Electronic Supplementary Information

Alkyne aza-Prins cyclization of *N*-(hexa-3,5-diynyl) tosylamides with aldehydes using triflic acid and binuclear aluminum complex

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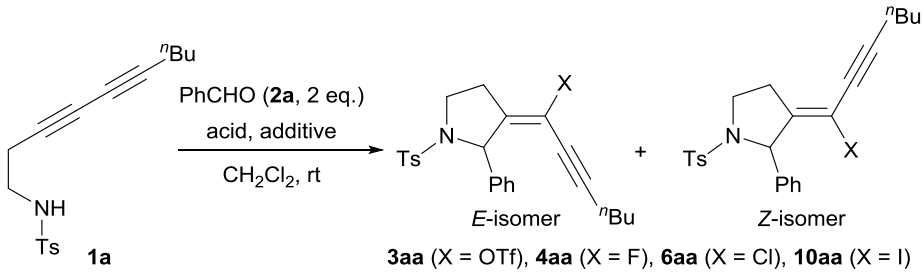
Screening of Acids and Additives for Alkyne Aza-Prins Cyclization

Table S1. Screening of acids and additives for alkyne aza-Prins cyclization of **1a** with **2a**.



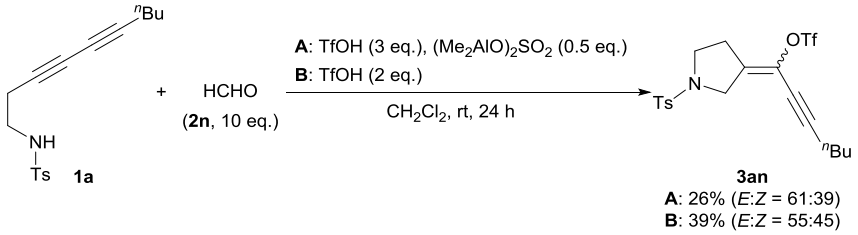
3aa (X = OTf), **4aa** (X = F), **6aa** (X = Cl), **10aa** (X = I)

Entry	Acid (eq.)	Additive (eq.)	Temp. (°C)	Time (h)	Product	Yield[a] (%)	*E:Z*	1a[a] (%)
1	$HBF_4{\cdot}OEt_2$ (3)	MeOH (3)	rt	8	**4aa**	17	76:24	50
2	$HBF_4{\cdot}OEt_2$ (3)		rt	8	**4aa**	0[b]	-	0
3	$HBF_4{\cdot}OEt_2$ (3)		-40	18	**4aa**	47	64:36	0
4	$HBF_4{\cdot}OEt_2$ (3)		-78	18	**4aa**	2	nd[c]	53
5	$HBF_4{\cdot}OEt_2$ (3)	$TBABF_4$ (3)	-40	18	**4aa**	28	58:42	29
6	$HBF_4{\cdot}OEt_2$ (3)	$TBABF_4$ (2)	-40	18	**4aa**	50[d]	59:41	0
7	$HBF_4{\cdot}OEt_2$ (3)	$TBABF_4$ (1)	-40	18	**4aa**	45[d]	61:39	0
8	$HBF_4{\cdot}OEt_2$ (2)	$TBABF_4$ (2)	-40	18	**4aa**	36[d]	69:31	13
9	$HBF_4{\cdot}OEt_2$ (2)	$TBABF_4$ (2)	rt	4	**4aa**	12	67:33	29
10	$BF_3{\cdot}OEt_2$ (3)		rt	18	**4aa**	21	67:33	38
11	$BF_3{\cdot}MeCN$ (3)		rt	18	**4aa**	8	nd[c]	57
12	DMPU·HF (10)		rt	18	**4aa**	0	-	Quant.
13[e]	Py·HF (576)		rt	24	**4aa**	12	67:33	0
14	$HBF_4{\cdot}OEt_2$ (3)	$(Me_2AlO)_2SO_2$ (0.5)	rt	24	**4aa**	13	nd[c]	0
15	$HBF_4{\cdot}OEt_2$ (3)	$(Me_2AlO)_2SO_2$ (0.5)	-40	24	**4aa**	0	-	97
16[f]	Py·HF (3)	$(Me_2AlO)_2SO_2$ (0.5)	80	24	**4aa**	0	-	92
17	TfOH (3)		rt	1	**3aa**	67	75:25	0
18	TfOH (2)		rt	2	**3aa**	67[d]	75:25	0
19	TMSOTf (3)		rt	8	**3aa**	49	69:31	0
20[g]	TMSOTf (3)		rt	8	**3aa**	51	20:80	0
21[g]	TfOH (3)		rt	18	**3aa**	trace	nd[c]	50
22[h]	TfOH (2)	$Al(OTf)_3$ (2)	rt	18	**3aa**	58[d]	74:26	0
23[h]	TfOH (2)	$Zn(OTf)_2$ (2)	rt	18	**3aa**	42	69:31	0
24[h]	TfOH (2)	$Sn(OTf)_2$ (2)	rt	18	**3aa**	42	81:19	0
25	TfOH (4)	Me_3Al (1)	rt	18	**3aa**	46	83:17	0
26	TfOH (4)	Et_3B (1)	rt	18	**3aa**	59	71:29	0
27	TfOH (3)	Et_2Zn (1)	rt	18	**3aa**	21	62:38	34
28	TfOH (5)	Et_2Zn (1.5)	rt	18	**3aa**	56[d]	73:27	34
29	TfOH (4)	Et_2Zn (1)	rt	18	**3aa**	55	69:41	0
30	TfOH (6.5)	Et_2Zn (1.5)	rt	18	**3aa**	59	71:29	0
31	TfOH (5)	Bu_3SnH (1)	rt	2	**3aa**	55	69:31	0
32	TfOH (4)	$(Me_2Al)_2O$ (0.5)	rt	18	**3aa**	66[d]	83:17	0
33	TfOH (4)	Me_3Al (1), EG (0.5)	rt	18	**3aa**	59[d]	83:17	0
34	TfOH (4)	$(Me_2Al)_2NTf$ (0.5)	rt	18	**3aa**	61[d]	84:16	0
35	TfOH (4)	$(Me_2AlO)_2SO_2$ (0.5)	rt	2	**3aa**	66[d]	86:14	0
36	TfOH (3)	$(Me_2AlO)_2SO_2$ (0.5)	rt	2	**3aa**	63[d]	92: 8	0
37	$FeCl_3$ (1.5)		rt	18	**6aa**	23	nd[c]	46
38	$FeCl_3$ (1.5)	TMSCl (1.5)	rt	18	**6aa**	25	nd[c]	0
39	$FeCl_3$ (1)	TMSCl (1)	rt	18	**6aa**	60[d]	78:22	0
40	$FeCl_3$ (0.2)	TMSCl (1.5)	rt	18	**6aa**	21	nd[c]	76
41	I_2 (1.5)		rt	18	**10aa**	0[b]	-	0
42	TMSCl (1)	NaI (1) /MeCN	rt	18	**10aa**	trace	nd[c]	88
43	TMSCl (3)	NaI (3) /MeCN	rt	18	**10aa**	0[b]	-	0

TBA = tetrabutylammonium. DMPU = *N*,*N*'-dimethylpropyleneurea. Py = pyridine. TMS = Me_3Si. EG = ethylene glycol. [a] Values were determined by ^1H NMR analysis. [b] Complex mixture. [c] Not determined. [d] Isolated yields. [e] Neat condition. [f] Solvent: 1,2-dichloroethane. [f] Solvent: Et_2O. [h] These metal triflates was practically insoluble in CH_2Cl_2 even in the presence of TfOH.

Alkyne Aza-Prins Cyclization of 1a with Formaldehyde

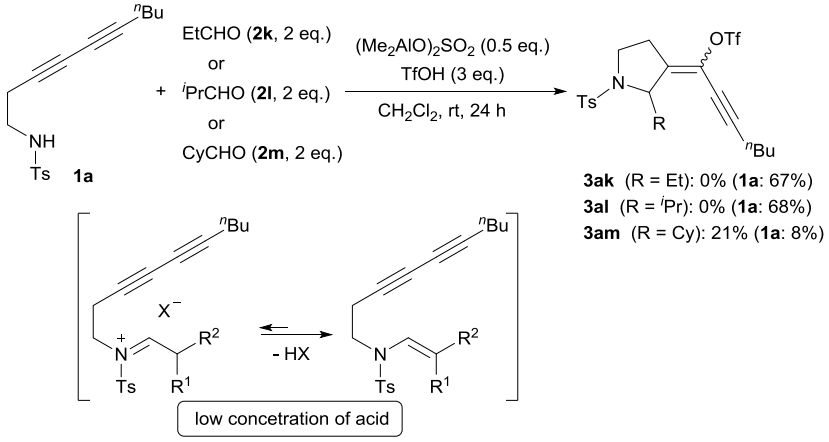
Under the conditions **A** using TfOH (3 eq.) with $(MeAlO)_2SO_2$ (0.5 eq.) and under conditions **B** solely using TfOH (2 eq.), the reactions of 3,5-diynyl tosylamide **1a** with paraformaldehyde (10 eq.) were examined (Scheme S1). Consequently, the desired products were obtained as a mixture of geometric isomers in 26% (E:Z = 61:39) and 39% (E:Z = 55:45) yields, respectively. Similar to the reactions of other aldehydes (entries 1-9, Table 2 in the text), the conditions **A** showed higher *E*-selectivities than the conditions **B**. However, compoared with the steroselectivities of 2-substituted pyrrolidines **3aa**-**3am**, the *E*-selectivities of **3an** under the both conditions **A** and **B** were reduced. The decrease in the *E*-selectivities is in accord with the results of DFT calculations (Figure 1 in the text and Figure S1 in ESI).



Scheme S1. Alkyne aza-Prins cyclization of **1a** with formaldehyde.

Comments on Reactions with Aliphatic Aldehydes under the Conditions A

In the reactions of 3,5-diynyl tosylamides **1a** with aliphatic aldehyde **2k** or **2l**, starting material **1a** were recovered in 67% and 68%, respectively, along with complex mixture (Scheme S2). Under the conditions **A**, proton (TfOH) concentration would be lower than that under conditions **C** (TfOH: 3 eq.) due to the generation of complexes with $(MeAlO)_2SO_2$ and thus aliphatic iminium ions having α-hydrogen would be easily converted to enamines (or the regeneration of iminium ions from enamines would be slow). Therefore, remaining in the enamine intermediates and/or the consquent side reaction such as aldol reaction may not afford the desired products **3ak** and **3al**. On the other hand, in the case of CyCHO (**2m**), **3am** was obtained in low yield likely because the ring strain and/or the steric hindrance of methylenecyclohexane structure in the enamines somewhat inhibited the formation of enamine and/or side reactions.



Scheme S2. Reactions of **1a** with aliphatic aldehydes **2k**-**2m** under the conditions **A**.

Determination of Stereochemistries of Products

The stereochemistry of pyrrolidine *E*-**3ag** and structure of tricyclic compound **7** were confirmed by single crystal X-ray analysis (Figures S1 and S2). Furthermore, the stereochemistries of the other 2-aryl pyrrolidines **3aa-3af**, **3ah-3ai**, **4aa** and **6aa** were determined by comparison with chemical shifts of alkyne carbons of their *E*- and *Z*-isomers (Table S2). As shown in Figure S1, alkyne carbon at terminus side (hereinafter, such carbons are called "C^{α}") in *E*-**3ag** is located near the aromatic ring at 2-position of pyrrolidine. Therefore, compared with the chemical shift of C^{α} of *Z*-**3ag**, the significant downfield shift of C^{α} of *E*-**3ag**, which likely caused by the magnetic anisotropy effect based on ring current of the aromatic ring, was obsereved ($\Delta_C{}^{\alpha}{}_{E\text{-}Z}$ = 0.7 ppm, Table S2). In addition to the chemical shift of C^{α}, that of another alkyne carbon C^{β} of *E*-**3ag** shifted slightly downfield ($\Delta_C{}^{\beta}{}_{E\text{-}Z}$ = 0.3 ppm). The similar observations were showed in the spectra of the other pyrrolidines **3aa-3af**, **3ah-3ai**, **4aa** and **6aa**. Thus, compared with the chemical shift of C^{α} and C^{β} of their minor isomers, those of C^{α} of their major isomers shifted significantly downfield ($\Delta_C{}^{\alpha}{}_{E\text{-}Z}$ = 0.8 to 1.2 ppm) and those of C^{α} of some major isomers shifted downfield ($\Delta_C{}^{\beta}{}_{E\text{-}Z}$ = -0.1 to 0.2 ppm). Hence, their major isomers were detemined as *E*-isomers.

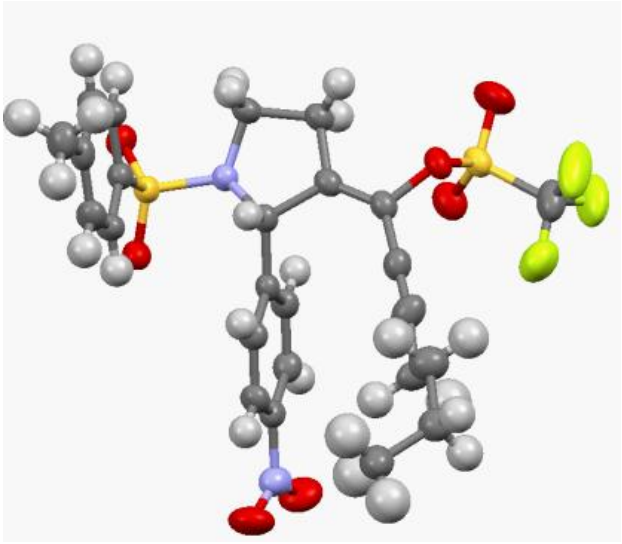


Figure S1. X-ray structure of *E*-**3ag**.

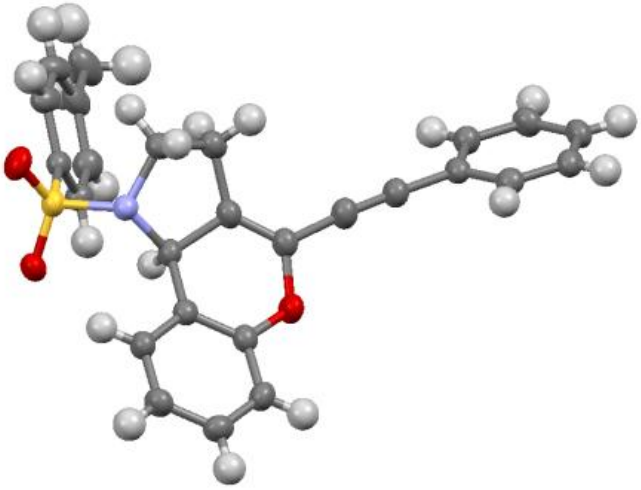
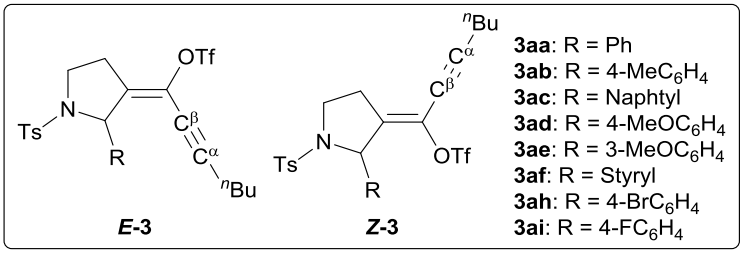
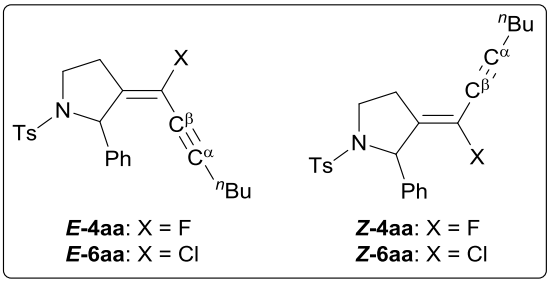


Figure S2. X-ray structure of **7**.

Table S2. Chemical Shifts of C^{α} and C^{β} of products **3aa-ai**, **4aa** and **6aa**.





E-**3**	$\delta_C{}^{\alpha}$ ppm	$\delta_C{}^{\beta}$ ppm	*Z*-**3**	$\delta_C{}^{\alpha}$ ppm	$\delta_C{}^{\beta}$ ppm	$\Delta_C{}^{\alpha}{}_{E\text{-}Z}$ ppm	$\Delta_C{}^{\beta}{}_{E\text{-}Z}$ ppm
E-**3ag**	102.7	70.9	*Z*-**3ag**	102.0	70.6	0.7	0.3
E-**3aa**	101.8	71.0	*Z*-**3aa**	101.0	70.9	0.8	0.1
E-**3ab**	101.7	71.1	*Z*-**3ab**	100.8	71.0	0.9	0.1
E-**3ac**	102.0	71.0	*Z*-**3ac**	101.1	71.0	0.9	0
E-**3ad**	101.7	71.0	*Z*-**3ad**	100.8	71.0	0.9	0
E-**3ae**	101.7	71.1	*Z*-**3ae**	101.0	70.9	0.9	0.2
E-**3af**	101.9	70.9	*Z*-**3af**	100.9	71.0	1.0	-0.1
E-**3ah**	102.2	70.9	*Z*-**3ah**	101.3	70.8	0.9	0.1
E-**3ai**	102.0	70.9	*Z*-**3ai**	101.2	70.8	0.8	0.1
E-**4aa**	99.0	71.1	*Z*-**4aa**	97.8	70.9	1.2	0.2
E-**6aa**	97.5	76.1	*Z*-**6aa**	96.4	76.0	1.1	0.1

On the other hand, the stereochemistries of the 2-alkyl pyrrolidines **3ak-3am** (Figures S3-S6) and the ring-opening products **5ba-5ca** (Figures S7-S9) were determined by NOESY spectra. As shown in Figure S3, NOE correlations between H^b and H^c in spectra of ***E*-3ak** (Figure S4), those between H^b and H^c in spectra of ***E*-3al** (Figure S5), or those between H^b and H^d and between H^c and H^d in spectra of ***E*-3am** (Figure S6) were obseved. Thus, those products were detemined as *E*-isomers. Furthermore, as shown in Figure S7, NOE correlations between H^c and H^d and between H^c and H^e in spectra of **5ba** (Figure S8) or those between H^a and H^a and between H^a and H^d in spectra of **5ca** (Figure S9) were obseved. Hence, those products were detemined as *E*-isomers.

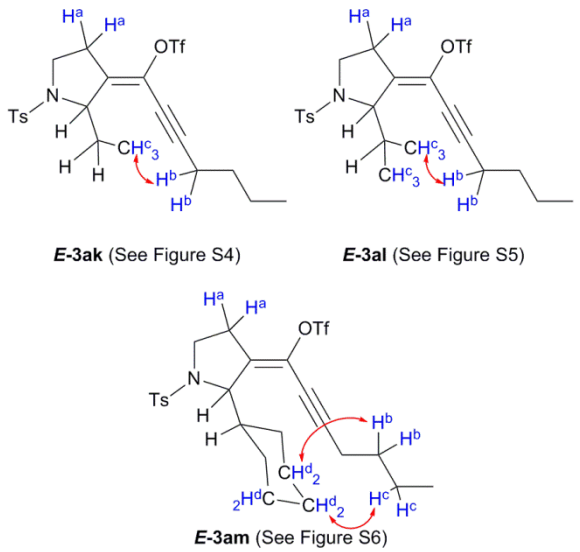


Figure S3. Summarization of NOESY correlations of ***E*-3ak**, ***E*-3al** and ***E*-3am**.

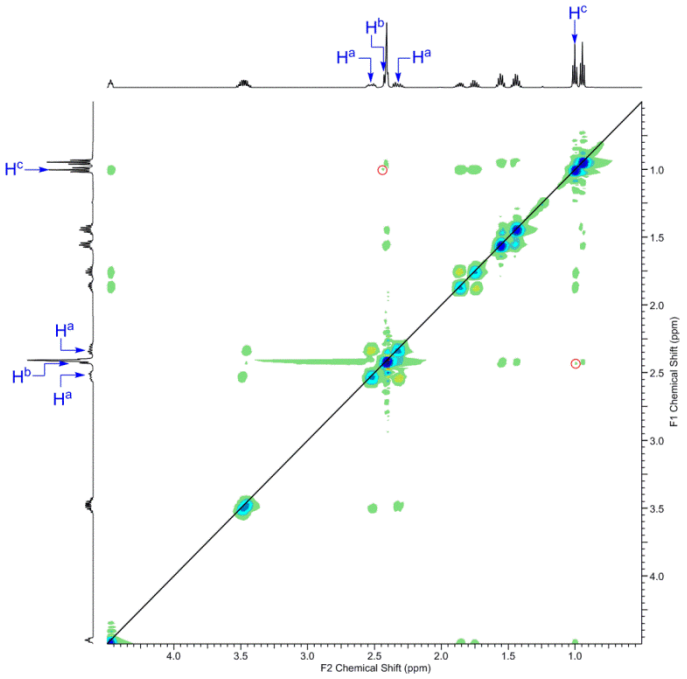


Figure S4. NOESY spectrum of ***E*-3ak**.

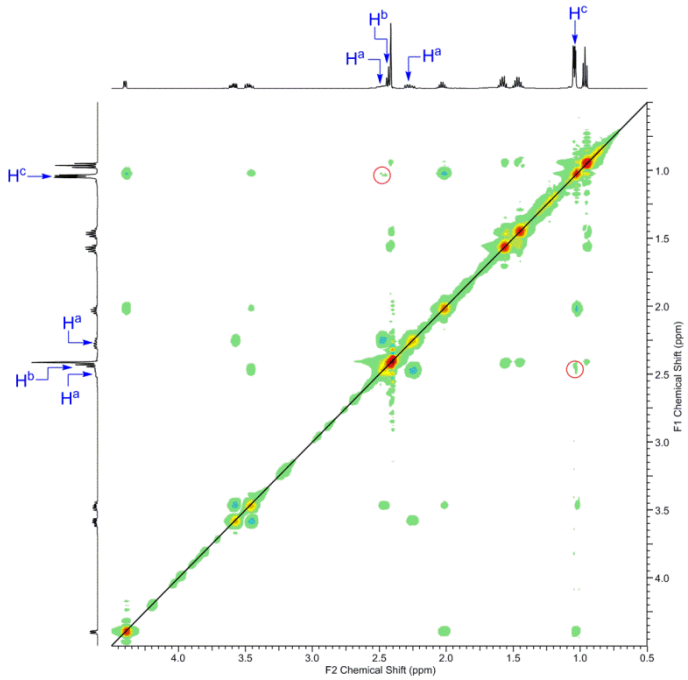


Figure S5. NOESY spectrum of ***E*-3al**.

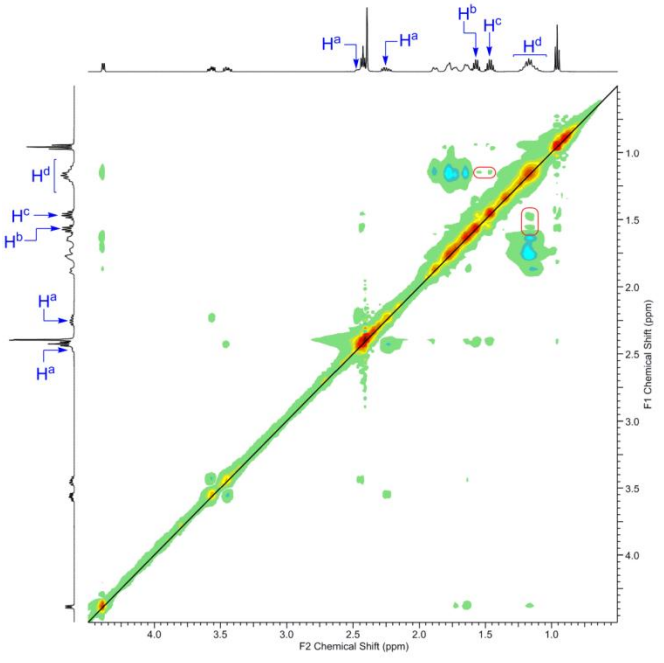
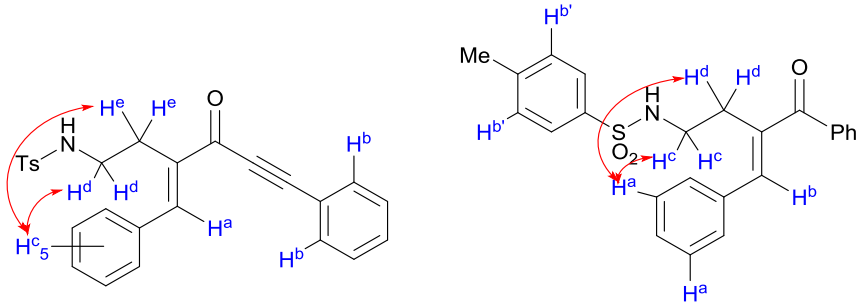


Figure S6. NOESY spectrum of ***E*-3am**.



5ba (See Figure S8) **5ca** (See Figure S9)

Figure S7. Summarization of NOESY correlations of **5ba** and **5ca**.

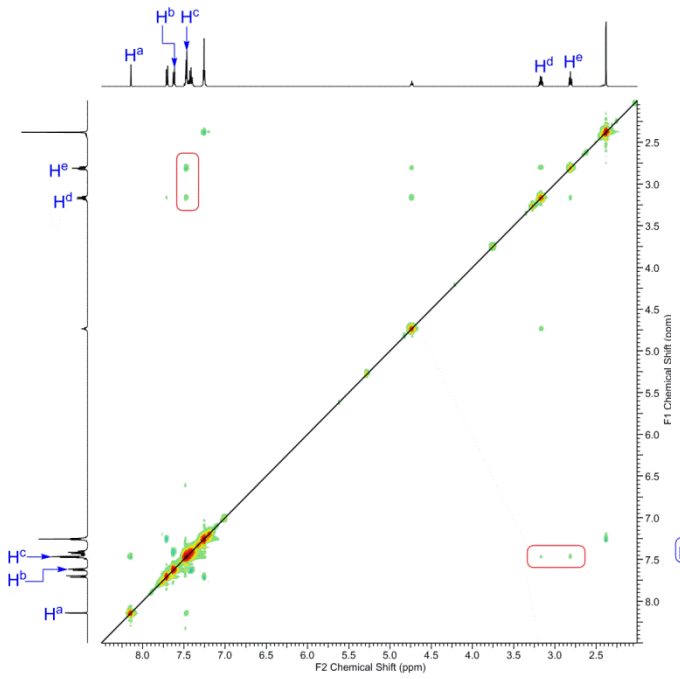


Figure S8. NOESY spectrum of **5ba**.

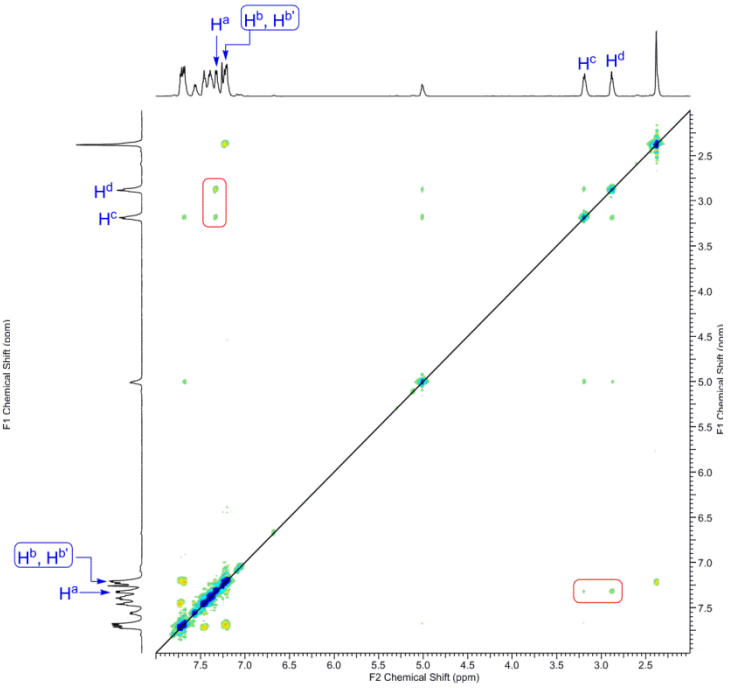


Figure S9. NOESY spectrum of **5ca**.

DFT Calculations on 6-endo and 5-exo Cyclization Pathways

All calculations were performed with the Gaussian 09 package.[1] All local minima and transition states were optimized at B3LYP/6-31+G* with the polarized continuum model (PCM, CH_2Cl_2). Frequency calculation were carried out to characterize the stationary points and to estimate Gibbs free energies.

We explored 6-*endo* and 5-*exo* cyclization pathways in the present aza-Prins cyclization (Figure S10). Though 6-*endo* product **PDc** is 1.8 kcal/mol more stable than 5-*exo* product **PDa_E**, the concerted 6-*endo* process directly affording **PDc** is overwhelmingly higher energy level than the stepwise 5-*exo* process via formation of the cationic cyclized intermediate.

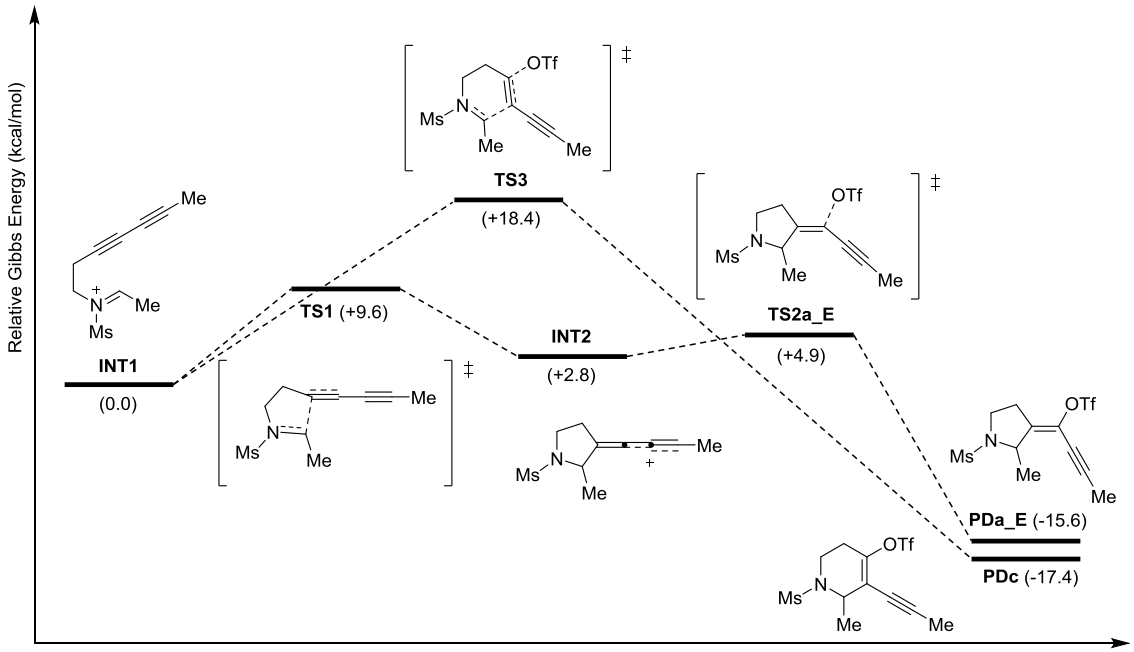


Figure S10. Gibbs free energy profile (in kcal/mol) of 6-*endo* and 5-*exo* cyclization pathways.

[1] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; and Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.

DFT Calculations of Models Derived from Benzaldehyde instead of Acetaldehyde

Focusing on the *E*/*Z*-selectivity of TfO^- addition, **TS2a_E** is 0.7 kcal/mol more stable than **TS2a_Z** (Figure 1 in the text) in qualitatively good agreement with the experimental results. Therefore, the calculations were carried out using models derived from benzaldehyde instead of acetaldehyde (Figure S11). As a results, the energy difference between **TS2'a_Z** and **TS2'a_E** increases to 0.9 kcal/mol. The *E*-selectivity is due to the enhancement of strain energy of carbocation moiety in **TS2'a_Z** (1.8 kcal/mol more compared with strain energy of **TS-2'a_E**, 2.5º less compared with cation-centered angle in **TS-2'a_E**) caused by the mitigation of steric hindrance between 2-phenyl group and TfO^-.

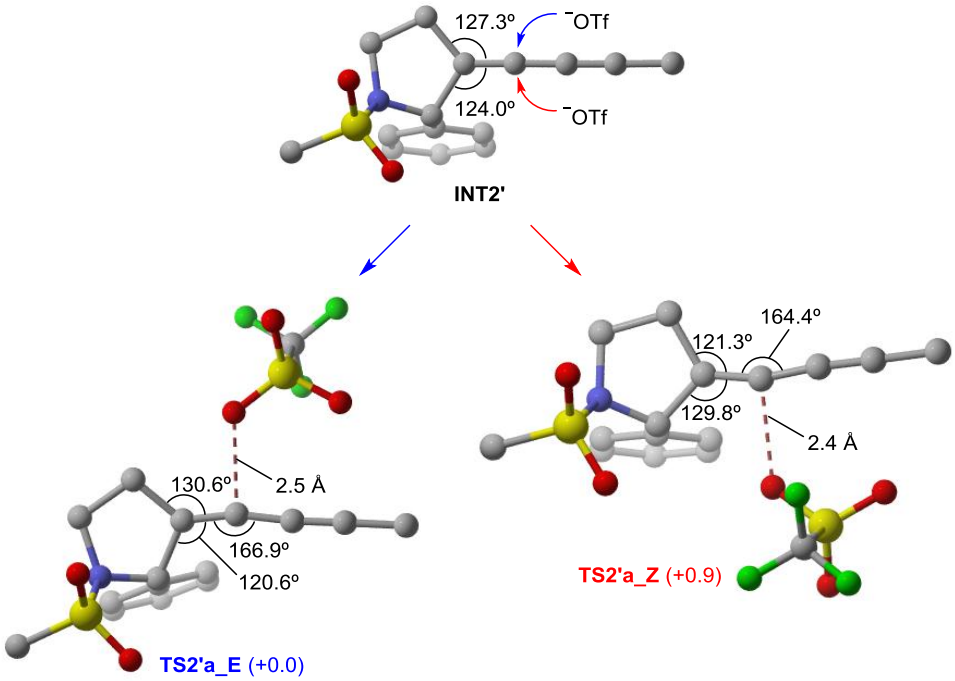
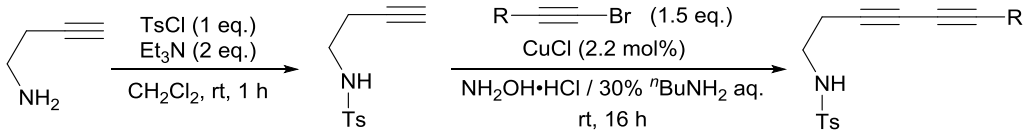


Figure S11. 3D structures of **INT2'**, **TS2'a_E** and **TS2'a_Z**.

General Information

All reactions were carried out under an argon atmosphere. *N*-Homopropargyl tsylamide **1c** and **1d** were prepared by the method reported in the literatures.[2] Triflic acid (TfOH), Me_3Al, bis(trimethylsilyl)sulfate [$(TMSO)_2SO_2$] and aldehydes **2a-n** are commercially available. Dichloromethane were purchased as the "anhydrous" and used without further purification. For the TLC analysis, Merck precoated TLC plates (silica gel 60 F254) were used. Column chromatography was performed on silica gel 60N (63-200 μm, neutral, Kanto Kagaku Co., Ltd.). Medium-pressure liquid chromatography (MPLC) was carried out on YAMAZEN W-Prep 2XY. ^{1}H and ^{13}C NMR spectra were measured at 500 (or 300) and 125 (or 75) MHz in $CDCl_3$, and the chemical shifts are given in ppm using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for 1H NMR and $CDCl_3$ (77.0 ppm) for ^{13}C NMR as an internal standard, respectively. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broadened). IR spectra were obtained on a JASCO FT/IR-6200. Mass spectra and HRMS were recorded on a JEOL MStation MS700 (double-focusing magnetic sector) by FAB methods.

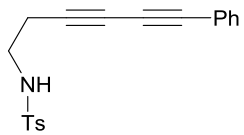
Synthesis and Characterization of 3,5-Diynyl Tosylamides 1a and 1b



To a solution of 3-butyn-1-amine (0.8 mL, 10 mmol) and triethylamine (2.8 mL, 20 mmol) in CH_2Cl_2 (30 mL) was added *p*-toluenesulfonyl chloride (1.9 g, 10 mmol) at 0 ºC. After being stirred at room temperature for 1 h, the reaction mixture was quenched with H_2O and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by silica gel column chromatography (hexane:AcOEt = 3:1) to give ***N*-3-butyn-1-yl-4-methyl-benzenesulfonamide**[3] (2.15 g, 96%).

CuCl (6.5 mg, 66 μmol) was added to a 30% ^{n}BuNH$_2$ aqueous solution (9 mL) at room temperature. And then, until the resulting blue solution became colorless, hydroxylamine hydrochloride were added. After the solution was cooled to 0 ºC, ***N*-3-butyn-1-yl-4-methyl-benzenesulfonamide** (670 mg, 3 mmol) was added, thereby forming in a yellow acetylide suspension. Subsequently, 1-bromohex-1-yne[4] (725 mg, 4.5 mmol) or (bromoethynyl)benzene[3] (815 mg, 4.5 mmol) was added at same temperature. After being stirred at room temperature for 16 h, the reaction mixture was extracted with Et_2O. The organic layer was washed with sat. NH_4Cl, dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by silica gel column chromatography (hexane:AcOEt = 3:1) to give **1a** (600 mg, 67%) or **1b** (762 mg, 80%).

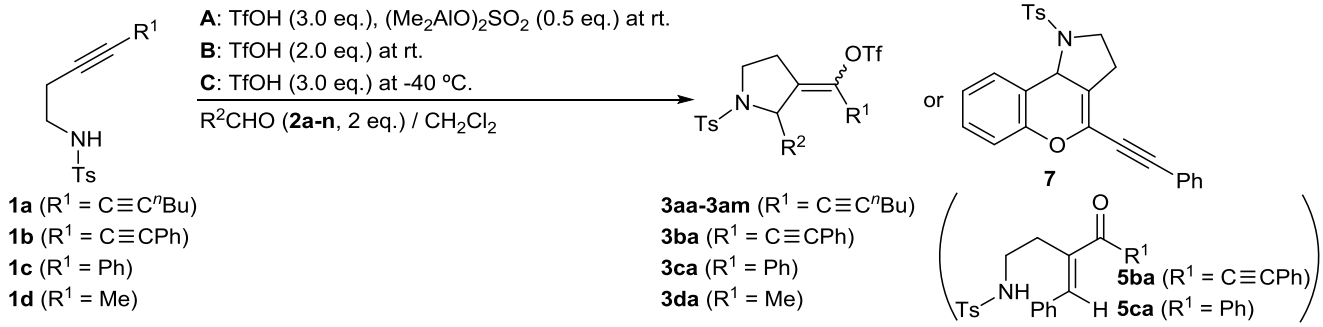
***N*-(Deca-3,5-diyn-1-yl)-4-methylbenzenesulfonamide (1a)**: R_f = 0.37 (hexane:AcOEt = 3:1). White solid. MP: 45-46ºC. IR (KBr) ν cm^{-1}; 2259, 1317, 1153. ^{1}H NMR (500 MHz) δ ppm; 7.75 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.70 (br.t, *J* = 6.6 Hz, 1H), 3.10 (q, *J* = 6.6 Hz, 2H), 2.43 (s, 3H), 2.41 (t, *J* = 6.3 Hz, 3H), 2.26 (t, *J* = 6.8 Hz, 2H), 1.55-1.47 (m, 2H), 1.46-1.38 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 143.6, 136.8, 129.7, 127.0, 78.8, 72.6, 67.6, 64.6, 41.5, 30.1, 21.8, 21.5, 20.6, 18.8, 13.4. FAB-LM *m/z*: 304 [M+H]. FAB-HM Calcd for $C_{17}H_{22}NO_2S$ [M+H]: 304.1371; found: 304.1407.



4-Methyl-*N*-(6-phenylhexa-3,5-diyn-1-yl)benzenesulfonamide (1b): R_f = 0.26 (hexane:AcOEt = 3:1). Colorless solid. MP: 106-107 ºC. IR (KBr) ν cm^{-1}; 2243, 1316, 1153. ^{1}H NMR (500 MHz) δ ppm; 7.78 (d, *J* = 8.0 Hz, 2H), 7.49-7.44 (m, 2H), 7.38-7.33 (m, 1H), 7.33-7.28 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.11 (t, *J* = 6.3 Hz, 1H), 3.15 (td, *J* = 6.6, 6.3 Hz, 2H), 2.53 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (125 MHz) δ ppm; 143.6, 136.7, 132.5, 129.8, 129.1, 128.4, 127.0, 121.4, 80.0, 75.7, 73.6, 67.2, 41.4, 21.5, 21.0. FAB-LM *m/z*: 324 [M+H]. FAB-HM Calcd for $C_{19}H_{18}NO_2S$ [M+H]: 324.1058; found: 324.1026.

[2] Y. Yin, W. Ma, Z. Chai and G. Zhao, *J. Org. Chem.*, **2007**, *72*, 5731.
[3] H. Park, H.-K. Lee and T.-L. Choi, *J. Am. Chem. Soc.*, **2013**, *135*, 10769.
[4] J. P. Marino and H. N. Nguyen *J. Org. Chem.*, **2002**, *67*, 6841.

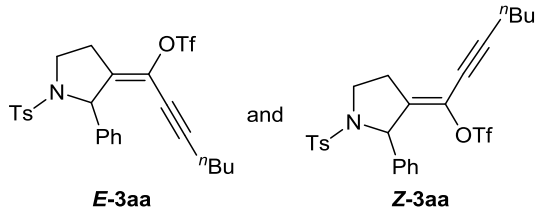
Synthesis and Characterization of TfO-Substituted Pyrrolidines 3, Ring-Opening Products 5ba, 5ca and Tricyclic Compound 7



Method **A**: To a solution of $(Me_2AlO)_2SO_2$, which was prepared by the treatment of $(TMSO)_2SO_2$ (48.5 mg, 0.20 mmol) in CH_2Cl_2 (2.5 mL) with Me_3Al (15% solution in hexane, 0.3 mL, 0.4 mmol) at room temperature for 30 min,[5] was added TfOH (105.9 μL, 1.2 mmol) at 0 ºC. After being stirred at room temperature for 30 min, aldehyde **2** (0.80 mmol) and homopropargyl amide **1** (**1a**, 121.4 mg, 0.40 mmol; **1b**, 129.4 mg, 0.40 mmol; **1c**, 119.8 mg, 0.4 mmol; or **1d**, 94.9 mg, 0.4 mmol) were added in turn and then the reaction mixture was stirred at room temperature until amide **1** was consumed completely (by TLC analysis). The reaction mixture was quenched with sat. NH_4Cl and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC to give **3aa-3aj**, **3am**, **3an**, **3ba** (and **5ba**), **3ca** (and **5ca**) or **3da**.

Method **B**: To a solution of aldehyde **2a-f** or **2n** (0.80 mmol) and homopropargyl amide **1** (**1a**, 121.4 mg, 0.40 mmol; **1b**, 129.4 mg, 0.40 mmol; **1c**, 119.8 mg, 0.4 mmol; or **1d**, 94.9 mg, 0.4 mmol) in CH_2Cl_2 (2.5 mL) was added TfOH (70.6 μL, 0.8 mmol) at 0 ºC. After being stirred at room temperature until amide **1** was consumed completely (by TLC analysis), the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC to give **3aa**-**3af**, **3an**, **3ba** (and **5ba**), **3ca** (and **5ca**), **3da** or **7**.

Method **C**: To a solution of aldehyde **2g-m** (0.80 mmol) and 3,5-diynyl amide **1a** (121.4 mg, 0.40 mmol) in CH_2Cl_2 (2.5 mL) was added TfOH (105.9 μL, 1.2 mmol) at -40 ºC. After being stirred at same temperature until amide **1a** was consumed completely (by TLC analysis), the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC to give **3ag-3am**.

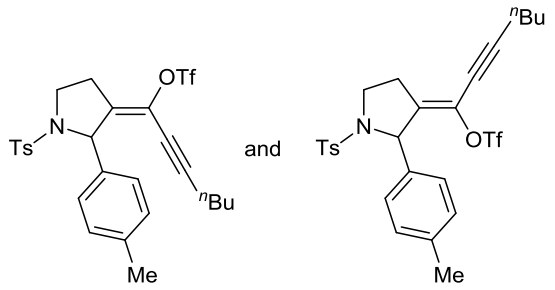


***E*-3aa** ***Z*-3aa**

(*E*)-1-(2-Phenyl-1-tosylpyrrolidin-3-ylidene)hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3aa)
Method **A** (2 h): 125.6 mg (58%). Method **B** (2 h): 101.8 mg (47%). R_f = 0.40 (hexane:AcOEt = 3:1). Yellow oil. IR (neat) ν cm^{-1}; 2225, 1599, 1420, 1351, 1214, 1164, 1093. ^{1}H NMR (500 MHz) δ ppm; 7.58 (d, *J* = 8.0 Hz, 2H), 7.37-7.33 (m, 2H), 7.32-7.28 (m, 3H), 7.24 (dd, *J* = 8.0 Hz, 2H), 5.61 (s, 1H), 3.67-3.60 (m, 1H), 3.54-3.46 (m, 1H), 2.73-2.64 (m, 1H), 2.63-2.54 (m, 1H), 2.40 (s, 3H), 2.30 (t, *J* = 6.8 Hz, 2H), 1.47-1.38 (m, 2H), 1.35-1.24 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 144.0, 141.3, 137.7, 134.9, 129.7, 128.5, 128.1, 127.2, 126.5, 118.1 (q, J_{C-F} = 320.3 Hz), 101.8, 71.0, 65.5, 46.4, 29.7, 28.7, 21.7, 21.4, 18.9, 13.4 (note that two carbon peaks overlap with each other). ^{19}F NMR (282 MHz) δ ppm; -75.1. FAB-LM *m/z*: 542 [M+H]. FAB-HM Calcd for $C_{25}H_{27}F_3NO_5S_2$ [M+H]: 542.1283; found: 542.1298.

(*Z*)-1-(2-Phenyl-1-tosylpyrrolidin-3-ylidene)hept-2-yn-1-yl trifluoromethanesulfonate (*Z*-3aa)
Method **A** (2 h): 10.9 mg (5%). Method **B** (2 h): 34.7 mg (16%). R_f = 0.23 (hexane:AcOEt = 3:1). Yellow oil. IR (neat) ν cm^{-1}; 2224, 1599, 1420, 1352, 1222, 1163, 1093. ^{1}H NMR (500 MHz) δ ppm; 7.58 (d, *J* = 8.1 Hz, 2H), 7.34-27 (m, 5H), 7.25 (d, *J* = 8.1 Hz, 2H), 5.56 (d, *J* = 1.8 Hz, 1H), 3.72-3.63 (m, 1H), 3.55-3.47 (m, 1H), 2.89-2.78 (m, 1H), 2.68-2.59 (m, 1H), 2.40 (s, 3H), 2.33 (t, *J* = 7.2 Hz, 2H), 1.53-1.44 (m, 2H), 1.41-1.32 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz) δ (ppm); 143.8, 140.7, 138.5, 134.3, 129.7, 128.6, 128.2 127.5, 127.4, 124.4, 118.1 (q, J_{C-F} = 320.3 Hz), 101.0, 70.9, 64.7, 46.8, 29.8, 29.7, 21.8, 21.5, 19.0, 13.4. ^{19}F NMR (282 MHz) δ ppm; -74.9. FAB-LM *m/z*: 542 [M+H]. FAB-HM Calcd for $C_{25}H_{27}F_3NO_5S_2$ [M+H]: 542.1283; found: 542.1291.

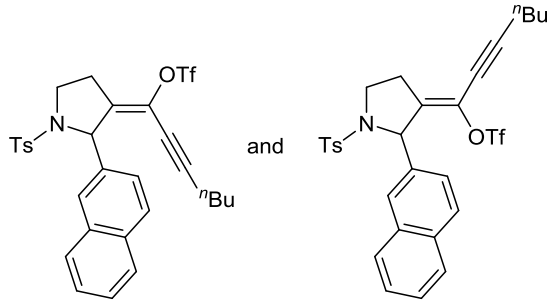
[5] H. Hanawa, N. Maekawa and K. Maruoka, *Tetrahedron Lett.*, **1999**, *40*, 8379.



