Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Photoinduced copper-catalyzed selective three-component 1,2-amino oxygenation of 1,3-dienes

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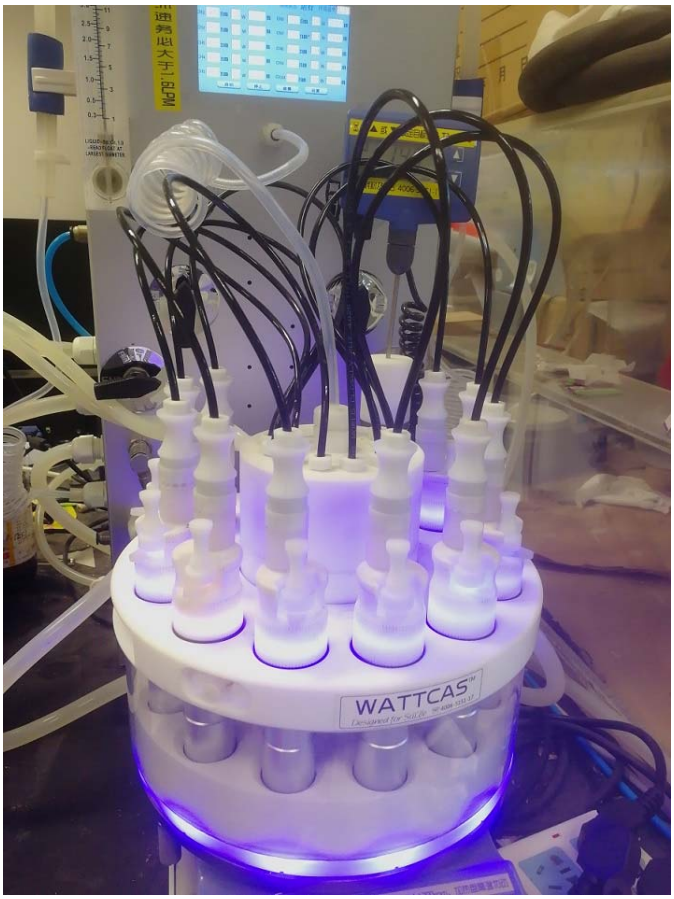
S1 General Information

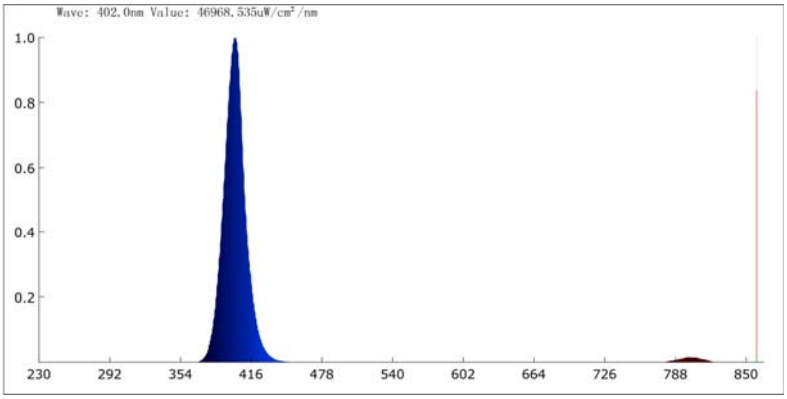
Unless otherwise noted, all reactions of substrates preparation were conducted in flame – dried glassware under a nitrogen atmosphere using anhydrous solvent passed through an activated alumina column (Innovative Technology). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using Huanghai TLC silica gel plates HSG F254 and visualized using UV light, anisaldehyde or potassium permanganate. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP – TEC – 1020L) with 10W LED. HP 8453 spectrometer was used as the light source for the UV-Vis data. The fluorescence emission spectra were collected on an Edinburgh Instruments (FLS1000). Cyclic voltammetry (CV) was taken using a CHI760E potentiostation. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker 400M spectrometer. Chemical shifts in ^{1}H NMR spectra were reported in parts per million (ppm) on the δ scale from an internal standard of residual $CDCl_3$ (7.26 ppm). Data for ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz) and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift in ppm from the central peak of $CDCl_3$ (77.00 ppm). High performance liquid chromatography (HPLC) was carried out with Agress 1100 HPLC gradient system on a D1100 UV spectrophotometric detector (ELITE).

S2 Picture of Reaction Set – Up

The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP – TEC – 1020L).

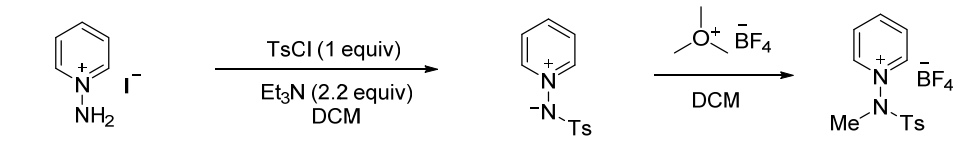


Picture of the photoreactor



Emission spectra of the 10 W blue LED lamp (maximum emission at λ = 402 nm). Wave length: 395 nm-405 nm Quartz glass was used as reaction vessel. Distance between light source and quartz tube was approximately 0.5 cm and no filter was used for the reaction.

S3 Preparation of **3**



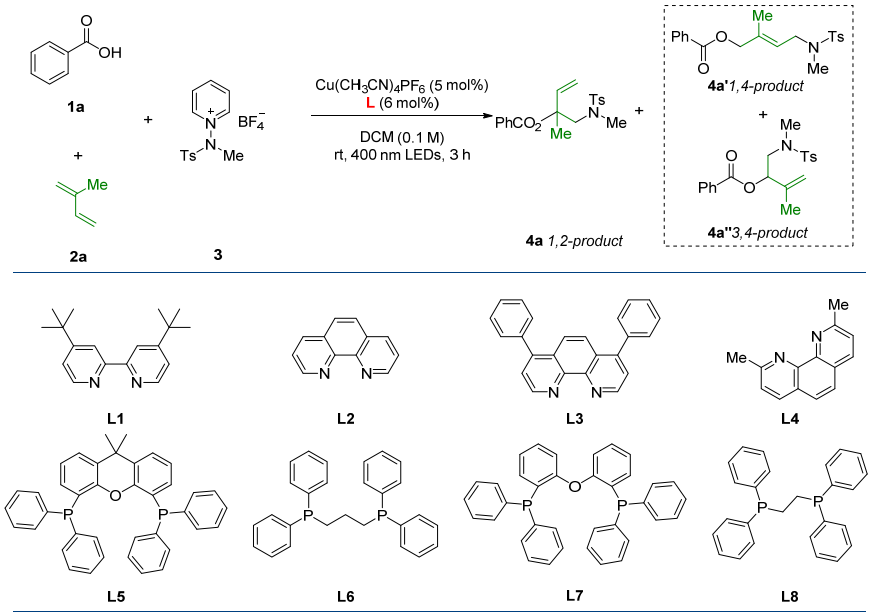
1-aminopyridinium *N*-tosyl 1-aminopyridinium **3**

A round bottom flask equipped with a magnetic stir bar was charged with the raw material 1-aminopyridinium (20.0 mmol, 1.0 equiv.) and tosyl chloride (20.0 mmol, 1.1 equiv.) was added DCM (100 mL) and triethylamine (44.0 mmol, 2.2 equiv) at room temperature. The reaction mixture was stirred at room temperature for overnight. The resulting mixture was extracted with dichloromethane and water for three times, and washed with water. The combined organic layers were dried over magnessium sulfate, filtered and concentrated in vacuum. The resulting mixture was purified by flash column chromatography on silica gel (CH_2Cl_2 : MeOH = 20 : 1) to obtain *N*-tosyl 1-aminopyridinium ylides. Then, to a solution of *N*-tosyl 1-aminopyridinium ylide (10.0 mmol, 1.0 equiv) in dichloromethane (50 mL) were added trimethyloxonium tetrafluoroborate (Meerwein's reagent, 12 mmol, 1.1 equiv) at room temperature. The reaction mixture was stirred at room temperature for 5 h. The resulting mixture was concentrated under reduced pressure. The product was recrystallized with diethylether from CH_2Cl_2 and MeOH (20:1) solution at - 20 ℃. A solid product **3a** was obtained.

N-tosyl 1-aminopyridinium tetrafluoroborate salts (3), ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.27 – 8.95 (m, 3H), 8.26 (dd, J = 7.1, 1.5 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 3.55 (s, 3H), 2.48 (s, 3H). (*J. Am. Chem. Soc.* 2020, 142, 26, 11370–11375)

S4 Optimization of Reaction Conditions

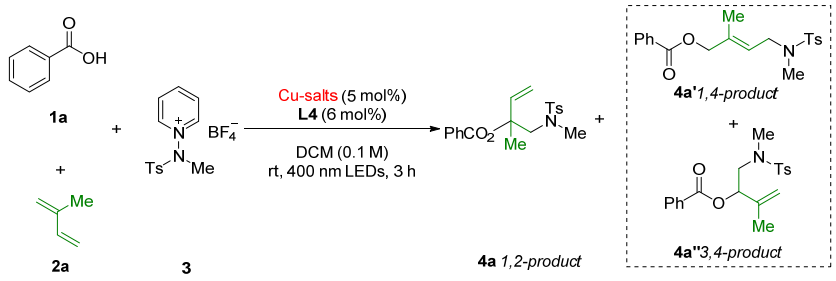
S4.1. The Effect of ligands



Entry [a]	[L]	yield of **4a** (%)[b]	**4a**:**4a'**:**4a''**
1	**L1**	19	10:0:1
2	**L2**	trace	ND
3	**L3**	57	9:1:1
4	**L4**	85	21:1:2
5	**L5**	46	10:0:1
6	**L6**	24	10:0:1
7	**L7**	trace	ND
8	**L8**	trace	ND

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **3** (0.3 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol%), **L** (6 mol%) in DCM (0.1 M) under 400 nm LEDs reaction for 3 h. [b] Yields were determined by ^1H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

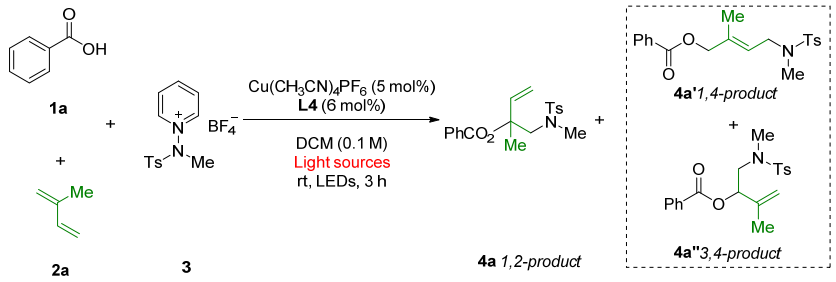
S4.2. The Effect of Copper Salts



Entry [a]	[**Cu**]	Yield of **4a** (%)[b]	**4a**:**4a'**:**4a''**
1	$Cu(OTf)_2$	64	14:1:2
2	CuI	71	15:1:2
3	CuCl	72	15:1:2

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **3** (0.3 mmol), Cu (5 mol%), **L4** (6 mol%) in DCM (0.1 M) under 400 nm LEDs reaction for 3 h. [b] Yields were determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

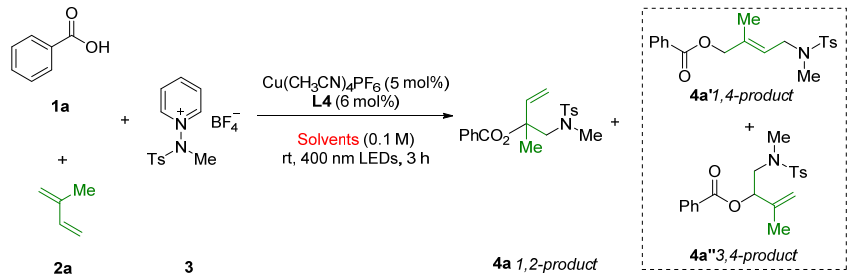
S4.3. The Effect of Light sources



Entry [a]	[**Light source**]	Yield of **4a** (%)[b]	**4a**:**4a'**:**4a''**
1	400-405 nm	85	21:1:2
2	450-455 nm	62	21:1:2

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **3** (0.3 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol%), **L4** (6 mol%) in solvents (0.1 M) under LEDs reaction for 3 h. [b] Yields were determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

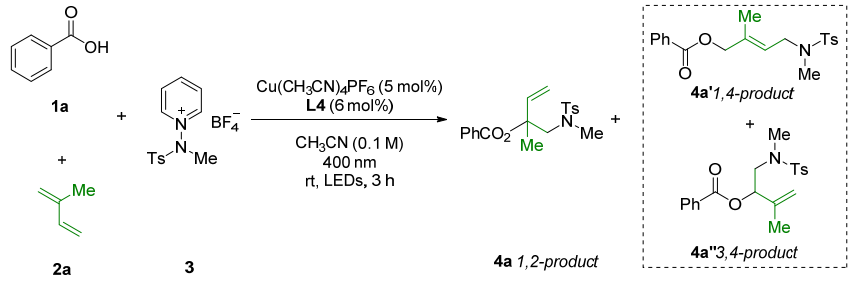
S4.4. The Effect of Solvents



Entry [a]	[**Solvent**]	Yield of **4a** (%)[b]	**4a**:**4a'**:**4a''**
1	THF	63	9:0:1
2	CH_3CN	89	18:0:1
3	DCE	85	20:2:3

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **3** (0.3 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol%), **L4** (6 mol%) in solvents (0.1 M) under 400 nm LEDs reaction for 3 h. [b] Yields were determined by ^1H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

S5. Control Experiments



Entry [a]	[**variation from standard conditions**]	Yield of **4a** (%)[b]	**4a**:**4a′**:**4a″**
1	none	89	18:0:1
2	No ligands	trace	ND
3	No $Cu(CH_3CN)_4PF_6$	0	-
4	No Light	0	-
5	**3** (1.3 equiv instead of 1.5 equiv)	89(87)[c]	18:0:1
6	**3** (1.0 equiv instead of 1.5 equiv)	75	18:0:1

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **3** (0.3 mmol), $Cu(CH_3CN)_4PF_6$ (5 mol%), **L4** (6 mol%) in solvents (0.1 M) under 400 nm LEDs reaction for 3 h. [b] Yields were determined by ^1H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.[c] Isolated yield.

S6 The Mechanism Studies

6.1 UV-Vis Absorption Spectra

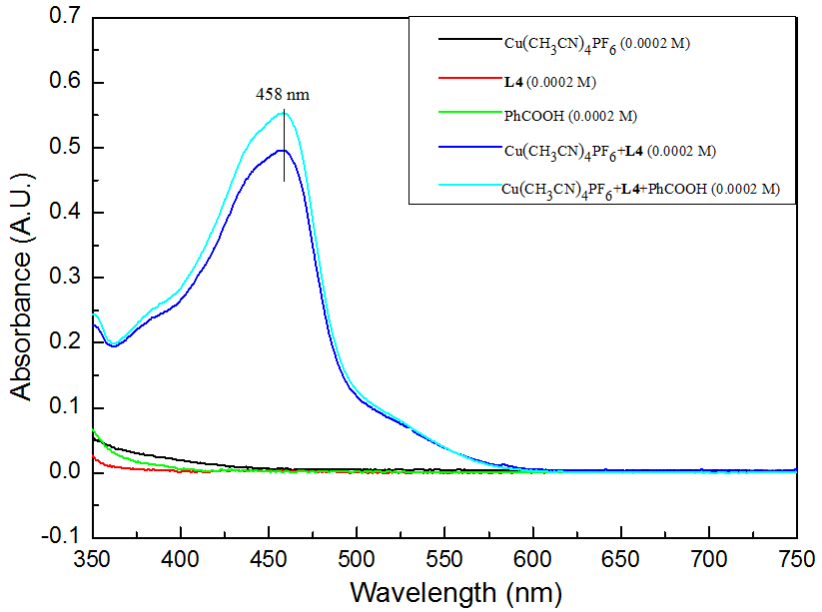


Figure S1 UV-vis spectrum of the $Cu(CH_3CN)_4PF_6$ in DCM, **L4** in DCM, PhCOOH in DCM, $Cu(CH_3CN)_4PF_6$ + **L4** in DCM and $Cu(CH_3CN)_4PF_6$ + **L4**+PhCOOH in DCM**,** the peak at 458 nm.

6.2 Luminescence Experiments

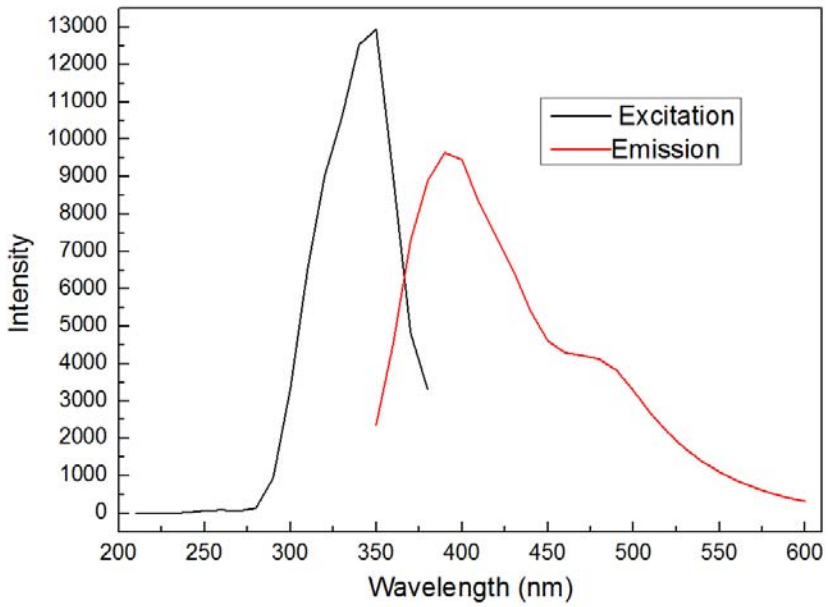


Figure S2 Excitation and emission wavelengths of $Cu(CH_3CN)_4PF_6$/**L4**

Fluorescence spectra was collected on Edinburgh Instruments (FLS1000) for all experiments. All solutions were excited at 349 nm and the emission intensity was collected at 355 nm, slit is 3 nm. The concentration of $Cu(CH_3CN)_4PF_6$/**L4** was 0.0002 M. The results revealed that the maximum excitation and emission peaks of $Cu(CH_3CN)_4PF_6$/**L4** complex were found at 349 nm and 392 nm, and the cross peak was found at 366 nm.

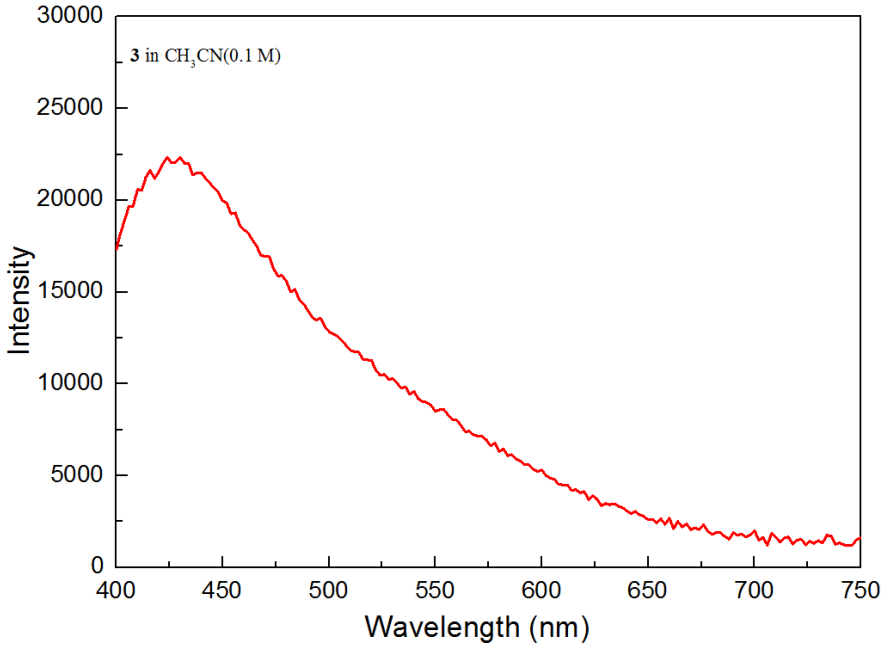


Figure S3 Fluorescence spectra of **3**

Fluorescence spectra was collected on Edinburgh Instruments (FLS1000) for all experiments. All solutions were excited at 360 nm and the emission intensity was collected at 400 nm, slit is 4 nm. The

concentration of **3** was 0.1 M. The results suggest that **3** had obvious fluorescence at the 430 nm emission peak.

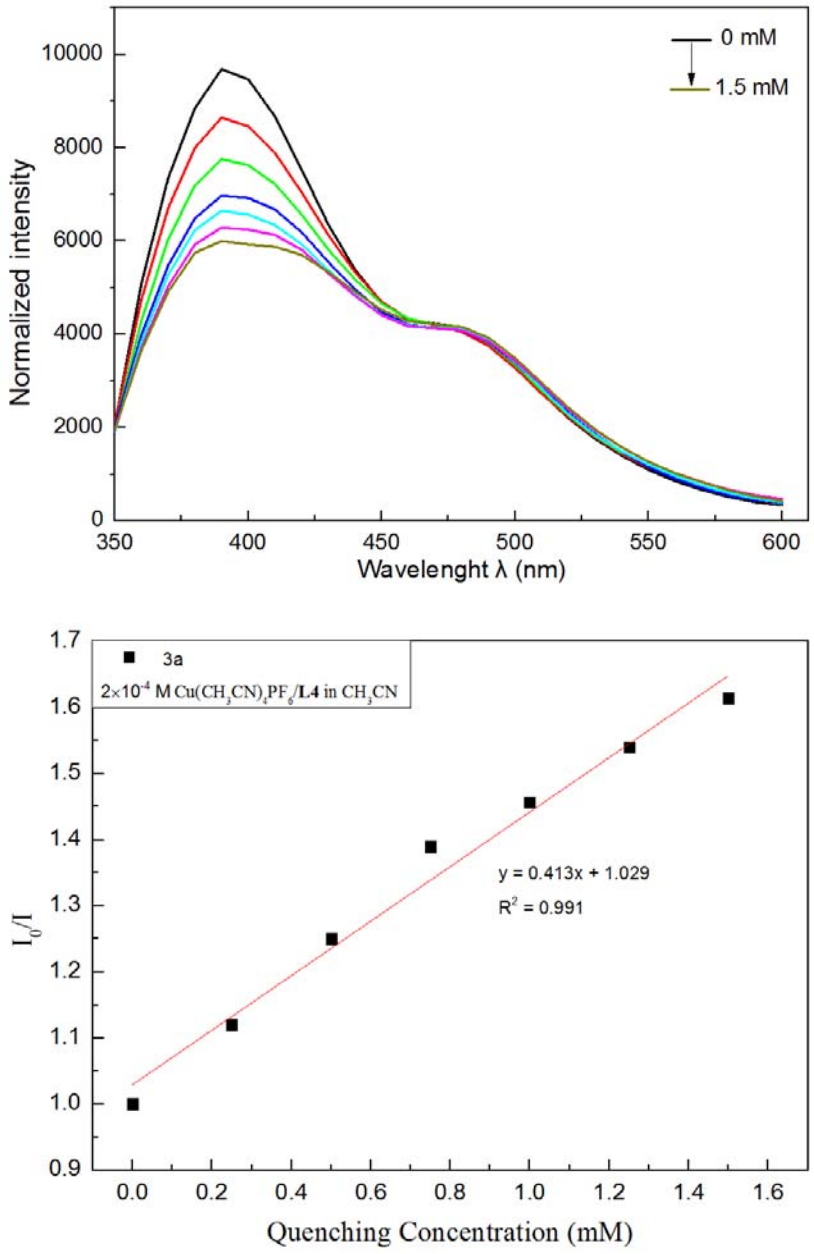


Figure S4 Stern−volmer quenching studies of $Cu(CH_3CN)_4PF_6$/**L4** by **3**

All solutions were excited at 349 nm and the emission intensity was collected at 392 nm, slit is 3 nm. The concentration of $Cu(CH_3CN)_4PF_6$/**L4** was 0.0002 M. The significant decrease of [Cu]/**L4** luminescence could be observed in the presence of substrate **3**.

6.3 Lifetime Chromatogram of $Cu(CH_3CN)_4PF_6$/L4

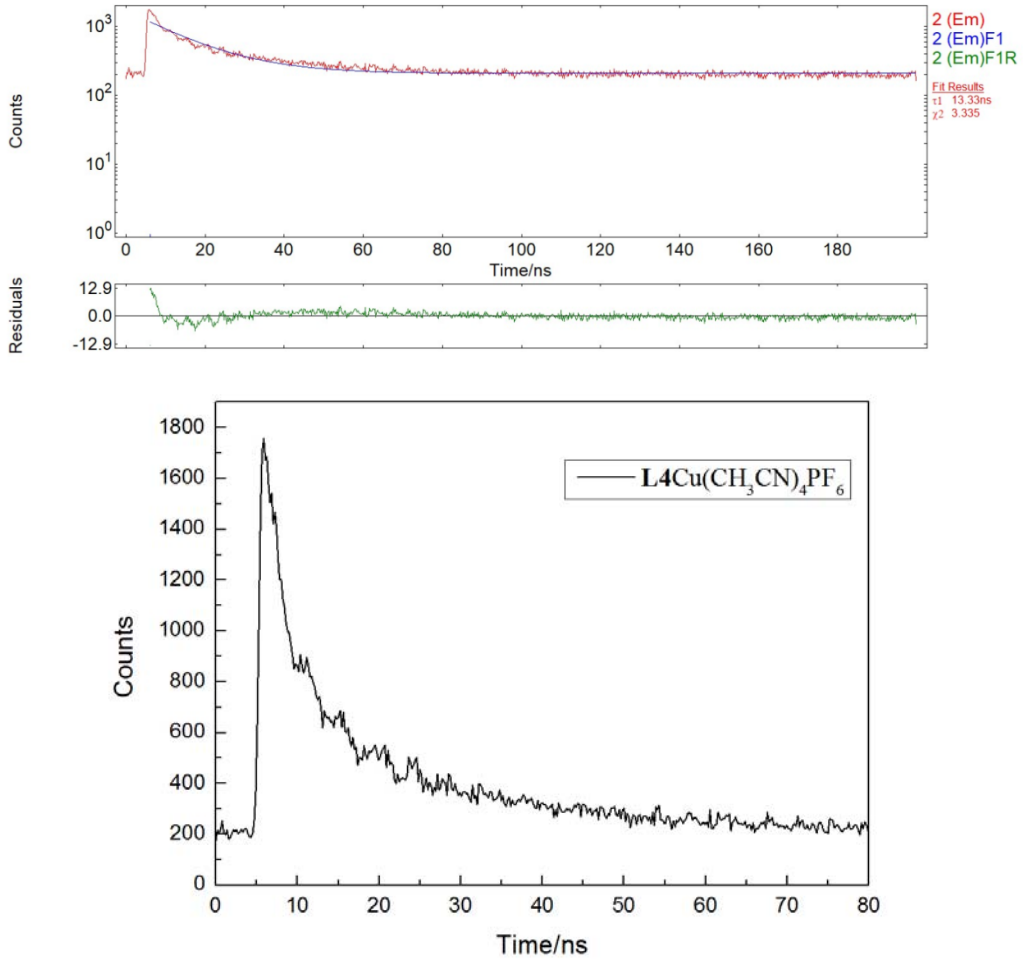


Figure S5 Lifetime chromatogram of $Cu(CH_3CN)_4PF_6$/**L4** excited at 405 nm EPL, 0.0002 M solution in CH_3CN (recorded on an Edinburgh Instrument FLS1000).

Lifetime: $\tau = 13.33$ ns.

6.4 Cyclic Voltammetry of $Cu(CH_3CN)_4PF_6$/L4

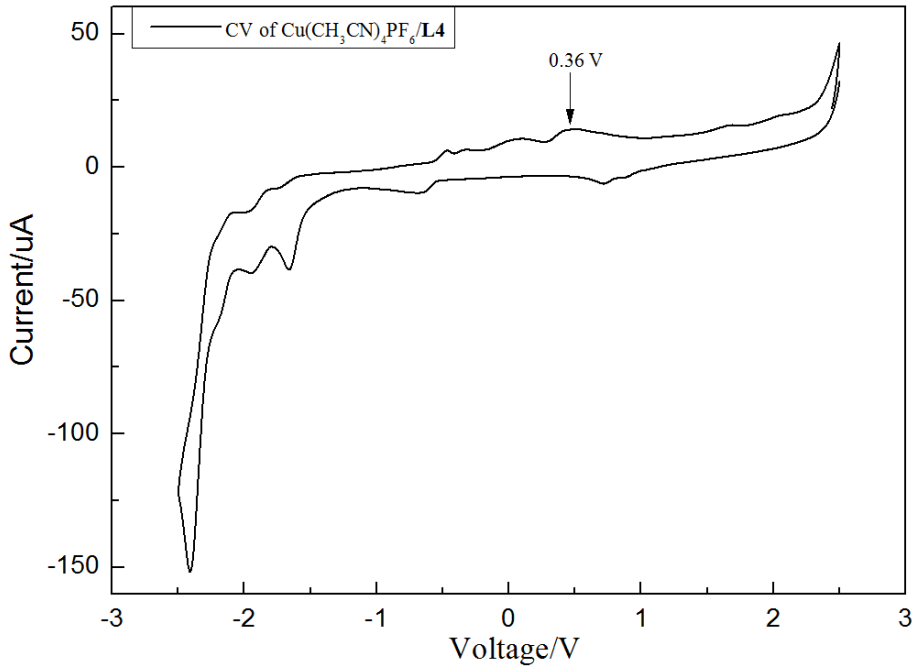
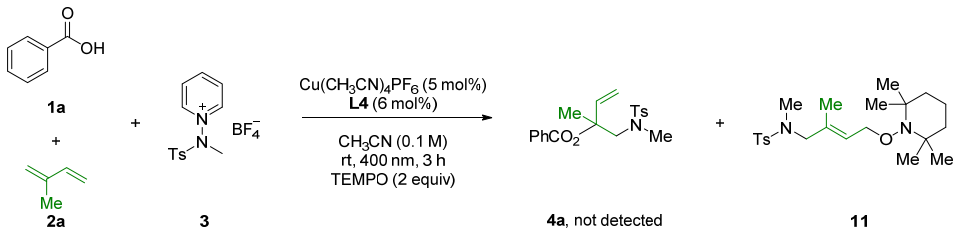


Figure S6 Cyclic voltammograms of $Cu(CH_3CN)_4PF_6$/**L4** (generated in situ by stirring a 1:1 mixture of $Cu(CH_3CN)_4PF_6$ and ligand **L4**) in CH_3CN.

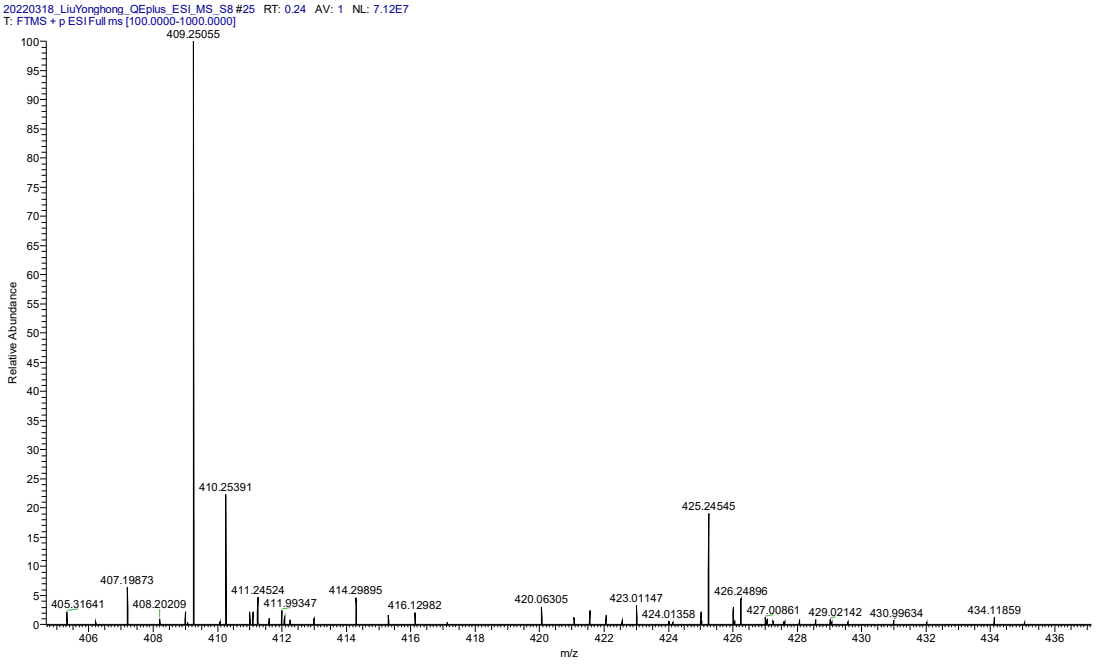
Cyclic voltammetry (CV) was taken using a CHI760E potentiostation. CV measurement was carried out in 0.1 M of nBu_4NPF_6/CH_3CN at a scan rate of 100 mV/s with the protection of Ar. The working electrode was a glassy carbon, the counter electrode was a Pt wire, and the reference electrode was Ag/AgCl. The results were as follow: $Cu(CH_3CN)_4PF_6$/**L4** ($E_{p/2}$ = 0.36 V *vs* SCE in CH_3CN).

6.5 Radical Trapping Experiment

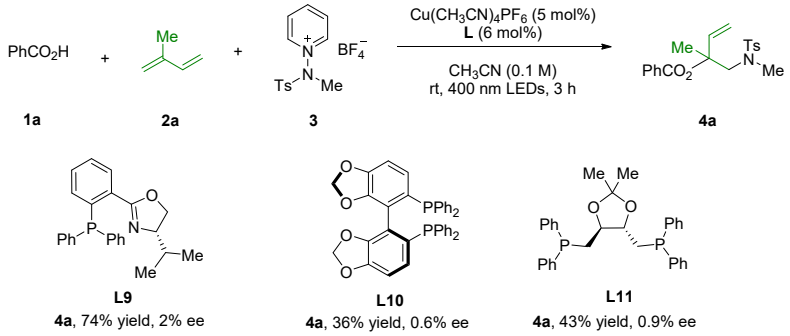


In a flame-dried 10 mL reaction tube equipped with a magnetic stirrer bar was charged sequentially with $Cu(CH_3CN)_4PF_6$ (0.05 equiv), **L4** (0.06 equiv), **1a** (0.2 mmol, 1.0 equiv). The Schlenk flask was transferred to an argon-filled glovebox and followed by the addition of dry CH_3CN (0.1 M). Then the mixture was stirred at room temperature for 30 min. To the resulting mixture were added **2a** (0.6 mmol, 3.0 equiv), **3** (0.26 mmol, 1.3 equiv) and TEMPO (0.4 mmol, 2.0 equiv). Next, the resulting mixture was removed out the glovebox. At last, the reaction mixture was stirred at room temperature with irradiation of 10 W 400 nm LED for 3 h. (the reaction solution was detected by ^1H NMR and HRMS analysis and the **4a** was not found, **11** was detected by HRMS)

HRMS of **11**: Calc'd for $C_{22}H_{37}N_2O_3S$, $[M+H]^+$ 409.2519 (100.0%), 410.2553 (23.8%), 411.2477 (4.5%); Found 409.2506, 410.2539, 411.2452.

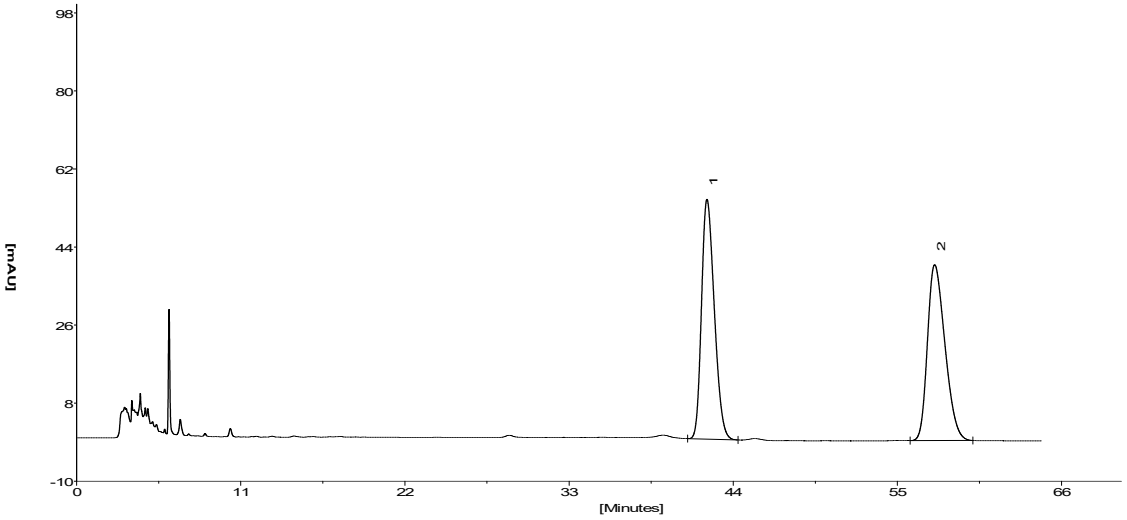


S7 Photoinduced copper-catalyzed asymmetric 1,2-amino oxygenation of 1,3-dienes



In a flame-dried 10 mL reaction tube equipped with a magnetic stirrer bar was charged sequentially with $Cu(CH_3CN)_4PF_6$ (0.05 equiv), **L** (0.06 equiv). The Schlenk flask was transferred to an argon-filled glovebox and followed by the addition of dry CH_3CN (2 mL). Then the mixture was stirred at room temperature for 30 min. To the resulting mixture were added **1** (0.2 mmol, 1.0 equiv), **2** (0.6 mmol, 3.0 equiv) and **3** (0.26 mmol, 1.3 equiv). Next, the resulting mixture was removed out the glovebox. At last, the reaction mixture was stirred at room temperature with irradiation of 10 W 400 nm LED for 3 h. After completion of the reaction, the solvent was evaporated in vacuo and the crude material was purified by flash column chromatography to furnish the desired product.

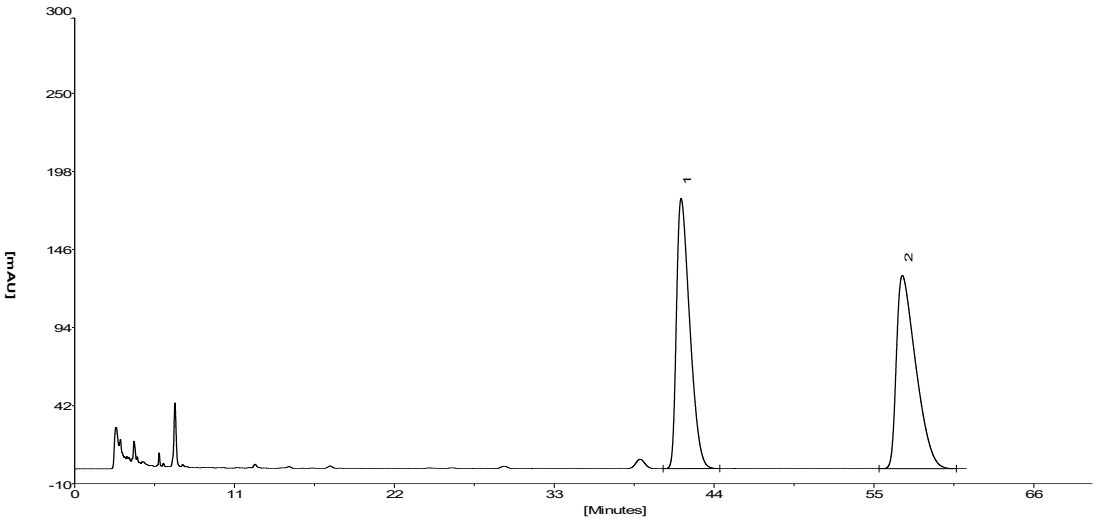
Racemic (**4a**)



	Retention time (min)	Height (mV)	Area (mV.sec)
1	42.23792	55.34	3294.85
2	57.49917	40.55	3299.59

HPLC analysis (Chiralpak AD-H column, n-hexane and i-PrOH, 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C), t_R (major) = 42.24 min, t_R (minor) = 57.50 min

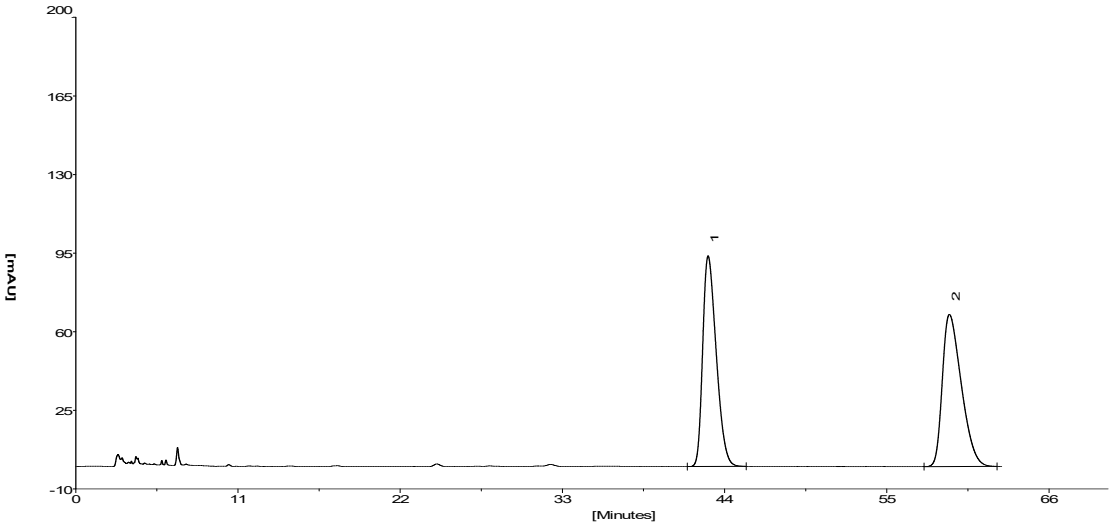
L9



	Retention time (min)	Height (mV)	Area (mV.sec)
1	41.73083	179.94	11410.09
2	56.95417	128.73	11887.60

HPLC analysis (Chiralpak AD-H column, n-hexane and i-PrOH, 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ^{o}C), t_R (major) = 41.73 min, t_R (minor) = 56.95 min

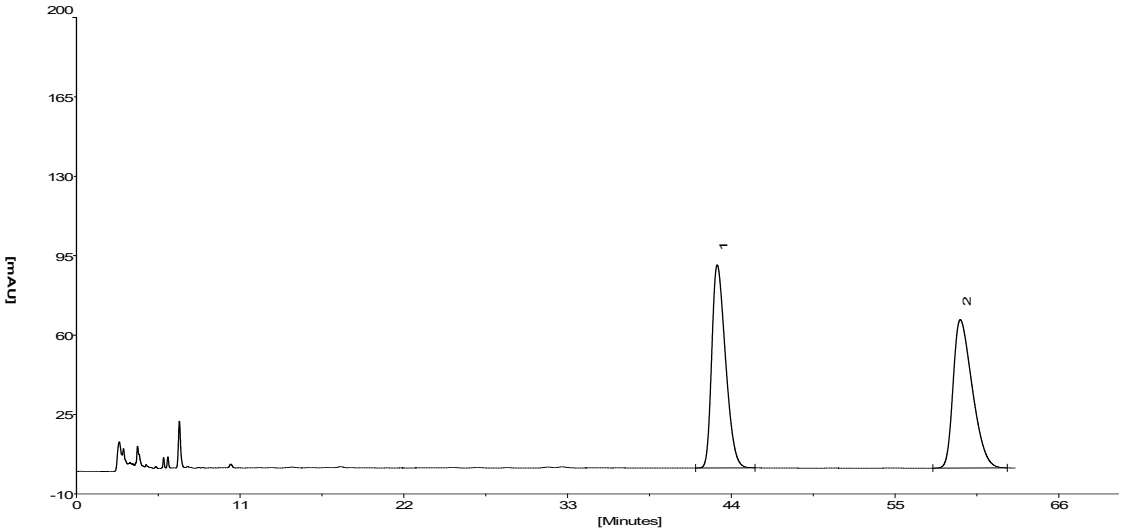
L10



	Retention time (min)	Height (mV)	Area (mV.sec)
1	42.88333	93.75	5969.25
2	59.24833	67.73	6045.58

HPLC analysis (Chiralpak AD-H column, n-hexane and i-PrOH, 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ^{o}C), t_R (major) = 41.73 min, t_R (minor) = 56.95 min

L11

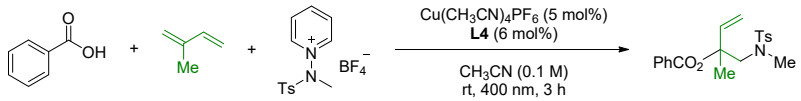


	Retention time (min)	Height (mV)	Area (mV.sec)
1	43.05167	89.52	5731.38
2	59.38083	65.39	5835.76

HPLC analysis (Chiralpak AD-H column, n-hexane and i-PrOH, 98:2 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ^{o}C), t_R (major) = 41.73 min, t_R (minor) = 56.95 min

S8 Synthetic Application of the Reaction

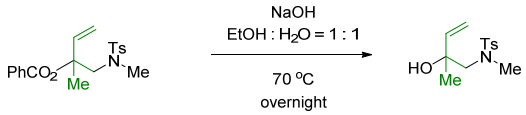
S8.1 Gram-Scale Reaction



1a **2a** **3** **4a**, 88% (1.31 g)

In a flame-dried 25 mL reaction tube equipped with a magnetic stirrer bar was charged sequentially with $Cu(CH_3CN)_4PF_6$ (0.05 equiv), **L4** (0.06 equiv), **1a** (3.0 mmol, 1.0 equiv). The Schlenk flask was transferred to an argon-filled glovebox and followed by the addition of dry CH_3CN (15 mL). Then the mixture was stirred at room temperature for 30 min. To the resulting mixture were added **2a** (9.0 mmol, 3.0 equiv) and **3** (3.9 mmol, 1.3 equiv). Next, the resulting mixture was removed out the glovebox. At last, the reaction mixture was stirred at room temperature with irradiation of 10 W 400 nm LED for 3 h. After completion of the reaction, the solvent was evaporated in vacuo and the crude material was purified by flash column chromatography to furnish the desired product **4a** (88%, 1.31 g).

