Palladium-catalyzed double strain-release (3+3) cycloaddition for the synthesis of vinylbicyclo[3.1.1]heptanes

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Supporting Information

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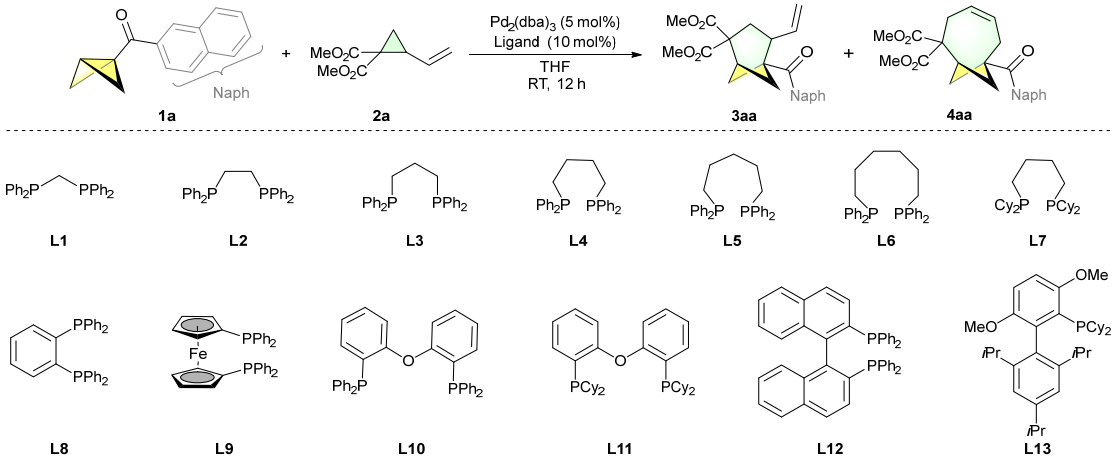
1 General Information

All reactions were performed in oven-dried glassware using conventional Schlenk techniques under a static pressure of nitrogen unless otherwise stated. Liquids and solutions were transferred with syringes. Bicyclo[1.1.0]butanes (BCBs),[1] vinyl cyclopropanes (**VCPs**)[2] and spirovinylcyclopropane oxindoles (**SVCPs**)[3] were prepared according to reported procedures. $Pd_2(dba)_3{\cdot}CHCl_3$ (98%, *Energy Chemical*) and other commercially available reagents were purchased from *Sigma-Adrich*, *Leyan*, *Energy Chemical* and *Bide* Chemical Company and used as received. Ethyl acetate (EtOAc) was purchased from *Energy Chemical* (99%, Extra Dry) and used as received. All other solvents (Et_2O, THF, toluene and 1,2-dichloroethane *etc*.) were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography (petroleum ether, CH_2Cl_2, and ethyl acetate) were distilled prior to use. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) by *Grace* using the indicated solvents. ^1H, ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_3OD on Bruker AV400 or 600 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm for ^1H NMR and $CDCl_3$: δ = 77.0 ppm for ^{13}C NMR, CD_3OD: δ = 3.31 ppm for ^1H NMR and CD_3OD: δ = 49.0 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplett, q = quartet, m = multiplet), coupling constants (Hz), and integration. The full-scan mass spectra were taken on a hybrid quadrupole-orbitrap mass spectrometer equipped with a heated electrospray ionization source (ThermoFischer Scientific, Bremen, Germany). The configuration was determined by single crystal X-ray diffraction analysis on Bruker D8 Venture dual system with a Cu micro-focus source. Acknowledgement: the ^1H, ^{13}C NMR spectra, single crystal X-ray diffraction and HRMS (ESI) were performed at Analytical Instrumentation Center of Hunan University.

2 Optimization Study

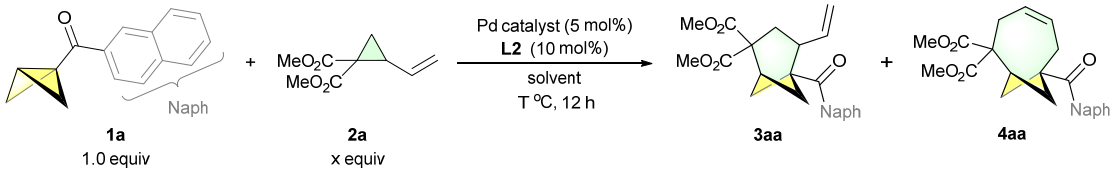
Table S1. Ligand screening for the (3+3) cycloaddition of BCB 1a and VCP 2a.[a]



Entry	Ligand	Conversion of **1a** [%][b]	Yield of **3aa** [%][b]	Yield of **4aa** [%][b]
1	**L1**	16	5	0
2	**L2**	**86**	**79**	**<5**
3	**L3**	77	49	<5
4	**L4**	90	77	<5
5	**L5**	52	29	<5
6	**L6**	35	15	<5
7	**L7**	98	60	<5
8	**L8**	83	64	<5
9	**L9**	32	16	0
10	**L10**	33	15	0
11	**L11**	95	68	6
12	**L12**	41	33	0
13	**L13**	20	12	<5

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.12 mmol), $Pd_2(dba)_3$ (5 mol%) and ligand (10 mol%), THF (1 mL), 25 °C, under N_2 for 12 h. [b] Determined by ^1H NMR analysis using CH_2Br_2 as an internal standard.

Table S2. Further optimization of the conditions for the (3+3) cycloaddition involving BCB 1a and VCP 2a.[a]

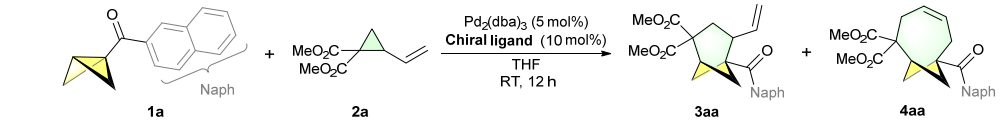


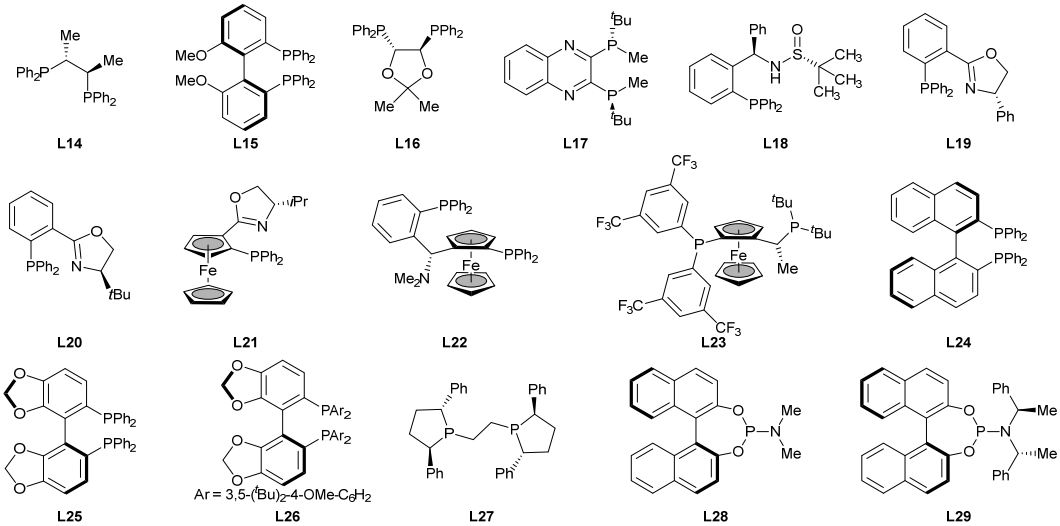
1a 1.0 equiv + **2a** x equiv → **3aa** + **4aa**

Entry	solvent	[Pd]	**1a** (equiv)	**2a** (x equiv)	T (°C)	Yield of **3aa** [%][b]	Yield of **4aa** [%][b]
1	THF	$Pd_2(dba)_3$	1.0	1.2	25	79	<5
2	toluene	$Pd_2(dba)_3$	1.0	1.2	25	6	0
3	CH_2Cl_2	$Pd_2(dba)_3$	1.0	1.2	25	74	<5
4	EtOAc	$Pd_2(dba)_3$	1.0	1.2	25	69	<5
5	CH_3CN	$Pd_2(dba)_3$	1.0	1.2	25	60	<5
6	1,4-dioxane	$Pd_2(dba)_3$	1.0	1.2	25	15	0
7	PhCl	$Pd_2(dba)_3$	1.0	1.2	25	79	0
8	HFIP	$Pd_2(dba)_3$	1.0	1.2	25	0	0
9	**THF**	**$Pd_2(dba)_3·CHCl_3$**	**1.0**	**1.2**	**25**	**86**	<5
10	THF	$Pd(PPh_3)_4$	1.0	1.2	25	79	7
11	THF	$Pd(OAc)_2$	1.0	1.2	25	53	0
12	THF	$CpPd(\eta^3\text{-}C_3H_5)$	1.0	1.2	25	62	0
13	THF	$Pd_2(dba)_3·CHCl_3$	1.0	2.0	25	69	<5
14	THF	$Pd_2(dba)_3·CHCl_3$	1.0	1.2	0	31	0
15	THF	$Pd_2(dba)_3·CHCl_3$	1.0	1.2	40	79	0
16	THF	$Pd_2(dba)_3·CHCl_3$	1.0	1.2	60	46	0

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2a** (x equiv), Pd catalyst (5 mol%) and **L2** (10 mol%), solvent (1 mL), T °C, under N_2 for 12 h. [b] Determined by ^1H NMR analysis using CH_2Br_2 as an internal standard.

Table S3. Chiral ligand screening for the catalytic asymmetric (3+3) cycloaddition of BCB 1a and VCP 2a.[a]

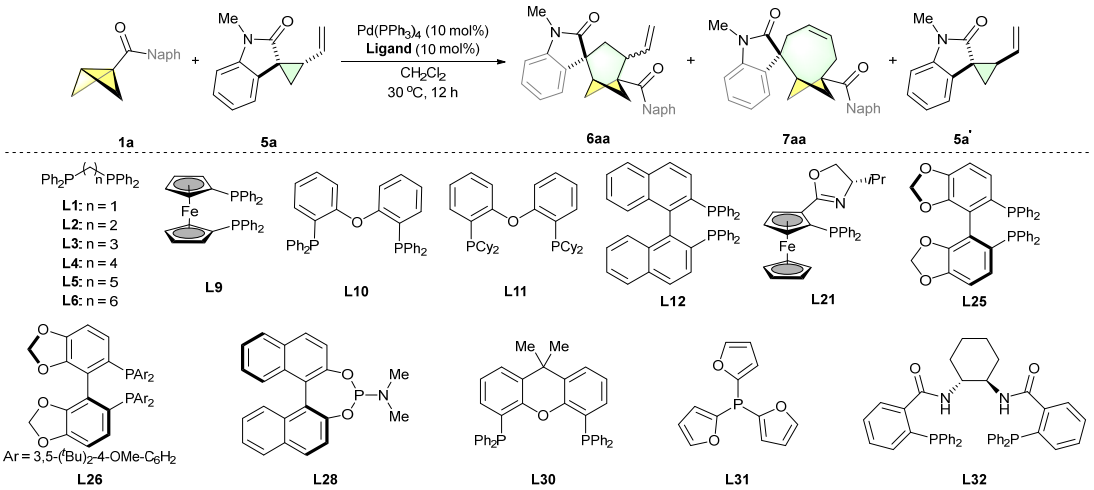




Entry	Ligand	Conversion of **1a** [%][b]	Yield of **3aa** [%][b]	*ee* of **3aa** [%][c]	Yield of **4aa** [%][b]
1	**L14**	**97**	**87**	**20**	**7**
2	**L15**	**17**	**5**	**-58**	**0**
3	**L16**	60	25	-10	<5
4	**L17**	45	39	-6	0
5	**L18**	13	0	-	0
6	**L19**	35	19	-21	0
7	**L20**	96	72	34	<5
8	**L21**	61	52	-19	<5
9	**L22**	29	15	54	0
10	**L23**	12	0	-	0
11	**L24**	36	27	27	0
12	**L25**	32	18	-31	0
13	**L26**	48	29	33	0
14	**L27**	50	39	-13	0
15	**L28**	24	0	-	0
16	**L29**	13	0	-	0

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.12 mmol), $Pd_2(dba)_3$ (5 mol%) and ligand (10 mol%), THF (1 mL), 25 °C, under N_2 for 12 h. [b] Determined by ^1H NMR analysis using CH_2Br_2 as an internal standard. [c] The *ee* value was determined by chiral HPLC with hexane/2-propanol.

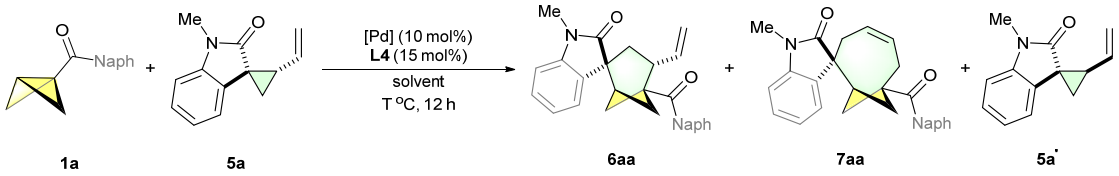
Table S4. Ligand screening for the (3+3) cycloaddition of BCB 1a and SVCP 5a.[a]



Entry	Ligand	Conversion of **1a** [%][b]	Yield of **6aa** [%][b],[c]	**6aa** *d.r.*[b]	Yield of **7aa** [%][b]	Yield of **5a'** [%][b]
1	**L1**	89	0	0	0	-
2	**L2**	100	33	45:55	10	0
3	**L3**	100	41	56:44	12	0
4	**L4**	**100**	**47**	**70:30**	**9**	**0**
5	**L5**	100	45	53:47	14	0
6	**L6**	96	39	67:33	11	0
7	**L9**	100	43	63:37	10	0
8	**L10**	100	46	54:46	16	13
9	**L11**	**100**	**56**	**52:48**	**19**	**0**
10	**L12**	99	31	68:32	4	0
11	**L21**	100	18	50:50	12	0
12	**L25**	100	32	69:31	-	0
13	**L26**	100	32	75:25	-	32
14	**L28**	85	9	44:56	6	52
15	**L30**	94	24	58:42	12	52
16	**L31**	93	40	55:45	-	31
17	**L32**	95	13	46:54	4	48
18[d]	**L4**	**100**	**84**	**71:29**	**15**	**0**

[a] Reaction conditions: **1a** (0.10 mmol), **5a** (0.12 mmol), $Pd(PPh_3)_4$ (10 mol%) and ligand (10 mol%), CH_2Cl_2 (1 mL), 30 °C, under N_2 for 12 h. [b] Determined by ^1H NMR spectroscopic analysis of the crude reaction product using CH_2Br_2 as an internal standard. [c] Combined NMR yield of the diastereomers. [d] 15 mol% **L4** was used.

Table S5. Further optimization of the conditions for the (3+3) cycloaddition involving BCB 1a and SVCP 5a.[a]

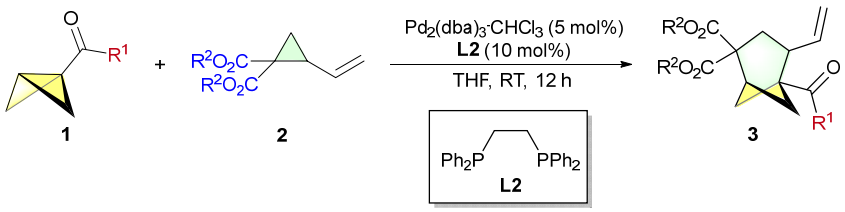


1a **5a** **6aa** **7aa** **5a'**

Entry	[Pd]	solvent	T (°C)	Yield of **6aa** [%][b], [c]	**6aa** *d.r.* [b]	Yield of **7aa** [%][b]	Yield of **5a'** [%][b]
1	$Pd_2(dba)_3$	THF	30	61	52:48	15	10
2	$Pd(PPh_3)_4$	THF	30	65	77:23	19	18
3	$Pd(OAc)_2$	THF	30	18	28:72	7	0
4	$Pd(dba)_2$	THF	30	52	54:46	15	12
5	$Pd(acac)_2$	THF	30	54	61:39	12	0
6	$[Pd(\eta^3\text{-allyl})Cl]_2$	THF	30	19	53:47	8	6
7	$Pd_2(dba)_3{\cdot}CHCl_3$	THF	30	55	60:40	13	19
8	$CpPd(\eta^3\text{-}C_3H_5)$	THF	30	79	71:29	14	0
9	$CpPd(\eta^3\text{-}C_3H_5)$	CH_2Cl_2	30	84	79:21	13	0
10	$CpPd(\eta^3\text{-}C_3H_5)$	toluene	30	58	59:41	17	0
11	$CpPd(\eta^3\text{-}C_3H_5)$	EtOAc	30	74	58:42	21	0
12	$CpPd(\eta^3\text{-}C_3H_5)$	MeCN	30	62	60:40	15	0
13	$CpPd(\eta^3\text{-}C_3H_5)$	1,4-dioxane	30	75	71:29	13	0
14	$CpPd(\eta^3\text{-}C_3H_5)$	PhCl	30	87	72:28	13	0
15	$CpPd(\eta^3\text{-}C_3H_5)$	DCE	30	59	71:29	13	10
16	$CpPd(\eta^3\text{-}C_3H_5)$	$CHCl_3$	30	0	0	0	65
17	$Pd(PPh_3)_4$	CH_2Cl_2	0	74	73:27	13	0
18	$Pd(PPh_3)_4$	CH_2Cl_2	40	73	75:25	14	0
19[d]	$CpPd(\eta^3\text{-}C_3H_5)$	CH_2Cl_2	30	75	77:23	16	0
20[d]	**$Pd(PPh_3)_4$**	**CH_2Cl_2**	**30**	**78**	**76:24**	**12**	**0**

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **5a** (x equiv), [Pd] (10 mol%) and **L4** (15 mol%), solvent (1 mL), T °C, under N_2 for 12 h. [b] Determined by ^1H NMR spectroscopic analysis of the crude reaction product using CH_2Br_2 as an internal standard. [c] Combined NMR yield of the diastereomers. [d] 0.2 mmol **1a** and 0.24 mmol **5a** were used.

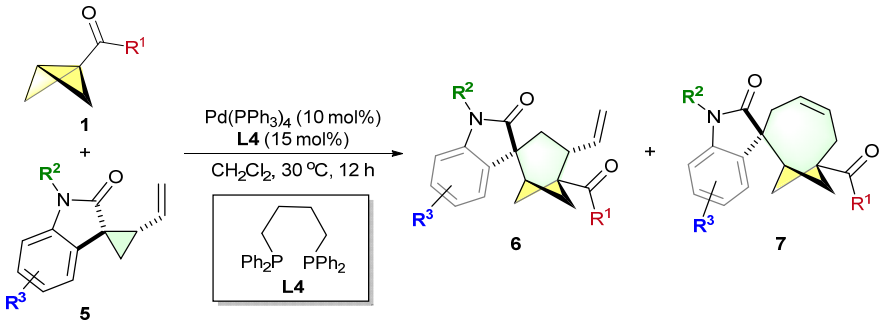
3 General Procedure for the (3+3) Cycloadditions of BCBs 1 and VCPs 2 (GP1)



Under a nitrogen atmosphere, a 25 mL oven-dried Schlenk tube was charged with BCBs **1** (0.20 mmol, 1.0 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$ (10.24 mg, 0.010 mmol, 5 mol%), **L2** (8.0 mg, 0.020 mmol, 10 mol%), VCPs **2** (0.24 mmol, 1.2 equiv) and THF (2.0 mL). The resulting mixture was stirred at 25 °C for 12 hours. After removing the solvent under reduced pressure, the residue was subjected to column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as the eluent, yielding the desired product **3**.

Note: *trace amounts of (5+3) cycloadducts were detected (< 5% NMR yield).*

4 General Procedure for the (3+3) Cycloadditions of BCBs 1 and SVCPs 5 (GP2)

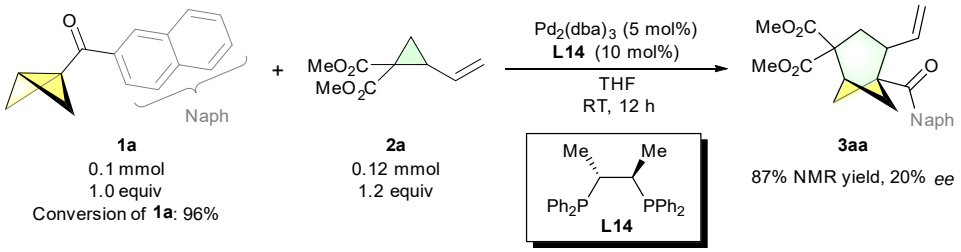


Under a nitrogen atmosphere, a 25 mL oven-dried Schlenk tube was charged with BCBs **1** (0.20 mmol, 1.0 equiv), SVCPs **5** (0.24 mmol, 2.4 equiv), $Pd(PPh_3)_4$ (23.11 mg, 0.020 mmol, 10 mol%), **L4** (12.79 mg, 0.030 mmol, 15 mol%) and CH_2Cl_2 (2.0 mL). The resulting mixture was stirred at room temperature (30 °C) for 12 hours. After removing the solvent under reduced pressure, the residue was subjected to column

chromatography purification using petroleum ether/EtOAc (15:1 to 10:1, v/v) as the eluent, yielding the desired product **6**.

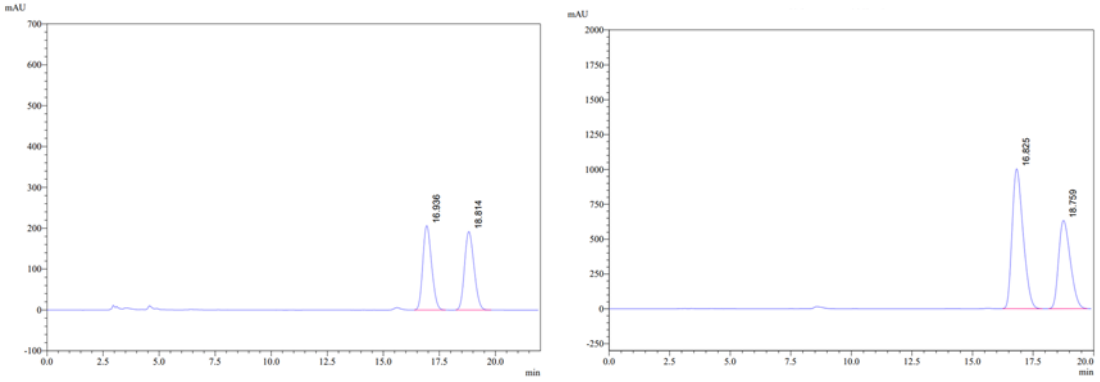
Note: *In most cases, the major diastereomer of compound **6** can be separated using chromatography. However, the minor diastereomer of compound **6** and the corresponding (5+3) cycloadduct **7** cannot be separated using chromatography.*

5 Procedure for the Catalytic Asymmetric (3+3) Cycloadditions of BCBs



Under a nitrogen atmosphere, a 25 mL oven-dried Schlenk tube was charged with BCB **1a** (20.83 mg, 0.10 mmol, 1.0 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$ (5.12 mg, 0.005 mmol, 5 mol%), **L14** (4.26 mg, 0.010 mmol, 10 mol%), VCP **2a** (22.10 mg, 0.12 mmol, 1.2 equiv) and THF (1.0 mL). The reaction mixture was stirred at 25 °C for 12 hours. Subsequently, the solvent was removed under reduced pressure, and the residue was dissolved in $CDCl_3$ (0.5 mL). The conversions of **1a** (96%) and the NMR yield of **3aa** (87%) were determined by ^1H NMR analysis using CH_2Br_2 as the internal standard.

ent-**3aa:** HPLC analysis (Chiralpak AD-H, ^{i}PrOH/hexane = 05/95, 1.0 mL/min, 254 nm; tr (major) = 16.83 min, tr (minor) = 18.76 min) gave the isomeric composition of the product: 20% *ee*.



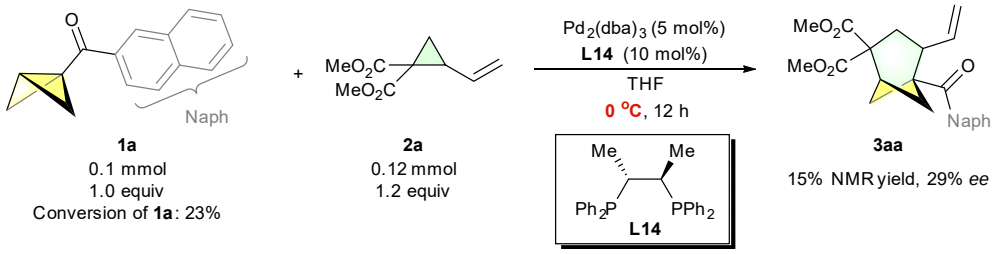
Detector A Channel 1 254nm

Peak#	Ret. Time [min]	Peak Start [min]	Height [mAU]	Area [mAU*min]	Area%
1	16.936	16.383	206042	5591474	49.761
2	18.814	18.233	191675	5645139	50.239
Total			397718	11236613	100.000

Detector A Channel 1 254nm

Peak#	Ret. Time [min]	Peak Start [min]	Height [mAU]	Area [mAU*min]	Area%
1	16.825	16.250	1002534	31608580	59.819
2	18.759	18.133	632782	21231470	40.181
Total			1635316	52840051	100.000

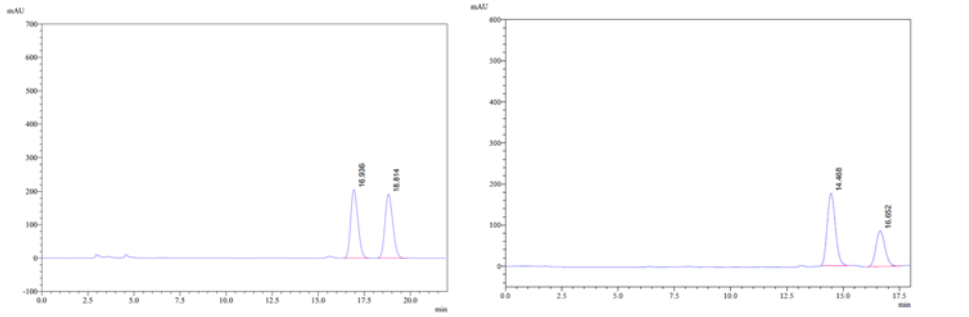
When the reaction was conducted at 0 °C, the desired product **3aa** was obtained with higher ee values (29% *ee*). However, the yield was unsatisfactory, with only a 15% NMR yield of **3aa** being observed.



1a
0.1 mmol
1.0 equiv
Conversion of **1a**: 23%

2a
0.12 mmol
1.2 equiv

3aa
15% NMR yield, 29% *ee*

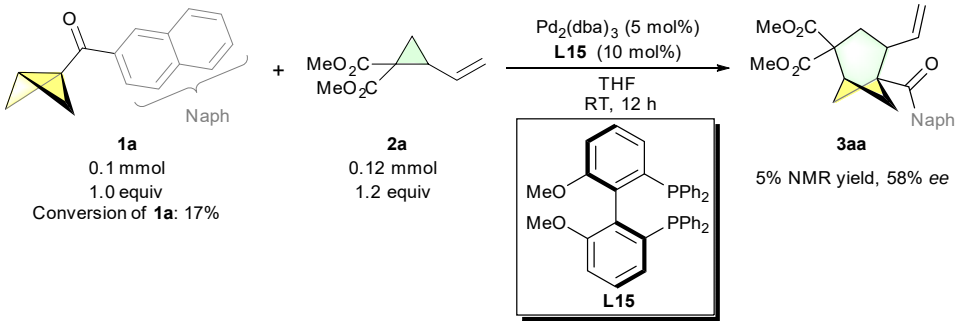


Detector A Channel 1 254nm

Peak#	Ret. Time [min]	Peak Start [min]	Height [mAU]	Area [mAU*min]	Area%
1	16.936	16.383	206042	5591474	49.761
2	18.814	18.233	191675	5645139	50.239
Total			397718	11236613	100.000

Detector A Channel 1 254nm

Peak#	Ret. Time [min]	Peak Start [min]	Height [mAU]	Area [mAU*min]	Area%
1	14.468	14.033	175840	4436251	64.738
2	16.652	16.092	86815	2416352	35.262
Total			262655	6852603	100.000



1a
0.1 mmol
1.0 equiv
Conversion of **1a**: 17%

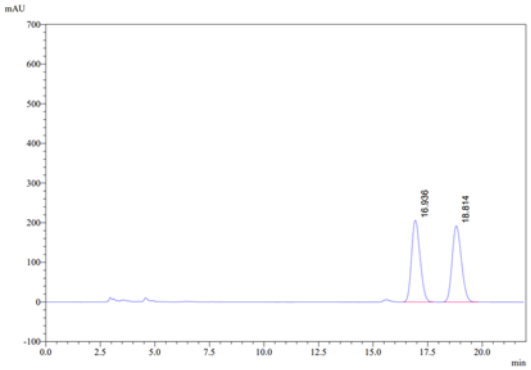
2a
0.12 mmol
1.2 equiv

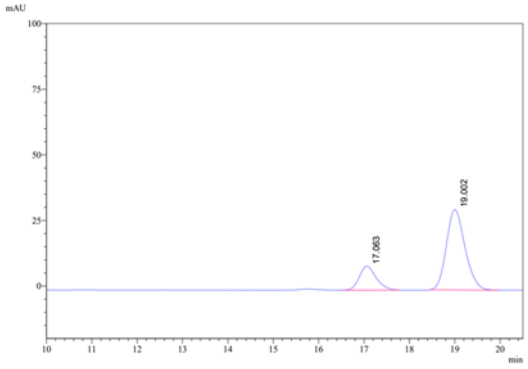
3aa
5% NMR yield, 58% *ee*

Under a nitrogen atmosphere, a 25 mL oven-dried Schlenk tube was charged with BCB **1a** (20.83 mg, 0.10 mmol, 1.0 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$ (5.12 mg, 0.005 mmol, 5 mol%), **L15** (5.83 mg, 0.010 mmol, 10 mol%), VCP **2a** (22.10 mg, 0.12 mmol, 1.2 equiv) and THF (1.0 mL). The reaction mixture was stirred at 25 °C for 12 hours. Subsequently, the solvent was removed under reduced pressure, and the residue was dissolved in

$CDCl_3$ (0.5 mL). The conversions of **1a** (17%) and the NMR yield of **3aa** (5%) were determined by ^1H NMR analysis using CH_2Br_2 as the internal standard.

ent-**3aa:** HPLC analysis (Chiralpak AD-H, ^{i}PrOH/hexane = 05/95, 1.0 mL/min, 254 nm; tr (minor) = 17.06 min, tr (major) = 19.00 min) gave the isomeric composition of the product: 58% *ee*.





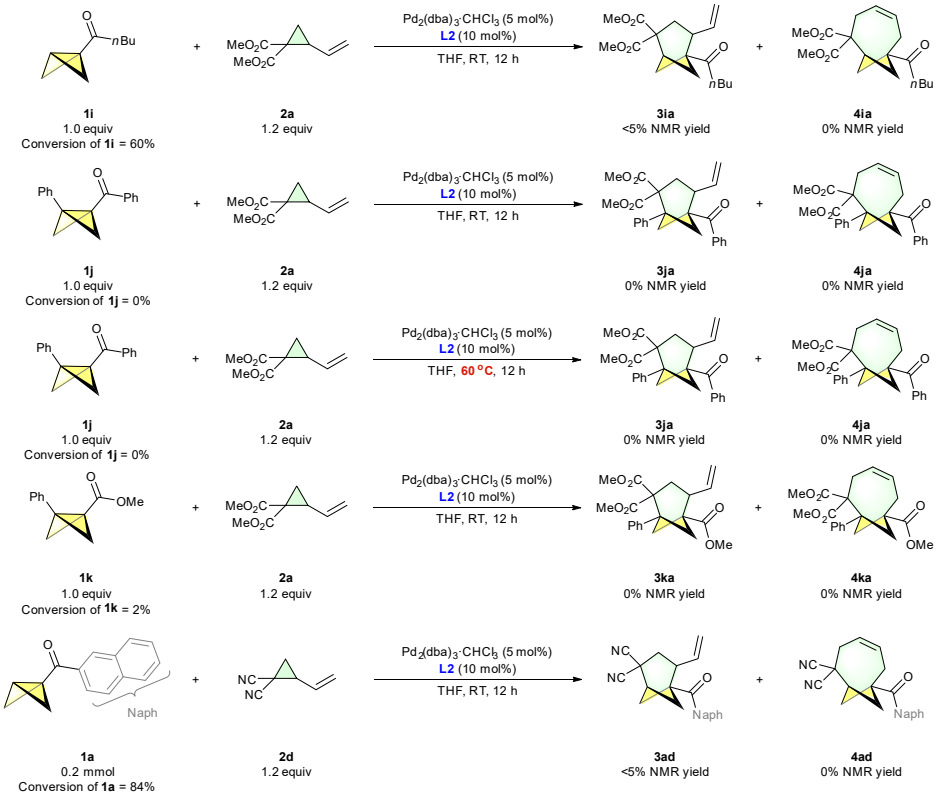
Detector A Channel 1 254nm

Peak#	Ret. Time [min]	Peak Start [min]	Height [mAU]	Area [mAU*min]	Area%
1	16.936	16.383	206042	5591474	49.761
2	18.814	18.233	191675	5645139	50.239
Total			397718	11236613	100.000

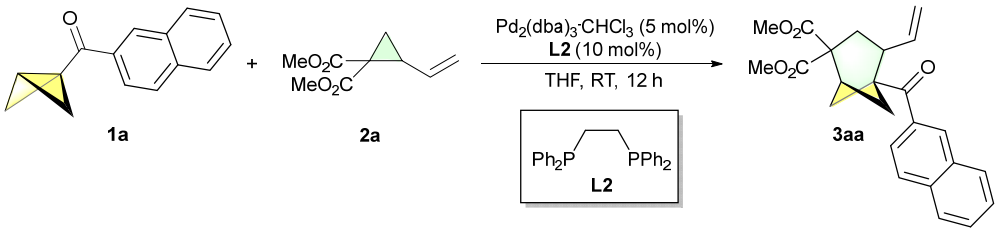
Detector A Channel 1 254nm

Peak#	Ret. Time [min]	Peak Start [min]	Height [mAU]	Area [mAU*min]	Area%
1	17.063	16.525	9070	233420	21.142
2	19.002	18.458	30604	870617	78.858
Total			39674	1104037	100.000

6 Unsuccessful Substrates

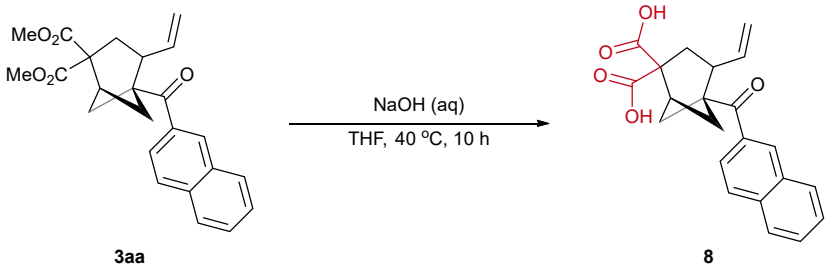


7 Scale-Up Experiment

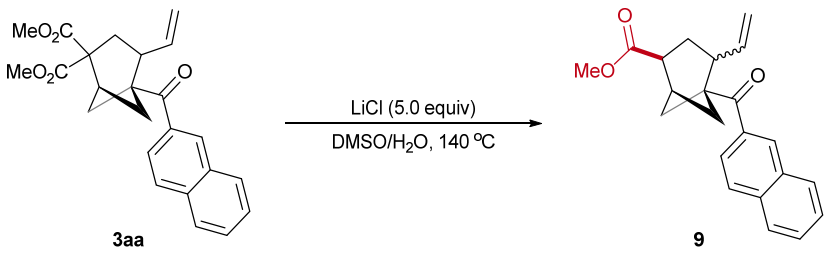


Under an atmosphere of N_2, to a 100 mL oven-dried Schlenk tube were added BCB **1a** (208.3 mg, 1.00 mmol, 1.0 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$ (51.1 mg, 0.05 mmol, 5 mol%), **L2** (39.8 mg, 0.1 mmol, 10 mol%), dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **2a** (221.0 mg, 1.2 mmol, 1.2 equiv) and THF (10.0 mL). Then the resulting mixture was stirred at room temperature (25 °C) for 12 h. After removal of the solvents under reduced pressure, the crude product was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford analytically pure product **3aa** as a viscous liquid (313.9 mg, 80% yield).

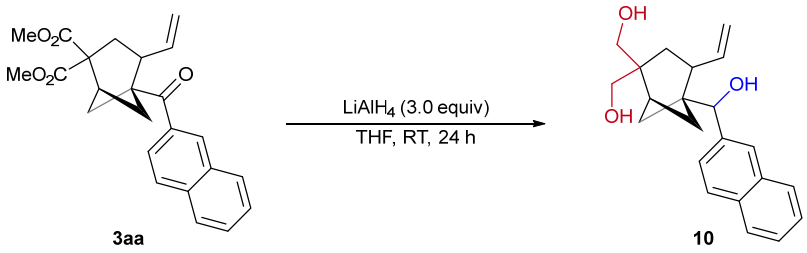
8 Synthetic Transformations



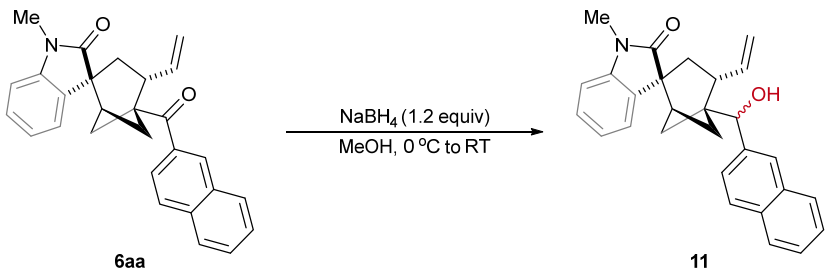
Synthesis of (8) [4a]**:** A solution of **3aa** (39.25 mg, 0.10 mmol) in THF (1.0 mL) was prepared, and then 3M aqueous NaOH (1.5 mL) was added. The mixture was heated at 140 °C for 7 hours. After cooling the mixture to room temperature, EtOAc was added to extract the reaction solution, and the organic phase was subsequently removed. The aqueous phase was acidified to pH 1.0 using 2 N HCl, followed by extraction with EtOAc. The combined organic phase was then dried over $MgSO_4$. After filtration and evaporation of the solvent, the desired product **8** was obtained as a white solid (24.4 mg, 76%).



Synthesis of (9) [4a]**:** A mixture of **3aa** (39.25 mg, 0.10 mmol) and LiCl (21.20 mg, 0.50 mmol) in a mixed solvent of DMSO/H_2O (v/v = 9:1, 2.0 mL) was heated at 140 °C for 7 h. The mixture was then cooled to room temperature, diluted with water, and extracted with EtOAc three times. The combined organic phase was then dried over $MgSO_4$. After filtration and evaporation of the solvent, the residue was subjected to column chromatography purification using petroleum ether/EtOAc (20:1 to 10:1, v/v) as the eluent, yielding the desired product **9** as a colorless oil (24.1 mg, 72% yield, 1:1 *d.r.*).

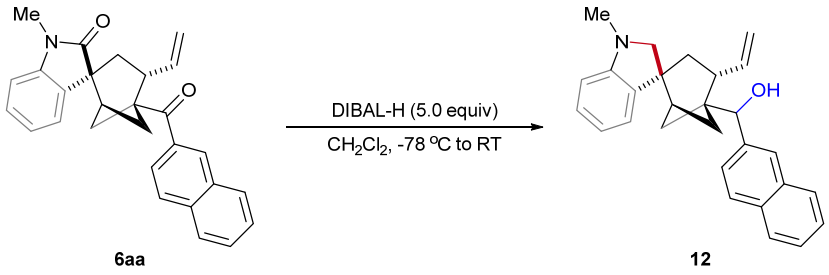


Synthesis of (10) [4b]**:** A solution of **3aa** (0.10 mmol, 39.25 mg, 1.0 equiv) in 2.0 mL of THF was prepared, to which lithium aluminum hydride (0.30 mmol, 11.39 mg, 3.0 equiv) was added in a single portion. The reaction mixture was stirred at room temperature until completion, as determined by TLC analysis. Subsequently, 1 N hydrochloric acid was added, and the mixture was extracted with ethyl acetate. The solution was then concentrated under reduced pressure and purified by silica gel chromatography (EtOAc/petroleum ether = 1/1), yielding the desired product **10** as a white solid (14.5 mg, 43% yield, >20:1 *d.r.*).



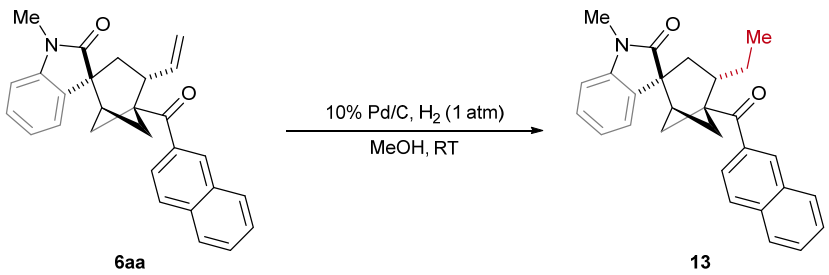
6aa **11**

Synthesis of (11) [4c]**:** To a solution of **6aa** (0.10 mmol, 40.75 mg, 1.0 equiv, >20:1 *d.r.*) in the MeOH (2.0 mL) was added $NaBH_4$ (4.5 mg, 0.12 mmol, 1.2 equiv) at 0 °C. The mixture was slowly warmed to room temperature and stirred overnight. Then aqueous saturated NH_4Cl solution (5 mL) was added to quench the reaction. The aqueous phase was extracted with EtOAc. The combined organic phases were washed by brine and dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 5/1) to afford **11** as a white solid (34.8 mg, 85% yield, 85:15 *d.r.*).

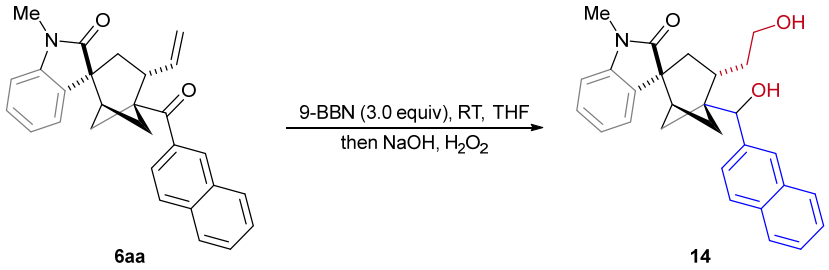


6aa **12**

Synthesis of (12) [4d]**:** A solution of **6aa** (40.75 mg, 0.10 mmol, >20:1 *d.r.*) in CH_2Cl_2 (2 mL) was cooled to -78 °C. Then, DIBAL-H (1.5 M in toluene) (0.34 mL, 0.50 mmol, 5.0 equiv) was added dropwise to the reaction mixture at -78 °C. Then the reaction vessel was taken out of the cooling bath and left to reach room temperature. It was then stirred overnight. Then the reaction was cooled back down to 0 °C and quenched by dropwise addition of Rochell's salt and the reaction was stirred until the mixture became two distinct layers. The layers were then separated and the aqueous layer was extracted with EtOAc (2×5 mL), washed with brine, dried over Na_2SO_4, filtered and concentrated on rotavapor under reduced pressure. The residue was purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afforded **12** as a colorless oil (33.1 mg, 84%, >20:1 *d.r.*).

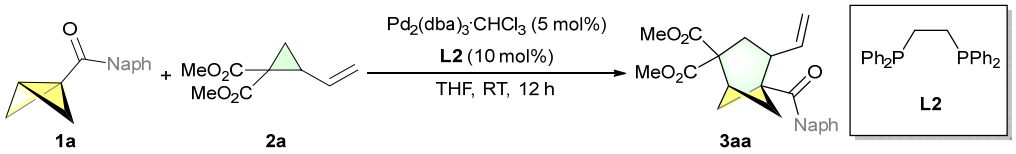


Synthesis of (13) [4e]**:** To a solution of **6aa** (0.10 mmol, 40.75 mg, 1.0 equiv, >20:1 *d.r.*) in MeOH (2.0 mL) was added Pd/C (10 wt%) (4.2 mg). This flask was in a vacuum and back-filled with H_2 (1 atm). After being stirred at room temperature overnight, the reaction solution was filtered, and the filtered-cake was washed with EtOAc (5.0 mL). The filtrate was evaporated under *vacuo*, and purified by silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford **13** as a white solid (34.8 mg, 85% yield, >20:1 *d.r.*).



Synthesis of (14) [4a]**:** A solution of **6aa** (0.10 mmol, 40.75 mg, 1.0 equiv, >20:1 *d.r.*) in dry THF (2.0 mL) was treated with 9-BBN (0.5 M in THF, 0.6 mL) added dropwise at room temperature. The mixture was stirred at 25 °C for 2 hours. Subsequently, water (0.3 mL), 30% aqueous NaOH (3 M, 1.5 mL), and 30% aqueous H_2O_2 (1.5 mL) were added dropwise. After stirring at 40 °C for 2 hours, the mixture was extracted three times with EtOAc (3 × 15 mL). The organic layer was combined and dried over anhydrous Na_2SO_4. After removing all solvents under reduced pressure, the residue was purified by column chromatography using a petroleum ether/EtOAc (5:1) solvent system, yielding compound **14** as a white solid (16.9 mg, 40% yield, >20:1 *d.r.*).

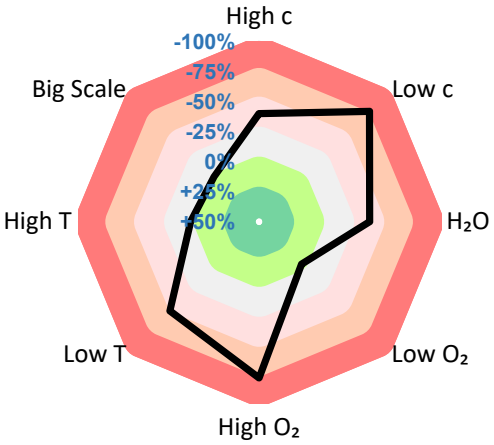
9 Sensitivity Assessment [5]



Standard conditions: Under an atmosphere of N_2, to a 25 mL oven-dried Schlenk tube were added BCB **1a** (0.10 mmol, 20.8 mg, 1.0 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$ (5.12 mg, 0.005 mmol, 5 mol%), **L2** (3.98 mg, 0.01 mmol, 10 mol%), dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **2a** (22.1 mg, 0.12 mmol, 1.2 equiv) and THF (1.0 mL). Then the resulting mixture was stirred at room temperature for 12 h. After the solvent was removed under reduced pressure, CH_2Br_2 (0.10 mmol, 17.4 mg) was added as an internal standard, and the yield was determined by ^1H NMR analysis of the crude mixture.

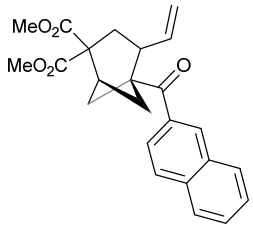
Table S6. Sensitivity assessment

Entry	Description	Deviation from standard condition	Yield	Deviation
1	High *c*	THF (0.5 mL)	46%	-40%
2	Low *c*	THF (2 mL)	6%	-80%
3	H_2O	+5 μL H_2O	44%	-42%
4	Low O_2	degassed solvent	86%	0%
5	High O_2	+5 mL air	6%	-80%
6	Low *T*	at 0°C	31%	-55%
7	High *T*	at 40 °C	79%	-7%
8	Big Scale	1.0 mmol scale	83%	-3%
9	control	-	86%	-



Comment: we conducted condition-based sensitivity screening, revealing that the amplification effect had no significant impact on the reaction. However, this reaction exhibited certain sensitivity to O_2 level, concentration, moisture, and temperature.

10 Characterization Data of the Products

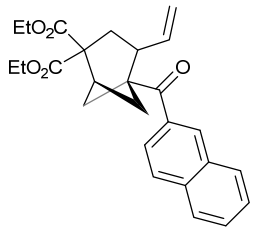


3aa
$C_{24}H_{24}O_5$
M = 392.45 g/mol

dimethyl 5-(2-naphthoyl)-4-vinylbicyclo[3.1.1]heptane-2,2-dicarboxylate (**3aa**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2a**, 44.2 mg, 0.24 mmol) according to the **GP1** at 25 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (15/1) afforded **3aa** as a colorless oil (64.3 mg, 82% yield).

3aa: $\mathbf{R_f}$ = 0.25 (petroleum ether/EtOAc = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.88-7.83 (m, 3H), 7.60-7.51 (m, 2H), 5.68-5.59 (m, 1H), 4.75 (d, *J* = 10.0 Hz, 1H), 4.70 (d, *J* = 16.8 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.33-3.27 (m, 1H), 2.94 (t, *J* = 8.0 Hz, 1H), 2.78-2.72 (m, 1H), 2.57 (t, *J* = 7.2 Hz, 1H), 2.48-

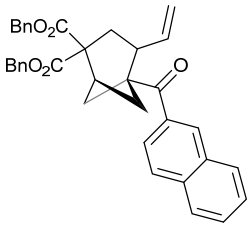
2.45 (m, 1H), 2.17 (t, *J* = 8.4 Hz, 1H), 2.05-1.96 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.5, 171.9, 137.6, 135.3, 133.2, 132.3, 129.9, 129.6, 128.3, 128.2, 127.7, 126.6, 124.5, 116.3, 57.2, 55.3, 52.7, 52.6, 45.0, 38.2, 34.6, 30.4, 28.8 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{24}H_{25}O_5$: 393.1697; found: 393.1694.



3ab
$C_{26}H_{28}O_5$
M = 420.51 g/mol

diethyl 5-(2-naphthoyl)-4-vinylbicyclo[3.1.1]heptane-2,2-dicarboxylate (**3ab**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2b,** 50.9 mg, 0.24 mmol) according to the **GP1** at 25 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (15/1) afforded **3ab** as a colorless oil (44.3 mg, 53% yield).

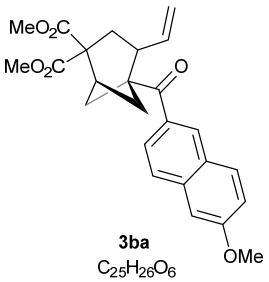
3ab: **R_f** = 0.30 (petroleum ether/EtOAc = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.88-7.83 (m, 3H), 7.60-7.52 (m, 2H), 5.68-5.59 (m, 1H), 4.75 (d, *J* = 10.0 Hz, 1H), 4.69 (d, *J* = 17.2 Hz, 1H), 4.35-4.16 (m, 4H), 3.34-3.28 (m, 1H), 2.93 (t, *J* = 6.4 Hz, 1H), 2.73 (dd, *J* = 14.8 Hz, 7.6 Hz, 1H), 2.57 (dd, *J* = 10.0 Hz, 7.2 Hz, 1H), 2.46 (dd, *J* = 10.8 Hz, 6.4 Hz, 1H), 2.19-2.14 (m, 1H), 2.03-2.00 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.7, 171.5, 137.7, 135.3, 133.2, 132.4, 130.0, 129.6, 128.33, 128.26, 127.7, 126.6, 124.6, 116.3, 61.5, 61.4, 57.1, 55.4, 45.1, 38.1, 34.5, 30.3, 28.8, 14.1, 14.0 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{26}H_{29}O_5$: 421.2010; found: 421.2009.



3ac
$C_{36}H_{32}O_5$
M = 544.65 g/mol

dibenzyl 5-(2-naphthoyl)-4-vinylbicyclo[3.1.1]heptane-2,2-dicarboxylate (**3ac**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and dibenzyl 2-vinylcyclopropane-1,1-dicarboxylate (**2c,** 80.7 mg, 0.24 mmol) according to the **GP1** at 25 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (15/1) afforded **3ac** as a colorless oil (39.0 mg, 36% yield).

