Supporting Information

NHCs and Visible Light-mediated Photoredox Co-catalyzed 1,4-Sulfonylacylation of 1,3-Enynes for Tetrasubstituted Allenyl Ketones

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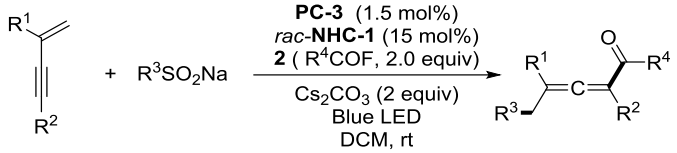
I. General Information

All reactions were carried out under nitrogen atmosphere. Reagents were purchased from commercial sources and used without further purification, unless otherwise noted. All of the solvents were anhydrous according 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 °C on a Bruker 600 or 500, Varian 500 MHz, **^{13}C NMR** spectra were recorded at 25 °C on a Bruker 151, Varian 126 MHz, respectively in $CDCl_3$ by using TMS as internal standard. **^{19}F NMR** spectra were recorded at 25 °C 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 manufactured by Beijing Rogertech Co.ltd base in Beijing PRC. This Photo reactor we used has equipped 8 blue light 10 W LED. This blue light 10 W LED's energy peak wavelength is 453.6 nm, peak width at half-height is 20.4 nm. Irradiation vessel is borosilicate glass test tube, LED irradiate through a high-reflection channel to the test tube, path length is 2 cm and no filter between LED and test tube. **NHC 1-5** were purchased from Daicelchiraltech. **NHC-6** was prepared according to the literature procedures[1]. Preparation of *Rac*-**NHC-1**: (5a*R*, 10b*S*)-**NHC-1** (250 mg) and (5a*S*, 10b*R*)-**NHC-1** (250 mg) are completely dissolved in dry DCM and concentrated to remove DCM.

II. General Procedure for the Synthesis of Tetrasubstituted Allenyl Ketones



1 **3** **4**

Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol), sulfinate (71.3 mg, 0.4 mmol) and DCM (8.0 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 room temperature for 4 hours. After the reaction finished that monitored by TLC, the reaction mixture was quenched by water. The mixture was extracted with EtOAc (3 x 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 = 10 : 1) to give the corresponding product **4**.

III. Preparation of the Starting Materials

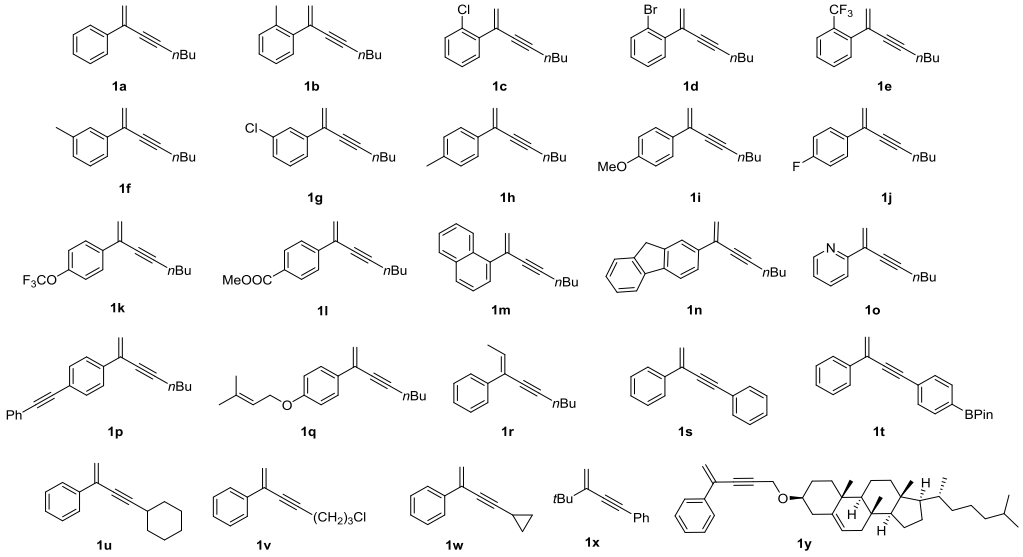
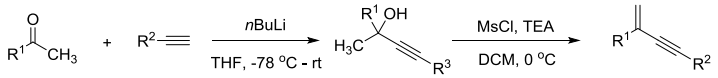


Table **S1**. The Substrates for 1,3-Enynes

Method A:

General Procedure for Preparation of 1,3-Enynes **1a–1o, 1r, 1s, 1u–1x**.

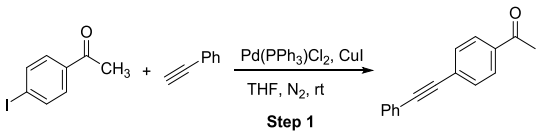


Step 1: A 100.0 mL round-bottomed flask equipped with a magnetic stir bar was charged with compound **S2** (20.0 mmol, 1.0 equiv) and 40.0 mL of THF. The solution was cooled to -78 ℃ and *n*BuLi (2.5 M in THF, 8.0 mL, 20.0 mmol, 1.0 equiv) was added. The resulting solution was stirred for 20 minutes at room temperature and then cooled to -78 ℃ again. Ketone **S1** (20.0 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 (40.0 mL). The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine (30.0 mL), dried over Na_2SO_4 and filtered, then concentrated under reduced pressure to afford the crude material **S3**.

Step 2 : The resulting crude material **S3** was dissolved in dry DCM (40 mL) and poured into 100.0 mL round-bottomed flask equipped with a magnetic stir bar, then the mixture was cooled to 0 ℃ with a cooling bath. To this solution was added TEA (100.0 mmol, 5.0 equiv) and methylsulfonyl chloride (50.0 mmol, 2.5 equiv) sequentially. After 30 min, the reaction was monitored by TLC for completion. On completion, the reaction was quenched with saturated aqueous NH_4Cl (40.0 mL). The aqueous layer was extracted with DCM, and the combined organic layers were washed with brine (30.0 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography to yield the 1,3-enynes.[2]

Method B:

Procedure for Preparation of 1,3-Enyne **1p**.

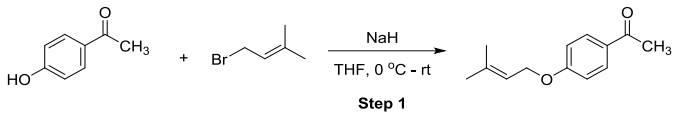


Step 1 : A 100.0 mL round bottomed flask equipped with a magnetic stir bar was charged with 20.0

mmol of 4'-Iodoacetophenone, 701.0 mg of $Pd(PPh_3)_2Cl_2$, 76.0 mg of CuI, 30.0 mmol of phenylacetylene, 30.0 mmol of triethylamine and 50.0 mL of THF. Then the mixture was stirred at room temperature for 16 h; afterward, the solvent was evaporated, and the residue was treated with pentane. Filtration through celite and evaporation of the solvent, the crude material was purified by flash chromatography to yield 1-(4-(phenylethynyl)phenyl)ethan-1-one.[3] The product was next used for Method A.

Method C:

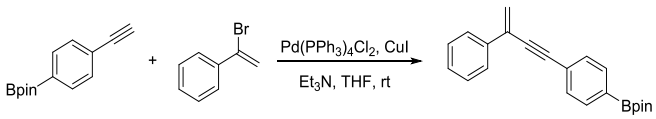
Procedure for Preparation of 1,3-Enyne **1q**.



A 50.0 mL round-bottomed flask equipped with a magnetic stir bar was charged with 4'-Hydroxyacetophenone (20.0 mmol, 1.0 equiv) and THF (30.0 mL). The solution was slowly added NaH (1.5 equiv) open to air at 0 ℃. The reaction mixture was allowed naturally to come to room temperature while stirring for 30 minutes. Then 3,3-Dimethylallyl bromide (1.2 equiv) was added dropwise. The reaction mixture was monitored by TLC for completion. After completion, the reaction was quenched with NH_4Cl (30.0 mL) and the aqueous phase extracted with DCM (3 x 20 mL). The combined organic layers were washed with saturated aqueous NaCl (30.0 mL) and dried over anhydrous Na_2SO_4, filtered off, and the solvent was removed in vacuo; the crude material was purified by flash chromatography to yield the 1-(4-((3-methylbut-2-en-1-yl)oxy)phenyl)ethan-1-one. The product was next used for Method A.

Method D:

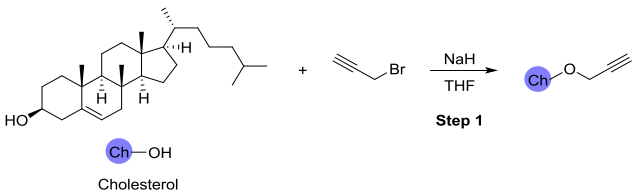
Procedure for Preparation of 1,3-Enyne **1t**.



A 50.0 mL round-bottomed flask equipped with a magnetic stir bar was charged with a mixture of 5.0 mmol of 2-(4-ethynylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 175.0 mg of $Pd(PPh_3)_2Cl_2$, 12.0 mg of CuI, 7.5 mmol of (1-bromovinyl)benzene, 7.5 mmol of triethylamine and THF (20.0 mL). Then the mixture was stirred at room temperature for 16 h; afterward, the solvent was evaporated, and the residue was treated with pentane. Filtration through celite and evaporation of the solvent, the crude material was purified by flash chromatography to yield the 1,3-enyne **1t**.[3]

Method E:

Procedure for Preparation of 1,3-Enyne **1y**.



A 100.0 mL round-bottomed flask equipped with a magnetic stir bar was charged with cholesterol (20.0 mmol, 1.0 equiv) and THF (50.0 mL); the solution was slowly added NaH (1.5 equiv) open to air at 0 ℃. The reaction mixture was allowed naturally to come to room temperature while stirring for 30 minutes. Then 3-Bromopropyne (1.2 equiv) was added dropwise. The reaction mixture was monitored by TLC for completion. After completion, the reaction was quenched with NH_4Cl (40.0 mL) and the aqueous phase extracted with DCM (3 x 30.0 mL). The combined organic layers were washed with saturated

aqueous NaCl (30.0 mL) and dried over anhydrous Na_2SO_4, filtered off, and the solvent was removed in vacuo. The crude material was purified by flash chromatography to yield the cholesterol ethyne. The product was next used for Method D.

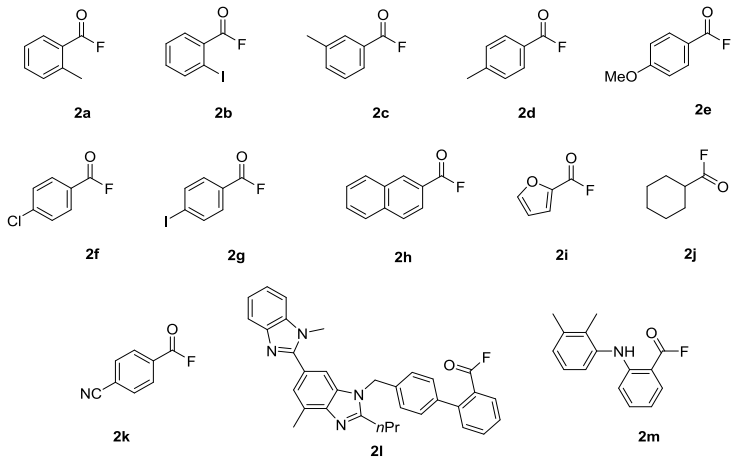
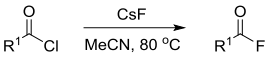


Table **S2**. The Substrates for Acyl Fluorides

Method F:

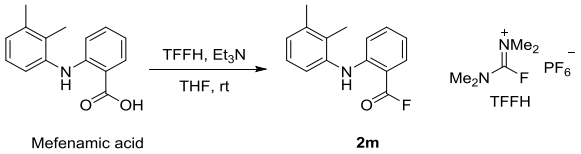
General Procedure for Preparation of Acyl Fluorides **2b–2i, 2k**.



A 25.0 mL round-bottomed flask equipped with a magnetic stir bar was charged with benzoyl chloride (5.0 mmol) and anhydrous acetonitrile (5.0 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 x 5 mL) and the combined organic solutions concentrated under vacuum. The resulting crude product was purified by column chromatography to yield the acyl fluorides.[4]

Method G:

Procedure for Preparation of Acyl Fluoride **2m**.



A 50.0 mL round bottom flask with a magnetic stirring bar was charged with carboxylic acid (5.0 mmol, 1.0 equiv), TFFH (5.5 mmol, 1.1 equiv), triethylamine (15.0 mmol, 3.0 equiv), and anhydrous THF (20.0 mL). The reaction mixture was stirred at room temperature. Within 5 min, the carboxylic acid and TFFH completely dissolve to form a homogeneous colorless solution. After 15 min, the reaction mixture was diluted with EtOAc (20.0 mL) and washed with ice-cold water (2 x 20.0 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting crude product was purified by column chromatography to yield **2m**.[5]

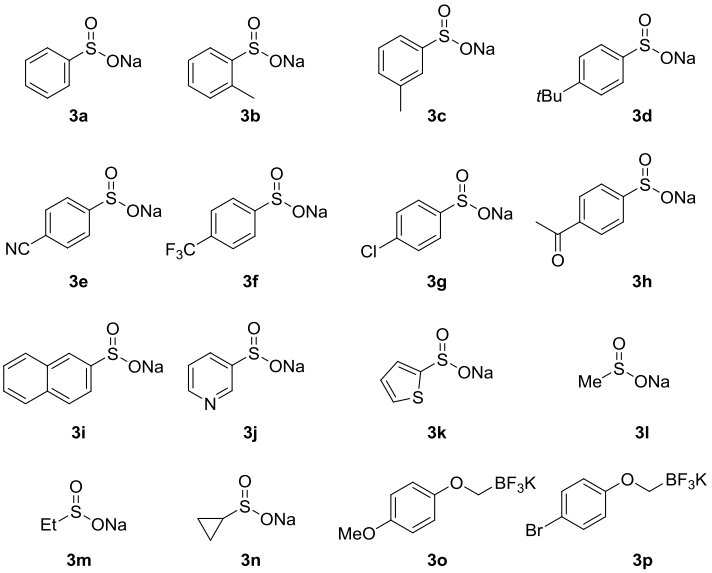
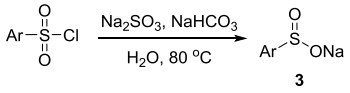


Table **S3**. The Substrates for Sulfinates and BF_3K

Method H:

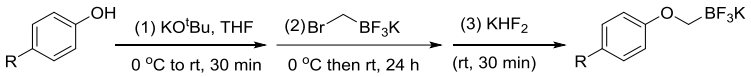
General Procedure for Preparation of Sulfinates **3b–3k**.



A 25.0 mL round bottom flask with a magnetic stirring bar were 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 ℃. After cooling to room temperature, the volatiles was removed in vacuo. The resultant solids were repeatedly washed with ethanol. The combined ethanol were evaporated under reduced pressure to yield the sulfinates.[6]

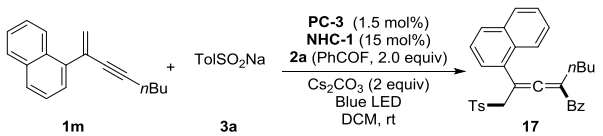
Method I:

Procedure for the Preparation of **3o** and **3p**.



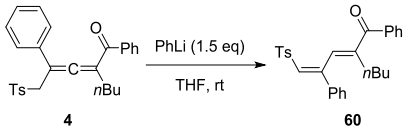
A 100 mL round bottom flask with a magnetic stirring bar was added potassium *tert*-butoxide (3.0 equiv) phenol (3.0 equiv) and anhydrous THF, at 0 ℃ under N_2. The reaction mixture was stirred at 0 ℃ for 15 min and then was allowed to warm to room temperature over 30 min. Potassium bromomehtyltrifluoroborate (10 mmol) was added in one batch at 0 ℃. The resulting reaction mixture was stirred at room temperature for 23 h, and 4.5 M KHF_2 (2.1 equiv) solution was added. The reaction mixture was stirred at room temperature for 30 min, and the white suspension was added with toluene (2–3 times). The solvent was removed, and the resulting solid was washed with Et_2O, followed by hot acetone.

IV. Procedure for Large-Scale Synthesis



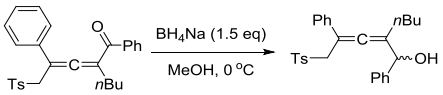
Into a nitrogen-filled glove box, a round-bottom flask (250.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (126.0 mg, 0.3 mmol), Cs_2CO_3 (1303.0 mg, 4.0 mmol), **PC-3** (27.0 mg, 0.03 mmol) sulfinate **3a** (713.0 mg, 4.0 mmol) and DCM (100.0 mL). Then **1m** (2.0 mmol) and **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 room temperature for 4 hours. After the reaction finished that monitored by TLC, the reaction mixture was quenched by water. The mixture was extracted with EtOAc (3 x 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 **17** (81%).

V. Derivatization Reactions



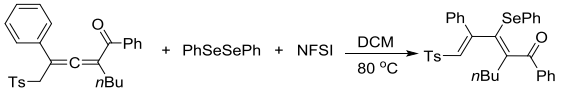
4 **60**

A vial (10.0 mL) equipped with a magnetic stir bar was charged with **4** (0.2 mmol) and THF (2.0 mL), then PhLi (1.5 eq) was added, and the mixture was stirred at rt for 5 h. After the reaction finished that monitored by TLC, the reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 15 : 1) to give the product **60** as a colorless oil (69.4 mg, 78% yield).



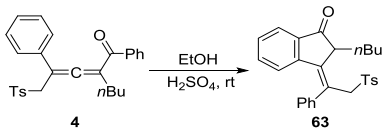
4 **61**

A 25.0 mL round-bottomed flask equipped with a magnetic stir bar was charged with compound **4** (0.2 mmol) and 2.0 mL MeOH under air. The solution was cooled to 0 °C, then $NaBH_4$ (15.1 mg, 2.0 equiv) was added. After 1 h, H_2O was added, extracted with EtOAc. The organic phase was washed with brine, dried with Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography to give the product **61** as a colorless oil (82.2 mg, 92% yield).[7]



4 **62**

A vial (10.0 mL) equipped with a magnetic stir bar was charged with **4** (0.2 mmol) and DCM (2.0 mL), Then NFSI (1.5 eq) and PhSeSePh (1.5 eq) were added. Afterward, the mixture was stirred at rt for 12 h. After the reaction finished that monitored by TLC, the reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10 : 1) to give the product **62** as a colorless oil (60.0 mg, 50% yield).



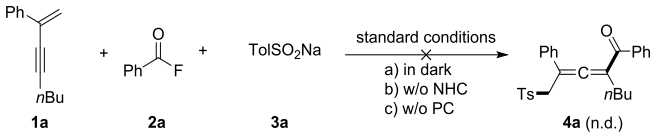
4 **63**

A vial (10.0 mL) equipped with a magnetic stir bar was charged with **4** (0.2 mmol), EtOH (0.2 mL), and H_2SO_4 (2.0 mL). Then the mixture was stirred at room temperature for 10 minutes. On completion, the reaction was quenched with H_2O (20.0 mL). The aqueous layer was extracted with EtOAc, and the combined organic layers were washed with brine (20.0 mL), dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography to afford product **63** as a colorless oil

(76.5 mg, 86% yield).

VI. Mechanistic Studies

Control Experiment

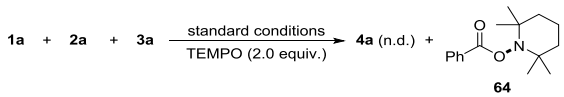


Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) **3a** (71.3 mg, 0.4 mmol) and DCM (8.0 mL). Then **1a** (0.2 mmol) and **2a** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was stirred in the dark for 4 hours at rt. Afterward, the reaction mixture was quenched by water. The mixture was extracted with EtOAc (3 x 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, the product **4a** was not detected.

Into a nitrogen-filled glove box, a vial (10.0 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 (8.0 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 room temperature for 4 hours. Afterward, the reaction mixture was quenched by water. The mixture was extracted with EtOAc (3 x 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 **4a** was not detected.

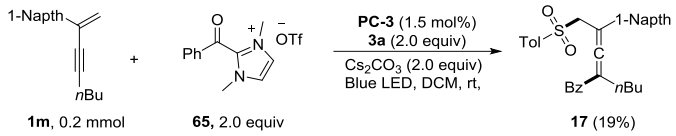
Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with **NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **3a** (71.3 mg, 0.4 mmol) and DCM (8.0 mL). Then **1a** (0.2 mmol) and **2a** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. Afterward, the reaction mixture was quenched by water. The mixture was extracted with EtOAc (3 x 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, the product **4a** was not detected.

The Radical Scavenger Experiment



Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 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 (8.0 mL). Then **1a** (0.2 mmol) and **2a** (0.4 mmol) were added. Finally, TEMPO (0.4 mmol, 2.0 equiv) was added to the mixture. The vial was removed from the glovebox and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After the reaction finished that monitored by TLC, the reaction mixture was quenched by water. The mixture was extracted with EtOAc (3 x 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, the product **4a** was not detected, then the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20 : 1) to give the corresponding product **64** with 55% yield (28.8 mg).

Possible Intermediate



Into a nitrogen-filled glove box, a vial (10.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 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 (8.0 mL). Then **1m** (0.2 mmol) and **65** (0.4 mmol) were added. The vial was removed from the glovebox, and then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After the reaction finished that monitored by TLC, the reaction mixture was quenched by water. The mixture was extracted with EtOAc (3 x 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 **17** (19%).

Emission Quenching Experiment

Emission intensities were recorded using a 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 nm was observed. Firstly, the emission spectrum of a 5 x 10^{-5} M solution of $[Ir(dtbbpy)(ppy)_2]PF_6$ in CH_3CN and H_2O (10 : 1) 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 **67** are easier than sodium benzenesulfinate **3a** and 1,3-enynes **1a** to quench the excited photosensitizer.

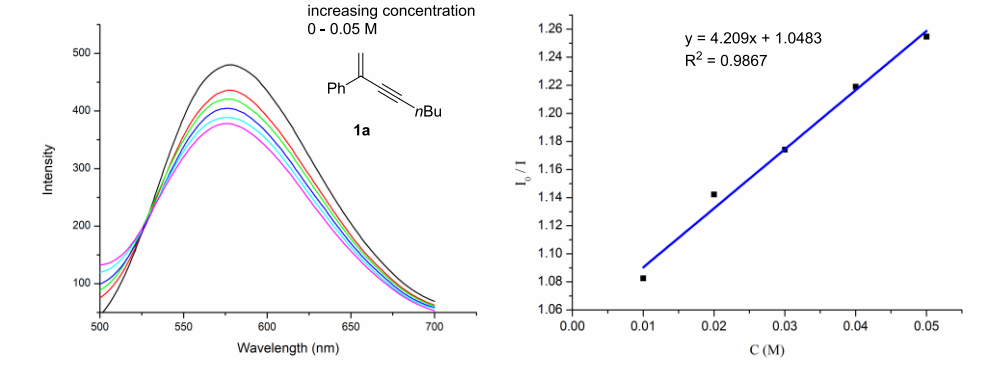


Figure **S1**. $[Ir(dtbbpy)(ppy)_2]PF_6$ emission quenching by 1,3-enynes **1a**

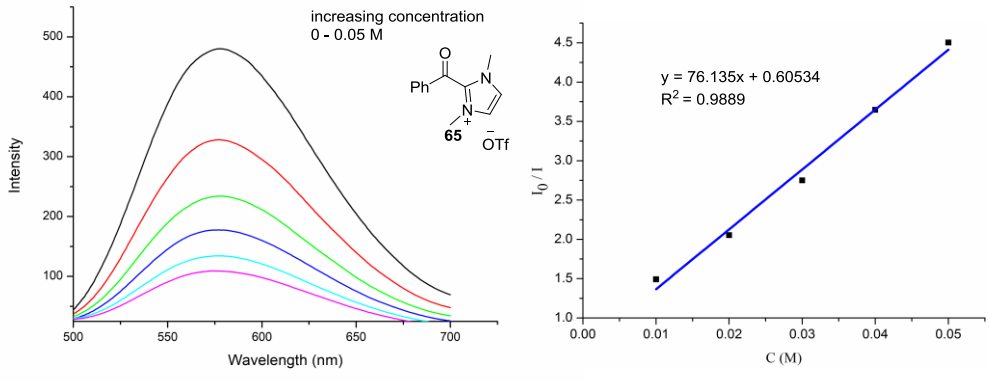


Figure **S2**. $[Ir(dtbbpy)(ppy)_2]PF_6$ emission quenching by acyl azolium ion **65**

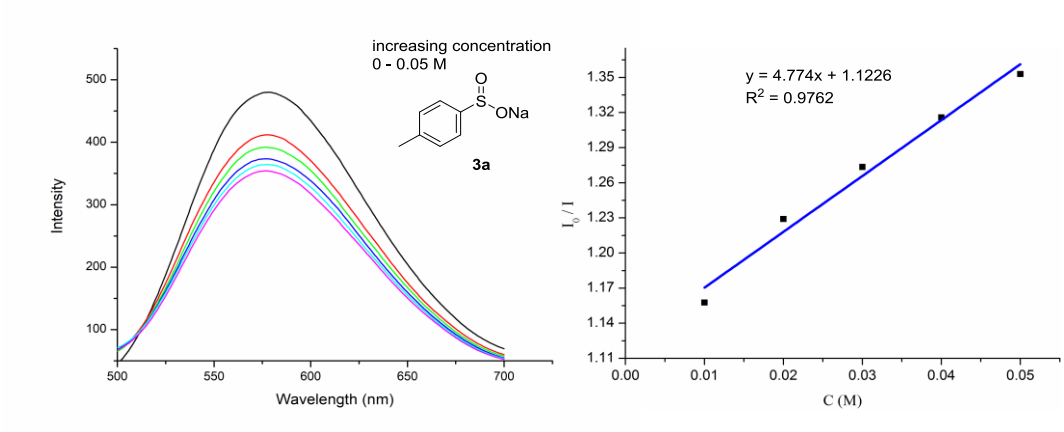


Figure **S3**. $[Ir(dtbbpy)(ppy)_2]PF_6$ emission quenching by sodium benzenesulfinate **3a**

Light on-off Experiment

Into a nitrogen-filled glove box, a vial (15.0 mL) equipped with a magnetic stir bar was charged with *rac*-**NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) sodium benzenesulfinate **3a** (71.3 mg, 0.4 mmol) and $CDCl_3$ (8.0 mL). Then **1m** (0.2 mmol), **2a** (0.4 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 10 minutes intervals at room temperature. Yields of the **17** were determined by ^1H 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 the continuous irradiation of visible light is essential for this catalytic reaction.

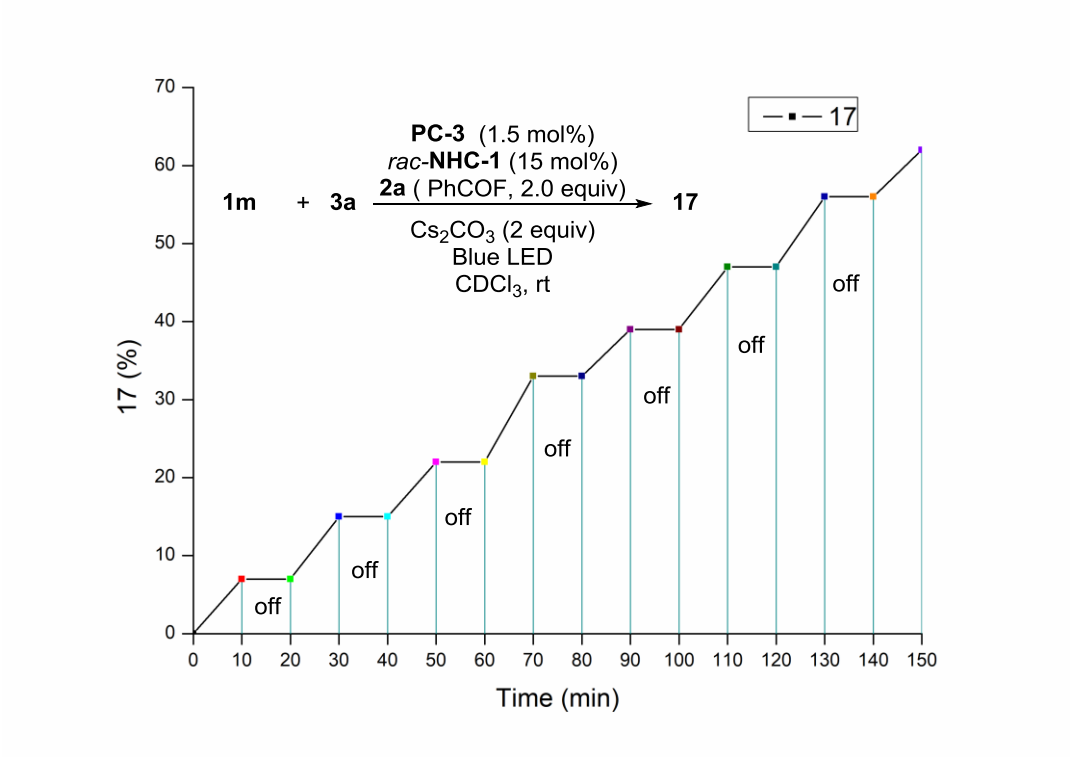


Figure **S4.** Light on-off Experiment

VII. X-ray Single Crystal Structure of 28

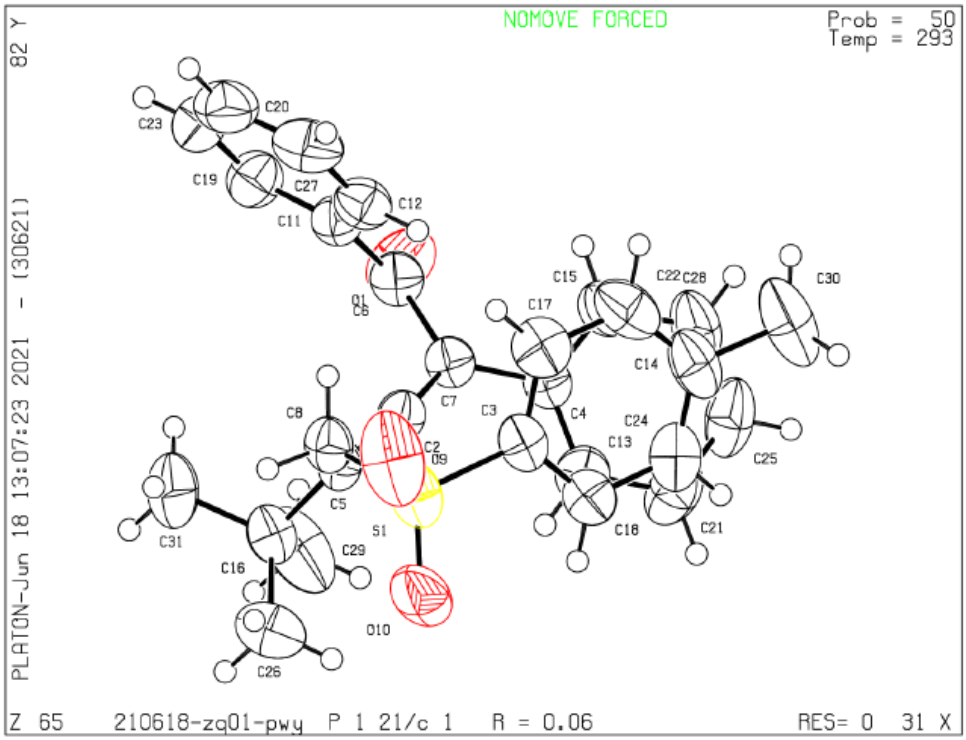


Figure **S5**. X-Ray Crystallography of **28**

CCDC number	2090996
Empirical formula	$C_{28}H_{28}O_3S$
Formula weight	444.56
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, Space group	monoclinic, P 2_1/C
Unit cell dimensions	a = 14.1193A alpha = 90 deg. b = 10.6583 A beta = 95.636 deg. c = 16.1923 A gamma = 90 deg.
Volume	2425.0 A^3
Z	4
Reflections collected / unique	10944 / 5671 [Rint = 0.0258]
F(000)	944.0
Absorption correction	Multi-Scan
Crystal size	0.15*0.15*0.1 mm^3
Data / restraints / parameters	5671/ 0 / 293
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0573, wR2 =0.1243
Final R indices (all data)	R1 = 0.1045, wR2 = 0.1551
Largest diff. peak and hole	0.25 and -0.45 e A^-3
$^aR_1 = \Sigma\|\|F_o\|-\|Fc\|\|/\Sigma\|Fo\|$; $^bwR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$	

VIII. References

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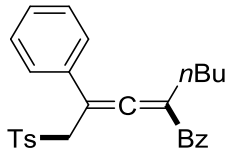
IX. Characterization Data of New Compounds



1-phenyl-2-(2-phenyl-3-tosylprop-1-en-1-ylidene)hexan-1-one (4)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a yellow oil (yield 66.6 mg, 75%).

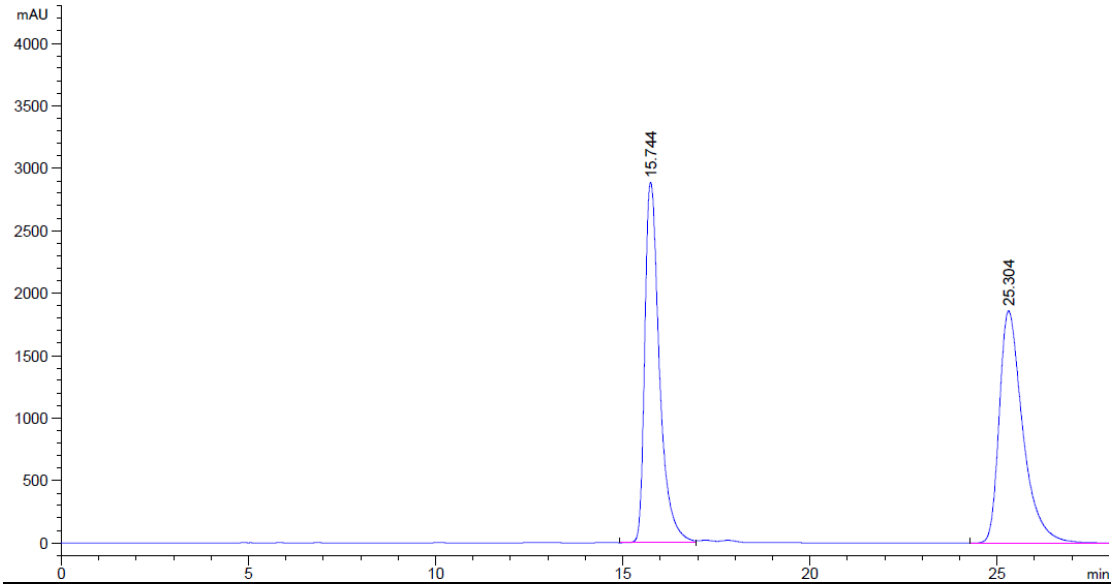
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2, 2H), 7.55 (d, *J* = 8.4, 2H), 7.43 (t, *J* = 7.4, 1H), 7.28 – 7.27 (m, 1H), 7.26 – 7.21 (m, 4H), 7.20 – 7.14 (m, 4H), 4.23 (d, *J* = 14.5 Hz, 1H), 4.04 (d, *J* = 14.6 Hz, 1H), 2.48 – 2.43 (m, 1H), 2.37 (s, 3H), 2.31 – 2.26 (m, 1H), 1.50 – 1.46(m, 2H), 1.41 – 1.36 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 215.24, 193.52, 144.74, 138.07, 135.65, 133.21, 132.42, 129.63, 128.63, 128.59, 128.42, 128.00, 127.86, 126.34, 110.06, 99.79, 57.80, 30.38, 28.71, 22.62, 21.50, 13.82.

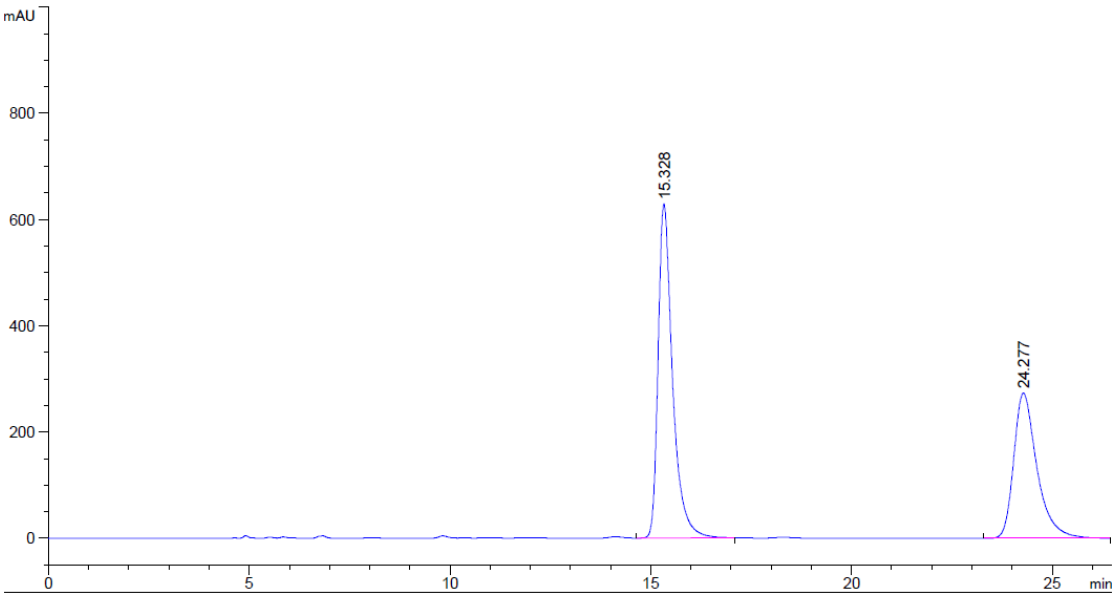
HRMS (ESI) (m/z): calcd for $C_{28}H_{28}NaO_3S$ ([M + Na] $^{+}$), 467.1651; found, 467.1663.

IR (neat): ν (cm^{-1}) 3029, 2957, 2928, 2871, 1929, 1655, 1596, 1578, 1494, 1448, 1402, 1320, 1303, 1269, 1209, 1154, 1134, 1085, 814, 746, 695.

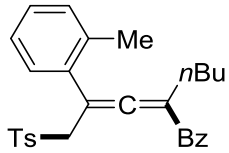
HPLC analysis (IA, Hexane/IPA = 80/20, 0.8 mL/min, 254 nm) indicated 59:41 e.r. tR (major) = 15.328 min, tR (minor) = 24.277 min.



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	15.744	MF R	0.4542	7.86457e4	2885.89526	49.2579
2	25.304	BB	0.6580	8.10154e4	1857.02283	50.7421



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	15.328	BB	0.3725	1.56488e4	628.53644	58.7840
2	24.277	BBA	0.6005	1.09721e4	273.20340	41.2160



1-phenyl-2-(2-(o-tolyl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (6)

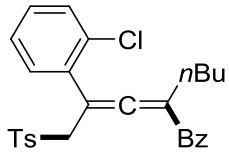
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 74.1 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.15 (td, *J* = 7.4, 1.4 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.84 (dd, *J* = 7.6, 1.3 Hz, 1H), 4.04 (d, *J* = 14.3 Hz, 1H), 4.00 (d, *J* = 14.3 Hz, 1H), 2.45 – 2.39 (m, 4H), 2.33 – 2.32 (m, 1H), 1.94 (s, 3H), 1.55 – 1.46 (m, 2H), 1.38 (p, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.04, 194.38, 144.72, 138.61, 136.14, 135.43, 133.91, 132.27, 130.63, 129.70, 128.80, 128.76, 128.17, 128.13, 128.05, 125.96, 107.88, 98.14, 60.10, 30.40, 28.32, 22.65, 21.58, 19.88, 13.88.

HRMS (ESI) (m/z): calcd for $C_{29}H_{30}NaO_3S$ ([M + Na] $^+$), 481.1808; found, 481.1813.

IR (neat): ν (cm^{-1}) 3061, 2957, 2927, 2871, 1938, 1654, 1596, 1446, 1320, 1303, 1270, 1151, 1135, 1086, 815, 759, 717, 697.



2-(2-(2-chlorophenyl)-3-tosylprop-1-en-1-ylidene)-1-phenylhexan-1-one (7)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a white solid (yield 70.7 mg, 74%), mp 90 – 91 °C.

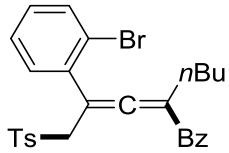
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.60 – 7.56 (m, 2H), 7.51 – 7.48 (m, 1H), 7.33 – 7.28 (m, 3H), 7.25 – 7.20 (m, 3H), 7.18 (td, *J* = 7.5, 1.4 Hz, 1H), 7.07 (dd, *J* = 7.6, 1.8 Hz, 1H), 4.24 (d,

J = 14.5 Hz, 1H), 4.06 (d, *J* = 14.5 Hz, 1H), 2.45 – 2.39 (m, 4H), 2.31 – 2.26 (m, 1H), 1.54 – 1.43 (m, 2H), 1.39 – 1.33 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.51, 193.77, 144.73, 138.21, 135.90, 133.21, 132.43, 132.35, 131.18, 129.93, 129.70, 129.49, 128.79, 128.25, 128.12, 126.90, 108.36, 97.54, 59.21, 30.22, 28.42, 22.60, 21.58, 13.86.

HRMS (ESI) (m/z): calcd for $C_{28}H_{27}ClNaO_3S$ ([M + Na] $^+$), 501.1262; found, 501.1264.

IR (neat): ν (cm^{-1}) 3062, 2957, 2928, 2871, 1941, 1655, 1596, 1446, 1321, 1270, 1152, 1136, 1085, 755, 700.



2-(2-(2-bromophenyl)-3-tosylprop-1-en-1-ylidene)-1-phenylhexan-1-one (8)

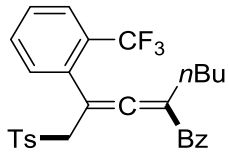
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 76.2 mg, 73%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.20 (m, 3H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H), 7.05 (d, *J* = 7.6, 1H), 4.23 (d, *J* = 14.4 Hz, 1H), 4.09 (d, *J* = 14.4 Hz, 1H), 2.47 – 2.39 (m, 4H), 2.32 – 2.30 (m, 1H), 1.57 – 1.44 (m, 2H), 1.40 – 1.34 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.00, 193.80, 144.72, 138.33, 135.96, 135.27, 133.06, 132.44, 131.51, 129.71, 129.65, 128.86, 128.19, 127.39, 122.11, 108.49, 98.85, 59.31, 30.26, 28.49, 22.57, 21.57, 13.87.

HRMS (ESI) (m/z): calcd for $C_{28}H_{27}BrNaO_3S$ ([M + Na] $^+$), 545.0756; found, 545.0766.

IR (neat): ν (cm^{-1}) 3061, 2957, 2928, 2870, 1941, 1656, 1596, 1468, 1446, 1433, 1321, 1303, 1270, 1151, 1135, 1085, 941, 814, 761, 719, 697.



1-phenyl-2-(3-tosyl-2-(2-(trifluoromethyl)phenyl)prop-1-en-1-ylidene)hexan-1-one (9)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 74.8 mg, 73%).

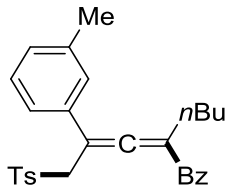
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.63 – 7.60 (m, 2H), 7.59 – 7.58 (m, 1H), 7.56 – 7.53 (m, 1H), 7.46 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.27 – 7.23 (m, 2H), 7.21 – 7.18 (m, 1H), 4.04 (d, *J* = 3.3 Hz, 1H), 4.01 (d, *J* = 3.3 Hz, 1H), 2.48 – 2.45 (m, 1H), 2.42 (s, 3H), 2.40 – 2.35 (m, 1H), 1.55 – 1.46 (m, 2H), 1.39 – 1.33 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.36, 193.82, 144.84, 138.49, 136.20, 133.51, 132.64, 132.05, 131.84, 129.83, 128.97, 128.48, 128.07, 127.81 (q, *J* = 60.6 Hz), 126.53 (q, *J* = 10.1 Hz), 123.65 (q, *J* = 273.9 Hz), 108.59, 96.24, 60.13, 30.25, 29.042, 22.53, 21.57, 13.80.

^{19}F NMR (565 MHz, $CDCl_3$) δ -59.00.

HRMS (ESI) (m/z): calcd for $C_{29}H_{27}F_3NaO_3S$ ([M + Na] $^+$), 535.1525; found, 535.1515.

IR (neat): ν (cm^{-1}) 3063, 2958, 2930, 2872, 1943, 1658, 1598, 1492, 1447, 1315, 1270, 1171, 1137, 1086, 1065, 1035, 941, 815, 768, 720, 698.



1-phenyl-2-(2-(m-tolyl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (10)

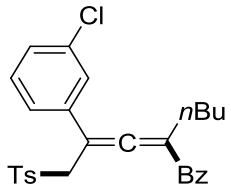
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 62.2 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.16 – 7.15 (m, 3H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.83 (s, 1H), 4.22 (d, *J* = 14.5 Hz, 1H), 4.03 (d, *J* = 14.5 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.38 (s, 3H), 2.33 – 2.28 (m, 1H), 2.26 (s, 3H), 1.52 – 1.43 (m, 2H), 1.42 – 1.36 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 215.39, 193.65, 144.72, 138.22, 138.18, 135.70, 133.09, 132.41, 129.60, 128.66, 128.55, 128.50, 128.03, 126.90, 123.61, 110.00, 99.82, 57.91, 30.41, 28.73, 22.65, 21.54, 21.37, 13.89.

HRMS (ESI) (m/z): calcd for $C_{29}H_{30}NaO_3S$ ([M + Na] $^+$), 481.1808; found, 481.1808.

IR (neat): ν (cm^{-1}) 3057, 2957, 2927, 2870, 1930, 1655, 1597, 1446, 1402, 1321, 1303, 1269, 1155, 1134, 1086, 871, 814, 788, 758, 696.



2-(2-(3-chlorophenyl)-3-tosylprop-1-en-1-ylidene)-1-phenylhexan-1-one (11)

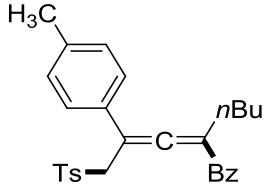
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 66.9 mg, 70%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.54 – 7.53 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.8, 2H), 7.22 – 7.16 (m, 4H), 7.07 – 7.06 (m, 1H), 6.95 (s, 1H), 4.17 (d, *J* = 14.6 Hz, 1H), 4.01 (d, *J* = 14.6 Hz, 1H), 2.50 – 2.45 (m, 1H), 2.39 (s, 3H), 2.37 – 2.31 (m, 1H), 1.52 –1.47 (m, 2H), 1.44 – 1.36 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 215.12, 193.25, 145.08, 138.05, 135.45, 135.31, 134.65, 132.65, 129.84, 129.76, 128.62, 128.46, 128.15, 127.87, 126.30, 124.61, 110.48, 98.96, 57.83, 30.35, 28.80, 22.64, 21.57, 13.86.

HRMS (ESI) (m/z): calcd for $C_{28}H_{27}ClNaO_3S$ ([M + Na] $^+$), 501.1262; found, 501.1251.

IR (neat): ν (cm^{-1}) 3059, 2957, 2927, 2871, 1941, 1655, 1596, 1446, 1320, 1303, 1270, 1151, 1136, 1085, 814, 754, 700.



1-phenyl-2-(2-(p-tolyl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (12)

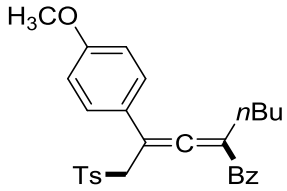
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 70.6 mg, 77%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.58 – 7.54 (m, 2H), 7.43 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.06 (m, 4H), 4.22 (d, *J* = 14.5 Hz, 1H), 4.01 (d, *J* = 14.5 Hz, 1H), 2.45 – 2.38 (m, 4H), 2.33 (s, 3H), 2.26 – 2.18 (m, 1H), 1.48 – 1.41 (m, 2H), 1.41 – 1.33 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 215.24, 193.64, 144.74, 138.11, 137.93, 135.69, 132.41, 130.14, 129.65, 129.42, 128.64, 128.48, 128.02, 126.31, 110.00, 99.72, 57.88, 30.46, 28.72, 22.67, 21.57, 21.11, 13.88.

HRMS (ESI) (m/z): calcd for $C_{29}H_{30}NaO_3S$ ([M + Na] $^+$), 481.1808; found, 481.1802.

IR (neat): ν (cm^{-1}) 3027, 2957, 2926, 2870, 1928, 1654, 1596, 1510, 1446, 1319, 1303, 1268, 1181, 1150, 1135, 815, 709.



2-(2-(4-methoxyphenyl)-3-tosylprop-1-en-1-ylidene)-1-phenylhexan-1-one (13)

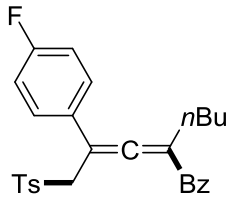
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow solid (yield 74.0 mg, 78%), mp 35 – 36 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.25(t, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.09 (m, 2H), 6.85 – 6.81 (m, 2H), 4.21 (d, *J* = 14.5 Hz, 1H), 4.01 (d, *J* = 14.5 Hz, 1H), 3.81 (s, 3H), 2.42 – 2.36 (m, 4H), 2.23 – 2.16 (m, 1H), 1.47 – 1.41 (m, 2H), 1.39 – 1.33 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 215.07, 193.68, 159.40, 144.74, 138.09, 135.65, 132.42, 129.66, 128.65, 128.48, 128.02, 127.70, 125.19, 114.18, 109.95, 99.45, 58.00, 55.31, 30.48, 28.74, 22.68, 21.58, 13.89.

HRMS (ESI) (m/z): calcd for $C_{29}H_{30}NaO_4S$ ([M + Na] $^+$), 497.1757; found, 497.1743.

IR (neat): ν (cm^{-1}) 3027, 2955, 2923, 2853, 1925, 1656, 1606, 1512, 1462, 1315, 1246, 1135, 1084, 1016, 839, 813, 764, 714, 697.



2-(2-(4-fluorophenyl)-3-tosylprop-1-en-1-ylidene)-1-phenylhexan-1-one (14)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 69.3 mg, 75%).

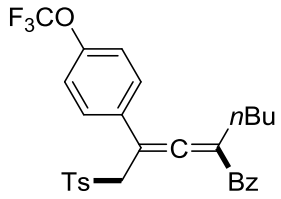
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 4H), 7.47 – 7.44 (m, 1H), 7.29 – 7.24 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.13 (m, 2H), 7.02 – 6.94 (m, 2H), 4.20 (d, *J* = 14.5 Hz, 1H), 4.02 (d, *J* = 14.5 Hz, 1H), 2.47 – 2.35 (m, 4H), 2.28 – 2.23 (m, 1H), 1.52 – 1.42 (m, 2H), 1.41 – 1.33 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.88, 193.42, 162.32 (d, *J* = 248 Hz), 144.95, 137.95, 135.53, 132.58, 129.27, 128.58, 128.42, 128.15 (d, *J* = 8.9 Hz), 128.07, 115.72 (d, *J* = 22.65 Hz), 110.10, 99.00, 58.02, 30.39, 28.73, 22.63, 21.56, 13.84.

^{19}F NMR (565 MHz, $CDCl_3$) δ -113.45 – -113.47.

HRMS (ESI) (m/z): calcd for $C_{28}H_{27}FNaO_3S$ ([M + Na] $^+$), 485.1557; found, 485.1546.

IR (neat): ν (cm^{-1}) 3062, 2958, 2929, 2871, 1929, 1655, 1597, 1509, 1447, 1320, 1303, 1234, 1164, 1133, 1086, 711.



1-phenyl-2-(3-tosyl-2-(4-(trifluoromethoxy)phenyl)prop-1-en-1-ylidene)hexan-1-one (15)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 73.9 mg, 70%).

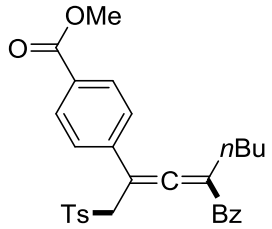
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.58 – 7.54 (m, 2H), 7.47 (t, *J* = 7.4, 1H), 7.29 – 7.25 (m, 2H), 7.20 – 7.17 (m, *J* = 8.6, 4H), 7.14 – 7.09 (m, 2H), 4.21 (d, *J* = 14.5 Hz, 1H), 4.04 (d, *J* = 14.5 Hz, 1H), 2.47 – 2.42 (m, 1H), 2.38 (s, 3H), 2.33 – 2.28 (m, 1H), 1.52 – 1.44 (m, 2H), 1.43 – 1.36 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.97, 193.25, 148.68, 145.07, 137.96, 135.55, 132.69, 132.05, 129.73, 128.60, 128.46, 128.14, 127.80, 121.05, 120.37 (q, *J* = 257.6 Hz), 110.40, 98.87, 57.96, 30.40, 28.84, 22.66, 21.51, 13.86.

^{19}F NMR (565 MHz, $CDCl_3$) δ -57.87.

HRMS (ESI) (m/z): calcd for $C_{29}H_{27}F_3NaO_4S$ ([M + Na] $^+$), 551.1474; found, 551.1485.

IR (neat): ν (cm^{-1}) 3062, 2958, 2929, 2872, 1930, 1657, 1596, 1508, 1447, 1321, 1260, 1161, 1135, 1086, 813, 698.



Methyl-4-(4-benzoyl-1-tosylocta-2,3-dien-2-yl)benzoate (16)

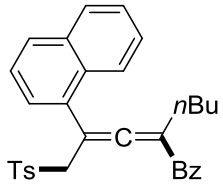
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 40.2 mg, 40%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.1, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.27 – 7.22 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.24 (d, *J* = 14.5 Hz, 1H), 4.05 (d, *J* = 14.4 Hz, 1H), 3.92 (s, 3H), 2.50 – 2.45 (m, 1H), 2.38 (s, 3H), 2.33 – 2.28 (m, 1H), 1.52 – 1.46 (m, 2H), 1.42 – 1.37 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 215.62, 193.09, 166.43, 145.04, 137.97, 137.96, 135.52, 132.66, 129.90, 129.75, 129.42, 128.56, 128.45, 128.13, 126.26, 110.47, 99.40, 57.61, 52.17, 30.38, 28.80, 22.63, 21.53, 13.83.

HRMS (ESI) (m/z): calcd for $C_{30}H_{30}NaO_5S$ ([M + Na] $^+$), 525.1706; found, 525.1701.

IR (neat): ν (cm^{-1}) 3061, 2955, 2929, 2871, 1929, 1721, 1656, 1606, 1446, 1435, 1320, 1279, 1186, 1135, 1111, 1086, 1013, 858, 814, 750, 698.



2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)-1-phenylhexan-1-one (17)

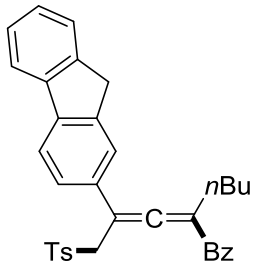
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 91.9 mg, 93%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.57 – 7.54 (m, 4H), 7.49 (td, *J* = 7.4, 1.3 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.32 (t, *J* = 8.2 Hz, 1H), 7.27 – 7.21 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 4.21 (d, *J* = 14.2 Hz, 1H), 4.13 (d, *J* = 14.2 Hz, 1H), 2.54 – 2.48 (m,1H), 2.43 – 2.34 (m, 4H), 1.63 – 1.48 (m, 2H), 1.44 – 1.36 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.77, 194.30, 144.62, 138.76, 135.99, 133.81, 132.17, 132.11, 130.27, 129.56, 128.76, 128.69, 128.53, 128.15, 128.12, 126.75, 126.28, 125.98, 125.19, 124.61, 108.27, 97.31, 60.33, 30.39, 28.31, 22.64, 21.52, 13.93.

HRMS (ESI) (m/z): calcd for $C_{32}H_{30}NaO_3S$ ([M + Na] $^+$), 517.1808; found, 517.1777.

IR (neat): ν (cm^{-1}) 3058, 2956, 2927, 2870, 1939, 1655, 1595, 1446, 1320, 1303, 1271, 1153, 1137, 1086, 1018, 803, 778, 706.



2-(2-(9H-fluoren-2-yl)-3-tosylprop-1-en-1-ylidene)-1-phenylhexan-1-one (18)

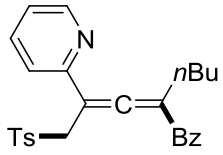
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 85.2mg, 80%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.71 – 7.62 (m, 3H), 7.60 – 7.51 (m, 3H), 7.46 – 7.39 (m, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.27 – 7.17 (m, 4H), 7.18 – 7.11 (m, 2H), 4.29 (d, *J* = 14.6 Hz, 1H), 4.08 (d, *J* = 14.6 Hz, 1H), 3.81 (s, 2H), 2.51 – 2.46 (m, 1H), 2.39 – 2.24 (m, 4H), 1.56 – 1.49 (m, 2H), 1.44 – 1.40 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 215.52, 193.57, 144.74, 143.64, 143.34, 141.64, 140.89, 138.14, 135.74, 132.41, 131.46, 129.58, 128.64, 128.46, 128.02, 127.07, 126.88, 125.40, 125.01, 122.82, 119.97, 110.02, 100.23, 58.06, 36.81, 30.42, 28.80, 22.65, 21.43, 13.87.

HRMS (ESI) (m/z): calcd for $C_{35}H_{32}NaO_3S$ ([M + Na] $^+$), 555.1964; found, 555.1973.

IR (neat): ν (cm^{-1}) 3056, 2956, 2926, 2858, 1926, 1653, 1596, 1456, 1446, 1320, 1302, 1269, 1149, 1134, 1085, 1019, 941, 881, 814, 753, 736, 707.



1-phenyl-2-(2-(pyridin-2-yl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (19)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords

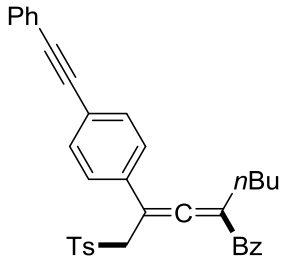
the title compound as a brown oil (yield 45.8 mg, 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 13.1 Hz, 2H), 7.59 (t, *J* = 8.3, 4H), 7.53 – 7.44 (m, 2H), 7.30 – 7.26 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 3H), 4.21 (d, *J* = 14.5 Hz, 1H), 4.03 (d, *J* = 14.5 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.40 (s, 3H), 1.52 – 1.43 (m, 2H), 1.42 – 1.32 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.71, 193.08, 148.84, 147.87, 145.16, 137.93, 135.36, 133.38, 132.76, 129.86, 128.57, 128.44, 128.17, 123.35, 110.58, 97.12, 57.57, 30.38, 28.81, 22.65, 21.59, 13.83.

HRMS (ESI) (m/z): calcd for $C_{27}H_{27}NNaO_3S$ ([M + Na] $^+$), 468.1604; found, 468.1595.

IR (neat): ν (cm^{-1}) 3061, 2957, 2926, 2870, 1922, 1717, 1684, 1596, 1492, 1448, 1316, 1266, 1146, 1085, 815, 762, 700.



1-phenyl-2-(2-(4-(phenylethynyl)phenyl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (20)

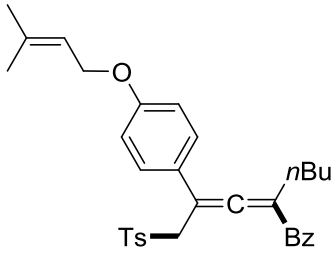
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow solid (yield 50.0 mg, 46%), mp 90 – 91 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.57 – 7.51 (m, 4H), 7.47 – 7.42 (m, 3H), 7.38 – 7.34 (m, 3H), 7.27 – 7.24 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.13 (m, 2H), 4.22 (d, *J* = 14.6 Hz, 1H), 4.03 (d, *J* = 14.6 Hz, 1H), 2.50 – 2.42 (m, 1H), 2.39 (s, 3H), 2.33 – 2.28 (m, 1H), 1.52 – 1.46 (m, 2H), 1.42 – 1.36 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 215.51, 193.30, 144.99, 138.04, 135.59, 133.00, 132.58, 131.84, 131.59, 129.72, 128.60, 128.44, 128.36, 128.11, 126.26, 122.98, 122.85, 110.42, 99.58, 90.67, 88.83, 57.64, 30.41, 28.81, 22.65, 21.56, 13.85.

HRMS (ESI) (m/z): calcd for $C_{36}H_{32}NaO_3S$ ([M + Na] $^+$), 567.1964; found, 567.1958.

IR (neat): ν (cm^{-1}) 3060, 2957, 2928, 2870, 1925, 1656, 1596, 1578, 1509, 1445, 1321, 1268, 1158, 1134, 1086, 838, 814, 757, 692.



2-(2-(4-((3-methylbut-2-en-1-yl)oxy)phenyl)-3-tosylprop-1-en-1-ylidene)-1-phenylhexan-1-one (21)

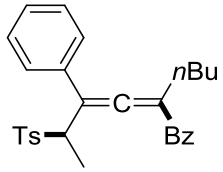
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 52.8 mg, 50%).

^{1}H NMR (500 MHz,$CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.49 (t, *J* = 7.0 Hz, 1H), 4.50 (d, *J* = 6.5 Hz, 2H); 4.21 (d, *J* = 14.5 Hz, 1H), 4.01 (d, *J* = 14.5 Hz, 1H), 2.43 – 2.37 (m, 4H), 2.24 – 2.18 (m, 1H), 1.81 (s, 3H), 1.75 (s, 3H), 1.47 – 1.40 (m, 2H), 1.40 – 1.34 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 215.04, 193.66, 158.69, 144.69, 138.42, 138.07, 135.63, 132.37, 129.63, 128.61, 128.43, 127.98, 127.61, 125.00, 119.32, 114.84, 109.93, 99.45, 64.81, 57.96, 30.42, 28.72, 25.78, 22.64, 21.54, 18.16, 13.85.

