

**Ni-Catalyzed Enantioselective Reductive Aryl-
Alkenylation of Alkenes: Application to the Synthesis of
(+)-Physovenine and (+)-Physostigmine**

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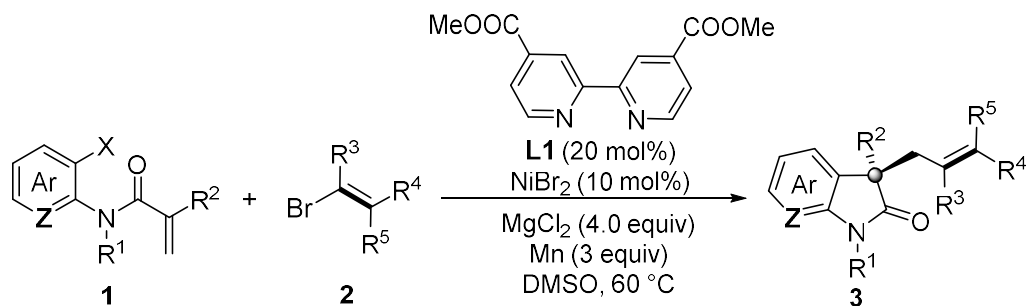
1. General Information

^1H and ^{13}C NMR data were recorded with Bruker ADVANCE III (400 MHz) or JNM-ECZ400S/L1 (400 MHz) spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual ^1H and ^{13}C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (b). ^{19}F NMR spectra were recorded using CFCl_3 as internal standard. Gas chromatography were determined with a Varian GC 2000 gas chromatography instrument with a FID detector. High-resolution mass spectra (HRMS) were recorded on DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer. Enantiomeric excesses were determined with a SHIMADZU LC-20ADXR system using chiral stationary phase columns (DAICEL) by comparing the samples with the corresponding racemic samples. Column and elution details were specified in each entry.

Materials and Methods: Unless otherwise stated, starting materials were purchased from commercial suppliers (Adamas-beta[®], Alfa, Aldrich and so on). All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Solvents were purchased in HPLC quality, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. More sensitive compounds were stored in a desiccator or in a glove-box if required. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (200-400 mesh).

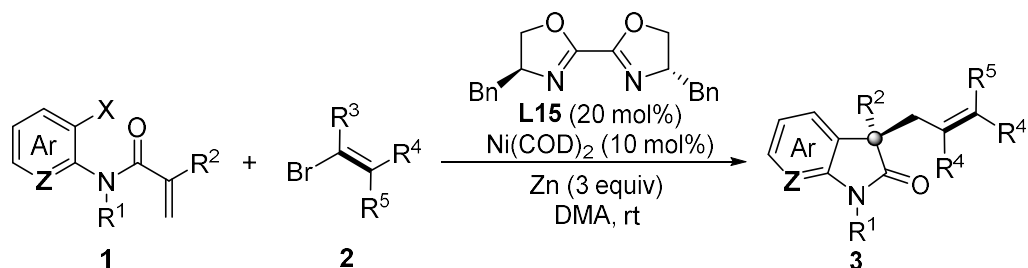
2. General Procedures

2.1 General Procedure for Racemic Aryl-Alkenylation Reaction:



To a mixture of **1** (0.1 mmol), NiBr₂ (10 mol%), **L1** (20 mol%), Mn (3 equiv), MgCl₂ (4 equiv) and dry DMSO (2 mL) in a sealed tube was added alkenyl bromide **2** (0.3 mmol) under Argon. The reaction mixture was heated at 60 °C until the reaction was complete (monitored by TLC). The resulting mixture was quenched with sat. NH₄Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with EtOAc (3 x 15 mL) and the combined organic layers were washed with brine (2 x 20 mL), dried with MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:40~1:5 (v/v) to afford the desired product **3**.

2.2 General Procedure for Asymmetric Aryl-Alkenylation Reaction:

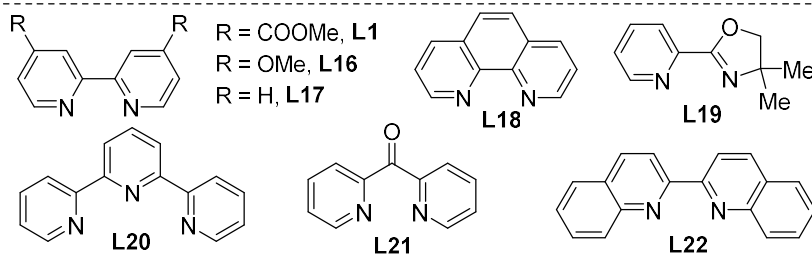
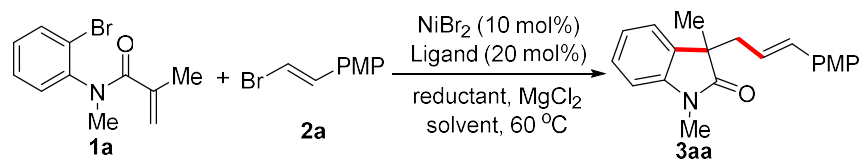


To a mixture of **1** (0.1 mmol), Ni(COD)₂ (10 mol%), **L15** (20 mol%), Zn (3 equiv) and dry DMA (2 mL) in a sealed tube was added alkenyl bromide **2** (0.3 mmol) under Argon. The reaction mixture was heated at room temperature until the reaction was complete (monitored by TLC). The resulting mixture was quenched with sat. NH₄Cl solution (5 mL) and further diluted with water (10 mL). The aqueous layer was extracted with

EtOAc (3 x 15 mL) and the combined organic layers were washed with brine (2 x 20 mL), dried with MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:40~1:5 (v/v) to afford the desired product **3**.

3. Additional experiments

Table S1. Optimization of reaction conditions^a

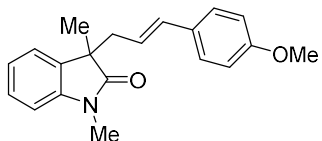


entry	ligand	solvent	reductant	yield of 3aa (%) ^b
1	L1	DMA	Mn	83
2	L16	DMA	Mn	33
3	L17	DMA	Mn	40
4	L18	DMA	Mn	57
5	L19	DMA	Mn	44
6	L20	DMA	Mn	trace
7	L21	DMA	Mn	trace
8	L22	DMA	Mn	5
9	L1	DMA	Zn	21
10	L1	DMA	Mg	trace
11	L1	DMA	TDAE	0
12	L1	DMSO	Mn	90
13	L1	DMF	Mn	65
14	L1	THF	Mn	33
15	L1	MeCN	Mn	33
16 ^c	L1	DMSO	Mn	0
17	L1	DMSO	-	0

^aReactions were carried out with **1a** (0.1 mmol), **2a** (0.3 mmol), NiBr₂ (10 mol%), ligand (20 mol%), Mn (0.3 mmol), MgCl₂ (0.4 mmol) in 2 mL solvent at 60 °C for 12 h, unless noted otherwise. ^bIsolated yields. ^cWithout NiBr₂.

4. Characterization data of products

(*E*)-3-(3-(4-Methoxyphenyl)allyl)-1,3-dimethylindolin-2-one (**3aa**)



Chemical Formula: C₂₀H₂₁NO₂

Exact Mass: 307.1572

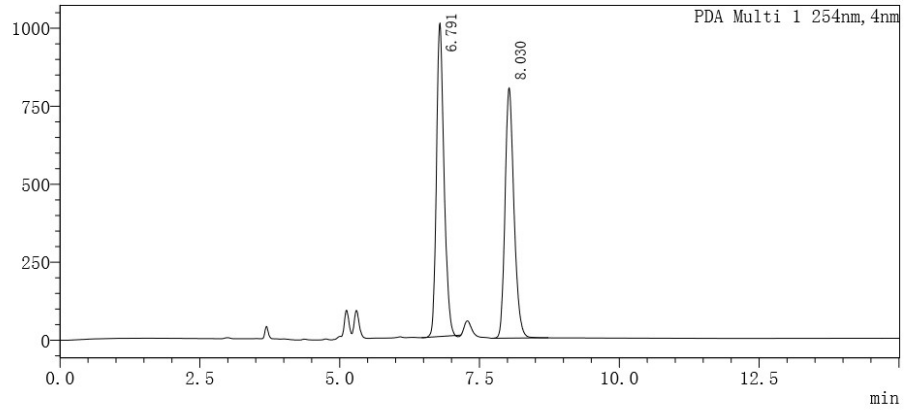
3aa was prepared according to general procedure 2.1 using **1a** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3aa** as yellow oil (90% yield). The ¹H NMR data matched those reported in the literature:¹ ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.24 (m, 1H), 7.22 (dd, *J* = 7.3, 0.7 Hz, 1H), 7.16-7.10 (m, 2H), 7.07 (td, *J* = 7.5, 0.9 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.80-6.75 (m, 2H), 6.29 (d, *J* = 15.7 Hz, 1H), 5.74 (ddd, *J* = 15.5, 8.0, 7.1 Hz, 1H), 3.77 (s, 3H), 3.18 (s, 3H), 2.70-2.52 (m, 2H), 1.41 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.3, 158.8, 143.1, 133.6, 133.0, 130.0, 127.7, 127.2, 122.9, 122.3, 121.8, 113.7, 107.9, 55.2, 48.7, 41.6, 26.1, 22.4.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 6.7 min (minor), 8.0 min (major).

Optical Rotation: [α]_D³³ +4.6 (c 0.2, *i*PrOH) for 82% ee.

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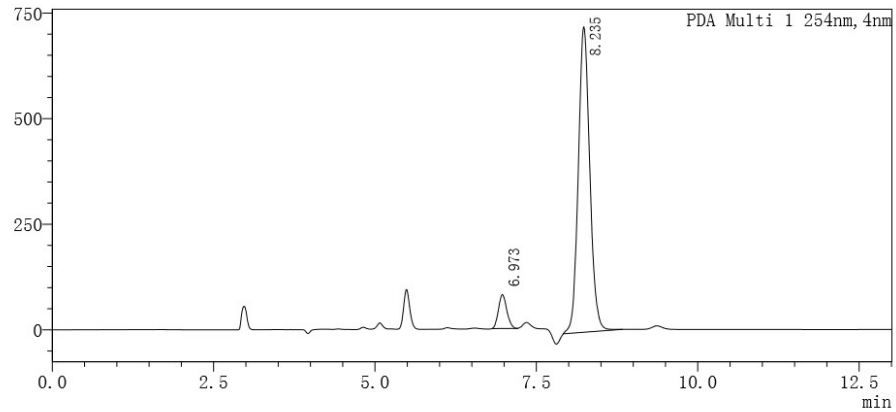
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.791	9427568	1005492	0.000		M	
2	8.030	8914918	803087	0.000		M	
总计		18342485	1808579				

peak number
retention time
area
height

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mAU



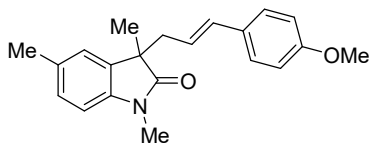
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PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.973	720009	80407	0.000		M	
2	8.235	8935544	723294	0.000		M	
总计		9655554	803701				

peak number
retention time
area
height

(*E*)-3-(3-(4-Methoxyphenyl)allyl)-1,3,5-trimethylindolin-2-one (**3ba**)



Chemical Formula: C₂₁H₂₃NO₂
Exact Mass: 321.1729

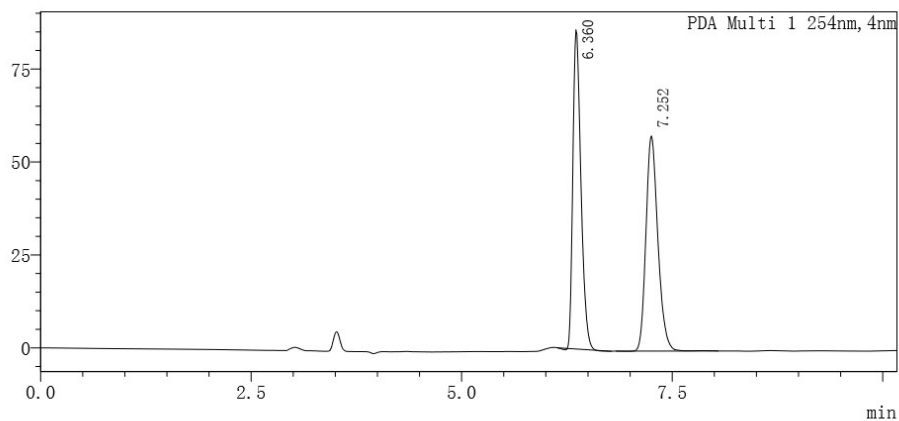
3ba was prepared according to general procedure 2.2 using **1b** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ba** as yellow oil (81% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.16-7.09 (m, 2H), 7.08-7.02 (m, 2H), 6.81-6.74 (m, 2H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.29 (d, *J* = 15.7 Hz, 1H), 5.77-5.66 (m, 1H), 3.77 (s, 3H), 3.15 (s, 3H), 2.61 (dd, *J* = 7.6, 1.0 Hz, 2H), 2.35 (s, 3H), 1.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.2, 158.8, 140.8, 133.7, 132.9, 131.8, 130.2, 127.9, 127.2, 123.8, 122.1, 113.8, 107.6, 55.2, 48.7, 41.7, 26.1, 22.5, 21.2; HRMS: (ESI) calcd for C₂₁H₂₄NO₂⁺[M+H]⁺ 322.1802; found 322.1795.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 6.3 min (minor), 7.2 min (major).

Optical Rotation: [α]_D³² +38.0 (c 0.5, *i*PrOH) for 90% ee.

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PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.360	568548	85891	0.000		M	
2	7.252	570176	57902	0.000		M	
总计		1138724	143793				

peak number

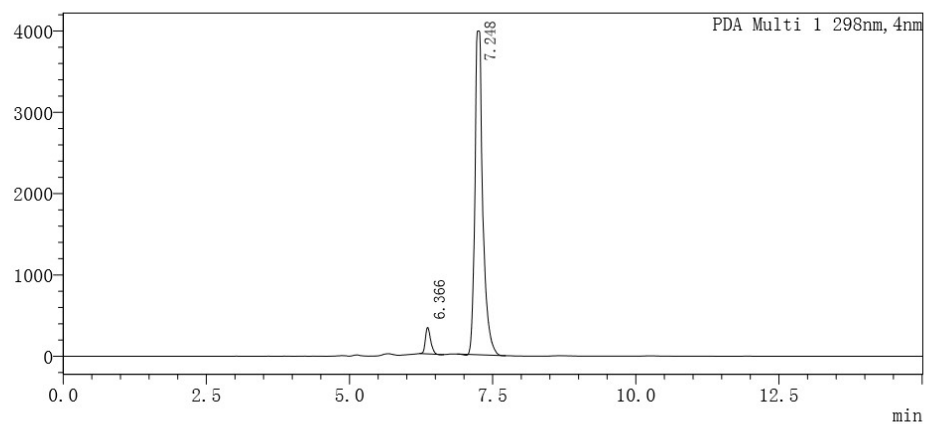
retention time

area

height

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mAU



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PDA Ch1 298nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.366	2058009	325509	5.128		M	
2	7.248	38073549	3981463	94.872		M	
总计		40131558	4306973				

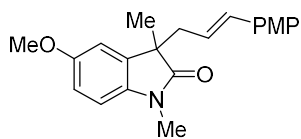
peak number

retention time

area

height

(*E*)-5-Methoxy-3-(3-(4-methoxyphenyl)allyl)-1,3-dimethylindolin-2-one (**3ca**)



Chemical Formula: C₂₁H₂₃NO₃
Exact Mass: 337.1678

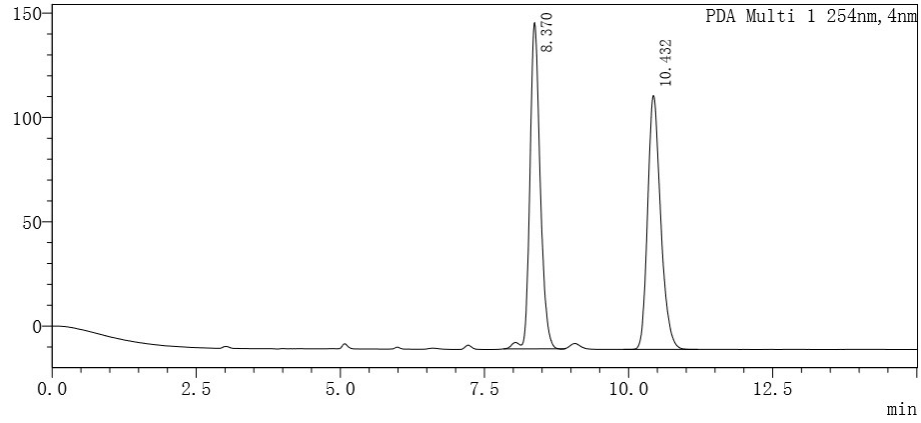
3ca was prepared according to general procedure 2.1 using **1c** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ca** as yellow oil (67% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.17-7.09 (m, 2H), 6.85 (d, *J* = 2.4 Hz, 1H), 6.81-6.75 (m, 3H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 15.7 Hz, 1H), 5.73 (dt, *J* = 15.5, 7.5 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.15 (s, 3H), 2.62 (dd, *J* = 7.5, 1.0 Hz, 2H), 1.40 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 179.9, 158.8, 155.8, 136.7, 135.0, 133.0, 130.0, 127.2, 121.8, 113.7, 111.6, 110.6, 108.1, 55.8, 55.2, 49.1, 41.6, 26.2, 22.6; HRMS: (ESI) calcd for C₂₁H₂₄NO₃⁺[M+H]⁺ 338.1751; found 338.1743.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. tR = 8.4 min (minor), 10.4 min (major).

Optical Rotation: [α]_D³³ +51.6 (c 0.2, *i*PrOH) for 80% ee.

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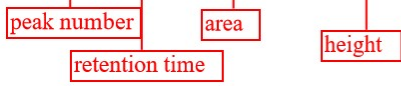
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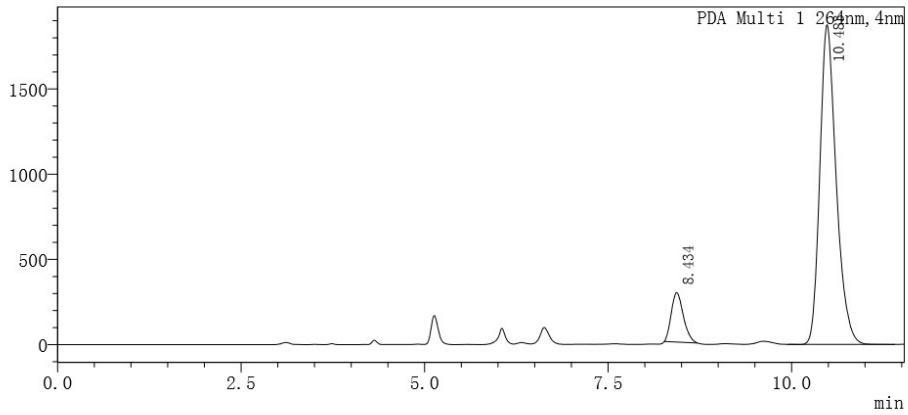
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.370	1935394	156420	0.000		M	
2	10.432	1915029	121790	0.000		M	
总计		3850423	278210				



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mAU



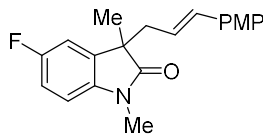
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PDA Ch1 264nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.434	3307516	289962	10.222		M	
2	10.483	29048073	1876373	89.778		M	
总计		32355588	2166335				



(*E*)-5-Fluoro-3-(3-(4-methoxyphenyl)allyl)-1,3-dimethylindolin-2-one (**3da**)



Chemical Formula: C₂₀H₂₀FNO₂
Exact Mass: 325.1478

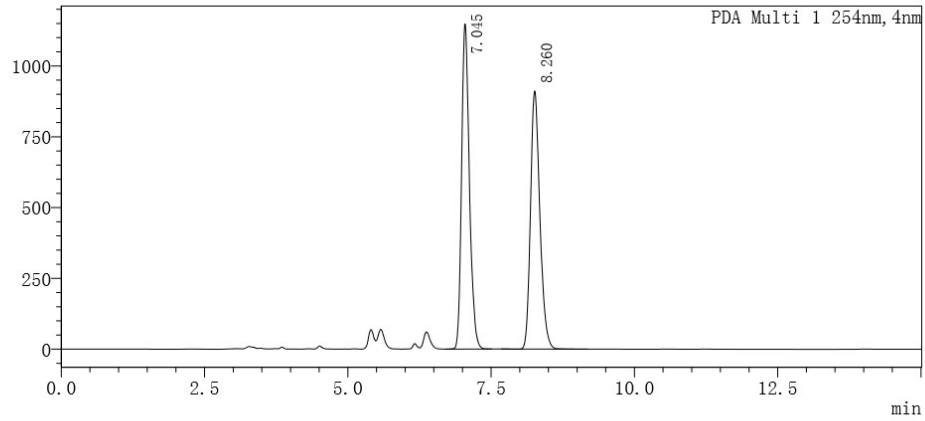
3da was prepared according to general procedure 2.2 using **1d** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3da** as yellow oil (74% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.17-7.11 (m, 2H), 7.00-6.92 (m, 2H), 6.82-6.75 (m, 2H), 6.73 (dt, *J* = 8.3, 3.3 Hz, 1H), 6.30 (t, *J* = 13.5 Hz, 1H), 5.70 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.78 (s, 3H), 3.17 (s, 3H), 2.70-2.53 (m, 2H), 1.39 (d, *J* = 11.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 179.9, 159.2 (d, *J* = 240.3 Hz), 158.9, 139.0, 135.3 (d, *J* = 7.8 Hz), 133.3, 129.8, 127.3, 121.3, 113.9 (d, *J* = 21.8 Hz), 113.8, 111.1 (d, *J* = 24.6 Hz), 108.3 (d, *J* = 8.1 Hz), 55.2, 49.2, 41.6, 26.3, 22.5; ¹⁹F NMR (377 MHz, CDCl₃) δ -120.83; HRMS: (ESI) calcd for C₂₀H₂₁FNO₂⁺[M+H]⁺ 326.1551; found 326.1550.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 7.0 min (minor), 8.2 min (major).

Optical Rotation: [α]_D³² +3.7 (c 0.5, ^tPrOH) for 89% ee.

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PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.045	10857885	1147868	0.000		M	
2	8.260	10307206	911310	0.000		M	
总计		21165092	2059178				

peak number

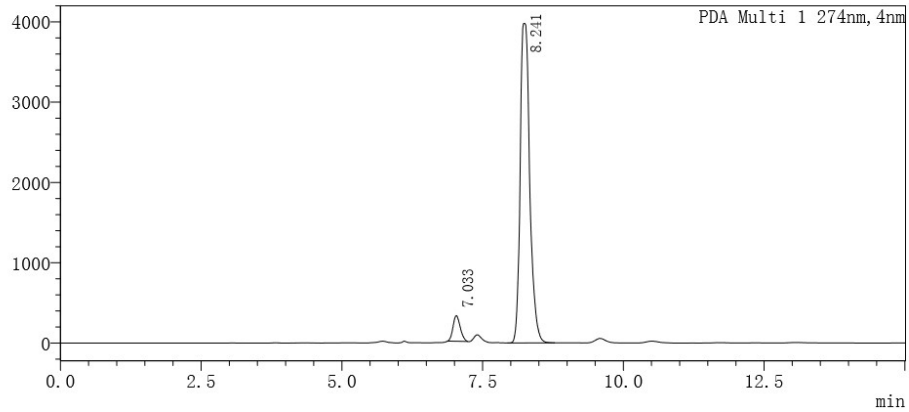
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area

height

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PDA Ch1 274nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.033	2833135	318813	0.000		M	
2	8.241	47093285	3978539	0.000		M	
总计		49926421	4297353				

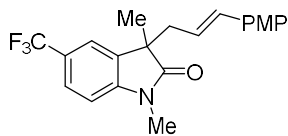
peak number

retention time

area

height

(*E*)-3-(3-(4-Methoxyphenyl)allyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (**3ea**)



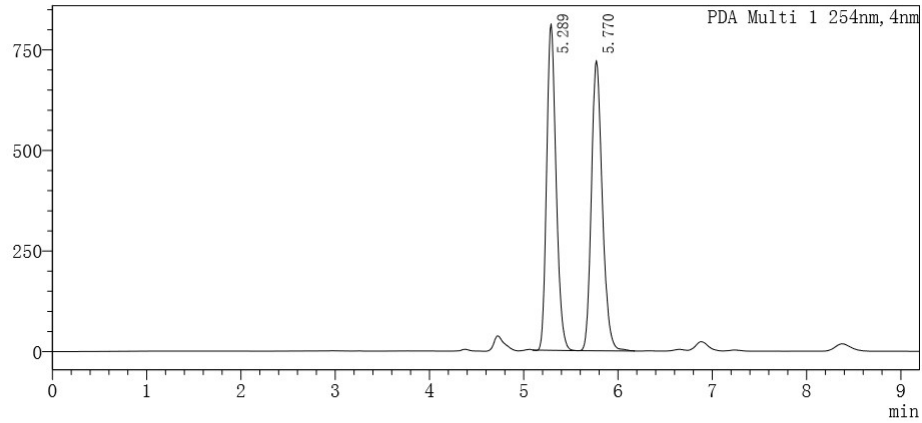
Chemical Formula: C₂₁H₂₀F₃NO₂
Exact Mass: 375.1446

3ea was prepared according to general procedure 2.1 using **1e** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ea** as yellow oil (67% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.55 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.45 (d, *J* = 1.1 Hz, 1H), 7.15-7.08 (m, 2H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.82-6.74 (m, 2H), 6.28 (d, *J* = 15.7 Hz, 1H), 5.67 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.77 (s, 3H), 3.20 (s, 3H), 2.65 (dd, *J* = 7.6, 1.0 Hz, 2H), 1.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.2, 159.0, 146.2, 134.2, 133.8, 129.8, 127.3, 126.1 (d, *J* = 58.0 Hz), 125.7 (q, *J* = 4.1 Hz), 124.6 (d, *J* = 32.6 Hz), 120.9, 119.9 (q, *J* = 3.6 Hz), 113.9, 107.7, 55.3, 48.8, 41.6, 26.4, 22.4; ¹⁹F NMR (377 MHz, CDCl₃) δ -61.27; HRMS: (ESI) calcd for C₂₁H₂₁F₃NO₂⁺[M+H]⁺ 376.1519; found 376.1525.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 5.3 min (minor), 5.8 min (major).

Optical Rotation: [α]_D³⁴ +17.6 (c 0.5, *i*PrOH) for 82% ee.

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PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.289	5650133	811595	0.000		M	
2	5.770	5808626	721863	0.000		M	
总计		11458759	1533458				

peak number

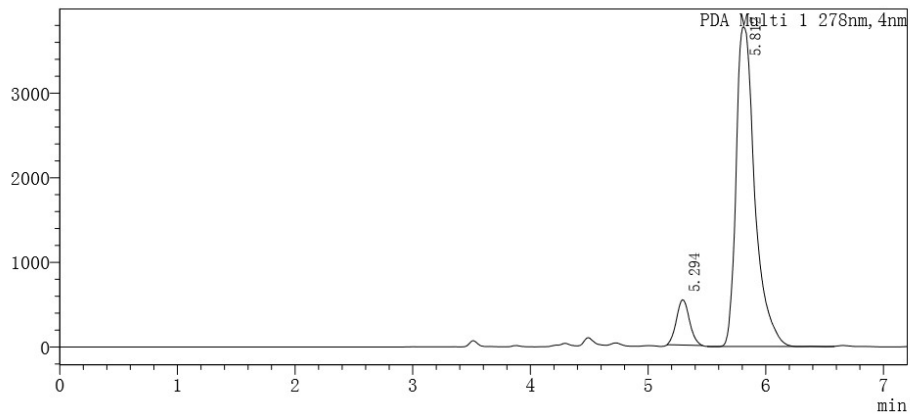
area

height

retention time

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mAU



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PDA Ch1 278nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.294	4095710	534662	8.956		M	
2	5.812	41634265	3779279	91.044		M	
总计		45729975	4313942				

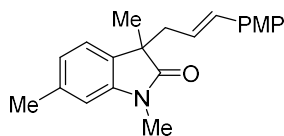
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area

height

retention time

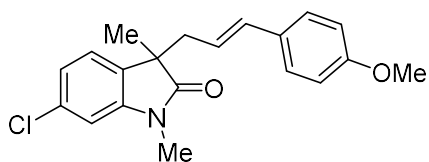
(*E*)-3-(3-(4-Methoxyphenyl)allyl)-1,3,6-trimethylindolin-2-one (**3fa**)



Chemical Formula: C₂₁H₂₃NO₂
Exact Mass: 321.1729

3fa was prepared according to general procedure 2.1 using **1f** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3fa** as yellow oil (64% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.15 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.78 (t, *J* = 5.8 Hz, 2H), 6.65 (s, 1H), 6.29 (d, *J* = 15.7 Hz, 1H), 5.76 (ddd, *J* = 15.5, 8.0, 7.1 Hz, 1H), 3.78 (s, 3H), 3.16 (s, 3H), 2.70-2.48 (m, 2H), 2.38 (s, 3H), 1.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.6, 158.8, 143.1, 137.8, 132.9, 130.7, 130.1, 127.2, 122.8, 122.7, 122.1, 113.7, 108.9, 55.2, 48.4, 41.6, 26.1, 22.6, 21.8; HRMS: (ESI) calcd for C₂₁H₂₄NO₂⁺[M+H]⁺ 322.1802; found 322.1804.

(*E*)-6-chloro-3-(3-(4-methoxyphenyl)allyl)-1,3-dimethylindolin-2-one (**3ga**)



Chemical Formula: C₂₀H₂₀ClNO₂

Exact Mass: 341.1183

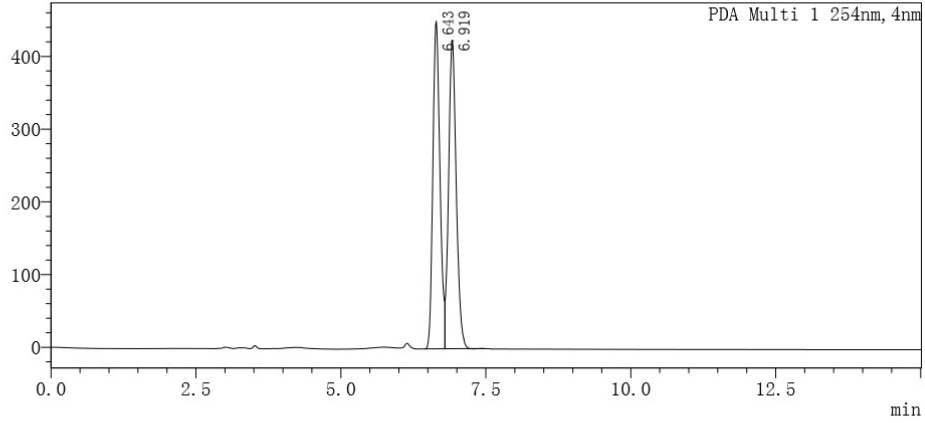
3ga was prepared according to general procedure 2.2 using **1g** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ga** as yellow oil (44% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.17-7.10 (m, 3H), 7.03 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.81 (d, *J* = 1.8 Hz, 1H), 6.80-6.76 (m, 2H), 6.28 (d, *J* = 15.7 Hz, 1H), 5.70 (dt, *J* = 15.4, 7.6 Hz, 1H), 3.78 (s, 3H), 3.16 (s, 3H), 2.68-2.49 (m, 2H), 1.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.1, 159.0, 144.3, 133.5, 133.4, 131.9, 129.8, 127.3, 123.8, 122.1, 121.3, 113.8, 108.7, 55.3, 48.5, 41.5, 26.2, 22.5; HRMS: (ESI) calcd for C₂₀H₂₁ClNO₂⁺[M+H]⁺ 342.1255; found 342.1253.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 6.6 min (minor), 6.9 min (major).

Optical Rotation: [α]_D³³ +7.9 (c 0.2, *i*PrOH) for 85% ee.

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.643	3835833	450841	0.000		M	
2	6.919	3877884	424547	0.000		V M	
总计		7713716	875388				

peak number

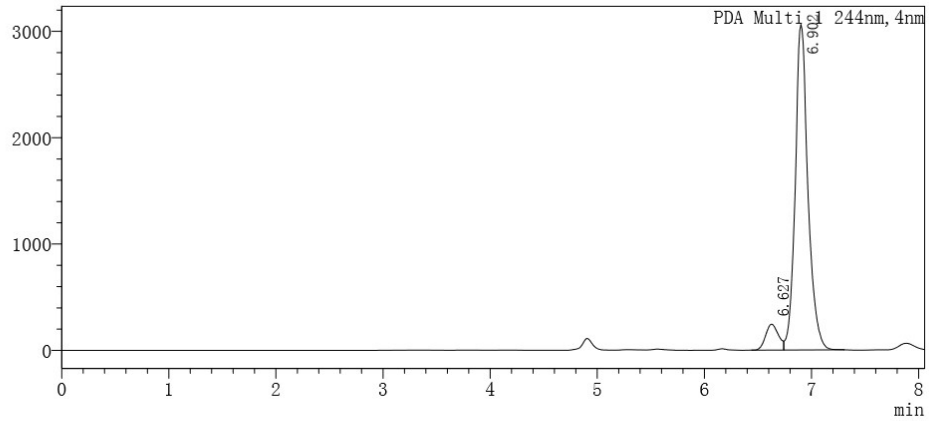
area

height

retention time

<色谱图>

mAU



<峰表>

PDA Ch1 244nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.627	2053514	243995	7.523		M	
2	6.902	25242984	3062902	92.477		V M	
总计		27296499	3306897				

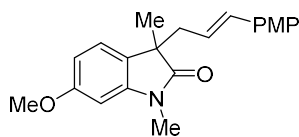
peak number

area

height

retention time

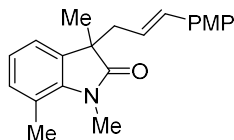
(*E*)-6-Methoxy-3-(3-(4-methoxyphenyl)allyl)-1,3-dimethylindolin-2-one (**3ha**)



Chemical Formula: C₂₁H₂₃NO₃
Exact Mass: 337.1678

3ha was prepared according to general procedure 2.1 using **1h** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ha** as yellow oil (74% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.18-7.12 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 6.82-6.75 (m, 2H), 6.56 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.41 (d, *J* = 2.3 Hz, 1H), 6.29 (d, *J* = 15.8 Hz, 1H), 5.80-5.68 (m, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.15 (s, 3H), 2.67-2.50 (m, 2H), 1.38 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.8, 159.8, 158.8, 144.3, 132.9, 130.1, 127.2, 125.6, 123.4, 122.1, 113.7, 106.0, 96.0, 55.5, 55.2, 48.2, 41.8, 26.1, 22.6; HRMS: (ESI) calcd for C₂₁H₂₄NO₃⁺[M+H]⁺ 338.1751; found 338.1747.

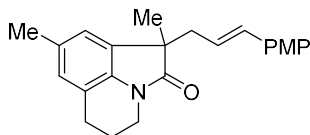
(*E*)-3-(3-(4-Methoxyphenyl)allyl)-1,3,7-trimethylindolin-2-one (**3ia**)



Chemical Formula: C₂₁H₂₃NO₂
Exact Mass: 321.1729

3ha was prepared according to general procedure 2.1 using **1h** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ha** as yellow oil (63% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.19-7.10 (m, 2H), 7.06 (dd, *J* = 6.9, 1.4 Hz, 1H), 7.01-6.90 (m, 2H), 6.82-6.75 (m, 2H), 6.28 (d, *J* = 15.7 Hz, 1H), 5.73 (dt, *J* = 15.5, 7.5 Hz, 1H), 3.78 (s, 3H), 3.46 (s, 3H), 2.63-2.58 (m, 2H), 2.56 (s, 3H), 1.38 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 181.0, 158.8, 140.84 134.3, 132.9, 131.5, 130.1, 127.3, 122.2, 122.1, 120.8, 119.5, 113.8, 55.2, 47.9, 41.9, 29.5, 22.9, 19.1; HRMS: (ESI) calcd for C₂₁H₂₄NO₂⁺[M+H]⁺ 322.1802; found 322.1809.

