Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Cyclization reactions of 1,6-dienes and 1,6-enynes by dual cobalt photocatalysis

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Supplementary Information

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1. General information

The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AVANCE III-400 MHz, a Bruker AVANCE III HD 400 MHz, or an INOVA600 MHz spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent. In $CDCl_3$, the chemical shifts in ^{1}H NMR spectra were determined with $Si(CH_3)_4$ as the internal standard (δ = 0.00 ppm); the chemical shifts in ^{13}C NMR spectra were determined based on the chemical shift of $CDCl_3$ (δ = 77.00 ppm). In DMSO-d_6, the chemical shifts in ^{1}H NMR spectra and ^{13}C NMR spectra were determined based on the chemical shift of DMSO-d_6 (δ = 2.50 ppm for ^{1}H NMR spectra and δ = 39.60 ppm for ^{13}C NMR spectra, respectively). The ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) or broad (br). The high resolution mass spectra (HRMS) were measured on a Thermo Scientific ORBITRAP ELITE by ESI. Melting points (m.p.) were measured on an XT-4 melting point apparatus and are uncorrected. Luminescence quenching experiments were conducted on a RF-5301PC spectrofluorophotometer. Cyclic voltammetry data were measured at a CORRTEST potentiostat. Thin layer chromatography (TLC) analyses were performed using Merck silica gel 60 F254 plates and visualized under UV light. Flash column chromatography (FCC) was conducted on silica gel (200–300 mesh). Anhydrous acetonitrile was purchased from Energy Chemical and used without further treatment. Deuterium oxide was purchased from J&K Scientific and acetonitrile-d_3 was purchased from Energy Chemical. Unless otherwise noted, all other materials were obtained from commercial suppliers, and were used without further purification.

A Kessil PR 160 L blue LED lamps (427 nm, 40 W) was used as the light source, the reaction vessel is a 15 mL common glass tube (inner diameter: 1.5 cm), which was put into the reactor at the distance of about 5.0 cm from the light source. The reactor was used to keep the reaction temperature constant.

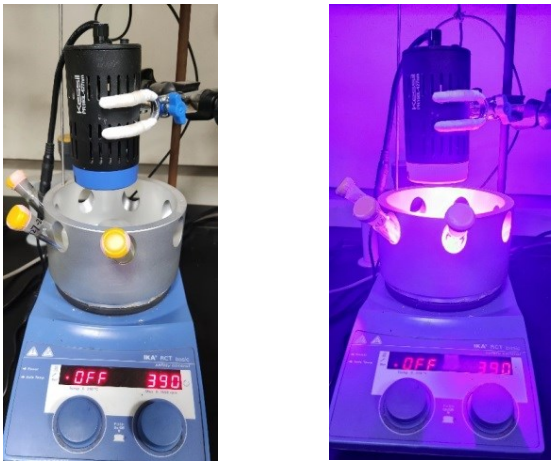
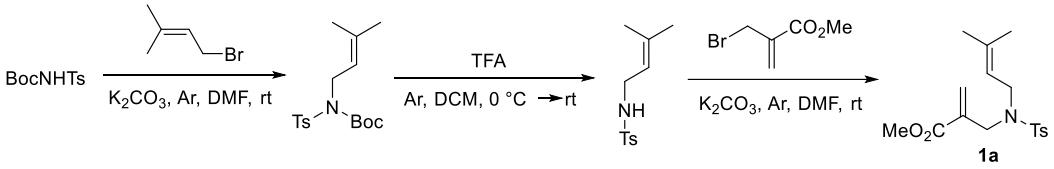


Figure S1 The photoreaction setup.

2. Preparation of the substrates

2.1 Synthesis of 1a[1]



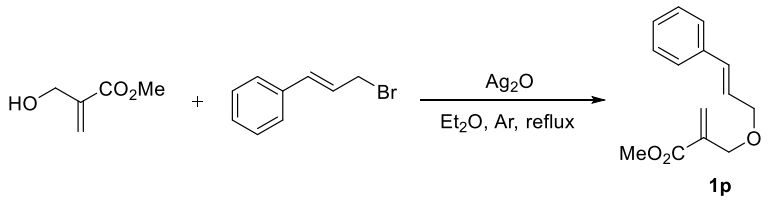
Step 1: To a stirred solution of *tert*-butyl tosylcarbamate (1.5 g, 5.5 mmol) and prenyl bromide (989 mg, 1.2 equiv) in DMF (15 mL) was added K_2CO_3 (1.53 g, 2.0 equiv) and the mixture was stirred at room temperature for 12 h. After the reaction was complete as monitored by TLC analysis, 10 mL of water was added into the reaction mixture, and the product was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was treated with flash chromatography on silica gel (petroleum ether (PE)/ethyl acetate (EA) = 10/1, v/v) to give dimethyl 2-(3-methylbut-2-enyl)malonate (1.54 g, 82%) as a colorless oil.

Step 2: To a stirred solution of *tert*-butyl(3-methylbut-2-en-1-yl)(tosyl)carbamate (1.86 g, 5.5 mmol) in dichloromethane (DCM) (25 mL) was added trifluoroacetic acid (1.63 mL) at 0 °C. The reaction mixture was allowed to warm up to room temperature overnight. After the reaction was complete as monitored by TLC analysis, the reaction mixture was cooled down to 0 °C and quenched by slowly adding saturated $NaHCO_3$ aqueous solution. The product was extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine (20 mL)**,** dried over anhydrous Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The residual was treated with flash chromatography on silica gel (PE/EA = 5/1, v/v) to give 4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide (0.59 g, 45%) as a colorless oil.

Step 3: To a stirred solution of 4-methyl-*N*-(3-methylbut-2-en-1-yl) benzenesulfonamide (700 mg, 2.9 mmol) and methyl 2-(bromomethyl)acrylate (628 mg, 1.2 equiv) in DMF (15 mL) was added K_2CO_3 (807 mg, 2.0 equiv) and the mixture was stirred at room temperature for 12 h. After the reaction was complete as monitored by TLC analysis, 10 mL of water was added into the reaction mixture, and the product was extracted with EA (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was treated with flash chromatography on silica gel (PE/ EA = 10/1, v/v) to give **1a** (798 mg, 81%) as a colorless oil.

1a–**1o**, **1aa**, **3b**, **3o** and **3p** were prepared following the same procedure.

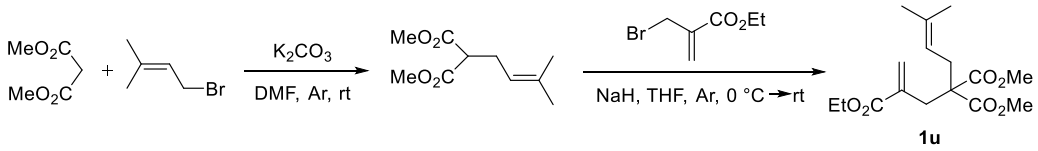
2.2 Synthesis of 1p[2]



To a stirred solution of methyl 2-(hydroxymethyl)acrylate (1.50 g, 1.2 equiv) and (*Z*)-(3-bromoprop-1-en-1-yl)benzene (2.12 g, 1.0 equiv) in Et_2O (15 mL) was added Ag_2O (5.00 g, 2.0 equiv) at room temperature. The mixture was stirred under reflux overnight. After the reaction was complete as monitored by TLC analysis, the insoluble substance was filtered off through a pad of celite, and the filtrate was concentrated under reduced pressure on a rotary evaporator. The residual was treated with flash chromatography on silica gel (PE/EA = 20/1, v/v) to give **1p** (1.06 g, 35%) as a colorless oil.

1p, **1q** and **1r** were prepared following the same procedure.

Synthesis of 1u[2]

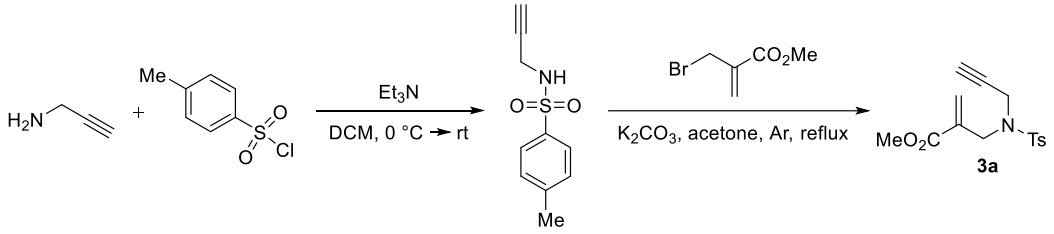


Step 1: To a stirred solution of dimethyl malonate (2.64 g, 20.0 mmol) and prenyl bromide (3.28 g, 1.1 equiv) in DMF (25 mL) was added K_2CO_3 (3.00 g, 1.1 equiv) at room temperature. The mixture was stirred for 12 h. After the reaction was complete as monitored by TLC analysis, 10 mL of water was added into the reaction mixture, and the product was extracted with EA (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was treated with flash chromatography on silica gel (PE/EA = 10/1, v/v) to give dimethyl 2-(3-methylbut-2-enyl)malonate (3.08 g, 77%) as a colorless oil.

Step 2: To a suspension of NaH (60 % dispersion in mineral oil, 554 mg, 1.5 equiv) in dry THF (25 mL) was added slowly dimethyl 2-(3-methylbut-2-enyl)malonate (3.08 g, 15.4 mmol) at 0 °C. After the mixture was stirred for 1 h, ethyl 2-(bromomethyl)-acrylate (3.56 g, 1.2 equiv) was added into it. The reaction mixture was stirred overnight at room temperature. After the reaction was complete as monitored by TLC analysis, 10 mL of water was added into the reaction mixture, and the product was extracted with EA (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The residual was treated with flash chromatography on silica gel (PE/EA = 20/1, v/v) to give **1u** (3.91 g, 81%) as a colorless oil.

1s–**1z** and **3t**–**3v** were prepared following the same procedure.

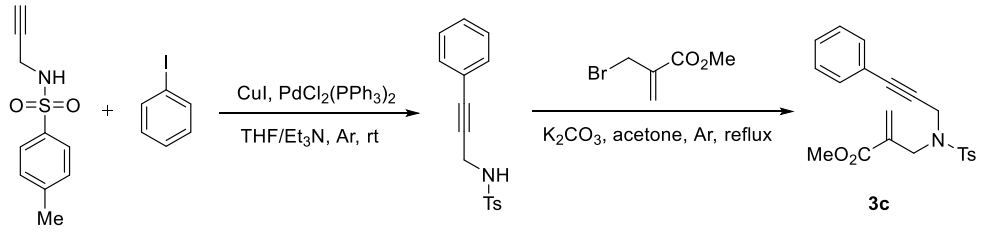
2.4 Synthesis of 3a[3]



Step 1: To a stirred solution of prop-2-yn-1-amine (500 mg, 9.1 mmol), Et_3N (3.8 mL, 3.0 equiv) in DCM (20 mL) was slowly added 4-methoxybenzenesulfonyl chloride (2.10 g, 1.2 equiv) at 0 °C. The reaction mixture was further stirred at room temperature overnight. After the reaction was complete as monitored by TLC analysis, 10 mL of water was added into the reaction mixture, and the product was extracted with EA (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The residual was treated with flash chromatography on silica gel (PE/EA = 8/1, v/v) to give 4-methyl-*N*-(prop-2-yn-1-yl)- benzenesulfonamide (1.24 g, 66%) as a white solid.

Step 2: To a stirred solution of the above sulfonamide 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (600 mg, 2.9 mmol) in acetone (15 mL) was added methyl 2-(bromomethyl)acrylate (0.45 mL, 1.3 equiv) and K_2CO_3 (1.20 g, 3.0 equiv). The mixture was stirred under reflux for 10 h. After the reaction was complete as monitored by TLC analysis, 10 mL of water was added into the reaction mixture, and the product was extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The residual was treated with flash chromatography on silica gel (PE/EA) = 5/1, v/v) to give **3a** (871 mg, 99%) as a white solid.

2.5 Synthesis of 3c[4]



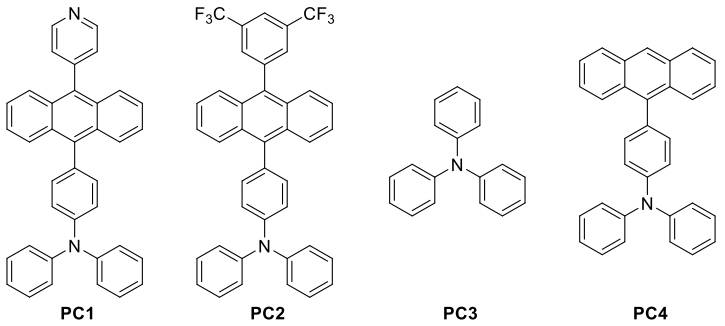
Step 1: To a stirred solution of 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (837 mg, 4.0 mmol) and iodobenzene (979 mg, 1.2 equiv) in THF-Et_3N (15 mL, THF/Et_3N = 1:1, v/v) was added $PdCl_2(PPh_3)_2$ (56 mg, 0.02 equiv) and CuI (30 mg, 0.04 equiv). The reaction mixture was stirred at room temperature overnight under an argon atmosphere. After the reaction was complete as monitored by TLC analysis, 10 mL of water was added into the reaction mixture, and the product was extracted with DCM

(3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The residual was treated with flash chromatography on silica gel (PE/EA = 5/1, v/v) to give 4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (684 mg, 60%) as a white solid.

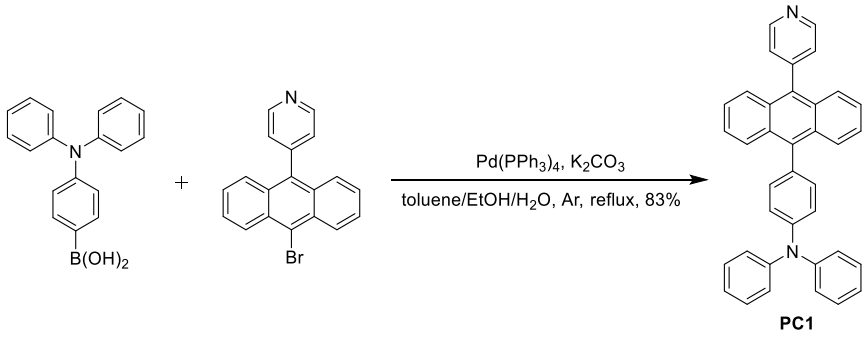
3c was prepared from 4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide in the same way as that for step 2 in the synthesis of **3a** (800 mg, 87%).

3c–**3n, 3q**–**3s** and **3w** were prepared following the same procedure.

3. Synthesis and characterization of the photocatalysts

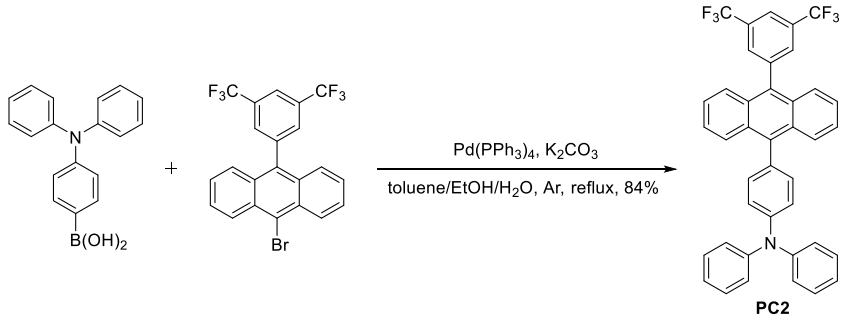


3.1 Synthesis of the photocatalysts

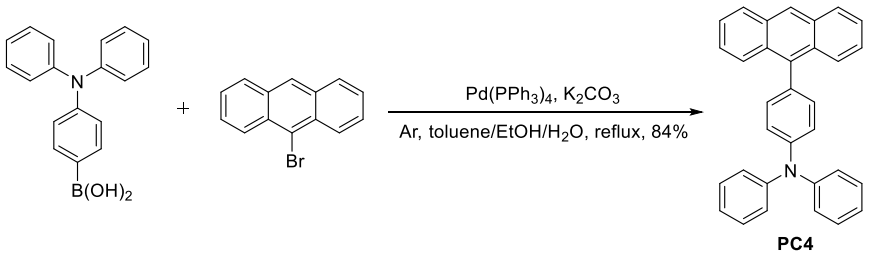


To a stirred solution of (4-(diphenylamino)phenyl)boronic acid (1.25 g, 1.2 equiv), 4-(10-bromoanthracen-9-yl)pyridine (1.20 g, 3.6 mmol) and $Pd(PPh_3)_4$ (208 mg, 0.05 equiv) in toluene/EtOH/H_2O (20 mL/10 mL/5 mL) was added K_2CO_3 (1.99 g, 4.0 equiv). The mixture was stirred under reflux for 10 h. After the reaction was complete as monitored by TLC analysis, the reaction mixture was cooled to room temperature and diluted with H_2O (20 mL). The product was extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The crude product was purified by flash chromatography on silica gel (PE/EA = 3/1, v/v) to give **PC1**[5] as a yellow solid (1.50 g, 83%). mp 288–289 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.88–8.86 (m, 2H), 7.89–7.86 (m, 2H), 7.60–7.58 (m, 2H), 7.47–7.45 (m, 2H), 7.43–7.38 (m, 4H), 7.36–7.33 (m, 4H), 7.32–7.25 (m, 8H), 7.11–7.08 (m, 2H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 149.9, 148.0, 147.7, 147.3, 138.2, 133.4, 132.0, 131.9, 129.9, 129.4, 129.1, 127.3, 126.6, 126.0, 125.7, 125.1, 124.7, 123.2, 122.9. HRMS (ESI): m/z calcd for $C_{37}H_{27}N_2$ $[M+H]^+$ 499.2169, found 499.2171.



PC2 was prepared following the same procedure of **PC1**. **PC2** was obtained as a yellow solid (1.50 g, 84%). mp 235–236 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.98–7.97 (m, 2H), 7.91–7.89 (m, 2H), 7.50–7.48 (m, 2H), 7.42–7.39 (m, 4H), 7.34–7.26 (m, 12H), 7.08–7.06 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 147.4, 141.7, 138.7, 132.5 (d, $J_{C\text{-}F}$ = 54.7 Hz), 132.0, 131.9, 131.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.9 (d, $J_{C\text{-}F}$ = 26.6 Hz), 129.4, 127.5, 126.1, 125.7, 125.2, 124.8, 123.2, 122.9, 122.1, 123.4 (q, $J_{C\text{-}F}$ = 271.2 Hz), 121.7 (q, $J_{C\text{-}F}$ = 11.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. HRMS (ESI): m/z calcd for $C_{40}H_{26}F_6N$ $[M+H]^+$ 634.1964, found 634.1961.



PC4 was prepared according to method in the literature.[6] **PC4** was obtained as a yellow solid (493 mg, 84%). mp 209–211 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.05 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H), 7.50–7.46 (m, 2H), 7.43–7.39 (m, 2H), 7.37–7.32 (m, 4H), 7.31–7.26 (m, 8H), 7.11–7.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 147.1, 136.9, 132.4, 132.0, 131.4, 130.4, 129.4, 128.3, 126.9, 126.4, 125.3, 125.1, 124.6, 123.1, 123.0. HRMS (ESI): m/z calcd for $C_{32}H_{24}N$ $[M+H]^+$ 422.1903, found 422.1907.

3.2 Characterization of photocatalysts

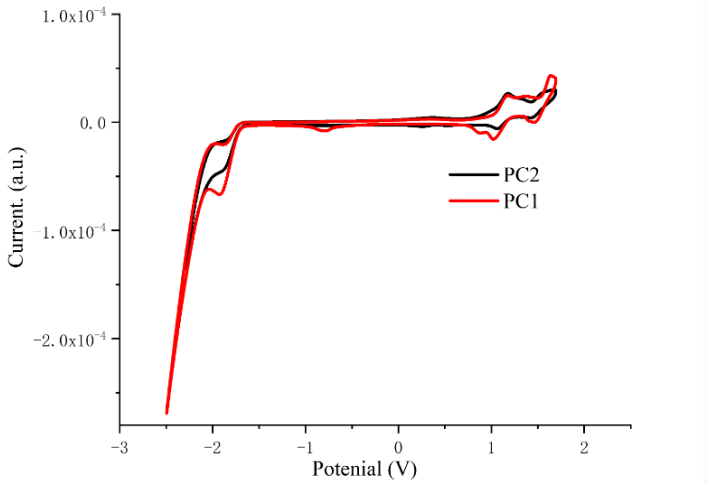


Figure S2 Cyclic voltammograms measurements were performed with the three-electrode CORRTEST electrochemical workstation by using a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel as reference electrode. The voltammograms were taken in a degassed DCM solution ([*n*-Bu_4NBF_4]) = 0.1 M, **PC** = 1 mM. The scan rate was 0.1 V/s.

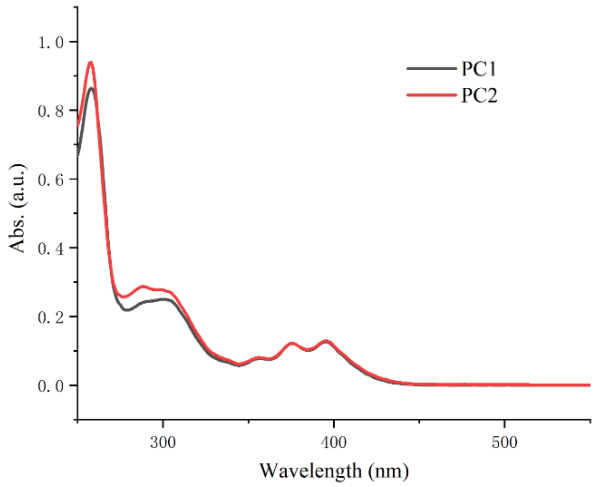


Figure S3 UV-vis spectrum of **PC1** and **PC2** in DCM solution (1×10^{-5} M).

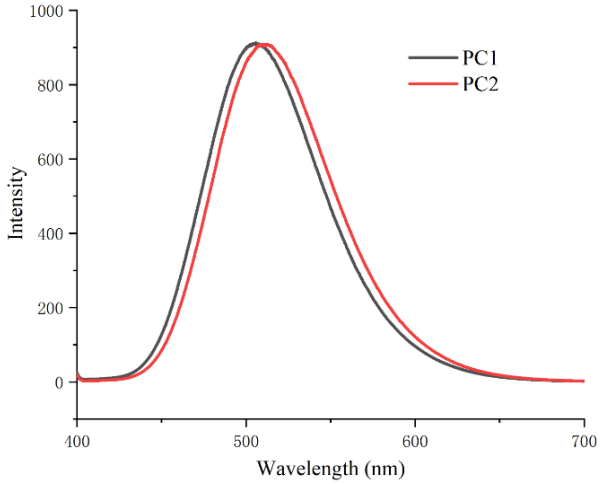


Figure S4 Emission spectra of **PC1** and **PC2** in DCM solution (1×10^{-5} M).

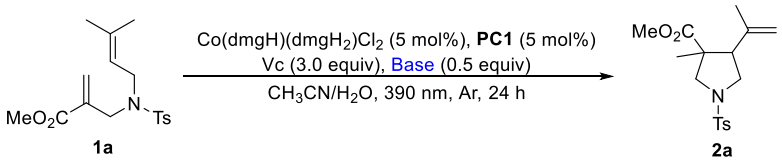
The ground state reduction and oxidation potential of **PC** are determined according to the reported method.[7,8] $E_{1/2}$(**PC1**/**PC1**$^{\bullet-}$) = -1.95 V vs. SCE; $E_{1/2}$(**PC1**$^{\bullet+}$/**PC1**) = +1.10 V vs. SCE. $E_{1/2}$(**PC2**/**PC2**$^{\bullet-}$) = -1.93 V vs. SCE; $E_{1/2}$(**PC2**$^{\bullet+}$/**PC2**) = +1.12 V vs. SCE. Excited state oxidation and reduction potentials were calculated by the following formulas:[7]

$E_{1/2}(PC^*/PC^{\bullet-}) = E_{1/2}(PC/PC^{\bullet-}) + E_{0,0}$

$E_{1/2}(PC^{\bullet+}/PC^*) = E_{1/2}(PC^{\bullet+}/PC) - E_{0,0}$

4. Optimization of the reaction conditions

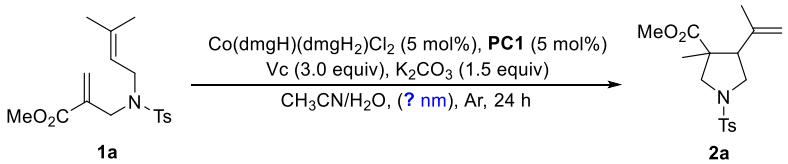
Table S1 Effect of base



Entry	Base	Yield (%)
1	K_2CO_3	47
2	K_3PO_4	39
3	Cs_2CO_3	40
4	CsF	trace[a]
5	KH_2PO_4	N.R.
6	Na_2CO_3	35
7	K_2CO_3	57[b]

The reaction was conducted on 0.2 mmol scale in CH_3CN (3.0 mL) and H_2O (0.5 mL) with 40 W 390 nm Kessil LED as the light source. System temperature of 30 °C. Isolated yield. N.R. = no reaction. [a]**1a** decomposed. [b]K_2CO_3 (1.5 equiv).

Table S2 Effect of light source

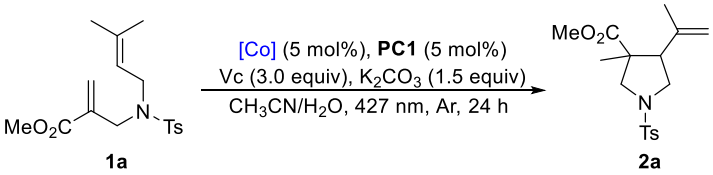


Entry	Light source	Yield (%)
1	390	57[a]
2	390	63[b]
3	455	N.R.[c]
4	427	91[d]
5	427	N.R.[e]
6	427	70[f]

The reaction was conducted on 0.2 mmol scale in CH_3CN (3.0 mL) and H_2O (0.5 mL). System

temperature of 30 °C. Isolated yield. [a]40 W 390 nm Kessil LED as the light source. [b]40 W 390 nm Kessil LED as the light source. System temperature of 50 °C. [c]18 W 455 nm blue LEDs. [d]40 W 427 nm Kessil LED as the light source. System temperature of 50 °C. [e]Vc (2.0 equiv), K_2CO_3 (1.5 equiv). [f]Vc (2.0 equiv), K_2CO_3 (1.0 equiv).

Table S3 The effect of cobalt catalyst



Entry	[Co]	Yield (%)
1	$Co(dmgH)(dmgH_2)Cl_2$	91
2	$Co(acac)_2$	N.R.
3	$CoBr_2$	N.R.
4	Salen **Co-1**	81
5	Salen **Co-2**	38
6	$Co(dmgH)_2{}^t$BuPyBr	N.R.[a]

The reaction was conducted on 0.2 mmol scale in CH_3CN (3.0 mL) and H_2O (0.5 mL) with a 40 W 427 nm Kessil LED as the light source. System temperature of 50 °C. Isolated yield. [a]In the absence of **PC1**.

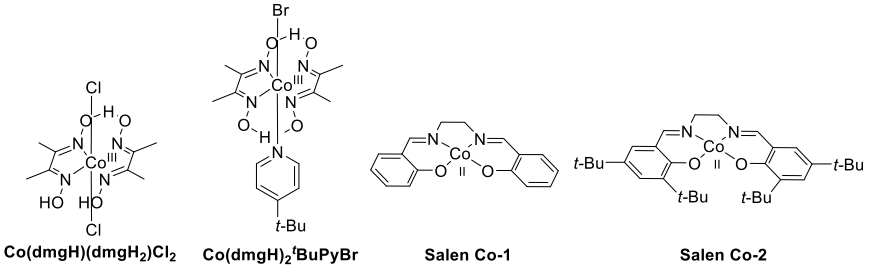
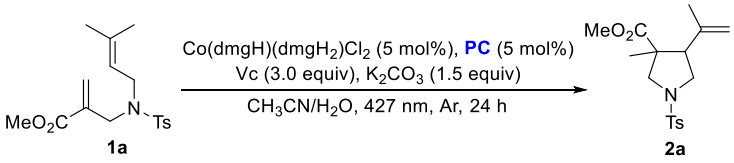


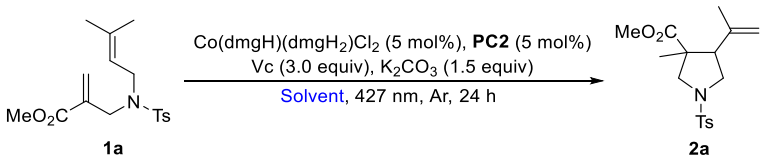
Table S4 Effect of **PC**



Entry	**PC** (5 mol%)	Yield (%)
1	**PC1**	91
2	**PC2**	90
3	**PC3**	N.R.
4	**PC4**	53

The reaction was conducted on 0.2 mmol scale in CH_3CN (3.0 mL) and H_2O (0.5 mL) with a 40 W 427 nm Kessil LED as the light source. System temperature of 50 °C. Isolated yield.

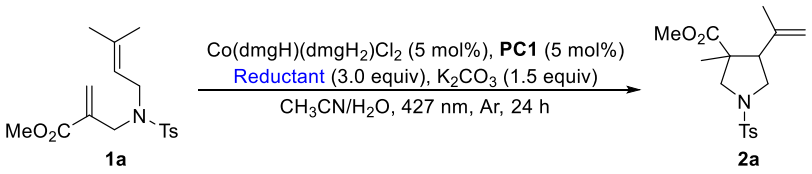
Table S5 Effect of solvent



Entry	Solvent	Yield (%)
1	CH_3CN/H_2O	91
2	DCM/H_2O	trace[a]
3	DCE/H_2O	trace[a]
4	THF/H_2O	68
5	$PhCH_3/H_2O$	N.R.
6	$EtOH/H_2O$	34
7	CH_3CN/H_2O	80[b]
8	CH_3CN	81

The reaction was conducted on 0.2 mmol scale in CH_3CN (3.0 mL) and H_2O (0.5 mL) with a 40 W 427 nm Kessil LED light. System temperature of 50 °C. Isolated yield. [a]**1a** decomposed. [b]CH_3CN = 2.0 mL.

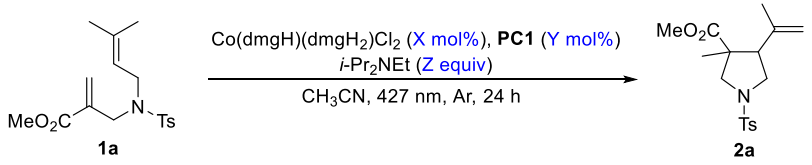
Table S6 The effect of reductant



Entry	Reductant	Yield (%)
1	Vc	91
2	VcNa	N.R.[a]
3	*i*-Pr_2NEt	96[a,b]
4	*i*-Pr_2NEt	80[a,b,c]

The reaction was conducted on 0.2 mmol scale in CH_3CN (3.0 mL) and H_2O (0.5 mL) with a 40 W 427 nm Kessil LED as the light source. System temperature of 50 °C. Isolated yield. [a]In the absence of K_2CO_3, [b]CH_3CN = 3.0 mL. [c]System temperature of 30 °C.

Table S7 The effect of *i*-Pr_2NEt/$Co(dmgH)(dmgH_2)Cl_2$/**PC1** equivalent

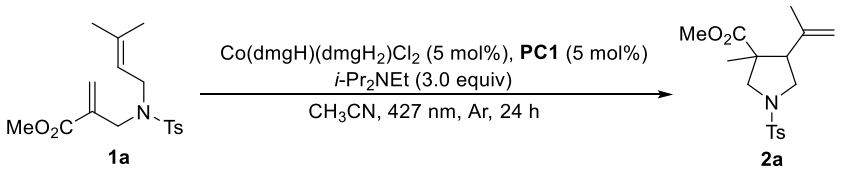


Entry	[Co] (X mol%)	**PC1** (Y mol%)	*i*-Pr_2NEt (Z equiv)	Yield (%)
1	5	5	3	96
2	5	5	0.5	83

3	5	5	1.5	94
4	3	5	3	84
5	5	3	3	86

The reaction was conducted on 0.2 mmol scale in CH_3CN (3.0 mL) and H_2O (0.5 mL) with a 40 W 427 nm Kessil LED as the light source. System temperature of 50 °C. Isolated yield.

Table S8 Control experiments

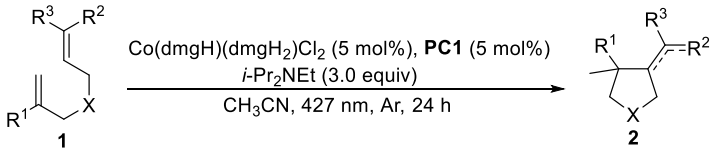


Entry	Variation	Yield (%)
1	without $Co(dmgH)(dmgH_2)Cl_2$	N.R.
2	without *i*-Pr_2NEt	N.R.
3	without **PC1**	N.R.
4	without Ar	N.R.
5	without light	N.R.

The reaction was conducted on 0.2 mmol scale with a 40 W 427 nm Kessil LED as the light source. System temperature of 50 °C. Isolated yield.

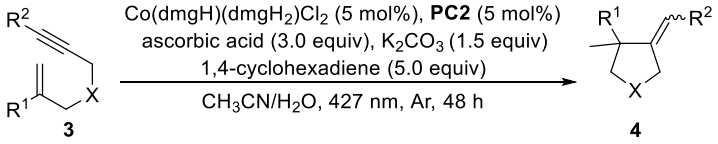
5. Experimental procedures

5.1 General procedure for the preparation of 2 (Protocol A)



1 (0.2 mmol) was added into a 15 mL oven-dried glass tube equipped with a magnetic stirring bar and a rubber stopper, followed by the addition of $Co(dmgH)(dmgH_2)Cl_2$ (0.01 mmol, 5 mol%), **PC1** (0.01 mmol, 5 mol%) and acetonitrile (3.0 mL). The tube was evacuated and backfilled with argon (repeated three times). *i*-Pr_2NEt (0.6 mmol, 3.0 equiv) was added into the reaction mixture, which was irradiated with a 40 W 427 nm Kessil light at 50 °C (system temperature) for 24 h. After the reaction was complete as monitored by TLC, the solvent was removed under reduced pressure with a rotatory evaporator. The residual was treated with flash chromatography on silica gel (eluted with PE and EA) to afford product **2**.

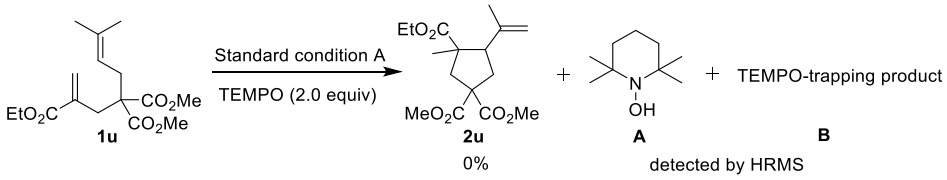
5.2 General procedure for the preparation of 4 (Protocol B)



3 (0.2 mmol) was added into a 15 mL oven-dried glass tube equipped with a magnetic stirring bar and a rubber stopper, followed by the addition of $Co(dmgH)(dmgH_2)Cl_2$ (0.01 mmol, 5 mol%), **PC2** (0.01 mmol, 5 mol%), ascorbic acid (0.6 mmol, 3.0 equiv), K_2CO_3 (0.3 mmol, 1.5 equiv), acetonitrile (3.0 mL) and deionized water (0.5 mL). The tube was evacuated and backfilled with argon (repeated three times). 1,4-Cyclohexadiene (1.0 mmol, 5.0 equiv) was added into the reaction mixture, which was irradiated with a 40 W 427 nm Kessil light at 50 ^{o}C (system temperature) for 48 h. After the reaction was complete as monitored by TLC the solvent was removed under reduced pressure with a rotatory evaporator. The residual was treated with flash chromatography on silica gel (eluted with PE and EA) to afford product **4**.

6. Mechanistic studies

6.1 Inhibition experiment for 1,6-diene cycloisomerization



1u (62.5 mg, 0.2 mmol) was added into a 15 mL oven-dried glass tube equipped with a magnetic stirring bar and a rubber stopper, followed by the addition of $Co(dmgH)(dmgH_2)Cl_2$ (3.6 mg, 0.01 mmol, 5 mol%), **PC1** (5.0 mg, 0.01 mmol, 5 mol%), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv) and acetonitrile (3.0 mL). The tube was evacuated and backfilled with argon (repeated three times). *i*-Pr_2NEt (105 μL, 0.6 mmol, 3.0 equiv) was added into the reaction mixture, which was irradiated with a 40 W 427 nm Kessil light at 50 ^{o}C (system temperature) for 24 h. The formation of **2u** was completely inhibited with the addition of a radical scavenger (TEMPO). TEMPO-trapping product (**B**) was detected by HRMS (Figure S5). This result indicates that the cycloisomerization of 1,6-dienes proceeded through a radical process.

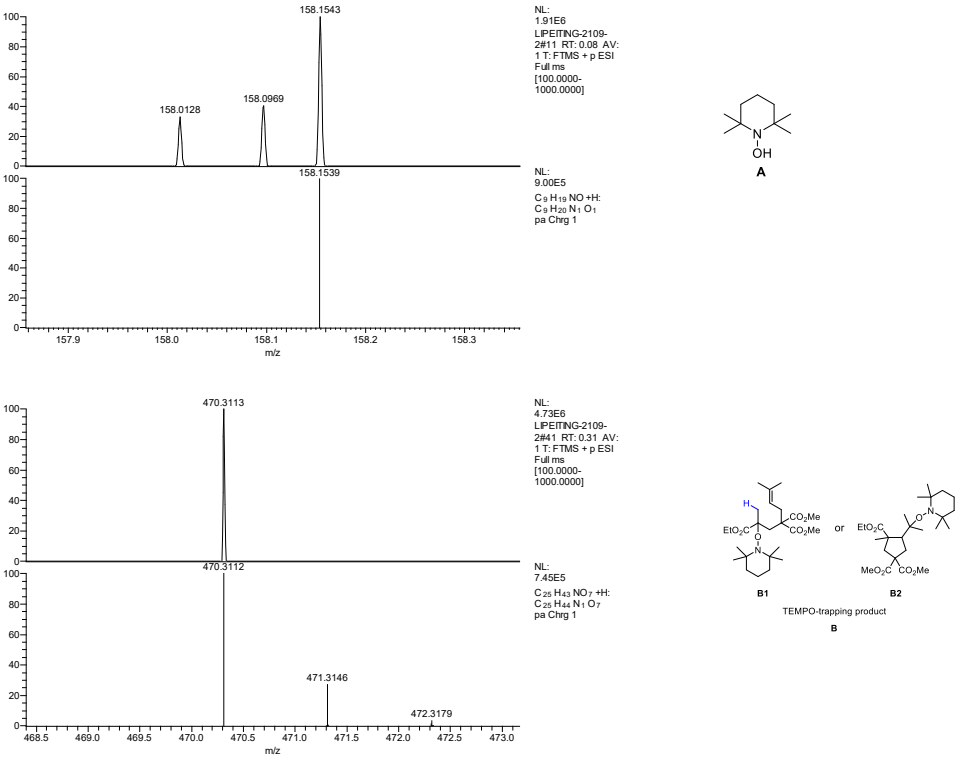
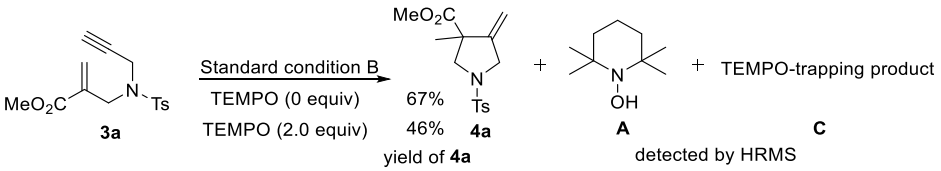


Figure S5 The HRMS of 1,6-diene cycloisomerization trapping experiments.

6.2 Inhibition experiment for 1,6-enyne cyclization



3a (61.5 mg, 0.2 mmol) was added into a 15 mL oven-dried glass tube equipped with a magnetic stirring bar and a rubber stopper, followed by the addition of $Co(dmgH)(dmgH_2)Cl_2$ (3.6 mg, 0.01 mmol, 5 mol%), **PC2** (6.3 mg, 0.01 mmol, 5 mol%), ascorbic acid (105.6 mg, 0.6 mmol, 3.0 equiv), K_2CO_3 (41.46 mg, 0.3 mmol, 1.5 equiv), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv), acetonitrile (3.0 mL) and deionized water (0.5 mL). The tube was evacuated and backfilled with argon (repeated three times). 1,4-Cyclohexadiene (95 μL, 1.0 mmol, 5.0 equiv) was added into the reaction mixture, which was irradiated with a 40 W 427 nm Kessil light at 50 ^oC (system temperature) for 48 h. **4a** was obtained in a yield of 46% (28 mg) after flash chromatography. TEMPO-trapping products (**C**) were detected by HRMS (Figure S6).

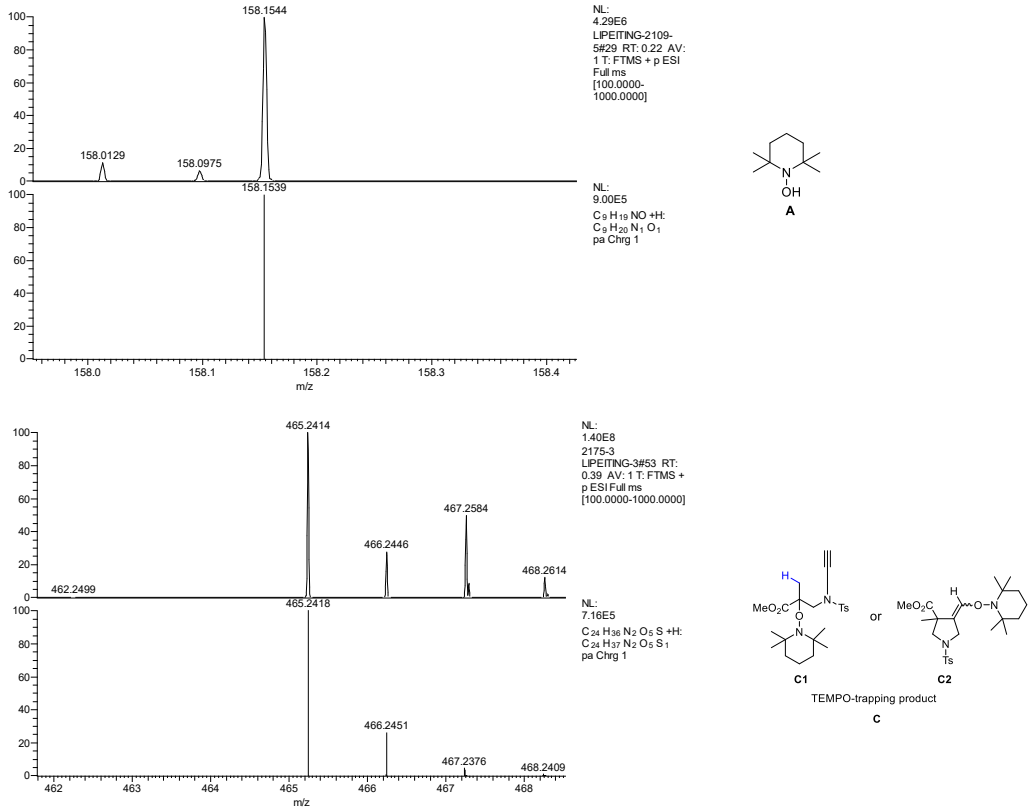
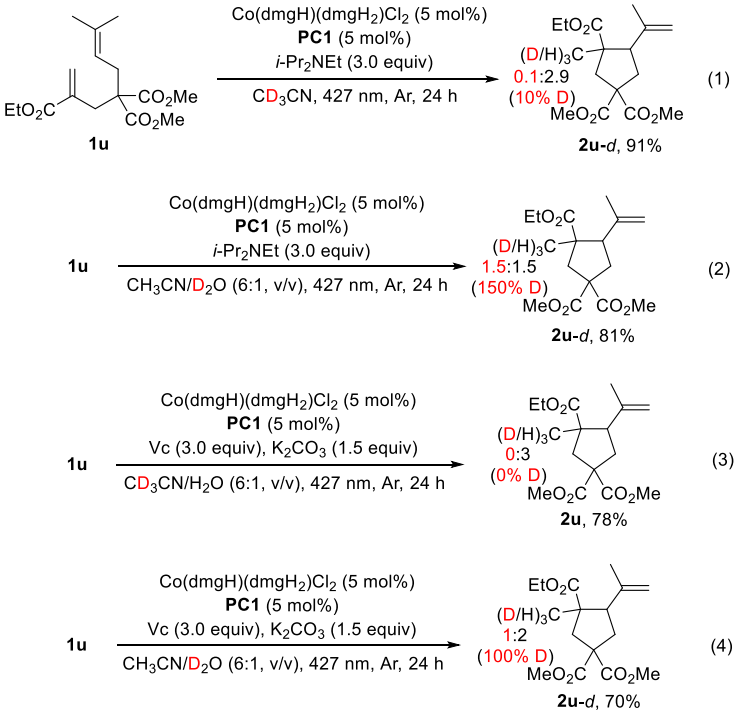


Figure S6 The HRMS of 1,6-enyne cyclization trapping experiments.

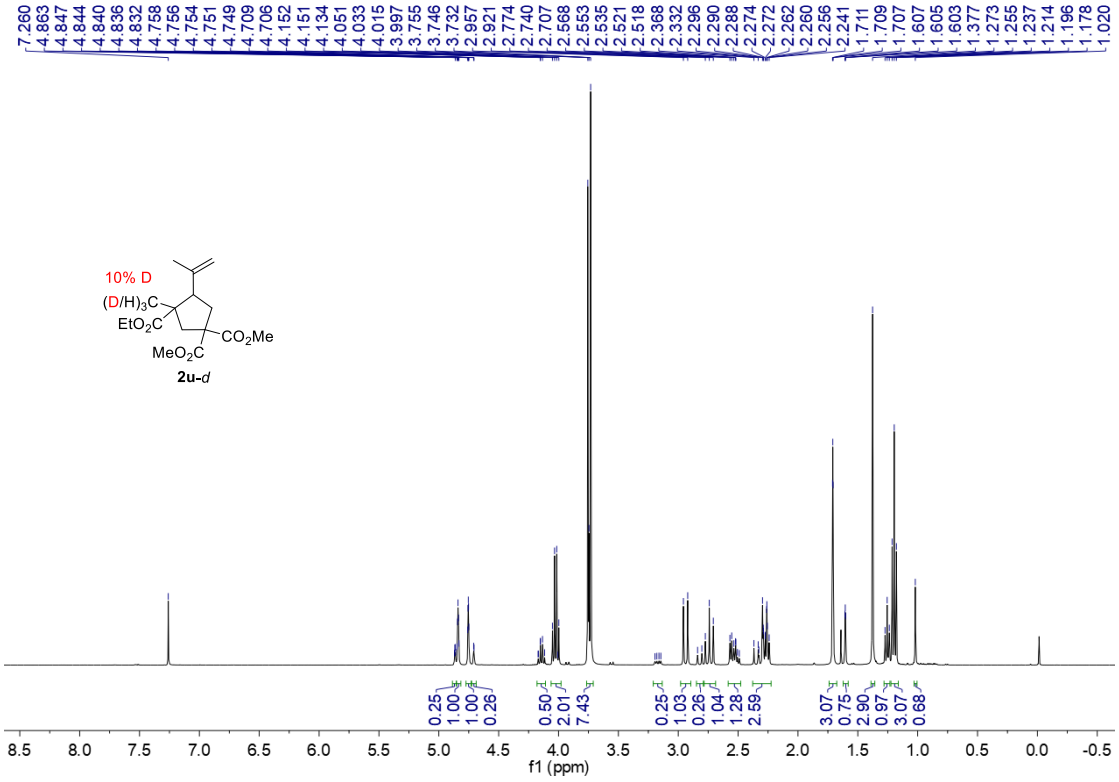
6.3 Deuterium labeling experiments for 1,6-diene cycloisomerization



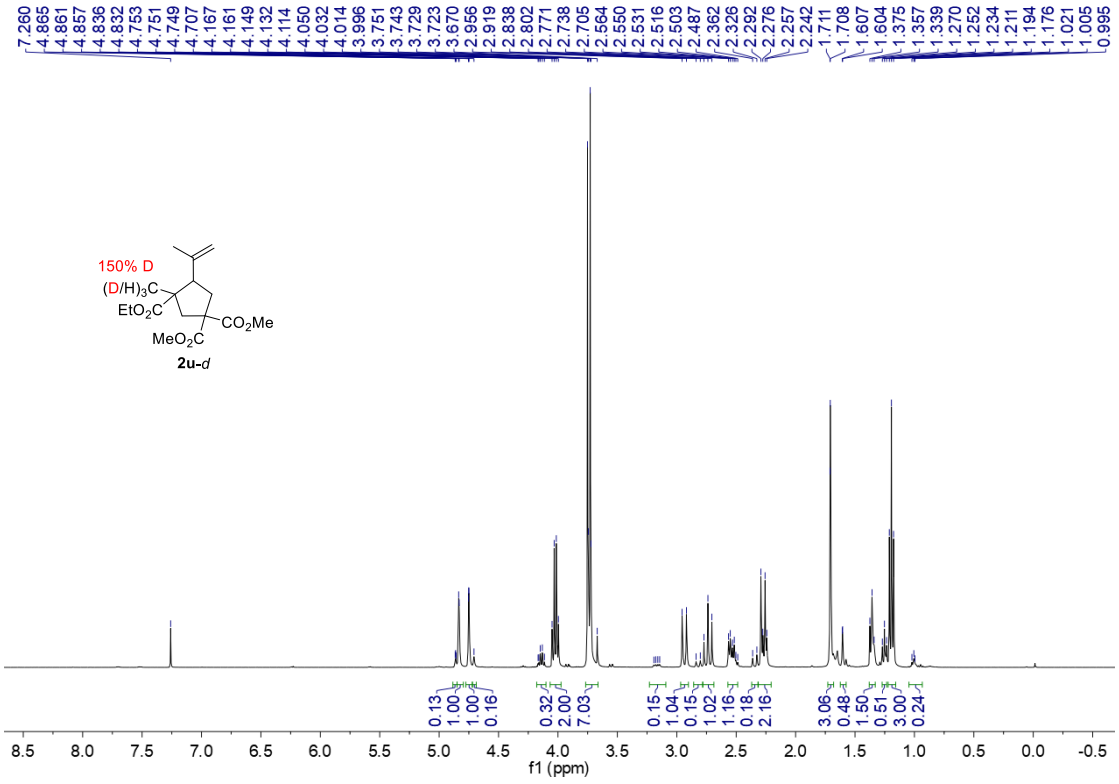
Scheme S1 Deuterium labeling experiments for the cycloisomerization of **1u**.

^{1}H NMR spectra

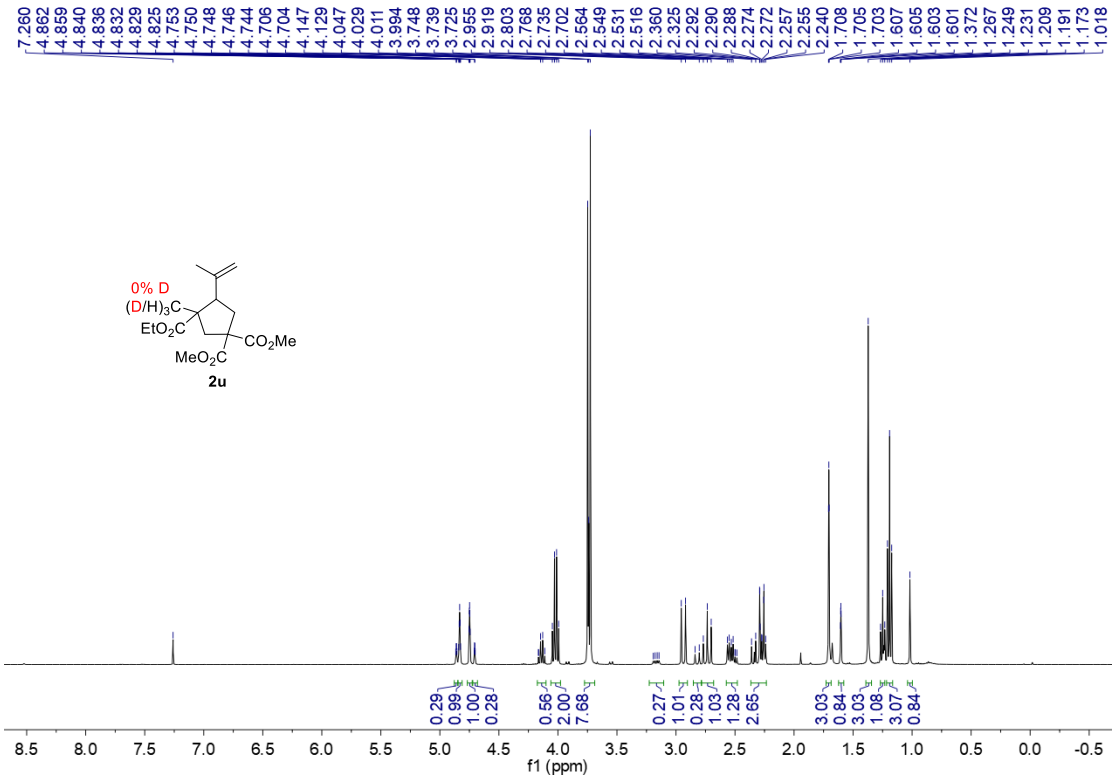
^{1}H NMR ($CDCl_3$, 400 MHz) (Scheme S1 (1), in CD_3CN)



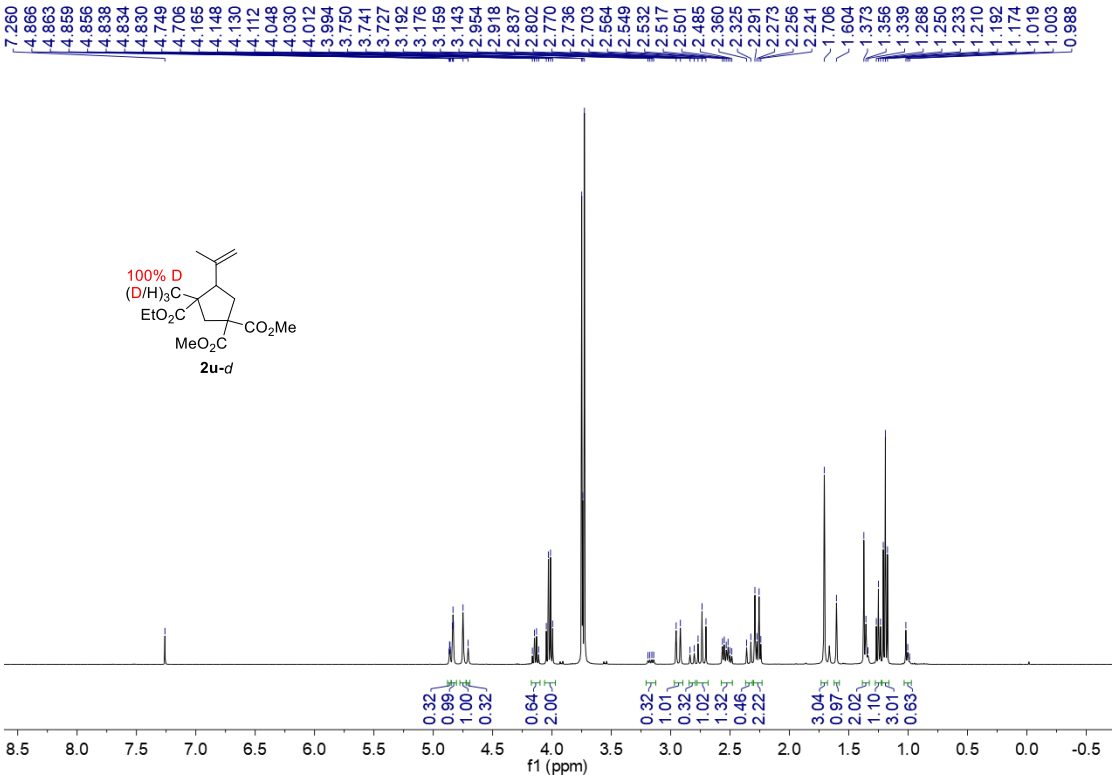
^{1}H NMR ($CDCl_3$, 400 MHz) (Scheme S1 (2), in CH_3CN-D_2O)



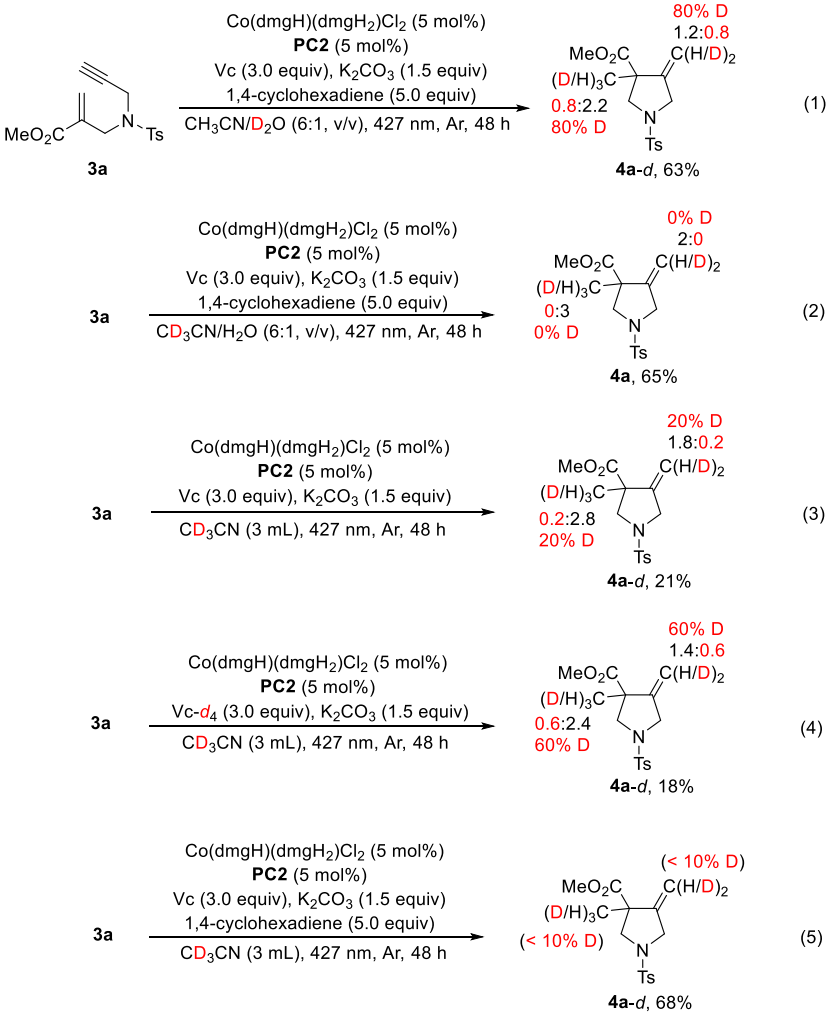
^{1}H NMR ($CDCl_3$, 400 MHz) (Scheme S1 (3), in CD_3CN-H_2O)



^{1}H NMR ($CDCl_3$, 400 MHz) (Scheme S1 (4), in CH_3CN-D_2O)



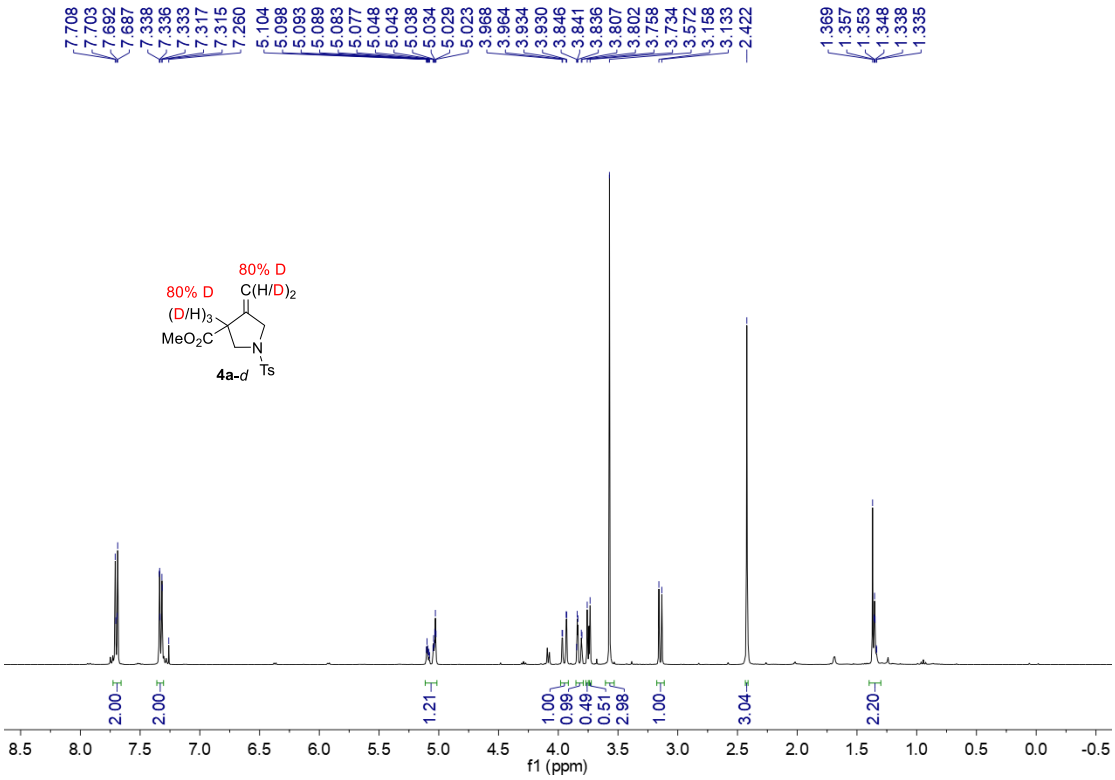
6.4 Deuterium labeling experiments for 1,6-enyne cyclization



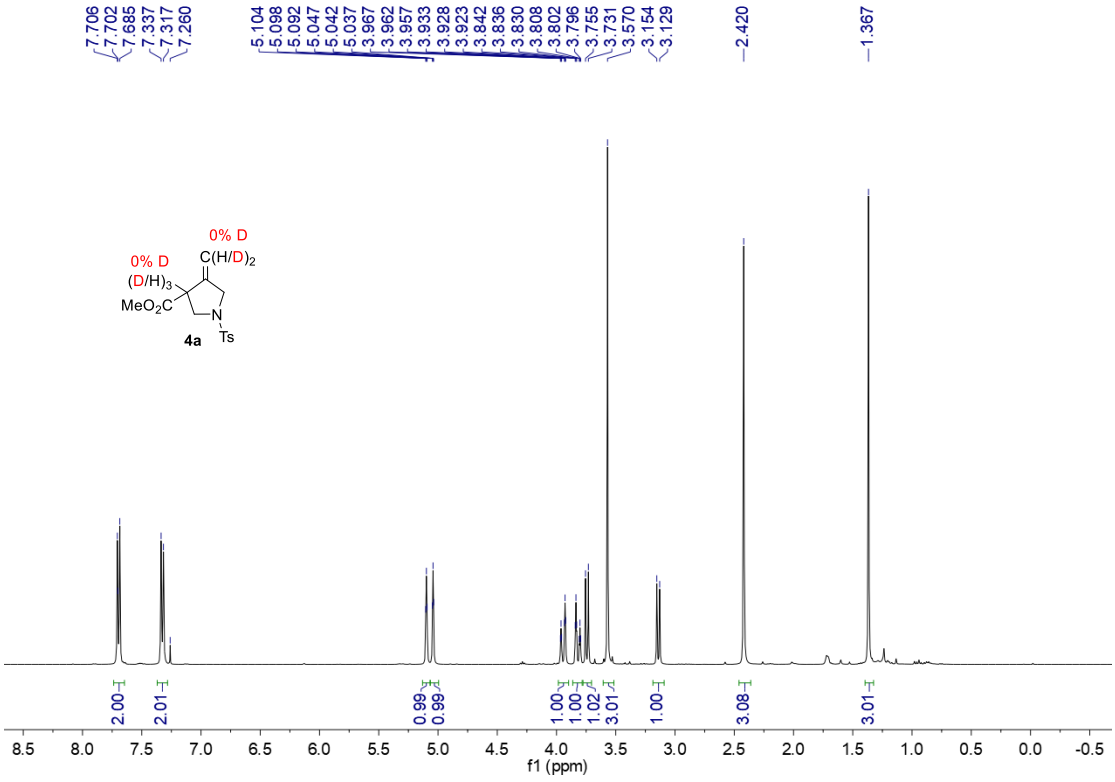
Scheme S2 Deuterium labeling experiments for the cyclization of **3a**.

^{1}H NMR spectra

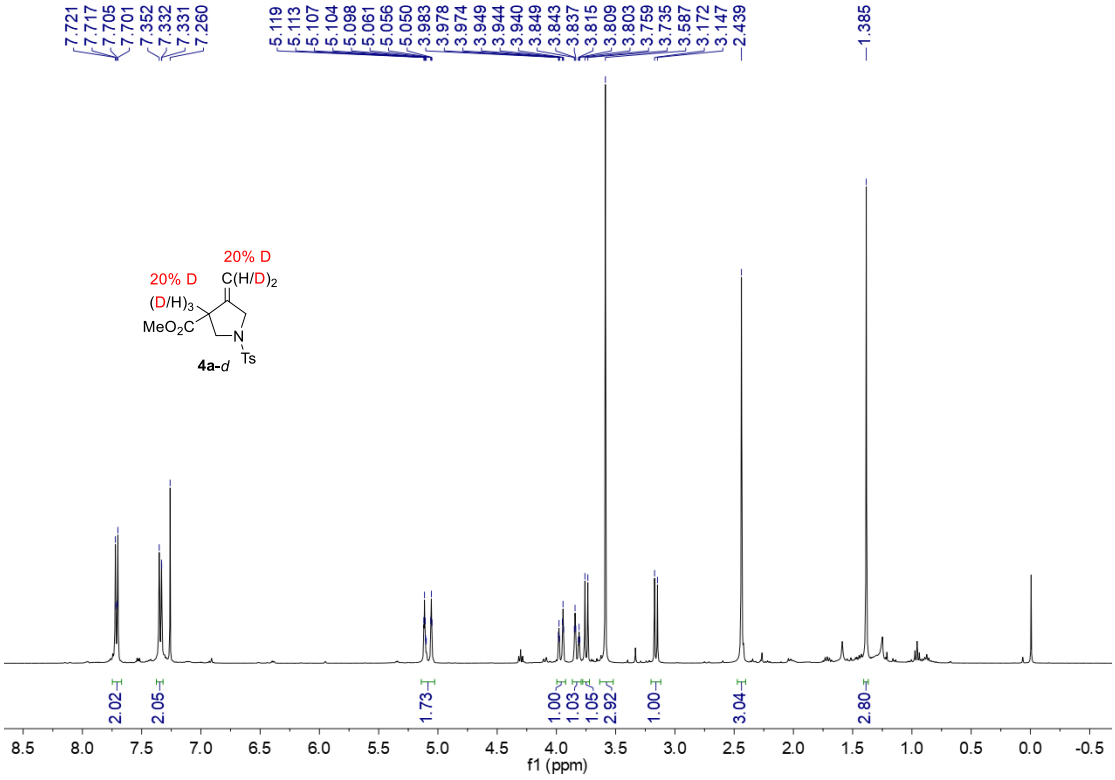
^{1}H NMR ($CDCl_3$, 400 MHz) (Scheme S2 (1), in CH_3CN-D_2O)



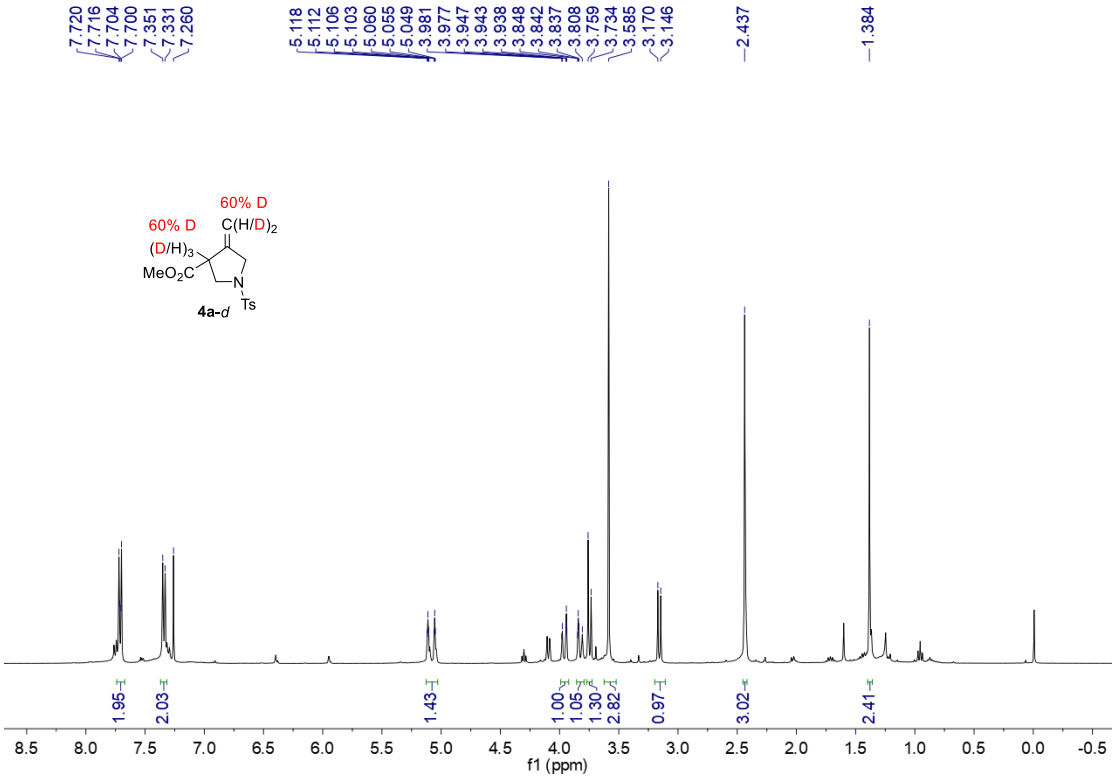
^{1}H NMR ($CDCl_3$, 400 MHz) (Scheme S2 (2), in CD_3CN-H_2O)



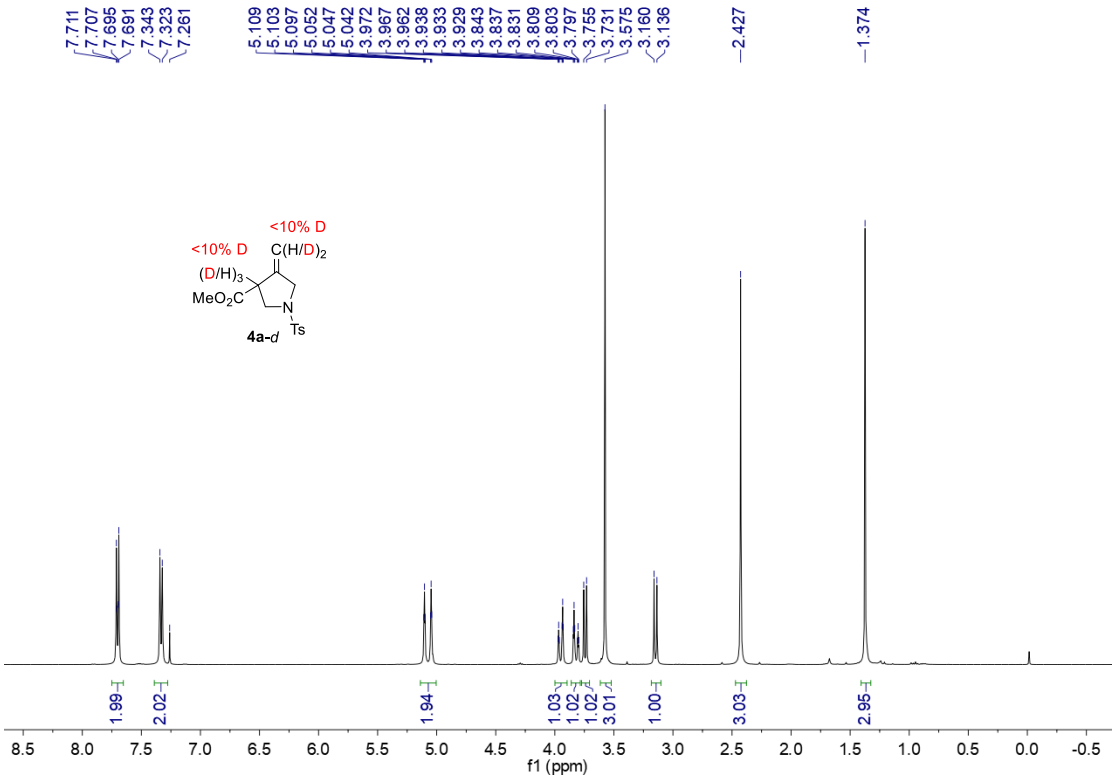
^{1}H NMR ($CDCl_3$, 400 MHz) (Scheme S2 (3), in CD_3CN in the absence of 1,4-cyclohexadiene)



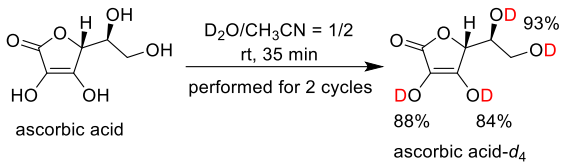
^{1}H NMR ($CDCl_3$, 400 MHz) (Scheme S2 (4), in CD_3CN with Vc-d_4 in the absence 1,4-cyclohexadiene)



^{1}H NMR ($CDCl_3$, 400 MHz) (Scheme S2 (5), in CD_3CN)



Synthesis of ascorbic acid-d_4[9]

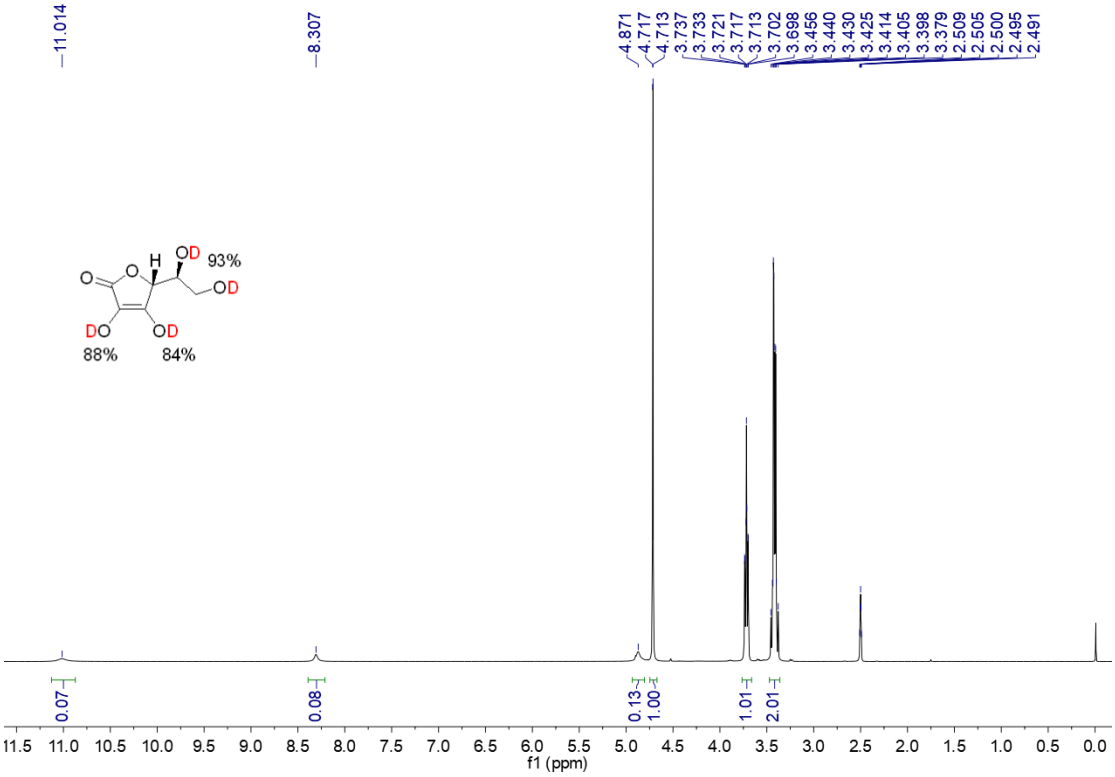


In a 50 mL round-bottom flask containing D_2O (5 mL) and CH_3CN (10 mL) was added ascorbic acid (2.52 g, 14.3 mmol). The mixture was stirred for 35 min at room temperature. The solvent was removed under reduced pressure on a rotary evaporator, then the residual was dissolved in a mixed solvent of D_2O (5 mL) and CH_3CN (10 mL), stirred 35 min at room temperature, and the solvent was removed under reduced pressure with a rotatory evaporator. The resulting solid was dried under vacuum overnight at 50 °C, and ascorbic acid-d_4 was obtained as a colorless solid. Ascorbic acid-d_4: **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.01 (br, 0.07H, 84% D), 8.31 (br, 0.08H, 88% D), 4.87 (br, 0.13H, 93% D), 4.72 (d, J = 1.6 Hz, 1H), 3.74–3.70 (m, 1H), 3.46–3.38 (m, 2H).

For comparison, ascorbic acid: **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.00 (br, 0.92H), 8.28 (br, 0.96H), 4.85 (br, 1.8H), 4.70 (d, J = 1.6 Hz, 1H), 3.74–3.70 (m, 1H), 3.46–3.39 (m, 2H).

^{1}H NMR spectra

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



6.5 Luminescence quenching experiment

6.5.1 **PC1** emission quenching by Co(dmgH)(dmgH$_2$)Cl$_2$ or *i*-Pr$_2$NEt

The measurement was run with acetonitrile as the solvent under an argon atmosphere. The solution was irradiated at 373 nm and the luminescence was measured from 450 nm to 750 nm (emission maximum is at 542 nm). The concentration of **PC1** stock solution was 0.1 mM in CH_3CN. The concentration of quencher Co(dmgH)(dmgH$_2$)Cl$_2$ and *i*-Pr$_2$NEt stock solution was 1 mM in CH_3CN.

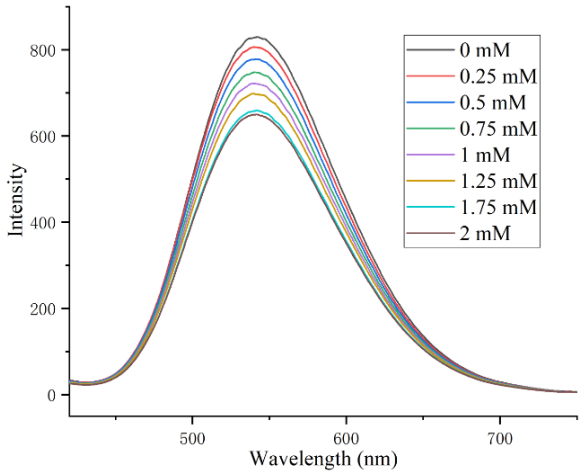


Figure S7 Fluorescence spectra of for **PC1** in CH_3CN with progressive addition of Co(dmgH)(dmgH$_2$)Cl$_2$.

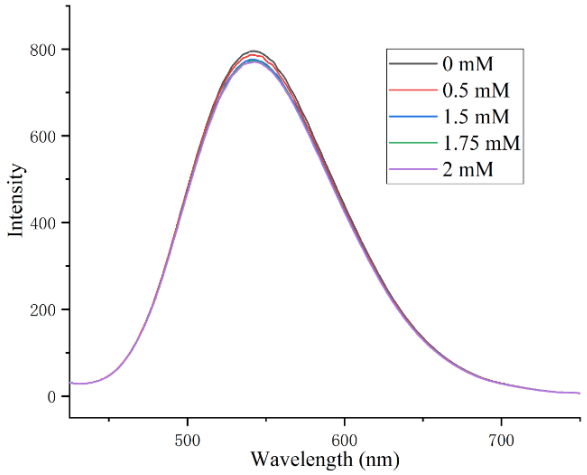


Figure S8 Fluorescence spectra of for **PC1** in CH_3CN with progressive addition of *i*-Pr_2NEt.