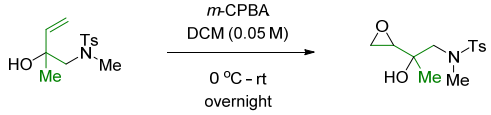
S8.2 Reduction of 4a



4a **9**, 98%

To a solution of **4a** (0.5 mmol, 1.0 equiv) in EtOH (5 mL) was added NaOH (1.5 mmol, 3.0 equiv) in H_2O (5 mL) and the reaction mixture was stirred for overnight at 70 °C. After completion of the reaction (TLC), the reaction was cooled to room temperature and DCM (5 mL) was aedded. The layers were separated and the aqueous layer extracted with DCM (50 mL x 3). The combined organic layers were washed with brine (20 mL), dried with Na_2SO_4, and concentrated in *vacuo* to yield the crude material. The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 6:1) to provide the *β*-amino alcohol compound **9** as a colorless oil in 98% yield (132 mg)**.** Rf = 0.33 (PE:EA = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.91 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.36 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.14 (dd, *J* = 10.8, 1.3 Hz, 1H), 3.14 (d, *J* = 14.4 Hz, 1H), 2.86 (d, *J* = 14.4 Hz, 1H), 2.84 (s, 3H), 2.54 (s, 1H), 2.42 (s, 3H), 1.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.57, 142.59, 134.17, 129.71, 127.40, 113.79, 73.32, 59.76, 38.44, 25.76, 21.46. **HRMS**: Calc'd for $C_{13}H_{19}NNaO_3S$, $[M+Na]^+$ 292.0983; found 292.0965.

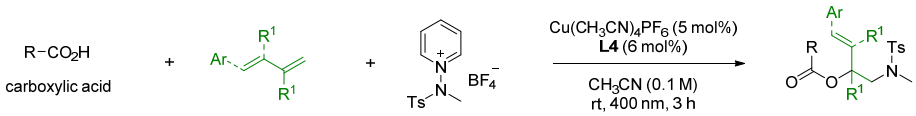
S8.3 Epoxidation of 9



9 **10**, 93% dr = 1:1

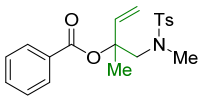
A solution of **9** (0.5 mmol, 1.0 equiv) in DCM (10 mL) was cooled by an ice bath and *m*-CPBA (2.0 mmol, 4 equiv) was added portion wise. The reaction mixture was allowed to warm to r.t. slowly and stirred vigorously overnight at r.t., then the reaction was quenched with saturated $Na_2S_2O_3$ solution and extracted with DCM. The concentrated organic layer was dried over anhydrous Na_2SO_4. The organic layer was then concentrated under reduced pressure and the crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the **10** as a white soild in 93% yield (133 mg). Rf = 0.2 and 0.21 (PE:EA = 2:1).. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (dd,*J* = 8.2, 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.17 (d, *J* = 12 Hz, 1H), 3.10 – 3.00 (m, 2H), 2.87 (s, 3H), 2.79 – 2.71 (m, 1H), 2.41 (s, 3H), 2.35 (d, *J* = 16.2 Hz, 1H), 1.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ143.56, 134.28, 129.71, 127.42, 70.78, 58.68, 56.16, 44.46, 38.28, 24.22, 21.44. (Another Diastereomeric, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (dd,*J* = 8.2, 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.16 (d, *J* = 16 Hz, 1H), 3.10 – 3.00 (m, 2H), 2.85 (s, 3H), 2.79 – 2.71 (m, 1H), 2.41 (s, 3H), 2.35 (d, *J* = 16.2 Hz, 1H), 1.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.52, 134.12, 129.71, 127.25, 70.14, 56.73, 56.07, 43.14, 37.91, 21.57, 21.44.) **HRMS**: Calc'd for $C_{13}H_{20}NO_4S$, $[M+H]^+$ 286.1108; found 286.1104.

S9 General Procedure and Characterization Data



1 **2** **3** **4 - 8**

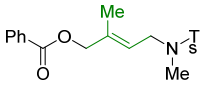
In a flame-dried 10 mL reaction tube equipped with a magnetic stirrer bar was charged sequentially with $Cu(CH_3CN)_4PF_6$ (0.05 equiv), **L4** (0.06 equiv). The Schlenk flask was transferred to an argon-filled glovebox and followed by the addition of dry CH_3CN (2 mL). Then the mixture was stirred at room temperature for 30 min. To the resulting mixture were added **1** (0.2 mmol, 1.0 equiv), **2** (0.6 mmol, 3.0 equiv) and **3** (0.26 mmol, 1.3 equiv). Specification when alcohols were used (alcohols (5 equiv), **2a** (3 equiv), **3** (0.2 mmol, 1 equiv), stirred for 12 h). Next, the resulting mixture was removed out the glovebox. At last, the reaction mixture was stirred at room temperature with irradiation of 10 W 400 nm LED for 3 h. After completion of the reaction (TLC), the solvent was evaporated in vacuo and the crude material was purified by flash column chromatography to furnish the desired product.



4a

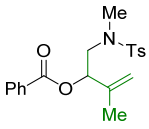
1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl benzoate, Rf = 0.5 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc =

10:1) to provide the title compound as a colorless oil in 87% yield (65 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 – 7.93 (m, 2H), 7.73 – 7.61 (m, 2H), 7.58 – 7.50 (m, 1H), 7.42 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.16 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.44 – 5.21 (m, 2H), 3.59 (d, *J* = 14.5 Hz, 1H), 3.45 (d, *J* = 14.5 Hz, 1H), 2.85 (s, 3H), 2.42 (s, 3H), 1.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.24, 143.44, 139.38, 134.69, 132.92, 130.90, 129.70, 129.41, 128.35, 127.30, 115.23, 83.78, 57.50, 37.45, 22.05, 21.43. **HRMS**: Calc'd for $C_{20}H_{24}NO_4S$, $[M+H]^+$ 374.1421; found 374.1413.



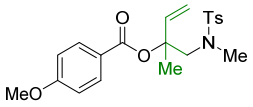
4a'

Rf = 0.46 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.99 (m, 2H), 7.70 – 7.66 (m, 2H), 7.61 – 7.54 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.49 (tq, *J* = 7.0, 1.4 Hz, 1H), 4.69 (s, 2H), 3.72 (d, *J* = 7.0 Hz, 2H), 2.68 (s, 3H), 2.41 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.14, 143.39, 135.49, 134.34, 133.09, 129.95, 129.65, 129.58, 128.41, 127.50, 121.75, 68.98, 47.24, 34.33, 21.49, 14.05.



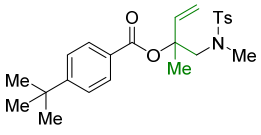
4a''

Rf = 0.48 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.51 (m, 1H), 7.45 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.33 – 7.12 (m, 2H), 5.57 (dd, *J* = 8.1, 4.3 Hz, 1H), 5.15 – 5.08 (m, 1H), 5.08 – 4.98 (m, 1H), 3.48 (dd, *J* = 14.1, 8.1 Hz, 1H), 3.28 (dd, *J* = 14.1, 4.4 Hz, 1H), 2.84 (s, 3H), 2.39 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.46, 143.41, 140.76, 134.73, 133.13, 129.88, 129.67, 128.41, 127.31, 114.37, 75.03, 52.13, 35.82, 21.45, 18.54.



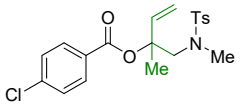
4b

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 4-methoxybenzoate, Rf = 0.3 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 6:1) to provide the title compound as a colorless oil in 94% yield (76 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 – 7.86 (m, 2H), 7.80 – 7.59 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.01 – 6.80 (m, 2H), 6.16 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.48 – 5.18 (m, 2H), 3.84 (s, 3H), 3.58 (d, *J* = 14.5 Hz, 1H), 3.44 (d, *J* = 14.5 Hz, 1H), 2.83 (s, 3H), 2.42 (s, 3H), 1.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.06, 163.35, 143.42, 139.66, 134.74, 131.49, 129.70, 127.31, 123.28, 115.00, 113.60, 83.38, 57.45, 55.38, 37.39, 22.22, 21.44. **HRMS**: Calc'd for $C_{21}H_{25}NNaO_5S$, $[M+Na]^+$ 426.1351; found 426.1333.



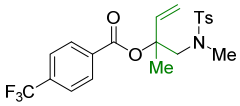
4c

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 4-(tert-butyl)benzoate, Rf = 5 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 91% yield (78 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.79 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.15 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.46 – 5.11 (m, 2H), 3.58 (s, 1H), 3.46 (s, 1H), 2.85 (s, 3H), 2.43 (s, 3H), 1.80 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.30, 156.63, 143.42, 139.53, 134.75, 129.71, 129.68, 129.34, 129.31, 128.13, 127.32, 127.30, 125.36, 125.33, 115.09, 83.57, 57.48, 37.41, 37.38, 35.02, 31.04, 31.02, 22.16, 21.45, 21.43. **HRMS**: Calc'd for $C_{24}H_{31}NNaO_4S$, $[M+Na]^+$ 452.1871; found 452.1853.



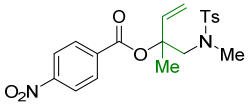
4d

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 4-chlorobenzoate, Rf = 0.5 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 88% yield (72 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.15 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.43 – 5.21 (m, 2H), 3.57 (d, *J* = 14.5 Hz, 1H), 3.43 (d, *J* = 14.6 Hz, 1H), 2.82 (s, 3H), 2.42 (s, 3H), 1.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.39, 143.49, 139.35, 139.18, 134.62, 130.85, 129.72, 129.37, 128.69, 127.31, 115.43, 84.01, 57.57, 37.60, 21.97, 21.43. **HRMS**: Calc'd for $C_{20}H_{23}ClNO_4S$, $[M+H]^+$ 408.1031; found 408.1017.



4e

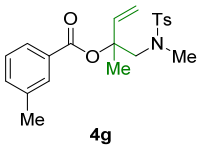
1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 4-(trifluoromethyl)benzoate, Rf = 0.4 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 87% yield (77 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 2H), 7.67 (dd, *J* = 8.3, 6.5 Hz, 4H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.16 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.44 – 5.23 (m, 2H), 3.59 (d, *J* = 14.6 Hz, 1H), 3.44 (d, *J* = 14.6 Hz, 1H), 2.84 (s, 3H), 2.42 (s, 3H), 1.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.06, 143.57, 138.98, 134.59, 134.34 (q, J_{C-F} = 32.1 Hz), 134.22, 129.88, 129.75, 127.34, 125.40 (q, J_{C-F} = 3.9 Hz), 123.56 (d, J_{C-F} = 272.6 Hz), 115.67, 84.36, 77.32, 77.00, 76.68, 57.68, 37.74, 21.88, 21.43. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -63.12. **HRMS**: Calc'd for $C_{21}H_{22}F_3NNaO_4S$, $[M+Na]^+$ 464.1119; found 464.1102.



4f

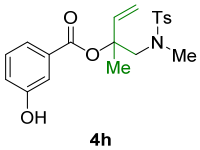
1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 4-nitrobenzoate, Rf = 0.4 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a pale-yellow oil in 69% yield (58 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 8.8, 2.1 Hz, 2H), 8.23 – 8.12 (m, 2H), 7.76 – 7.61 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.16 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.42 – 5.27 (m, 2H), 3.58 (d, *J* = 14.7 Hz,

1H), 3.44 (d, *J* = 14.7 Hz, 1H), 2.84 (s, 15H), 2.44 (s, 3H), 1.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.45, 150.46, 143.65, 138.77, 136.43, 134.52, 130.66, 129.80, 127.39, 123.54, 115.98, 84.70, 57.79, 38.01, 21.81, 21.49. **HRMS**: Calc'd for $C_{20}H_{23}N_2O_6S$, $[M+H]^+$ 419.1271; found 419.1262.



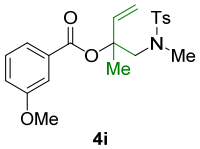
4g

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 3-methylbenzoate, Rf = 0.5 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 90% yield (70 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 2H), 7.71 – 7.62 (m, 2H), 7.43 – 7.18 (m, 4H), 6.16 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.52 – 5.19 (m, 2H), 3.60 (d, *J* = 14.5 Hz, 1H), 3.46 (d, *J* = 14.5 Hz, 1H), 2.84 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.42, 143.42, 139.42, 138.13, 134.69, 133.67, 130.82, 129.99, 129.68, 128.24, 127.29, 126.51, 115.16, 83.68, 57.39, 37.40, 22.11, 21.42, 21.20. **HRMS**: Calc'd for $C_{21}H_{26}NO_4S$, $[M+Na]^+$ 388.1577; found 388.1571.



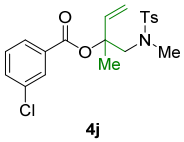
4h

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 3-hydroxybenzoate, Rf = 0.33 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a colorless oil in 63% yield (49 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ7.66 (d, *J* = 7.9 Hz, 2H), 7.60 – 7.48 (m, 2H), 7.41 – 7.20 (m, 3H), 7.10 – 6.98 (m, 1H), 6.32 – 5.92 (m, 2H), 5.45 – 5.12 (m, 2H), 3.57 (d, *J* = 14.6 Hz, 1H), 3.40 (d, *J* = 14.5 Hz, 1H), 2.84 (s, 3H), 2.42 (s, 3H), 1.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.27, 155.98, 143.62, 139.23, 134.55, 132.21, 129.79, 129.66, 127.34, 121.66, 120.31, 116.27, 115.46, 83.88, 57.75, 37.61, 21.97, 21.48. **HRMS**: Calc'd for $C_{20}H_{23}NNaO_5S$, $[M+Na]^+$ 412.1195; found 412.1178.



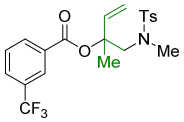
4i

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 3-methoxybenzoate, Rf = 0.3 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 5:1) to provide the title compound as a colorless oil in 90% yield (83 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.63 (m, 2H), 7.60 – 7.52 (m, 2H), 7.38 – 7.27 (m, 3H), 7.08 (ddd, *J* = 8.3, 2.7, 1.1 Hz, 1H), 6.15 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.42 – 5.23 (m, 2H), 3.82 (s, 3H), 3.58 (d, *J* = 14.5 Hz, 1H), 3.42 (d, *J* = 14.5 Hz, 1H), 2.85 (s, 3H), 2.42 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.12, 159.54, 143.46, 139.35, 134.70, 132.21, 129.71, 129.36, 127.32, 121.77, 119.41, 115.28, 114.01, 83.77, 57.72, 55.38, 37.53, 21.95, 21.44. **HRMS**: Calc'd for $C_{21}H_{25}NNaO_5S$, $[M+Na]^+$ 426.1351; found 426.1337.



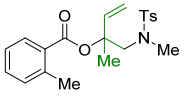
4j

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 3-chlorobenzoate, Rf = 4 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 91% yield (74 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.9 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.51 (ddd, *J* = 8.1, 2.2, 1.1 Hz, 1H), 7.40 – 7.29 (m, 3H), 6.15 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.42 – 5.17 (m, 2H), 3.58 (d, *J* = 14.6 Hz, 1H), 3.44 (d, *J* = 14.6 Hz, 1H), 2.83 (s, 3H), 2.43 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.03, 143.52, 139.05, 134.64, 134.51, 132.94, 132.70, 129.74, 129.72, 129.53, 127.60, 127.34, 115.60, 84.30, 57.53, 37.62, 21.96, 21.46. **HRMS**: Calc'd for $C_{20}H_{22}ClNNaO_4S$, $[M+Na]^+$ 430.0856; found 430.0839.



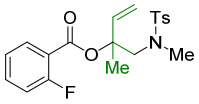
4k

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 3-(trifluoromethyl)benzoate, Rf = 0.4 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 94% yield (83 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 5.4 Hz, 2H), 6.16 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.52 – 5.22 (m, 2H), 3.59 (d, *J* = 14.6 Hz, 1H), 3.45 (d, *J* = 14.6 Hz, 1H), 2.85 (d, *J* = 3.4 Hz, 3H), 2.43 (d, *J* = 3.4 Hz, 3H), 1.83 (d, *J* = 3.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.94, 143.57, 138.95, 134.62, 132.70, 131.03 (q, J_{C-F} = 33.2 Hz), 130.54, 129.76, 129.44, 129.42 (d, J_{C-F} = 3.6 Hz), 127.36, 126.36 (d, J_{C-F} = 4.2 Hz), 123.59 (d, J_{C-F} = 272.2 Hz), 115.74, 84.46, 57.73, 37.73, 21.85, 21.45. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.84. **HRMS**: Calc'd for $C_{21}H_{22}F_3NNaO_4S$, $[M+Na]^+$ 464.1119; found 464.1099.



4l

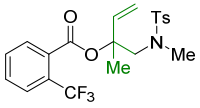
1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 2-methylbenzoate, Rf = 0.35 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 92% yield (71 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.38 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.4 Hz, 2H), 6.18 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.43 – 5.22 (m, 2H), 3.57 (d, *J* = 14.5 Hz, 1H), 3.44 (d, *J* = 14.5 Hz, 1H), 2.83 (s, 3H), 2.56 (s, 3H), 2.43 (s, 3H), 1.82 (s, 3H. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.29, 143.44, 140.05, 139.60, 134.69, 131.82, 131.71, 130.38, 130.11, 129.71, 127.35, 125.69, 115.23, 83.71, 57.53, 37.55, 22.10, 21.55, 21.46. **HRMS**: Calc'd for $C_{21}H_{26}NO_4S$, $[M+H]^+$ 388.1577; found 388.1566.



4m

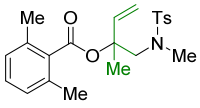
1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 2-fluorobenzoate, Rf = 0.4 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 93% yield (73 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (td, *J* = 7.6, 1.9 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.53 – 7.45 (m, 1H),

7.31 (d, J = 8.0 Hz, 2H), 7.18 (td, J = 7.6, 1.2 Hz, 1H), 7.09 (ddd, J = 11.0, 8.3, 1.1 Hz, 1H), 6.13 (dd, J = 17.5, 11.0 Hz, 1H), 5.50 – 5.14 (m, 2H), 3.56 (d, J = 14.6 Hz, 1H), 3.37 (d, J = 14.5 Hz, 1H), 2.84 (s, 3H), 2.42 (s, 3H), 1.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.05 (d, J_{C-F} = 3.6 Hz), 161.62 (d, J_{C-F} = 258.7 Hz), 143.42, 139.07, 134.69, 134.38 (d, J_{C-F} = 9.2 Hz), 132.05, 129.69, 127.32, 124.01 (d, J_{C-F} = 3.8 Hz), 119.52 (d, J_{C-F} = 10.2 Hz), 116.89 (d, J_{C-F} = 22.6 Hz), 115.55, 84.69, 57.78, 37.32, 37.29, 21.83, 21.44. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -109.38. **HRMS**: Calc'd for $C_{20}H_{23}FNO_4S$, $[M+H]^+$ 392.1326; found 392.1313.



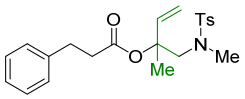
4n

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 2-(trifluoromethyl)benzoate, Rf = 0.5 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 91% yield (80 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 2H), 7.68 – 7.62 (m, 2H), 7.62 – 7.53 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.17 (dd, J = 17.6, 11.0 Hz, 1H), 5.45 – 5.26 (m, 2H), 3.50 (d, J = 14.6 Hz, 1H), 3.38 (d, J = 14.6 Hz, 1H), 2.76 (s, 3H), 2.42 (s, 3H), 1.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.32, 143.50, 138.48, 134.54, 132.13, 131.81, 130.87, 129.83, 129.72, 128.11 (d, J_{C-F} = 32.1 Hz), 127.34, 126.56 (d, J_{C-F} = 5.7 Hz), 123.37 (d, J_{C-F} = 273.3 Hz) 85.32, 77.32, 77.00, 76.68, 57.68, 37.65, 21.43, 21.12. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.78. **HRMS**: Calc'd for $C_{21}H_{23}F_3NO_4S$, $[M+H]^+$ 442.1294; found 442.1283.



4o

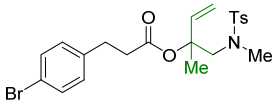
1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 2,6-dimethylbenzoate, Rf = 5 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 91% yield (73 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 7.6, 7.6 Hz, 1H), 7.00 (d, J = 7.6 Hz, 2H), 6.21 (dd, J = 17.6, 11.0 Hz, 1H), 5.46 – 5.28 (m, 2H), 3.40 (d, J = 14.4 Hz, 1H), 3.22 (d, J = 14.3 Hz, 1H), 2.76 (s, 3H), 2.42 (s, 3H), 2.32 (s, 6H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.27, 143.46, 139.20, 134.49, 134.36, 134.17, 129.68, 129.06, 127.54, 127.33, 116.16, 84.33, 58.81, 37.75, 21.42, 20.74, 19.49. **HRMS**: Calc'd for $C_{22}H_{28}NO_4S$, $[M+H]^+$ 402.1734; found 402.1721.



5a

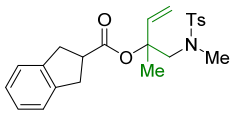
1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 3-phenylpropanoate, Rf = 0.4 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 92% yield (74 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.57 (m, 2H), 7.34 – 7.24 (m, 4H), 7.22 – 7.15 (m, 3H), 5.97 (dd, J = 17.8, 10.8 Hz, 1H), 5.33 – 5.12 (m, 2H), 3.36 (d, J = 14.5 Hz, 1H), 3.17 (d, J = 14.4 Hz, 1H), 2.91 (t, J = 7.7 Hz, 2H), 2.72 (s, 3H), 2.59 (dd, J = 8.3, 7.2 Hz, 2H), 2.43 (s, 3H), 1.65 (s, 3H). **^{13}C NMR** (101

MHz, $CDCl_3$) δ 171.41, 143.39, 140.27, 139.20, 134.65, 129.67, 128.41, 128.26, 127.30, 126.23, 115.17, 83.25, 57.64, 37.44, 36.77, 30.77, 21.52, 21.43. **HRMS**: Calc'd for $C_{22}H_{28}NO_4S$, $[M+H]^+$ 402.1734; found 402.1723.



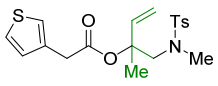
5b

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 3-(4-bromophenyl)propanoate, Rf = 0.4 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 94% yield (90 mg)**.** ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.56 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.00 (m, 2H), 5.96 (dd, *J* = 17.4, 11.2 Hz, 1H), 5.29 – 5.09 (m, 2H), 3.36 (d, *J* = 14.5 Hz, 1H), 3.17 (d, *J* = 14.5 Hz, 1H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.73 (s, 3H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.64 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 171.11, 143.42, 139.31, 139.14, 134.57, 131.43, 130.08, 129.69, 127.29, 119.98, 115.24, 83.30, 57.57, 37.56, 36.44, 30.10, 21.56, 21.43. **HRMS**: Calc'd for $C_{22}H_{27}BrNO_4S$, $[M+H]^+$ 480.0839; found 480.0822.



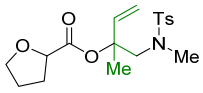
5c

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 2,3-dihydro-1H-indene-2-carboxylate, Rf = 0.4 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 88% yield (73 mg)**.** ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.08 (m, 4H), 6.04 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.32 – 5.17 (m, 2H), 3.43 (d, *J* = 14.5 Hz, 1H), 3.36 – 3.09 (m, 6H), 2.79 (s, 3H), 2.43 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.69, 143.43, 141.34, 139.28, 134.63, 129.70, 127.32, 126.58, 124.26, 115.24, 83.31, 57.85, 44.36, 37.52, 36.01, 35.97, 21.52, 21.44. **HRMS**: Calc'd for $C_{23}H_{28}NO_4S$, $[M+H]^+$ 414.1734; found 414.1720.



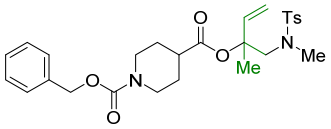
5d

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 2-(thiophen-3-yl)acetate, Rf = 0.35 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 65% yield (51 mg)**.** ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.52 (m, 2H), 7.40 – 7.20 (m, 3H), 7.10 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.00 (dd, *J* = 4.9, 1.3 Hz, 1H), 5.99 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.33 – 5.09 (m, 2H), 3.61 (s, 2H), 3.39 (d, *J* = 14.5 Hz, 1H), 3.16 (d, *J* = 14.5 Hz, 1H), 2.65 (s, 3H), 2.42 (s, 3H), 1.68 (s, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 169.55, 143.41, 138.98, 134.63, 133.49, 129.68, 128.37, 127.29, 125.79, 122.84, 115.35, 83.73, 57.62, 37.26, 36.93, 21.51, 21.44. **HRMS**: Calc'd for $C_{19}H_{24}NO_4S_2$, $[M+H]^+$ 394.1141; found 394.1133.



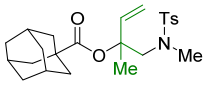
5e

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl tetrahydrofuran-2-carboxylate, Rf = 0.3 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a colorless oil in 79% yield (58 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.01 (ddd, *J* = 17.5, 11.0, 4.1 Hz, 1H), 5.35 – 5.07 (m, 2H), 4.34 (ddd, *J* = 8.5, 5.2, 2.0 Hz, 1H), 3.99 – 3.80 (m, 2H), 3.40 (dd, *J* = 19.7, 14.5 Hz, 1H), 3.20 (dd, *J* = 14.5, 13.1 Hz, 1H), 2.82 (s, 3H), 2.41 (s, 3H), 2.18 (ddd, *J* = 10.9, 6.2, 3.2 Hz, 1H), 2.05 – 1.79 (m, 3H), 1.69 (d, *J* = 2.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.82, 143.43, 138.77, 134.53, 129.68, 127.29, 115.54, 83.84, 69.22, 57.84, 57.73, 37.49, 29.94, 29.90, 25.19, 21.41. **HRMS**: Calc'd for C18H26NO5S, $[M+H]^+$ 368.1526; found 368.1515.



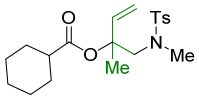
5f

1-benzyl 4-(1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl) piperidine-1,4-dicarboxylate, Rf = 0.4 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 5:1) to provide the title compound as a pale yellow oil in 92% yield (95 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.27 (m, 7H), 5.99 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.34 – 5.18 (m, 2H), 5.11 (s, 2H), 4.09 (d, *J* = 12.9 Hz, 2H), 3.41 (d, *J* = 14.6 Hz, 1H), 3.22 (d, *J* = 14.6 Hz, 1H), 2.89 (t, *J* = 12.2 Hz, 2H), 2.79 (s, 3H),2.46 – 2.38 (m, 4H), 1.87 (d, *J* = 13.5 Hz, 2H), 1.66 (s, 3H), 1.64 – 1.51 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.91, 155.04, 143.44, 139.20, 136.63, 134.49, 129.67, 128.39, 127.90, 127.77, 127.27, 115.22, 83.14, 67.01, 57.55, 43.12, 41.66, 37.74, 27.76, 21.64, 21.40. **HRMS**: Calc'd for $C_{27}H_{35}N_2O_6S$, $[M+H]^+$ 515.2210; found 515.2168.



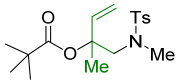
5g

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl adamantane-1-carboxylate, Rf = 0.55 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 88% yield (76 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.97 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.40 – 5.03 (m, 2H), 3.43 (d, *J* = 14.4 Hz, 1H), 3.21 (d, *J* = 14.5 Hz, 1H), 2.81 (s, 3H), 2.41 (s, 3H), 2.06 – 1.90 (m, 3H), 1.83 (d, *J* = 2.9 Hz, 6H), 1.79 – 1.56 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.24, 143.36, 139.73, 134.67, 129.66, 127.28, 114.68, 82.57, 57.65, 41.06, 38.75, 37.44, 36.37, 27.83, 21.77, 21.42. **HRMS**: Calc'd for $C_{24}H_{34}NO_4S$, $[M+H]^+$ 432.2203; found 432.2190.



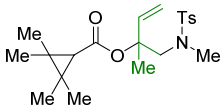
5h

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl cyclohexanecarboxylate, Rf = 0.55 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 90% yield (68 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.00 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.37 – 5.16 (m, 2H), 3.41 (d, *J* = 14.4 Hz, 1H), 3.21 (d, *J* = 14.4 Hz, 1H), 2.81 (s, 3H), 2.43 (s, 3H), 2.21 (tt, *J* = 11.3, 3.6 Hz, 1H), 1.93 – 1.80 (m, 2H), 1.77 – 1.69 (m, 2H), 1.67 – 1.58 (m, 4H), 1.44 – 1.32 (m, 2H), 1.31 – 1.12 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.70, 143.41, 139.60, 134.73, 129.70, 127.35, 114.94, 82.75, 57.72, 43.97, 37.50, 28.93, 25.70, 25.38, 21.73, 21.48. **HRMS**: Calc'd for $C_{20}H_{30}NO_4S$, $[M+H]^+$ 380.1890; found 380.1882.



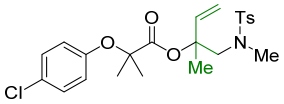
5i

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl pivalate, Rf = 0.55 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 64% yield (45 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.99 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.33 – 5.16 (m, 2H), 3.43 (d, *J* = 14.4 Hz, 1H), 3.21 (d, *J* = 14.5 Hz, 1H), 2.82 (s, 3H), 2.42 (s, 3H), 1.66 (s, 3H), 1.16 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.05, 143.42, 139.64, 134.70, 129.70, 127.33, 114.83, 82.79, 57.88, 39.15, 37.45, 27.08, 21.55, 21.46. **HRMS**: Calc'd for $C_{18}H_{28}NO_4S$, $[M+H]^+$ 354.1734; found 354.1724.



5j

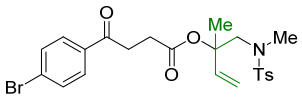
1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl
2,2,3,3-tetramethylcyclopropane-1-carboxylate, Rf = 0.6 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a white solid in 92% yield (73 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.02 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.35 – 4.98 (m, 2H), 3.38 (d, *J* = 14.3 Hz, 1H), 3.21 (d, *J* = 14.3 Hz, 1H), 2.82 (s, 3H), 2.41 (s, 3H), 1.64 (s, 3H), 1.18 (s, 3H), 1.16 (s, 3H), 1.14 (s, 3H), 1.13 (s, 3H), 1.07 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.72, 143.31, 140.12, 134.69, 129.64, 127.26, 114.45, 82.53, 57.59, 37.32, 36.13, 29.97, 23.48, 23.46, 21.93, 21.41, 16.42, 16.34. **HRMS**: Calc'd for $C_{21}H_{32}NO_4S$, $[M+H]^+$ 394.2047; found 394.2036.



5k

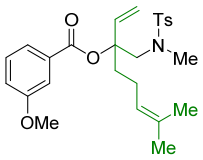
1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl
2-(4-chlorophenoxy)-2-methylpropanoate，Rf = 0.5 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 90% yield (84 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.44 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 8.9 Hz, 2H), 5.96 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.26 (dd, *J* = 14.3, 3.2 Hz, 2H), 3.30 (d, *J* = 14.5 Hz, 1H), 2.97 (d, *J* = 14.5 Hz, 1H), 2.71 (s, 3H), 2.42 (s, 3H), 1.71 (s, 3H), 1.56 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.27, 153.92, 143.49,

138.36, 134.51, 129.71, 129.09, 127.35, 126.88, 119.69, 116.15, 84.52, 79.46, 58.60, 37.41, 25.21, 25.09, 21.46, 20.34. **HRMS**: Calc'd for $C_{23}H_{29}ClNO_5S$, $[M+H]^+$ 466.1449; found 466.1438.



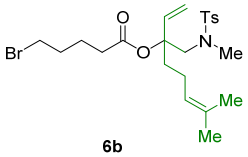
5l

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 4-(4-bromophenyl)-4-oxobutanoate, Rf = 0.27 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 7:1) to provide the title compound as a colorless oil in 89% yield (90 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.01 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.34 – 5.13 (m, 2H), 3.40 (d, *J* = 14.5 Hz, 1H), 3.32 – 3.13 (m, 3H), 2.84 (s, 3H), 2.71 (td, *J* = 6.4, 3.9 Hz, 2H), 2.42 (s, 3H), 1.67 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.05, 171.34, 143.42, 139.16, 135.17, 134.62, 131.86, 129.70, 129.49, 128.33, 127.32, 127.28, 115.22, 83.50, 57.61, 37.65, 33.12, 28.99, 21.61, 21.46. **HRMS**: Calc'd for $C_{23}H_{27}BrNO_5S$, $[M+H]^+$ 508.0788; found 508.0771.



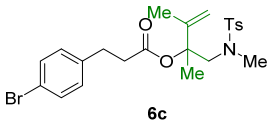
6a

3-(((N,4-dimethylphenyl)sulfonamido)methyl)-7-methylocta-1,6-dien-3-yl 3-methoxybenzoate, Rf = 0.4 (PE:EA = 5:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 77% yield (73 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 14.7, 7.8 Hz, 3H), 7.53 (s, 1H), 7.39 – 7.27 (m, 3H), 7.10 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.01 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.51 – 5.31 (m, 2H), 5.11 (t, *J* = 7.2 Hz, 1H), 3.83 (s, 3H), 3.78 (d, *J* = 14.6 Hz, 1H), 3.66 (d, *J* = 14.6 Hz, 1H), 2.72 (s, 3H), 2.51 – 2.31 (m, 4H), 2.18 – 1.92 (m, 2H), 1.86 (ddd, *J* = 13.7, 11.1, 5.0 Hz, 1H), 1.62 (s, 3H), 1.55 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.25, 159.55, 143.41, 138.43, 134.63, 132.15, 132.12, 129.70, 129.46, 127.31, 123.39, 121.85, 119.42, 115.22, 114.08, 86.31, 55.37, 54.75, 37.08, 35.28, 25.60, 21.67, 21.46, 17.59. **HRMS**: Calc'd for $C_{26}H_{33}NNaO_5S$, $[M+Na]^+$ 494.1977; found 494.1953.



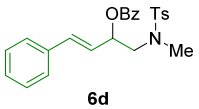
6b

3-(((N,4-dimethylphenyl)sulfonamido)methyl)-7-methylocta-1,6-dien-3-yl 5-bromopentanoate, Rf = 0.4 (PE:EA = 5:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 67% yield (67 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.98 – 5.74 (m, 1H), 5.37 – 5.20 (m, 2H), 5.07 (t, *J* = 1.5 Hz, 1H), 3.61 (d, *J* = 14.7 Hz, 1H), 3.48 – 3.33 (m, 3H), 2.73 (s, 3H), 2.42 (s, 3H), 2.35 (t, *J* = 7.3 Hz, 2H), 2.27 (ddd, *J* = 13.6, 11.5, 5.3 Hz, 1H), 1.99 (qd, *J* = 11.7, 10.6, 5.2 Hz, 1H), 1.94 – 1.83 (m, 3H), 1.80 – 1.70 (m, 3H), 1.66 (s, 3H), 1.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.03, 143.43, 138.27, 134.45, 132.11, 129.70, 127.35, 123.31, 115.26, 85.35, 54.84, 37.62, 34.92, 34.16, 33.06, 31.90, 25.66, 23.29, 21.63, 21.47, 17.61. **HRMS**: Calc'd for $C_{23}H_{35}BrNO_4S$, $[M+H]^+$ 500.1465; found 500.1270.



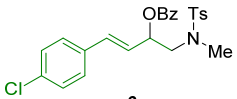
6c

1-((N,4-dimethylphenyl)sulfonamido)-2,3-dimethylbut-3-en-2-yl 3-(4-bromophenyl)propanoate, Rf = 0.4 (PE:EA = 5:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 92% yield (91 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 5.06 – 4.91 (m, 1H), 4.88 (s, 1H), 3.32 (d, *J* = 14.4 Hz, 1H), 3.06 (d, *J* = 14.4 Hz, 1H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.76 (s, 3H), 2.56 (t, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 1.71 (s, 3H), 1.69 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.75, 145.07, 143.47, 139.31, 134.57, 131.49, 130.10, 129.73, 127.34, 120.04, 112.65, 85.36, 57.77, 37.48, 36.35, 30.09, 21.49, 21.04, 19.26. **HRMS**: Calc'd for $C_{23}H_{29}BrNO_4S$, $[M+H]^+$ 494.0995; found 494.0983.



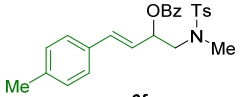
6d

(E)-1-((N,4-dimethylphenyl)sulfonamido)-4-phenylbut-3-en-2-yl benzoate, Rf = 0.5 (PE:EA = 5:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 47% yield (41 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 – 8.05 (m, 2H), 7.71 – 7.64 (m, 2H), 7.61 – 7.55 (m, 1H), 7.47– 7.42 (m, 2H), 7.39 (d, *J* = 7.1 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.29 – 7.22 (m, 3H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.26 (dd, *J* = 16.0, 7.1 Hz, 1H), 5.86 (td, *J* = 7.3, 4.7 Hz, 1H), 3.59 (dd, *J* = 14.1, 7.6 Hz, 1H), 3.33 (dd, *J* = 14.1, 4.7 Hz, 1H), 2.88 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.63, 143.44, 135.87, 134.84, 134.39, 133.16, 129.95, 129.74, 129.71, 128.58, 128.42, 128.37, 128.26, 127.34, 126.75, 124.26, 72.59, 53.35, 36.19, 21.47. **HRMS**: Calc'd for $C_{25}H_{25}NO_4SNa$, $[M+Na]^+$ 458.1402; found 458.1396.



6e

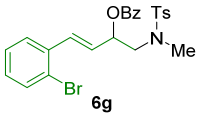
(E)-4-(4-chlorophenyl)-1-((N,4-dimethylphenyl)sulfonamido)but-3-en-2-yl benzoate, Rf = 0.5 (PE:EA = 5:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title c ompound as a colorless oil in 44% yield (41 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.70 – 7.64 (m, 2H), 7.60 – 7.55 (m, 1H), 7.48 – 7.42 (m, 2H), 7.29 (ddd, *J* = 16.6, 9.0, 4.9 Hz, 6H), 6.72 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 16.0, 6.9 Hz, 1H), 5.94 – 5.81 (m, 1H), 3.56 (dd, *J* = 14.1, 7.4 Hz, 1H), 3.34 (dd, *J* = 14.1, 4.9 Hz, 1H), 2.88 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.57, 143.49, 134.74, 134.40, 133.89, 133.23, 132.98, 129.80, 129.71, 128.86, 128.74, 128.44, 128.35, 127.96, 127.59, 127.40, 127.29, 125.02, 72.47, 53.26, 36.25, 21.45. **HRMS**: Calc'd for $C_{25}H_{25}ClNO_4S$, $[M+H]^+$ 470.1187; found 470.1185.



6f

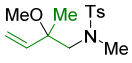
(E)-1-((N,4-dimethylphenyl)sulfonamido)-4-(p-tolyl)but-3-en-2-yl benzoate, Rf = 0.5 (PE:EA = 5:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 58% yield (52 mg). **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.0 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.48 – 7.42 (m, 2H), 7.33 – 7.21 (m, 4H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.20 (dd, *J* = 15.9, 7.2 Hz, 1H), 5.85 (td, *J* = 7.3, 4.4 Hz, 1H), 3.59 (dd, *J* = 14.1, 7.7 Hz, 1H), 3.31 (dd, *J* = 14.1, 4.6 Hz, 1H), 2.88 (s, 3H), 2.39 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.63, 143.40, 138.19, 134.85, 134.35, 133.10, 133.06, 129.99, 129.72, 129.68, 129.26, 128.39, 128.31, 127.32, 126.65, 123.14, 72.68, 53.38, 36.15, 21.45, 21.20. **HRMS**: Calc'd for $C_{26}H_{27}NO_4SNa$, $[M+Na]^+$ 472.1558; found 472.1552.



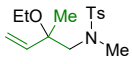
6g

(E)-4-(2-bromophenyl)-1-((N,4-dimethylphenyl)sulfonamido)but-3-en-2-yl benzoate, Rf = 0.5 (PE:EA = 5:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 36% yield (37 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.9 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.56 (dddd, *J* = 13.5, 7.8, 6.3, 1.3 Hz, 3H), 7.49 – 7.43 (m, 2H), 7.34 – 7.20 (m, 3H), 7.19 – 7.03 (m, 2H), 6.26 (dd, *J* = 15.9, 6.6 Hz, 1H), 5.88 (dtd, *J* = 7.4, 5.8, 5.4, 2.7 Hz, 1H), 3.58 (dd, *J* = 14.1, 7.0 Hz, 1H), 3.37 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.90 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.55, 143.49, 135.93, 134.79, 133.24, 132.89, 132.64, 129.76, 129.73, 129.43, 128.46, 127.58, 127.41, 127.32, 123.85, 72.23, 53.21, 36.22, 21.48. **HRMS**: Calc'd for $C_{25}H_{25}BrNO_4S$, $[M+H]^+$ 514.0682; found 514.0679.



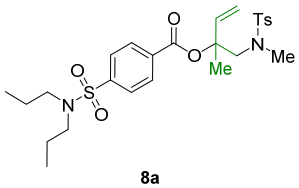
7a

N-(2-methoxy-2-methylbut-3-en-1-yl)-N,4-dimethylbenzenesulfonamide, Rf = 0.6 (PE:EA = 5:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 41% yield (23 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.35 – 5.14 (m, 2H), 3.16 –3.08 (m, 4H), 2.91 – 2.81 (m, 4H), 1.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.14, 139.98, 134.86, 129.59, 127.35, 116.79, 78.83, 58.83, 50.07, 37.52, 21.46, 18.37. **HRMS**: Calc'd for $C_{14}H_{22}NO_3S$, $[M+H]^+$ 284.1315; found 284.1314.



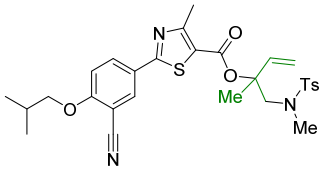
7b

N-(2-ethoxy-2-methylbut-3-en-1-yl)-N,4-dimethylbenzenesulfonamide, Rf = 0.6 (PE:EA = 5:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 10:1) to provide the title compound as a colorless oil in 37% yield (22 mg)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.87 – 5.65 (m, 1H), 5.32 – 5.16 (m, 2H), 3.39 – 3.22 (m, 2H), 3.12 (d, *J* = 13.8 Hz, 1H), 2.91 – 2.81 (m, 4H), 2.42 (s, 3H), 1.39 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.09, 140.62, 134.89, 129.58, 127.36, 116.18, 78.54, 59.09, 57.66, 37.52, 21.46, 19.12, 15.87. **HRMS**: Calc'd for $C_{15}H_{24}NO_3S$, $[M+H]^+$ 298.1471; found 298.1470.