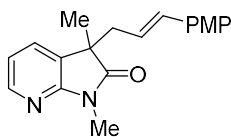
(*E*)-1-(3-(4-Methoxyphenyl)allyl)-1,8-dimethyl-5,6-dihydro-4H-pyrrolo[3,2-*i*]quinolin-2(1H)-one (**3ja**)



Chemical Formula: $C_{23}H_{25}NO_2$
Exact Mass: 347.1885

3ja was prepared according to general procedure 2.1 using **1j** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ja** as yellow oil (74% yield). 1H NMR (400 MHz, $CDCl_3$): δ 7.14 (t, J = 5.7 Hz, 2H), 6.85 (d, J = 16.4 Hz, 2H), 6.81-6.75 (m, 2H), 6.30 (d, J = 15.8 Hz, 1H), 5.78 (dt, J = 15.4, 7.5 Hz, 1H), 3.77 (s, 3H), 3.65 (td, J = 6.8, 4.7 Hz, 2H), 2.70 (t, J = 6.0 Hz, 2H), 2.65-2.50 (m, 2H), 2.32 (s, 3H), 2.03-1.80 (m, 2H), 1.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 158.8, 136.4, 132.8, 132.2, 131.3, 130.2, 127.2, 126.9, 122.3, 121.6, 119.7, 113.8, 55.2, 50.1, 41.4, 38.7, 24.5, 22.1, 21.4, 21.4; HRMS: (ESI) calcd for $C_{23}H_{26}NO_2^+[M+H]^+$ 348.1958; found 348.1953.

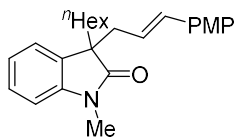
(*E*)-3-(3-(4-Methoxyphenyl)allyl)-1,3-dimethyl-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (**3ka**)



Chemical Formula: $C_{19}H_{20}N_2O_2$
Exact Mass: 308.1525

3ka was prepared according to general procedure 2.1 using **1k** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ka** as yellow oil (89% yield). 1H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, J = 5.3, 1.5 Hz, 1H), 7.43 (dd, J = 7.2, 1.5 Hz, 1H), 7.15 (t, J = 5.7 Hz, 2H), 6.95 (dd, J = 7.2, 5.3 Hz, 1H), 6.82-6.76 (m, 2H), 6.30 (d, J = 15.7 Hz, 1H), 5.77 (dt, J = 15.5, 7.6 Hz, 1H), 3.78 (s, 3H), 3.28 (s, 3H), 2.73-2.52 (m, 2H), 1.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.9, 159.0, 156.6, 146.7, 133.7, 130.4, 129.7, 128.0, 127.3, 120.9, 117.9, 113.9, 55.3, 48.3, 41.1, 25.3, 21.9; HRMS: (ESI) calcd for $C_{19}H_{21}N_2O_2^+[M+H]^+$ 305.1598; found 309.1593.

(*E*)-3-Hexyl-3-(3-(4-methoxyphenyl)allyl)-1-methylindolin-2-one (**3la**)



Chemical Formula: C₂₅H₃₁NO₂
Exact Mass: 377.2355

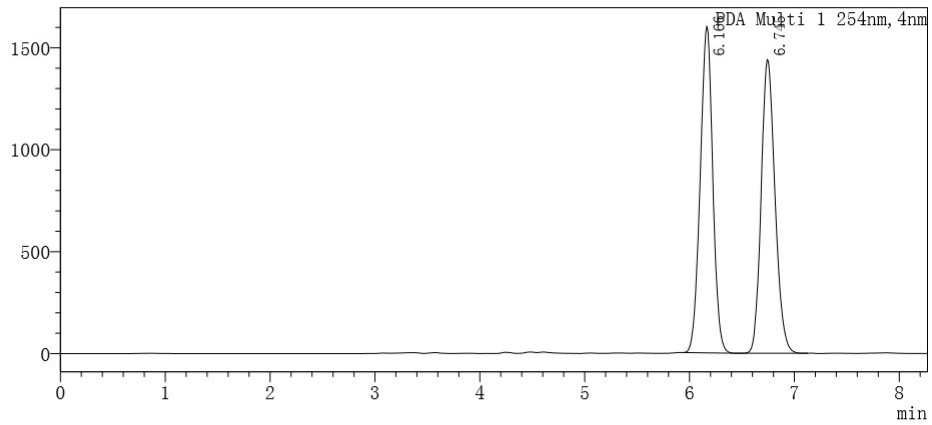
3la was prepared according to general procedure 2.1 using **11** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3la** as yellow oil (82% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.22 (m, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.15-7.03 (m, 3H), 6.79 (dd, *J* = 15.0, 8.2 Hz, 3H), 6.26 (d, *J* = 15.7 Hz, 1H), 5.70 (dt, *J* = 15.5, 7.5 Hz, 1H), 3.77 (s, 3H), 3.17 (s, 3H), 2.71-2.53 (m, 2H), 1.95 (td, *J* = 12.8, 4.6 Hz, 1H), 1.81 (td, *J* = 12.8, 4.4 Hz, 1H), 1.32-1.06 (m, 7H), 1.03-0.89 (m, 1H), 0.80 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 179.7, 158.8, 143.8, 132.8, 132.0, 130.1, 127.6, 127.2, 123.0, 122.3, 121.9, 113.7, 107.8, 55.2, 53.4, 41.4, 36.8, 31.5, 29.4, 26.0, 24.2, 22.5, 14.0; HRMS: (ESI) calcd for C₂₅H₃₂NO₂⁺[M+H]⁺ 378.2428; found 378.2427.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 6.2 min (minor), 7.0 min (major).

Optical Rotation: [α]_D³⁵ +3.8 (c 0.5, ^tPrOH) for 80% ee.

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.166	13318316	1604660	0.000		M	
2	6.745	13257997	1442081	0.000		M	
总计		26576312	3046742				

peak number

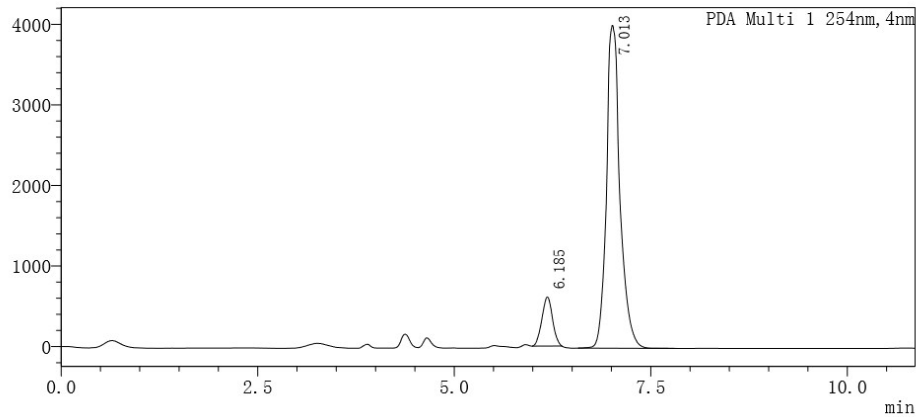
area

height

retention time

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.185	5698373	609996	0.000		M	
2	7.013	48023861	4007492	0.000		M	
总计		53722234	4617488				

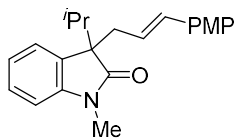
peak number

area

height

retention time

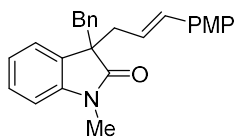
(*E*)-3-Isopropyl-3-(3-(4-methoxyphenyl)allyl)-1-methylindolin-2-one (**3ma**)



Chemical Formula: C₂₂H₂₅NO₂
Exact Mass: 335.1885

3ma was prepared according to general procedure 2.1 using **1m** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ma** as yellow oil (55% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.21 (m, 2H), 7.06 (ddd, *J* = 7.6, 4.6, 1.6 Hz, 3H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.76-6.70 (m, 2H), 6.24 (d, *J* = 15.7 Hz, 1H), 5.66-5.53 (m, 1H), 3.75 (s, 3H), 3.14 (s, 3H), 2.73 (dddd, *J* = 13.5, 9.1, 7.5, 1.0 Hz, 2H), 2.25 (hept, *J* = 6.8 Hz, 1H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 179.4, 158.7, 144.1, 132.5, 130.9, 130.2, 127.6, 127.1, 123.7, 122.2, 122.0, 113.7, 107.6, 56.6, 55.2, 38.7, 34.6, 25.8, 17.4, 17.3; HRMS: (ESI) calcd for C₂₂H₂₆NO₂⁺[M+H]⁺ 336.1958; found 336.1956.

(*E*)-3-Benzyl-3-(3-(4-methoxyphenyl)allyl)-1-methylindolin-2-one (**3na**)



Chemical Formula: C₂₆H₂₅NO₂
Exact Mass: 383.1885

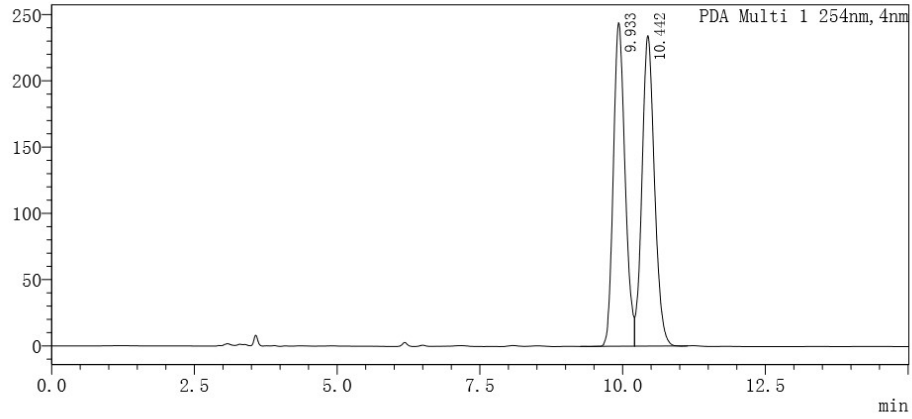
3na was prepared according to general procedure 2.1 using **1n** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3na** as yellow oil (82% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.22 (dd, *J* = 7.3, 0.7 Hz, 1H), 7.19-7.14 (m, 1H), 7.14-7.10 (m, 2H), 7.08-6.98 (m, 4H), 6.85 (dd, *J* = 7.2, 2.2 Hz, 2H), 6.81-6.72 (m, 2H), 6.56 (d, *J* = 7.7 Hz, 1H), 6.33 (d, *J* = 15.7 Hz, 1H), 5.80-5.66 (m, 1H), 3.76 (s, 3H), 3.20 (d, *J* = 13.0 Hz, 1H), 3.09 (d, *J* = 13.0 Hz, 1H), 2.93 (s, 3H), 2.86-2.74 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 178.7, 158.8, 143.6, 135.9, 133.1, 130.7, 130.0, 129.8, 127.8, 127.5, 127.3, 126.3, 123.8, 121.9, 121.7, 113.7, 107.7, 55.2, 54.8, 43.1, 40.5, 25.8; HRMS: (ESI) calcd for C₂₆H₂₆NO₂⁺[M+H]⁺ 384.1958; found 384.1962.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 9.9 min (major), 10.4 min (minor).

Optical Rotation: [α]_D³² -9.8 (c 0.5, ^tPrOH) for 76% ee.

<色谱图>

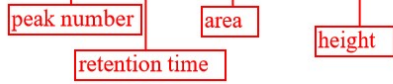
mAU



<峰表>

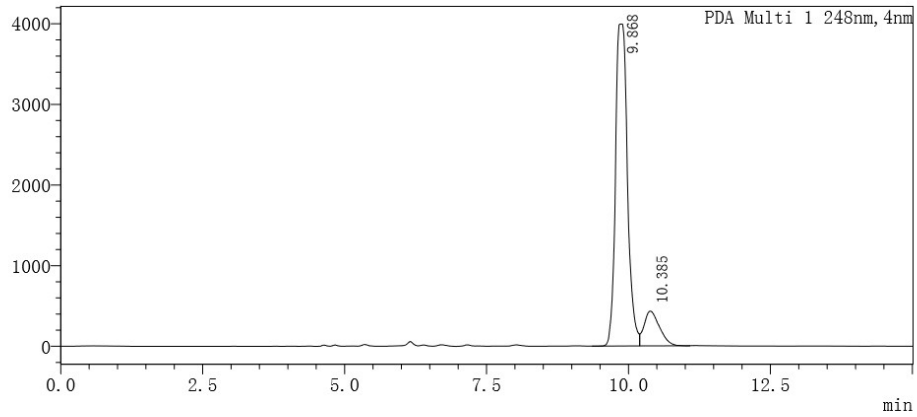
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.933	3478099	244178	0.000		M	
2	10.442	3557691	234336	0.000		V M	
总计		7035789	478514				



<色谱图>

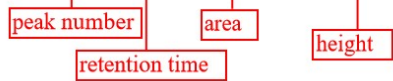
mAU



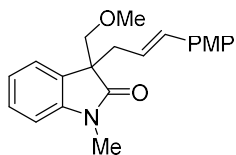
<峰表>

PDA Ch1 248nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.868	58440116	3992110	87.789		M	
2	10.385	8128827	432931	12.211		V M	
总计		66568943	4425041				



(*E*)-3-(Methoxymethyl)-3-(3-(4-methoxyphenyl)allyl)-1-methylindolin-2-one (**3oa**)



Chemical Formula: C₂₁H₂₃NO₃
Exact Mass: 337.1678

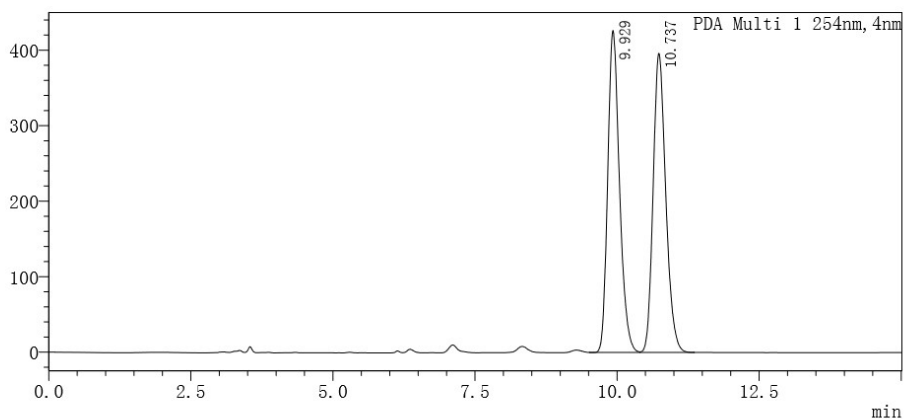
3oa was prepared according to general procedure 2.1 using **1o** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3oa** as yellow oil (63% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.32 (dd, *J* = 7.3, 0.7 Hz, 1H), 7.30-7.26 (m, 2H), 7.16-7.04 (m, 3H), 6.86-6.72 (m, 3H), 6.29 (d, *J* = 15.7 Hz, 1H), 5.69 (ddd, *J* = 15.5, 8.2, 7.0 Hz, 1H), 3.77 (s, 3H), 3.72 (q, *J* = 9.0 Hz, 2H), 3.25 (d, *J* = 4.8 Hz, 3H), 3.22 (d, *J* = 3.4 Hz, 1H), 3.18 (s, 3H), 2.72 (ddd, *J* = 13.5, 6.9, 1.2 Hz, 1H), 2.61 (ddd, *J* = 13.6, 8.2, 0.8 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 177.9, 158.8, 143.9, 133.1, 130.6, 129.9, 128.1, 127.2, 123.4, 122.3, 121.0, 113.7, 107.9, 76.1, 59.5, 55.2, 54.0, 37.5, 26.2; HRMS: (ESI) calcd for C₂₁H₂₄NO₃⁺[M+H]⁺ 338.1751; found 338.1752.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 9.9 min (major), 10.7 min (minor).

Optical Rotation: [α]_D³⁴ +5.6 (c 0.5, *i*PrOH) for 89% ee.

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.929	6125839	426724	0.000		M	
2	10.737	6130416	396211	0.000		V M	
总计		12256254	822935				

peak number

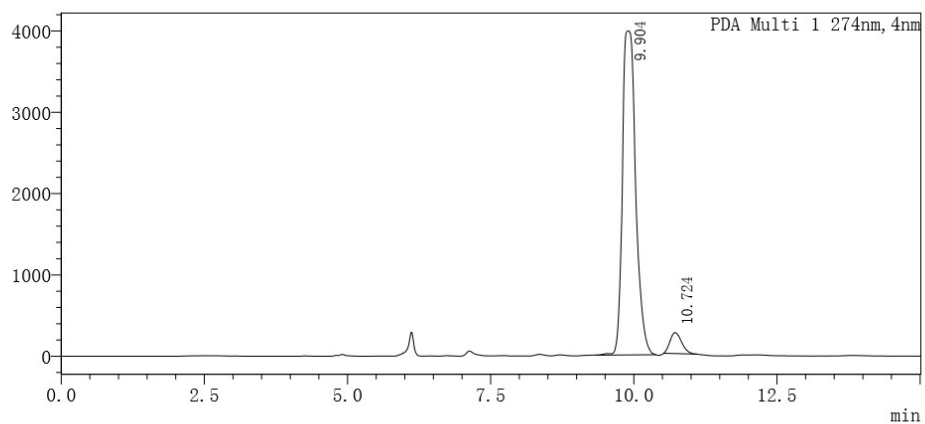
retention time

area

height

<色谱图>

mAU



<峰表>

PDA Ch1 274nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.904	64224535	3983537	0.000		M	
2	10.724	3645680	259869	0.000		M	
总计		67870215	4243407				

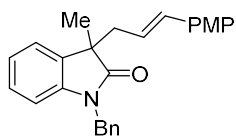
peak number

retention time

area

height

(*E*)-1-Benzyl-3-(3-(4-methoxyphenyl)allyl)-3-methylindolin-2-one (**3pa**)

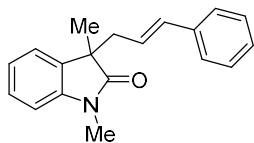


Chemical Formula: C₂₆H₂₅NO₂

Exact Mass: 383.1885

3pa was prepared according to general procedure 2.1 using **1p** and **2a** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3pa** as yellow oil (84% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.22 (m, 1H), 7.12 (ddd, *J* = 18.0, 11.9, 5.0 Hz, 6H), 7.04 (td, *J* = 7.6, 1.0 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.82-6.74 (m, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 5.74-5.54 (m, 1H), 5.17 (d, *J* = 15.8 Hz, 1H), 4.60 (d, *J* = 15.8 Hz, 1H), 3.79 (s, 3H), 2.85-2.59 (m, 2H), 1.48 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.3, 158.9, 142.3, 135.7, 133.5, 133.2, 130.0, 128.7, 127.8, 127.4, 127.3, 127.0, 122.9, 122.5, 121.9, 113.8, 109.2, 55.3, 49.0, 43.7, 42.0, 23.4; HRMS: (ESI) calcd for C₂₆H₂₆NO₂⁺[M+H]⁺ 384.1958; found 384.1959.

(*E*)-3-Cinnamyl-1,3-dimethylindolin-2-one (**3ab**)



Chemical Formula: C₁₉H₁₉NO
Exact Mass: 277.1467

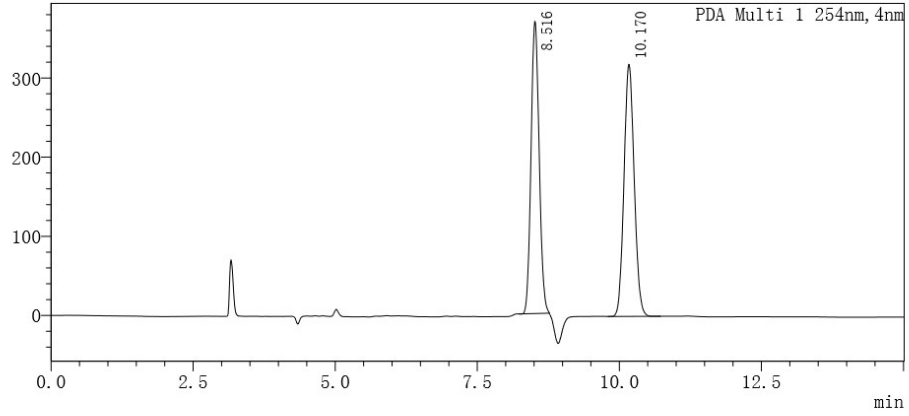
3ab was prepared according to general procedure 2.1 using **1a** and **2b** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ab** as yellow oil (60% yield). The ¹H NMR data matched those reported in the literature:¹ ¹H NMR (400 MHz, CDCl₃): δ 7.31-7.14 (m, 7H), 7.11-7.03 (m, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 5.95-5.82 (m, 1H), 3.18 (s, 3H), 2.72-2.58 (m, 2H), 1.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.2, 143.1, 137.2, 133.6, 133.5, 128.4, 127.8, 127.2, 126.1, 124.2, 122.9, 122.4, 108.0, 77.3, 77.0, 76.7, 48.6, 41.6, 26.1, 22.5.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 8.5 min (minor), 10.2 min (major).

Optical Rotation: [α]_D³³ +4.6 (c 0.2, ^tPrOH) for 83% ee.

<色谱图>

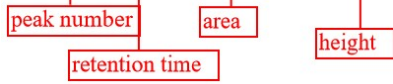
mAU



<峰表>

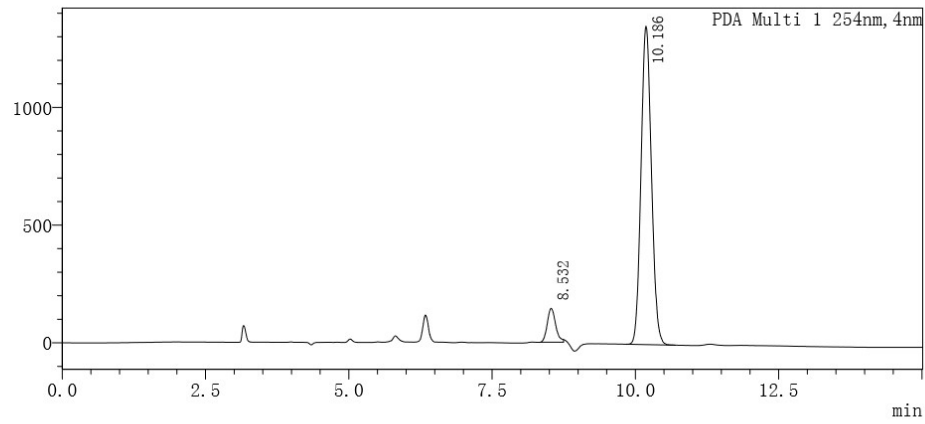
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.516	3671666	369354	0.000		M	
2	10.170	3975765	318585	0.000		M	
总计		7647431	687939				



<色谱图>

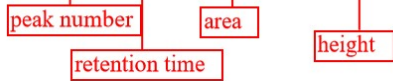
mAU



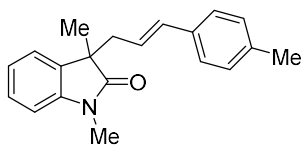
<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.532	1446426	143771	0.000		M	
2	10.186	17057563	1353348	0.000		M	
总计		18503989	1497120				



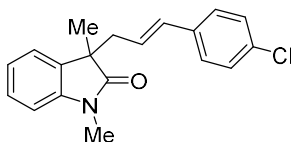
(E)-1,3-Dimethyl-3-(3-(p-tolyl)allyl)indolin-2-one (3ac)



Chemical Formula: C₂₀H₂₁NO
Exact Mass: 291.1623

3ac was prepared according to general procedure 2.1 using **1a** and **2c** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ac** as yellow oil (75% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.25 (td, *J* = 7.6, 1.3 Hz, 1H), 7.23-7.20 (m, 1H), 7.11-7.02 (m, 5H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.31 (d, *J* = 15.6 Hz, 1H), 5.90-5.75 (m, 1H), 3.17 (s, 3H), 2.69-2.57 (m, 2H), 2.29 (s, 3H), 1.41 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.2, 143.1, 136.9, 134.5, 133.5, 129.1, 127.8, 126.0, 123.1, 122.9, 122.3, 107.9, 48.6, 41.6, 26.1, 22.5, 21.1; HRMS: (ESI) calcd for C₂₀H₂₂NO⁺[M+H]⁺ 292.1696; found 292.1703.

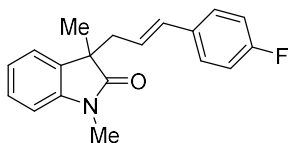
(E)-3-(3-(4-Chlorophenyl)allyl)-1,3-dimethylindolin-2-one (3ad)



Chemical Formula: C₁₉H₁₈ClNO
Exact Mass: 311.1077

3ad was prepared according to general procedure 2.1 using **1a** and **2d** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ad** as yellow oil (75% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.27 (td, *J* = 7.7, 1.3 Hz, 1H), 7.24-7.17 (m, 3H), 7.13-7.03 (m, 3H), 6.82 (m, 1H), 6.29 (d, *J* = 15.8 Hz, 1H), 5.90-5.79 (m, 1H), 3.18 (s, 3H), 2.64 (dd, *J* = 7.6, 1.1 Hz, 2H), 1.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.1, 143.1, 135.7, 133.5, 132.8, 132.5, 128.6, 127.9, 127.3, 125.0, 122.9, 122.5, 108.1, 48.6, 41.6, 26.2, 22.6; HRMS: (ESI) calcd for C₁₉H₁₉ClNO⁺[M+H]⁺ 312.1150; found 312.1149.

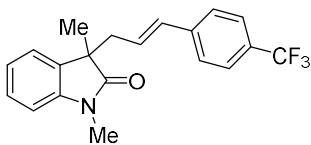
(E)-3-(3-(4-Fluorophenyl)allyl)-1,3-dimethylindolin-2-one (3ae)



Chemical Formula: $C_{19}H_{18}FNO$
Exact Mass: 295.1372

3ae was prepared according to general procedure 2.1 using **1a** and **2e** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ae** as yellow oil (70% yield). 1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.25 (m, 1H), 7.24-7.20 (m, 1H), 7.18-7.11 (m, 2H), 7.08 (td, $J = 7.5, 0.9$ Hz, 1H), 6.97-6.88 (m, 2H), 6.83 (d, $J = 7.8$ Hz, 1H), 6.30 (d, $J = 15.8$ Hz, 1H), 5.78 (dt, $J = 15.4, 7.5$ Hz, 1H), 3.18 (s, 3H), 2.70-2.58 (m, 2H), 1.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 163.3, 143.1, δ 133.4 (d, $J = 3.3$ Hz), 133.4, 132.5, 127.9, 127.6 (d, $J = 7.9$ Hz), 123.9 (d, $J = 2.2$ Hz), 122.9, 122.4, 115.3 (d, $J = 21.5$ Hz), 108.0, 48.7, 41.6, 26.2, 22.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.06; HRMS: (ESI) calcd for $C_{19}H_{19}FNO^+[M+H]^+$ 296.1145; found 296.1439.

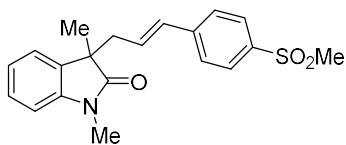
(*E*)-1,3-Dimethyl-3-(3-(4-(trifluoromethyl)phenyl)allyl)indolin-2-one (**3af**)



Chemical Formula: $C_{20}H_{18}F_3NO$
Exact Mass: 345.1340

3af was prepared according to general procedure 2.1 using **1a** and **2f** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3af** as yellow oil (43% yield). 1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, $J = 8.2$ Hz, 2H), 7.30-7.26 (m, 2H), 7.25 (d, $J = 2.4$ Hz, 1H), 7.24-7.21 (m, 1H), 7.08 (td, $J = 7.5, 1.0$ Hz, 1H), 6.83 (d, $J = 7.7$ Hz, 1H), 6.36 (d, $J = 14.8$ Hz, 1H), 5.95 (dq, $J = 15.9, 7.9$ Hz, 1H), 3.18 (s, 3H), 2.72-2.65 (m, 2H), 1.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.1, 173.8, 158.3, 143.2, 133.4, 132.5, 128.1, 127.2, 126.3, 125.5 (q, $J = 3.8$ Hz), 123.2, 122.9, 122.6, 108.2, 48.7, 41.7, 26.3, 22.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4; HRMS: (ESI) calcd for $C_{20}H_{19}F_3NO^+[M+H]^+$ 346.1413; found 346.1419.

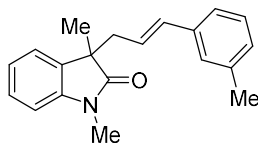
(*E*)-1,3-Dimethyl-3-(3-(4-(methylsulfonyl)phenyl)allyl)indolin-2-one (**3ag**)



Chemical Formula: C₂₀H₂₁NO₃S
Exact Mass: 355.1242

3ag was prepared according to general procedure 2.1 using **1a** and **2g** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ag** as yellow oil (41% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.76 (m, 2H), 7.36-7.32 (m, 2H), 7.31-7.27 (m, 1H), 7.23 (ddd, *J* = 7.4, 1.3, 0.5 Hz, 1H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.04 (ddd, *J* = 15.7, 8.0, 7.1 Hz, 1H), 3.18 (s, 3H), 3.02 (s, 3H), 2.75-2.65 (m, 2H), 1.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 179.8, 143.0, 142.6, 138.7, 133.2, 131.9, 128.9, 128.1, 127.6, 126.8, 122.8, 122.6, 108.1, 48.5, 44.5, 41.6, 26.2, 22.7; HRMS: (ESI) calcd for C₂₀H₂₂NO₃S⁺[M+H]⁺ 378.1134; found 378.1126.

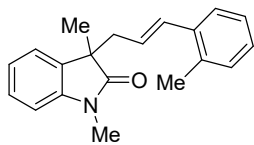
(*E*)-1,3-Dimethyl-3-(3-(*m*-tolyl)allyl)indolin-2-one (**3ah**)



Chemical Formula: C₂₀H₂₁NO
Exact Mass: 291.1623

3ah was prepared according to general procedure 2.1 using **1a** and **2h** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ah** as yellow oil (70% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.27 (td, *J* = 7.7, 1.2 Hz, 2H), 7.24-7.21 (m, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 (td, *J* = 7.5, 0.9 Hz, 1H), 7.04-6.97 (m, 3H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.31 (d, *J* = 15.7 Hz, 1H), 5.95-5.83 (m, 1H), 3.19 (s, 3H), 2.71-2.55 (m, 2H), 2.29 (s, 3H), 1.41 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.2, 143.1, 137.9, 137.2, 133.8, 133.6, 128.3, 128.0, 127.8, 126.9, 123.9, 123.2, 122.9, 122.4, 108.0, 77.3, 77.0, 76.7, 48.6, 41.6, 26.2, 22.5, 21.3; HRMS: (ESI) calcd for C₂₀H₂₂NO⁺[M+H]⁺ 292.1696; found 292.1698.

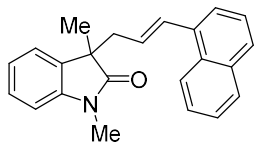
(*E*)-1,3-Dimethyl-3-(3-(*o*-tolyl)allyl)indolin-2-one (**3ai**)



Chemical Formula: C₂₀H₂₁NO
Exact Mass: 291.1623

3ai was prepared according to general procedure 2.1 using **1a** and **2i** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ai** as yellow oil (70% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.22 (m, 3H), 7.14 (dd, *J* = 7.3, 2.3 Hz, 1H), 7.10-7.04 (m, 4H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 5.70 (dt, *J* = 15.4, 7.6 Hz, 1H), 3.18 (s, 3H), 2.68 (d, *J* = 7.8 Hz, 2H), 2.17 (s, 3H), 1.43 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.2, 143.1, 136.6, 135.2, 133.5, 132.0, 130.0, 127.8, 127.1, 125.9, 125.8, 125.7, 122.9, 122.3, 108.0, 48.8, 41.9, 26.1, 22.7, 19.7; HRMS: (ESI) calcd for C₂₀H₂₁NONa⁺[M+Na]⁺ 314.1515; found 314.1511.

(*E*)-1,3-Dimethyl-3-(3-(naphthalen-1-yl)allyl)indolin-2-one (**3aj**)



Chemical Formula: C₂₃H₂₁NO
Exact Mass: 327.1623

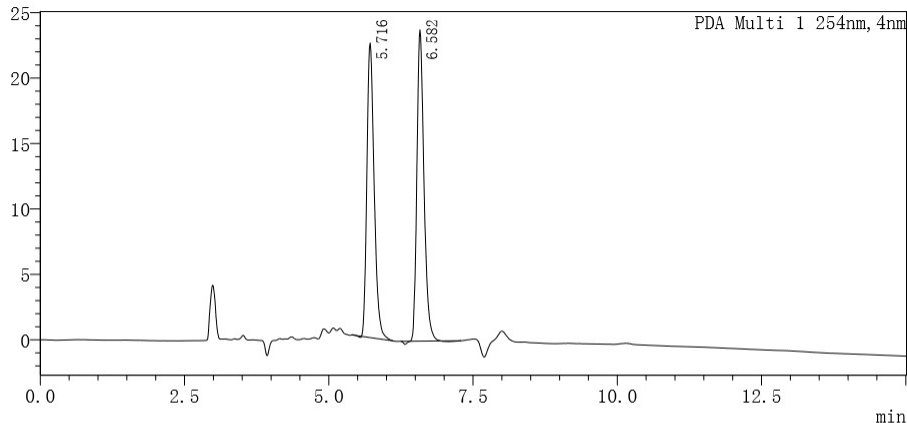
3aj was prepared according to general procedure 2.2 using **1a** and **2j** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3aj** as yellow oil (72% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.79 (dt, *J* = 3.9, 2.8 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.47-7.39 (m, 2H), 7.38-7.23 (m, 5H), 7.14-7.07 (m, 1H), 7.00 (d, *J* = 15.5 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 5.81 (dt, *J* = 15.3, 7.6 Hz, 1H), 3.17 (s, 3H), 2.88-2.66 (m, 2H), 1.48 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.1, 143.2, 135.3, 133.5, 133.3, 131.6, 131.0, 128.3, 127.8, 127.6, 127.5, 125.8, 125.7, 125.5, 124.1, 123.8, 122.9, 122.4, 108.0, 77.3, 77.0, 76.7, 48.9, 42.0, 26.1, 22.7; HRMS: (ESI) calcd for C₂₃H₂₂NO⁺[M+H]⁺ 328.1696; found 328.1696.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 5.7 min (minor), 6.5 min (major).

Optical Rotation: [α]_D³³ +47.7 (c 0.2, *i*PrOH) for 84% ee.