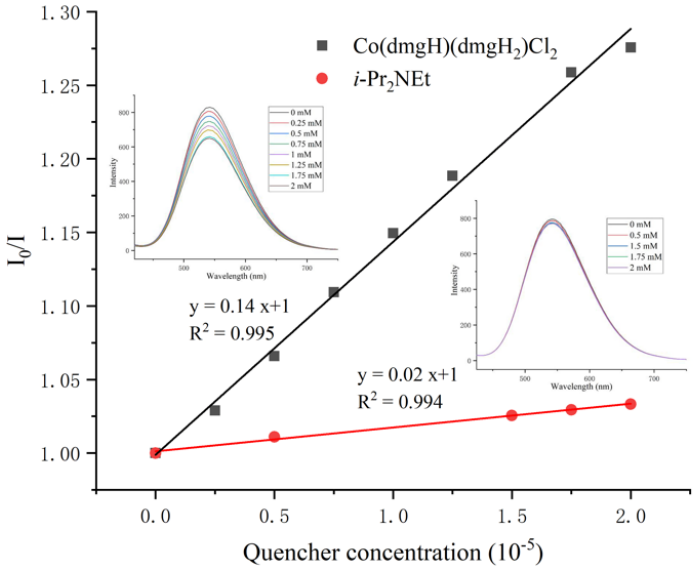


Figure S9 Stern-Volmer plot for the luminescence quenching of **PC1** by $Co(dmgH)(dmgH_2)Cl_2$ and *i*-Pr_2NEt respectively in CH_3CN solution (intensity data was collected at 542 nm).

6.5.2 **PC2** emission quenching by $Co(dmgH)(dmgH_2)Cl_2$ or Vc

The measurement was run with acetonitrile as the solvent under an argon atmosphere. The solution was irradiated at 383 nm and the luminescence was measured from 450 nm to 750 nm (emission maximum is at 550 nm). The concentration of **PC2** stock solution was 0.1 mM in CH_3CN. The concentration of quencher $Co(dmgH)(dmgH_2)Cl_2$ and Vc stock solution was 1 mM in CH_3CN.

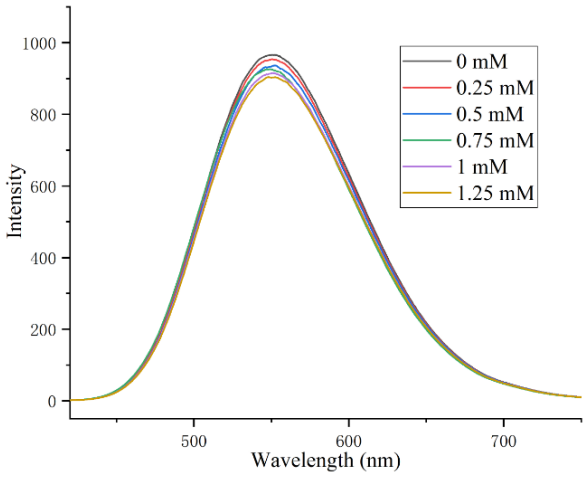


Figure S10 Fluorescence spectra of for **PC2** in CH_3CN with progressive addition of $Co(dmgH)(dmgH_2)Cl_2$.

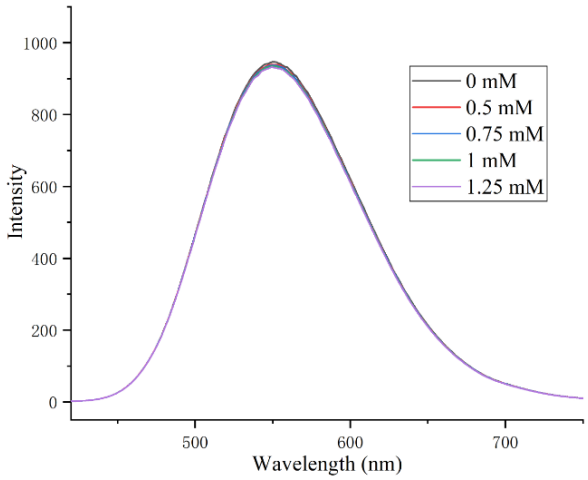


Figure S11 Fluorescence spectra of for **PC2** in CH_3CN with progressive addition of Vc.

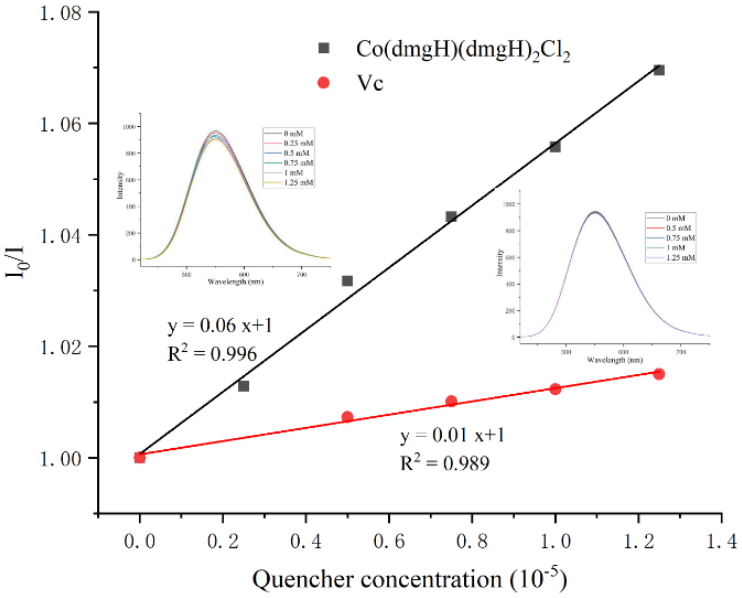
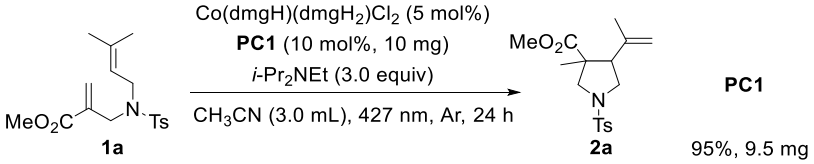


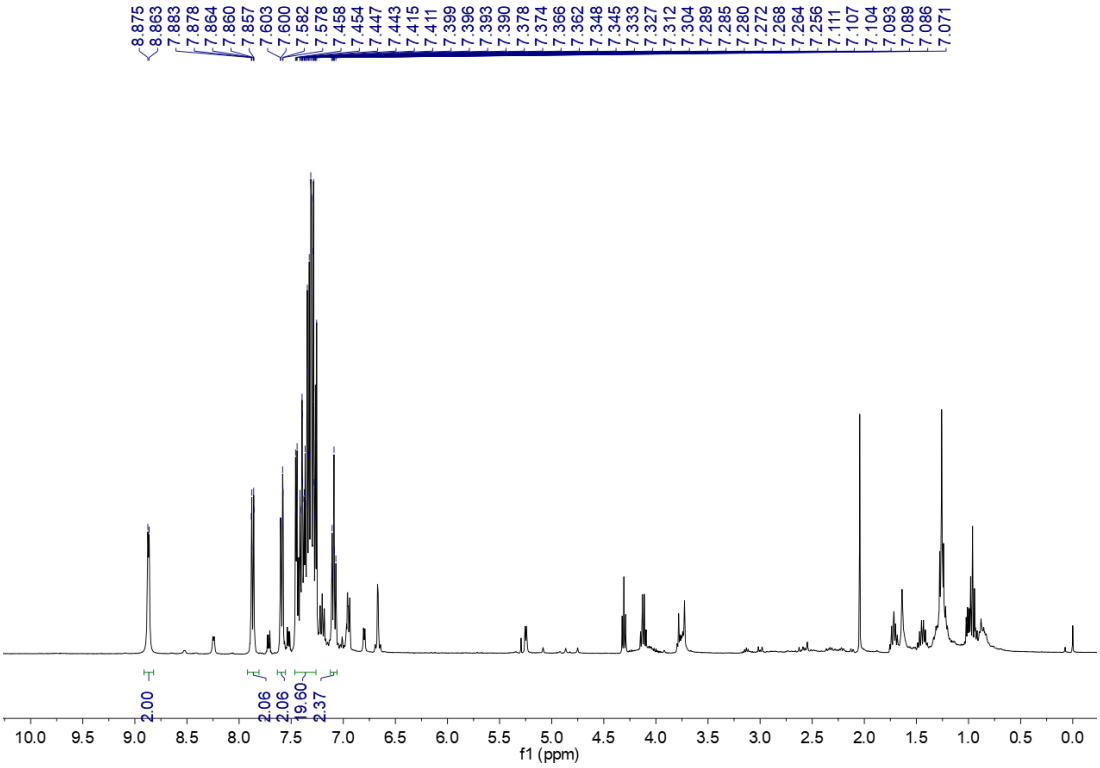
Figure S12 Stern-Volmer plot for the luminescence quenching of **PC2** by $Co(dmgH)(dmgH_2)Cl_2$ and Vc respectively in CH_3CN solution (intensity data was collected at 550 nm).

PC1 stability examination

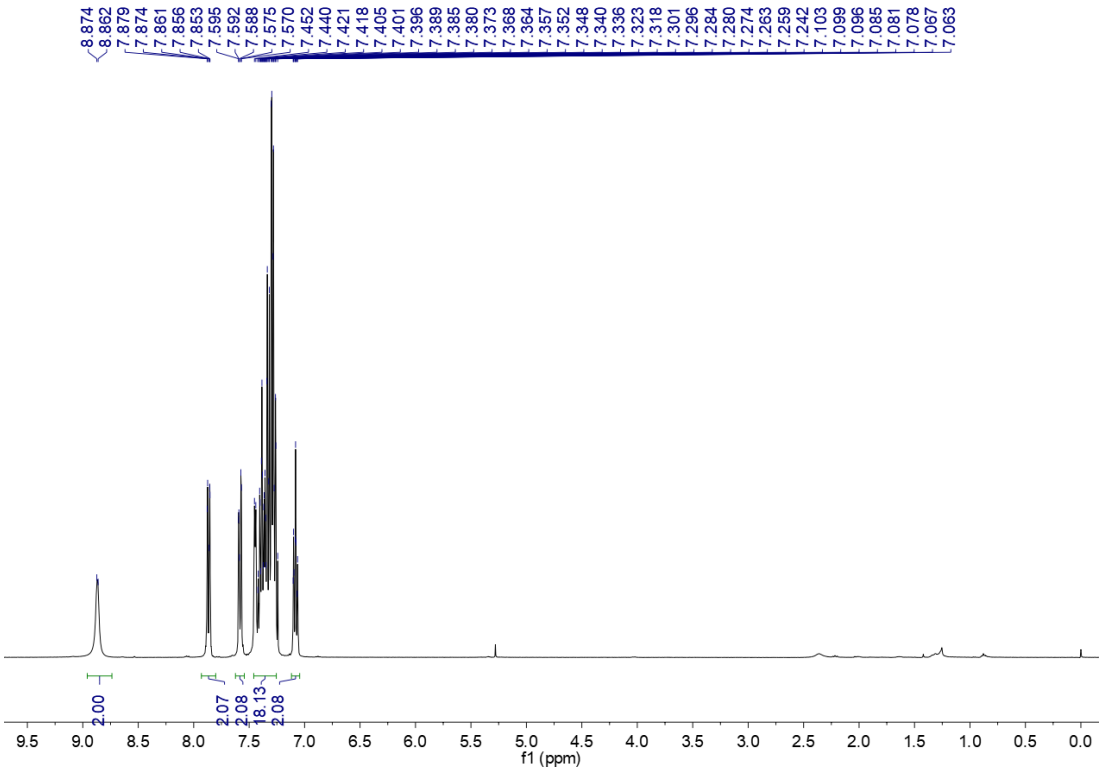
To examine the stability of **PC1** in the reaction system, it was isolated after reaction and identified by ^{1}H NMR. For the convenience of isolation, 10 mg **PC1** (10 mol%) was added into the reaction system. After reaction, 9.5 mg **PC1** was isolated. This result demonstrated that most of **PC1** remained intact after the reaction.



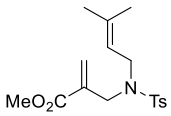
^{1}H NMR spectra of **PC1** isolated after reaction



^{1}H NMR spectra for **PC1**

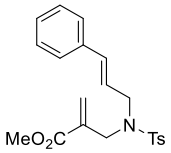


7. Characterization Data of Products



Methyl 2-(((4-methyl-*N*-(3-methylbut-2-en-1-yl)phenyl)sulfonamido)methyl)acrylate (1a)

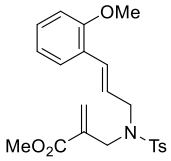
Colorless oil (798 mg, 81% on 2.9 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.27 (s, 1H), 5.84 (s, 1H), 4.82 (t, *J* = 7.2 Hz, 1H), 3.89 (s, 2H), 3.73 (d, *J* = 7.2 Hz, 2H), 3.64 (d, *J* = 2.0 Hz, 3H), 2.33 (s, 3H), 1.52 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 143.1, 137.6, 137.2, 135.6, 129.5, 127.2, 126.8, 118.3, 51.8, 46.8, 45.7, 25.6, 21.4, 17.6.



Methyl (*E*)-2-(((4-methyl-*N*-(3-phenylallyl)phenyl)sulfonamido)methyl)acrylate (1b)

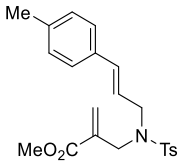
White solid (645 mg, 75% on 2.2 mmol scale). mp 68–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.32–7.26 (m, 4H), 7.25–7.19 (m, 3H), 6.39–6.35

(m, 2H), 5.96 (d, J = 0.8 Hz, 1H), 5.92–5.84 (m, 1H), 4.06 (s, 2H), 3.98 (dd, J = 7.2, 1.2 Hz, 2H), 3.67 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 143.4, 137.1, 136.1, 135.6, 134.4, 129.7, 128.5, 127.9, 127.5, 127.3, 126.4, 123.3, 51.9, 50.6, 47.2, 21.5. HRMS (ESI): m/z calcd for $C_{21}H_{24}NO_4S$ $[M+H]^+$ 386.1421, found 386.1428.



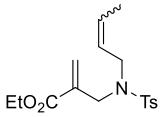
Methyl (*E*)-2-(((4-methyl-*N*-(3-(p-tolyl)allyl)phenyl)sulfonamido)methyl)acrylate (1c)

White solid (416 mg, 56% on 1.8 mmol scale). mp 99–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.23–7.17 (m, 2H), 6.89–6.82 (m, 2H), 6.70 (d, J = 16.0 Hz, 1H), 6.38 (d, J = 0.8 Hz, 1H), 5.98 (d, J = 0.8 Hz, 1H), 5.92–5.85 (m, 1H), 4.05 (s, 2H), 3.99–3.98 (m, 2H), 3.79 (s, 3H), 3.68 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 156.7, 143.3, 137.1, 135.7, 129.7, 129.5, 129.0, 127.3, 127.29, 127.0, 125.1, 123.8, 120.5, 110.8, 55.3, 51.8, 51.1, 47.0, 21.4. HRMS (ESI): m/z calcd for $C_{22}H_{26}NO_5S$ $[M+H]^+$ 416.1526, found 416.1530.



Methyl (*E*)-2-(((4-methyl-*N*-(3-(p-tolyl)allyl)phenyl)sulfonamido)methyl)acrylate (1d)

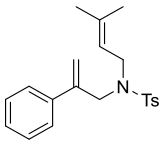
White solid (255 mg, 68% on 0.9 mmol scale). mp 64–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.11–7.06 (m, 4H), 6.36–6.32 (m, 2H), 5.95 (d, J = 0.8 Hz, 1H), 5.85–5.78 (m, 1H), 4.05 (s, 2H), 3.96 (dd, J = 6.8, 0.8 Hz, 2H), 3.67 (s, 3H), 2.42 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 143.3, 137.8, 137.1, 135.6, 134.2, 133.2, 129.7, 129.2, 127.3, 127.2, 126.3, 122.2, 51.8, 50.6, 47.0, 21.4, 21.1. HRMS (ESI): m/z calcd for $C_{22}H_{26}NO_4S$ $[M+H]^+$ 400.1577, found 400.1584.



Ethyl 2-(((*N*-(but-2-en-1-yl)-4-methylphenyl)sulfonamido)methyl)acrylate (1f)

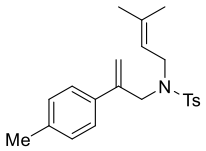
Colorless oil (433 mg, 76% on 1.7 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.69 (m, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.33 (s, 1H), 5.88 (s, 1H), 5.56–5.46 (m, 1H), 5.20–5.13 (m, 1H), 4.20–4.14 (m, 2H), 3.97 (s, 2H), 3.73 (d, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.57 (d, J = 6.4 Hz, 3H), 1.27 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 143.2, 137.1, 135.8, 131.1, 129.6, 129.58, 127.2, 126.8, 124.9, 60.8, 50.3, 46.6,

21.4, 17.6, 14.1. HRMS (ESI): m/z calcd for $C_{17}H_{24}NO_4S$ $[M+H]^+$ 338.1421, found 338.1425.



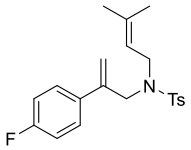
4-Methyl-*N*-(3-methylbut-2-en-1-yl)-*N*-(2-phenylallyl)benzenesulfonamide (1g)

White solid (637 mg, 80% on 2.2 mmol scale). mp 84–85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.41–7.38 (m, 2H), 7.34–7.25 (m, 5H), 5.44 (s, 1H), 5.22 (s, 1H), 4.85 (t, *J* = 7.2 Hz, 1H), 4.20 (s, 2H), 3.74 (d, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 1.57 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.05, 143.0, 138.7, 137.3, 136.7, 129.5, 128.3, 127.9, 127.3, 126.4, 118.5, 115.6, 50.2, 44.5, 25.7, 21.5, 17.7. HRMS (ESI): m/z calcd for $C_{21}H_{26}NO_2S$ $[M+H]^+$ 356.1679, found 356.1684.



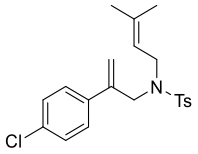
4-Methyl-*N*-(3-methylbut-2-en-1-yl)-*N*-(2-(p-tolyl)allyl)benzenesulfonamide (1h)

White solid (993 mg, 73% on 3.7 mmol scale). mp 64–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.64 (m, 2H), 7.30–7.25 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.40 (d, *J* = 0.8 Hz, 1H), 5.16 (d, *J* = 1.2 Hz, 1H), 4.86–4.82 (m, 1H), 4.18 (s, 2H), 3.74 (d, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 1.57 (d, *J* = 0.8 Hz, 3H), 1.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 142.8, 137.7, 137.3, 136.6, 135.8, 129.4, 129.0, 127.3, 126.3, 118.5, 114.8, 50.3, 44.5, 25.7, 21.5, 21.1, 17.7. HRMS (ESI): m/z calcd for $C_{22}H_{28}NO_2S$ $[M+H]^+$ 370.18345, found 370.1830.



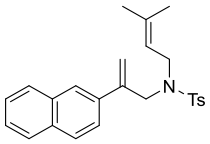
***N*-(2-(4-Fluorophenyl)allyl)-4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide (1i)**

White solid (1.09 g, 75% on 3.9 mmol scale). mp 80–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.63 (m, 2H), 7.40–7.37 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.02–6.98 (m, 2H), 5.39 (s, 1H), 5.19 (d, *J* = 1.2 Hz, 1H), 4.83–4.79 (m, 1H), 4.17 (s, 2H), 3.72 (d, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.56 (d, *J* = 0.8 Hz, 3H), 1.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}F}$ = 248.6 Hz), 143.1, 142.1, 137.1, 136.6, 134.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 129.5, 128.2 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.3, 118.4, 115.7, 115.2 (d, $J_{C\text{-}F}$ = 21.2 Hz), 50.5, 44.6, 25.7, 21.6, 17.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.3. HRMS (ESI): m/z calcd for $C_{21}H_{25}FNO_2S$ $[M+H]^+$ 374.1585, found 374.1581.



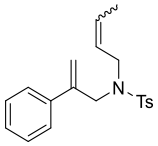
***N*-(2-(4-Chlorophenyl)allyl)-4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide (1j)**

White solid (1.18g, 79% on 3.8 mmol scale). mp 72–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.36–7.33 (m, 2H), 7.27–7.25 (m, 4H), 5.42 (s, 1H), 5.22 (s, 1H), 4.80 (t, *J* = 6.8 Hz, 1H), 4.17 (s, 2H), 3.71 (d, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 1.55 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 142.0, 136.9, 136.85, 136.5, 133.6, 129.4, 128.3, 127.7, 127.1, 118.3, 116.2, 50.4, 44.5, 25.6, 21.3, 17.6. HRMS (ESI): m/z calcd for $C_{21}H_{25}ClNO_2S$ $[M+H]^+$ 390.1289, found 390.1283.



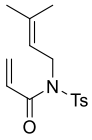
4-Methyl-*N*-(3-methylbut-2-en-1-yl)-*N*-(2-(naphthalen-2-yl)allyl)benzenesulfonamide (1k)

White solid (433 mg, 38% on 2.8 mmol scale). mp 87–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.79 (m, 4H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.57 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.49–7.47 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.61 (s, 1H), 5.35 (d, *J* = 0.8 Hz, 1H), 4.94–4.90 (m, 1H), 4.35 (s, 2H), 3.81 (d, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 1.60 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 142.8, 137.2, 136.6, 135.9, 133.1, 132.9, 129.4, 128.2, 127.8, 127.4, 127.2, 126.1, 126.0, 125.3, 124.5, 118.5, 116.2, 50.3, 44.6, 25.6, 21.4, 17.7. HRMS (ESI): m/z calcd for $C_{25}H_{28}NO_2S$ $[M+H]^+$ 406.1835, found 406.1830.



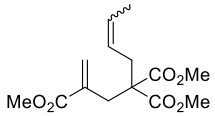
***N*-(but-2-en-1-yl)-4-methyl-*N*-(2-phenylallyl)benzenesulfonamide (1l)**

Colorless oil (341 mg, 62% on 1.6 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.63 (m, 2H), 7.43–7.37 (m, 2H), 7.31–7.25 (m, 5H), 5.53–5.46 (m, 1H), 5.46–5.43 (m, 1H), 5.24–5.22 (m, 1H), 5.19–5.11 (m, 1H), 4.22–4.21 (m, 2H), 3.82–3.66 (m, 2H), 2.42 (s, 3H), 1.58–1.51 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 142.8, 138.7, 137.2, 130.8, 129.5, 128.3, 127.9, 127.4, 126.5, 124.8, 115.9, 50.0, 48.8, 21.5, 17.6. HRMS (ESI): m/z calcd for $C_{20}H_{24}NO_2S$ $[M+H]^+$ 342.1522, found 342.1526.



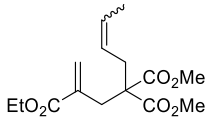
***N*-(3-Methylbut-2-en-1-yl)-*N*-tosylacrylamide (1o)**

Colorless oil (357 mg, 29% on 4.2 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.76 (m, 2H), 7.31–7.26 (m, 2H), 6.92–6.85 (m, 1H), 6.38–6.33 (m, 1H), 5.76–5.72 (m, 1H), 5.22–5.17 (m, 1H), 4.47 (d, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 1.74–1.71 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 144.6, 137.0, 136.6, 131.1, 129.6, 128.6, 127.6, 119.6, 44.7, 25.6, 21.6, 18.0. HRMS (ESI): m/z calcd for $C_{15}H_{20}NO_3S$ $[M+H]^+$ 294.1158, found 294.1165.



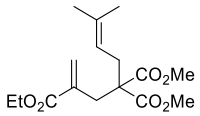
Trimethyl octa-1,6-diene-2,4,4-tricarboxylate (1s)

Colorless oil (827 mg, 80% on 2.7 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (s, 1H), 5.63 (s, 1H), 5.51–5.46 (m, 1H), 5.32–5.24 (m, 1H), 3.69–3.66 (m, 9H), 2.93 (s, 2H), 2.50 (d, *J* = 7.2 Hz, 2H), 1.62 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 167.3, 135.9, 130.0, 129.0, 124.5, 57.9, 52.2, 51.9, 36.1, 33.8, 18.0. HRMS (ESI): m/z calcd for $C_{14}H_{21}O_6$ $[M+H]^+$ 285.1333, found 285.1337.



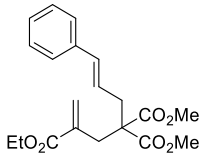
2-Ethyl 4,4-dimethyl octa-1,6-diene-2,4,4-tricarboxylate (1t)

Colorless oil (1.35 g, 84% on 5.4 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22–6.21 (m, 1H), 5.59 (s, 1H), 5.50–5.44 (m, 1H), 5.30–5.25 (m, 1H), 4.16–4.10 (m, 2H), 3.64–3.63 (m, 6H), 2.94–2.91 (m, 2H), 2.58–2.48 (m, 2H), 1.60–1.55 (m, 3H), 1.27–1.22 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 166.8, 136.2, 129.8, 128.6, 124.6, 60.8, 58.0, 52.1, 36.1, 33.7, 17.9, 14.0. HRMS (ESI): m/z calcd for $C_{15}H_{23}O_6$ $[M+H]^+$ 299.1489, found 299.1492.



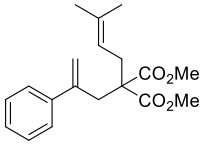
2-Ethyl 4,4-dimethyl 7-methylocta-1,6-diene-2,4,4-tricarboxylate (1u)

Colorless oil (2.0 g, 70% on 9.2 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (d, *J* = 1.2 Hz, 1H), 5.54 (d, *J* = 1.2 Hz, 1H), 4.97–4.93 (m, 1H), 4.10 (q, *J* = 14.4, 7.2 Hz, 2H), 3.62 (s, 6H), 2.90 (d, *J* = 1.2 Hz, 2H), 2.50 (d, *J* = 7.2 Hz, 2H), 1.63 (s, 3H), 1.53 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 166.7, 136.1, 135.4, 128.5, 117.5, 60.7, 57.7, 52.1, 33.7, 31.3, 25.8, 17.8, 14.0. HRMS (ESI): m/z calcd for $C_{16}H_{25}O_6$ $[M+H]^+$ 313.1646, found 313.1648.



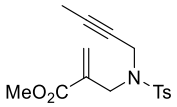
2-Ethyl 4,4-dimethyl (*E*)-7-phenylhepta-1,6-diene-2,4,4-tricarboxylate (1v)

Colorless oil (1.0 g, 71% on 4.0 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.26 (m, 4H), 7.23–7.19 (m, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.29 (d, *J* = 1.2 Hz, 1H), 6.14–6.10 (m, 1H), 5.67 (s, 1H), 4.17 (q, *J* = 14.4, 7.2 Hz, 2H), 3.70 (s, 6H), 3.04 (s, 2H), 2.75 (d, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 166.9, 137.0, 136.1, 134.0, 128.9, 128.5, 127.4, 126.2, 124.0, 60.9, 58.3, 52.4, 36.7, 34.2, 14.1. HRMS (ESI): m/z calcd for $C_{20}H_{25}O_6$ $[M + H]^+$ 361.1646, found 361.1651.



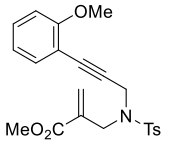
Dimethyl 2-(3-methylbut-2-en-1-yl)-2-(2-phenylallyl)malonate (1w)

Colorless oil (808 mg, 73% on 3.5 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.22 (m, 5H), 5.25 (d, *J* = 1.6 Hz, 1H), 5.10 (d, *J* = 0.8 Hz, 1H), 4.95–4.91 (m, 1H), 3.41 (s, 6H), 3.16 (s, 2H), 2.54 (d, *J* = 7.2 Hz, 2H), 1.67 (d, *J* = 0.8 Hz, 3H), 1.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 144.5, 141.5, 135.5, 127.9, 127.4, 126.9, 118.4, 117.6, 57.4, 52.0, 37.3, 30.3, 26.0, 17.9. HRMS (ESI): m/z calcd for $C_{19}H_{25}O_4$ $[M+H]^+$ 317.1747, found 317.1752.



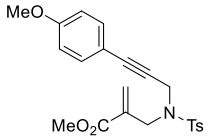
Methyl 2-(((*N*-(but-2-yn-1-yl)-4-methylphenyl)sulfonamido)methyl)acrylate (3b)

Colorless oil (546 mg, 81% on 2.4 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.36 (d, *J* = 1.2 Hz, 1H), 5.92 (d, *J* = 0.8 Hz, 1H), 4.04 (s, 2H), 4.01 (q, *J* = 4.8, 2.4 Hz, 2H), 3.74 (s, 3H), 2.41 (s, 3H), 1.52 (t, *J* = 2.0 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 143.4, 136.0, 134.9, 129.3, 127.8, 127.3, 81.9, 71.6, 51.9, 46.6, 37.4, 21.4, 3.2. HRMS (ESI): m/z calcd for $C_{16}H_{20}NO_4S$ $[M+H]^+$ 322.1108, found 322.1110.



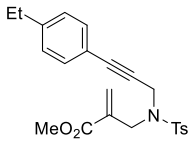
Methyl 2-(((*N*-(3-(2-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)methyl)acrylate (3d)

White solid (378 mg, 72% on 1.3 mmol scale). mp 86–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.26–7.20 (m, 3H), 6.91 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.83–6.79 (m, 2H), 6.41 (s, 1H), 6.03 (s, 1H), 4.35 (s, 2H), 4.17 (s, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 160.0, 143.5, 135.8, 134.8, 133.3, 129.8, 129.4, 127.8, 127.7, 120.1, 111.3, 110.4, 85.6, 82.5, 55.5, 52.0, 46.8, 38.0, 21.3. HRMS (ESI): m/z calcd for $C_{22}H_{24}NO_5S$ $[M+H]^+$ 414.1370, found 414.1374.



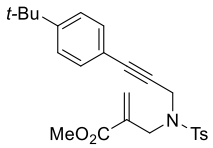
Methyl 2-(((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)methyl)acrylate (3e)

White solid (507 mg, 54% on 2.3 mmol scale). mp 72–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.02–6.98 (m, 2H), 6.77–6.74 (m, 2H), 6.41 (d, *J* = 0.8 Hz, 1H), 5.99 (d, *J* = 1.2 Hz, 1H), 4.29 (s, 2H), 4.14 (s, 2H), 3.78 (s, 3H), 3.76 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 159.6, 143.5, 135.9, 134.9, 132.9, 129.5, 127.8, 127.5, 114.0, 113.7, 85.8, 80.1, 55.2, 52.0, 46.8, 37.8, 21.4. HRMS (ESI): m/z calcd for $C_{22}H_{24}NO_5S$ $[M+H]^+$ 414.1370, found 414.1374.



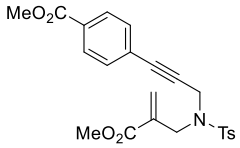
Methyl 2-(((*N*-(3-(4-ethylphenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)methyl)acrylate (3f)

Colorless oil (364 mg, 77% on 1.2 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.99–6.97 (m, 2H), 6.42 (d, *J* = 0.8 Hz, 1H), 6.00 (d, *J* = 1.2 Hz, 1H), 4.31 (s, 2H), 4.14 (s, 2H), 3.77 (s, 3H), 2.62 (q, *J* = 15.2, 7.6 Hz, 2H), 2.35 (s, 3H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 144.9, 143.6, 136.0, 134.9, 131.5, 129.6, 127.8, 127.7, 119.2, 86.1, 80.9, 52.0, 46.9, 37.8, 28.8, 21.4, 15.3. HRMS (ESI): m/z calcd for $C_{23}H_{26}NO_4S$ $[M+H]^+$ 412.1577, found 412.1580.



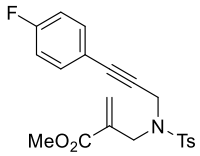
Methyl 2-(((*N*-(3-(4-(*tert*-butyl)phenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)methyl)acrylate (3g)

White solid (326 mg, 79% on 0.9 mmol scale). mp 46–47 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.4 Hz, 2H), 7.29–7.26 (m, 4H), 7.04–7.01 (m, 2H), 6.44 (d, J = 0.8 Hz, 1H), 6.01 (d, J = 1.2 Hz, 1H), 4.33 (s, 2H), 4.16 (s, 2H), 3.78 (s, 3H), 2.35 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 151.7, 143.5, 135.9, 134.9, 131.2, 129.5, 127.7, 127.6, 125.0, 119.0, 86.0, 80.8, 52.0, 46.8, 37.8, 34.7, 31.0, 21.4. HRMS (ESI): m/z calcd for $C_{25}H_{30}NO_4S$ $[M+H]^+$ 440.1890, found 440.1897.



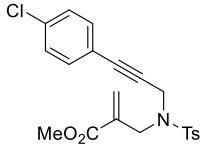
Methyl 4-(3-((*N*-(2-(methoxycarbonyl)allyl)-4-methylphenyl)sulfonamido)-prop-1-yn-1-yl)benzoate (3h)

Gray solid (438 mg, 74% on 1.3 mmol scale). mp 87–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.90 (m, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.12–7.10 (m, 2H), 6.43 (d, J = 0.8 Hz, 1H), 6.00 (d, J = 0.8 Hz, 1H), 4.33 (s, 2H), 4.15 (s, 2H), 3.91 (s, 3H), 3.77 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 166.2, 143.8, 135.9, 134.8, 131.4, 129.8, 129.6, 129.3, 127.8, 127.75, 126.6, 85.1, 84.8, 52.3, 52.1, 47.1, 37.8, 21.5. HRMS (ESI): m/z calcd for $C_{23}H_{24}NO_6S$ $[M+H]^+$ 442.1319, found 442.1325.



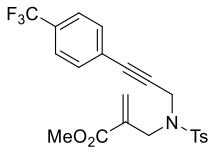
Methyl 2-(((*N*-(3-(4-fluorophenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)-methyl)acrylate (3i)

White solid (342 mg, 74% on 1.2 mmol scale). mp 99–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.07–7.03 (m, 2H), 6.95–6.91 (m, 2H), 6.42 (s, 1H), 5.99 (s, 1H), 4.29 (s, 2H), 4.14 (s, 2H), 3.76 (d, J = 1.6 Hz, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 162.5 (d, $J_{C\text{-}F}$ = 248.6 Hz), 143.6, 136.0 , 134.9, 133.4 (d, $J_{C\text{-}F}$ = 8.4 Hz), 129.5, 127.8, 127.6, 118.1 (d, $J_{C\text{-}F}$ = 3.4 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.9 Hz), 84.8, 81.5, 52.0, 47.0, 37.7, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.4. HRMS (ESI): m/z calcd for $C_{21}H_{21}FNO_4S$ $[M+H]^+$ 402.1170, found 402.1176.



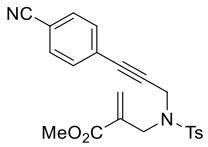
Methyl 2-(((*N*-(3-(4-chlorophenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)methyl)acrylate (3j)

White solid (351 mg, 77% on 1.1 mmol scale). mp 125–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.23–7.20 (m, 2H), 7.00–6.98 (m, 2H), 6.42 (d, *J* = 1.2 Hz, 1H), 6.00 (d, *J* = 0.8 Hz, 1H), 4.30 (s, 2H), 4.14 (s, 2H), 3.77 (s, 3H), 2.35 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 143.7, 136.0, 134.8, 134.6, 132.7, 129.6, 128.5, 127.8, 127.7, 120.5, 84.7, 82.8, 52.1, 47.0, 37.7, 21.5. HRMS (ESI): m/z calcd for $C_{21}H_{21}ClNO_4S$ $[M+H]^+$ 418.0874, found 418.0878.



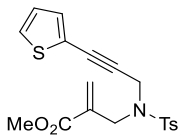
Methyl 2-(((4-methyl-*N*-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)phenyl)-sulfonamido)methyl)acrylate (3k)

White solid (349 mg, 78% on 1.0 mmol scale). mp 105–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 0.8 Hz, 1H), 6.00 (d, *J* = 1.2 Hz, 1H), 4.33 (s, 2H), 4.15 (s, 2H), 3.77 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 143.7, 135.9, 134.8, 131.7, 130.2 (q, $J_{C\text{-}F}$ = 32.7 Hz), 129.6, 127.8, 127.7, 125.8, 125.81, 123.7 (q, $J_{C\text{-}F}$ = 271 Hz), 125.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 84.44, 52.1, 47.1, 37.7, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9. HRMS (ESI): m/z calcd for $C_{22}H_{21}F_3NO_4S$ $[M+H]^+$ 452.1138, found 452.1144.



Methyl 2-(((*N*-(3-(4-cyanophenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)-methyl)acrylate (3l)

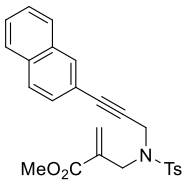
White solid (337 mg, 73% on 1.1 mmol scale). mp 167–168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.54–7.52 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.16–7.14 (m, 2H), 6.42 (d, *J* = 0.8 Hz, 1H), 5.99 (d, *J* = 1.2 Hz, 1H), 4.33 (s, 2H), 4.14 (s, 2H), 3.76 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 143.8, 135.9, 134.7, 132.0, 131.8, 129.6, 127.8, 126.9, 118.2, 111.9, 86.5, 84.1, 52.1, 47.1, 37.7, 21.4. HRMS (ESI): m/z calcd for $C_{22}H_{21}N_2O_4S$ $[M+H]^+$ 409.1217, found 409.1222.



Methyl 2-(((4-methyl-*N*-(3-(thiophen-2-yl)prop-2-yn-1-yl)phenyl)sulfonamido)-methyl)acrylate (3m)

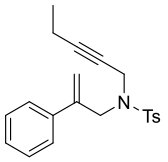
White solid (355 mg, 76% on 1.2 mmol scale). mp 78–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.77 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 5.2, 1.2 Hz, 1H),

6.94–6.89 (m, 2H), 6.42 (d, *J* = 1.2 Hz, 1H), 5.98 (d, *J* = 1.2 Hz, 1H), 4.33 (s, 2H), 4.12 (s, 2H), 3.77 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 143.7, 135.8, 134.9, 132.3, 129.7, 127.7, 127.3, 126.7, 121.9, 85.7, 79.1, 52.0, 47.0, 37.9, 21.5. HRMS (ESI): m/z calcd for $C_{19}H_{20}NO_4S_2$ $[M+H]^+$ 390.0828, found 390.0830.



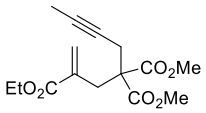
Methyl 2-(((4-methyl-*N*-(3-(naphthalen-2-yl)prop-2-yn-1-yl)phenyl)sulfonamido)methyl)acrylate (3n)

White solid (312 mg, 72% on 1.0 mmol scale). mp 97–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.83 (m, 2H), 7.80–7.69 (m, 3H), 7.58 (s, 1H), 7.51–7.47 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.10 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.45 (d, *J* = 0.8 Hz, 1H), 6.04 (d, *J* = 1.2 Hz, 1H), 4.37 (s, 2H), 4.20 (s, 2H), 3.78 (s, 3H), 2.31 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 143.7, 136.0, 134.9, 132.8, 132.7, 131.5, 129.6, 128.0, 127.9, 127.8, 127.7, 127.5, 126.8, 126.6, 119.3, 86.2, 82.0, 52.1, 47.0, 37.9, 21.5. HRMS (ESI): m/z calcd for $C_{25}H_{24}NO_4S$ $[M+H]^+$ 434.1421, found 434.1426.



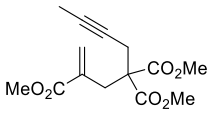
4-Methyl-*N*-(pent-2-yn-1-yl)-*N*-(2-phenylallyl)benzenesulfonamide (3p)

White solid (697 mg, 67% on 3.0 mmol scale). mp 89–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.37–7.28 (m, 5H), 5.57 (s, 1H), 5.34 (s, 1H), 4.24 (s, 2H), 3.96 (t, *J* = 2.0 Hz, 2H), 2.43 (s, 3H), 1.92–1.85 (m, 2H), 0.88 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.5, 137.8, 135.8, 129.2, 128.4, 128.04, 128.0, 126.4, 116.9, 87.9, 71.4, 49.9, 36.0, 21.4, 13.5, 12.0. HRMS (ESI): m/z calcd for $C_{21}H_{24}NO_2S$ $[M+H]^+$ 354.1522, found 354.1527.



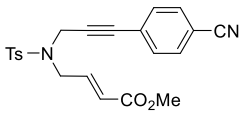
2-Ethyl 4,4-dimethyl oct-1-en-6-yne-2,4,4-tricarboxylate (3u)

Colorless oil (531 mg, 75% on 2.4 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (d, *J* = 1.6 Hz, 1H), 5.78 (d, *J* = 1.6 Hz, 1H), 4.10 (q, *J* = 14.4, 7.2 Hz, 2H), 3.67 (s, 6H), 3.05 (s, 2H), 2.65 (q, *J* = 5.2, 2.4 Hz, 2H), 1.72 (t, *J* = 2.8 Hz, 3H), 1.23 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 166.5, 135.5, 129.4, 79.2, 73.4, 60.7, 56.6, 52.5, 33.4, 23.0, 14.0, 3.3. HRMS (ESI): m/z calcd for $C_{15}H_{21}O_6$ $[M+H]^+$ 297.1333, found 297.1339.



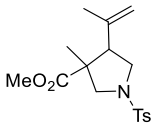
Trimethyl oct-1-en-6-yne-2,4,4-tricarboxylate (**3v**)

White solid (546 mg, 81% on 2.4 mmol scale). mp 59–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28–6.27 (m, 1H), 5.80 (s, 1H), 3.68–3.66 (m, 9H), 3.06 (d, *J* = 3.2 Hz, 2H), 2.67–2.64 (m, 2H), 1.74–1.72 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 167.0, 135.2, 129.9, 79.3, 73.3, 56.5, 52.6, 51.8, 33.5, 23.0, 3.3. HRMS (ESI): m/z calcd for $C_{14}H_{19}O_6$ $[M+H]^+$ 283.1176, found 283.1180.



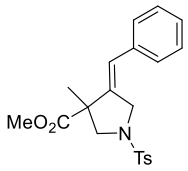
Methyl (*E*)-4-((*N*-(3-(4-cyanophenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)but-2-enoate (**3w**)

White solid (129 mg, 72% on 0.5 mmol scale). mp 141–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.75 (m, 2H), 7.56–7.54 (m, 2H), 7.29–7.27 (m, 2H), 7.19–7.17 (m, 2H), 6.90–6.83 (m, 1H), 6.09–6.05 (m, 1H), 4.32 (s, 2H), 4.04 (dd, *J* = 6.0, 1.6 Hz, 2H), 3.74 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 144.0, 141.5, 135.6, 132.0, 131.8, 129.7, 127.8, 126.7, 124.3, 118.1, 112.0, 86.0, 84.4, 51.8, 47.7, 37.5, 21.5. HRMS (ESI): m/z calcd for $C_{22}H_{21}N_2O_4S$ $[M+H]^+$ 409.1217, found 409.1214.



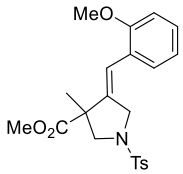
Methyl 3-methyl-4-(prop-1-en-2-yl)-1-tosylpyrrolidine-3-carboxylate (**2a**)

Prepared with protocol A. **2a** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 96%, dr = 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.69 (m, 4H), 7.33–7.31 (m, 4H), 4.87 (s, 1H), 4.76 (s, 1H), 4.63 (s, 1H), 4.57 (s, 1H), 3.73 (d, *J* = 10.4 Hz, 1H), 3.66 (d, *J* = 9.6 Hz, 1H), 3.62–3.57 (m, 4H), 3.49 (dd, *J* = 10.0, 8.0 Hz, 1H), 3.39 (s, 3H), 3.32 (t, *J* = 8.8 Hz, 2H), 3.25 (dd, *J* = 9.6, 2.4 Hz, 2H), 3.13 (t, *J* = 8.4 Hz, 1H), 2.62 (t, *J* = 7.6 Hz, 1H), 2.42 (s, 6H), 1.57 (d, *J* = 5.6 Hz, 6H), 1.25 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 173.6, 143.5, 143.4, 141.5, 140.6, 134.0, 133.8, 129.6, 129.5, 127.5, 127.4, 113.8, 113.76, 58.3, 56.5, 54.5, 52.4, 52.3, 51.6, 51.0, 50.8, 50.6, 49.7, 23.6, 22.7, 22.0, 21.5, 21.4, 16.5. HRMS (ESI): m/z calcd for $C_{17}H_{24}NO_4S$ $[M+H]^+$ 338.1421, found 338.1418.



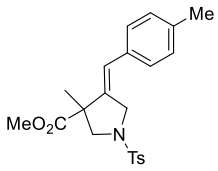
Methyl (*Z*)-4-benzylidene-3-methyl-1-tosylpyrrolidine-3-carboxylate (2b)

Prepared with protocol A. **2b** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.37–7.32 (m, 4H), 7.28–7.24 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 6.43 (t, *J* = 2.8 Hz, 1H), 4.26 (dd, *J* = 14.0, 2.0 Hz, 1H), 4.14 (dd, *J* = 14.4, 2.8 Hz, 1H), 3.82 (d, *J* = 9.6 Hz, 1H), 3.62 (s, 3H), 3.15 (d, *J* = 9.6 Hz, 1H), 2.42 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 143.7, 139.3, 135.8, 132.9, 129.7, 128.5, 128.3, 127.8, 127.5, 124.5, 56.4, 53.2, 52.6, 50.8, 22.8, 21.5. HRMS (ESI): m/z calcd for $C_{21}H_{24}NO_4S$ $[M+H]^+$ 386.1421, found 386.1426.



Methyl (*Z*)-4-(2-methoxybenzylidene)-3-methyl-1-tosylpyrrolidine-3-carboxylate (2c)

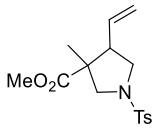
Prepared with protocol A. **2c** was obtained as a yellow oily liquid after flash chromatography (PE/EA = 8/1) (0.2 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.27–7.23 (m, 1H), 7.04 (dd, *J* = 7.6, 2.0 Hz, 1H), 6.96–6.92 (m, 1H), 6.87–6.85 (m, 1H), 6.69 (t, *J* = 2.4 Hz, 1H), 4.17 (dd, *J* = 14.0, 2.0 Hz, 1H), 4.08 (dd, *J* = 14.0, 2.8 Hz, 1H), 3.83–3.80 (m, 4H), 3.61 (s, 3H), 3.15 (d, *J* = 9.6 Hz, 1H), 2.43 (s, 4H), 1.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 156.8, 143.6, 139.0, 133.1, 129.7, 129.0, 128.7, 127.8, 124.9, 120.4, 119.6, 110.6, 56.6, 55.5, 53.1, 52.6, 50.8, 22.7, 21.5. HRMS (ESI): m/z calcd for $C_{22}H_{26}NO_5S$ $[M+H]^+$ 416.1526, found 416.1531.



Methyl (*Z*)-3-methyl-4-(4-methylbenzylidene)-1-tosylpyrrolidine-3-carboxylate (2d)

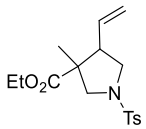
Prepared with protocol A. **2d** was obtained as a colorless oil after flash chromatography (PE/EA = 8/1) (0.2 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0

Hz, 2H), 6.39 (t, *J* = 2.4 Hz, 1H), 4.25 (dd, *J* = 14.4, 2.4 Hz, 1H), 4.13 (dd, *J* = 14.0, 2.4 Hz, 1H), 3.81 (d, *J* = 9.6 Hz, 1H), 3.61 (s, 3H), 3.13 (d, *J* = 9.6 Hz, 1H), 2.42 (s, 3H), 2.35 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 143.7, 138.2, 137.4, 133.0, 132.9, 129.7, 129.2, 128.2, 127.8, 124.3, 56.4, 53.1, 52.6, 50.8, 22.8, 21.5, 21.1. HRMS (ESI): m/z calcd for $C_{22}H_{26}NO_4S$ $[M+H]^+$ 400.1577, found 400.1580.



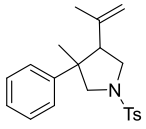
Methyl 3-methyl-1-tosyl-4-vinylpyrrolidine-3-carboxylate (**2e**)

Prepared with protocol A. **2e** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 85%, dr = 1/0.86). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.70 (m, 3.72H), 7.33 (d, *J* = 8.0 Hz, 3.72H), 5.63–5.54 (m, 0.86H), 5.46–5.37 (m, 1H), 5.12–5.01 (m, 3.72H), 3.68 (d, *J* = 10.4 Hz, 1H), 3.64–3.57 (m, 4.86H), 3.48 (dd, *J* = 9.6, 7.6 Hz, 0.86H), 3.40 (s, 2.58H), 3.28–3.09 (m, 3.72H), 3.04 (dd, *J* = 16.0, 7.6 Hz, 0.86H), 2.58 (dd, *J* = 15.6, 7.8 Hz, 1H), 2.43 (s, 5.58H), 1.20 (s, 3H), 1.00 (s, 2.58H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 173.5, 143.6, 143.4, 134.1, 133.8, 133.3, 133.2, 129.7, 129.6, 127.5, 127.4, 118.7, 118.6, 57.0, 56.0, 52.4, 52.3, 52.2, 51.7, 51.4, 51.3, 50.3, 48.4, 21.7, 21.5, 21.48, 17.2. HRMS (ESI): m/z calcd for $C_{16}H_{22}NO_4S$ $[M+H]^+$ 324.1264, found 324.1270.



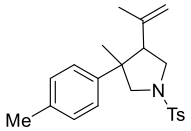
Ethyl 3-methyl-1-tosyl-4-vinylpyrrolidine-3-carboxylate (**2f**)

Prepared with protocol A. **2f** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 87%, dr = 1/0.72). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.69 (m, 3.44H), 7.31 (d, *J* = 8.4 Hz, 3.44H), 5.62–5.53 (m, 0.72H), 5.48–5.39 (m, 1H), 5.10–4.99 (m, 3.44H), 4.09–3.83 (m, 3.44H), 3.73–3.57 (m, 2.72H), 3.48 (dd, *J* = 10.0, 8.0 Hz, 0.72H), 3.27–3.08 (m, 3.44H), 3.03 (dd, *J* = 16.0, 7.6 Hz, 0.72H), 2.55 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.41 (s, 5.16H), 1.19–1.14 (m, 5.16H), 1.05 (t, *J* = 7.2 Hz, 3H), 0.97 (s, 2.16H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 172.9, 143.5, 143.4, 134.1, 133.8, 133.3, 133.2, 129.6, 129.5, 127.4, 127.36, 118.5, 118.47, 61.1, 60.7, 57.0, 55.9, 52.3, 52.0, 51.4, 51.2, 50.3, 48.3, 21.8, 21.4, 21.42, 17.1, 14.0, 13.95. HRMS (ESI): m/z calcd for $C_{17}H_{24}NO_4S$ $[M+H]^+$ 338.1421, found 338.1423.



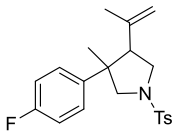
3-Methyl-3-phenyl-4-(prop-1-en-2-yl)-1-tosylpyrrolidine (**2g**)

Prepared with protocol A. **2g** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 96%, dr = 1/0.55). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.76 (m, 3.1H), 7.36 (d, *J* = 8.0 Hz, 3.1H), 7.28–7.26 (m, 4H), 7.23–7.17 (m, 2.75H), 7.14–7.12 (m, 1H), 4.79 (s, 1H), 4.66 (t, *J* = 1.6 Hz, 0.55H), 4.54 (s, 1.55H), 3.89 (d, *J* = 9.6 Hz, 0.55H), 3.66–3.60 (m, 2.55H), 3.46 (t, *J* = 10.0 Hz, 1H), 3.41–3.30 (m, 2.1H), 2.98 (t, *J* = 8.8 Hz, 1H), 2.66 (t, *J* = 7.6 Hz, 0.55H), 2.46–2.45 (m, 4.65H), 1.31 (s, 1.65H), 1.23 (s, 3H), 1.09 (s, 3H), 0.97 (s, 1.65H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 143.4, 142.8, 142.5, 141.2, 134.2, 134.1, 129.7, 129.66, 128.3, 127.9, 127.3, 127.31, 126.6, 126.56, 126.4, 126.0, 115.0, 112.9, 62.3, 59.0, 55.8, 54.7, 50.7, 50.1, 48.6, 47.2, 28.0, 26.8, 23.6, 21.5, 21.48, 20.4, 19.1. HRMS (ESI): m/z calcd for $C_{21}H_{26}NO_2S$ $[M+H]^+$ 356.1679, found 356.1685.



3-Methyl-4-(prop-1-en-2-yl)-3-(p-tolyl)-1-tosylpyrrolidine (**2h**)

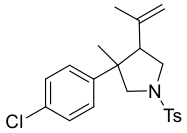
Prepared with protocol A. **2h** was obtained as a colorless oil after flash chromatography (PE/EA = 20/1) (0.2 mmol, 99%, dr = 1/0.52). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.76 (m, 3.04H), 7.36 (d, *J* = 8.0 Hz, 3.04H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.02 (s, 2.08H), 4.79 (s, 1H), 4.67 (t, *J* = 1.6 Hz, 0.52H), 4.54 (s, 1.52H), 3.87 (d, *J* = 9.6 Hz, 0.52H), 3.65–3.59 (m, 2.52H), 3.46 (t, *J* = 10.0 Hz, 1H), 3.39–3.30 (m, 2.04H), 2.96 (t, *J* = 8.8 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 0.52H), 2.46 (s, 3H), 2.45 (s, 1.56H), 2.30 (s, 3H), 2.29 (s, 1.56H), 1.29 (s, 1.56H), 1.25 (s, 3H), 1.07 (s, 3H), 1.00 (s, 1.56H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 142.6, 141.3, 141.2, 139.7, 136.1, 135.9, 134.3, 134.2, 129.7, 129.6, 129.0, 128.6, 127.34, 127.3, 126.5, 125.9, 114.8, 112.7, 62.3, 59.1, 55.8, 54.6, 50.7, 50.1, 48.3, 46.9, 28.0, 23.6, 21.5, 20.8, 20.75, 20.5, 19.1. HRMS (ESI): m/z calcd for $C_{22}H_{28}NO_2S$ $[M+H]^+$ 370.1835, found 370.1839.



3-(4-Fluorophenyl)-3-methyl-4-(prop-1-en-2-yl)-1-tosylpyrrolidine (**2i**)

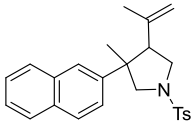
Prepared with protocol A. **2i** was obtained as a colorless oil after flash chromatography (PE/EA = 20/1) (0.2 mmol, 98%, dr = 1/0.58). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.75 (m, 3.16H), 7.36 (d, *J* = 8.0 Hz, 3.16H), 7.27–7.22 (m, 2H), 7.14–7.10 (m, 1.16H), 6.98 – 6.88 (m, 3.16H), 4.80 (s, 1H), 4.69 (t, *J* = 1.2 Hz, 0.58H), 4.53 (s, 1.58H), 3.85 (d, *J* = 9.6 Hz, 0.58H), 3.64–3.58 (m, 2.58H), 3.44 (t, *J* = 10.0 Hz, 1H), 3.37–3.34 (m, 1.58H), 3.30 (dd, *J* = 10.4, 8.0 Hz, 0.58H), 2.93 (t, *J* =

8.8 Hz, 1H), 2.62 (t, J = 8.0 Hz, 0.58H), 2.46 (s, 3H), 2.45 (s, 1.74H),1.30 (s, 1.74H), 1.25 (s, 3H), 1.07 (s, 3H), 1.01 (s, 1.74H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, $J_{C\text{-}F}$ = 244.4 Hz), 143.5, 143.51, 142.1, 141.0, 140.1(d, $J_{C\text{-}F}$ = 3.2 Hz), 138.5 (d, $J_{C\text{-}F}$ = 3.3 Hz), 134.1, 134.06, 129.7, 129.69, 128.2 (d, $J_{C\text{-}F}$ = 7.7 Hz), 127.7 (d, $J_{C\text{-}F}$ = 7.9 Hz), 127.3, 127.31, 115.2, 115.1 (d, $J_{C\text{-}F}$ = 20.8 Hz) 114.7 (d, $J_{C\text{-}F}$ = 21 Hz), 113.1, 62.2, 59.2, 55.8, 54.9, 50.5, 50.1, 48.2, 46.9, 29.6, 27.9, 23.6, 21.5, 20.6, 19.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.3. HRMS (ESI): m/z calcd for $C_{21}H_{25}FNO_2S$ $[M+H]^+$ 374.1585, found 374.1588.



3-(4-Chlorophenyl)-3-methyl-4-(prop-1-en-2-yl)-1-tosylpyrrolidine (2j)

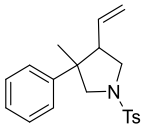
Prepared with protocol A. **2j** was obtained as a white solid after flash chromatography (PE/EA = 20/1) (0.2 mmol, 99%, dr = 1/0.55). mp 150–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.75 (m, 3.1H), 7.36 (d, J = 8.0 Hz, 3.1H), 7.27–7.17 (m, 5.1H), 7.09–7.07 (m, 1.1H), 4.81 (s, 1H), 4.69 (t, J = 1.2 Hz, 0.55H), 4.54 (s, 1.55H), 3.83 (d, J = 9.6 Hz, 0.55H), 3.65–3.57 (m, 2.55H), 3.44 (t, J = 10.0 Hz, 1H), 3.38–3.28 (m, 2.1H), 2.93 (t, J = 8.8 Hz, 1H), 2.64 (t, J = 7.6 Hz, 0.55H), 2.46 (s, 3H), 2.45 (s, 1.65H), 1.29 (s, 1.65H), 1.26 (s, 3H), 1.07 (s, 3H), 1.02 (s, 1.65H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 143.1, 142.0, 141.3, 140.9, 134.1, 134.0, 132.4, 132.3, 129.7, 129.69, 128.4, 128.1, 128.0, 127.5, 127.33, 127.3, 115.3, 113.2, 62.1, 59.0, 55.7, 54.8, 50.5, 50.1, 48.3, 47.0, 27.9, 23.6, 21.5, 20.6, 19.2. HRMS (ESI): m/z calcd for $C_{21}H_{25}ClNO_2S$ $[M+H]^+$ 390.1289, found 390.1294.



3-Methyl-3-(naphthalen-2-yl)-4-(prop-1-en-2-yl)-1-tosylpyrrolidine (2k)

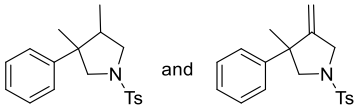
Prepared with protocol A. **2k** was obtained as a colorless oil after flash chromatography (PE/EA = 20/1) (0.2 mmol, 95%, dr = 1/0.32). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.85–7.65 (m, 7.6H), 7.53 (d, J = 1.6 Hz, 0.32H), 7.47–7.34 (m, 6.28H), 7.29 (dd, J = 8.4, 2.0 Hz, 0.32H), 4.80 (s, 1H), 4.64 (t, J = 1.6 Hz, 0.32H), 4.59 (s, 0.32H), 4.58 (s, 1H), 4.03 (d, J = 10.0 Hz, 0.32H), 3.75 (d, J = 10.4 Hz, 1H), 3.72–3.65 (m, 1.32H), 3.54–3.49 (m, 1.32H), 3.43–3.36 (m, 1.32H), 3.12 (t, J = 8.4 Hz,1H), 2.79 (t, J = 7.2 Hz, 0.32H), 2.45 (s, 3H), 2.44 (s, 0.96H), 1.37 (s, 0.96H), 1.23 (s, 3H), 1.19 (s, 3H), 1.00 (s, 0.96H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 142.7, 141.7, 141.3, 140.5, 134.4, 134.1, 133.0, 132.9, 132.0, 131.9, 129.7, 129.68, 128.1, 127.9, 127.4, 127.3, 127.28, 126.1, 125.9, 125.7, 125.5, 124.9, 124.7, 124.2, 115.1, 112.9,

62.0, 58.9, 55.8, 54.3, 50.9, 50.2, 48.9, 47.5, 28.5, 23.7, 21.5, 21.47, 20.6, 19.4. HRMS (ESI): m/z calcd for $C_{25}H_{28}NO_2S$ $[M+H]^+$ 406.1832, found 406.1839.



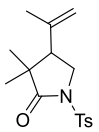
3-Methyl-3-phenyl-1-tosyl-4-vinylpyrrolidine (**2l**)

Prepared with protocol A. **2l** was obtained as a colorless oil after flash chromatography (PE/EA = 20/1) (0.2 mmol, 89%, dr = 1/0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.37–7.33 (m, 3H), 7.30–7.18 (m, 6.5H), 7.11–7.09 (m, 1H), 5.66–5.57 (m, 1H), 5.10–5.06 (m, 1H), 5.01 (t, *J* = 1.2 Hz, 0.5H), 4.96 (t, *J* = 1.2, 0.5 Hz, 1H), 4.95–4.92 (m, 1H), 4.89–4.85 (m, 0.5H), 3.83 (d, *J* = 9.6 Hz, 0.5H), 3.64–3.54 (m, 1.5H), 3.51 (s, 2H), 3.38 (d, *J* = 9.6 Hz, 0.5H), 3.30 (t, *J* = 9.6 Hz, 1H), 3.19 (dd, *J* = 10.0, 7.2 Hz, 0.5H), 2.94 (dd, *J* = 17.2, 8.0 Hz, 1H), 2.57–2.51 (m, 0.5H), 2.45 (s, 1.5H), 2.44 (s, 3H), 1.28 (s, 1.5H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 143.4, 142.4, 135.1, 134.3, 134.0, 133.9, 129.7, 129.66, 128.4, 128.0, 127.3, 127.31, 126.85, 126.6, 126.4, 125.7, 118.3, 117.5, 60.6, 58.6, 53.1, 51.5, 51.4, 50.9, 48.6, 47.7, 26.3, 21.5, 20.9. HRMS (ESI): m/z calcd for $C_{20}H_{24}NO_2S$ $[M+H]^+$ 342.1522, found 342.1530.



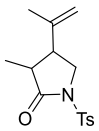
3,**4-Dimethyl-3-phenyl-1-tosylpyrrolidine** (**2m**) **and**
3-Methyl-4-methylene-3-phenyl-1-tosylpyrrolidine (**2m'**)

Prepared with protocol A. **2m** and **2m'** mixture were obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 35%, **2m**/**2m'** = 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.33–7.17 (m, 14H), 5.08 (t, *J* = 2.0 Hz, 1H), 4.88 (t, *J* = 2.4 Hz, 1H), 3.99–3.90 (m, 2H), 3.74 (d, *J* = 9.6 Hz, 1H), 3.57 (dd, *J* = 10.0, 8.0 Hz, 1H), 3.42 (s, 2H), 3.21 (d, *J* = 9.6 Hz, 1H), 3.03 (t, *J* = 10.0 Hz, 1H), 2.43–2.40 (m, 7H), 1.42 (s, 3H), 1.08 (s, 3H), 0.82 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 144.2, 144.1, 143.4, 143.3, 134.3, 133.1, 129.6, 129.58, 128.4, 128.37, 127.6, 127.4, 126.6, 126.5, 126.3, 125.8, 108.4, 61.3, 61.27, 53.4, 52.3, 50.2, 47.3, 42.0, 25.5, 21.52, 21.50, 19.2, 11.8. HRMS (ESI): m/z calcd for $C_{19}H_{24}NO_2S$ $[M+H]^+$ 330.1522, found 330.1525 (**2m**). HRMS (ESI): m/z calcd for $C_{19}H_{22}NO_2S$ $[M+H]^+$ 328.1366, found 328.1369 (**2m'**).



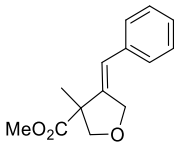
3,3-Dimethyl-4-(prop-1-en-2-yl)-1-tosylpyrrolidin-2-one (**2n**)

Prepared with protocol A. **2n** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.89 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.93 (t, *J* = 1.6 Hz, 1H), 4.73 (d, *J* = 0.8 Hz, 1H), 3.93 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.67 (dd, *J* = 10.0, 8.0 Hz, 1H), 2.60 (t, *J* = 7.6 Hz, 1H), 2.41 (s, 3H), 1.66 (s, 3H), 1.16 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 145.1, 140.8, 134.9, 129.6, 127.9, 114.3, 49.4, 47.1, 45.1, 24.4, 22.5, 21.6, 18.5. HRMS (ESI): m/z calcd for $C_{16}H_{22}NO_3S$ $[M+H]^+$ 308.1315, found 308.1316.



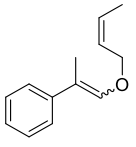
3-Methyl-4-(prop-1-en-2-yl)-1-tosylpyrrolidin-2-one (**2o**)

Prepared with protocol A. **2o** was obtained as a white solid after flash chromatography (PE/EA = 10/1) (0.2 mmol, 29%). mp 108–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.91 (m, 2H), 7.35–7.32 (m, 2H), 4.93–4.91 (m, 1H), 4.83 (d, *J* = 1.2 Hz, 1H), 4.03 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.44 (t, *J* = 10.0 Hz, 1H), 2.60–2.53 (m, 1H), 2.45–2.37 (m, 4H), 1.72 (s, 3H), 1.10 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 145.1, 140.9, 135.2, 129.7, 128.0, 113.8, 49.3, 47.8, 41.7, 21.7, 19.7, 13.3. HRMS (ESI): m/z calcd for $C_{15}H_{20}NO_3S$ $[M+H]^+$ 294.1158, found 294.1162.



Methyl (*Z*)-4-benzylidene-3-methyltetrahydrofuran-3-carboxylate (**2p**)

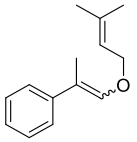
Prepared with protocol A. **2p** was obtained as a colorless oil after flash chromatography (PE/EA = 20/1) (0.2 mmol, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.34 (m, 2H), 7.25–7.22 (m, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.46 (t, *J* = 2.4 Hz, 1H), 4.79–4.69 (m, 2H), 4.41 (d, *J* = 8.8 Hz, 1H), 3.74 (s, 3H), 3.66 (d, *J* = 8.4 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 144.2, 136.7, 128.6, 128.2, 127.1, 122.3, 76.8, 70.7, 53.9, 52.6, 22.3. HRMS (ESI): m/z calcd for $C_{14}H_{17}O_3$ $[M+H]^+$ 233.1172, found 233.1178.



4-Ethylidene-3-methyl-3-phenyltetrahydrofuran (**2q**)

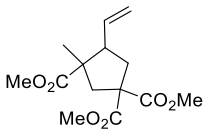
Prepared with protocol A. **2q** was obtained as a colorless oil after flash chromatography (PE/EA = 40/1) (0.2 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 0.54H), 7.30–7.21 (m, 4.54H), 7.15–7.12 (m, 1.27H), 6.46 (d, *J* =

1.2 Hz, 1H), 6.16 (s, 0.27H), 5.80–5.68 (m, 1.27H), 5.66–5.57 (m, 1.27H), 4.40 (dd, *J* = 14.8, 6.4 Hz, 0.54H), 4.25 (dd, *J* = 15.2, 6.4 Hz, 2H), 1.97 (d, *J* = 0.8 Hz, 3H), 1.88 (d, *J* = 0.8 Hz, 0.81H), 1.70 (d, *J* = 6.4 Hz, 4.81H); 13C NMR (101 MHz, $CDCl_3$) δ 143.4, 142.9, 140.8, 138.4, 130.23, 129.98, 128.3, 127.8, 127.4, 126.89, 126.86, 125.85, 125.76, 125.0, 114.7, 114.3, 73.2, 72.9, 18.4, 17.8, 13.3, 12.7. HRMS (ESI): m/z calcd for $C_{13}H_{17}O$ $[M + H]^+$ 189.1274, found 189.1276.



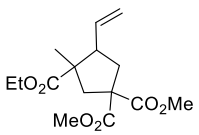
(1-((3-Methylbut-2-en-1-yl)oxy)prop-1-en-2-yl)benzene (**2r**)

Prepared with protocol A. **2r** was obtained as a colorless oil after flash chromatography (PE/EA = 40/1) (0.2 mmol, 77%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.66–7.63 (m, 0.94H), 7.33–7.26 (m, 4.94H), 7.19–7.15 (m, 1.47H), 6.51 (dd, *J* = 2.4, 1.2 Hz, 1H), 6.20 (d, *J* = 2.8, 1.6 Hz, 0.47H), 5.44–5.40 (m, 1.47H), 4.38 (d, *J* = 6.8 Hz, 2H), 4.34 (d, *J* = 6.8 Hz, 0.94H), 2.00 (d, *J* = 1.2 Hz, 3H), 1.92 (d, *J* = 1.6 Hz, 1.41H), 1.78–1.77 (m, 4.41H), 1.73–1.71 (m, 4.41H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 143.1, 140.9, 138.5, 137.9, 137.6, 128.3, 127.8, 127.4, 125.8, 125.7, 124.9, 120.5, 120.4, 114.4, 110.5, 69.1, 68.8, 25.8, 25.79, 18.4, 18.2, 12.7. HRMS (ESI): m/z calcd for $C_{14}H_{19}O$ $[M+H]^+$ 203.1430, found 203.1426.



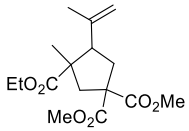
Trimethyl 3-methyl-4-vinylcyclopentane-1,1,3-tricarboxylate (**2s**)

Prepared with protocol A. **2s** was obtained as a colorless oil after flash chromatography (PE/EA = 12/1) (0.2 mmol, 92%, dr = 1/0.8). ^1H NMR (400 MHz, $CDCl_3$) δ 5.77–5.68 (m, 0.8H), 5.65–5.56 (m, 1H), 5.08–5.02 (m, 3.6H), 3.73–3.71 (m, 10.8H), 3.66 (s, 2.4H), 3.58 (s, 3H), 3.08–3.01 (m, 0.8H), 2.91 (d, *J* = 14.4 Hz, 1H), 2.82 (d, *J* = 14.0 Hz, 0.8H), 2.56–2.46 (m, 2.8H), 2.39–2.31 (m, 1.8H), 2.25–2.14 (m, 1.8H), 1.26 (s, 3H), 1.07 (s, 2.4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 175.6, 173.4, 172.4, 172.0, 135.9, 135.7, 117.0, 116.8, 58.6, 57.8, 54.6, 52.9, 52.93, 52.87, 52.85, 52.7, 52.0, 51.9, 51.5, 49.7, 44.8, 44.7, 38.8, 37.4, 22.7, 18.9. HRMS (ESI): m/z calcd for $C_{14}H_{21}O_6$ $[M+H]^+$ 285.1333, found 285.1336.



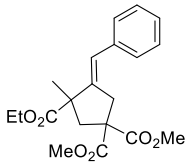
3-Ethyl 1,1-dimethyl 3-methyl-4-vinylcyclopentane-1,1,3-tricarboxylate (**2t**)

Prepared with protocol A. **2t** was obtained as a colorless oil after flash chromatography (PE/EA = 12/1) (0.2 mmol, 84%, dr = 1/0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77–5.59 (m, 1.5H), 5.08–5.02 (m, 3H), 4.14–4.01 (m, 3H), 3.73–3.71 (m, 9H), 3.08–3.01 (m, 0.5H), 2.92 (d, *J* = 14.4 Hz, 1H), 2.83 (d, *J* = 14.4 Hz, 0.5H), 2.58–2.47 (m, 2.5H), 2.36–2.31 (m, 1.5H), 2.25–2.14 (m, 1.5H), 1.26 (s, 3H), 1.24–1.17 (m, 4.5H), 1.07 (s, 1.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 175.1, 173.5, 172.5, 172.4, 172.0, 136.0, 135.7, 117.0, 116.7, 60.7, 60.5, 58.7, 57.8, 54.5, 52.9, 52.86, 52.8, 52.76, 52.7, 51.8, 49.6, 44.7, 44.67, 38.9, 37.5, 29.6, 22.8, 18.9, 14.1. HRMS (ESI): m/z calcd for $C_{15}H_{23}O_6$ $[M+H]^+$ 299.1489, found 299.1491.



3-Ethyl 1,1-dimethyl 3-methyl-4-(prop-1-en-2-yl)cyclopentane-1,1,3-tricarboxylate (2u)

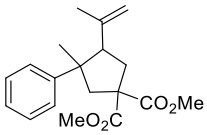
Prepared with protocol A. **2u** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 98%, dr = 1/0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (s, 0.5H), 4.82 (s, 1H), 4.74 (s, 1H), 4.69 (s, 0.5H), 4.13 (q, *J* = 14.4, 7.2 Hz, 1H), 4.01 (q, *J* = 14.4, 7.2 Hz, 2H), 3.74–3.71 (m, 9H), 3.16 (dd, *J* = 13.2, 6.0 Hz, 0.5H), 2.92 (d, *J* = 14.4 Hz, 1H), 2.81 (d, *J* = 14.0 Hz, 0.5H), 2.72 (t, *J* = 13.2 Hz, 1H), 2.55–2.47 (m, 1.5H), 2.35–2.23 (m, 3H), 1.69 (s, 3H), 1.59 (s, 1.5H), 1.36 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 1.5H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.01 (s, 1.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 175.5, 173.5, 172.4, 172.3, 172.0, 142.7, 142.3, 112.7, 112.3, 60.8, 60.5, 58.1, 57.6, 56.4, 52.9, 52.8, 52.81, 52.6, 52.3, 52.1, 50.3, 46.5, 45.2, 38.3, 36.8, 24.3, 23.0, 22.4, 18.5, 14.0, 13.96. HRMS (ESI): m/z calcd for $C_{16}H_{25}O_6$ $[M+H]^+$ 313.1646, found 313.1647.



3-Ethyl 1,1-dimethyl (*E*)-4-Benzylidene-3-methylcyclopentane-1,1,3-tricarboxylate (2v)

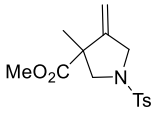
Prepared with protocol A. **2v** was obtained as a colorless oil after flash chromatography (PE/EA = 15/1) (0.2 mmol, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.28 (m, 4H), 7.24–7.21 (m, 1H), 6.44 (t, *J* = 2.4 Hz, 1H), 4.12 (q, *J* = 14.0, 7.2 Hz, 2H), 3.75 (s, 3H), 3.70 (s, 3H), 3.49 (dd, *J* = 17.2, 2.8 Hz, 1H), 3.23 (dd, *J* = 17.2, 2.0 Hz, 1H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.41 (d, *J* = 14.0 Hz, 1H), 1.48 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 172.2, 171.7, 144.4, 137.2,

128.6, 128.3, 126.8, 124.4, 61.2, 58.9, 53.6, 53.0, 52.9, 43.7, 38.8, 24.8, 14.0. HRMS (ESI): m/z calcd for $C_{20}H_{25}O_6$ $[M + H]^+$ 361.1646, found 356.1654.



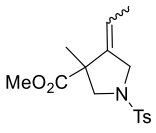
Dimethyl 3-methyl-3-phenyl-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarboxylate (2w)

Prepared with protocol A. **2w** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 99%, dr = 1/0.64). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.45 (m, 1.28H), 7.33–7.29 (m, 1.28H), 7.26–7.16 (m, 5.64H), 4.77 (s, 0.64H), 4.68 (t, *J* = 1.6 Hz, 1H), 4.62 (s, 1.64H), 3.79–3.76 (m, 9.84H), 3.06–2.99 (m, 1.64H), 2.87 (d, *J* = 14.8 Hz, 0.64H), 2.72–2.65 (m, 2.64H), 2.50–2.42 (m, 3.28H), 1.53 (s, 3H), 1.23 (s, 1.92H), 1.17 (s, 1.92H), 1.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 173.3, 173.0, 172.6, 148.0, 145.9, 144.0, 143.4, 128.1, 127.6, 127.1, 126.3, 125.9, 125.8, 113.3, 111.7, 58.3, 57.3, 57.0, 56.4, 52.9, 52.8, 52.76, 51.3, 49.0, 47.8, 47.6, 38.0, 37.6, 29.8, 23.6, 20.9, 20.4. HRMS (ESI): m/z calcd for $C_{21}H_{26}NO_2S$ $[M+H]^+$ 356.1679, found 356.1684.



Methyl 3-methyl-4-methylene-1-tosylpyrrolidine-3-carboxylate (4a)

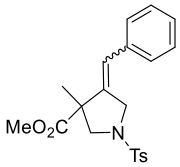
Prepared with protocol B. **4a** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.11 (t, *J* = 2.0 Hz, 1H), 5.05 (t, *J* = 2.0 Hz, 1H), 3.96 (dt, *J* = 13.6, 2.0 Hz, 1H), 3.83 (dt, *J* = 13.6, 2.4 Hz, 1H), 3.75 (d, *J* = 10 Hz, 1H), 3.59 (s, 3H), 3.16 (d, *J* = 9.6 Hz, 1H), 2.44 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 147.2, 143.8, 132.7, 129.7, 127.9, 109.0, 57.4, 52.6, 52.1, 52.08, 22.8, 21.5. HRMS (ESI): m/z calcd for $C_{15}H_{20}NO_4S$ $[M+H]^+$ 310.1108, found 310.1105.



Methyl 4-ethylidene-3-methyl-1-tosylpyrrolidine-3-carboxylate (4b)

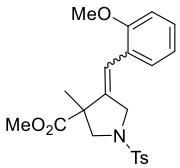
Prepared with protocol B. **4b** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 83%, *E*/*Z* = 1/0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.66 (m, 3H), 7.34–7.32 (m, 3H), 5.50–5.44 (m, 0.5H), 5.41–5.34 (m, 1H), 3.97–3.93 (m, 1.5H), 3.75–3.71 (m, 1H), 3.65–3.61 (m, 4H), 3.57 (s, 1.5H), 3.35 (d, *J* = 9.6 Hz, 1H), 3.29 (d, *J* = 9.2 Hz, 1H), 3.10 (d, *J* = 9.6 Hz, 0.5H), 2.43 (s, 4.5H),

1.56–1.54 (m, 1.5H), 1.52–1.49 (m, 3H), 1.42 (s, 3H), 1.34 (s, 1.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 173.8, 143.8, 143.7, 138.8, 138.7, 132.7, 131.9, 129.6, 129.63, 128.0, 127.8, 119.4, 119.2, 56.0, 57.4, 53.3, 52.4, 52.41, 51.8, 50.8, 49.5, 23.0, 21.8, 21.5, 14.6, 13.4. HRMS (ESI): m/z calcd for $C_{16}H_{22}NO_4S$ $[M+H]^+$ 324.1264, found 324.1271.



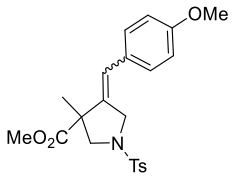
Methyl 4-benzylidene-3-methyl-1-tosylpyrrolidine-3-carboxylate (**4c**)

Prepared with protocol B. **4c** was obtained as a white solid after flash chromatography (PE/EA = 10/1) (0.2 mmol, 62%, *E*/*Z* = 1/0.1). mp 68–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.73 (m, 2.2H), 7.38–7.34 (m, 2.2H), 7.30–7.20 (m, 3.3H), 7.17 (d, *J* = 7.6 Hz, 0.2H), 7.07 (d, *J* = 7.2 Hz, 2H), 6.49 (s, 1H), 6.44 (t, *J* = 2.4 Hz, 0.1H), 4.27 (dd, *J* = 14.4, 2.4 Hz, 0.1H), 4.20–4.13 (m, 1.1H), 4.03 (dd, *J* = 13.6, 2.0 Hz, 1H), 3.83 (d, *J* = 9.6 Hz, 0.1H), 3.63 (s, 0.3H), 3.52 (d, *J* = 9.2 Hz, 1H), 3.33–3.31 (m, 4H), 3.16 (d, *J* = 9.6 Hz, 0.1H), 2.47 (s, 3H), 2.44 (s, 0.3H), 1.51 (s, 0.3H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 173.4, 143.8, 143.75, 140.0, 139.3, 135.8, 135.6, 132.9, 132.8, 129.7, 128.5, 128.3, 128.26, 128.0, 127.8, 127.78, 127.5, 127.3, 124.7, 124.5, 60.4, 56.4, 54.1, 53.2, 52.6, 52.2, 51.4, 50.8, 29.6, 22.9, 21.5. HRMS (ESI): m/z calcd for $C_{21}H_{24}NO_4S$ $[M+H]^+$ 386.1421, found 386.1423.

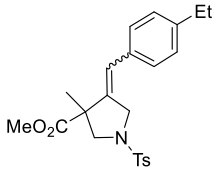


Methyl 4-(2-methoxybenzylidene)-3-methyl-1-tosylpyrrolidine-3-carboxylate (**4d**)

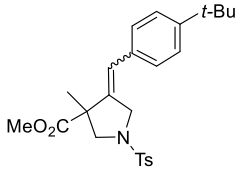
Prepared with protocol B. **4d** was obtained as a white solid after flash chromatography (PE/EA = 6/1) (0.2 mmol, 56%, *E*/*Z* = 1/0.12). mp 168–169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2.24H), 7.36–7.31 (m, 2.24H), 7.23–7.19 (m, 1.12H), 7.04 (dd, *J* = 7.6, 1.2 Hz, 0.12H), 6.97 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.82–6.79 (m, 1.24H), 6.69 (t, *J* = 3.2 Hz, 0.12H), 6.47 (s, 1H), 4.19–4.09 (m, 2.24H), 3.81 (d, *J* = 9.6 Hz, 0.12H), 3.79 (s, 0.36H), 3.76 (s, 3H), 3.60 (d, *J* = 3.6 Hz, 1H), 3.57 (s, 0.36H), 3.33 (s, 3H), 3.25 (d, *J* = 9.6 Hz, 1H), 3.15 (d, *J* = 9.6 Hz, 0.12H), 2.45 (s, 3H), 2.42 (s, 0.36H), 1.25 (s, 0.36H), 1.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 156.8, 143.7, 139.8, 133.3, 129.7, 129.65, 129.0, 127.7, 124.6, 120.8, 119.9, 110.1, 60.3, 55.3, 54.1, 52.1, 51.4, 21.5, 20.9. HRMS (ESI): m/z calcd for $C_{22}H_{26}NO_5S$ $[M+H]^+$ 416.1526, found 416.1531.



