
Supplementary information

Kinetic resolution of bromonitroalkenes atropisomers enabling divergent access to multi-stereogenic molecules

Guishun Bai, Ruoqi Liu, Hua Chen, Hong Wang, Damien Bonne, Xiaoze Bao

Contents

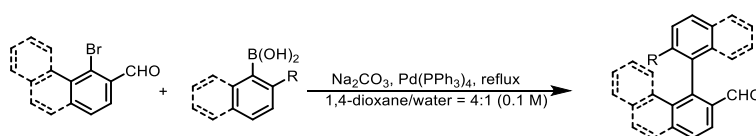
1. General Information	2
2. General Procedure	2
2.1 General procedure A: synthesis of substrates 1	2
2.2 General procedure for the synthesis of 3	3
2.3 Gram scale synthesis of 3aa	3
2.4 General Procedure for the Applications	4
2.5 Control experiments	6
2.6 Determination of the rotation barrier	7
3. Characterization Data for the Products	10
4. X-ray Crystallographic Data	39
5. NMR spectra	61

1. General Information

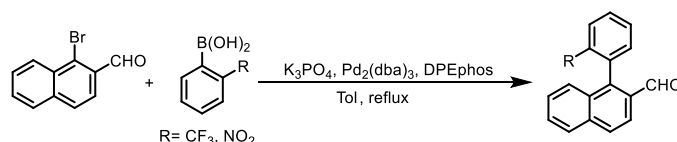
Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (100 ~ 200 mesh). Enantiomeric excesses (*ee*) were determined by HPLC using corresponding commercial chiral columns as stated at 30 °C with UV detector at 254 nm. All ¹H NMR and ¹⁹F NMR spectra were recorded on a Bruker AvanceII 500 MHz and Bruker Avance III 376 MHz respectively, ¹³C NMR spectra were recorded on a Bruker AvanceII Bruker Avance III 126 MHz with chemical shifts reported as ppm (in DMSO-d₆ or CDCl₃, TMS as internal standard). Data for ¹H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet, dd = doublet doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XL TM).

2. General Procedure

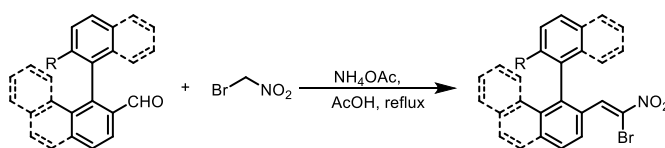
2.1 General procedure A: synthesis of substrates 1



Added Pd(PPh₃)₄ (5 mol%) to a solution of 2-bromoquinolin-7-ol (5 mmol), Na₂CO₃ (2.0 equiv.), aryl boronic acid (1.5 equiv.) in 1,4-dioxane/water (4:1, 50 mL) under argon atmosphere. Heated the mixture at 100 °C in an oil bath until the aldehyde substrates was completely consumed. Subsequently, added saturated aqueous ammonium chloride solution (20 mL) to the reaction mixture and extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography to afford the product S1-S5, S8-S11.

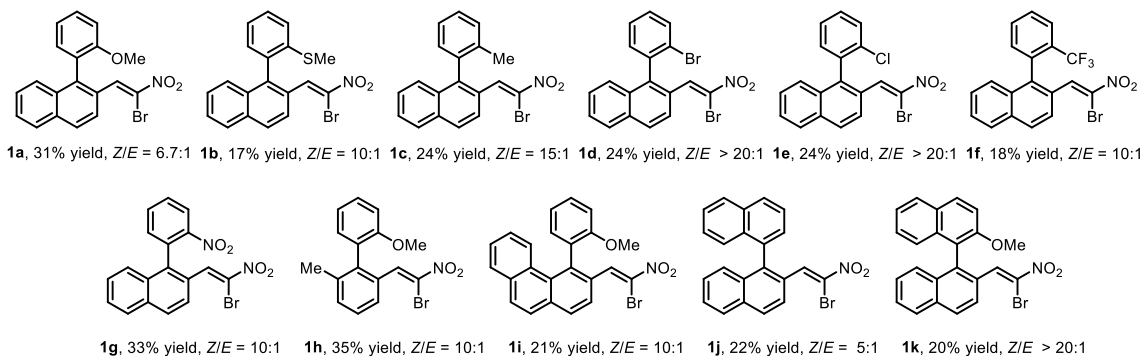


Added Pd₂(dba)₃ (5 mol%) and DPEphos (10 mol%) to a solution of 2-bromoquinolin-7-ol (5 mmol), K₃PO₄ (3.0 equiv.), aryl boronic acid (1.5 equiv.) in toluene (20 mL) under argon atmosphere. Heated the mixture at 100 °C in an oil bath until the aldehyde substrates was completely consumed. Subsequently, added saturated aqueous ammonium chloride solution (20 mL) to the reaction mixture and extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography to afford the product S6 and S7.

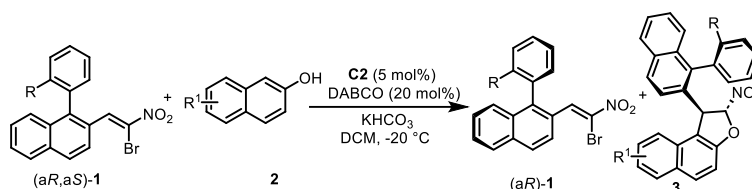


A mixture of aldehyde derivative (1.0 equiv., 3 mmol), bromonitromethane (2.0 equiv., 6

mmol), ammonium acetate (2.0 equiv., 6 mmol) in acetic acid (10 mL) was refluxed in an oil bath for 4 h. The reaction mixture was cooled to room temperature and quenched with H₂O. The mixture was then extracted with ether (3 × 10 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography to afford the product.



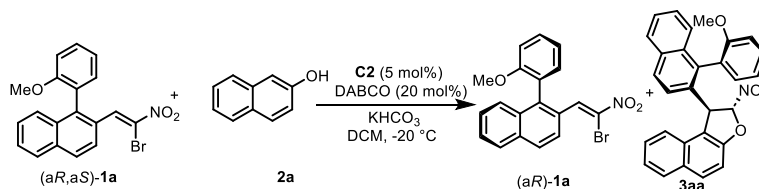
2.2 General procedure for the synthesis of 3



A solution of naphthol **2** (0.15 mmol, 0.75 equiv.), **C2** (0.01 mmol, 5 mol%), DABCO (0.04 mmol, 20 mol%), and potassium bicarbonate (0.2 mmol, 1.0 equiv.) in dichloromethane (4 mL) was stirred at -20 °C for 5 minutes. Then, the corresponding α -bromonitroalkenes **1** (0.2 mmol, 1.0 equiv.) was added and reaction mixture was stirred at same temperature. After the reaction was complete as indicated by TLC analysis, the crude product was quenched with hydrochloric acid (1M, 5 mL) and the mixture was extracted with dichloromethane (DCM, 2 × 5 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography to afford the products.

The selectivity factor was calculated as following: Conversion (C) = $ee_s / (ee_s + ee_p)$. Selectivity factor (S) = $\ln[(1-C)(1-ee_s)] / \ln[(1-C)(1+ee_s)]$. ee_s : ee of the recovered starting material; ee_p : ee of the product;

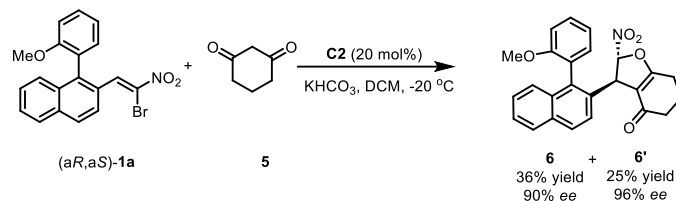
2.3 Gram scale synthesis of 3aa



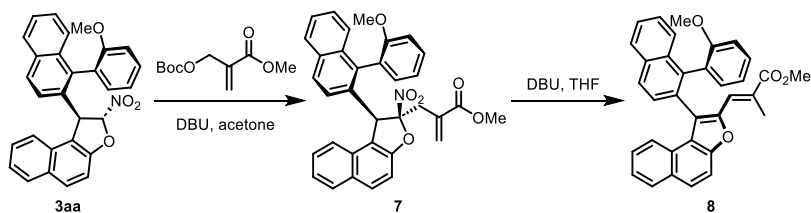
A solution of naphthol **2a** (1.5 mmol, 0.75 equiv.), **C2** (0.1 mmol, 5 mol%), DABCO (0.4 mmol, 20 mol%), and potassium bicarbonate (2.0 mmol, 1.0 equiv.) in dichloromethane (40 mL) was stirred at -20 °C for 10 minutes. Then, the corresponding α -bromonitroalkenes **1a** (2.0 mmol, 1.0 equiv.) was added and reaction mixture was stirred at same temperature. After the reaction was complete as indicated by TLC analysis, the crude product was quenched with hydrochloric acid (1M,

30 mL) and the mixture was extracted with dichloromethane (DCM, 20 × 4 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography to afford 314 mg of (*aR*)-**1a** (41% yield, 97% *ee*) and 411 mg of **3aa** (46% yield, *dr* = 10:1, 94% *ee*), respectively.

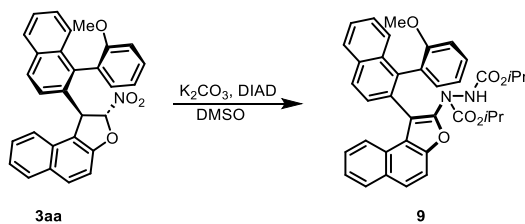
2.4 General Procedure for the Applications



A solution of 1,3-cyclohexanedione **5** (28.0 mg, 0.25 mmol), **C2** (12.6 mg, 0.02 mmol, 20 mol%) and potassium bicarbonate (80.8 mg, 0.8 mmol, 4.0 equiv.) in dichloromethane (4 mL) was stirred at -20 °C for 5 minutes. Then, the α -bromonitroalkene **1a** (76.6 mg, 0.2 mmol, 1.0 equiv.) was added and reaction mixture was stirred at same temperature. After the reaction was complete as indicated by TLC analysis, the crude product was quenched with hydrochloric acid (1M, 5 mL) and the mixture was extracted with dichloromethane (DCM, 2 × 5 mL). The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography to afford the product.

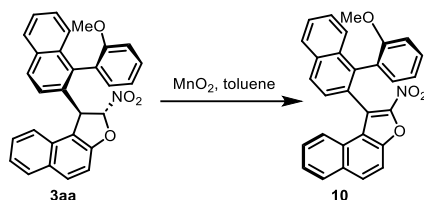


A solution of the benzodihydrofuran derivative **3aa** (44.7 mg, 0.1 mmol, 1.0 equiv.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 15 μ L, 0.1 mmol, 1.0 equiv.) in acetone (1 mL) was stirred at room temperature (25-30 °C). Then, Morita–Baylis–Hillman (MBH) carbonic ester (32.4 mg, 0.15 mmol, 1.5 equiv.) was added, and the mixture was stirred at the same temperature for 10 minutes to get the product **7**. And then, the reaction mixture was concentrated under reduced pressure to remove volatile solvents. The residue was redissolved in THF (1 mL), treated with DBU (75 μ L, 0.5 mmol, 5.0 equiv.), and stirred at room temperature for 24 h. Upon completion, the mixture was concentrated and purified by flash column chromatography on silica gel to afford the desired product **8**.



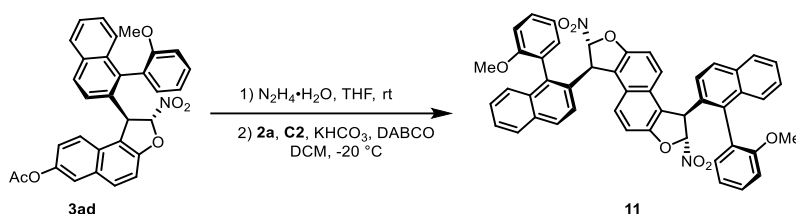
A solution of the benzodihydrofuran derivative **3aa** (44.7 mg, 0.1 mmol, 1.0 equiv.) and potassium carbonate (27.6 mg, 0.2 mmol, 2.0 equiv.) in DMSO (1 mL) was stirred at room temperature (25-30 °C). Then, diisopropyl azodicarboxylate (39 μ L, 0.2 mmol, 2.0 equiv.) was added

and the reaction mixture was stirred at rt for 12h. And then, added saturated ammonium chloride (NH₄Cl, 10 mL) to the reaction mixture and extracted with Et₂O (2 × 5 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the desired product **9**.



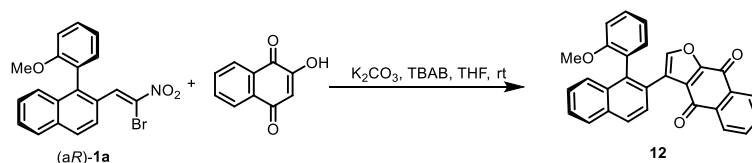
Activated manganese dioxide (348 mg, 4 mmol, 40 equiv.) was added in a solution of the corresponding dihydrofuran **3aa** (44.7 mg, 0.1 mmol, 1.0 equiv.) in toluene (1 mL) at room temperature was stirred for 3 days at rt. After the reaction was finished, filter the reaction mixture with Celite to remove the insoluble manganese dioxide and washed with ethyl acetate. The combined organic phase concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the desired product **10**.

Note: The manganese dioxide was activated by heating at 250 °C for 12 hours in a muffle furnace prior to use.

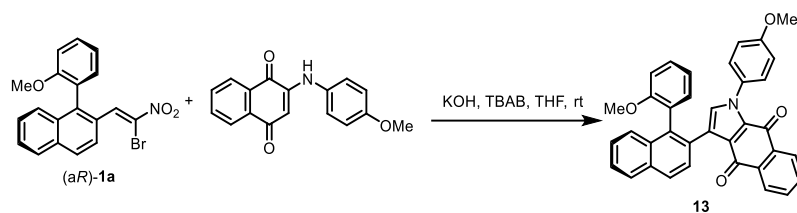


A solution of the benzodihydrofuran derivative **3ad** (25.3 mg, 0.05 mmol, 1.0 equiv.) in THF (1 mL) was treated with hydrazine hydrate (15 μL, 1 mmol) at room temperature. The mixture was stirred for 20 minutes. Upon completion, the reaction mixture was quenched with hydrochloric acid (1M, 5 mL) and the mixture was extracted with EtOAc (2 × 5 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated under reduced pressure to afford the deacetylated intermediate, which was used directly in the next step.

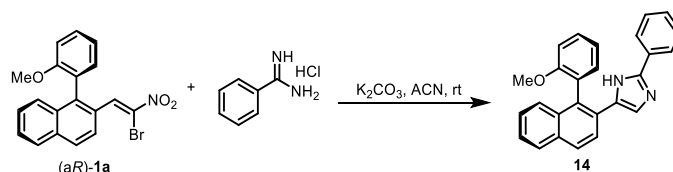
The crude intermediate from the previous step was dissolved in DCM (1 mL). To this solution, catalyst (3.2 mg, 0.005 mmol, 10 mol%) and potassium bicarbonate (10.1 mg, 0.1 mmol, 2.0 equiv.) were added. The mixture was cooled to -20 °C and stirred for 5 minutes, followed by the addition of the corresponding α-bromonitroalkene (15 mg). Stirring was continued at the same temperature until the reaction was complete, as monitored by TLC. The crude mixture was then quenched with hydrochloric acid (1 M, 5 mL) and extracted with dichloromethane (DCM, 2 × 5 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography to yield the desired product **11**.



A solution of the chirally resolved α -bromonitroalkene (38.3 mg, 0.1 mmol, 1.0 equiv.), potassium carbonate (27.6 mg, 0.2 mmol, 2.0 equiv.) and tetrabutylammonium bromide (48.3 mg, 0.15 mmol, 1.5 equiv.) in THF (1 mL) was stirred at room temperature (25-30 °C). Then, 2-hydroxy-1,4-naphthoquinone (34.8 mg, 0.2 mmol, 2.0 equiv.) was added and the reaction mixture was stirred at rt for 12h. After the material was completely consumed, added saturated ammonium chloride (NH₄Cl, 10 mL) to quench the reaction mixture and extracted with EtOAc (2 $\times$ 5 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the desired product.

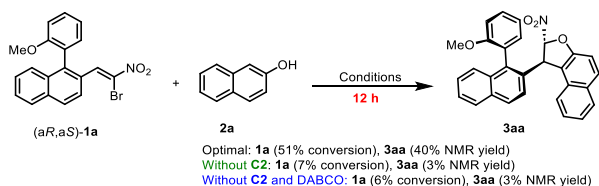


A solution of the chirally resolved α -bromonitroalkene (38.3 mg, 0.1 mmol, 1.0 equiv.) potassium hydroxide (27.6 mg, 0.2 mmol, 2.0 equiv.) and tetrabutylammonium bromide (48.3 mg, 0.15 mmol, 1.5 equiv.) in THF (1 mL) was stirred at room temperature (25-30 °C). Then, 2-[(4-methoxyphenyl)amino] -1,4-naphthoquinone (55.8 mg, 0.2 mmol, 2.0 equiv.) was added and the reaction mixture was stirred at rt for 12h. After the material was completely consumed, added saturated ammonium chloride (NH₄Cl, 10 mL) to quench the reaction mixture and extracted with EtOAc (2 $\times$ 5 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the desired product.



A solution of the chirally resolved α -bromonitroalkene (38.3 mg, 0.1 mmol, 1.0 equiv.) and potassium carbonate (27.6 mg, 0.2 mmol, 2.0 equiv.) in acetonitrile (ACN, 2 mL) was stirred at room temperature (25-30 °C). Then, benzimidamide hydrochloride (30.2 mg, 0.2 mmol, 2.0 equiv.) was added and the reaction mixture was stirred at rt for 3h. After the material was completely consumed, the organic solvent concentrated under reduced pressure. After that, the residue was purified by flash column chromatography to afford the desired product.

