Supporting Information

Tandem Catalytic Allylic C−H Amination and Asymmetric [2,3]-Rearrangement via Bimetallic Relay Catalysis

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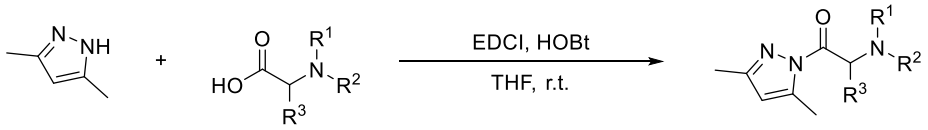
1. General information

All solvents were dried and distilled according to general practice prior to use. All reagents were purchased from commercial sources and used without further purification unless specified otherwise. Solvents for flash column chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed using Huanghai silica gel plates with HSGF 254. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) and appropriate stains. Flash column chromatography was performed using silica gel (200-300 mesh, from Leyan.com) with the indicated solvent system according to standard techniques. CDCl3 was also bought from Leyan.com. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker NMR 400 (400MHz, 101MHz). Multiplicities are described as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); and coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded with total proton decoupling. Melting points were recorded on a Shanghai Jingke SGWX-4B melting-point Meter and are uncorrected. Chiral HPLC was recorded on a Shimadzu LC-20AD spectrometer using Daicel Chiralcel columns. HRMS (ESI) analysis was performed by the Analytical Instrumentation Center at Peking University Shenzhen Graduate School and (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units.

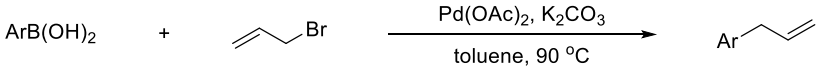
2. General procedure for the synthesis of amino amide



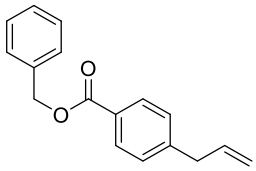
A solution of amino acid (1.1 equiv.) in anhydrous THF was cooled to 0 °C. The 3,5-dimethyl-1H-pyrazole (1.0 equiv.), EDCI (1.2 equiv.), HOBt (1.2 equiv.) and DMAP (0.1 equiv.) were successively added, the reaction mixture was stirred for 24 h at room temperature. To the mixture was added brine and the aqueous layer was separated and extracted with dichloromethane. The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated. The residue was subjected to column chromatography to give the product.

3. Preparation of allylbenzene derivatives

3.1 Method A



Under N_2 atmosphere, to a solution of arylboronic acid (1.0 equiv.), $Pd(OAc)_2$ (2.5 mol%) and K_2CO_3 (2.0 equiv.) in toluene, allyl bromide (2.0 equiv.) was added via syringe. After being heated at 90 °C overnight, the mixture was cooled to room temperature, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography to afford the product.



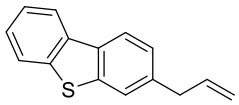
benzyl 4-allylbenzoate (1p): Following the general procedure, (4-((benzyloxy)carbonyl)phenyl)boronic acid (1.6 g, 6.25 mmol) to yield **1p** as a colorless oil (1.12 g, 71% yield).

TLC: R_f = 0.9 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.32 (m, 6H), 7.27 (s, 1H), 7.25 (s, 1H), 6.02 – 5.89 (m, 1H), 5.36 (s, 2H), 5.14 – 5.06 (m, 2H), 3.44 (d, *J* = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 145.7, 136.5, 136.2, 133.1, 130.0, 128.7, 128.7, 128.3, 128.2, 116.7, 66.6, 40.2.

HRMS m/z $[M+H]^+$ calcd for $C_{17}H_{17}O_2^+$ = 253.1223, found 253.1225.



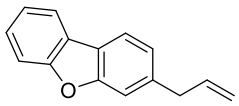
3-allyldibenzo[*b*,*d*]thiophene (1t): Following the general procedure, dibenzo[*b*,*d*]thiophen-3-ylboronic acid (1.5 g, 6.25 mmol) to yield **1t** as white solid (0.96 g, 65% yield), M.p. 50 – 51 ℃.

TLC: R_f = 0.9 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.87 – 7.82 (m, 1H), 7.68 (s, 1H), 7.46 – 7.41 (m, 2H), 7.30 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.14 – 5.96 (m, 1H), 5.20 – 5.09 (m, 2H), 3.55 (d, *J* = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 139.4, 139.1, 137.3, 135.5, 133.9, 126.4, 125.5, 124.4, 122.9, 122.5, 121.5, 121.4, 116.3, 40.4.

HRMS m/z $[M+H]^+$ calcd for $C_{15}H_{13}S^+$ = 225.0732, found 225.0736.



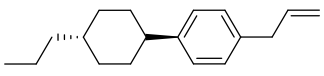
3-allyldibenzo[*b*,*d*]furan (1u): Following the general procedure, dibenzo[*b*,*d*]furan-3-ylboronic acid (1.5 g, 7.08 mmol) to yield **1u** as a colorless oil (1.02 g, 69% yield).

TLC: R_f = 0.9 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.78 (s, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.39 – 7.27 (m, 2H), 6.18 – 6.01 (m, 1H), 5.21 – 5.07 (m, 2H), 3.57 (d, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 155.0, 137.9, 134.6, 127.9, 127.1, 124.4, 124.3, 122.7, 120.7, 120.4, 115.9, 111.7, 111.5, 40.2.

HRMS m/z $[M+H]^+$ calcd for $C_{15}H_{13}O^+$ = 209.0961, found 209.0964.



1-allyl-4-((1*r*,4*s*)-4-propylcyclohexyl)benzene (1x): Following the general procedure, (4-((1*r*,4*s*)-4-propylcyclohexyl)phenyl)boronic acid (1.8 g, 7.31 mmol) to yield **1x** as a colorless oil (1.23 g, 69% yield).

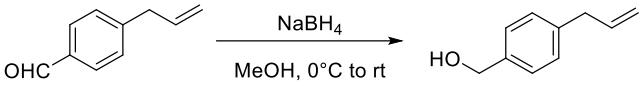
TLC: R_f = 0.9 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.09 (m, 4H), 6.05 – 5.87 (m, 1H), 5.16 – 5.01 (m, 2H), 3.37 (d, *J* = 6.8 Hz, 2H), 2.54 – 2.35 (m, 1H), 1.98 – 1.78 (m, 4H), 1.52 – 1.40 (m, 2H), 1.40 – 1.26 (m, 3H), 1.26 – 1.19 (m, 2H), 1.12 – 0.97 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

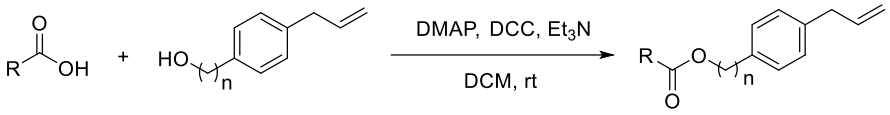
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 137.7, 137.5, 128.5, 126.9, 115.7, 44.3, 39.9, 39.8, 37.1, 34.5, 33.7, 20.1, 14.5.

HRMS m/z $[M+H]^+$ calcd for $C_{18}H_{27}^+$ = 243.2107, found 243.2110.

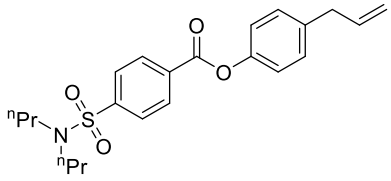
3.2 Method B



To a solution of 4-allylbenzaldehyde (5.0 mmol) in MeOH (20 mL) at 0 °C, $NaBH_4$ (0.38 g, 10 mmol) was slowly added. The reaction mixture was slowly warmed to room temperature and stirred overnight. After washed with 5% HCl (aq.), brine, and H_2O, the combined organic layers were dried over Na_2SO_4, filtrated, and then concentrated under vacuum. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1) to afford the desired product.



Under nitrogen atmosphere, to a solution of carboxylic acid compound (1.0 equiv.), DMAP (0.2 equiv.), DCC (1.1 equiv.), Et_3N (2.0 equiv.) and alcohol in dichloromethane was added at rt. The mixture was stirred at room temperature overnight. After the reaction was completed, the suspension was filtered through a celite pad. The filtrate was concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product.



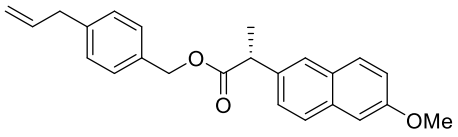
4-Allylphenyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (1ca): Following the general procedure, dibenzo[*b*,*d*]furan-3-ylboronic acid (1.0 g, 3.5 mmol) to yield **1ca** as a white solid (0.87 g, 62% yield), M.p. 66 – 68 °C.

TLC: R_f = 0.7 (petroleum ether/ethyl acetate 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 – 8.30 (m, 2H), 7.95 – 7.93 (m, 2H), 7.31 – 7.22 (m, 2H), 7.15 – 7.13 (m, 2H), 6.04 – 5.90 (m, 1H), 5.15 – 5.07 (m, 2H), 3.42 (d, *J* = 6.6 Hz, 2H), 3.18 – 3.09 (m, 4H), 1.61 – 1.52 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.1, 149.0, 144.9, 138.2, 137.1, 133.0, 130.9, 129.8, 127.2, 121.4, 116.3, 50.0, 39.7, 22.0, 11.2.

HRMS m/z $[M+H]^+$ calcd for $C_{22}H_{28}NO_4S^+$ = 402.1734, found 402.1733.



4-allylbenzyl (*R*)-2-(6-methoxynaphthalen-2-yl)propanoate (1cb): Following the general procedure, Naproxen (1.0 g, 4.3 mmol) to yield **1cb** as a white solid (1.14 g, 73% yield), M.p. 61 – 63 °C.

TLC: R_f = 0.8 (petroleum ether/ethyl acetate 10/1).

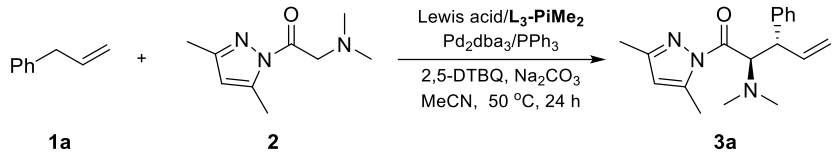
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.67 (m, 3H), 7.51 – 7.44 (m, 1H), 7.34 – 7.15 (m, 6H), 6.07 – 5.93 (m, 1H), 5.23 – 5.07 (m, 4H), 3.97 (s, 4H), 3.42 (d, *J* = 6.7 Hz, 2H), 1.65 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 157.7, 140.1, 137.3, 135.7, 133.82, 133.77, 129.4, 129.0, 128.8, 128.3, 127.2, 126.4, 126.1, 119.0, 116.1, 105.6, 66.5, 55.4, 45.5, 40.0, 18.7.

HRMS m/z $[M+H]^+$ calcd for $C_{24}H_{25}O_3^+$ = 361.1798, found 361.1800.

4. Reaction optimization for [2,3]-rearrangement

***Table S1*: Screening of Lewis acids**

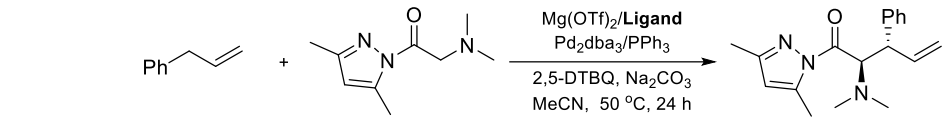


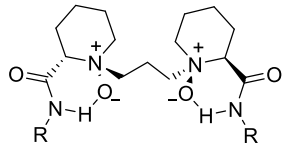
1a **2** **3a**

Entry[a]	Lewis Acid	Yield	*dr* (*anti*:*syn*)	*er*
1	$Sc(OTf)_3$	No product	N.D.[e]	N.D.
2	$Ni(OTf)_2$	No product	N.D.	N.D.
3	$Zn(OTf)_2$	No product	N.D.	N.D.
4	$Fe(OTf)_2$	No product	N.D.	N.D.
5	$Yb(OTf)_3$	No product	N.D.	N.D.
6	$Mg(OTf)_2$	trace	N.D.	N.D.
7	$Co(BF_4)_2•6H_2O$	No product	N.D.	N.D.

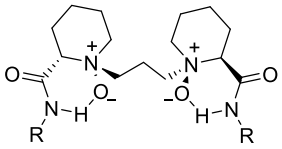
Reaction conditions: **1a** (0.2 mmol, 2.0 equiv.), **2** (0.1 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (4 mol%), PPh_3 (8 mol%), 2,5-DTBQ (0.11 mmol, 1.1 equiv.), Lewis acid (10 mol%), **L_3-PiMe$_2$** (10 mol%), and Na_2CO_3 (0.12 mmol, 1.2 equiv.) in MeCN (2.0 mL) at 50 °C for 24 h. The yield and diastereomeric ratio (*dr*) were determined via ^1H NMR analysis of the crude reaction mixtures using 4-methylanisole as the internal standard. The enantiomeric ratio (*er*) was determined by chiral HPLC analysis. Compound **3a** was converted into its methyl ester derivative quantitatively with MeOH at 60 °C to determine its *er* value. [b] N.D. = no detection. 2,5-DTBQ = 2,5-ditertbutylquinone.

***Table S2*: Screening of chiral *N,N'*-dioxide ligands**

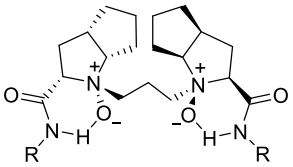




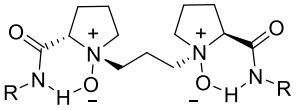
L_3-PiMe$_2$: R = 2,6-$Me_2C_6H_3$



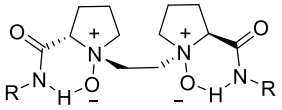
L_3-PiAd: R = 1-adamantyl



L_3-RaAd: R = 1-adamantyl



L_3-PrAd: R = 1-adamantyl
L_3-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$
L_3-PrMe$_2$: R = 2,6-$Me_2C_6H_3$
L_3-PrcH: R = cyclohexyl
L_3-PrCHPh$_2$: R = $CHPh_2$
L_3-PrEt$_2$: R = 2,6-$Et_2C_6H_3$
L_3-PrAdMe: (*ent*-)R = 1-adam(Me)$_2$
L_3-PrCH$_2$Ad: R = 1-CH_2-adam
L_3-PrcP: R = cyclopentyl

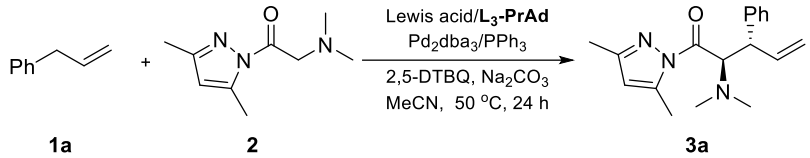


L_2-PrAd: R = 1-adamantyl

Entry	Ligand	Yield	*dr* (*anti*:*syn*)	*er*
1	**L_3-PiMe$_2$**	trace	N.D.	N.D.
2	**L_3-PiAd**	44	2:1	54:46/51:49
3	**L_3-RaAd**	47	3:1	82:18/62:38
4	**L_3-PrAd**	55	5:1	78:22/62:38
5	**L_3-Pr^{i}Pr$_2$**	38	3:1	57:43/60:40
6	**L_3-PrMe$_2$**	35	2:1	56:44/53:47
7	**L_3-PrcH**	48	3:1	60:40/57:43
8	**L_3-PrCHPh$_2$**	30	3:1	56:44/57:43
9	**L_3-PrEt$_2$**	35	2:1	56:44/57:43
10	**L_3-PrAdMe$_2$**	36	3:1	62:38/55:45
11	**L_3-PrCH$_2$Ad**	35	2:1	60:40/56:44
12	**L_3-PrcP**	35	2.5:1	66:34/76:24
13	**L_2-PrAd**	30	1.5:1	57:43/59:41

Reaction conditions: **1a** (0.2 mmol, 2.0 equiv.), **2** (0.1 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (4 mol%), PPh_3 (8 mol%), 2,5-DTBQ (0.11 mmol, 1.1 equiv.), $Mg(OTf)_2$ (10 mol%), **Ligand** (10 mol%), and Na_2CO_3 (0.12 mmol, 1.2 equiv.) in MeCN (2.0 mL) at 50 °C for 24 h. The yield and diastereomeric ratio (*dr*) were determined via ^{1}H NMR analysis of the crude reaction mixtures using 4-methylanisole as the internal standard. The enantiomeric ratio (*er*) was determined by chiral HPLC analysis. Compound **3a** was converted into its methyl ester derivative quantitatively with MeOH at 60 °C to determine its *er* value.

Table S3: **Screening of Lewis acids again with the use of L_3-PrAd**

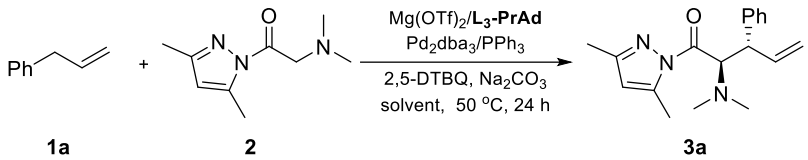


1a **2** **3a**

Entry	Lewis Acid	Yield	*dr* (*anti*:*syn*)	*er*
1	$Sc(OTf)_3$	trace	N.D.	N.D.
2	$Ni(OTf)_2$	trace	N.D.	N.D.

Reaction conditions: **1a** (0.2 mmol, 2.0 equiv.), **2** (0.1 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (4 mol%), PPh_3 (8 mol%), 2,5-DTBQ (0.11 mmol, 1.1 equiv.), lewis acid (10 mol%), **L_3-PrAd** (10 mol%), Na_2CO_3 (1.2 equiv.) in MeCN (2.0 mL) at 50 °C for 24 h. The yield and diastereomeric ratio (*dr*) were determined via ^1H NMR analysis of the crude reaction mixtures using 4-methylanisole as the internal standard. The enantiomeric ratio (*er*) was determined by chiral HPLC analysis. Compound **3a** was converted into its methyl ester derivative quantitatively with MeOH at 60 °C to determine its *er* value.

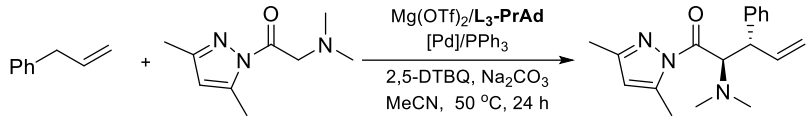
***Table S4*: Screening of solvent**



Entry	Solvent	Yield	*dr* (*anti*:*syn*)	*er*
1	Dichloromethane	trace	N.D.	N.D.
2	Toluene	No product	N.D.	N.D.
3	Tetrahydrofuran	No product	N.D.	N.D.
4	2-Methyltetrahydrofuran	15	2.5:1	N.D.
5	1,4-Dioxane	61	1:1	54:46/50:50
6	Ethyl acetate	67	1.5:1	53:47/52:48
7	Acetonitrile	55	5:1	78:22/62:38
8	Isobutyronitrile	No product	N.D.	N.D.
9	Benzonitrile	No product	N.D.	N.D.

Reaction conditions: **1a** (0.2 mmol, 2.0 equiv.), **2** (0.1 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (4 mol%), PPh_3 (8 mol%), 2,5-DTBQ (0.11 mmol, 1.1 equiv.), $Mg(OTf)_2$ (10 mol%), **L_3-PrAd** (10 mol%), Na_2CO_3 (1.2 equiv.) in solvent (2.0 mL) at 50 °C for 24 h. The yield and diastereomeric ratio (*dr*) were determined via ^1H NMR analysis of the crude reaction mixtures using 4-methylanisole as the internal standard. The enantiomeric ratio (*er*) was determined by chiral HPLC analysis. Compound **3a** was converted into its methyl ester derivative quantitatively with MeOH at 60 °C to determine its *er* value.

***Table S5*: Screening of palladium catalyst**

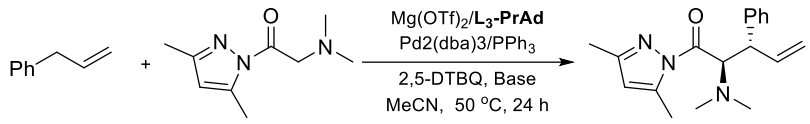


1a **2** **3a**

Entry	[Pd]	Yield	*dr* (*anti*:*syn*)	*er*
1	$Pd(PPh_3)_4$	trace	N.D.	N.D.
2	$Pd(MeCN)_2Cl_2$	trace	N.D.	N.D.
3	$Pd(MeCN)_4(BF_4)_2$	trace	N.D.	N.D.
4	$Pd(TFA)_2$	48	3.5:1	76:24/54:46
5	$Pd_2(dba)_3$	55	5:1	78:22/62:38
6	$Pd_2(dba)_3{\cdot}CHCl_3$	69	4.5:1	77:23/61:39

Reaction conditions: **1a** (0.2 mmol, 2.0 equiv), **2** (0.1 mmol, 1.0 equiv), **[Pd]** (4 or 8 mol% for dimer or monomer), PPh_3 (8 mol%), 2,5-DTBQ (0.11 mmol, 1.1 equiv.), $Mg(OTf)_2$ (10 mol%), **L_3-PrAd** (10 mol%), and Na_2CO_3 (0.12 mmol, 1.2 equiv.) in MeCN (2.0 mL) at 50 °C for 24 h. The yield and diastereomeric ratio (*dr*) were determined via ^1H NMR analysis of the crude reaction mixtures using 4-methylanisole as the internal standard. The enantiomeric ratio (*er*) was determined by chiral HPLC analysis. Compound **3a** was converted into its methyl ester derivative quantitatively with MeOH at 60 °C to determine its *er* value.

***Table S6*: Screening of base**

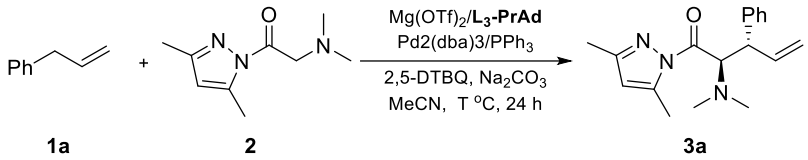


1a **2** **3a**

Entry	Base	Yield	*dr* (*anti*:*syn*)	*er*
1	DABCO	trace	N.D.[e]	N.D.
2	Et_3N	29	1:1	65:35/55:45
3	$^{i}Pr_2NEt$	48	3.5:1	76:24/54:46
4	$KO^{t}Bu$	trace	N.D.	N.D.
5	LiOAc	No product	N.D.	N.D.
6	KOAc	37	1:1	0/0
7	K_2CO_3	59	1:1	53:47/52:48
8	Na_2CO_3	55	5:1	78:22/62:38
9	Na_2HPO_4	47	3:1	77:24/61:39
10	K_2HPO_4	52	4.5:1.	78:22/63:37
11	No base	41	3:1	80:20/62:38

Reaction conditions: **1a** (0.2 mmol, 2.0 equiv.), **2** (0.1 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (4 mol%), PPh_3 (8 mol%), 2,5-DTBQ (0.11 mmol, 1.1 equiv.), $Mg(OTf)_2$ (10 mol%), **L_3-PrAd** (10 mol%), and base (0.12 mmol, 1.2 equiv.) in MeCN (2.0 mL) at 50 °C for 24 h. The yield and diastereomeric ratio (*dr*) were determined via ^1H NMR analysis of the crude reaction mixtures using 4-methylanisole as the internal standard. The enantiomeric ratio (*er*) was determined by chiral HPLC analysis. Compound **3a** was converted into its methyl ester derivative quantitatively with MeOH at 60 °C to determine its *er* value.

***Table S7*: Screening of temperature**

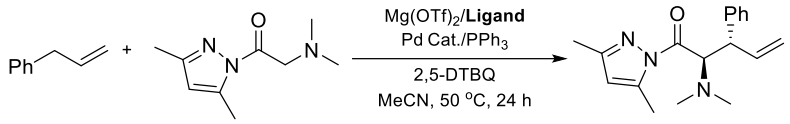


1a **2** **3a**

Entry	T °C	Yield	*dr* (*anti*:*syn*)	*er*
1	50	55	5:1	78:22/62:38
2	45	50	4:1	80:20/65:35
3	40	58	6:1	82:18/67:33
4	35	19	7:1	N.D.

Reaction conditions: **1a** (0.2 mmol, 2.0 equiv.), **2** (0.1 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (4 mol%), PPh_3 (8 mol%), 2,5-DTBQ (0.11 mmol, 1.1 equiv.), $Mg(OTf)_2$ (10 mol%), **L_3-PrAd** (10 mol%), and Na_2CO_3 (0.12 mmol, 1.2 equiv.) in MeCN (2.0 mL) at T °C for 24 h. The yield and diastereomeric ratio (*dr*) were determined via ^1H NMR analysis of the crude reaction mixtures using 4-methylanisole as the internal standard. The enantiomeric ratio (*er*) was determined by chiral HPLC analysis. Compound **3a** was converted into its methyl ester derivative quantitatively with MeOH at 60 °C to determine its *er* value.

***Table S8*: Optimization for reaction of dimethylglycine pyrazoleamide 1a with allylbenzene 2.**

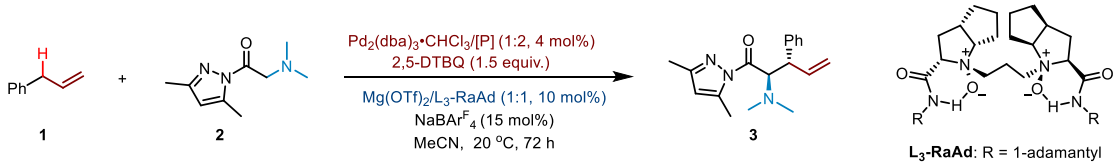


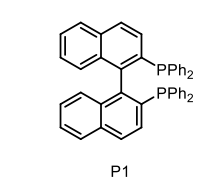
1a **2** **3a**

Entry	**[Pd]**	Additive	Yield	*dr* (*anti*:*syn*)	*er*
1	Pd_2dba_3	-	47	3:1	82:18/62:38
2 [a]	Pd_2dba_3	-	60	4.5:1	83:17/60:40
3 [a]	$Pd_2(dba)_3{\cdot}CHCl_3$	-	65	4.5:1	84:16/60:40
4 [a,b]	$Pd_2(dba)_3{\cdot}CHCl_3$	-	62	5:1	87:13/63:37
5 [a,b,c]	$Pd_2(dba)_3{\cdot}CHCl_3$	-	56	5:1	93:7/60:40
6 [a,b,c]	$Pd_2(dba)_3{\cdot}CHCl_3$	40 mg 4Å MS	trace	N.D.[e]	N.D.
7 [a,b,c]	$Pd_2(dba)_3{\cdot}CHCl_3$	TBAB	trace	N.D.	N.D.
8 [a,b,c]	$Pd_2(dba)_3{\cdot}CHCl_3$	15% mmol $NaBAr^F_4$	67	8:1	95:5/-

Reaction conditions: **1a** (0.2 mmol, 2.0 equiv.), **2** (0.1 mmol, 1.0 equiv.), **[Pd]** (4 or 8 mol% for dimer or monomer), PPh_3 (8 mol%), 2,5-DTBQ (0.11 mmol, 1.1 equiv.), $Mg(OTf)_2$ (10 mol%), **L_3-PrAd** (10 mol%), and Na_2CO_3 (0.12 mmol, 1.2 equiv.) in MeCN (2.0 mL) at T °C for 24 h. The yield and diastereomeric ratio (*dr*) were determined via ^1H NMR analysis of the crude reaction mixtures using 4-methylanisole as the internal standard. The enantiomeric ratio (*er*) was determined by chiral HPLC analysis. Compound **3a** was converted into its methyl ester derivative quantitatively with MeOH at 60 °C to determine its *er* value. [a] 2,5-DTBQ (1.5 equiv.). [b] At 20 °C for 72 h. [c] No base.

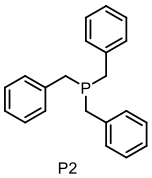
Table S9: Screening of achiral phosphorus ligands



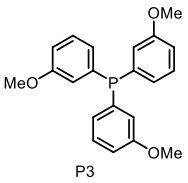


P1

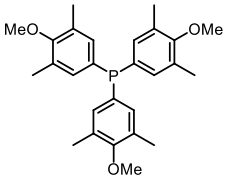
Pd2(dba)3•CHCl3/[P] (1:1, 4 mol%)



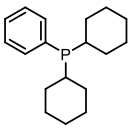
P2



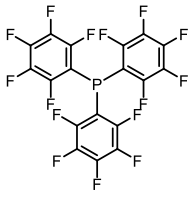
P3



P4



P5

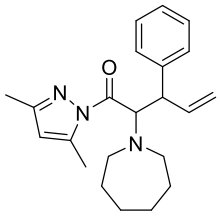


P6

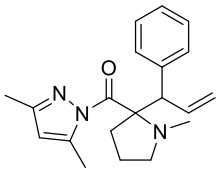
Entry	[P]	Yield
1	P1	N.D.
2	P2	trace
3	P3	trace
4	P4	trace
5	P5	<10%
6	P6	N.D.

Reaction conditions: **1a** (0.2 mmol, 2.0 equiv.), **2** (0.1 mmol, 1.0 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$ (4 mol%), [P] (4 or 8 mol% for dimer or monomer), 2,5-DTBQ (0.15 mmol, 1.5 equiv.), $Mg(OTf)_2$ (10 mol%), **L_3-PrAd** (10 mol%) in MeCN (2.0 mL) at 20 °C for 72 h. The yield was determined via ^1H NMR analysis of the crude reaction mixtures using 4-methylanisole as the internal standard.

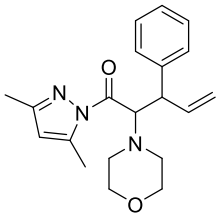
5. Scope Limitation



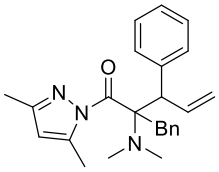
trace



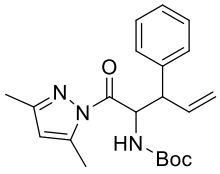
trace



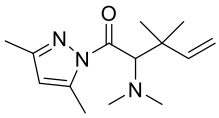
trace



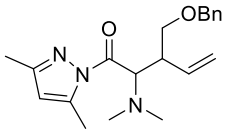
N.D.



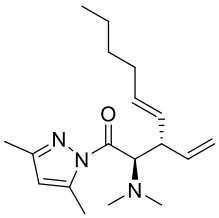
N.D.



N.D.

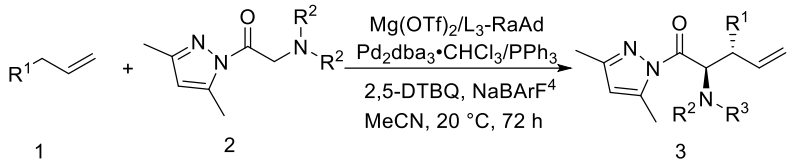


N.D.



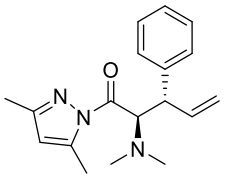
N.D.

6. General procedure for synthesis of [2,3]-rearrangement products



Under an Ar atmosphere, a tube was added $Mg(OTf)_2$ (0.02 mmol, 10mol%), *N,N'*-dioxide ligand **L_3-RaAd** (0.02 mmol, 10 mol%), amino amide **2** (0.2 mmol, 1.0 equiv.) and MeCN (1.5 mL). Another tube was added $Pd_2(dba)_3{\cdot}CHCl_3$ (4 mol%), PPh_3 (8 mol%) and MeCN (0.5 mL). After being stirred at 35 °C for 1 h, two tubes were mixed. Then, 2,5-DTBQ (1.5 equiv.), terminal alkene **1** (0.4 mmol, 2.0 equiv.) and MeCN (2.0 mL) were added sequentially. The reaction mixture was stirred at 20 °C for 48-72 h. After the reaction was completed, the suspension was filtered through a celite pad. The filtrate was concentrated under vacuum, and the residue was purified by silica gel chromatography to give the desired product **3**.

The product **3** was dissolved in 1.0 mL of methanol. The reaction was stirred at 60 °C overnight. The reaction mixture was subjected to column chromatography on silica gel to afford the corresponding methyl ester derivative. The *er* value was determined by HPLC using a Daicel chiral column. The analytical data of the products were summarized below.



(2*R*,3*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)-3-phenylpent-4-en-1-one (3a): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3a** was obtained as a colorless liquid (38.1 mg, 64% yield, *anti:syn* = 8:1).

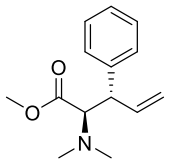
TLC: R_f = 0.7 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_D$ = +49.7 (*c* = 0.40, in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H), 7.18-7.11 (m, 2H), 7.09-7.03 (m, 1H), 6.25 – 6.14 (m, 1H), 5.77 (s, 1H), 5.36 (d, *J* = 11.7 Hz, 1H), 5.18 – 5.09 (m, 2H), 3.91 (m, 1H), 2.44 (s, 6H), 2.31 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 151.3, 143.3, 140.4, 139.7, 128.5, 128.3, 126.6, 115.9, 111.2, 66.4, 49.9, 41.3, 14.4, 13.8.

HRMS m/z $[M+H]^+$ calcd for $C_{18}H_{24}N_3O^+$ = 298.1919, found 298.1920.



Methyl (2*R*,3*S*)-2-(dimethylamino)-3-phenylpent-4-enoate (3a-methyl ester): Following the general procedure, product **3a-methyl ester** was obtained as a colorless liquid, 22.4 mg, 48% yield in two steps,

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_D$ = +26.1 (*c* = 0.12, in CH_2Cl_2).

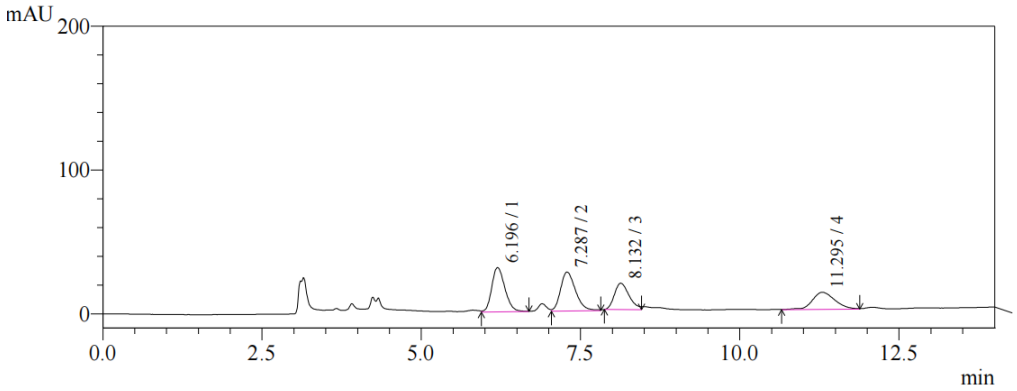
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 – 7.25 (m, 2H), 7.23 – 7.16 (m, 3H), 6.12 (m, 1H), 5.19 – 5.04 (m, 2H), 3.82 – 3.68 (m, 1H), 3.58 (d, *J*=11.7 Hz, 1H), 3.42 (s, 3H), 2.40 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.3, 140.8, 138.9, 128.6, 128.3, 126.9, 116.2, 71.8, 50.6, 49.8, 41.4.

HPLC: 95:5 *er*, chiral stationary column: OJ-H, mobile phase: hexane/^{i}PrOH = 99/1, flow rate 0.8 mL/min, λ = 254 nm, 30 °C, major isomer: t_r (major) = 6.3 min, t_r (minor) = 7.4 min.

HRMS m/z $[M+H]^+$ calcd for $C_{14}H_{20}NO_2^+$ = 234.1494, found 234.1493.

Racemic **3a-methyl ester**



1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

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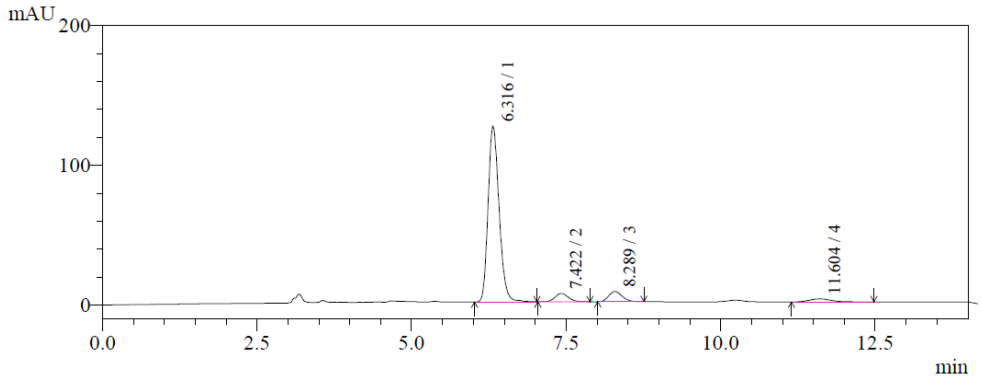
2	7.287	449643	27207	30.341	30.823
3	8.132	295599	18377	19.946	20.819
4	11.295	291136	11795	19.645	13.363
Total		1481983	88268	100.000	100.000

Enantioenriched **3a-methyl ester**

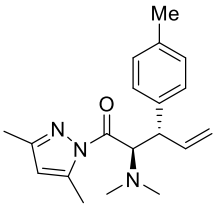


1 PDA Multi 1 / 220nm,4nm

PeakTable

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.316	1561485	125926	85.963	88.994
2	7.422	88696	5972	4.883	4.220
3	8.289	112649	7394	6.202	5.225
4	11.604	53640	2208	2.953	1.560
Total		1816469	141499	100.000	100.000



(2*R*,3*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)-3-(*p*-tolyl)pent-4-en-1-one (3b)

Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3b** was obtained as a colorless liquid (25.0 mg, 40% yield, *anti:syn* = 7:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}_{D}$ = +66.7 (*c* = 0.14, in CH_2Cl_2).

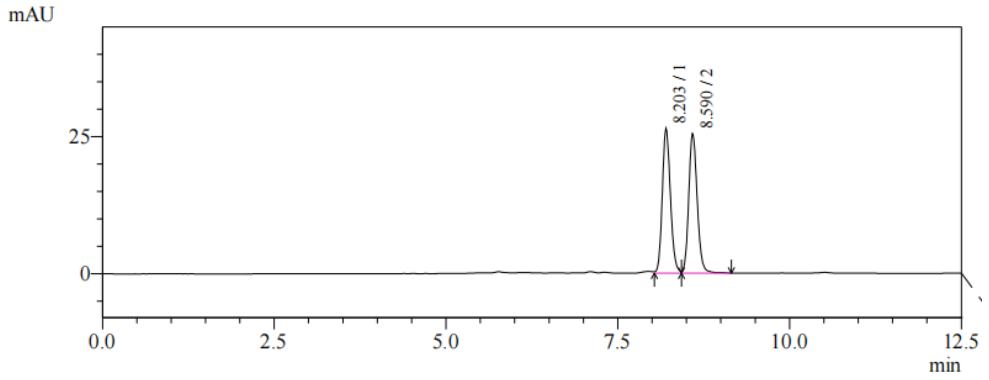
^{1}H NMR (500 MHz, $CDCl_3$**)** δ 7.12 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.21 – 6.12 (m, 1H), 5.79 (s, 1H), 5.34 (d, *J* = 11.7 Hz, 1H), 5.11 (s, 1H), 5.09 (d, *J* = 4.2 Hz, 1H), 3.88 (dd, *J* = 11.7, 8.6 Hz, 1H), 2.43 (s, 6H), 2.32 (s, 3H), 2.21 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 151.3, 143.4, 140.0, 137.4, 136.1, 129.0, 128.3, 115.6, 111.2, 66.3, 49.4, 41.3, 21.0, 14.4, 13.9.

HPLC: 93:7 *er*, chiral stationary column: AD-H, mobile phase: hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, t_r (major) = 8.6 min, t_r (minor) = 8.2 min.

HRMS m/z $[M+H]^+$ calcd for $C_{19}H_{26}N_3O^+$ = 312.2076, found 312.2076.

Racemic **3b**



1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

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1	8.203	216224	26399	49.761	50.913
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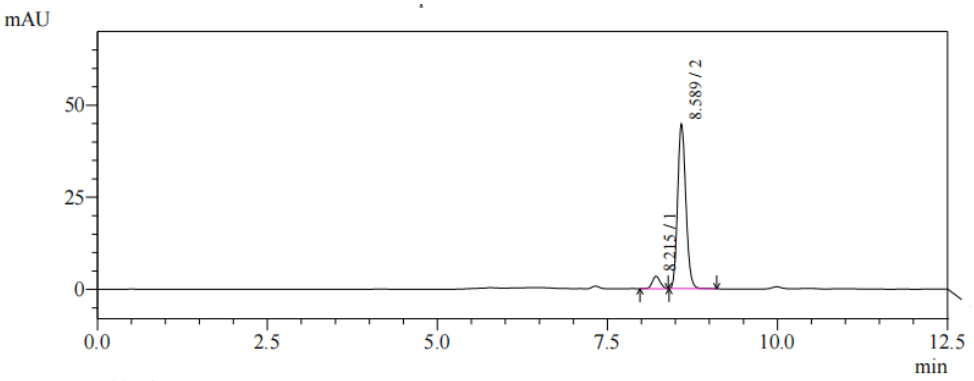
Total		434524	51851	100.000	100.000

Enantioenriched **3b**



1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
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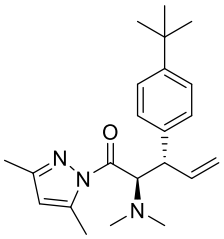
2	8.589	376632	44664	92.873	92.876
Total		405536	48090	100.000	100.000



(2*R*,3*S*)-3-(4-(*tert*-butyl)phenyl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)pent-4-en-1-one (3c) Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3c** was obtained as a colorless liquid (49.8 mg, 70% yield, *anti:syn* =9:1).

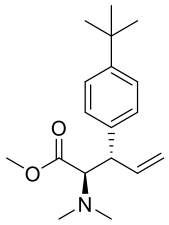
TLC: R_f = 0.7 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +44.8 (*c* = 0.21, in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.09 (m, 4H), 6.18 (m, 1H), 5.74 (s, 1H), 5.31 (d, *J* = 11.6 Hz, 1H), 5.16-5.10 (m, 2H), 3.93-3.80 (m, 1H), 2.46 (s, 6H), 2.27 (s, 3H), 2.17 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 150.1, 148.2, 142.2, 138.7, 136.0, 126.9, 124.0, 114.6, 109.9, 65.5, 48.6, 40.3, 33.2, 30.2, 13.2, 12.7.

HRMS m/z $[M+H]^+$ calcd for $C_{22}H_{32}N_3O^+$ = 354.2545, found 354.2546.



Methyl (2*R*,3*S*)-3-(4-(*tert*-butyl)phenyl)-2-(dimethylamino)pent-4-enoate (3c-methyl ester): Following the general procedure, product **3c-methyl ester** was obtained as a colorless liquid, 35.9 mg, 62% yield in two steps,

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +63.8 (*c* = 0.28, in CH_2Cl_2).

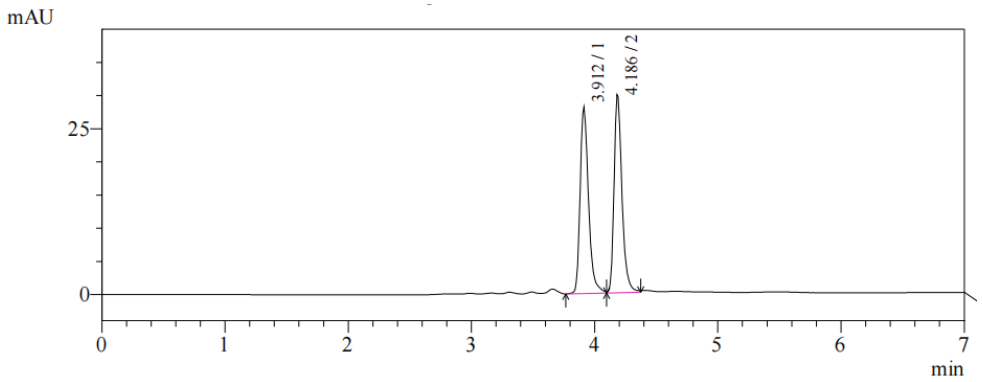
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 3H), 7.14 – 7.08 (m, 2H), 6.18 – 6.02 (m, 1H), 5.19 – 5.05 (m, 2H), 3.73 (dd, *J* = 12.0, 8.5 Hz, 1H), 3.56 (d, *J* = 11.6 Hz, 1H), 3.41 (s, 3H), 2.39 (s, 6H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 149.7, 139.1, 137.6, 127.7, 125.5, 115.9, 71.8, 50.6, 49.4, 41.4, 34.4, 31.4.

HPLC: 94:6 *er*, chiral stationary column: OD-H, mobile phase: hexane/^{i}PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm, 30 ^{o}C, t_r (major) = 3.9 min, t_r (minor) = 4.2 min.

HRMS m/z $[M+H]^+$ calcd for $C_{18}H_{28}NO_2^+$ = 290.2115, found 290.2116.

Racemic **3c-methyl ester**



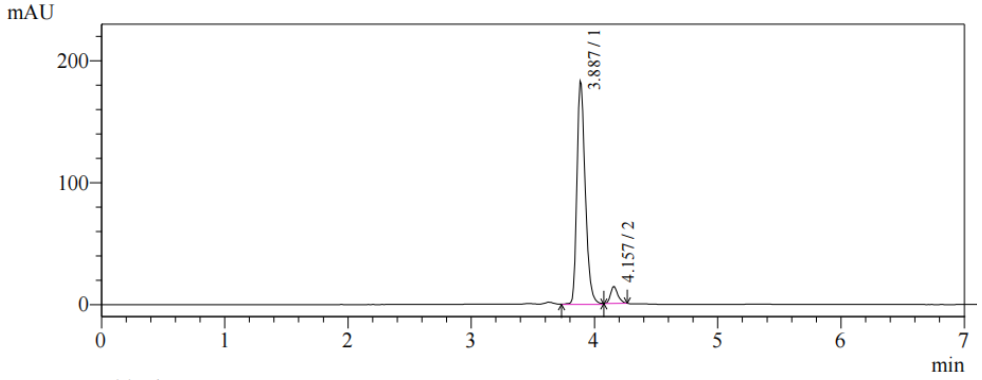
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.912	132809	28167	50.014	48.532
2	4.186	132734	29871	49.986	51.468
Total		265543	58039	100.000	100.000

Enantioenriched **3c-methyl ester**

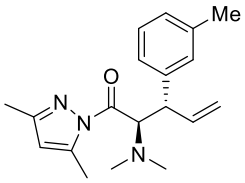


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.887	864134	183429	93.755	92.929
2	4.157	57562	13958	6.245	7.071
Total		921696	197387	100.000	100.000



(2*S*,3*R*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)-3-(m-tolyl)pent-4-en-1-one (3d): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3d** was obtained as a colorless liquid (44.0 mg, 71% yield, *anti:syn* >19:1).

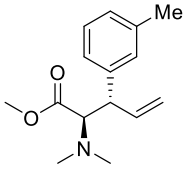
TLC: R_f = 0.7 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}_{D}$ = +54.9 (*c* = 0.46, in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 6.98 (m, 3H), 6.87 (d, *J* = 6.0 Hz, 1H), 6.26 – 6.09 (m, 1H), 5.77 (s, 1H), 5.36 (d, *J* = 11.7 Hz, 1H), 5.17 – 5.10 (m, 2H), 3.87 (dd, *J* = 11.7, 8.7 Hz, 1H), 2.45 (s, 6H), 2.30 (s, 3H), 2.21 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 151.3, 143.3, 140.1, 139.8, 137.8, 129.3, 128.1, 127.4, 125.5, 115.8, 111.1, 66.3, 50.0, 41.3, 21.3, 14.4, 13.8.

HRMS m/z $[M+H]^+$ calcd for $C_{19}H_{26}N_3O^+$ = 312.2076, found 312.2072.



Methyl (2*R*,3*S*)-2-(dimethylamino)-3-(*m*-tolyl)pent-4-enoate (3d-methyl ester): Following the general procedure, product **3d-methyl ester** was obtained as a colorless liquid, 31.5 mg, 64% yield in two steps,

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}_{D}$ = +41.6 (*c* = 0.30, in CH_2Cl_2).

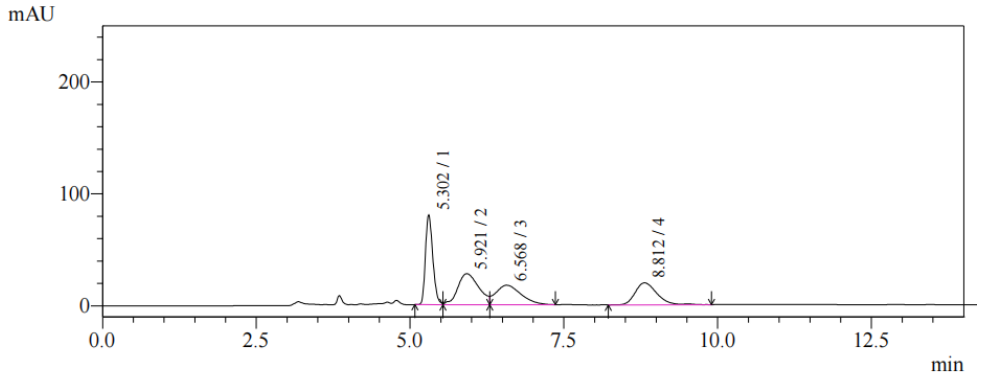
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.12 (m, 1H), 7.04-6.96 (m, 3H), 6.18-6.03 (m, 1H), 5.17 – 5.06 (m, 2H), 3.75 – 3.68 (m, 1H), 3.57 (d, *J* = 11.7 Hz, 1H), 3.43 (s, 3H), 2.39 (s, 6H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.3, 140.8, 139.1, 138.2, 129.0, 128.5, 127.7, 125.2, 116.0, 71.7, 50.6, 49.8, 41.4, 21.5.

HPLC: 93.5:6.5 *er*, chiral stationary column: OJ-H, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm, 30 °C, major isomer: t_r (major) = 5.2 min, t_r (minor) = 5.9 min.

HRMS m/z $[M+H]^+$ calcd for $C_{15}H_{22}NO_2^+$ = 248.1651, found 248.1646.

Racemic **3d-methyl ester**



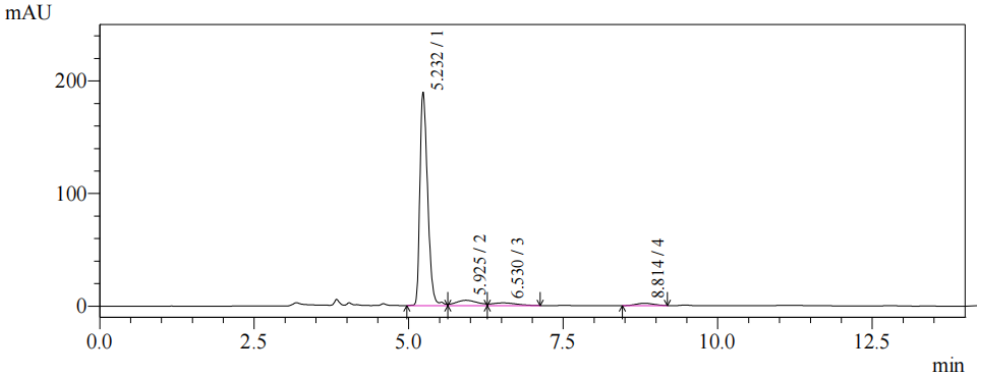
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.302	666116	80217	28.980	55.334
2	5.921	656847	27690	28.577	19.101
3	6.568	492649	17374	21.433	11.984
4	8.812	482926	19689	21.010	13.581
Total		2298538	144969	100.000	100.000

Enantioenriched **3d-methyl ester**

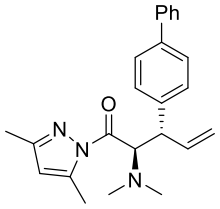


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.232	1656741	189413	88.184	95.382
2	5.925	114247	4669	6.081	2.351
3	6.530	65555	2388	3.489	1.203
4	8.814	42182	2114	2.245	1.064
Total		1878725	198583	100.000	100.000



(2*R*,3*S*)-3-([1,1'-biphenyl]-4-yl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)pent-4-en-1-one (3e): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3e** was obtained as a colorless liquid (53.0 mg, 71% yield, *anti:syn* = 6:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}_{D}$ = +78.5 (*c* = 0.40, in CH_2Cl_2).

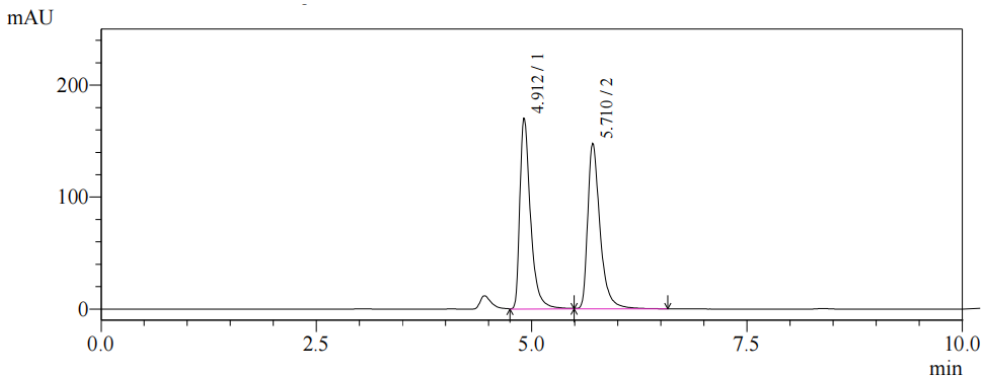
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 – 7.46 (m, 2H), 7.41 – 7.35 (m, 4H), 7.33 – 7.27 (m, 3H), 6.29 – 6.15 (m, 1H), 5.77 (s, 1H), 5.39 (d, *J* = 11.7 Hz, 1H), 5.22 – 5.12 (m, 2H), 3.99 – 3.94 (m, 1H), 2.46 (s, 6H), 2.32 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.0, 151.4, 143.4, 140.9, 139.7, 139.6, 139.4, 128.9, 128.7, 127.1, 127.0, 127.0, 116.0, 111.3, 66.4, 49.6, 41.4, 14.4, 13.9.

HPLC: 95:5 *er*, chiral stationary column: AD-H, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm, 30 °C, t_r (major) = 6.1 min, t_r (minor) = 5.2 min.

HRMS m/z $[M+H]^+$ calcd for $C_{24}H_{28}N_3O^+$ = 374.2227, found 374.2229.

Racemic **3e**



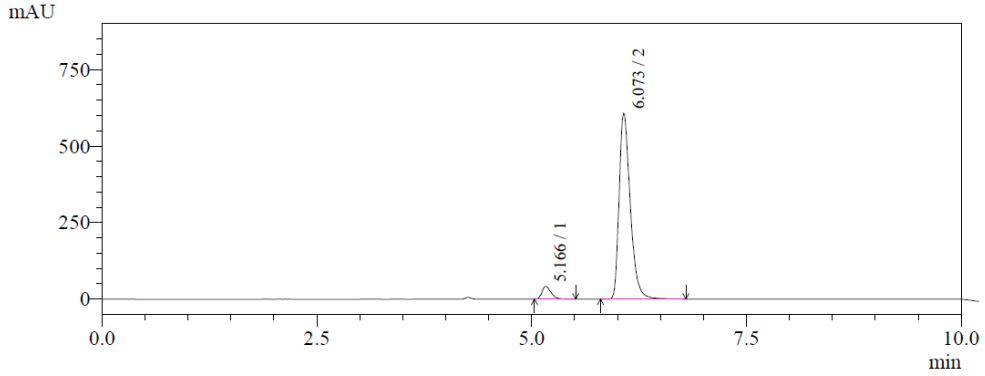
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.912	1474243	170445	49.979	53.520
2	5.710	1475477	148027	50.021	46.480
Total		2949720	318472	100.000	100.000

Enantioenriched **3e**

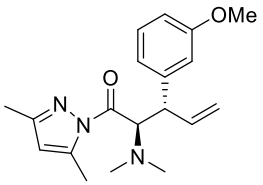


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.166	310006	41507	5.355	6.396
2	6.073	5478892	607479	94.645	93.604
Total		5788899	648985	100.000	100.000



(2*R*,3*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)-3-(3-methoxyphenyl)pent-4-en-1-one (3f): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3f** was obtained as a colorless liquid (42.0 mg, 64% yield, *anti:syn* = 10:1).

TLC: R_f = 0.8 (petroleum ether/ethyl acetate 10/1).

[α] $^{20}_{D}$ = +75.7 (*c* = 0.74, in CH_2Cl_2).