Methyl 4-(4-methoxybenzylidene)-3-methyl-1-tosylpyrrolidine-3-carboxylate (**4e**)
Prepared with protocol B. **4e** was obtained as a white solid after flash chromatography (PE/EA = 5/1) (0.2 mmol, 67%, *E*/*Z* = 1/0.18). mp 136–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.71 (m, 2.36H), 7.36–7.32 (m, 2.36H), 7.09 (d, *J* = 8.4 Hz, 0.36H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 0.36H), 6.81–6.77 (m, 2H), 6.39 (s, 1H), 6.35 (t, *J* = 2.4 Hz, 0.18H), 4.23 (dd, *J* = 14.0, 2.0 Hz, 0.18H), 4.15–4.09 (m, 1.18H), 3.99 (dd, *J* = 13.6, 2.0 Hz, 1H), 3.81–3.79 (m, 0.72H), 3.76 (s, 3H), 3.60 (s, 0.54H), 3.49 (d, *J* = 9.2 Hz, 1H), 3.35 (s, 3H), 3.29 (d, *J* = 9.6 Hz, 1H), 3.12 (d, *J* = 9.6 Hz, 0.18H), 2.44 (s, 3H), 2.42 (s, 0.54H), 1.47 (s, 0.54H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 173.6, 158.9, 158.7, 143.8, 143.7, 138.5, 136.9, 132.9, 132.7, 129.7, 129.67, 129.6, 128.6, 128.0, 127.8, 127.75, 124.3, 123.8, 114.0, 113.4, 60.5, 56.4, 55.2, 55.1, 54.2, 53.1, 52.6, 52.3, 51.3, 50.8, 22.8, 21.5, 21.3. HRMS (ESI): m/z calcd for $C_{22}H_{26}NO_5S$ $[M+H]^+$ 416.1526, found 416.1529.

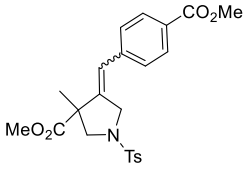


Methyl 4-(4-ethylbenzylidene)-3-methyl-1-tosylpyrrolidine-3-carboxylate (**4f**)
Prepared with protocol B. **4f** was obtained as a white solid after flash chromatography (PE/EA = 8/1) (0.2 mmol, 62%, *E*/*Z* = 47/4). mp 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.44 (s, 1H), 4.18–4.14 (m, 1H), 4.02–3.99 (m, 1H), 3.49 (d, *J* = 9.6 Hz, 1H), 3.32–3.30 (m, 4H), 2.60 (q, *J* =15.2, 7.6 Hz, 2H), 2.45 (s, 3H), 1.33 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 143.8, 143.5, 139.3, 132.9, 132.85, 129.7, 128.3, 127.8, 127.5, 124.7, 60.5, 54.2, 52.2, 51.4, 28.5, 21.5, 21.48, 15.4. HRMS (ESI): m/z calcd for $C_{23}H_{28}NO_4S$ $[M+H]^+$ 414.1734, found 414.1739.



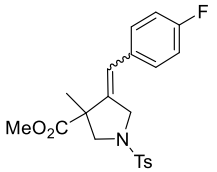
Methyl 4-(4-(*tert*-butyl)benzylidene)-3-methyl-1-tosylpyrrolidine-3-carboxylate (**4g**)

Prepared with protocol B. **4g** was obtained as a colorless oil after flash chromatography (PE/EA = 7/1) (0.2 mmol, 44%, *E*/*Z* = 7.7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.43 (s, 1H), 4.17 (dd, *J* = 13.6, 2.0 Hz, 1H), 4.00 (dd, *J* = 13.6, 2.0 Hz, 1H), 3.48 (d, *J* = 9.2 Hz, 1H), 3.32 (d, *J* = 9.6 Hz, 1H), 3.28 (s, 3H), 2.45 (s, 3H), 1.35 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 150.4, 143.8, 139.4, 132.9, 132.6, 129.7, 128.0, 127.8, 124.9, 124.6, 60.5, 54.2, 52.2, 51.4, 34.5, 31.2, 21.6. HRMS (ESI): m/z calcd for $C_{25}H_{32}NO_4S$ $[M+H]^+$ 442.2047, found 442.2051.



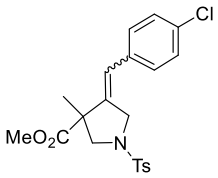
Methyl 4-(4-(methoxycarbonyl)benzylidene)-3-methyl-1-tosylpyrrolidine-3-carboxylate (4h)

Prepared with protocol B. **4h** was obtained as a white solid after flash chromatography (PE/EA = 5/1) (0.2 mmol, 66%, *E*/*Z* = 1/0.13). mp 130–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.48 (s, 1H), 4.17 (dd, *J* = 14.0, 2.0 Hz, 1H), 4.03 (dd, *J* = 14.0, 2.0 Hz, 1H), 3.89 (s, 3H), 3.51 (d, *J* = 9.2 Hz, 1H), 3.33 (s, 3H), 3.30 (d, *J* = 9.6 Hz, 1H), 2.45 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 166.6, 144.0, 141.9, 140.3, 132.7, 129.8, 129.4, 129.0, 128.3, 127.8, 123.8, 60.4, 54.2, 52.4, 52.1, 51.6, 21.6, 21.5. HRMS (ESI): m/z calcd for $C_{23}H_{26}NO_6S$ $[M+H]^+$ 444.1475, found 444.1480.



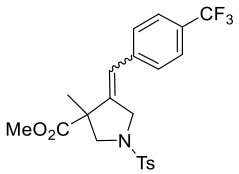
Methyl 4-(4-fluorobenzylidene)-3-methyl-1-tosylpyrrolidine-3-carboxylate (4i)

Prepared with protocol B. **4i** was obtained as a white solid after flash chromatography (PE/EA = 7/1) (0.2 mmol, 70%, *E*/*Z* = 56/5). mp 139–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.04–7.01 (m, 2H), 6.97–6.92 (m, 2H), 6.41 (s, 1H), 4.16–4.12 (m, 1H), 4.02–3.98 (m, 1H), 3.51 (d, *J* = 9.2 Hz, 1H), 3.34 (s, 3H), 3.28 (d, *J* = 9.2 Hz, 1H), 2.44 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 161.9 (d, $J_{C\text{-}F}$ = 245.8 Hz), 143.9, 140.3, 132.7, 131.6, (d, $J_{C\text{-}F}$ = 3.5 Hz), 130.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.7, 127.8, 123.7, 115.0 (d, $J_{C\text{-}F}$ = 21.3 Hz), 60.4, 54.1, 52.3, 51.4, 21.5, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.2. HRMS (ESI): m/z calcd for $C_{21}H_{23}FNO_4S$ $[M+H]^+$ 404.1326, found 404.1330.



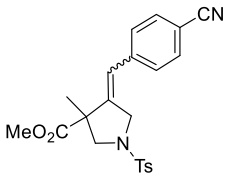
Methyl 4-(4-chlorobenzylidene)-3-methyl-1-tosylpyrrolidine-3-carboxylate (**4j**)

Prepared with protocol B. **4j** was obtained as a white solid after flash chromatography (PE/EA = 7/1) (0.2 mmol, 69%, *E*/*Z* = 43/15). mp 137–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.70 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.25–7.21 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.40 (s, 1H), 4.16–4.12 (m, 1H), 4.02–3.98 (m, 1H), 3.51 (d, *J* = 9.2 Hz, 1H), 3.35 (s, 3H), 3.28 (d, *J* = 9.2 Hz, 1H), 2.44 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 143.9, 140.8, 134.0, 133.2, 132.7, 129.7, 129.65, 128.2, 127.8, 123.5, 60.4, 54.1, 52.3, 51.5, 21.5, 21.4. HRMS (ESI): m/z calcd for $C_{21}H_{23}ClNO_4S$ $[M+H]^+$ 420.1031, found 420.1034.



Methyl 3-methyl-1-tosyl-4-(4-(trifluoromethyl)benzylidene)pyrrolidine-3-carboxylate (**4k**)

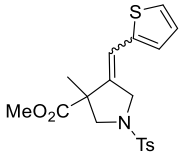
Prepared with protocol B. **4k** was obtained as a white solid after flash chromatography (PE/EA = 7/1) (0.2 mmol, 71%, *E*/*Z* = 55/9). mp 126–127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.48 (s, 1H), 4.19–4.15 (m, 1H), 4.05–4.01 (m, 1H), 3.53 (d, *J* = 9.6 Hz, 1H), 3.33 (s, 3H), 3.29 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 144.0, 142.1, 139.2, 132.7, 129.8, 129.4 (q, $J_{C\text{-}F}$ = 32.3 Hz), 128.7, 127.8, 125.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.9 (q, $J_{C\text{-}F}$ = 270.4 Hz), 123.4, 60.3, 54.1, 52.3, 51.6, 21.5, 21.48; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. HRMS (ESI): m/z calcd for $C_{22}H_{23}F_3NO_4S$ $[M+H]^+$ 454.1294, found 454.1302.



Methyl 4-(4-cyanobenzylidene)-3-methyl-1-tosylpyrrolidine-3-carboxylate (**4l**)

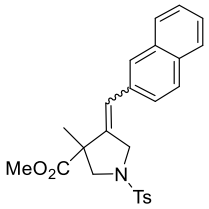
Prepared with protocol B. **4l** was obtained as a white solid after flash chromatography (PE/EA = 5/1) (0.2 mmol, 56%, *E*/*Z* = 40/6). mp 161–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.70 (m, 2H), 7.57–7.55 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.45 (s, 1H), 4.18–4.14 (m, 1H), 4.05–4.01 (m, 1H), 3.53 (d, *J* = 9.6 Hz,

1H), 3.36 (s, 3H), 3.28 (d, *J* = 9.6 Hz, 1H), 2.45 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 144.0, 143.0, 140.3, 132.6, 131.8, 129.8, 129.0, 127.8, 123.1, 118.5, 111.0, 60.3, 54.2, 52.4, 51.7, 21.5, 21.4. HRMS (ESI): m/z calcd for $C_{22}H_{23}N_2O_4S$ $[M+H]^+$ 411.1373, found 411.1378.



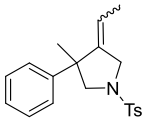
Methyl 3-methyl-4-(thiophen-2-ylmethylene)-1-tosylpyrrolidine-3-carboxylate (4m)

Prepared with protocol B. **4m** was obtained as a colorless oil after flash chromatography (PE/EA = 7/1) (0.2 mmol, 47%, *E*/*Z* = 1/0.26). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 0.52 H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.36–7.33 (m, 2.78H), 7.23 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.05–7.03 (m, 0.26H), 6.95–6.93 (m, 1.26H), 6.80 (d, *J* = 3.2 Hz, 1H), 6.63 (t, *J* = 2.4 Hz, 0.26 H), 6.46 (s, 1H), 4.25–4.21 (m, 0.26 H), 4.18–4.14 (m, 1H), 4.08–4.04 (m, 0.26 H), 3.94–3.90 (m, 1H), 3.83 (d, *J* = 9.6 Hz, 0.26H), 3.64 (s, 0.78 H), 3.48 (s, 3H), 3.40–3.35 (m, 2H), 3.14 (d, *J* = 9.6 Hz, 0.26 H), 2.45 (s, 3H), 2.43 (s, 0.78 H), 1.49 (s, 3H), 1.47 (s, 0.78H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 144.0, 139.9, 137.6, 132.2, 129.8, 127.9, 127.4, 127.2, 126.0, 116.8, 60.7, 54.5, 52.5, 51.6, 21.5, 20.9. HRMS (ESI): m/z calcd for $C_{19}H_{22}NO_4S_2$ $[M+H]^+$ 392.0985, found 392.0988.



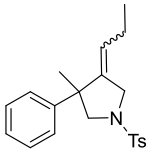
Methyl 3-methyl-4-(naphthalen-2-ylmethylene)-1-tosylpyrrolidine-3-carboxylate (4n)

Prepared with protocol B. **4n** was obtained as a colorless oil after flash chromatography (PE/EA = 7/1) (0.2 mmol, 53%, *E*/*Z* = 38/8). mp 137–139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.73 (m, 5H), 7.52 (s, 1H), 7.48–7.43 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.62 (s, 1H), 4.25–4.21 (m, 1H), 4.10–4.06 (m, 1H), 3.53 (d, *J* = 9.2 Hz, 1H), 3.34 (d, *J* = 9.6 Hz, 1H), 3.25 (s, 3H), 2.46 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 143.9, 140.4, 133.1, 132.9, 132.8, 132.3, 129.8, 127.9, 127.8, 127.6, 127.5, 127.3, 126.3, 126.27, 126.2, 124.7, 60.5, 54.3, 52.2, 51.6, 21.6, 21.5. HRMS (ESI): m/z calcd for $C_{25}H_{26}NO_4S$ $[M+H]^+$ 436.1577, found 436.1581.



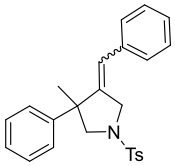
4-Ethylidene-3-methyl-3-phenyl-1-tosylpyrrolidine (**4o**)

Prepared with protocol B. **4o** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 90%, *E*/*Z* = 1/0.68). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.55 (m, 3.36H), 7.24–7.10 (m, 11.76H), 5.31 (dd, *J* = 14.4, 7.2 Hz, 1H), 5.18–5.13 (m, 0.68H), 4.00 (d, *J* = 12.8 Hz, 1H), 3.90 (d, *J* = 14.0 Hz, 0.68H), 3.79 (d, *J* = 14.0 Hz, 0.68H), 3.67 (d, *J* = 12.8 Hz, 1H), 3.62 (d, *J* = 9.2 Hz, 0.68H), 3.29 (d, *J* = 9.2 Hz, 1H), 3.09 (d, *J* = 9.2 Hz, 0.68H), 3.00 (d, *J* = 9.2 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 2.04H), 1.54 (s, 3H), 1.52 (dd, *J* = 6.8, 1.2 Hz, 2.04H), 1.34 (s, 2.04H), 1.08 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 144.6, 143.6, 143.4, 143.2, 142.8, 133.0, 131.9, 129.6, 128.4, 128.2, 128.0, 127.6, 126.4, 126.3, 118.5, 118.3, 65.1, 61.5, 54.3, 49.8, 49.7, 48.7, 25.6, 23.8, 21.5, 21.48, 14.4, 13.9. HRMS (ESI): m/z calcd for $C_{20}H_{24}NO_2S$ $[M+H]^+$ 342.1522, found 342.1523.



3-Methyl-3-phenyl-4-propylidene-1-tosylpyrrolidine (**4p**)

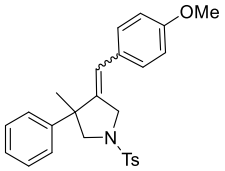
Prepared with protocol B. **4p** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 89%, *E*/*Z* = 1/0.54). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.62 (m, 3.08H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.27–7.23 (m, 7.24H), 7.21–7.16 (m, 1.54H), 5.28–5.23 (m, 1H), 5.19–5.15 (m, 0.54H), 4.08 (dd, *J* = 12.8, 1.2 Hz, 1H), 4.00–3.96 (m, 0.54H), 3.88–3.83 (m, 0.54H), 3.78–3.73 (m, 1H), 3.69 (d, *J* = 9.2 Hz, 0.54H), 3.35 (d, *J* = 9.2 Hz, 1H), 3.17 (d, *J* = 9.6 Hz, 0.54H), 3.07 (d, *J* = 9.2 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 1.62H), 2.00–1.93 (m, 1H), 1.61–1.51 (m, 4.08H), 1.50–1.44 (m, 1H), 1.42 (s, 1.62H), 0.94 (t, *J* = 7.6 Hz, 1.62H), 0.66 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 145.0, 143.6, 143.4, 141.6, 141.5, 133.1, 131.9, 129.6, 129.5, 128.3, 128.2, 128.0, 127.6, 126.4, 126.0, 125.8, 65.1, 61.4, 54.3, 49.7, 49.5, 48.9, 25.7, 24.4, 22.5, 21.6, 21.5, 21.47, 13.6, 13.3. HRMS (ESI): m/z calcd for $C_{21}H_{26}NO_2S$ $[M+H]^+$ 356.1679, found 356.1681.



4-Benzylidene-3-methyl-3-phenyl-1-tosylpyrrolidine (**4q**)

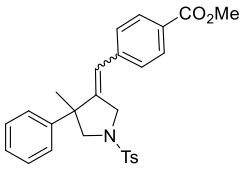
Prepared with protocol B. **4q** was obtained as a white solid after flash chromatography (PE/EA = 10/1) (0.2 mmol, 72%, *E*/*Z* = 1/0.73). mp 139–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.56 (m, 3.46H), 7.30–7.07 (m, 16.3H), 6.96–6.91

(m, 2.73H), 6.72–6.70 (m, 1.73H), 6.45 (s, 1H), 6.11 (t, *J* = 2.4 Hz, 0.73H), 4.22 (dd, *J* = 14.8, 2.4 Hz, 0.73H), 4.16 (dd, *J* = 14.8, 2.4 Hz, 0.73H), 4.10 (d, *J* = 2.0 Hz, 2H), 3.65 (d, *J* = 9.6 Hz, 0.73H), 3.34 (d, *J* = 9.2 Hz, 1H), 3.21 (d, *J* = 9.2 Hz, 1H), 3.16 (d, *J* = 9.6 Hz, 0.73H), 2.36 (s, 3H), 2.33 (s, 2.19H), 1.49 (s, 2.19H), 1.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 144.6, 144.4, 143.7, 143.6, 143.5, 136.2, 135.5, 133.1, 132.5, 129.7, 129.6, 128.8, 128.6, 128.4, 128.39, 128.3, 127.8, 127.6, 127.5, 127.2, 126.7, 126.6, 126.5, 126.4, 124.4, 124.1, 65.4, 60.3, 55.5, 51.4, 50.9, 49.6, 25.7, 23.2, 21.54, 21.5. HRMS (ESI): m/z calcd for $C_{25}H_{26}NO_2S$ $[M+H]^+$ 404.1679, found 404.1680.



4-(4-Methoxybenzylidene)-3-methyl-3-phenyl-1-tosylpyrrolidine (**4r**)

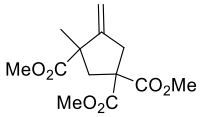
Prepared with protocol B. **4r** was obtained as a white solid after flash chromatography (PE/EA = 10/1) (0.2 mmol, 72%, *E*/*Z* = 1/0.23). mp 133–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.64 (m, 2.46H), 7.31–7.17 (m, 8.61H), 7.10 (d, *J* = 8.8 Hz, 0.46H), 6.90 (d, *J* = 8.8 Hz, 0.46H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 6.47 (s, 1H), 6.14 (s, 0.23H), 4.30–4.21 (m, 0.46H), 4.16 (d, *J* = 1.6 Hz, 2H), 3.82 (s, 0.69H), 3.74 (d, *J* = 9.2 Hz, 0.23H), 3.68 (s, 3H), 3.40 (d, *J* = 9.6 Hz, 1H), 3.29 (d, *J* = 9.6 Hz, 1H), 3.22 (d, *J* = 9.6 Hz, 0.23H), 2.43 (s, 3H), 2.41 (s, 0.69H), 1.56 (s, 0.69H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 158.3, 144.8, 143.5, 143.46, 141.9, 141.7, 133.1, 132.4, 130.1, 129.6, 129.56, 129.54, 129.0, 128.4, 128.36, 128.0, 127.8, 127.5, 126.6, 126.5, 126.48, 126.3, 123.9, 123.4, 114.0, 113.0, 65.4, 60.3, 55.6, 55.3, 55.0, 51.2, 50.9, 49.5, 25.6, 23.0, 21.5, 21.45. HRMS (ESI): m/z calcd for $C_{26}H_{28}NO_3S$ $[M+H]^+$ 434.1784, found 434.1788.



Methyl 4-((4-methyl-4-phenyl-1-tosylpyrrolidin-3-ylidene)methyl)benzoate (**4s**)

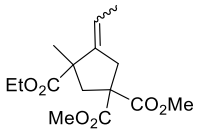
Prepared with protocol B. **4s** was obtained as a white solid after flash chromatography (PE/EA = 6/1) (0.2 mmol, 60%, *E*/*Z* = 1/0.18). mp 124–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 0.36H), 7.76–7.73 (m, 4.36H), 7.40–7.34 (m, 4.36H), 7.29–7.23 (m, 4.26H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.60 (s, 1H), 6.29 (t, *J* = 2.8 Hz, 0.18H), 4.36–4.23 (m, 2.36H), 4.01 (s, 0.54H), 3.92 (s, 3H), 3.81 (d, *J* = 9.2 Hz, 0.18H), 3.46 (d, *J* = 9.6 Hz, 1H), 3.39 (d, *J* = 9.6 Hz, 1H), 3.34 (d, *J* = 9.2 Hz, 0.18H), 2.53 (s, 3H), 2.49 (s, 0.54H), 1.67 (s, 0.54H), 1.57 (s, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 166.7, 146.4, 144.2, 143.7, 140.2, 132.4, 129.7, 128.8, 128.7, 128.5, 128.2, 127.9, 126.8, 126.3, 123.3, 65.3, 55.6, 52.0, 49.7, 23.2, 21.6. HRMS (ESI): m/z calcd for $C_{27}H_{28}NO_4S$ $[M+H]^+$ 462.1734, found 462.1738.



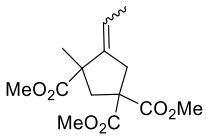
Trimethyl 3-methyl-4-methylenecyclopentane-1,1,3-tricarboxylate (**4t**)

Prepared with protocol B. **4t** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (t, *J* = 2.0 Hz, 1H), 5.01 (t, *J* = 2.0 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.63 (s, 3H), 3.21 (dt, *J* = 16.4, 2.4 Hz, 1H), 3.03 (d, *J* = 14.0 Hz, 1H), 2.91 (d, *J* = 16.4 Hz, 1H), 2.37 (d, *J* = 14.0 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 172.1, 171.6, 151.7, 109.2, 57.9, 52.9, 52.85, 52.4, 51.8, 44.6, 41.1, 24.7. HRMS (ESI): m/z calcd for $C_{13}H_{19}O_6$ $[M+H]^+$ 271.1176, found 271.1172.



3-Ethyl 1,1-dimethyl 4-ethylidene-3-methylcyclopentane-1,1,3-tricarboxylate (**4u**)

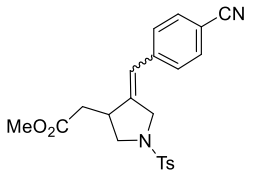
Prepared with protocol B. **4u** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 82%, *E*/*Z* = 1/0.73). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47–5.41 (m, 1.73H), 4.18–4.03 (m, 3.46H), 3.72–3.71 (m, 10.38H), 3.10–2.89 (m, 5.19H), 2.41 (d, *J* = 14 Hz, 1H), 2.31 (d, *J* = 14.0 Hz, 0.73H), 1.62 (d, *J* = 6.8 Hz, 2.19H), 1.52 (d, *J* = 7.2 Hz, 3H), 1.35 (s, 3H), 1.30 (s, 2.19H), 1.23–1.17 (m, 5.19H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 175.4, 172.4, 172.0, 171.8, 171.3, 142.8, 142.6, 119.5, 118.9, 60.9, 58.6, 58.1, 52.8, 52.7, 52.69, 51.9, 50.0, 47.5, 44.5, 42.6, 37.0, 24.9, 23.4, 14.7, 14.1, 14.0, 13.8. HRMS (ESI): m/z calcd for $C_{15}H_{23}O_6$ $[M+H]^+$ 299.1489, found 299.1490.



Trimethyl 4-ethylidene-3-methylcyclopentane-1,1,3-tricarboxylate (**4v**)

Prepared with protocol B. **4v** was obtained as a colorless oil after flash chromatography (PE/EA = 10/1) (0.2 mmol, 85%, *E*/*Z* = 1/0.72). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46–5.40 (m, 1.72H), 3.72–3.71 (m, 10.32H), 3.65 (s, 3H), 3.60 (s, 2.16H), 3.11–2.87 (m, 5.16H), 2.42 (dd, *J* = 13.6, 0.4 Hz, 1H), 2.31 (d, *J* = 14.0 Hz, 0.72H), 1.62 (dt, *J* = 6.8, 1.6 Hz, 2.16H), 1.51 (dt, *J* = 7.2, 2.0 Hz, 3H), 1.36 (s, 3H), 1.31 (s, 2.16H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 175.9, 172.3, 171.9, 171.8, 171.3, 142.7, 142.5, 119.6, 119.1, 58.6, 58.1, 52.8, 52.76, 52.7, 52.2, 52.1, 51.9, 49.9, 47.5,

44.6, 42.5, 36.9, 24.9, 23.4, 14.7, 13.6. HRMS (ESI): m/z calcd for $C_{14}H_{21}O_6$ $[M+H]^+$ 285.1333, found 285.1335.



Methyl 2-(4-(4-cyanobenzylidene)-1-tosylpyrrolidin-3-yl)acetate (4w)

Prepared with protocol B. **4w** was obtained as a white solid after flash chromatography (PE/EA = 3/1) (0.2 mmol, 60%, *E*/*Z* = 27/16). mp 157–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.70 (m, 2H), 7.64–7.61 (m, 2H), 7.34–7.32 (m, 2H), 7.22–7.19 (m, 2H), 6.32–6.30 (m, 1H), 4.18–4.13 (m, 1H), 4.02 (dd, *J* = 2.4 Hz, *J* = 15.2 Hz, 1H), 3.69 (s, 3H), 3.48–3.44 (m, 1H), 3.29–3.23 (m, 1H), 3.14–3.10 (m, 1H), 2.65–2.60 (m, 1H), 2.53–2.47 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 144.0, 143.3, 140.5, 132.5, 132.4, 129.9, 128.6, 127.8, 122.3, 118.6, 110.7, 51.9, 50.5, 41.2, 37.6, 21.5. HRMS (ESI): m/z calcd for $C_{22}H_{23}N_2O_4S$ $[M+H]^+$ 411.1373, found 411.1370.

8. References

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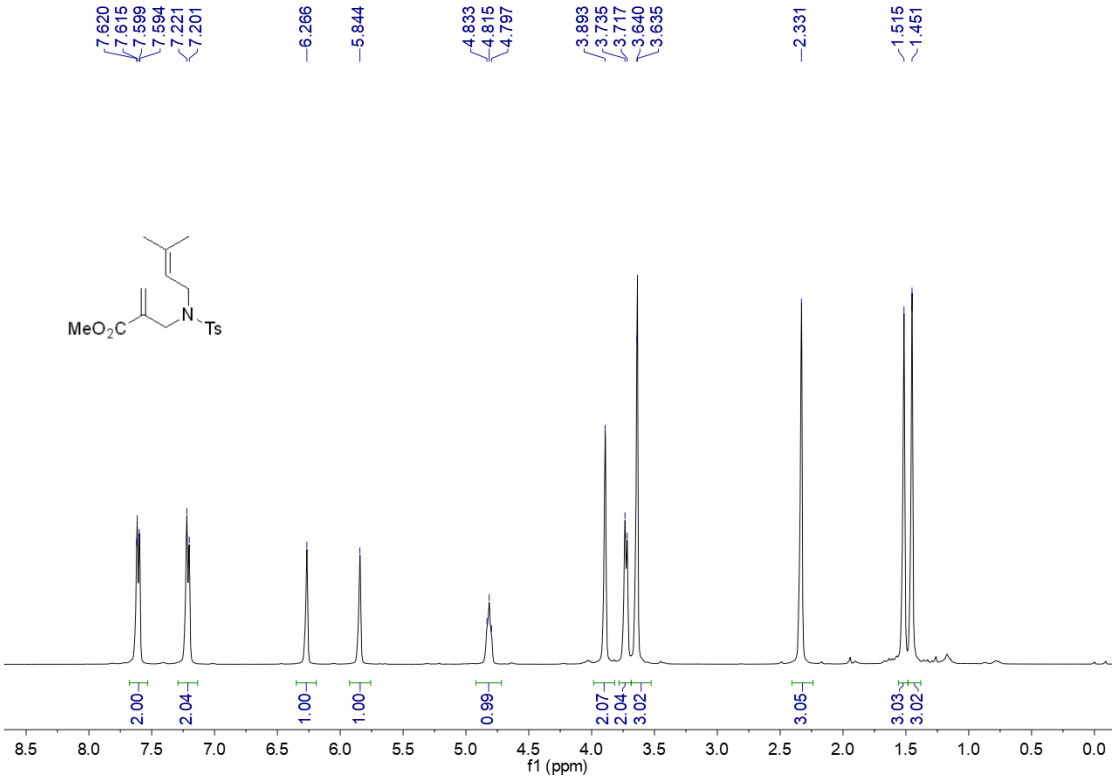
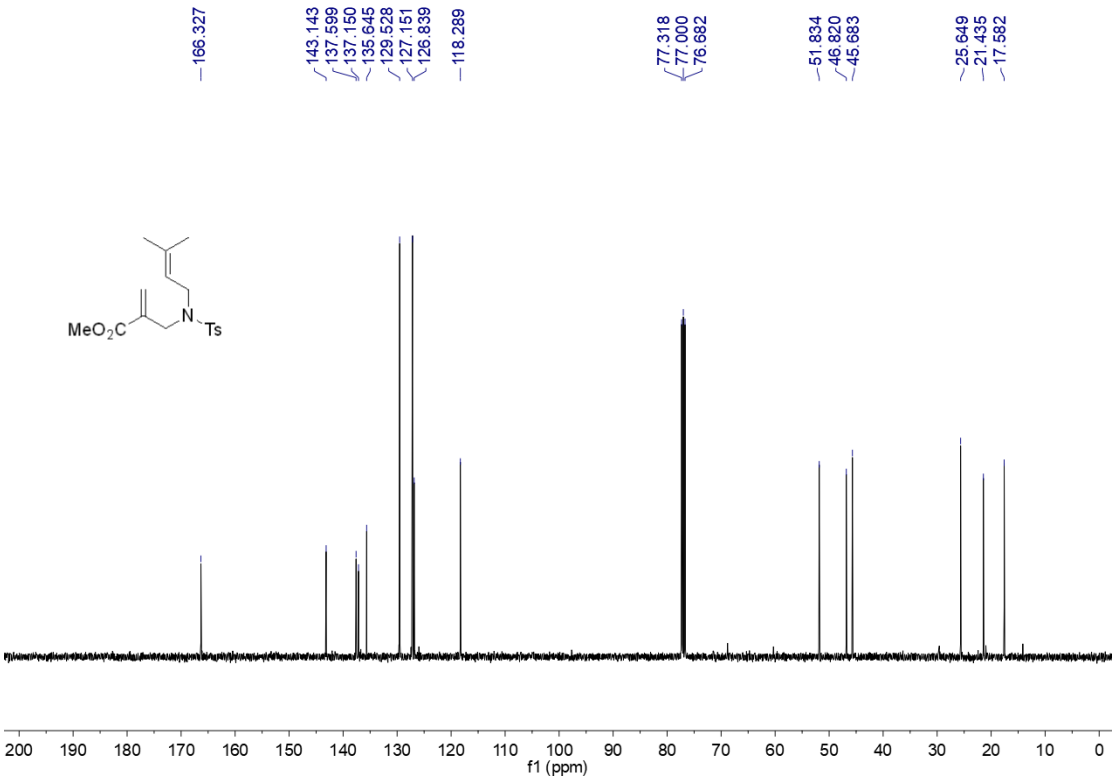
9. Copies of ^{1}H NMR and ^{13}C NMR spectra

(1a)

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

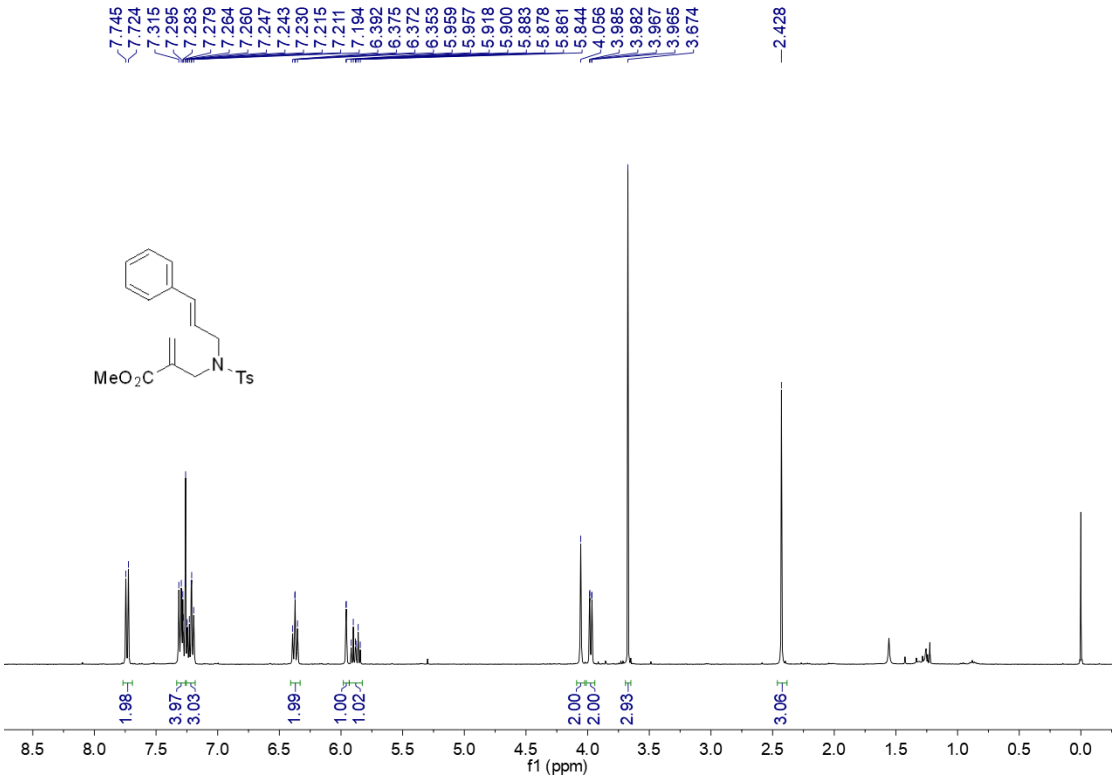


^{13}C NMR ($CDCl_3$, 101 MHz)

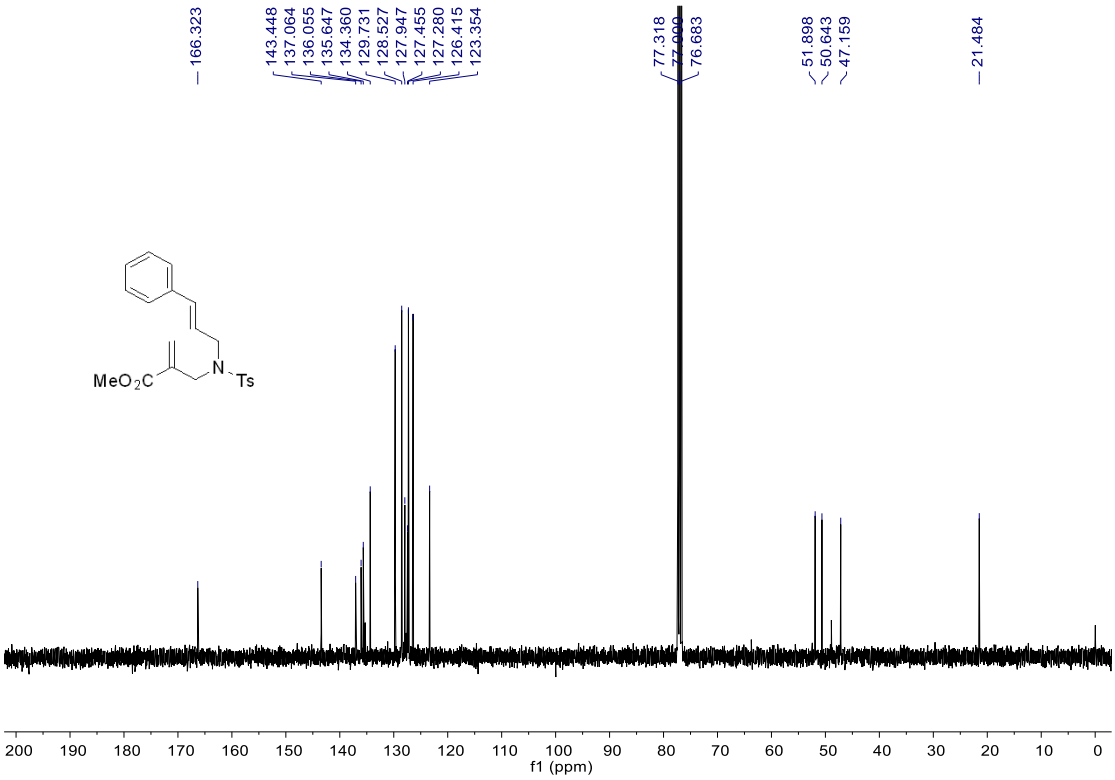


(1b)

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



^{13}C NMR ($CDCl_3$, 101 MHz)



(1c)

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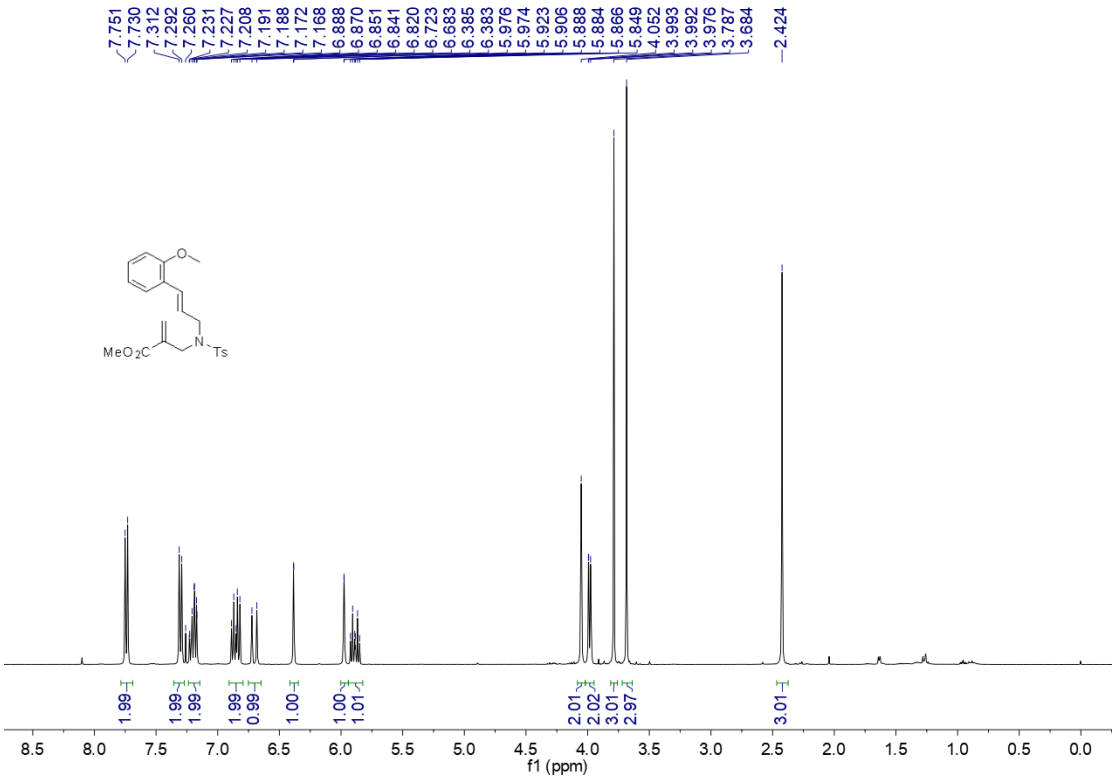

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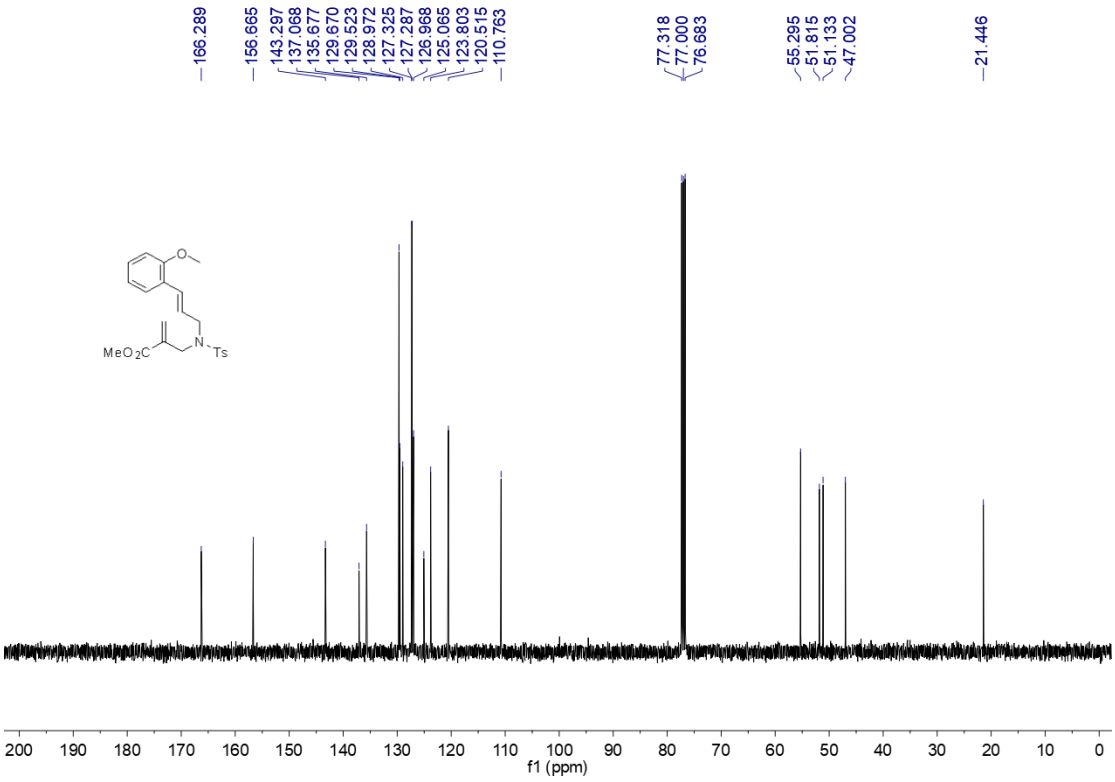

(1d)

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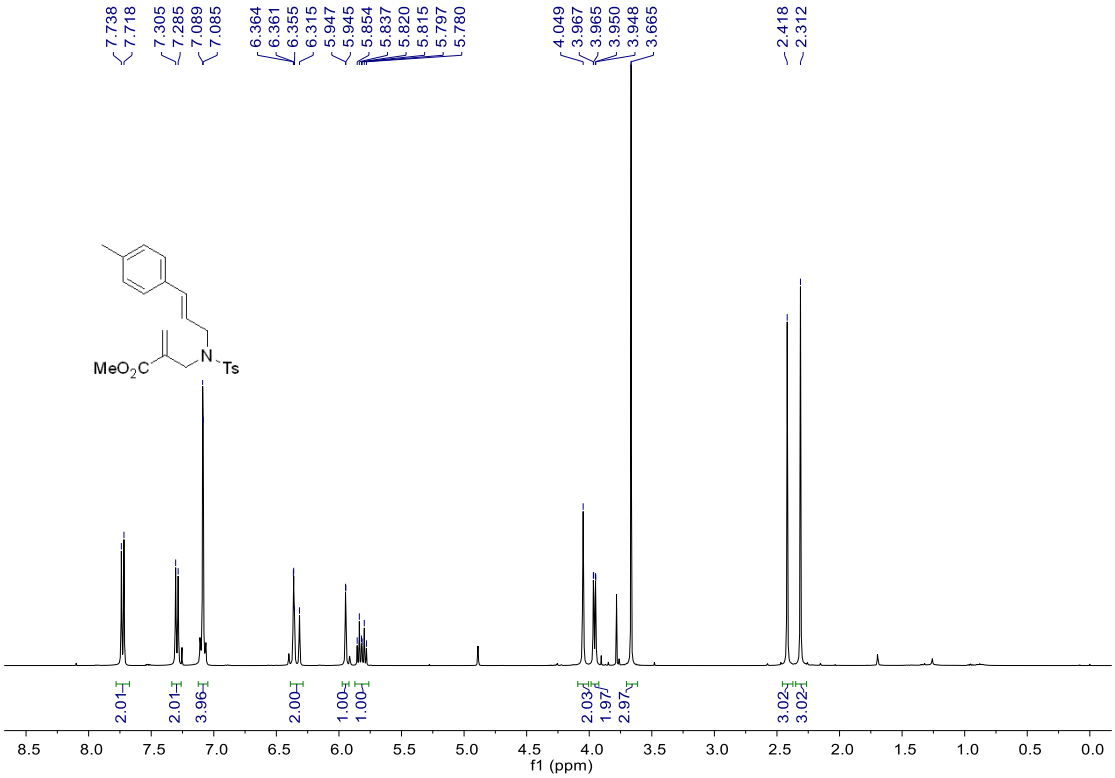
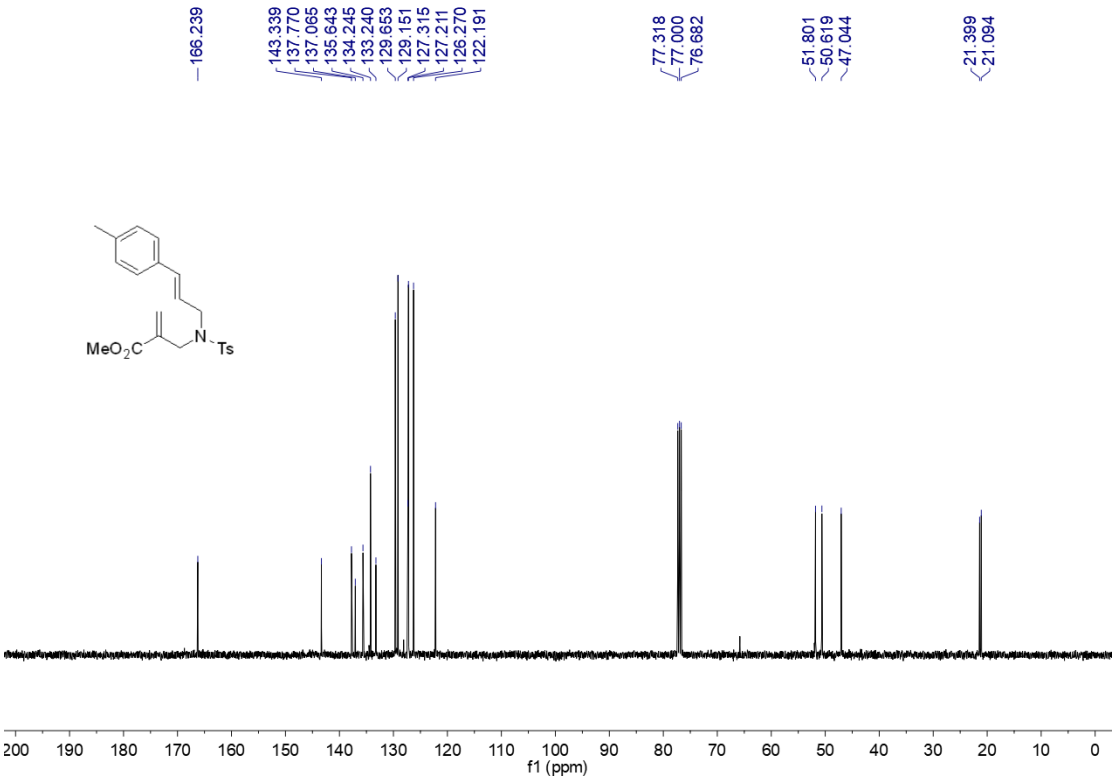


^{13}C NMR ($CDCl_3$, 101 MHz)



(1f)

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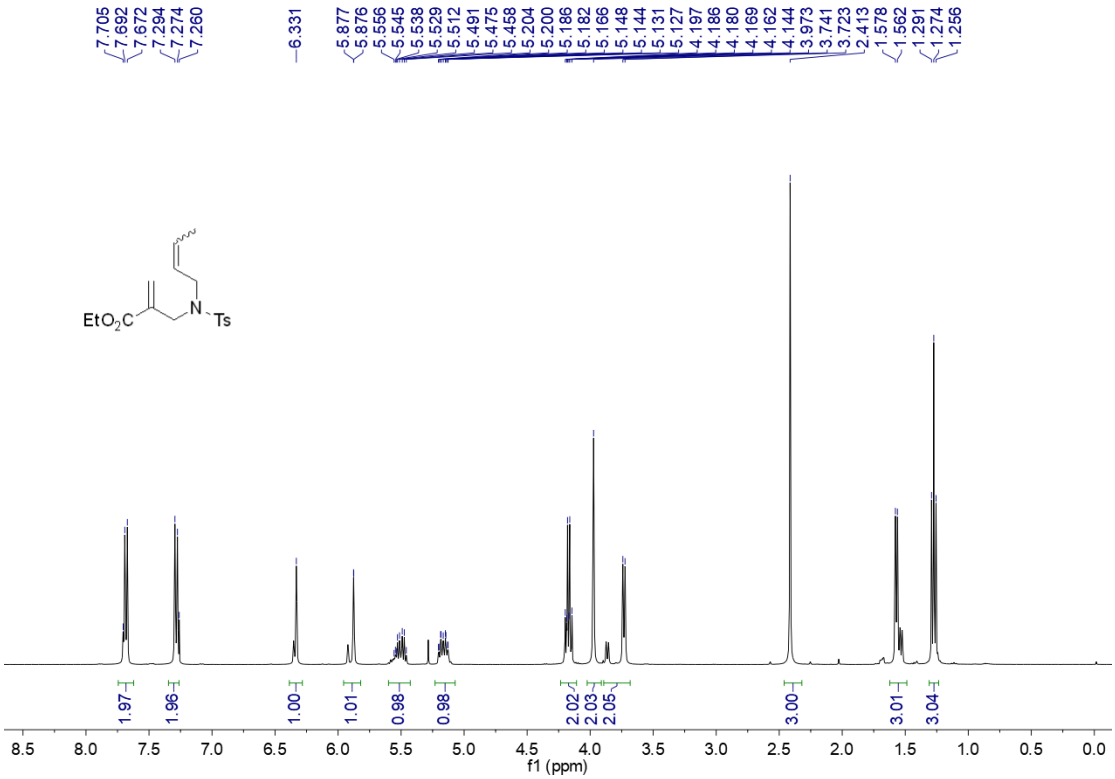
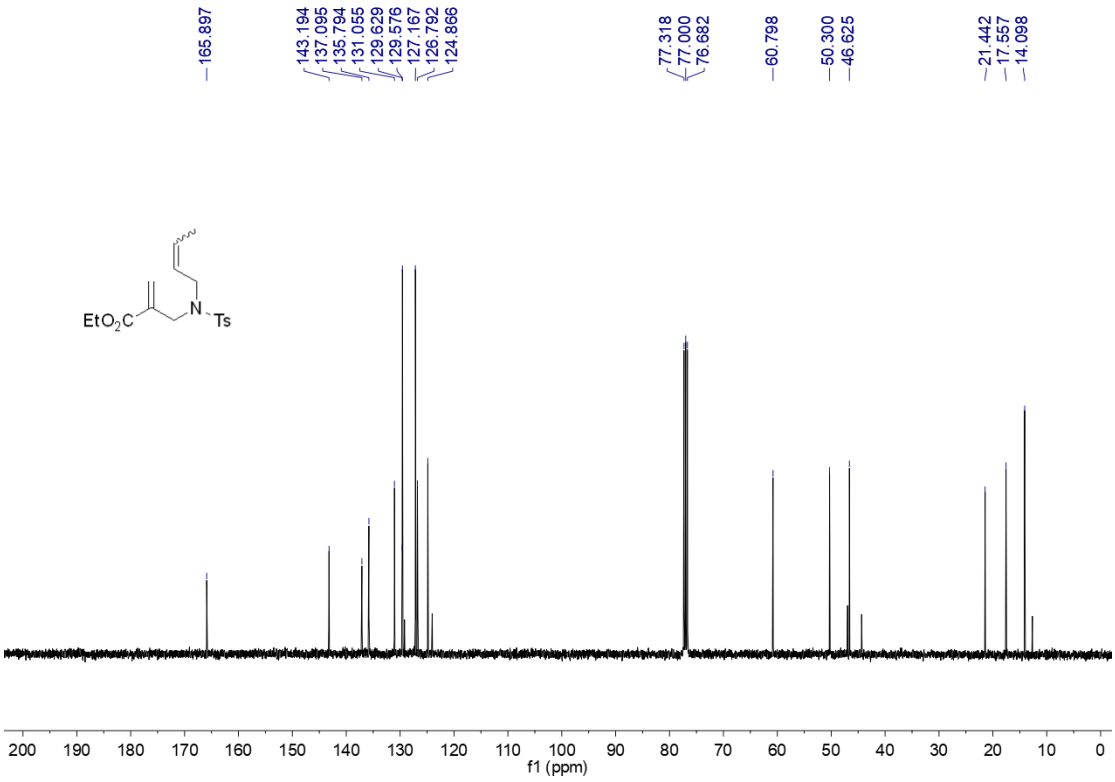
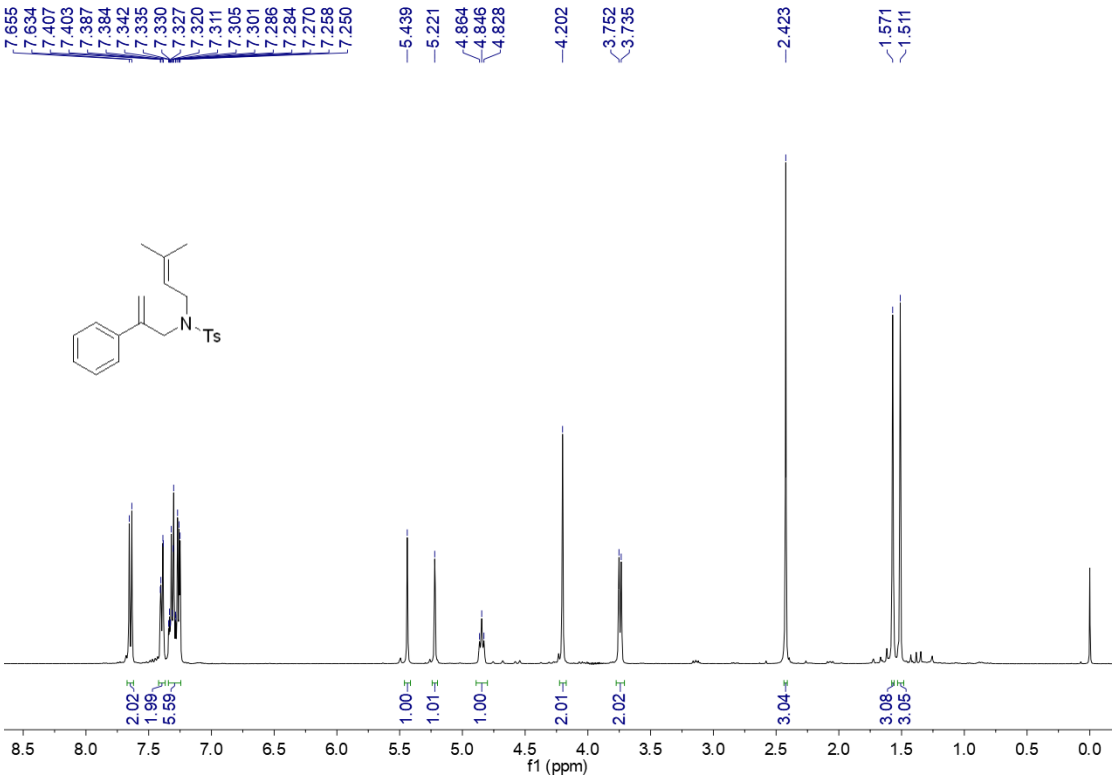


^{13}C NMR ($CDCl_3$, 101 MHz)

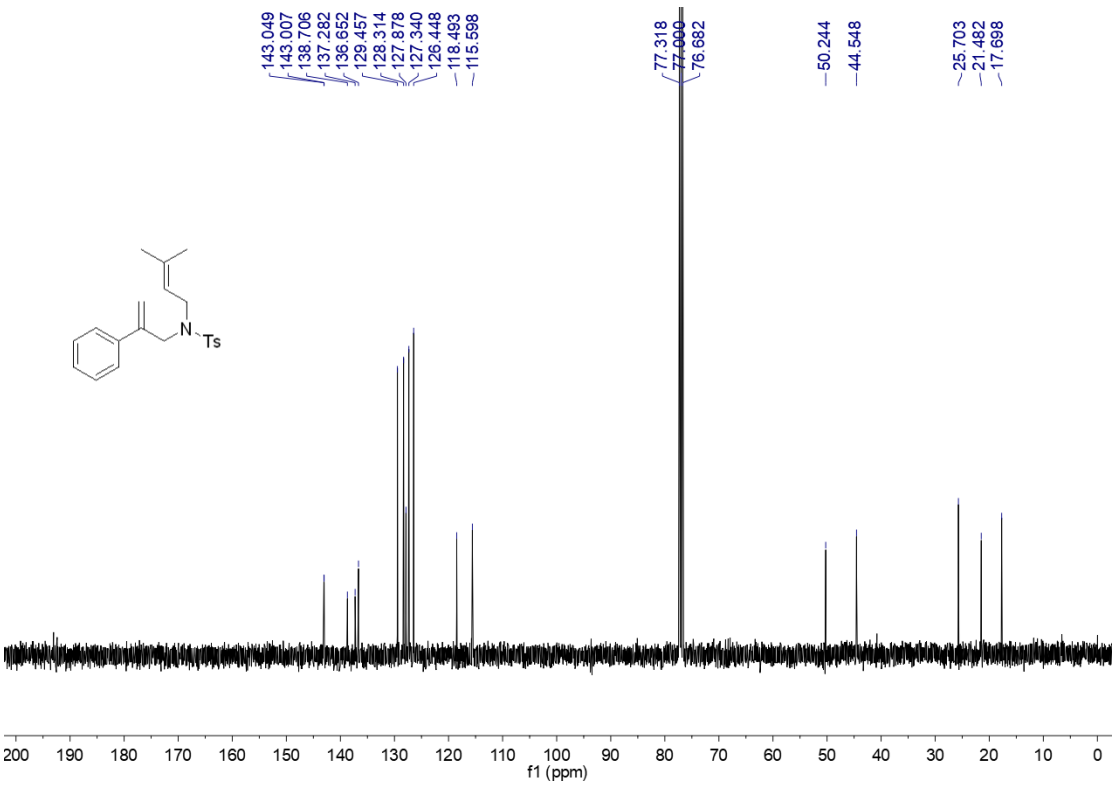


(1g)

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

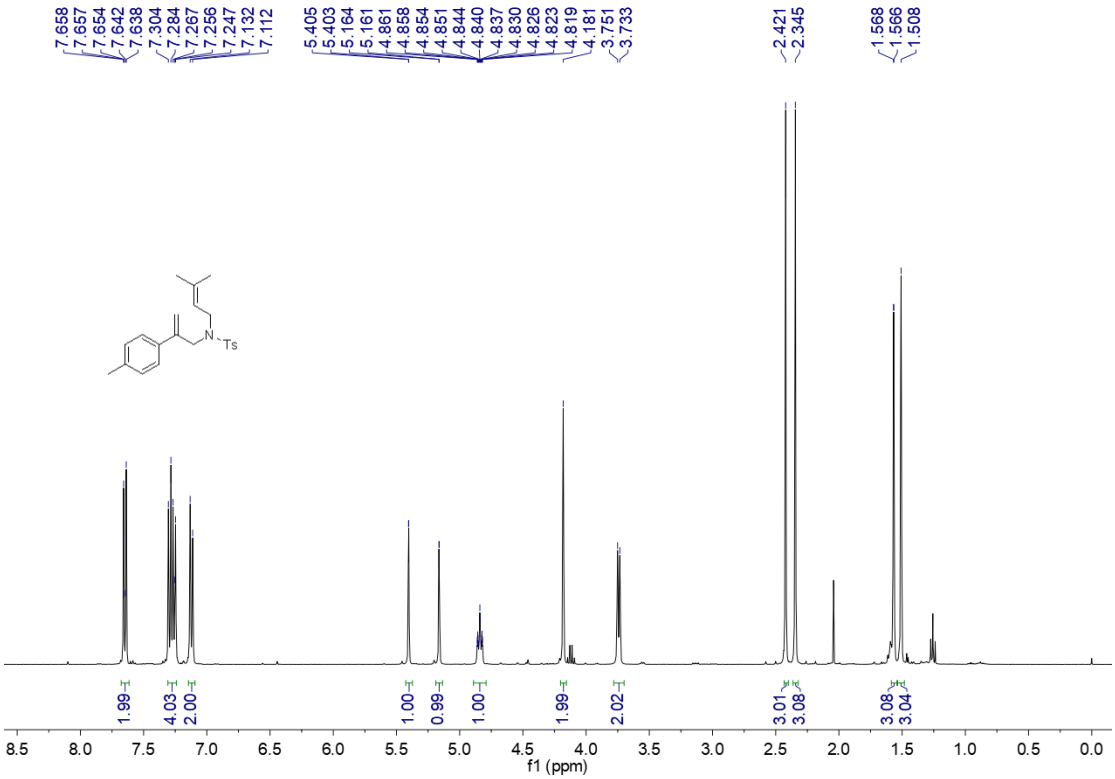


^{13}C NMR ($CDCl_3$, 101 MHz)

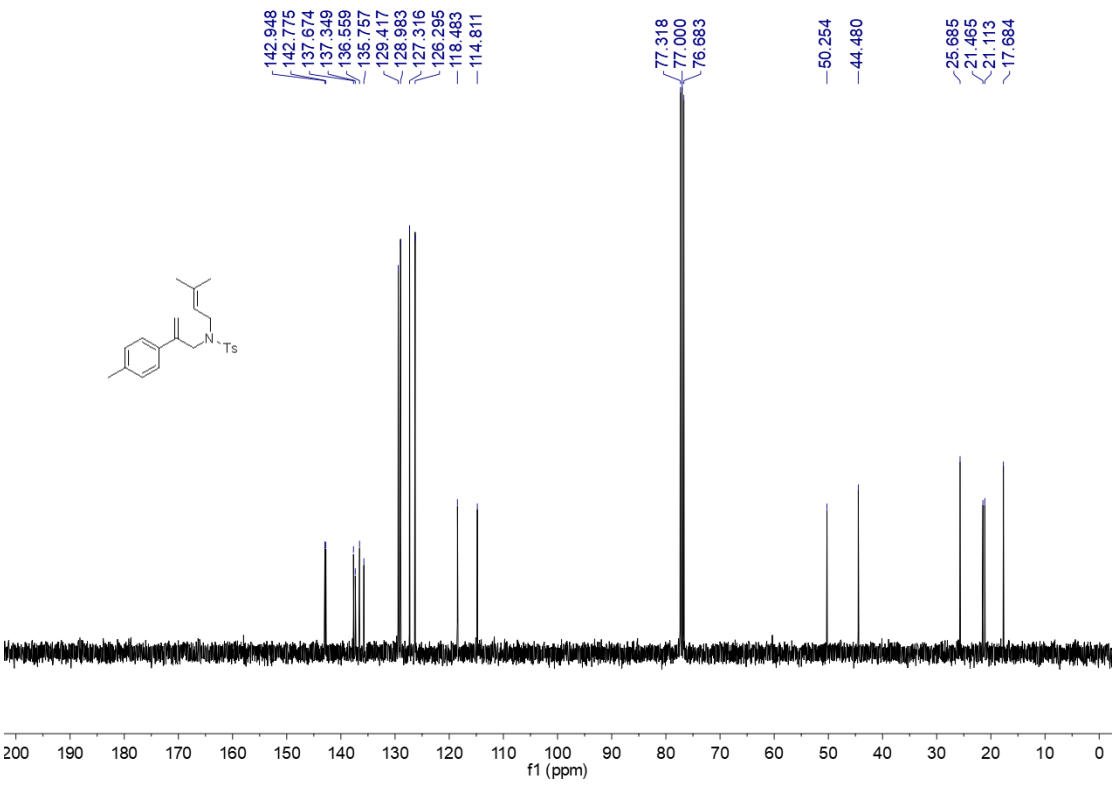


(1h)

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

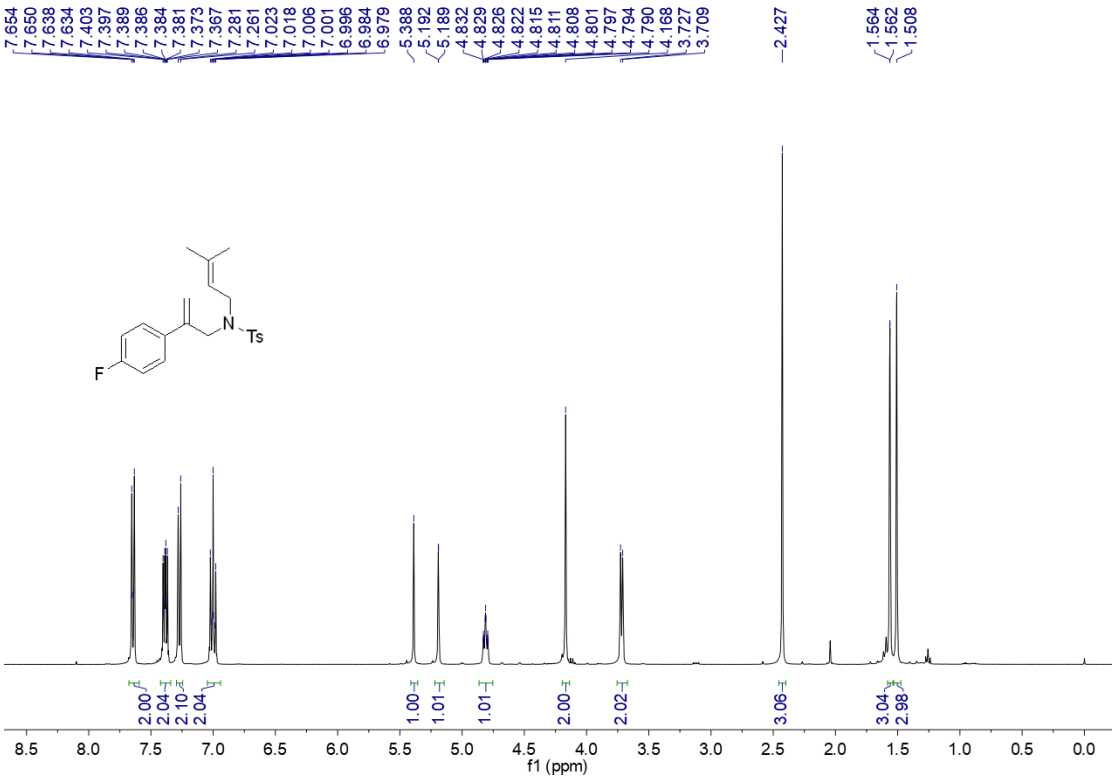


^{13}C NMR ($CDCl_3$, 101 MHz)

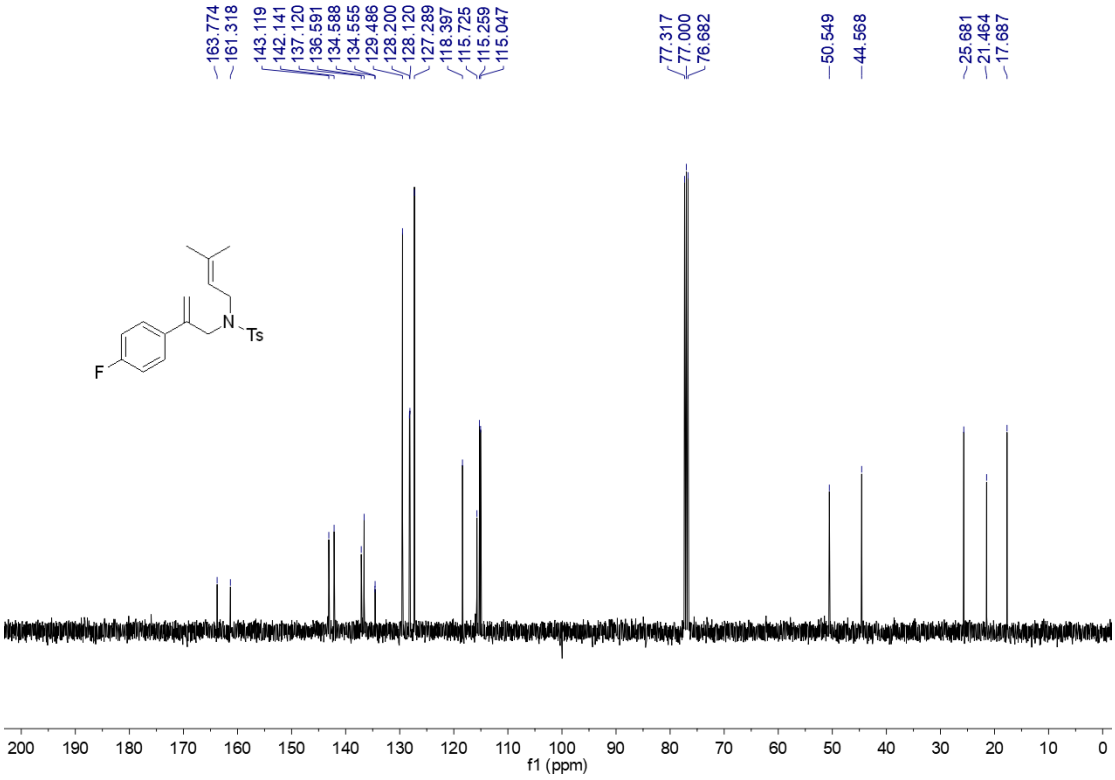


(1i)

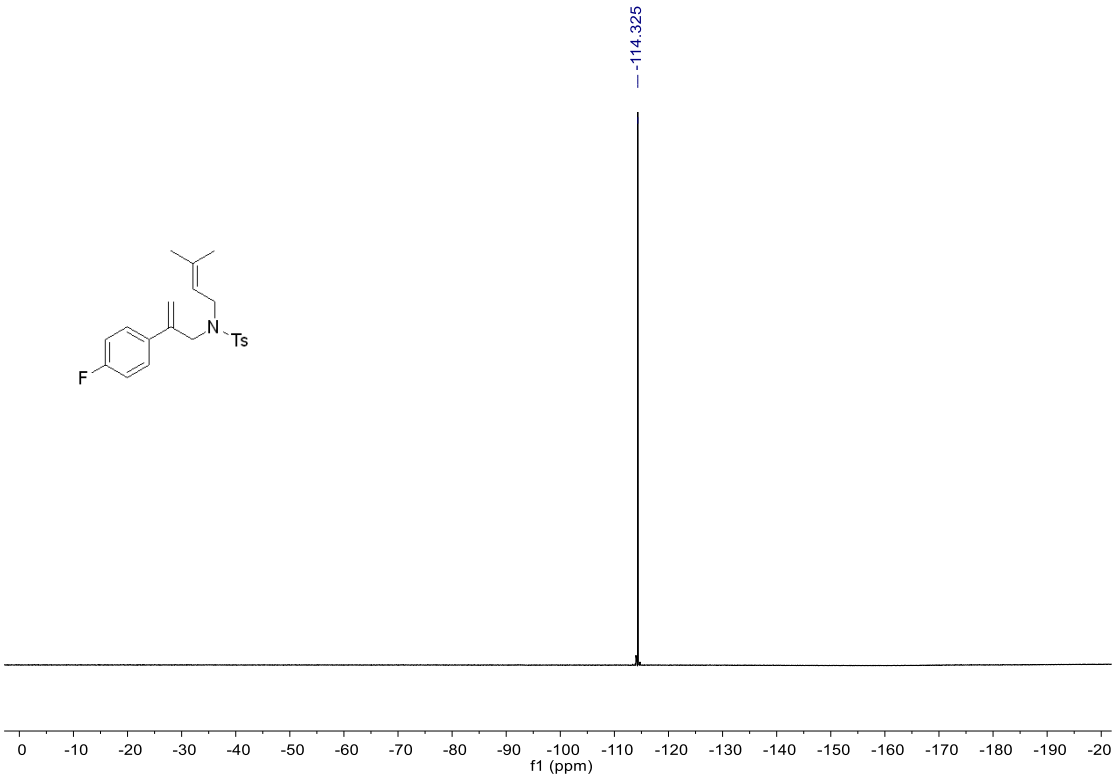
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

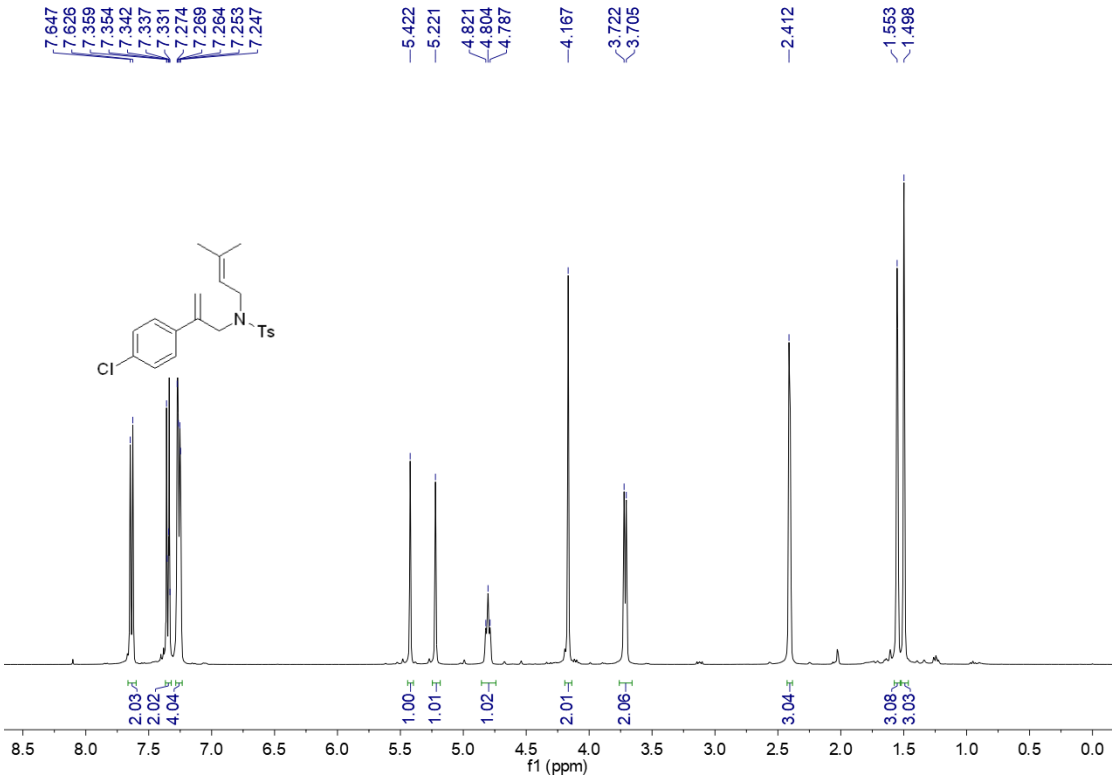


^{19}F NMR ($CDCl_3$, 376 MHz)

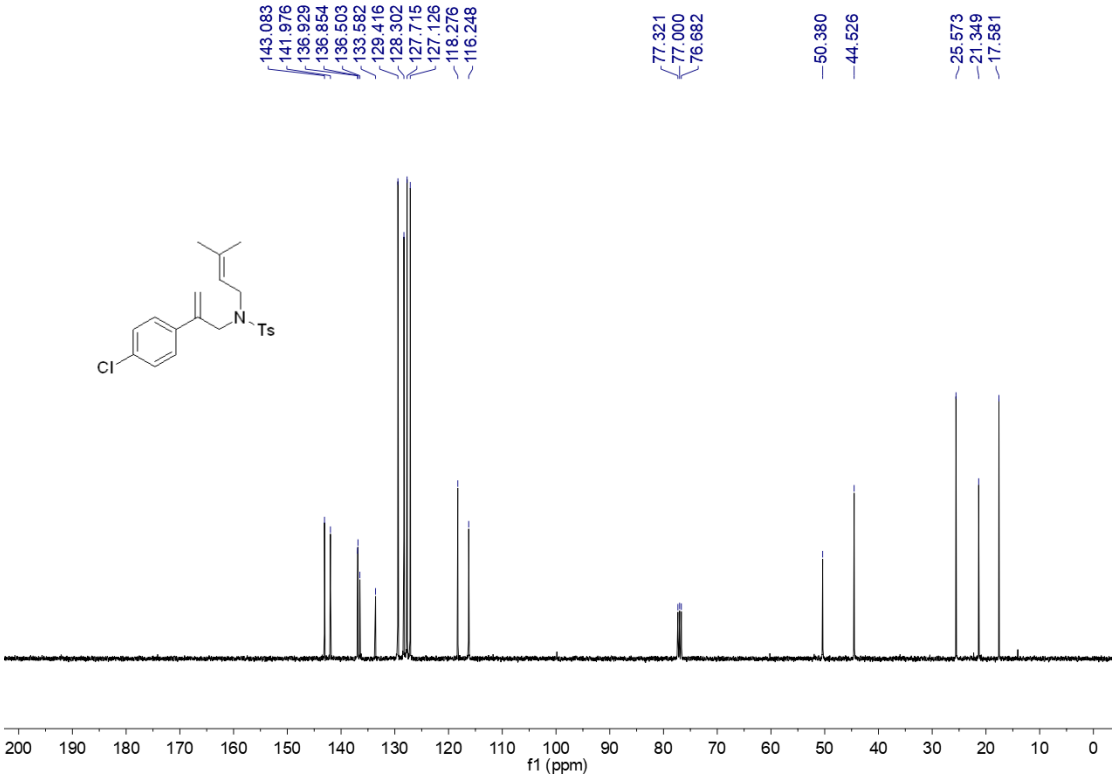


(1j)

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

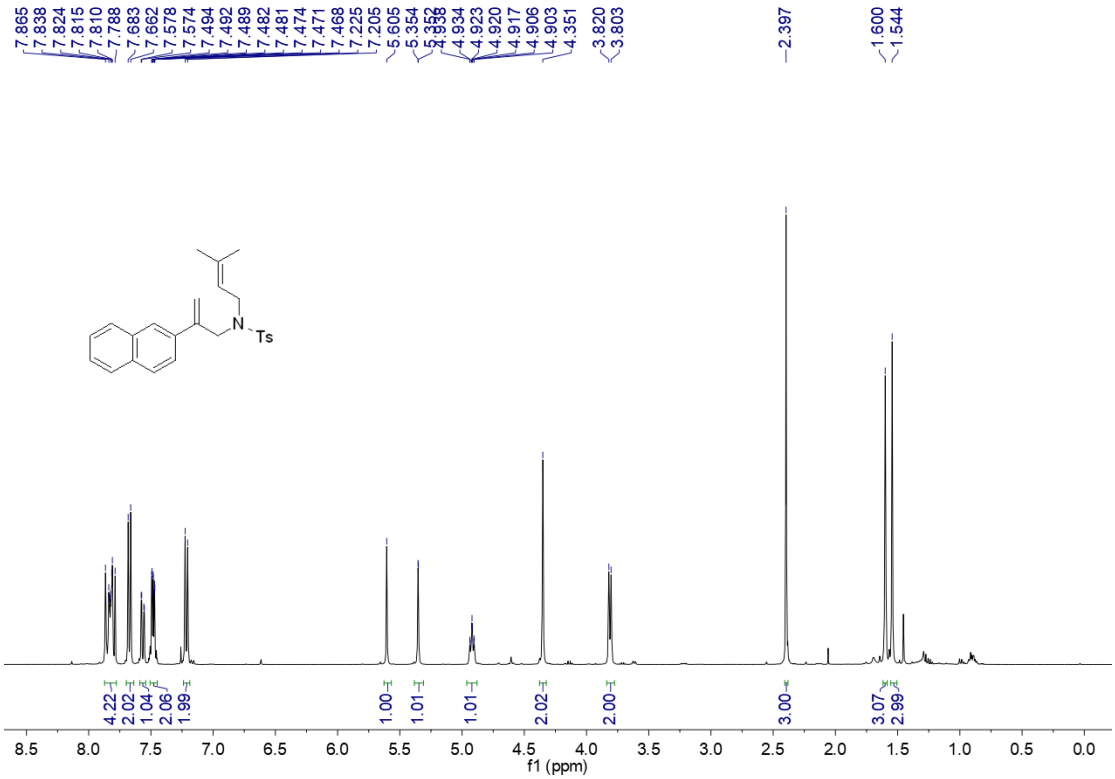


^{13}C NMR ($CDCl_3$, 101 MHz)