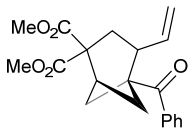
3ac: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.86-7.82 (m, 3H), 7.60-7.51 (m, 2H), 7.31-7.25 (m, 10H), 5.65-5.56 (m, 1H), 5.20 (dd, *J* = 20.4 Hz, 12.4 Hz, 2H), 5.14 (s, 2H), 4.73 (d, *J* = 10.0 Hz, 1H), 4.66 (d, *J* = 16.8 Hz, 1H), 3.31-3.25 (m, 1H), 2.98 (t, *J* = 6.0 Hz, 1H), 2.76 (dd, *J* = 14.8 Hz, 7.2 Hz, 1H), 2.53-2.49 (m, 1H), 2.46-2.42 (m, 1H), 2.15 (t, *J* = 9.2 Hz, 1H), 2.02 (dd, *J* = 14.4 Hz, 8.4 Hz, 1H), 1.92 (t, *J* = 9.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.5, 171.1, 171.0, 137.5, 135.4, 135.32, 135.27, 133.1, 132.3, 130.0, 129.6, 128.5, 128.34, 128.28, 128.26, 128.1, 127.9, 127.7, 126.6, 124.5, 116.4, 67.2, 67.1, 57.3, 55.3, 45.0, 38.0, 34.6, 30.3, 28.7 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{36}H_{33}O_5$: 545.2323; found: 545.2322.



3ba
$C_{25}H_{26}O_6$
M = 422.48 g/mol

dimethyl 5-(6-methoxy-2-naphthoyl)-4-vinylbicyclo[3.1.1]heptane-2,2-dicarboxylate (**3ba**): Prepared from bicyclo[1.1.0]butan-1-yl(6-methoxynaphthalen-2-yl)methanone (**1b**, 47.7 mg, 0.20 mmol) and dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2a**, 44.2 mg, 0.24 mmol) according to the **GP1** at 25 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (15/1) afforded **3ba** as a colorless oil (54.5 mg, 64% yield).

3ba: $\mathbf{R_f}$ = 0.20 (petroleum ether/EtOAc = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.84-7.82 (m, 2H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.20-7.17 (m, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 5.67-5.58 (m, 1H), 4.75 (d, *J* = 10.4 Hz, 1H), 4.70 (d, *J* = 17.2 Hz, 1H), 3.94 (s, 3H), 3.81 (s, 3H), 3.76 (s, 3H), 3.32-3.25 (m, 1H), 2.92 (t, *J* = 6.4 Hz, 1H), 2.74 (dd, *J* = 14.8 Hz, 7.6 Hz, 1H), 2.56 (dd, *J* = 10.0 Hz, 6.8 Hz, 1H), 2.45 (dd, *J* = 10.8 Hz, 6.0 Hz, 1H), 2.18-2.13 (m, 1H), 2.04-1.93 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.3, 171.9, 171.9, 159.7, 137.6, 137.0, 131.20, 131.18, 129.9, 127.7, 126.9, 125.3, 119.6, 116.3, 105.7, 57.2, 55.4, 55.3, 52.72, 52.67, 45.1, 38.2, 34.6, 30.4, 28.8 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{25}H_{27}O_6$: 423.1808; found: 423.1801.

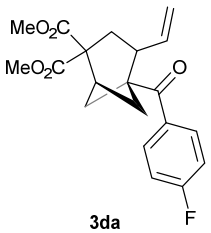


3ca
$C_{20}H_{22}O_5$
M = 342.39 g/mol

dimethyl 5-benzoyl-4-vinylbicyclo[3.1.1]heptane-2,2-dicarboxylate (**3ca**): Prepared from bicyclo[1.1.0]butan-1-yl(phenyl)methanone (**1c**, 31.6 mg, 0.20 mmol) and dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2a**, 44.2 mg, 0.24 mmol) according to the **GP1** at 25 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (15/1) afforded **3ca** as a colorless oil (38.4 mg, 56% yield).

3ca: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.42-7.38 (m, 2H), 5.62-5.53 (m, 1H), 4.77 (d, *J* = 10.0 Hz, 1H), 4.70 (d, *J* = 17.2 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.23-3.17 (m, 1H), 2.90 (t, *J* = 6.8 Hz, 1H), 2.70 (dd, *J* = 15.2 Hz, 7.6 Hz, 1H), 2.51-2.46 (m, 1H),

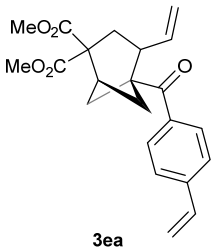
2.43-2.38 (m, 1H), 2.11-2.07 (m, 1H), 1.97 (dd, *J* = 14.8 Hz, 8.8 Hz, 1H), 1.86 (t, *J* = 8.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.5, 171.9, 171.8, 137.5, 135.9, 132.6, 128.6, 128.4, 116.3, 57.2, 55.2, 52.7, 52.6, 44.8, 38.1, 34.5, 30.4, 28.5 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{23}O_5$: 343.1540; found: 343.1539.



3da
$C_{20}H_{21}FO_5$
M = 360.38 g/mol

dimethyl 5-(4-fluorobenzoyl)-4-vinylbicyclo[3.1.1]heptane-2,2-dicarboxylate (**3da**): Prepared from bicyclo[1.1.0]butan-1-yl(4-fluorophenyl)methanone (**1d**, 35.2 mg, 0.20 mmol) and dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2a**, 44.2 mg, 0.24 mmol) according to the **GP1** at 25 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (15/1) afforded **3da** as a colorless oil (49.7 mg, 69% yield).

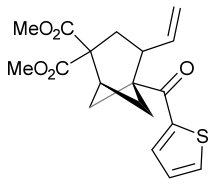
3da: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82-7.79 (m, 2H), 7.08 (t, *J* = 8.4 Hz, 2H), 5.61-5.52 (m, 1H), 4.78 (d, *J* = 10.0 Hz, 1H), 4.71 (d, *J* = 16.8 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.19-3.13 (m, 1H), 2.90 (t, *J* = 6.0 Hz, 1H), 2.70 (dd, *J* = 14.8 Hz, 7.2 Hz, 1H), 2.50-2.46 (m, 1H), 2.39 (dd, *J* = 10.8 Hz, 6.0 Hz, 1H), 2.12-2.07 (m, 1H), 1.96 (dd, *J* = 14.8 Hz, 8.8 Hz, 1H), 1.84 (t, *J* = 8.4 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.9, 171.8, 171.7, 165.3 (d, *J* = 253.0 Hz), 137.4, 132.2 (d, *J* = 2.9 Hz), 131.2 (d, *J* = 9.1 Hz), 116.3, 115.5 (d, *J* = 21.7 Hz), 57.1, 55.1, 52.6, 44.9, 38.0, 34.5, 30.4, 28.6 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.53 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{20}H_{22}FO_5$: 361.1446; found: 361.1443.



3ea
$C_{22}H_{24}O_5$
M = 368.43 g/mol

dimethyl 4-vinyl-5-(4-vinylbenzoyl)bicyclo[3.1.1]heptane-2,2-dicarboxylate (**3ea**): Prepared from bicyclo[1.1.0]butan-1-yl(4-vinylphenyl)methanone (**1e**, 36.8 mg, 0.20 mmol) and dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2a**, 44.2 mg, 0.24 mmol) according to the **GP1** at 25 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ea** as a colorless oil (32.6 mg, 44% yield).

3ea: $\mathbf{R_f}$ = 0.25 (petroleum ether/EtOAc = 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76-7.73 (m, 2H), 7.44- 7.42 (m, 2H), 6.73 (dd, *J* = 17.6 Hz, 10.8 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.62- 5.53 (m, 1H), 5.38 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 9.6 Hz, 1H), 4.72 (d, *J* = 17.2 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.23-3.17 (m, 1H), 2.89 (t, *J* = 6.4 Hz, 1H), 2.70 (dd, *J* = 14.4 Hz, 7.2 Hz, 1H), 2.48 (dd, *J* = 10.0 Hz, 6.8 Hz, 1H), 2.39 (dd, *J* = 10.8 Hz, 6.0 Hz, 1H), 2.09 (dd, *J* = 10.8 Hz, 8.0 Hz, 1H), 1.95 (dd, *J* = 14.8 Hz, 8.8 Hz, 1H), 1.85 (dd, *J* = 9.6 Hz, 8.0 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.0, 171.9, 171.8, 141.7, 137.5, 135.9, 134.9, 129.0, 126.2, 116.6, 116.4, 57.2, 55.2, 52.74, 52.71, 44.9, 38.1, 34.5, 30.5, 28.6 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{25}O_5$: 369.1702; found: 369.1708.

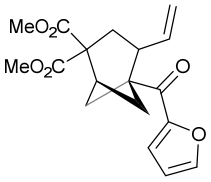


3fa
$C_{18}H_{20}O_5S$
M = 348.41 g/mol

dimethyl 5-(thiophene-2-carbonyl)-4-vinylbicyclo[3.1.1]heptane-2,2-dicarboxylate (**3fa**): Prepared from bicyclo[1.1.0]butan-1-yl(thiophen-2-yl)methanone (**1f**, 29.6 mg,

0.20 mmol) and dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2a**, 44.2 mg, 0.24 mmol) according to the **GP1** at 25 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (15/1) afforded **3fa** as a colorless oil (53.8 mg, 77% yield).

3fa: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 15/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.60 (d, *J* = 4.8 Hz, 1H), 7.58 (d, *J* = 4.2 Hz, 1H), 7.09 (t, *J* = 4.2 Hz, 1H), 5.63-5.57 (m, 1H), 4.83 (d, *J* = 9.0 Hz, 1H), 4.81 (d, *J* = 16.8 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.20-3.16 (m, 1H), 2.90 (t, *J* = 6.6 Hz, 1H), 2.71 (dd, *J* = 15.0 Hz, 7.8 Hz, 1H), 2.46 (dd, *J* = 10.2 Hz, 6.6 Hz, 1H), 2.38 (dd, *J* = 10.8 Hz, 6.0 Hz, 1H), 2.09 (dd, *J* = 10.8 Hz, 7.8 Hz, 1H), 1.95 (dd, *J* = 15.0 Hz, 9.0 Hz, 1H), 1.81-1.78 (m, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 195.4, 171.8, 171.6, 142.2, 137.4, 133.1, 131.7, 127.9, 116.4, 57.0, 54.9, 52.68, 52.66, 45.2, 37.6, 34.5, 30.4, 28.2 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{21}O_5S$: 349.1104; found: 349.1105.

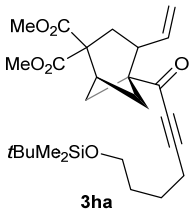


3ga
$C_{18}H_{20}O_6$
M = 332.35 g/mol

dimethyl 5-(furan-2-carbonyl)-4-vinylbicyclo[3.1.1]heptane-2,2-dicarboxylate (**3ga**): Prepared from bicyclo[1.1.0]butan-1-yl(furan-2-yl)methanone (**1g**, 29.6 mg, 0.20 mmol) and dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2a**, 44.2 mg, 0.24 mmol) according to the **GP1** at 25 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (15/1) afforded **3ga** as a colorless oil (52.5 mg, 79% yield).

3ga: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 15/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.09 (d, *J* = 3.6 Hz, 1H), 6.50-6.49 (m, 1H), 5.61-5.55 (m, 1H), 4.82-4.79 (m, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.28-3.23 (m, 1H), 2.89 (t, *J* = 6.6 Hz, 1H), 2.70 (dd, *J* = 15.0 Hz, 7.8 Hz, 1H), 2.36-2.33 (m, 2H), 2.08-2.04 (m, 1H), 1.93-1.89 (m, 1H), 1.80-1.77

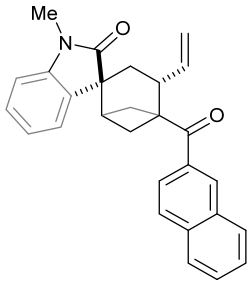
(m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.3, 171.8, 171.6, 151.9, 145.8, 137.7, 117.3, 116.1, 111.9, 57.0, 53.9, 52.6, 44.2, 37.0, 34.5, 30.4, 27.3 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{21}O_6$: 333.1333; found: 333.1335.



3ha
$C_{26}H_{40}O_6Si$
M = 476.69 g/mol

dimethyl 5-(7-((tert-butyldimethylsilyl)oxy)hept-2-ynoyl)-4-vinylbicyclo[3.1.1]heptane-2,2-dicarboxylate (**3ha**): Prepared from 1-(bicyclo[1.1.0]butan-1-yl)-8-((*tert*-butyldimethylsilyl)oxy)oct-3-yn-1-one (**1h**, 58.5 mg, 0.20 mmol) and dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2a**, 44.2 mg, 0.24 mmol) according to the **GP1** at 25 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (15/1) afforded **3ha** as a colorless oil (71.4 mg, 75% yield).

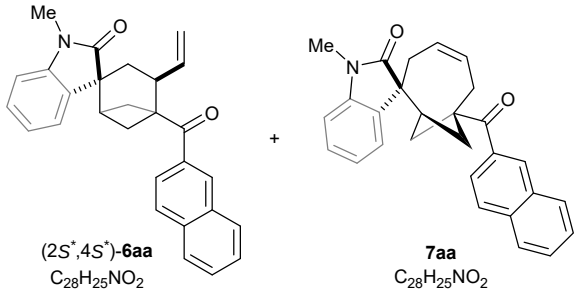
3ha: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.67-5.58 (m, 1H), 5.10 (d, *J* = 16.8 Hz, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.64-3.61 (m, 2H), 3.12-3.06 (m, 1H), 2.84-2.81 (m, 1H), 2.65 (dd, *J* = 14.8 Hz, 7.6 Hz, 1H), 2.41-2.38 (m, 2H), 2.30-2.26 (m, 1H), 2.19-2.15 (m, 1H), 1.91 (dd, *J* = 14.8 Hz, 8.0 Hz, 1H), 1.82-1.77 (m, 1H), 1.67-1.61 (m, 4H), 1.54 (t, *J* = 9.2 Hz, 1H), 0.89 (s, 9H), 0.05 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.7, 171.8, 171.5, 137.6, 116.6, 97.0, 78.8, 62.2, 57.0, 55.7, 52.6, 42.8, 35.9, 33.7, 31.7, 30.0, 26.3, 25.9, 24.4, 18.8, 18.2, -5.4 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{26}H_{41}O_6Si$: 477.2672; found: 477.2669.



6aa
$C_{28}H_{25}NO_2$
M = 407.51 g/mol

Racemic (2*S,4*R**)-5-(2-naphthoyl)-1'-methyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6aa**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-1'-methyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5a**, 47.8 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6aa** as a white solid (46.5 mg, 57% yield). **Note:** A mixture of (2*S**,4*S**)-**6aa** (the minor diastereomer) and the (5+3) cycloadduct **7aa** was also obtained, which could not be separated using flash chromatography on silica gel (18.7 mg, 23% combined isolated yield).

(2*S**,4*R**)-**6aa**: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.03-7.98 (m, 2H), 7.89-7.85 (m, 2H), 7.61-7.53 (m, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 5.79-5.70 (m, 1H), 4.78 (d, *J* = 10.0 Hz, 1H), 4.68 (d, *J* = 17.2 Hz, 1H), 3.69-3.63 (m, 1H), 3.55 (t, *J* = 8.8 Hz, 1H), 3.24 (s, 3H), 2.59-2.49 (m, 2H), 2.43 (dd, *J* = 9.2 Hz, 6.8 Hz, 1H), 2.32 (dd, *J* = 15.2 Hz, 8.0 Hz, 1H), 2.19 (t, *J* = 6.0 Hz, 1H), 2.09 (dd, *J* = 14.8 Hz, 8.4 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 203.2, 180.8, 142.6, 138.2, 135.4, 135.1, 133.2, 132.5, 130.2, 129.7, 128.3, 128.1, 127.7, 126.6, 124.7, 122.6, 122.5, 116.1, 108.1, 55.6, 49.2, 44.4, 38.6, 35.4, 31.9, 29.0, 26.2 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{26}NO_2$: 408.1958; found: 408.1961.



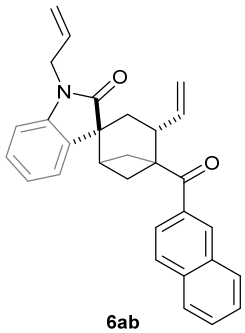
(2*S**,4*S**)-**6aa**
$C_{28}H_{25}NO_2$
M = 407.51 g/mol

7aa
$C_{28}H_{25}NO_2$
M = 407.51 g/mol

(2*S**,4*S**)-**6aa: R*f*** = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.39 (s, 1H), 8.00-7.85 (m, 4H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.60-7.54 (m, 2H), 7.33-7.29 (m, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.86 (t, *J* = 7.8 Hz, 1H), 5.99-5.93 (m, 1H), 4.79 (d, *J* = 5.4 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 3.45-3.41 (m, 1H), 3.21 (s, 3H), 3.13-3.10 (m, 1H), 3.07-2.96 (m, 2H), 2.71-2.68 (m, 1H), 2.48-2.45 (m, 1H), 2.44-2.36 (m, 1H), 2.17-2.09 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{26}NO_2$: 408.1958; found: 408.1960.

7aa: R*f* = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.00-7.85 (m, 3H), 7.60-7.54 (m, 3H), 7.33-7.29 (m, 1H), 7.25 (s, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.86 (t, *J* = 7.8 Hz, 1H), 6.33 (dt, *J* = 9.6 Hz, 9.0 Hz, 1H), 6.17 (dt, *J* = 9.0 Hz, 8.4 Hz, 1H), 3.36-3.33 (m, 1H), 3.19 (s, 3H), 2.90-2.82 (m, 2H), 2.71-2.68 (m, 1H), 2.48-2.45 (m, 1H), 2.44-2.36 (m, 2H), 2.17-2.09 (m, 2H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{26}NO_2$: 408.1958; found: 408.1962.

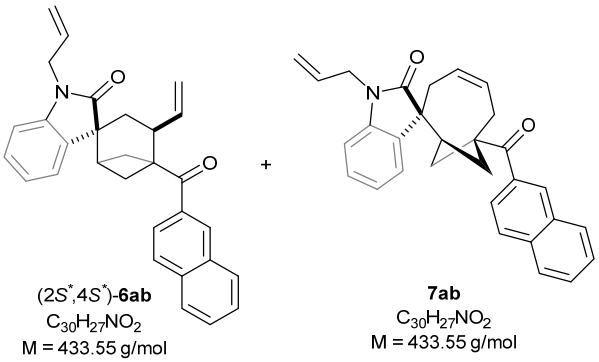
^{13}C NMR (150 MHz, $CDCl_3$): δ 203.7 (for (2*S**,4*S**)-**6aa**), 203.0 (for **7aa**), 180.4 (for (2*S**,4*S**)-**6aa**), 179.4 (for **7aa**), 143.0, 142.5, 138.7, 135.24, 135.17, 134.6, 133.6, 133.3, 132.4, 132.3, 131.5, 131.4, 130.8, 130.6, 130.2, 129.6, 128.33, 128.27, 128.2, 128.0, 127.9, 127.64, 127.62, 126.60, 126.57, 124.9, 124.7, 123.90, 123.86, 122.2, 122.1, 116.0, 108.10, 108.08, 55.4, 50.3, 49.7, 48.9, 45.7, 38.5, 37.5, 36.4, 35.1, 34.6, 31.0, 30.7, 30.5, 28.5, 26.2, 26.0 ppm.



6ab
$C_{30}H_{27}NO_2$
M = 433.55 g/mol

Racemic (2*S,4*R**)-5-(2-naphthoyl)-1'-allyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6ab**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-1'-allyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5b**, 54.1 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6ab** as a white solid (36.1 mg, 42% yield). **Note:** A mixture of (2*S**,4*S**)-**6ab** (the minor diastereomer) and the (5+3) cycloadduct **7ab** was also obtained, which could not be separated using flash chromatography on silica gel (16.1 mg, 19% combined isolated yield).

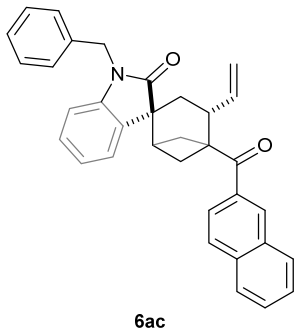
(2*S**,4*R**)-**6ab**: $\mathbf{R_f}$ = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.01-7.98 (m, 2H), 7.88-7.85 (m, 2H), 7.60-7.52 (m, 2H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.92-5.83 (m, 1H), 5.79-5.70 (m, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 5.22 (d, *J* = 16.8 Hz, 1H), 4.78 (d, *J* = 10.0 Hz, 1H), 4.68 (d, *J* = 16.8 Hz, 1H), 4.44 (d, *J* = 16.4 Hz, 1H), 4.31 (d, *J* = 16.4 Hz, 1H), 3.70-3.55 (m, 1H), 3.57 (t, *J* = 8.0 Hz, 1H), 2.61-2.51 (m, 2H), 2.46-2.42 (m, 1H), 2.33 (dd, *J* = 14.8 Hz, 7.6 Hz, 1H), 2.23-2.21 (m, 1H), 2.11 (dd, *J* = 14.8 Hz, 8.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.0, 180.5, 141.8, 138.2, 135.4, 135.1, 133.2, 132.5, 131.4, 130.2, 129.7, 128.3, 128.0, 127.7, 126.6, 124.7, 122.6, 117.3, 116.1, 108.9, 55.7, 49.2, 44.4, 42.1, 38.7, 35.5, 32.2, 29.0 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{30}H_{28}NO_2$: 434.2115; found: 434.2113.



(2*S**,4*S**)-**6ab: R_f** = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.00-7.93 (m, 2H), 7.90-7.86 (m, 2H), 7.65-7.55 (m, 3H), 7.31-7.25 (m, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.88-6.85 (m, 1H), 6.00-5.93 (m, 1H), 5.90-5.79 (m, 1H), 5.23-5.19 (m, 2H), 4.80-4.75 (m, 2H), 4.49-4.44 (m, 1H), 4.38-4.22 (m, 1H), 3.46-3.40 (m, 1H), 3.14-3.06 (m, 2H), 2.73-2.67 (m, 1H), 2.51-2.37 (m, 2H), 2.22-2.10 (m, 2H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{30}H_{28}NO_2$: 434.2115; found: 434.2114.

7ab: R_f = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.00-7.93 (m, 1H), 7.90-7.86 (m, 2H), 7.65-7.55 (m, 2H), 7.39-7.37 (m, 1H), 7.31-7.25 (m, 2H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.88-6.85 (m, 1H), 6.34 (dt, *J* = 9.6 Hz, 9.2 Hz, 1H), 6.18 (dt, *J* = 9.2 Hz, 8.4 Hz, 1H), 5.90-5.79 (m, 1H), 5.23-5.19 (m, 2H), 4.38-4.22 (m, 2H), 3.34 (d, *J* = 13.6 Hz, 1H), 3.02-2.98 (m, 1H), 2.92-2.82 (m, 2H), 2.73-2.67 (m, 1H), 2.51-2.37 (m, 3H), 2.22-2.10 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{30}H_{28}NO_2$: 434.2115; found: 434.2112.

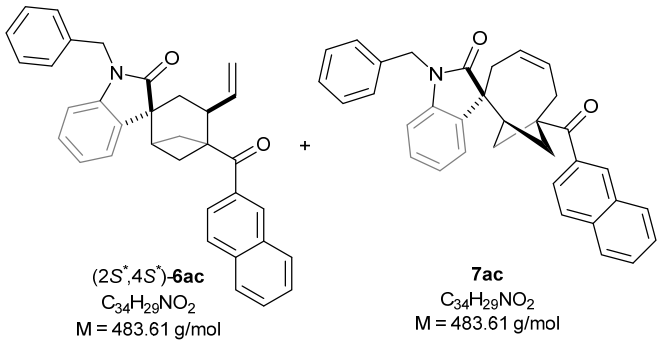
^{13}C NMR (100 MHz, $CDCl_3$): δ 203.7 (for (2*S**,4*S**)-**6ab**), 203.1 (for **7ab**), 180.2 (for (2*S**,4*S**)-**6ab**), 179.3 (for **7ab**), 142.3, 141.8, 138.8, 135.4, 135.3, 134.7, 133.8, 133.4, 132.5, 132.4, 131.7, 131.5, 131.4, 130.9, 130.3, 129.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 126.7, 126.6, 125.1, 124.8, 124.12, 124.05, 122.3, 122.1, 117.4, 116.1, 109.1, 55.5, 50.5, 49.8, 48.9, 45.8, 42.3, 41.9, 38.9, 37.6, 36.7, 35.2, 34.8, 31.2, 30.8, 28.7 ppm.



6ac
$C_{34}H_{29}NO_2$
M = 483.61 g/mol

Racemic (2*S,4*R**)-5-(2-naphthoyl)-1'-benzyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6ac**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-1'-benzyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5c**, 66.1 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6ac** as a white solid (49.3 mg, 51% yield). **Note:** A mixture of (2*S**,4*S**)-**6ac** (the minor diastereomer) and the (5+3) cycloadduct **7ac** was also obtained, which could not be separated using flash chromatography on silica gel (22.1 mg, 23% combined isolated yield).

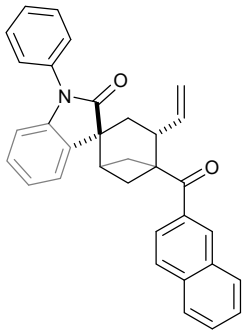
(2*S**,4*R**)-**6ac**: $\mathbf{R_f}$ = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.02-8.00 (m, 2H), 7.88-7.85 (m, 2H), 7.59-7.56 (m, 1H), 7.55-7.52 (m, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.33-7.29 (m, 4H), 7.27-7.24 (m, 1H), 7.18-7.16 (m, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 5.79-5.73 (m, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.89 (d, *J* = 15.6 Hz, 1H), 4.79 (d, *J* = 10.2 Hz, 1H), 4.70 (d, *J* = 17.4 Hz, 1H), 3.72-3.68 (m, 1H), 3.62 (dd, *J* = 9.6 Hz, 7.8 Hz, 1H), 2.60 (dd, *J* = 10.8 Hz, 7.8 Hz, 1H), 2.54 (dd, *J* = 10.2 Hz, 5.4 Hz, 1H), 2.48 (dd, *J* = 9.6 Hz, 6.6 Hz, 1H), 2.39 (dd, *J* = 15.0 Hz, 7.8 Hz, 1H), 2.27 (t, *J* = 6.0 Hz, 1H), 2.14 (dd, *J* = 15.0 Hz, 8.4 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 203.1, 180.8, 141.7, 138.1, 135.9, 135.3, 135.0, 133.2, 132.4, 130.2, 129.7, 128.8, 128.28, 128.27, 128.0, 127.64, 127.55, 127.1, 126.6, 124.7, 122.7, 122.6, 116.2, 109.0, 55.6, 49.2, 44.4, 43.5, 38.6, 35.4, 32.1, 29.0 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{34}H_{30}NO_2$: 484.2271; found: 484.2272.



(2*S**,4*S**)-**6ac: R_f** = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.97-7.95 (m, 1H), 7.93-7.87 (m, 3H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.62-7.55 (m, 3H), 7.33-7.23 (m, 3H), 7.22-7.17 (m, 2H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.77 (t, *J* = 7.8 Hz, 1H), 6.00-5.94 (m, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 4.80 (d, *J* = 10.2 Hz, 2H), 4.77 (d, *J* = 9.0 Hz, 1H), 3.47-3.43 (m, 1H), 3.18-3.11 (m, 1H), 2.74-2.69 (m, 1H), 2.56-2.41 (m, 4H), 2.27-2.21 (m, 1H), 2.16 (dd, *J* = 14.4 Hz, 7.8 Hz, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{34}H_{30}NO_2$: 484.2271; found: 484.2274.

7ac: R_f = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.01-7.98 (m, 2H), 7.93-7.87 (m, 2H), 7.62-7.55 (m, 2H), 7.33-7.23 (m, 7H), 7.04-7.01 (m, 1H), 6.77 (t, *J* = 7.8 Hz, 1H), 6.36 (dt, *J* = 9.0 Hz, 8.4 Hz, 1H), 6.20 (dt, *J* = 8.4 Hz, 8.4 Hz, 1H), 4.93 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 3.39 (d, *J* = 12.6 Hz, 1H), 3.18-3.11 (m, 2H), 3.01 (d, *J* = 13.2 Hz, 1H), 2.92 (dd, *J* = 15.0 Hz, 6.6 Hz, 1H), 2.88-2.84 (m, 1H), 2.74-2.69 (m, 1H), 2.27-2.21 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{34}H_{30}NO_2$: 484.2271; found: 484.2275.

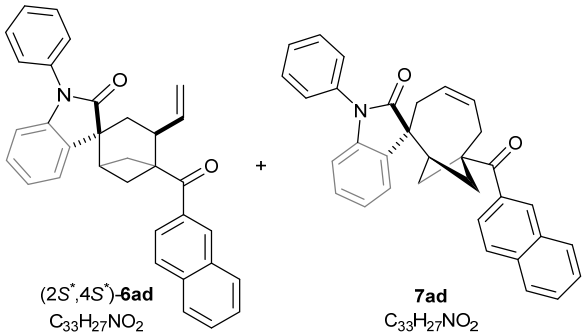
^{13}C NMR (150 MHz, $CDCl_3$): δ 203.7 (for (2*S**,4*S**)-**6ac**), 203.1 (for **7ac**), 180.5 (for (2*S**,4*S**)-**6ac**), 179.6 (for **7ac**), 142.2, 141.6, 138.8, 136.0, 135.9, 135.34, 135.27, 134.6, 133.7, 133.3, 132.5, 132.4, 131.8, 131.3, 130.9, 130.7, 130.3, 129.6, 128.8, 128.42, 128.36, 128.2, 128.0, 127.9, 127.73, 127.70, 127.6, 127.2, 126.69, 126.65, 125.0, 124.7, 124.14, 124.09, 122.3, 122.2, 116.1, 109.2, 55.5, 50.5, 49.8, 48.9, 45.9, 43.7, 43.3, 38.8, 37.6, 36.6, 35.2, 34.9, 31.2, 30.8, 30.7, 28.8 ppm.



6ad
$C_{33}H_{27}NO_2$
M = 469.58 g/mol

Racemic (2*S,4*R**)-5-(2-naphthoyl)-1'-phenyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6ad**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-1'-phenyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5d**, 62.7 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6ad** as a white solid (50.0 mg, 53% yield). **Note:** A mixture of (2*S**,4*S**)-**6ad** (the minor diastereomer) and the (5+3) cycloadduct **7ad** was also obtained, which could not be separated using flash chromatography on silica gel (25.0 mg, 26% combined isolated yield).

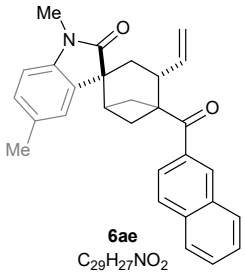
(2*S**,4*R**)-**6ad**: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.00 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.87-7.84 (m, 2H), 7.59-7.51 (m, 5H), 7.46-7.41 (m, 3H), 7.23-7.21 (m, 1H), 7.14-7.11 (m, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.79-5.73 (m, 1H), 4.79 (dd, *J* = 10.2 Hz, 1.2 Hz, 1H), 4.70 (d, *J* = 17.4 Hz, 1H), 3.72-3.68 (m, 1H), 3.60 (dd, *J* = 9.6 Hz, 8.4 Hz, 1H), 2.63 (dd, *J* = 10.8 Hz, 8.4 Hz, 1H), 2.57 (dd, *J* = 10.8 Hz, 6.0 Hz, 1H), 2.47-2.43 (m, 2H), 2.38 (t, *J* = 6.0 Hz, 1H), 2.20 (dd, *J* = 15.0 Hz, 8.4 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 203.0, 180.1, 142.5, 138.0, 135.3, 134.8, 134.4, 133.1, 132.4, 130.2, 129.7, 129.5, 128.29, 128.26, 128.0, 127.6, 126.57, 126.56, 124.7, 123.1, 122.8, 116.2, 109.4, 55.6, 49.2, 44.4, 38.8, 35.4, 32.4, 29.0 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{33}H_{28}NO_2$: 470.2115; found: 470.2118.



(2*S**,4*S**)-**6ad: R_f** = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.40-8.39 (m, 1H), 8.01-7.94 (m, 2H), 7.91-7.86 (m, 1H), 7.72-7.69 (m, 1H), 7.64-7.49 (m, 5H), 7.44-7.37 (m, 2H), 7.27-7.21 (m, 2H), 7.19-7.16 (m, 1H), 6.89-6.86 (m, 1H), 6.02-5.95 (m, 1H), 4.81-4.77 (m, 2H), 3.50-3.44 (m, 1H), 3.17-3.08 (m, 2H), 2.76-2.70 (m, 1H), 2.59-2.51 (m, 1H), 2.46-2.43 (m, 1H), 2.39-2.32 (m, 1H), 2.28-2.23 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{33}H_{28}NO_2$: 470.2115; found: 470.2116.

7ad: R_f = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.31-8.30 (m, 1H), 8.01-7.94 (m, 1H), 7.91-7.86 (m, 4H), 7.64-7.49 (m, 3H), 7.44-7.37 (m, 4H), 7.27-7.21 (m, 1H), 7.11-7.08 (m, 1H), 6.89-6.86 (m, 1H), 6.42-6.36 (m, 1H), 6.23-6.18 (m, 1H), 3.38-3.34 (m, 1H), 3.06-3.02 (m, 1H), 2.93-2.87 (m, 2H), 2.76-2.70 (m, 1H), 2.59-2.51 (m, 3H), 2.39-2.32 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{33}H_{28}NO_2$: 470.2115; found: 470.2114.

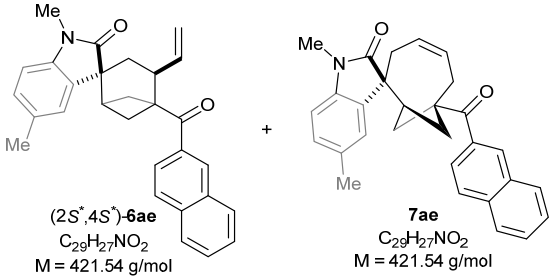
^{13}C NMR (150 MHz, $CDCl_3$): δ 203.7 (for (2*S**,4*S**)-**6ad**), 203.1 (for **7ad**), 179.7 (for (2*S**,4*S**)-**6ad**), 178.9 (for **7ad**), 142.9, 142.4, 138.8, 135.33, 135.26, 134.5, 134.4, 134.3, 133.6, 133.2, 132.5, 132.4, 131.8, 131.3, 130.9, 130.7, 130.3, 129.62, 129.56, 129.53, 129.48, 128.41, 128.35, 128.2, 127.98, 127.97, 127.91, 127.89, 127.72, 127.69, 126.7, 126.64, 126.56, 126.5, 125.0, 124.7, 124.3, 124.2, 122.7, 122.6, 116.1, 109.5, 55.5, 50.4, 50.0, 49.0, 45.8, 39.1, 37.4, 36.8, 35.1, 34.7, 31.2, 30.9, 30.7, 28.6 ppm.



6ae
$C_{29}H_{27}NO_2$
M = 421.54 g/mol

Racemic (2*S,4*R**)-5-(2-naphthoyl)-1',5'-dimethyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6ae**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-1',5'-dimethyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5e**, 51.2 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6ae** as a white solid (43.3 mg,51% yield). **Note:** A mixture of (2*S**,4*S**)-**6ae** (the minor diastereomer) and the (5+3) cycloadduct **7ae** was also obtained, which could not be separated using flash chromatography on silica gel (15.4 mg, 18% combined isolated yield).

(2*S**,4*R**)-**6ae**: $\mathbf{R_f}$ = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.02-7.99 (m, 2H), 7.88-7.84 (m, 2H), 7.60-7.52 (m, 2H), 7.26 (s, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 5.80-5.71 (m, 1H), 4.78 (d, *J* = 10.0 Hz, 1H), 4.68 (d, *J* = 16.8 Hz, 1H), 3.69-3.63 (m, 1H), 3.56 (t, *J* = 8.4 Hz, 1H), 3.21 (s, 3H), 2.60-2.49 (m, 2H), 2.44-2.40 (m, 1H), 2.37 (s, 3H), 2.30 (dd, *J* = 15.2 Hz, 8.0 Hz, 1H), 2.18 (t, *J* = 5.6 Hz, 1H), 2.07 (dd, *J* = 14.8 Hz, 8.4 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.1, 180.7, 140.3, 138.3, 135.3, 135.2, 133.3, 132.5, 132.1, 130.1, 129.7, 128.2, 127.6, 126.5, 124.7, 123.4, 116.0, 107.7, 55.7, 49.3, 44.4, 38.6, 35.5, 32.1, 29.1, 21.2 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{29}H_{28}NO_2$: 422.2115; found: 422.2116.



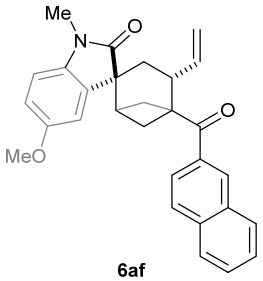
(2*S**,4*S**)-**6ae**
$C_{29}H_{27}NO_2$
M = 421.54 g/mol

7ae
$C_{29}H_{27}NO_2$
M = 421.54 g/mol

(2*S**,4*S**)-**6ae: R_f** = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.96-7.87 (m, 2H), 7.62-7.56 (m, 3H), 7.44 (s, 1H), 7.13-7.10 (m, 1H), 6.77-6.75 (m, 1H), 6.01-5.95 (m, 1H), 4.82-4.79 (m, 2H), 3.43-3.40 (m, 1H), 3.21 (s, 3H), 3.04-2.95 (m, 2H), 2.72-2.66 (m, 1H), 2.48-2.41 (m, 2H), 2.44 (s, 3H), 2.18-2.09 (m, 2H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{29}H_{28}NO_2$: 422.2115; found: 422.2117.

7ae: R_f = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.96-7.87 (m, 5H), 7.34 (s, 1H), 7.13-7.10 (m, 1H), 6.77-6.75 (m, 1H), 6.34 (dt, *J* = 9.6 Hz, 9.0 Hz, 1H), 6.18 (dt, *J* = 9.0 Hz, 8.4 Hz, 1H), 3.39-3.36 (m, 1H), 3.18 (s, 3H), 3.15 (t, *J* = 9.0 Hz, 2H), 2.92-2.85 (m, 2H), 2.72-2.66 (m, 1H), 2.48-2.41 (m, 2H), 2.38 (s, 3H), 2.18-2.09 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{29}H_{28}NO_2$: 422.2115; found: 422.2118.

^{13}C NMR (150 MHz, $CDCl_3$): δ 204.1 (for (2*S**,4*S**)-**6ae**), 203.2 (for **7ae**), 180.5 (for (2*S**,4*S**)-**6ae**), 179.5 (for **7ae**), 140.7, 140.2, 138.9, 135.34, 135.26, 134.8, 133.7, 133.6, 132.5, 132.4, 131.8, 131.7, 131.5, 130.9, 130.7, 130.4, 129.7, 129.6, 128.4, 128.34, 128.26, 128.2, 127.72, 127.69, 126.67, 126.6, 125.0, 124.9, 124.81, 124.78, 116.0, 107.9, 107.8, 55.4, 50.4, 49.8, 49.0, 45.9, 38.7, 37.5, 36.5, 35.2, 34.7, 31.0, 30.9, 30.7, 28.9, 26.3, 26.1, 21.30, 21.28 ppm.

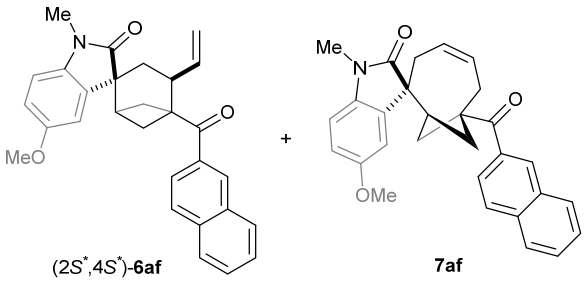


6af
$C_{29}H_{27}NO_3$
M = 437.54 g/mol

Racemic (2*S,4*R**)-5-(2-naphthoyl)-5'-methoxy-1'-methyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6af**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-5'-methoxy-1'-methyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5f**, 55.0 mg, 0.24 mmol)

according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6af** as a white solid (44.4 mg, 51% yield). **Note:** A mixture of (2*S**,4*S**)-**6af** (the minor diastereomer) and the (5+3) cycloadduct **7af** was also obtained, which could not be separated using flash chromatography on silica gel (20.9 mg, 24% combined isolated yield).

(2*S**,4*R**)-**6af**: **R_f** = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.02-7.98 (m, 2H), 7.88-7.85 (m, 2H), 7.60-7.52 (m, 2H), 7.07 (s, 1H), 6.82-6.73 (m, 2H), 5.78-5.70 (m, 1H), 4.79 (d, *J* = 10.0 Hz, 1H), 4.69 (d, *J* = 17.2 Hz, 1H), 3.82 (s, 3H), 3.69-3.63 (m, 1H), 3.56 (t, *J* = 6.4 Hz, 1H), 3.21 (s, 3H), 2.57-2.49 (m, 2H), 2.43 (t, *J* = 7.6 Hz, 1H), 2.36-2.30 (m, 1H), 2.21-2.17 (m, 1H), 2.09-2.03 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.1, 180.4, 156.1, 138.2, 136.4, 136.2, 135.4, 133.3, 132.5, 130.2, 129.7, 128.3, 127.7, 126.6, 124.7, 116.1, 111.9, 110.6, 108.2, 55.8, 55.6, 49.6, 44.4, 38.6, 35.5, 32.0, 29.0, 26.2 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{29}H_{28}NO_3$: 438.2064; found: 438.2071.



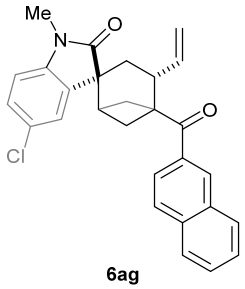
(2*S**,4*S**)-**6af**
$C_{29}H_{27}NO_3$
M = 437.54 g/mol

7af
$C_{29}H_{27}NO_3$
M = 437.54 g/mol

(2*S**,4*S**)-**6af: R_f** = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.94-7.93 (m, 1H), 7.90-7.87 (m, 2H), 7.61-7.55 (m, 2H), 7.27 (s, 1H), 6.85-6.82 (m, 1H), 6.78-6.76 (m, 1H), 5.99-5.93 (m, 1H), 4.79 (d, *J* = 6.0 Hz, 1H), 4.76 (d, *J* = 16.2 Hz, 1H), 3.88 (s, 3H), 3.42-3.38 (m, 1H), 3.20 (s, 3H), 3.14-3.11 (m, 1H), 2.72-2.66 (m, 1H), 2.49-2.40 (m, 3H), 2.19-2.14 (m, 1H), 2.11 (dd, *J* = 15.0 Hz, 7.8 Hz, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{29}H_{28}NO_3$: 438.2064; found: 438.2065.

7af: $\mathbf{R_f}$ = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.90-7.87 (m, 3H), 7.61-7.55 (m, 2H), 7.19 (s, 1H), 6.85-6.82 (m, 1H), 6.78-6.76 (m, 1H), 6.34 (dt, *J* = 9.6 Hz, 8.4 Hz, 1H), 6.17 (dt, *J* = 9.0 Hz, 8.4 Hz, 1H), 3.83 (s, 3H), 3.34 (d, *J* = 13.2 Hz, 1H), 3.17 (s, 3H), 3.09-3.02 (m, 2H), 2.97 (d, *J* = 12.6 Hz, 1H), 2.90-2.82 (m, 2H), 2.72-2.66 (m, 1H), 2.37 (dd, *J* = 14.4 Hz, 8.4 Hz, 1H), 2.19-2.14 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{29}H_{28}NO_3$: 438.2064; found: 438.2066.

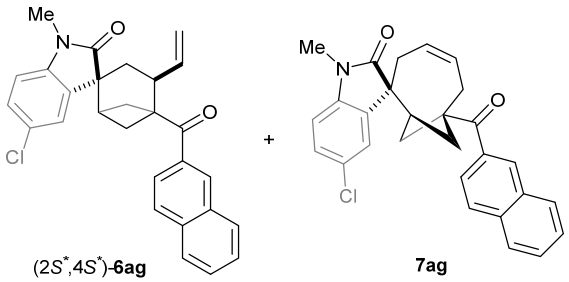
^{13}C NMR (150 MHz, $CDCl_3$): δ 203.8 (for (2*S**,4*S**)-**6af**), 203.1 (for **7af**), 180.1 (for (2*S**,4*S**)-**6af**), 179.2 (for **7af**), 155.7, 155.5, 138.8, 136.7, 136.24, 136.16, 135.34, 135.25, 134.7, 133.7, 132.5, 132.4, 131.7, 131.3, 130.9, 130.7, 130.3, 129.7, 129.6, 128.4, 128.3, 128.2, 127.71, 127.69, 126.7, 126.6, 125.0, 124.7, 116.1, 112.7, 112.5, 111.2, 111.1, 108.12, 108.10, 55.9, 55.8, 55.4, 50.4, 50.1, 49.3, 45.8, 38.7, 37.4, 36.5, 35.1, 34.7, 31.0, 30.7, 30.6, 28.7, 26.4, 26.1 ppm.



6ag
$C_{28}H_{24}ClNO_2$
M = 441.96 g/mol

Racemic (2*S,4*R**)-5-(2-naphthoyl)-5'-chloro-1'-methyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6ag**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-5'-chloro-1'-methyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5g**, 56.1 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6ag** as a white solid (51.4 mg, 58% yield). **Note:** A mixture of (2*S**,4*S**)-**6ag** (the minor diastereomer) and the (5+3) cycloadduct **7ag** was also obtained, which could not be separated using flash chromatography on silica gel (23.8 mg, 27% combined isolated yield).

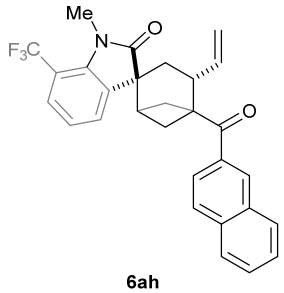
(2*S**,4*R**)-**6ag**: **R*f*** = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.02-7.97 (m, 2H), 7.89-7.85 (m, 2H), 7.61-7.53 (m, 2H), 7.41 (s, 1H), 7.28-7.25 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.77-5.68 (m, 1H), 4.79 (d, *J* = 10.4 Hz, 1H), 4.69 (d, *J* = 16.8 Hz, 1H), 3.68-3.61 (m, 1H), 3.54-3.50 (m, 1H), 3.22 (s, 3H), 2.56-2.48 (m, 2H), 2.45-2.41 (m, 1H), 2.31 (dd, *J* = 14.8 Hz, 7.6 Hz, 1H), 2.19 (t, *J* = 5.2 Hz, 1H), 2.04 (dd, *J* = 15.2 Hz, 8.4 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.8, 180.2, 141.2, 138.0, 136.7, 135.4, 133.2, 132.5, 130.1, 129.7, 128.3, 128.0, 127.7, 126.6, 123.1, 116.3, 108.9, 55.6, 49.5, 44.3, 38.5, 35.3, 31.9, 29.0, 26.3 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{25}ClNO_2$: 442.1568; found: 442.1573.



(2*S**,4*S**)-**6ag: R*f*** = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.94-7.87 (m, 3H), 7.62-7.55 (m, 3H), 7.31-7.26 (m, 1H), 6.79 (t, *J* = 7.2 Hz, 1H), 5.98-5.92 (m, 1H), 4.81 (d, *J* = 4.8 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 3.42-3.38 (m, 1H), 3.21 (s, 3H), 3.11-3.01 (m, 1H), 2.63-2.60 (m, 1H), 2.51 (dd, *J* = 10.2 Hz, 6.6 Hz, 1H), 2.45-2.41 (m, 2H), 2.17-2.09 (m, 2H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{25}ClNO_2$: 442.1568; found: 442.1569.

7ag: R*f* = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.94-7.87 (m, 2H), 7.62-7.55 (m, 2H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.31-7.26 (m, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.32 (dt, *J* = 9.0 Hz, 8.4 Hz, 1H), 6.21 (dt, *J* = 10.2 Hz, 7.8 Hz, 1H), 3.32-3.29 (m, 1H), 3.18 (s, 3H), 3.11-3.01 (m, 2H), 2.94-2.84 (m, 3H), 2.71 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 2.37 (dd, *J* = 13.8 Hz, 7.8 Hz, 1H), 2.17-2.09 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{25}ClNO_2$: 442.1568; found: 442.1571.

^{13}C NMR (150 MHz, $CDCl_3$): δ 203.6 (for (2*S**,4*S**)-**6aa**), 202.9 (for **7ag**), 180.0 (for (2*S**,4*S**)-**6aa**), 179.0 (for **7ag**), 141.6, 141.2, 138.5, 136.3, 135.4, 135.3, 134.9, 133.6, 132.5, 132.4, 132.1, 130.84, 130.82, 130.6, 130.3, 129.7, 129.6, 128.45, 128.39, 128.3, 128.0, 127.9, 127.73, 127.70, 127.6, 127.5, 126.71, 126.69, 125.0, 124.7, 124.4, 116.3, 109.01, 108.99, 55.4, 50.3, 50.1, 49.2, 45.6, 38.5, 37.4, 36.4, 35.1, 34.5, 30.9, 30.8, 30.4, 28.5, 26.4, 26.2 ppm.

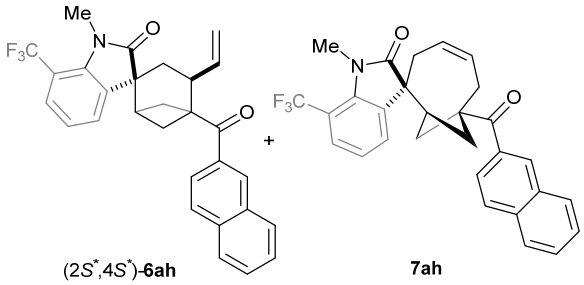


6ah
$C_{29}H_{24}F_3NO_2$
M = 475.51g/mol

Racemic (2*S,4*R**)-5-(2-naphthoyl)-1'-methyl-7'-(trifluoromethyl)-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6ah**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-1'-methyl-7'-(trifluoromethyl)-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5h**, 64.1 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6ah** as a white solid (51.3 mg, 54% yield). **Note:** A mixture of (2*S**,4*S**)-**6ah** (the minor diastereomer) and the (5+3) cycloadduct **7ah** was also obtained, which could not be separated using flash chromatography on silica gel (20.8 mg, 22% combined isolated yield).

(2*S**,4*R**)-**6ah**: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.03-7.98 (m, 2H), 7.89-7.85 (m, 2H), 7.64-7.53 (m, 4H), 7.14 (t, *J* = 8.0 Hz, 1H), 5.77-5.68 (m, 1H), 4.79 (d, *J* = 10.4 Hz, 1H), 4.70 (d, *J* = 17.2 Hz, 1H), 3.72-3.66 (m, 1H), 3.56-3.52 (m, 1H), 3.45 (s, 3H), 2.58-2.51 (m, 2H), 2.44-2.40 (m, 1H), 2.28 (dd, *J* = 14.8 Hz, 7.6 Hz, 1H), 2.17 (t, *J* = 5.2 Hz, 1H), 2.08 (dd, *J* = 14.8 Hz, 8.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.7, 181.4, 140.6, 137.9, 137.6, 135.4, 133.2, 132.5, 130.2, 129.7, 128.4, 128.3, 127.7, 126.6, 126.0 (q, *J* = 5.9 Hz), 125.7,

124.7, 123.6 (q, *J* = 270.1 Hz), 121.9, 116.4, 112.4 (q, *J* = 32.5 Hz), 55.6, 47.6, 44.2, 38.9, 35.4, 32.4, 28.9, 28.7 (q, *J* = 6.7 Hz) ppm. **^{19}F NMR** (376 MHz, CDCl3) δ -52.95 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{29}H_{25}F_3NO_2$: 476.1832; found: 476.1833.



(2*S**,4*S**)-**6ah**
$C_{29}H_{24}F_3NO_2$
M = 475.51g/mol

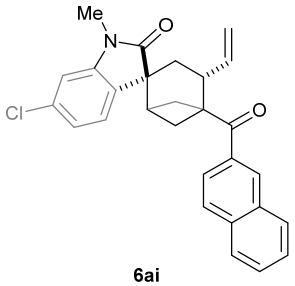
7ah
$C_{29}H_{24}F_3NO_2$
M = 475.51g/mol

(2*S**,4*S**)-**6ah: R_f** = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.99 (t, *J* = 7.8 Hz, 1H), 7.94-7.87 (m, 3H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.62-7.56 (m, 3H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.02-5.96 (m, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.79 (d, *J* = 17.4 Hz, 1H), 3.50-3.38 (m, 1H), 3.44 (s, 3H), 3.13-3.10 (m, 1H), 3.03-2.88 (m, 2H), 2.62 (t, *J* = 10.2 Hz, 1H), 2.49-2.41 (m, 3H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{29}H_{25}F_3NO_2$: 476.1832; found: 476.1831.

7ah: R_f = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.99 (t, *J* = 7.8 Hz, 1H), 7.94-7.87 (m, 3H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.62-7.56 (m, 3H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.32 (dt, *J* = 9.6 Hz, 8.4 Hz, 1H), 6.21 (dt, *J* = 9.6 Hz, 7.8 Hz, 1H), 3.41 (s, 3H), 3.03-2.88 (m, 3H), 2.71 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 2.49-2.41 (m, 1H), 2.16 (t, *J* = 7.8 Hz, 2H), 2.12 (t, *J* = 6.6 Hz, 2H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{29}H_{25}F_3NO_2$: 476.1832; found: 476.1829.

