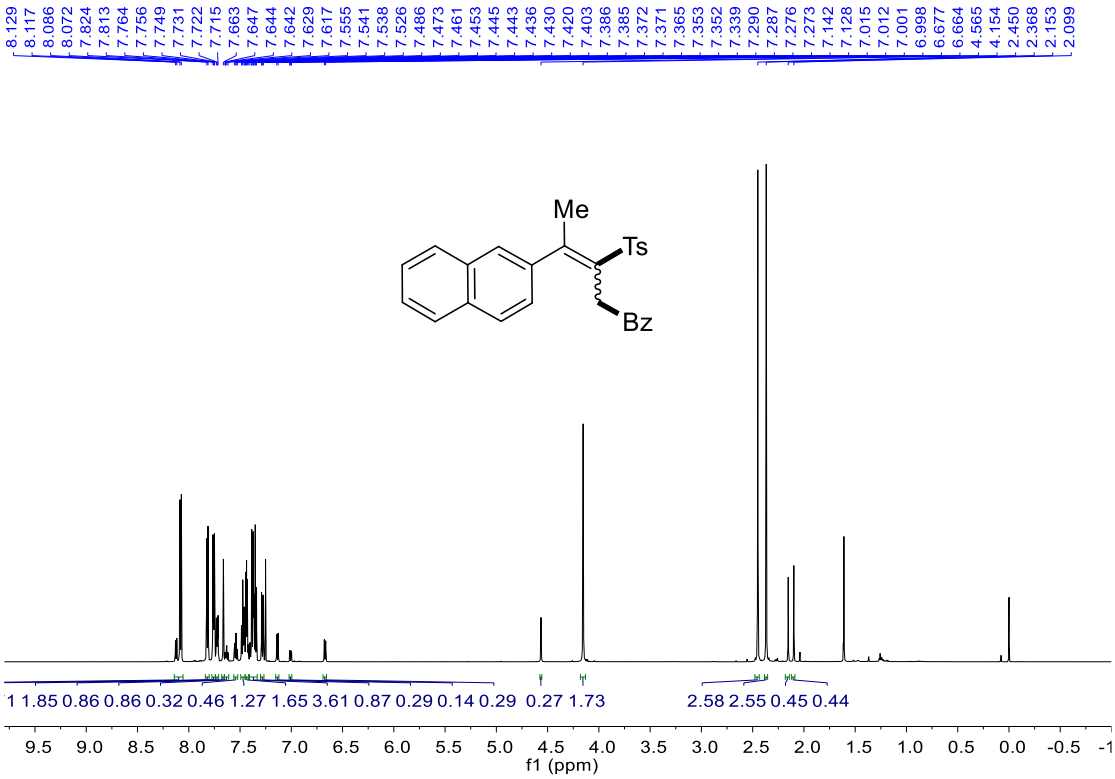
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **24**



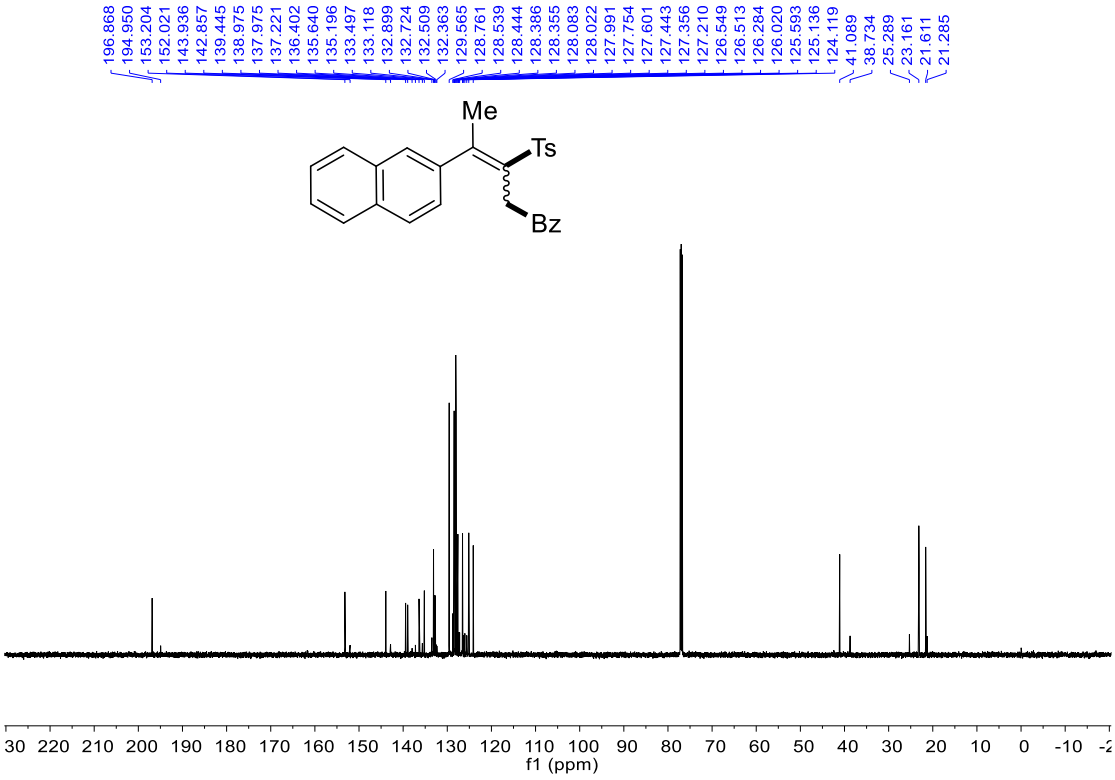
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **24**



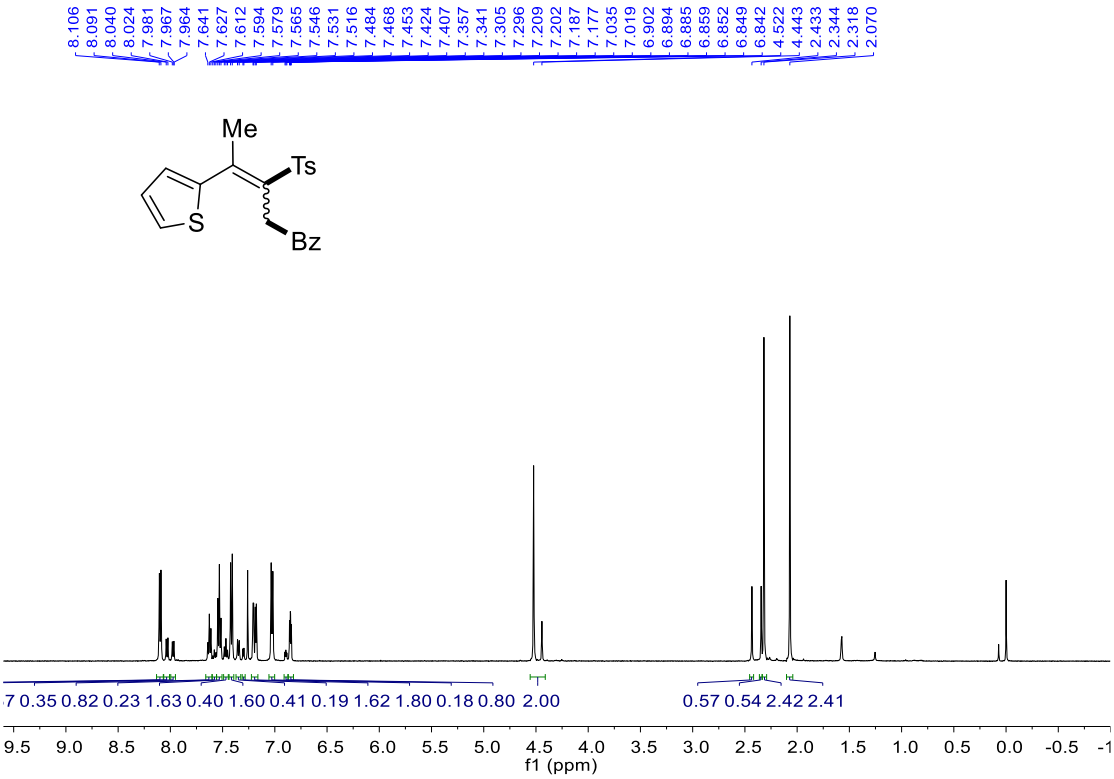
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **25**



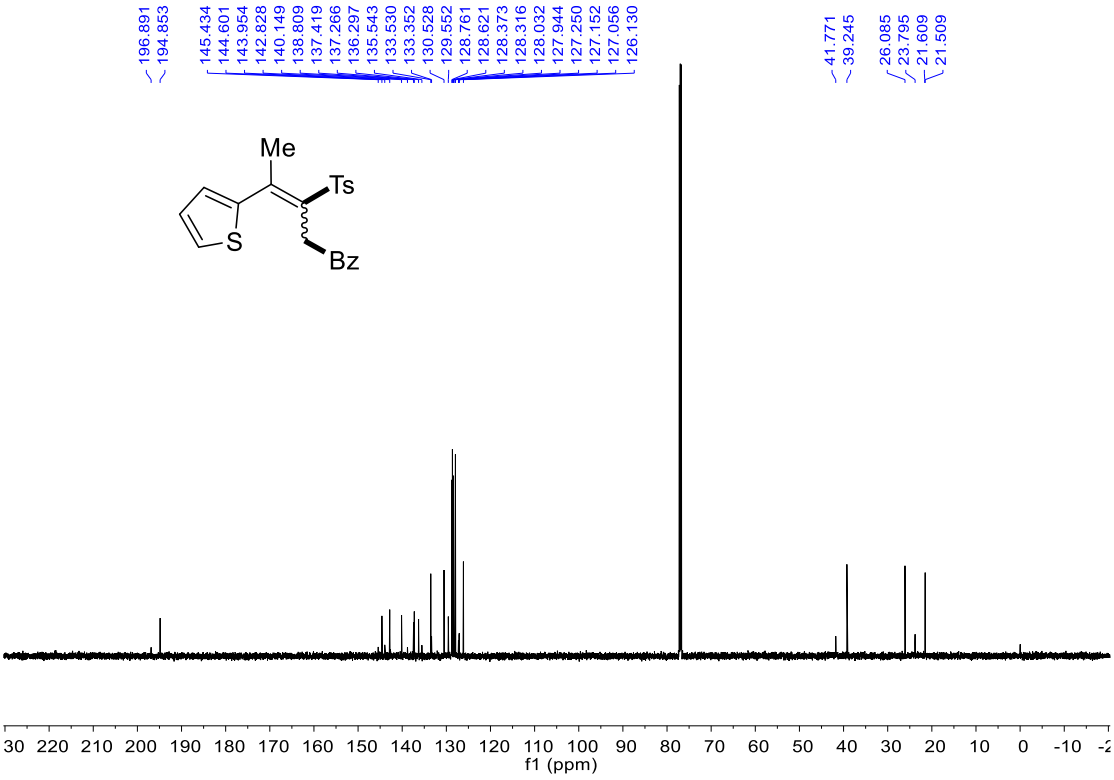
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **25**



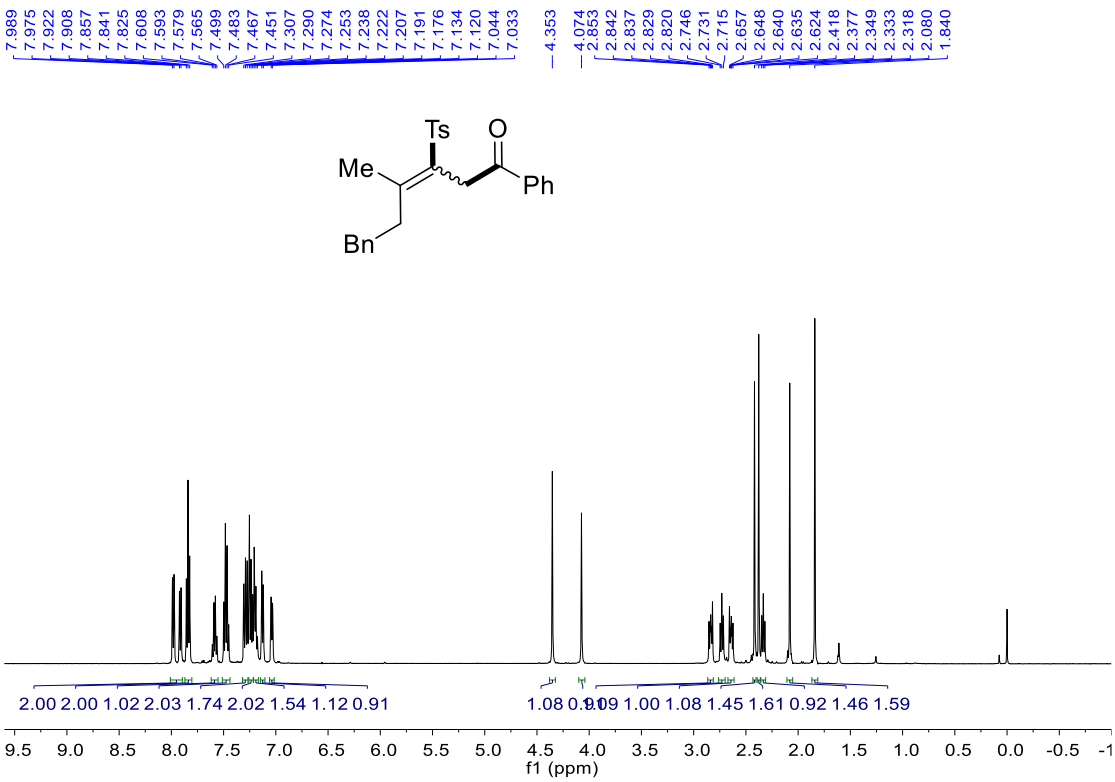
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **26**



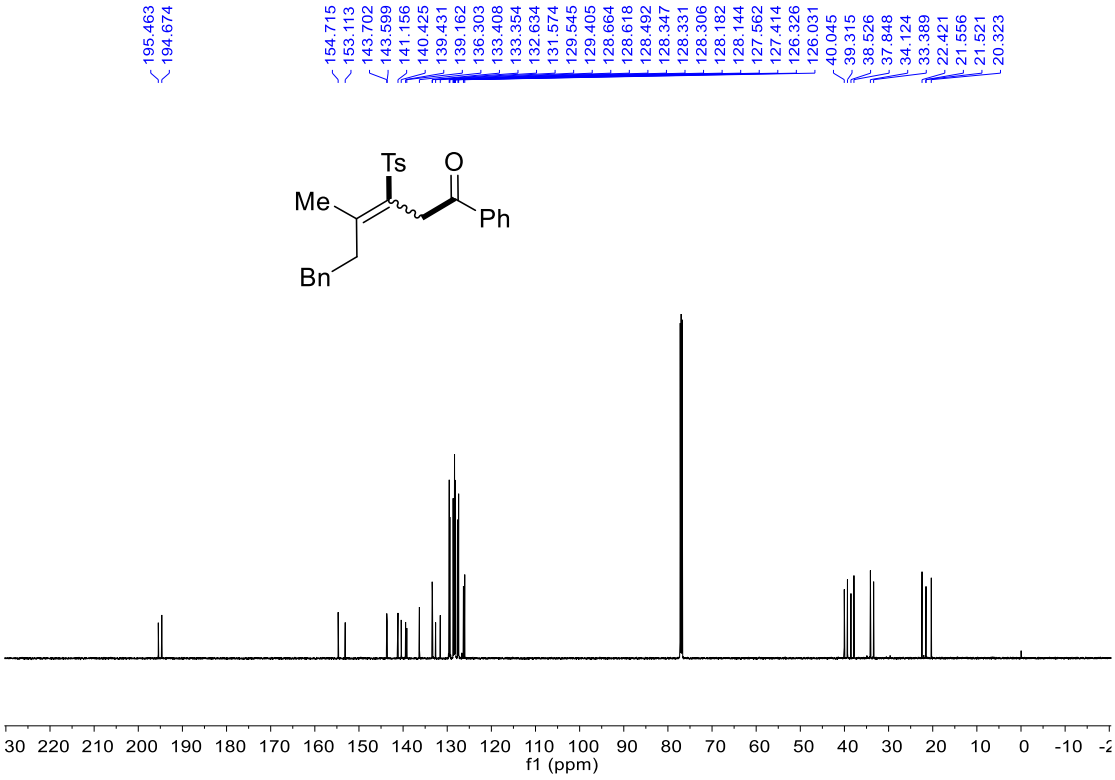
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **26**



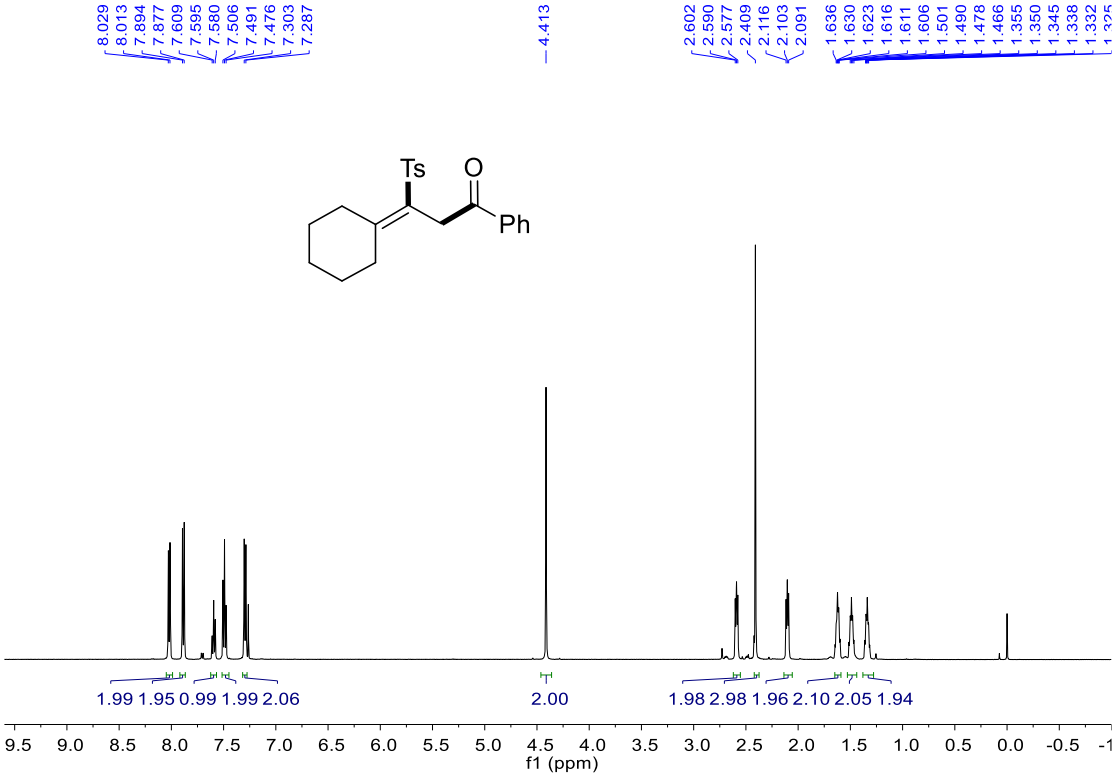
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **27**



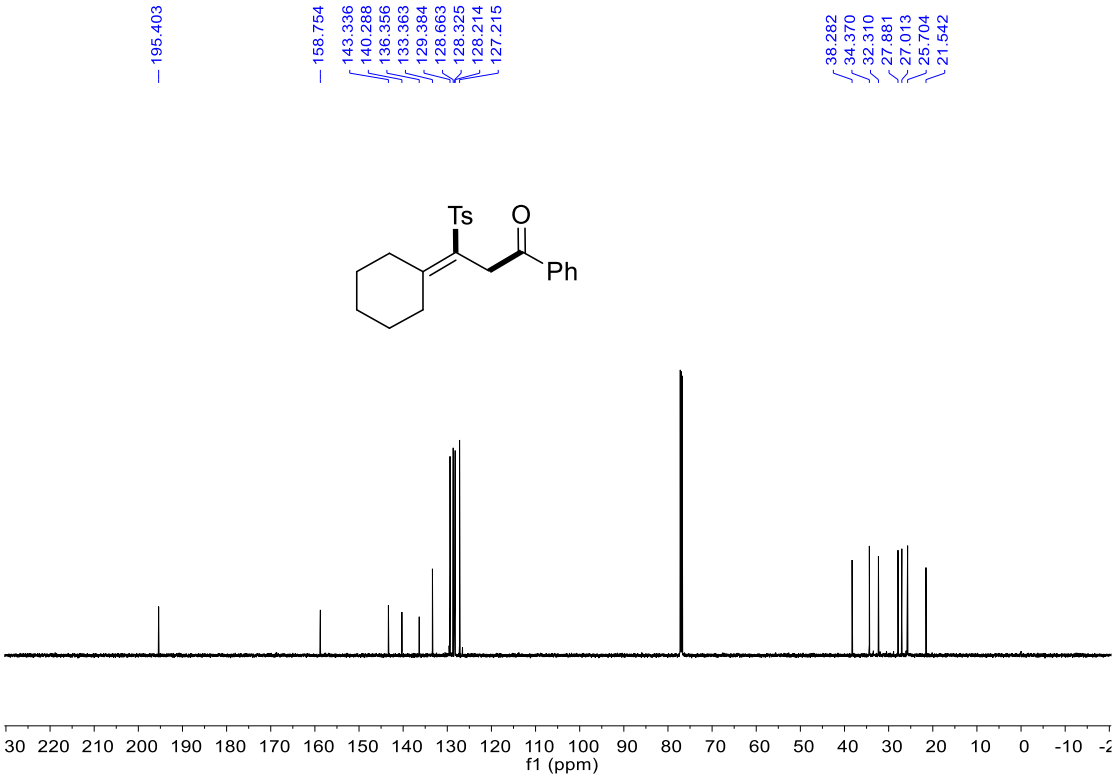
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **27**