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.716	196535	22517	0.000		M	
2	6.582	200509	23803	0.000		M	
总计		397044	46320				

peak number

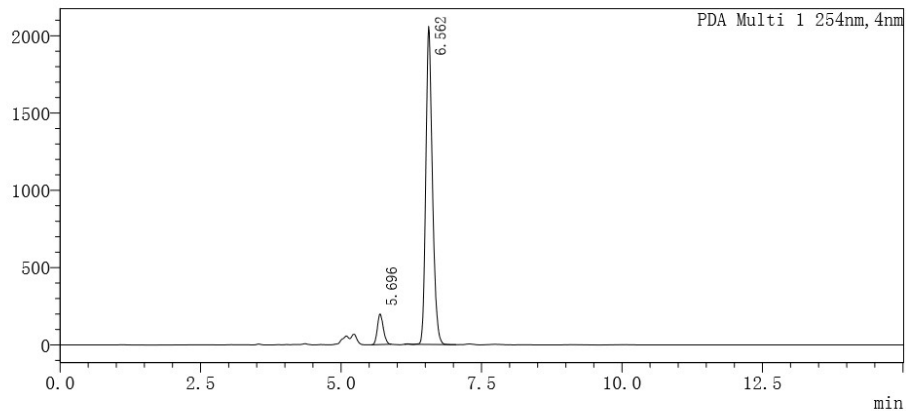
area

height

retention time

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.696	1457932	198580	0.000		M	
2	6.562	16728897	2058676	0.000		M	
总计		18186828	2257256				

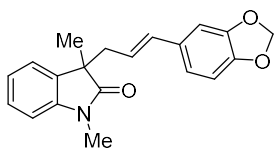
peak number

area

height

retention time

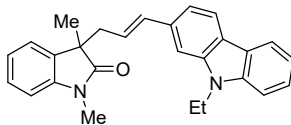
(*E*)-3-(3-(Benzo[*d*][1,3]dioxol-5-yl)allyl)-1,3-dimethylindolin-2-one (**3ak**)



Chemical Formula: C₂₀H₁₉NO₃
Exact Mass: 321.1365

3ak was prepared according to general procedure 2.1 using **1a** and **2k** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3ak** as yellow oil (73% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.23 (m, 1H), 7.21 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 1.7 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.63 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.25 (d, *J* = 15.7 Hz, 1H), 5.90 (s, 2H), 5.69 (dt, *J* = 15.4, 7.5 Hz, 1H), 3.18 (s, 3H), 2.68-2.55 (m, 2H), 1.40 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.3, 147.9, 146.9, 143.2, 133.7, 133.3, 131.8, 127.9, 123.0, 122.5, 120.8, 108.2, 108.1, 105.5, 101.0, 48.8, 41.7, 26.2, 22.6; HRMS: (ESI) calcd for C₂₀H₂₀NO₃⁺[M+H]⁺ 322.1438; found 322.1443.

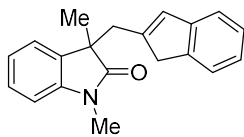
(*E*)-3-(3-(9-Ethyl-9*H*-carbazol-2-yl)allyl)-1,3-dimethylindolin-2-one (**3al**)



Chemical Formula: C₂₇H₂₆N₂O
Exact Mass: 394.2045

3al was prepared according to general procedure 2.1 using **1a** and **2l** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3al** as yellow oil (64% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, *J* = 6.8, 0.8 Hz, 1H), 7.91 (d, *J* = 1.5 Hz, 1H), 7.44 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.38-7.33 (m, 2H), 7.29-7.24 (m, 3H), 7.20 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 7.12-7.05 (m, 1H), 6.84-6.79 (m, 1H), 6.52 (d, *J* = 15.7 Hz, 1H), 5.91 (ddd, *J* = 15.5, 8.0, 7.1 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.19 (s, 3H), 2.78-2.56 (m, 2H), 1.45 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 211.8, 174.6, 171.6, 170.8, 165.8, 165.2, 159.9, 159.1, 157.1, 155.5, 154.4, 154.4, 154.3, 153.7, 152.6, 151.8, 150.2, 149.6, 139.9, 139.7, 139.4, 80.2, 73.2, 68.9, 57.6, 53.8, 45.2; HRMS: (ESI) calcd for C₂₇H₂₆N₂ONa⁺[M+Na]⁺ 417.1937; found 417.1929.

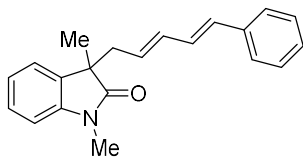
3-(2-(1*H*-Inden-2-yl)ethyl)-1,3-dimethylindolin-2-one (**3am**)



Chemical Formula: C₂₀H₁₉NO
Exact Mass: 289.1467

3am was prepared according to general procedure 2.1 using **1a** and **2m** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3am** as yellow oil (70% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.18 (m, 3H), 7.18-7.11 (m, 2H), 7.08 (td, *J* = 7.7, 0.9 Hz, 1H), 7.05-7.00 (m, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.32 (d, *J* = 0.7 Hz, 1H), 3.15 (d, *J* = 13.9 Hz, 1H), 3.11 (s, 3H), 2.95 (dd, *J* = 18.1, 15.1 Hz, 2H), 2.74 (d, *J* = 22.8 Hz, 1H), 1.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.1, 144.8, 144.4, 143.3, 143.1, 133.6, 129.8, 127.9, 125.9, 123.8, 123.2, 122.7, 122.4, 120.2, 108.1, 49.3, 42.0, 39.5, 26.1, 24.2; HRMS: (ESI) calcd for C₂₀H₂₀NO⁺[M+H]⁺ 290.1539; found 290.1546.

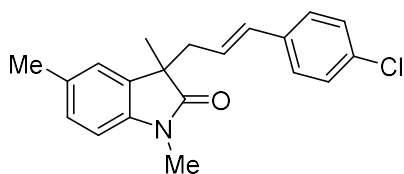
1,3-Dimethyl-3-((2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl)indolin-2-one (**3an**)



Chemical Formula: C₂₂H₂₁NO
Exact Mass: 303.1623

3an was prepared according to general procedure 2.1 using **1a** and **2n** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3an** as yellow oil (90% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.30 (m, 2H), 7.30-7.24 (m, 3H), 7.23-7.15 (m, 2H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.64-6.52 (m, 1H), 6.39 (d, *J* = 15.7 Hz, 1H), 6.16 (ddd, *J* = 15.0, 10.4, 0.5 Hz, 1H), 5.46 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.19 (s, 3H), 2.59 (d, *J* = 7.7 Hz, 2H), 1.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.3, 143.2, 137.4, 134.3, 133.7, 131.4, 128.7, 128.6, 128.6, 127.9, 127.4, 126.3, 123.0, 122.5, 108.1, 48.7, 41.6, 26.3, 22.7; HRMS: (ESI) calcd for C₂₁H₂₂NO⁺[M+H]⁺ 304.1696; found 304.1689.

(*E*)-3-(3-(4-chlorophenyl)allyl)-1,3,5-trimethylindolin-2-one (**3bd**)



Chemical Formula: C₂₀H₂₀ClNO

Exact Mass: 325.1233

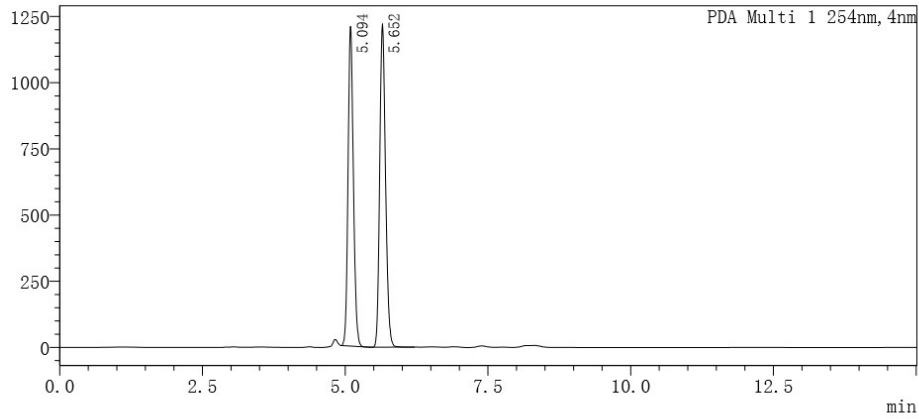
3bd was prepared according to general procedure 2.2 using **1b** and **2d** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3bd** as yellow oil (66% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.16 (m, 2H), 7.13-7.08 (m, 2H), 7.08-7.04 (m, 1H), 7.04-7.00 (m, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.30 (d, *J* = 15.7 Hz, 1H), 5.97-5.74 (m, 1H), 3.15 (s, 3H), 2.63 (dt, *J* = 7.1, 1.2 Hz, 2H), 2.35 (s, 3H), 1.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.0, 140.7, 135.7, 133.5, 132.7, 132.3, 131.9, 128.5, 128.1, 127.3, 125.1, 123.7, 107.7, 48.7, 41.7, 26.2, 22.6, 21.2; HRMS: (ESI) calcd for C₂₀H₂₀ClNONa⁺[M+Na]⁺ 348.1126; found 348.1116.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 5.1 min (minor), 5.6 min (major).

Optical Rotation: [α]_D³³ +51.4 (c 0.5, ^tPrOH) for 77% ee.

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.094	7807822	1206229	0.000		M	
2	5.652	8671609	1222243	0.000		M	
总计		16479431	2428472				

peak number

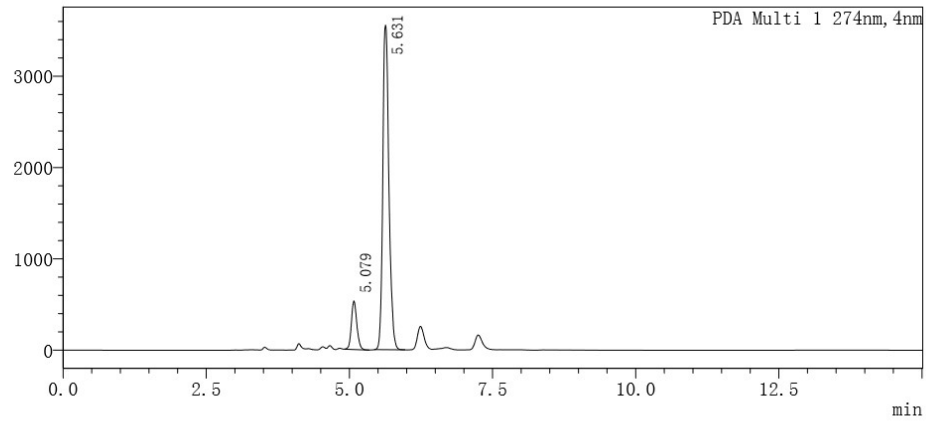
retention time

area

height

<色谱图>

mAU



<峰表>

PDA Ch1 274nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.079	3516280	533018	11.747		M	
2	5.631	26416868	3556478	88.253		M	
总计		29933148	4089497				

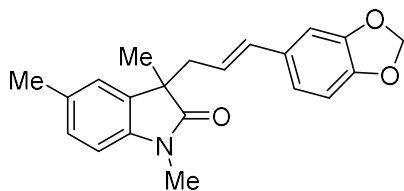
peak number

retention time

area

height

(*E*)-3-(3-(benzo[d][1,3]dioxol-5-yl)allyl)-1,3,5-trimethylindolin-2-one (**3bk**)



Chemical Formula: C₂₁H₂₁NO₃

Exact Mass: 335.1521

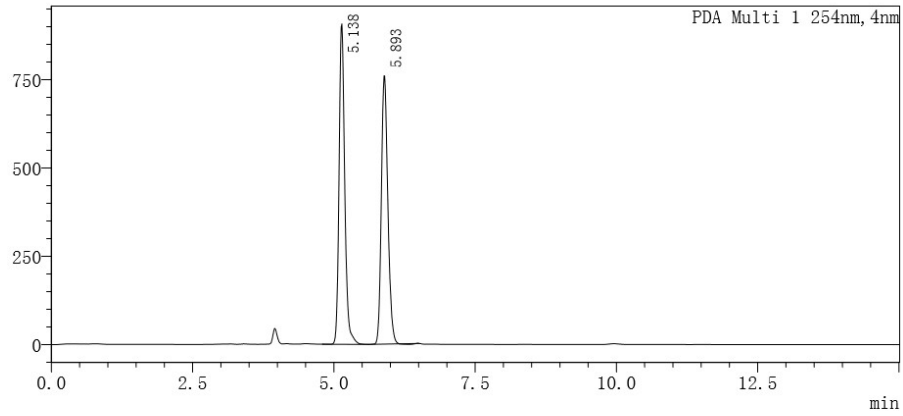
3bk was prepared according to general procedure 2.2 using **1b** and **2k** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3bk** as yellow oil (75% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.09-7.02 (m, 2H), 6.73-6.66 (m, 3H), 6.66-6.60 (m, 1H), 6.26 (d, *J* = 15.5 Hz, 1H), 5.90 (s, 2H), 5.74-5.62 (m, 1H), 3.15 (s, 3H), 2.60 (d, *J* = 7.5 Hz, 2H), 2.36 (s, 3H), 1.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.2, 147.8, 146.8, 140.8, 133.7, 133.1, 131.9, 128.0, 123.7, 122.6, 120.7, 108.1, 107.7, 105.5, 100.9, 48.7, 41.6, 26.2, 22.6, 21.2; HRMS: (ESI) calcd for C₂₁H₂₁NO₃Na⁺[M+Na]⁺ 358.1414; found 358.1390.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. t_R = 5.1 min (minor), 5.9 min (major).

Optical Rotation: [α]_D³¹ +11.4 (c 0.1, *i*PrOH) for 81% ee.

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.138	6339024	907229	0.000		M	
2	5.893	6035640	759778	0.000		M	
总计		12374664	1667006				

peak number

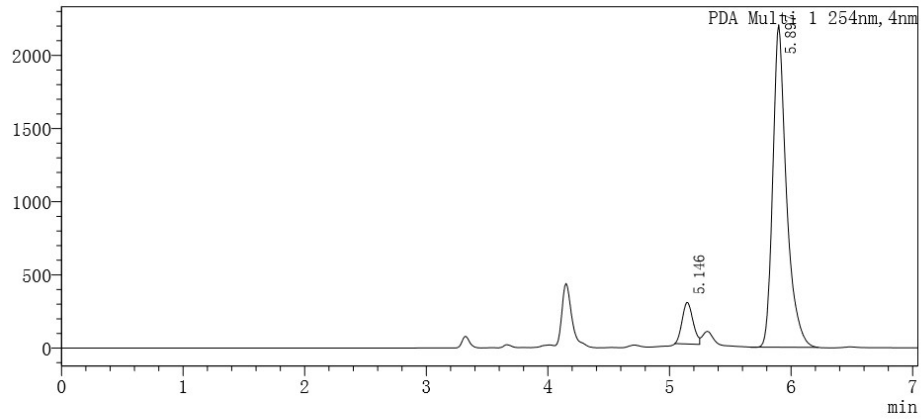
retention time

area

height

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.146	1778907	284348	0.000		M	
2	5.897	17109412	2204867	0.000		M	
总计		18888319	2489215				

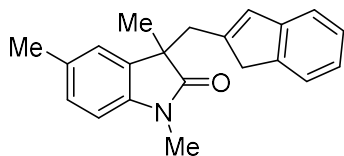
peak number

retention time

area

height

3-((1*H*-inden-2-yl)methyl)-1,3,5-trimethylindolin-2-one (**2bm**)



Chemical Formula: C₂₁H₂₁NO

Exact Mass: 303.1623

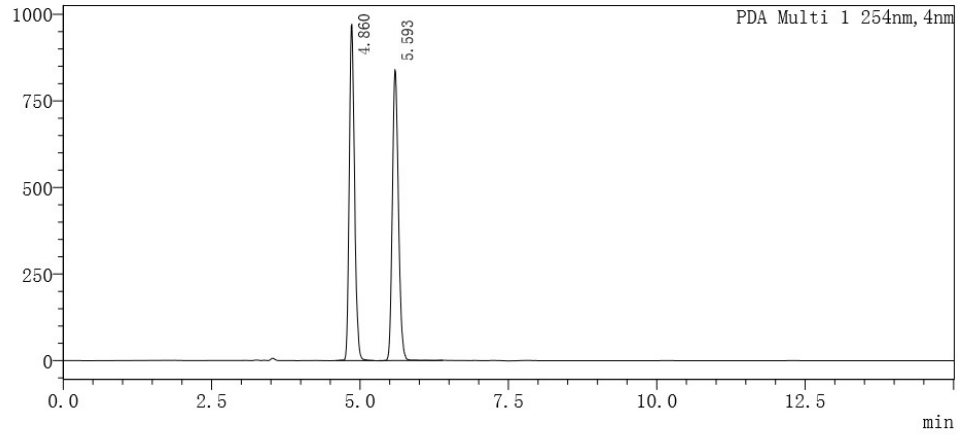
3bm was prepared according to general procedure 2.2 using **1b** and **2m** and was purified by silica gel column chromatography (PE/EA = 40/1~5/1) to obtain **3bm** as yellow oil (62% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.20 (m, 1H), 7.19-7.11 (m, 2H), 7.08-7.06 (m, 1H), 7.06-7.00 (m, 2H), 6.62 (d, *J* = 7.9 Hz, 1H), 6.31 (s, 1H), 3.14 (d, *J* = 13.1 Hz, 1H), 3.09 (s, 3H), 2.97 (d, *J* = 22.1 Hz, 1H), 2.90 (d, *J* = 14.5 Hz, 1H), 2.76 (d, *J* = 22.1 Hz, 1H), 2.37 (s, 3H), 1.45 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.1, 144.9, 144.6, 143.4, 140.8, 133.7, 131.9, 129.6, 128.2, 125.0, 123.8, 123.5, 123.2, 120.2, 107.8, 49.3, 42.0, 39.6, 26.2, 24.4, 21.2; HRMS: (ESI) calcd for C₂₁H₂₂NO⁺[M+H]⁺ 304.1696; found 304.1688.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. t_R = 4.9 min (minor), 5.6 min (major).

Optical Rotation: [α]_D³³ +56.2 (c 0.2, *i*PrOH) for 73% ee.

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mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.860	6008217	971803	0.000		M	
2	5.593	5969741	841042	0.000		M	
总计		11977958	1812845				

peak number

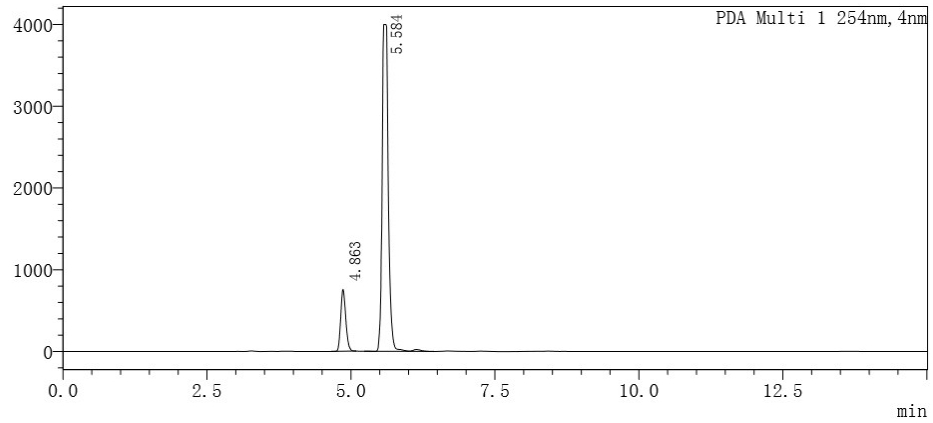
area

height

retention time

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.863	4587032	759227	0.000		M	
2	5.584	29777410	3997483	0.000		M	
总计		34364442	4756710				

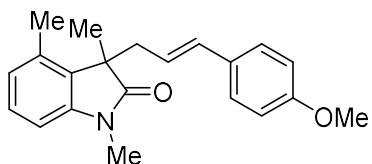
peak number

area

height

retention time

(E)-3-(3-(4-methoxyphenyl)allyl)-1,3,4-trimethylindolin-2-one (3qa)



Chemical Formula: $C_{21}H_{23}NO_2$

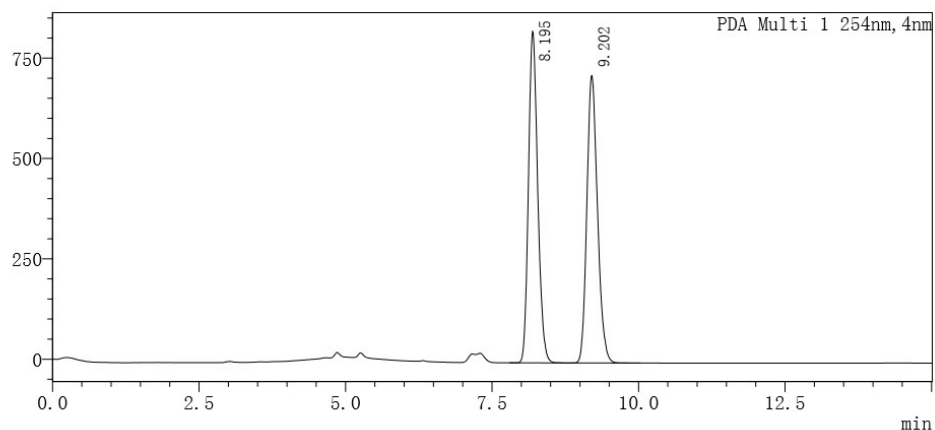
Exact Mass: 321.1729

1H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, $J = 7.8$ Hz, 1H), 7.06-6.98 (m, 2H), 6.84 (d, $J = 7.7$ Hz, 1H), 6.76-6.69 (m, 2H), 6.67-6.61 (m, 1H), 6.26 (d, $J = 15.6$ Hz, 1H), 5.53-5.40 (m, 1H), 3.74 (s, 3H), 3.14 (s, 3H), 2.90-2.74 (m, 2H), 2.44 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.1, 158.8, 143.5, 134.0, 132.1, 130.2, 130.1, 127.6, 127.2, 125.0, 122.3, 113.7, 105.7, 55.2, 50.0, 39.7, 26.2, 21.5, 18.4; HRMS: (ESI) calcd for $C_{21}H_{23}NO_2H^+$ $[M+H]^+$ 322.1802; found 322.1797.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. $t_R = 8.2$ min (minor), 9.2 min (major).

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.195	9045045	826938	0.000		M	
2	9.202	9026436	716594	0.000		M	
总计		18071481	1543531				

peak number

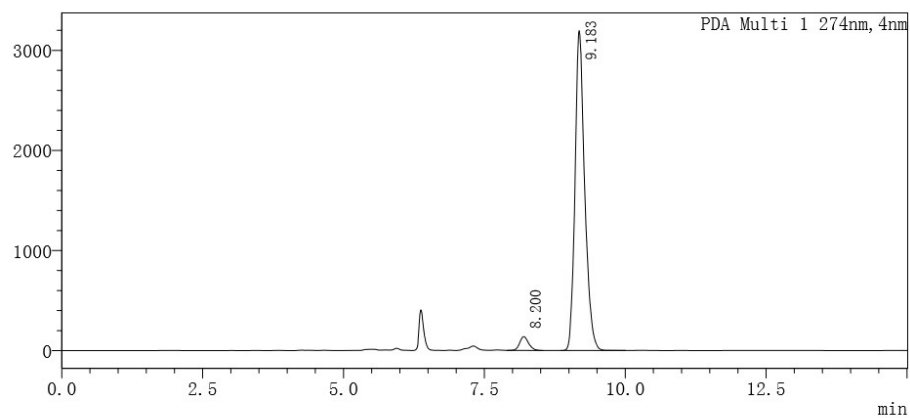
area

height

retention time

<色谱图>

mAU



<峰表>

PDA Ch1 274nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.200	1518990	138972	0.000		M	
2	9.183	38063939	3196894	0.000		M	
总计		39582928	3335866				

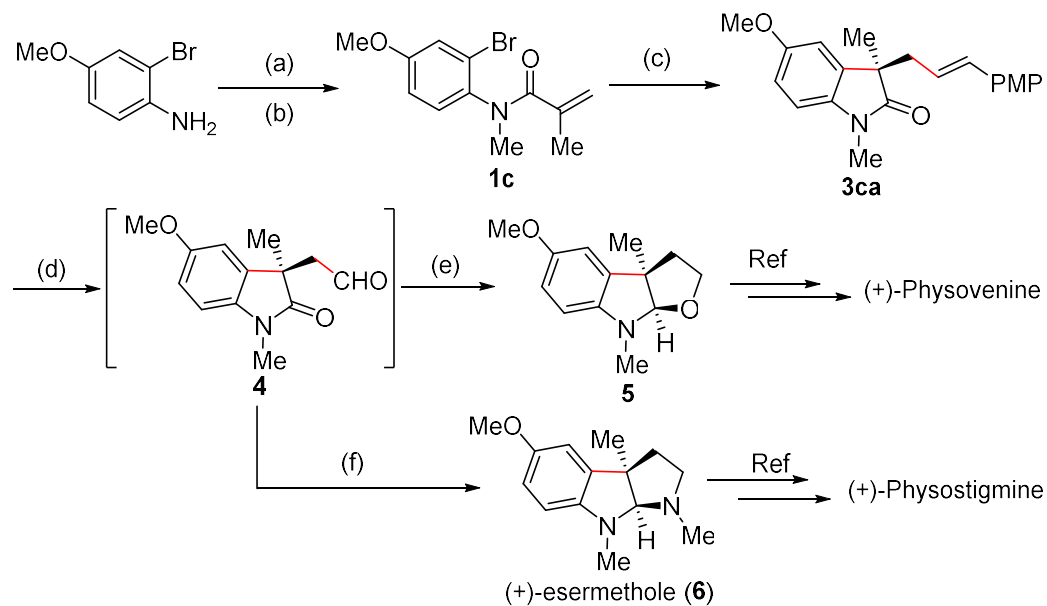
peak number

area

height

retention time

5. Synthetic Applications²



Scheme S1. Formal total synthesis of (+)-physovene and (+)-physostigmine.

Procedure for the synthesis of the aldehyde intermediate 4: To a solution of **3ca** (100 mg, 0.3 mmol) in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (3 mL/3 mL), O_3 was bubbled at -78°C until the reaction was complete (monitored by TLC). Argon was bubbled into the solution for 5 min to remove the excess O_3 . PPh_3 was added at -78°C and the mixture was kept stirring for another hour. The reaction mixture was passed through a short pad of silica gel, and eluted with EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel (PE/ethyl acetate = 5/1 to 2/1) to afford the aldehyde intermediate **4** as a white solid (42.1 mg, 60% yield).

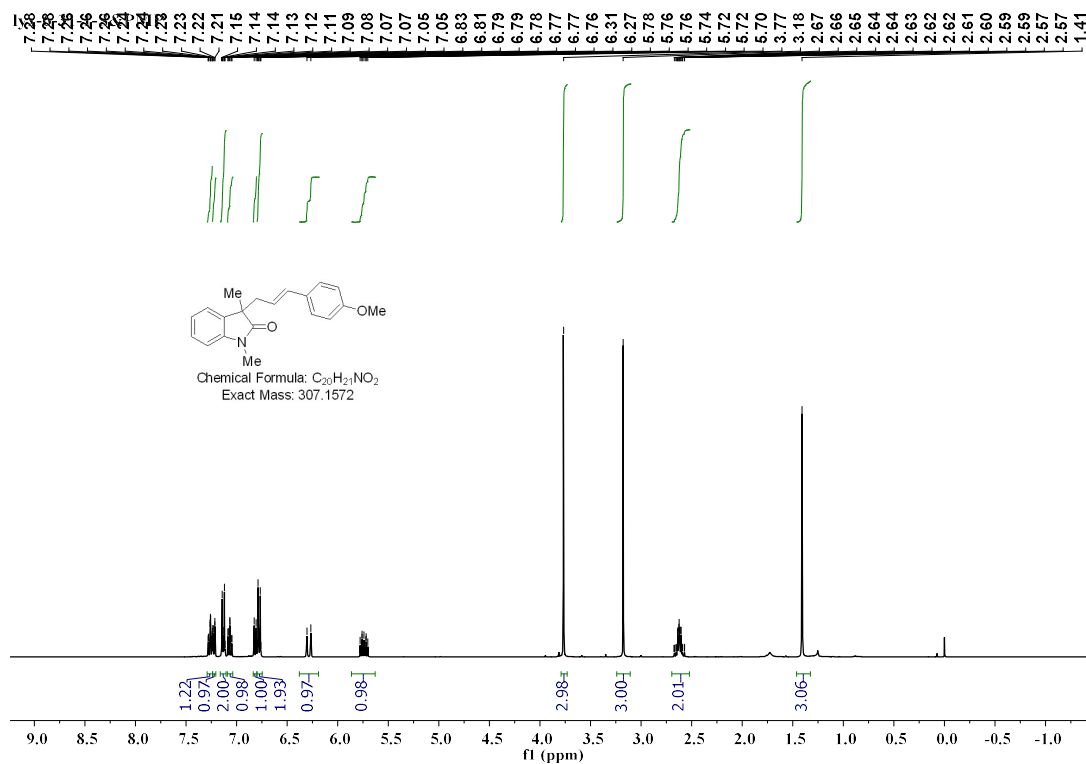
Procedure for the synthesis of 5: To a solution of LiAlH_4 (260 μL , 0.65 mmol, 2.5 mol/L in THF) in dry THF (3 mL), the aldehyde intermediate **4** (15.1 mg, 0.065 mmol) was added under Ar, the mixture was stirred at room temperature for 40 min. The reaction was quenched by EtOAc and saturated aqueous NaHCO_3 successively. The phases were separated, the aqueous layer was extracted with EtOAc, and the combined organic extracts were dried with Na_2SO_4 and concentrated. The residue was

purified by silica gel column chromatography (PE/acetone/ $\text{NEt}_3 = 10/1/0.1$) to afford **5** as a pale yellow oil (13.0 mg, 91%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.74-6.62 (m, 2H), 6.29 (d, $J = 8.3$ Hz, 1H), 5.03 (s, 1H), 4.03-3.86 (m, 1H), 3.75 (s, 3H), 3.47 (ddd, $J = 10.9, 8.6, 5.4$ Hz, 1H), 2.88 (s, 3H), 2.13 (ddd, $J = 11.8, 5.3, 1.5$ Hz, 1H), 2.09-1.99 (m, 1H), 1.45 (s, 3H); $[\alpha]_{\text{D}}^{30} +24$ (c 0.25, EtOH), literature value $[\alpha]_{\text{D}}^{22} -81.2$ (c 0.6, EtOH) for the opposite enantiomer.³

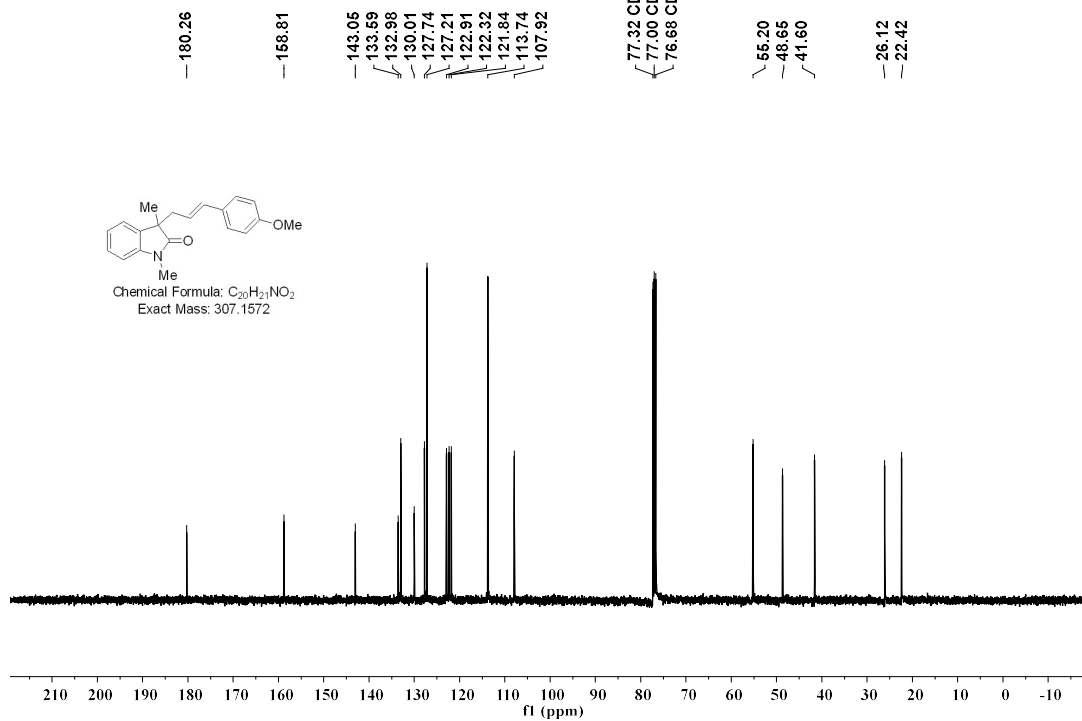
Procedure for the synthesis of 6: To a solution of the aldehyde intermediate **4** (15.1 mg, 0.065 mmol) and TEA (90 μL , 0.65 mmol) in anhydrous THF (3 mL), $\text{MeNH}_2\cdot\text{HCl}$ (43.9 mg, 0.65 mmol) and MgSO_4 (50 mg) was added under Ar, the mixture was stirred at room temperature for 16 h. Then LiAlH_4 (260 μL , 0.65 mmol, 2.5 mol/L in THF) was added and the mixture was refluxed at 80 °C for 1.5 h. The reaction was quenched by EtOAc and saturated aqueous NaHCO_3 successively. The phases were separated, the aqueous layer was extracted with EtOAc, and the combined organic extracts were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (PE/acetone/ $\text{NEt}_3 = 8/1/0.1$) to afford **6** as a pale yellow oil (12.8 mg, 86%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.65 (dt, $J = 4.0, 2.4$ Hz, 2H), 6.36 (d, $J = 8.2$ Hz, 1H), 4.05 (s, 1H), 3.75 (s, 3H), 2.89 (s, 3H), 2.73 (dt, $J = 9.5, 5.4$ Hz, 1H), 2.68-2.60 (m, 1H), 2.54 (s, 3H), 1.95 (dd, $J = 7.4, 5.4$ Hz, 2H), 1.43 (s, 3H); $[\alpha]_{\text{D}}^{30} +62$ (c 0.2, MeOH), literature value $[\alpha]_{\text{D}}^{22} -98$ (c 1.0, MeOH) for the opposite enantiomer.³