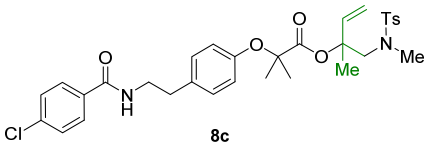
8a

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 4-(N,N-dipropylsulfamoyl)benzoate, Rf = 0.4 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 6:1) to provide the title compound as a colorless oil in 85% yield (91 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 – 8.00 (m, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.74 – 7.59 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.14 (ddd, *J* = 17.6, 11.0, 1.0 Hz, 1H), 5.46 – 5.18 (m, 2H), 3.56 (d, *J* = 14.6 Hz, 1H), 3.40 (d, *J* = 14.6 Hz, 1H), 3.15 – 2.99 (m, 4H), 2.83 (s, 3H), 2.42 (s, 3H), 1.81 (s, 3H), 1.53 (q, *J* = 7.8 Hz, 4H), 0.85 (td, *J* = 7.3, 1.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.93, 144.07, 143.60, 138.88, 134.40, 134.19, 130.11, 129.76, 127.32, 126.97, 115.78, 84.37, 57.79, 49.94, 37.87, 21.92, 21.73, 21.47, 11.10. **HRMS**: Calc'd for $C_{26}H_{37}N_2O_6S_2$, $[M+H]^+$ 537.2088; found 537.2070.



8b

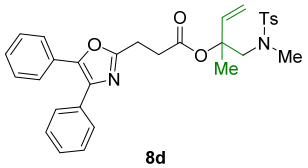
1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate, Rf = 0.33 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 5:1) to provide the title compound as a white solid in 73% yield (83 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.3 Hz, 1H), 8.07 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.13 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.50 – 5.07 (m, 2H), 3.88 (d, *J* = 6.5 Hz, 2H), 3.54 (d, *J* = 14.6 Hz, 1H), 3.35 (d, *J* = 14.6 Hz, 1H), 2.87 (s, 3H), 2.71 (s, 3H), 2.42 (s, 3H), 2.18 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.80 (s, 3H), 1.08 (s, 3H), 1.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.91, 162.46, 161.76, 160.55, 143.53, 138.90, 134.55, 132.51, 132.01, 129.74, 127.29, 125.75, 121.57, 115.68, 115.31, 112.58, 102.82, 84.97, 77.20, 75.60, 57.62, 37.66, 28.06, 21.91, 21.45, 18.96, 17.37. **HRMS**: Calc'd for $C_{29}H_{34}N_3O_5S_2$, $[M+H]^+$ 568.1934; found 568.1921.



8c

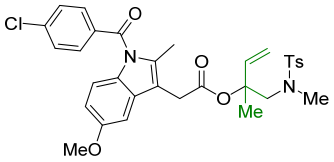
1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoate, Rf = 0.2 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 2:1) to provide the title compound as a white solid in 67% yield (82 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 6.0 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 2H), 5.94 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.41 – 5.17 (m, 2H), 3.67 (dt, *J* = 12.5, 6.4 Hz, 1H), 3.57 (dt, *J* = 13.2, 6.4 Hz, 1H), 3.25 (d, *J* = 14.5 Hz, 1H), 2.88 (td, *J* = 14.0, 7.8 Hz, 3H), 2.53 (s, 3H), 2.40 (s, 3H), 1.68 (s, 3H), 1.58 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.70, 166.62, 153.82, 143.56, 138.37, 137.30, 134.15, 133.04, 132.43,

129.69, 129.64, 128.61, 128.49, 127.17, 117.43, 116.06, 84.33, 78.55, 59.09, 41.85, 37.36, 34.48, 26.31, 23.97, 21.44, 19.77. **HRMS**: Calc'd for $C_{32}H_{38}ClN_2O_6S$, $[M+H]^+$ 613.2134; found 613.2116.



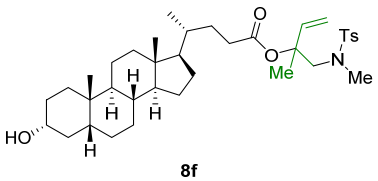
8d

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 3-(4,5-diphenyloxazol-2-yl)propanoate, Rf = 0.25 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 5:1) to provide the title compound as a yellow solid in 82% yield (89 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.57 – 7.52 (m, 2H), 7.40 – 7.26 (m, 8H), 6.02 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.34 – 5.16 (m, 2H), 3.39 (d, *J* = 14.5 Hz, 1H), 3.20 (d, *J* = 14.6 Hz, 1H), 3.14 (t, *J* = 7.1 Hz, 2H), 2.88 (t, *J* = 7.0 Hz, 2H), 2.79 (s, 3H), 2.41 (s, 3H), 1.70 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.56, 161.65, 145.36, 143.37, 139.04, 134.94, 134.54, 132.28, 129.66, 128.80, 128.56, 128.47, 128.41, 127.99, 127.76, 127.27, 126.40, 115.35, 83.69, 57.52, 37.61, 31.87, 23.27, 21.57, 21.43. **HRMS**: Calc'd for $C_{31}H_{33}N_2O_5S$, $[M+H]^+$ 545.2105; found 545.2093.



8e

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate, Rf = 0.46 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 2:1) to provide the title compound as a yellow oil in 77% yield (94 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 12.6, 8.4 Hz, 4H), 7.52 – 7.41 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.99 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.19 (dd, *J* = 14.3, 3.2 Hz, 2H), 3.80 (s, 3H), 3.64 (s, 2H), 3.37 (d, *J* = 14.6 Hz, 1H), 3.15 (d, *J* = 14.6 Hz, 1H), 2.62 (s, 3H), 2.41 (s, 3H), 2.35 (s, 2H), 1.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.40, 168.18, 155.95, 143.46, 139.20, 138.97, 135.65, 134.40, 133.72, 131.08, 130.62, 130.49, 129.69, 129.61, 129.05, 129.02, 127.26, 127.16, 115.35, 114.87, 112.53, 111.78, 100.96, 83.75, 57.45, 55.59, 37.38, 31.38, 21.60, 21.43, 13.29. **HRMS**: Calc'd for $C_{32}H_{34}ClN_2O_6S$, $[M+H]^+$ 609.1821; found 609.1806.



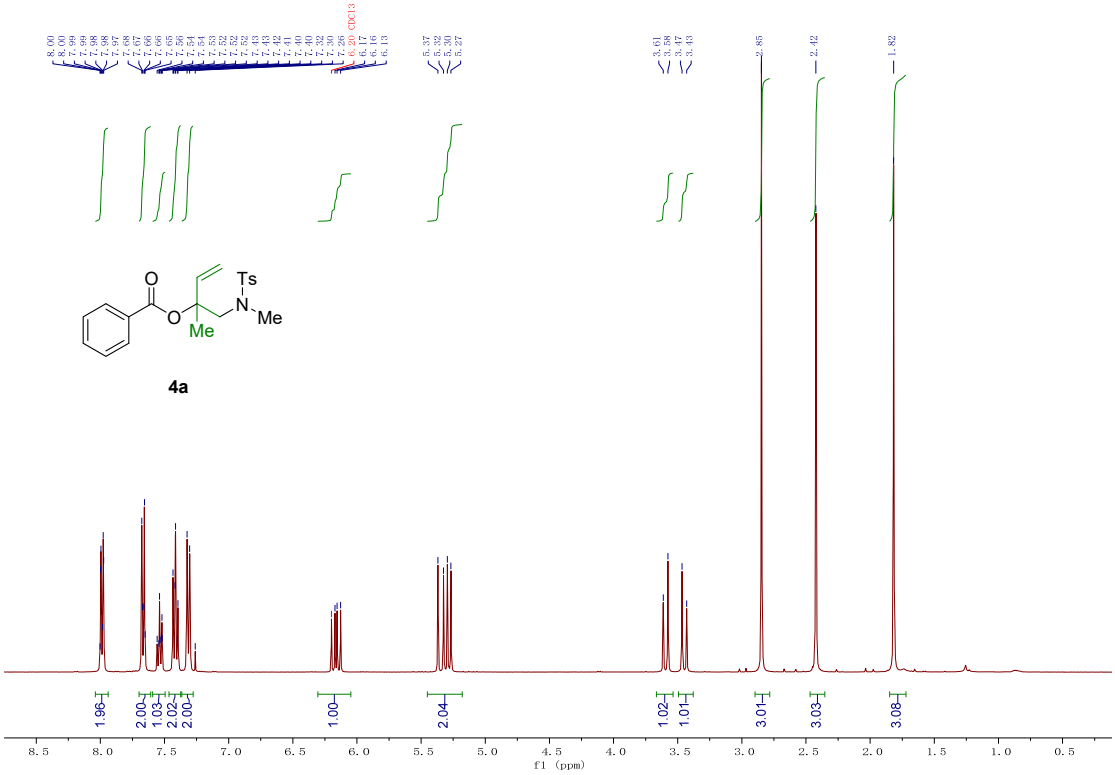
8f

1-((N,4-dimethylphenyl)sulfonamido)-2-methylbut-3-en-2-yl (4R)-4-((3R,5R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate, Rf = 0.23 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 5:1) to provide the title compound as a colorless oil in 69% yield (87 mg)**.** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.48 (m, 2H), 7.35 – 7.22 (m, 2H), 6.00 (ddd, *J* = 17.5, 11.0, 2.2 Hz, 1H), 5.35 – 5.10 (m, 2H), 3.66 – 3.49 (m, 1H), 3.37 (dd,

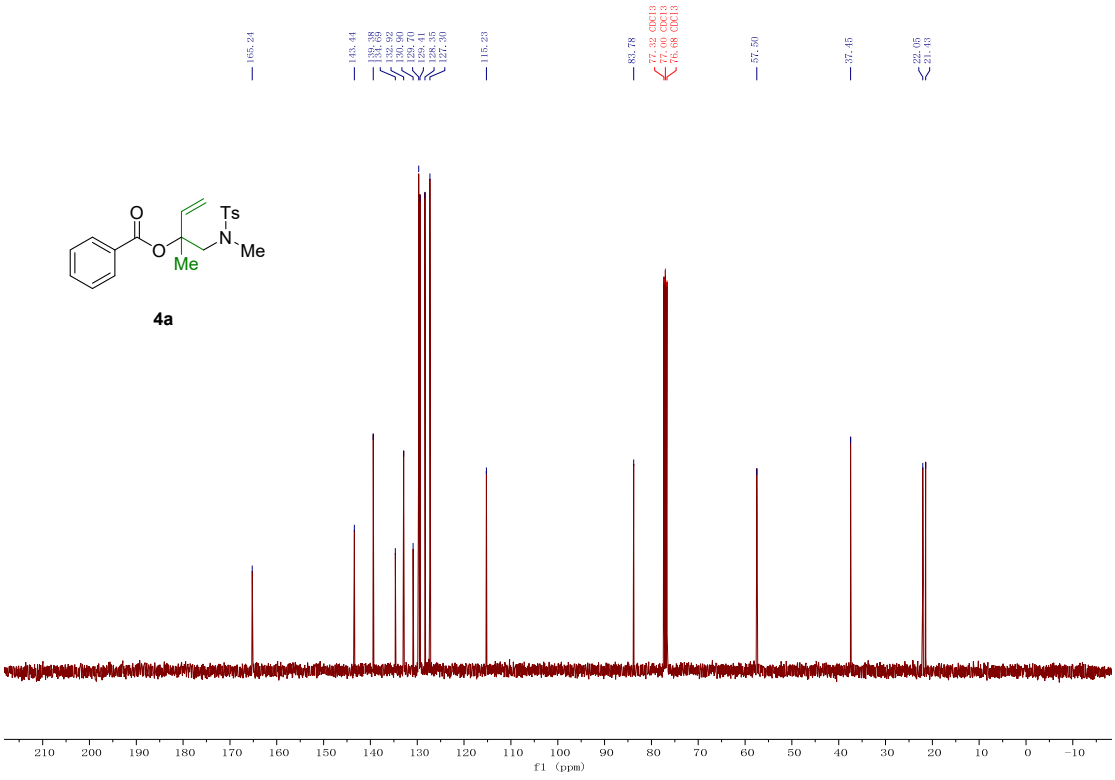
J = 14.5, 2.5 Hz, 1H), 3.18 (dd, *J* = 14.4, 4.7 Hz, 1H), 2.81 (s, 3H), 2.42 (s, 3H), 2.28 (dddd, *J* = 15.4, 10.2, 5.3, 1.7 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.92 (dt, *J* = 12.3, 2.9 Hz, 1H), 1.85 – 1.62 (m, 10H), 1.58 – 1.45 (m, 2H), 1.41 – 1.31 (m, 6H), 1.28 – 1.17 (m, 4H), 1.14 – 0.97 (m, 6H), 0.91 – 0.81 (m, 7H), 0.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.84, 143.40, 139.37, 134.56, 129.68, 127.31, 115.11, 82.92, 71.74, 57.73, 56.38, 55.82, 42.63, 41.98, 40.30, 40.06, 37.53, 36.32, 35.74, 35.25, 35.18, 34.48, 32.18, 30.80, 30.42, 28.12, 27.10, 26.33, 24.11, 23.30, 21.50, 21.47, 20.72, 18.19, 11.96. **HRMS**: Calc'd for $C_{37}H_{58}NO_5S$, $[M+H]^+$ 628.4030; found 628.4013.

S10 NMR Spectra

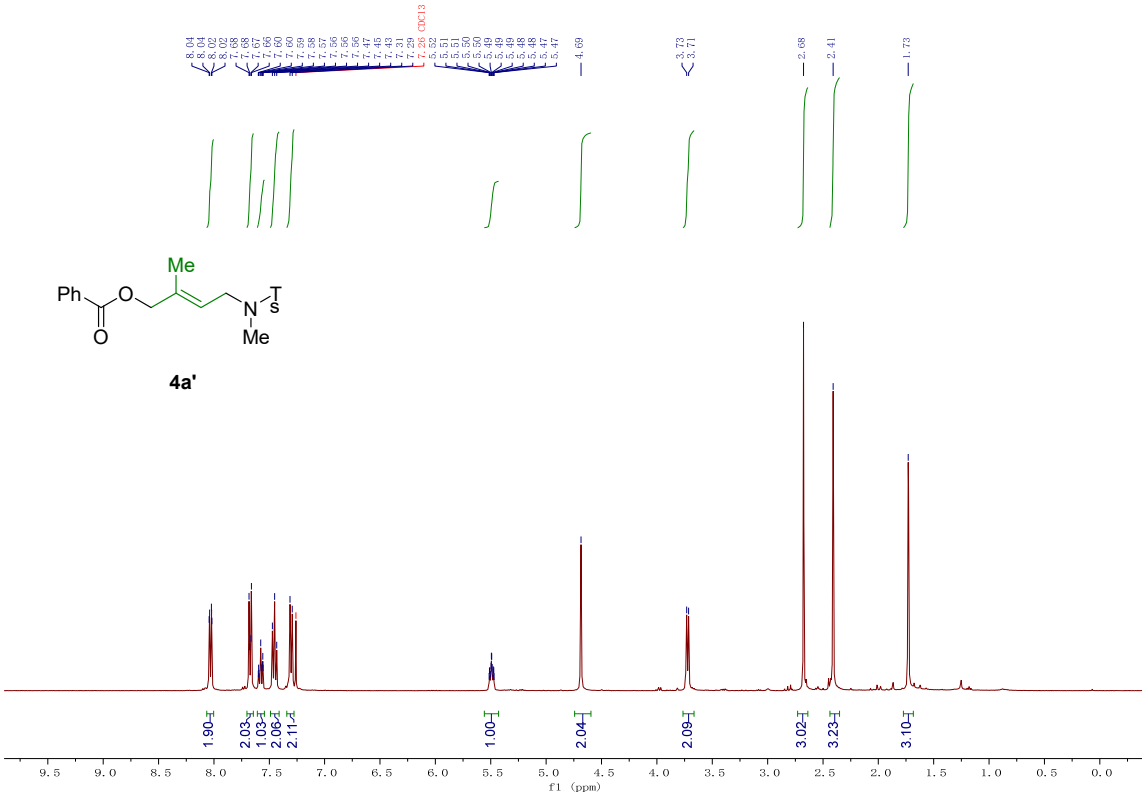
^{1}H NMR (400 MHz, $CDCl_3$)



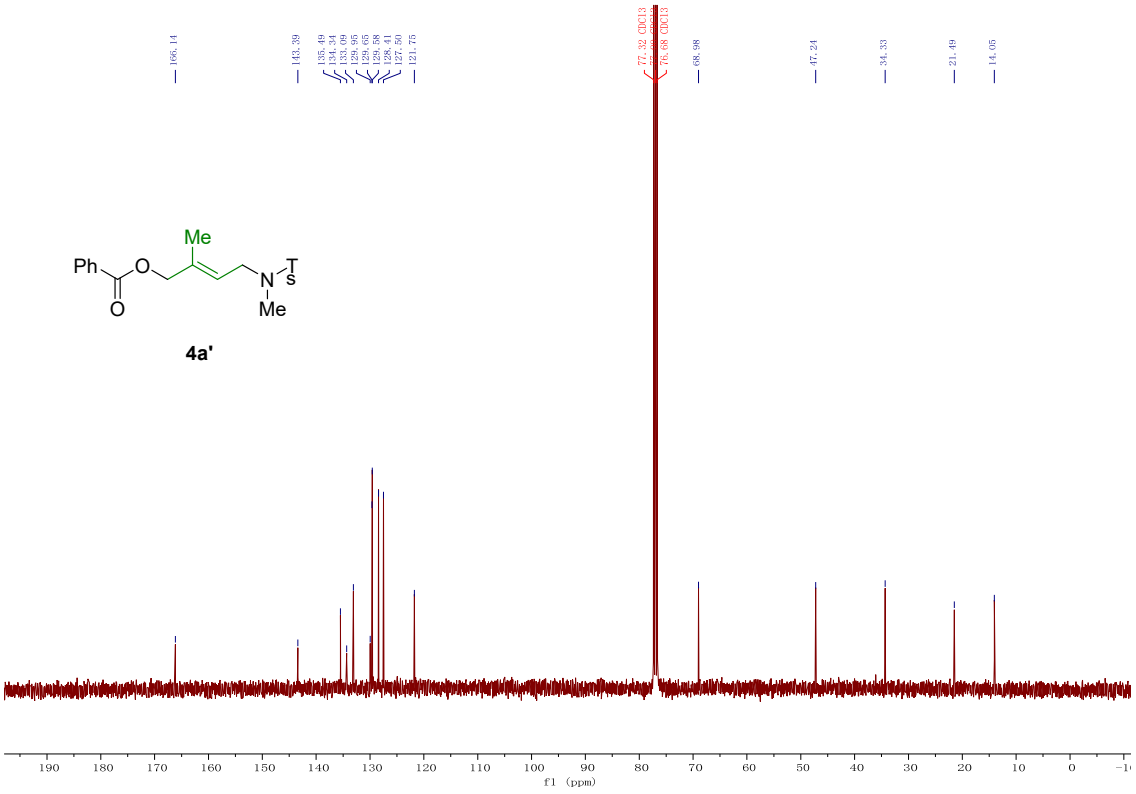
^{13}C NMR (101 MHz, $CDCl_3$)



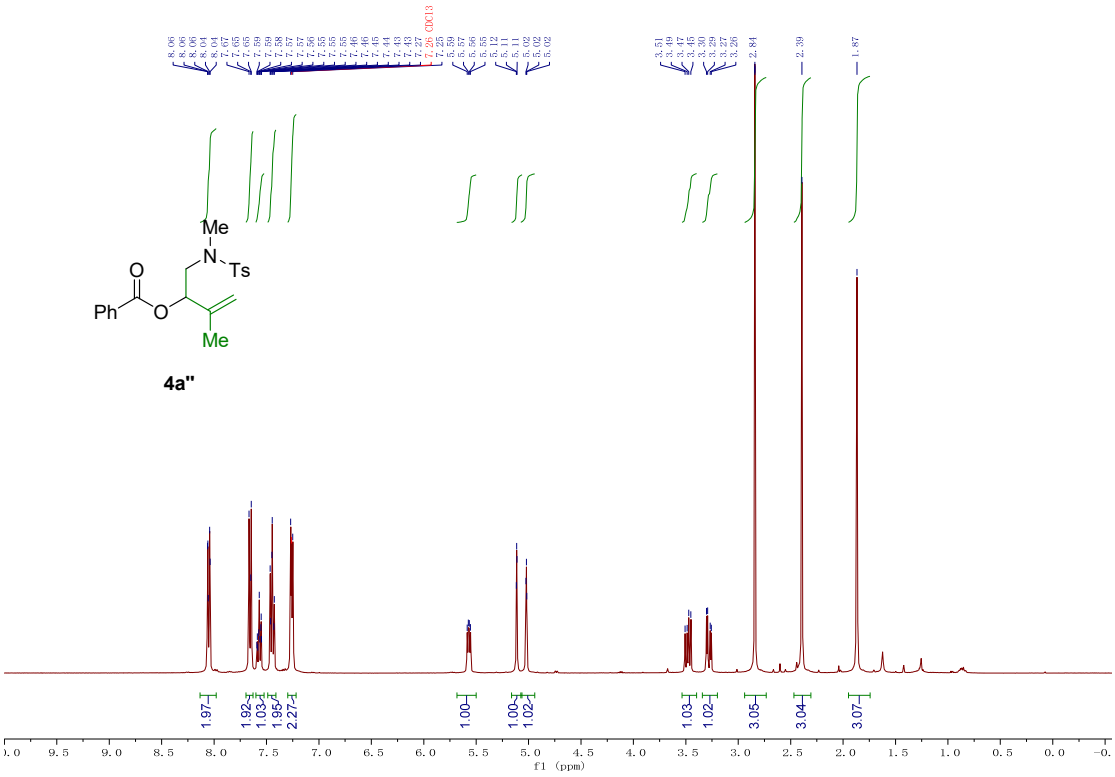
^{1}H NMR (400 MHz, $CDCl_3$)



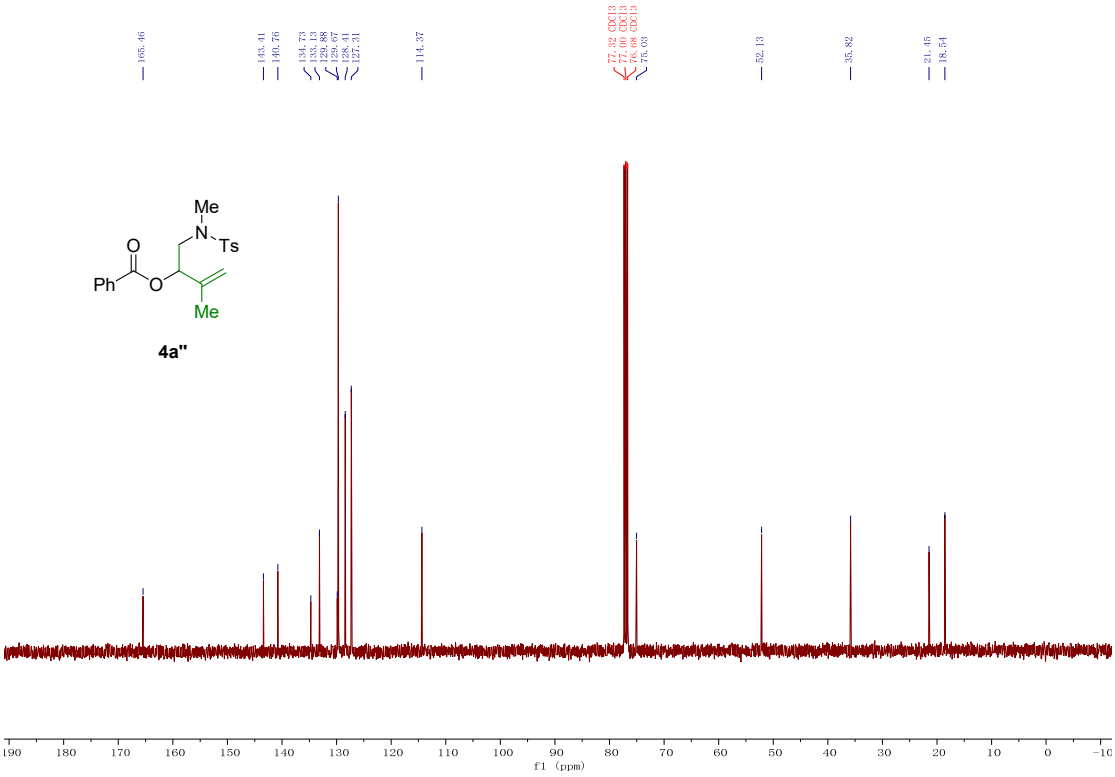
^{13}C NMR (101 MHz, $CDCl_3$)



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



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



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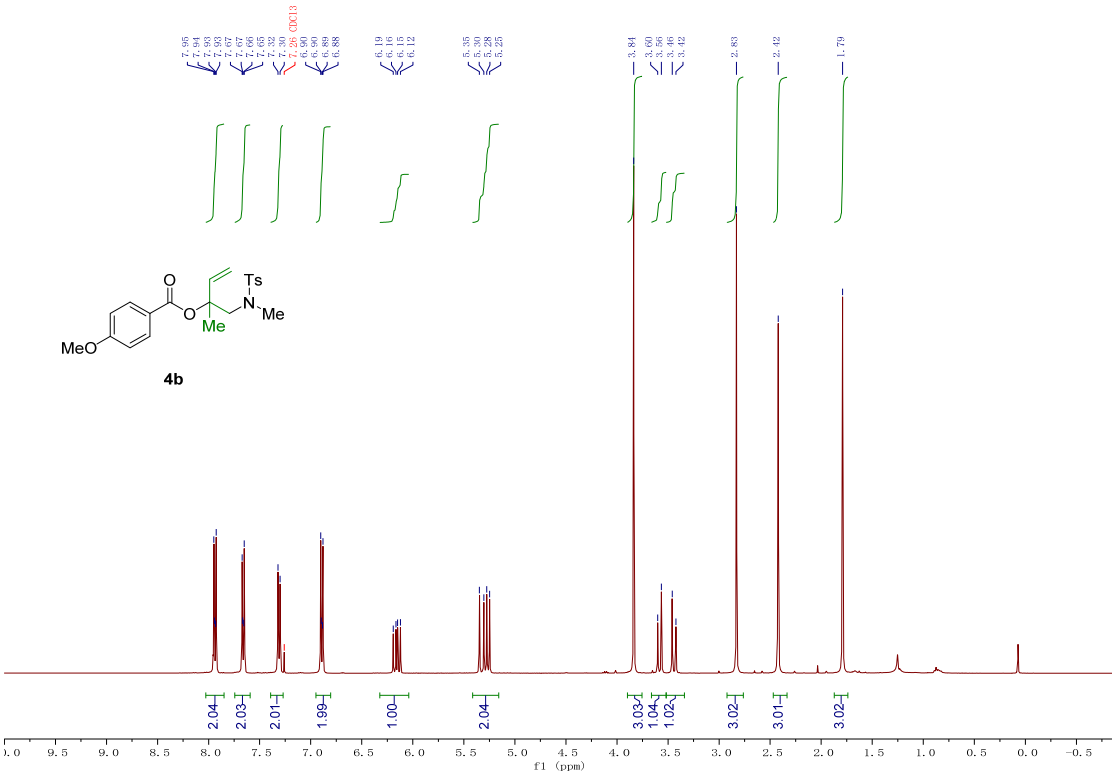
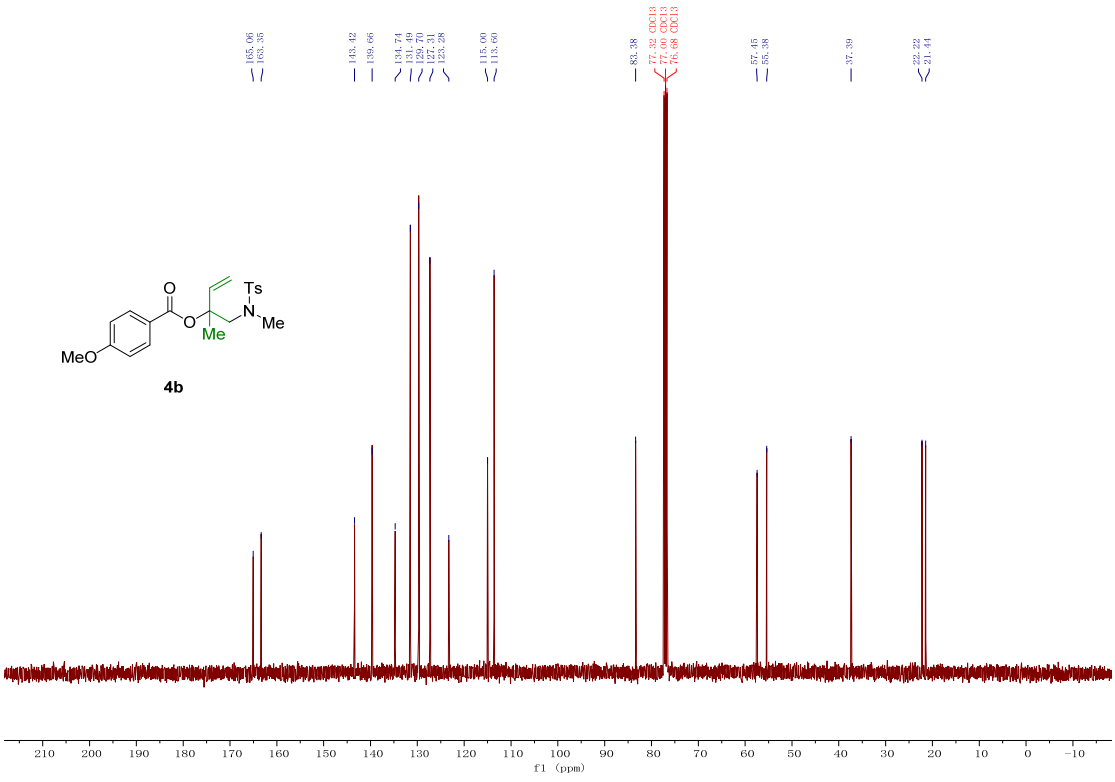
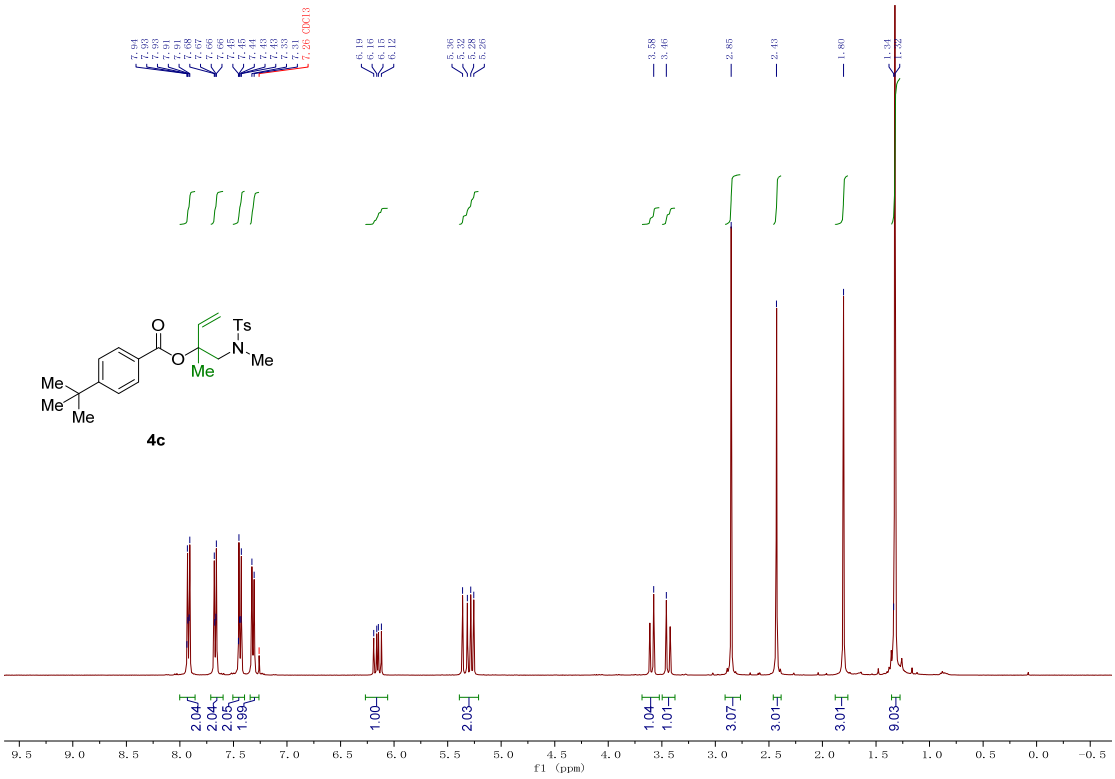


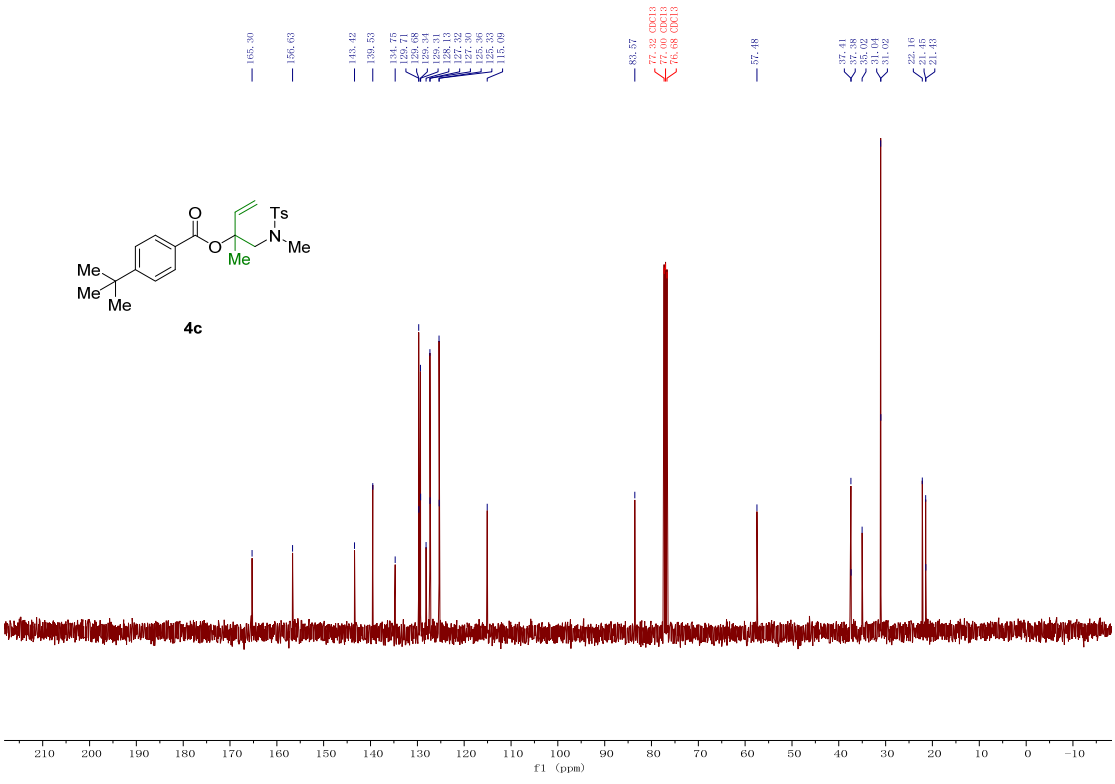
^{13}C NMR (101 MHz, $CDCl_3$)



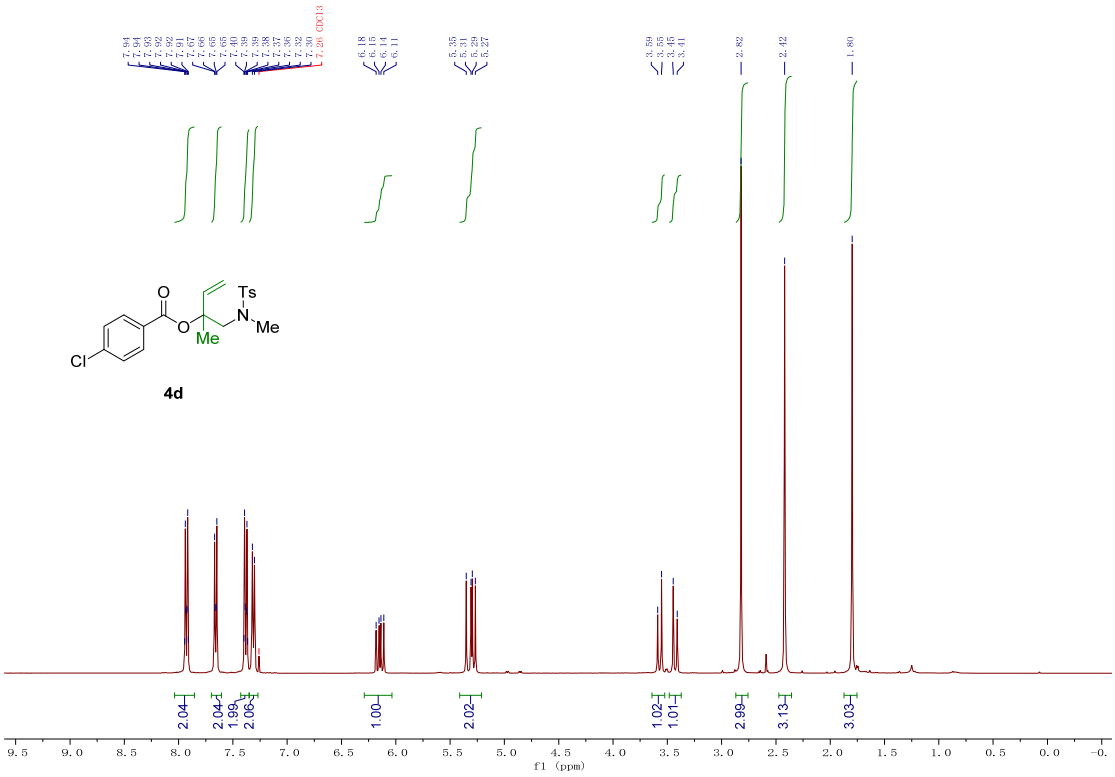
^{1}H NMR (400 MHz, $CDCl_3$)



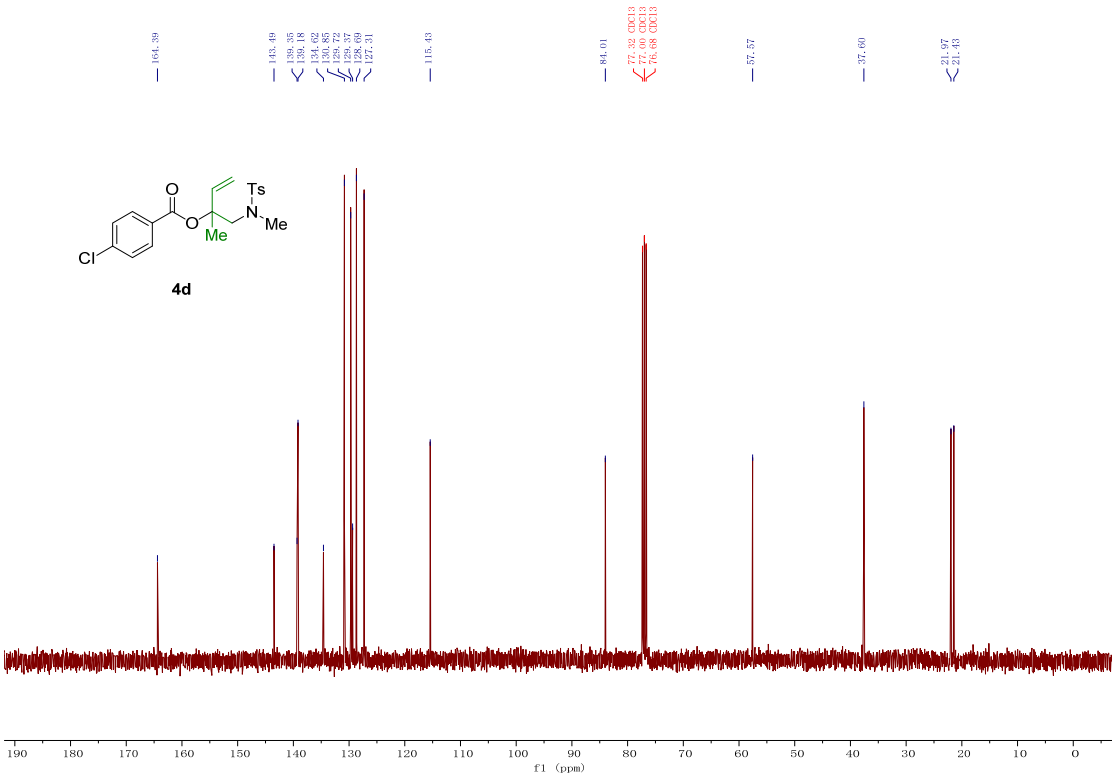
^{13}C NMR (101 MHz, $CDCl_3$)