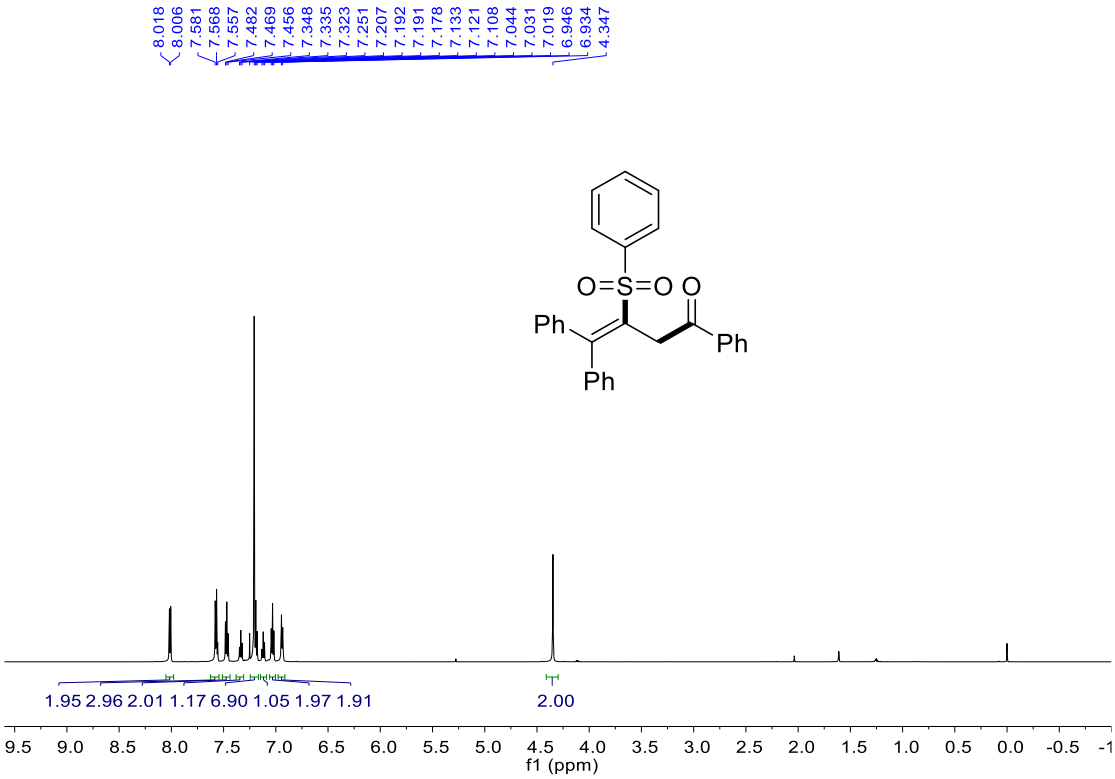
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **28**



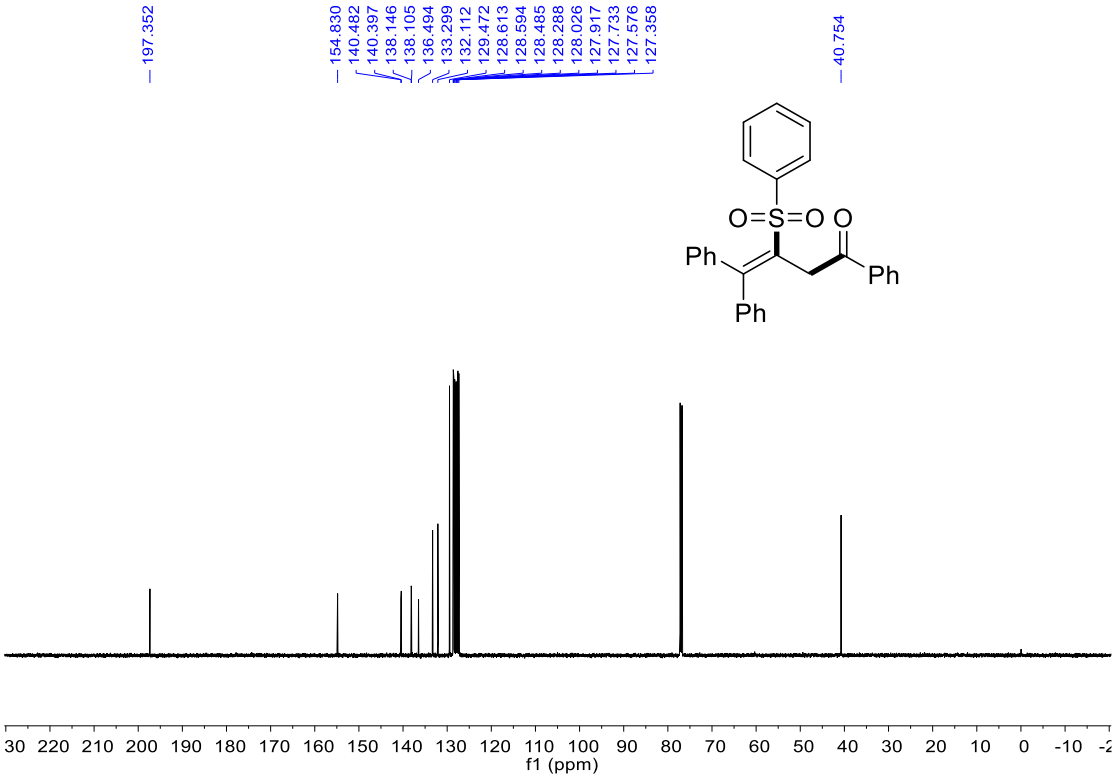
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **28**



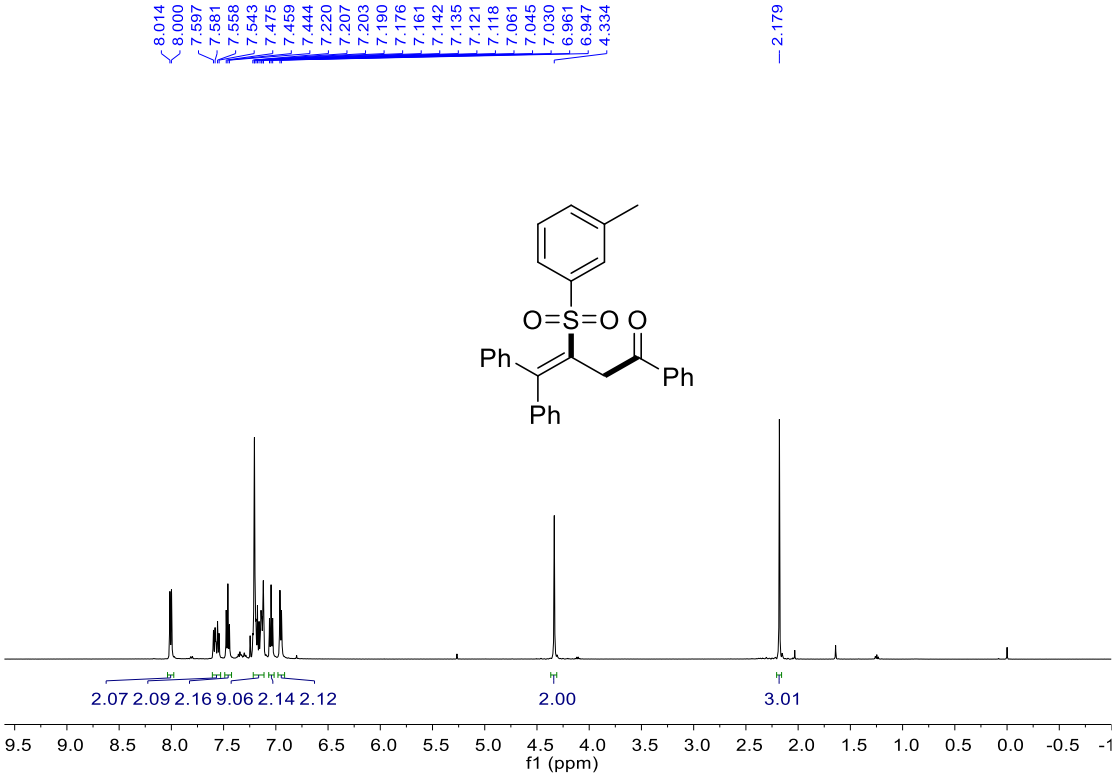
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **30**



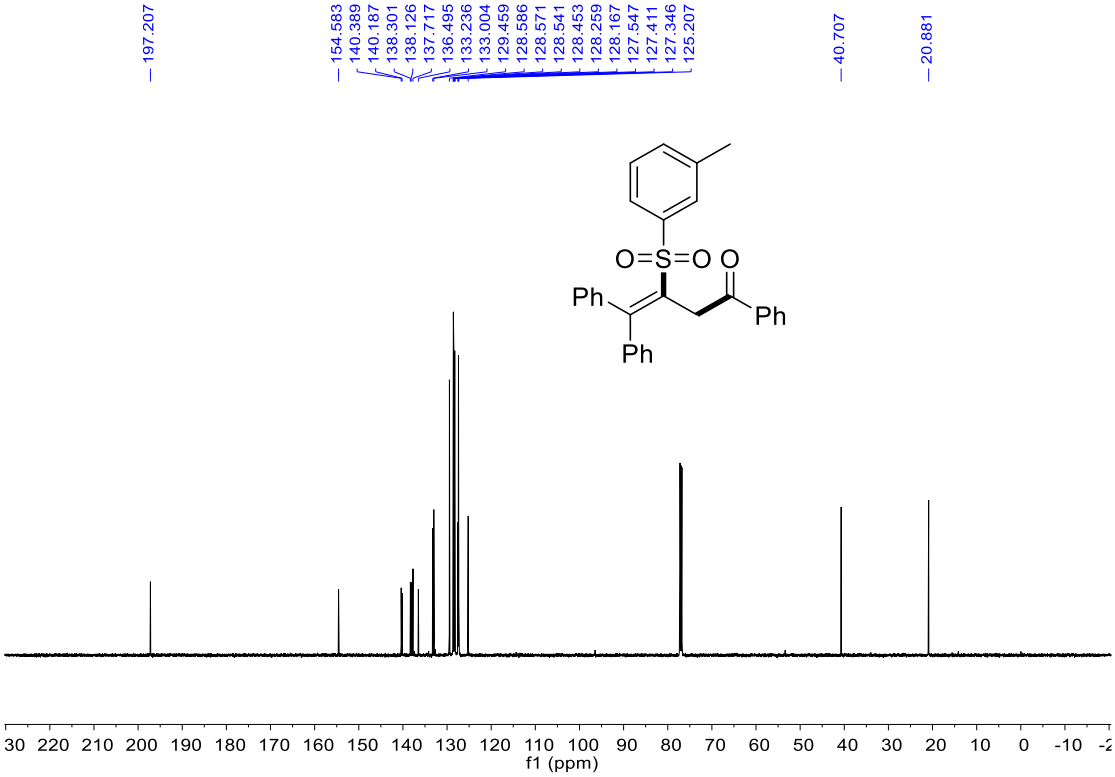
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **30**



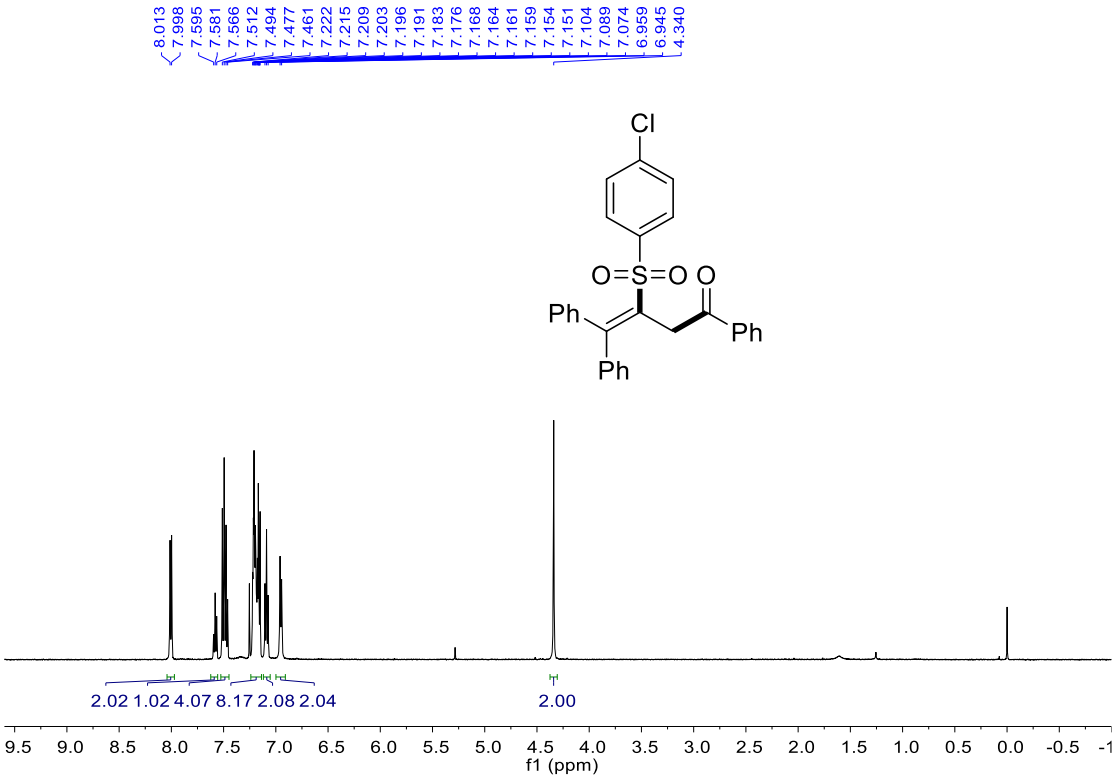
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **31**



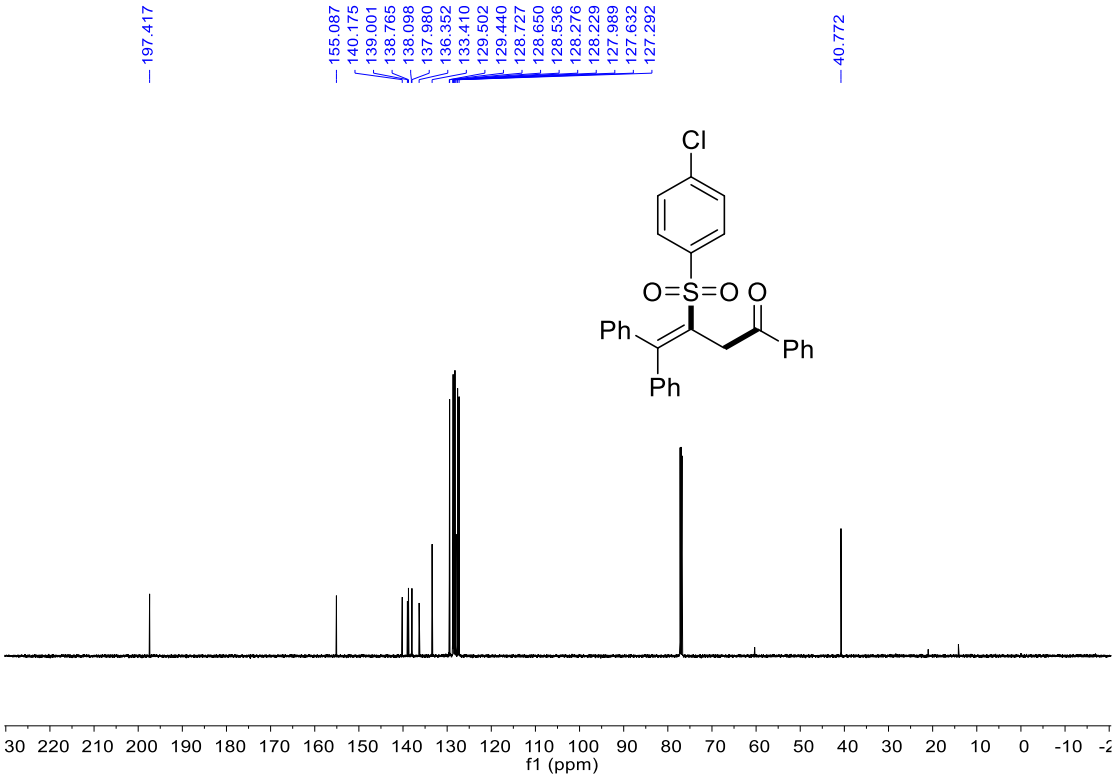
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **31**



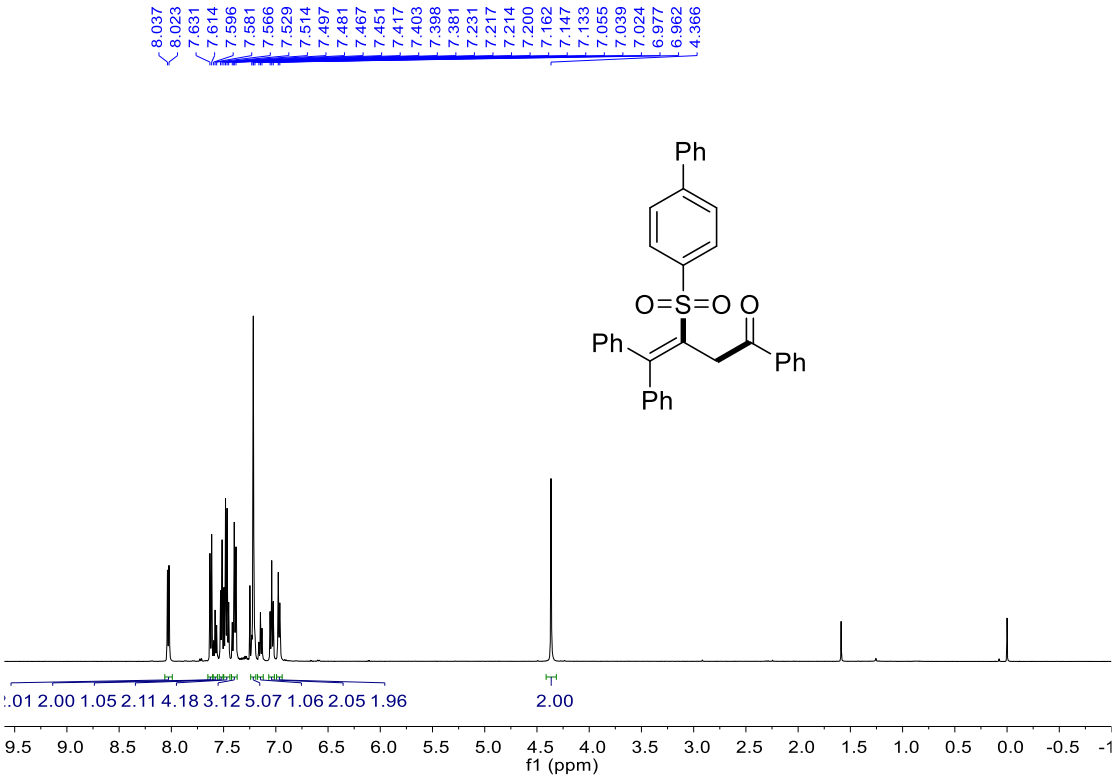
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **32**



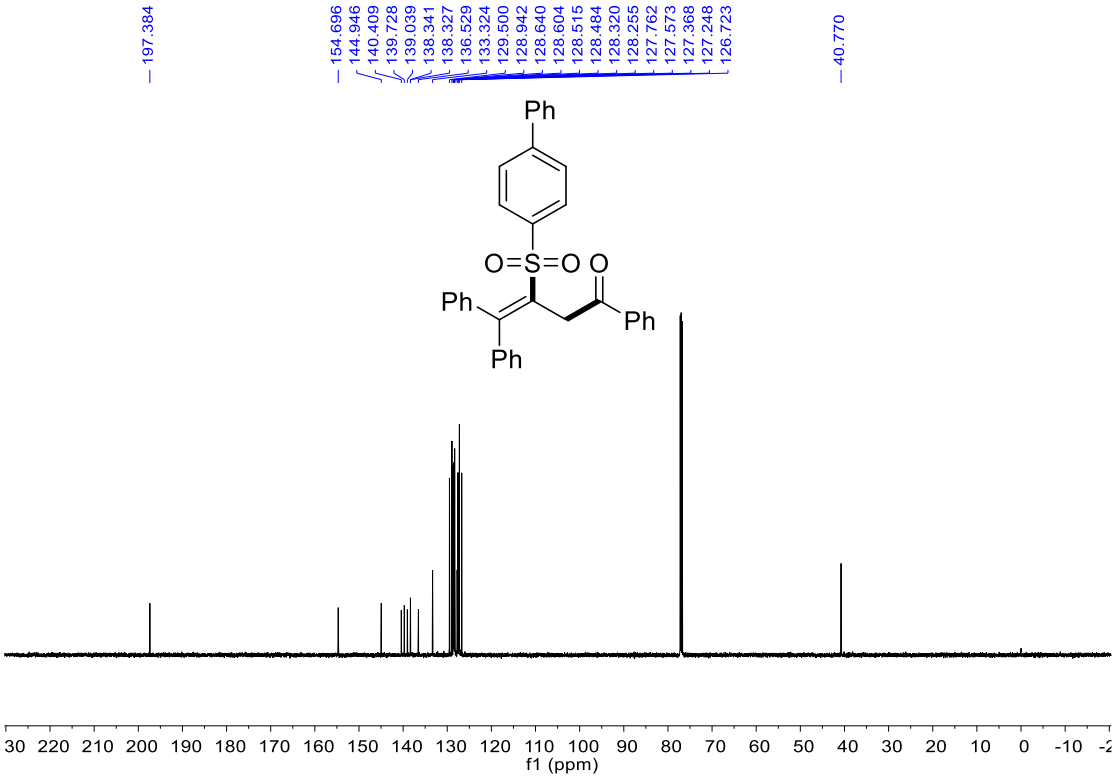
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **32**