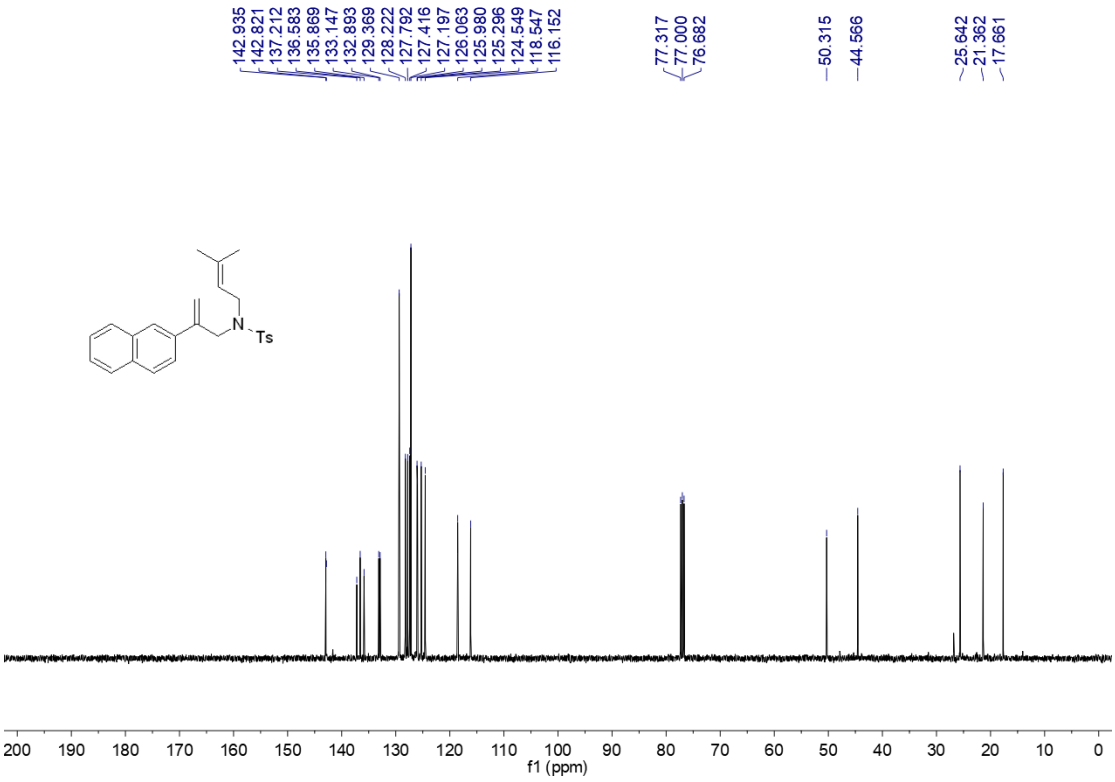


(1k)

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

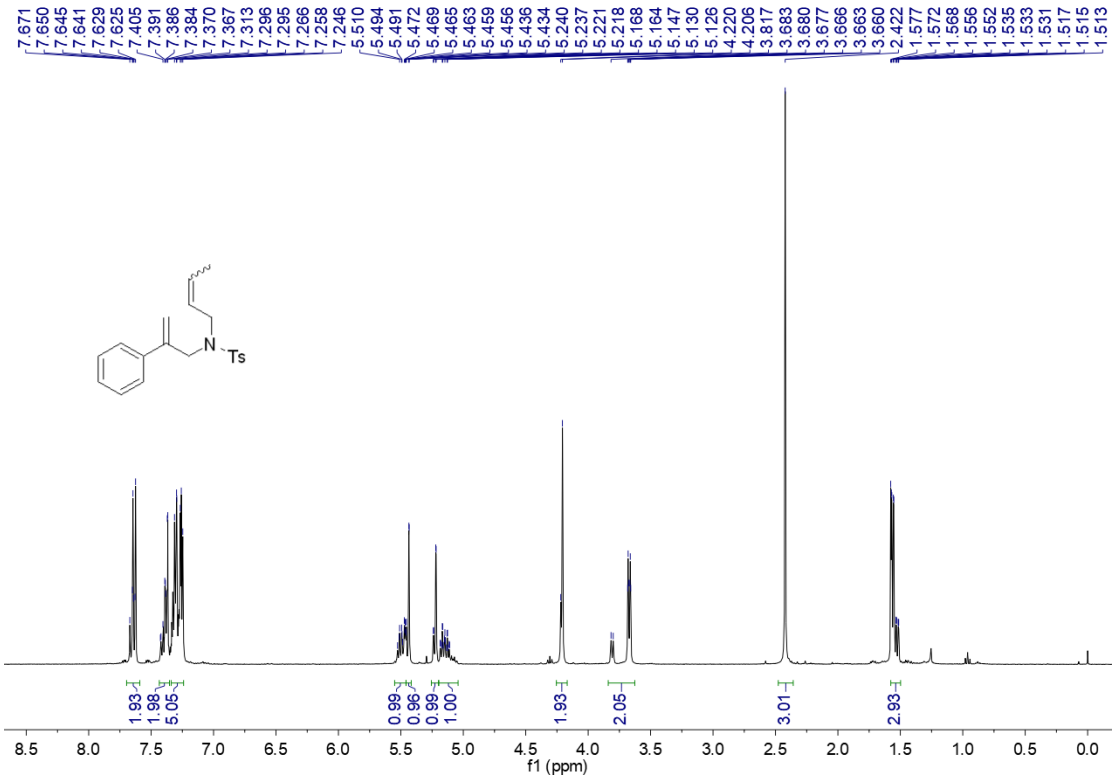


^{13}C NMR ($CDCl_3$, 101 MHz)

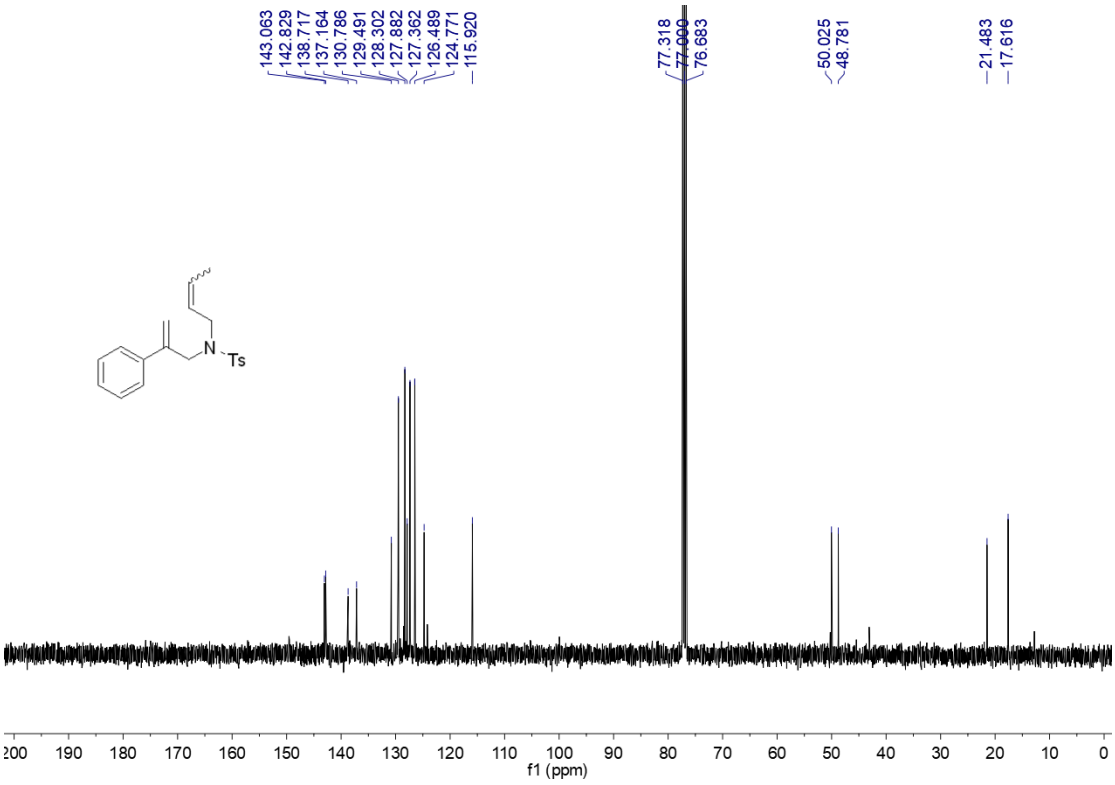


(1l)

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

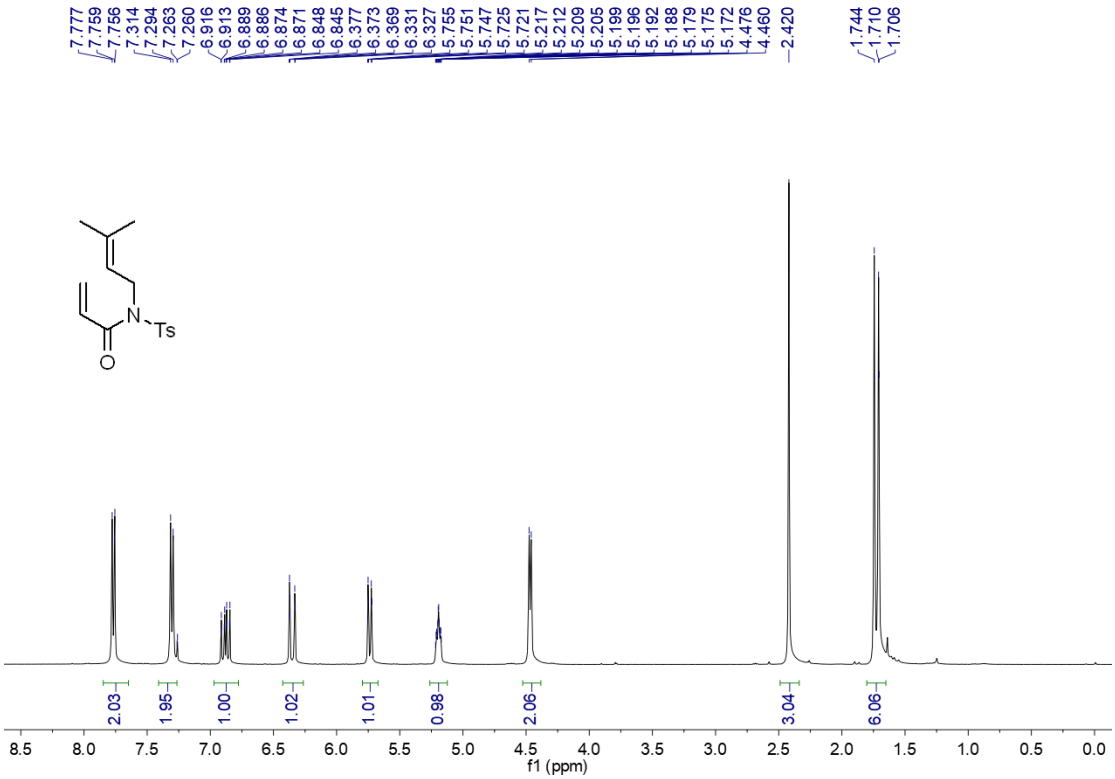


^{13}C NMR ($CDCl_3$, 101 MHz)

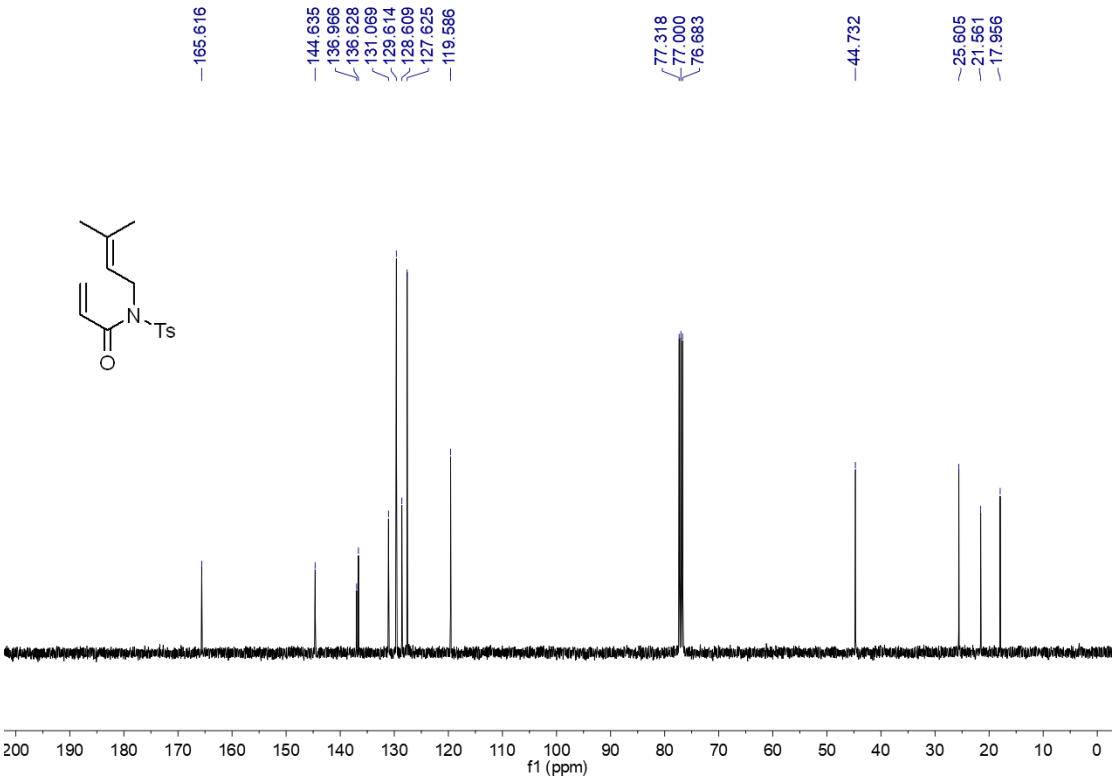


(1o)

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

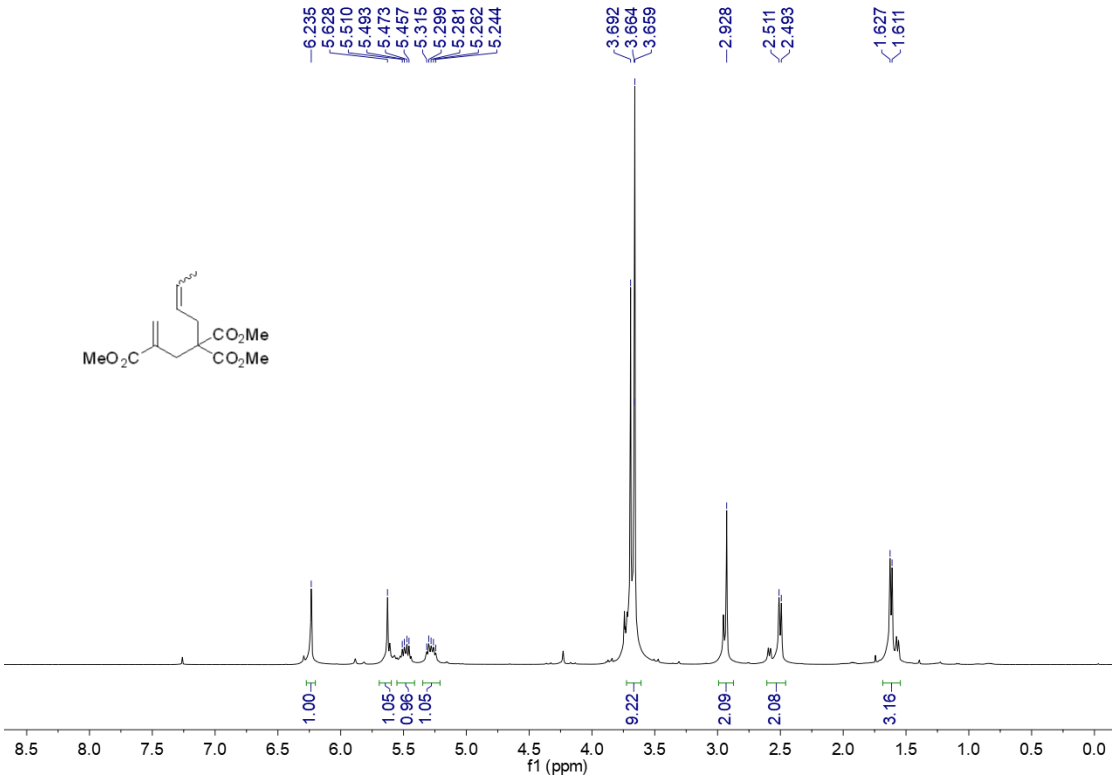


^{13}C NMR ($CDCl_3$, 101 MHz)

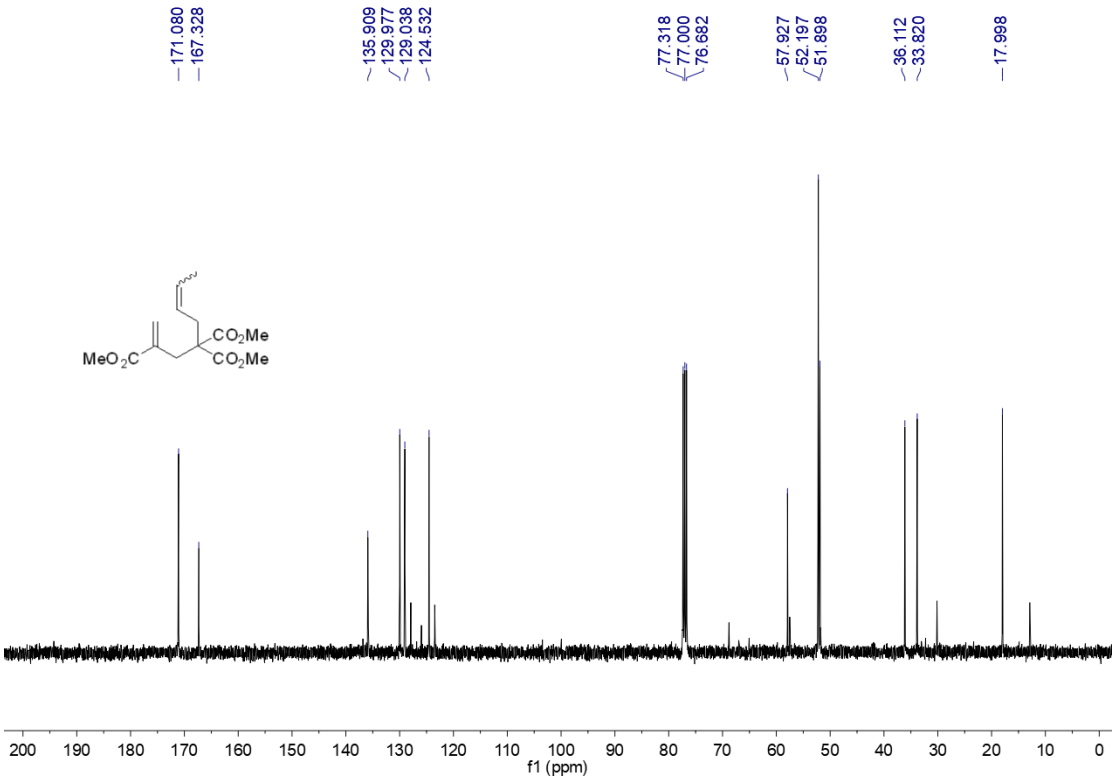


(1s)

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

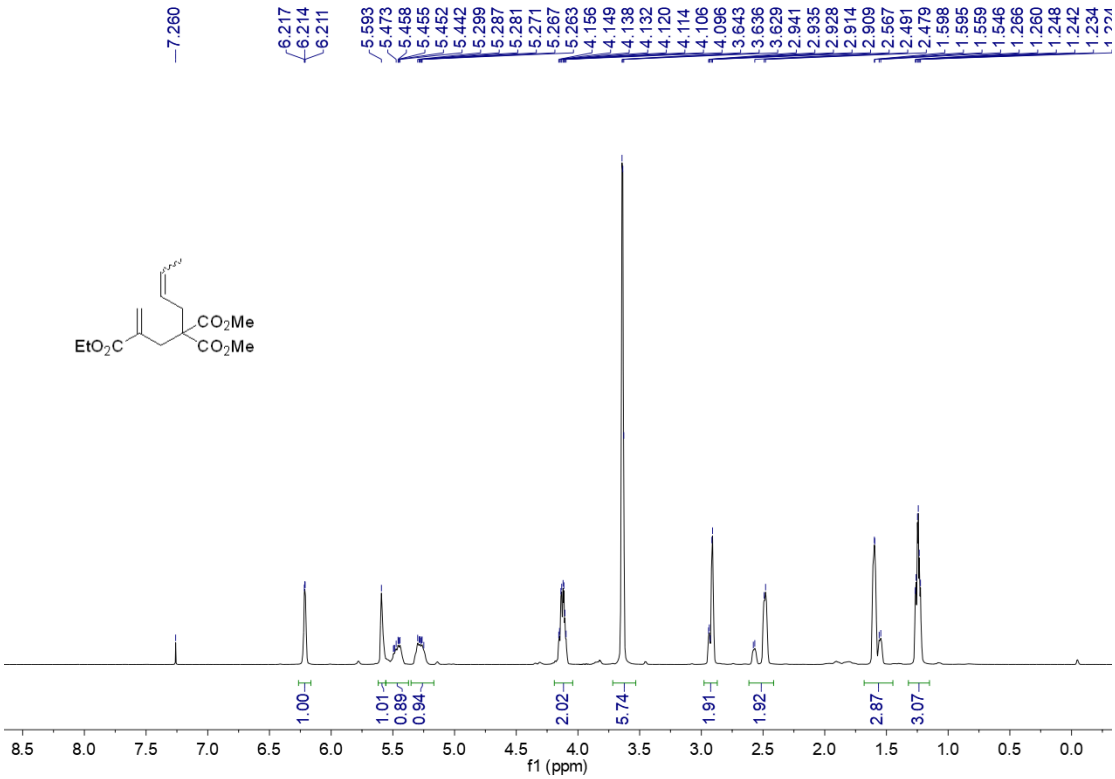


^{13}C NMR ($CDCl_3$, 101 MHz)

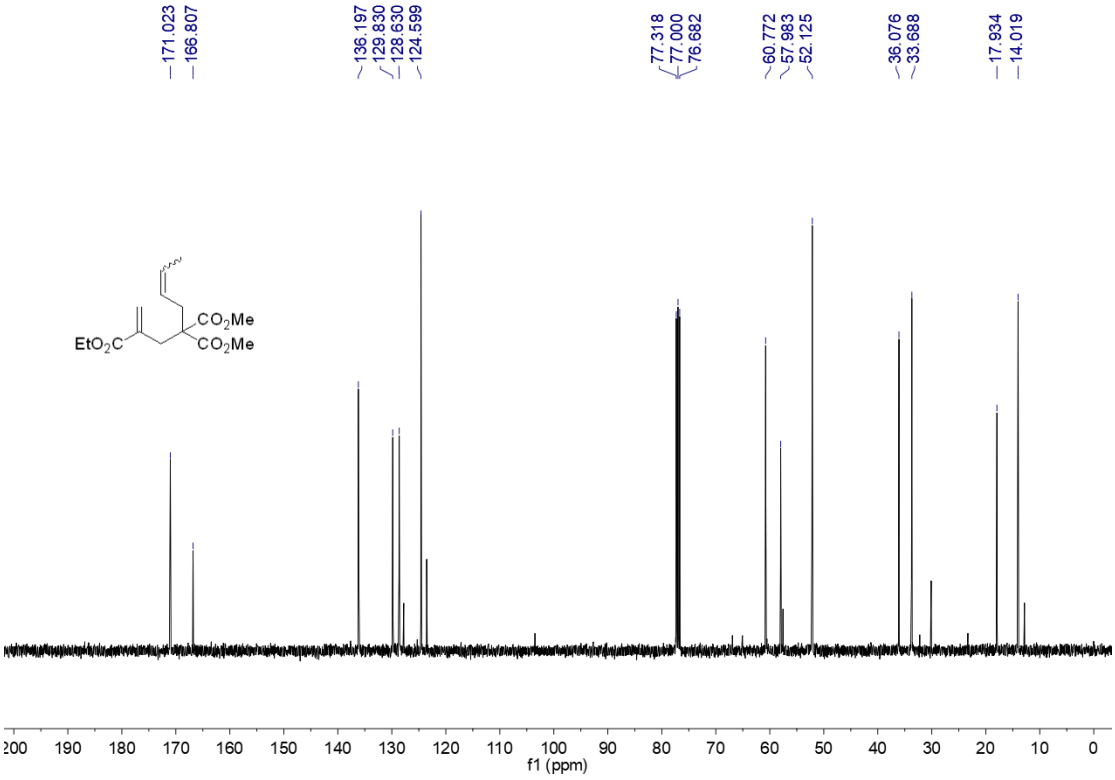


(1t)

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

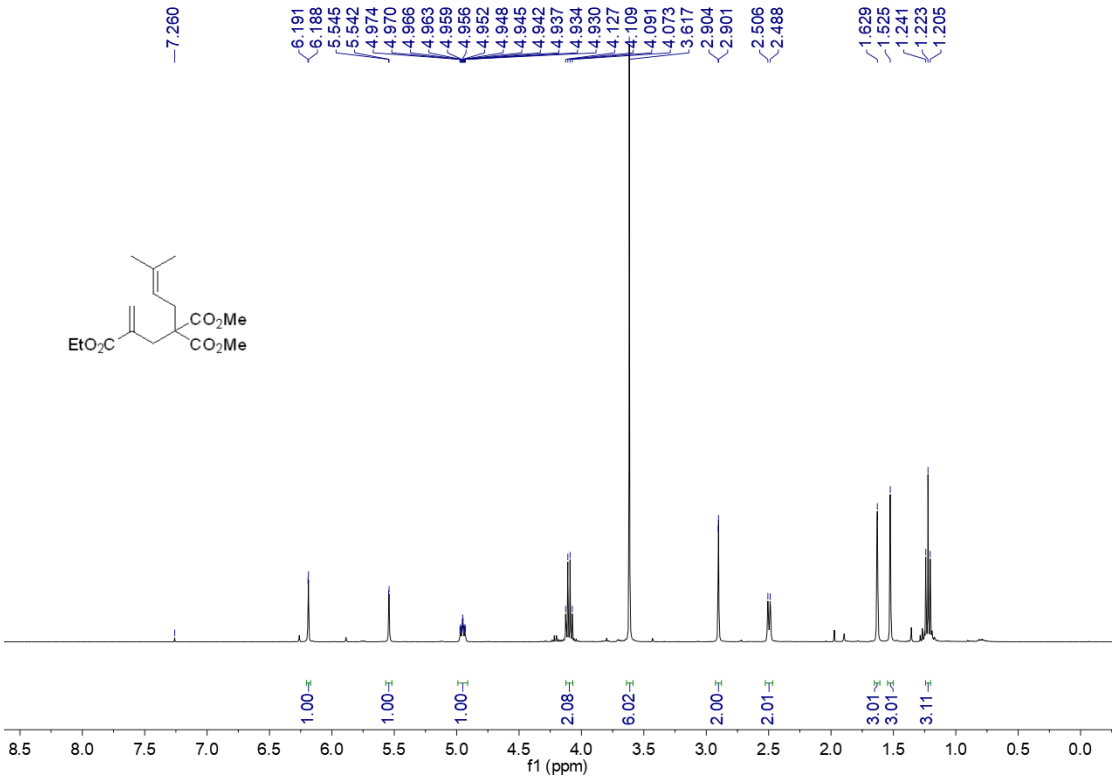


^{13}C NMR ($CDCl_3$, 101 MHz)

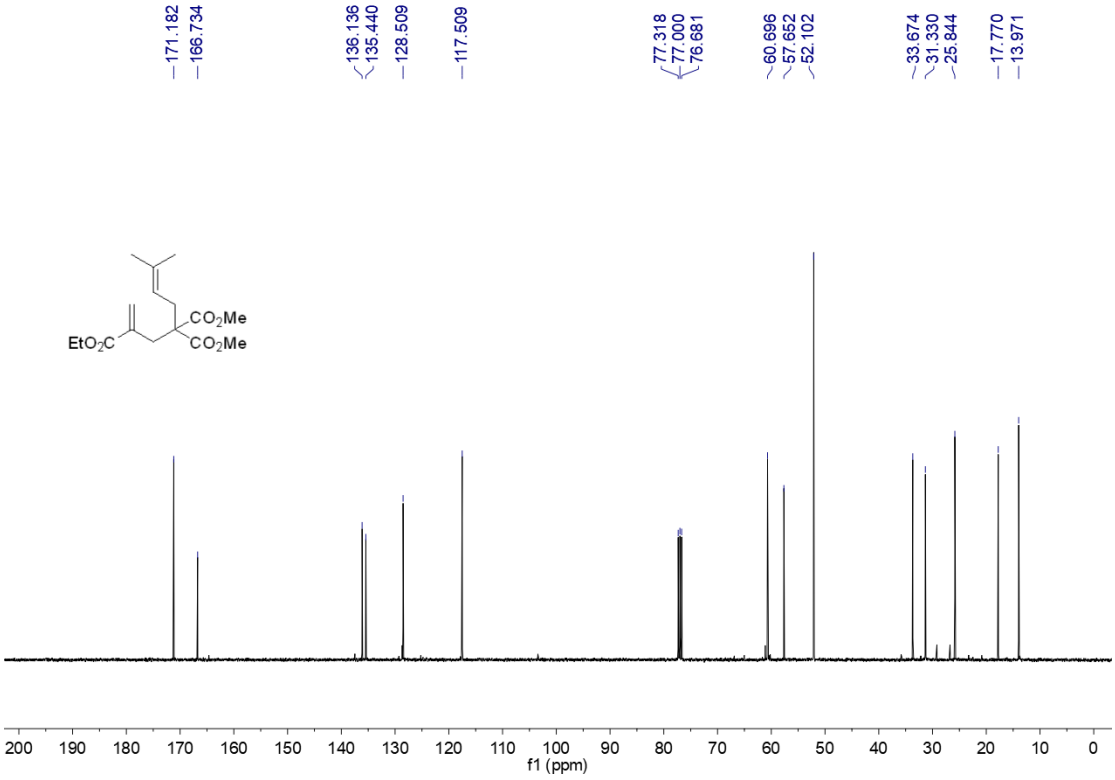


(1u)

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

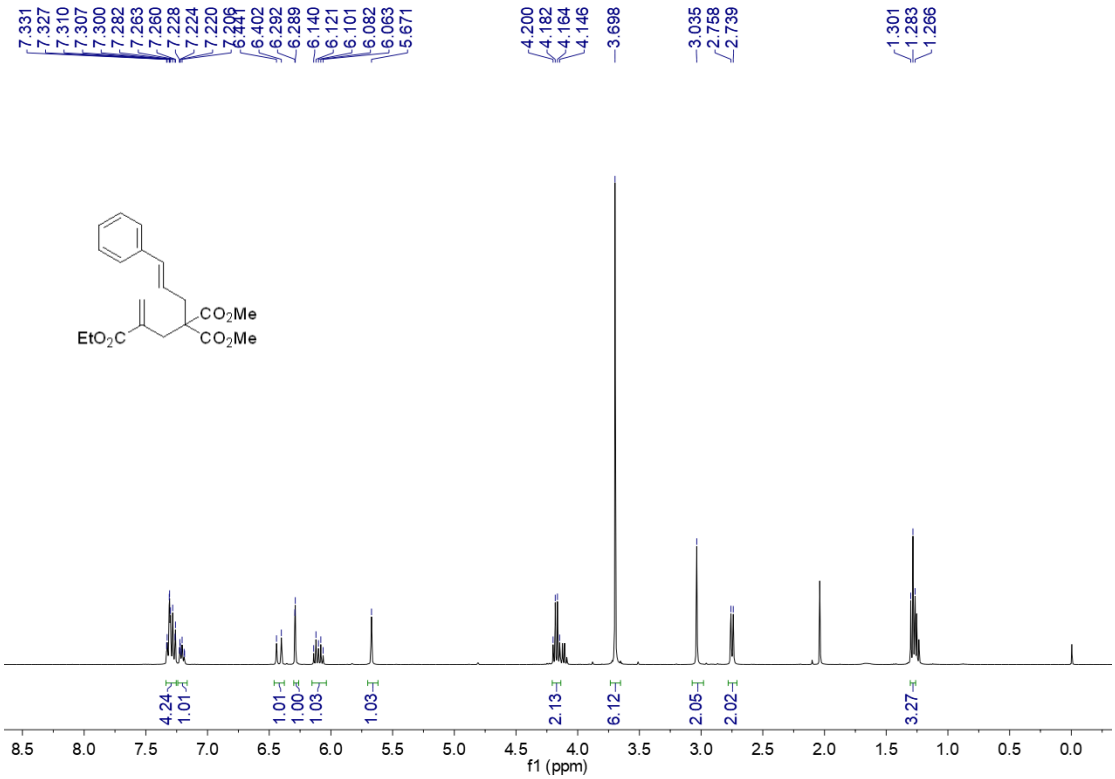


^{13}C NMR ($CDCl_3$, 101 MHz)

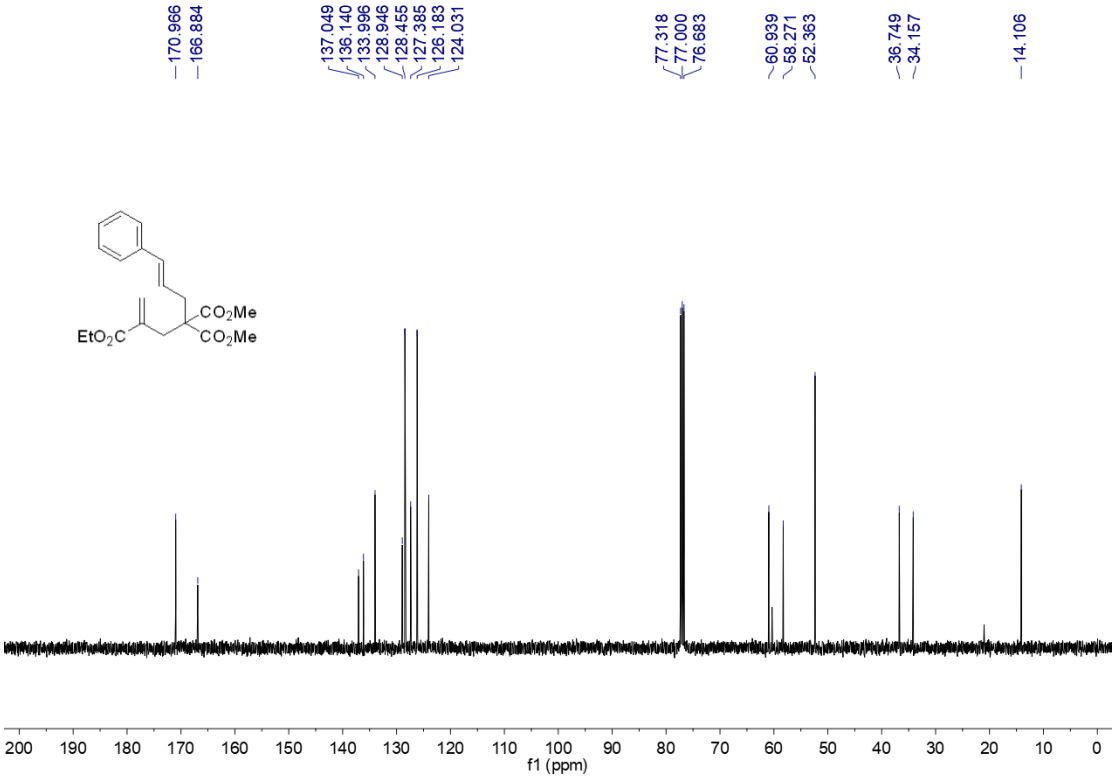


(1v)

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

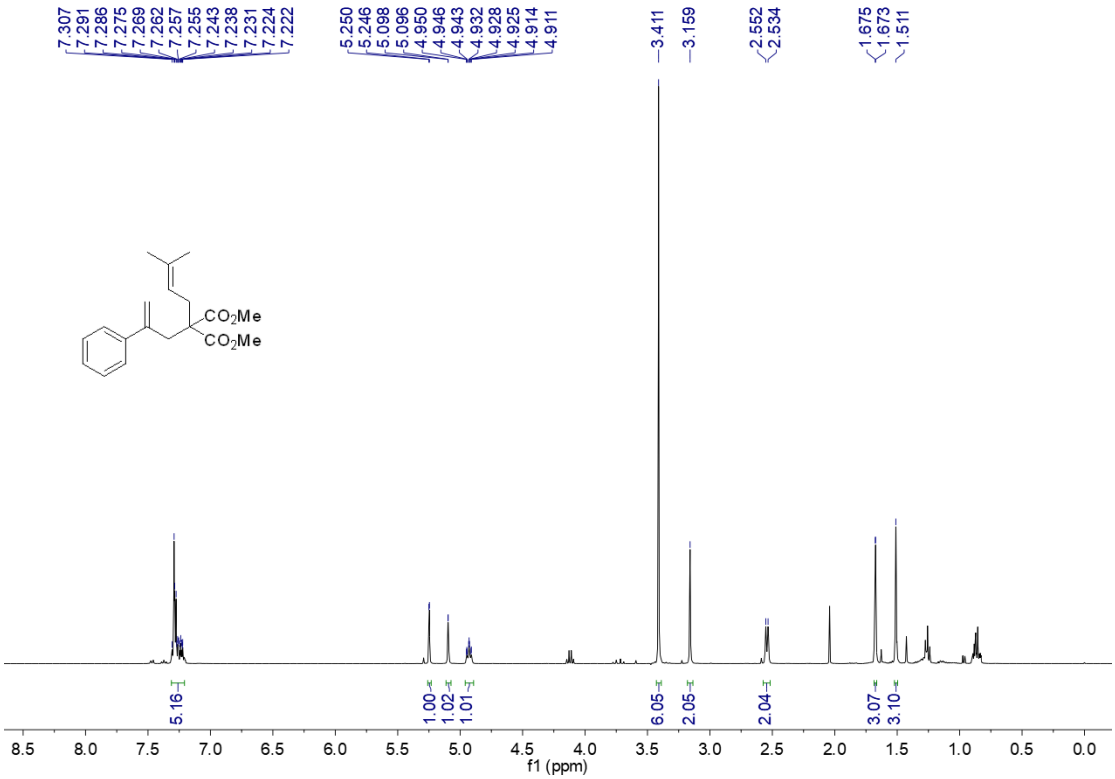


^{13}C NMR ($CDCl_3$, 101 MHz)

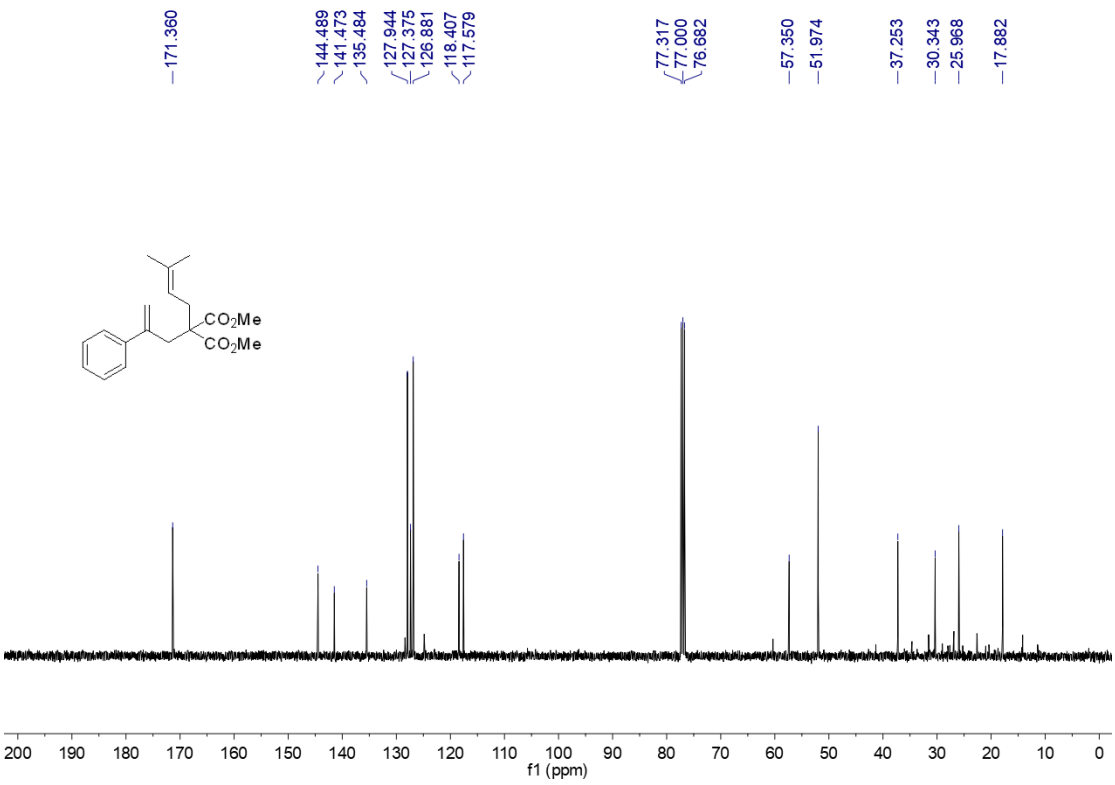


(1w)

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

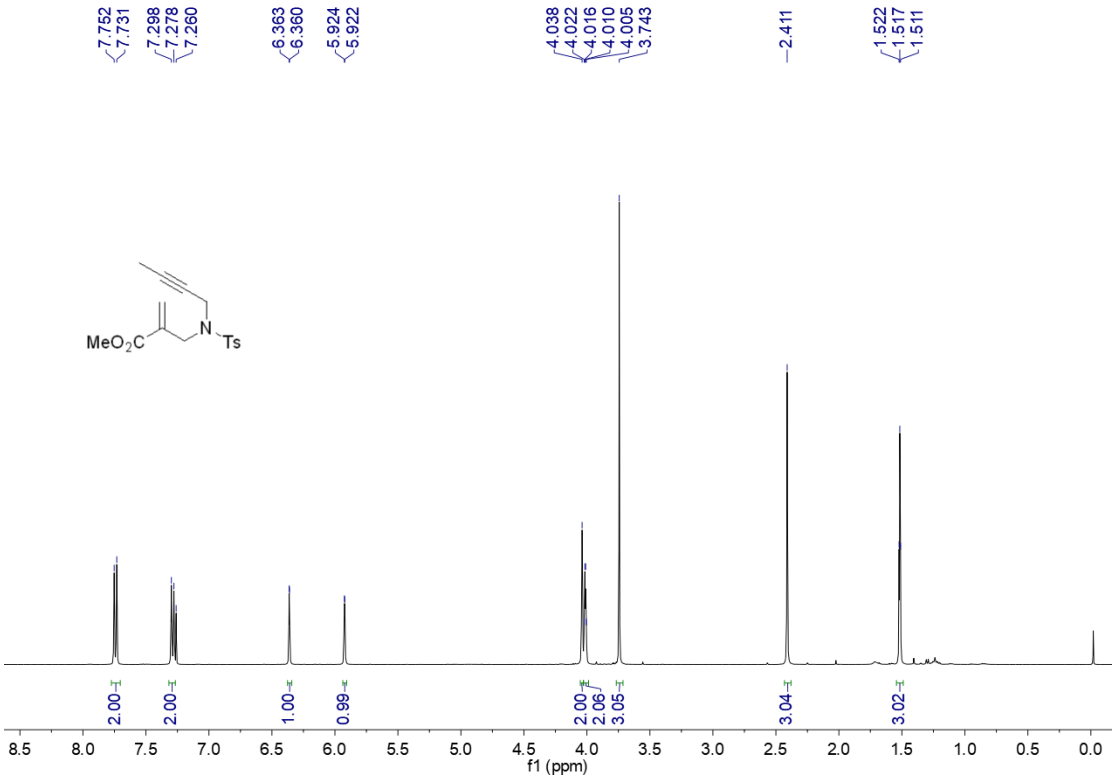


^{13}C NMR ($CDCl_3$, 101 MHz)

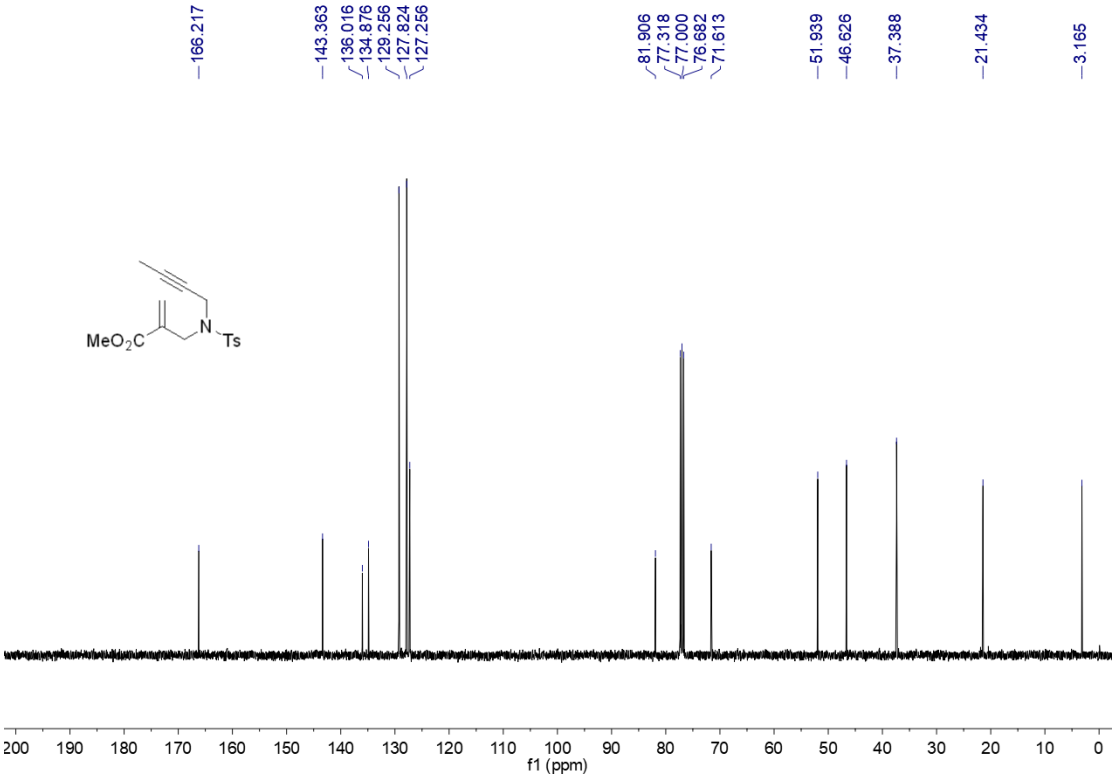


(3b)

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

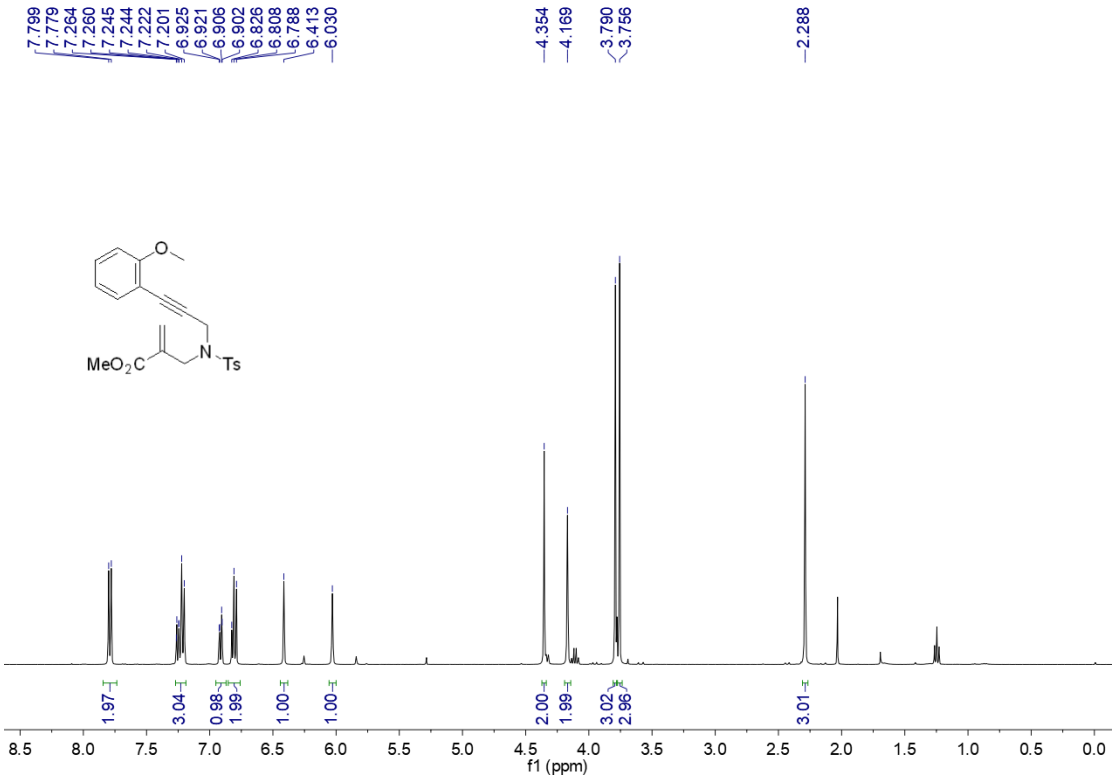


^{13}C NMR ($CDCl_3$, 101 MHz)

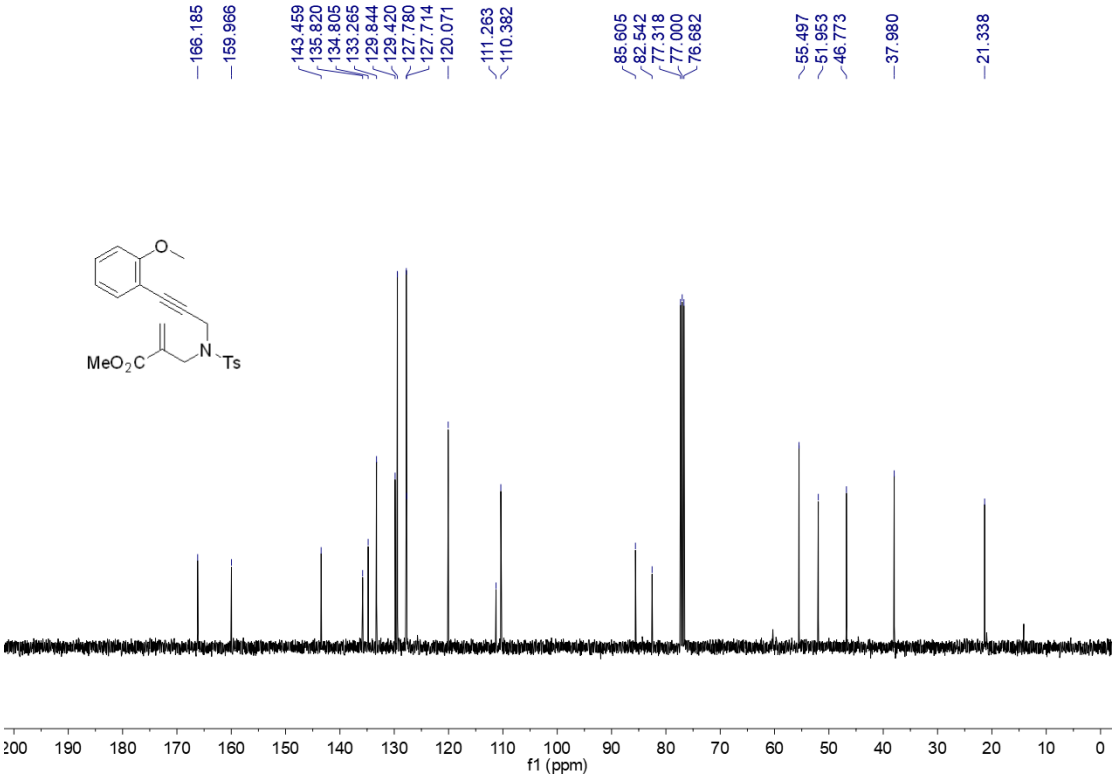


(3d)

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

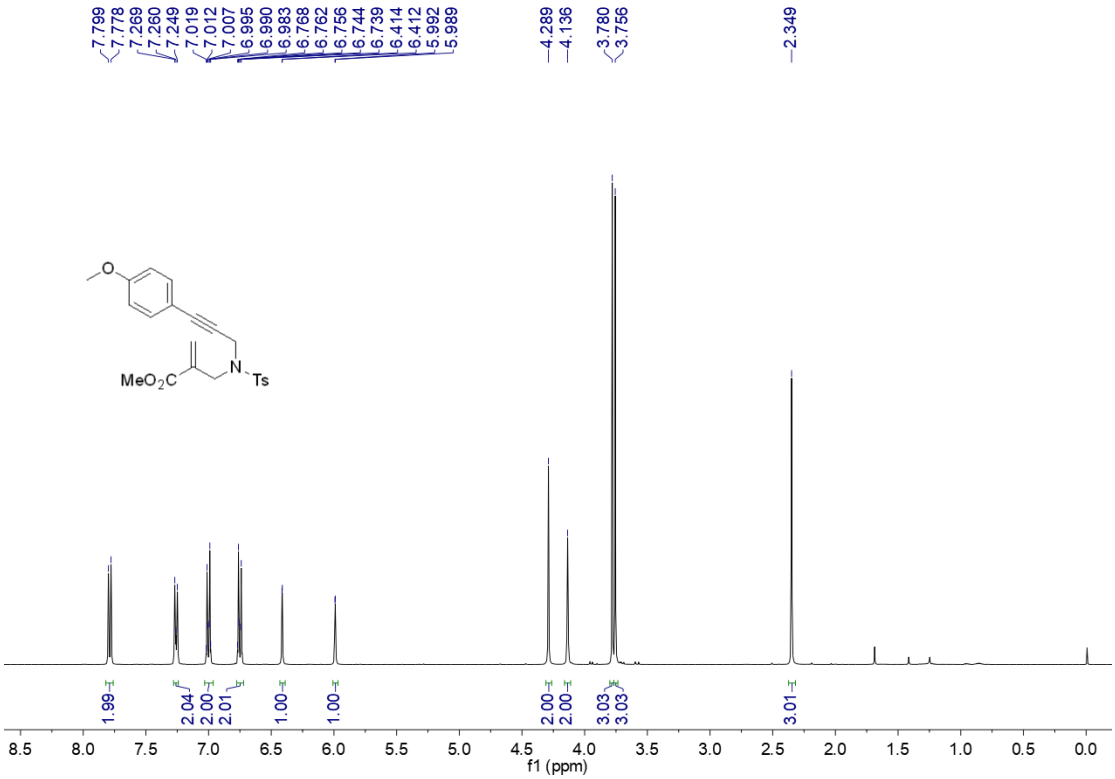


^{13}C NMR ($CDCl_3$, 101 MHz)

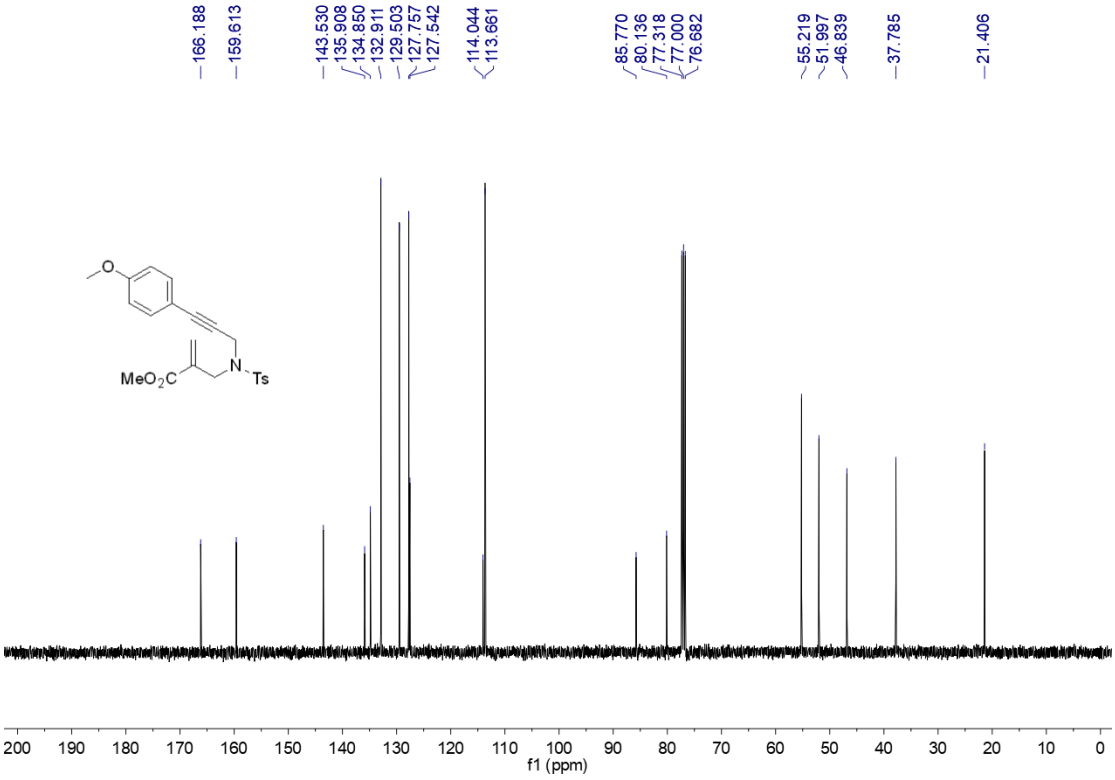


(3e)

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

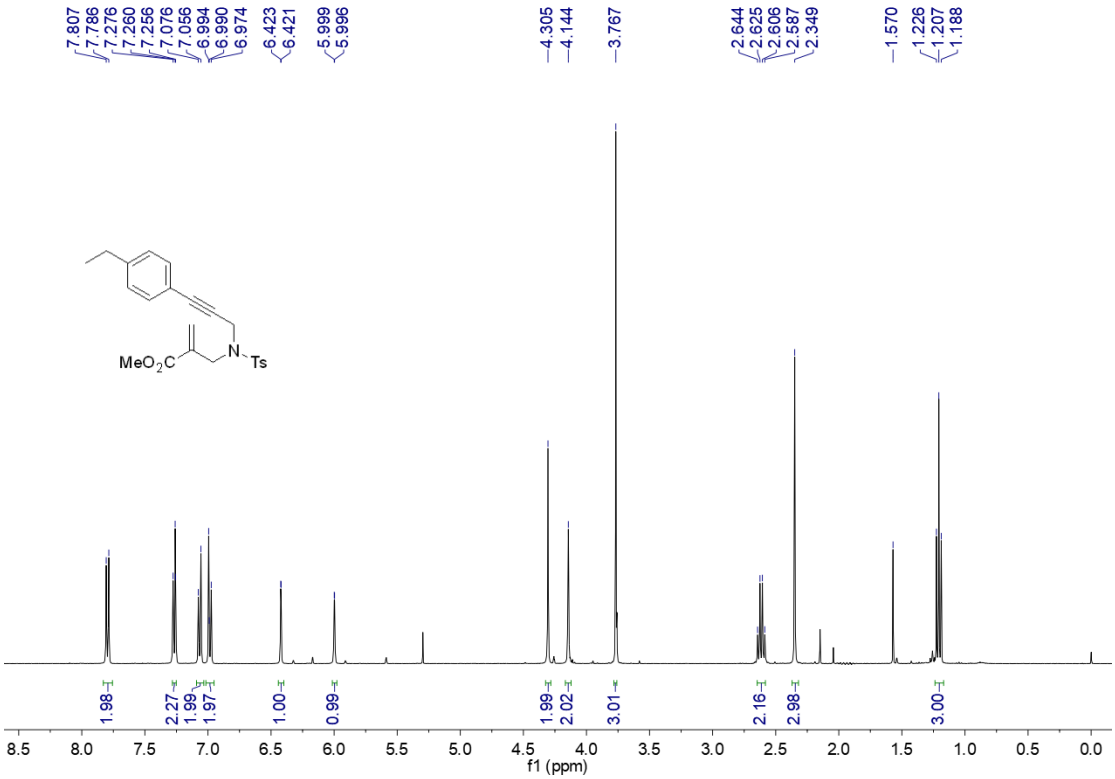


^{13}C NMR ($CDCl_3$, 101 MHz)

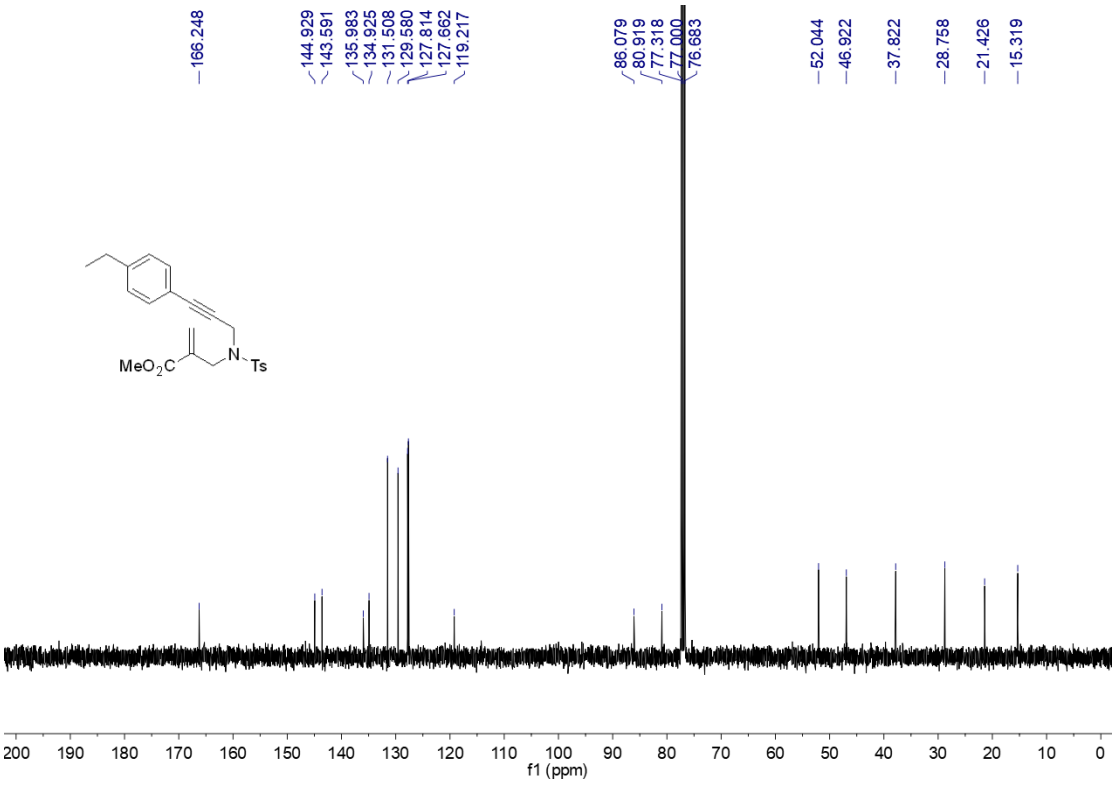


(3f)

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

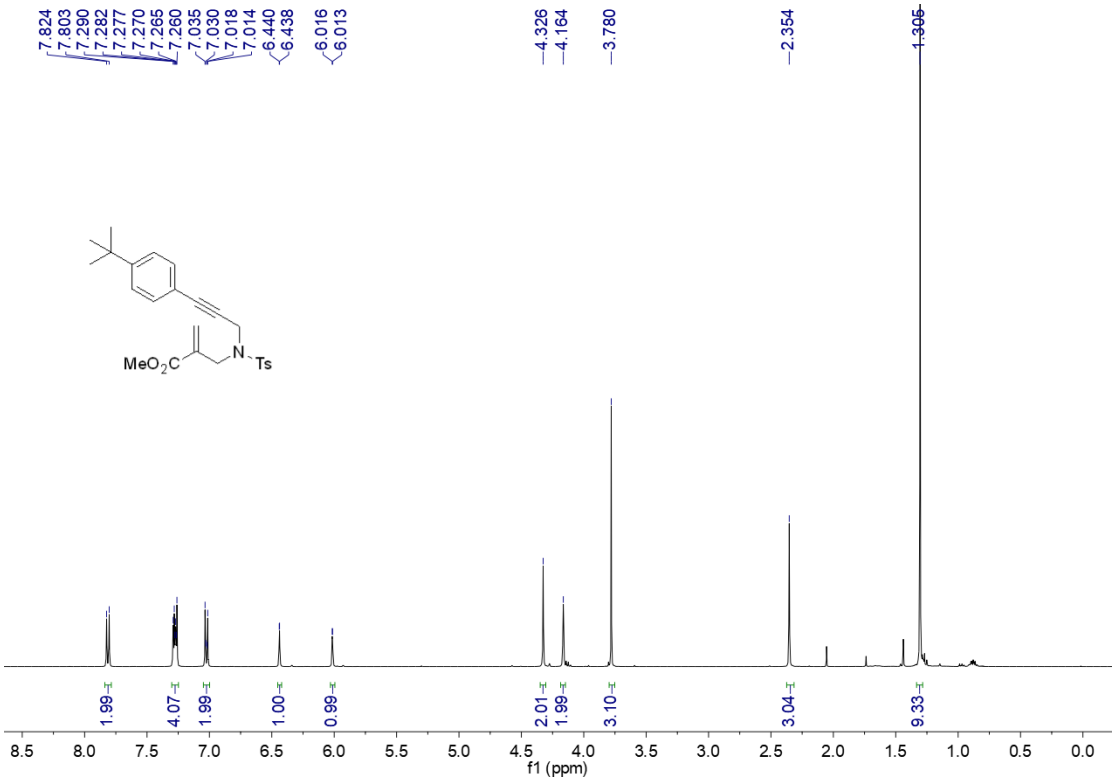


^{13}C NMR ($CDCl_3$, 101 MHz)

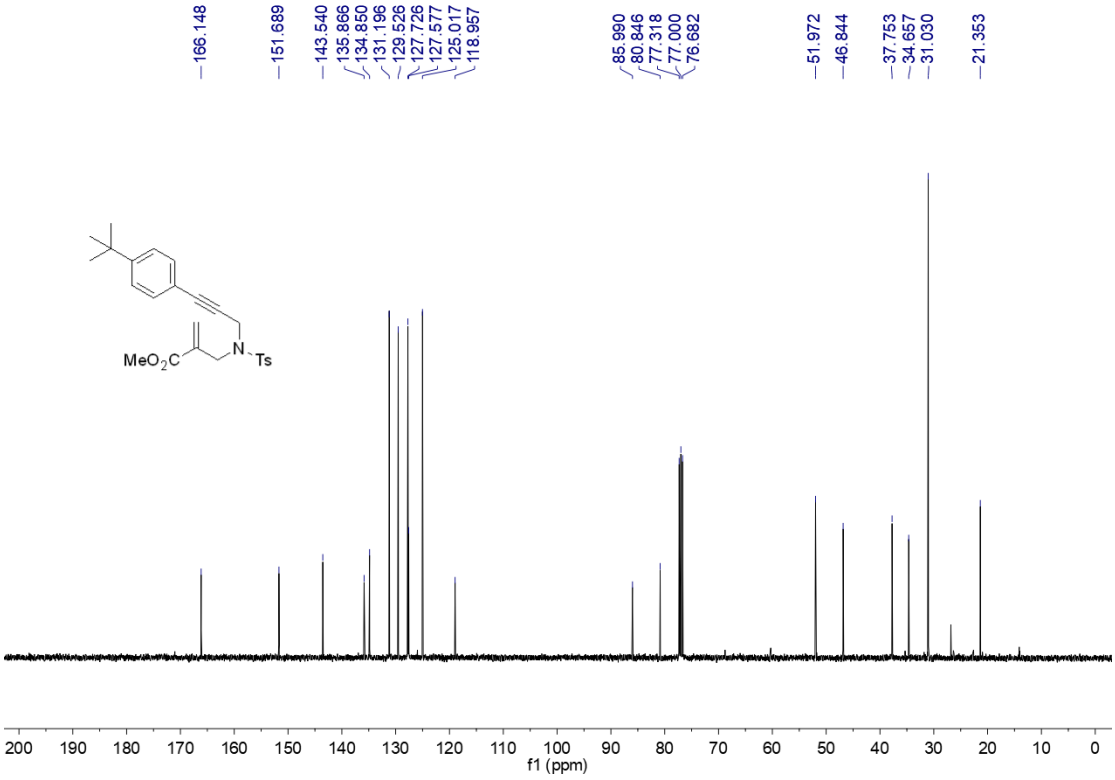


(3g)

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

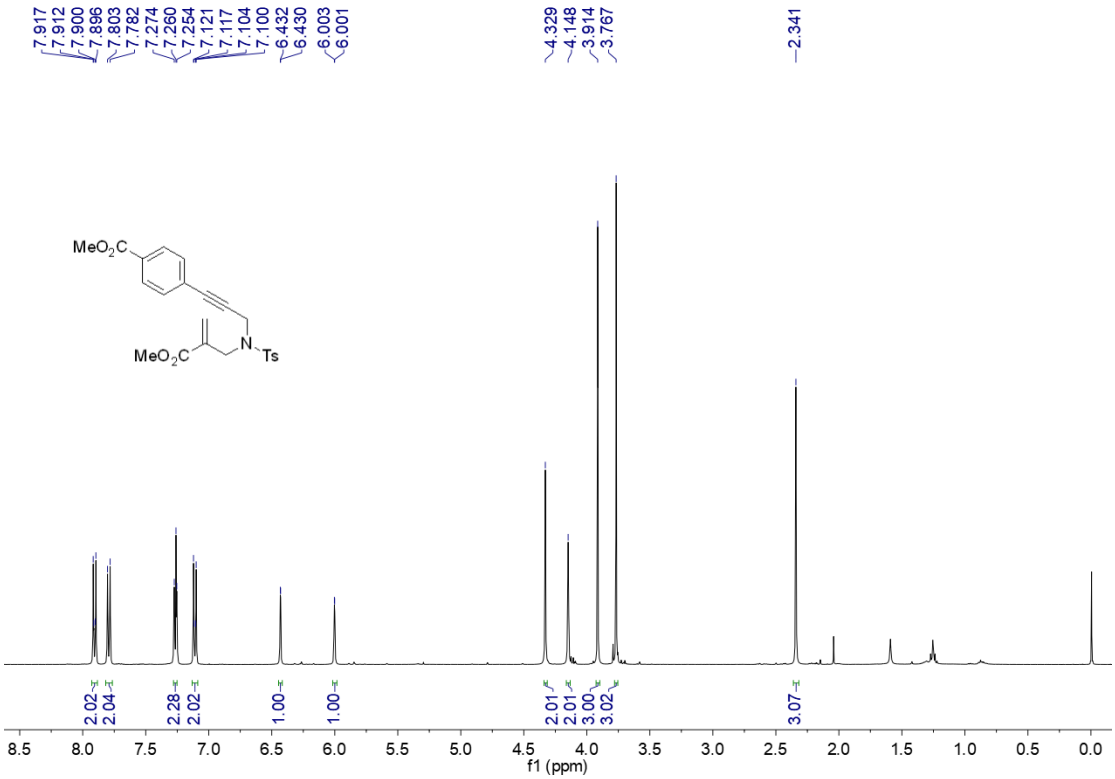


^{13}C NMR ($CDCl_3$, 101 MHz)

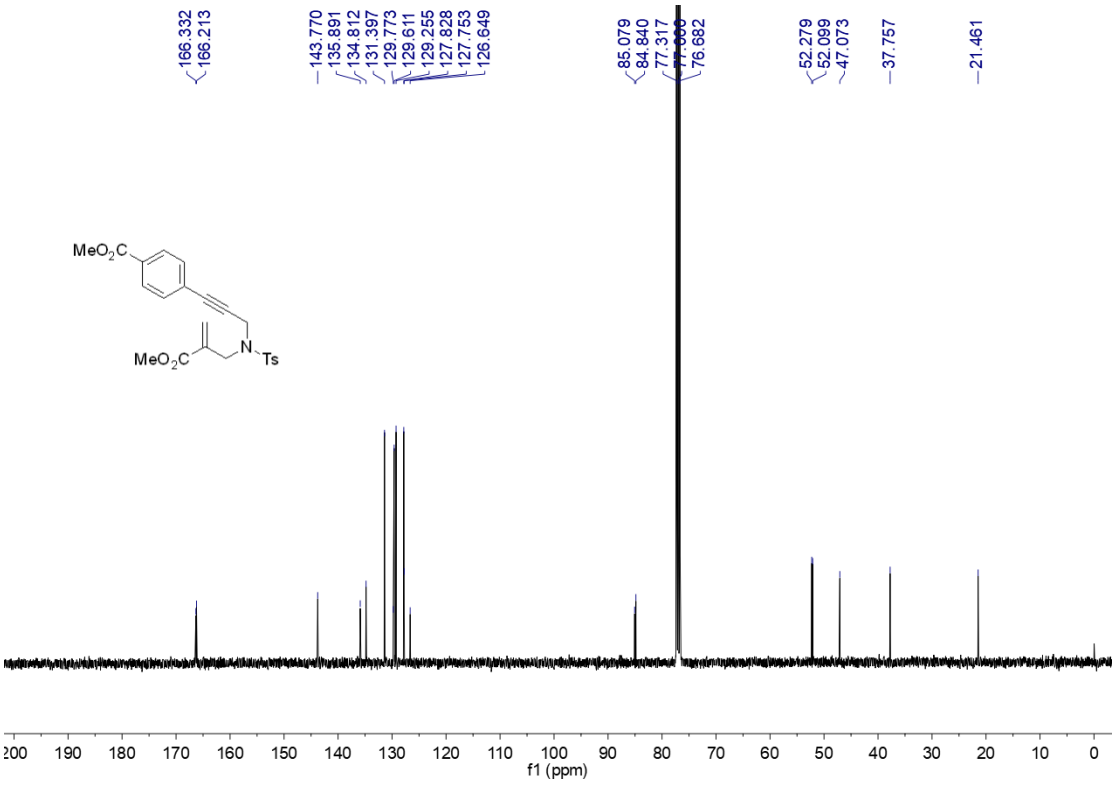


(3h)

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

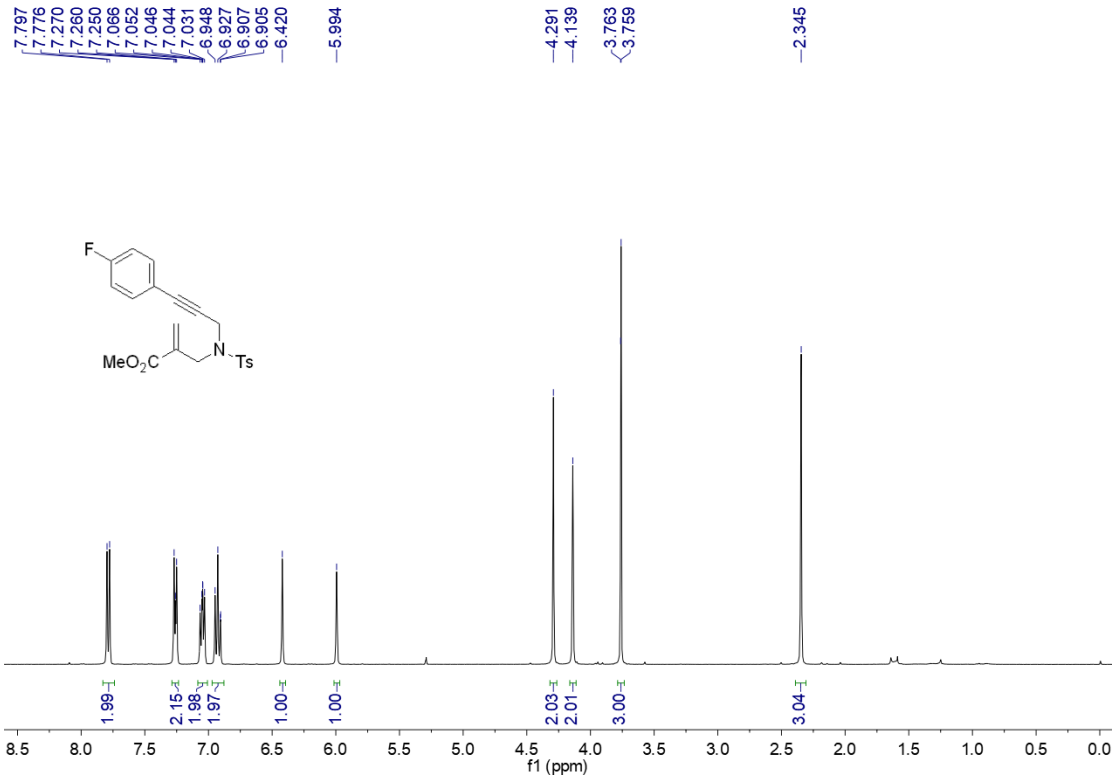


^{13}C NMR ($CDCl_3$, 101 MHz)

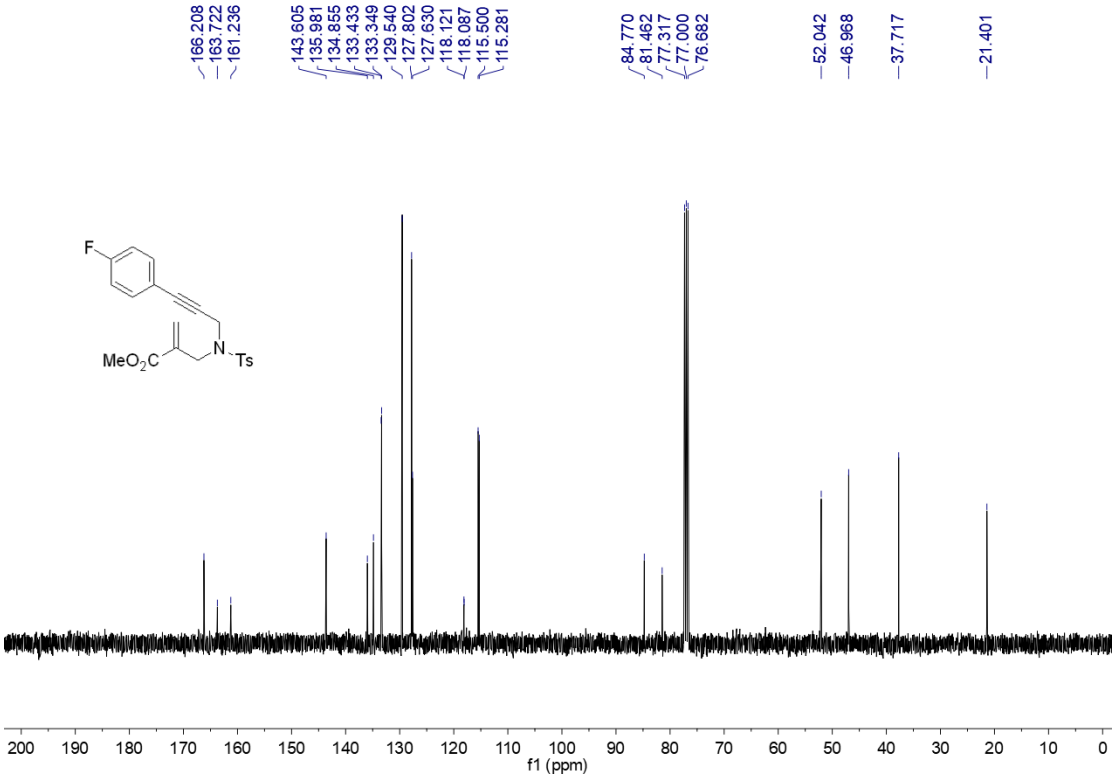


(3i)

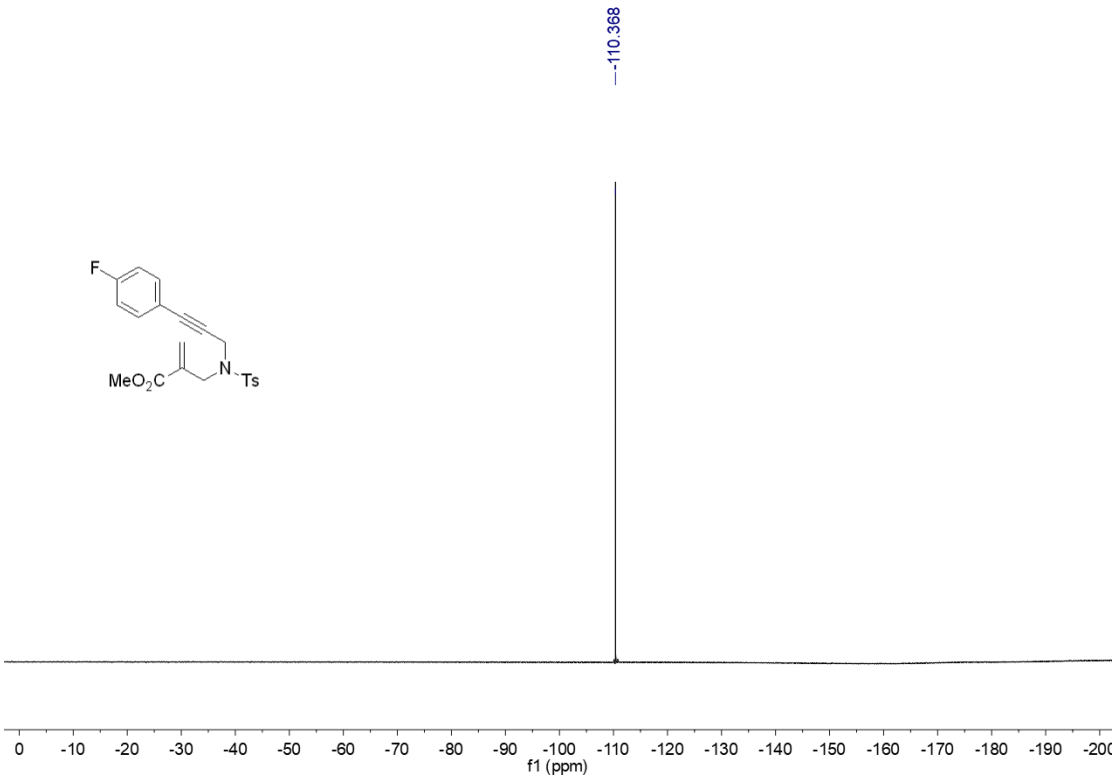
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