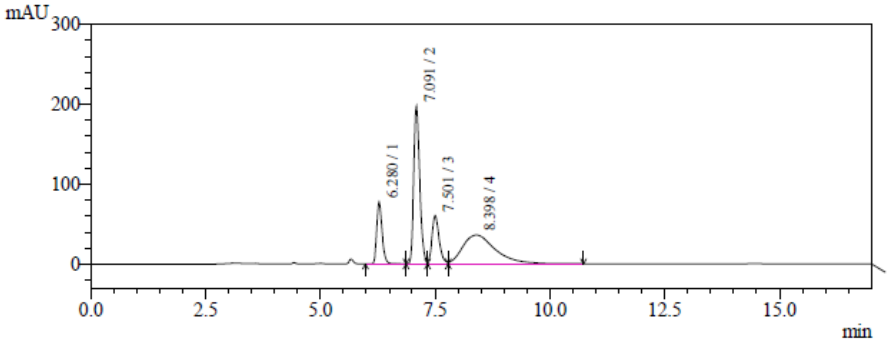
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.9 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.70 – 6.62 (m, 1.0 Hz, 1H), 6.26 – 6.15 (m, 1H), 5.83 (d, *J* = 1.1 Hz, 1H), 5.42 (d, *J* = 11.8 Hz, 1H), 5.19 (dd, *J* = 2.0, 1.0 Hz, 1H), 5.18 – 5.14 (m, 1H), 3.93 (dd, *J* = 11.8, 8.5 Hz, 1H), 3.73 (s, 3H), 2.48 (s, 6H), 2.36 (d, *J* = 1.1 Hz, 3H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 170.8, 159.7, 159.5, 151.6, 151.3, 143.6, 143.4, 143.0, 141.9, 139.6, 138.6, 129.5, 129.3, 121.1, 120.7, 116.6, 115.9, 114.6, 113.1, 113.0, 111.6, 111.4, 111.2, 66.1, 65.8, 55.2, 55.1, 50.2, 49.9, 41.3, 14.7, 14.4, 14.0, 13.8.

HPLC: 95:5 *er*, chiral stationary column: AD, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm, 30 °C, t_r (major) = 6.4 min, t_r (minor) = 7.5 min.

HRMS m/z $[M+H]^+$ calcd for $C_{19}H_{26}N_3O_2^+$ = 328.2020, found 328.2019.

Racemic **3f**



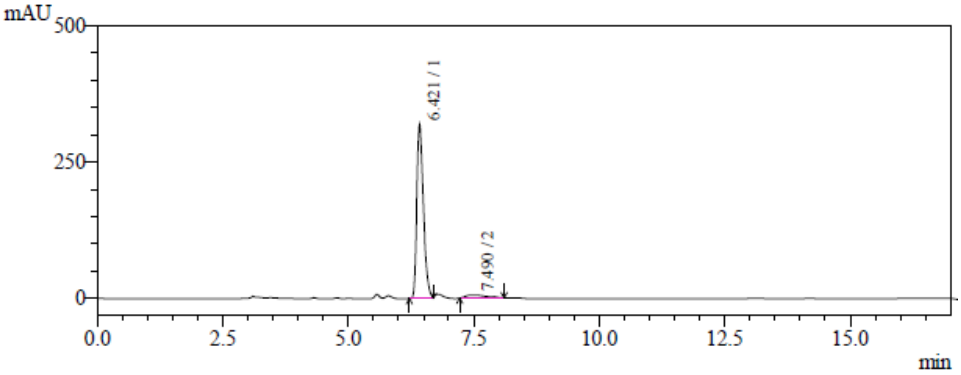
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.280	639648	77720	13.001	20.888
2	7.091	1809276	197633	36.774	53.115
3	7.501	659902	60702	13.413	16.314
4	8.398	1811197	36029	36.813	9.683
Total		4920023	372084	100.000	100.000

Enantioenriched **3f**

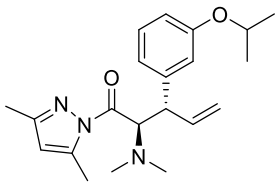


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.421	2949775	319695	94.989	98.318
2	7.490	155620	5470	5.011	1.682
Total		3105395	325166	100.000	100.000



(2*R*,3*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)-3-(3-isopropoxyphenyl)pent-4-en-1-one (3g): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3g** was obtained as a colorless liquid (42.0 mg, 59% yield, *anti:syn* = 15:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{20}{}_{D}$ = +99.9 (*c* = 0.24, in CH_2Cl_2).

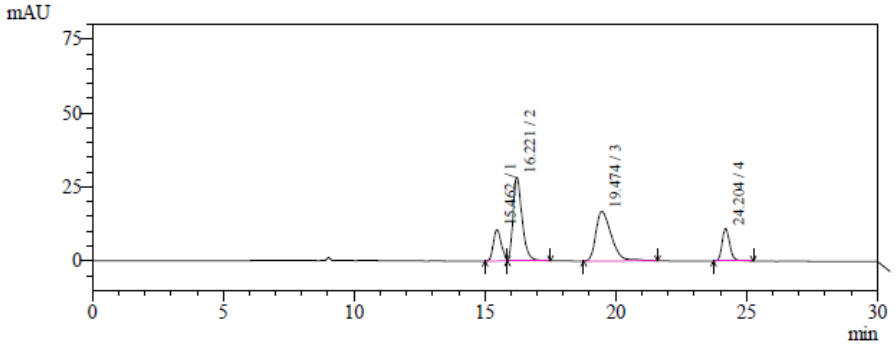
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.64 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.27 – 6.14 (m, 1H), 5.82 (s, 1H), 5.39 (d, *J* = 11.7 Hz, 1H), 5.20 – 5.13 (m, 2H), 4.51 – 4.40 (m, 1H), 3.91 (dd, *J* = 11.7, 8.6 Hz, 1H), 2.47 (s, 6H), 2.36 (s, 3H), 2.20 (s, 3H), 1.29 (d, *J* = 6.0 Hz, 3H), 1.24 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 157.8, 151.3, 143.4, 141.8, 139.6, 129.3, 121.1, 115.9, 115.3, 115.1, 111.2, 69.7, 66.2, 49.9, 41.3, 22.1, 22.0, 14.4, 13.8.

HPLC: 93:7 *er*, chiral stationary column: OD, mobile phase: hexane/^{i}PrOH = 99.7/0.3, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, t_r (major) = 16.3 min, t_r (minor) = 19.1 min.

HRMS m/z $[M+H]^+$ calcd for $C_{21}H_{30}N_3O_2^+$ = 356.2333, found 356.2332.

Racemic **3g**



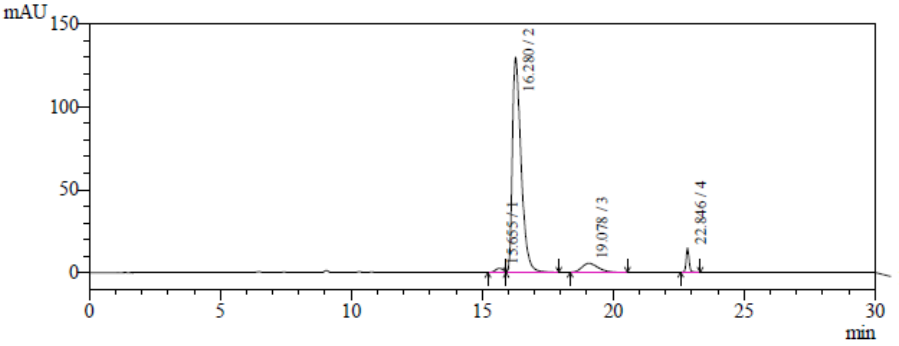
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.462	227498	10587	12.426	15.867
2	16.221	685805	28355	37.460	42.495
3	19.474	689733	16741	37.675	25.090
4	24.204	227717	11042	12.438	16.548
Total		1830753	66725	100.000	100.000

Enantioenriched **3g**

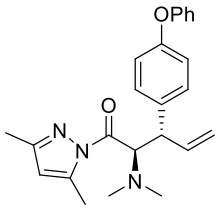


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.655	50783	2464	1.495	1.625
2	16.280	3006226	129365	88.486	85.317
3	19.078	229811	5340	6.764	3.522
4	22.846	110572	14459	3.255	9.536
Total		3397391	151629	100.000	100.000



(2*R*,3*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)-3-(4-phenoxyphenyl)pent-4-en-1-one (3h):Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3h** was obtained as a colorless liquid (55.0 mg, 71% yield, *anti:syn* = 6:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}_{D}$ = +103.5 (*c* = 0.42, in CH_2Cl_2).

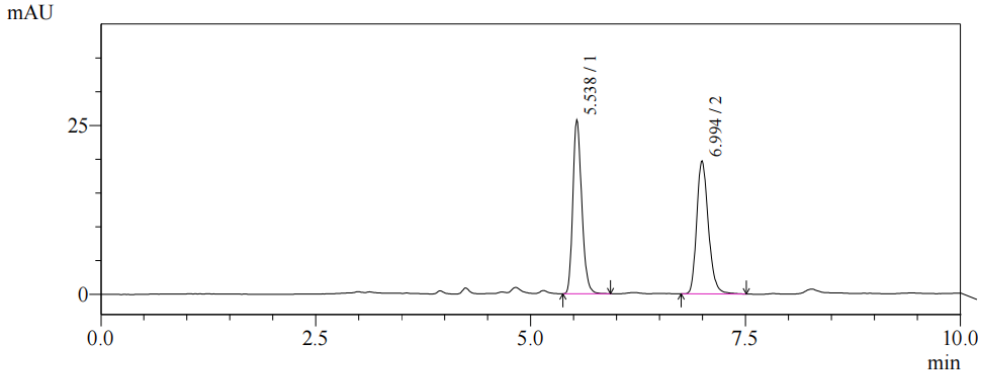
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 – 7.24 (m, 3H), 7.21 – 7.17 (m, 2H), 7.08 – 7.02 (m, 1H), 6.86 – 6.78 (m, 4H), 6.25 –6.17 (m, 1H), 5.82 (s, 1H), 5.32 (d, *J* = 11.7 Hz, 1H), 5.20 – 5.12 (m, 2H), 3.92 – 3.87 (m, 1H), 2.46 (s, 6H), 2.34 (d, *J* =0.8 Hz, 3H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.5, 155.5, 151.4, 143.3, 139.5, 135.4, 129.9, 129.6, 122.9, 119.1, 118.4, 116.1, 111.2, 66.7, 49.4, 41.3, 14.5, 13.8.

HPLC: 93:7 *er*, chiral stationary column: AD-H, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm, 30 °C, t_r (major) = 7.2 min, t_r (minor) = 5.7 min.

HRMS m/z $[M+H]^+$ calcd for $C_{24}H_{28}N_3O_2^+$ = 390.2176, found 390.2175.

Racemic **3h**



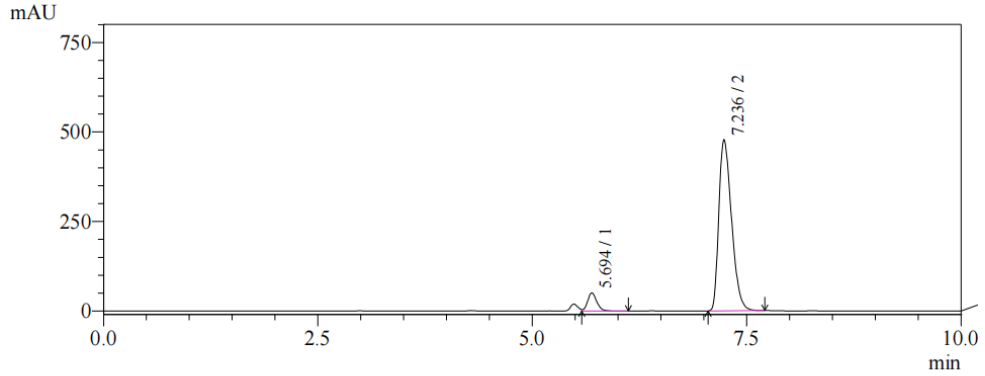
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.538	185481	25766	49.908	56.640
2	6.994	186167	19725	50.092	43.360
Total		371648	45491	100.000	100.000

Enantioenriched **3h**

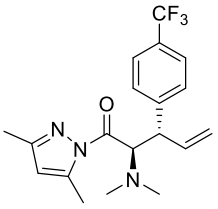


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.694	373811	51009	7.046	9.637
2	7.236	4931170	478299	92.954	90.363
Total		5304981	529308	100.000	100.000



(2*R*,3*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)-3-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (3i) Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3i** was obtained as a colorless liquid (38.0 mg, 52% yield, *anti:syn* = 2:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}_{D}$ = +57.5 (*c* = 0.69, in CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 6.24-6.13 (m, 1H), 5.81 (s, 1H), 5.36 (d, *J* = 11.7 Hz, 1H), 5.17 (d, *J* = 10.2 Hz, 1H), 5.10 (d, *J* = 17.1 Hz, 1H), 3.98 (dd, *J* = 11.7, 8.3 Hz, 1H), 2.44 (s, 6H), 2.33 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 151.7, 144.8, 143.5, 139.0, 129.0, 125.4, 125.3 (q, J_{C-F} = 3.9 Hz, J_{C-F} = 8.0 Hz), 123.2, 116.7, 111.5, 66.3, 49.6, 41.4, 14.4, 13.8.

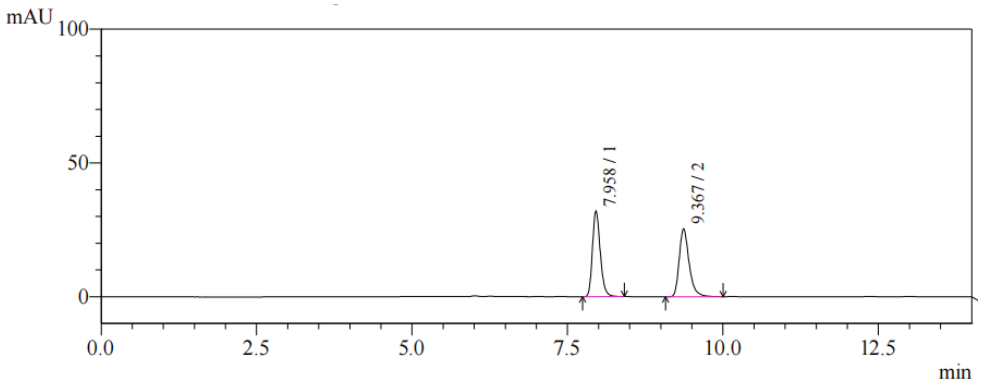
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.51.

HPLC: major isomer, 90:10 *er*, chiral stationary column: IA, mobile phase: hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, t_r (major) = 9.2 min, t_r (minor) = 7.6 min.

minor isomer, 65:35 *er*, chiral stationary column: IA, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, t_r (major) = 10.1 min, t_r (minor) = 8.6 min.

HRMS m/z $[M+H]^+$ calcd for $C_{19}H_{23}F_3N_3O^+$ = 366.1793, found 366.1790.

Racemic-major **3i**



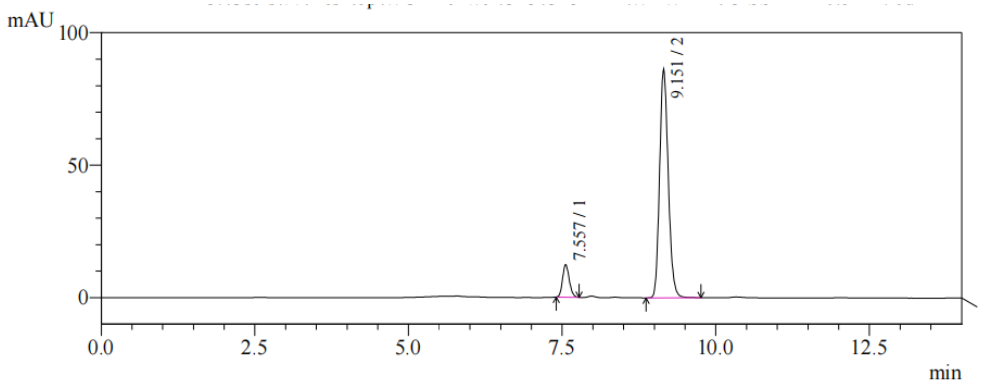
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.958	281450	32111	49.896	55.818
2	9.367	282621	25416	50.104	44.182
Total		564071	57527	100.000	100.000

Enantioenriched-major **3i**



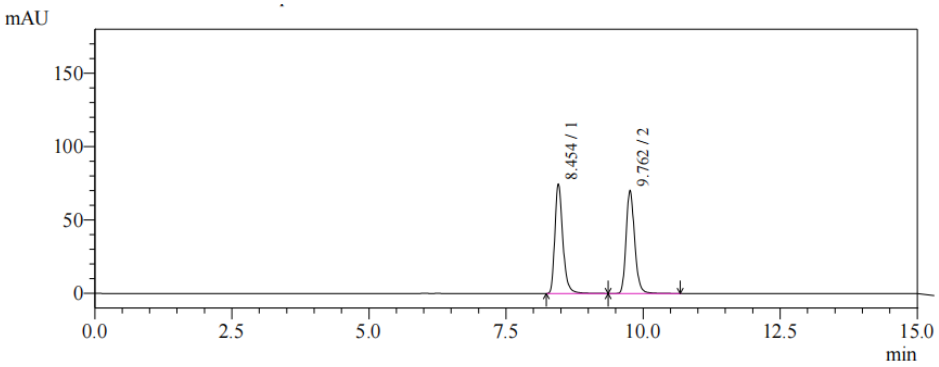
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.557	93462	12223	9.972	12.384
2	9.151	843785	86476	90.028	87.616
Total		937247	98698	100.000	100.000

Racemic-minor **3i**



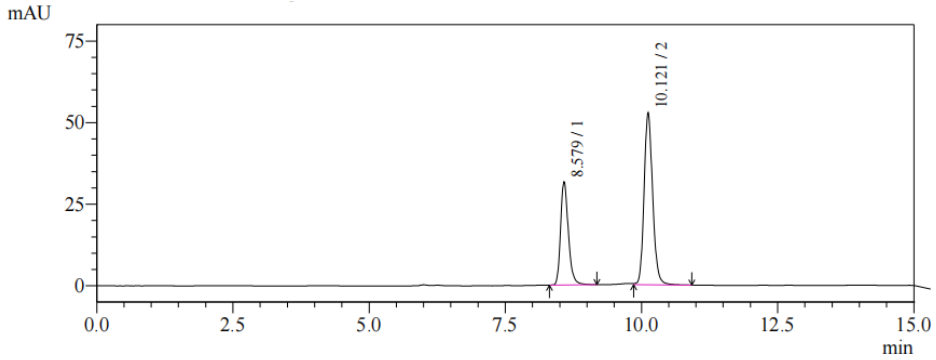
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.454	757561	74752	49.756	51.520
2	9.762	764988	70341	50.244	48.480
Total		1522549	145092	100.000	100.000

Enantioenriched-minor **3i**

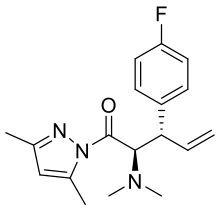


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.579	314524	31702	35.137	37.493
2	10.121	580614	52853	64.863	62.507
Total		895137	84555	100.000	100.000



(2*R*,3*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)-3-(4-fluorophenyl)pent-4-en-1-one (3j): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3j** was obtained as a colorless liquid (29.0 mg, 46% yield, *anti:syn* = 5:1).

TLC: R_f = 0.7 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +46.4 (*c* = 0.54, in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 – 7.16 (m, 2H), 6.90 – 6.79 (m, 2H), 6.22 – 6.13 (m, 1H), 5.80 (s, 1H), 5.31 (d, *J*=11.8 Hz, 1H), 5.19 – 5.05 (m, 2H), 2.43 (s, 6H), 2.33 (s, 3H), 2.17 (s, 3H).

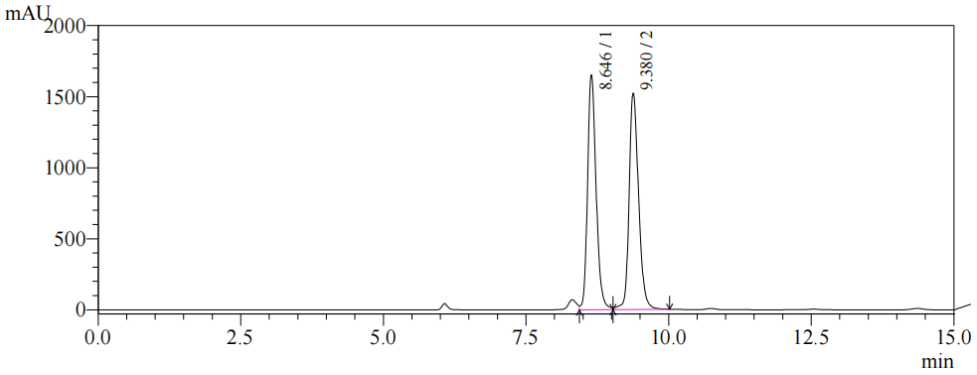
^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.9, 161.6 (d, $J_{C\text{-}F}$ = 243.3 Hz) 151.5, 143.4, 139.5, 136.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.1 (d, $J_{C\text{-}F}$ = 7.9 Hz), 116.1, 115.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), 111.4, 66.5, 49.0, 41.3, 14.4, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -72.98.

HPLC: 92.5:7.5 *er*, chiral stationary column: IA, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, t_r (major) = 9.1 min, t_r (minor) = 8.4 min.

HRMS m/z $[M+H]^+$ calcd for $C_{18}H_{23}FN_3O^+$ = 316.1825, found 316.1822.

Racemic **3j**



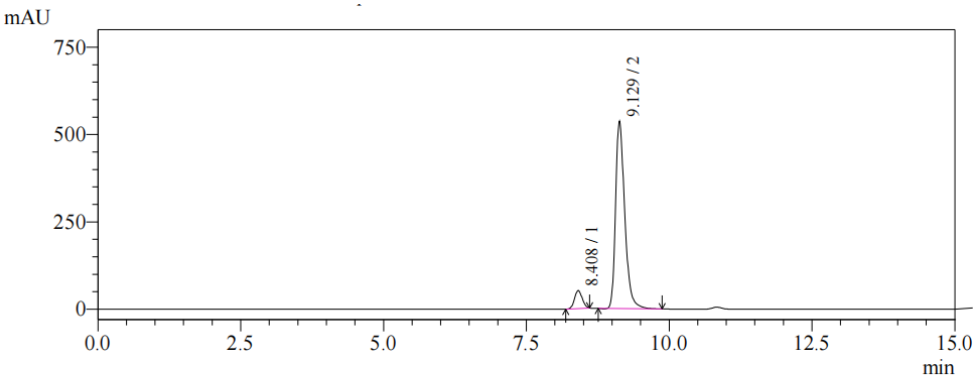
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.646	17231323	1652374	49.417	52.037
2	9.380	17637861	1523032	50.583	47.963
Total		34869184	3175406	100.000	100.000

Enantioenriched **3j**

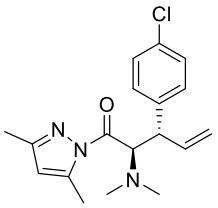


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.408	489580	51931	7.562	8.812
2	9.129	5984910	537378	92.438	91.188
Total		6474489	589309	100.000	100.000



(2R,3S)-3-(4-chlorophenyl)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-(dimethylamino)pent-4-en-1-one (3k): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3k** was obtained as a colorless liquid (31.9 mg, 48% yield, *anti:syn* = 5:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +88.3 (*c* = 0.24, in CH_2Cl_2).

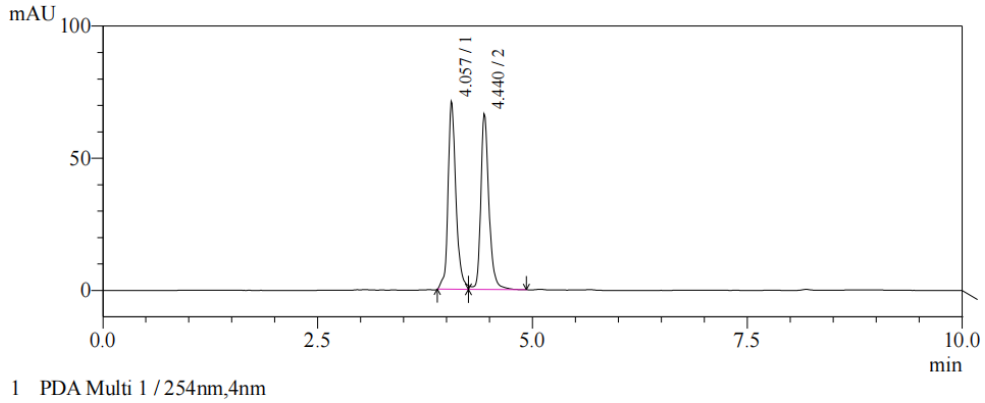
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 – 7.10 (m, 4H), 6.23 – 6.09 (m, 1H), 5.82 (s, 1H), 5.31 (d, *J* = 11.8 Hz, 1H), 5.19 – 5.04 (m, 2H), 3.94 – 3.84 (m, 1H), 2.42 (s, 6H), 2.35 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.6, 151.6, 143.4, 139.3, 139.1, 132.4, 129.9, 128.5, 116.3, 111.4, 66.3, 49.1, 41.3, 14.5, 13.9.

HPLC: 90:10 *er*, chiral stationary column: IA, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm, 30 °C, t_r (major) = 4.8 min, t_r (minor) = 4.3 min.

HRMS m/z $[M+H]^+$ calcd for $C_{18}H_{23}ClN_3O^+$ = 332.1530, found 332.1530.

Racemic **3k**



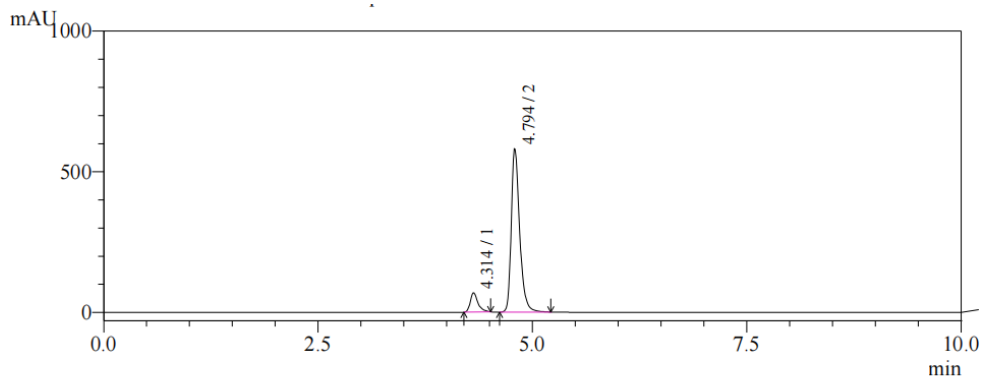
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.057	453036	71161	50.893	51.715
2	4.440	437136	66441	49.107	48.285
Total		890173	137602	100.000	100.000

Enantioenriched **3k**

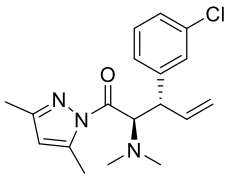


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.314	425555	68551	9.647	10.542
2	4.794	3985822	581701	90.353	89.458
Total		4411378	650252	100.000	100.000



(2*R*,3*S*)-3-(3-chlorophenyl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)pent-4-en-1-one (3l) Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3l** was obtained as a colorless liquid (34.0 mg, 51% yield, *anti:syn* = 17:1).

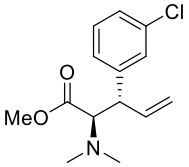
TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_D$ = +42.6 (*c* = 0.26, in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 1H), 7.12 – 7.01 (m, 3H), 6.21 – 6.22 (m, 1H), 5.80 (s, 1H), 5.33 (d, *J* = 11.7 Hz, 1H), 5.19 – 5.08 (m, 2H), 3.87 (dd, *J* = 11.7, 8.4 Hz, 1H), 2.44 (s, 6H), 2.33 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 151.7, 143.4, 142.5, 139.1, 134.1, 129.5, 128.9, 126.9, 126.9, 116.6, 111.4, 66.3, 49.7, 41.3, 14.4, 13.8.

HRMS m/z $[M+H]^+$ calcd for $C_{18}H_{23}ClN_3O^+$ = 332.1530, found 332.1527.



methyl (2*R*,3*S*)-3-(3-chlorophenyl)-2-(dimethylamino)pent-4-enoate (3l-methyl ester) Following the general procedure, product **3l-methyl ester** was obtained as a colorless liquid, 24.1 mg, 48% yield in two steps,

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_D$ = +63.3 (*c* = 0.34, in CH_2Cl_2).

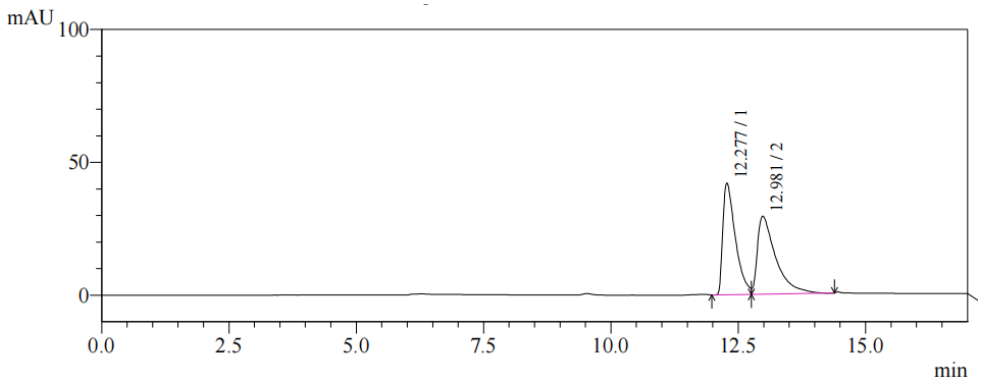
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 3H), 7.08 (d, *J* = 7.0 Hz, 1H), 6.17 – 5.99 (m, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 5.09 (d, *J* = 17.1 Hz, 1H), 3.73 (dd, *J* = 11.6, 8.5 Hz, 1H), 3.53 (d, *J* = 11.7 Hz, 1H), 3.46 (s, 3H), 2.38 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 142.9, 138.2, 134.3, 129.8, 128.5, 127.1, 126.5, 116.7, 71.5, 50.8, 49.4, 41.3.

HPLC: 92:8 *er*, chiral stationary column: AD-H, mobile phase: hexane/^{i}PrOH = 99.8/0.2, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, t_r (major) = 13.1 min, t_r (minor) = 12.4 min.

HRMS m/z $[M+H]^+$ calcd for $C_{14}H_{19}ClNO_2^+$ = 268.1104, found 268.1100.

Racemic **3l-methyl ester**



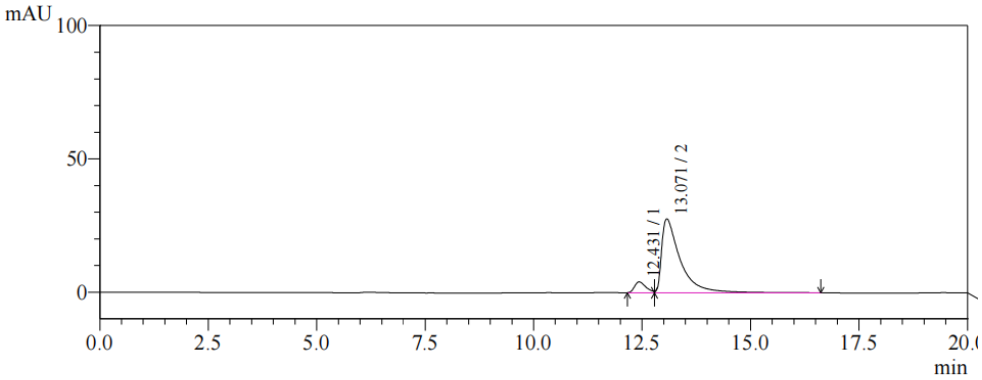
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.277	718670	41997	49.511	58.859
2	12.981	732863	29355	50.489	41.141
Total		1451533	71352	100.000	100.000

Enantioenriched **3l-methyl ester**

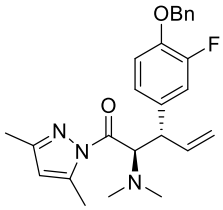


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.431	73751	4076	8.148	12.808
2	13.071	831436	27749	91.852	87.192
Total		905187	31825	100.000	100.000



(2*R*,3*S*)-3-(4-(benzyloxy)-3-fluorophenyl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)pent-4-en-1-one (3m): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3m** was obtained as a colorless liquid (36.2 mg, 43% yield, *anti:syn* = 9:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +72.6 (*c* = 0.62, in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.29 (m, 5H), 7.03 – 7.00 (m, 1H), 6.89 – 6.87 (m, 1H), 6.80 –6.76 (m, 1H), 6.18 – 6.09 (m, 1H), 5.79 (s, 1H), 5.28 (d, *J* = 11.7 Hz, 1H), 5.16 – 5.08 (m, 2H), 5.02 (s, 2H), 3.86 – 3.81 (m, 1H), 2.42 (s, 6H), 2.33 (d, *J* = 0.8 Hz, 3H), 2.17 (s, 3H).

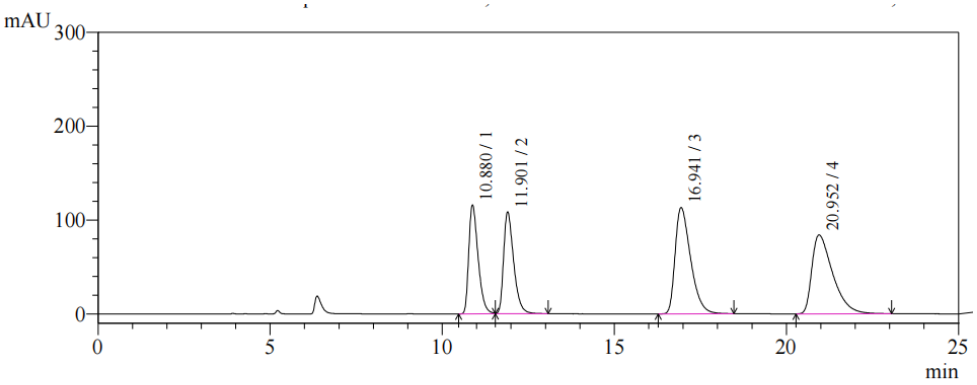
^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.0, 152.6 (d, $J_{C\text{-}F}$ = 244.6 Hz), 151.6, 145.3 (d, $J_{C\text{-}F}$ = 10.8 Hz), 143.4, 139.3, 136.7, 135.1 (d, $J_{C\text{-}F}$ = 5.9 Hz), 128.6, 128.1, 127.4, 124.2 (d, $J_{C\text{-}F}$ = 3.5 Hz), 116.4 (d, $J_{C\text{-}F}$ = 18.9 Hz), 116.1, 115.4 (d, $J_{C\text{-}F}$ = 2.1 Hz), 111.4, 71.4, 66.4, 48.9, 41.3, 14.4, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ = –133.76.

HPLC: 94.5:5.5 *er*, chiral stationary column: OD-H, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm, 30 °C, major isomer: t_r (major) = 10.5 min, t_r (minor) = 11.7 min.

HRMS m/z $[M+H]^+$ calcd for $C_{25}H_{29}FN_3O_2^+$ = 422.2238, found 422.2237.

Racemic **3m**



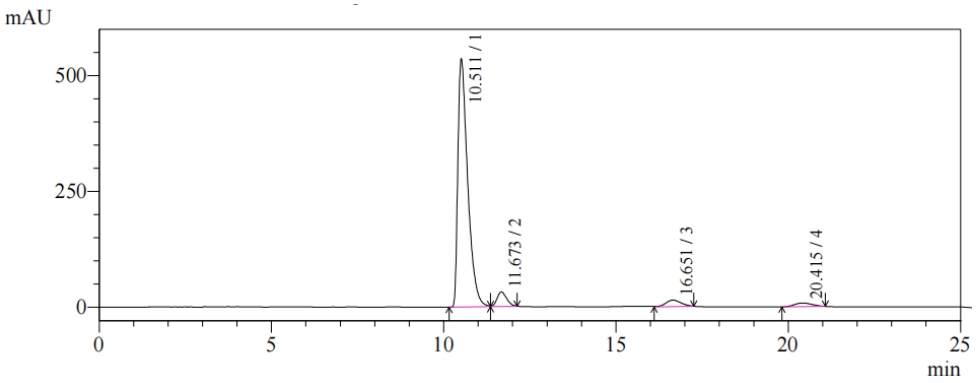
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.880	2196099	116314	19.105	27.517
2	11.901	2210197	108694	19.228	25.714
3	16.941	3545538	113510	30.845	26.854
4	20.952	3542945	84178	30.822	19.914
Total		11494779	422695	100.000	100.000

Enantioenriched **3m**

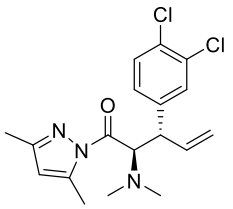


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.511	10586914	536678	88.936	90.969
2	11.673	600474	31272	5.044	5.301
3	16.651	434917	14130	3.654	2.395
4	20.415	281706	7876	2.366	1.335
Total		11904011	589956	100.000	100.000



(2*R*,3*S*)-3-(3,4-dichlorophenyl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)pent-4-en-1-one (3n) Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3n** was obtained as a colorless liquid (47.4 mg, 65% yield, *anti:syn* = 8:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}_{D}$ = +54.8 (*c* = 0.70, in CH_2Cl_2).

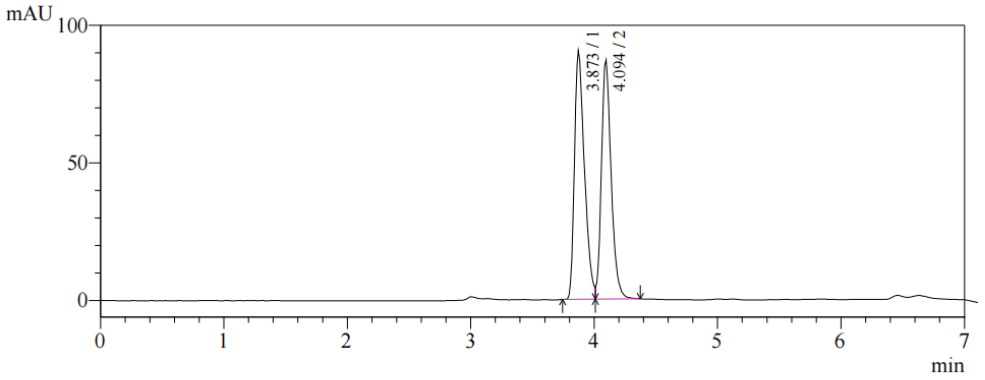
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 2.1 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.06 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.19-6.08 (m, 1H), 5.83 (s, 1H), 5.30 (d, *J* = 11.7 Hz, 1H), 5.17 (dt, *J* = 10.1, 1.1 Hz, 1H), 5.10 (dt, *J* = 17.1, 1.3 Hz, 1H), 3.86 (dd, *J* = 11.7, 8.2 Hz, 1H), 2.42 (s, 6H), 2.36 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 151.9, 143.5, 140.9, 138.7, 132.3, 130.8, 130.7, 130.2, 128.1, 116.8, 111.6, 66.3, 49.0, 41.3, 14.4, 13.8.

HPLC: 89:11 *er* chiral stationary column: AD-H, mobile phase: hexane/^{i}PrOH = 100/0, flow rate 1.0 mL/min, λ = 254 nm, 30 °C, t_r (major) = 4.1 min, t_r (minor) = 3.9 min.

HRMS m/z $[M+H]^+$ calcd for $C_{18}H_{22}Cl_2N_3O^+$ = 366.1140, found 366.1142.

Racemic **3n**



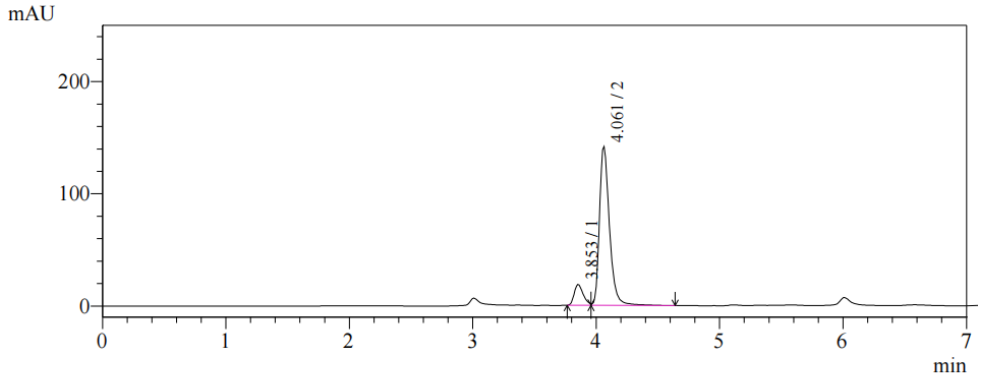
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.873	510068	90438	51.803	50.985
2	4.094	474561	86945	48.197	49.015
Total		984629	177384	100.000	100.000

Enantioenriched **3n**

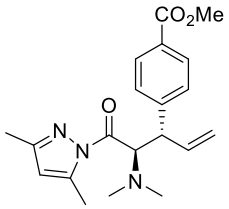


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.853	95764	18743	10.750	11.683
2	4.061	795043	141692	89.250	88.317
Total		890807	160436	100.000	100.000



Methyl 4-((3S,4R)-5-(3,5-dimethyl-1H-pyrazol-1-yl)-4-(dimethyllamino)-5-oxopent-1-en-3-yl) benzoate (3o): Following the general procedure, the reaction was conducted at 0.1 mmol scale, product **3o** was obtained as a colorless liquid (30.1 mg, 85% yield, *anti:syn* =4:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +49.7 (*c* = 0.48, in CH_2Cl_2).

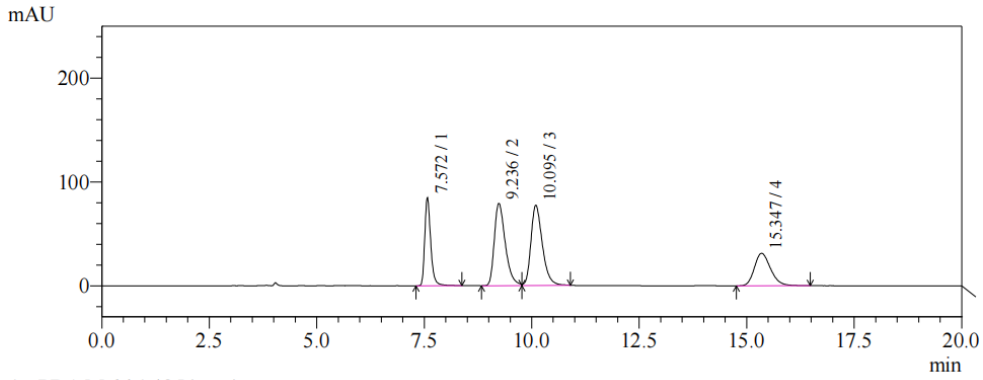
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 – 7.80 (m, 2H), 7.35 – 7.29 (m, 2H), 6.23 – 6.14 (m, 1H), 5.79 (s, 1H), 5.38 (d, *J* = 11.7 Hz, 1H), 5.20 – 5.05 (m, 2H), 4.01 – 3.96 (m, 1H), 3.85 (s, 3H), 2.43 (s, 6H), 2.31 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.5, 167.1, 151.6, 146.0, 143.4, 139.0, 137.9, 129.9, 129.7, 128.6, 128.5, 128.4, 117.3, 116.6, 111.7, 111.5, 66.1, 65.7, 52.1, 50.2, 49.7, 41.3, 41.2, 14.7, 14.4, 14.0, 13.8.

HPLC: 92.5:7.5 *er*, chiral stationary column: OD-H, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm, 30 °C, major isomer: t_r (major) = 7.3 min, t_r (minor) = 15.3 min.

HRMS m/z $[M+H]^+$ calcd for $C_{20}H_{26}N_3O_3^+$ = 356.1969, found 356.1967.

Racemic **3o**



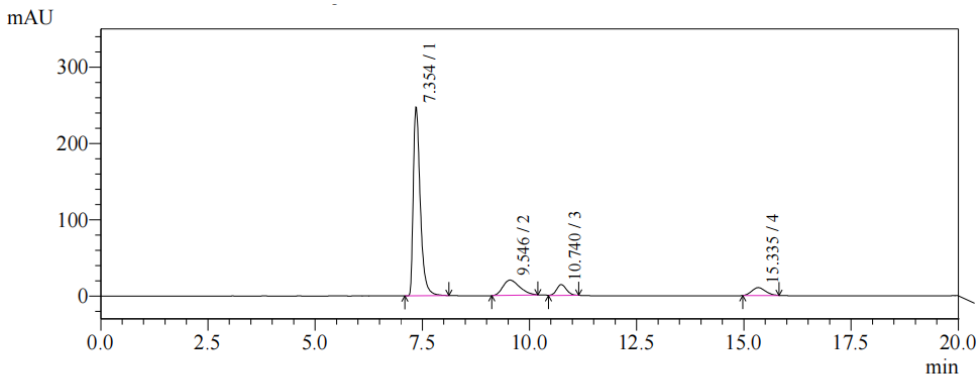
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.572	819197	84937	18.305	31.099
2	9.236	1408407	79405	31.471	29.074
3	10.095	1426418	77406	31.874	28.342
4	15.347	821205	31365	18.350	11.484
Total		4475228	273113	100.000	100.000

Enantioenriched **3o**

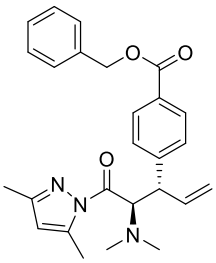


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.354	2805185	247351	73.702	84.727
2	9.546	544126	20004	14.296	6.852
3	10.740	228203	14294	5.996	4.896
4	15.335	228583	10289	6.006	3.525
Total		3806097	291938	100.000	100.000



Benzyl 4-((3*S*,4*R*)-5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-4-(dimethylamino)-5-oxopent-1-en-3-yl)benzoate (3p) Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3p** was obtained as a colorless liquid (39.0 mg, 45% yield, *anti:syn* = 3:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +64.4 (*c* = 0.54, in CH_2Cl_2).

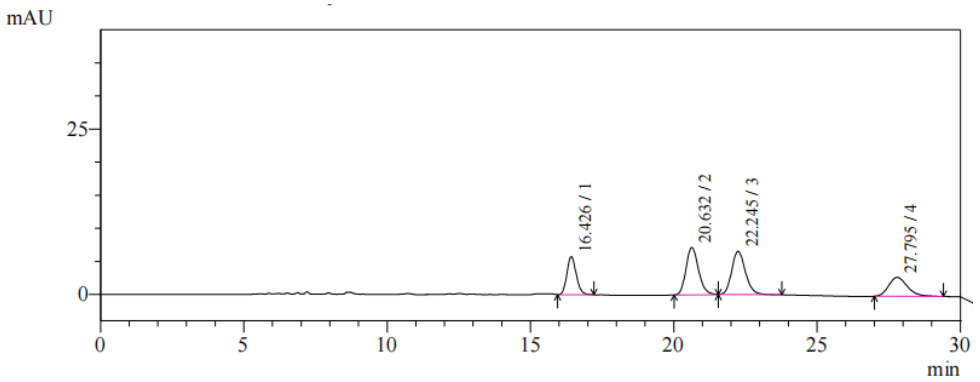
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.30 (m, 7H), 6.24 – 6.12 (m, 1H), 5.80 (s, 1H), 5.38 (d, *J* = 11.8 Hz, 1H), 5.30 (s, 2H), 5.19 – 5.07 (m, 2H), 3.99 (dd, *J* = 11.7, 8.4 Hz, 1H), 2.42 (s, 6H), 2.32 (s, 3H), 2.24 (s, 1H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 170.4, 166.4, 166.3, 151.7, 151.6, 147.1, 146.1, 143.7, 143.4, 140.0, 137.9, 136.3, 136.1, 130.0, 129.8, 128.61, 128.57, 128.5, 128.43, 128.36, 128.21, 128.17, 128.15, 128.12, 117.2, 116.5, 111.6, 111.4, 66.6, 66.5, 66.1, 65.7, 50.1, 49.6, 41.3, 41.2, 14.6, 14.4, 13.9, 13.8.

HPLC: 90:10 *er*, chiral stationary column: OD-H, mobile phase: hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, major isomer: t_r (major) = 16.4 min, t_r (minor) = 27.8 min.

HRMS m/z $[M+H]^+$ calcd for $C_{26}H_{30}N_3O_3^+$ = 432.2282, found 432.2283.

Racemic **3p**



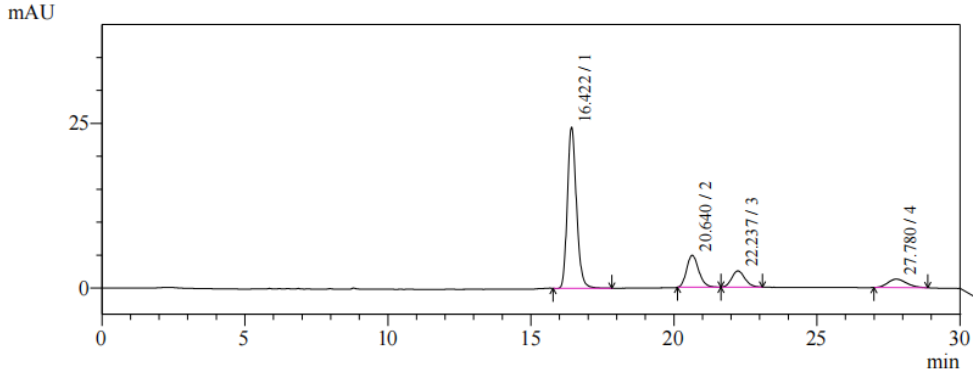
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.426	130694	5755	18.713	25.718
2	20.632	218973	7205	31.352	32.195
3	22.245	217422	6547	31.130	29.257
4	27.795	131337	2871	18.805	12.830
Total		698425	22378	100.000	100.000

Enantioenriched **3p**

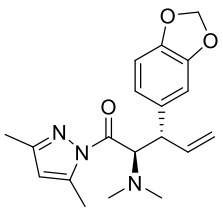


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.422	541260	24479	65.939	73.960
2	20.640	141783	4868	17.273	14.707
3	22.237	78750	2463	9.594	7.442
4	27.780	59053	1288	7.194	3.891
Total		820847	33097	100.000	100.000



(2*R*,3*S*)-3-(benzo[*d*][1,3]dioxol-5-yl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)pent-4-en-1-one (3q): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3q** was obtained as a white solid (55.0 mg, 81% yield, *anti:syn* =10:1), M.p. 30 – 31 ℃.

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +65.0 (*c* = 0.90, in CH_2Cl_2).

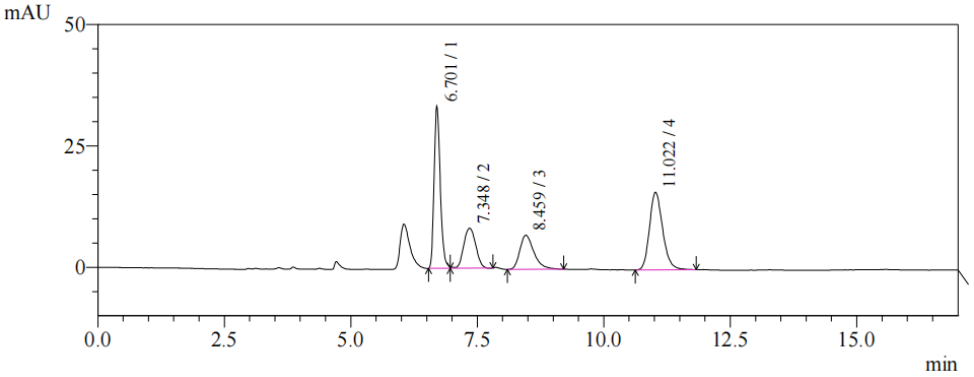
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.77 – 6.74 (m, 1H), 6.70 – 6.68 (m, 1H), 6.61 – 6.59 (m, 1H), 6.19 – 6.10 (m, 1H), 5.85 – 5.80 (m, 3H), 5.28 (d, *J* =11.7 Hz, 1H), 5.16 – 5.07 (m, 2H), 3.85 – 3.80 (m, 1H), 2.41 (s, 6H), 2.36 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.9, 151.4, 147.5, 146.1, 143.4, 139.8, 134.3, 121.6, 115.8, 111.3, 109.0, 108.1, 100.8, 66.4, 49.4, 41.3, 14.5, 13.8.

HPLC: 94:6 *er*, chiral stationary column: OD-H, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm, 30 ºC, t_r (major) = 6.3 min, t_r (minor) = 11.1 min.

HRMS m/z $[M+H]^+$ calcd for $C_{19}H_{24}N_3O_3^+$ = 342.1812, found 342.1811.

Racemic **3q**



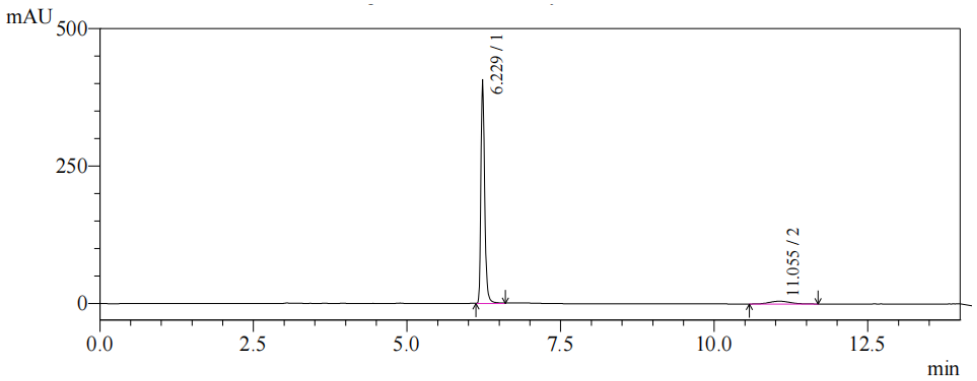
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.701	283649	33441	33.583	51.660
2	7.348	135101	8225	15.995	12.705
3	8.459	136260	7059	16.132	10.905
4	11.022	289622	16009	34.290	24.730
Total		844631	64733	100.000	100.000

Enantioenriched **3q**

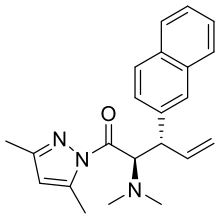


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.229	1728381	408275	93.636	98.789
2	11.055	117464	5003	6.364	1.211
Total		1845846	413278	100.000	100.000



(2*R*,3*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)-3-(naphthalen-2-yl)pent-4-en-1-one (3r): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3r** was obtained as a colorless liquid (45.0 mg, 65% yield, *anti:syn* = 10:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +110.2 (*c* = 0.12, in CH_2Cl_2).

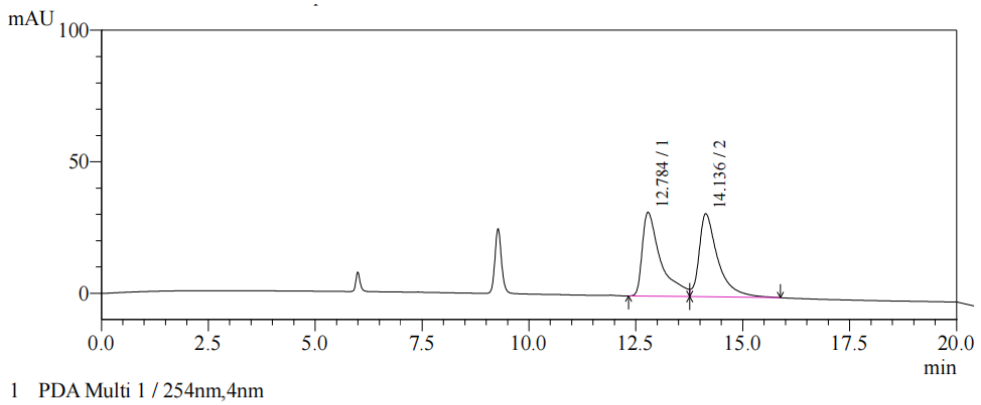
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 – 7.63 (m, 4H), 7.41 – 7.33 (m, 3H), 6.34 – 6.21 (m, 1H), 5.69 (s, 1H), 5.51 (d, *J* = 11.7 Hz, 1H), 5.17 – 5.13 (m, 2H), 4.12 – 4.07 (m, 1H), 2.48 (s, 6H), 2.24 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.9, 151.4, 143.4, 139.7, 138.0, 133.5, 132.4, 127.9, 127.8, 127.5, 127.10, 127.08, 125.8, 125.4, 116.2, 111.3, 66.2, 49.9, 41.4, 14.4, 13.8.

HPLC: 95:5 *er*, chiral stationary column: IA, mobile phase: hexane/^{i}PrOH = 99.8/0.2, flow rate 0.5 mL/min, λ = 254 nm, 30 ^{o}C, t_r (major) = 13.7 min, t_r (minor) = 12.7 min.

HRMS m/z $[M+H]^+$ calcd for $C_{22}H_{26}N_3O^+$ = 348.2076, found 348.2077.