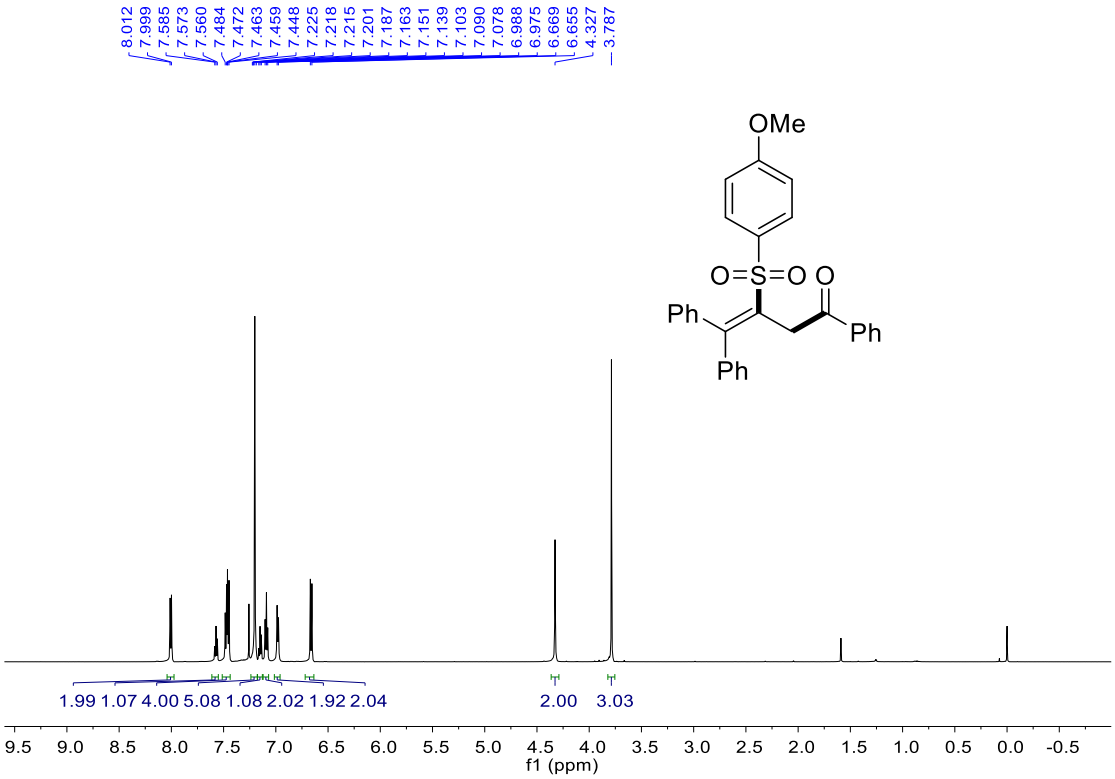
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **33**



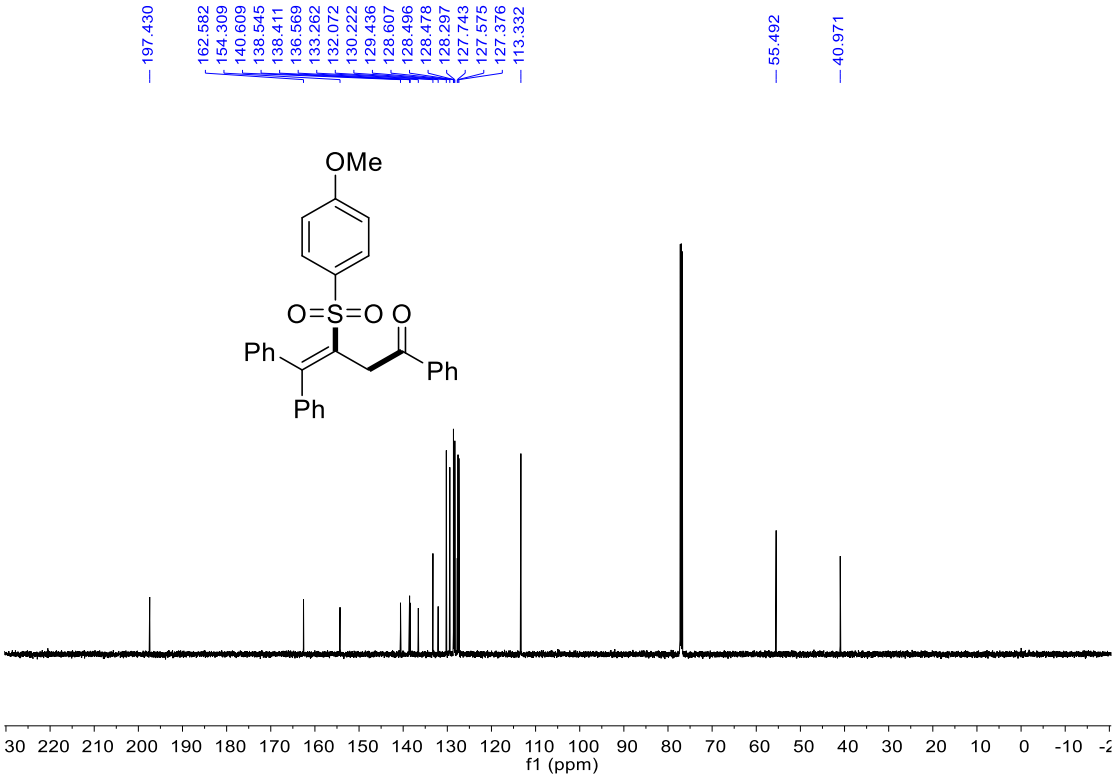
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **33**



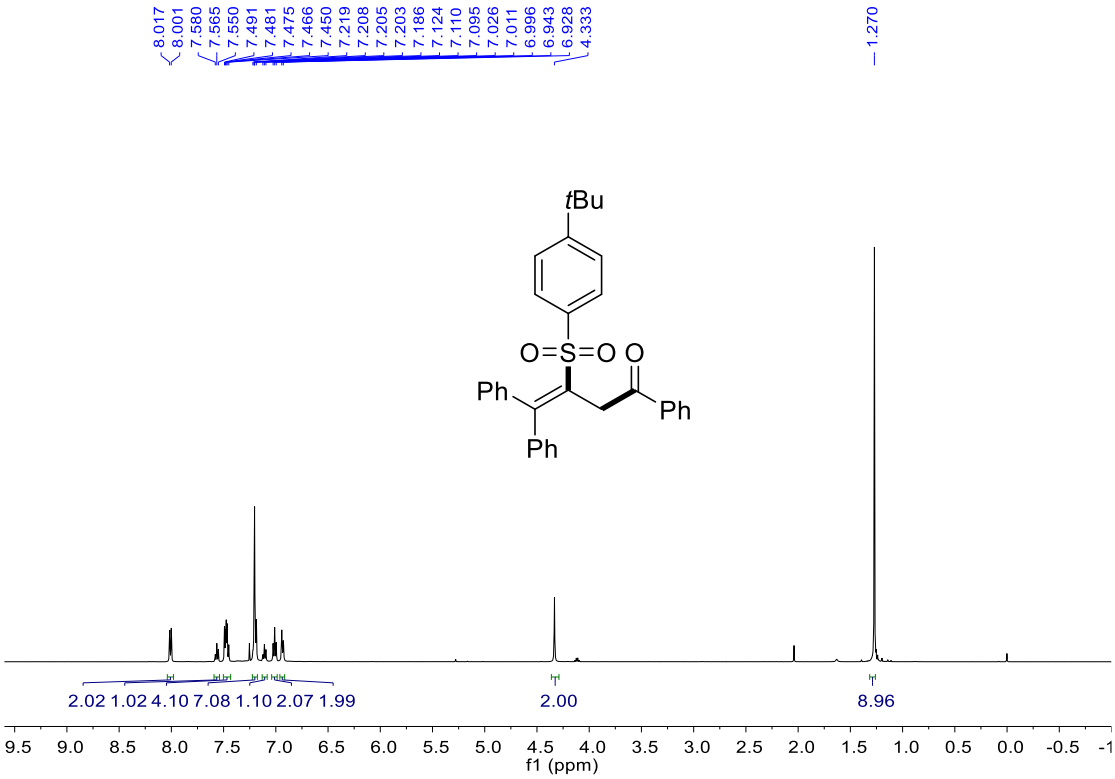
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **34**



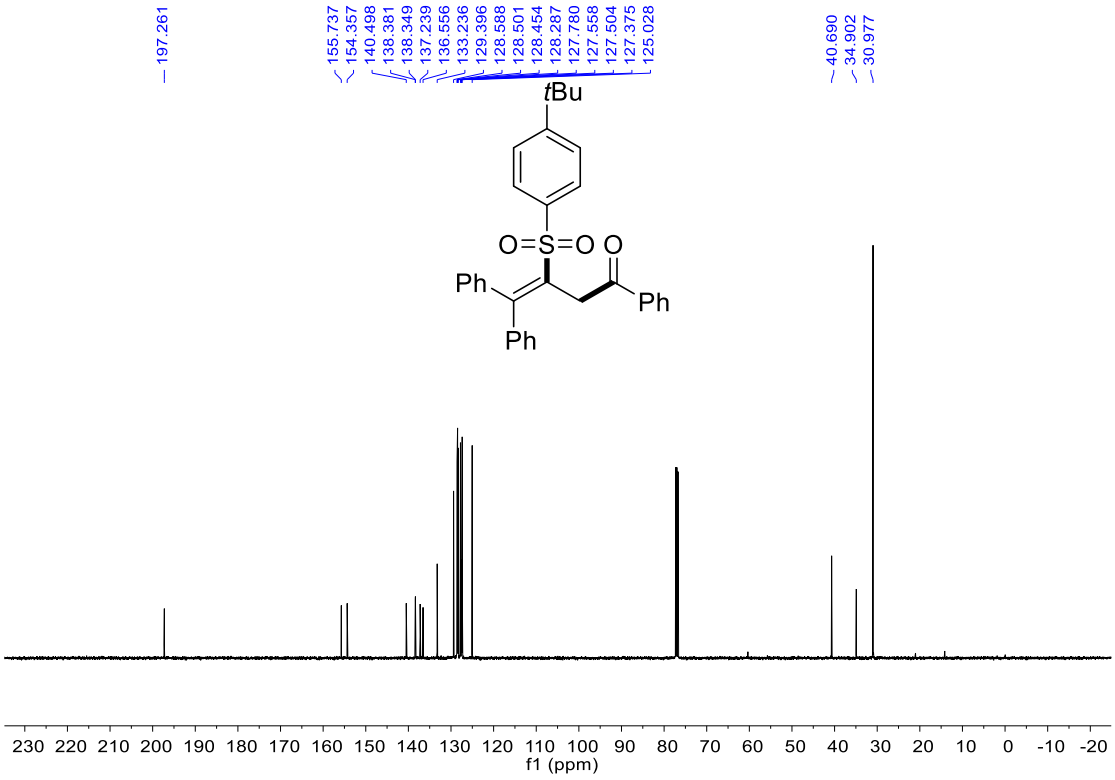
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **34**



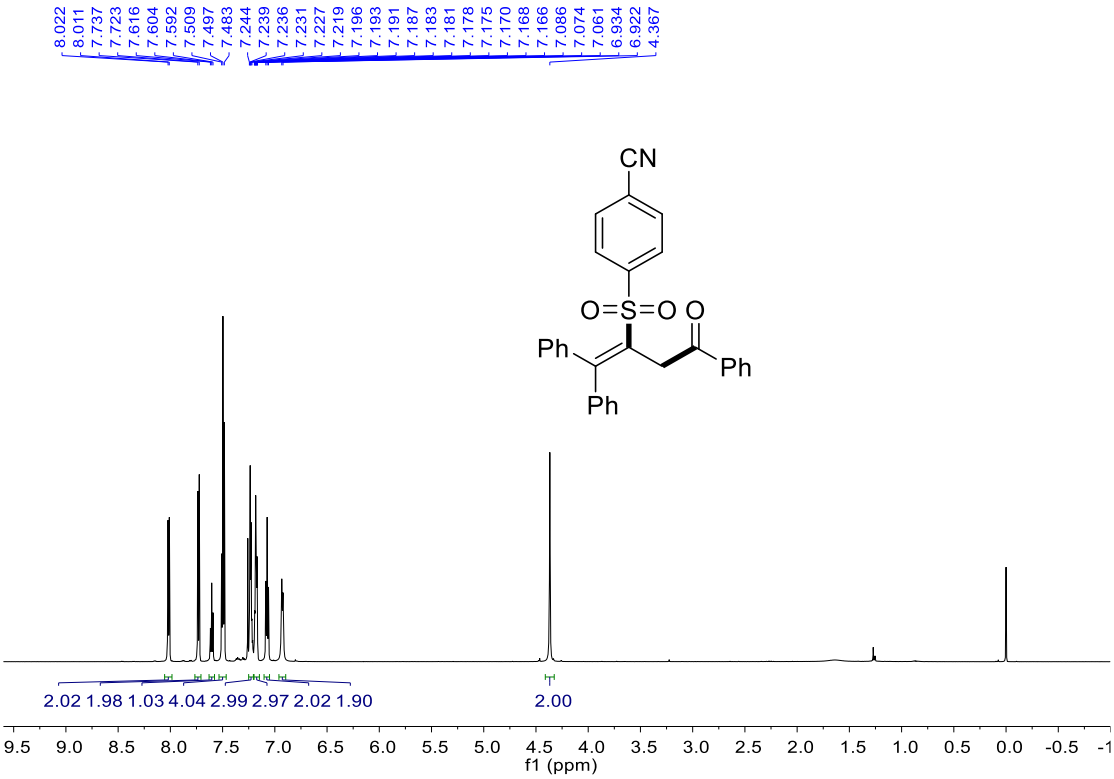
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **35**



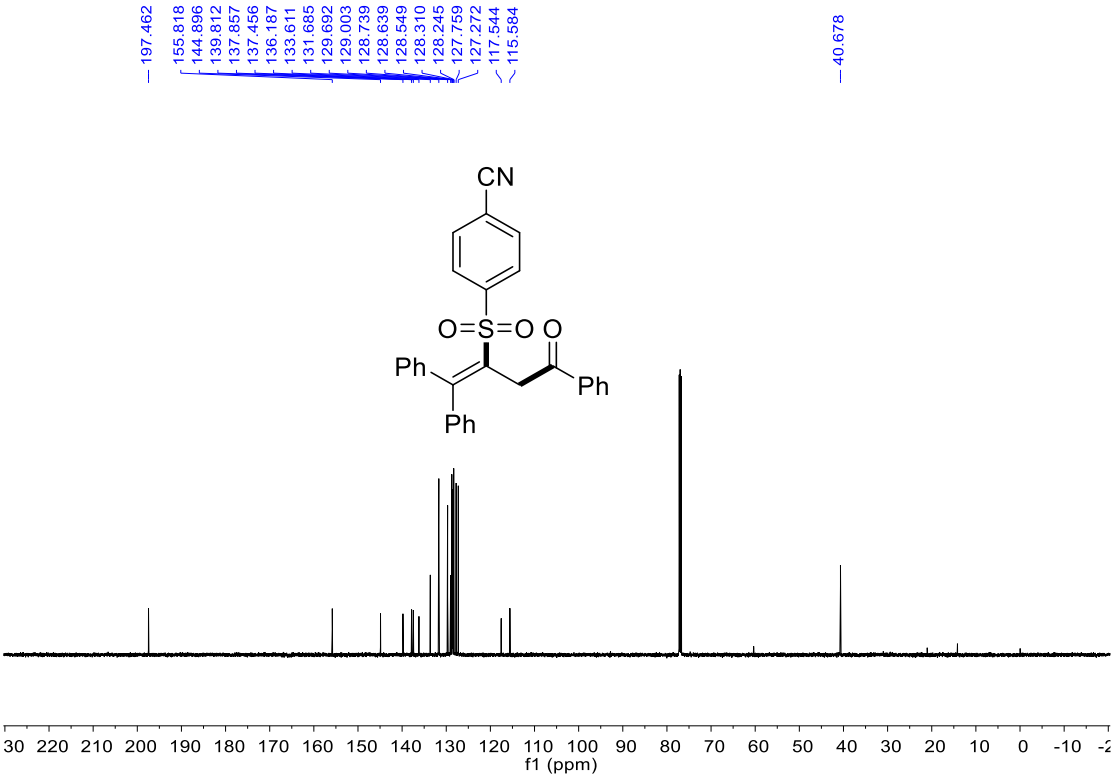
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **35**



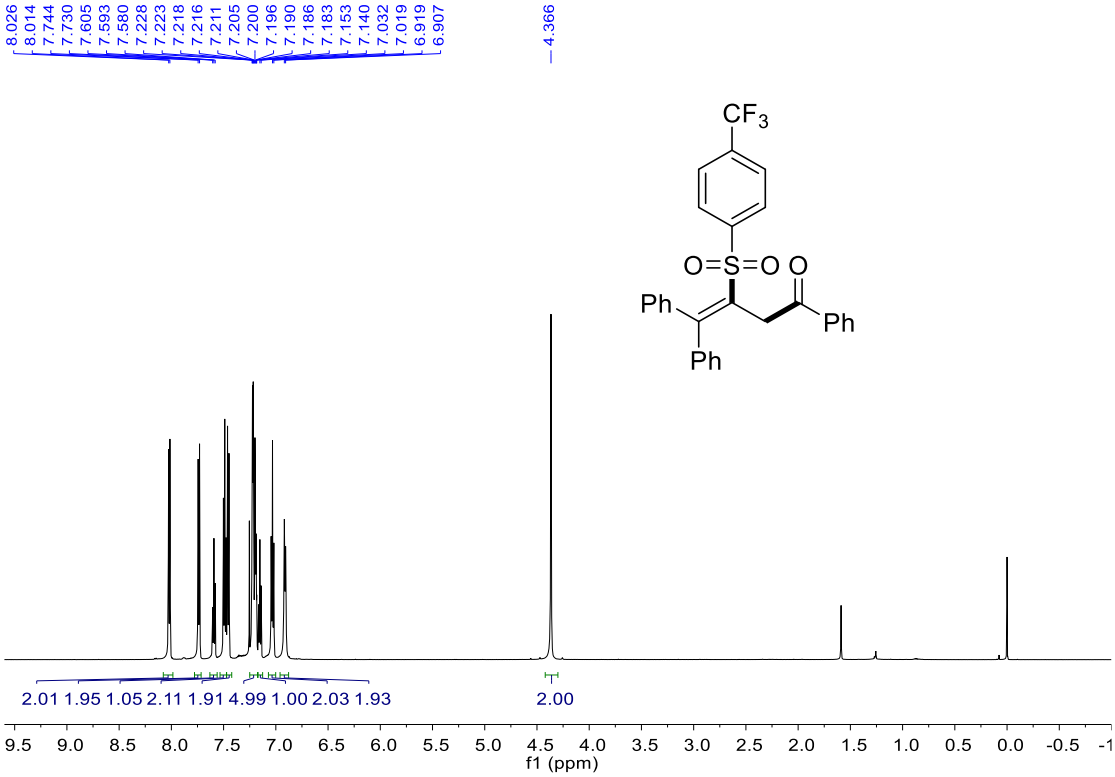
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **36**