2.5 Control experiments

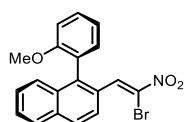


Three reactions were conducted in parallel under the following conditions: (A) with **C2** and

DABCO; (B) with DABCO only; (C) without **C2** and DABCO. A solution of naphthol **2** (0.075 mmol, 0.75 equiv.), the appropriate additive (**C2** (0.05 mmol, 5 mol%) and/or DABCO (0.02 mmol, 20 mol%) as indicated), and potassium bicarbonate (0.1 mmol, 1.0 equiv.) in dichloromethane (2 mL) was stirred at -20 °C for 5 minutes. Then, the corresponding α -bromonitroalkenes **1** (0.1 mmol, 1.0 equiv.) was added and reaction mixture was stirred at same temperature for 12 h. The crude product was quenched with hydrochloric acid (1M, 5 mL) and the mixture was extracted with dichloromethane (DCM, 2 $\times$ 5 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and concentrated in vacuo. The yield and conversion were determined by ¹H NMR spectroscopy using trimethoxybenzene as the internal standard.

2.6 Determination of the rotation barrier.

Enantiomerisation barrier for (1a)



(aR)-**1a**

About 3 mg of enantio-enriched (**1a**) were refluxed in 15 mL of Isopropanol. Samples of 10 μ L of this solution were injected on Chiralpak OD-H (hexane / isopropanol 95/5, 1 mL/min, UV detection at 254 nm) to monitor the percentage decrease of the first eluted enantiomer over time.

Solvent: Isopropanol

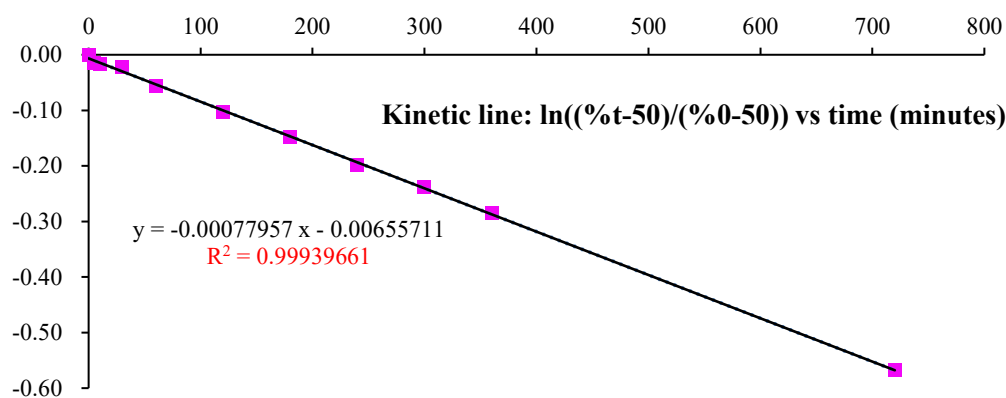
Temperature = 70.00 °C

Time (min)	% first eluted enantiomer (%t)	ln ((%t-50)/(%0-50))
0	95.15	0.0000
5	94.50	-0.0144
10	94.41	-0.0164
30	94.15	-0.0224
60	92.65	-0.0569
120	90.75	-0.1026
180	88.94	-0.1480
240	87.01	-0.1988
300	85.58	-0.2383
360	83.92	-0.2860
720	75.61	-0.5669

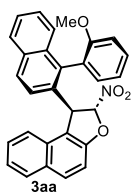
k racemisation	=	1.29928E-05	s ⁻¹
k enantiomerisation	=	6.49642E-06	s ⁻¹
$\Delta G^\ddagger$ enantiomerisation	=	118.20	kJ.mol ⁻¹
		28.25	kcal.mol ⁻¹
half-life time t _{1/2}	=	53337	seconds
		888.95	minutes

14.82 hours

0.617 days



Diastereoisomerisation barrier for (3aa)



About 5 mg of enantio-enriched (**3aa**) were heated in 0.20 mL of DMSO-*d*₆ at 100 °C. Sample of this solution was detected by ¹H-NMR to monitor the percentage decrease of the major diastereomer over time.

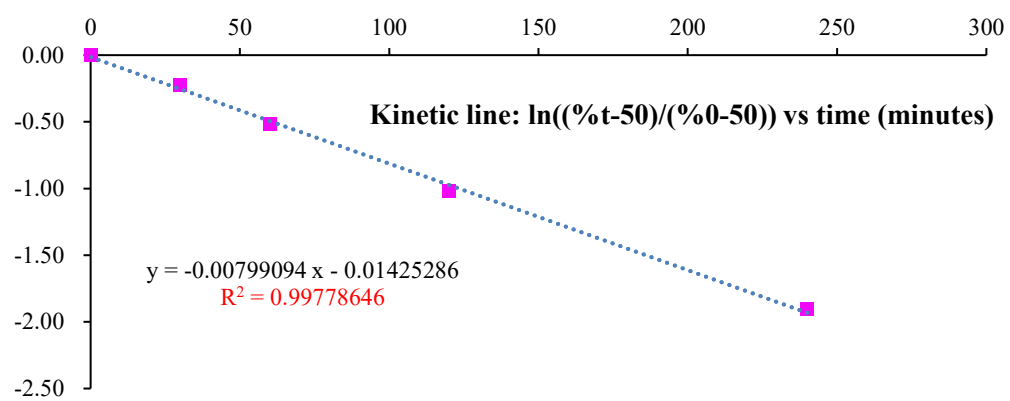
Solvent: DMSO-*d*₆

Temperature = 100.00 °C

Time (min)	% major diastereomer (%t)	In ((%t-50)/(%0-50))
0	95.10	0.0000
30	86.17	-0.2207
60	76.85	-0.5186
120	66.22	-1.0226
240	56.71	-1.9053

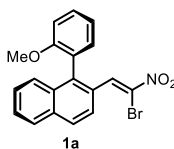
k racemisation	=	1.33182E-04	s ⁻¹
k enantiomerisation	=	6.65912E-05	s ⁻¹
ΔG [‡] diastereoisomerisation	=	121.75	kJ.mol ⁻¹
		29.10	kcal.mol ⁻¹
half-life time t _{1/2}	=	5204	seconds
		86.73	minutes

1.446 hours

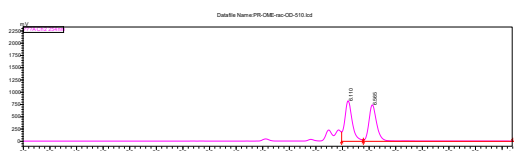


3. Characterization Data for the Products

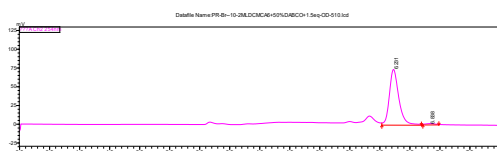
(a*R*,*Z*)-2-(2-bromo-2-nitrovinyl)-1-(2-methoxyphenyl)naphthalene (1a)



Isolated according to the general procedure with a reaction time of 16 h (34.6 mg, 45% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *Z*/*E* = 6.7:1. **MP** = 93.2–98.8 °C. **Rf**: 0.16 (petroleum ether/ethyl acetate = 100:1). **¹H NMR (500 MHz, CDCl₃)** δ 8.42 (s, 1H), 8.10 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.56 – 7.54 (m, 1H), 7.52 – 7.49 (m, 1H), 7.44 – 7.41 (m, 1H), 7.16 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.12 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 3.68 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 157.1, 140.3, 137.4, 134.4, 132.5, 132.1, 130.5, 128.9, 128.1, 127.72, 127.69, 127.5, 127.2, 126.8, 125.4, 124.5, 120.8, 111.4, 55.5. **HRMS (ESI)** *m/z* Calcd. for C₁₉H₁₅BrNO₃⁺ ([*M*+H]⁺) = 384.0230, found: 384.0237. **[α]_D²⁵** (DCM, *c* = 0.1) = +136. **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 96% ee, *t*_{major} : 6.231 min, *t*_{min} : 6.838 min.

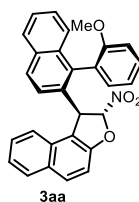


Peak#	Ret. Time	Height	Area	Area%
1	6.110	821020	7936087	51.493
2	6.565	738159	7475764	48.507
Total		1559178	15411851	100.000



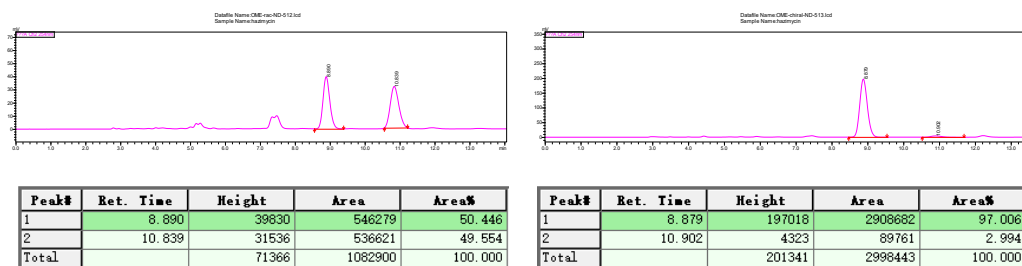
Peak#	Ret. Time	Height	Area	Area%
1	6.231	73973	808664	97.939
2	6.838	1498	17016	2.061
Total		75471	825680	100.000

(1*R*,2*R*)-1-((a*S*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan (3aa)

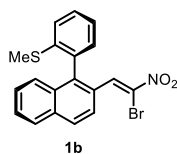


Prepared according to the general procedure with a reaction time of 16 h as pale pink foam (43.1 mg, 48% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* = 10:1. **Rf**: 0.09 (petroleum ether/ethyl acetate = 100:1). **MP** = 85.2–94.5 °C. **¹H NMR (500 MHz, CDCl₃)** δ 7.91 (d, *J* = 8.9 Hz, 1H), 7.88 – 7.85 (m, 1H), 7.83 – 7.80 (m, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.55 – 7.53 (m, 2H), 7.51 – 7.48 (m, 1H), 7.48 – 7.44 (m, 2H), 7.35 – 7.32 (m, 3H), 7.31 – 7.28 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.24 (s, 1H), 5.38 (s, 1H), 3.77 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 157.8, 156.3, 135.4, 133.4, 133.13, 133.10, 131.1, 130.9, 130.2, 129.5, 128.94, 128.87, 127.9, 127.5, 127.3, 126.9, 126.5, 126.2, 124.4, 124.0, 123.1, 120.9, 120.2, 112.9, 111.7, 111.4, 55.2, 51.5. **HRMS (ESI)** *m/z* Calcd. for C₂₉H₂₁O₂⁺ ([*M*-HNO₂]+H)⁺ = 401.1536, found: 401.1551. **[α]_D²⁵** (MeOH, *c* = 0.1) = -476. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 94% ee, *t*_{major} :

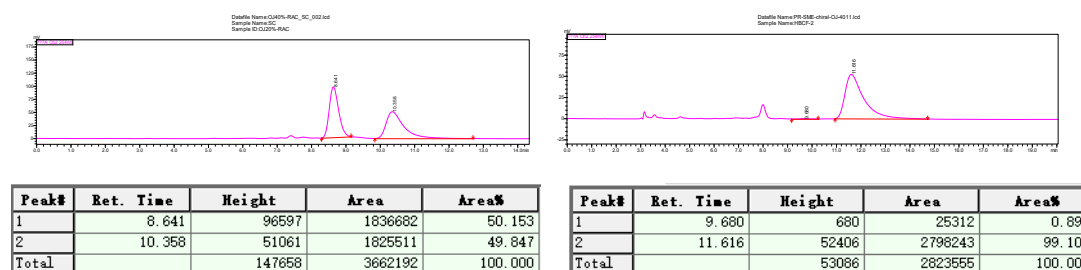
8.879 min, $t_{\min}$: 10.902 min.



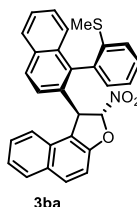
(aR,Z)-(2-(2-(2-bromo-2-nitrovinyl)naphthalen-1-yl)phenyl)(methyl)sulfane (1b)



Isolated according to the general procedure with a reaction time of 24 h (36.1 mg, 45% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). Z/E = 10:1. **MP** = 125.1–130.2 °C. **Rf**: 0.24 (petroleum ether/ethyl acetate = 60:1). **¹H NMR (500 MHz, CDCl₃)** δ 8.35 (s, 1H), 8.15 (d, J = 8.8 Hz, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.93 (dd, J = 8.3, 1.1 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.53 – 7.50 (m, 1H), 7.44 – 7.40 (m, 2H), 7.39 – 7.37 (m, 1H), 7.32 – 7.29 (m, 1H), 7.14 (dd, J = 7.5, 1.5 Hz, 1H), 2.33 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 141.6, 139.0, 136.5, 135.0, 134.4, 132.1, 130.7, 129.5, 129.3, 128.3, 128.2, 128.0, 127.5, 127.1, 126.8, 125.0, 124.9, 124.5, 15.4. **HRMS (ESI)** m/z Calcd. for $^+$ ([M+H] $^+$) = 384.0230, found: 384.0237. **$[\alpha]_D^{25}$** (DCM, c = 0.1) = +114. **HPLC analysis** (Chiralpak OJ, Hexane/Isopropanol (60/40), 1 mL/min, 30 °C, 254 nm) indicated 98% ee , t_{major} : 11.616 min, t_{min} : 9.680 min.

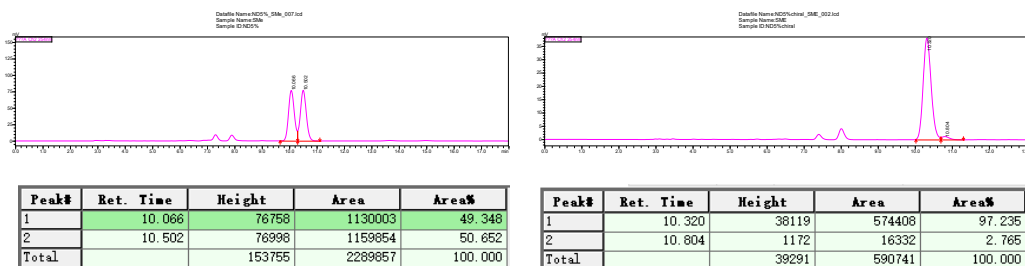


(1R,2R)-1-((aS)-1-(2-(methylthio)phenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-b]furan (3ba)

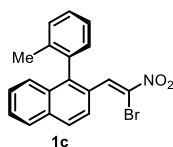


Prepared according to the general procedure with a reaction time of 24 h as beige foam (43.0 mg, 46% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). dr = 12.5:1. **Rf**: 0.13 (petroleum ether/ethyl acetate = 60:1). **MP** = 120.8–126.3 °C. **¹H NMR (500 MHz, CDCl₃)** δ 7.92 (d, J = 8.9 Hz, 1H), 7.88 (dd, J = 6.7, 2.1 Hz, 1H), 7.83 (d, J = 8.0, 1H), 7.71 (d, J = 8.7 Hz,

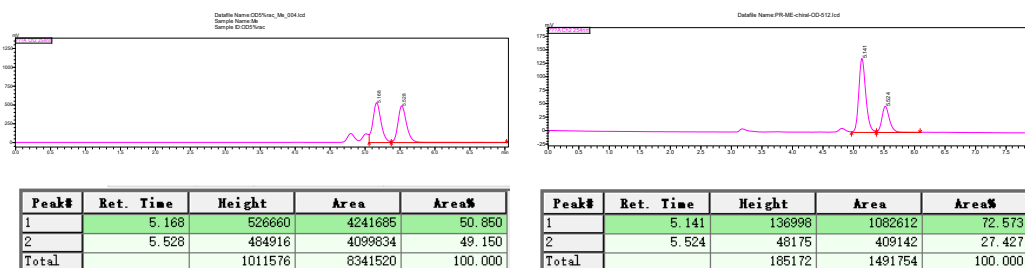
1H), 7.64 – 7.59 (m, 2H), 7.53 – 7.51 (m, 1H), 7.50 – 7.49 (m, 2H), 7.49 – 7.47 (m, 2H), 7.47 – 7.46 (m, 1H), 7.39 – 7.37 (m, 2H), 7.36 – 7.33 (m, 1H), 6.80 (d, $J = 8.6$ Hz, 1H), 6.54 (d, $J = 1.3$ Hz, 1H), 5.33 (s, 1H), 2.43 (s, 3H). **^{13}C NMR (126 MHz, CDCl_3)** δ 156.4, 140.3, 136.7, 135.4, 133.1, 132.7, 132.6, 131.2, 131.0, 129.7, 129.5, 129.5, 129.4, 129.0, 128.1, 127.5, 126.9, 126.53, 126.51, 124.9, 124.43, 124.37, 124.2, 123.0, 120.0, 112.1, 111.8, 51.3, 14.5. **HRMS (ESI)** m/z Calcd. for $\text{C}_{29}\text{H}_{21}\text{OS}^+$ ($[(\text{M}-\text{HNO}_2)+\text{H}]^+$) = 417.1308, found: 417.1297. $[\alpha]^{25}_{\text{D}}$ (MeOH, $c = 0.1$) = -549. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 94% ee, t_{major} : 10.320 min, t_{min} : 10.804 min.