HRMS (ESI) (m/z): calcd for $C_{33}H_{36}NaO_4S$ ([M + Na] $^+$), 551.2227; found, 551.2226.

IR (neat): ν (cm^{-1}) 3061, 2957, 2928, 2871, 1927, 1654, 1604, 1577, 1509, 1446, 1381, 1320, 1290, 1268, 1242, 1179, 1158, 1134, 1086, 999, 831, 814, 761, 713.



2-butyl-1,4-diphenyl-5-tosylhexa-2,3-dien-1-one (22)

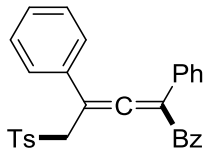
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 60.5 mg, 66%). The products could not readily be separated by silica gel chromatography, so they were characterized as a mixture. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 3:1 mixture based on the peak at δ 1.00 and at δ 0.90.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2, 0.63H), 7.60 (d, *J* = 8.4, 2H), 7.53 (t, *J* = 7.4, 0.33H), 7.38 – 7.34 (m, 3.88H), 7.33 – 7.29 (m, 2.21H), 7.28 – 7.26 (m, 0.87H), 7.26 – 7.20 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.15 – 7.08 (m, 4.48H), 7.00 (d, *J* = 8.0 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 1.32H), 2.59 – 2.46 (m, 1.72H), 2.36 (s, 3H), 2.33 – 2.26 (m, 2H), 1.64 – 1.60 (m, 1H), 1.56 (d, *J* = 7.1 Hz, 1H), 1.54 – 1.36 (m, 4.31H), 1.16 (d, *J* = 6.9 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 215.81, 213.42, 194.08, 193.72, 144.63, 144.41, 138.60, 137.96, 134.90, 134.64, 134.27, 134.13, 132.35, 132.02, 129.37, 129.21, 128.96, 128.92, 128.65, 128.47, 128.34, 128.18, 127.83, 127.70, 127.60, 126.62, 126.59, 112.28, 112.13, 106.83, 106.27, 61.29, 60.71, 30.71, 30.25, 29.42, 27.90, 22.76, 22.59, 21.48, 21.45, 15.06, 13.92, 13.85, 13.81.

HRMS (ESI) (m/z): calcd for $C_{29}H_{30}NaO_3S$ ([M + Na] $^+$), 481.1808; found, 481.1813.

IR (neat): ν (cm^{-1}) 3059, 2957, 2930, 2871, 1929, 1655, 1596, 1493, 1448, 1315, 1303, 1269, 1147, 1086, 1054, 940, 815, 765, 724, 696.



1,2,4-triphenyl-5-tosylpenta-2,3-dien-1-one (23)

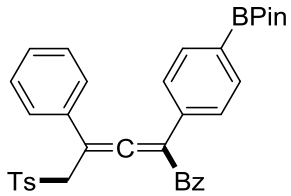
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a white solid (yield 55.6 mg, 60%), mp 110 – 111 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.31 (m, 7H), 7.29 – 7.24 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.33 (d, *J* = 14.5 Hz, 1H), 4.24 (d, *J* = 14.5 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.09, 192.03, 144.77, 137.57, 135.15, 133.45, 132.93, 131.99, 129.67, 129.43, 128.75, 128.73, 128.40, 128.37, 128.33, 128.27, 128.05, 126.58, 111.79, 102.70, 57.79, 21.59.

HRMS (ESI) (m/z): calcd for $C_{30}H_{24}NaO_3S$ ([M + Na] $^+$), 487.1338; found, 487.1346.

IR (neat): ν (cm^{-1}) 3058, 2925, 1923, 1662, 1596, 1493, 1446, 1319, 1267, 1153, 1132, 1086, 1020, 844, 814, 744, 693.



1,4-diphenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-5-tosylpenta-2,3-dien-1-one (24)

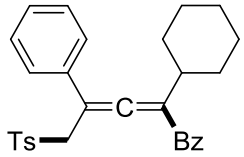
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow solid (yield 70.8 mg, 60%), mp 50 – 51 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.56 – 7.53 (m, 2H), 7.52 – 7.50 (m, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.27(m, 6H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.35 (d, *J* = 14.5 Hz, 1H), 4.26 (d, *J* = 14.5 Hz, 1H), 2.28 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.30, 191.79, 144.81, 137.47, 135.12, 135.05, 134.77, 133.45, 132.82, 129.72, 129.46, 128.76, 128.42, 128.34, 127.17, 126.64, 111.85, 102.88, 83.88, 57.73, 24.85, 21.57.

HRMS (ESI) (m/z): calcd for $C_{36}H_{35}BNaO_5S$ ([M + Na] $^+$), 613.2197; found, 613.2188.

IR (neat): ν (cm^{-1}) 3058, 2978, 2928, 1923, 1665, 1606, 1597, 1448, 1398, 1360, 1322, 1269, 1143, 1089, 1020, 858, 814, 742, 695.



2-cyclohexyl-1,4-diphenyl-5-tosylpenta-2,3-dien-1-one (25)

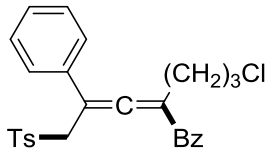
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow solid (yield 73.3 mg, 78%), mp 100 – 101 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.22 (m, 5H), 7.19 – 7.10 (m, 4H), 4.21 (d, *J* = 14.5 Hz, 1H), 4.05 (d, *J* = 14.5 Hz, 1H), 2.73 (tt, *J* = 11.8, 3.4 Hz, 1H), 2.36 (s, 3H), 1.90 – 1.69 (m, 5H), 1.40 – 1.33 (m, 2H), 1.29 – 1.13 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.86, 193.60, 144.70, 138.28, 135.71, 133.35, 132.49, 129.65, 128.78, 128.75, 128.57, 128.39, 127.79, 126.19, 115.46, 101.22, 58.06, 38.24, 32.20, 32.03, 26.41, 26.33, 25.86, 21.54.

HRMS (ESI) (m/z): calcd for $C_{30}H_{30}NaO_3S$ ([M + Na] $^+$), 493.1808; found, 493.1811.

IR (neat): ν (cm^{-1}) 3059, 2926, 2851, 1924, 1655, 1596, 1494, 1448, 1320, 1264, 1154, 1134, 1086, 1019, 937, 813, 766, 746, 732, 694.



2-(2-chloroethyl)-1,4-diphenyl-5-tosylpenta-2,3-dien-1-one (26)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 74.3 mg, 80%), mp 90 – 91 °C.

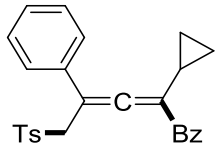
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 –7.58 (m, 4H), 7.44 (t, *J* = 7.4, 1H), 7.30 – 7.23 (m, 5H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.16 – 7.11 (m, 2H), 4.23 (d, *J* = 14.5 Hz, 1H), 4.03 (d, *J* = 14.5 Hz, 1H), 3.62 – 3.59 (m, 2H), 2.66 – 2.51 (m, 1H), 2.55 – 2.50 (m, 1H), 2.39 (s, 3H), 2.09 – 2.01 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 215.48, 193.27, 144.94, 137.89, 135.67, 133.01, 132.58, 129.77, 128.77,

128.58, 128.41, 128.10, 128.08, 126.37, 108.78, 100.39, 57.79, 44.53, 30.83, 26.59, 21.55.

HRMS (ESI) (m/z): calcd for $C_{27}H_{25}ClNaO_3S$ ([M + Na] $^+$), 487.1105; found, 487.1104.

IR (neat): ν (cm^{-1}) 3059, 2926, 1931, 1654, 1596, 1578, 1494, 1447, 1403, 1319, 1303, 1266, 1152, 1134, 1086, 1017, 975, 877, 814, 746, 695.



2-cyclopropyl-1,4-diphenyl-5-tosylpenta-2,3-dien-1-one (27)

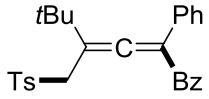
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 64.2 mg, 75%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.22 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.08 (m, 2H), 4.19 (d, *J* = 14.4 Hz, 1H), 4.00 (d, *J* = 14.5 Hz, 1H), 2.36 (s, 3H), 1.85 – 1.81 (m, 1H), 0.94 – 0.89 (m, 2H), 0.69 – 0.65 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.65, 193.69, 144.80, 137.98, 135.79, 133.21, 132.47, 129.71, 128.67, 128.30, 128.01, 126.25, 114.12, 102.17, 58.05, 21.53, 9.38, 8.05, 7.68.

HRMS (ESI) (m/z): calcd for $C_{27}H_{24}NaO_3S$ ([M + Na] $^+$), 451.1338; found, 451.1331.

IR (neat): ν (cm^{-1}) 3060, 3003, 2926, 1926, 1656, 1596, 1494, 1448, 1402, 1320, 1303, 1266, 1151, 1136, 1086, 1022, 941, 815, 745, 724, 695.



5,5-dimethyl-1,2-diphenyl-4-(tosylmethyl)hexa-2,3-dien-1-one (28)

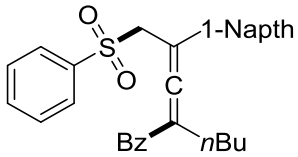
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as light yellow solid (yield 63.0 mg, 71%), mp 64 – 65 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.2, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.51 (m, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.33 (m, 5H), 7.06 (d, *J* = 8.0 Hz, 2H), 3.86 (d, *J* = 15.0 Hz, 1H), 3.74 (d, *J* = 15.0 Hz, 1H), 2.33 (s, 3H), 0.88 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.27, 194.14, 144.72, 139.29, 135.45, 132.77, 132.53, 129.56, 128.87, 128.42, 128.14, 128.00, 113.28, 108.15, 55.07, 35.91, 28.49, 21.58.

HRMS (ESI) (m/z): calcd for $C_{28}H_{28}NaO_3S$ ([M + Na] $^+$), 467.1651; found, 467.1656.

IR (neat): ν (cm^{-1}) 3059, 2964, 2927, 2868, 1932, 1659, 1596, 1579, 1494, 1447, 1396, 1365, 1319, 1273, 1141, 1087, 1019, 882, 815, 763, 738, 696.



2-(2-(naphthalen-1-yl)-3-(phenylsulfonyl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (29)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 78.7 mg, 82%).

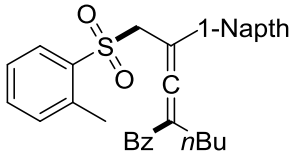
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.55 (d, *J* = 6.8 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.45 – 7.40 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.27 – 7.21 (m, 4H), 7.08 – 7.04 (m, 1H), 4.22 (d, *J* = 14.3 Hz, 1H), 4.15 (d, *J* = 14.3 Hz, 1H), 2.55 – 2.50 (m, 1H), 2.44 – 2.39 (m, 1H), 1.65 – 1.51 (m, 2H), 1.45 – 1.33 (m, 2H), 0.96 (t, *J* = 7.3 Hz,

3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.74, 194.27, 138.93, 138.72, 133.77, 133.59, 132.11, 132.06, 130.22, 128.94, 128.79, 128.74, 128.54, 128.11, 128.07, 126.68, 126.32, 125.99, 125.18, 124.53, 108.32, 97.13, 60.19, 30.35, 28.29, 22.59, 13.91.

HRMS (ESI) (m/z): calcd for $C_{31}H_{28}NaO_3S$ ([M + Na] $^+$), 503.1651; found, 503.1642.

IR (neat): ν (cm^{-1}) 3059, 2957, 2928, 2871, 1940, 1652, 1595, 1578, 1507, 1446, 1399, 1320, 1271, 1155, 1138, 1084, 933, 863, 803, 778, 735, 688.



2-(2-(naphthalen-1-yl)-3-(o-tolylsulfonyl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (30)

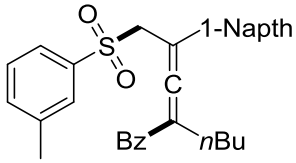
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 79.0 mg, 80%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.50 – 7.48 (m, 1H), 7.44 – 7.41 (m, 1H), 7.39 – 7.37 (m, 1H), 7.30 – 7.17 (m, 6H), 7.10 – 7.09 (m, 1H), 6.99 – 6.90 (m, 1H), 4.28 (d, *J* = 13.9 Hz, 1H), 4.18 (d, *J* = 13.9 Hz, 1H), 2.57 – 2.48 (m, 1H), 2.43 – 2.32 (m, 4H), 1.60 – 1.51 (m, 2H), 1.43 – 1.39 (m, 2H), 0.96 (t, *J* = 6.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.73, 194.30, 138.81, 137.79, 137.01, 133.74, 133.65, 132.43, 132.10, 132.07, 130.51, 130.18, 128.74, 128.54, 128.12, 126.62, 126.32, 125.99, 125.16, 124.50, 108.36, 97.23, 59.26, 30.38, 28.26, 22.62, 19.95, 13.93.

HRMS (ESI) (m/z): calcd for $C_{32}H_{30}NaO_3S$ ([M + Na] $^+$), 517.1808; found, 517.1797.

IR (neat): ν (cm^{-1}) 3059, 2956, 2928, 2870, 1940, 1655, 1595, 1577, 1507, 1446, 1315, 1271, 1155, 1127, 1059, 805, 778, 757, 735, 707.



2-(2-(naphthalen-1-yl)-3-(m-tolylsulfonyl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (31)

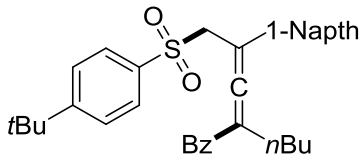
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 85.0 mg, 86%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.46 (m, 2H), 7.44 – 7.42 (m, 2H), 7.33 – 7.26 (m, 3H), 7.26 – 7.21 (m, 4H), 7.07 (d, *J* = 6.7 Hz, 1H), 4.22 (d, *J* = 14.2 Hz, 1H), 4.16 (d, *J* = 14.3 Hz, 1H), 2.56 – 2.51 (m, 1H), 2.45 – 2.37 (m, 1H), 2.24 (s, 3H), 1.62 – 1.52 (m, 2H), 1.44 – 1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.84, 194.25, 139.24, 138.82, 138.72, 134.34, 133.79, 132.09, 132.04, 130.29, 128.79, 128.75, 128.73, 128.52, 128.41, 128.10, 126.62, 126.28, 125.98, 125.16, 125.14, 124.62, 108.26, 97.24, 60.26, 30.37, 28.31, 22.63, 21.07, 13.91.

HRMS (ESI) (m/z): calcd for $C_{32}H_{30}NaO_3S$ ([M + Na] $^+$), 517.1808; found, 517.1803.

IR (neat): ν (cm^{-1}) 3058, 2957, 2928, 2870, 1940, 1653, 1595, 1578, 1477, 1446, 1321, 1271, 1133, 1082, 933, 874, 803, 778, 735, 707.



2-(3-((4-(tert-butyl)phenyl)sulfonyl)-2-(naphthalen-1-yl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (32)

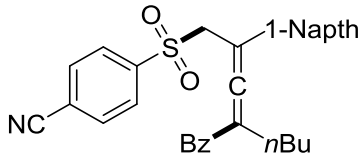
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 85.8 mg, 80%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.53 (m, 4H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.28 – 7.21 (m, 5H), 7.02 (d, *J* = 6.9 Hz, 1H), 4.22 (d, *J* = 14.3 Hz, 1H), 4.15 (d, *J* = 14.3 Hz, 1H), 2.58 – 2.53 (m, 1H), 2.43 – 2.38 (m, 1H), 1.65 – 1.55 (m, 2H), 1.44 – 1.37 (m, 2H), 1.27 (s, 9H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.86, 194.27, 157.48, 138.73, 135.79, 133.71, 132.07, 130.25, 128.72, 128.69, 128.48, 128.09, 127.97, 127.93, 126.57, 126.26, 125.95, 125.86, 125.09, 124.62, 108.20, 97.27, 60.22, 35.08, 30.92, 30.38, 28.24, 22.58, 13.94.

HRMS (ESI) (m/z): calcd for $C_{35}H_{36}NaO_3S$ ([M + Na] $^+$), 559.2277; found, 559.2272.

IR (neat): ν (cm^{-1}) 3058, 2961, 2870, 1940, 1653, 1594, 1507, 1464, 1446, 1398, 1320, 1293, 1270, 1156, 1141, 1107, 1083, 933, 803, 778, 761, 735, 707.



4-((4-benzoyl-2-(naphthalen-1-yl)octa-2,3-dien-1-yl)sulfonyl)benzonitrile (33)

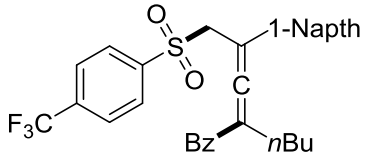
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 86.9 mg, 86%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (d, *J* = 2.3 Hz, 1H), 8.63 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.51 – 7.48 (m, 1H), 7.46 – 7.44 (m, 1H), 7.34 – 7.27 (m, 3H), 7.26 – 7.22 (m, 2H), 7.15 – 7.13 (m, 1H), 7.10 (d, *J* = 7.0 Hz, 1H), 4.30 – 4.23 (m, 2H), 2.59 – 2.55 (m, 1H), 2.51 – 2.46 (m, 1H), 1.67 – 1.55 (m, 2H), 1.46 – 1.40 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.76, 193.95, 153.87, 148.90, 138.49, 135.51, 135.37, 133.76, 132.25, 131.48, 130.05, 129.05, 128.73, 128.63, 128.16, 126.77, 126.55, 126.18, 125.18, 124.31, 123.19, 108.40, 96.81, 60.71, 30.33, 28.37, 22.58, 13.90.

HRMS (ESI) (m/z): calcd for $C_{32}H_{27}NNaO_3S$ ([M + Na] $^+$), 528.1604; found, 528.1602.

IR (neat): ν (cm^{-1}) 3060, 2957, 2928, 2871, 2233, 1940, 1652, 1595, 1507, 1446, 1398, 1327, 1271, 1181, 1136, 1083, 1018, 934, 862, 840, 803, 778, 736, 706.



2-(2-(naphthalen-1-yl)-3-((4-(trifluoromethyl)phenyl)sulfonyl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (34)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 98.6 mg, 90%).

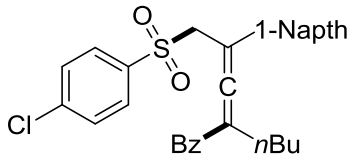
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.46 – 7.41 (m, 3H), 7.31 – 7.21 (m, 5H), 7.03 (d, *J* = 7.1, 1H), 4.30 (d, *J* = 14.5 Hz, 1H), 4.26 (d, *J* = 14.5 Hz, 1H), 2.60 – 2.55 (m, 1H), 2.50 – 2.45 (m, 1H), 1.63 – 1.56 (m, 2H), 1.47 – 1.38 (m, 2H), 0.97 (t, *J* = 7.3, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.72, 193.91, 142.13, 138.46, 134.95 (q, *J* = 33.2 Hz,), 133.73, 132.25, 131.39, 130.07, 129.03, 128.79, 128.68, 128.46, 128.18, 126.73, 126.47, 126.15, 125.68 (q, *J* = 3.6 Hz), 125.07, 124.34, 122.86 (q, *J* = 274.1 Hz,), 108.32, 96.92, 60.28, 30.34, 28.41, 22.57, 13.91.

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.37.

HRMS (ESI) (m/z): calcd for $C_{32}H_{27}F_3NaO_3S$ ([M + Na] $^+$), 571.1525; found, 571.1523.

IR (neat): ν (cm^{-1}) 3059, 2958, 2929, 2872, 1940, 1653, 1595, 1507, 1446, 1403, 1322, 1271, 1138, 1107, 1087, 1062, 1016, 933, 845, 803, 778, 709.



2-(3-((4-chlorophenyl)sulfonyl)-2-(naphthalen-1-yl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (35)

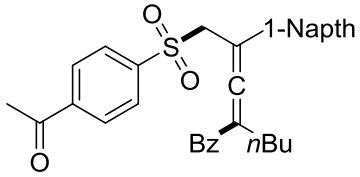
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 80.2 mg, 78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.52 – 7.47 (m, 3H), 7.46 – 7.43 (m, 1H), 7.33 – 7.30 (m, 1H), 7.29 – 7.18 (m, 6H), 7.07 (dd, *J* = 7.0, 1.1 Hz, 1H), 4.21 (s, 2H), 2.58 – 2.52 (m, 1H), 2.49 – 2.43 (m, 1H), 1.63 – 1.51 (m, 2H), 1.46 – 1.39 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.66, 194.02, 140.25, 138.52, 137.16, 133.76, 132.19, 131.68, 130.14, 129.39, 129.05, 128.85, 128.76, 128.64, 128.13, 126.72, 126.39, 126.09, 125.14, 124.41, 108.25, 97.07, 60.36, 30.34, 28.39, 22.59, 13.91.

HRMS (ESI) (m/z): calcd for $C_{31}H_{27}ClNaO_3S$ ([M + Na] $^+$), 537.1262; found, 537.1273.

IR (neat): ν (cm^{-1}) 3059, 2957, 2928, 2870, 1940, 1655, 1579, 1507, 1475, 1446, 1395, 1324, 1272, 1156, 1139, 1088, 1013, 933, 803, 778, 760, 707.



2-(3-((4-acetylphenyl)sulfonyl)-2-(naphthalen-1-yl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (36)

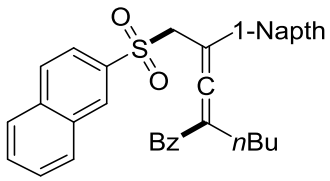
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 75.2 mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 3H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.50 – 7.48 (m, 1H), 7.44 – 7.41 (m, 1H), 7.30 – 7.26 (m, 3H), 7.24 (t, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 7.1 Hz, 1H), 4.26 (s, 2H), 2.57 – 2.52 (m, 4H), 2.50 – 2.42 (m, 1H), 1.66 – 1.54 (m, 2H), 1.46 – 1.38 (m, 2H), 1.00 – 0.92 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.63, 196.31, 193.92, 142.37, 140.34, 138.44, 133.70, 132.20, 131.63, 130.10, 128.82, 128.73, 128.49, 128.31, 128.24, 128.12, 126.73, 126.36, 126.07, 125.11, 124.44, 108.23, 96.88, 60.25, 30.28, 28.37, 26.72, 22.55, 13.88.

HRMS (ESI) (m/z): calcd for $C_{33}H_{30}NaO_4S$ ([M + Na] $^+$), 545.1757; found, 545.1747.

IR (neat): ν (cm^{-1}) 3059, 2957, 2928, 2870, 1940, 1692, 1655, 1595, 1577, 1446, 1397, 1359, 1324, 1299, 1261, 1156, 1138, 1088, 1071, 1014, 959, 835, 804, 779, 735, 707.



2-(2-(naphthalen-1-yl)-3-(naphthalen-2-ylsulfonyl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (37)

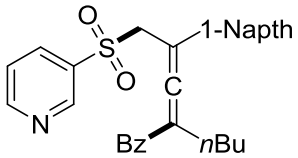
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 100.7 mg, 95%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.78 – 7.76 (m, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.55 (m, 4H), 7.52 – 7.51 (m, 2H), 7.47 – 7.45 (m, 1H), 7.40 – 7.37 (m, 1H), 7.31 – 7.15 (m, 5H), 7.06 (d, *J* = 7.1, 1H), 4.31 (d, *J* = 14.3 Hz, 1H), 4.26 (d, *J* = 14.4 Hz, 1H), 2.45 – 2.40 (m, 1H), 2.30 – 2.25 (m, 1H), 1.57 – 1.42 (m, 2H), 1.32 – 1.26 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.81, 194.21, 138.61, 135.57, 135.14, 133.71, 132.11, 131.81, 131.79, 130.27, 130.22, 129.30, 129.26, 128.71, 128.51, 128.09, 127.79, 127.57, 126.61, 126.26, 125.95, 125.04, 124.52, 122.41, 108.19, 97.26, 60.24, 30.32, 28.25, 22.54, 13.87.

HRMS (ESI) (m/z): calcd for $C_{35}H_{30}NaO_3S$ ([M + Na] $^+$), 553.1808; found, 553.1792.

IR (neat): ν (cm^{-1}) 3057, 2956, 2928, 2870, 1939, 1654, 1593, 1505, 1446, 1317, 1270, 1153,1140, 1126, 1071, 777, 759, 706.



2-(2-(naphthalen-1-yl)-3-(pyridin-3-ylsulfonyl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (38)

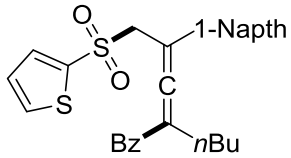
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 91.4 mg, 95%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.56(m, 4H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.45 (m, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.26 – 7.23 (m, 2H), 7.06 (d, *J* = 7.0 Hz, 1H), 4.31 (d, *J* = 14.5 Hz, 1H), 4.26 (d, *J* = 14.5 Hz, 1H), 2.62 – 2.55 (m, 1H), 2.54 – 2.49 (m, 1H), 1.64 – 1.56 (m, 2H), 1.48 – 1.40 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.60, 193.72, 142.66, 138.33, 133.71, 132.30, 132.12, 131.30, 130.05, 129.04, 128.78, 128.68, 128.41, 128.18, 126.75, 126.53, 126.27, 125.10, 124.31, 116.90, 116.80, 108.31, 96.72, 60.32, 30.29, 28.46, 22.56, 13.90.

HRMS (ESI) (m/z): calcd for $C_{30}H_{27}NNaO_3S$ ([M + Na] $^+$), 504.1604; found, 504.1599.

IR (neat): ν (cm^{-1}) 3058, 2957, 2928, 2870, 1940, 1655, 1595, 1574, 1416, 1319, 1271, 1159, 1142, 1120, 1100, 1019, 934, 803, 778, 701.



2-(2-(naphthalen-1-yl)-3-(thiophen-2-ylsulfonyl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (39)

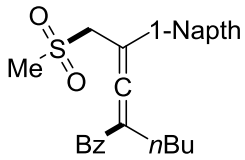
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 95.3 mg, 98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.35 (t, *J* = 7.0 Hz 1H), 7.28 – 7.21 (m, 4H), 7.17 (d, *J* = 7.1 Hz, 1H), 6.95 – 6.93 (m, 1H), 4.32 (d, *J* = 14.2 Hz, 1H), 4.22 (d, *J* = 14.3 Hz, 1H), 2.59 – 2.53 (m, 1H), 2.51 – 2.45 (m, 1H), 1.64 – 1.54 (m, 2H), 1.45 – 1.40 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.74, 194.20, 139.81, 138.69, 134.59, 134.17, 133.76, 132.14, 132.04, 130.19, 128.83, 128.71, 128.54, 128.11, 127.60, 126.69, 126.34, 126.00, 125.21, 124.49, 108.38, 97.16, 61.74, 30.35, 28.35, 22.59, 13.91.

HRMS (ESI) (m/z): calcd for $C_{29}H_{26}NaO_3S_2$ ([M + Na] $^+$), 509.1216; found, 509.1222.

IR (neat): ν (cm^{-1}) 3091, 3058, 2956, 2928, 2870, 1940, 1654, 1595, 1577, 1506, 1446, 1402, 1325, 1271, 1226, 1135, 1090, 1071, 1014, 940, 855, 803, 726.



2-(3-(methylsulfonyl)-2-(naphthalen-1-yl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (40)

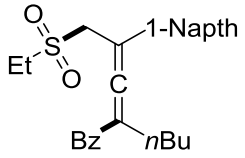
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 66.9 mg, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (t, *J* = 7.5 Hz, 2H), 7.60 – 7.59 (m, 2H), 7.53 – 7.47 (m, 3H), 7.44 – 7.39 (m, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.24 (m, 2H), 4.08 (d, *J* = 14.6 Hz, 1H), 4.04 (d, *J* = 14.4 Hz, 1H), 2.64 – 2.60 (m, 2H), 2.55 (s, 3H), 1.69 – 1.60 (m, 2H), 1.48 – 1.42 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.52, 194.14, 138.60, 133.94, 132.25, 131.97, 130.29, 129.24, 128.75, 128.72, 128.18, 127.01, 126.75, 126.32, 125.39, 124.40, 108.58, 97.40, 59.46, 40.97, 30.33, 28.36, 22.57, 13.90.

HRMS (ESI) (m/z): calcd for $C_{26}H_{26}NaO_3S$ ([M + Na] $^+$), 441.1495; found, 441.1486.

IR (neat): ν (cm^{-1}) 3058, 2957, 2928, 2870, 1941, 1654, 1595, 1577, 1507, 1446, 1400, 1314, 1272, 1128, 1099, 964, 932, 865, 804, 779, 709.



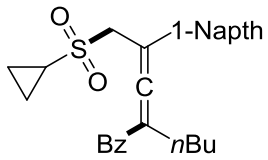
2-(3-(ethylsulfonyl)-2-(naphthalen-1-yl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (41)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 60.6 mg, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (t, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 7.1 Hz, 2H), 7.55 – 7.46 (m, 3H), 7.43 (d, *J* = 7.0 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.30 – 7.25 (m, 2H), 4.01 (s, 2H), 2.72 – 2.56 (m, 4H), 1.70 – 1.59 (m, 2H), 1.48 – 1.40(m, 2H), 1.10 (t, *J* = 7.5 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.57, 194.21, 138.68, 133.91, 132.22, 132.10, 130.31, 129.19, 128.74, 128.72, 128.17, 127.02, 126.69, 126.28, 125.38, 124.44, 108.59, 97.24, 56.56, 47.37, 30.34, 28.36, 22.59, 13.92, 6.34.

HRMS (ESI) (m/z): calcd for $C_{27}H_{28}NaO_3S$ ([M + Na] $^+$), 455.1651; found, 455.1654.



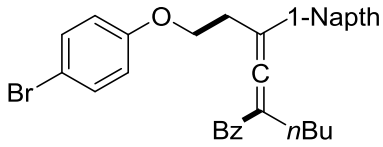
2-(3-(cyclopropylsulfonyl)-2-(naphthalen-1-yl)prop-1-en-1-ylidene)-1-phenylhexan-1-one (42)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a light yellow oil (yield 67.6 mg, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 2H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.54 – 7.43 (m, 5H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 2H), 4.13 – 4.04 (dd, *J* = 14.5, 14.5Hz, 2H), 2.63 – 2.60 (m, 2H), 1.97 – 1.92 (m, 1H), 1.74 – 1.60 (m, 2H), 1.47 – 1.40 (m, 2H), 1.15 – 1.10 (m, 1H), 1.04 – 0.98 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.73 – 0.72 (m, 1H), 0.63 – 0.60 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.73, 194.32, 138.74, 133.92, 132.44, 132.22, 130.45, 129.06, 128.77, 128.71, 128.18, 126.99, 126.62, 126.23, 125.39, 124.59, 108.44, 97.30, 58.37, 30.39, 30.03, 28.41, 22.62, 13.94, 5.19, 5.12.

HRMS (ESI) (m/z): calcd for $C_{28}H_{28}NaO_3S$ ([M + Na] $^+$), 467.1651; found, 467.1649.



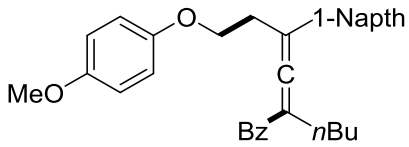
6-(4-bromophenoxy)-2-butyl-4-(naphthalen-1-yl)-1-phenylhexa-2,3-dien-1-one (43)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a light yellow oil (yield 77.8 mg, 74%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.35 – 7.31 (m, 4H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 6.63 (d, *J* = 8.9 Hz, 2H), 4.0 – 3.95 (m, 1H), 3.94 – 3.90 (m, 1H), 3.03 – 2.98 (m, 1H), 2.89 – 2.83 (m, 1H), 2.50 (t, *J* =7.5 Hz 2H), 1.68 – 1.55 (m, 2H), 1.46 – 1.38 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.71, 195.53, 157.59, 139.26, 133.85, 133.61, 132.20, 131.70, 130.92, 128.78, 128.36, 128.31, 127.96, 126.15, 126.06, 125.99, 125.33, 125.23, 116.11, 112.96, 107.92, 104.48, 65.39, 34.53, 30.45, 28.11, 22.55, 13.98.

HRMS (ESI) (m/z): calcd for $C_{32}H_{29}BrNaO_2$ ([M + Na] +), 547.1243; found, 547.1242.



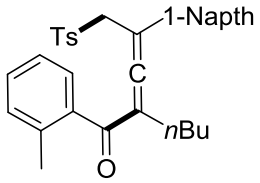
2-butyl-6-(4-methoxyphenoxy)-4-(naphthalen-1-yl)-1-phenylhexa-2,3-dien-1-one (44)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords the title compound as a light yellow oil (yield 47.7 mg, 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 9.1 Hz, 2H), 4.00 – 3.96(m, 1H), 3.94 – 3.90 (m, 1H), 3.76 (s, 3H), 3.03 – 2.98 (m, 1H), 2.87 – 2.82 (m, 1H), 2.51 – 2.48 (m, 2H), 1.67 – 1.55 (m, 2H), 1.42 (q, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.88, 195.68, 153.88, 152.67, 139.38, 133.84, 133.81, 131.62, 130.97, 128.77, 128.30, 128.21, 127.95, 126.10, 126.05, 125.94, 125.32, 115.33, 114.58, 107.91, 104.71, 65.85, 55.69, 34.77, 30.45, 28.09, 22.57, 13.99.

HRMS (ESI) (m/z): calcd for $C_{33}H_{32}NaO_3$ ([M + Na] +), 499.2244; found, 499.2247.



2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)-1-(o-tolyl)hexan-1-one (45)

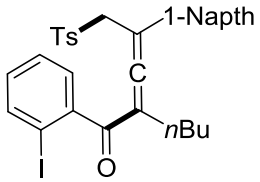
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 93.5 mg, 92%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.18 – 7.11 (m, 4H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 2H), 4.08 (d, *J* = 14.2 Hz, 1H), 3.96 (d, *J* = 14.2 Hz, 1H), 2.49 – 2.45 (m, 1H), 2.41 – 2.36 (m, 1H), 2.34 (s, 3H), 2.09 (s, 3H), 1.63 – 1.55(m, 2H), 1.45 – 1.38 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 216.45, 197.17, 144.59, 140.20, 135.93, 135.90, 133.56, 131.73, 130.84, 130.09, 129.80, 129.48, 128.55, 128.30, 128.05, 127.33, 126.70, 126.28, 125.86, 124.98, 124.96, 124.43, 110.67, 97.79, 59.90, 30.26, 27.05, 22.61, 21.45, 19.23, 13.89.

HRMS (ESI) (m/z): calcd for $C_{33}H_{32}NaO_3S$ ([M + Na] $^{+}$), 531.1964; found, 531.1965.

IR (neat): ν (cm^{-1}) 3059, 2956, 2927, 2871, 1941, 1654, 1596, 1507, 1456, 1399, 1379, 1319, 1302, 1136, 1086, 1018, 937, 925, 864, 803, 777, 746, 704.



1-(2-iodophenyl)-2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (46)

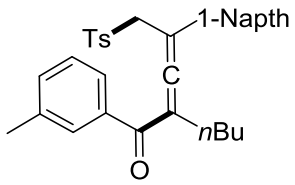
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 50.8 mg, 41%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.24 – 7.17 (m, 2H), 7.16 – 7.09 (m, 3H), 6.99 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.94 (d, *J* = 7.1 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.27 (d, *J* = 14.1 Hz, 1H), 3.97 (d, *J* = 14.1 Hz, 1H), 2.49 – 2.43 (m, 1H), 2.40 – 2.31 (m, 4H), 1.72 – 1.58 (m, 2H), 1.46 – 1.42 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 217.46, 196.50, 146.15, 144.61, 139.22, 136.05, 133.66, 131.12, 130.57, 130.13, 129.50, 128.75, 128.43, 128.09, 127.86, 127.35, 127.07, 126.33, 125.86, 125.09, 124.40, 109.82, 99.17, 91.23, 59.20, 30.14, 26.74, 22.69, 21.49, 13.91.

HRMS (ESI) (m/z): calcd for $C_{32}H_{29}INaO_3S$ ([M + Na] $^{+}$), 643.0774; found, 643.0775.

IR (neat): ν (cm^{-1}) 3058, 2956, 2927, 2870, 1941, 1666, 1595, 1459, 1320, 1153, 1136, 1085, 1016, 802, 777, 731.



2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)-1-(m-tolyl)hexan-1-one (47)

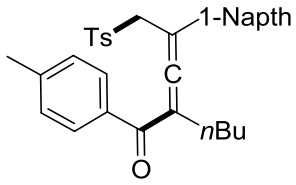
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 89.4 mg, 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.43 (m, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.29 – 7.26 (m, 2H), 7.25 – 7.23 (m, 2H), 7.17 – 7.09 (m, 4H), 4.18 (d, *J* = 14.2 Hz, 1H), 4.14 (d, *J* = 14.2 Hz, 1H), 2.54 – 2,48 (m, 1H), 2.40 – 2.31 (m, 4H), 1.98 (s, 3H), 1.56 – 1.52 (m, 2H), 1.44 – 1.37 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.54, 194.52, 144.58, 138.67, 137.81, 135.88, 133.81, 132.91, 132.16, 130.20, 129.52, 129.35, 128.62, 128.52, 128.12, 127.97, 126.72, 126.27, 125.95, 125.82, 125.20, 124.53, 108.09, 97.16, 60.27, 30.35, 28.30, 22.62, 21.48, 20.82, 13.90.

HRMS (ESI) (m/z): calcd for $C_{33}H_{32}NaO_3S$ ([M + Na] $^+$), 531.1964; found, 531.1957.

IR (neat): ν (cm^{-1}) 3058, 2956, 2926, 2870, 1940, 1654, 1596, 1456, 1320, 1276, 1193, 1154, 1137, 1086, 802, 778.



2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)-1-(p-tolyl)hexan-1-one (48)

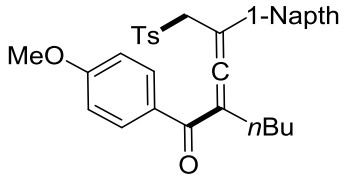
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 91.5 mg, 90%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 6.8 Hz, 2H), 7.46 – 7.42 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.14 – 7.12 (m, *J* = 7.5, 4.6 Hz, 3H), 7.00 (d, *J* = 7.8 Hz, 2H), 4.21 (d, *J* = 14.8 Hz, 1H), 4.15 (d, *J* = 14.2 Hz, 1H), 2.53 – 2.46 (m, 1H), 2.38 – 2.33 (m, 7H), 1.60 – 1.48 (m, 2H), 1.39 (p, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.3, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.24, 193.85, 144.57, 142.86, 135.92, 135.89, 133.76, 132.23, 130.24, 129.51, 128.92, 128.73, 128.60, 128.48, 128.11, 126.73, 126.07, 125.90, 125.17, 124.69, 108.03, 96.99, 60.32, 30.33, 28.37, 22.59, 21.53, 21.47, 13.89.

HRMS (ESI) (m/z): calcd for $C_{33}H_{32}NaO_3S$ ([M + Na] $^+$), 531.1964; found, 531.1969.

IR (neat): ν (cm^{-1}) 3047, 2956, 2926, 2870, 1939, 1651, 1606, 1320, 1272, 1180, 1154, 1137, 1086, 939, 925, 803, 778, 759.



1-(4-methoxyphenyl)-2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (49)

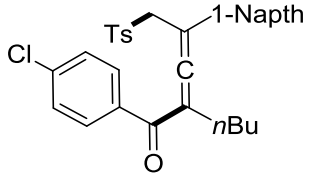
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 95.4 mg, 91%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.53 (m, 4H), 7.47 – 7.43 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.30 – 7.27 (m, 1H), 7.16 (d, *J* = 7.1, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 4.22 (d, *J* = 14.3 Hz, 1H), 4.19 (d, *J* = 14.3 Hz, 1H), 3.77 (s, 3H), 2.52 – 2.47 (m, 1H), 2.38 – 2.31 (m, 4H), 1.57 – 1.48 (m, 2H), 1.41 – 1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.45, 192.49, 163.01, 144.55, 135.86, 133.80, 132.32, 131.19, 130.99, 130.24, 129.50, 128.62, 128.54, 128.11, 126.80, 126.12, 125.92, 125.19, 124.77, 113.27, 107.66, 96.76, 60.35, 55.33, 30.33, 28.64, 22.58, 21.47, 13.88.

HRMS (ESI) (m/z): calcd for $C_{33}H_{32}NaO_4S$ ([M + Na] $^+$), 547.1914; found, 547.1904.

IR (neat): ν (cm^{-1}) 3058, 2957, 2929, 2870, 1939, 1651, 1600, 1574, 1508, 1458, 1418, 1400, 1378, 1319, 1258, 1171, 1137, 1086, 1028, 939, 926, 843, 803, 777, 737.



1-(4-chlorophenyl)-2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (50)

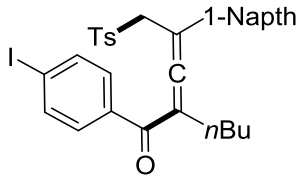
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 58.1 mg, 55%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.48 –7.46 (m, 3H), 7.36 – 7.27 (m, 3H), 7.18 – 7.12 (m, 4H), 7.10 (d, *J* = 7.1 Hz, 1H), 4.17 (d, *J* = 2.1 Hz, 2H), 2.53 – 2.49 (m, 1H), 2.43 – 2.34 (m, 4H), 1.61 – 1.50 (m, 2H), 1.43 – 1.37 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.62, 193.03, 144.69, 138.40, 136.93, 135.91, 133.80, 131.92, 130.15, 130.12, 129.56, 128.83, 128.61, 128.38, 128.08, 126.72, 126.35, 126.13, 125.22, 124.48, 108.21, 97.64, 60.15, 30.32, 28.24, 22.61, 21.50, 13.90.

HRMS (ESI) (m/z): calcd for $C_{32}H_{29}ClNaO_3S$ ([M + Na] $^+$), 551.1418; found, 551.1411.

IR (neat): ν (cm^{-1}) 3059, 2957, 2928, 2870, 1938, 1656, 1590, 1398, 1320, 1302, 1269, 1137, 1087, 1014, 841, 802, 777, 743.



1-(4-iodophenyl)-2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (51)

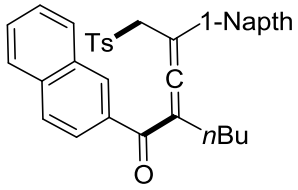
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 52.1 mg, 42%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.54 (t, *J* = 8.4 Hz, 4H), 7.49 – 7.46 (m, 1H), 7.36 – 7.30 (m, 2H), 7.25 – 7.20 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.10 (dd, *J* = 7.1, 1.2 Hz, 1H), 4.15 (d, *J* = 3.4 Hz, 2H), 2.55 – 2.45 (m, 1H), 2.43 – 2.36 (m, 4H), 1.60 – 1.52(m, 2H), 1.44 – 1.36 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.75, 193.54, 144.69, 138.02, 137.36, 135.98, 133.81, 131.94, 130.15, 130.09, 129.59, 128.85, 128.61, 128.10, 126.80, 126.45, 126.16, 125.23, 124.49, 108.25, 99.46, 97.78, 60.16, 30.32, 28.16, 22.61, 21.52, 13.90.

HRMS (ESI) (m/z): calcd for $C_{32}H_{29}INaO_3S$ ([M + Na] $^+$), 643.0774; found, 643.0783.

IR (neat): ν (cm^{-1}) 3057, 2956, 2926, 2869, 1939, 1654, 1579, 1389, 1320, 1269, 1153, 1136, 1085, 1006, 802, 777, 762.



2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)-1-(naphthalen-2-yl)hexan-1-one (52)

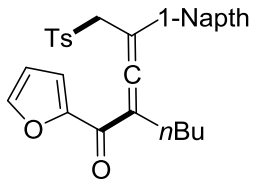
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 91.4 mg, 84%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.85 – 7.73 (m, 5H), 7.53 (t, *J* = 7.4, 1H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.35 (q, *J* = 8.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 2H), 7.01 (t, *J* = 7.1 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 4.17 (d, *J* = 14.3 Hz, 1H), 4.13 (d, *J* = 14.3 Hz, 1H), 2.63 – 2.55 (m, 1H), 2.46 – 2.41 (m, 1H), 2.33 (s, 3H), 1.65 – 1.57 (m, 2H), 1.47 – 1.41 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.54, 194.04, 144.57, 135.84, 135.60, 135.15, 133.80, 132.16, 131.98, 130.47, 130.28, 129.51, 129.23, 128.68, 128.50, 128.14, 128.06, 128.02, 127.53, 126.76, 126.43, 126.26, 126.03, 125.15, 124.79, 124.48, 108.15, 97.19, 60.19, 30.45, 28.54, 22.68, 21.46, 13.93.

HRMS (ESI) (m/z): calcd for $C_{36}H_{32}NaO_3S$ ([M + Na] $^+$), 567.1964; found, 567.1954.

IR (neat): ν (cm^{-1}) 3057, 2956, 2927, 2870, 1940, 1651, 1595, 1464, 1320, 1283, 1154, 1136, 1086, 802, 776, 761.



1-(furan-2-yl)-2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (53)

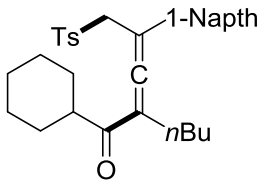
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a brown oil (yield 50.4 mg, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.44 – 7.32 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 3.6 Hz, 1H), 6.34 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.38 (s, 2H), 2.50 – 2.44 (m, 1H), 2.36 – 2.29 (m, 4H), 1.53 – 1.46 (m, 2H), 1.40 – 1.29 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 213.21, 179.61, 152.05, 146.50, 144.59, 135.89, 133.92, 131.94, 130.30, 129.49, 128.80, 128.74, 128.05, 126.89, 126.32, 126.04, 125.35, 124.56, 118.90, 111.92, 106.84, 97.43, 60.43, 30.33, 28.34, 22.53, 21.49, 13.88.

HRMS (ESI) (m/z): calcd for $C_{30}H_{28}NaO_4S$ ([M + Na] $^+$), 507.1601; found, 507.1602.

IR (neat): ν (cm^{-1}) 3058, 2957, 2929, 2871, 1941, 1643, 1596, 1464, 1391, 1319, 1302, 1152, 1137, 1085, 1018, 804, 778, 736.



cyclohexyl-2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (54)

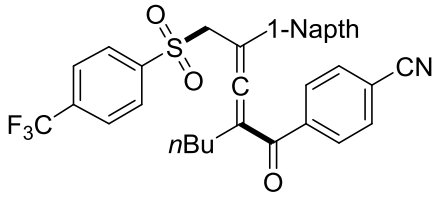
In situ reaction: In a nitrogen-filled glovebox, the benzoyl chloride (1.0 mmol) was dissolved in anhydrous acetonitrile (2.0 mL). Cesium fluoride (227.9 mg, 1.5 mmol, 1.5 equiv) was added and the mixture was stirred for 4 h at 80 ℃. After completion, the reaction mixture was filtered, the filtration residue washed with *n*-pentane (3 x 5.0 mL) and the combined organic solutions concentrated under vacuum. A pre-mixed solution of **NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.003 mmol) sulfinate (71.3 mg, 0.4 mmol) in DCM (8.0 mL) were added in the vial (10.0 mL) charged with crude acid fluorides. Then 1,3-enyne **1m** (0.2 mmol) was added. The vial was removed from the glovebox and then then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After the reaction finished that monitored by TLC, the reaction mixture was quenched by water. The mixture was extracted with EtOAc (3 x 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 = 10:1, v/v) to give the corresponding product **50** as a light yellow oil (yield 42.1 mg, 42%).[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 1H), 7.86 – 7.83 (m, 1H), 7.76 (d, *J* = 1.7 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.39 – 7.32 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.38 (d, *J* = 14.0 Hz, 1H), 4.32 (d, *J* = 14.0 Hz, 1H), 3.21 – 3.20 (m, 1H), 2.35 (s, 3H), 2.23 – 2.16 (m, 2H), 1.94 –1.93 (m , 1H), 1.86 – 1.84 (m, 2H), 1.77 – 1.61 (m, 3H), 1.49 – 1.48 (m, 1H), 1.45 – 1.34 (m, 4H), 1.33 – 1.18 (m, 3H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.27, 203.72, 144.61, 136.32, 133.88, 132.08, 130.44, 129.56, 128.80, 128.73, 128.01, 127.04, 126.48, 126.08, 125.33, 124.49, 108.49, 97.86, 60.44, 47.87, 38.28, 36.31, 30.33, 29.74, 29.17, 27.05, 25.84, 25.71, 22.51, 13.88.

HRMS (ESI) (m/z): calcd for $C_{32}H_{36}NaO_3S$ ([M + Na] $^+$), 523.2277; found, 523.2289.

IR (neat): ν (cm^{-1}) 513, 650, 777, 803, 1018, 1086, 1137, 1153, 1187, 1244, 1321, 1450, 1595, 1675, 1595, 1450, 1321, 1244, 1187, 1153, 1137, 1086, 1018, 803, 777, 759.



4-(2-(2-(naphthalen-1-yl)-3-((4-(trifluoromethyl)phenyl)sulfonyl)prop-1-en-1-ylidene)hexanoyl)benzonitrile (55)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 27.5 mg, 24%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.43 (m, 5H), 7.36 – 7.29 (m, 2H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.06 (dd, *J* = 7.1, 1.2 Hz, 1H), 4.28 (d, *J* = 14.4 Hz, 1H), 4.21 (d, *J* = 14.4 Hz, 1H), 2.63 – 2.47 (m, 2H), 1.70 – 1.58 (m, 2H), 1.50 – 1.39 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H).

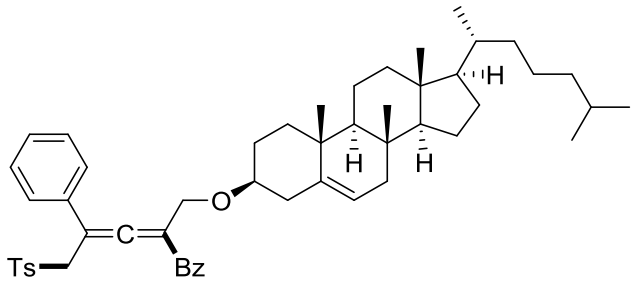
^{13}C NMR (151 MHz, $CDCl_3$) δ 215.39, 192.61, 142.18, 142.02, 135.172 (q, *J* = 34.13 Hz), 133.83,

132.00, 130.84, 129.83, 129.46, 129.08, 128.97, 128.40, 126.81, 126.67, 126.48, 125.79, 125.24, 123.94, 122.83 (q, *J* = 272.25 Hz), 117.89, 115.34, 108.55, 98.11, 60.01, 30.30, 28.12, 22.58, 13.88.

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.45.

HRMS (ESI) (m/z): calcd for $C_{33}H_{26}F_3NNaO_3S$ ([M + Na] $^+$), 596.1478; found, 596.1473.

IR (neat): ν (cm^{-1}) 3060, 2959, 2928, 2871, 2231, 1940, 1661, 1403, 1323, 1270, 1171, 1138, 1107, 1087, 1062, 1016, 846, 778, 763.



1,4-diphenyl-5-tosyl-2-((((3S,8S,9S,10R,13R,14R,17R)-8,10,13-trimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)penta-2,3-dien-1-one (57)

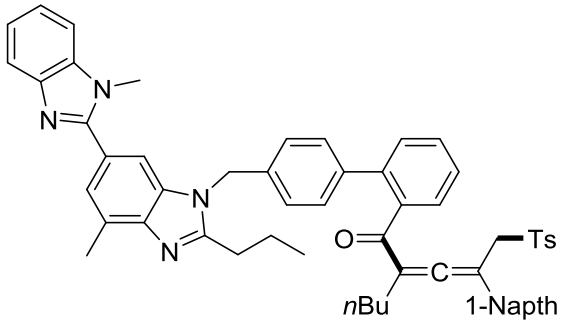
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 92.9 mg, 58%). The products could not readily be separated by silica gel chromatography, so they were characterized as a mixture. The ratio of the isomer was determined by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 1:1 mixture of compounds based on the peak at δ 5.36 – 5.35 and at δ 5.31 – 5.29.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 2H), 7.59 – 7.57 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.22 (m, 8H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.36 – 5.35 (m, 0.5H), 5.31 – 5.29 (m, 0.5H), 4.51 (d, *J* = 11.7, 1H), 4.24 (d, *J* = 14.6 Hz, 1H), 4.21 – 1.89 (m, 1H), 4.08 (d, *J* = 14.6 Hz, 1H), 3.31 – 3.23 (m, 1H), 2.37 (s, 3H), 2.36 – 2.32 (m, 1H), 2.21 – 2.03 (m, 1H), 2.03 – 1.95 (m, 2H), 1.90 – 1.80 (m, 3H), 1.58 – 1.41 (m, 8H), 1.39 – 1.32 (m, 3H), 1.28 – 1.24 (m, 1H), 1.19 – 1.08 (m, 7H), 1.04 – 0.99 (m, 6H), 0.92 (d, *J* = 6.5 Hz, 4H), 0.87 – 0.86 (m, 6H), 0.68 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.99, 214.98, 192.01, 144.77, 144.74, 140.76, 140.65, 137.61, 135.55, 132.77, 129.65, 128.87, 128.85, 128.71, 128.53, 128.51, 128.14, 128.11, 126.64, 121.70, 121.67, 107.80, 107.72, 100.65, 100.63, 79.40, 79.08, 65.16, 64.94, 57.51, 57.49, 56.76, 56.16, 50.17, 42.31, 39.78, 39.50, 39.18, 38.95, 37.24, 37.19, 36.86, 36.84, 36.18, 35.76, 31.94, 31.88, 28.43, 28.32, 28.21, 27.98, 24.27, 23.81, 22.79, 22.54, 21.58, 21.05, 19.36, 18.70, 11.84.

HRMS (ESI) (m/z): calcd for $C_{52}H_{66}NaO_4S$ ([M + Na] $^+$), 809.4574; found, 809.4565.

IR (neat): ν (cm^{-1}) 3058, 2935, 2866, 1939, 1659, 1596, 1494, 1448, 1380, 1322, 1272, 1157, 1134, 1086, 813, 740.



1-(4'-((1,7'-dimethyl-2'-propyl-1H,3'H-[2,5'-bibenzo[d]imidazol]-3'-yl)methyl)-[1,1'-biphenyl]-2-yl)-2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (58)

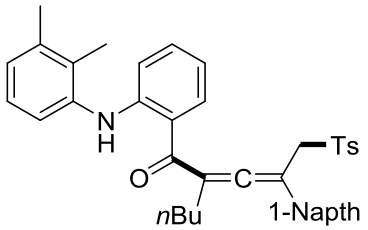
In situ reaction: In a nitrogen-filled glovebox, a vial (10.0 mL) was charged with Telmisartan (1.0 equiv, 0.6 mmol), tetramethylfluoroformamidinium hexafluorophosphate (TFFH) (1.1 equiv, 0.66 mmol), and triethylamine (1.8 mmol, 3.0 equiv). THF (2.0 mL) was added, and the reacti on mixture was stirred at room temperature for 15 min. Then the reaction mixture was diluted with EtOAc (10.0 mL) and washed with ice-cold water (2 x 10.0 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo to form the acid fluoride.[4] A pre-mixed solution of **NHC-1** (12.6 mg, 0.03 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), **PC-3** (2.7 mg, 0.0 03 mmol) sulfinate (71.3 mg, 0.4 mmol) in DCM (8.0 mL) were added. Then 1,3-enyne **1m** (0.2 mmol) was added. The vial was removed from the glovebox and then then the reaction mixture was irradiated with Blue LED at room temperature for 4 hours. After the reaction fini shed that monitored by TLC, the reaction mixture was quenched by water. The mixture was e xtracted with EtOAc (3 x 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 colu mn chromatography (petroleum ether/ethyl acetate = 1:1) to give the corresponding product **54** as a light yellow oil (yield 150.8 mg, 85%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.38 – 7.31 (m, 5H), 7.31 – 7.26 (m, 4H), 7.16 – 7.1 (m, 2H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 7.0 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 2H), 6.50 (d, *J* = 7.8 Hz, 2H), 5.23 (s, 2H), 3.93 (d, *J* = 1.9 Hz, 2H), 3.74 (s, 3H), 2.83 (t, *J* = 7.9 Hz, 2H), 2.77 (s, 3H), 2.27 (s, 3H), 2.22 – 2.17 (m, 1H), 2.15 – 2.10 (m, 1H), 1.85 – 1.82 (m, 2H), 1.30 – 1.24 (m, 2H), 1.19 – 1.63 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.84 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 216.27, 197.48, 156.21, 154.58, 144.45, 143.07, 142.87, 140.47, 139.13, 138.83, 136.63, 135.78, 134.90, 134.63, 133.50, 130.93, 130.26, 129.88, 129.74, 129.34, 129.02, 128.54, 128.28, 127.88, 127.22, 126.87, 126.75, 126.28, 125.84, 125.71, 124.95, 124.35, 123.84, 123.77, 122.42, 122.22, 119.49, 111.15, 109.49, 108.79, 108.75, 98.18, 59.87, 46.75, 31.72, 29.81, 29.70, 26.90, 22.35, 21.73, 21.38, 16.82, 14.02, 13.77.

HRMS (ESI) (m/z): calcd for $C_{58}H_{55}N_4O_3S$ ([M + Na] $^+$), 887.3989; found, 887.3994.

IR (neat): ν (cm^{-1}) 3056, 2959, 2929, 2871, 1940, 1661, 1595, 1508, 1454, 1403, 1320, 1281, 1247, 1153, 1136, 1085, 1005, 803, 778, 737.



1-(2-((2,3-dimethylphenyl)amino)phenyl)-2-(2-(naphthalen-1-yl)-3-tosylprop-1-en-1-ylidene)hexan-1-one (59)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 74.8 mg, 61%).

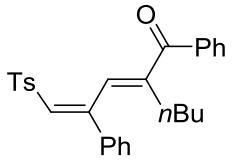
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 8.2 Hz, 2H), 7.44 – 7.43 (m, 1H), 7.35 – 7.30 (m, 2H), 7.21 – 7.18 (m, 1H), 7.17 – 7.12 (m, 3H), 7.06 – 7.02 (m, 2H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 8.6, 1H), 6.29 (t, *J* = 6.8,

1H), 4.30 (d, *J* = 14.2 Hz, 1H), 4.19 (d, *J* = 14.2 Hz, 1H), 2.55 – 2.49 (m, 1H), 2.44 – 2.35 (m, 1H), 2.35 (s, 3H), 2.29 (s, 3H), 2.11 (s, 3H), 1.60 – 1.51 (m, 2H), 1.40 – 1.39 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.58, 195.48, 148.48, 144.55, 138.56, 138.08, 136.07, 134.10, 133.81, 132.98, 132.50, 131.54, 130.55, 129.55, 128.50, 128.48, 128.24, 126.70, 126.41, 126.29, 125.87, 125.77, 125.13, 124.77, 122.04, 120.12, 115.69, 114.39, 108.34, 96.25, 60.37, 30.34, 29.10, 22.66, 21.49, 20.54, 13.92, 13.88.

HRMS (ESI) (m/z): calcd for $C_{40}H_{39}NNaO_3S$ ([M + Na] $^+$), 636.2543; found, 636.2535.

IR (neat): ν (cm^{-1}) 3052, 2956, 2870, 1941, 1616, 1507, 1319, 1031, 1008, 928, 810, 742.



(*E*)-1-phenyl-2-((*E*)-2-phenyl-3-tosylallylidene)hexan-1-one (60)

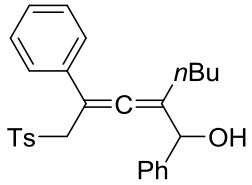
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 91.2 mg, 78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 3.6 Hz, 5H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.14 (s, 1H), 6.66 (d, *J* = 1.7 Hz, 1H), 2.42 (s, 3H), 2.05 – 1.97 (m, 2H), 1.14 – 1.07 (m, 2H), 1.07 – 1.01 (m, 2H), 0.66 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.83, 149.40, 147.71, 144.53, 138.34, 137.91, 137.36, 132.87, 132.59, 130.32, 129.90, 129.88, 129.08, 129.00, 128.44, 127.54, 127.47, 29.68, 29.24, 22.64, 21.59, 13.57.

HRMS (ESI) (m/z): calcd for $C_{28}H_{28}NaO_3S$ ([M + Na] $^+$), 467.1651; found, 467.1659.

IR (neat): ν (cm^{-1}) 3059, 2957, 2927, 2870, 1651, 1596, 1492, 1446, 1315, 1302, 1263, 1146, 1085, 835, 813, 717.



1-phenyl-2-(2-phenyl-3-tosylprop-1-en-1-ylidene)hexan-1-ol (61)

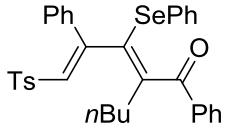
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 82.2 mg, 92%). The products could not readily be separated by silica gel chromatography. The ratio of the isomer was determined by 1H NMR Spectroscopy. The ^{1}H NMR spectrum of the product showed a 1.4:1 mixture based on the peak at δ 0.80 and at δ 0.75.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.49 – 7.47 (m, 2H), 7.42 – 7.34 (m, 2H), 7.34 – 7.31 (m, 1H), 7.18 – 7.08 (m, 7H), 5.27 – 5.24 (m, 1H), 4.41 – 4.29 (m, 1.57H), 4.15 – 4.09 (m, 1H), 3.82 – 3.79 (m, 0.39H), 2.33 (s, 3H), 1.94 – 1.83 (m, 2H), 1.38 – 1.17 (m, 4H), 0.80 (t, *J* = 8.0 Hz, 1.74H), 0.76 (t, *J* = 8.0 Hz, 1.23H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 205.128, 204.37, 144.93, 144.88, 142.10, 141.39, 135.72, 135.62, 134.68, 134.55, 129.69, 129.65, 128.67, 128.61, 128.55, 128.44, 128.28, 128.24, 128.02, 127.84, 127.43, 126.92, 126.89, 126.86, 125.84, 125.71, 115.84, 114.46, 100.62, 99.89, 75.42, 75.26, 58.75, 58.69, 29.71, 29.60, 29.47, 28.73, 22.40, 21.49, 13.80, 13.75.