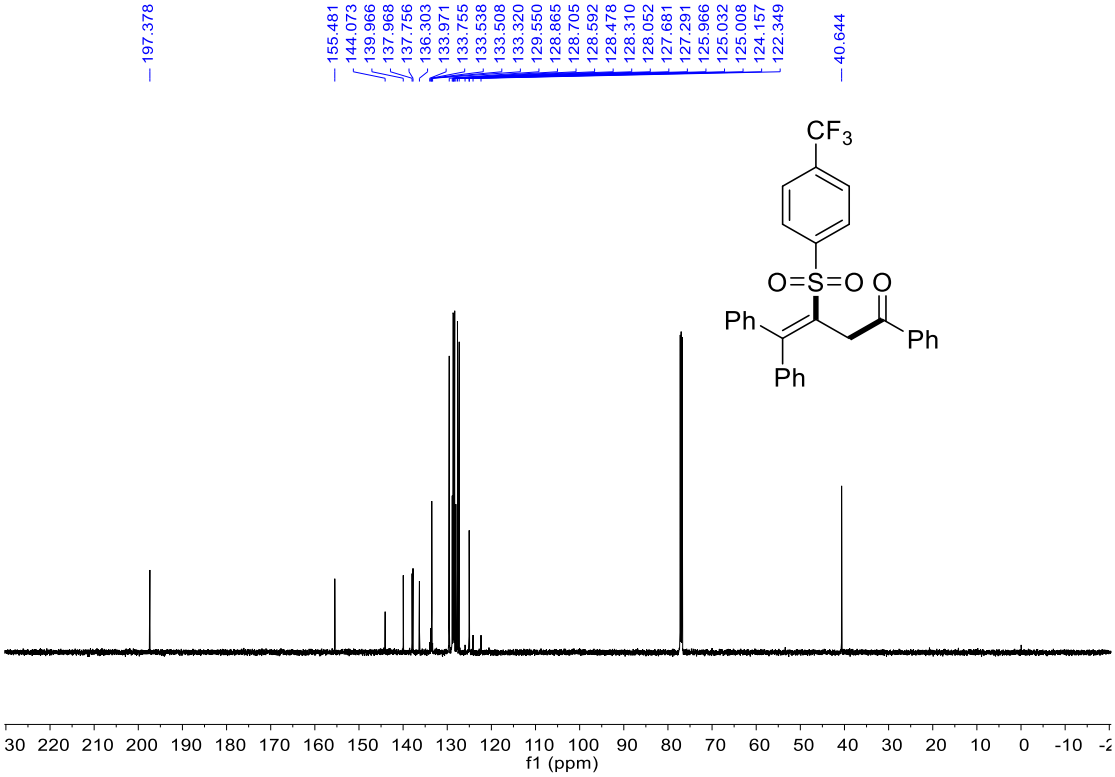
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **36**



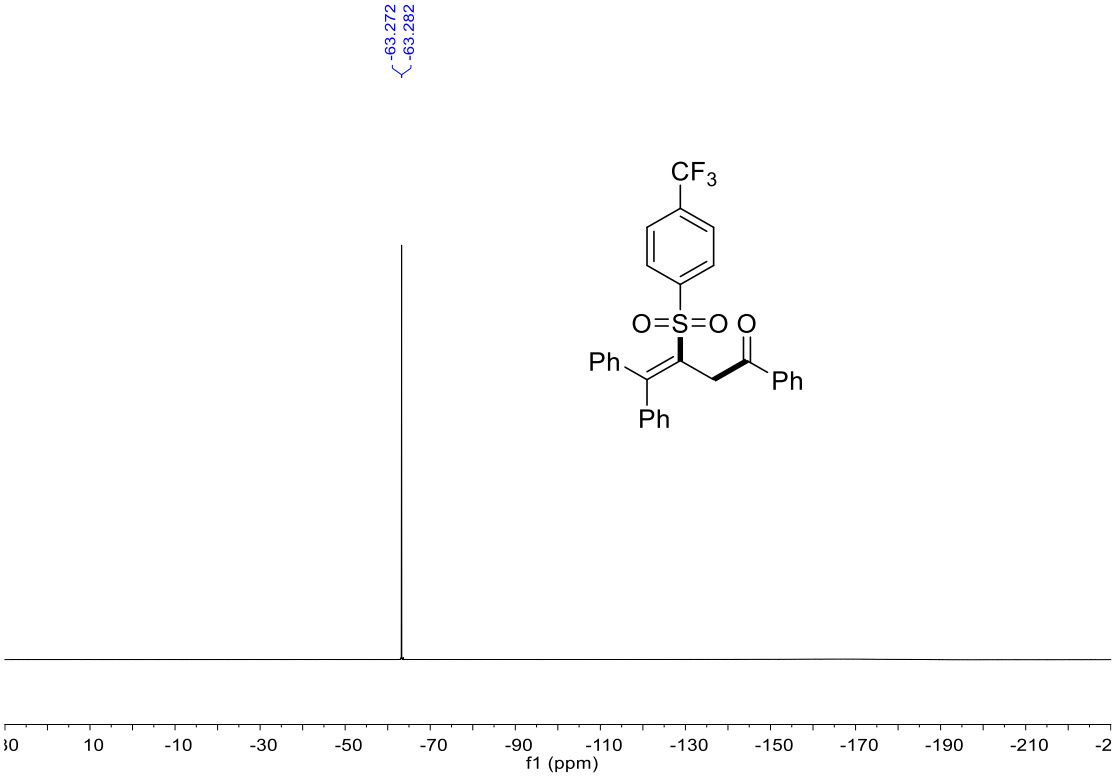
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **37**



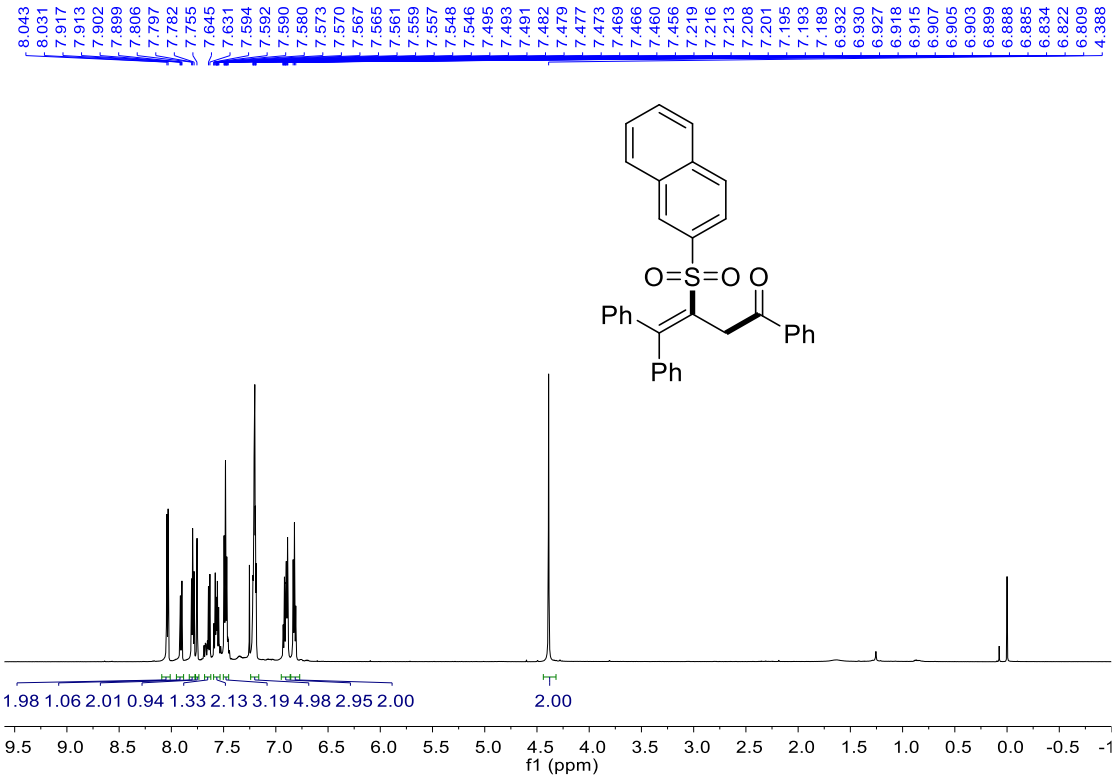
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **37**



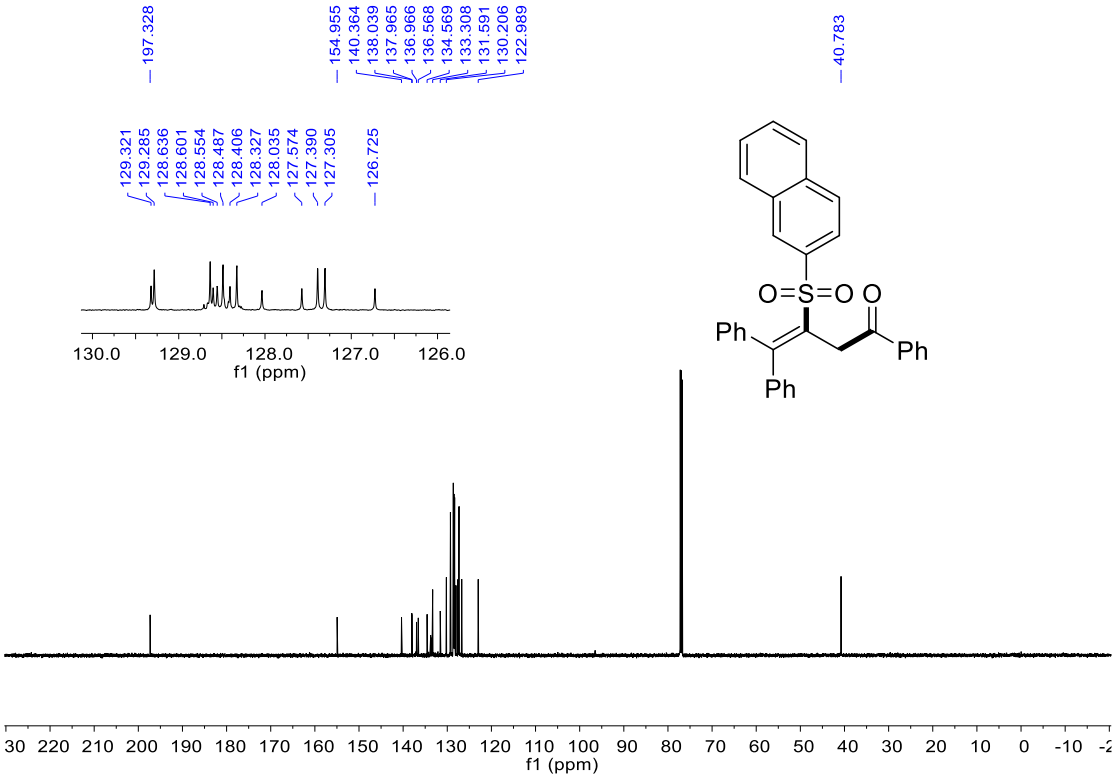
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **37**



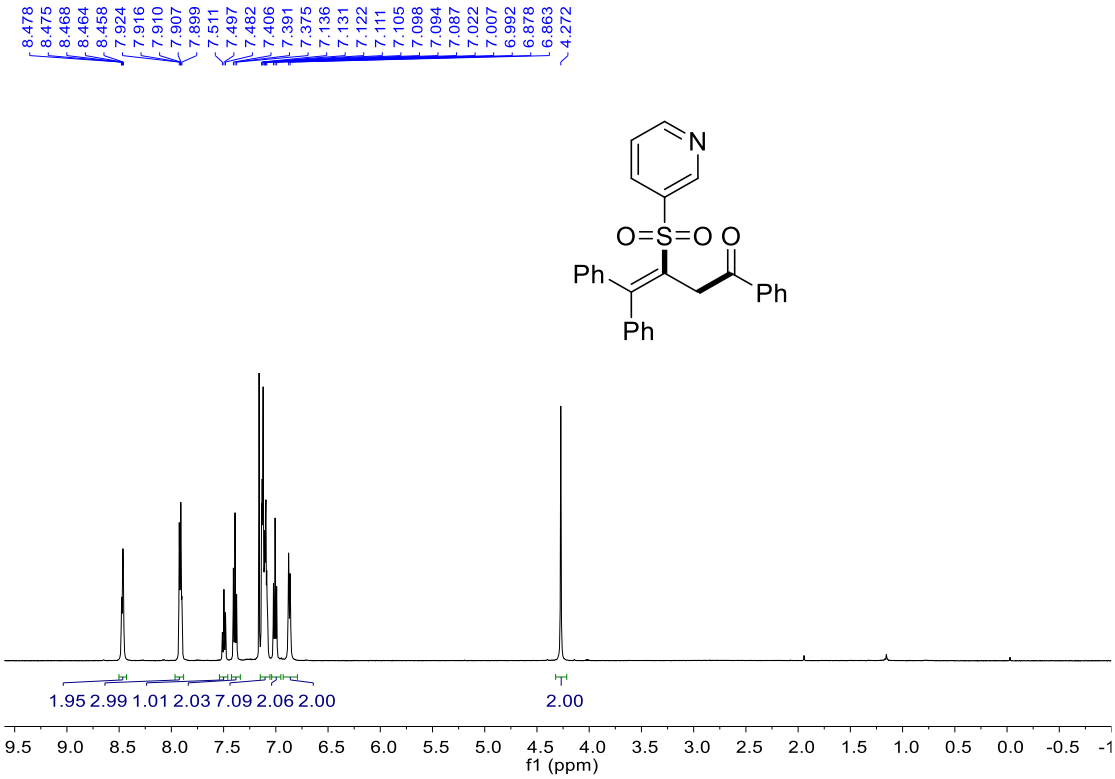
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **38**



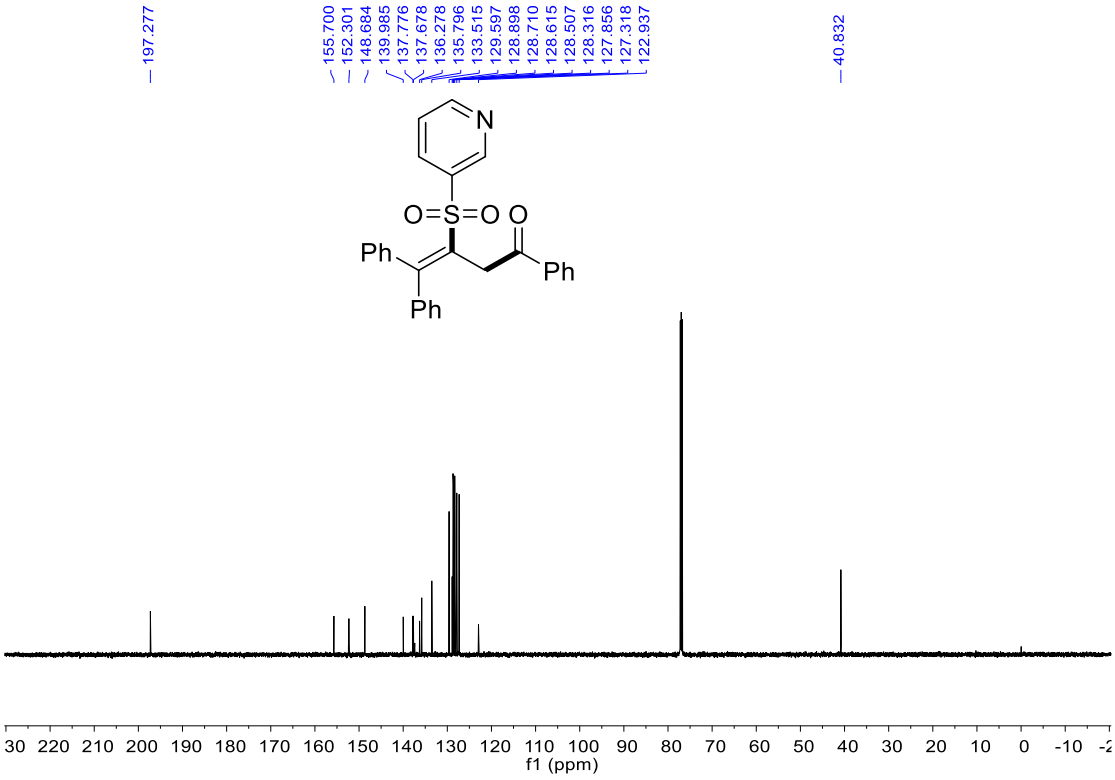
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **38**



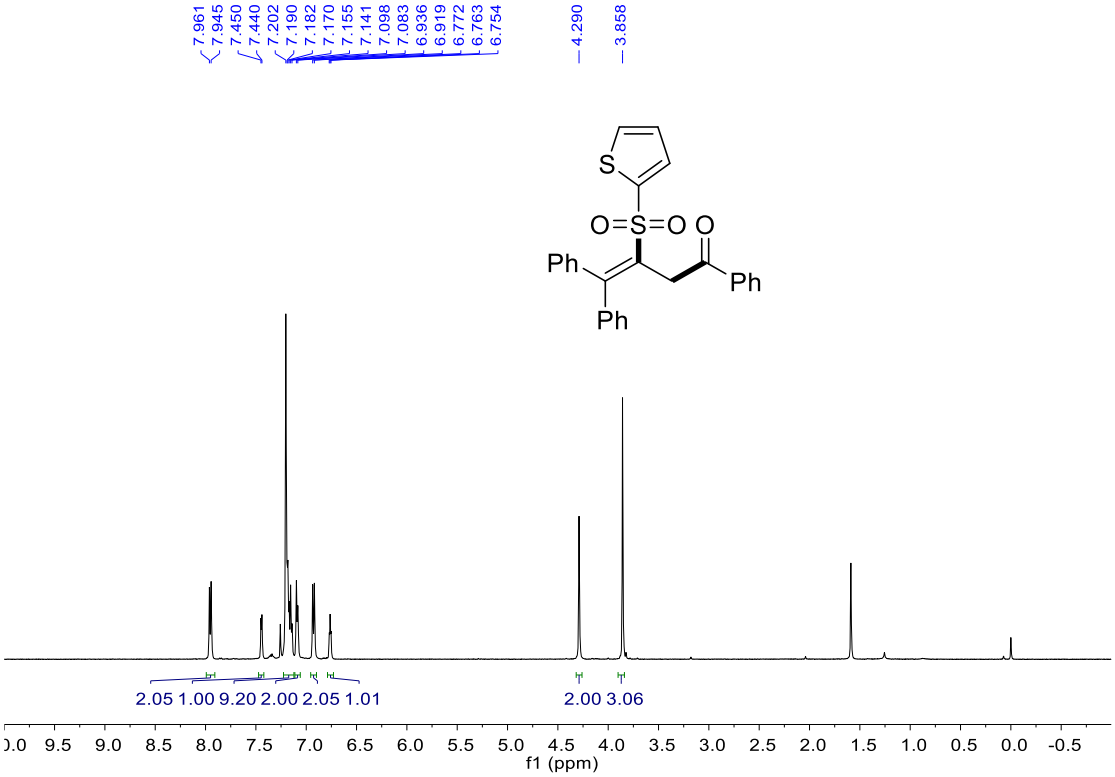
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **39**



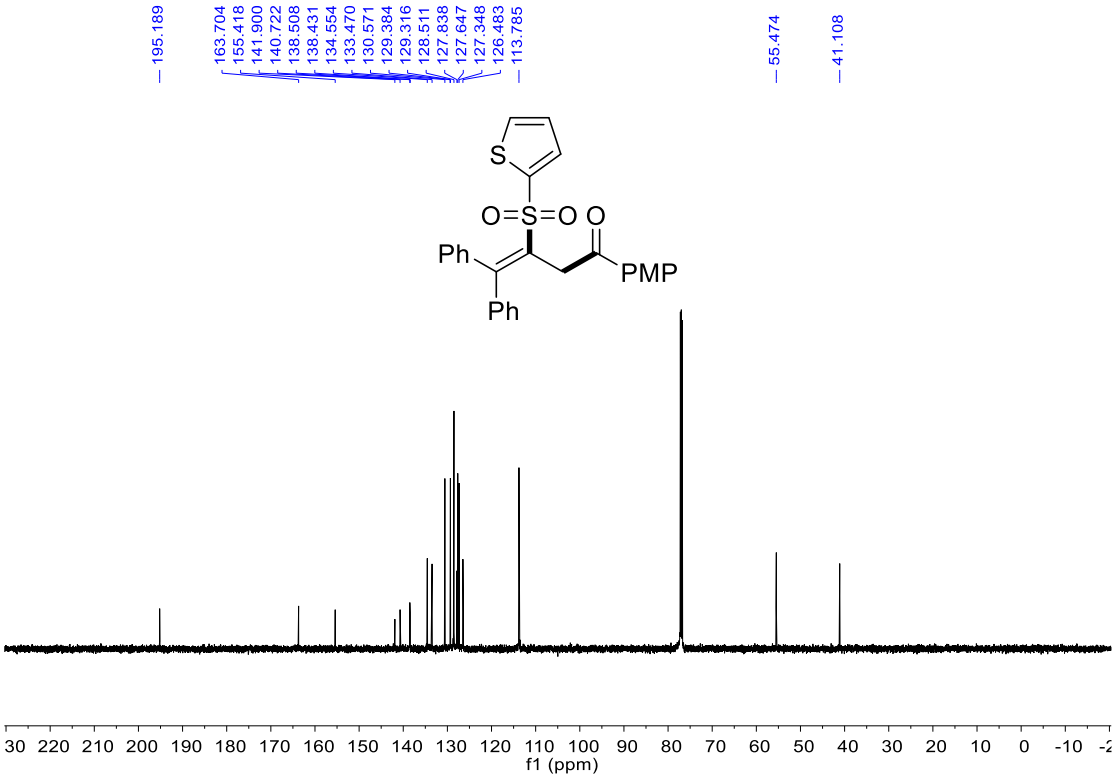
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **39**