***E*-3ab** ***Z*-3ab**

(*E*)-1-(2-(p-Tolyl)-1-tosylpyrrolidin-3-ylidene)hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3ab)
Method **A** (4 h): 113.3 mg (51%). Method **B** (2 h): 60.0 mg (27%). R_f = 0.51 (hexane:AcOEt = 3:1). White solid. MP: 50-51 ºC. IR (KBr) ν cm^{-1}; 2225, 1596, 1419, 1352, 1215, 1164, 1092. ^{1}H NMR (500 MHz) δ ppm; 7.58 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 5.57 (s, 1H), 3.65-3.58 (m, 1H), 3.53-3.45 (m, 1H), 2.71-2.63 (m, 1H), 2.61-2.53 (m, 1H), 2.40 (s, 3H), 2.32 (s, 3H), 2.29 (t, *J* = 7.2 Hz, 2H), 1.46-1.39 (m, 2H), 1.34-1.25 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 143.9, 141.4, 137.8, 135.0, 134.8, 129.7, 129.2, 127.2, 127.1, 126.4, 118.2 (q, J_{C-F} = 320.3 Hz), 101.7, 71.1, 65.4, 46.4, 29.7, 28.7, 21.7, 21.5, 21.1, 19.0, 13.4. ^{19}F NMR (282 MHz) δ ppm; -75.2. FAB-LM m/z: 556 [M+H]. FAB-HM Calcd for $C_{26}H_{29}F_3NO_5S_2$ [M+H]: 556.1439; found 556.1433.

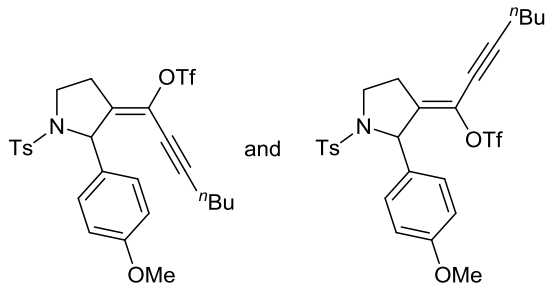
(*Z*)-1-[2-(p-Tolyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*Z*-3ab)
Method **A** (4 h): 20.0 mg (9%). Method **B** (2 h): 28.9 mg (13%). R_f = 0.34 (hexane:AcOEt = 3:1). Brown oil. IR (neat) ν cm^{-1}; 2224, 1598, 1420, 1351, 1220, 1163, 1093. ^{1}H NMR (500 MHz) δ ppm; 7.57 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.51 (s, 1H), 3.70-3.62 (m, 1H), 3.51-3.44 (m, 1H), 2.86-2.76 (m, 1H), 2.65-2.56 (m, 1H), 2.39 (s, 3H), 2.32 (t, *J* = 6.9 Hz, 2H), 2.31 (s, 3H), 1.51-1.43 (m, 2H), 1.40-1.30 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 143.7, 140.9, 138.0, 135.6, 134.3, 129.7, 129.3, 127.5, 127.2, 124.3, 118.1 (q, J_{C-F} = 320.3 Hz), 100.8, 71.0, 64.5, 46.8, 29.8, 29.7, 21.8, 21.5, 21.1, 19.0, 13.4. ^{19}F NMR (282 MHz) δ ppm; -74.9. FAB-LM m/z: 556 [M+H]. FAB-HM Calcd for $C_{26}H_{29}F_3NO_5S_2$ [M+H]: 556.1439; found 556.1449.



***E*-3ac** ***Z*-3ac**

(*E*)-1-[2-(Naphthalene-2-yl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3ac)
Method **A** (4 h): 120.7 mg (51%). Method **B** (4 h): 89.9 mg (38%). R_f = 0.40 (hexane:AcOEt = 3:1). Brown solid. MP: 60-62 ºC. IR (KBr) ν cm^{-1}; 2223, 1596, 1420, 1353, 1224, 1166, 1093. ^{1}H NMR (500 MHz) δ ppm; 7.84-7.77 (m, 3H), 7.75 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.52-7.46 (m, 3H), 7.17 (d, *J* = 8.6 Hz, 2H), 5.78 (s, 1H), 3.78-3.66 (1H), 3.63-3.53 (m, 1H), 2.85-2.74 (m, 1H), 2.72-2.62 (m, 1H), 2.36 (s, 3H), 2.25 (t, *J* = 7.2 Hz, 2H), 1.40-1.30 (m, 2H), 1.26-1.16 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR(125 MHz) δ ppm; 143.9, 141.3, 135.0, 134.8, 133.0, 132.9, 129.7, 128.5, 128.1, 127.5, 127.2, 126.7, 126.6, 126.3, 126.2, 124.9, 118.2 (q, J_{C-F} = 320.3 Hz), 102.0, 71.0, 65.8, 46.5, 29.6, 28.8, 21.6, 21.4, 18.9, 13.2. ^{19}F NMR (282 MHz) δ ppm; -75.1. FAB-LM m/z: 592 [M+H]. FAB-HM Calcd for $C_{29}H_{29}F_3NO_5S_2$ [M+H]: 592.1439; found 592.1468.

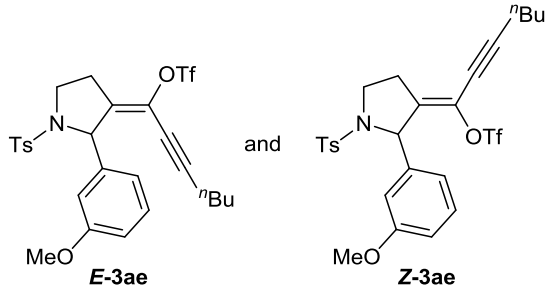
(*Z*)-1-[2-(Naphthalene-2-yl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*Z*-3ac)
Method **A** (4 h): 33.1 mg (14%). Method **B** (4 h): 40.2 mg (17%). R_f = 0.29 (hexane:AcOEt = 3:1). Colorless oil. IR (neat) ν cm^{-1}; 2224, 1599, 1420, 1352, 1219, 1163, 1093. ^{1}H NMR (500 MHz) δ ppm; 7.83-7.77 (m, 2H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.73 (s, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.52-7.45 (m, 2H), 7.39 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 5.74 (s, 1H), 3.79-3.72 (m, 1H), 3.64-3.56 (m, 1H), 2.97-2.87 (m, 1H), 2.75-2.65 (m, 1H), 2.35 (d, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.53-1.44 (m, 2H), 1.42-1.33 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 143.8, 140.6, 135.5, 134.4, 133.1, 133.0, 129.6, 128.6, 128.2, 127.5, 127.4, 126.8, 126.3, 126.2, 124.8, 124.6, 118.1 (q, J_{C-F} = 320.3 Hz), 101.1, 71.0, 64.9, 46.9, 29.8, 21.8, 21.4, 19.0, 13.4 (note that two carbon peaks overlap with each other). ^{19}F NMR (282 MHz) δ ppm; -74.9. FAB-LM m/z: 592 [M+H]. FAB-HM Calcd for $C_{29}H_{29}F_3NO_5S_2$ [M+H]: 592.1439; found 592.1463.



***E*-3ad** ***Z*-3ad**

(*E*)-1-[2-(4-Methoxyphenyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3ad)
Method **A** (24 h): 96.0 mg (42%). Method **B** (24 h): 89.2 mg (39%). R_f = 0.49 (hexane:AcOEt = 3:1). White solid. MP: 79-80 ºC. IR (KBr) ν cm^{-1}; 2220, 1597, 1419, 1350, 1212, 1163, 1095 . ^{1}H NMR (500 MHz) δ ppm; 7.58 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.57 (s, 1H), 3.79 (s, 3H), 3.66-3.59 (m, 1H), 3.53-3.46 (m, 1H), 2.74-2.65 (m, 1H), 2.62-2.53 (m, 1H), 2.41 (s, 3H), 2.30 (t, *J* = 7.2 Hz, 2H), 1.47-1.40 (m, 2H), 1.35-1.26 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 159.4, 143.9, 141.6, 135.1, 129.8, 129.7, 128.5, 127.2, 126.4, 118.2 (q, J_{C-F} = 320.3 Hz), 113.8, 101.7, 71.0, 65.1, 55.2, 46.3, 29.7, 28.7, 21.7, 21.4, 18.9, 13.4. ^{19}F NMR (282 MHz) δ ppm; -75.1. FAB-LM m/z: 572 [M+H]. FAB-HM Calcd for $C_{26}H_{29}F_3NO_6S_2$ [M+H]: 572.1388; found 572.1418.

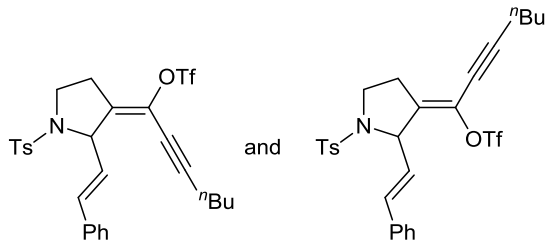
(*Z*)-1-[2-(4-Methoxyphenyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*Z*-3ad)
Method **A** (24 h): 18.3 mg (8%). Method **B** (24 h): 54.9 mg (24%). R_f = 0.34 (hexane:AcOEt = 3:1). Red oil. IR (neat) ν cm^{-1}; 2224, 1599, 1419, 1349, 1217, 1162, 1092. ^{1}H NMR (500 MHz) δ ppm; 7.58 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 9.1 Hz, 2H), 6.82 (d, *J* = 9.1 Hz, 2H), 5.52 (d, J = 1.7 Hz, 1H), 3.79 (s, 3H), 3.69-3.62 (m, 1H), 3.54-3.46 (m, 1H), 2.88-2.78 (m, 1H), 2.66-2.58 (m, 1H), 2.41 (s, 3H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.52-1.45 (m, 2H), 1.41-1.32 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 159.5, 143.7, 141.1, 134.4, 130.6, 129.6, 128.6, 127.4, 124.3, 118.1 (q, J_{C-F} = 320.3 Hz), 113.9, 100.8, 71.0, 64.2, 55.2, 46.6, 29.8, 29.7, 21.8, 21.5, 18.9, 13.4. ^{19}F NMR (282 MHz) δ ppm; -74.9. FAB-LM m/z: 572 [M+H]. FAB-HM Calcd for $C_{26}H_{29}F_3NO_6S_2$ [M+H]: 572.1388; found 572.1407.



***E*-3ae** ***Z*-3ae**

(*E*)-1-[2-(3-Methoxyphenyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3ae)
Method **A** (24 h): 116.6 mg (51%). Method **B** (24 h): 86.9 mg (38%). R_f = 0.43 (hexane:AcOEt = 3:1). White solid. MP: 84-86 ºC. IR (KBr) ν cm^{-1}; 2222, 1597, 1419, 1353, 1214, 1167, 1090. ^{1}H NMR (500 MHz) δ ppm; 7.61 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 2H), 6.97 (dd, *J* = 8.0, 2.3 Hz, 1H), 6.89 (t, *J* = 2.3 Hz, 1H), 6.82 (dd, *J* = 8.0, 2.3 Hz, 1H), 5.61 (s, 1H), 3.76 (s, 3H), 3.70-3.63 (m, 1H), 3.53-3.45 (m, 1H), 2.72-2.62 (m, 1H), 2.61-2.53 (m, 1H), 2.41 (s, 3H), 2.32 (t, *J* = 7.2 Hz, 2H), 1.49-1.40 (m, 2H), 1.36-1.27 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 159.7, 144.0, 141.1, 139.0, 135.0, 129.7, 129.5, 127.2, 126.4, 119.5, 118.2 (q, J_{C-F} = 320.3 Hz), 113.8, 112.5, 101.7, 71.1, 65.5, 55.1, 46.4, 29.7, 28.6, 21.7, 21.4, 18.9, 13.4. FAB-LM m/z: 572 [M+H]. ^{19}F NMR (282 MHz) δ ppm; -75.1. FAB-HM Calcd for $C_{29}H_{29}F_3NO_6S_2$ [M+H]: 572.1388; found 572.1418.

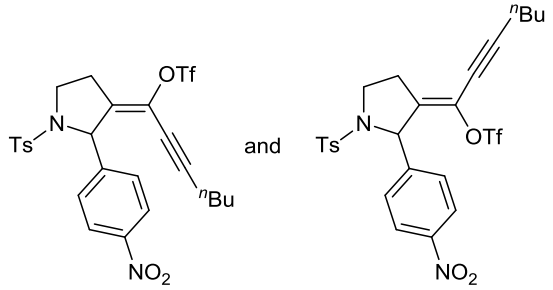
(*Z*)-1-[2-(3-Methoxyphenyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*Z*-3ae)
Method **A** (24 h): 20.6 mg (9%). Method **B** (24 h): 32.0 mg (14%). R_f = 0.31 (hexane:AcOEt = 3:1). Brown oil. IR (neat) ν cm^{-1}; 2224, 1601, 1420, 1352, 1221, 1163, 1093. ^{1}H NMR (500 MHz) δ ppm; 7.59 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 2H), 6.88 (dd, *J* = 8.0, 2.3 Hz, 1H), 6.84-6.80 (m, 2H), 5.54 (d, J = 1.7 Hz, 1H), 3.78 (s, 3H), 3.71-3.64 (m, 1H), 3.56-3.50 (m, 1H), 2.87-2.77 (m, 1H), 2.69-2.58 (m, 1H), 2.41 (s, 3H), 2.33 (t, *J* = 7.2 Hz, 2H), 1.53-1.44 (m, 2H), 1.41-1.34 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 159.7, 143.8, 140.6, 139.9, 134.4, 129.7, 129.6, 127.5, 124.5, 119.6, 118.1 (q, J_{C-F} = 320.3 Hz), 113.9, 113.0, 101.0, 70.9, 64.6, 55.2, 46.8, 29.8, 29.7, 21.8, 21.5, 19.0, 13.4. ^{19}F NMR (282 MHz) δ ppm; -74.9. FAB-LM m/z: 572 [M+H]. FAB-HM Calcd for $C_{29}H_{29}F_3NO_6S_2$ [M+H]: 572.1388; found 572.1407.



***E*-3af** ***Z*-3af**

(*E*)-1-[2-((*E*-styryl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3af)
Method **A** (24 h): 81.8 mg (36%). Method **B** (24 h): 52.2 mg (23%). R_f = 0.71 (hexane:AcOEt = 3:1). Brown oil. IR (neat) ν cm^{-1}; 2224, 1598, 1419, 1351, 1215, 1164, 1094. ^{1}H NMR (500 MHz) δ ppm; 7.69 (d, *J* = 8.0 Hz, 2H), 7.34-7.29 (m, 4H), 7.28-7.24 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.62 (dd, *J* = 16.1, 1.4 Hz, 1H), 5.97 (dd, *J* = 16.1, 6.3 Hz, 1H), 5.21 (d, *J* = 6.3 Hz, 1H), 3.66-3.59 (m, 1H), 3.56-3.49 (m, 1H), 2.72-2.63 (m, 1H), 2.61-2.62 (m, 1H), 2.40 (s, 3H), 2.39 (t, *J* = 6.8 Hz, 2H), 1.55-1.47 (m, 2H), 1.44-1.34 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 144.1, 140.4, 135.9, 135.2, 132.7, 129.8, 128.5, 128.1, 127.4, 126.7, 126.0, 123.7, 118.2 (q, $J_{C\text{-}F}$ = 320.3 Hz), 101.9, 70.9, 64.1, 46.4, 29.9, 28.4, 21.8, 21.4, 19.1, 13.4. ^{19}F NMR (282 MHz) δ ppm; -75.1. FAB-LM m/z: 568 [M+H]. FAB-HM Calcd for $C_{27}H_{29}F_3NO_5S_2$ [M+H]: 568.1439; found 568.1464.

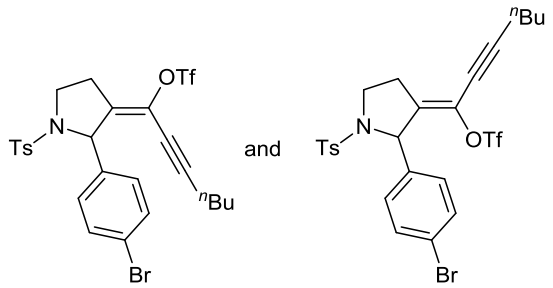
(*Z*)-1-[2-((*E*-styryl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*Z*-3af)
Method **A** (24 h): 0 mg (0%). Method **B** (24 h): 31.8 mg (14%). R_f = 0.69 (hexane:AcOEt = 3:1). Brown oil. IR (neat) ν cm^{-1}; 2224, 1599, 1420, 1352, 1218, 1164, 1094. ^{1}H NMR (500 MHz) δ ppm; 7.70 (d, *J* = 8.0 Hz, 2H), 7.33-7.28 (m, 4H), 7.28-7.22 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.66 (dd, *J* = 16.0, 1.1 Hz, 1H), 5.91 (dd, J = 16.0, 6.9 Hz, 1H), 5.24 (d, *J* = 6.9 Hz, 1H), 3.64-3.50 (m, 2H), 2.77-2.66 (m, 1H), 2.61-2.51 (m, 1H), 2.39 (s, 3H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.55-1.47 (m, 2H), 1.43-1.34 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 143.9, 139.8, 136.0, 134.8, 133.3, 129.8, 128.4, 128.0, 127.7, 126.8, 124.5, 123.7, 118.2 (q, $J_{C\text{-}F}$ = 320.3 Hz), 100.9, 71.0, 63.1, 46.5, 29.8, 29.3, 21.8 21.5, 19.0, 13.4. ^{19}F NMR (282 MHz) δ ppm; -74.9. FAB-LM m/z: 568 [M+H]. FAB-HM Calcd for $C_{27}H_{29}F_3NO_5S_2$ [M+H]: 568.1439; found 568.1469.



***E*-3ag** ***Z*-3ag**

(*E*)-1-[2-(4-Nitrophenyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3ag)
Method **A** (2 h): 91.5 mg (39%). Method **C** (24 h): 79.8 mg (34%). R_f = 0.69 (hexane:AcOEt = 3:1). White solid. MP: 101-103 ºC. IR (KBr) ν cm^{-1}; 2227, 1597, 1415, 1345, 1207, 1163, 1092. ^{1}H NMR (500 MHz) δ ppm; 8.17 (d, *J* = 8.9 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.58 (s, 1H), 3.63-3.52 (m, 2H), 2.79-2.63 (m, 2H), 2.42 (s, 3H), 2.31 (t, *J* = 7.2 Hz, 2H), 1.49-1.38 (m, 2H), 1.35-1.25 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR(125 MHz) δ ppm; 147.7, 145.3, 144.6, 140.4, 134.2, 129.9, 128.4, 127.3, 126.9, 123.7, 118.1 (q, $J_{C\text{-}F}$ = 320.3 Hz), 102.7, 70.9, 64.7, 46.9, 29.6, 28.7, 21.7, 21.5, 18.9, 13.3. ^{19}F NMR (282 MHz) δ (ppm); -74.7. FAB-LM m/z: 587 [M+H]. FAB-HM Calcd for $C_{25}H_{26}F_3N_2O_7S_2$ [M+H]: 587.1134; found 587.1167.

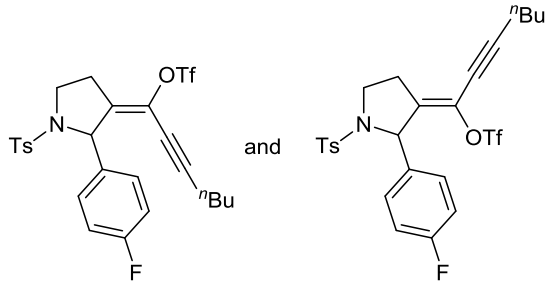
(*Z*)-1-[2-(4-Nitrophenyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*Z*-3ag)
Method **A** (2 h): 25.8 mg (11%). Method **C** (24 h): 46.9 mg (20%). R_f = 0.37. Colorless oil. IR (neat) ν cm^{-1}; 2224, 1598, 1526, 1422, 1382, 1349, 1220, 1165, 1094. ^{1}H NMR (500 MHz) δ ppm; 8.17 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 5.51 (d, *J* = 1.8 Hz, 1H), 3.80-3.74 (m, 1H), 3.48-3.41 (m, 1H), 2.94-2.84 (m, 1H), 2.76-2.67 (m, 1H), 2.42 (s, 3H), 2.34 (t, J = 6.9 Hz, 2H), 1.52-1.45 (m, 2H), 1.41-1.32 (m, 2H), 0.88 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 147.7, 145.9, 144.5, 139.6, 133.4, 129.9, 128.5, 127.5, 125.2, 123.9, 118.0 (q, $J_{C\text{-}F}$ = 320.3 Hz), 102.0, 70.6, 63.8, 47.3, 29.71, 29.66, 21.8, 21.5, 19.0, 13.4. ^{19}F NMR (282 MHz) δ (ppm); -74.6. FAB-LM m/z: 587 [M+H]. FAB-HM Calcd for $C_{25}H_{26}F_3N_2O_7S_2$ [M+H]: 587.1134; found 587.1166.



***E*-3ah** ***Z*-3ah**

(*E*)-1-[2-(4-Bromophenyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3ah)
Method **A** (2 h): 119.1 mg (48%). Method **C** (24 h): 99.3 mg (40%). R_f = 0.69 (hexane:AcOEt = 3:1). White solid. MP: 85-86 ºC. IR (KBr) ν cm^{-1}; 2225, 1596, 1417, 1349, 1216, 1162, 1092. ^{1}H NMR (500 MHz) δ ppm; 7.57 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 5.51 (s, 1H), 3.65-3.58 (m, 1H), 3.54-3.47 (m, 1H), 2.74-2.57 (m, 2H), 2.40 (s, 3H), 2.30 (t, *J* = 6.9 Hz, 2H), 1.46-1.39 (m, 2H), 1.34-1.24 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 144.2, 141.0, 136.9, 134.7, 131.5, 129.8, 129.1, 127.2, 126.6, 122.2, 118.1 (q, J_{C-F} = 320.3 Hz), 102.2, 70.9, 64.9, 46.5, 29.7, 28.7, 21.7, 21.4, 18.9, 13.4. ^{19}F NMR (282 MHz) δ ppm; -75.1. FAB-LM m/z: 620 [M+H]. FAB-HM Calcd for $C_{25}H_{26}BrF_3NO_5S_2$ [M+H]: 620.0388; found 620.0381.

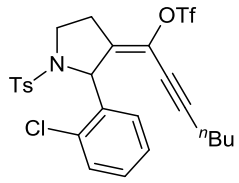
(*Z*)-1-[2-(4-Bromophenyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*Z*-3ah)
Method **A** (2 h): 32.3 mg (13%). Method **C** (24 h): 54.6 mg (22%). R_f = 0.40 (hexane:AcOEt = 3:1). Colorless oil. IR (neat) ν cm^{-1}; 2224, 1597, 1421, 1352, 1223, 1163, 1094, 1031. ^{1}H NMR (500 MHz) δ ppm; 7.57 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 5.47 (d, *J* = 1.7 Hz, 1H), 3.73-3.65 (m, 1H), 3.53-3.45 (m, 1H), 2.88-2.77 (m, 1H), 2.71-2.61 (m, 1H), 2.42 (s, 3H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.53-1.45 (m, 2H), 1.41-1.32 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 144.0, 140.3, 137.6, 134.0, 131.7, 129.7, 129.1, 127.4, 124.7, 122.4, 118.1 (q, J_{C-F} = 320.3 Hz), 101.3, 70.8, 64.0, 46.9, 29.8, 29.6, 21.8, 21.5, 18.9, 13.4. ^{19}F NMR (282 MHz) δ ppm; -74.9. FAB-LM m/z: 620 [M+H]. FAB-HM Calcd for $C_{25}H_{26}BrF_3NO_5S_2$ [M+H]: 620.0388; found 620.0388.



***E*-3ai** ***Z*-3ai**

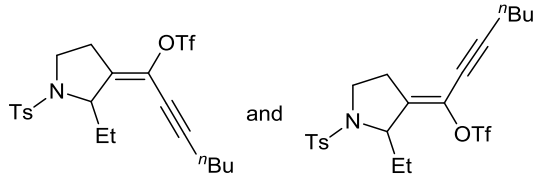
(*E*)-1-[2-(4-Fluorophenyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3ai)
Method **A** (2 h): 105.2 mg (47%). Method **C** (24 h): 98.5 mg (44%). R_f = 0.40 (hexane:AcOEt = 3:1). Yellow oil. IR (neat) ν cm^{-1}; 2224, 1604, 1422, 1352, 1218, 1164, 1095. ^{1}H NMR (500 MHz) δ ppm; 7.58 (d, *J* = 8.6 Hz, 2H), 7.33 (dd, $J_{H-H,H-F}$ = 8.6, 5.2 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.99 (dd, $J_{H-H,H-F}$ = 8.6, 8.6 Hz, 2H), 5.56 (s, 1H), 3.66-3.58 (m, 1H), 3.54-3.47 (m, 1H), 2.74-2.65 (m, 1H), 2.64-2.56 (m, 1H), 2.41 (s, 3H), 2.30 (t, *J* = 6.9 Hz, 2H), 1.46-1.39 (m, 2H), 1.34-1.25 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 162.5 (d, J_{C-F} = 247.1 Hz), 144.1, 141.2, 134.8, 133.6 (d, J_{C-F} = 3.6 Hz), 129.8, 129.1 (d, J_{C-F} = 8.4 Hz), 127.2, 126.5, 118.1 (q, J_{C-F} = 320.3 Hz), 115.3 (d, J_{C-F} = 21.6 Hz), 102.0, 70.9, 64.9, 46.4, 29.7, 28.7, 21.7, 21.4, 18.9, 13.3. ^{19}F NMR (282 MHz) δ ppm; -75.1. FAB-LM m/z: 560 [M+H]. FAB-HM Calcd for $C_{25}H_{26}F_4NO_5S_2$ [M+H]: 560.1189; found 560.1180.

(*Z*)-1-[2-(4-Fluorophenyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*Z*-3ai)
Method **A** (2 h): 24.6 mg (11%). Method **C** (24 h): 51.5 mg (23%). R_f = 0.29 (hexane:AcOEt = 3:1).White solid. MP: 69-70 ºC. IR (KBr) ν cm^{-1}; 2227, 1604, 1425, 1352, 1231, 1164, 1093. ^{1}H NMR (500 MHz) δ ppm; 7.57 (d, *J* = 8.0 Hz, 2H), 7.30-7.24 (m, 4H), 6.98 (dd, $J_{H-H,H-F}$ = 8.6, 8.6 Hz, 2H), 5.51 (d, *J* = 1.7 Hz, 1H), 3.71-3.63 (m, 1H), 3.53-3.45 (m, 1H), 2.88-2.78 (m, 1H), 2.69-2.60 (m, 1H), 2.41 (s, 3H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.54-1.44 (m, 2H), 1.41-1.32 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 162.6 (d, J_{C-F} = 247.1 Hz), 144.0, 140.6, 134.4 (d, J_{C-F} = 3.6 Hz), 134.2, 129.7, 129.2 (d, J_{C-F} = 8.4 Hz), 127.4, 124.6, 118.1 (q, J_{C-F} = 320.3 Hz), 115.5 (d, J_{C-F} = 22.8 Hz), 101.2, 70.8, 64.0, 46.8, 29.8, 29.7, 21.8, 21.5, 19.0, 13.4. ^{19}F NMR (282 MHz) δ ppm; -74.9. FAB-LM m/z: 560 [M+H]. FAB-HM Calcd for $C_{25}H_{26}F_4NO_5S_2$ [M+H]: 560.1189; found 560.1216.



***E*-3aj**

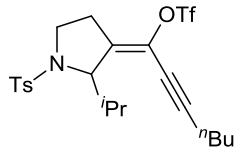
(*E*)-1-[2-(2-Chlorophenyl)-1-tosylpyrrolidin-3-ylidene]hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3aj)
Method **A** (2 h): 96.8 mg (42%). Method **C** (24 h): 126.7 mg (55%). R_f = 0.43 (hexane:AcOEt = 3:1). Brown solid. MP: 66-67 ºC. IR (KBr) ν cm^{-1}; 2221, 1599, 1411, 1351, 1211, 1168, 1093. ^{1}H NMR (500 MHz) δ ppm; 7.64 (d, *J* = 8.0 Hz, 2H), 7.33-7.29 (m, 1H), 7.27-7.22 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.74 (d, *J* = 2.3 Hz, 1H), 3.90-3.84 (m, 1H), 3.56-3.48 (m, 1H), 3.15-3.06 (m, 1H), 2.99-2.88 (m, 1H), 2.44 (s, 3H), 2.29-2.16 (m, 2H), 1.43-1.34 (m, 2H), 1.32-1.22 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 143.8, 143.3, 136.8, 134.0, 133.9, 130.9, 129.5, 129.23, 129.19, 127.7, 126.9, 126.7, 118.1 (q, J_{C-F} = 320.3 Hz), 103.1, 70.2, 62.0, 47.7, 29.6, 29.4, 21.7, 21.4, 19.1, 13.1. ^{19}F NMR (282 MHz) δ ppm; -75.1. FAB-LM m/z: 576 [M+H]. FAB-HM Calcd for $C_{25}H_{26}ClF_3NO_5S_2$ [M+H]: 576.0893; found 576.0908.



***E*-3ak** ***Z*-3ak**

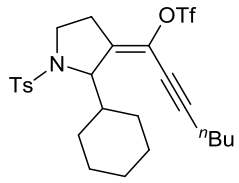
(*E*)-1-(2-Ethyl-1-tosylpyrrolidin-3-ylidene)hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3ak)
Method **C** (24 h): 116.5 mg (59%). R_f = 0.60 (hexane:AcOEt = 3:1). Brown oil. IR (neat) ν cm^{-1}; 2224, 1599, 1420, 1353, 1214, 1165, 1093. ^{1}H NMR (500 MHz) δ ppm; 7.66 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.47 (t, *J* = 5.7 Hz, 1H), 3.55-3.41 (m, 2H), 2.58-2.48 (m, 1H), 2.42 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 2.37-2.26 (m, 1H), 1.92-1.82 (m, 1H), 1.80-1.69 (m, 1H), 1.61-1.52 (m, 2H), 1.49-1.39 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 1H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 144.0, 142.3, 134.5, 129.9, 127.2, 124.7, 118.1 (q, J_{C-F} = 320.3 Hz), 101.0, 70.9, 64.1, 46.5, 29.9, 28.5, 27.0, 21.8, 21.4, 19.0, 13.4, 9.6. ^{19}F NMR (282 MHz) δ ppm; -75.2. FAB-LM m/z: 494 [M+H]. FAB-HM Calcd for $C_{21}H_{27}F_3NO_5S_2$ [M+H]: 494.1283; found 494.1301.

(*Z*)-1-(2-Ethyl-1-tosylpyrrolidin-3-ylidene)hept-2-yn-1-yl trifluoromethanesulfonate (*Z*-3ak)
Method **C** (24 h): 35.5 mg (18%). R_f = 0.46 (hexane:AcOEt = 3:1). Brown oil. IR (neat) ν cm^{-1}; 2224, 1598, 1419, 1354, 1216, 1165, 1093. ^{1}H NMR (500 MHz) δ ppm; 7.79 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.56 (ddd, *J* = 6.6, 4.9, 1.7 Hz, 1H), 3.60-3.52 (m, 1H), 3.43-3.35 (m, 1H), 2.58-2.48 (m, 1H), 2.42 (s, 3H), 2.33 (t, *J* = 7.2 Hz, 3H), 2.31-2.23 (m, 1H), 1.95-1.84 (m, 1H), 1.79-1.68 (m, 1H), 1.52-1.44 (m, 2H), 1.41-1.32 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 1H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 143.9, 141.4, 134.1, 129.9, 127.5, 123.4, 118.2 (q, J_{C-F} = 320.3 Hz), 100.3, 71.0, 63.2, 46.7, 29.9, 29.7, 27.2, 21.8, 21.5, 18.9, 13.4, 9.5. ^{19}F NMR (282 MHz) δ ppm; -75.1. FAB-LM m/z: 494 [M+H]. FAB-HM Calcd for $C_{21}H_{27}F_3NO_5S_2$ [M+H]: 494.1283; found 494.1289.



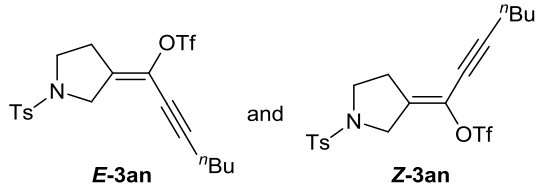
***E*-3al**

(*E*)-1-(2-Isopropyl-1-tosylpyrrolidin-3-ylidene)hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3al)
Method **C** (24 h): 75.1 mg (37%). R_f = 0.66 (hexane:AcOEt = 3:1). Brown oil. IR (neat) ν cm^{-1}; 2225, 1599, 1420, 1351, 1214, 1164, 1092. ^{1}H NMR (500 MHz) δ ppm; 7.65 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 4.40 (dd, *J* = 6.3, 1.2 Hz, 1H), 3.63-3.56 (m, 1H), 3.51-3.43 (m, 1H), 2.53-2.46 (m, 1H), 2.43 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 2.32-2.23 (m, 1H), 2.03 (qd, *J* = 6.9, 6.9 Hz, 1H), 1.63-1.54 (m, 2H), 1.51-1.41 (m, 2H), 1.05 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 144.0, 141.1, 134.8, 129.9, 127.2, 125.4, 118.2 (q, J_{C-F} = 320.3 Hz), 100.4, 71.5, 68.9, 46.8, 33.5, 29.9, 28.4, 21.9, 21.5, 19.2, 19.0, 13.4. ^{19}F NMR (282 MHz) δ ppm; 75.2. FAB-LM m/z: 508 [M+H]. FAB-HM Calcd for $C_{22}H_{29}F_3NO_5S_2$ [M+H]: 508.1439; found 508.1474.



***E*-3am**

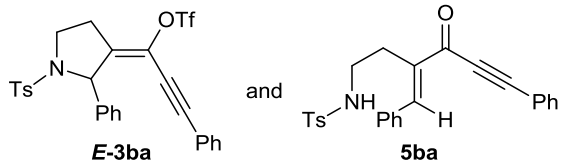
(*E*)-1-(2-Cyclohexyl-1-tosylpyrrolidin-3-ylidene)hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3am)
Method **A** (6 h): 45.9 mg (21%). Method **C** (24 h): 105.1 mg (48%). R_f = 0.54 (hexane:AcOEt = 3:1). Red oil. IR (neat) ν cm^{-1}; 2225, 1598, 1419, 1348, 1218, 1163, 1092. ^{1}H NMR (500 MHz) δ ppm; 7.63 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 4.39 (d, *J* = 6.3 Hz, 1H), 3.62-3.53 (m, 1H), 3.49-3.40 (m, 1H), 2.50-2.41 (m, 1H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 2.31-2.20 (m, 1H), 1.93-1.85 (m, 1H), 1.93-1.85 (m, 1H), 1.83-1.69 (m, 3H), 1.69-1.61 (m, 2H), 1.61-1.53 (m, 2H), 1.52-1.41 (m, 2H), 1.26-1.07 (m, 5H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 144.0, 140.8, 134.8, 129.8, 127.1, 125.3, 118.2 (q, $J_{C\text{-}F}$ = 320.3 Hz), 100.3, 71.6, 68.3, 46.6, 42.8, 29.9, 29.6, 29.5, 28.4, 26.13, 26.10, 26.0, 21.8, 21.4, 19.0, 13.4. ^{19}F NMR (282 MHz) δ ppm; -75.2. FAB-LM m/z: 548 [M+H]. FAB-HM Calcd for $C_{25}H_{33}F_3NO_5S_2$ [M+H]: 548.1752; found 548.1789.



***E*-3an** and ***Z*-3an**

(*E*)-1-(1-Tosylpyrrolidin-3-ylidene)hept-2-yn-1-yl trifluoromethanesulfonate (*E*-3an)
Method **A** (24 h): 29.5 mg (16%). Method **B** (24 h): 40.1 mg (22%). R_f = 0.57 (hexane:AcOEt = 3:1). Brown solid. MP: 53-55 ºC. IR (KBr) ν cm^{-1}; 2224, 1598, 1419, 1351, 1217, 1165, 1093. ^{1}H NMR (500 MHz) δ ppm; 7.71 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 3.95 (s, 2H), 3.34 (t, *J* = 6.9 Hz, 2H), 2.68 (t, *J* = 6.9 Hz, 2H), 2.45 (s, 3H), 2.40 (t, *J* = 6.9 Hz, 2H), 1.58-1.50 (m, 2H), 1.47-1.37 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 144.3, 138.5, 132.1, 129.9, 127.8, 124.3, 118.2 (q, $J_{C\text{-}F}$ = 321.5 Hz), 101.4, 70.7, 50.8, 47.9, 29.9, 28.9, 21.8, 21.5, 19.0, 13.4. ^{19}F NMR (282 MHz) δ ppm; -75.1. FAB-LM *m/z*: 466 [M+H]. FAB-HM Calcd for $C_{19}H_{23}F_3NO_5S_2$ [M+H]: 466.0970; found: 466.0975.

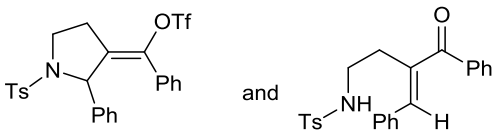
(*Z*)-1-(1-Tosylpyrrolidin-3-ylidene)hept-2-yn-1-yl trifluoromethanesulfonate (*Z*-3an)
Method **A** (24 h): 18.5 mg (10%). Method **B** (24 h): 32.7 mg (17%). R_f = 0.51 (hexane:AcOEt = 3:1). Brown oil. IR (neat) ν cm^{-1}; 2224, 1597, 1423, 1349, 1226, 1168, 1094. ^{1}H NMR (500 MHz) δ ppm; 7.71 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.01 (s, 2H), 3.35 (t, *J* = 6.9 Hz, 2H), 2.64 (t, *J* = 6.9 Hz, 2H), 2.45 (s, 3H), 2.36 (t, *J* = 6.9 Hz, 2H), 1.55-1.46 (m, 2H), 1.44-1.33 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz) δ (ppm); 144.3, 138.0, 131.9, 129.9, 127.9, 124.2, 118.2 (q, $J_{C\text{-}F}$ = 320.3 Hz), 100.7, 70.9, 49.8, 47.7, 29.9, 29.8, 21.8, 21.5, 19.0, 13.4. ^{19}F NMR (282 MHz) δ ppm; -74.9. FAB-LM *m/z*: 466 [M+H]. FAB-HM Calcd for $C_{19}H_{23}F_3NO_5S_2$ [M+H]: 466.0970; found: 466.0975.



***E*-3ba** and **5ba**

(*E*)-3-Phenyl-1-(2-phenyl-1-tosylpyrrolidin-3-ylidene)prop-2-yn-1-yl trifluoromethanesulfonate (*E*-3ba)
Method **A** (2 h): 49.0 mg (22%). Method **B** (2 h): 71.2 mg (32%). R_f = 0.49 (hexane:AcOEt = 3:1). Yellow solid. MP: 97-99 ºC. IR (KBr) ν cm^{-1}; 2212, 1598, 1423, 1351, 1217, 1168, 1091 ^{1}H NMR (500 MHz) δ ppm; 7.58 (d, *J* = 8.0 Hz, 2H), 7.41-7.36 (m, 3H), 7.35-7.27 (m, 7H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.68 (s, 1H), 3.74-3.64 (m, 1H), 3.62-3.53 (m, 1H), 2.85-2.76 (m, 1H), 2.75-2.65 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz) δ ppm; 144.0, 143.3, 137.7, 134.8, 131.5, 130.1, 129.8, 128.6, 128.5, 128.2, 127.4, 127.2, 126.2, 120.3, 118.2 (q, $J_{C\text{-}F}$ = 320.3 Hz), 99.0, 78.7, 65.7, 46.5, 29.1, 21.5. ^{19}F NMR (282 MHz) δ ppm; -75.0. FAB-LM m/z: 562 [M+H]. FAB-HM Calcd for $C_{27}H_{23}F_3NO_5S_2$ [M+H]: 562.0970; found 562.1001.

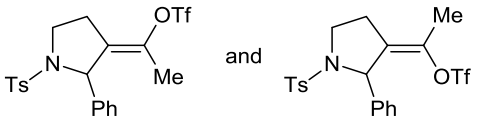
(*E*)-*N*-(3-Benzylidene-4-oxo-6-phenylhex-5-yn-1-yl)-4-methylbenzenesulfonamide (5ba)
Method **A** (2 h): 32.7 mg (19%). Method **B** (2 h): 26.1 mg (15%). R_f = 0.34 (hexane:AcOEt = 3:1).Yellow oil. IR (neat) ν cm^{-1}; 3284, 2200, 1617, 1330, 1159. ^{1}H NMR (500 MHz) δ ppm; 8.15 (s, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.65-7.60 (m, 2H), 7.51-7.37 (m, 8H), 7.26 (d, *J* = 8.6 Hz, 2H), 4.82 (t, *J* = 6.9 Hz, 1H), 3.17 (q, *J* = 6.9 Hz, 2H), 2.82 (t, *J* = 6.9 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (125 MHz) δ ppm; 180.8, 148.6, 143.3, 138.6, 136.9, 134.4, 132.8, 130.7, 129.9, 129.7, 129.0, 128.7, 127.0, 120.0, 93.0, 85.8, 41.9, 26.2, 21.5 (note that two carbon peaks overlap with each other). FAB-LM m/z: 430 [M+H]. FAB-HM Calcd for $C_{26}H_{24}NO_3S$ [M+H]: 430.1477; found 430.1503.



***E*-3ca** **5ca**

(*E*)-Phenyl(2-phenyl-1-tosylpyrrolidin-3-ylidene)methyl trifluoromethanesulfonate (*E*-3ca)
Method **A** (2 h): 30.5 mg (14%). Method **B** (2 h): 10.9 mg (5%). R_f = 0.51 (hexane:AcOEt = 3:1). White solid. MP: 113-114 ºC. IR (KBr) ν cm^{-1}; 1598, 1415, 1346, 1226, 1161, 1091. ^{1}H NMR (500 MHz) δ ppm; 7.42 (d, *J* = 8.1 Hz, 2H), 7.40-7.26 (m, 8H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 5.51 (s, 1H), 3.80-3.70 (m, 1H), 3.48-3.36 (m, 1H), 2.87-2.76 (m, 1H), 2.76-2.67 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz) δ ppm; 143.8, 142.0, 138.2, 134.9, 133.4, 131.3, 130.2, 129.7, 128.8, 128.5, 128.2, 127.4, 127.2, 127.1, 118.0 (q, $J_{C\text{-}F}$ = 320.3 Hz), 64.9, 45.2, 29.1, 21.4. ^{19}F NMR (282 MHz) δ ppm; -75.5. FAB-LM m/z: 538 [M+H]. FAB-HM Calcd for $C_{25}H_{23}F_3NO_5S_2$ [M+H]: 538.0970; found 538.0941.

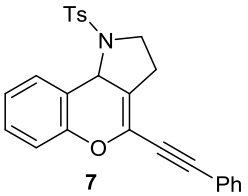
(*E*)-*N*-(3-Benzoyl-4-phenylbut-3-en-1-yl)-4-methylbenzenesulfonamide (5ca)
Method **A** (2 h): 106.7 mg (66%). Method **B** (2 h): 121.7 mg (75%). R_f = 0.20 (hexane:AcOEt = 3:1). White solid. MP: 116-117 ºC. IR (KBr) ν cm^{-1}; 3289, 1644, 1320, 1152. ^{1}H NMR (300 MHz) δ ppm; 7.85-7.65 (m, 4H), 7.62-7.28 (m, 9H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.10 (t, *J* = 5.4 Hz, 1H), 3.19 (td, *J* = 6.6, 5.4 Hz, 2H), 2.89 (t, *J* = 6.6 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (75 MHz) δ ppm; 199.7, 145.0, 143.2, 137.9, 137.5, 136.8, 134.7, 132.0, 129.7, 129.6, 129.20, 129.15, 128.8, 128.3, 127.0, 41.9, 27.6, 21.3. FAB-LM m/z: 406 [M+H]. FAB-HM Calcd for $C_{24}H_{24}NO_3S$ $[M+H]^+$ 406.1477; found 406.1439.



***E*-3da** ***Z*-3da**

(*E*)-1-(2-Phenyl-1-tosylpyrrolidin-3-ylidene)ethyl trifluoromethanesulfonate (*E*-3da)
Method **A** (8 h): 55.6 mg (29%). Method **B** (8 h): 53.3 mg (28%). R_f = 0.37 (hexane:AcOEt = 3:1). White solid. MP: 128-129 ºC. IR (KBr) ν cm^{-1}; 1599, 1406, 1342, 1216, 1164, 1092. ^{1}H NMR (500 MHz) δ ppm; 7.55 (d, *J* = 8.0 Hz, 2H), 7.36-7.27 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.45 (s, 1H), 3.69-3.60 (m, 1H), 3.48-3.40 (m, 1H), 2.76-2.65 (m, 1H), 2.64-2.52 (m, 1H), 2.41 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (125 MHz) δ ppm; 143.9, 140.8, 137.9, 135.1, 132.8, 129.7, 128.8, 128.3, 127.5, 127.1, 118.1 (q, $J_{C\text{-}F}$ = 320.3 Hz), 64.4, 46.3, 28.5, 21.5, 17.0. ^{19}F NMR (282 MHz) δ ppm; -76.2. FAB-LM m/z: 476 [M+H]. FAB-HM Calcd for $C_{20}H_{21}F_3NO_5S_2$ [M+H]: 476.0813; found 476.0851.

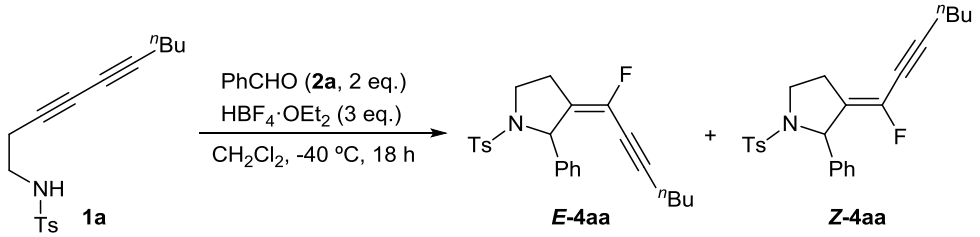
(*Z*)-1-(2-Phenyl-1-tosylpyrrolidin-3-ylidene)ethyl trifluoromethanesulfonate (*Z*-3da)
Method **A** (8 h): 20.5 mg (11%). Method **B** (8 h): 22.8 mg (12%). R_f = 0.20 (hexane:AcOEt = 3:1). Yellow oil. IR (neat) ν cm^{-1}; 1599, 1407, 1341, 1223, 1163, 1093. ^{1}H NMR (300 MHz) δ ppm; 7.62 (d, *J* = 8.1 Hz, 2H), 7.36-7.26 (m, 5H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.58 (s, 1H), 3.70-3.59 (m, 1H), 3.58-3.47 (m, 1H), 2.80-2.60 (m, 2H), 2.42 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (75 MHz) δ ppm; 143.8, 139.1, 134.3, 132.2, 129.7, 128.5, 128.1, 127.5, 127.3, 118.0 (q, $J_{C\text{-}F}$ = 322.6 Hz), 64.2, 46.8, 28.2, 21.4, 17.1 (note that two carbon peaks overlap with each other). ^{19}F NMR (282 MHz) δ ppm; -75.9. FAB-LM m/z: 476 [M+H]. FAB-HM Calcd for $C_{20}H_{21}F_3NO_5S_2$ [M+H]: 476.0813; found 476.0844.



7

4-(Phenylethynyl)-1-tosyl-1, 2, 3, 9b-tetrahydrochromeno-[4,3-*b*]pyrrole (7)
Method **B** (18 h): 107.8 mg (63%). R_f = 0.34 (hexane:AcOEt = 3:1). White solid. MP: 136-137 ºC. IR (KBr) ν cm^{-1}; 2219, 1344, 1159. ^{1}H-NMR (500 MHz) δ ppm; 7.99 (d, *J* = 7.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.50-7.44 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.36-7.23 (m, 5H), 7.13 (dd, *J* = 8.0, 1.1 Hz, 1H), 5.14 (s, 1H), 3.92 (dd, *J* = 12.6, 8.0 Hz, 1H), 3.32-3.21 (m, 1H), 2.54 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.46 (s, 3H), 1.97-1.86 (m, 1H) ^{13}C NMR (125 MHz) δ ppm; 151.4, 144.2, 135.0, 131.6, 130.1, 129.2, 128.4, 128.3, 127.9, 127.7, 124.6, 122.0, 121.4, 120.8, 115.9, 99.8, 93.6, 81.1, 55.6, 48.7, 28.4, 21.6. FAB-LM m/z: 428 [M+H]. FAB-HM Calcd for $C_{26}H_{22}NO_3S$ [M+H]: 428.1320; found 428.1309.

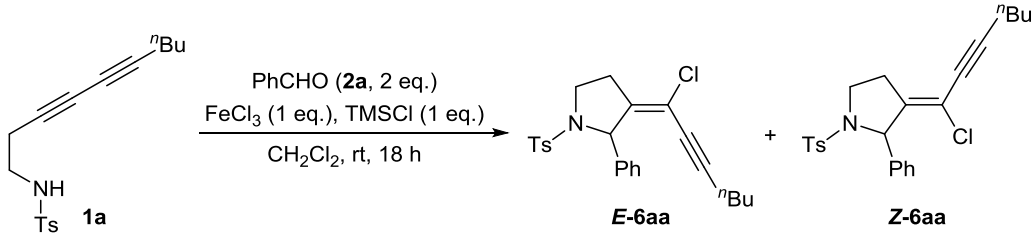
Synthesis and Characterization of F-Substituted Pyrrolidines 4aa



To a solution of 3,5-diynyl amide **1a** (121.4 mg, 0.40 mmol) and benzaldehyde (**2a**, 81.6 μL, 0.80 mmol) in CH_2Cl_2 (2.5 mL) was added $HBF_4{\cdot}OEt_2$ (163.3 μL, 1.2 mmol) at -40 ºC. After being stirred at same temperature for 18 h, the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC to give **4aa** (77.5 mg, 47%) as as a mixture of geometric isomers (*E*:*Z* = 64:36).