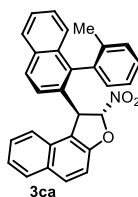
(aR,Z)-2-(2-bromo-2-nitrovinyl)-1-(o-tolyl)naphthalene (1c)



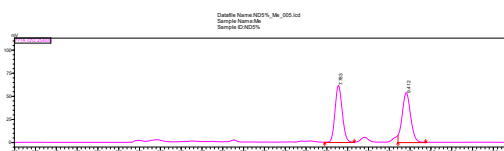
Isolated according to the general procedure with a reaction time of 16 h (30.8 mg, 42% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). Z/E = 15:1. **MP** = 69.2–71.8 °C. **Rf**: 0.22 (petroleum ether/ethyl acetate = 100:1). **^1H NMR (500 MHz, CDCl_3)** δ 8.33 (s, 1H), 8.15 (d, $J = 8.8$ Hz, 1H), 7.97 (d, $J = 8.8$ Hz, 1H), 7.94 (d, $J = 8.3$ Hz, 1H), 7.61 – 7.57 (m, 1H), 7.45 – 7.43 (m, 1H), 7.43 – 7.40 (m, 2H), 7.40 – 7.38 (m, 1H), 7.36 – 7.32 (m, 1H), 7.13 (dd, $J = 7.6, 1.4$ Hz, 1H), 1.92 (s, 3H). **^{13}C NMR (126 MHz, CDCl_3)** δ 143.5, 136.9, 136.5, 136.4, 134.4, 132.1, 130.5, 130.2, 129.0, 128.9, 128.2, 128.0, 127.7, 127.09, 127.06, 126.9, 126.2, 124.6, 19.7. **HRMS (ESI)** m/z Calcd. for $\text{C}_{19}\text{H}_{15}\text{BrNO}_2$ ($[\text{M}+\text{H}]^+$) = 368.0281, found: 368.0290. $[\alpha]^{25}_{\text{D}}$ (DCM, $c = 0.1$) = -16. **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 45% ee, t_{major} : 5.141 min, t_{min} : 5.524 min.



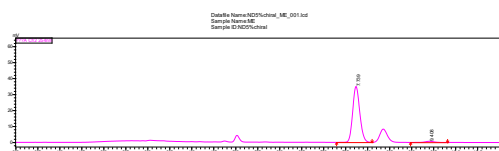
(1*R*,2*R*)-2-nitro-1-((*aS*)-1-(*o*-tolyl)naphthalen-2-yl)-1,2-dihydronaphtho[2,1-*b*]furan (3ca)



Prepared according to the general procedure with a reaction time of 16 h as pale pink foam (36.8 mg, 43% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* = 4:1. **Rf**: 0.16 (petroleum ether/ethyl acetate = 100:1). **MP** = 82.9-84.4 °C. **¹H NMR (500 MHz, CDCl₃)** δ 7.93 (d, *J* = 8.9 Hz, 1H), 7.89 – 7.87 (m, 1H), 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.54 (d, *J* = 5.7 Hz, 1H), 7.52 – 7.49 (m, 3H), 7.48 (d, *J* = 9.1 Hz, 2H), 7.45 – 7.43 (m, 2H), 7.40 – 7.37 (m, 1H), 7.36 – 7.32 (m, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.07 (d, *J* = 1.6 Hz, 1H), 5.33 (d, *J* = 1.0 Hz, 1H), 2.14 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 156.4, 138.4, 138.3, 137.1, 133.1, 132.71, 132.69, 132.0, 131.4, 131.0, 130.9, 129.5, 129.0, 128.7, 128.0, 127.5, 126.93, 126.87, 126.5, 126.3, 124.5, 124.4, 124.2, 123.1, 119.9, 112.1, 111.7, 52.4, 20.2. **HRMS (ESI)** *m/z* Calcd. for C₂₉H₂₁O⁺ [(M-HNO₂)+H]⁺ = 385.1587, found: 385.1579. **[α]²⁵_D** (MeOH, *c* = 0.1) = -382. **HPLC analysis** (Chiralpak ND, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 95% ee, *t*_{major} : 7.739 min, *t*_{min} : 9.408 min.

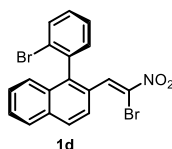


Peak#	Ret. Time	Height	Area	Area%
1	7.783	61510	739725	49.463
2	9.412	53687	755794	50.537
Total		115197	1495519	100.000

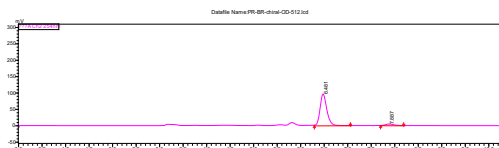
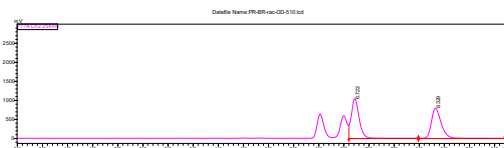


Peak#	Ret. Time	Height	Area	Area%
1	7.739	34984	393644	97.503
2	9.408	713	10080	2.497
Total		35697	403724	100.000

(*aR,Z*)-2-(2-bromo-2-nitrovinyl)-1-(2-bromophenyl)naphthalene (1d)



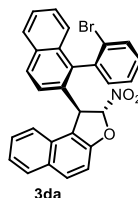
Isolated according to the general procedure with a reaction time of 24 h (40.4 mg, 47% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *Z/E* > 20:1. **MP** = 82.6-87.5 °C. **Rf**: 0.22 (petroleum ether/ethyl acetate = 100:1). **¹H NMR (500 MHz, CDCl₃)** δ 8.31 (s, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.50 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.42 – 7.39 (m, 1H), 7.38 – 7.36 (m, 1H), 7.28 – 7.26 (m, 1H). **¹³C NMR (126 MHz, CDCl₃)** δ 142.0, 137.9, 136.0, 134.3, 133.3, 133.2, 132.4, 131.9, 131.8, 130.4, 129.8, 128.4, 128.2, 128.0, 127.8, 127.2, 126.7, 124.5. **HRMS (ESI)** *m/z* Calcd. for C₁₈H₁₂Br₂NO₂⁺ ([M+H]⁺) = 431.9229, found: 431.9230. **[α]²⁵_D** (DCM, *c* = 0.1) = -11. **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 90% ee, *t*_{major} : 6.481 min, *t*_{min} : 7.887 min.



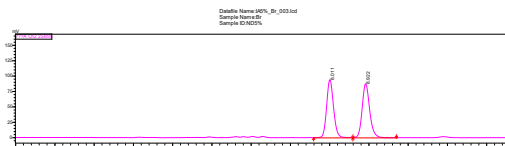
Peak#	Ret. Time	Height	Area	Area%
1	6.722	1040621	11243389	51.666
2	8.329	787707	10518455	48.334
Total		1828327	21761845	100.000

Peak#	Ret. Time	Height	Area	Area%
1	6.481	96482	963231	94.773
2	7.887	4548	53127	5.227
Total		101031	1016358	100.000

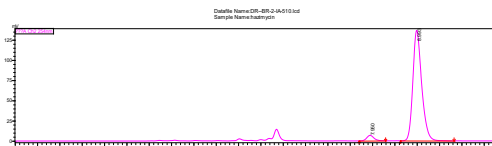
(1*R*,2*R*)-1-((*aS*)-1-(2-bromophenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan (3da)



Prepared according to the general procedure with a reaction time of 24 h as pale pink foam (43.0 mg, 43% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* = 10:1. **Rf**: 0.13 (petroleum ether/ethyl acetate = 100:1). **MP** = 110.1-117.0 °C. **¹H NMR (500 MHz, CDCl₃)** δ 7.91 (d, *J* = 8.9 Hz, 1H), 7.88 – 7.85 (m, 1H), 7.83 – 7.80 (m, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.55 – 7.53 (m, 2H), 7.51 – 7.48 (m, 1H), 7.48 – 7.44 (m, 2H), 7.35 – 7.32 (m, 3H), 7.31 – 7.28 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.24 (s, 1H), 5.38 (s, 1H), 3.77 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 156.5, 138.9, 138.1, 133.7, 133.0, 132.3, 132.2, 131.4, 131.0, 130.9, 130.3, 129.6, 129.5, 129.1, 128.3, 128.0, 127.6, 127.0, 126.6, 126.5, 126.3, 124.5, 124.1, 122.9, 119.4, 111.9, 111.5, 51.8. **HRMS (ESI)** *m/z* Calcd. for C₂₈H₁₈BrO⁺ ([M-HNO₂]+H)⁺ = 449.0536, found: 449.0524. **[α]_D²⁵** (MeOH, *c* = 0.1) = -412. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 92% ee, *t*_{major} : 8.993 min, *t*_{min} : 7.950 min.

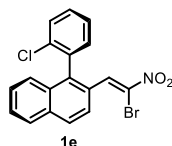


Peak#	Ret. Time	Height	Area	Area%
1	8.011	94174	1152702	49.726
2	8.922	87525	1165402	50.274
Total		181699	2318104	100.000



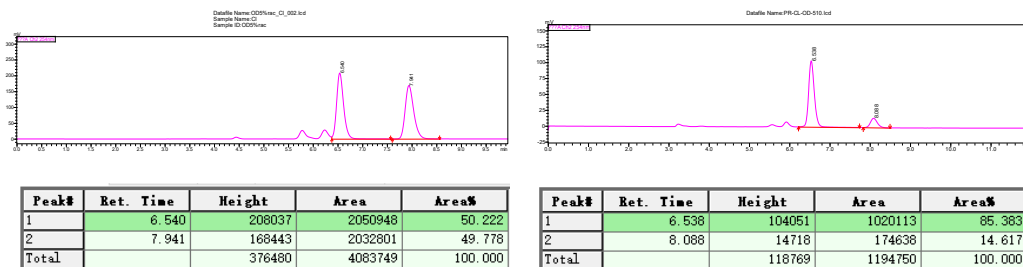
Peak#	Ret. Time	Height	Area	Area%
1	7.950	6775	75375	3.856
2	8.993	136645	1879385	96.144
Total		143420	1954760	100.000

(*aR,Z*)-2-(2-bromo-2-nitrovinyl)-1-(2-chlorophenyl)naphthalene (1e)

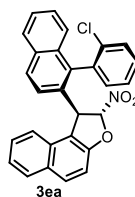


Isolated according to the general procedure with a reaction time of 24 h (33.8 mg, 43% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *Z/E* > 20:1. **Rf**: 0.20 (petroleum ether/ethyl acetate = 100:1). **MP** = 98.1-100.2 °C. **¹H NMR (500 MHz, CDCl₃)** δ 8.33 (s, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.51 – 7.47 (m, 1H), 7.47 – 7.42 (m, 2H), 7.41 – 7.38 (m, 1H), 7.27 (dd, *J* = 7.5, 1.8 Hz, 1H). **¹³C NMR (126 MHz, CDCl₃)** δ 140.3, 136.0, 135.9, 134.32, 134.26, 132.0, 131.9, 130.3, 130.1, 129.9, 128.5, 128.2, 128.0, 127.4, 127.3, 127.2, 126.7, 124.5. **HRMS (ESI)** *m/z* Calcd. for C₁₈H₁₁BrClNNaO₂⁺ ([M+Na]⁺) = 409.9554, found: 409.9558. **[α]_D²⁵** (DCM, *c* = 0.1) = +104.

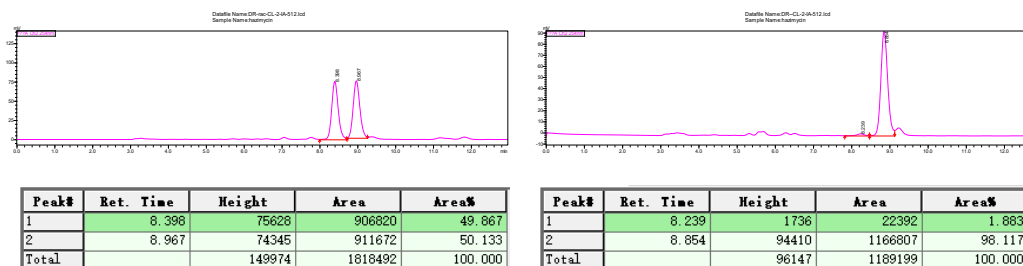
HPLC analysis (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 70% ee, t_{major} : 6.538 min, t_{min} : 8.088 min.



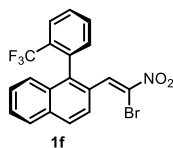
(1*R*,2*R*)-1-((*aS*)-1-(2-chlorophenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan (3ea)



Prepared according to the general procedure with a reaction time of 24 h as pale orange foam (40.9 mg, 45% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* = 14.3:1. **Rf**: 0.13 (petroleum ether/ethyl acetate = 100:1). **MP** = 105.6–109.0 °C. **¹H NMR (500 MHz, CDCl₃)** δ 7.93 (d, J = 8.9 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.84 – 7.81 (m, 1H), 7.75 (dd, J = 7.8, 1.5 Hz, 1H), 7.70 (d, J = 8.6 Hz, 1H), 7.68 – 7.66 (m, 1H), 7.63 – 7.59 (m, 1H), 7.59 – 7.56 (m, 1H), 7.53 – 7.50 (m, 1H), 7.48 (d, J = 4.9 Hz, 1H), 7.46 (dd, J = 6.8, 1.4 Hz, 1H), 7.41 – 7.39 (m, 1H), 7.37 – 7.34 (m, 2H), 7.34 – 7.31 (m, 1H), 6.73 (d, J = 8.7 Hz, 1H), 6.21 (d, J = 1.3 Hz, 1H), 5.32 (s, 1H). **¹³C NMR (126 MHz, CDCl₃)** δ 156.5, 136.8, 136.3, 135.7, 133.0, 132.6, 132.4, 131.4, 131.0, 130.9, 130.6, 130.2, 129.6, 129.4, 129.1, 128.0, 127.6, 127.0, 126.6, 126.4, 124.5, 124.1, 122.9, 119.4, 111.9, 111.7, 51.8. **HRMS (ESI)** m/z Calcd. for C₂₈H₁₈ClO⁺ [(M-HNO₂)+H]⁺ = 405.1041, found: 405.1032. **[α]²⁵_D** (MeOH, c = 0.1) = -416. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 96% ee, t_{major} : 8.854 min, t_{min} : 8.239 min.

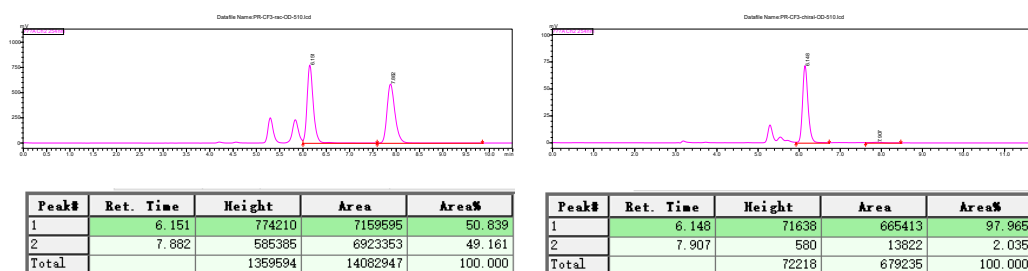


(*aR*,*Z*)-2-(2-bromo-2-nitrovinyl)-1-(2-(trifluoromethyl)phenyl)naphthalene (1f)

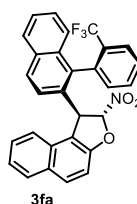


Isolated according to the general procedure with a reaction time of 24 h (35.9 mg, 43% yield)

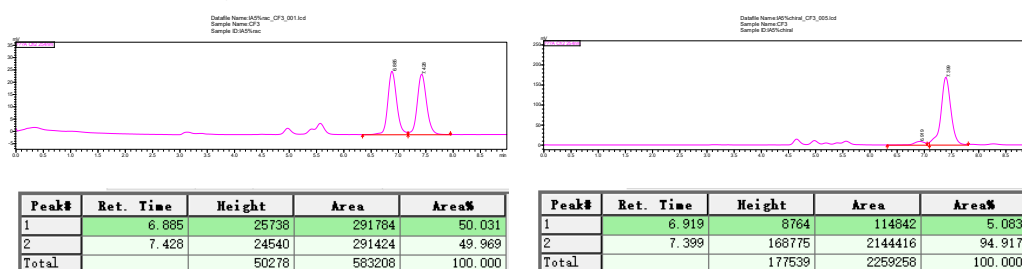
after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). Z/E = 10:1. **MP** = 87.4–91.2 °C. **Rf**: 0.18 (petroleum ether/ethyl acetate = 100:1). **¹H NMR (500 MHz, CDCl₃)** δ 8.27 (s, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.73 – 7.69 (m, 1H), 7.69 – 7.65 (m, 1H), 7.60 – 7.56 (m, 1H), 7.44 – 7.40 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.23 (d, *J* = 8.5 Hz, 1H). **¹³C NMR (126 MHz, CDCl₃)** δ 140.1, 135.9, 133.9, 132.6, 132.2, 132.1, 129.8 (q, *J*_{C-F} = 24.2 Hz), 129.7, 129.1, 128.6, 128.0, 127.9, 127.5, 127.2, 127.0, 126.8 (q, *J*_{C-F} = 5.1 Hz), 124.2, 123.6 (q, *J*_{C-F} = 219.2 Hz). **HRMS (ESI)** *m/z* Calcd. for ⁺ ([M+H]⁺) = 384.0230, found: 384.0237. **[α]_D²⁵** (DCM, *c* = 0.1) = -26. **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 96% ee, *t*_{major} : 6.148 min, *t*_{min} : 7.907 min.