HRMS (ESI) (m/z): calcd for $C_{28}H_{30}NaO_3S$ ([M + Na] $^+$), 469.1808; found, 469.1811.

IR (neat): ν (cm^{-1}) 3475, 3060, 3029, 2956, 2928, 2859, 1945, 1597, 1494, 1453, 1403, 1379, 1314, 1301, 1186, 1151, 1132, 1085, 1039, 1025, 912, 815, 748, 700.



(*Z*)-1-phenyl-2-((*E*)-2-phenyl-1-(phenylselanyl)-3-tosylallylidene)hexan-1-one (62)

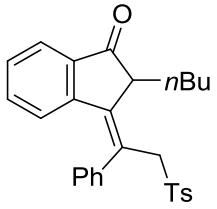
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 60.0 mg, 50%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 – 8.39 (m, 2H), 7.66 – 7.62(m, 3H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.31 (m, 3H), 7.28 – 7.19 (m, 7H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.42 (s, 1H), 2.66 – 2.62 (m, 1H), 2.59 – 2.54 (m, 1H), 2.45 (s, 3H), 1.52 – 1.49 (m, 1H), 1.32 – 1.28 (m, 1H), 1.20 – 1.16 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.15, 148.48, 147.13, 144.38, 138.25, 137.22, 136.73, 136.30, 133.47, 130.12, 130.09, 129.78, 128.76, 128.63, 128.57, 128.46, 127.68, 127.56, 127.40, 126.43, 125.27, 34.83, 29.81, 22.79, 21.62, 13.58.

HRMS (ESI) (m/z): calcd for $C_{34}H_{32}NaO_3SSe$ ([M + Na] $^{+}$), 623.1132; found, 623.1125.

IR (neat): ν (cm^{-1}) 3059, 2958, 2928, 2872, 1655, 1596, 1448, 1438, 1315, 1302, 1265, 1150, 1086, 1021, 909, 812, 739.



(*E*)-2-butyl-3-(1-phenyl-2-tosylethylidene)-2,3-dihydro-1H-inden-1-one (63)

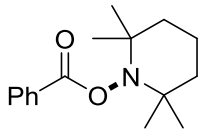
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) affords the title compound as a light yellow oil (yield 76.5 mg, 86%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.44 (s, 1H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 3H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.37 (d, *J* = 8.1 Hz, 1H), 4.44 (d, *J* = 14.0 Hz, 1H), 4.30 (d, *J* = 14.0 Hz, 1H), 3.15 (dd, *J* = 8.4, 3.7 Hz, 1H), 2.41 (s, 3H), 1.99 – 1.90 (m, 1H), 1.80 – 1.71 (m, 1H), 1.40 – 1.14 (m, 4H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.40, 147.96, 144.90, 142.36, 139.66, 137.76, 137.08, 134.01, 129.79, 129.32, 129.13, 128.57, 128.23, 127.96, 125.78, 125.72, 123.40, 63.74, 50.60, 32.36, 27.75, 22.73, 21.56, 13.83.

HRMS (ESI) (m/z): calcd for $C_{28}H_{28}NaO_3S$ ([M + Na] $^{+}$), 467.1651; found, 467.1653.

IR (neat): ν (cm^{-1}) 3064, 2989, 2953, 2928, 1710, 1595, 1467, 1314, 1298, 1240, 1171, 1136,1085, 809, 771, 747, 731.



2-butyl-3-(1-phenyl-2-tosylethylidene)-2,3-dihydro-1H-inden-1-one (64)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) affords

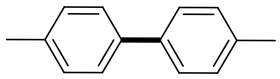
the title compound as a light yellow oil (yield 28.7 mg, 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.8 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 1.83 – 1.74 (m, 2H), 1.75 – 1.67 (m, 1H), 1.61 – 1.57 (m, 2H), 1.48 – 1.44 (m, *J* = 13.5, 3.4 Hz, 1H), 1.28 (s, 6H), 1.12 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.32, 132.78, 129.75, 129.51, 128.40, 60.37, 39.07, 31.94, 20.83, 16.99.

HRMS (ESI) (m/z): calcd for $C_{16}H_{23}NNaO_2$([M + Na] $^+$), 284.1621; found, 284.1614.

IR (neat): ν (cm^{-1}) 2974, 2935, 1749, 1450, 1378, 1364, 1255, 1236, 1176, 1132, 1080, 1061, 1024, 706.

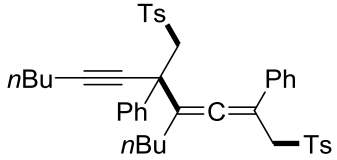


4,4'-dimethyl-1,1'-biphenyl (66)

Purification by column chromatography on silica gel (petroleum ether) affords the title compound as a light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.3 Hz, 4H), 7.10 (d, *J* = 7.9 Hz, 4H), 2.32 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.45, 133.93, 129.77, 128.58, 21.04.[8]



4,4'-(4-butyl-5-(hex-1-yn-1-yl)-2,5-diphenylhexa-2,3-diene-1,6-diyldisulfonyl)bis(methylbenzene) (5) and (5').

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1, v/v) affords the title compound as a light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.05 (m, 8H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.90 (d, *J* = 14.8 Hz, 1H), 4.44 (d, *J* = 14.5 Hz, 1H), 4.13 (d, *J* = 14.4 Hz, 1H), 3.88 (d, *J* = 14.8 Hz, 1H), 2.38 (t, *J* = 7.0 Hz, 2H), 2.33 (s, 3H), 2.30 (s, 3H), 2.14 – 2.08 (m, 1H), 1.64 – 1.61 (m, 2H), 1.54 – 1.44 (m, 3H), 1.17 – 1.09 (m, 1H), 1.06 – 1.04 (m, 3H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.63 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 203.79, 144.90, 142.96, 137.75, 137.52, 135.75, 133.91, 129.78, 128.99, 128.62, 128.36, 128.01, 127.95, 127.90, 127.16, 127.05, 125.47, 116.42, 101.16, 88.38, 78.86, 64.79, 58.34, 46.50, 30.82, 29.62, 28.42, 22.18, 22.06, 21.49, 21.43, 18.75, 13.67.

HRMS (ESI) (m/z): calcd for $C_{42}H_{46}NaO_4S_2$ ([M + Na] $^+$), 701.2730; found, 701.2748.

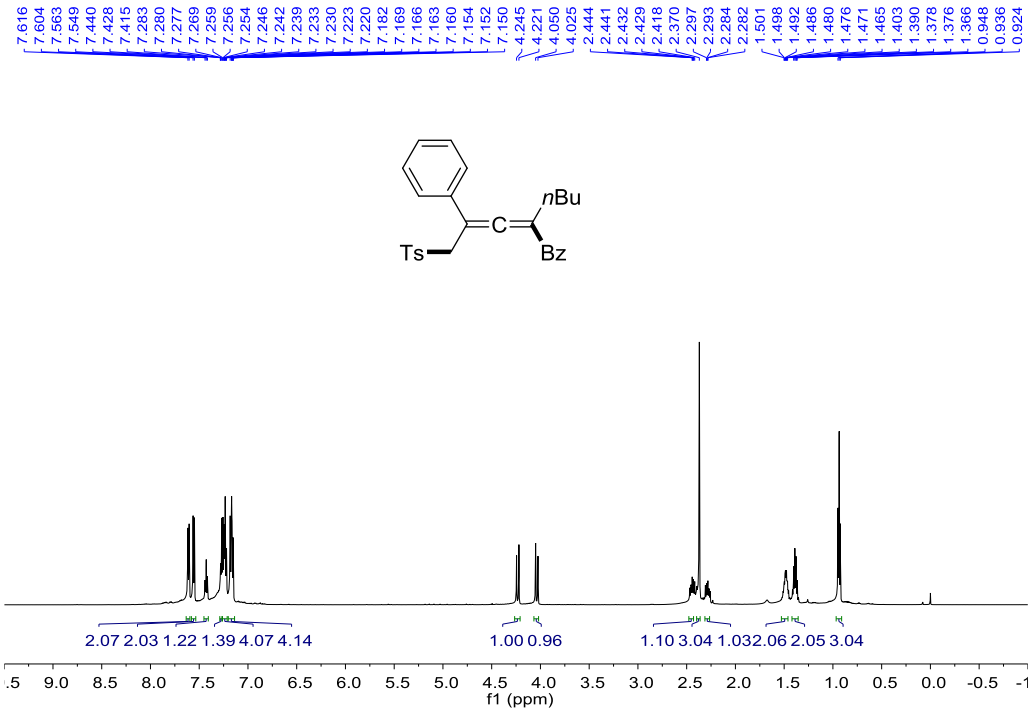
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.38 (m, 2H), 7.24 – 7.18 (m, 10H), 7.17 – 7.13 (m, 2H), 4.44 – 4.32 (m, 2H), 3.70 (d, *J* = 14.6 Hz, 1H), 2.37 (s, 6H), 2.08 (t, *J* = 6.9 Hz, 2H), 2.06 – 2.00 (m, 1H), 1.67 – 1.62 (m, 1H), 1.50 – 1.40 (m, 4H), 1.24 – 1.17 (m, 2H), 1.16 – 1.05 (m, 3H), 0.94 (t, *J* = 7.0 Hz, 3H), 0.72 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 204.19, 144.54, 143.63, 139.50, 138.32, 136.38, 134.61, 129.64, 129.16, 128.52, 128.44, 128.37, 128.09, 127.42, 127.36, 126.07, 114.89, 102.03, 89.29, 77.57, 64.71, 58.66, 46.39, 30.59, 29.78, 29.69, 28.98, 22.42, 22.12, 21.54, 18.69, 13.75, 13.63.

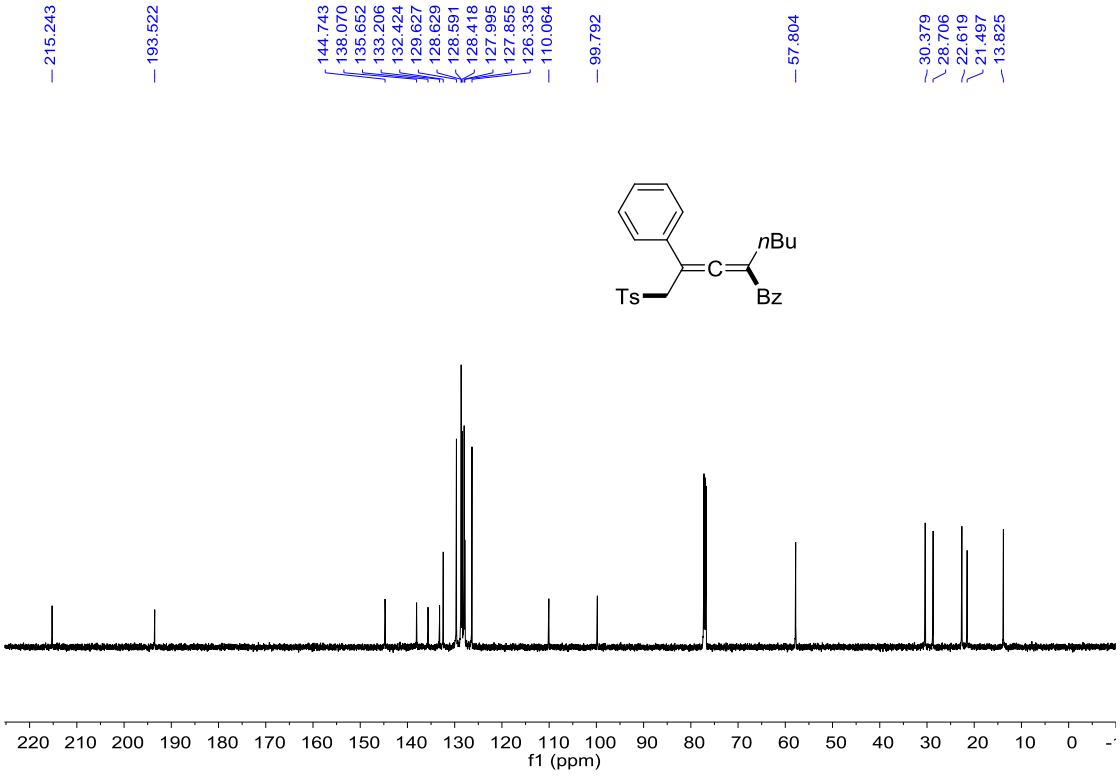
HRMS (ESI) (m/z): calcd for $C_{42}H_{46}NaO_4S_2$ ([M + Na] $^+$), 701.2730; found, 701.2733.

IR (neat): ν (cm^{-1}) 3060, 3028, 2957, 2929, 2871, 2238, 1942, 1597, 1493, 1449, 1319, 1303, 1154, 1133, 1086, 929, 814, 767, 749.

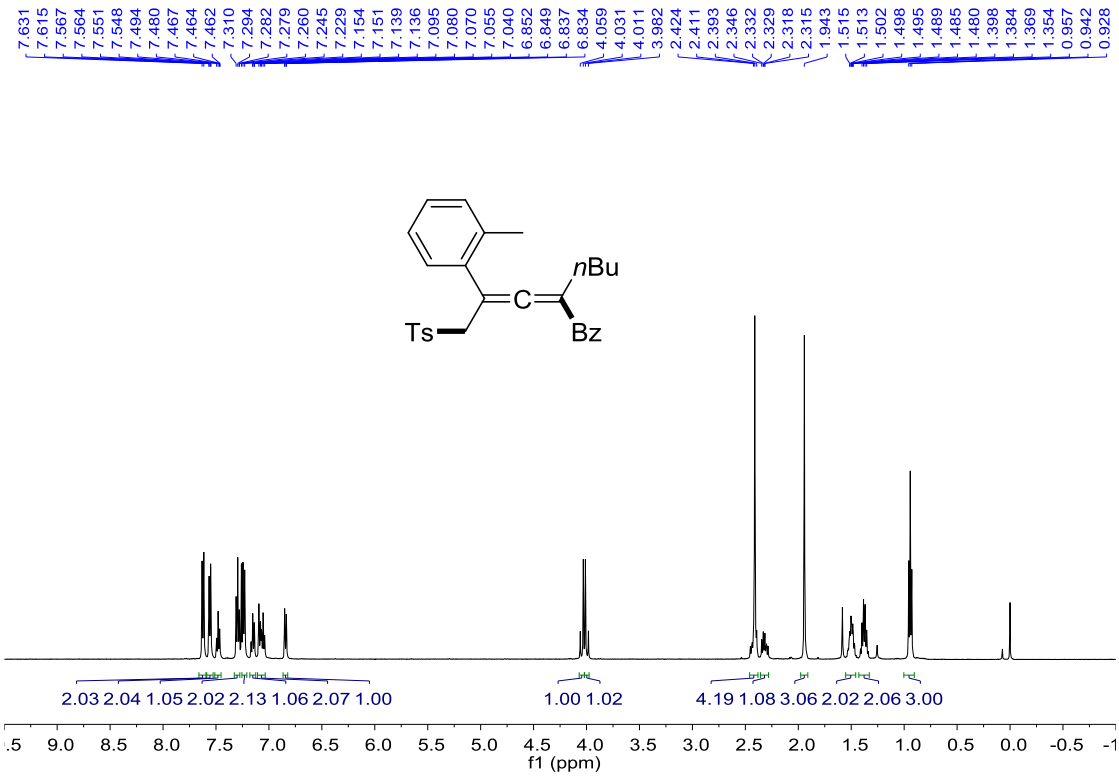
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **4**.



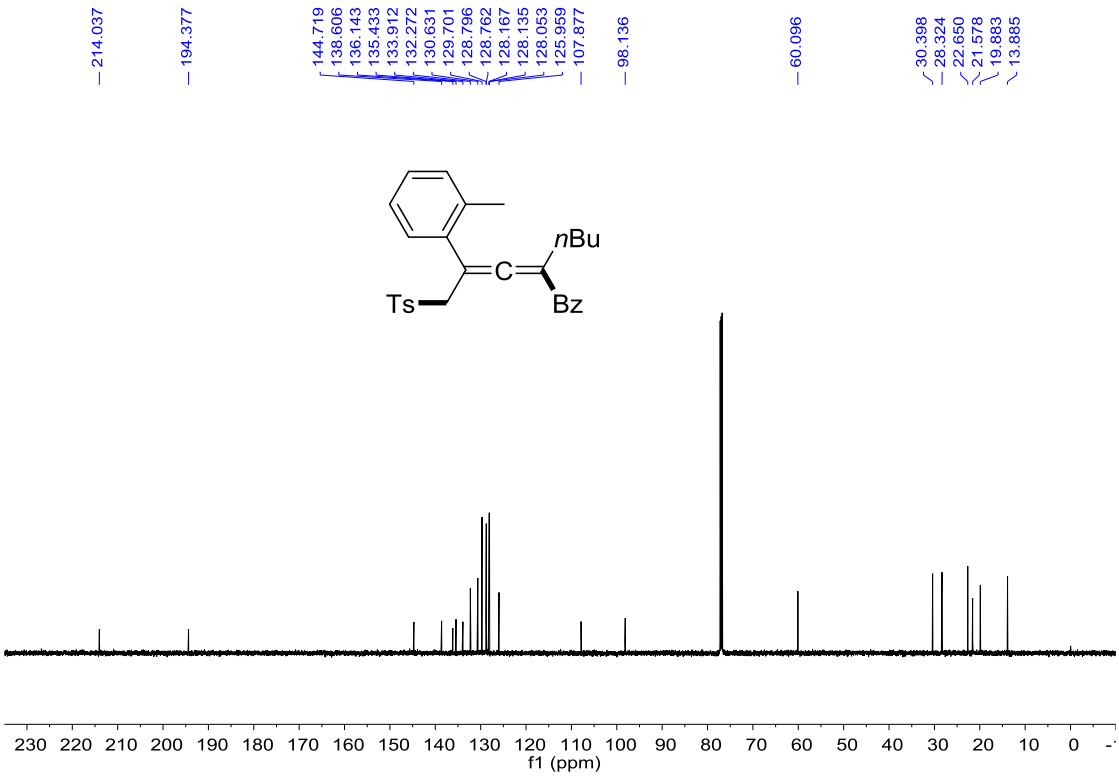
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **4**.



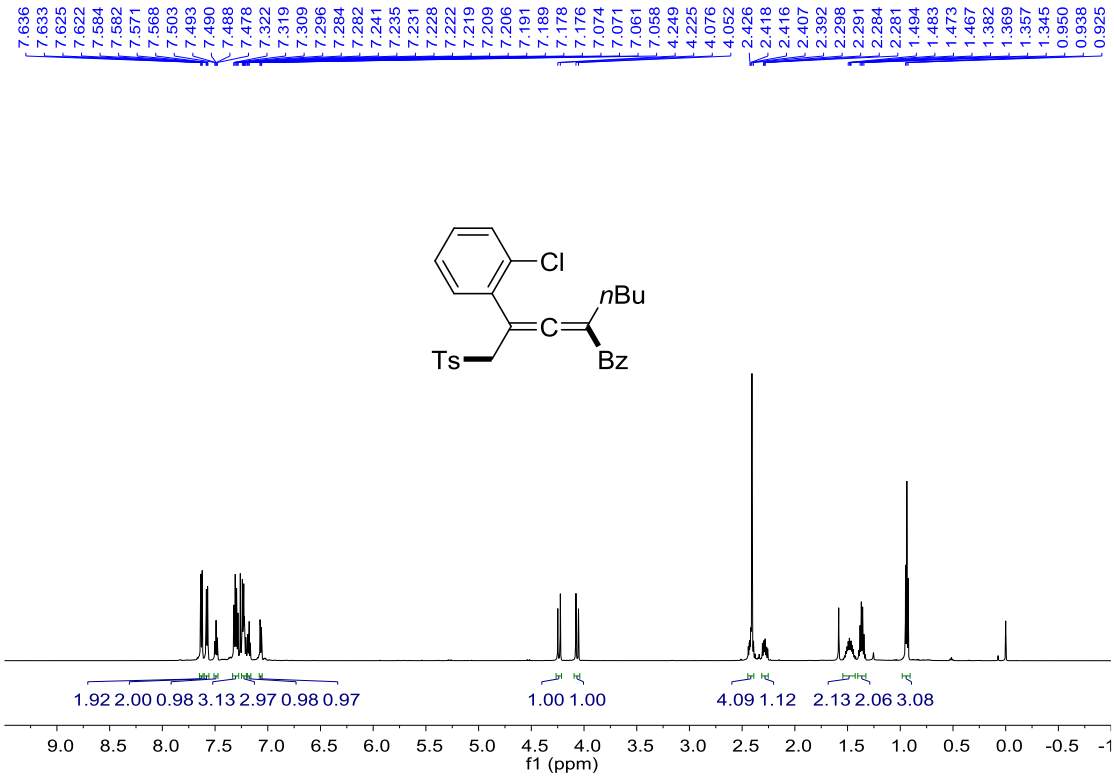
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **6**.



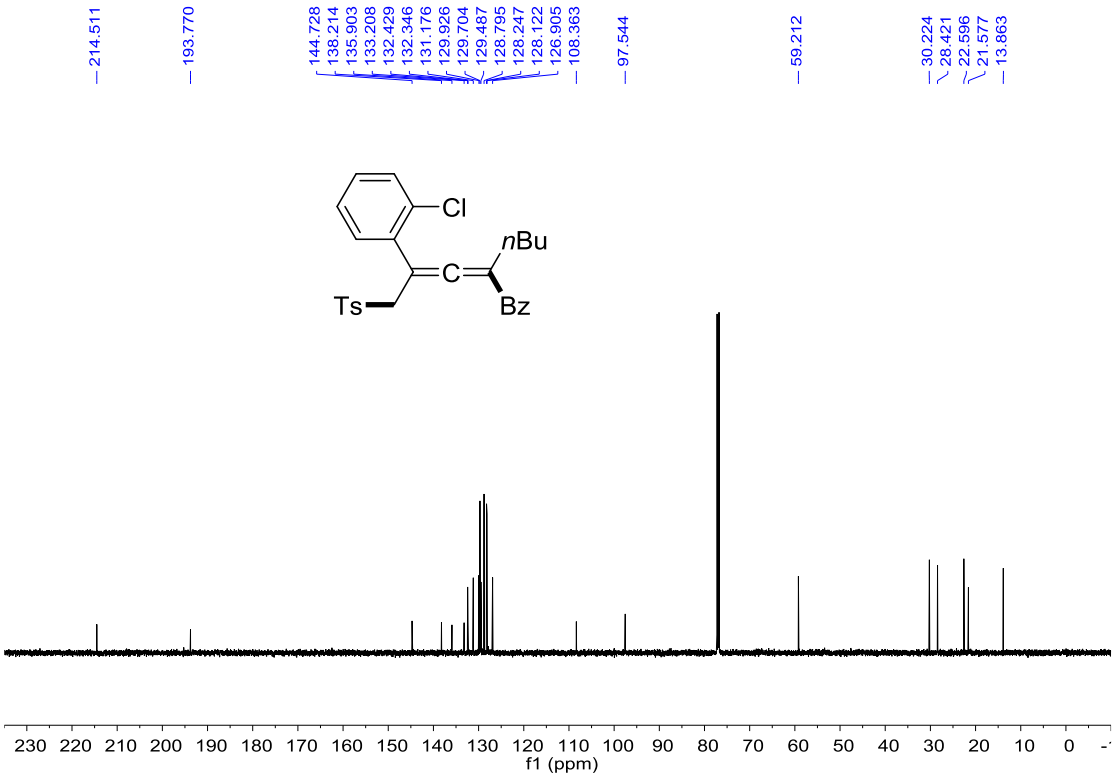
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **6**.



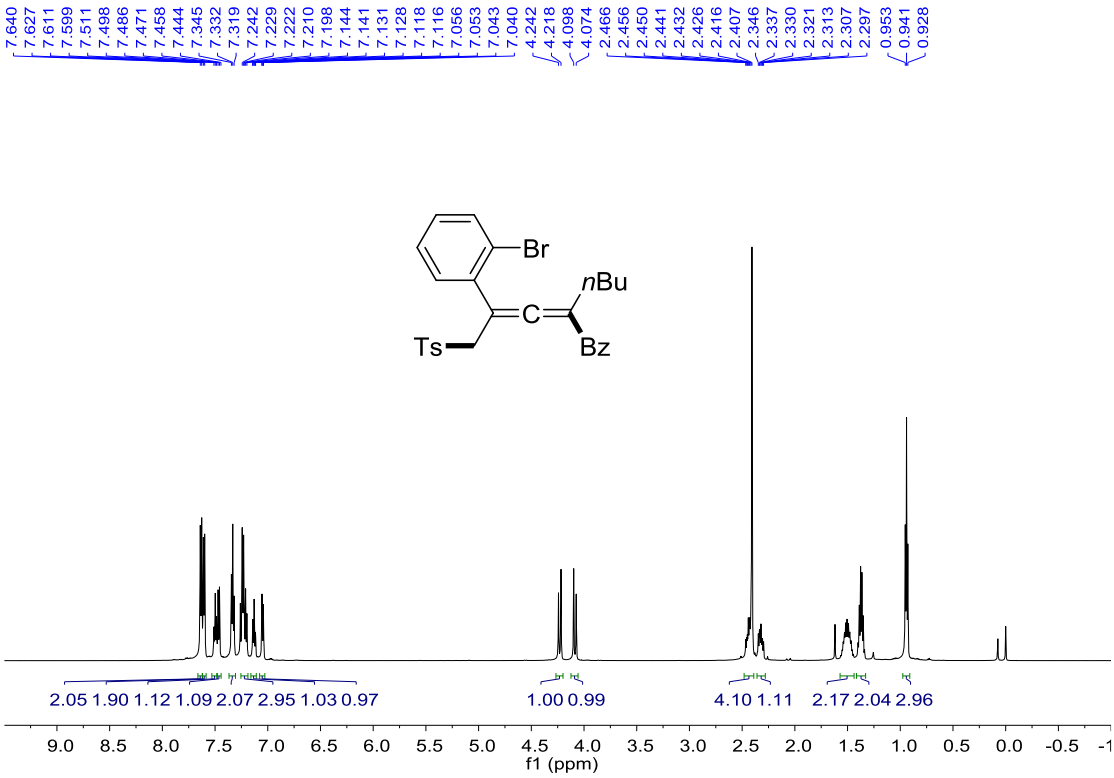
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **7**.



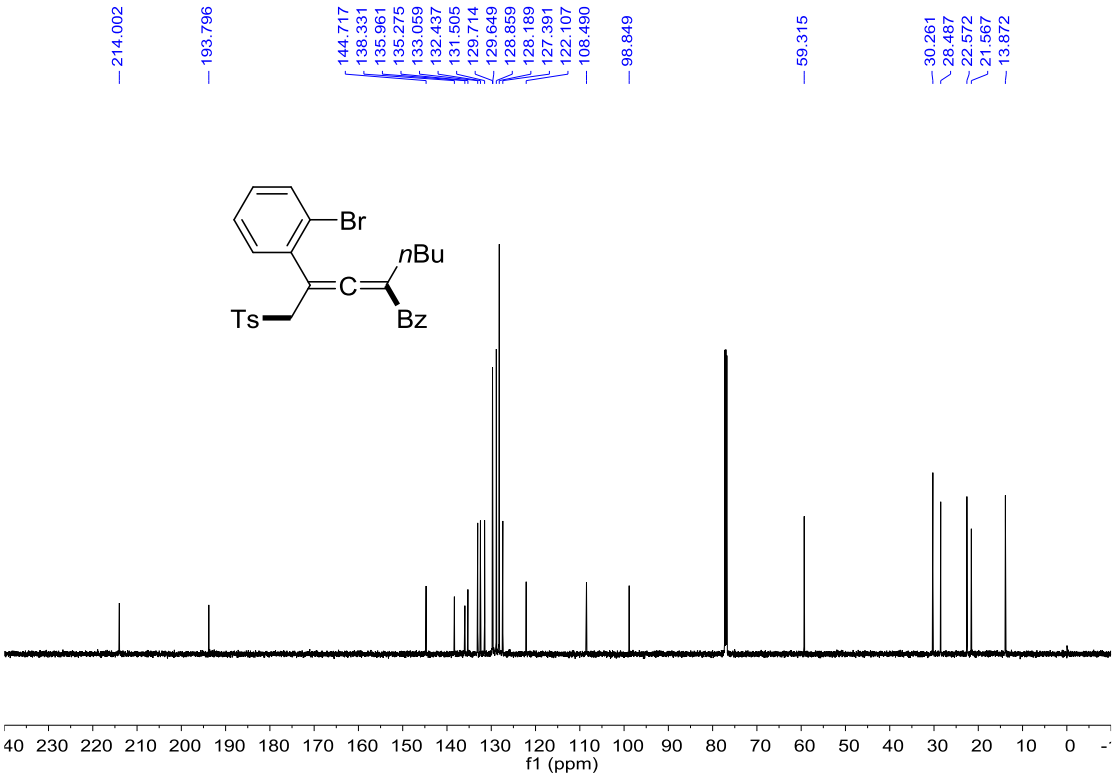
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **7**.



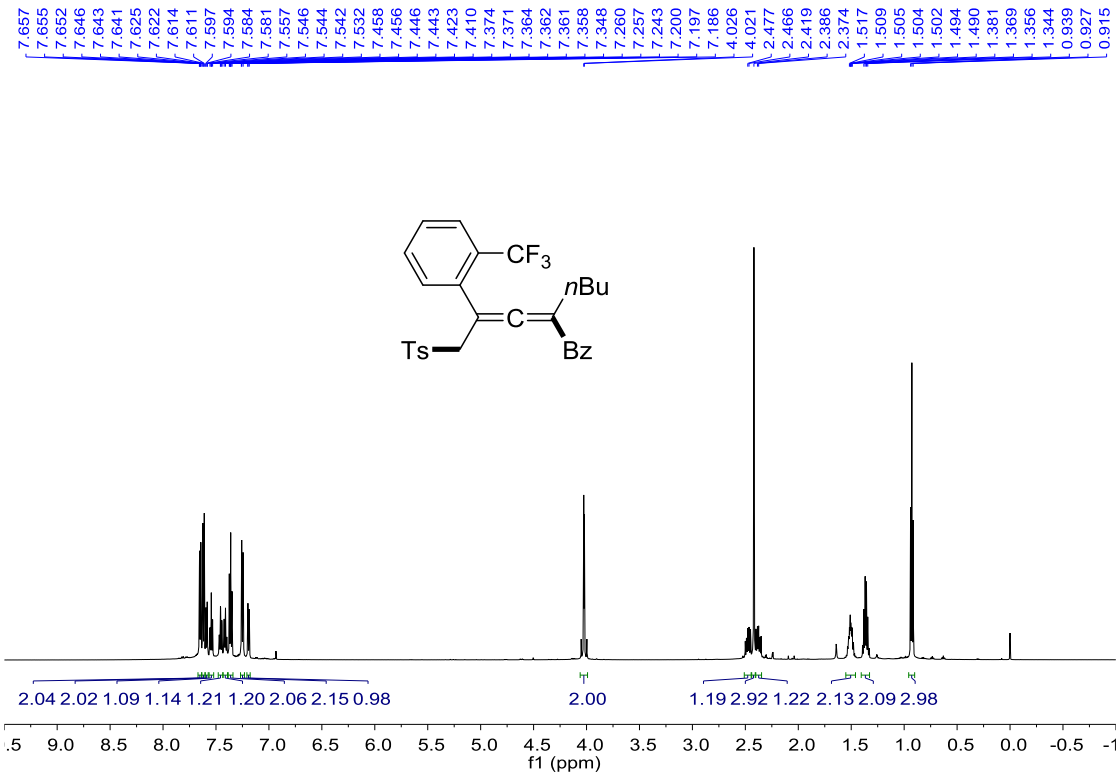
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **8**.



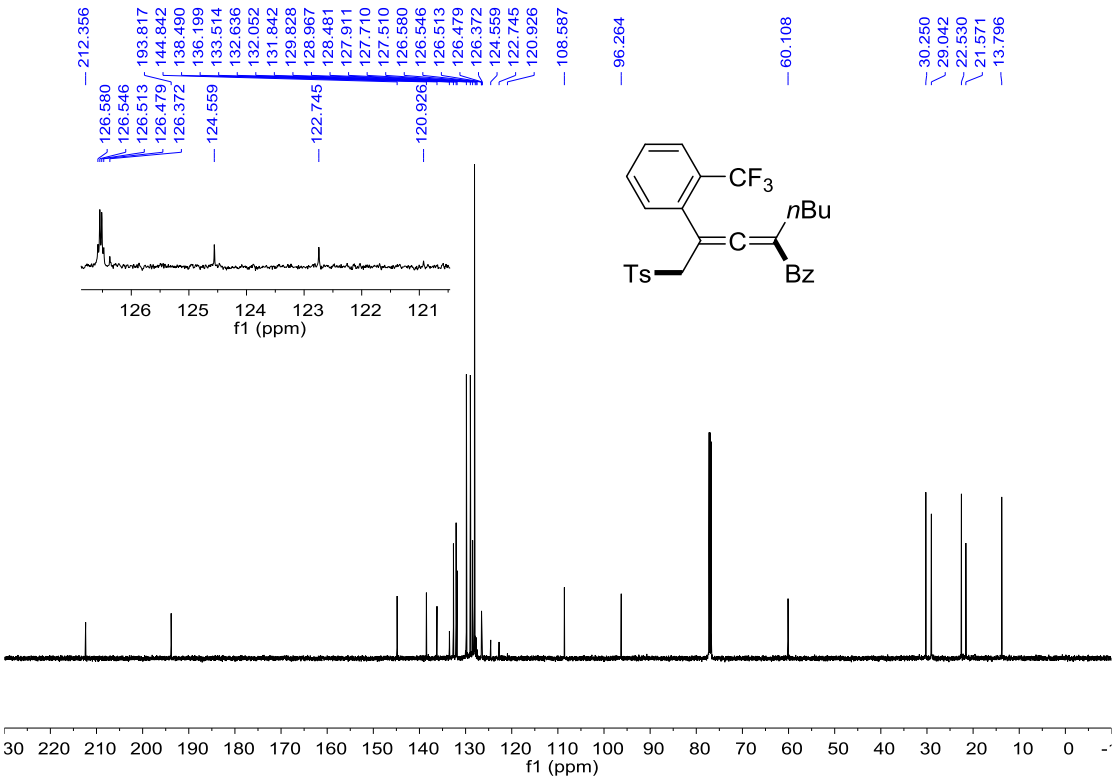
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **8**.



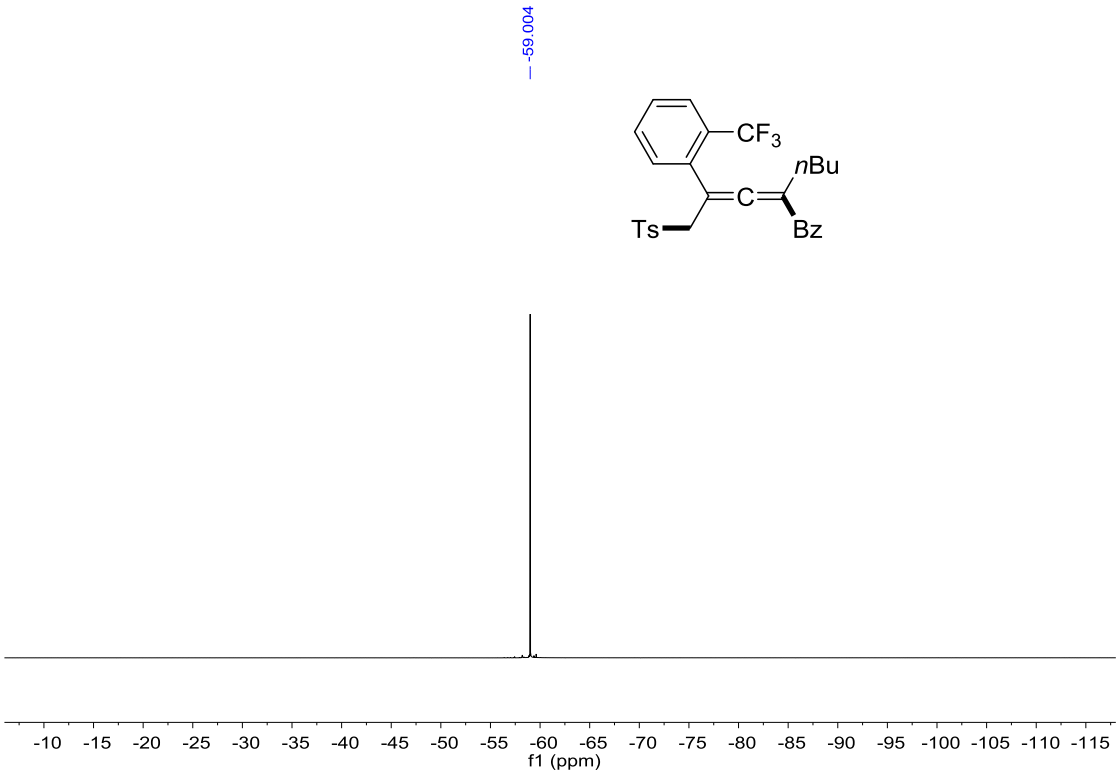
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **9**.



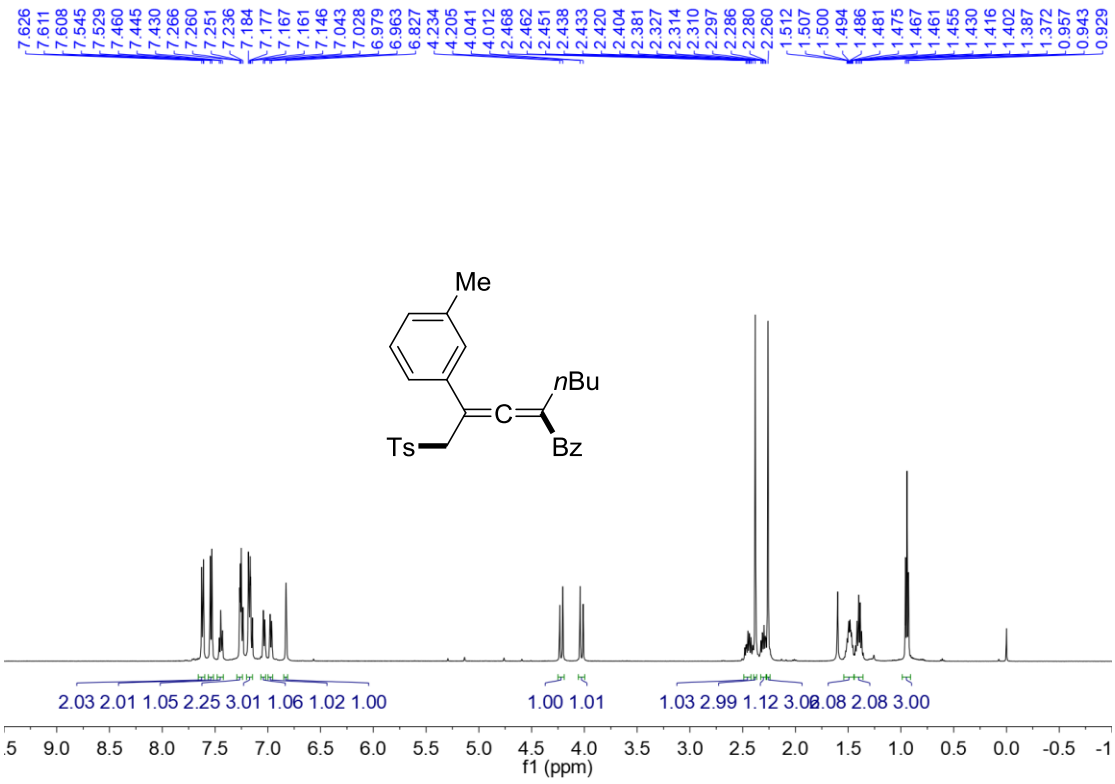
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **9**.



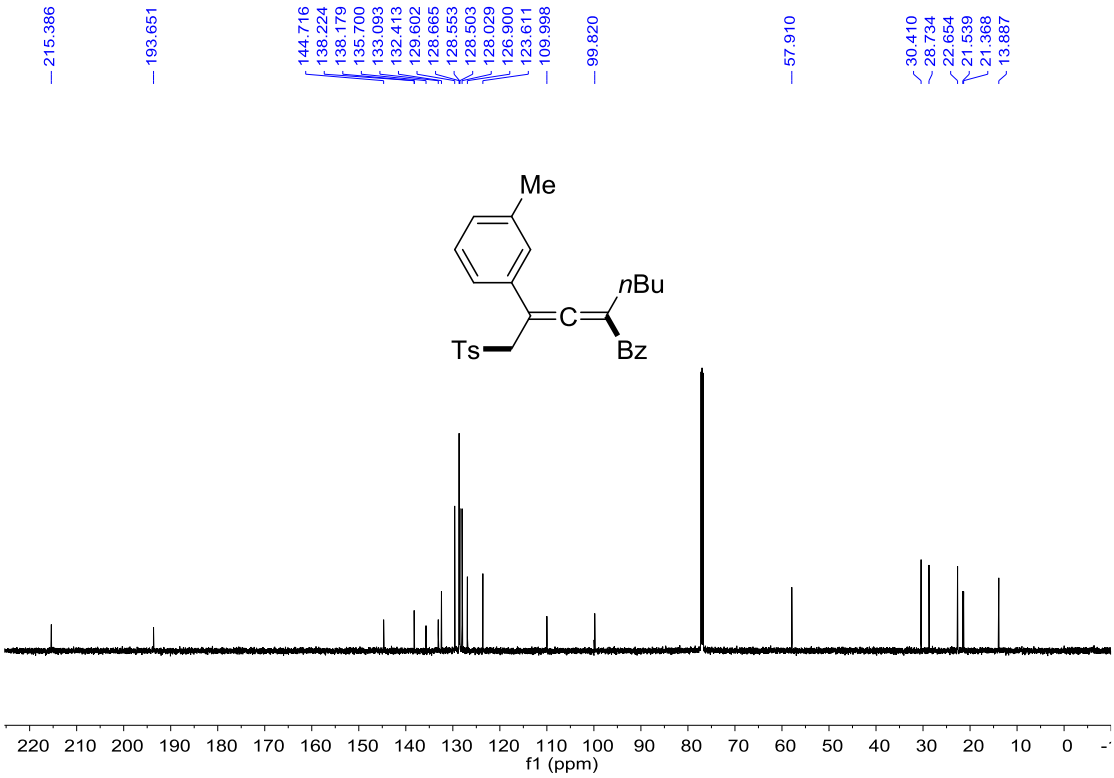
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **9**.



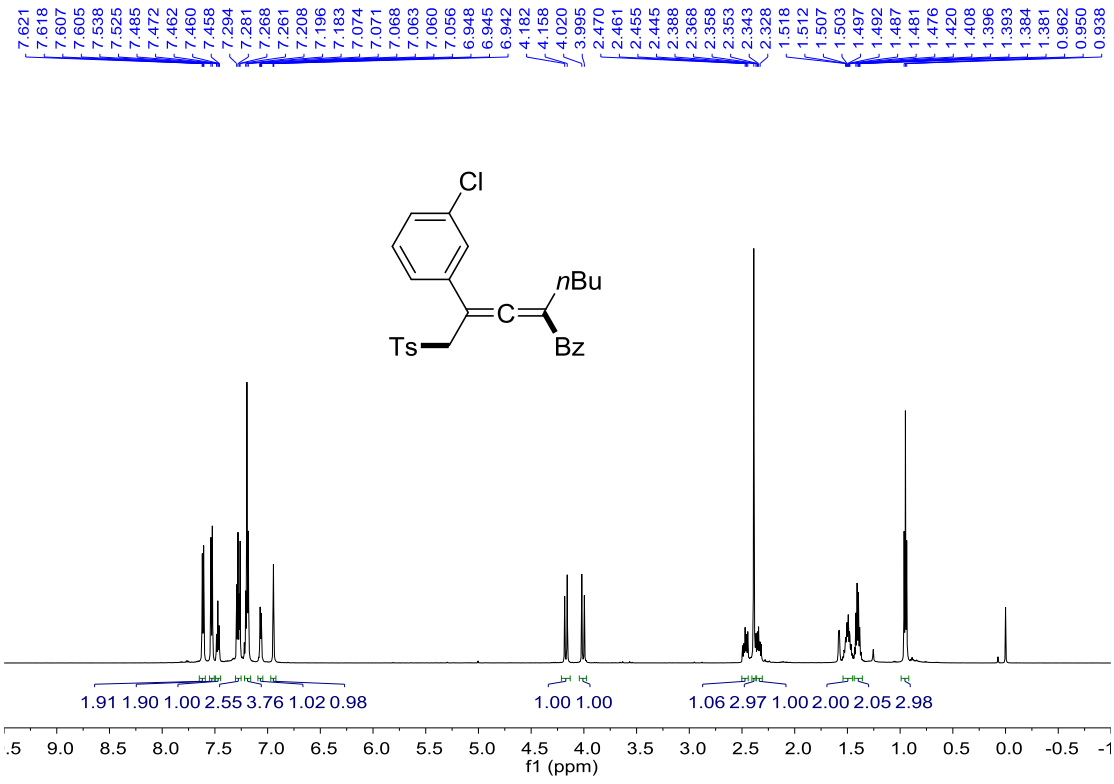
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **10**.



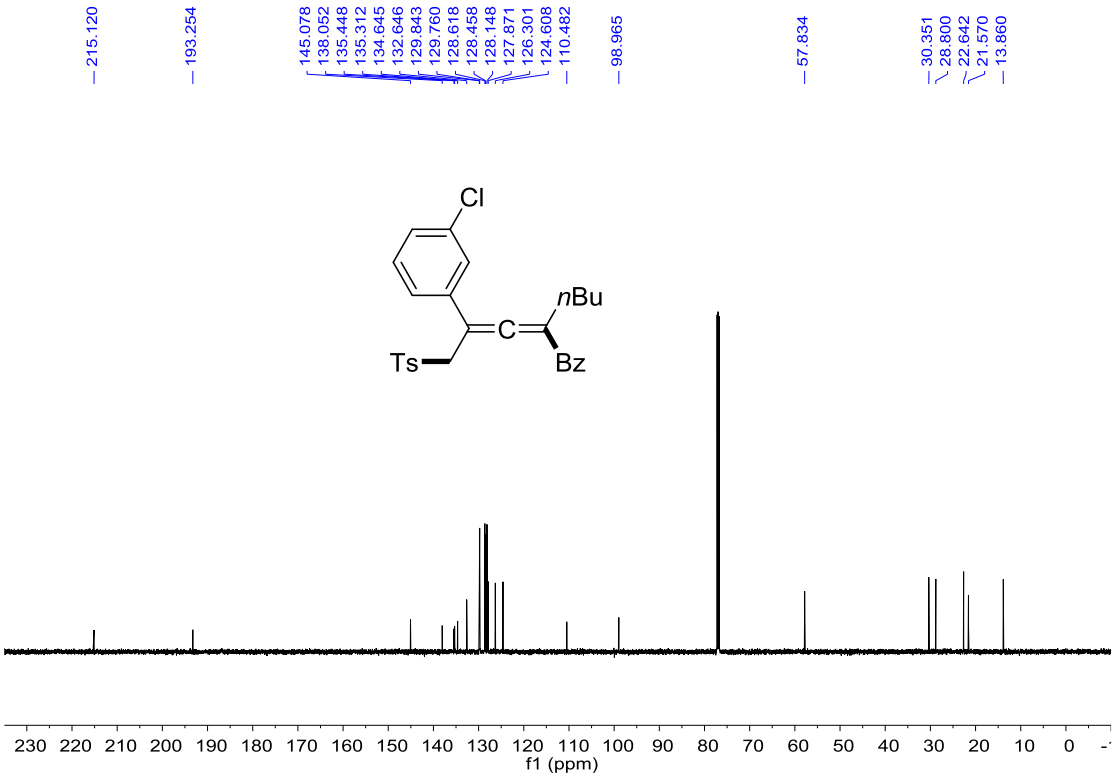
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **10**.



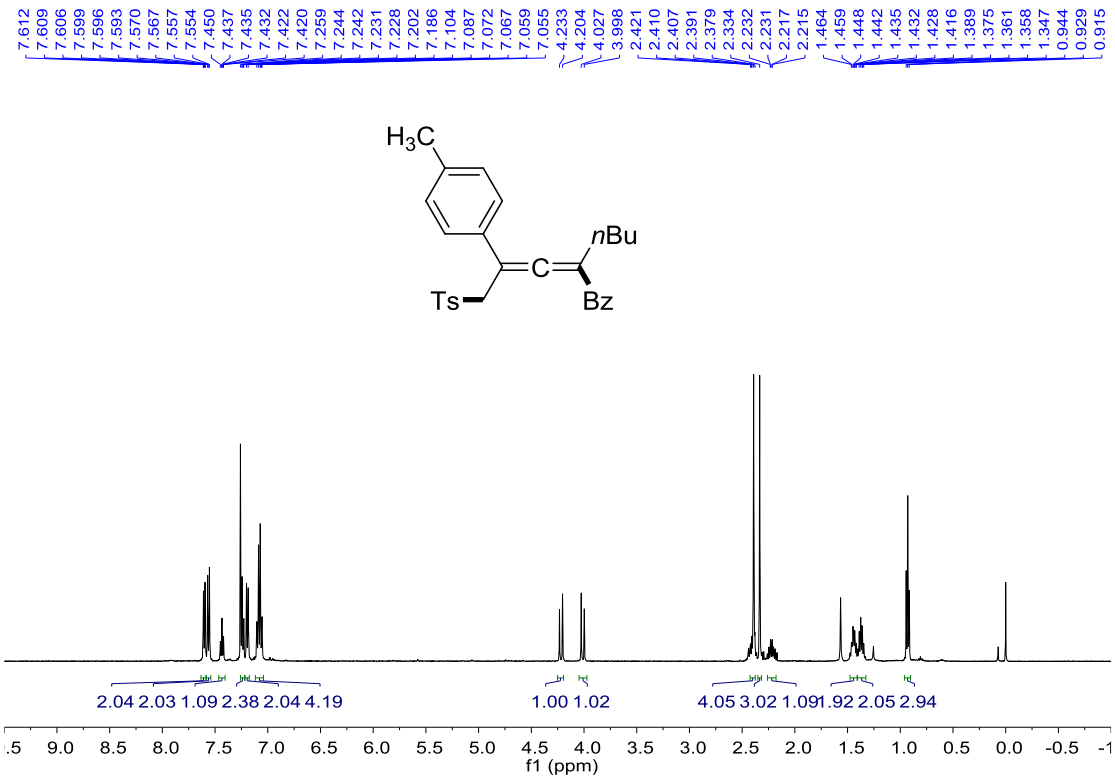
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **11**.



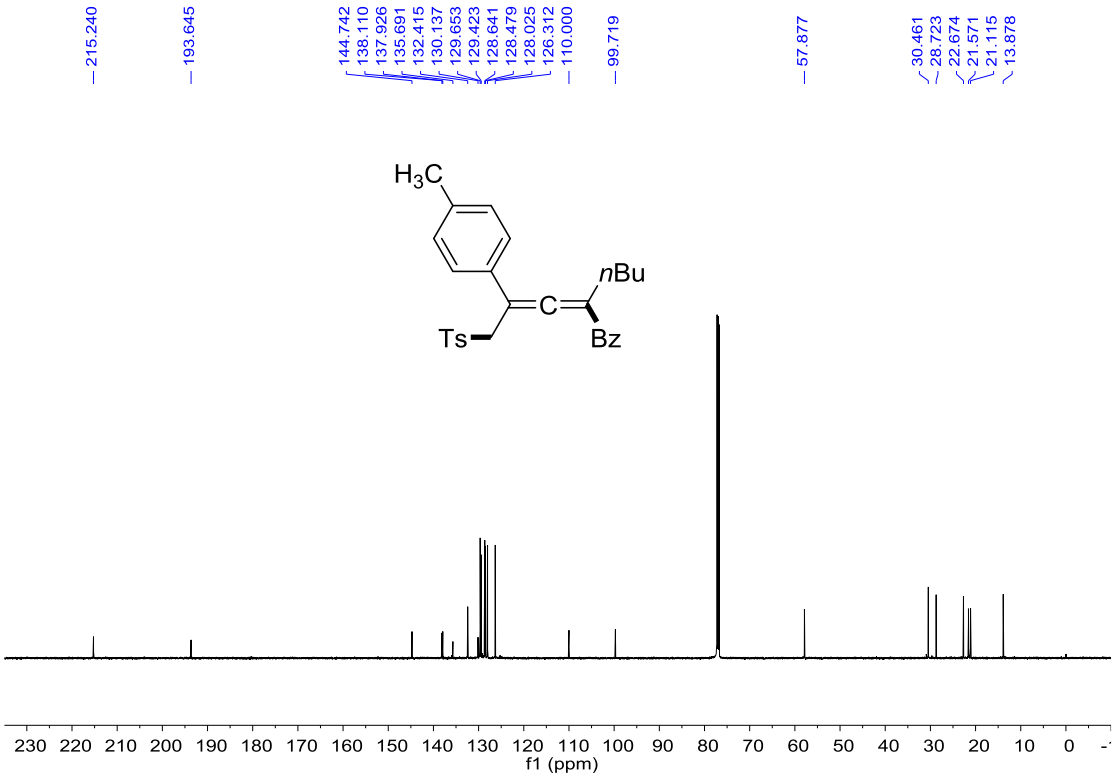
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **11**.



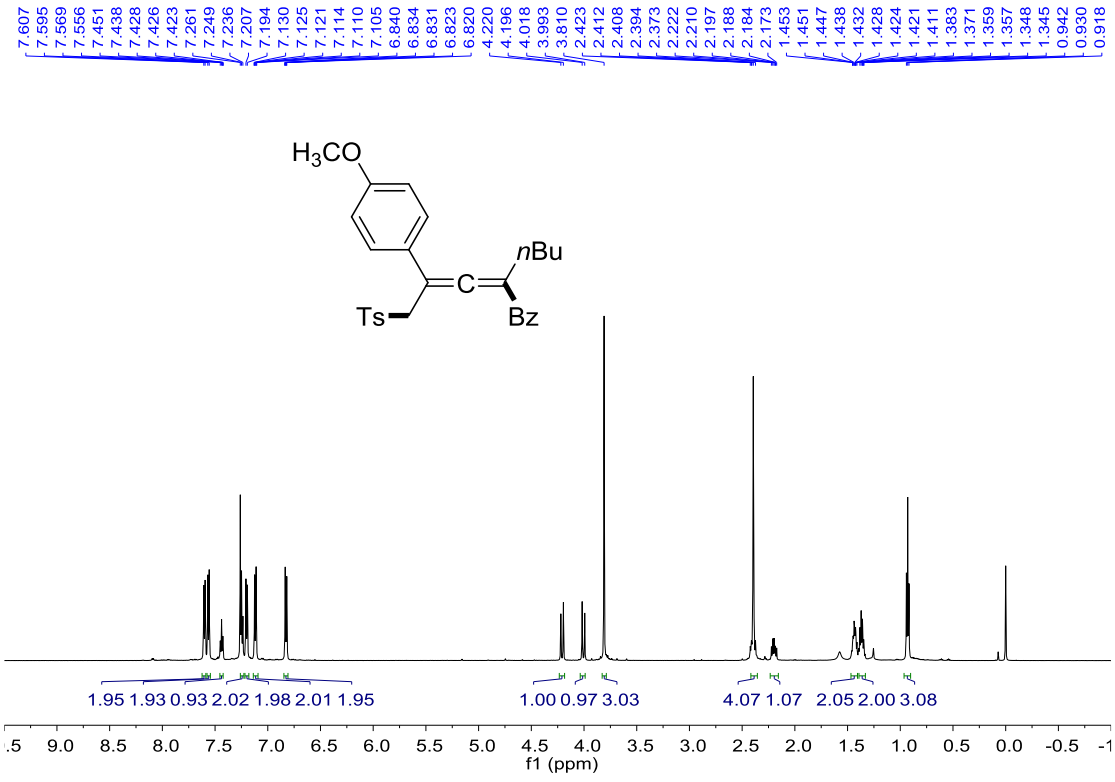
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **12**.



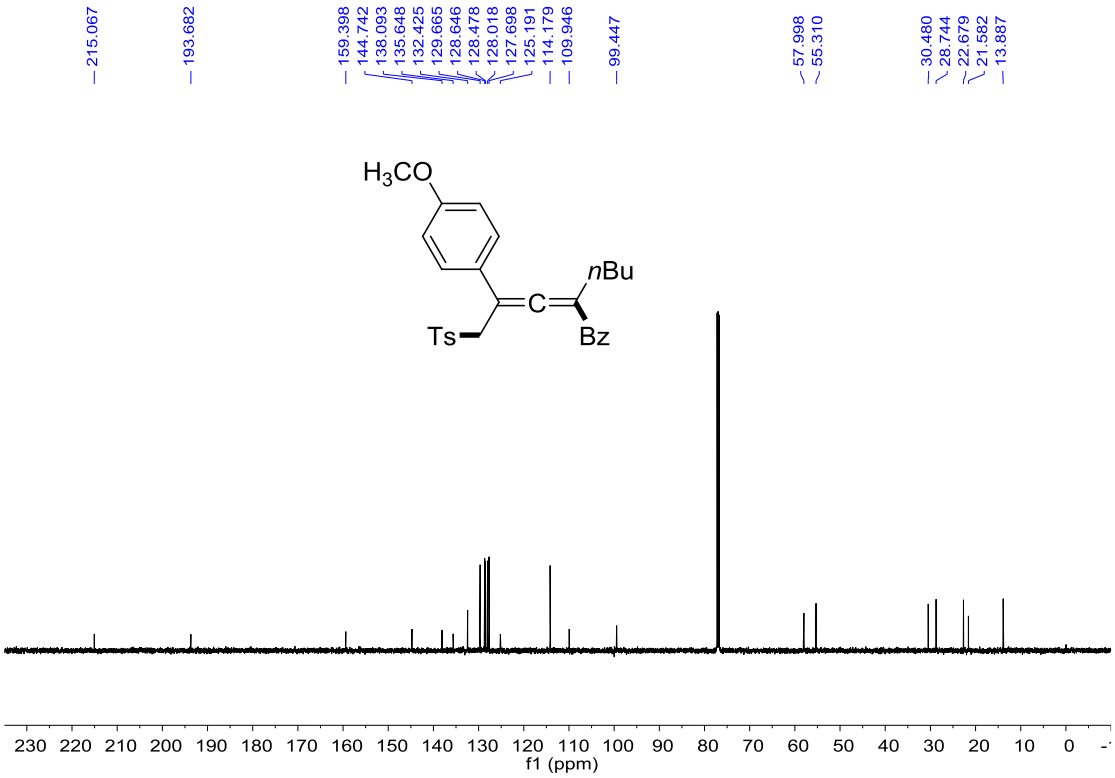
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **12**.



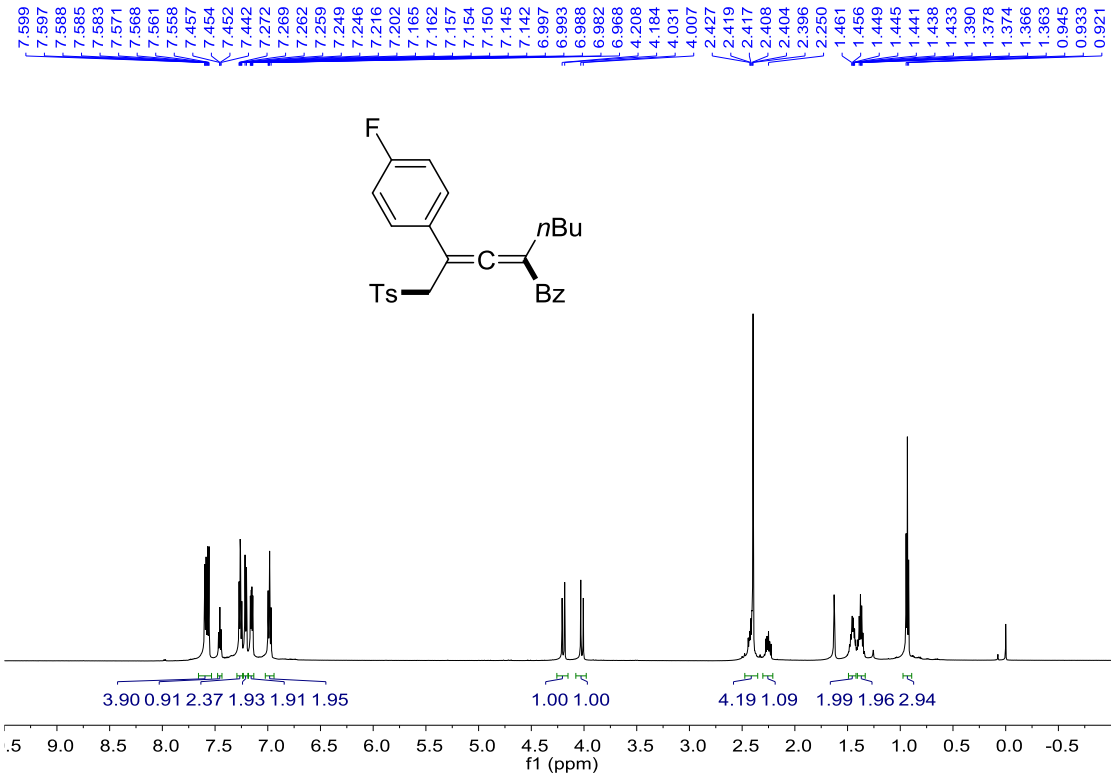
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **13**.