Racemic **3r**



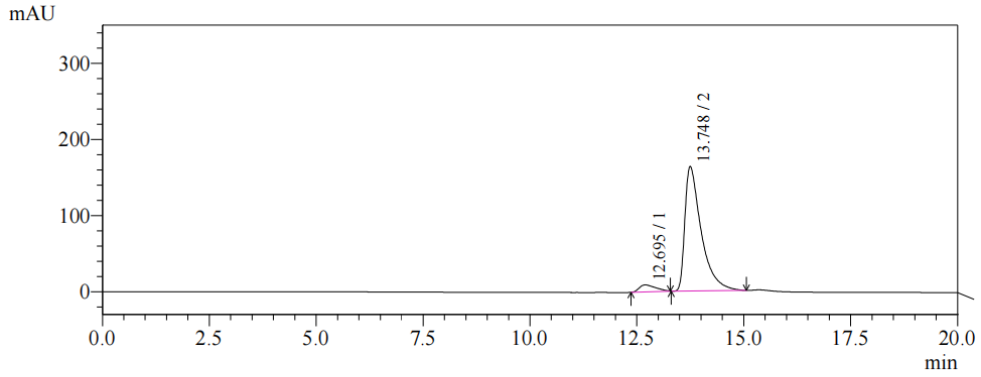
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.784	954532	31925	49.711	50.211
2	14.136	965640	31657	50.289	49.789
Total		1920172	63582	100.000	100.000

Enantioenriched **3r**

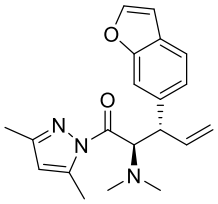


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.695	242558	9208	5.275	5.321
2	13.748	4356002	163842	94.725	94.679
Total		4598560	173050	100.000	100.000



(2*R*,3*S*)-3-(benzofuran-6-yl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)pent-4-en-1-one (3s) Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3s** was obtained as a colorless liquid (25.6 mg, 38% yield, *anti:syn* =10:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_D$ = +63.5 (*c* = 0.26, in CH_2Cl_2).

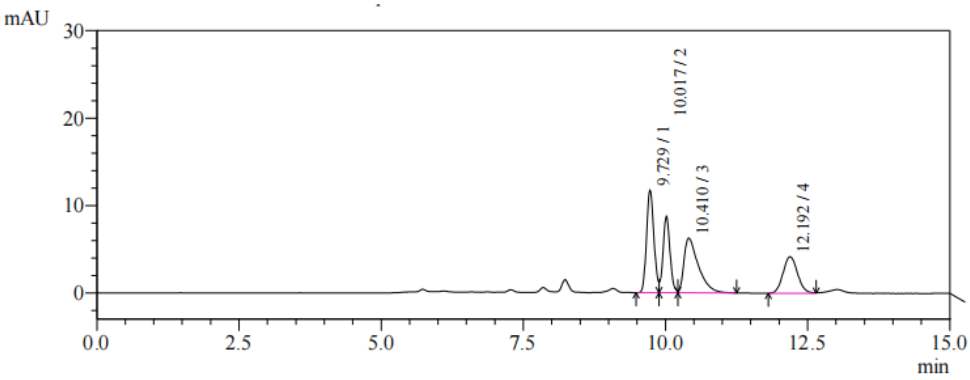
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.2 Hz, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.18 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.63 (dd, *J* = 2.1, 0.8 Hz, 1H), 6.31-6.19 (m, 1H), 5.72 (s, 1H), 5.40 (d, *J* = 11.7 Hz, 1H), 5.18 – 5.10 (m, 2H), 4.01 (dd, *J* = 11.7, 8.6 Hz, 1H), 2.46 (s, 6H), 2.27 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 171.1, 154.0, 153.9, 151.6, 151.3, 145.1, 145.0, 143.7, 143.3, 140.1, 139.2, 135.8, 135.0, 127.8, 127.4, 124.9, 124.5, 121.1, 120.6, 116.3, 115.8, 111.6, 111.5, 111.2, 111.0, 106.7, 106.6, 66.7, 66.1, 50.1, 49.7, 41.33, 41.28, 14.7, 14.4, 14.0, 13.8.

HPLC: 93.5:6.5 *er*, chiral stationary column: AD-H, mobile phase: hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, major isomer: t_r (major) = 10.7 min, t_r (minor) = 9.8 min.

HRMS m/z $[M+H]^+$ calcd for $C_{20}H_{24}N_3O_2^+$ = 338.1863, found 338.1863.

Racemic **3s**



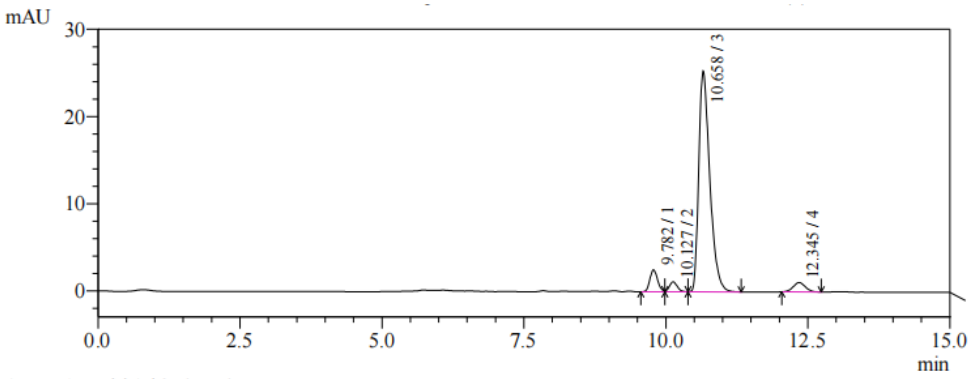
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.729	105995	11727	29.056	37.896
2	10.017	74316	8753	20.372	28.288
3	10.410	110761	6288	30.362	20.319
4	12.192	73724	4177	20.210	13.497
Total		364797	30944	100.000	100.000

Enantioenriched **3s**

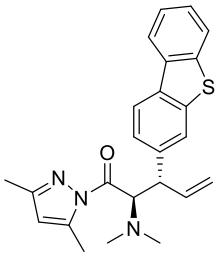


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.782	24007	2539	6.095	8.441
2	10.127	11073	1146	2.811	3.810
3	10.658	342836	25323	87.046	84.203
4	12.345	15942	1066	4.048	3.546
Total		393857	30074	100.000	100.000



(2*R*,3*S*)-3-(dibenzo[*b*,*d*]thiophen-3-yl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)pent-4-en-1-one (3t) Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3t** was obtained as a colorless liquid (24.4 mg, 30% yield, *anti:syn* =19:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +91.0 (*c* = 0.27, in CH_2Cl_2).

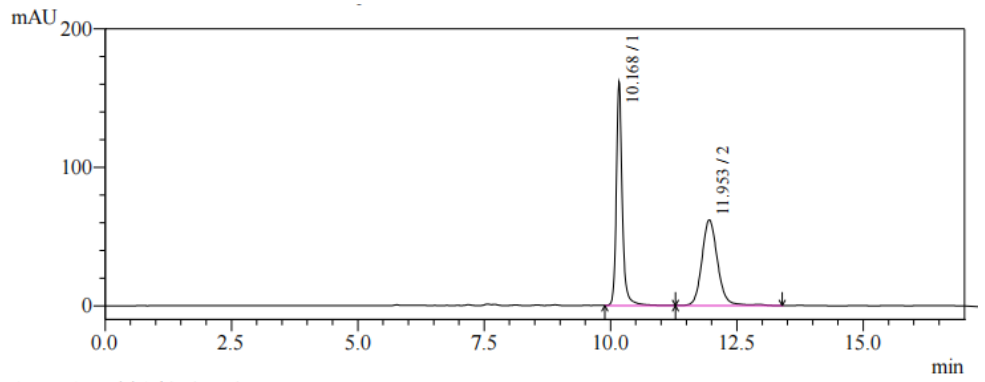
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.43 – 7.36 (m, 2H), 7.34 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.36 – 6.22 (m, 1H), 5.70 (s, 1H), 5.47 (d, *J* = 11.7 Hz, 1H), 5.20 (s, 1H), 5.16 (d, *J* = 7.4 Hz, 1H), 4.07 (dd, *J* = 11.7, 8.5 Hz, 1H), 2.48 (s, 6H), 2.27 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 151.6, 143.4, 139.6, 139.5, 139.3, 135.4, 134.2, 126.5, 125.2, 124.3, 122.8, 122.7, 121.43, 121.37, 116.3, 111.4, 66.5, 50.0, 41.4, 14.4, 13.8.

HPLC: 95:5 *er*, chiral stationary column: IA, mobile phase: hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm, 30 ^{o}C, t_r (major) = 11.8 min, t_r (minor) = 10.3 min.

HRMS m/z $[M+H]^+$ calcd for $C_{24}H_{26}N_3OS^+$ = 404.1791, found 404.1793.

Racemic **3t**



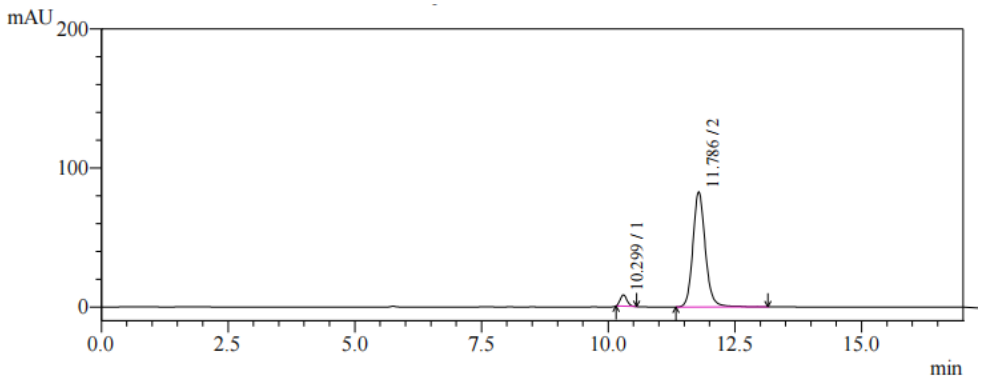
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.168	1324564	161761	49.691	72.307
2	11.953	1341013	61955	50.309	27.693
Total		2665577	223716	100.000	100.000

Enantioenriched **3t**

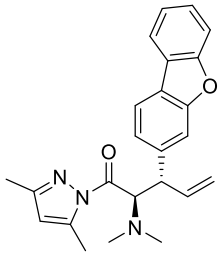


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.299	76414	8174	5.139	8.984
2	11.786	1410566	82812	94.861	91.016
Total		1486981	90986	100.000	100.000



(2*R*,3*S*)-3-(dibenzo[*b*,*d*]furan-3-yl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)pent-4-en-1-one (3u) Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3u** was obtained as a colorless liquid (39.2 mg, 51% yield, *anti:syn* =19:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}_{D}$ = +38.8 (*c* = 0.32, in CH_2Cl_2).

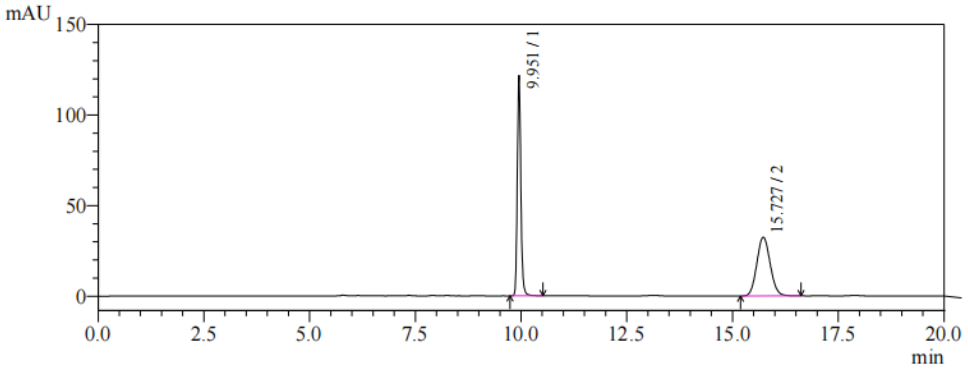
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.43-7.38 (m, 1H), 7.38 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 6.36 – 6.23 (m, 1H), 5.68 (s, 1H), 5.50 (d, *J* = 11.8 Hz, 1H), 5.20 – 5.13 (m, 2H), 4.08 (dd, *J* = 11.8, 8.3 Hz, 1H), 2.49 (s, 6H), 2.25 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 156.4, 155.1, 151.5, 143.3, 140.0, 134.9, 127.9, 127.0, 124.3, 124.2, 122.6, 120.6, 116.0, 111.6, 111.32, 111.27, 66.6, 49.7, 41.3, 14.4, 13.8.

HPLC: 90:10 *er*, chiral stationary column: AD-H, mobile phase: hexane/^{i}PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, t_r (major) = 15.6 min, t_r (minor) = 10.5 min.

HRMS m/z $[M+H]^+$ calcd for $C_{24}H_{26}N_3O_2^+$ = 388.2020, found 388.2020.

Racemic **3u**



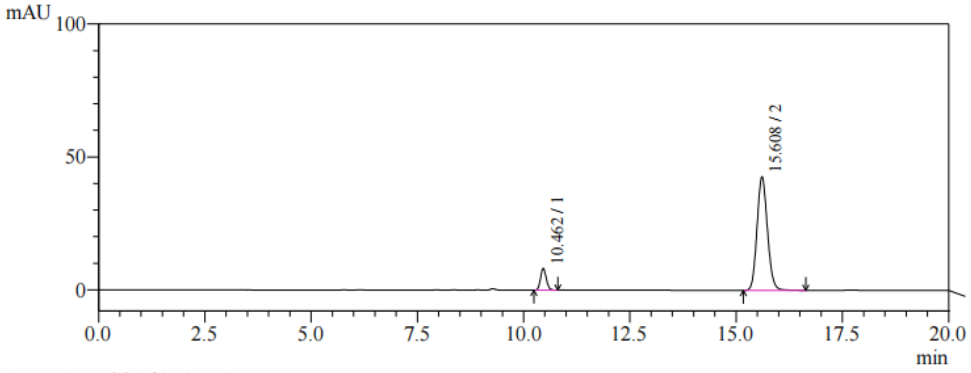
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.951	704952	121808	49.760	78.946
2	15.727	711763	32485	50.240	21.054
Total		1416715	154293	100.000	100.000

Enantioenriched **3u**

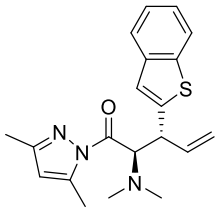


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.462	78029	8239	9.692	16.149
2	15.608	727076	42780	90.308	83.851
Total		805105	51020	100.000	100.000



(2*R*,3*R*)-3-(benzo[*b*]thiophen-2-yl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)pent-4-en-1-one (3v): Following the general procedure, the reaction was conducted at 0.1 mmol scale, product **3v** was obtained as a colorless liquid (32.3 mg, 46% yield, *anti:syn* = 10:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +88.1 (*c* = 0.24, in CH_2Cl_2).

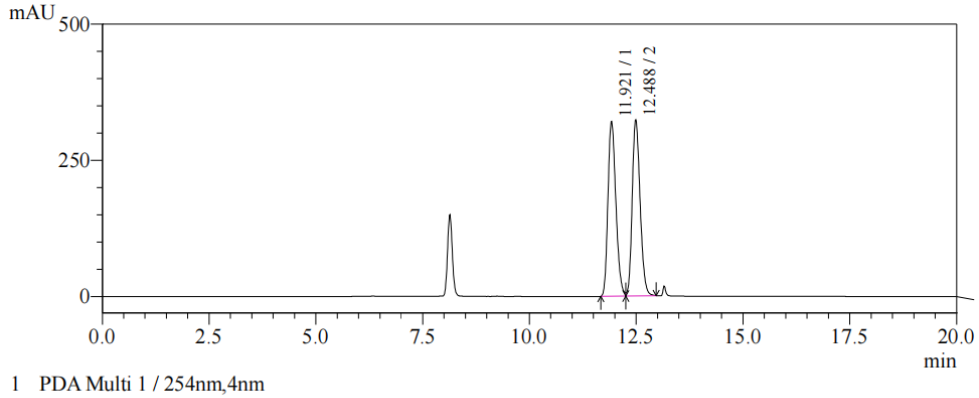
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 – 7.69 (m, 1H), 7.60 – 7.56 (m, 1H), 7.24 – 7.18 (m, 2H), 7.12 (s, 1H), 6.22 – 6.13 (m, 1H), 5.83 (s, 1H), 5.39 (d, *J* = 11.6 Hz, 1H), 5.28 – 5.17 (m, 2H), 4.33 – 4.28 (m, 1H), 2.41 (s, 9H), 2.20 (s, 3H).

^{13}C NMR δ = 169.9, 151.7, 145.0, 143.7, 139.9, 139.5, 138.6, 124.0, 123.7, 123.2, 122.2, 121.4, 116.7, 111.6, 66.7, 45.1, 41.3, 14.6, 13.9.

HPLC: 96:4 *er*, chiral stationary column: OD-H, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, t_r (major) = 11.4 min, t_r (minor) = 12.1 min.

HRMS m/z $[M+H]^+$ calcd for $C_{20}H_{24}N_3OS^+$ = 354.1640, found 354.1639.

Racemic **3v**



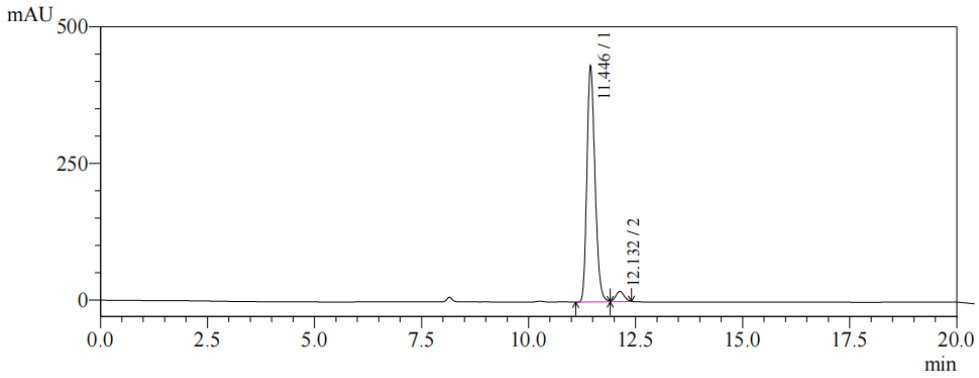
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.921	4141381	320937	49.906	49.822
2	12.488	4156979	323227	50.094	50.178
Total		8298361	644164	100.000	100.000

Enantioenriched **3v**

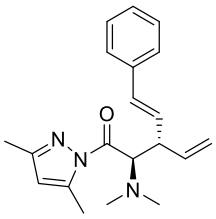


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.446	5678224	432895	95.710	95.885
2	12.132	254523	18576	4.290	4.115
Total		5932747	451472	100.000	100.000



(2*R*,3*S*,*E*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)-5-phenyl-3-vinylpent-4-en-1-one (3w): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3w** was obtained as a colorless liquid (26.0 mg, 41% yield, *anti:syn* >19:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +14.6 (*c* = 0.54, in CH_2Cl_2).

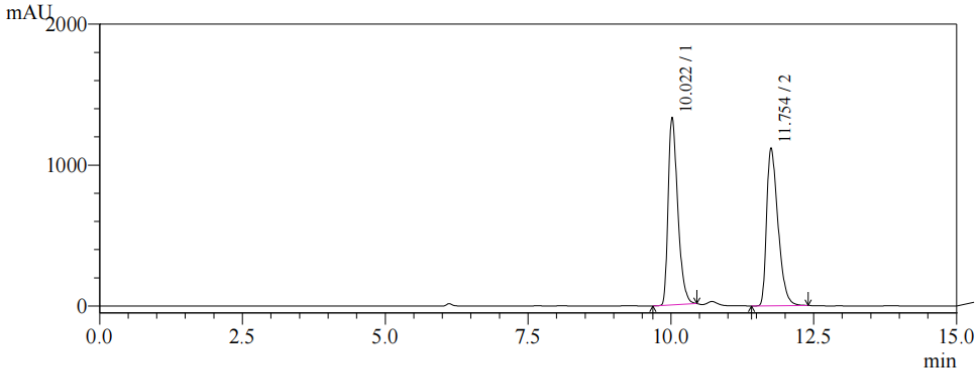
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 – 7.12 (m, 5H), 6.43 – 6.40 (m, 1H), 6.08 – 5.99 (m, 2H), 5.87 (s, 1H), 5.27 – 5.14 (m, 2H), 5.05 (d, *J* = 11.2 Hz, 1H), 3.60 – 3.48 (m, 1H), 2.46 (s, 3H), 2.42 (s, 6H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.7, 151.7, 143.7, 138.2, 137.4, 131.8, 128.5, 128.4, 127.3, 126.3, 116.3, 111.6, 66.0, 47.7, 41.3, 14.6, 13.9.

HPLC: 96:4 *er*, chiral stationary column: OD-H, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, t_r (major) = 10.0 min, t_r (minor) = 11.7 min.

HRMS m/z $[M+H]^+$ calcd for $C_{20}H_{26}N_3O^+$ = 324.2076, found 324.2069.

Racemic **3w**



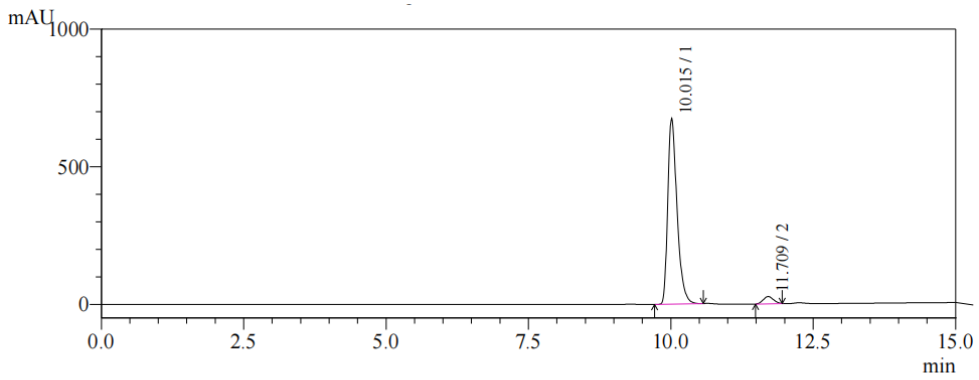
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.022	15560947	1331159	50.064	54.250
2	11.754	15520964	1122590	49.936	45.750
Total		31081911	2453749	100.000	100.000

Enantioenriched **3w**

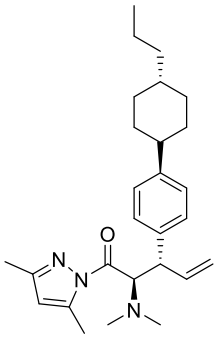


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.015	7643000	675180	95.871	96.253
2	11.709	329162	26285	4.129	3.747
Total		7972161	701465	100.000	100.000



(2*R*,3*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(dimethylamino)-3-(4-((1*r*,4*R*)-4-propylcyclohexyl)phenyl)pent-4-en-1-one (3x) Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3x** was obtained as a colorless liquid (45.3 mg, 54% yield, *anti:syn* = 7:1).

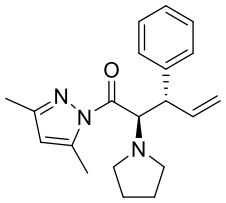
TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +61.7 (*c* = 0.51, in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.27 – 6.09 (m, 1H), 5.74 (s, 1H), 5.32 (d, *J* = 11.6 Hz, 1H), 5.18 – 5.08 (m, 2H), 3.86 (dd, *J* = 11.7, 8.7 Hz, 1H), 2.46 (s, 6H), 2.36 – 2.29 (m, 1H), 2.27 (s, 3H), 2.16 (s, 3H), 1.85 – 1.71 (m, 4H), 1.38 – 1.14 (m, 7H), 1.05 – 0.92 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 151.2, 146.1, 143.3, 139.8, 137.4, 128.2, 126.6, 115.8, 111.0, 66.5, 49.8, 44.2, 41.3, 39.8, 37.1, 34.3, 34.2, 33.6, 20.1, 14.5, 14.3, 13.8.

HRMS m/z $[M+H]^+$ calcd for $C_{27}H_{40}N_3O^+$ = 422.3166, found 422.3167.



(2*R*,3*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-phenyl-2-(pyrrolidin-1-yl)pent-4-en-1-one (3aa): Following the general procedure, the reaction performed at 50 °C and was conducted at 0.2 mmol scale, product **3aa** was obtained as a white solid (24.0 mg, 37% yield, *anti:syn* = 10:1), M.p. 62 – 64 °C.

TLC: R_f = 0.8 (petroleum ether/ethyl acetate 10/1).

[α] $^{20}_{D}$ = +75.0 (*c* = 0.16, in CH_2Cl_2).

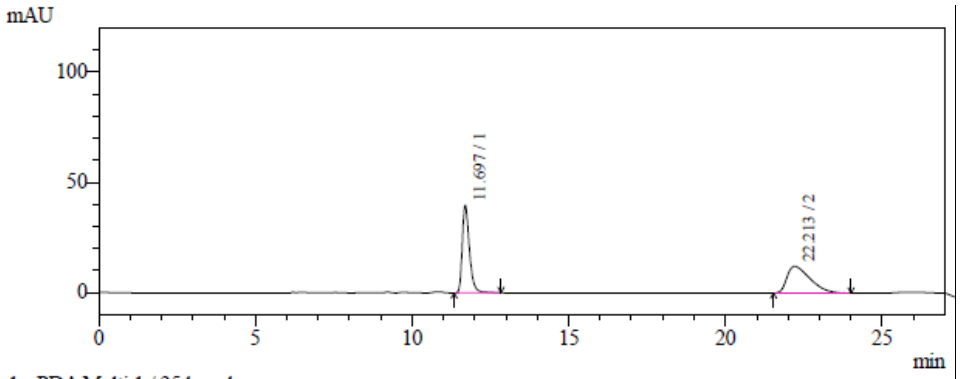
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.33 – 6.16 (m, 1H), 5.77 (s, 1H), 5.62 – 5.52 (m, 1H), 5.15 – 5.02 (m, 2H), 4.00 – 3.90 (m, 1H), 2.92 (s, 2H), 2.74 (s, 2H), 2.28 (s, 3H), 2.18 (s, 3H), 1.79 – 1.64 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 151.4, 143.4, 140.7, 140.0, 128.5, 128.3, 126.6, 115.7, 111.1, 63.3, 50.8, 48.3, 23.6, 14.4, 13.9.

HPLC: 89:11 *er*, chiral stationary column: OD, mobile phase: hexane/^{i}PrOH = 99.7/0.3, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, t_r (major) = 11.6 min, t_r (minor) = 21.7 min.

HRMS m/z $[M+H]^+$ calcd for $C_{20}H_{26}N_3O^+$ = 324.2070, found 324.2071.

Racemic **3aa**



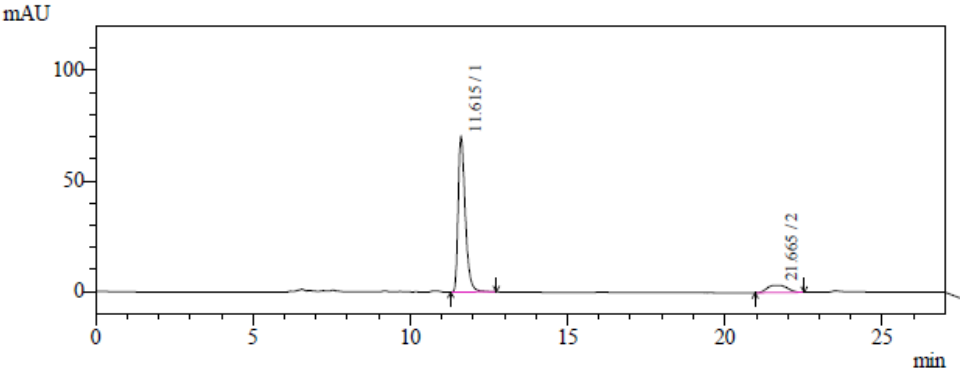
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.697	632521	39779	50.298	76.608
2	22.213	625026	12147	49.702	23.392
Total		1257547	51925	100.000	100.000

Enantioenriched **3aa**

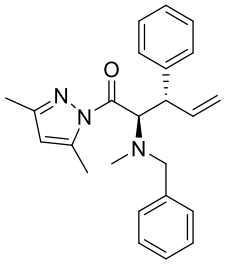


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.615	1112486	70588	88.545	95.661
2	21.665	143915	3202	11.455	4.339
Total		1256401	73790	100.000	100.000



(2*R*,3*S*)-2-(benzyl(methyl)amino)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-phenylpent-4-en-1-one (3ab): Following the general procedure, the reaction performed at 50 °C and was conducted at 0.2 mmol scale, product **3ab** was obtained as a white solid (39.0 mg, 52% yield, *anti:syn* = 5:1), M.p. 75 – 86 °C.

TLC: R_f = 0.8 (petroleum ether/ethyl acetate 10/1).

[α] $^{20}_{D}$ = +42.5 (*c* = 0.32, in CH_2Cl_2).

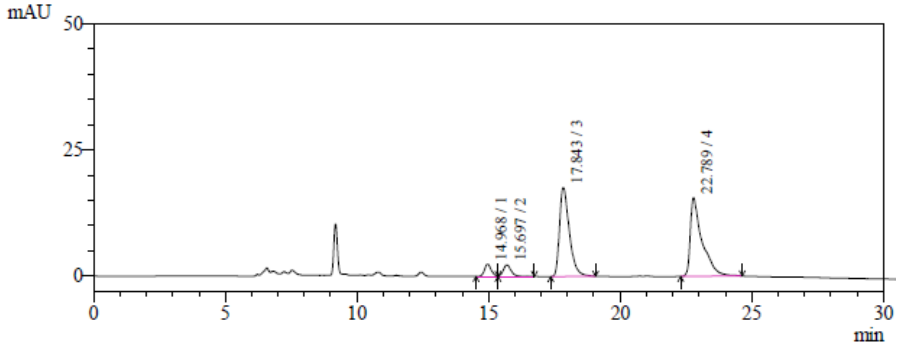
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.23 (m, 3H), 7.20 – 7.14 (m, 2H), 7.12 – 7.08 (m, 1H), 6.38 – 6.26 (m, 1H), 5.81 (s, 1H), 5.50 (d, *J* = 11.7 Hz, 1H), 5.14 (dd, *J* = 29.6, 13.7 Hz, 2H), 4.04 (dd, *J* = 11.6, 8.2 Hz, 1H), 3.86 (d, *J* = 13.9 Hz, 1H), 3.75 (d, *J* = 13.9 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 171.3, 151.7, 151.3, 143.7, 143.4, 141.2, 140.5, 140.1, 140.0, 139.9, 138.7, 128.7, 128.6, 128.5, 128.3, 128.1, 127.9, 126.8, 126.6, 126.5, 116.6, 116.0, 111.7, 111.2, 66.5, 66.0, 58.1, 57.9, 50.3, 49.8, 37.6, 37.5, 14.7, 14.4, 14.0, 13.8.

HPLC: 75:25 *er*, chiral stationary column: OD, mobile phase: hexane/^{i}PrOH = 99.7/0.3, flow rate 0.5 mL/min, λ = 254 nm, 30 °C, t_r (major) = 17.1 min, t_r (minor) = 22.2 min.

HRMS m/z $[M+H]^+$ calcd for $C_{24}H_{28}N_3O^+$ = 374.2227, found 374.2227.

Racemic **3ab**



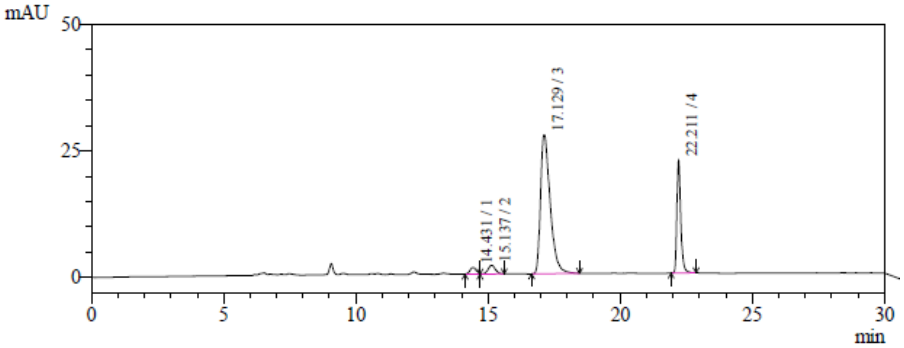
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.968	43940	2436	4.238	6.414
2	15.697	48730	2295	4.700	6.044
3	17.843	458449	17639	44.215	46.443
4	22.789	485745	15610	46.848	41.100
Total		1036864	37980	100.000	100.000

Enantioenriched **3ab**

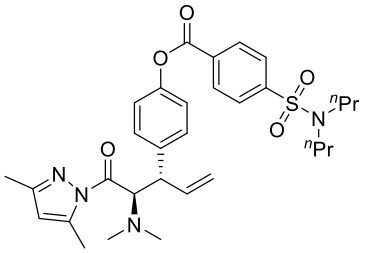


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.431	21773	1317	2.216	2.491
2	15.137	33150	1719	3.374	3.252
3	17.129	698452	27536	71.085	52.100
4	22.211	229184	22281	23.325	42.156
Total		982559	52852	100.000	100.000



4-((3*S*,4*R*)-5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-4-(dimethylamino)-5-oxopent-1-en-3-yl)phenyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (3ca): Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3ca** was obtained as a colorless liquid (52.0 mg, 45% yield, *anti:syn* = 8:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +28.2 (*c* = 0.95, in CH_2Cl_2).

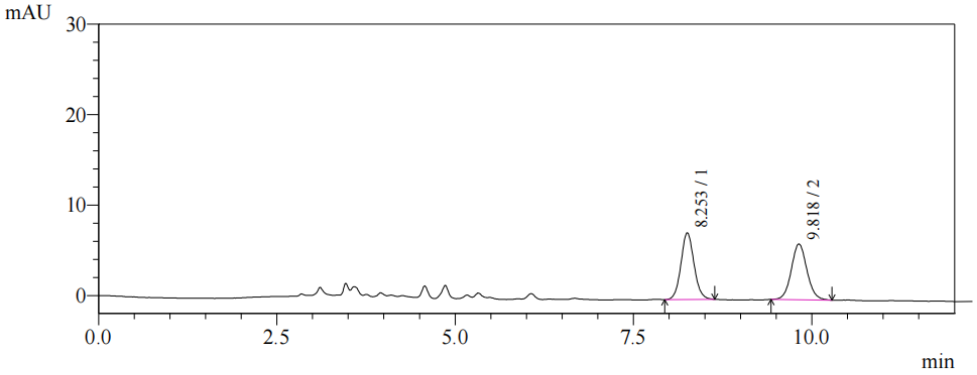
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 – 8.25 (m, 2H), 7.97 – 7.90 (m, 2H), 7.37 – 7.31 (m, 2H), 7.10 – 7.02 (m, 2H), 6.27 – 6.18 (m, 1H), 5.86 (s, 1H), 5.40 (d, *J* = 11.7 Hz, 1H), 5.23 – 5.13 (m, 2H), 4.02 – 3.97 (m, 1H), 3.18 – 3.11 (m, 4H), 2.48 (s, 6H), 2.39 (s, 3H), 2.21 (s, 3H), 1.63 – 1.54 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.7, 163.7, 151.6, 149.3, 144.9, 143.5, 139.4, 138.5, 138.4, 133.0, 130.9, 130.8, 129.7, 129.5, 127.2, 121.5, 121.2, 116.9, 116.3, 111.7, 111.5, 66.3, 50.0, 49.2, 41.3, 22.0, 14.7, 14.5, 13.9, 11.2.

HPLC: 93:7 *er*, chiral stationary column: IA, mobile phase: hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, 30 °C, t_r (major) = 9.7 min, t_r (minor) = 8.2 min.

HRMS m/z $[M+H]^+$ calcd for $C_{31}H_{41}N_4O_5S^+$ = 581.2792, found 581.2797.

Racemic **3ca**



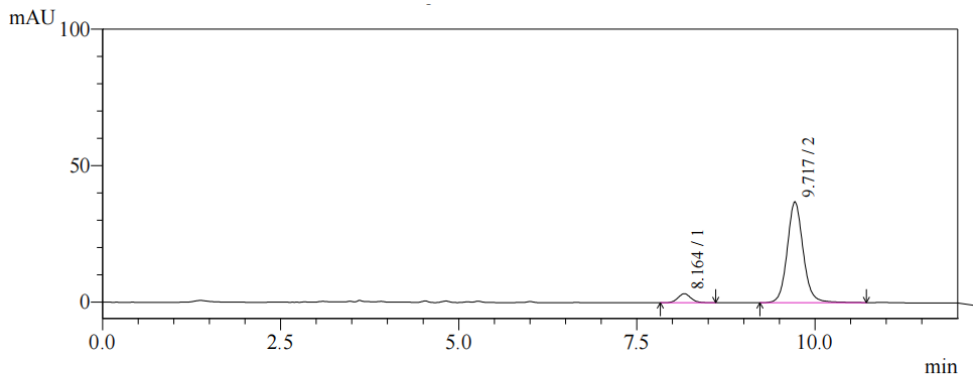
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.253	94449	7399	50.141	54.522
2	9.818	93917	6171	49.859	45.478
Total		188366	13570	100.000	100.000

Enantioenriched **3ca**

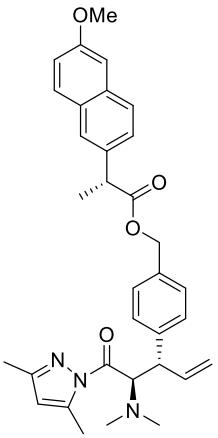


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.164	42875	3334	6.927	8.262
2	9.717	576058	37019	93.073	91.738
Total		618933	40353	100.000	100.000



4-((3*S*,4*R*)-5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-4-(dimethylamino)-5-oxopent-1-en-3-yl)benzyl (*R*)-2-(6-methoxynaphthalen-2-yl)propanoate (3cb) Following the general procedure, the reaction was conducted at 0.2 mmol scale, product **3cb** was obtained as a colorless liquid (61.7 mg, 57% yield, *anti:syn* = 10:1).

TLC: R_f = 0.6 (petroleum ether/ethyl acetate 10/1).

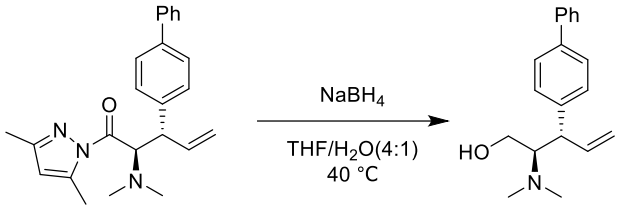
[α] $^{28}{}_{D}$ = +40.5 (*c* = 0.60, in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.6, 4.7 Hz, 2H), 7.84 (s, 1H), 7.58 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.42 – 7.32 (m, 4H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.45 – 6.33 (m, 1H), 5.97 (s, 1H), 5.56 (d, *J* = 11.7 Hz, 1H), 5.38 – 5.29 (m, 2H), 5.26 (d, *J* = 12.5 Hz, 1H), 5.16 (d, *J* = 12.5 Hz, 1H), 4.15 – 4.05 (m, 5H), 2.66 (s, 6H), 2.52 (s, 3H), 2.37 (s, 3H), 1.78 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 174.4, 170.7, 170.6, 157.7, 157.6, 151.5, 151.4, 143.4, 143.3, 140.4, 140.3, 139.5, 139.4, 135.6, 135.5, 134.3, 134.2, 133.7, 133.6, 129.34, 129.25, 129.0, 128.9, 128.6, 128.5, 128.0, 127.9, 127.2, 127.1, 126.3, 126.2, 126.0, 125.9, 119.0, 118.9, 116.1, 116.0, 111.3, 111.2, 105.6, 105.5, 66.3, 66.2, 55.4, 55.3, 49.6, 49.5, 45.5, 45.4, 41.3, 41.2, 18.7, 18.6, 14.4, 14.3, 13.8, 13.7.

HRMS m/z $[M+H]^+$ calcd for $C_{33}H_{38}N_3O_4^+$ = 540.2857, found 540.2858.

7. Synthetic applications



3e **4**

The product **3e** (0.1 mmol) in THF/H_2O (0.8 mL/0.2 mL) was added $NaBH_4$ (8.0 equiv.) at 0 °C, and the resulting solution was stirred 36 h at 40 °C. After quenching with 1.0 M HCl, the resultant mixture was extracted with EtOAc. The combined organic layer was washed with brine and dried over Na_2SO_4. After evaporation of the organic solvent under reduced pressure, the crude mixture was purified by silica gel column chromatography to give **4.**

(2*R*,3*S*)-3-([1,1'-biphenyl]-4-yl)-2-(dimethylamino)pent-4-en-1-ol (4) the reaction was conducted at 0.1 mmol scale, product **4** was obtained as a white solid (24.0 mg, 85% yield, *anti:syn* =19:1), M.p. 135 – 137 ℃.

TLC: R_f = 0.2 (ethyl acetate).

[α] $^{28}_{D}$ = +88.03 (*c* = 0.44, in CH_2Cl_2).

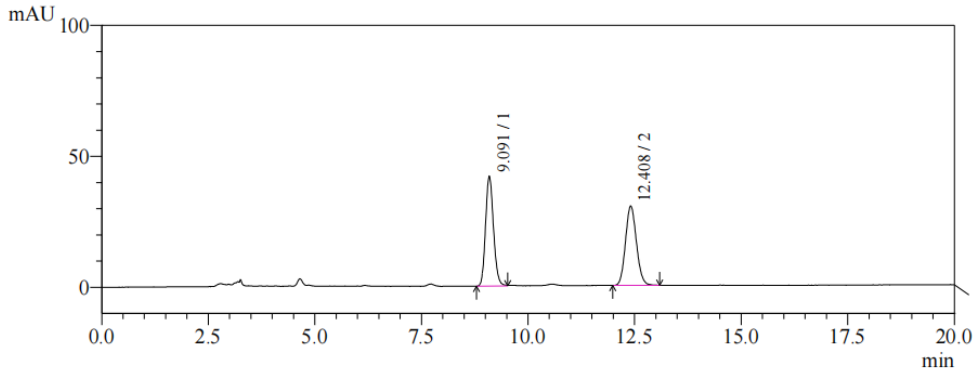
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.52 (m, 4H), 7.52 – 7.42 (m, 2H), 7.42 – 7.33 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.31 – 6.18 (m, 1H), 5.21 (dd, *J* = 16.9, 1.3 Hz, 1H), 5.14 – 5.10 (M, 1H), 3.58 (t, *J* = 8.9 Hz, 1H), 3.20 – 3.08 (m, 3H), 2.65 – 2.60 (m, 6H), 2.50 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 140.8, 140.7, 139.7, 128.8, 127.9, 127.7, 127.3, 127.1, 115.8, 68.1, 59.8, 51.2, 40.7.

HPLC: 95:5 *er*, chiral stationary column: OD-H, mobile phase: hexane/^{i}PrOH = 97/3, flow rate 1.0 mL/min, λ = 254 nm, 30 ^{o}C, t_r (major) = 9.0 min, t_r (minor) = 12.3 min.

HRMS m/z $[M+H]^+$ calcd for $C_{19}H_{24}NO^+$ = 282.1852, found 282.1850.

Racemic **4**



1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

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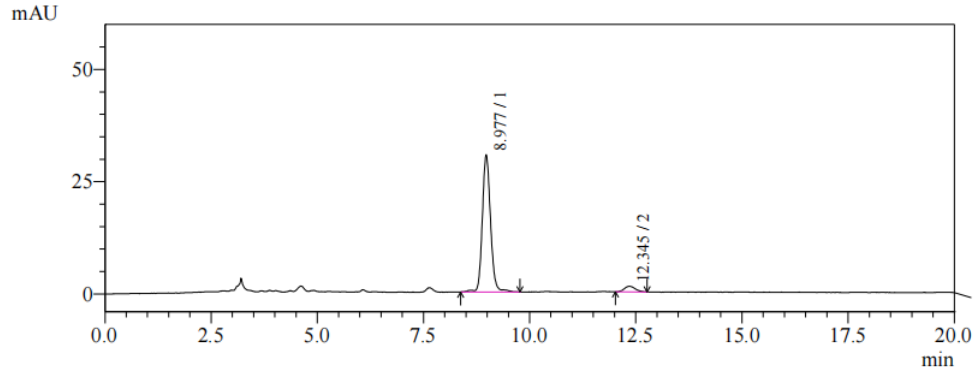
2	12.408	541563	30378	49.896	41.978
Total		1085374	72366	100.000	100.000

Enantioenriched **4**



1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
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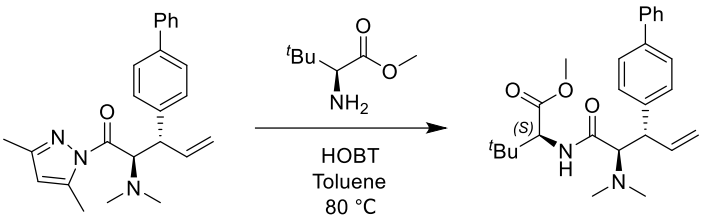
2	12.345	22602	1254	5.199	3.939
Total		434766	31828	100.000	100.000



3e **5**

The product **3e** (0.1 mmol), methyl (2*S*)-2-amino-3,3-dimethylbutanoate (2.0 equiv.), HOBT (2.0 equiv.) and toluene (1.0 mL) was added into a reaction tube equipped with a stirring bar. Then the tube was stirred 24h at 80 °C. The mixture was concentrated under reduced pressure and the crude residue was purified by silica gel column chromatography to give product **5**.

Methyl (*S*)-2-((2*R*,3*S*)-3-([1,1'-biphenyl]-4-yl)-2-(dimethylamino)pent-4-enamido)-3,3-dimethylbutanoate (5) the reaction was conducted at 0.1 mmol scale, product **5** was obtained as a white solid (31.9 mg, 76% yield, *anti:syn* =19:1), M.p. 156 – 158 ℃.

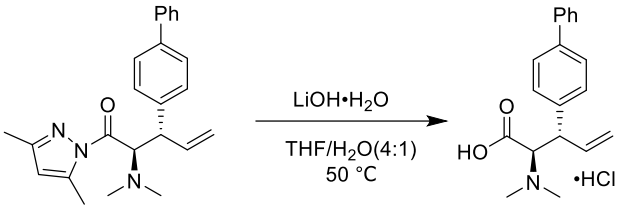
TLC: R_f = 0.2 (petroleum ether/ethyl acetate 1/1).

[α] $^{28}{}_{D}$ = +30.63 (*c* = 0.37, in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 4H), 7.48 – 7.43 (m, 2H), 7.39 – 7.33 (m, 3H), 6.33 – 6.15 (m, 1H), 5.89 (d, *J* = 9.5 Hz, 1H), 5.21 (dd, *J* = 14.1, 2.7 Hz, 2H), 4.29 (d, *J* = 9.4 Hz, 1H), 4.00 – 3.87 (m, 1H), 3.71 (s, 3H), 3.40 (d, *J* = 10.9 Hz, 1H), 2.48 (s, 6H), 0.58 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 168.5, 141.1, 140.3, 140.1, 138.9, 128.9, 128.8, 127.6, 127.2, 127.1, 116.4, 73.6, 59.2, 51.8, 49.6, 41.5, 34.7, 26.1.

HRMS m/z $[M+H]^+$ calcd for $C_{26}H_{35}N_2O_3^+$ = 423.2642, found 423.2639.



3e **6**

The product **3e** (0.1 mmol) in THF/H_2O (0.8 mL/0.2 mL) was added LiOH·H_2O(8.0 equiv.) at 0 °C, and the resulting solution was stirred 36h at 50 °C. After quenching with 4.0 M HCl, the resultant mixture was extracted with EtOAc (3 × equal volume) and dried over Na_2SO_4. After evaporation of the organic solvent under reduced pressure, the crude mixture was purified by silica gel column chromatography to give **6.**

(2*R*,3*S*)-3-([1,1'-biphenyl]-4-yl)-2-(dimethylamino)pent-4-enoic acid hydrochloride (6) the reaction was conducted at 0.1 mmol scale, product **6** was obtained as a white solid (21.2 mg, 64% yield, *anti:syn* =19:1), M.p. 89 – 91 °C.

TLC: R_f = 0.2 (dichloromethane/CH_3OH 10/1).

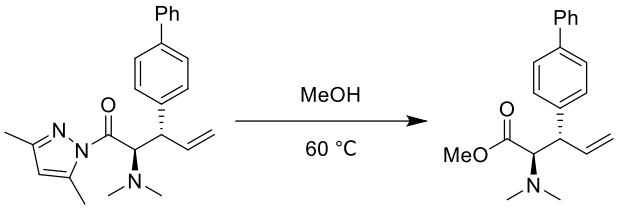
[α] $^{28}{}_D$ = -1.61 (*c* = 0.31, in CH_3OH).

^{1}H NMR (400 MHz, MeOD) δ 7.55 – 7.47 (m, 4H), 7.41 – 7.32 (m, 4H), 7.30 – 7.21 (m, 1H), 6.19 – 6.07 (m, 1H), 5.32 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.20 (dd, *J* = 10.1, 1.3 Hz, 1H), 4.02 – 3.88 (m, 2H), 2.87 (s, 6H).

^{13}C NMR (101 MHz, MeOD) δ 169.0, 140.6, 140.2, 138.1, 137.1, 128.7, 128.5, 127.04, 126.95, 126.5, 117.9, 73.2, 49.6, 40.7.

Er was determined on the corresponding **3e** (95:5 *er*, see compound **3e**).

HRMS m/z $[M+H]^+$ calcd for $C_{19}H_{22}NO_2^+$ = 296.1645, found 296.1646.



3e **7**

The product **3e** (0.1 mmol) was dissolved in 1.0 mL of methanol. The reaction was stirred at 60 °C overnight. After the reaction was completed, the solution was concentrated under vacuum, and the residue was purified by silica gel chromatography to give the desired product **7**.

methyl (2*R*,3*S*)-3-([1,1'-biphenyl]-4-yl)-2-(dimethylamino)pent-4-enoate (7) the reaction was conducted at 0.1 mmol scale, product **7** was obtained as a white solid (27.8 mg, 90% yield, *anti:syn* =19:1), M.p. 98 – 99 ℃.

TLC: R_f = 0.5 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = -4.8 (*c* = 0.08, in CH_2Cl_2).

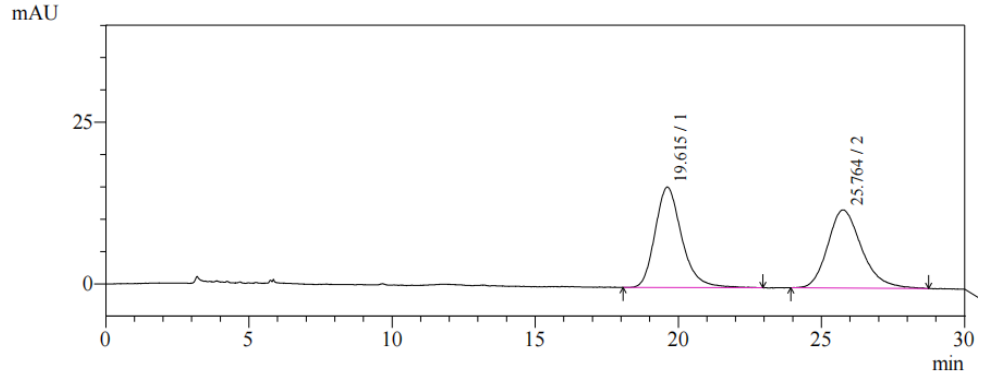
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.54 – 7.49 (m, 2H), 7.45 – 7.39 (m, 2H), 7.35 – 7.29 (m, 1H), 7.29 – 7.25 (m, 2H), 6.23 – 6.08 (m, 1H), 5.19 – 5.10 (m, 2H), 3.81 (dd, *J* = 11.7, 8.6 Hz, 1H), 3.62 (d, *J* = 11.7 Hz, 1H), 3.45 (s, 3H), 2.41 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 140.8, 139.9, 139.7, 138.8, 128.8, 128.6, 127.32, 127.25, 127.0, 116.3, 71.7, 50.7, 49.5, 41.4.

HPLC: 96:4 *er*, chiral stationary column: OJ-H, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm, 30 ^{o}C, t_r (major) = 19.8 min, t_r (minor) = 26.4 min.

HRMS m/z $[M+H]^+$ calcd for $C_{20}H_{24}NO_2^+$ = 310.1802, found 310.1800.

Racemic **7**



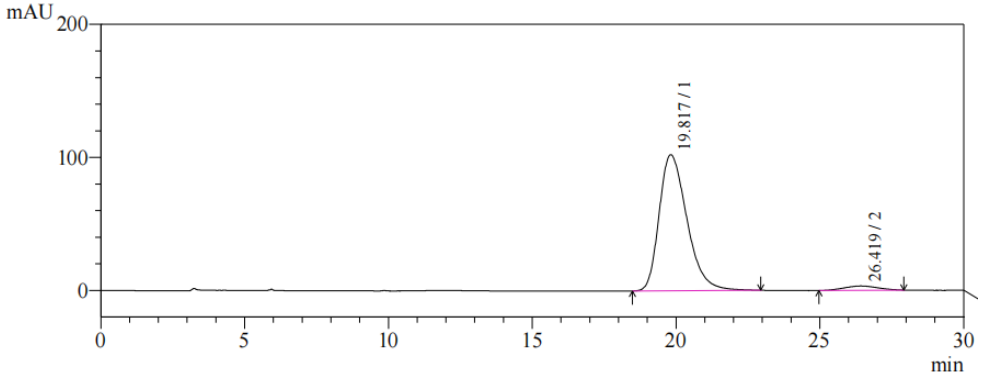
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.615	1004039	15554	50.247	56.292
2	25.764	994160	12077	49.753	43.708
Total		1998198	27630	100.000	100.000

Enantioenriched **7**

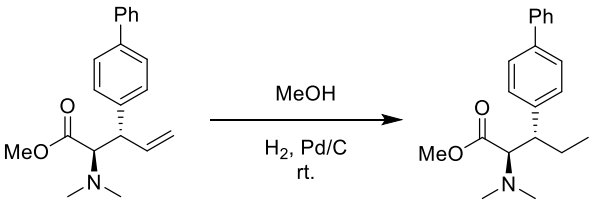


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.817	6877815	102285	96.096	96.821
2	26.419	279455	3358	3.904	3.179
Total		7157270	105643	100.000	100.000



7 **8**

The product **7** (0.1 mmol) and 10% Pd/C was dissolved in 1 mL MeOH under H_2 atmosphere. The reaction was stirred at rt. overnight. After the reaction was completed, the solution was concentrated under vacuum, and the residue was purified by silica gel chromatography to give the desired product **8**.

methyl (2*R*,3*S*)-3-([1,1'-biphenyl]-4-yl)-2-(dimethylamino)pentanoate (8) the reaction was conducted at 0.1 mmol scale, product **8** was obtained as a white solid (28.3 mg, 91% yield, *anti:syn* =19:1), M.p. 133 – 135 ℃.

TLC: R_f = 0.7 (petroleum ether/ethyl acetate 10/1).

[α] $^{28}{}_{D}$ = +98.4 (*c* = 0.1, in CH_2Cl_2).

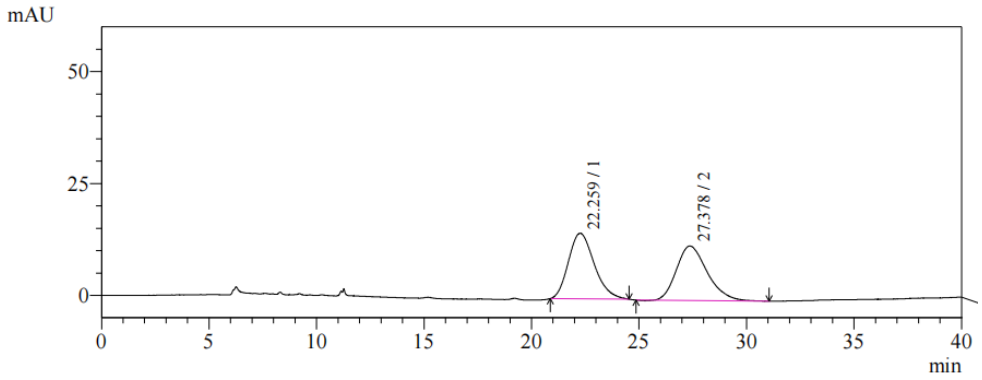
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.54 – 7.48 (m, 2H), 7.42 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.42 (d, *J* = 11.4 Hz, 1H), 3.38 (s, 3H), 2.98 – 2.87 (m, 1H), 2.39 (s, 6H), 2.20 – 2.03 (m, 1H), 1.57 – 1.48 (m, 1H), 0.76 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 140.9, 140.5, 139.3, 129.0, 128.7, 127.1, 126.92, 126.86, 72.4, 50.3, 46.6, 41.4, 24.8, 11.6.

HPLC: 95:5 *er*, chiral stationary column: OJ-H, mobile phase: hexane/^{i}PrOH = 99.5/0.5, flow rate 0.5 mL/min, λ = 254 nm, 30 ºC, t_r (major) = 22.6 min, t_r (minor) = 27.5 min.

HRMS m/z $[M+H]^+$ calcd for $C_{20}H_{26}NO_2^+$ = 312.1958, found 312.1955.