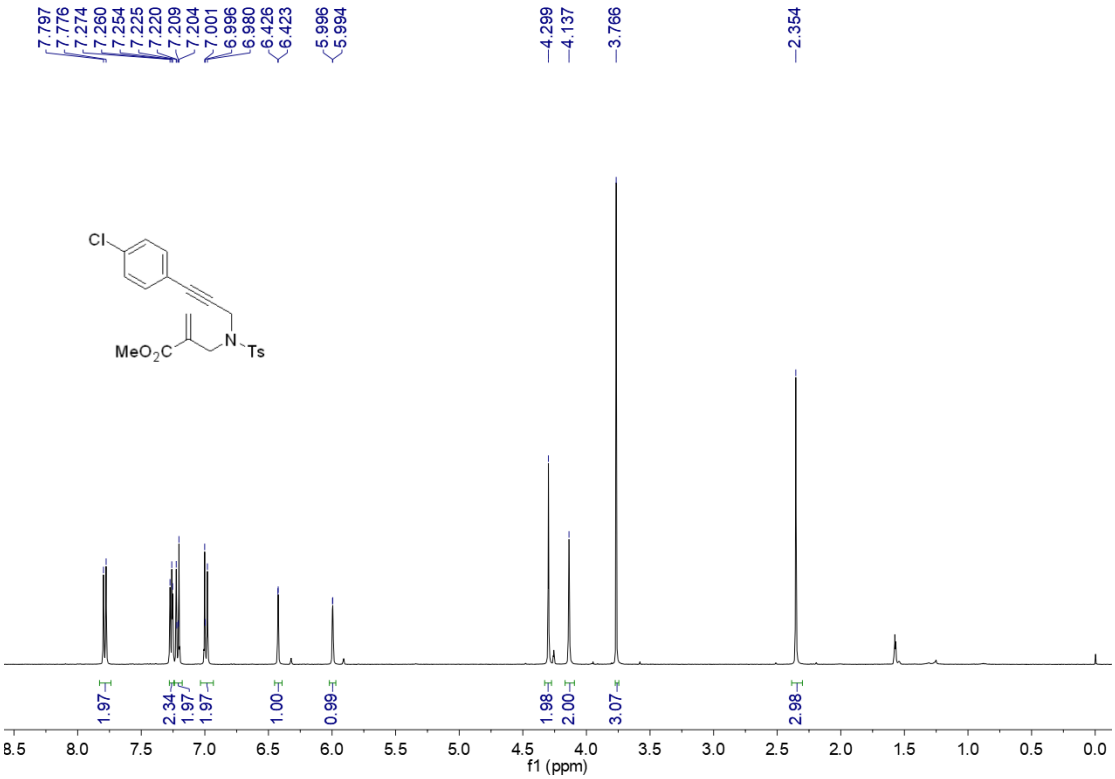


^{19}F NMR ($CDCl_3$, 376 MHz)

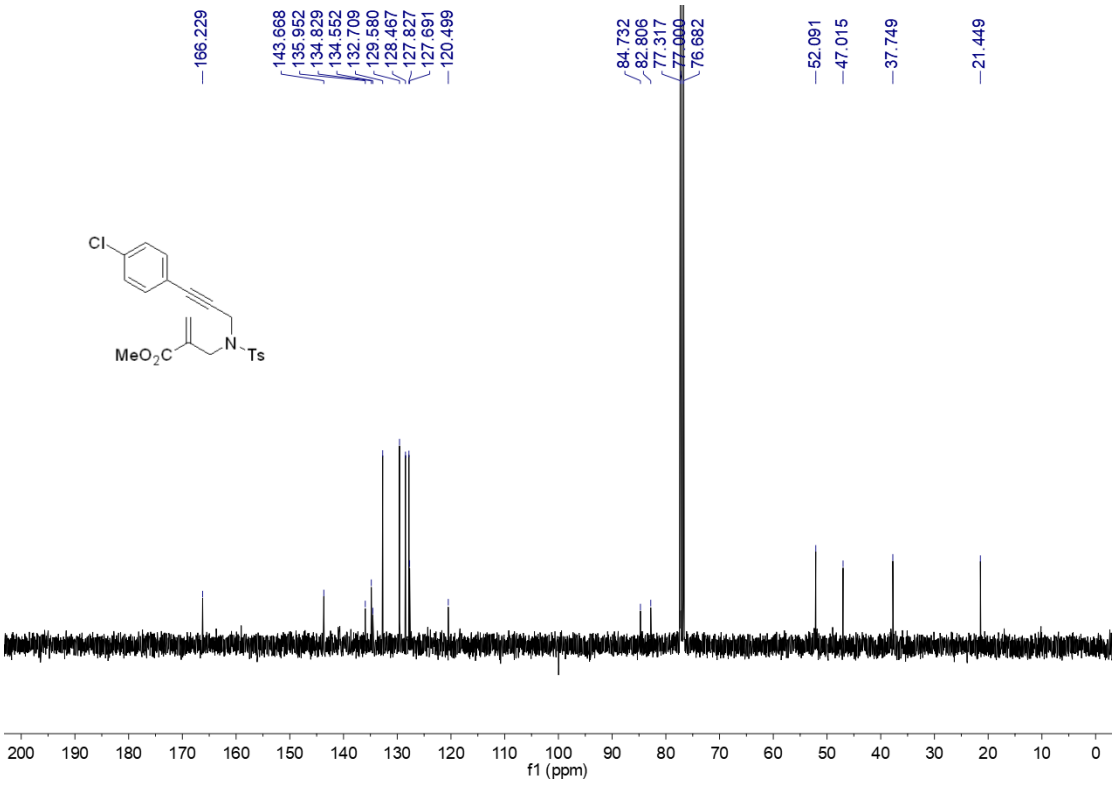


(3j)

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

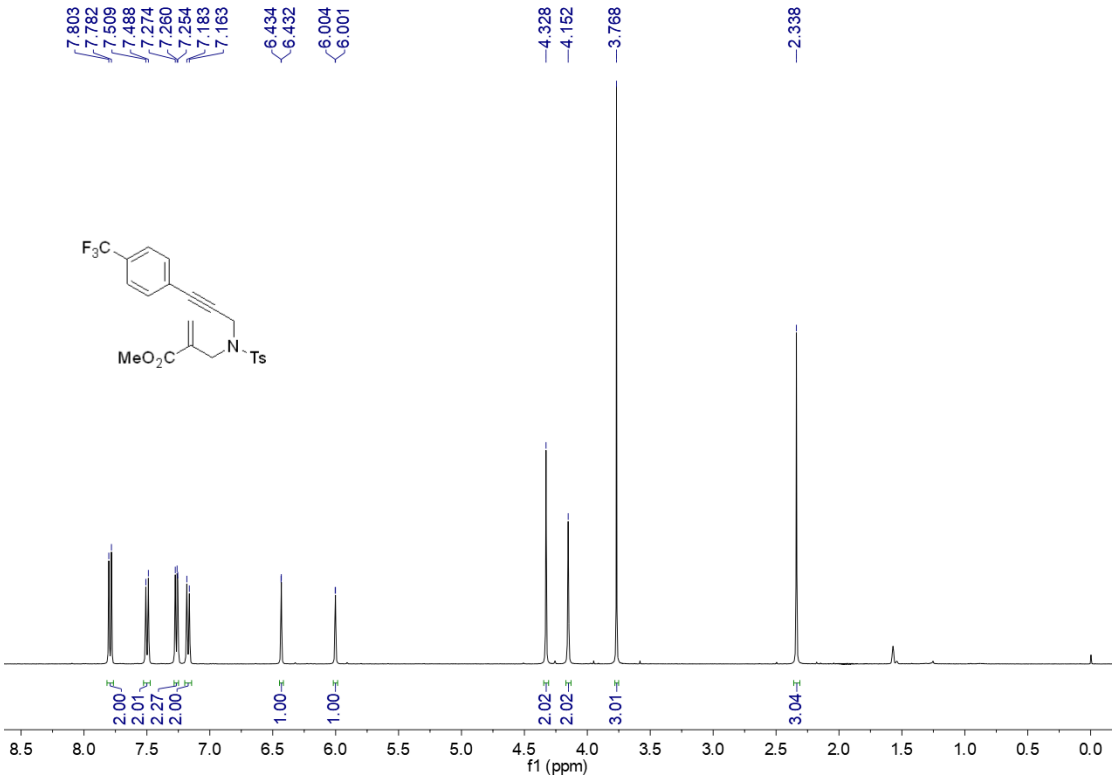


^{13}C NMR ($CDCl_3$, 101 MHz)

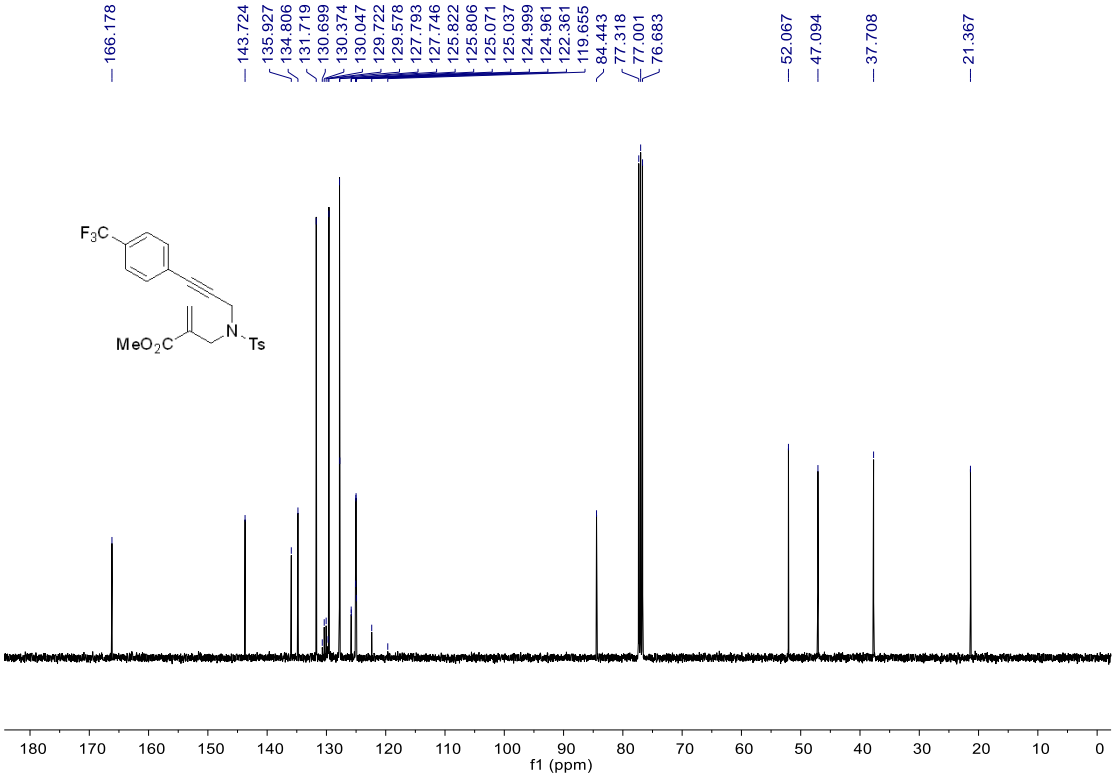


(3k)

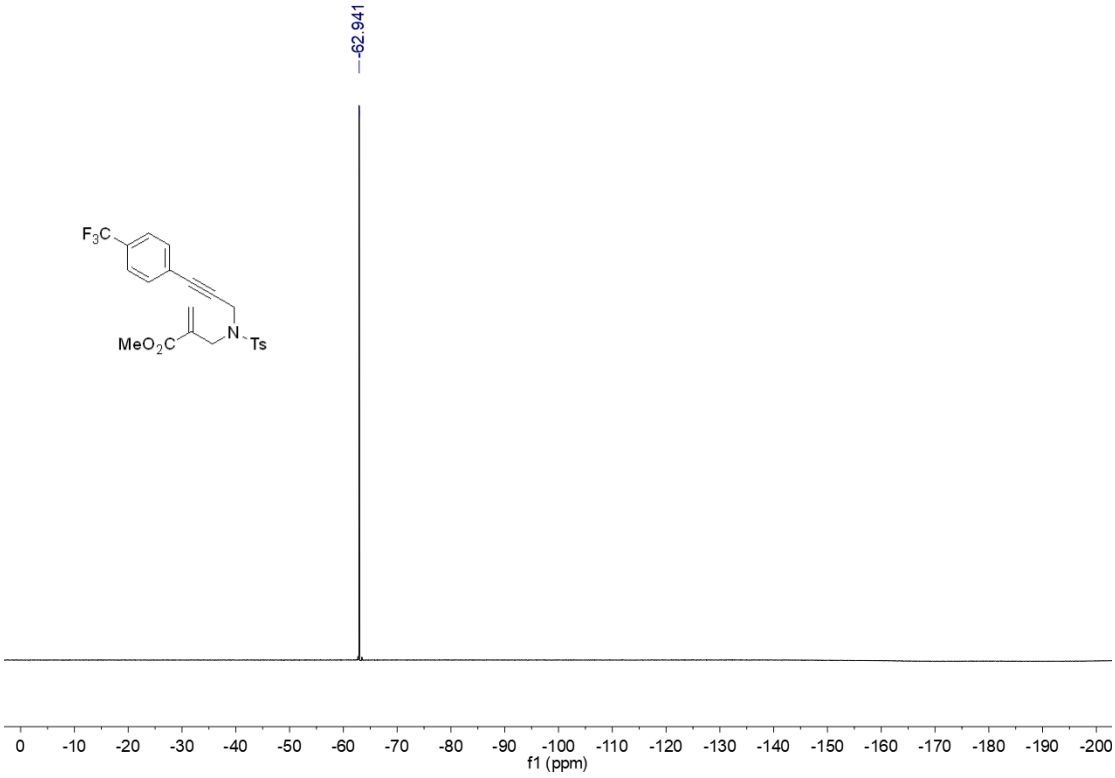
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

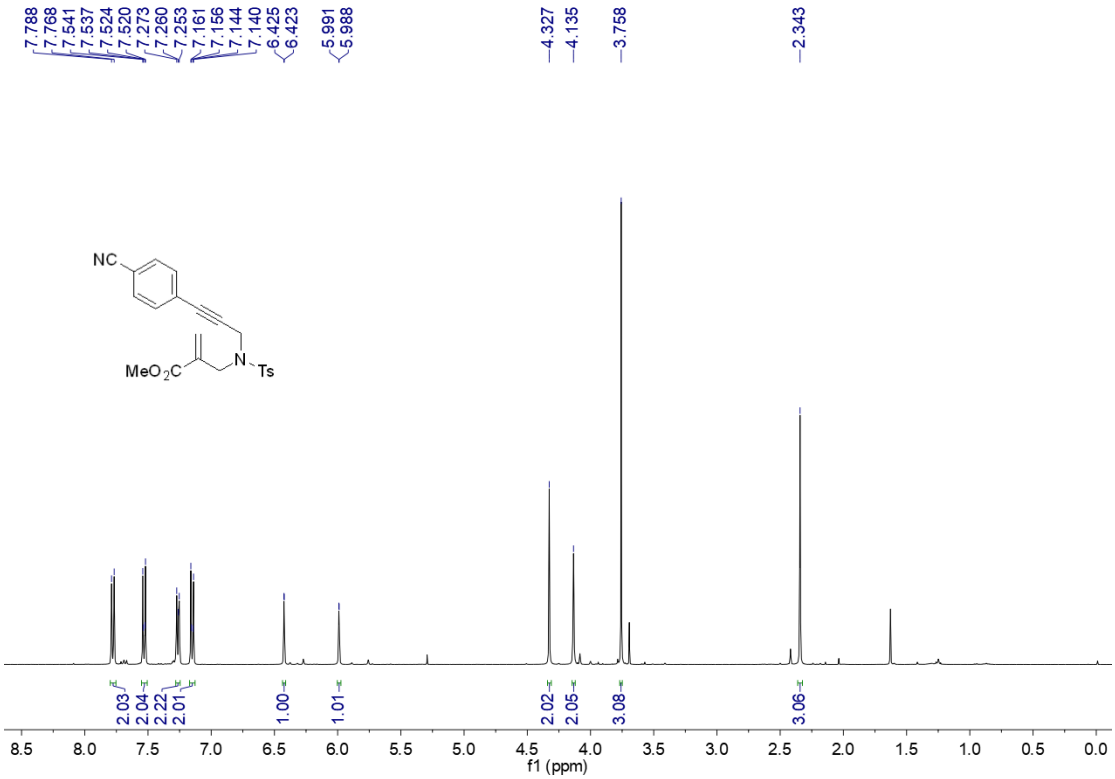


^{19}F NMR ($CDCl_3$, 376 MHz)

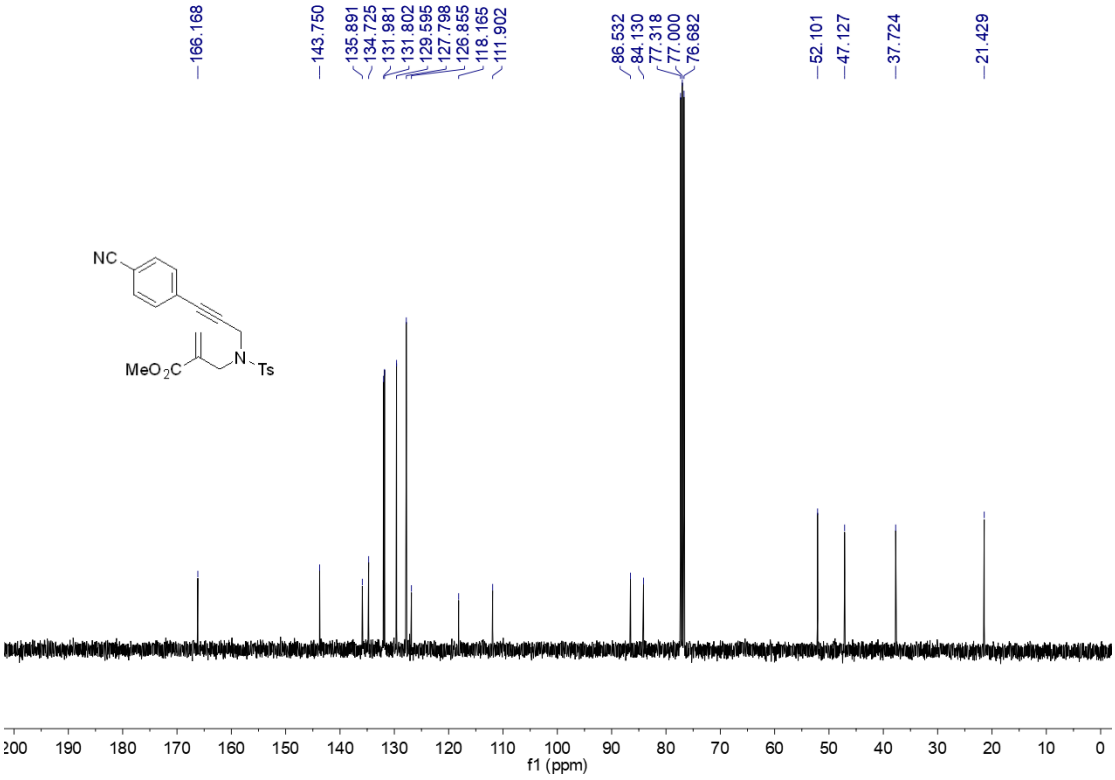


(3l)

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

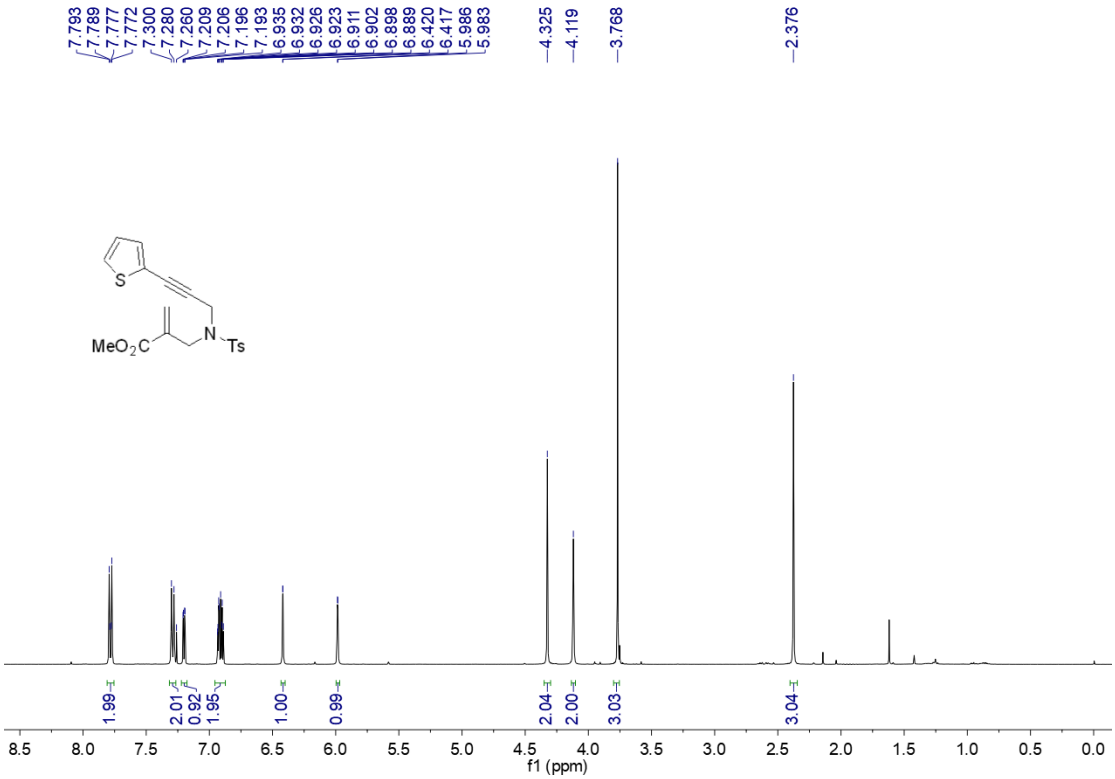


^{13}C NMR ($CDCl_3$, 101 MHz)

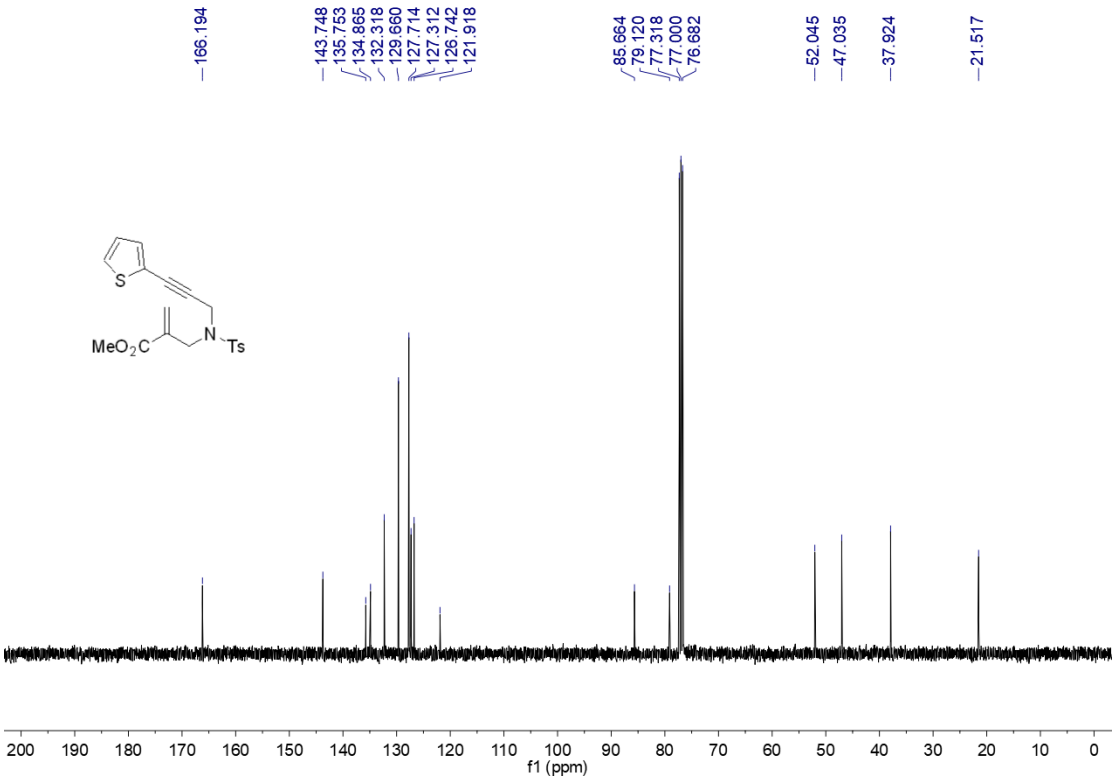


(3m)

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

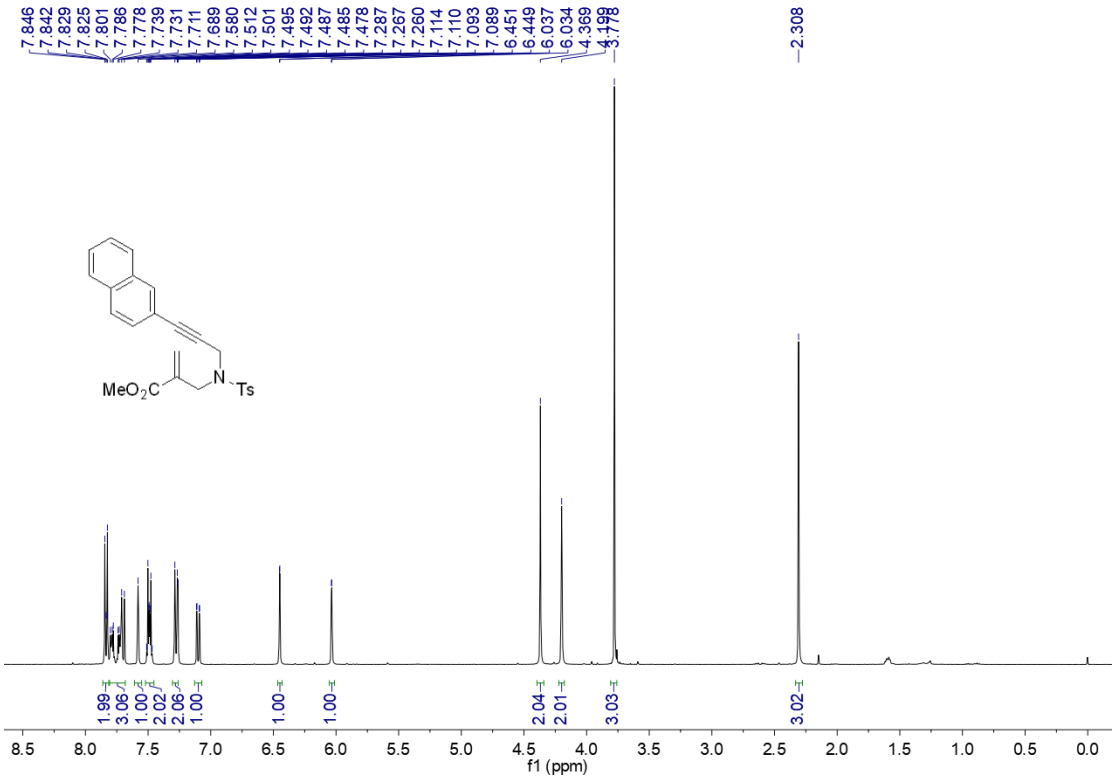


^{13}C NMR ($CDCl_3$, 101 MHz)

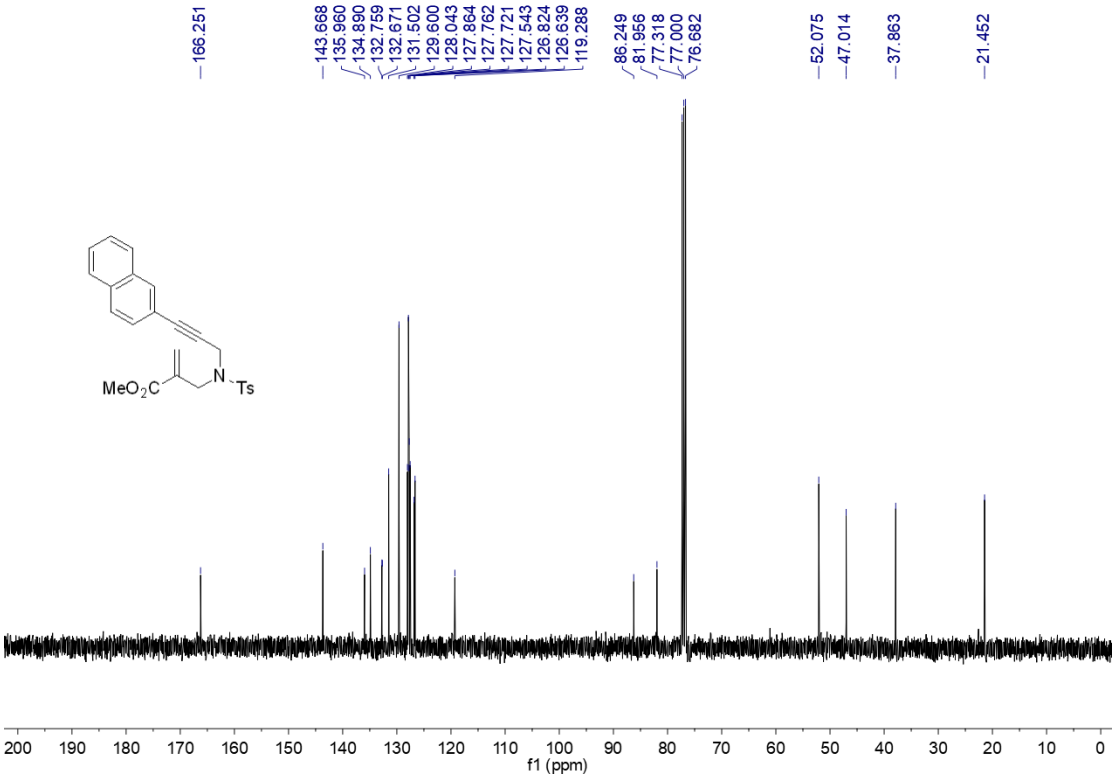


(3n)

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

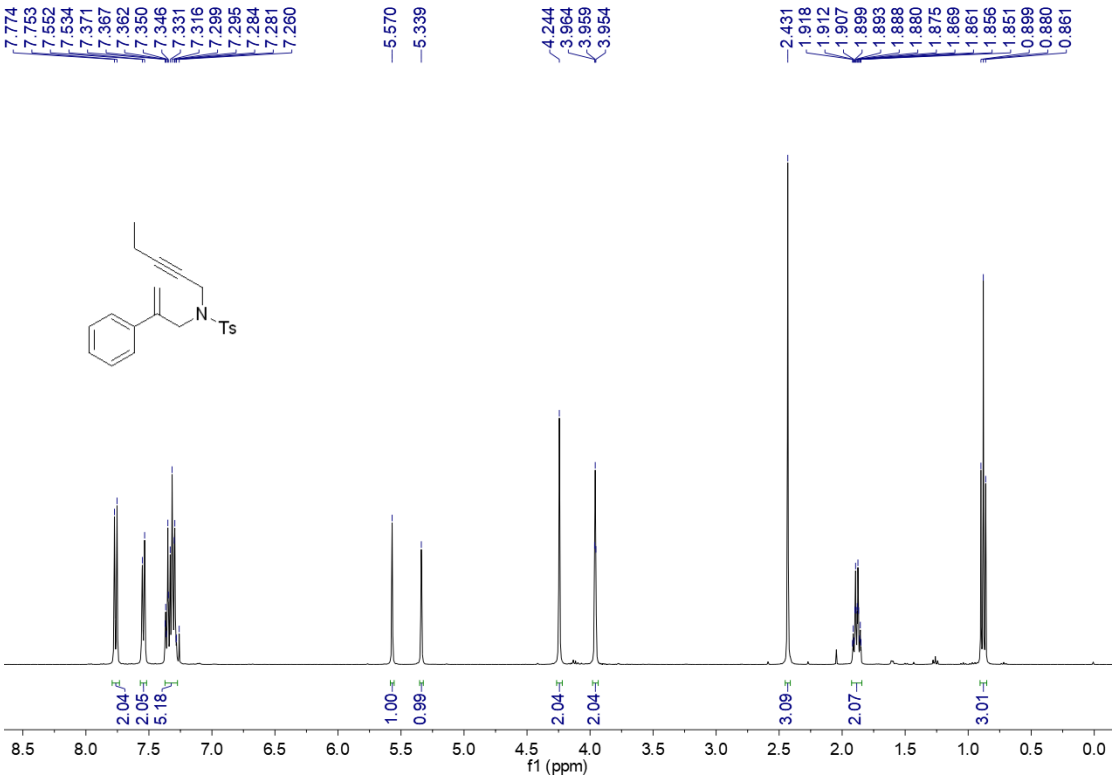


^{13}C NMR ($CDCl_3$, 101 MHz)

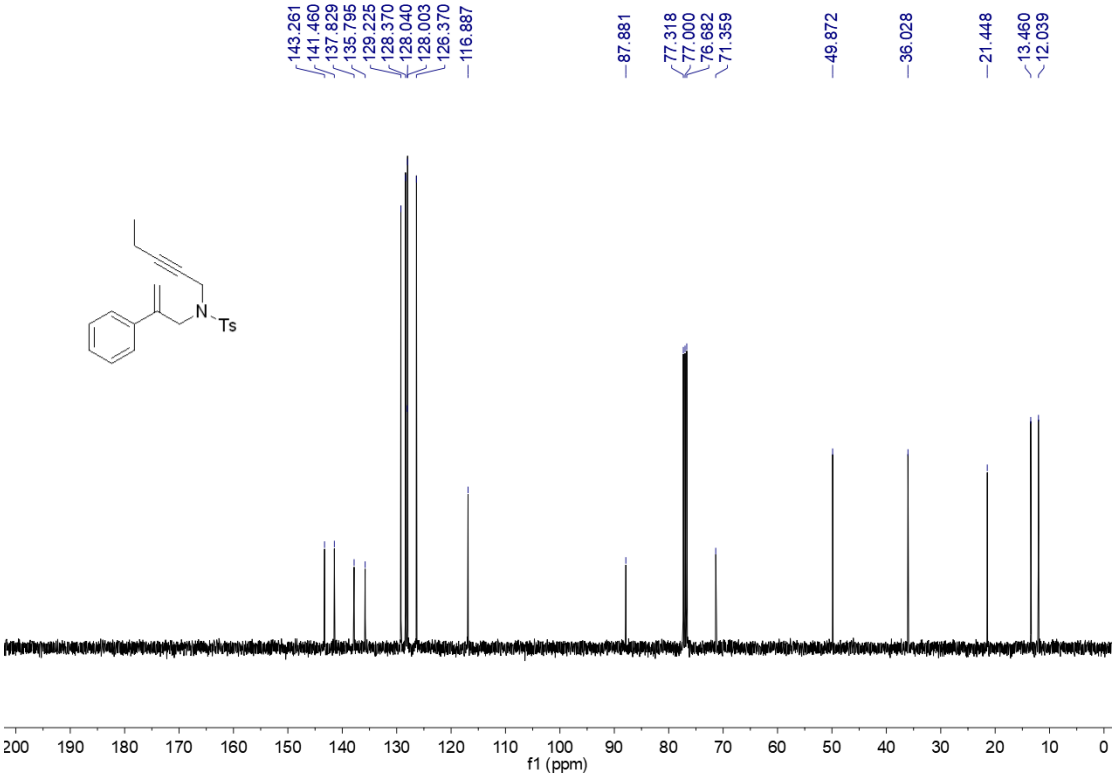


(3p)

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

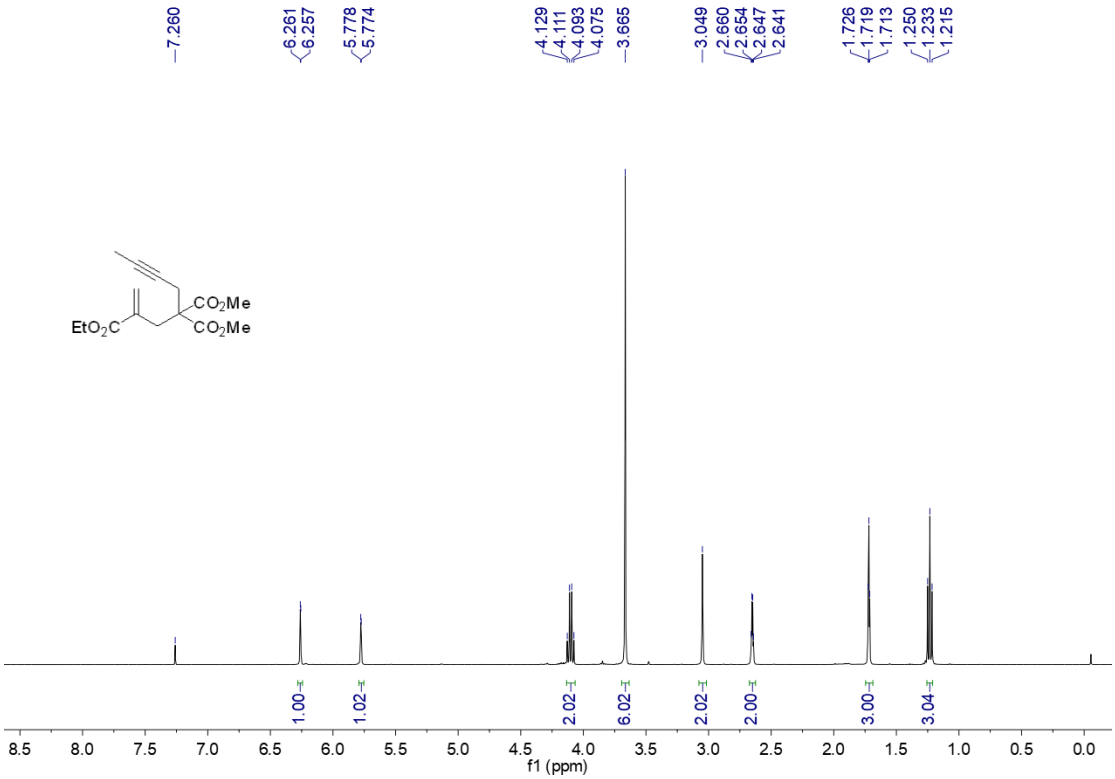


^{13}C NMR ($CDCl_3$, 101 MHz)

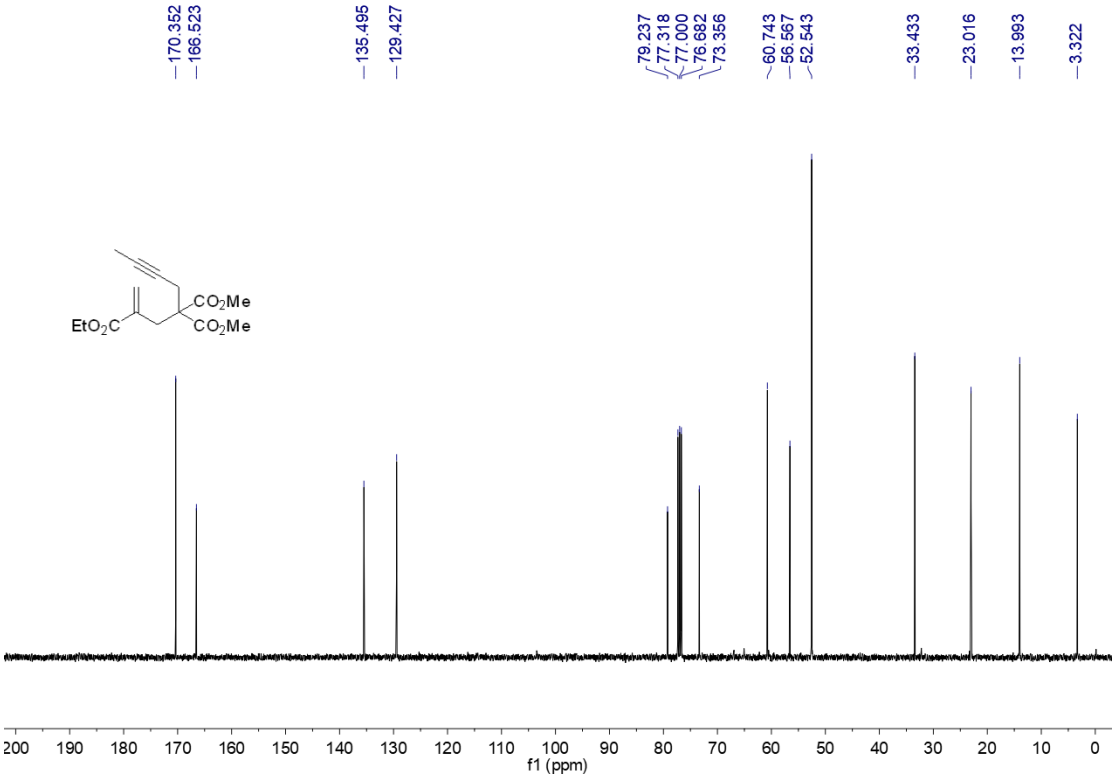


(3u)

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

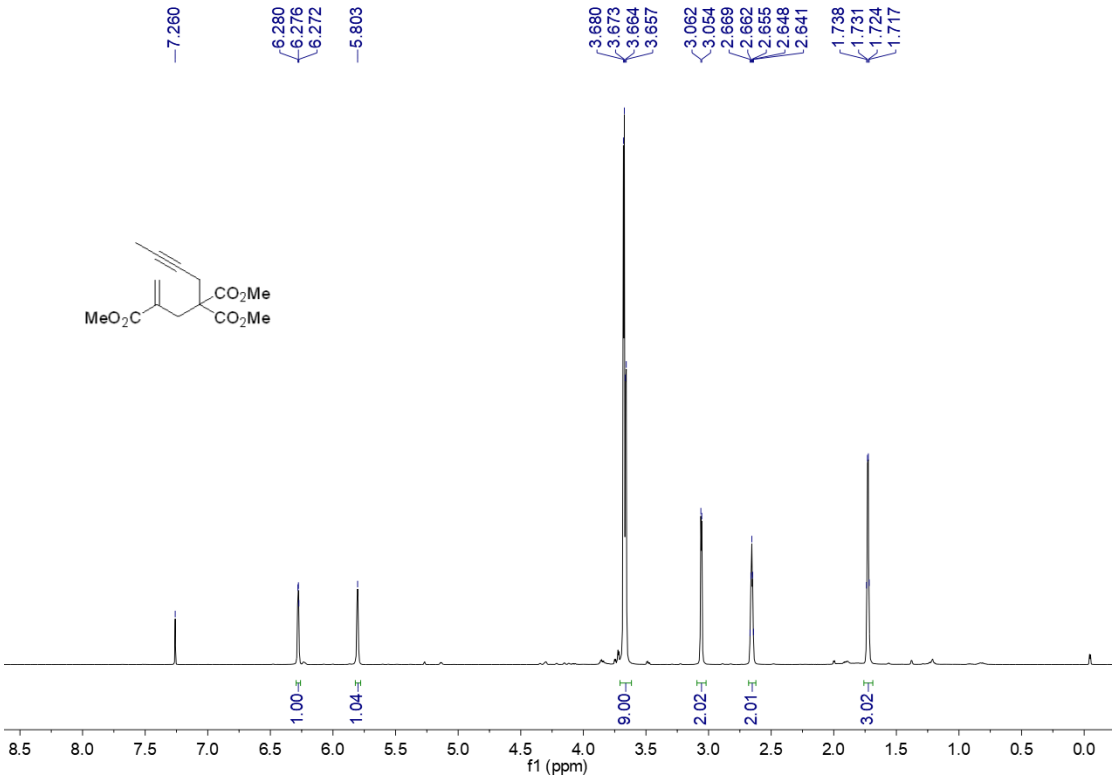


^{13}C NMR ($CDCl_3$, 101 MHz)

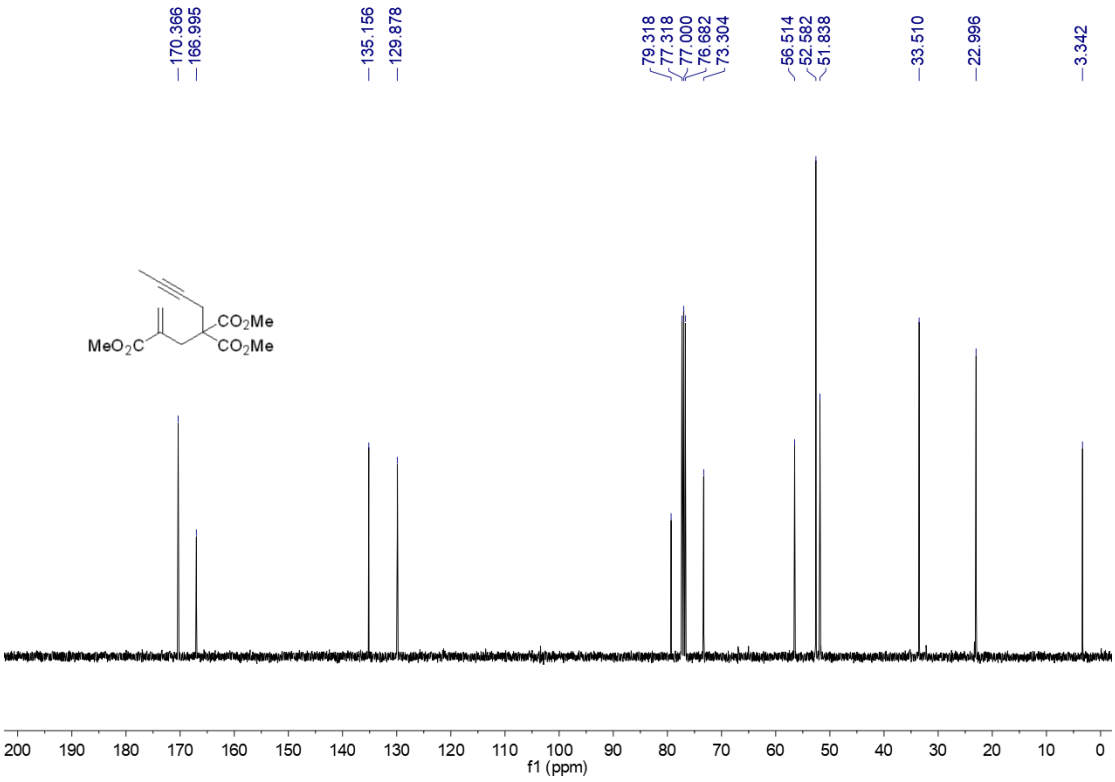


(3v)

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

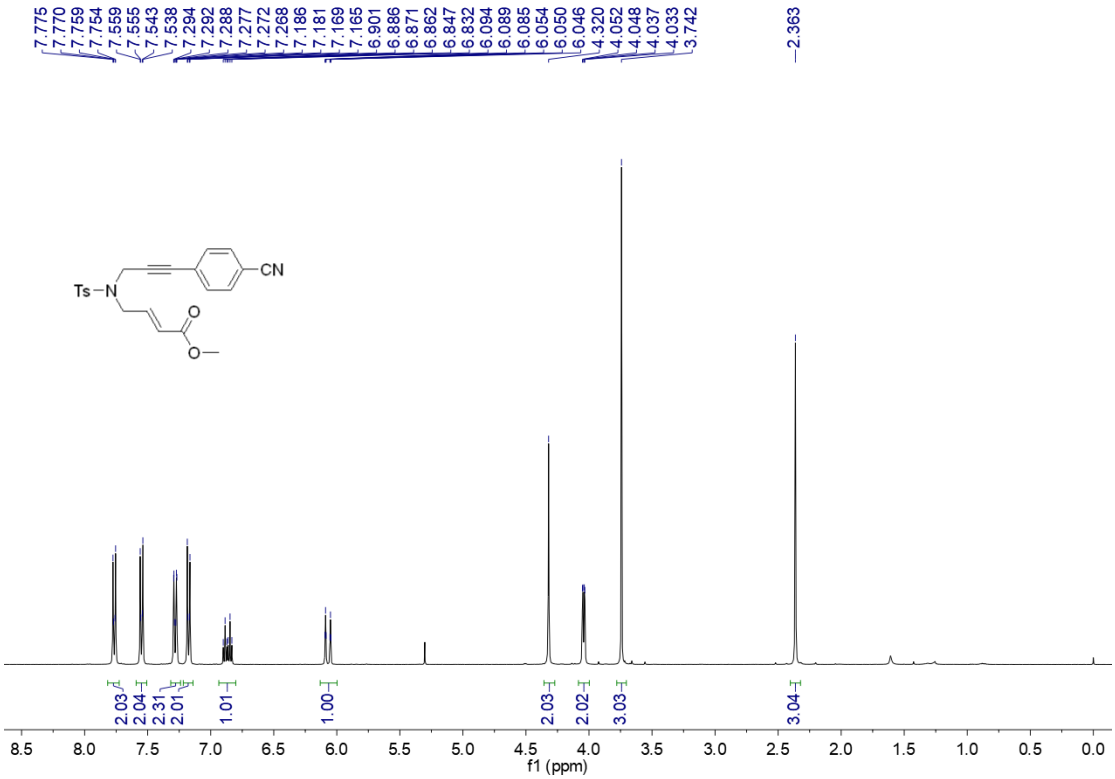


^{13}C NMR ($CDCl_3$, 101 MHz)

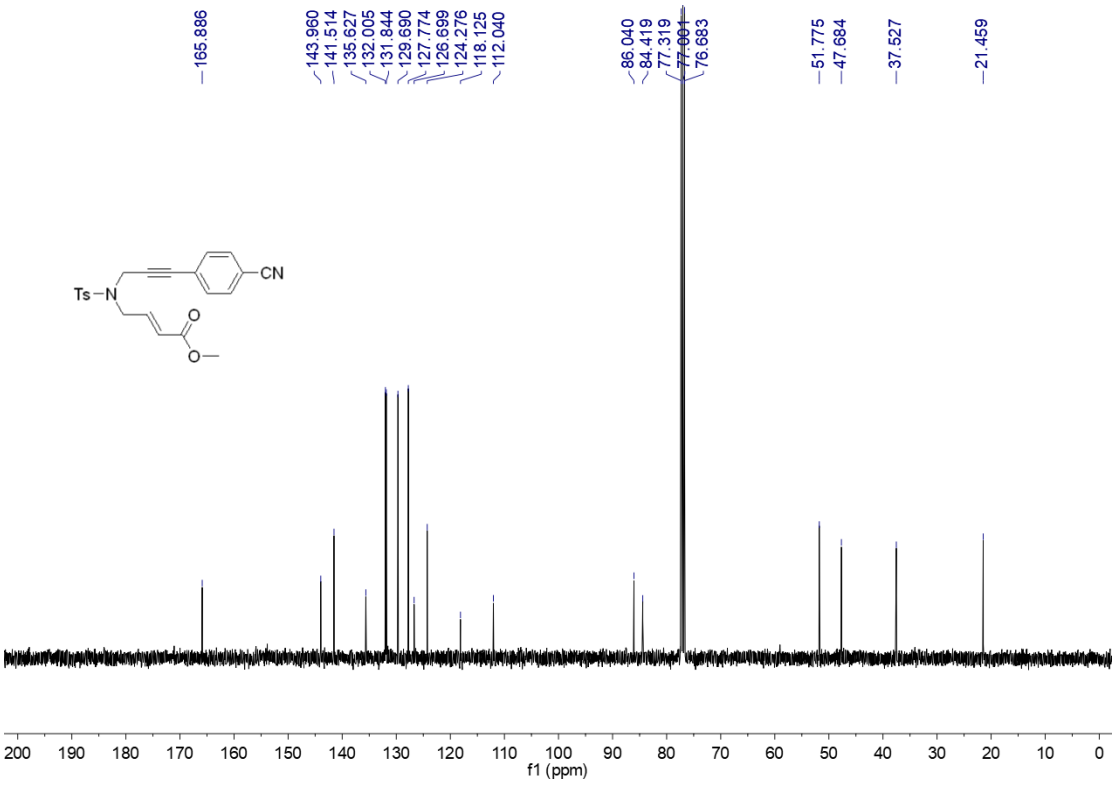


(3w)

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

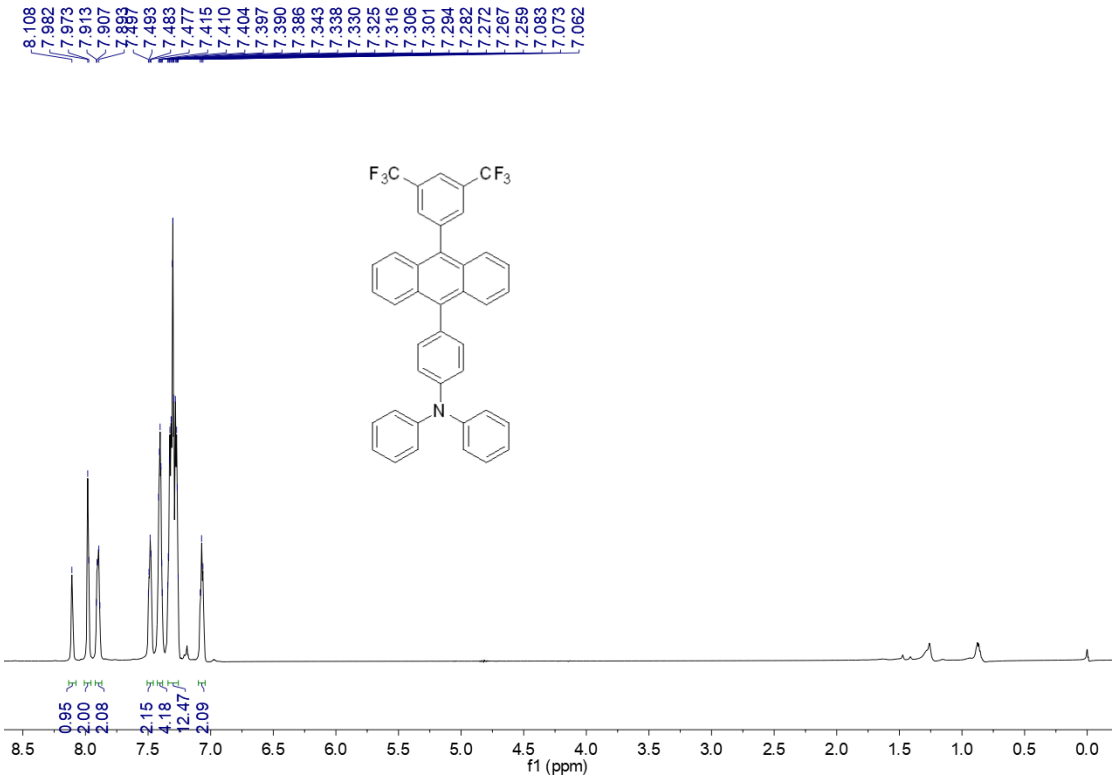


^{13}C NMR ($CDCl_3$, 101 MHz)

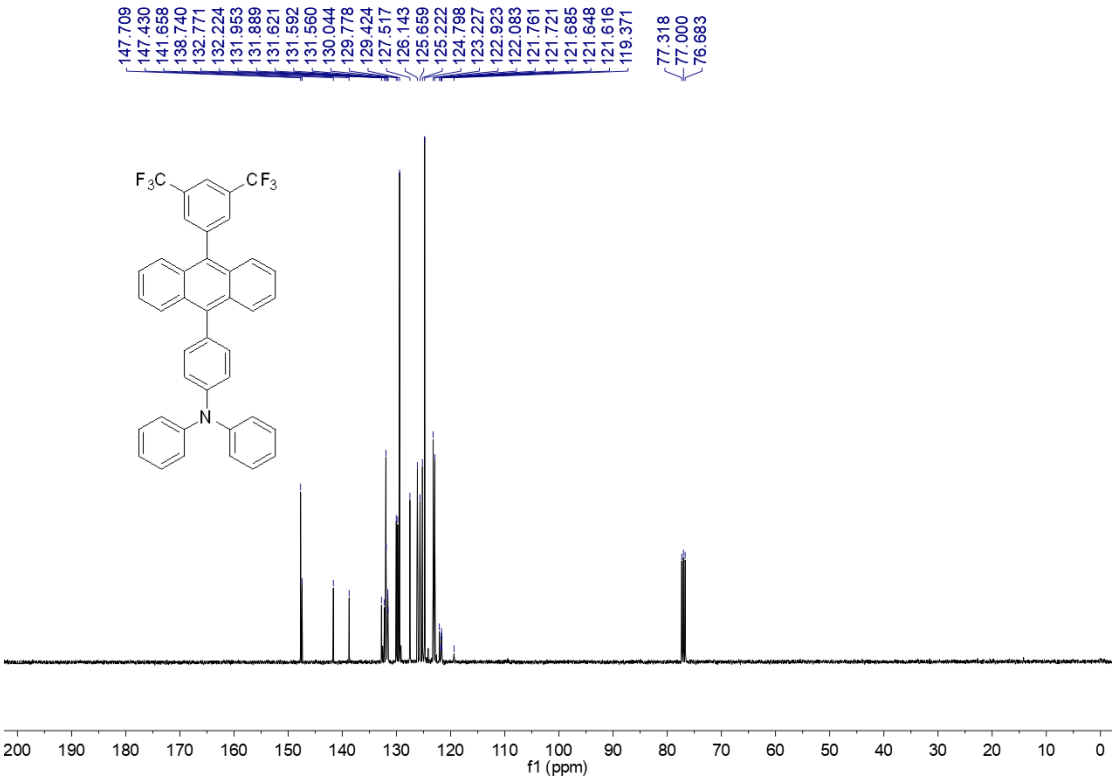


PC2

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



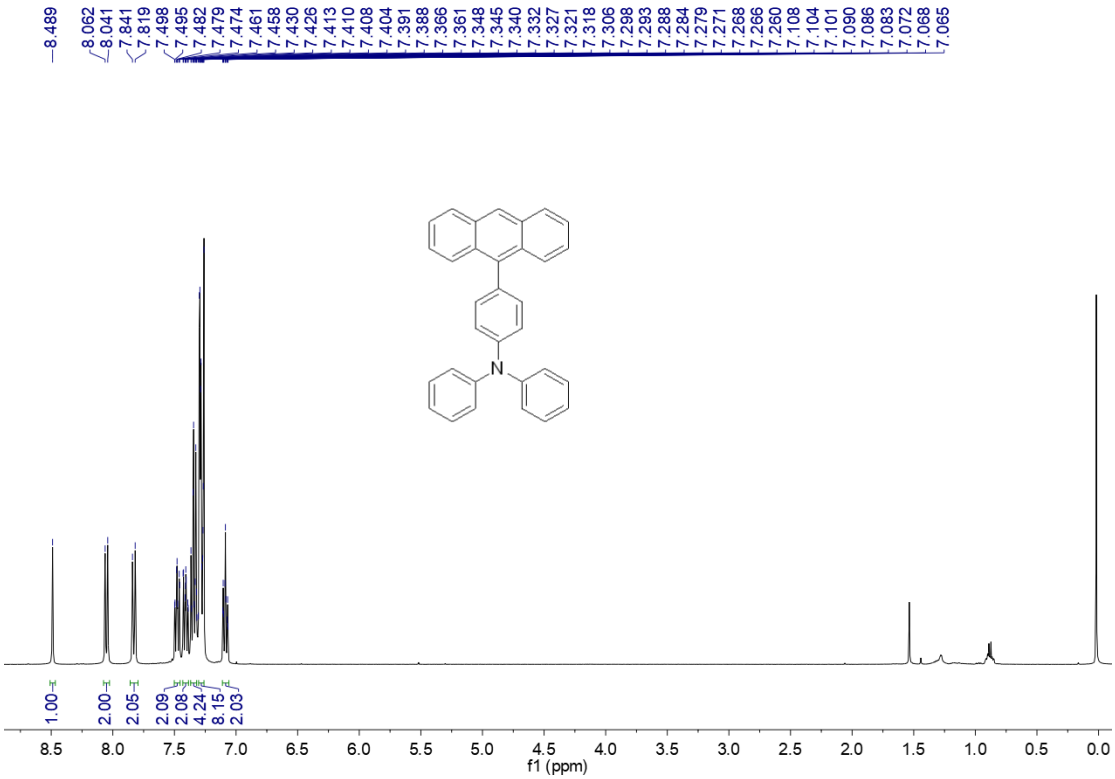
^{13}C NMR ($CDCl_3$, 101 MHz)



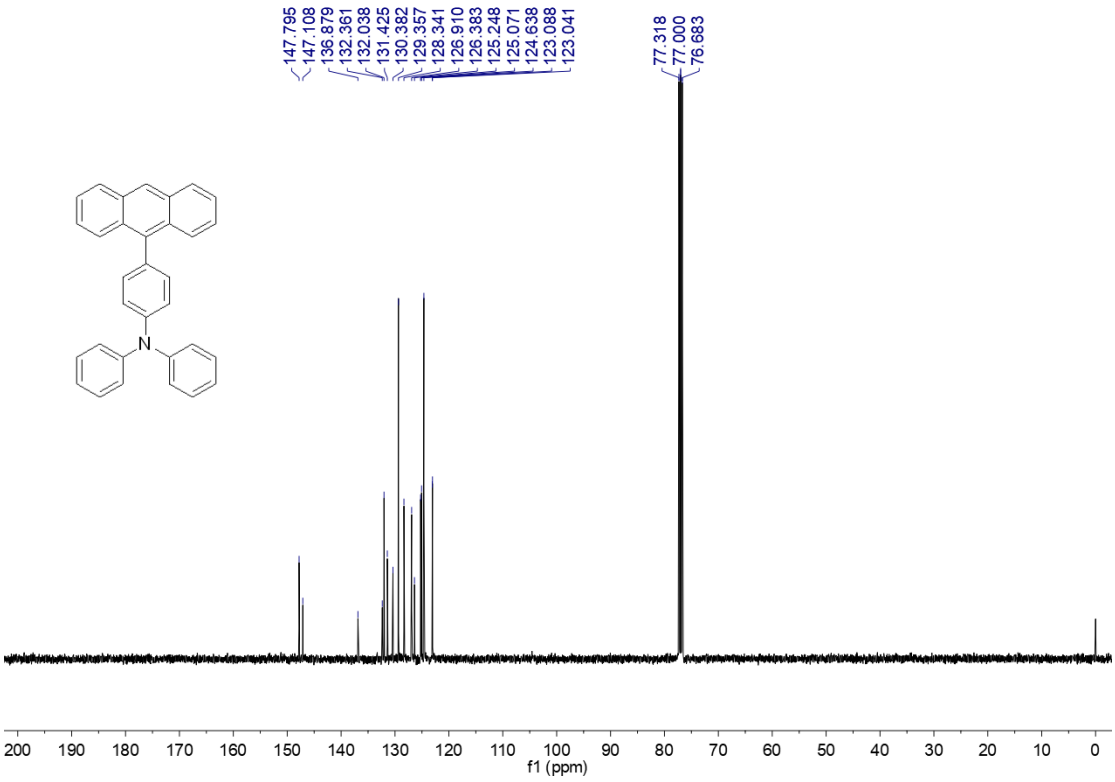
^{19}F NMR ($CDCl_3$, 376 MHz)

PC4

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

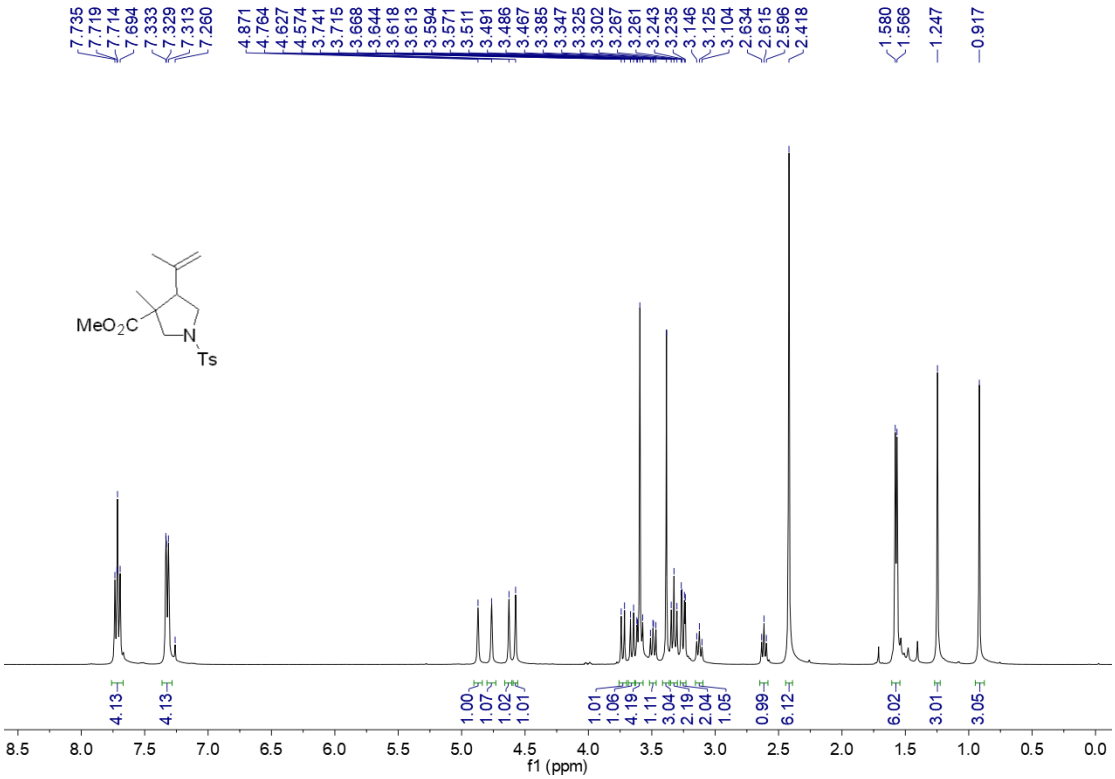


^{13}C NMR ($CDCl_3$, 101 MHz)

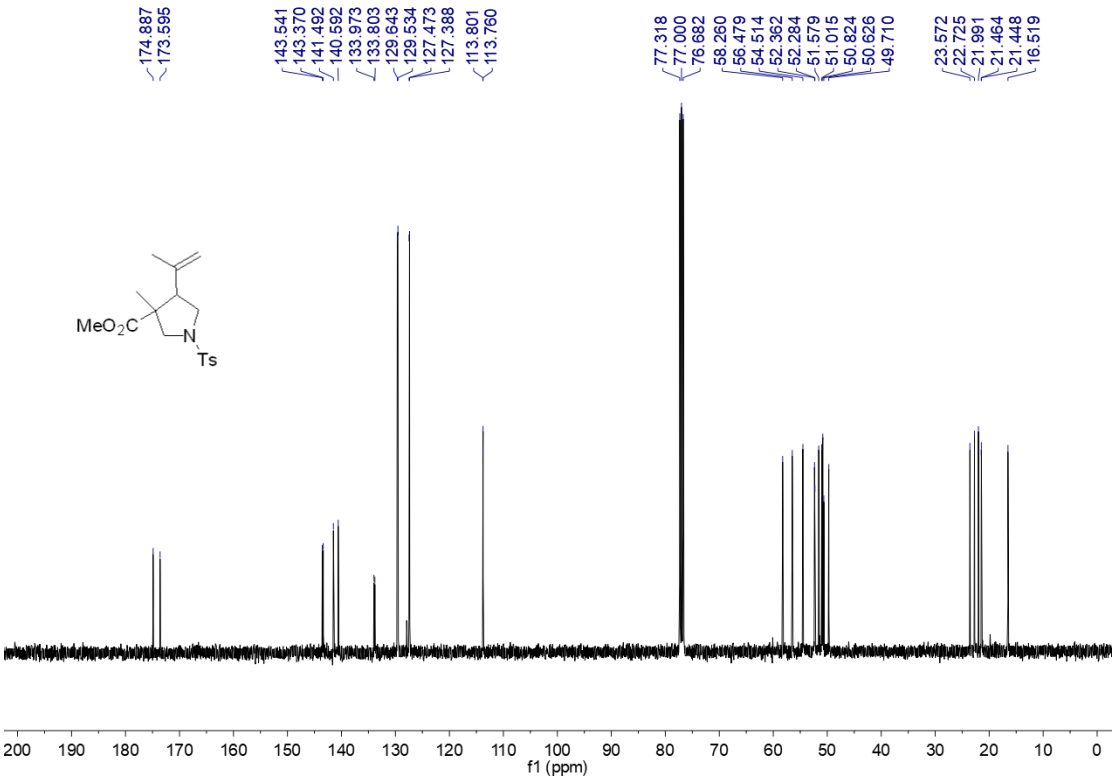


(**2a**)

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

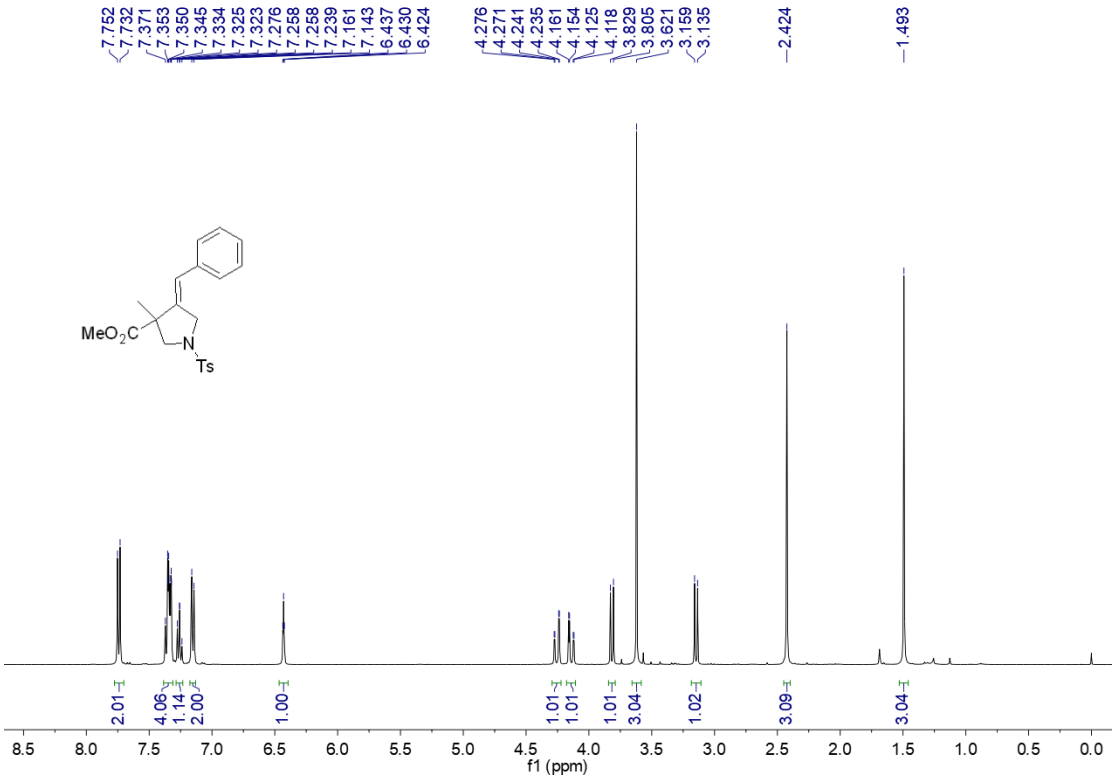


^{13}C NMR ($CDCl_3$, 101 MHz)

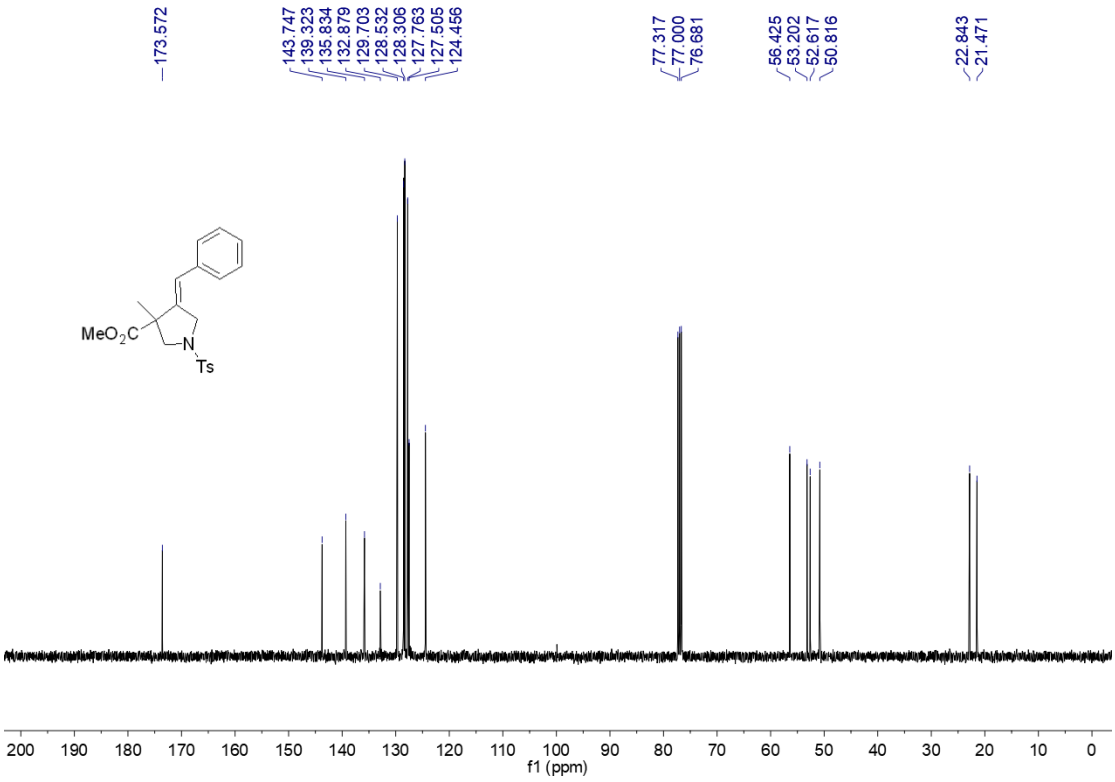


(2b)

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

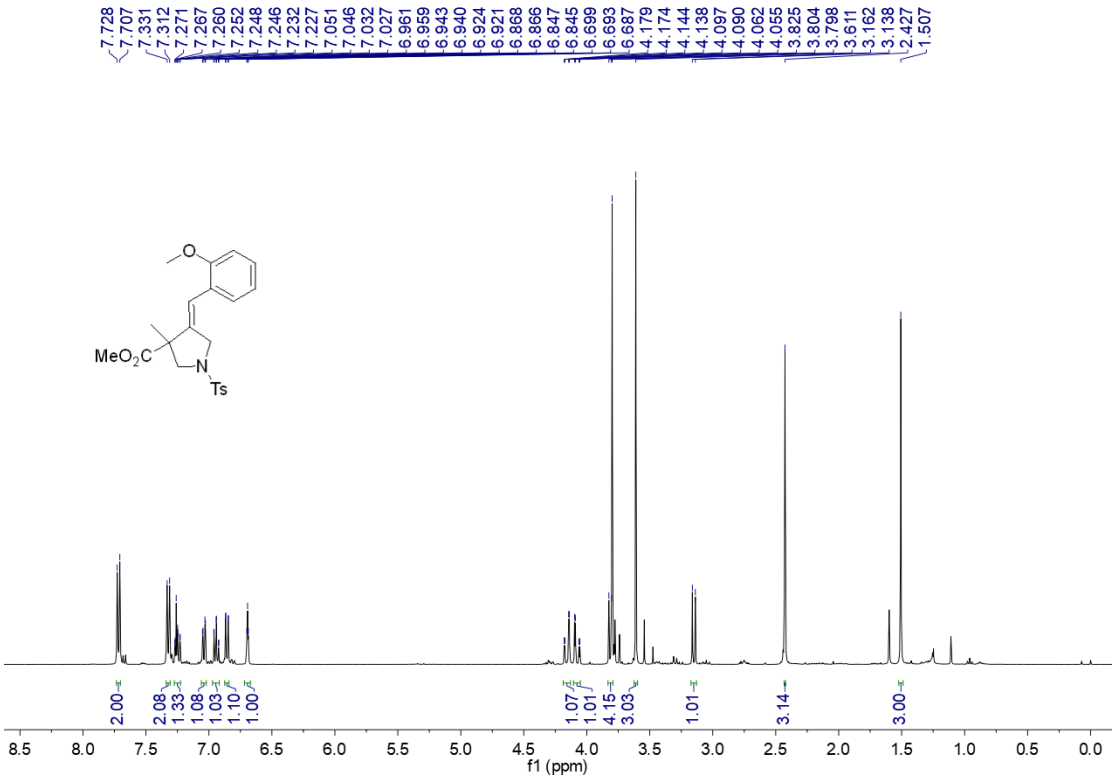


^{13}C NMR ($CDCl_3$, 101 MHz)

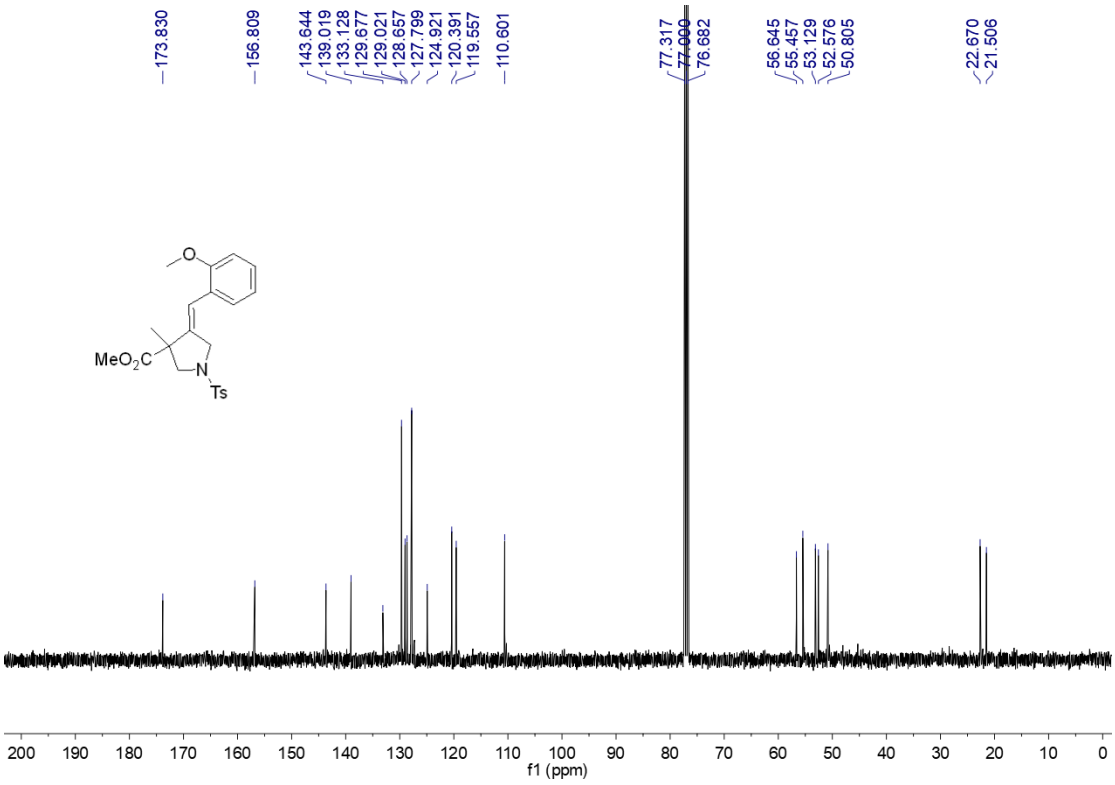


(2c)