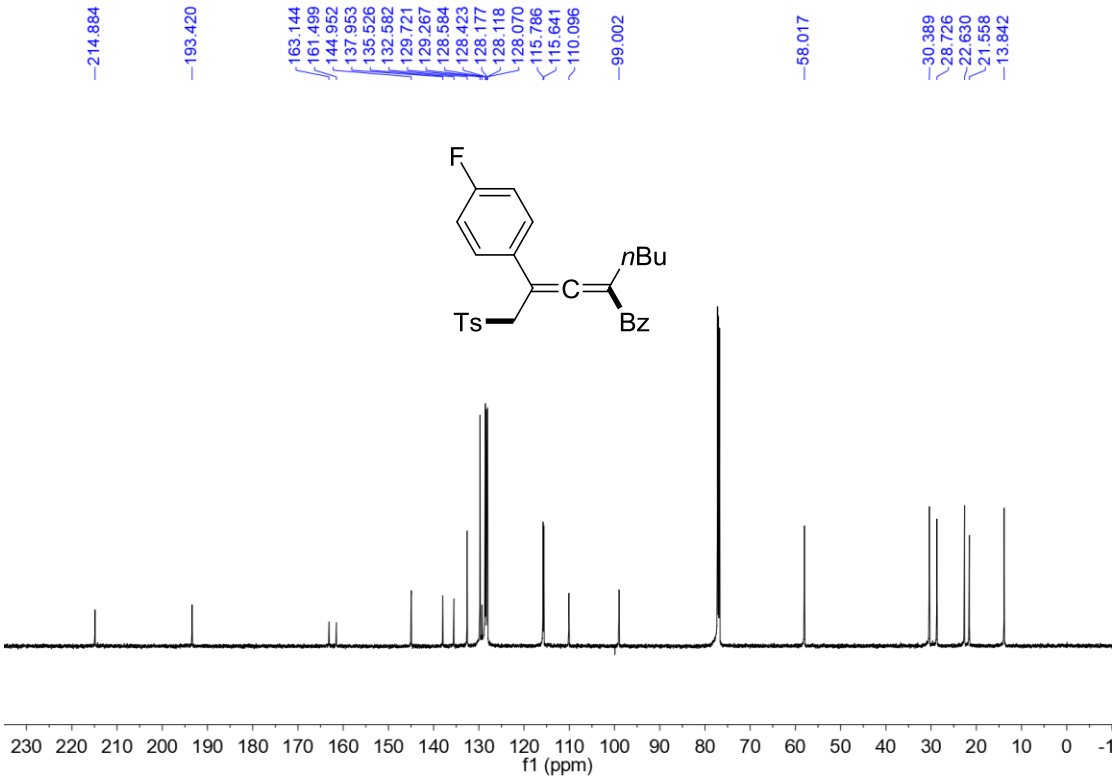
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **13**.



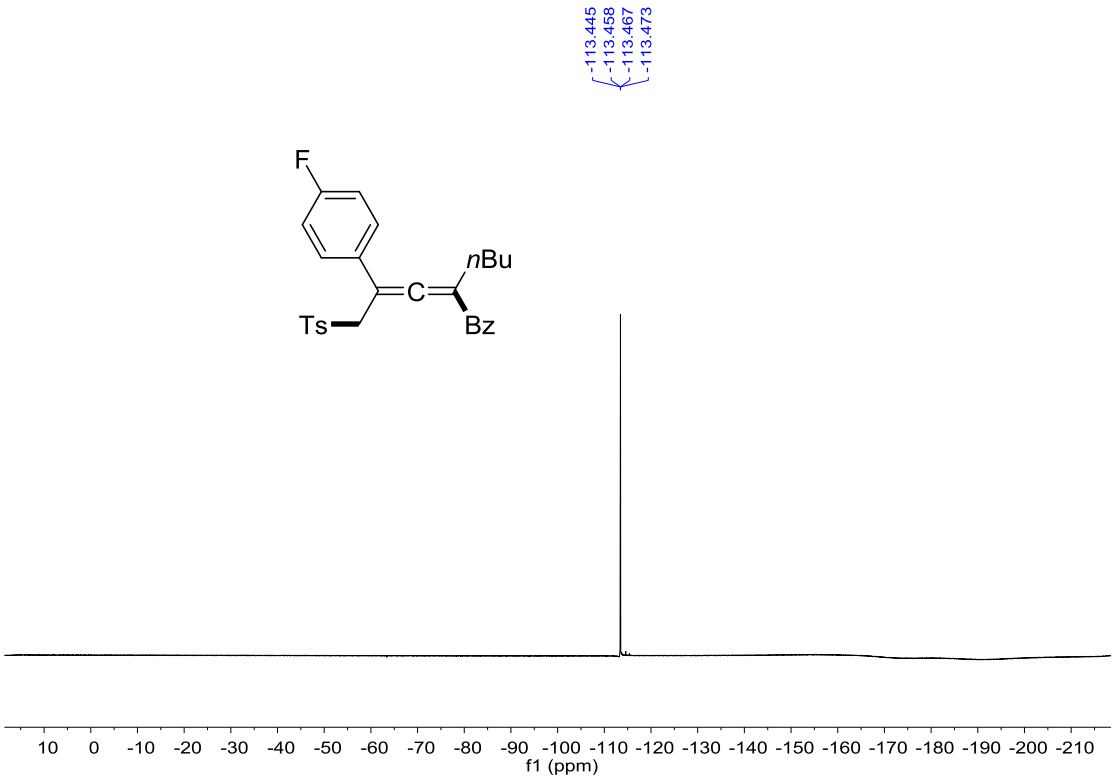
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **14**.



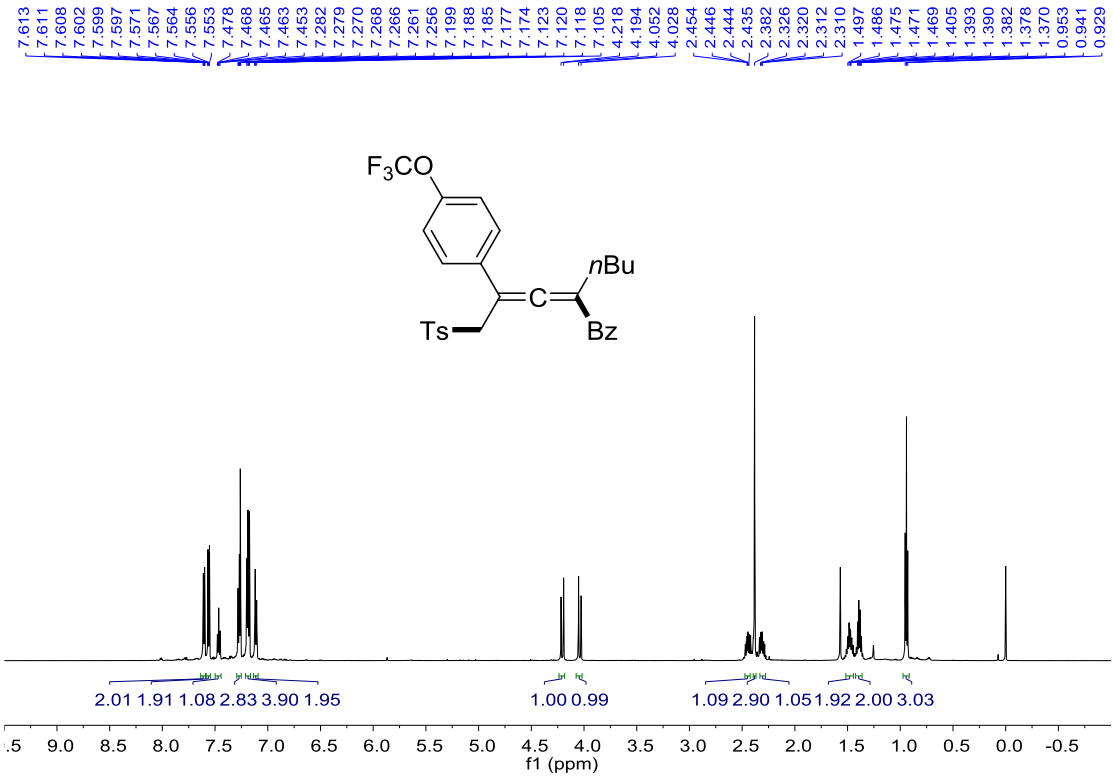
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **14**.



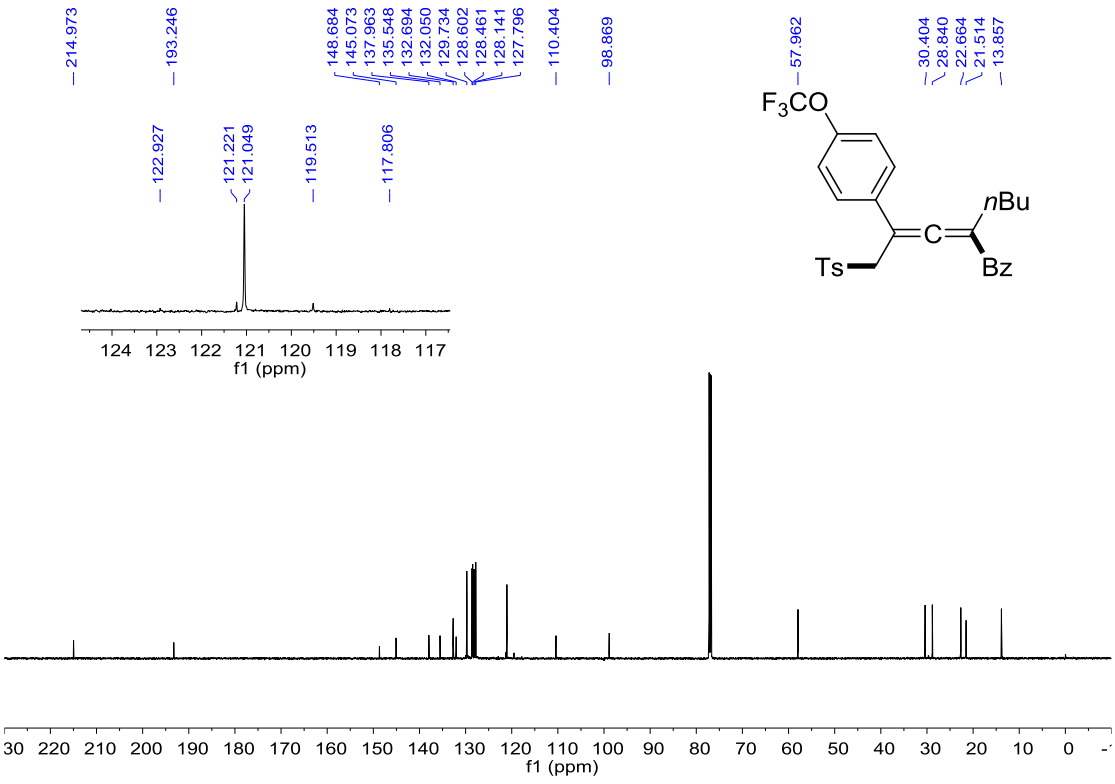
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **14**.



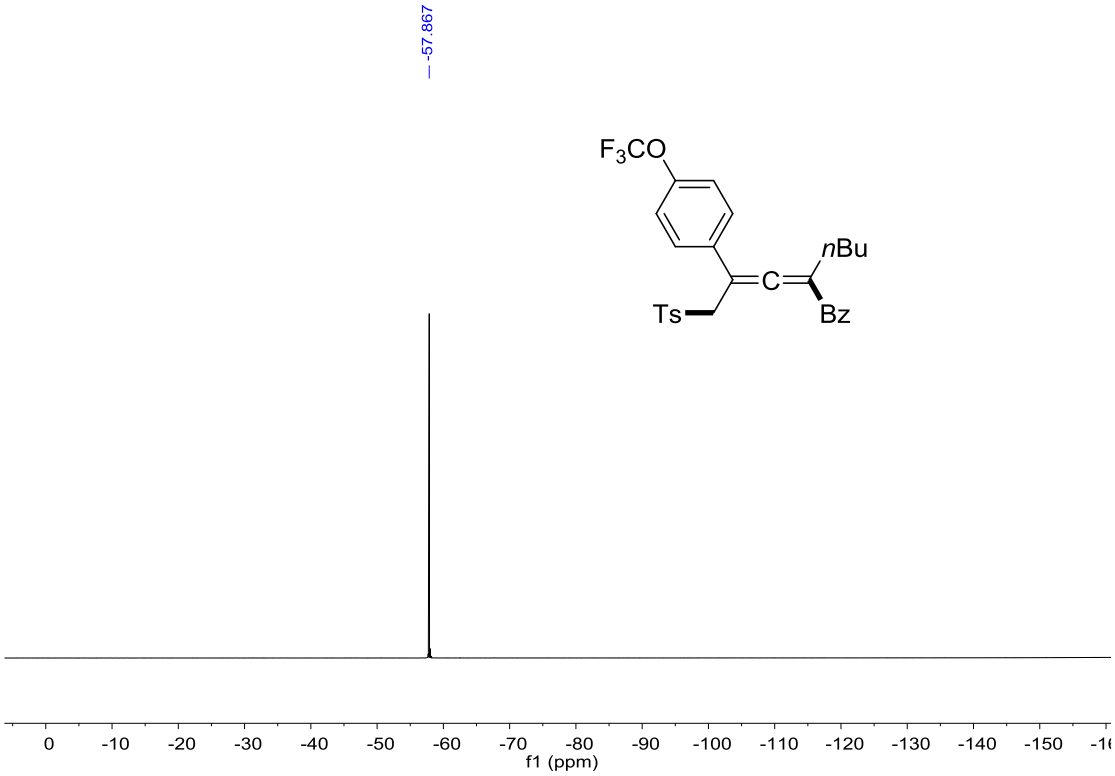
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **15**.



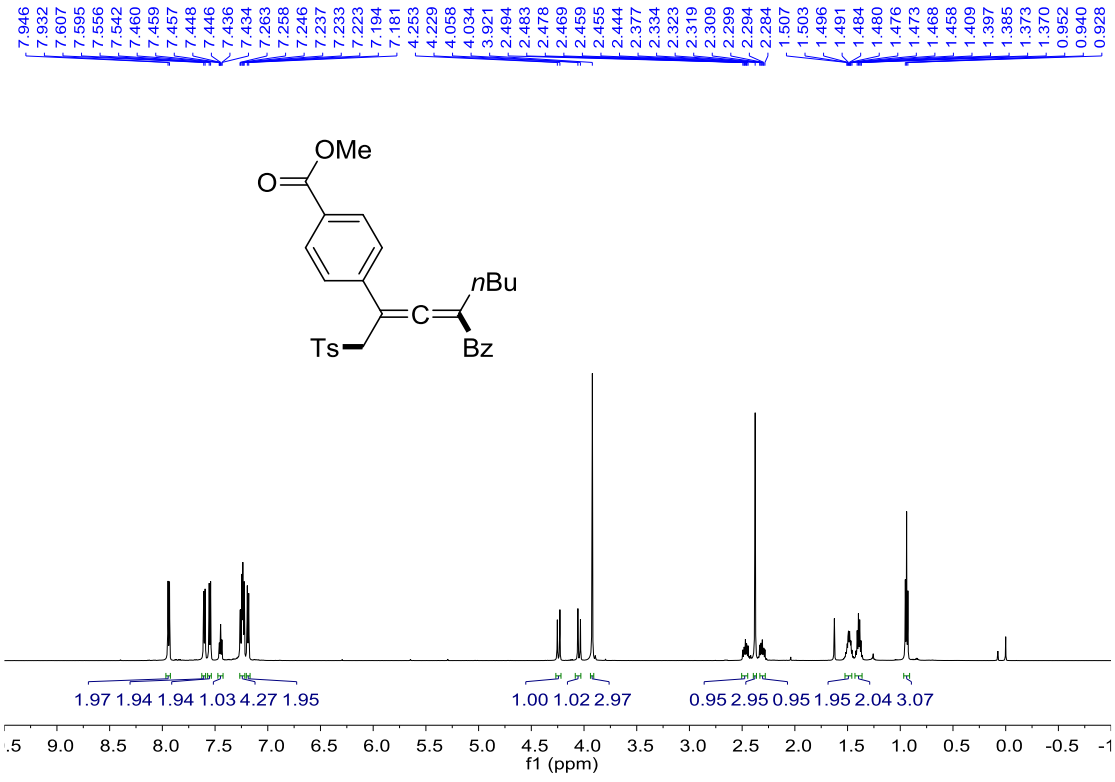
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **15**.



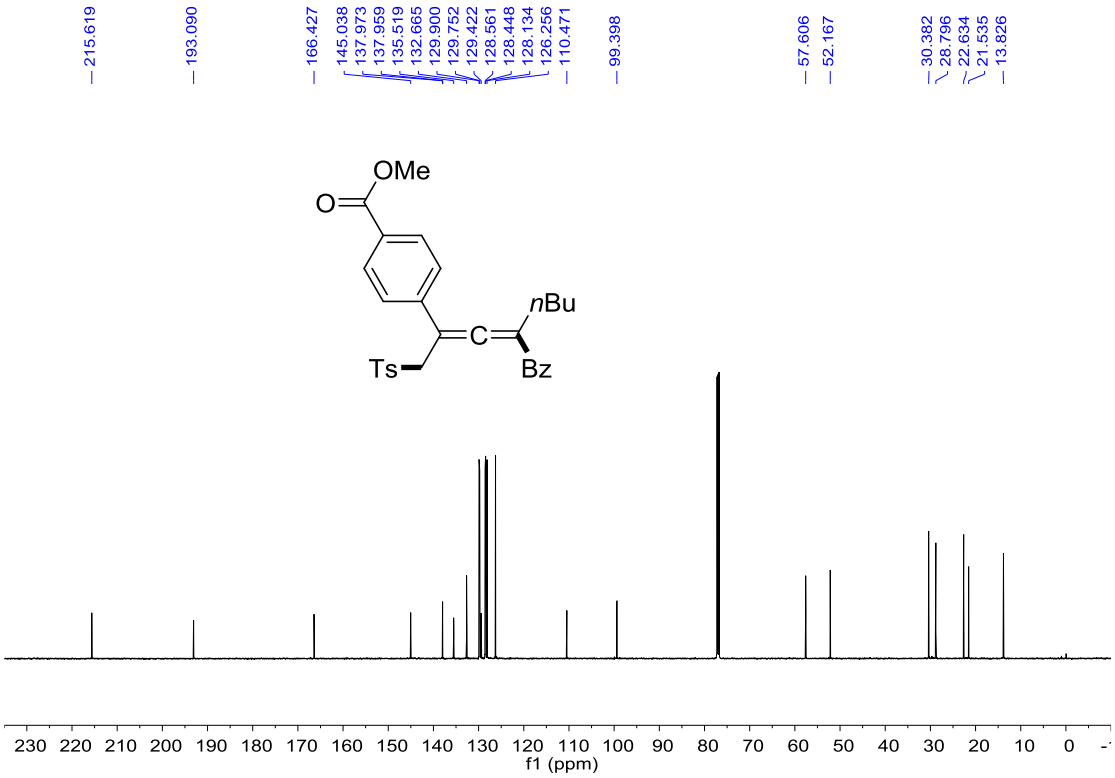
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **15**.



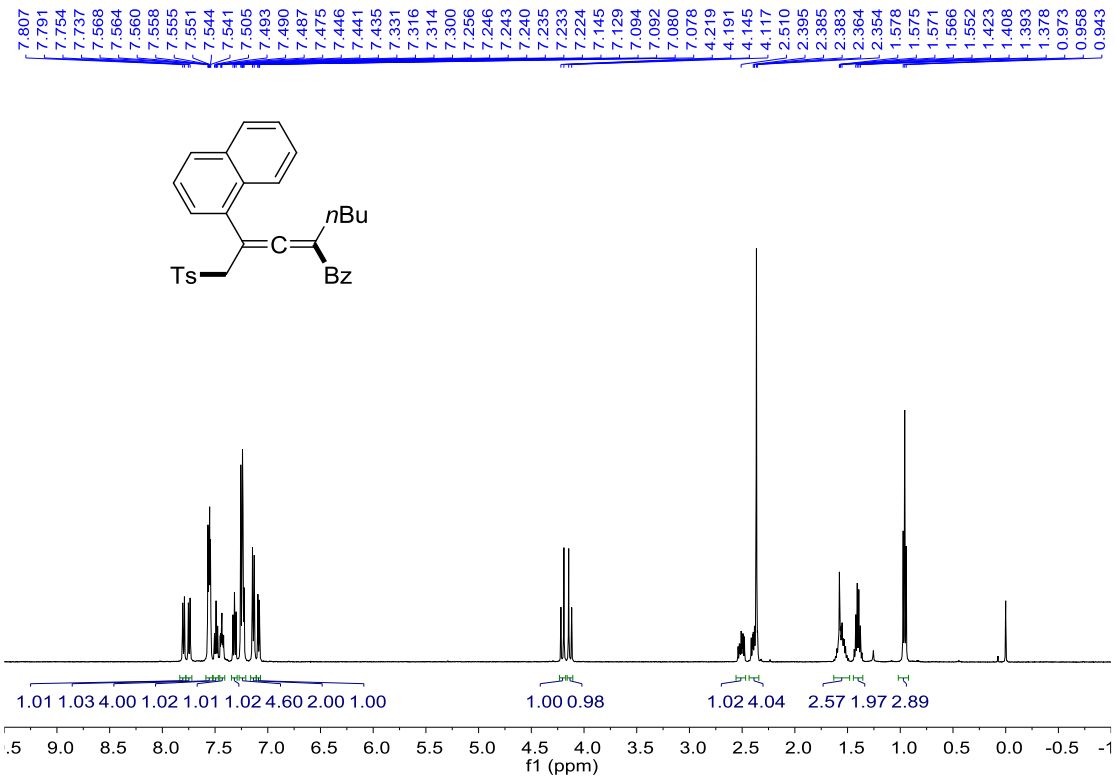
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **16**.



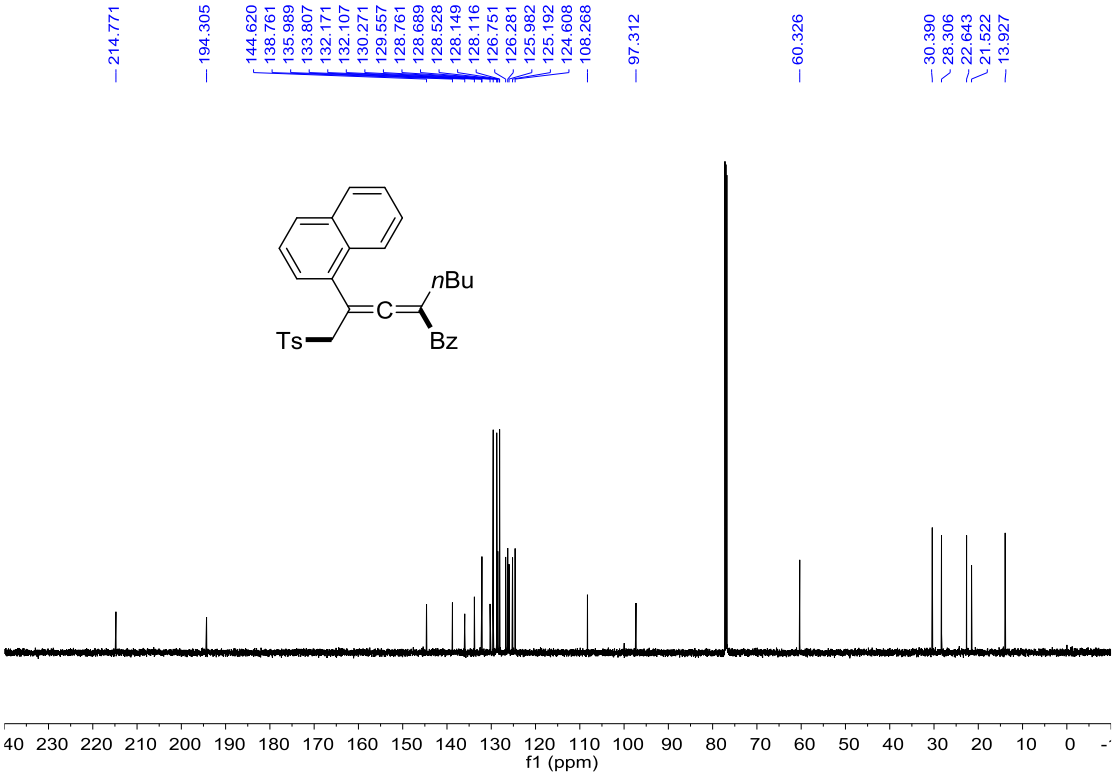
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **16**.



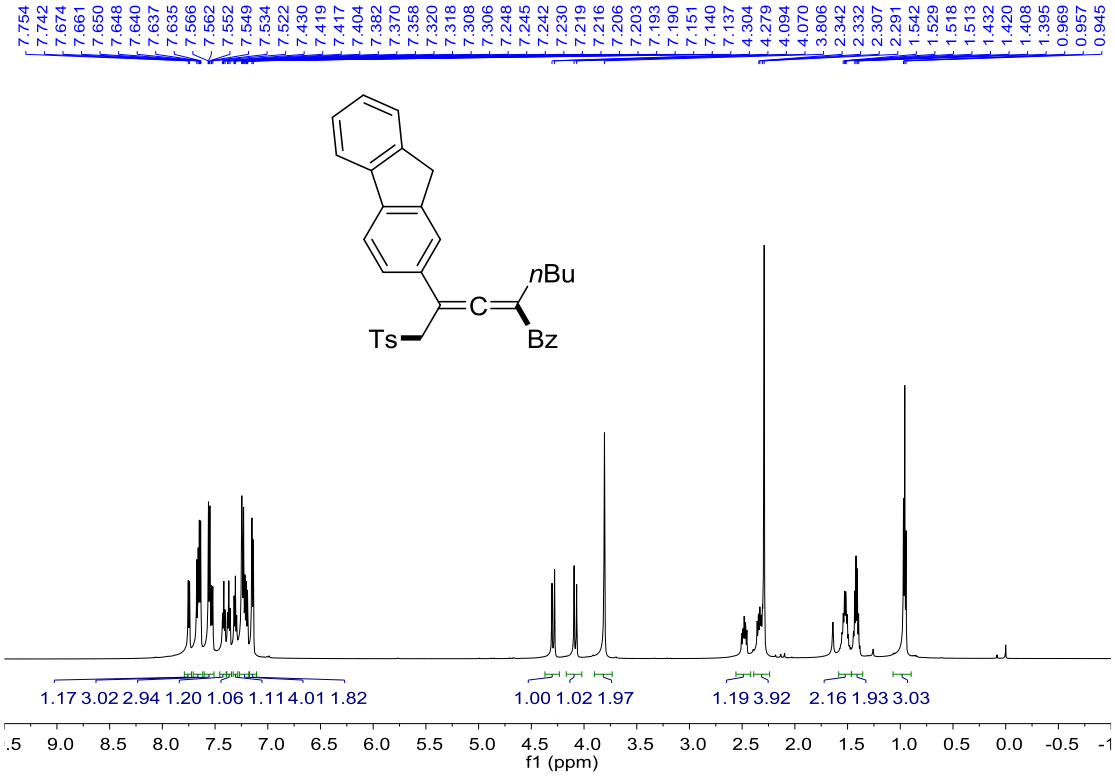
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **17**.



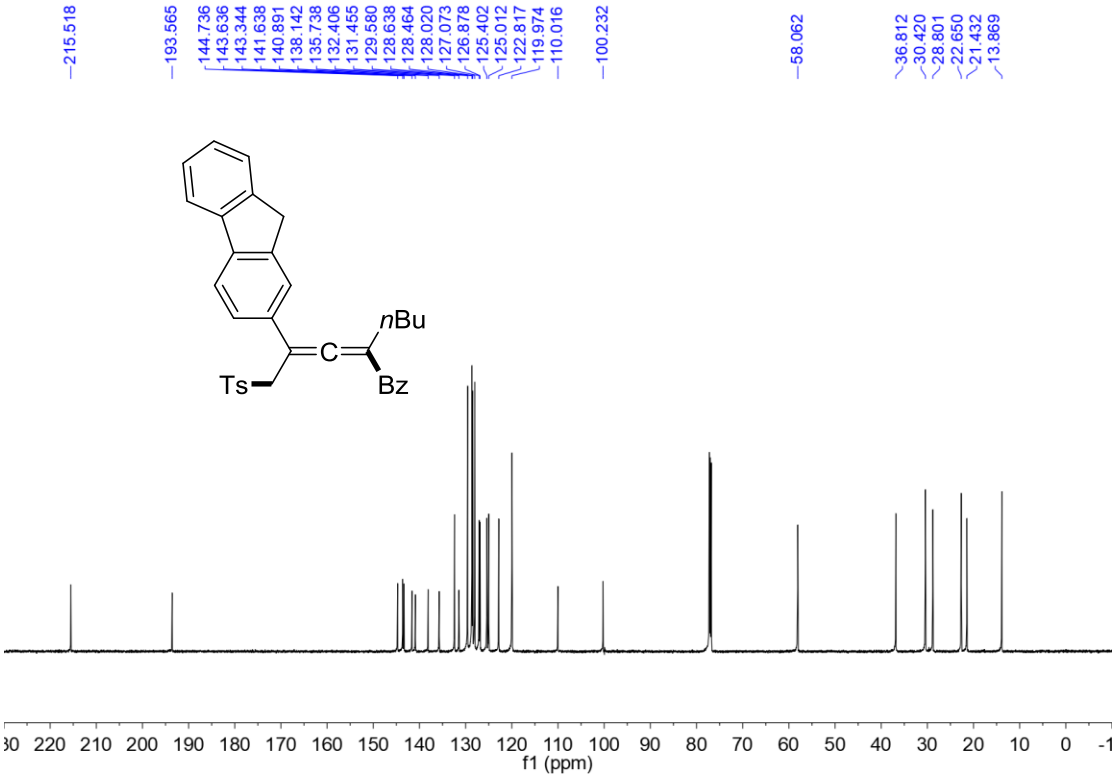
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **17**



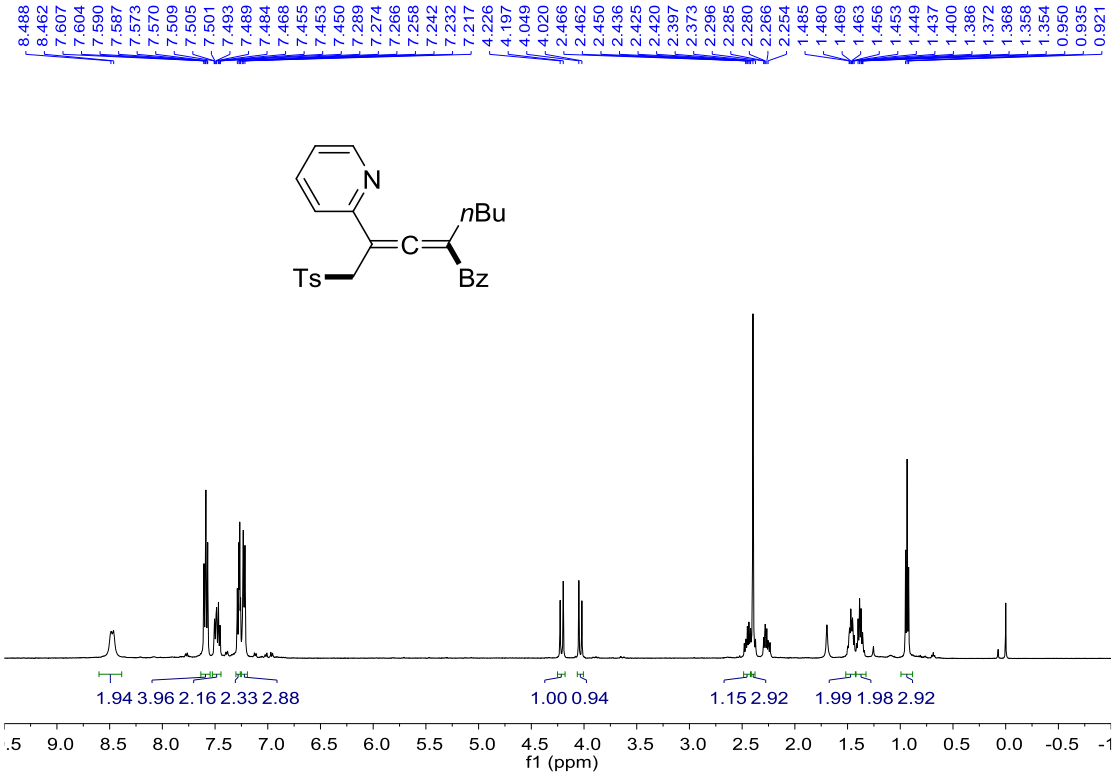
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **18**.



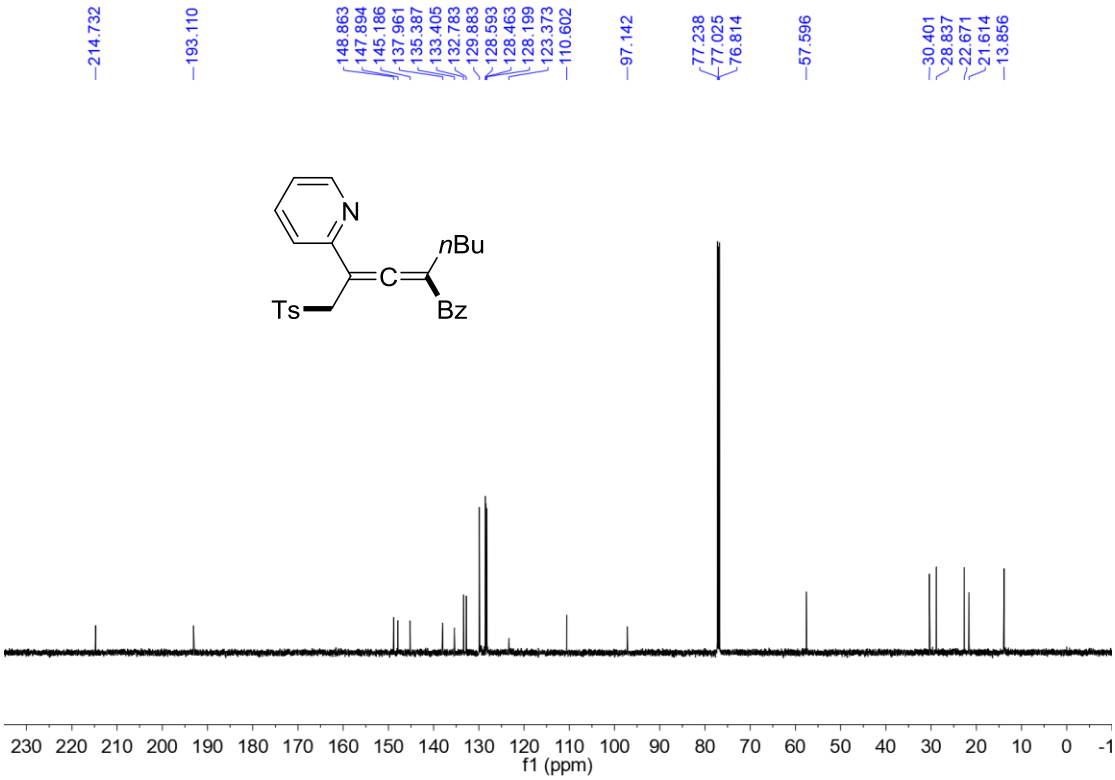
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **18**.



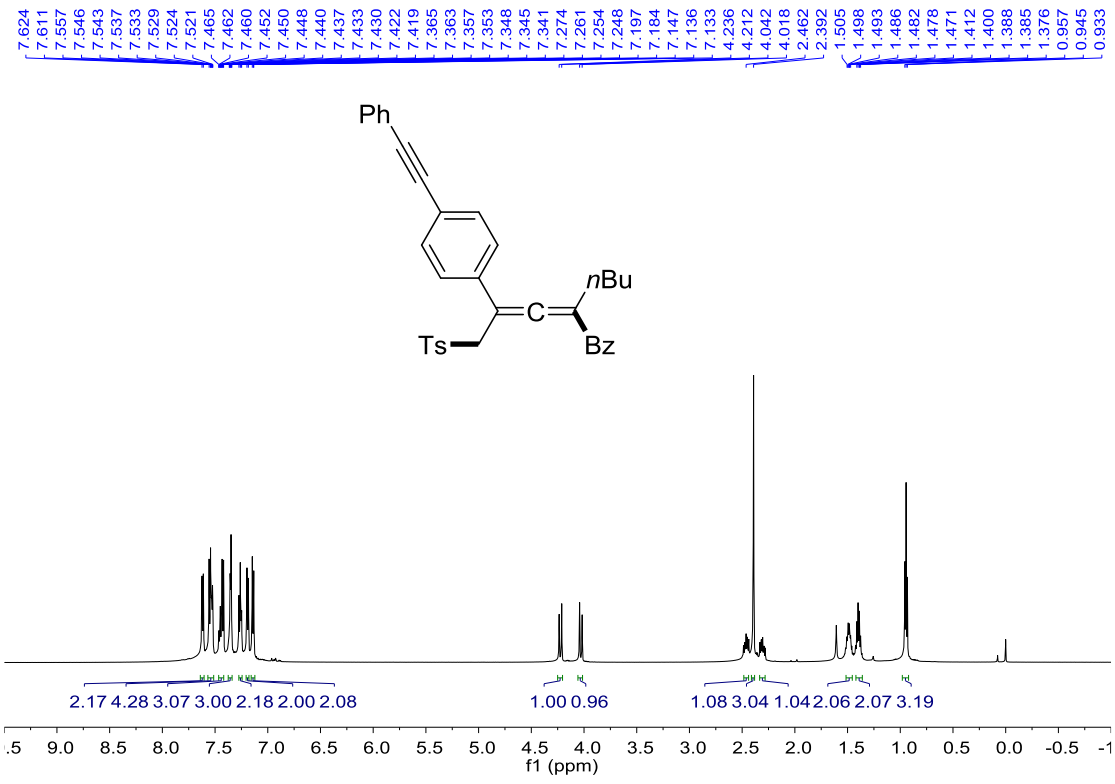
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **19**.



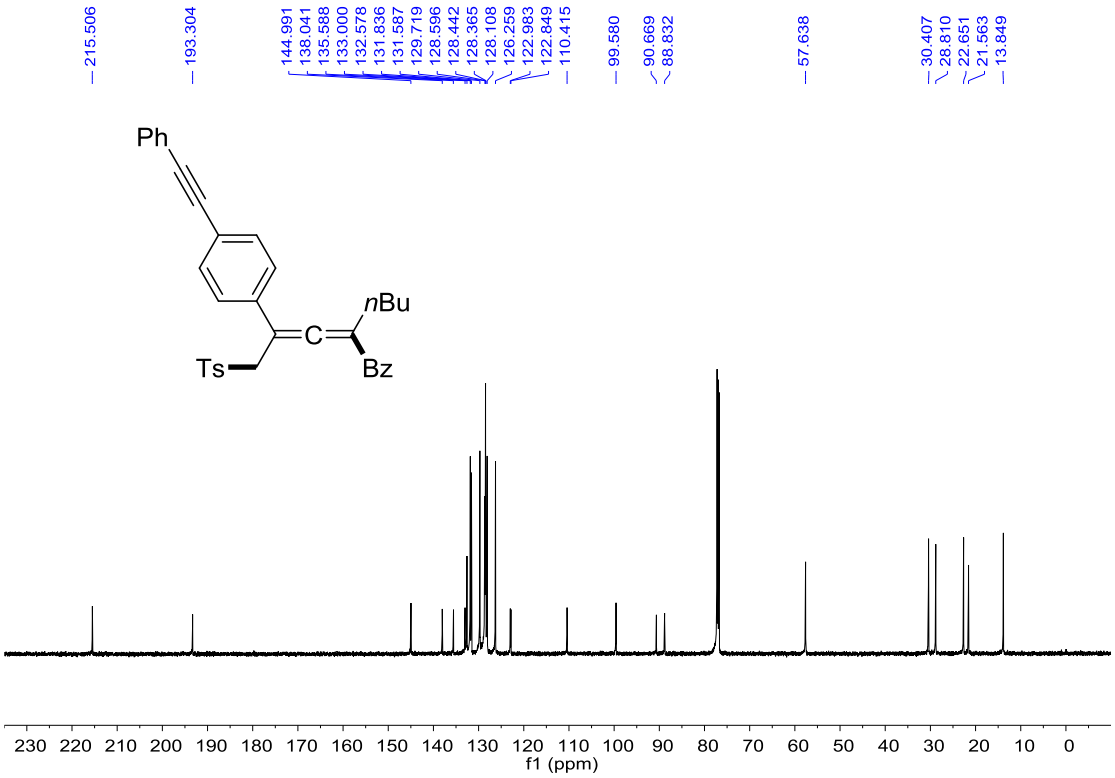
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **19**.



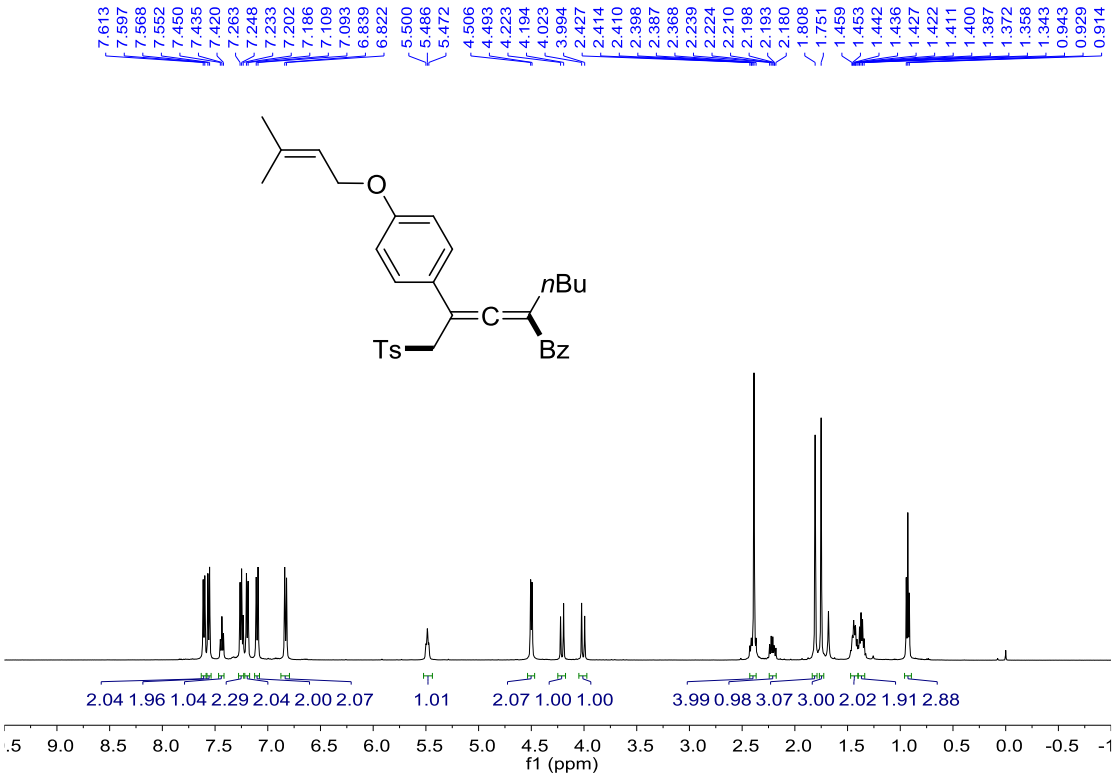
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **20**.



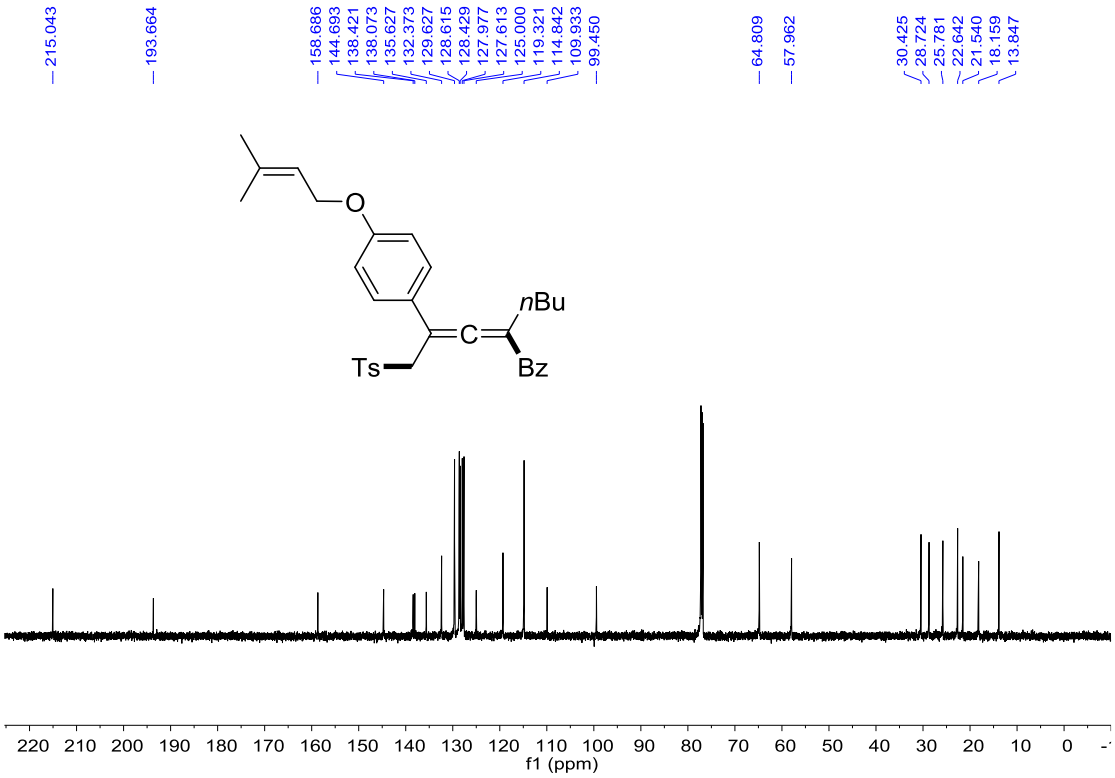
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **20**.



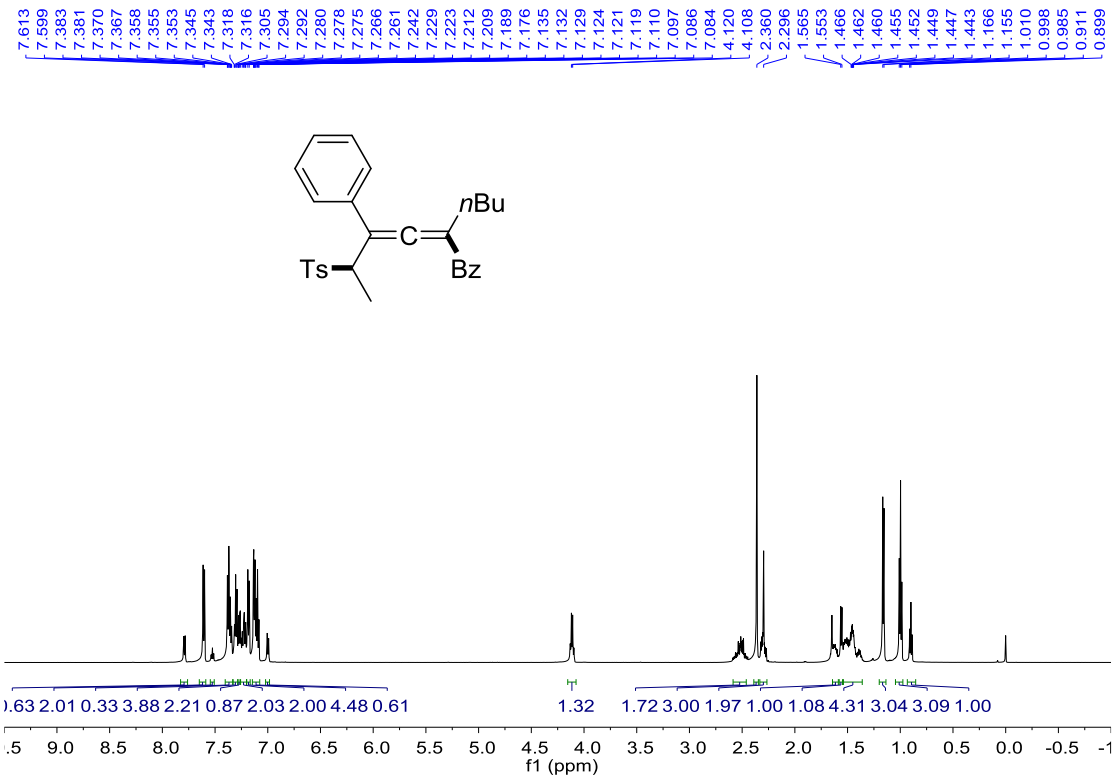
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **21**.



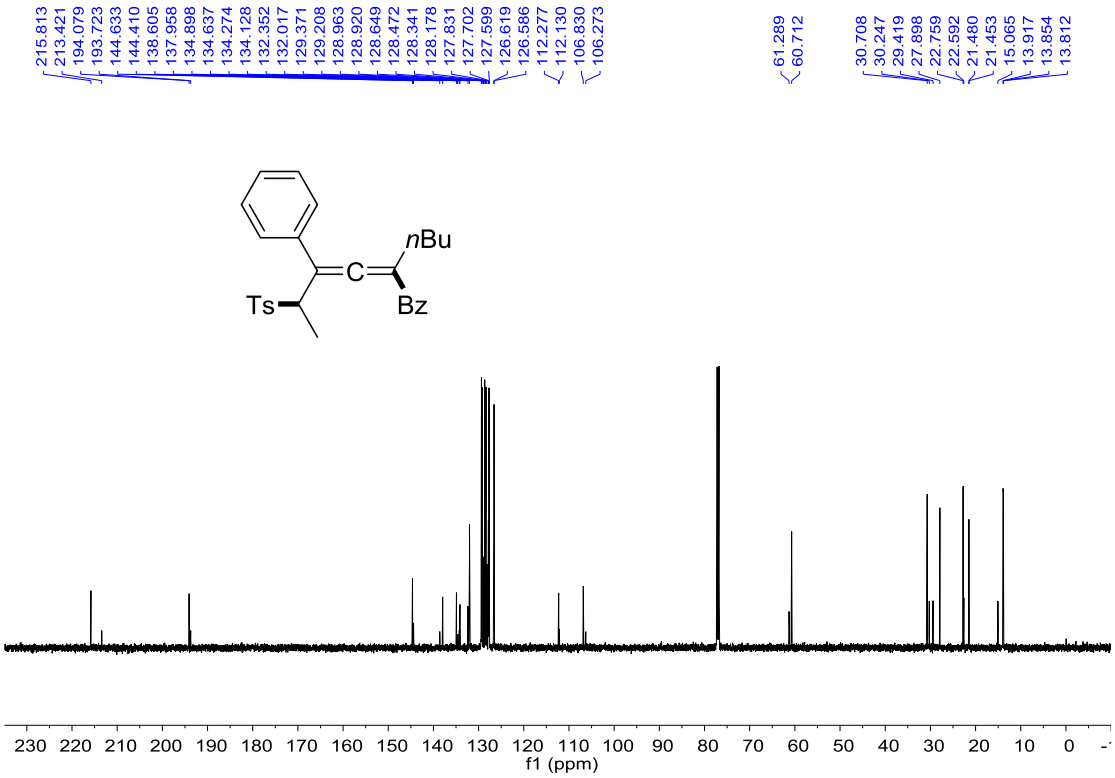
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **21**.



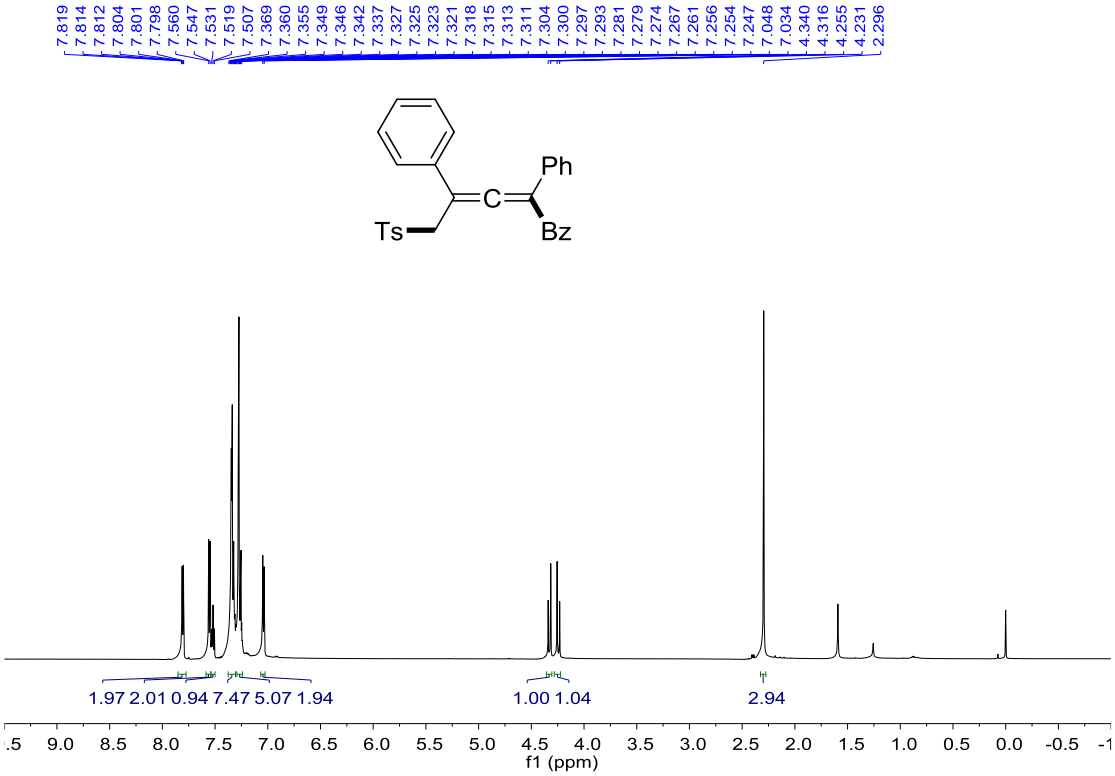
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **22**.



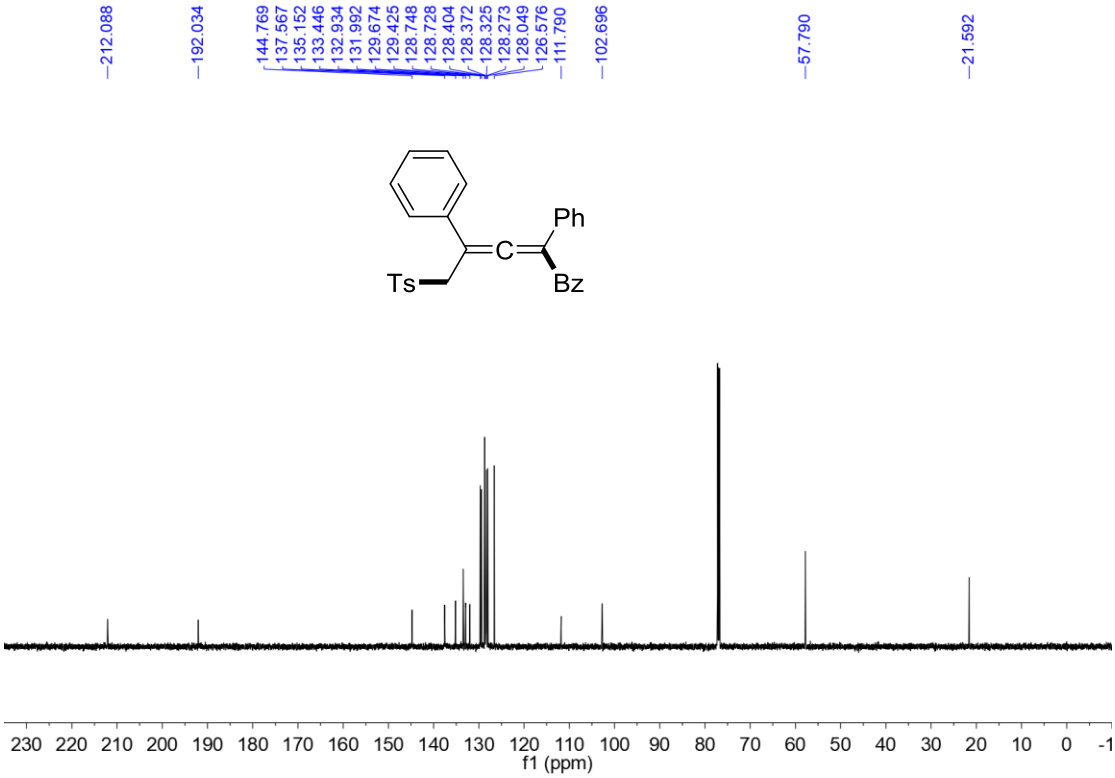
^{13}H NMR (151 MHz, $CDCl_3$) spectrum for **22**.



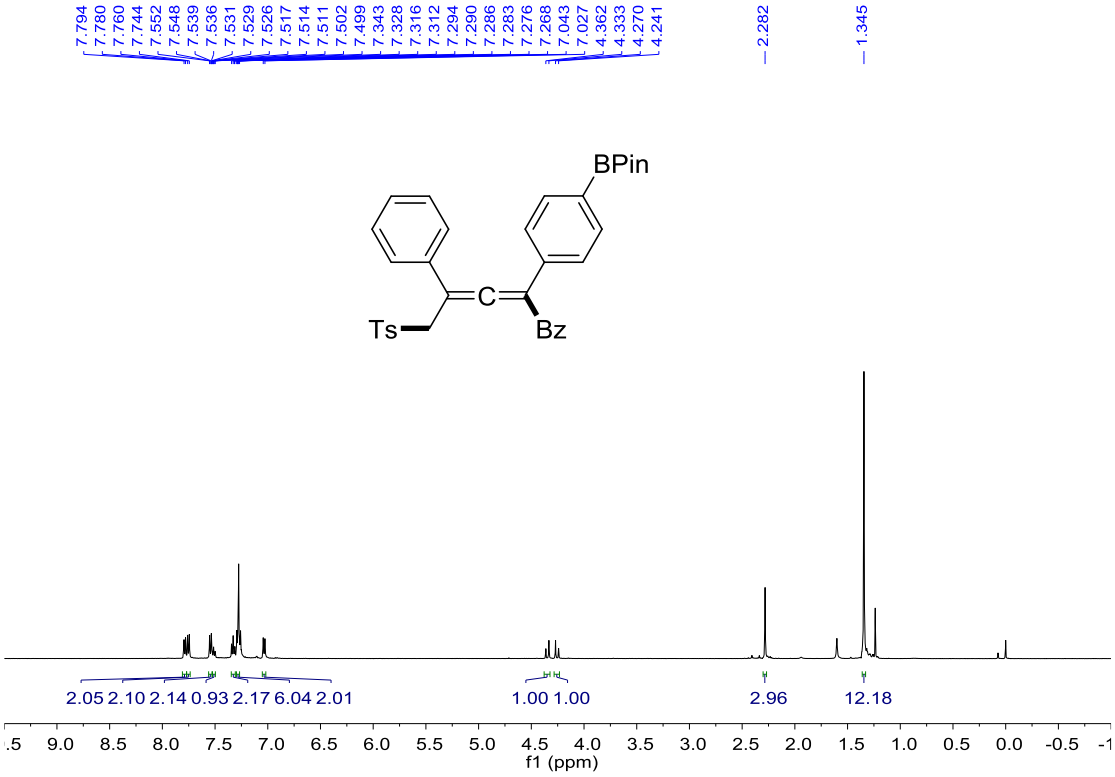
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **23**.



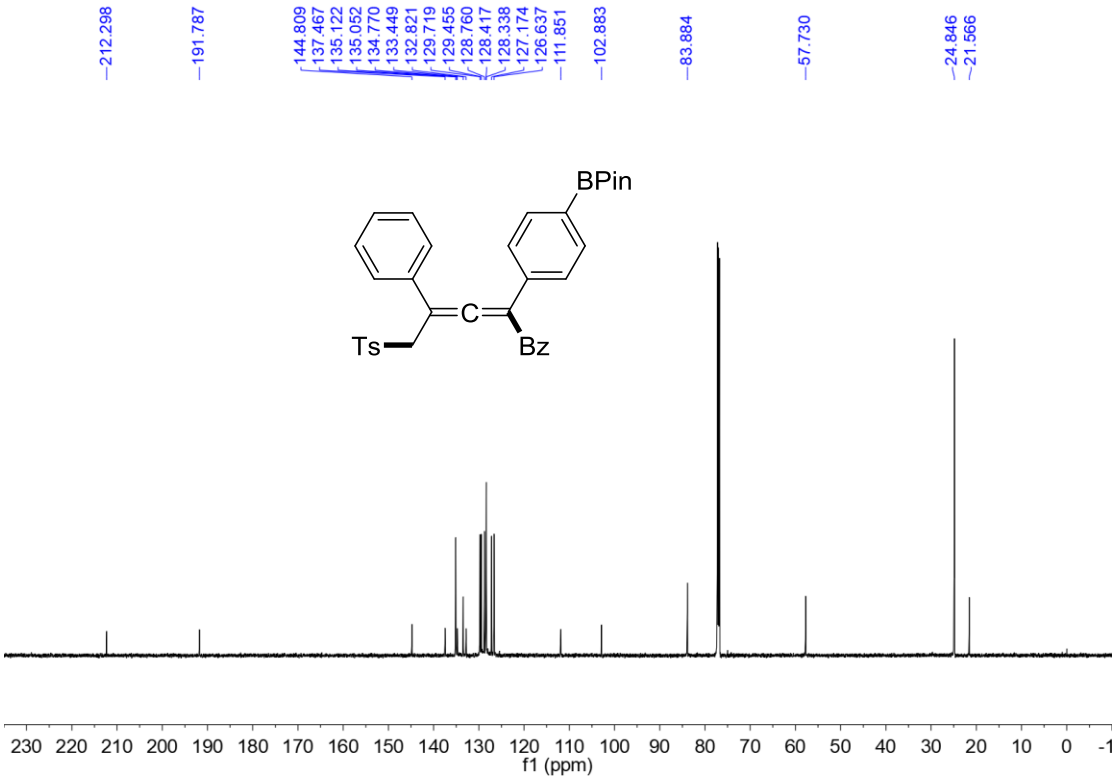
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **23**.