Racemic **8**



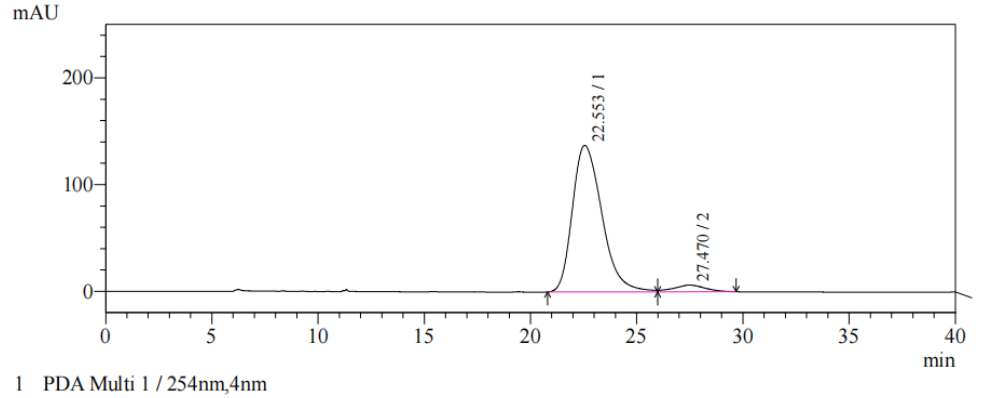
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.259	1226100	14668	50.285	54.626
2	27.378	1212220	12184	49.715	45.374
Total		2438319	26851	100.000	100.000

Enantioenriched **8**

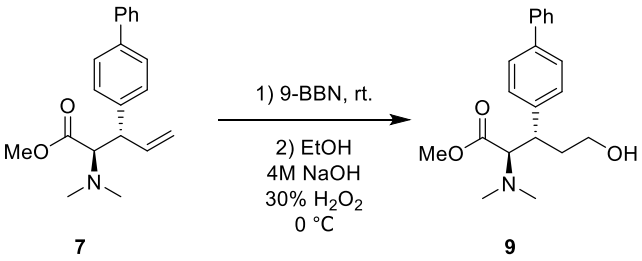


1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.553	13268654	137314	95.383	95.624
2	27.470	642274	6285	4.617	4.376
Total		13910928	143598	100.000	100.000



7 **9**

The product **7** (0.1 mmol) was dissolved in 9-BBN (0.5 M in tetrahydrofuran, 0.4 mL, 0.20 mmol) under N_2 atmosphere, and the resulting solution was stirred 24 h at room temperature. The reaction was diluted with ethanol (1.0 mL) and treated with 4 M sodium hydroxide (0.2 mL). Then 30% hydrogen peroxide (0.3 mL) was added dropwise at 0 °C. The reaction was stirred at 0 °C for 1 h, then quenched by addition of saturated NH_4Cl. The mixture was extracted with diethyl ether. The combine organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography to give the desired product **9.**

methyl (2*R*,3*S*)-3-([1,1'-biphenyl]-4-yl)-2-(dimethylamino)-5-hydroxypentanoate (9) the reaction was conducted at 0.1 mmol scale, product **9** was obtained as a white solid (27.2 mg, 83% yield, *anti:syn* =19:1), M.p. 79 – 81 °C.

TLC: R_f = 0.2 (petroleum ether/ethyl acetate 2/1).

[α] $^{28}{}_D$ = -0.95 (*c* = 0.35, in CH_2Cl_2).

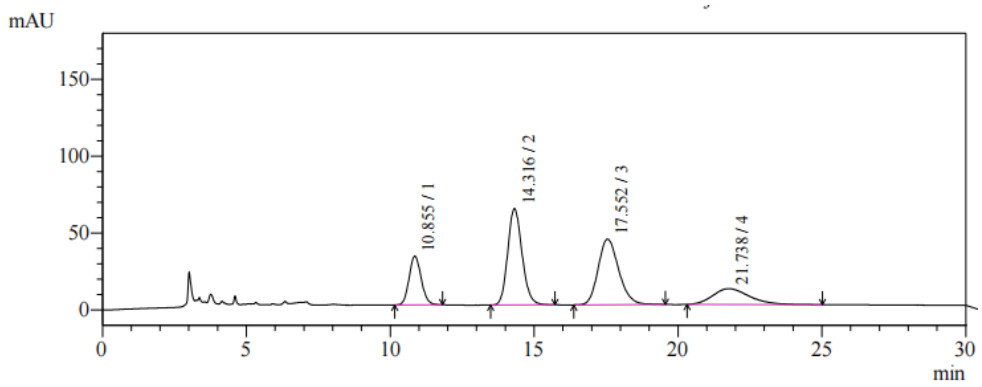
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.57 – 7.52 (m, 2H), 7.51 – 7.41 (m, 2H), 7.40 – 7.32 (m, 1H), 7.32 – 7.24 (m, 2H), 3.80 – 3.69 (m, 1H), 3.65 – 3.53 (m, 2H), 3.40 (s, 3H), 3.30 – 3.21 (m, 1H), 2.49 (s, 6H), 2.26 – 2.14 (m, 1H), 2.06 – 1.96 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 141.2, 140.7, 139.7, 128.8, 128.5, 127.3, 127.2, 127.0, 72.3, 61.3, 50.8, 44.5, 41.6, 39.0.

HPLC: 95:5 *er*, chiral stationary column: OJ-H, mobile phase: hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, 30 °C, t_r (major) = 14.4 min, t_r (minor) = 17.6 min.

HRMS m/z $[M+H]^+$ calcd for $C_{20}H_{26}NO_3^+$ = 328.1907, found 328.1905.

Racemic **9**



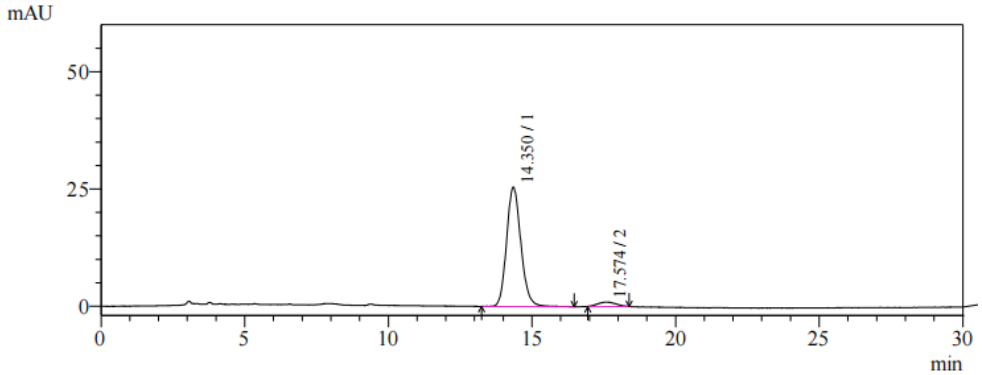
1 PDA Multi 1 / 254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.855	928805	31781	15.125	21.540
2	14.316	2178817	62784	35.480	42.552
3	17.552	2128407	42733	34.659	28.963
4	21.738	904956	10246	14.736	6.945
Total		6140986	147545	100.000	100.000

Enantioenriched **9**



1 PDA Multi 1 / 254nm,4nm

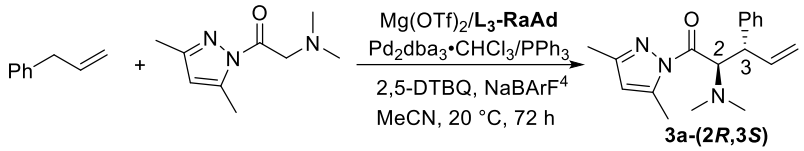
PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.350	883880	25501	95.251	96.293
2	17.574	44070	982	4.749	3.707
Total		927950	26483	100.000	100.000

8. Determination of the absolute configuration

a) This work:

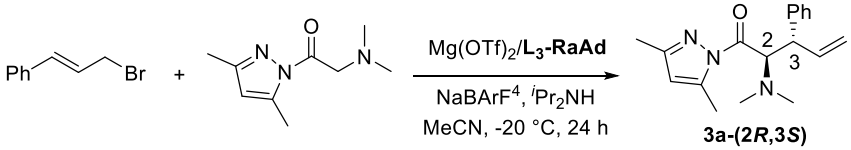


3a-(2*R*,3*S*)

64% yield, >8:1 *dr*, 95:5 *er*

$[a]^{28}_{D}$ = +49.7 (c = 0.40, in CH_2Cl_2).

b) Our previous work: *Chem. Sci.,* **2020**, *11*, 3068-3073.



3a-(2*R*,3*S*)

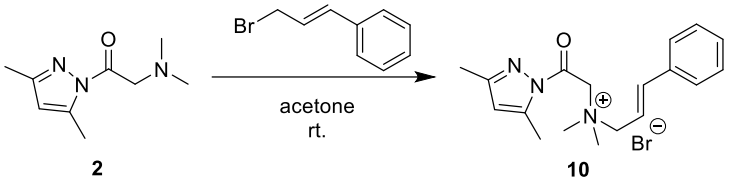
91% yield, >19:1 *dr*, 97:3 *er*

$[a]^{24}_{D}$ = +82.0 (c = 1.02, in CH_2Cl_2).

The reaction depicted in Eq (b) was run according to our previous report (*Chem. Sci.* **2020**, *11*, 3068-3073). The compound **3a** prepared by our previous method is (2*R*,3*S*) configuration in 97:3 *er*, and its optical rotation has been measured as $[\alpha]^{24}_{D}$ = +82.0 (c = 1.02, CH_2Cl_2, λ = 589 mm).

In the present manuscript, the sample of **3a** was prepared in 95:5 *er* and its optical rotation was measured as $[\alpha]^{28}_{D}$ = +49.7 (c = 0.40, CH_2Cl_2, λ = 589 mm). Therefore, we assigned **3a** as (2*R*,3*S*) configuration.

9. Control experiment



2 **10**

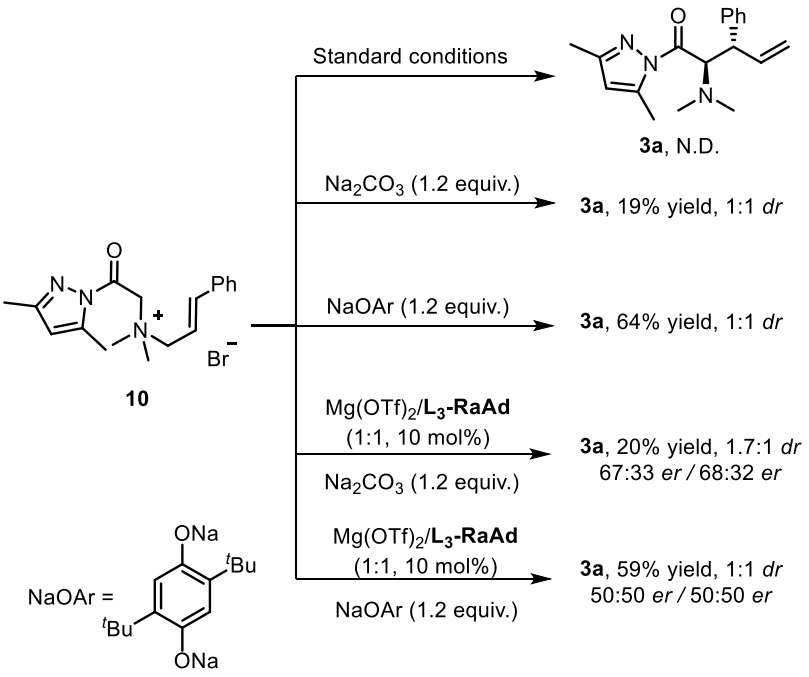
The reaction was conducted with dimethylglycine pyrazoleamide (**2**, 0.1 mmol) and cinnamyl bromide (0.1 mmol) in 2.0 mL of acetone. The mixture was stirred at room temperature overnight under a N_2 atmosphere, and then concentrated in vacuo to give product **10**.

^{1}H NMR (400 MHz, D_2O) δ 7.26 (d, *J* = 7.1 Hz, 2H), 7.18 (d, *J* = 6.9 Hz, 3H), 6.67 (d, *J* = 15.7 Hz, 1H), 6.23 – 6.11 (m, 1H), 5.97 (s, 1H), 4.60 (s, 2H), 4.15 (d, *J* = 7.7 Hz, 2H), 3.19 (s, 5H), 2.31 (s, 3H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, D_2O) δ 163.7, 155.8, 145.8, 143.5, 134.7, 129.6, 128.9, 127.2, 114.3, 112.7, 67.6, 61.1, 51.9, 13.6, 12.8.

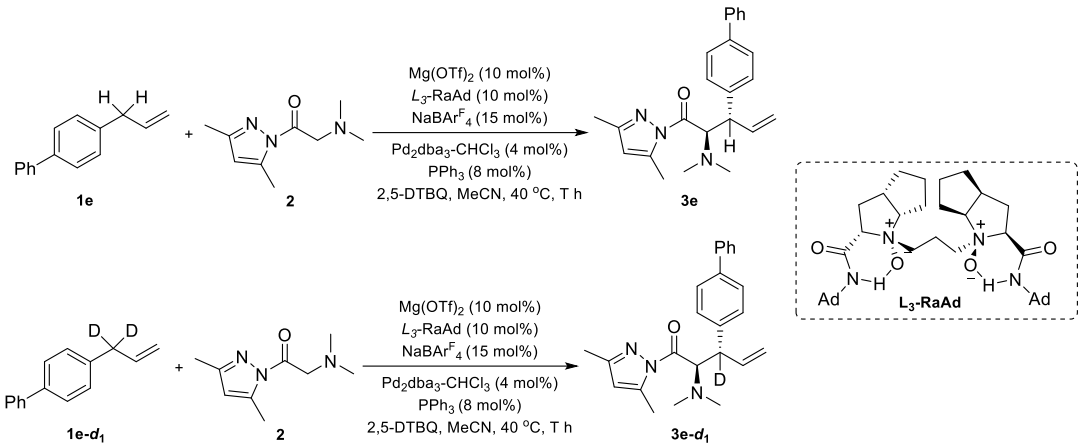
HRMS m/z $[M+H]^+$ calcd for $C_{18}H_{24}N_3O^+$ = 298.1914, found 298.1906.

In order to gain insight into the catalytic mechanism, a series of control experiments to investigate the [2,3]-rearrangement of allylic ammonium salt **10** were subsequently performed. The results summarized as below:



Note: All the reactions were conducted at MeCN, 20 °C, 72 h

10. Initial Rate Kinetic Isotope Effects (KIE) study



Under an N_2 atmosphere, the tube was added $Mg(OTf)_2$ (0.01 mmol, 10mol%), *N*,*N*′-dioxides ligand L_3-RaAd (0.01 mmol, 10 mol%), amino amide **2** (0.1 mmol, 1.0 equiv.) and MeCN (0.5 mL). Another tube was added $Pd_2(dba)_3{\cdot}CHCl_3$ (4 mol%), PPh_3 (8 mol%) and MeCN (0.5 mL). After being stirred at 35 °C for 1 h, two tubes were mixed, and 2,5-DTBQ (1.5 equiv.) and terminal alkene **1e**/**1e-*d*$_2$** (0.2 mmol, 2.0 equiv.) were added sequently. Then the reaction mixture was stirred at 40 °C. The concentration of **3e** and **3e-*d*$_1$** was monitored by NMR ^{1}H analysis. The results were shown in Figure S1. The KIE (k_H/k_D) was calculated to be 2.9 (Figure S1).

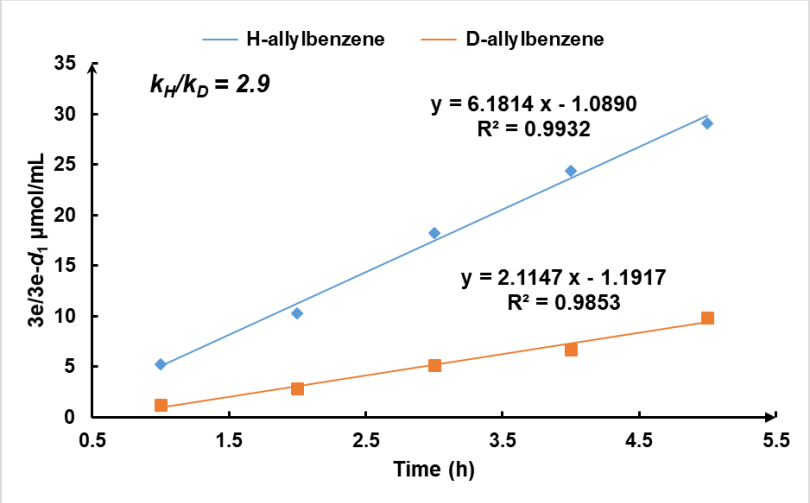
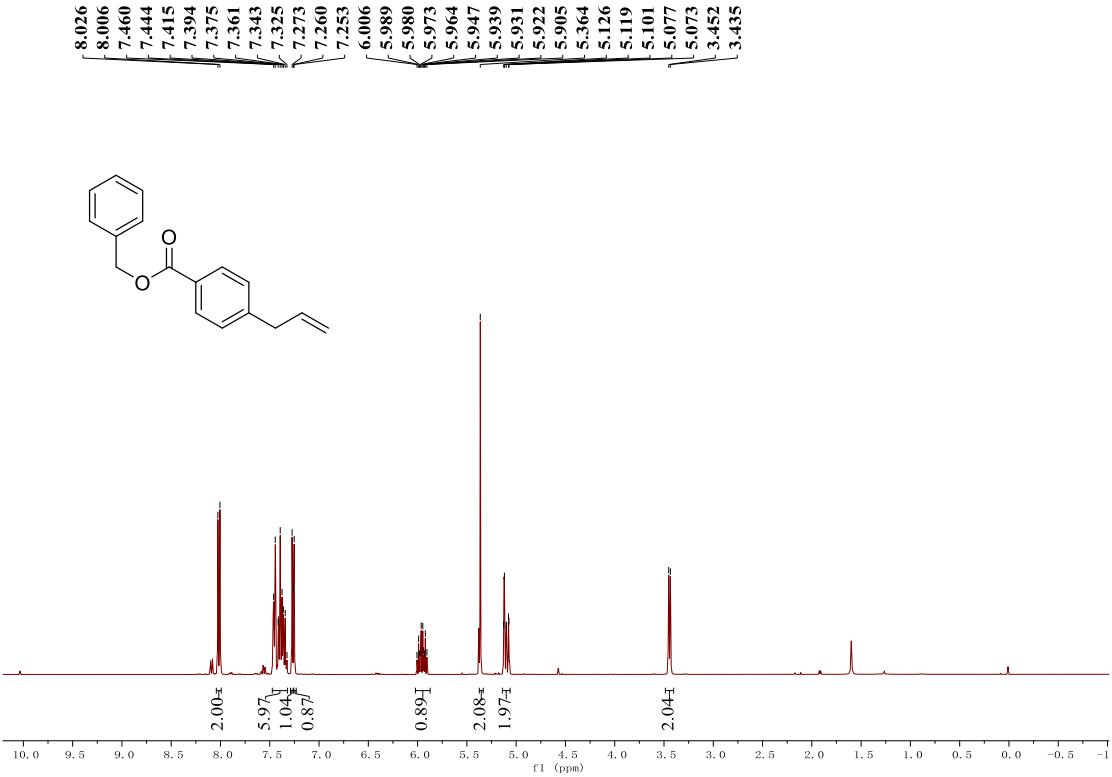
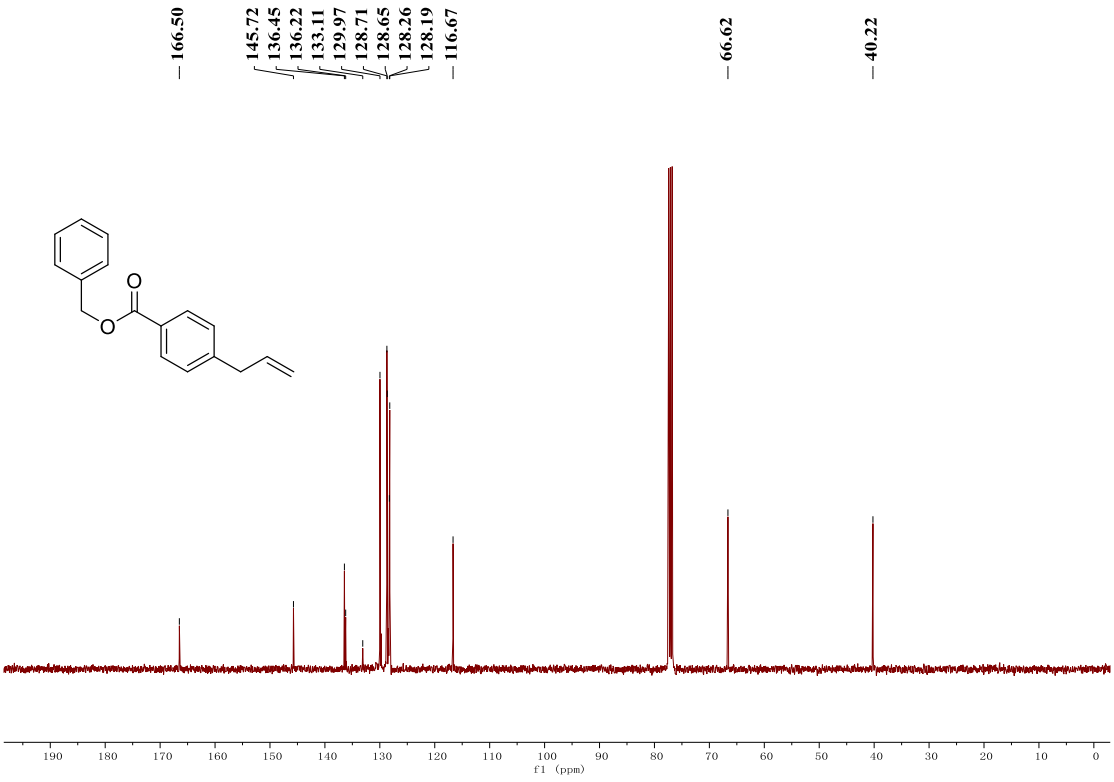


Figure S1: Graph illustrating the KIE data. Slopes were fit using a least square linear regression model.

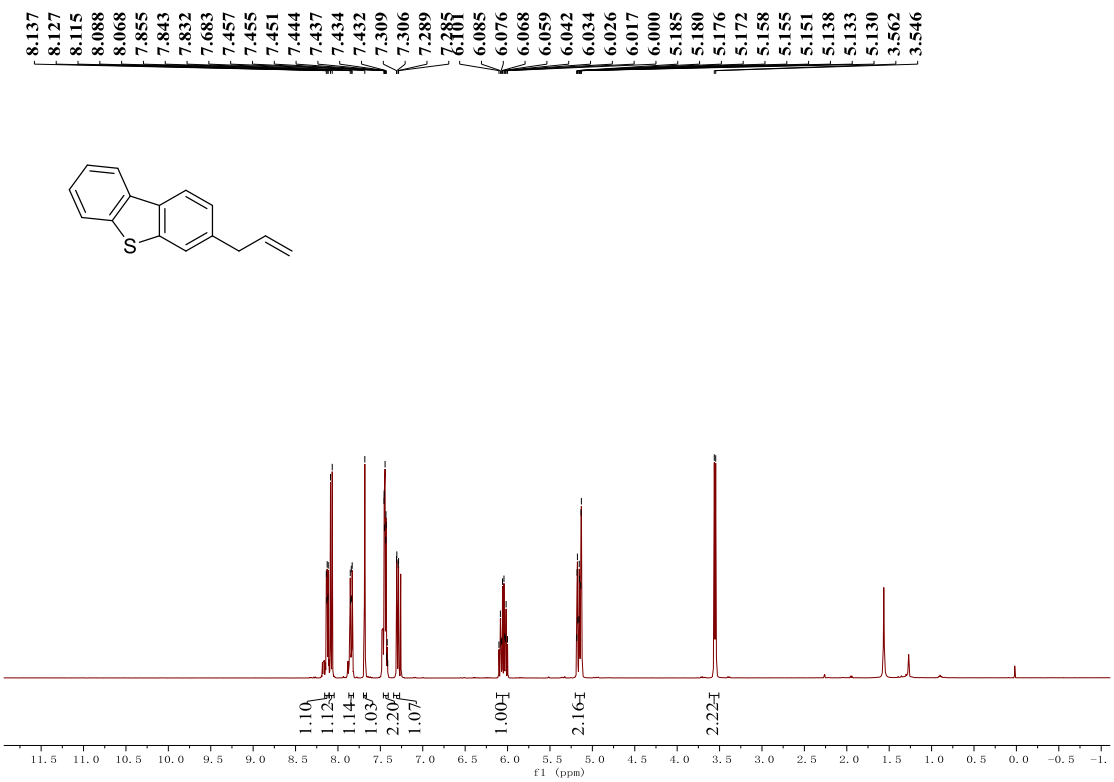
11. NMR spectrum



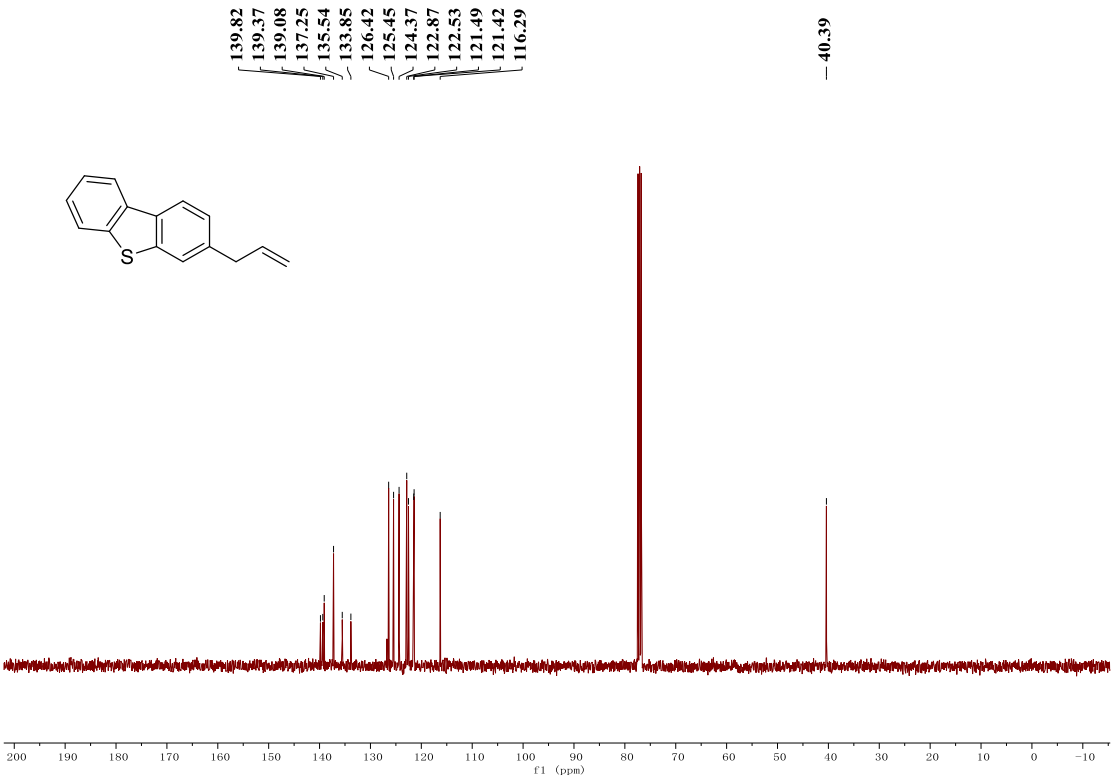
^{1}H NMR of Compound **1p** (400 MHz, $CDCl_3$)



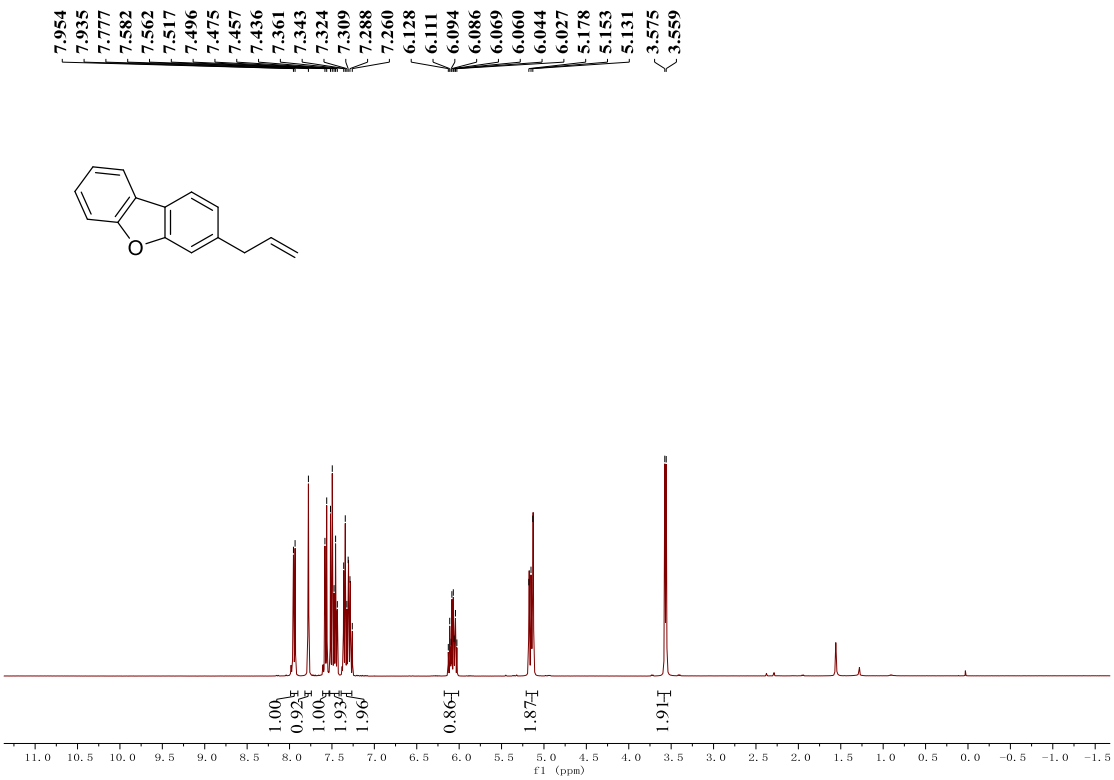
^{13}C NMR of Compound **1p** (101 MHz, $CDCl_3$)



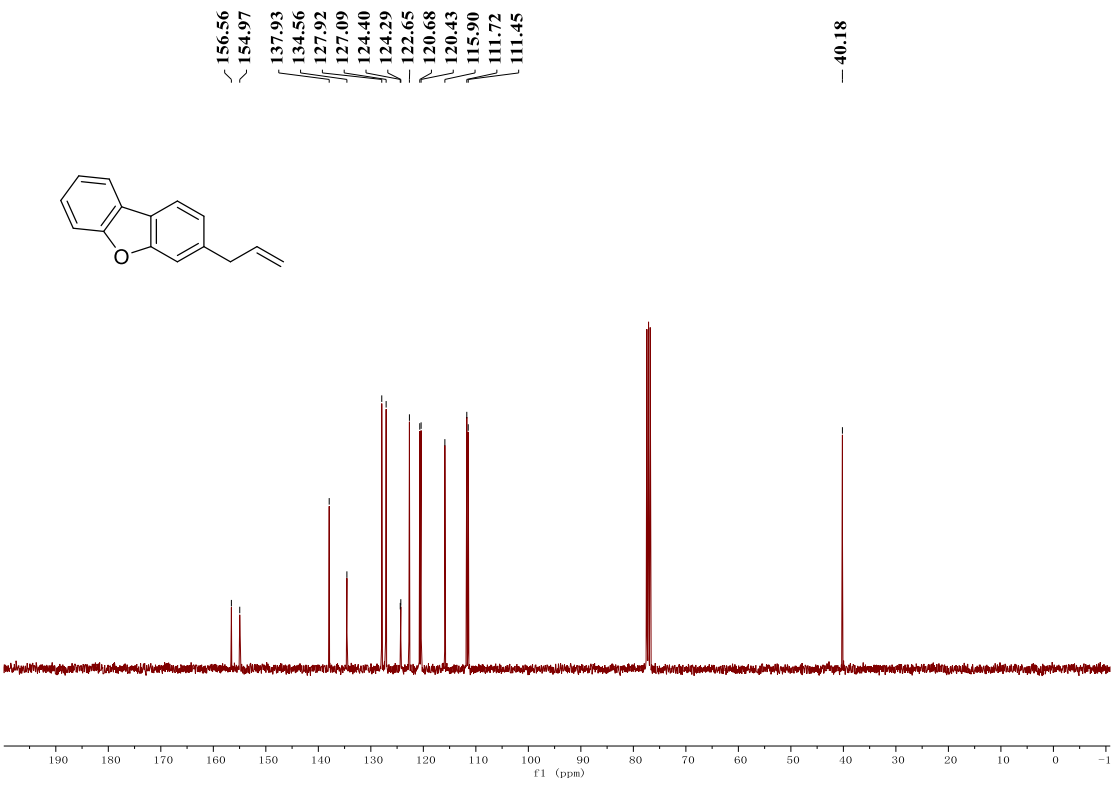
^{1}H NMR of Compound **1t** (400 MHz, $CDCl_3$)



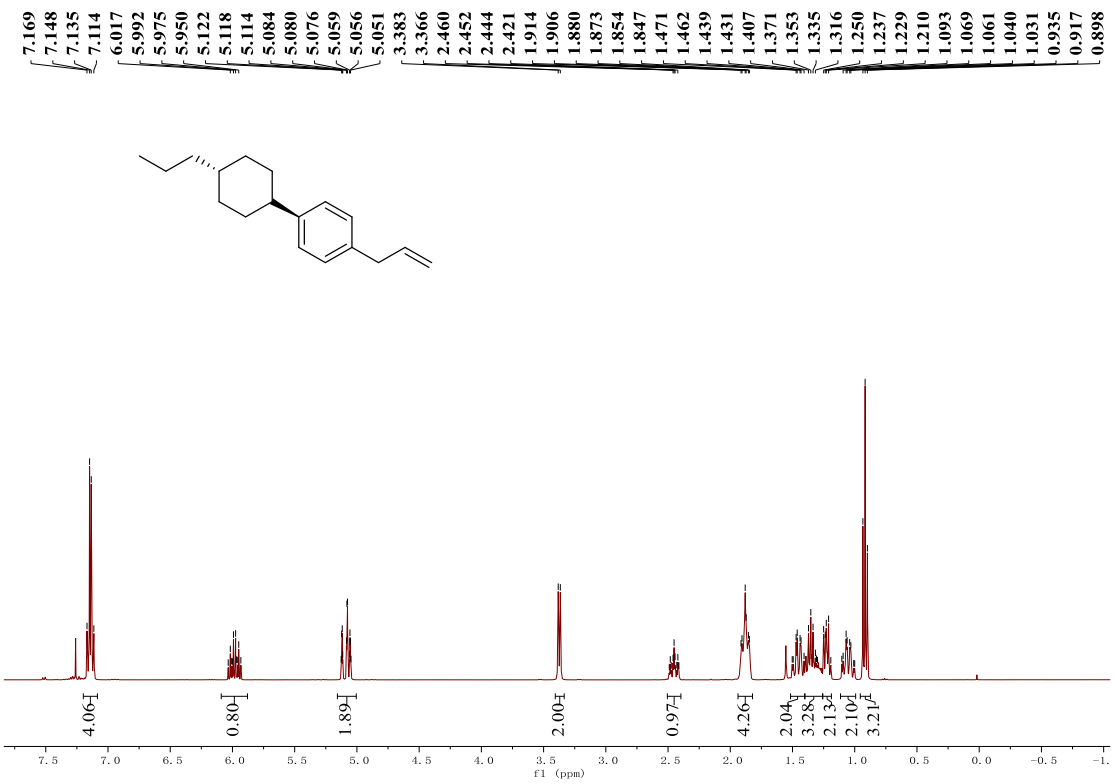
^{13}C NMR of Compound **1t** (101 MHz, $CDCl_3$)



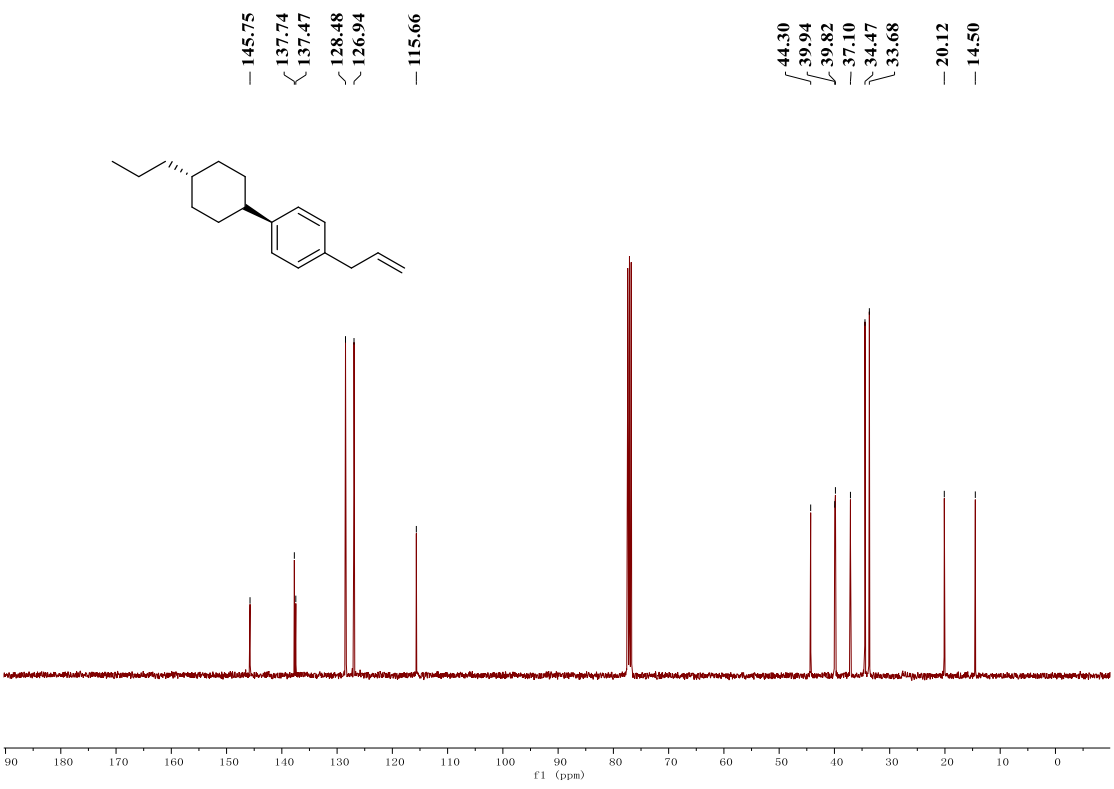
^{1}H NMR of Compound **1u** (400 MHz, $CDCl_3$)



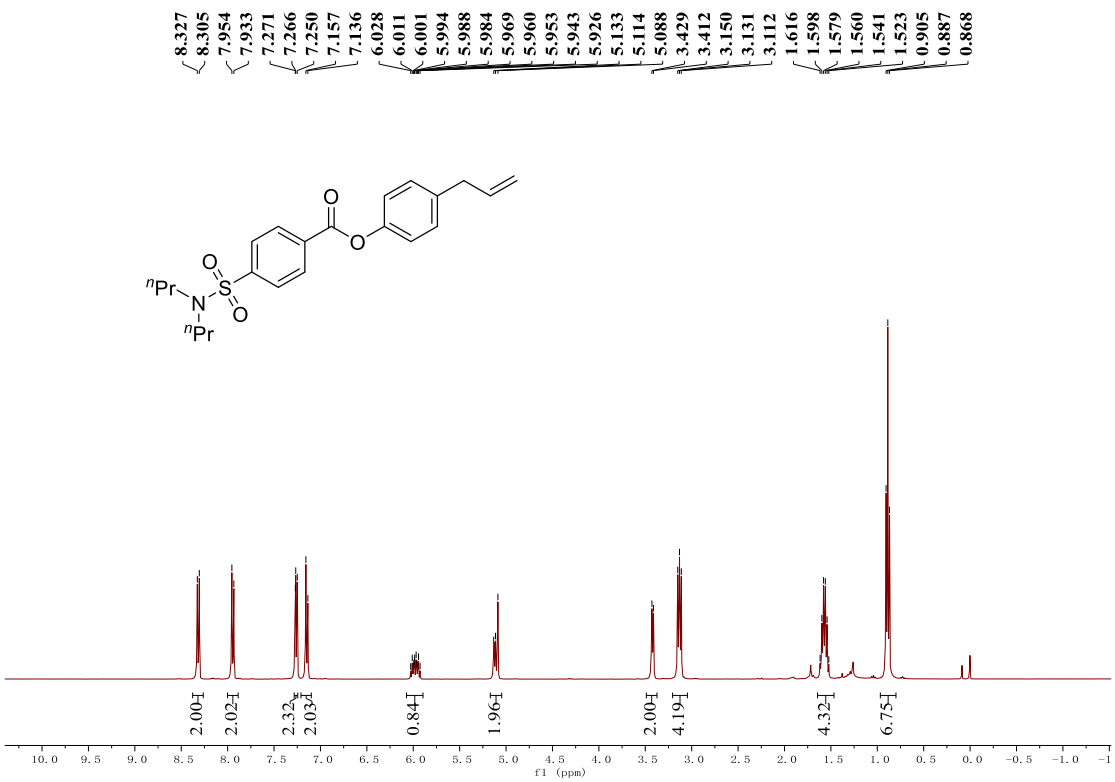
^{13}C NMR of Compound **1u** (101 MHz, $CDCl_3$)



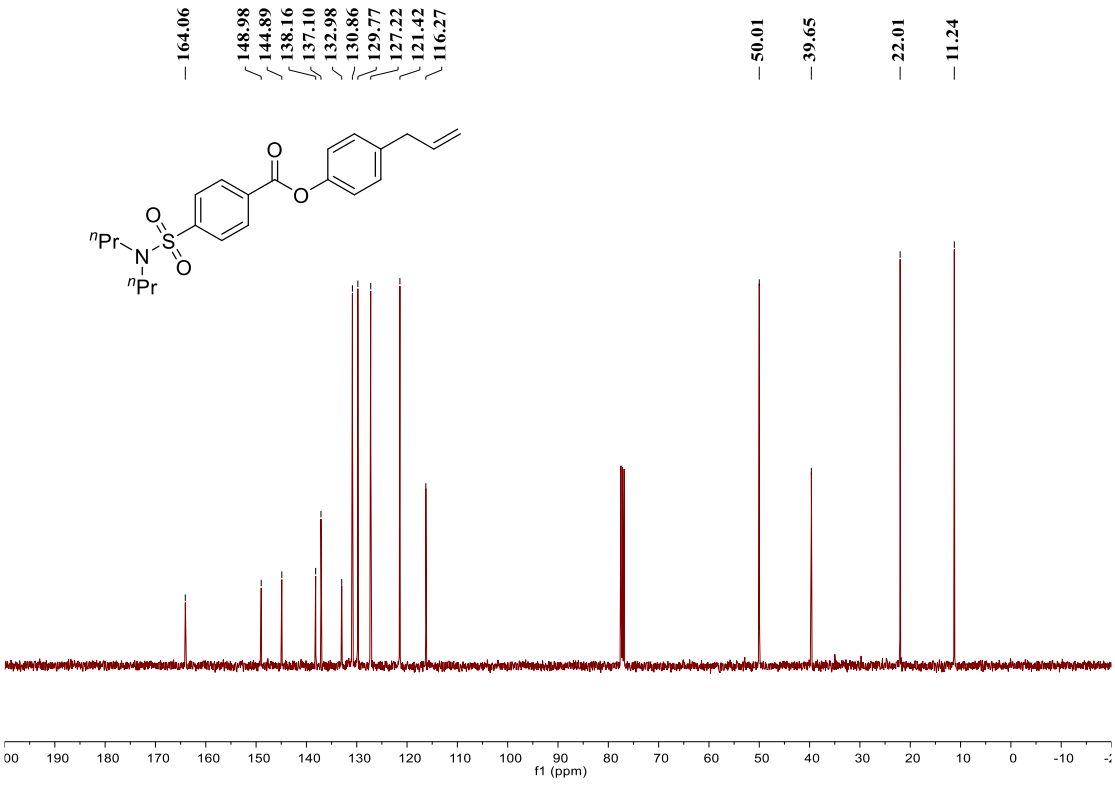
^{1}H NMR of Compound **1x** (400 MHz, $CDCl_3$)



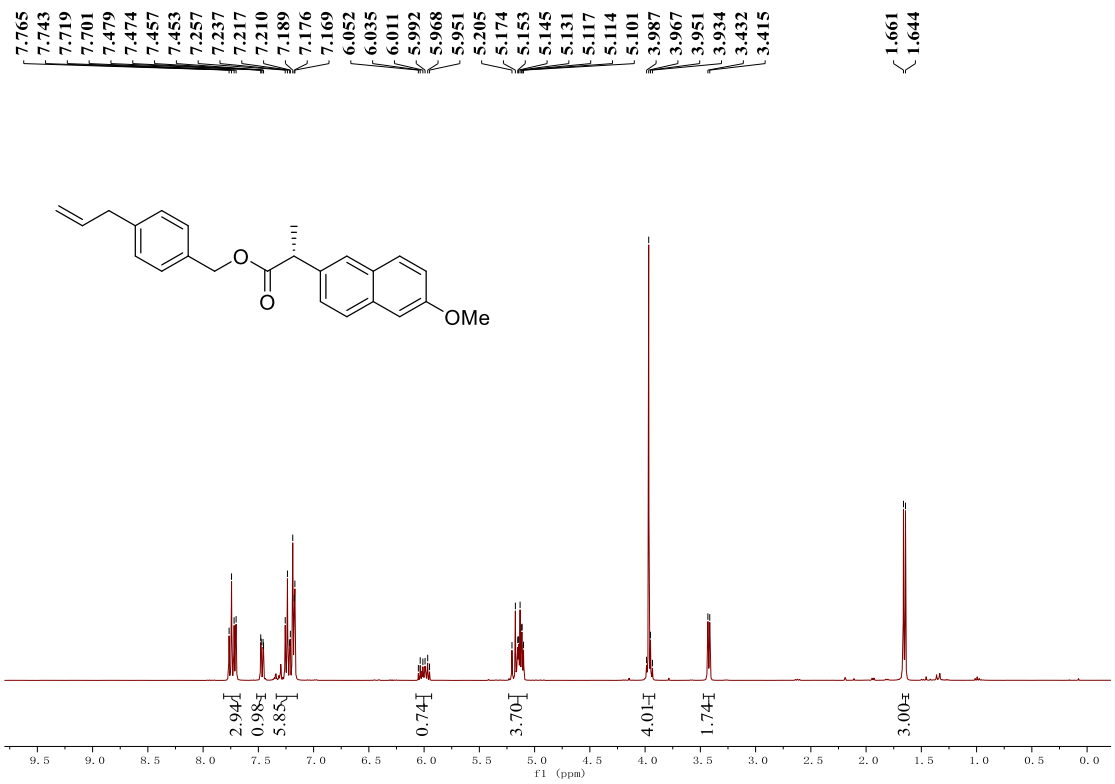
^{13}C NMR of Compound **1x** (101 MHz, $CDCl_3$)



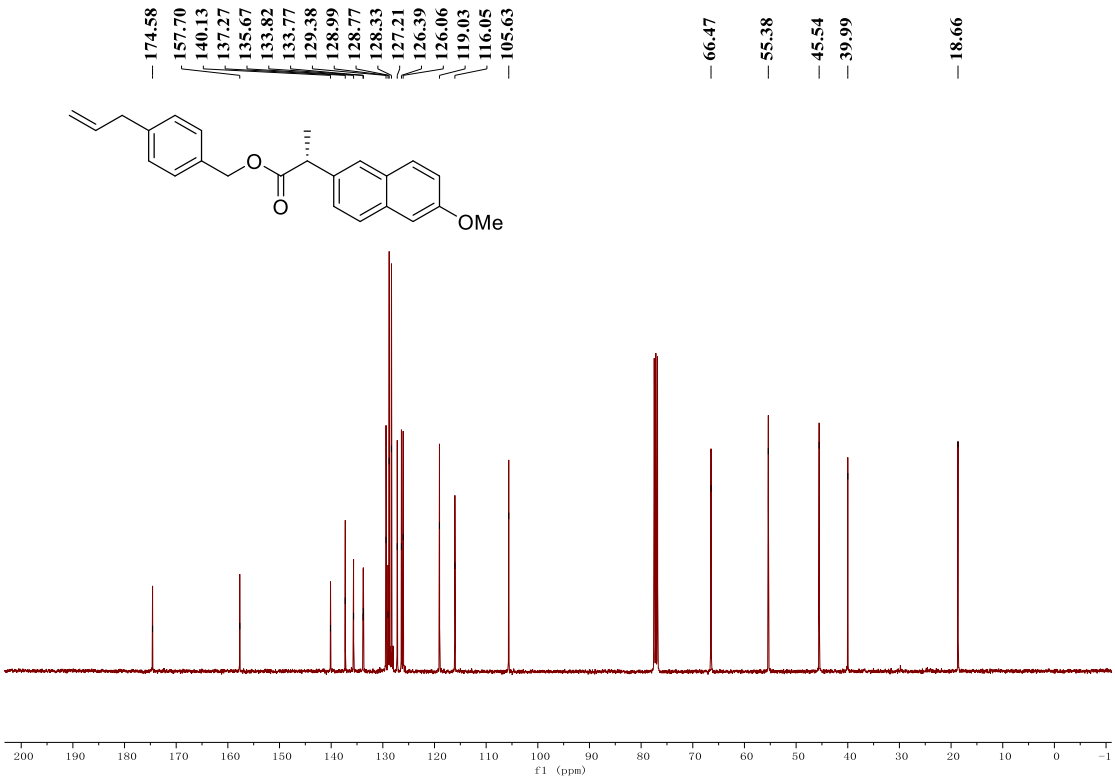
^{1}H NMR of Compound **1ca** (400 MHz, $CDCl_3$)



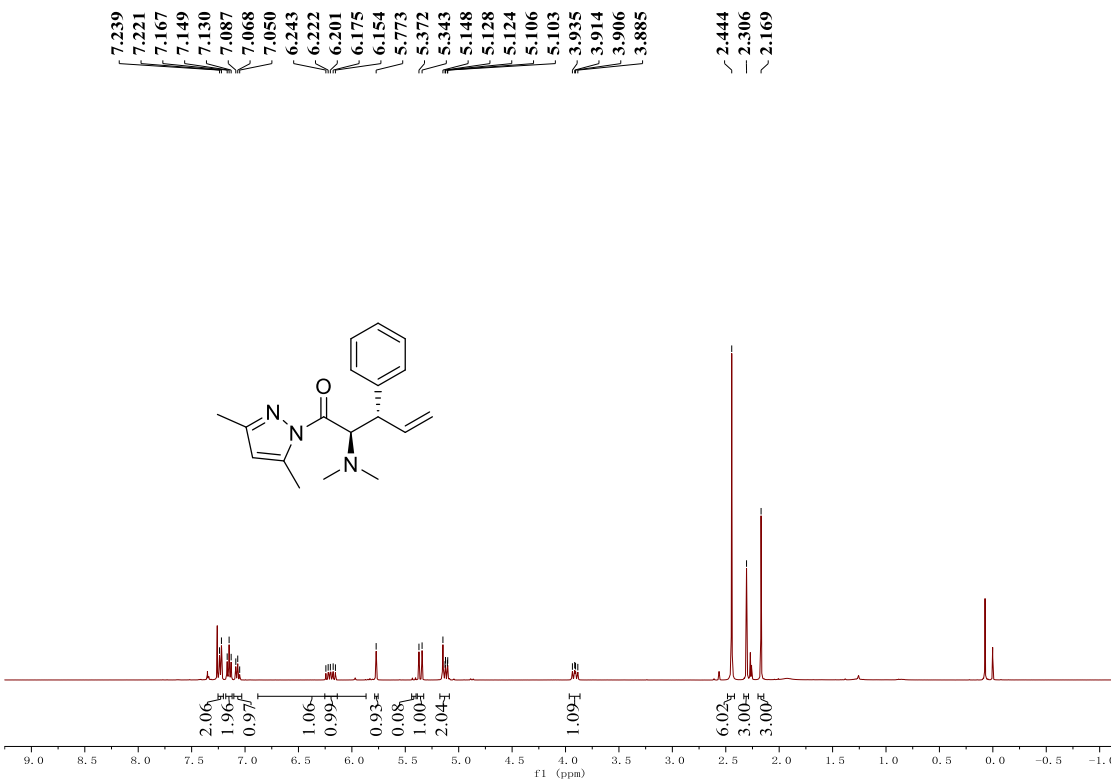
^{13}C NMR of Compound **1ca** (101 MHz, $CDCl_3$)



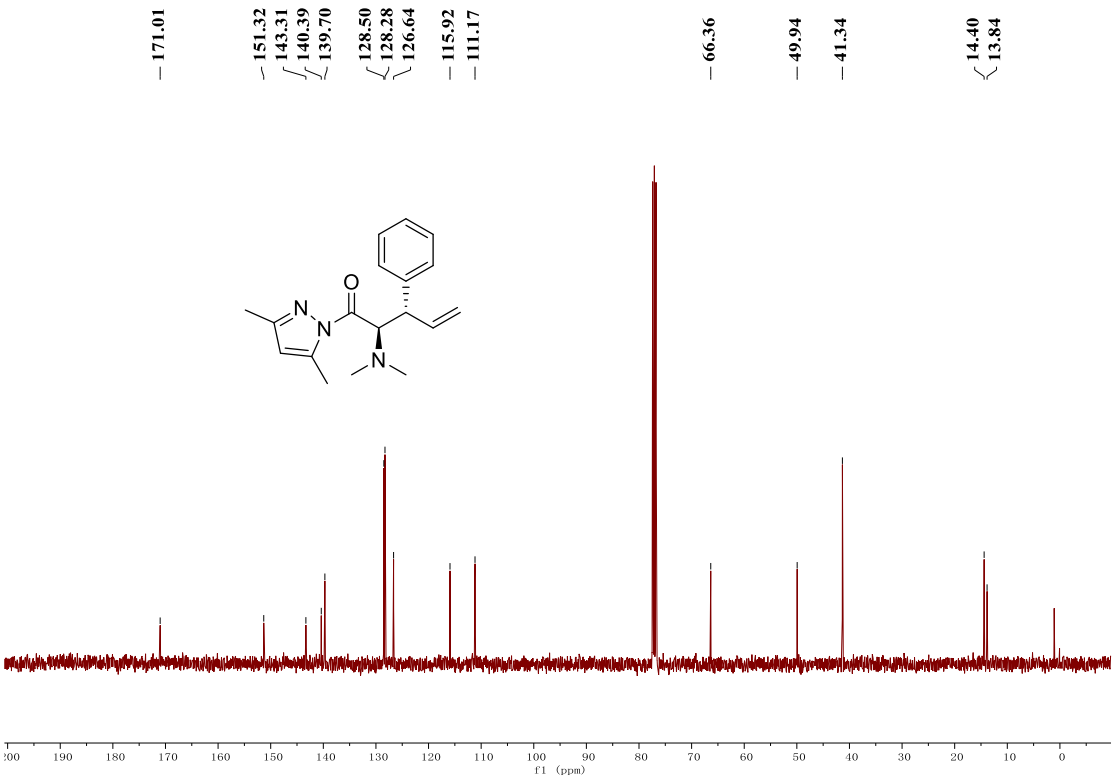
^{1}H NMR of Compound **1cb** (400 MHz, $CDCl_3$)



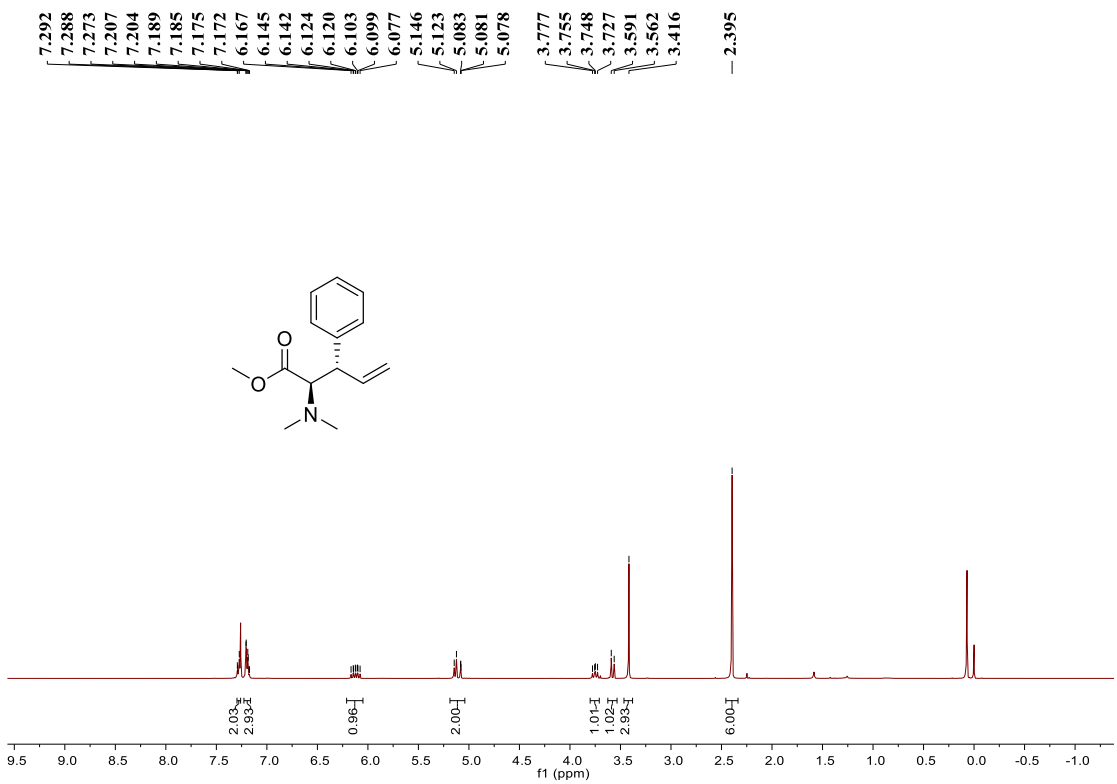
^{13}C NMR of Compound **1cb** (101 MHz, $CDCl_3$)