(*E*)- and (*Z*)-3-(1-Fluorohept-2-yn-1-ylidene)-2-phenyl-1-tosylpyrrolidine (*E*-4aa and *Z*-4aa)
R_f = 0.57 (hexane:AcOEt = 3:1). Colorless oil. IR (neat) ν cm^{-1}; 2224, 1351, 1163, 1118. ^{1}H NMR (500 MHz, mixture of *E* and *Z* isomers) δ ppm for ***E*-4aa**; 7.60 (d, 2H, *J* = 8.1 Hz), 7.38-7.33 (m, 2H), 7.32-7.27 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.48 (s, 1H), 3.59-3.51 (m, 2H), 2.61-2.51 (m, 2H), 2.42 (s, 3H), 2.36-2.29 (m, 2H), 1.53-1.44 (m, 2H), 1.41-1.31 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); δ ppm for ***Z*-4aa**; 7.62 (d, 2H, *J* = 8.1 Hz), 7.38-7.33 (m, 2H), 7.32-7.27 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.55 (s, 1H), 3.68-3.60 (m, 1H), 3.51-3.42 (m, 1H), 2.70-2.61 (m, 1H), 2.48-2.44 (m, 1H), 2.42 (s, 3H), 2.36-2.29 (m, 2H), 1.53-1.44 (m, 2H), 1.41-1.31 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, mixture of *E* and *Z* isomers) δ ppm for ***E*-4aa**; 143.4, 139.3, 137.1 (d, *J* = 233.9 Hz), 134.6, 129.3, 128.0, 127.43, 127.1, 126.8, 126.4 (d, *J* = 22.8 Hz), 99.0 (d, *J* = 6.0 Hz), 71.1 (d, *J* = 42.0 Hz), 64.4 (d, *J* = 3.6 Hz), 46.8, 29.7, 26.3, 21.53, 21.19, 18.61, 13.24; δ ppm for ***Z*-4aa**; 143.5, 139.5, 135.5 (d, *J* = 233.9 Hz), 134.1, 129.4, 128.1, 127.37, 127.2, 126.6, 126.1 (d, *J* = 21.6 Hz), 97.8 (d, *J* = 7.2 Hz), 70.9 (d, *J* = 42.0 Hz), 63.1, 46.9, 29.8, 27.4, 21.51, 21.21, 18.56, 13.21. ^{19}F NMR (282 MHz) δ (ppm) for ***E*-4aa**; -108.2; δ (ppm) for ***Z*-4aa**; -106.5. FAB-LM m/z: 412 [M+H]. FAB-HM Calcd for $C_{26}H_{23}FNO_2S$ [M+H]: 412.1747; found 412.1720.

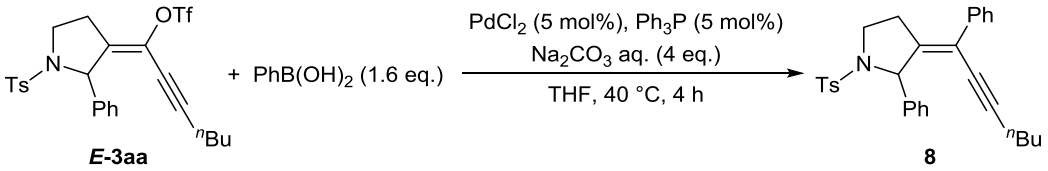
Synthesis and Characterization of Cl-Substituted Pyrrolidines 6aa



To a solution of 3,5-diynyl amide **1a** (121.4 mg, 0.40 mmol) and benzaldehyde (**2a**, 81.6 μL, 0.80 mmol) in CH_2Cl_2 (2.5 mL) was added $FeCl_3$ (64.9 mg, 0.4 mmol) and chlorotrimethylsilane (50.5 μL, 0.4 mmol) at 0 ºC. After being stirred at room temperature for 18 h, the reaction mixture was quenched with sat. NH_4Cl and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC to give **6aa** (101.4 mg, 59%) as as a mixture of geometric isomers (*E*:*Z* = 78:22).

(*E*)- and (*Z*)-3-(1-Chlorohept-2-yn-1-yliden)-2-phenyl-1-tosylpyrrilidine (*E*-6aa and *Z*-6aa)
R_f = 0.31 (hexane:AcOEt = 3:1). Brown oil. IR (neat) ν cm^{-1}; 2220, 1351, 1163, 1118, 1093. ^{1}H NMR (500 MHz, mixture of *E* and *Z* isomers) δ ppm; 7.61-7.55 (m, 2H), 7.37-7.31 (m, 2H), 7.31-7.18 (m, 5H), 5.59 (s, 0.78H for ***E*-6aa**), 5.56 (s, 0.22H for ***E*-6aa**), 3.68-3.44 (m, 2H), 2.83-2.42 (m, 2H), 2.40 (s, 3H), 2.35-2.27 (m, 2H), 1.52-1.40 (m, 2H), 1.40-1.26 (m, 2H), 0.91-0.85 (m, 3H). ^{13}C NMR (125 MHz, mixture of *E* and *Z* isomers) δ ppm for ***E*-4aa**; 145.4, 143.7, 138.5, 134.9, 129.5, 128.2, 127.7, 127.3, 127.2, 109.5, 97.5, 76.1, 66.7, 46.3, 30.8, 30.0, 21.8, 21.5, 19.0, 13.5; δ ppm for ***Z*-4aa**; 144.9, 143.6, 138.1, 134.7, 129.5, 128.3, 127.8, 127.5, 127.3, 108.2, 96.4, 76.0, 66.1, 46.7, 31.3, 30.2, 21.8, 21.5, 18.9, 13.6. FAB-LM m/z: 428 [M+H]. FAB-HM Calcd for $C_{24}H_{26}ClNO_2S$ [M+H]: 428.1451; found 428.1486.

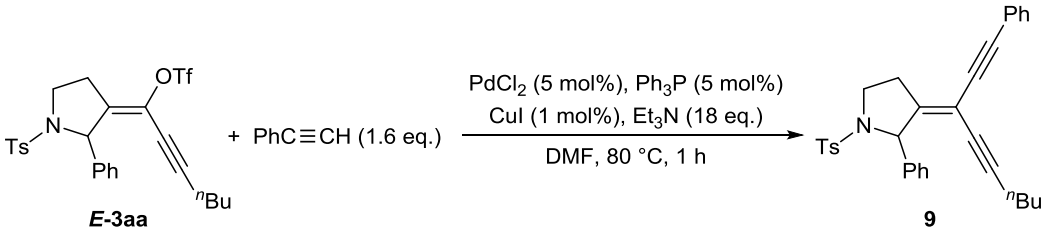
Suzuki-Miyaura Coupling Reaction of E-3aa



To a solution of $PdCl_2$ (1.8 mg, 10 μmol), Ph_3P (2.6 mg, 10 μmol) and ***E*-3aa** (108.3 mg, 0.2 mmol) in THF (2.5 mL) was added phenylboronic acid (39.0 mg, 0.32 mmol) and Na_2CO_3 (2M soultion in H_2O, 0.4 mL, 0.8 mmol) at room temperature. After being stirred at 40 ºC for 4 h, the reaction mixture was quenched with H_2O and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by silica gel column chromatography (hexane:AcOEt = 3:1) to give **8** (66.2 mg, 70 %).

(*Z*)-2-Phenyl-3-(1-phenylhept-2-yn-1-yliden)-1-tosylpyrrolidine (8)
R_f = 0.51 (hexane:AcOEt = 3:1). Brown oil. IR (neat) ν cm^{-1}; 2219, 1350, 1162. ^{1}H-NMR (500 MHz) δ ppm; 7.44 (d, *J* = 8.0 Hz, 2H), 7.26-7.20 (m, 6H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.18-7.14 (m, 2H), 7.05-6.99 (m, 2H), 5.51 (s, 1H), 3.68-3.60 (m, 1H), 3.52-3.43 (m, 1H), 2.85-2.69 (m, 2H), 2.43 (s, 3H), 2.32 (t, *J* = 7.2 Hz, 2H), 1.55-1.46 (m, 2H), 1.45-1.35 (m, 2H), 0.92 (q, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz) δ ppm; 145.0, 143.2, 139.9, 137.8, 135.0, 129.4, 128.3, 128.1, 127.7, 127.55, 127.52, 127.50, 127.2, 119.8, 95.5, 79.6, 65.1, 45.5, 32.2, 30.8, 21.8, 21.5, 19.1, 13.5. FAB-LM m/z: 470 [M+H]. FAB-HM Calcd for $C_{30}H_{32}NO_2S$ [M+H]: 470.2154; found 470.2150.

Sonogashira Coupling Reaction of E-3aa

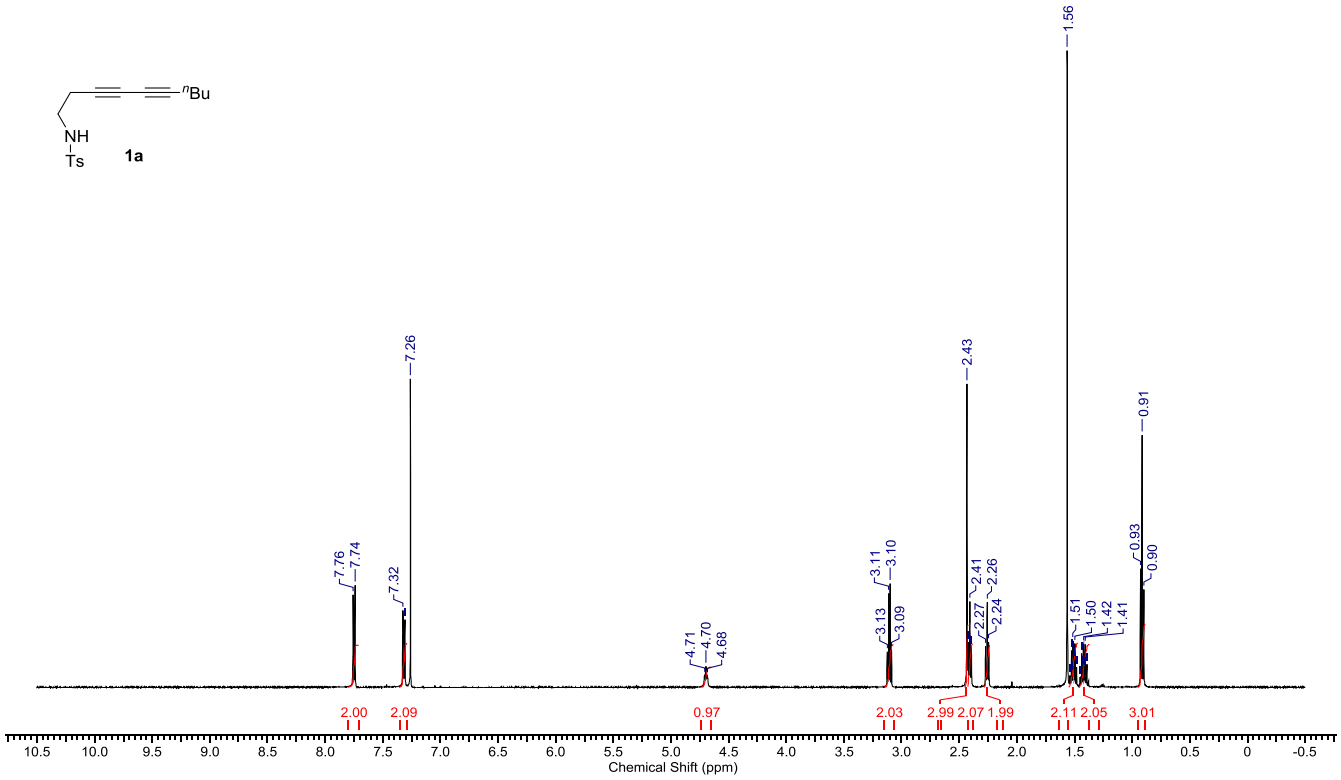


To a solution of $PdCl_2$ (1.8 mg, 10 μmol), Ph_3P (2.6 mg, 10 μmol), CuI (0.4 mg, 2 μmol) and ***E*-3aa** (108.3 mg, 0.2 mmol) in DMF (2.5 mL) was added ethynylbenzene (35.1 μL, 0.32 mmol) and Et_3N (0.5 mL, 3.6 mmol) at room temperature. After being stirred at 80 ºC for 1 h, the reaction mixture was quenched with sat. NH_4Cl and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by silica gel column chromatography (hexane:AcOEt = 3:1) to give **8** (62.8 mg, 64 %).

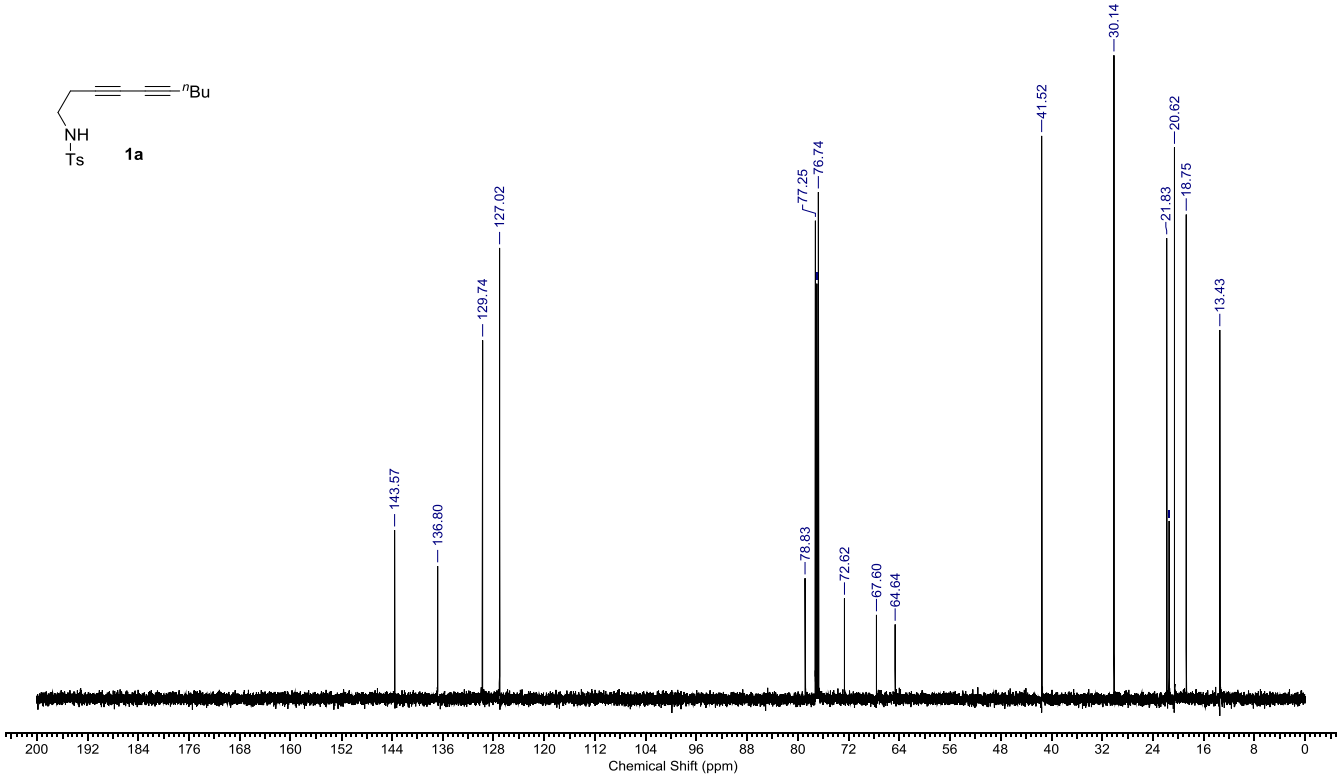
(*E*)-2-Phenyl-3-(1-phenylnona-1,4-diyn-3-ylidene)-1-tosylpyrrolidine (9)
R_f = 0.37 (hexane:AcOEt = 3:1). Brown oil. IR (neat) ν cm^{-1}; 2227, 1350, 1163. ^{1}H-NMR (500 MHz) δ ppm; 7.69 (d, *J* = 8.6 Hz, 2H), 7.43-7.38 (m, 2H), 7.37-7.25 (m, 8H), 7.23 (d, *J* = 8.6 Hz, 2H), 5.68 (s, 1H), 3.68-3.54 (m, 2H), 2.85-2.72 (m, 2H), 2.40 (s, 3H), 2.32 (t, *J* = 7.2 Hz, 2H), 1.56-1.46 (m, 2H), 1.45-1.35 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H) ^{13}C NMR (125 MHz) δ ppm; 156.4, 143.5, 139.3, 134.9, 131.4, 129.5, 128.6, 128.3, 127.6, 127.5, 127.3, 122.5, 101.0, 94.4, 92.9, 85.4, 76.3, 66.6, 46.7, 31.2, 30.5, 21.9, 21.5, 19.0, 13.5 (note that two carbon peaks overlap with each other). FAB-LM m/z: 494 [M+H]. FAB-HM Calcd for $C_{32}H_{32}NO_2S$ [M+H]: 494.2154; found 494.2191.