6. Copies of the ^1H , ^{19}F and ^{13}C NMR spectra

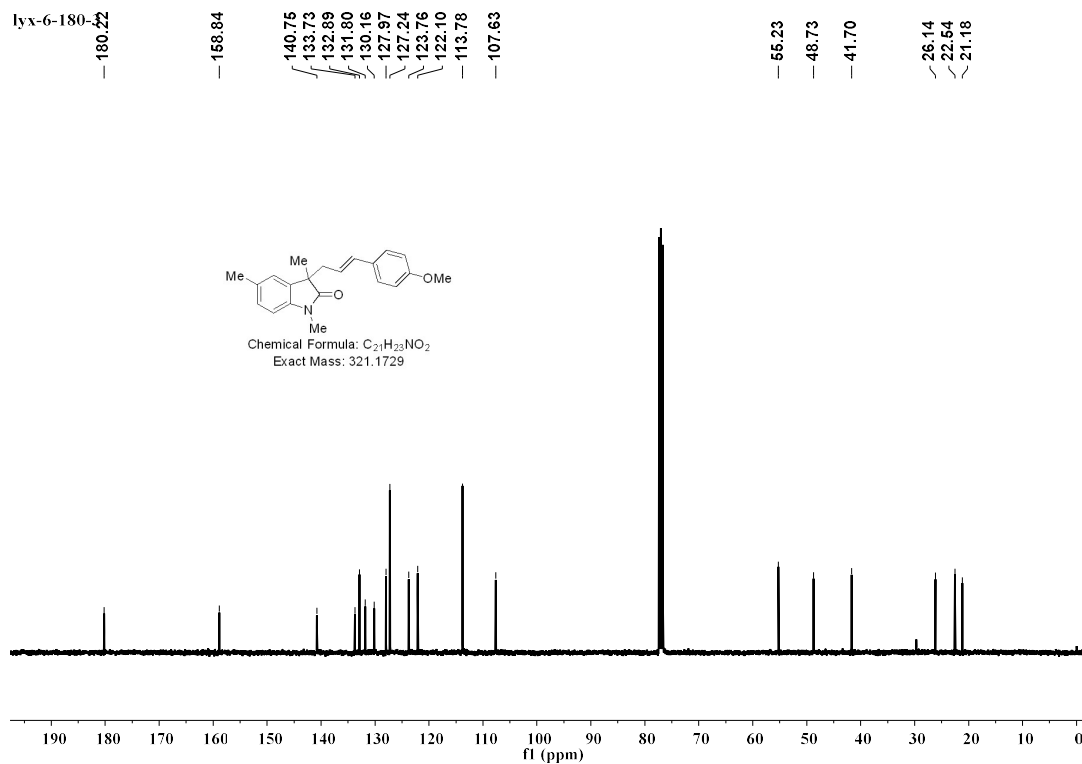
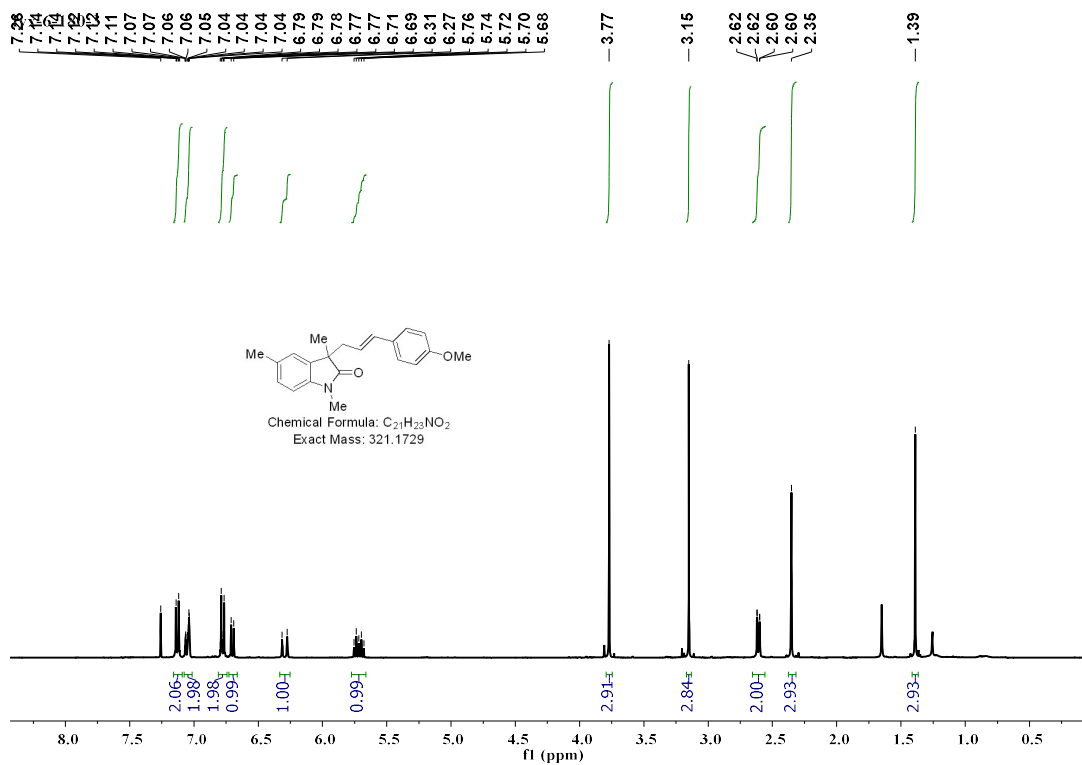
3aa



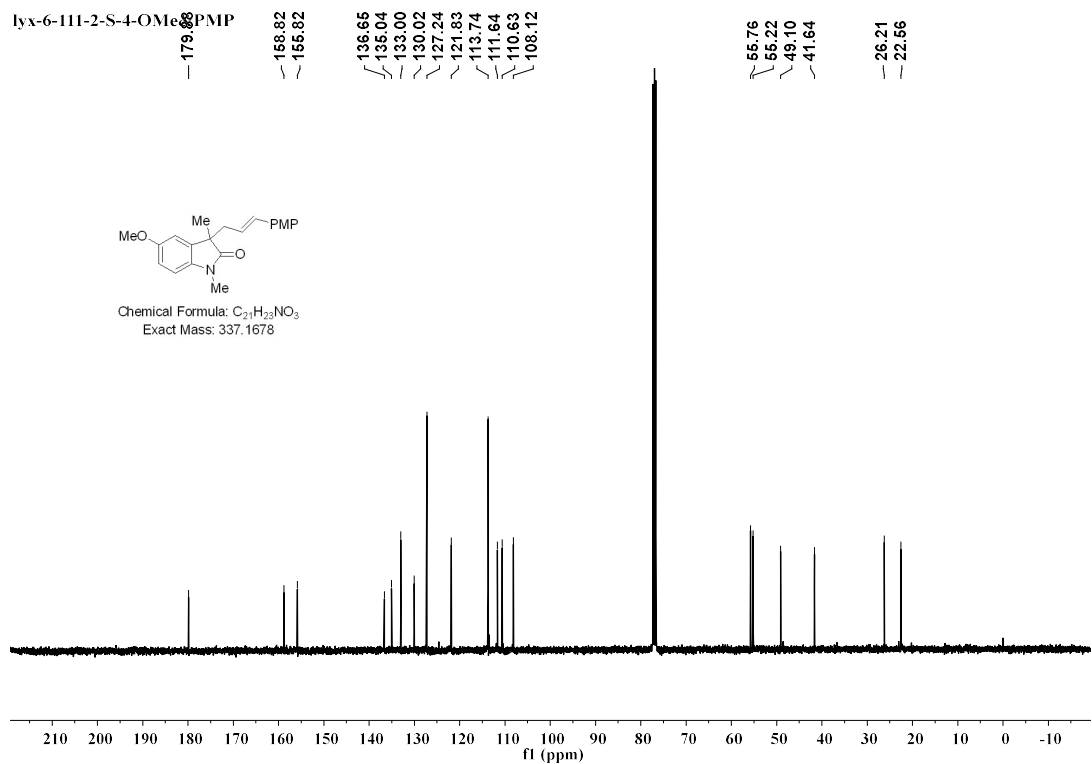
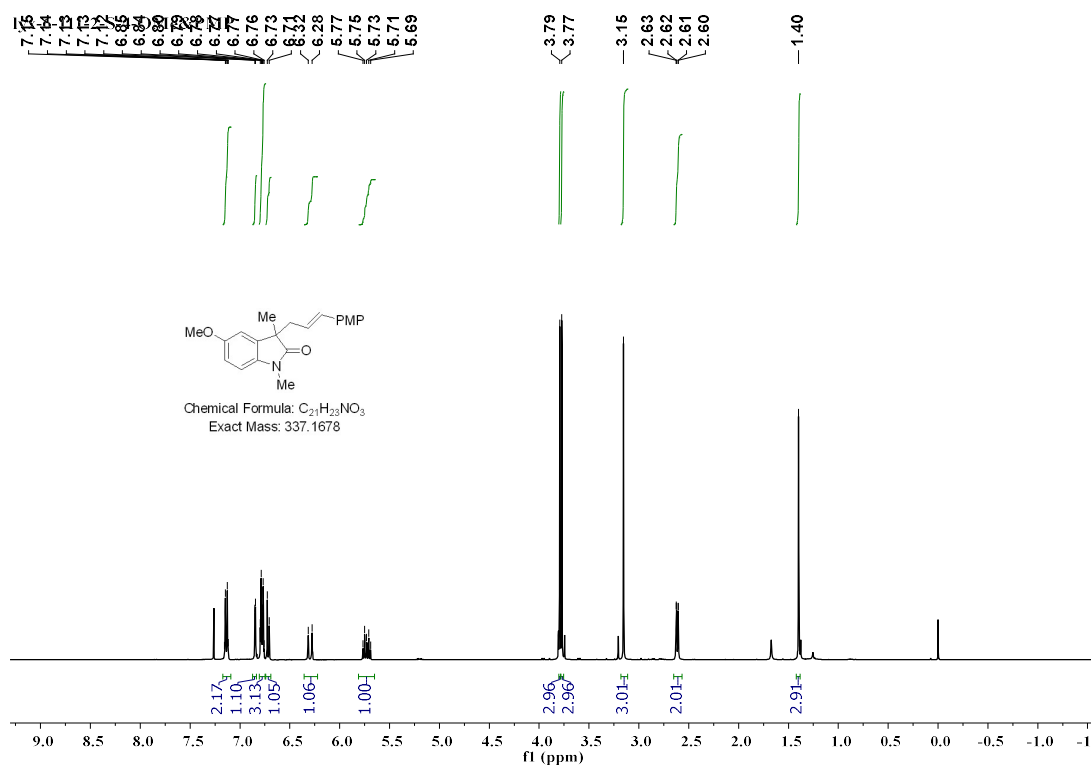
lyx-6-31-1-S&PMP



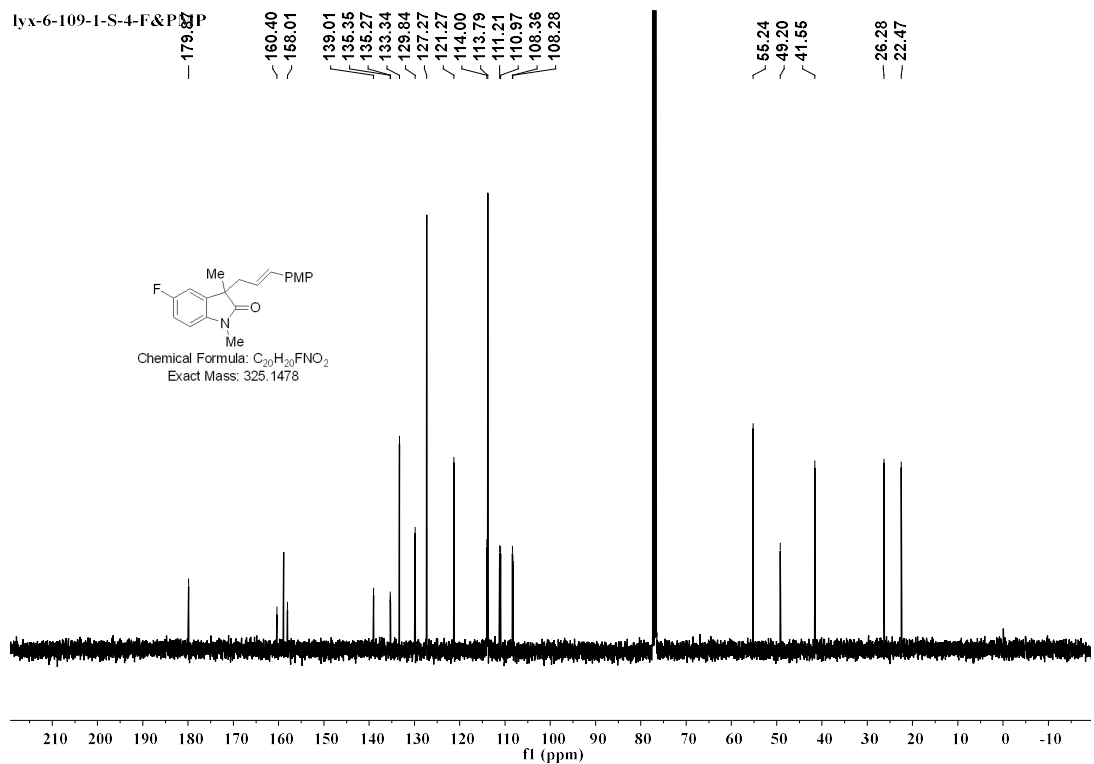
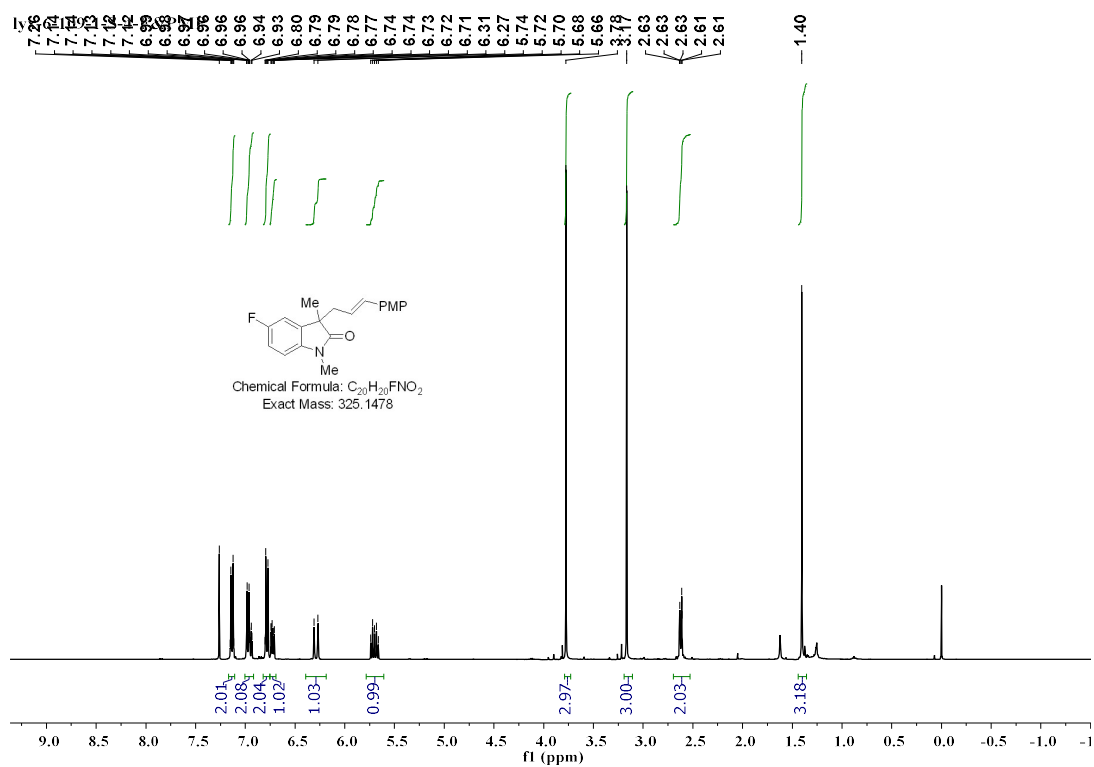
3ba



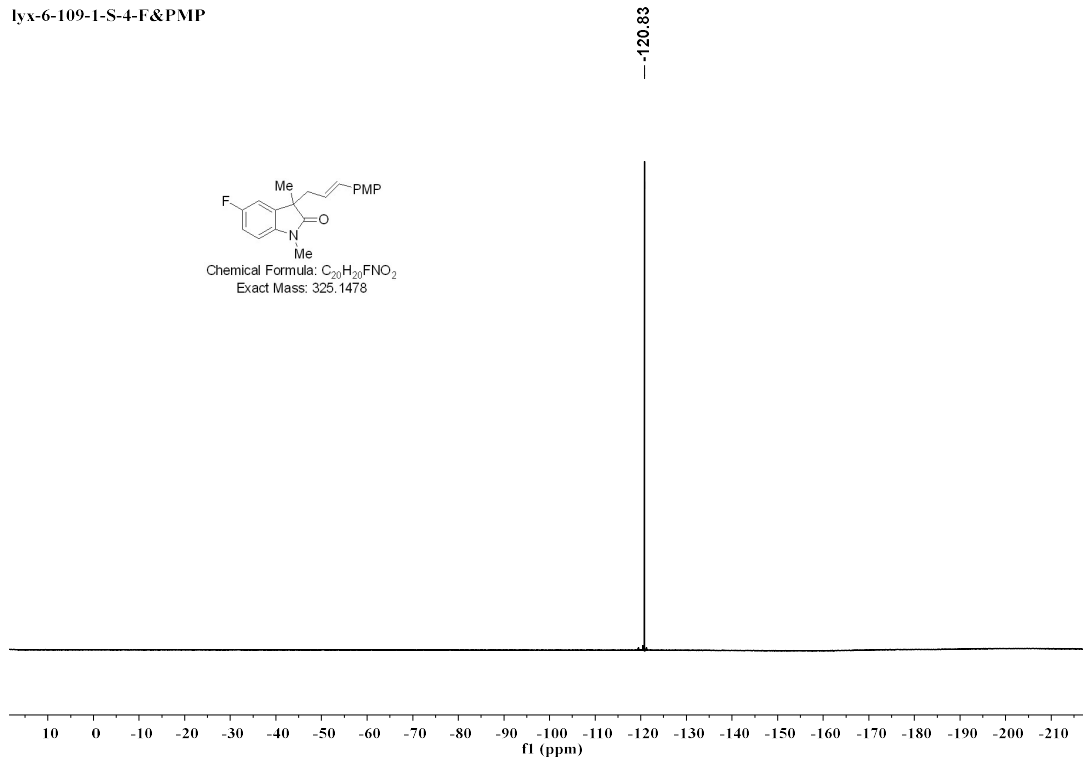
3ca



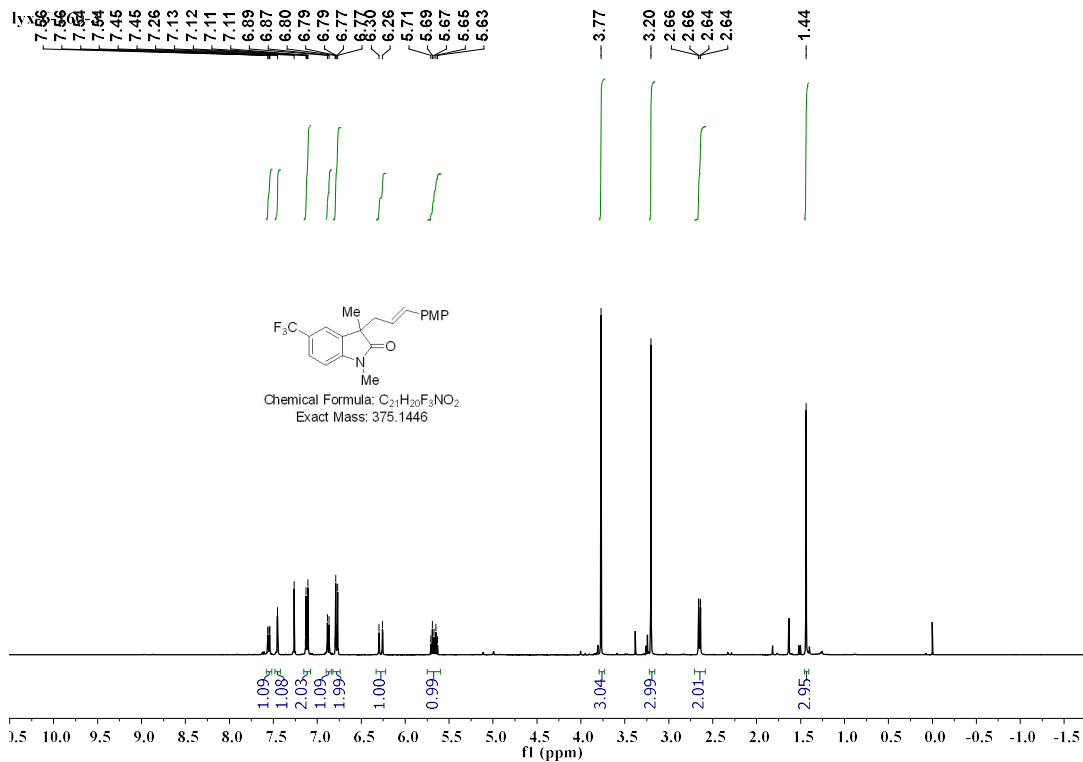
3da



lyx-6-109-1-S-4-F&PMP

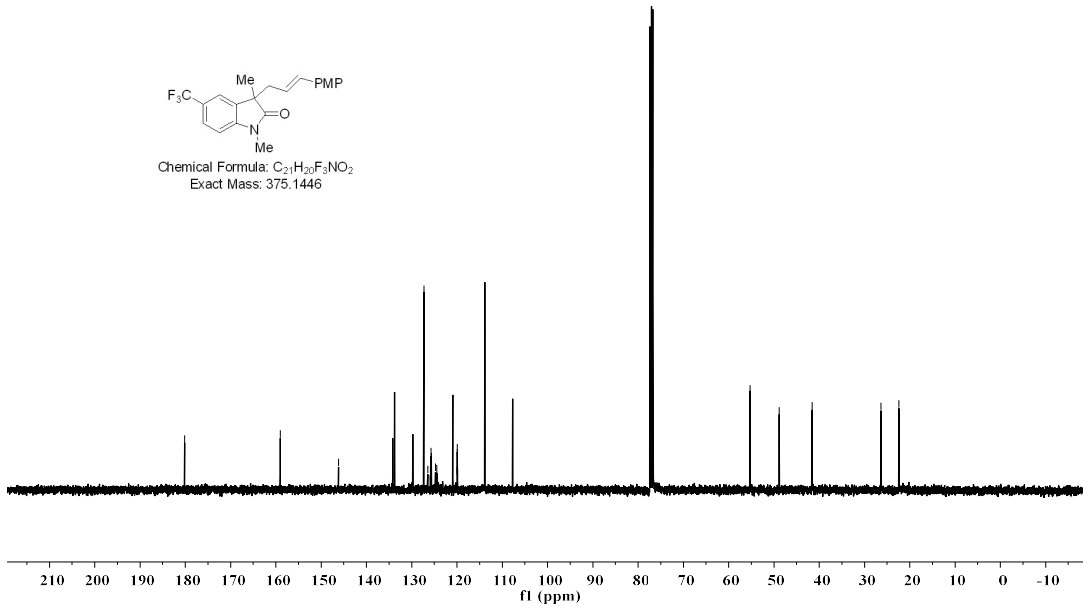
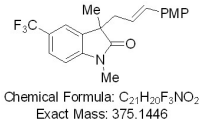


3ea



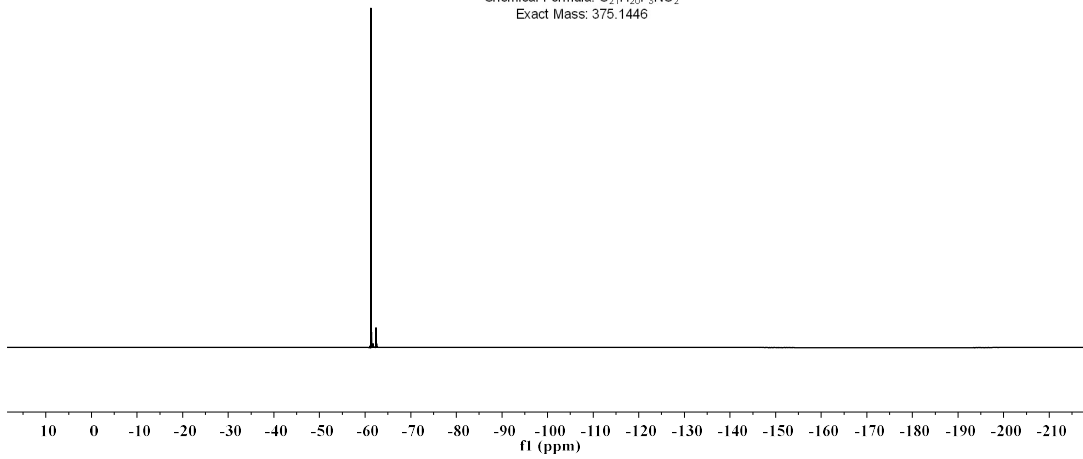
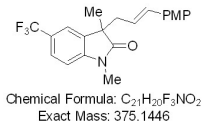
lyx-6-160-3

180.16
159.03
146.15
127.32
126.42
125.85
125.75
125.71
125.67
125.63
124.75
124.43
120.00
119.96
119.93
119.89
56.27
48.84
41.58
26.38
22.42

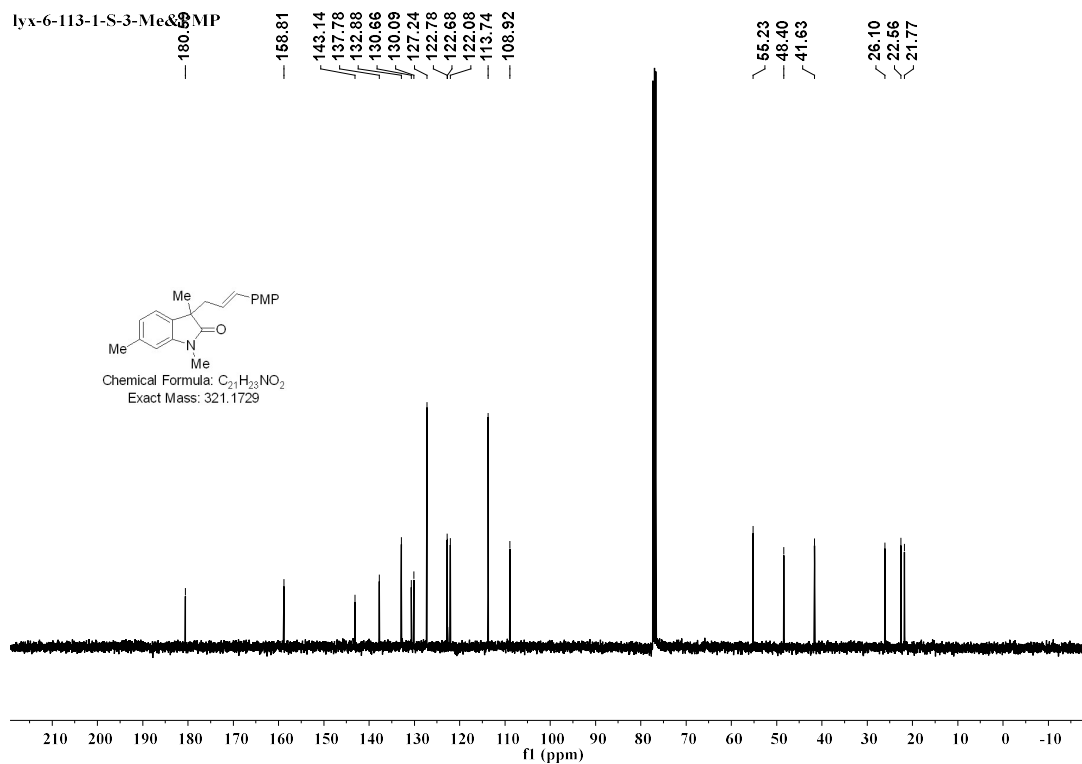
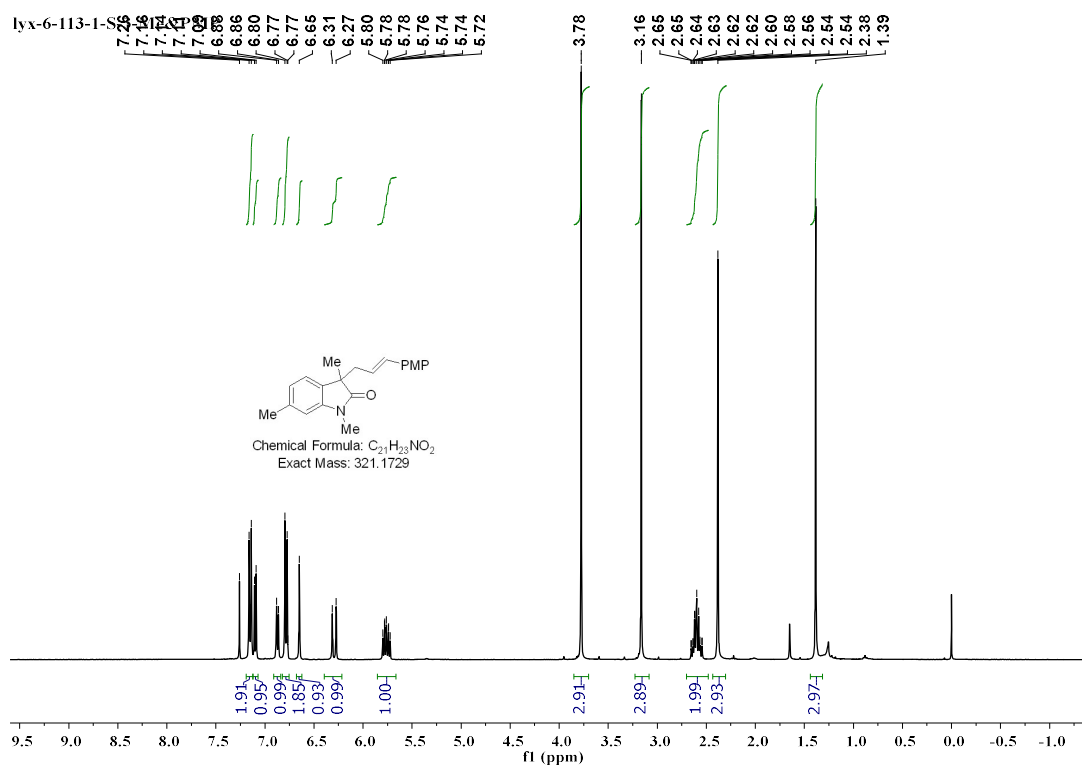


lyx-6-160-3

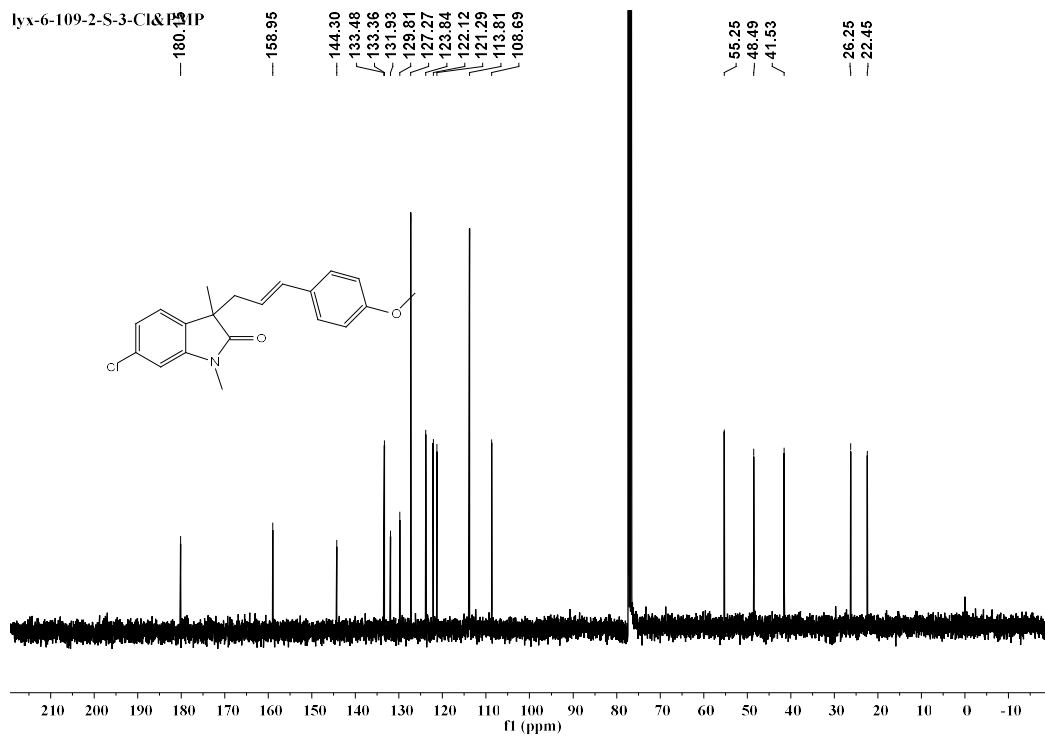
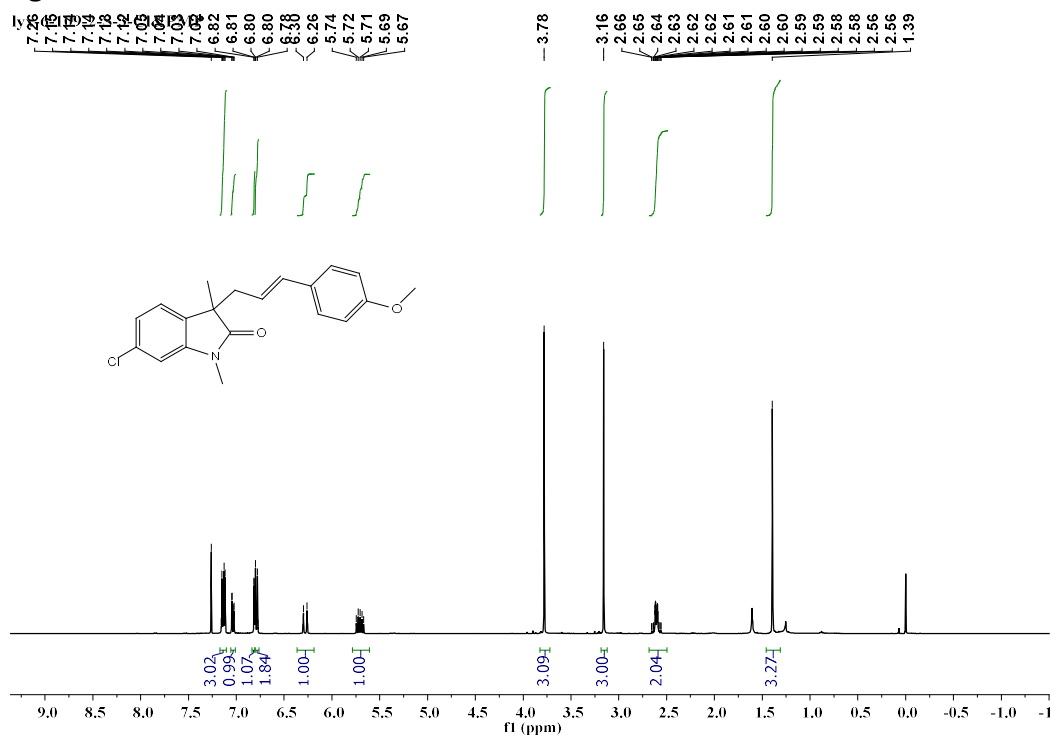
-61.27



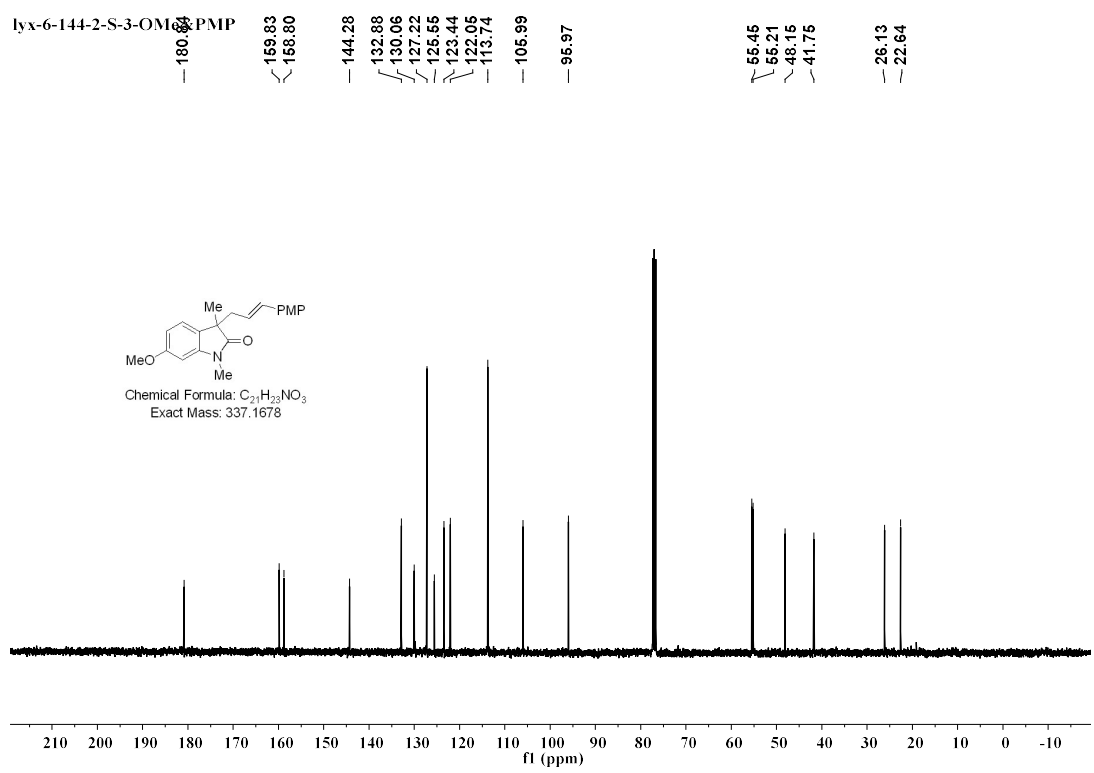
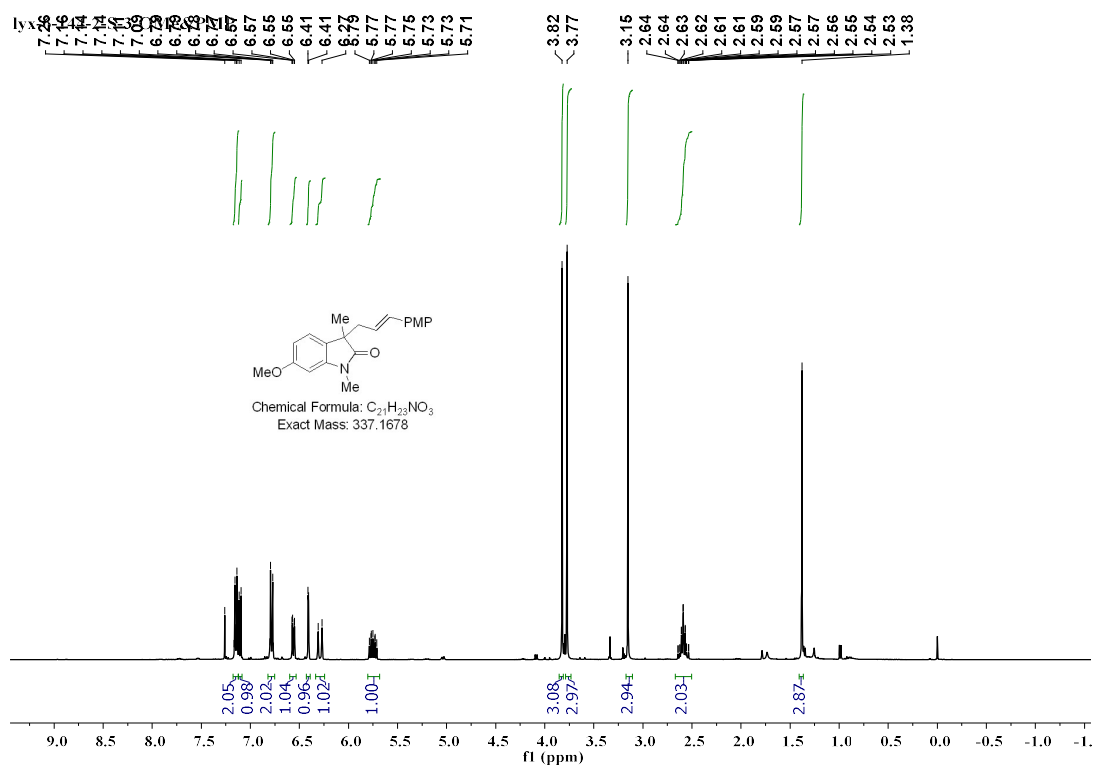
3fa