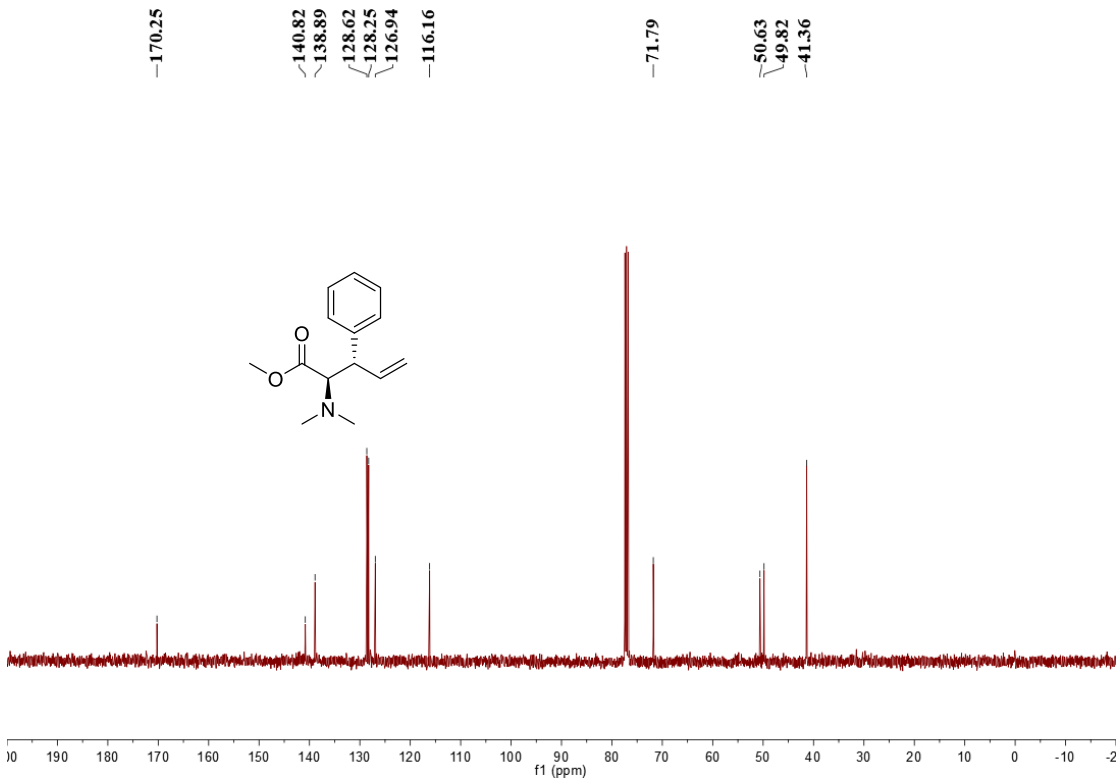
^{1}H NMR of Compound **3a** (400 MHz, $CDCl_3$)



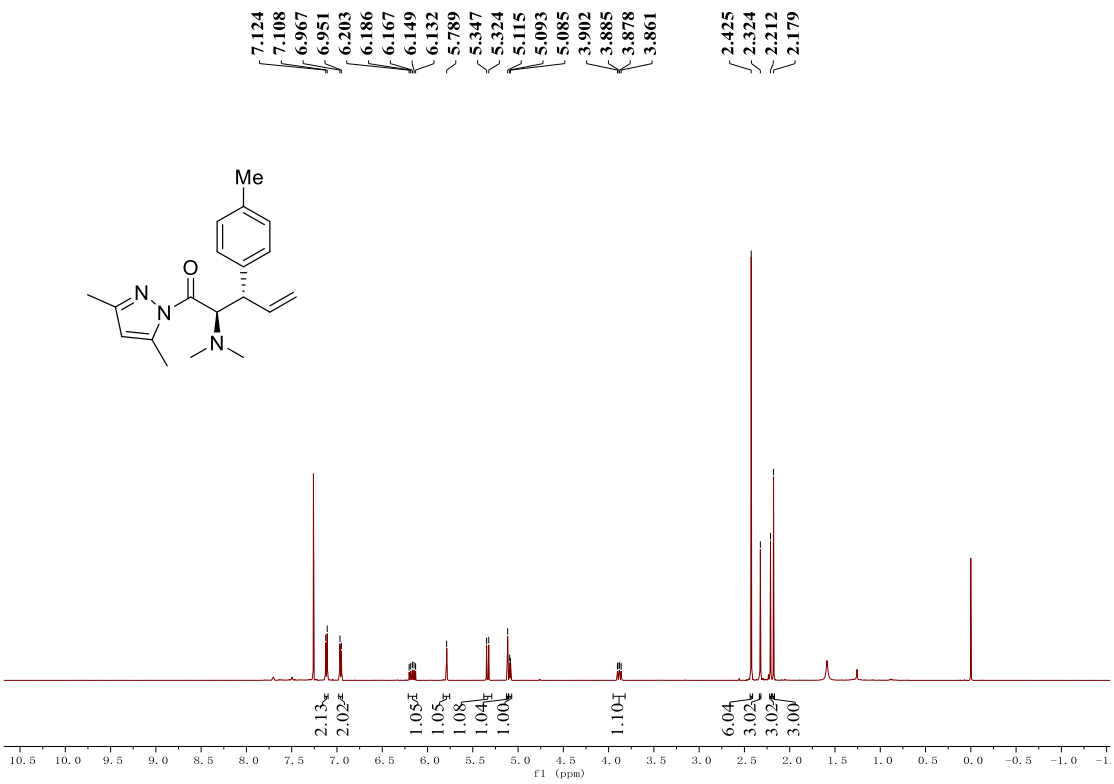
^{13}C NMR of Compound **3a** (101 MHz, $CDCl_3$)



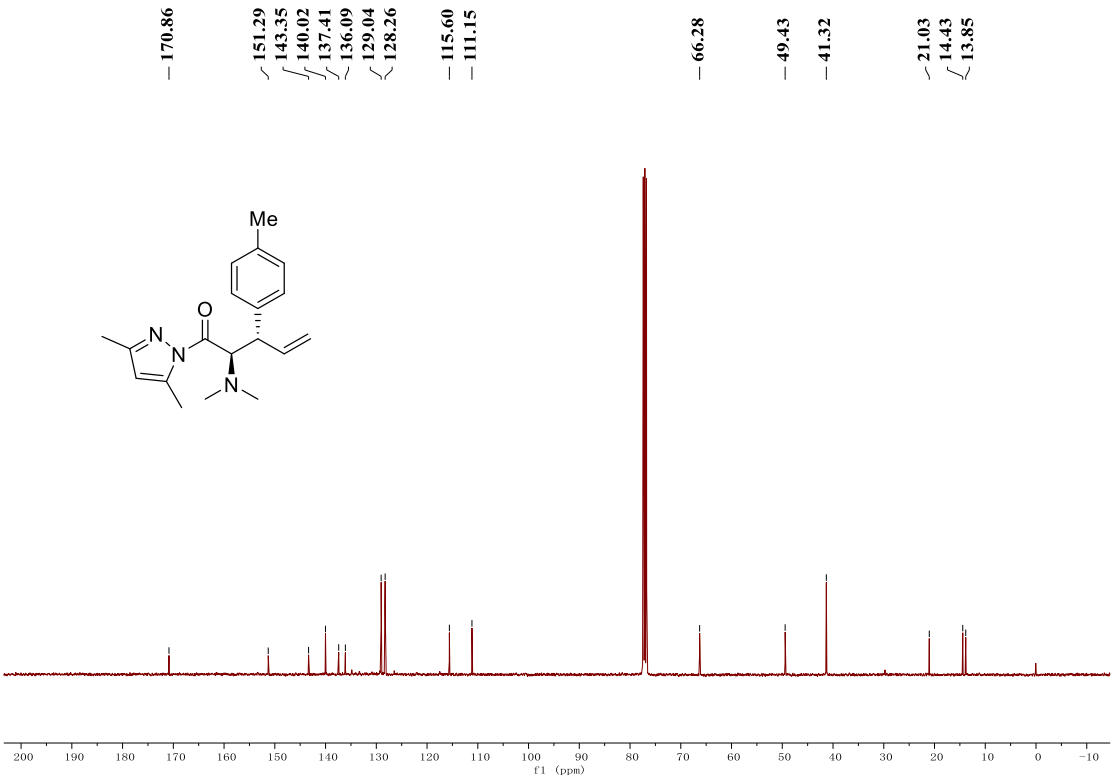
^{1}H NMR of Compound **3a-methyl ester** (400 MHz, $CDCl_3$)



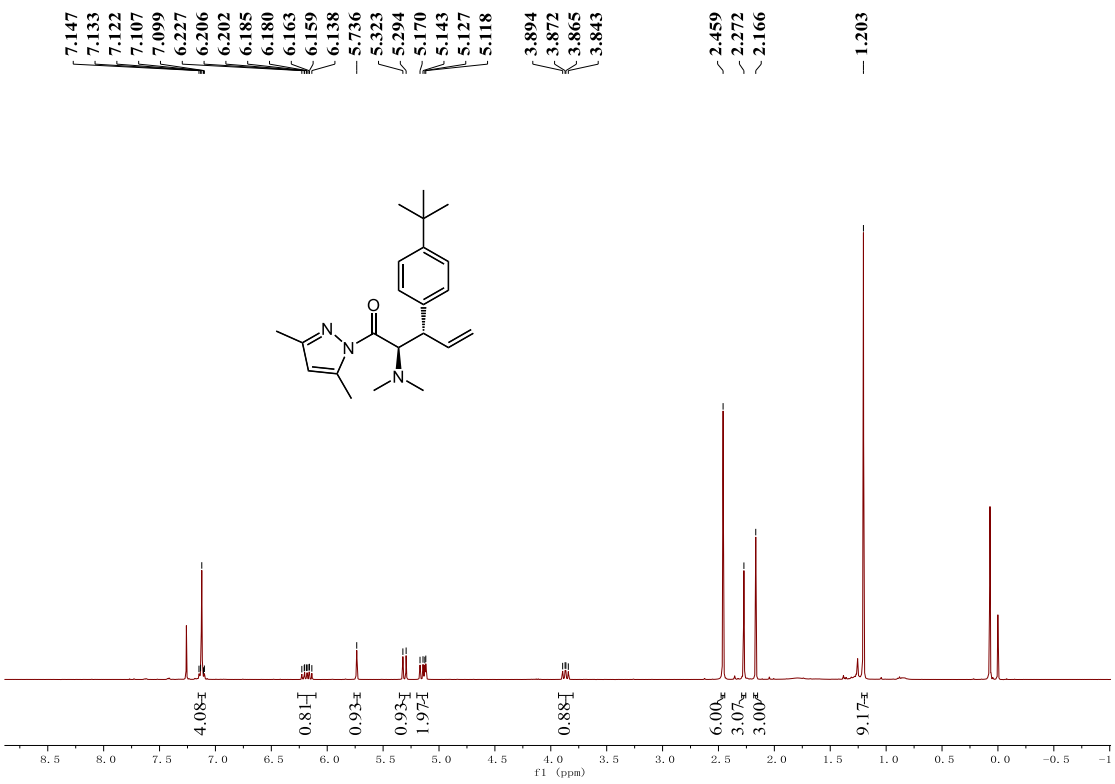
^{13}C NMR of Compound **3a-methyl ester** (101 MHz, $CDCl_3$)



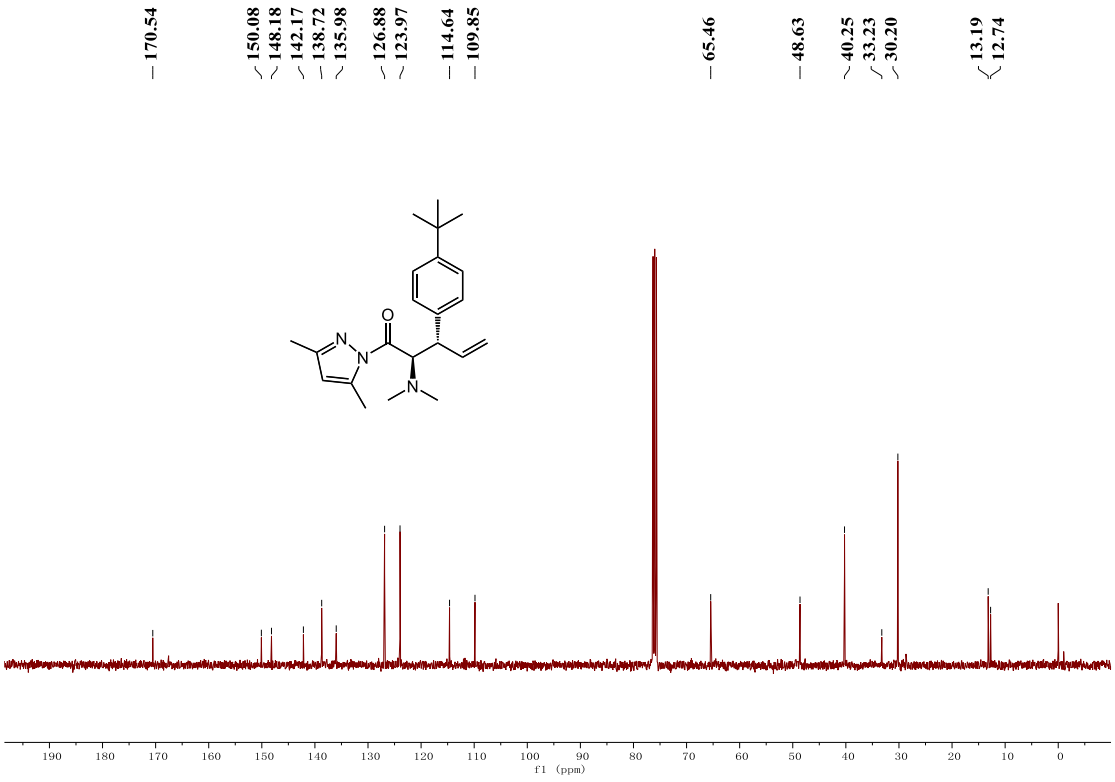
^{1}H NMR of Compound **3b (**(500 MHz, $CDCl_3$)**)**



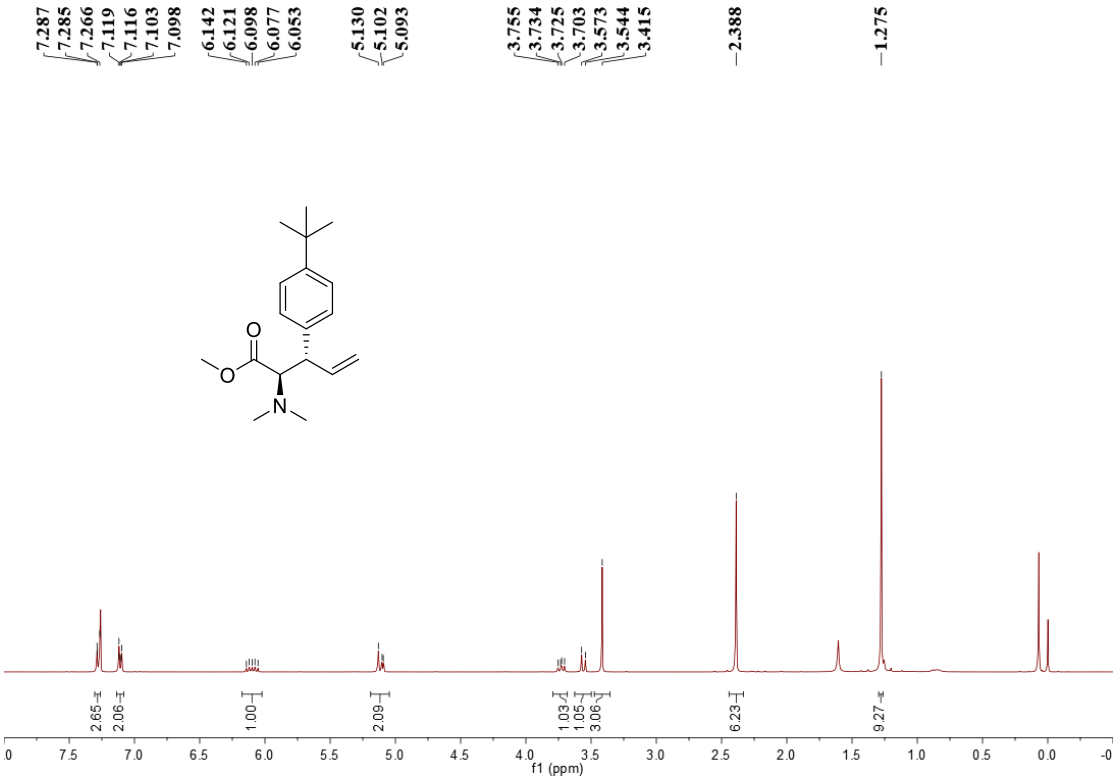
^{13}C NMR of Compound **3b** (101 MHz, $CDCl_3$)



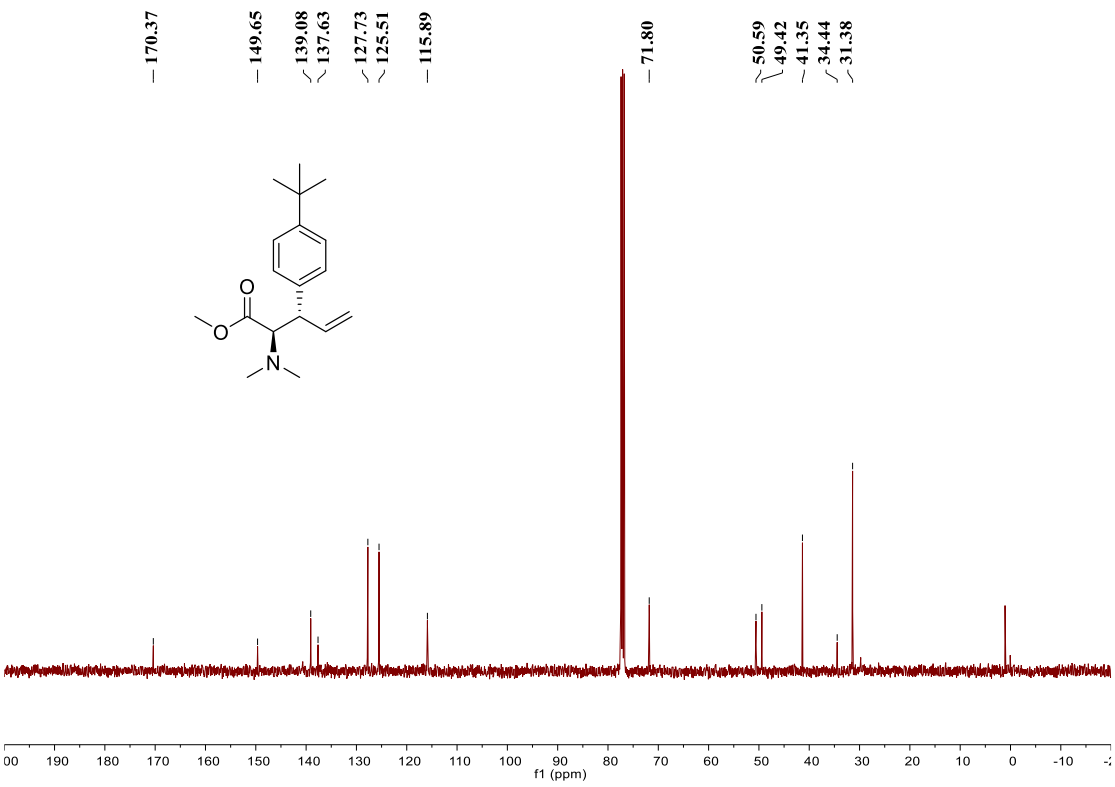
^{1}H NMR of Compound **3c** (400 MHz, $CDCl_3$)



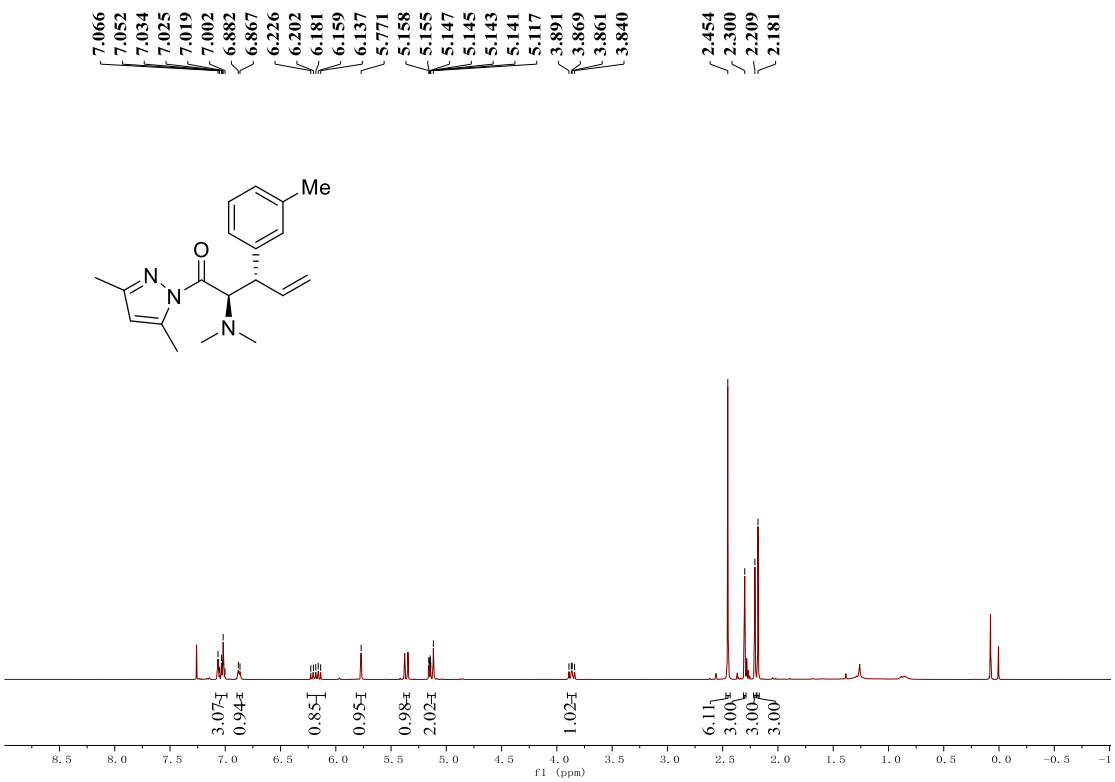
^{13}C NMR of Compound **3c** (101 MHz, $CDCl_3$)



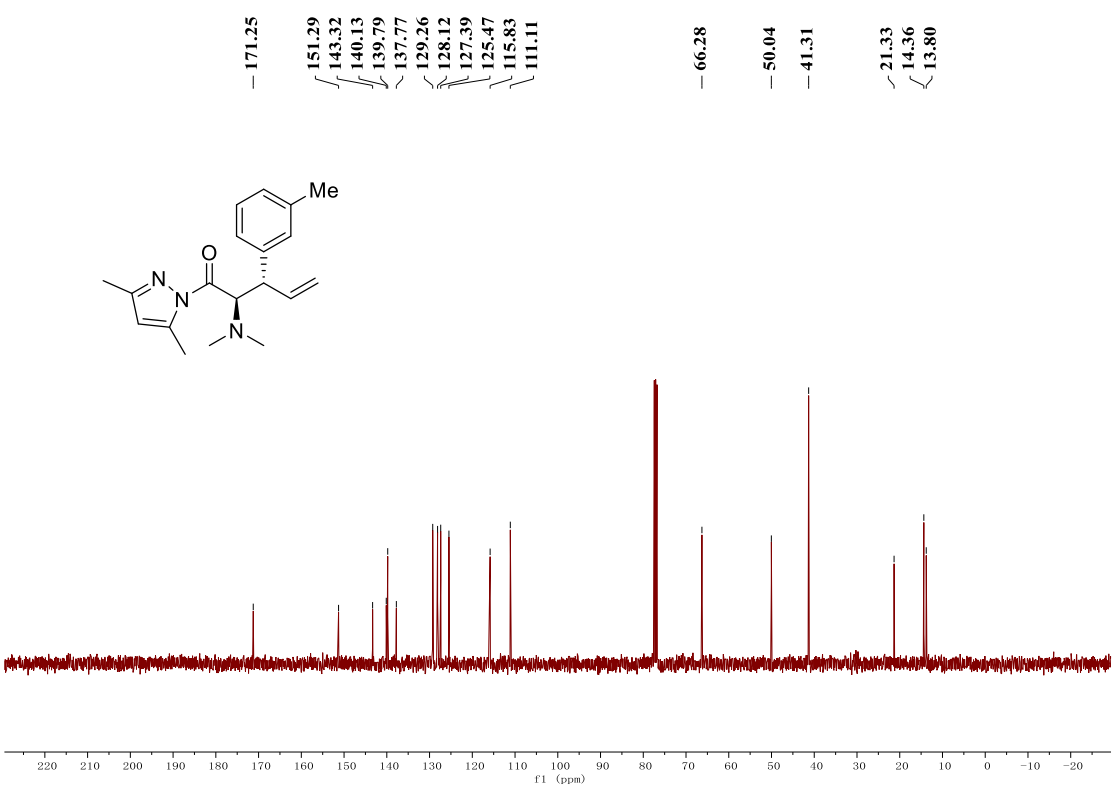
^{1}H NMR of Compound **3c-methyl ester** (400 MHz, $CDCl_3$)



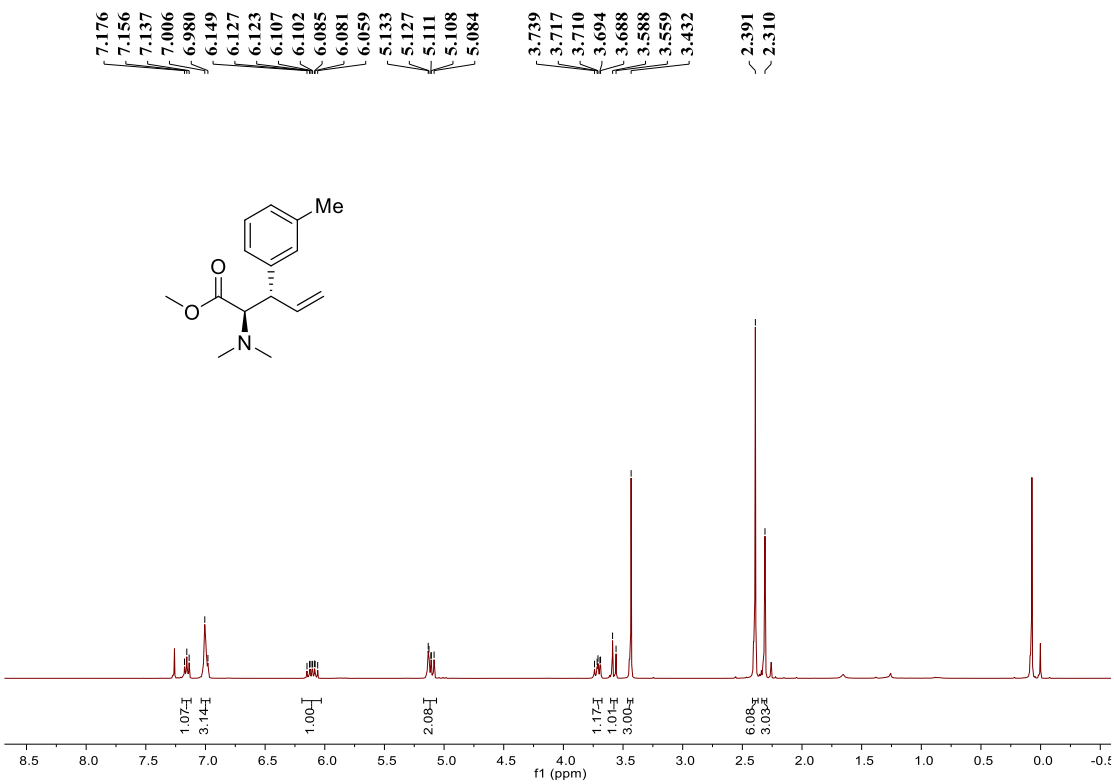
^{13}C NMR of Compound **3c-methyl ester** (101 MHz, $CDCl_3$)



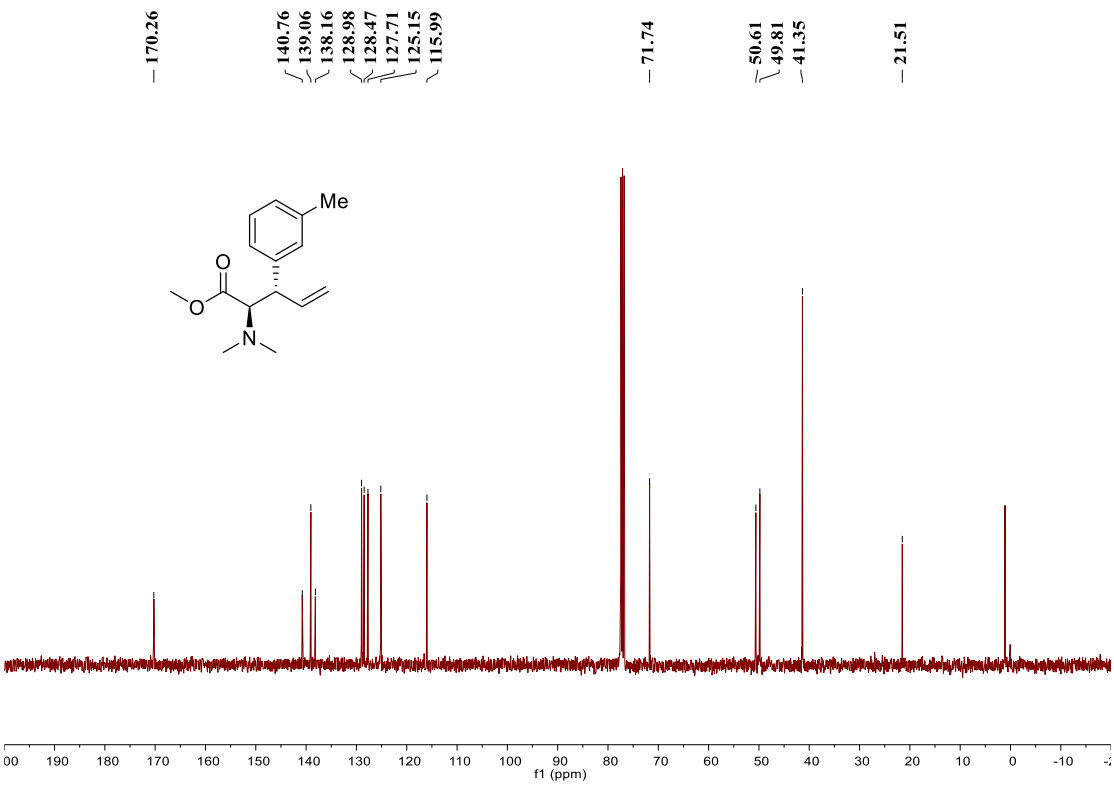
^{1}H NMR of Compound **3d** (400 MHz, $CDCl_3$)



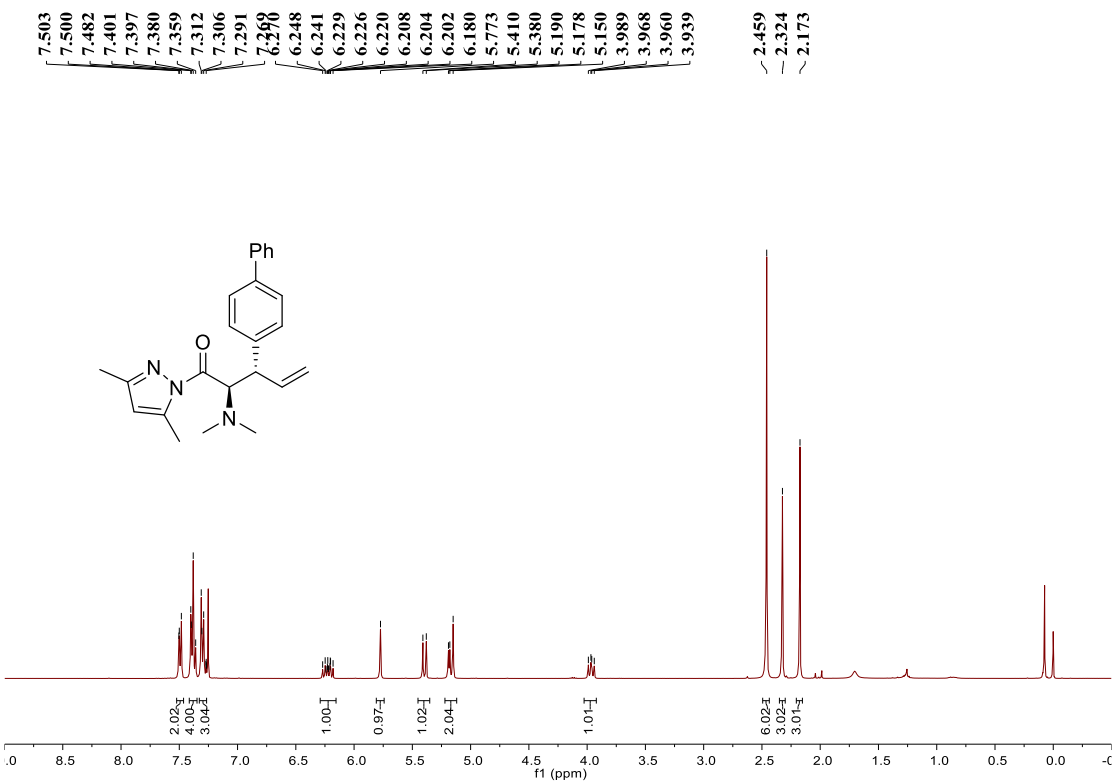
^{13}C NMR of Compound **3d** (101 MHz, $CDCl_3$)



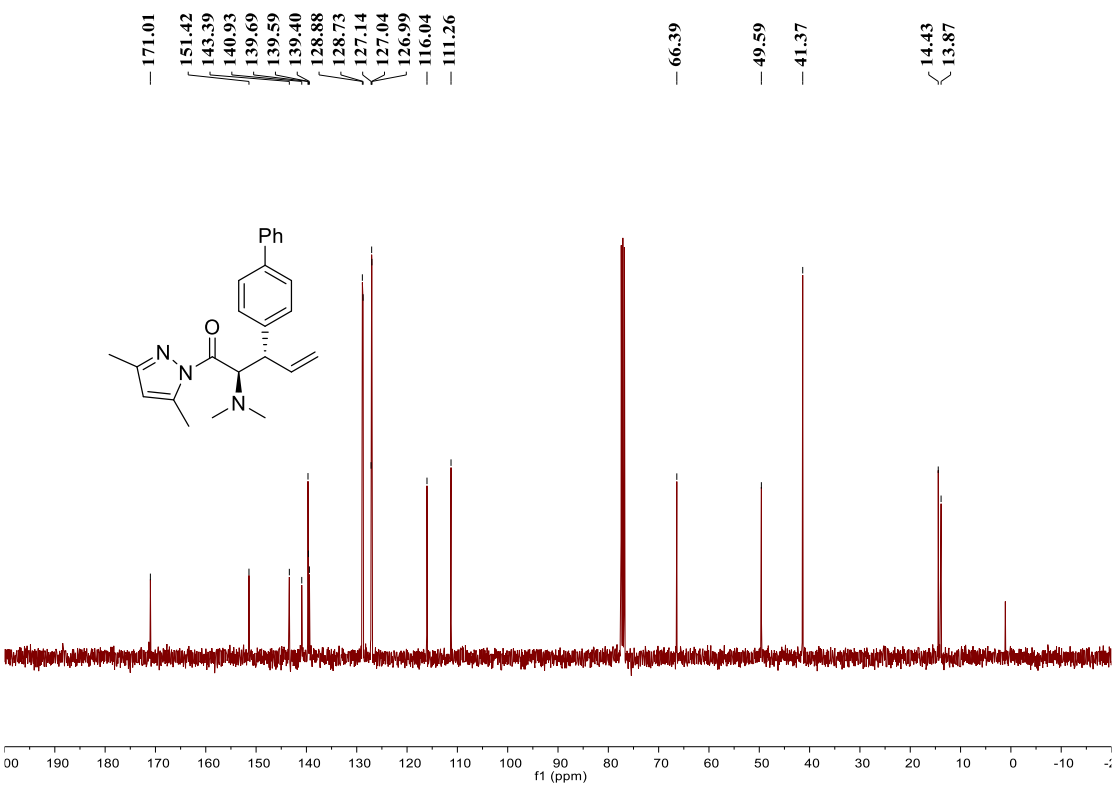
^{1}H NMR of Compound **3d-methyl ester** (400 MHz, $CDCl_3$)



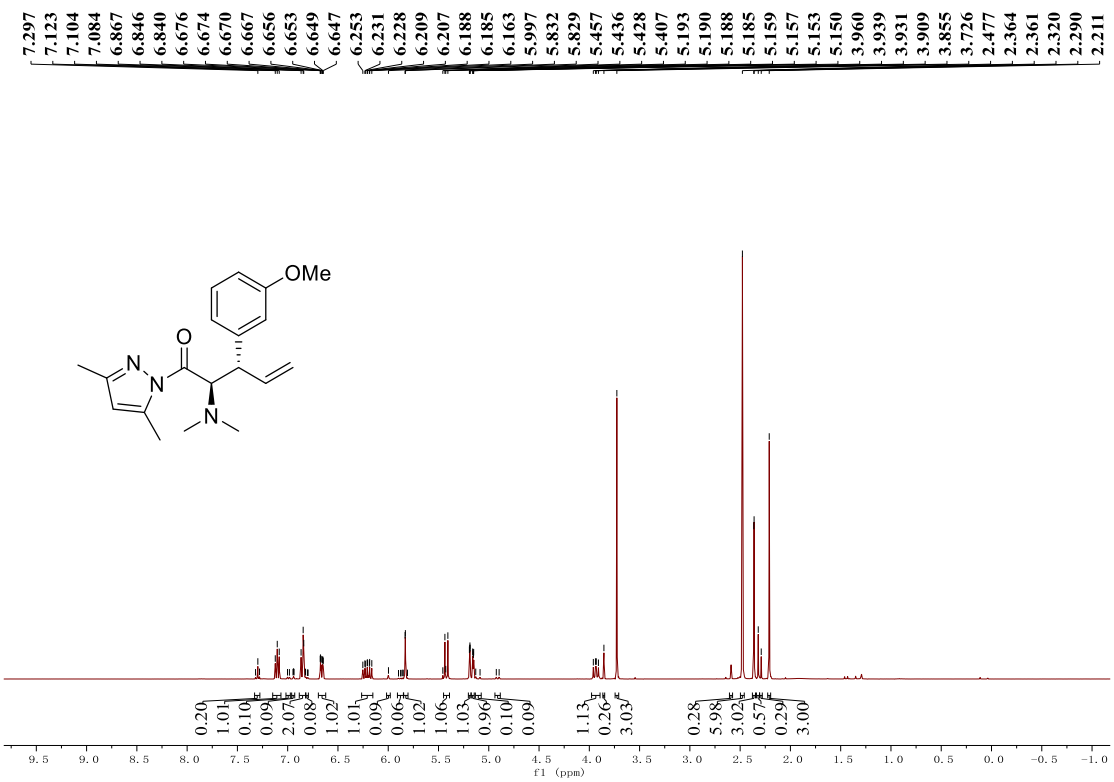
^{13}C NMR of Compound **3d-methyl ester** (101 MHz, $CDCl_3$)



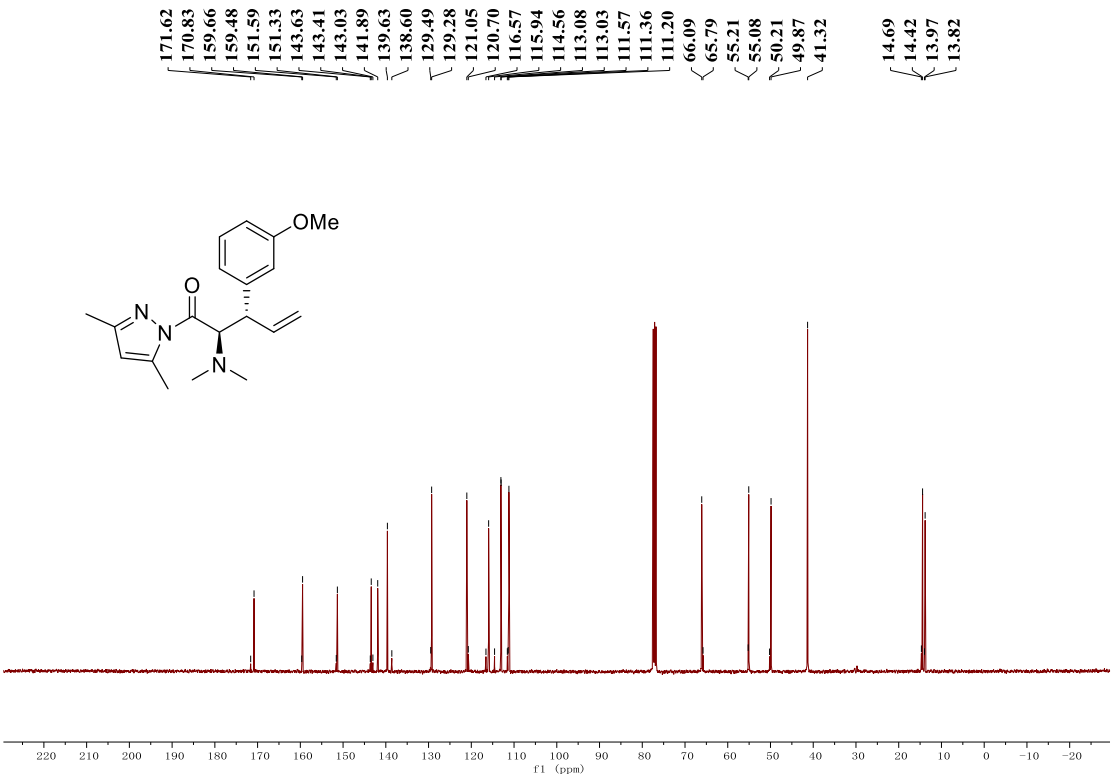
^{1}H NMR of Compound **3e** (400 MHz, $CDCl_3$)



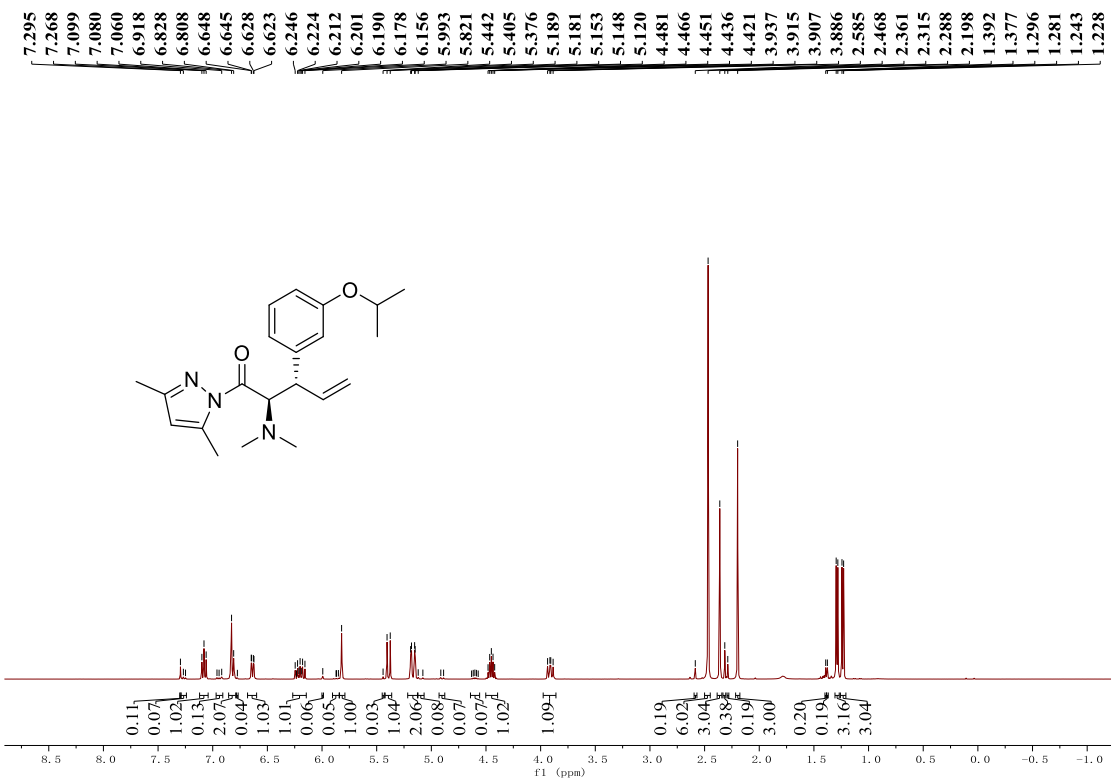
^{13}C NMR of Compound **3e** (101 MHz, $CDCl_3$)



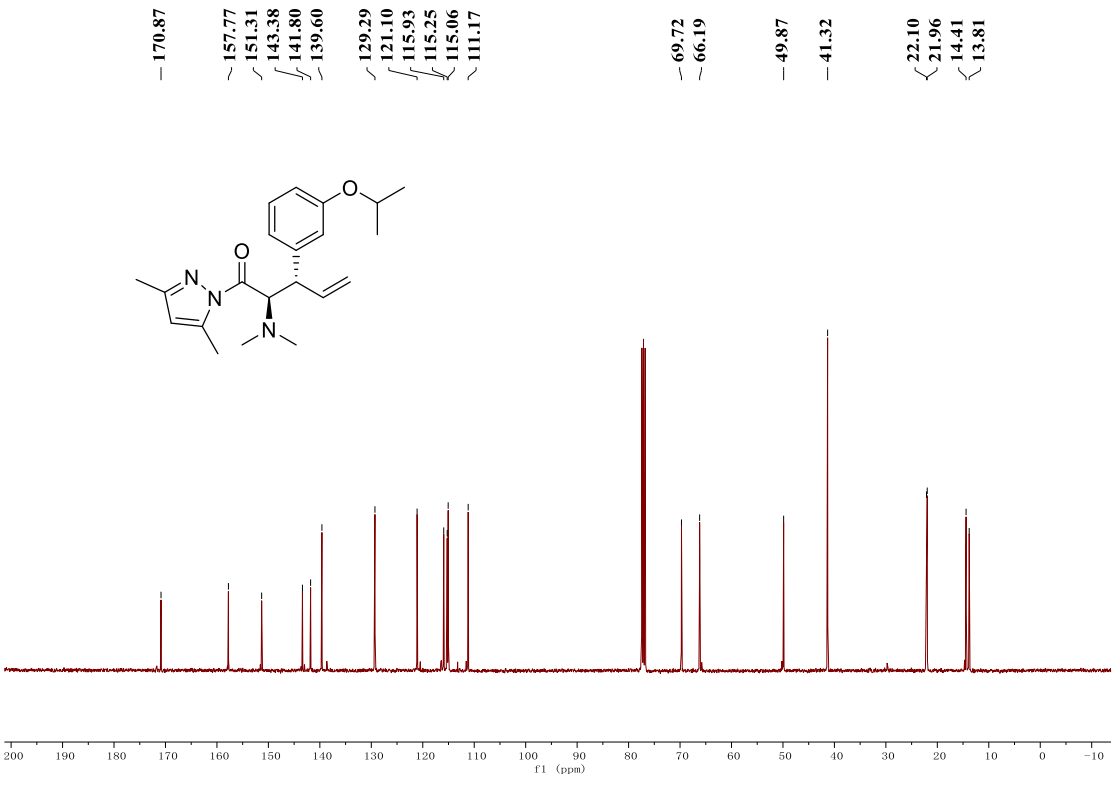
^{1}H NMR of Compound **3f** (400 MHz, $CDCl_3$)



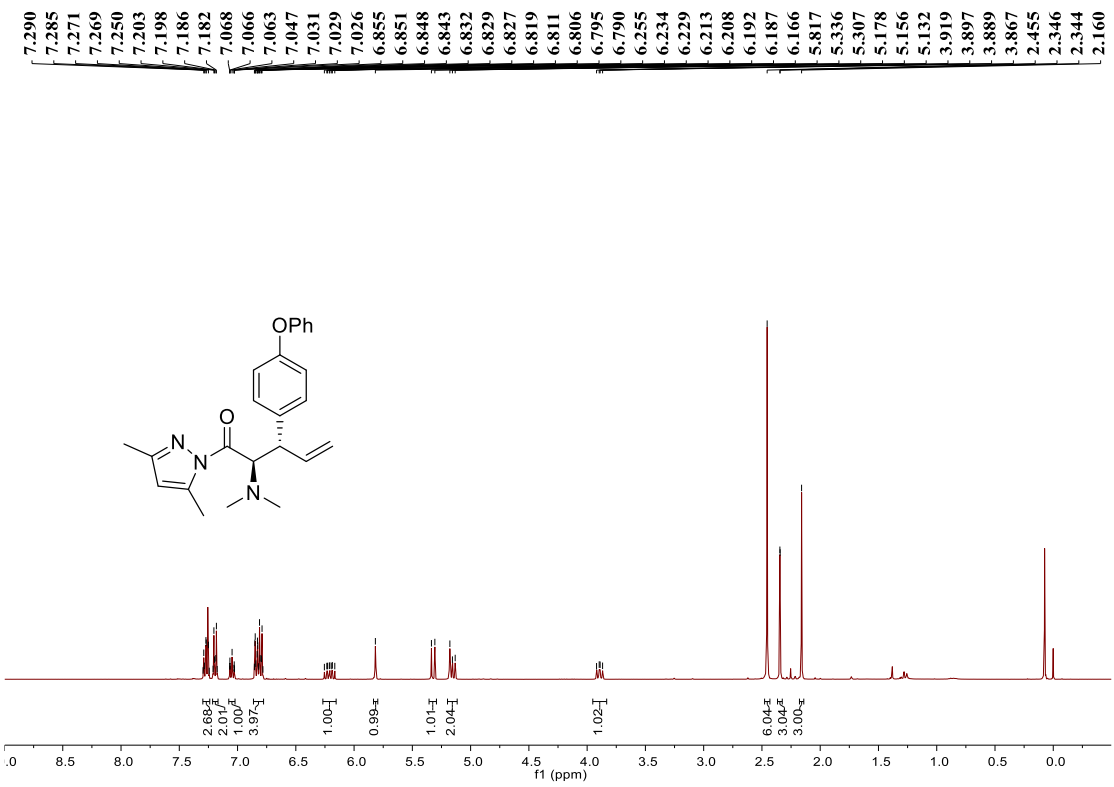
^{13}C NMR of Compound **3f** (101 MHz, $CDCl_3$)



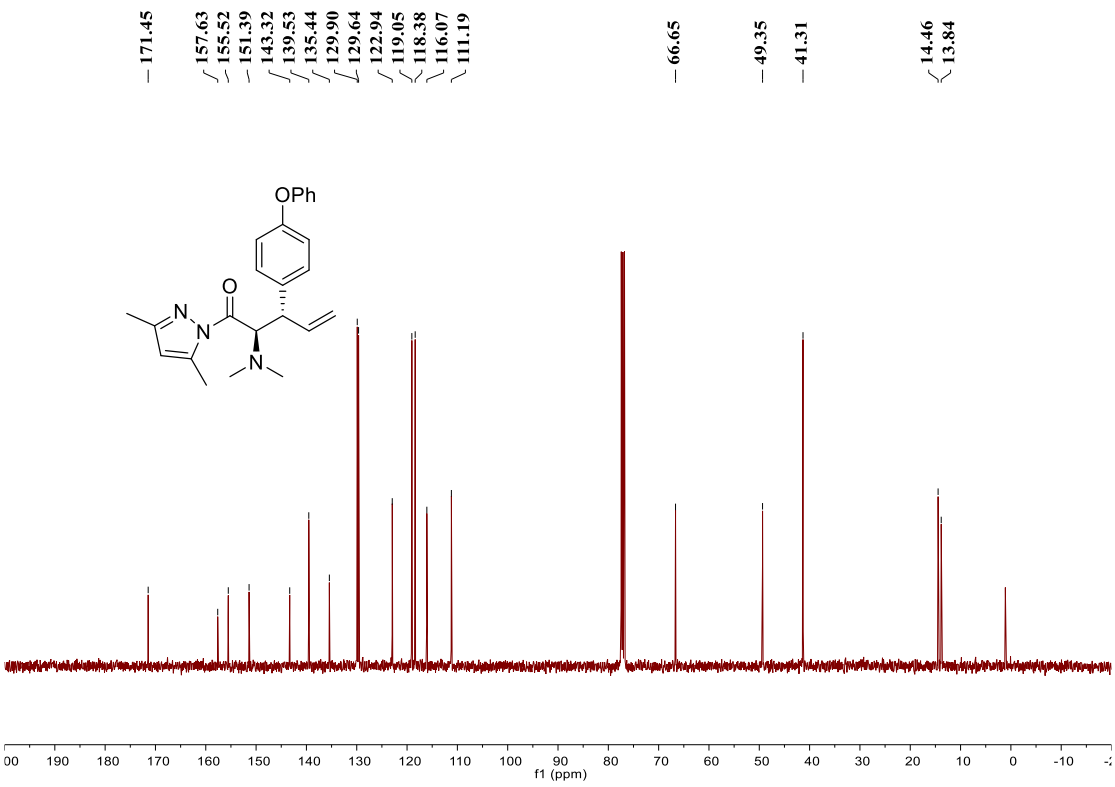
^{1}H NMR of Compound **3g** (400 MHz, $CDCl_3$)



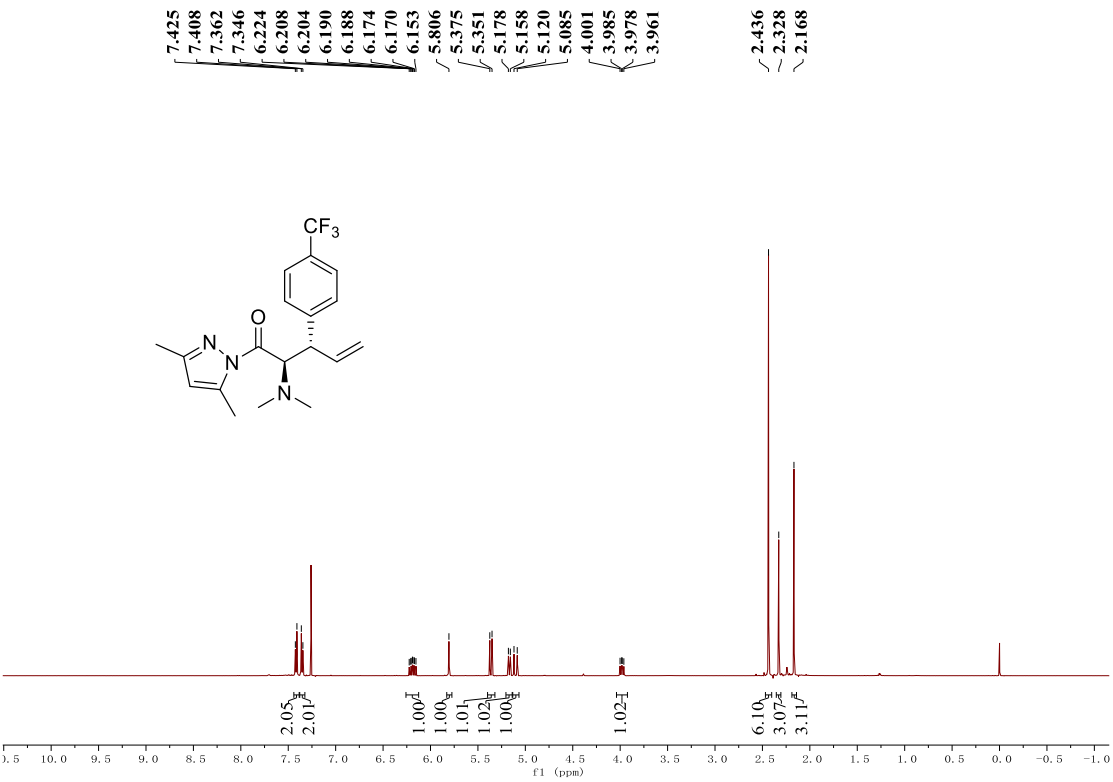
^{13}C NMR of Compound **3g** (101 MHz, $CDCl_3$)