^{1}H and ^{13}C NMR spectra of new compounds

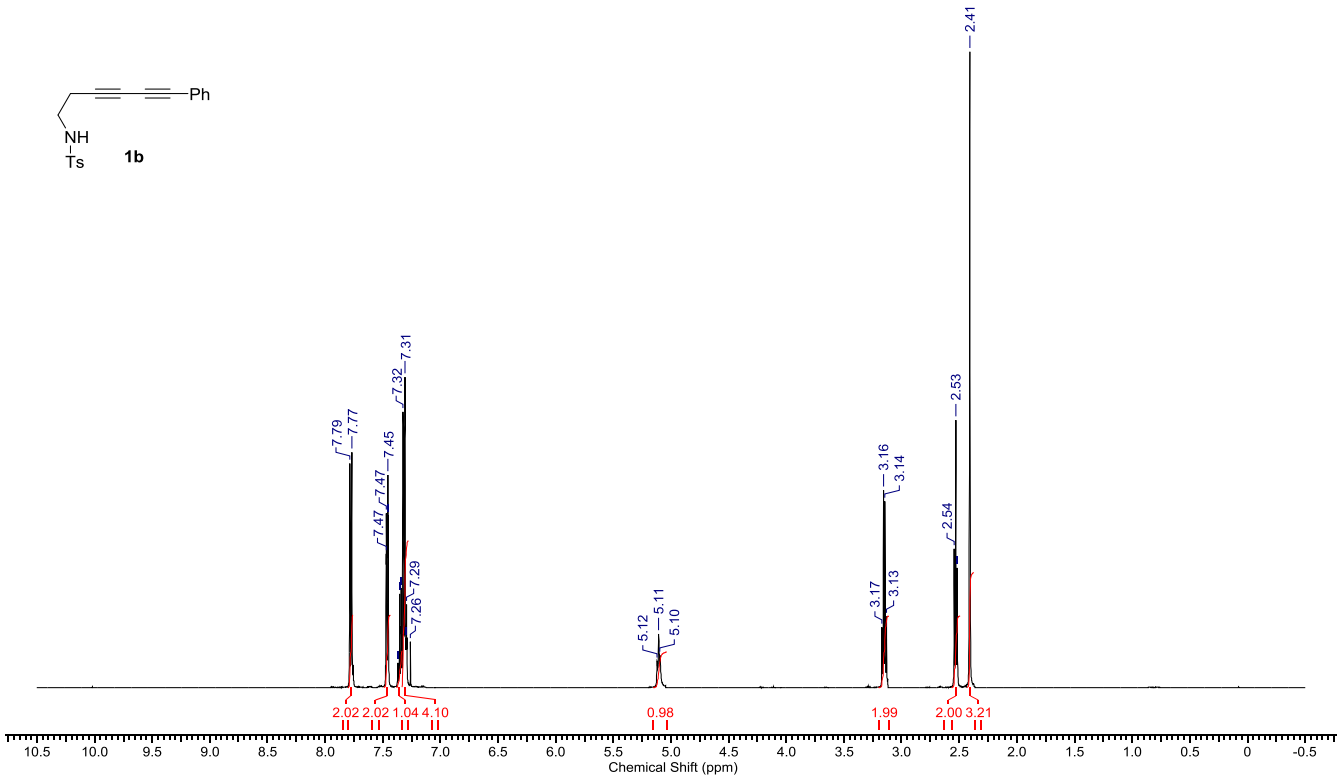
^{1}H NMR of **1a**



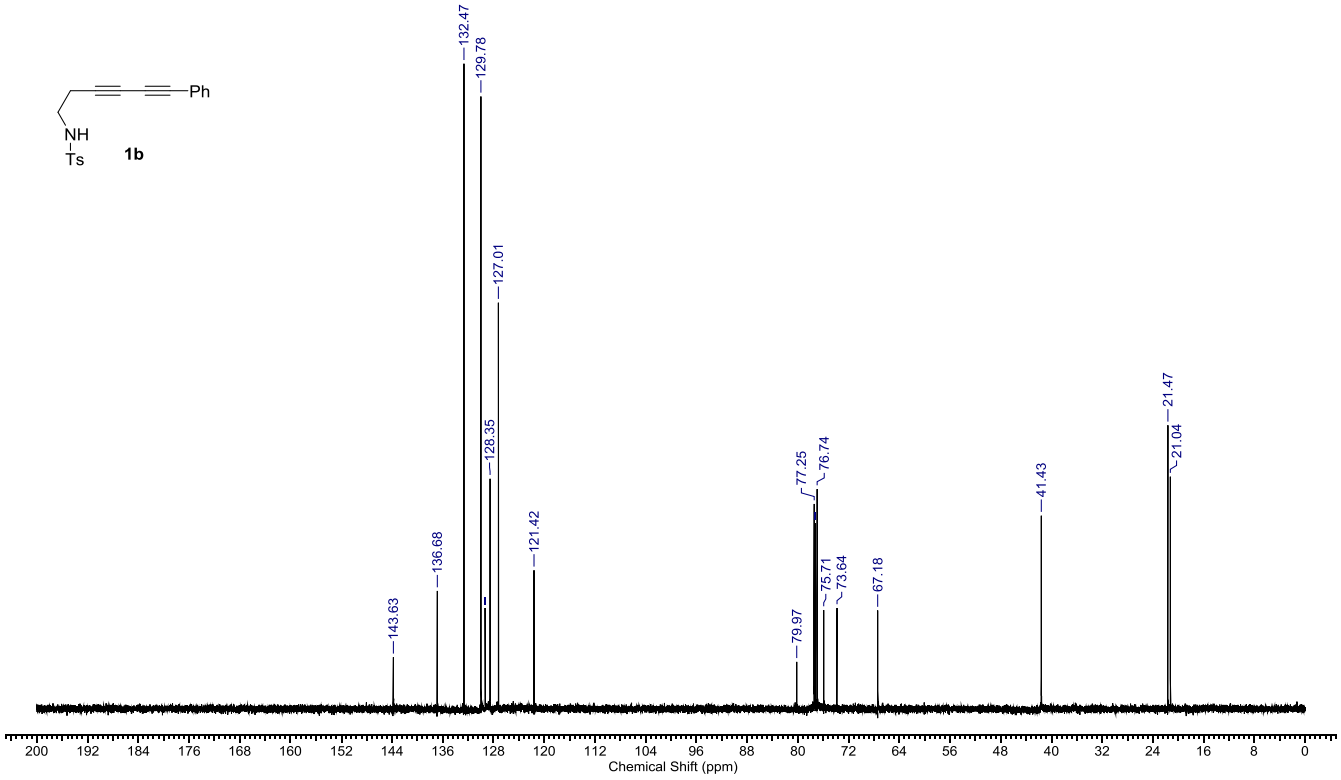
^{13}C NMR of **1a**



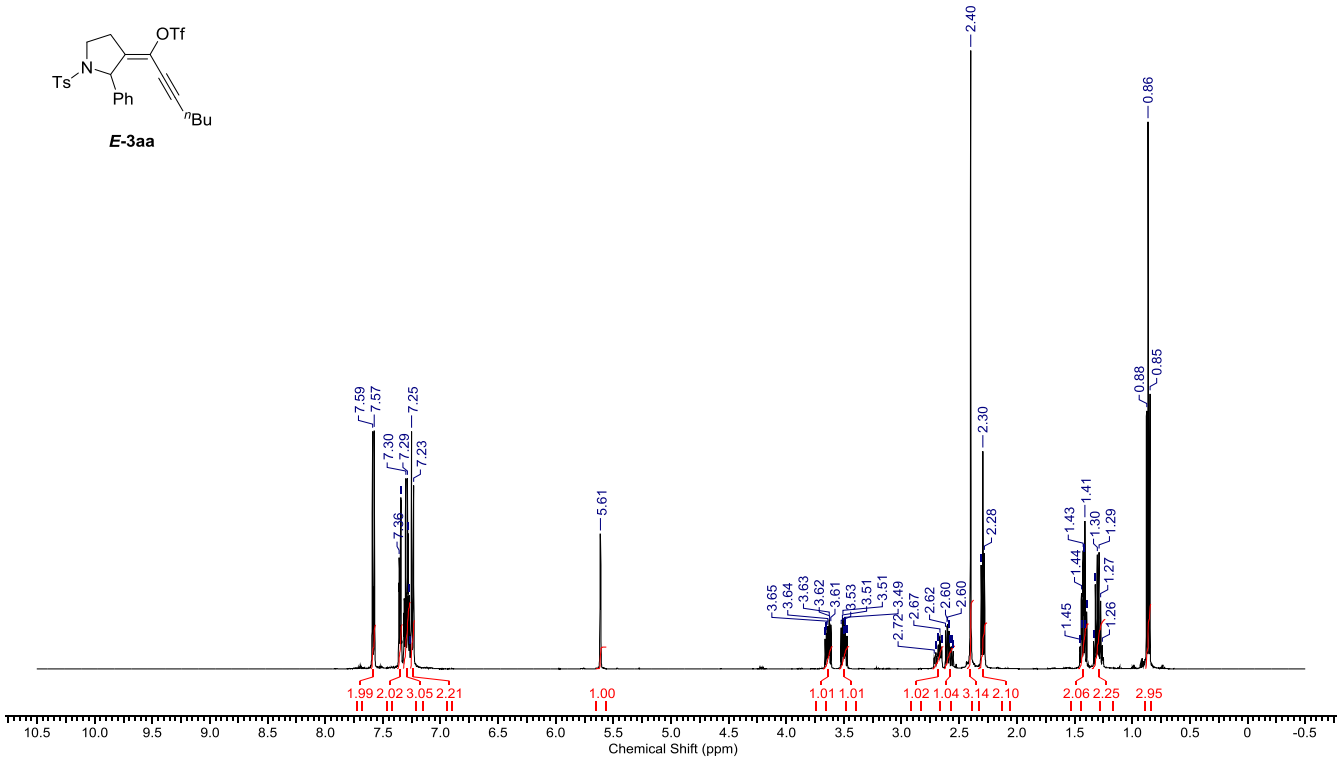
^{1}H NMR of **1b**



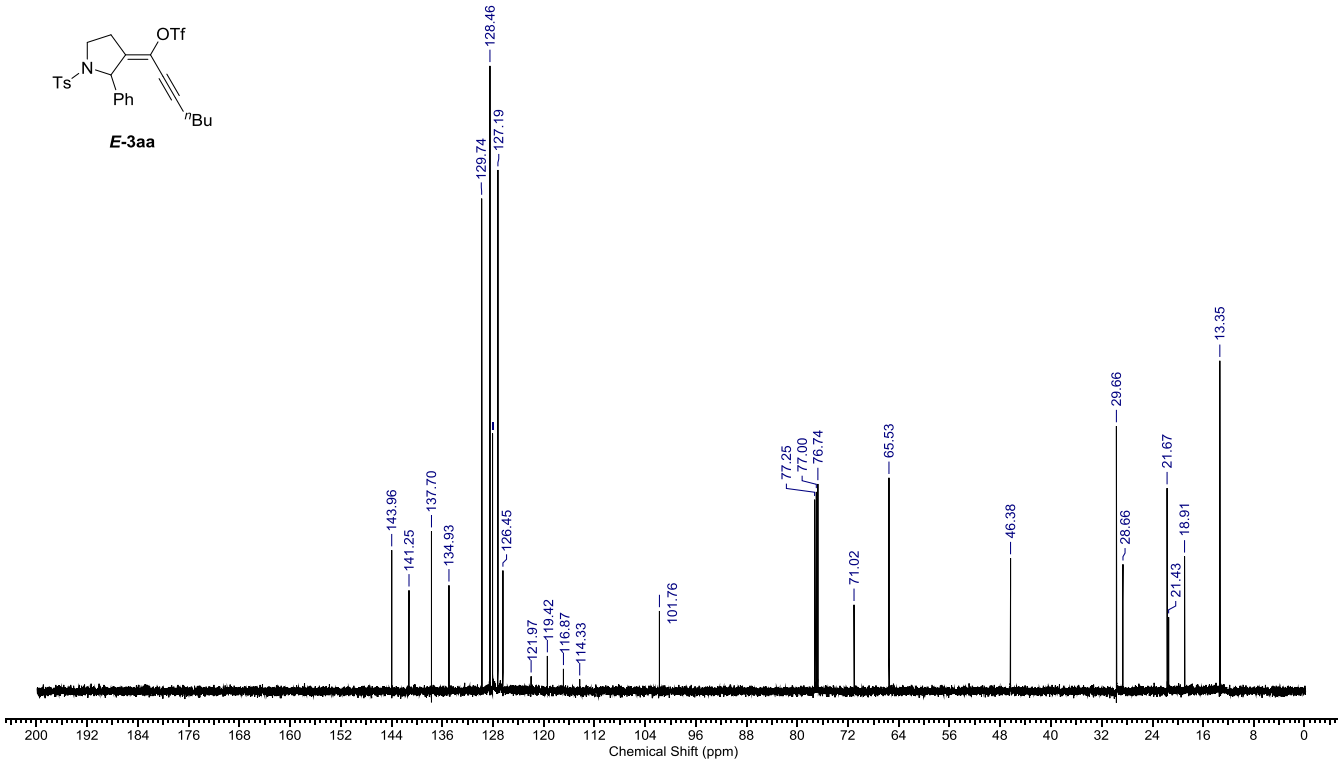
^{13}C NMR of **1b**



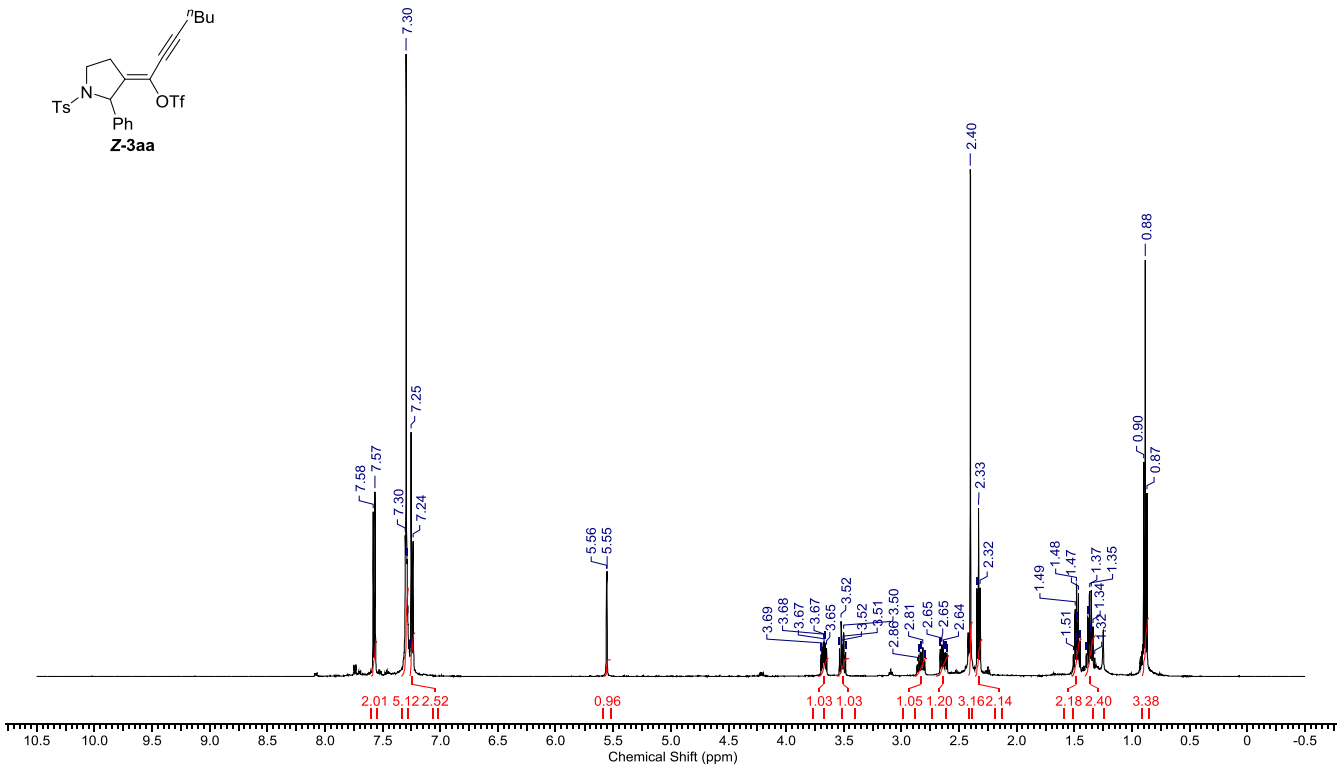
^{1}H NMR of ***E*-3aa**



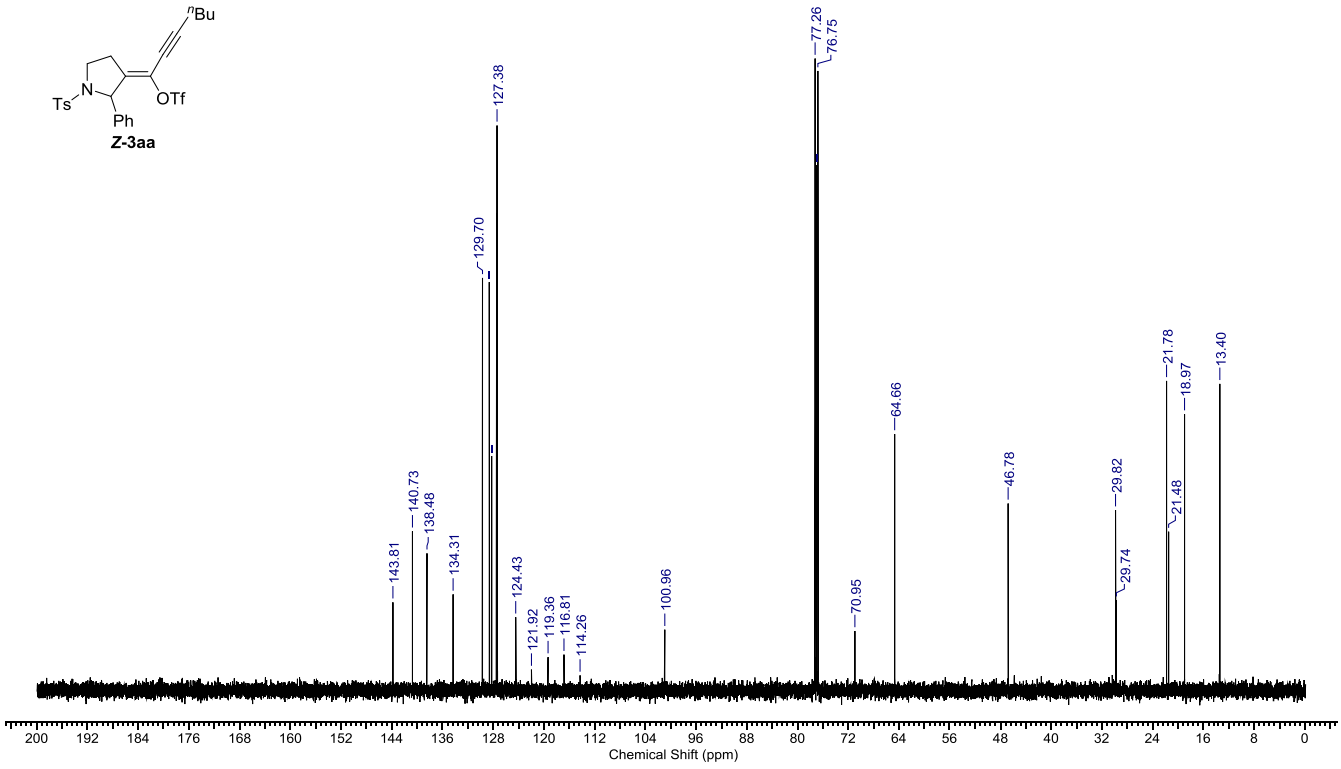
^{13}C NMR of ***E*-3aa**



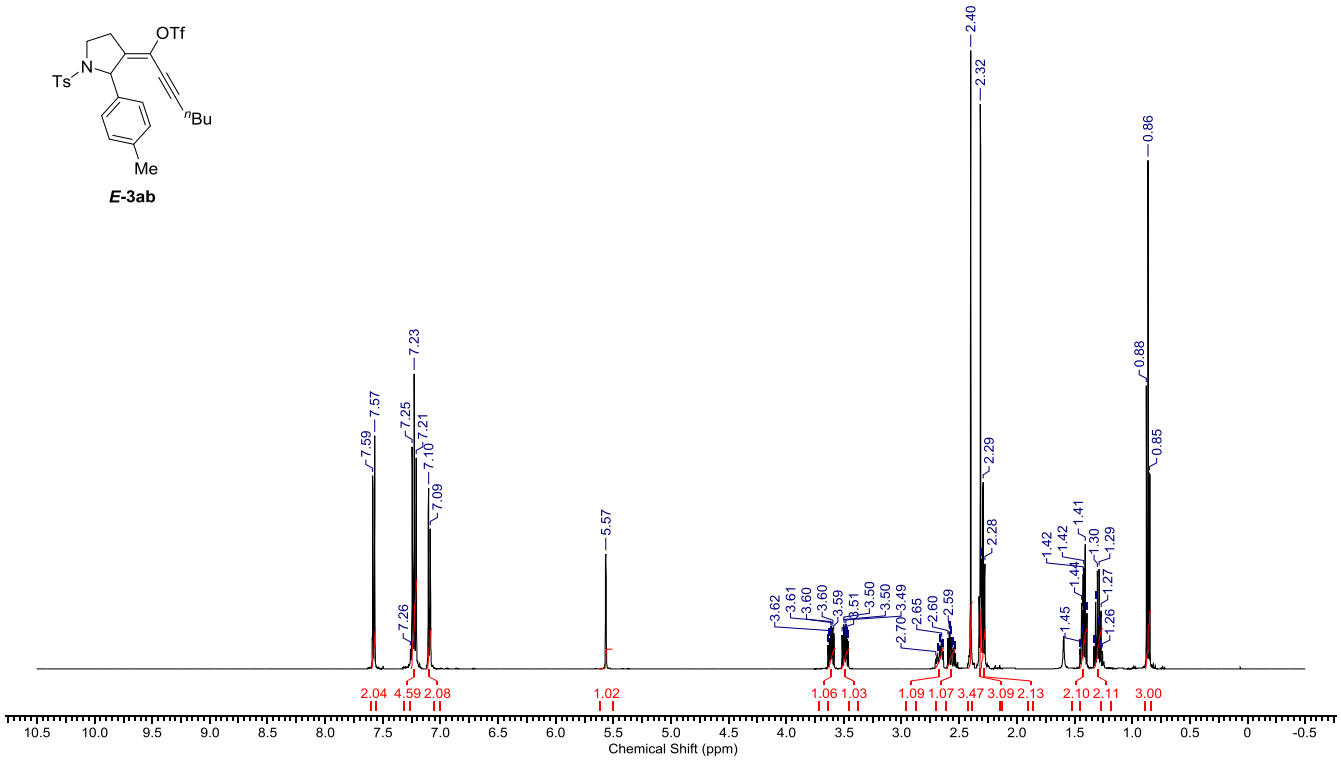
^{1}H NMR of ***Z*-3aa**



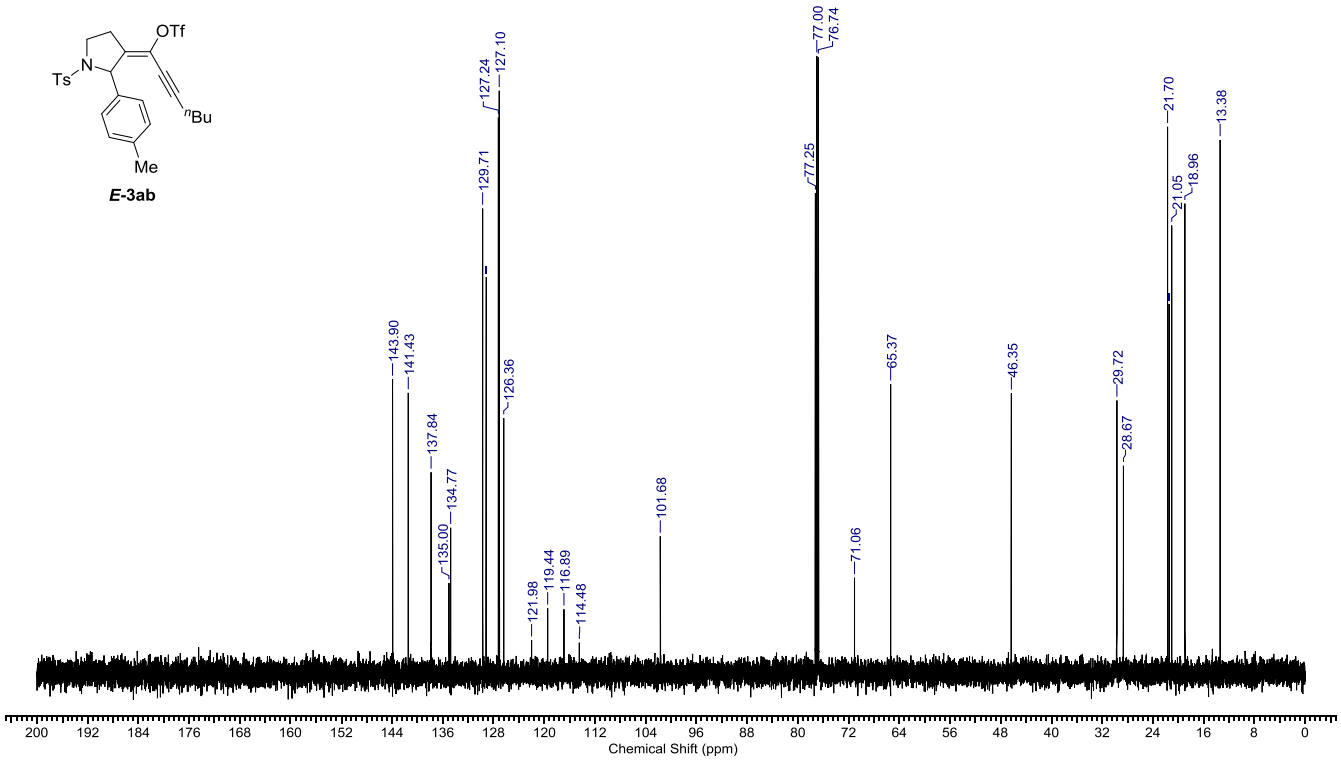
^{13}C NMR of ***Z*-3aa**



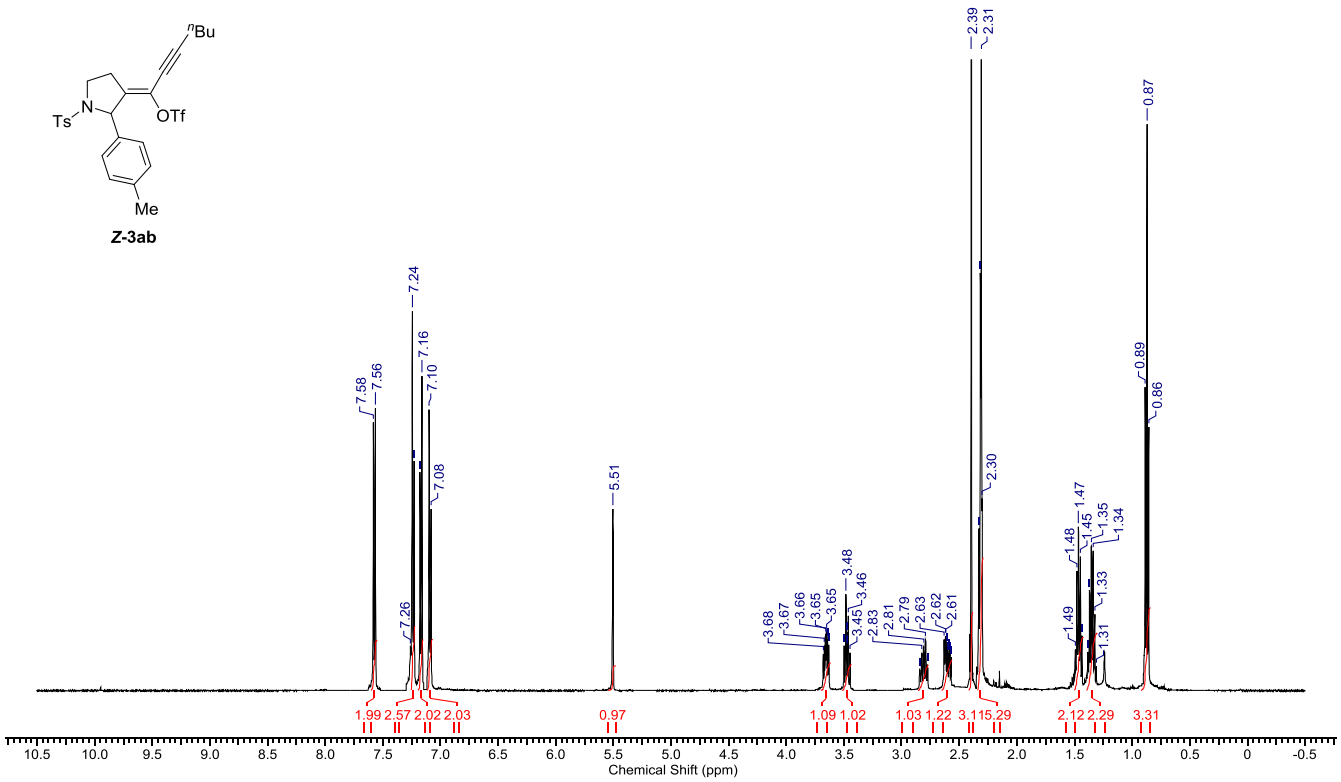
^{1}H NMR of ***E*-3ab**



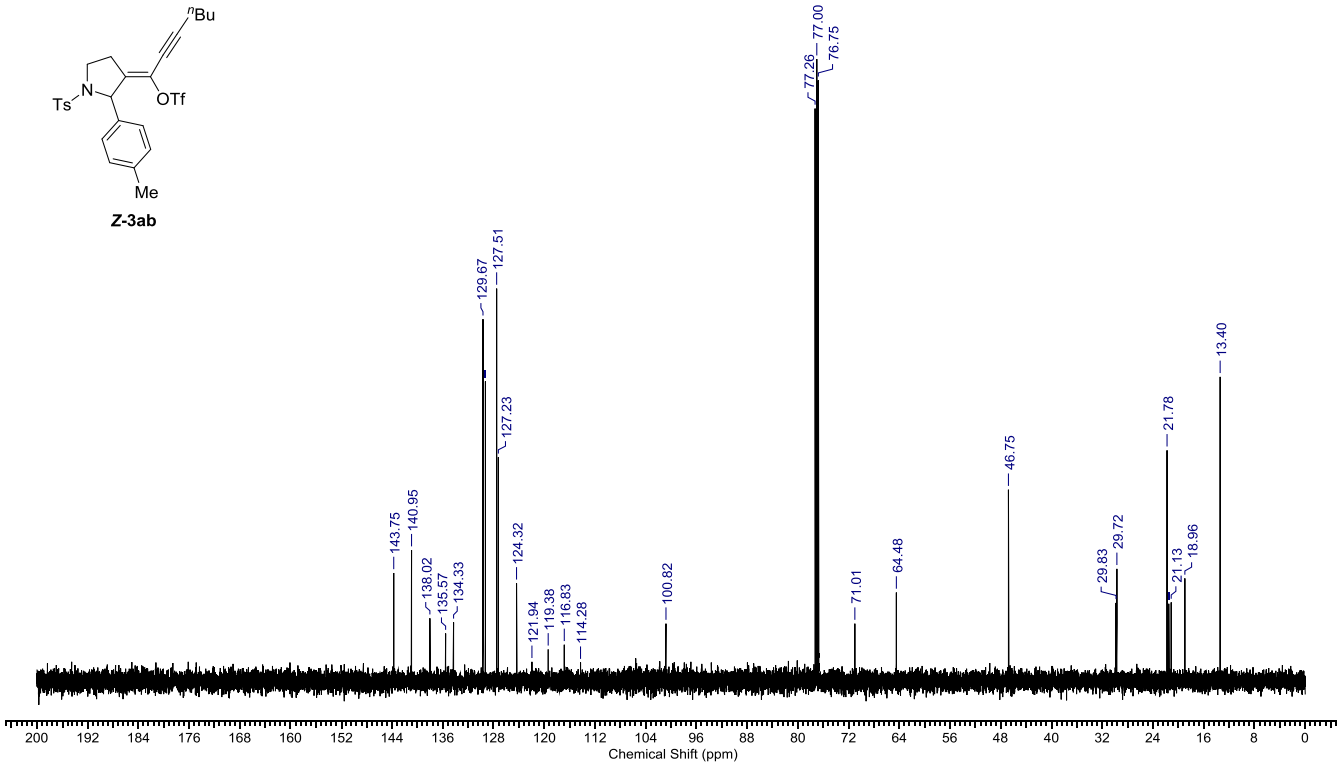
^{13}C NMR of ***E*-3ab**



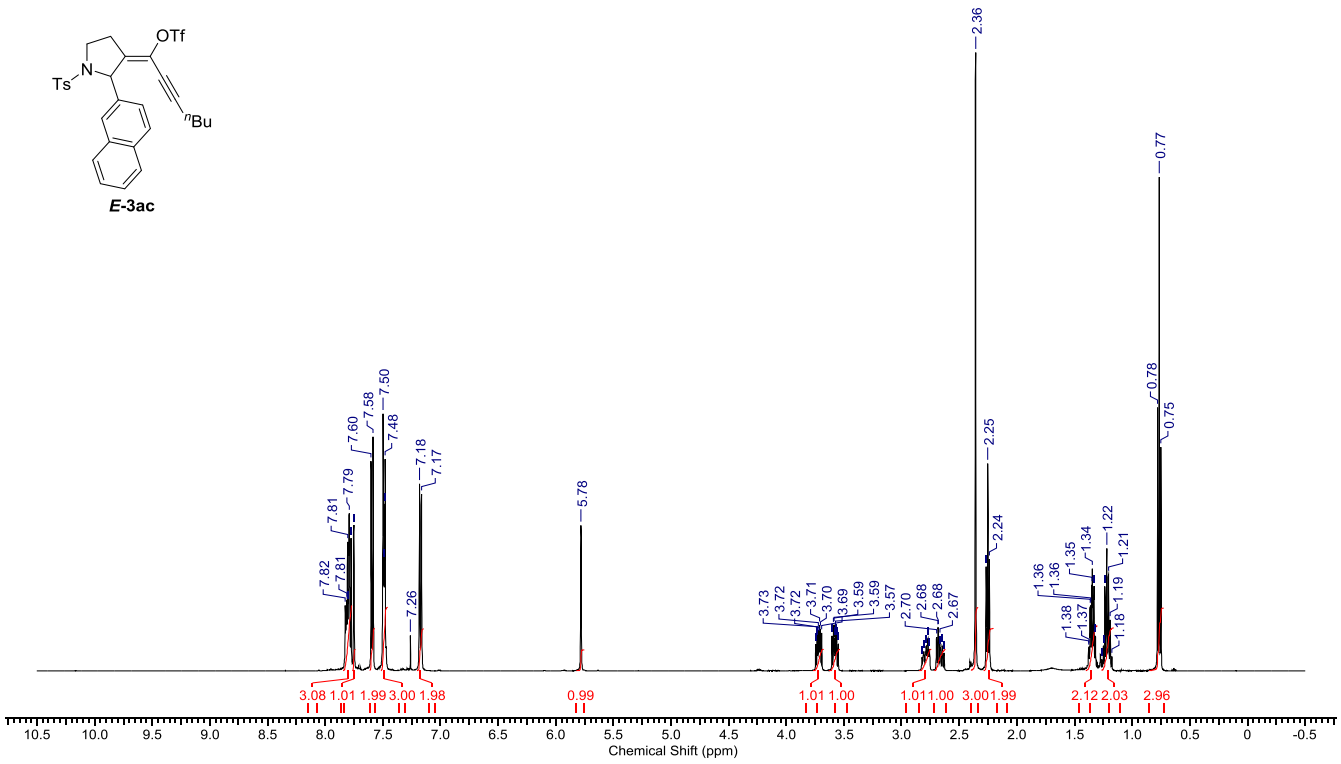
^{1}H NMR of ***Z*-3ab**



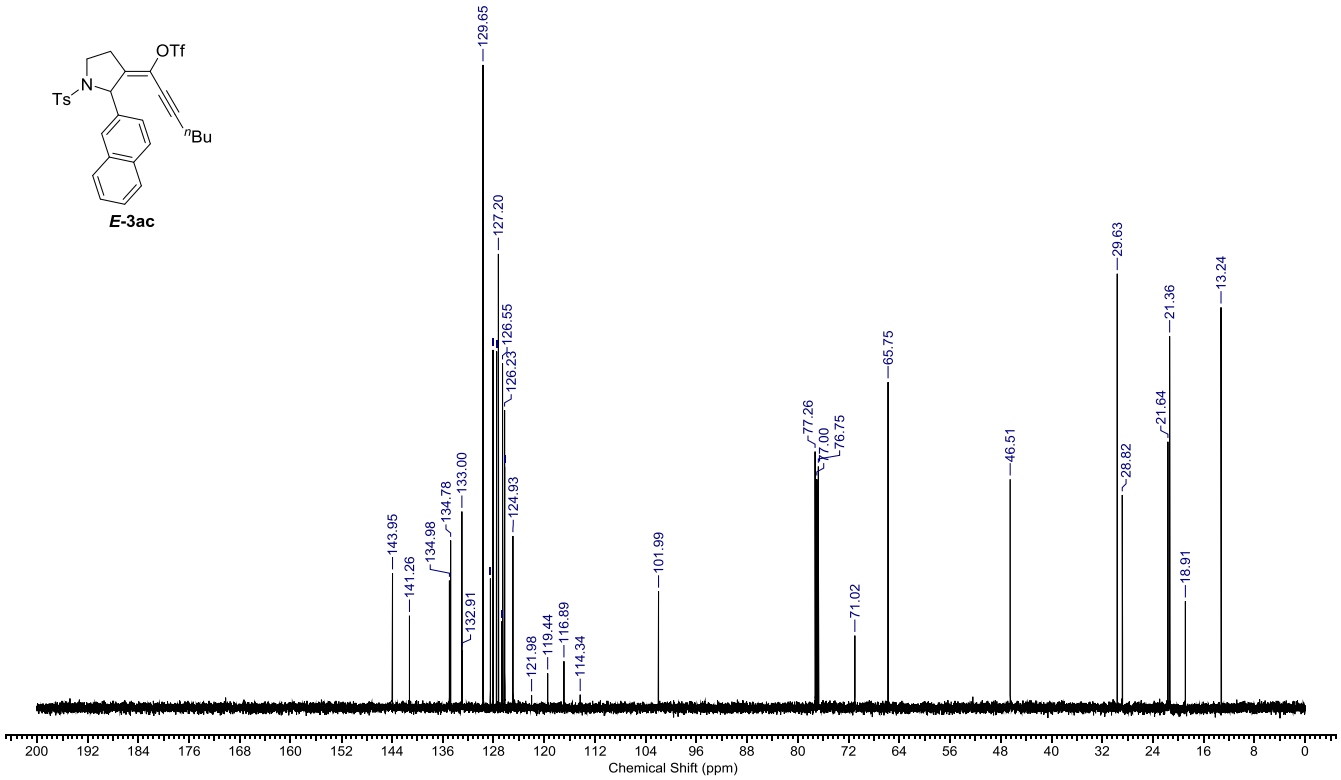
^{13}C NMR of ***Z*-3ab**



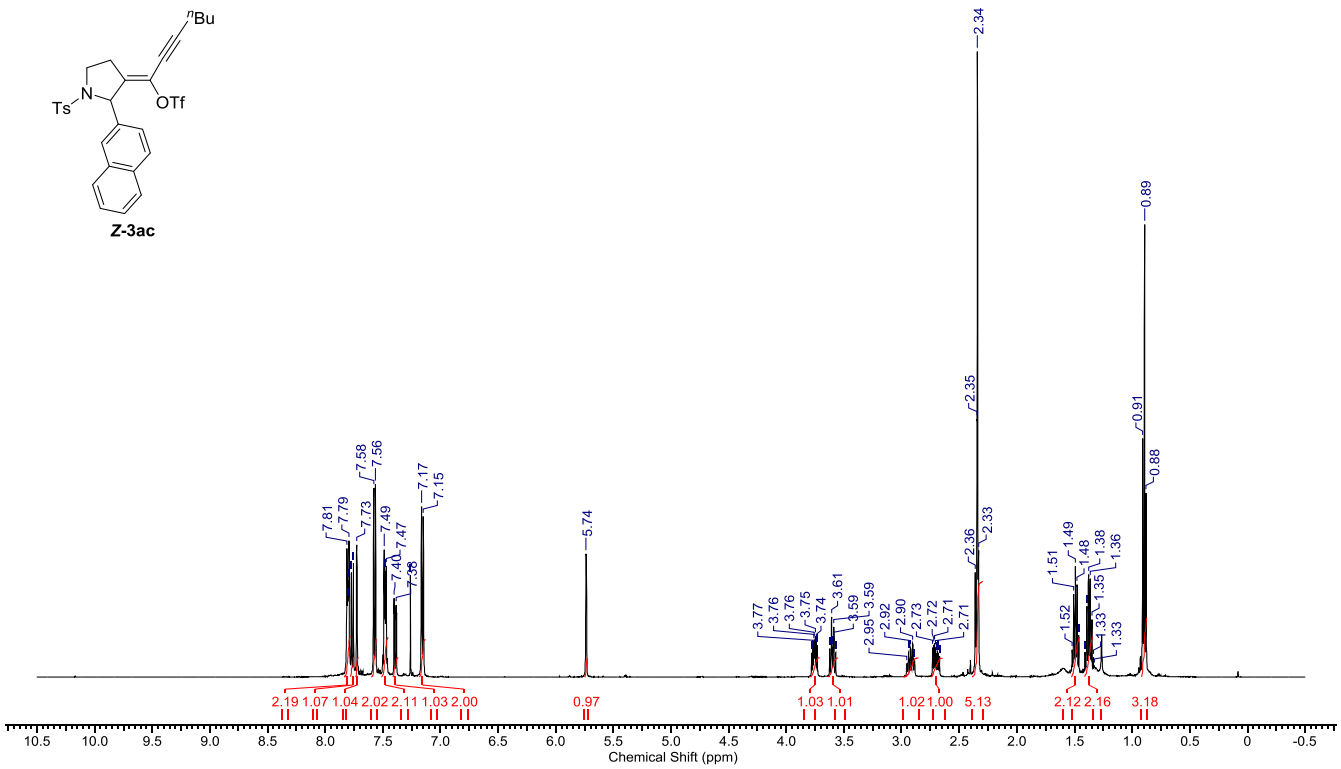
^{1}H NMR of ***E*-3ac**



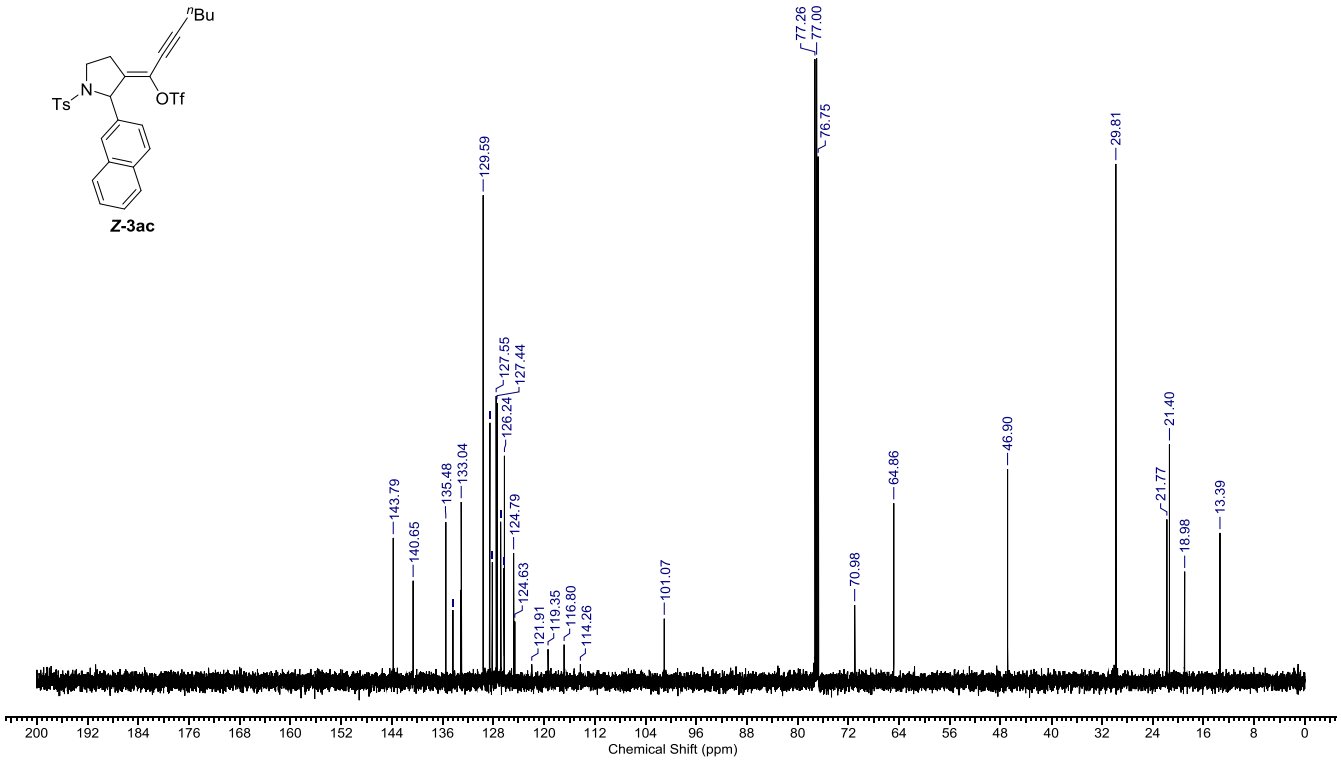
^{13}C NMR of ***E*-3ac**



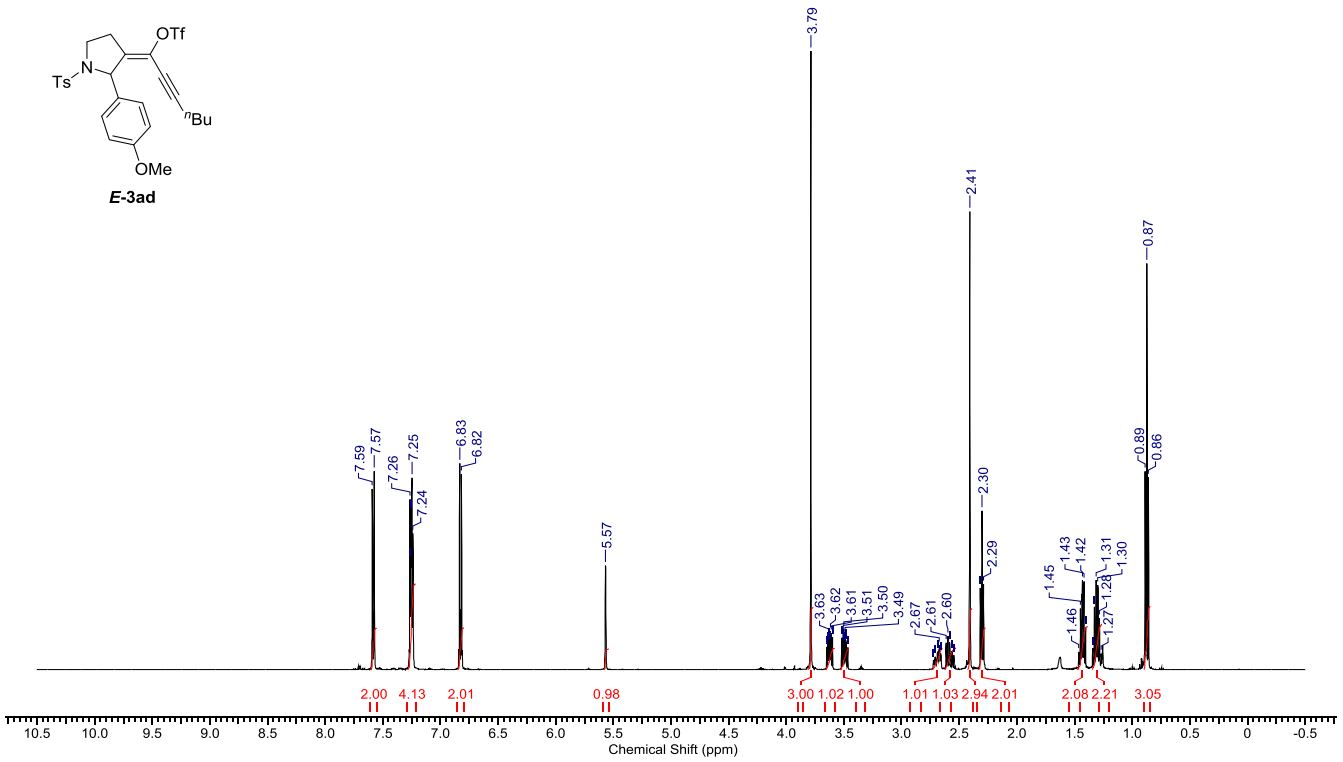
^{1}H NMR of ***Z*-3ac**



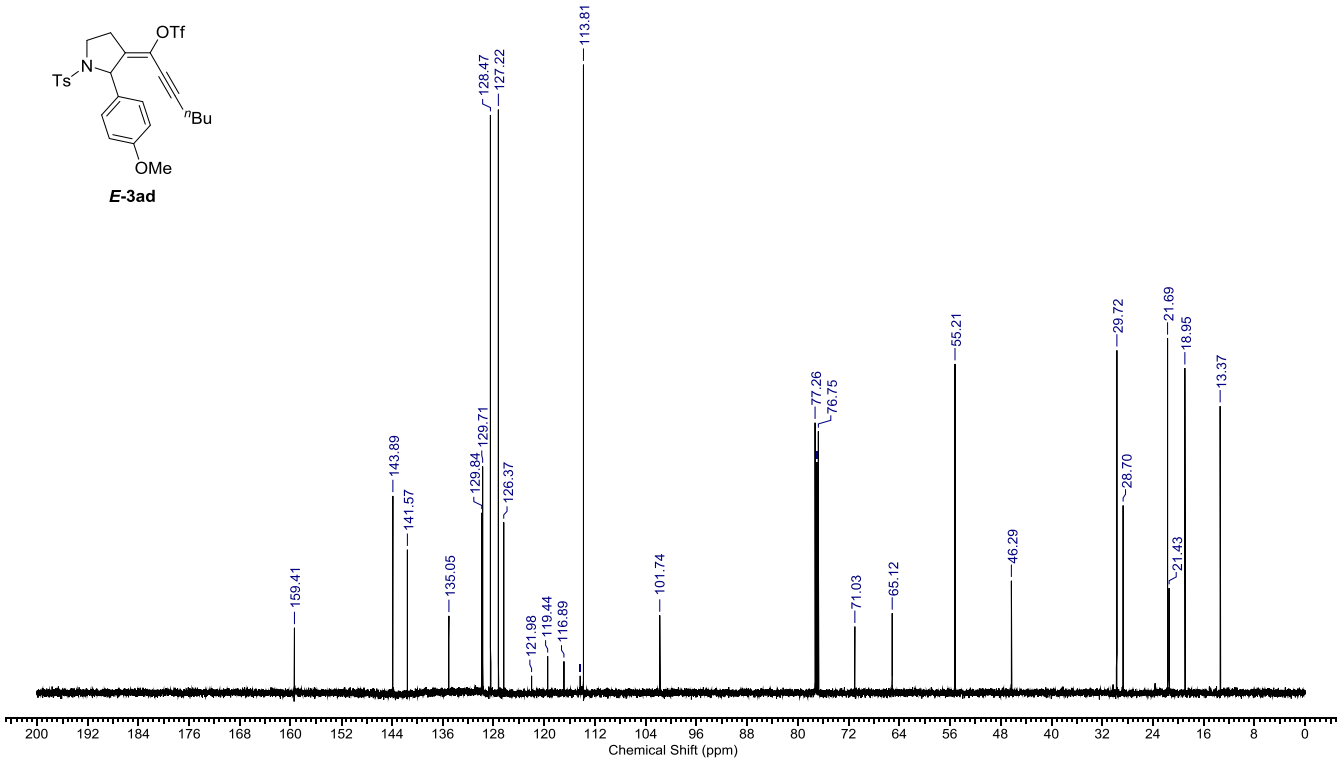
^{13}C NMR of ***Z*-3ac**



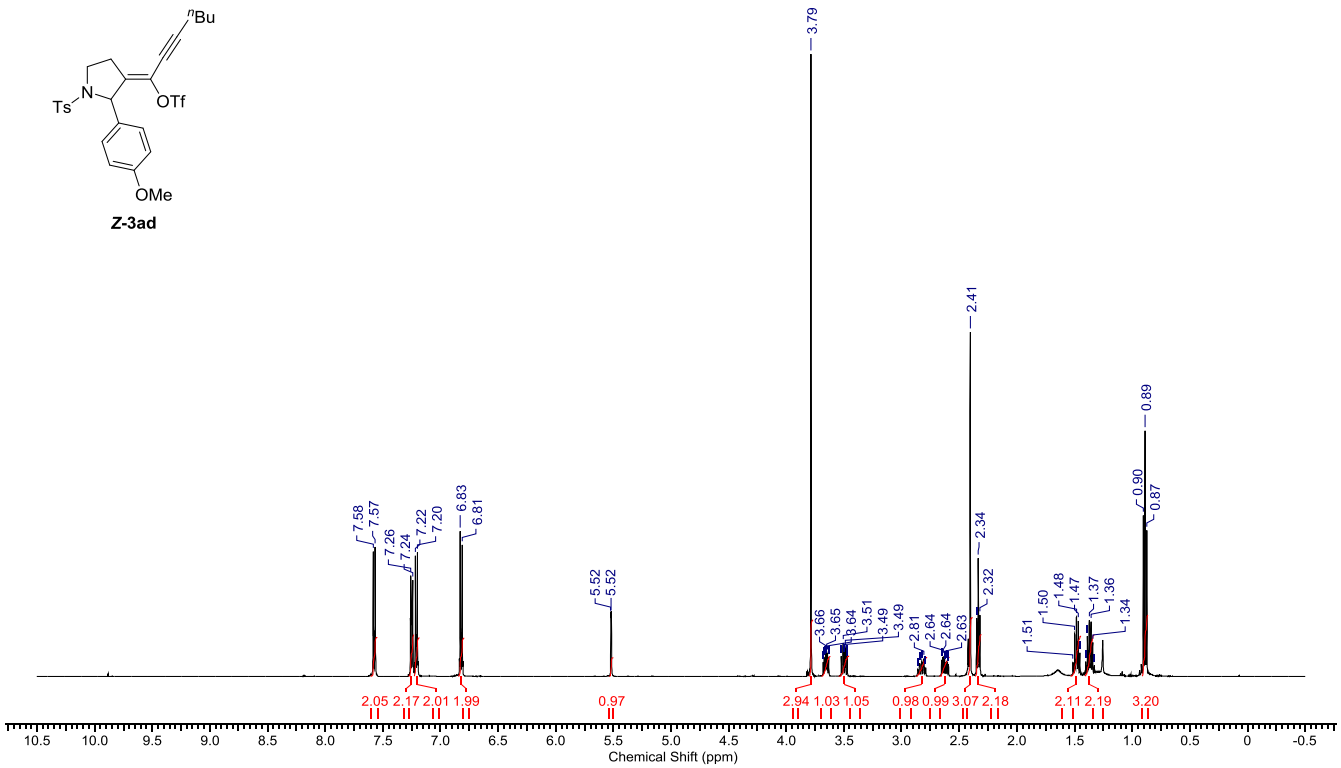
^{1}H NMR of ***E*-3ad**