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



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



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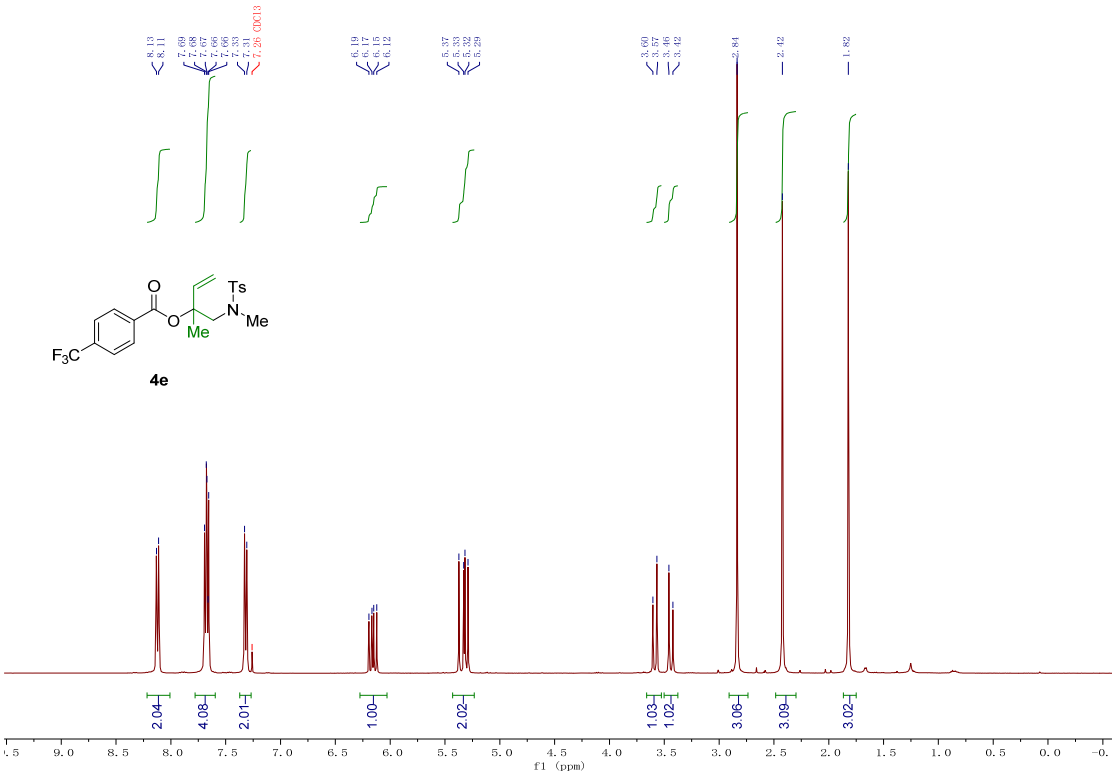
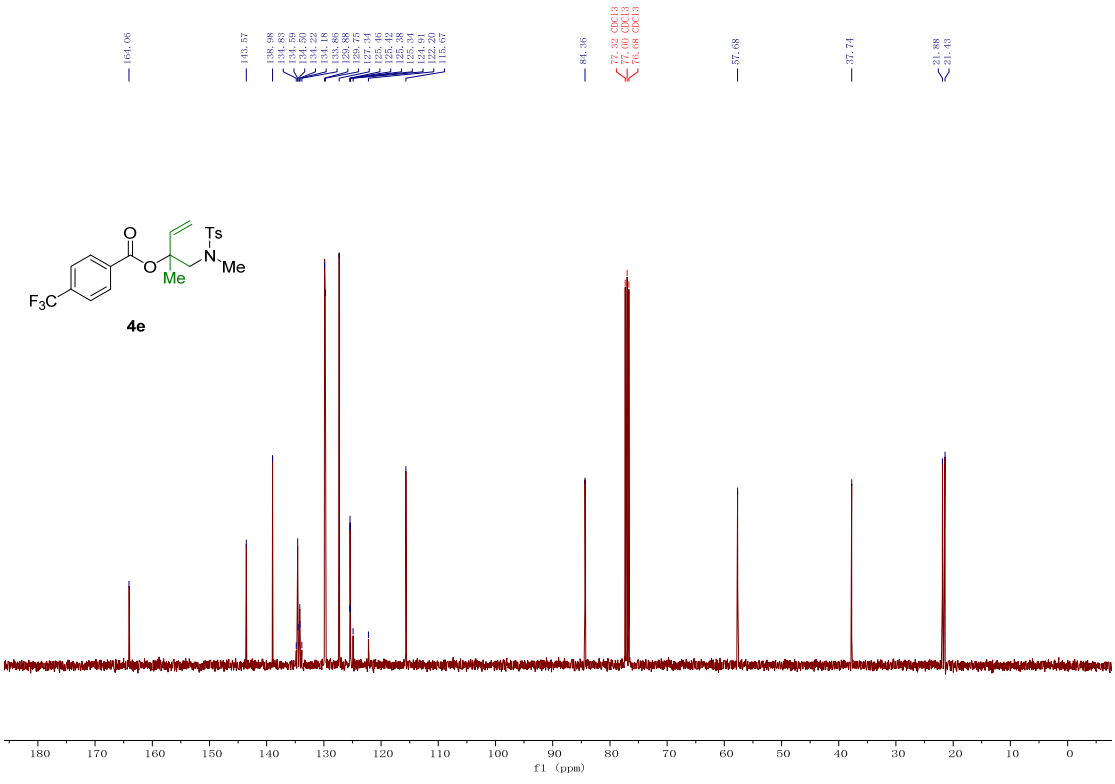
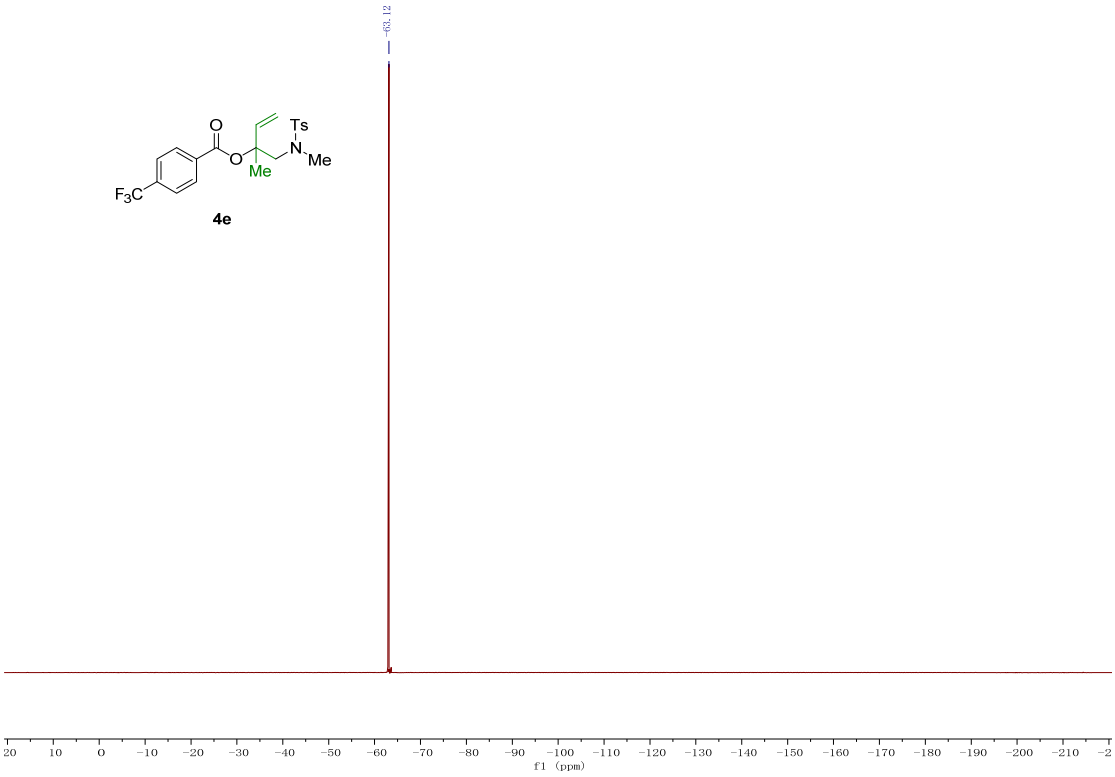


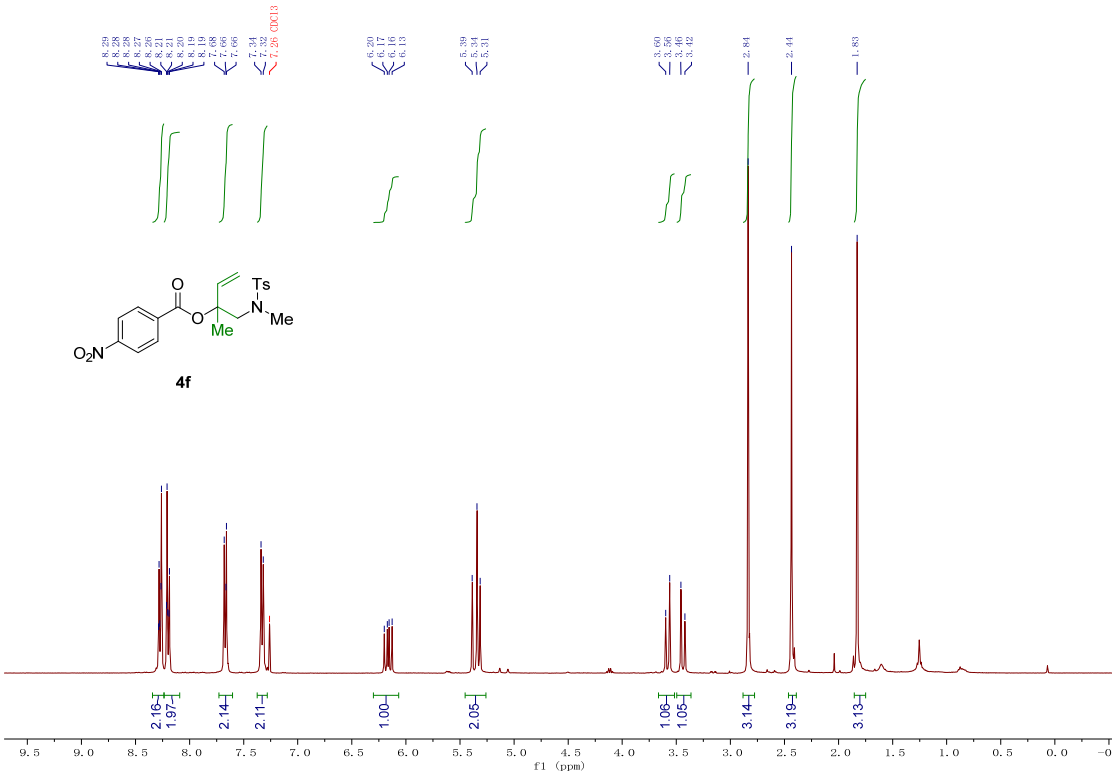
^{13}C NMR (101 MHz, $CDCl_3$)



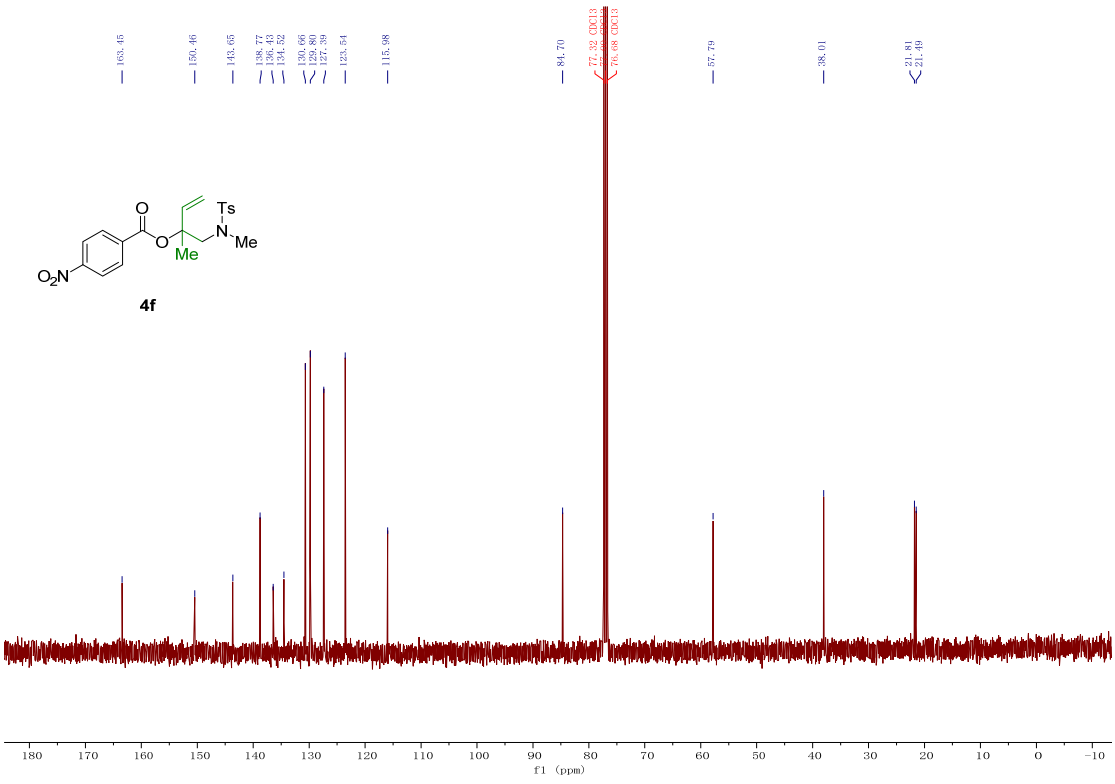
^{19}F NMR (377 MHz, $CDCl_3$)



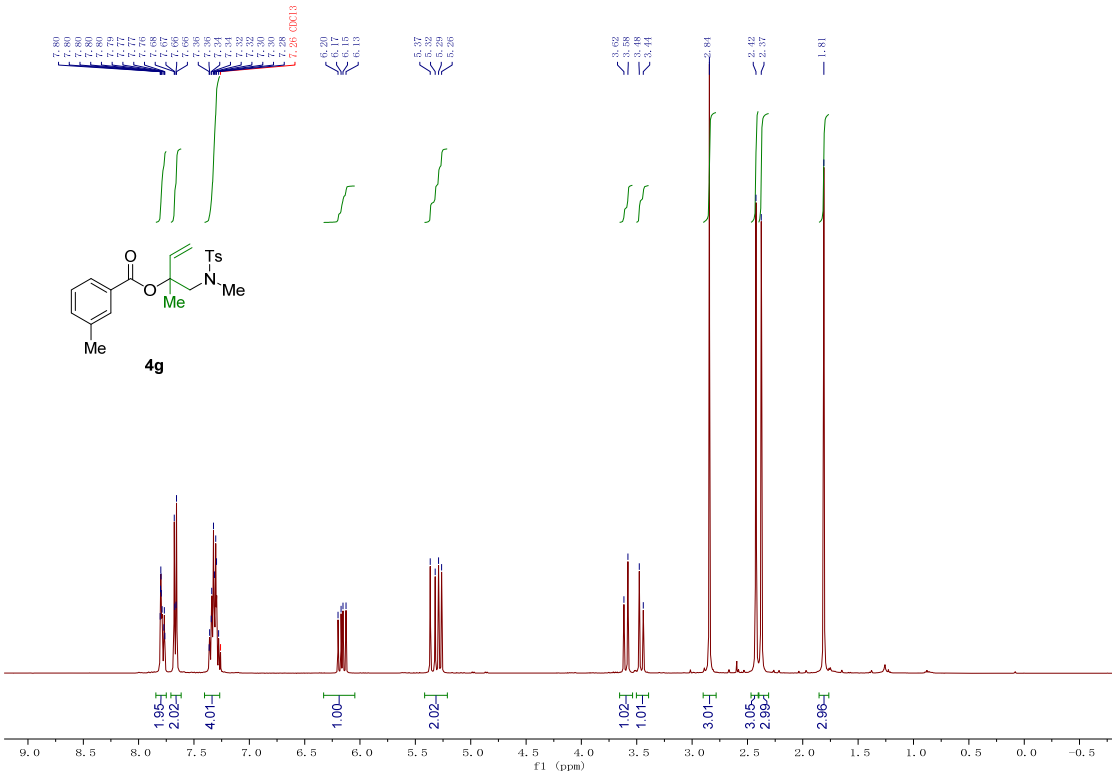
^{1}H NMR (400 MHz, $CDCl_3$)



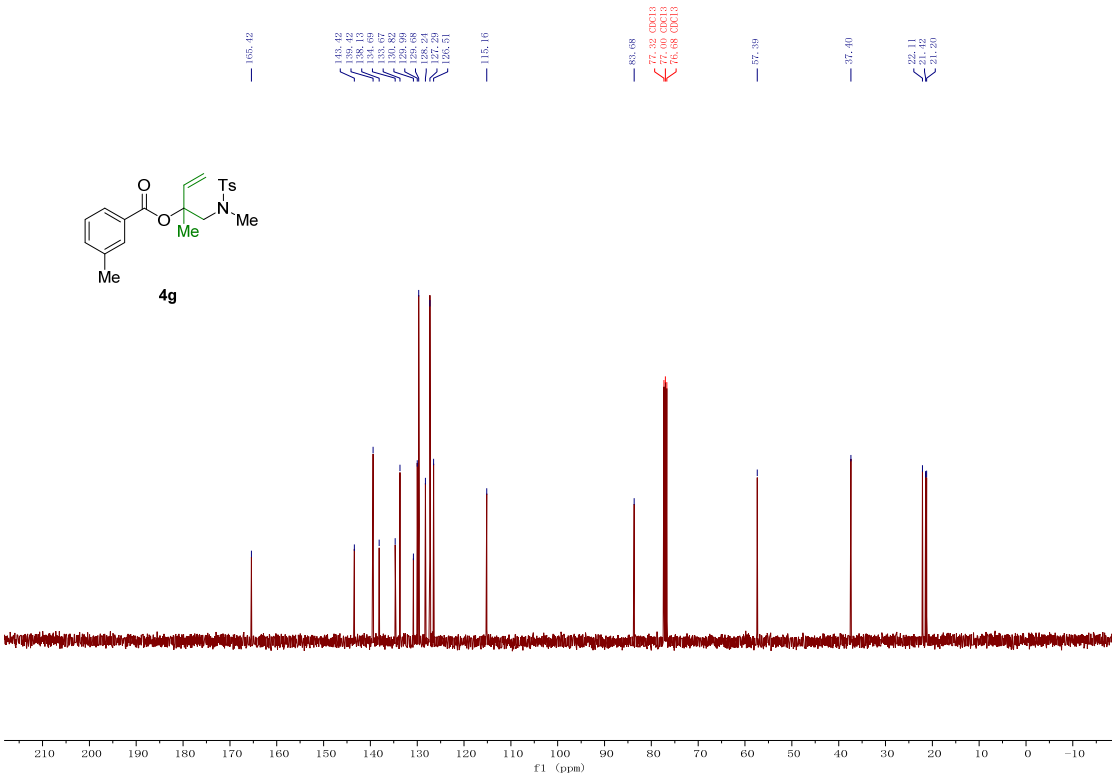
^{13}C NMR (101 MHz, $CDCl_3$)



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



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



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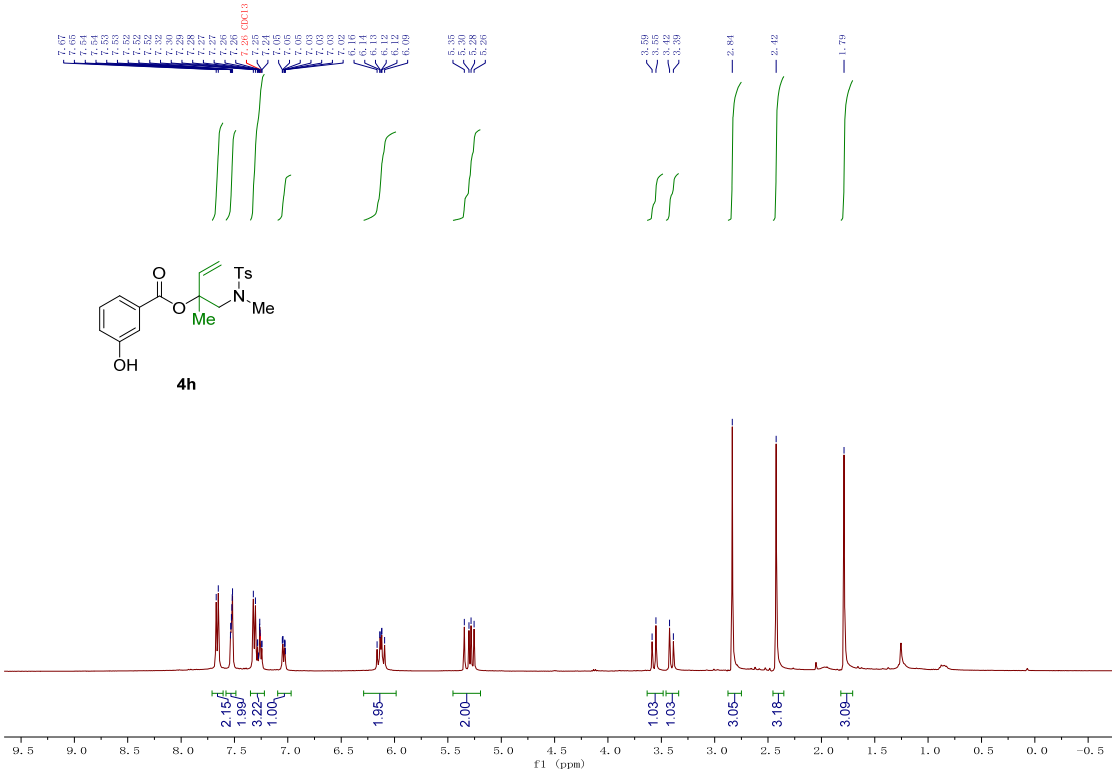
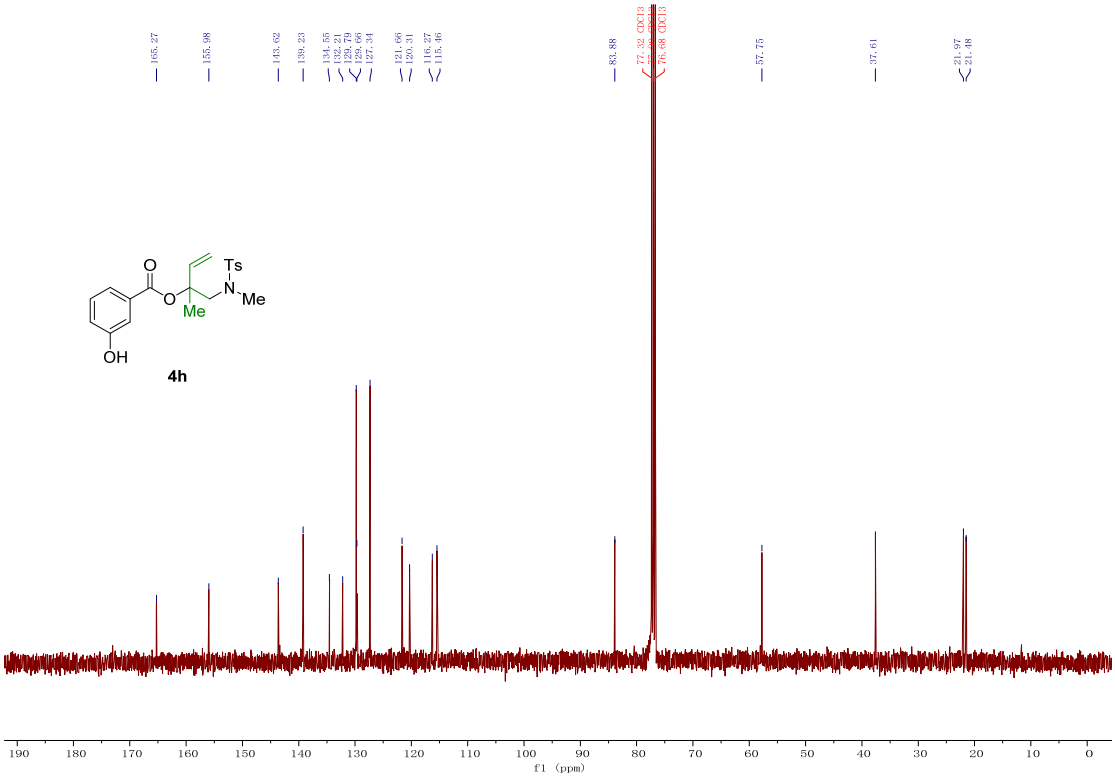
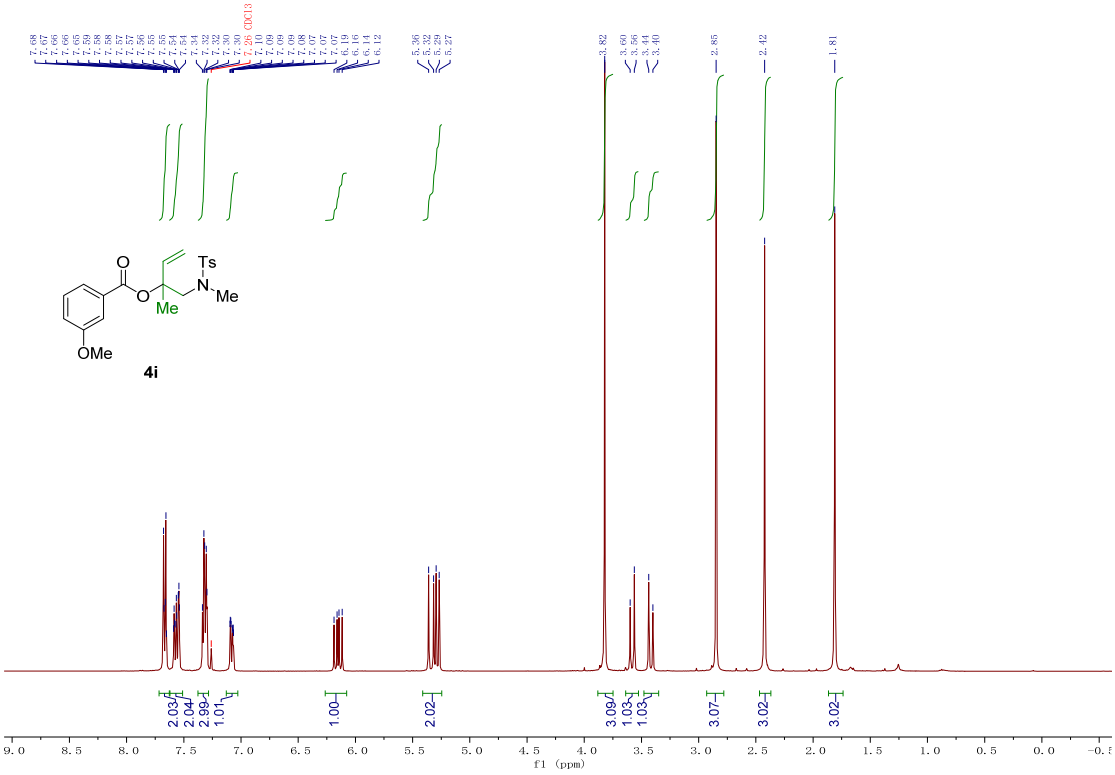


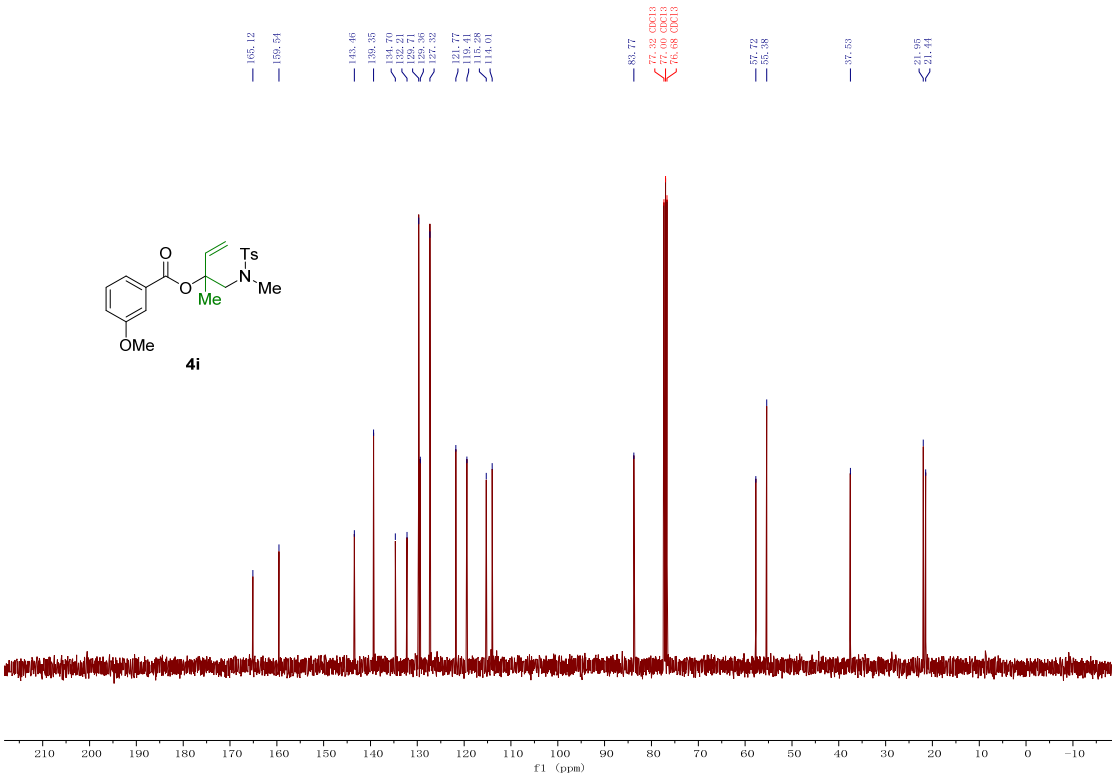
^{13}C NMR (101 MHz, $CDCl_3$)



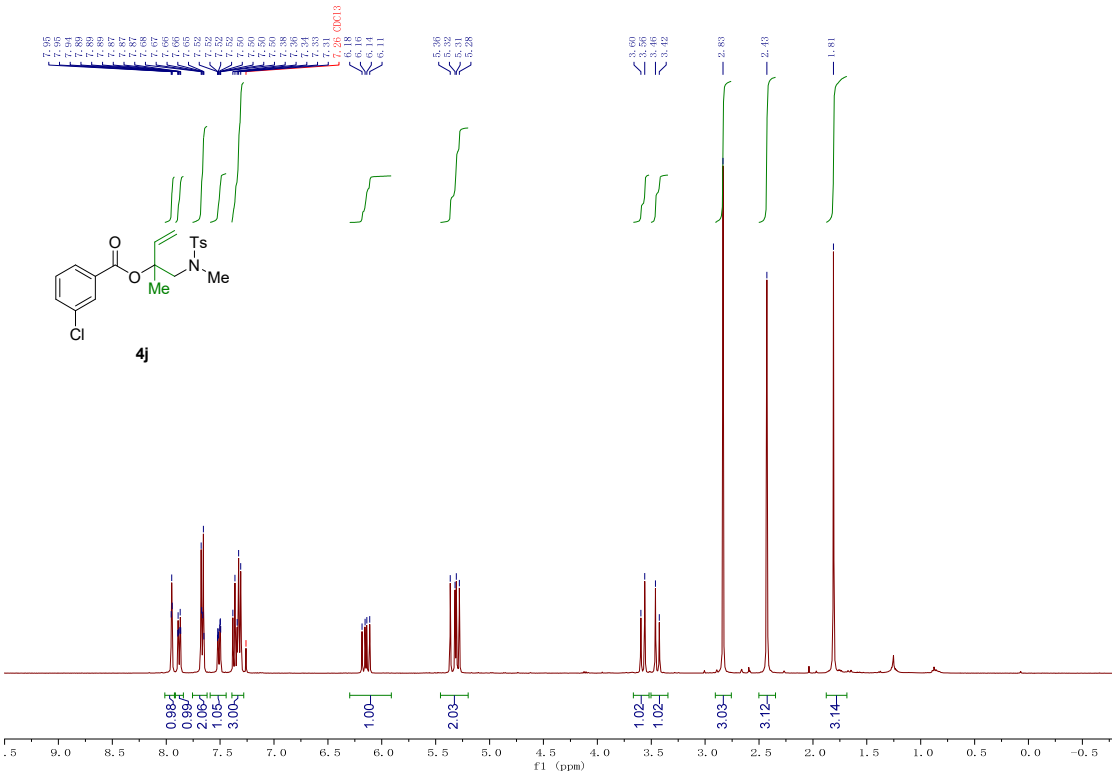
^{1}H NMR (400 MHz, $CDCl_3$)



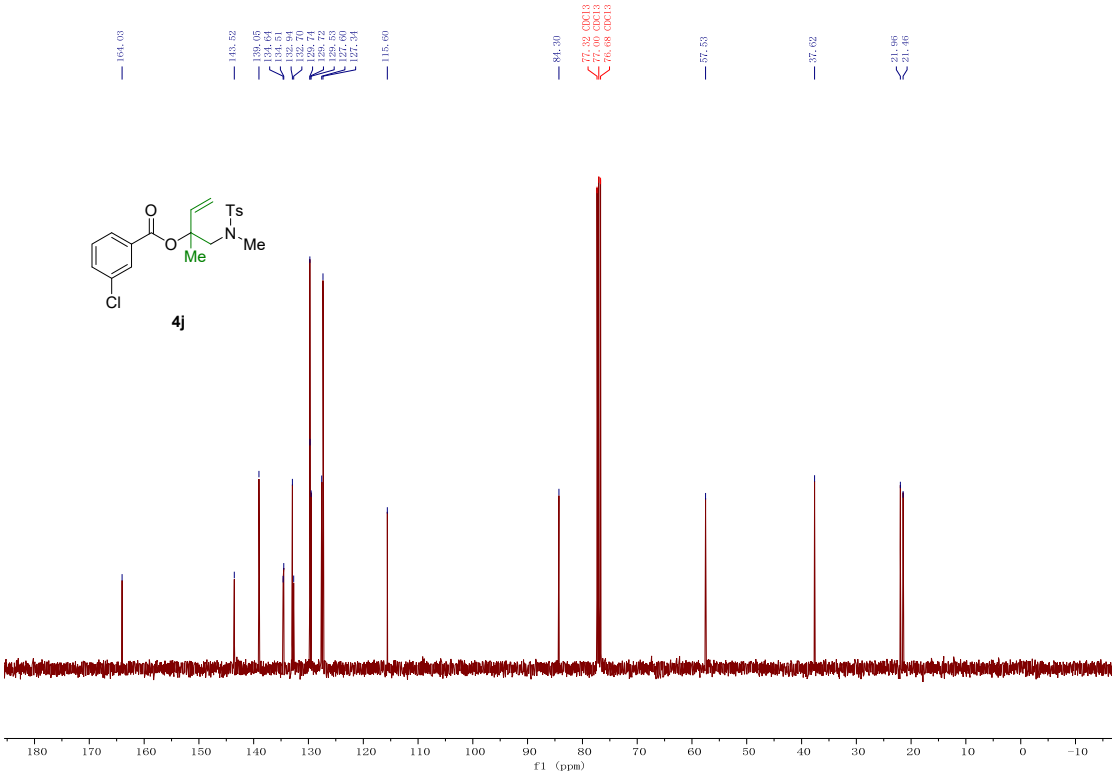
^{13}C NMR (101 MHz, $CDCl_3$)



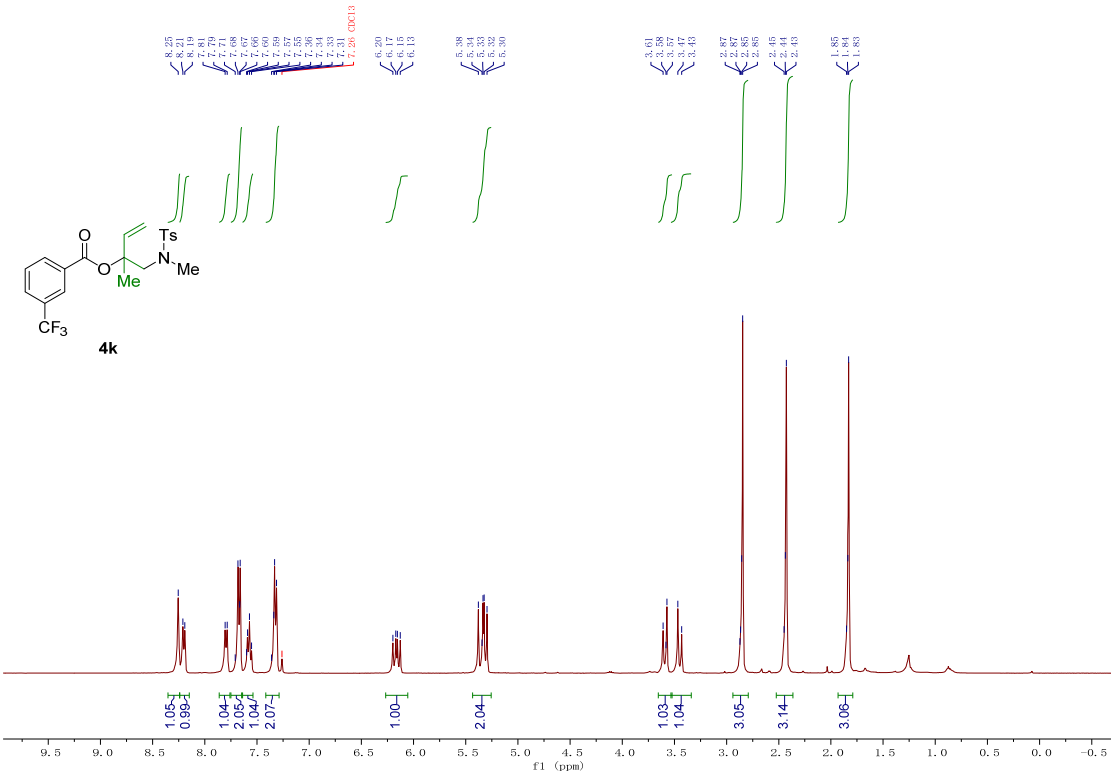
^{1}H NMR (400 MHz, $CDCl_3$)



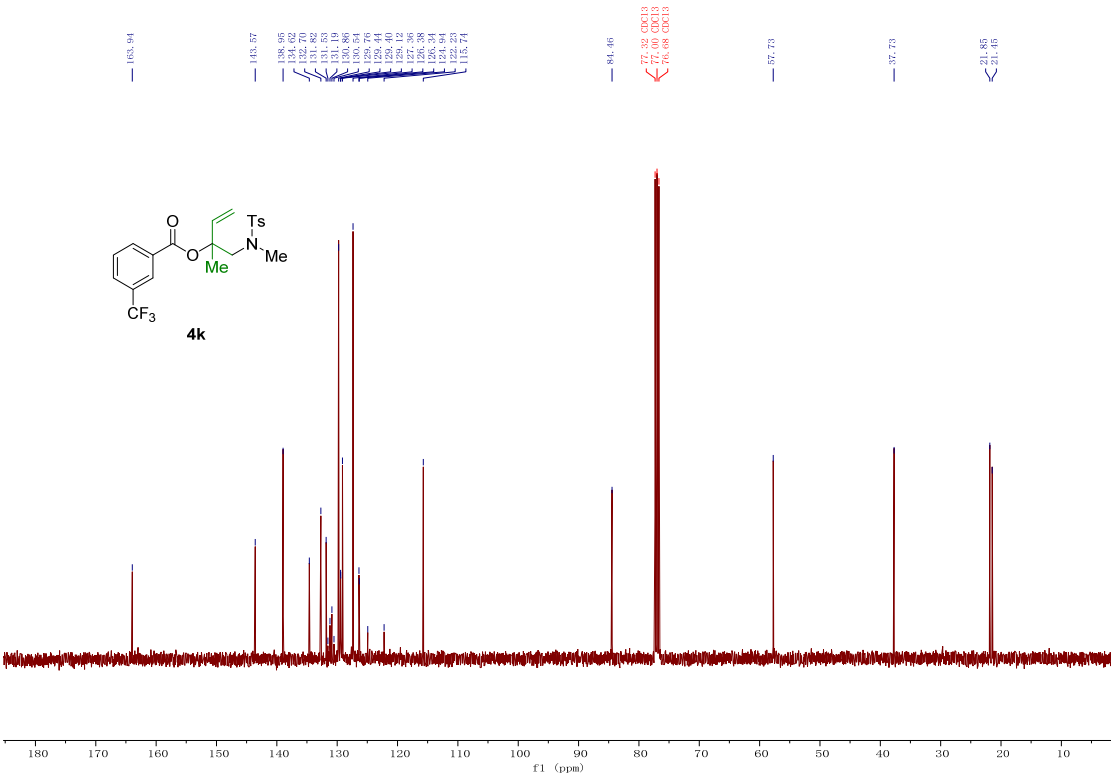
^{13}C NMR (101 MHz, $CDCl_3$)



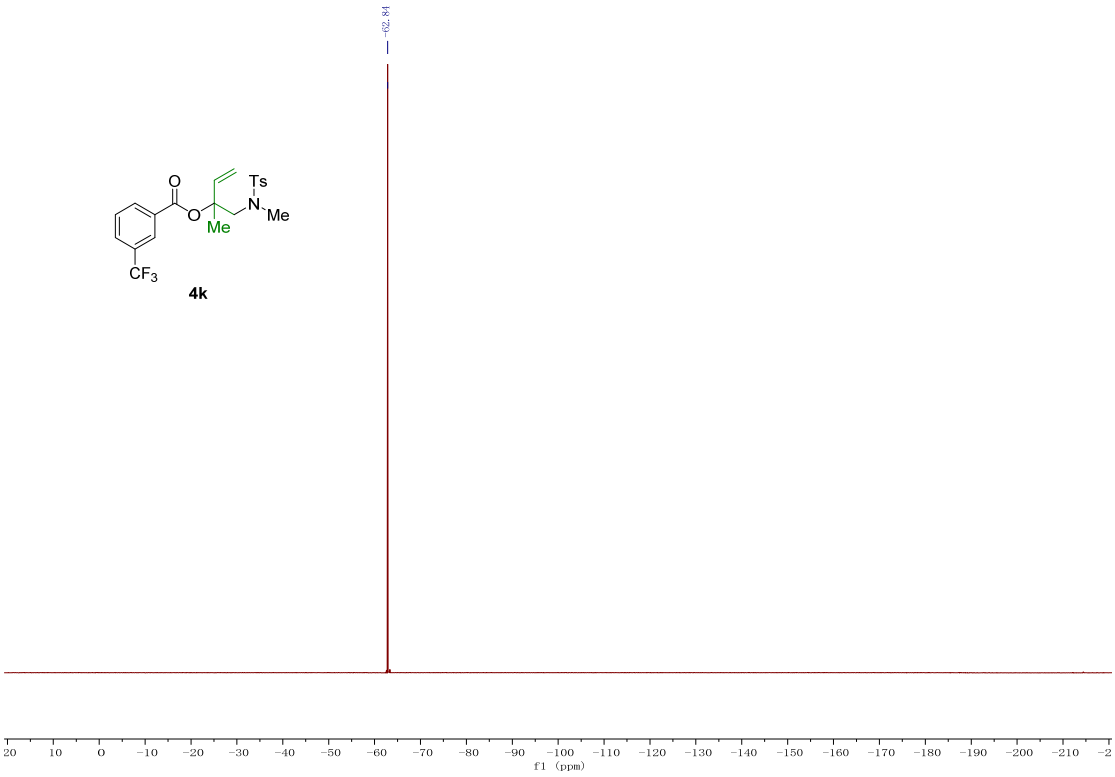
^{1}H NMR (400 MHz, $CDCl_3$)



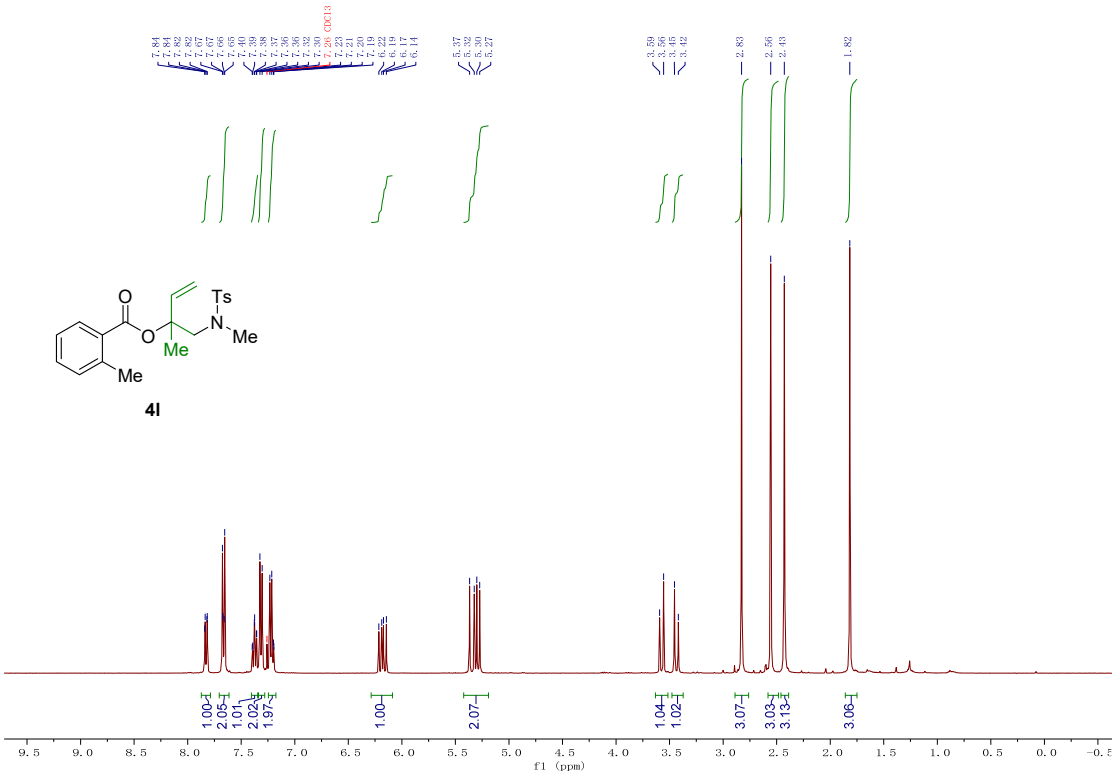
^{13}C NMR (101 MHz, $CDCl_3$)