^{13}C NMR (150 MHz, $CDCl_3$): δ 203.6 (for (2*S**,4*S**)-**6ah**), 202.9 (for **7ah**), 181.2 (for (2*S**,4*S**)-**6ah**), 180.0 (for **7ah**), 141.0, 140.5, 138.6, 137.2, 136.0, 135.4, 135.3, 133.6, 132.7, 132.5, 132.4, 132.1, 130.88, 130.86, 130.6, 130.4, 129.64, 129.63, 128.5, 128.43, 128.41, 128.3, 128.2, 127.8, 127.7, 127.1, 127.0, 126.74, 126.71, 126.0 (q, *J* = 6.0 Hz), 125.9 (q, *J* = 6.5 Hz), 125.0, 124.7, 123. 6 (q, *J* = 270.0 Hz), 121.8 (q, *J* = 268.8 Hz), 121.51, 121.49, 116.4, 112.52 (q, *J* = 33.0 Hz), 112.46 (q, *J* = 32.0 Hz), 55.4, 50.5, 48.2, 47.1, 45.6, 39.1, 37.0, 36.7, 35.2, 34.2, 31.0, 30.8, 29.0 (q, *J* = 6.5

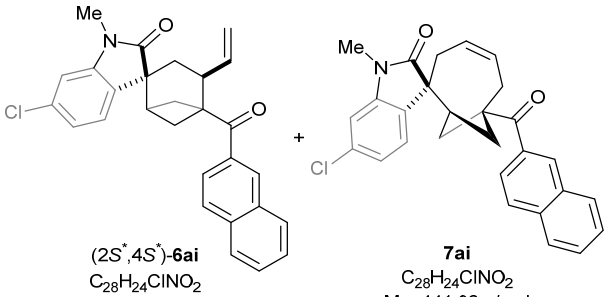
Hz), 28.65 (q, *J* = 6.5 Hz), 28.58 ppm. **^{19}F NMR** (565 MHz, CDCl3) δ -52.84, -52.95 ppm.



6ai
$C_{28}H_{24}ClNO_2$
M = 441.96 g/mol

Racemic (2*S,4*R**)-5-(2-naphthoyl)-6'-chloro-1'-methyl-4-vinylspiro[bicyclo[3.1.1] heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6ai**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-6'-chloro-1'-methyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5i**, 56.1 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6ai** as a white solid (46.8 mg, 53% yield). **Note:** A mixture of (2*S**,4*S**)-**6ai** (the minor diastereomer) and the (5+3) cycloadduct **7ai** was also obtained, which could not be separated using flash chromatography on silica gel (23.5 mg, 27% combined isolated yield).

(2*S**,4*R**)-**6ai**: **R_f** = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.02-7.97 (m, 2H), 7.88-7.85 (m, 2H), 7.60-7.52 (m, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.84 (s, 1H), 5.77-5.68 (m, 1H), 4.79 (d, *J* = 10.0 Hz, 1H), 4.69 (d, *J* = 17.2 Hz, 1H), 3.67-3.61 (m, 1H), 3.52-3.49 (m, 1H), 3.21 (s, 3H), 2.54-2.47 (m, 2H), 2.45-2.41 (m, 1H), 2.31 (dd, *J* = 15.2 Hz, 8.0 Hz, 1H), 2.17-2.14 (m, 1H), 2.03 (dd, *J* = 14.8 Hz, 8.0 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.8, 180.6, 143.9, 138.0, 135.4, 133.9, 133.4, 133.2, 132.5, 130.1, 129.7, 128.3, 127.7, 126.6, 124.7, 123.4, 122.3, 116.2, 108.7, 55.6, 49.0, 44.2, 38.5, 35.3, 31.8, 28.9, 26.2 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{25}ClNO_2$: 442.1568; found: 442.1576.



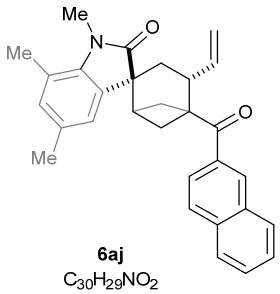
(2*S**,4*S**)-**6ai**
$C_{28}H_{24}ClNO_2$
M = 441.96 g/mol

7ai
$C_{28}H_{24}ClNO_2$
M = 441.96 g/mol

(2*S**,4*S**)-**6ai: R_f** = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.99 (t, *J* = 7.8 Hz, 1H), 7.93-7.87 (m, 4H), 7.61-7.53 (m, 3H), 7.10 (d, *J* = 7.8 Hz, 1H), 5.97-5.91 (m, 1H), 4.80 (d, *J* = 9.0 Hz, 1H), 4.78 (d, *J* = 15.6 Hz, 1H), 3.41-3.37 (m, 1H), 3.20 (s, 3H), 3.10-3.00 (m, 1H), 2.93-2.82 (m, 1H), 2.60 (t, *J* = 9.6 Hz, 1H), 2.50-2.41 (m, 2H), 2.16-2.11 (m, 1H), 2.08 (dd, *J* = 15.6 Hz, 7.8 Hz, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{25}ClNO_2$: 442.1568; found: 442.1572.

7ai: R_f = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.99 (t, *J* = 7.8 Hz, 1H), 7.93-7.87 (m, 2H), 7.61-7.53 (m, 2H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.88-6.86 (m, 2H), 6.29 (dt, *J* = 9.6 Hz, 9.0 Hz, 1H), 6.18 (dt, *J* = 9.0 Hz, 8.4 Hz, 1H), 3.33-3.29 (m, 1H), 3.18 (s, 3H), 3.10-3.00 (m, 2H), 2.93-2.82 (m, 2H), 2.69 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 2.50-2.41 (m, 1H), 2.36 (dd, *J* = 14.4 Hz, 8.4 Hz, 1H), 2.16-2.11 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{25}ClNO_2$: 442.1568; found: 442.1570.

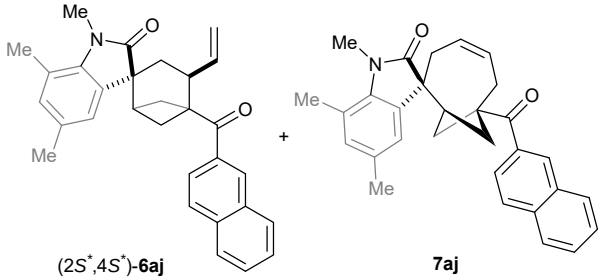
^{13}C NMR (150 MHz, $CDCl_3$): δ 203.6 (for (2*S**,4*S**)-**6ai**), 202.9 (for **7ai**), 180.3 (for (2*S**,4*S**)-**6ai**), 179.4 (for **7ai**), 144.3, 143.9, 138.6, 135.33, 135.25, 133.94, 133.91, 133.6, 133.0, 132.5, 132.3, 132.0, 131.6, 130.9, 130.8, 130.6, 130.3, 129.6, 128.44, 128.37, 128.36, 128.2, 127.72, 127.69, 126.70, 126.66, 125.0, 124.8, 124.71, 124.68, 122.0, 121.9, 116.2, 108.88, 108.85, 55.4, 50.4, 49.6, 48.7, 45.7, 38.5, 37.4, 36.4, 35.1, 34.6, 30.9, 30.5, 28.5, 26.4, 26.1 ppm.



6aj
$C_{30}H_{29}NO_2$
M = 435.57 g/mol

Racemic (2*S,4*R**)-5-(2-naphthoyl)-1',5',7'-trimethyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6aj**): Prepared from bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (**1a**, 41.7 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-1',5',7'-trimethyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5j**, 54.6 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6aj** as a white solid (44.5 mg, 51% yield). **Note:** A mixture of (2*S**,4*S**)-**6aj** (the minor diastereomer) and the (5+3) cycloadduct **7aj** was also obtained, which could not be separated using flash chromatography on silica gel (18.8 mg, 22% combined isolated yield).

(2*S**,4*R**)-**6aj**: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.02-7.98 (m, 2H), 7.88-7.85 (m, 2H), 7.60-7.52 (m, 2H), 7.10 (s, 1H), 6.82 (s, 1H), 5.77-5.68 (m, 1H), 4.76 (d, *J* = 10.4 Hz, 1H), 4.67 (d, *J* = 17.2 Hz, 1H), 3.69-3.63 (m, 1H), 3.59-3.53 (m, 1H), 3.49 (s, 3H), 2.59-2.47 (m, 2H), 2.54 (s, 3H), 2.42-2.38 (m, 1H), 2.31 (s, 3H), 2.27-2.21 (m, 1H), 2.14 (t, *J* = 6.0 Hz, 1H), 2.05 (dd, *J* = 14.8 Hz, 8.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.2, 181.5, 138.3, 137.9, 136.0, 135.4, 133.3, 132.5, 132.2, 131.9, 130.2, 129.7, 128.2, 127.7, 126.5, 124.7, 121.1, 119.3, 116.0, 55.7, 48.5, 44.5, 38.9, 35.7, 32.6, 29.4, 29.0, 20.9, 18.9 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{30}H_{30}NO_2$: 436.2771; found: 436.2772.



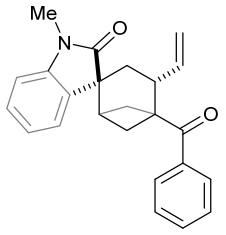
(2*S**,4*S**)-**6aj**
$C_{30}H_{29}NO_2$
M = 435.57 g/mol

7aj
$C_{30}H_{29}NO_2$
M = 435.57 g/mol

(2*S**,4*S**)-**6aj: R_f** = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.95-7.87 (m, 3H), 7.61-7.55 (m, 2H), 7.26 (d, *J* = 7.2 Hz, 1H), 6.03-5.97 (m, 1H), 4.81 (d, *J* = 7.8 Hz, 1H), 4.79 (d, *J* = 10.2 Hz, 1H), 3.48 (s, 3H), 3.42-3.38 (m, 1H), 3.15 (t, *J* = 9.0 Hz, 1H), 3.01-2.86 (m, 3H), 2.71-2.66 (m, 2H), 2.55 (s, 3H), 2.45-2.41 (m, 1H), 2.38 (s, 3H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{30}H_{30}NO_2$: 436.2771; found: 436.2776.

7aj: R_f = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.95-7.87 (m, 2H), 7.61-7.55 (m, 2H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.19 (s, 1H), 6.86-6.84 (m, 2H), 6.34 (dt, *J* = 9.0 Hz, 8.4 Hz, 1H), 6.17 (dt, *J* = 9.0 Hz, 7.8 Hz, 1H), 3.46 (s, 3H), 3.42-3.38 (m, 1H), 3.01-2.86 (m, 1H), 2.54 (s, 3H), 2.45-2.41 (m, 3H), 2.32 (s, 3H), 2.16-2.08 (m, 4H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{30}H_{30}NO_2$: 436.2771; found: 436.2774.

^{13}C NMR (150 MHz, $CDCl_3$): δ 204.2 (for (2*S**,4*S**)-**6aj**), 203.2 (for **7aj**), 181.2 (for (2*S**,4*S**)-**6aj**), 180.1 (for **7aj**), 139.1, 138.3, 137.8, 135.6, 135.3, 135.2, 134.4, 133.7, 132.5, 132.4, 132.23, 132.16, 131.7, 131.53, 131.46, 131.3, 130.9, 130.7, 130.4, 129.65, 129.61, 128.4, 128.3, 128.2 127.71, 127.68, 126.65, 126.62, 125.1, 124.8, 122.7, 122.5, 119.42, 119.38, 116.0, 55.4, 50.4, 49.1, 48.2, 45.7, 39.1, 37.1, 36.8, 35.2, 31.2, 30.9, 29.7, 29.4, 28.9, 21.0, 20.9, 19.03, 19.01 ppm.

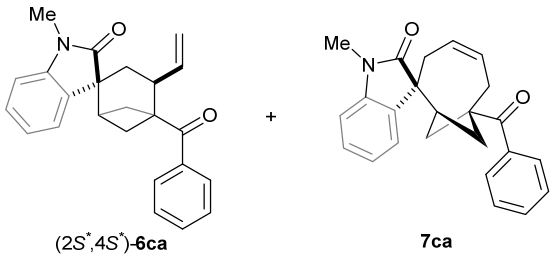


6ca
$C_{24}H_{23}NO_2$
M = 357.45 g/mol

Racemic (2*S,4*R**)-5-benzoyl-1'-methyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6ca**): Prepared from bicyclo[1.1.0]butan-1-yl(phenyl)methanone (**1c**, 31.6 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-1'-methyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5a**, 47.8 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using

petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6ca** as a colorless oil (38.0 mg, 53% yield). **Note:** A mixture of (2*S**,4*S**)-**6ca** (the minor diastereomer) and the (5+3) cycloadduct **7ca** was also obtained, which could not be separated using flash chromatography on silica gel (17.3 mg, 24% combined isolated yield).

(2*S**,4*R**)-**6ca**: **R_f** = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.46-7.42 (m, 3H), 7.30-7.28 (m, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.73-5.67 (m, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.70 (d, *J* = 17.4 Hz, 1H), 3.58-3.54 (m, 1H), 3.42 (dd, *J* = 10.2 Hz, 7.8 Hz, 1H), 3.22 (s, 3H), 2.53-2.50 (m, 1H), 2.46 (dd, *J* = 10.8 Hz, 6.0 Hz, 1H), 2.34 (dd, *J* = 9.6 Hz, 6.6 Hz, 1H), 2.27 (dd, *J* = 15.6 Hz, 7.8 Hz, 1H), 2.15 (t, *J* = 6.0 Hz, 1H), 2.05 (dd, *J* = 15.0 Hz, 8.4 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 203.1, 180.7, 142.6, 138.1, 135.8, 135.0, 132.7, 128.7, 128.4, 128.1, 122.6, 122.4, 116.0, 108.0, 55.4, 49.1, 44.2, 38.4, 35.2, 31.8, 28.8, 26.1 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{24}H_{24}NO_2$: 358.1802; found: 358.1801.



(2*S**,4*S**)-**6ca**
$C_{24}H_{23}NO_2$
M = 357.45 g/mol

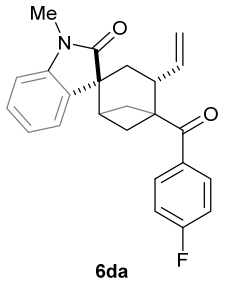
7ca
$C_{24}H_{23}NO_2$
M = 357.45 g/mol

(2*S**,4*S**)-**6ca: R_f** = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.55-7.51 (m, 1H), 7.47-7.45 (m, 2H), 7.33-7.29 (m, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.88-6.85 (m, 1H), 5.93-5.87 (m, 1H), 4.81 (d, *J* = 10.2 Hz, 1H), 4.76 (d, *J* = 16.8 Hz, 1H), 3.37-3.33 (m, 1H), 3.21 (s, 3H), 3.02-2.97 (m, 2H), 2.65-2.59 (m, 1H), 2.43-2.39 (m, 2H), 2.15-2.11 (m, 1H), 2.07 (dd, *J* = 15.0 Hz, 7.8 Hz, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{24}H_{24}NO_2$: 358.1802; found: 358.1879.

7ca: R_f = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.55-7.51 (m, 2H), 7.47-7.45 (m, 2H), 7.33-7.29 (m, 1H), 7.05 (t, *J* =

7.8 Hz, 1H), 6.88-6.85 (m, 1H), 6.30 (dt, *J* = 9.6 Hz, 9.0 Hz, 1H), 6.13 (dt, *J* = 8.4 Hz, 7.8 Hz, 1H), 3.25-3.24 (m, 1H), 3.19 (s, 3H), 2.92 (d, *J* = 13.2 Hz, 1H), 2.82-2.75 (m, 2H), 2.65-2.59 (m, 1H), 2.39-2.38 (m, 1H), 2.34 (dd, *J* = 10.8 Hz, 6.0 Hz, 2H), 2.15-2.11 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{24}H_{24}NO_2$: 358.1802; found: 358.1800.

^{13}C NMR (150 MHz, $CDCl_3$): δ 203.7 (for (2*S**,4*S**)-**6ca**), 203.0 (for **7ca**), 180.4 (for (2*S**,4*S**)-**6ca**), 179.5 (for **7ca**), 143.1, 142.6, 138.7, 136.3, 134.7, 133.4, 132.7, 132.6, 131.5, 131.4, 129.3, 128.8, 128.5, 128.4, 128.1, 128.0, 124.0, 123.9, 122.2, 122.1, 116.0, 108.14, 108.12, 55.4, 50.2, 49.8, 48.9, 45.6, 38.5, 37.4, 36.4, 34.9, 34.4, 31.0, 30.8, 30.6, 28.3, 26.3, 26.0 ppm.

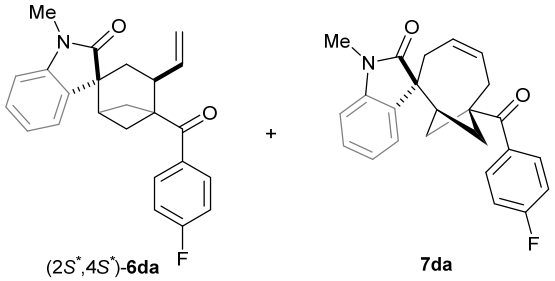


6da
$C_{24}H_{22}FNO_2$
M = 375.44 g/mol

Racemic (2*S,4*R**)-5-(4-fluorobenzoyl)-1'-methyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6da**): Prepared from bicyclo[1.1.0]butan-1-yl(4-fluorophenyl)methanone (**1d**, 35.2 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-1'-methyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5a,** 47.8 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6da** as a colorless oil (42.6 mg, 57% yield). **Note:** A mixture of (2*S**,4*S**)-**6da** (the minor diastereomer) and the (5+3) cycloadduct **7da** was also obtained, which could not be separated using flash chromatography on silica gel (18.7 mg, 25% combined isolated yield).

(2*S**,4*R**)-**6da**: $\mathbf{R_f}$ = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.00-7.96 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.14-7.10 (m, 2H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.71-5.65 (m, 1H), 4.80 (d, *J* =

10.2 Hz, 1H), 4.70 (d, *J* = 16.8 Hz, 1H), 3.54-3.49 (m, 1H), 3.42-3.39 (m, 1H), 3.23 (s, 3H), 2.52 (dd, *J* = 10.8 Hz, 7.8 Hz, 1H), 2.45 (dd, *J* = 10.8 Hz, 6.0 Hz, 1H), 2.32 (dd, *J* = 9.6 Hz, 6.6 Hz, 1H), 2.25 (dd, *J* = 15.0 Hz, 7.2 Hz, 1H), 2.16 (t, *J* = 6.0 Hz, 1H), 2.06 (dd, *J* = 15.0 Hz, 8.4 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 201.5, 180.6, 165.3 (d, *J* = 252.9 Hz), 142.6, 138.0, 134.9, 132.2 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 9.2 Hz), 128.1, 122.6, 122.4, 116.1, 115.5 (d, *J* = 21.5 Hz), 108.0, 55.3, 49.0, 44.3, 38.3, 35.1, 31.9, 28.8, 26.1 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$): δ -105.46 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{24}H_{23}FNO_2$: 376.1707; found: 376.1710.



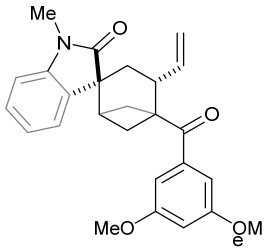
(2*S**,4*S**)-**6da**
$C_{24}H_{22}FNO_2$
M = 375.44 g/mol

7da
$C_{24}H_{22}FNO_2$
M = 375.44 g/mol

(2*S**,4*S**)-**6da: R_f** = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.91-7.89 (m, 2H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.34-7.29 (m, 1H), 7.15-7.10 (m, 3H), 6.88-6.86 (m, 1H), 5.91-5.85 (m, 1H), 4.81 (d, *J* = 10.2 Hz, 1H), 4.77 (d, *J* = 16.8 Hz, 1H), 3.33-3.28 (m, 1H), 3.23 (s, 3H), 3.01 (dd, *J* = 10.8 Hz, 7.8 Hz, 1H), 2.98-2.94 (m, 1H), 2.63-2.56 (m, 1H), 2.43-2.39 (m, 2H), 2.16-2.10 (m, 1H), 2.07 (dd, *J* = 15.0 Hz, 7.8 Hz, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{24}H_{23}FNO_2$: 376.1707; found: 376.1712.

7da: R_f = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.85-7.83 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.34-7.29 (m, 1H), 7.15-7.10 (m, 2H), 7.06-7.04 (m, 1H), 6.88-6.86 (m, 1H), 6.31 (dt, *J* = 9.0 Hz, 9.0 Hz, 1H), 6.11 (dt, *J* = 9.0 Hz, 7.8 Hz, 1H), 3.24-3.23 (m, 1H), 3.19 (s, 3H), 2.92-2.89 (m, 1H), 2.80-2.74 (m, 2H), 2.63-2.56 (m, 1H), 2.39-2.36 (m, 1H), 2.33 (dd, *J* = 10.2 Hz, 6.0 Hz, 2H), 2.16-2.10 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{24}H_{23}FNO_2$: 376.1707; found: 376.1713.

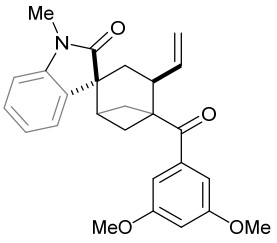
^{13}C NMR (150 MHz, $CDCl_3$): δ 202.1 (for (2*S**,4*S**)-**6da**), 201.5 (for **7da**), 180.4 (for (2*S**,4*S**)-**6da**), 179.4 (for **7da**), 165.4 (d, *J* = 253.4 Hz), 165.3 (d, *J* = 253.1 Hz), 143.1, 142.6, 138.7, 134.6, 133.3, 132.7 (d, *J* = 3.0 Hz), 131.9 (d, *J* = 9.2 Hz), 131.6, 131.4 (d, *J* = 9.2 Hz), 131.3, 129.7 (d, *J* = 2.9 Hz), 128.1, 128.0, 123.94, 123.92, 122.3, 122.2, 116.1, 115.7, 115.5 (d, *J* = 21.8 Hz), 108.19, 108.16, 55.2, 50.1, 49.7, 48.9, 45.7, 38.5, 37.4, 36.3, 34.8, 34.4, 31.0, 30.7, 30.6, 28.4, 26.3, 26.0 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -105.45, -105.59 ppm.



6la
$C_{26}H_{27}NO_2$
M = 417.51 g/mol

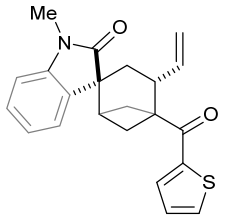
Racemic (2*S,4*R**)-5-(3,5-dimethoxybenzoyl)-1'-methyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6la**): Prepared from bicyclo[1.1.0]butan-1-yl(3,5-dimethoxyphenyl)methanone (**1l**, 43.7 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-1'-methyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5a**, 47.8 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6la** as a white solid (49.3 mg, 59% yield) and (2*S**,4*S**)-**6la** as a colorless oil (16.8 mg, 20% yield).

(2*S**,4*R**)-**6la**: R_f = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 6.4 Hz, 1H), 7.30-7.27 (m, 1H), 7.08-7.05 (m, 3H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.63 (s, 1H), 5.76-5.67 (m, 1H), 4.85 (d, *J* = 10.0 Hz, 1H), 4.79 (d, *J* = 17.2 Hz, 1H), 3.84 (s, 6H), 3.58-3.52 (m, 1H), 3.40 (t, *J* = 8.0 Hz, 1H), 3.21 (s, 3H), 2.53-2.49 (m, 1H), 2.45-2.41 (m, 1H), 2.35-2.25 (m, 2H), 2.14 (t, *J* = 6.0 Hz, 1H), 2.07-2.02 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.9, 180.7, 160.7, 142.7, 138.2, 137.7, 135.1, 128.1, 122.6, 122.5, 116.1, 108.0, 106.5, 105.2, 55.5, 49.1, 44.3, 38.5, 35.3, 31.9, 29.1, 26.1 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{26}H_{28}NO_2$: 418.2013; found: 418.2017.



(2*S**,4*S**)-**6la**
$C_{26}H_{27}NO_2$
M = 417.51 g/mol

(2*S**,4*S**)-**6la**: $\mathbf{R_f}$ = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 2H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.63 (s, 1H), 5.94-5.88 (m, 1H), 4.85 (d, *J* = 11.4 Hz, 1H), 4.82 (d, *J* = 18.0 Hz, 1H), 3.85 (s, 6H), 3.37-3.33 (m, 1H), 3.21 (s, 3H), 2.98 (dd, *J* = 10.2 Hz, 8.4 Hz, 1H), 2.59 (t, *J* = 9.6 Hz, 1H), 2.42-2.37 (m, 2H), 2.32 (dd, *J* = 10.8 Hz, 6.6 Hz, 1H), 2.10 (t, *J* = 6.6 Hz, 1H), 2.07 (dd, *J* = 15.0 Hz, 7.8 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 203.3, 180.4, 160.6, 143.1, 138.8, 138.1, 134.7, 128.1, 123.9, 122.3, 116.0, 108.1, 106.7, 104.6, 55.6, 55.4, 49.8, 45.6, 38.5, 37.5, 31.0, 28.3, 26.3 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{26}H_{28}NO_2$: 418.2013; found: 418.2014.

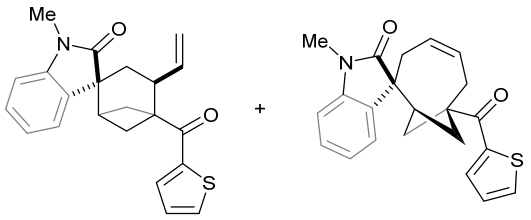


6fa
$C_{22}H_{21}NO_2S$
M = 363.48 g/mol

Racemic (2*S,4*R**)-1'-methyl-5-(thiophene-2-carbonyl)-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one** ((2*S**,4*R**)-**6fa**): Prepared from bicyclo[1.1.0]butan-1-yl(thiophen-2-yl)methanone (**1f**, 32.8 mg, 0.20 mmol) and *rac*-(1*S**,2*S**)-1'-methyl-2-vinylspiro[cyclopropane-1,3'-indolin]-2'-one (**5a**, 47.8 mg, 0.24 mmol) according to the **GP2** at 30 °C for 12 h. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded (2*S**,4*R**)-**6fa** as a yellow oil (40.7 mg, 56% yield). **Note:** A mixture of (2*S**,4*S**)-**6fa** (the minor diastereomer) and the (5+3)

cycloadduct **7fa** was also obtained, which could not be separated using flash chromatography on silica gel (12.8 mg, 18% combined isolated yield).

(2*S**,4*R**)-**6fa**: **R*f*** = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.61(d, *J* = 4.8 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.30-7.27 (m, 1H), 7.13 (t, *J* = 5.2 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.79-5.70 (m, 1H), 4.87 (d, *J* = 10.0 Hz, 1H), 4.81 (d, *J* = 17.2 Hz, 1H), 3.57-3.51 (m, 1H), 3.36 (t, *J* = 8.4 Hz, 1H), 3.22 (s, 3H), 2.53-2.48 (m, 1H), 2.43-2.39 (m, 1H), 2.32-2.24 (m, 2H), 2.15 (t, *J* = 5.6 Hz, 1H), 2.06 (dd, *J* = 14.8 Hz, 8.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.0, 180.6, 142.6, 142.4, 138.1, 135.0, 133.0, 131.9, 128.1, 128.0, 122.6, 122.4, 116.1, 108.0, 55.2, 49.1, 44.7, 38.5, 34.8, 31.9, 28.6, 26.1 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{22}NO_2S$: 364.1366; found: 364.1370.



(2*S**,4*S**)-**6fa**
$C_{22}H_{21}NO_2S$
M = 363.48 g/mol

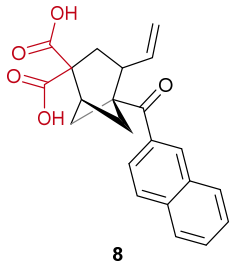
7fa
$C_{22}H_{21}NO_2S$
M = 363.48 g/mol

(2*S**,4*S**)-**6fa: R*f*** = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.71 (d, *J* = 4.2 Hz, 1H), 7.63 (d, *J* = 4.8 Hz, 1H), 7.33-7.29 (m, 1H), 7.16-7.09 (m, 2H), 6.87 (t, *J* = 6.6 Hz, 2H), 5.91-5.85 (m, 1H), 4.86-4.84 (m, 2H), 3.35-3.30 (m, 1H), 3.22 (s, 3H), 3.02-2.97 (m, 2H), 2.90 (d, *J* = 13.2 Hz, 1H), 2.56 (t, *J* = 9.6 Hz, 1H), 2.43-2.30 (m, 2H), 2.15-2.11 (m, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{22}NO_2S$: 364.1366; found: 364.1369.

7fa: R*f* = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.63 (d, *J* = 4.8 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 3.6 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.33-7.29 (m, 1H), 7.16-7.09 (m, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.27 (dt, *J* = 9.6 Hz, 9.0 Hz, 1H), 6.09 (dt, *J* = 9.0 Hz, 8.4 Hz, 1H), 3.26-3.23 (m, 1H), 3.19 (s, 3H), 3.02-2.97 (m, 1H), 2.83 (dd, *J* = 15.6 Hz, 6.6 Hz, 1H), 2.75 (t, *J* = 10.8 Hz, 1H), 2.69 (dd, *J* = 15.6 Hz, 9.0 Hz, 1H), 2.43-2.30 (m, 2H), 2.15-2.11 (m, 1H), 2.05 (dd, *J* = 15.0 Hz,

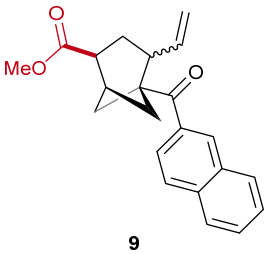
7.8 Hz, 1H) ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{22}NO_2S$: 364.1366; found: 364.1367.

^{13}C NMR (150 MHz, $CDCl_3$): δ 196.9 (for 7**fa**), 196.4 (for (2*S**,4*S**)-**6fa**), 180.4 (for (2*S**,4*S**)-**6fa**), 179.5 (for **7fa**), 143.1, 142.8, 142.6, 140.7, 138.6, 135.0, 134.6, 133.23, 133.16, 132.2, 132.0, 131.6, 131.2, 128.1, 128.02, 128.00, 127.9, 124.05, 123.99, 122.25, 122.15, 116.0, 108.2, 108.1, 55.2, 50.3, 49.7, 49.0, 46.0, 38.5, 36.9, 36.2, 35.3, 34.4, 31.1, 30.5, 30.2, 28.1, 26.3, 26.0 ppm.



8
$C_{22}H_{20}O_5$
M = 364.40 g/mol

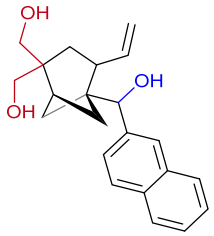
5-(2-naphthoyl)-4-vinylbicyclo[3.1.1]heptane-2,2-dicarboxylic acid (**8**): **R_f** = 0.25 (CH_2Cl_2/MeOH = 10/1). **^{1}H NMR** (400 MHz, CD_3OD): δ 8.33 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 1H, 7.90-7.82 (m, 3H), 7.62-7.54 (m, 2H), 5.69-5.60 (m, 1H), 4.70 (d, *J* = 10.4 Hz, 1H), 4.63 (d, *J* = 16.8 Hz, 1H), 3.32-3.31 (m, 1H), 3.27 (t, *J* = 8.0 Hz, 1H), 2.91 (t, *J* = 6.4 Hz, 1H), 2.69 (dd, *J* = 14.4 Hz, 7.2 Hz, 1H), 2.59-2.55 (m, 1H), 2.38 (dd, J = 10.0 Hz, 6.0 Hz, 1H), 2.19-2.09 (m, 2H), 2.02 (dd, *J* = 14.8 Hz, 8.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, CD_3OD): δ 205.0, 175.0, 174.8, 139.6, 136.8, 134.5, 133.8, 131.4, 130.7, 129.7, 129.4, 128.7, 127.9, 125.5, 116.3, 58.3, 56.8, 46.8, 39.5, 35.9, 31.8, 29.8 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{21}O_5$: 365.1384; found: 365.1381.



9
$C_{22}H_{22}O_3$
M = 334.42 g/mol

methyl 5-(2-naphthoyl)-4-vinylbicyclo[3.1.1]heptane-2-carboxylate (**9**): **The one isomer R_f** = 0.25 (petroleum ether/EtOAc = 20/1). **One of the diastereomers: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.91-7.85 (m, 3H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 5.71-5.65 (m, 1H), 4.81 (d, *J* = 10.2 Hz, 1H), 4.71 (d, *J* = 17.4 Hz, 1H), 3.76 (s, 3H), 3.34-3.31 (m, 1H), 3.08-3.05 (m, 1H), 2.66-2.64 (m, 1H), 2.54-2.50 (m, 1H), 2.49-2.46 (m, 1H), 2.43 (dd, *J* = 10.2 Hz, 6.6 Hz, 1H), 2.27 (t, *J* = 8.4 Hz, 1H), 1.97 (t, *J* = 8.4 Hz, 1H), 1.94-1.90 (m, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 203.1, 175.8, 138.1, 135.3, 133.1, 132.4, 130.2, 129.6, 128.31, 128.26, 127.7, 126.6, 124.7, 115.7, 56.1, 51.8, 44.5, 42.7, 36.9, 32.0, 31.0, 24.9 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{23}O_3$: 335.1642; found: 335.1637.

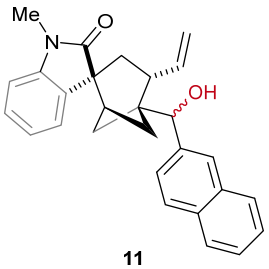
The other diastereomer: R_f = 0.20 (petroleum ether/EtOAc = 20/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.89-7.85 (m, 3H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 5.69-5.63 (m, 1H), 4.73 (d, *J* = 10.2 Hz, 1H), 4.66 (d, *J* = 16.8 Hz, 1H), 3.72 (s, 3H), 3.17-3.13 (m, 1H), 2.99 (t, *J* = 9.0 Hz, 1H), 2.70 (dd, *J* = 9.6 Hz, 7.2 Hz, 1H), 2.61 (t, *J* = 6.0 Hz, 1H), 2.32 (dd, *J* = 10.8 Hz, 6.0 Hz, 1H), 2.24-2.17 (m, 2H), 2.14-2.08 (m, 1H), 1.98 (t, *J* = 9.0 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 203.2, 175.5, 138.3, 135.3, 133.5, 132.4, 130.0, 129.5, 128.3, 128.2, 127.7, 126.6, 124.7, 115.8, 55.9, 51.8, 46.5, 44.1, 42.5, 32.1, 26.9, 26.7 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{23}O_3$: 335.1642; found: 335.1639.



10
$C_{22}H_{26}O_3$
M = 338.45 g/mol

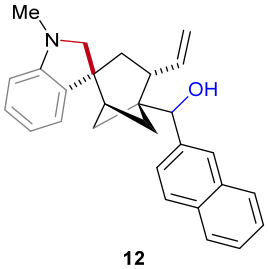
(5-(hydroxy(naphthalen-2-yl)methyl)-4-vinylbicyclo[3.1.1]heptane-2,2-diyl)dimethanol (**10**): **R_f** = 0.25 (petroleum ether/EtOAc = 1/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.84-7.79 (m, 3H), 7.70 (s, 1H), 7.49-7.45 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 5.98-5.92 (m, 1H), 5.14 (d, *J* = 16.8 Hz, 1H), 5.09 (d, *J* = 10.2 Hz, 1H), 4.77 (s, 1H), 3.65-3.59 (m, 2H),

3.55-3.49 (m, 2H), 2.84-2.80 (m, 1H), 2.64 (broad s, 2H), 2.20 (broad s, 1H), 2.10-2.06 (m, 1H), 1.85-1.83 (m, 1H), 1.59-1.52 (m, 2H), 1.41 (t, *J* = 9.0 Hz, 1H), 1.33-1.30 (m, 1H), 1.13 (dd, *J* = 15.0 Hz, 7.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.1, 139.3, 133.0, 132.8, 127.9, 127.6, 127.2, 126.0, 125.8, 125.7, 125.6, 115.4, 76.6, 69.0, 67.8, 49.4, 43.3, 41.2, 32.9, 30.6, 29.1, 26.9 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{22}H_{27}O_3$: 339.1955; found: 339.1960.



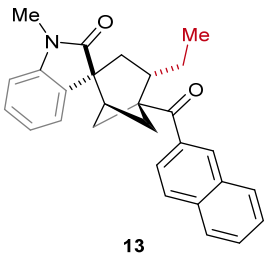
11
$C_{28}H_{27}NO_2$
M = 409.53 g/mol

5-(hydroxy(naphthalen-2-yl)methyl)-1'-methyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one (**11**): The major diastereomers: **R_f** = 0.25 (petroleum ether/EtOAc = 5/1). **^{1}H NMR:** (400 MHz, $CDCl_3$): δ 7.84-7.76 (m, 4H), 7.49-7.43 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.25-7.20 (m, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 7.2 Hz, 1H), 6.21-6.12 (m, 1H), 5.24 (d, *J* = 16.8 Hz, 1H), 5.18 (d, *J* = 10.0 Hz, 1H), 4.90 (s, 1H), 3.31-3.25 (m, 1H), 3.13 (s, 3H), 2.63 (t, *J* = 8.4 Hz, 1H), 2.36 (dd, *J* = 14.8 Hz, 8.8 Hz, 1H), 2.19-2.14 (m, 1H), 1.89-1.80 (m, 3H), 1.66 (broad s, 1H), 1.55-1.51 (m, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 180.8, 142.7, 140.7, 139.1, 135.4, 133.0, 132.7, 127.9, 127.8, 127.6, 127.3, 126.0, 125.9, 125.68, 125.66, 122.7, 122.2, 116.2, 107.8, 76.8, 49.8, 48.4, 42.9, 39.6, 32.3, 28.3, 28.2, 26.1 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{28}NO_2$: 410.2115; found: 410.2118.



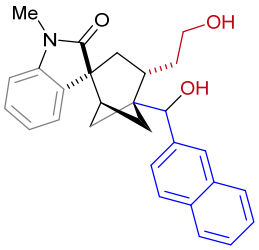
12
$C_{28}H_{29}NO$
M = 395.55 g/mol

(1'-methyl-4-vinylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-5-yl)(naphthalen-2-yl) methanol (**12**): $\mathbf{R_f}$ = 0.20 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.85-7.81 (m, 3H), 7.75 (s, 1H), 7.50-7.45 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.07-7.04 (m, 2H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 6.08-6.01 (m, 1H), 5.21 (d, *J* = 16.8 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 4.86 (s, 1H), 3.29 (d, *J* = 9.0 Hz, 1H), 2.99 (d, *J* = 8.4 Hz, 1H), 2.97-2.93 (m, 1H), 2.71 (s, 3H), 2.17-2.10 (m, 2H), 2.07 (t, *J* = 8.4 Hz, 2H), 1.95 (t, *J* = 8.4 Hz, 1H), 1.85 (dd, *J* = 15.0 Hz, 9.6 Hz, 1H), 1.44-1.41 (m, 1H), 1.37 (t, *J* = 9.0 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 152.3, 140.8, 139.2, 138.6, 133.0, 132.8, 127.9, 127.6, 127.2, 126.0, 125.9, 125.8, 125.7, 121.8, 117.9, 115.4, 107.3, 76.3, 67.2, 48.4, 46.9, 44.7, 39.6, 37.6, 35.9, 31.9, 27.4 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{30}NO$: 396.2322; found: 396.2324.



13
$C_{28}H_{27}NO_2$
M = 409.53 g/mol

5-(2-naphthoyl)-4-ethyl-1'-methylspiro[bicyclo[3.1.1]heptane-2,3'-indolin]-2'-one (**13**): $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.08-8.06 (m, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.53 (dd, *J* = 9.0 Hz, 7.8 Hz, 1H), 3.24 (s, 3H), 3.01-2.96 (m, 1H), 2.51 (dd, *J* = 10.2 Hz, 7.8 Hz, 1H), 2.46 (dd, *J* = 10.2 Hz, 6.0 Hz, 1H), 2.38-2.32 (m, 2H), 2.17 (t, *J* = 6.0 Hz, 1H), 1.91 (dd, *J* = 14.4 Hz, 9.0 Hz, 1H), 1.31-1.27 (m, 2H), 0.74 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 203.9, 181.1, 142.6, 135.53, 135.46, 132.9, 132.6, 130.3, 129.8, 128.44, 128.39, 128.1, 127.7, 126.6, 124.6, 122.6, 122.3, 108.0, 56.3, 49.4, 40.9, 38.9, 36.1, 32.1, 29.2, 26.5, 26.1, 11.1 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{28}NO_2$: 410.2115; found: 410.2117.

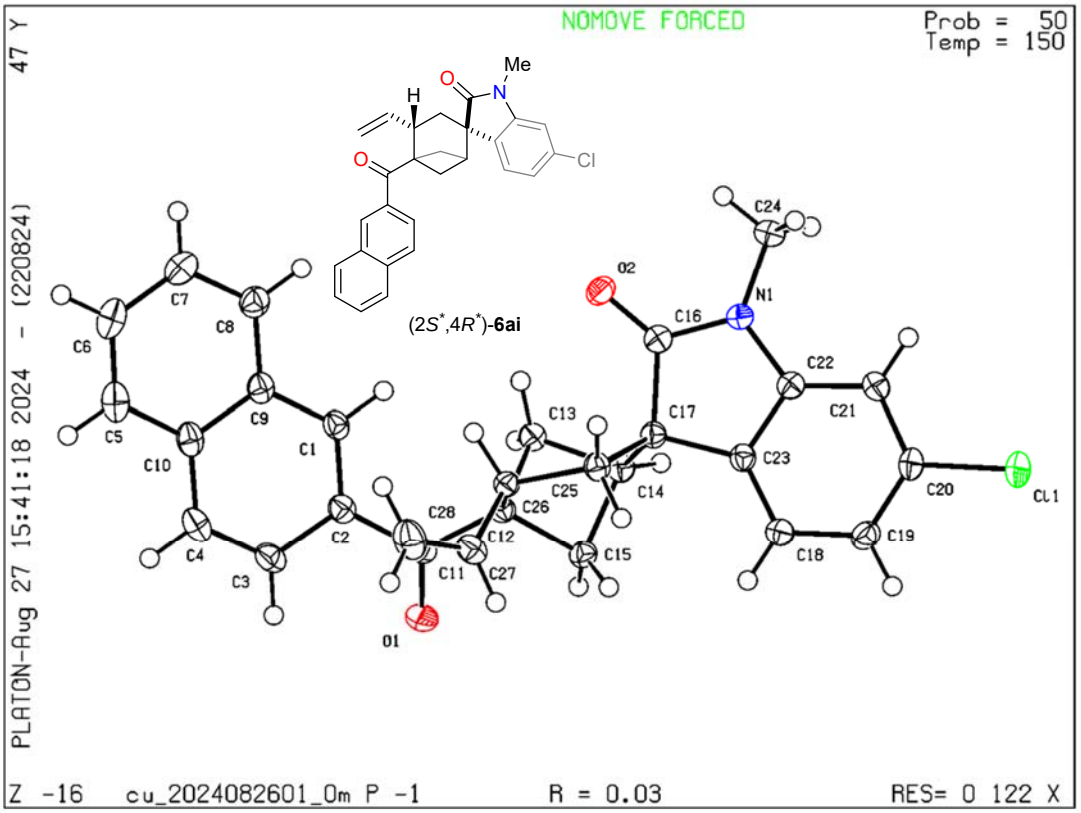


14
$C_{28}H_{29}NO_3$
M = 427.54 g/mol

5-(hydroxy(naphthalen-2-yl)methyl)-4-(2-hydroxyethyl)-1'-methylspiro[bicycle [3.1.1] heptane-2,3'-indolin]-2'-one (**14**): $\mathbf{R_f}$ = 0.25 (petroleum ether/EtOAc = 5/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.82-7.78 (m, 2H), 7.47-7.44 (m, 3H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.25-7.23 (m, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 3.13 (s, 3H), 2.78-2.72 (m, 1H), 2.40-2.32 (m, 2H), 2.24 (t, *J* = 9.0 Hz, 1H), 2.18 (dd, *J* = 13.8 Hz, 6.6 Hz, 1H), 2.10-2.06 (m, 4H), 1.93 (t, *J* = 6.0 Hz, 2H), 1.73-1.66 (m, 1H), 1.37 (dd, *J* = 9.0 Hz, 6.6 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 180.7, 143.4, 142.7, 135.8, 133.0, 132.3, 128.1, 127.8, 127.5, 127.4, 125.9, 125.5, 124.3, 122.9, 122.3, 121.9, 107.8, 82.3, 57.3, 48.4, 43.8, 43.6, 38.3, 34.2, 33.2, 31.0, 27.9, 26.0 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{28}H_{30}NO_3$: 428.2220; found: 428.2229.

11 Crystal Structure of (2*S**,4*R**)-6ai

Note: The thermal ellipsoids are 50% probability level. The crystals are grown by slow solvent (CH_2Cl_2/Et_2O) evaporation at room temperature. CCDC number of racemic **(2*S**,4*R**)-6ai** is 2417046.