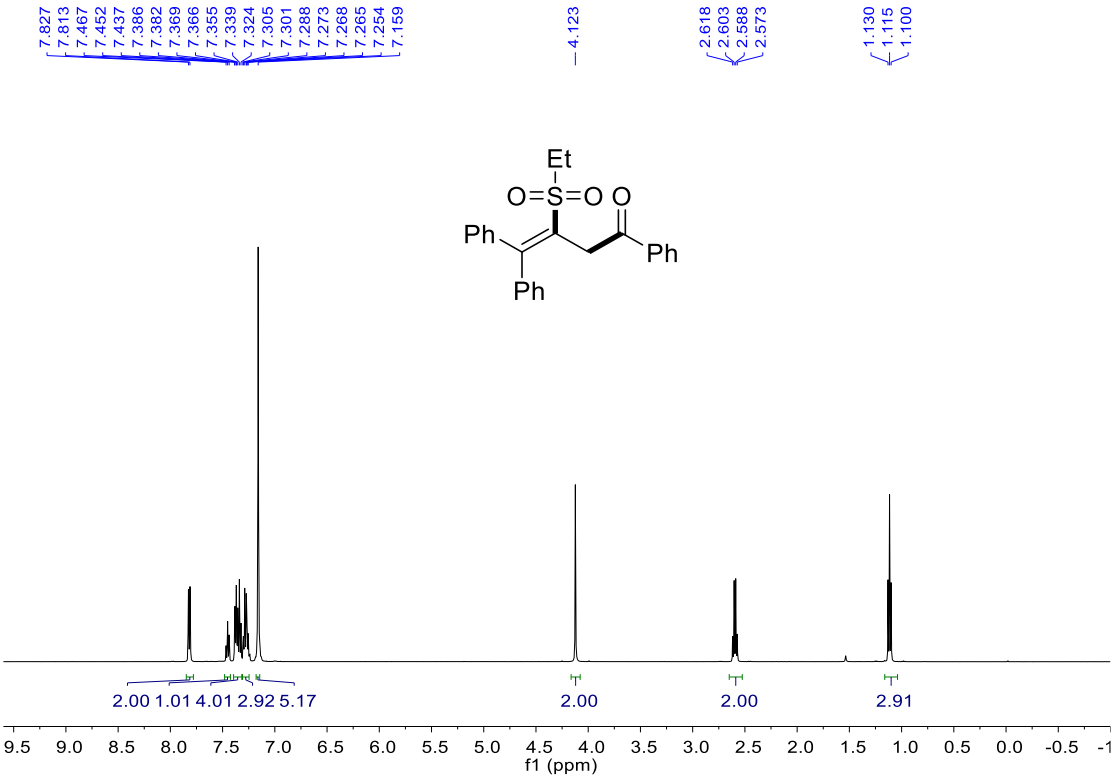
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **40**



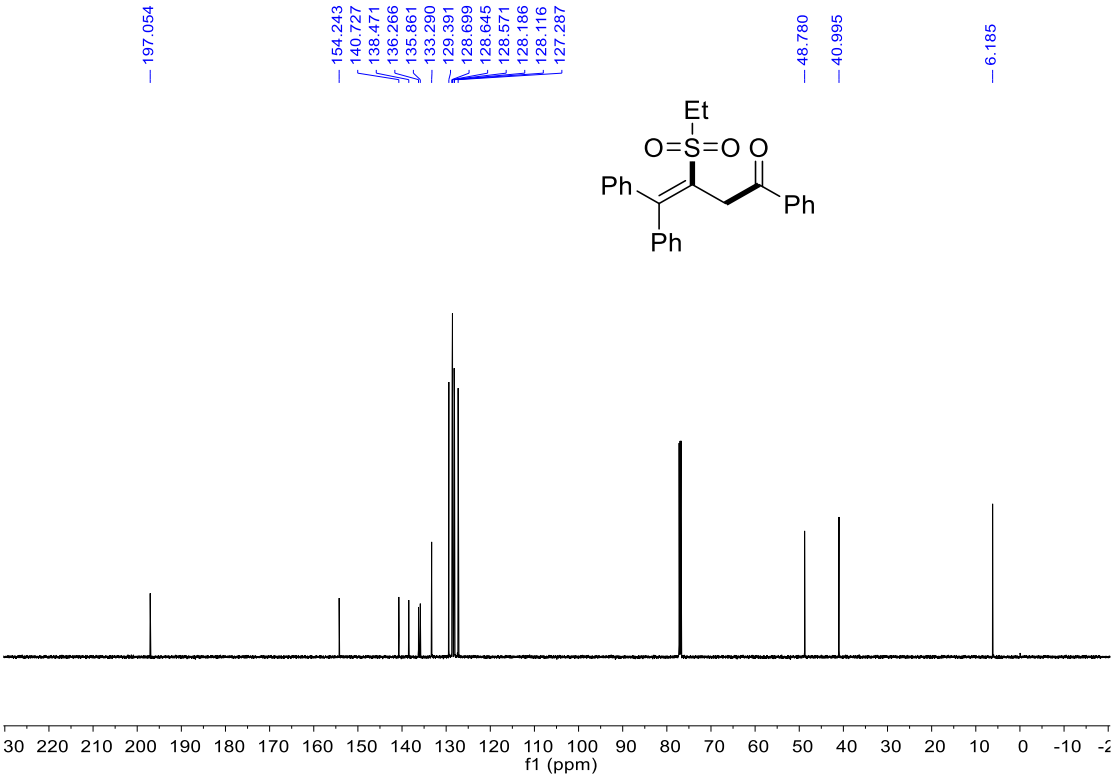
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **40**



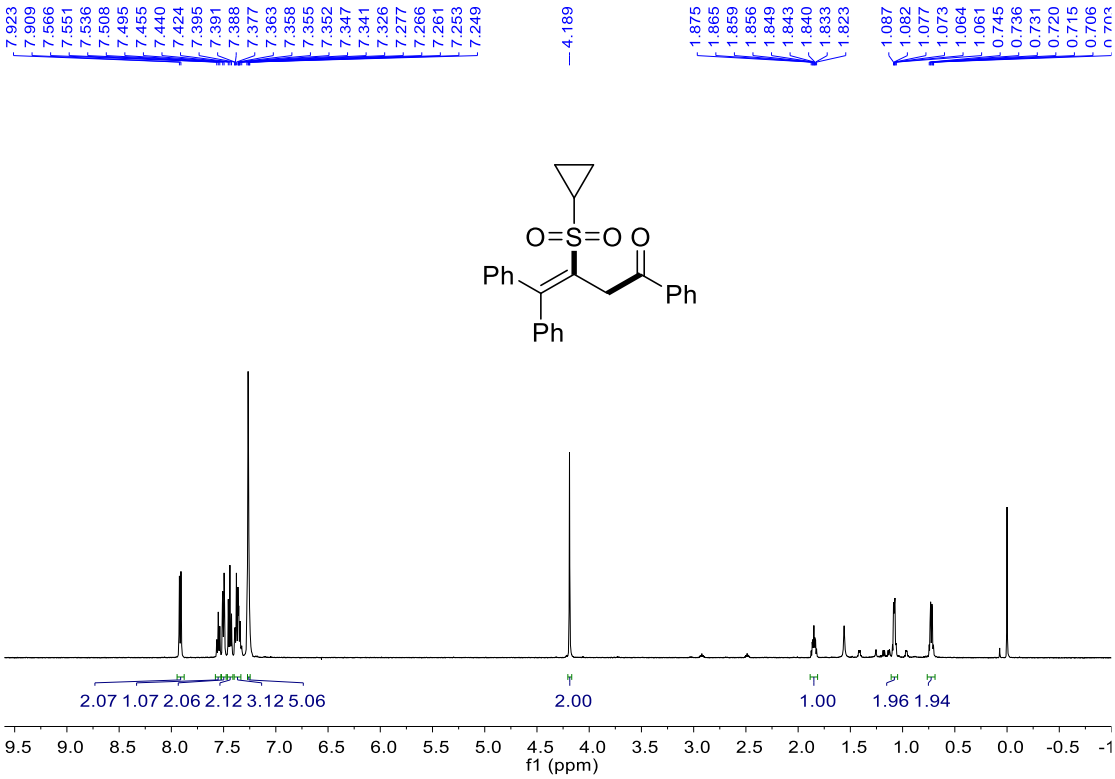
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **41**



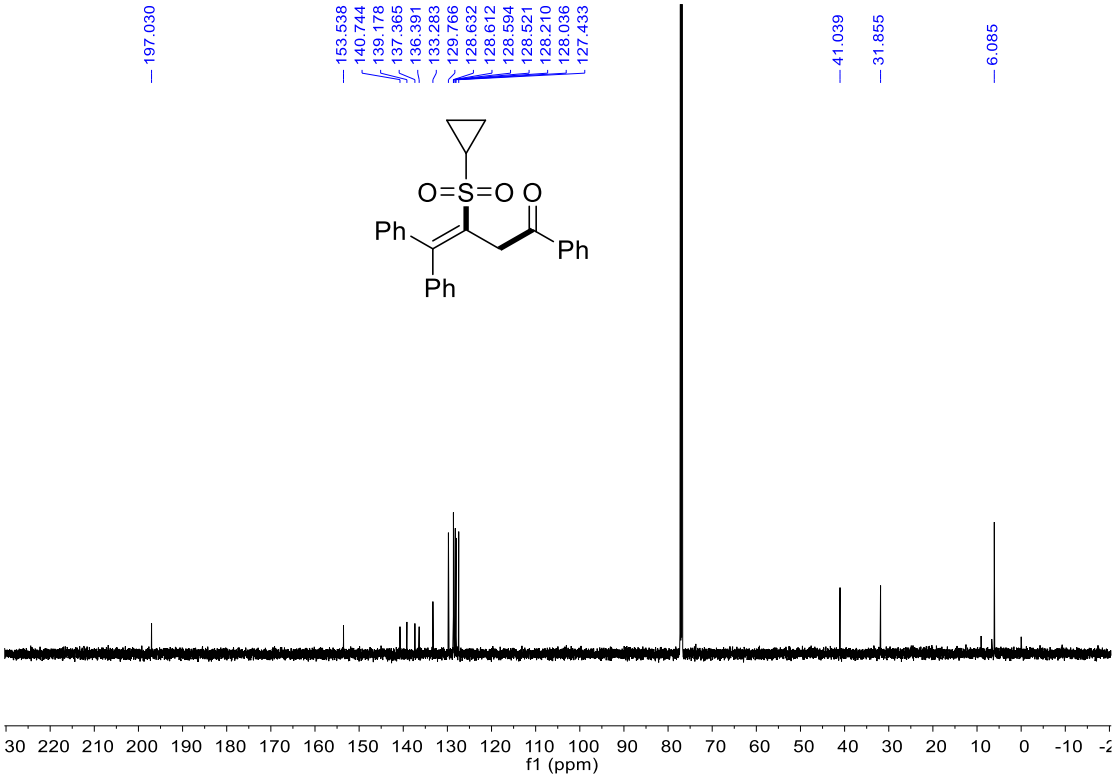
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **41**



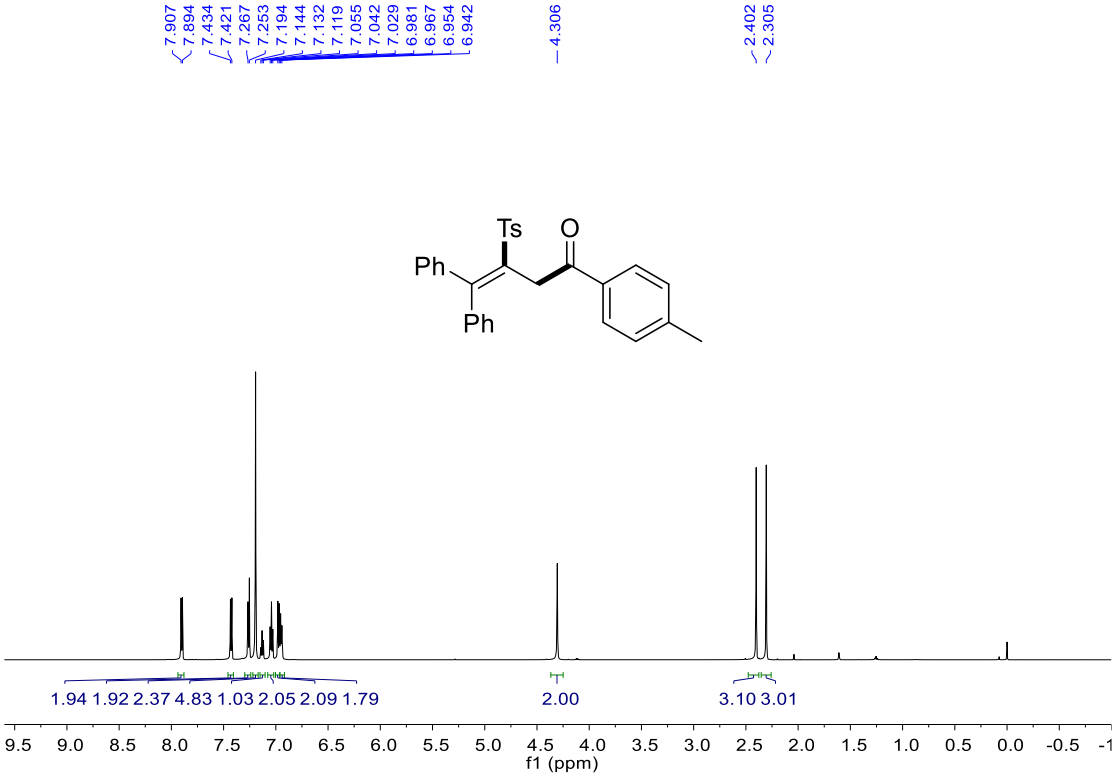
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **42**



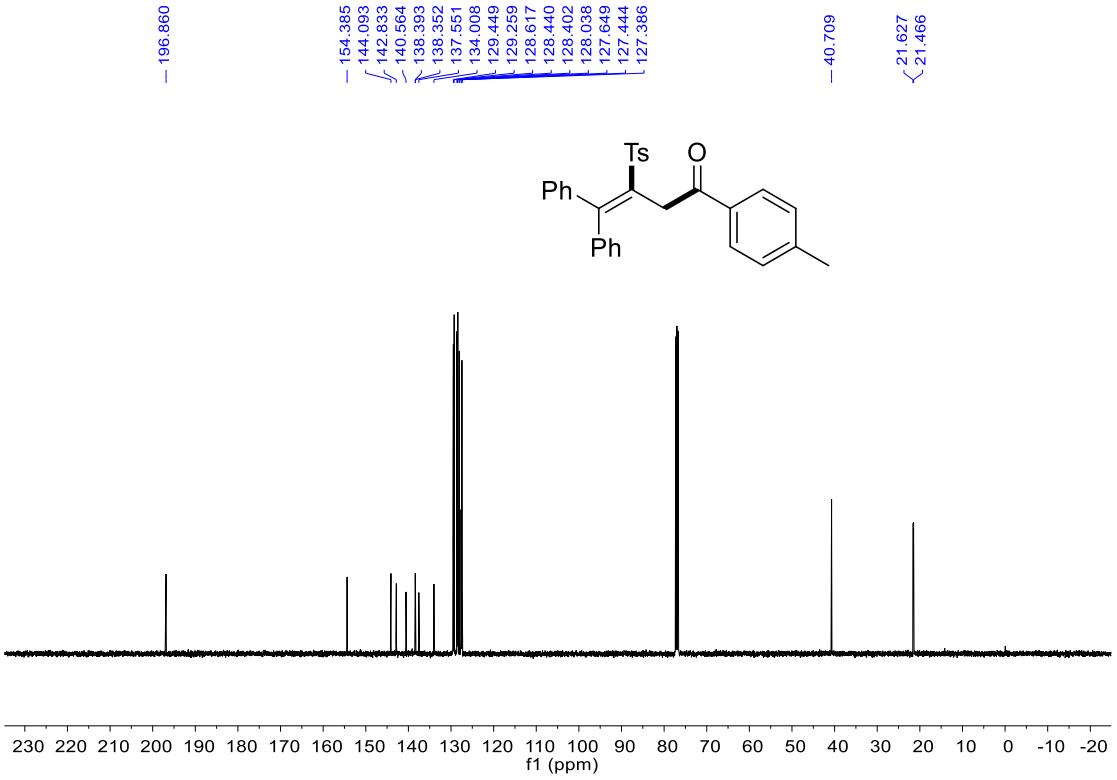
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **42**



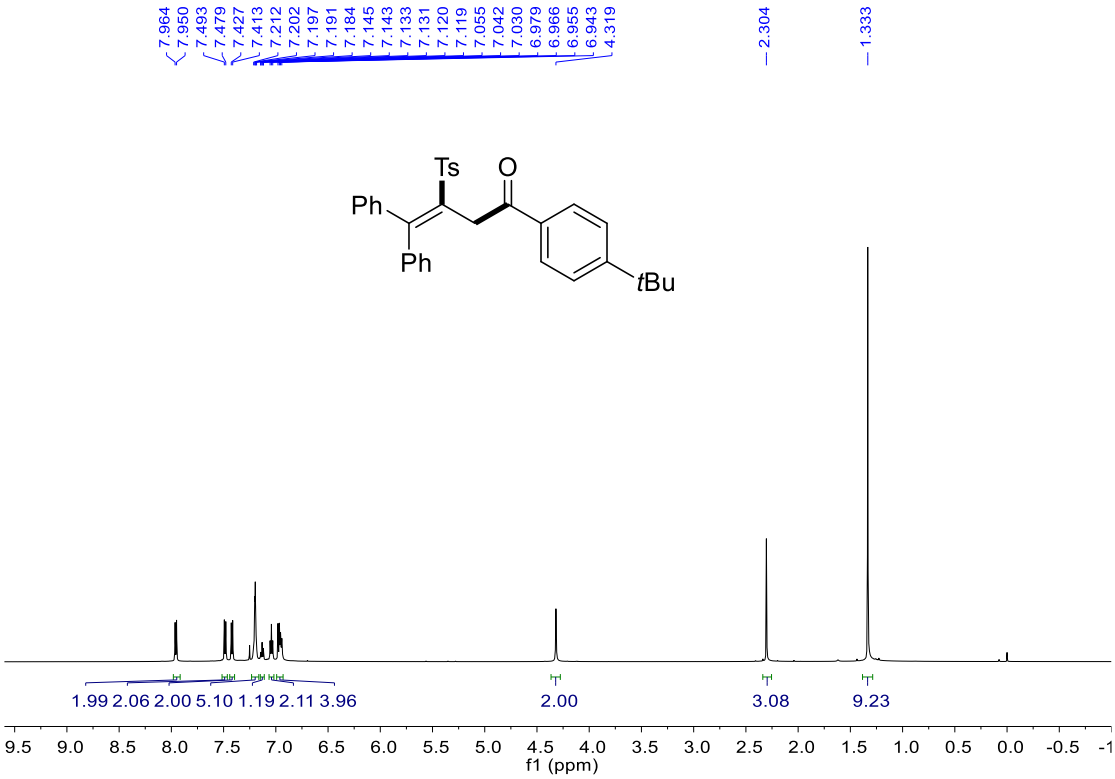
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **43**



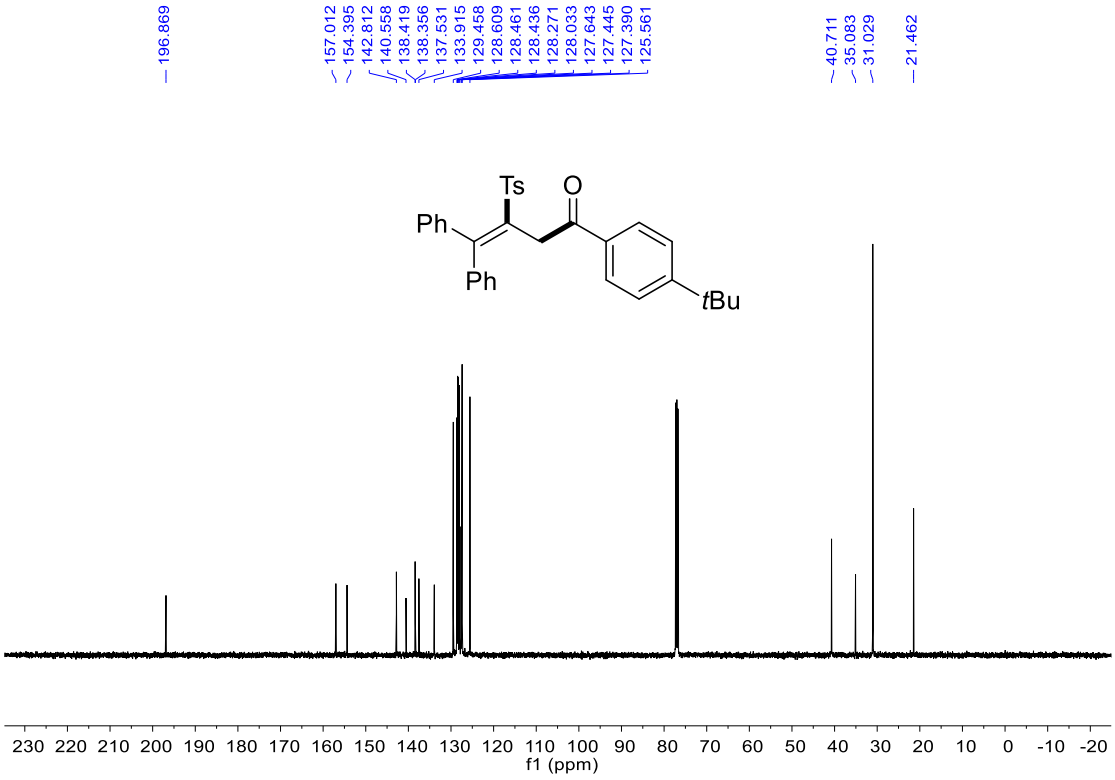
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **43**