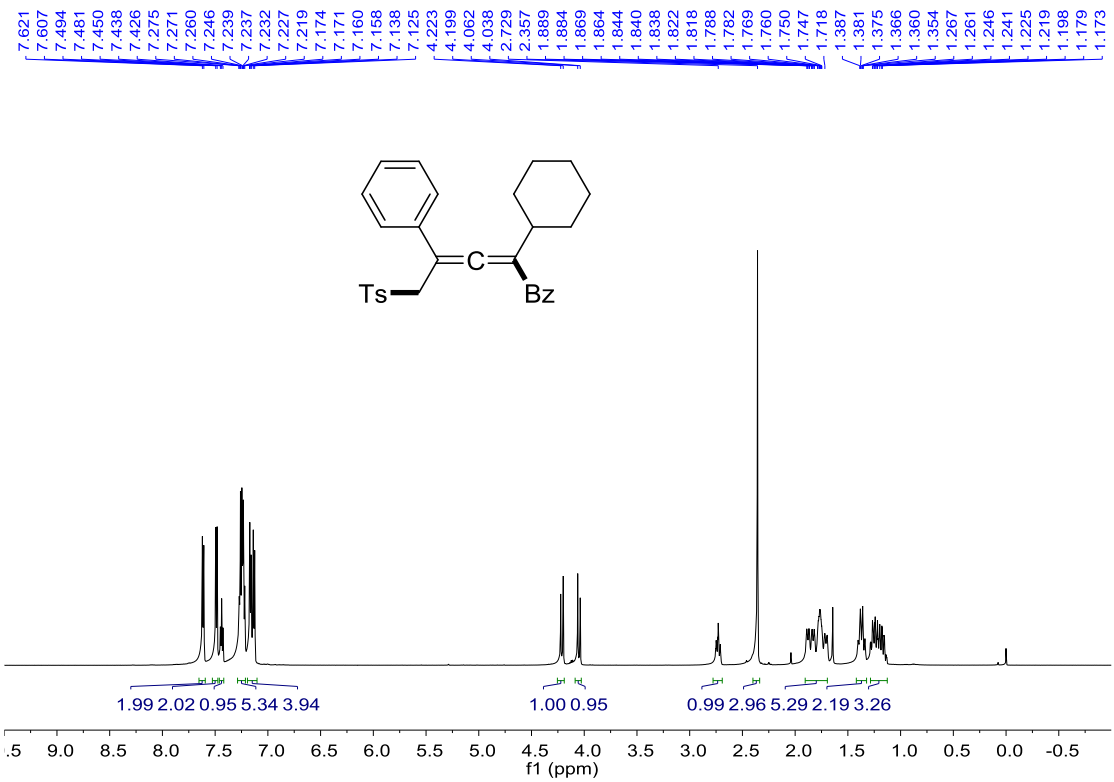
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **24**.



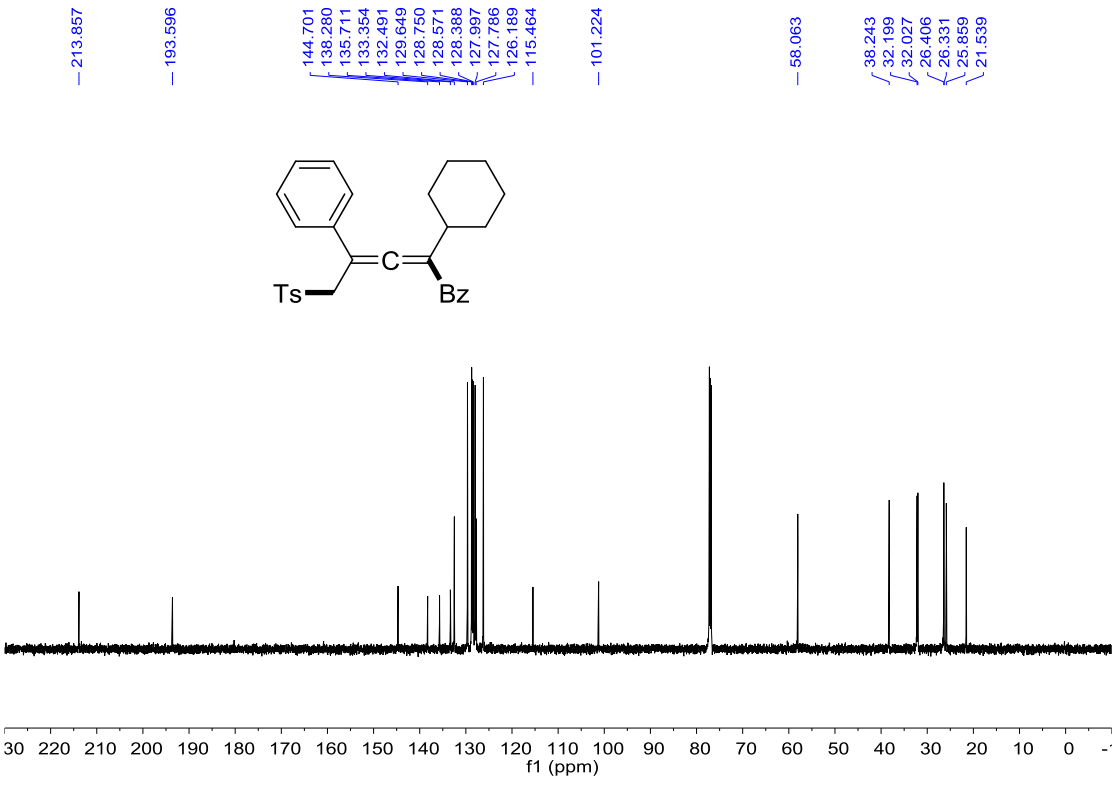
^{13}C NMR (500 MHz, $CDCl_3$) spectrum for **24**.



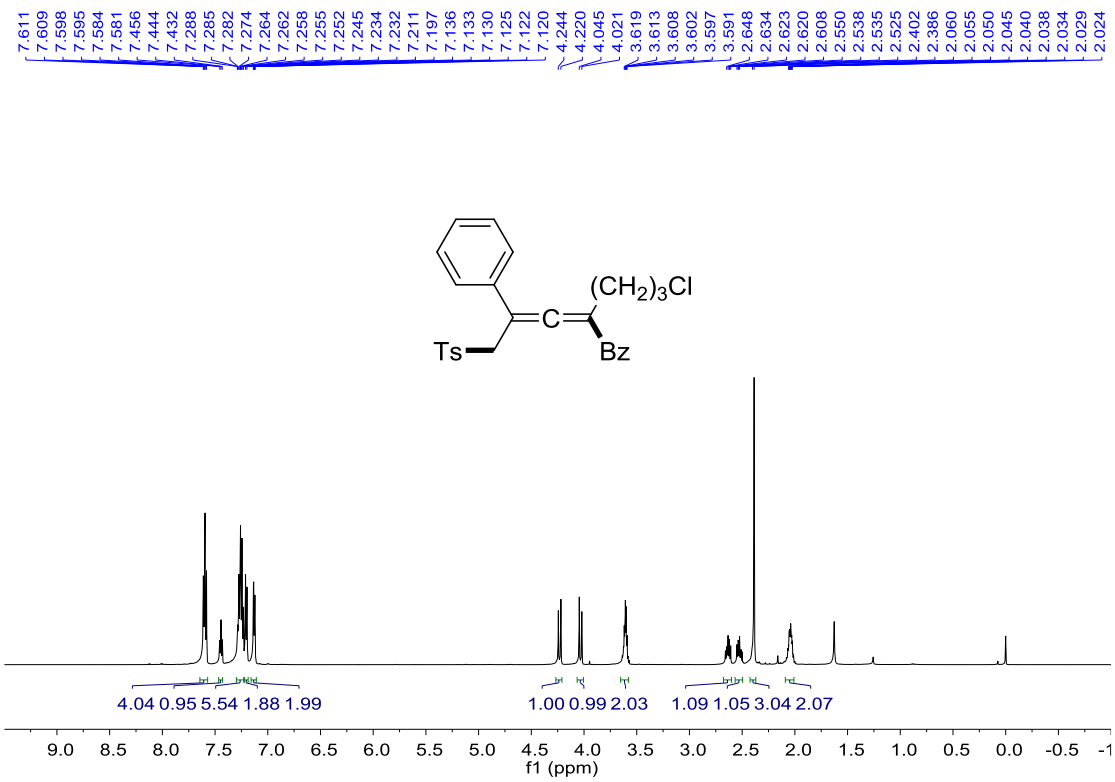
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **25**.



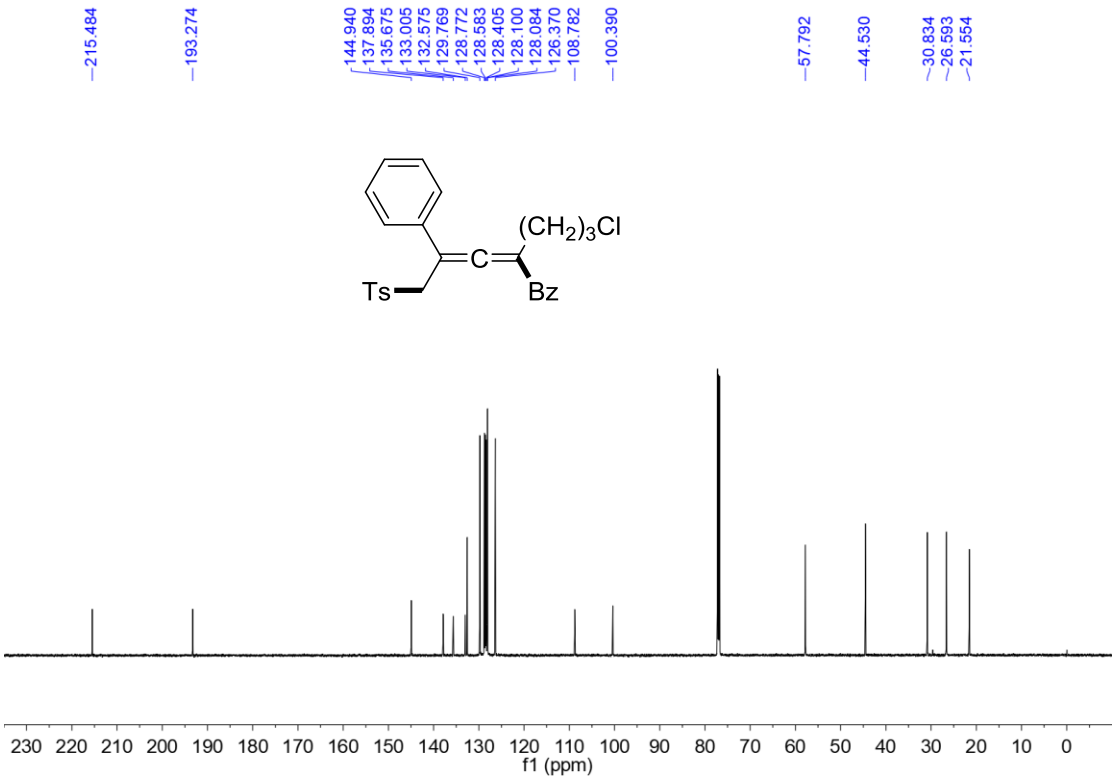
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **25**.



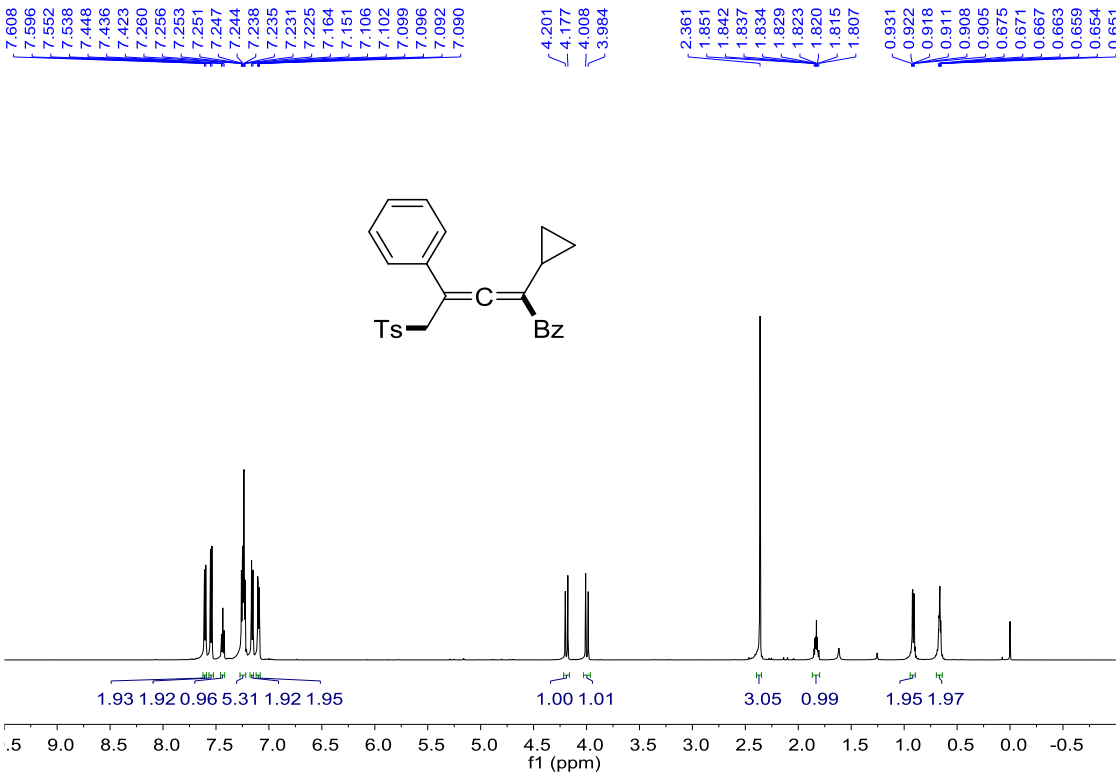
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **26**.



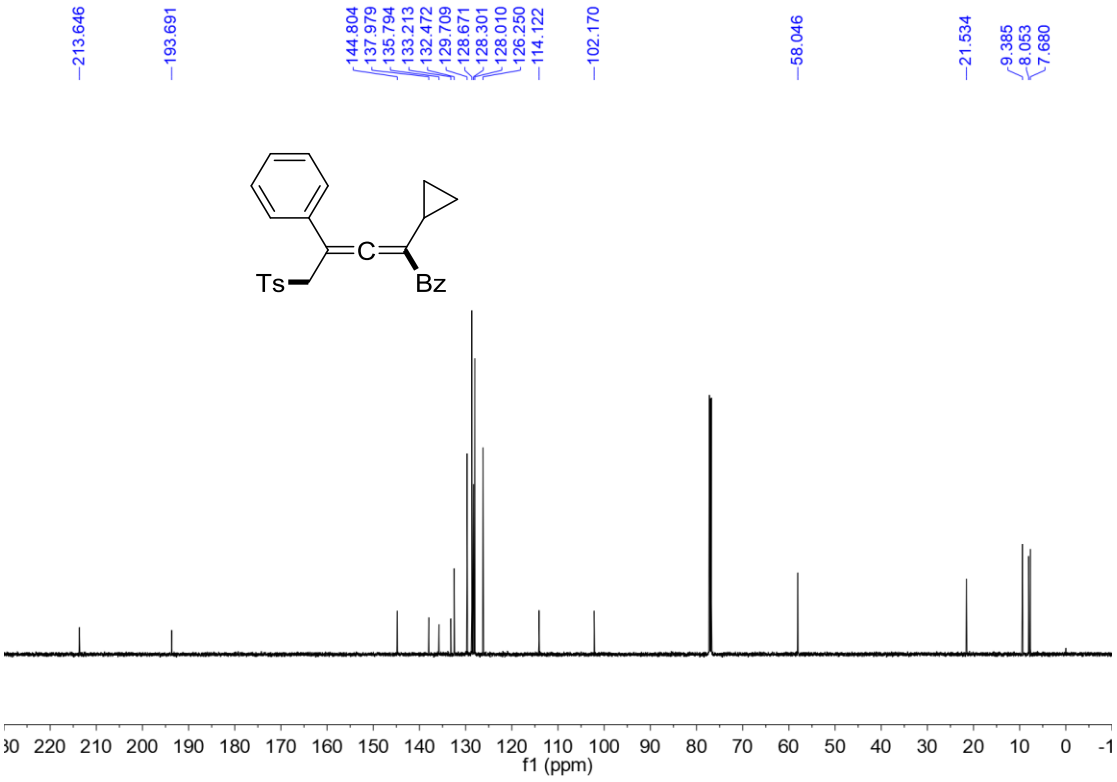
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **26**.



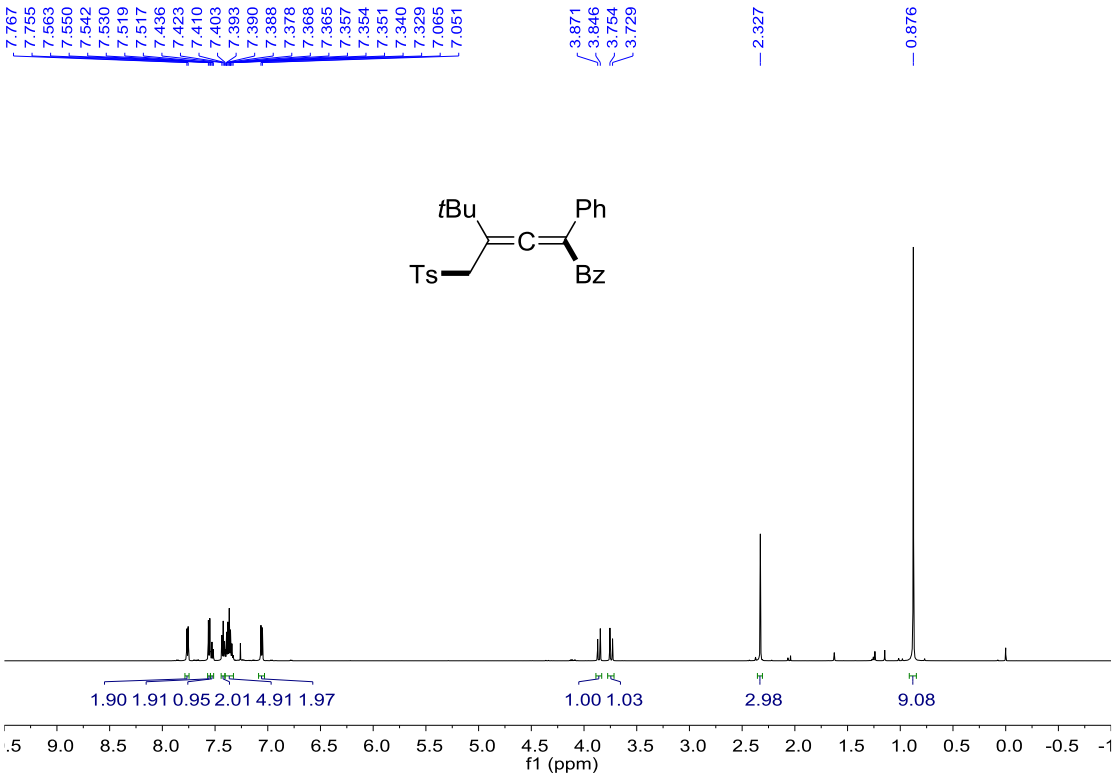
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **27**.



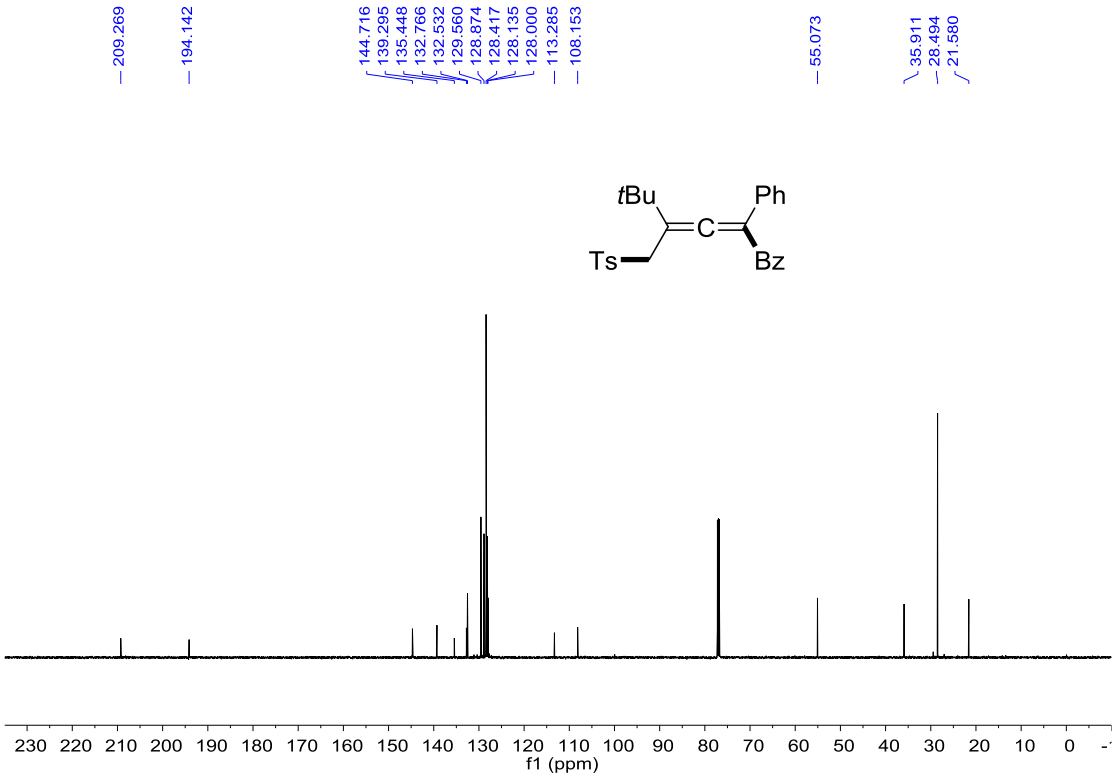
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **27**.



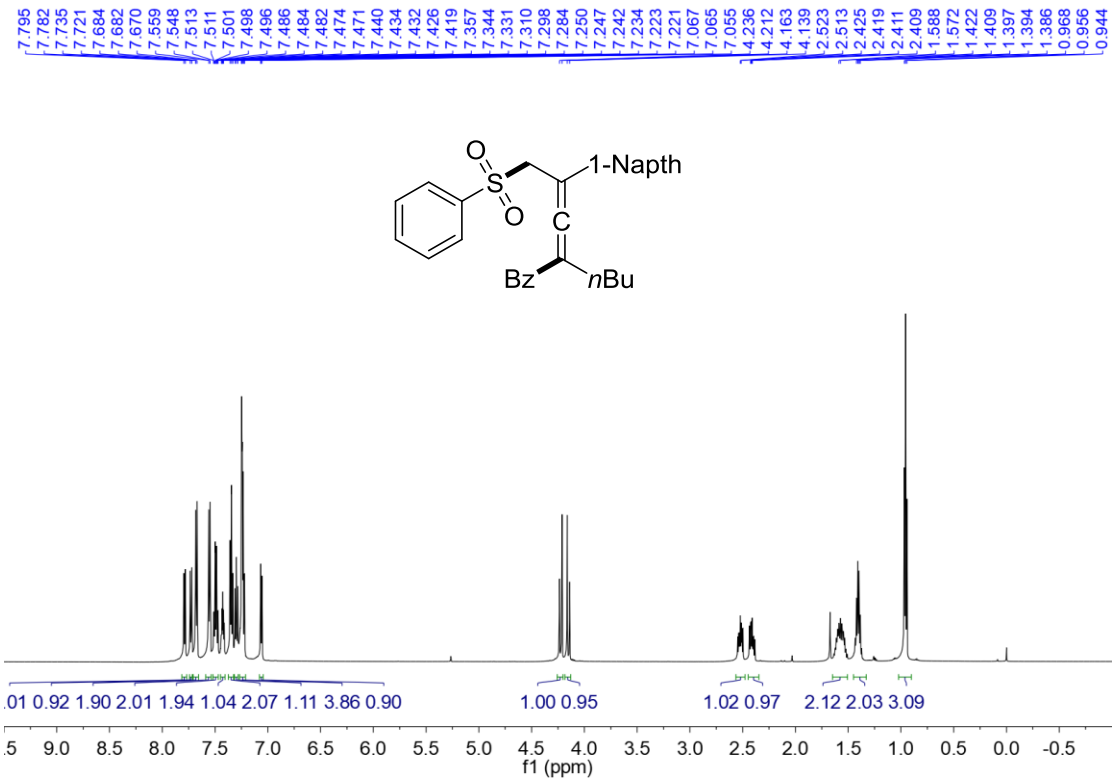
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **28**.



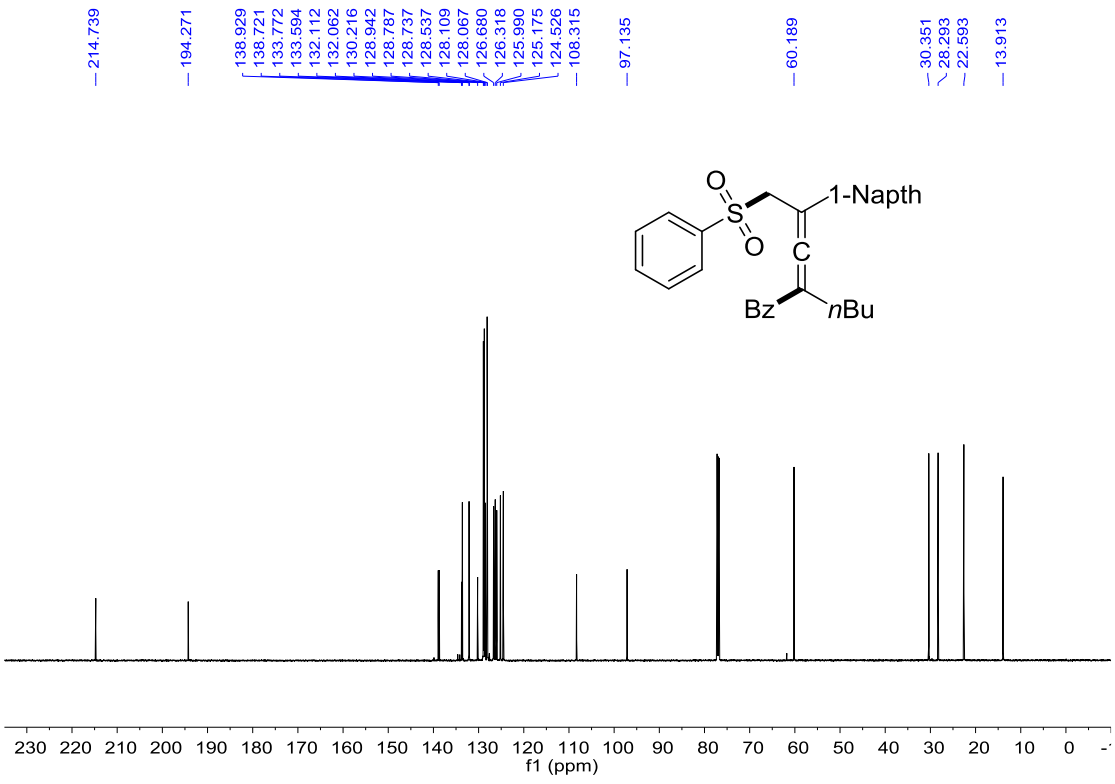
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **28**.



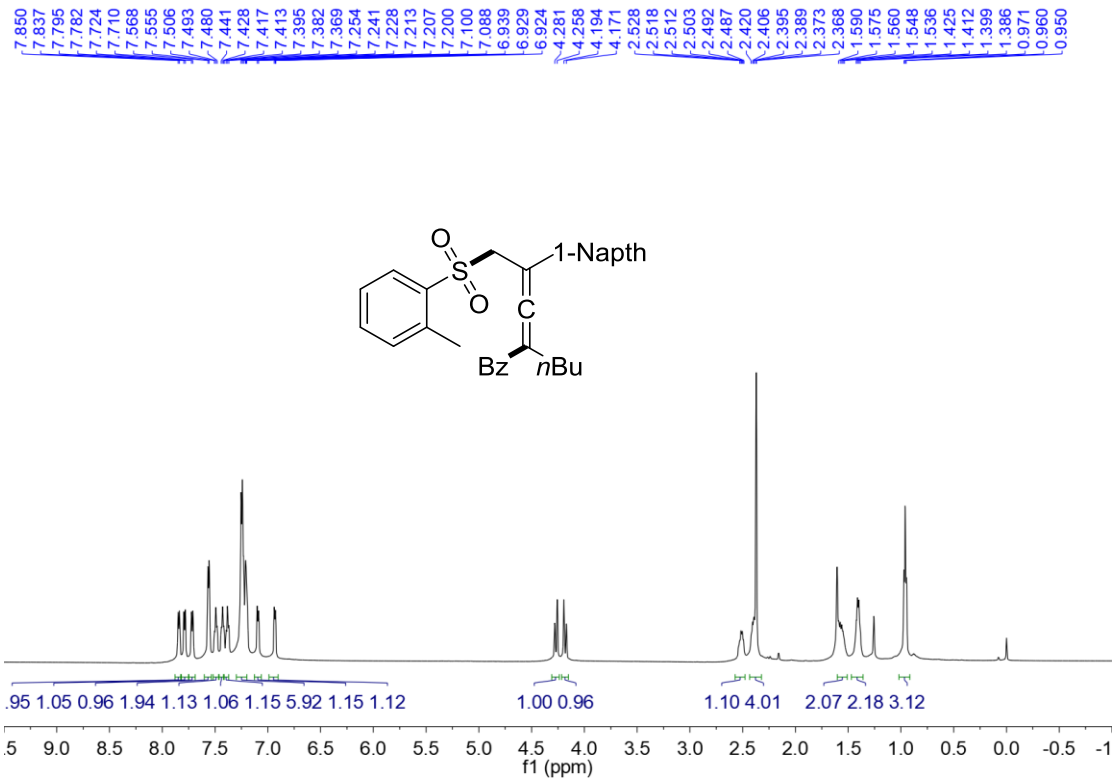
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **29**.



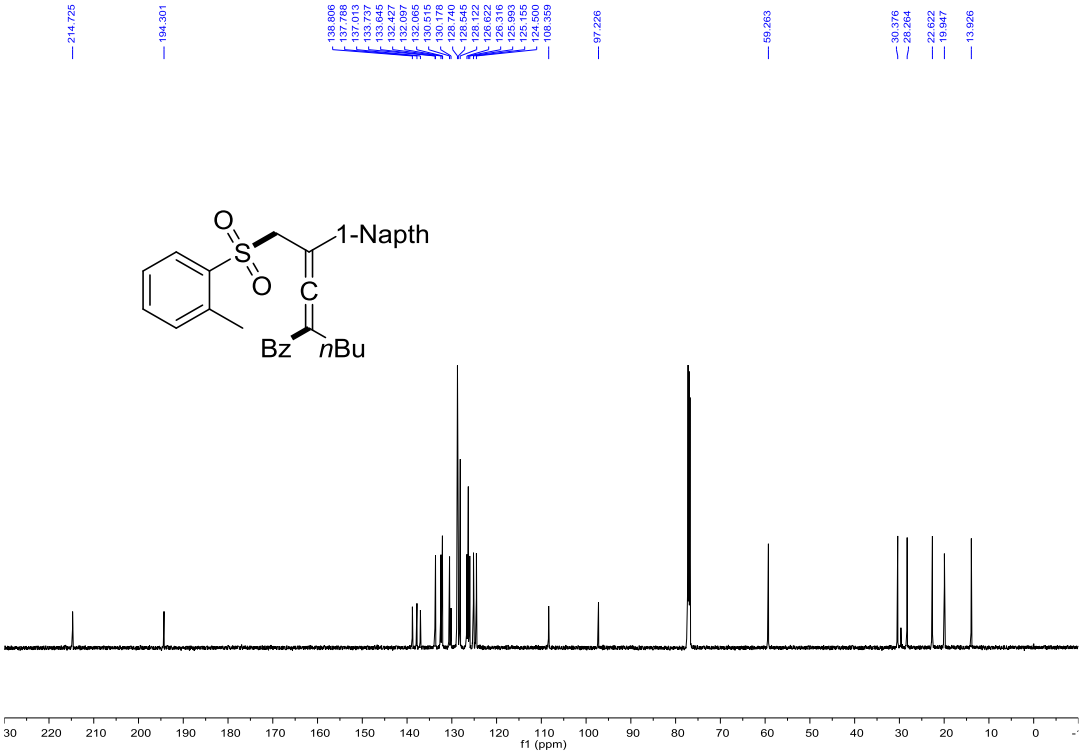
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **29**.



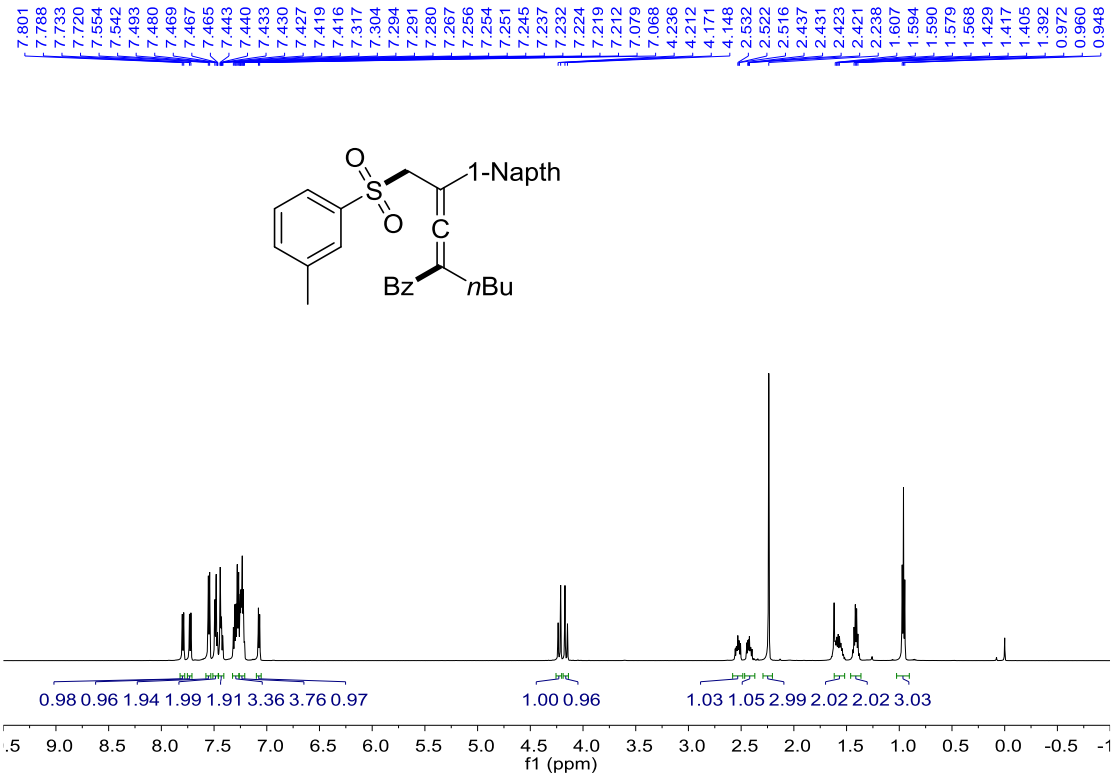
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **30**.



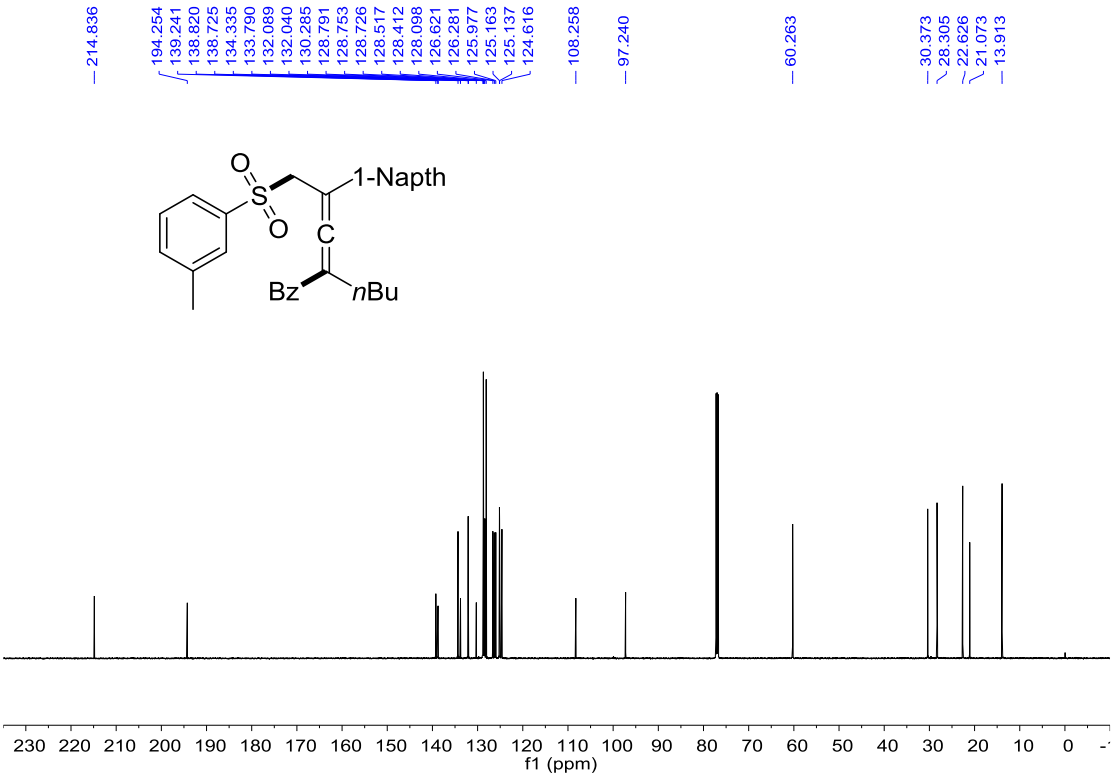
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **30**.



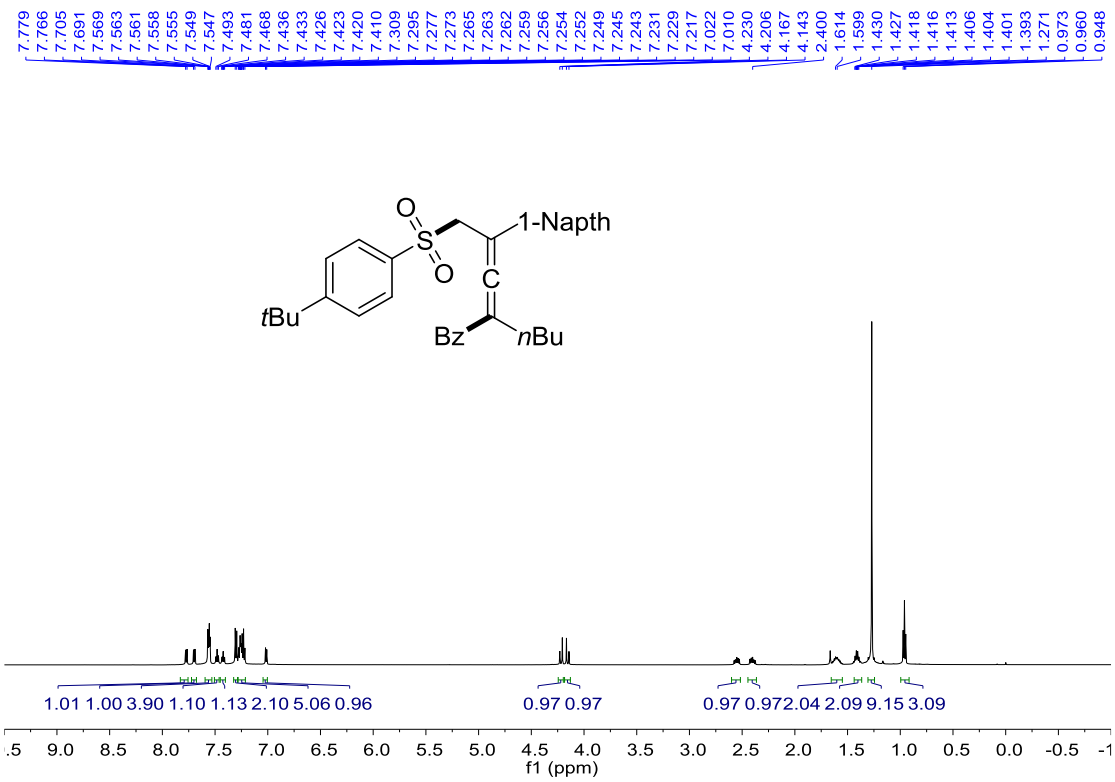
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **31**.



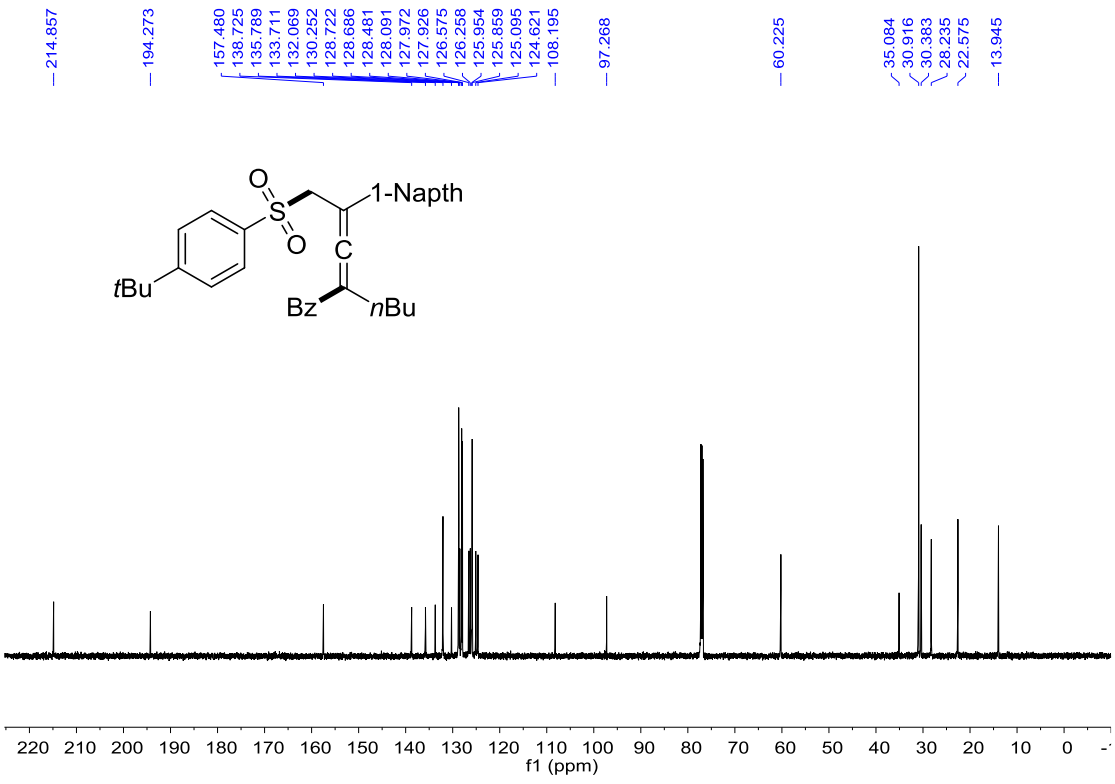
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **31**.



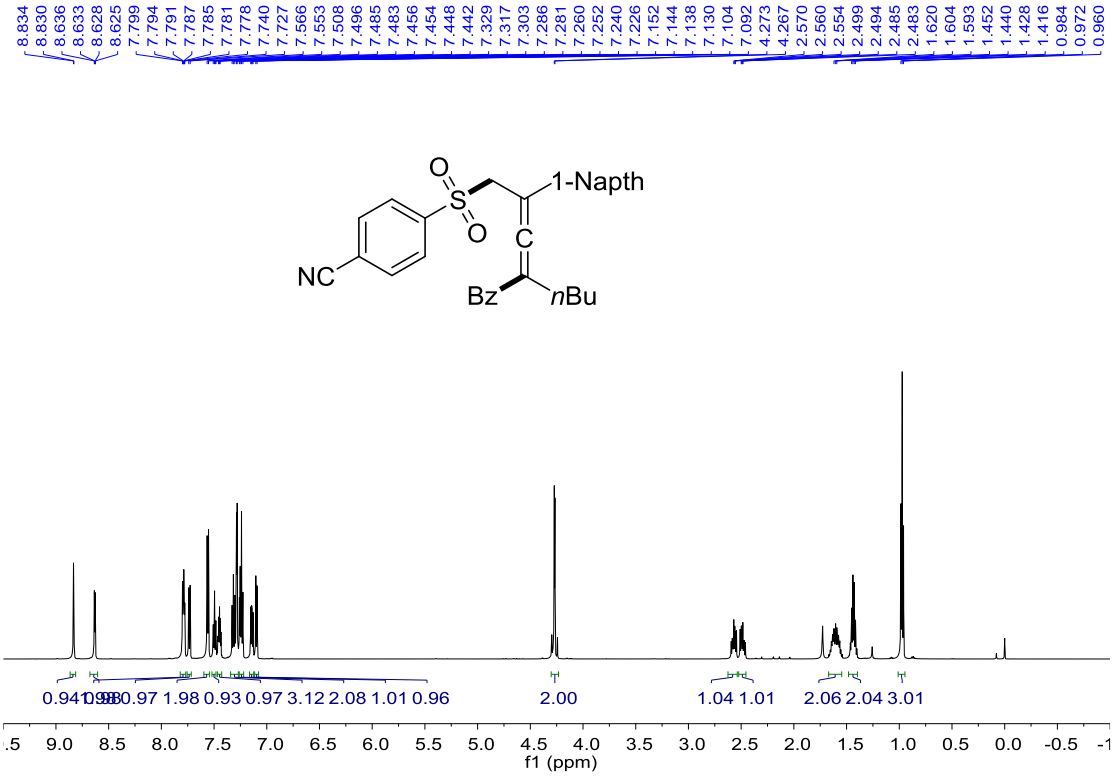
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **32**.



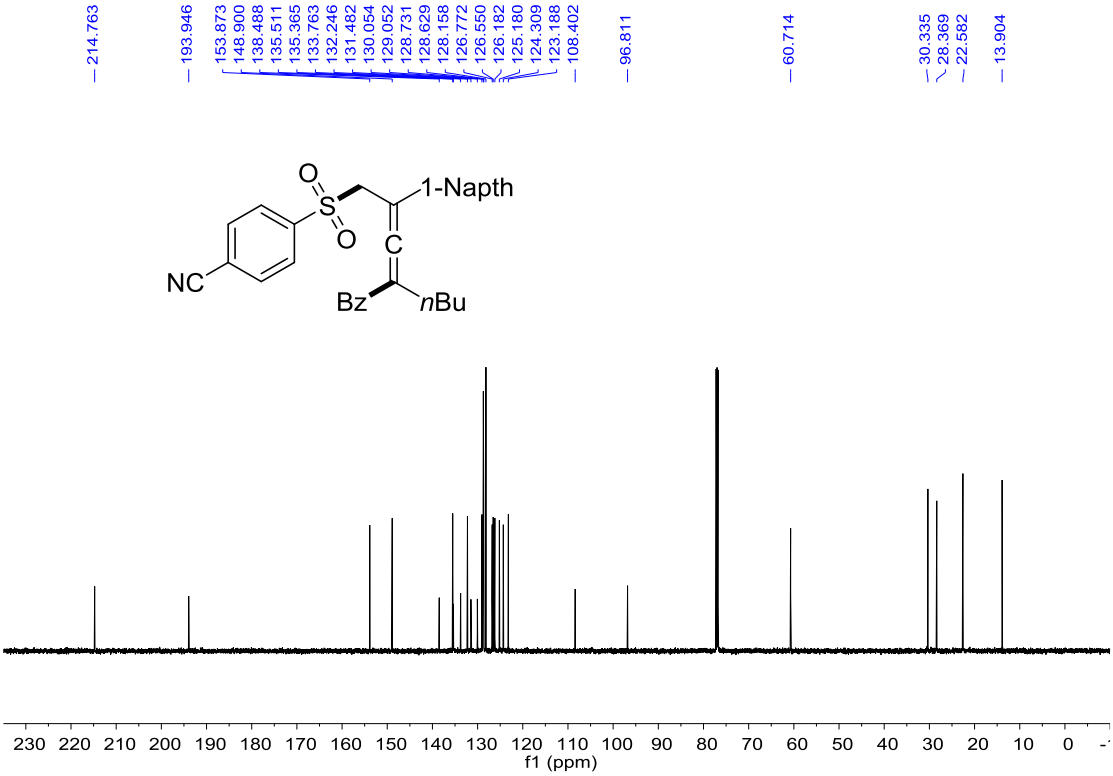
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **32**.



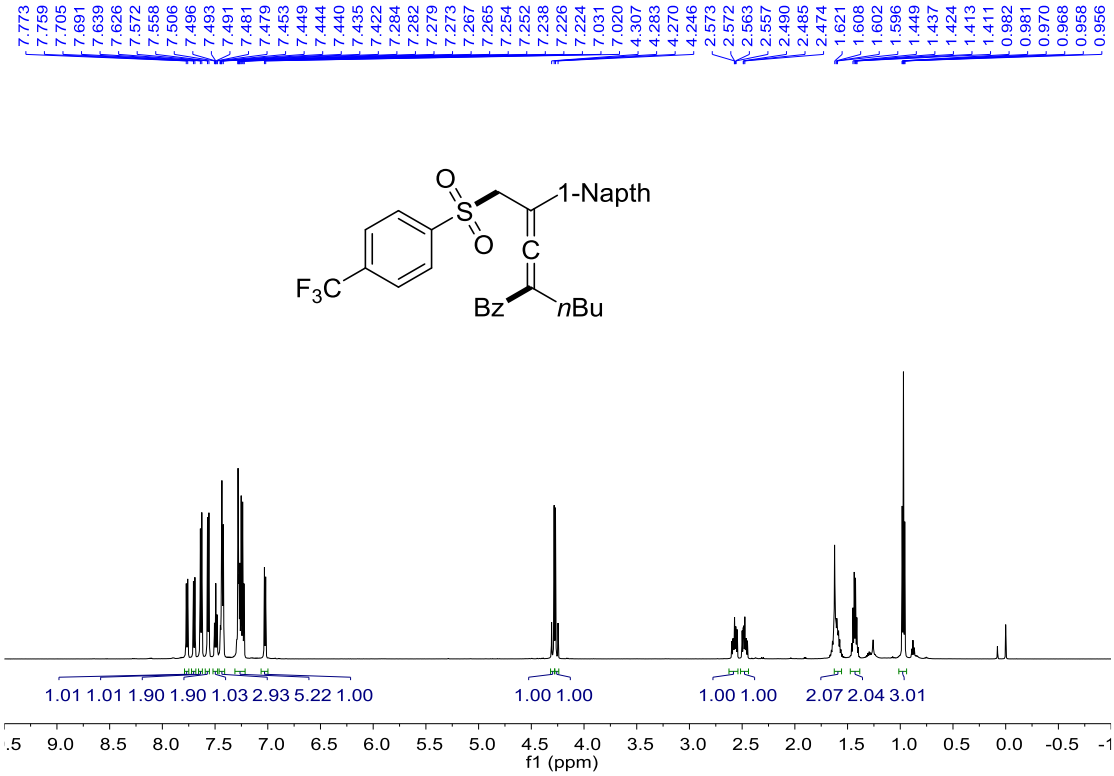
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **33**.



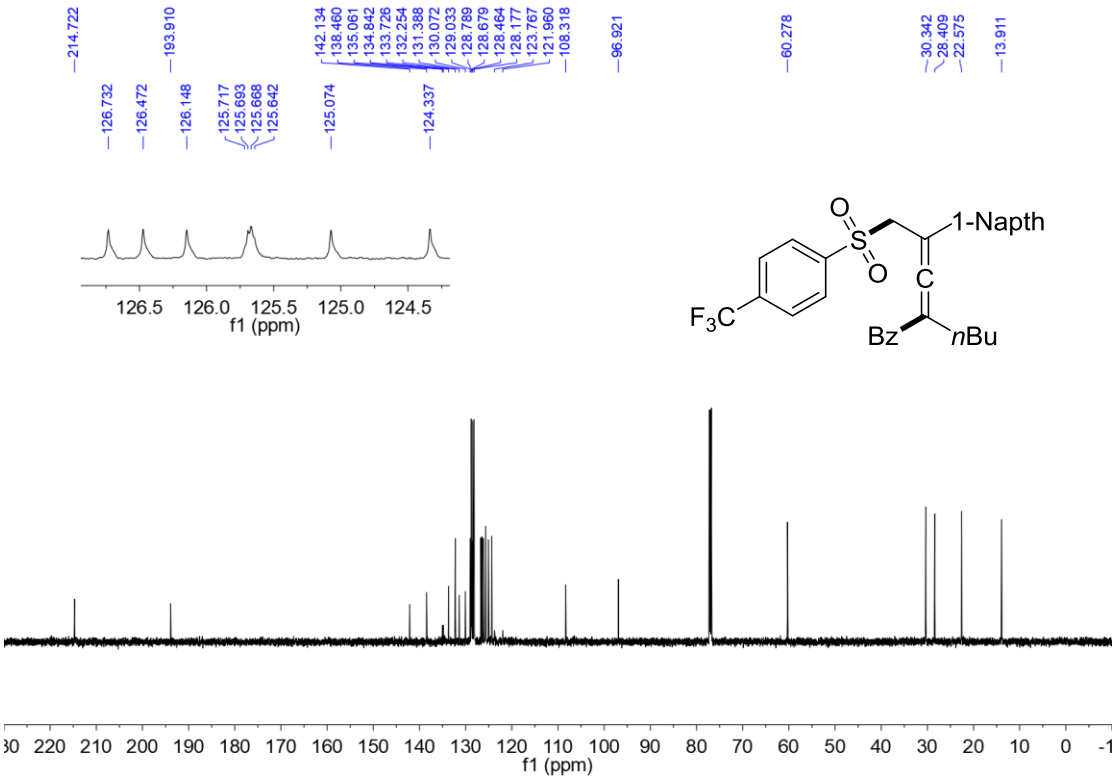
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **33**.



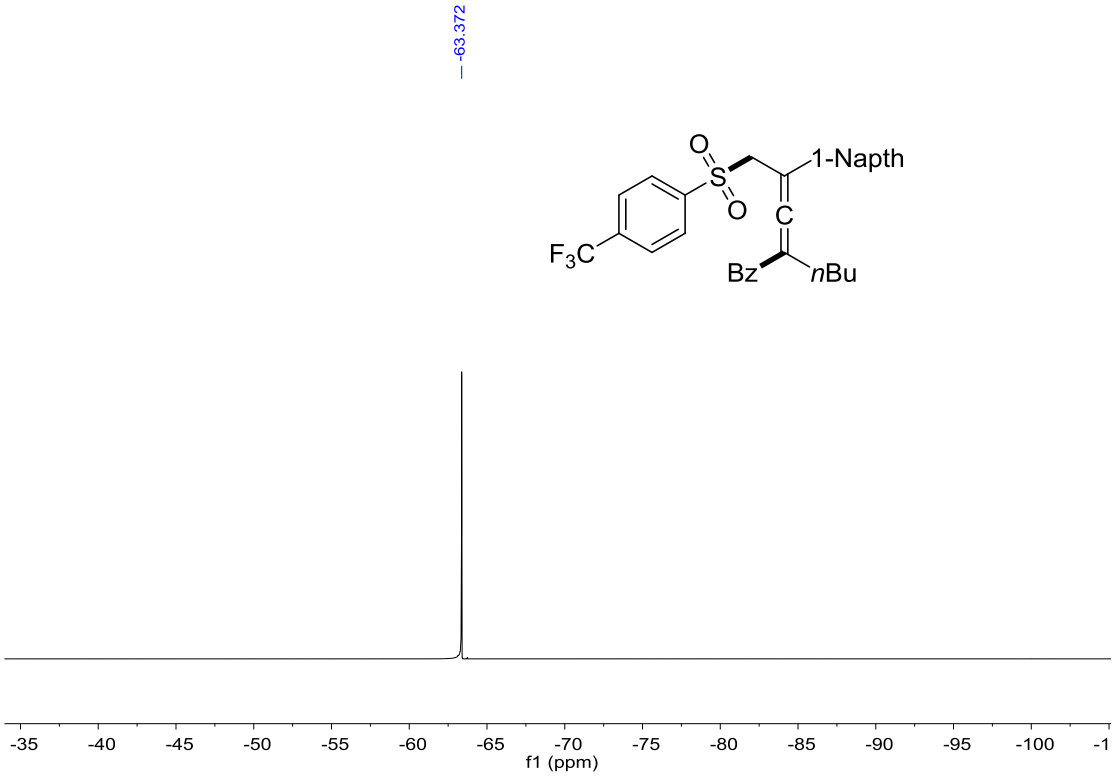
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **34**.



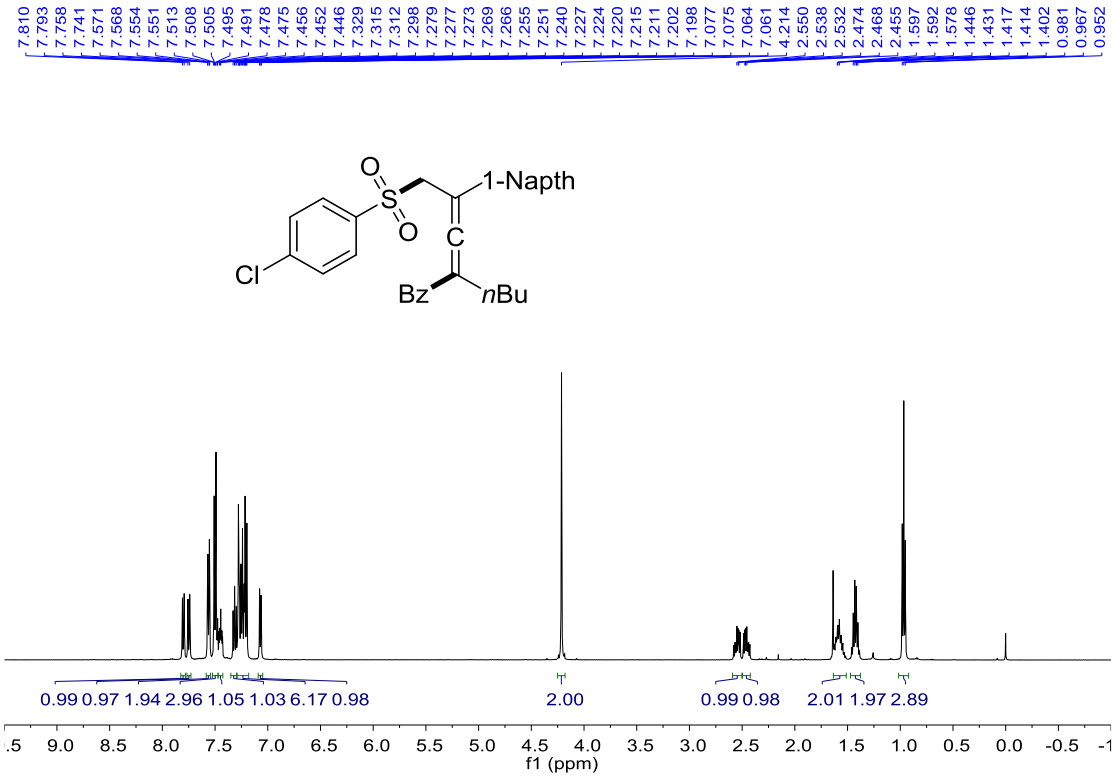
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **34**.



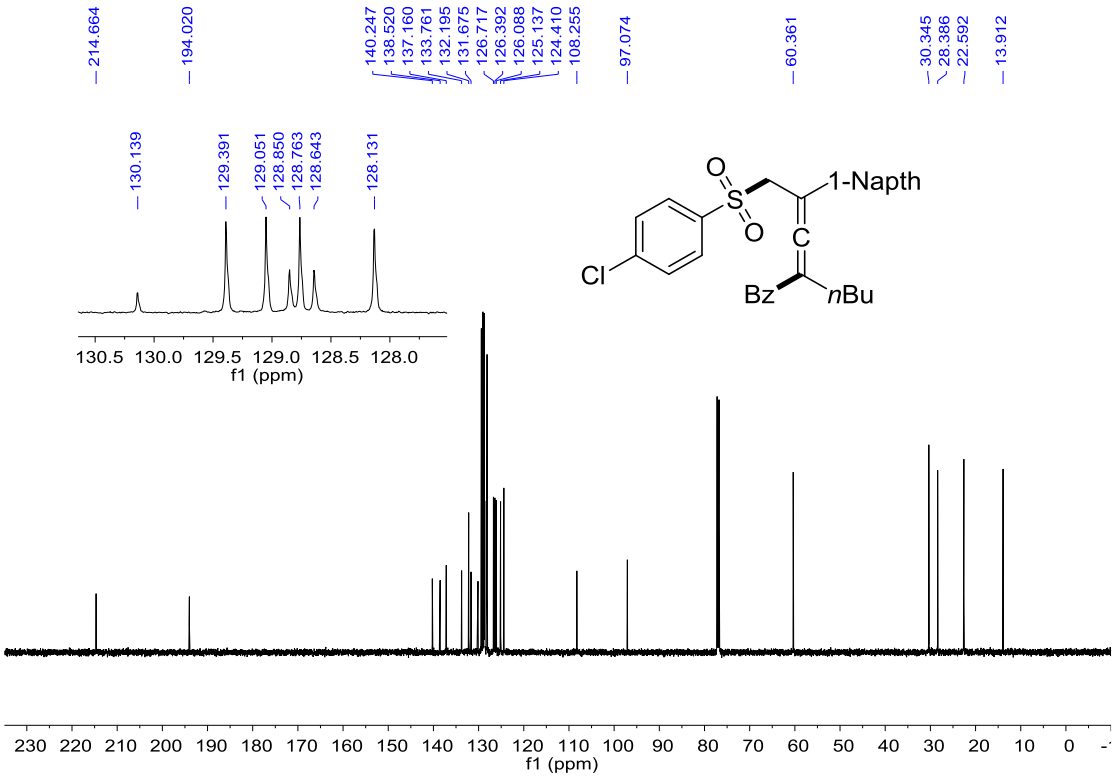
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **34**.