Datablock: cu_2024082601_0m

Bond precision: C-C = 0.0019 A Wavelength=1.54178

Cell: a=7.6756(2) b=12.5665(4) c=12.6858(4)
alpha=111.162(1) beta=96.177(1) gamma=102.052(1)
Temperature: 150 K

	Calculated	Reported
Volume	1093.26(6)	1093.25(6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C28 H24 Cl N O2	C28 H24 Cl N O2
Sum formula	C28 H24 Cl N O2	C28 H24 Cl N O2
Mr	441.93	441.93
Dx,g cm-3	1.342	1.342
Z	2	2
Mu (mm-1)	1.748	1.748
F000	464.0	464.0
F000'	465.95	
h,k,lmax	9,15,15	9,15,15
Nref	4343	4324
Tmin,Tmax	0.769,0.924	0.647,0.754
Tmin'	0.722	

Correction method= # Reported T Limits: Tmin=0.647 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 72.510

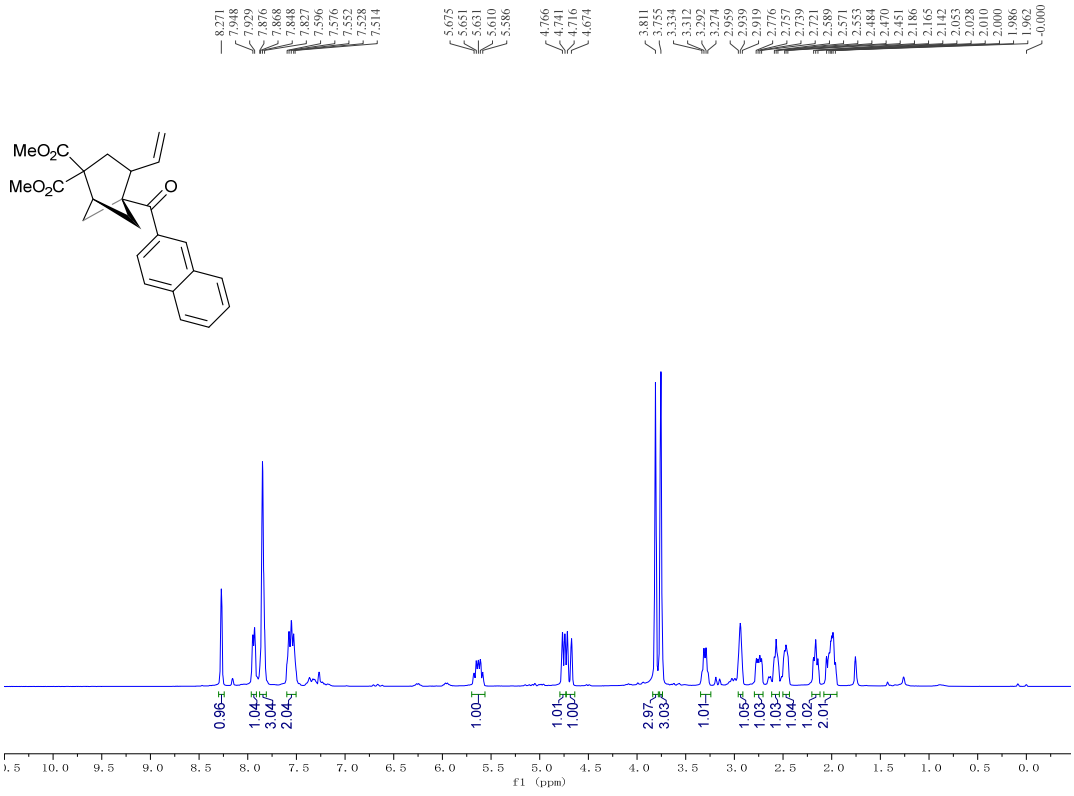
R(reflections)= 0.0322(3935) wR2(reflections)= 0.0860(4324)

S = 1.073 Npar= 298

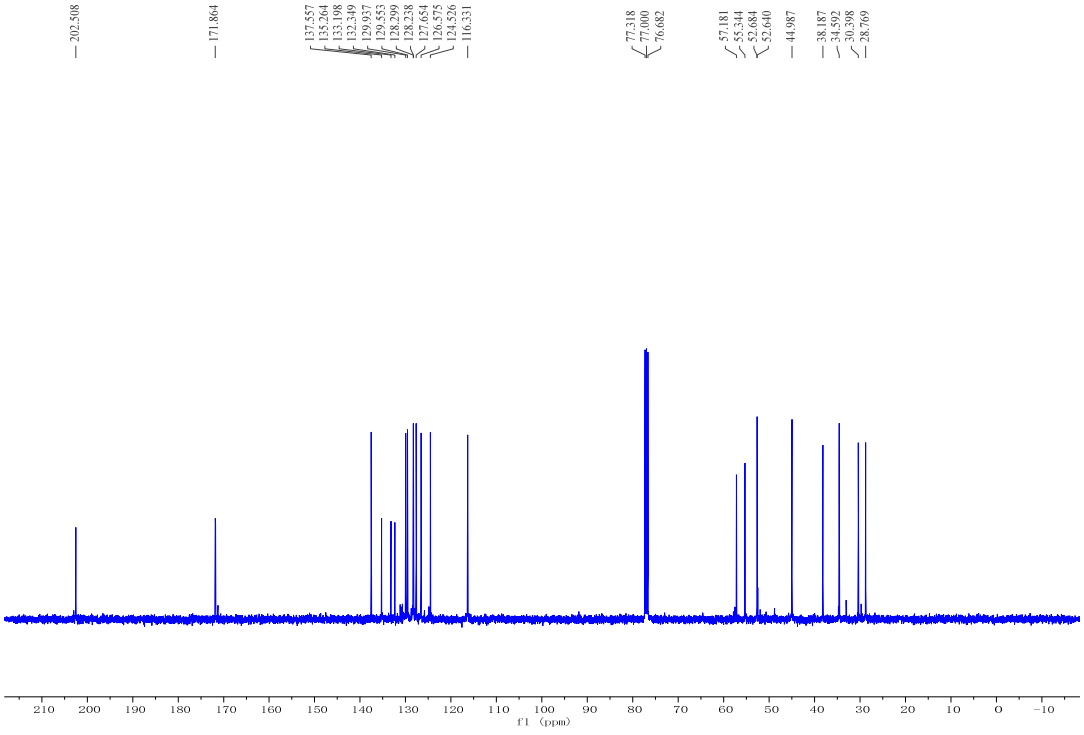
12 NMR Spectra

^{1}H and ^{13}C NMR Spectra for Compound 3aa:

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

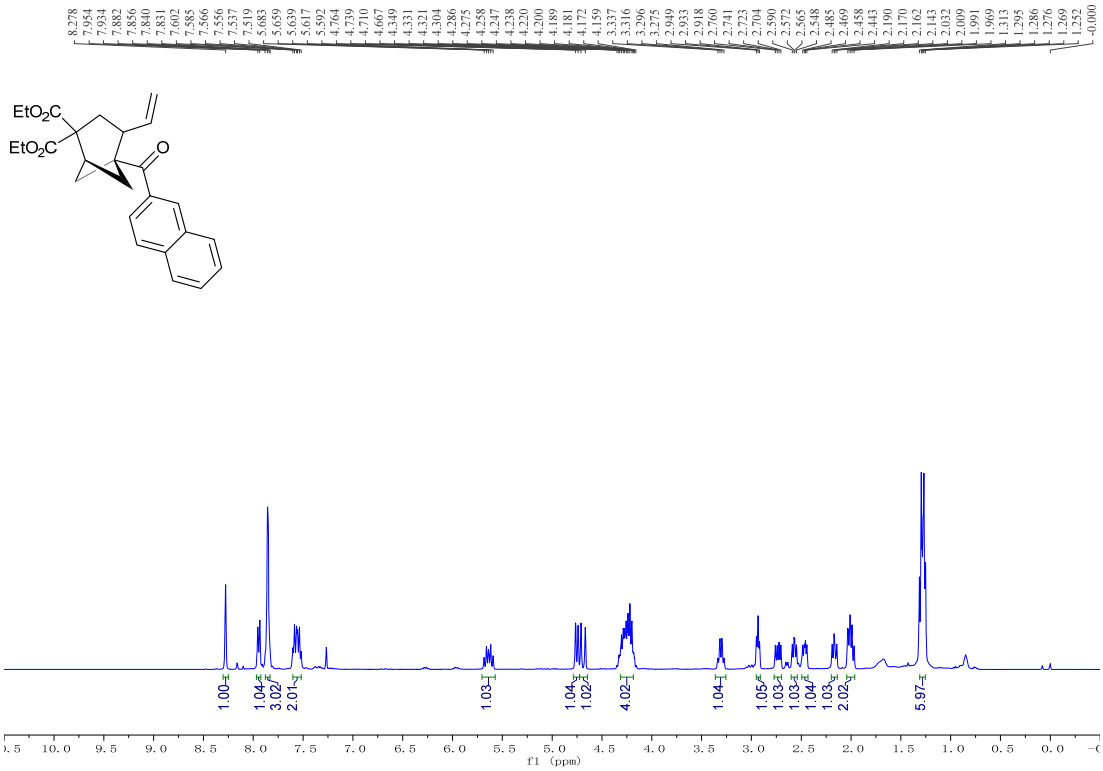


^{13}C NMR (100 MHz, $CDCl_3$)

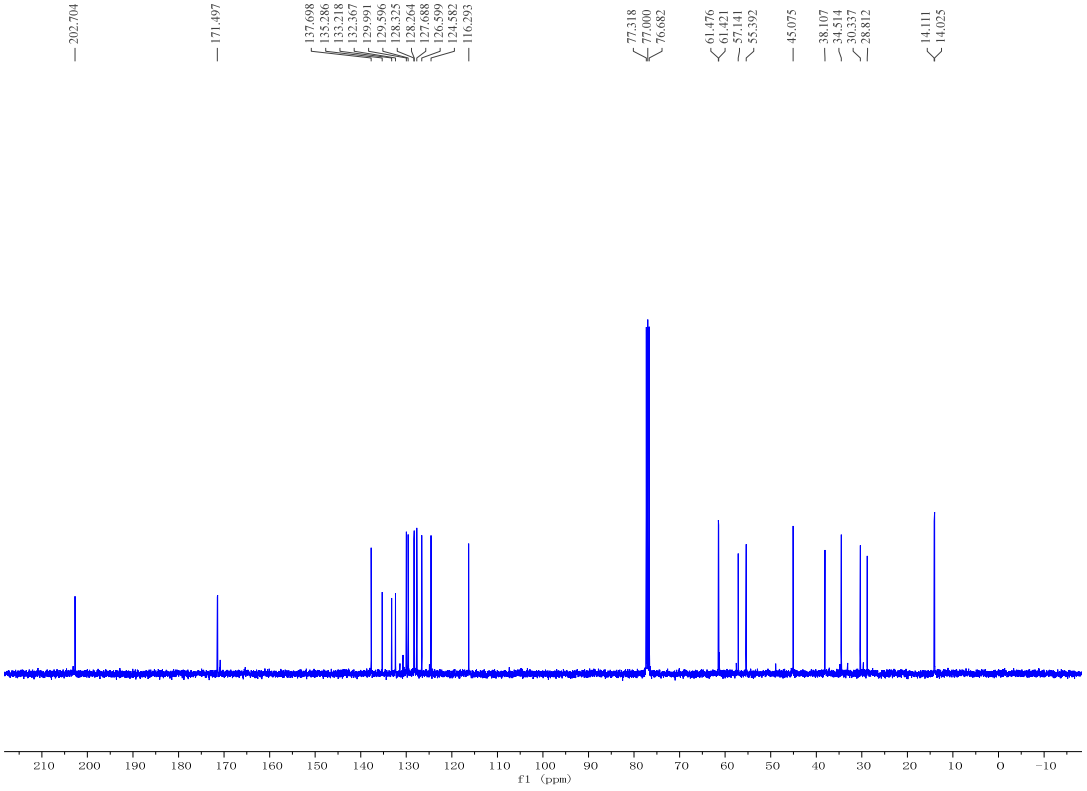


^{1}H and ^{13}C NMR Spectra for Compound 3ab:

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

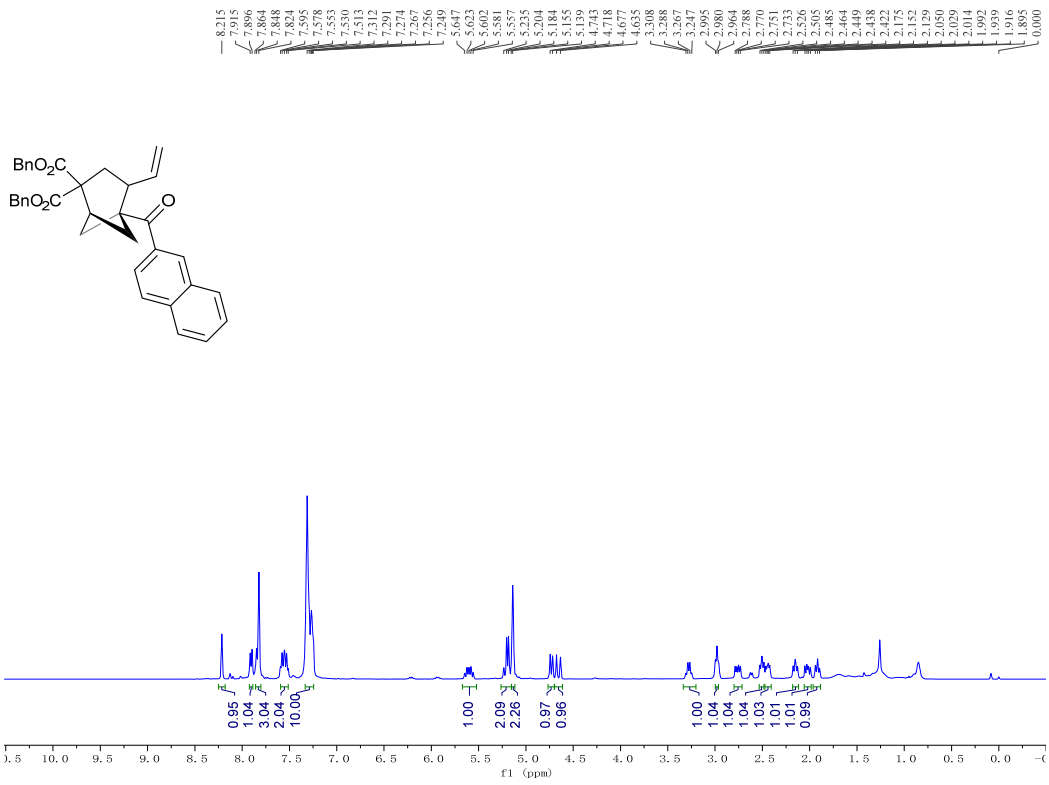


^{13}C NMR (100 MHz, $CDCl_3$)

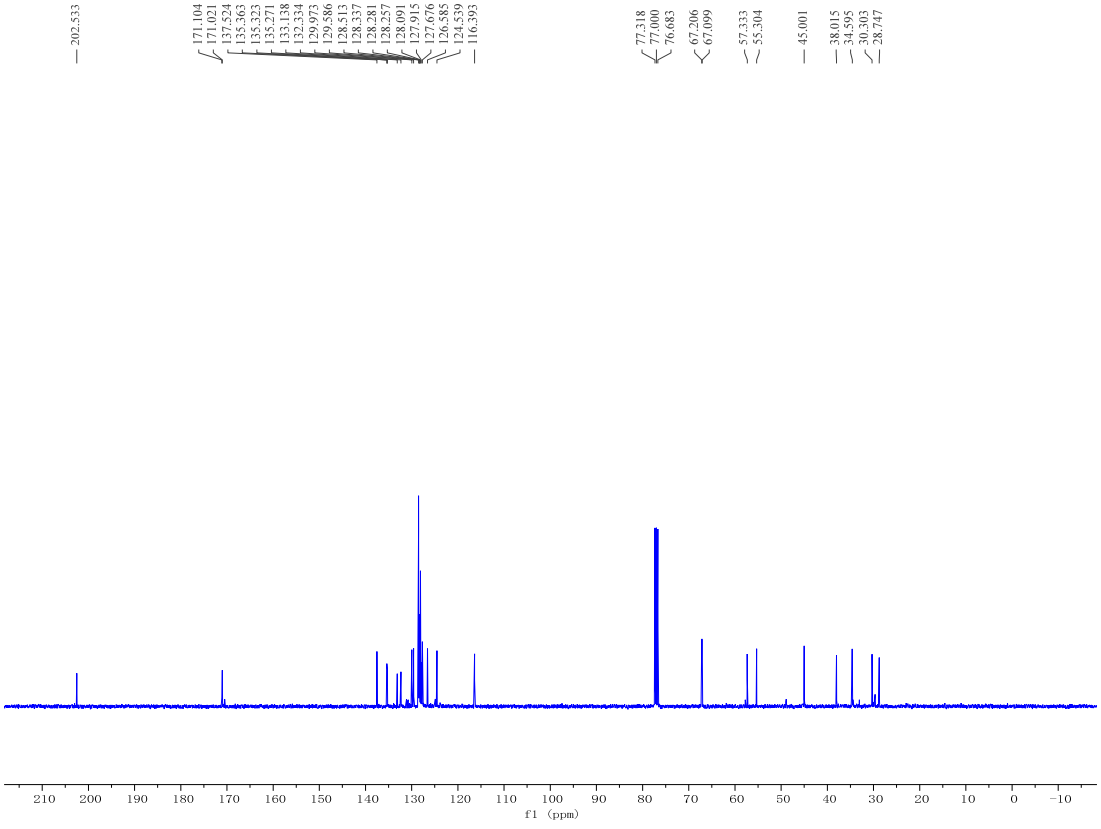


^{1}H and ^{13}C NMR Spectra for Compound 3ac:

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

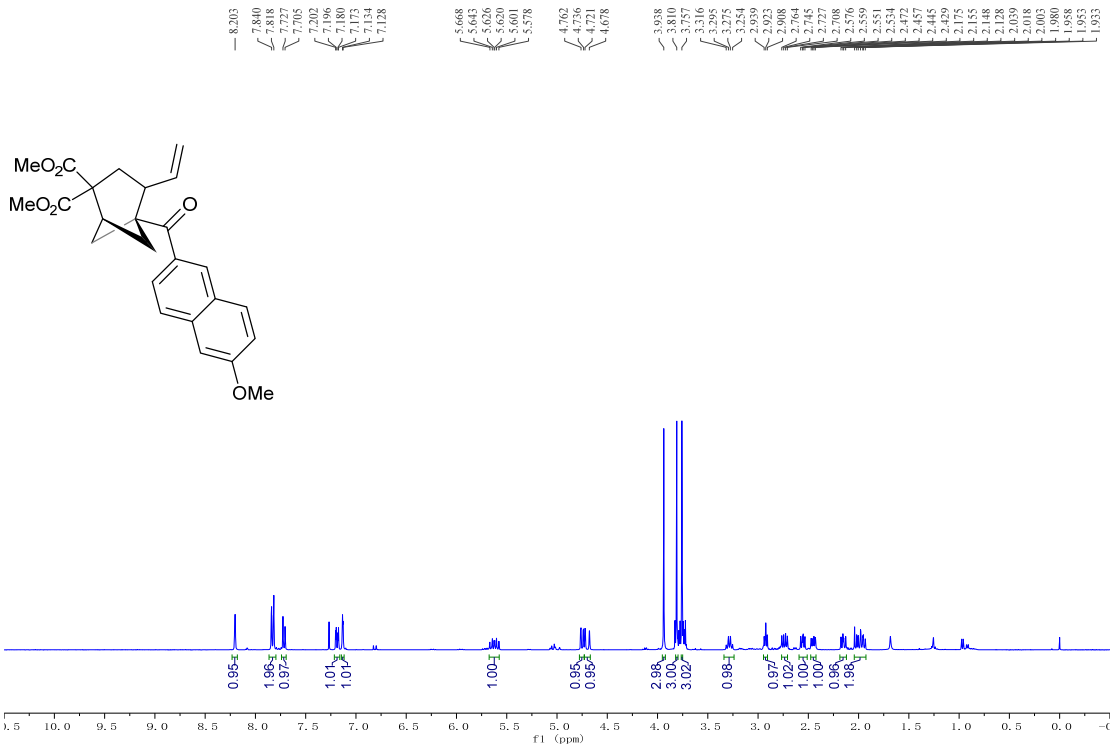


^{13}C NMR (100 MHz, $CDCl_3$)

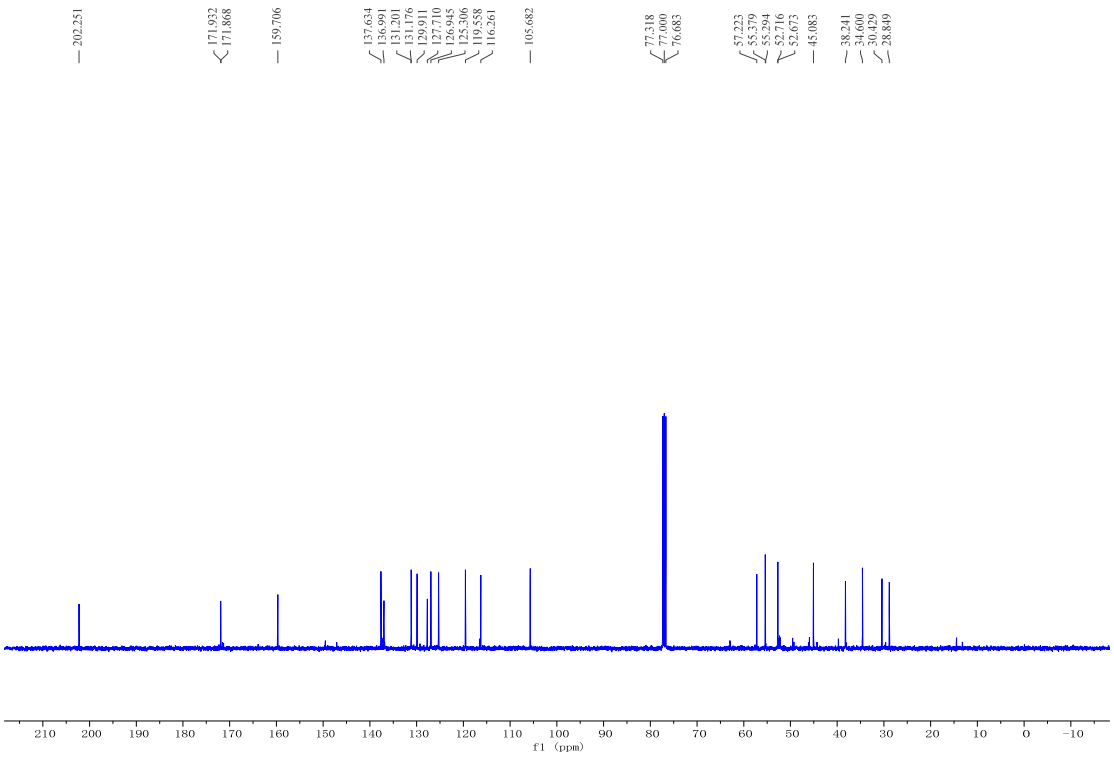


^{1}H and ^{13}C NMR Spectra for Compound 3ba:

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

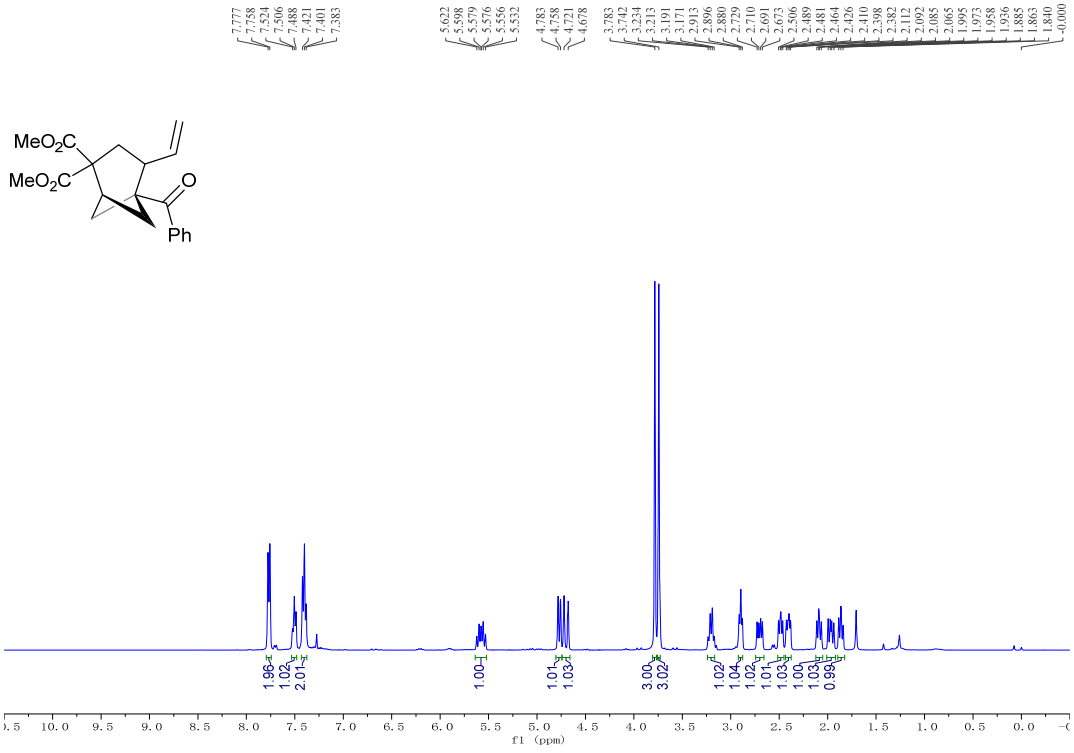


^{13}C NMR (100 MHz, $CDCl_3$)

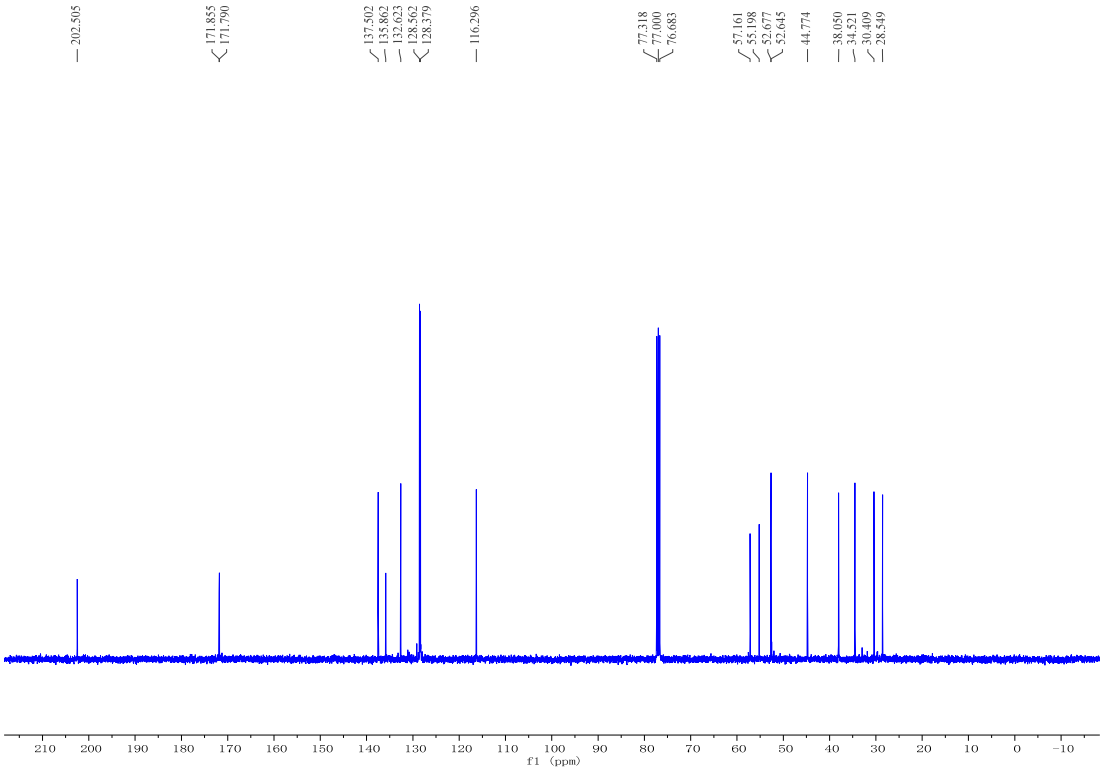


^{1}H and ^{13}C NMR Spectra for Compound 3ca:

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

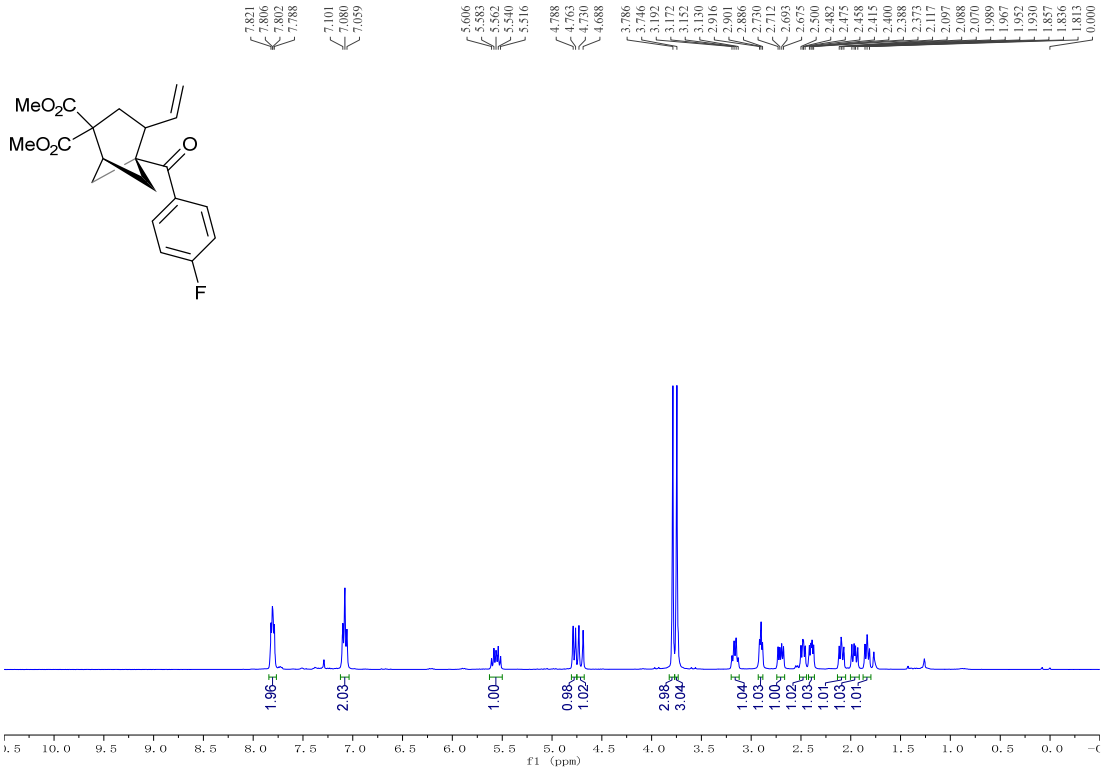


^{13}C NMR (100 MHz, $CDCl_3$)

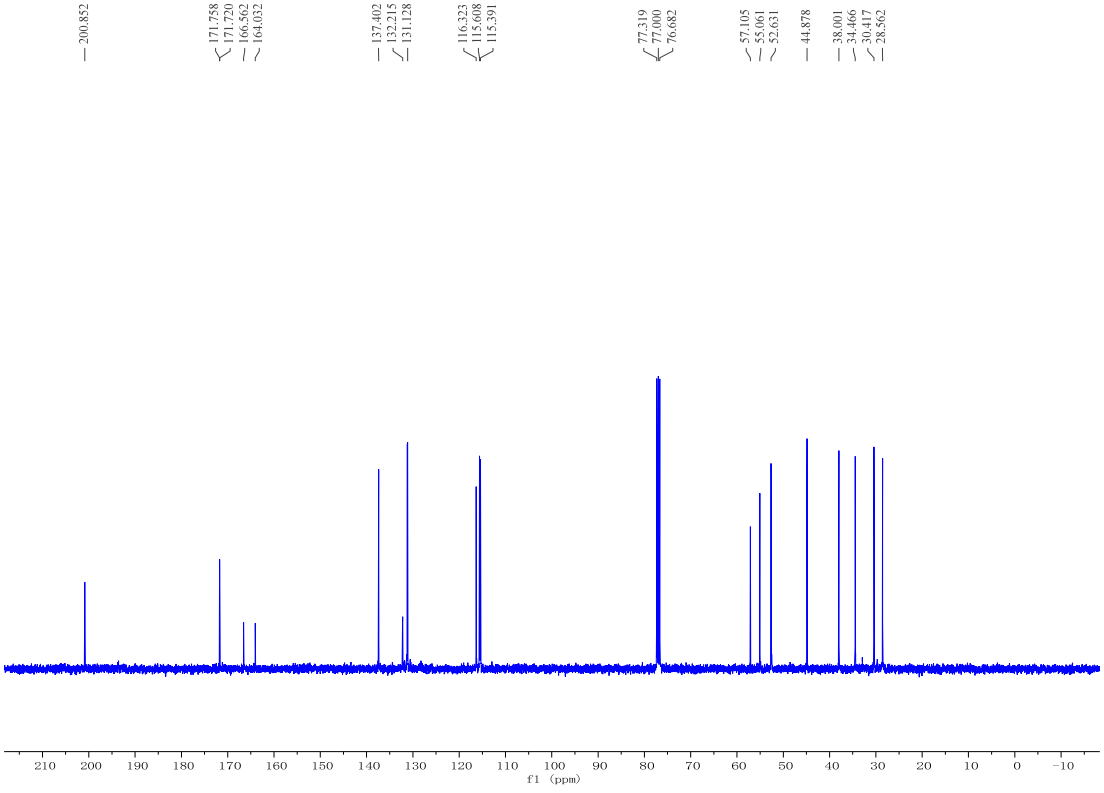


^{1}H ,^{13}C and ^{19}F NMR Spectra for Compound 3da:

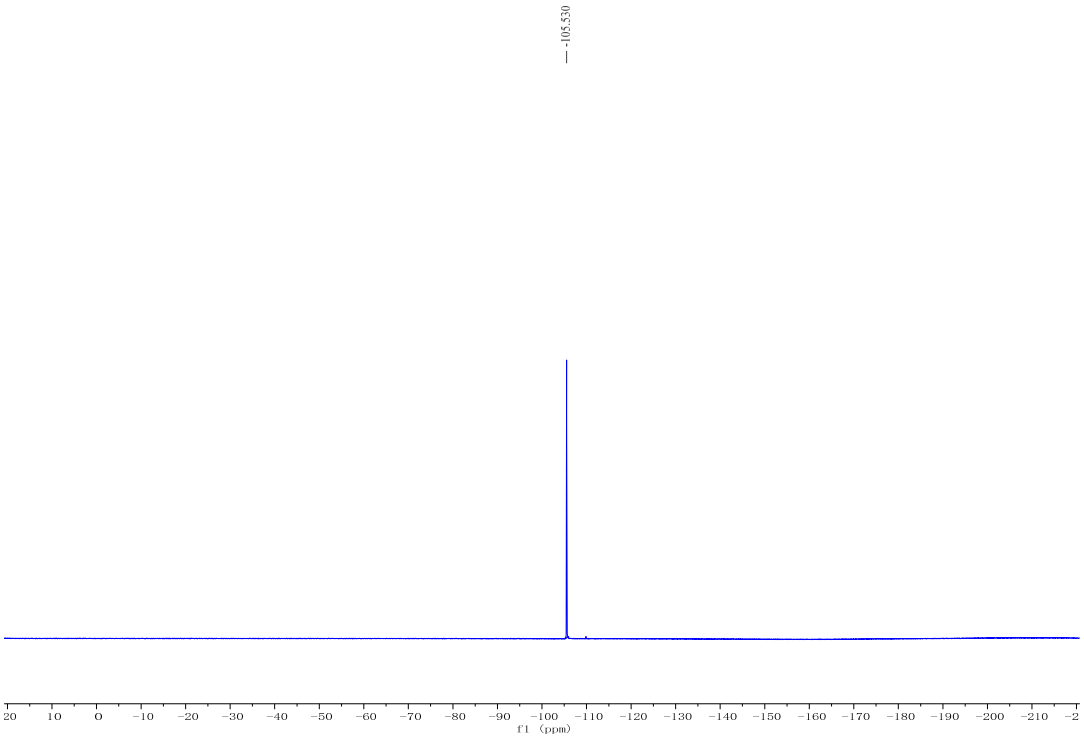
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

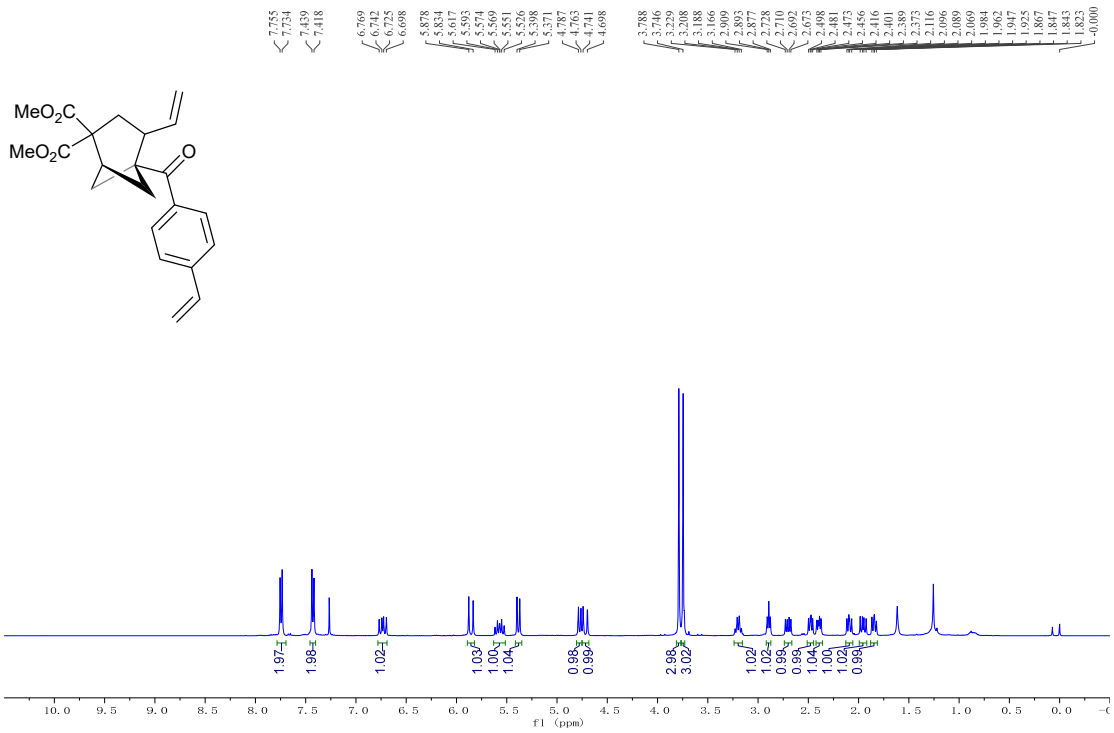


^{19}F NMR (376 MHz, $CDCl_3$)

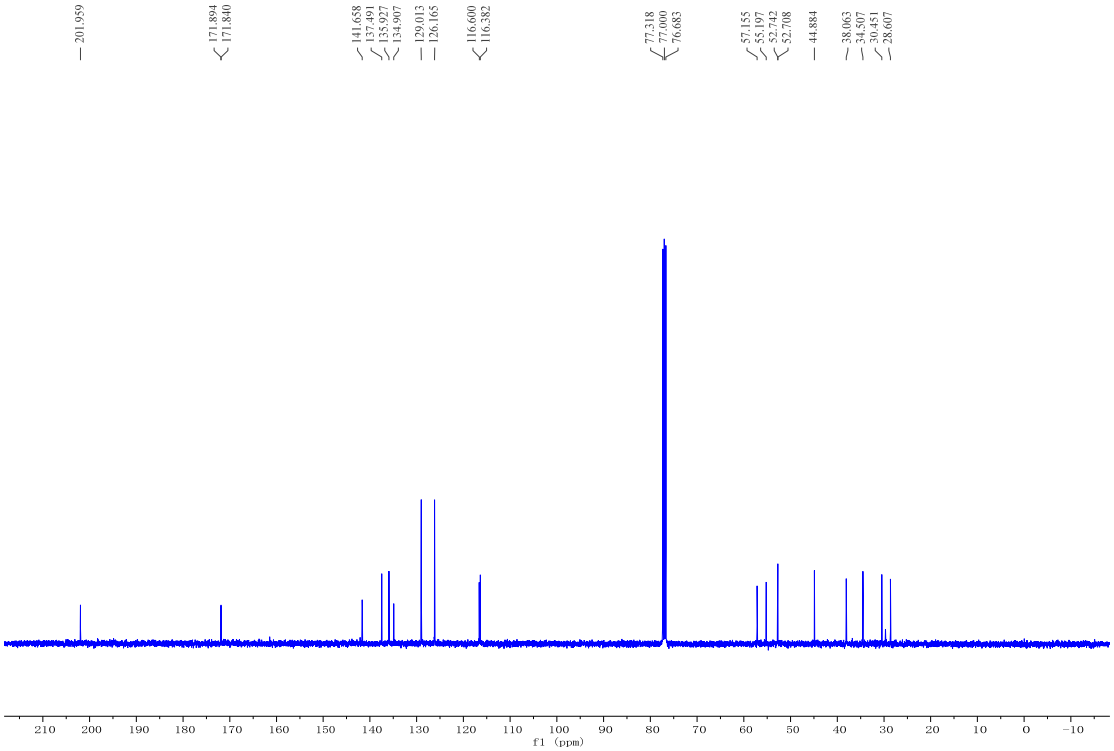


^{1}H and ^{13}C NMR Spectra for Compound 3ea:

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

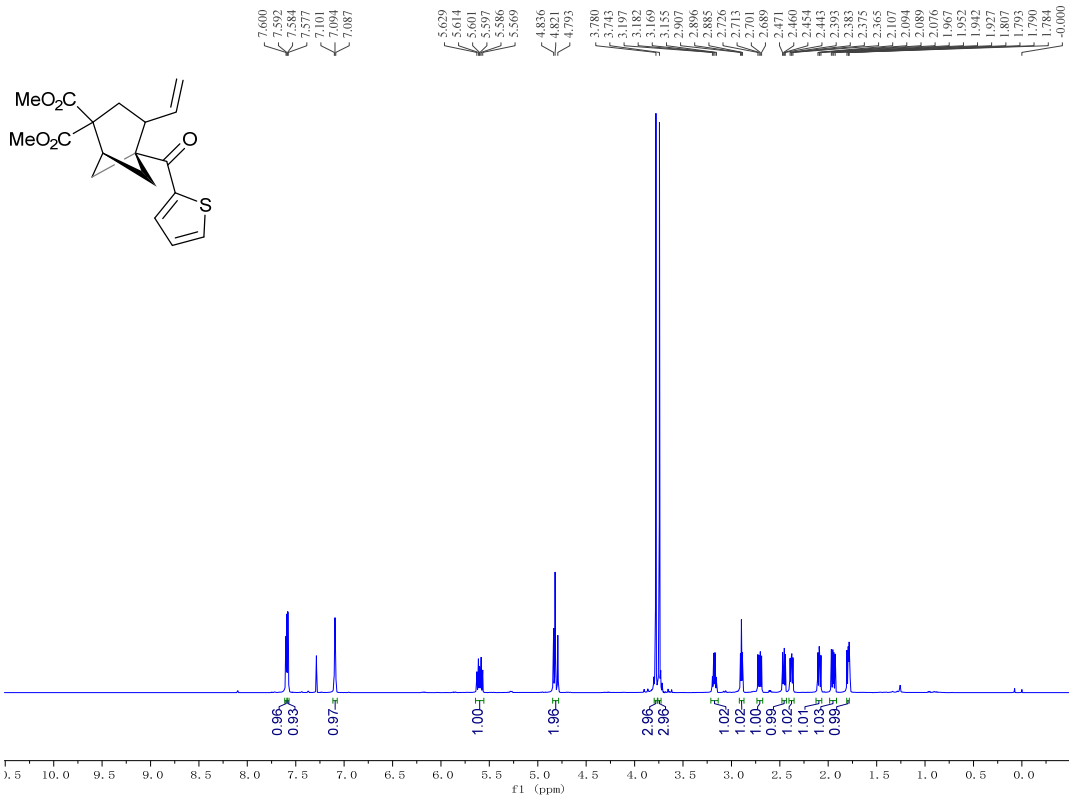


^{13}C NMR (100 MHz, $CDCl_3$)

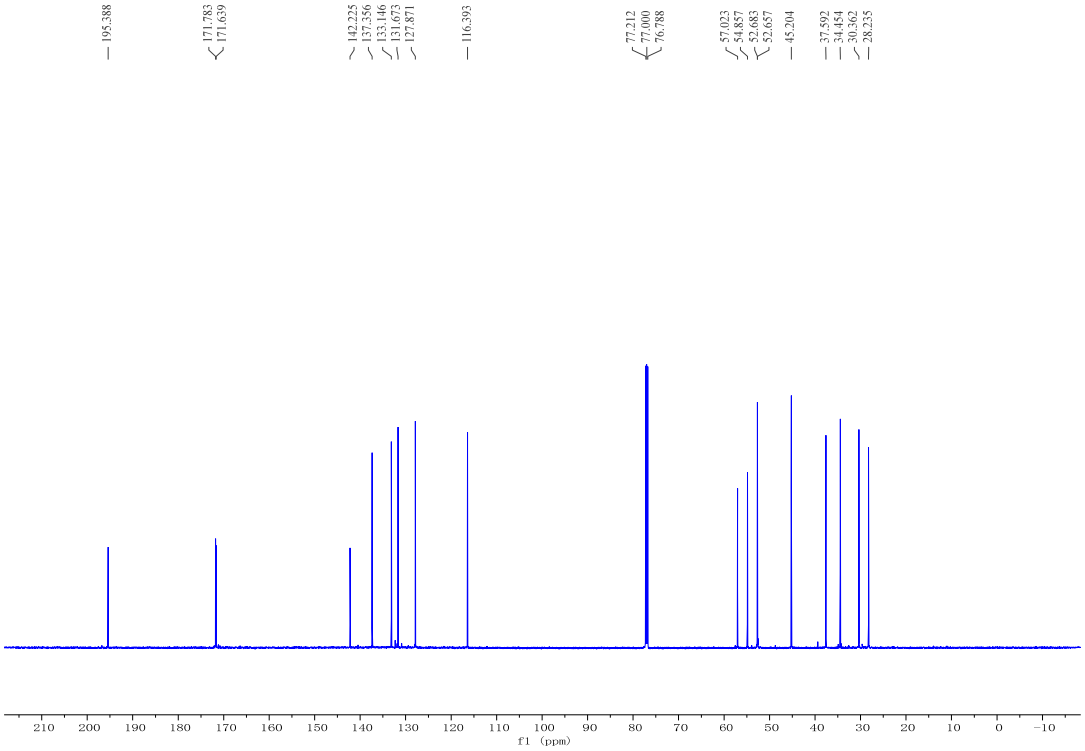


^{1}H and ^{13}C NMR Spectra for Compound 3fa:

^{1}H NMR (600 MHz, $CDCl_3$)

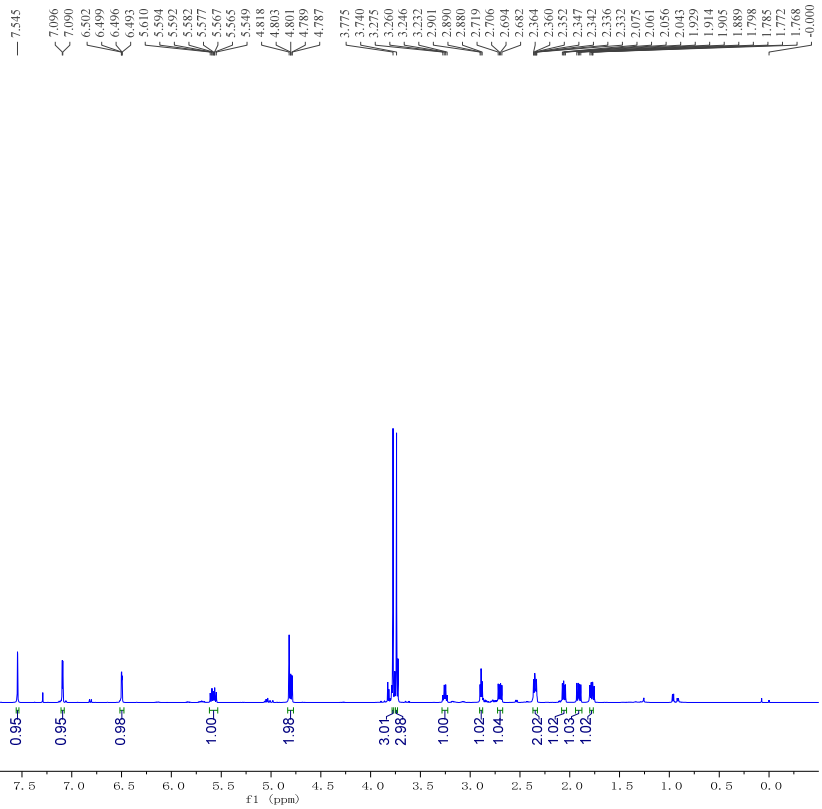


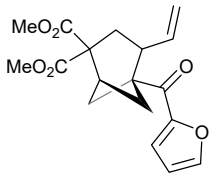
^{13}C NMR (150 MHz, $CDCl_3$)



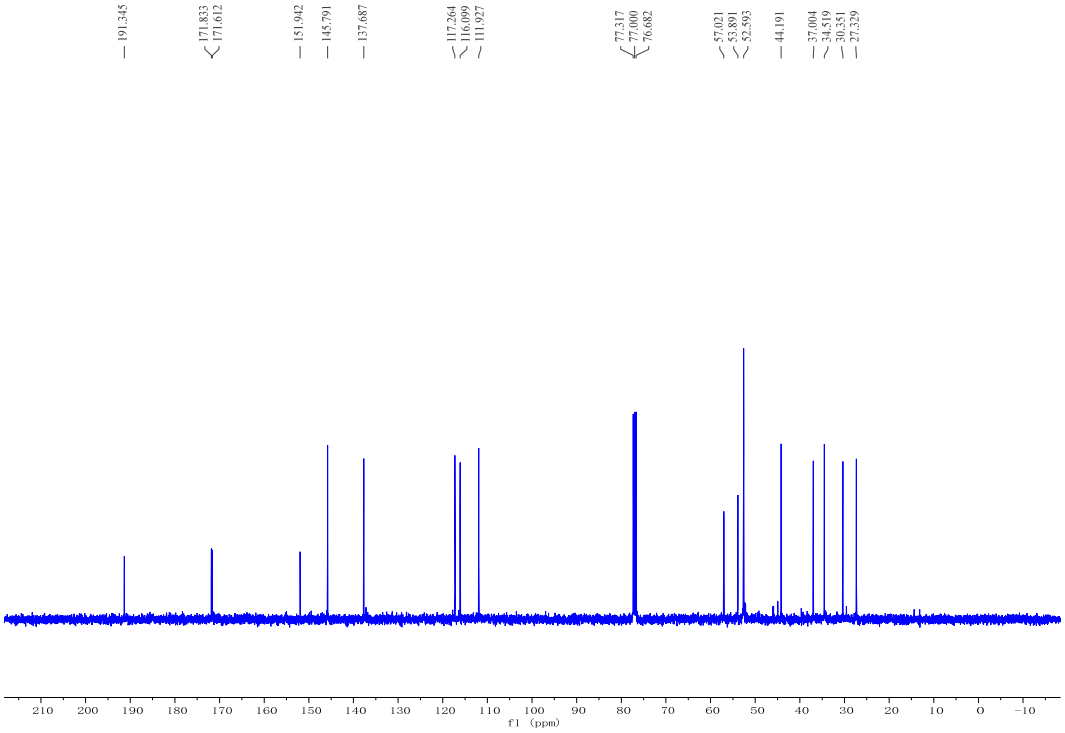
^{1}H and ^{13}C NMR Spectra for Compound 3ga:

^{1}H NMR (600 MHz, $CDCl_3$)



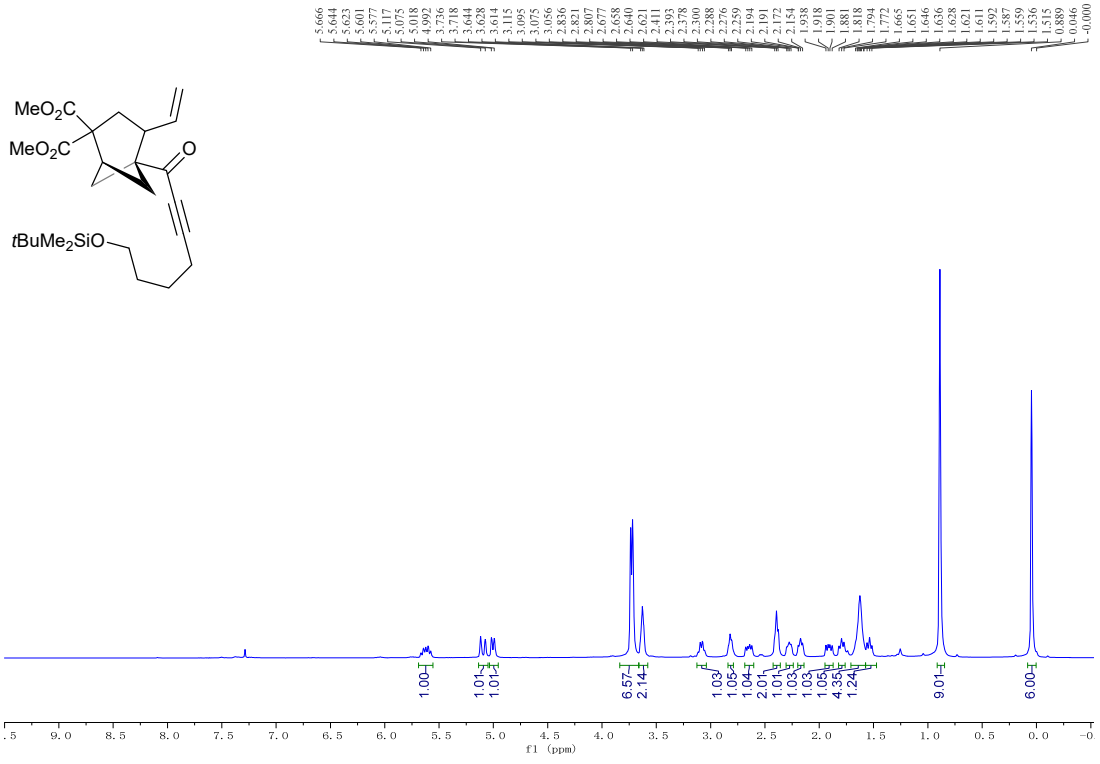


^{13}C NMR (100 MHz, $CDCl_3$)

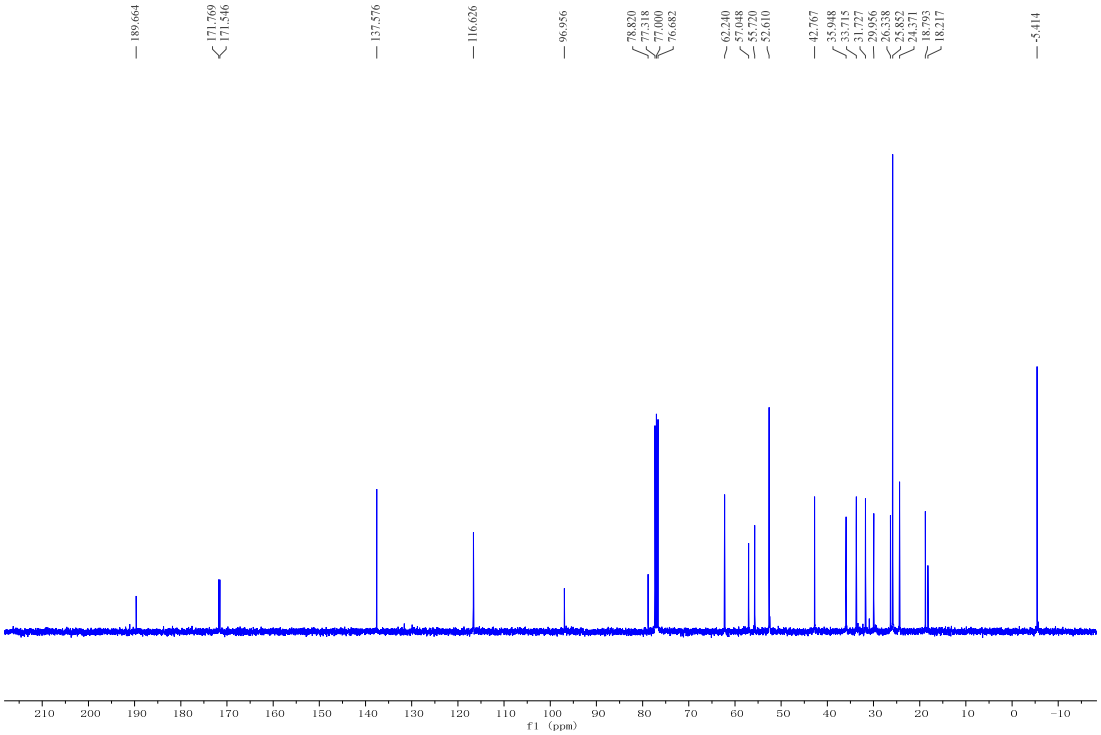


^{1}H and ^{13}C NMR Spectra for Compound 3ha:

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

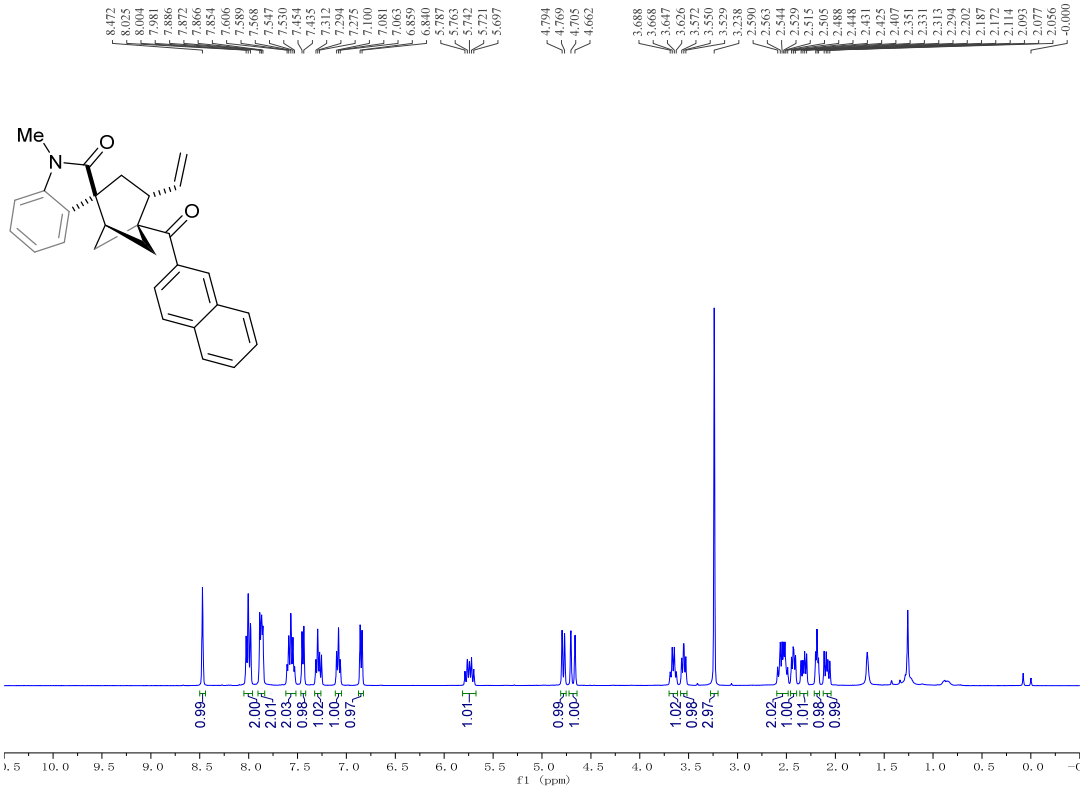


^{13}C NMR (100 MHz, $CDCl_3$)