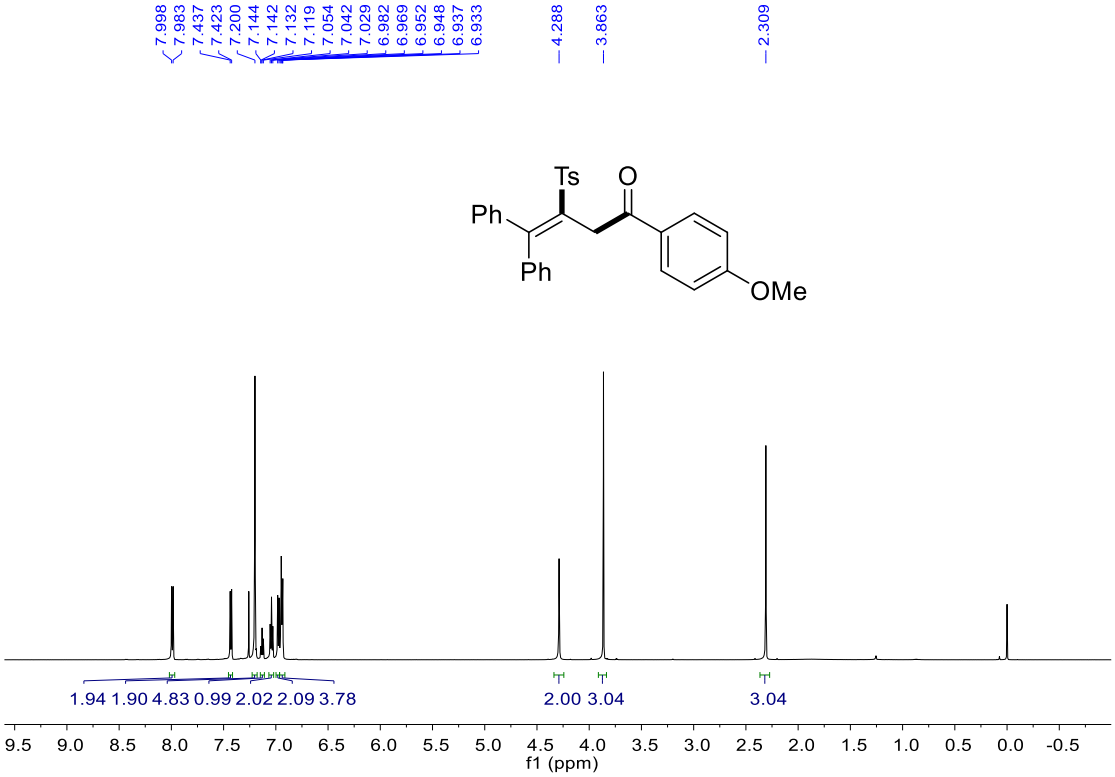
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **44**



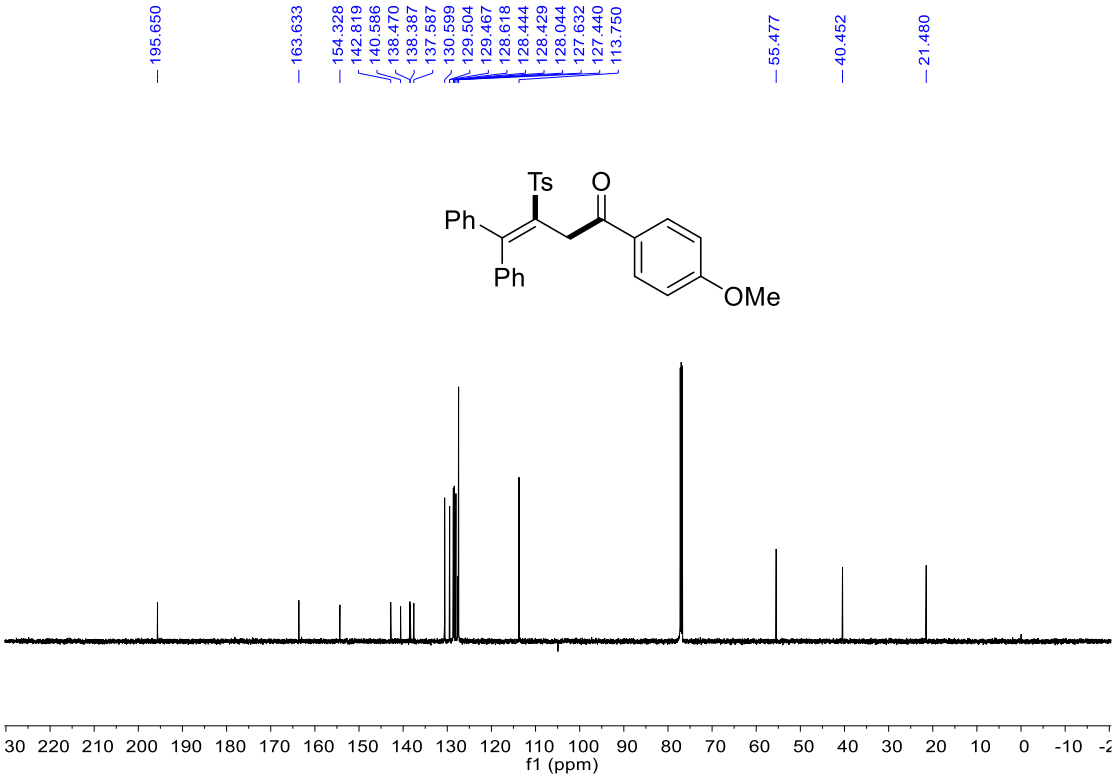
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **44**



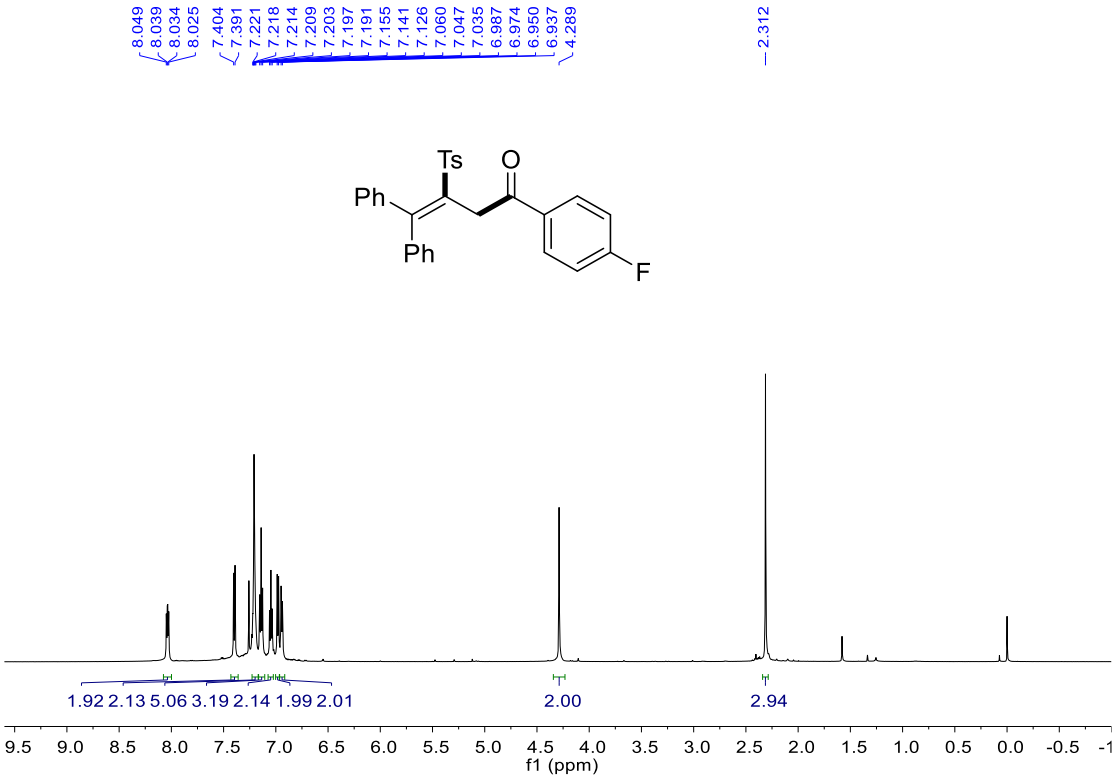
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **45**



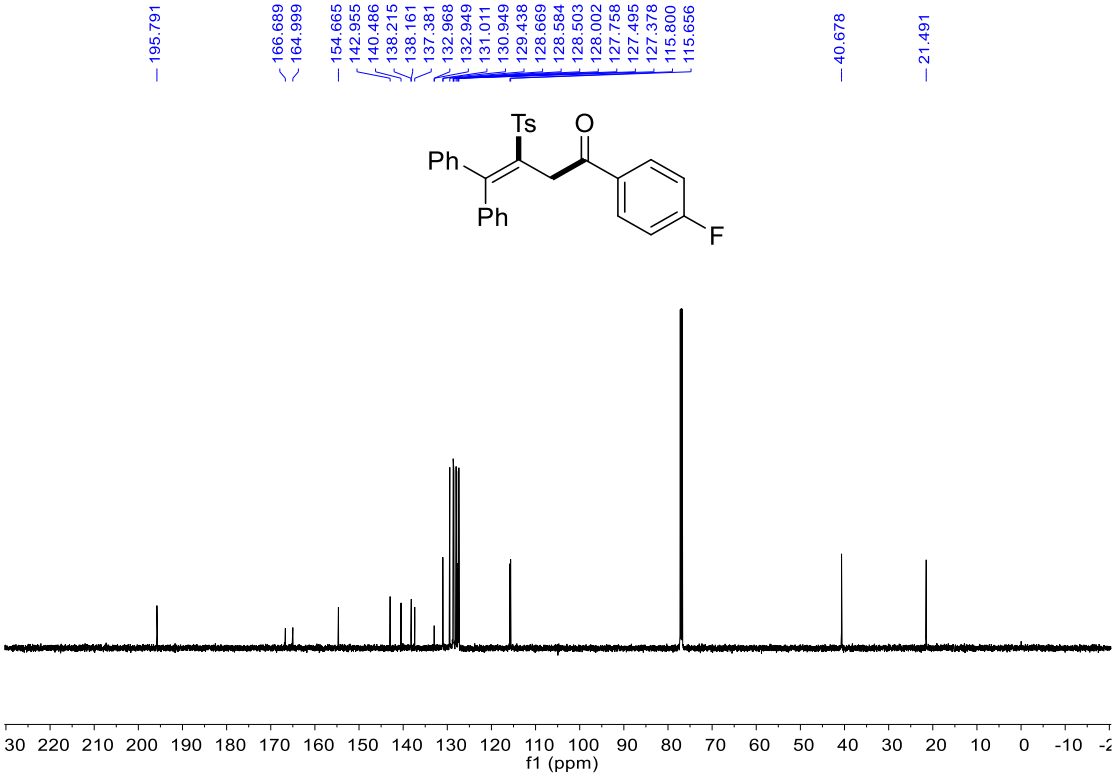
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **45**



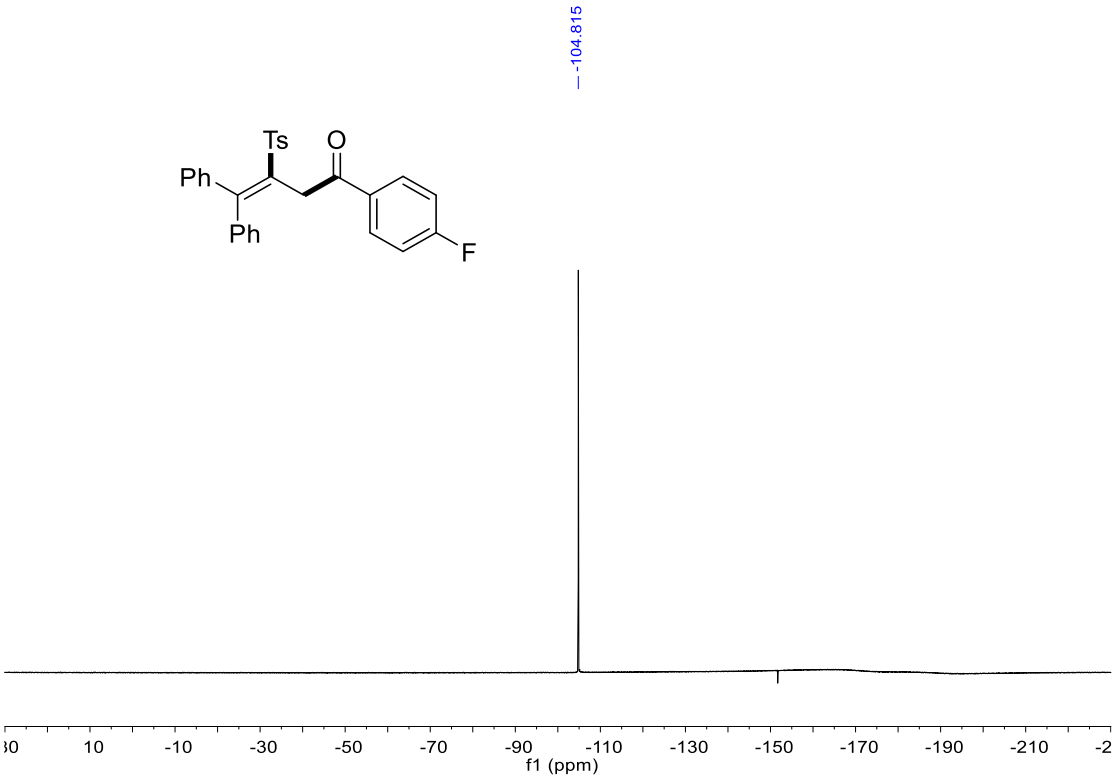
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **46**



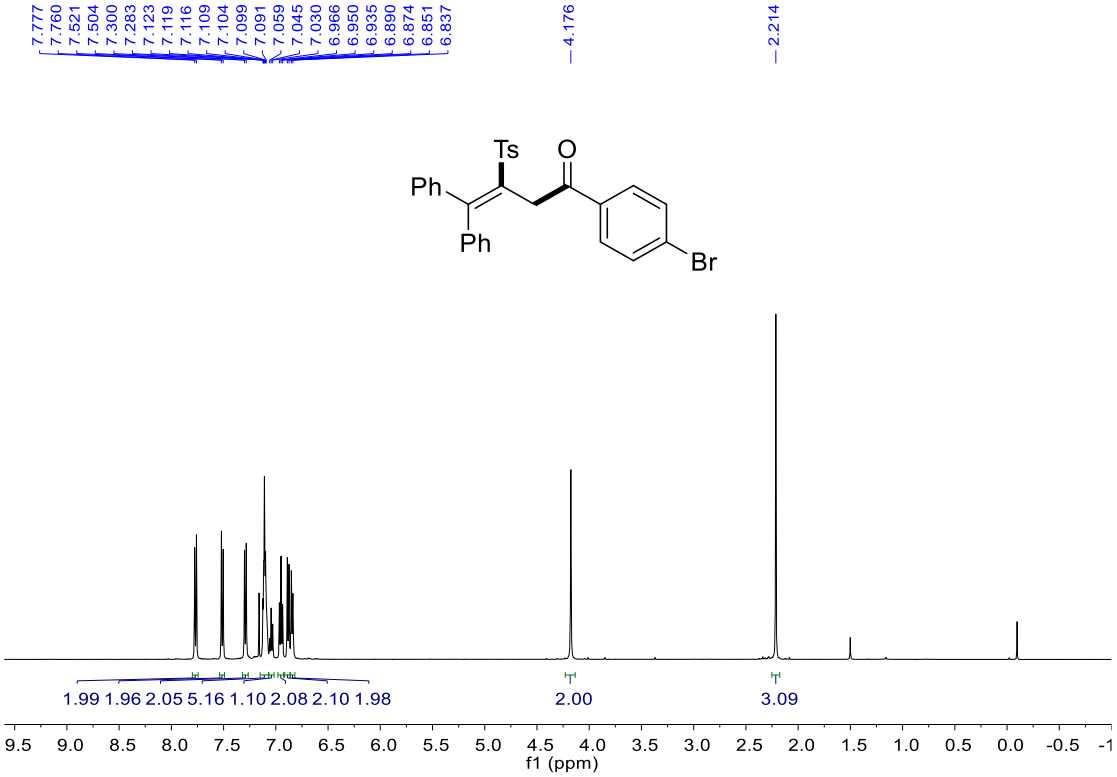
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **46**



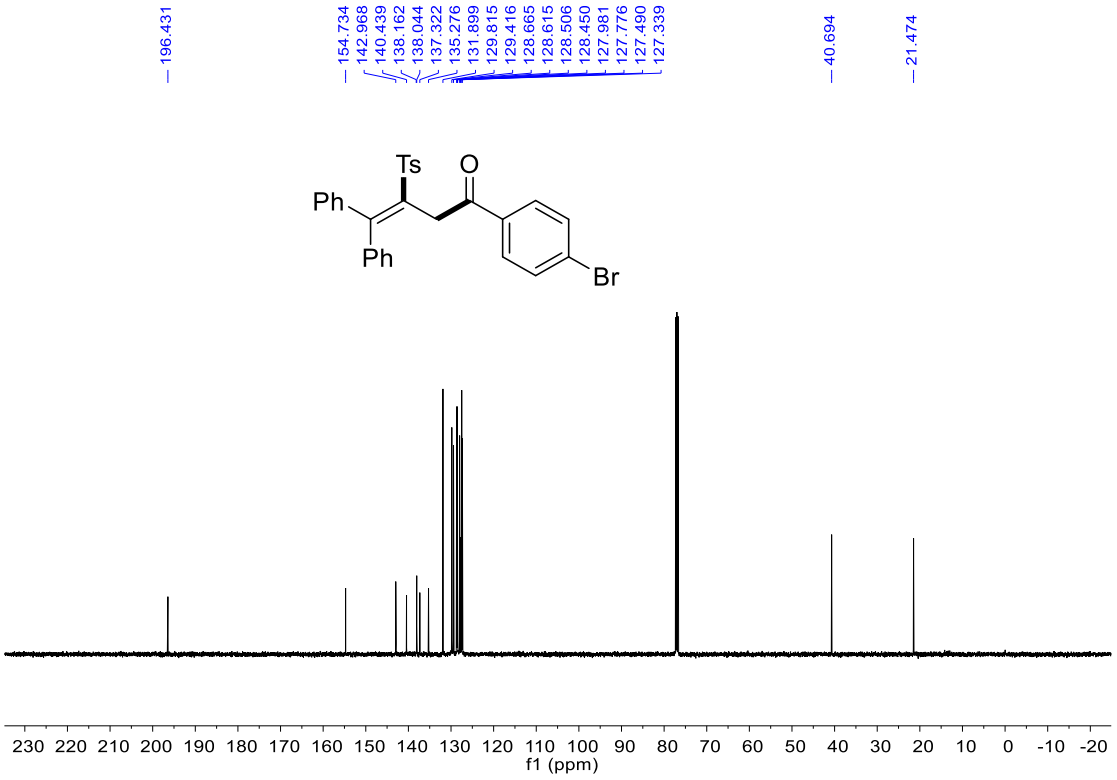
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **46**



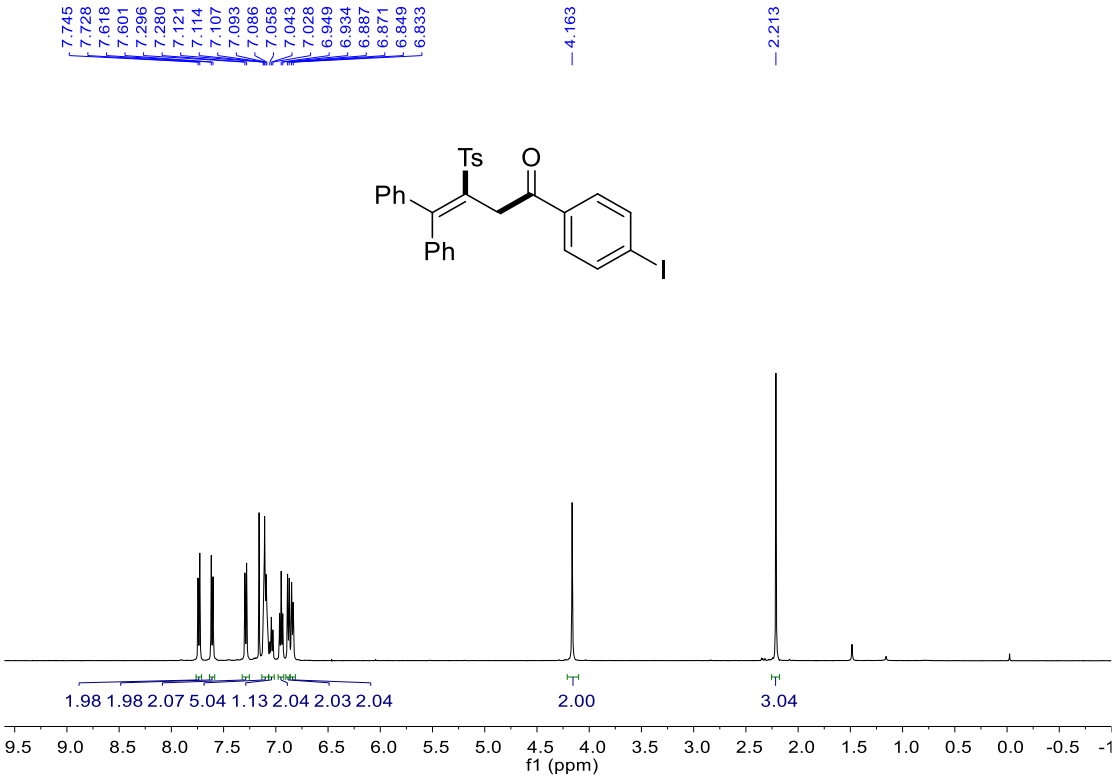
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **47**