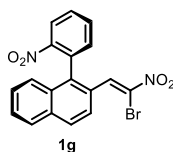
(1*R*,2*R*)-2-nitro-1-((*aS*)-1-(2-(trifluoromethyl)phenyl)naphthalen-2-yl)-1,2-dihydronaphtho[2,1-*b*]furan (3fa)



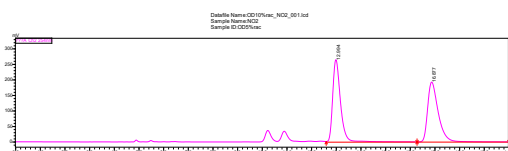
Prepared according to the general procedure with a reaction time of 24 h as pale pink foam (23.6 mg, 24% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* > 20:1 **Rf**: 0.08 (petroleum ether/ethyl acetate = 100:1). **MP** = 94.7–100.2 °C. **¹H NMR (500 MHz, CDCl₃)** δ 8.06 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.81 – 7.79 (m, 1H), 7.77 – 7.73 (m, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.43 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.37 – 7.33 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.11 (d, *J* = 1.3 Hz, 1H), 5.25 (s, 1H). **¹³C NMR (126 MHz, CDCl₃)** δ 156.5, 136.5, 135.8, 132.8, 132.3, 131.5, 131.3 (q, *J* = 23.2 Hz), 131.0, 129.7, 129.4, 129.2, 129.1, 127.8, 127.5 (q, *J* = 2.9 Hz), 127.2, 126.6, 126.5, 124.4, 124.1 (q, *J* = 272.5 Hz), 123.9, 122.7, 119.6, 111.9, 111.5, 111.4, 51.9. **HRMS (ESI)** *m/z* Calcd. for C₂₉H₁₈F₃O⁺ [(M-HNO₂)+H]⁺ = 439.1304, found: 439.1290. **[α]_D²⁵** (MeOH, *c* = 0.1) = -425. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 90% ee, *t*_{major} : 7.399 min, *t*_{min} : 6.919 min.



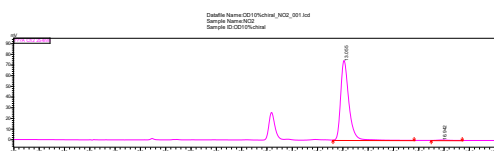
(aR,Z)-2-(2-bromo-2-nitrovinyl)-1-(2-nitrophenyl)naphthalene (1g)



Isolated according to the general procedure with a reaction time of 24 h (32.4 mg, 41% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *Z/E* = 10:1. **MP** = 106.4–110.8 °C. **Rf**: 0.24 (petroleum ether/ethyl acetate = 60:1). **¹H NMR (500 MHz, CDCl₃)** δ 8.31 (s, 1H), 8.22 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.74 – 7.70 (m, 1H), 7.60 – 7.55 (m, 1H), 7.44 – 7.40 (m, 1H), 7.37 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.26 – 7.24 (m, 1H). **¹³C NMR (126 MHz, CDCl₃)** δ 149.4, 138.4, 135.6, 134.1, 133.5, 133.0, 132.2, 131.5, 130.4, 130.2, 128.7, 128.5, 128.0, 127.6, 127.2, 125.7, 125.0, 124.6. **HRMS (ESI)** *m/z* Calcd. for C₁₈H₁₁BrN₂NaO₄⁺ ([*M*+Na]⁺) = 420.9794, found: 420.9806. **[α]_D²⁵** (DCM, *c* = 0.1) = +14. **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (90/10), 1 mL/min, 30 °C, 254 nm) indicated 98% ee, *t*_{major} : 13.055min, *t*_{min} : 16.942 min.

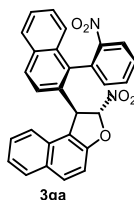


Peak#	Ret. Time	Height	Area	Area%
1	12.994	265033	5822348	50.369
2	16.877	192658	5737048	49.631
Total		457691	11559396	100.000

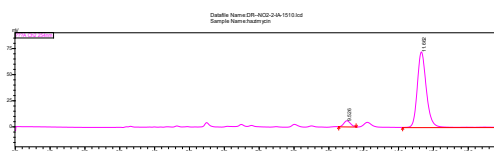
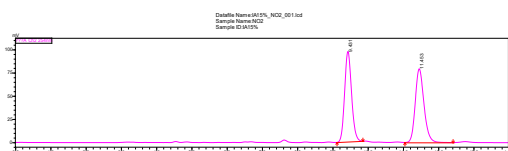


Peak#	Ret. Time	Height	Area	Area%
1	13.055	74723	1680911	99.353
2	16.942	399	10952	0.647
Total		75122	1691863	100.000

(1R,2R)-2-nitro-1-((aS)-1-(2-nitrophenyl)naphthalen-2-yl)-1,2-dihydronaphtho[2,1-b]furan (3ga)



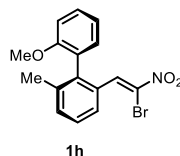
Prepared according to the general procedure with a reaction time of 24 h as beige foam (43.7 mg, 47% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* > 20:1 **Rf**: 0.18 (petroleum ether/ethyl acetate = 60:1). **MP** = 192.1–195.0 °C. **¹H NMR (500 MHz, CDCl₃)** δ 8.53 (d, *J* = 8.3 Hz, 1H), 8.00 – 7.93 (m, 2H), 7.91 (d, *J* = 7.4 Hz, 1H), 7.85 – 7.76 (m, 3H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.44 – 7.33 (m, 4H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.27 (s, 1H), 5.30 (s, 1H). **¹³C NMR (126 MHz, CDCl₃)** δ 156.8, 150.1, 135.3, 134.3, 133.7, 133.1, 132.2, 132.1, 131.8, 131.6, 131.0, 130.1, 129.6, 129.4, 129.3, 128.3, 127.7, 127.3, 126.6, 126.0, 125.4, 124.5, 124.0, 122.7, 118.7, 112.0, 111.1, 52.7. **HRMS (ESI)** *m/z* Calcd. for C₂₈H₁₈NO₃⁺ ([*M*-HNO₂]+H)⁺ = 416.1281, found: 416.1272. **[α]_D²⁵** (MeOH, *c* = 0.1) = -321. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (85/15), 1 mL/min, 30 °C, 254 nm) indicated 90% ee, *t*_{major} : 11.662 min, *t*_{min} : 9.526 min.



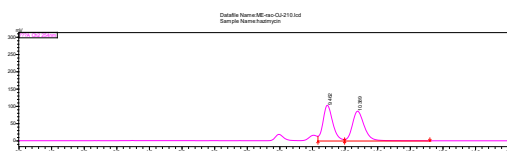
Peak#	Ret. Time	Height	Area	Area%
1	9.431	97282	1333277	49.248
2	11.453	79493	1373971	50.752
Total		176775	2707248	100.000

Peak#	Ret. Time	Height	Area	Area%
1	9.526	5682	73485	5.350
2	11.662	72228	1300002	94.650
Total		77910	1373487	100.000

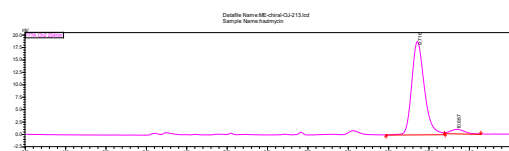
(a*S*,*Z*)-2-(2-bromo-2-nitrovinyl)-2'-methoxy-6-methyl-1,1'-biphenyl (1h)



Isolated according to the general procedure with a reaction time of 24 h (30.2 mg, 43% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *Z*/*E* = 10:1. **MP** = 50.8-55.0 °C. **Rf**: 0.18 (petroleum ether/ethyl acetate = 100:1). **¹H NMR (500 MHz, CDCl₃)** δ 8.19 (s, 1H), 7.86 – 7.81 (m, 1H), 7.43 – 7.40 (m, 2H), 7.40 – 7.38 (m, 1H), 7.06 – 7.02 (m, 1H), 7.01 (dd, *J* = 7.4, 1.9 Hz, 2H), 3.74 (s, 3H), 2.12 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 156.3, 140.3, 137.8, 137.3, 132.5, 131.1, 130.6, 130.0, 128.8, 127.2, 126.7, 126.1, 120.9, 111.2, 55.5, 20.3. **HRMS (ESI)** *m/z* Calcd. for C₁₆H₁₅BrNO₃⁺ ([*M*+H]⁺) = 348.0230, found: 348.0240. [*α*]_D²⁵ (DCM, *c* = 0.1) = +149. **HPLC analysis** (Chiralpak OJ, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 90% ee, *t*_{major} : 9.716 min, *t*_{min} : 10.687 min.

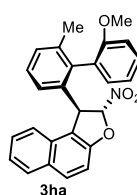


Peak#	Ret. Time	Height	Area	Area%
1	9.462	102643	2121565	49.729
2	10.389	85517	2144706	50.271
Total		188161	4266271	100.000

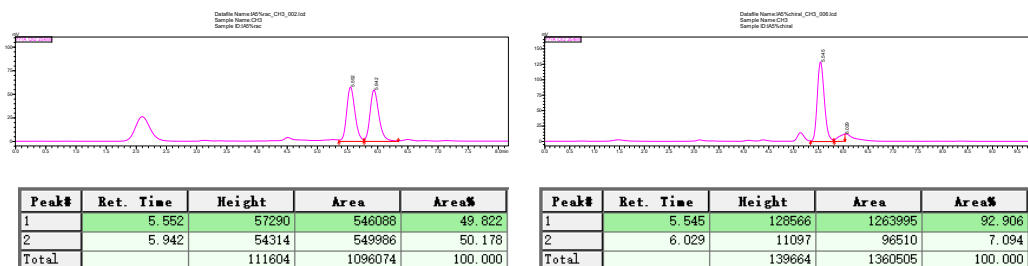


Peak#	Ret. Time	Height	Area	Area%
1	9.716	18757	405848	95.129
2	10.687	863	20780	4.871
Total		19620	426628	100.000

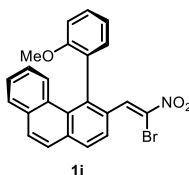
(1*R*,2*R*)-1-((a*R*)-2'-methoxy-6-methyl-[1,1'-biphenyl]-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan (3ha)



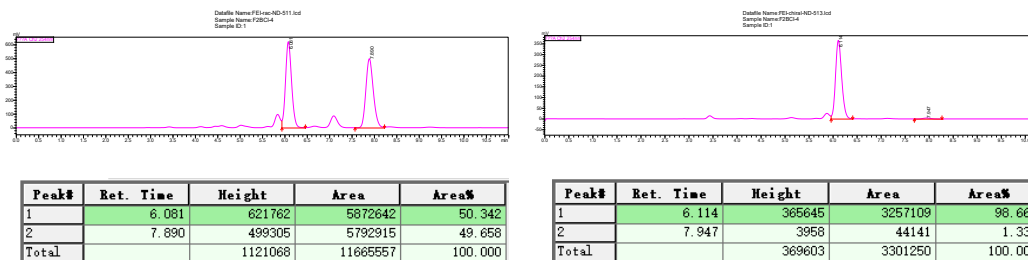
Prepared according to the general procedure with a reaction time of 24h as pale pink foam (38.9 mg, 47% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* > 20:1 **Rf**: 0.18 (petroleum ether/ethyl acetate = 100:1). **MP** = 110.2-117.9 °C. **¹H NMR (500 MHz, CDCl₃)** δ 7.89 – 7.85 (m, 2H), 7.51 – 7.47 (m, 1H), 7.42 – 7.39 (m, 2H), 7.38 – 7.35 (m, 2H), 7.34 – 7.32 (m, 1H), 7.24 – 7.22 (m, 1H), 7.21 – 7.18 (m, 1H), 7.13 – 7.09 (m, 1H), 7.08 – 7.05 (m, 1H), 6.48 (d, *J* = 7.9 Hz, 1H), 6.11 (d, *J* = 1.3 Hz, 1H), 5.17 (s, 1H), 3.81 (s, 3H), 2.11 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 157.0, 156.3, 138.1, 137.8, 136.2, 130.93, 130.89, 129.9, 129.74, 129.66, 129.5, 128.9, 128.1, 127.6, 127.4, 124.6, 124.3, 123.3, 121.1, 120.1, 112.9, 111.7, 111.3, 55.1, 51.3, 20.8. **HRMS (ESI)** *m/z* Calcd. for C₂₆H₂₁O₂⁺ ([*M*-HNO₂]+H]⁺) = 365.1536, found: 365.1527. [*α*]_D²⁵ (MeOH, *c* = 0.1) = -369. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 86% ee, *t*_{major} : 5.545 min, *t*_{min} : 6.029 min.



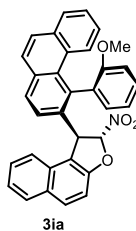
(aR,Z)-3-(2-bromo-2-nitrovinyl)-4-(2-methoxyphenyl)phenanthrene (1i)



Isolated according to the general procedure with a reaction time of 36 h (30.1 mg, 35% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **Z/E** = 10:1. **MP** = 104.2–108.2 °C. **Rf**: 0.18 (petroleum ether/ethyl acetate = 100:1). **¹H NMR (500 MHz, CDCl₃)** δ 8.28 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.48 – 7.44 (m, 1H), 7.17 – 7.14 (m, 1H), 7.13 – 7.11 (m, 1H), 7.11 – 7.07 (m, 1H), 7.04 (dd, *J* = 7.4, 1.8 Hz, 1H), 3.66 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 156.7, 138.53, 138.51, 135.0, 133.6, 130.9, 130.8, 130.6, 130.5, 129.9, 129.5, 129.2, 128.8, 128.6, 127.2, 127.1, 126.4, 126.0, 125.9, 122.0, 111.8, 55.6. **HRMS (ESI)** *m/z* Calcd. for C₂₃H₁₆BrNNaO₃⁺ ([M+Na]⁺) = 456.0206, found: 456.0206. **[α]_D²⁵** (DCM, *c* = 0.1) = -49. **HPLC analysis** (Chiralpak ND, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 97% ee, *t*_{major} : 6.114 min, *t*_{min} : 7.947 min.

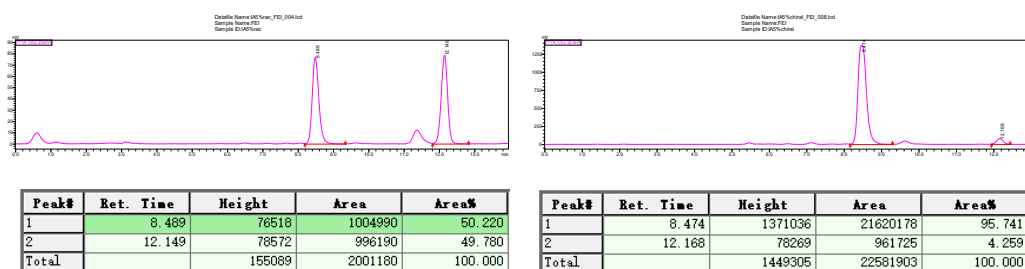


(1R,2R)-1-((aS)-4-(2-methoxyphenyl)phenanthren-3-yl)-2-nitro-1,2-dihydronaphtho[2,1-b]furan (3ia)

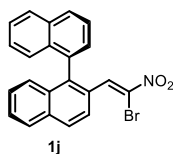


Prepared according to the general procedure with a reaction time of 36h as light brown foam (43.3 mg, 46% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **dr** > 20:1. **Rf**: 0.18 (petroleum ether/ethyl acetate = 100:1). **MP** = 108.3–113.1 °C. **¹H NMR (500 MHz,**

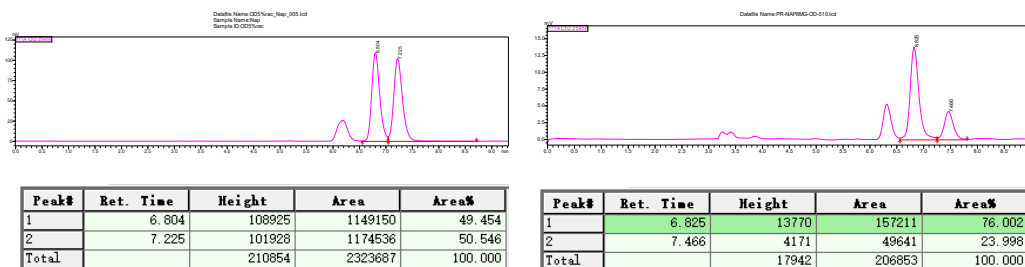
CDCl₃) δ 7.91 (d, J = 8.9 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.74 (d, J = 8.7 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.58 (d, J = 8.8 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.44 (dd, J = 7.6, 1.8 Hz, 1H), 7.33 – 7.31 (m, 1H), 7.31 – 7.29 (m, 2H), 7.29 – 7.26 (m, 1H), 7.26 – 7.23 (m, 1H), 7.19 (ddd, J = 8.7, 7.0, 1.6 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.29 (d, J = 1.4 Hz, 1H), 5.42 (s, 1H), 3.81 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 157.6, 156.3, 135.7, 135.5, 133.9, 133.4, 131.12, 131.10, 131.0, 130.6, 130.5, 130.1, 129.8, 129.7, 129.4, 129.0, 128.8, 128.3, 127.5, 127.3, 127.0, 126.1, 125.8, 125.0, 124.4, 123.2, 122.3, 121.0, 113.3, 112.1, 111.7, 55.4, 50.8. **HRMS (ESI)** m/z Calcd. for C₃₃H₂₃O₂⁺ ([M-HNO₂]+H)⁺ = 451.1693, found: 451.1681. **[α]²⁵_D** (MeOH, c = 0.1) = -580. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 92% ee, t_{major} : 8.474 min, t_{min} : 12.168 min.



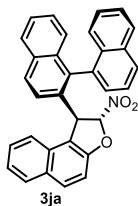
(aR,Z)-2-(2-bromo-2-nitrovinyl)-1,1'-binaphthalene (1j)



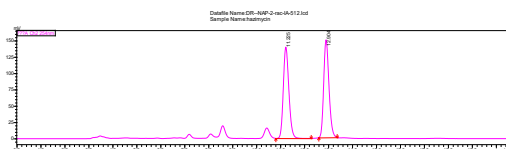
Isolated according to the general procedure with a reaction time of 16 h (35.5 mg, 44% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). Z/E = 6.7:1. **MP** = 116.7–119.6 °C. **Rf**: 0.20 (petroleum ether/ethyl acetate = 100:1). **¹H NMR (500 MHz, CDCl₃)** δ 8.22 (s, 1H), 8.19 (d, J = 8.8 Hz, 1H), 8.06 (d, J = 8.8 Hz, 1H), 8.03 (dd, J = 8.4, 1.1 Hz, 1H), 8.00 – 7.96 (m, 2H), 7.63 (dd, J = 8.3, 6.9 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.52 – 7.49 (m, 1H), 7.41 (dd, J = 6.9, 1.2 Hz, 1H), 7.32 – 7.29 (m, 3H), 7.16 (dd, J = 8.5, 1.0 Hz, 1H). **¹³C NMR (126 MHz, CDCl₃)** δ 141.9, 136.7, 134.5, 134.3, 133.7, 133.0, 132.4, 129.4, 129.2, 128.69, 128.66, 128.6, 128.2, 128.1, 127.9, 127.5, 127.0, 126.8, 126.4, 125.7, 125.4, 124.7. **HRMS (ESI)** m/z Calcd. for C₂₂H₁₄BrNNaO₂⁺ ([M+Na]⁺) = 426.0100, found: 426.0108. **[α]²⁵_D** (DCM, c = 0.1) = +125. **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 52% ee, t_{major} : 6.825 min, t_{min} : 7.466 min.