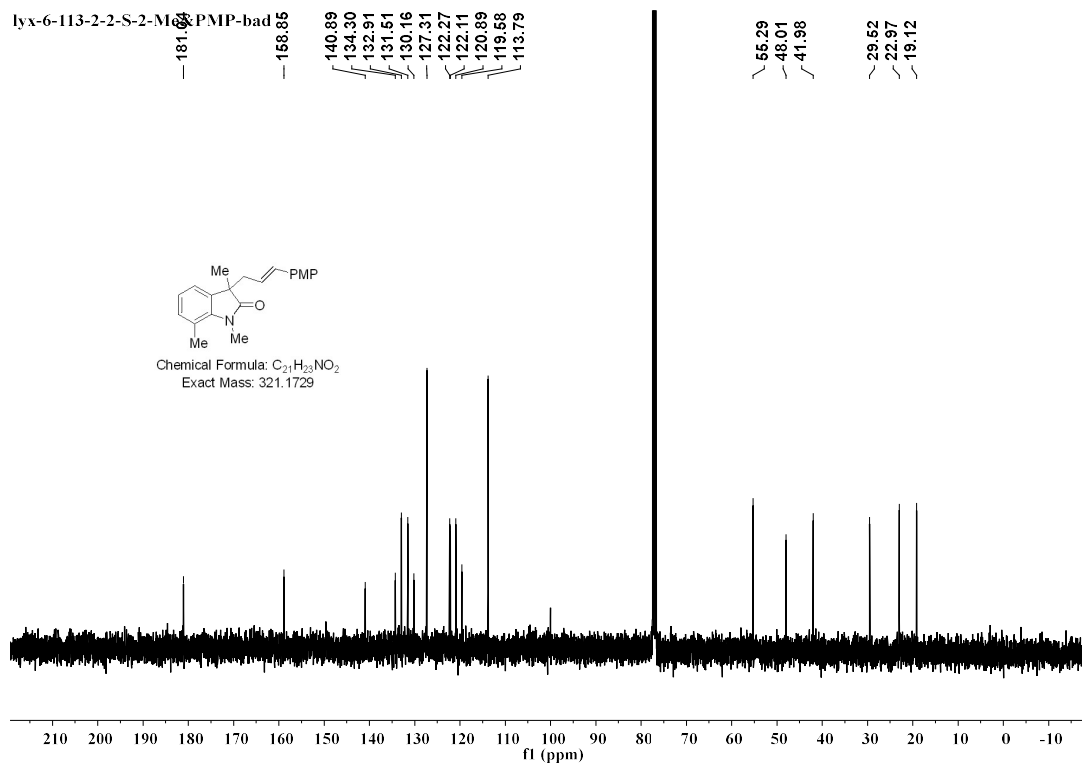
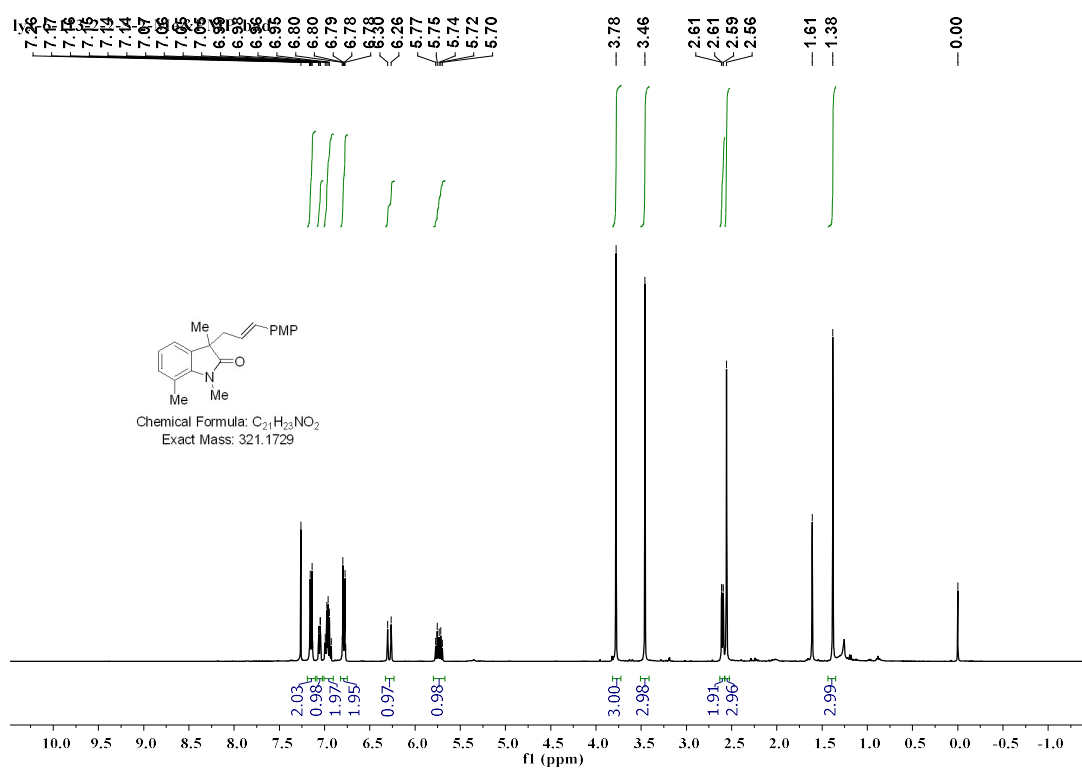
3ga



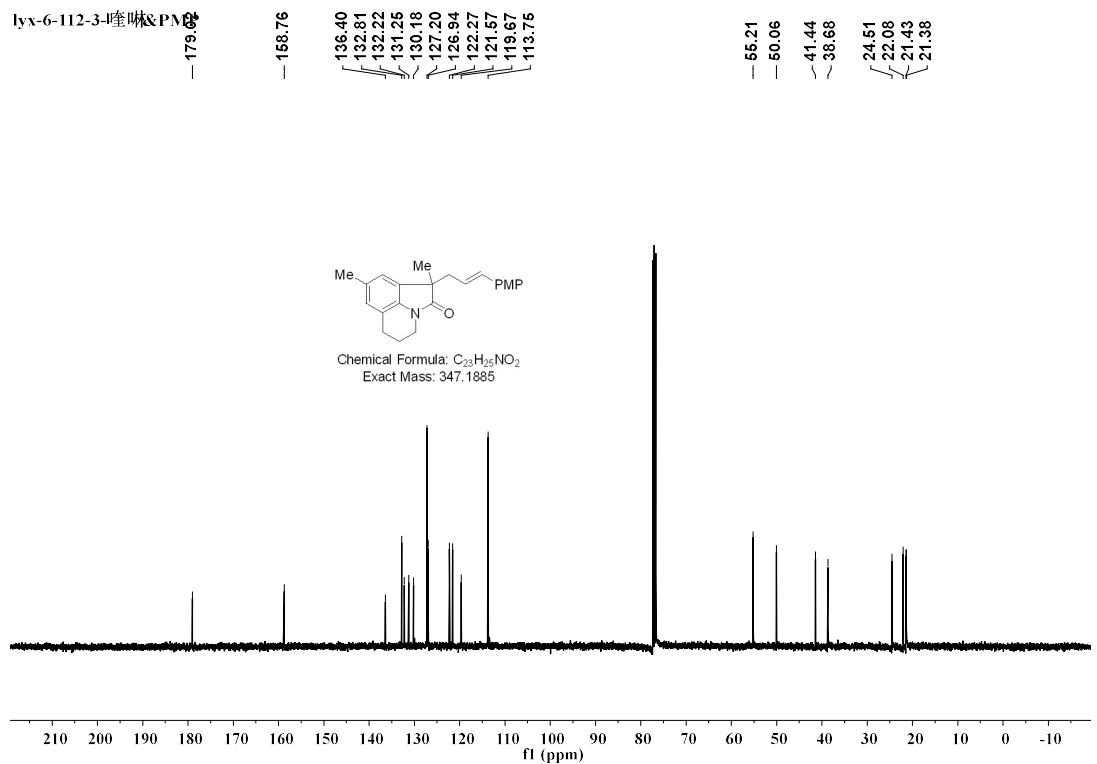
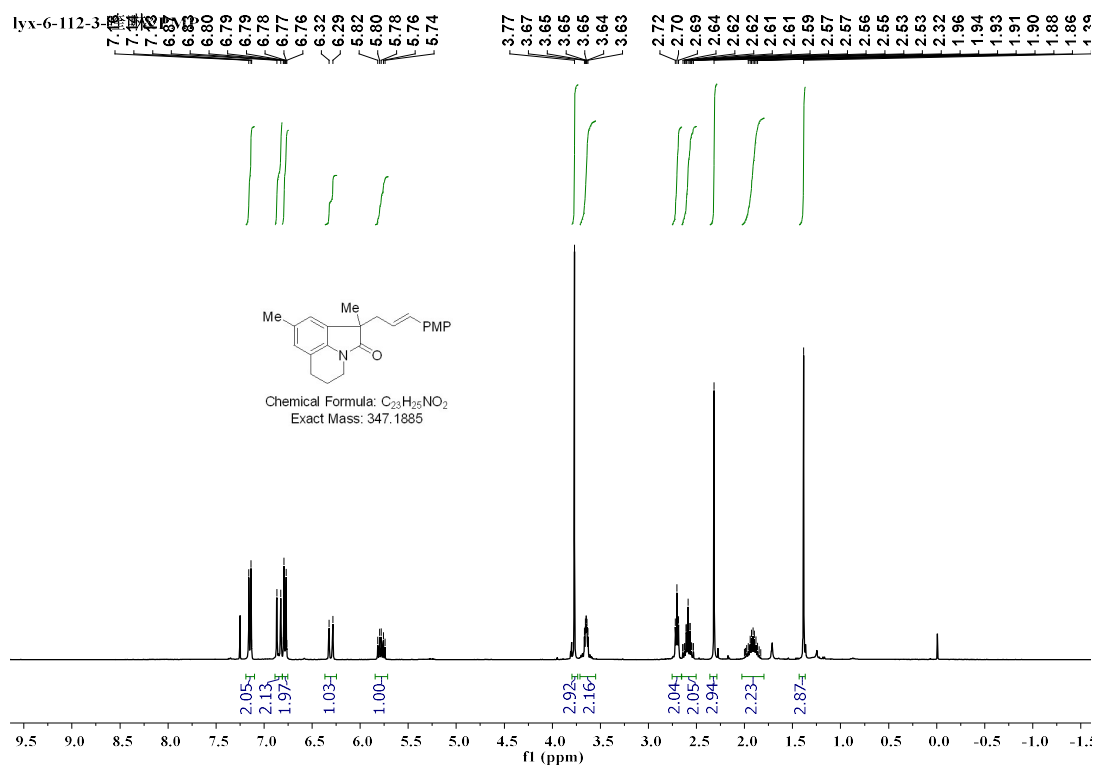
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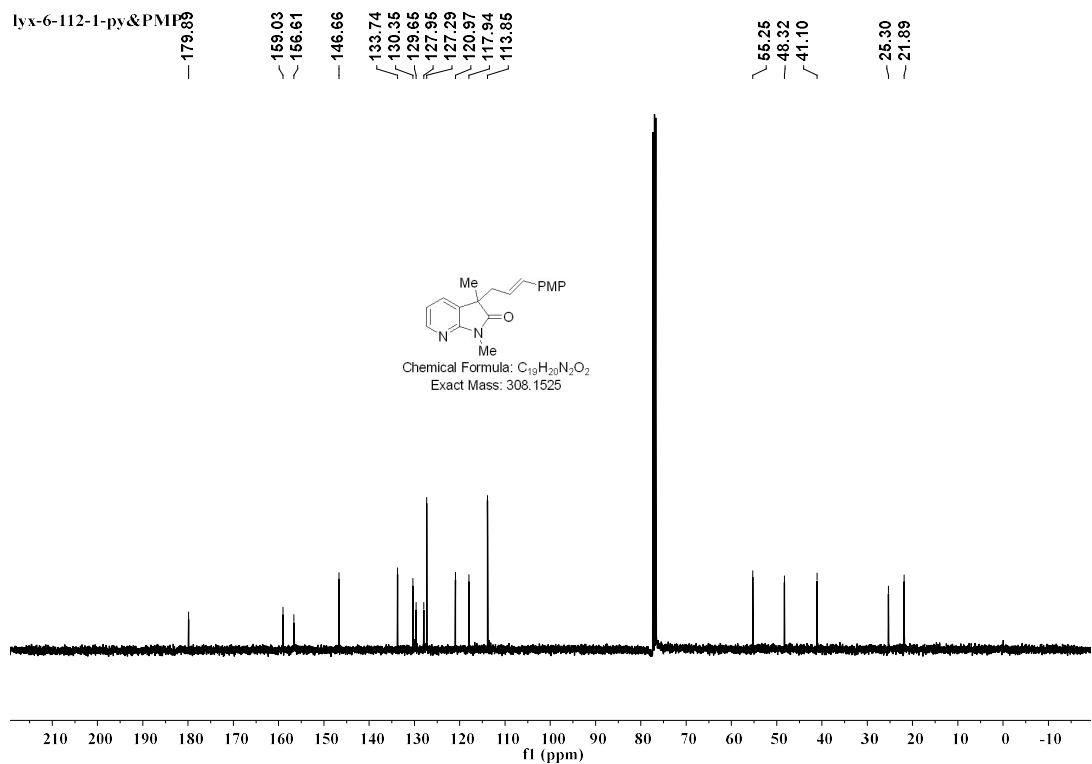
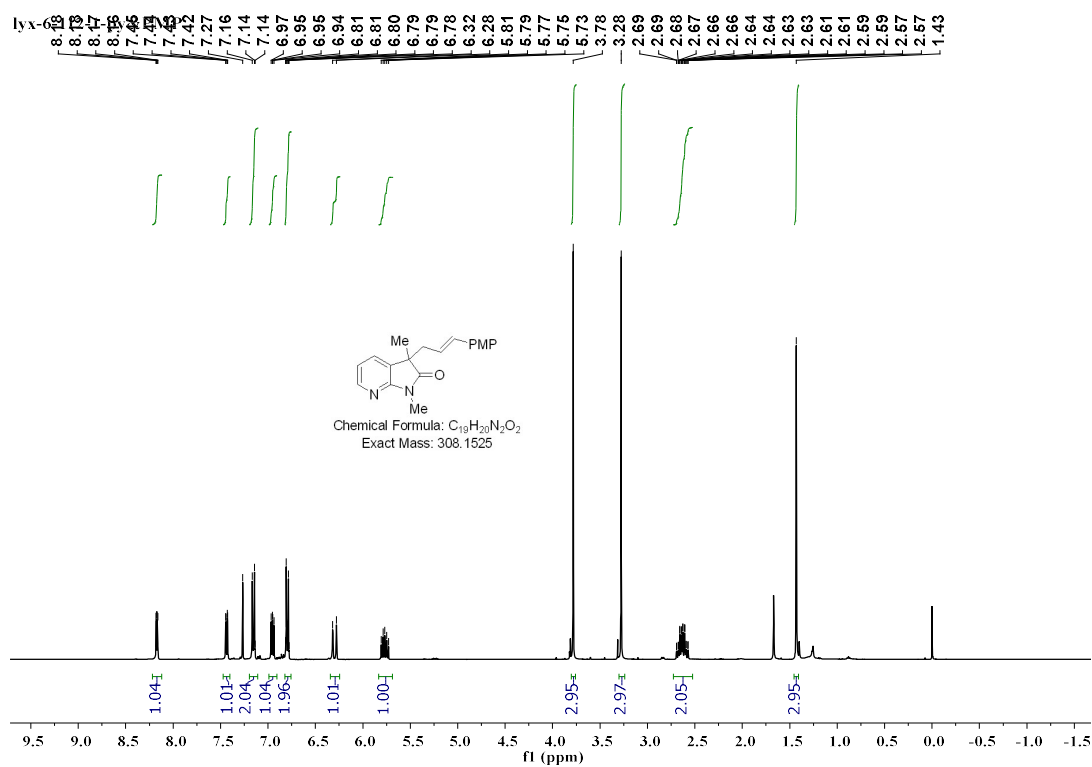
3ia