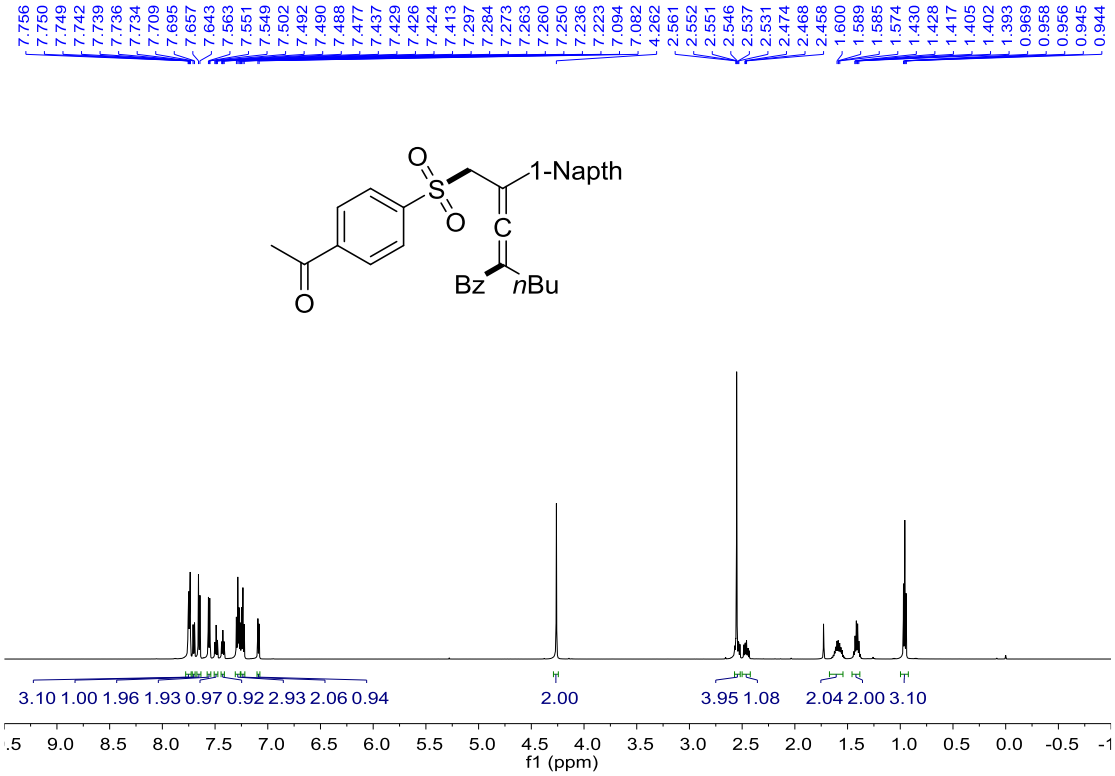
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **35**



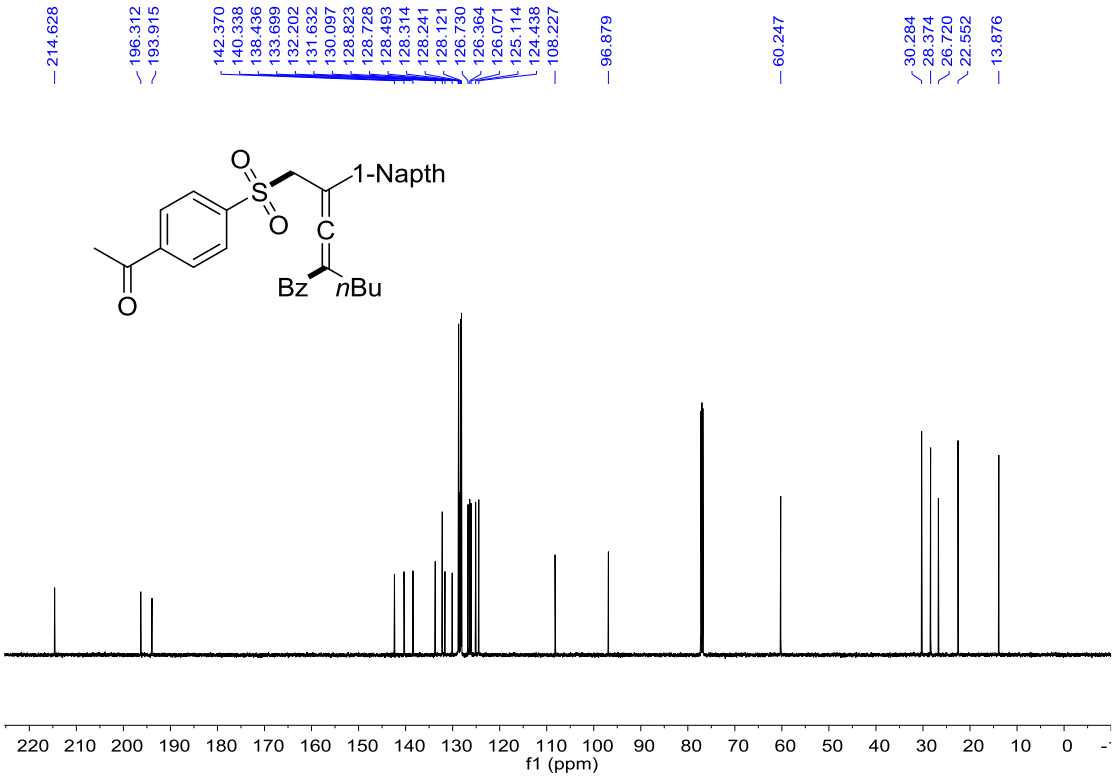
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **35**.



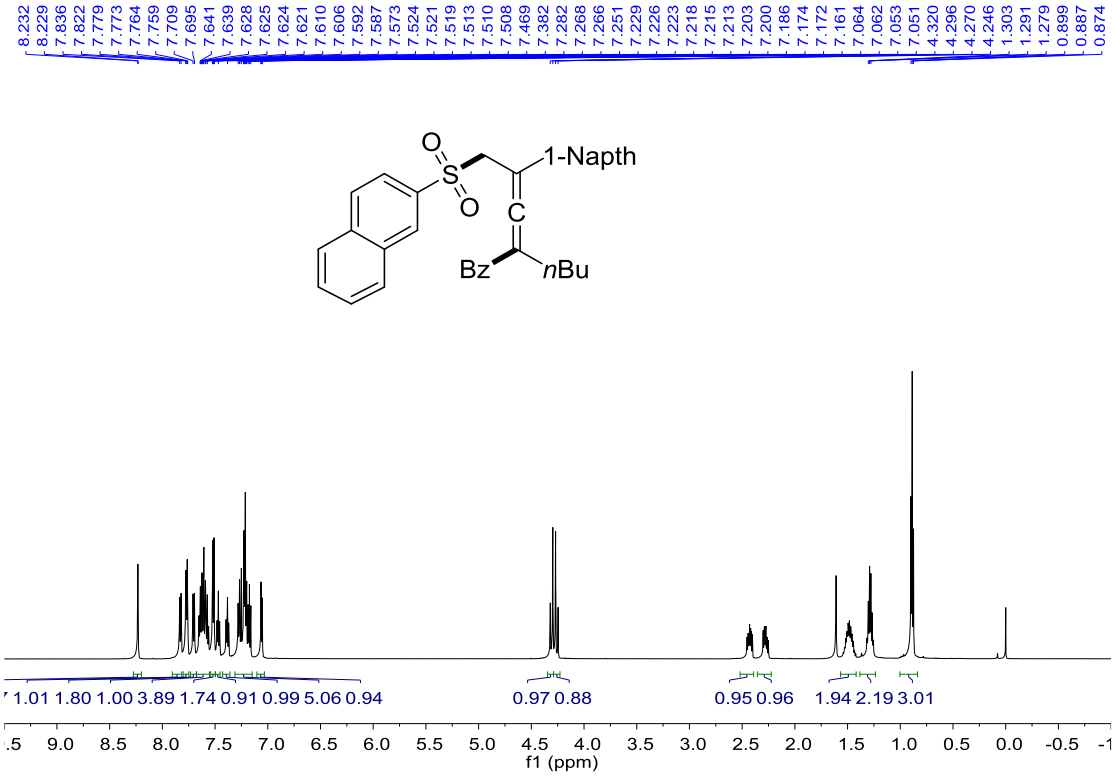
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **36**.



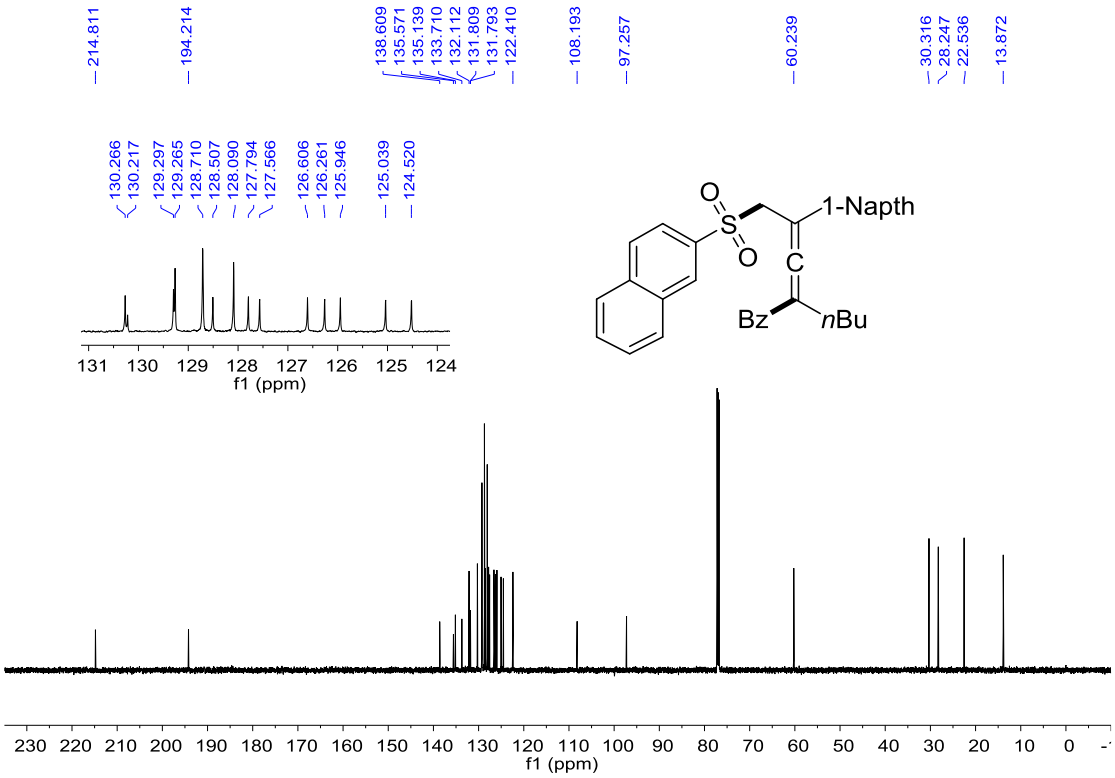
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **36**.



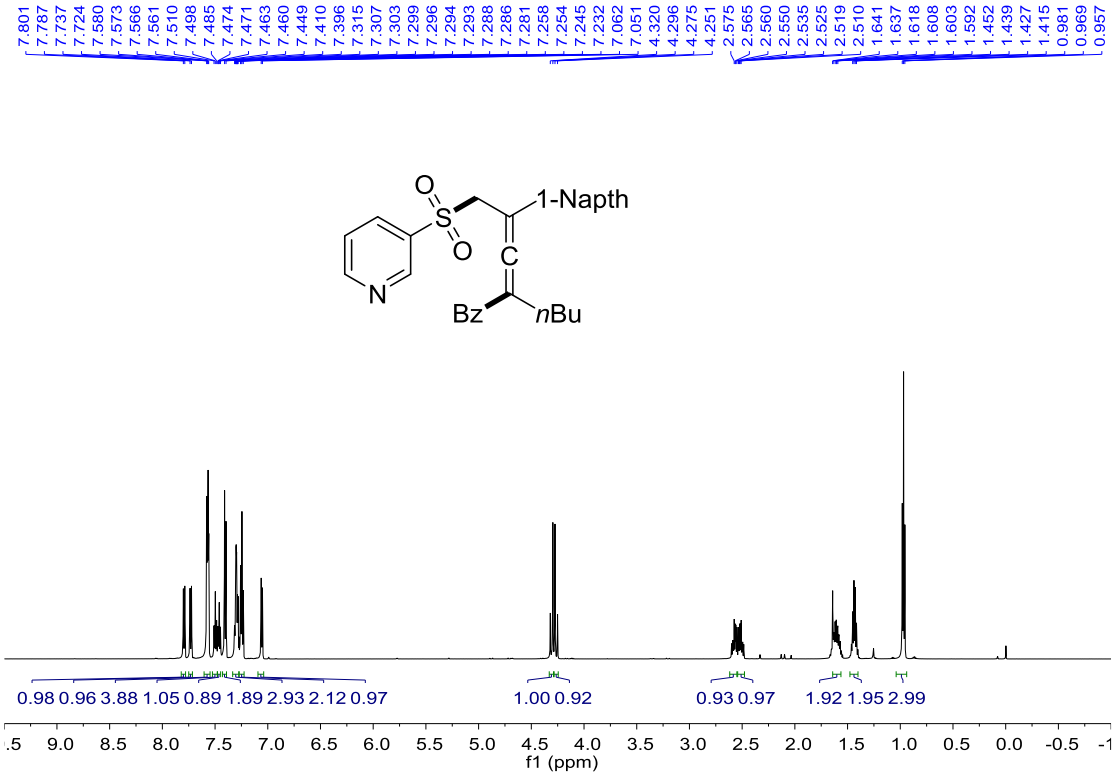
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **37**.



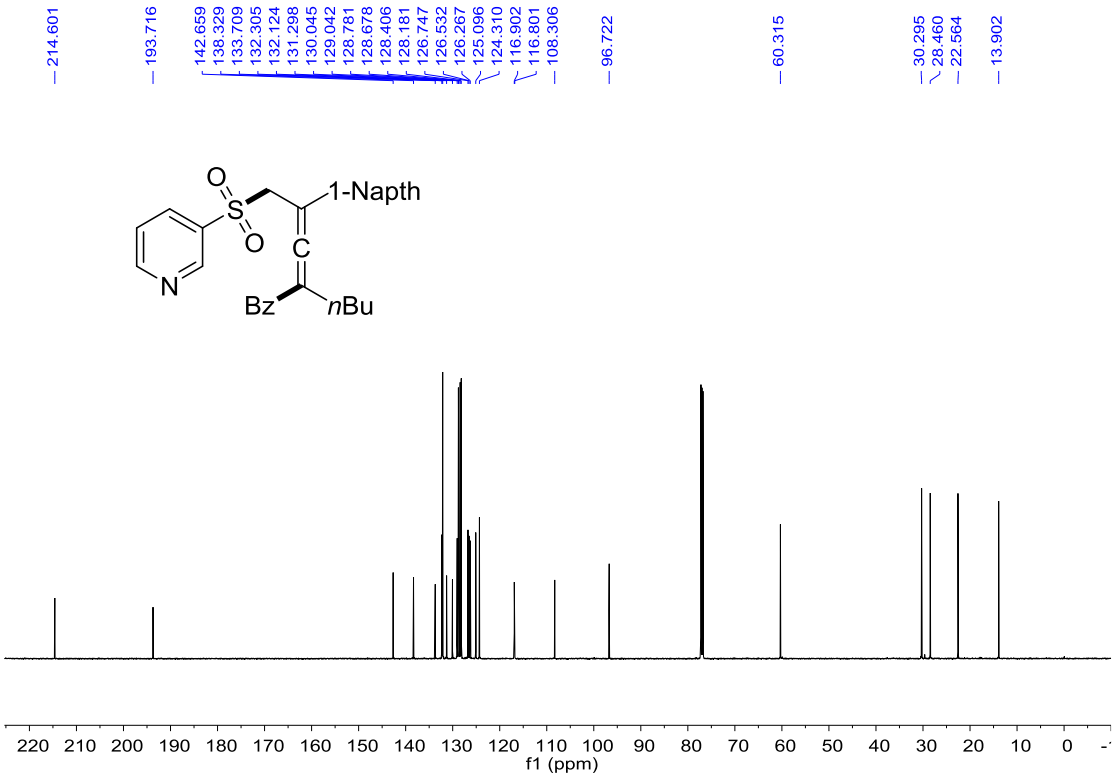
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **37**.



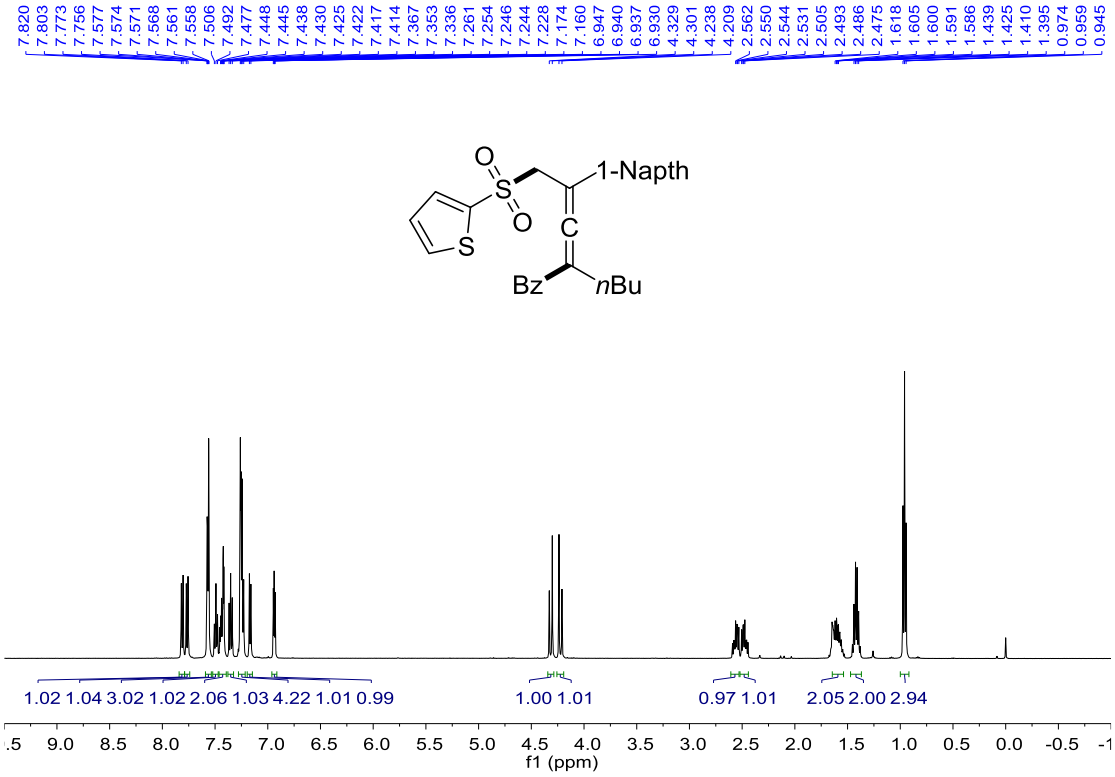
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **38**.



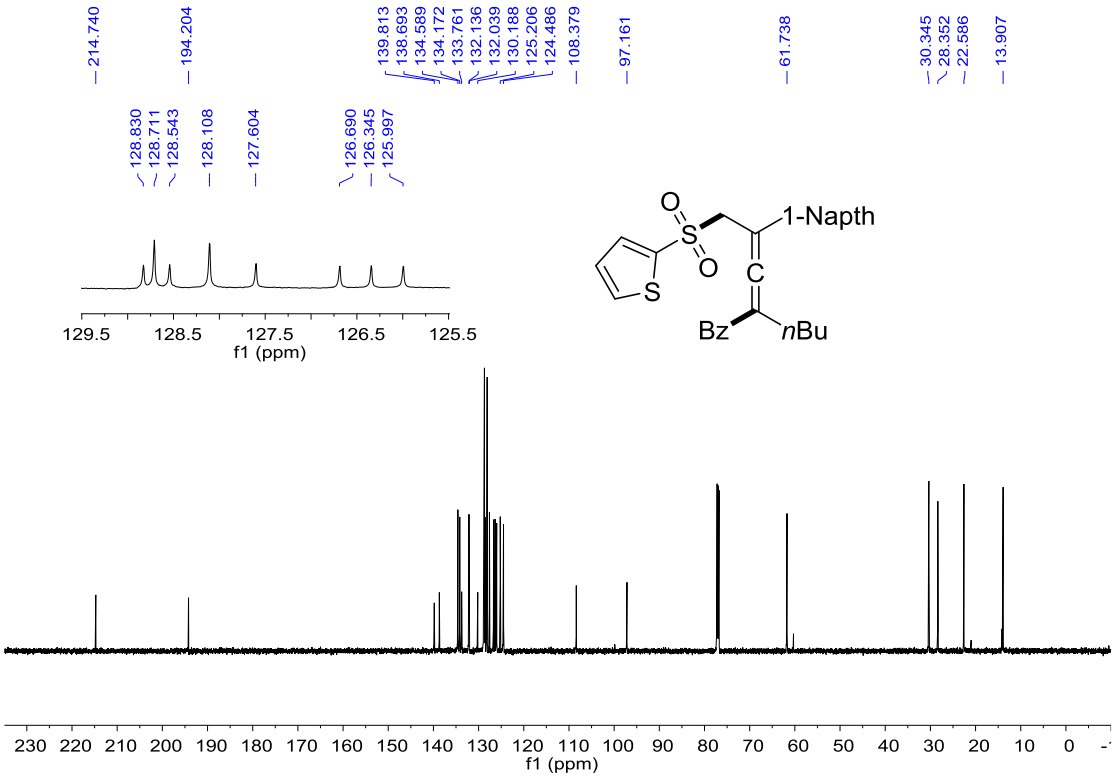
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **38**.



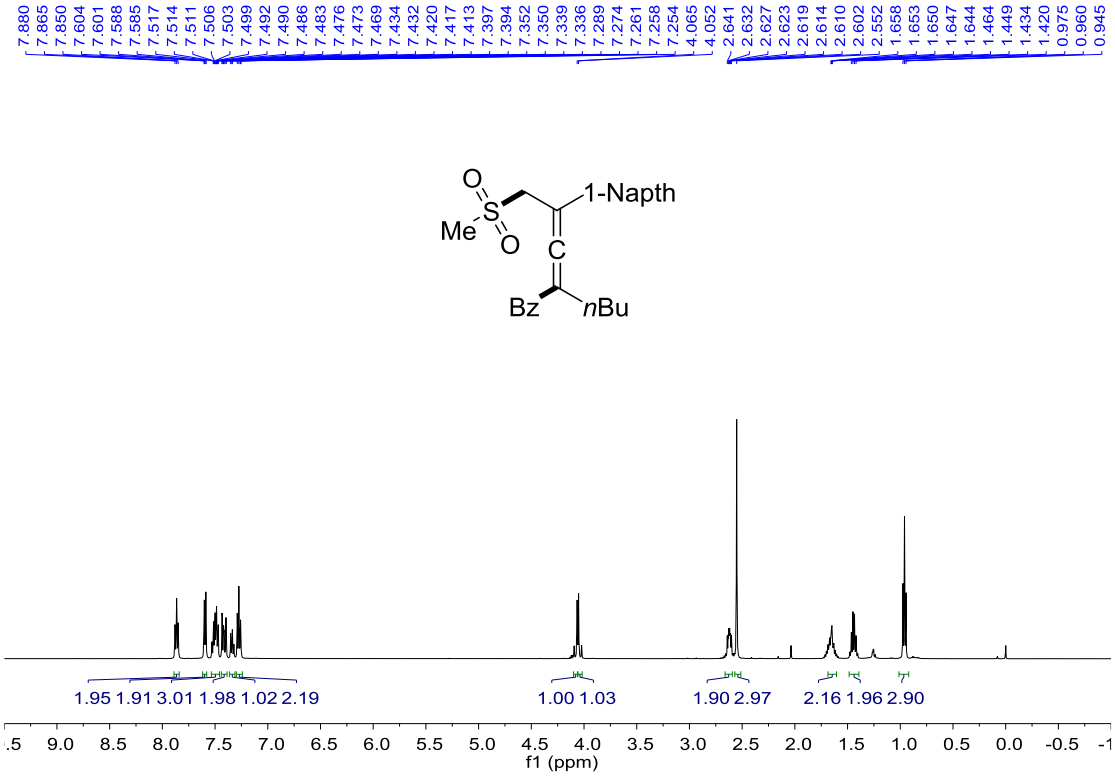
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **39**.



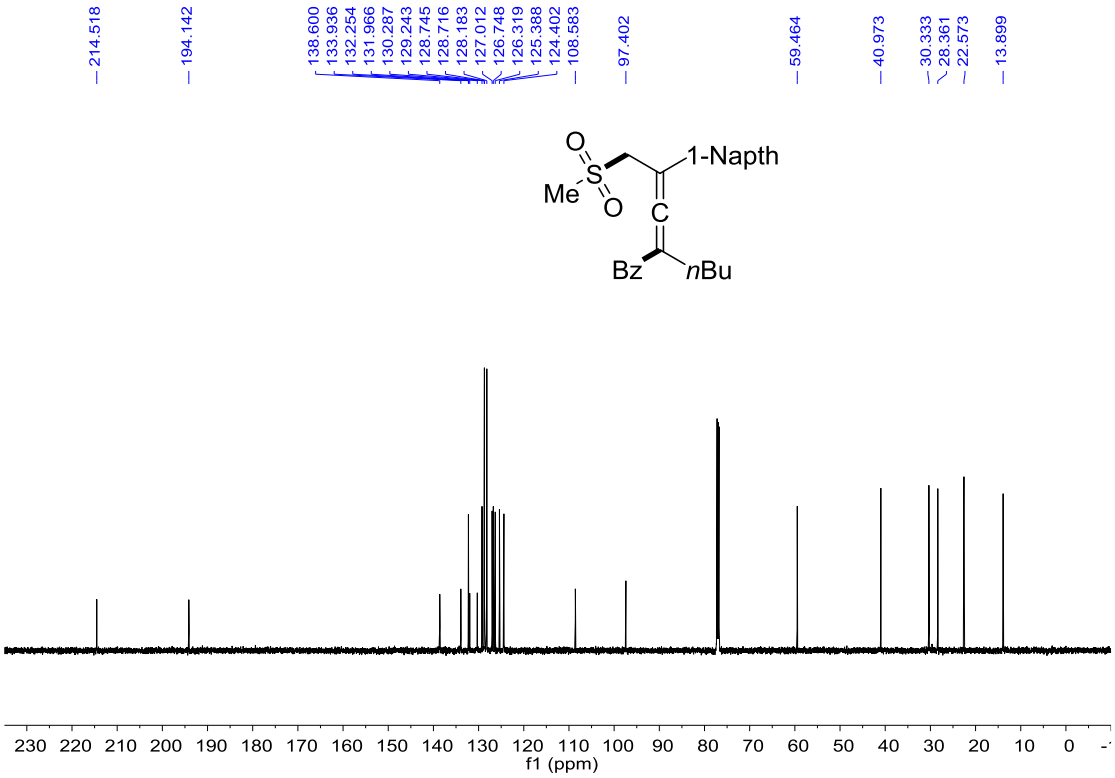
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **39**.



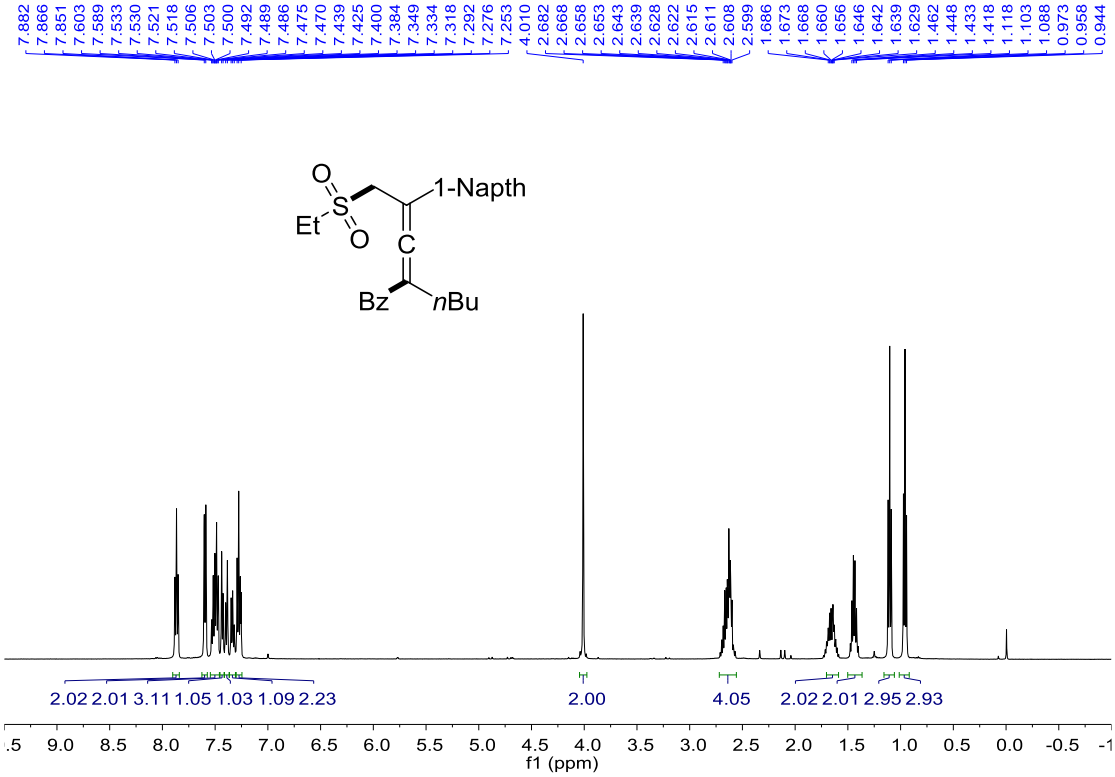
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **40**.



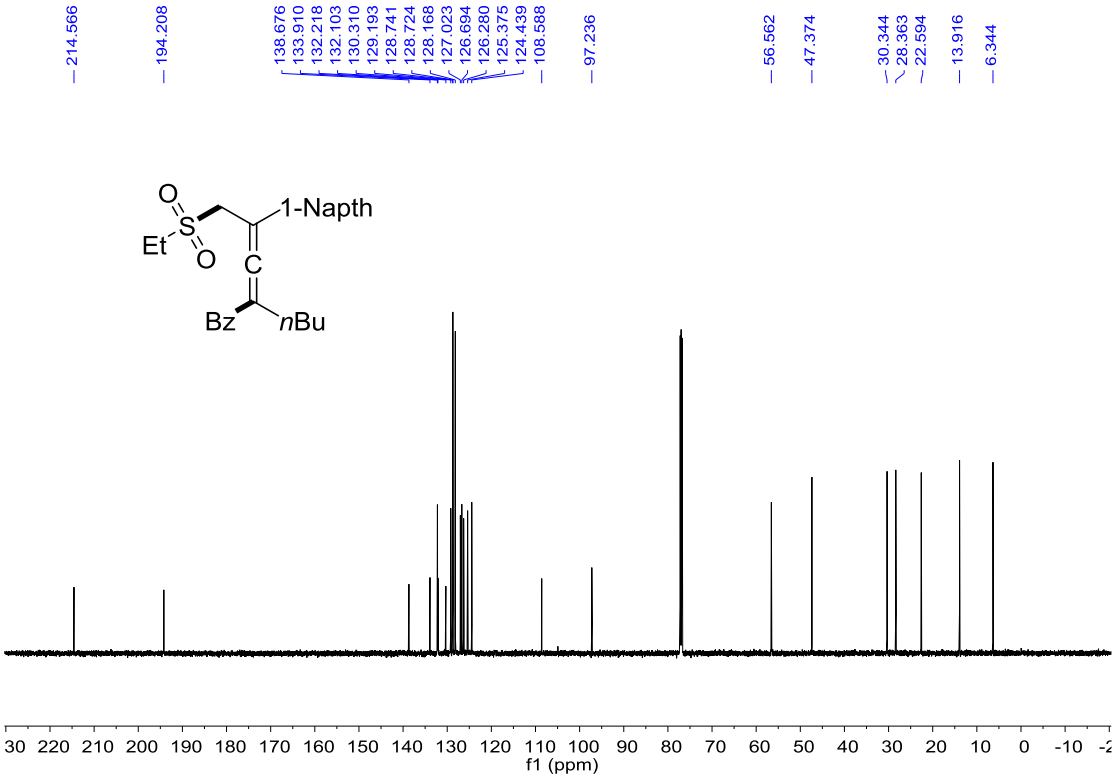
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **40**.



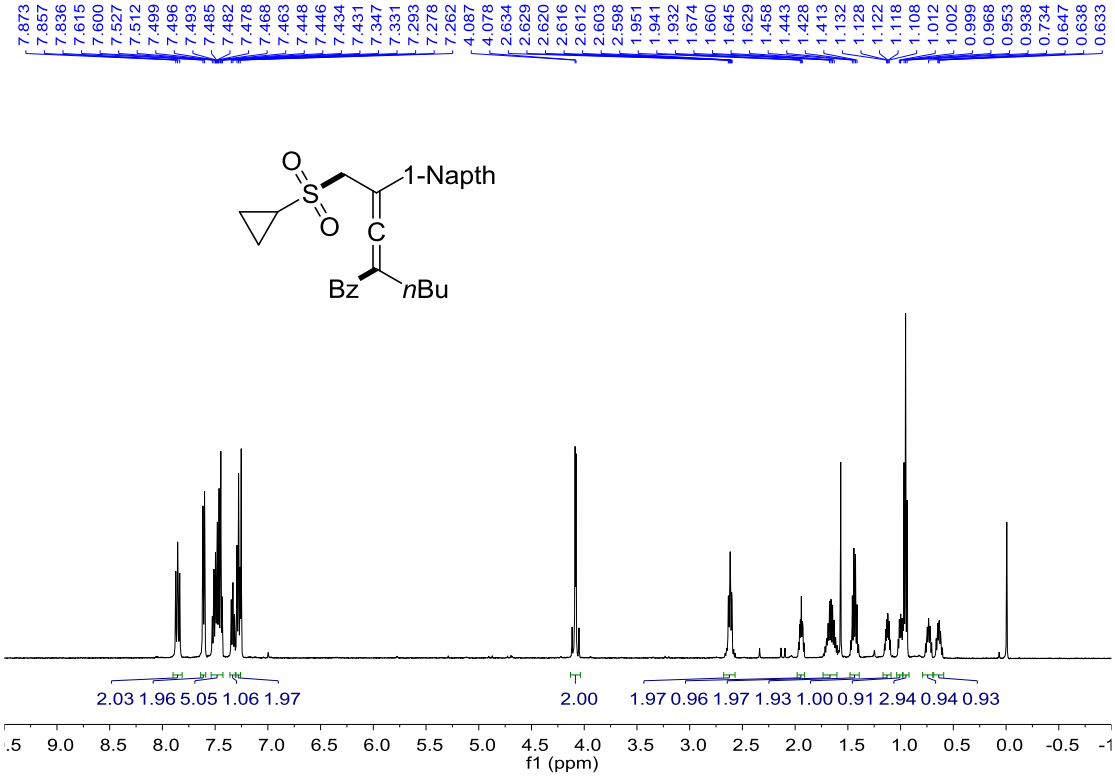
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **41**.



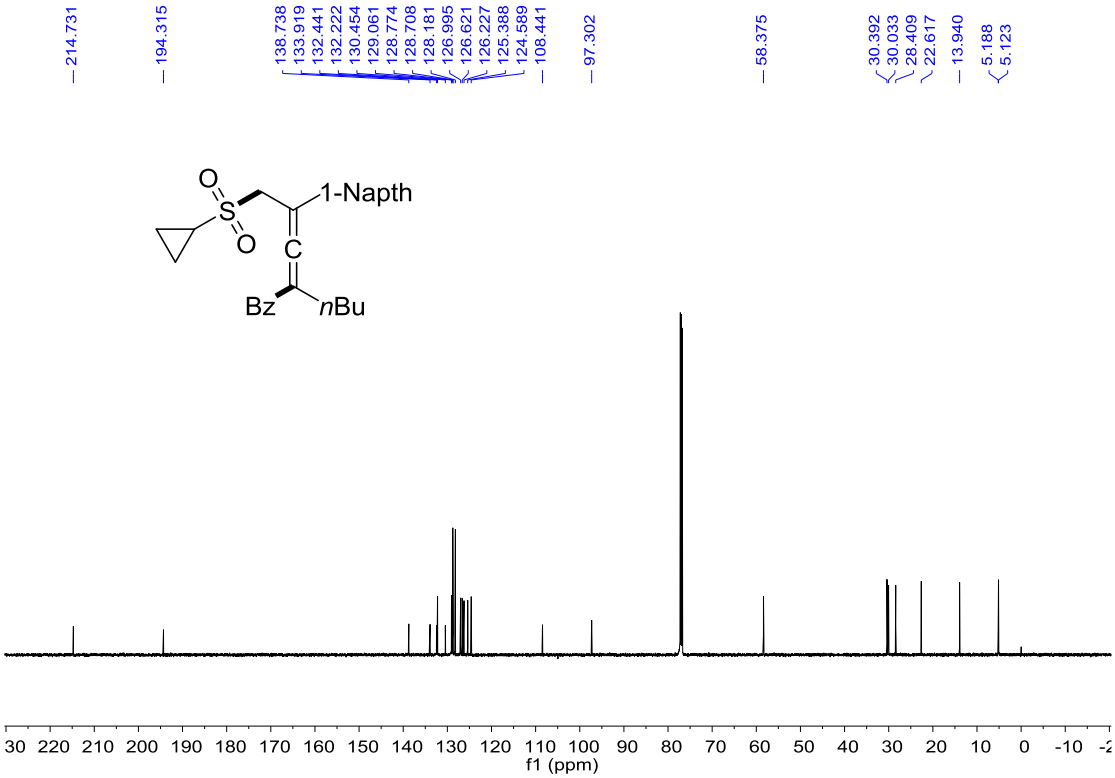
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **41**.



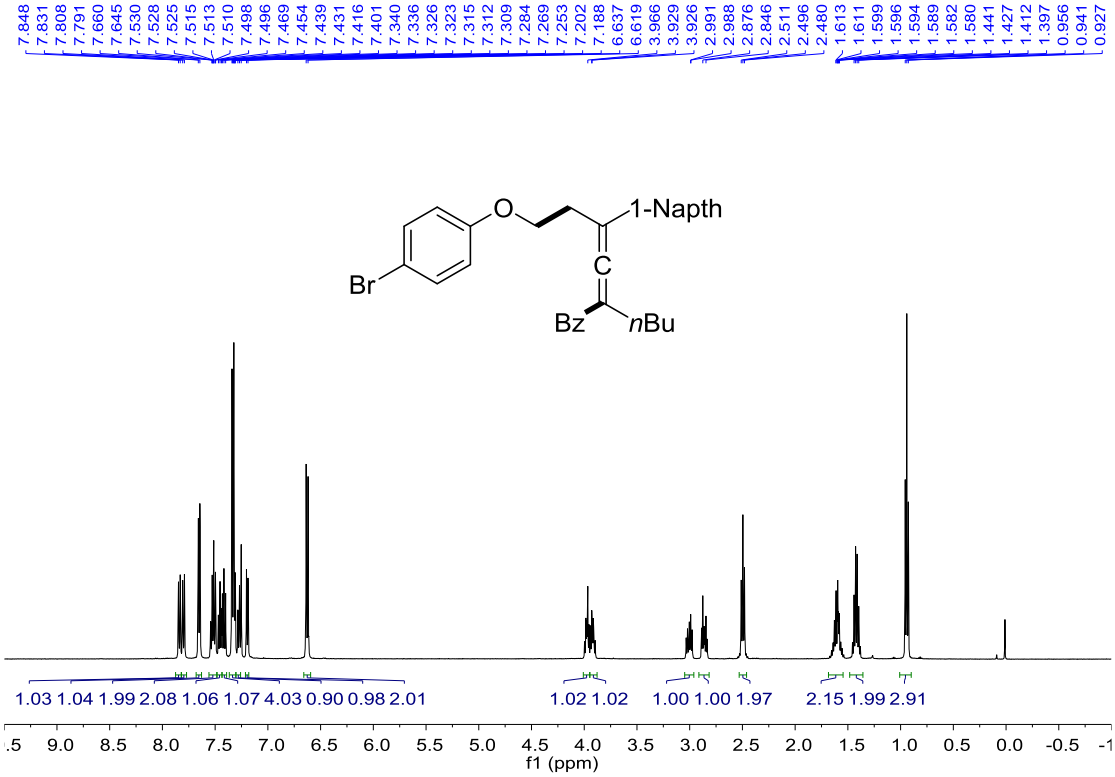
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **42**



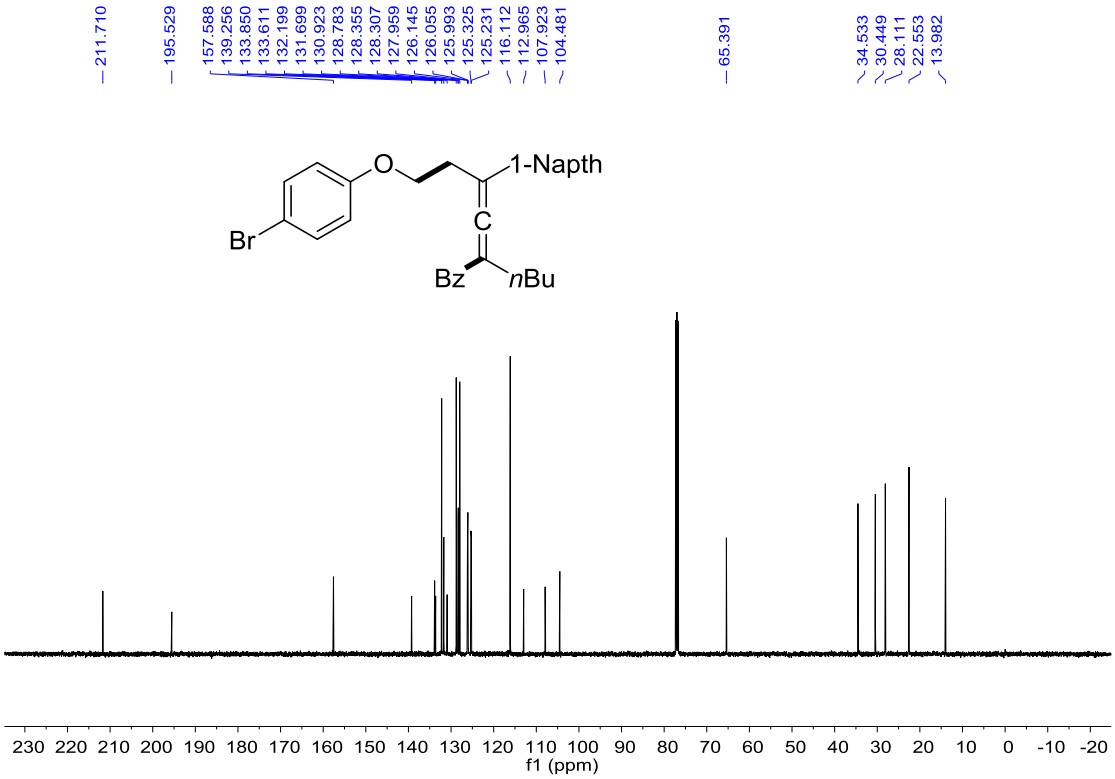
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **42**.



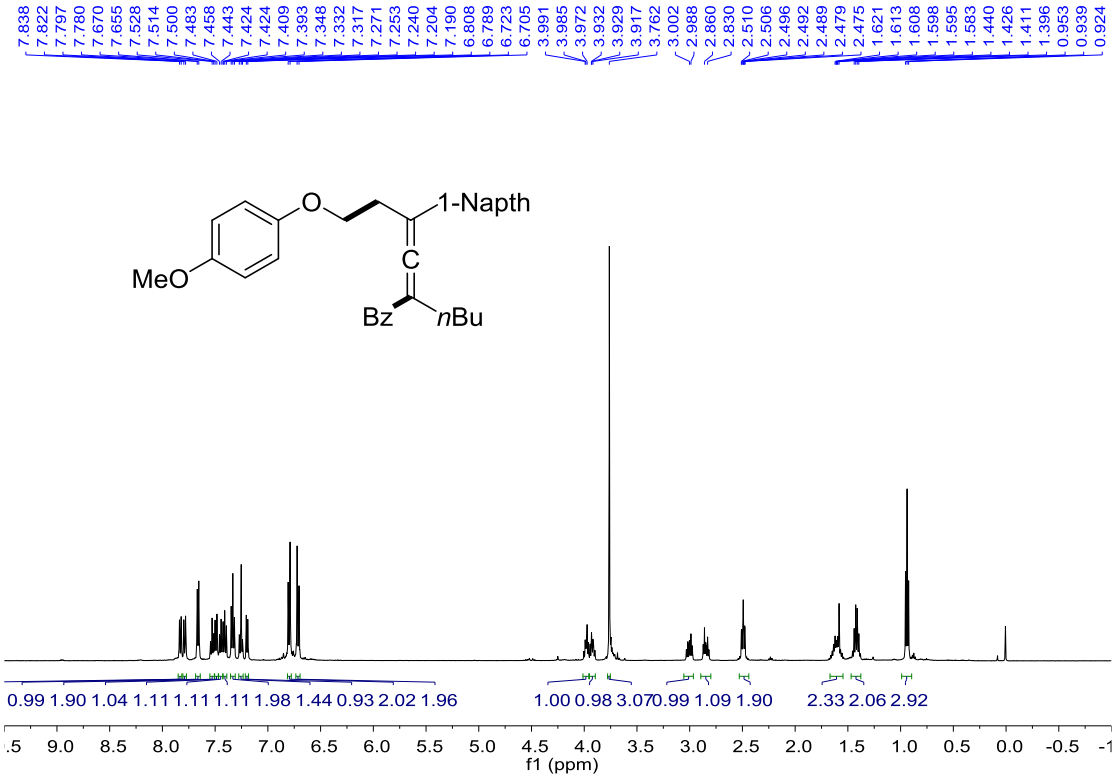
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **43**.



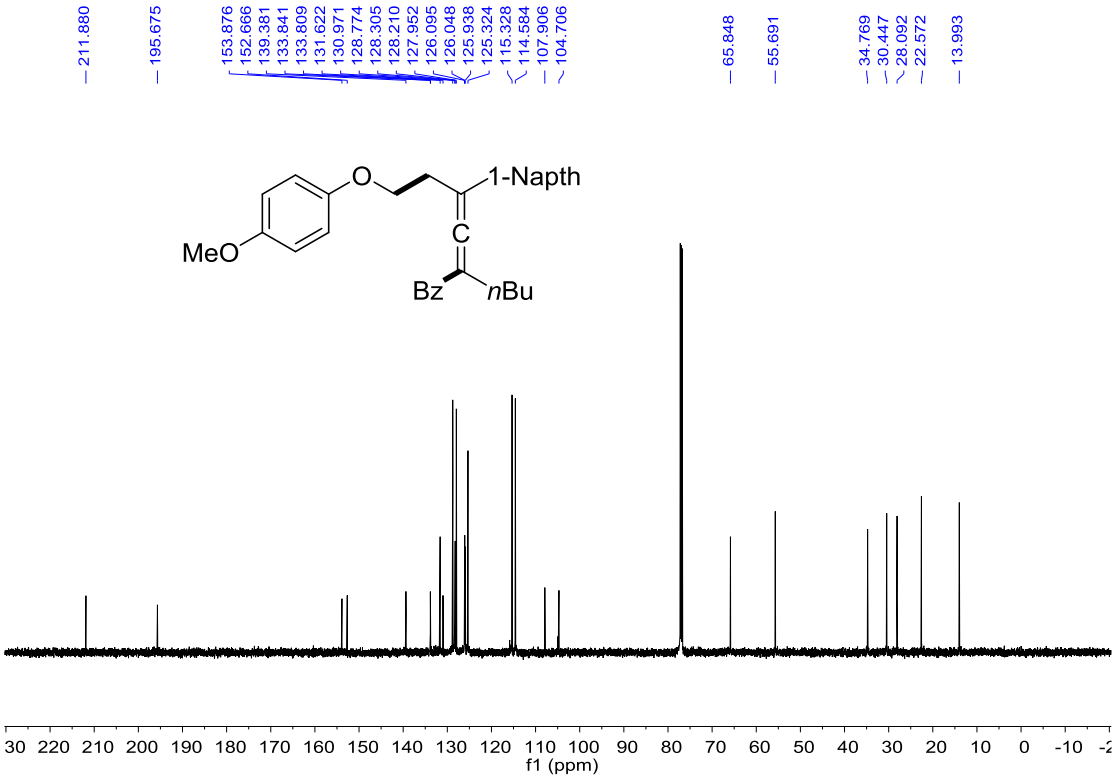
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **43**.



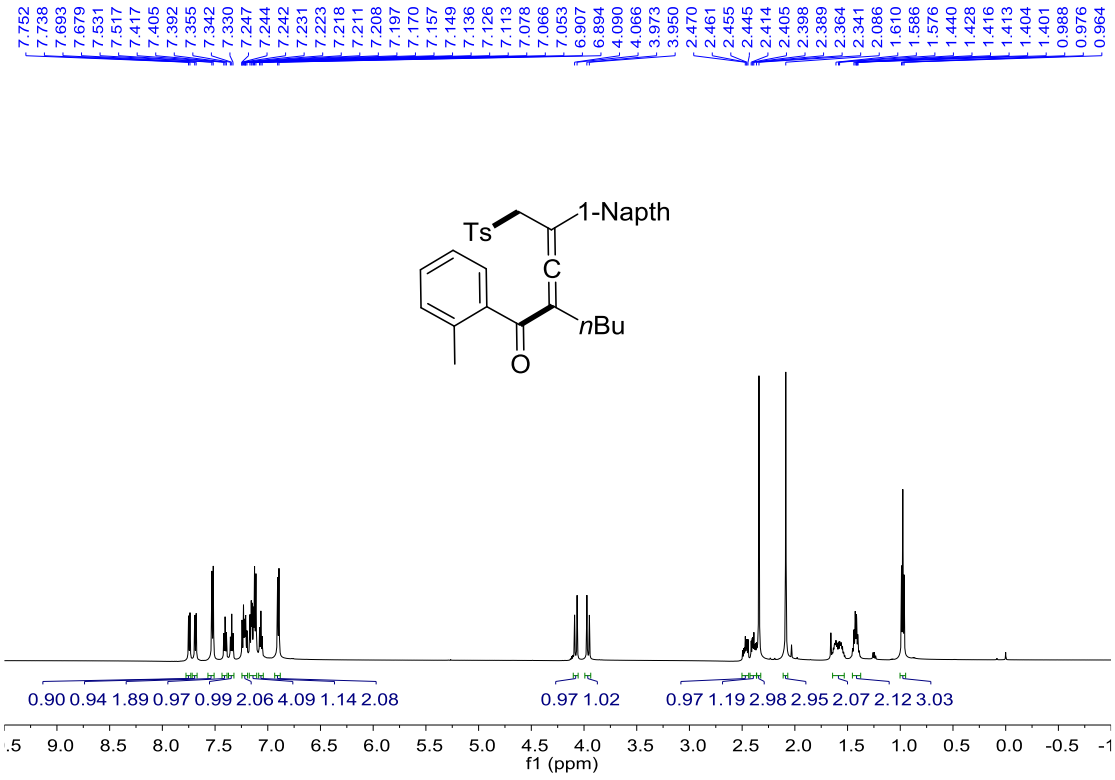
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **44**.



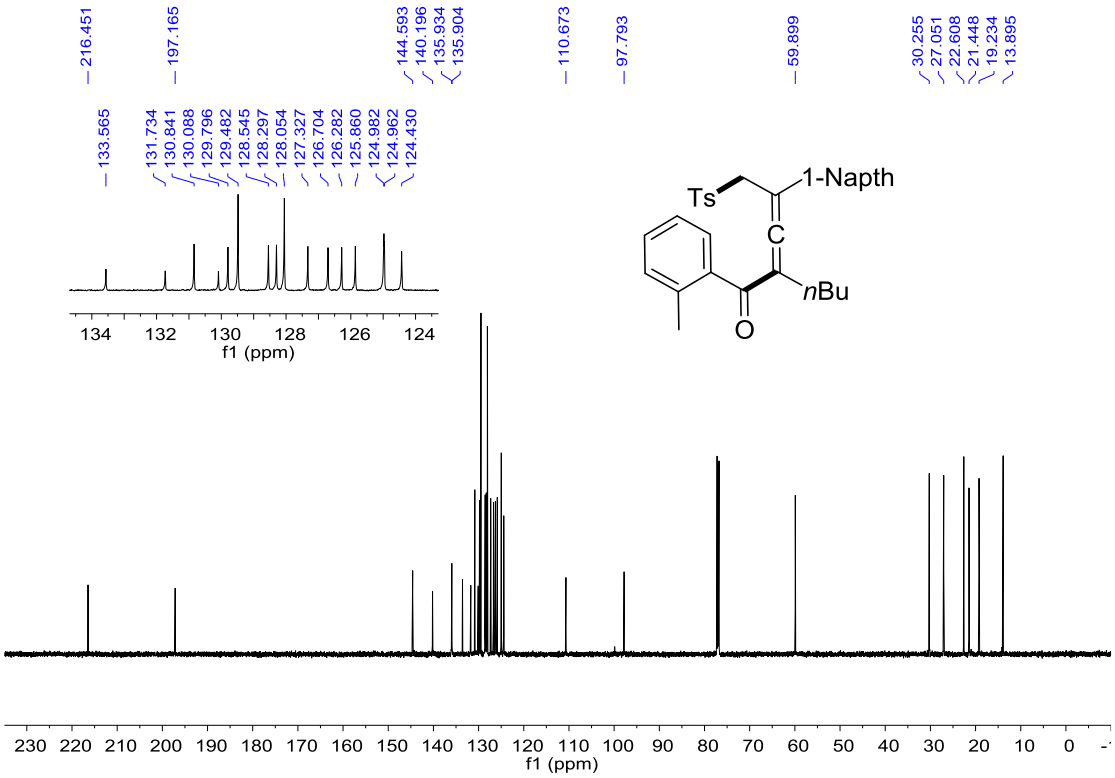
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **44**.



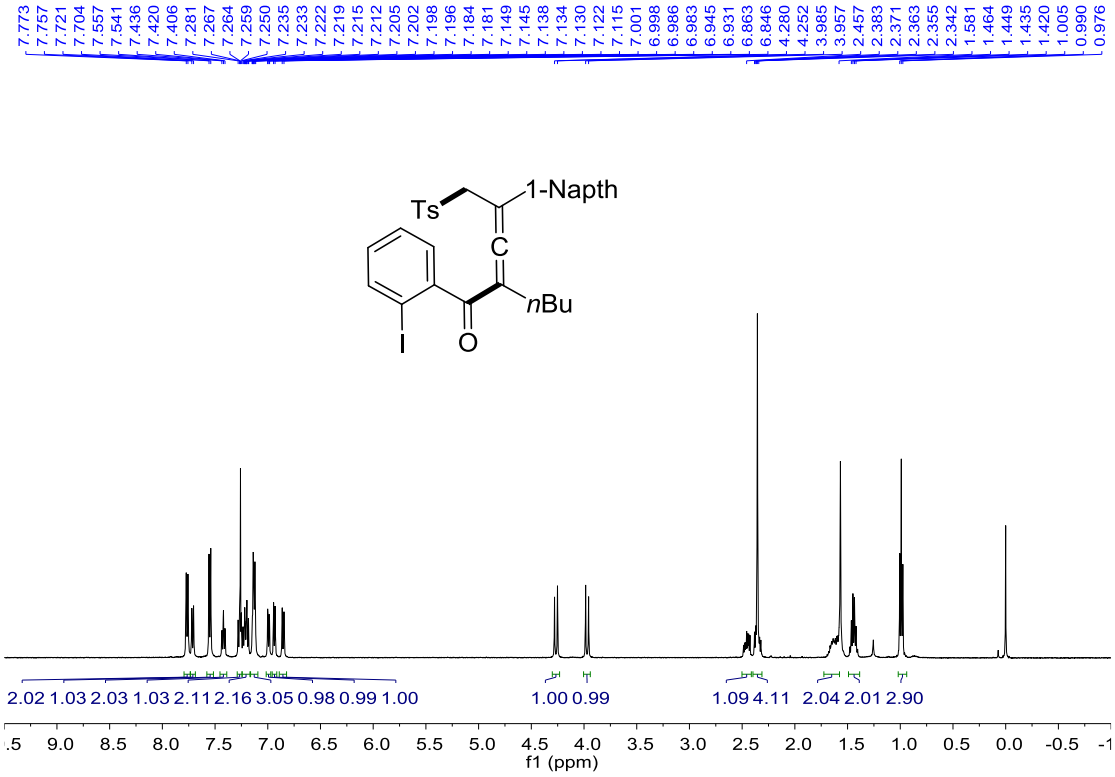
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **45**.



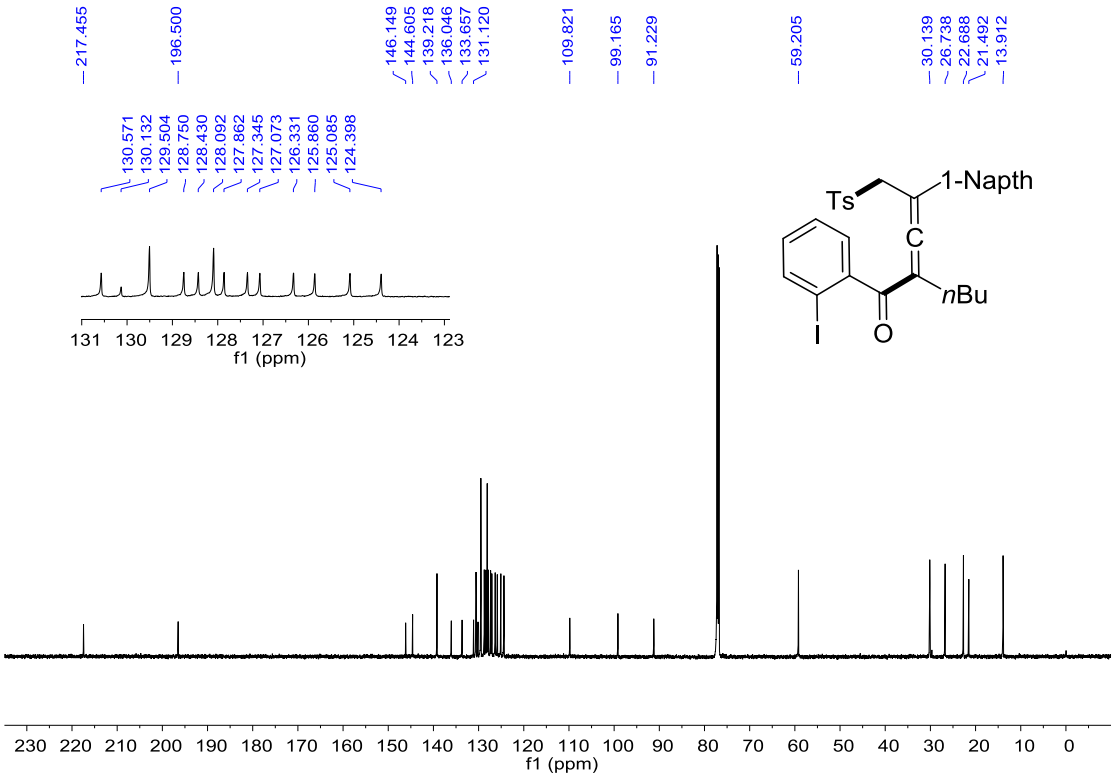
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **45**.