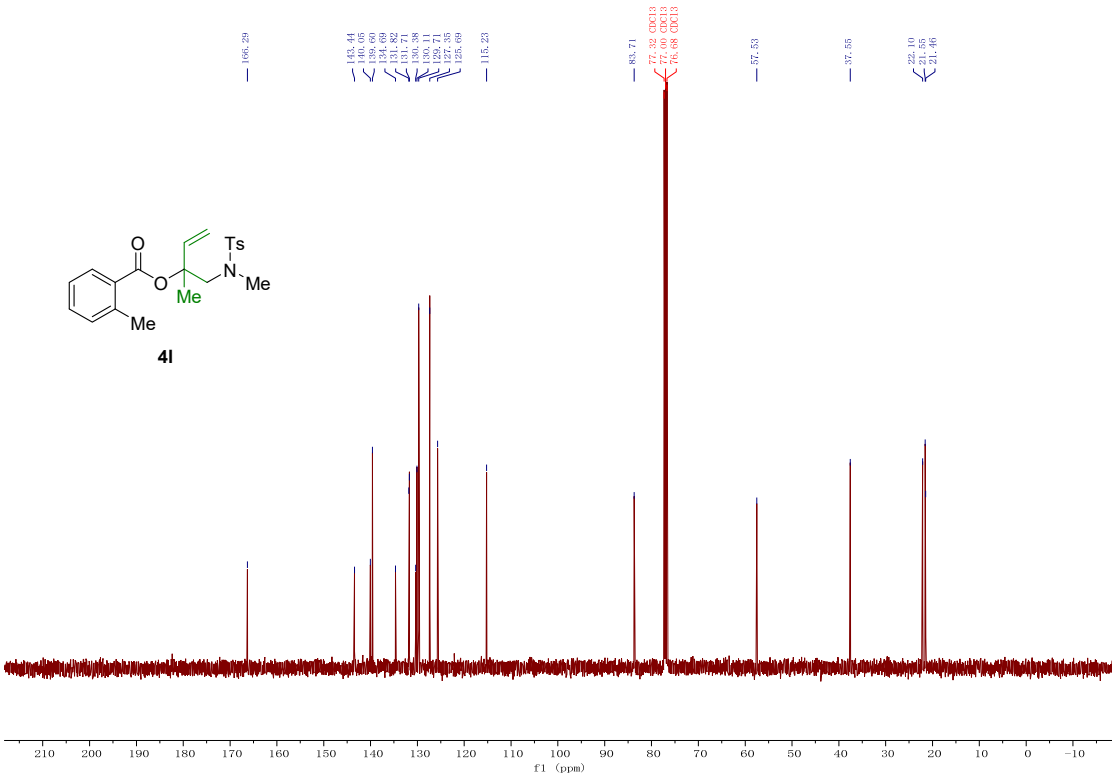
^{19}F NMR (377 MHz, $CDCl_3$)



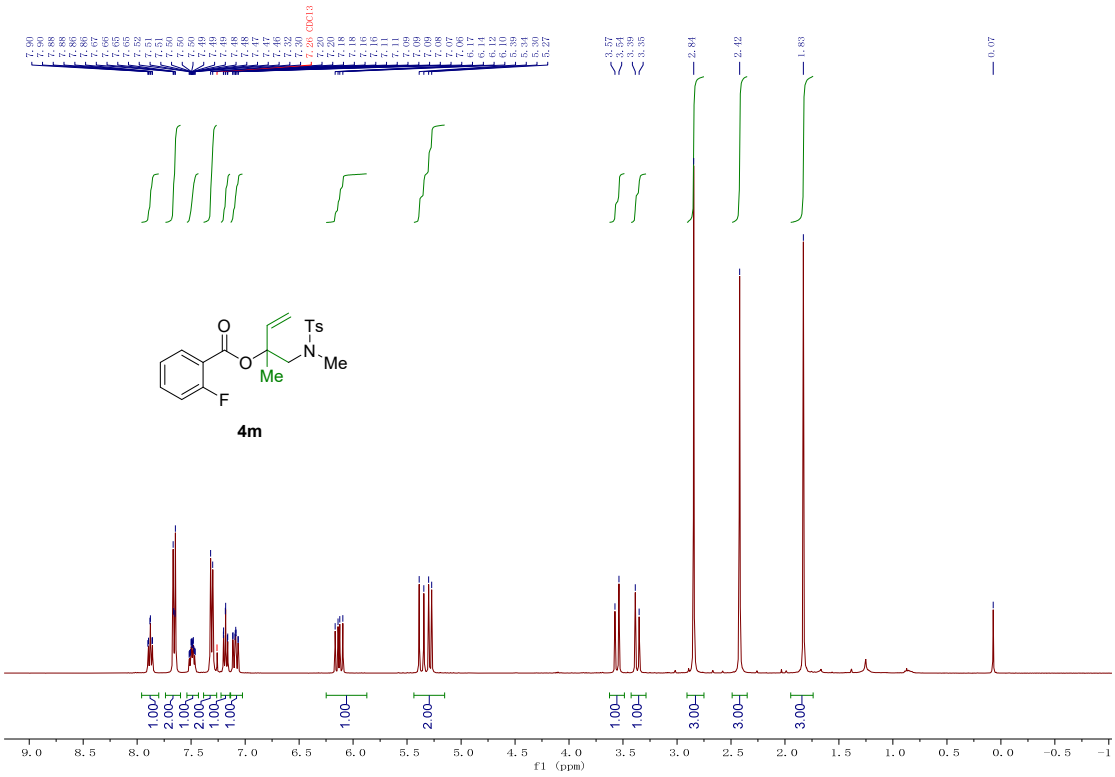
^{1}H NMR (400 MHz, $CDCl_3$)



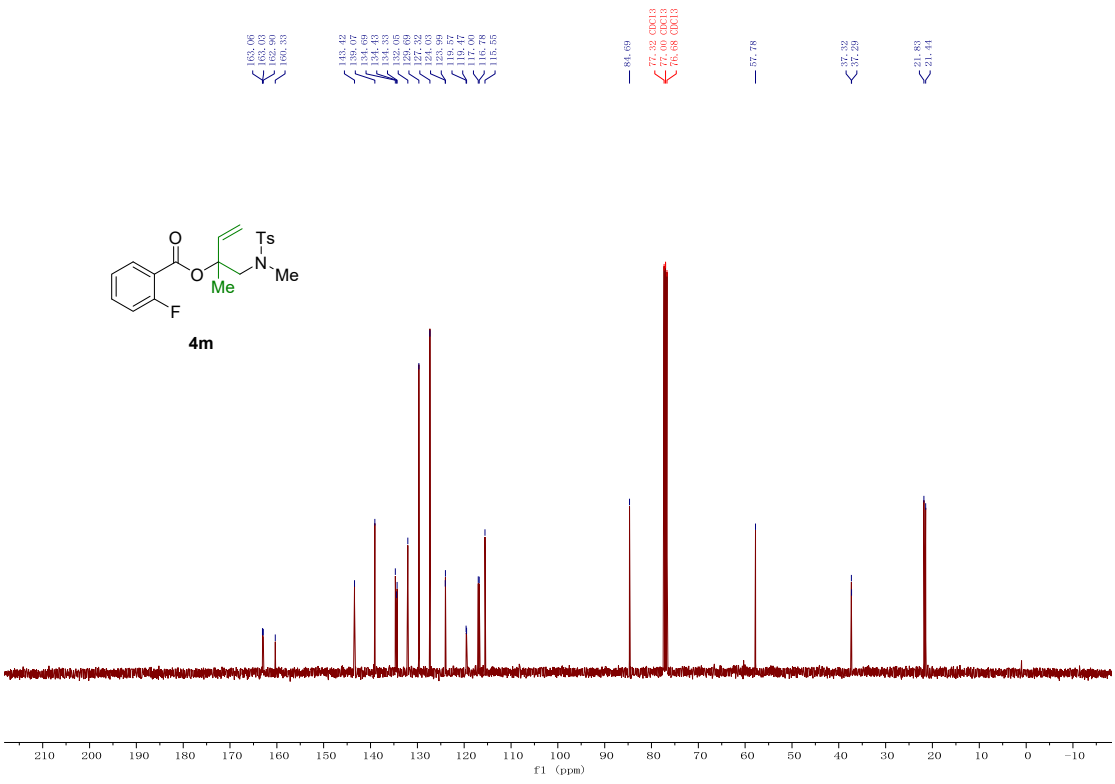
^{13}C NMR (101 MHz, $CDCl_3$)



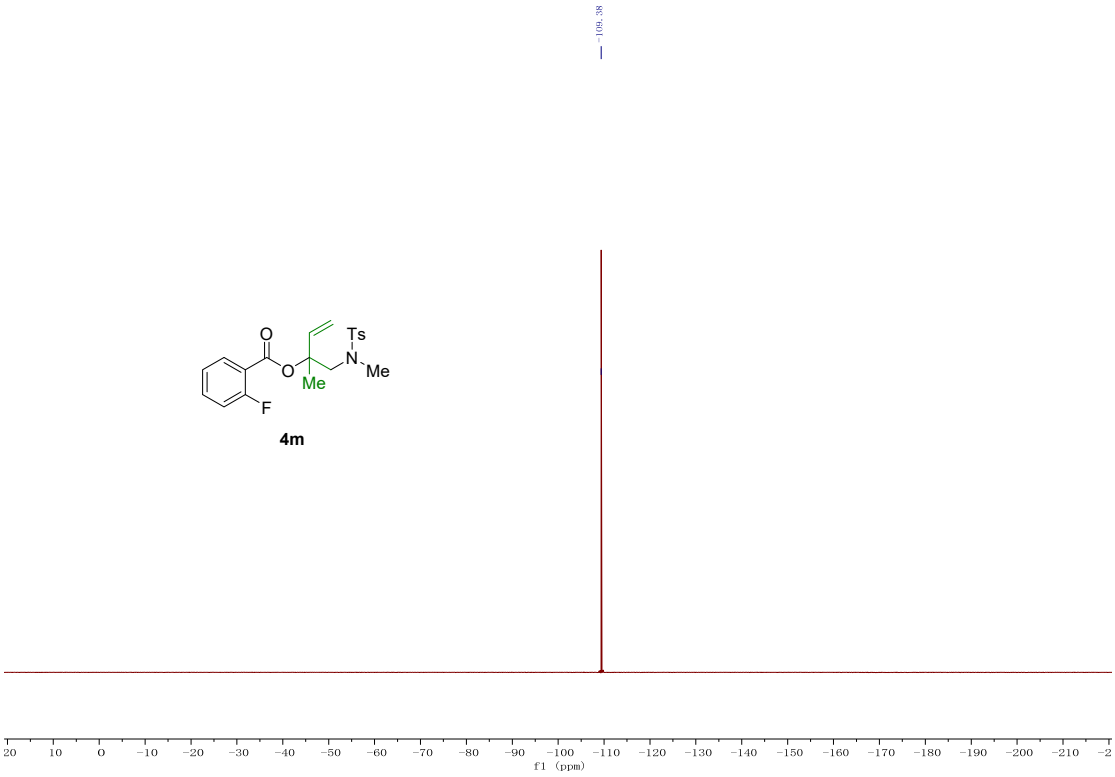
^{1}H NMR (400 MHz, $CDCl_3$)



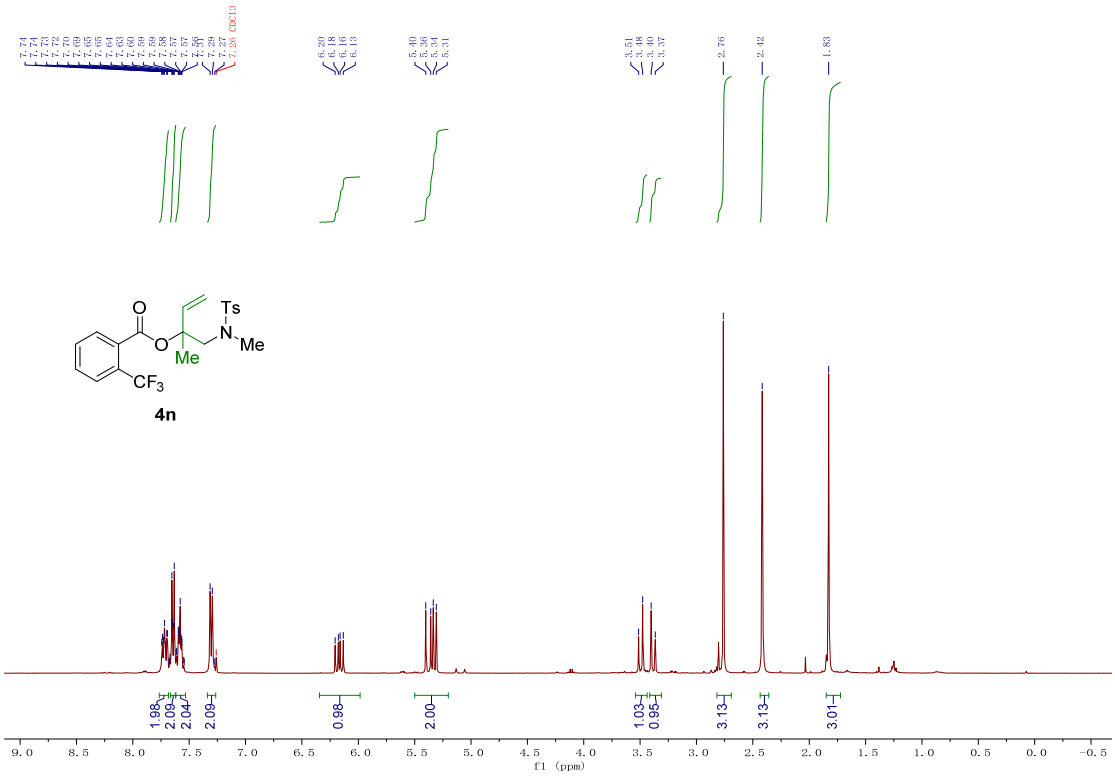
^{13}C NMR (101 MHz, $CDCl_3$)



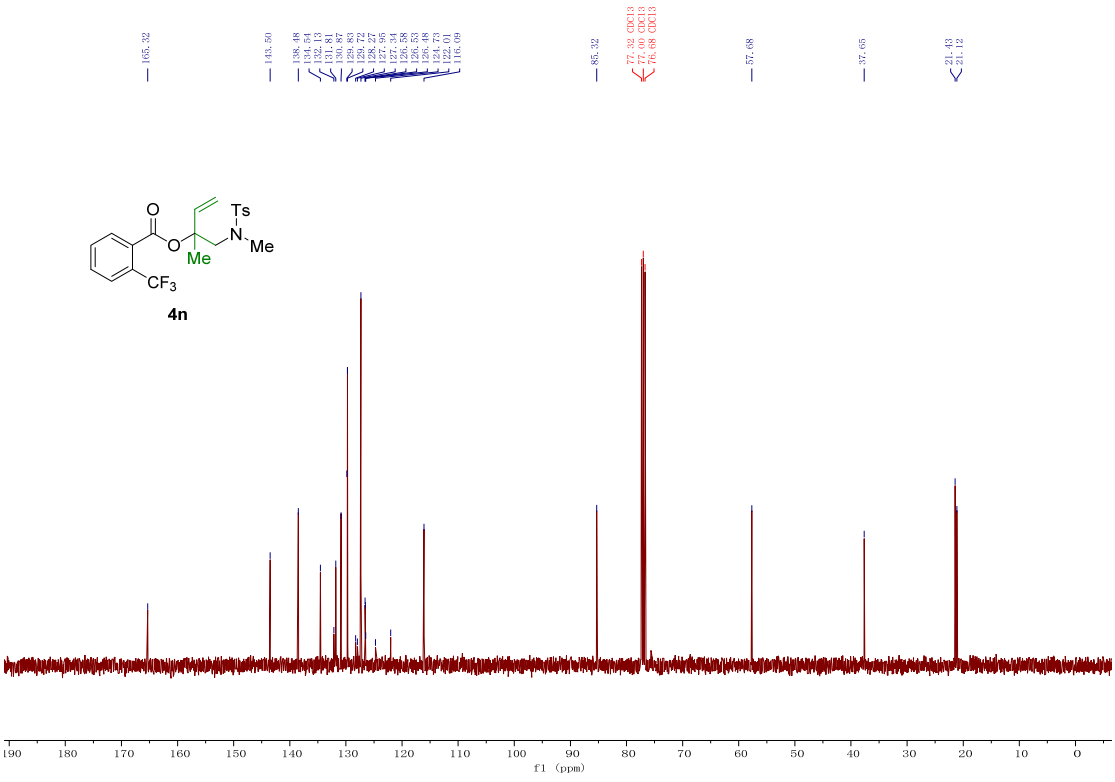
^{19}F NMR (377 MHz, $CDCl_3$)



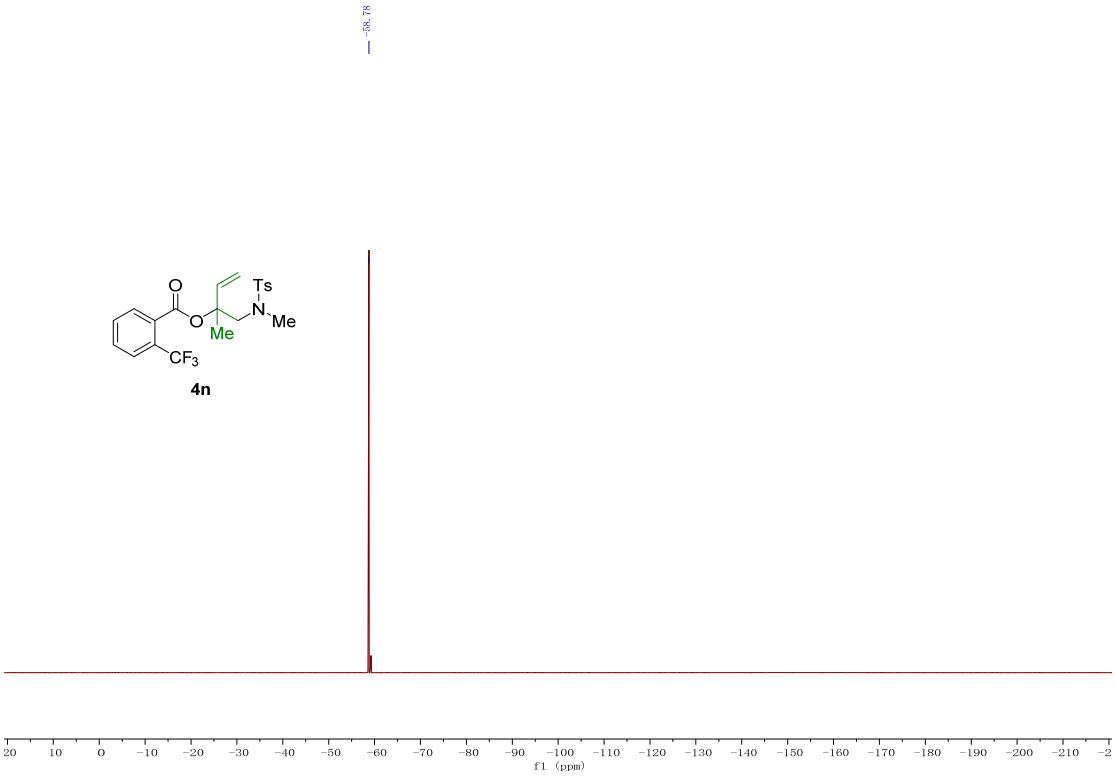
^{1}H NMR (400 MHz, $CDCl_3$)



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



^{19}F NMR (377 MHz, $CDCl_3$)



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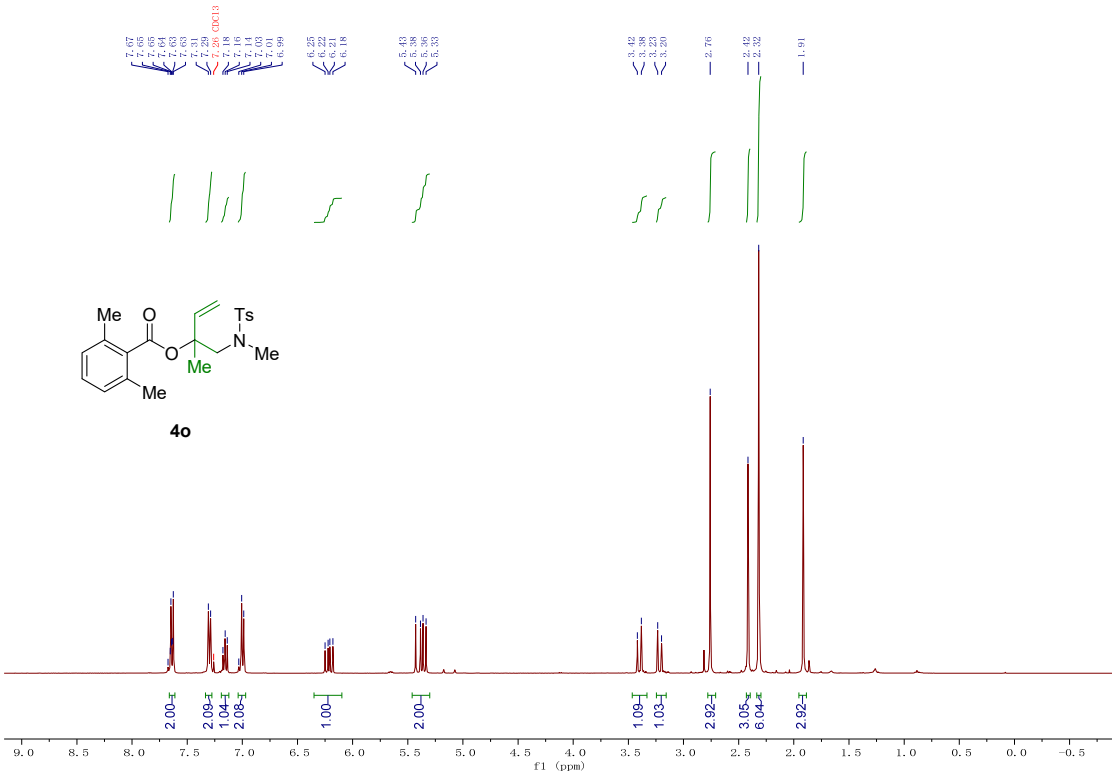

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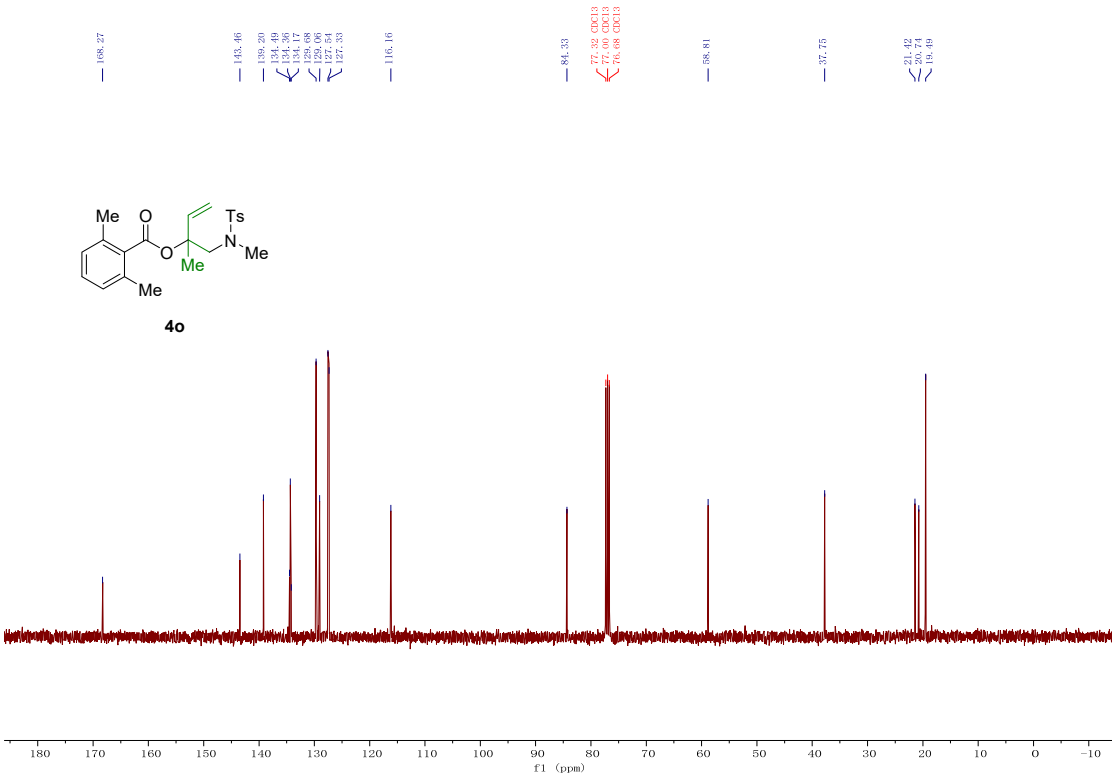

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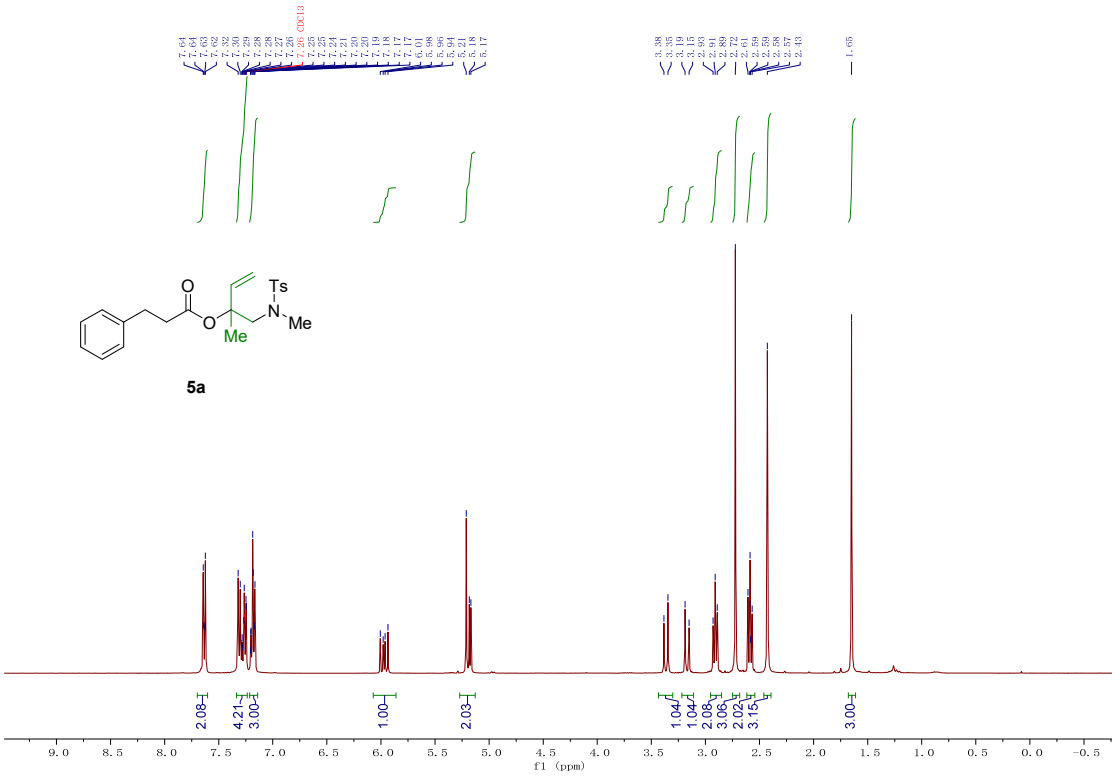

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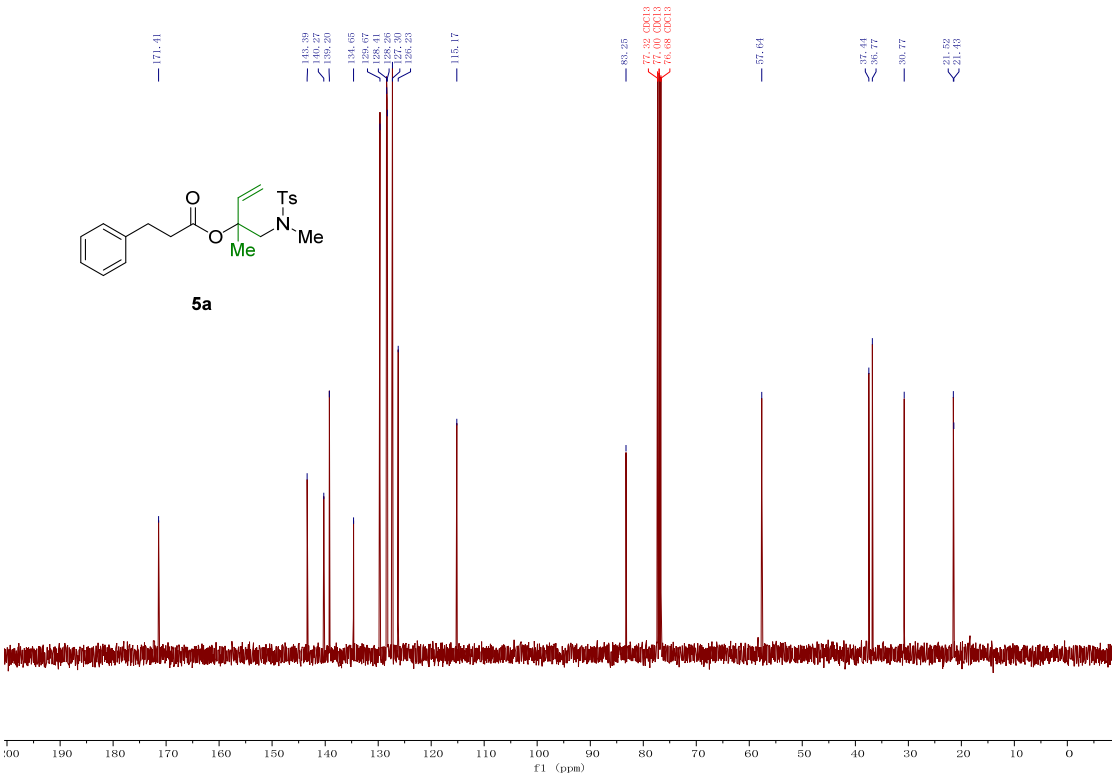

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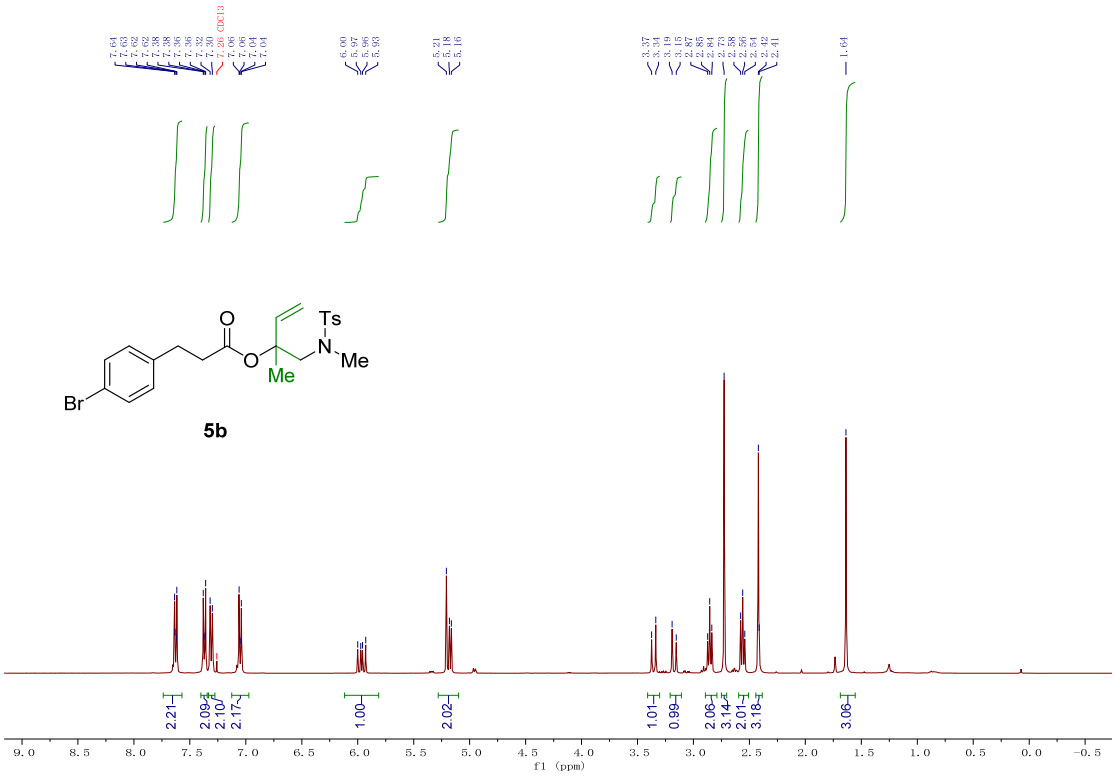

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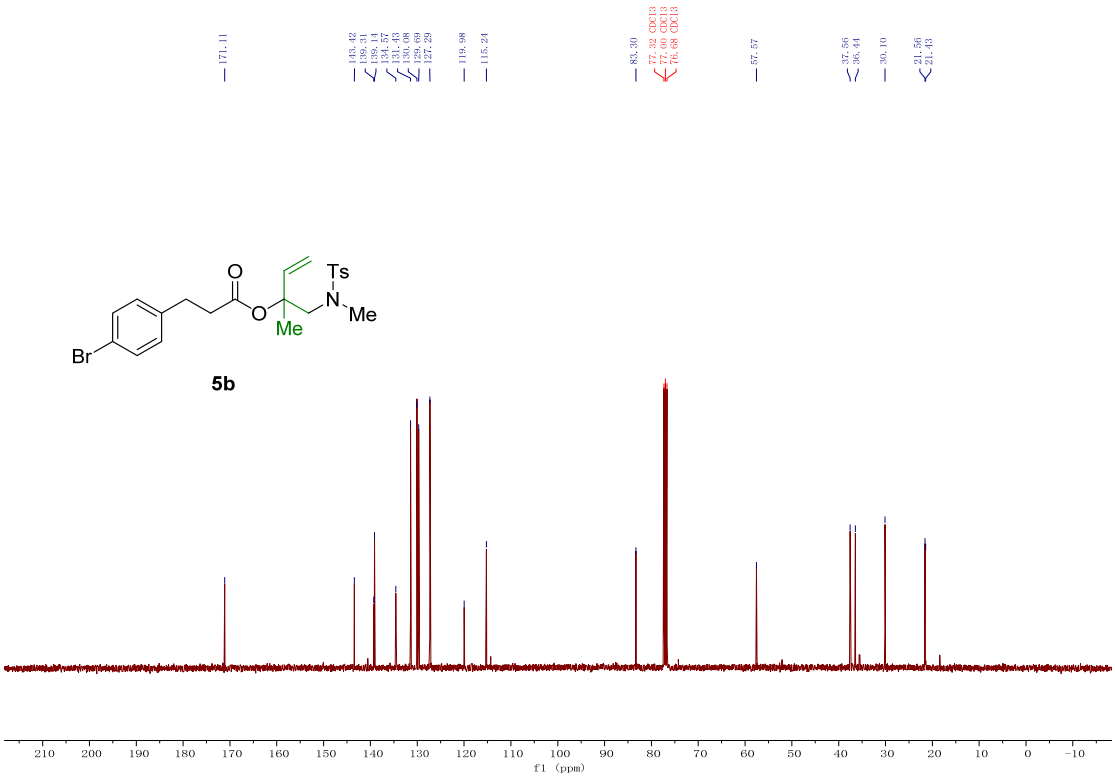

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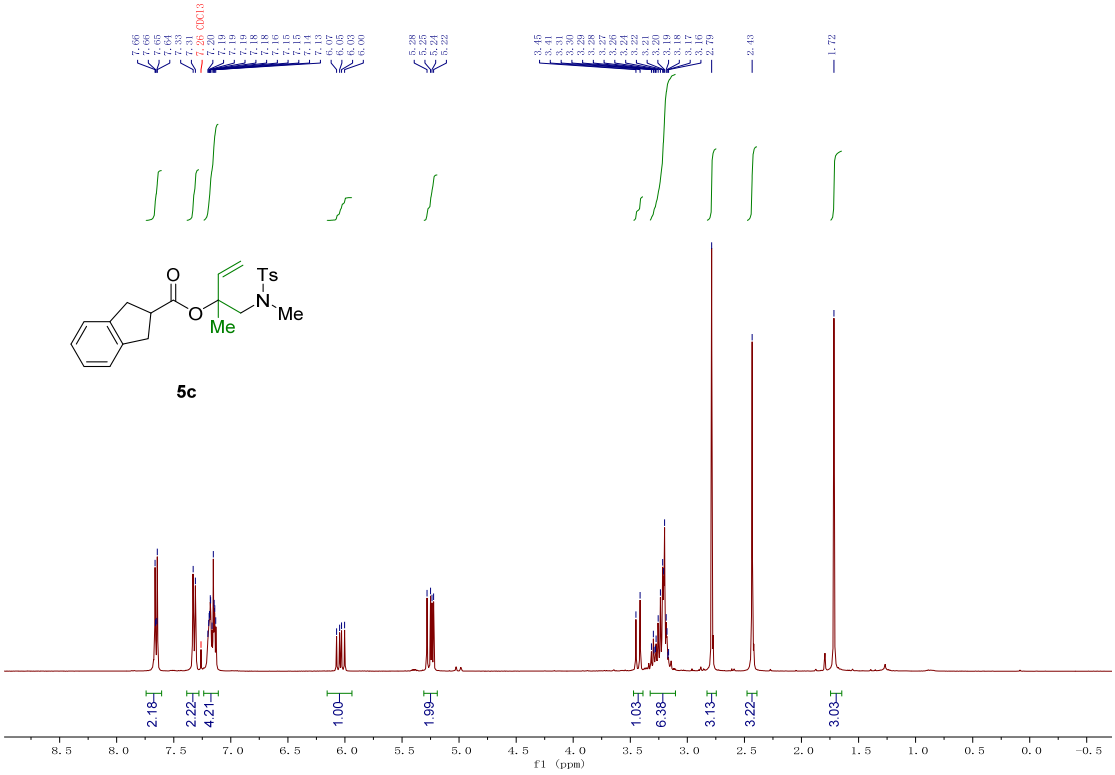

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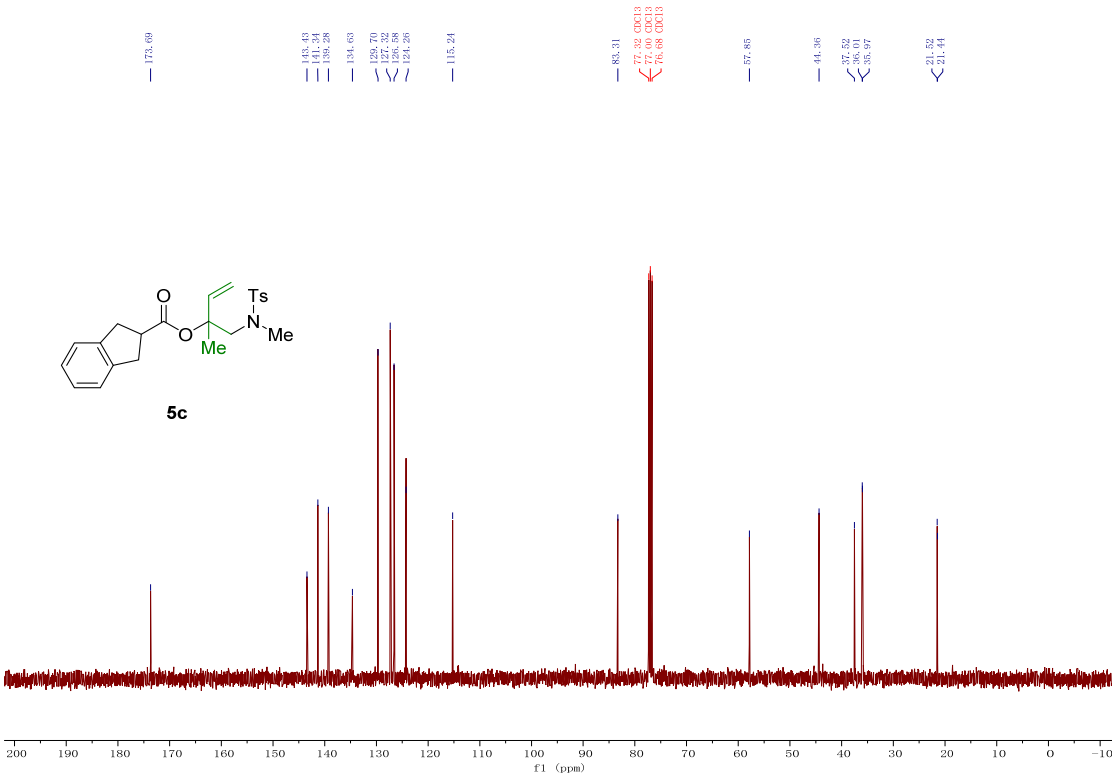

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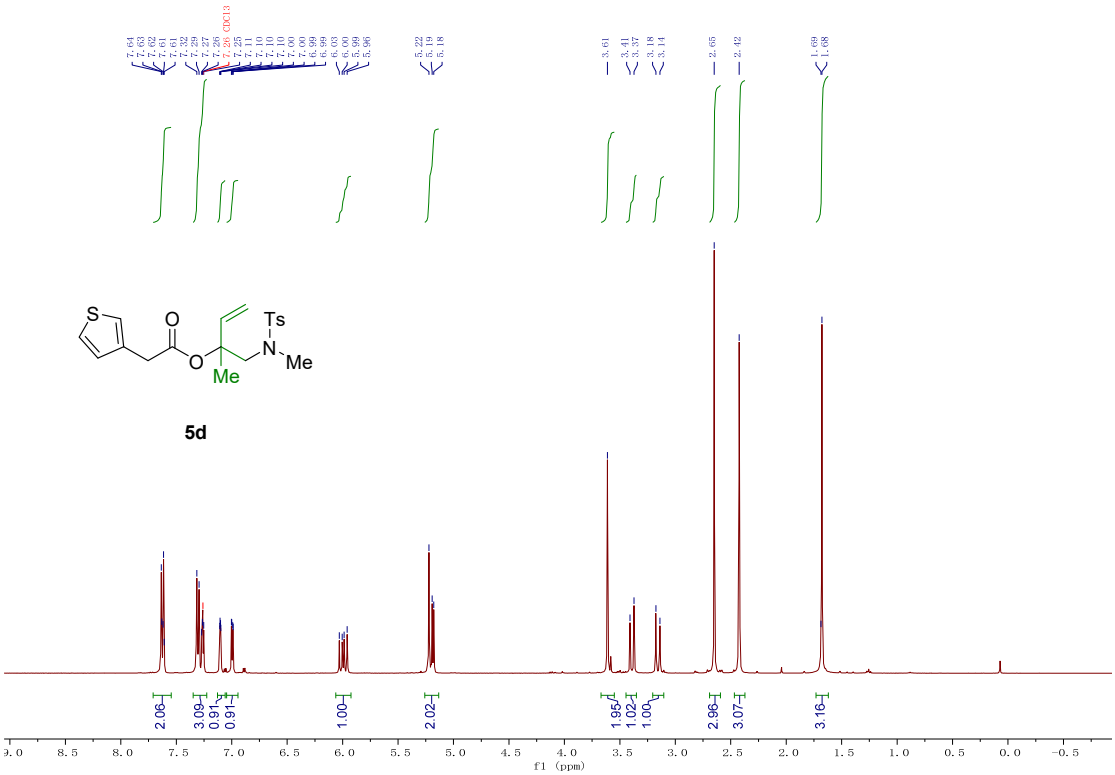

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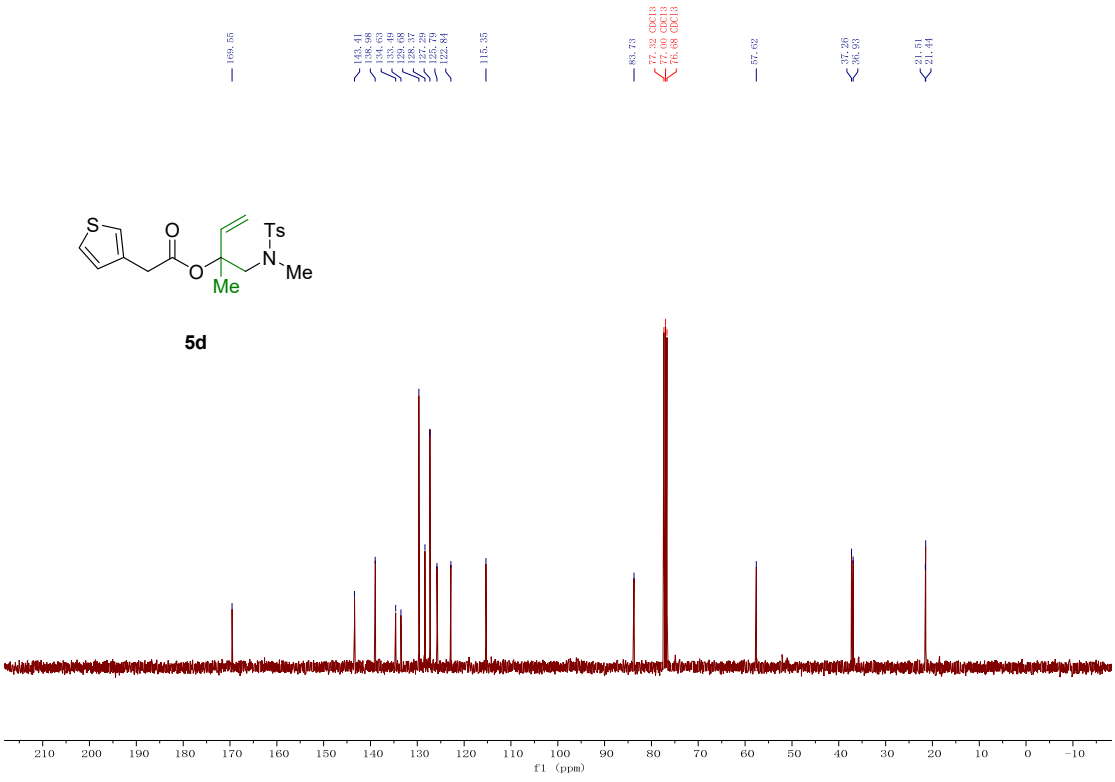