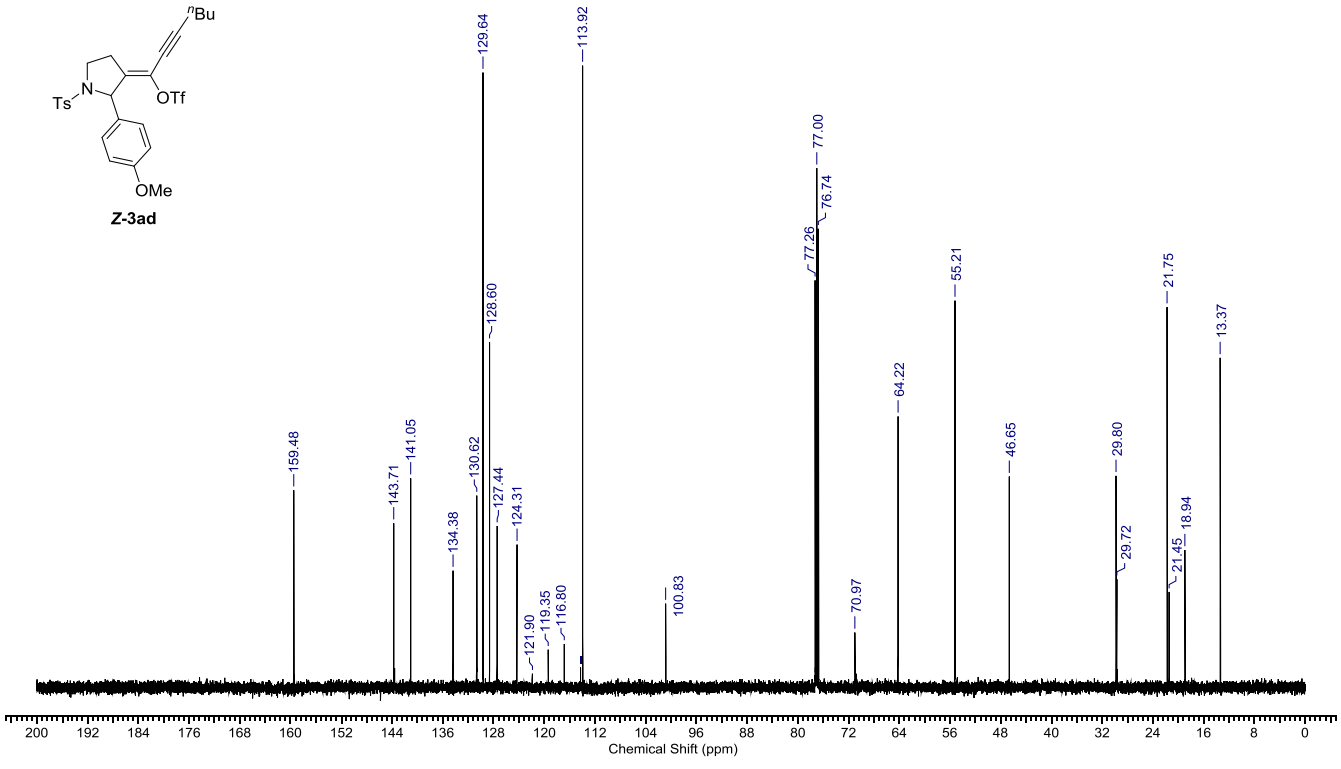
^{13}C NMR of ***E*-3ad**



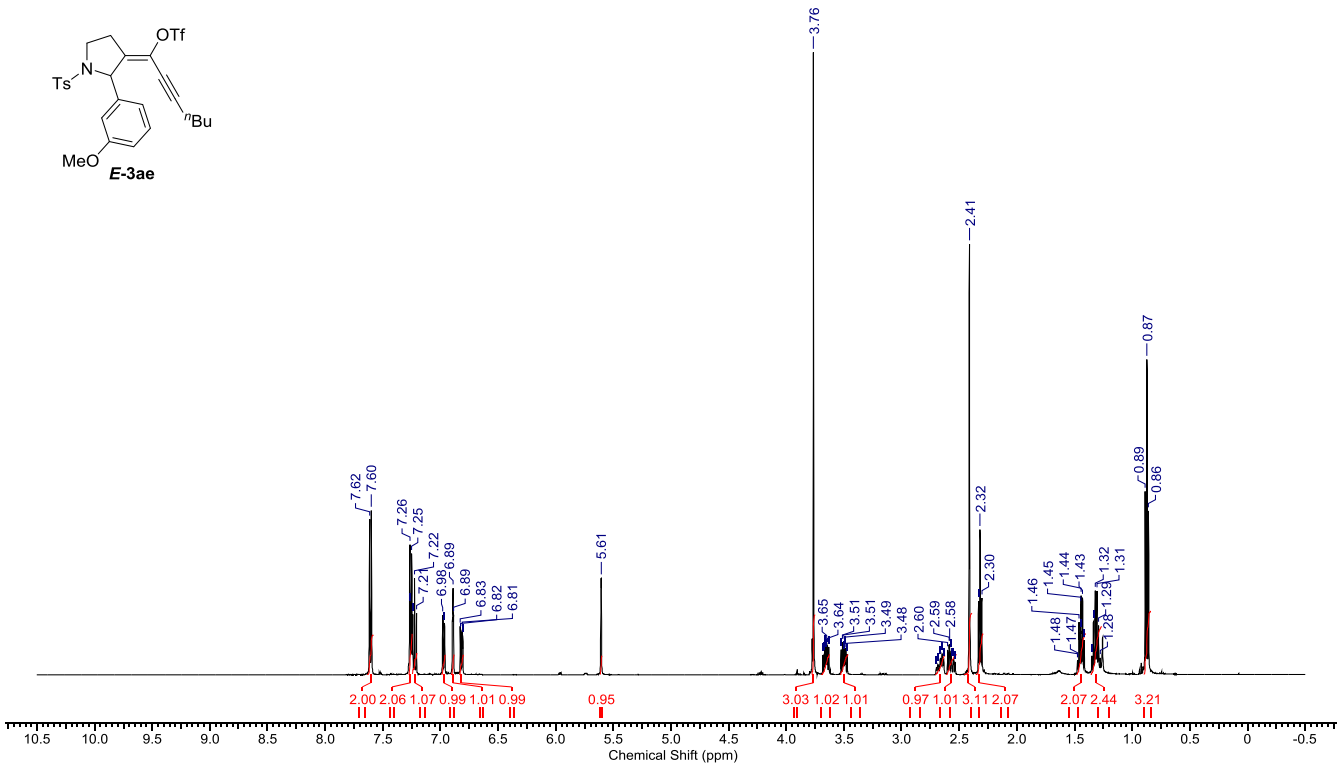
^{1}H NMR of ***Z*-3ad**



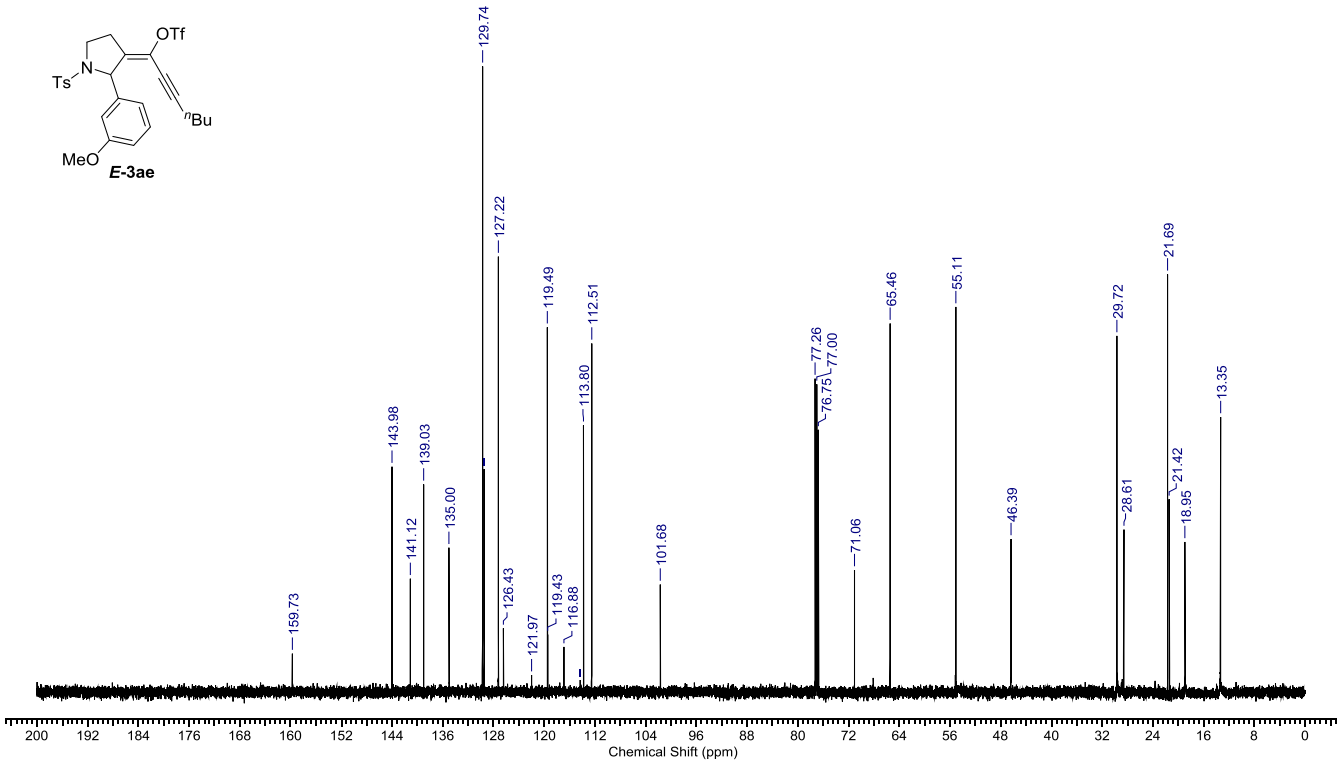
^{13}C NMR of ***Z*-3ad**



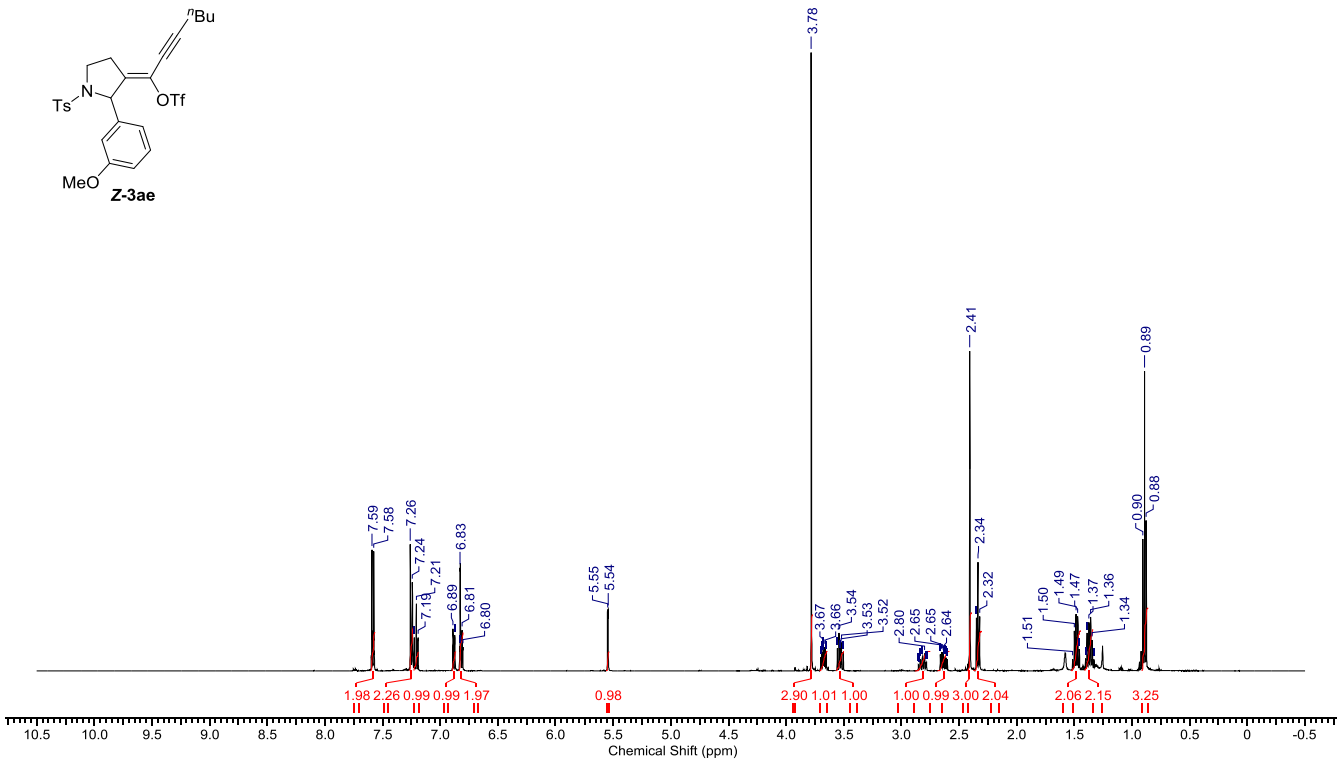
^{1}H NMR of ***E*-3ae**



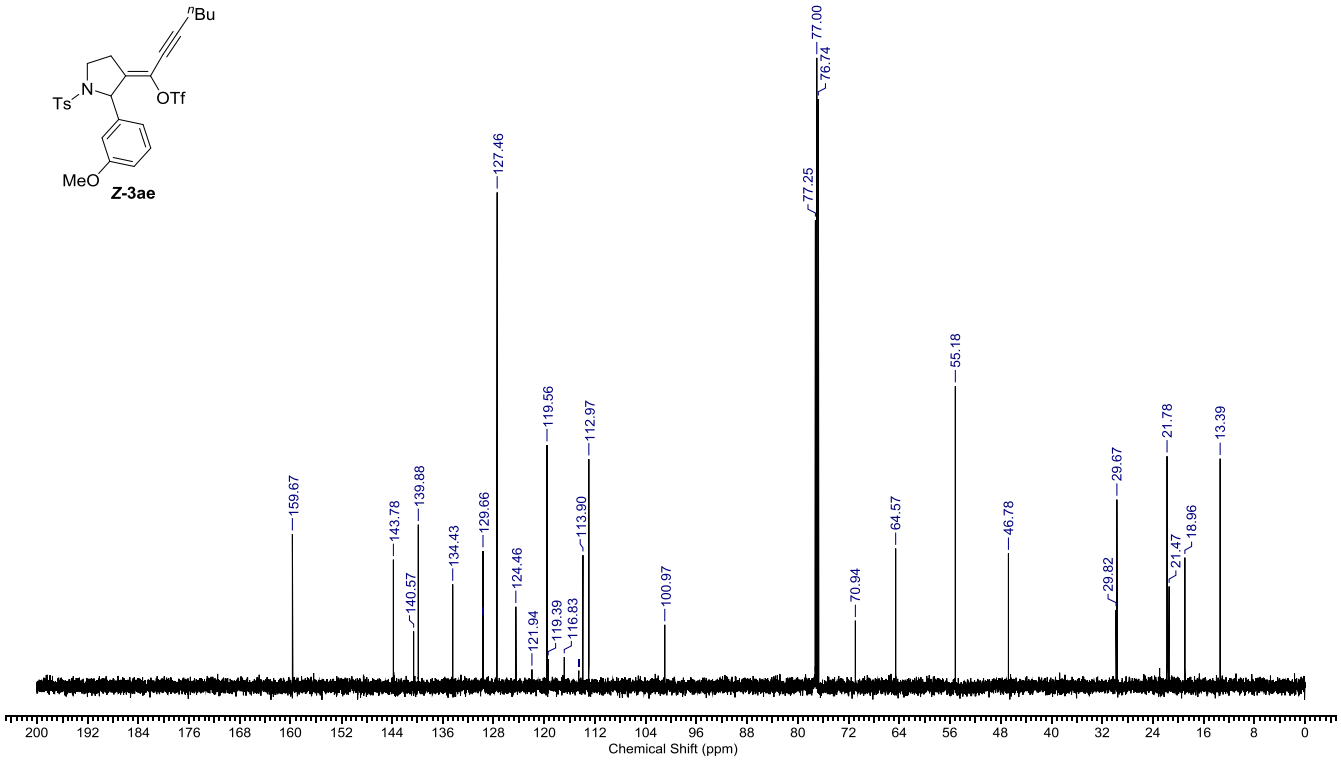
^{13}C NMR of ***E*-3ae**



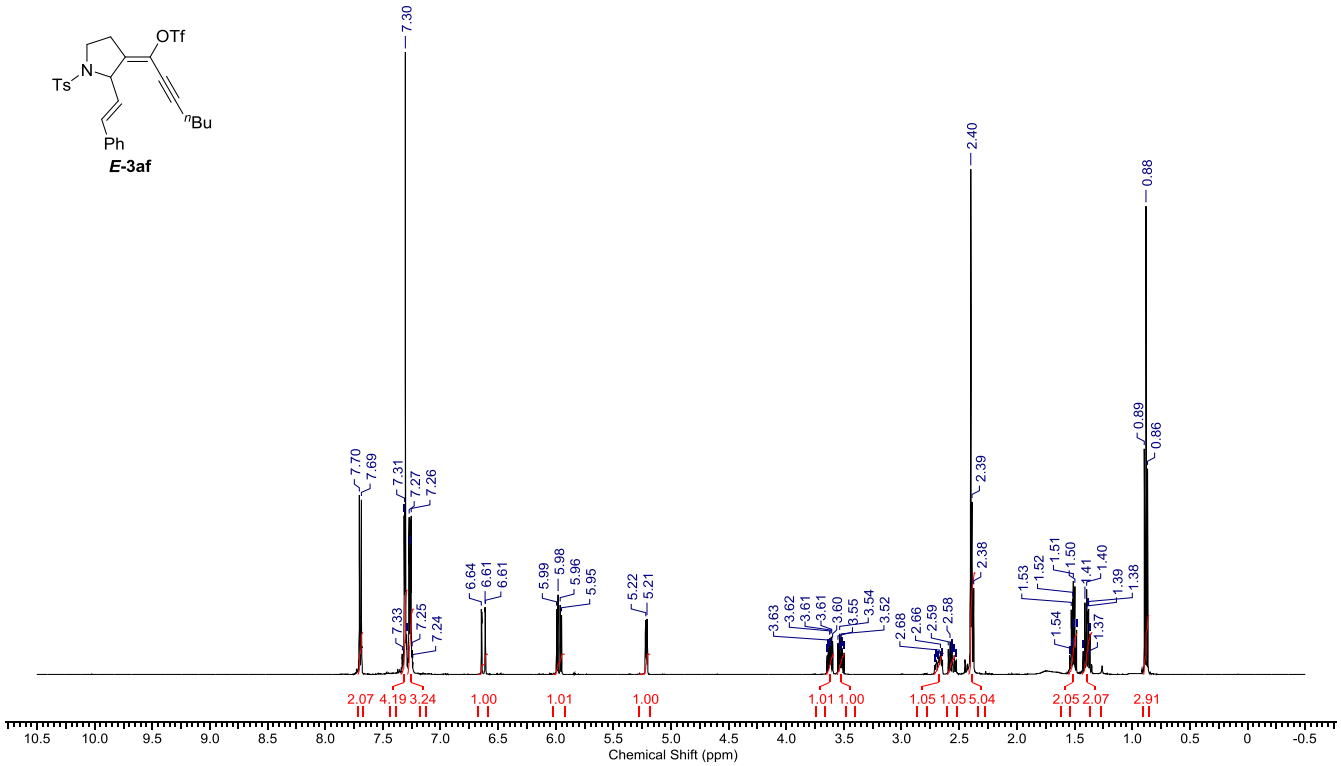
^{1}H NMR of ***Z*-3ae**



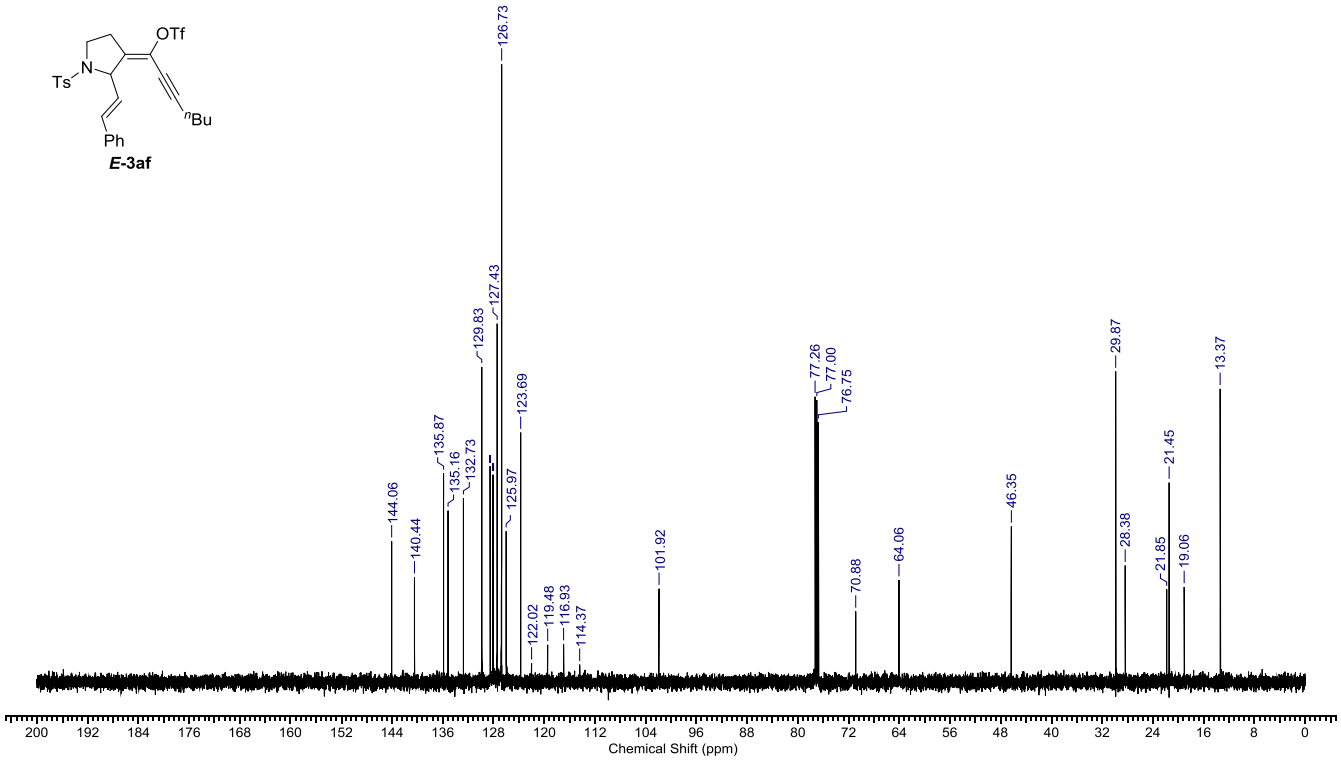
^{13}C NMR of ***Z*-3ae**



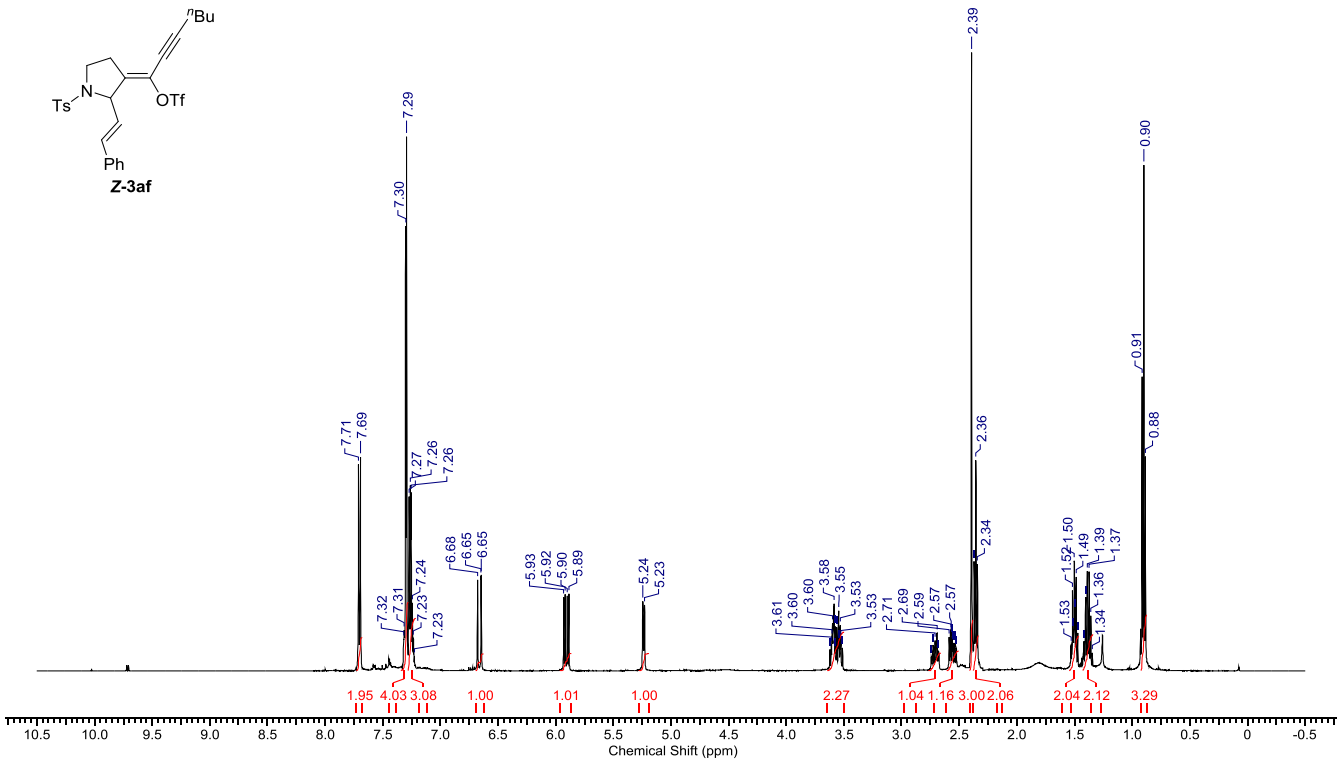
^{1}H NMR of ***E*-3af**



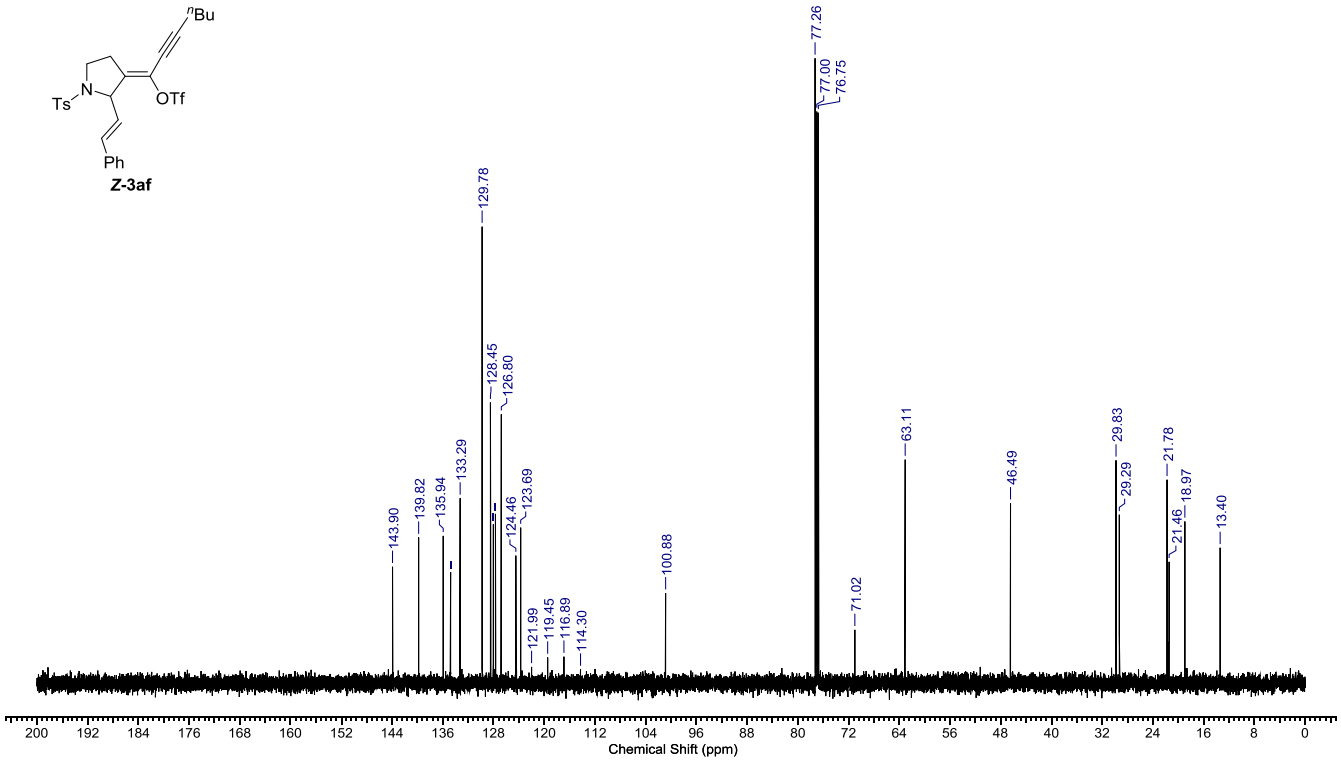
^{13}C NMR of ***E*-3af**



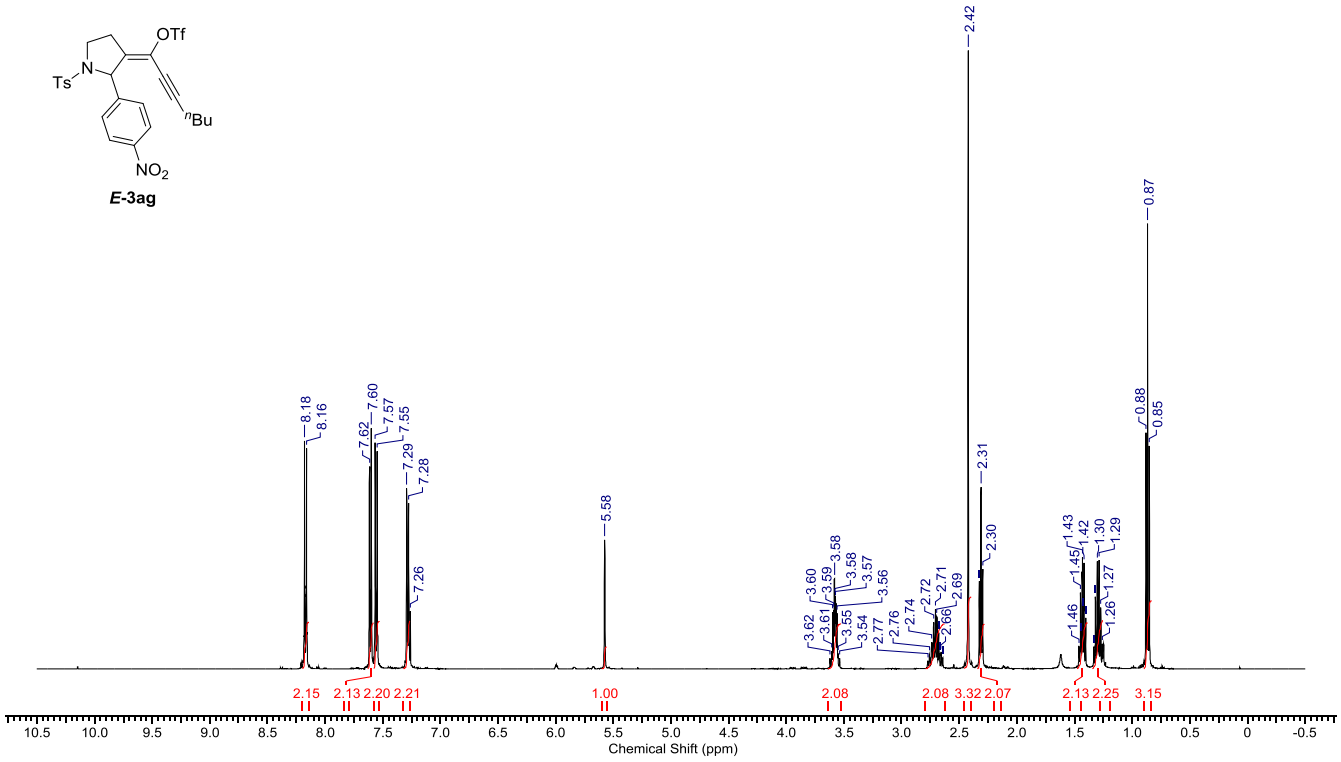
^{1}H NMR of ***Z*-3af**



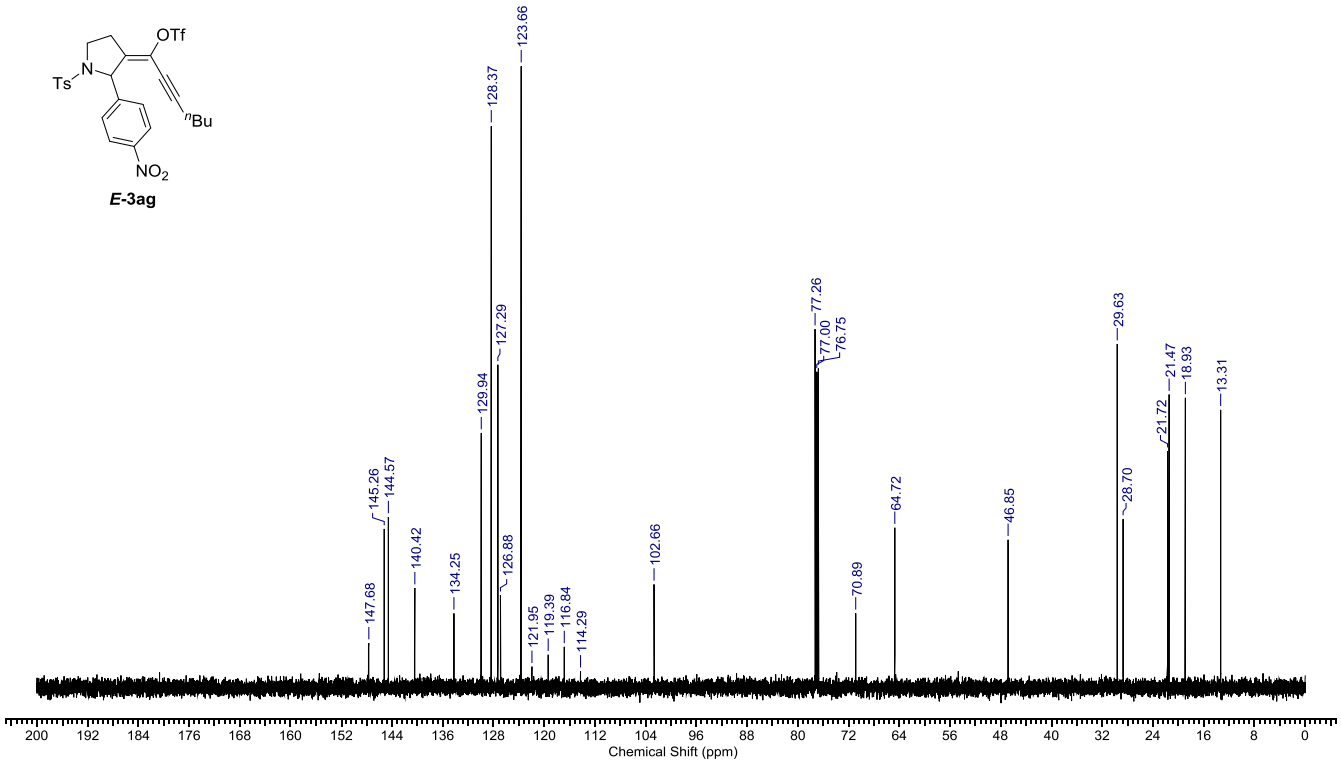
^{13}C NMR of ***Z*-3af**



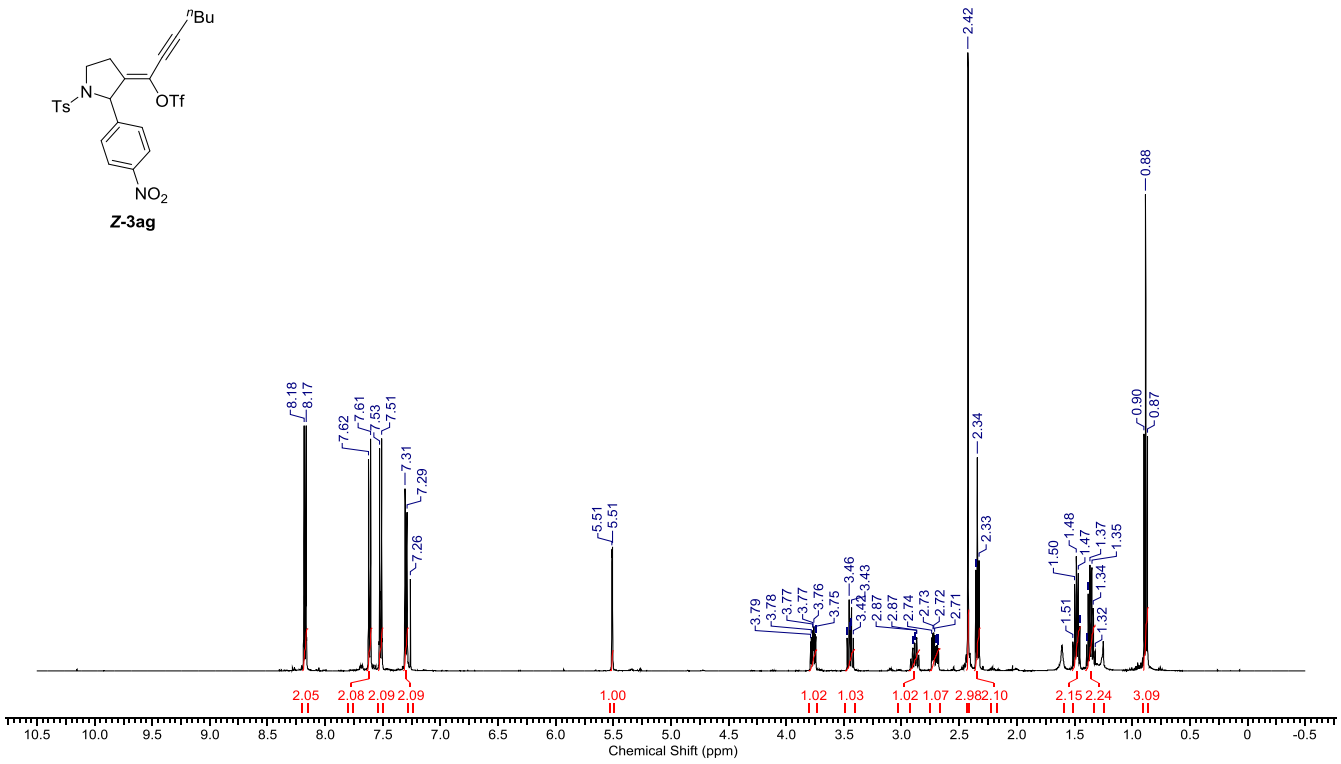
^{1}H NMR of ***E*-3ag**



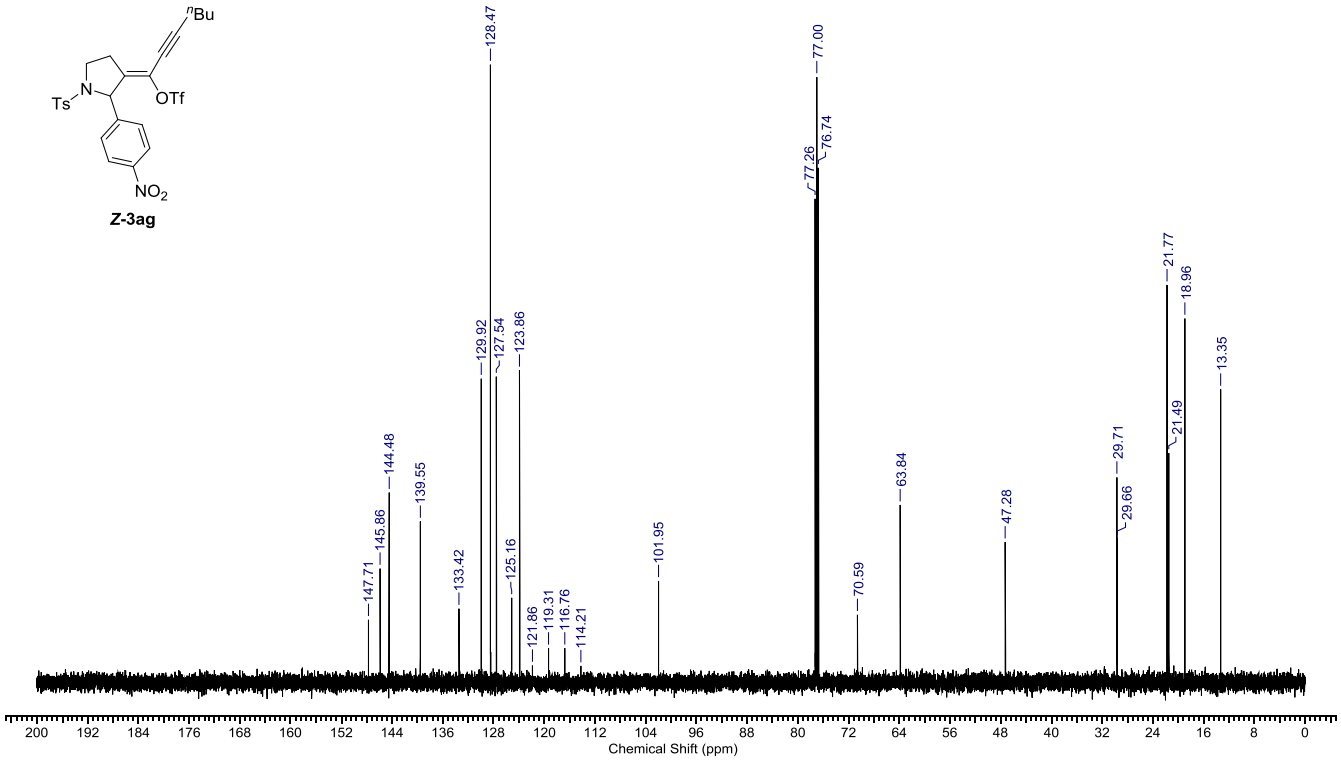
^{13}C NMR of ***E*-3ag**



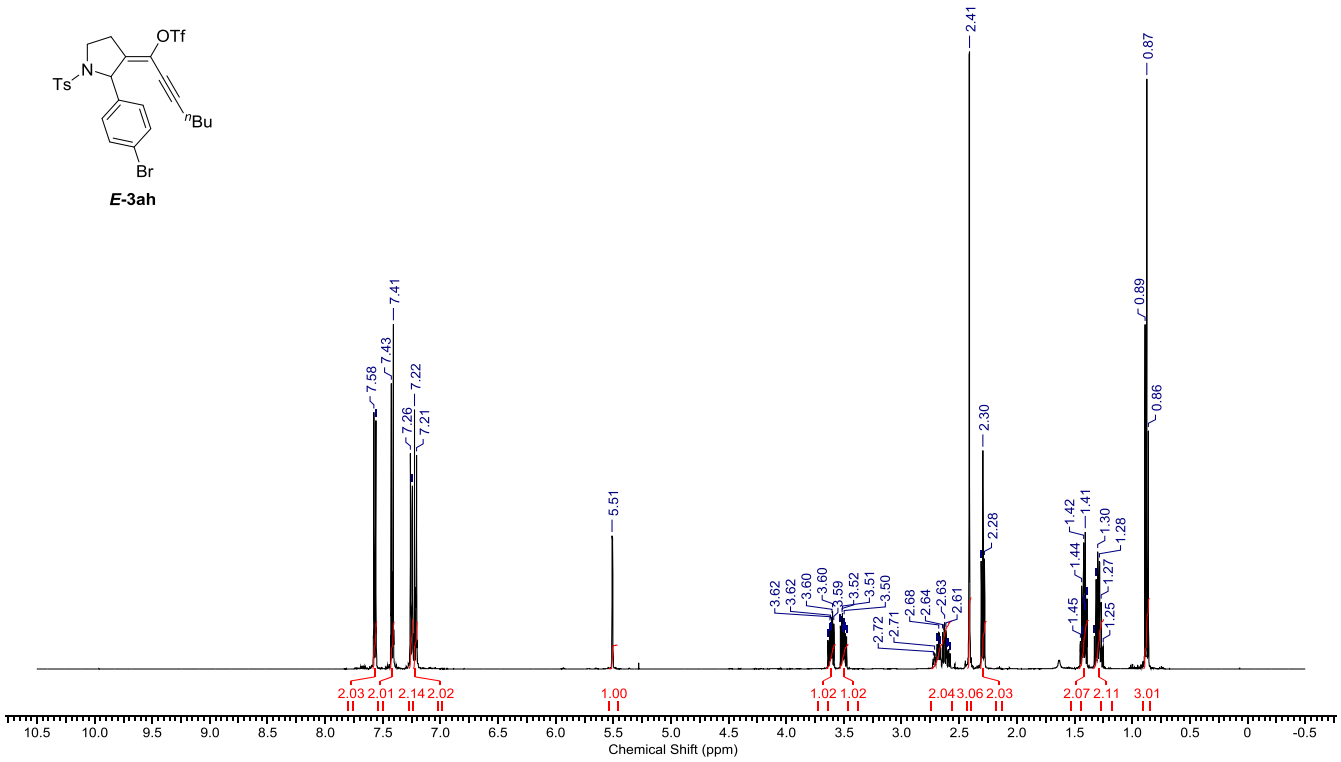
^{1}H NMR of ***Z*-3ag**



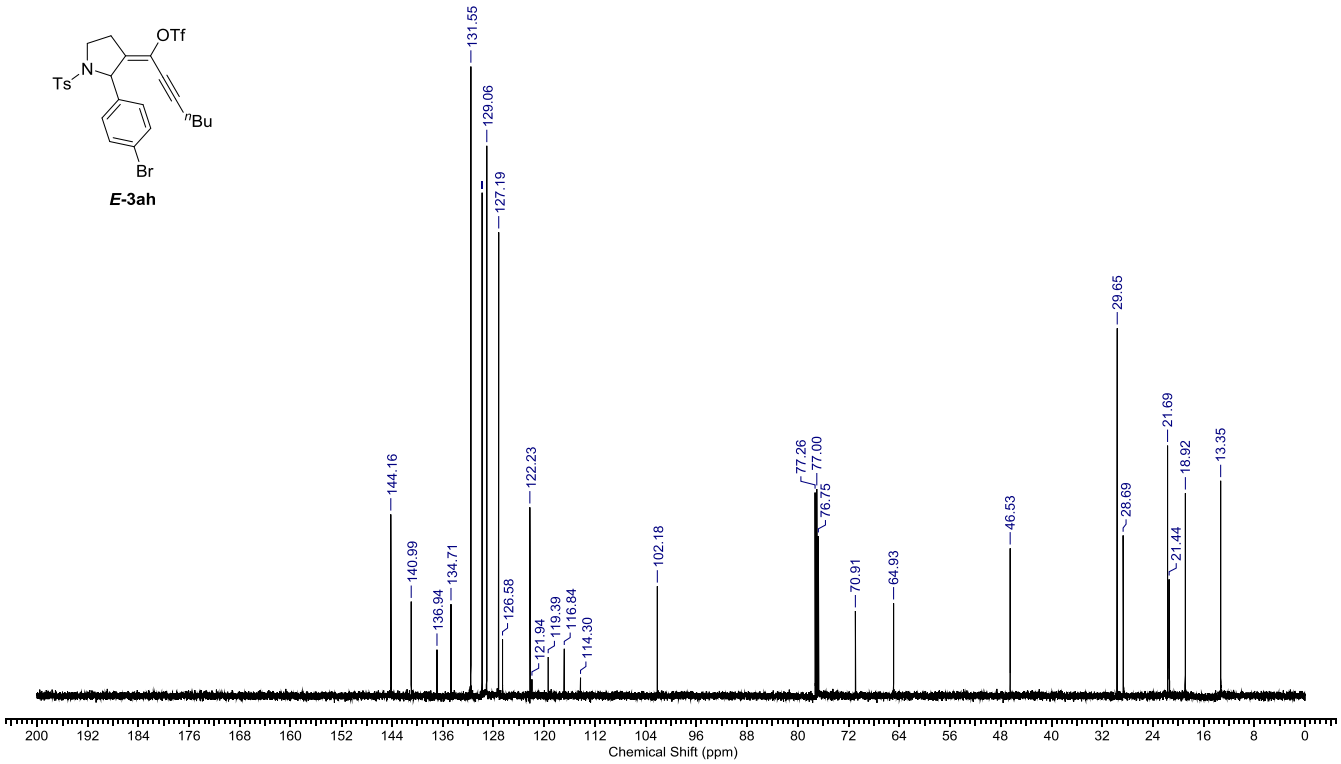
^{13}C NMR of ***Z*-3ag**



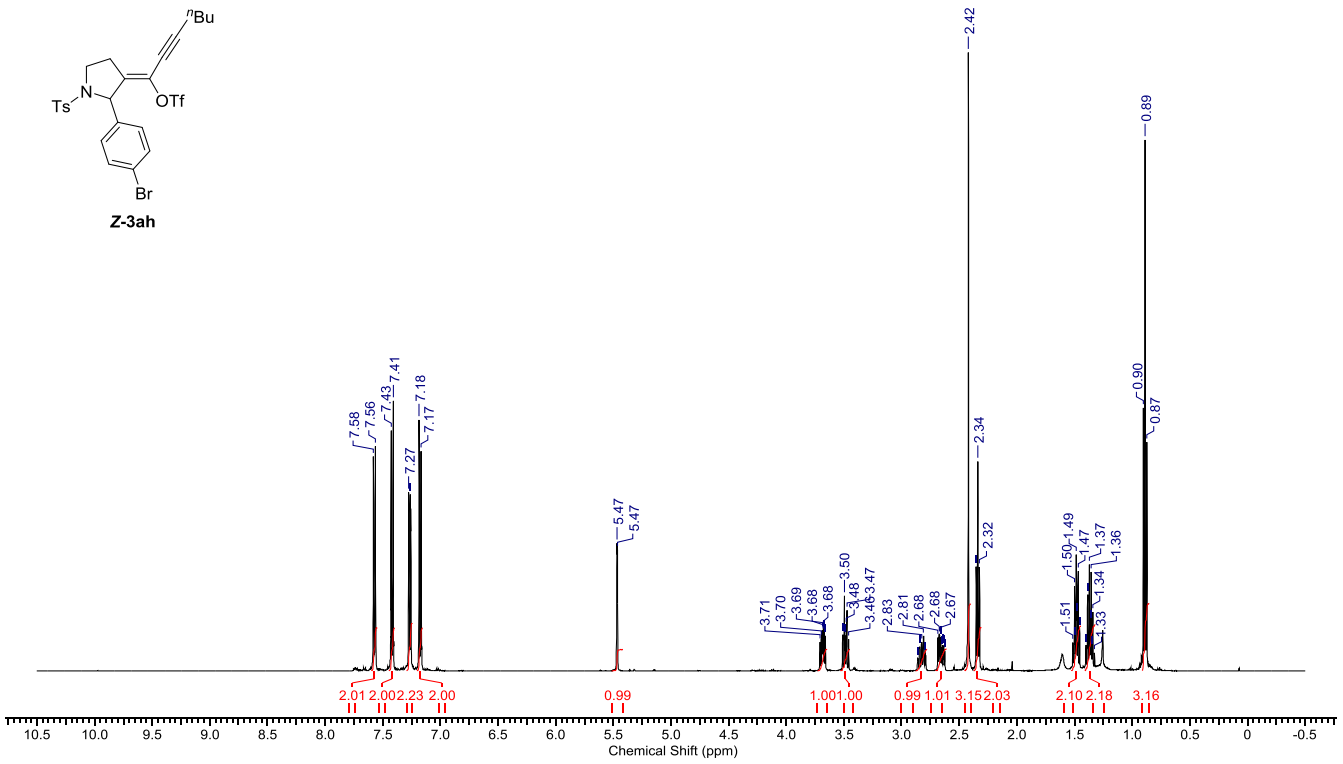
^{1}H NMR of ***E*-3ah**



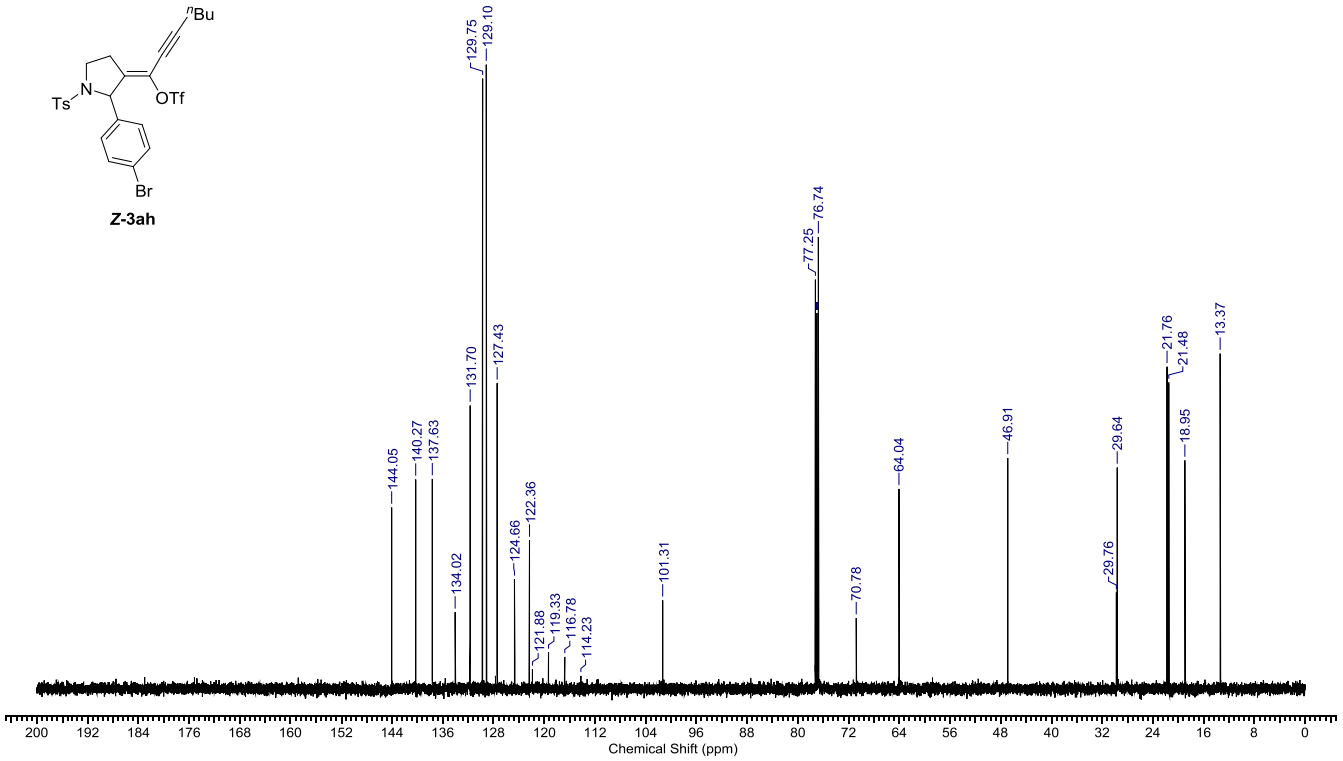
^{13}C NMR of ***E*-3ah**



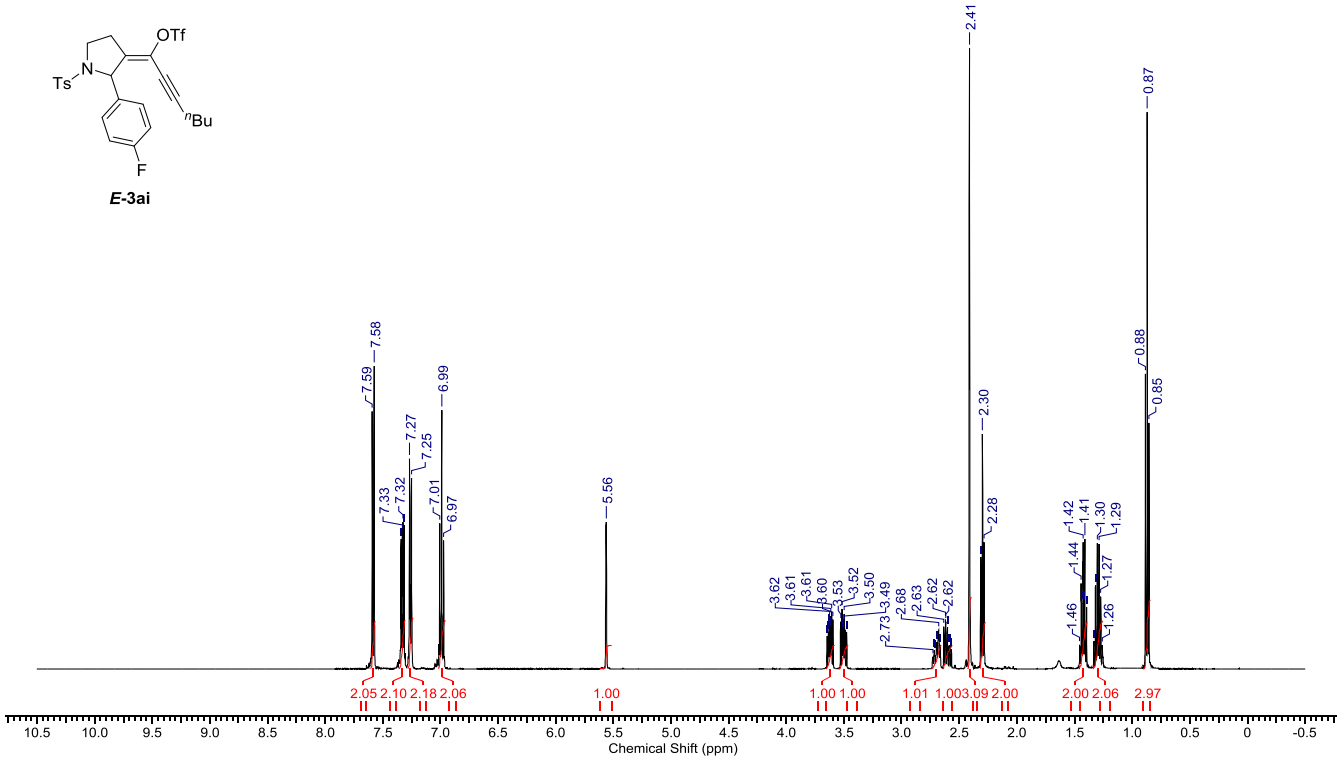
^{1}H NMR of ***Z*-3ah**