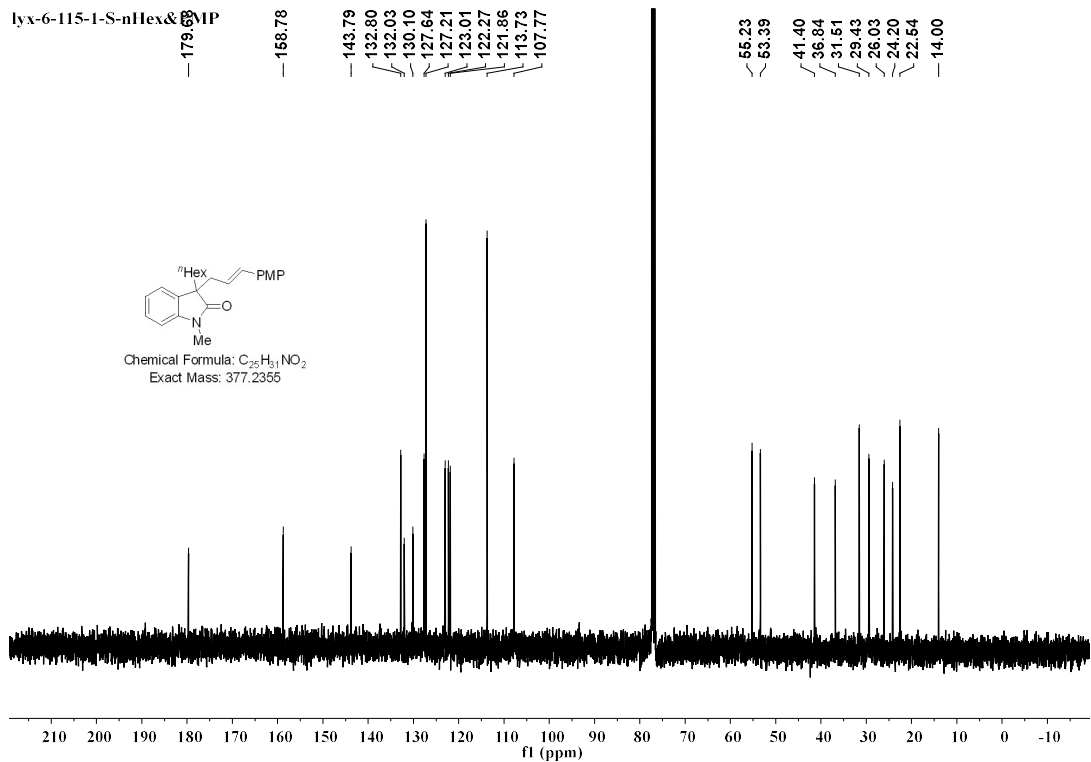
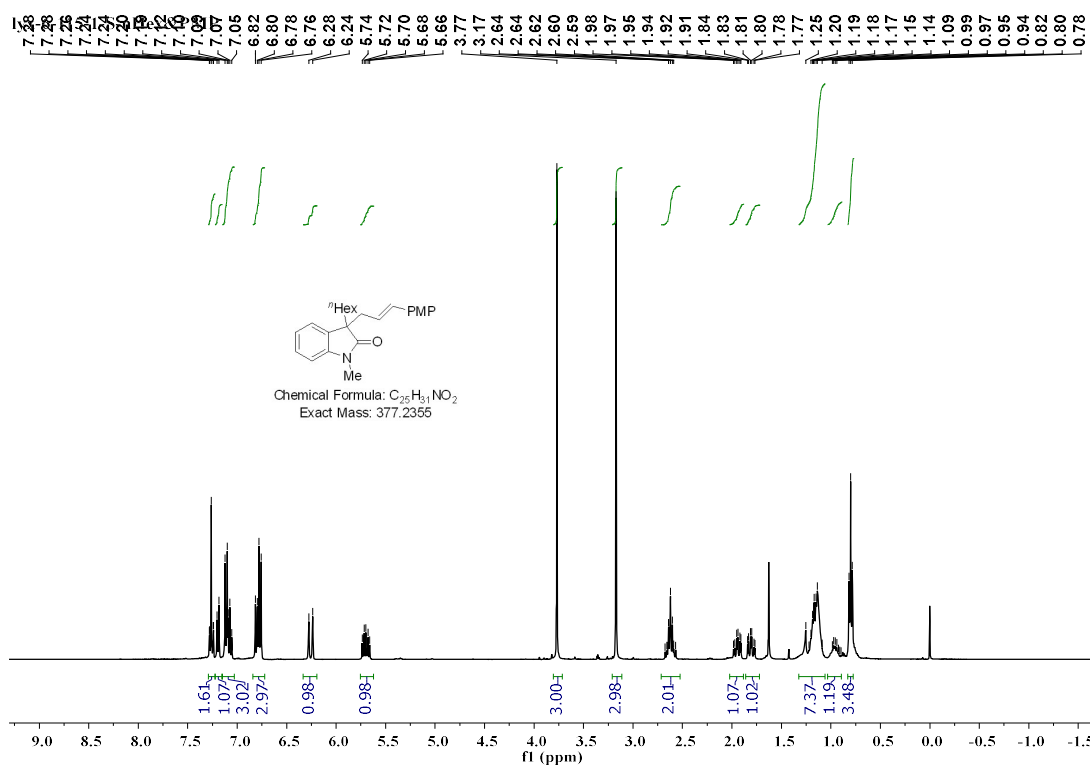
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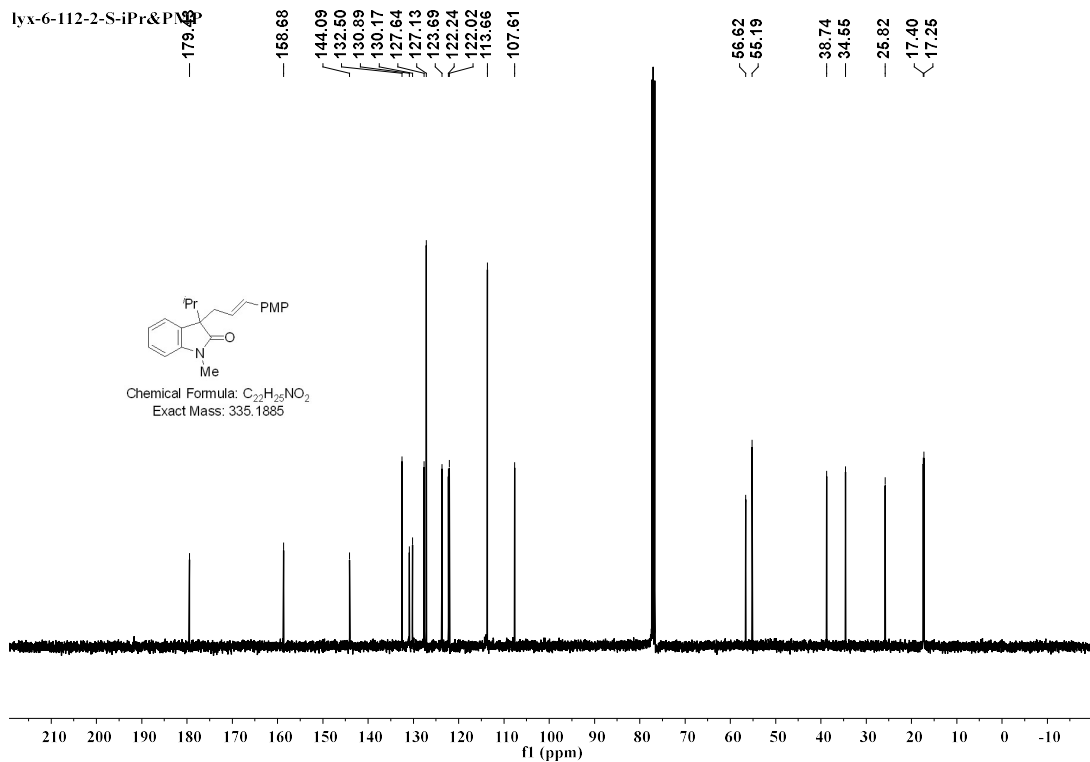
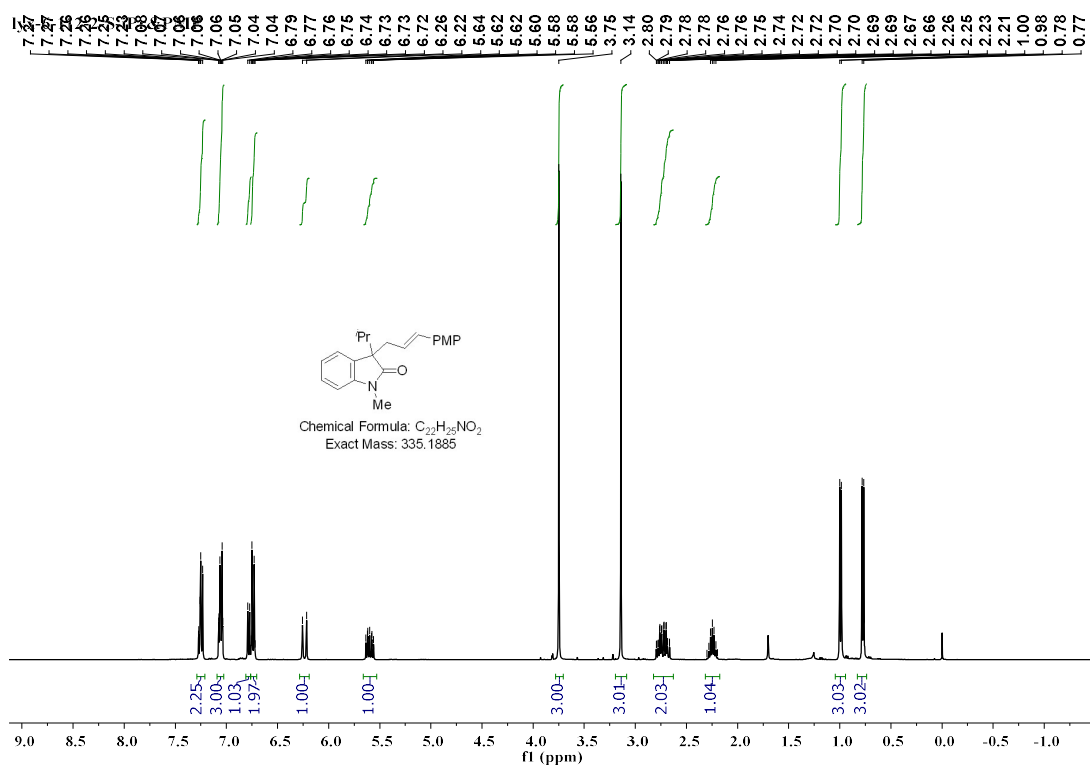
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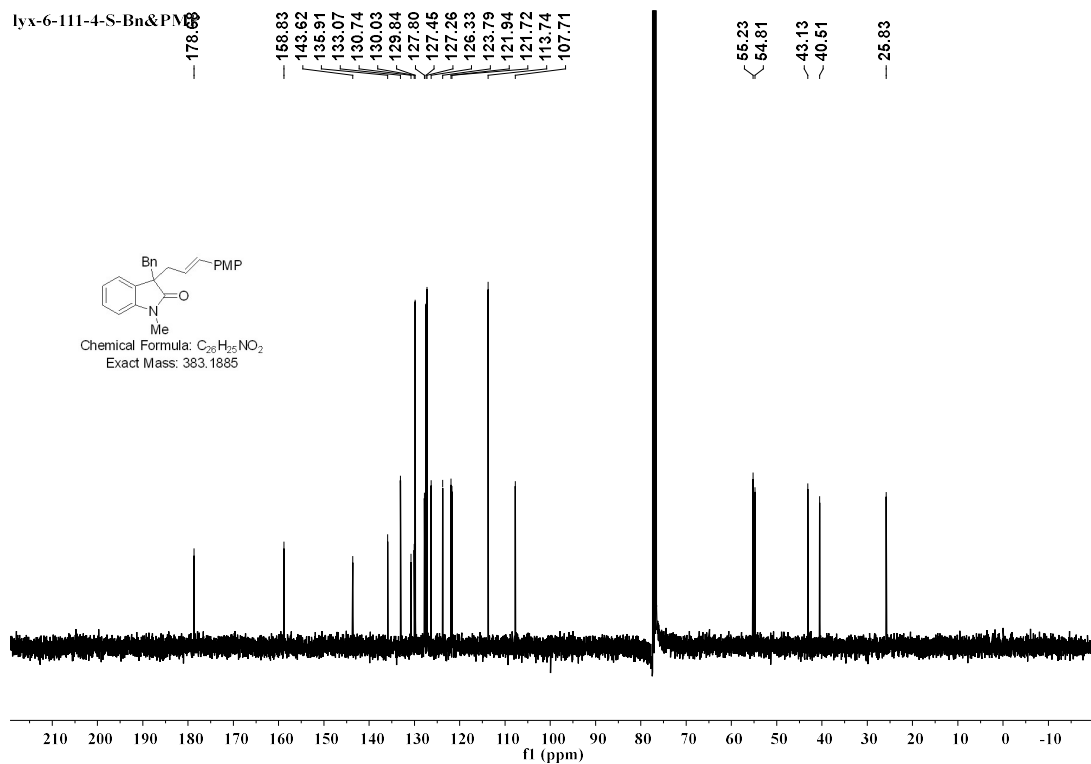
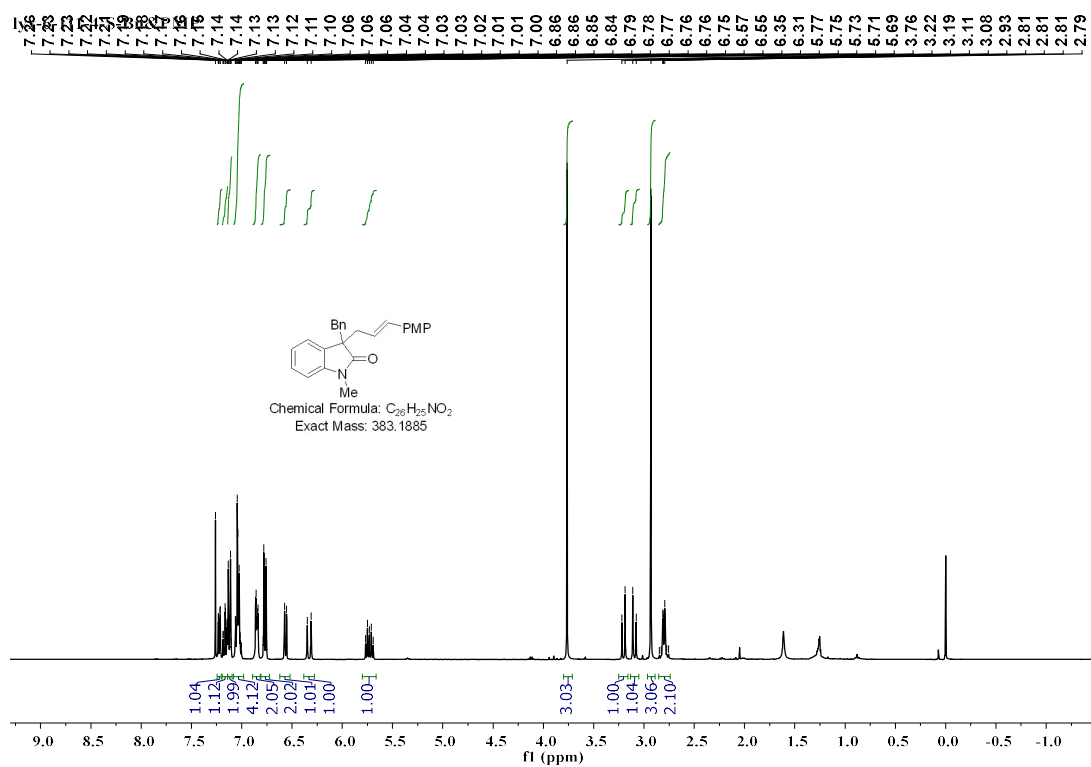
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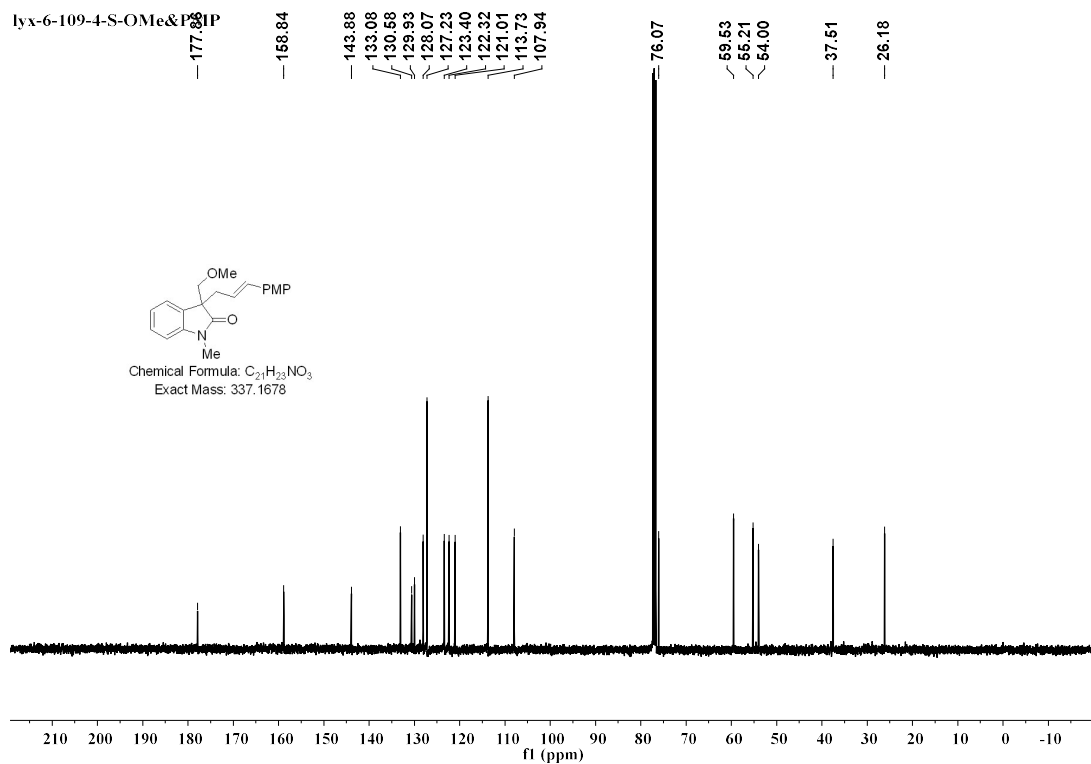
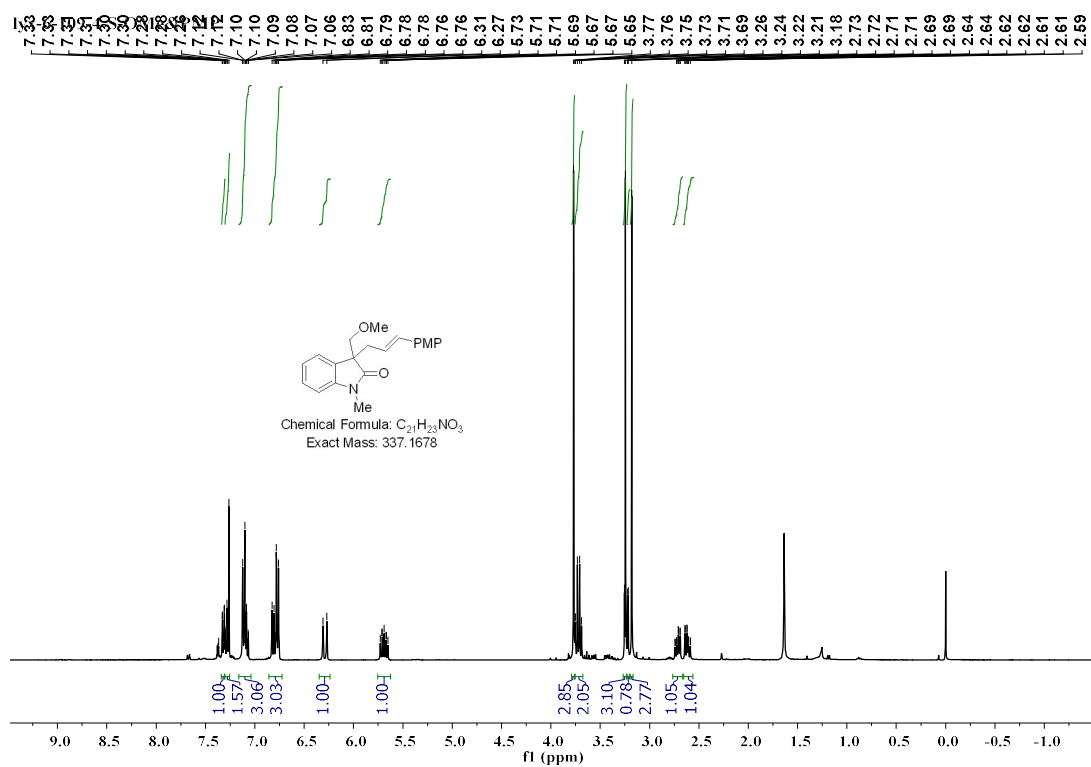
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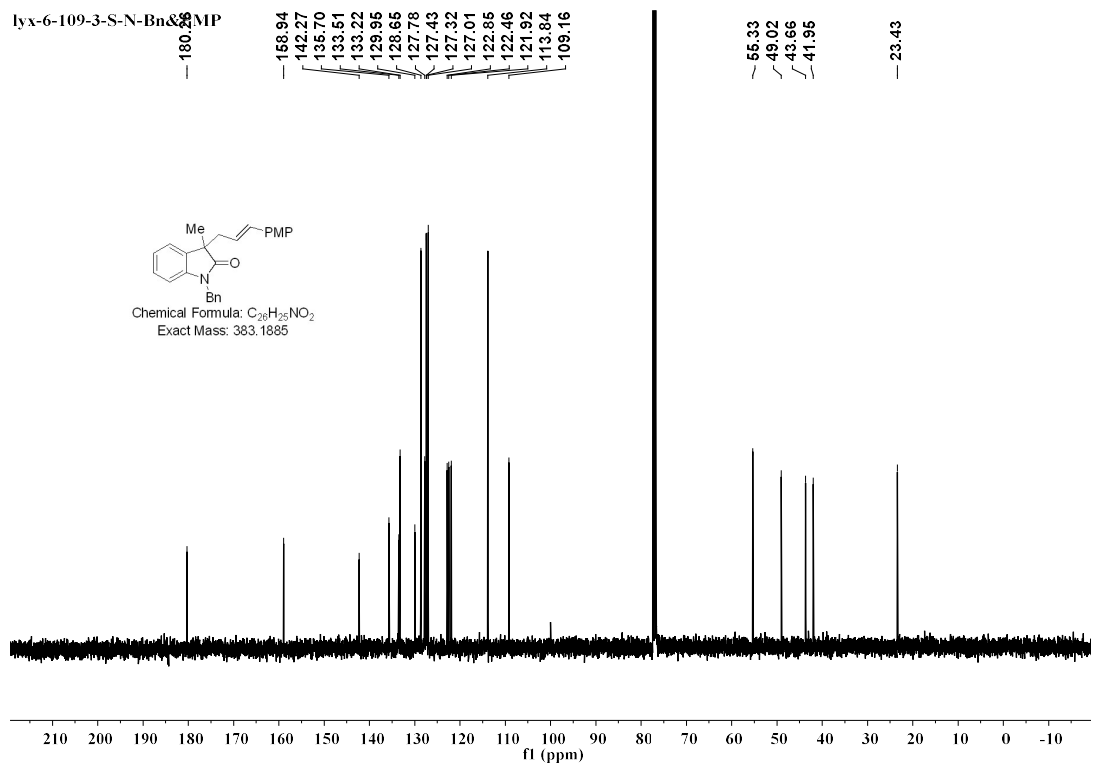
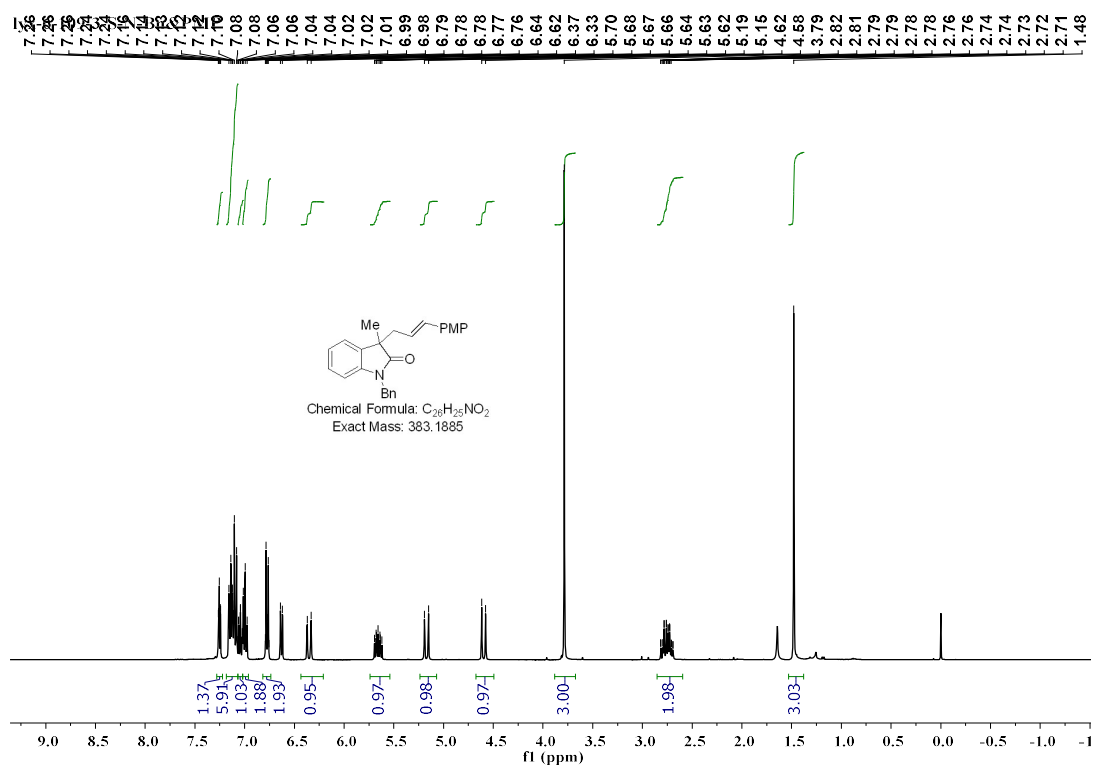
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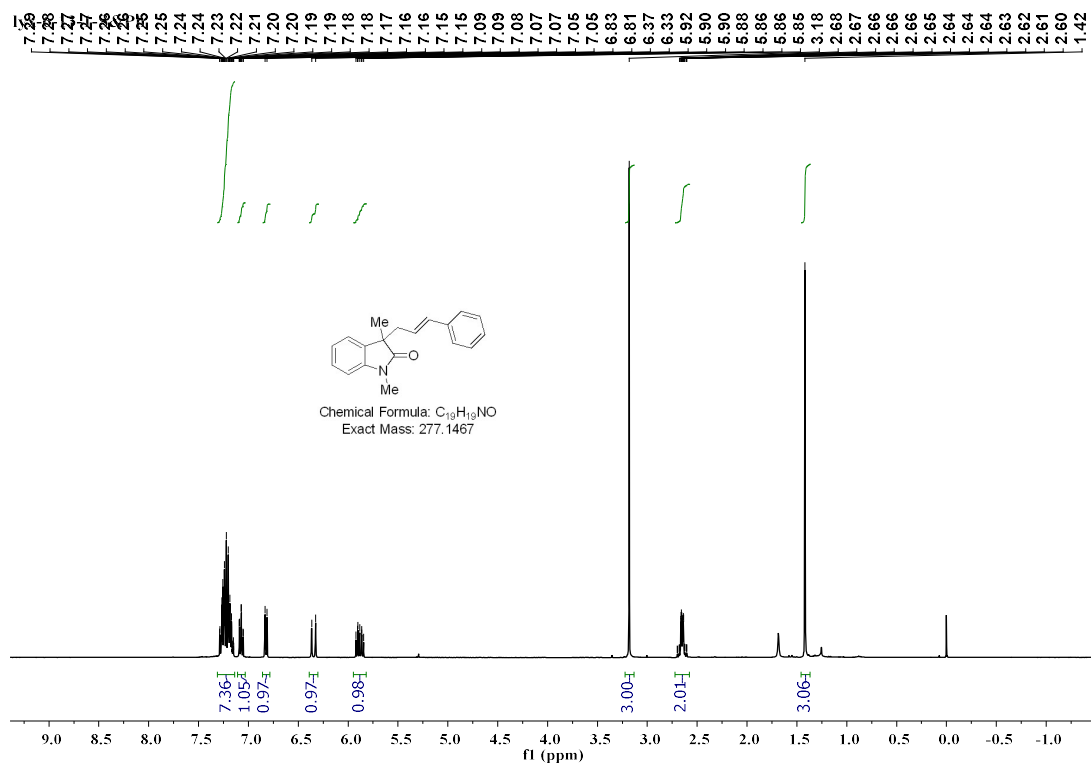
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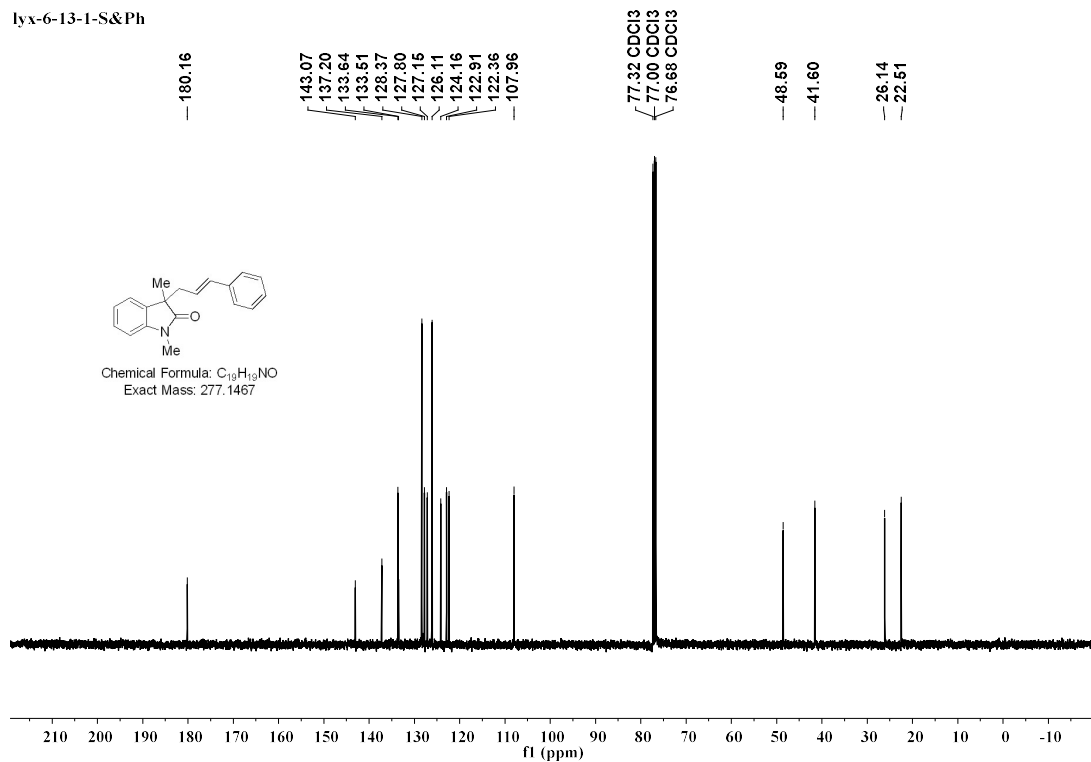
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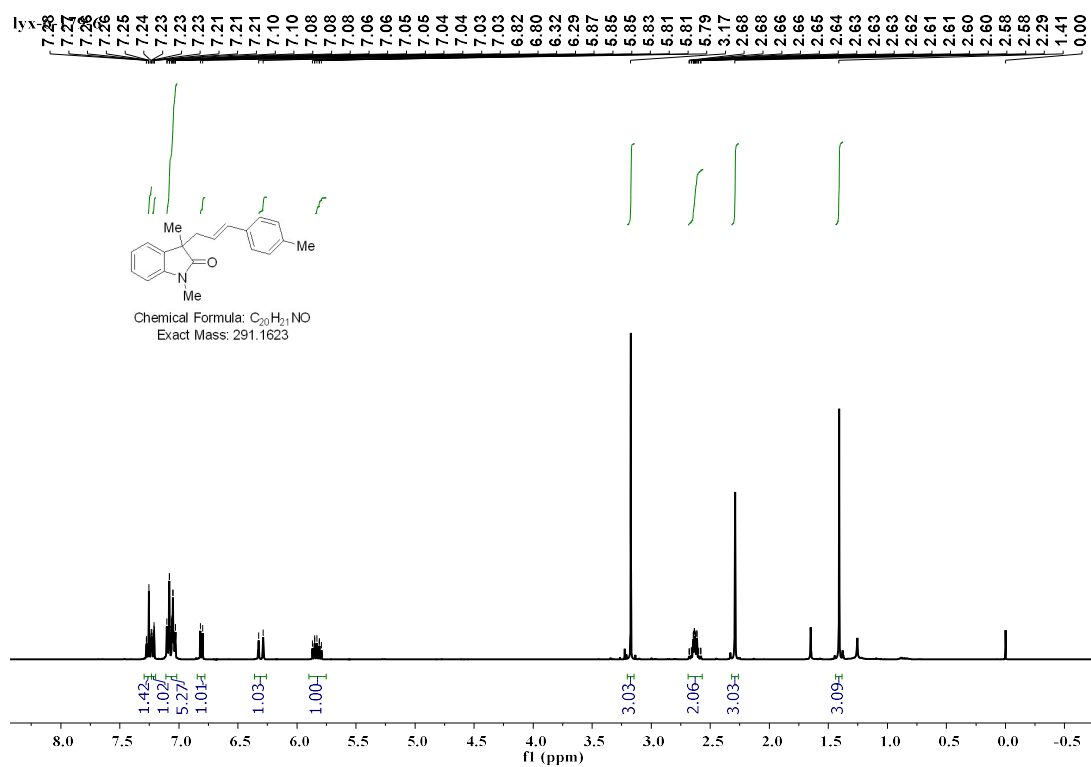
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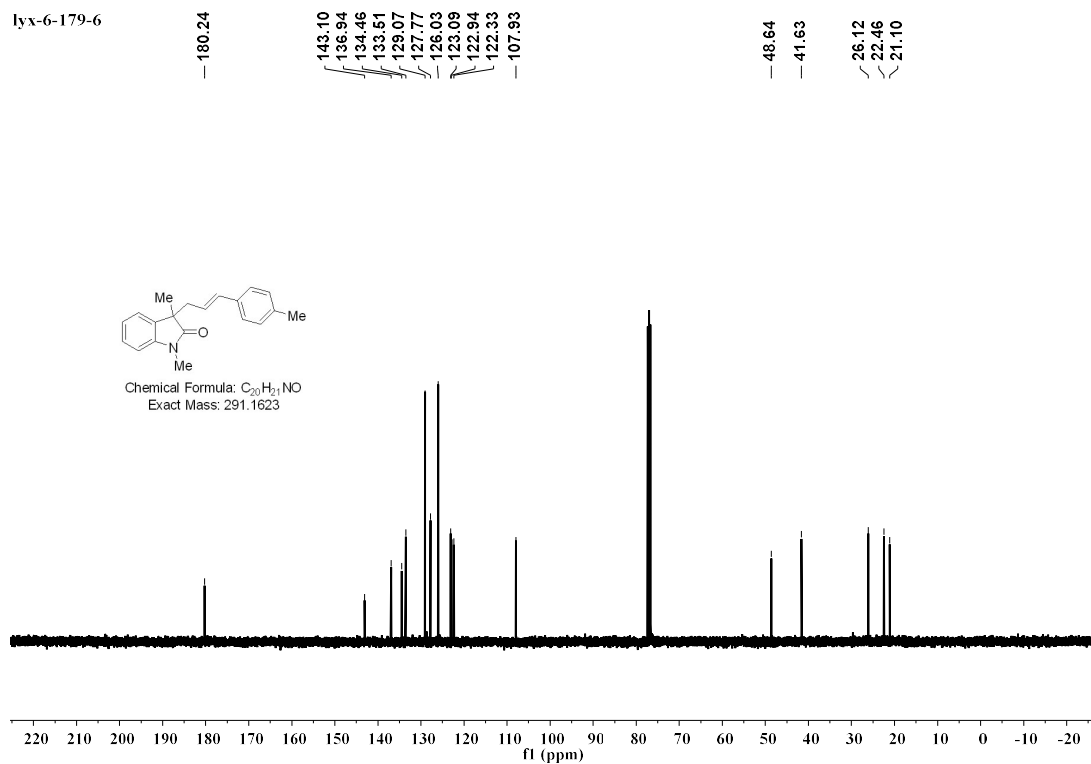
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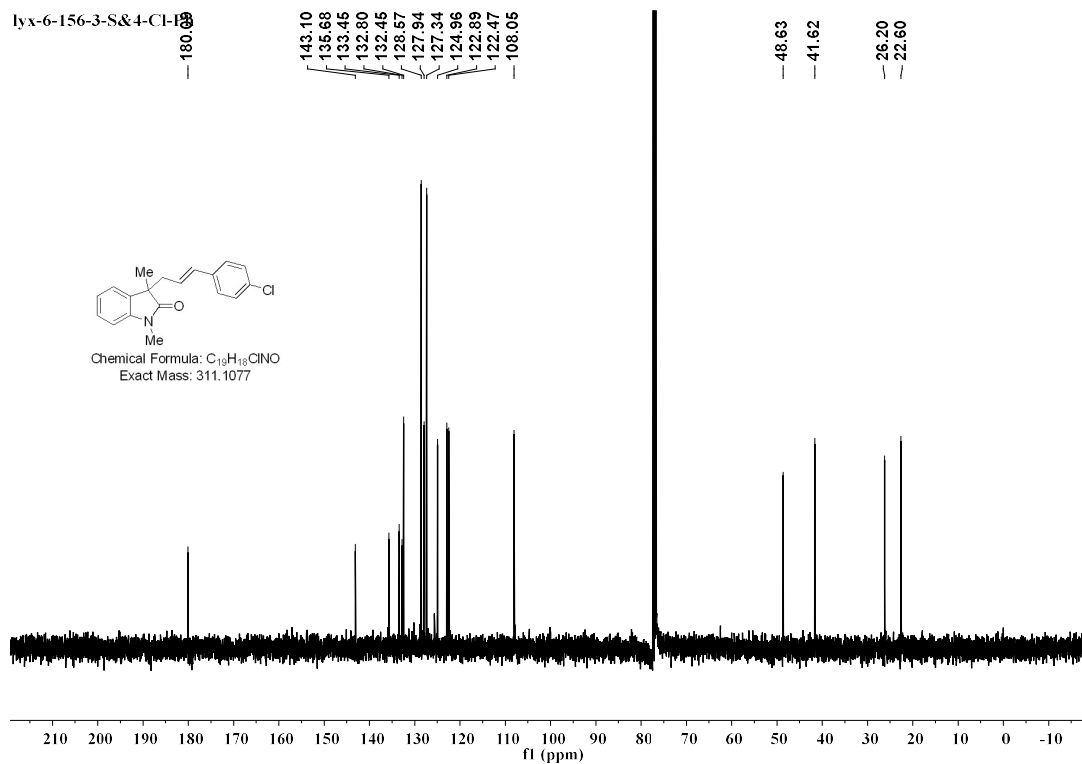
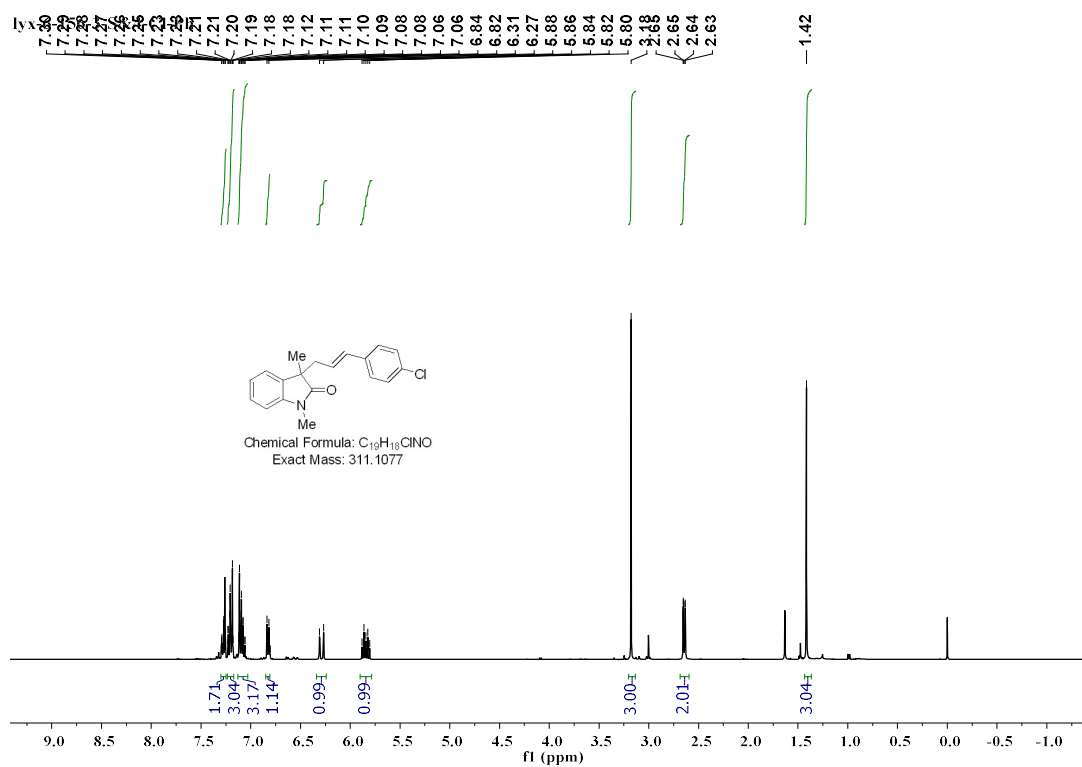
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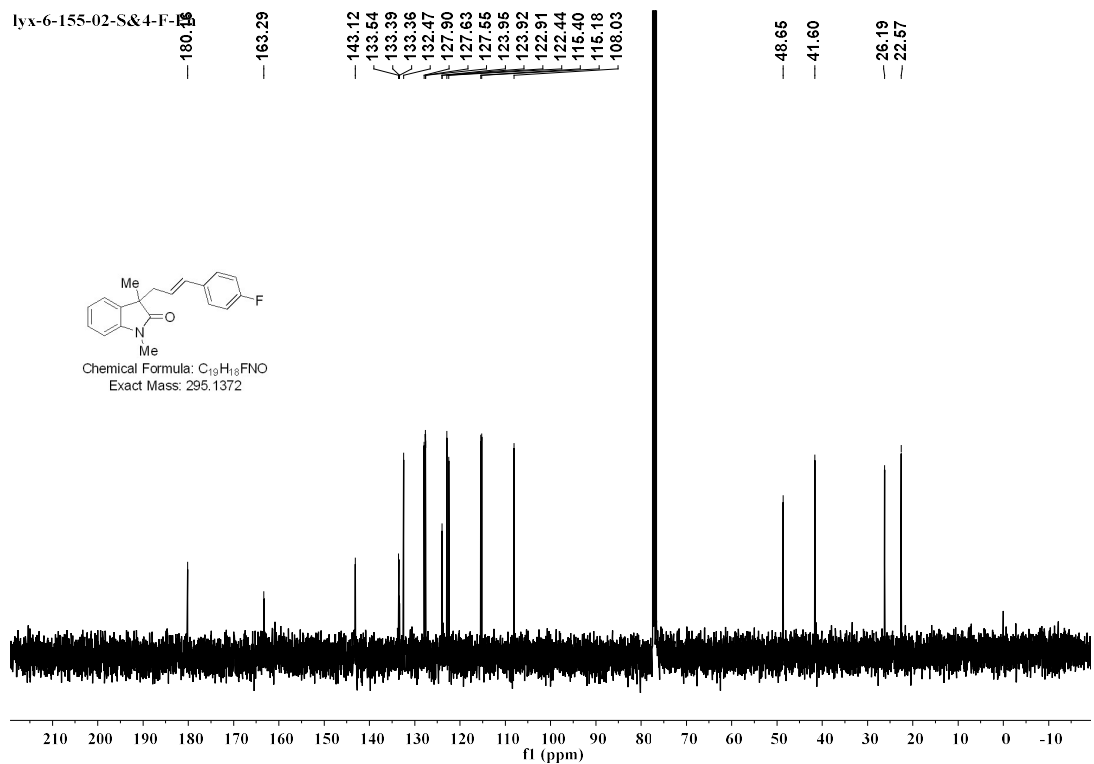
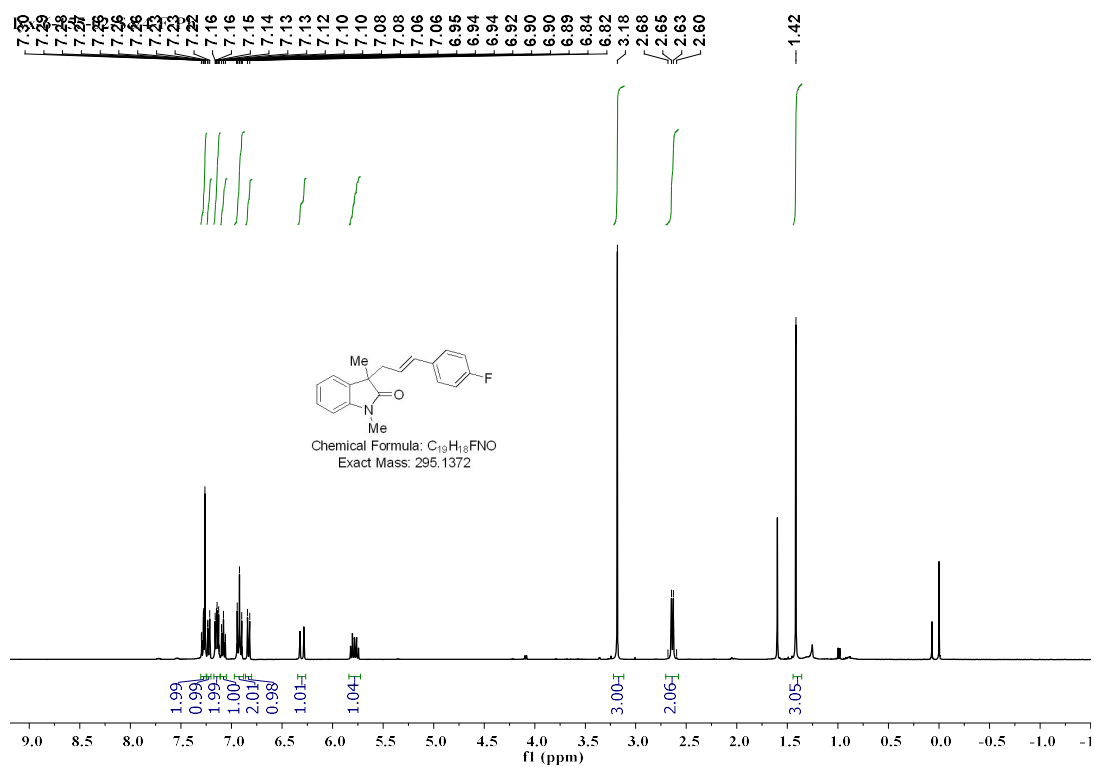
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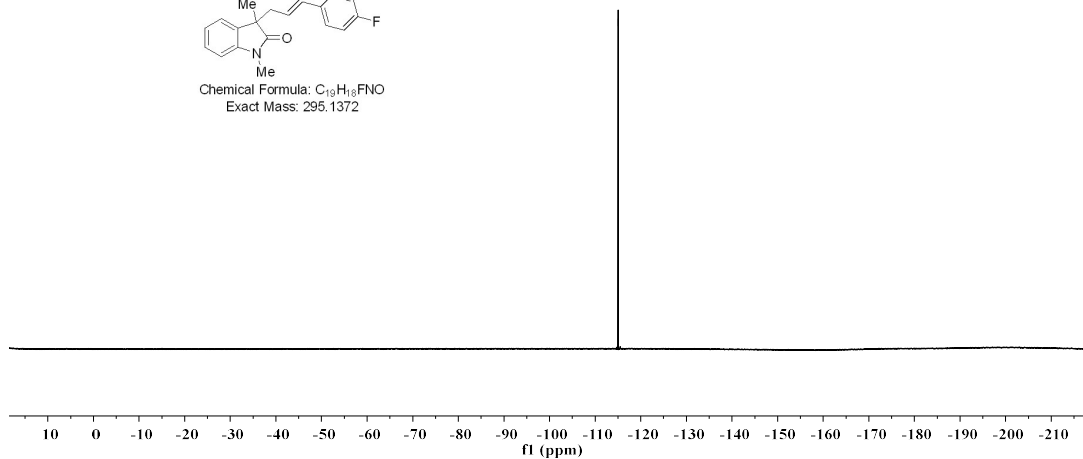
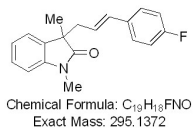


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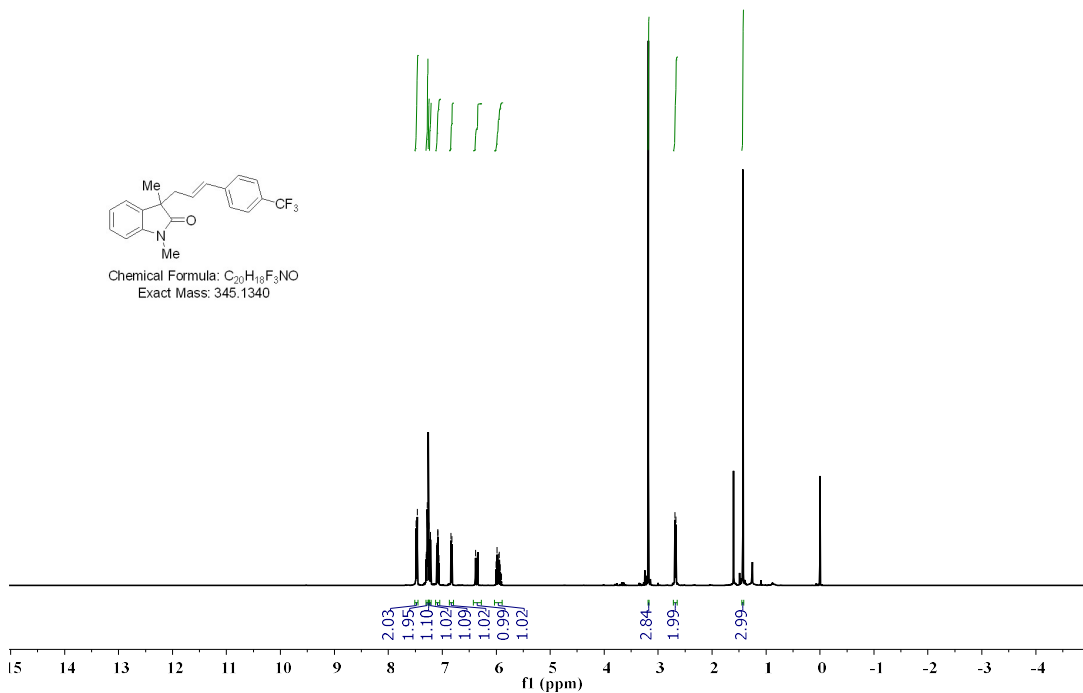
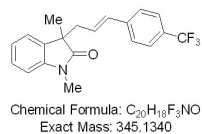
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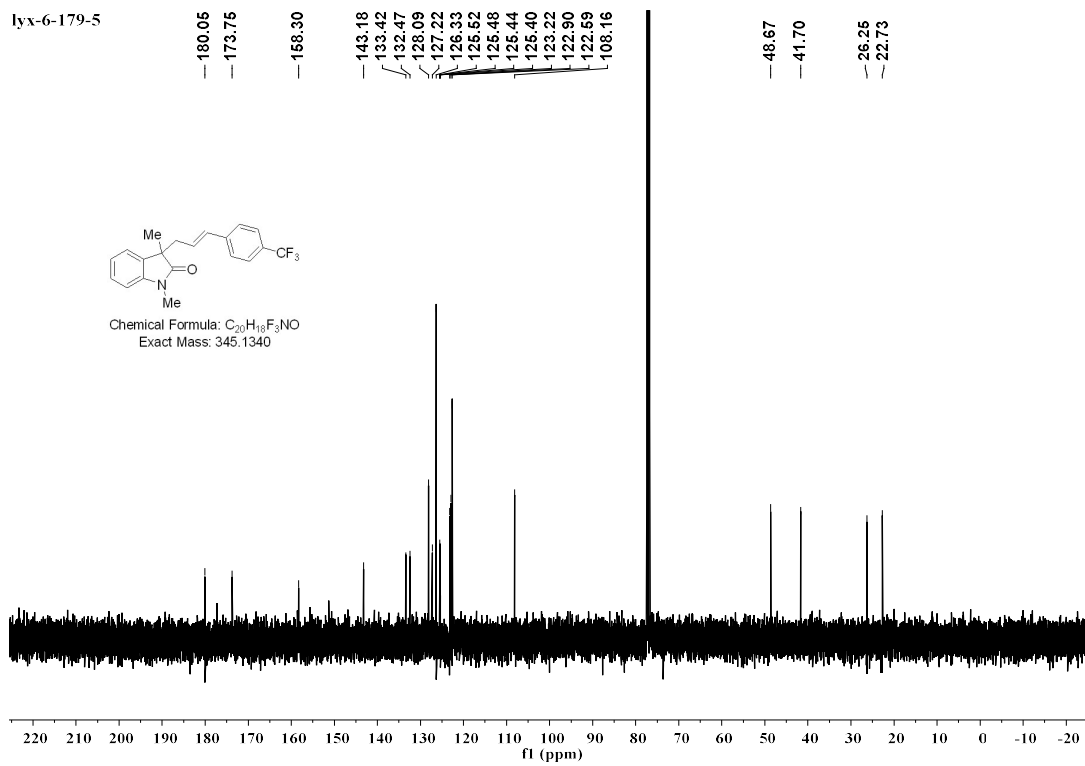
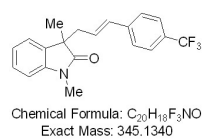