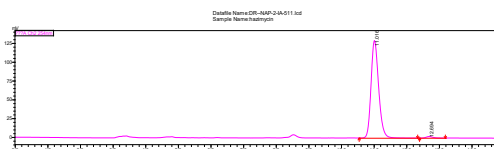
(1*R*,2*R*)-1-((a*S*)-[1,1'-binaphthalen]-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan (3ja)



Prepared according to the general procedure with a reaction time of 16 h as pale pink foam (46.1 mg, 49% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* = 5:1 **Rf**: 0.11 (petroleum ether/ethyl acetate = 100:1). **MP** = 106.3–109.1 °C. **¹H NMR (500 MHz, CDCl₃)** δ 8.11 – 8.08 (m, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.84 – 7.81 (m, 2H), 7.80 – 7.77 (m, 3H), 7.59 – 7.48 (m, 3H), 7.48 – 7.45 (m, 1H), 7.41 – 7.38 (m, 1H), 7.37 – 7.35 (m, 2H), 7.35 – 7.33 (m, 2H), 7.16 – 7.11 (m, 1H), 6.95 (d, *J* = 9.2 Hz, 1H), 5.92 (s, 1H), 5.32 (s, 1H). **¹³C NMR (126 MHz, CDCl₃)** δ 156.3, 137.5, 135.5, 134.0, 133.7, 133.51, 133.46, 133.0, 132.5, 131.2, 130.9, 130.2, 129.5, 129.2, 129.0, 128.7, 127.9, 127.5, 127.3, 126.8, 126.7, 126.5, 126.3, 125.6, 125.5, 124.4, 123.1, 119.4, 111.9, 111.6, 52.2. **HRMS (ESI)** *m/z* Calcd. for C₃₂H₂₁O⁺ ([*M*-HNO₂]+H)⁺ = 421.1587, found: 421.1570. **[α]_D²⁵** (MeOH, *c* = 0.1) = -405. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 98% ee, *t*_{major} : 11.016 min, *t*_{min} : 12.694 min.

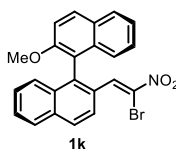


Peak#	Ret. Time	Height	Area	Area%
1	11.225	139767	2248746	49.578
2	12.904	149685	2287004	50.422
Total		289452	4535750	100.000



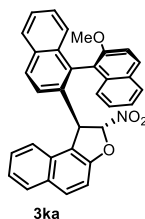
Peak#	Ret. Time	Height	Area	Area%
1	11.016	129549	2097619	98.669
2	12.694	2024	28297	1.331
Total		131573	2125916	100.000

(a*R*,*Z*)-3-(2-bromo-2-nitrovinyl)-4-(2-methoxyphenyl)phenanthrene (1k)

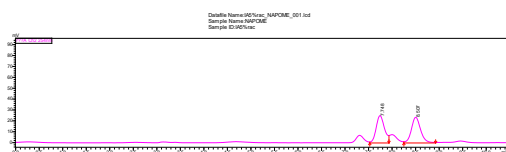


Isolated according to the general procedure with a reaction time of 36 h (40.7 mg, 47% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *Z/E* = 20:1. **MP** = 111.7–114.6 °C. **Rf**: 0.18 (petroleum ether/ethyl acetate = 100:1). **¹H NMR (500 MHz, CDCl₃)** δ 8.26 (s, 1H), 8.21 (d, *J* = 8.7 Hz, 1H), 8.08 – 8.04 (m, 2H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.90 (m, 1H), 7.56 (ddd, *J* = 8.1, 6.5, 1.5 Hz, 1H), 7.46 (d, *J* = 9.1 Hz, 1H), 7.36 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.28 – 7.26 (m, 1H), 7.26 – 7.22 (m, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 3.78 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 154.7, 138.6, 137.0, 134.5, 133.5, 132.8, 131.1, 129.1, 129.0, 128.7, 128.3, 128.2, 128.0, 127.8, 127.2, 127.1, 126.9, 124.9, 124.7, 124.0, 118.8, 113.2, 56.4. **HRMS (ESI)** *m/z* Calcd. for C₂₃H₁₆BrNNaO₃⁺ ([*M*+Na]⁺) = 456.0206, found: 456.0213. **[α]_D²⁵** (DCM, *c* = 0.1) = -30.

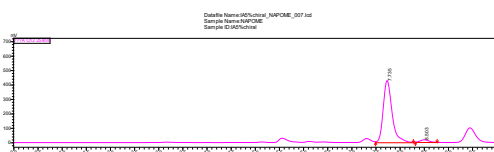
(1*R*,2*R*)-1-((*aS*)-2'-methoxy-[1,1'-binaphthalen]-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan (3ka)



Prepared according to the general procedure with a reaction time of 36h as pale pink foam (44.9 mg, 48% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* = 5:1. **Rf**: 0.18 (petroleum ether/ethyl acetate = 100:1). **MP** = 109.0-112.1 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 9.1 Hz, 1H), 8.02 – 7.98 (m, 1H), 7.89 – 7.82 (m, 3H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.59 (d, *J* = 9.1 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.46 – 7.43 (m, 3H), 7.32 – 7.28 (m, 4H), 7.19 – 7.16 (m, 2H), 6.80 (d, *J* = 8.7 Hz, 1H), 6.25 (d, *J* = 1.2 Hz, 1H), 5.13 (s, 1H), 3.88 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 156.5, 155.3, 134.3, 133.6, 133.5, 133.3, 133.2, 131.1, 130.8, 130.7, 129.5, 129.2, 129.0, 128.8, 128.6, 128.0, 127.1, 126.91, 126.86, 126.7, 126.3, 125.0, 124.32, 124.28, 123.9, 123.4, 119.7, 119.0, 113.1, 112.5, 111.7, 55.8, 51.5. **HRMS (ESI)** *m/z* Calcd. for C₃₃H₂₃O₂⁺ [(M-HNO₂)+H]⁺ = 451.1693, found: 451.1700. **[α]_D²⁵** (MeOH, *c* = 0.1) = -305. **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 93% ee, *t*_{major} : 7.735 min, *t*_{min} : 8.503 min.

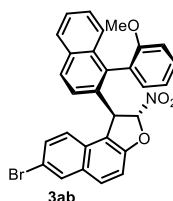


Peak#	Ret. Time	Height	Area	Area%
1	7.748	24917	304637	49.179
2	8.507	23418	314813	50.821
Total		48335	619450	100.000

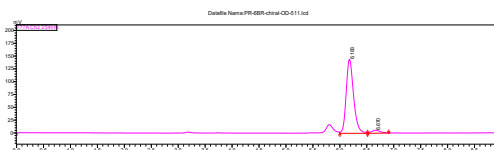
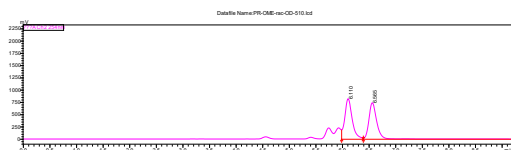


Peak#	Ret. Time	Height	Area	Area%
1	7.735	428493	5484919	96.421
2	8.503	16740	203619	3.579
Total		445232	5688538	100.000

(1*R*,2*R*)-7-bromo-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan (3ab)



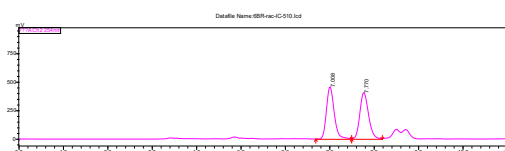
(*R*)-**1a** was isolated according to the general procedure with a reaction time of 24 h (33.0 mg, 43% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 92% ee, *t*_{major} : 6.183 min, *t*_{min} : 6.670 min.



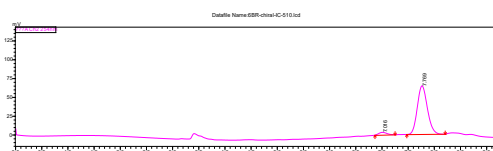
Peak#	Ret. Time	Height	Area	Area%
1	6.110	821020	7936087	51.493
2	6.565	738159	7475764	48.507
Total		1559178	15411851	100.000

Peak#	Ret. Time	Height	Area	Area%
1	6.183	144267	1361825	96.024
2	6.670	5412	56384	3.976
Total		149679	1418208	100.000

Prepared according to the general procedure with a reaction time of 24 h as pale pink foam (50.3 mg, 48% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* > 20:1. **Rf**: 0.27 (petroleum ether/ethyl acetate = 20:1). **MP** = 114.6-120.7 °C. **¹H NMR (500 MHz, CDCl₃)** δ 8.00 (d, *J* = 1.9 Hz, 1H), 7.82 – 7.80 (m, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.53 – 7.48 (m, 3H), 7.47 – 7.43 (m, 2H), 7.40 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.21 – 7.16 (m, 2H), 6.77 (s, 1H), 6.24 (d, *J* = 1.3 Hz, 1H), 5.35 (s, 1H), 3.75 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 157.8, 156.5, 135.5, 133.2, 133.1, 133.0, 132.0, 131.1, 130.9, 130.8, 130.31, 130.25, 129.0, 128.0, 127.9, 126.9, 126.7, 126.3, 126.1, 124.7, 123.8, 120.9, 120.7, 118.2, 112.9, 112.8, 111.4, 55.3, 51.4. **HRMS (ESI)** *m/z* Calcd. for C₂₉H₂₀BrO₂⁺ [(M-HNO₂)+H]⁺ = 479.0641, found: 479.0628. **[α]_D²⁵** (MeOH, *c* = 0.1) = -422. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 92% ee, *t*_{major} : 7.769 min, *t*_{min} : 7.016 min.

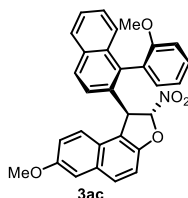


Peak#	Ret. Time	Height	Area	Area%
1	7.008	457004	5585716	50.182
2	7.770	406814	5545163	49.818
Total		863817	11130879	100.000

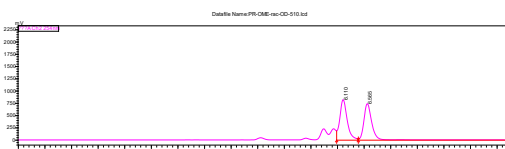


Peak#	Ret. Time	Height	Area	Area%
1	7.016	3476	36570	4.082
2	7.769	64308	859266	95.918
Total		67785	895837	100.000

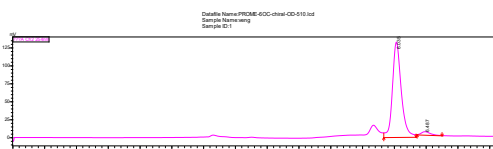
(1*R*,2*R*)-7-methoxy-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan (3*c*)



(*R*)-**1a** was isolated according to the general procedure with a reaction time of 3 days (35.8 mg, 47% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 94% ee, *t*_{major} : 6.035 min, *t*_{min} : 6.487 min.



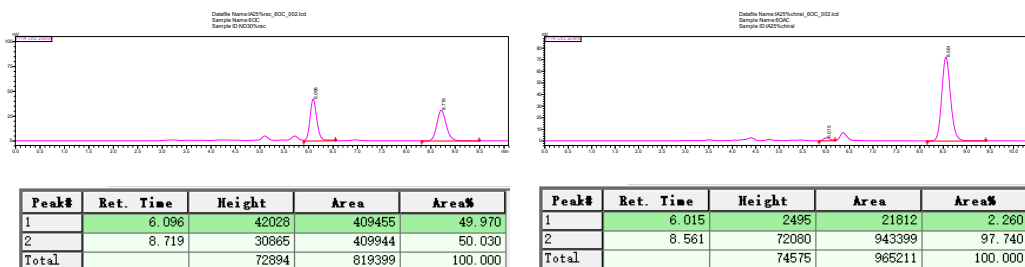
Peak#	Ret. Time	Height	Area	Area%
1	6.110	821020	7936087	51.493
2	6.565	738159	7475764	48.507
Total		1559178	15411851	100.000



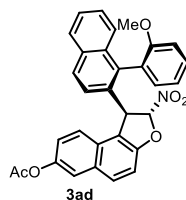
Peak#	Ret. Time	Height	Area	Area%
1	6.035	132562	1275959	96.745
2	6.487	4574	42930	3.255
Total		137136	1318889	100.000

Prepared according to the general procedure with a reaction time of 3 days as gray foam (45.3 mg, 47% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* = 14.3:1. **Rf**: 0.24 (petroleum ether/ethyl acetate = 20:1). **MP** = 108.9-114.4 °C. **¹H NMR (500 MHz, CDCl₃)**

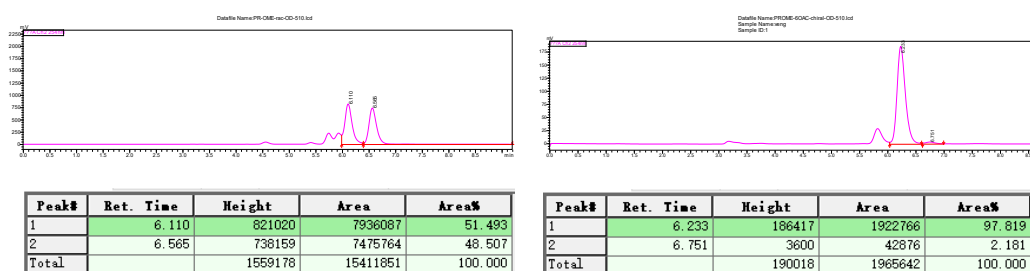
δ 7.80 – 7.76 (m, 2H), 7.66 (d, J = 8.7 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.51 – 7.46 (m, 3H), 7.43 – 7.39 (m, 2H), 7.28 – 7.26 (m, 1H), 7.20 – 7.17 (m, 2H), 7.16 (d, J = 2.5 Hz, 1H), 7.01 (dd, J = 9.0, 2.5 Hz, 1H), 6.77 (d, J = 8.6 Hz, 1H), 6.17 (d, J = 1.3 Hz, 1H), 5.31 (s, 1H), 3.85 (s, 3H), 3.75 (s, 3H). **^{13}C NMR (126 MHz, CDCl_3)** δ 157.8, 156.5, 154.8, 135.4, 133.4, 133.10, 133.07, 132.0, 131.1, 130.2, 129.5, 128.8, 127.9, 126.9, 126.5, 126.19, 126.17, 124.8, 124.5, 124.0, 120.9, 120.5, 120.2, 112.8, 112.0, 111.4, 107.2, 55.3, 55.2, 51.6. **HRMS (ESI)** m/z Calcd. for $\text{C}_{30}\text{H}_{23}\text{O}_3^+$ ($[(\text{M}-\text{HNO}_2)+\text{H}]^+$) : 431.1642, found: 431.1627. $[\alpha]_D^{25}$ (MeOH, c = 0.1) = -480. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (75/25), 1 mL/min, 30 °C, 254 nm) indicated 96% ee, t_{major} : 8.561 min, t_{min} : 6.015 min.



(1*R*,2*R*)-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan-7-yl acetate (3ad)

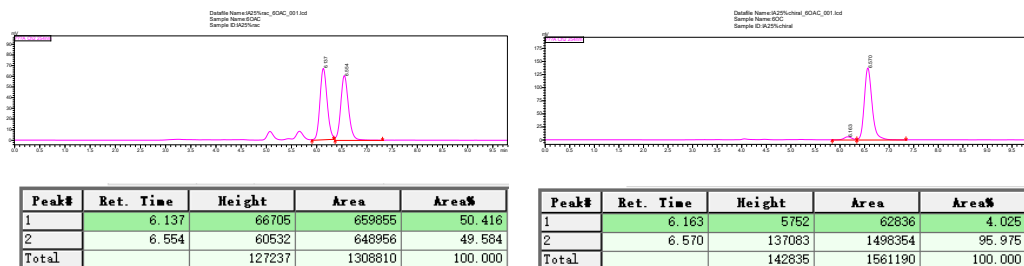


(*R*)-**1a** was isolated according to the general procedure with a reaction time of 60 h (32.2 mg, 42% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 96% ee, t_{major} : 6.233 min, t_{min} : 6.751 min.

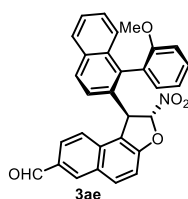


Prepared according to the general procedure with a reaction time of 60 h as gray foam (48.2 mg, 48% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* > 20:1 **Rf**: 0.20 (petroleum ether/ethyl acetate = 10:1). **MP** = 126.0–135.3 °C. **^1H NMR (500 MHz, CDCl_3)** δ 7.85 (d, J = 8.9 Hz, 1H), 7.83 – 7.80 (m, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.52 – 7.49 (m, 2H), 7.49 – 7.44 (m, 2H), 7.44 – 7.41 (m, 1H), 7.32 (d, J = 8.9 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.10 (dd, J = 9.0, 2.3 Hz, 1H), 6.80 (d, J = 8.6 Hz, 1H), 6.22 (d, J = 1.4 Hz, 1H), 5.34 (s, 1H), 3.74 (s, 3H), 2.31 (s, 3H). **^{13}C NMR (126 MHz, CDCl_3)** δ 169.6, 157.8, 156.2, 147.2, 135.4, 133.2, 133.13, 133.06, 131.2, 131.1, 130.7, 130.2, 129.0, 127.9, 127.6, 126.9, 126.6, 126.3, 126.1, 124.5, 123.9, 122.8, 120.9, 120.6, 119.7, 112.9, 112.5, 111.4, 55.2, 51.5, 21.1.