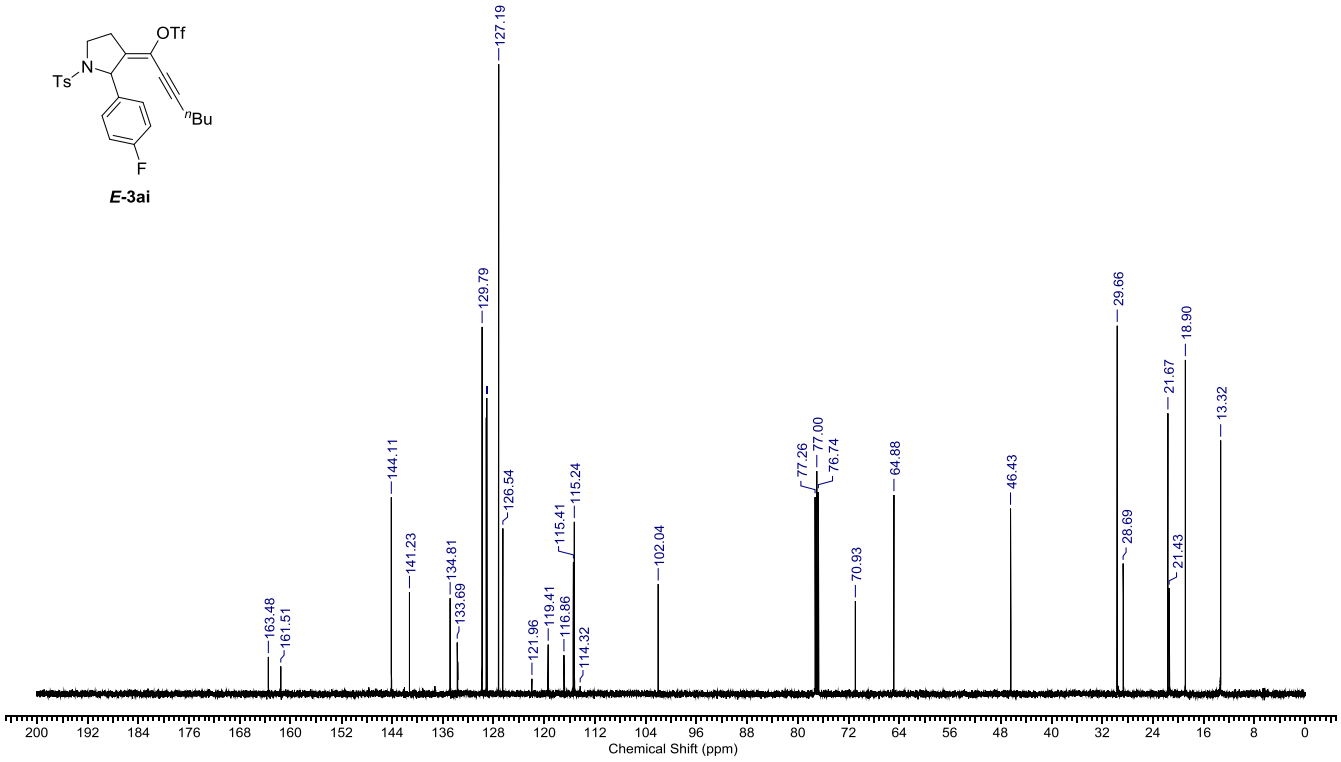
^{13}C NMR of ***Z*-3ah**



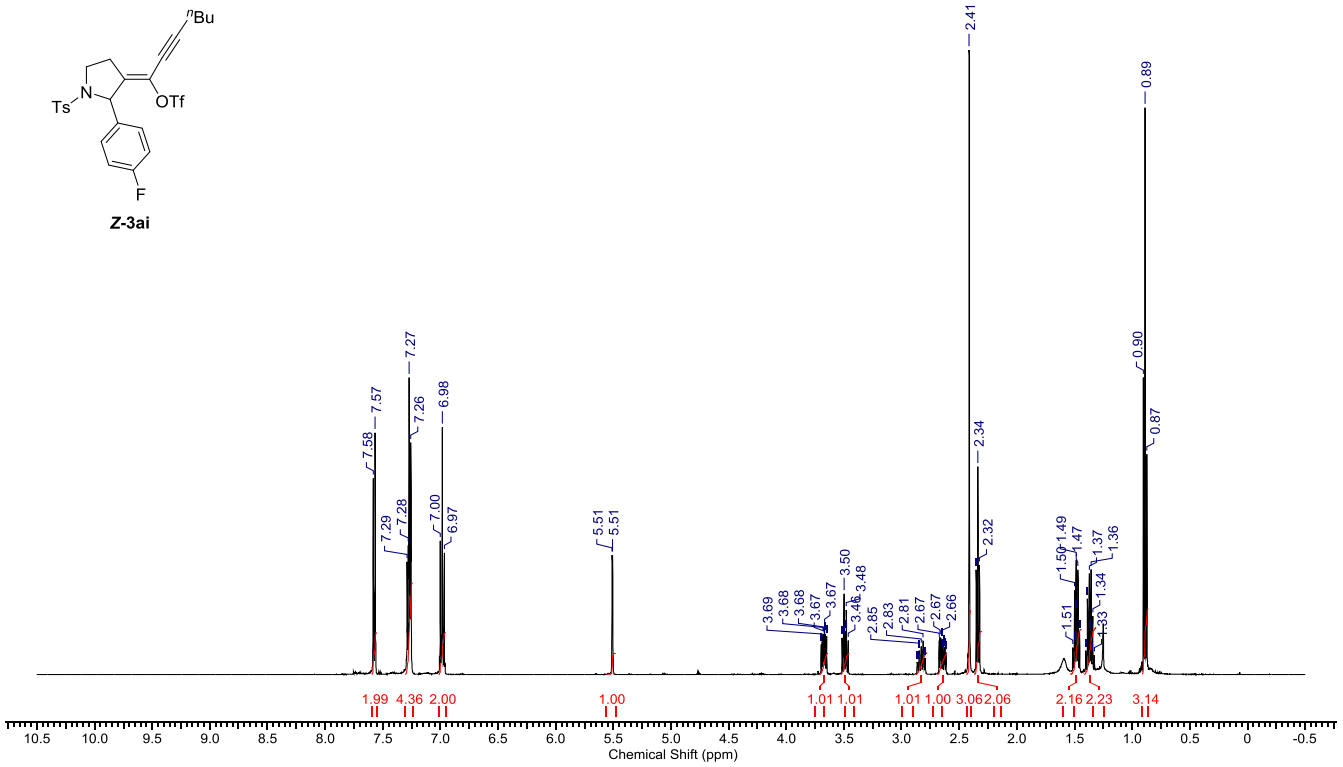
^{1}H NMR of ***E*-3ai**



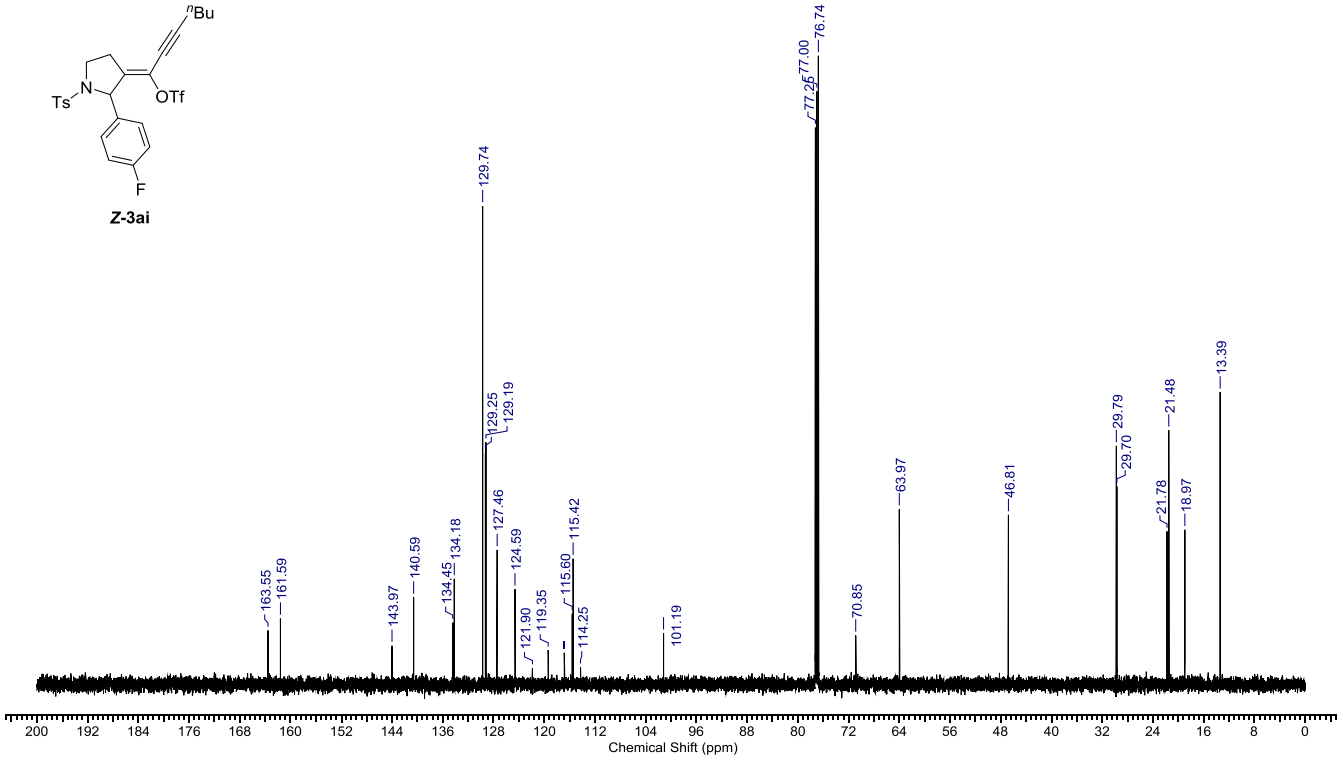
^{13}C NMR of ***E*-3ai**



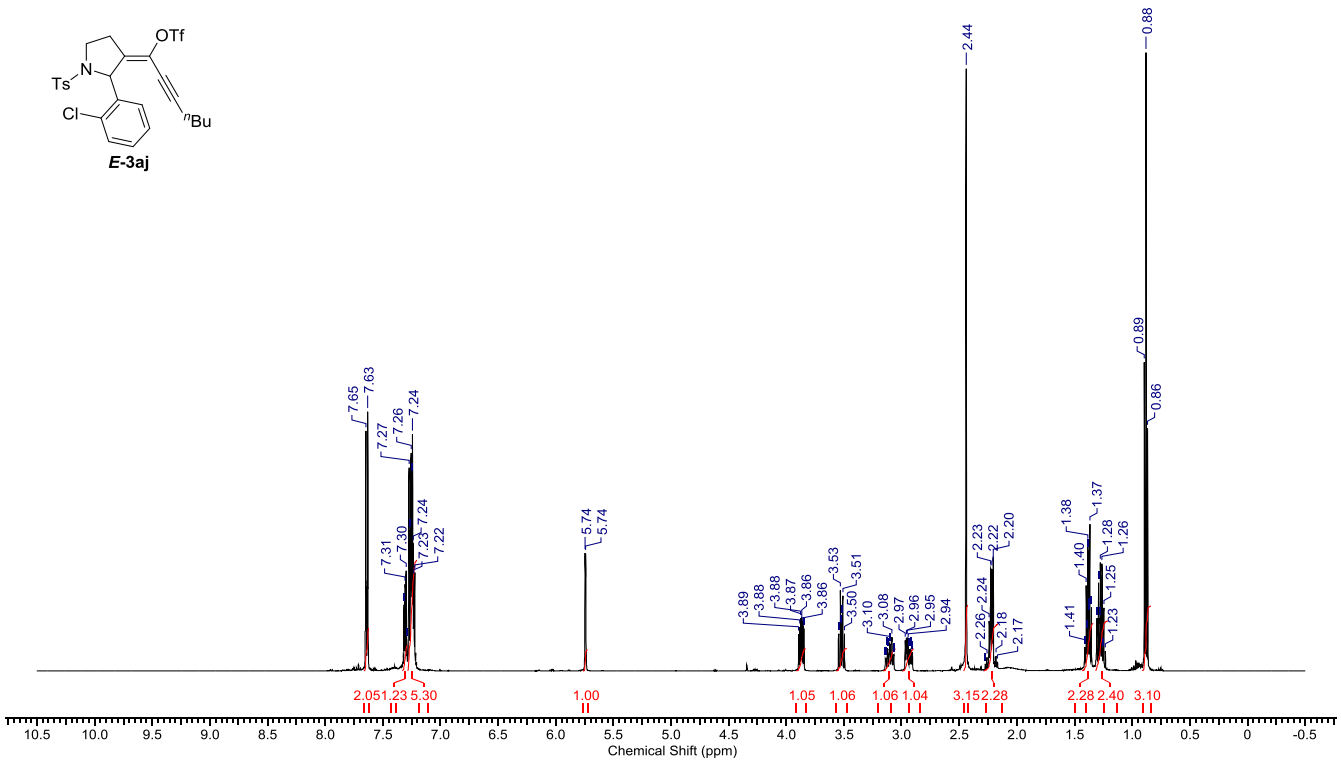
^{1}H NMR of ***Z*-3ai**



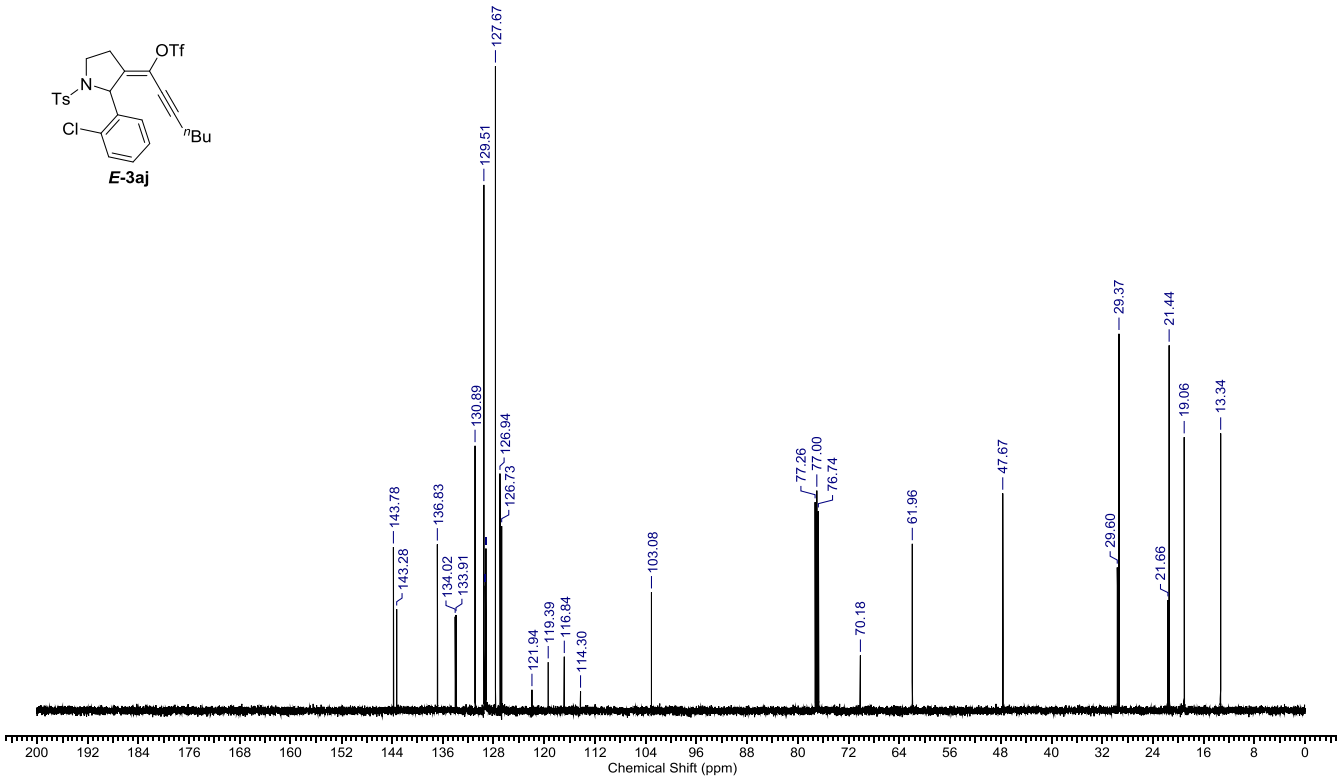
^{13}C NMR of ***Z*-3ai**



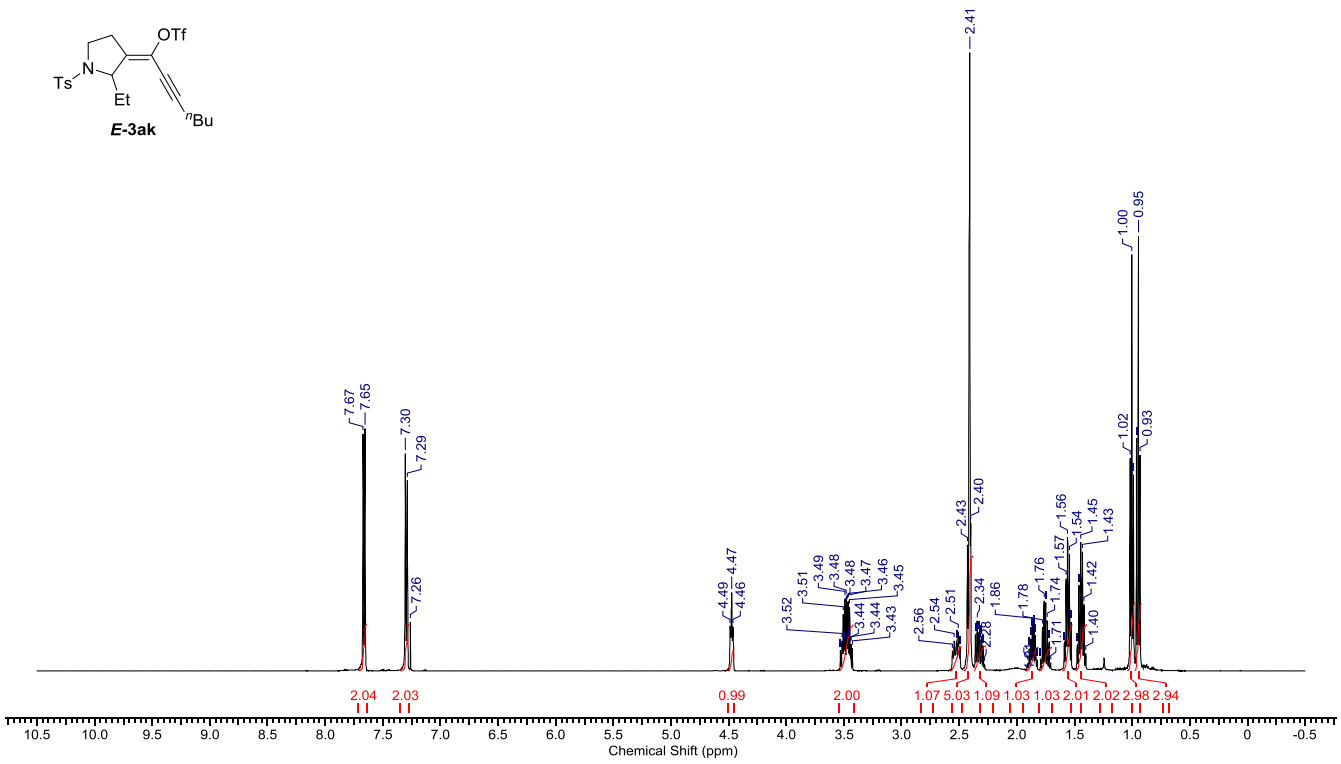
^{1}H NMR of ***E*-3aj**



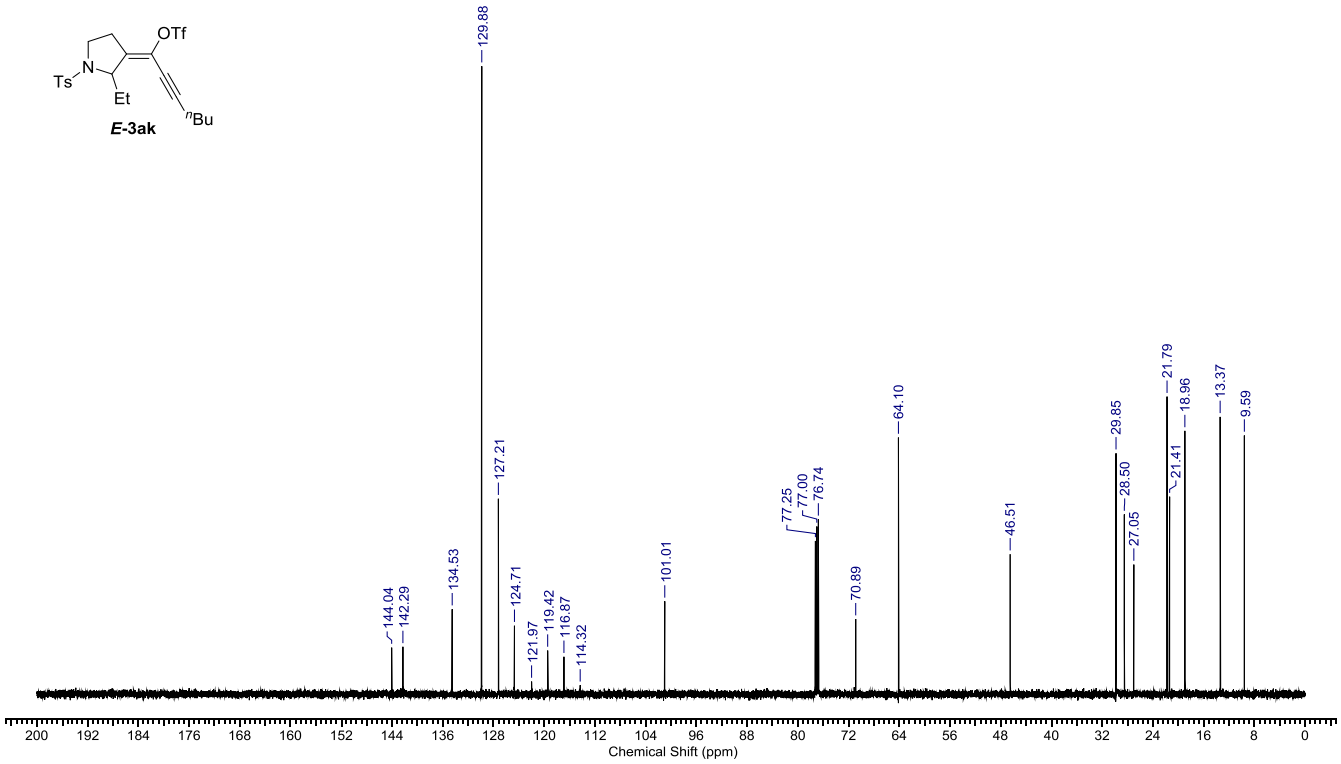
^{13}C NMR of ***E*-3aj**



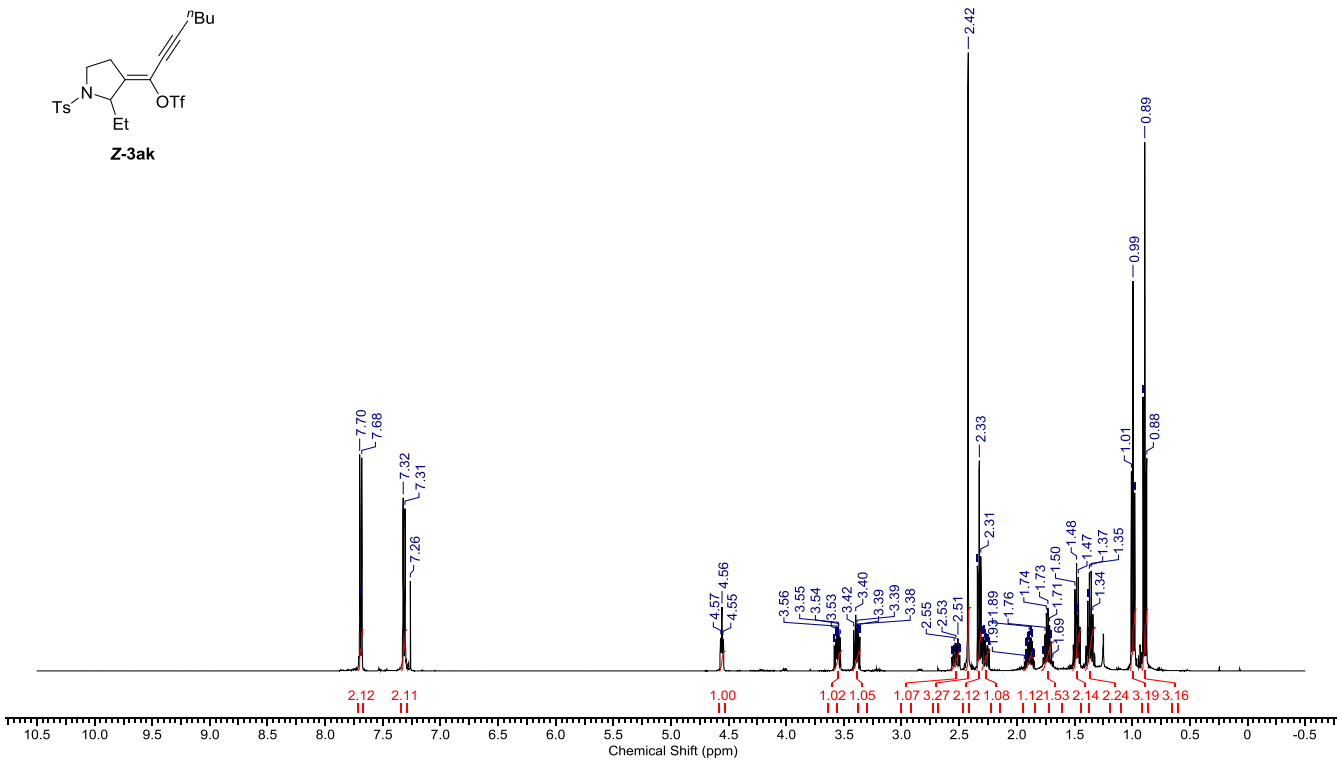
^{1}H NMR of ***E*-3ak**



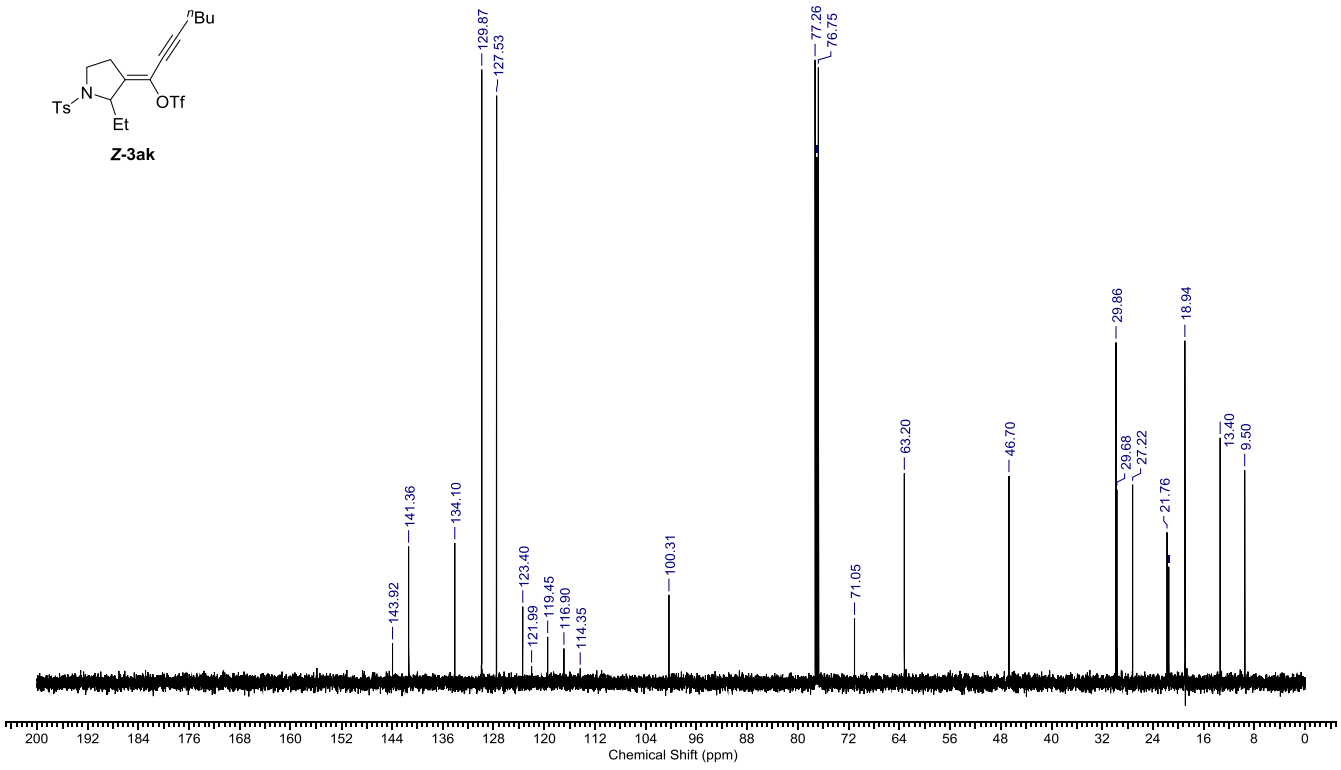
^{13}C NMR of ***E*-3ak**



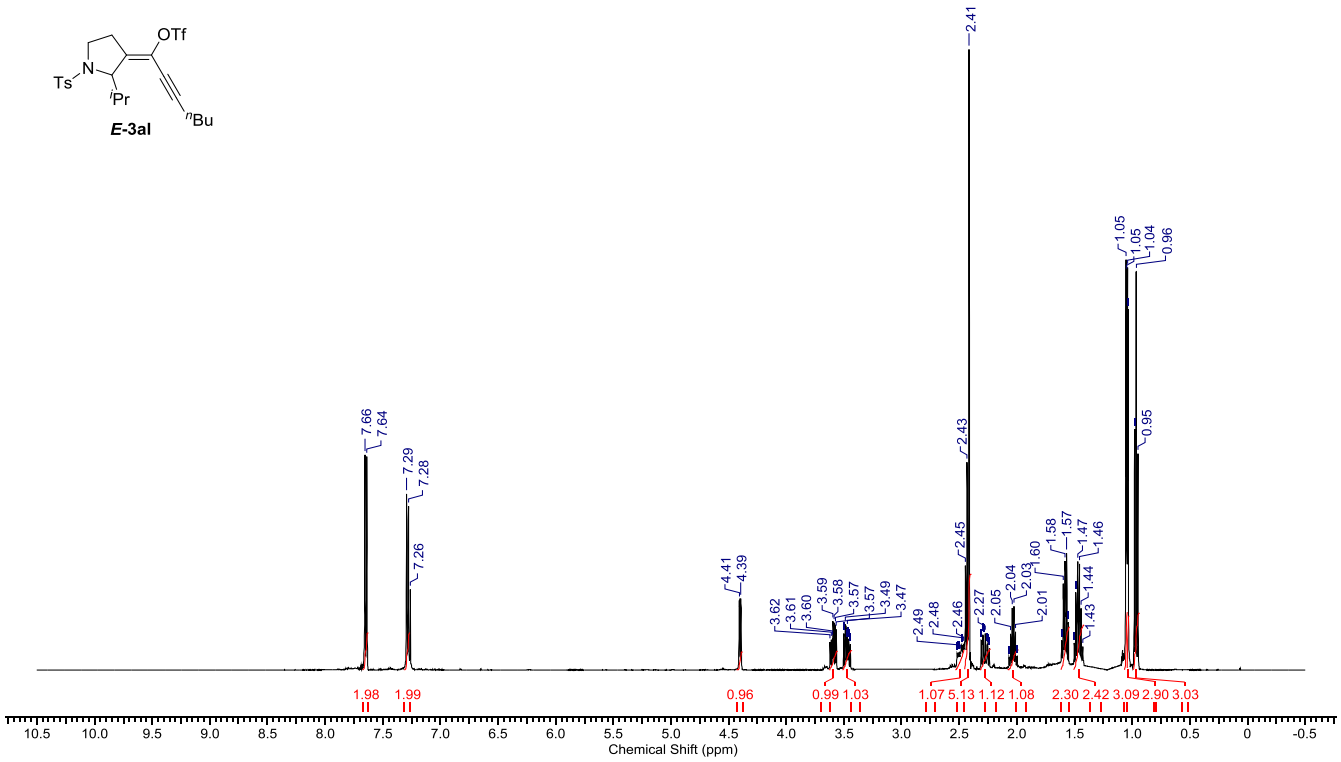
^{1}H NMR of ***Z*-3ak**



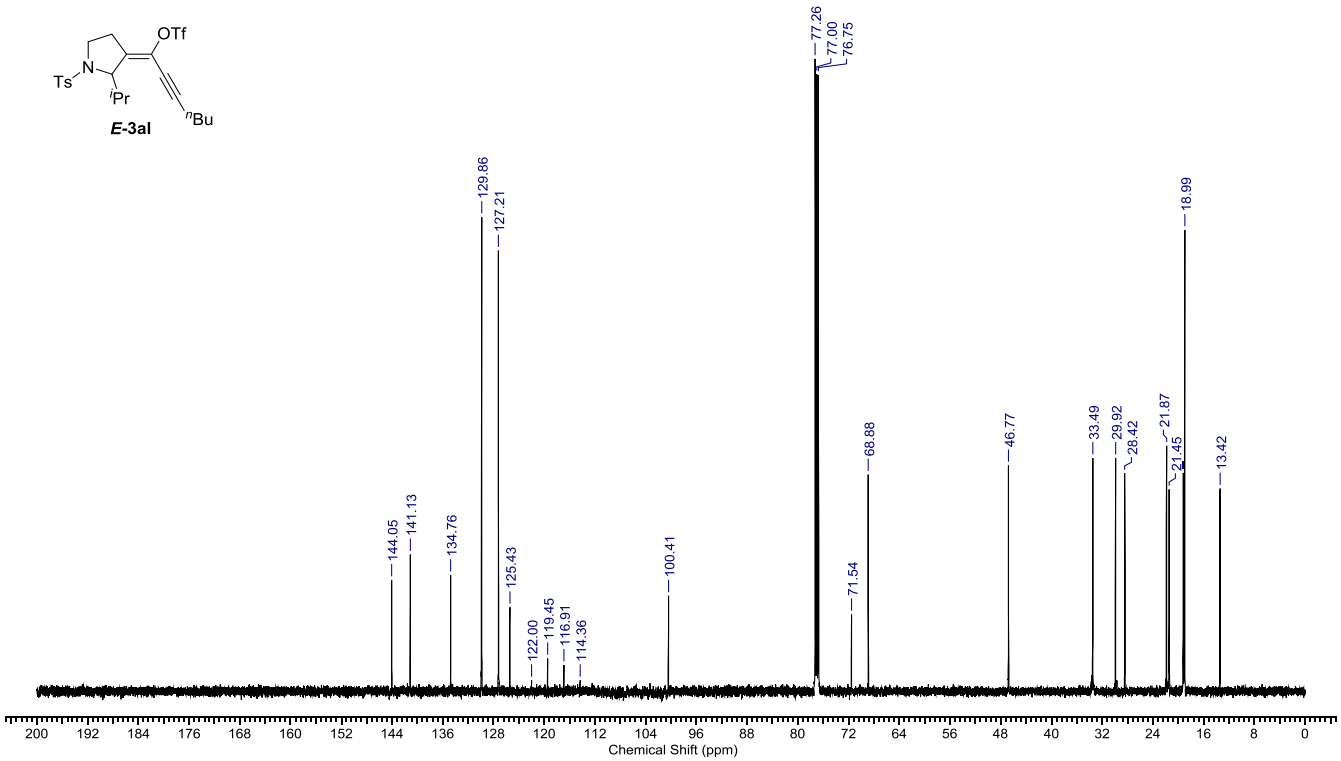
^{13}C NMR of ***Z*-3ak**



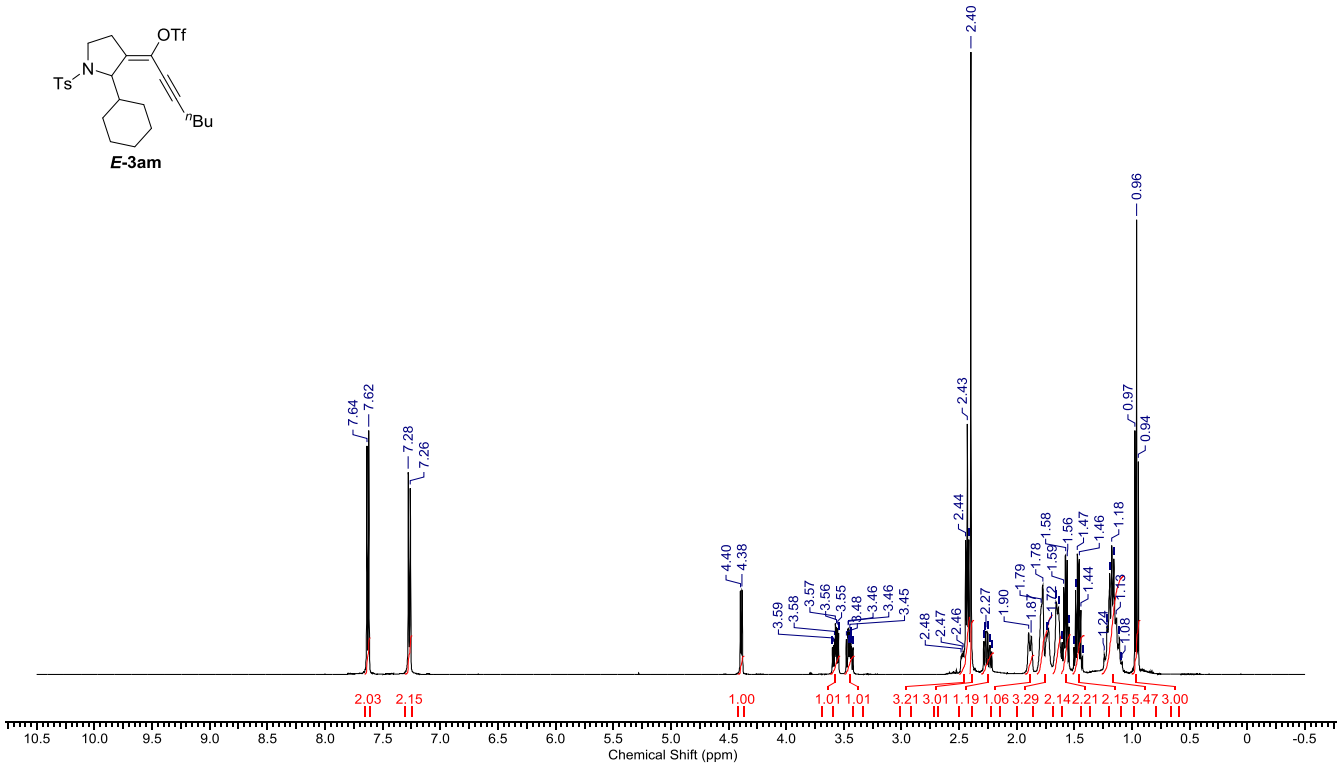
^{1}H NMR of ***E*-3al**



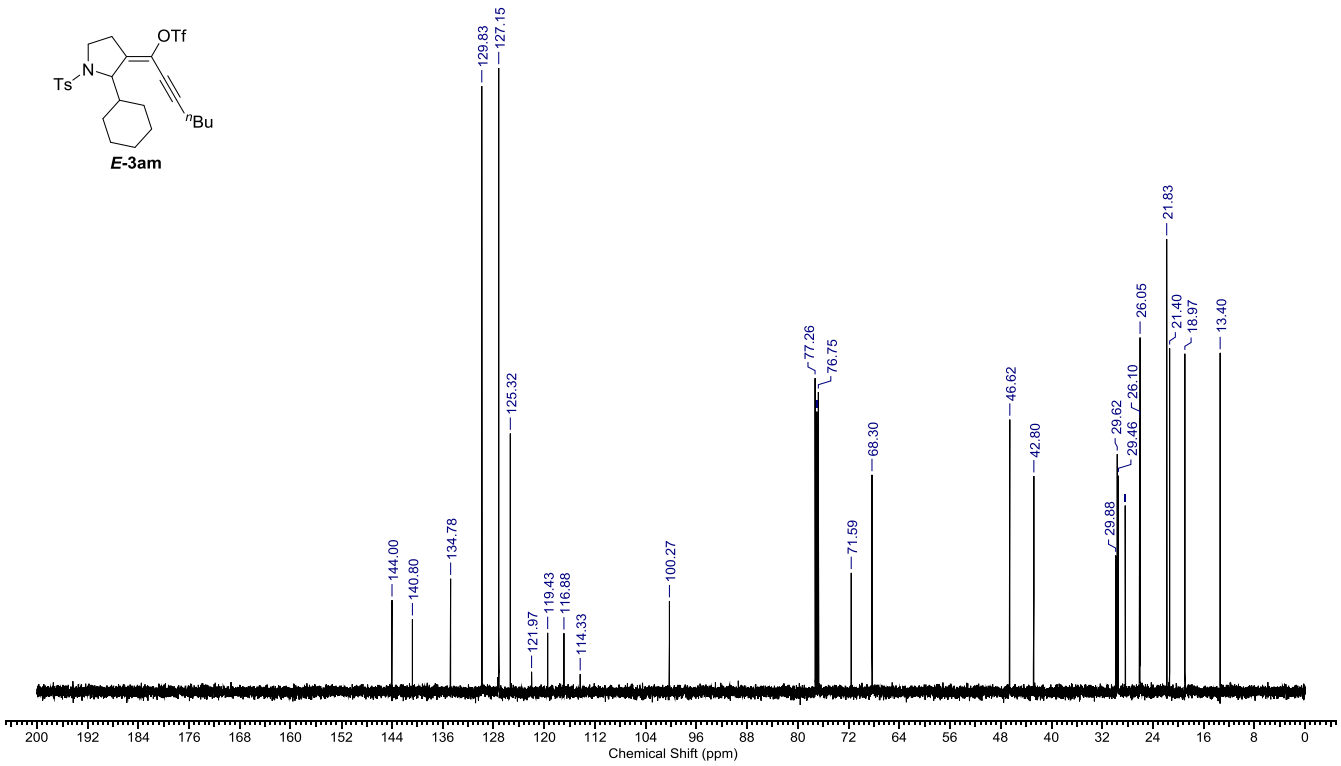
^{13}C NMR of ***E*-3al**



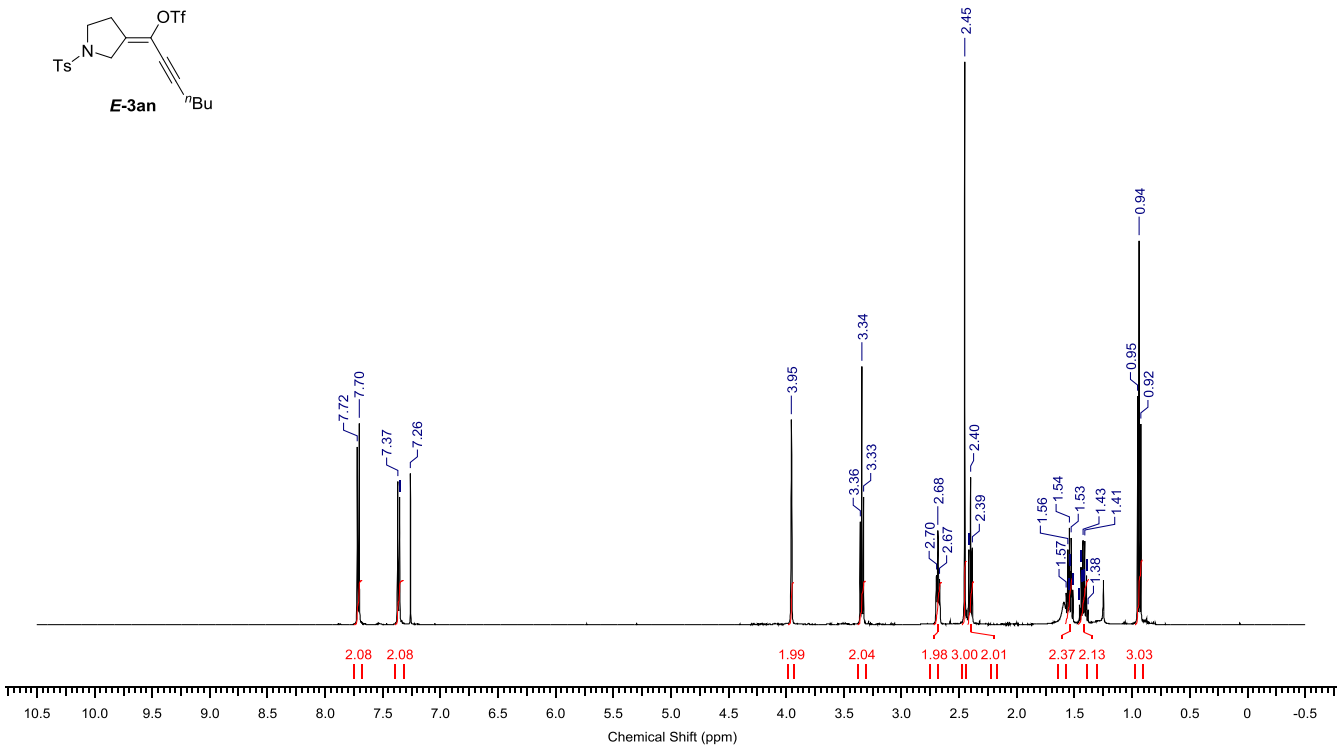
^{1}H NMR of ***E*-3am**



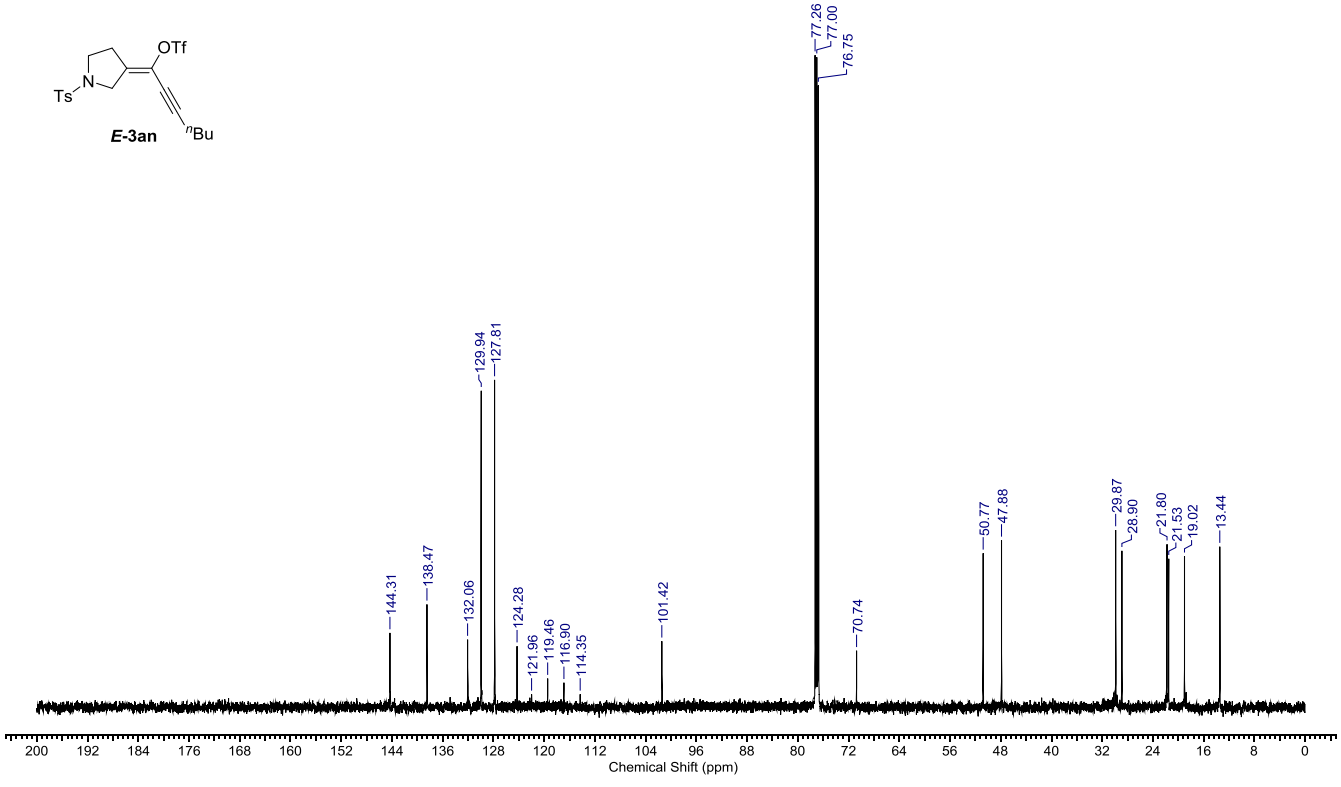
^{13}C NMR of ***E*-3am**



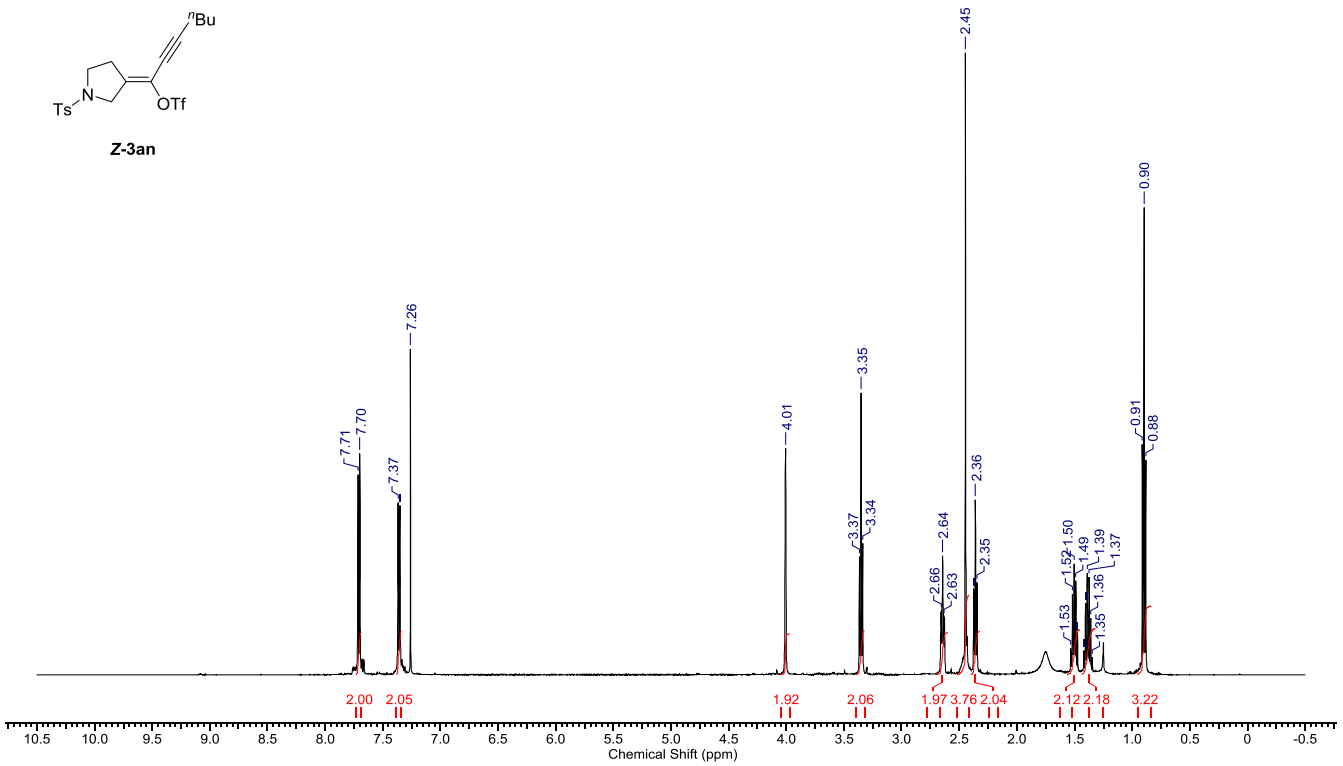
^{1}H NMR of ***E*-3an**



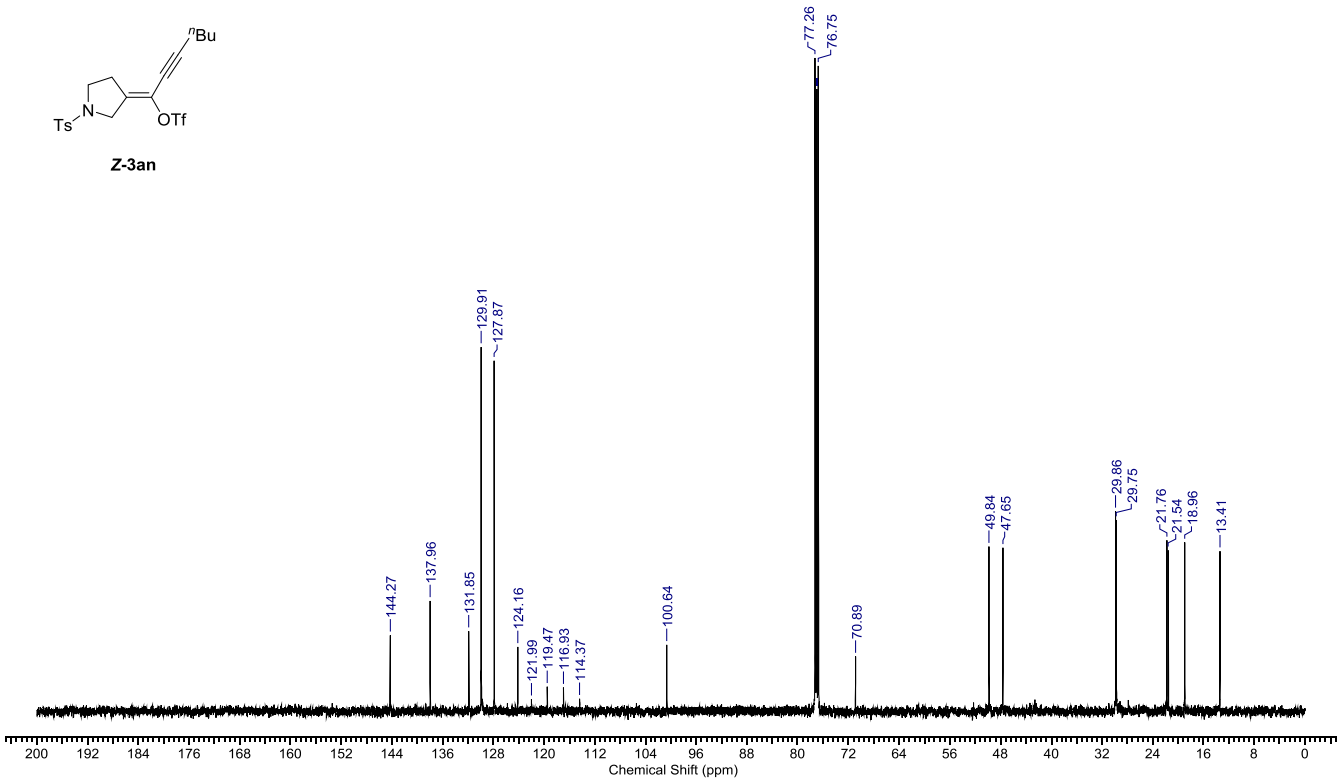
^{13}C NMR of ***E*-3an**



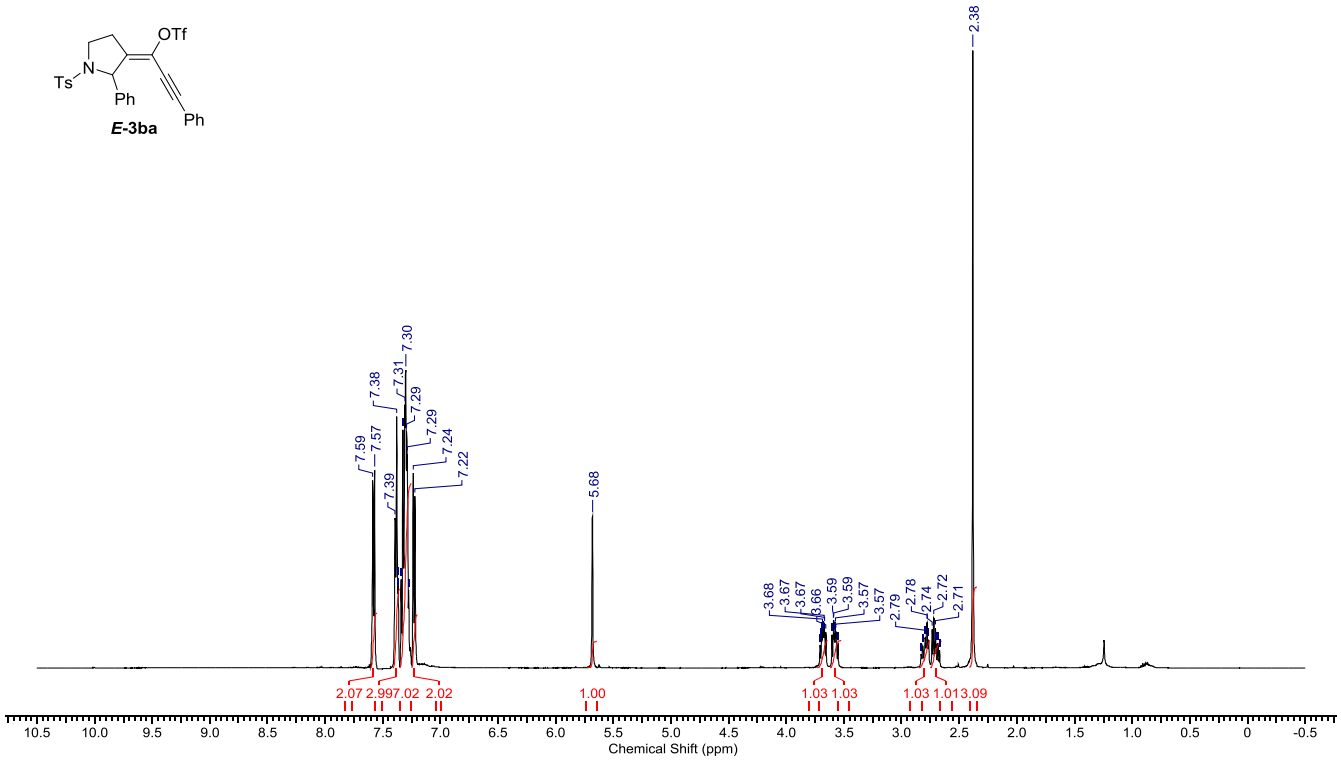