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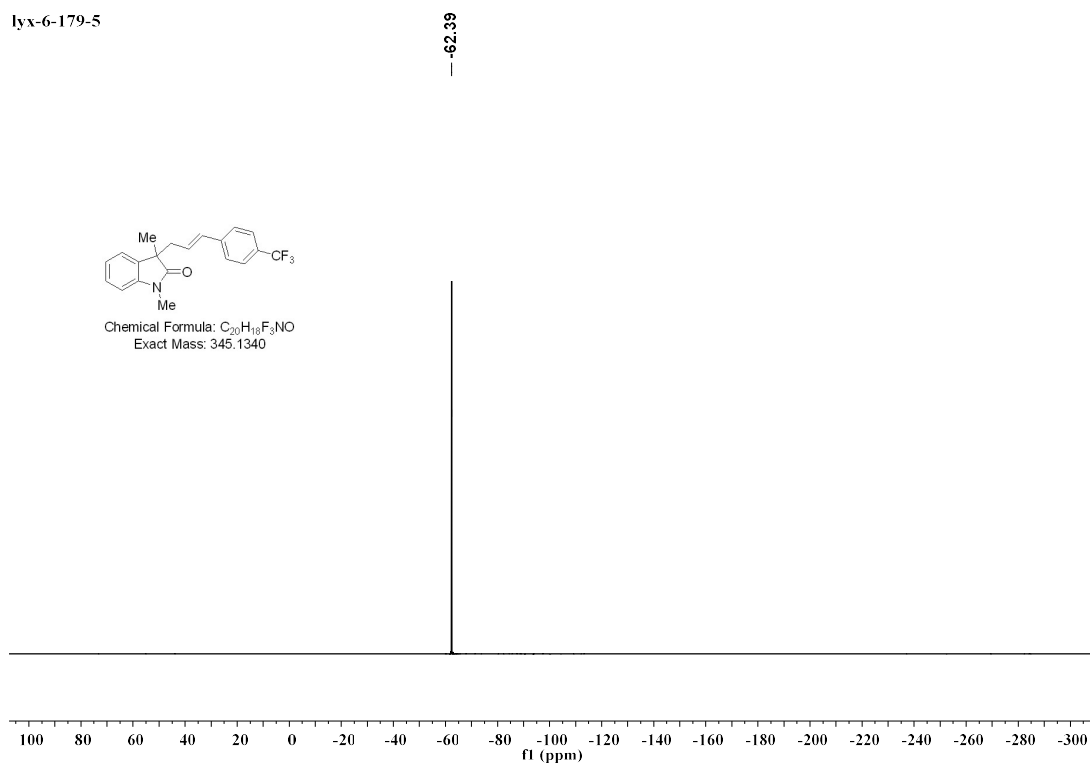
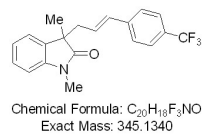
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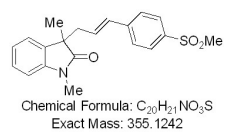
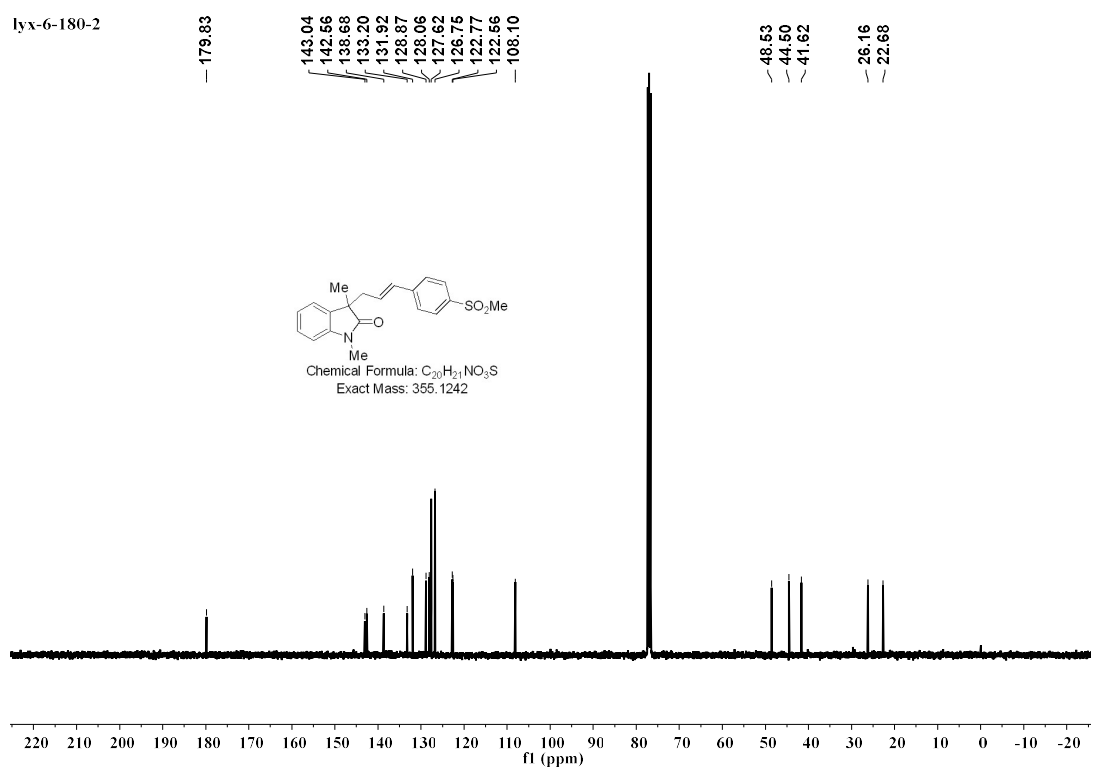
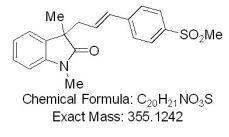
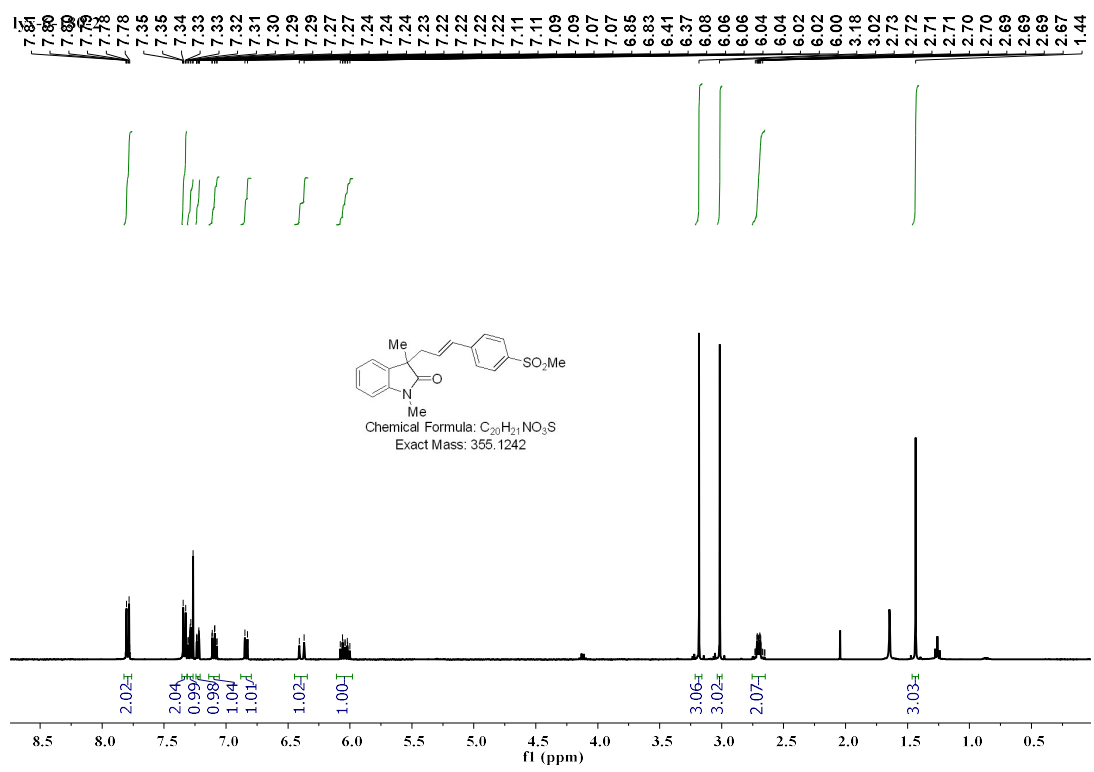
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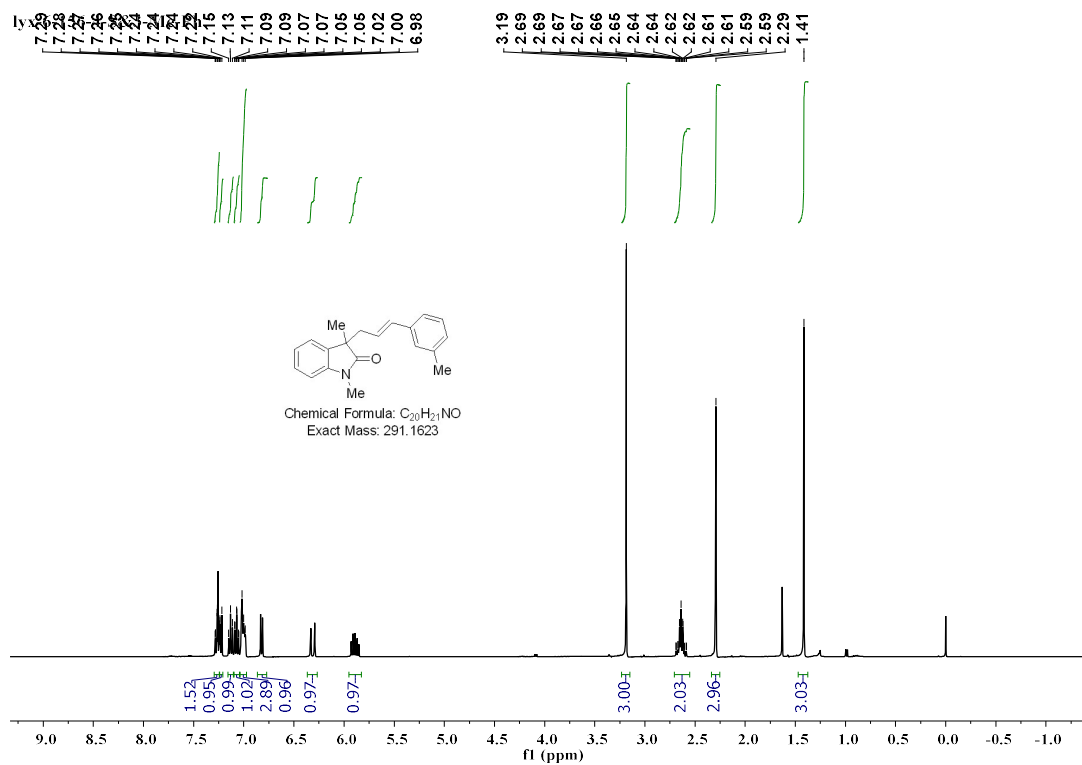
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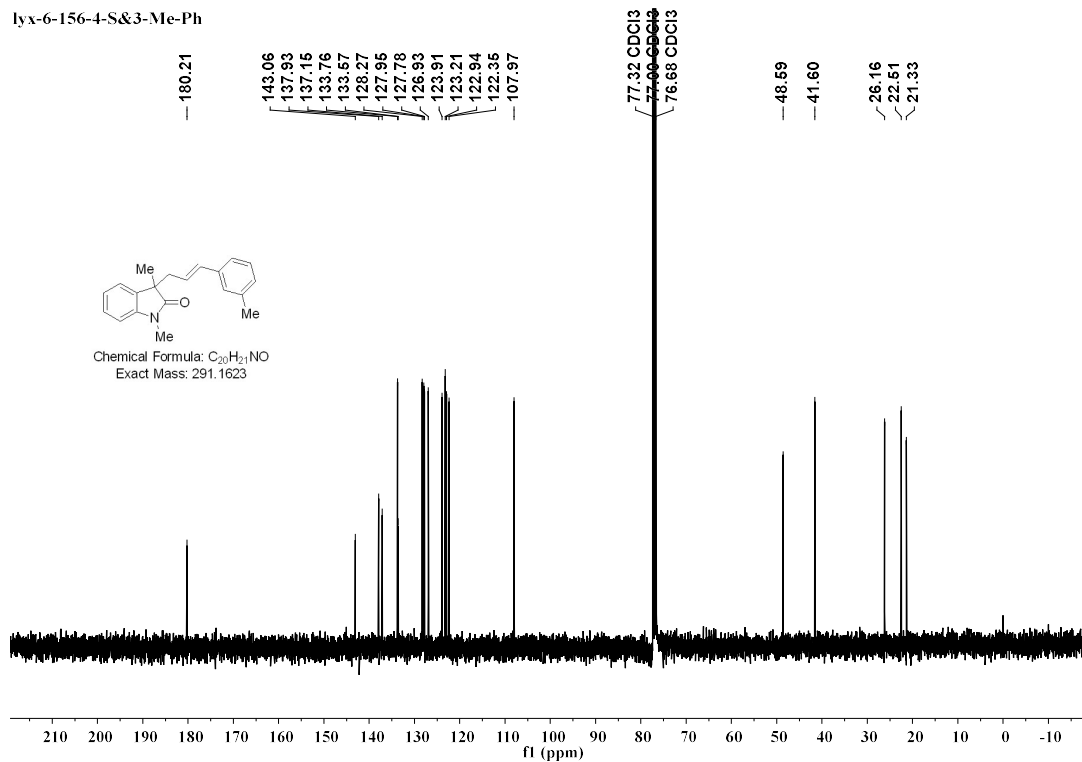
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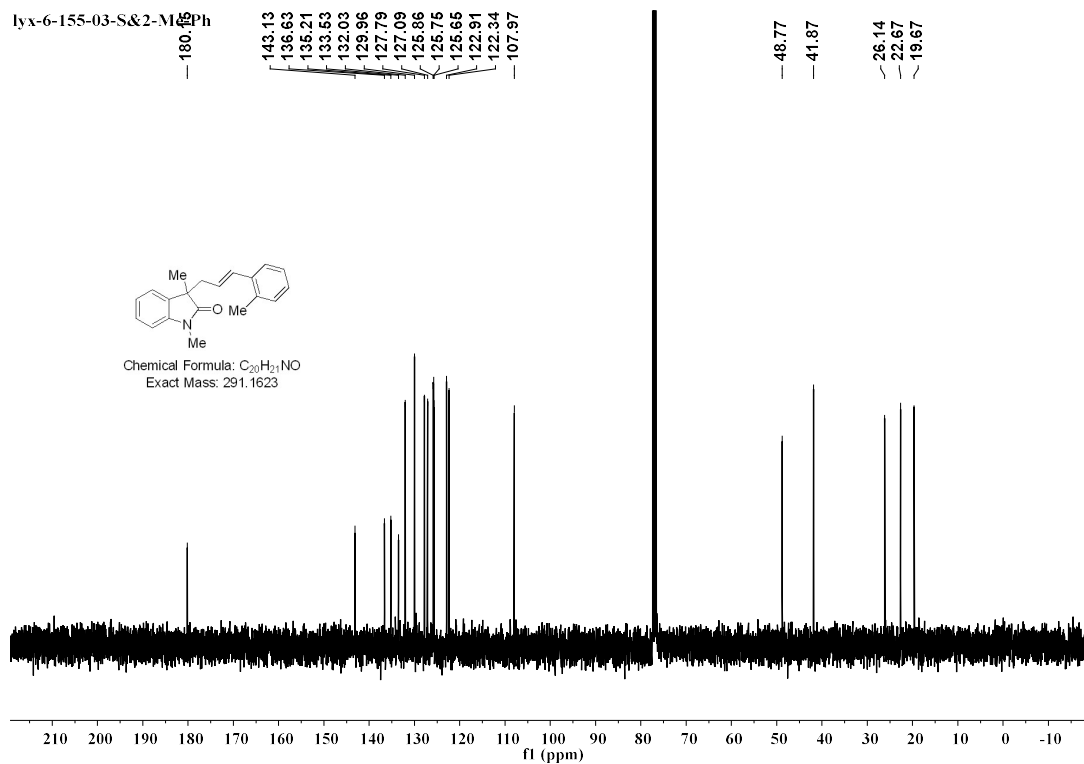
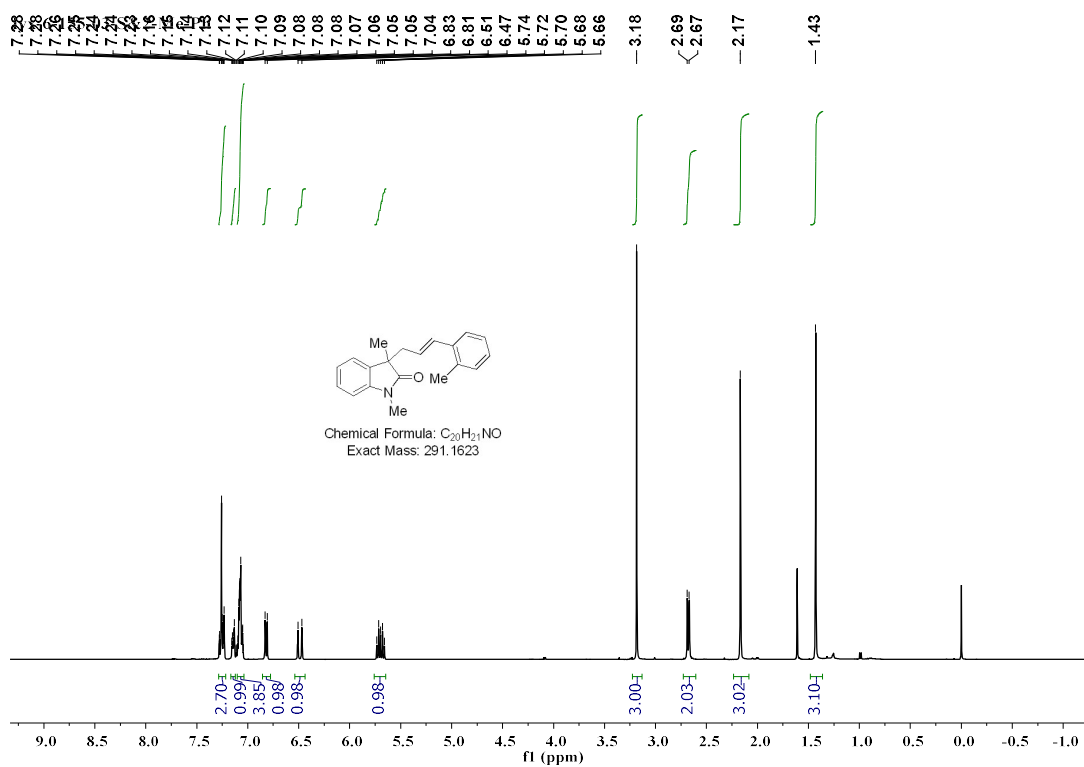
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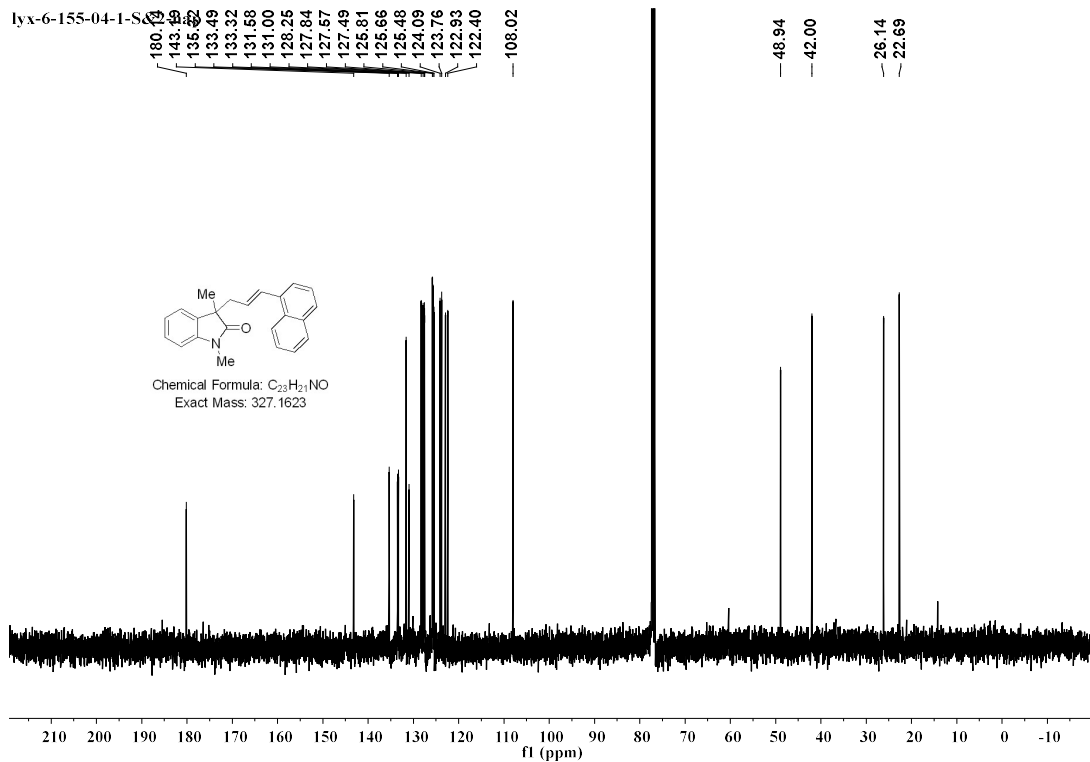
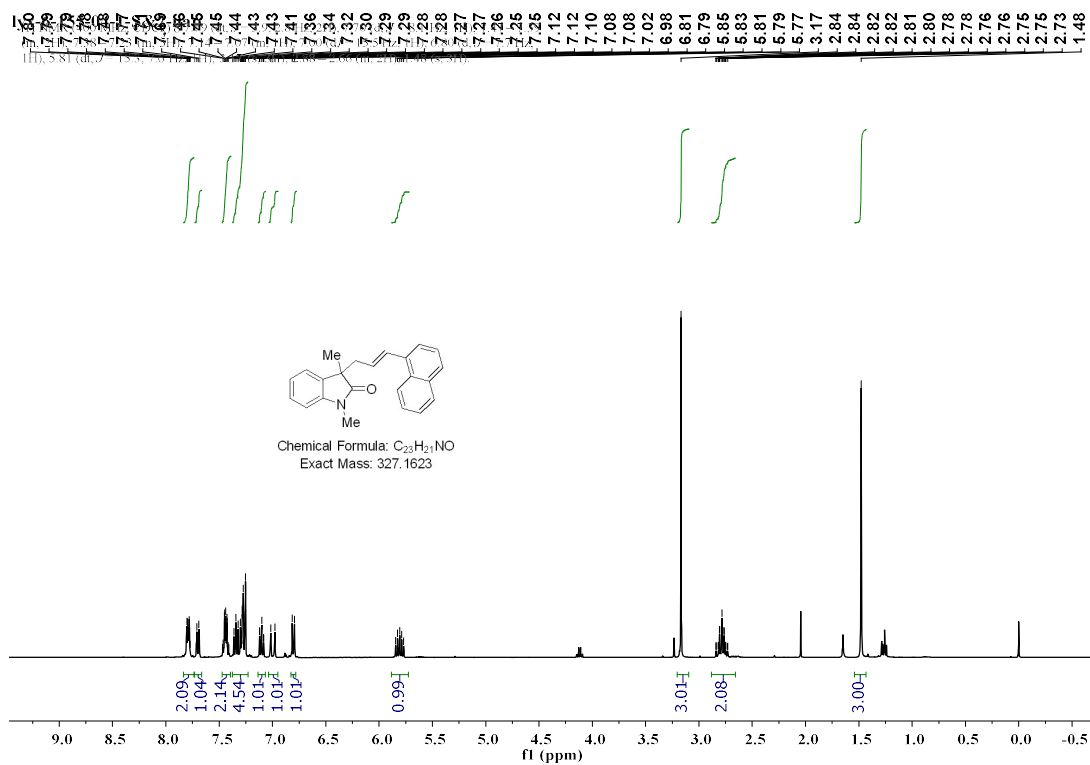
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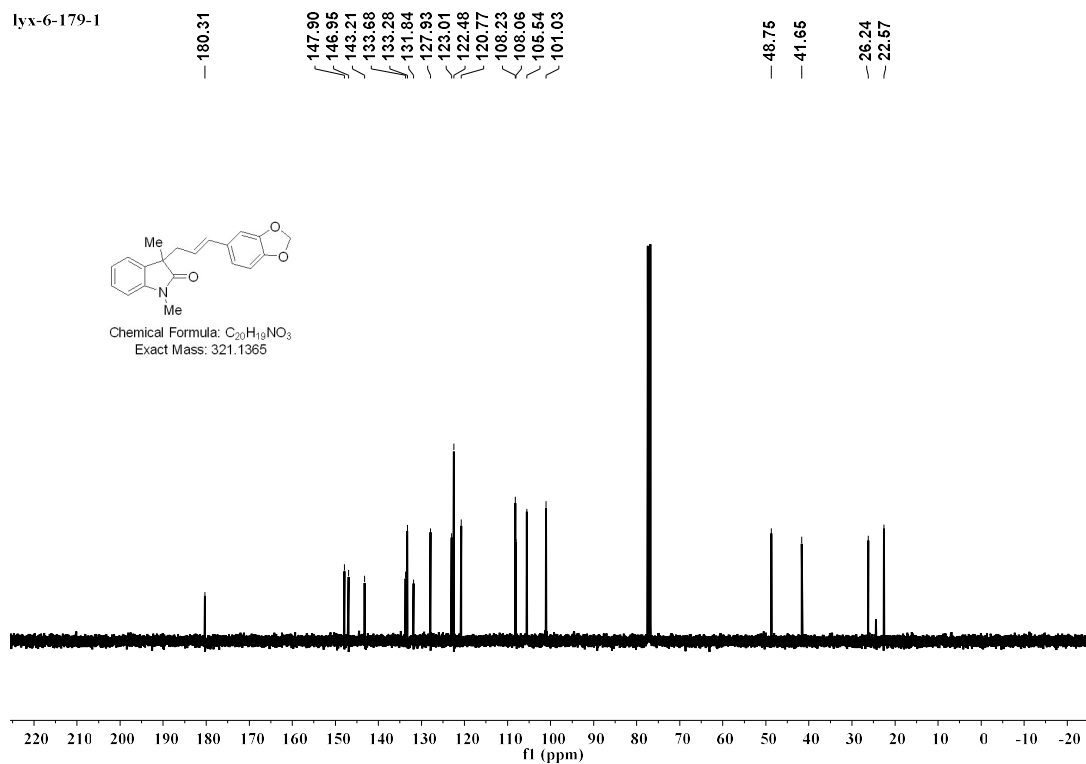
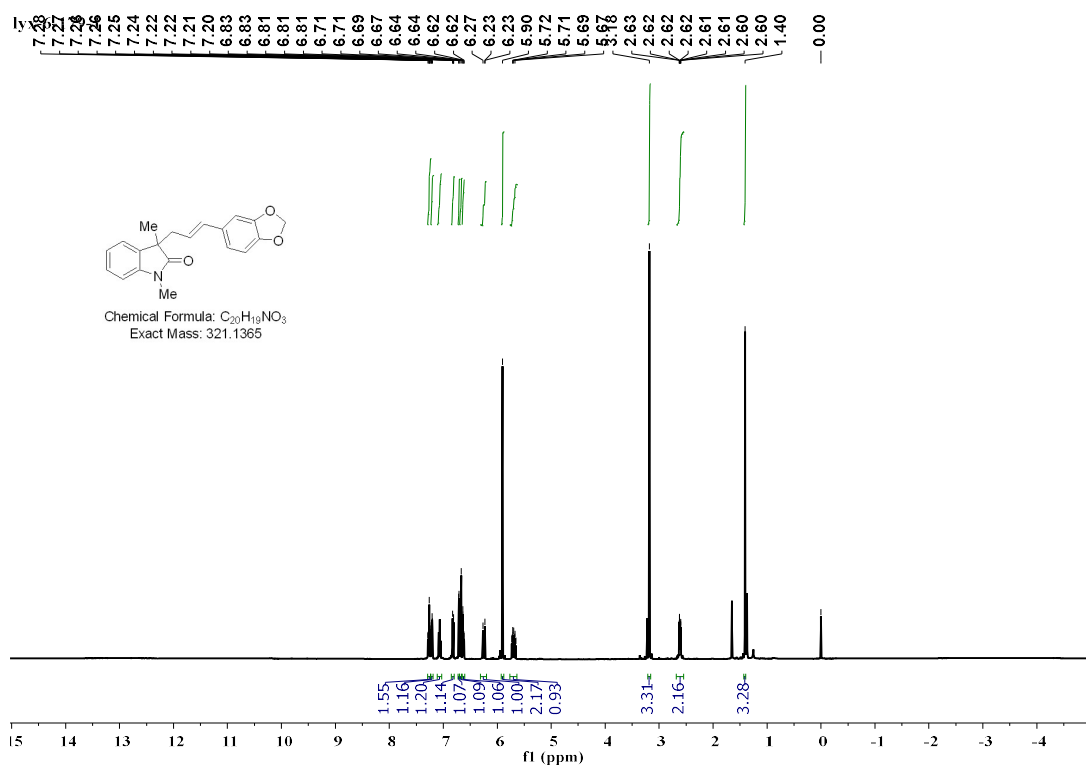
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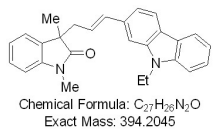
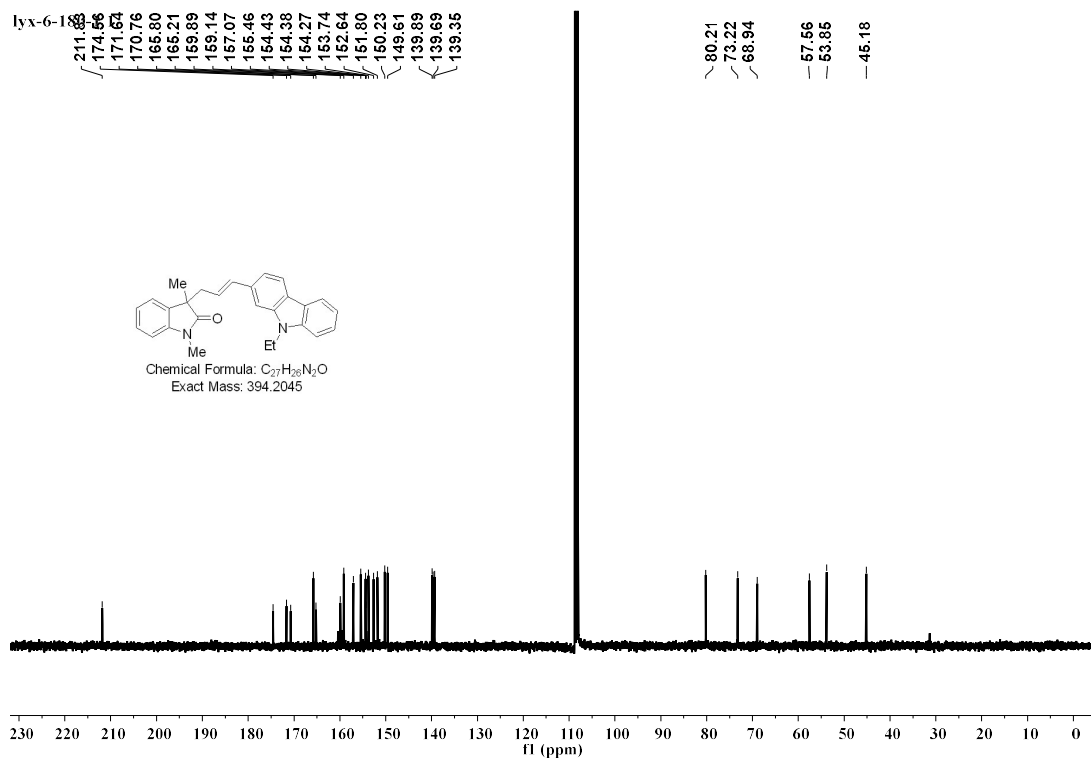
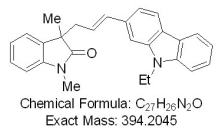
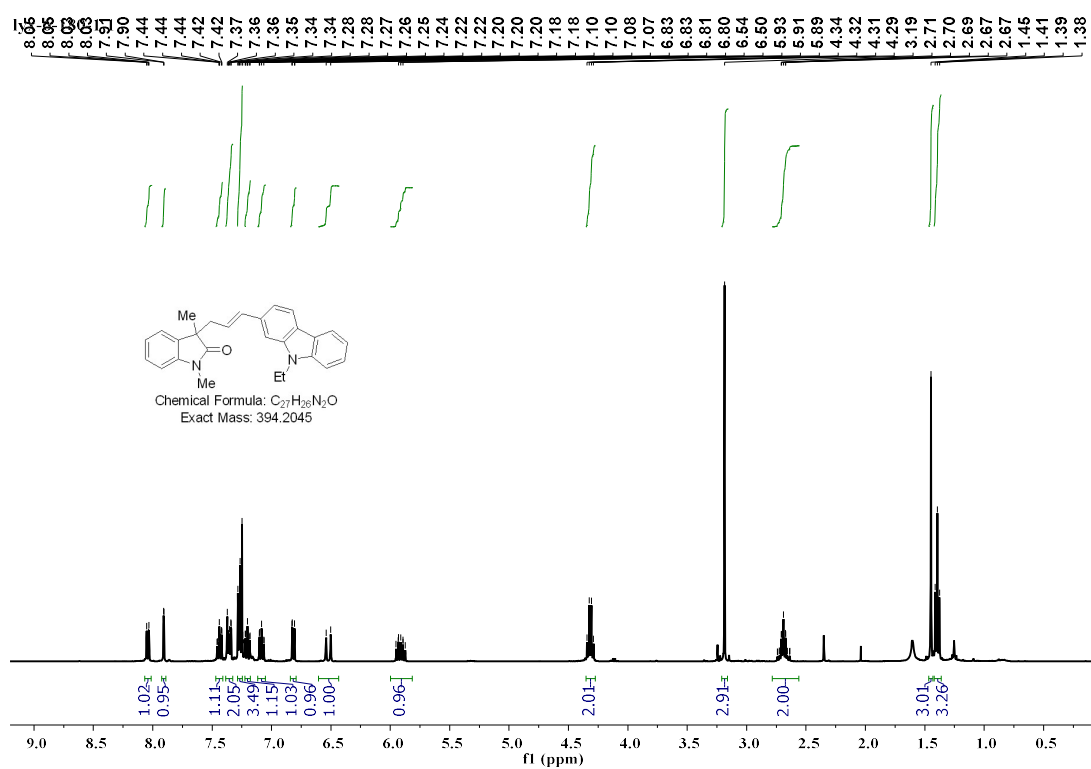
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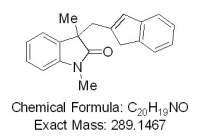