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

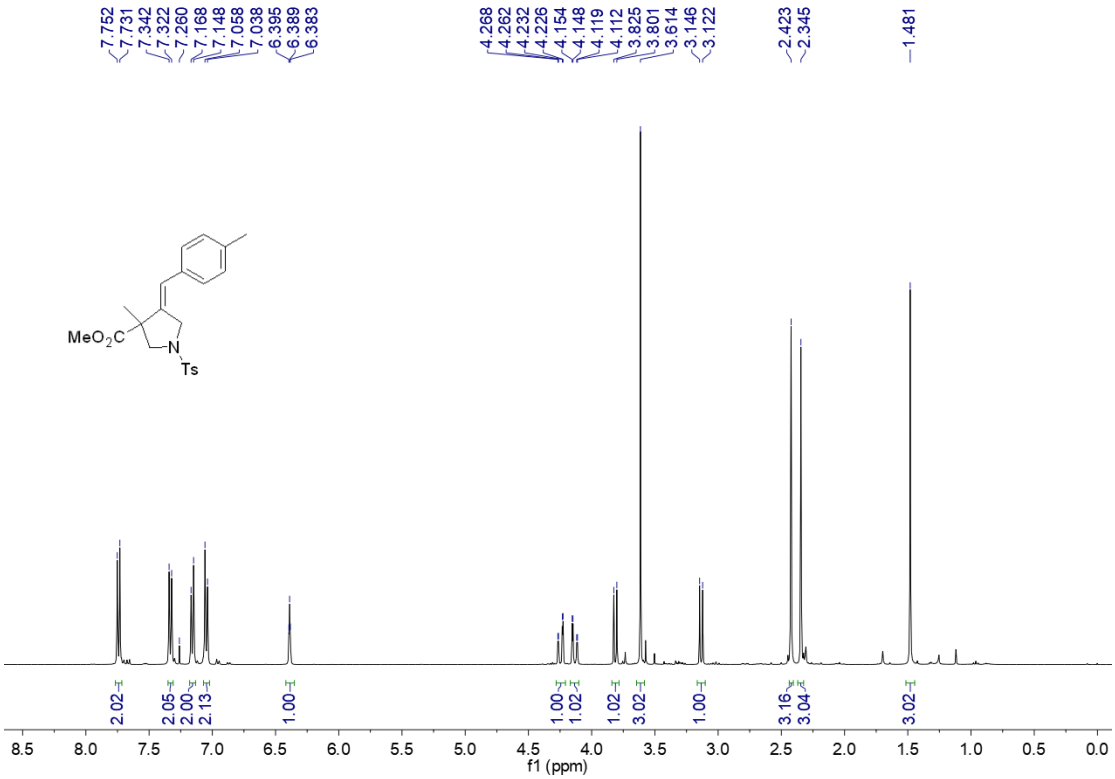


^{13}C NMR ($CDCl_3$, 101 MHz)

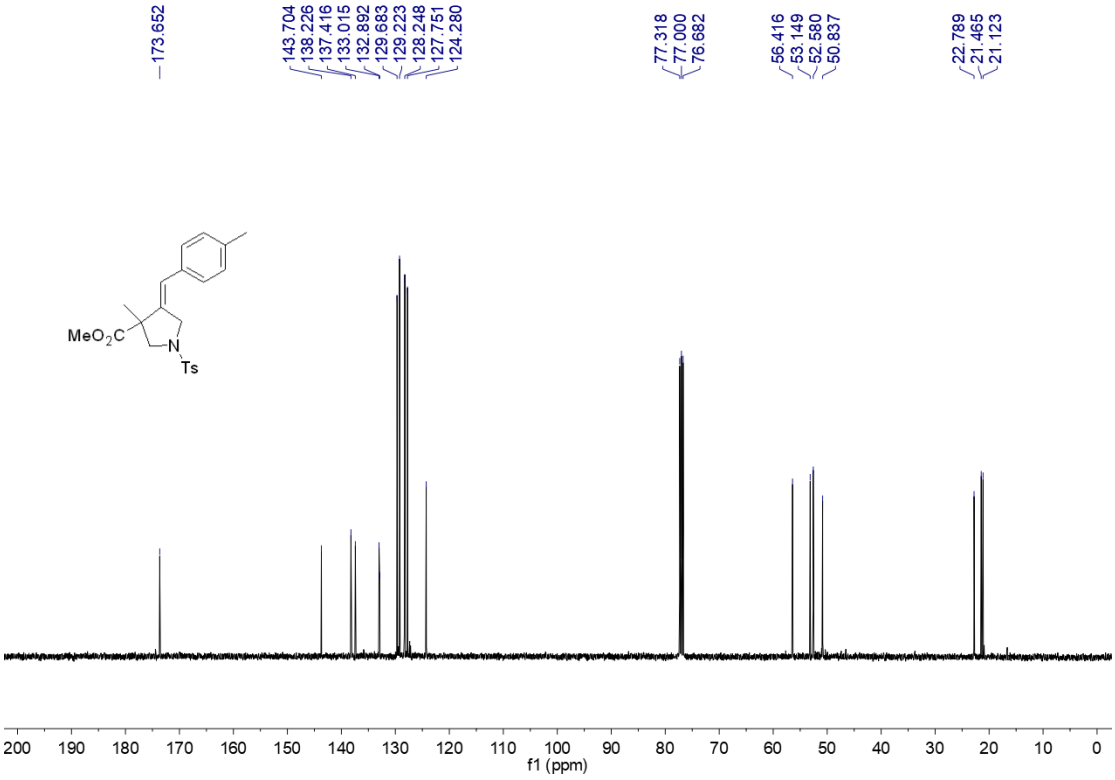


(2d)

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

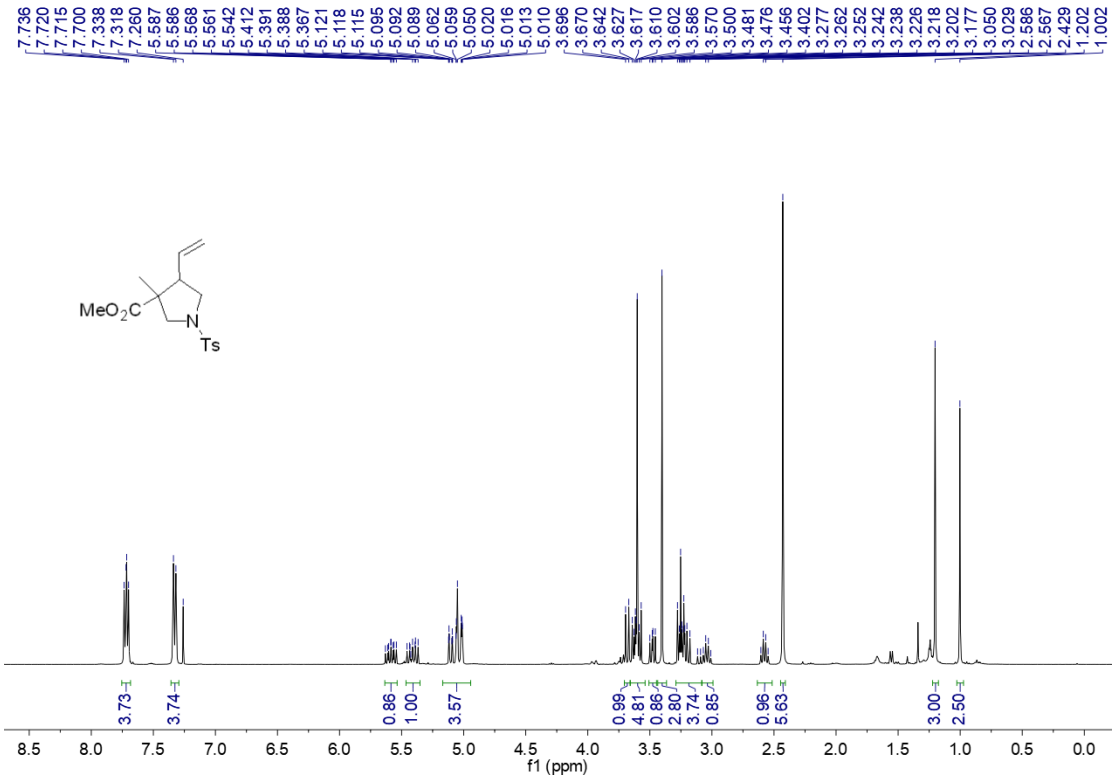


^{13}C NMR ($CDCl_3$, 101 MHz)

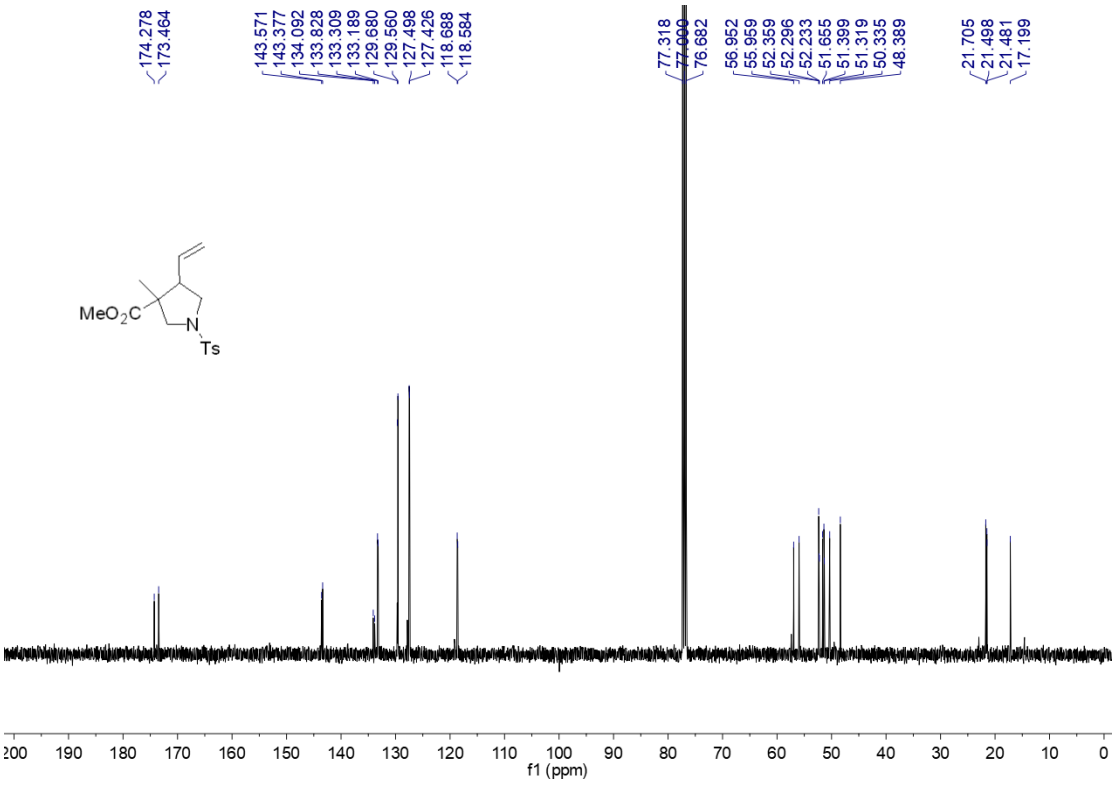


(**2e**)

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

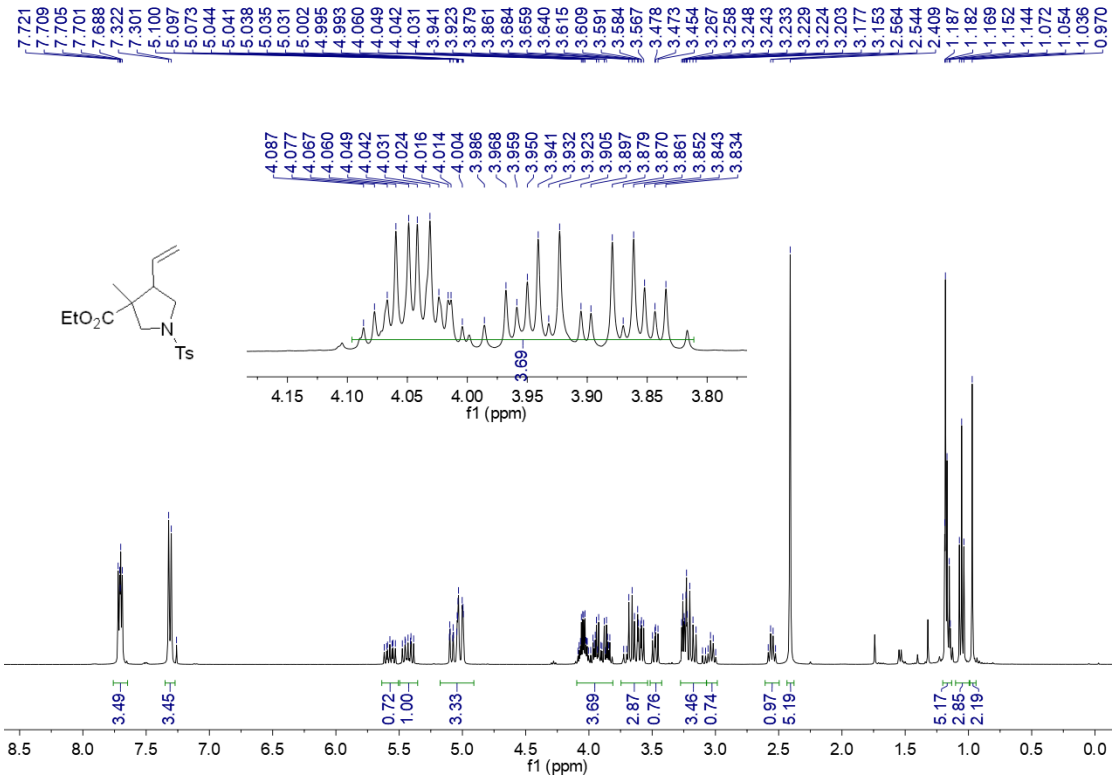


^{13}C NMR ($CDCl_3$, 101 MHz)

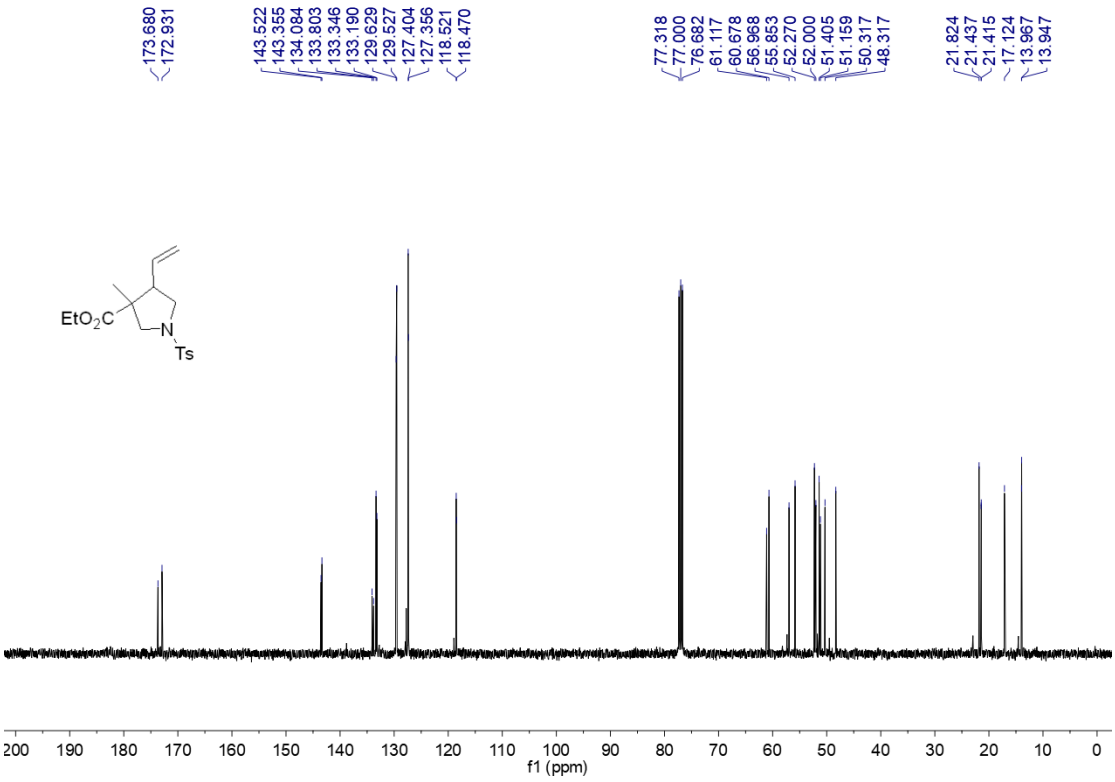


(2f)

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

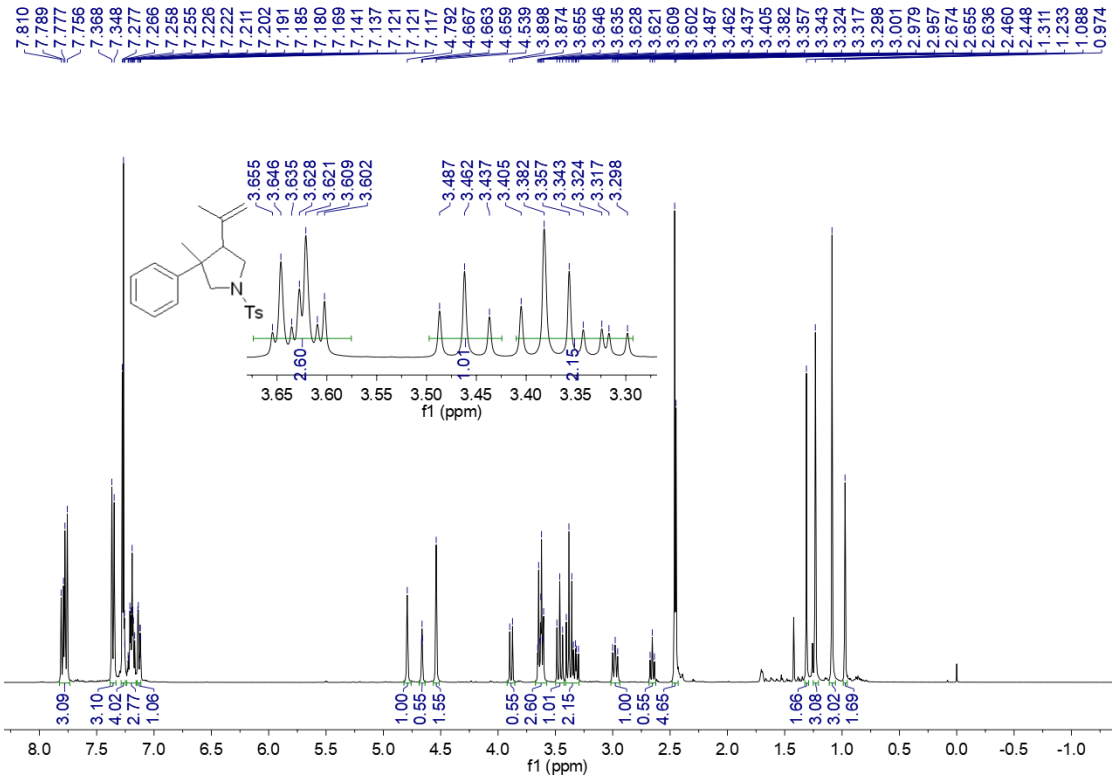


^{13}C NMR ($CDCl_3$, 101 MHz)

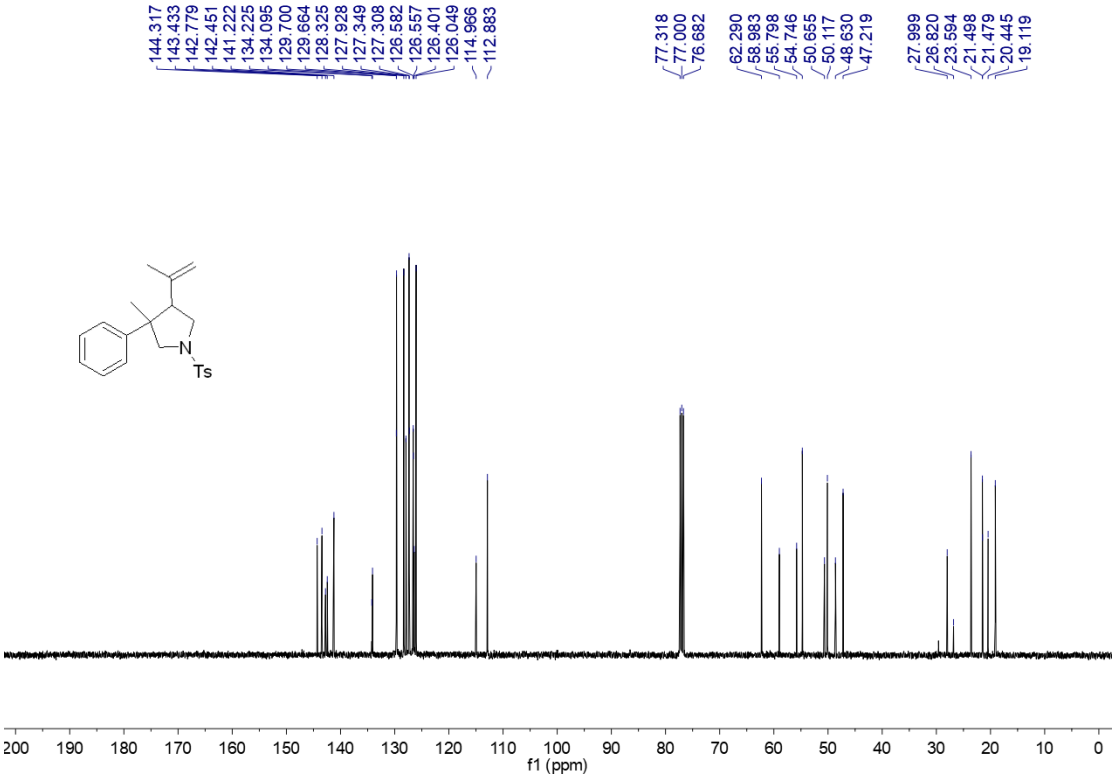


(2g)

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

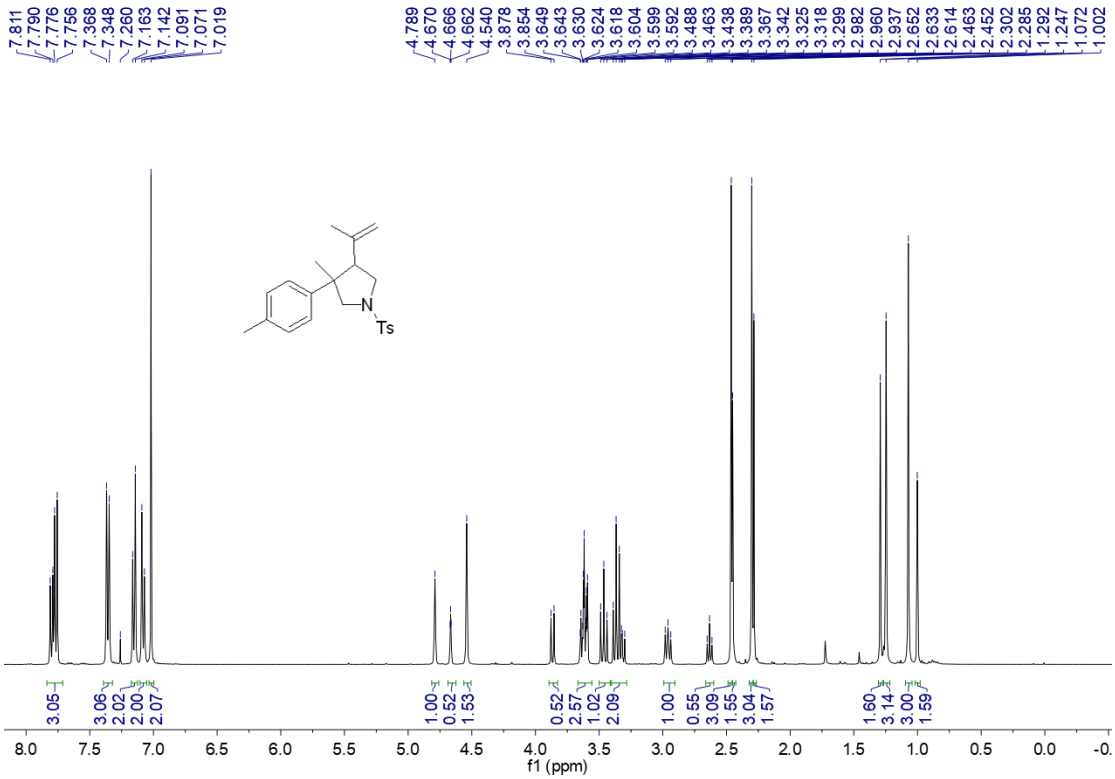


^{13}C NMR ($CDCl_3$, 101 MHz)

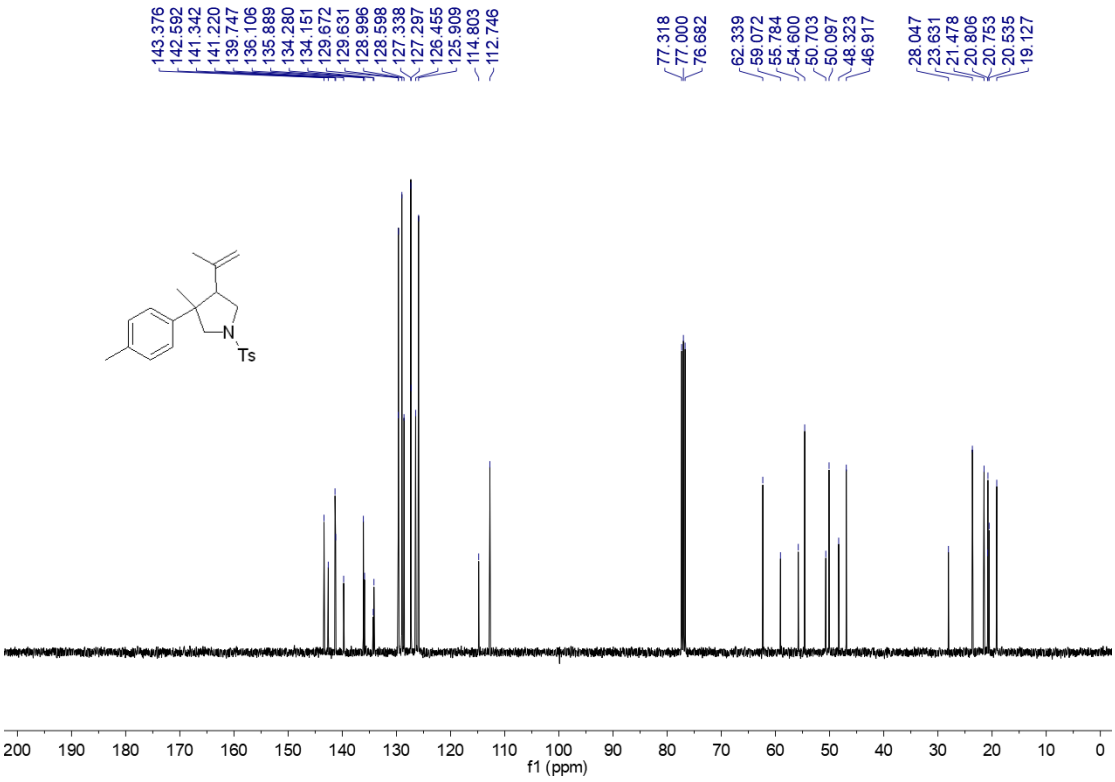


(2h)

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

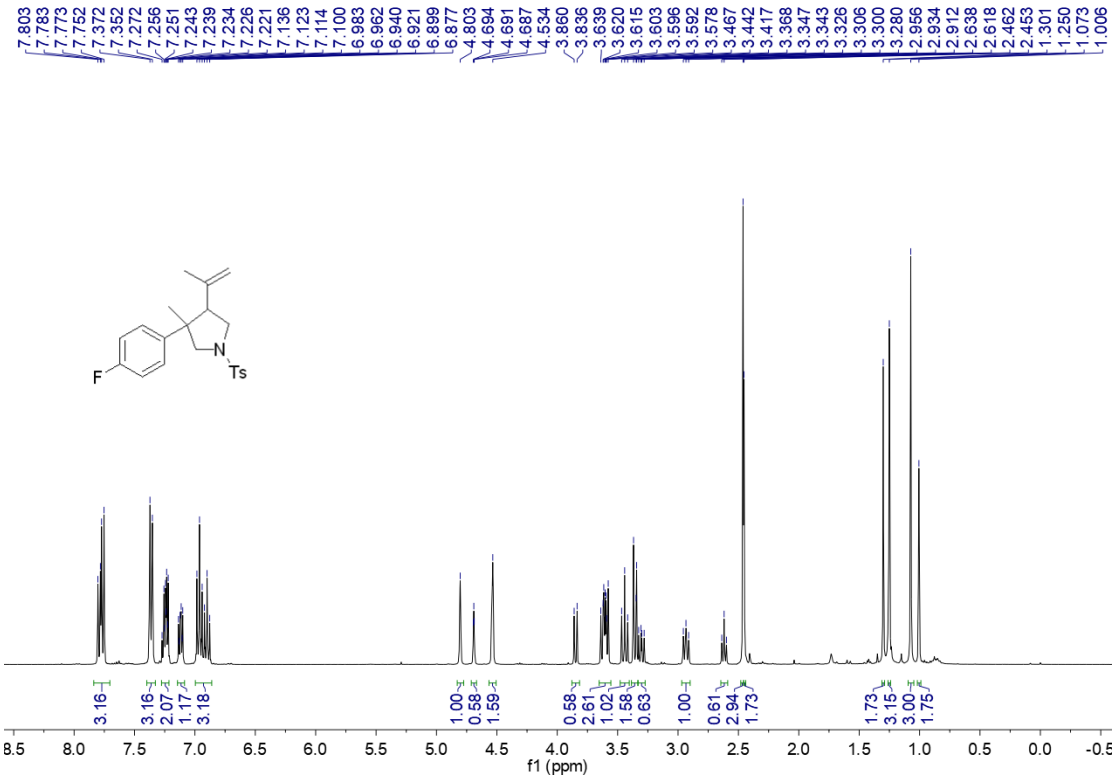


^{13}C NMR ($CDCl_3$, 101 MHz)

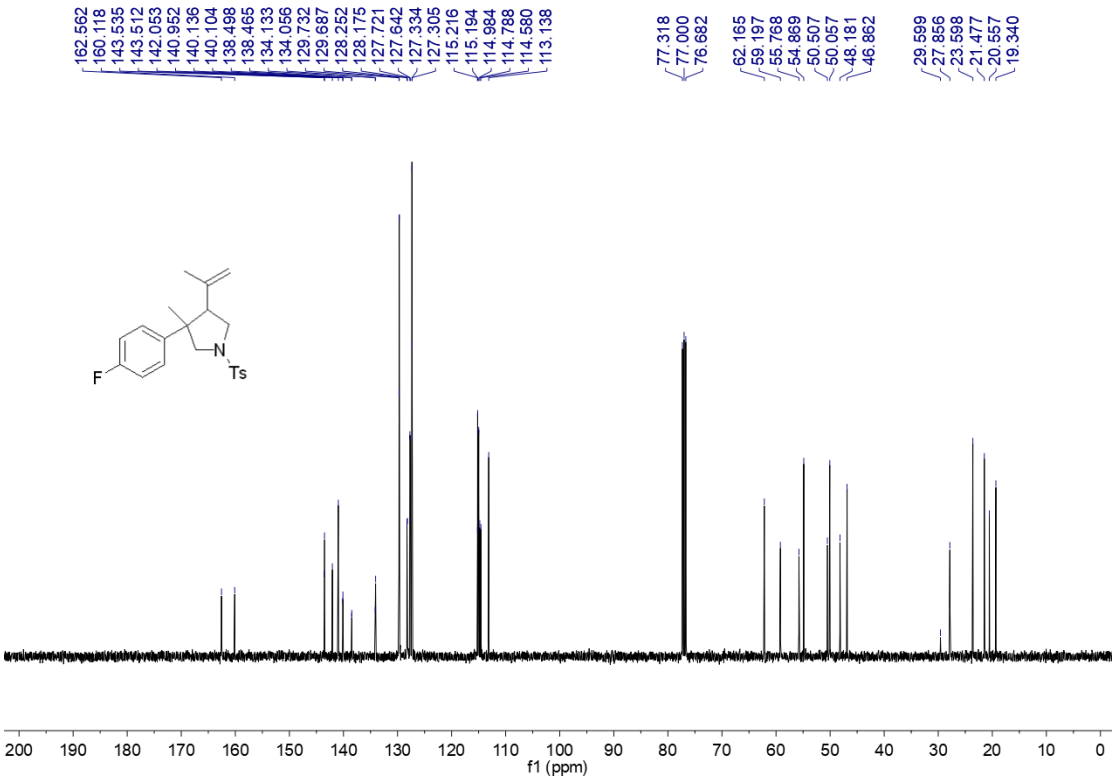


(2i)

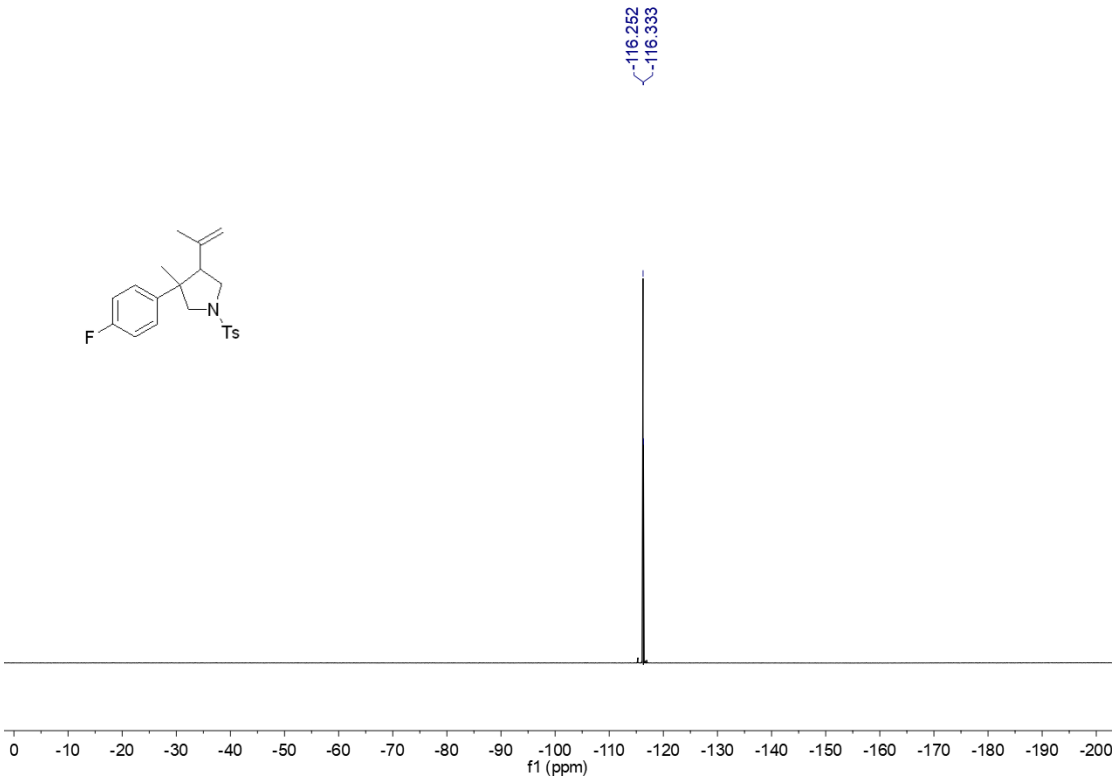
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

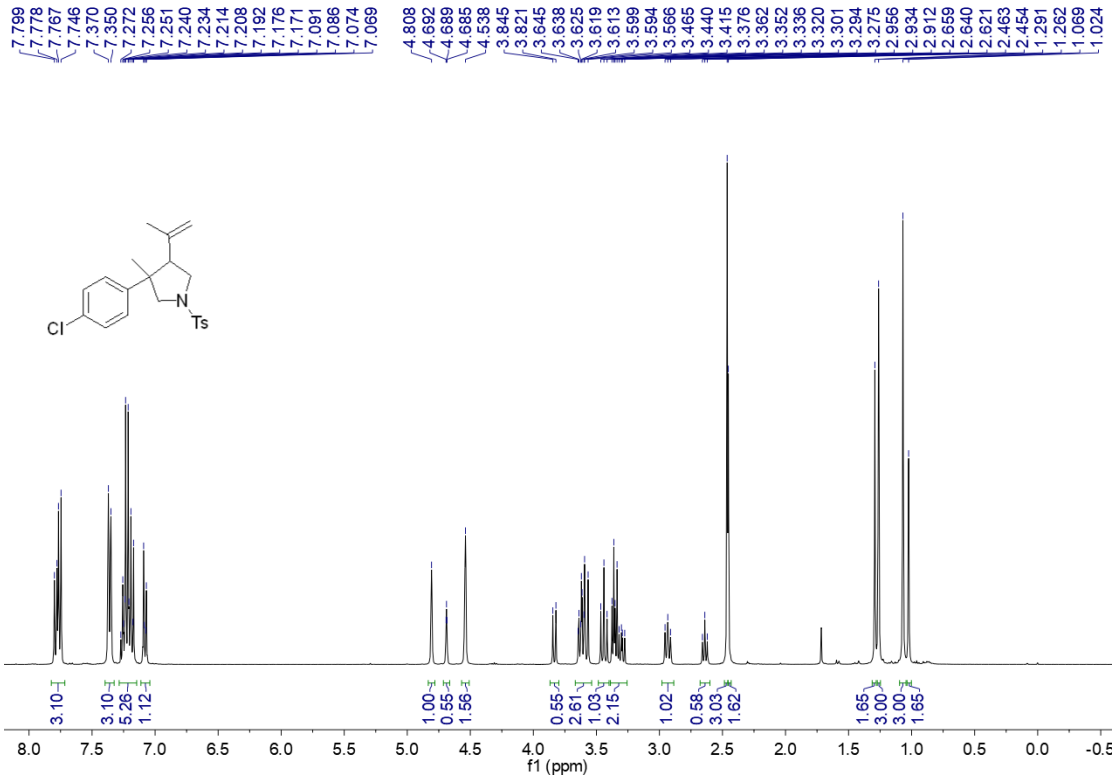


^{19}F NMR ($CDCl_3$, 376 MHz)

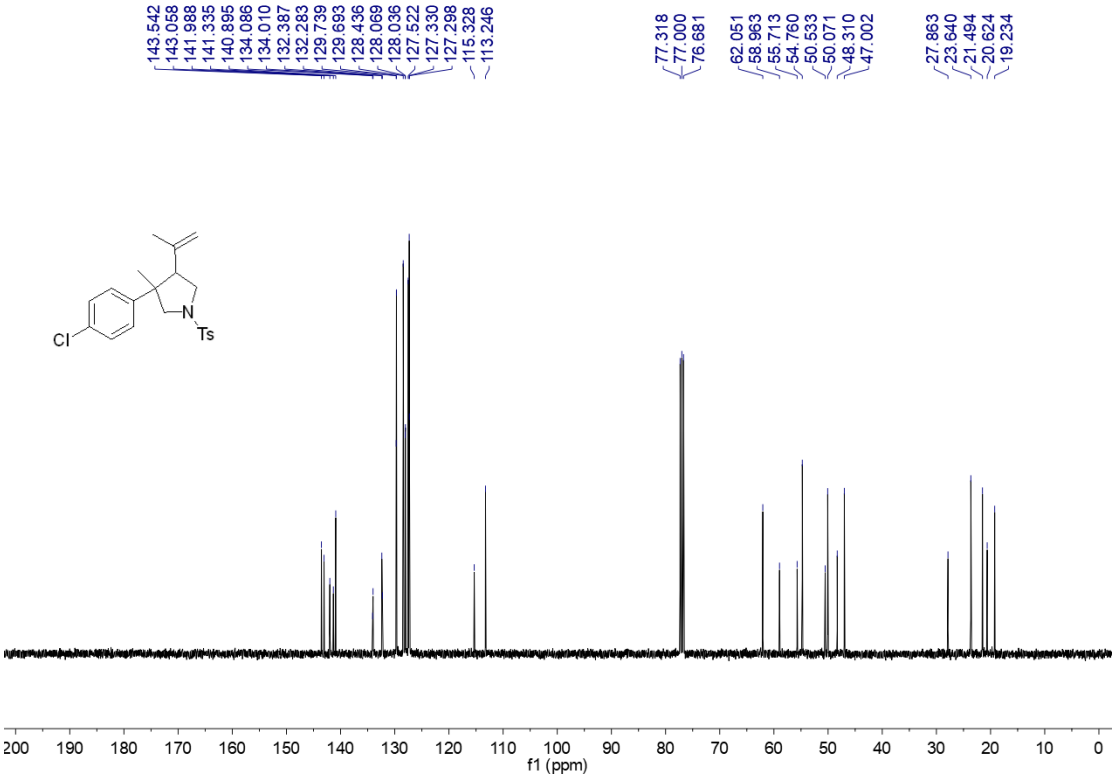


(2j)

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

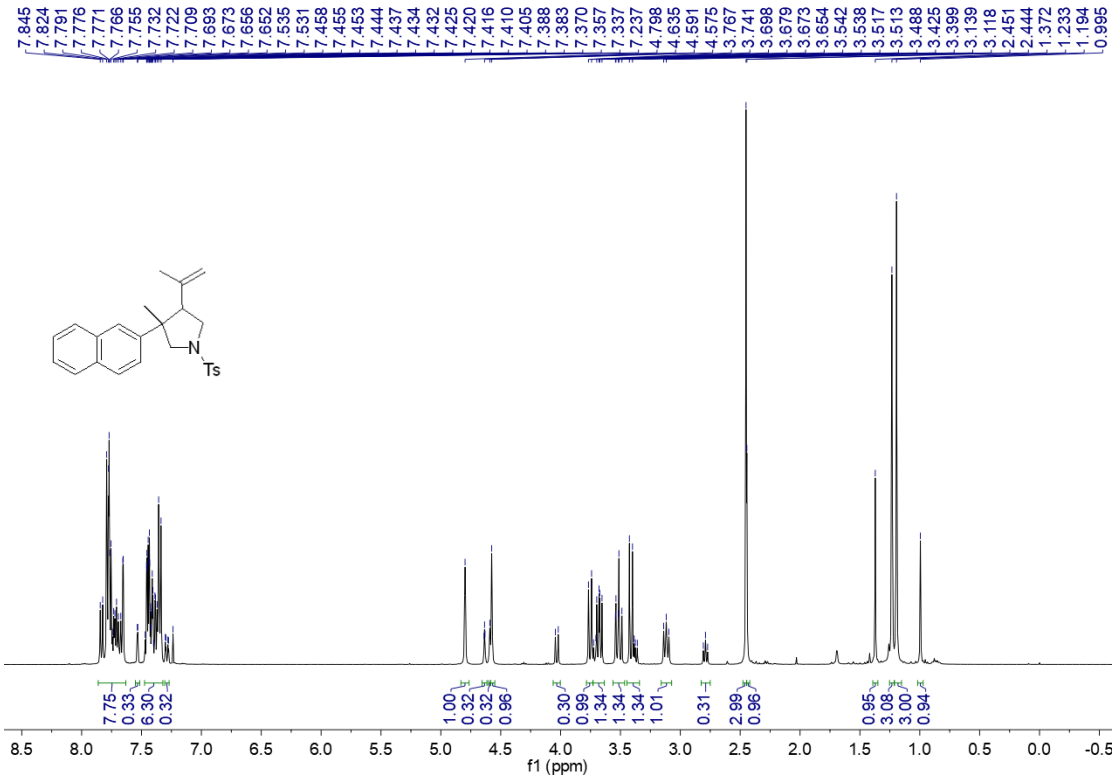


^{13}C NMR ($CDCl_3$, 101 MHz)

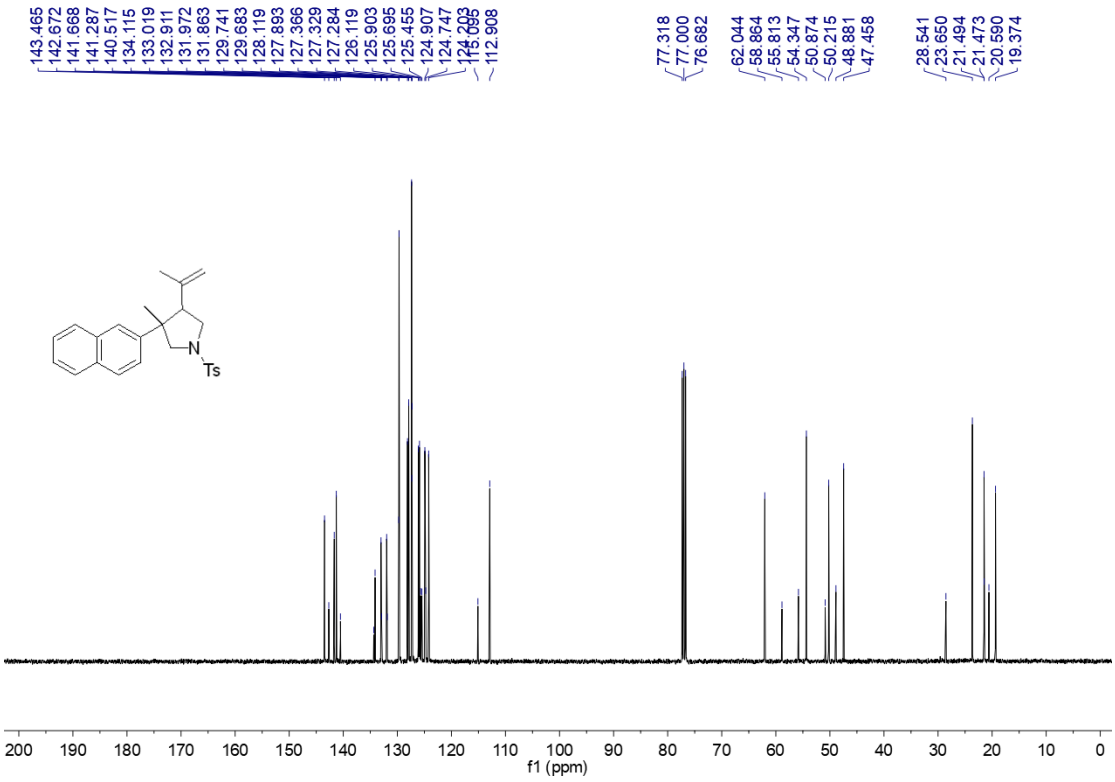


(2k)

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

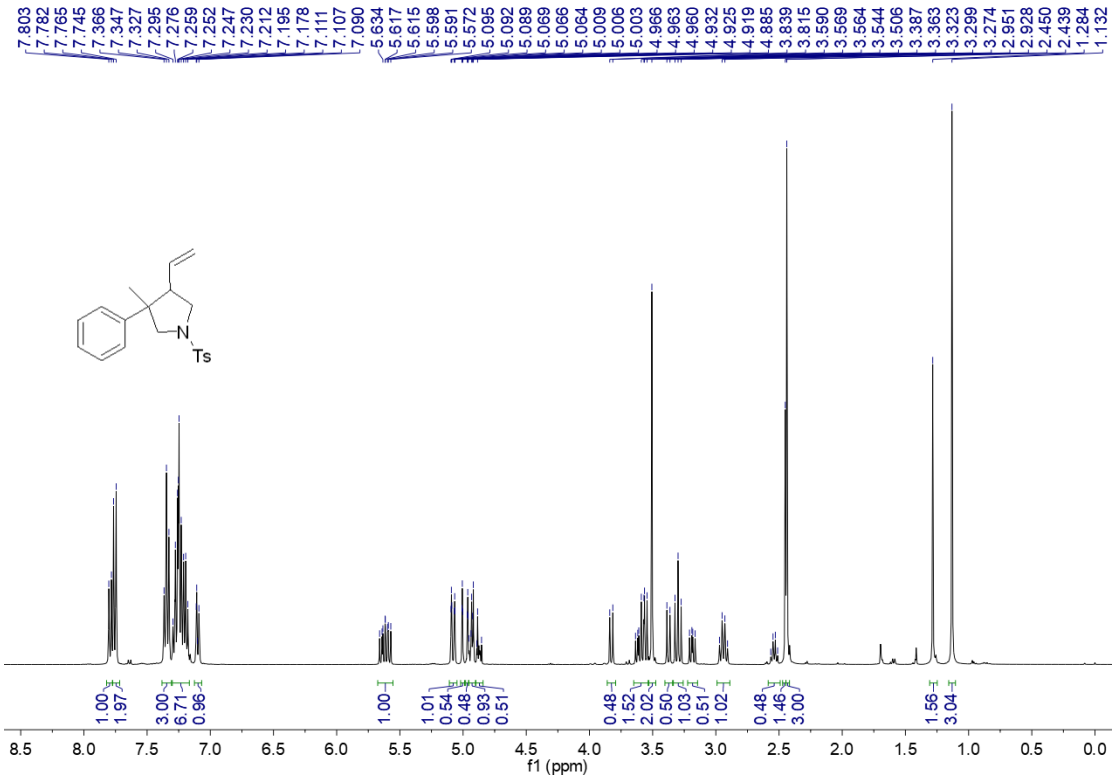


^{13}C NMR ($CDCl_3$, 101 MHz)

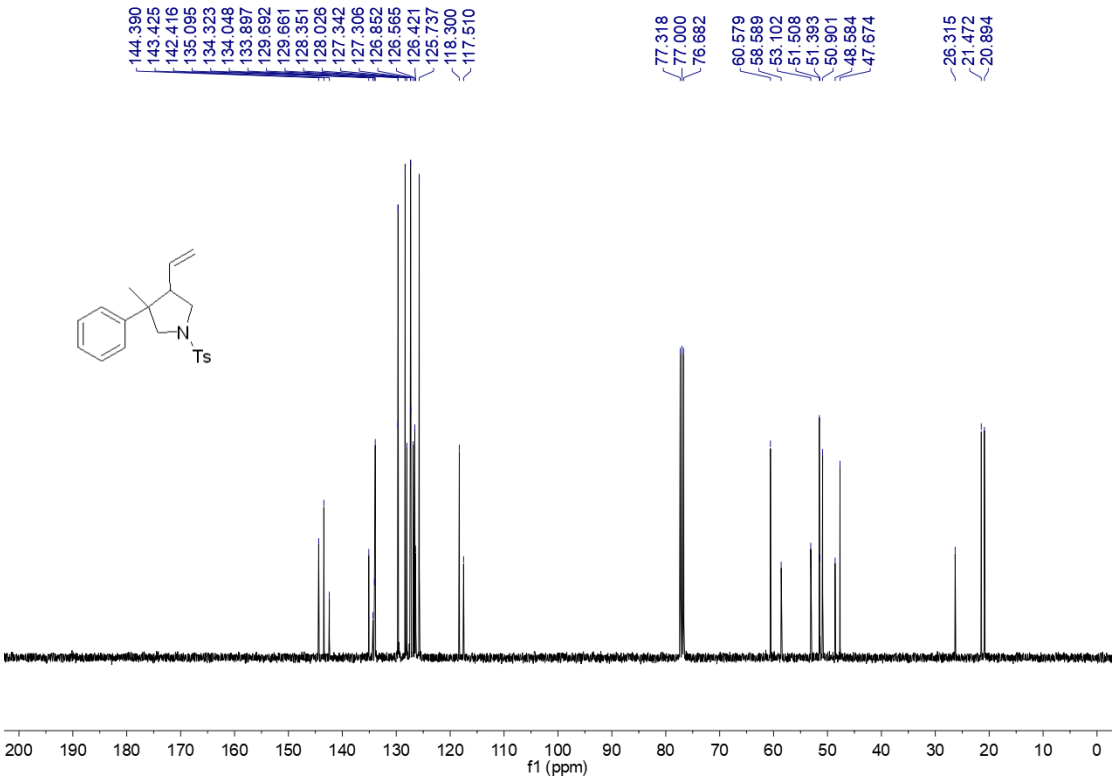


(2l)

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

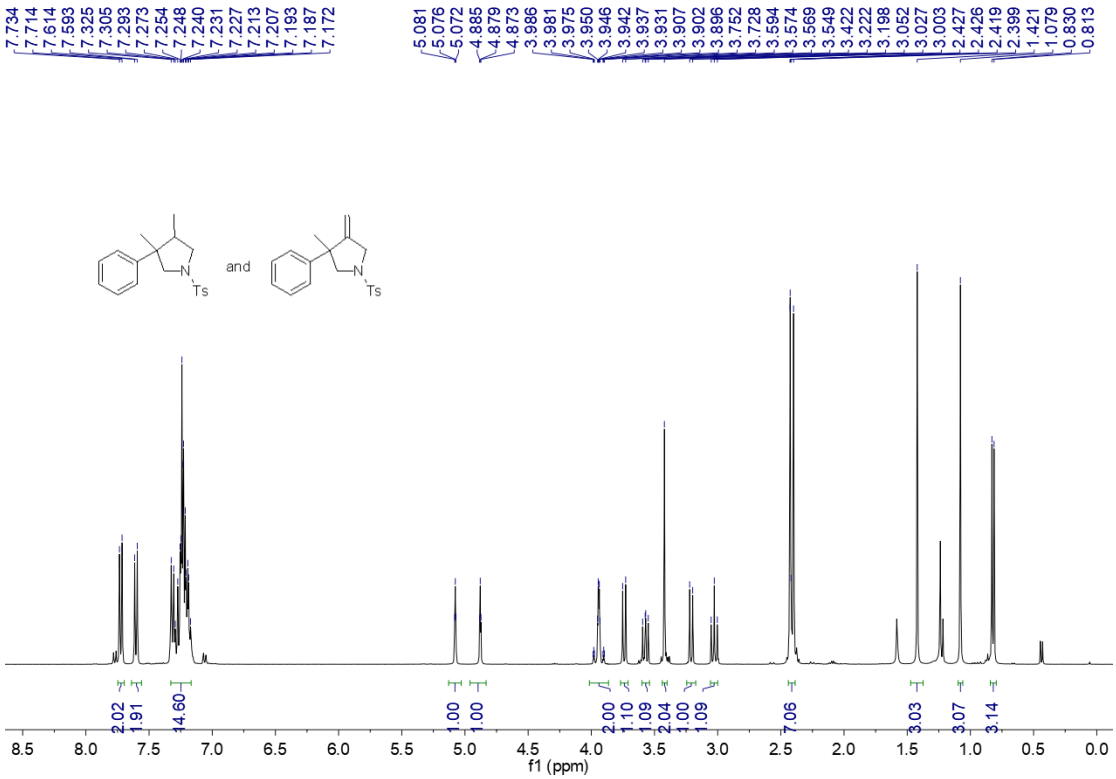


^{13}C NMR ($CDCl_3$, 101 MHz)

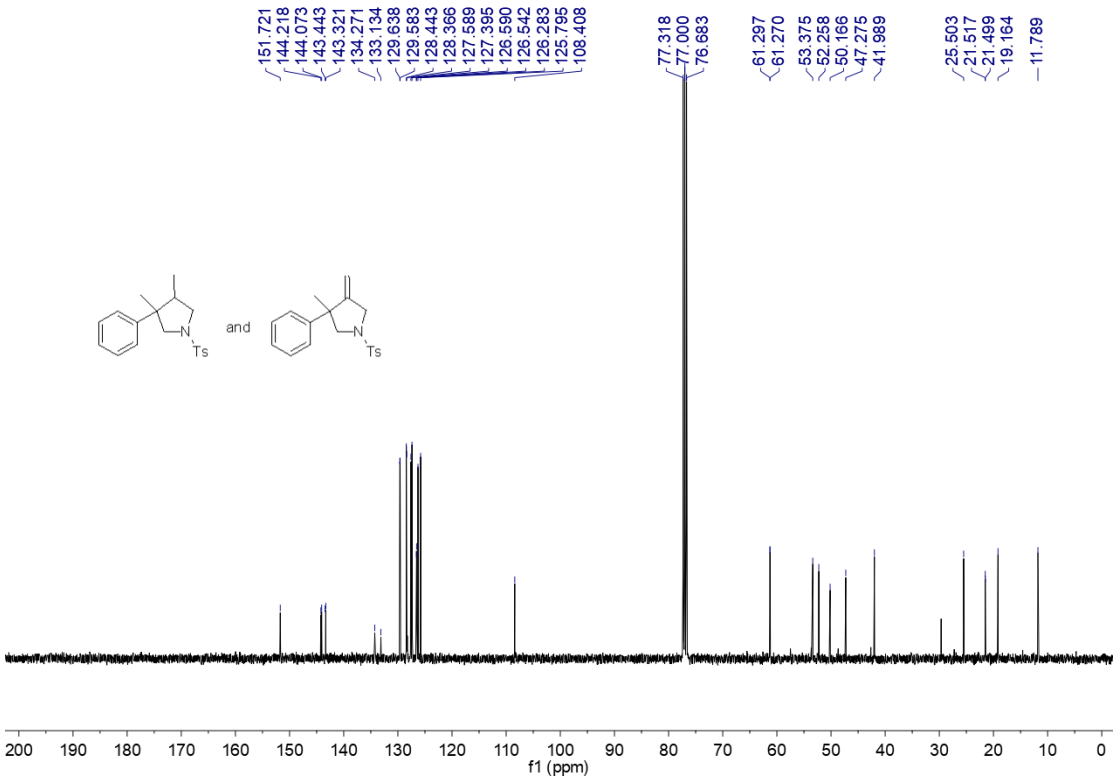


(**2m** and **2m'**)

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

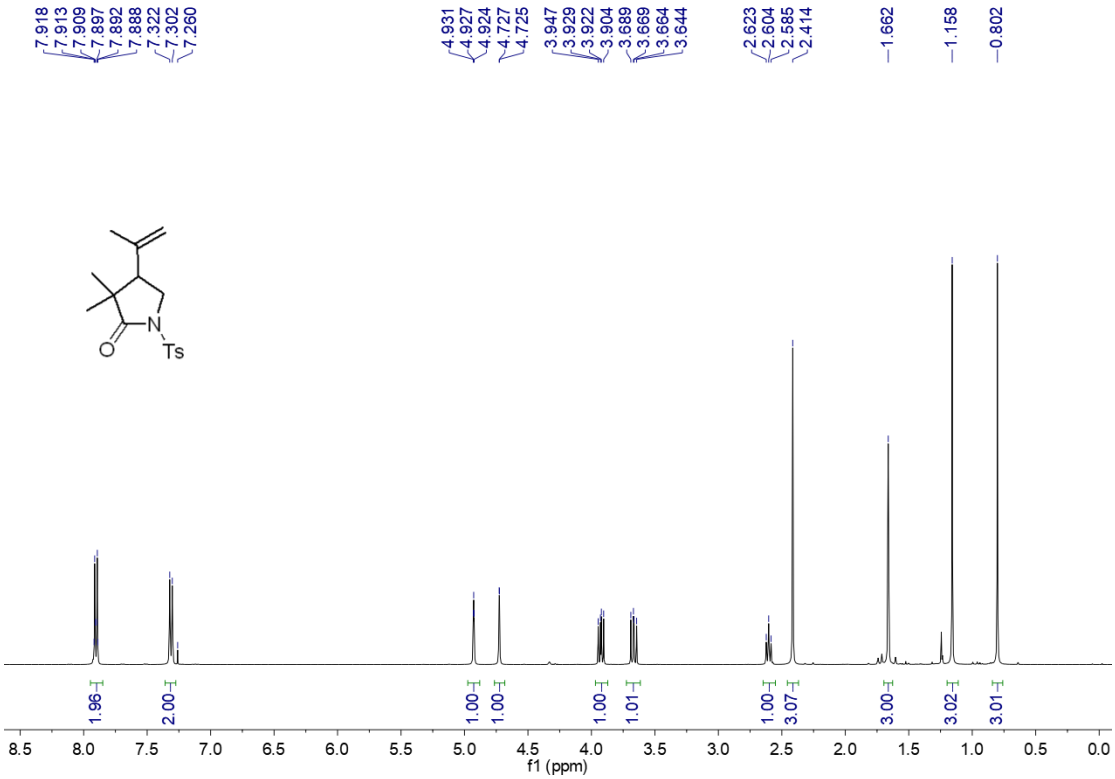


^{13}C NMR ($CDCl_3$, 101 MHz)

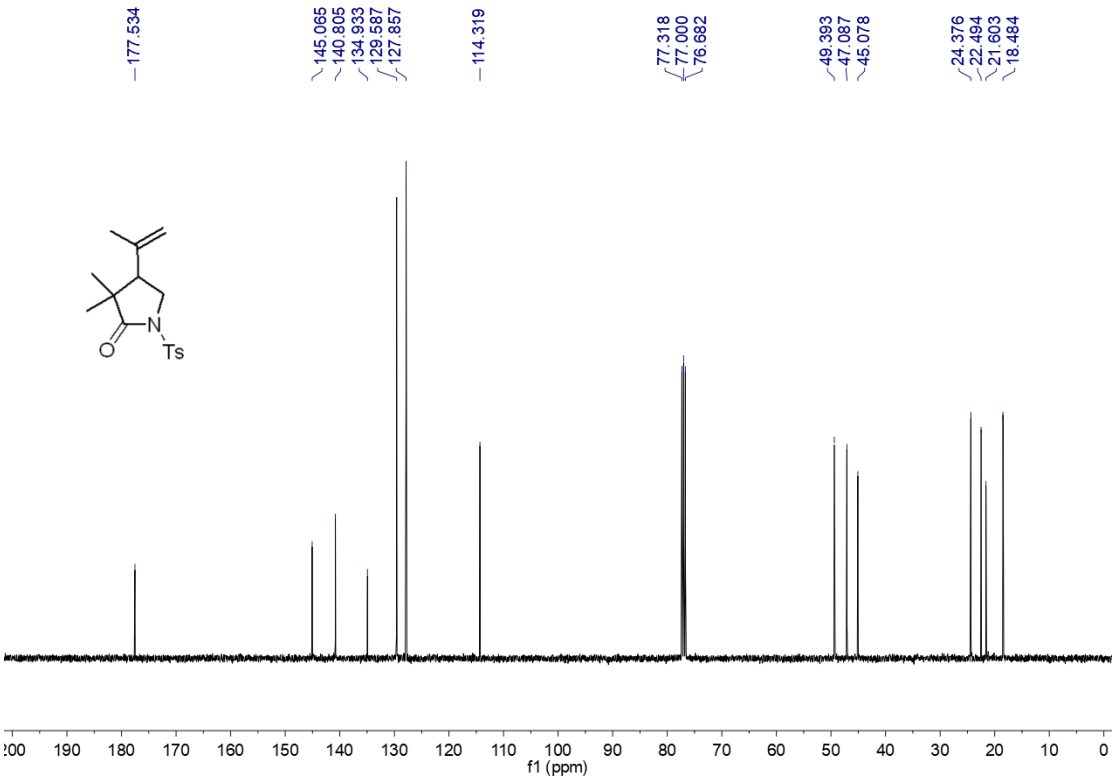


(2n)

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

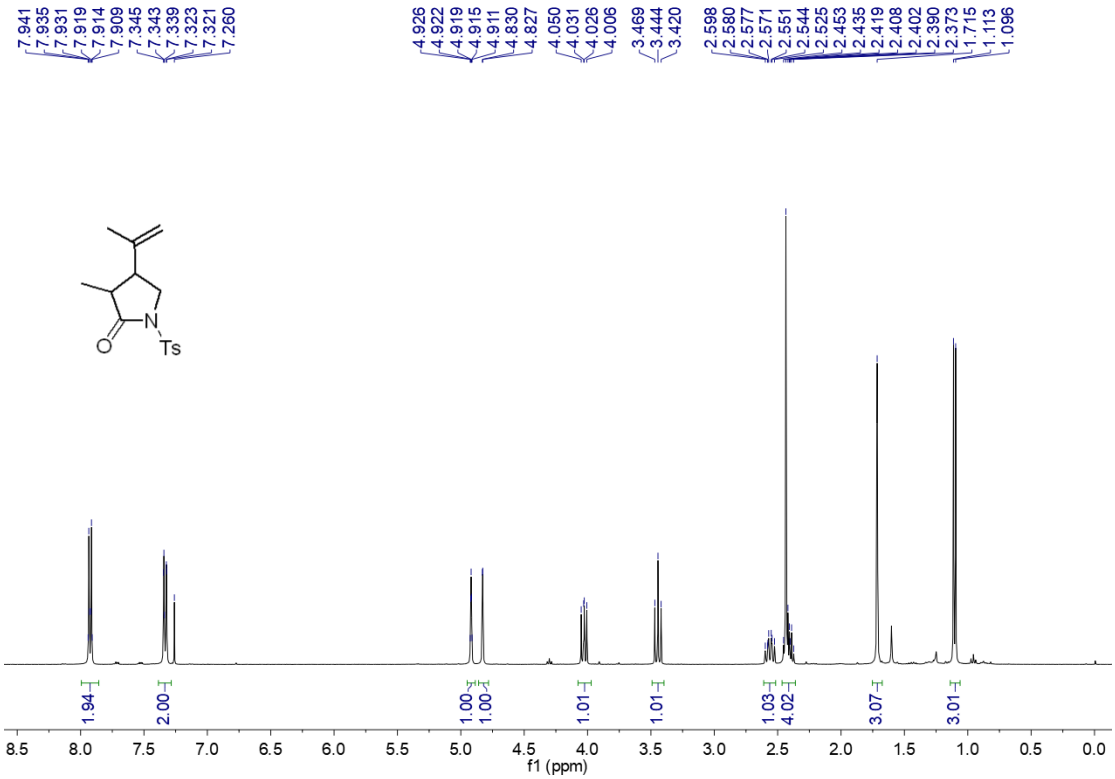


^{13}C NMR ($CDCl_3$, 101 MHz)

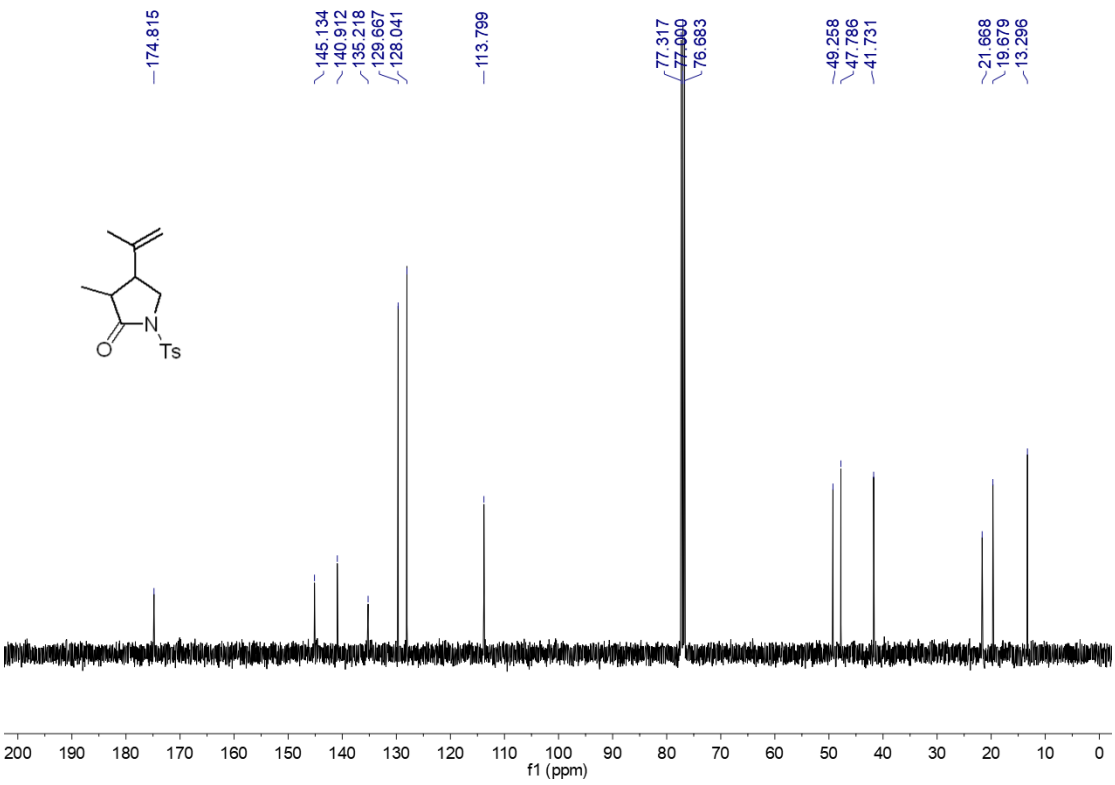


(**2o**)

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

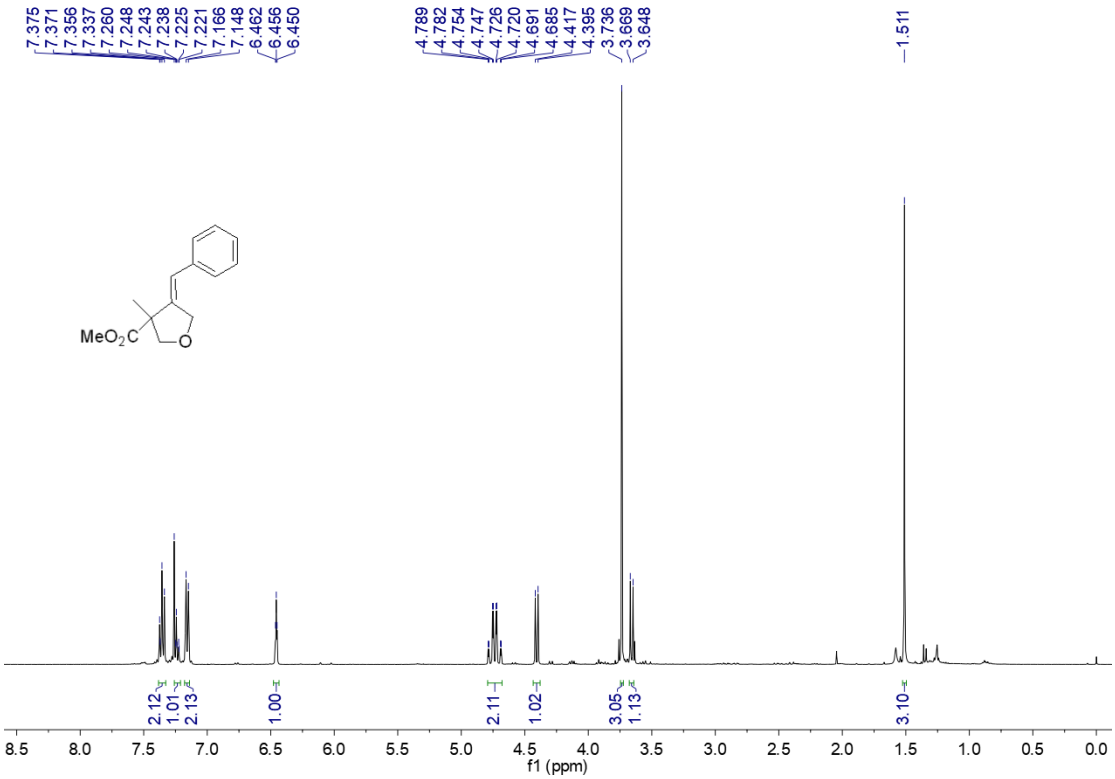


^{13}C NMR ($CDCl_3$, 101 MHz)

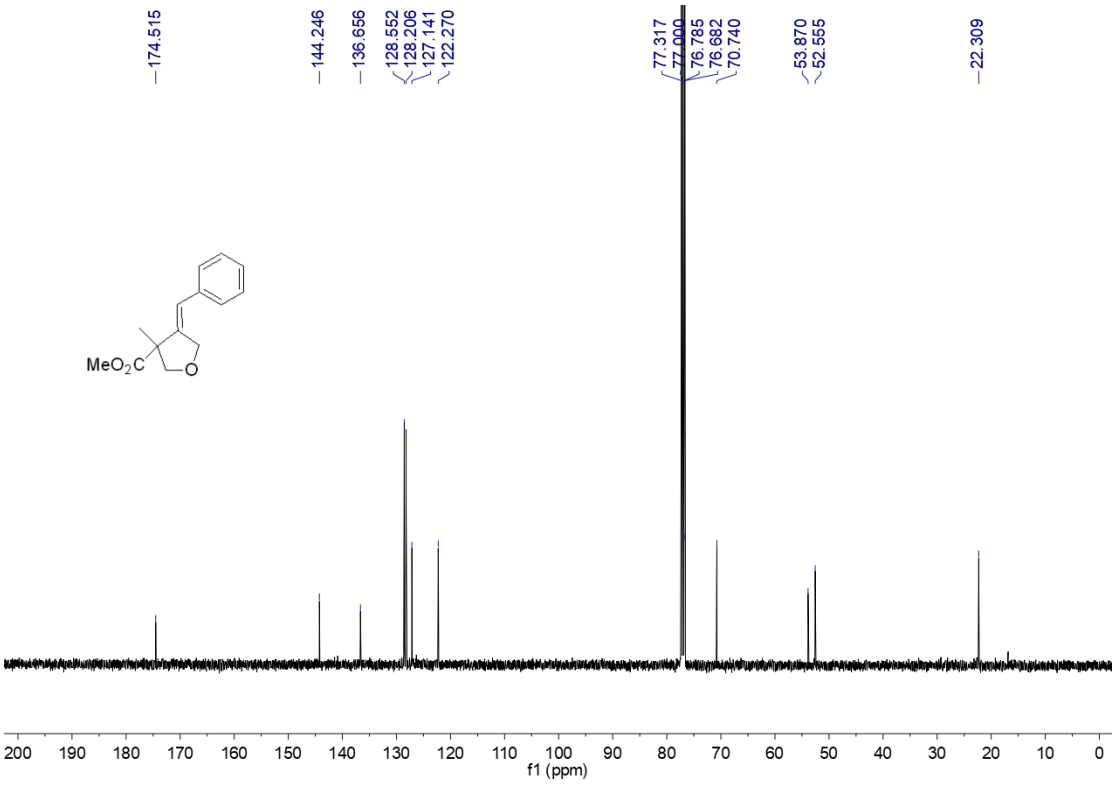


(2p)

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

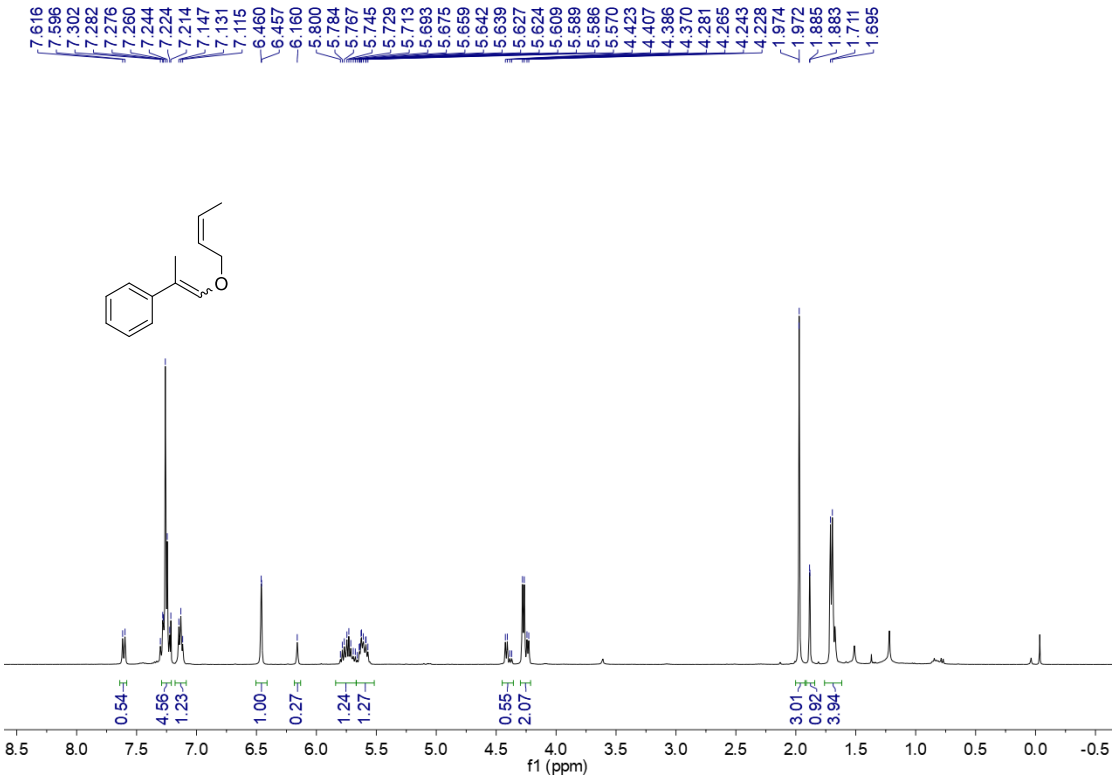


^{13}C NMR ($CDCl_3$, 101 MHz)

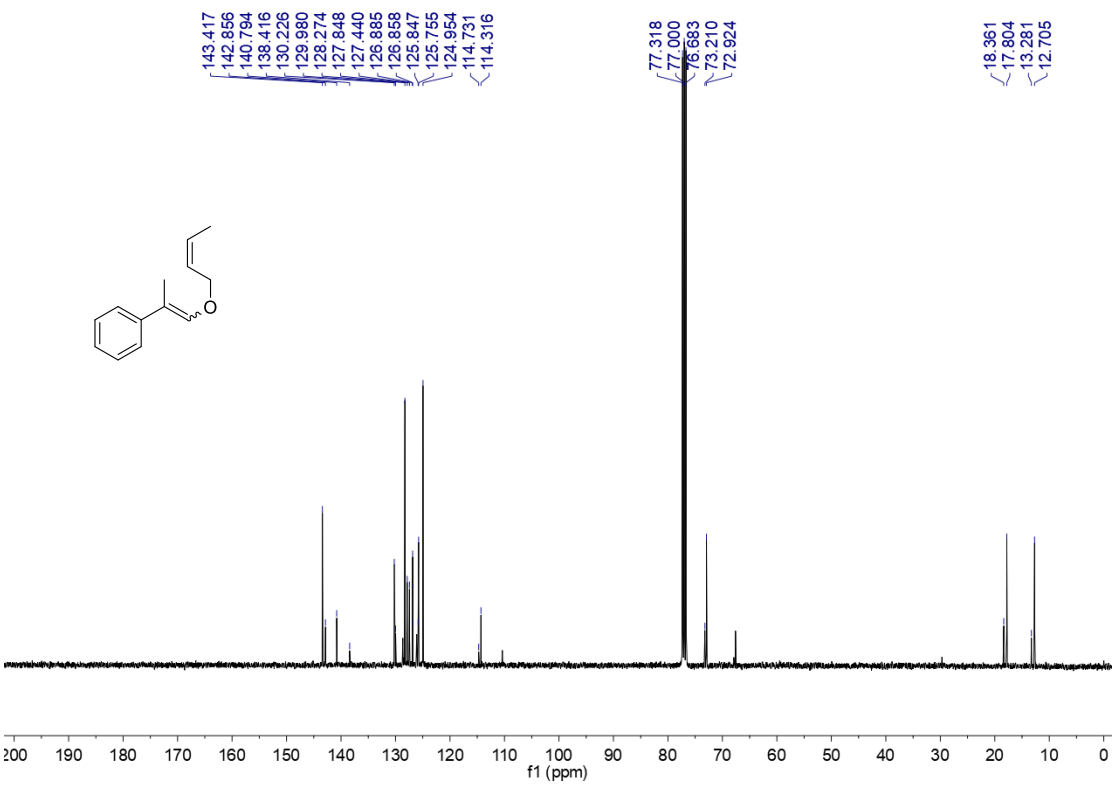


(2q)

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

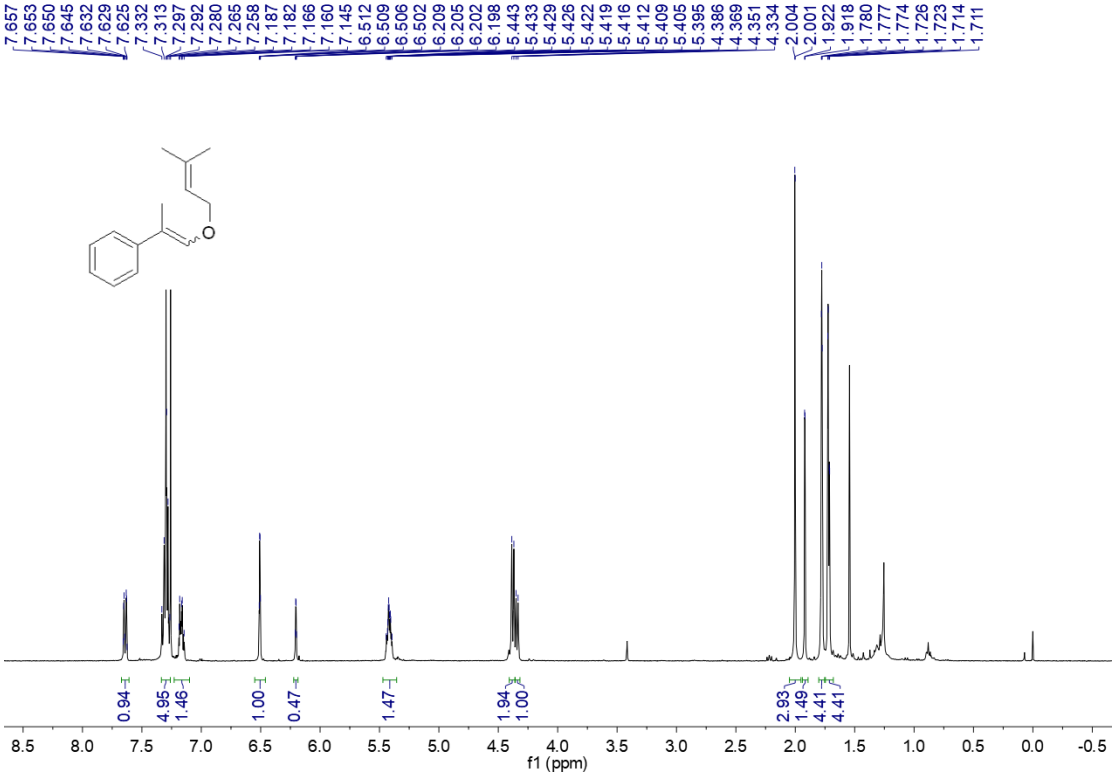


^{13}C NMR ($CDCl_3$, 101 MHz)