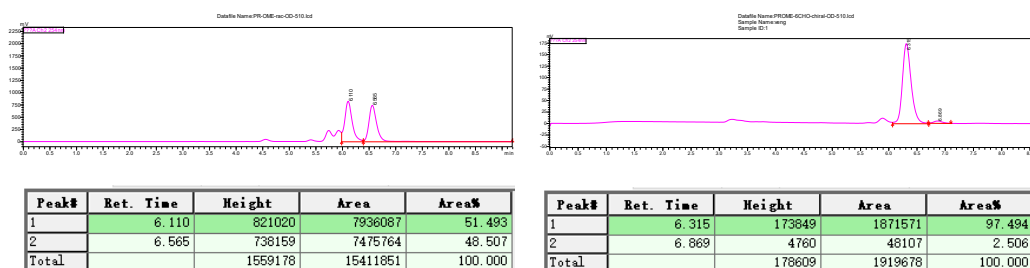
HRMS (ESI) m/z Calcd. for $C_{31}H_{23}O_4^+$ $[(M-HNO_2)+H]^+$ = 459.1591, found: 459.1579. $[\alpha]^{25}_D$ (MeOH, c = 0.1) = -586. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (75/25), 1 mL/min, 30 °C, 254 nm) indicated 92% ee, t_{major} : 6.570 min, t_{min} : 6.163 min.



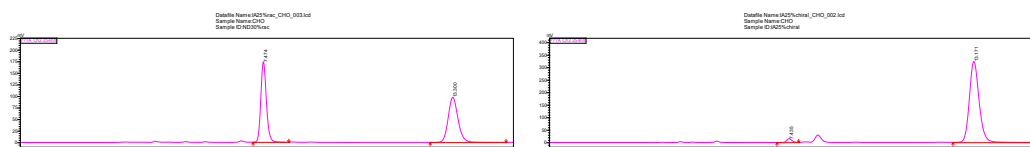
(1*R*,2*R*)-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan-7-carbaldehyde (3ae)



(*R*)-**1a** was isolated according to the general procedure with a reaction time of 4 days (32.1 mg, 42% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 95% ee, t_{major} : 6.315 min, t_{min} : 6.869 min.



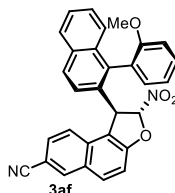
Prepared according to the general procedure with a reaction time of 4 days as light brown foam (46.3 mg, 49% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). dr = 20:1 **Rf**: 0.20 (petroleum ether/ethyl acetate = 10:1). **MP** = 115.2-128.0 °C. **¹H NMR (500 MHz, CDCl₃)** δ 10.04 (s, 1H), 8.33 (d, J = 1.6 Hz, 1H), 8.06 (d, J = 8.9 Hz, 1H), 7.83 – 7.79 (m, 2H), 7.68 (d, J = 8.7 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.55 – 7.51 (m, 3H), 7.50 – 7.47 (m, 1H), 7.46 – 7.42 (m, 1H), 7.39 (d, J = 8.6 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.18 (d, J = 8.4 Hz, 1H), 6.77 (d, J = 8.7 Hz, 1H), 6.28 (d, J = 1.5 Hz, 1H), 5.37 (s, 1H), 3.74 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 191.6, 158.7, 157.7, 135.6, 135.1, 133.2, 133.08, 133.06, 132.9, 132.8, 131.1, 130.4, 130.0, 129.1, 127.9, 126.9, 126.7, 126.4, 126.0, 124.8, 124.2, 123.6, 121.2, 121.0, 113.0, 112.9, 111.4, 55.3, 51.3. **HRMS (ESI)** m/z Calcd. for $C_{30}H_{21}O_3^+$ $[(M-HNO_2)+H]^+$ = 429.1485, found: 429.1491. $[\alpha]^{25}_D$ (MeOH, c = 0.1) = -679. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (75/25), 1 mL/min, 30 °C, 254 nm) indicated 95% ee, t_{major} : 13.171 min, t_{min} : 7.435 min.



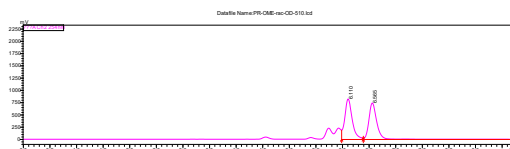
Peak#	Ret. Time	Height	Area	Area%
1	7.474	173526	2057727	50.114
2	13.300	97202	2046380	49.886
Total		270729	4106107	100.000

Peak#	Ret. Time	Height	Area	Area%
1	7.435	14355	164361	2.361
2	13.171	323546	6797478	97.639
Total		337901	6961839	100.000

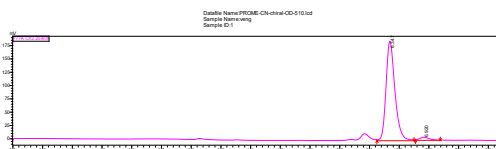
(1*R*,2*R*)-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan-7-carbonitrile (3af)



(*R*)-**1a** was isolated according to the general procedure with a reaction time of 48 h (30.7 mg, 40% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 94% ee, t_{major} : 6.347 min, t_{min} : 6.920 min.

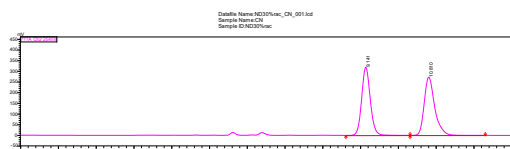


Peak#	Ret. Time	Height	Area	Area%
1	6.110	821020	7936087	51.493
2	6.565	738159	7475764	48.507
Total		1559178	15411851	100.000

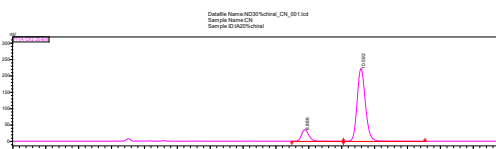


Peak#	Ret. Time	Height	Area	Area%
1	6.347	186345	1931660	97.126
2	6.920	5231	57167	2.874
Total		191576	1988827	100.000

Prepared according to the general procedure with a reaction time of 48 h as pale orange foam (47.1 mg, 50% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). $dr = 10:1$ **Rf**: 0.13 (petroleum ether/ethyl acetate = 20:1). **MP** = 123.6-130.1 °C. **¹H NMR (500 MHz, CDCl₃)** δ 8.22 (d, $J = 1.6$ Hz, 1H), 7.94 (d, $J = 8.7$ Hz, 1H), 7.81 (dd, $J = 7.3, 2.0$ Hz, 1H), 7.69 (d, $J = 8.7$ Hz, 1H), 7.61 – 7.57 (m, 1H), 7.55 (d, $J = 8.9$ Hz, 1H), 7.52 – 7.49 (m, 2H), 7.48 – 7.43 (m, 3H), 7.35 (d, $J = 8.6$ Hz, 1H), 7.28 (dd, $J = 7.5, 1.0$ Hz, 1H), 7.20 – 7.16 (m, 1H), 6.74 (d, $J = 8.7$ Hz, 1H), 6.28 (d, $J = 1.5$ Hz, 1H), 5.35 (s, 1H), 3.74 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 158.6, 157.7, 135.6, 135.0, 133.2, 133.1, 132.6, 132.0, 131.1, 131.0, 130.4, 129.7, 129.1, 128.1, 127.9, 126.9, 126.8, 126.5, 125.9, 124.3, 123.5, 121.2, 121.0, 119.0, 113.7, 112.9, 111.5, 107.9, 55.3, 51.2. **HRMS (ESI)** m/z Calcd. for C₃₀H₂₀NO₂⁺ [(M-HNO₂)+H]⁺ = 426.1489, found: 426.1473. $[\alpha]_D^{25}$ (MeOH, $c = 0.1$) = -527. **HPLC analysis** (Chiralpak ND, Hexane/Isopropanol (70/30), 1 mL/min, 30 °C, 254 nm) indicated 75% ee, t_{major} : 10.592 min, t_{min} : 8.886 min.

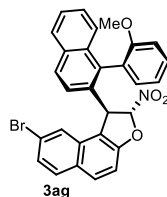


Peak#	Ret. Time	Height	Area	Area%
1	9.141	318764	5078981	49.027
2	10.810	272657	5280639	50.973
Total		591421	10359620	100.000

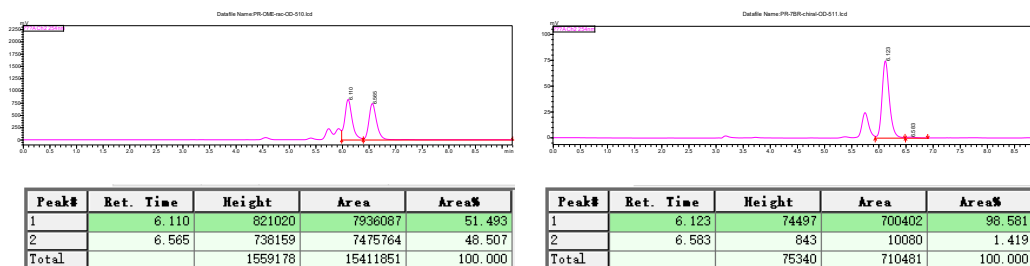


Peak#	Ret. Time	Height	Area	Area%
1	8.886	35251	542403	12.331
2	10.592	221899	3856216	87.669
Total		257150	4398619	100.000

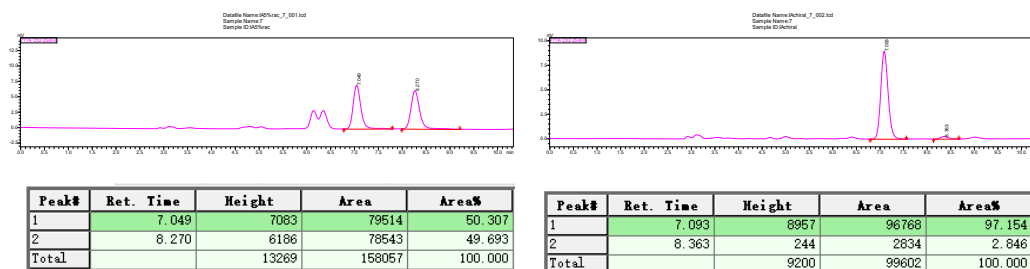
(1*R*,2*R*)-8-bromo-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan (3ag)



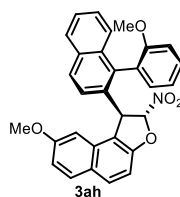
(*R*)-**1a** was isolated according to the general procedure with a reaction time of 24 h (32.9 mg, 43% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 97% ee, t_{major} : 6.123 min, t_{min} : 6.583 min.



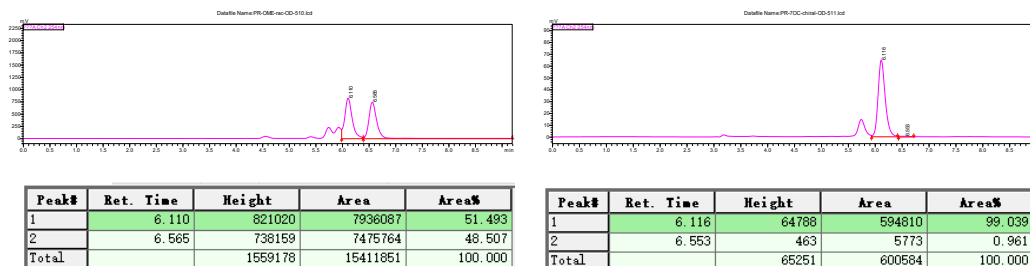
Prepared according to the general procedure with a reaction time of 24 h as pale pink foam (47.4 mg, 45% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* > 20:1 **Rf**: 0.24 (petroleum ether/ethyl acetate = 20:1). **MP** = 125.4–131.2 °C. **¹H NMR (500 MHz, CDCl₃)** δ 7.85 – 7.81 (m, 2H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.57 – 7.53 (m, 2H), 7.52 – 7.49 (m, 1H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.22 – 7.18 (m, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.26 (s, 1H), 5.27 (s, 1H), 3.78 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 157.6, 156.8, 135.2, 133.2, 133.0, 131.7, 131.1, 130.6, 130.4, 130.3, 129.2, 129.1, 128.0, 127.9, 127.0, 126.7, 126.4, 125.9, 125.4, 123.6, 122.0, 121.1, 120.2, 113.0, 112.2, 111.3, 55.3, 51.3. **HRMS (ESI)** *m/z* Calcd. for C₂₉H₂₀BrO₂⁺ [(M-HNO₂)+H]⁺ = 479.0641, found: 479.0628. **[α]_D²⁵** (MeOH, *c* = 0.1) = -469. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 94% ee, t_{major} : 7.093 min, t_{min} : 8.363 min.



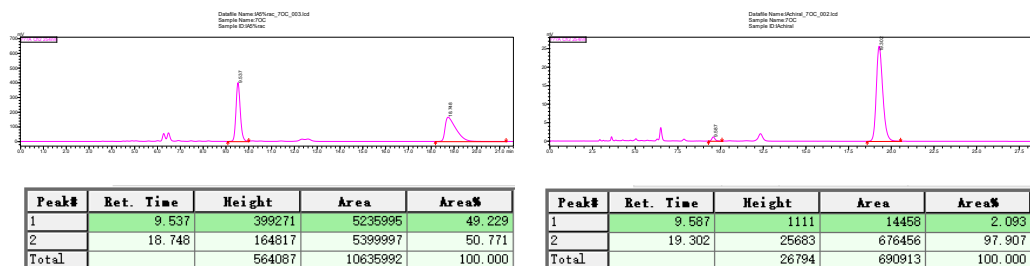
(1*R*,2*R*)-8-methoxy-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan (3ah)



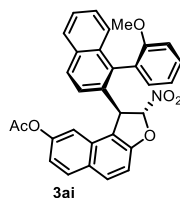
(*R*)-**1a** was isolated according to the general procedure with a reaction time of 48 h (31.6 mg, 41% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 98% ee, t_{major} : 6.116 min, t_{min} : 6.553 min.



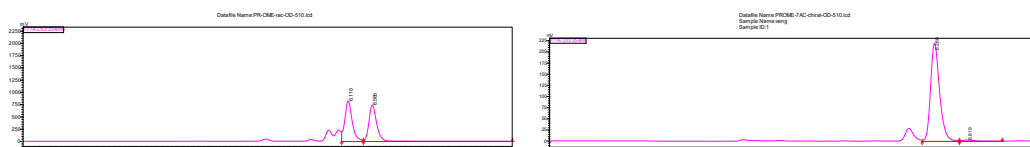
Prepared according to the general procedure with a reaction time of 48 h as beige foam (45.1 mg, 47% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). $dr > 20:1$. **Rf**: 0.24 (petroleum ether/ethyl acetate = 20:1). **MP** = 102.9–111.4 °C. **¹H NMR (500 MHz, CDCl₃)** δ 7.83 – 7.80 (m, 2H), 7.73 (d, J = 9.0 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.60 (ddd, J = 8.4, 7.5, 1.8 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.51 – 7.47 (m, 2H), 7.45 – 7.42 (m, 1H), 7.31 (d, J = 8.8 Hz, 1H), 7.24 – 7.20 (m, 2H), 6.98 (dd, J = 9.0, 2.5 Hz, 1H), 6.86 (d, J = 8.7 Hz, 1H), 6.55 (d, J = 2.5 Hz, 1H), 6.19 (d, J = 1.3 Hz, 1H), 5.30 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 158.9, 157.9, 156.8, 135.3, 133.20, 133.16, 133.0, 131.0, 130.9, 130.8, 130.5, 130.3, 129.0, 128.0, 126.9, 126.5, 126.3, 126.2, 123.9, 120.5, 119.4, 117.2, 113.0, 111.5, 109.0, 101.6, 55.3, 55.3, 51.2. **HRMS (ESI)** m/z Calcd. for C₃₀H₂₃O₃⁺ [(M-HNO₂)+H]⁺ : 431.1642, found: 431.1650. **[α]_D²⁵** (MeOH, c = 0.1) = -476. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 96% ee, t_{major} : 19.302 min, t_{min} : 9.587 min.



(1*R*,2*R*)-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan-8-yl acetate (**3ai**)



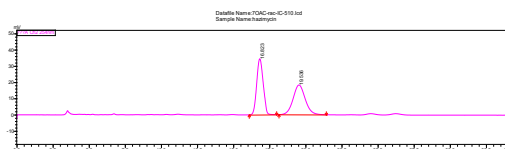
(*R*)-**1a** was isolated according to the general procedure with a reaction time of 60 h as gray foam (34.5 mg, 45% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 97% ee, t_{major} : 6.280 min, t_{min} : 6.819 min.