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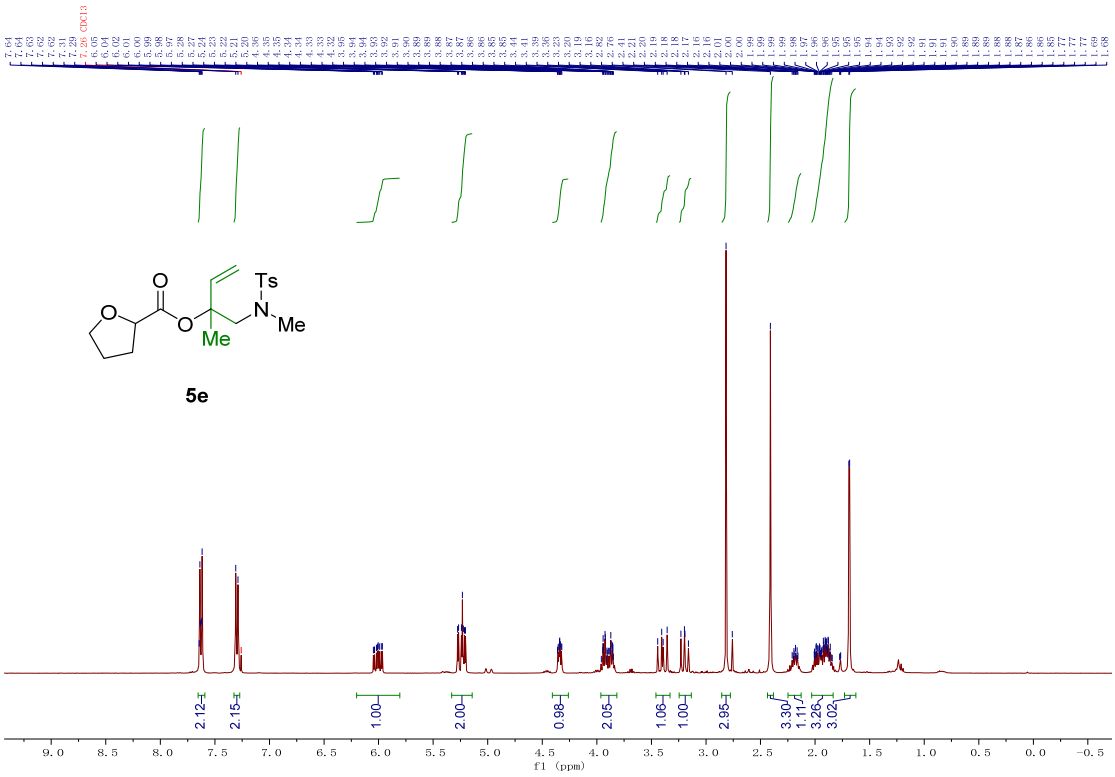

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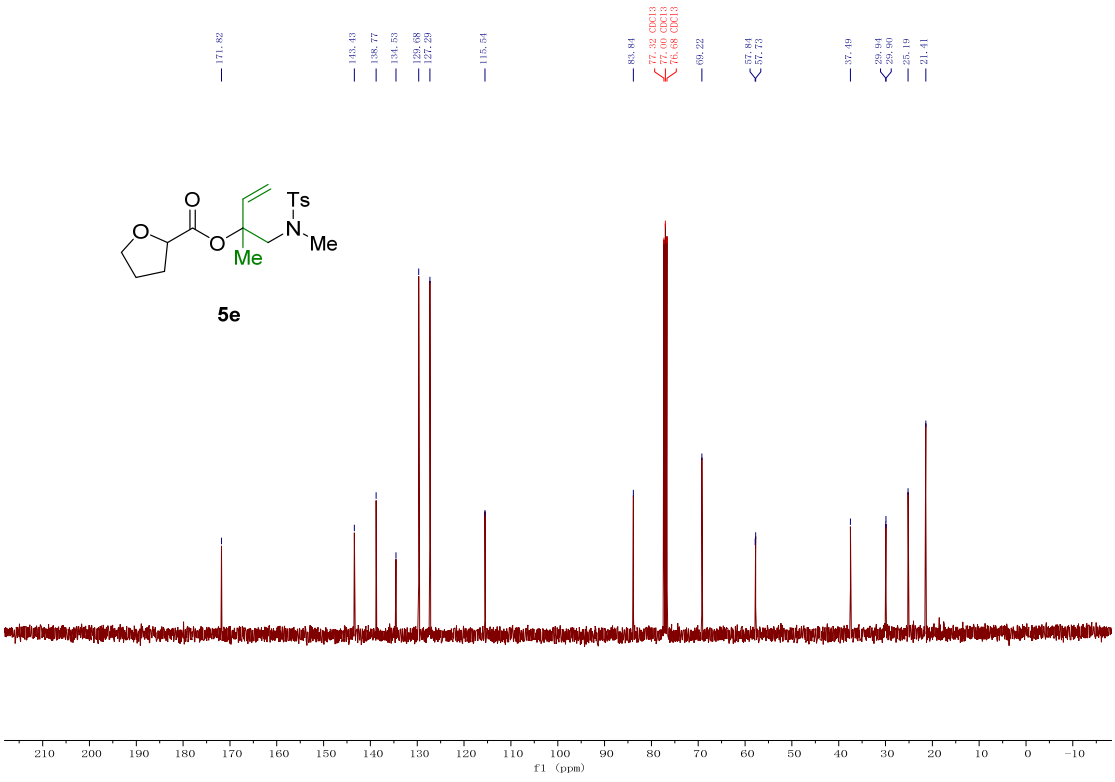

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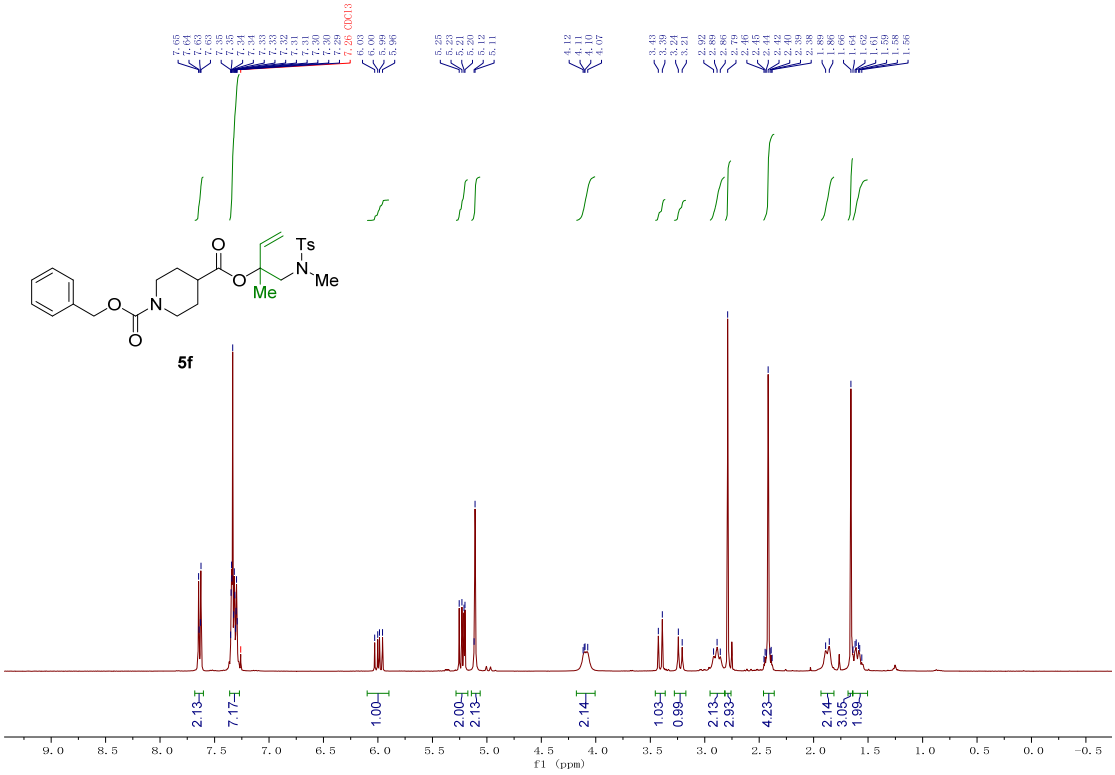

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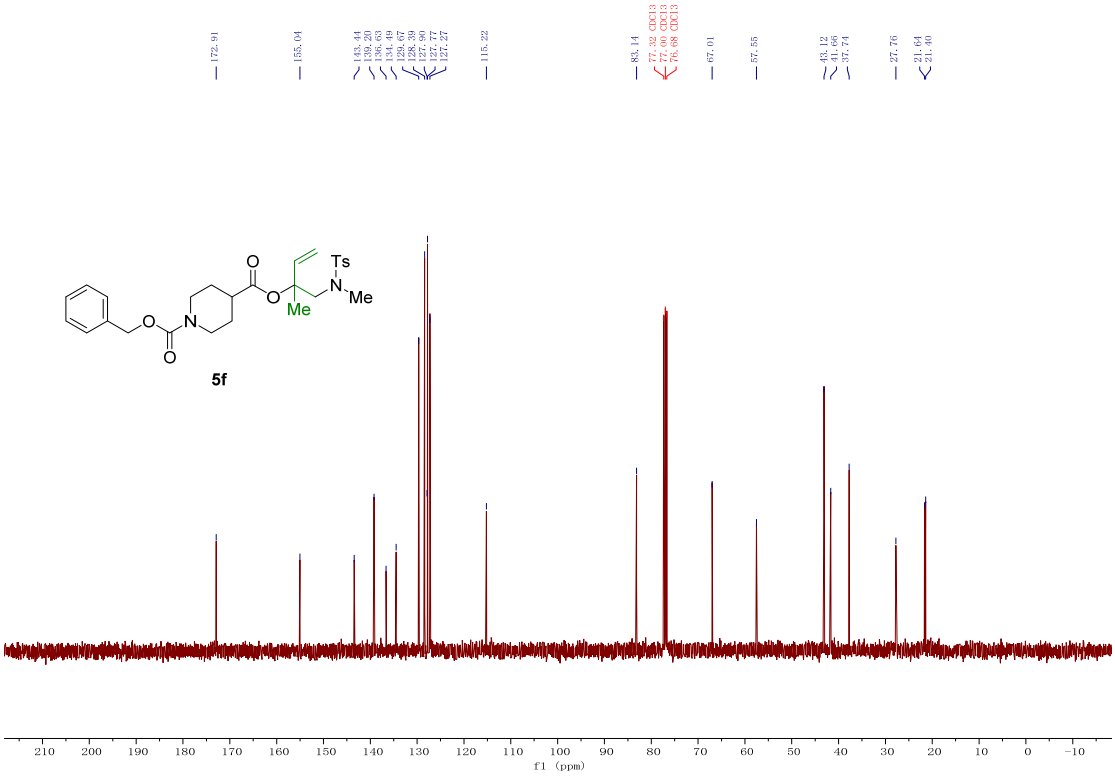

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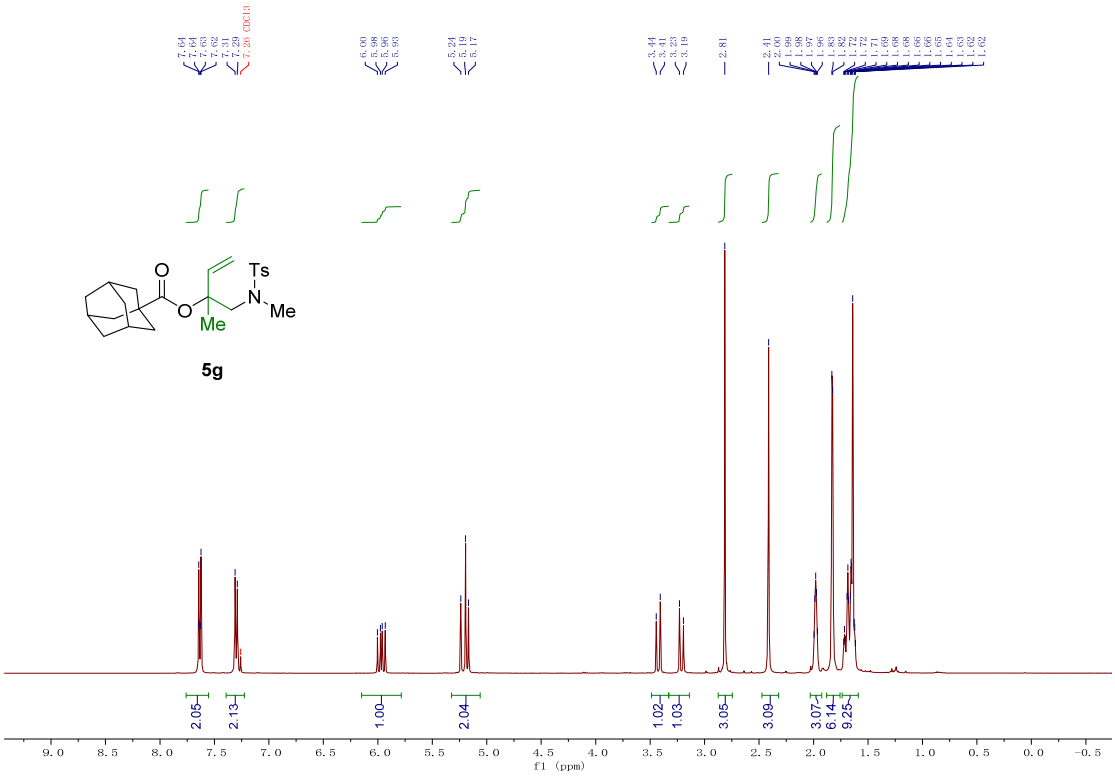

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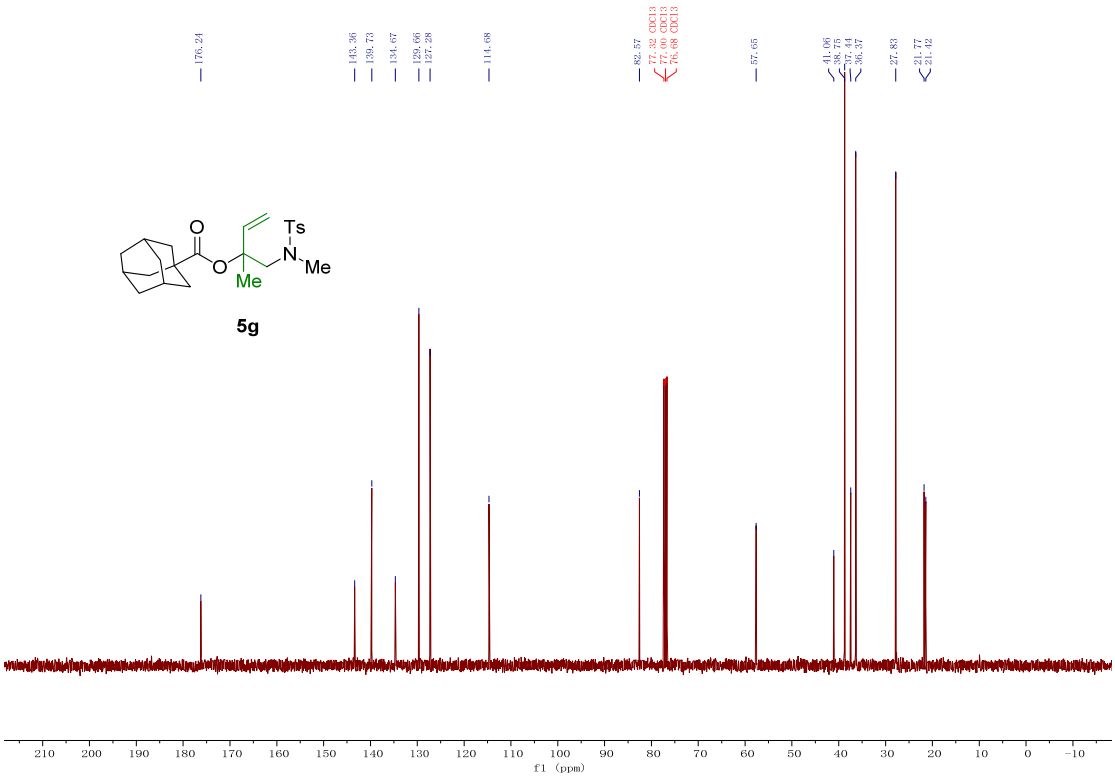

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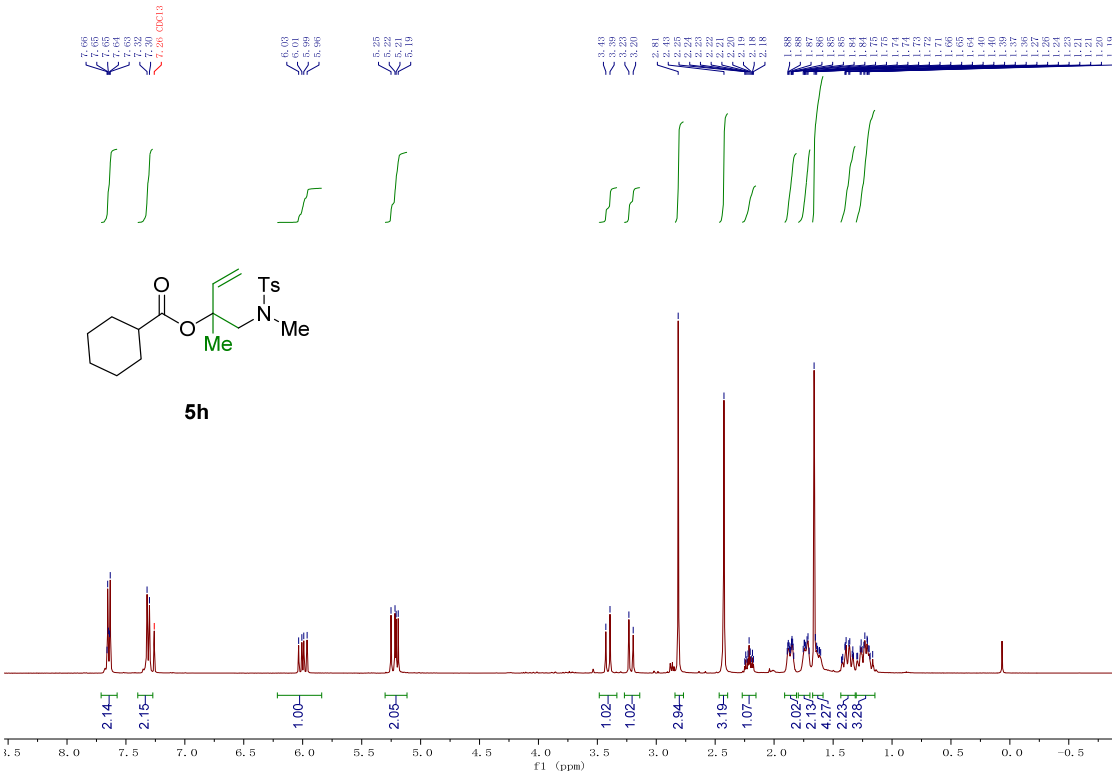

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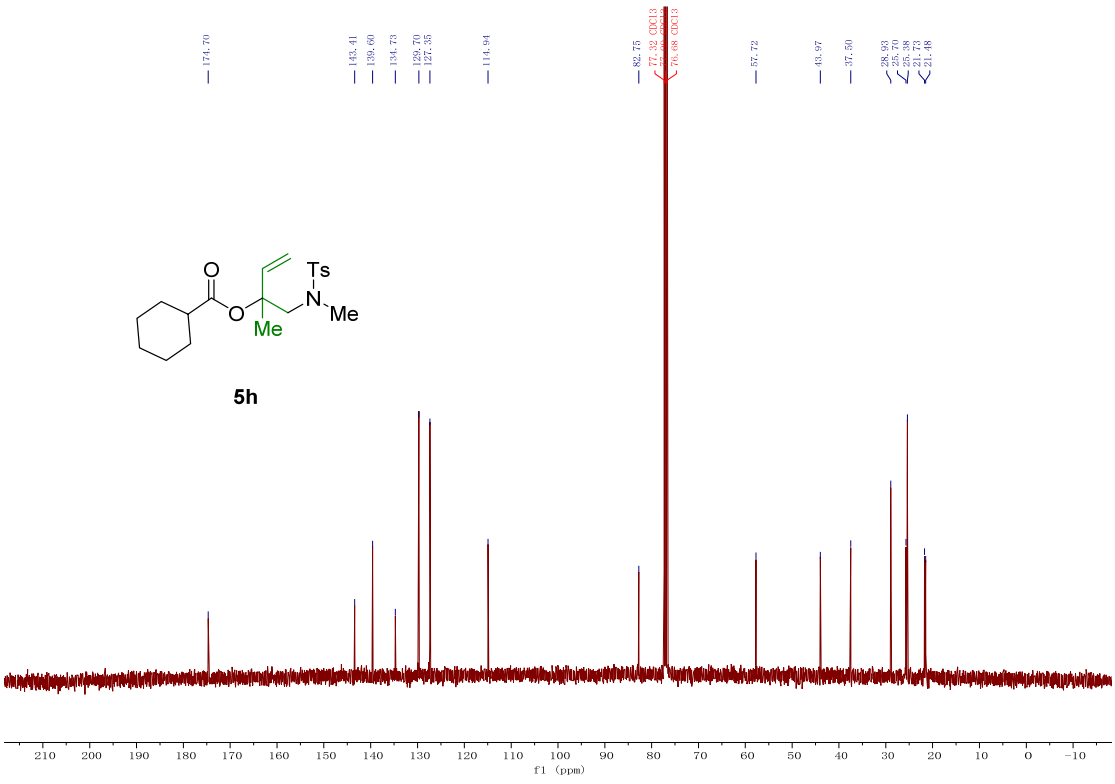

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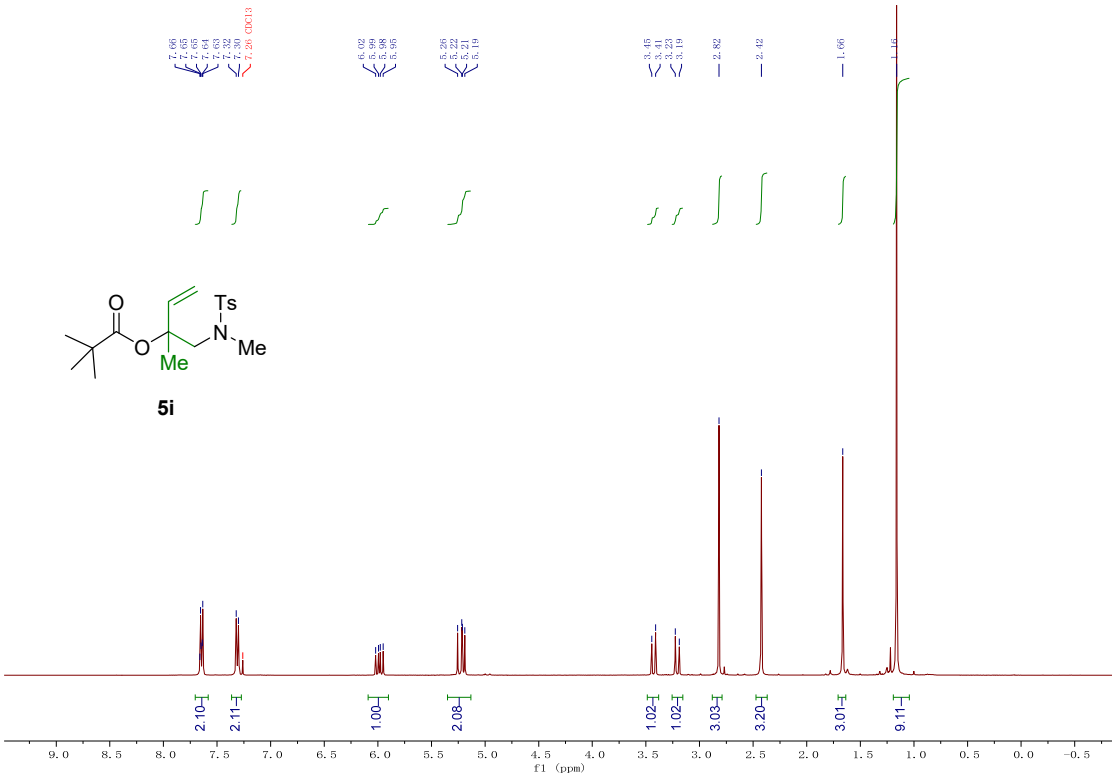

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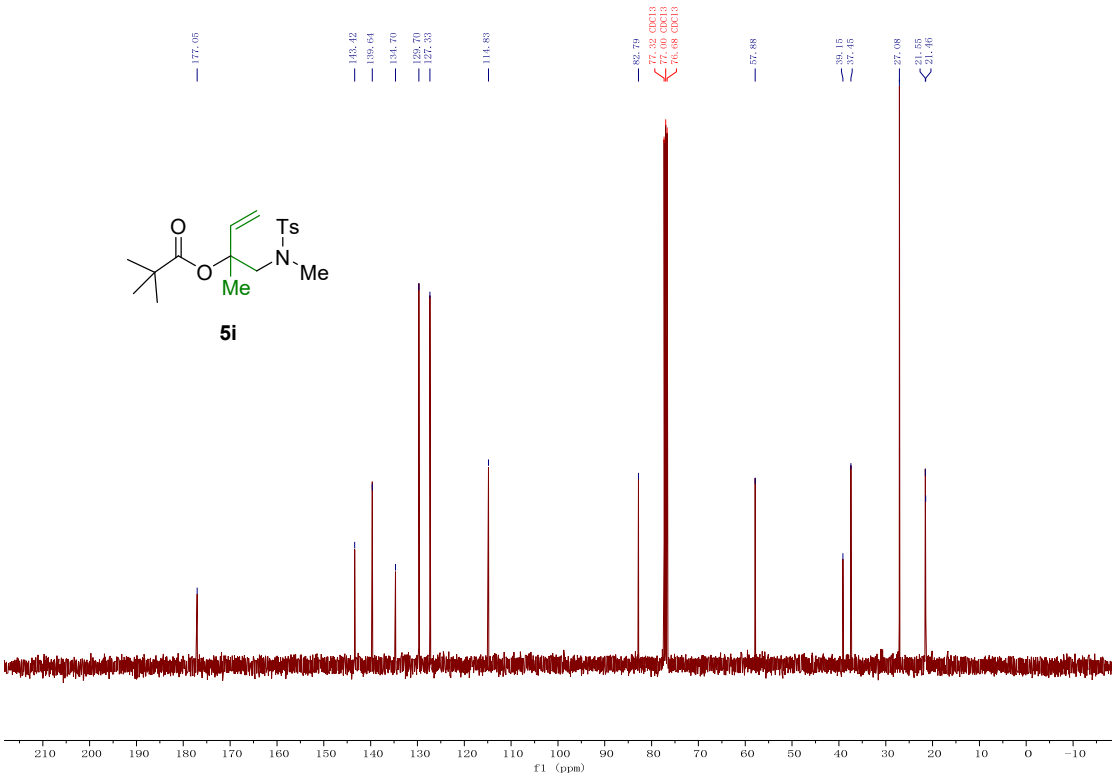

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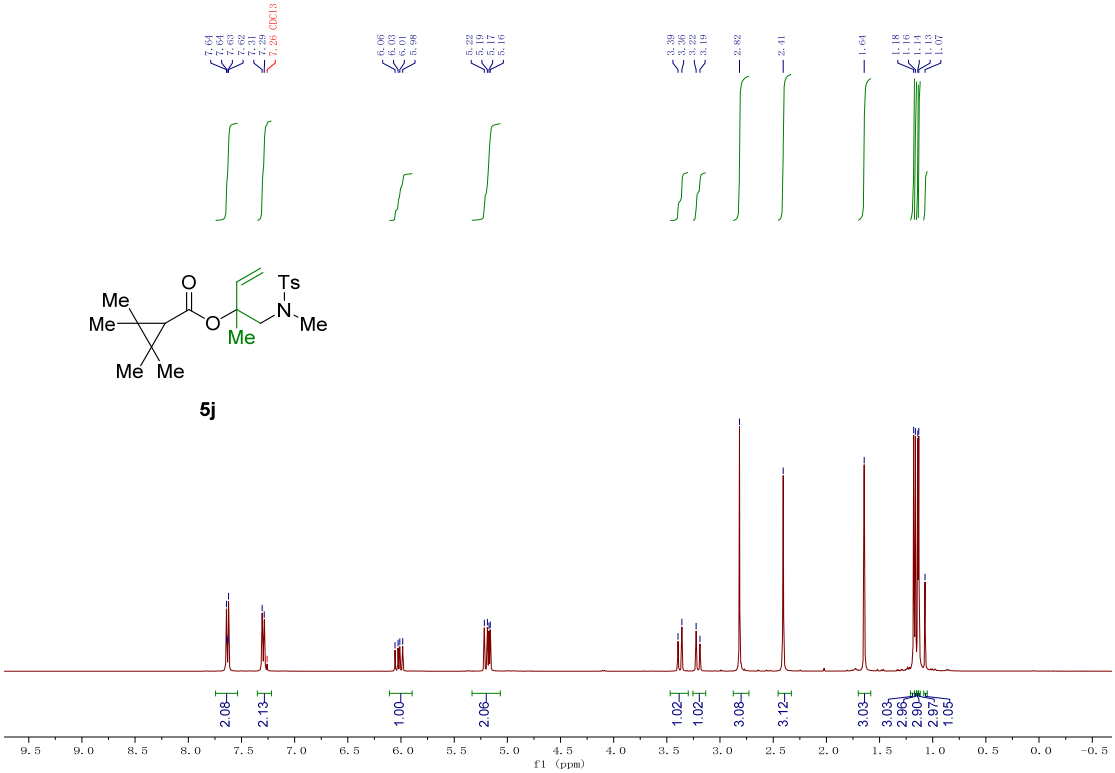

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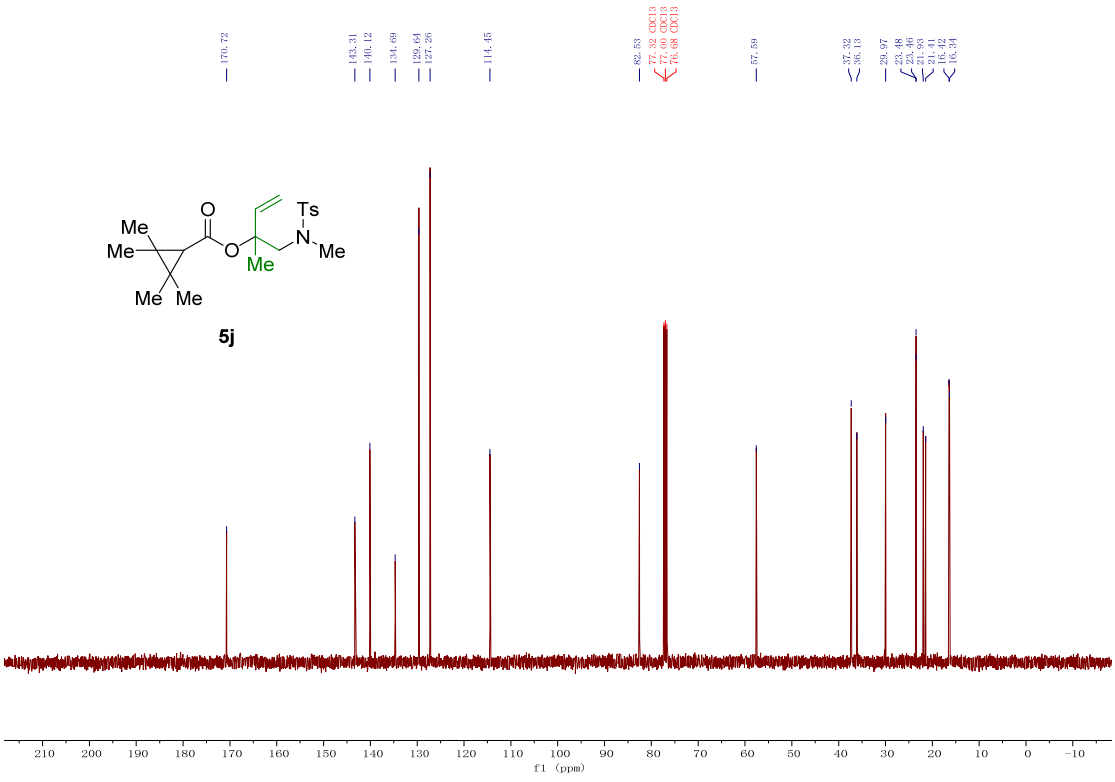

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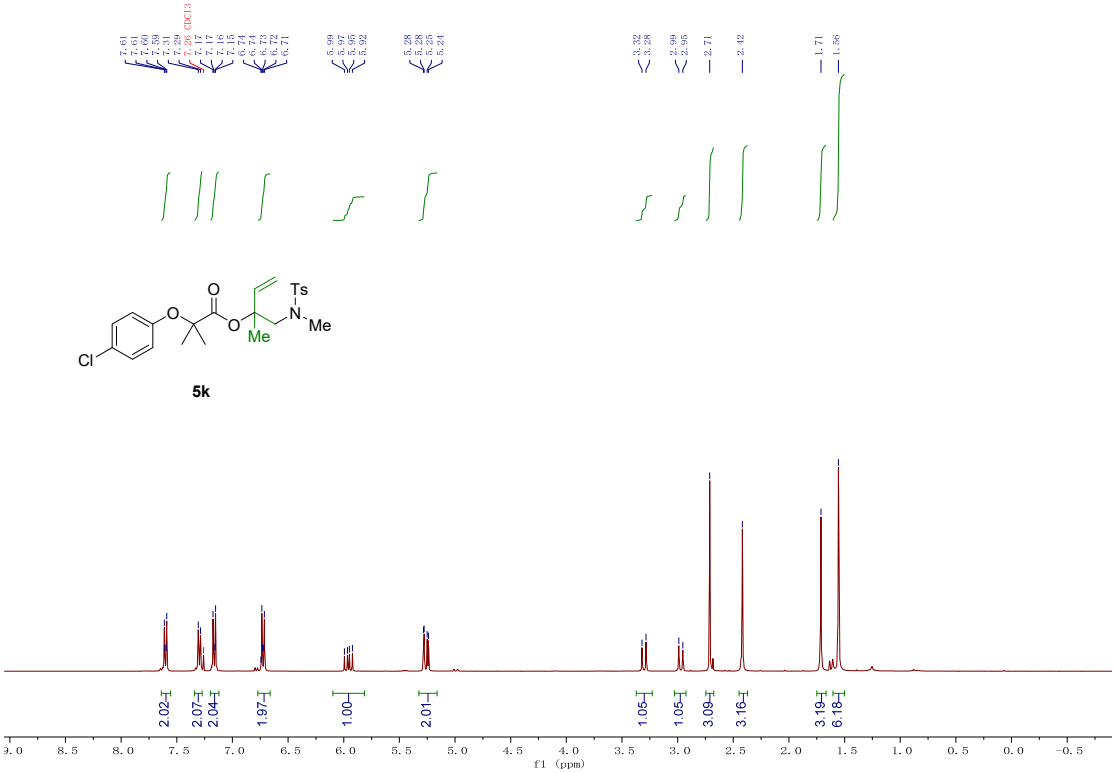

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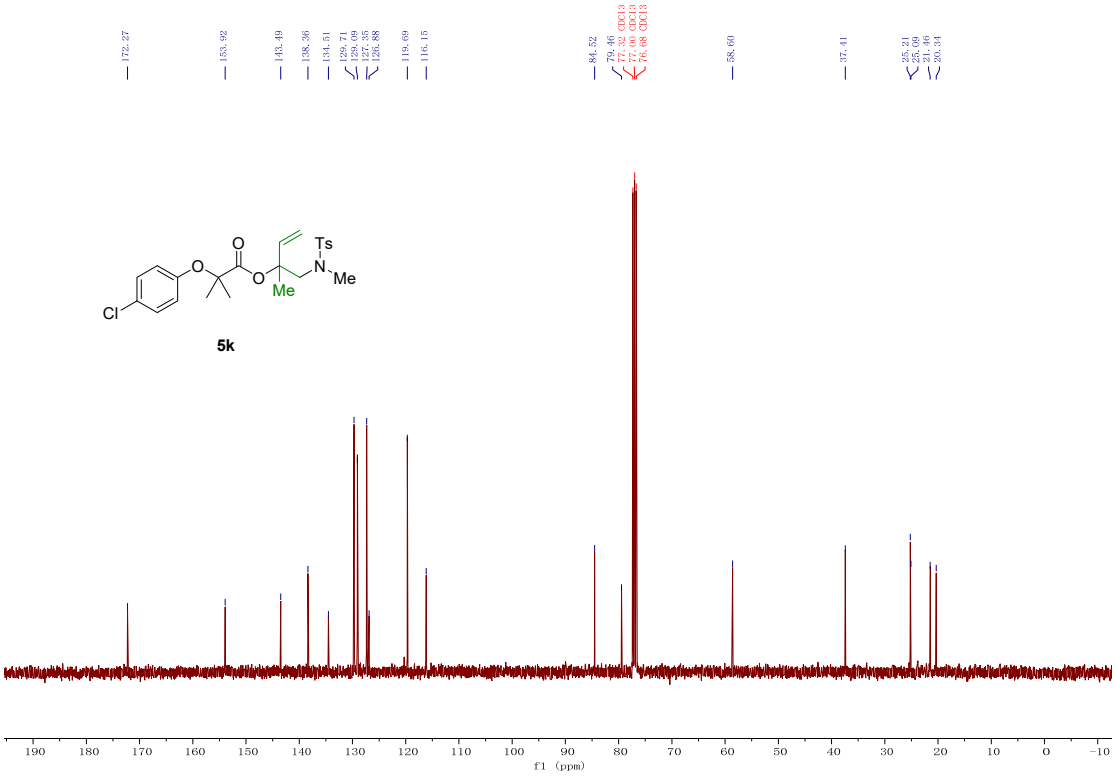

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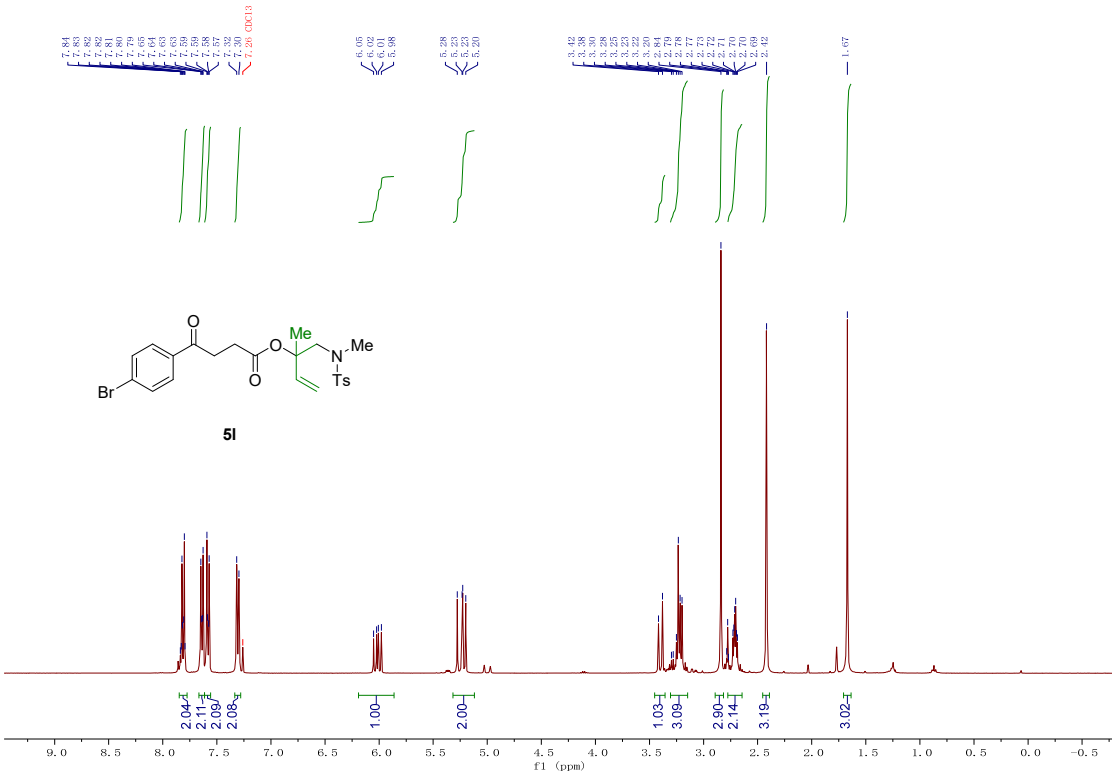

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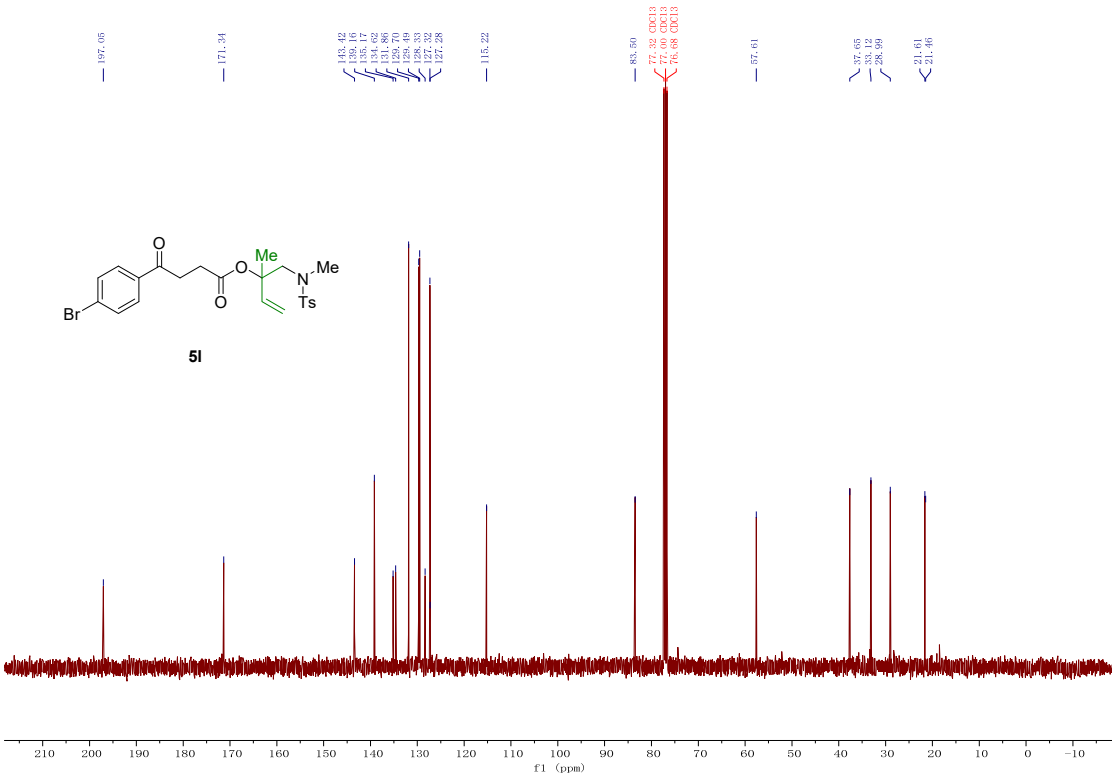