^{1}H NMR of ***Z*-3an**



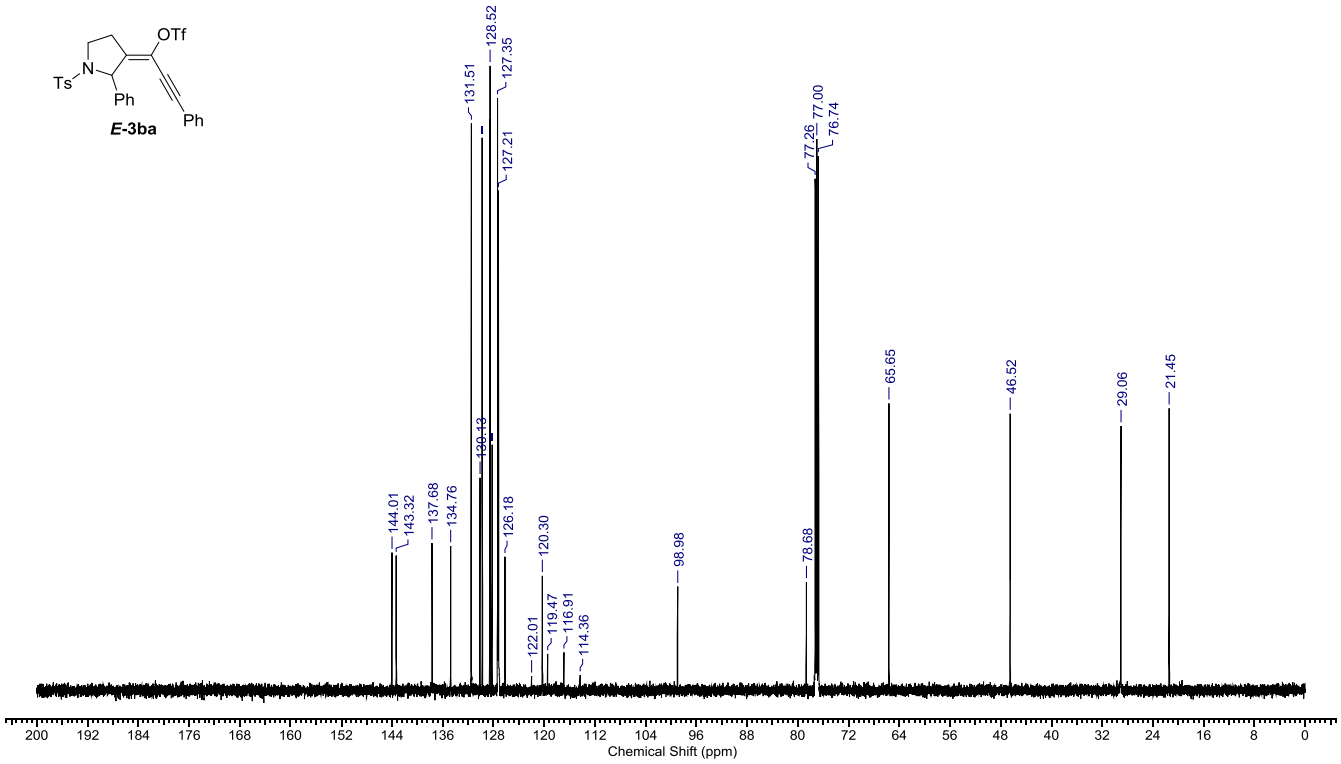
^{13}C NMR of ***Z*-3an**



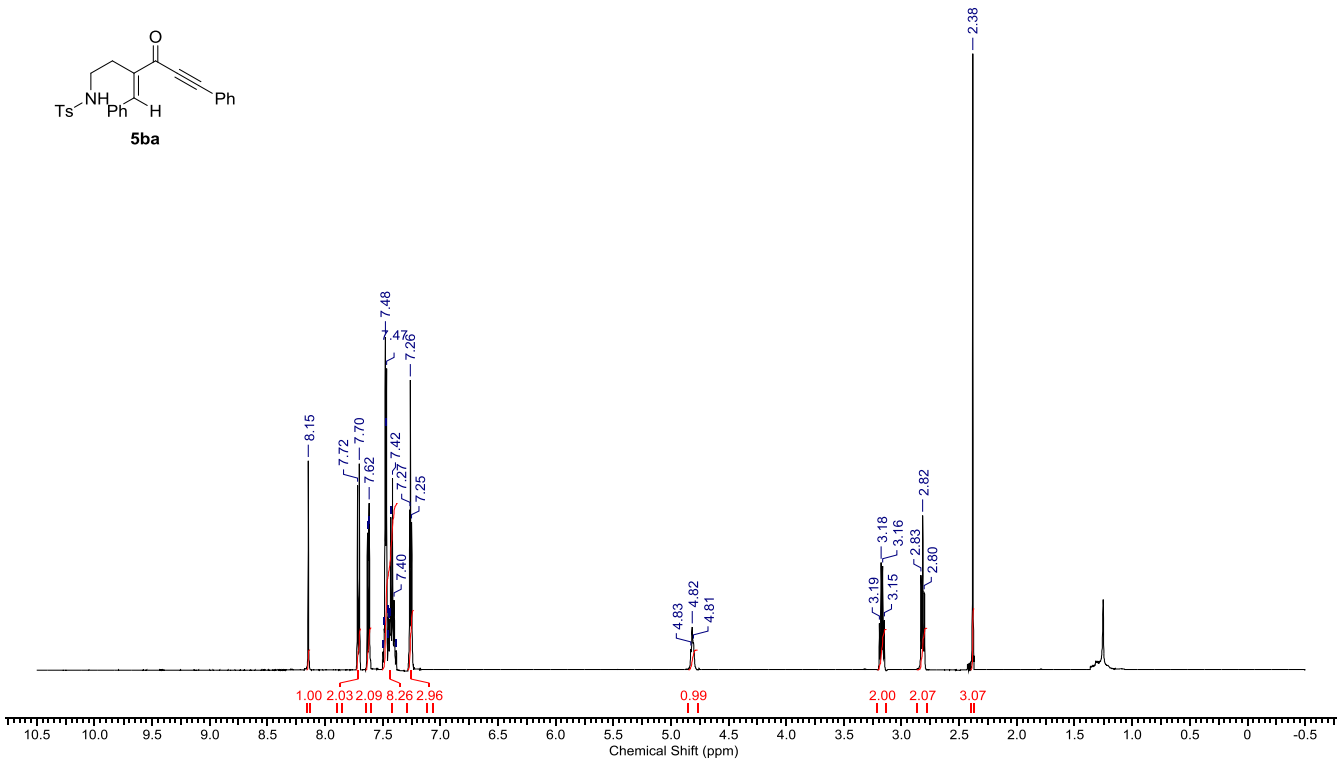
^{1}H NMR of ***E*-3ba**



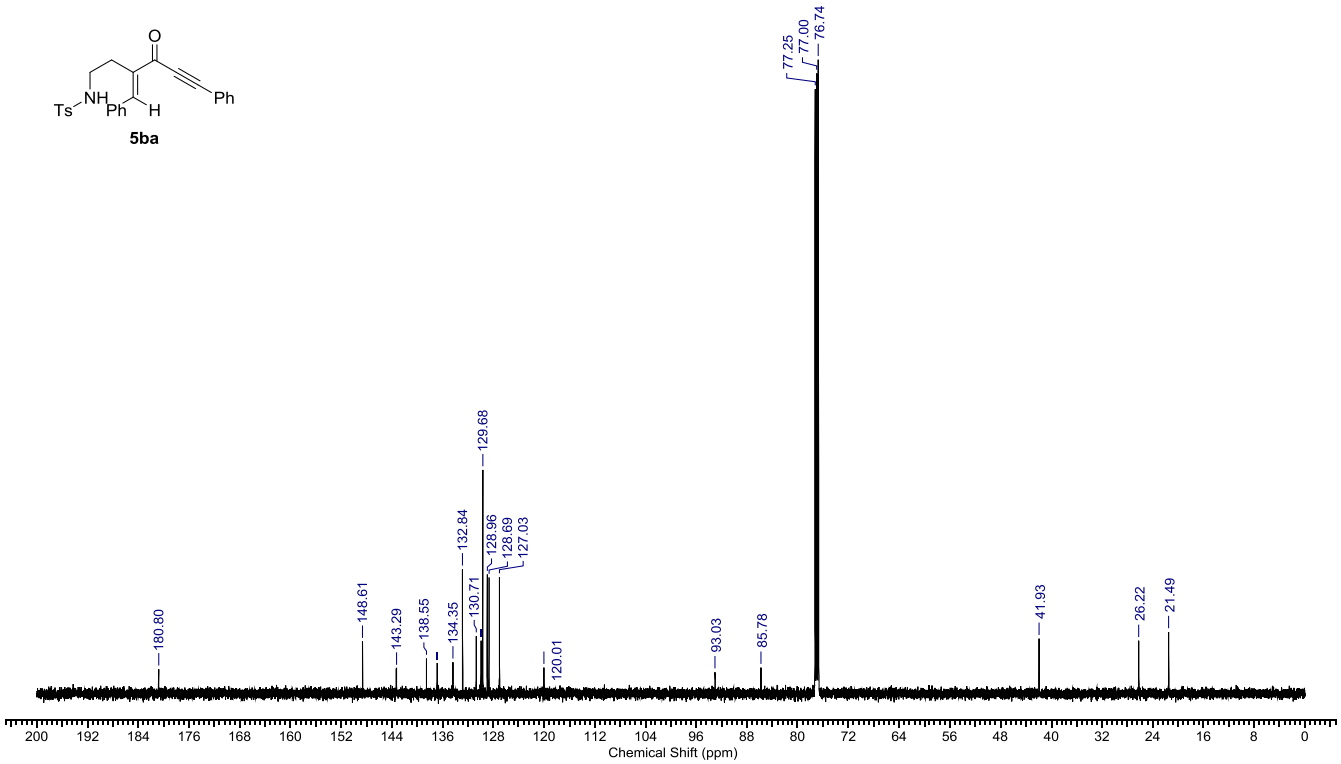
^{13}C NMR of ***E*-3ba**



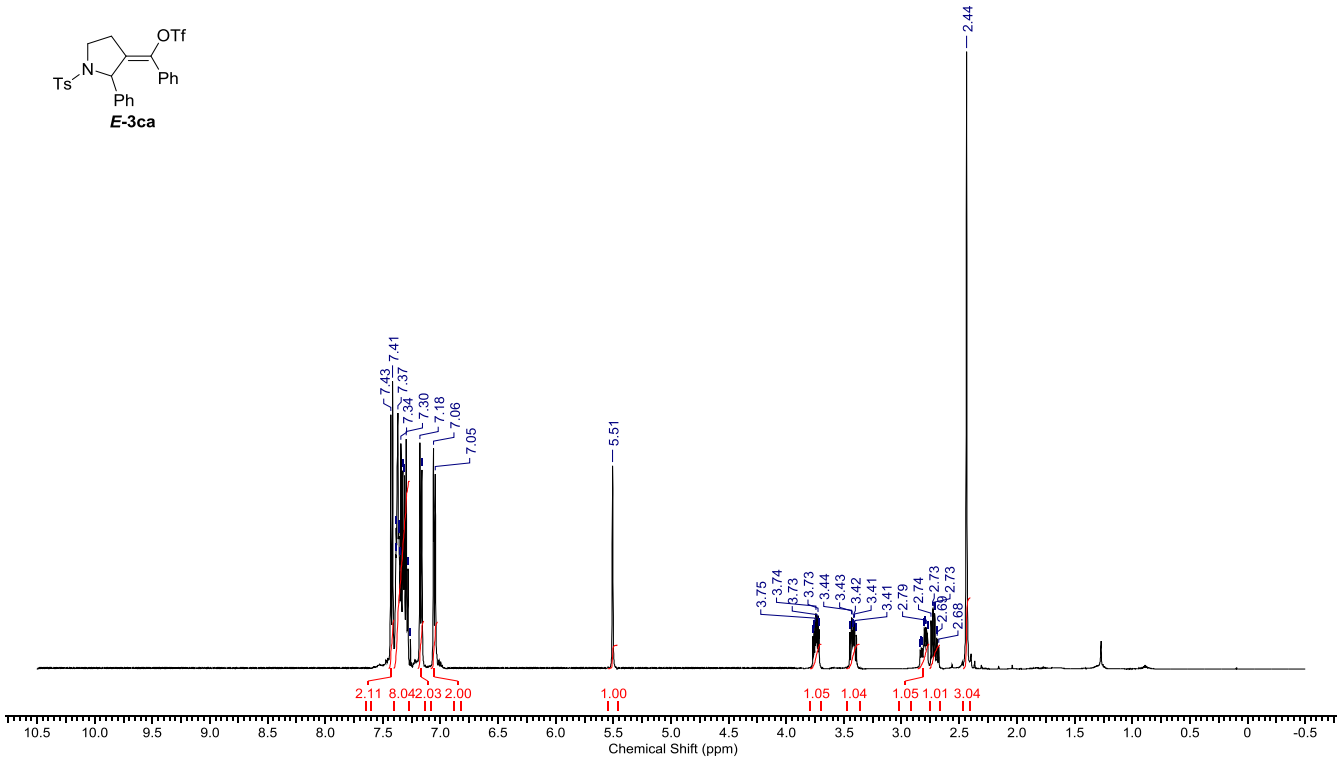
^{1}H NMR of **5ba**



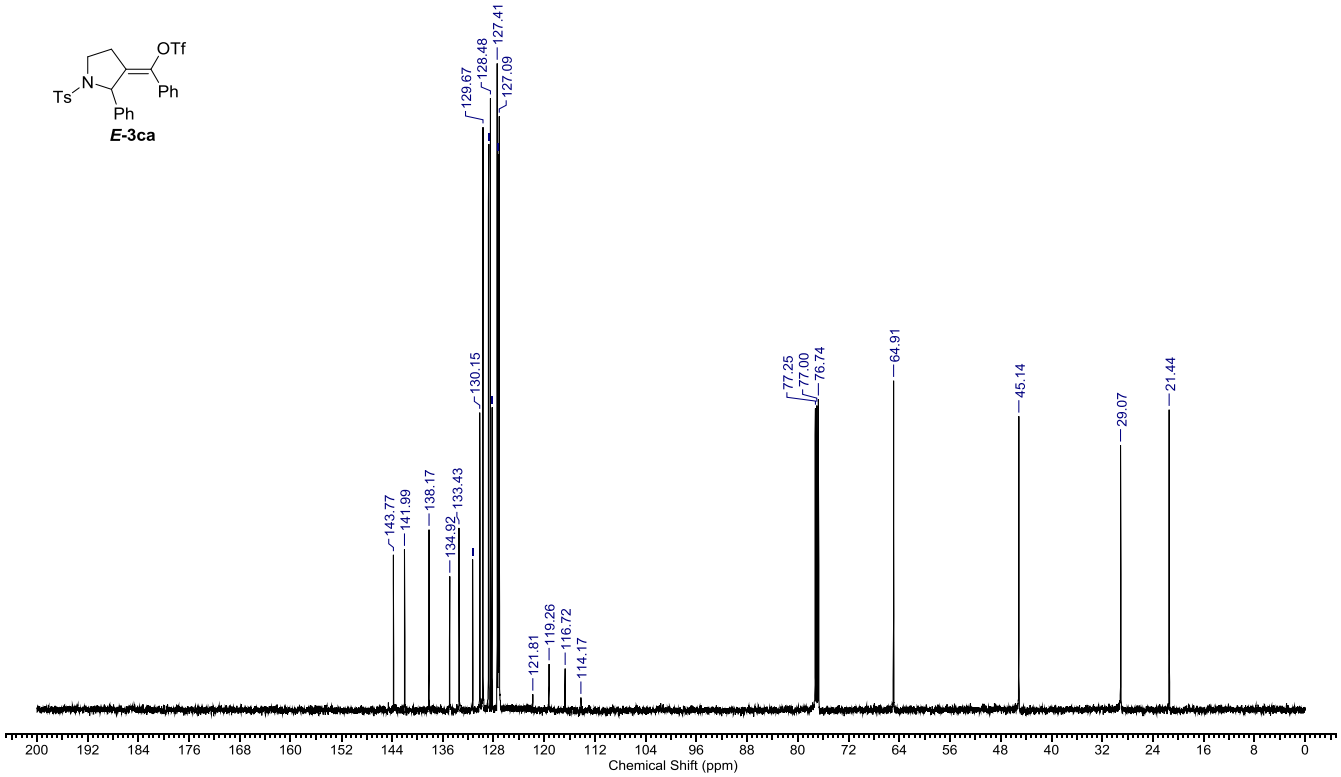
^{13}C NMR of **5ba**



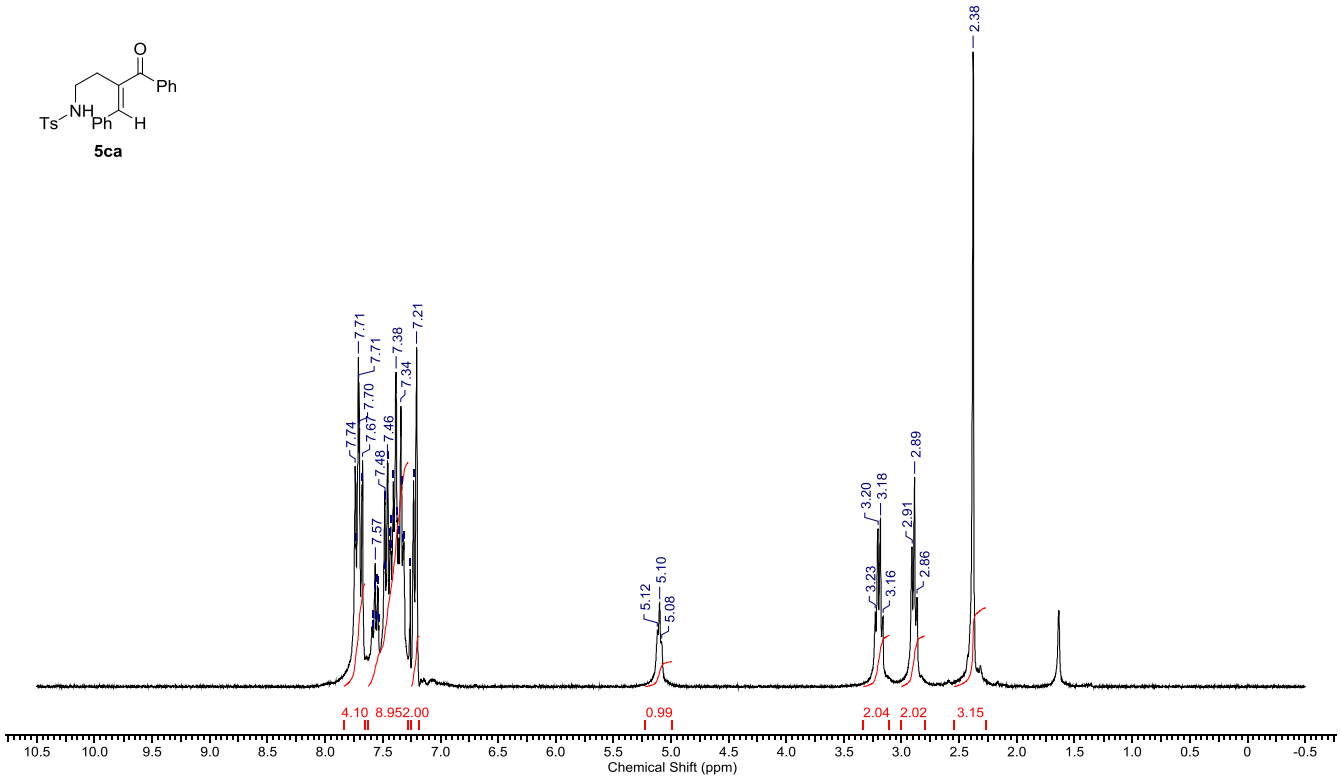
^{1}H NMR of ***E*-3ca**



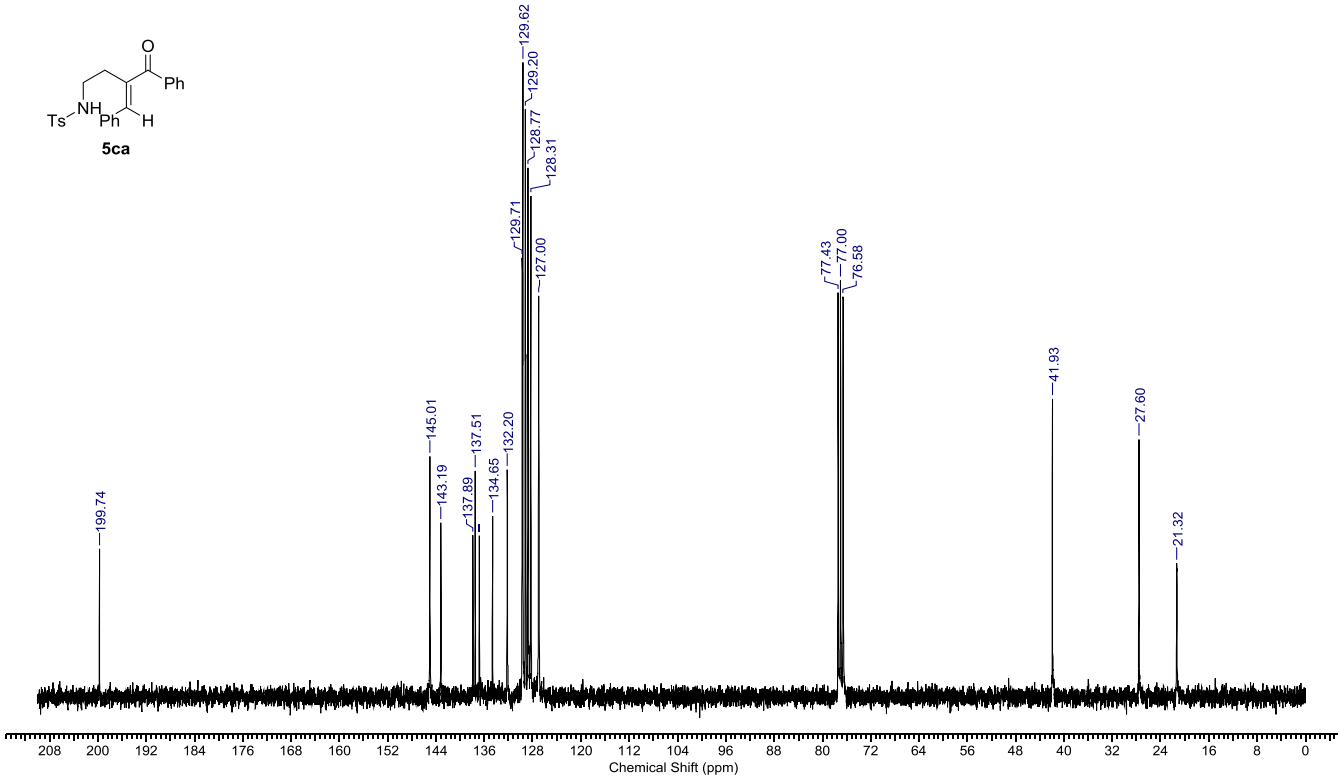
^{13}C NMR of ***E*-3ca**



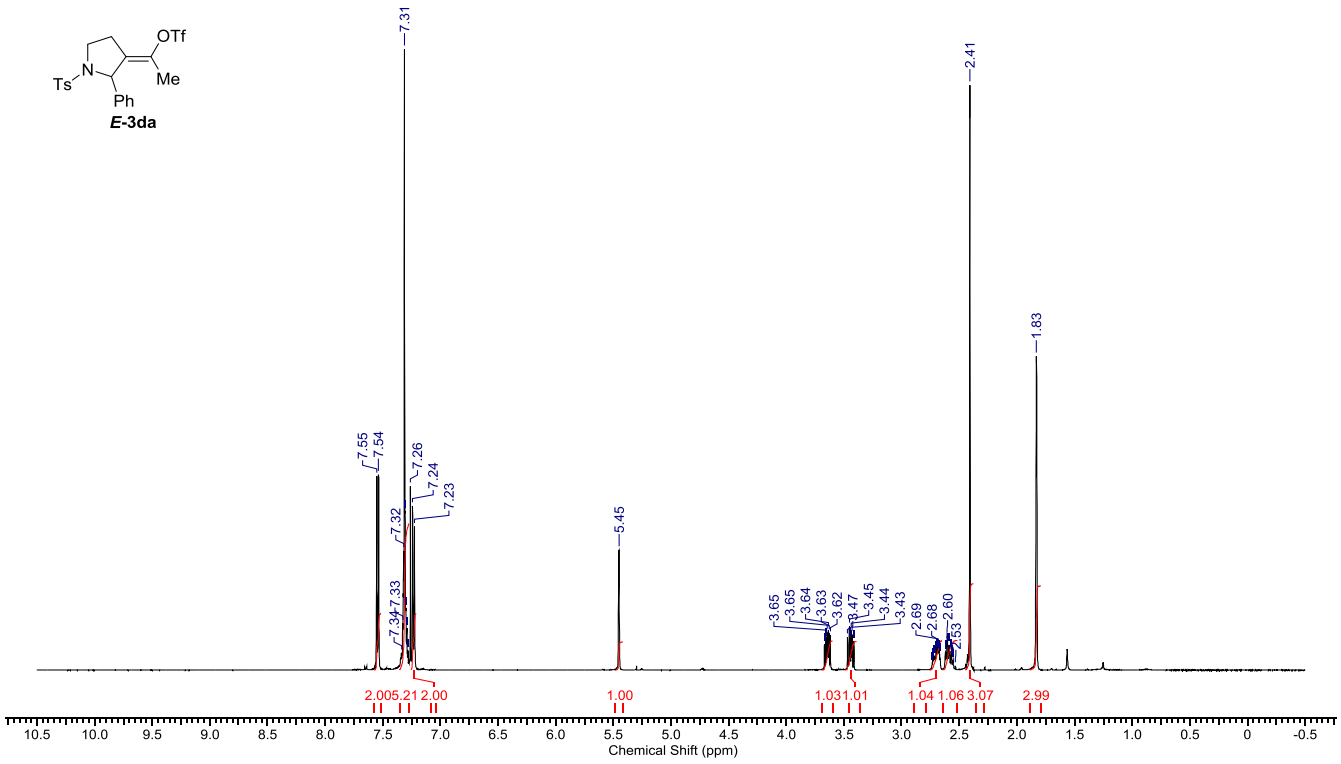
^{1}H NMR of **5ca**



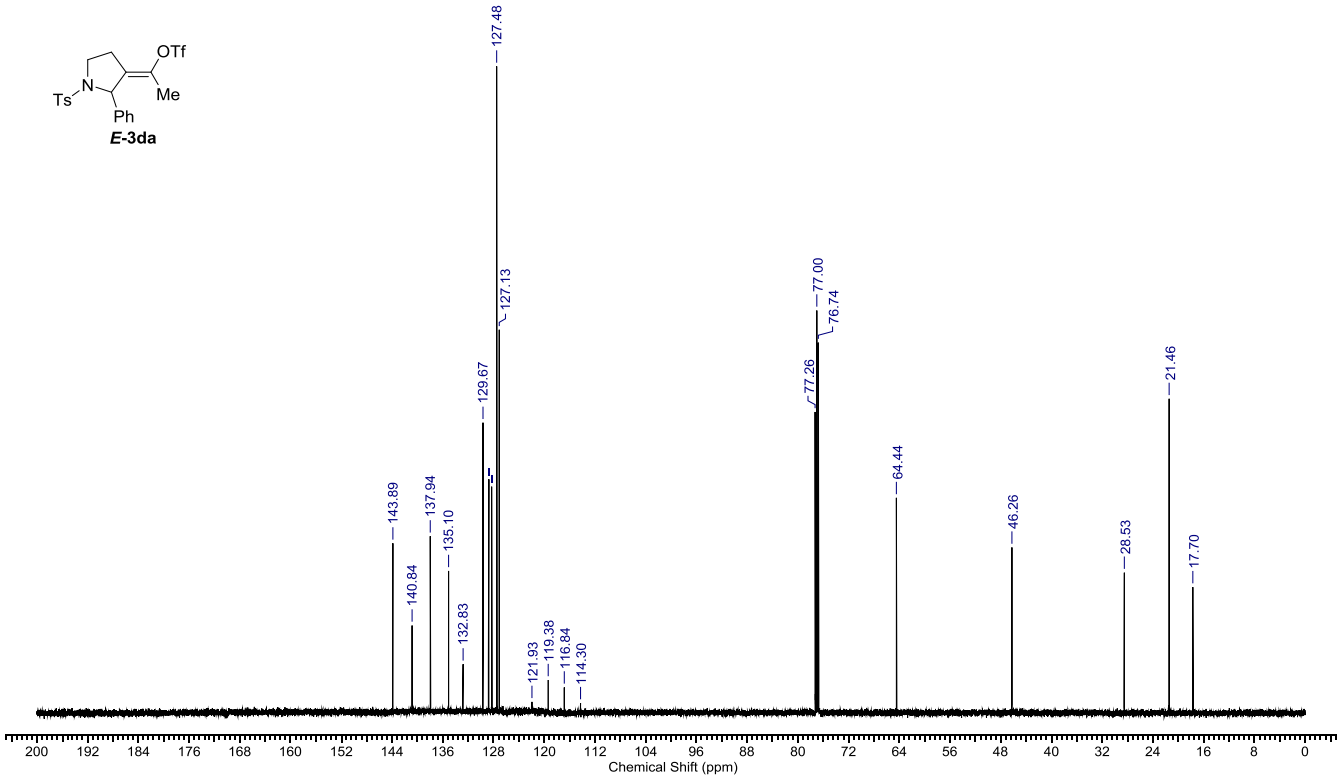
^{13}C NMR of **5ca**



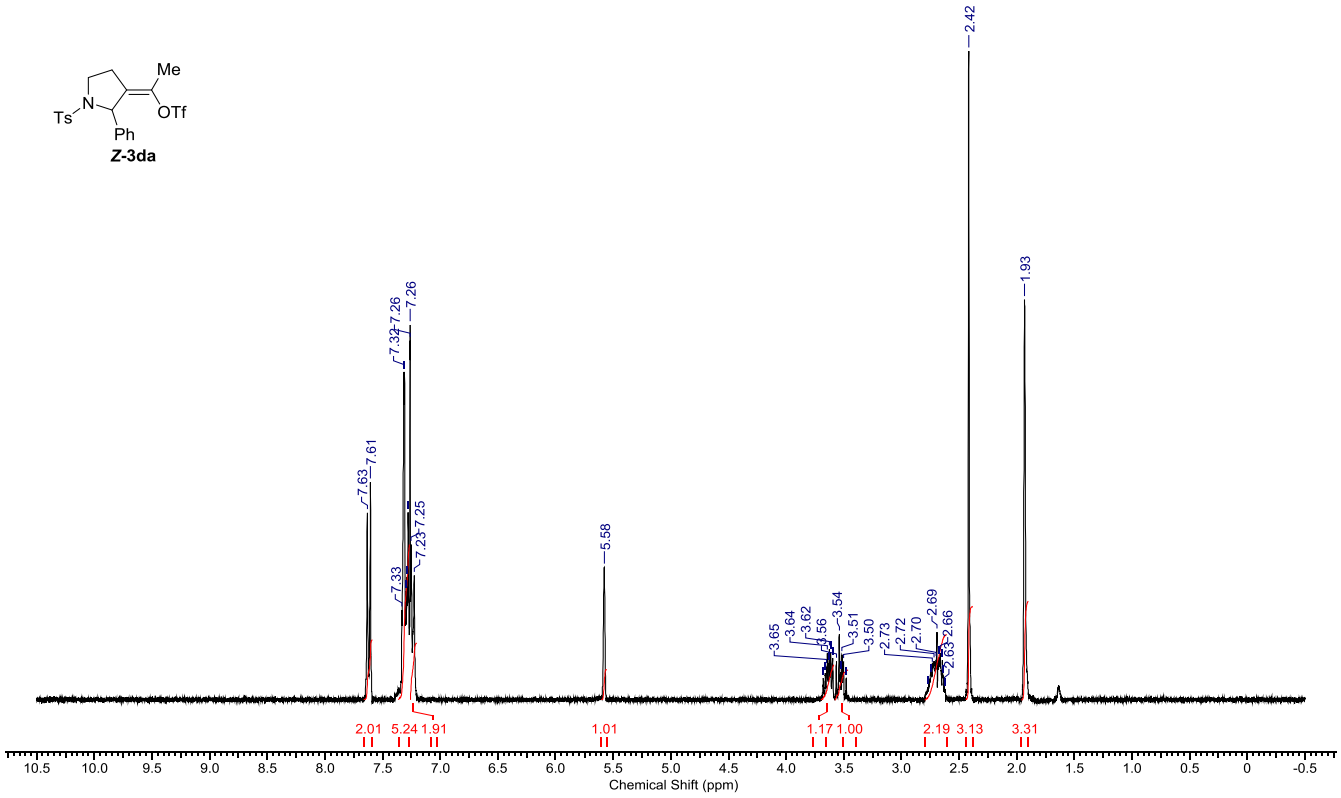
^{1}H NMR of ***E*-3da**



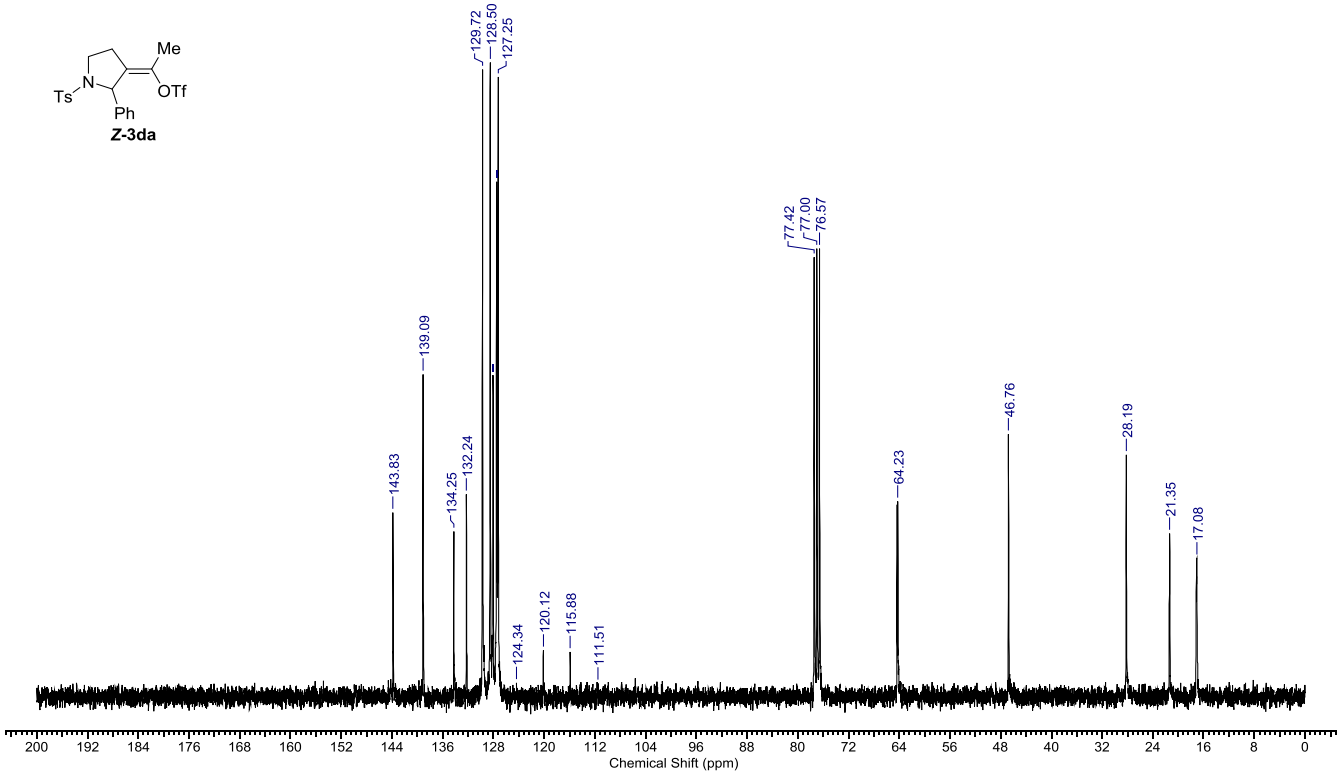
^{13}C NMR of ***E*-3da**



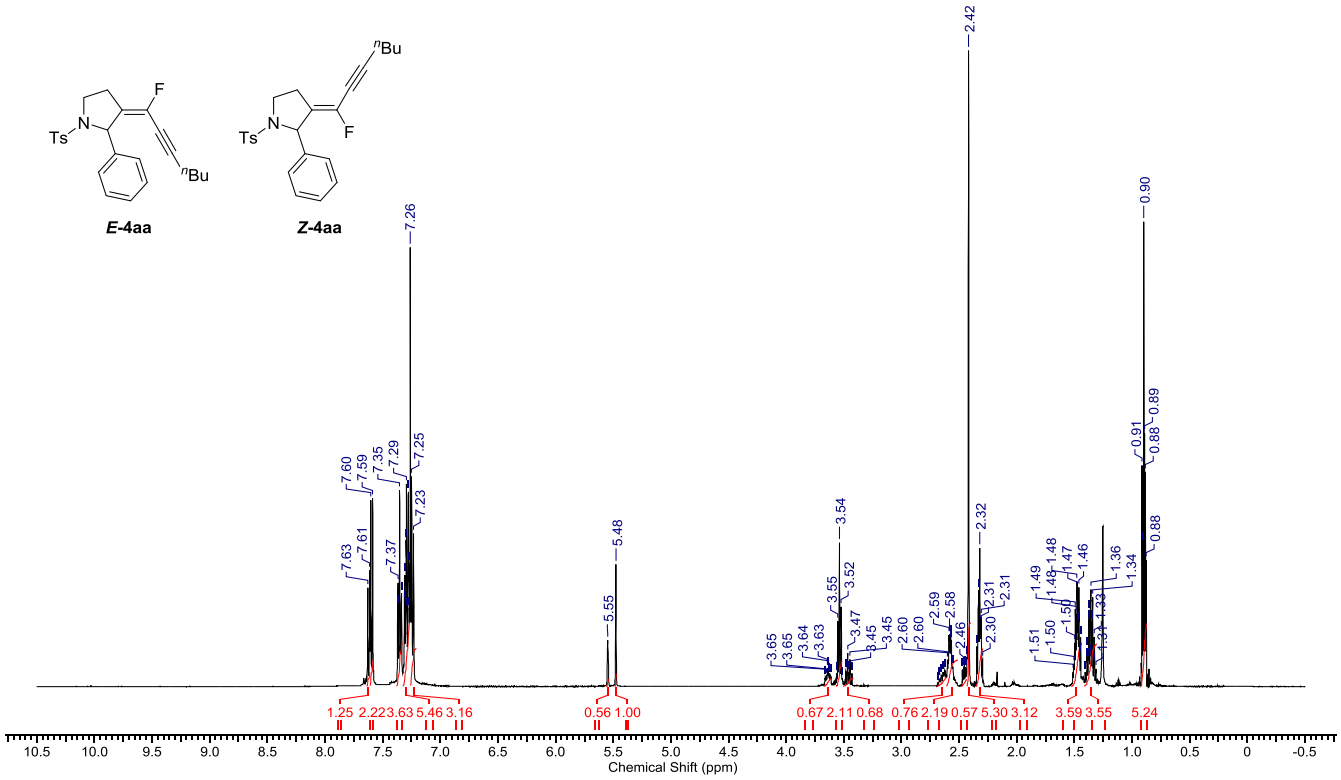
^{1}H NMR of ***Z*-3da**



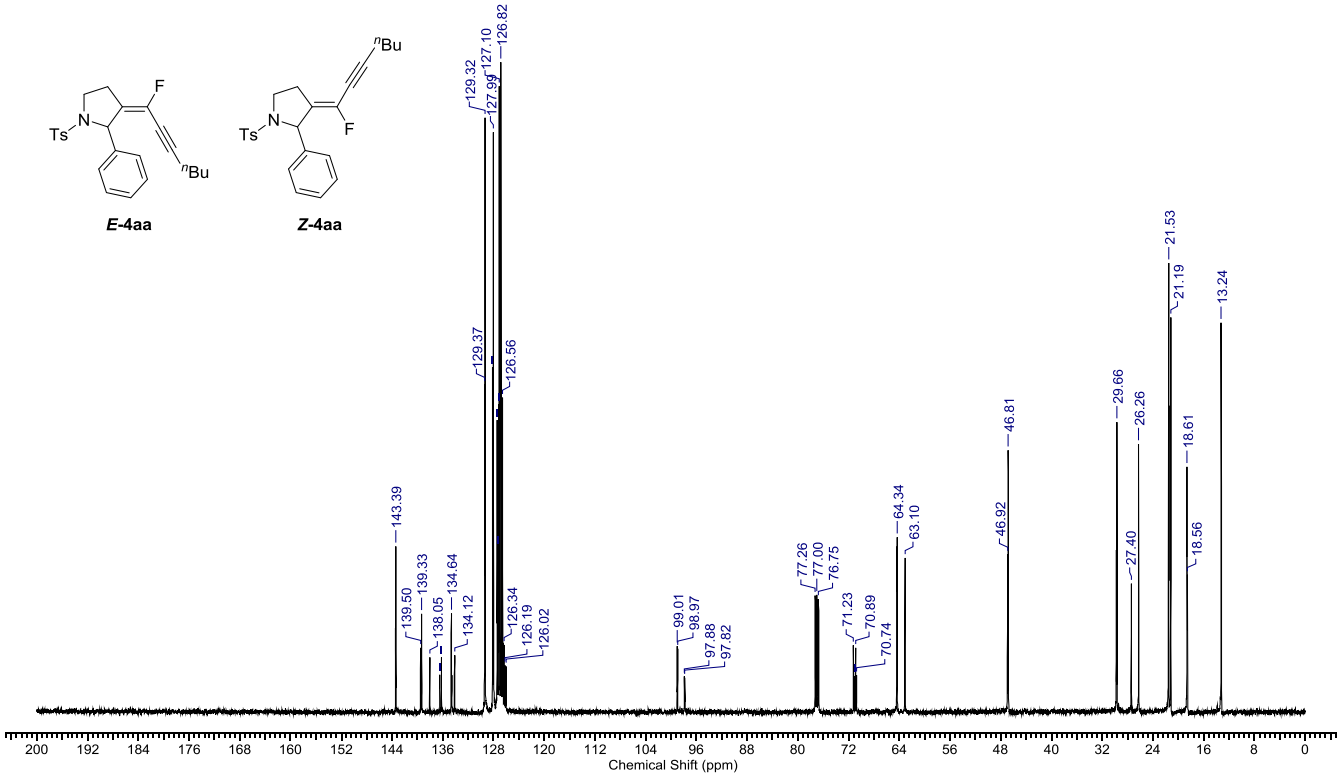
^{13}C NMR of ***Z*-3da**



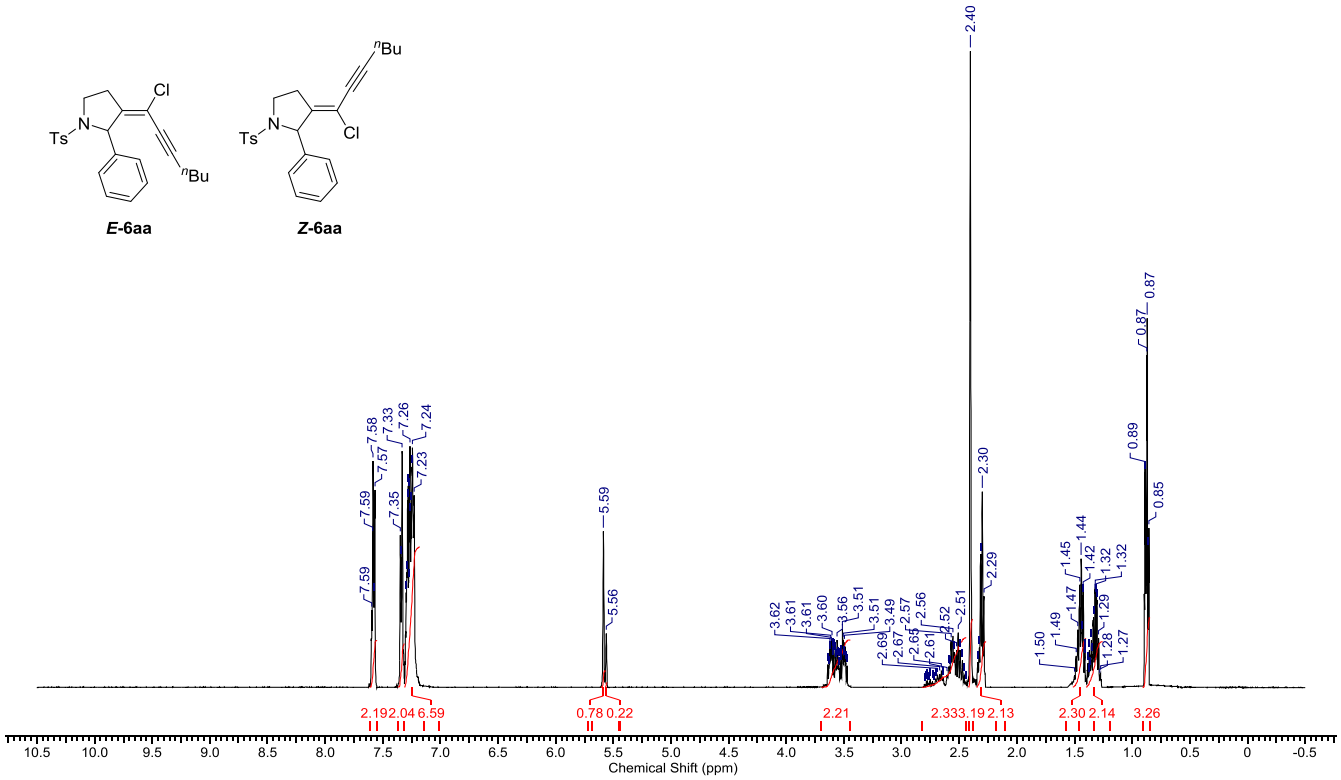
^{1}H NMR of **4aa** (mixture of *E* and *Z* isomers)



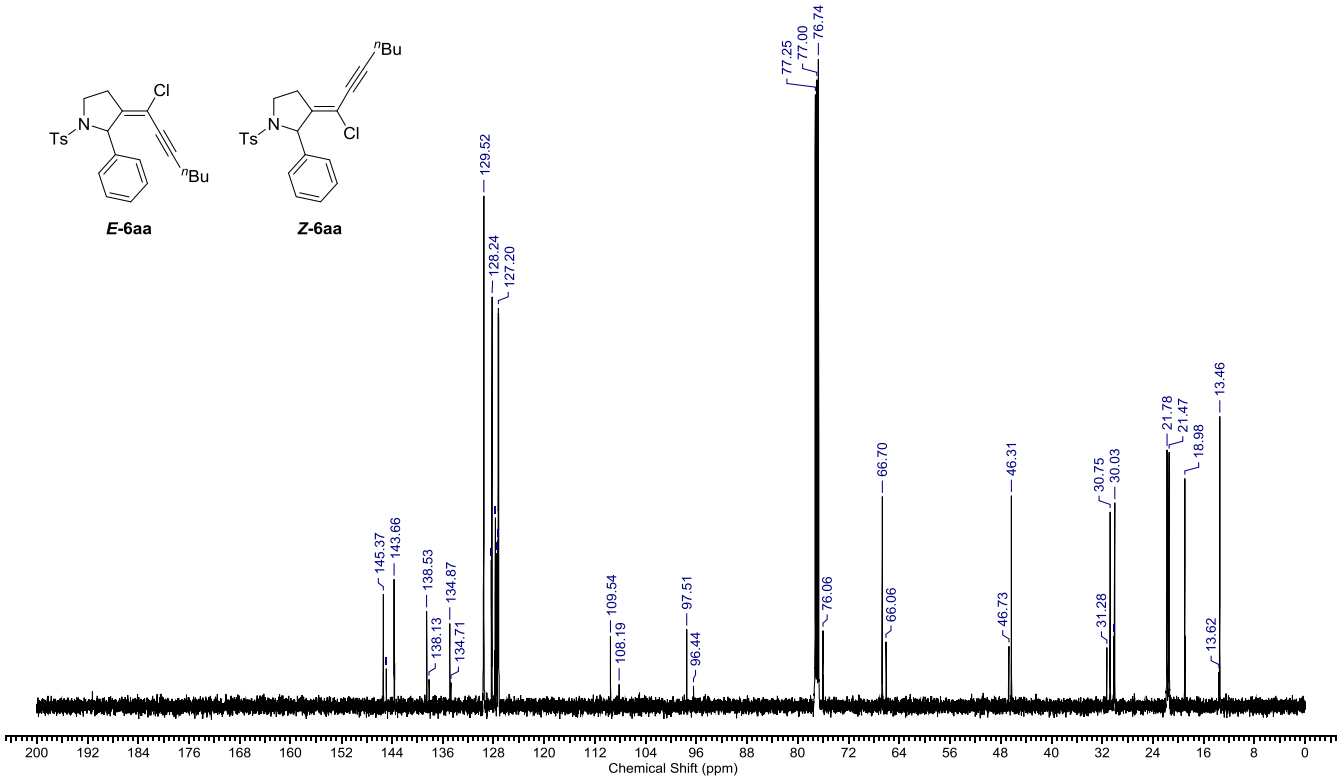
^{13}C NMR of **4aa** (mixture of *E* and *Z* isomers)



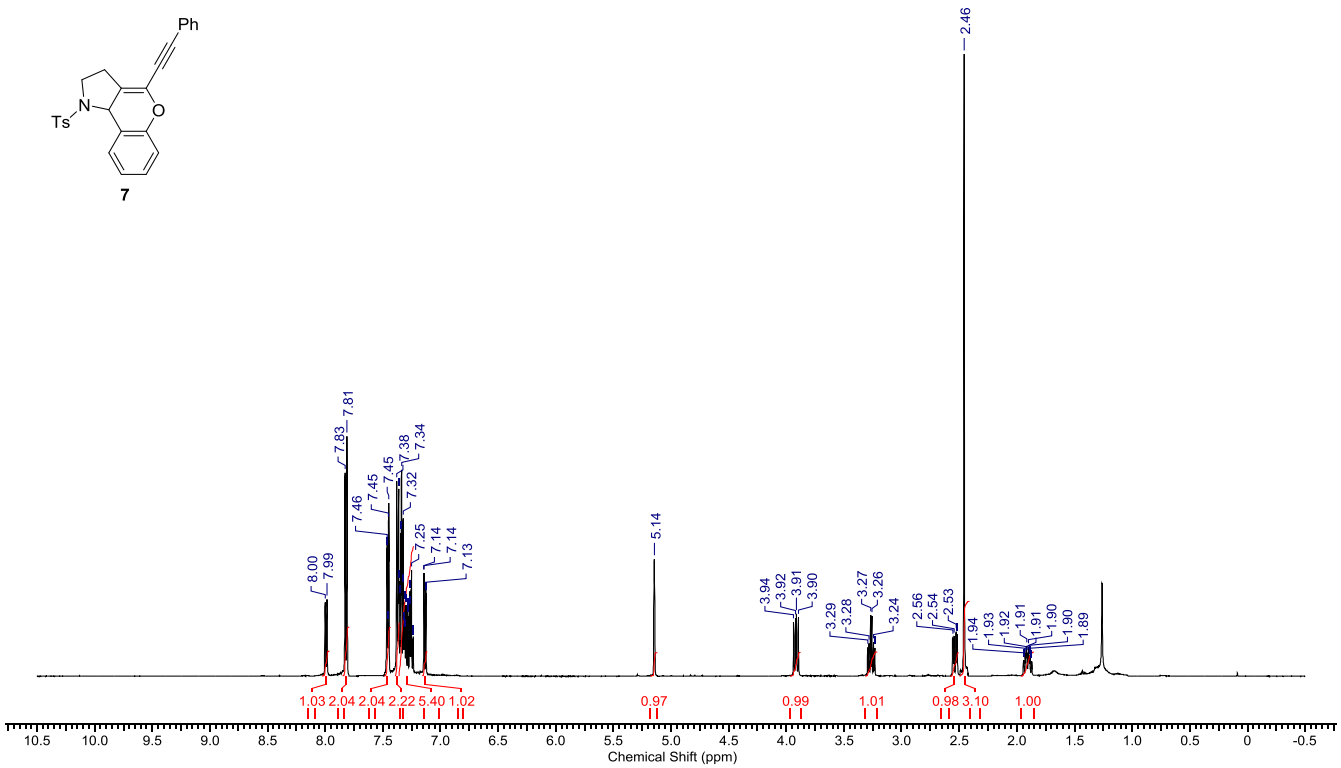
^{1}H NMR of **6aa** (mixture of *E* and *Z* isomers)