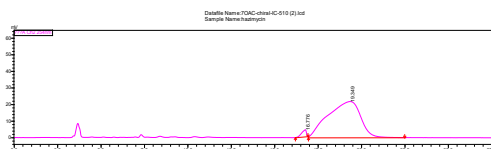
Peak#	Ret. Time	Height	Area	Area%
1	6.110	821020	7936087	51.493
2	6.565	738159	7475764	48.507
Total		1559178	15411851	100.000

Peak#	Ret. Time	Height	Area	Area%
1	6.280	219484	2246292	98.514
2	6.819	2460	33885	1.486
Total		221944	2280177	100.000

Prepared according to the general procedure with a reaction time of 60 h as gray foam (49.2 mg, 49% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* > 20:1. **Rf**: 0.20 (petroleum ether/ethyl acetate = 10:1). **MP** = 101.1–108.6 °C. **¹H NMR (500 MHz, CDCl₃)** δ 7.88 (d, *J* = 8.9 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.83 – 7.80 (m, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.52 – 7.48 (m, 2H), 7.48 – 7.46 (m, 1H), 7.45 – 7.40 (s, 2H), 7.27 – 7.24 (m, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.10 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.21 (d, *J* = 1.4 Hz, 1H), 5.30 (s, 1H), 3.75 (s, 3H), 2.29 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 169.0, 157.7, 156.9, 149.7, 135.5, 133.2, 133.1, 133.0, 131.3, 131.0, 130.4, 130.3, 130.2, 129.0, 128.8, 128.0, 126.9, 126.5, 126.2, 126.0, 123.9, 120.9, 120.3, 119.7, 113.8, 112.9, 111.5, 111.3, 55.2, 51.5, 21.2. **HRMS (ESI)** *m/z* Calcd. for C₃₁H₂₂NaO₄⁺ [(M-HNO₂)+Na]⁺: 481.1410, found: 481.1389. **[α]_D²⁵** (MeOH, *c* = 0.1) = -664. **HPLC analysis** (Chiralpak IC, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 94% ee, *t*_{major}: 19.349 min, *t*_{min}: 16.776 min.

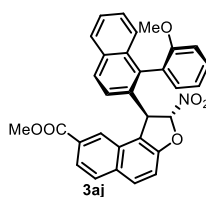


Peak#	Ret. Time	Height	Area	Area%
1	16.823	34492	1077034	50.350
2	19.536	18271	1062062	49.650
Total		52763	2139096	100.000

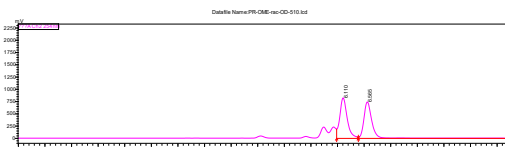


Peak#	Ret. Time	Height	Area	Area%
1	16.776	4186	77940	2.667
2	19.349	21740	2844573	97.333
Total		25926	2922513	100.000

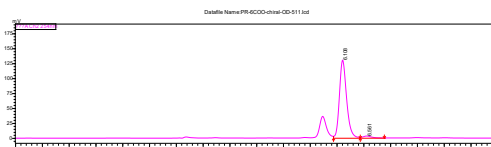
methyl (1*R*,2*R*)-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan-8-carboxylate (3aj)



(*R*)-**1a** was isolated according to the general procedure with a reaction time of 48 h (32.8 mg, 43% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 94% ee, *t*_{major}: 6.108 min, *t*_{min}: 6.561 min.



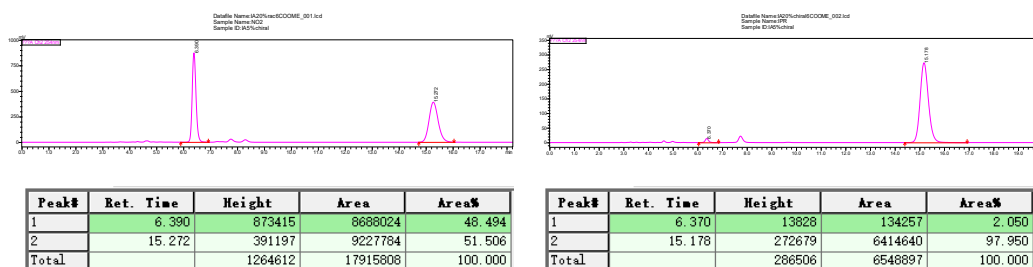
Peak#	Ret. Time	Height	Area	Area%
1	6.110	821020	7936087	51.493
2	6.565	738159	7475764	48.507
Total		1559178	15411851	100.000



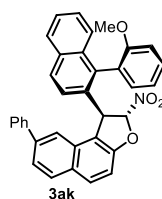
Peak#	Ret. Time	Height	Area	Area%
1	6.108	130457	1214716	97.136
2	6.561	3273	35815	2.864
Total		133730	1250531	100.000

Prepared according to the general procedure with a reaction time of 48 h as beige foam (42.1

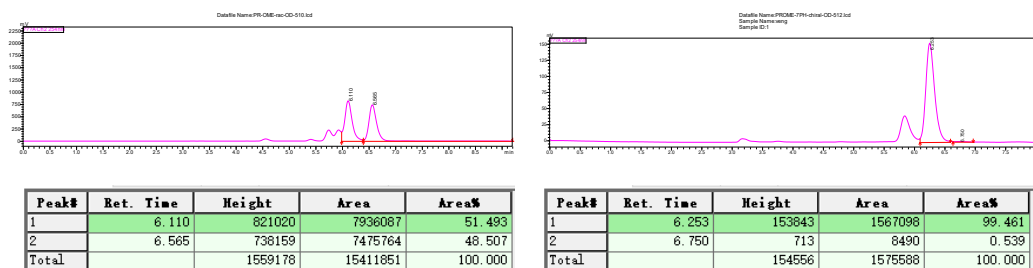
mg, 42% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* > 20:1 **Rf**: 0.27 (petroleum ether/ethyl acetate = 10:1). **MP** = 181.7-187.2 °C. **¹H NMR (500 MHz, CDCl₃)** δ 8.62 (d, *J* = 1.6 Hz, 1H), 8.01 (d, *J* = 8.9 Hz, 1H), 7.93 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.82 – 7.79 (m, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.53 – 7.51 (m, 2H), 7.51 – 7.47 (m, 2H), 7.45 – 7.41 (m, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.26 (d, *J* = 1.5 Hz, 1H), 5.36 (s, 1H), 3.93 (s, 3H), 3.75 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 166.9, 158.0, 157.7, 135.5, 133.2, 133.1, 133.0, 132.8, 132.0, 131.8, 131.1, 130.3, 130.0, 129.0, 127.9, 127.0, 126.9, 126.6, 126.3, 126.1, 126.0, 123.7, 123.3, 120.9, 120.7, 112.9, 112.6, 111.4, 55.2, 52.2, 51.3. **HRMS (ESI)** *m/z* Calcd. for C₃₁H₂₃O₄⁺ [(M-HNO₂)+H]⁺ = 459.1591, found: 459.1573. **[α]_D²⁵** (MeOH, *c* = 0.1) = -516. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (80/20), 1 mL/min, 30 °C, 254 nm) indicated 96% ee, *t*_{major} : 15.178 min, *t*_{min} : 6.370 min.



(1*R*,2*R*)-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-8-phenyl-1,2-dihydronaphtho[2,1-*b*]furan (3ak)

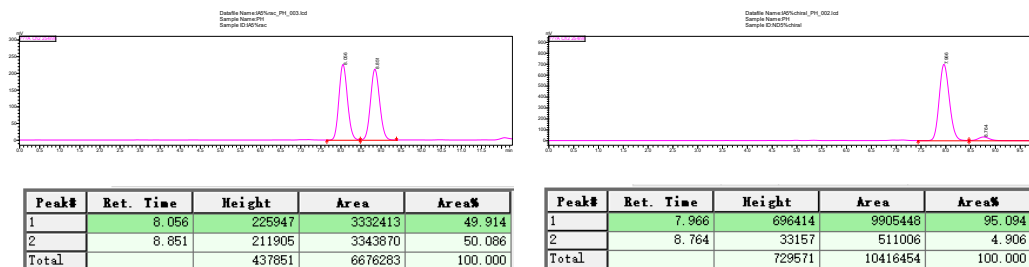


(*R*)-**1a** was isolated according to the general procedure with a reaction time of 24 h (30.4 mg, 40% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 99% ee, *t*_{major} : 6.253 min, *t*_{min} : 6.750 min.

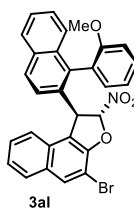


Prepared according to the general procedure with a reaction time of 24 h as pink foam (58.6 mg, 56% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). *dr* = 12.5:1 **Rf**: 0.24 (petroleum ether/ethyl acetate = 20:1). **MP** = 98.3-111.5 °C. **¹H NMR (500 MHz, CDCl₃)** δ 7.93 (d, *J* = 3.4 Hz, 1H), 7.91 (d, *J* = 3.0 Hz, 1H), 7.79 (d, *J* = 8.4, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.59 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.57 (d, *J* = 1.5 Hz, 1H), 7.55 – 7.54 (m, 2H), 7.52 – 7.49 (m, 2H), 7.48 – 7.46 (m, 3H), 7.45 (d, *J* = 1.6 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.40 – 7.37

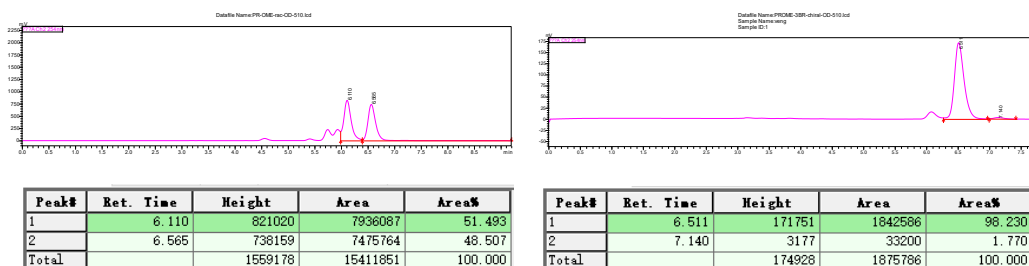
(m, 1H), 7.32 – 7.28 (m, 1H), 7.23 (d, $J = 8.3$ Hz, 1H), 6.92 (d, $J = 8.7$ Hz, 1H), 6.25 (d, $J = 1.3$ Hz, 1H), 5.41 (s, 1H), 3.79 (s, 3H). **^{13}C NMR (126 MHz, CDCl_3)** δ 157.8, 156.5, 140.8, 140.3, 135.0, 133.4, 133.2, 133.0, 131.7, 130.8, 130.3, 130.0, 129.8, 129.4, 129.0, 128.8, 128.7, 127.9, 127.8, 127.7, 127.6, 126.9, 126.5, 126.2, 124.3, 123.8, 121.2, 121.0, 120.7, 113.2, 111.7, 111.4, 55.3, 51.4. **HRMS (ESI)** m/z Calcd. for $\text{C}_{35}\text{H}_{25}\text{O}_2^+$ ($[(\text{M}-\text{HNO}_2)+\text{H}]^+$) = 477.1849, found: 477.1831. $[\alpha]_D^{25}$ (MeOH, $c = 0.1$) = -452. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 90% ee, t_{major} : 7.966 min, t_{min} : 8.764 min.



(1*R*,2*R*)-4-bromo-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan (3a)

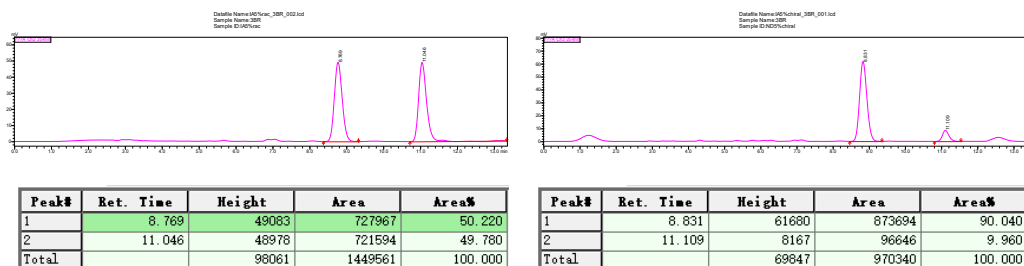


(*R*)-**1a** was isolated according to the general procedure with a reaction time of 24 h (33.5 mg, 44% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). **HPLC analysis** (Chiralpak OD, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 96% ee, t_{major} : 6.511 min, t_{min} : 7.140 min.

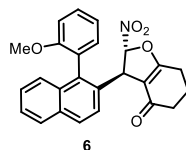


Prepared according to the general procedure with a reaction time of 24 h as pale pink foam (46.8 mg, 44% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 200:1). $dr > 20:1$ **Rf**: 0.24 (petroleum ether/ethyl acetate = 20:1). **MP** = 131.2-136.3 °C. **^1H NMR (500 MHz, CDCl_3)** δ 8.07 (s, 1H), 7.83 – 7.79 (m, 1H), 7.78 – 7.74 (m, 1H), 7.69 (d, $J = 8.7$ Hz, 1H), 7.59 – 7.54 (m, 1H), 7.51 – 7.48 (m, 1H), 7.48 – 7.45 (m, 2H), 7.44 – 7.40 (m, 1H), 7.35 – 7.30 (m, 2H), 7.26 – 7.23 (m, 2H), 7.15 (d, $J = 8.4$ Hz, 1H), 6.80 (d, $J = 8.6$ Hz, 1H), 6.25 (d, $J = 1.5$ Hz, 1H), 5.41 (s, 1H), 3.72 (s, 3H). **^{13}C NMR (126 MHz, CDCl_3)** δ 157.7, 153.4, 135.5, 133.2, 133.1, 133.0, 132.7, 131.9, 131.1, 130.3, 129.0, 128.5, 128.0, 127.9, 127.7, 126.9, 126.6, 126.3, 125.9, 125.3, 123.8, 123.2, 121.7, 120.9, 112.2, 111.4, 104.2, 55.2, 52.6. **HRMS (ESI)** m/z Calcd. for $\text{C}_{29}\text{H}_{20}\text{BrO}_2^+$ ($[(\text{M}-\text{HNO}_2)+\text{H}]^+$) = 479.0641, found: 479.0635. $[\alpha]_D^{25}$ (MeOH, $c = 0.1$) = -437.

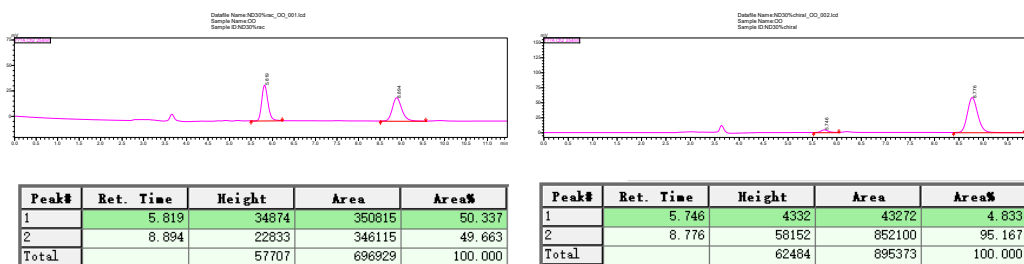
HPLC analysis (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 80% ee, t_{major} : 8.831 min, t_{min} : 11.109 min.



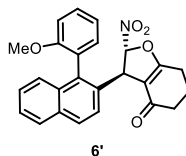
(2R,3R)-3-((aS)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (6)



Prepared according to the general procedure as off-white solid (29.8 mg, 36% yield) after silica gel chromatography (petroleum ether/ethyl acetate from 20:1 to 10:1). $dr > 20:1$. **Rf**: 0.22 (petroleum ether/ethyl acetate = 5:1). **MP** = 144.1-148.9 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.88 – 7.83 (m, 2H), 7.51 – 7.49 (m, 1H), 7.48 – 7.45 (m, 2H), 7.43 – 7.37 (m, 2H), 7.18 – 7.14 (m, 1H), 7.10 – 7.06 (m, 2H), 6.01 (d, $J = 2.1$ Hz, 1H), 4.65 (s, 1H), 3.70 (s, 3H), 2.82 – 2.73 (m, 2H), 2.41 – 2.33 (m, 2H), 2.22 – 2.15 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 193.2, 175.6, 157.5, 136.2, 133.2, 133.1, 132.3, 132.1, 129.8, 128.8, 127.8, 127.0, 126.5, 126.1, 125.9, 122.4, 120.8, 117.6, 111.6, 110.6, 77.4, 77.1, 76.9, 55.2, 50.0, 36.9, 23.4, 21.6. **HRMS (ESI)** m/z Calcd. for $\text{C}_{25}\text{H}_{21}\text{NNaO}_5^+$ ($[\text{M}+\text{Na}]^+$) = 438.1312, found: 438.1296. $[\alpha]_D^{25}$ (MeOH, $c = 0.1$) = -217. **HPLC analysis** (Chiralpak ND, Hexane/Isopropanol (70/30), 1 mL/min, 30 °C, 254 nm) indicated 90% ee, t_{major} : 8.776 min, t_{min} : 5.746 min.