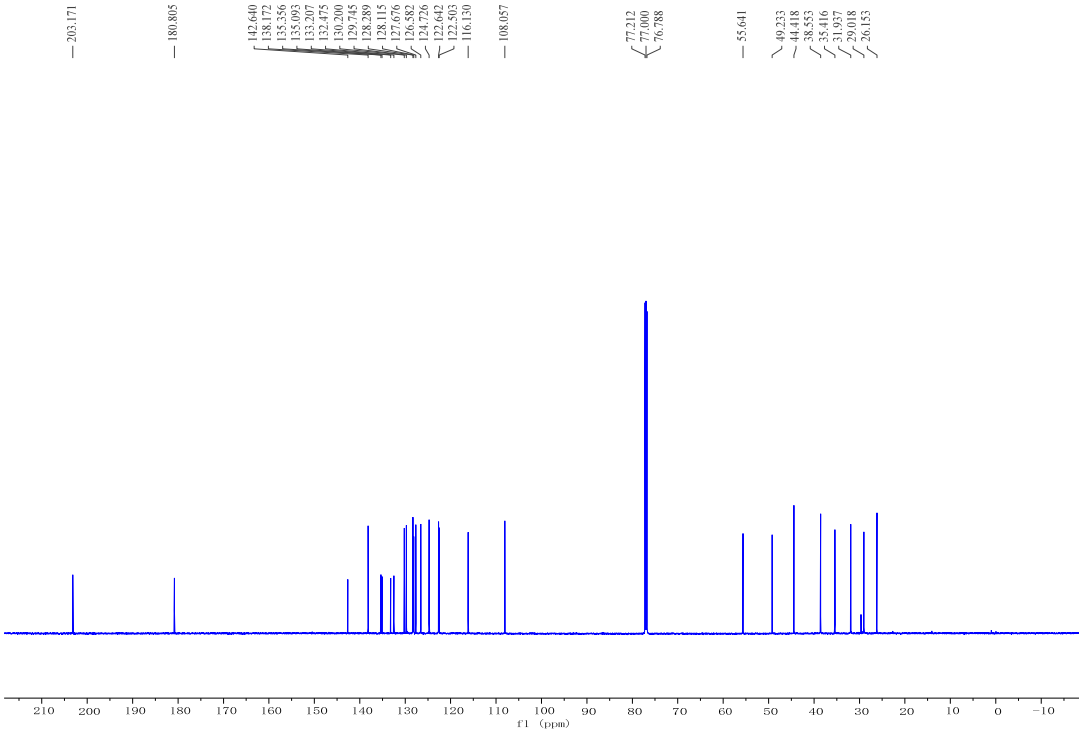


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)-**6aa**:

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

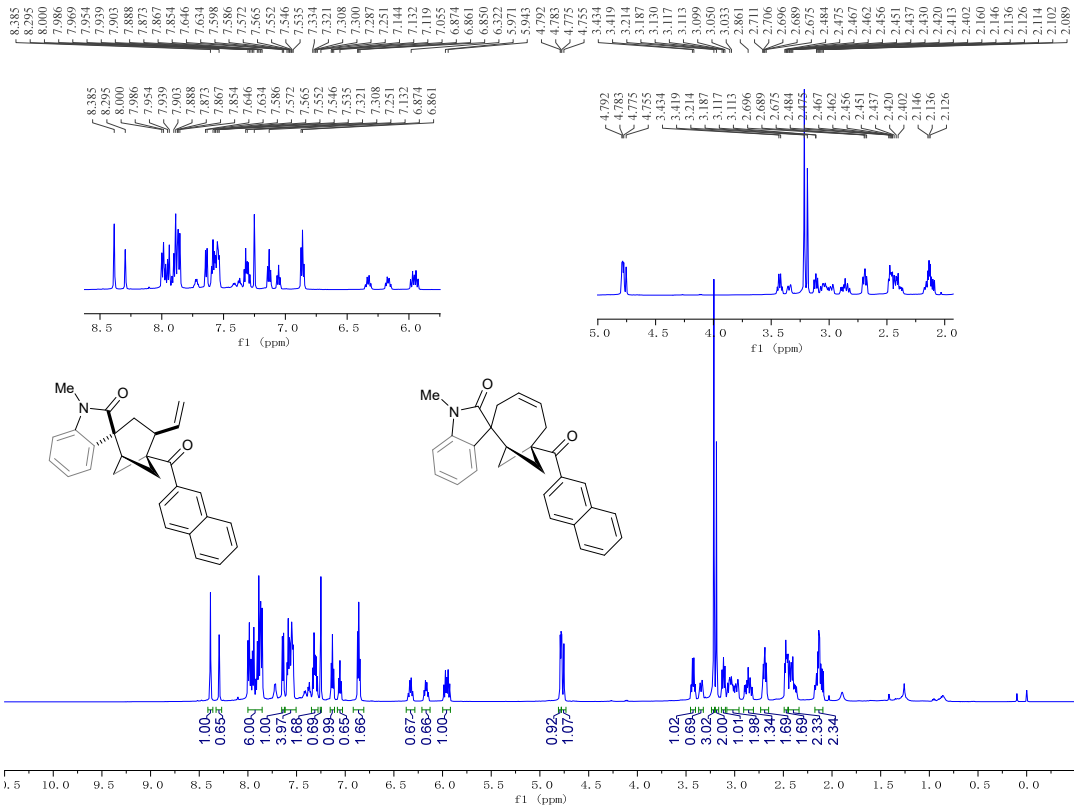


^{13}C NMR (150 MHz, $CDCl_3$)

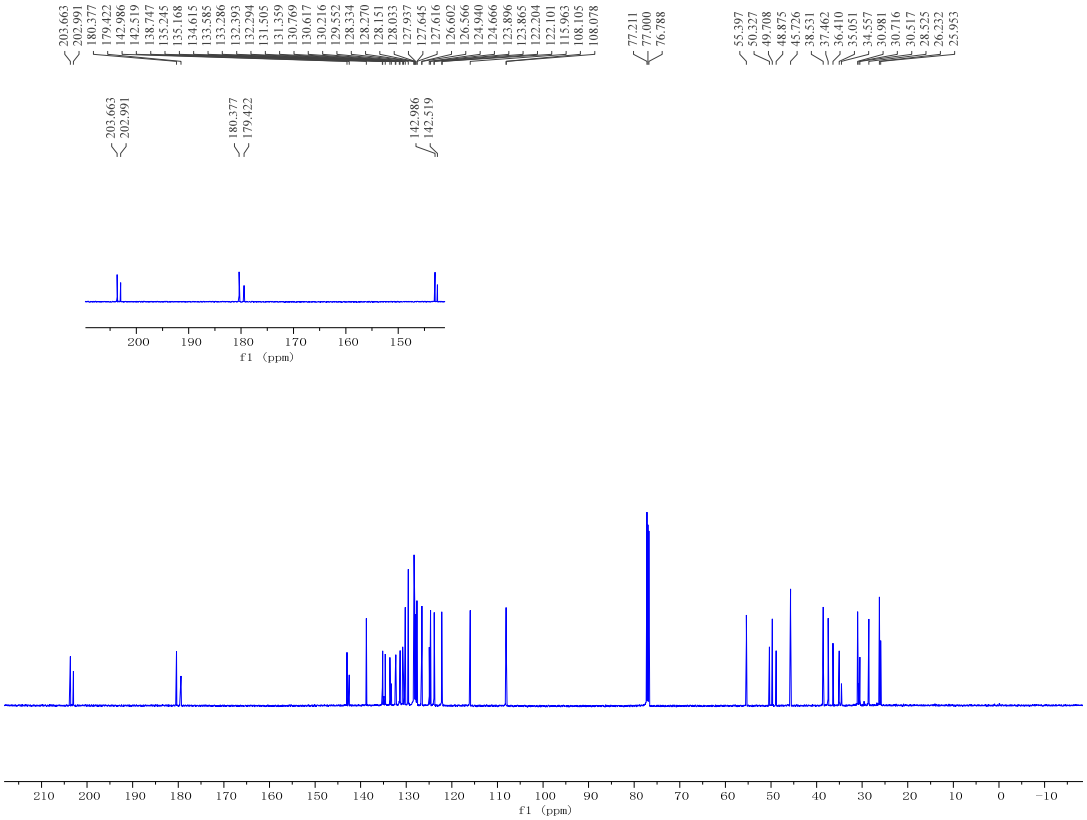


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)**-6aa and 7aa:**

^{1}H NMR (600 MHz, $CDCl_3$)

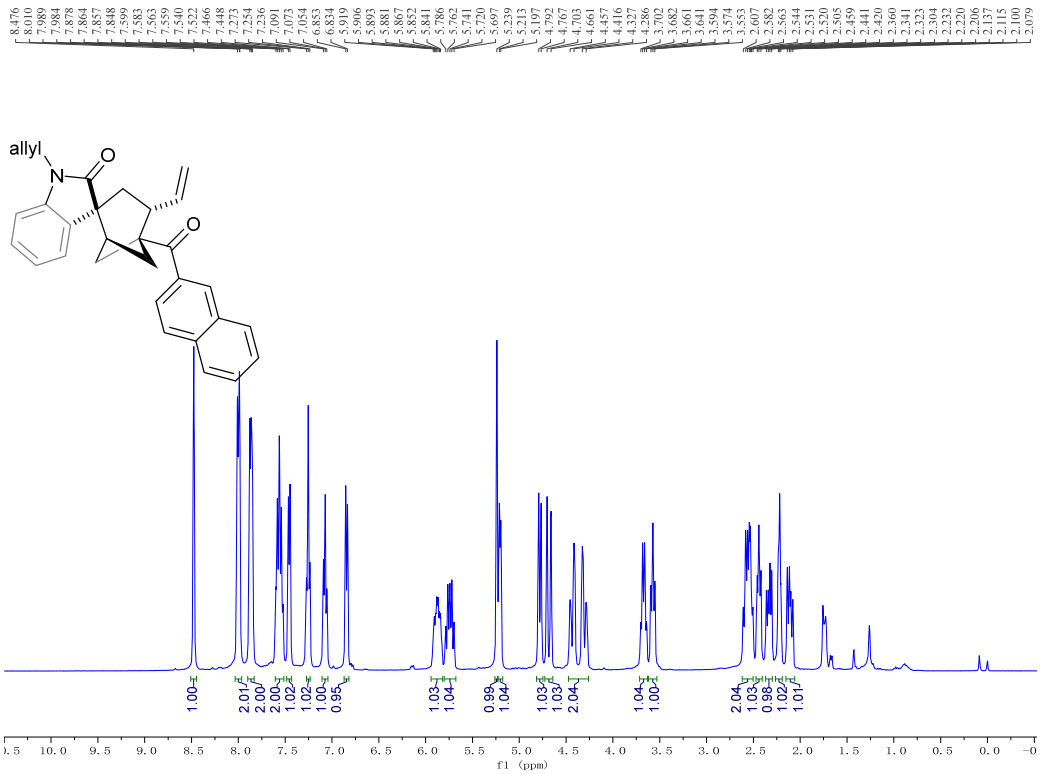


^{13}C NMR (150 MHz, $CDCl_3$)

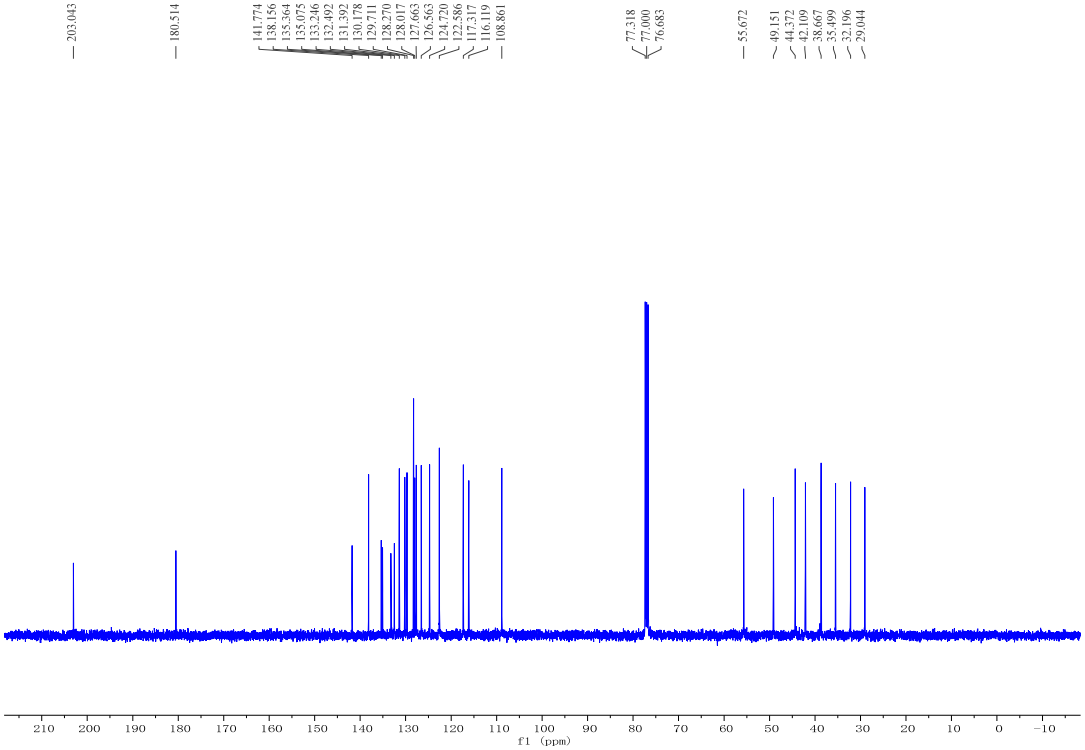


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)-**6ab**:

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

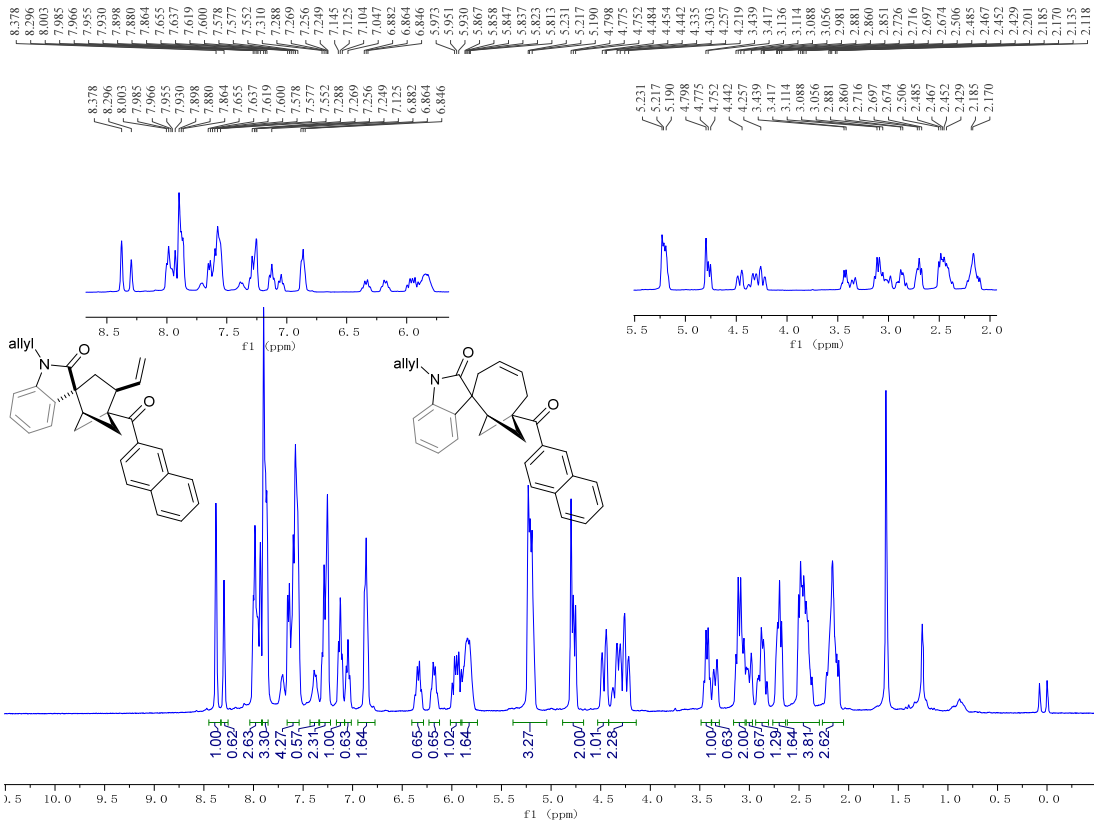


^{13}C NMR (100 MHz, $CDCl_3$)

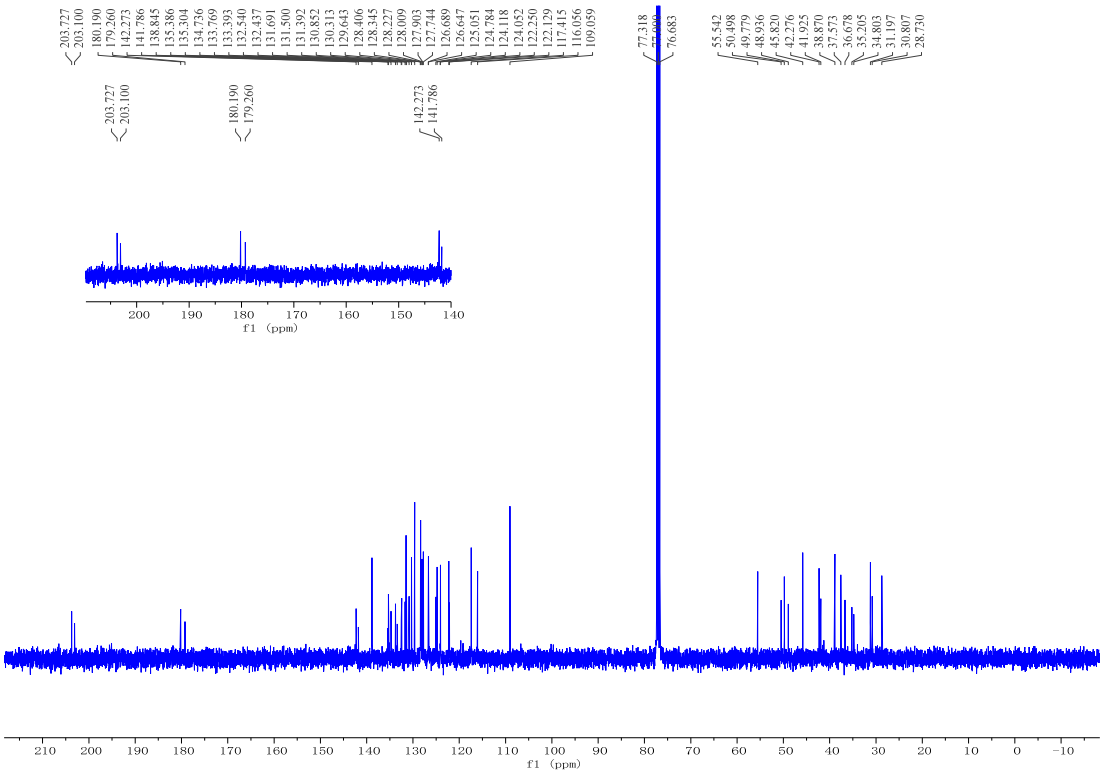


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)**-6ab and 7ab:**

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

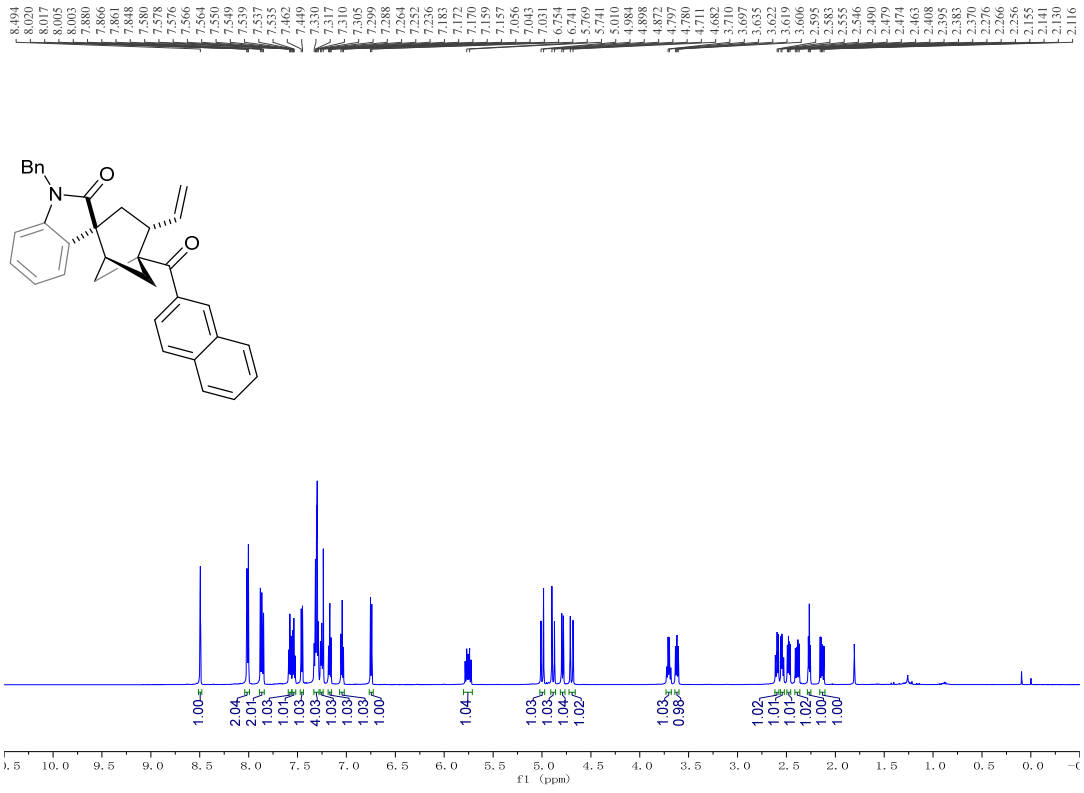


^{13}C NMR (100 MHz, $CDCl_3$)

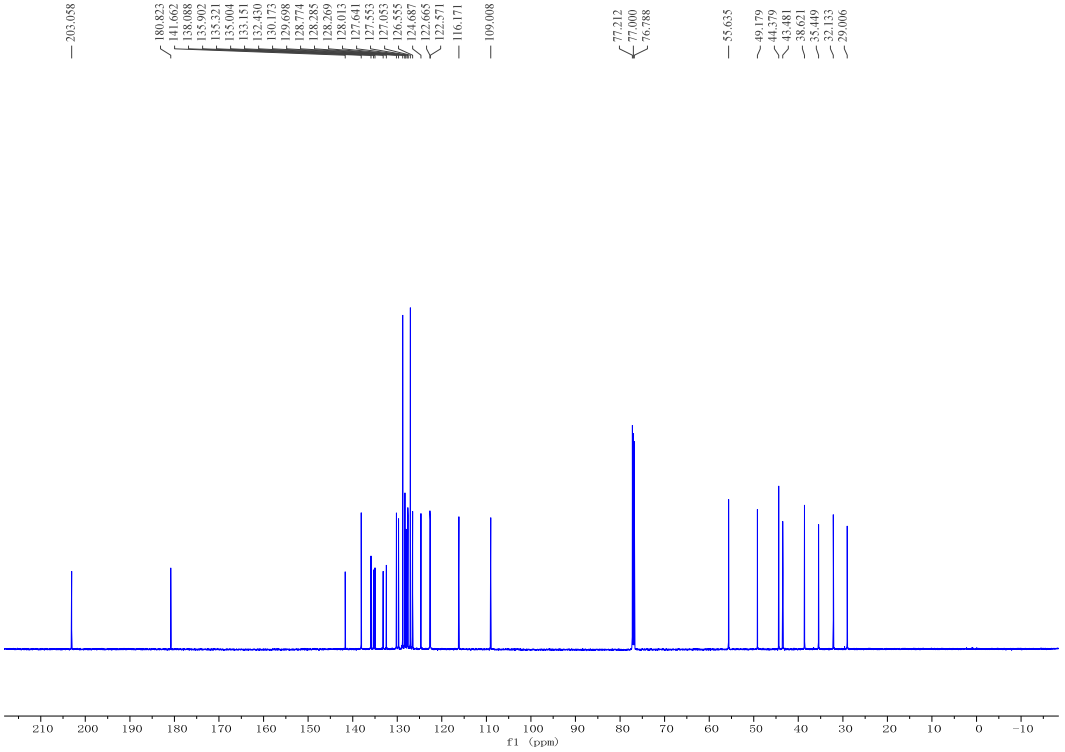


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)**-6ac**:

^{1}H NMR (600 MHz, $CDCl_3$)

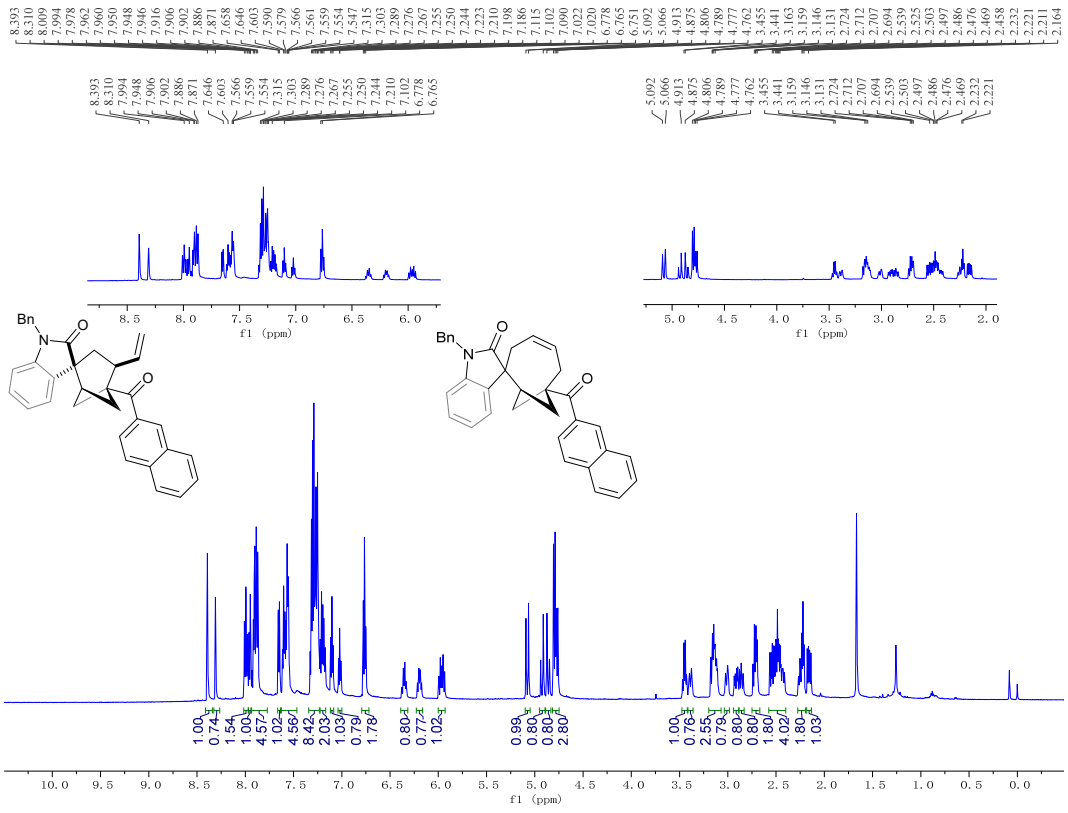


^{13}C NMR (150 MHz, $CDCl_3$)

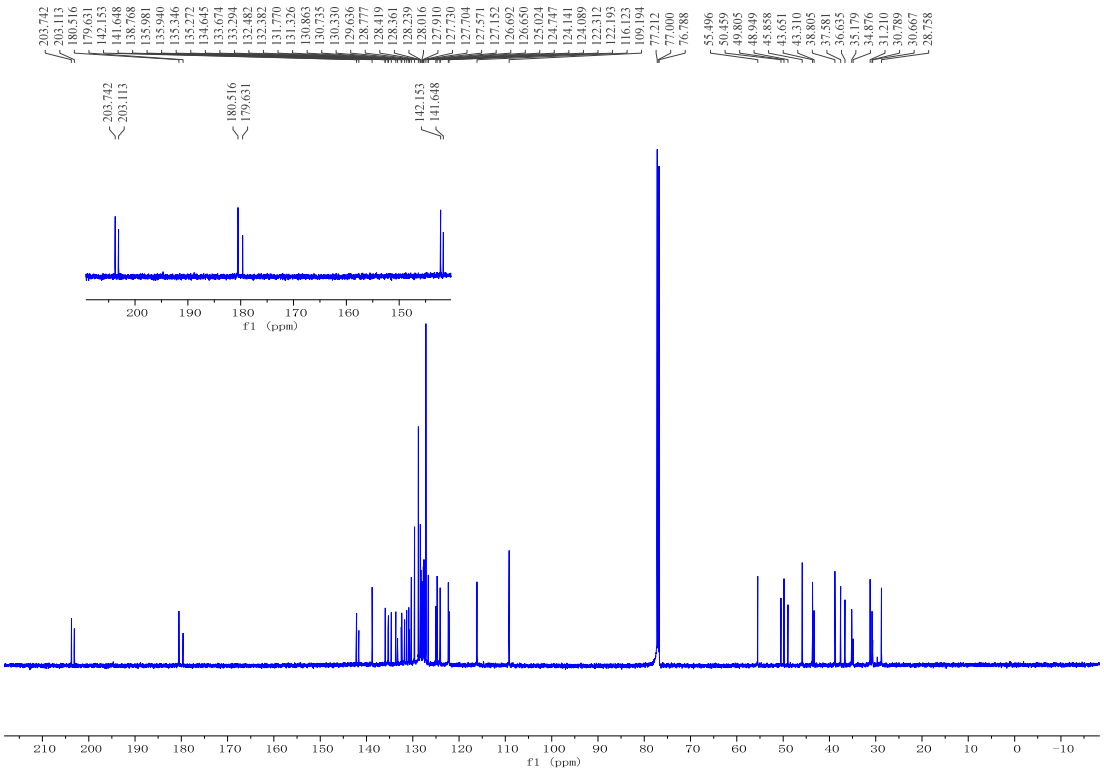


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)**-6ac and 7ac:**

^{1}H NMR (600 MHz, $CDCl_3$)

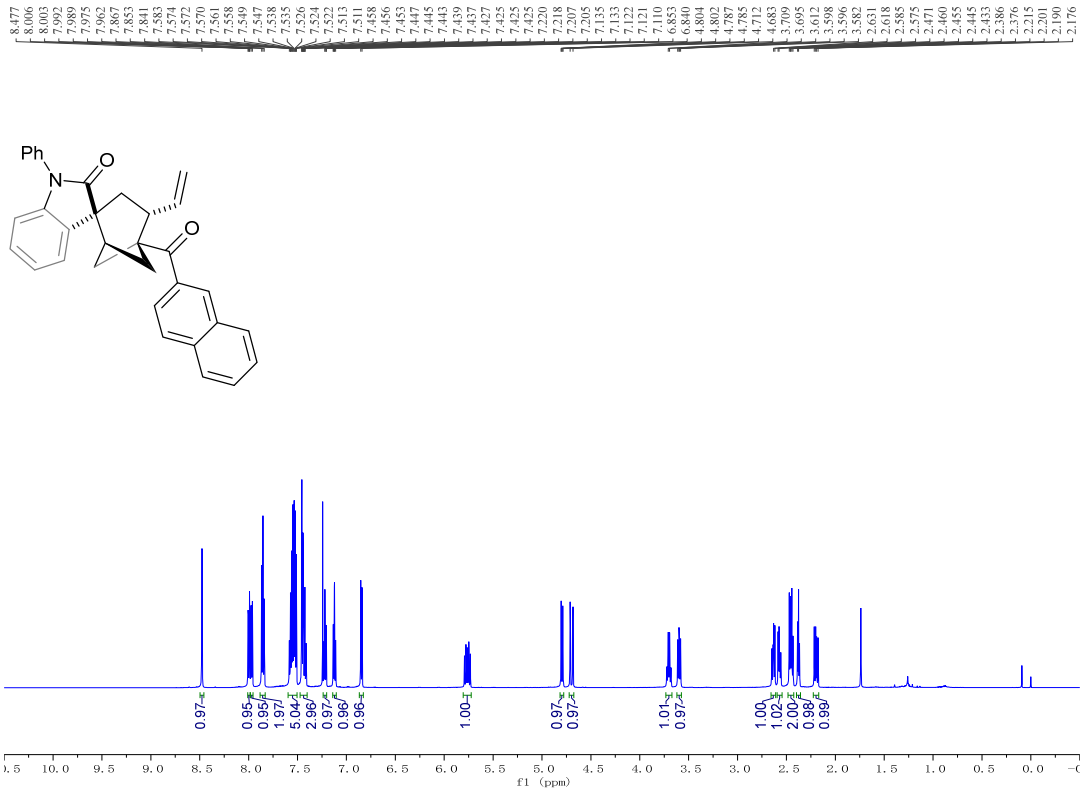


^{13}C NMR (150 MHz, $CDCl_3$)

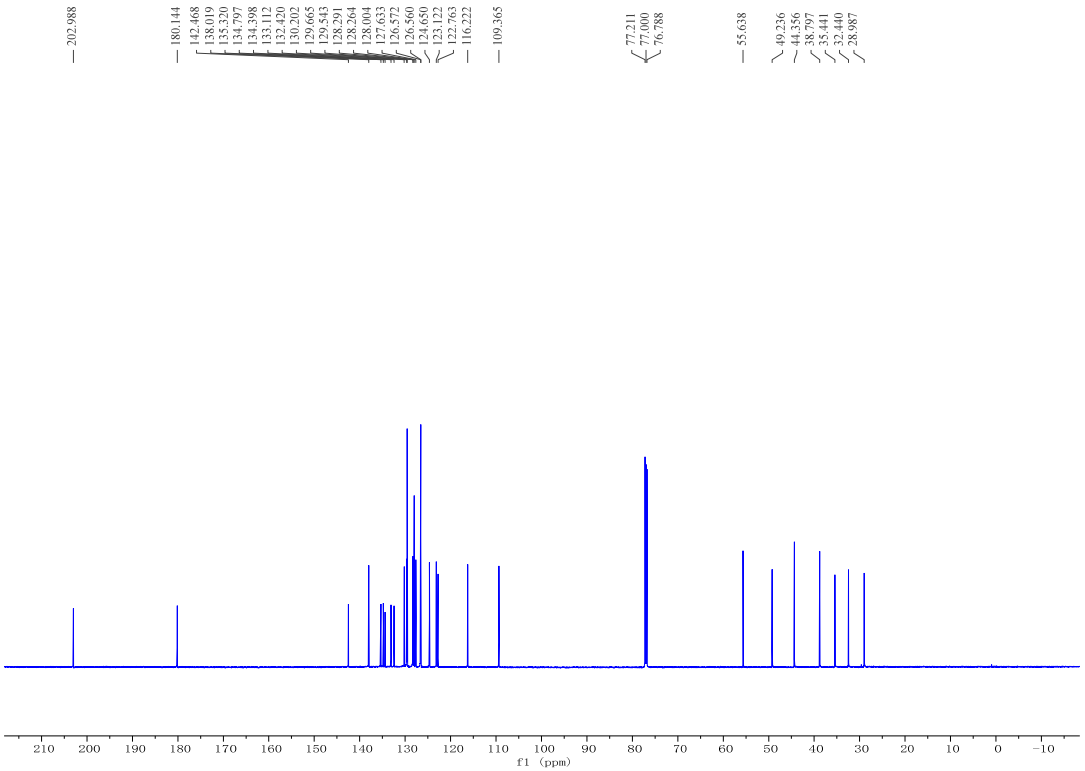


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)-**6ad**:

^{1}H NMR (600 MHz, $CDCl_3$)

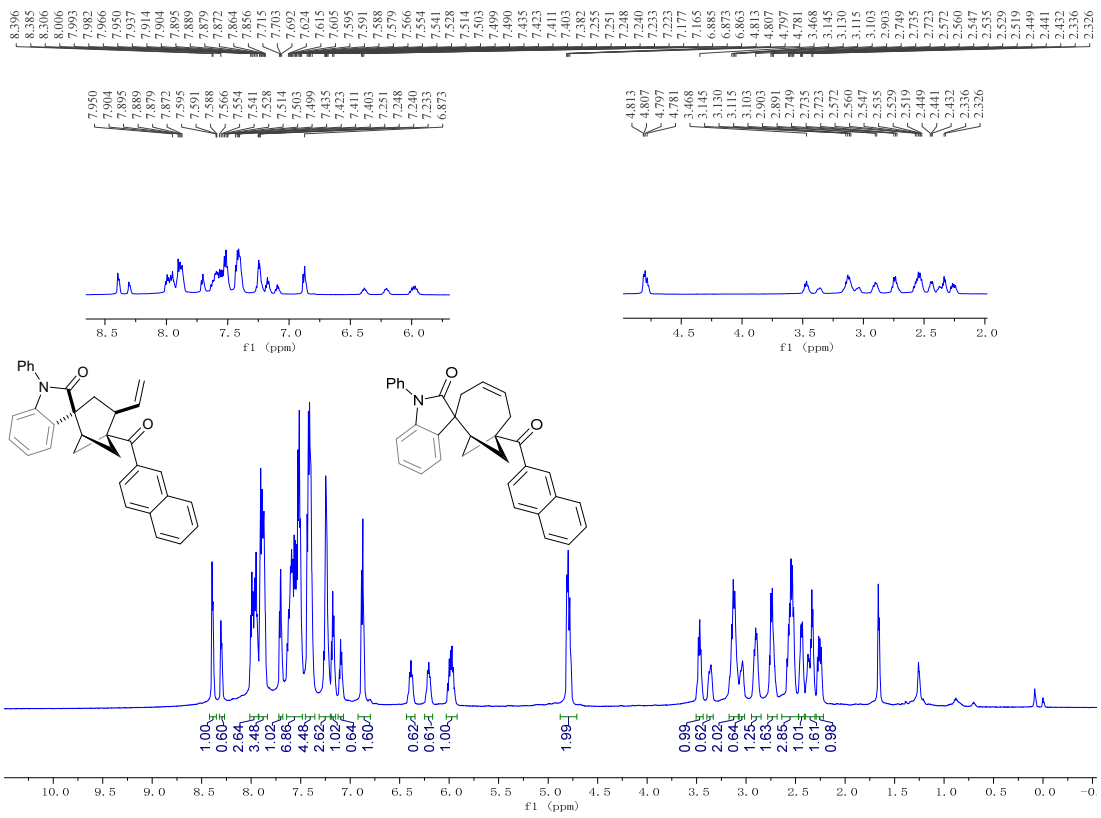


^{13}C NMR (150 MHz, $CDCl_3$)

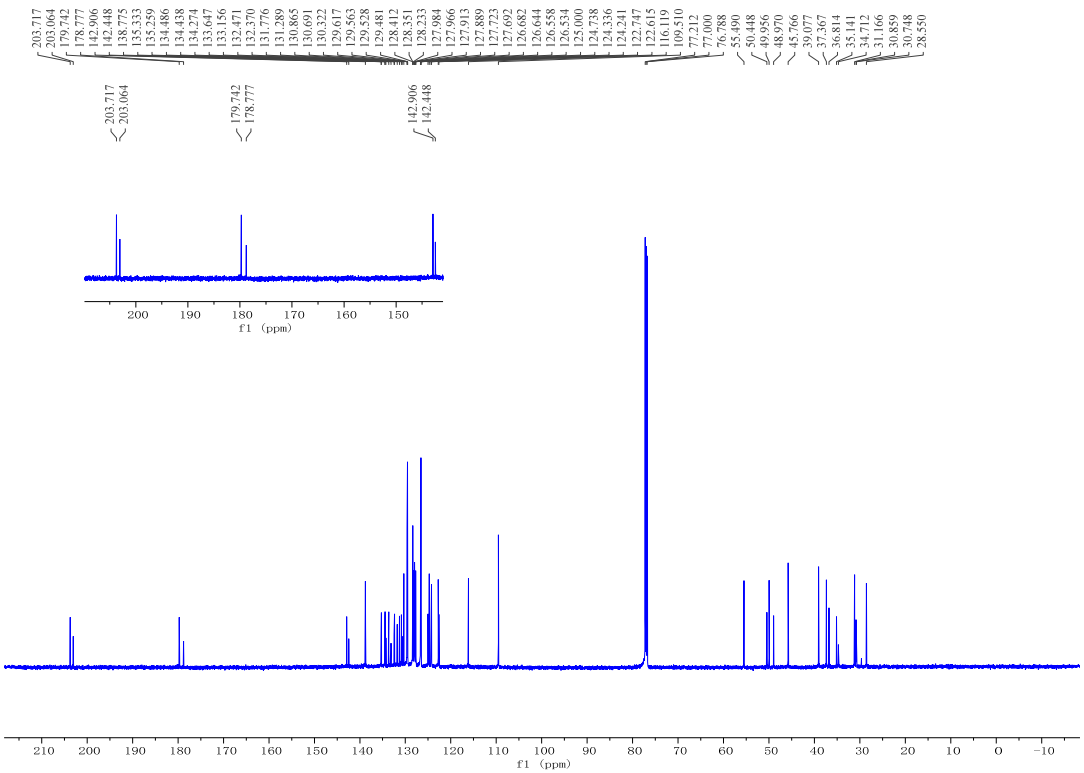


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)-**6ad and 7ad:**

^{1}H NMR (600 MHz, $CDCl_3$)

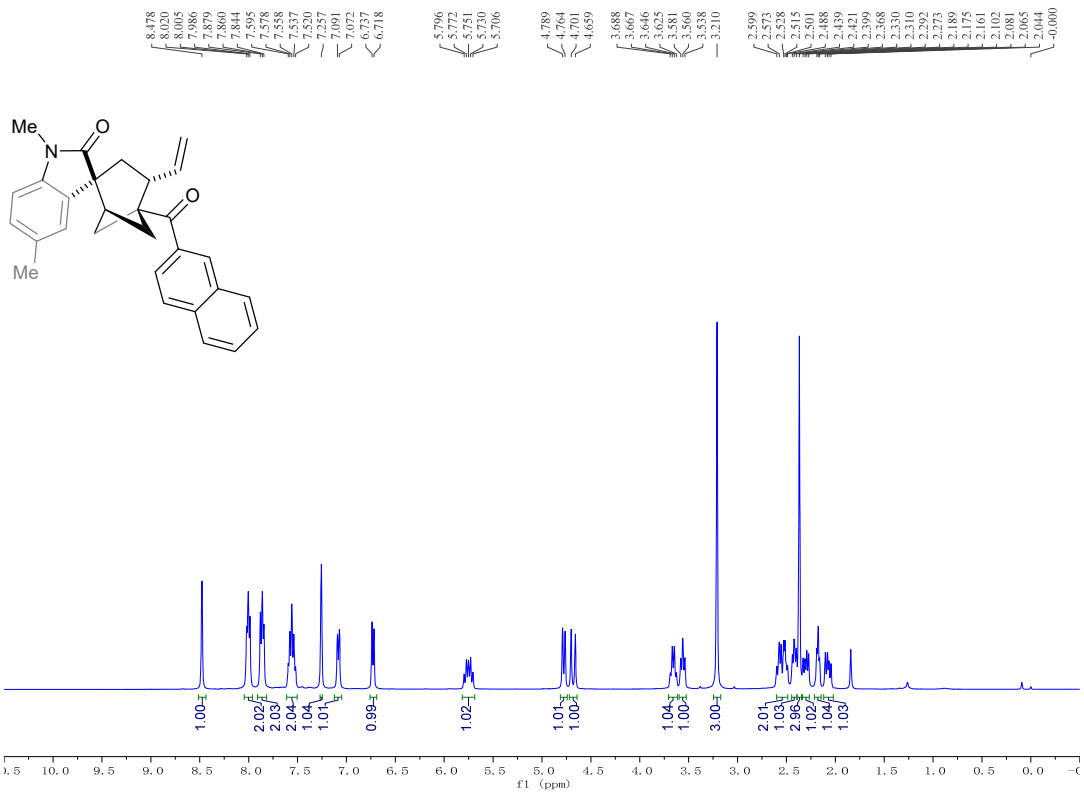


^{13}C NMR (150 MHz, $CDCl_3$)

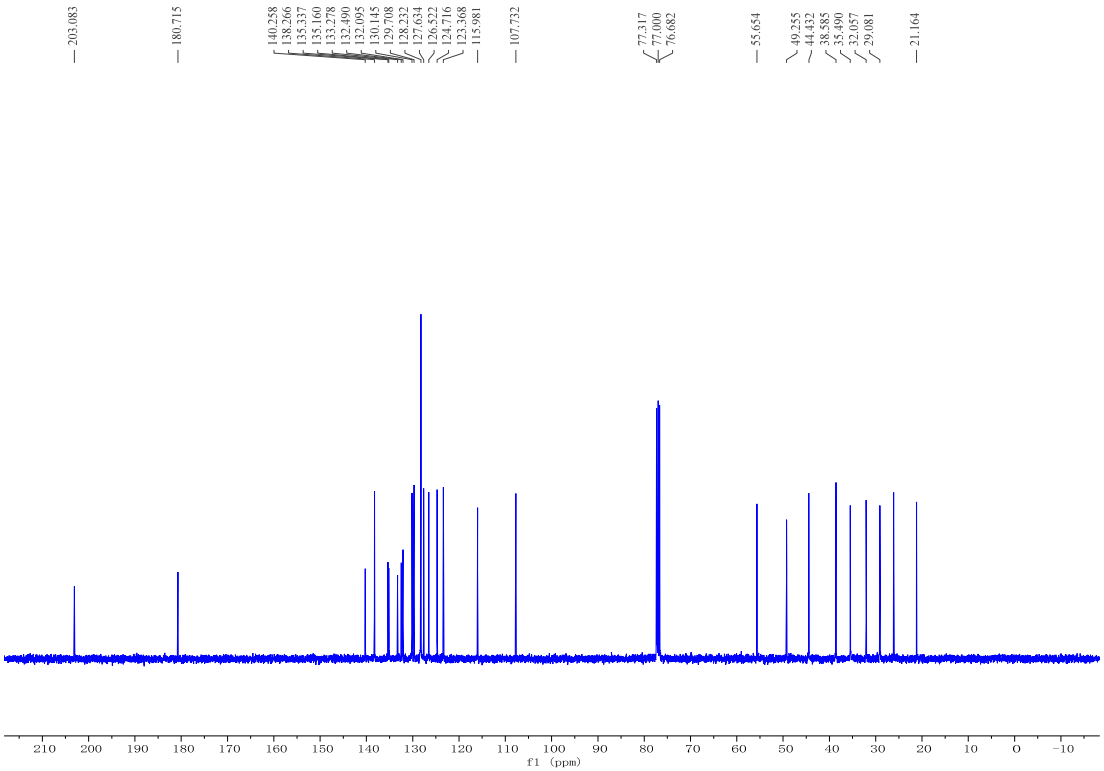


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)-**6ae**:

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

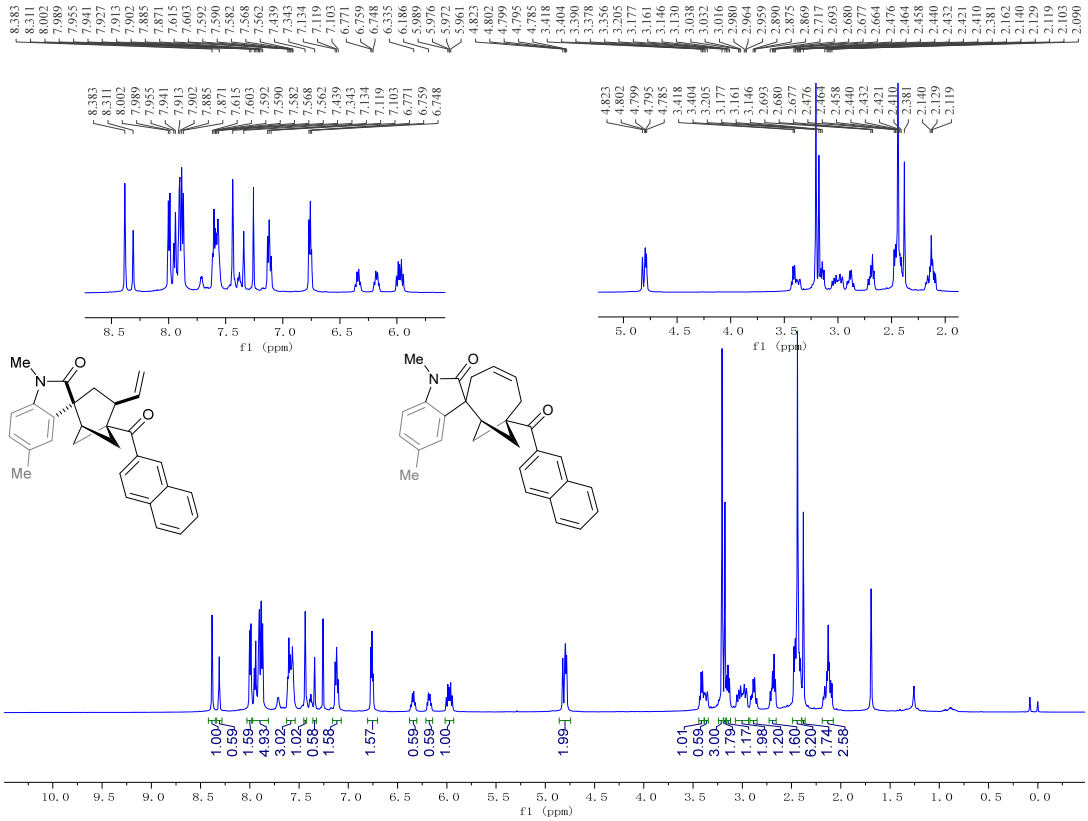


^{13}C NMR (100 MHz, $CDCl_3$)

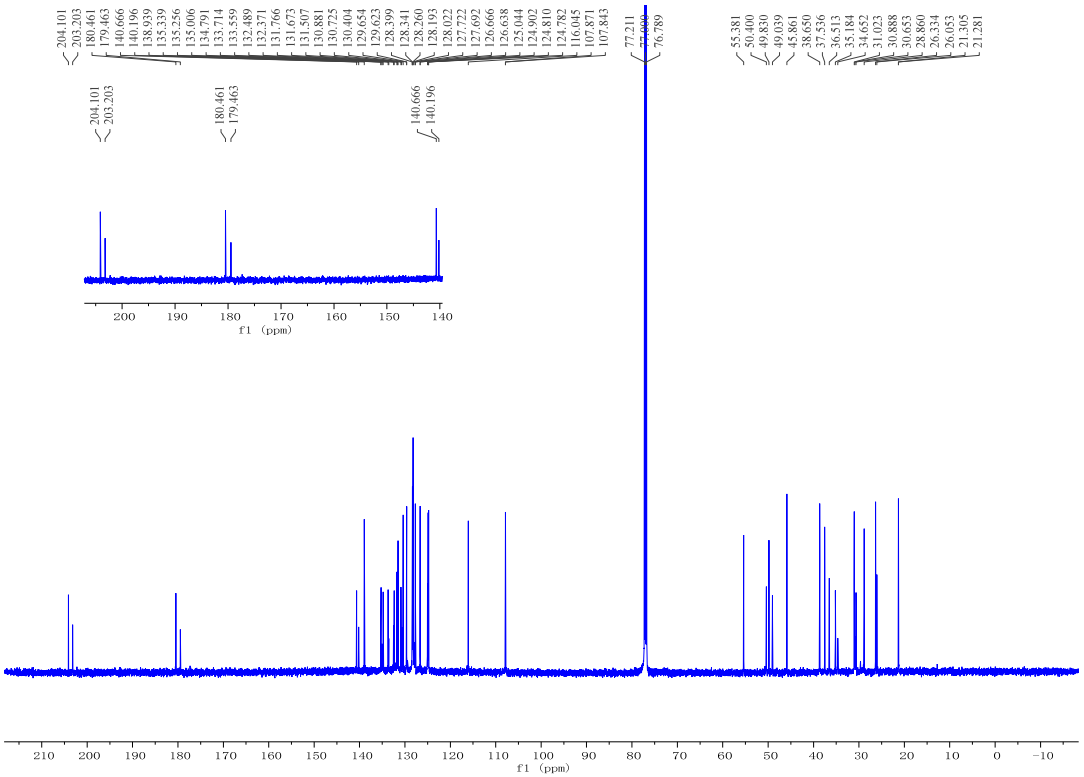


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)**-6ae and 7ae:**

^{1}H NMR (600 MHz, $CDCl_3$)