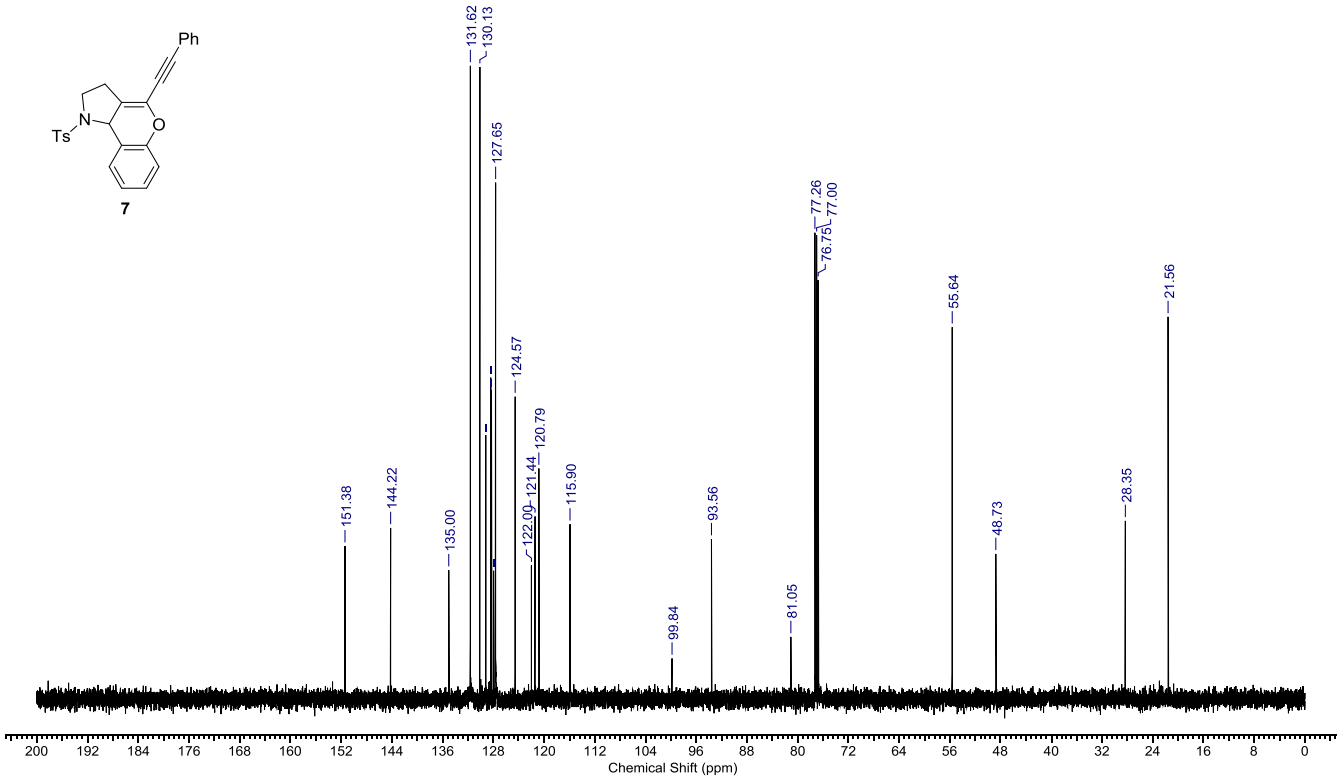
^{13}C NMR of **6aa** (mixture of *E* and *Z* isomers)



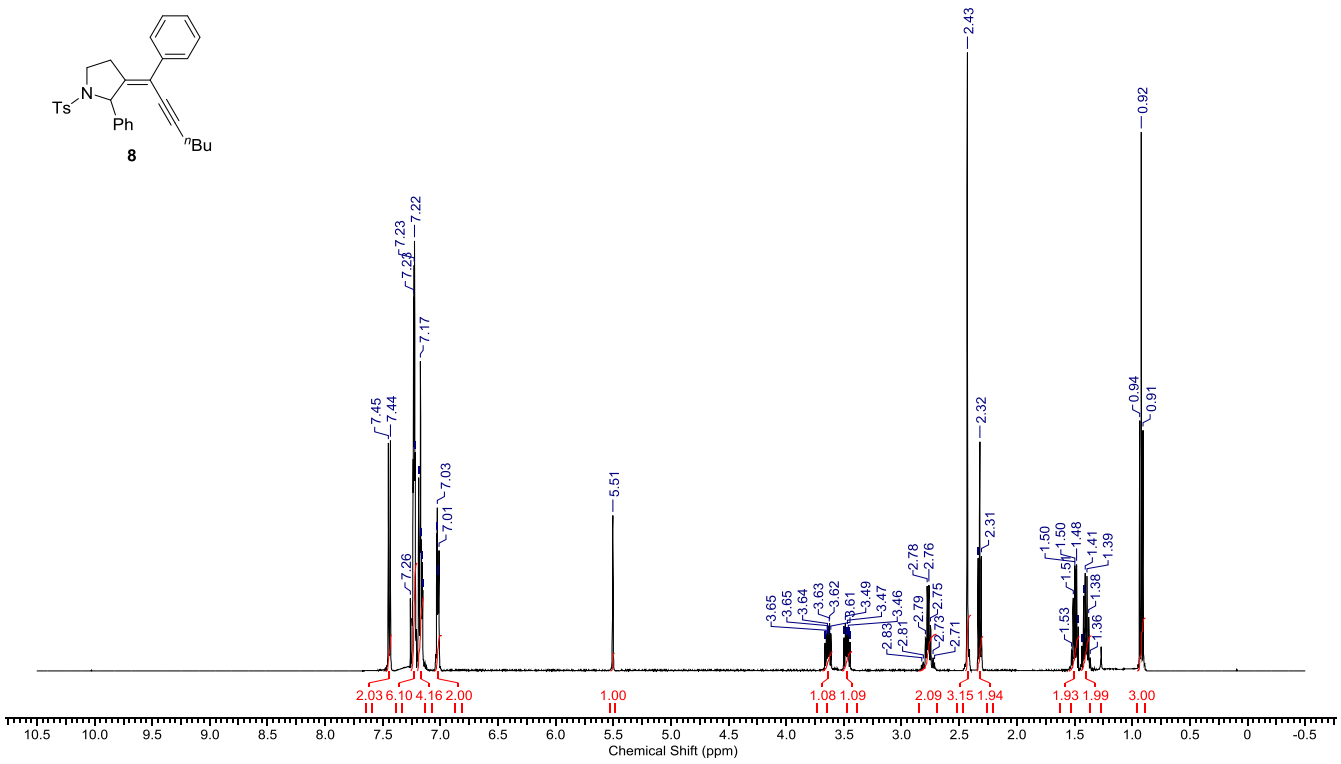
^{1}H NMR of **7**



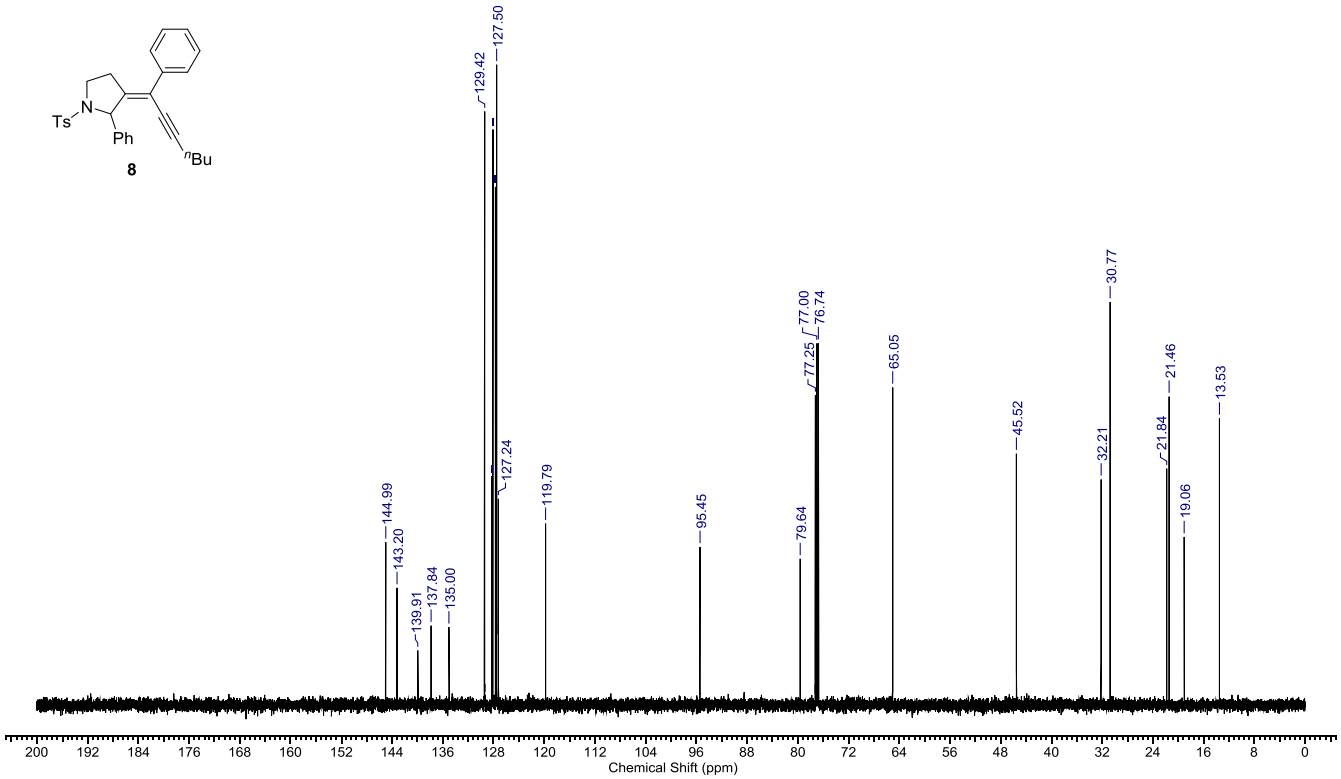
^{13}C NMR of **7**



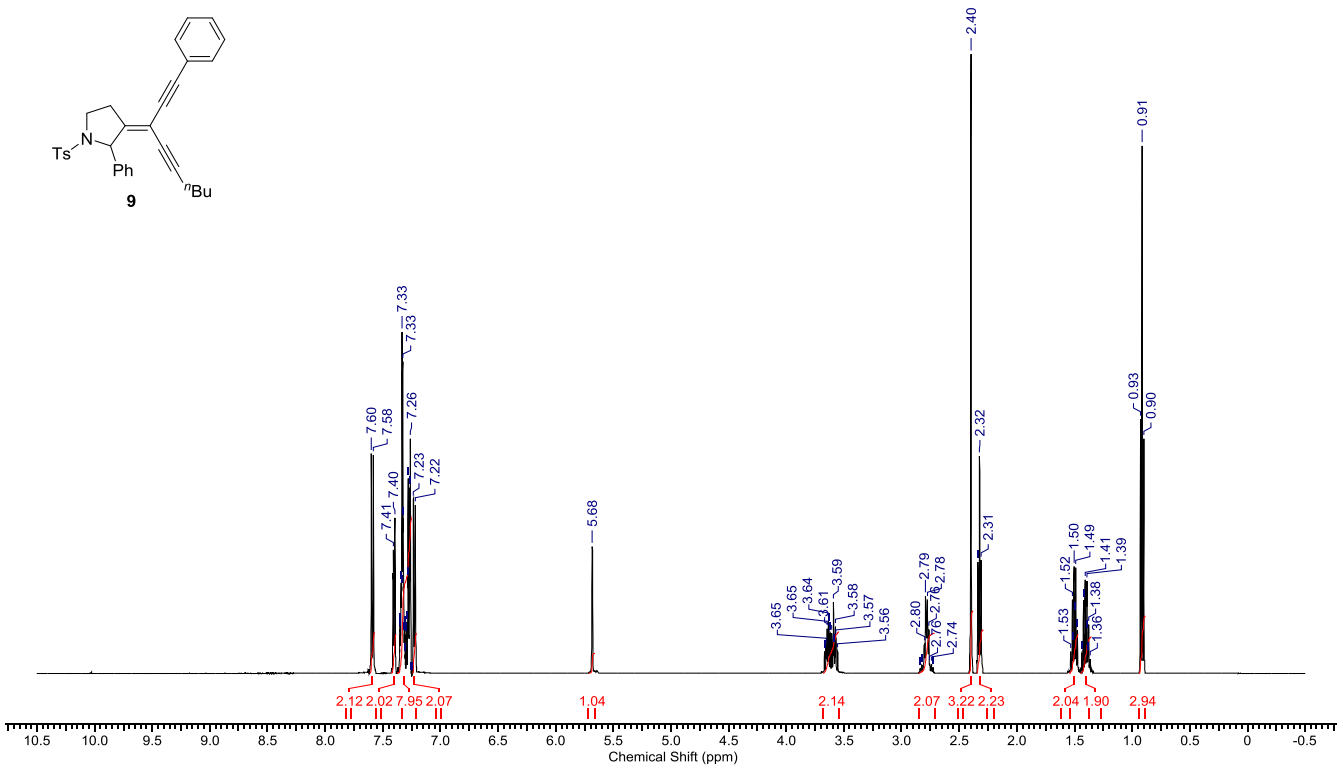
^{1}H NMR of **8**



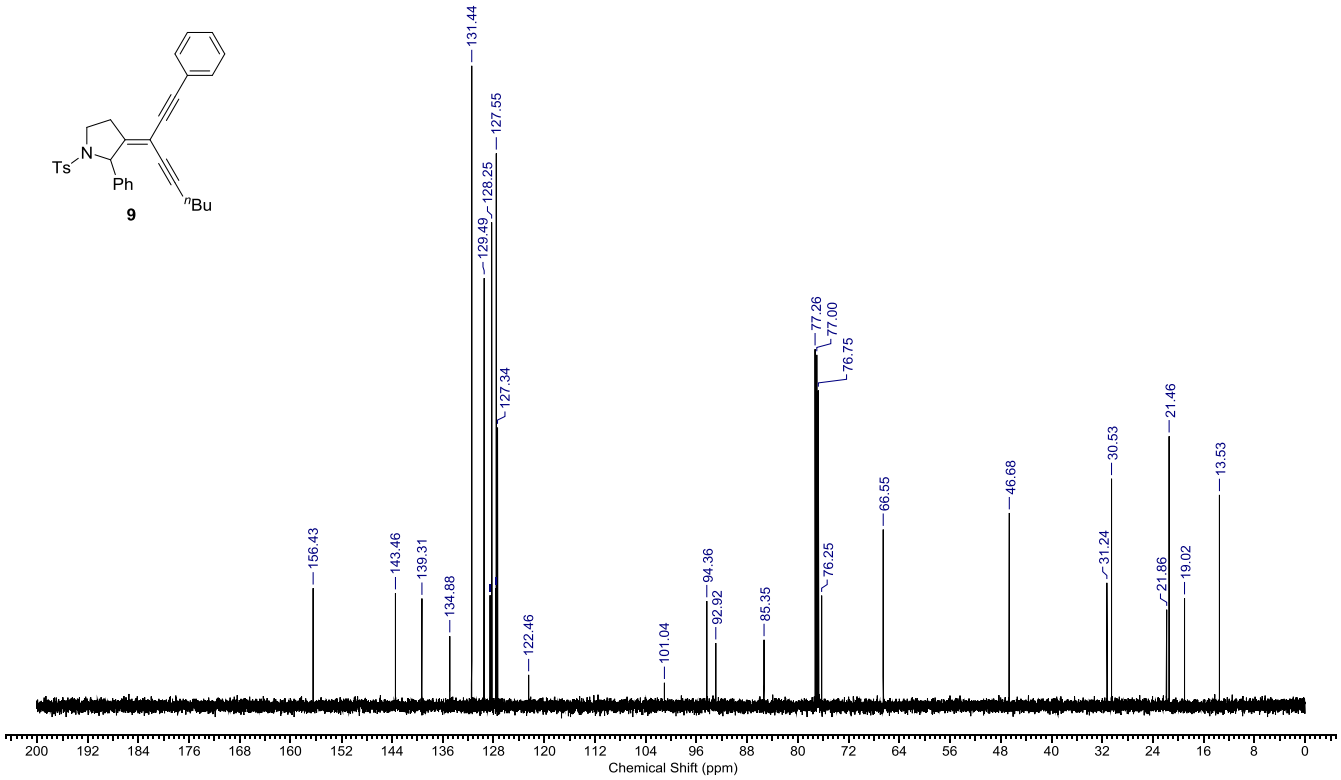
^{13}C NMR of **8**



^{1}H NMR of **9**



^{13}C NMR of **9**



Cartesian Coordinates and Absolute Electronic Energies of Intermediates and Transition States

INT1

SCF Done: E(RB3LYP) = -992.531991063 a.u.
Sum of electronic and thermal Free Energies= -992.353060 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.137332	-0.419958	-0.519068
2	6	0	-0.710923	-0.610285	-0.760851
3	6	0	0.092582	-0.427631	0.545286
4	1	0	-0.528590	-1.616359	-1.160828
5	1	0	-0.360439	0.105299	-1.514347
6	1	0	-0.060631	0.569384	0.955801
7	1	0	-0.198782	-1.163647	1.296695
8	7	0	1.555986	-0.606557	0.304048
9	16	0	2.501791	0.947554	-0.166973
10	8	0	3.387007	0.545581	-1.250764
11	8	0	1.439203	1.923221	-0.358238
12	6	0	3.416306	1.284326	1.341291
13	1	0	2.706537	1.441652	2.154539
14	1	0	4.095600	0.455286	1.539950
15	1	0	3.977670	2.199867	1.132667
16	6	0	-3.323951	-0.249158	-0.304302
17	6	0	-4.659927	-0.059273	-0.074692
18	6	0	-5.849283	0.111414	0.127204
19	6	0	-7.272903	0.316423	0.365017
20	1	0	-7.743510	0.817569	-0.489196
21	1	0	-7.786545	-0.639410	0.522228
22	1	0	-7.435654	0.938578	1.253138
23	6	0	2.096330	-1.782578	0.342412
24	1	0	1.405183	-2.588479	0.595490
25	6	0	3.496931	-2.187046	0.104448
26	1	0	4.191788	-1.382062	-0.118109
27	1	0	3.829491	-2.760718	0.979421
28	1	0	3.490666	-2.899733	-0.732674

OTf^-

SCF Done: E(RB3LYP) = -961.629263842 a.u.
Sum of electronic and thermal Free Energies= -961.635441 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.922311	0.000380	0.000000
2	8	0	1.253525	-0.723164	-1.252310
3	8	0	1.253527	-0.723631	1.252041
4	6	0	-0.959967	0.000227	0.000000
5	8	0	1.254591	1.446338	0.000268
6	9	0	-1.446758	-1.258832	-0.000217

7	9	0	-1.448306	0.629018	1.089817
8	9	0	-1.448305	0.629393	-1.089600

TS1

SCF Done: E(RB3LYP) = -992.518154903 a.u.

Sum of electronic and thermal Free Energies= -992.337839 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.096816	0.518504	1.043055
2	6	0	-0.898416	1.087624	-0.658192
3	6	0	0.193038	1.806581	-1.349076
4	6	0	1.471437	1.758182	-0.450114
5	1	0	-0.220957	-0.489251	1.300087
6	1	0	0.385713	1.310856	-2.306625
7	1	0	-0.096031	2.841481	-1.560631
8	1	0	2.381726	1.672416	-1.041212
9	1	0	1.552202	2.646255	0.177967
10	7	0	1.309558	0.580490	0.421442
11	16	0	2.024370	-0.950787	-0.136711
12	8	0	1.184459	-2.012984	0.422088
13	8	0	2.225048	-0.829648	-1.582602
14	6	0	3.604782	-0.912091	0.710518
15	1	0	4.156372	-0.027088	0.390053
16	1	0	3.416076	-0.904292	1.784776
17	1	0	4.129122	-1.823025	0.409858
18	6	0	-0.334526	1.602611	1.993048
19	1	0	-0.152254	2.614864	1.629561
20	1	0	-1.393712	1.489024	2.230699
21	1	0	0.242205	1.455597	2.917777
22	6	0	-2.019020	0.559331	-0.553898
23	6	0	-3.202808	-0.041128	-0.329227
24	6	0	-4.279520	-0.588713	-0.132714
25	6	0	-5.555169	-1.237538	0.089101
26	1	0	-6.221707	-1.039224	-0.760185
27	1	0	-5.433091	-2.322926	0.178942
28	1	0	-6.038228	-0.854646	0.995325

INT2

SCF Done: E(RB3LYP) = -992.530024000 a.u.

Sum of electronic and thermal Free Energies= -992.348614 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.074274	0.627809	-0.832586
2	6	0	0.936053	0.613437	0.374808
3	6	0	0.204129	1.062956	1.633382

4	6	0	-1.198594	1.451163	1.093394
5	1	0	0.004693	-0.285580	-1.422697
6	1	0	0.141352	0.216555	2.325556
7	1	0	0.717583	1.885646	2.138231
8	1	0	-1.988638	1.228409	1.810058
9	1	0	-1.238117	2.515593	0.846973
10	7	0	-1.366907	0.678928	-0.150834
11	16	0	-2.257750	-0.799798	-0.037145
12	8	0	-1.734778	-1.685321	-1.089287
13	8	0	-2.278918	-1.263886	1.360417
14	6	0	-3.909375	-0.259254	-0.488466
15	1	0	-4.242993	0.496577	0.224588
16	1	0	-3.875275	0.139562	-1.502913
17	1	0	-4.548221	-1.143973	-0.434723
18	6	0	0.167953	1.857194	-1.718889
19	1	0	0.115201	2.792305	-1.154389
20	1	0	1.153640	1.787434	-2.188525
21	1	0	-0.596183	1.875515	-2.502034
22	6	0	2.162762	0.236450	0.270035
23	6	0	3.409826	-0.158738	0.128118
24	6	0	4.580671	-0.533379	-0.003980
25	6	0	5.935962	-0.981419	-0.148141
26	1	0	6.303922	-1.311287	0.835375
27	1	0	5.970136	-1.860006	-0.807064
28	1	0	6.594140	-0.196147	-0.533381

TS2a_E

SCF Done: E(RB3LYP) = -1954.17399126 a.u.

Sum of electronic and thermal Free Energies= -1953.980627 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.345866	0.700337	1.028681
2	6	0	-1.011602	0.160022	0.415504
3	6	0	-1.155471	-1.324132	0.151854
4	6	0	-2.562567	-1.652029	0.703097
5	1	0	-2.656069	1.633152	0.557173
6	1	0	-1.095729	-1.498096	-0.927026
7	1	0	-0.356585	-1.899950	0.623881
8	1	0	-3.077288	-2.404229	0.104889
9	1	0	-2.510584	-2.010119	1.735123
10	7	0	-3.303281	-0.369391	0.702493
11	16	0	-4.351368	-0.092185	-0.630288
12	8	0	-4.514565	1.367532	-0.739120
13	8	0	-3.912961	-0.855994	-1.813126
14	6	0	-5.884639	-0.813063	-0.033236
15	1	0	-5.721155	-1.871826	0.175438
16	1	0	-6.192429	-0.275777	0.864357
17	1	0	-6.616190	-0.691940	-0.835822

18	6	0	-2.215564	0.898587	2.545037
19	1	0	-1.889491	-0.014110	3.052696
20	1	0	-1.488990	1.689583	2.755260
21	1	0	-3.188305	1.197435	2.947985
22	6	0	-0.025323	0.968127	0.179491
23	6	0	0.784231	2.001286	0.036928
24	6	0	1.611572	2.898801	-0.141296
25	6	0	2.563645	3.955934	-0.353098
26	1	0	3.432087	3.514112	-0.863279
27	1	0	2.152891	4.739160	-1.000964
28	1	0	2.905276	4.391092	0.592784
29	16	0	3.023114	-0.523037	-0.966465
30	8	0	1.564617	-0.728623	-0.710470
31	8	0	3.417460	0.889132	-1.178687
32	8	0	3.617518	-1.506231	-1.893074
33	6	0	3.800374	-0.947963	0.693076
34	9	0	5.136534	-0.793434	0.648213
35	9	0	3.320298	-0.147122	1.666469
36	9	0	3.537425	-2.222908	1.037282

TS2b_E

SCF Done: E(RB3LYP) = -1954.17410048 a.u.

Sum of electronic and thermal Free Energies= -1953.980455 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.564629	0.847003	0.849877
2	6	0	-1.230951	0.311735	0.267073
3	6	0	-1.359190	-1.178771	-0.006714
4	6	0	-2.685710	-1.537842	0.697172
5	1	0	-2.925949	1.704996	0.280713
6	1	0	-1.440541	-1.330176	-1.089300
7	1	0	-0.496612	-1.744822	0.350828
8	1	0	-3.209985	-2.356876	0.204177
9	1	0	-2.516097	-1.813480	1.742222
10	7	0	-3.488039	-0.293994	0.674606
11	16	0	-4.672556	-0.163598	-0.556262
12	8	0	-4.876983	1.275129	-0.799768
13	8	0	-4.347954	-1.045899	-1.693002
14	6	0	-6.125877	-0.826130	0.266575
15	1	0	-5.923113	-1.854481	0.570865
16	1	0	-6.350086	-0.196831	1.128478
17	1	0	-6.937712	-0.797630	-0.463990
18	6	0	-2.422882	1.230059	2.329848
19	1	0	-2.069480	0.389481	2.934899
20	1	0	-1.711782	2.055818	2.435023
21	1	0	-3.396794	1.553083	2.710220
22	6	0	-0.180450	1.044514	0.052723
23	6	0	0.843913	1.822350	-0.143759

24	6	0	1.887512	2.472973	-0.361241
25	6	0	2.877801	3.509457	-0.519345
26	1	0	3.731980	3.360212	0.148012
27	1	0	3.225891	3.572389	-1.555345
28	1	0	2.389362	4.460987	-0.260040
29	16	0	3.257583	-0.589903	-0.896410
30	8	0	1.871315	-1.060511	-0.689702
31	8	0	3.382214	0.889267	-1.128910
32	8	0	4.099026	-1.398100	-1.797801
33	6	0	4.060303	-0.812427	0.790243
34	9	0	5.348221	-0.425170	0.764679
35	9	0	3.421863	-0.079426	1.724144
36	9	0	4.015113	-2.102659	1.169232

TS2a_Z

SCF Done: E(RB3LYP) = -1954.17325527 a.u.

Sum of electronic and thermal Free Energies= -1953.979562 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.605756	0.317060	1.011156
2	6	0	1.011239	1.510622	0.239730
3	6	0	2.152465	2.396330	-0.274672
4	6	0	3.403289	1.738306	0.359296
5	1	0	1.132174	-0.615743	0.710876
6	1	0	2.189347	2.334351	-1.367177
7	1	0	2.029637	3.444834	0.009098
8	1	0	4.277754	1.810228	-0.287886
9	1	0	3.643321	2.200718	1.320854
10	7	0	3.028175	0.331613	0.605198
11	16	0	3.517481	-0.806592	-0.579947
12	8	0	2.553423	-1.918213	-0.535277
13	8	0	3.782280	-0.134764	-1.867417
14	6	0	5.087790	-1.370696	0.086320
15	1	0	5.760122	-0.516066	0.181607
16	1	0	4.902514	-1.836295	1.054939
17	1	0	5.487829	-2.094069	-0.628120
18	6	0	1.469377	0.506697	2.529843
19	1	0	1.938958	1.434836	2.869984
20	1	0	0.411629	0.522902	2.800548
21	1	0	1.954341	-0.335893	3.032827
22	6	0	-0.230624	1.797629	-0.011861
23	6	0	-1.353098	2.367612	-0.416738
24	6	0	-2.449906	2.818070	-0.753521
25	6	0	-3.725731	3.355214	-1.147065
26	1	0	-4.500373	2.686087	-0.745081
27	1	0	-3.887658	4.354632	-0.727217
28	1	0	-3.832603	3.385009	-2.237360
29	16	0	-2.671119	-0.596618	0.857300

30	8	0	-1.253874	-0.134490	1.010157
31	8	0	-3.624532	0.467580	0.470404
32	8	0	-3.114534	-1.508604	1.928688
33	6	0	-2.586506	-1.695643	-0.666378
34	9	0	-3.798949	-2.206573	-0.949990
35	9	0	-2.166504	-0.994497	-1.737548
36	9	0	-1.733706	-2.717236	-0.473690

TS2b_Z

SCF Done: E(RB3LYP) = -1954.17325527 a.u.

Sum of electronic and thermal Free Energies= -1953.979562 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.764918	0.411110	0.933892
2	6	0	1.330287	1.626459	0.075243
3	6	0	2.570099	2.357207	-0.425964
4	6	0	3.721929	1.613611	0.292866
5	1	0	1.212756	-0.485823	0.655114
6	1	0	2.643802	2.233635	-1.511967
7	1	0	2.542876	3.427465	-0.202894
8	1	0	4.624754	1.561555	-0.315564
9	1	0	3.969871	2.097978	1.241457
10	7	0	3.194542	0.264516	0.590328
11	16	0	3.614758	-0.981168	-0.512787
12	8	0	2.520742	-1.966061	-0.494898
13	8	0	4.043178	-0.403309	-1.801489
14	6	0	5.055862	-1.702241	0.281989
15	1	0	5.824356	-0.934491	0.387144
16	1	0	4.752683	-2.092647	1.254114
17	1	0	5.403986	-2.504665	-0.372667
18	6	0	1.575896	0.690346	2.431870
19	1	0	2.100870	1.596060	2.751374
20	1	0	0.510149	0.803073	2.646625
21	1	0	1.963569	-0.160075	3.001632
22	6	0	0.099196	1.940662	-0.190480
23	6	0	-1.124867	2.275582	-0.478814
24	6	0	-2.327618	2.514808	-0.714253
25	6	0	-3.574031	3.085516	-1.163203
26	1	0	-4.217182	3.354460	-0.319356
27	1	0	-3.325125	4.003246	-1.717223
28	1	0	-4.110573	2.407155	-1.833549
29	16	0	-2.857826	-0.441273	0.881200
30	8	0	-1.414545	-0.341919	1.185341
31	8	0	-3.471832	0.833699	0.375477
32	8	0	-3.692274	-1.138757	1.876912
33	6	0	-2.921303	-1.560685	-0.628773
34	9	0	-2.229189	-1.021804	-1.651075
35	9	0	-4.190617	-1.746676	-1.035028

36	9	0	-2.388400	-2.762959	-0.348134

PDa_E

SCF Done: E(RB3LYP) = -1954.21120381 a.u.

Sum of electronic and thermal Free Energies= -1954.013372 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.931380	0.613037	0.790715
2	6	0	-0.743351	-0.205933	0.306976
3	6	0	-1.121873	-1.666412	0.232713
4	6	0	-2.555285	-1.702878	0.802785
5	1	0	-2.095988	1.492744	0.165225
6	1	0	-1.106671	-2.003517	-0.811060
7	1	0	-0.441145	-2.315218	0.793685
8	1	0	-3.193495	-2.428499	0.297383
9	1	0	-2.552621	-1.938116	1.871409
10	7	0	-3.086005	-0.322788	0.647017
11	16	0	-4.130430	-0.063755	-0.669010
12	8	0	-4.141895	1.388185	-0.927958
13	8	0	-3.838919	-0.978398	-1.793361
14	6	0	-5.718566	-0.541900	0.025561
15	1	0	-5.669512	-1.584642	0.344714
16	1	0	-5.939636	0.116292	0.866392
17	1	0	-6.455820	-0.423658	-0.771999
18	6	0	-1.797706	1.060529	2.255918
19	1	0	-1.669236	0.205656	2.928004
20	1	0	-0.929610	1.717984	2.366845
21	1	0	-2.696003	1.609862	2.555123
22	6	0	0.430289	0.334668	-0.056217
23	6	0	0.778225	1.706067	-0.069326
24	6	0	1.075067	2.884345	-0.090309
25	6	0	1.432472	4.298419	-0.111861
26	1	0	2.513328	4.420587	-0.248023
27	1	0	0.926548	4.821500	-0.931889
28	1	0	1.152491	4.788213	0.828160
29	16	0	2.636977	-1.127223	0.309635
30	8	0	2.510009	-0.682971	1.690968
31	8	0	1.412882	-0.559224	-0.610698
32	8	0	2.825831	-2.525038	-0.048336
33	6	0	4.091028	-0.199037	-0.464638
34	9	0	4.113451	-0.410114	-1.780930
35	9	0	3.992413	1.106207	-0.219480
36	9	0	5.213898	-0.672747	0.083531

PDb_E

SCF Done: E(RB3LYP) = -1954.20193357 a.u.

Sum of electronic and thermal Free Energies= -1954.003638 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.974178	1.069834	0.122584
2	6	0	-1.761647	0.291442	0.644864
3	6	0	-2.230588	-0.935199	1.403428
4	6	0	-3.717562	-0.634580	1.657256
5	1	0	-2.943474	1.154171	-0.966263
6	1	0	-2.126201	-1.825030	0.769022
7	1	0	-1.663534	-1.107188	2.322910
8	1	0	-4.331797	-1.533850	1.718770
9	1	0	-3.854599	-0.059983	2.579206
10	7	0	-4.139023	0.224824	0.520181
11	16	0	-5.007645	-0.540107	-0.722020
12	8	0	-4.893849	0.317078	-1.916948
13	8	0	-4.651007	-1.969458	-0.843624
14	6	0	-6.693458	-0.451787	-0.102718
15	1	0	-6.749488	-0.974422	0.854116
16	1	0	-6.966775	0.598209	0.006682
17	1	0	-7.324969	-0.948147	-0.843271
18	6	0	-3.095150	2.475551	0.727534
19	1	0	-3.173660	2.433181	1.819049
20	1	0	-2.212542	3.069812	0.467818
21	1	0	-3.984069	2.975068	0.329373
22	6	0	-0.506926	0.655434	0.459422
23	6	0	0.699743	1.006647	0.279719
24	6	0	1.951381	1.379041	0.089004
25	6	0	2.470395	2.566357	-0.653406
26	1	0	3.124378	3.167775	-0.009826
27	1	0	3.052329	2.262827	-1.532744
28	1	0	1.637006	3.188223	-0.989390
29	16	0	3.519739	-0.792001	0.091790
30	8	0	2.980353	0.608178	0.739858
31	8	0	2.872162	-1.072511	-1.182190
32	8	0	3.594785	-1.774981	1.161885
33	6	0	5.300435	-0.275716	-0.275458
34	9	0	5.945423	-1.330358	-0.780423
35	9	0	5.312592	0.720512	-1.163873
36	9	0	5.900075	0.119928	0.847825

PDa_Z

SCF Done: E(RB3LYP) = -1954.20976511 a.u.

Sum of electronic and thermal Free Energies= -1954.012487 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.621043	-0.660503	0.602574
2	6	0	0.827811	0.637255	0.536123

3	6	0	1.725439	1.804901	0.880095
4	6	0	3.051239	1.135352	1.293580
5	1	0	1.461945	-1.276987	-0.284137
6	1	0	1.871804	2.437888	-0.003864
7	1	0	1.309302	2.436936	1.671726
8	1	0	3.929246	1.712369	1.001026
9	1	0	3.095997	0.971498	2.374618
10	7	0	3.041694	-0.199100	0.638040
11	16	0	3.937836	-0.333763	-0.800551
12	8	0	3.408789	-1.500593	-1.530817
13	8	0	4.035580	0.959036	-1.511371
14	6	0	5.573197	-0.734884	-0.170558
15	1	0	5.905988	0.067939	0.489926
16	1	0	5.512579	-1.683241	0.364241
17	1	0	6.233637	-0.812324	-1.037414
18	6	0	1.326920	-1.502129	1.856232
19	1	0	1.476367	-0.924788	2.774361
20	1	0	0.294682	-1.863118	1.841957
21	1	0	1.993507	-2.370108	1.874707
22	6	0	-0.451118	0.771152	0.149658
23	6	0	-1.166160	1.984925	0.018955
24	6	0	-1.766432	3.034975	-0.099112
25	6	0	-2.494863	4.291219	-0.239012
26	1	0	-3.572548	4.105629	-0.315894
27	1	0	-2.324936	4.940915	0.627456
28	1	0	-2.179570	4.834069	-1.137912
29	16	0	-2.362060	-1.067802	0.529013
30	8	0	-1.119886	-0.417904	-0.309863
31	8	0	-2.642432	-0.308680	1.739522
32	8	0	-2.165019	-2.509769	0.543184
33	6	0	-3.760808	-0.751932	-0.703188
34	9	0	-3.971713	0.555098	-0.843740
35	9	0	-4.864402	-1.333395	-0.224146
36	9	0	-3.449014	-1.287996	-1.883201

PDb_Z

SCF Done: E(RB3LYP) = -1954.20233596 a.u.

Sum of electronic and thermal Free Energies= -1954.003258 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.136177	-0.404264	0.294391
2	6	0	1.504486	0.990220	0.364713
3	6	0	2.549310	2.001698	0.797326
4	6	0	3.670558	1.117227	1.368049
5	1	0	2.056696	-0.816803	-0.714162
6	1	0	2.912800	2.554383	-0.078890
7	1	0	2.163653	2.727403	1.519367
8	1	0	4.661208	1.561229	1.262172

9	1	0	3.502433	0.897231	2.427477
10	7	0	3.573295	-0.160211	0.616062
11	16	0	4.709181	-0.406570	-0.618953
12	8	0	4.143360	-1.420910	-1.528102
13	8	0	5.180803	0.871513	-1.192895
14	6	0	6.084354	-1.138283	0.278925
15	1	0	6.422349	-0.437860	1.044950
16	1	0	5.745960	-2.074172	0.724855
17	1	0	6.877700	-1.314114	-0.451341
18	6	0	1.522391	-1.398607	1.289708
19	1	0	1.627317	-1.044477	2.320709
20	1	0	0.457009	-1.531058	1.076678
21	1	0	2.021118	-2.368829	1.198383
22	6	0	0.241228	1.258742	0.092984
23	6	0	-0.970946	1.531563	-0.168806
24	6	0	-2.216203	1.872759	-0.442216
25	6	0	-2.842670	3.228366	-0.385220
26	1	0	-3.685631	3.245206	0.316735
27	1	0	-2.105812	3.967422	-0.061252
28	1	0	-3.222830	3.515529	-1.373740
29	16	0	-4.175332	0.094048	-0.049498
30	8	0	-4.193098	0.641535	1.300820
31	8	0	-3.079402	0.855841	-0.989022
32	8	0	-5.383794	-0.070666	-0.842560
33	6	0	-3.371725	-1.613532	0.044679
34	9	0	-2.199541	-1.531014	0.676509
35	9	0	-3.186242	-2.098314	-1.183106
36	9	0	-4.189034	-2.421016	0.726341

INT2'

SCF Done: E(RB3LYP) = -1184.26972712 a.u.

Sum of electronic and thermal Free Energies= -1184.039589 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.157694	0.126902	-0.197092
2	6	0	0.826821	-0.650966	0.764838
3	6	0	0.081268	-0.991369	2.049323
4	6	0	-1.337714	-0.413073	1.794691
5	1	0	-0.043455	-0.229431	-1.222074
6	1	0	0.056271	-2.078200	2.173913
7	1	0	0.569609	-0.554908	2.925407
8	1	0	-2.121627	-1.058135	2.190269
9	1	0	-1.434445	0.579184	2.242466
10	7	0	-1.452267	-0.274075	0.331199
11	16	0	-2.308581	-1.509197	-0.523309
12	8	0	-1.688101	-1.609558	-1.853207
13	8	0	-2.410693	-2.704853	0.328274
14	6	0	-3.939164	-0.777981	-0.688467

15	1	0	-4.336444	-0.575411	0.307549
16	1	0	-3.847316	0.136968	-1.274886
17	1	0	-4.557229	-1.516012	-1.205523
18	6	0	2.019673	-1.006645	0.437673
19	6	0	3.233224	-1.374696	0.084486
20	6	0	4.373319	-1.726417	-0.239079
21	6	0	5.693450	-2.154174	-0.603626
22	1	0	6.042869	-2.868658	0.158505
23	1	0	5.679217	-2.687158	-1.562522
24	1	0	6.399184	-1.317359	-0.640818
25	6	0	0.085544	1.637022	-0.130536
26	6	0	-0.975547	2.520920	0.104503
27	6	0	1.363316	2.154315	-0.385507
28	6	0	-0.759447	3.901984	0.085676
29	1	0	-1.971352	2.130073	0.285992
30	6	0	1.576746	3.533367	-0.410540
31	1	0	2.201683	1.487472	-0.569909
32	6	0	0.515286	4.412669	-0.170513
33	1	0	-1.592042	4.575967	0.267739
34	1	0	2.571756	3.919321	-0.613609
35	1	0	0.682356	5.486096	-0.183464

TS2′a_E

SCF Done: E(RB3LYP) = -2145.91350287 a.u.

Sum of electronic and thermal Free Energies= -2145.670762 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.092632	0.194376	0.373919
2	6	0	0.637140	-0.242495	-0.010809
3	6	0	0.663251	-0.830120	-1.406418
4	6	0	2.167772	-0.830073	-1.774598
5	1	0	2.307276	-0.032370	1.419830
6	1	0	0.245761	-1.839381	-1.379666
7	1	0	0.054404	-0.240124	-2.096739
8	1	0	2.471082	-1.749372	-2.275811
9	1	0	2.417259	0.017795	-2.418353
10	7	0	2.898363	-0.662832	-0.496895
11	16	0	3.586909	-2.070803	0.204456
12	8	0	3.691176	-1.812762	1.650222
13	8	0	2.882106	-3.276057	-0.265869
14	6	0	5.230884	-2.062315	-0.518496
15	1	0	5.136874	-2.085090	-1.605741
16	1	0	5.749811	-1.162969	-0.185144
17	1	0	5.733905	-2.963394	-0.159617
18	6	0	-0.324745	-0.169773	0.855730
19	6	0	-1.084242	-0.010924	1.924902
20	6	0	-1.874063	0.094289	2.866163
21	6	0	-2.780732	0.205161	3.977249

22	1	0	-3.734366	-0.246781	3.667570
23	1	0	-2.410995	-0.347413	4.848963
24	1	0	-2.967109	1.250877	4.246541
25	16	0	-3.583731	-1.051764	-0.324708
26	8	0	-2.114452	-1.064398	-0.602489
27	8	0	-3.938499	-0.935475	1.108767
28	8	0	-4.351067	-2.044222	-1.102338
29	6	0	-4.128793	0.598330	-1.044792
30	9	0	-5.450865	0.780258	-0.870861
31	9	0	-3.484563	1.620213	-0.445385
32	9	0	-3.867152	0.659166	-2.364041
33	6	0	2.334741	1.686353	0.105835
34	6	0	3.493403	2.107266	-0.559922
35	6	0	1.440134	2.651081	0.590022
36	6	0	3.752489	3.469542	-0.738333
37	1	0	4.194941	1.368009	-0.931856
38	6	0	1.702109	4.011985	0.416307
39	1	0	0.532984	2.351816	1.106412
40	6	0	2.858654	4.426575	-0.251566
41	1	0	4.655699	3.778988	-1.257527
42	1	0	0.998695	4.746087	0.799667
43	1	0	3.059681	5.485260	-0.391153

TS2′a_Z

SCF Done: E(RB3LYP) = -2145.91207817 a.u.

Sum of electronic and thermal Free Energies= -2145.669301 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.492135	0.177410	0.129017
2	6	0	-0.760334	0.222184	1.486220
3	6	0	-1.755226	-0.148820	2.592337
4	6	0	-3.034808	-0.525084	1.795758
5	1	0	-0.834056	-0.220367	-0.642738
6	1	0	-1.375694	-0.998394	3.166698
7	1	0	-1.920041	0.685843	3.280169
8	1	0	-3.529041	-1.406524	2.202603
9	1	0	-3.743349	0.307581	1.788591
10	7	0	-2.591026	-0.759482	0.407181
11	16	0	-2.396240	-2.385859	-0.100704
12	8	0	-1.270845	-2.420639	-1.047923
13	8	0	-2.383340	-3.271201	1.078164
14	6	0	-3.919248	-2.686051	-1.005307
15	1	0	-4.765206	-2.526980	-0.334408
16	1	0	-3.955517	-2.004354	-1.855892
17	1	0	-3.884411	-3.725724	-1.339430
18	6	0	0.496675	0.419310	1.747285
19	6	0	1.662141	0.581158	2.351625
20	6	0	2.788310	0.742789	2.825410

21	6	0	4.098517	0.930546	3.390411
22	1	0	4.787537	1.140275	2.559433
23	1	0	4.122352	1.782432	4.079419
24	1	0	4.448496	0.026020	3.901161
25	16	0	2.746090	0.618747	-0.954690
26	8	0	1.317237	0.660360	-0.501950
27	8	0	3.728287	0.978289	0.092676
28	8	0	2.962255	1.220322	-2.283698
29	6	0	3.044128	-1.216929	-1.234789
30	9	0	4.307338	-1.430942	-1.648187
31	9	0	2.853074	-1.911413	-0.096472
32	9	0	2.207412	-1.701653	-2.168286
33	6	0	-2.019245	1.559938	-0.288858
34	6	0	-1.191376	2.689609	-0.224108
35	6	0	-3.317610	1.697582	-0.797387
36	6	0	-1.653941	3.932557	-0.663350
37	1	0	-0.177836	2.599966	0.151680
38	6	0	-3.780029	2.942310	-1.235437
39	1	0	-3.965983	0.829275	-0.853435
40	6	0	-2.950819	4.064921	-1.169089
41	1	0	-0.996939	4.796659	-0.610654
42	1	0	-4.789598	3.030225	-1.628535
43	1	0	-3.310283	5.032671	-1.508694

TS3

SCF Done: E(RB3LYP) = -1954.14975318 a.u.

Sum of electronic and thermal Free Energies= -1953.959136 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.018048	-1.608806	1.047807
2	6	0	-2.236327	0.801481	1.015789
3	6	0	-0.518268	0.990449	-0.007349
4	6	0	-0.289866	-0.243246	-0.005001
5	6	0	-0.687861	-1.612447	0.176401
6	1	0	-2.741968	1.612030	0.495316
7	1	0	-1.757462	-1.608435	2.106008
8	1	0	-2.582861	-2.514851	0.831654
9	1	0	-0.883300	-2.082375	-0.792747
10	1	0	0.076122	-2.189772	0.706619
11	7	0	-2.815999	-0.422753	0.764082
12	6	0	-0.197002	2.304261	-0.277449
13	6	0	0.042130	3.476368	-0.497733
14	6	0	0.354942	4.870489	-0.778532
15	1	0	1.331803	4.955481	-1.268206
16	1	0	-0.398997	5.312724	-1.440120
17	1	0	0.384017	5.457657	0.146712
18	16	0	-3.951802	-0.531818	-0.584956
19	8	0	-4.148078	0.838388	-1.066533
20	8	0	-3.466232	-1.583979	-1.482076
21	6	0	-5.433743	-1.093454	0.257937

22	1	0	-5.227408	-2.051121	0.738296
23	1	0	-5.723205	-0.333503	0.984787
24	1	0	-6.196961	-1.208922	-0.515661
25	6	0	-1.782644	1.125099	2.417949
26	1	0	-1.244864	2.075482	2.423884
27	1	0	-2.683017	1.238239	3.036404
28	1	0	-1.144890	0.359138	2.861331
29	16	0	2.961477	-1.337505	-0.439843
30	8	0	2.556860	-2.121732	0.751036
31	8	0	1.827125	-0.679625	-1.156216
32	8	0	3.957477	-1.975378	-1.326385
33	6	0	3.898458	0.118555	0.295481
34	9	0	3.116919	0.818586	1.142866
35	9	0	4.321032	0.958753	-0.668551
36	9	0	4.977864	-0.304808	0.981634

PDc

SCF Done: E(RB3LYP) = -1954.21555938 a.u.
Sum of electronic and thermal Free Energies= -1954.016222 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.051439	-1.488387	1.070390
2	6	0	-1.929810	0.973701	0.757385
3	6	0	-0.499931	0.764331	0.234288
4	6	0	-0.032788	-0.480234	0.020700
5	6	0	-0.789374	-1.752041	0.239515
6	1	0	-2.386362	1.727942	0.110251
7	1	0	-1.787515	-1.356658	2.124129
8	1	0	-2.743111	-2.327215	1.003246
9	1	0	-1.043263	-2.197723	-0.732587
10	1	0	-0.166068	-2.485694	0.766745
11	7	0	-2.745561	-0.256170	0.655450
12	6	0	0.256670	1.941742	-0.019353
13	6	0	0.833980	2.992370	-0.218920
14	6	0	1.555435	4.237778	-0.464169
15	1	0	2.620072	4.126813	-0.226878
16	1	0	1.474973	4.536942	-1.516221
17	1	0	1.153867	5.053095	0.148752
18	16	0	-3.814532	-0.362672	-0.655764
19	8	0	-3.300208	0.381831	-1.822580
20	8	0	-4.158302	-1.787331	-0.813693
21	6	0	-5.268585	0.510077	-0.054302
22	1	0	-5.645244	-0.013778	0.825081
23	1	0	-4.993506	1.538255	0.187774
24	1	0	-6.001426	0.495460	-0.864592
25	6	0	-1.939686	1.512309	2.198377
26	1	0	-1.345560	2.429381	2.258383
27	1	0	-2.965749	1.739858	2.503347
28	1	0	-1.516166	0.787887	2.900972
29	16	0	2.478420	-1.323687	0.166441
30	8	0	2.846330	-2.544694	-0.535438
31	8	0	2.270757	-1.295118	1.608975

32	8	0	1.225807	-0.616656	-0.619615
33	6	0	3.800924	-0.041757	-0.266867
34	9	0	4.981382	-0.541996	0.110188
35	9	0	3.571435	1.095133	0.384842
36	9	0	3.808774	0.179839	-1.580679