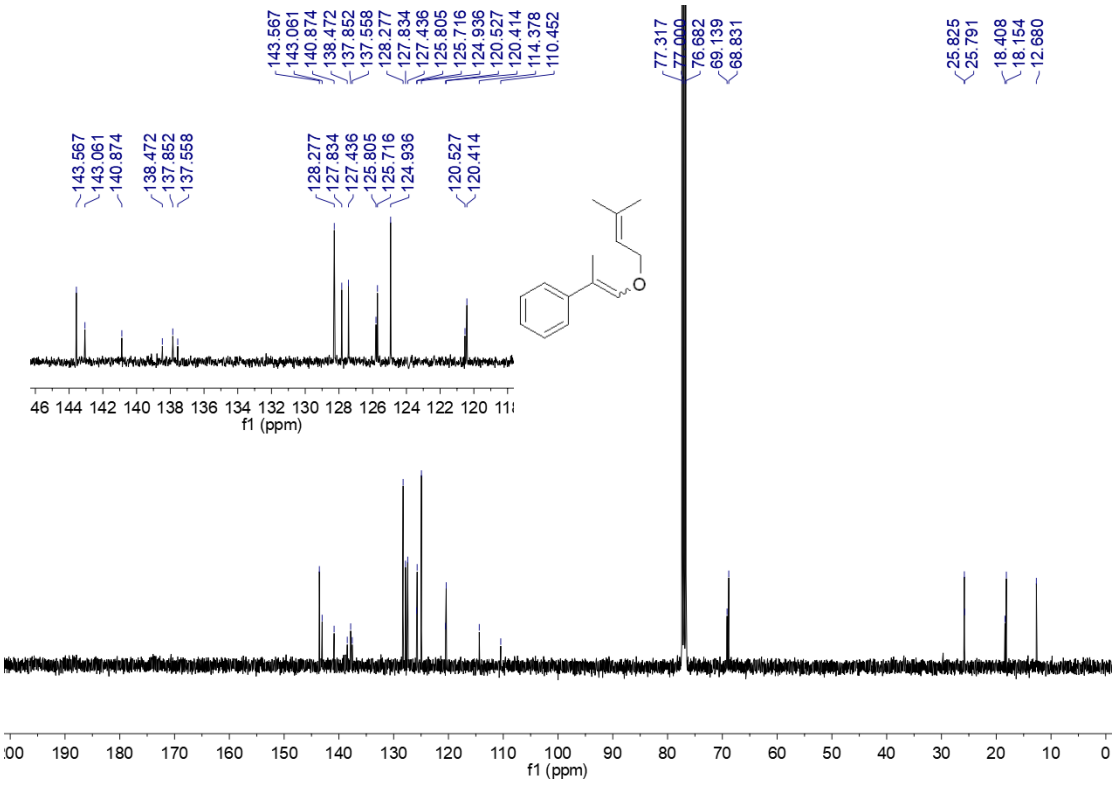


(2r)

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

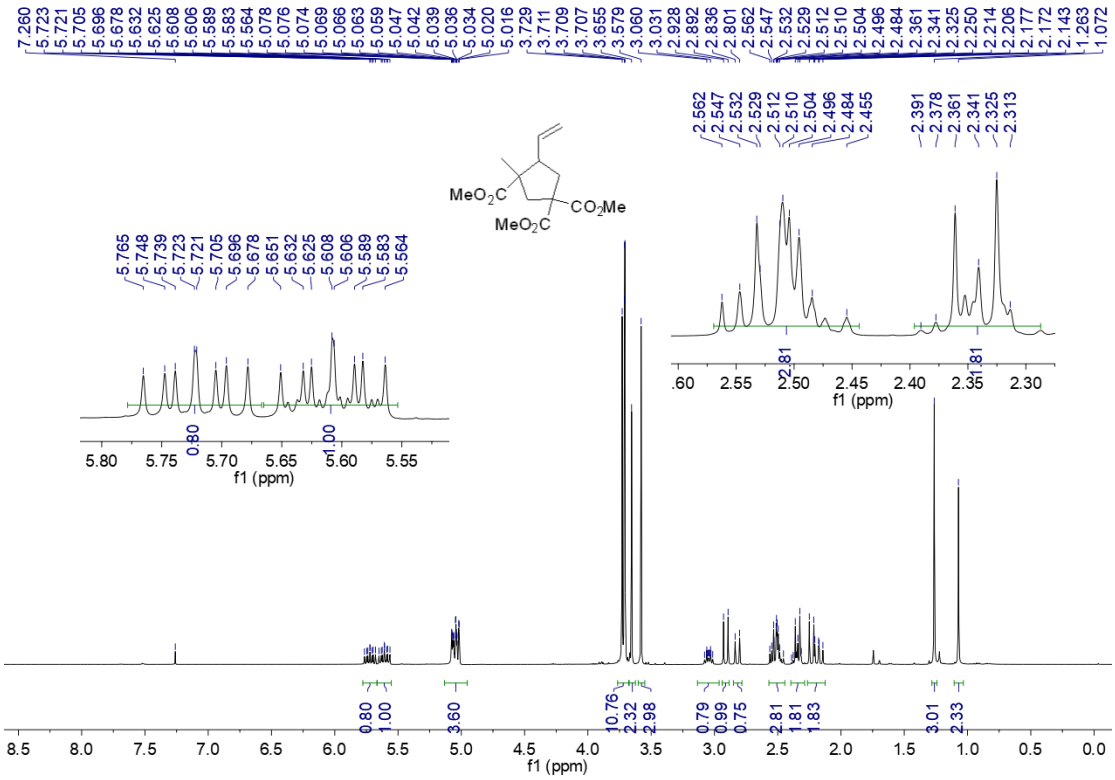


^{13}C NMR ($CDCl_3$, 101 MHz)

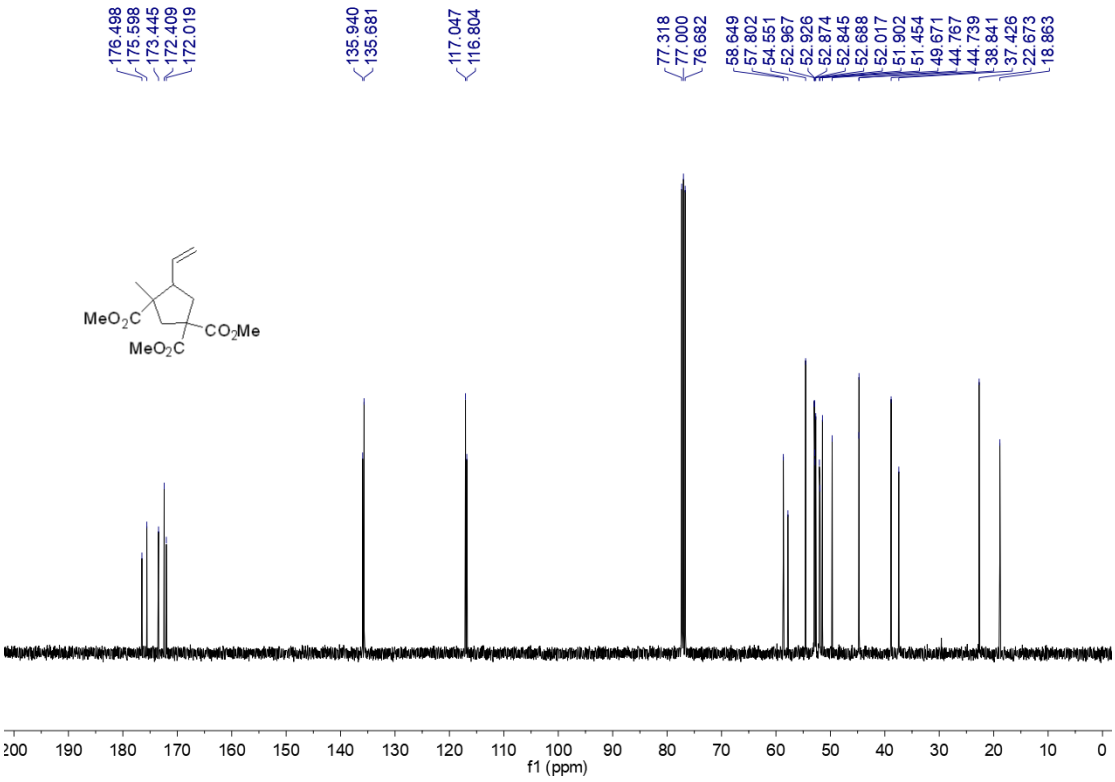


(2s)

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

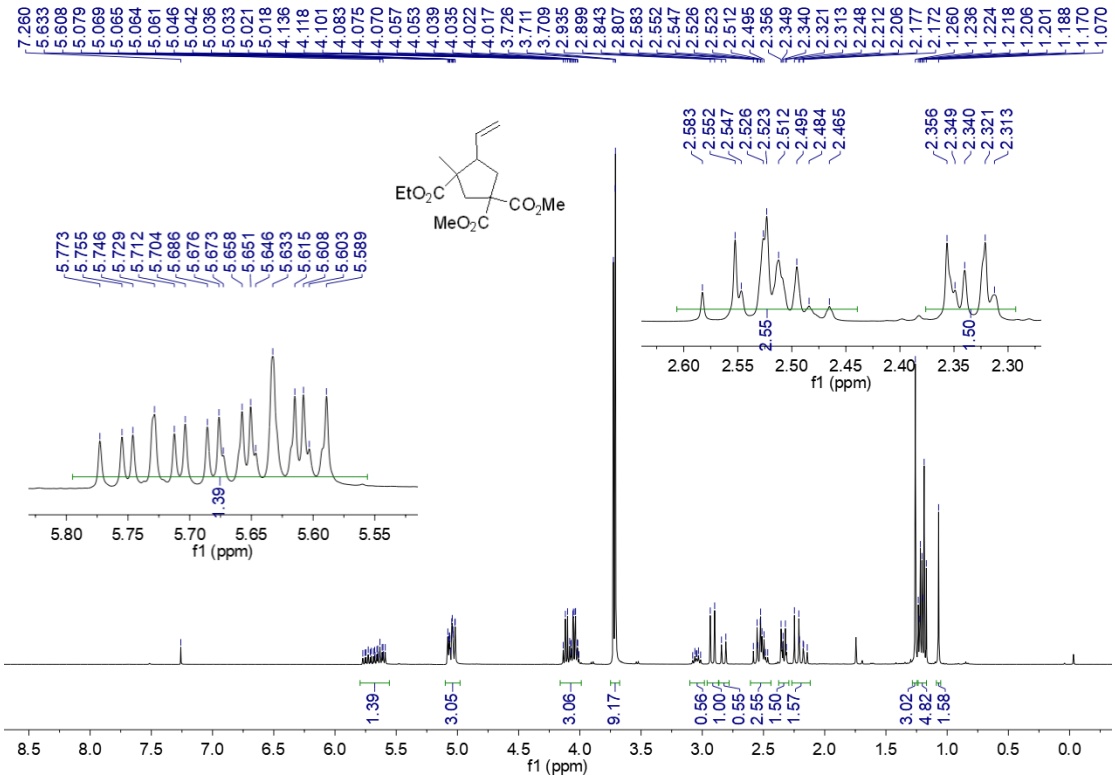


^{13}C NMR ($CDCl_3$, 101 MHz)

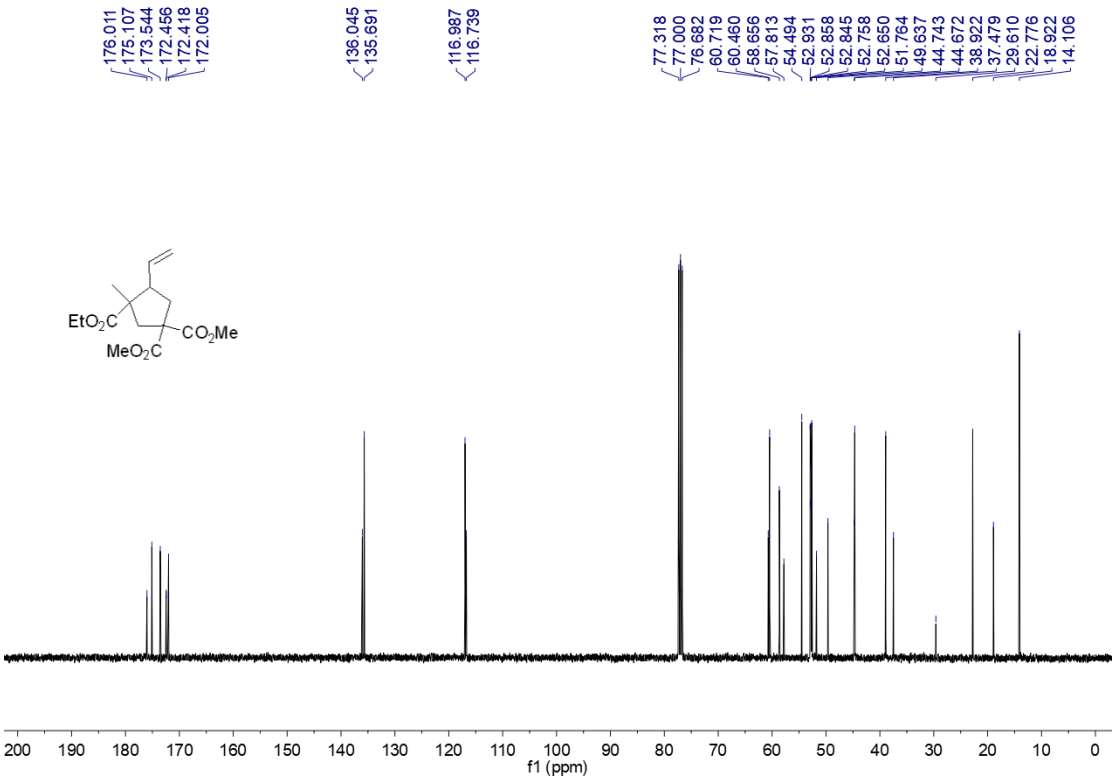


(2t)

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

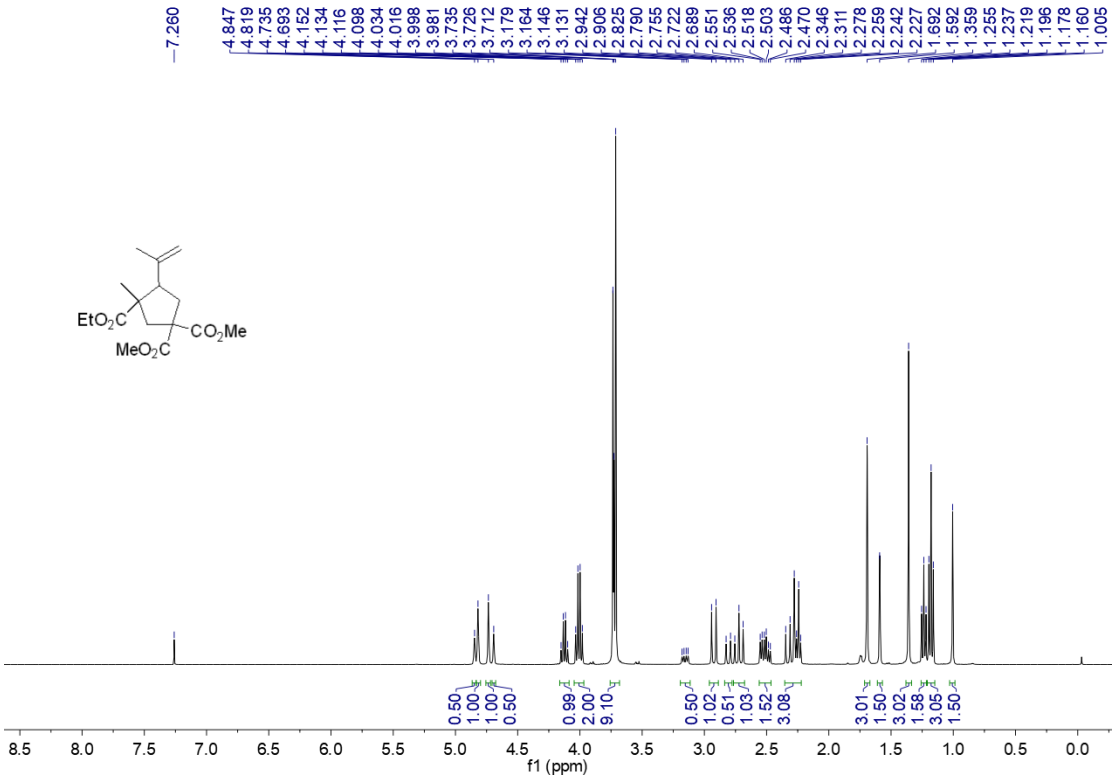


^{13}C NMR ($CDCl_3$, 101 MHz)

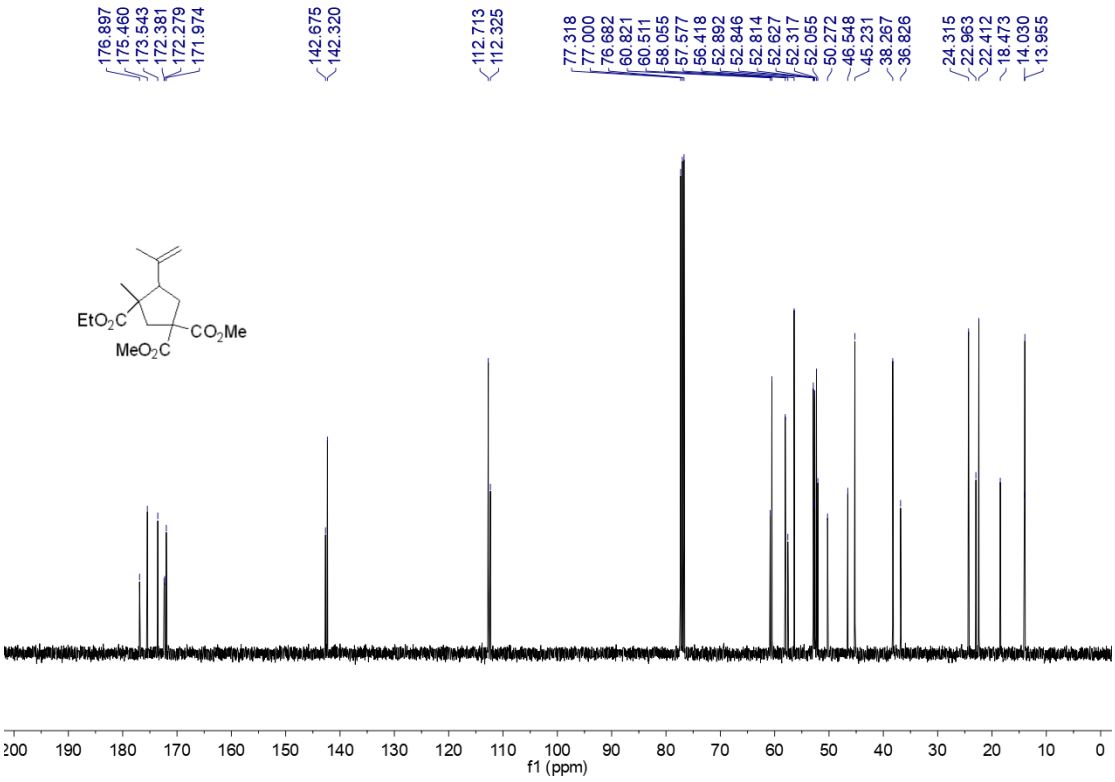


(2u)

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

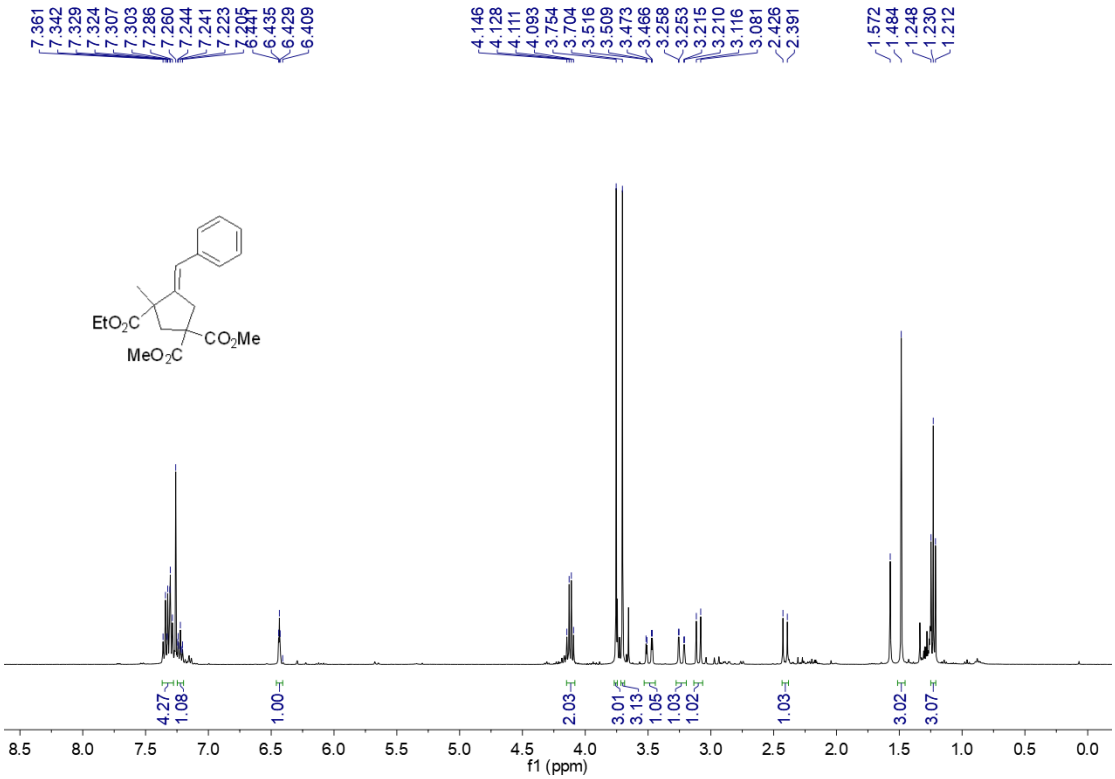


^{13}C NMR ($CDCl_3$, 101 MHz)

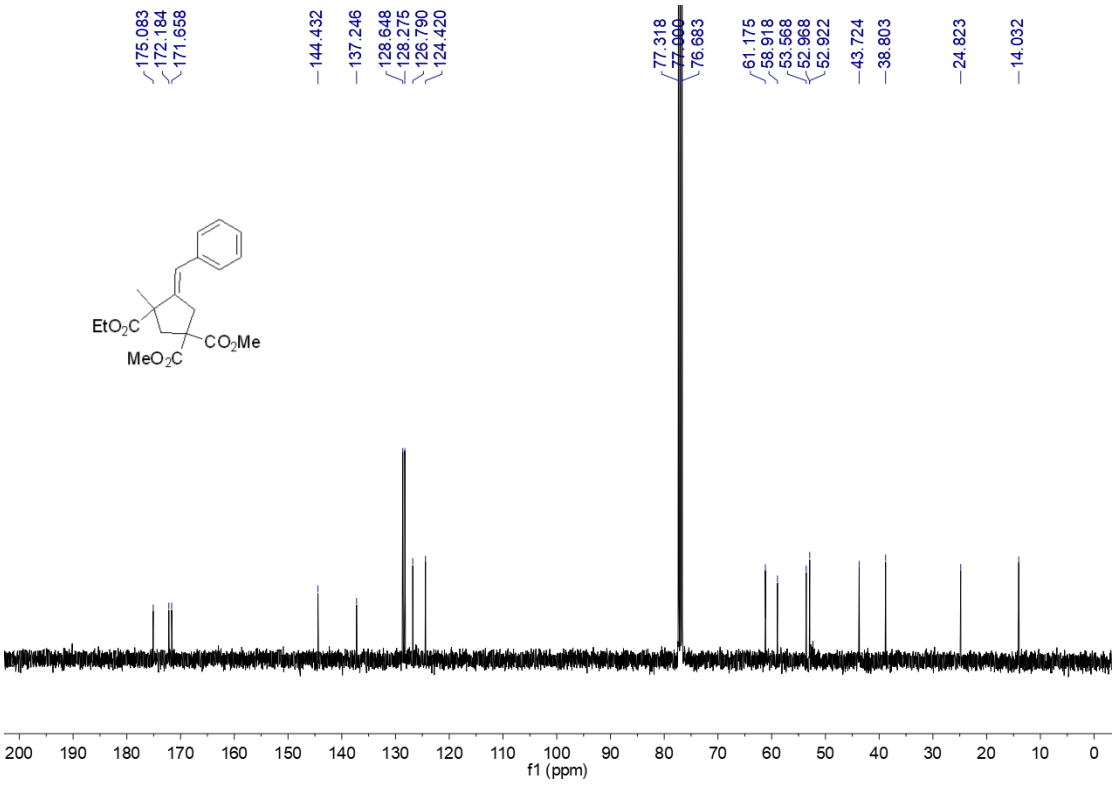


(2v)

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

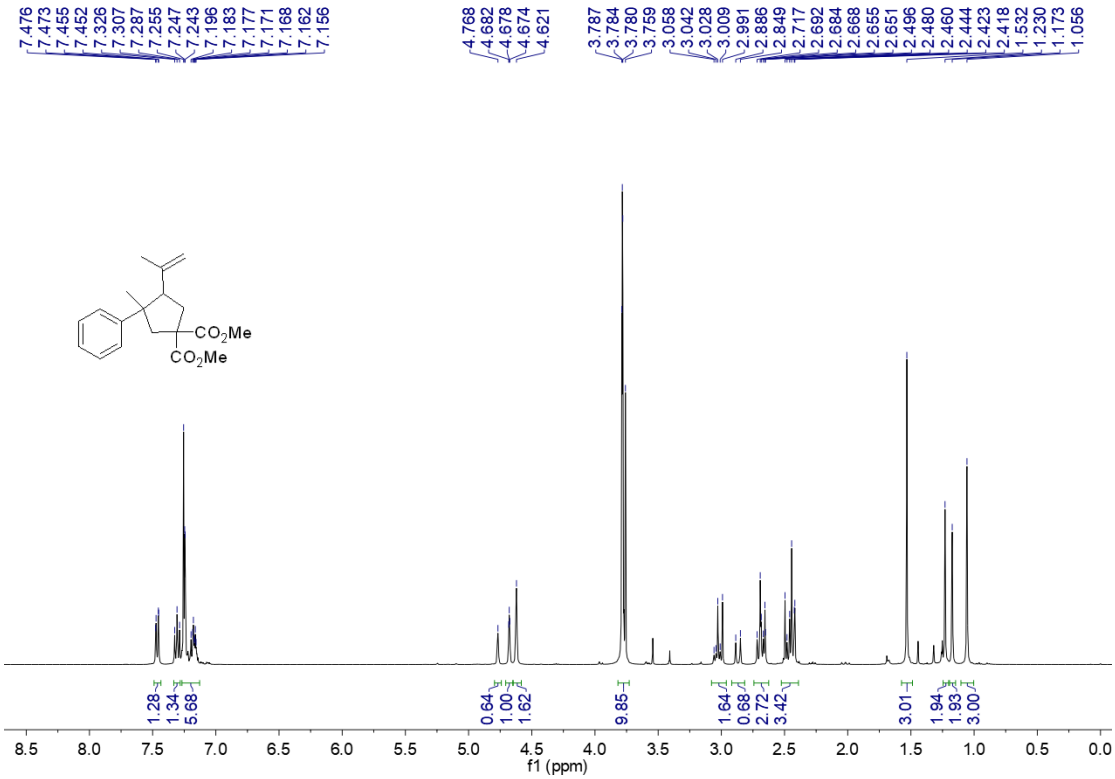


^{13}C NMR ($CDCl_3$, 101 MHz)

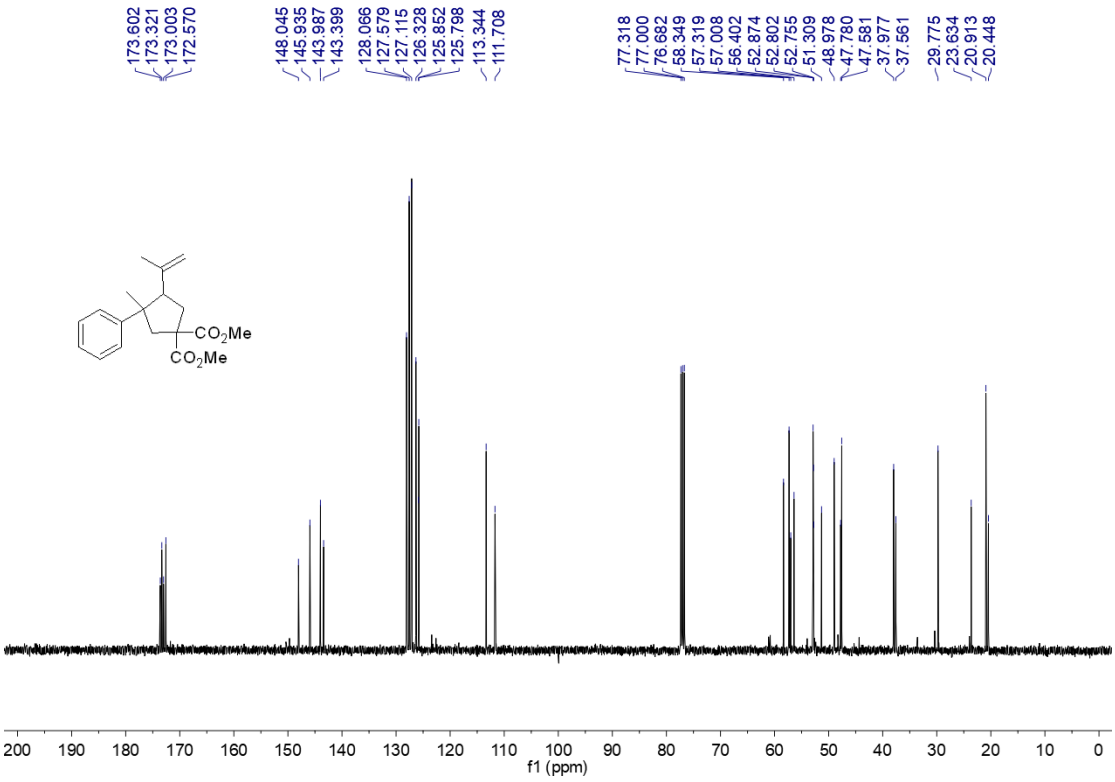


(2w)

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

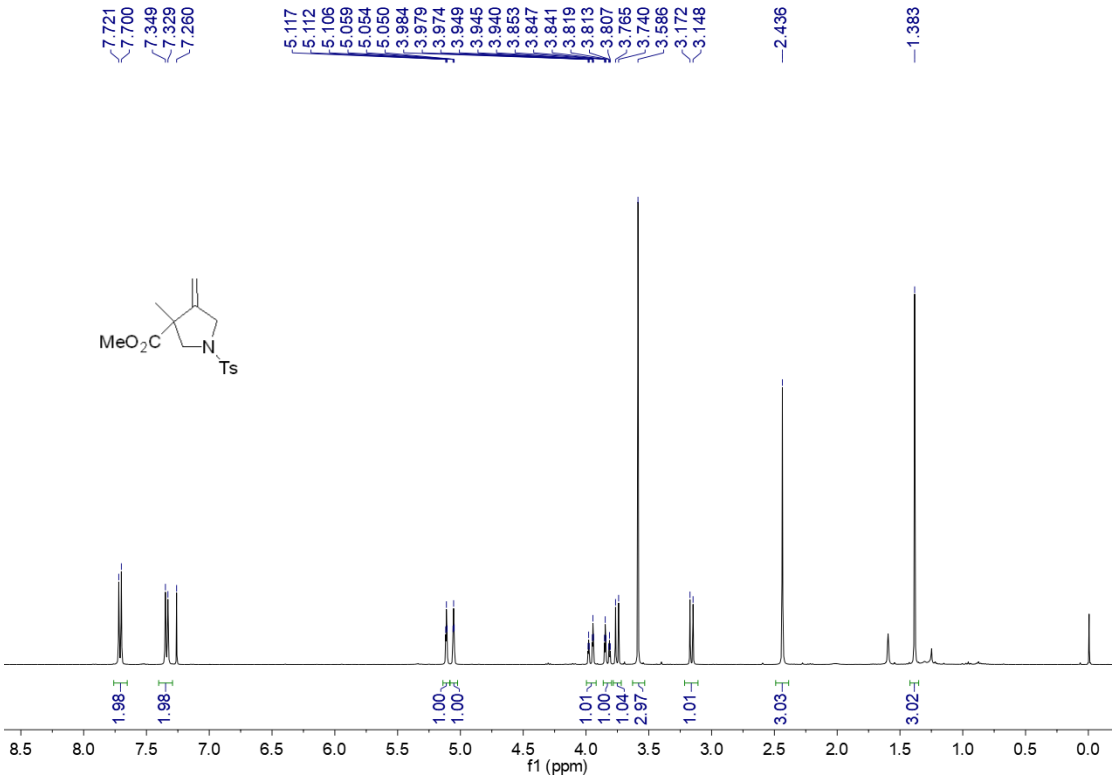


^{13}C NMR ($CDCl_3$, 101 MHz)

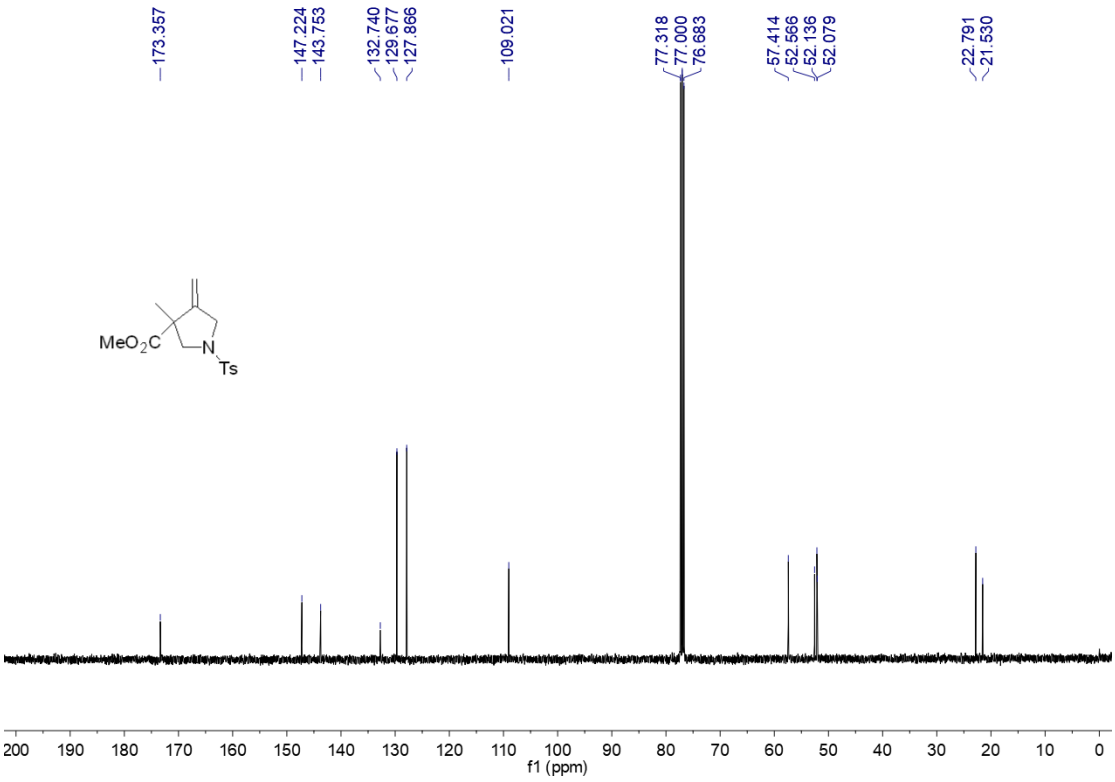


(4a)

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

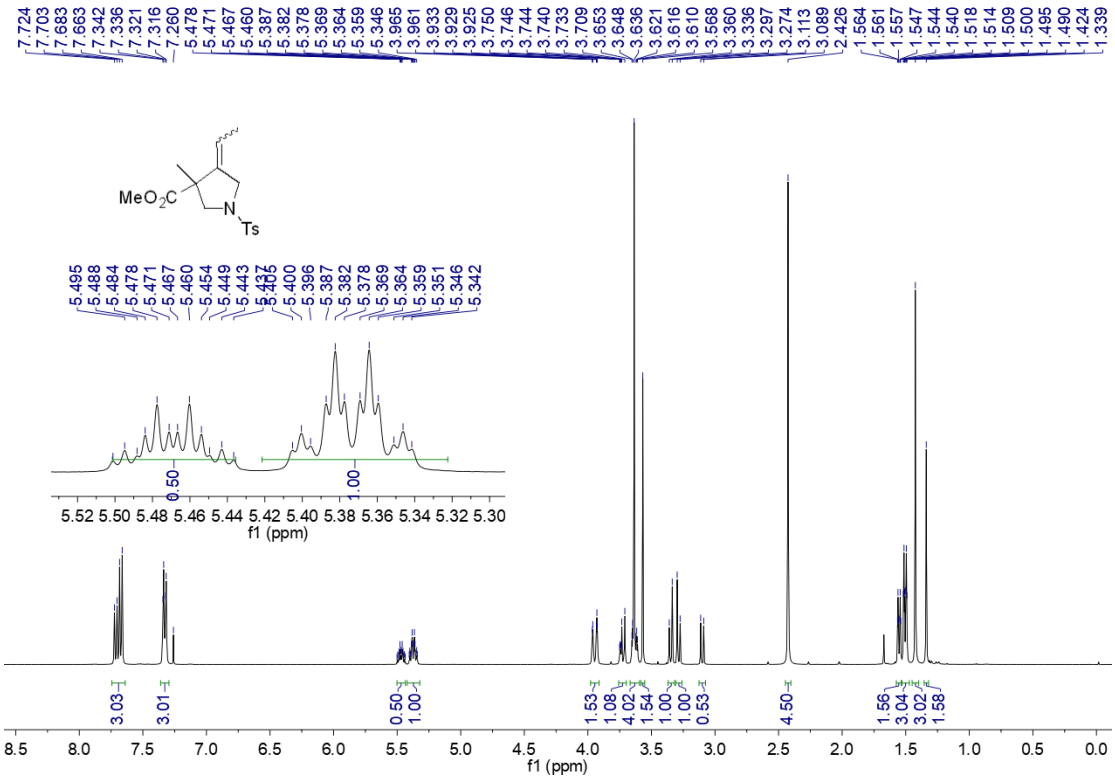


^{13}C NMR ($CDCl_3$, 101 MHz)

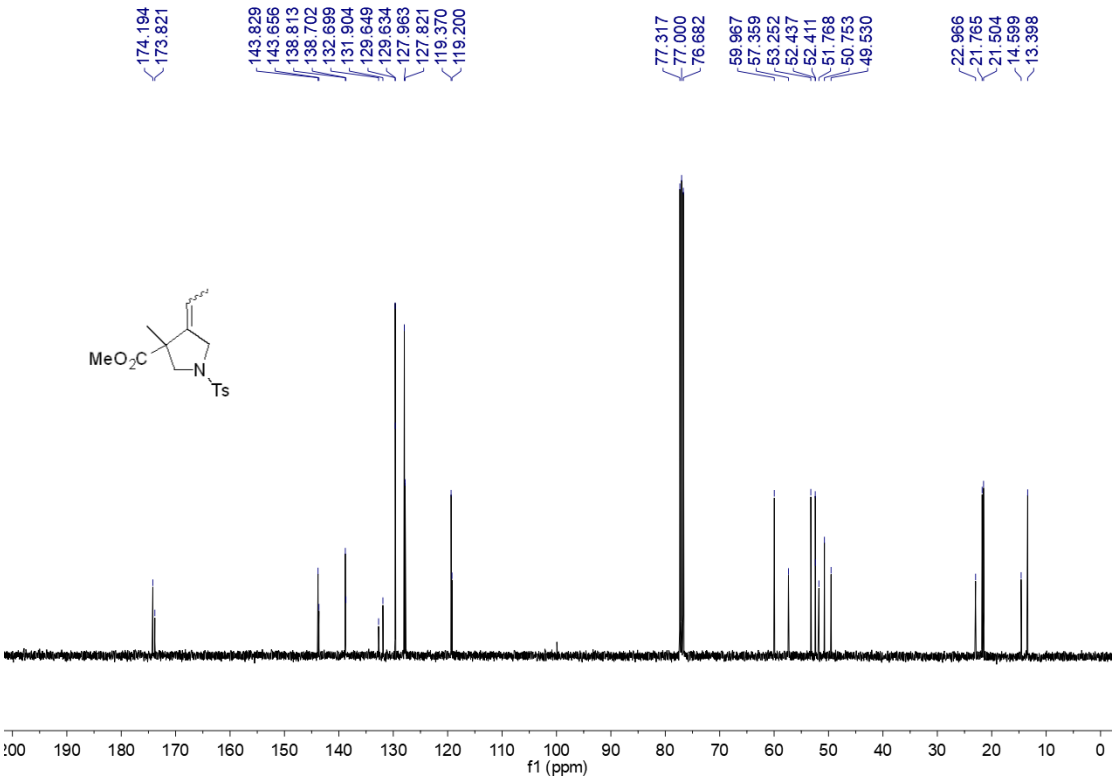


(4b)

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

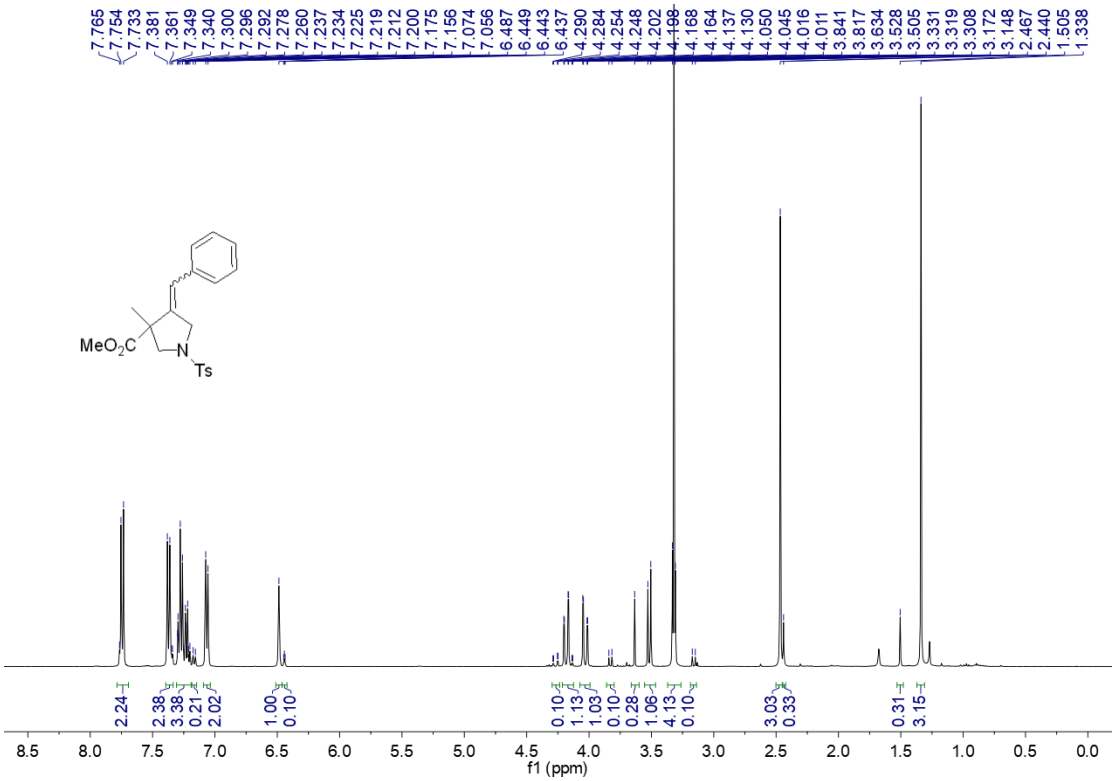


^{13}C NMR ($CDCl_3$, 101 MHz)

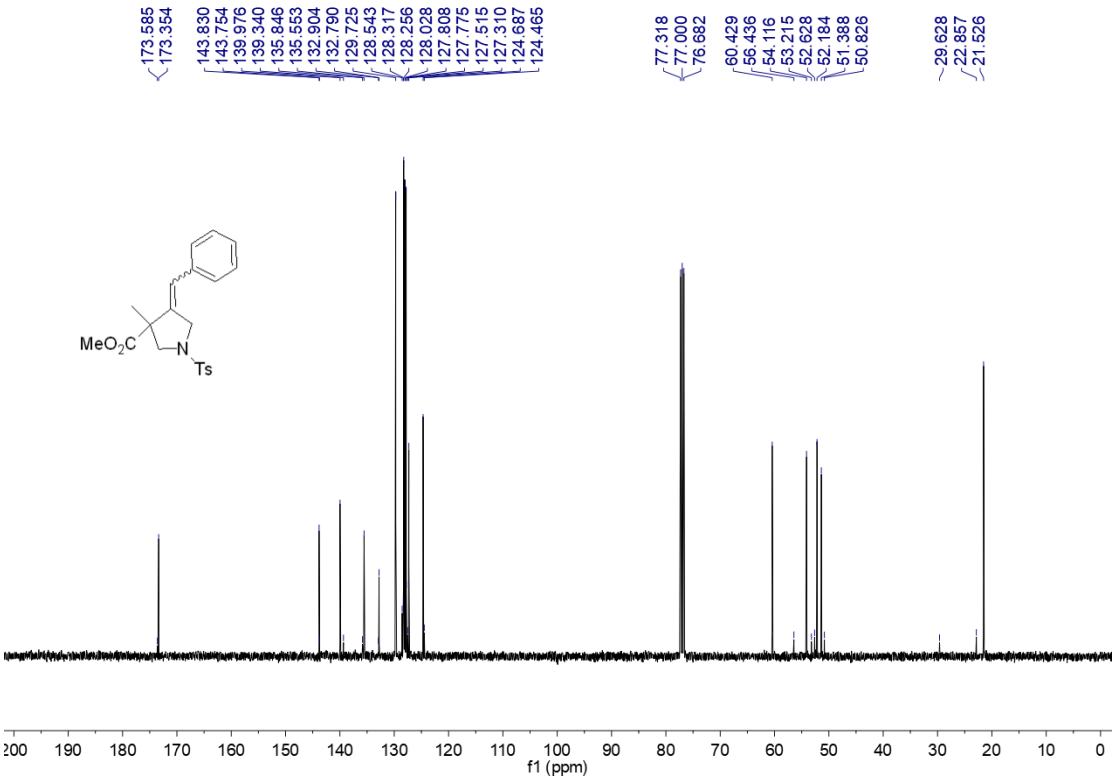


(4c)

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

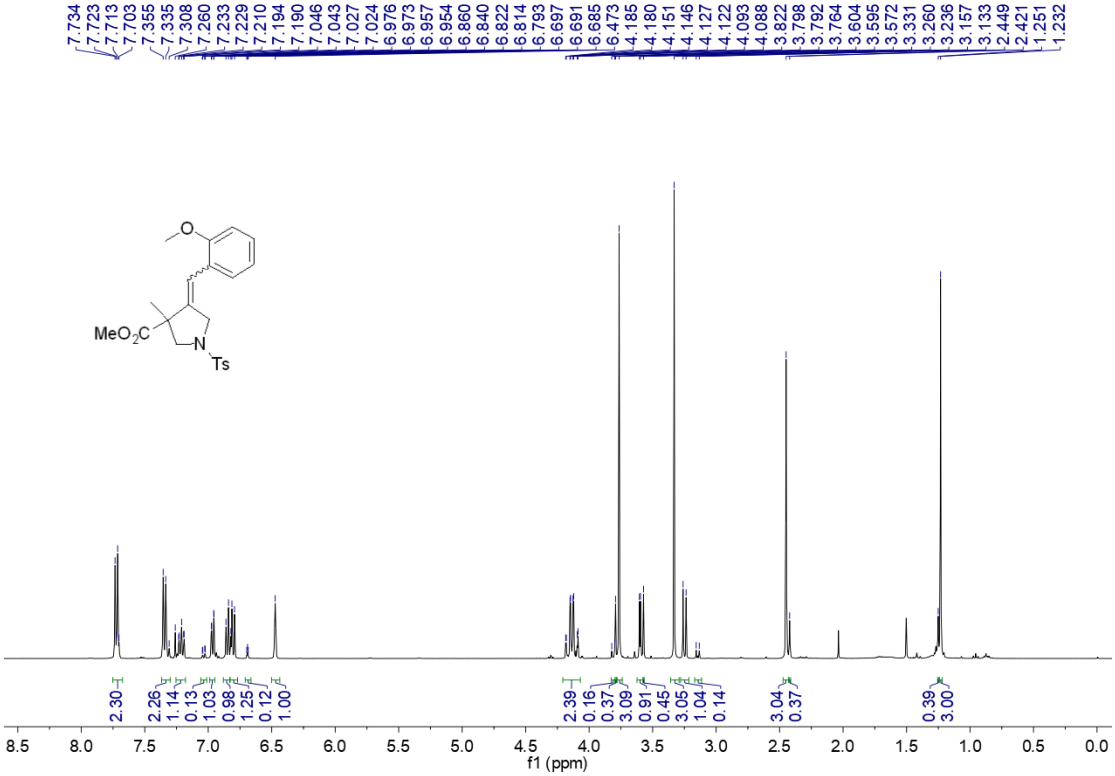


^{13}C NMR ($CDCl_3$, 101 MHz)

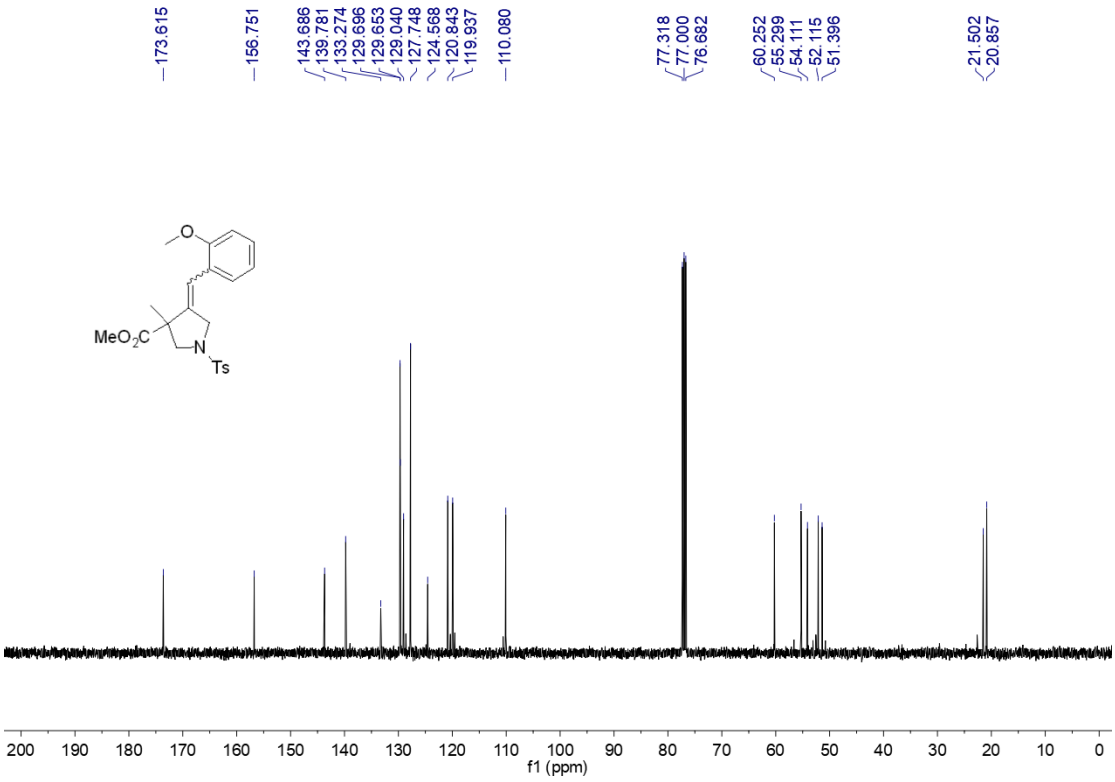


(4d)

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

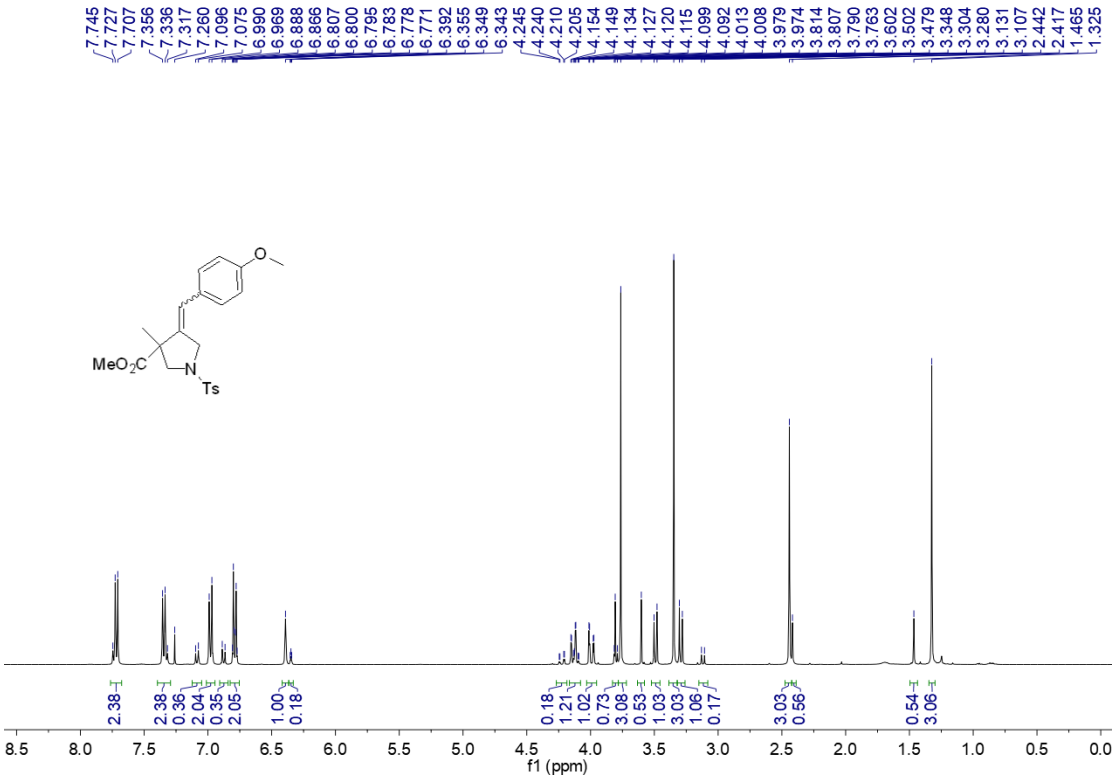


^{13}C NMR ($CDCl_3$, 101 MHz)

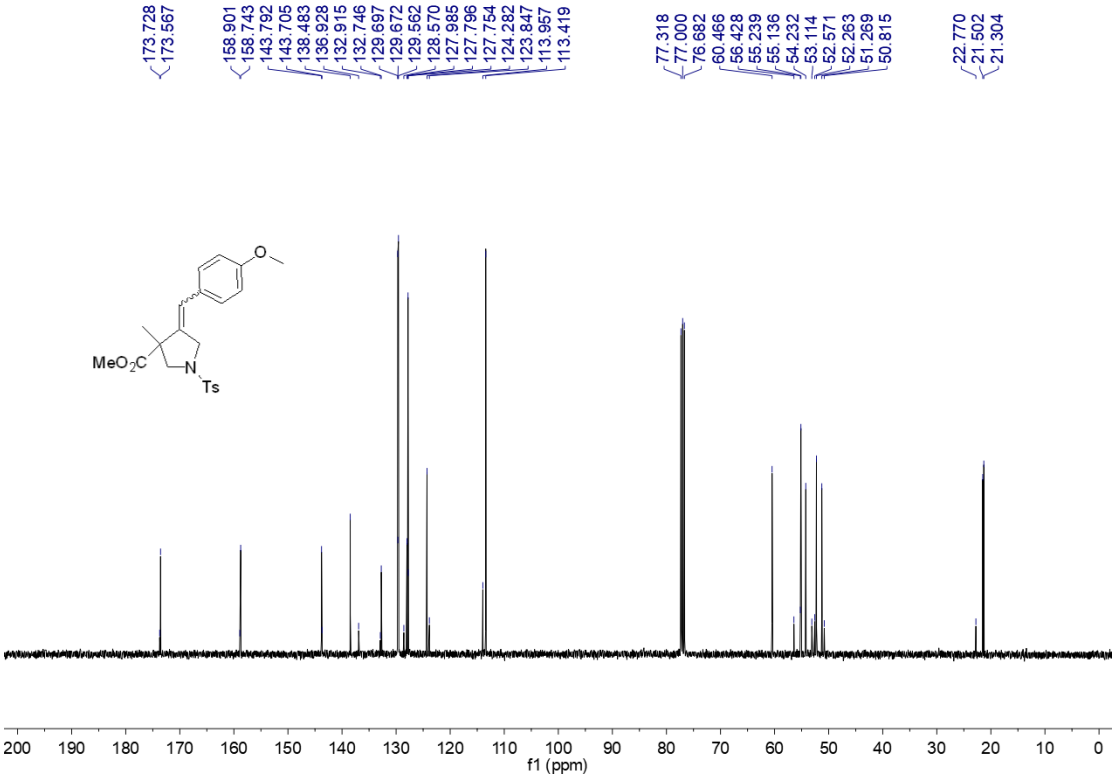


(4e)

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

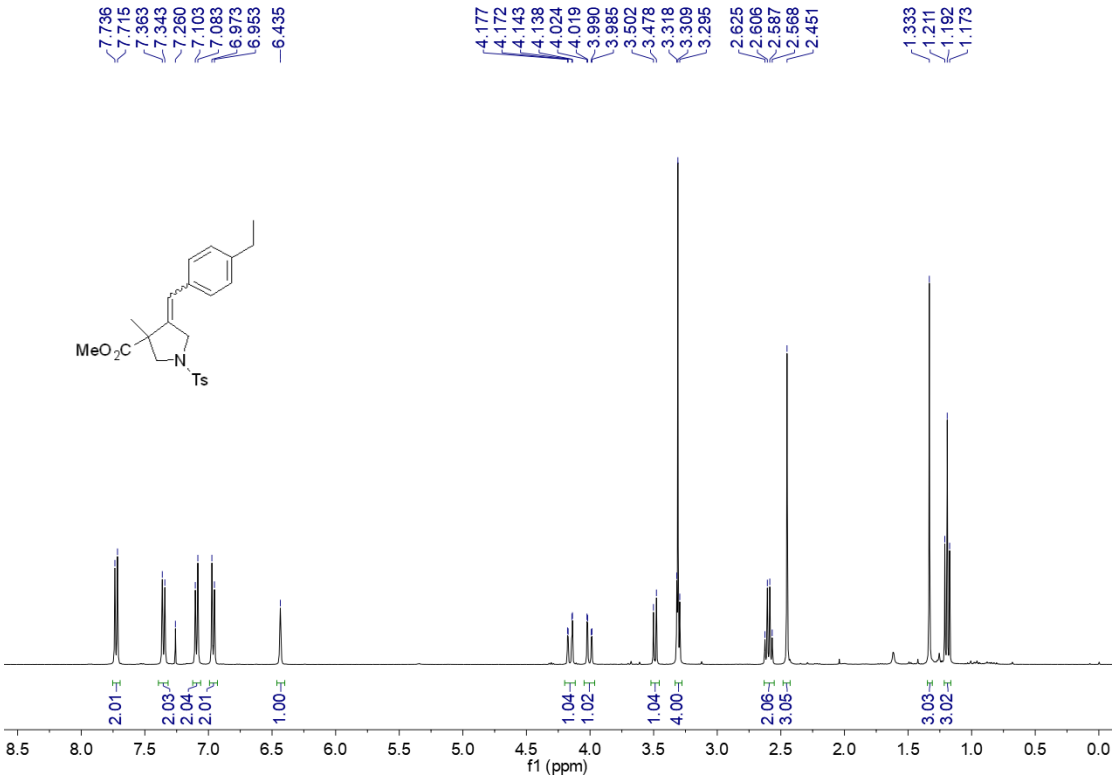


^{13}C NMR ($CDCl_3$, 101 MHz)

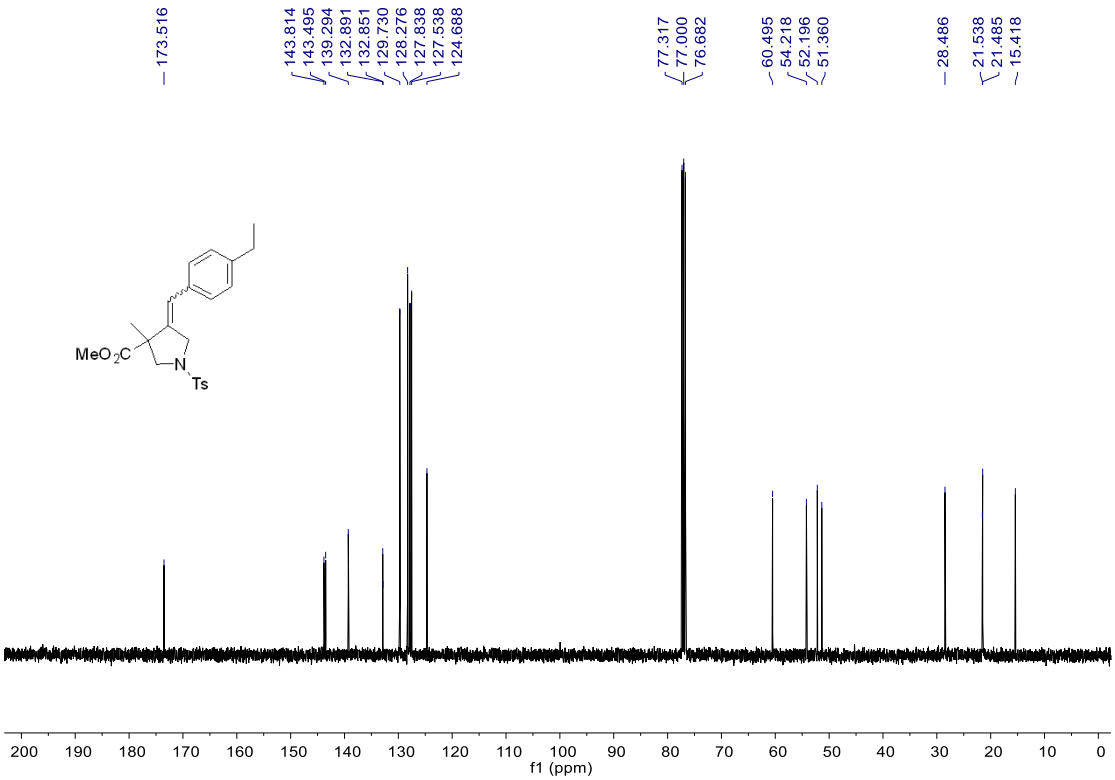


(4f)

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

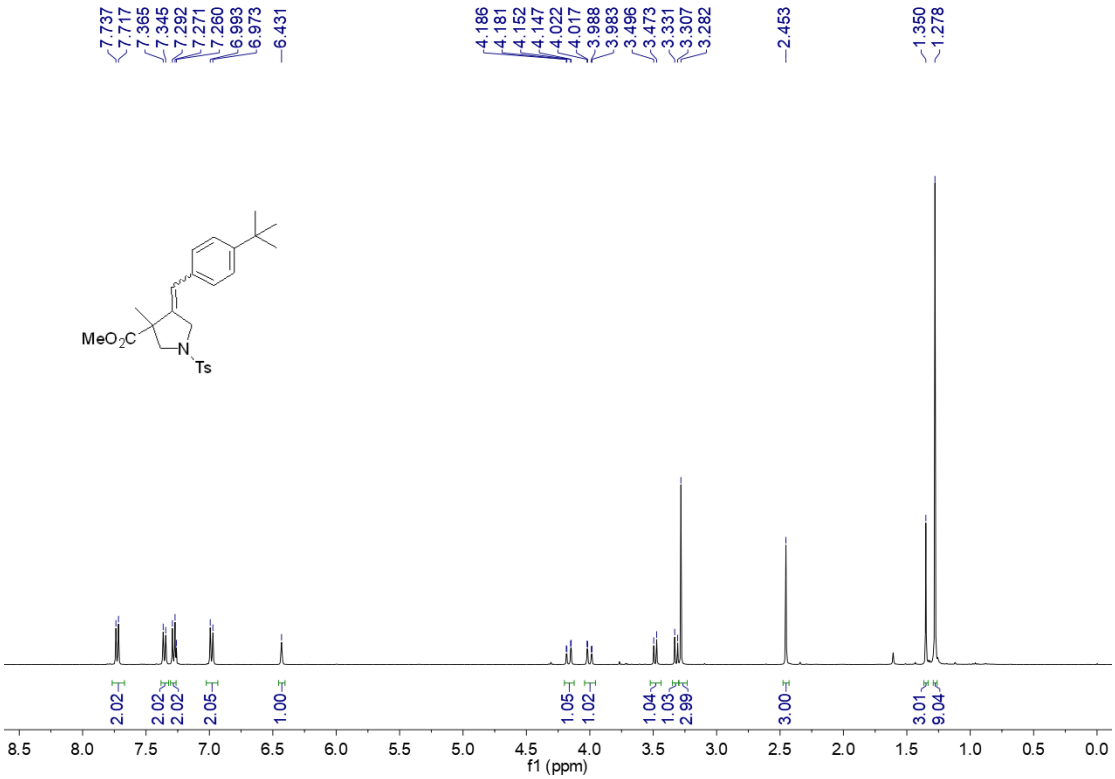


^{13}C NMR ($CDCl_3$, 101 MHz)

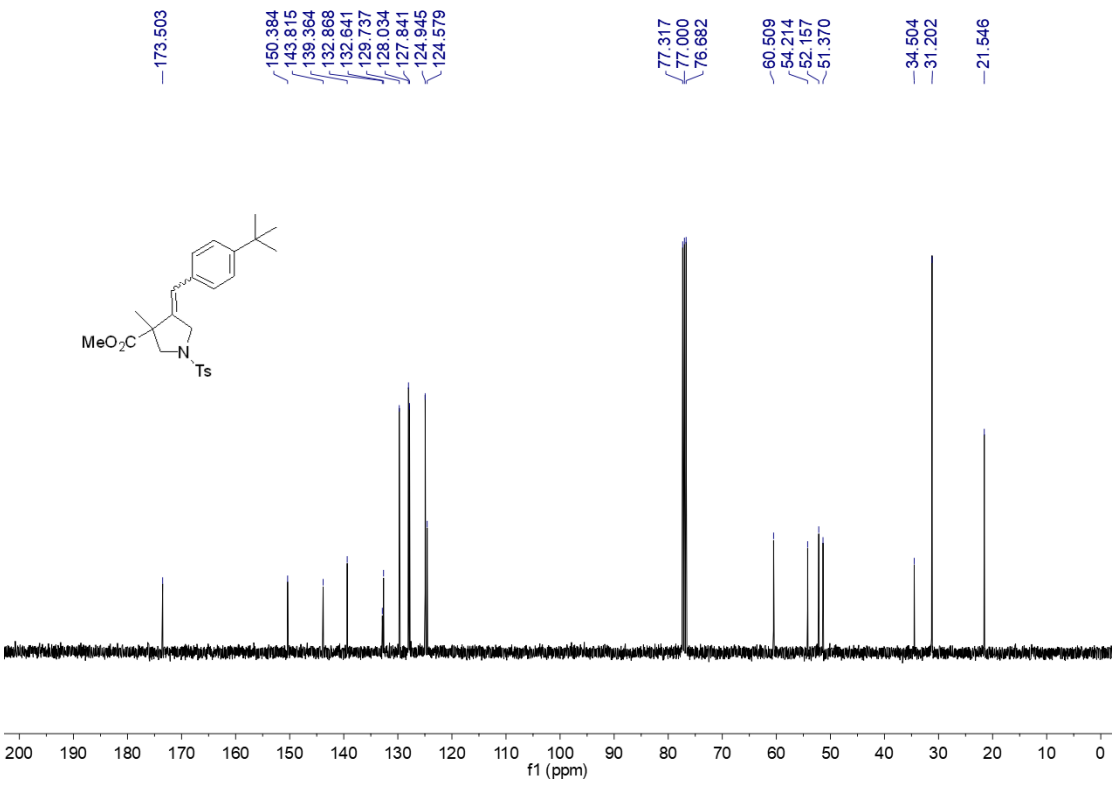


(4g)

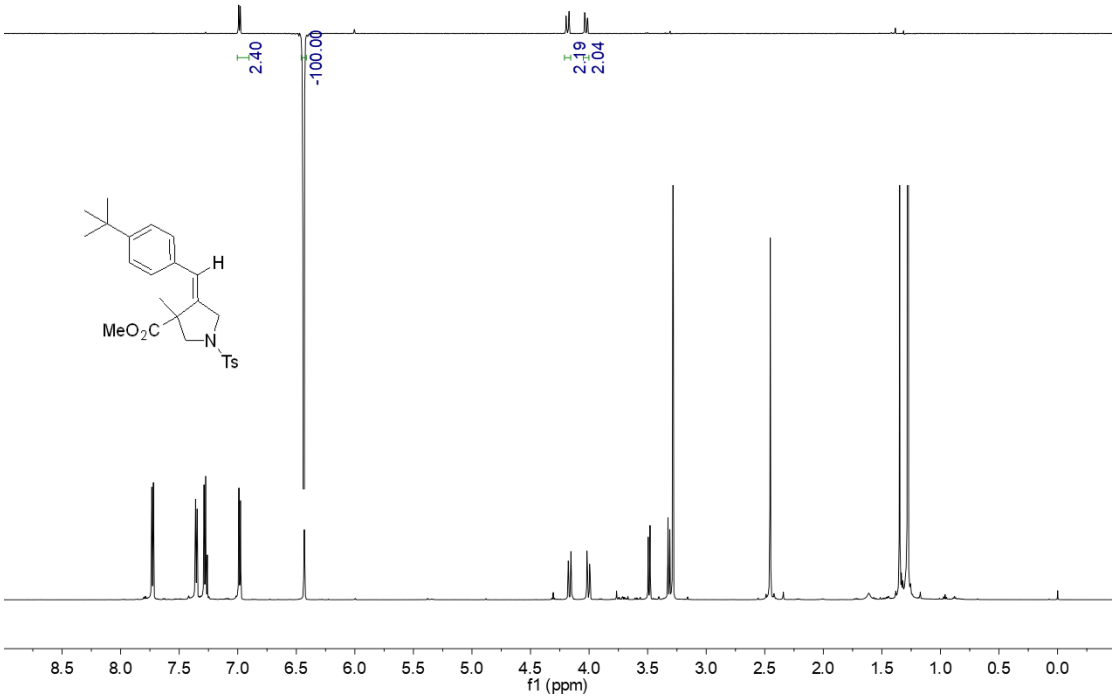
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

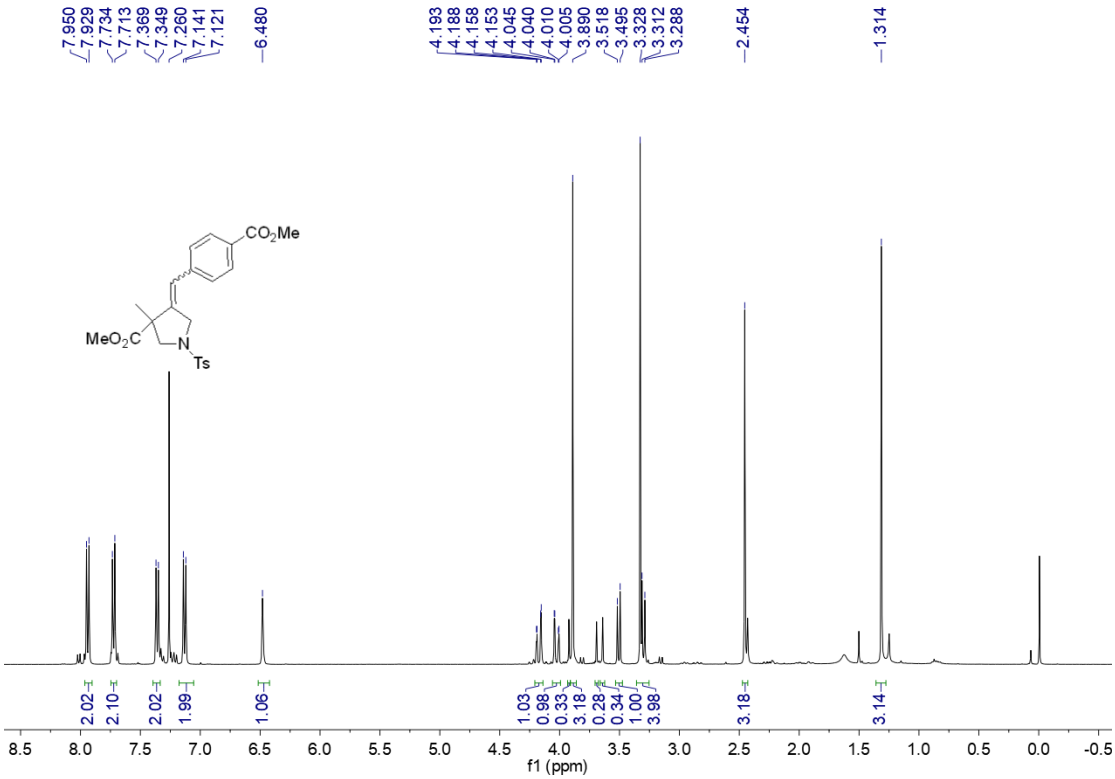


NOE Experiment ($CDCl_3$, 600 MHz)

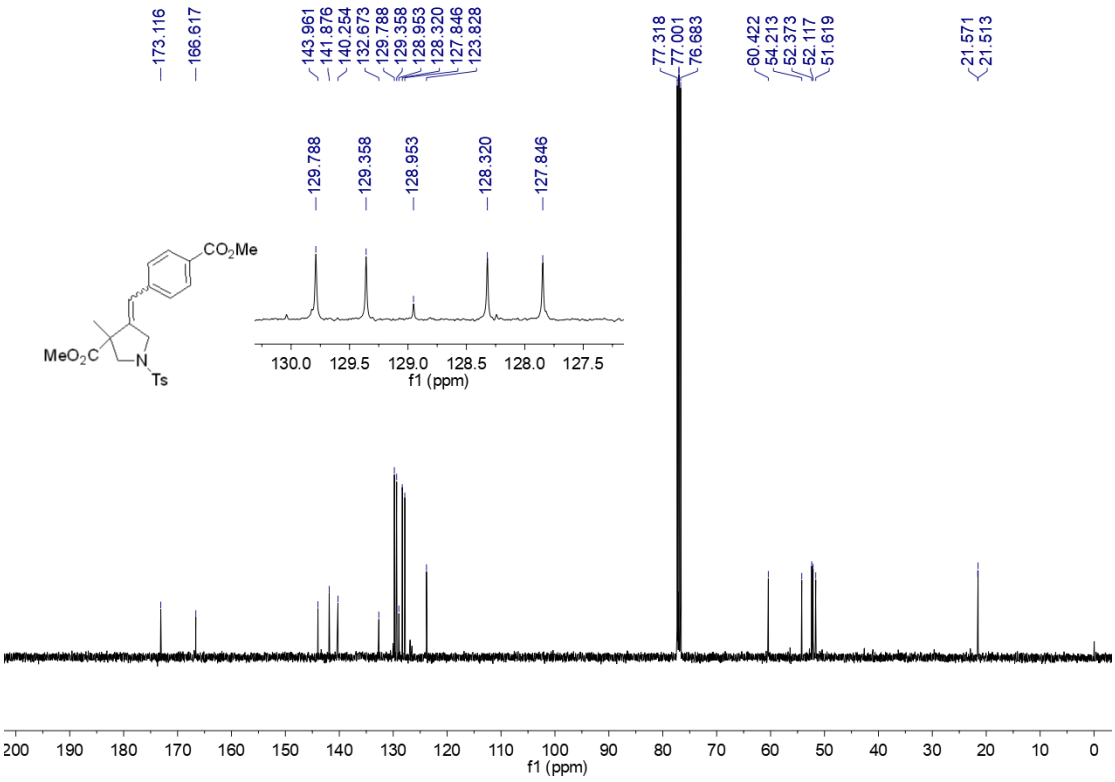


(4h)

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

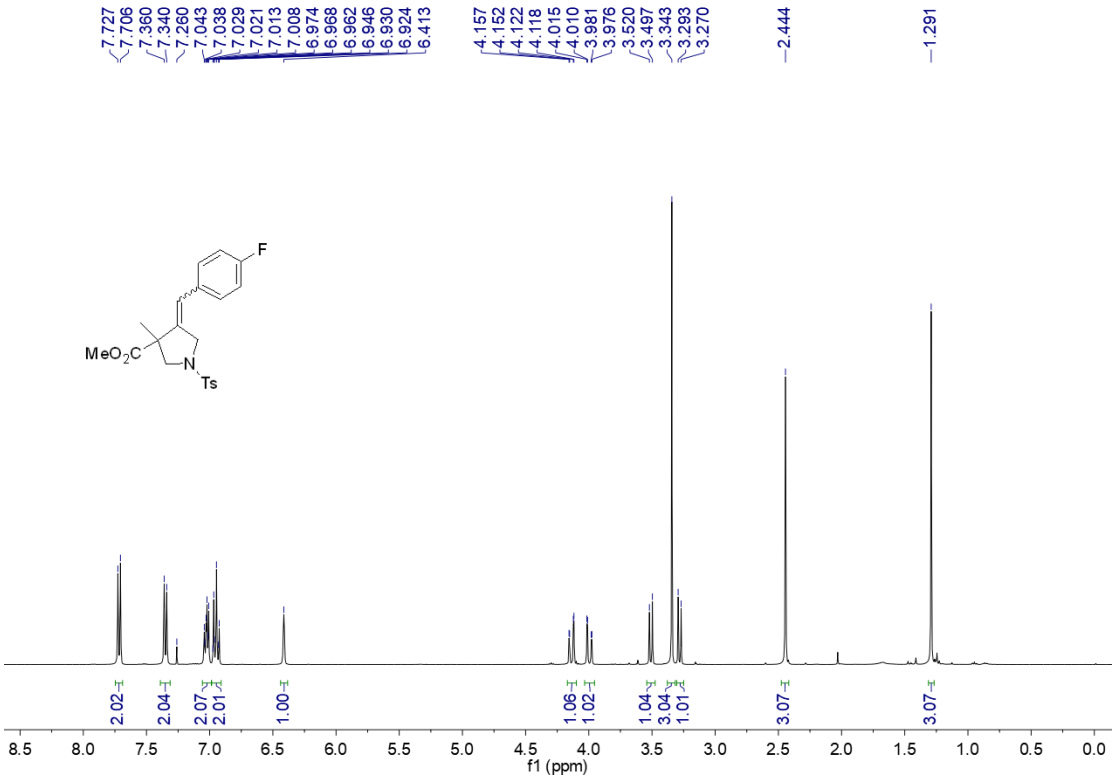


^{13}C NMR ($CDCl_3$, 101 MHz)