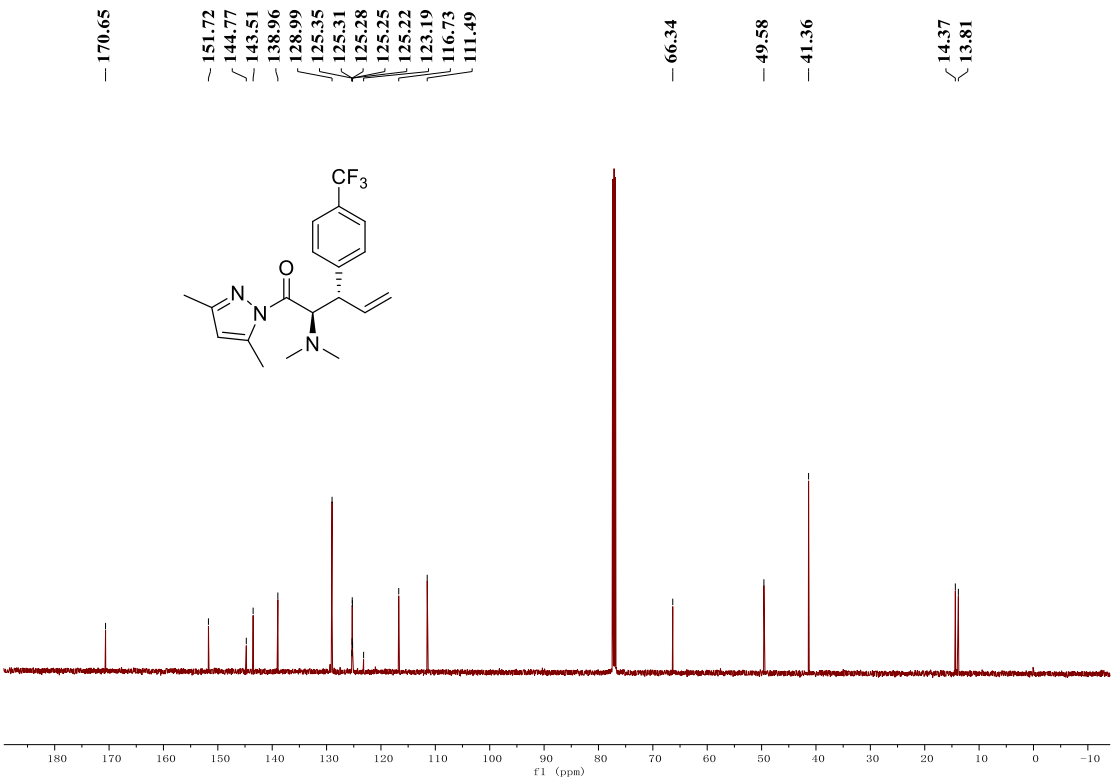
^{1}H NMR of Compound **3h** (400 MHz, $CDCl_3$)



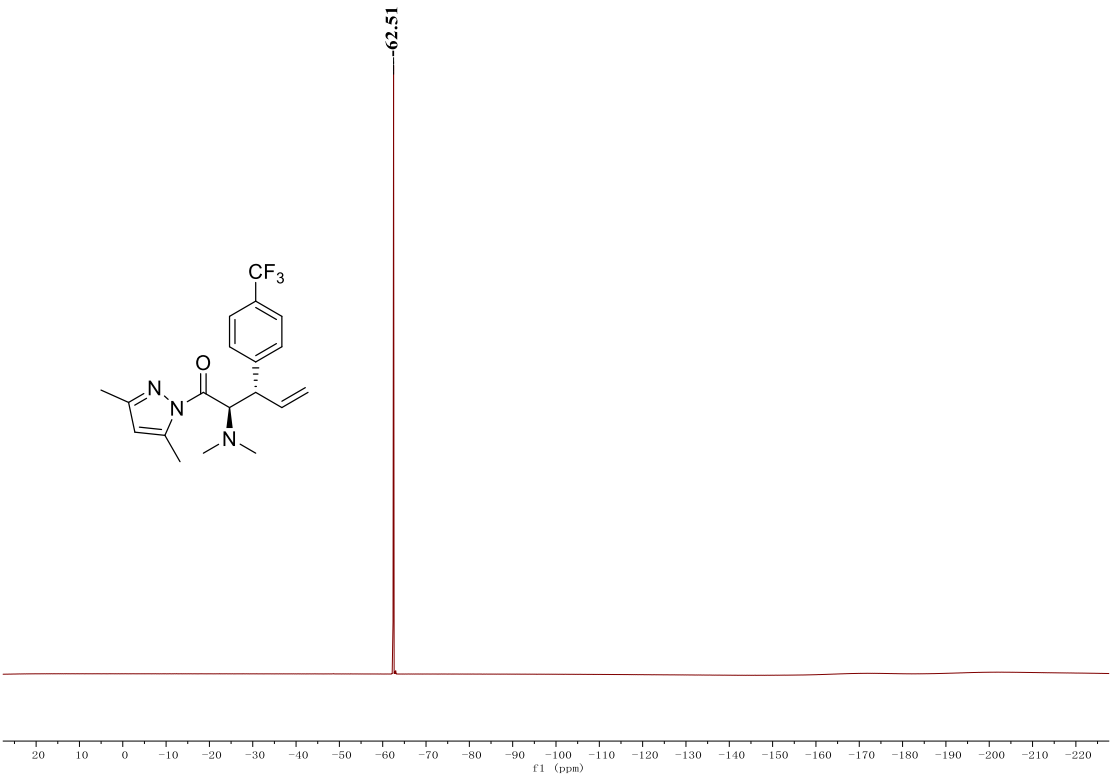
^{13}C NMR of Compound **3h** (101 MHz, $CDCl_3$)



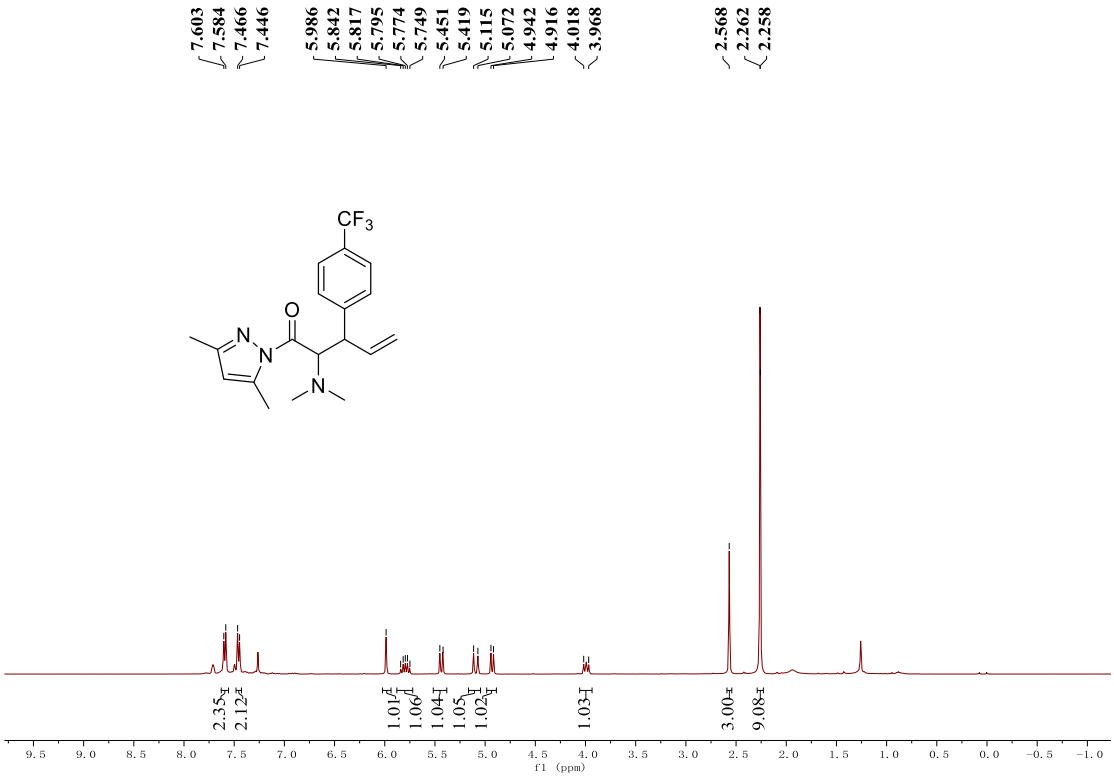
^{1}H NMR of Compound **3i** (500 MHz, $CDCl_3$)



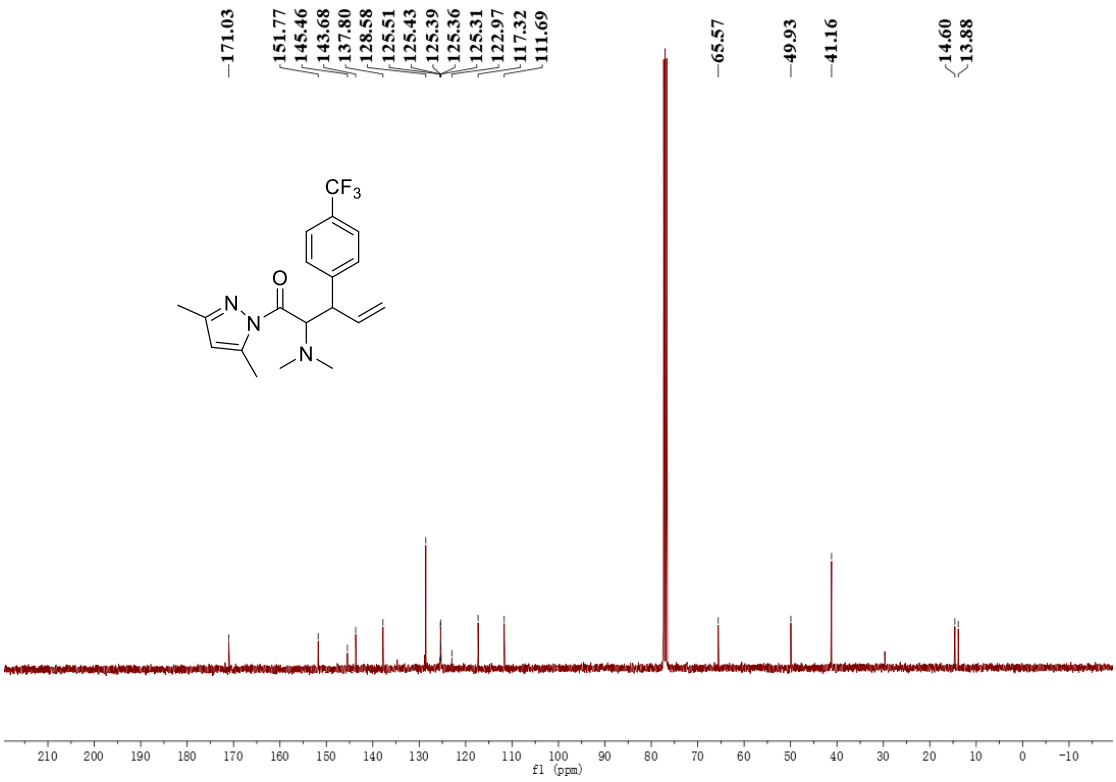
^{13}C NMR of Compound **3i** (125 MHz, $CDCl_3$)



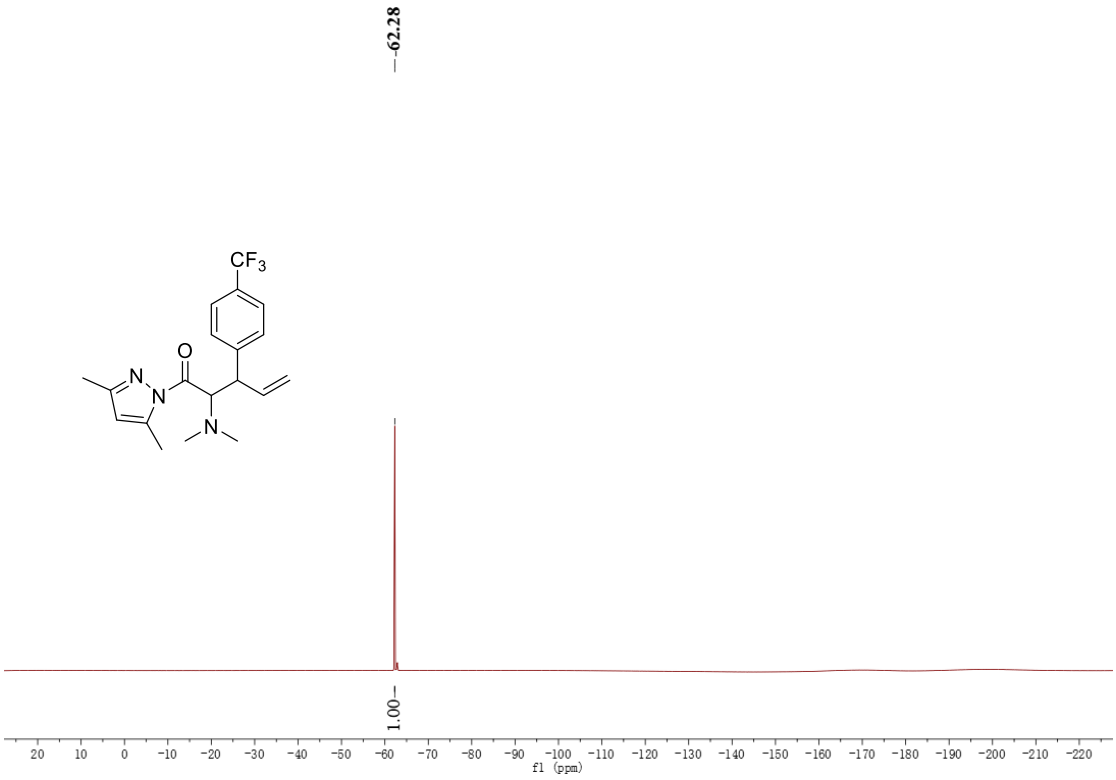
^{19}F NMR of Compound **3i** (376 MHz, $CDCl_3$)



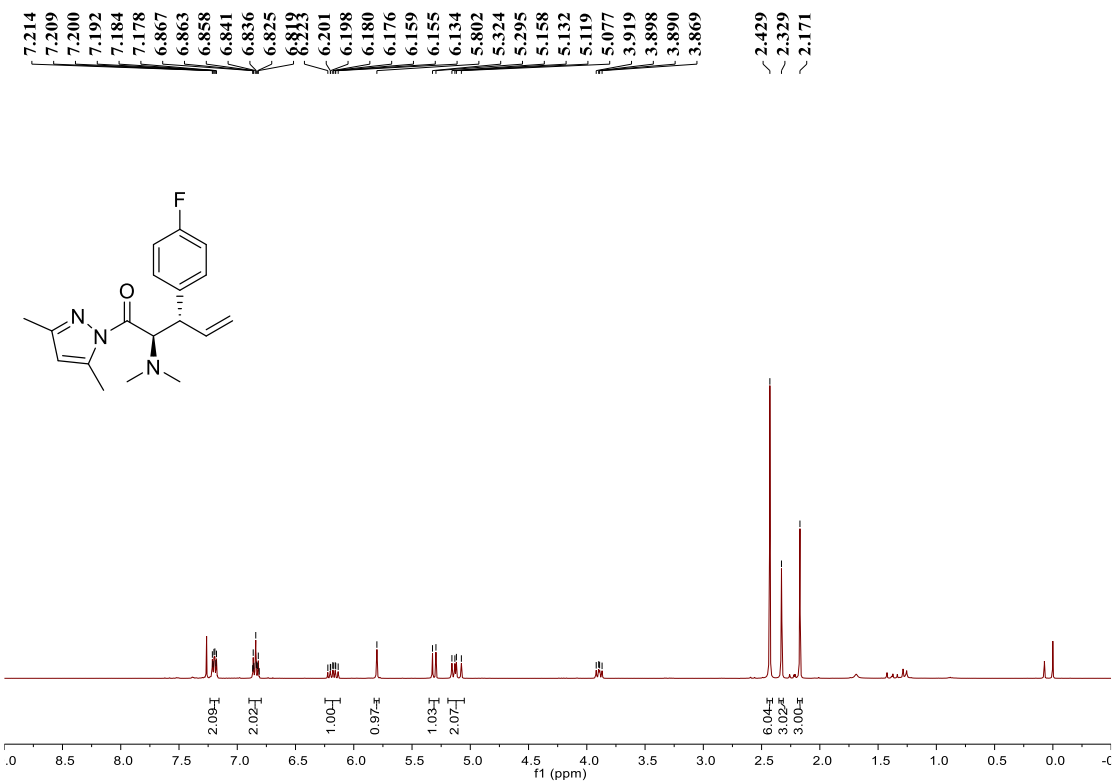
^{1}H NMR of Compound **3i-minor** (400 MHz, $CDCl_3$)



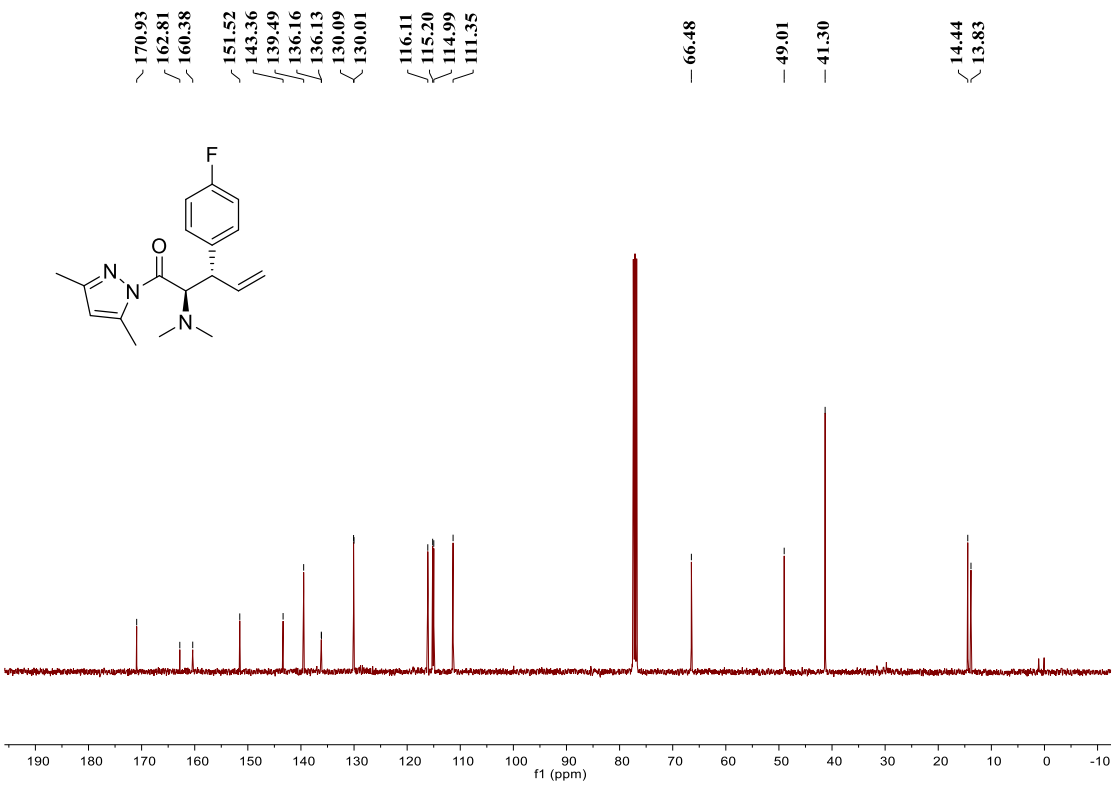
^{13}C NMR of Compound **3i-minor** (101 MHz, $CDCl_3$)



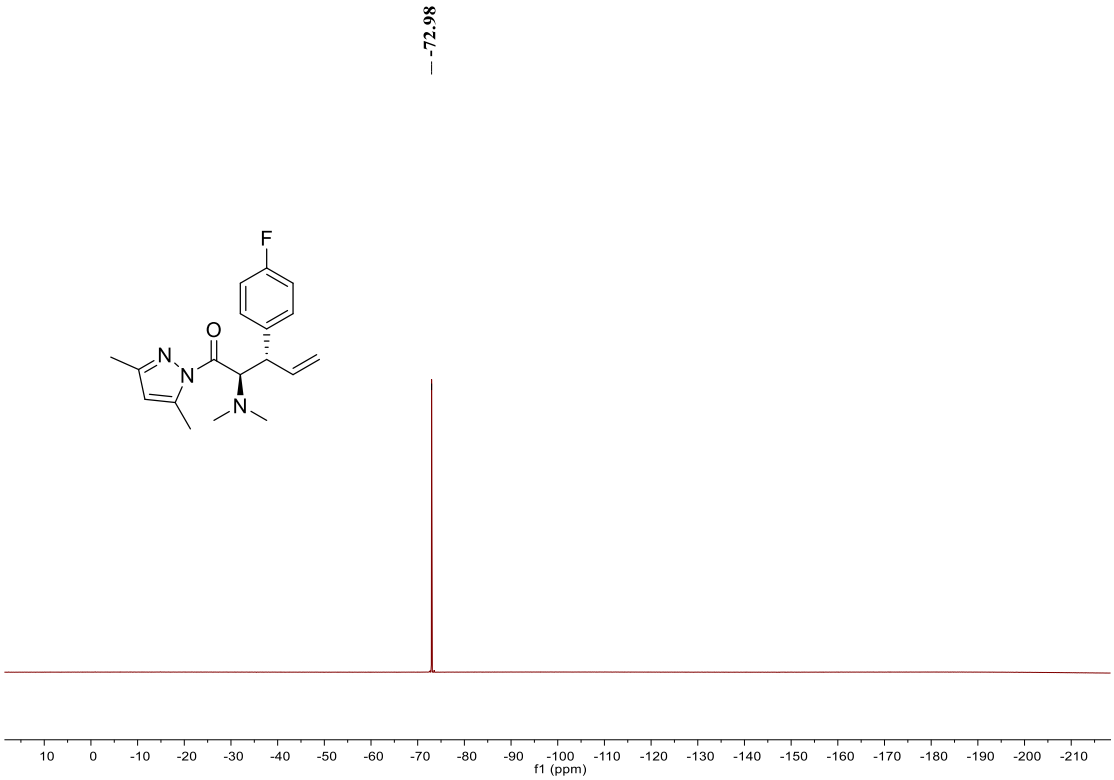
^{19}F NMR of Compound **3i-minor** (376 MHz, $CDCl_3$)



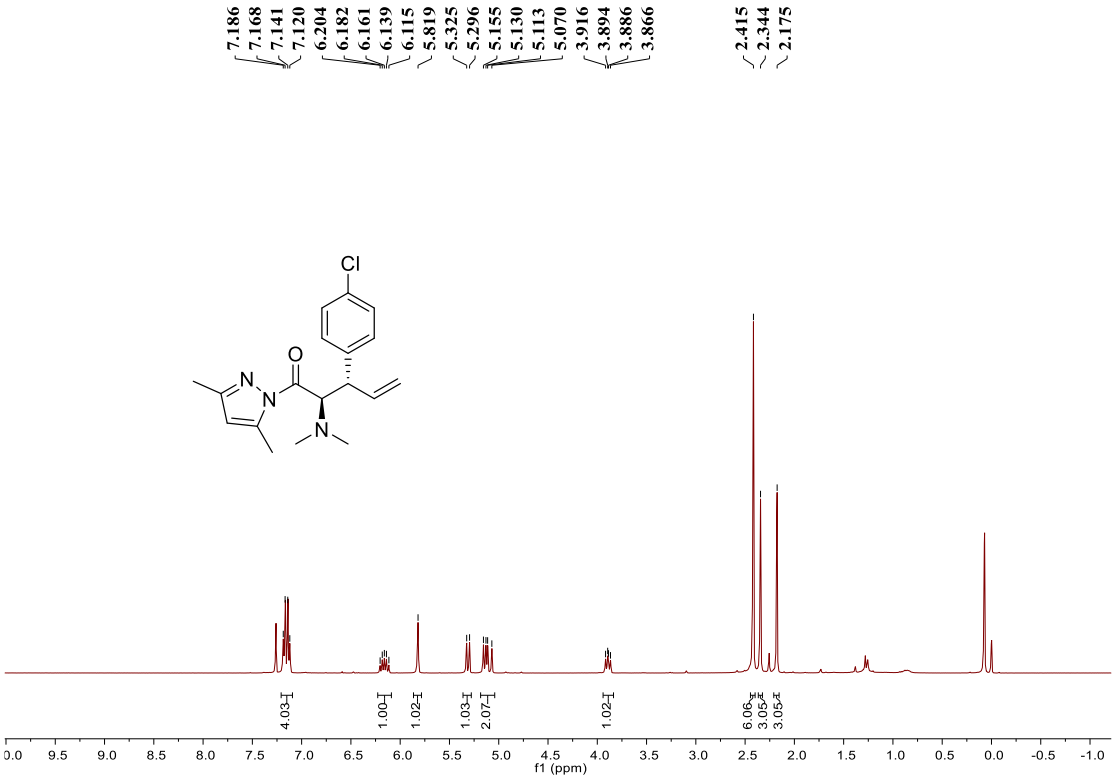
^{1}H NMR of Compound **3j** (400 MHz, $CDCl_3$)



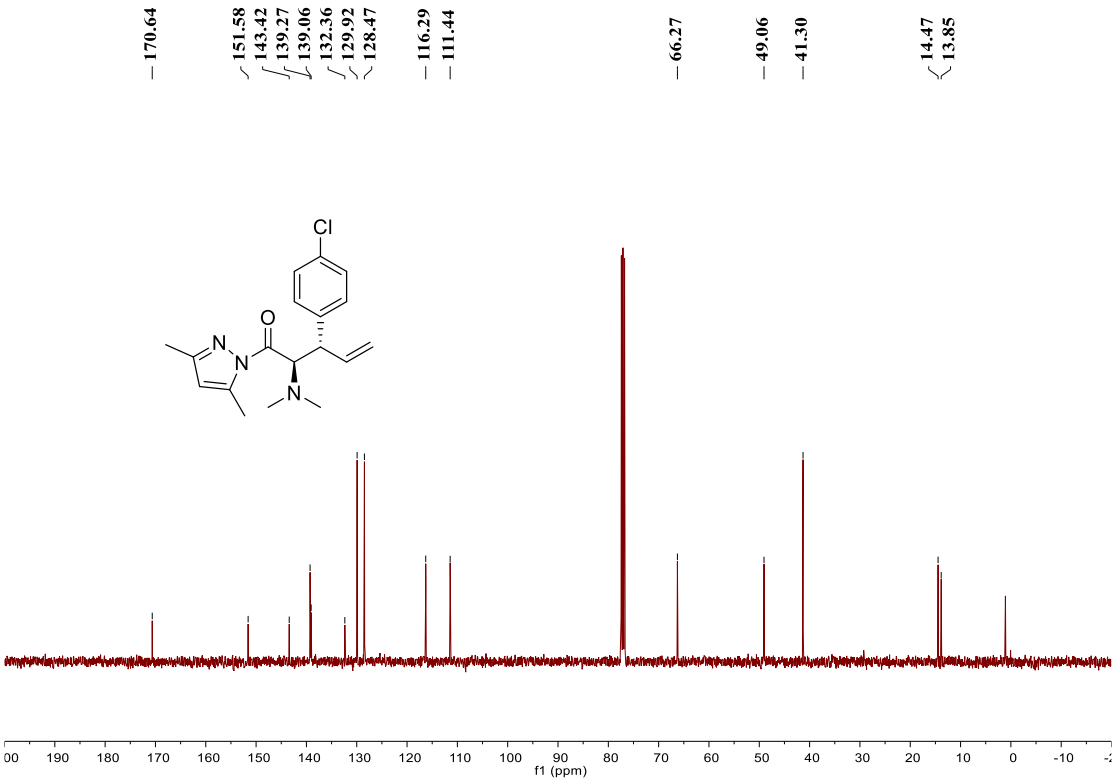
^{13}C NMR of Compound of **3j** (101 MHz, $CDCl_3$)



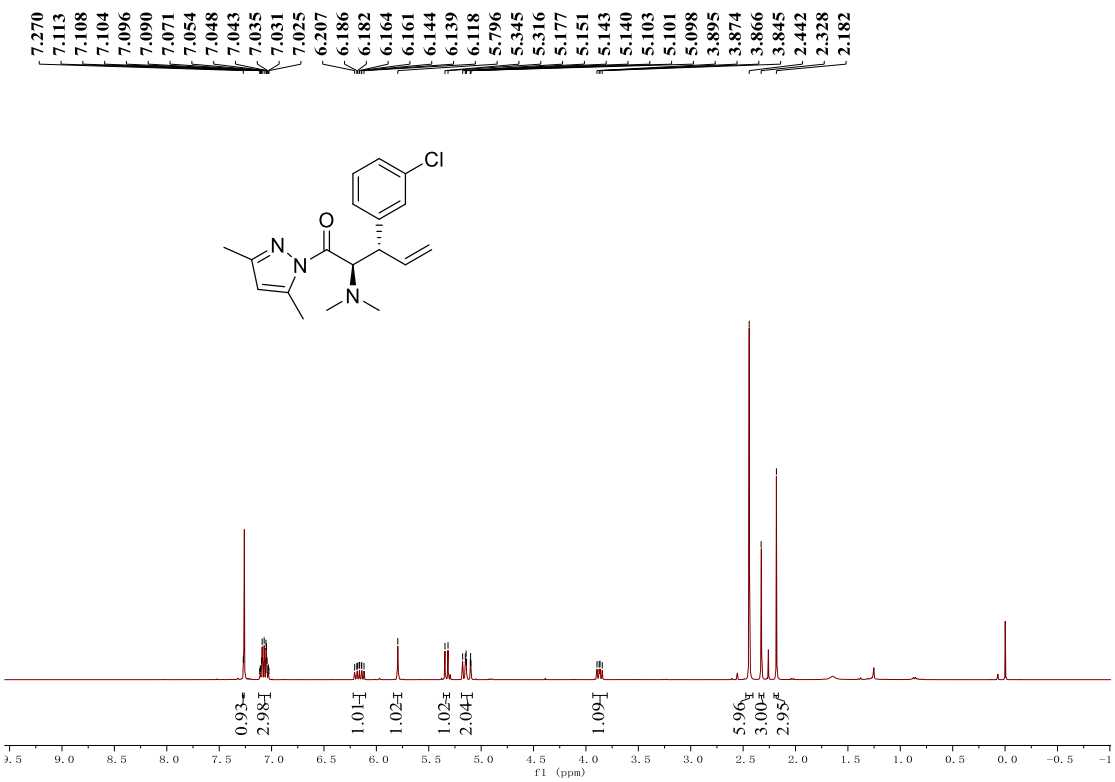
^{19}F NMR of Compound **3j** (376 MHz, $CDCl_3$)



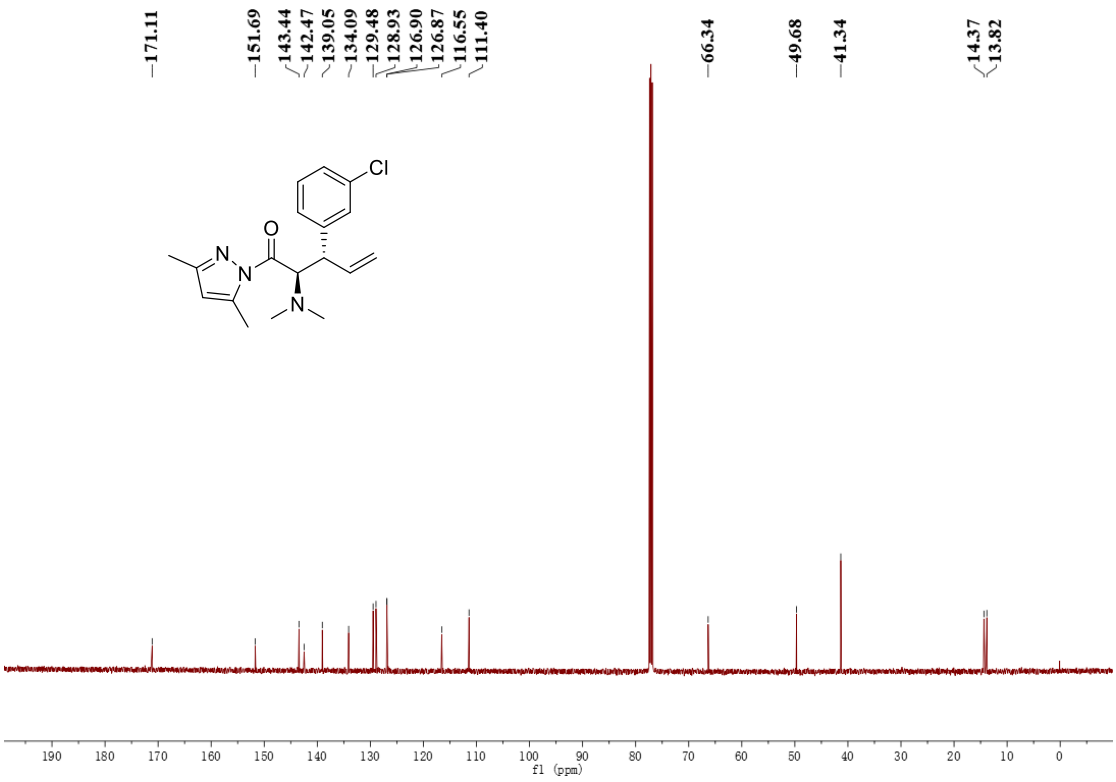
^{1}H NMR of Compound of **3k** (400 MHz, $CDCl_3$)



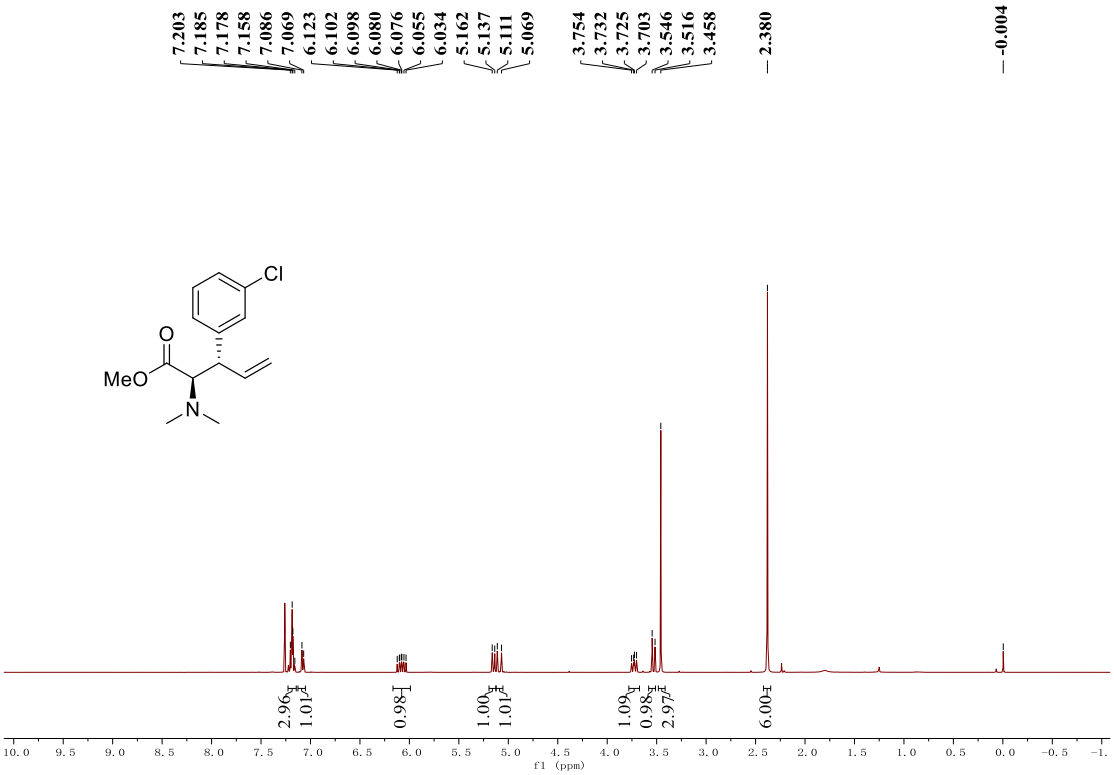
^{13}C NMR of Compound **3k** (101 MHz, $CDCl_3$)



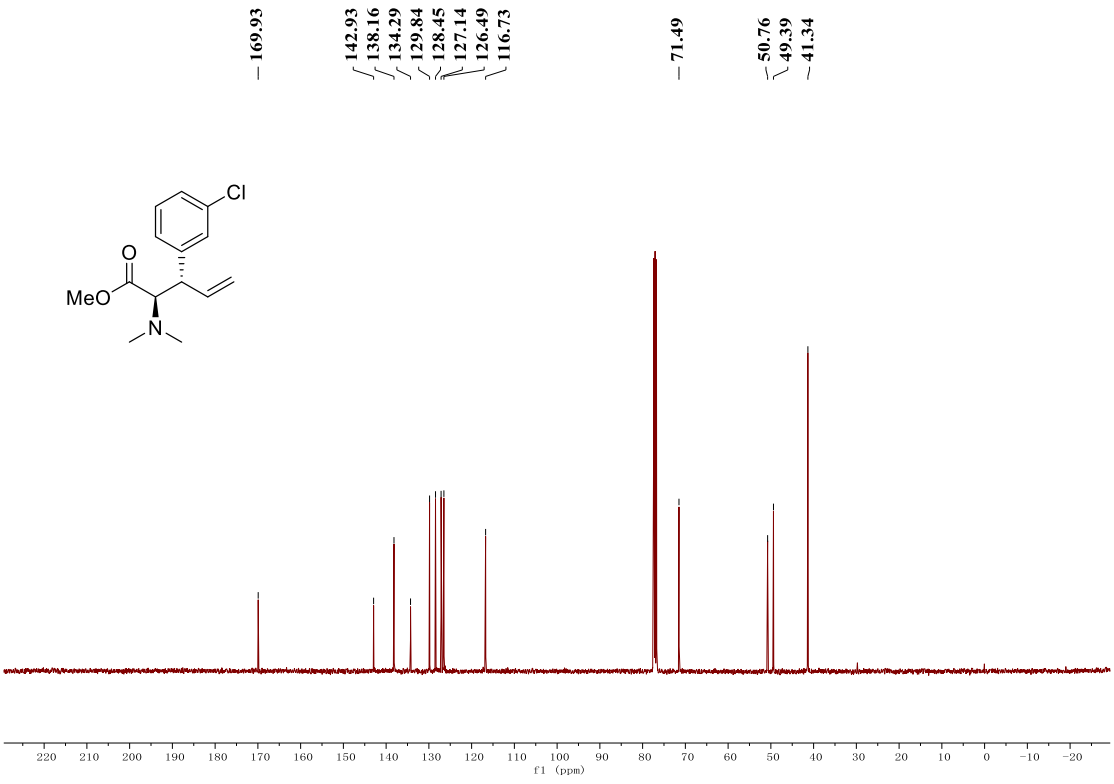
^{1}H NMR of Compound **3l** (400 MHz, $CDCl_3$)



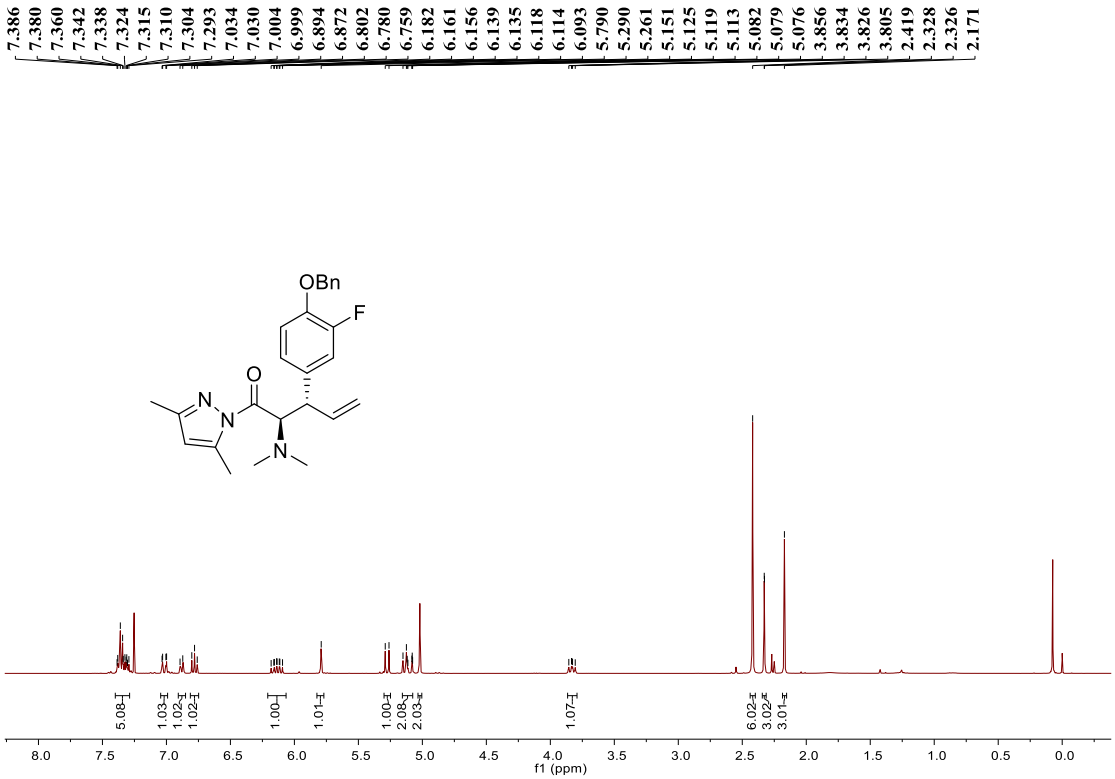
^{13}C NMR of Compound **3l** (125 MHz, $CDCl_3$)



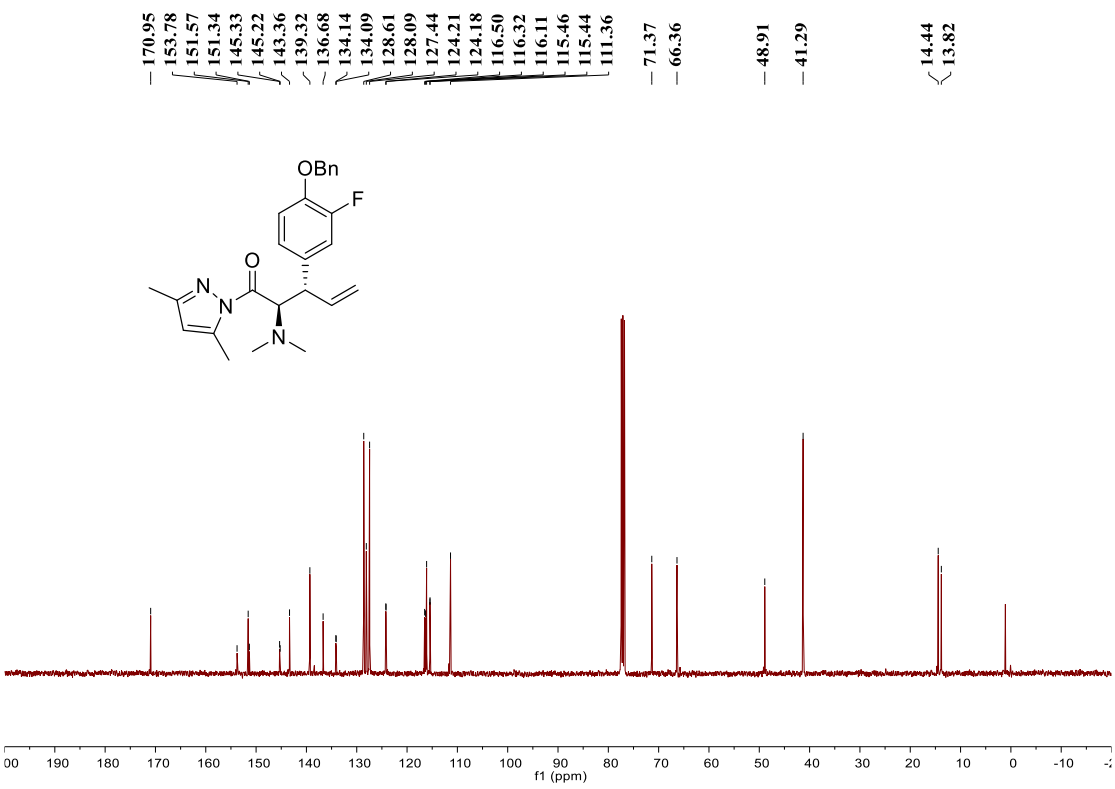
^{1}H NMR of Compound **3l-methyl ester** (400 MHz, $CDCl_3$)



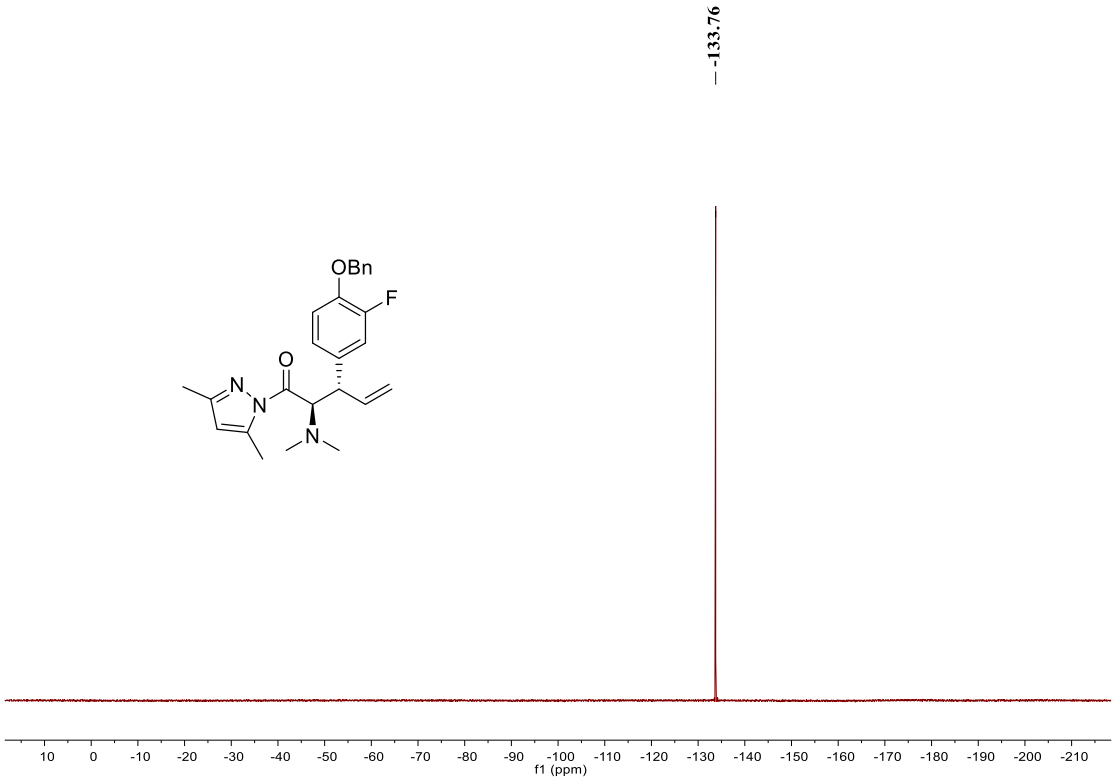
^{13}C NMR of Compound **3l-methyl ester** (101 MHz, $CDCl_3$)



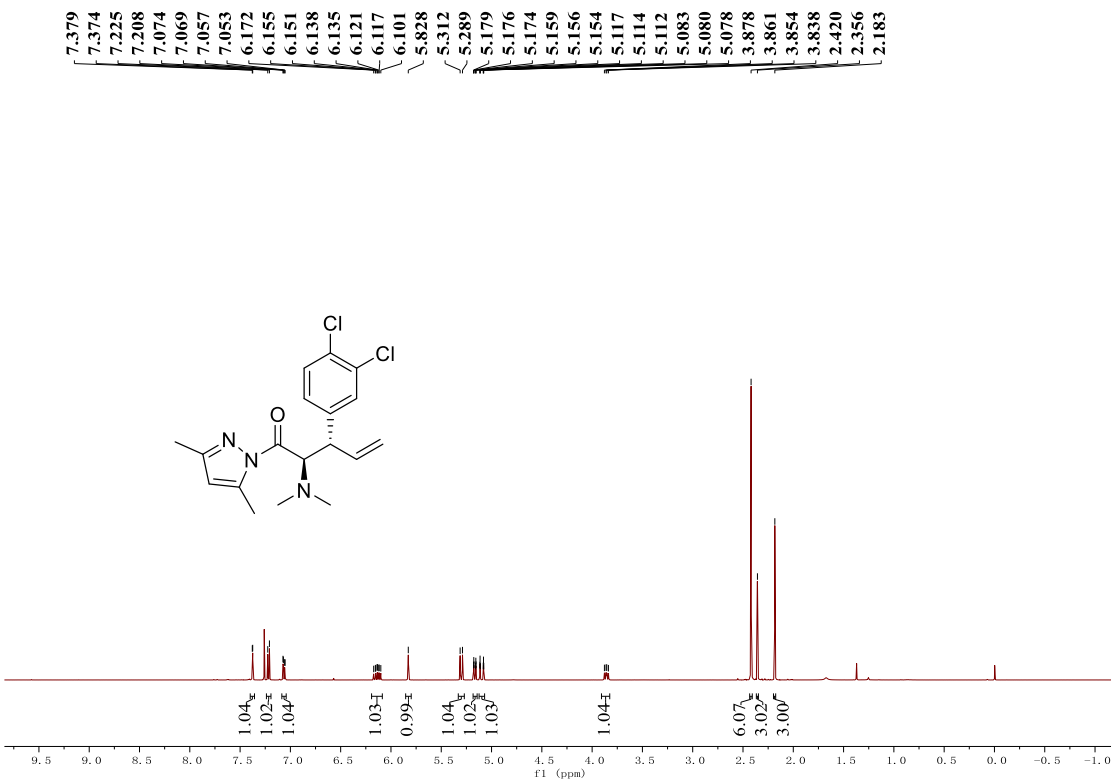
^{1}H NMR of Compound **3m** (400 MHz, $CDCl_3$)



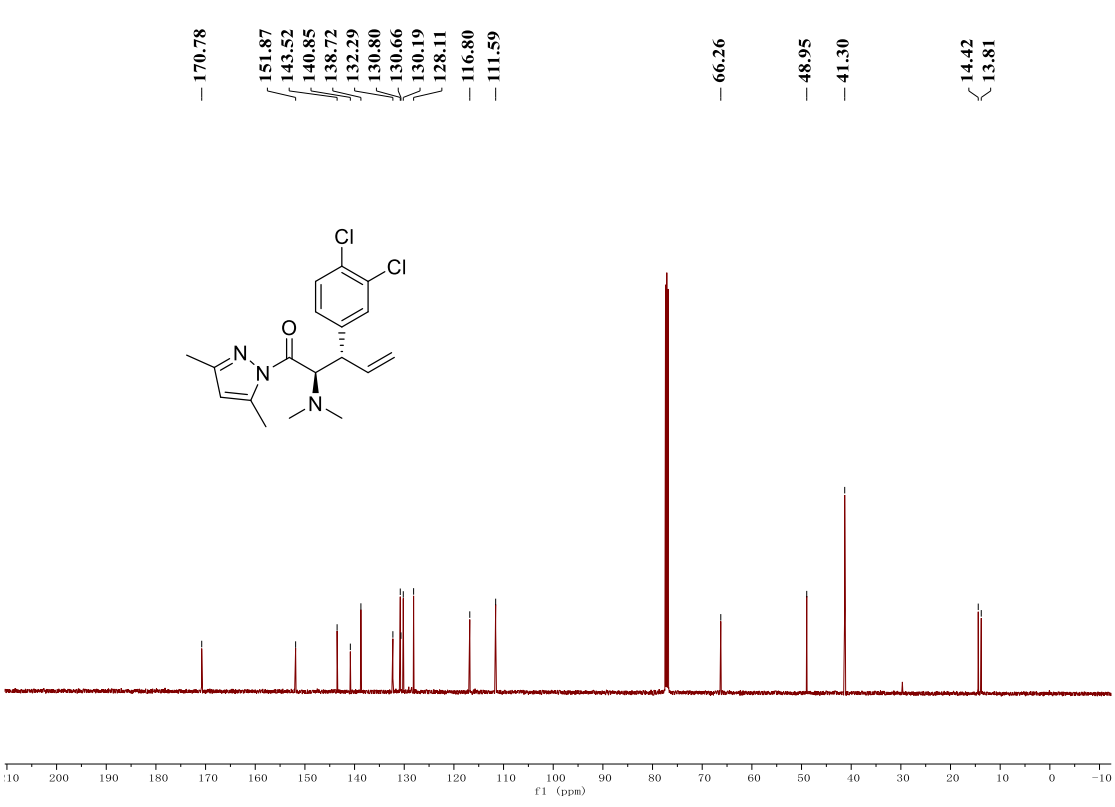
^{13}C NMR of Compound **3m** (101 MHz, $CDCl_3$)



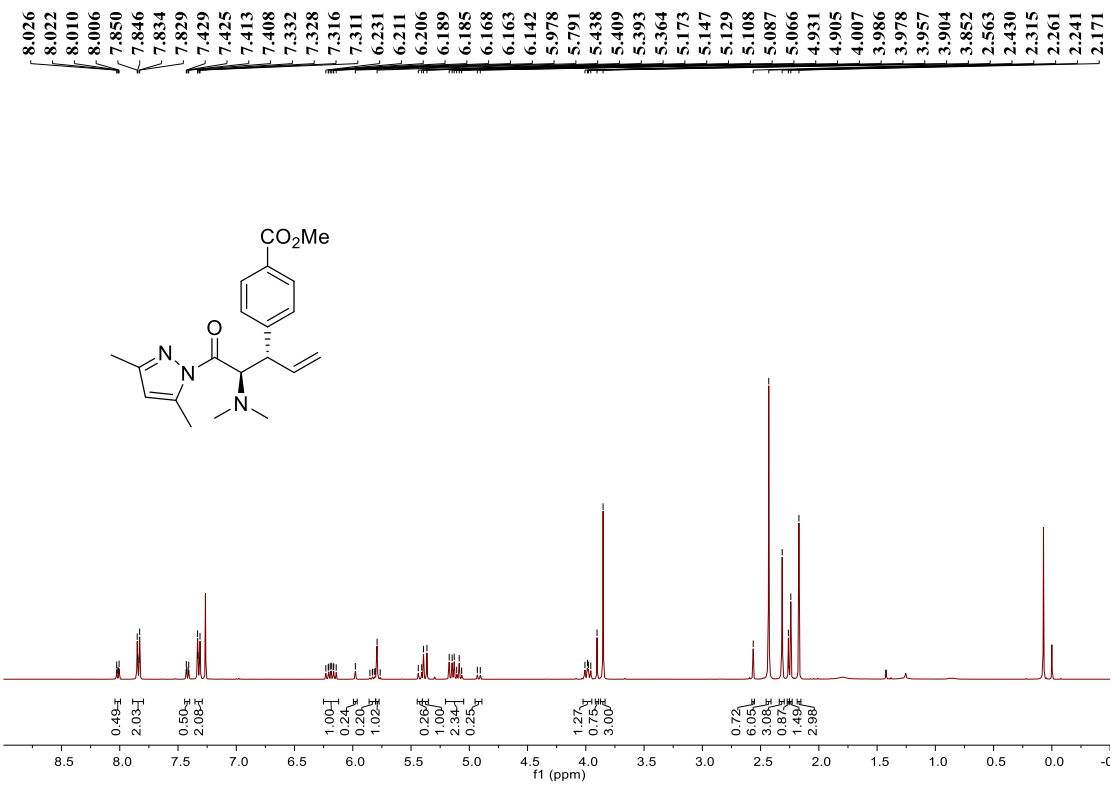
^{19}F NMR of Compound **3m** (376 MHz, $CDCl_3$)