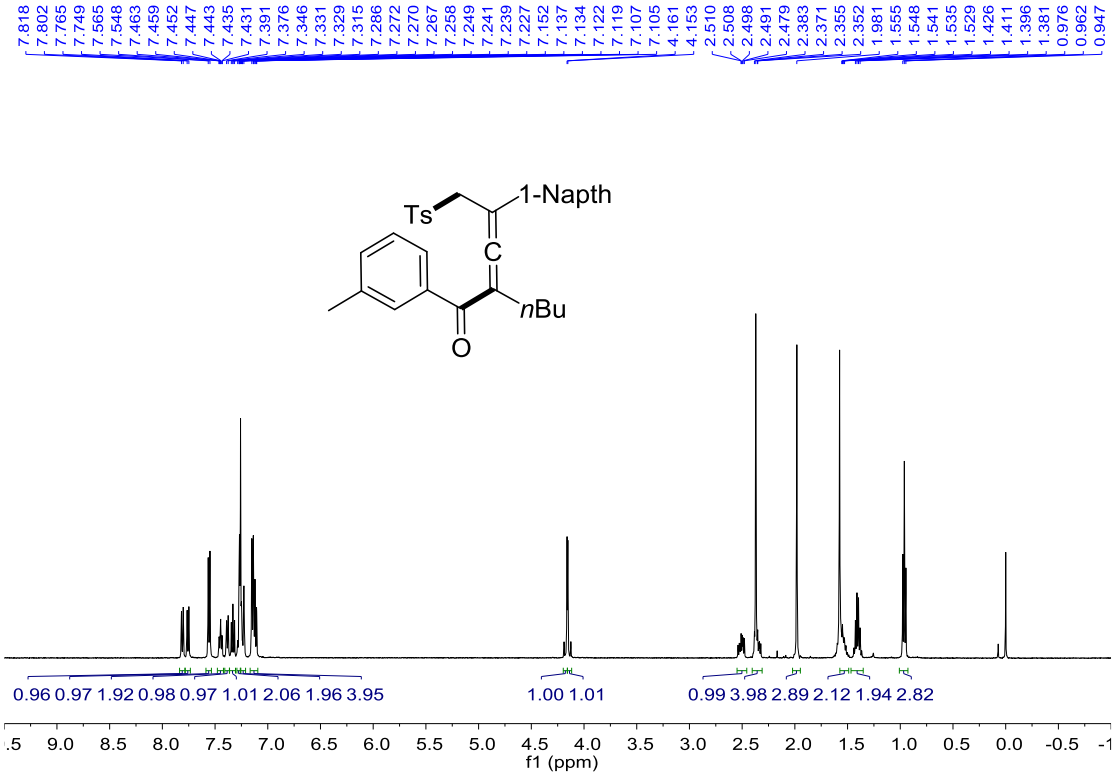
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **46**.



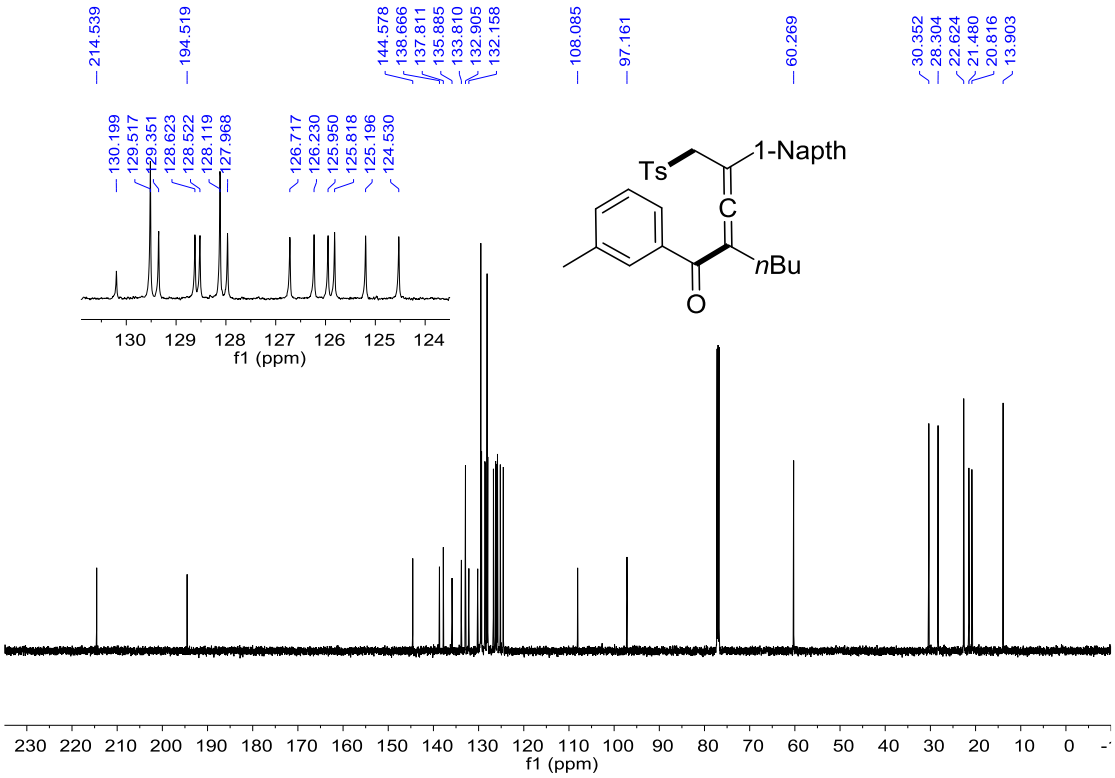
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **46**.



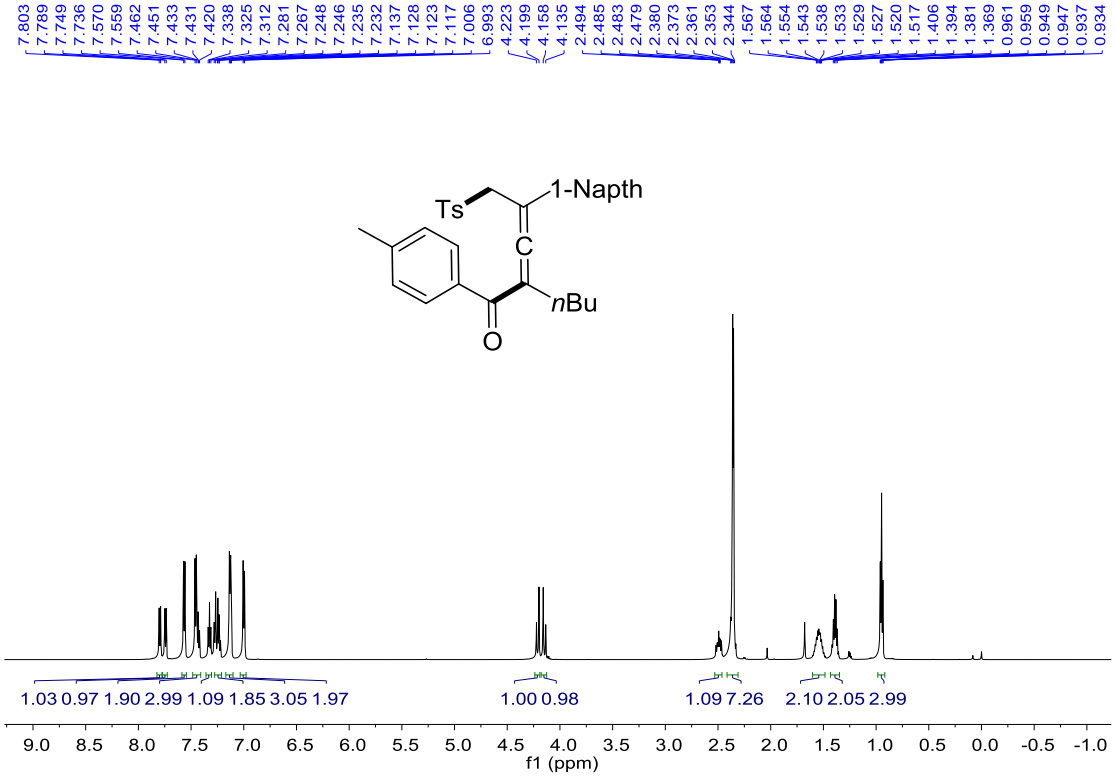
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **47**.



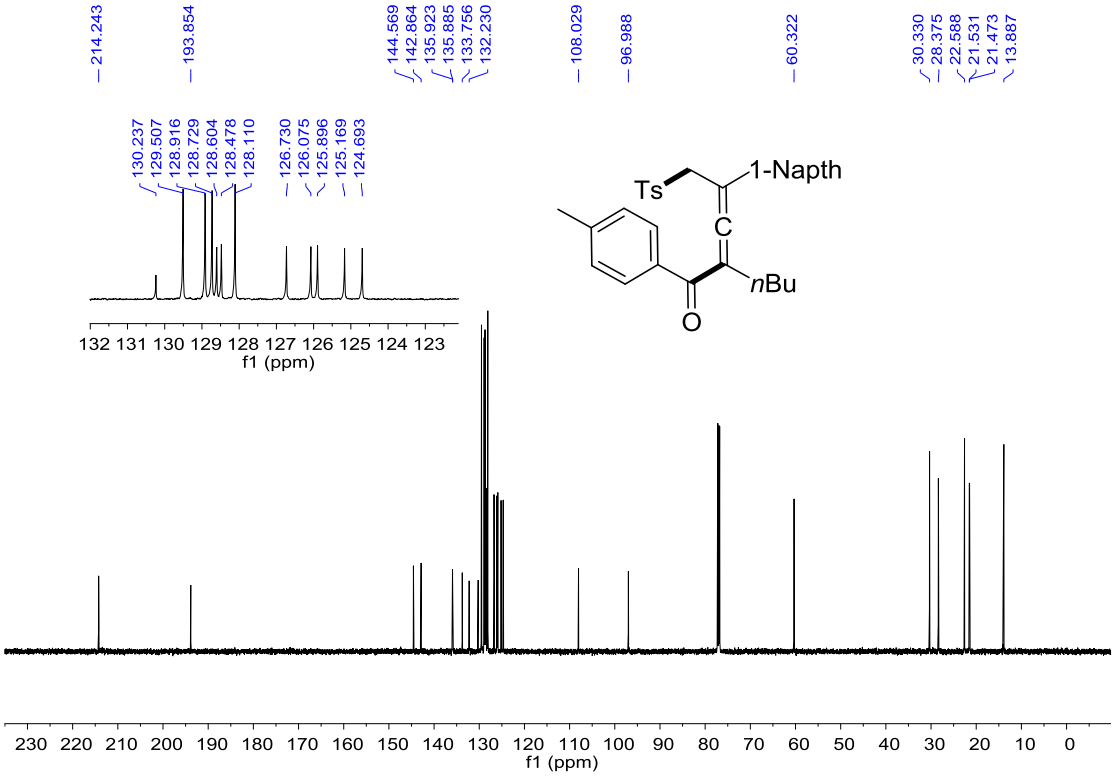
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **47**.



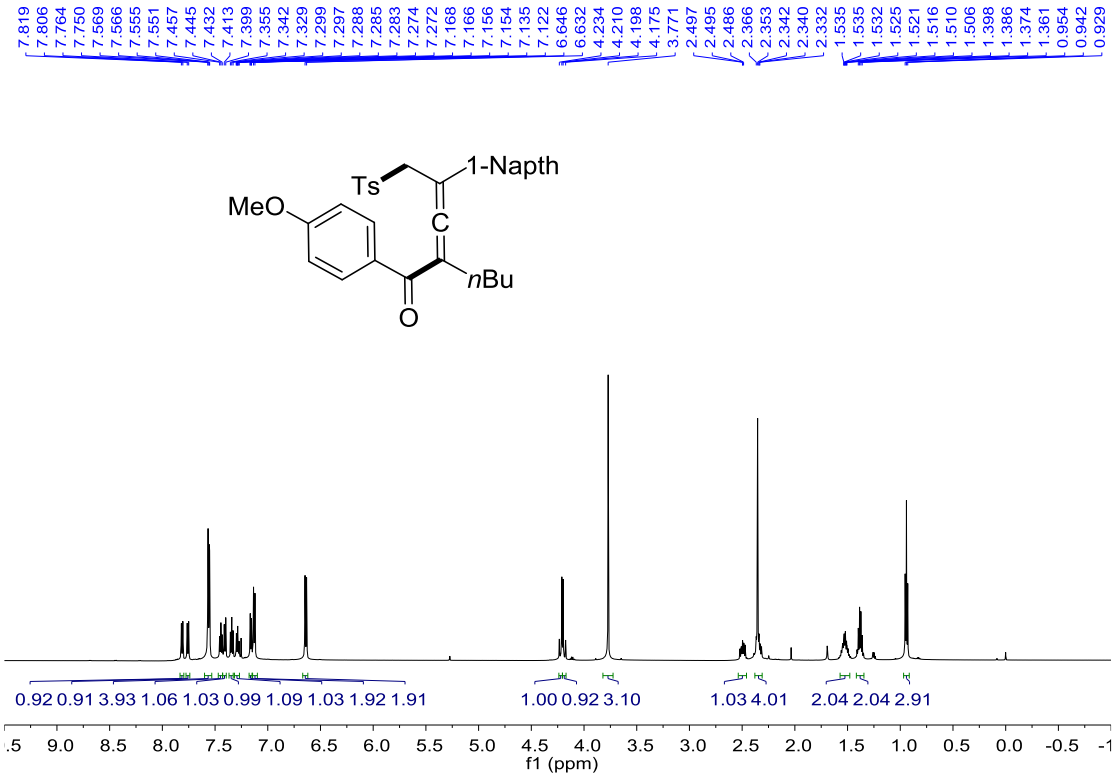
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **48**.



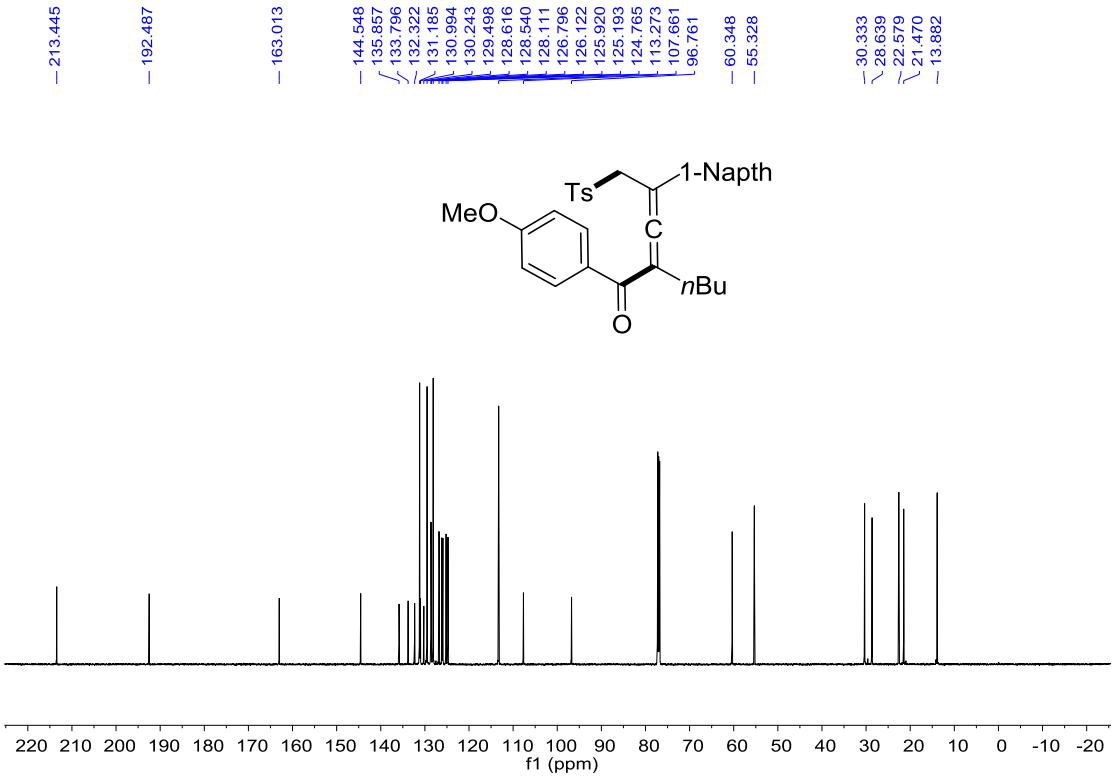
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **48**.



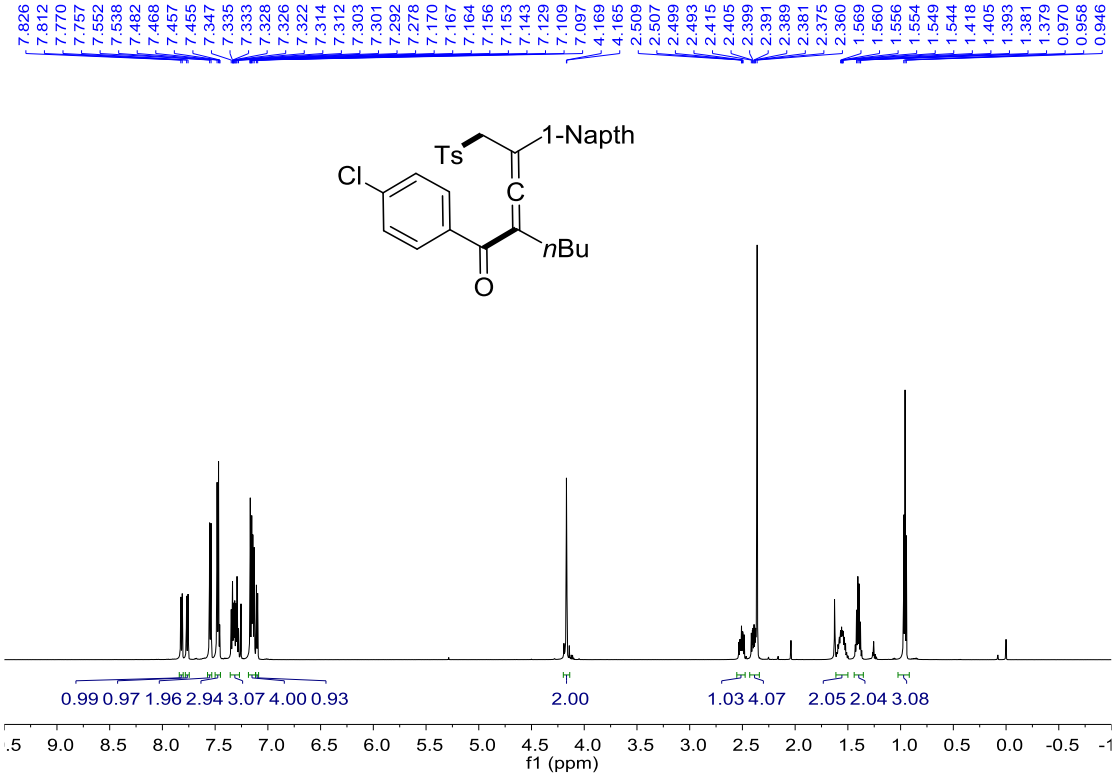
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **49**.



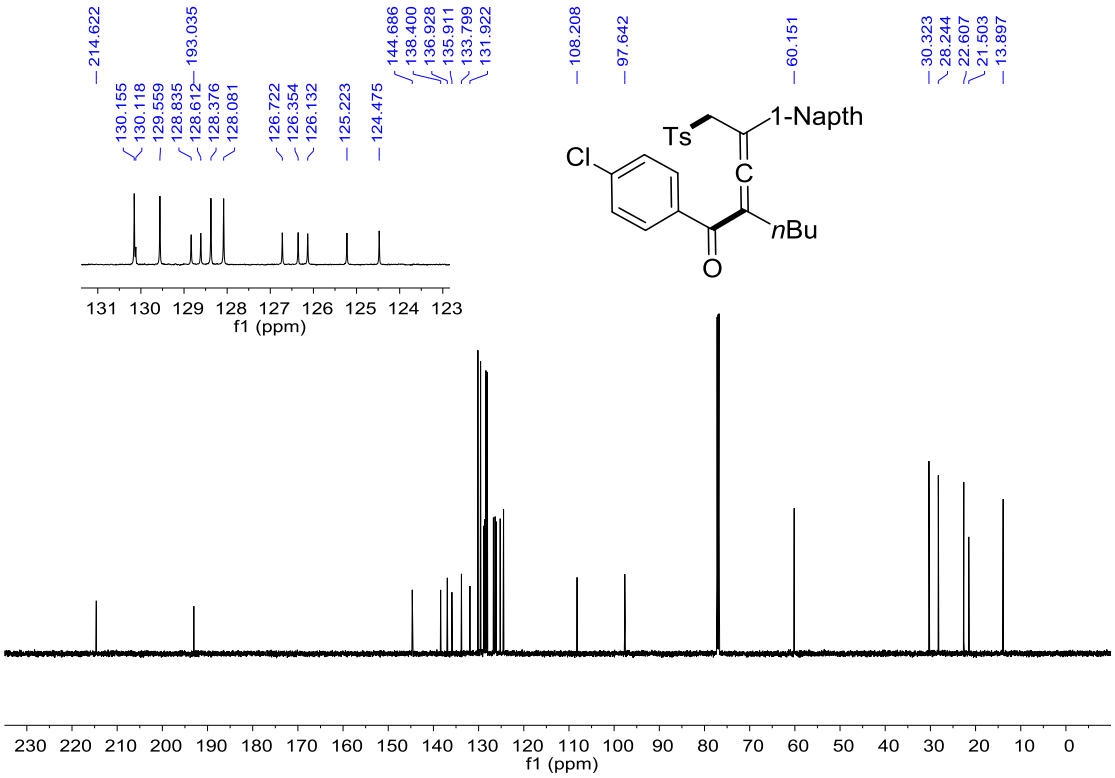
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **49**.



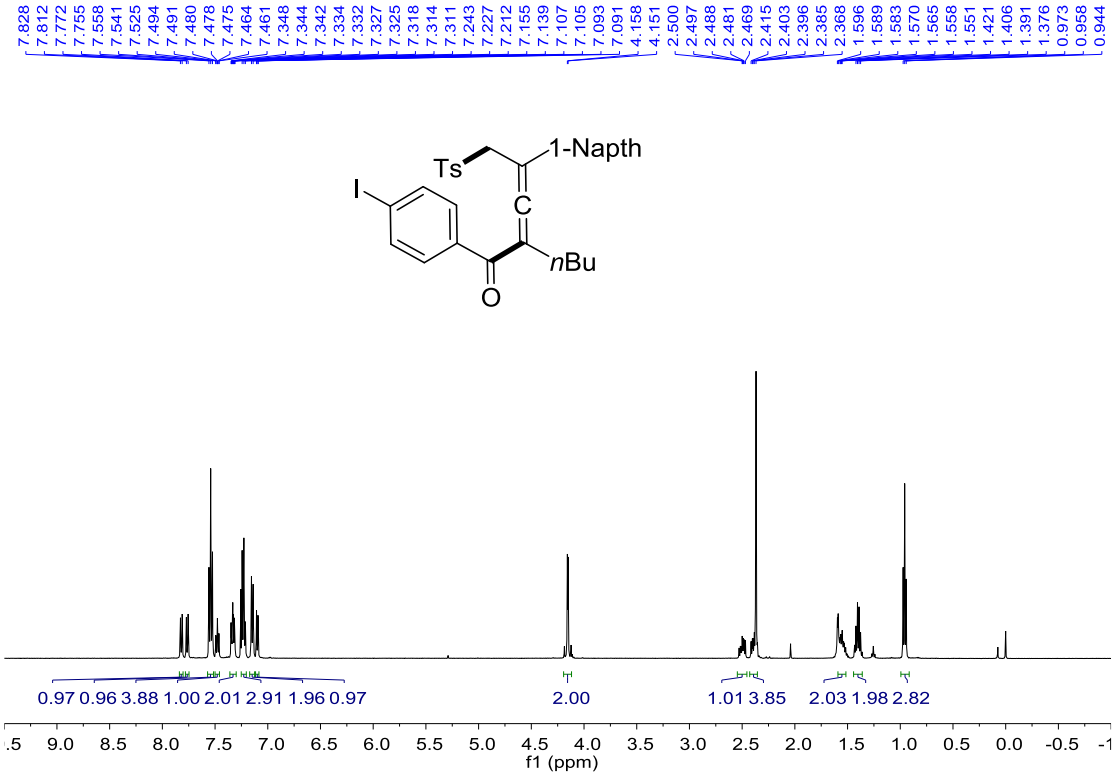
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **50**.



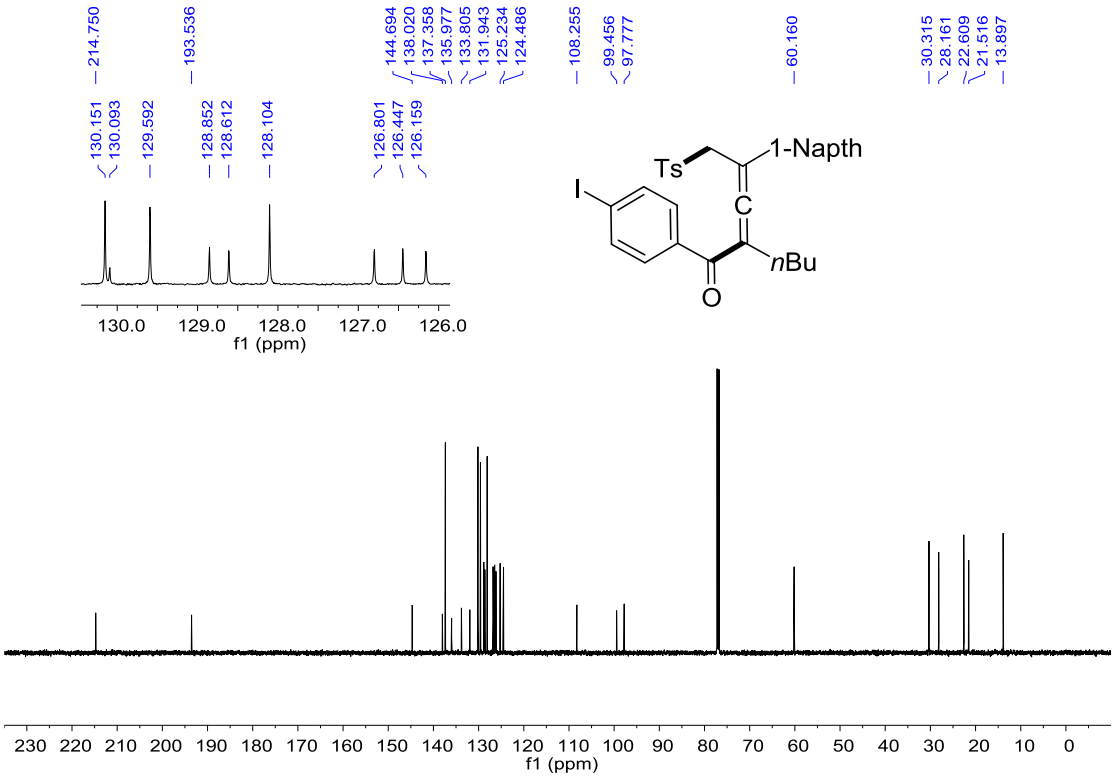
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **50**.



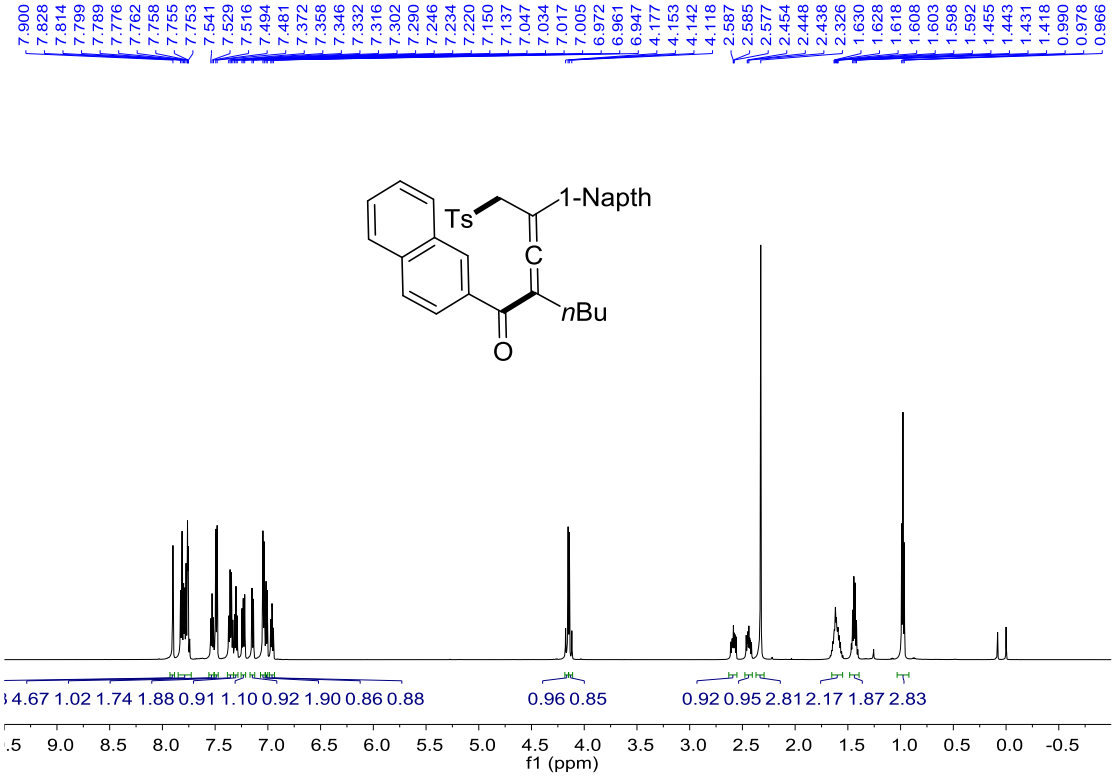
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **51**.



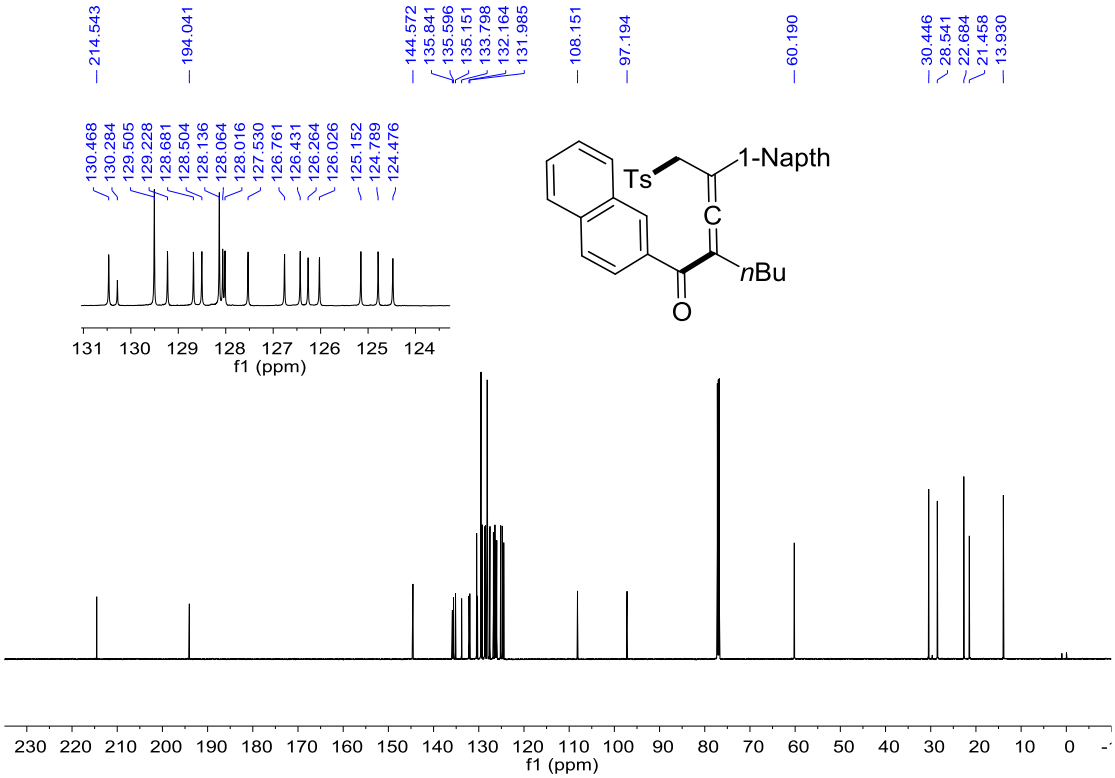
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **51**.



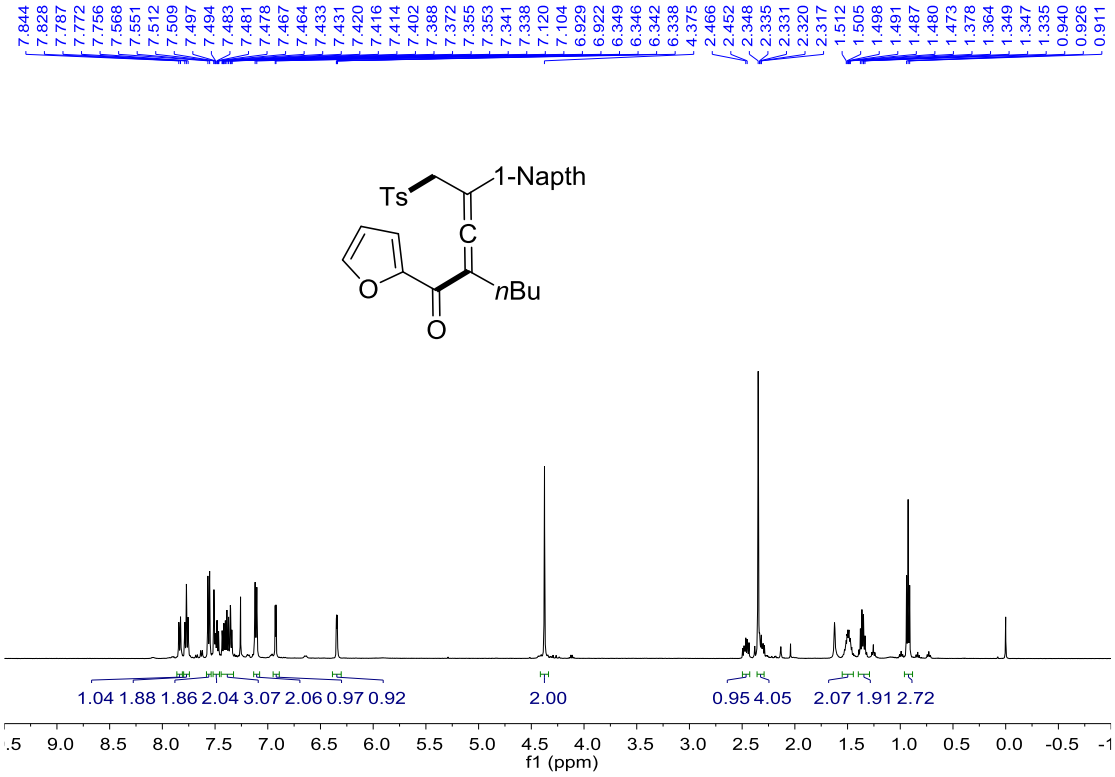
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **52**.



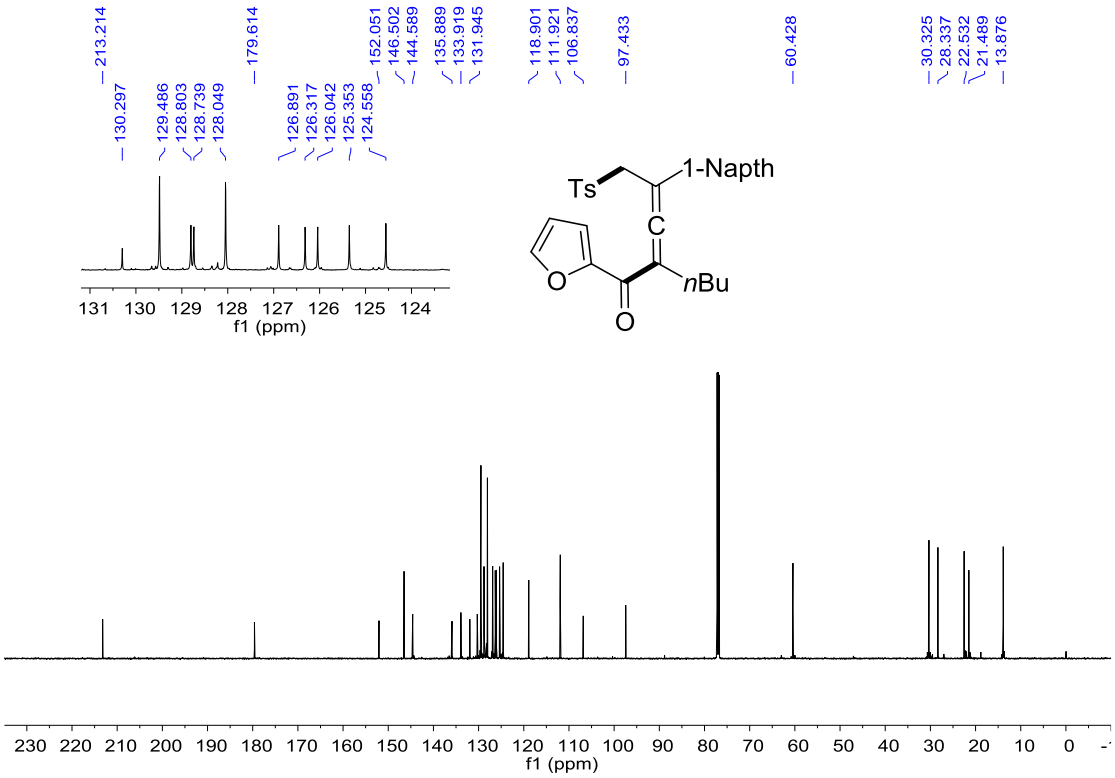
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **52**.



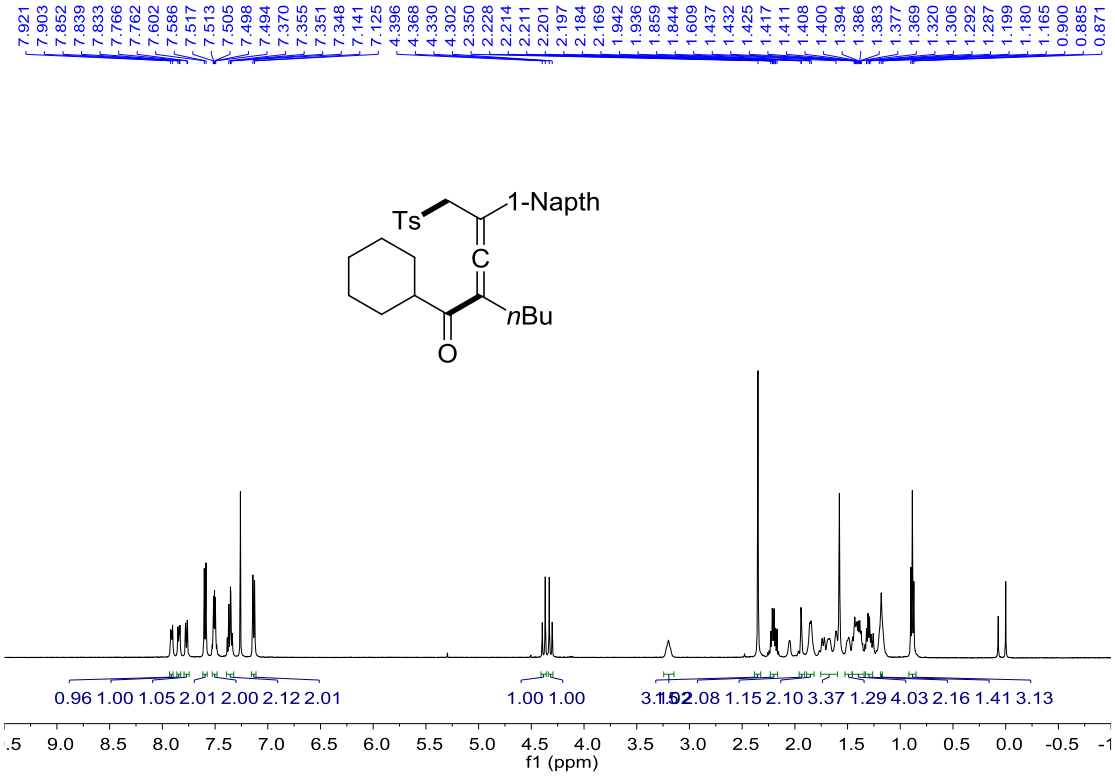
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **53**.



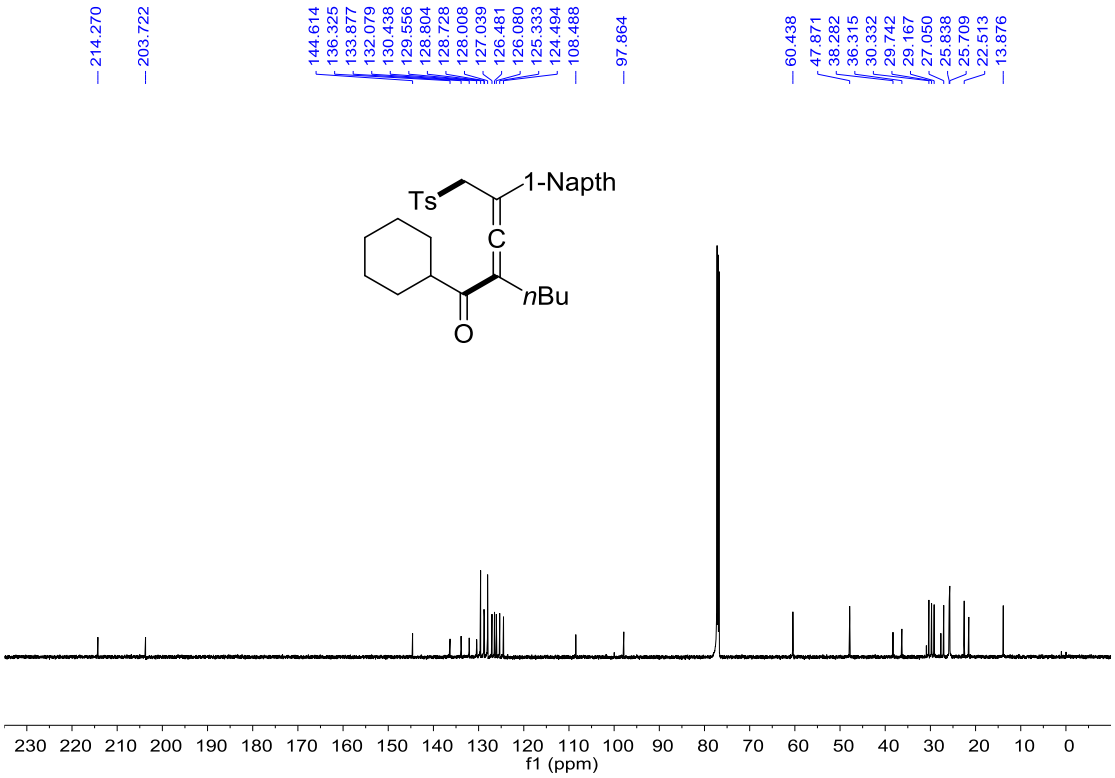
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **53**.



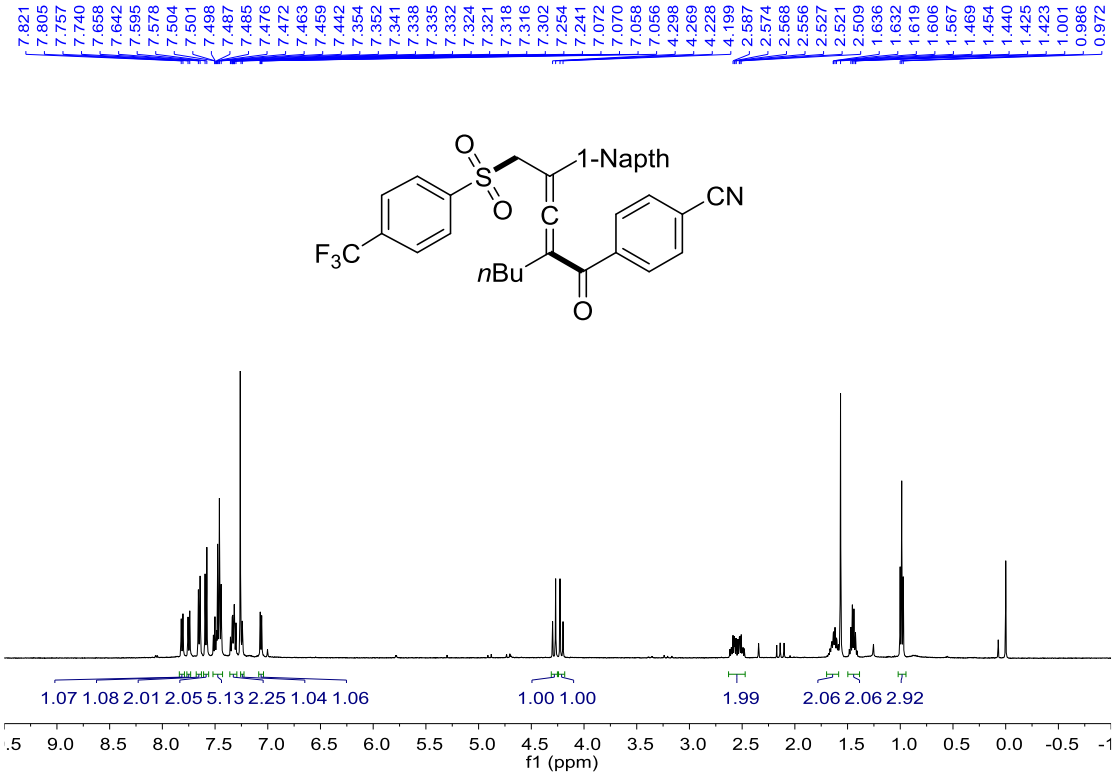
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **54**.



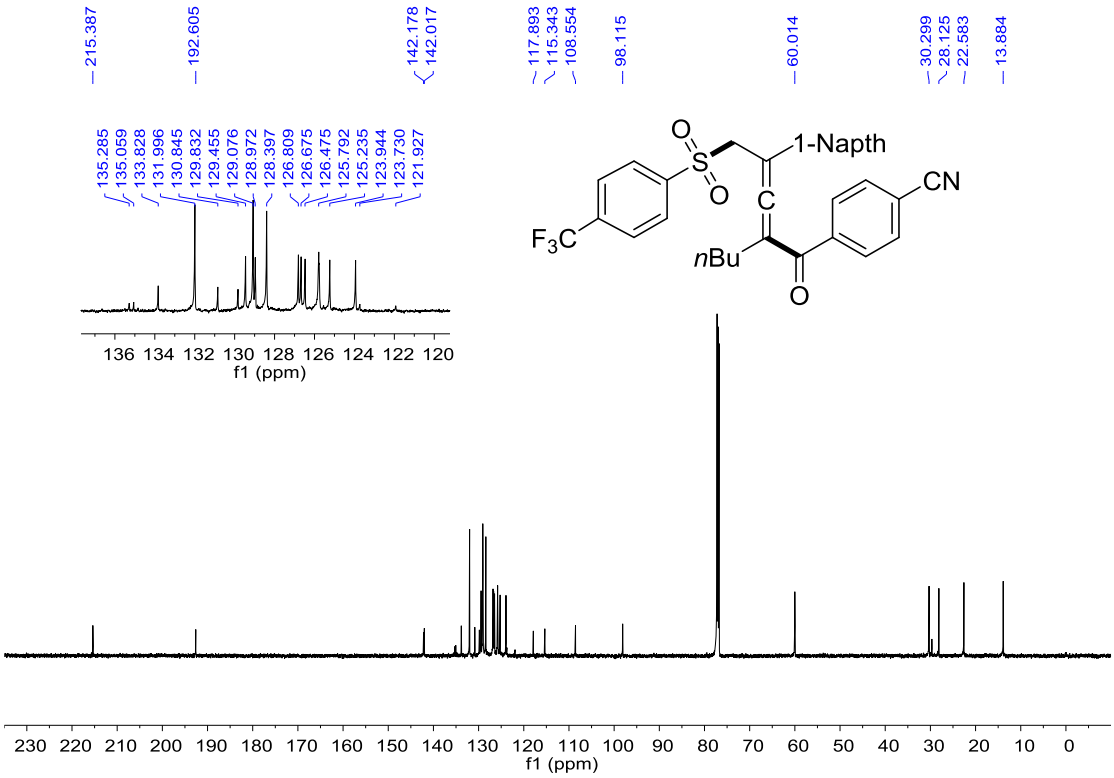
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **54**.



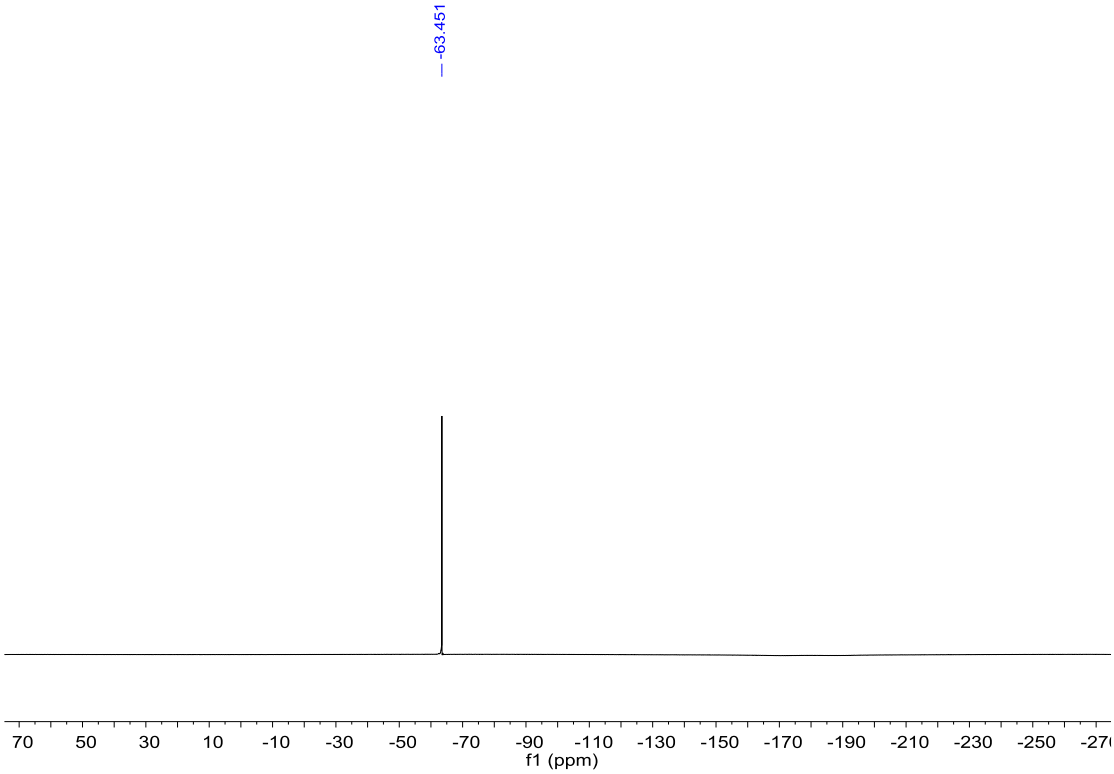
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **55**.



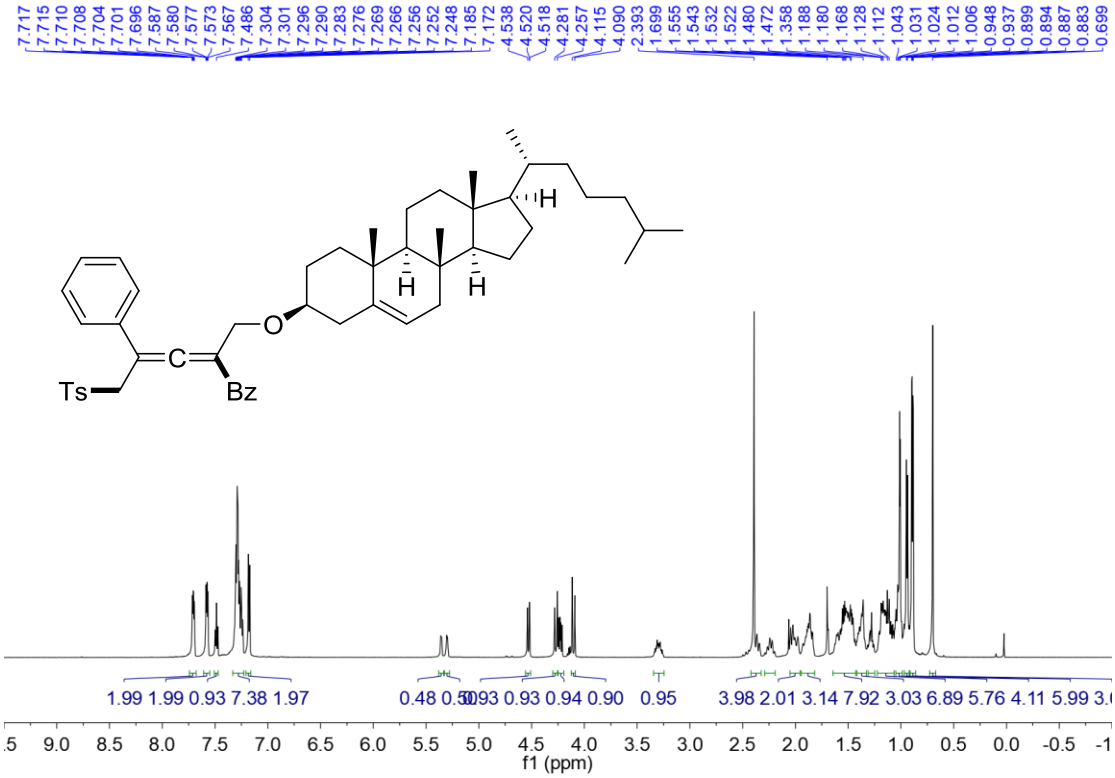
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **55**.



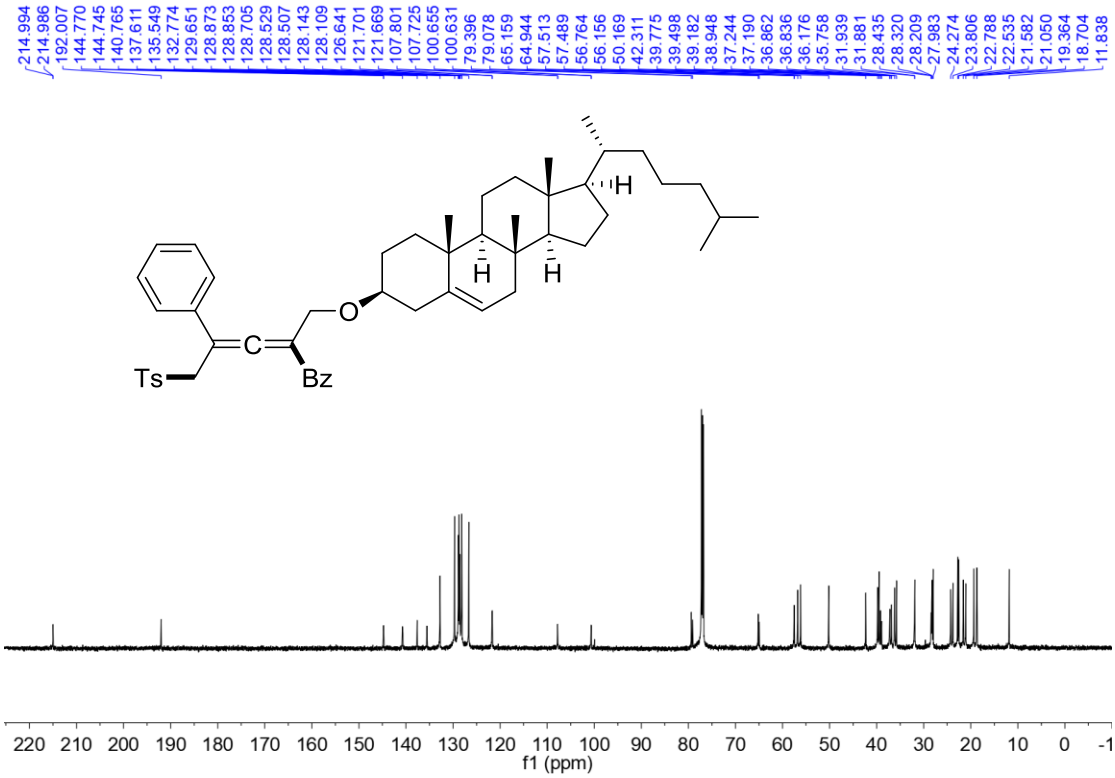
^{19}F NMR (565 MHz, $CDCl_3$) spectrum for **55**.



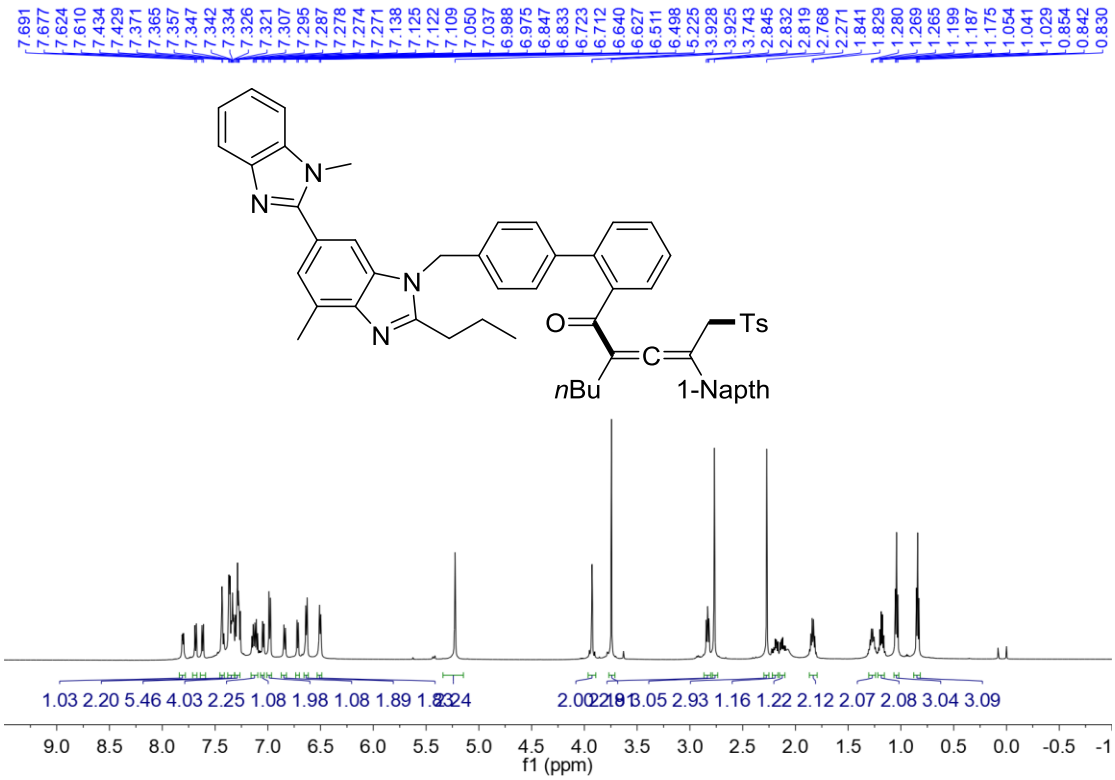
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **57**.



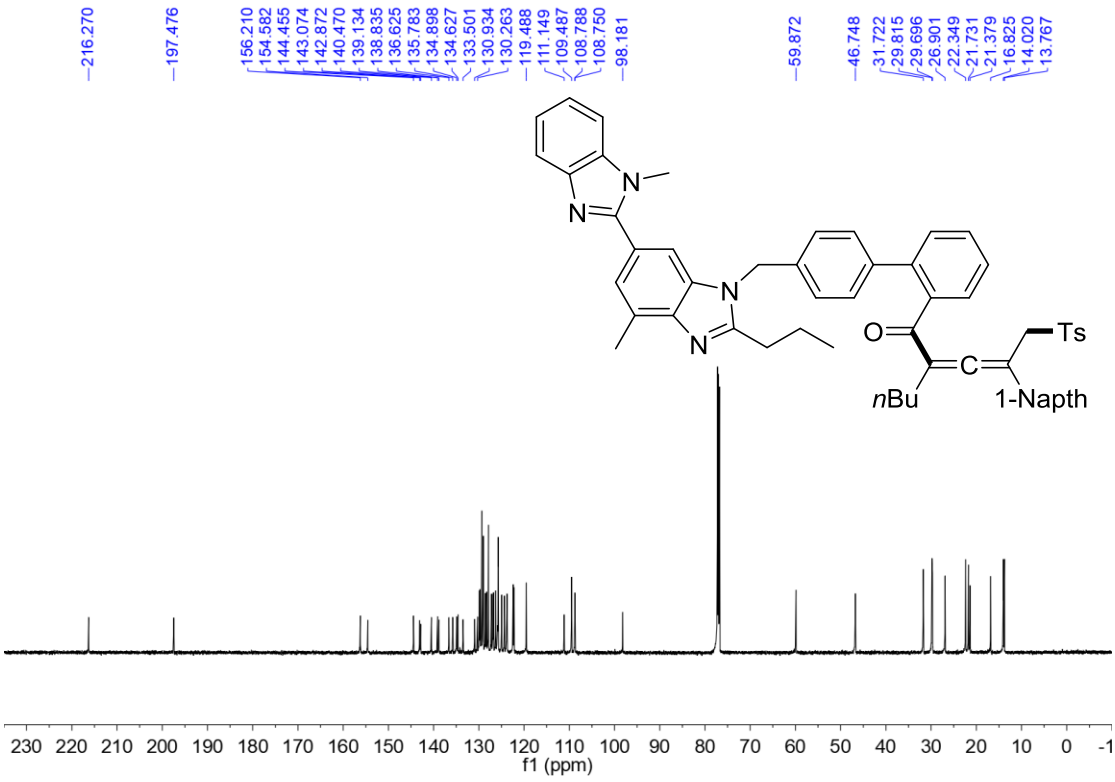
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **57**.