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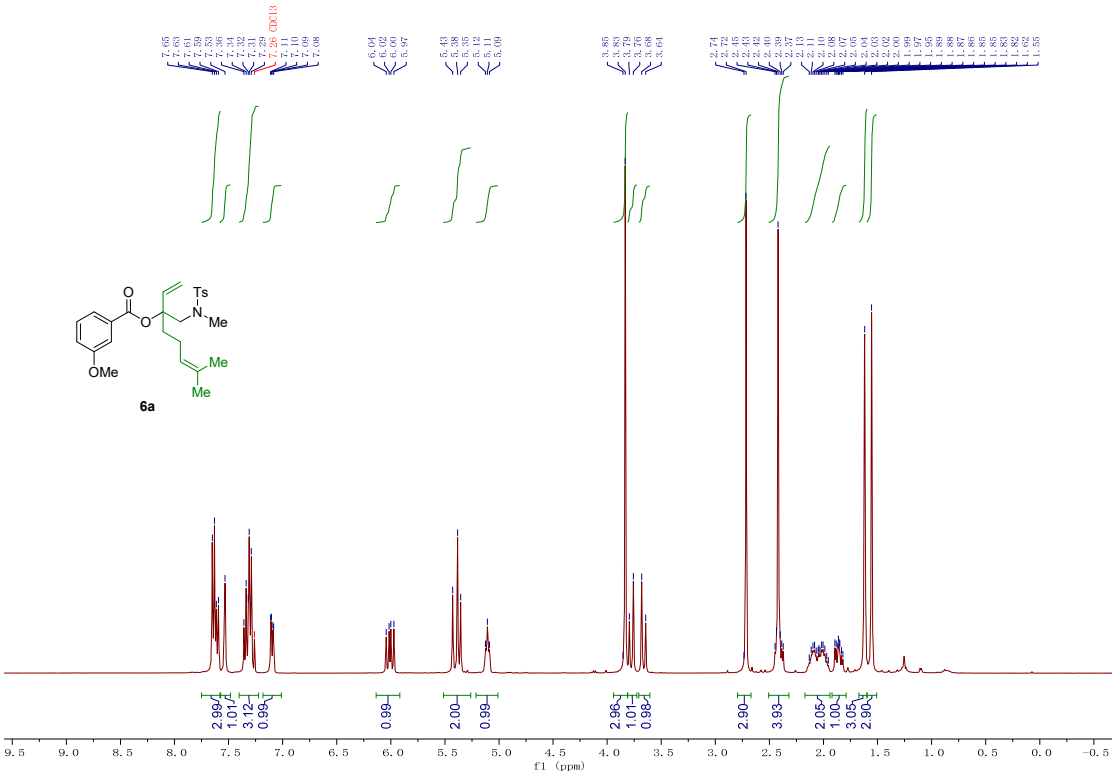

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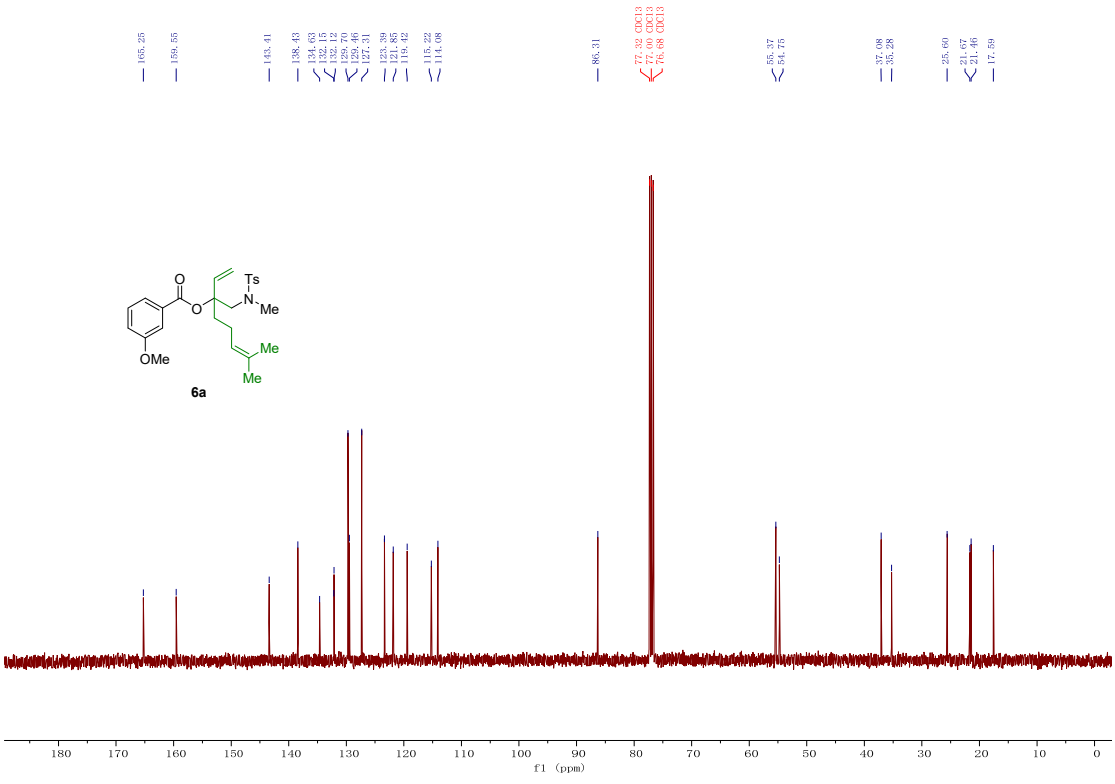

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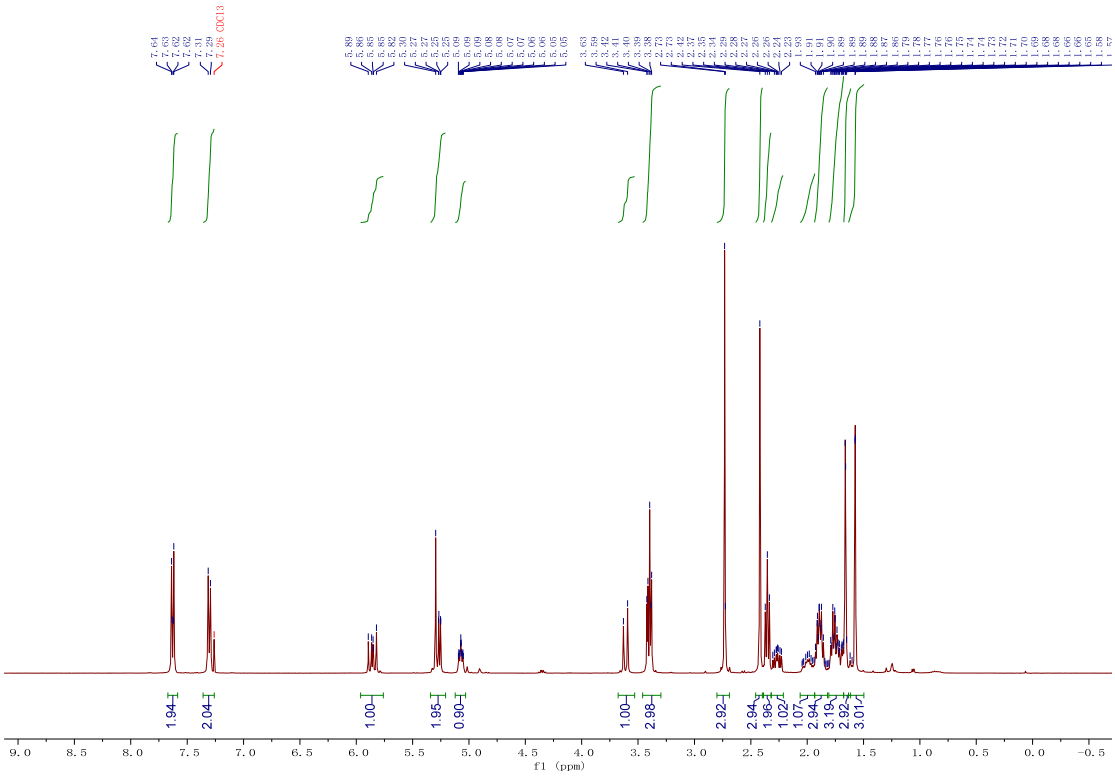

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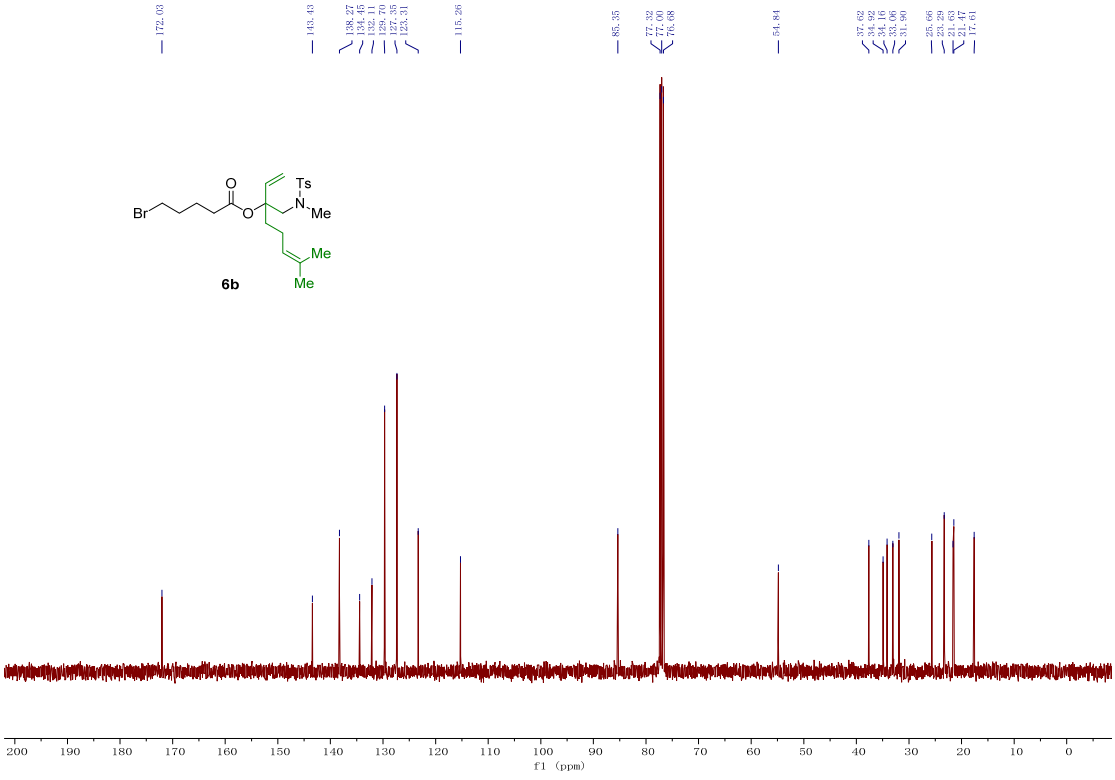

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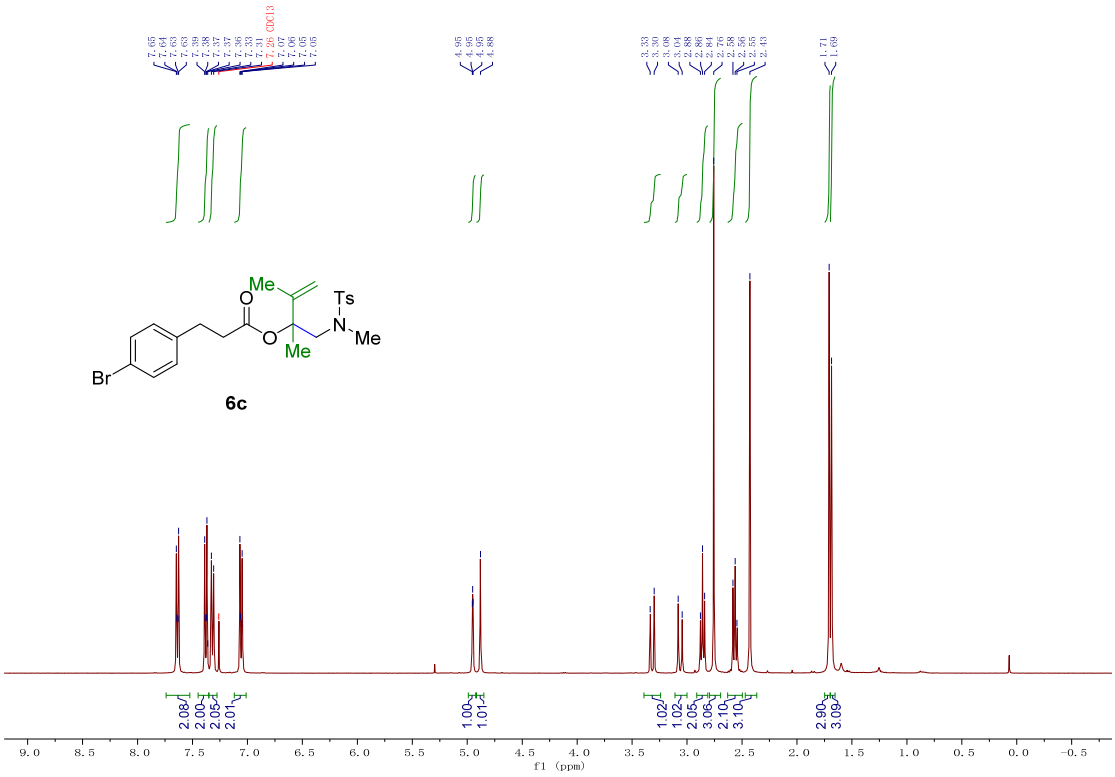

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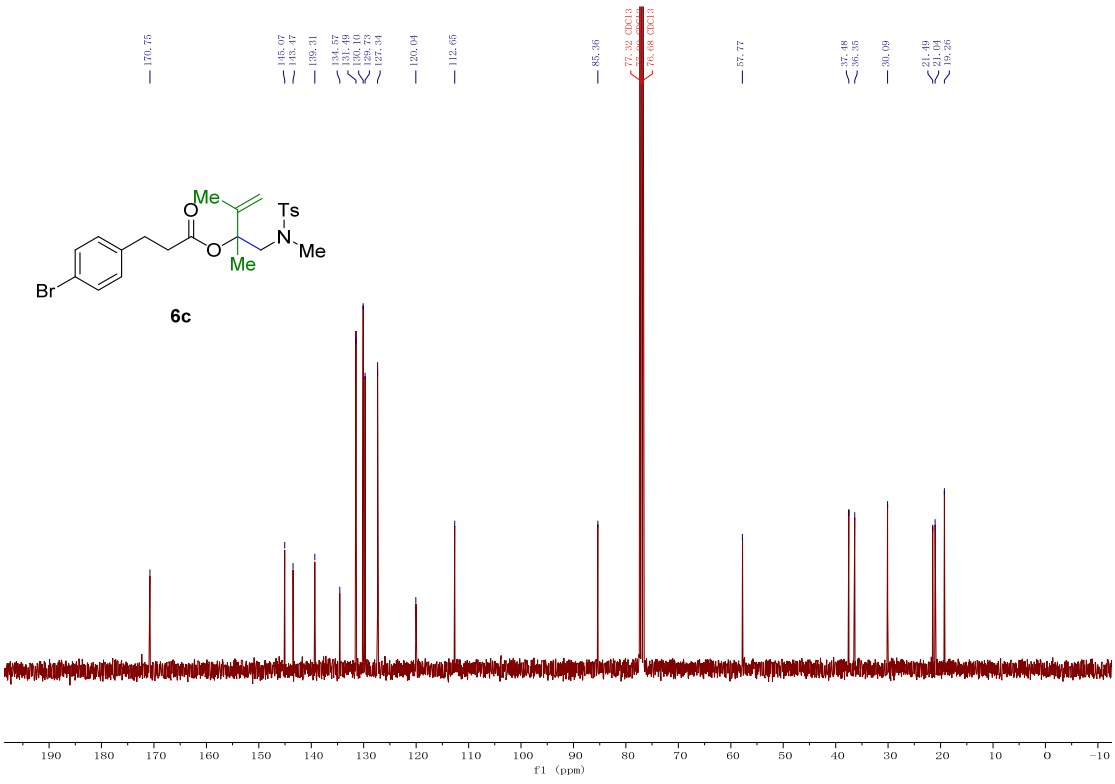

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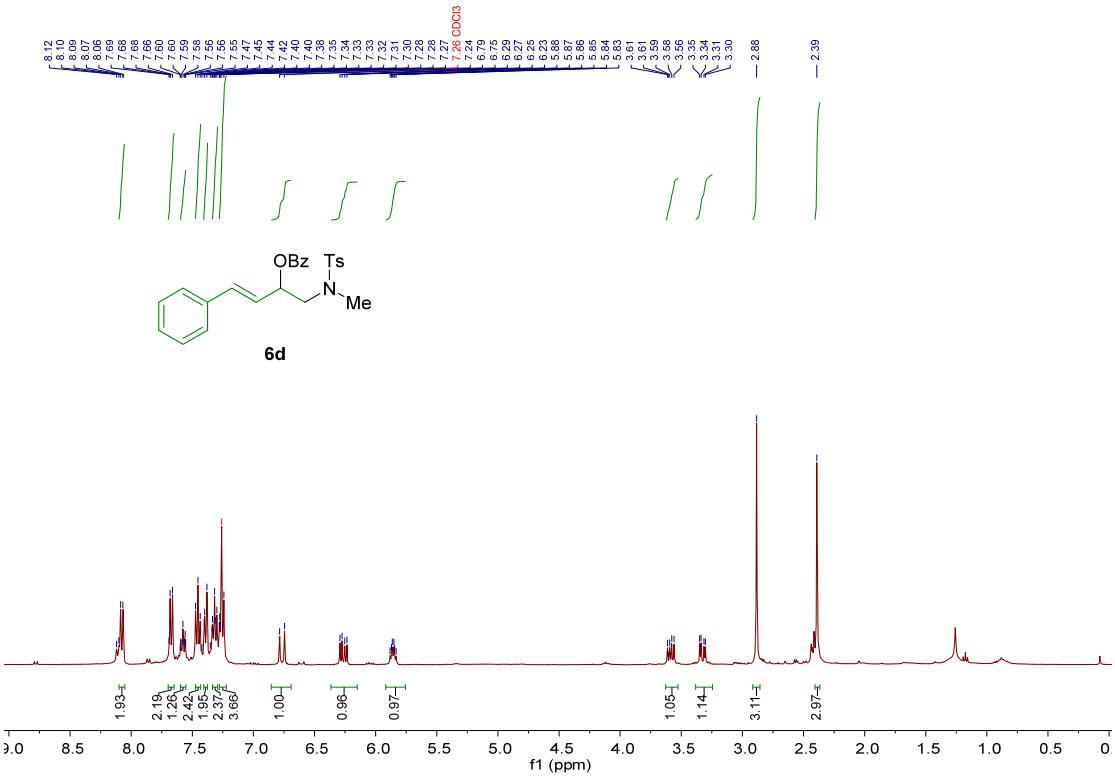

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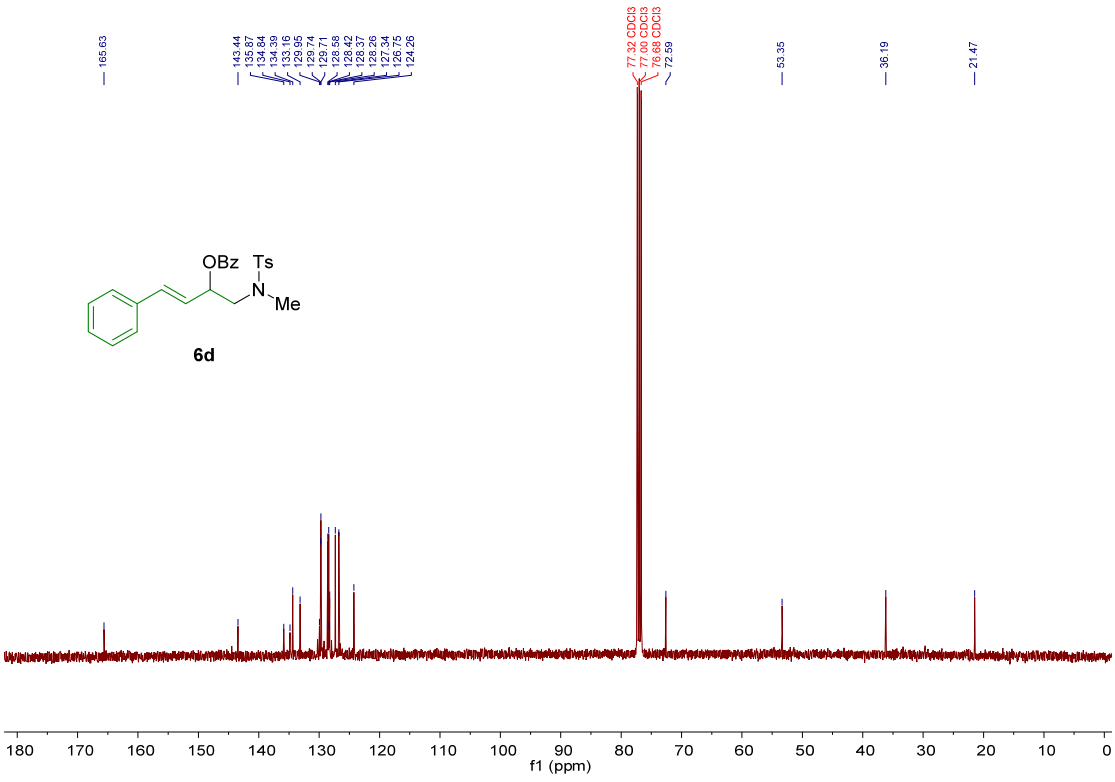

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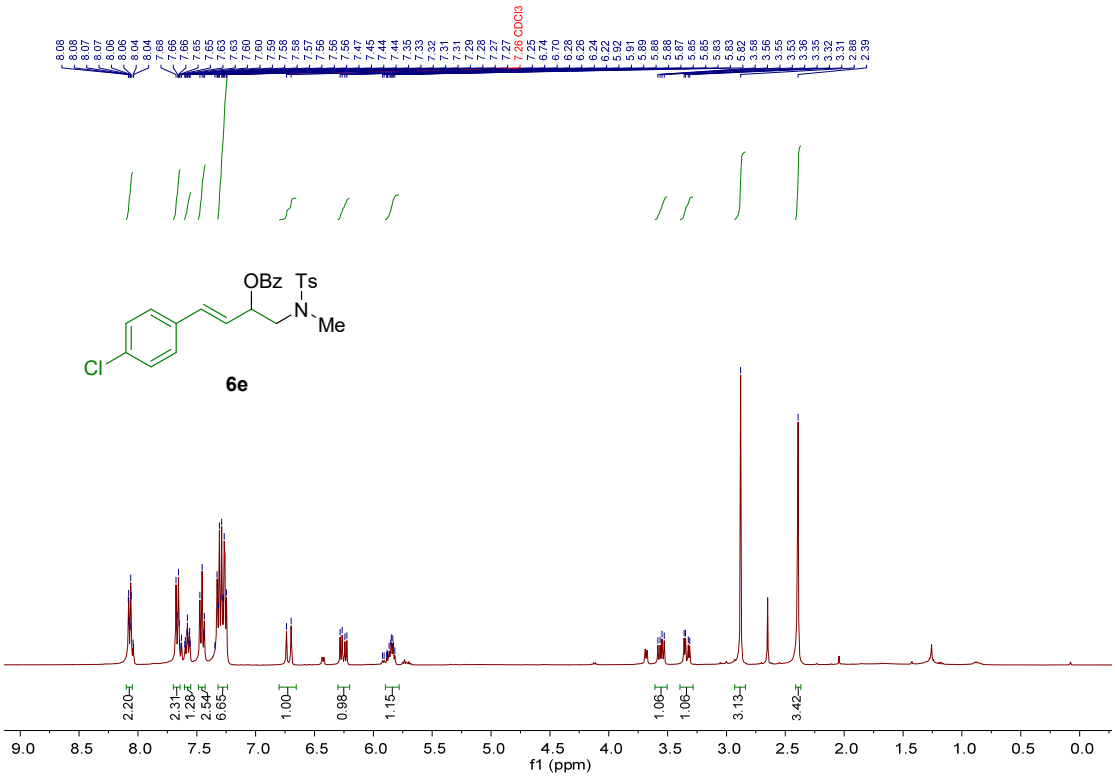

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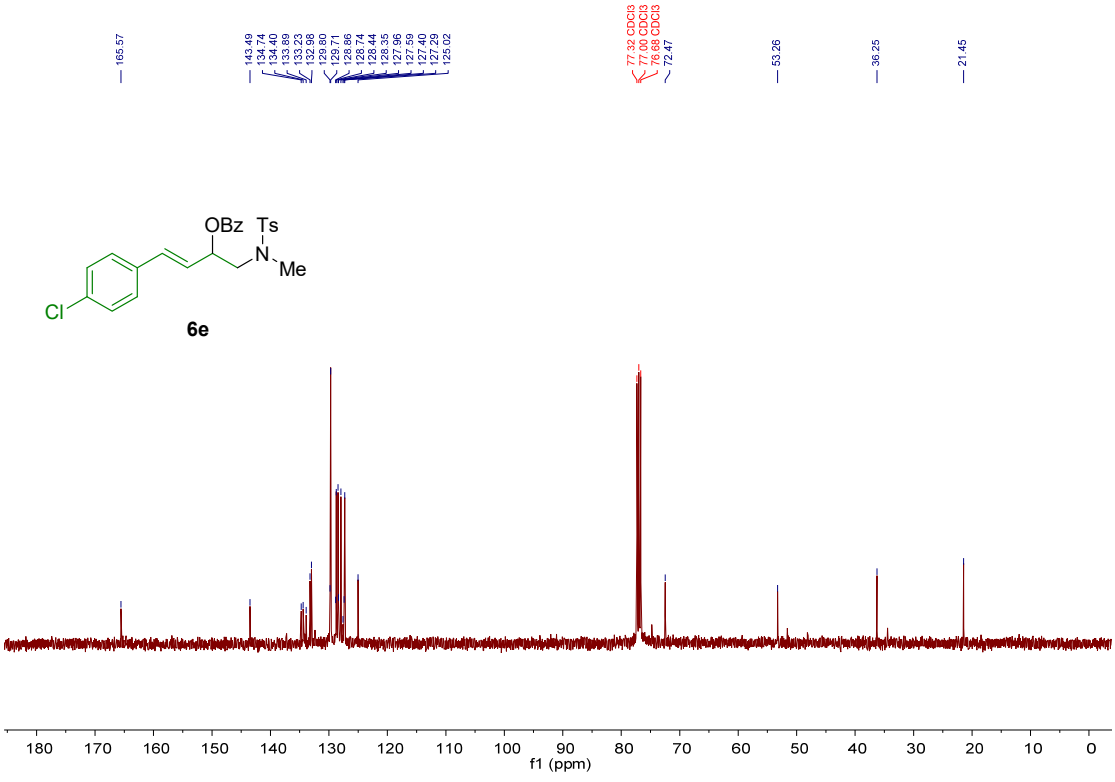

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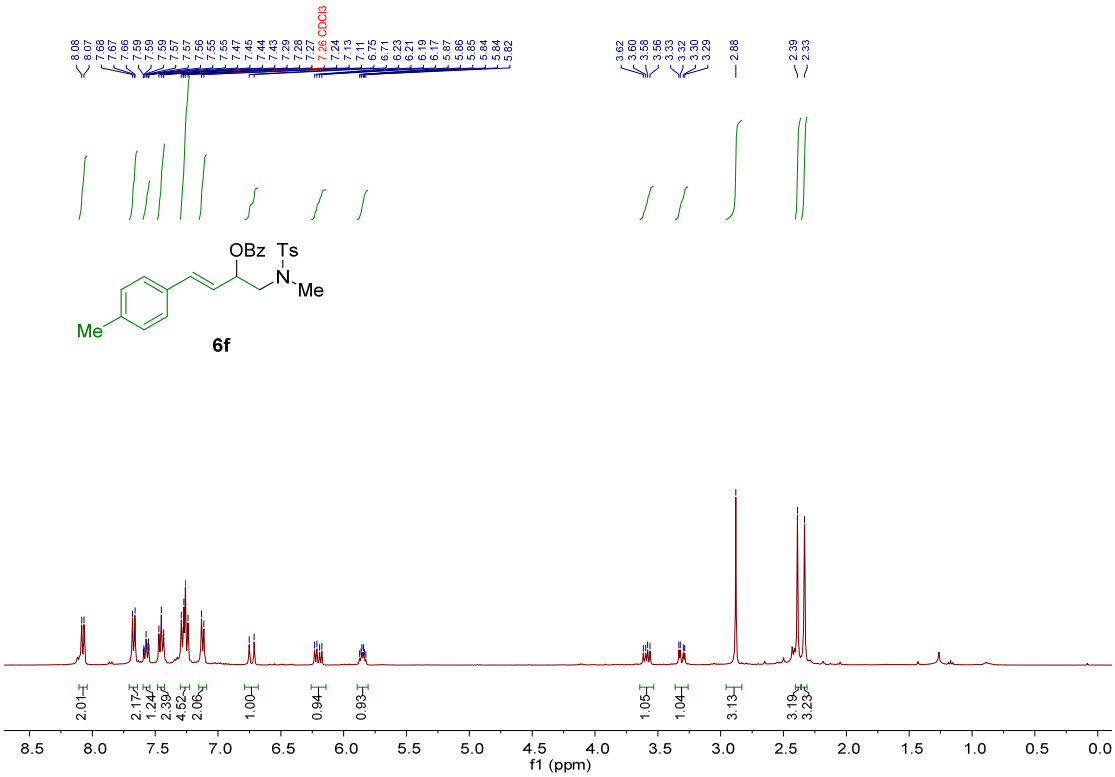

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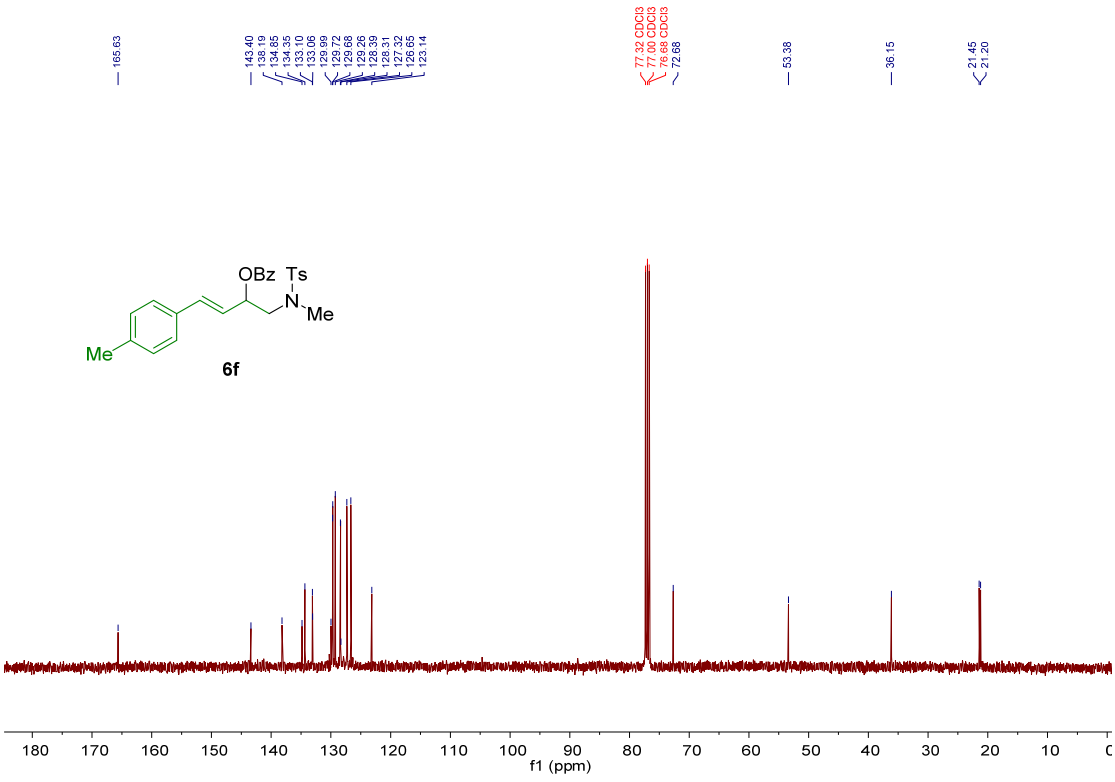

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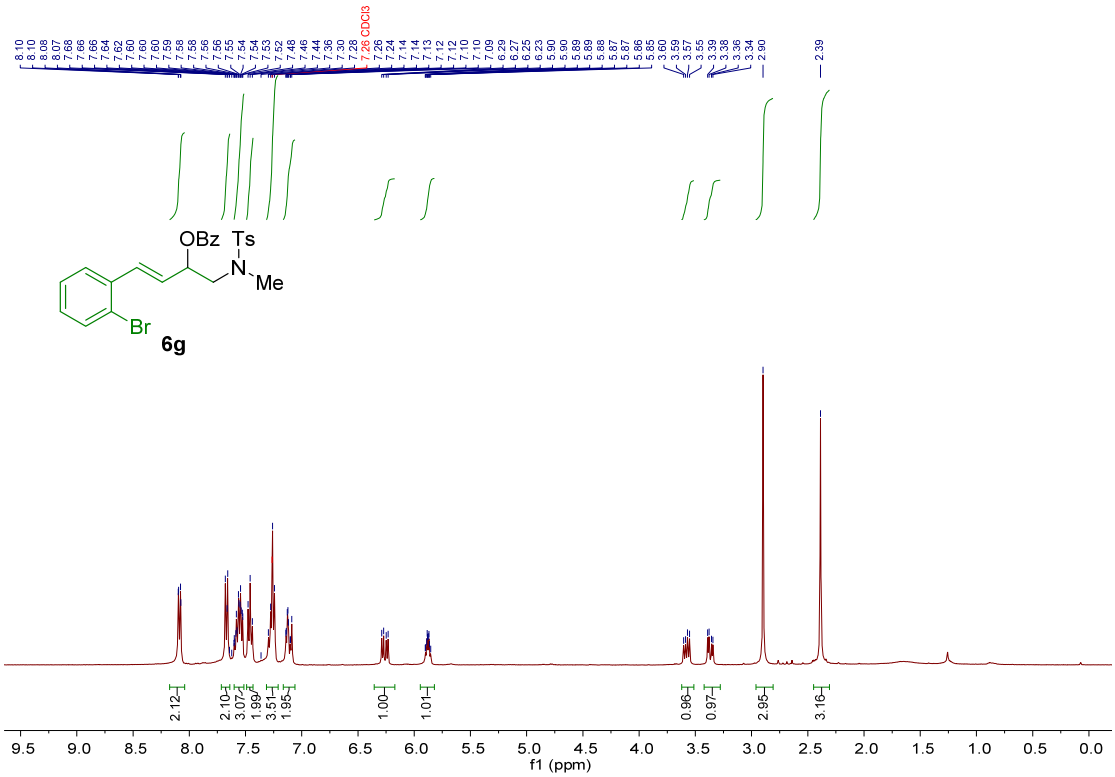

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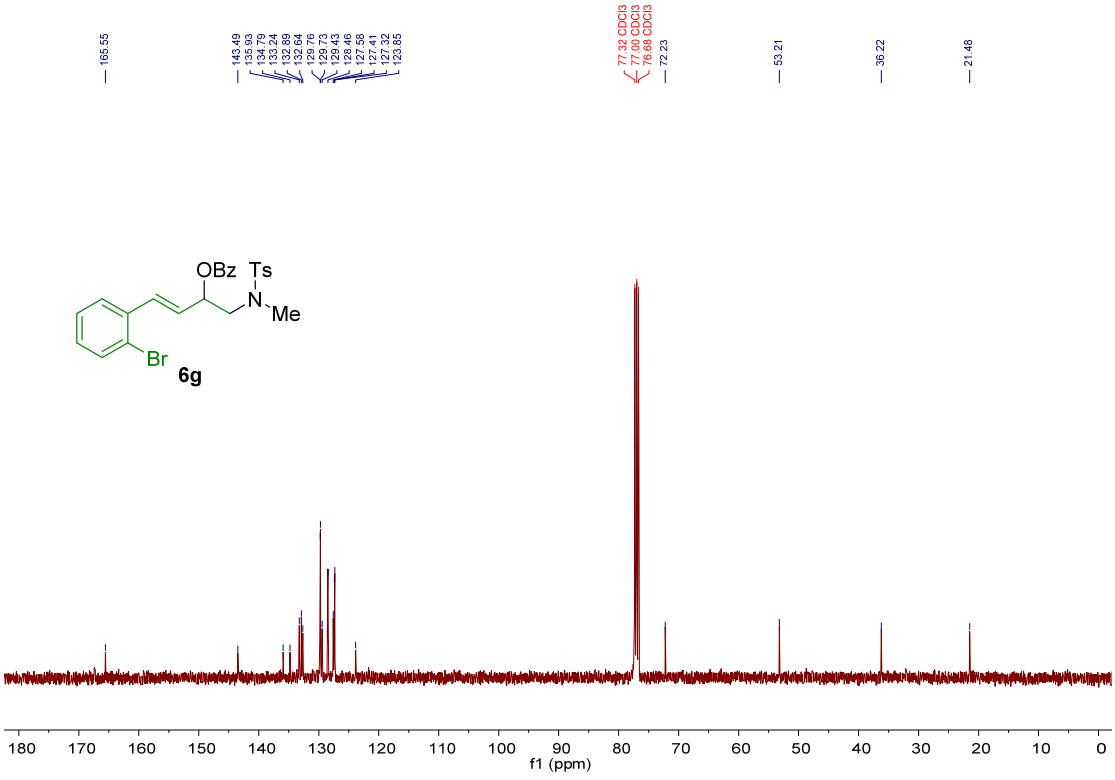

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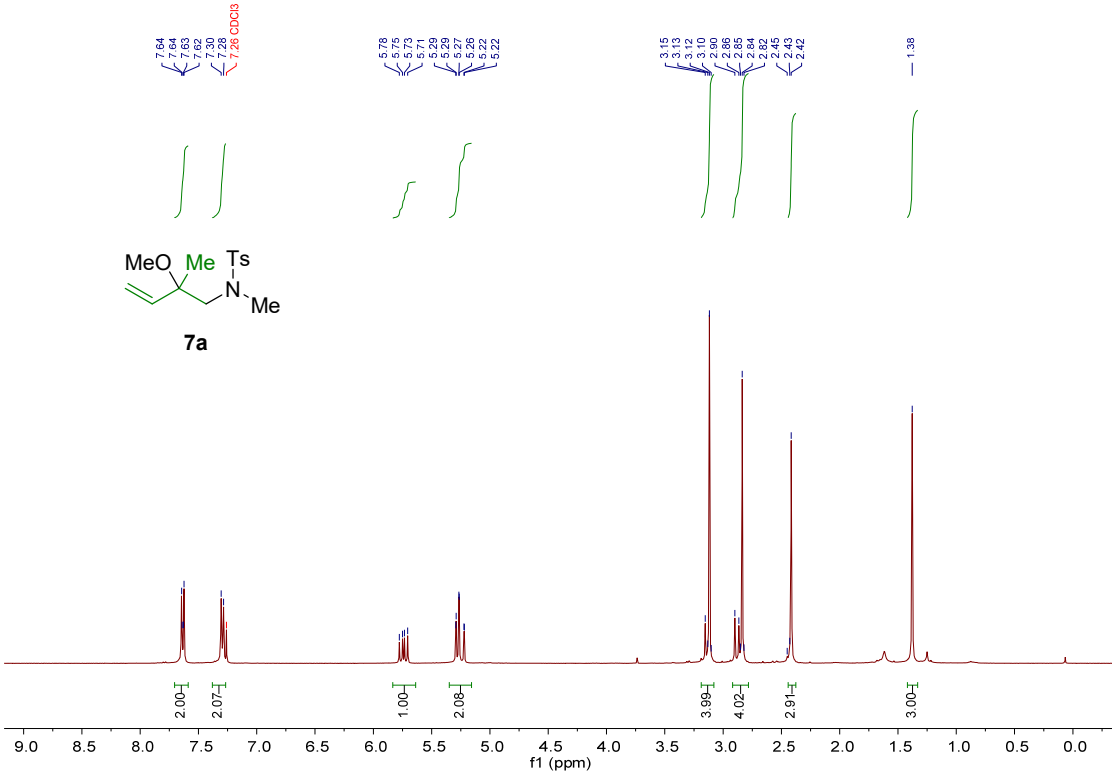

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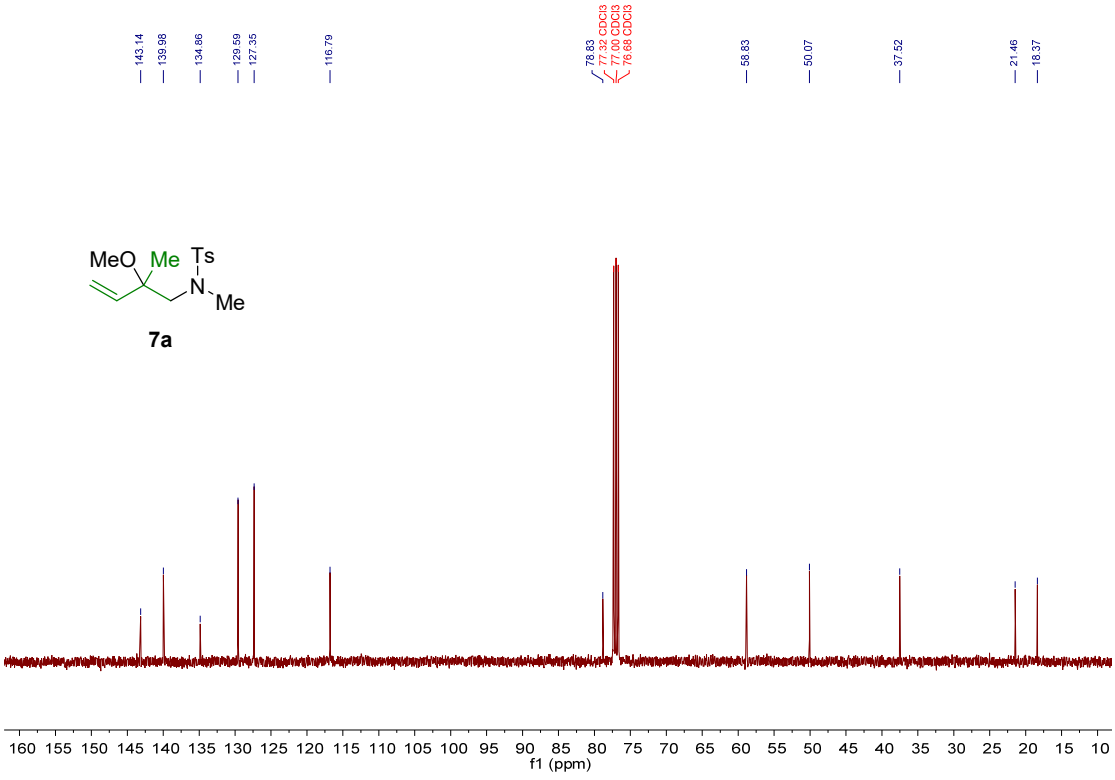

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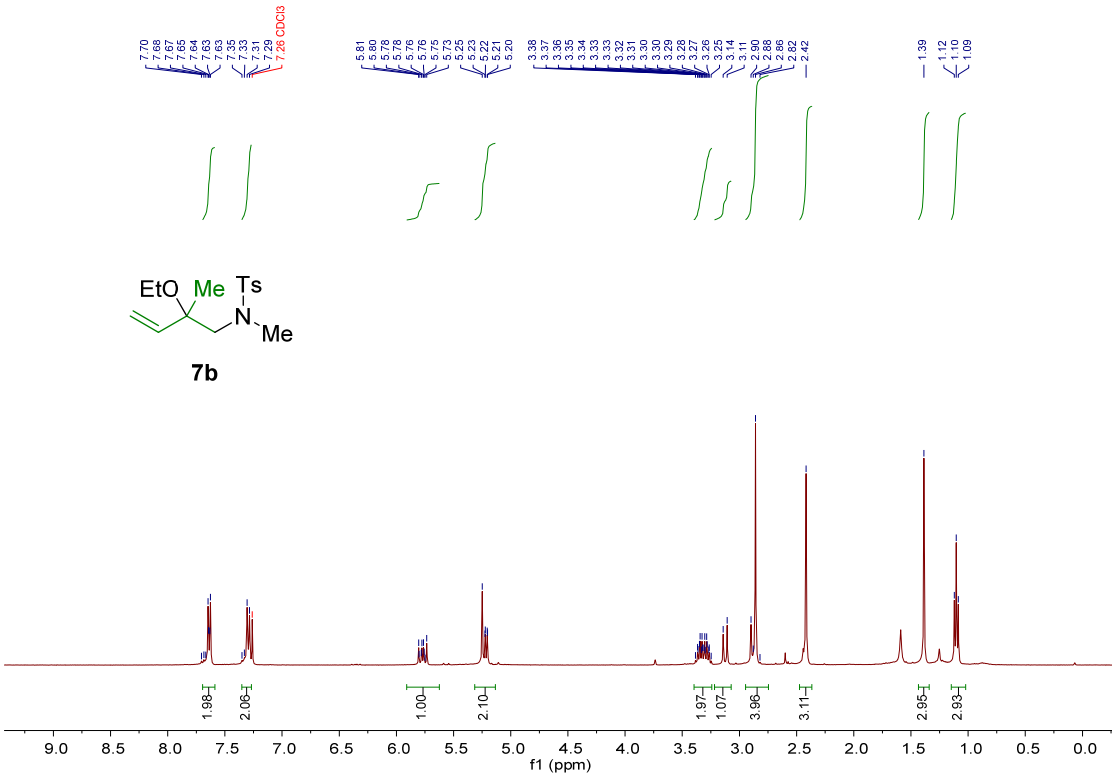