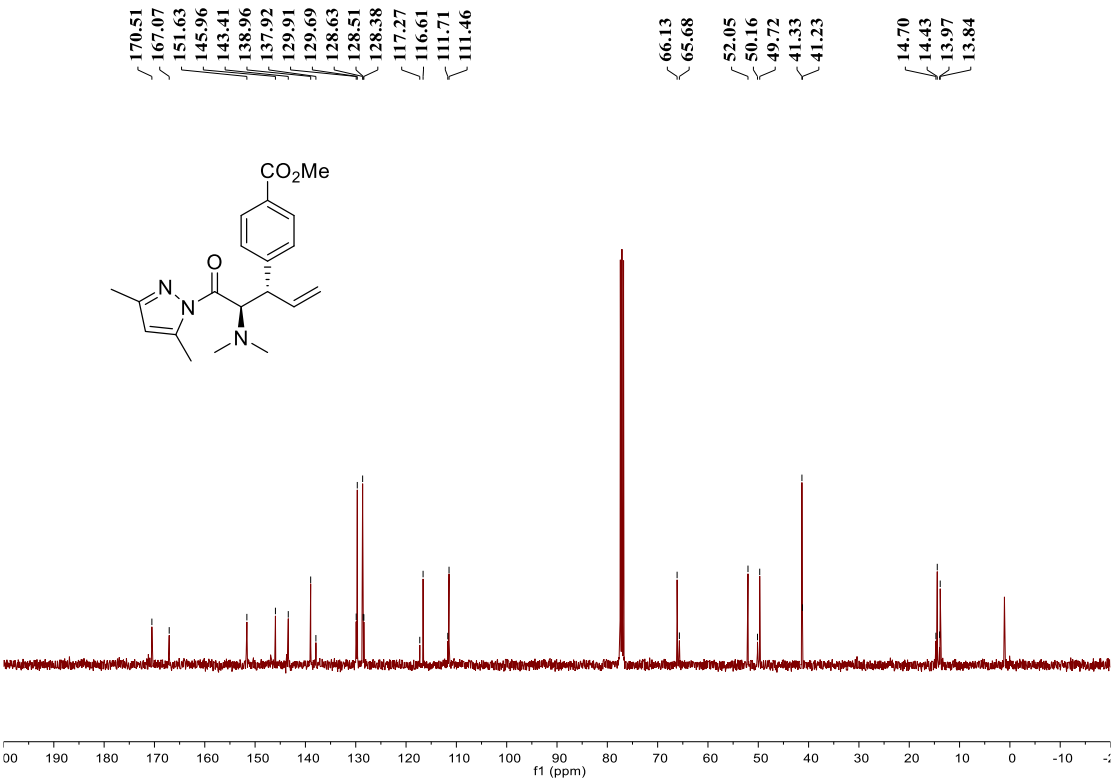
^{1}H NMR of Compound **3n** (500 MHz, $CDCl_3$)



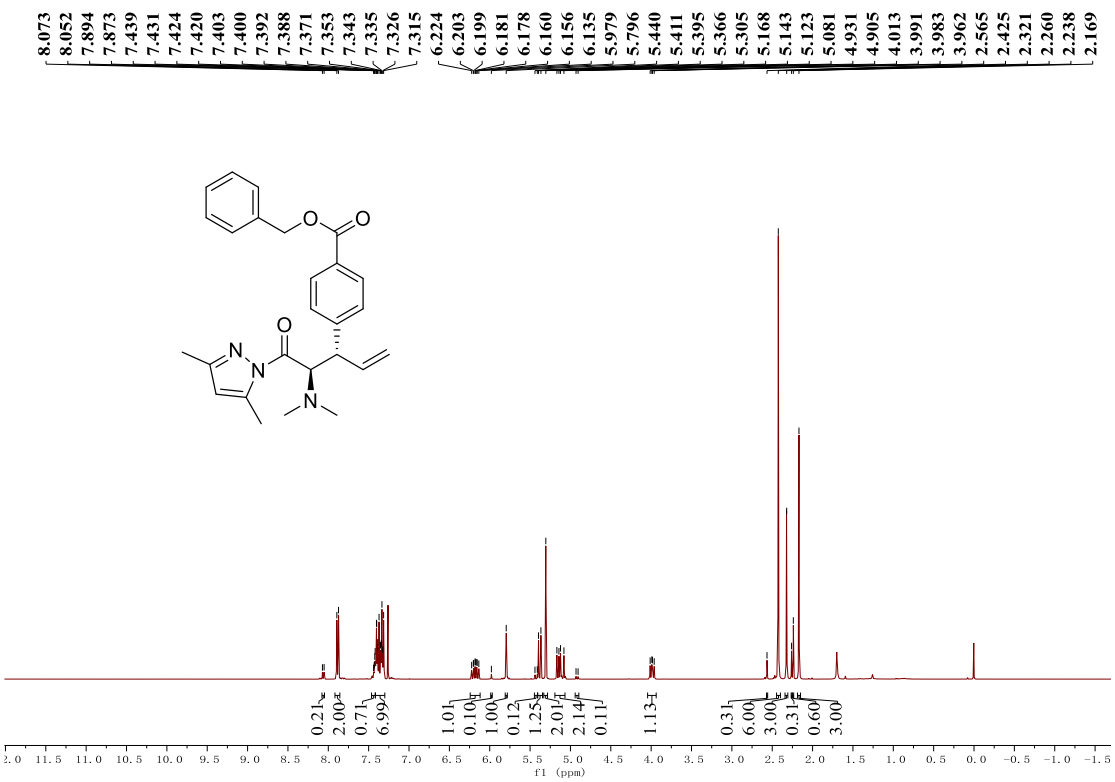
^{13}C NMR of Compound **3n** (125 MHz, $CDCl_3$)



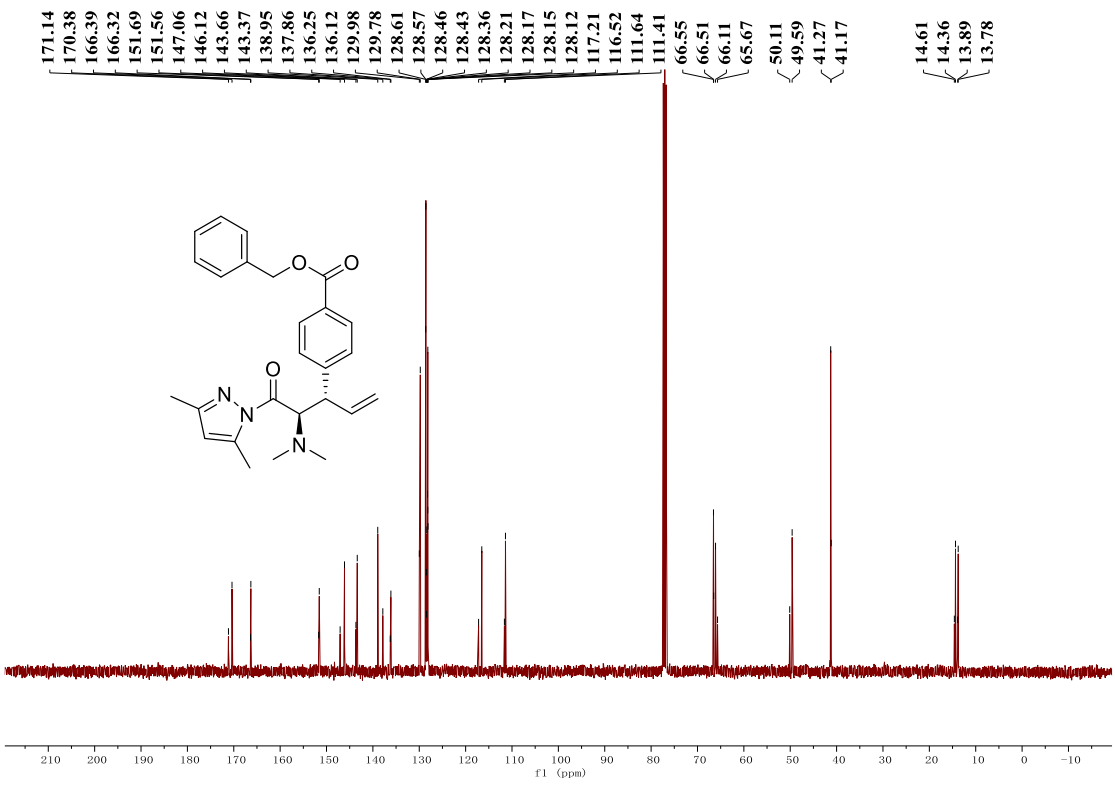
^{1}H NMR of Compound **3o** (400 MHz, $CDCl_3$)



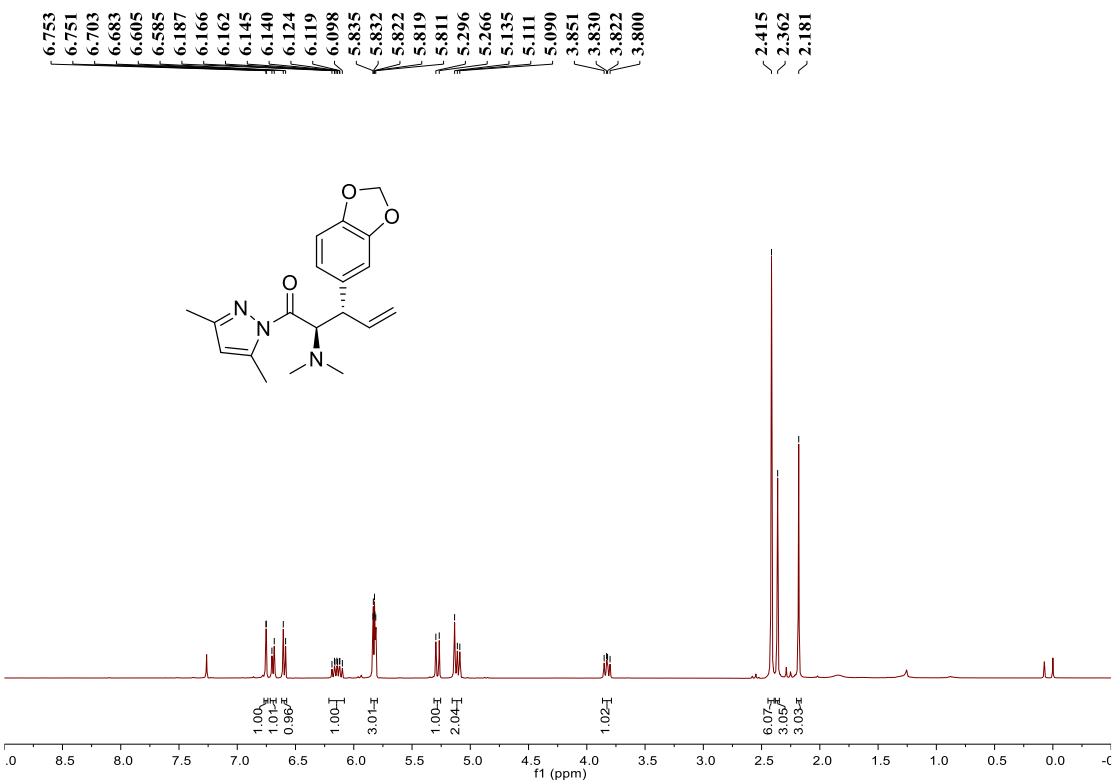
^{13}C NMR of Compound **3o** (101 MHz, $CDCl_3$)



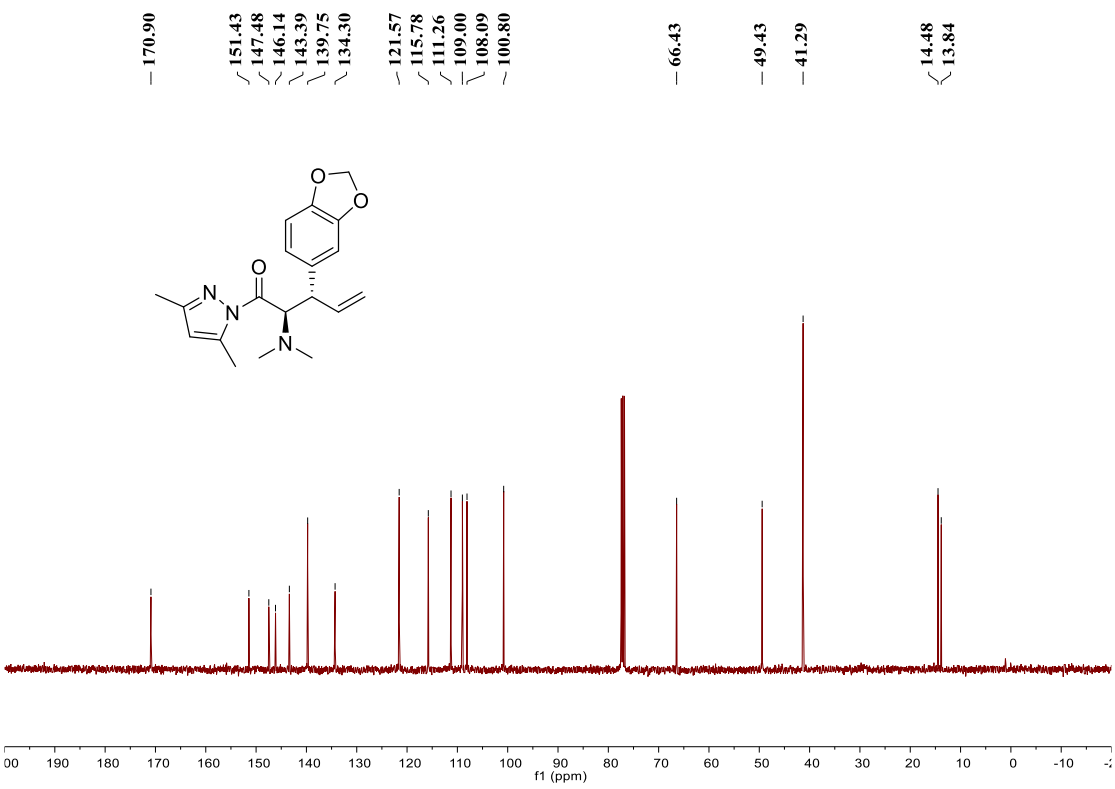
^{1}H NMR of Compound **3p** (400 MHz, $CDCl_3$)



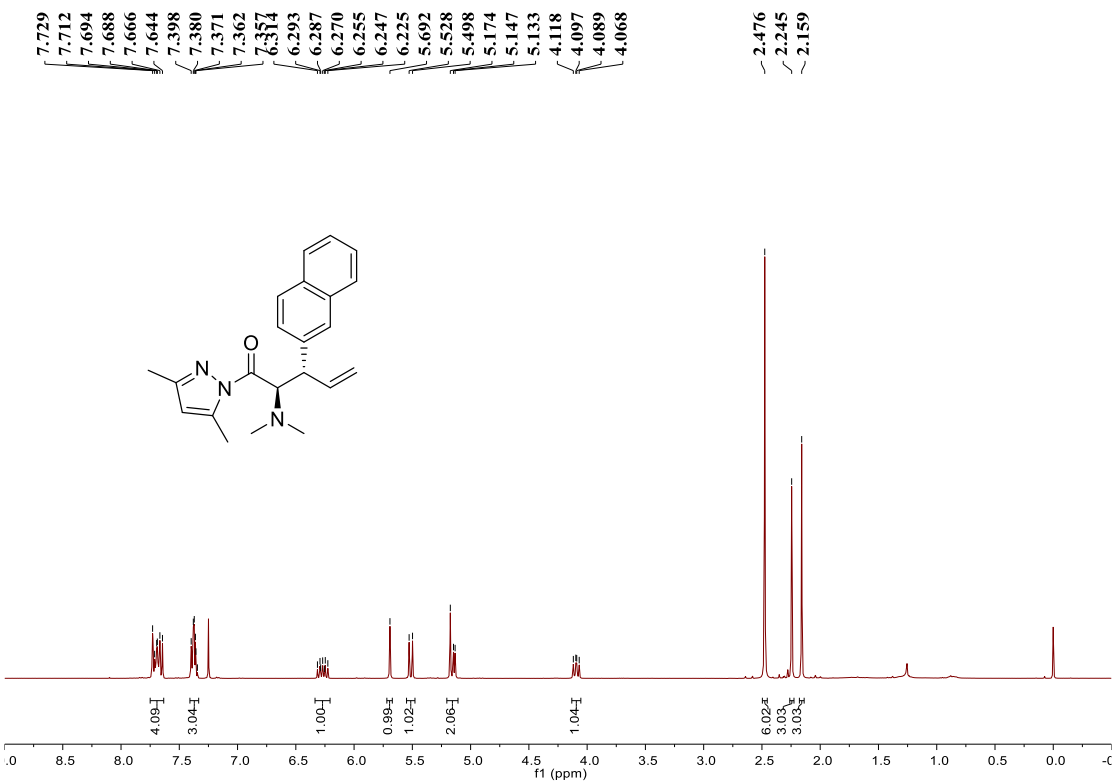
^{13}C NMR of Compound **3p** (101 MHz, $CDCl_3$)



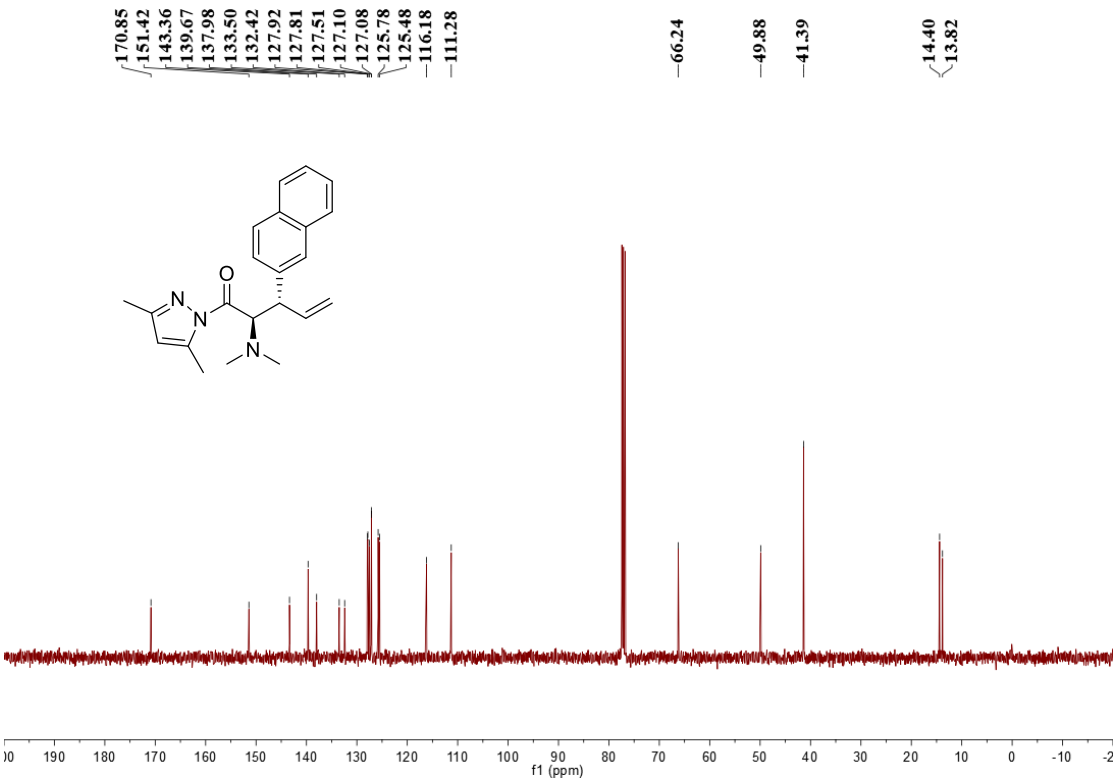
^{1}H NMR of Compound **3q** (400 MHz, $CDCl_3$)



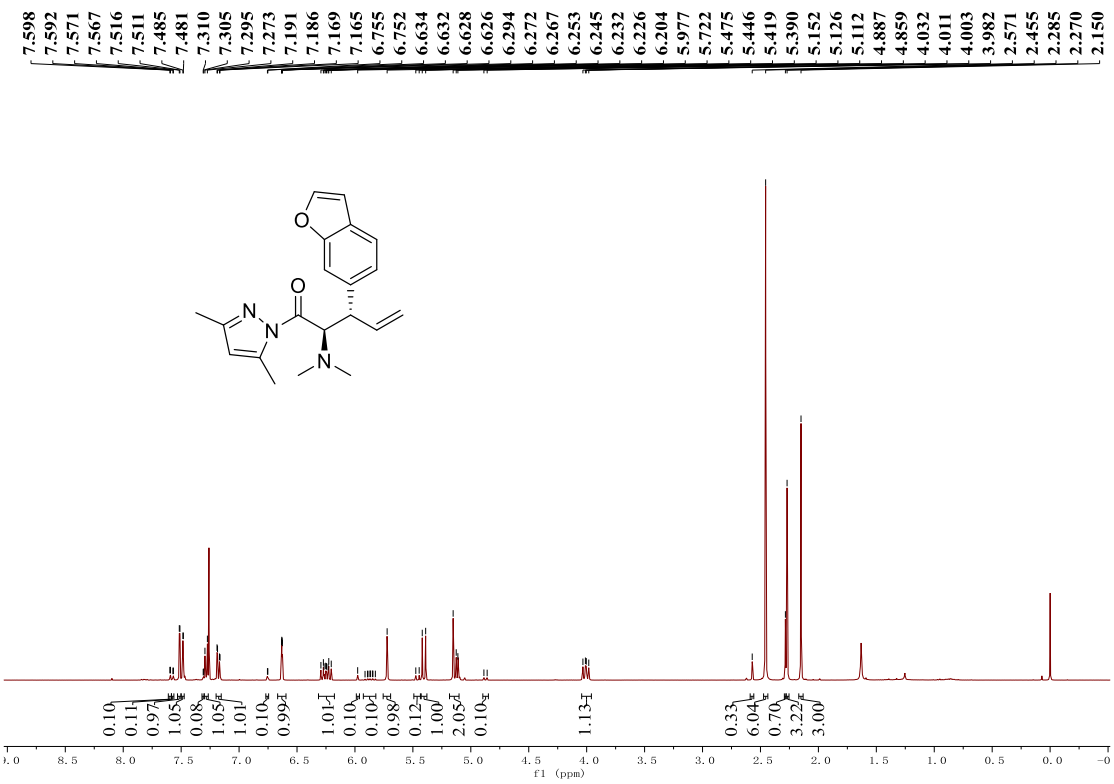
^{13}C NMR of Compound **3q** (101 MHz, $CDCl_3$)



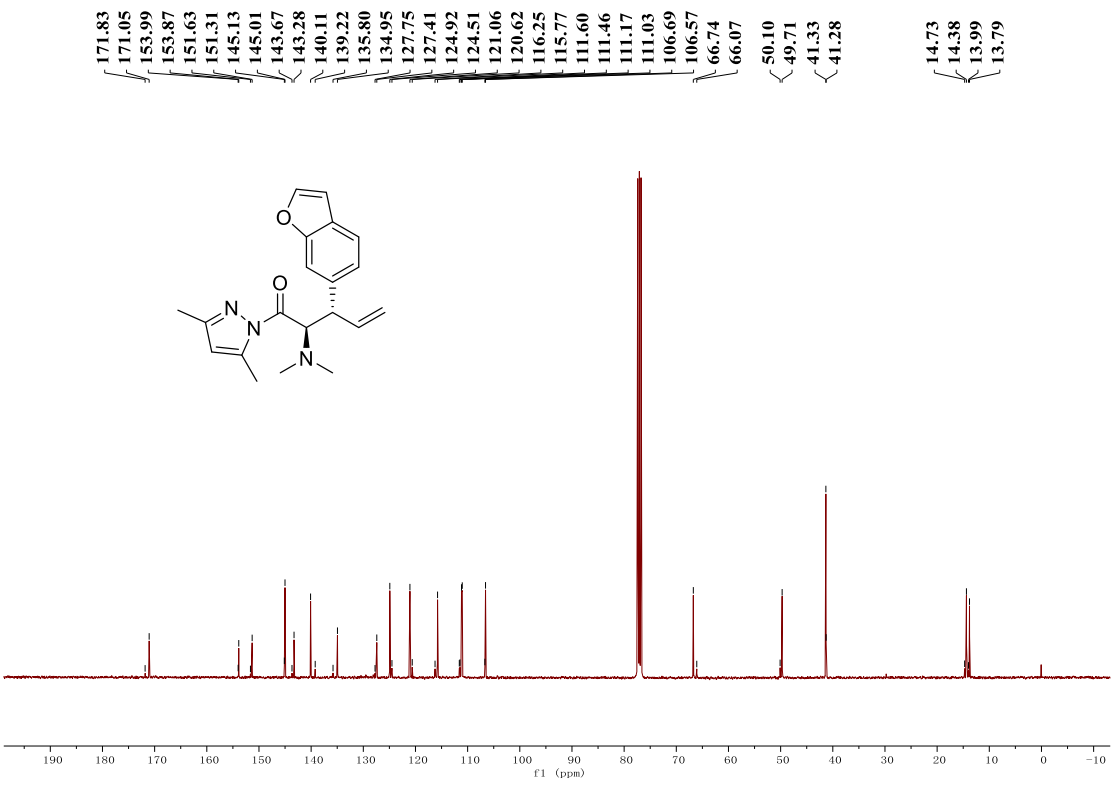
^{1}H NMR of Compound **3r** (400 MHz, $CDCl_3$)



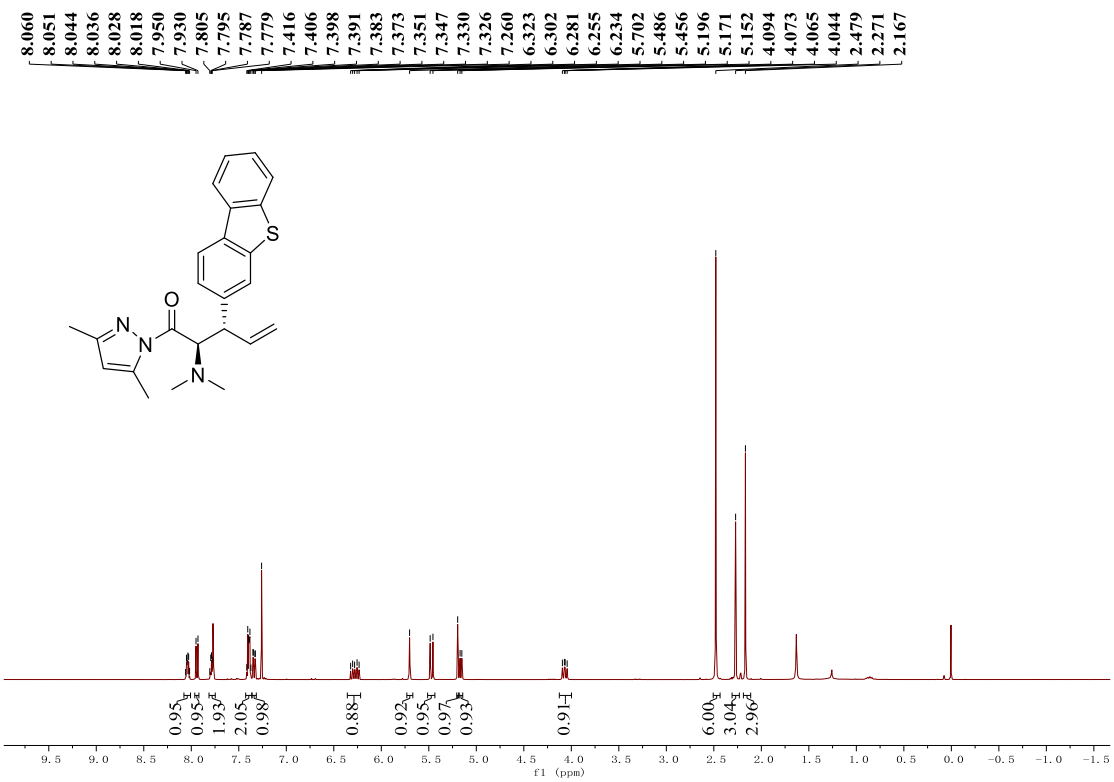
^{13}C NMR of Compound **3r** (101 MHz, $CDCl_3$)



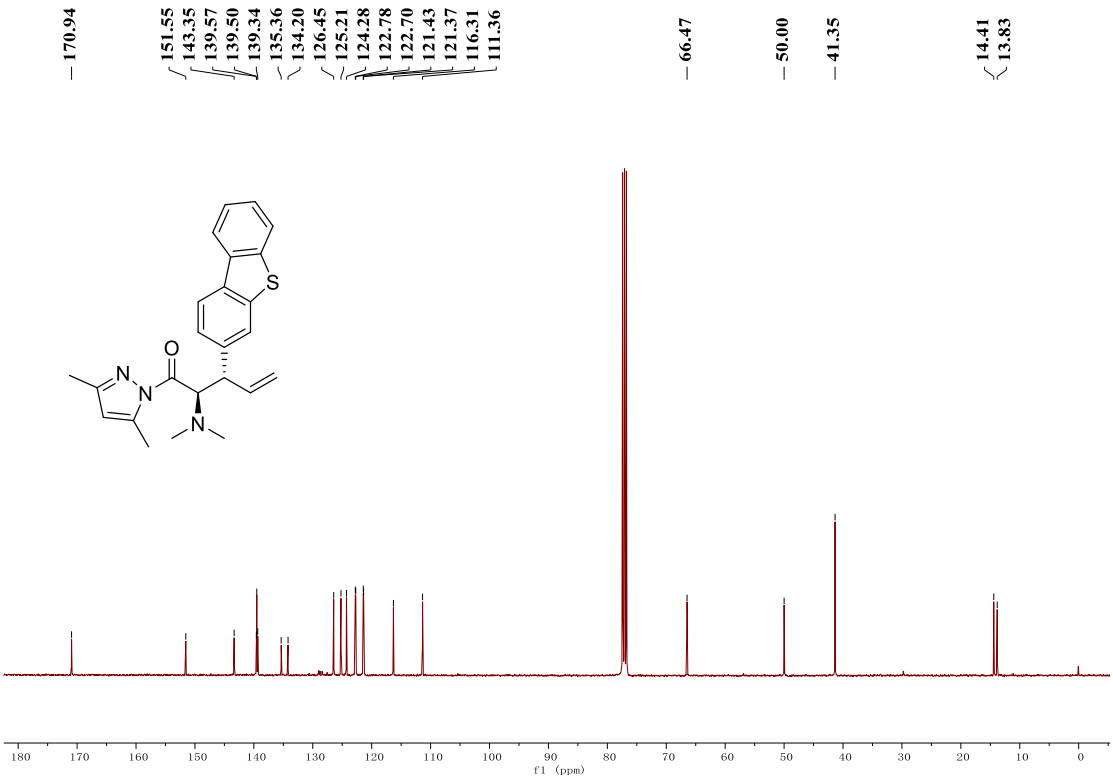
^{1}H NMR of Compound **3s** (400 MHz, $CDCl_3$)



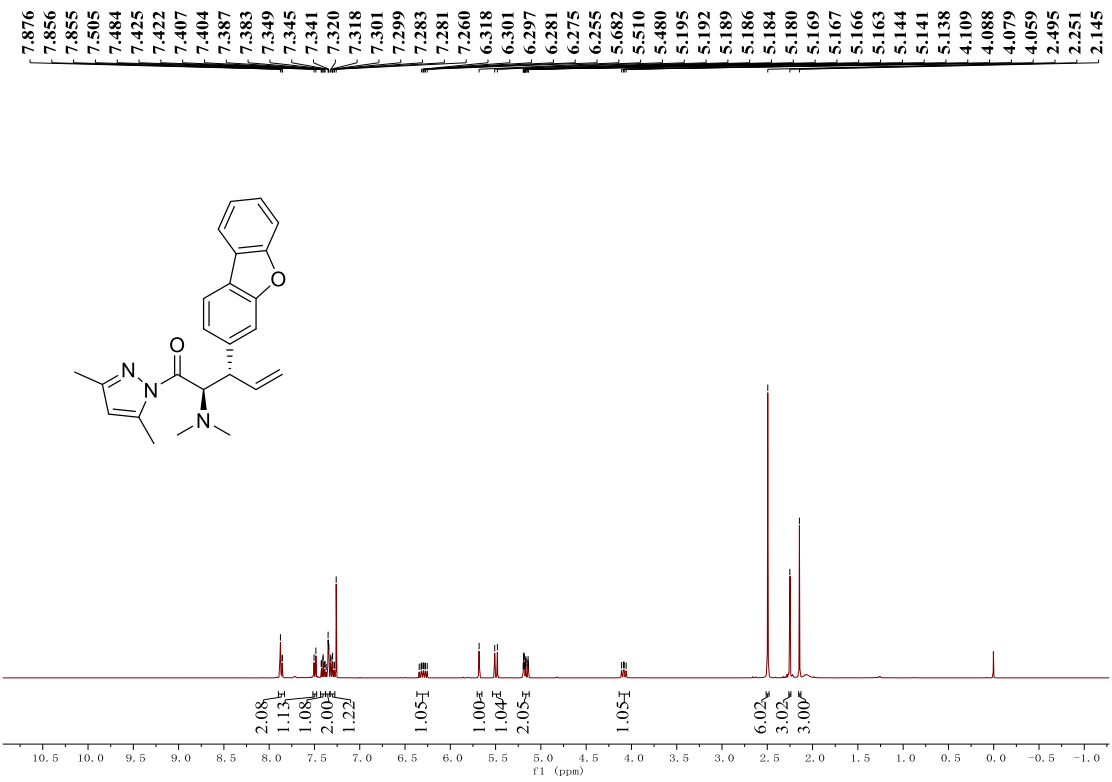
^{13}C NMR of Compound **3s** (101 MHz, $CDCl_3$)



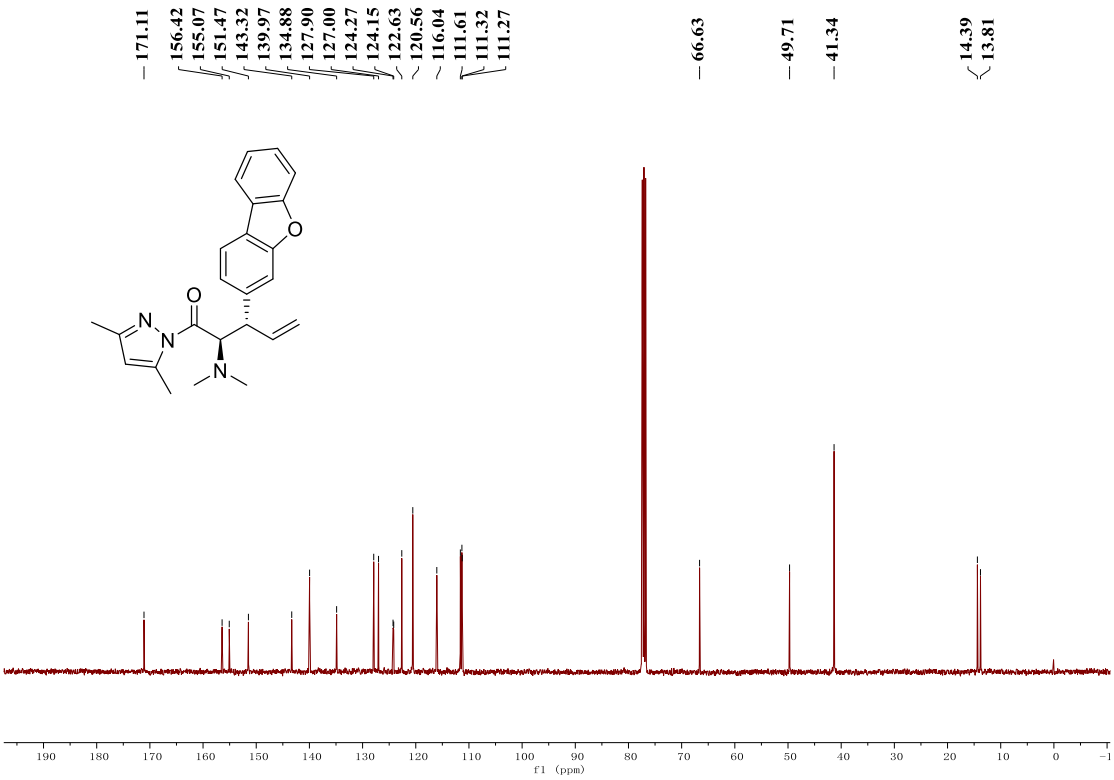
^{1}H NMR of Compound **3t** (400 MHz, $CDCl_3$)



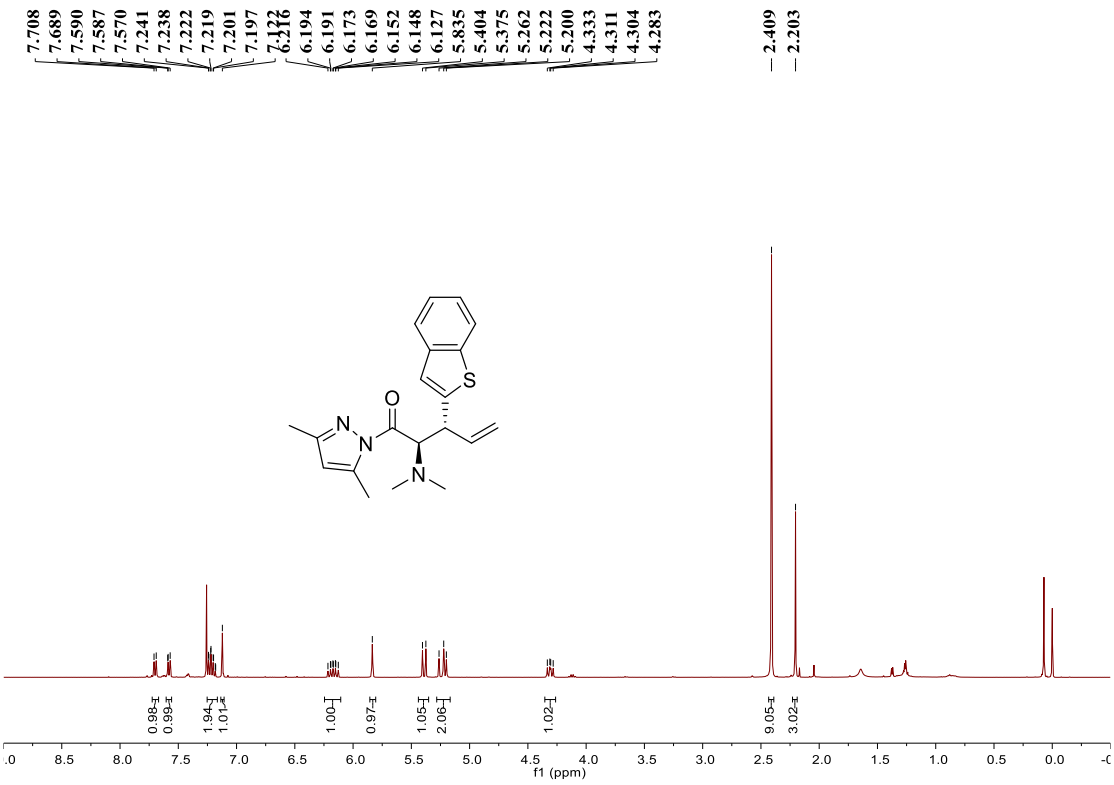
^{13}C NMR of Compound **3t** (101 MHz, $CDCl_3$)



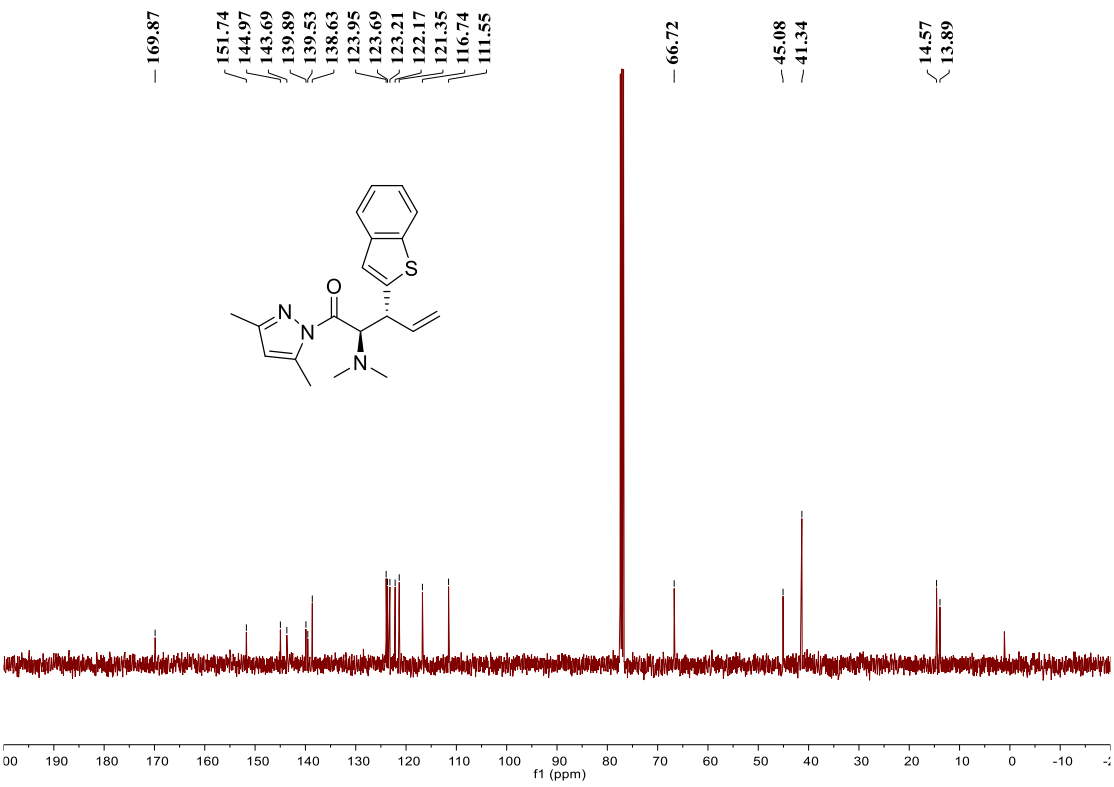
^{1}H NMR of Compound **3u** (400 MHz, $CDCl_3$)



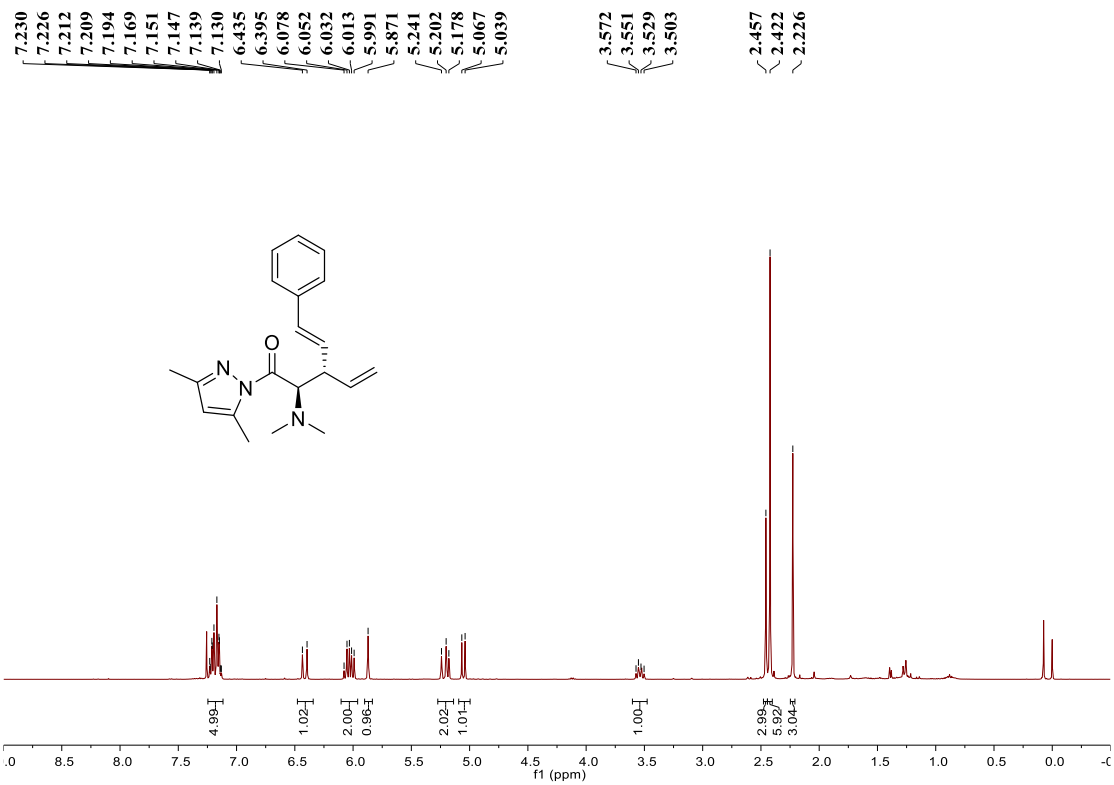
^{13}C NMR of Compound **3u** (101 MHz, $CDCl_3$)



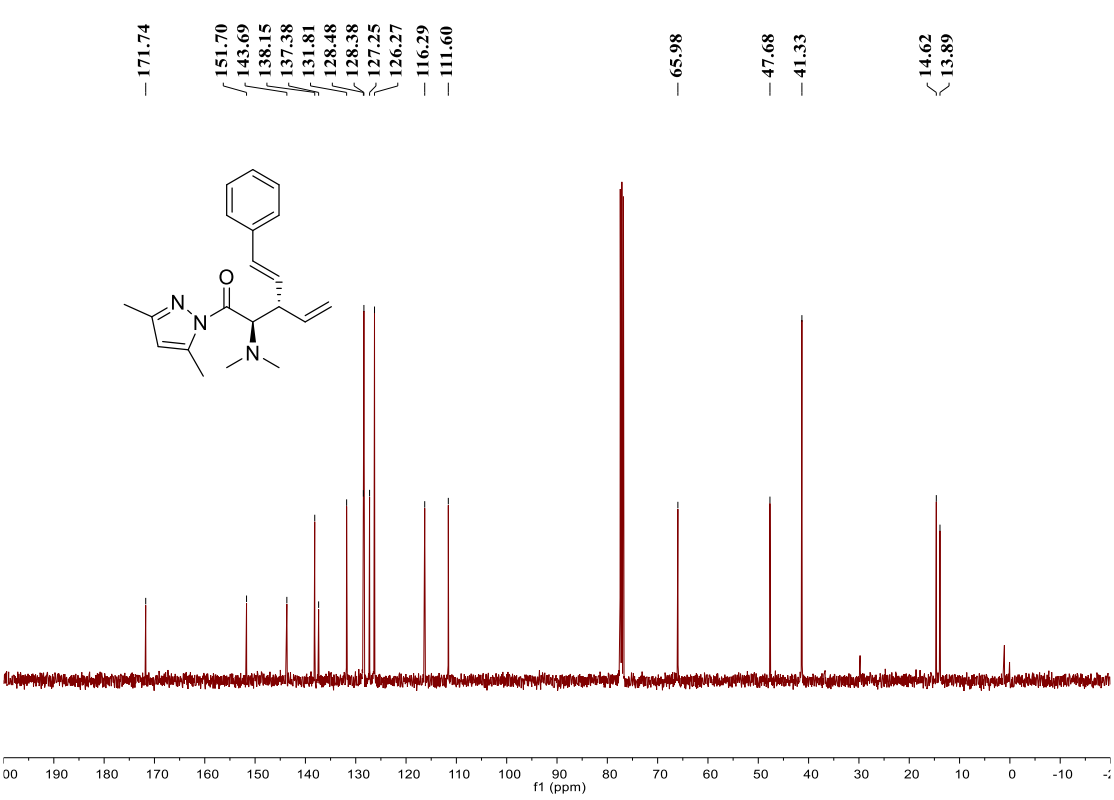
^{1}H NMR of Compound **3v** (400 MHz, $CDCl_3$)



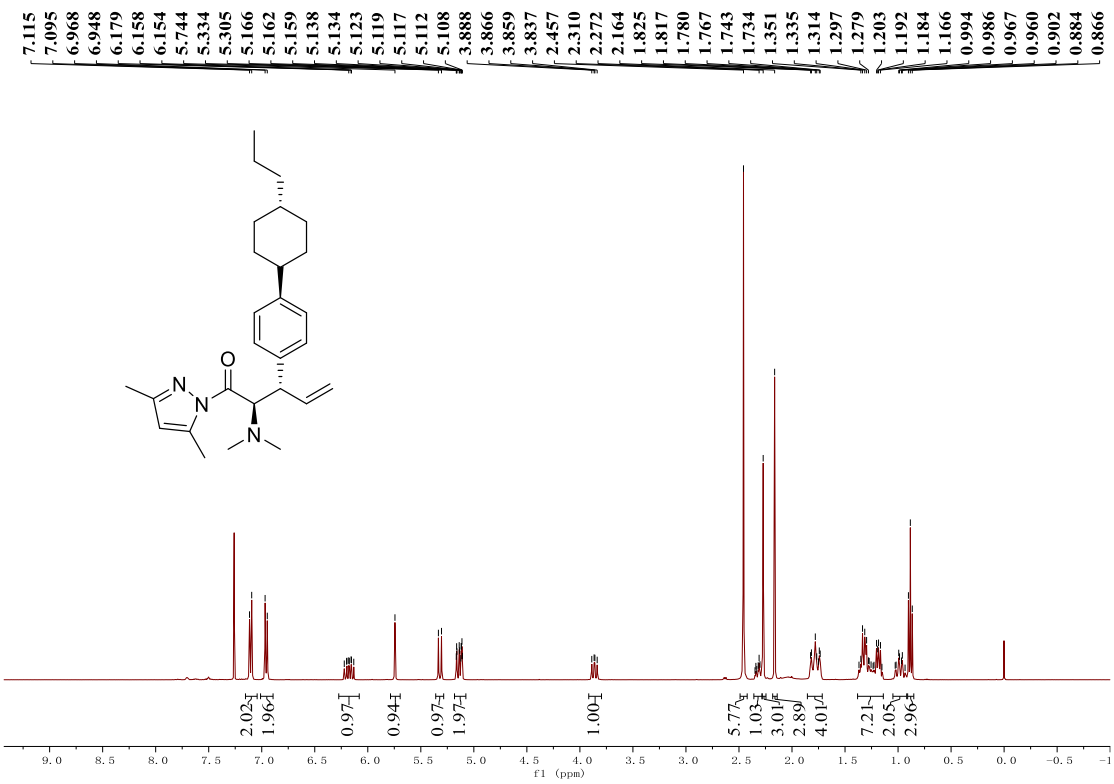
^{13}C NMR of Compound **3v** (101 MHz, $CDCl_3$)



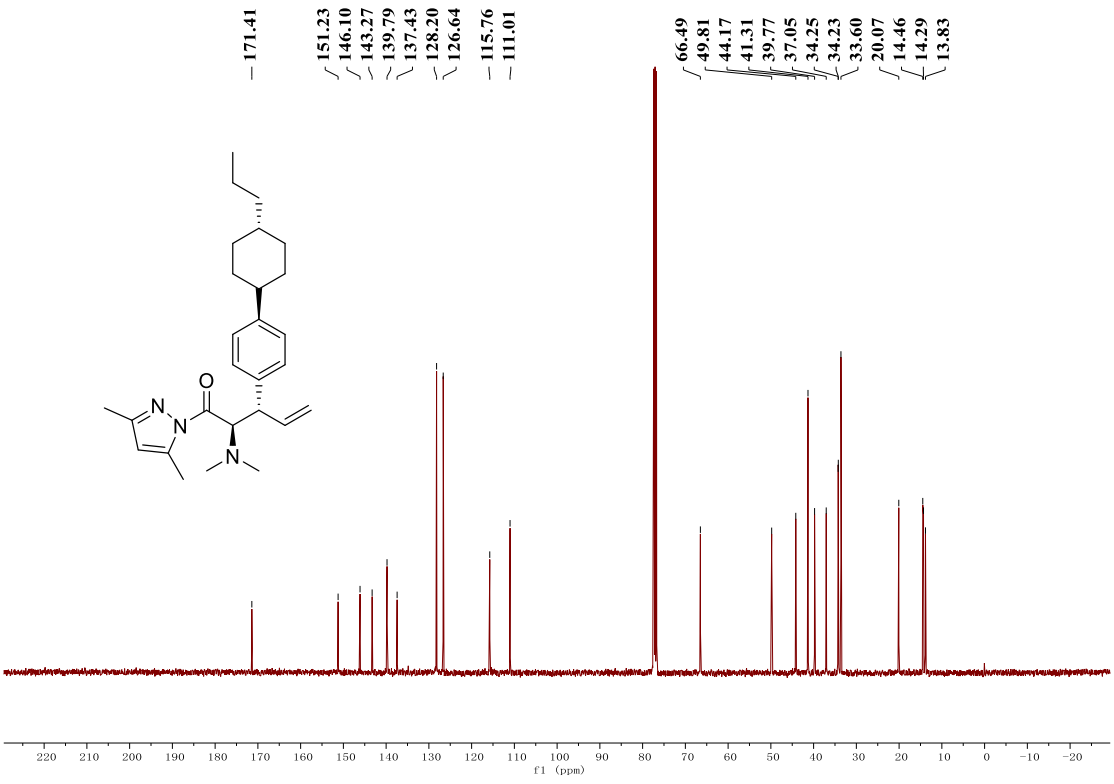
^{1}H NMR of Compound **3w** (400 MHz, $CDCl_3$)



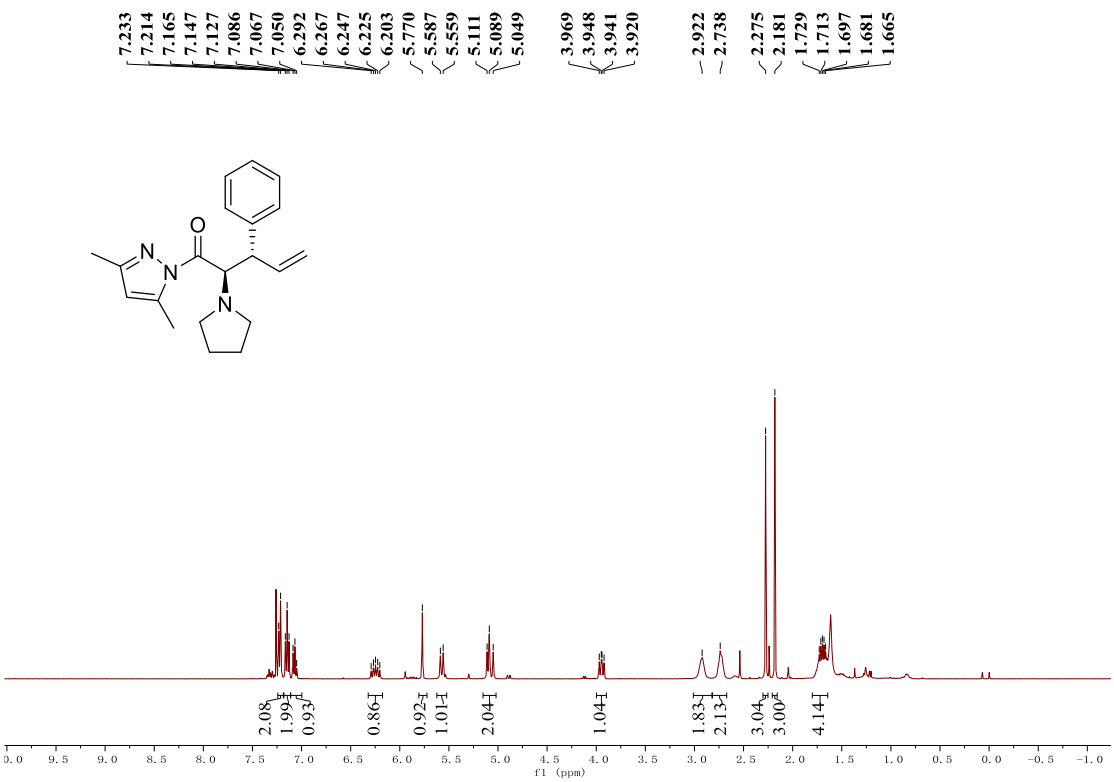
^{13}C NMR of Compound **3w** (101 MHz, $CDCl_3$)



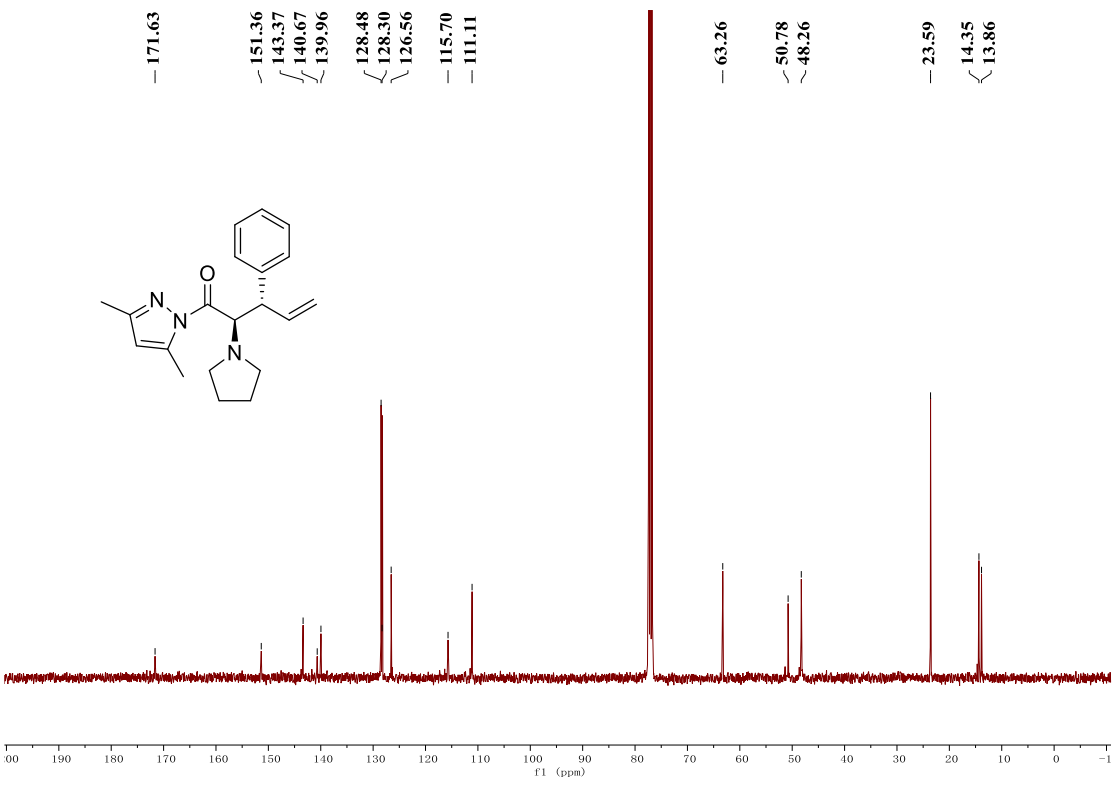
^{1}H NMR of Compound **3x** (400 MHz, $CDCl_3$)