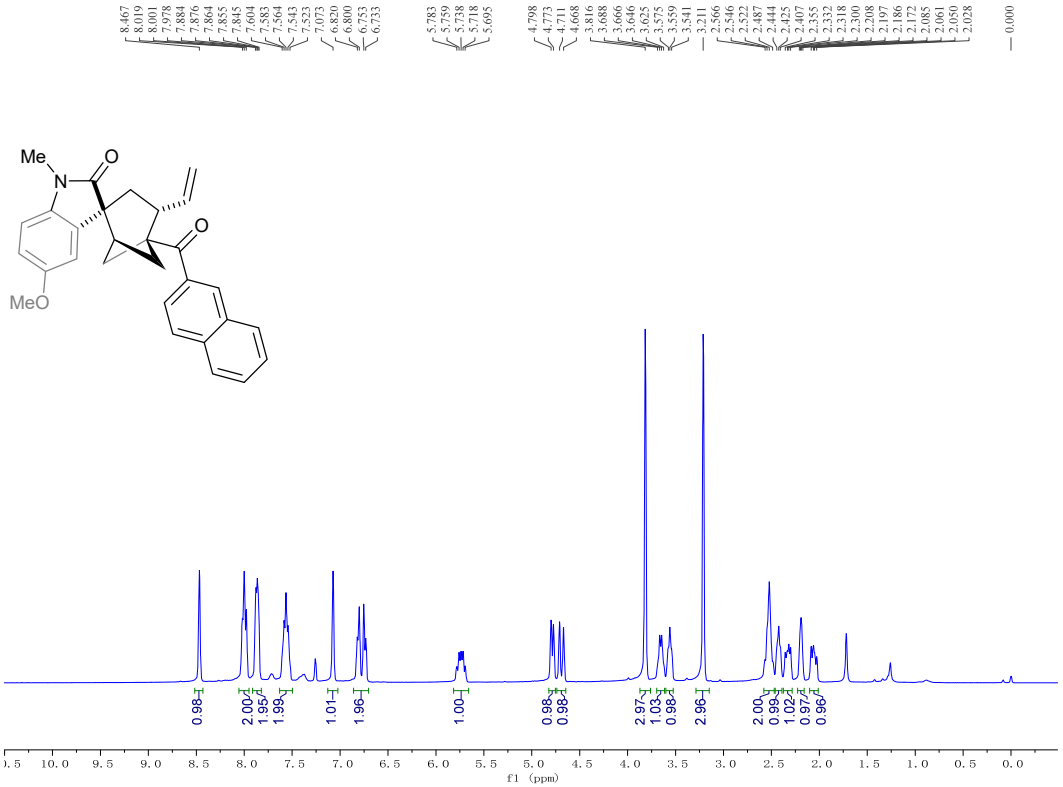


^{13}C NMR (150 MHz, $CDCl_3$)

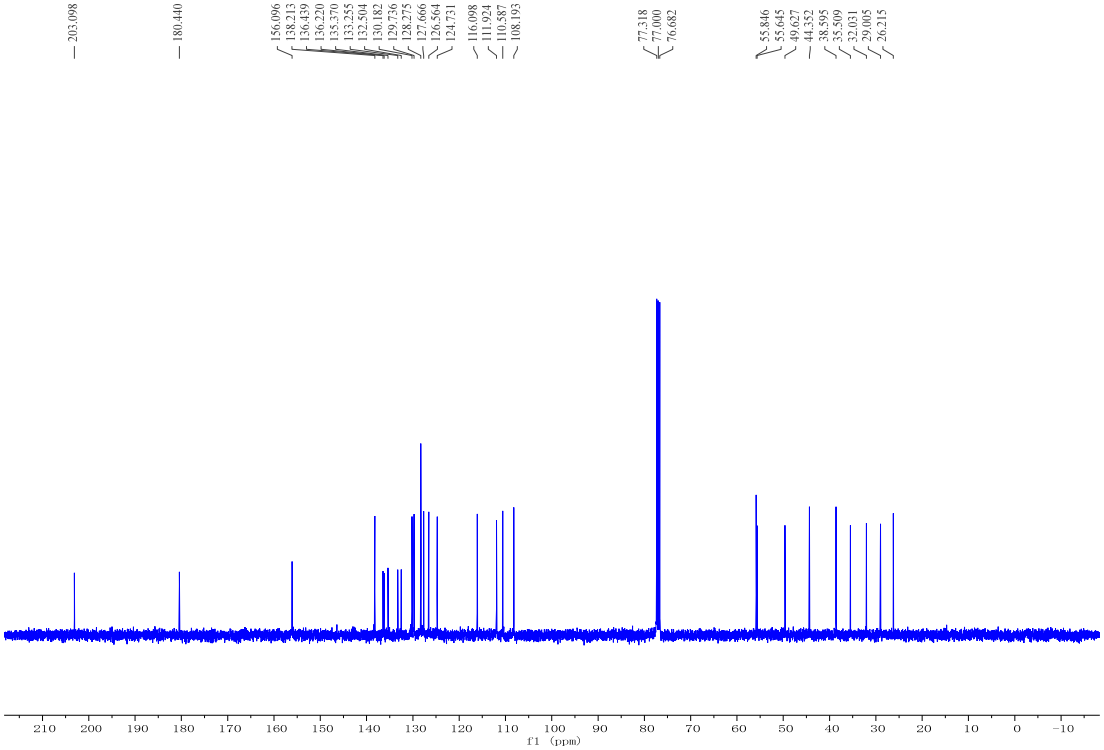


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)**-6af**:

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

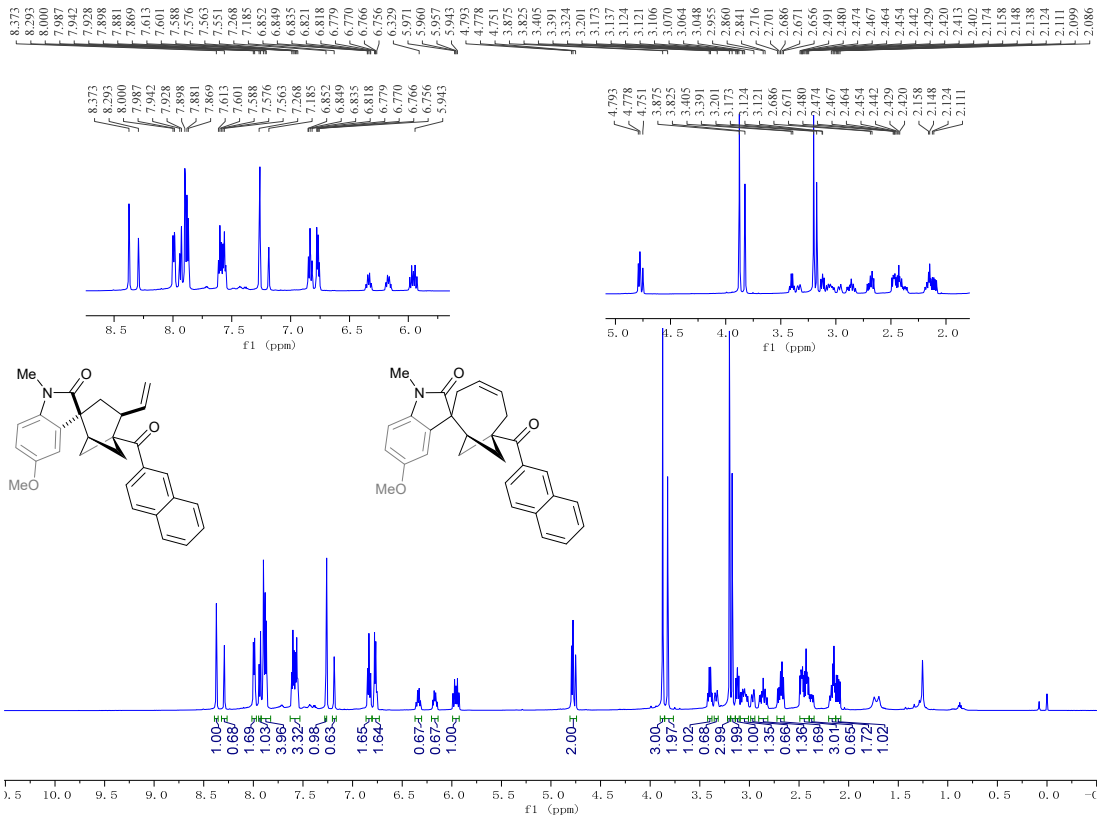


^{13}C NMR (100 MHz, $CDCl_3$)

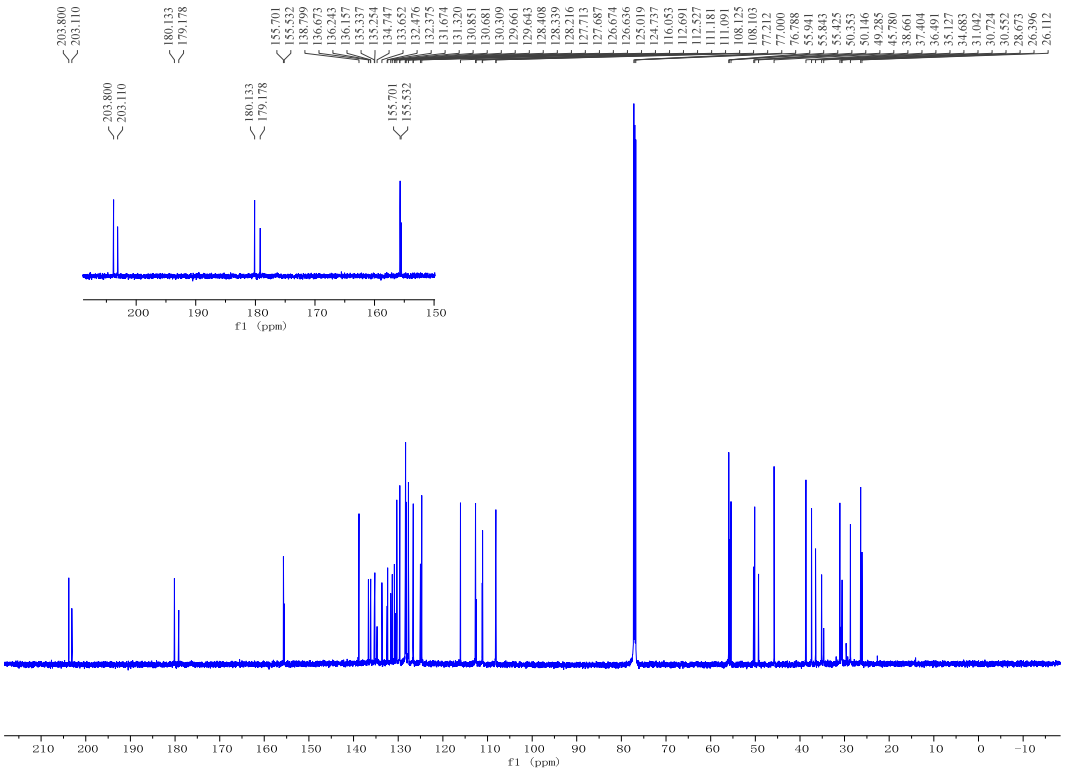


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)-**6af and 7af:**

^{1}H NMR (600 MHz, $CDCl_3$)

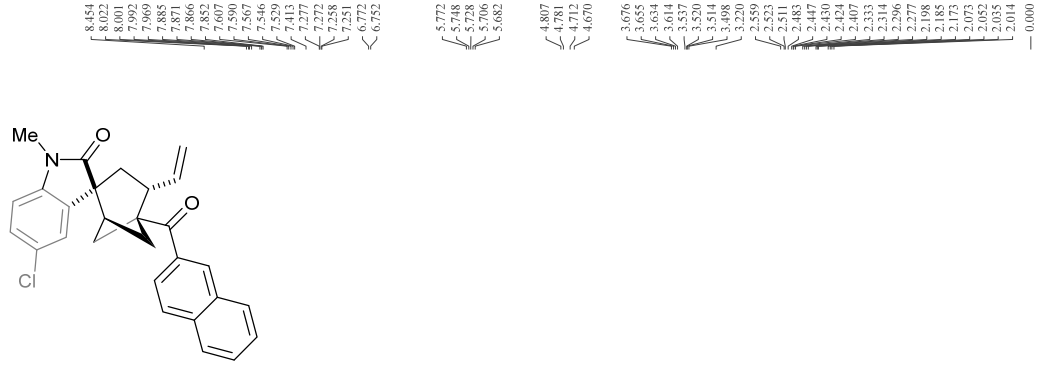


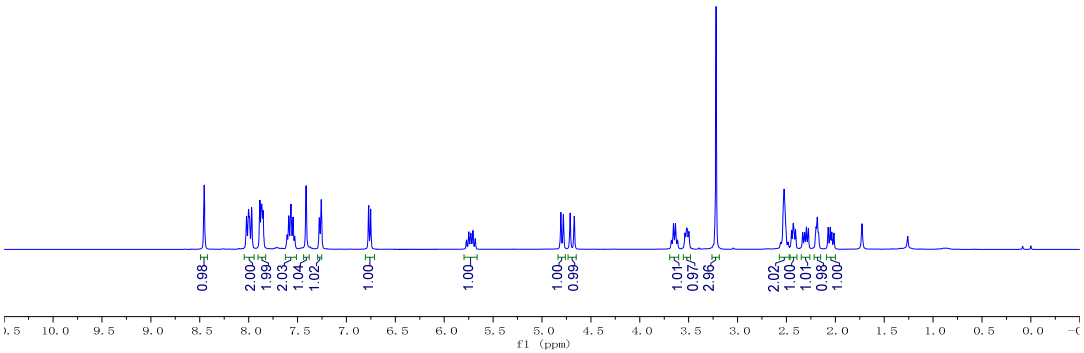
^{13}C NMR (150 MHz, $CDCl_3$)



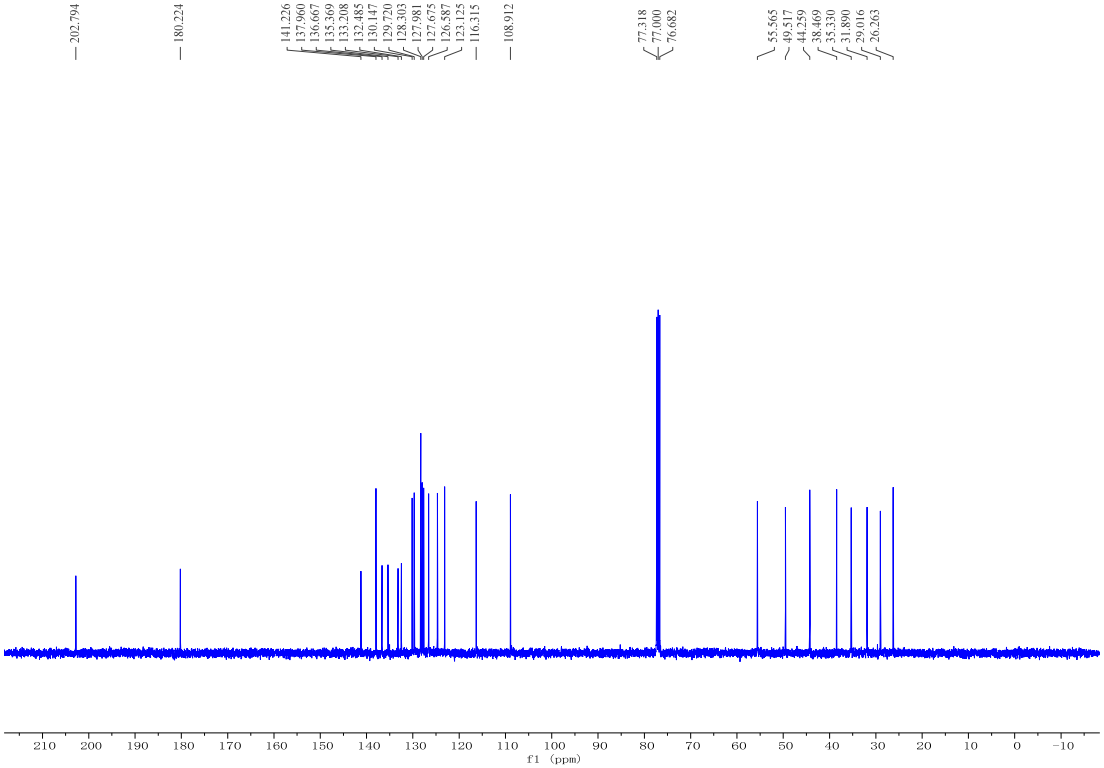
^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)-**6ag**:

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



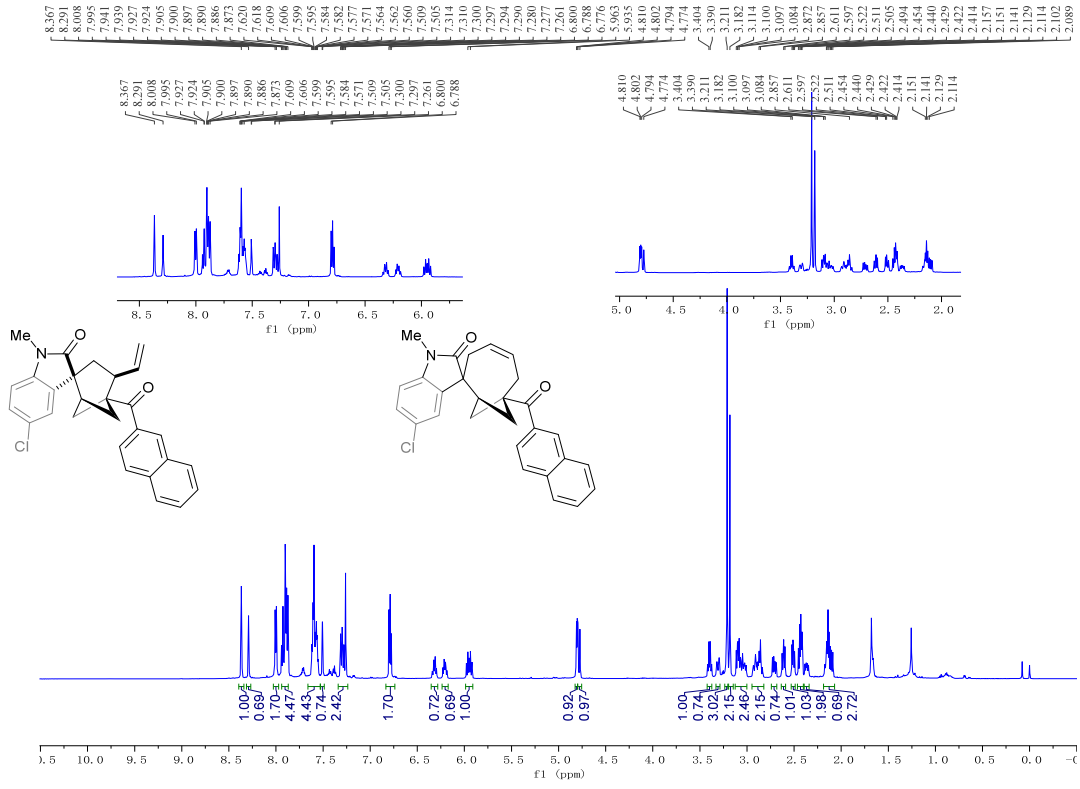


^{13}C NMR (100 MHz, $CDCl_3$)

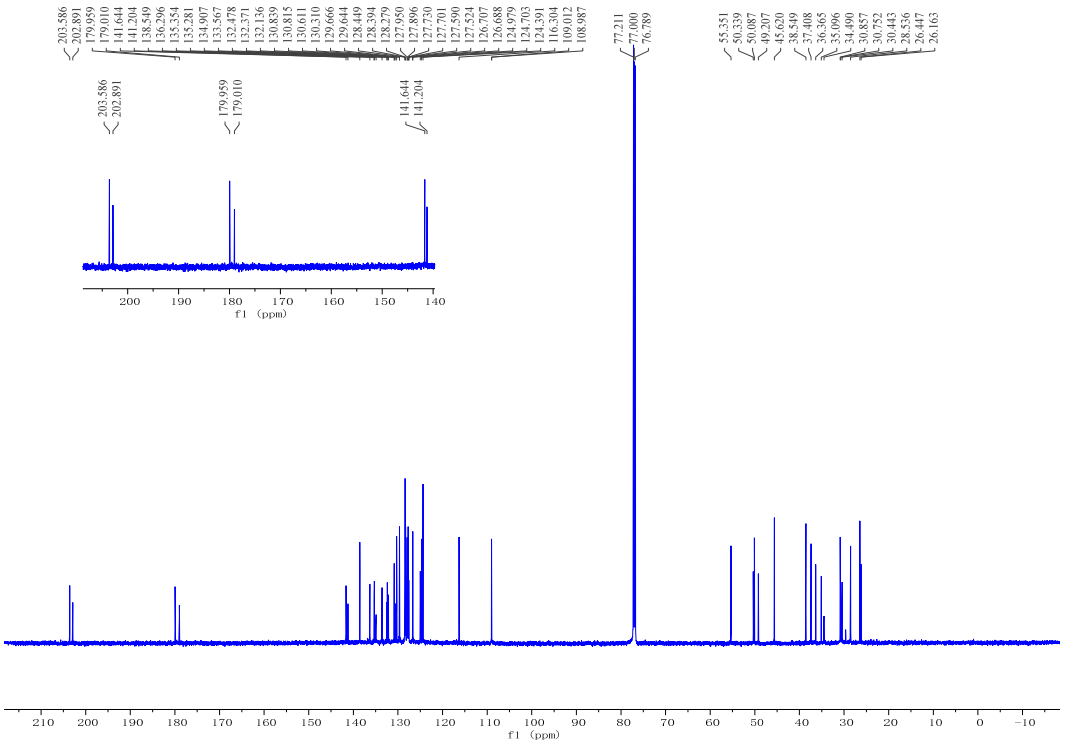


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)-**6ag and 7ag:**

^{1}H NMR (600 MHz, $CDCl_3$)

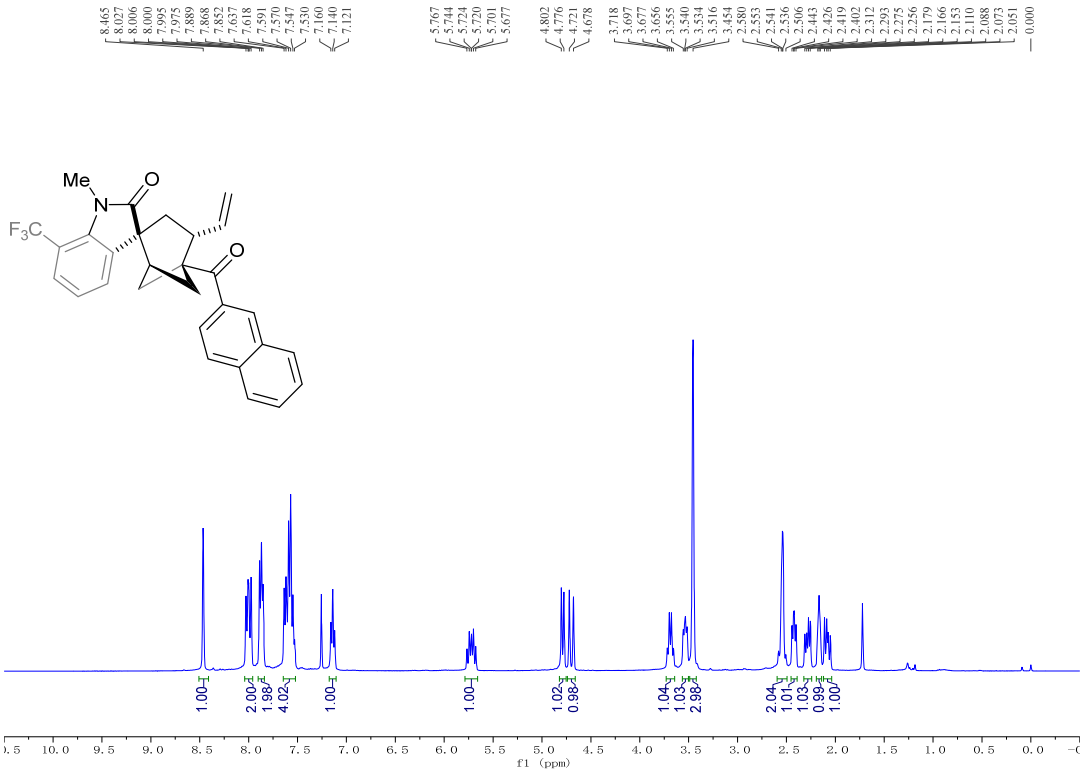


^{13}C NMR (150 MHz, $CDCl_3$)

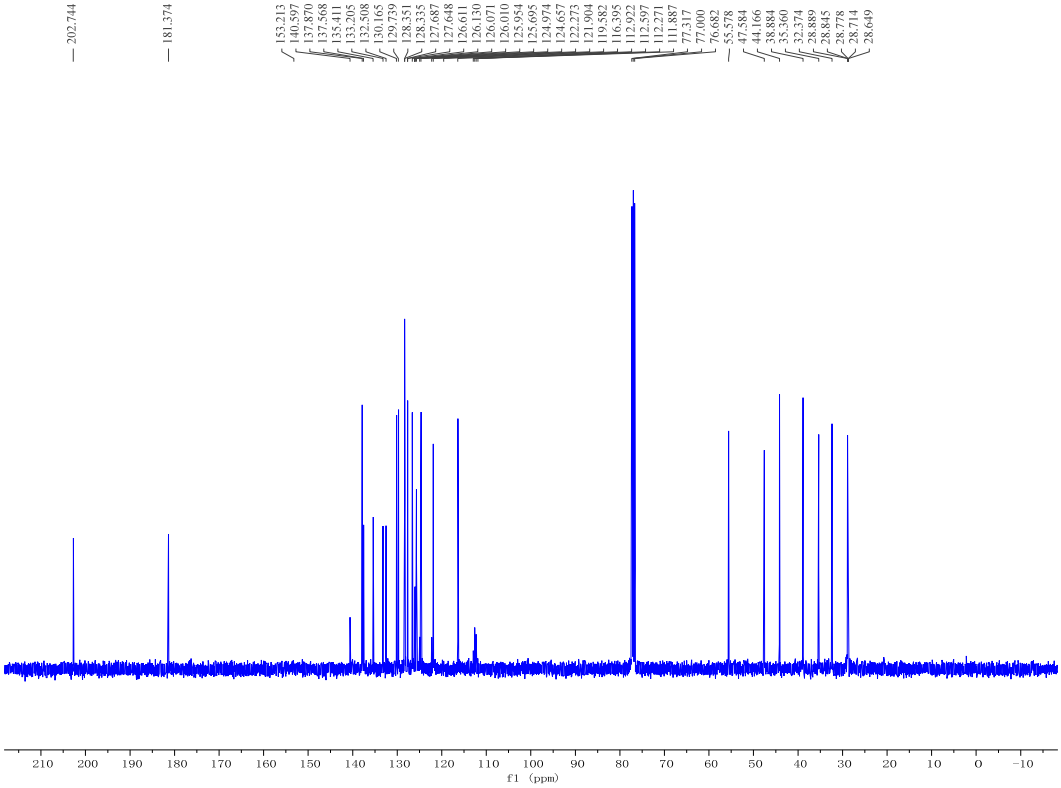


^{1}H ,^{13}C NMR and ^{19}F NMR Spectra for Compound (2*S**,4*R**)-**6ah**:

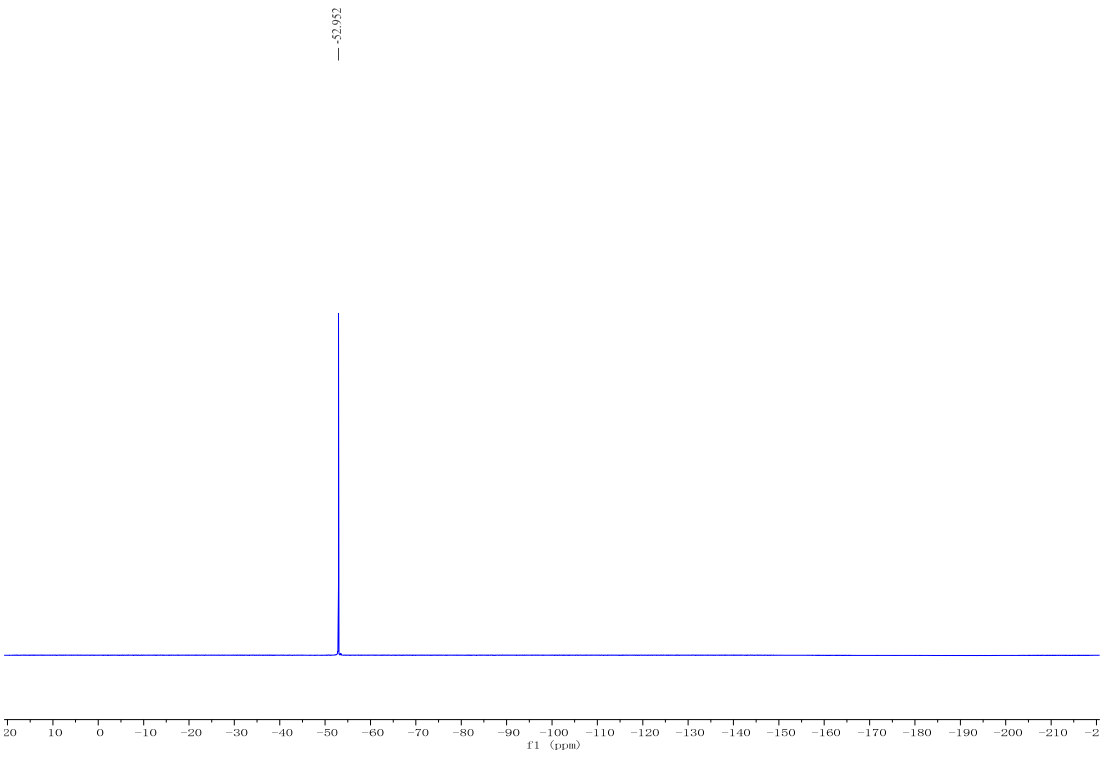
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

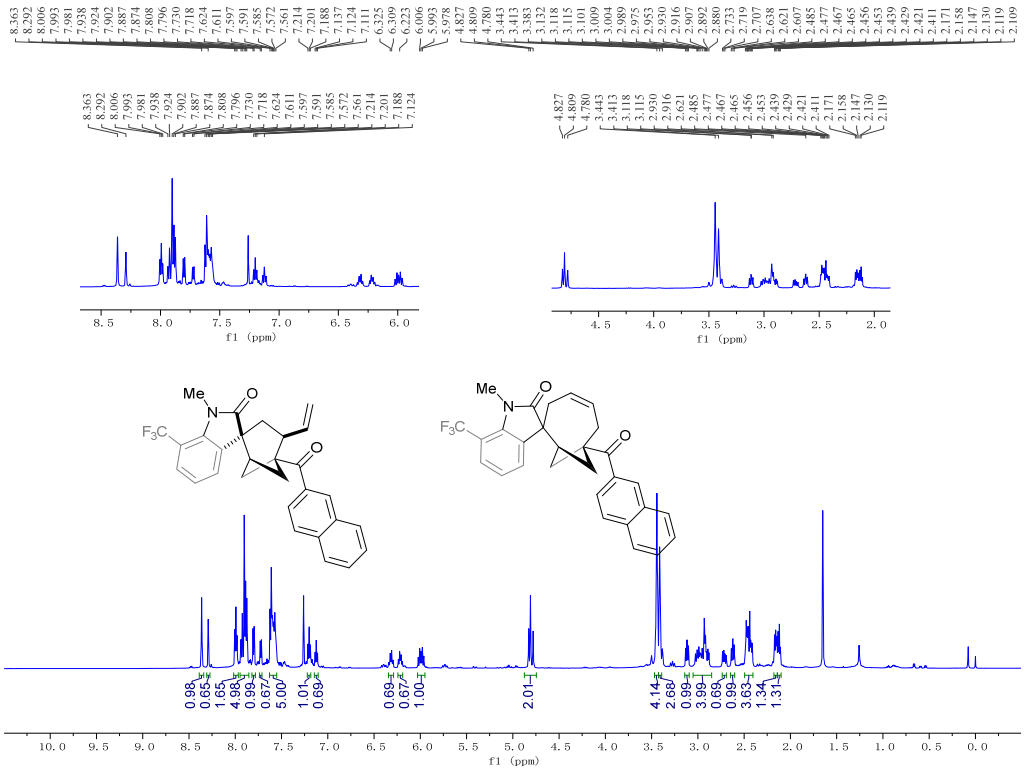


^{19}F NMR (376 MHz, $CDCl_3$)

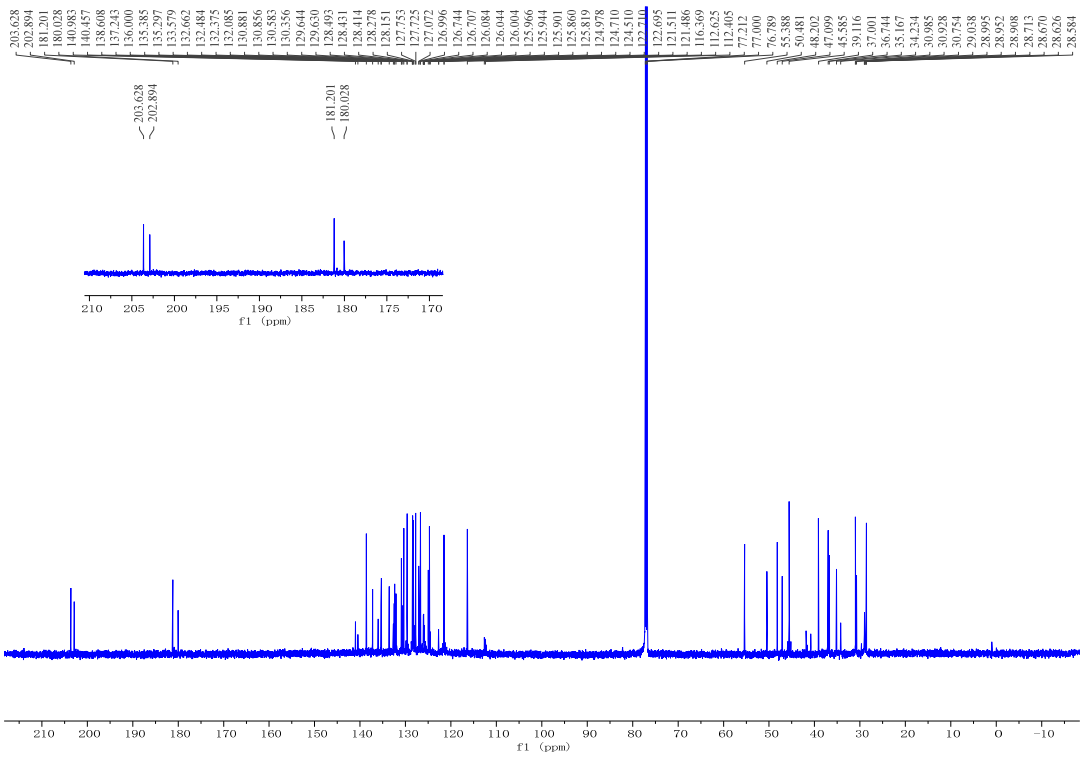


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)-6ah and 7ah:

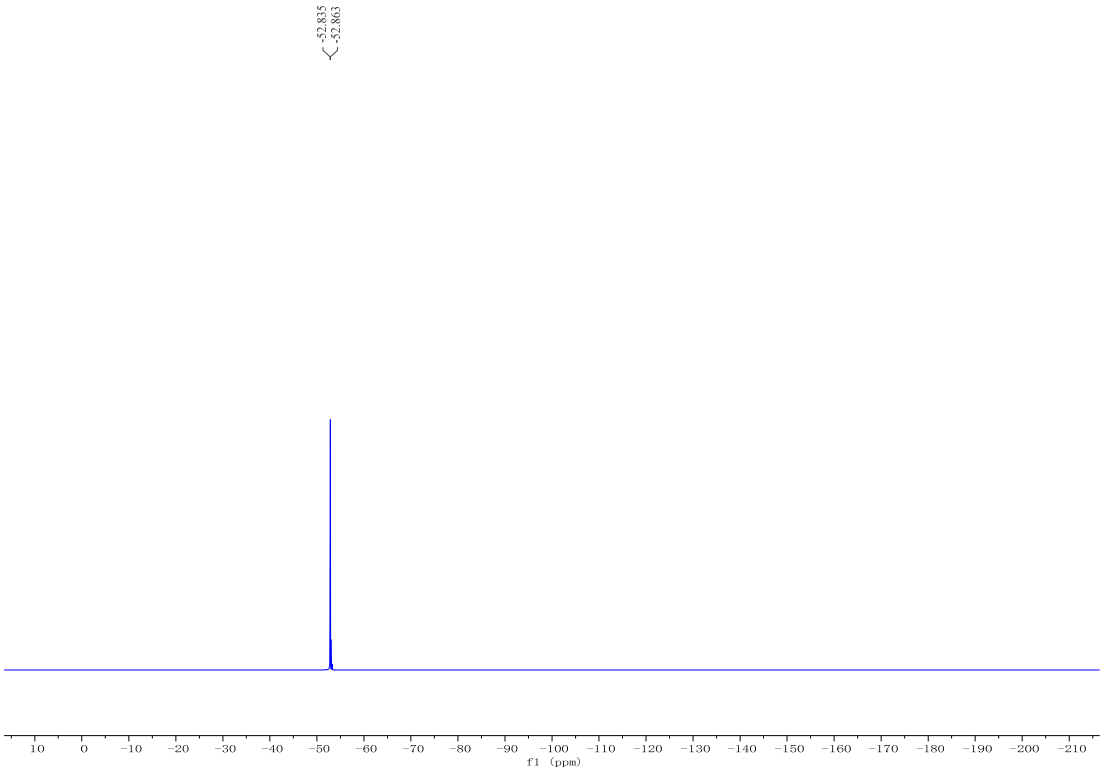
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

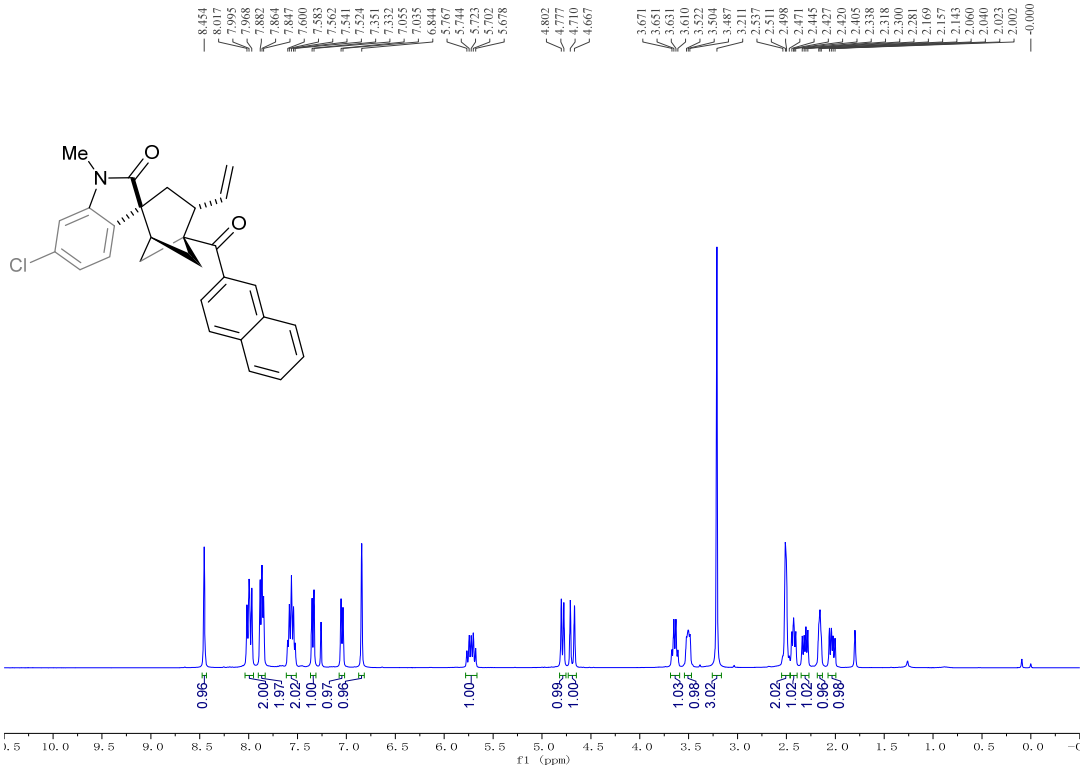


^{19}F NMR (565 MHz, $CDCl_3$)

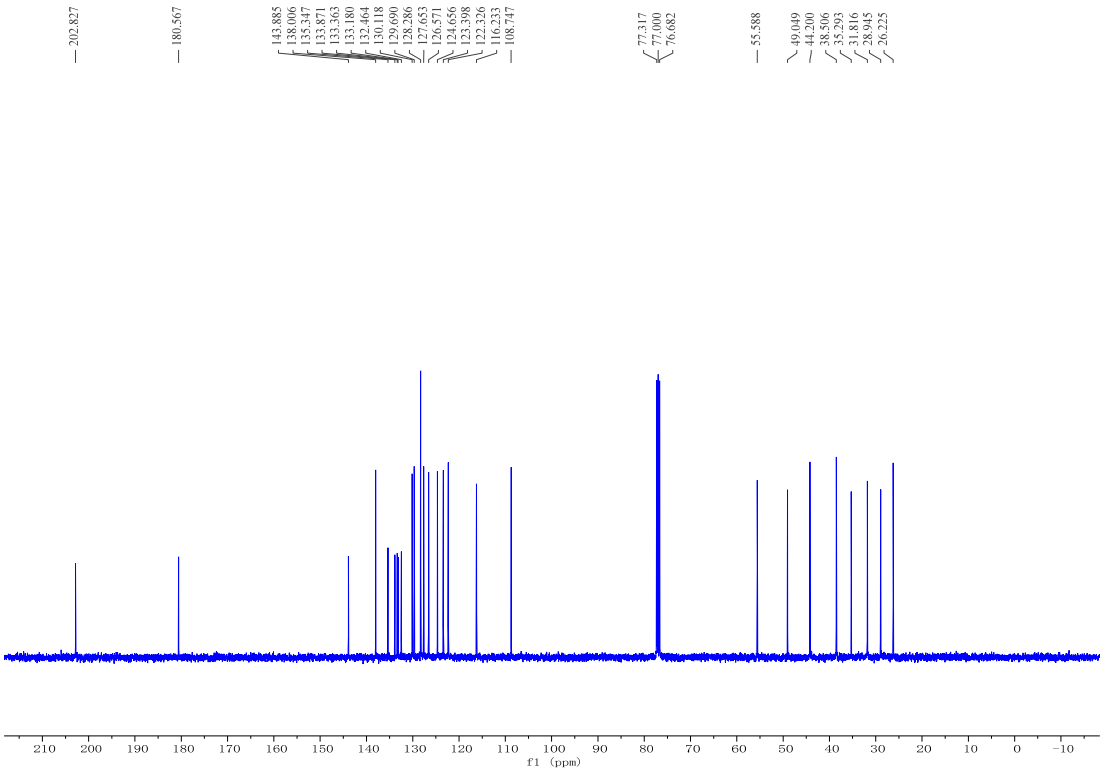


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)-**6ai**:

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

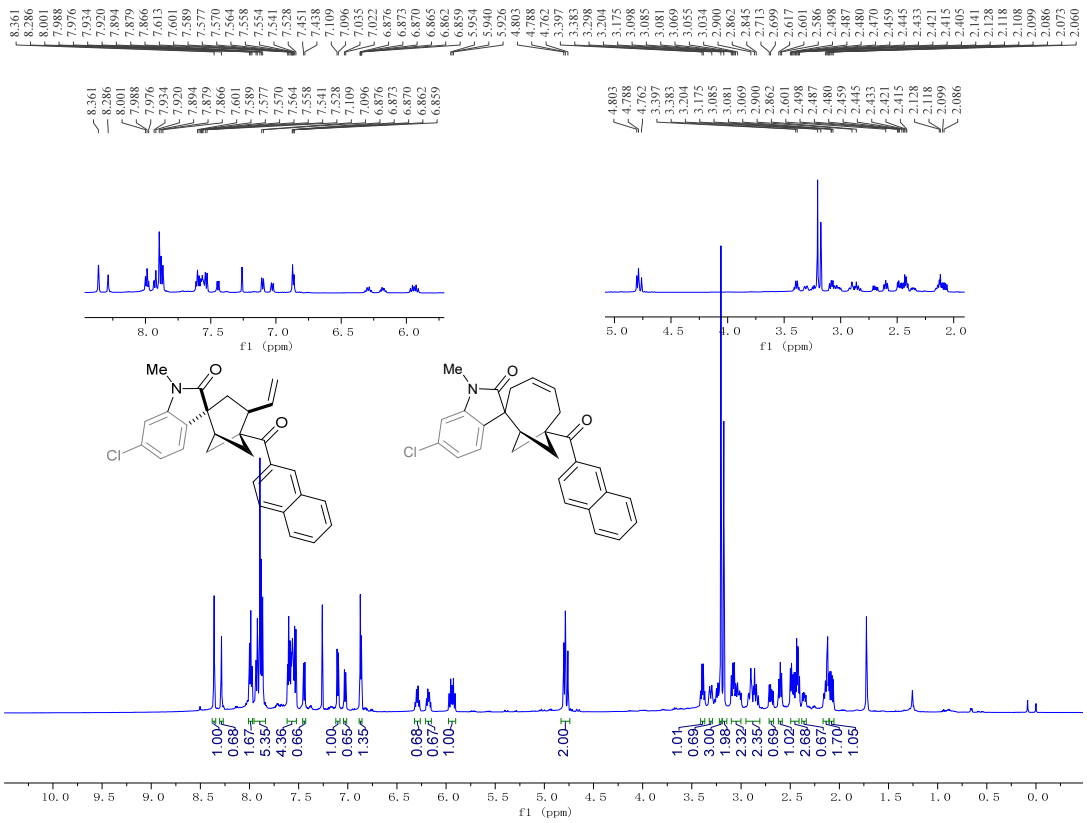


^{13}C NMR (100 MHz, $CDCl_3$)

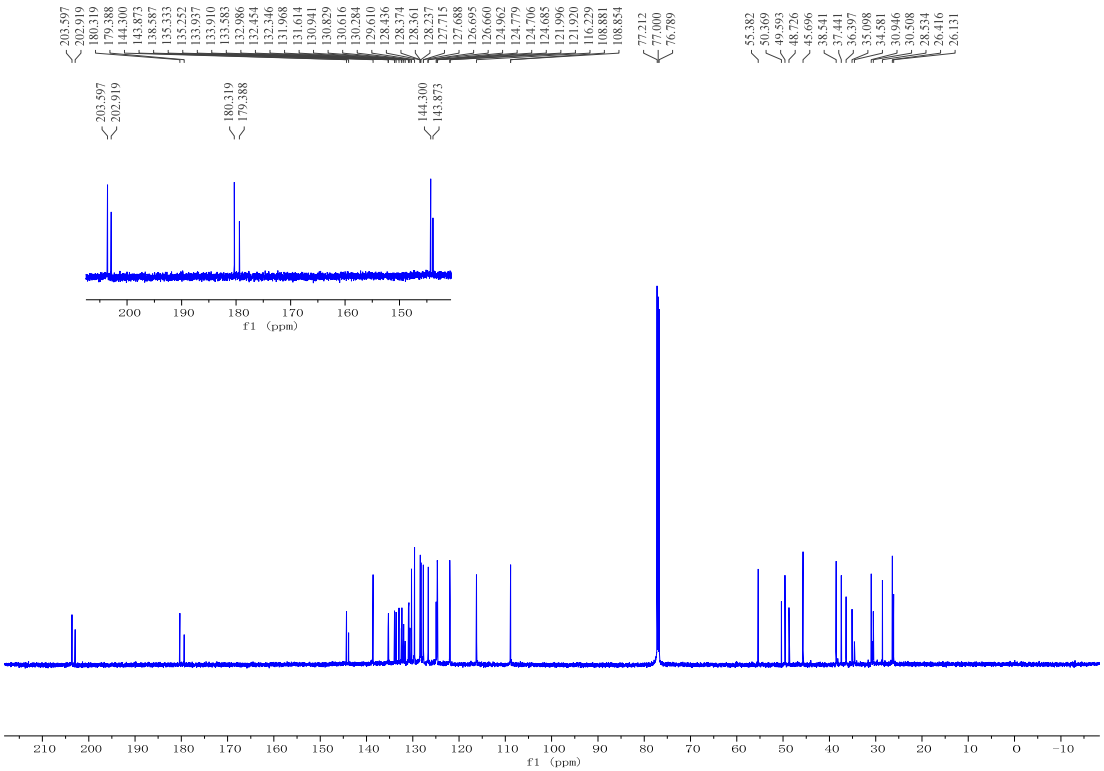


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)**-6ai and 7ai:**

^{1}H NMR (600 MHz, $CDCl_3$)

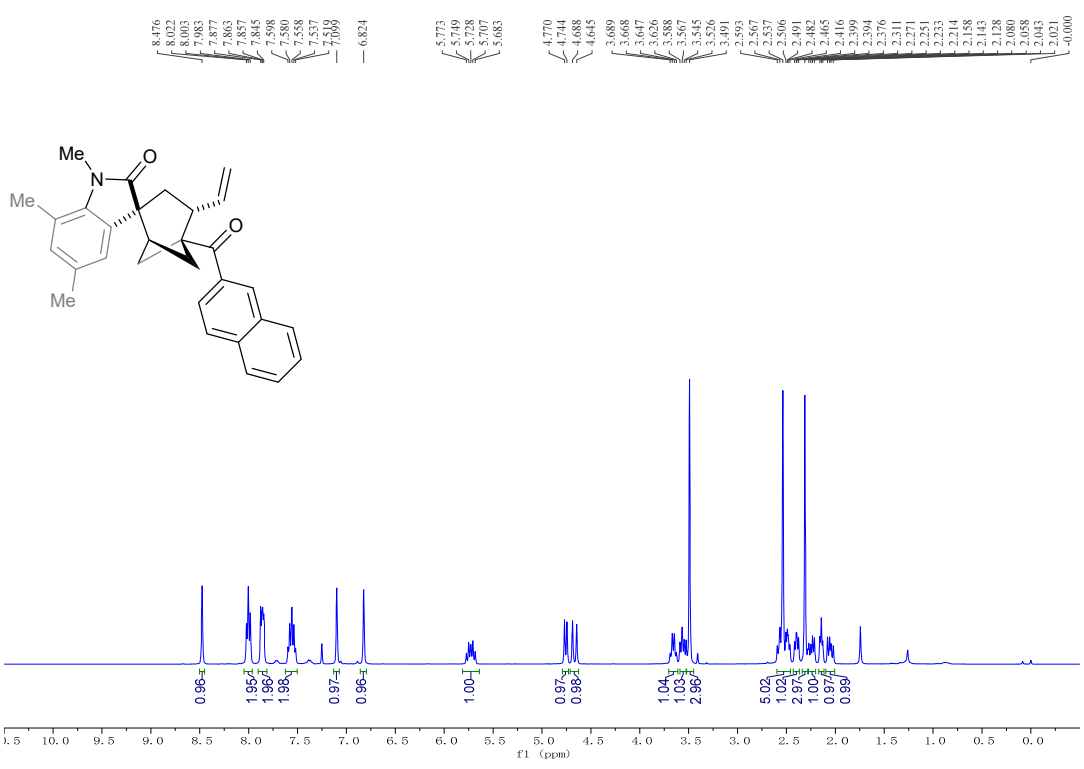


^{13}C NMR (150 MHz, $CDCl_3$)