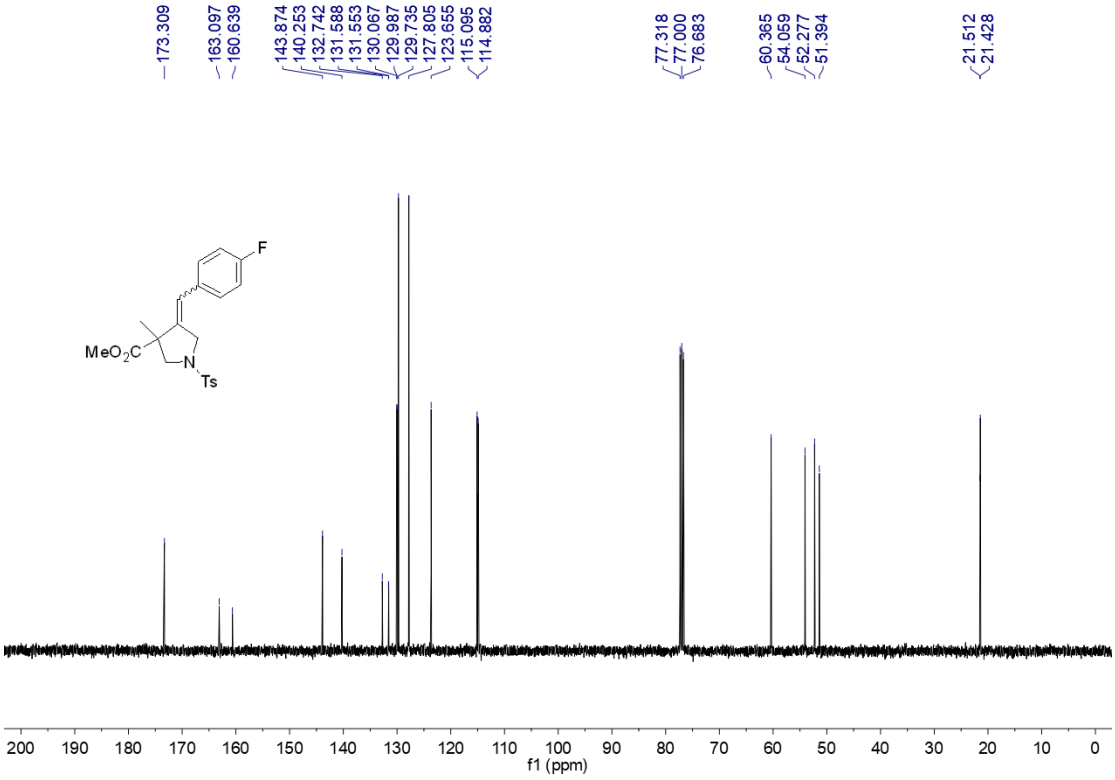


(4i)

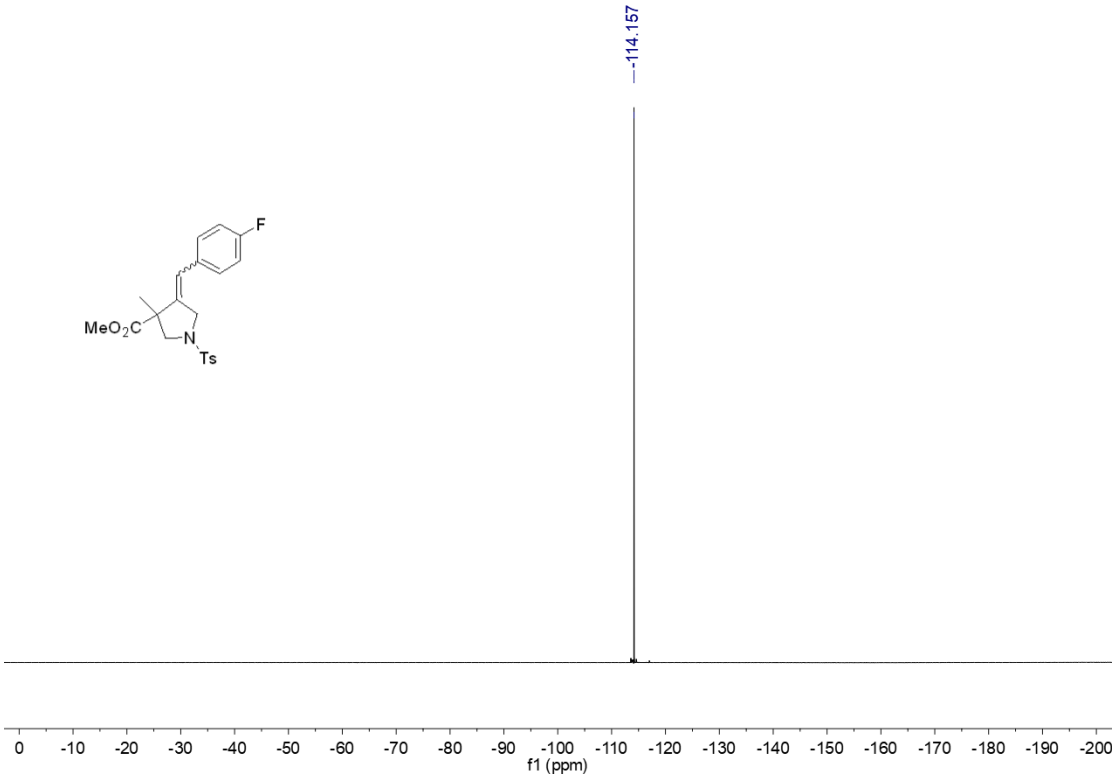
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

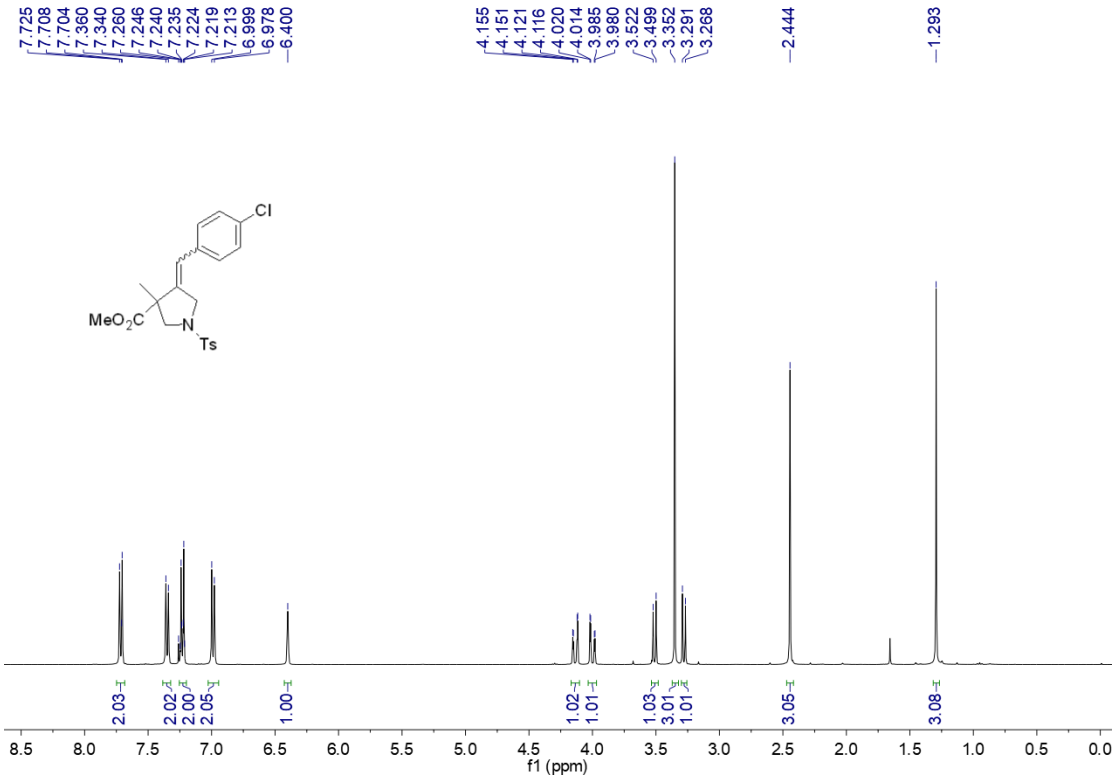


^{19}F NMR ($CDCl_3$, 376 MHz)

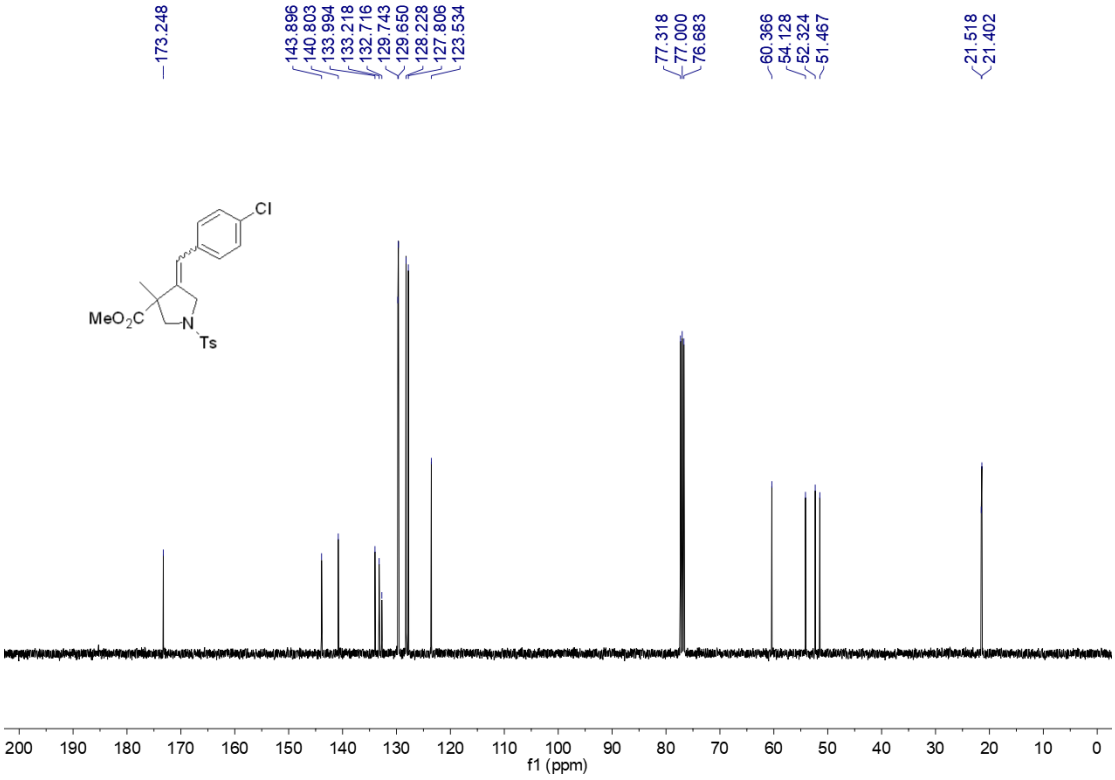


(4j)

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

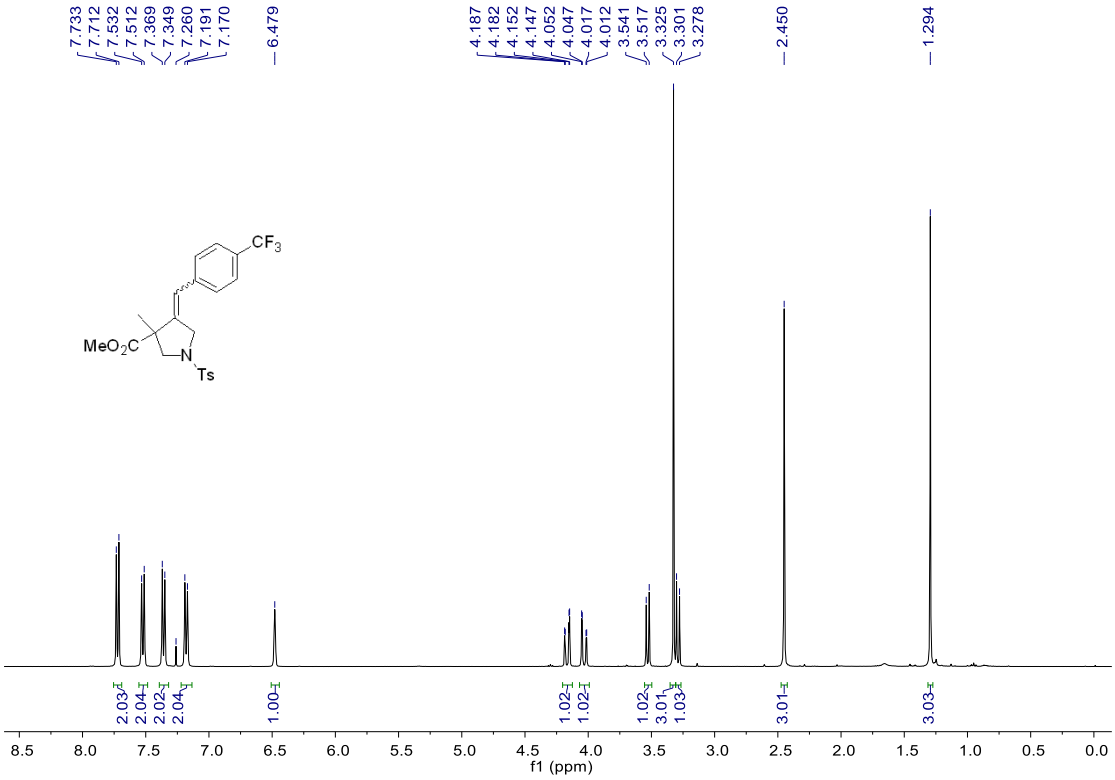


^{13}C NMR ($CDCl_3$, 101 MHz)

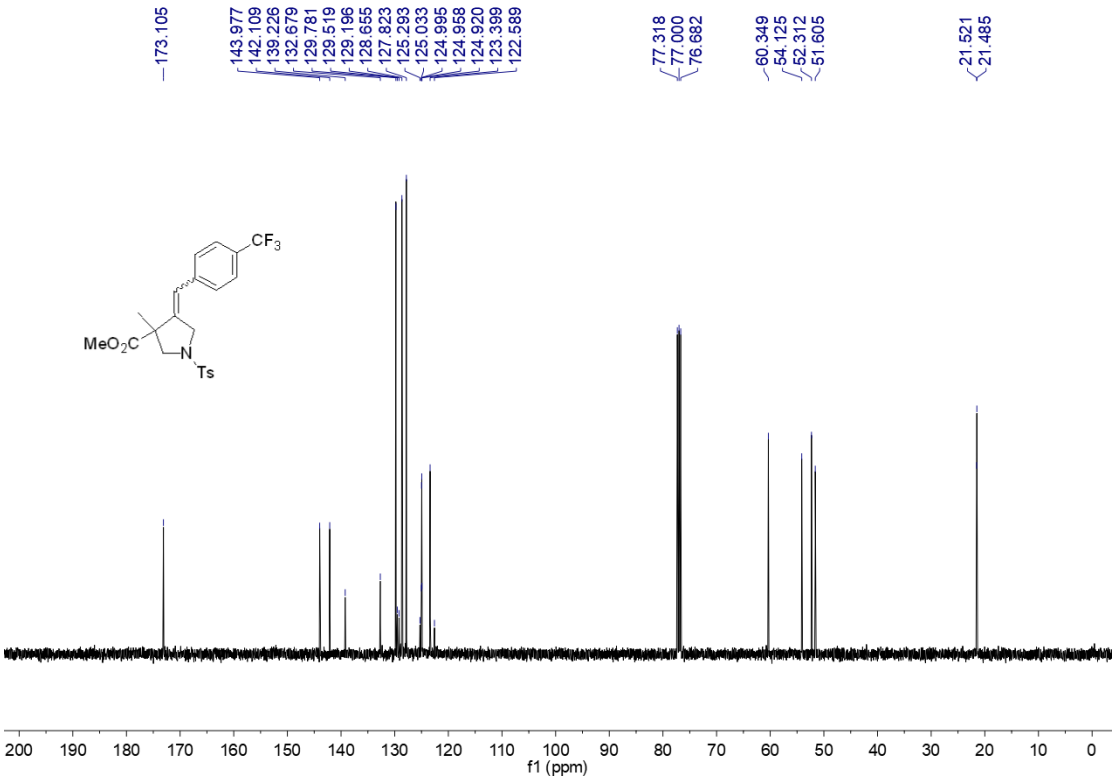


(4k)

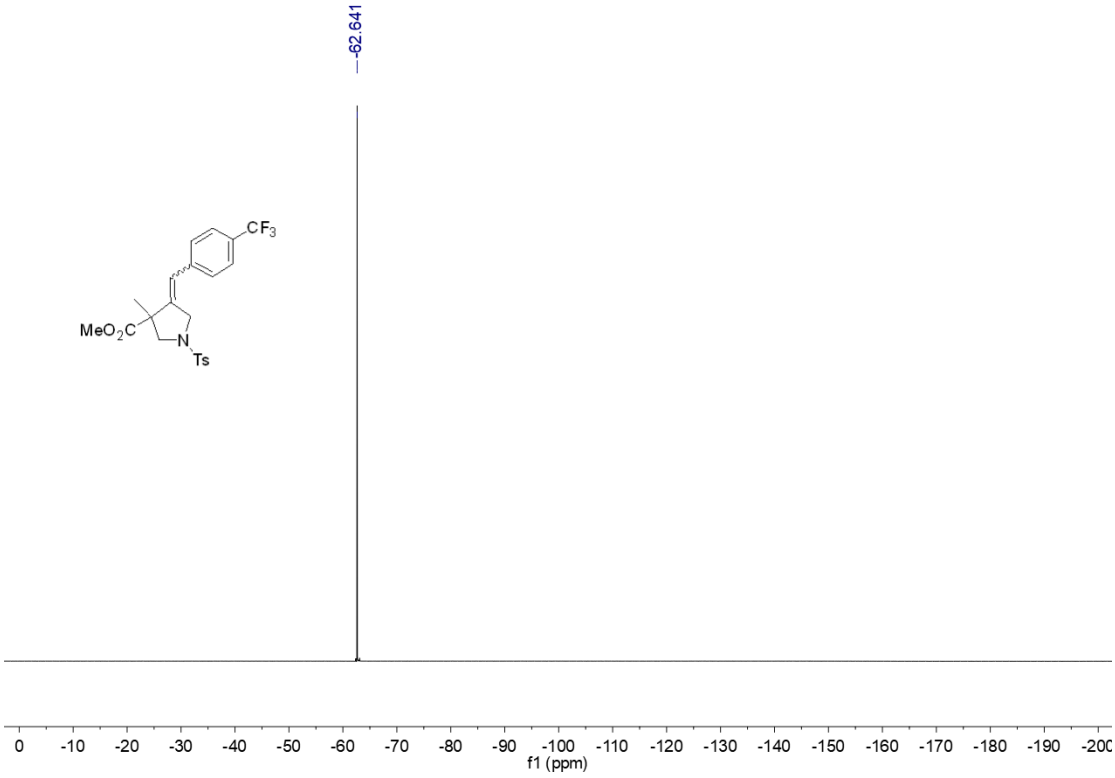
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

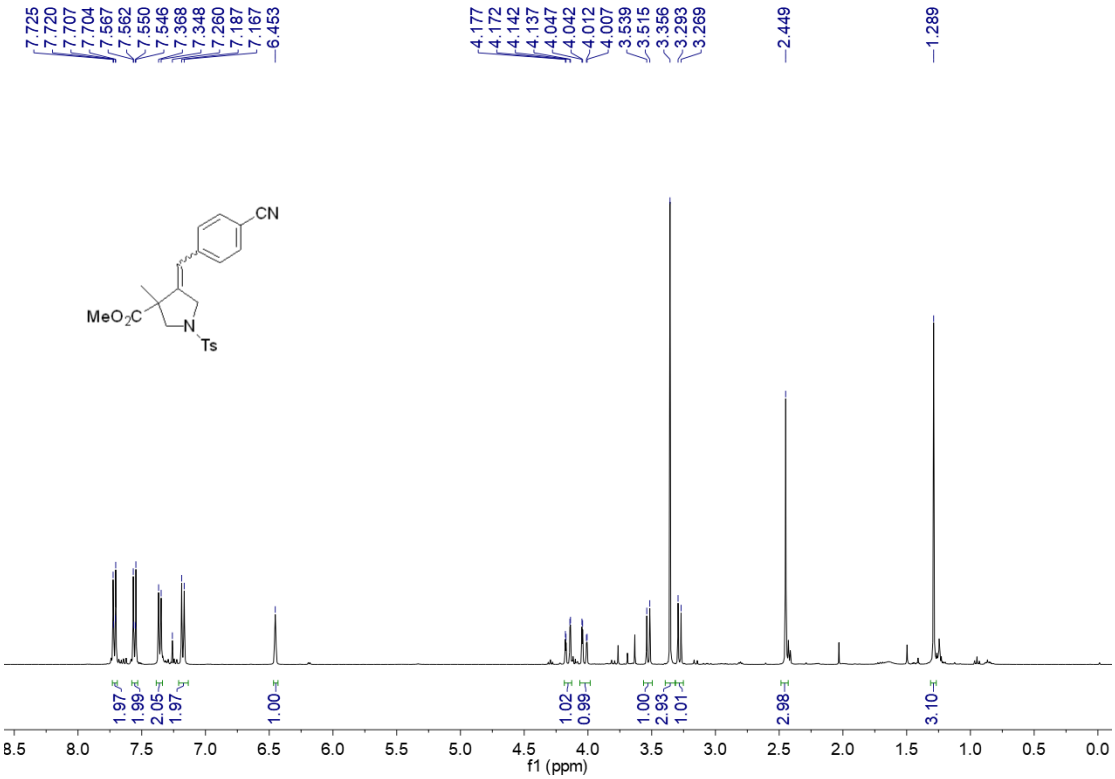


^{19}F NMR ($CDCl_3$, 376 MHz)

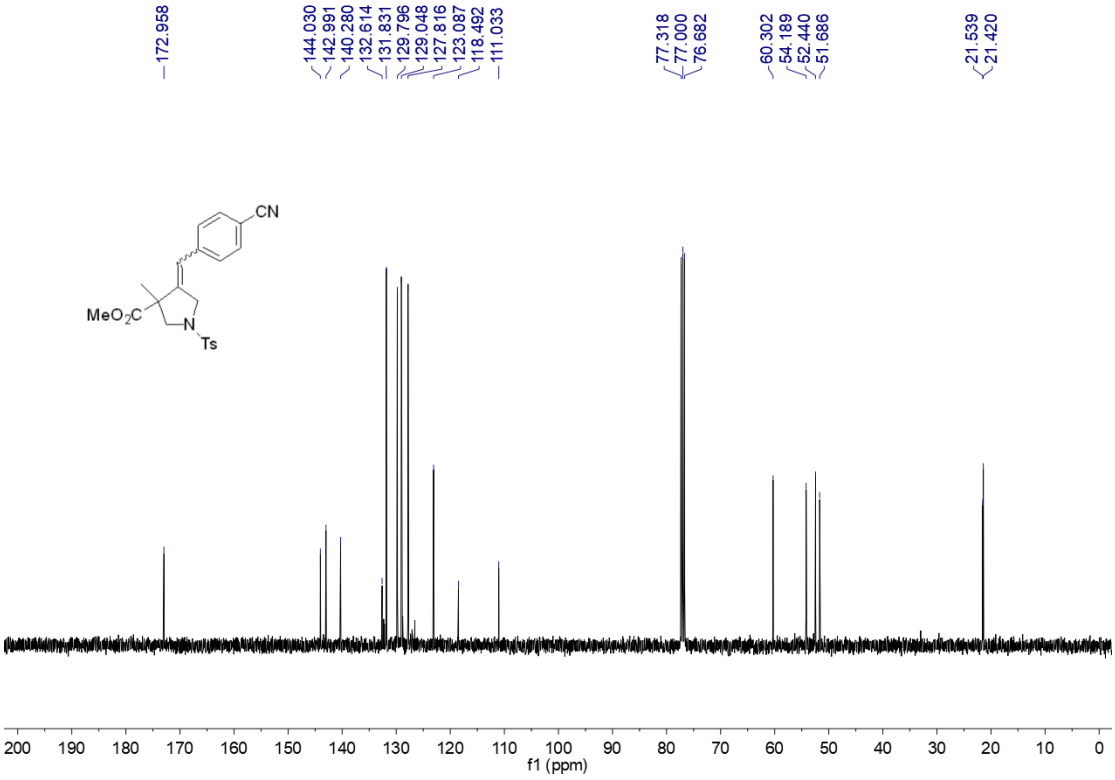


(4l)

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

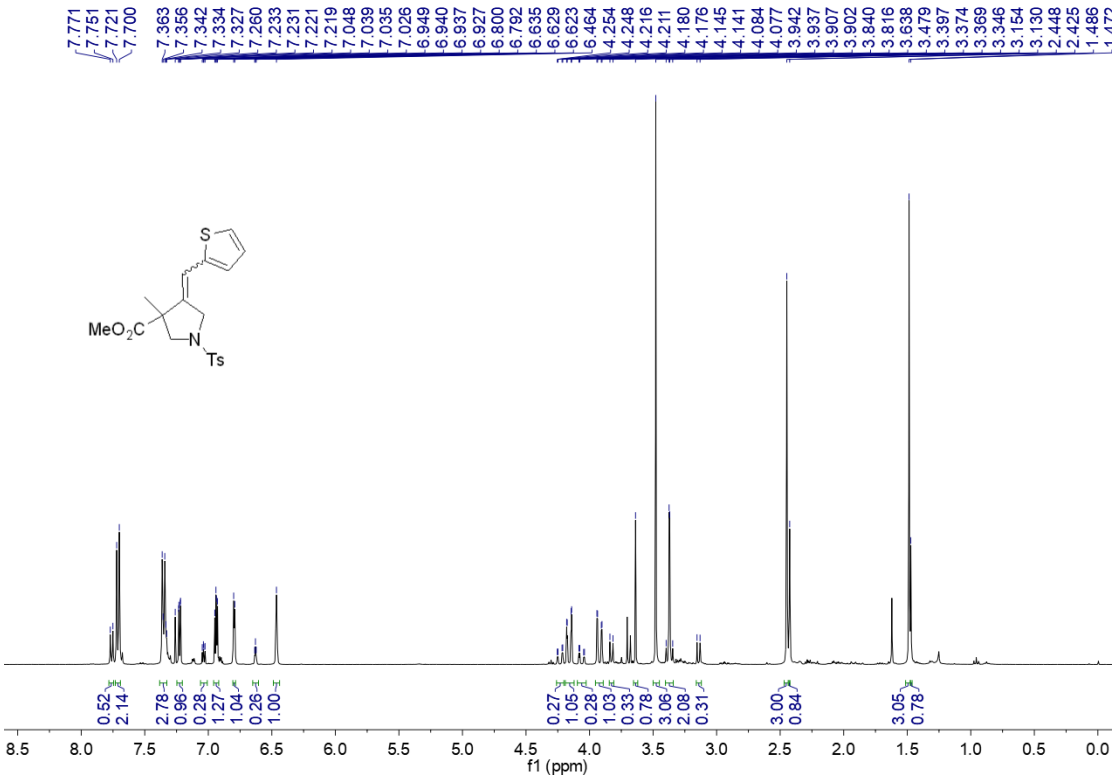


^{13}C NMR ($CDCl_3$, 101 MHz)

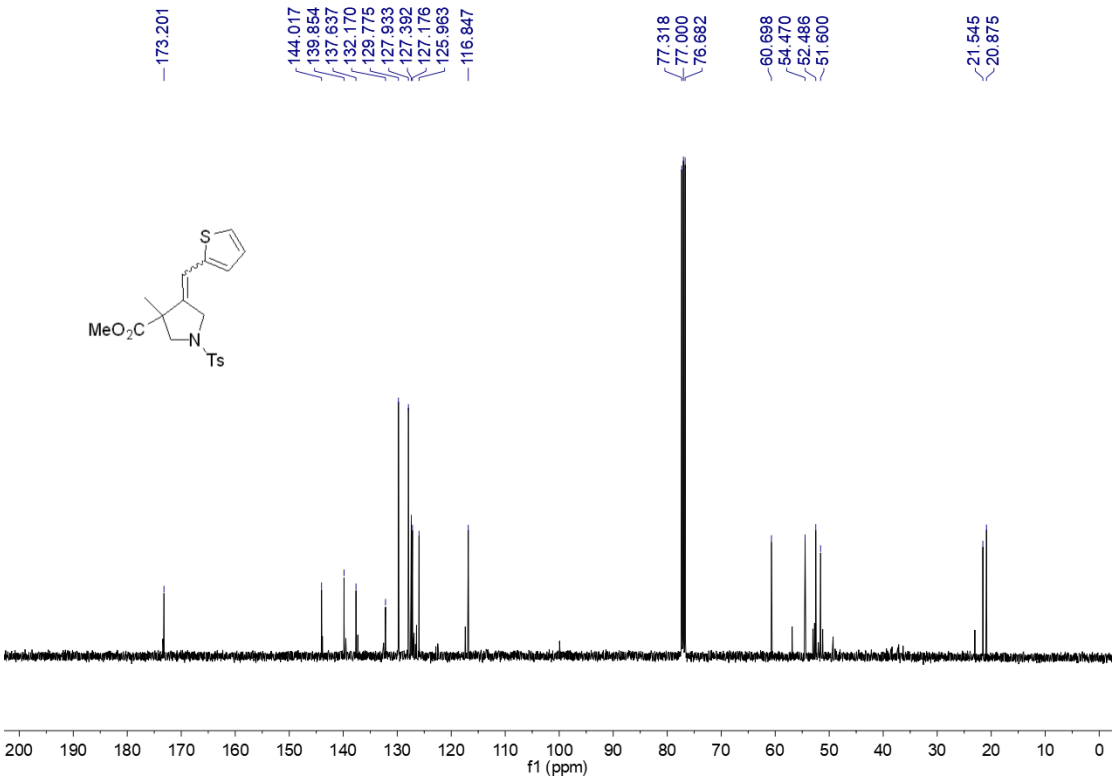


(4m)

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

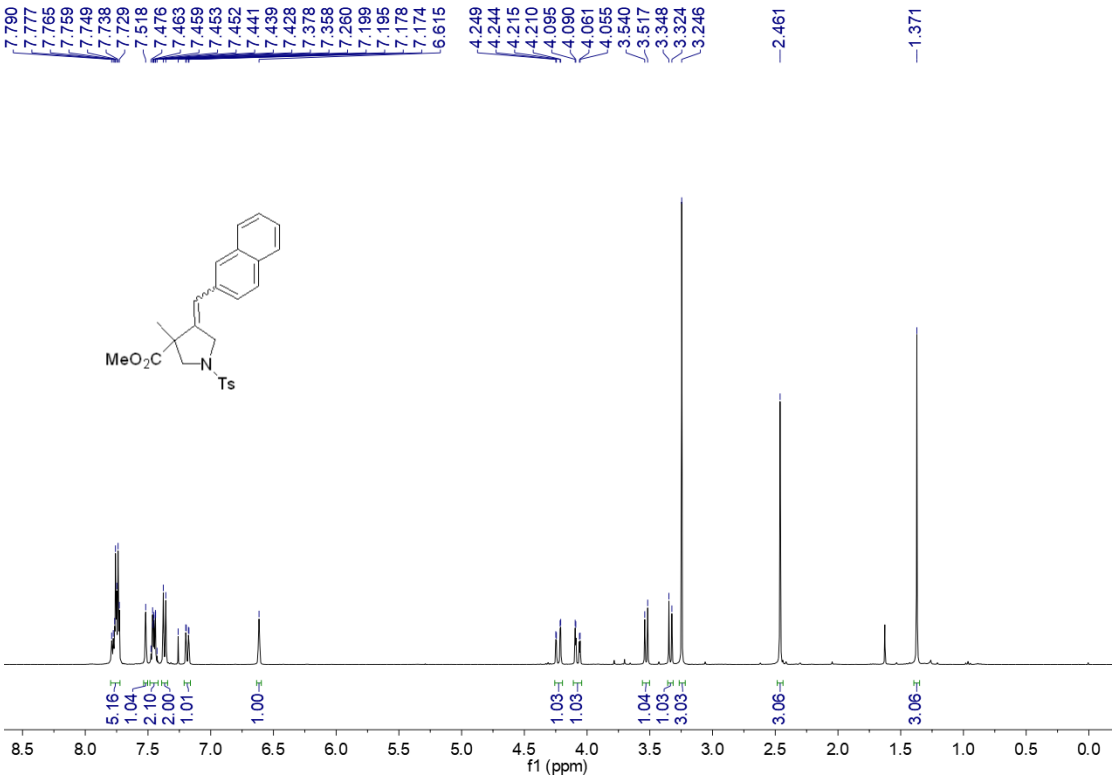


^{13}C NMR ($CDCl_3$, 101 MHz)

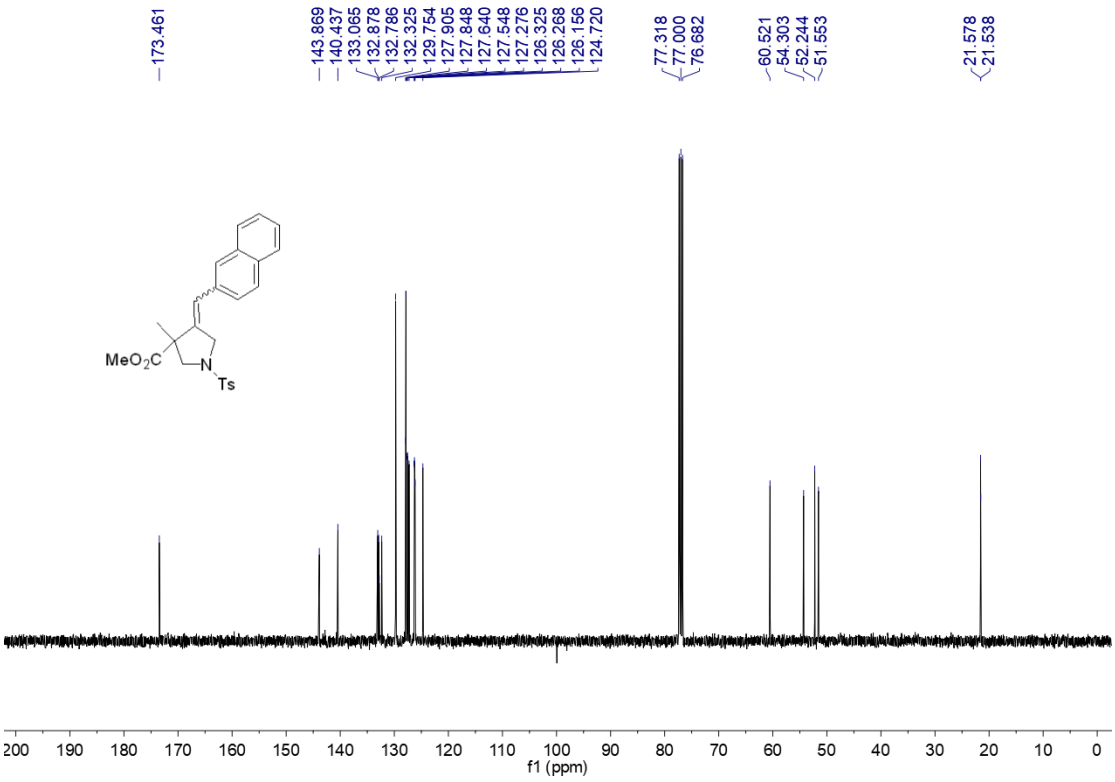


(4n)

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

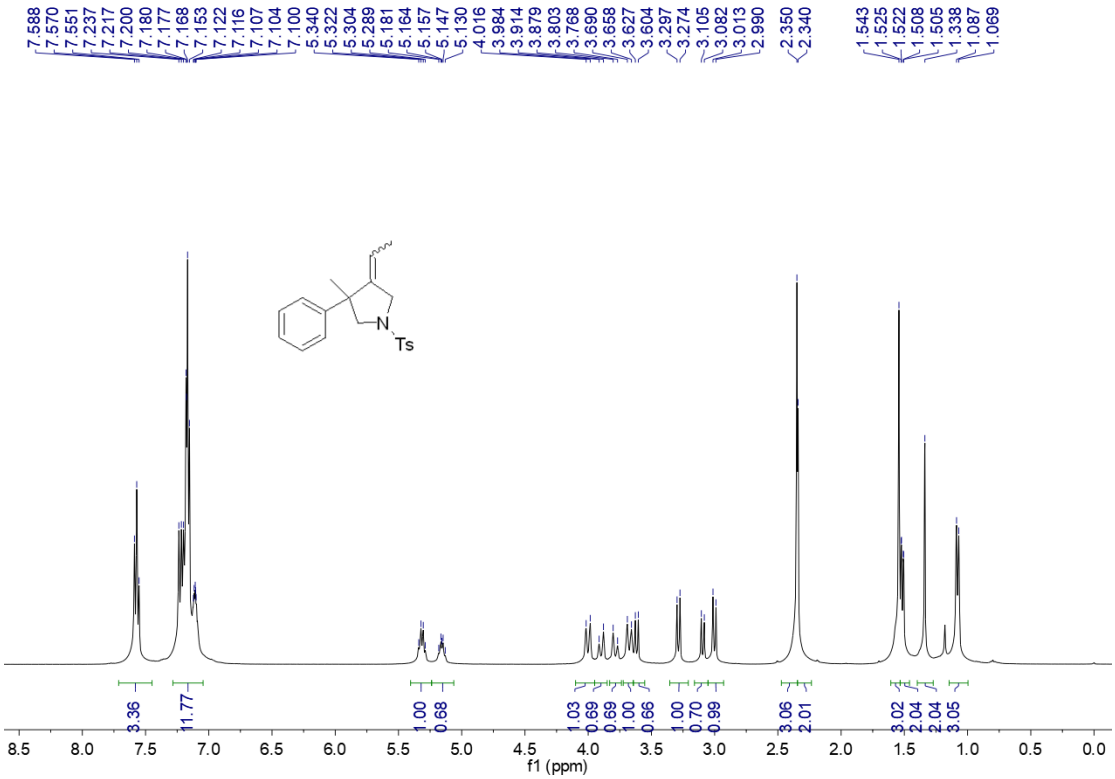


^{13}C NMR ($CDCl_3$, 101 MHz)

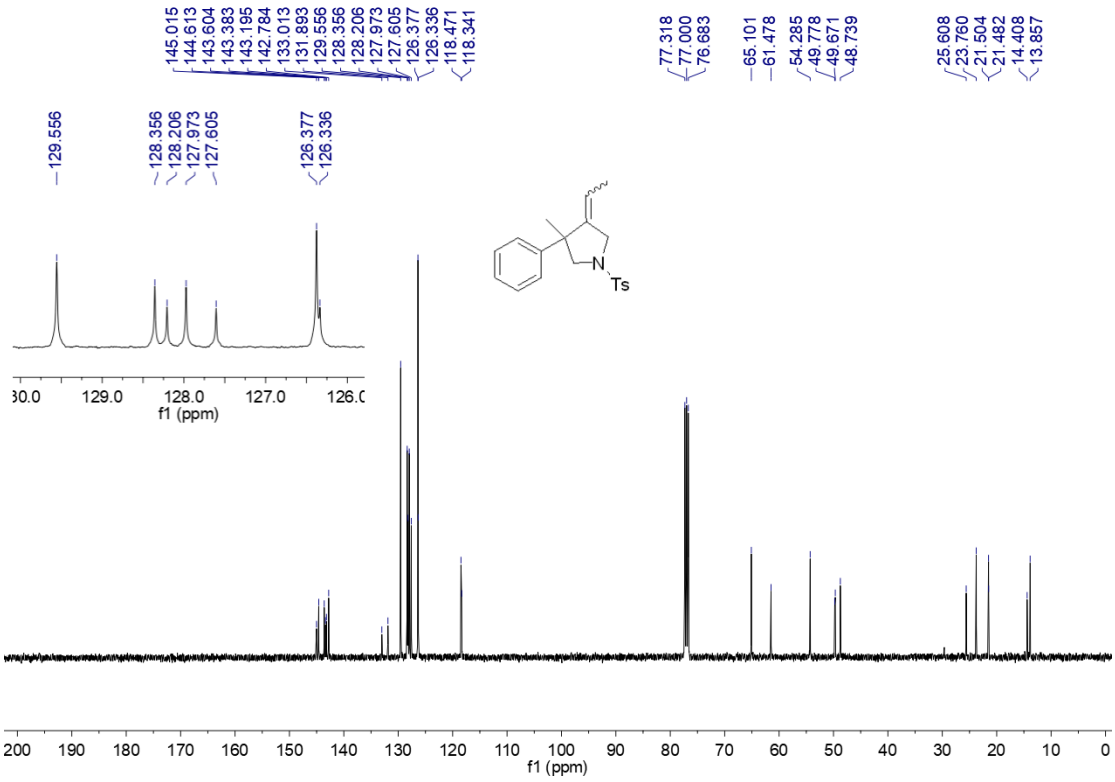


(4o)

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

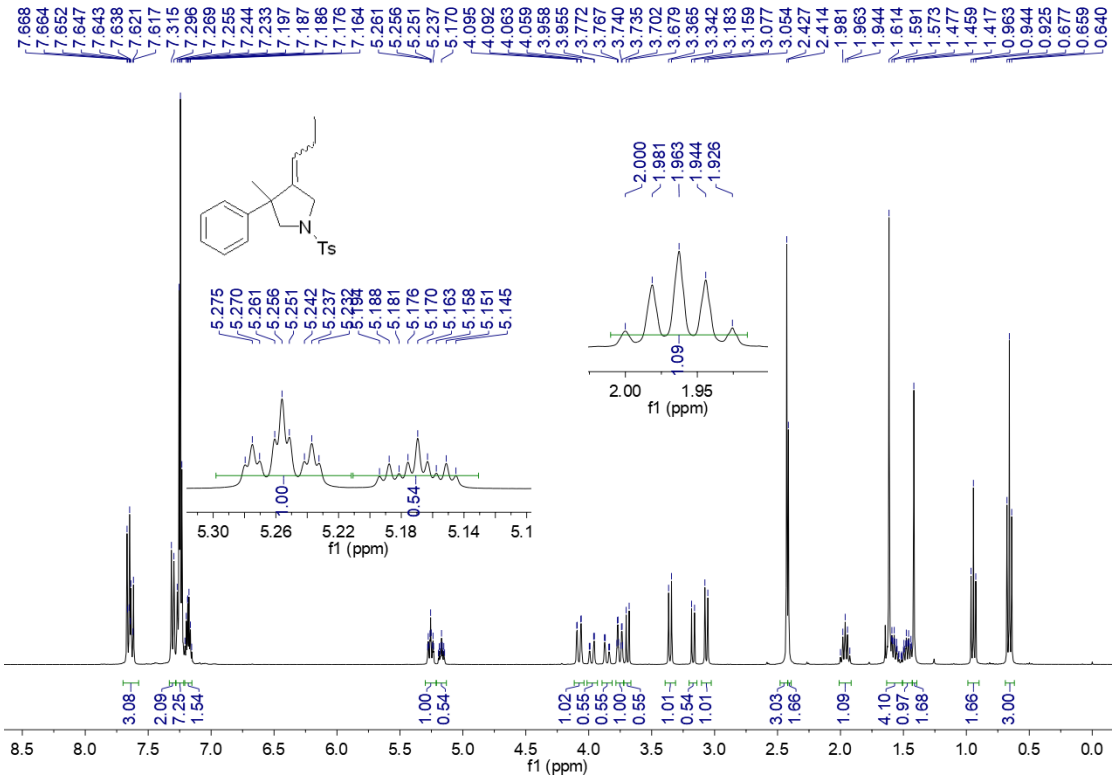


^{13}C NMR ($CDCl_3$, 101 MHz)

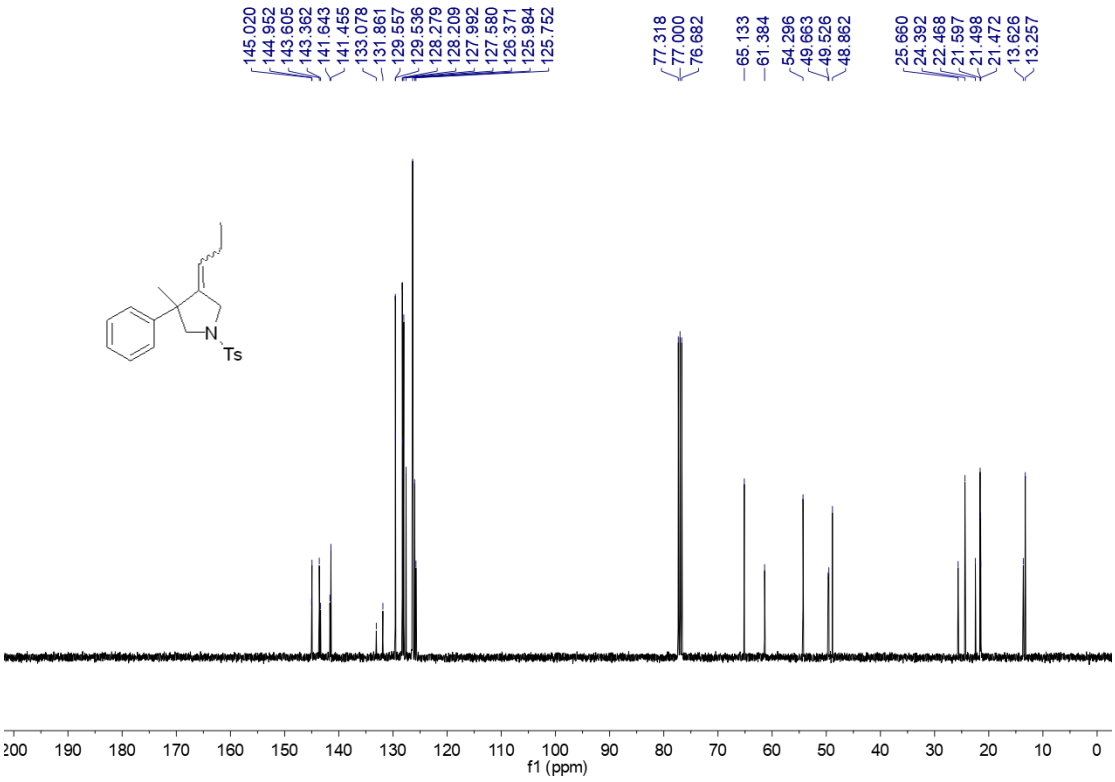


(4p)

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

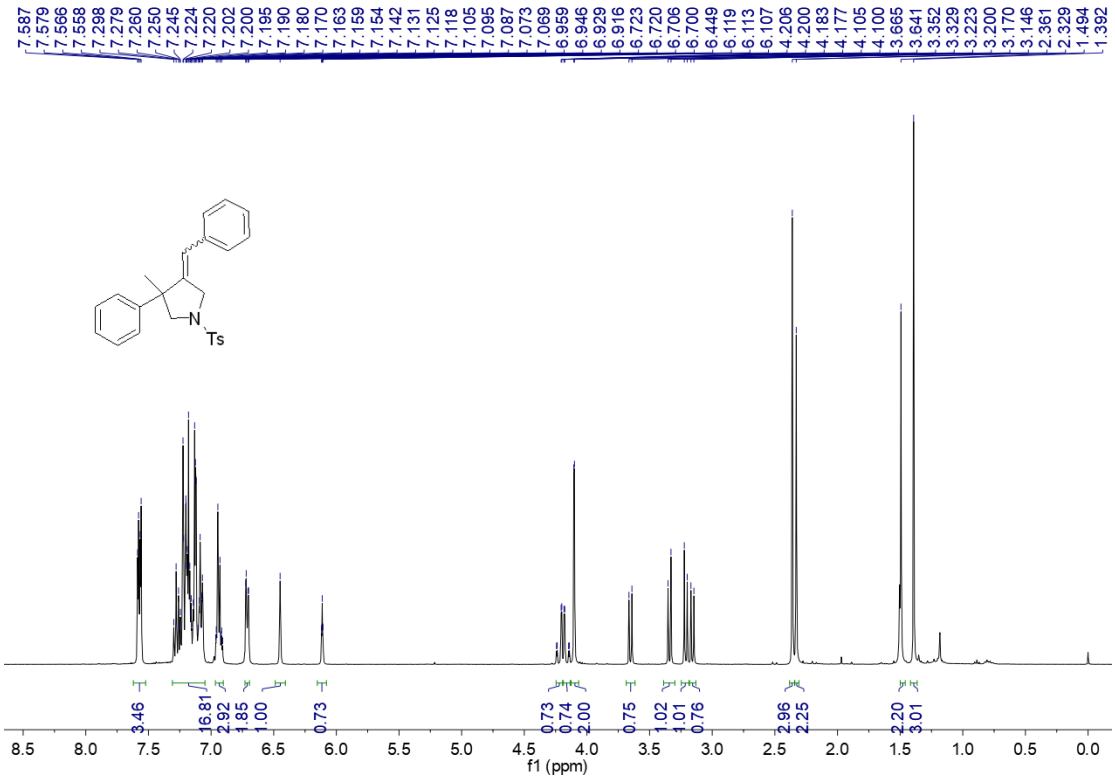


^{13}C NMR ($CDCl_3$, 101 MHz)

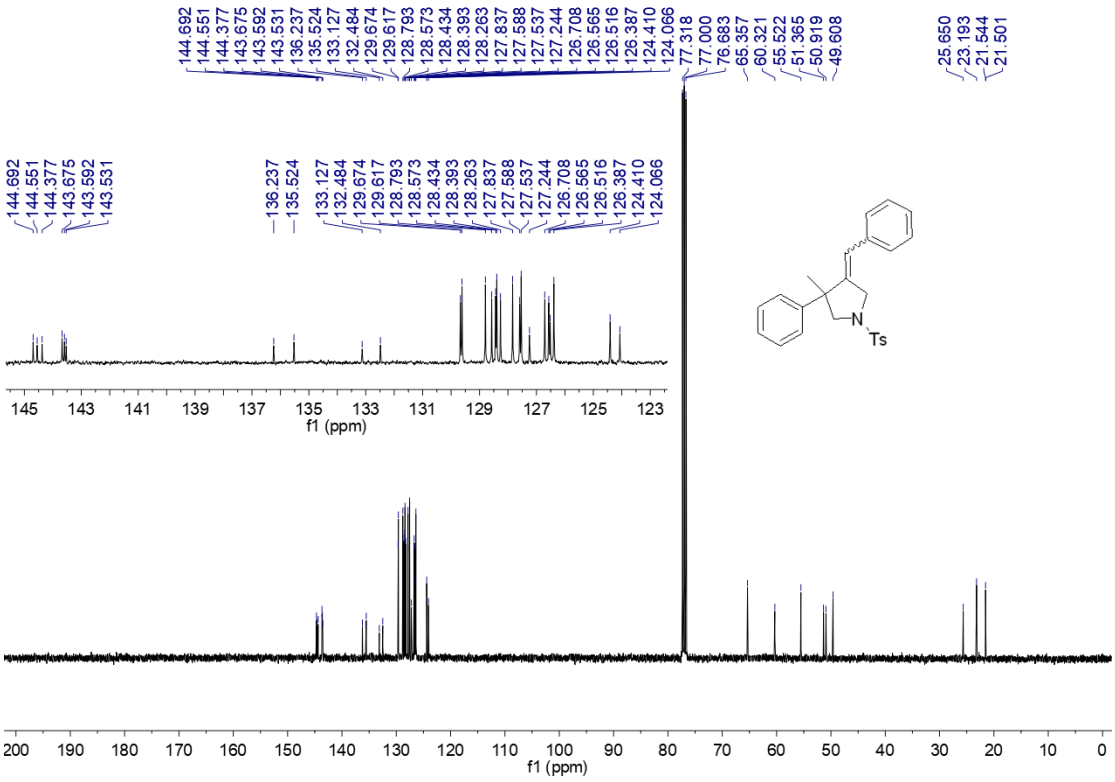


(4q)

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

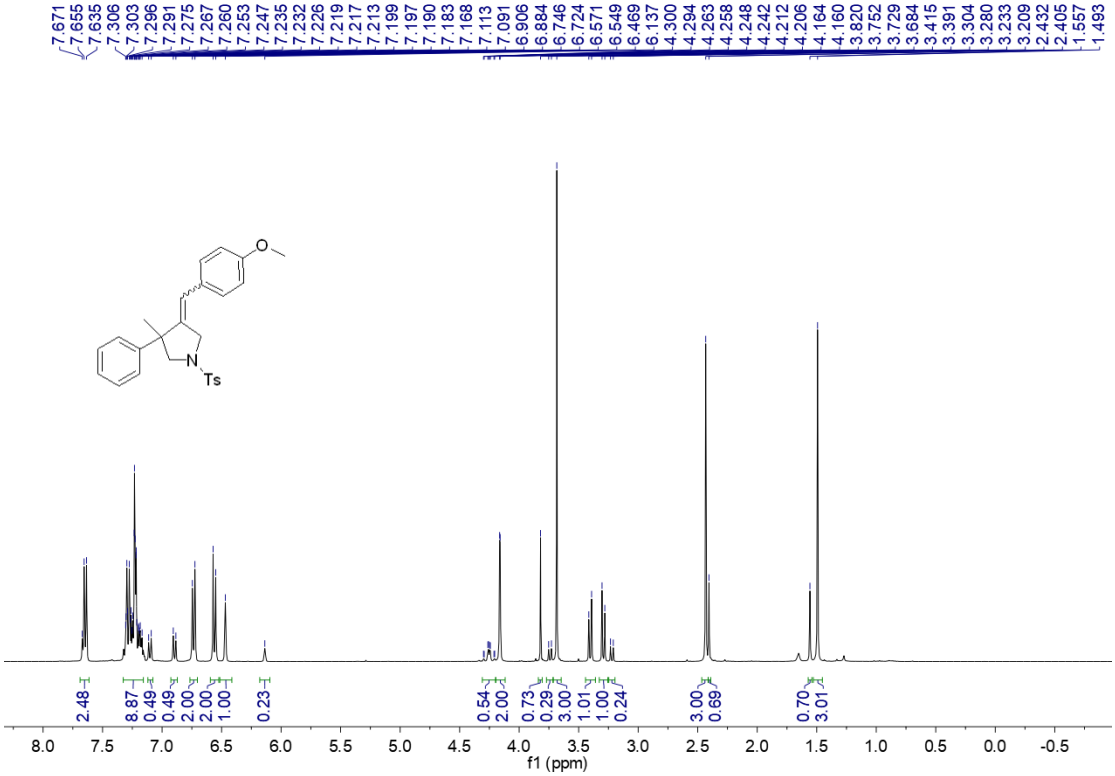


^{13}C NMR ($CDCl_3$, 101 MHz)

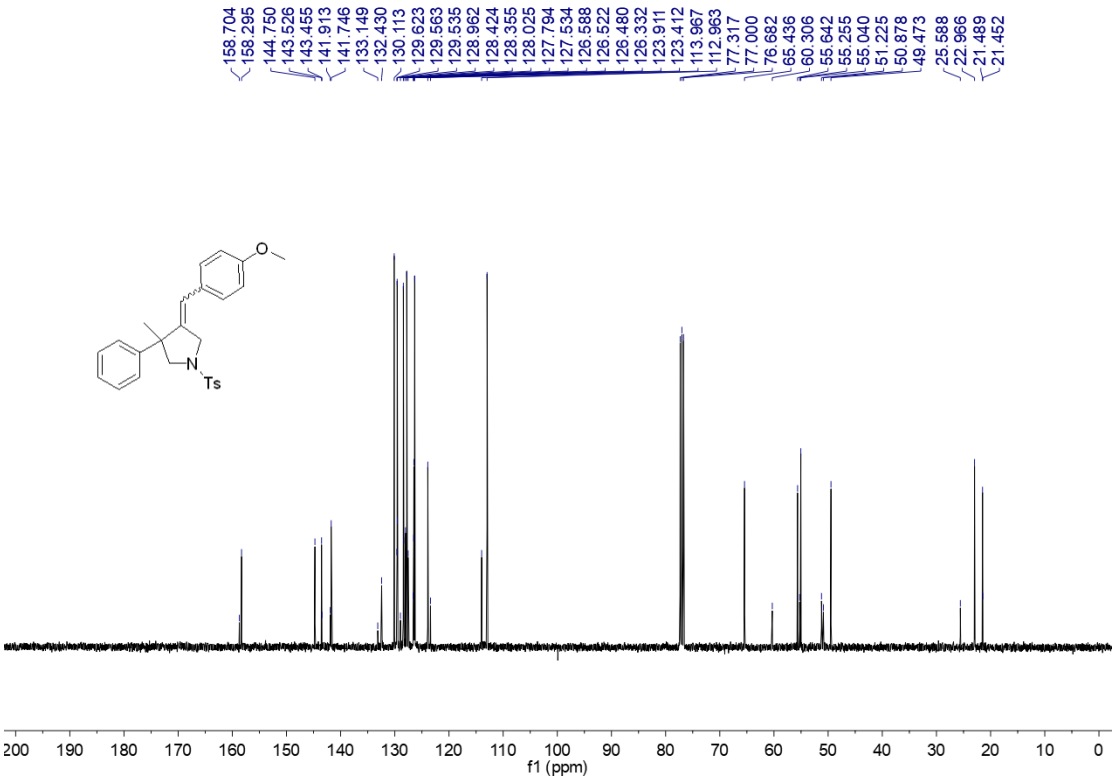


(4r)

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

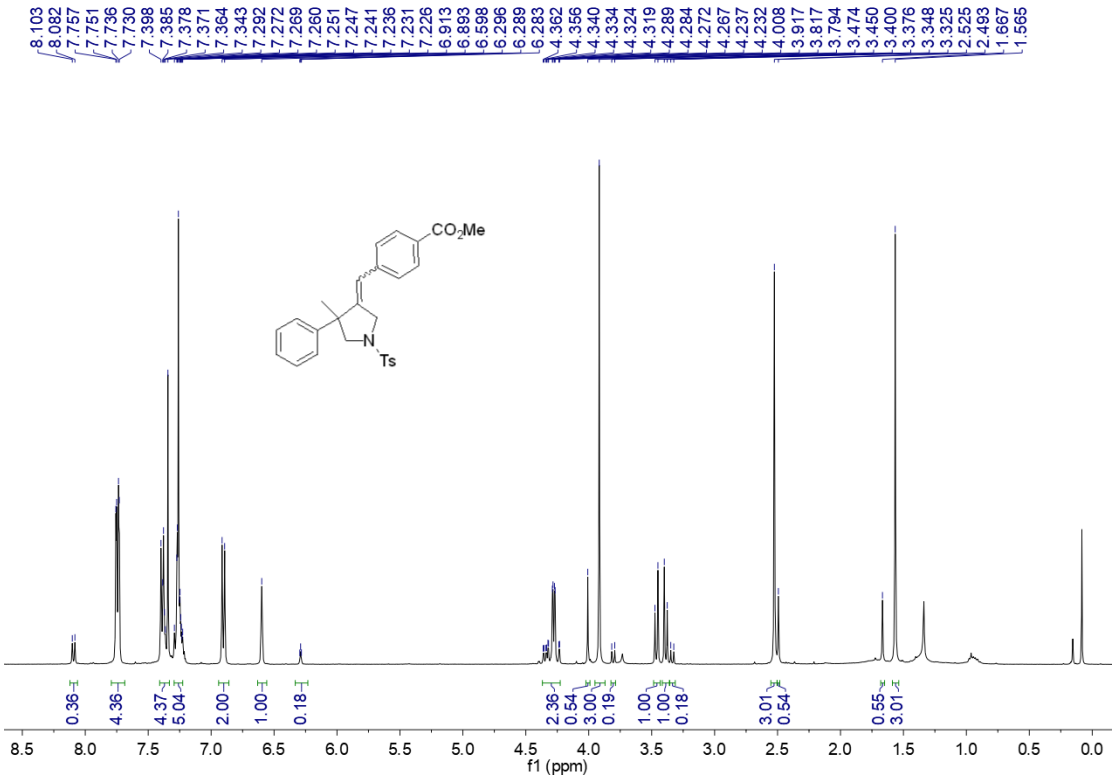


^{13}C NMR ($CDCl_3$, 101 MHz)

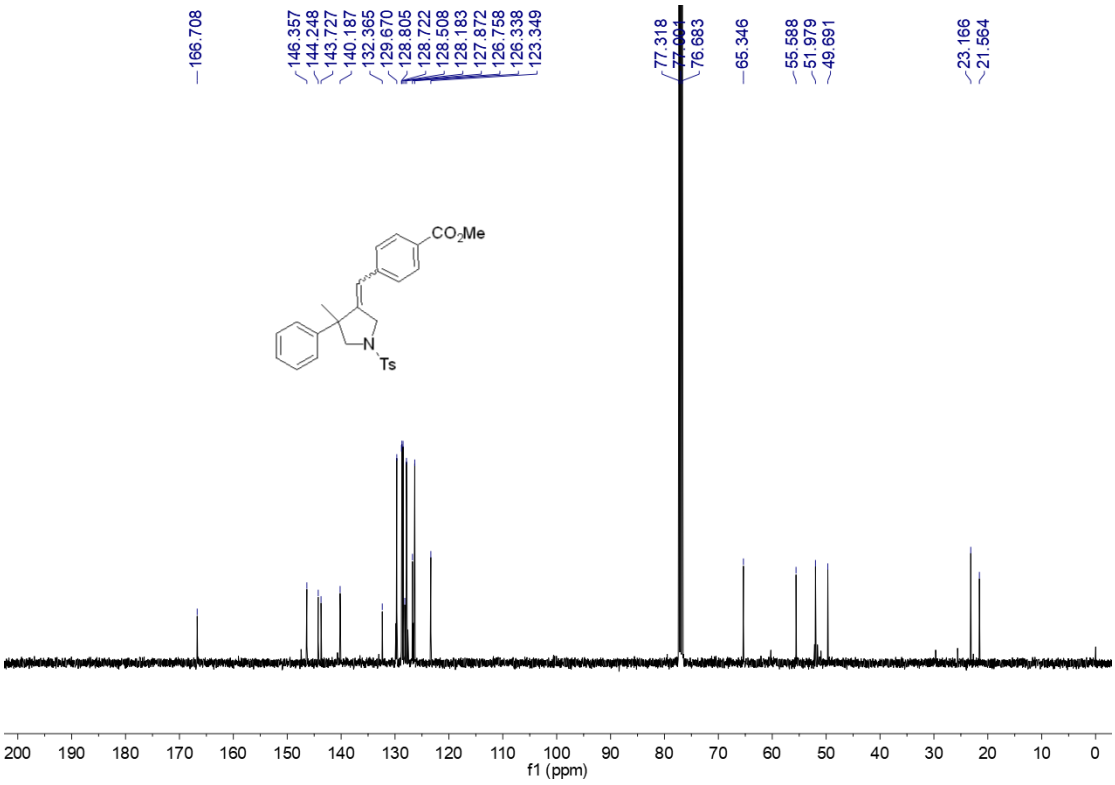


(4s)

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

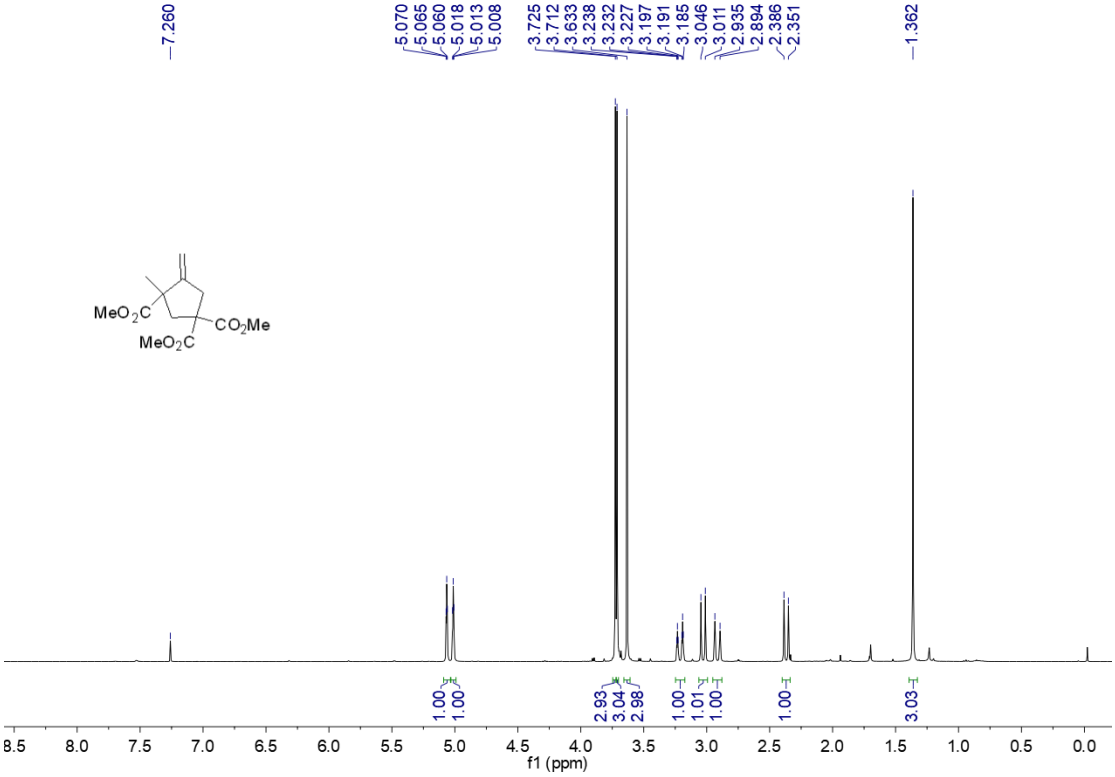


^{13}C NMR ($CDCl_3$, 101 MHz)

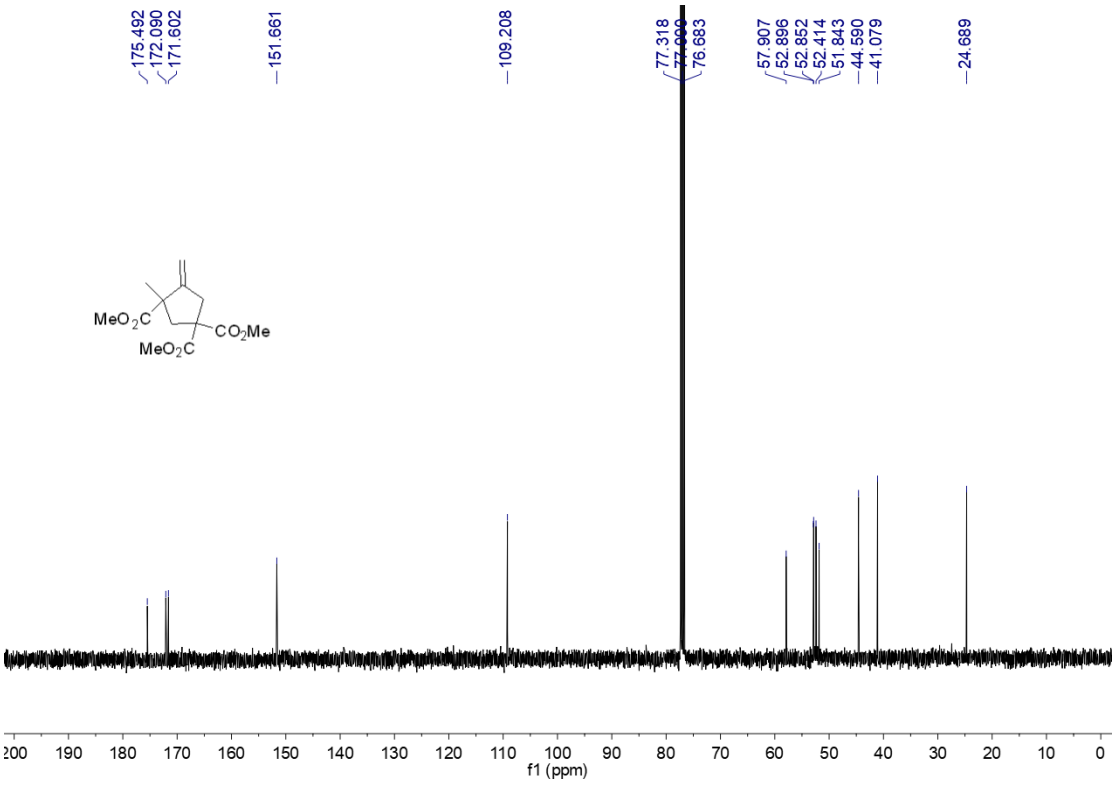


(4t)

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

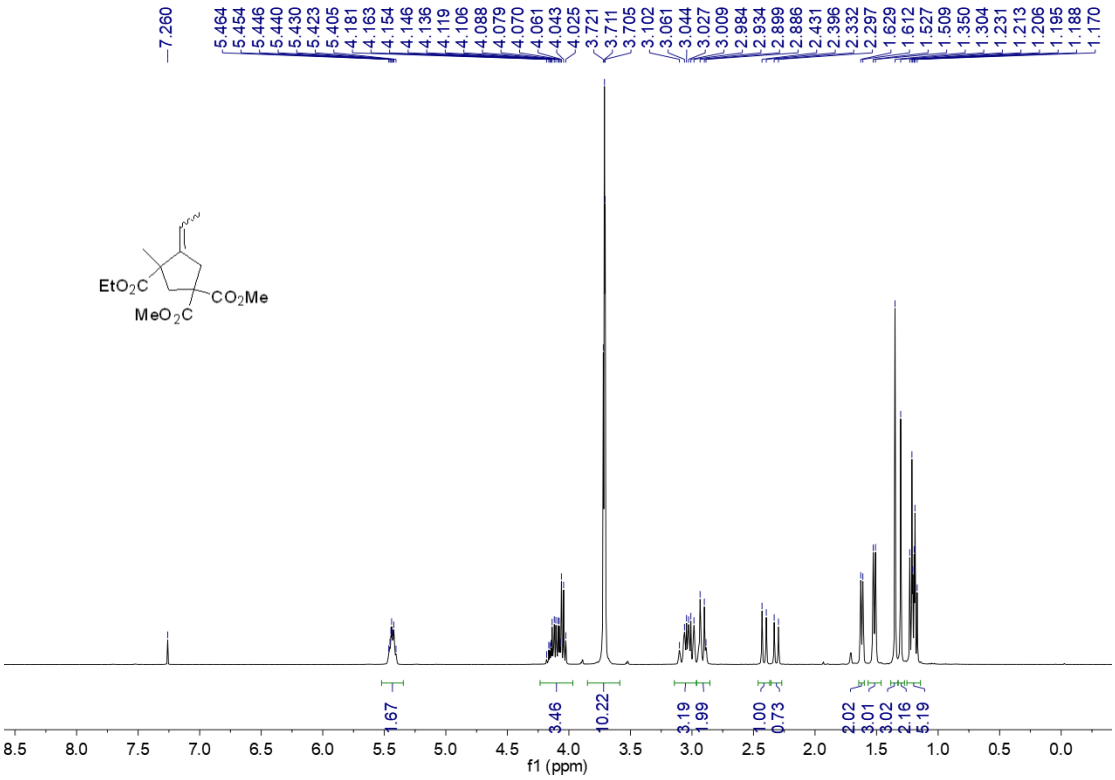


^{13}C NMR ($CDCl_3$, 101 MHz)

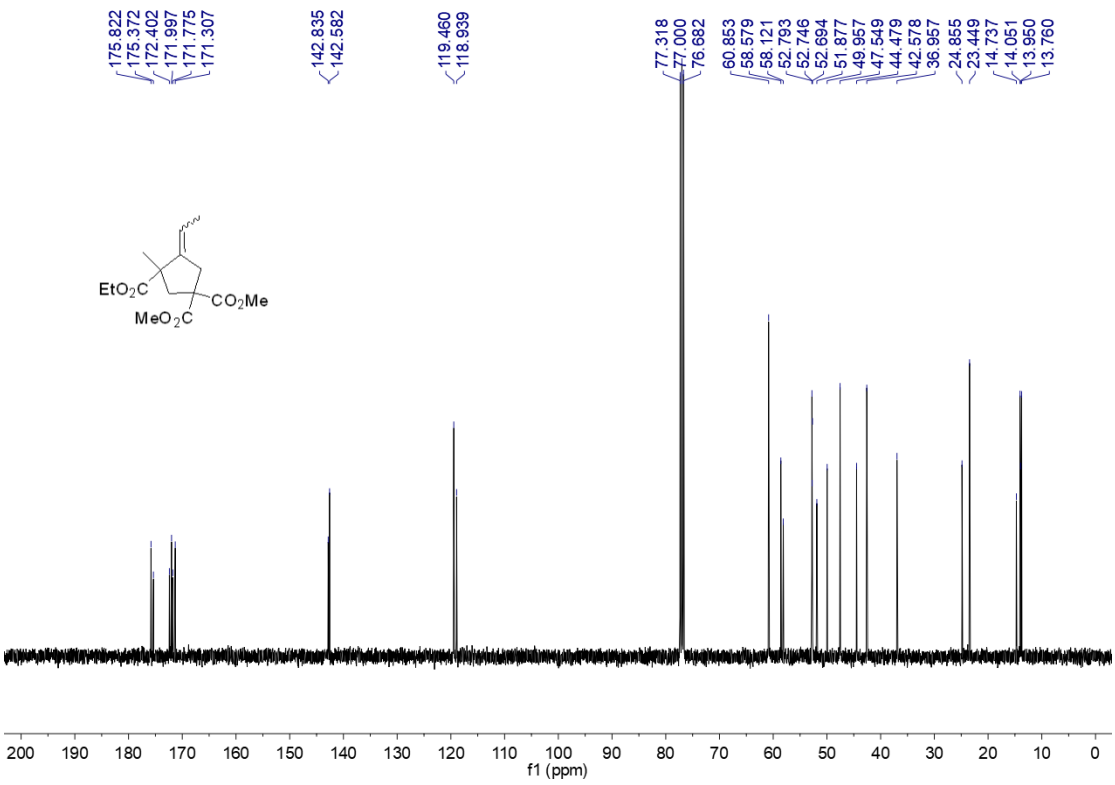


(4u)

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

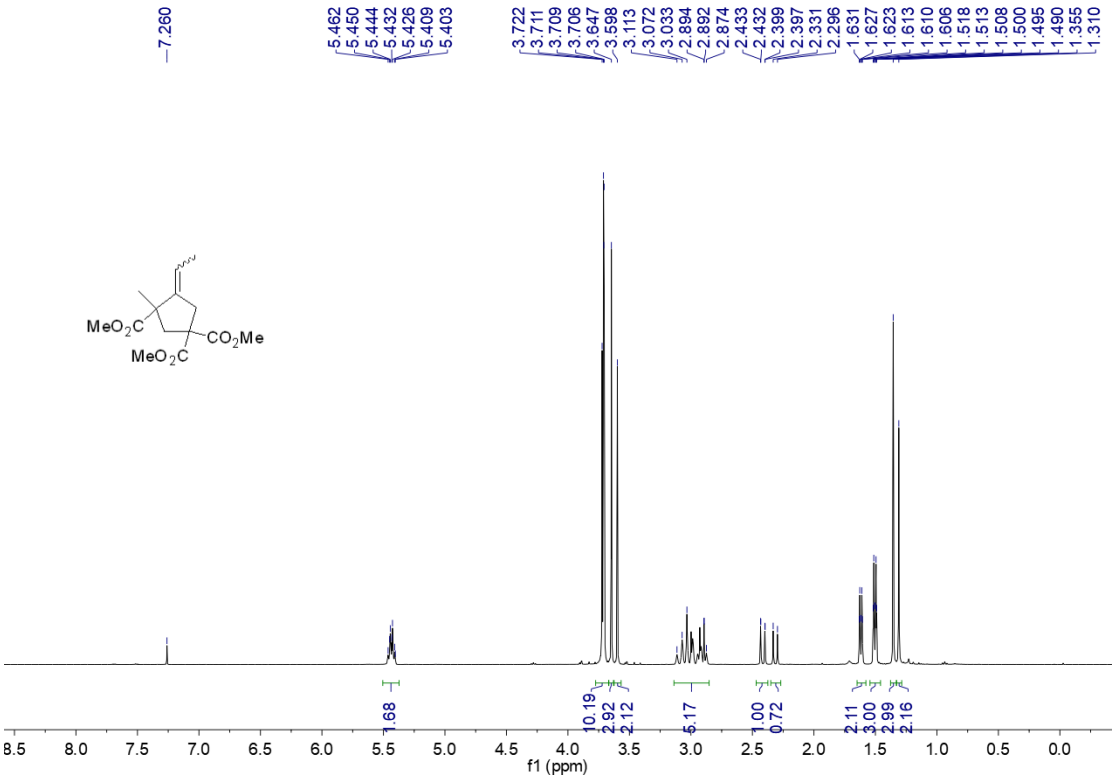


^{13}C NMR ($CDCl_3$, 101 MHz)

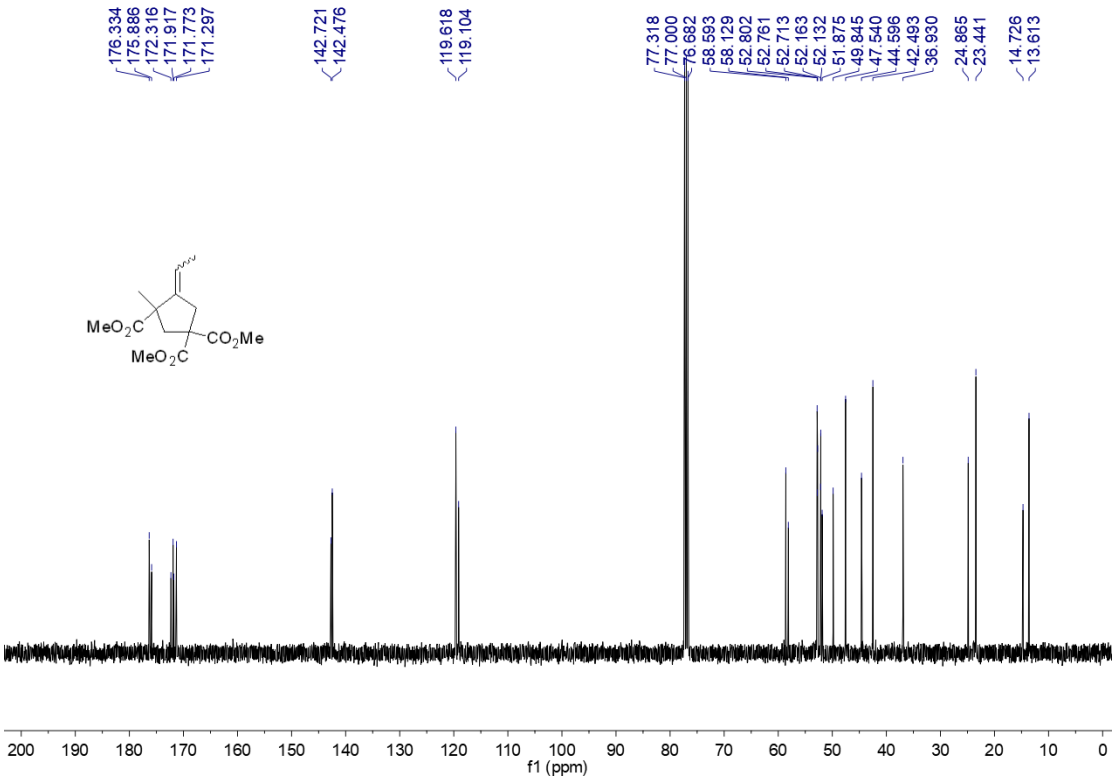


(4v)

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

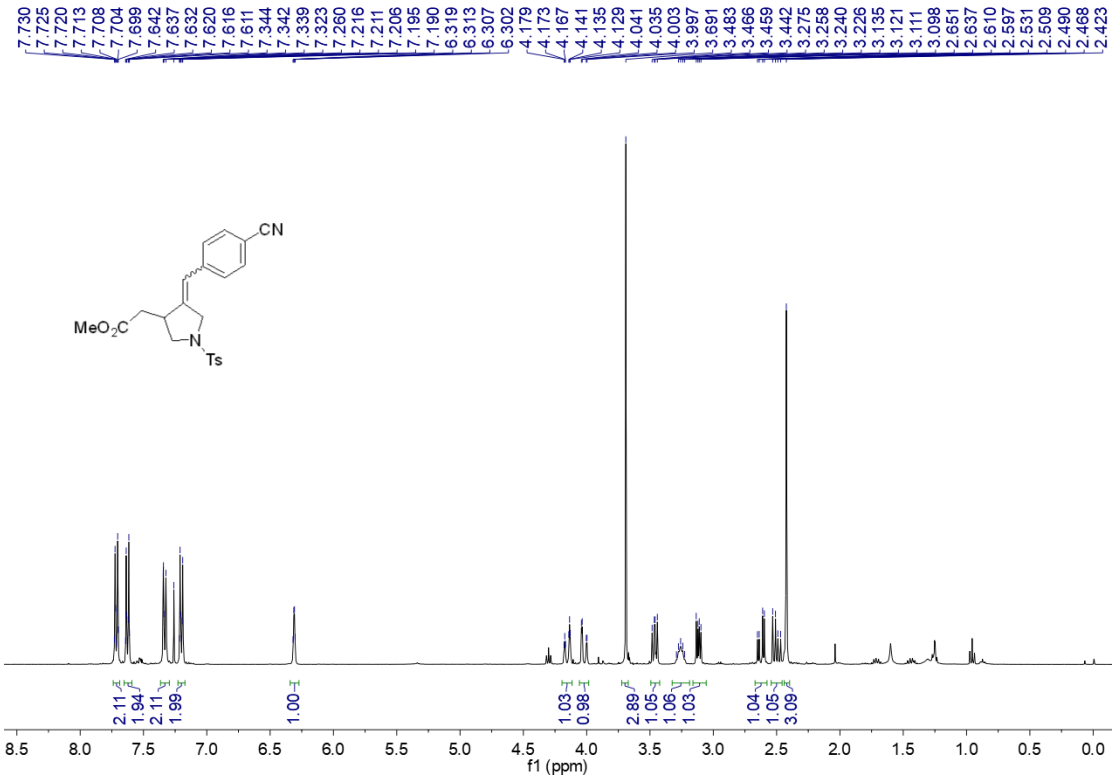


^{13}C NMR ($CDCl_3$, 101 MHz)



(4w)

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



^{13}C NMR ($CDCl_3$, 101 MHz)