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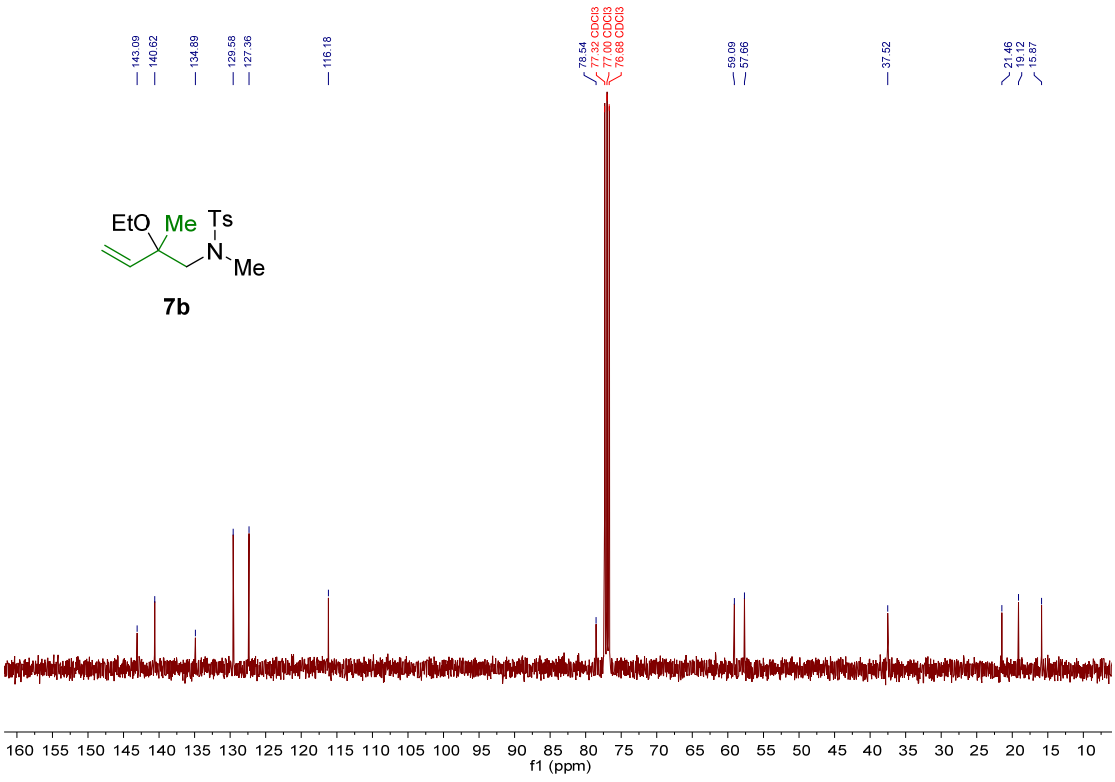

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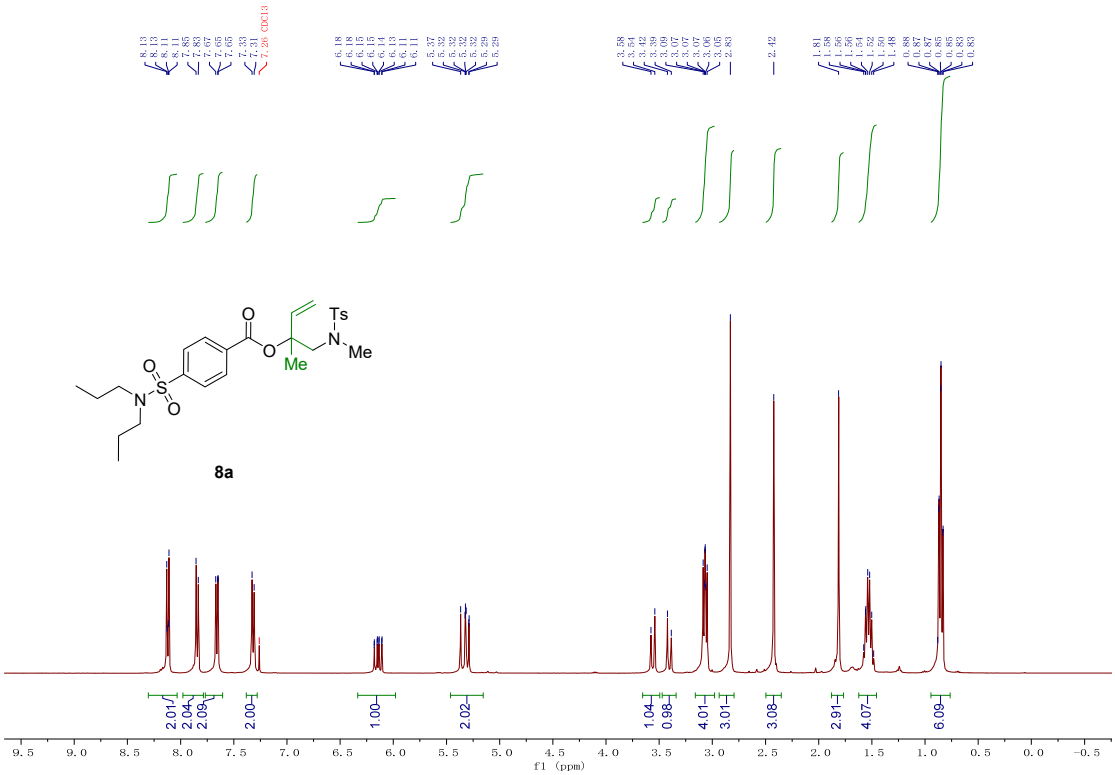

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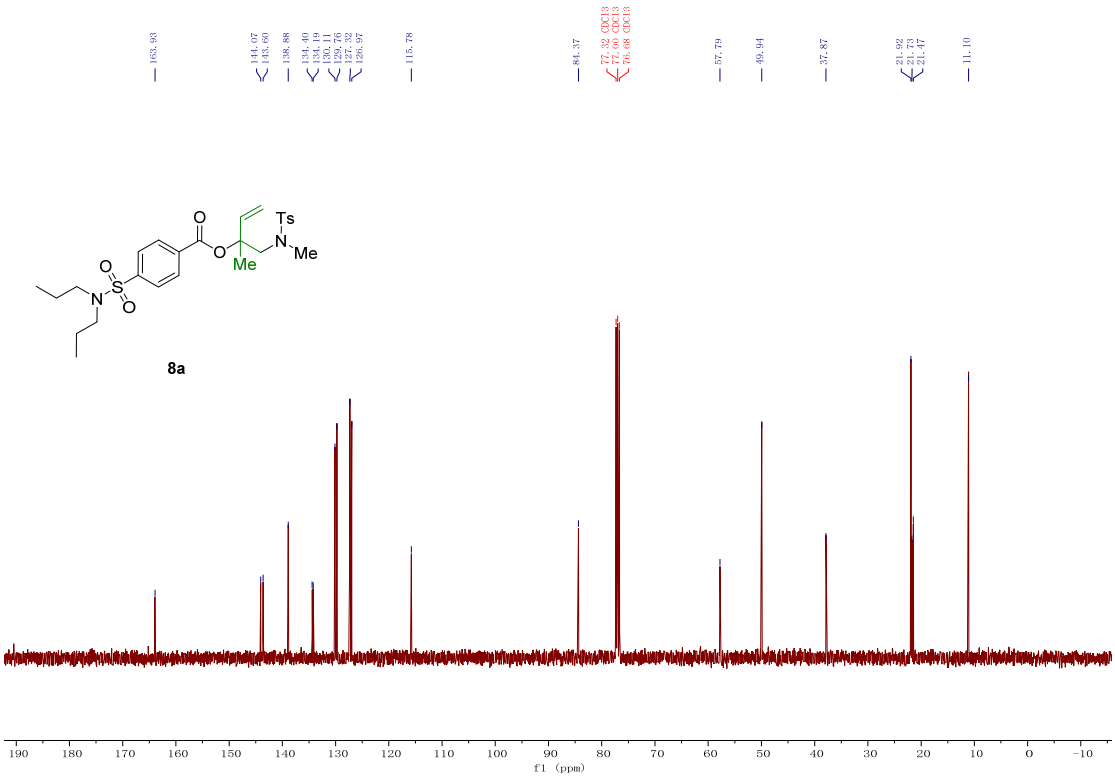

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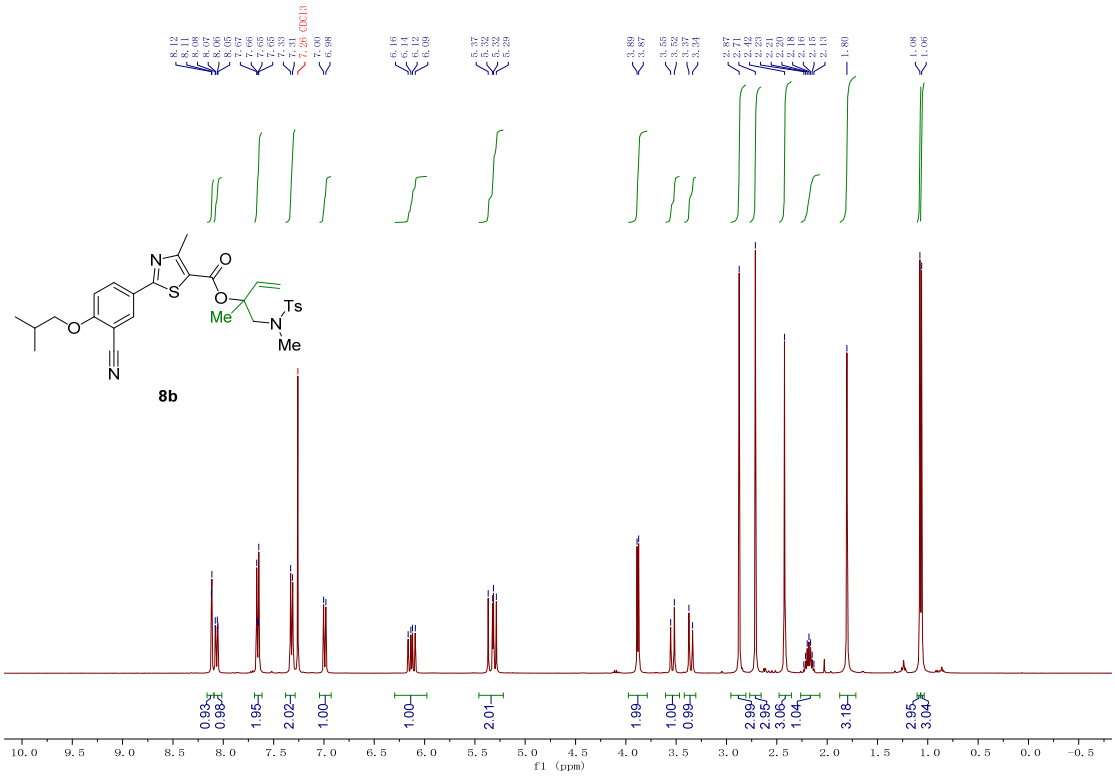

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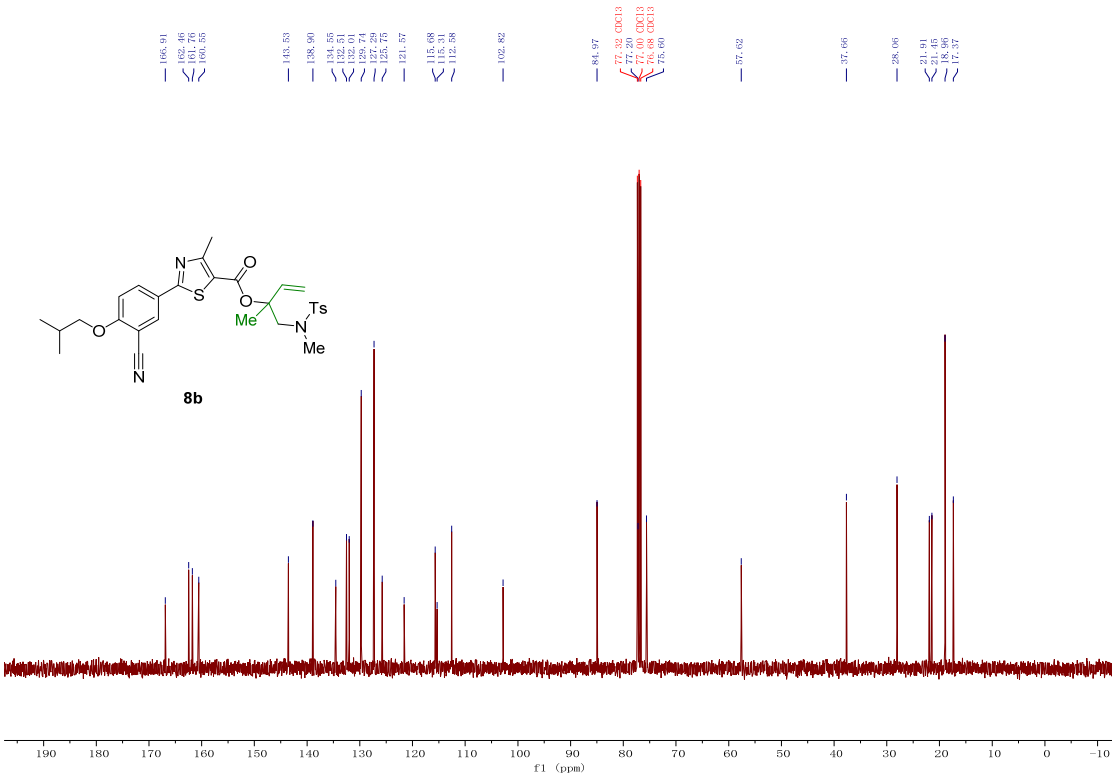

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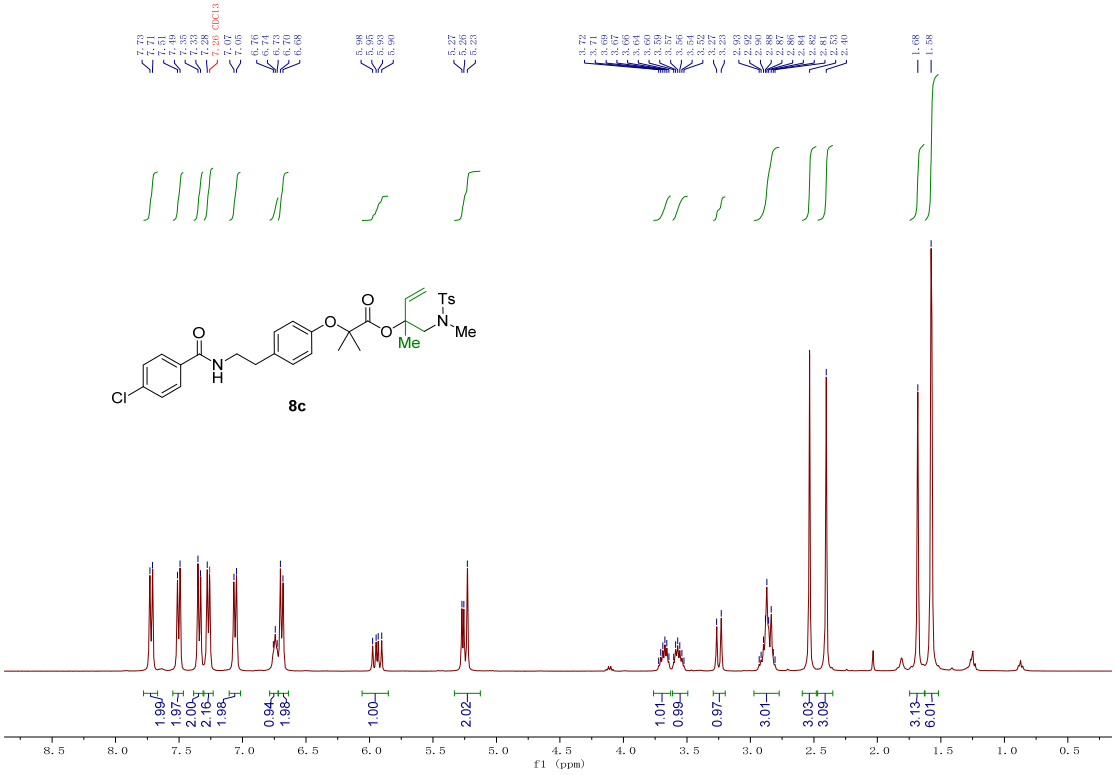
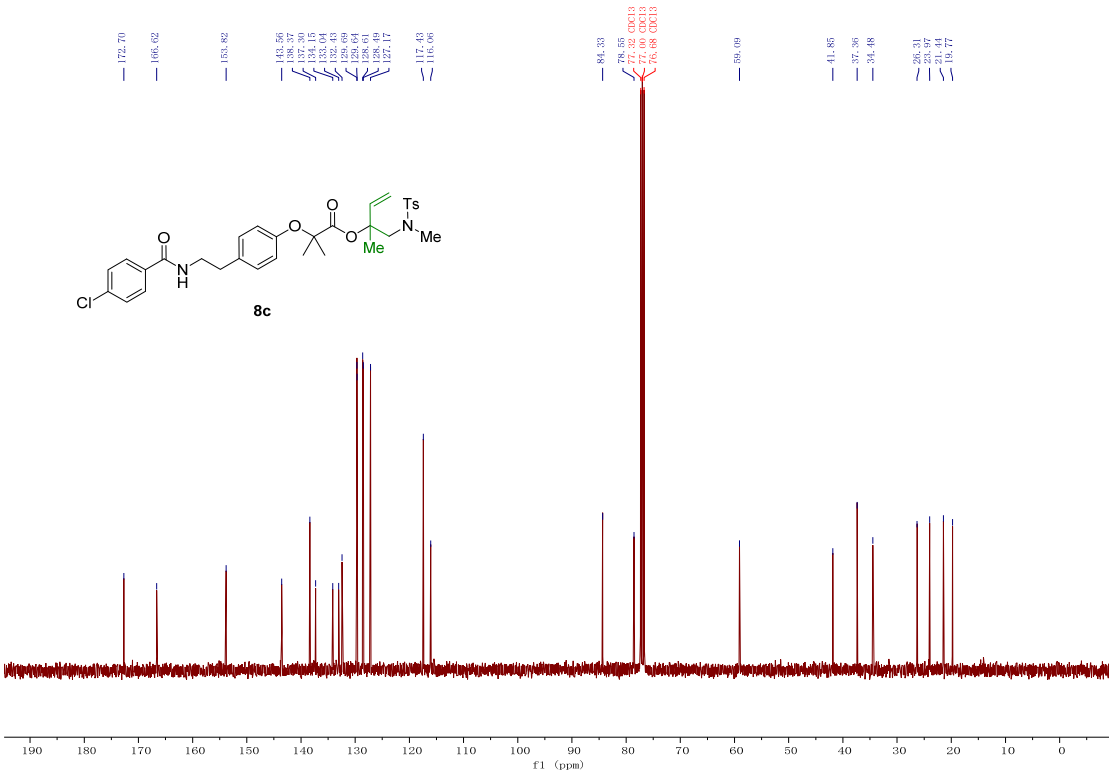
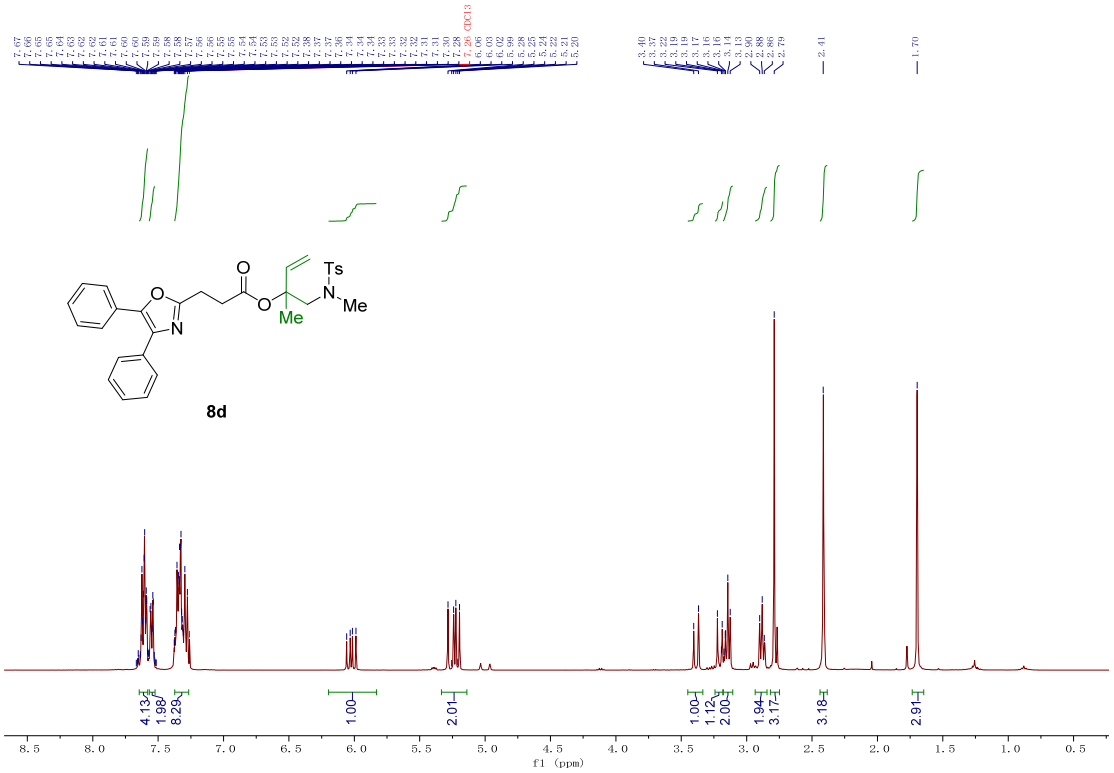


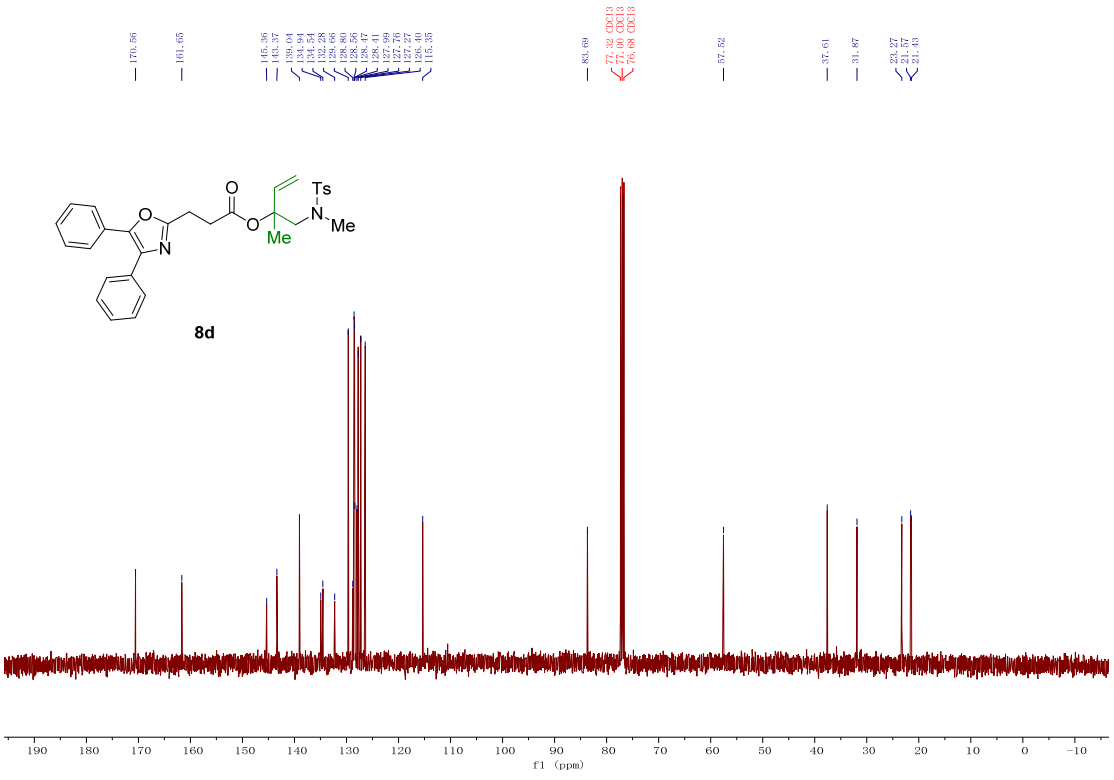
^{13}C NMR (101 MHz, $CDCl_3$)



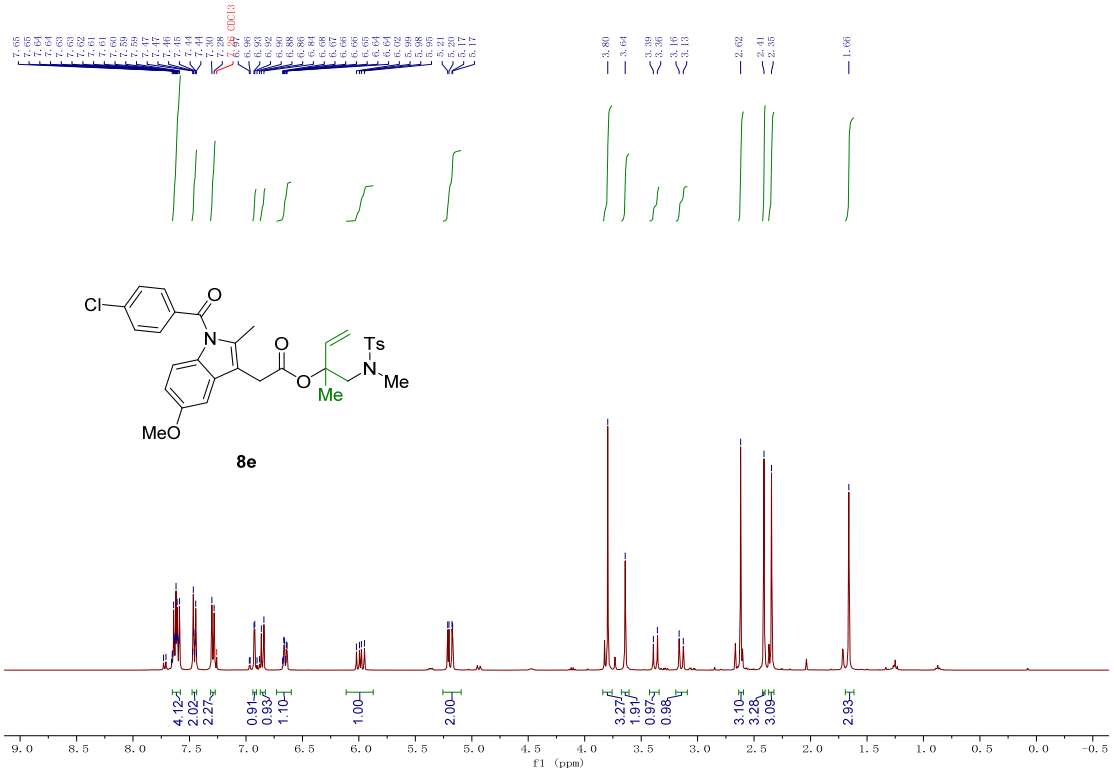
^{1}H NMR (400 MHz, $CDCl_3$)



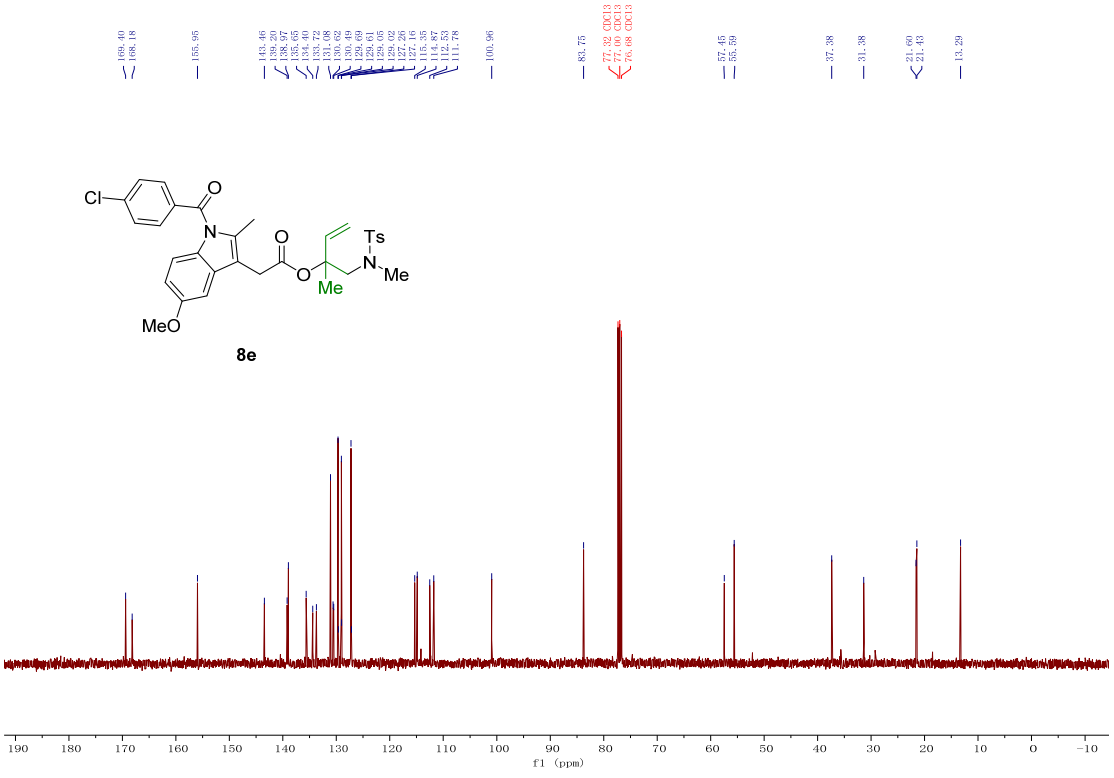
^{13}C NMR (101 MHz, $CDCl_3$)



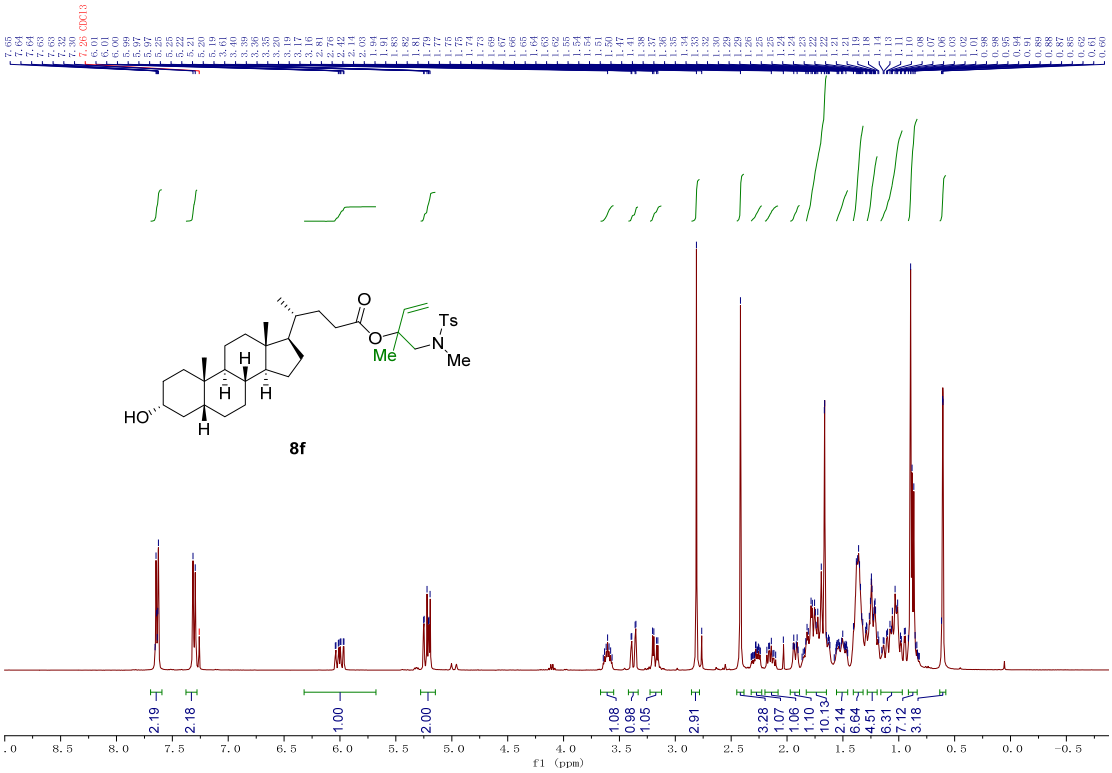
^{1}H NMR (400 MHz, $CDCl_3$)



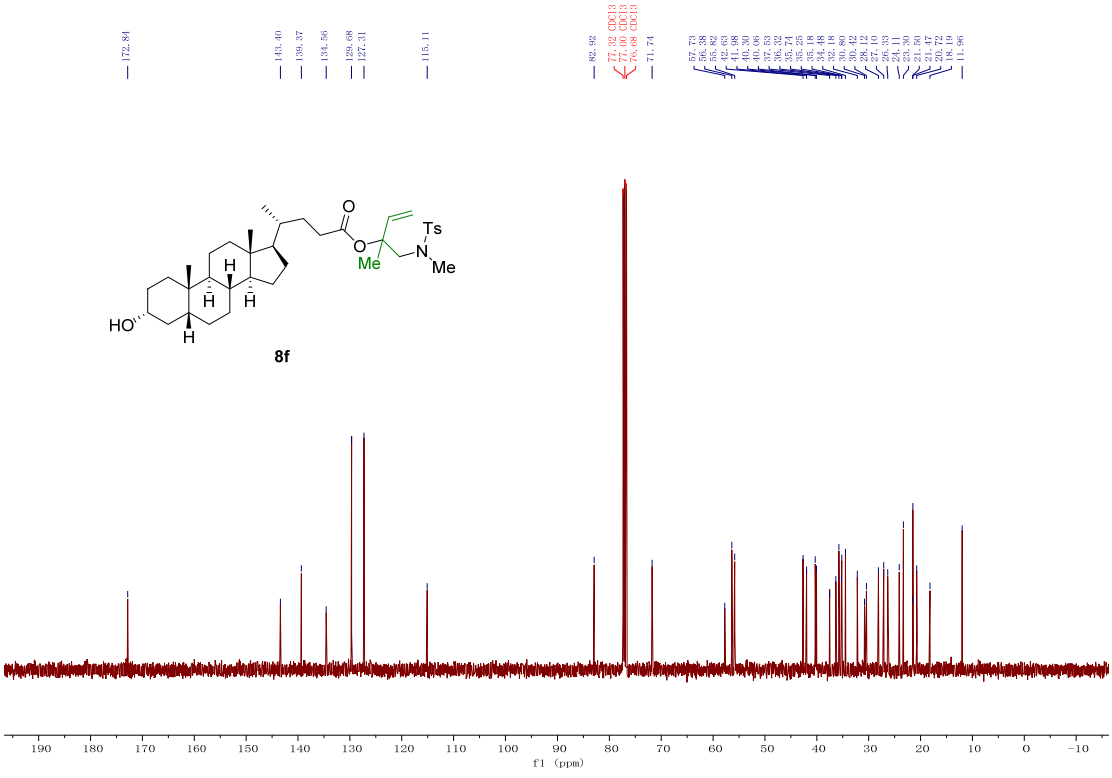
^{13}C NMR (101 MHz, $CDCl_3$)



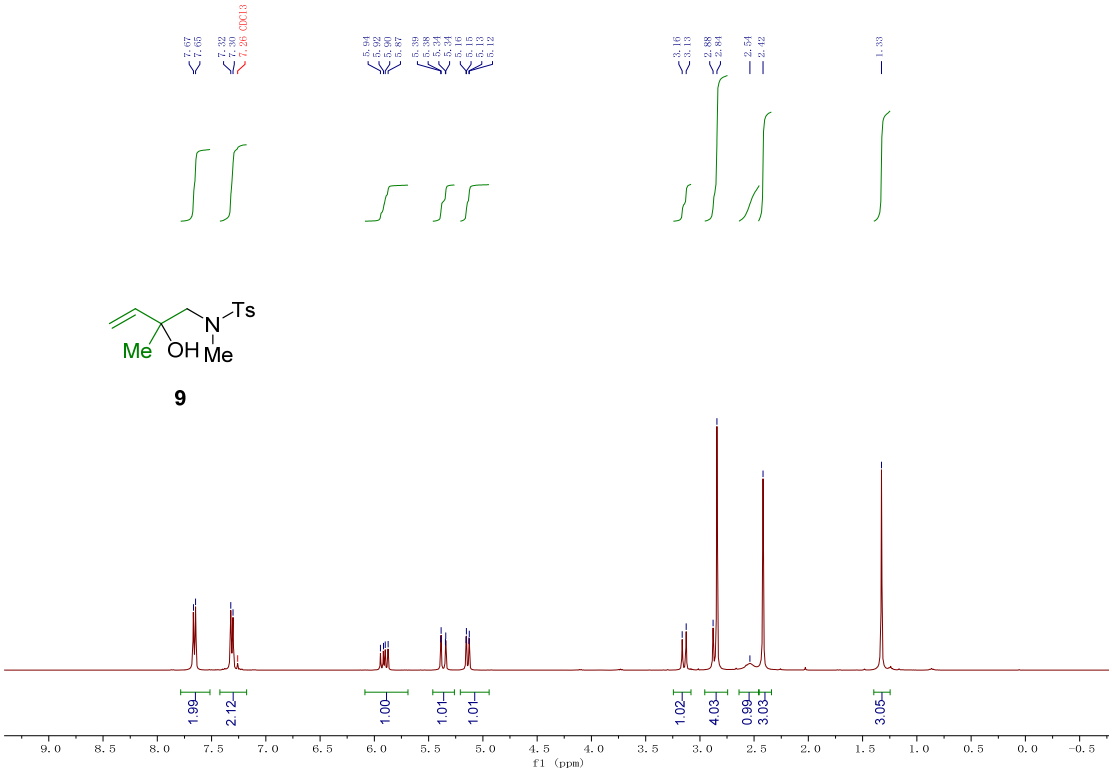
^{1}H NMR (400 MHz, $CDCl_3$)



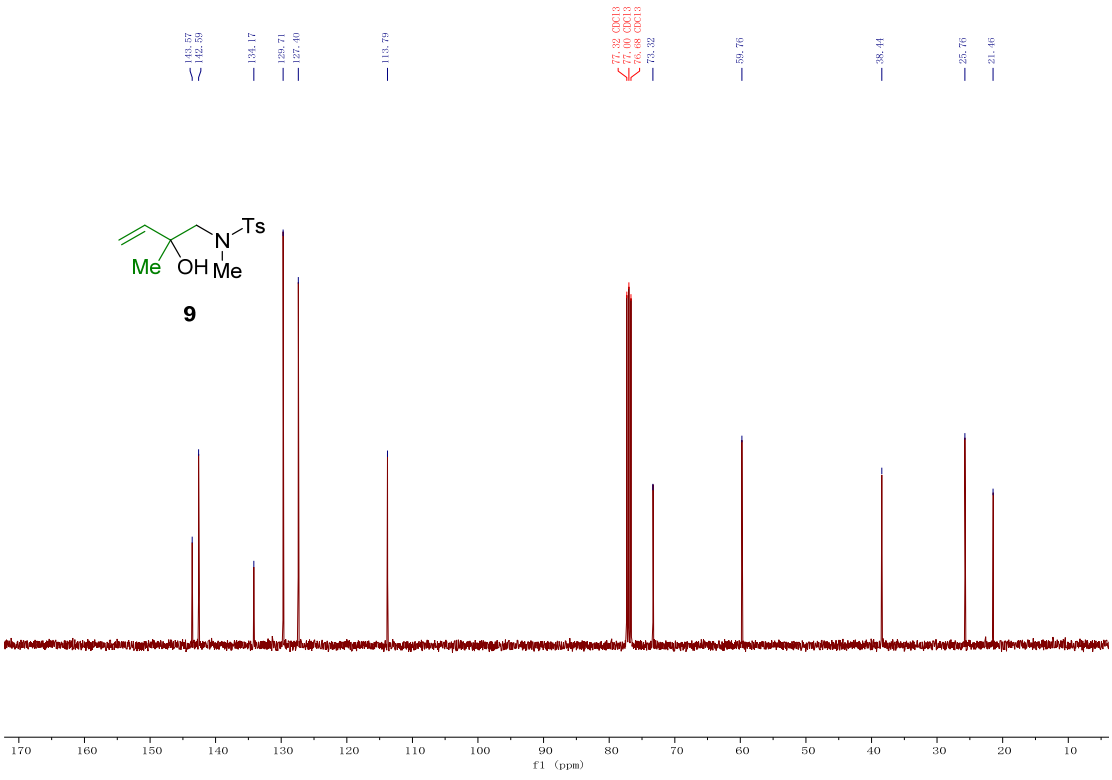
^{13}C NMR (101 MHz, $CDCl_3$)



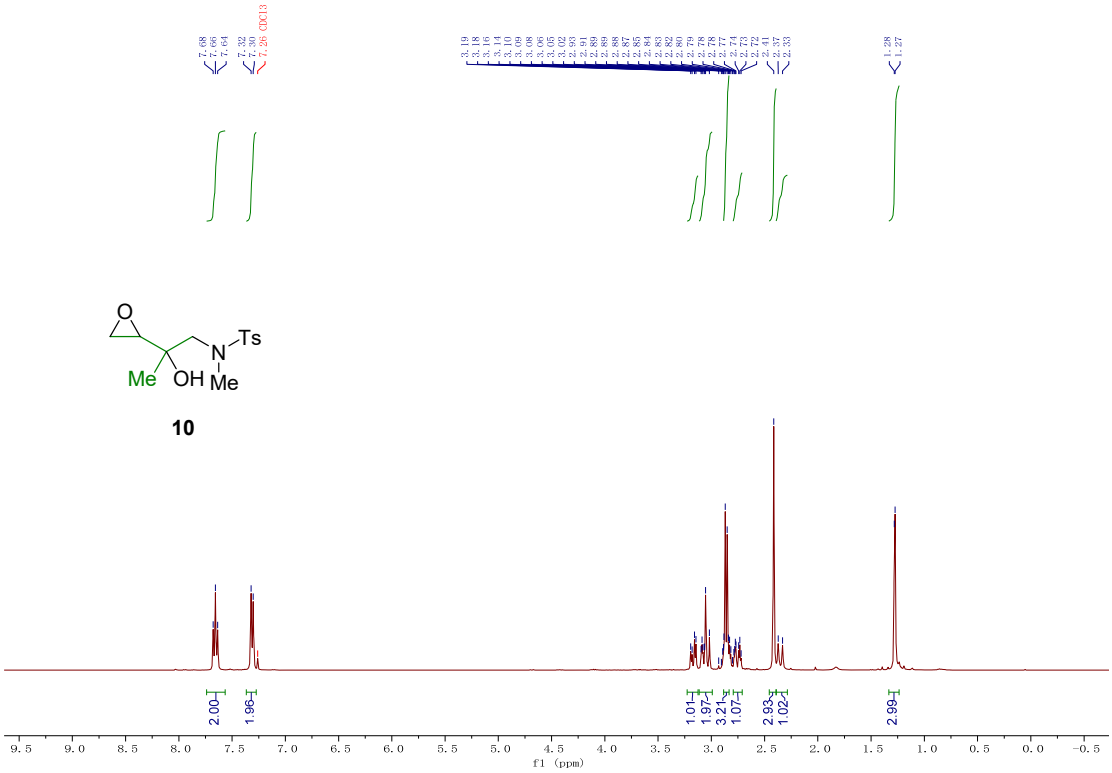
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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