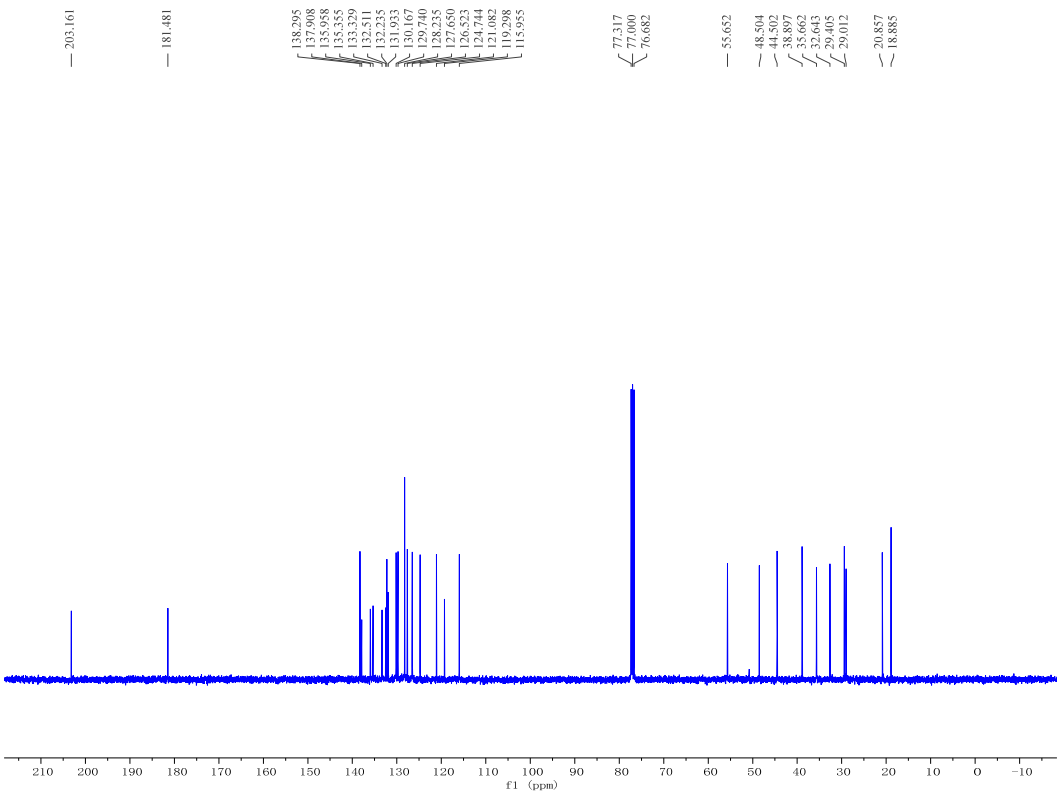


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)**-6aj**:

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

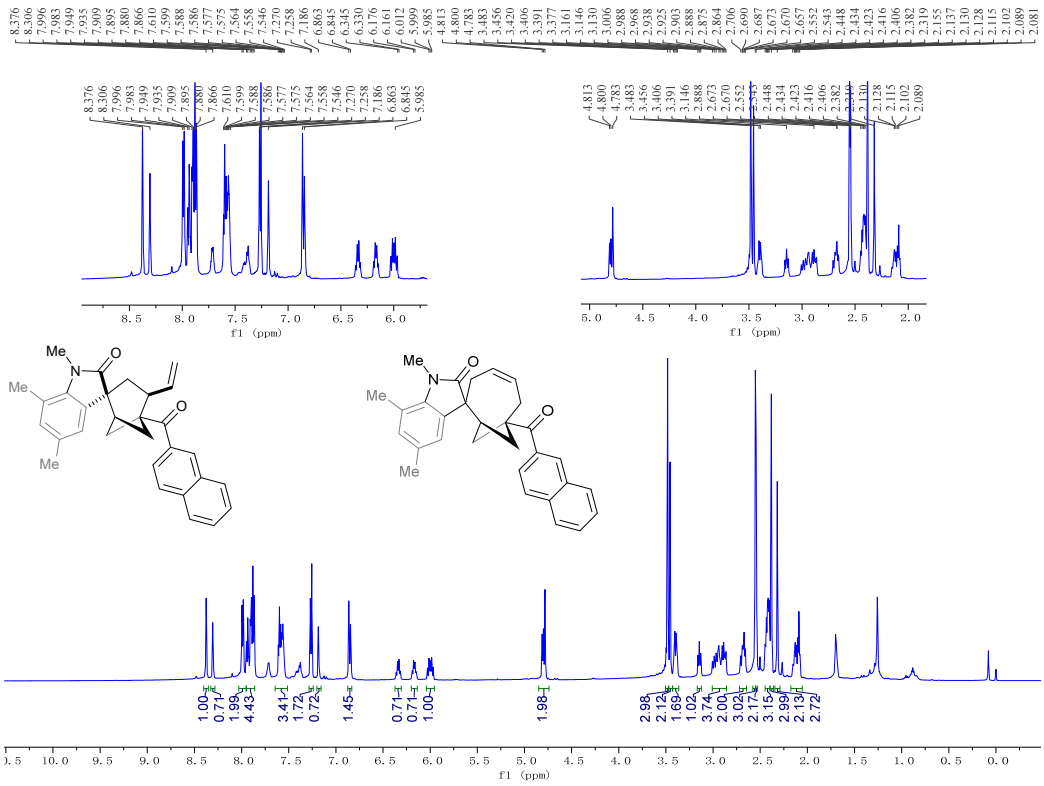


^{13}C NMR (100 MHz, $CDCl_3$)

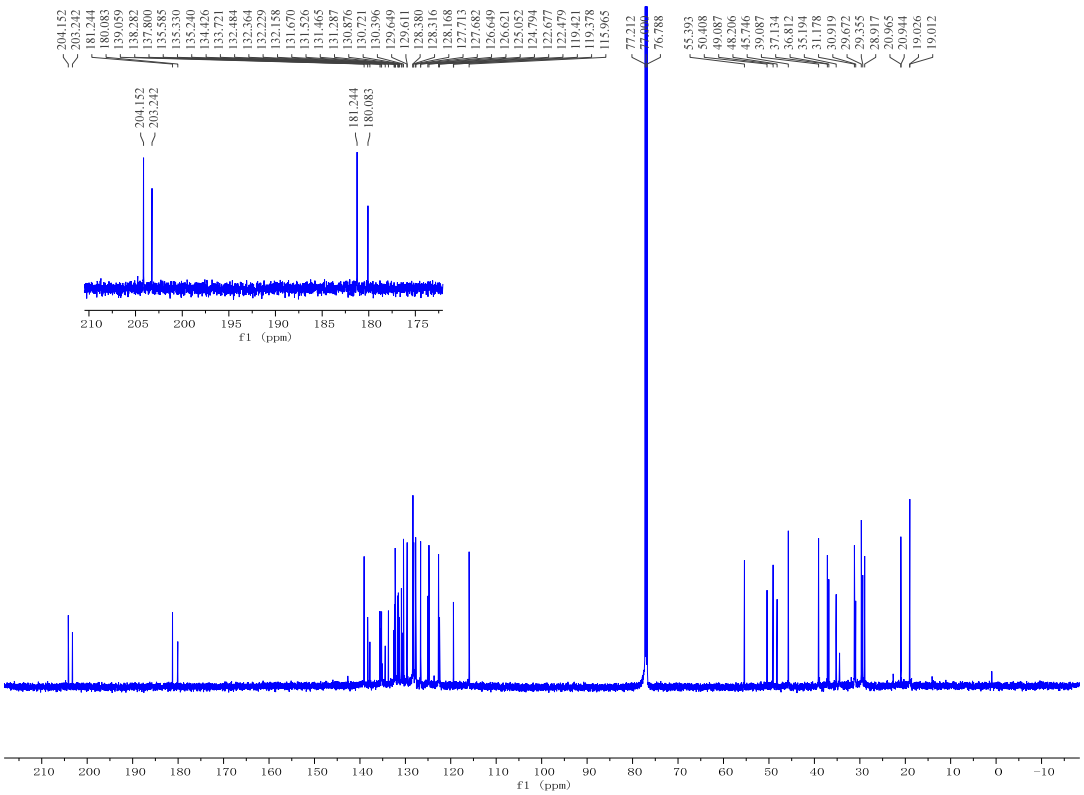


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)-**6aj and 7aj:**

^{1}H NMR (600 MHz, $CDCl_3$)

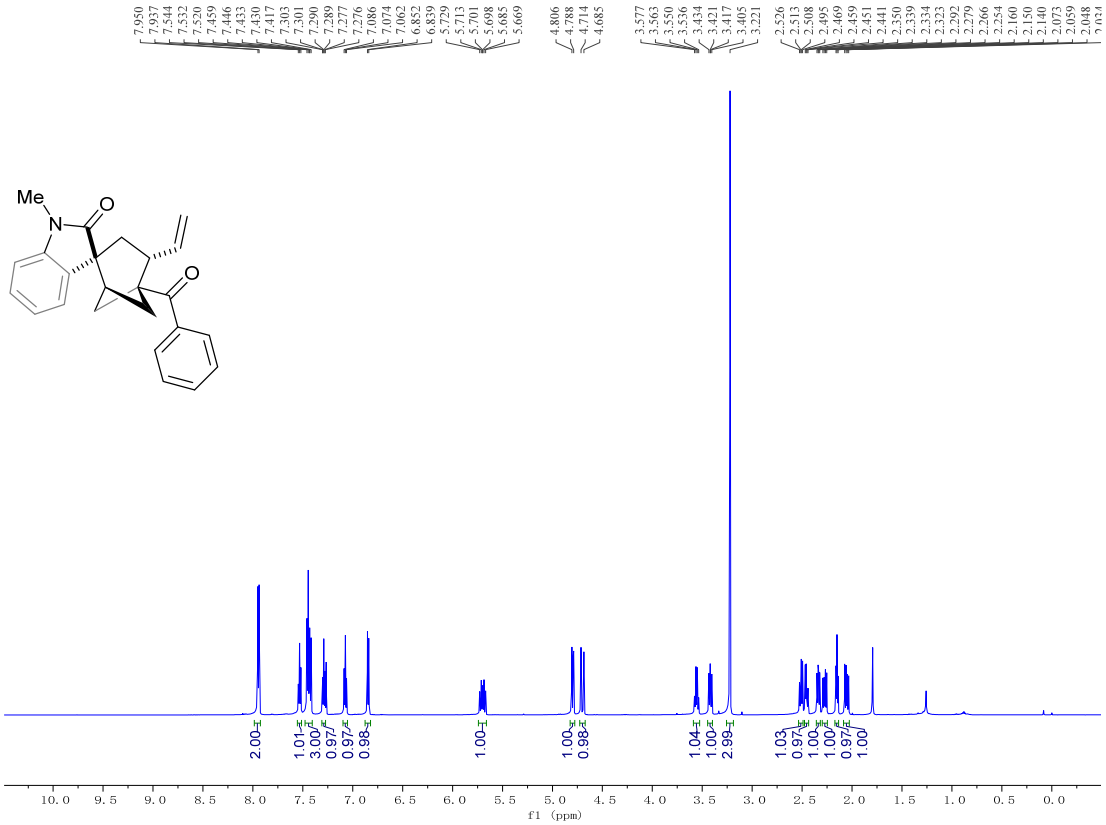


^{13}C NMR (150 MHz, $CDCl_3$)

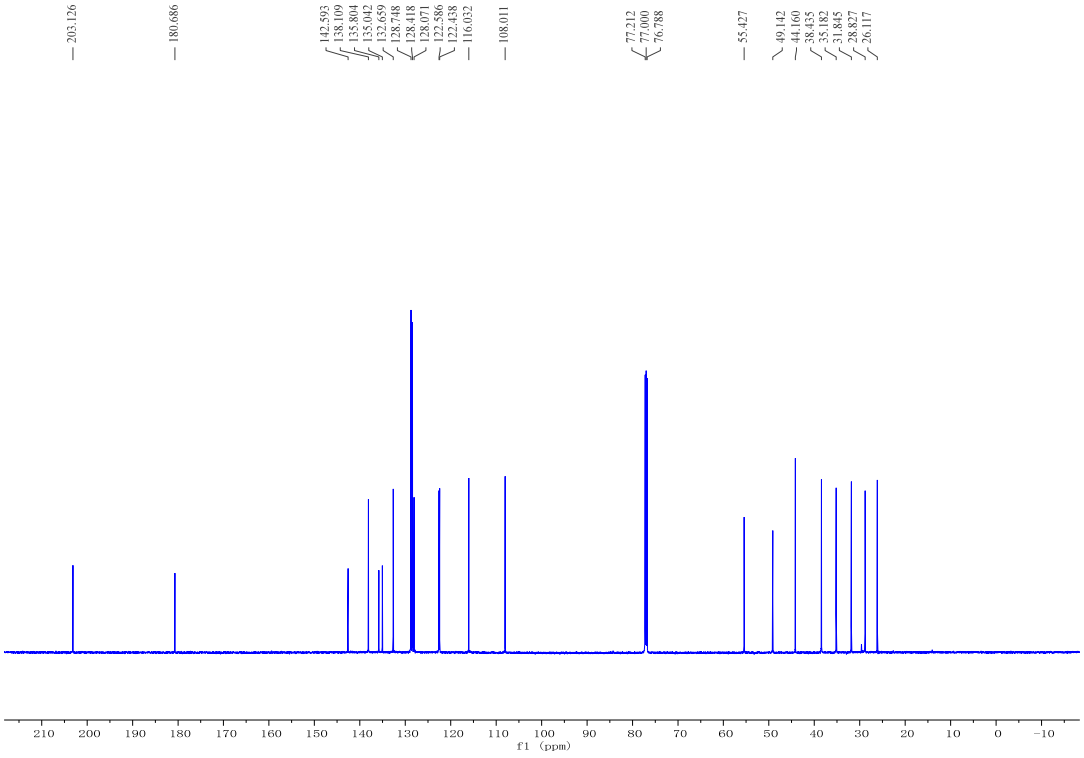


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)**-6ca**:

^{1}H NMR (600 MHz, $CDCl_3$)

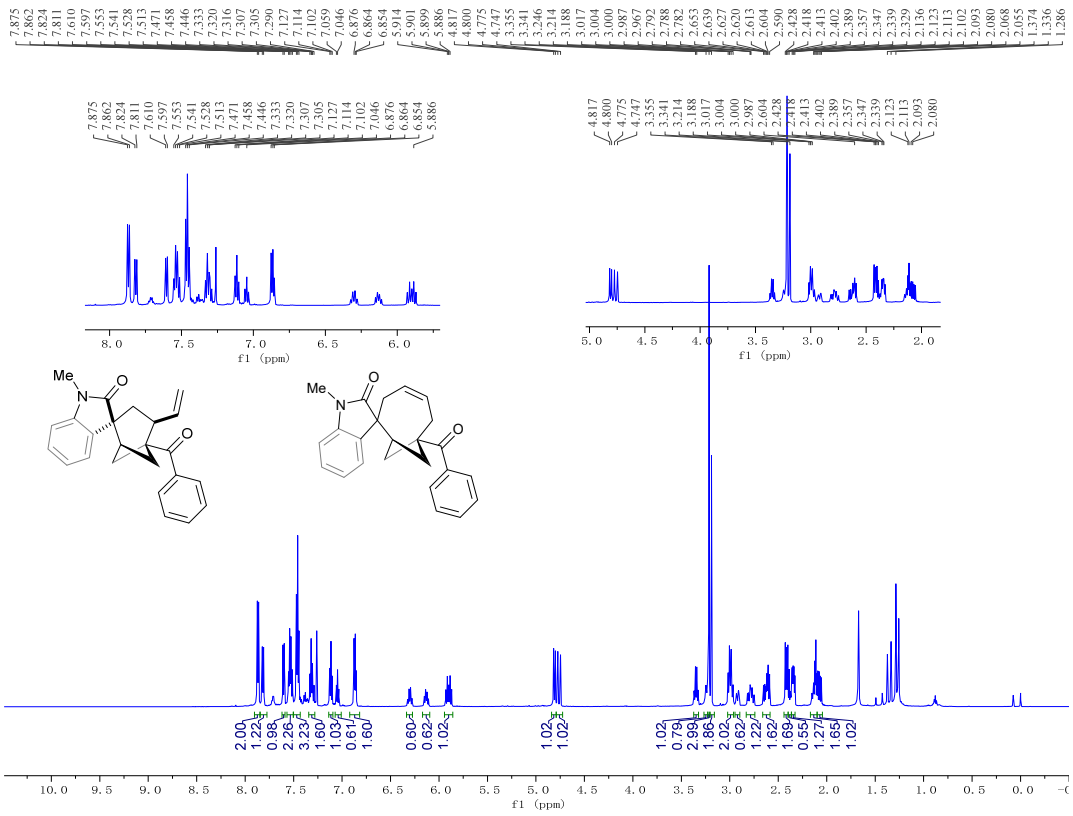


^{13}C NMR (150 MHz, $CDCl_3$)

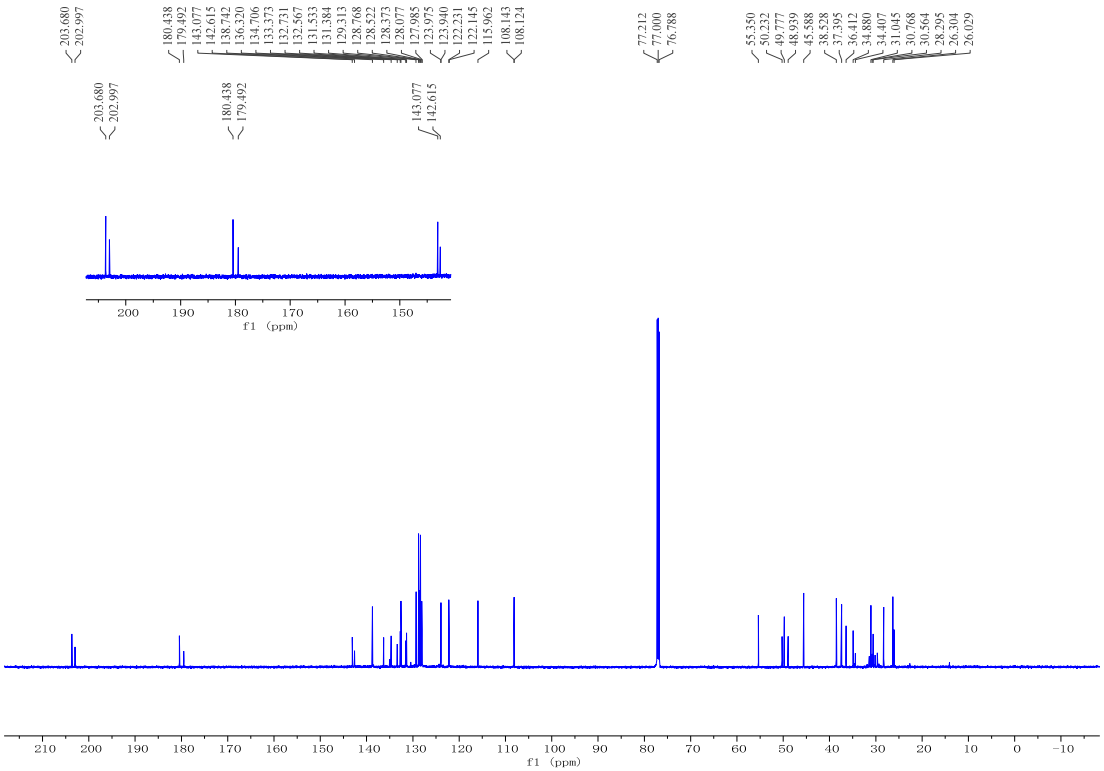


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)-**6ca and 7ca:**

^{1}H NMR (600 MHz, $CDCl_3$)

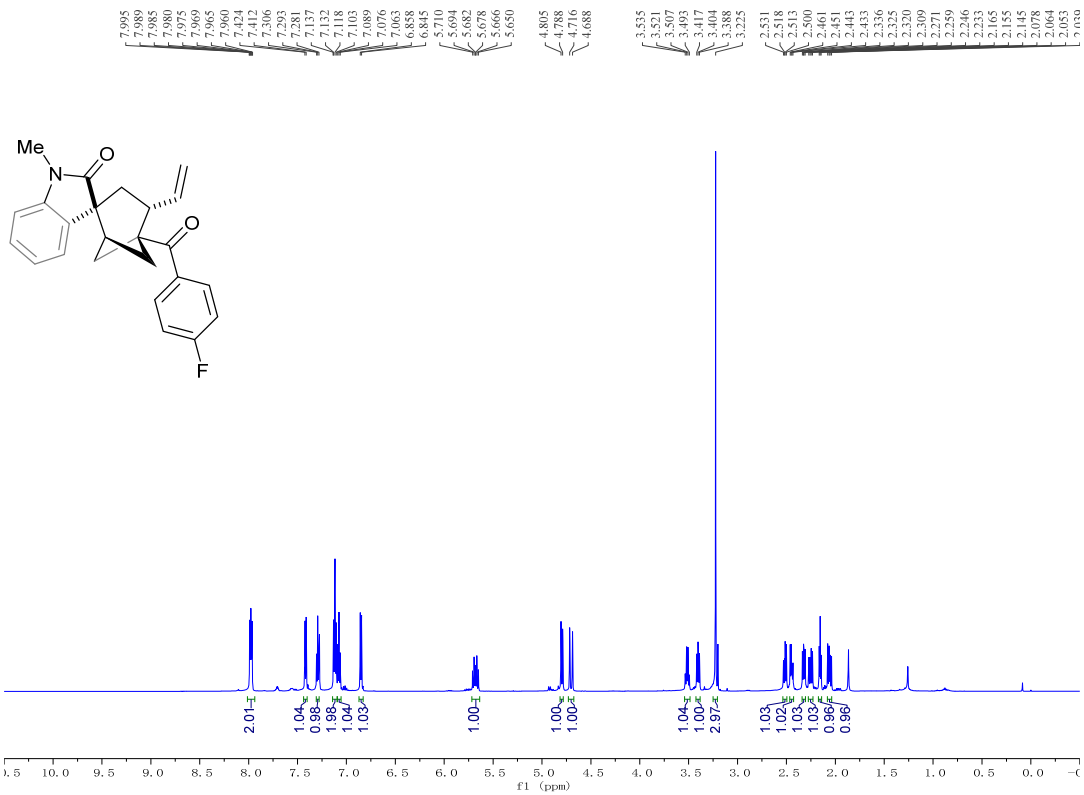


^{13}C NMR (150 MHz, $CDCl_3$)

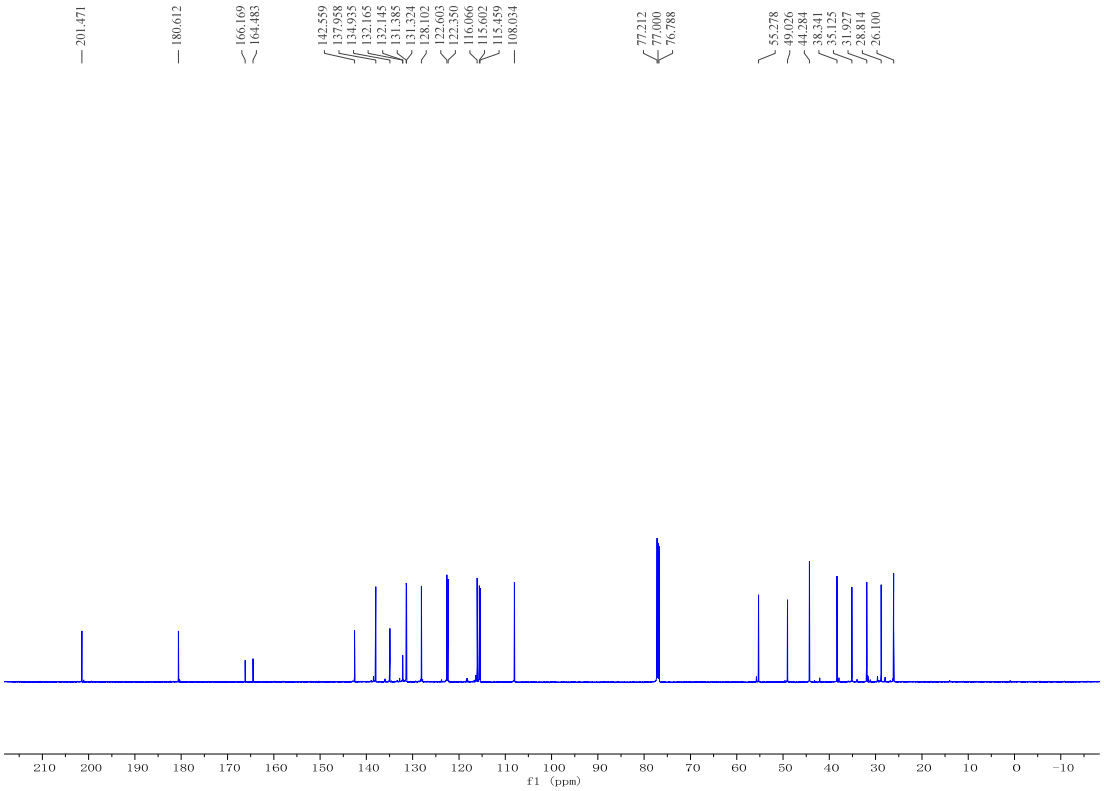


^{1}H ,^{13}C NMR and ^{19}F NMR Spectra for Compound (2*S**,4*R**)-**6da**:

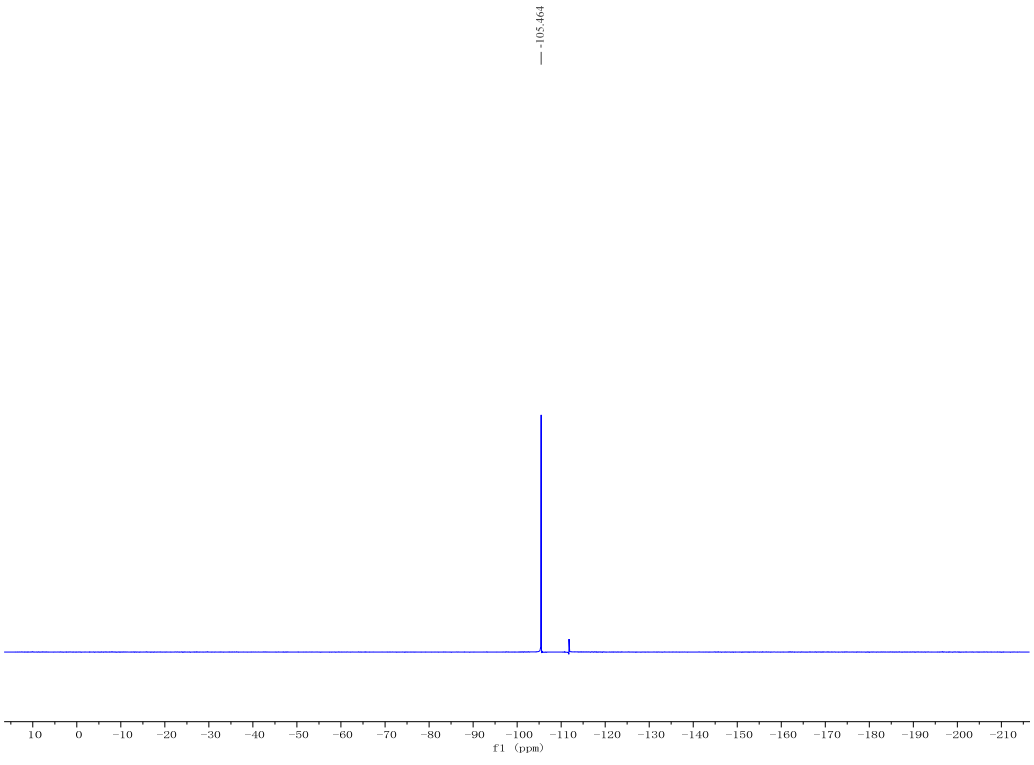
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

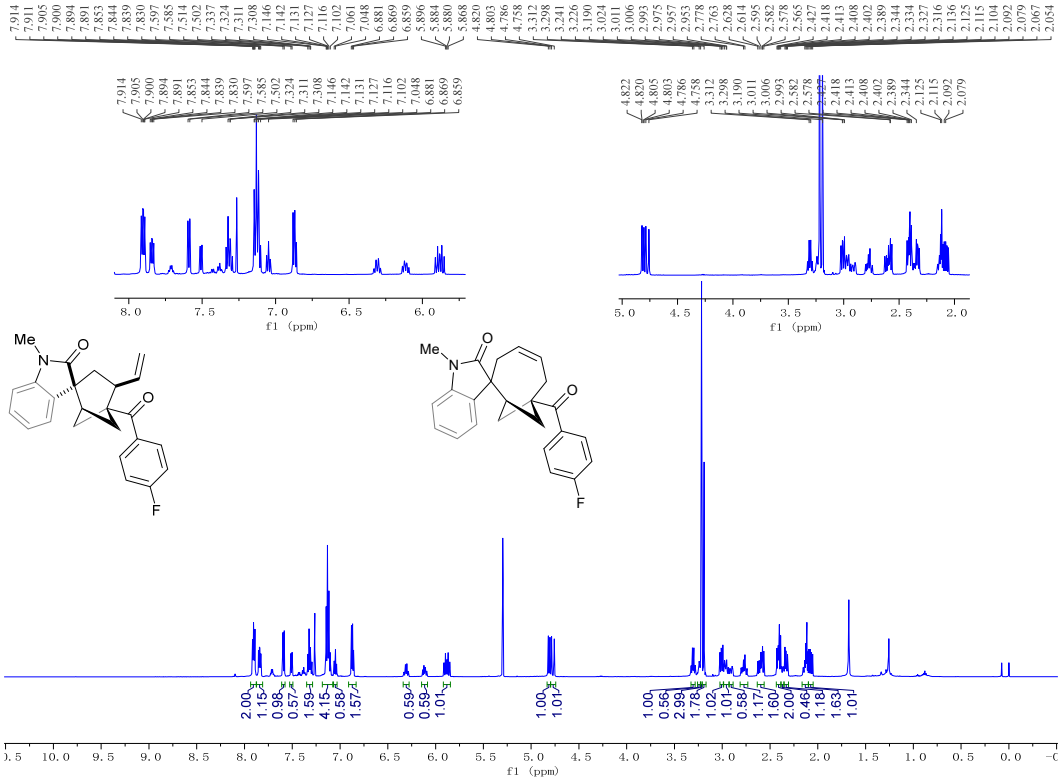


^{19}F NMR (565 MHz, $CDCl_3$)

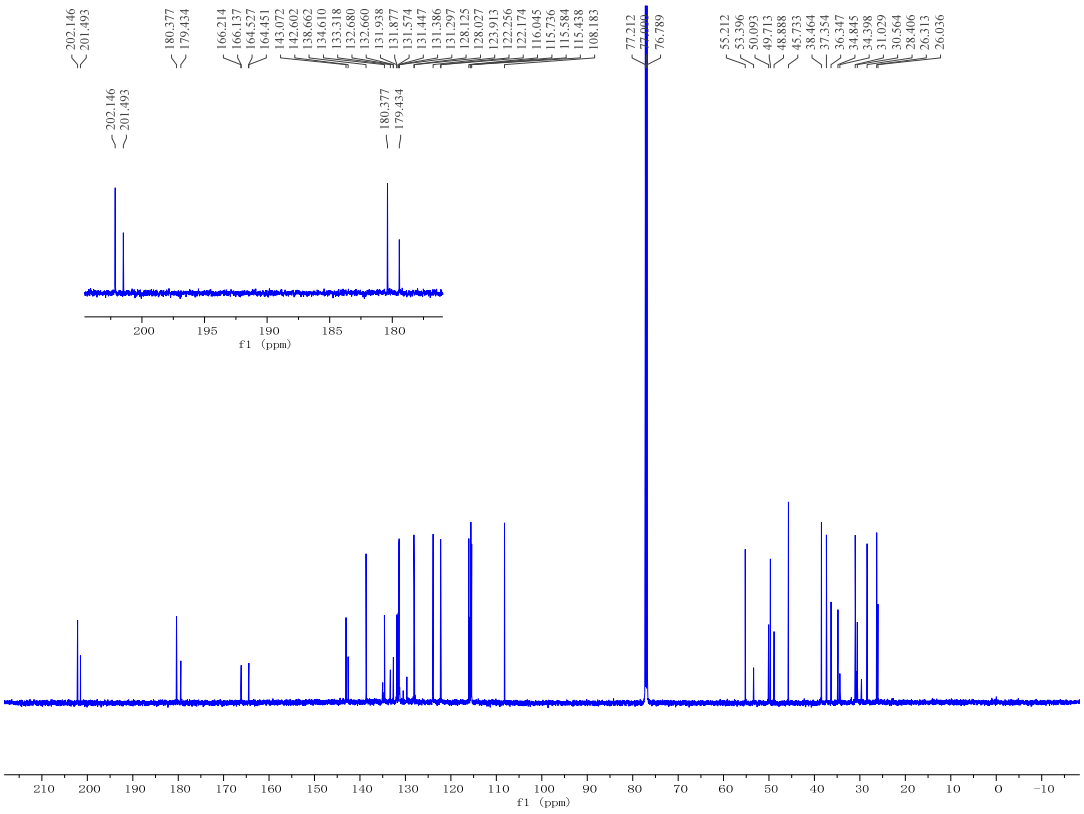


^{1}H ,^{13}C NMR and ^{19}F NMR Spectra for Compounds (2*S**,4*S**)-6da and 7da:

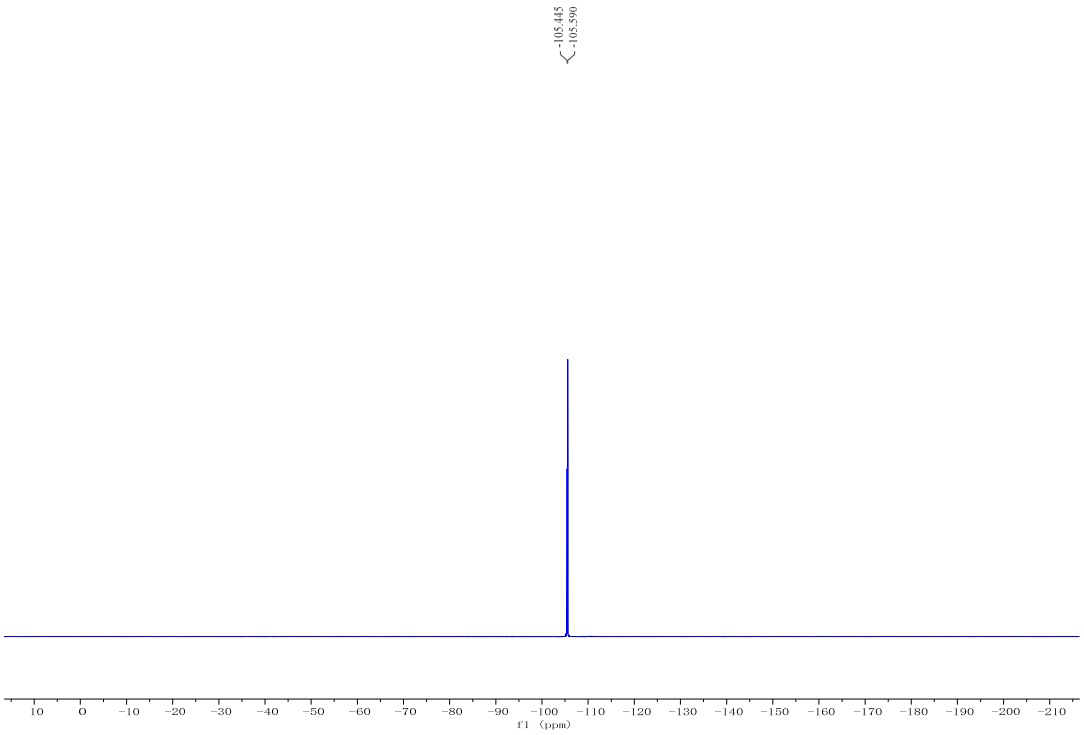
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

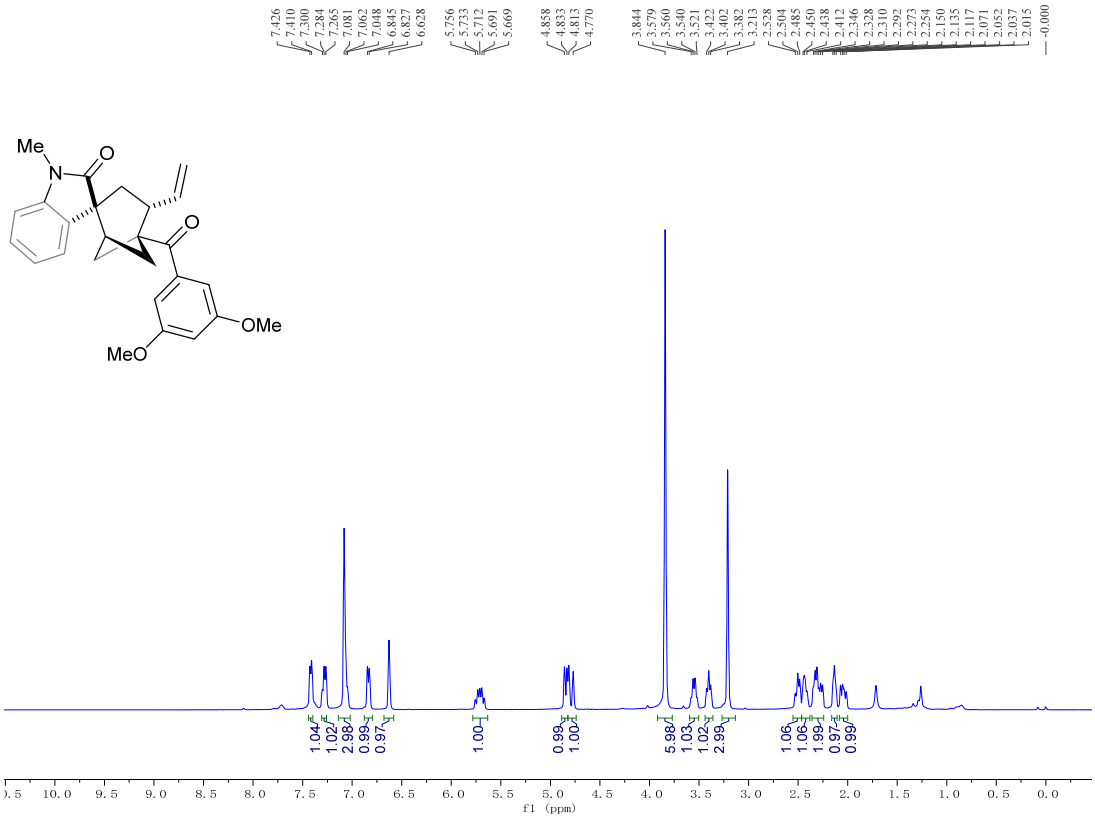


^{19}F NMR (565 MHz, $CDCl_3$)

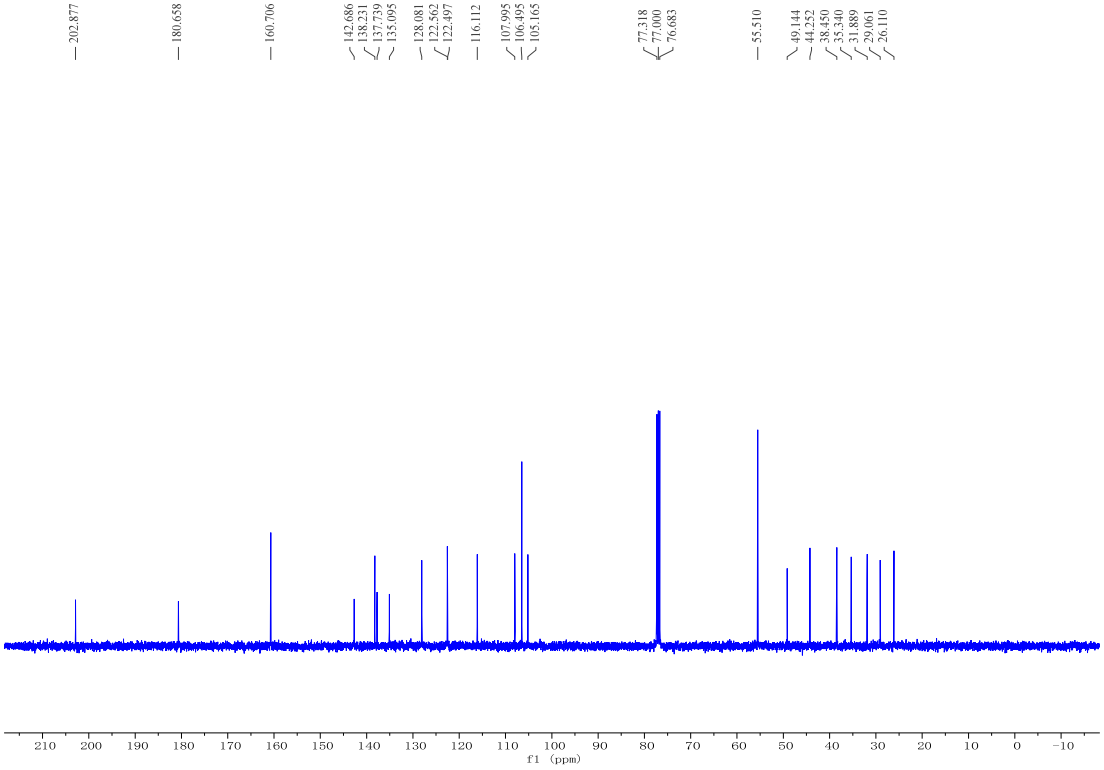


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)-**6la**:

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

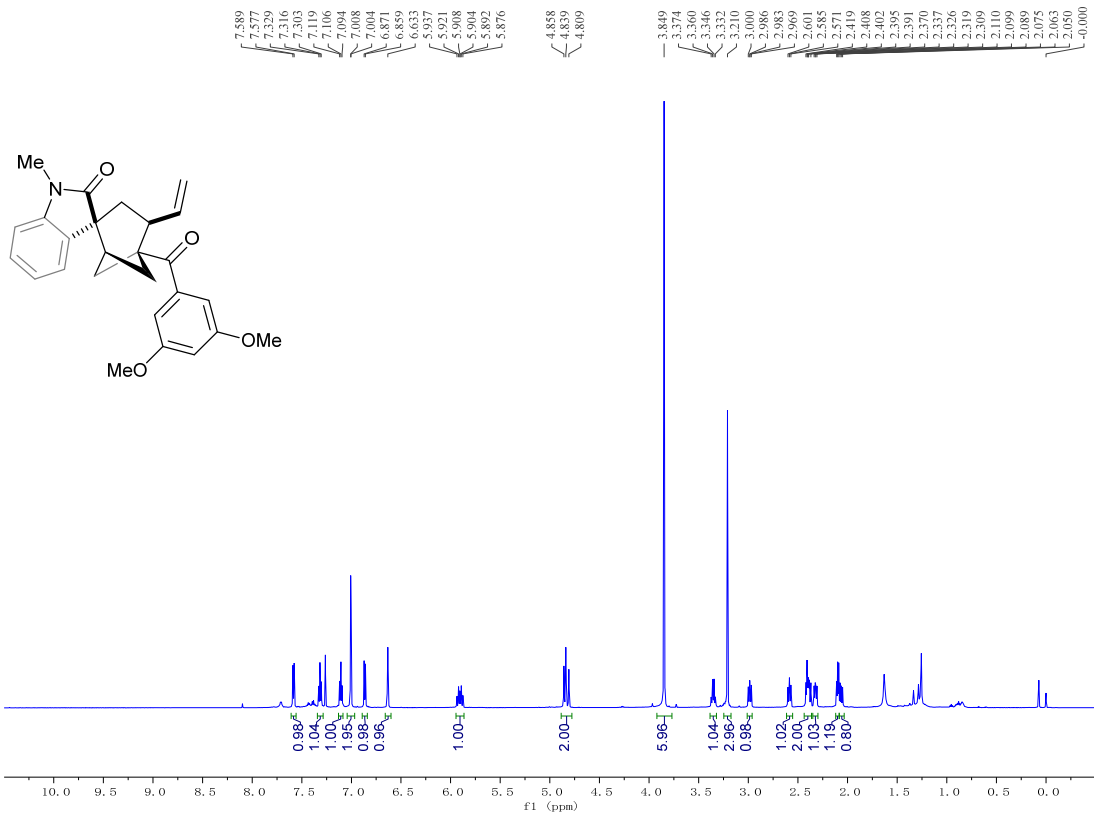


^{13}C NMR (100 MHz, $CDCl_3$)

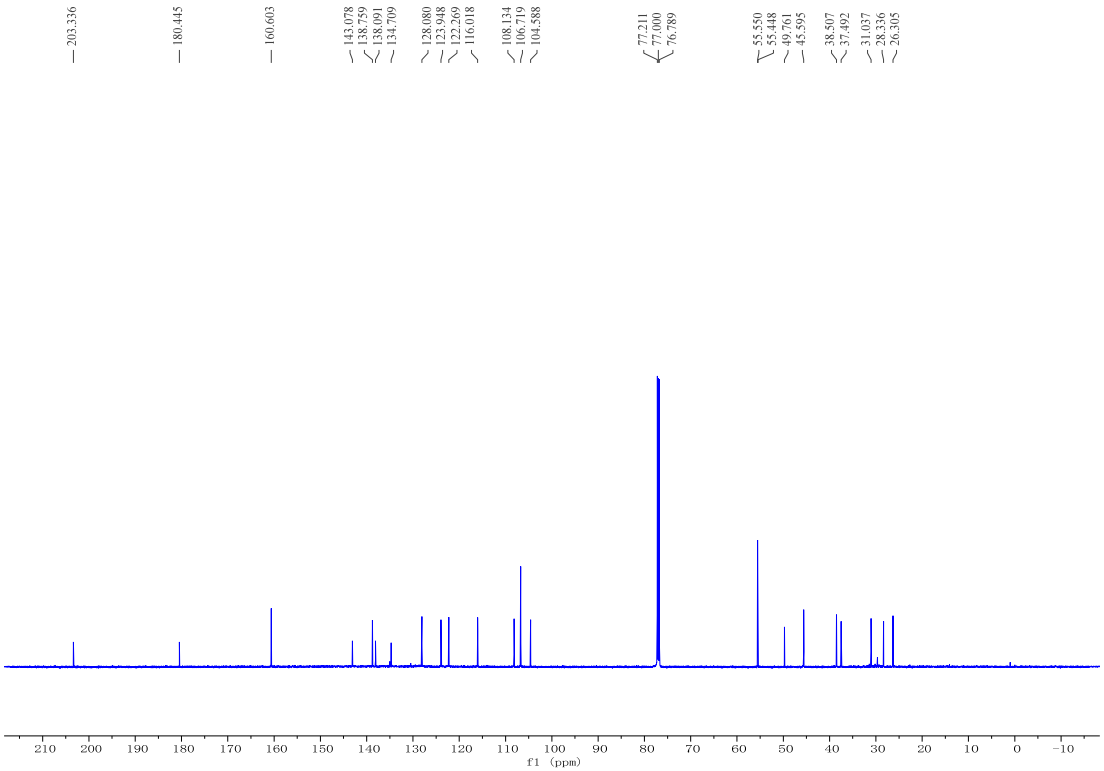


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*S**)**-6la:**

^{1}H NMR (600 MHz, $CDCl_3$)

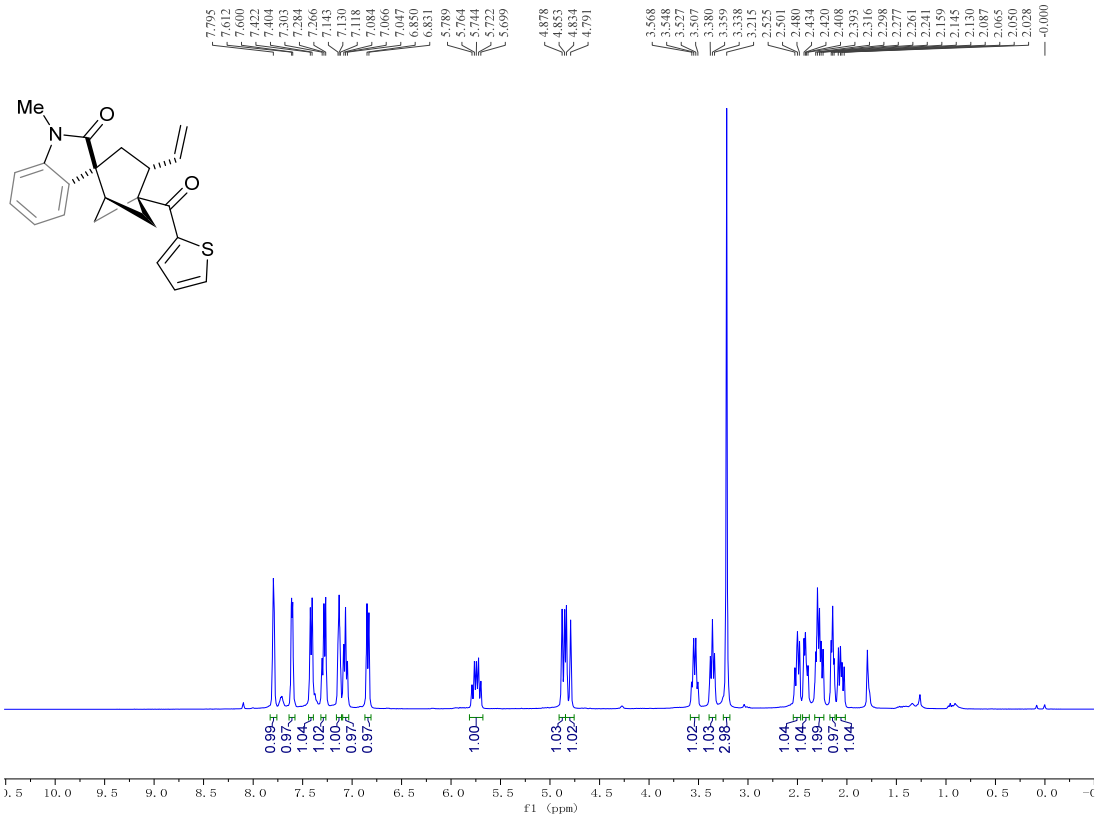


^{13}C NMR (150 MHz, $CDCl_3$)

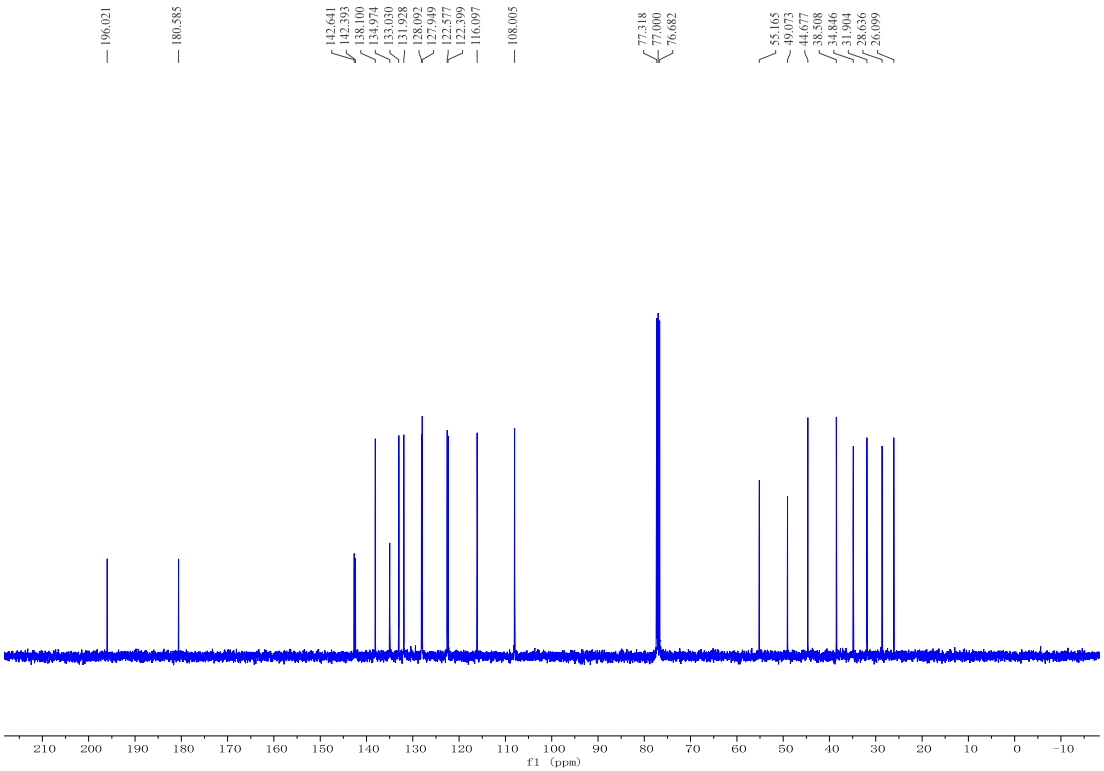


^{1}H and ^{13}C NMR Spectra for Compound (2*S**,4*R**)**-6fa**:

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

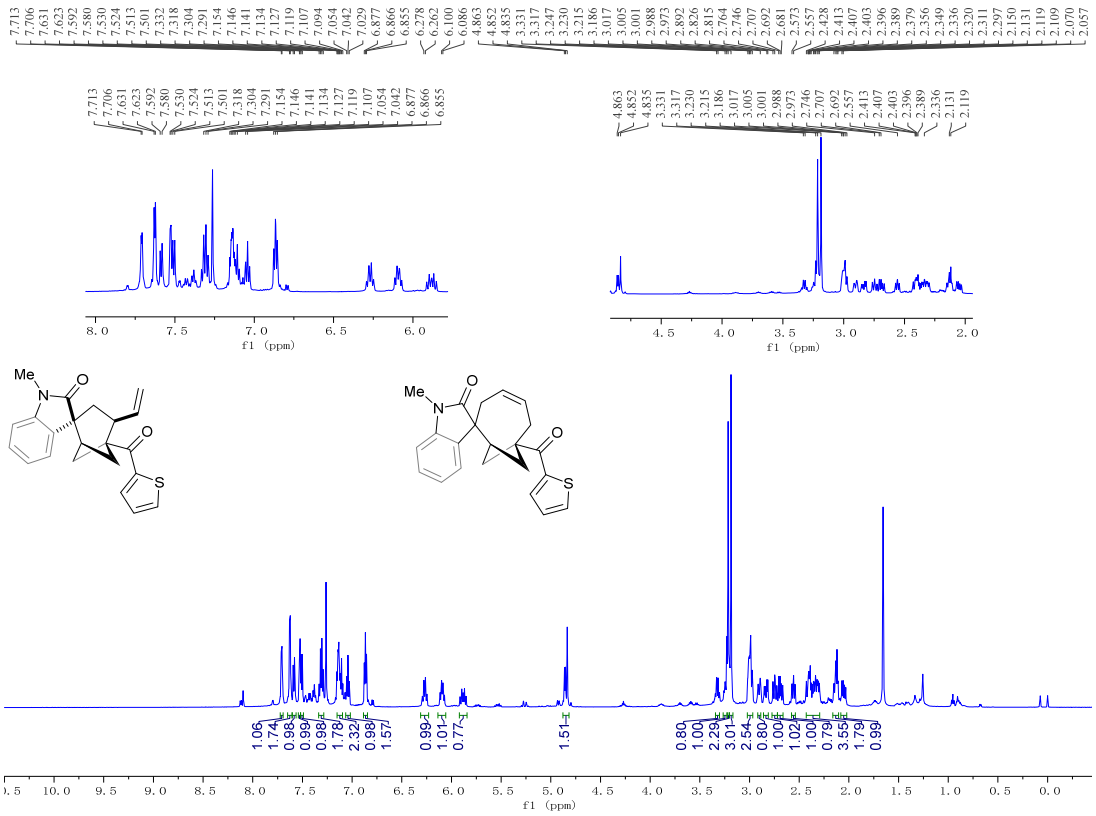


^{13}C NMR (100 MHz, $CDCl_3$)

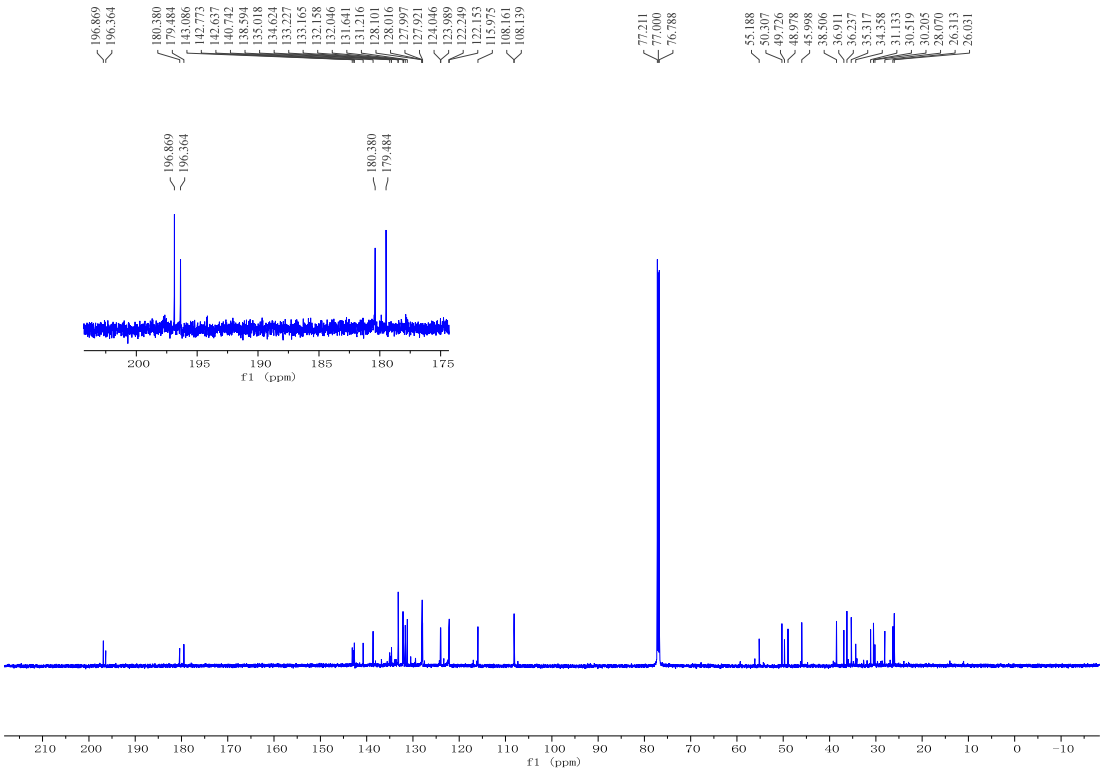


^{1}H and ^{13}C NMR Spectra for Compounds (2*S**,4*S**)**-6fa and 7fa:**

^{1}H NMR (600 MHz, $CDCl_3$)

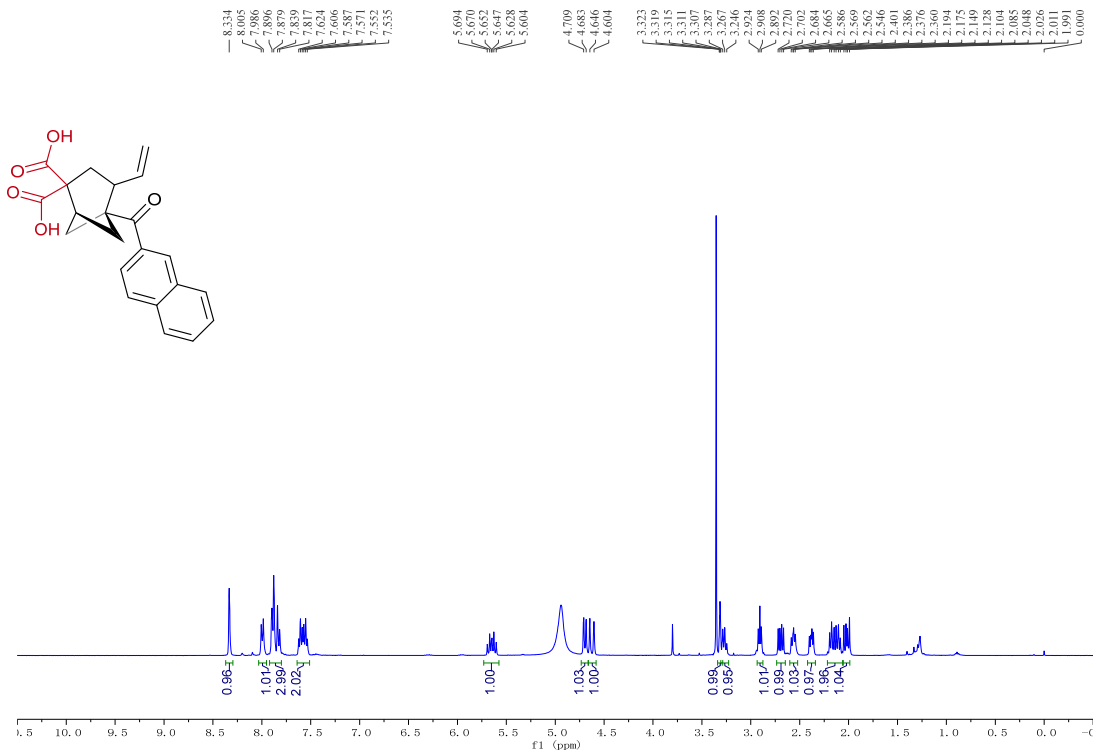


^{13}C NMR (150 MHz, $CDCl_3$)

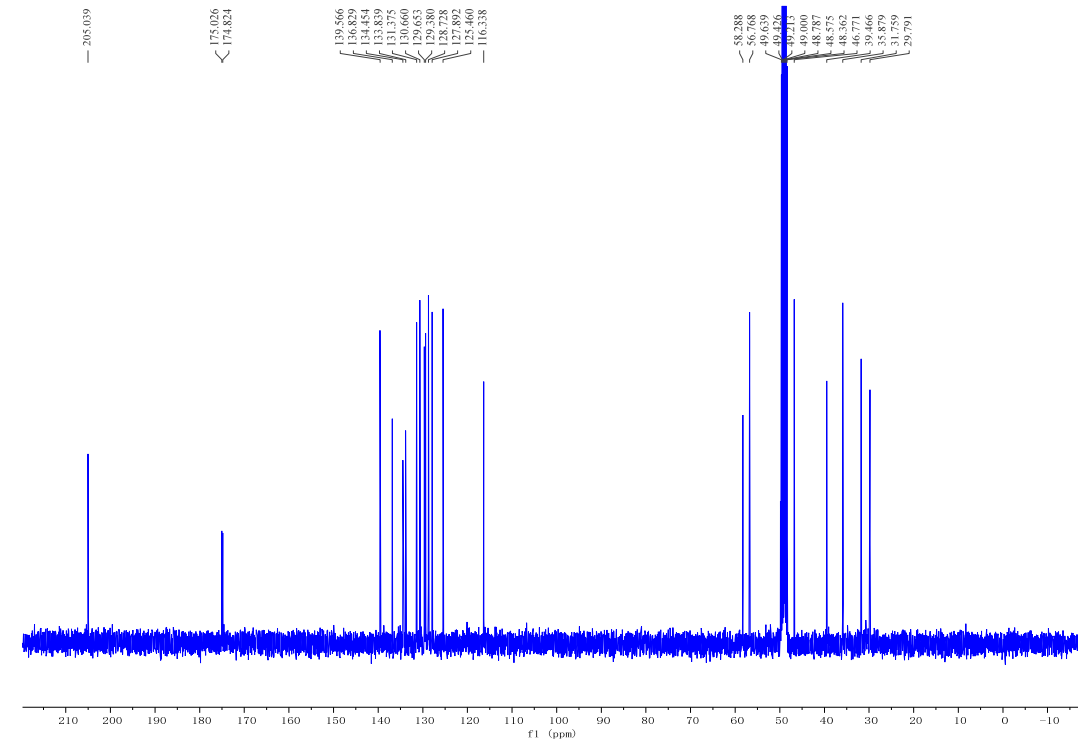


^{1}H and ^{13}C NMR Spectra for Compound 8

^{1}H NMR (400 MHz, CD_3OD)

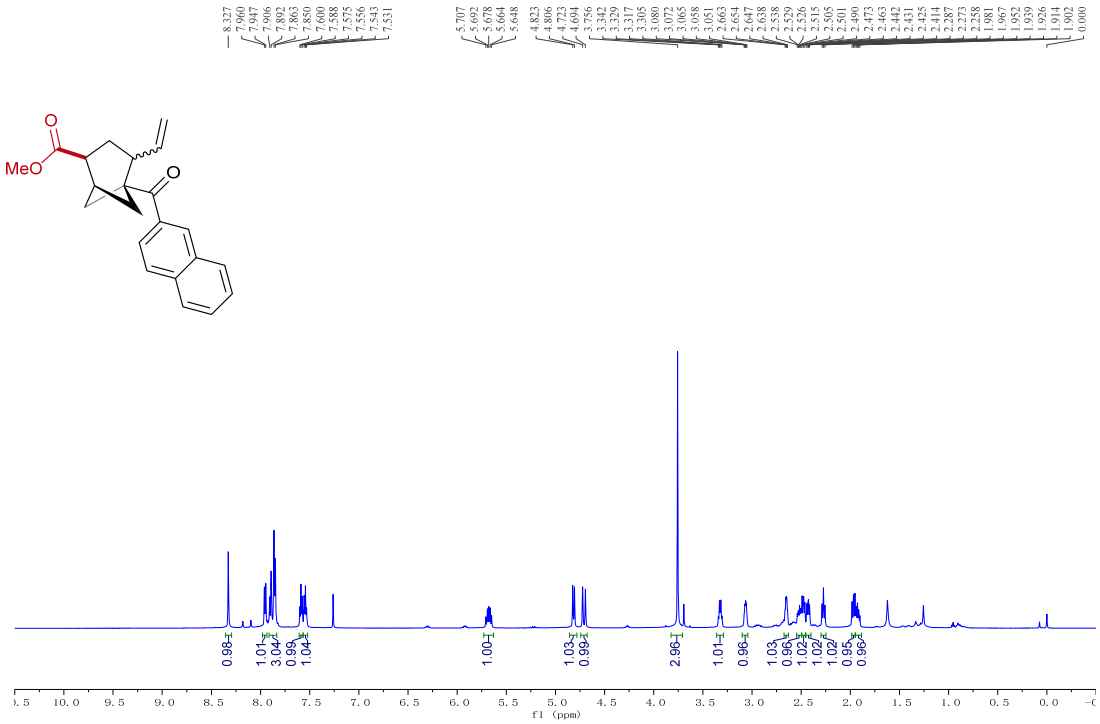


^{13}C NMR (100 MHz, CD_3OD)

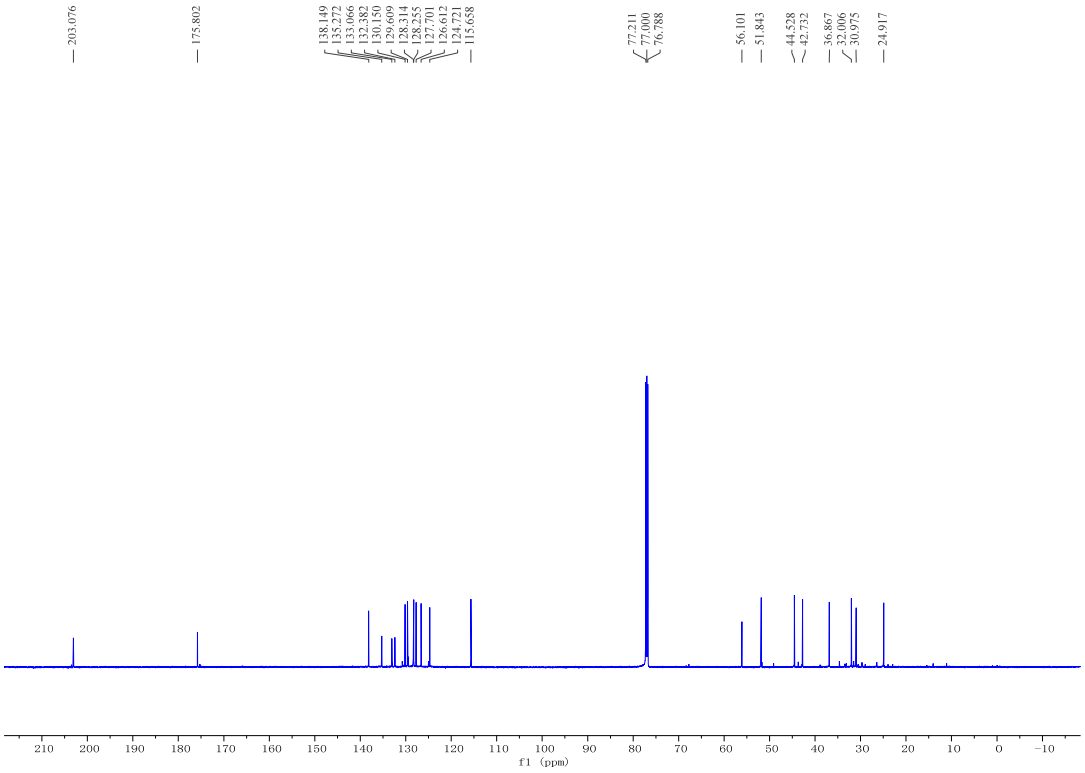


^{1}H and ^{13}C NMR Spectra for Compound 9 (1:1 *d.r.*)**:**

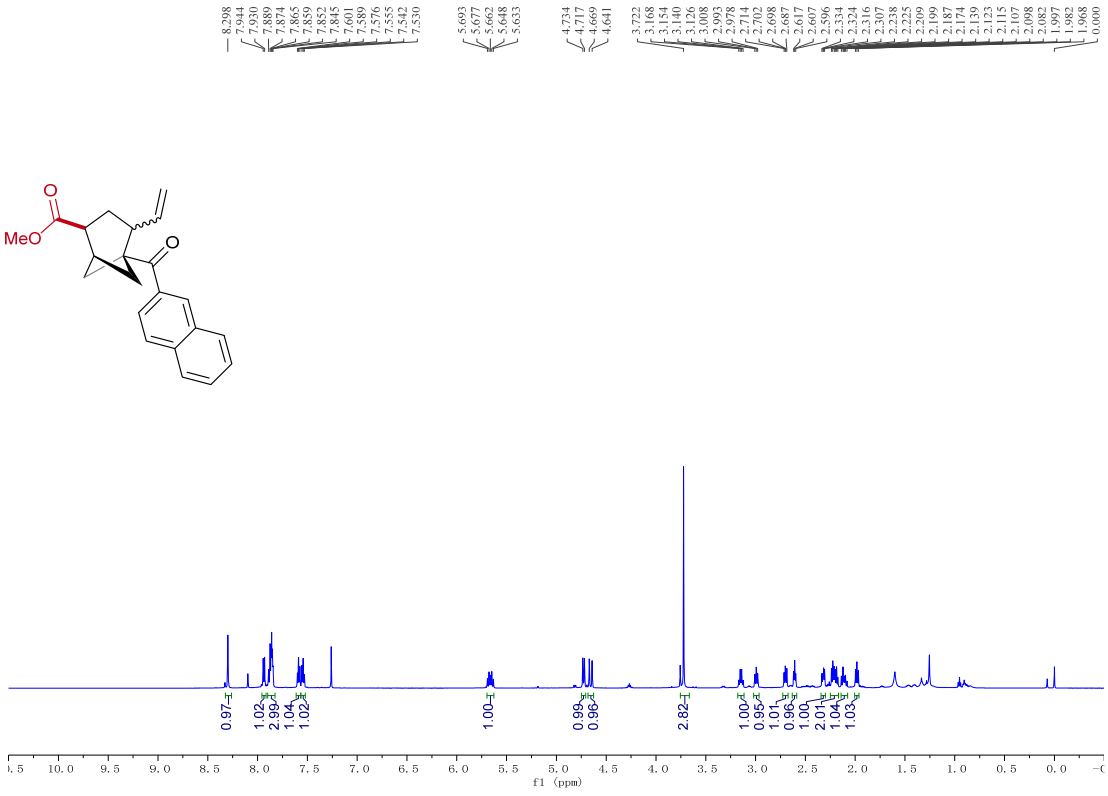
^{1}H NMR (600 MHz, $CDCl_3$), One of the diastereomers:



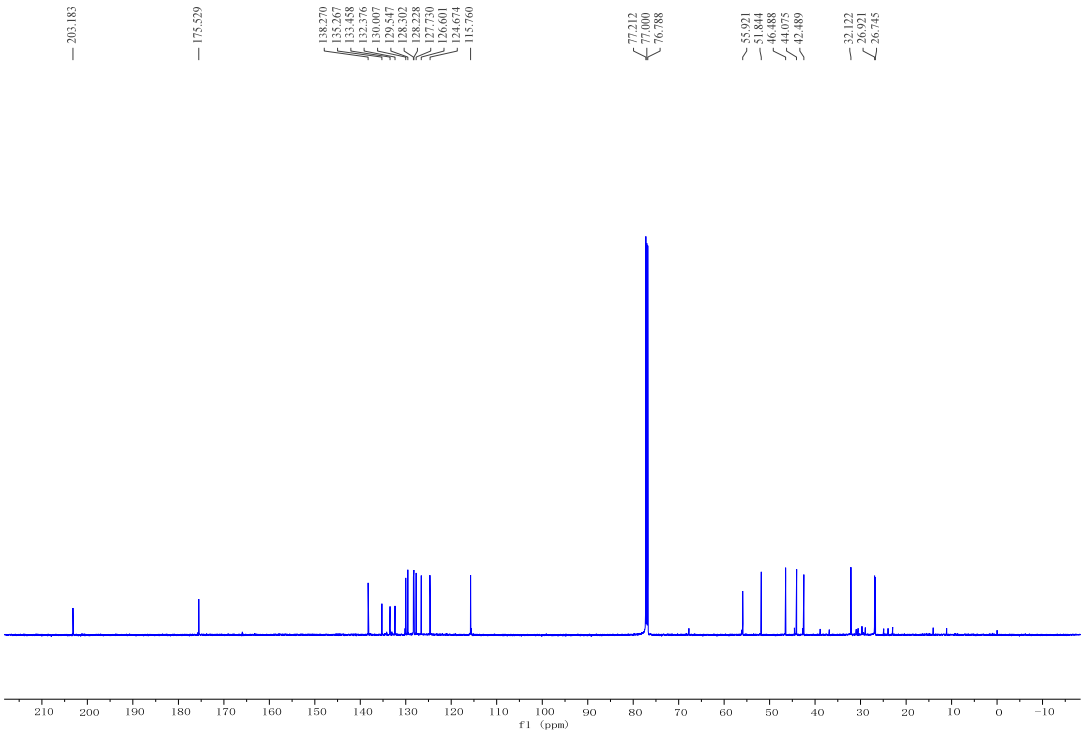
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$), The other diastereomer:

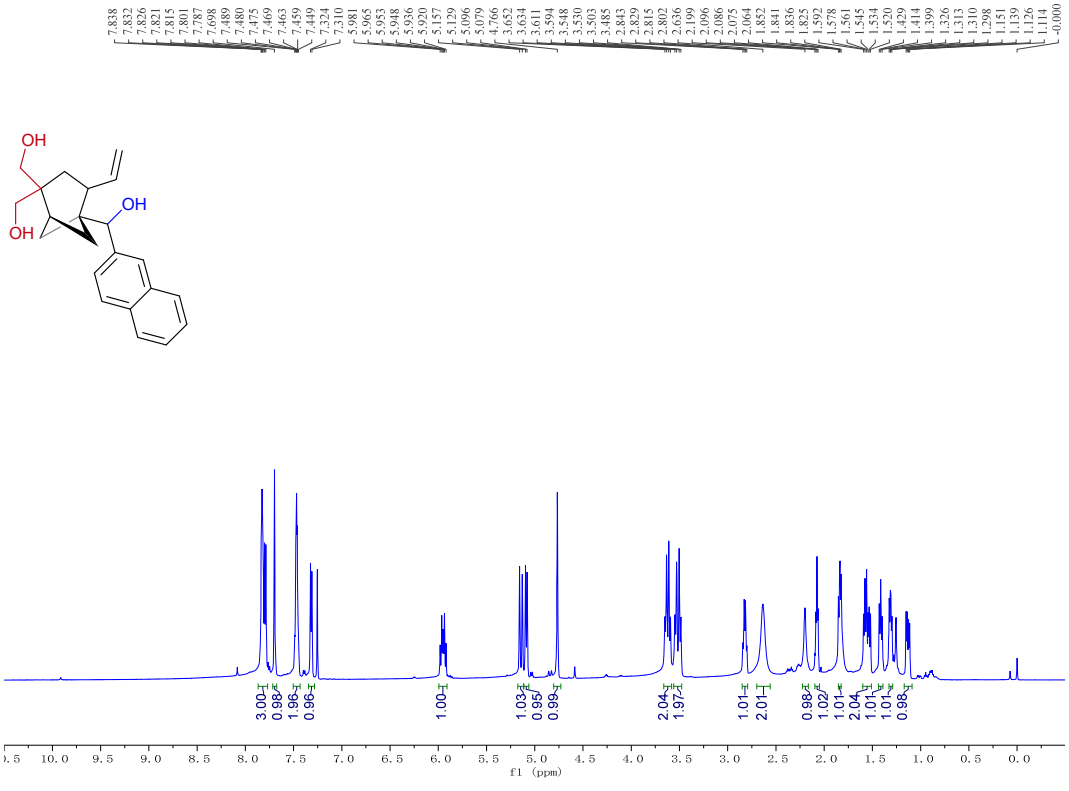


^{13}C NMR (150 MHz, $CDCl_3$)

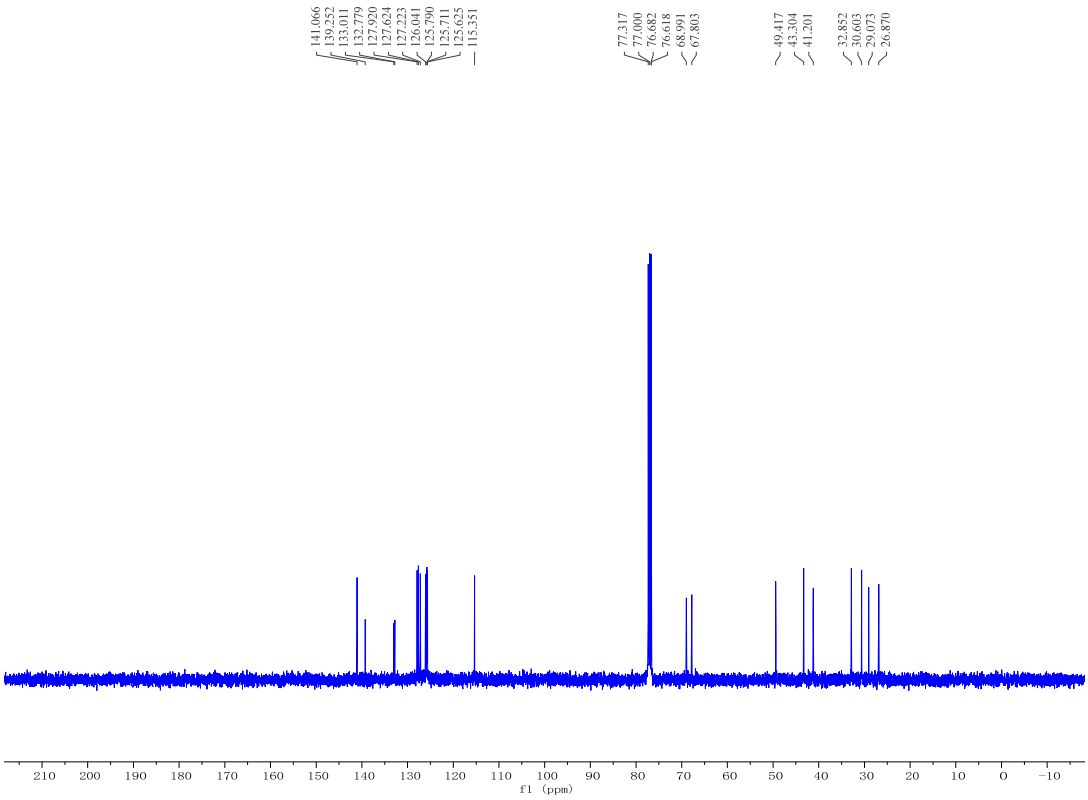


^{1}H and ^{13}C NMR Spectra for Compound 10:

^{1}H NMR (600 MHz, $CDCl_3$)

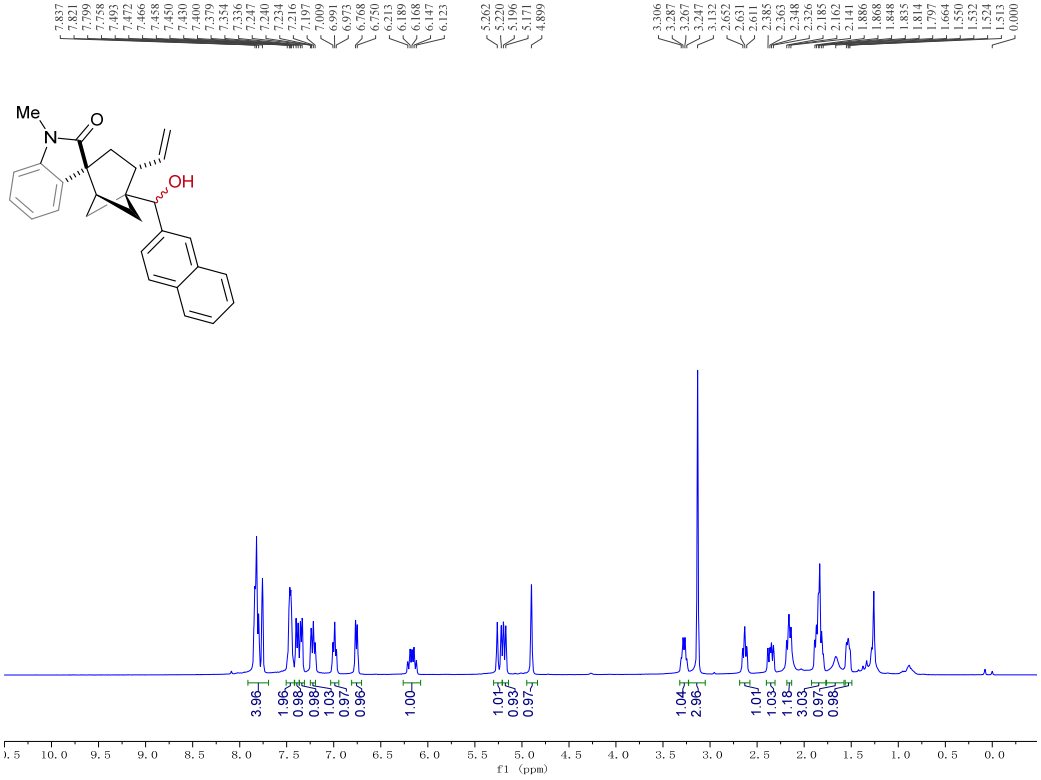


^{13}C NMR (100 MHz, $CDCl_3$)

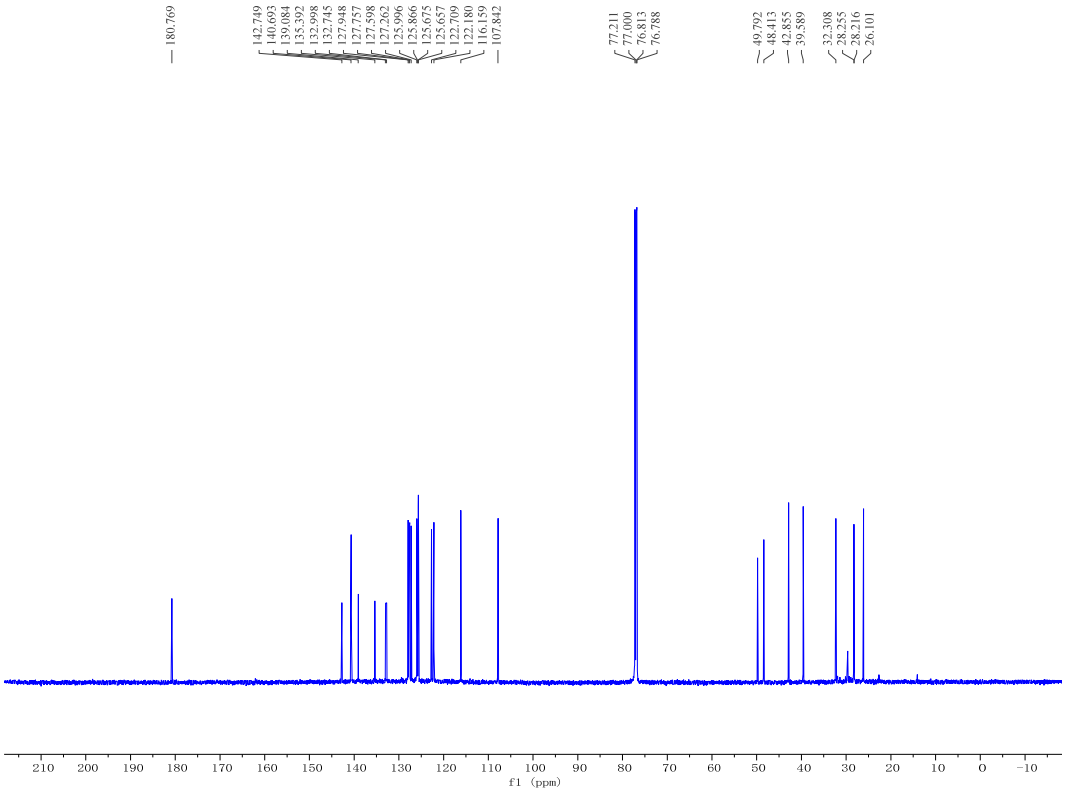


^{1}H and ^{13}C NMR Spectra for Compound 11 (the major isomer):

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

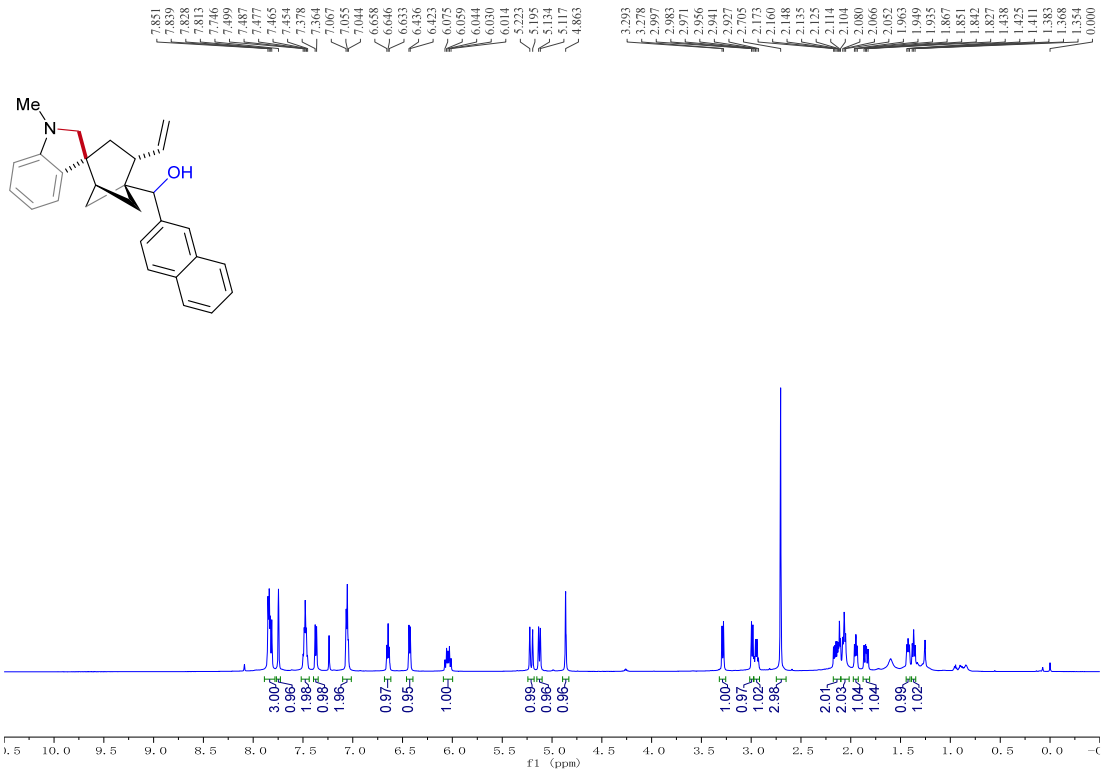


^{13}C NMR (150 MHz, $CDCl_3$)

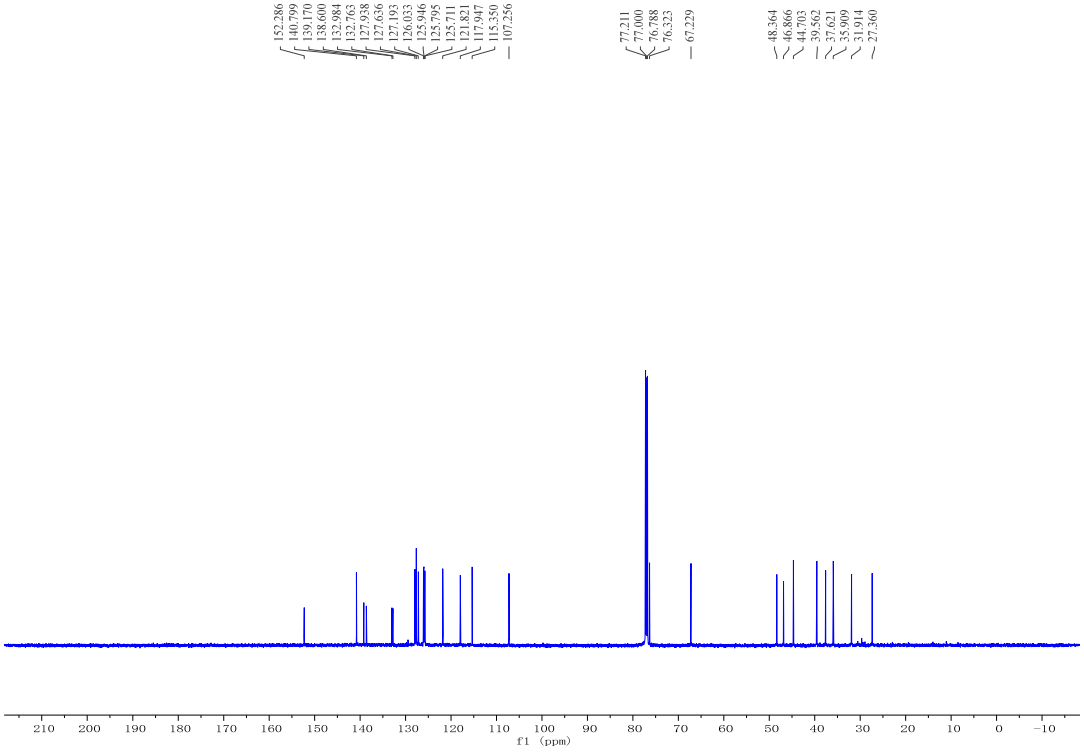


^{1}H and ^{13}C NMR Spectra for Compound 12:

^{1}H NMR (600 MHz, $CDCl_3$)

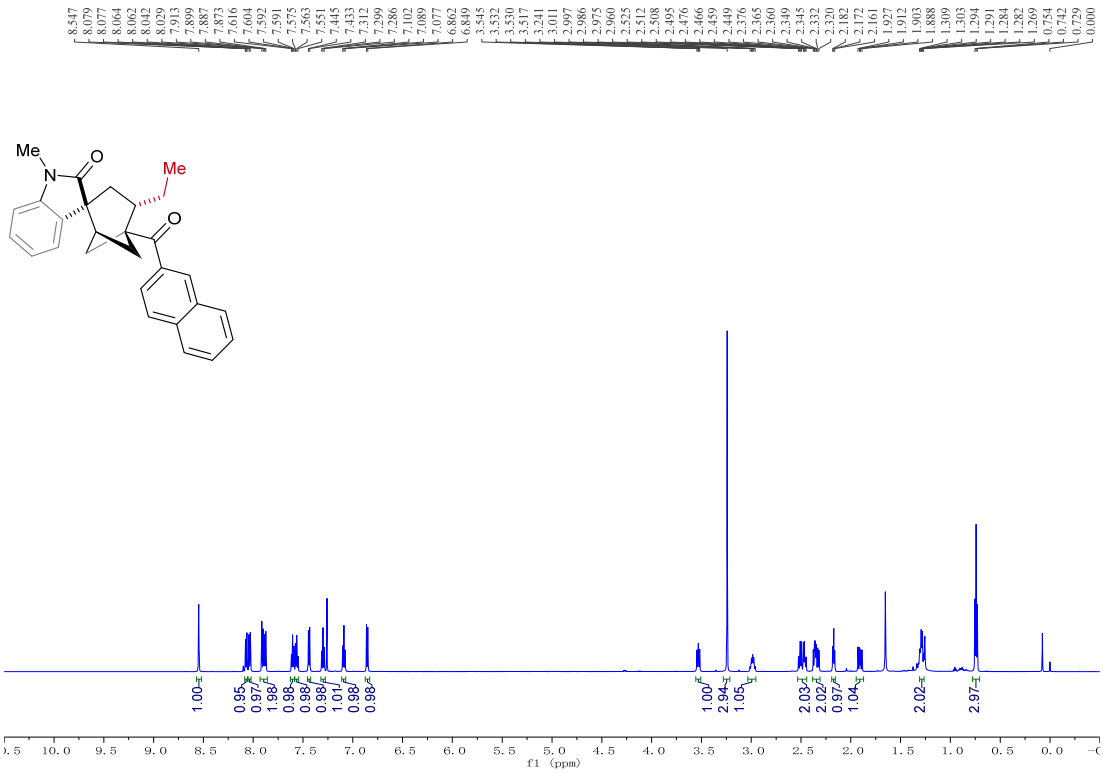


^{13}C NMR (150 MHz, $CDCl_3$)

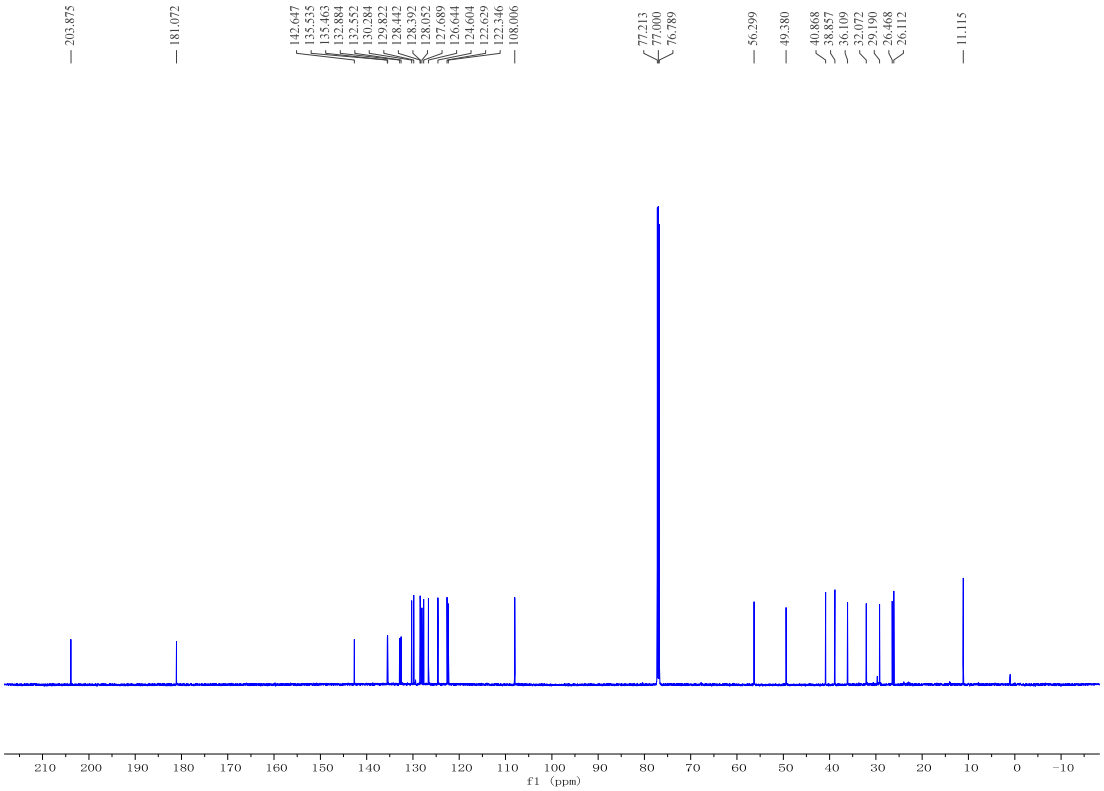


^{1}H and ^{13}C NMR Spectra for Compound 13

^{1}H NMR (600 MHz, $CDCl_3$)

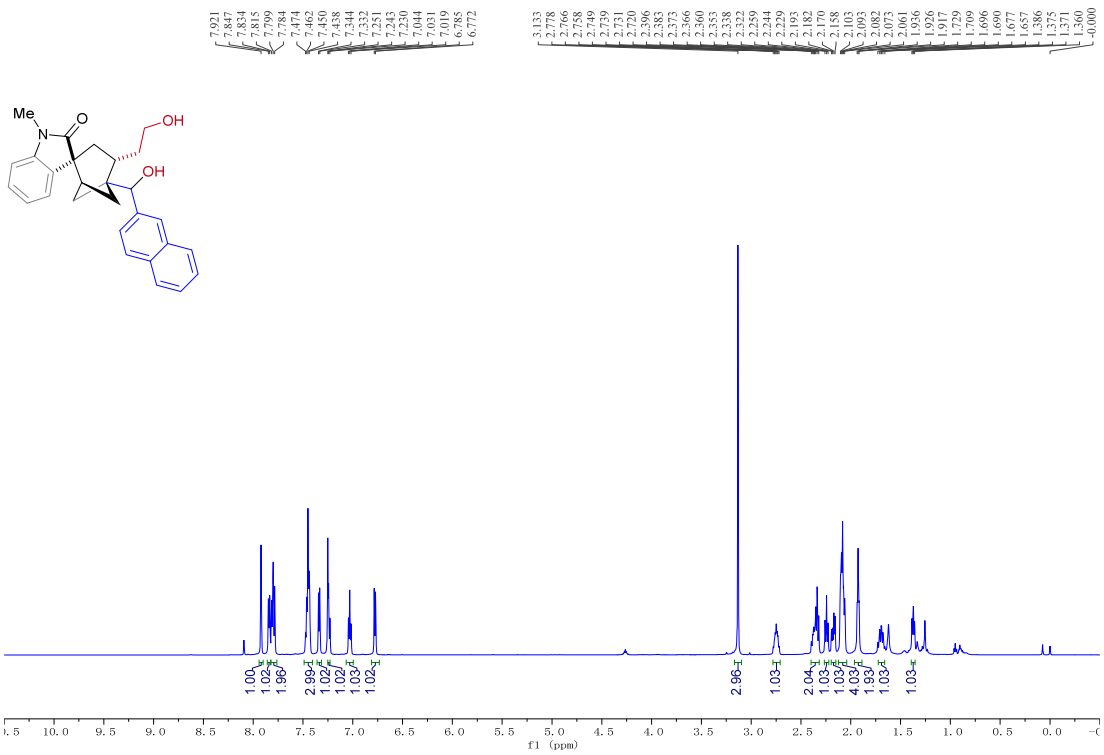


^{13}C NMR (150 MHz, $CDCl_3$)

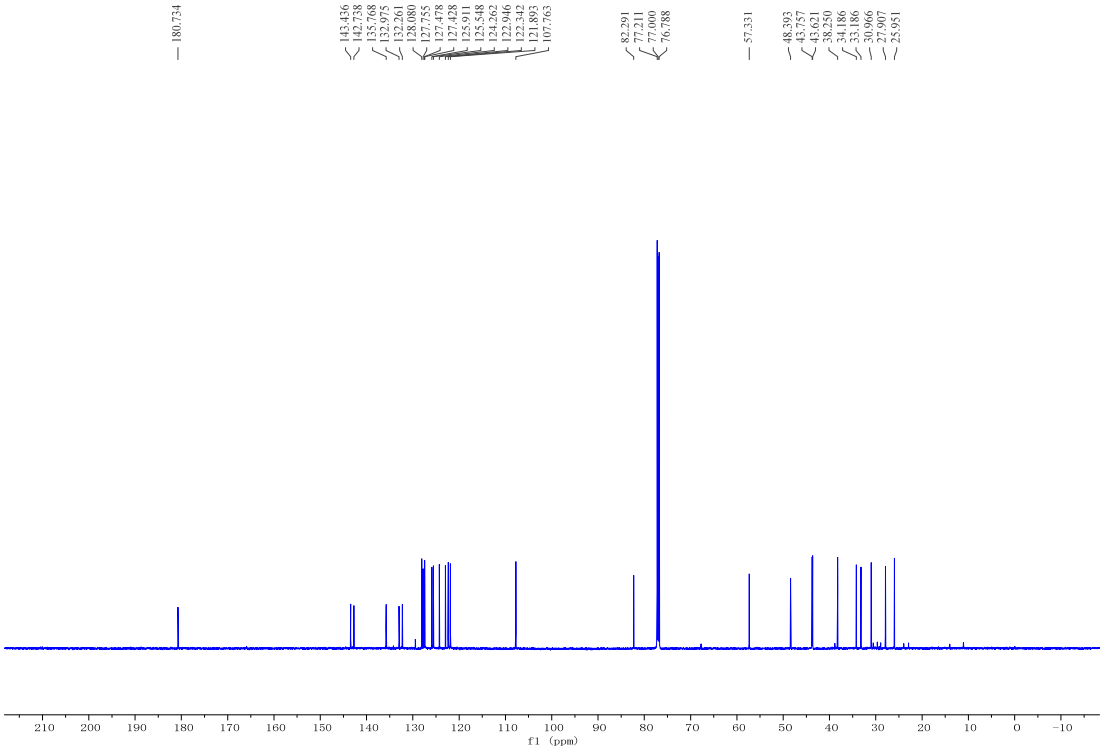


^{1}H and ^{13}C NMR Spectra for Compound 14:

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)



13 References

[1] (a) R. Guo, Y.-C. Chang, L. Herter, C. Salome, S. E. Braley, T. C. Fessard and M. K. Brown, Strain-Release [2π+2σ] Cycloadditions for the Synthesis of Bicyclo[2.1.1]hexanes Initiated by Energy Transfer. *J. Am. Chem. Soc.* **2022**, *144,* 7988−7994; (b) M. de Robichon, T. Kratz, F. Beyer, J. Zuber, C. Merten and T. Bach, Enantioselective, Intermolecular [$_{\pi}$2+$_{\sigma}$2] Photocycloaddition Reactions of 2(1*H*)‐Quinolones and Bicyclo[1.1.0]butanes. *J. Am. Chem. Soc.* **2023**, *145,* 24466−24470; (c) D. Ni, S. Hu, X. Tan, Y. Yu, Z. Li and L. Deng, Intermolecular Formal Cycloaddition of Indoles with Bicyclo[1.1.0]butanes by Lewis Acid Catalysis. *Angew. Chem. Int. Ed.* **2023**, *62,* e202308606; (d) B. D. Schwartz, M. Y. Zhang, R. H. Attard, M. G. Gardiner and L. R. Malins, Structurally Diverse Acyl Bicyclobutanes: Valuable Strained Electrophiles. *Chem. Eur. J.* **2020**, *26*, 2808–2812.

[2] A. P. Dieskau, M. S. Holzwarth and B. Plietker, Fe-Catalyzed Allylic C–C-Bond Activation: Vinylcyclopropanes As Versatile a1, a3, d5-Synthons in Traceless Allylic Substitutions and [3+2]-Cycloadditions. *J. Am. Chem. Soc.,* **2012**, *134*, 5048−5051.

[3] Q. Wan, L. Chen, S. Li, Q. Kang, Y. Yuan and Y. Du, Enantioselective Synthesis of Multisubstituted Spirocyclopentane Oxindoles Enabled by Pd/Chiral Rh(III) Complex Synergistic Catalysis. *Org. Lett.*, **2020**, *22*, 9539−9544.

[4] (a) H. Zhao, P. Shen, D. Sun, H. Zhai and Y. Zhao, Transition-Metal-Free [3+2] Dehydration Cycloaddition of Donor-Acceptor Cyclopropanes With 2-Naphthols. *Front. Chem.,* **2021**, *9*, 711257; (b) Z. Yuan, W. Wei, A. Lin and H. Yao, Bifunctional Organo/Metal Cooperatively Catalyzed [3+2] Annulation of *para*-Quinone Methides with Vinylcyclopropanes: Approach to Spiro[4.5]deca-6,9-diene-8-ones. *Org. Lett.,* **2016**, *18*, 3370-3373; (c) X.-Y. Gao, L. Tang, X. Zhang and J.-J. Feng, Palladium-catalyzed decarboxylative (4+3) cycloadditions of bicyclobutanes with 2-alkylidenetrimethylene carbonates for the synthesis of 2-oxabicyclo[4.1.1]octanes. *Chem. Sci.*, **2024**, *15*, 13942-13948; (d) J.-J. Wang, L. Tang, Y. Xiao, W.-B. Wu, G. Wang and J.-J. Feng, Switching between the [2π+2σ] and Hetero-[4π+2σ]

Cycloaddition Reactivity of Bicyclobutanes with Lewis Acid Catalysts Enables the Synthesis of Spirocycles and Bridged Heterocycles. *Angew. Chem. Int. Ed.,* **2024**, *63,* e202405222 (1 of 6); (e) B. Debnath, T. Sarkar, P. Karjee, S. K. Purkayastha, A. K. Guha and T. Punniyamurthy, Palladium-Catalyzed Annulative Coupling of Spirovinylcyclopropyl Oxindoles with *p*-Quinone Methides. *J. Org. Chem*., **2023**, *88*, 9704-9719.

[5] L. Pitzer, F. Schäfers and F. Glorius, Rapid Assessment of the Reaction-Condition-Based Sensitivity of Chemical Transformations. *Angew. Chem. Int. Ed.,* **2019**, *58*, 8572–8576.