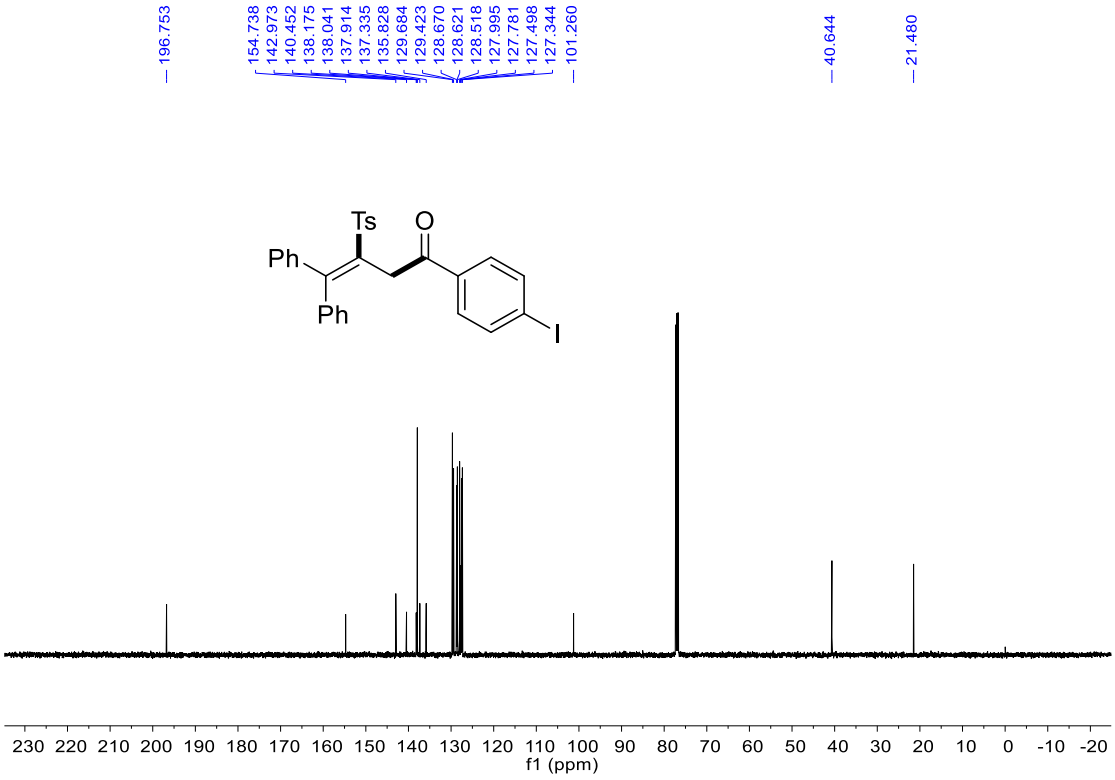
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **47**



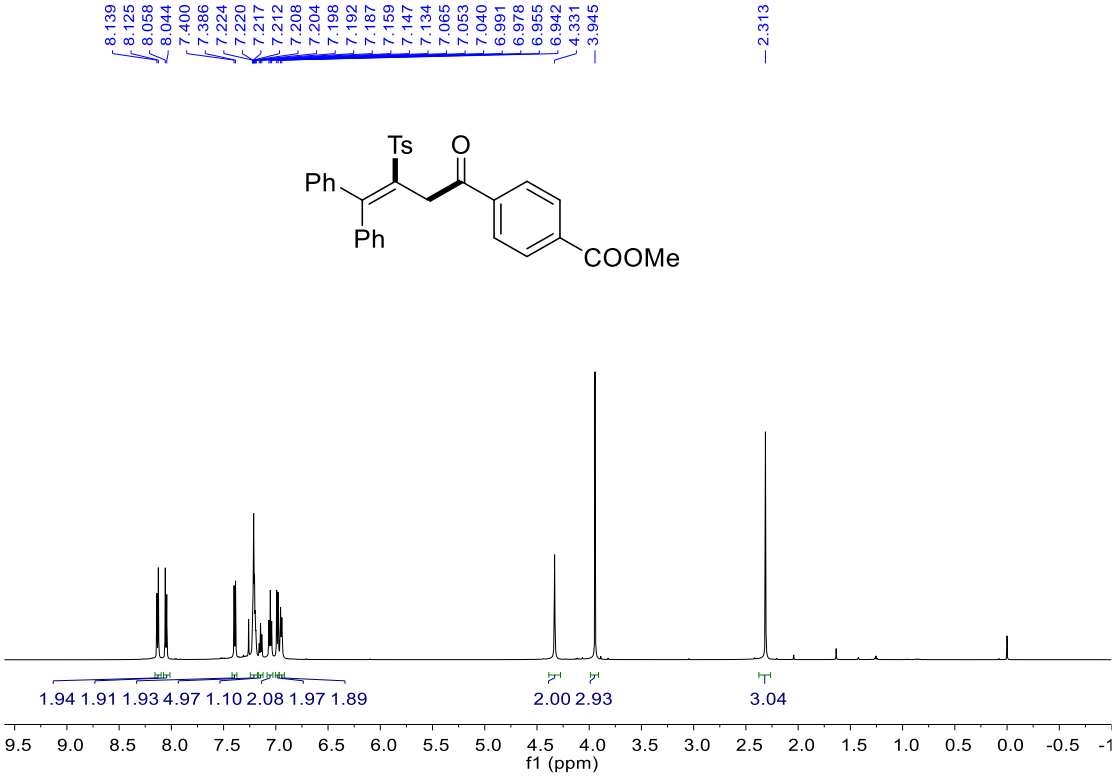
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **48**



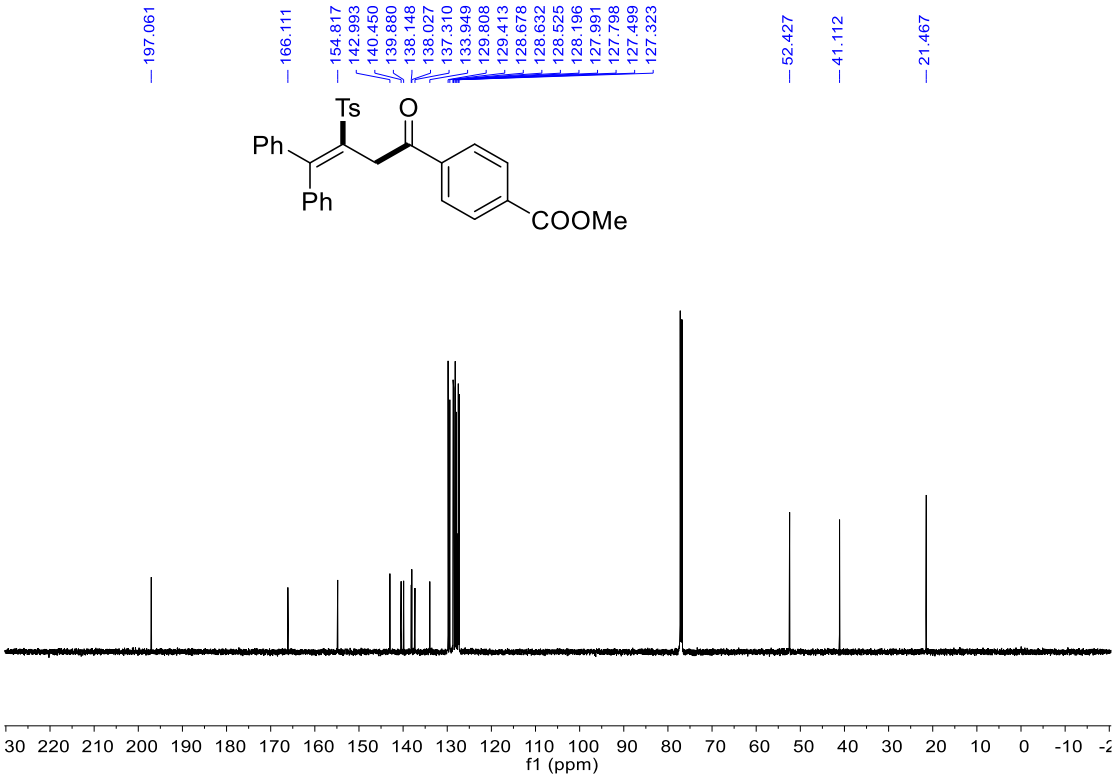
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **48**



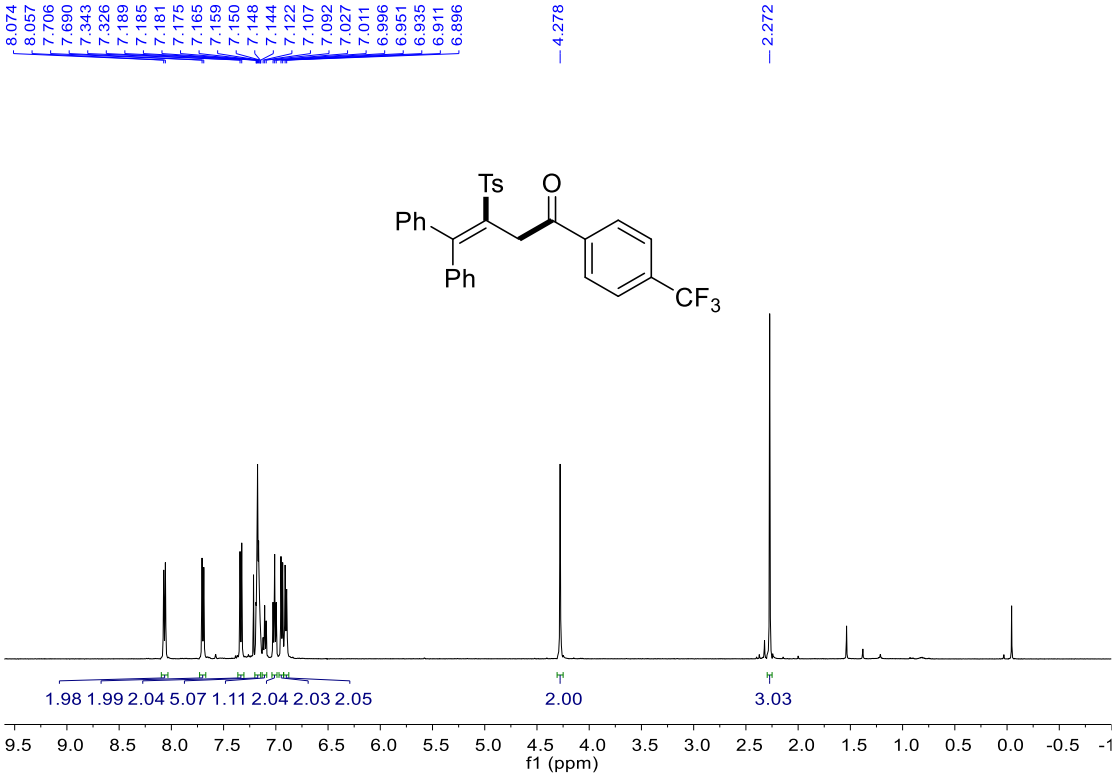
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **49**



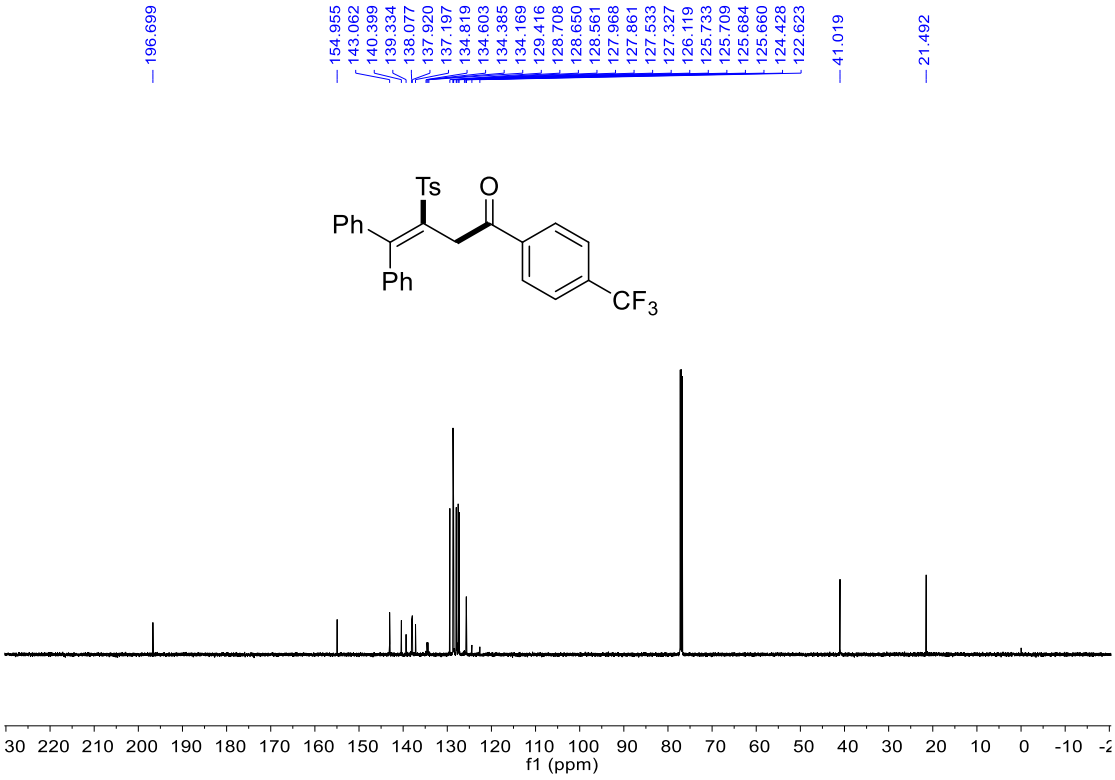
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **49**



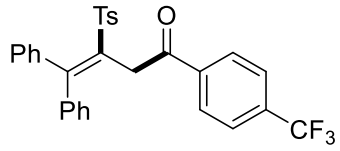
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **50**



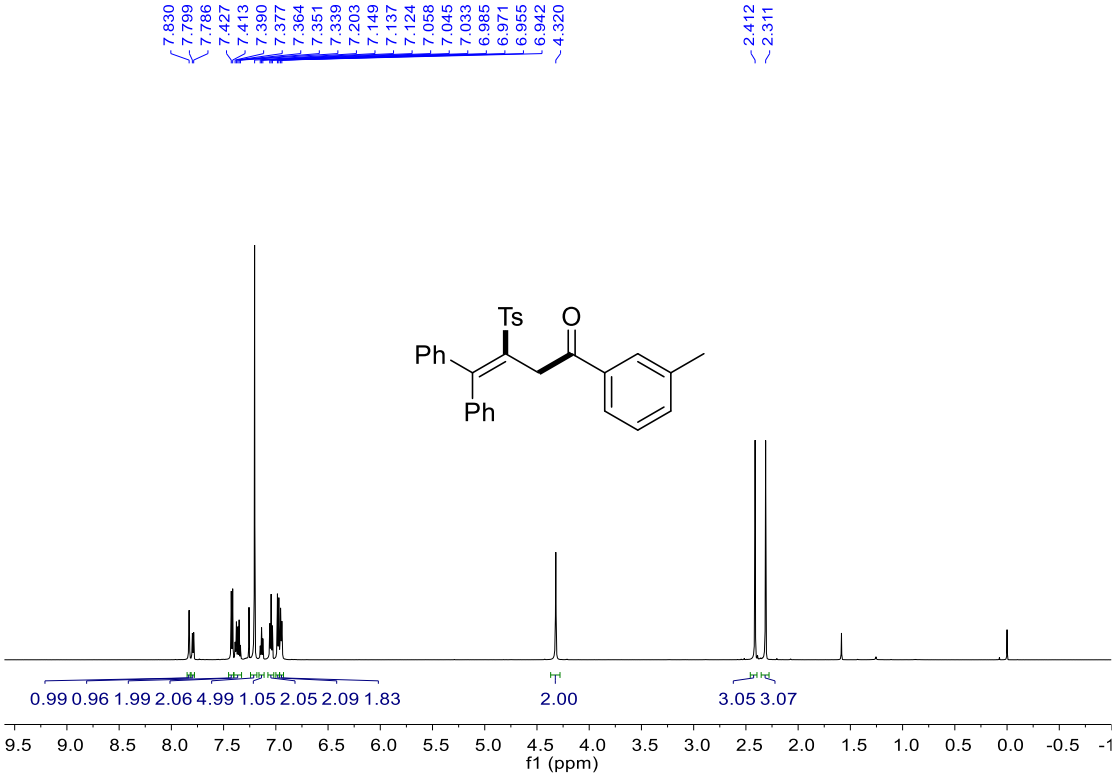
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **50**



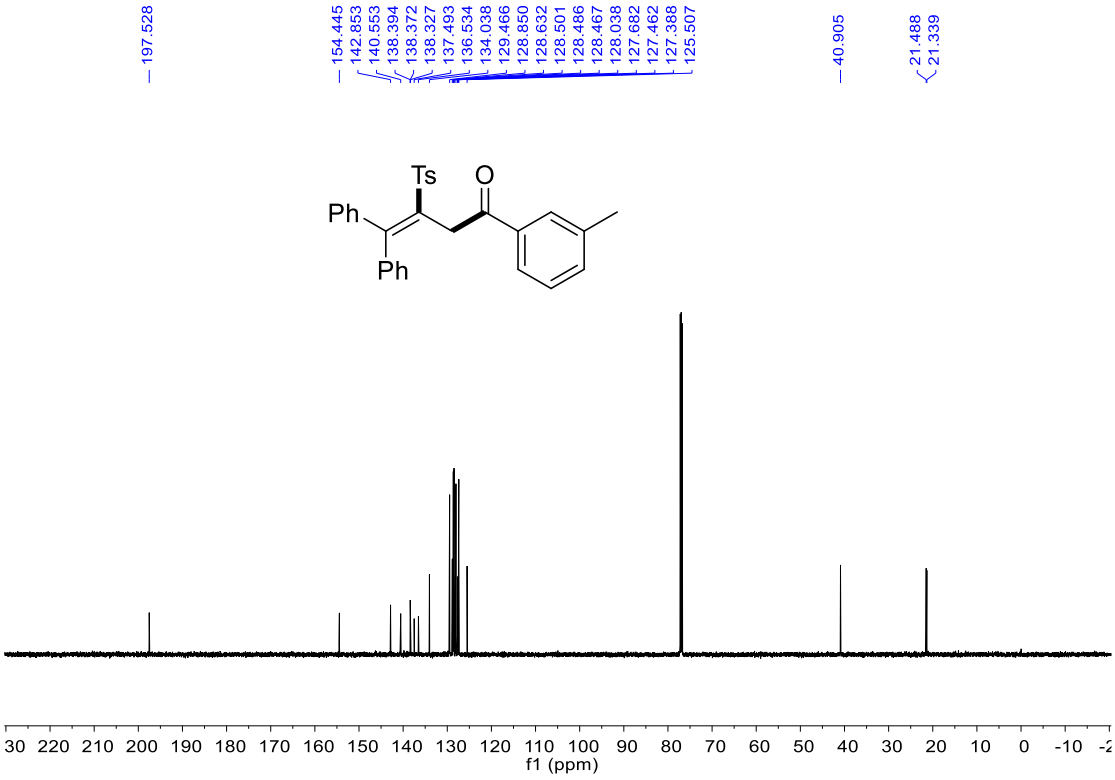
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **50**