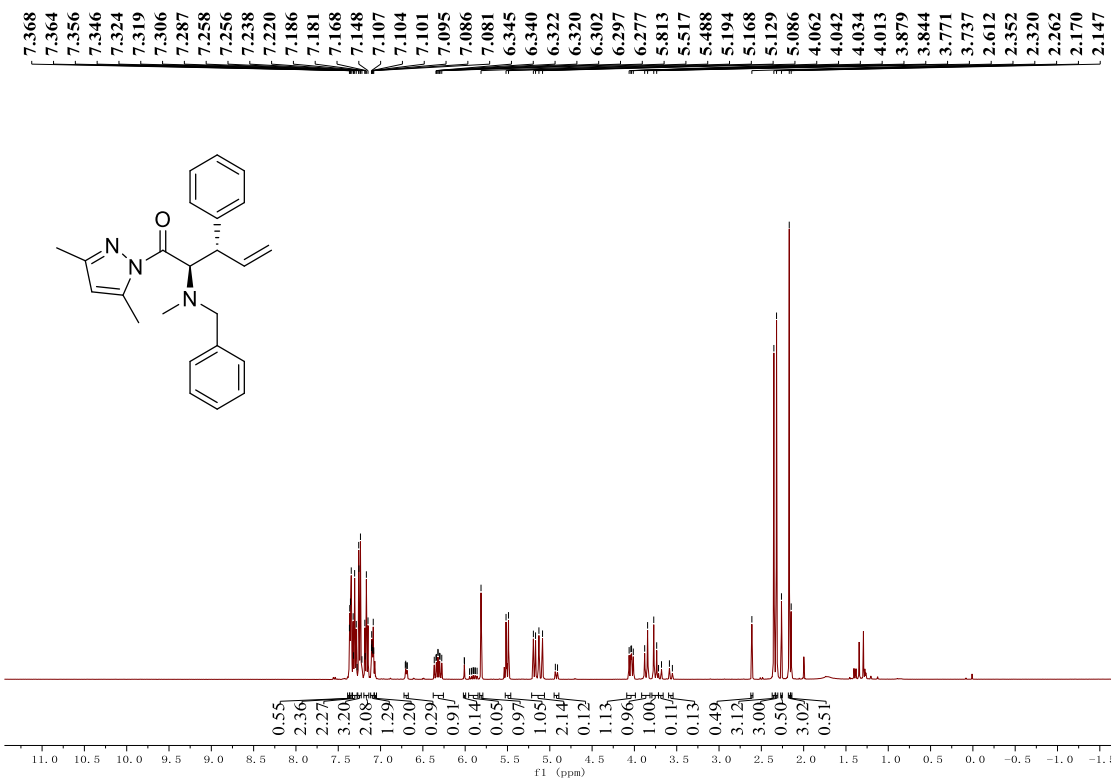
^{13}C NMR of Compound **3x** (101 MHz, $CDCl_3$)



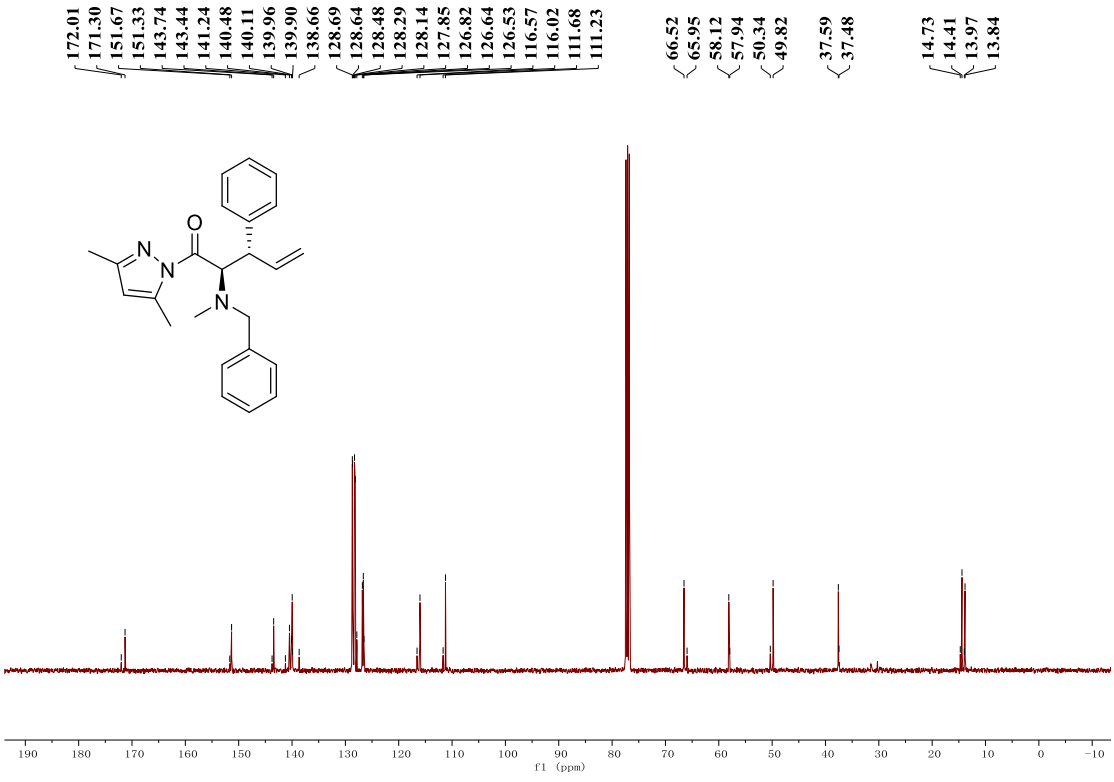
^{1}H NMR of Compound **3aa** (400 MHz, $CDCl_3$)



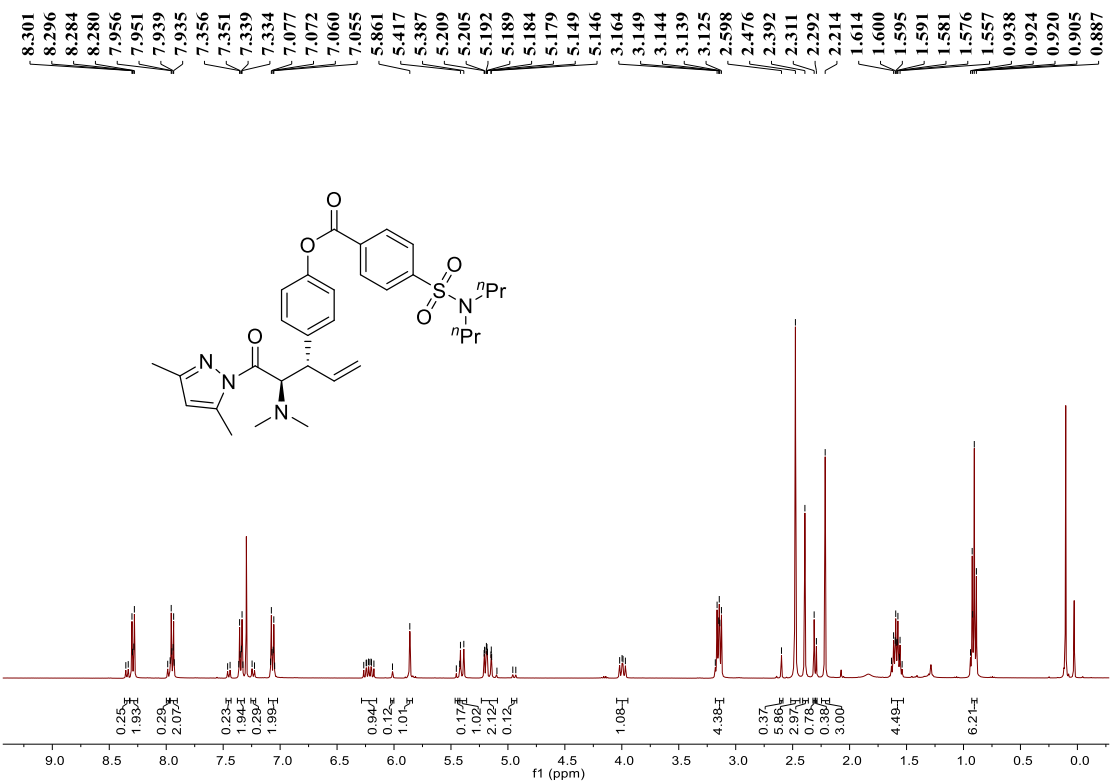
^{13}C NMR of Compound **3aa** (101 MHz, $CDCl_3$)



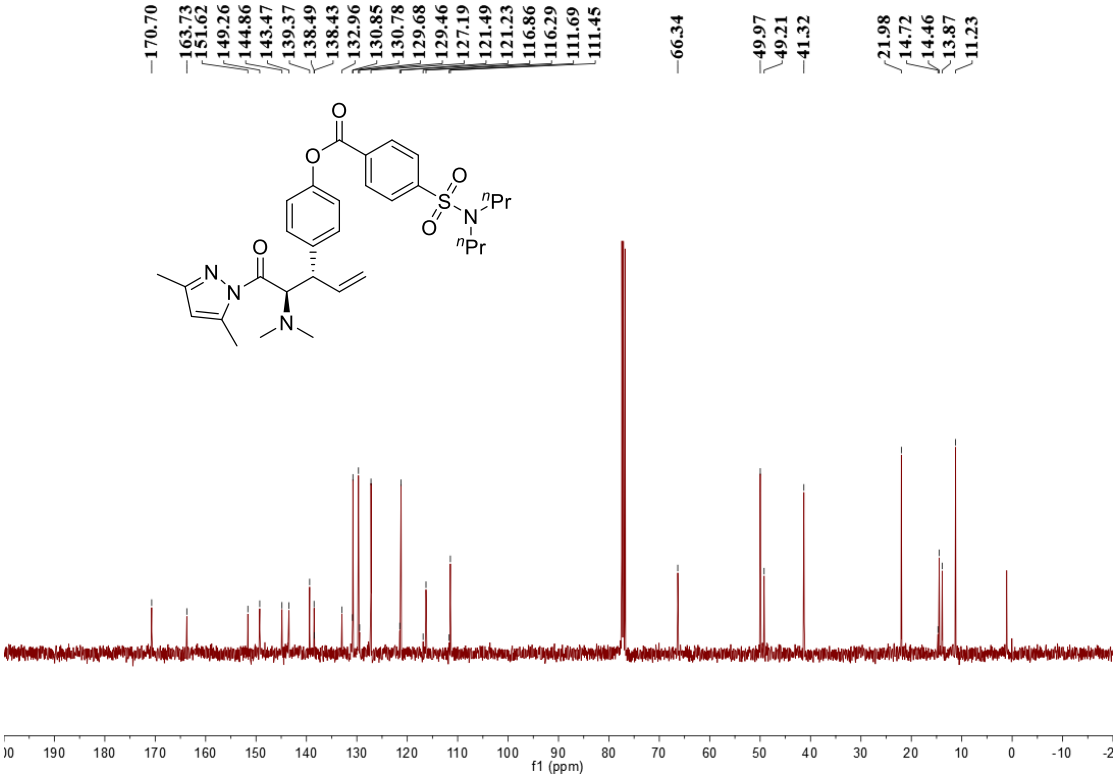
^{1}H NMR of Compound **3ab** (400 MHz, $CDCl_3$)



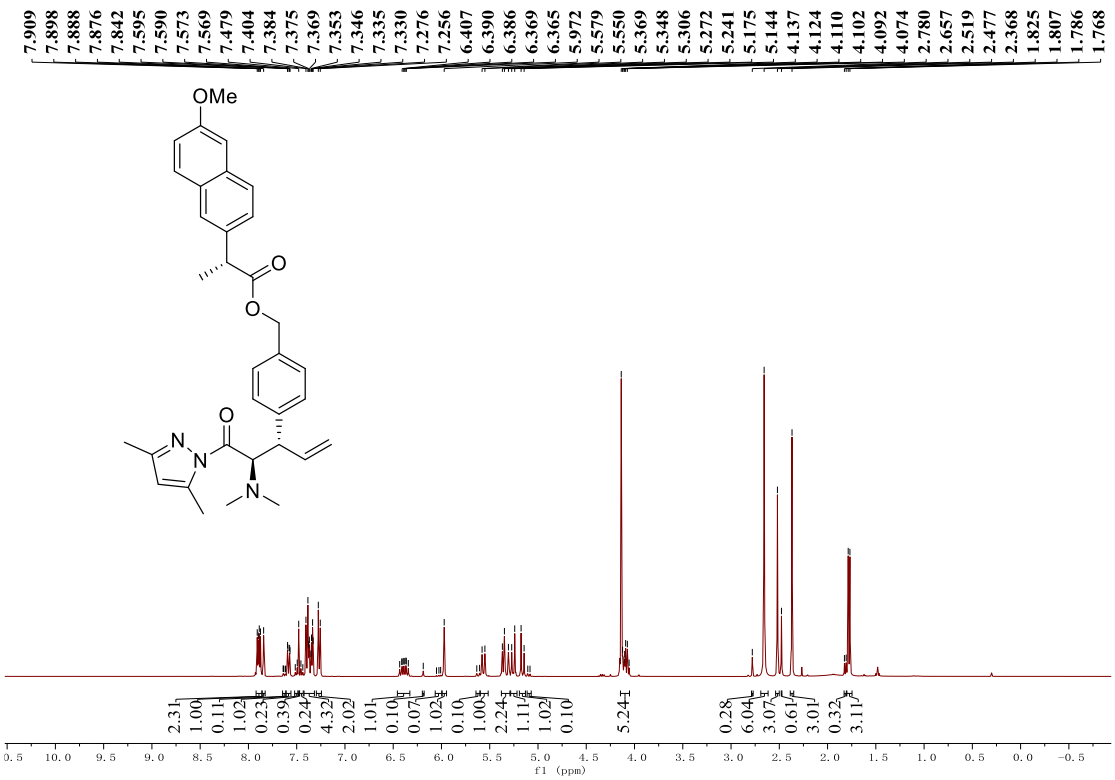
^{13}C NMR of Compound **3ab** (101 MHz, $CDCl_3$)



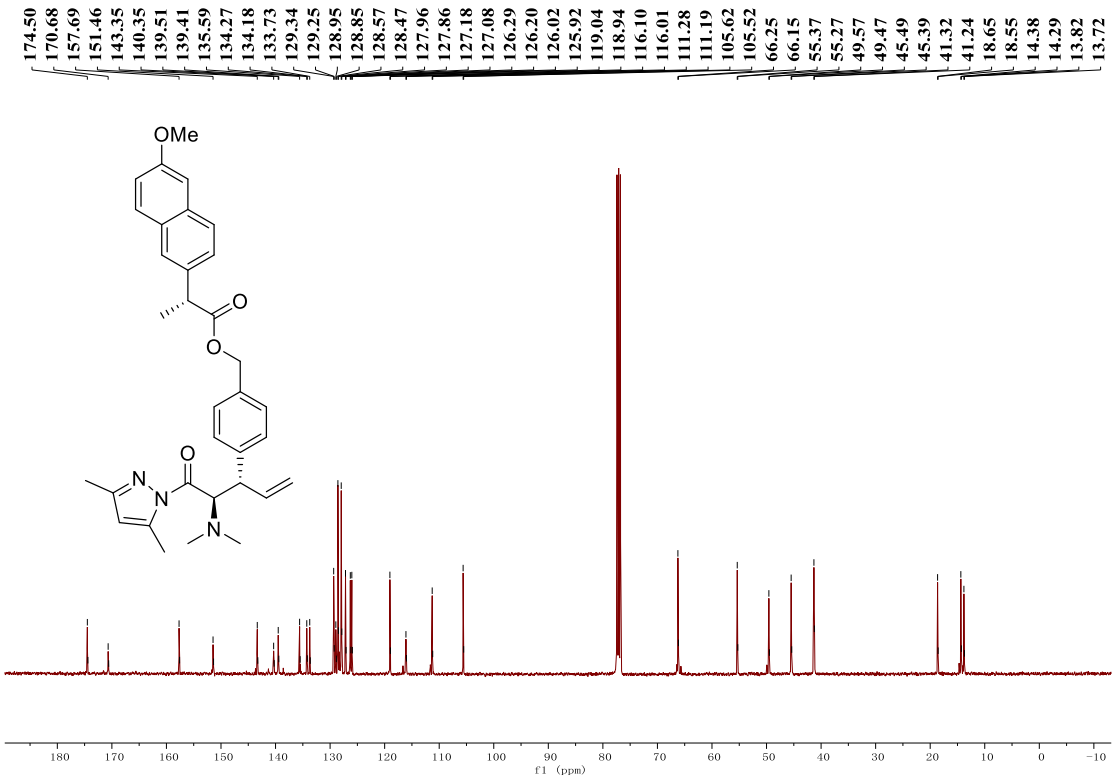
^{1}H NMR of Compound **3ca** (400 MHz, $CDCl_3$)



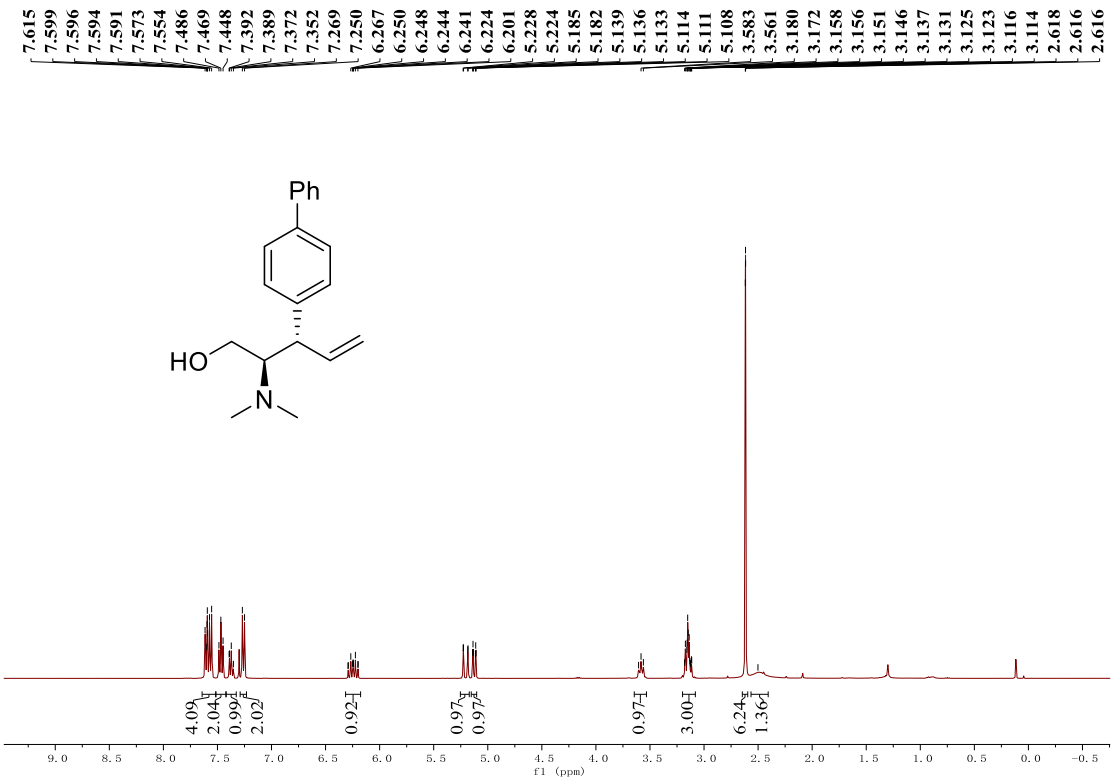
^{13}C NMR of Compound **3ca** (101 MHz, $CDCl_3$)



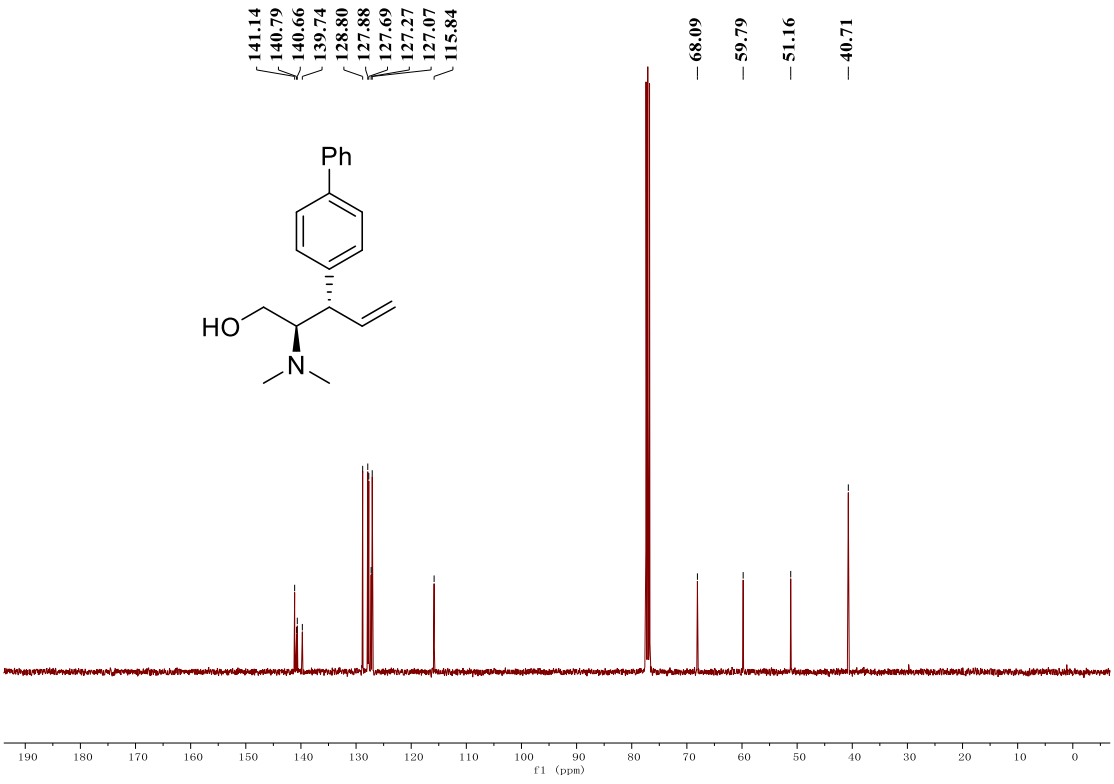
^{1}H NMR of Compound **3cb** (400 MHz, $CDCl_3$)



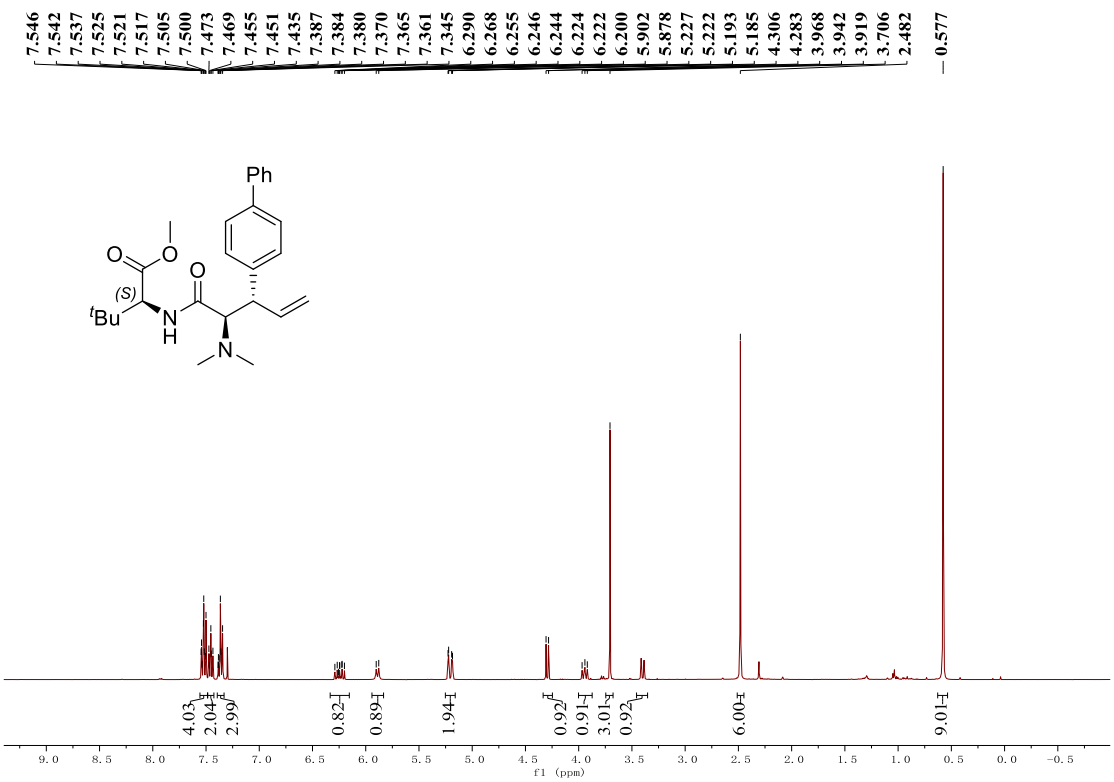
^{13}C NMR of Compound **3cb** (101 MHz, $CDCl_3$)



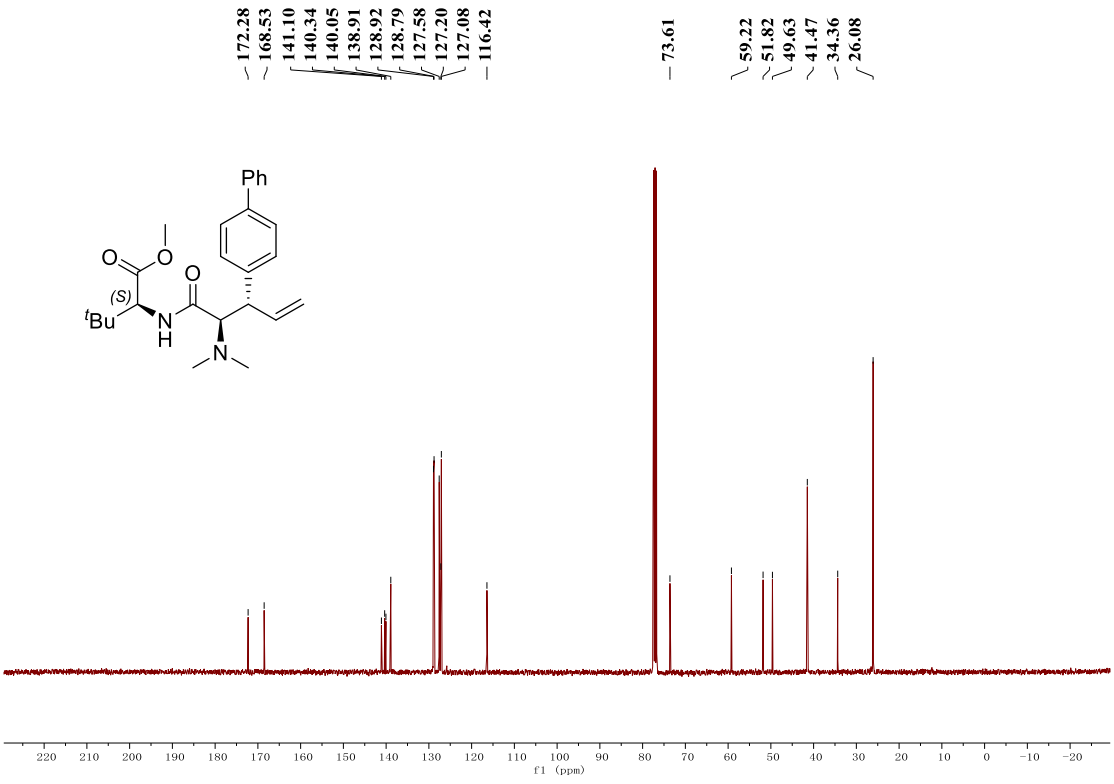
^{1}H NMR of Compound **4** (400 MHz, $CDCl_3$)



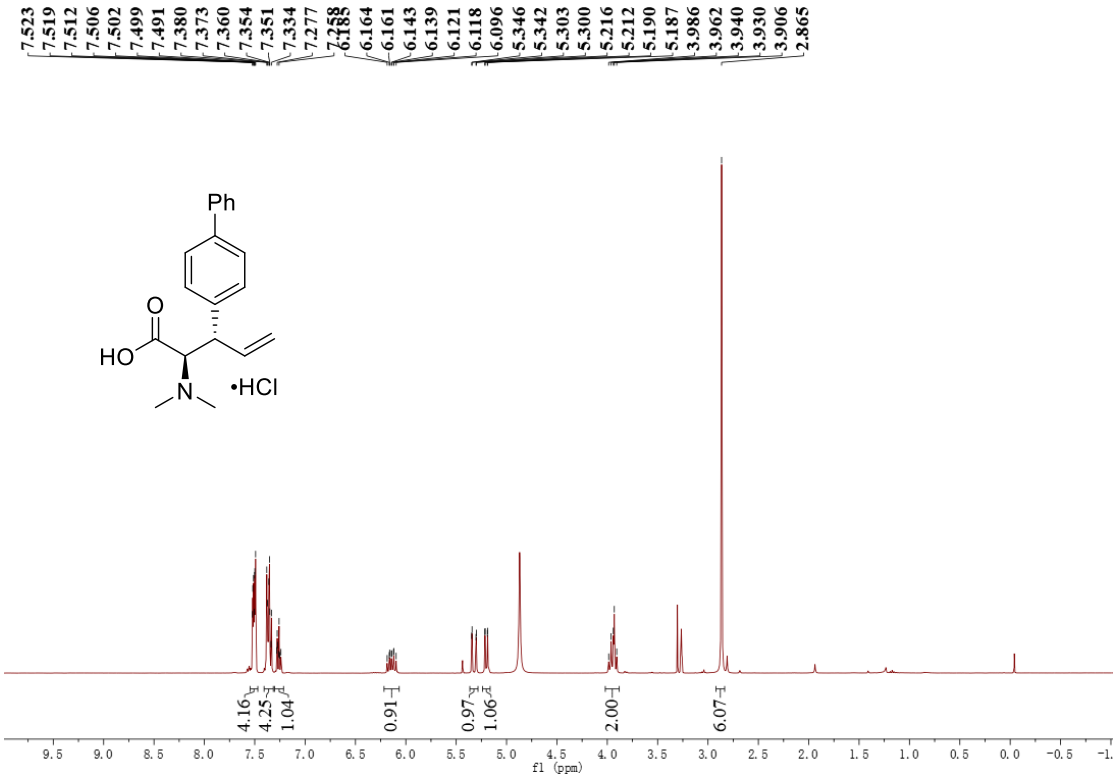
^{13}C NMR of Compound **4** (101 MHz, $CDCl_3$)



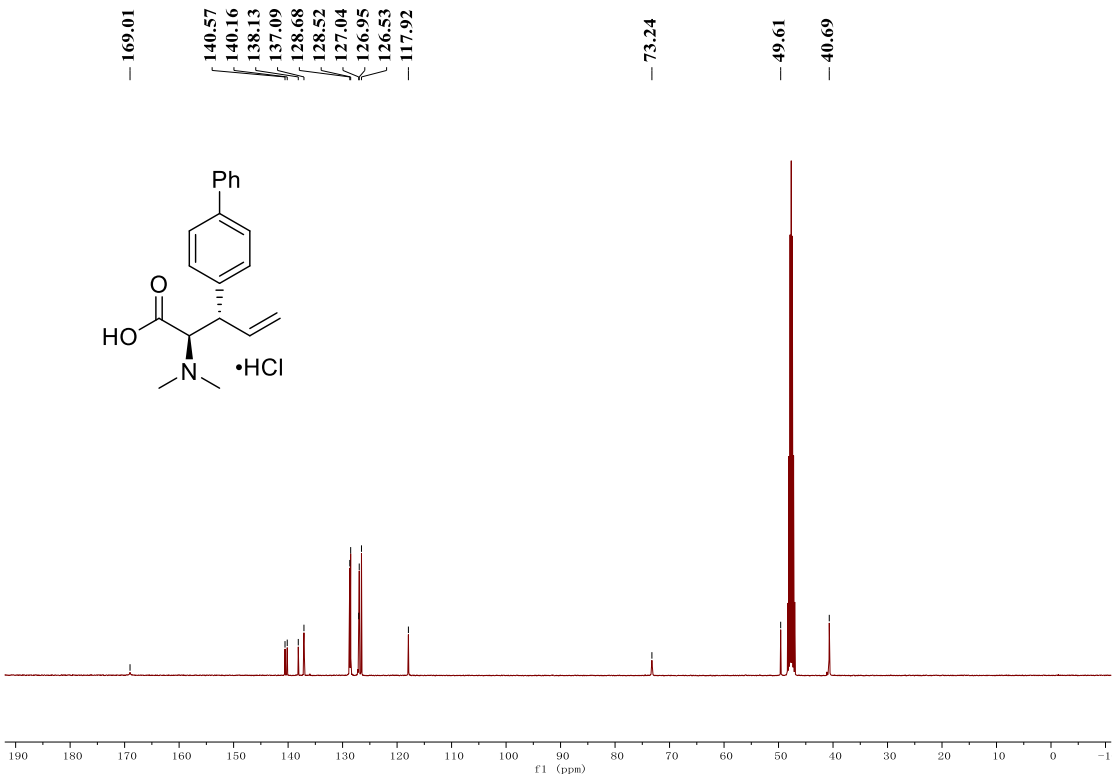
^{1}H NMR of Compound **5** (400 MHz, $CDCl_3$)



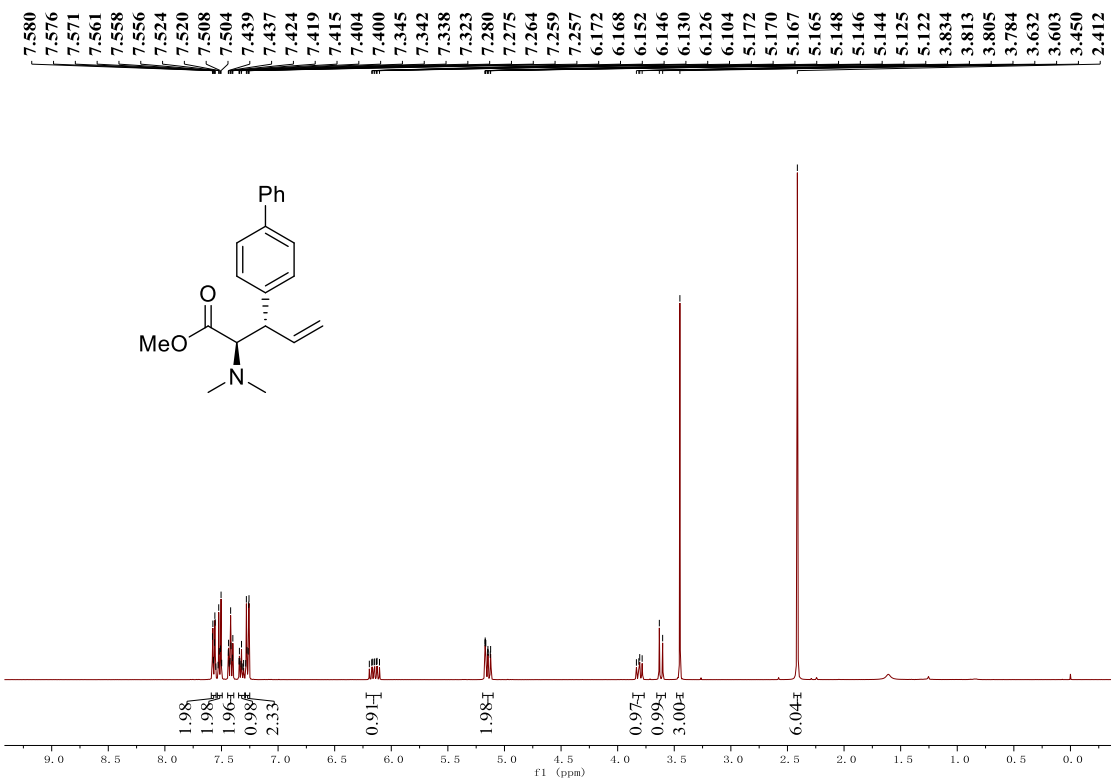
^{13}C NMR of Compound **5** (101 MHz, $CDCl_3$)



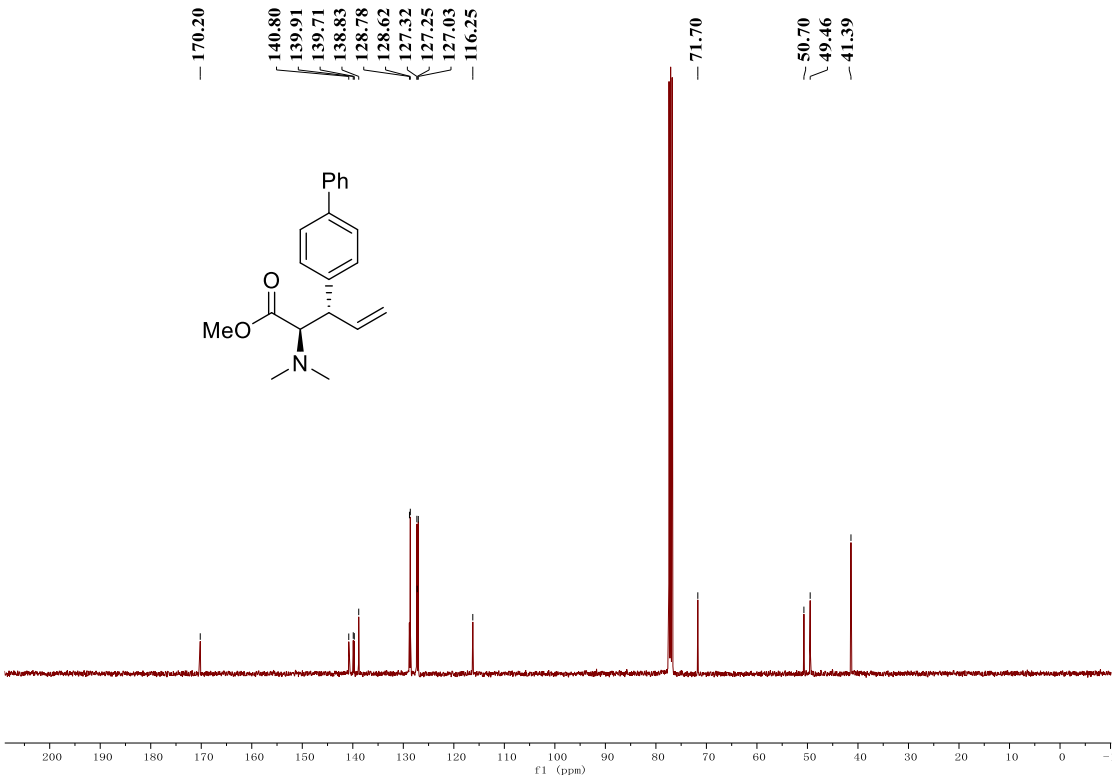
^{1}H NMR of Compound **6** (400 MHz, MeOD)



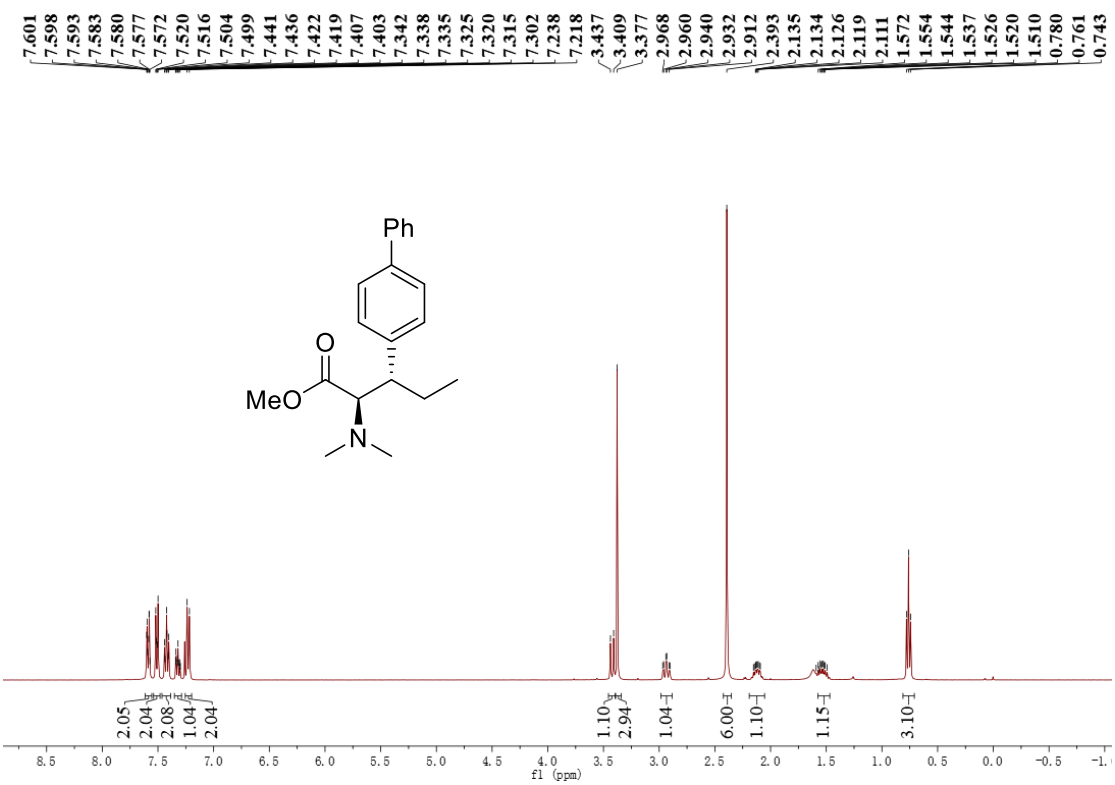
^{13}C NMR of Compound **7** (101 MHz, MeOD)



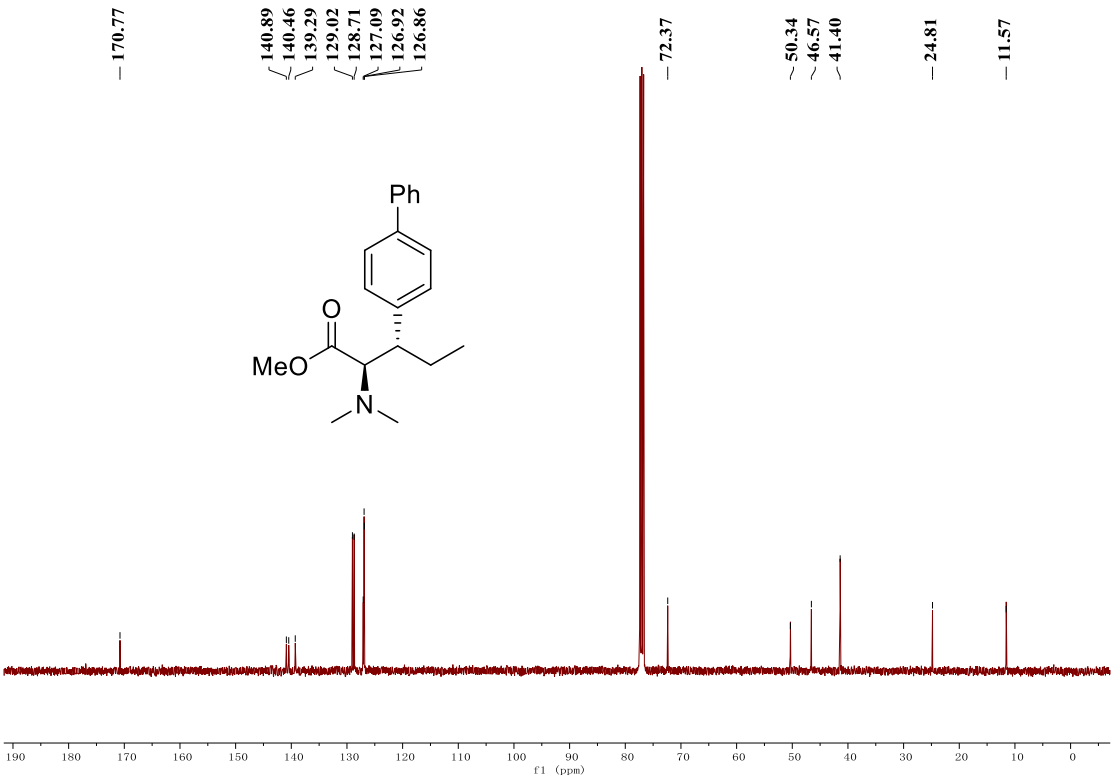
^{1}H NMR of Compound **7** (400 MHz, $CDCl_3$)



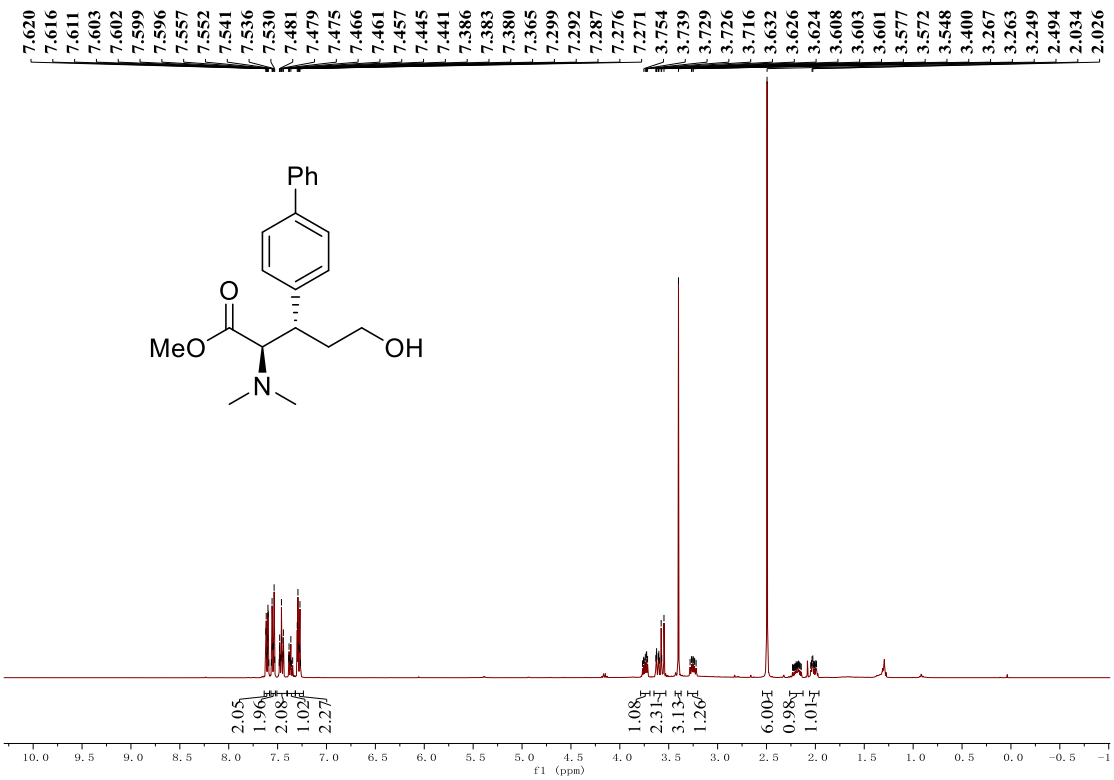
^{13}C NMR of Compound **7** (101 MHz, $CDCl_3$)



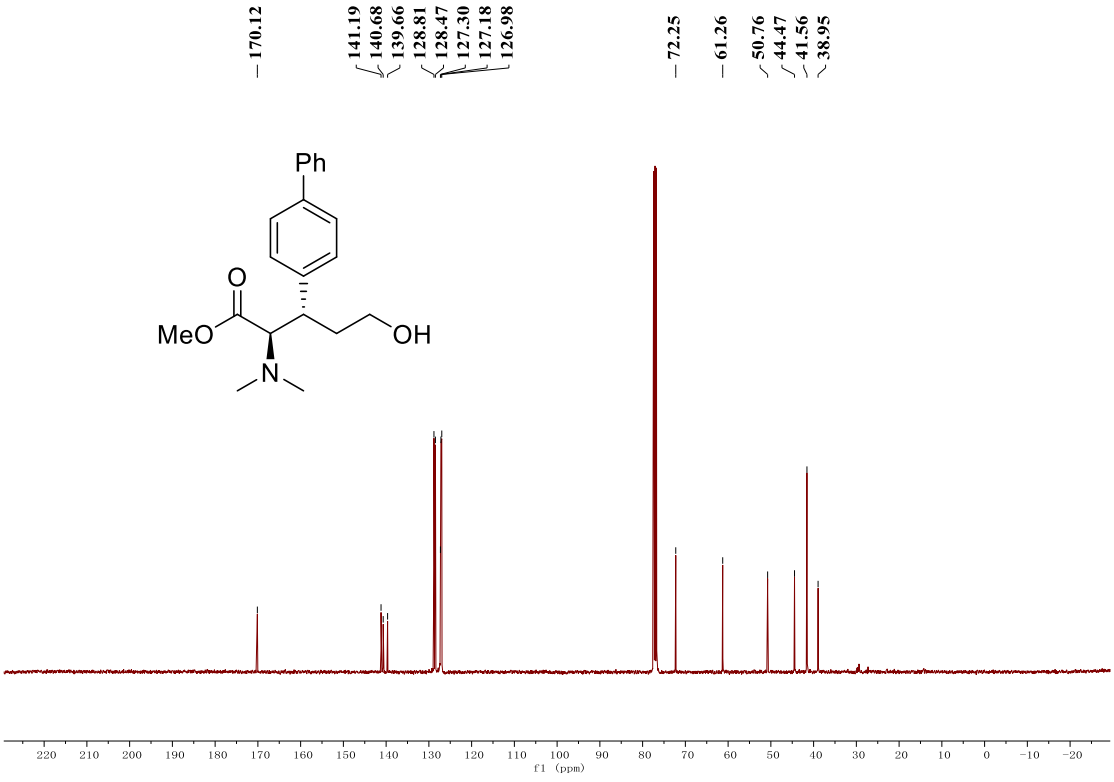
^{1}H NMR of Compound **8** (400 MHz, $CDCl_3$)



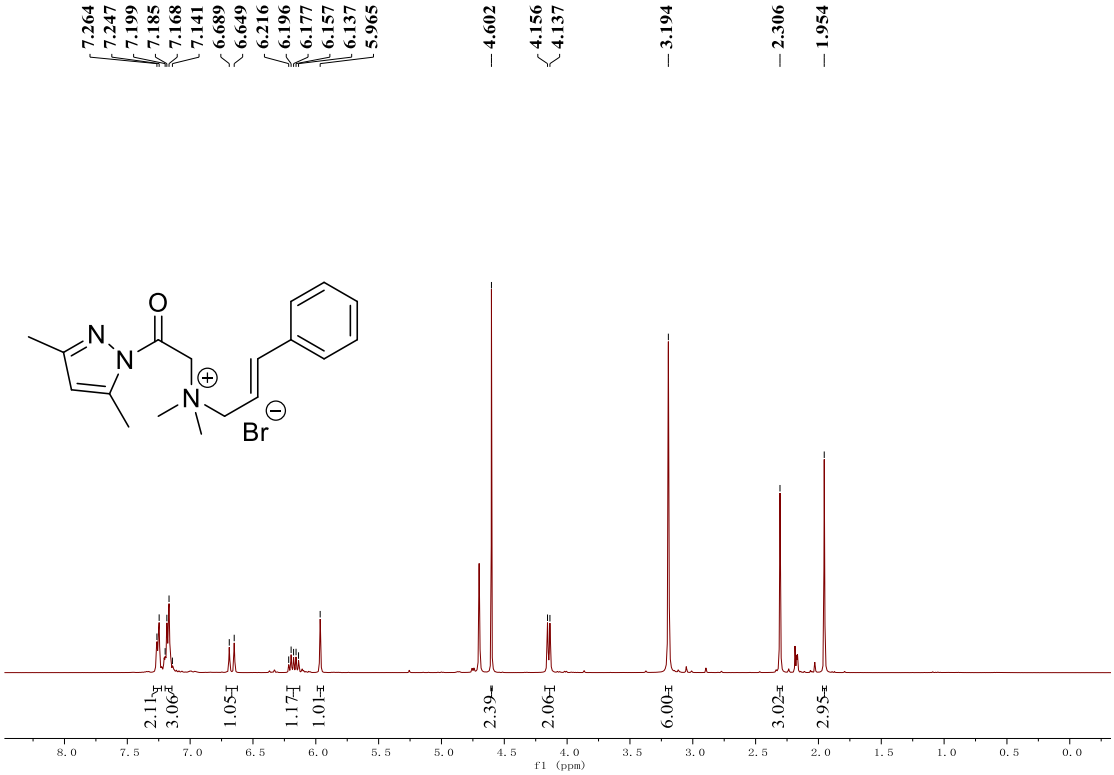
^{13}C NMR of Compound **8** (101 MHz, $CDCl_3$)



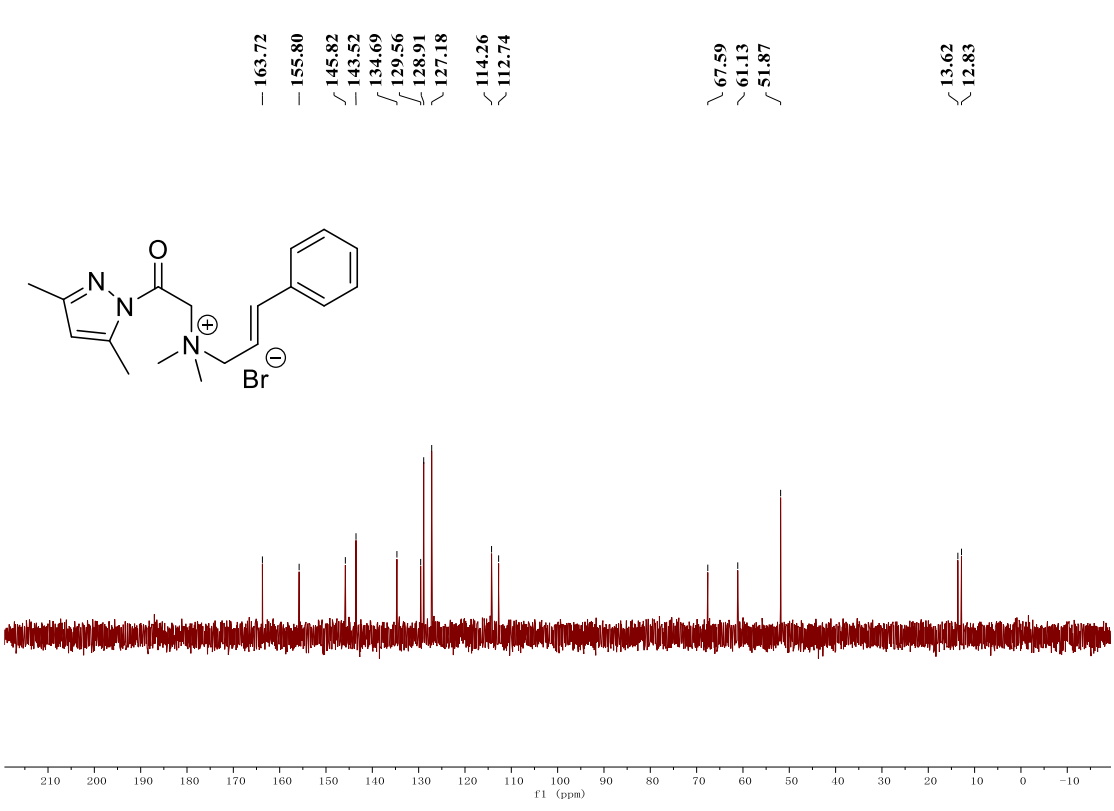
^{1}H NMR of Compound **9** (400 MHz, $CDCl_3$)



^{13}C NMR of Compound **9** (101 MHz, $CDCl_3$)



^{1}H NMR of Compound **10** (400 MHz, D_2O)



^{13}C NMR of Compound **10** (101 MHz, D_2O)