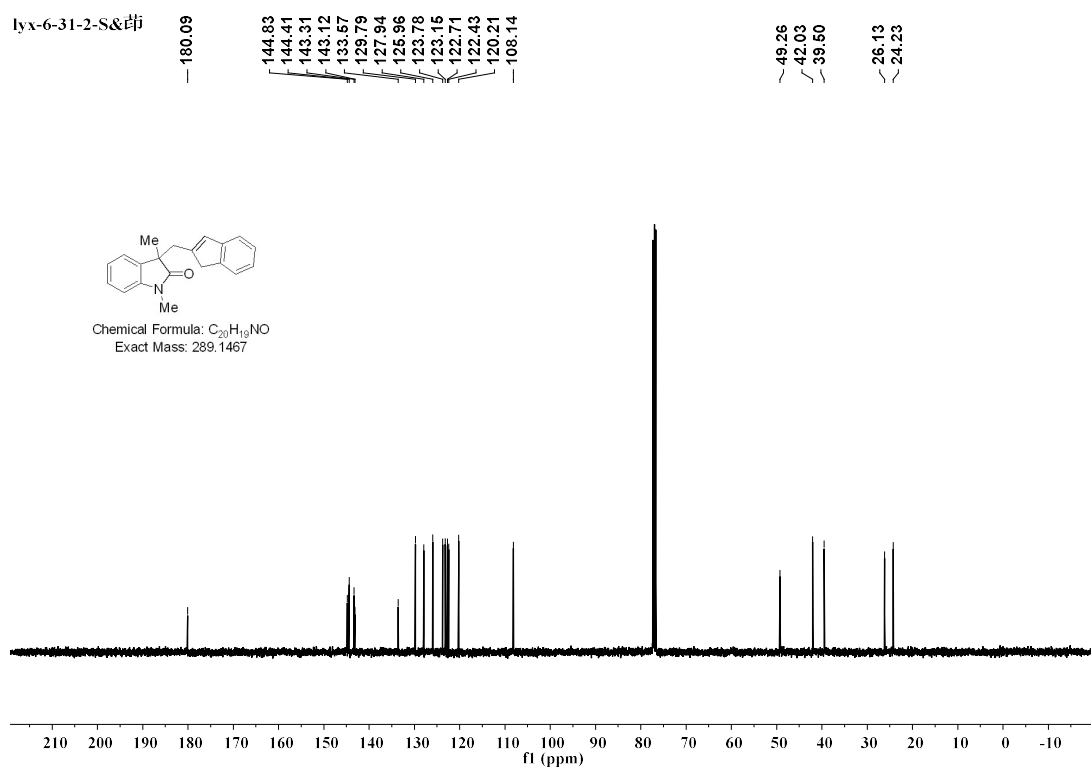
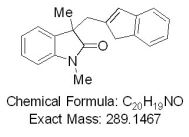
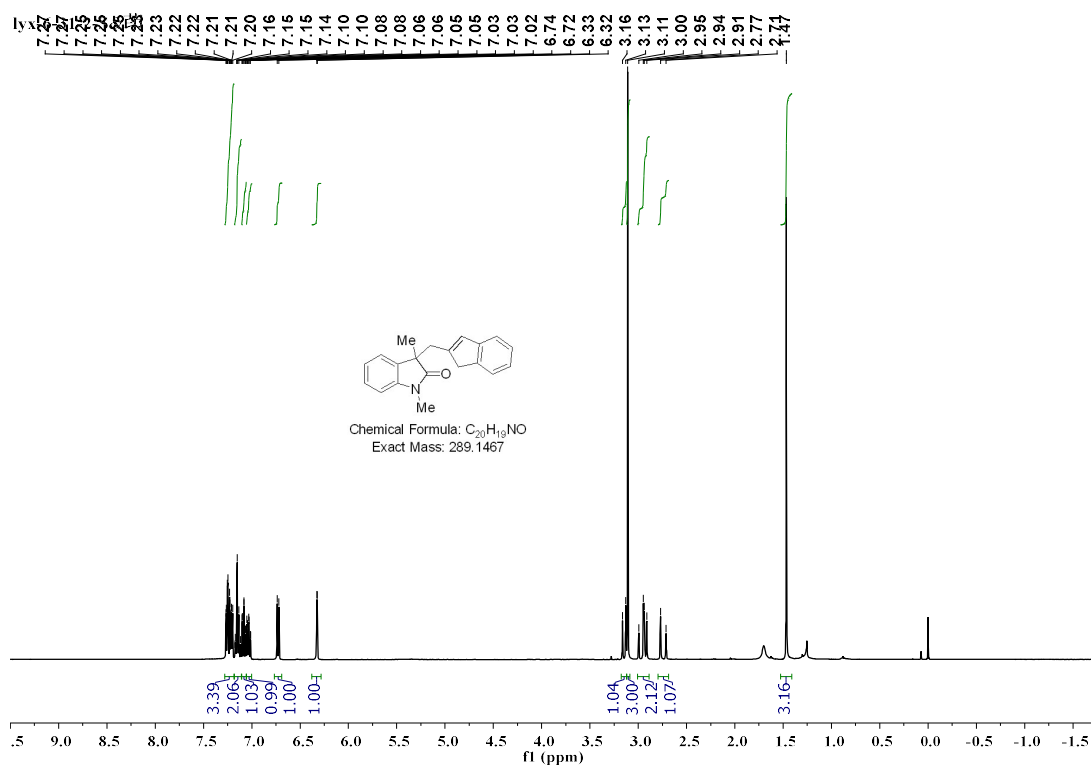
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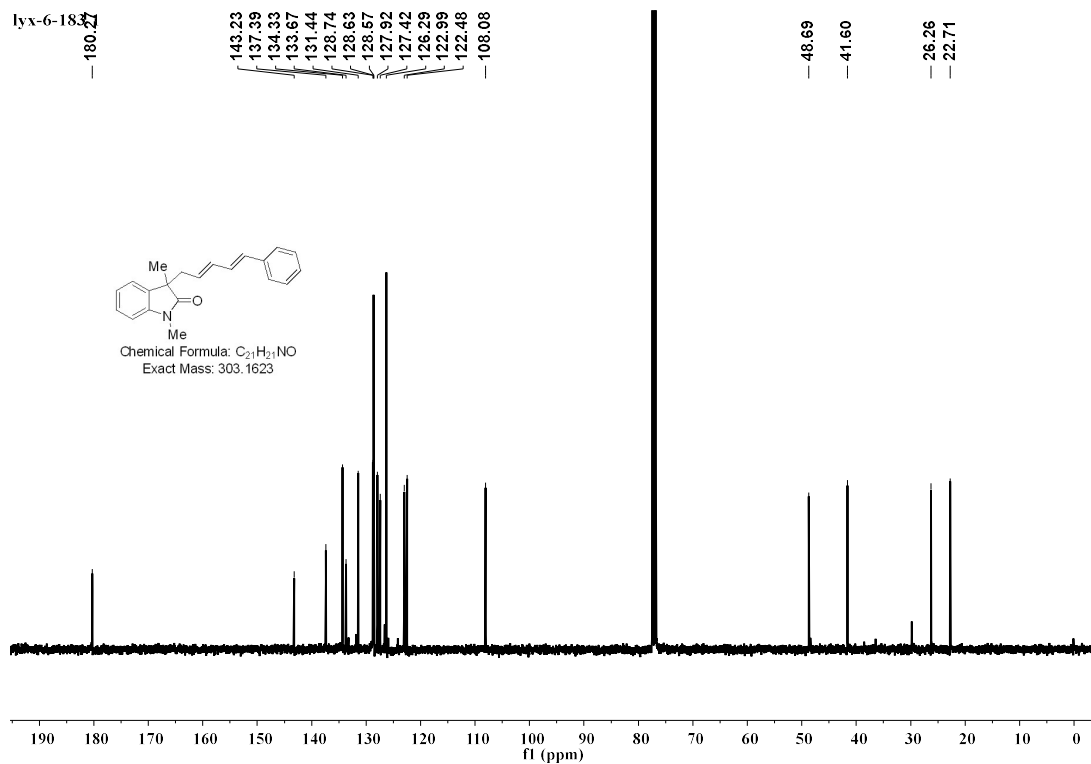
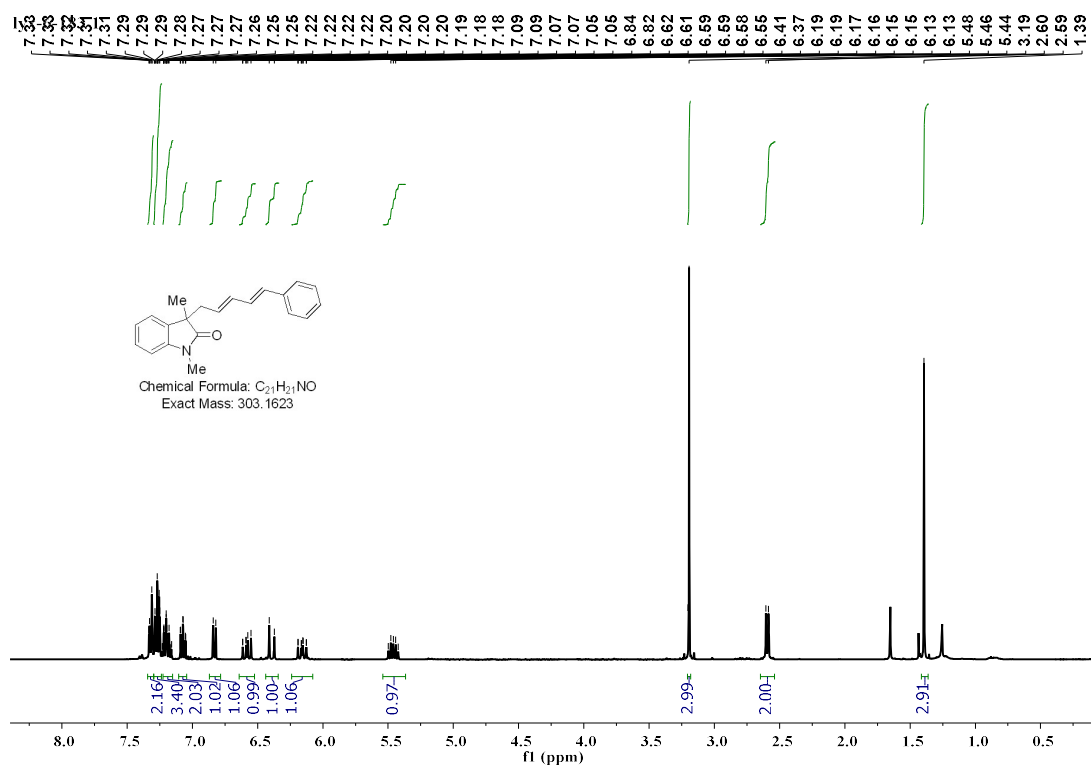
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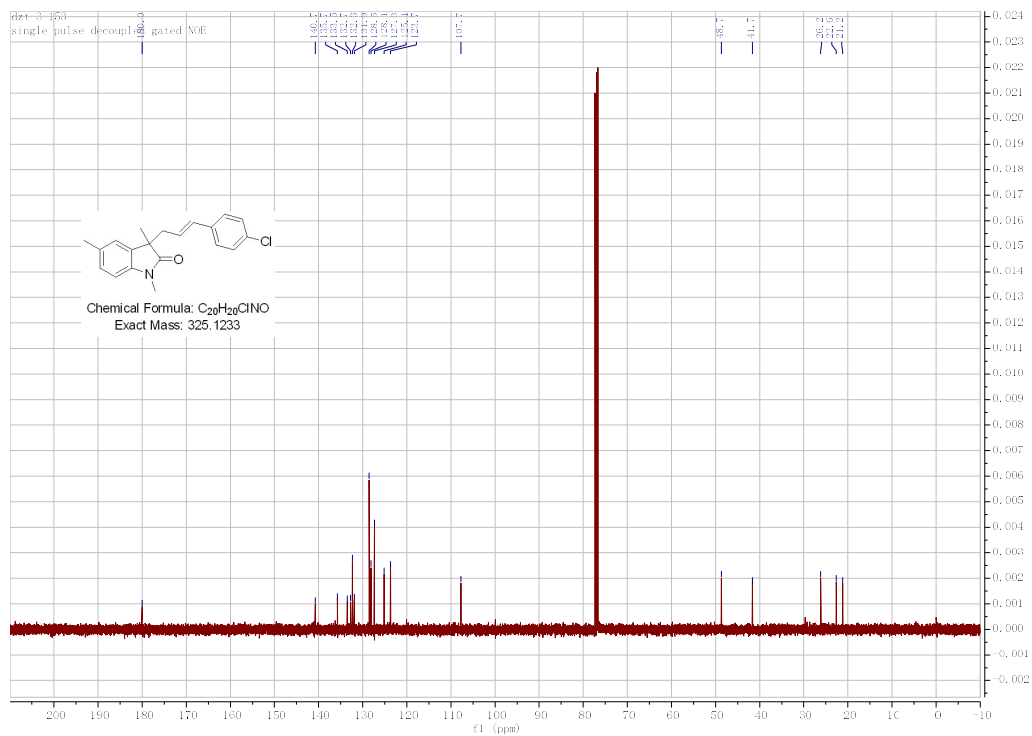
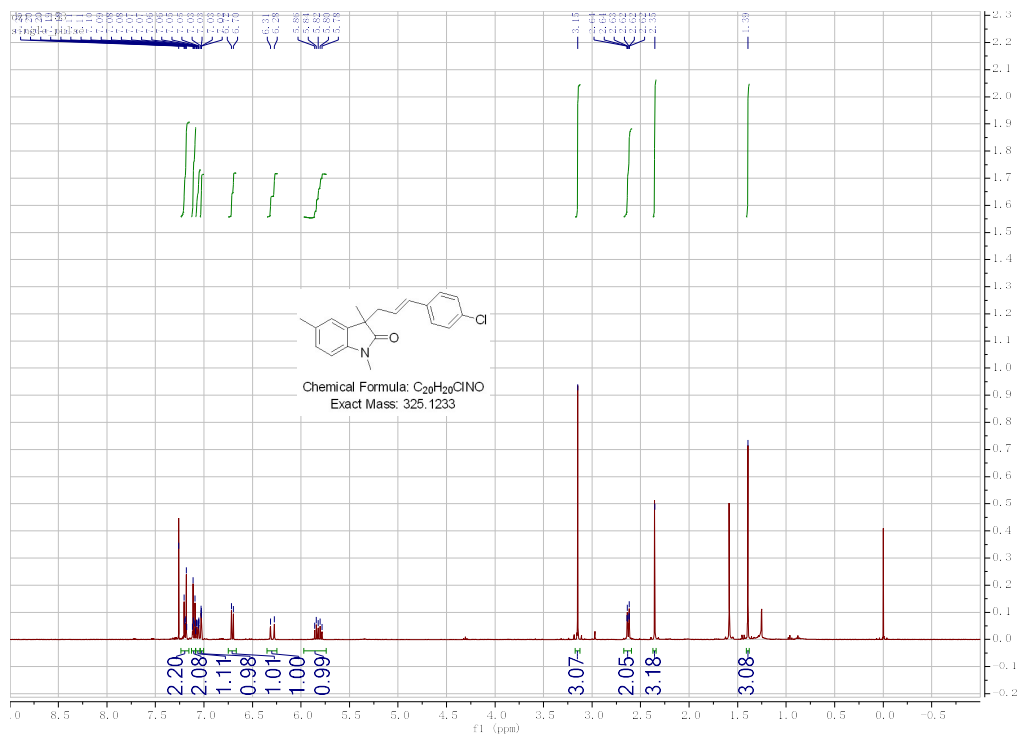
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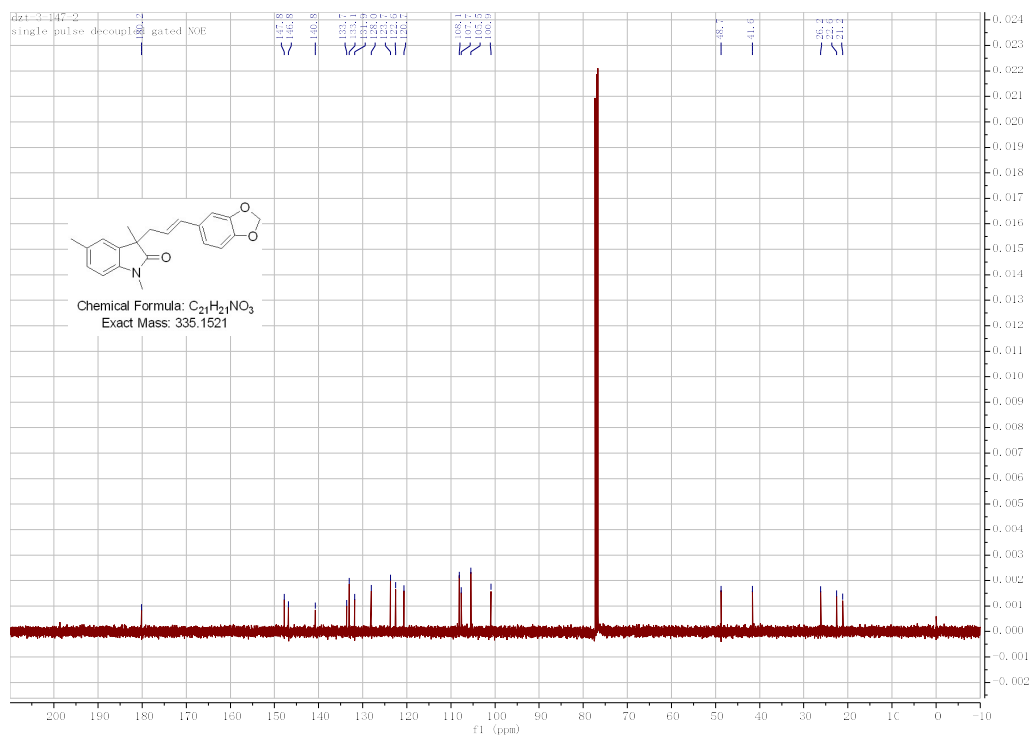
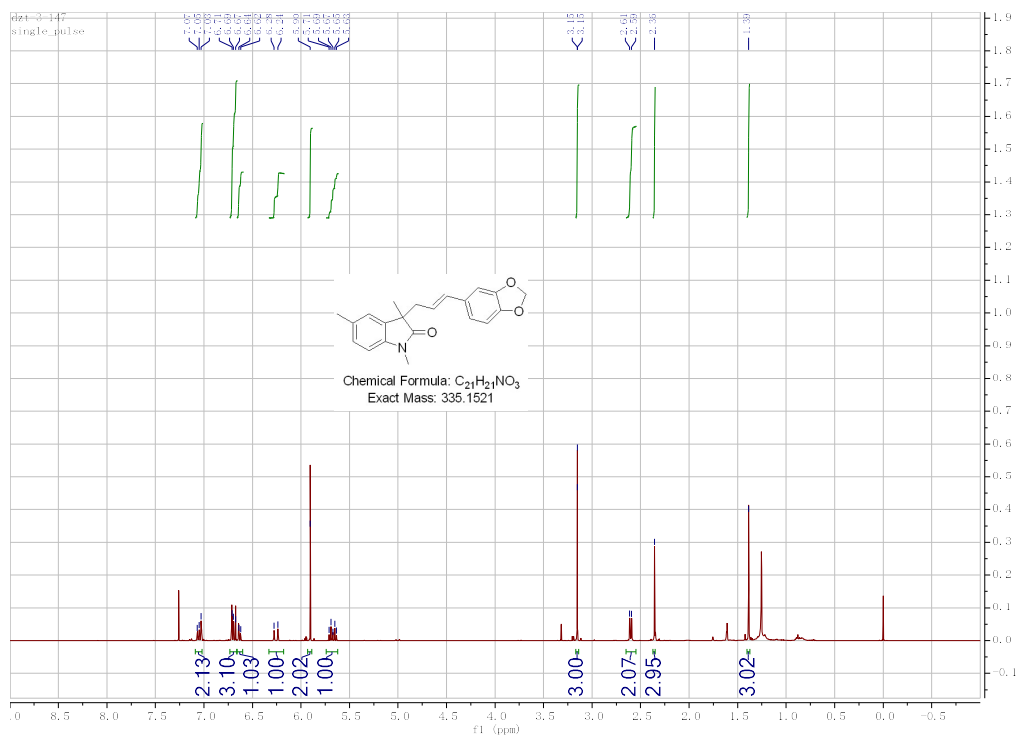
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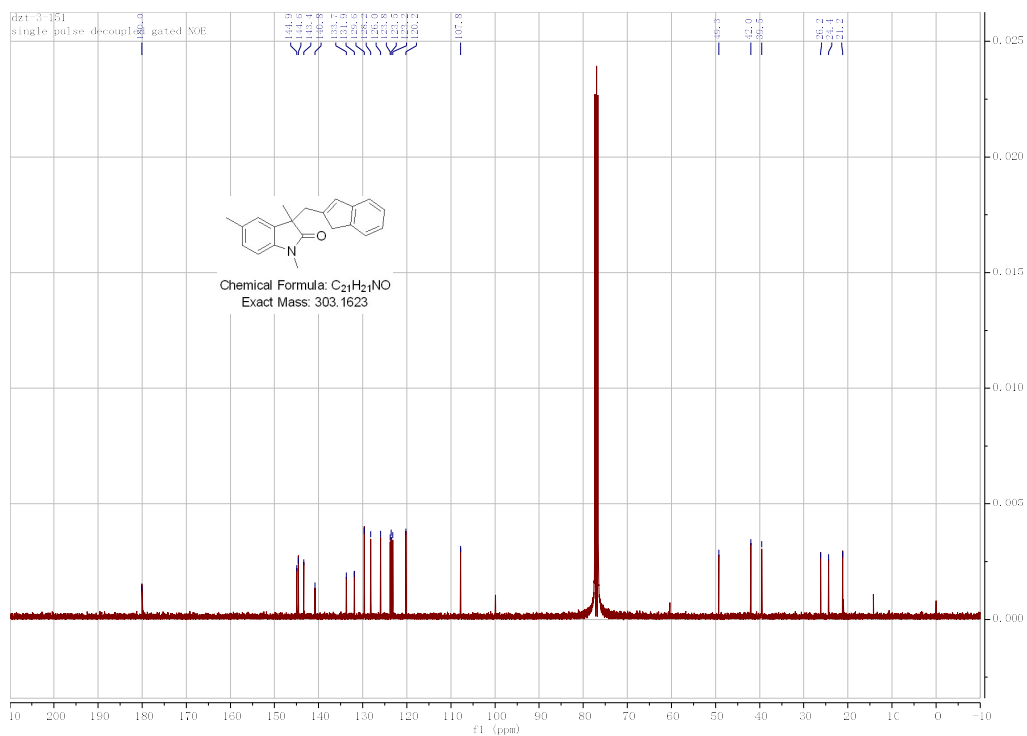
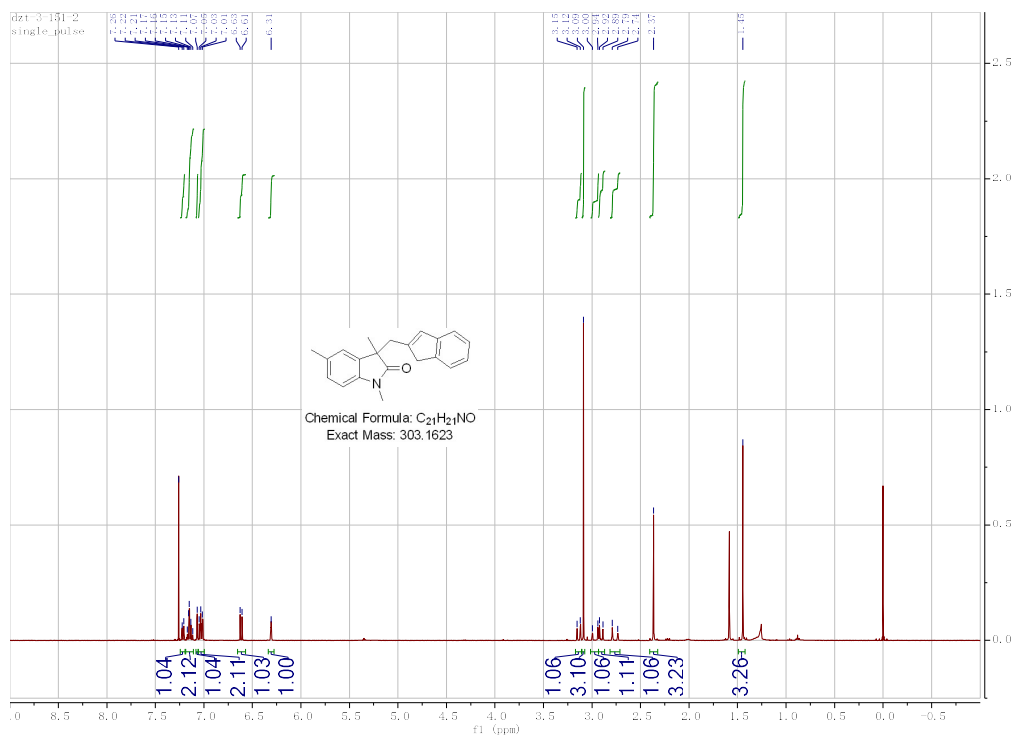
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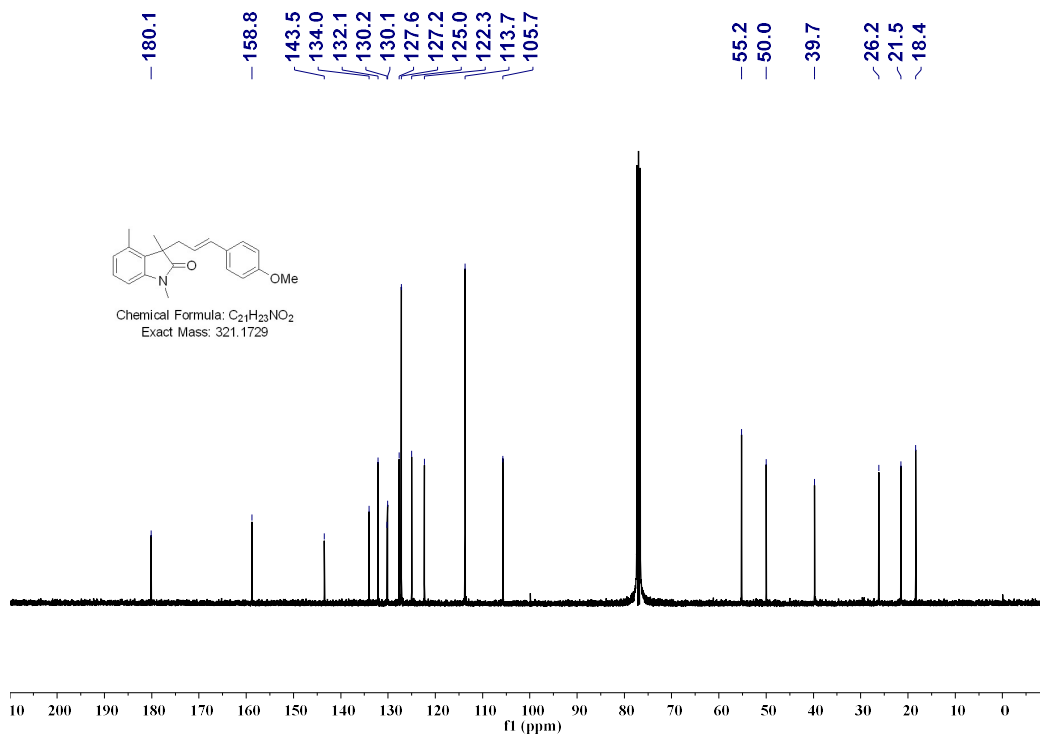
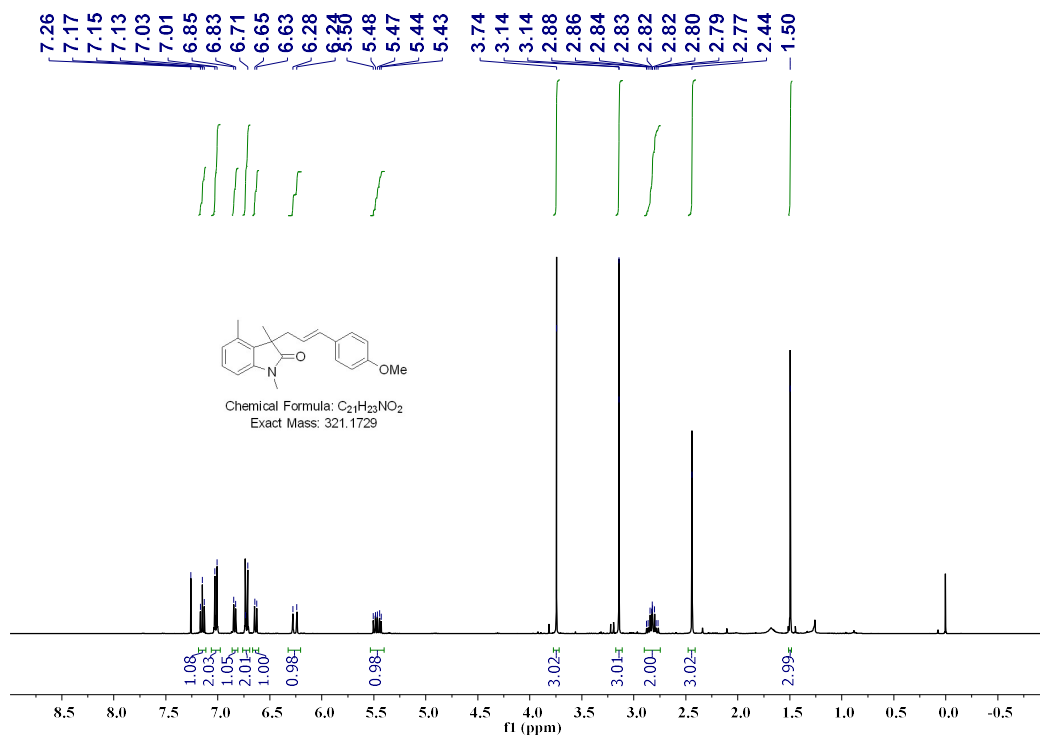
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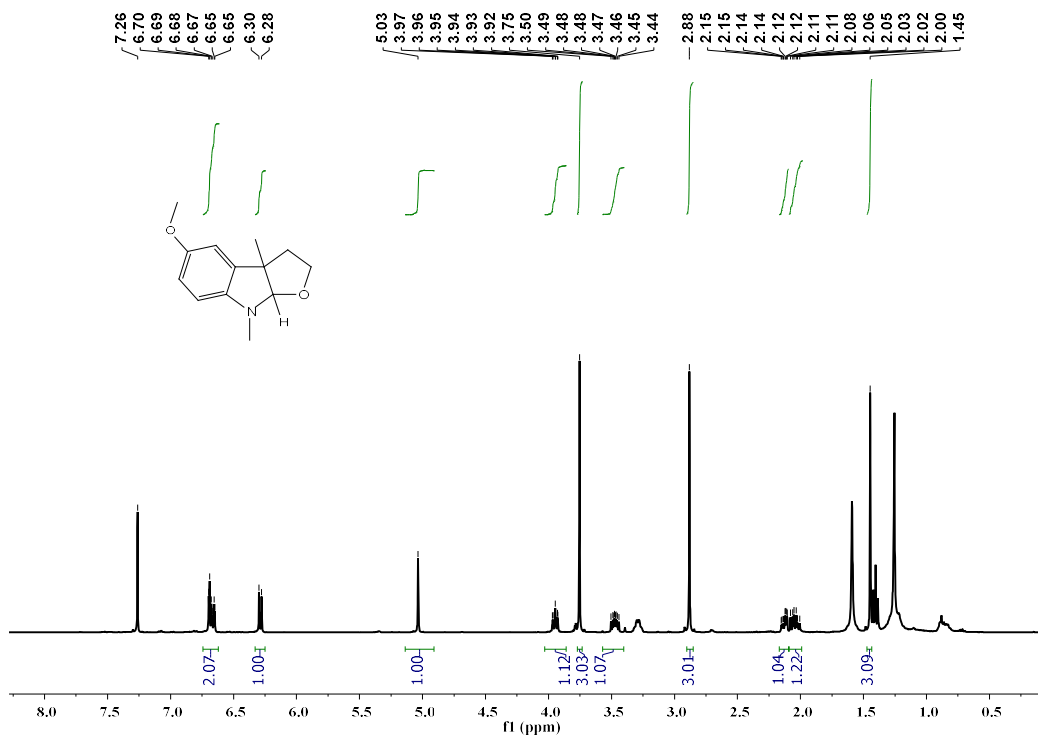
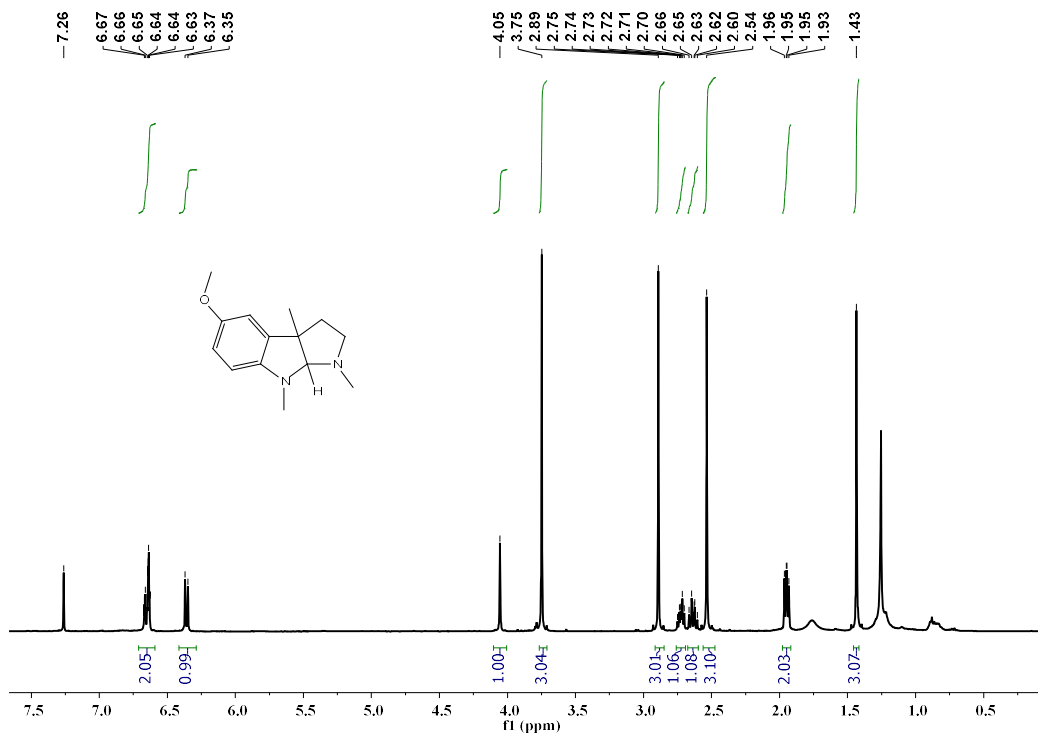


3bm



3qa



5**6**

7. References

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2. (a) Zhou, B.; Hou, W.; Yang, Y.; Feng, H.; Li, Y. *Org. Lett.* **2014**, *16*, 1322. (b) T. Wang, W. Yao, F. Zhong, G. Pang, Y. Lu. *Angew. Chem. Int. Ed.* **2014**, *53*, 2964.
3. Q. Yu, W. Luo, Y. Li, *Heterocycles*, **1993**, *36*, 1279.