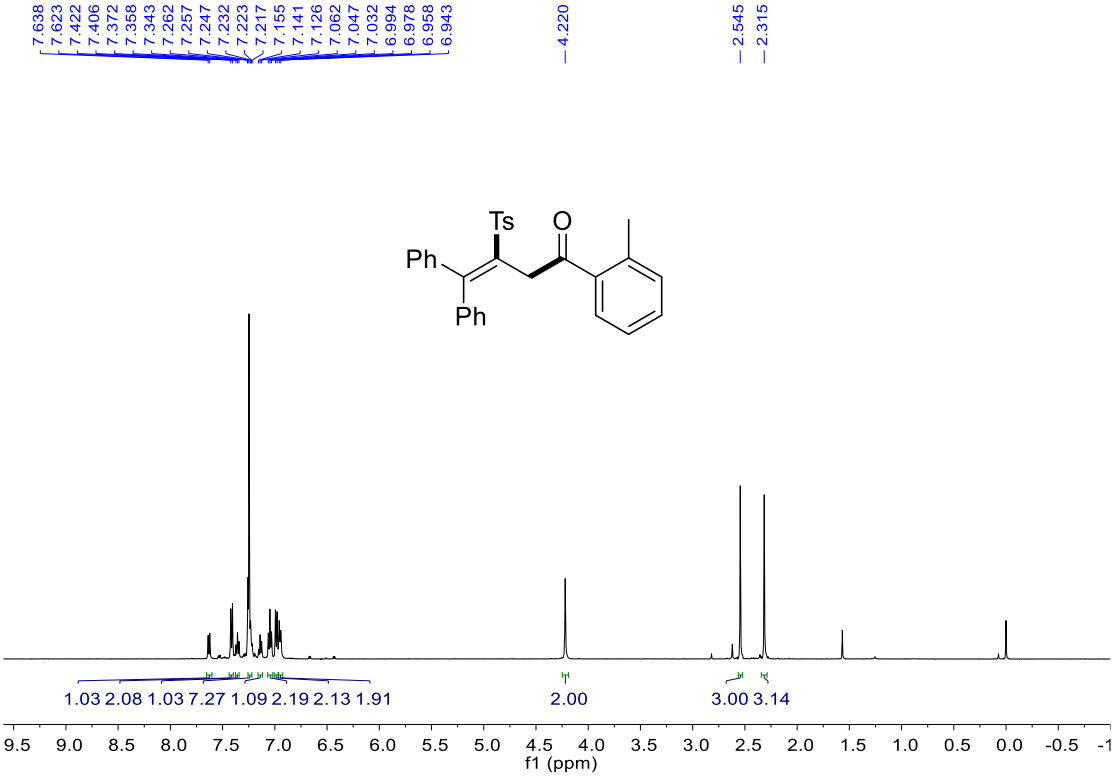
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **51**



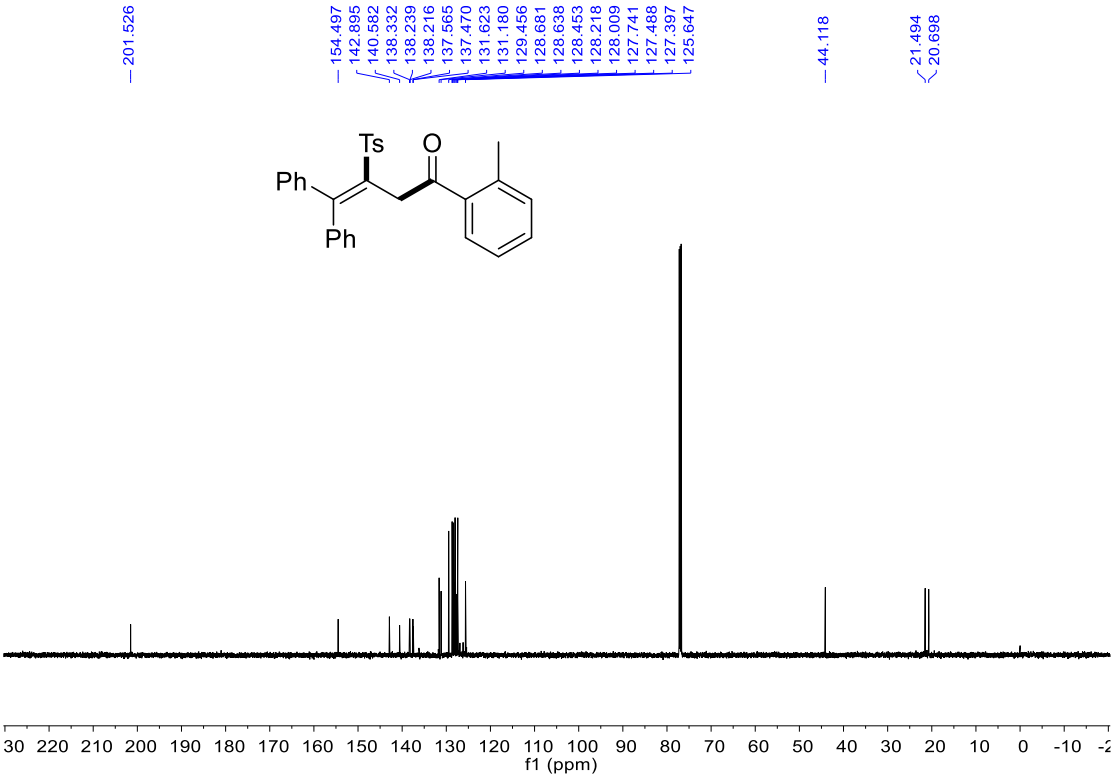
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **51**



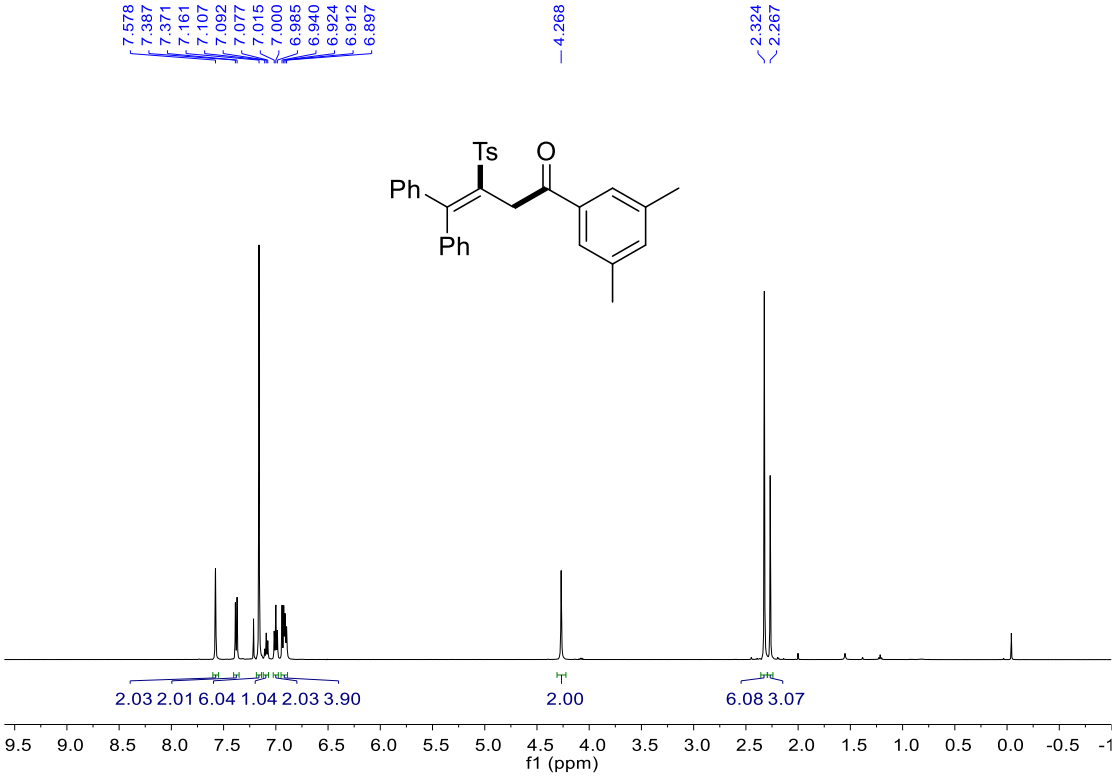
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **52**



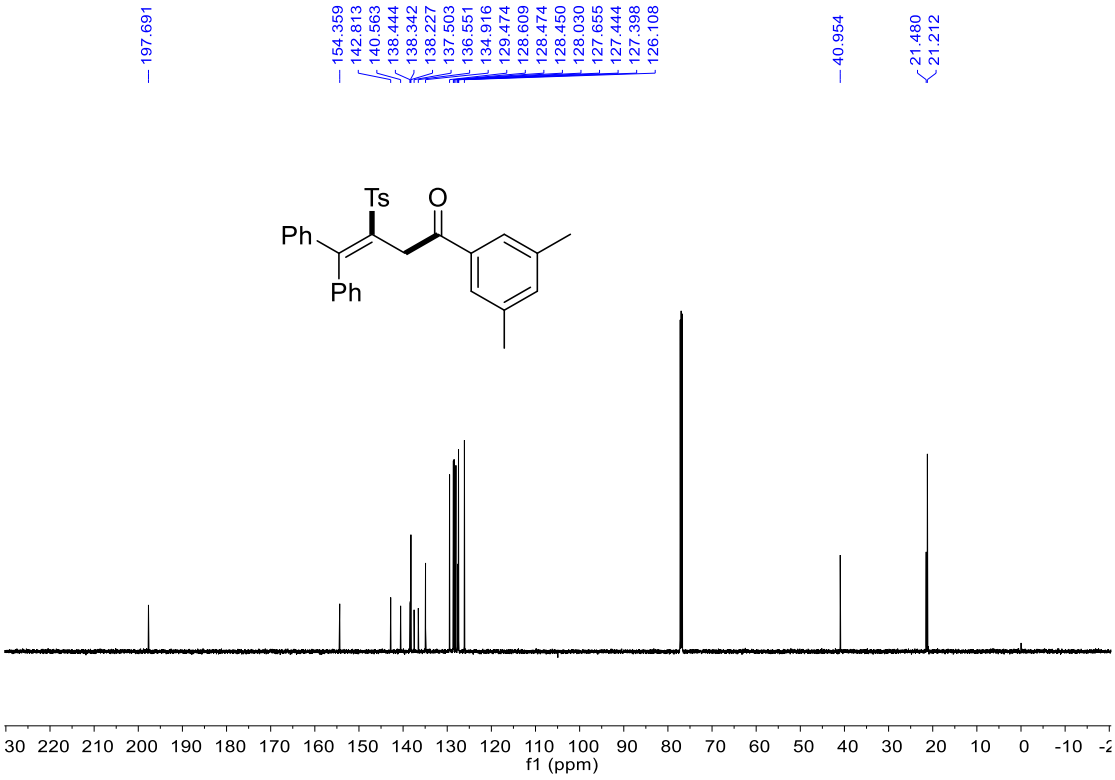
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **52**



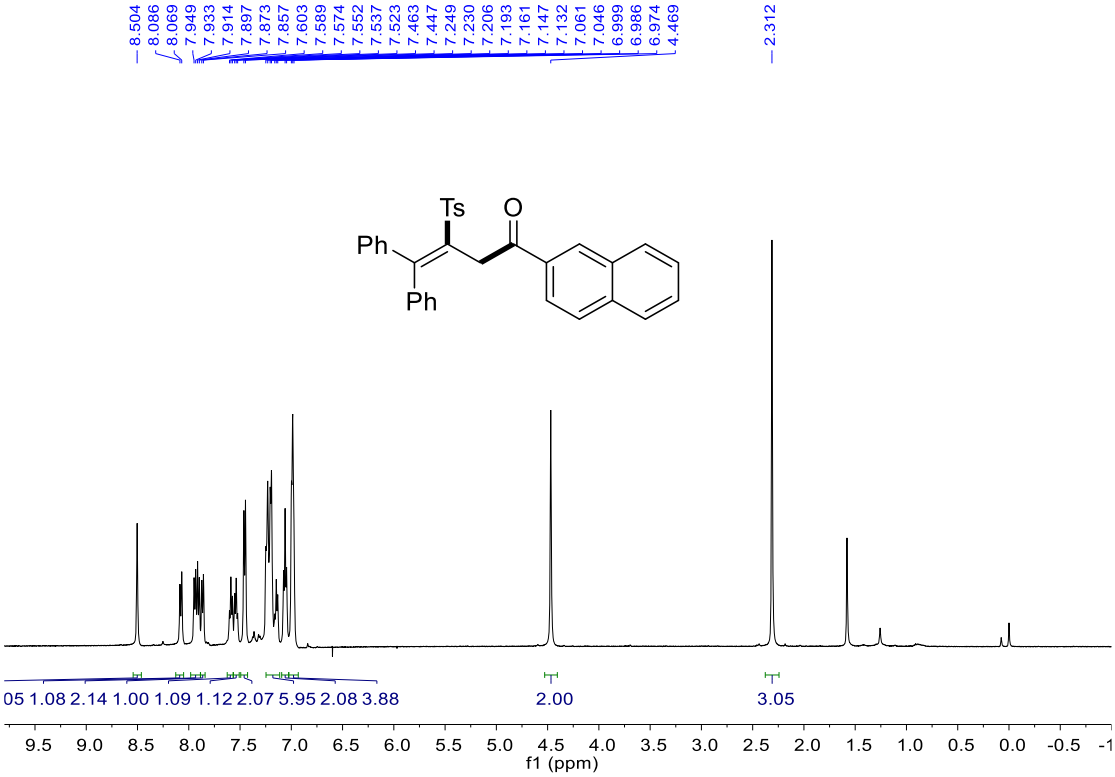
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **53**



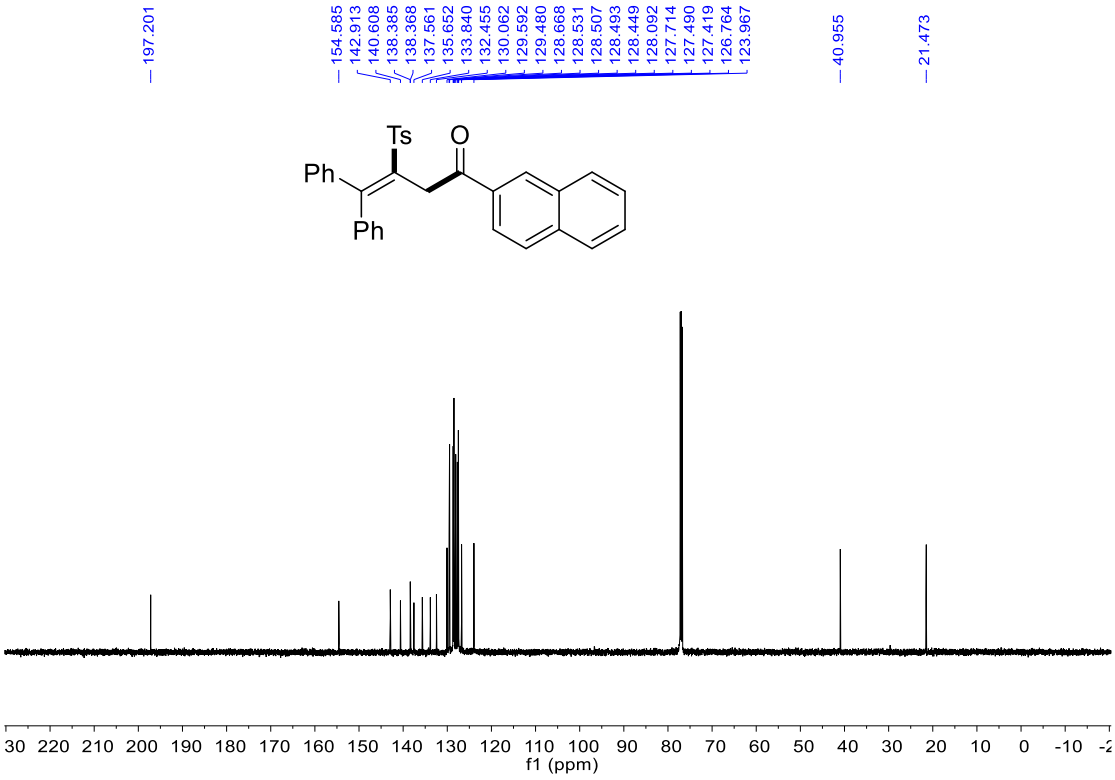
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **53**



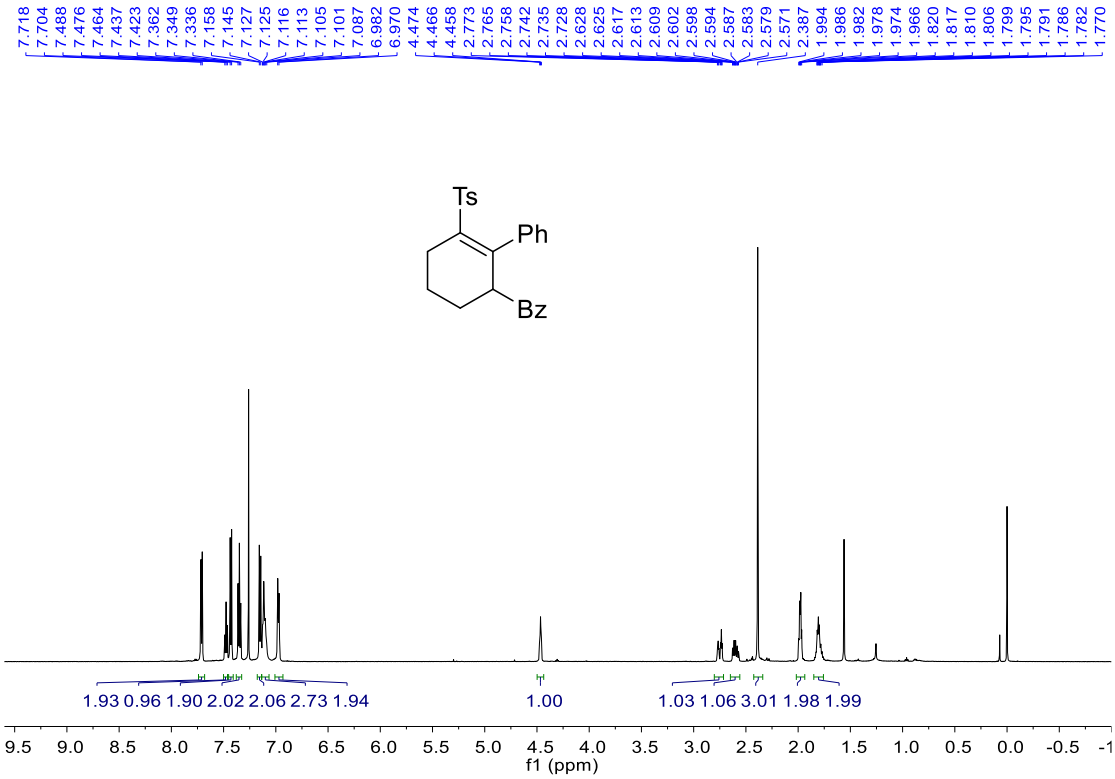
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **54**



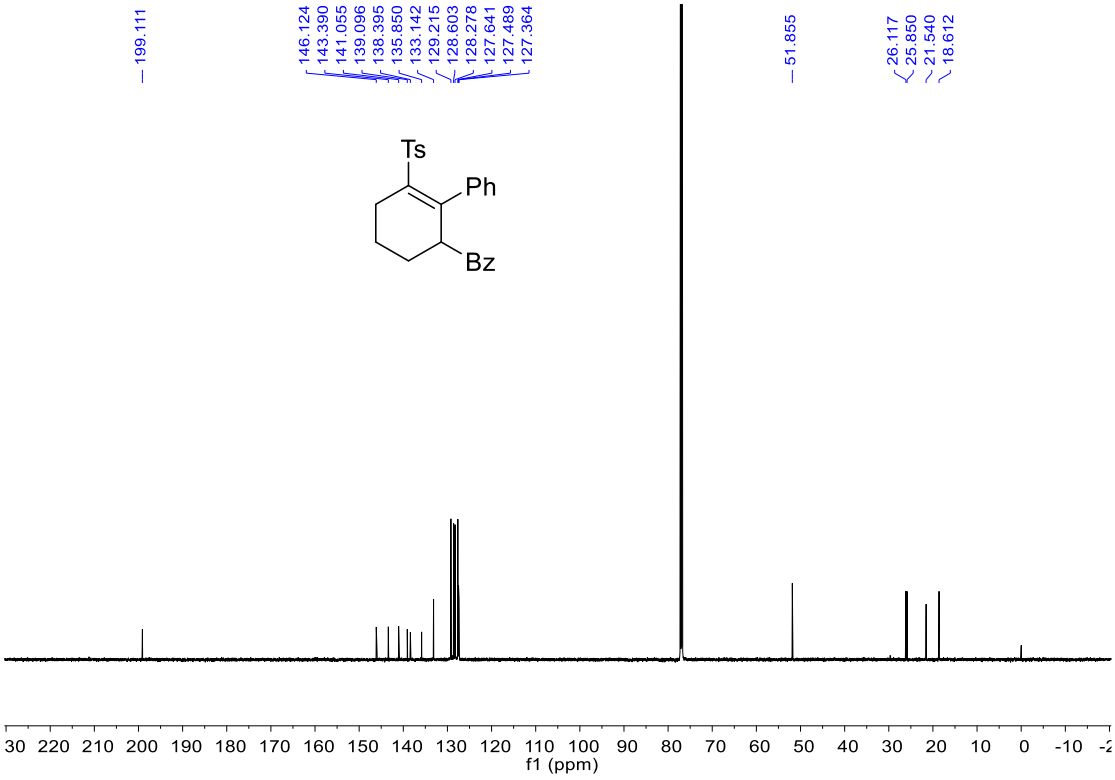
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **54**



H NMR (600 MHz, $CDCl_3$) spectrum for **58**



^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **58**



H NMR (500 MHz, $CDCl_3$) spectrum for **11'**