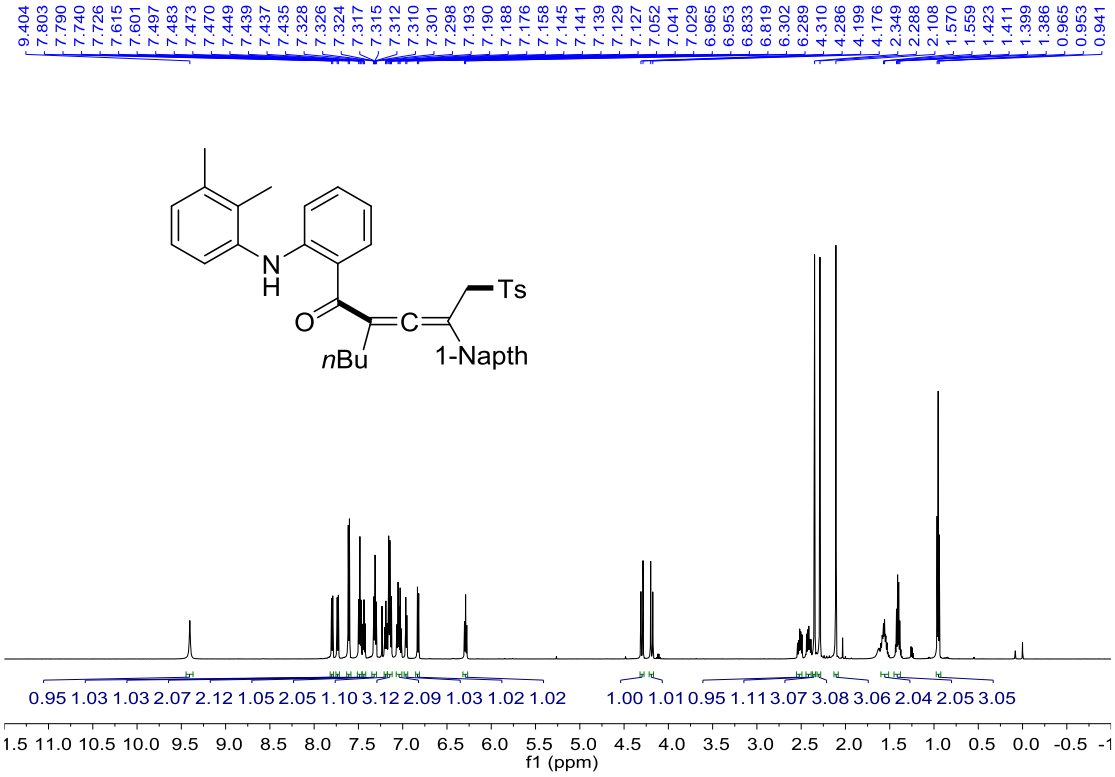
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **58**.



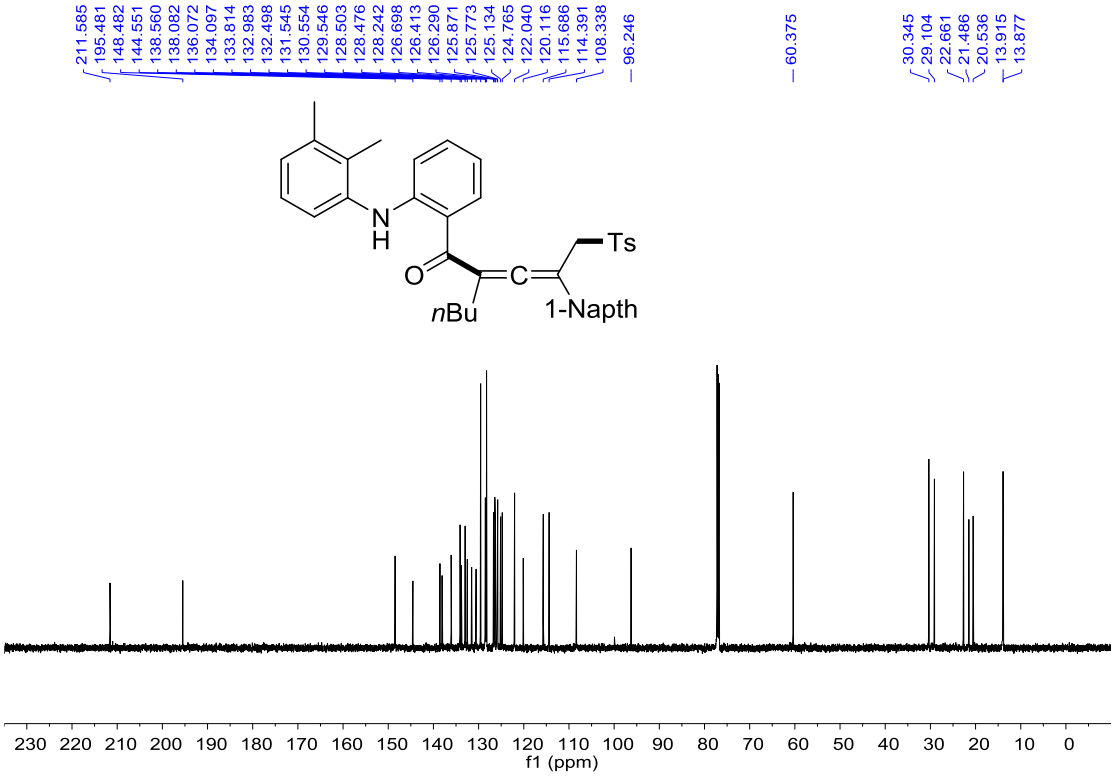
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **58**.



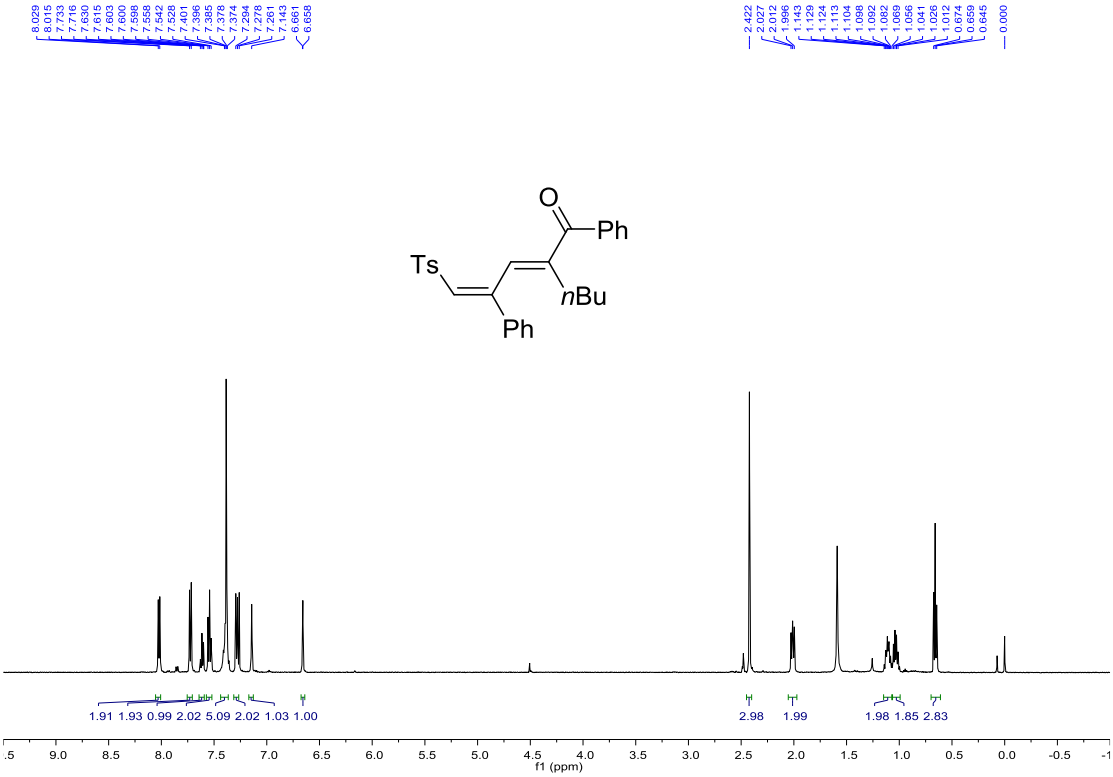
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **59**.



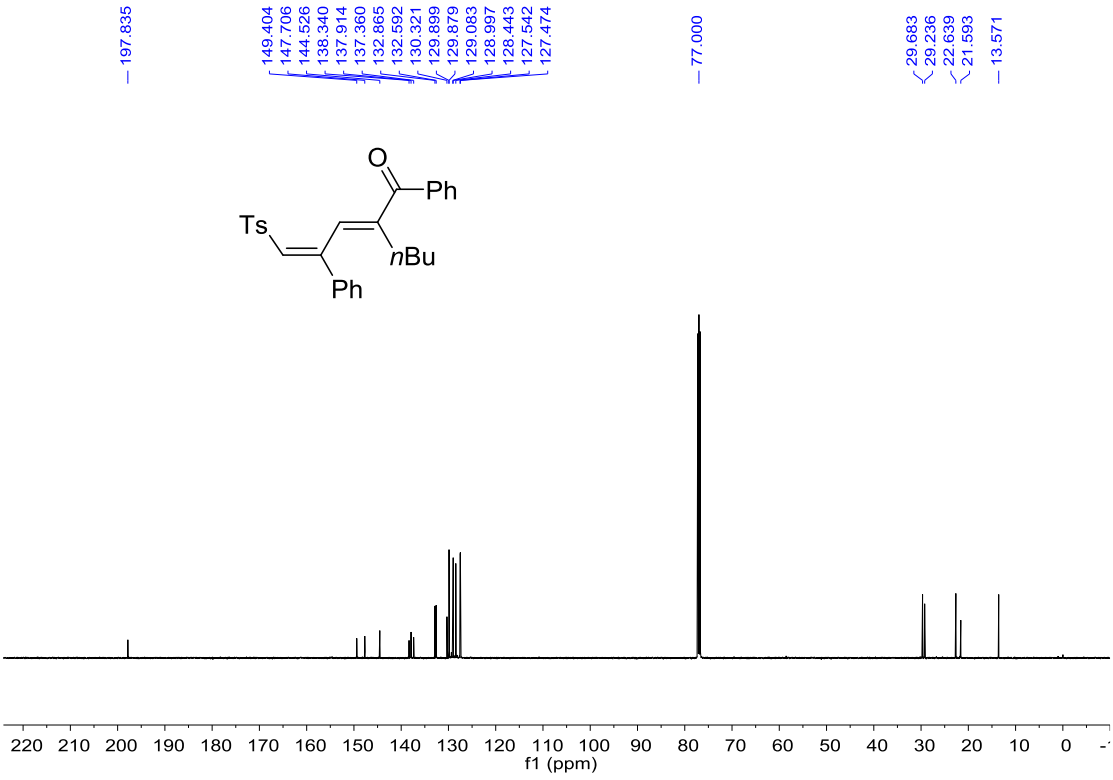
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **59**.



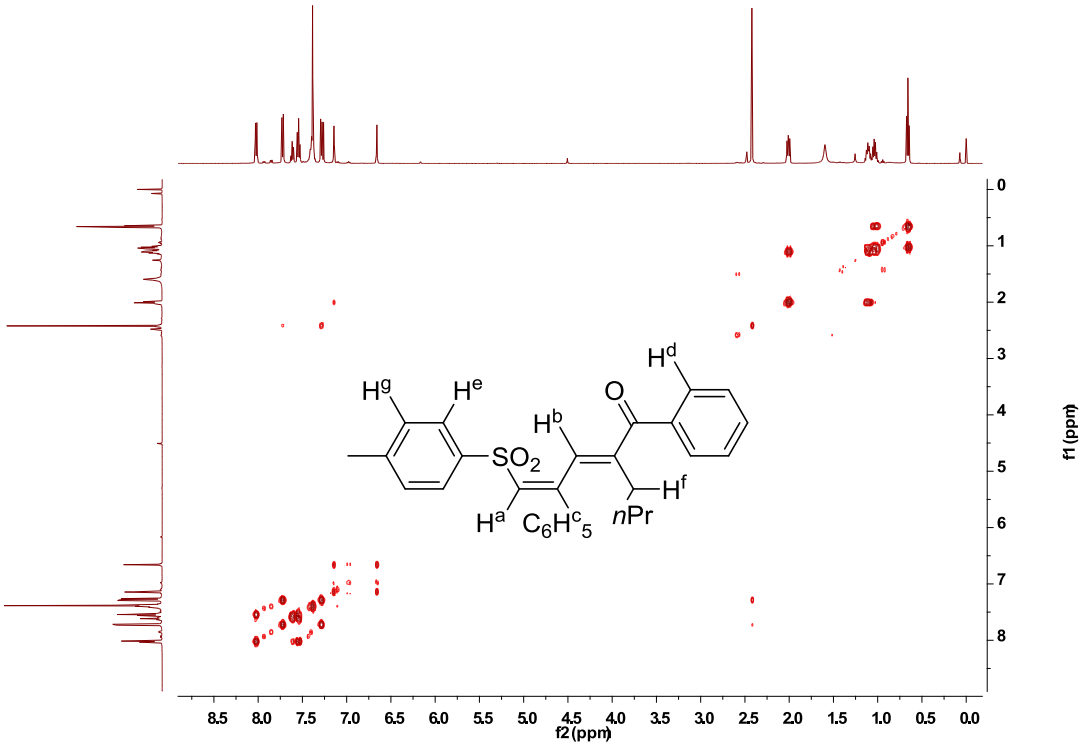
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **60**.



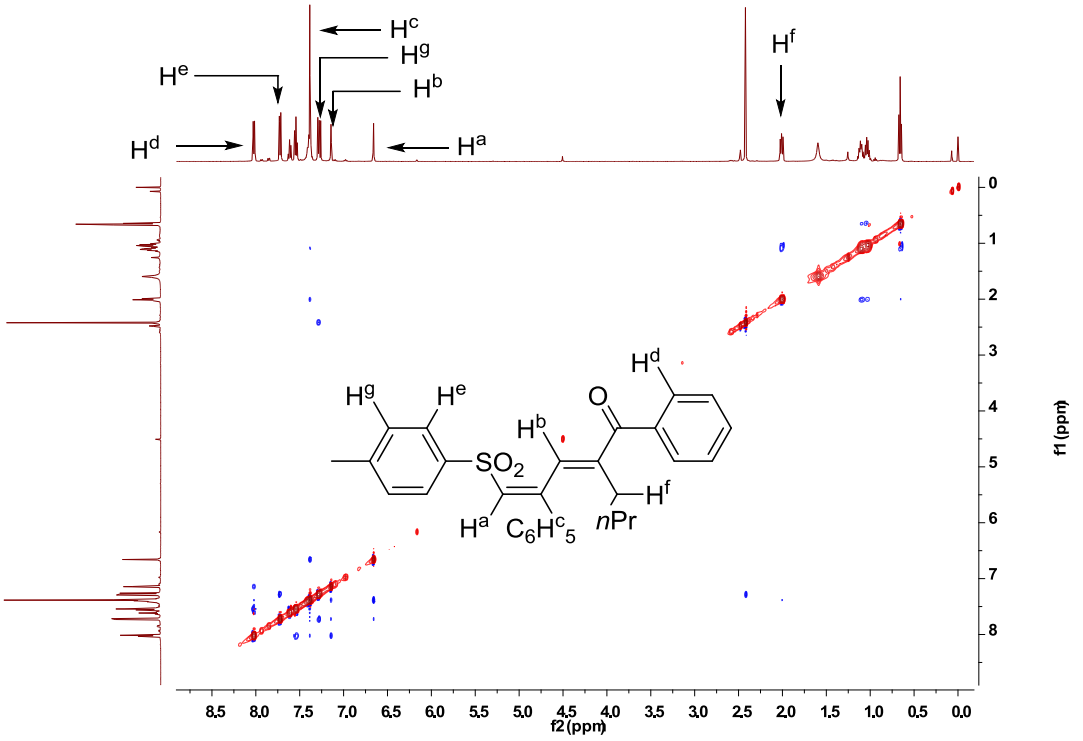
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **60**



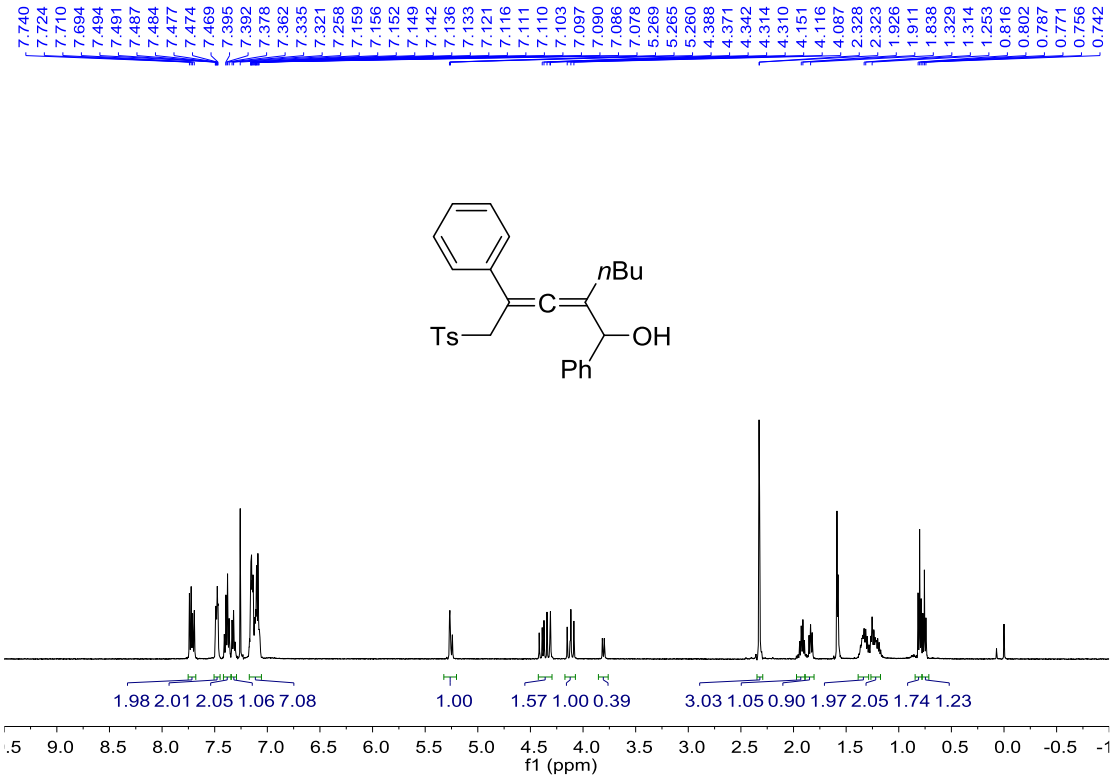
^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$) spectrum of **60**



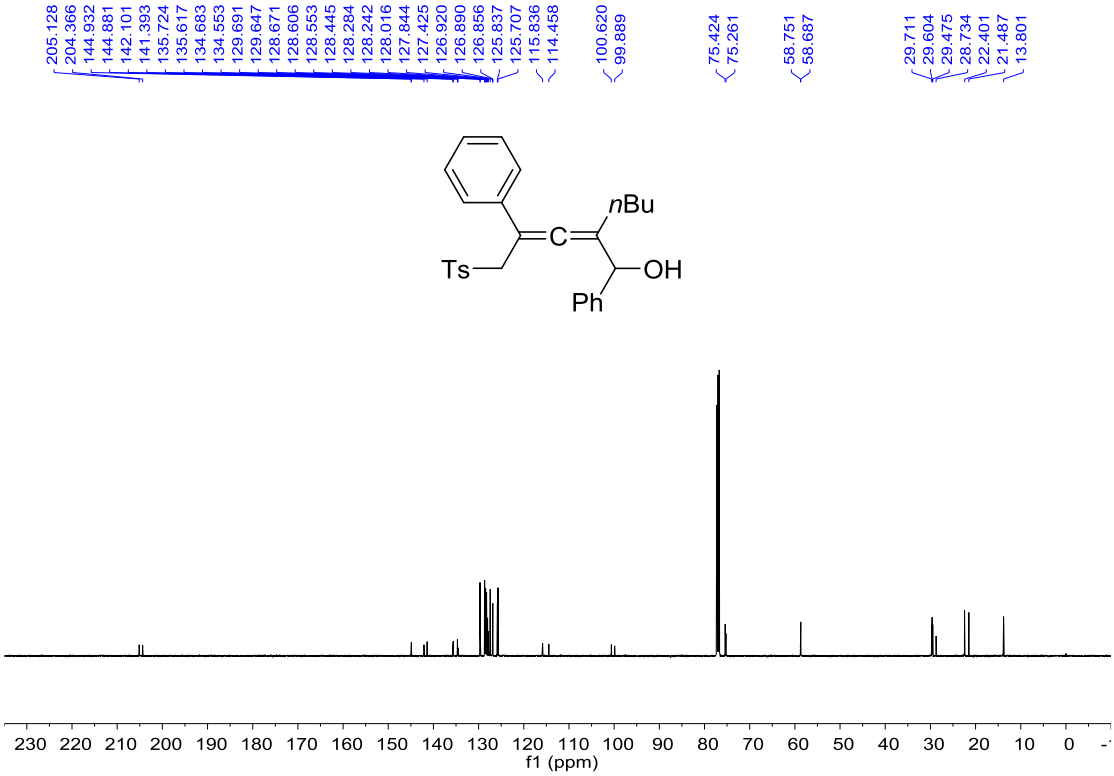
^{1}H-^{1}H NOESY (500 MHz, $CDCl_3$) spectrum of **60**



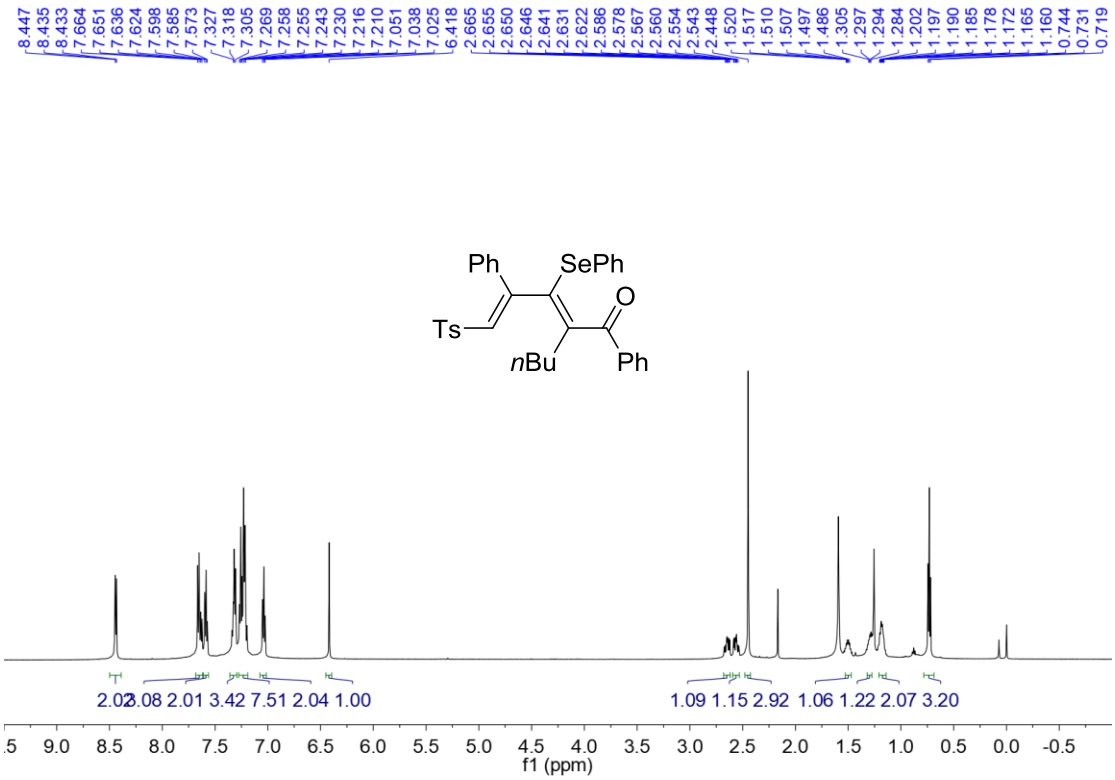
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **61**.



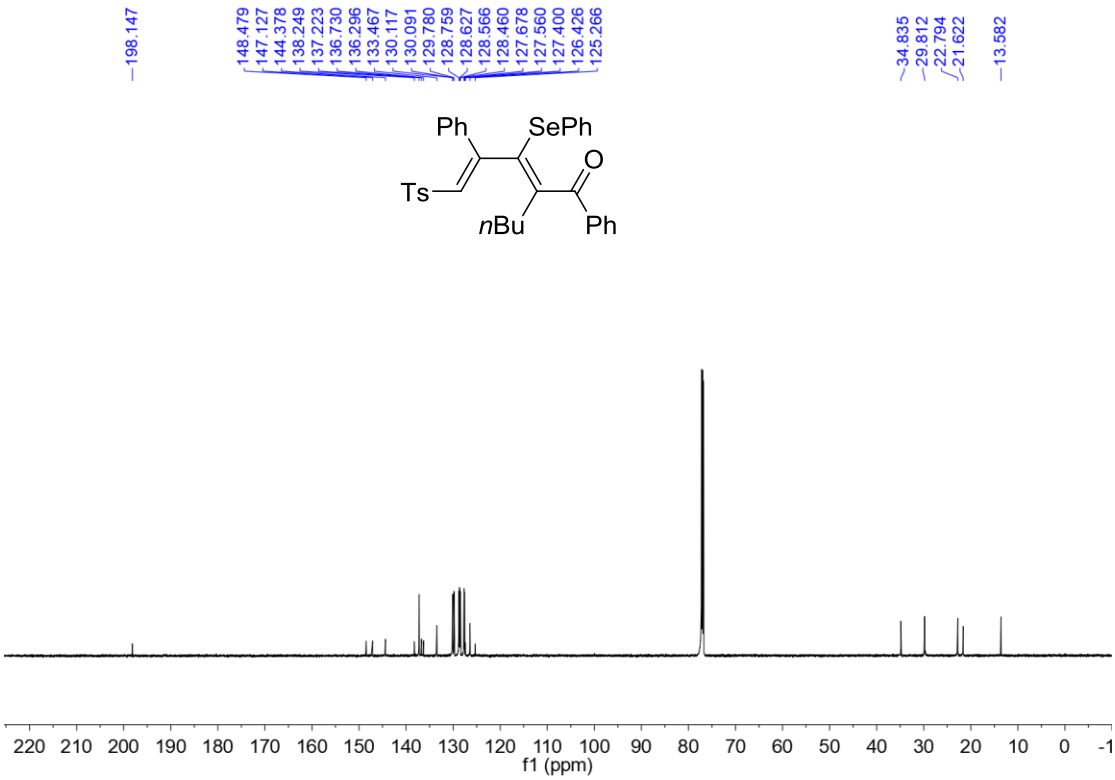
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **61**.



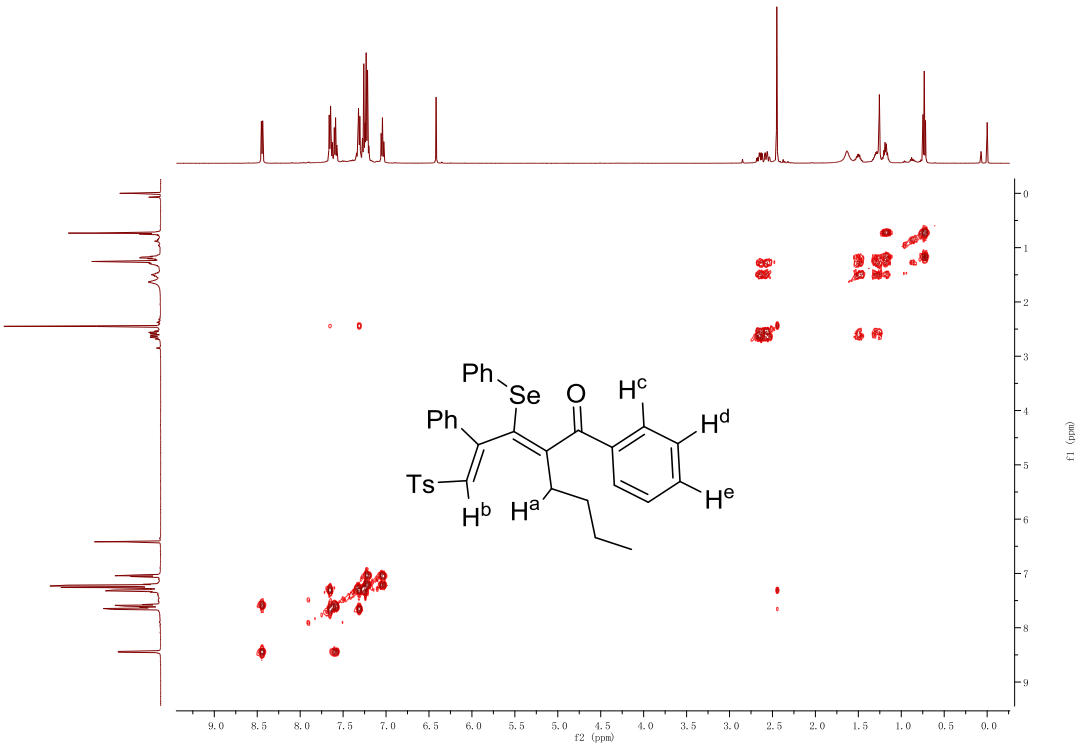
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **62**.



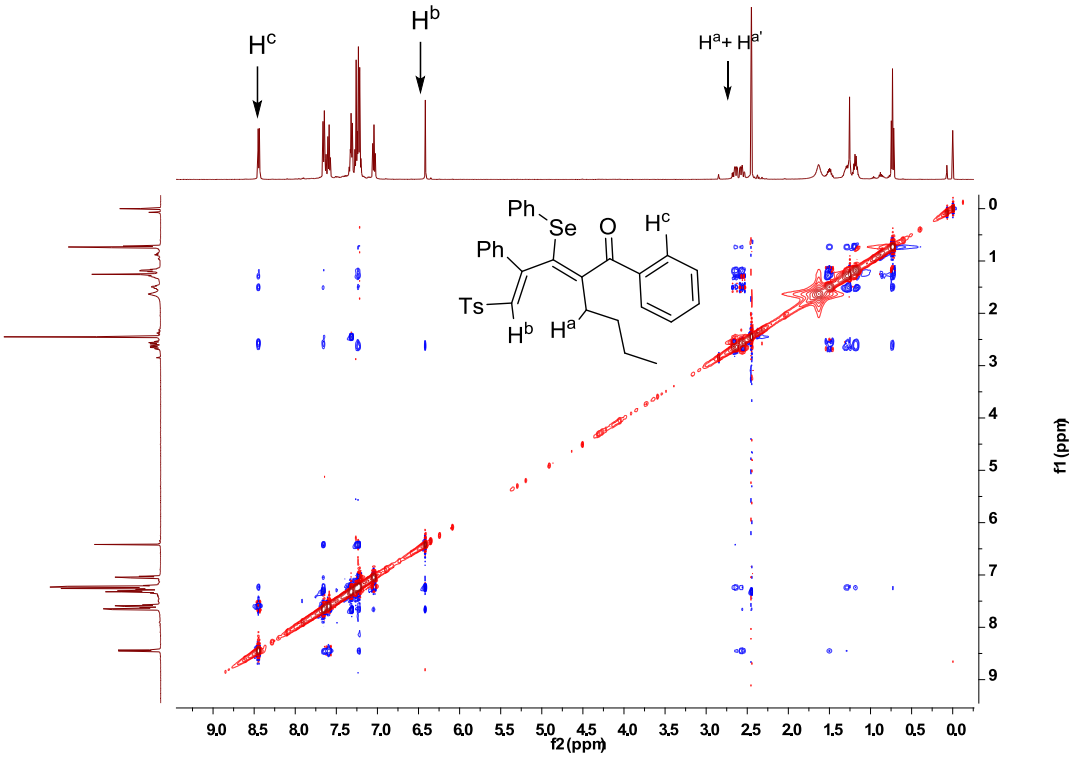
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **62**.



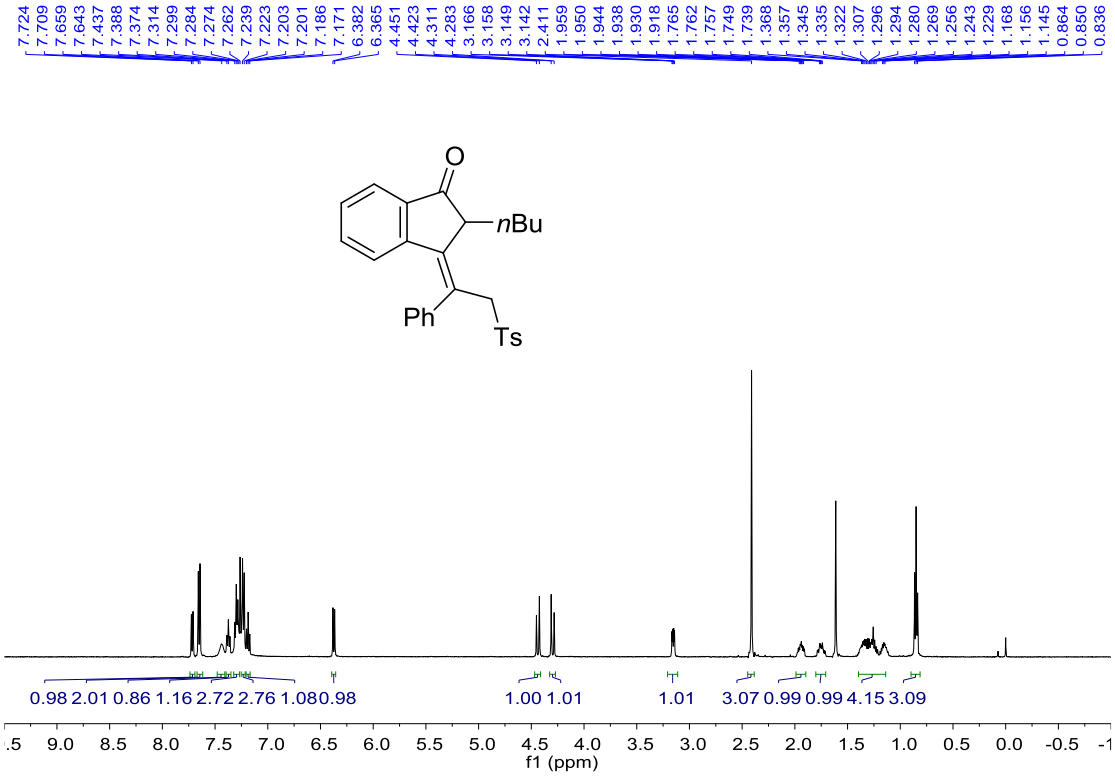
^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$) spectrum of **62**



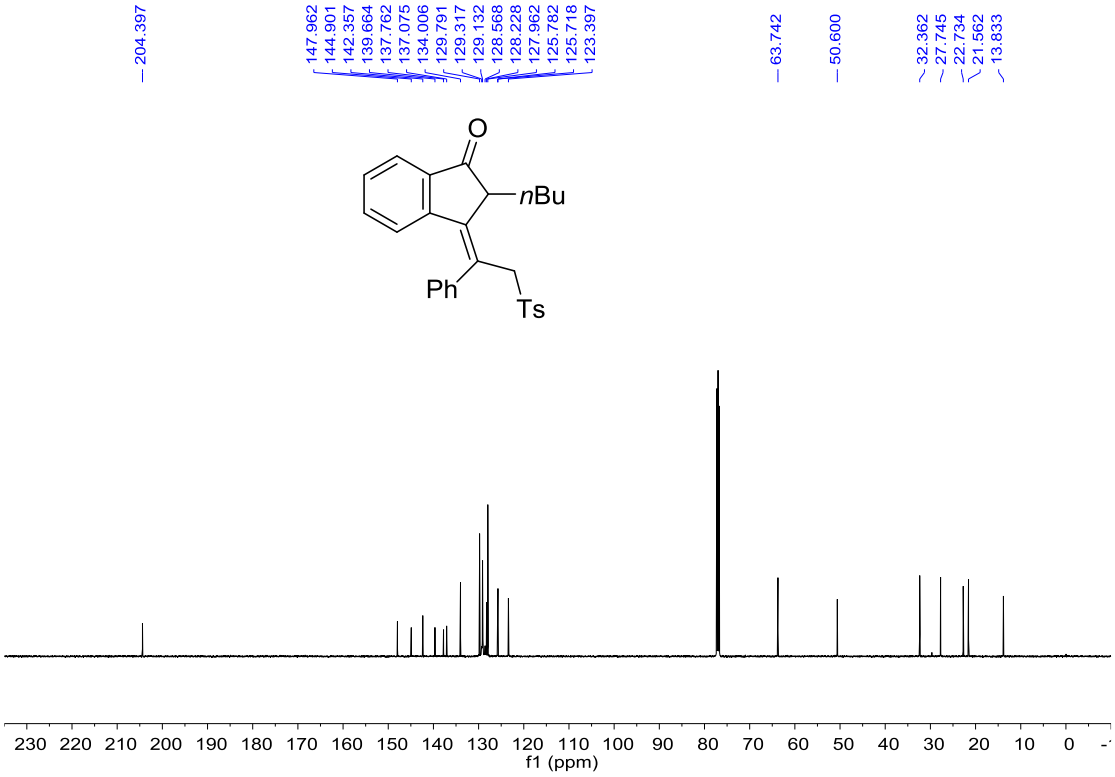
^{1}H-^{1}H NOESY NMR (500 MHz, $CDCl_3$) spectrum of **62**



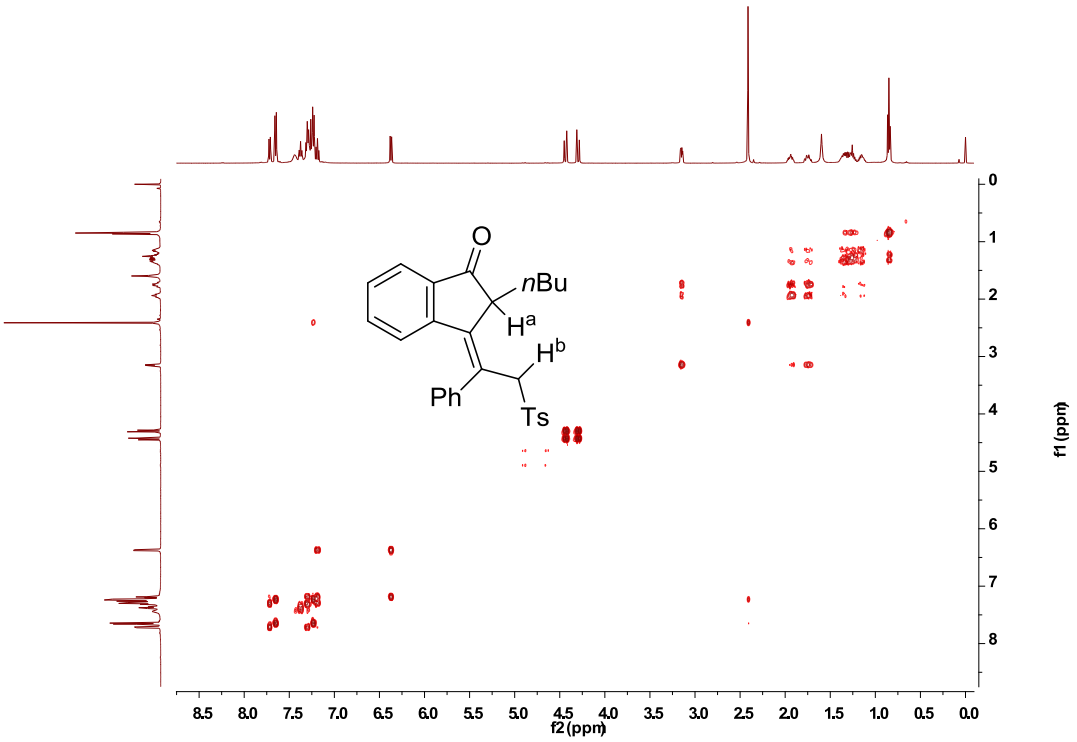
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **63**.



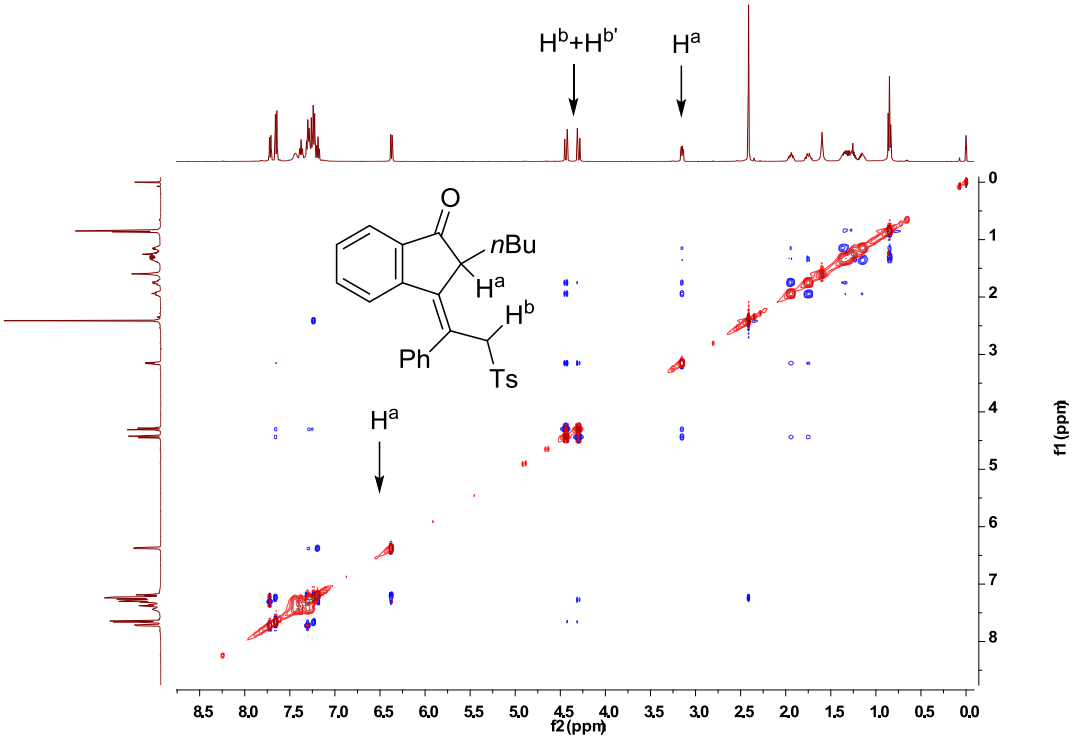
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for **63**.



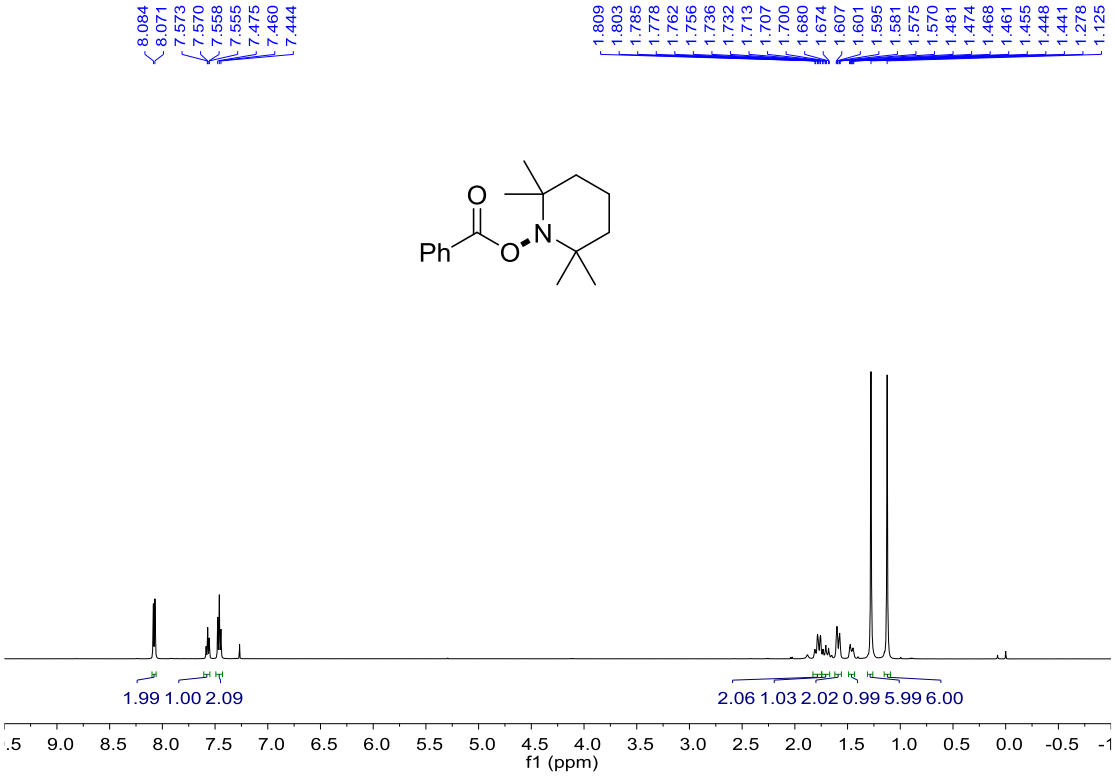
^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$) spectrum of **63**



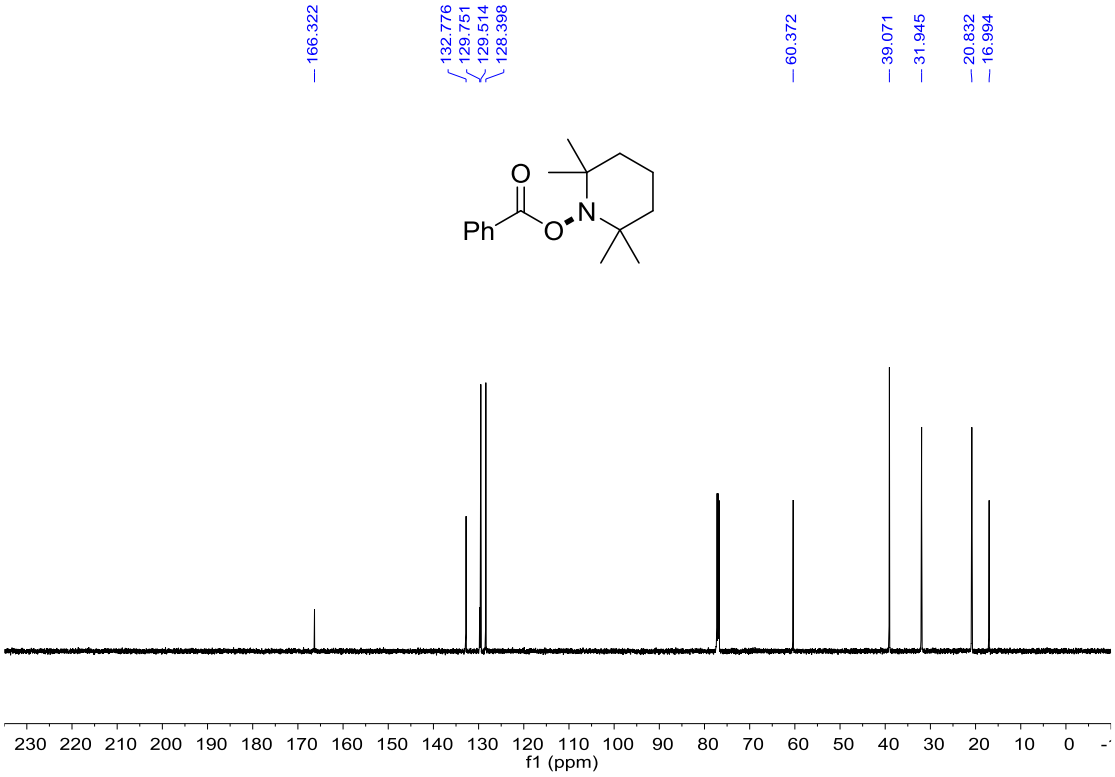
^{1}H-^{1}H NOESY NMR (500 MHz, $CDCl_3$) spectrum of **63**



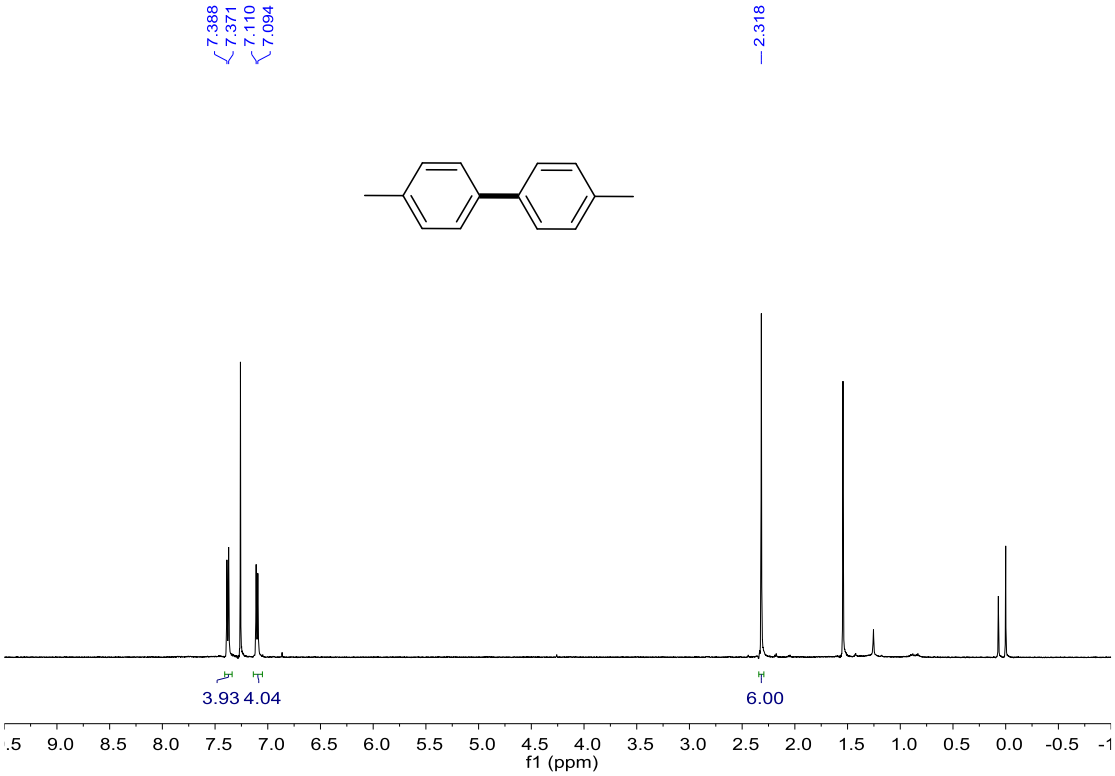
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **64**.



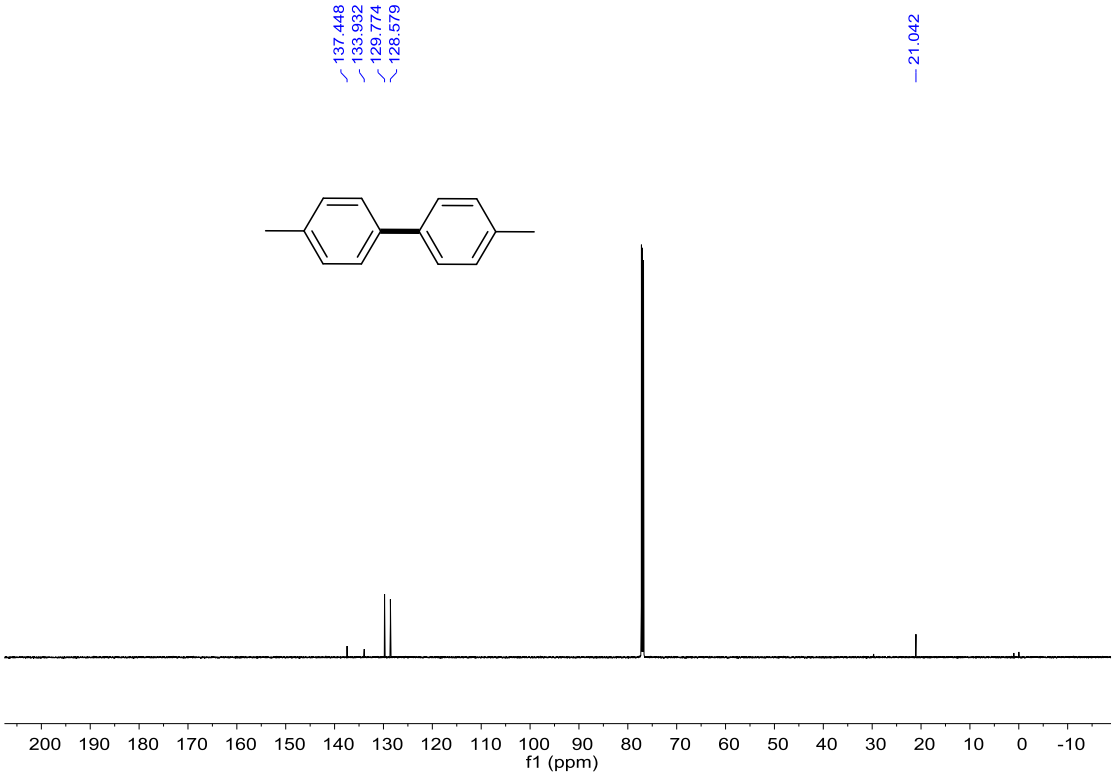
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **64**.



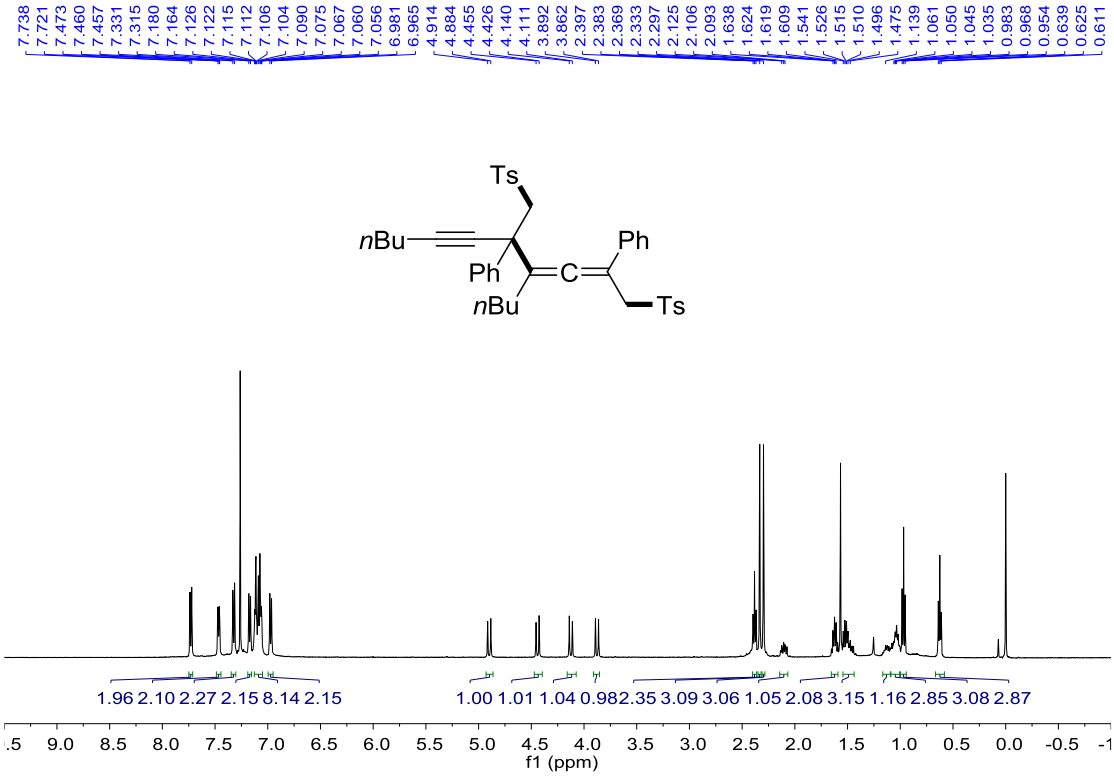
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **66**.



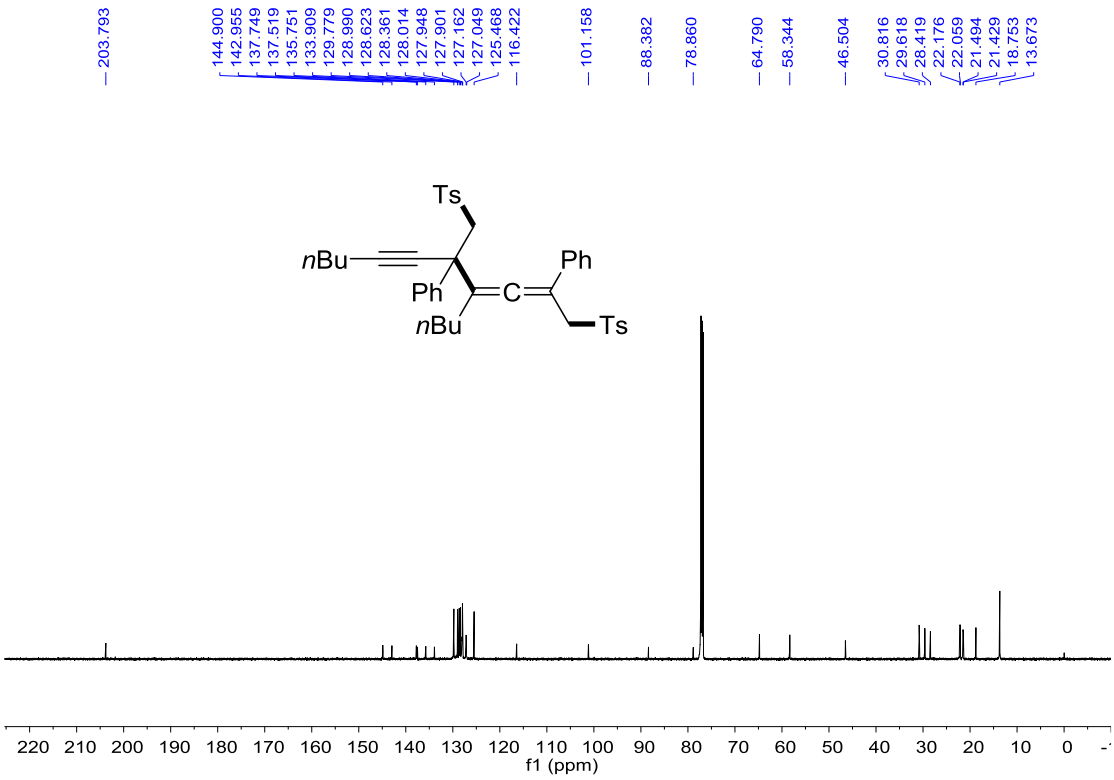
^{13}C NMR (151 MHz, $CDCl_3$) spectrum for **66**.



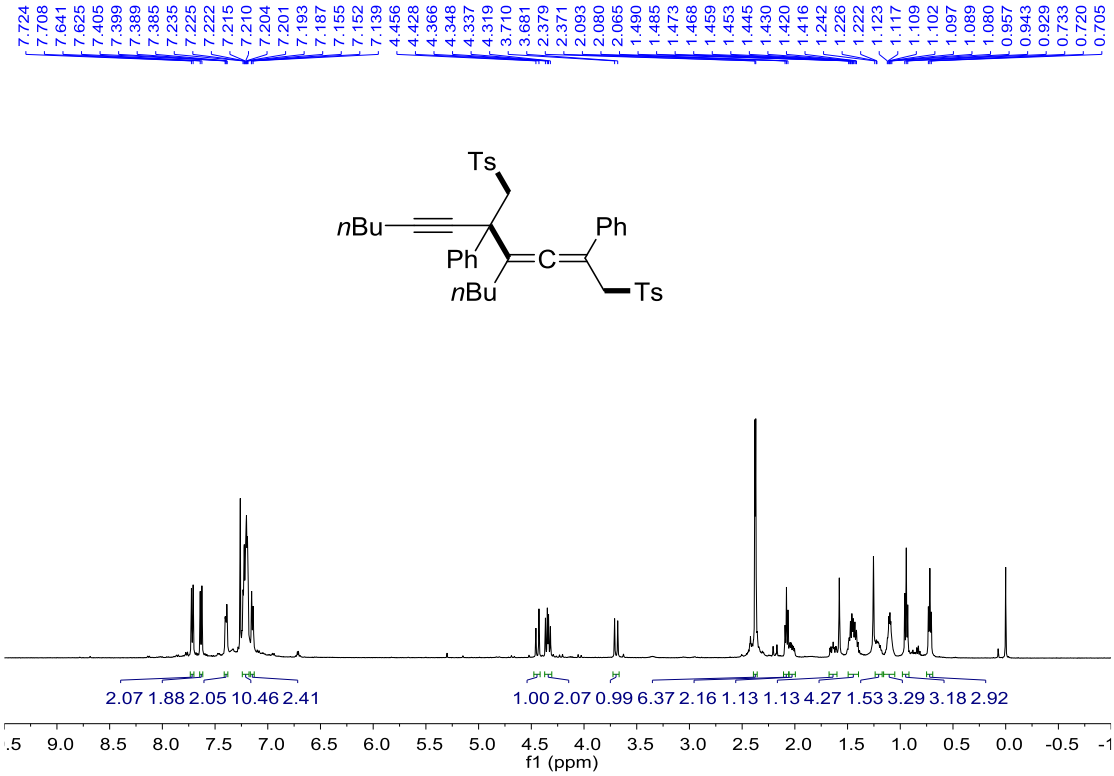
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **5**.



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



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



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