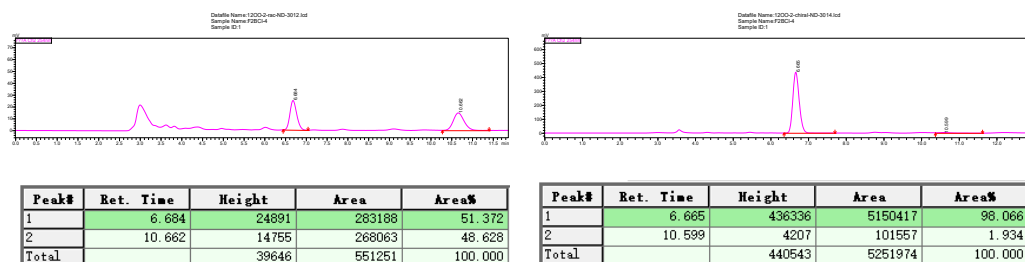


(2R,3R)-3-(1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (6')

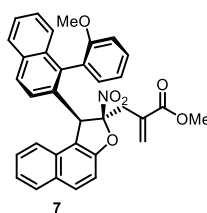


Prepared according to the general procedure as off-white solid (20.8 mg, 25% yield) after silica gel chromatography (petroleum ether/ethyl acetate from 20:1 to 5:1). $dr > 20:1$. **Rf**: 0.13 (petroleum ether/ethyl acetate = 5:1). **MP** = 180.7-185.1 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.90 – 7.83 (m,

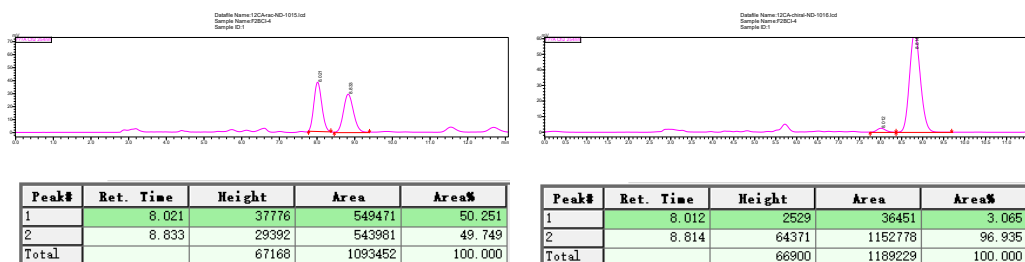
2H), 7.49 – 7.43 (m, 2H), 7.37 – 7.33 (m, 1H), 7.32 – 7.27 (m, 2H), 7.13 (dd, $J = 7.3, 2.0$ Hz, 1H), 7.11 – 7.05 (m, 2H), 6.04 (d, $J = 2.6$ Hz, 1H), 4.71 (s, 1H), 3.74 (s, 3H), 2.65 – 2.56 (m, 1H), 2.51 – 2.43 (m, 1H), 2.35 – 2.28 (m, 2H), 2.11 – 2.02 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 193.2, 175.5, 157.3, 135.8, 133.4, 133.2, 132.7, 131.9, 129.9, 128.8, 127.8, 126.6, 126.4, 126.1, 125.8, 125.3, 120.4, 116.6, 111.3, 111.2, 77.3, 77.1, 76.8, 55.6, 52.2, 36.7, 23.2, 21.3. $[\alpha]^{25}_D$ (MeOH, $c = 0.1$) = -182. **HRMS (ESI)** m/z Calcd. for $\text{C}_{25}\text{H}_{21}\text{NNaO}_5^+$ ($[\text{M}+\text{Na}]^+$) = 438.1312, found: 438.1293. **HPLC analysis** (Chiralpak ND, Hexane/Isopropanol (70/30), 1 mL/min, 30 °C, 254 nm) indicated 96% ee, t_{major} : 6.665 min, t_{min} : 10.599 min.



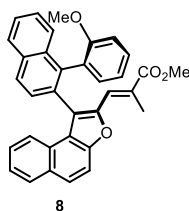
methyl 2-(((1*R*,2*S*)-1-((*aS*)-1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitro-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)methyl)acrylate (7)



Prepared according to the general procedure as beige foam (49.1 mg, 90% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 20:1). **dr** > 20:1. **Rf**: 0.33 (petroleum ether/ethyl acetate = 10:1). **MP** = 146.3-152.3 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.88 – 7.82 (m, 3H), 7.65 (d, $J = 8.7$ Hz, 1H), 7.56 – 7.52 (m, 1H), 7.52 – 7.48 (m, 1H), 7.44 – 7.39 (m, 3H), 7.32 – 7.27 (m, 2H), 7.18 (dd, $J = 8.3, 6.9$ Hz, 2H), 7.14 – 7.10 (m, 1H), 7.04 (d, $J = 8.4$ Hz, 1H), 6.93 (d, $J = 8.7$ Hz, 1H), 6.09 (s, 1H), 5.69 (s, 1H), 5.16 (s, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 3.61 (d, $J = 15.4$, 1H), 2.95 (d, $J = 15.3$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.0, 158.6, 156.7, 137.2, 133.5, 133.1, 132.7, 131.5, 131.1, 131.0, 130.9, 130.1, 129.8, 129.1, 128.8, 128.7, 128.2, 127.2, 127.08, 127.05, 126.3, 126.2, 125.0, 123.8, 122.7, 121.9, 121.0, 118.8, 111.5, 111.3, 55.4, 55.2, 52.1, 36.6. $[\alpha]^{25}_D$ (MeOH, $c = 0.1$) = -187. **HRMS (ESI)** m/z Calcd. for $\text{C}_{34}\text{H}_{27}\text{O}_4^+$ ($[(\text{M}-\text{HNO}_2)+\text{H}]^+$) = 499.1904, found: 499.1909. **HPLC analysis** (Chiralpak ND, Hexane/Isopropanol (90/10), 1 mL/min, 30 °C, 254 nm) indicated 94% ee, t_{major} : 8.814 min, t_{min} : 8.012 min.

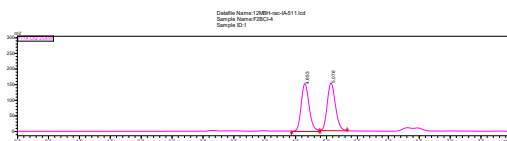


methyl (a*R,Z*)-3-(1-(1-(2-methoxyphenyl)naphthalen-2-yl)naphtho[2,1-b]furan-2-yl)-2-methylacrylate (8)

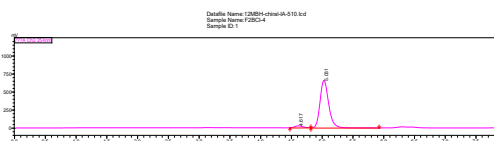


8

Prepared according to the general procedure as pale pink foam (38.7 mg, 78% yield) after silica gel chromatography (petroleum ether/ethyl acetate = 20:1). **Rf**: 0.44 (petroleum ether/ethyl acetate = 10:1). **MP** = 150.0-153.4 °C. **¹H NMR (500 MHz, CDCl₃)** δ 8.06 – 8.02 (m, 2H), 7.89 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.78 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.72 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.50 – 7.46 (m, 1H), 7.43 – 7.38 (m, 1H), 7.32 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.17 – 7.11 (m, 2H), 6.90 – 6.85 (m, 1H), 6.48 (dd, *J* = 8.3, 1.1 Hz, 1H), 3.73 (s, 3H), 2.55 (s, 3H), 2.30 (d, *J* = 1.3 Hz, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 169.1, 156.7, 152.7, 149.3, 137.1, 133.8, 133.3, 133.0, 130.7, 130.1, 128.7, 128.5, 128.3, 128.2, 128.1, 127.8, 127.1, 127.0, 126.6, 126.3, 126.2, 126.1, 125.8, 124.8, 124.7, 124.5, 122.8, 119.5, 112.2, 109.9, 53.7, 52.0, 14.3. **[α]_D²⁵** (MeOH, *c* = 0.1) = -210. **HRMS (ESI)** *m/z* Calcd. for C₃₄H₂₆NaO₄⁺ ([*M*+Na]⁺) = 521.1723, found: 521.1717. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 93% ee, *t*_{major} : 5.031 min, *t*_{min} : 4.617 min.

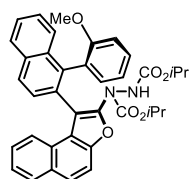


Peak#	Ret. Time	Height	Area	Area%
1	4.653	152722	1367761	49.647
2	5.076	152188	1387235	50.353
Total		304910	2754996	100.000



Peak#	Ret. Time	Height	Area	Area%
1	4.617	26164	223336	3.387
2	5.031	656270	6369722	96.613
Total		682434	6593058	100.000

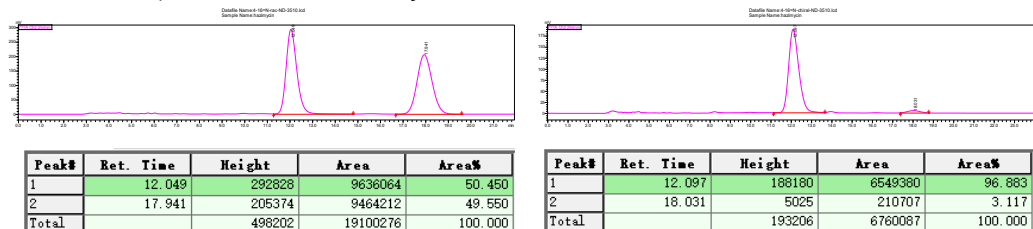
diisopropyl (a*R*)-1-(1-(1-(2-methoxyphenyl)naphthalen-2-yl)naphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (9)



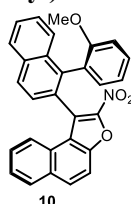
9

Prepared according to the general procedure as earthy yellow solid (40.6 mg, 67% yield) after silica gel chromatography (petroleum ether/ethyl acetate from 50:1 to 10:1). **Rf**: 0.36 (petroleum ether/ethyl acetate = 5:1). **MP** = 137.2-142.4 °C. **¹H NMR (500 MHz, CDCl₃)** δ 8.05 – 7.98 (m, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.76 – 7.66 (m, 2H), 7.65 – 7.54 (m, 2H), 7.49 – 7.45 (m, 1H), 7.44 – 7.33 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.13 (m, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 5.77 (s, 1H), 5.09 – 4.92 (m, 1H), 4.84 – 4.60 (m, 1H), 2.49 (s, 3H), 1.39 – 1.04 (m, 10H), 0.80 – 0.64 (m, 2H). **¹³C NMR (126 MHz, CDCl₃)** δ 157.5, 155.3, 152.8, 149.2, 143.2,

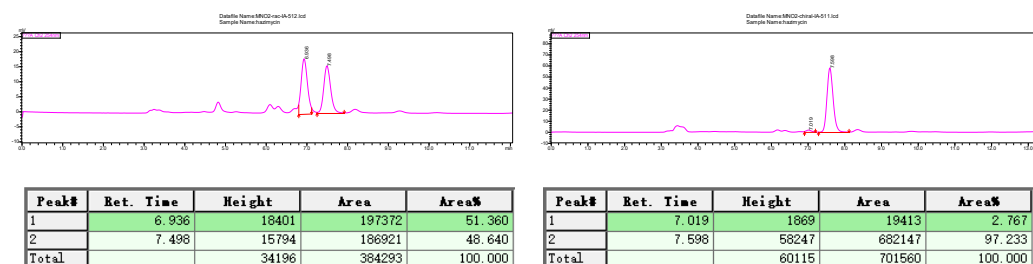
134.7, 133.7, 132.9, 130.7, 130.0, 129.6, 129.5, 128.7, 128.3, 128.1, 127.8, 127.3, 126.7, 126.3, 126.2, 125.9, 125.7, 124.2, 122.5, 118.9, 115.4, 112.6, 112.2, 111.6, 53.7, 22.1, 22.0, 21.6, 20.8. **HRMS (ESI)** m/z Calcd. for $C_{37}H_{34}N_2NaO_6^+$ ($[M+Na]^+$) = 625.2309, found: 625.2297. $[\alpha]^{25}_D$ (MeOH, $c = 0.1$) = -240. **HPLC analysis** (Chiralpak ND, Hexane/Isopropanol (65/35), 1 mL/min, 30 °C, 254 nm) indicated 94% ee, t_{major} : 12.097 min, t_{min} : 18.031 min.



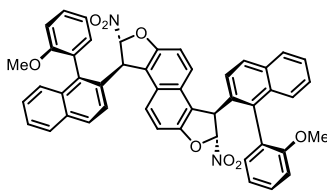
(aR)-1-(1-(2-methoxyphenyl)naphthalen-2-yl)-2-nitronaphtho[2,1-b]furan (10)



Prepared according to the general procedure as dark yellow solid (26.9 mg, 60% yield) after silica gel chromatography (petroleum ether/ethyl acetate from 50:1 to 15:1). $dr = 9:1$. **Rf**: 0.43 (petroleum ether/ethyl acetate = 5:1). **MP** = 234.2-236.6 °C. **1H NMR (500 MHz, $CDCl_3$)** δ 8.11 (d, $J = 8.4$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 9.1$ Hz, 1H), 7.92 (d, $J = 8.1$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.64 – 7.59 (m, 4H), 7.52 – 7.49 (m, 1H), 7.49 – 7.46 (m, 1H), 7.36 – 7.33 (m, 1H), 7.28 – 7.26 (m, 1H), 7.20 – 7.16 (m, 1H), 6.95 – 6.89 (m, 1H), 6.48 (d, $J = 8.3$ Hz, 1H), 2.52 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.5, 150.1, 136.5, 133.9, 133.3, 132.1, 131.6, 131.0, 129.4, 129.0, 128.7, 128.5, 128.3, 127.6, 127.4, 127.0, 126.62, 126.59, 126.1, 125.9, 125.5, 124.6, 124.5, 122.3, 120.1, 112.1, 109.8, 53.6. **HRMS (ESI)** m/z Calcd. for $C_{29}H_{19}NNaO_4^+$ ($[M+Na]^+$) : 468.1206, found: 468.1194. $[\alpha]^{25}_D$ (MeOH, $c = 0.1$) = -182. **HPLC analysis** (Chiralpak ND, Hexane/Isopropanol (95/5), 1 mL/min, 30 °C, 254 nm) indicated 94% ee, t_{major} : 7.598 min, t_{min} : 7.019 min.

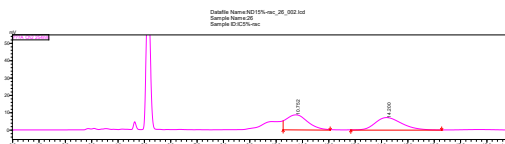


(2R,3R,7R,8R)-3,8-bis((aS)-1-(2-methoxyphenyl)naphthalen-2-yl)-2,7-dinitro-2,3,7,8-tetrahydronaphtho[2,1-b:6,5-b']difuran (11)

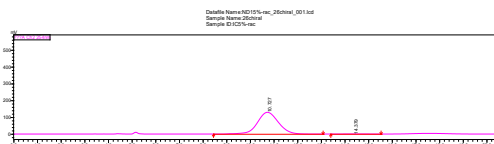


11

Prepared according to the general procedure as (30.9 mg, 40% yield) after silica gel chromatography (petroleum ether/ethyl acetate from 20:1 to 10:1). **Rf**: 0.27 (petroleum ether/ethyl acetate = 5:1). **MP** = 206.0–209.1 °C. **¹H NMR (500 MHz, CDCl₃)** δ 7.84 – 7.81 (m, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.55 – 7.53 (m, 1H), 7.53 – 7.49 (m, 2H), 7.47 – 7.43 (m, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 8.6 Hz, 1H), 6.16 (d, *J* = 1.4 Hz, 1H), 5.29 (d, *J* = 1.4 Hz, 1H), 3.74 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 157.7, 155.1, 135.3, 133.2, 133.1, 131.1, 130.3, 129.0, 127.9, 127.0, 126.9, 126.6, 126.3, 126.0, 125.9, 123.9, 121.8, 120.9, 113.3, 112.7, 111.4, 55.2, 51.7. **[α]_D²⁵** (MeOH, *c* = 0.1) = –315. **HPLC analysis** (Phenomenex Chiral ND (2), Hexane/Isopropanol (85/15), 1 mL/min, 30 °C, 254 nm) indicated % 99% *ee*, *t*_{major} : 10.727 min, *t*_{min} : 14.379 min.

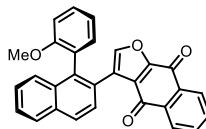


Peak#	Ret. Time	Height	Area	Area%
1	10.752	8520	476864	49.174
2	14.200	7120	492892	50.826
Total		15640	969755	100.000



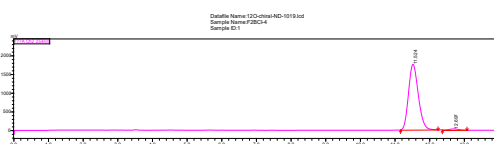
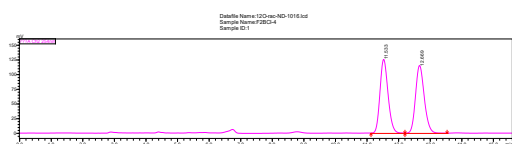
Peak#	Ret. Time	Height	Area	Area%
1	10.727	129380	7959672	99.631
2	14.379	481	29516	0.369
Total		129861	7989188	100.000

(aS)-3-(1-(2-methoxyphenyl)naphthalen-2-yl)naphtho[2,3-b]furan-4,9-dione (12)



12

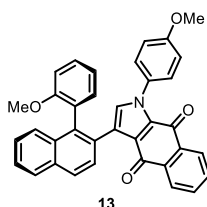
Prepared according to the general procedure as dark yellow solid (23.7 mg, 55% yield) after silica gel chromatography (petroleum ether/ethyl acetate from 50:1 to 20:1). **Rf**: 0.13 (petroleum ether/ethyl acetate = 20:1). **MP** = 218.1–221.7 °C. **¹H NMR (500 MHz, CDCl₃)** δ 8.23 – 8.17 (m, 1H), 8.15 – 8.10 (m, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.95 – 7.92 (m, 1H), 7.74 – 7.70 (m, 2H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.42 – 7.38 (m, 1H), 7.34 – 7.28 (m, 2H), 7.13 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.95 – 6.91 (m, 1H), 6.90 (dd, *J* = 8.3, 1.0 Hz, 1H), 3.56 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 180.3, 173.7, 157.3, 152.5, 146.9, 135.8, 133.9, 133.7, 133.5, 132.7, 132.3, 132.0, 129.4, 128.2, 128.1, 127.7, 127.5, 127.3, 127.0, 126.8, 126.6, 126.22, 126.16, 126.1, 125.8, 120.5, 110.9, 55.3. **HRMS (ESI)** *m/z* Calcd. for C₂₉H₁₈NaO₄⁺ ([M+Na]⁺) = 453.1097, found: 453.1090. **[α]_D²⁵** (MeOH, *c* = 0.1) = +98. **HPLC analysis** (Chiralpak ND, Hexane/Isopropanol (90/10), 1 mL/min, 30 °C, 254 nm) indicated 96% *ee*, *t*_{major} : 11.524 min, *t*_{min} : 12.697 min.



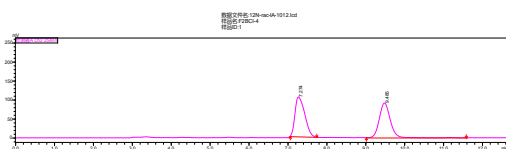
Peak#	Ret. Time	Height	Area	Area%
1	11.533	125614	2233719	50.105
2	12.669	115174	2224389	49.895
Total		240789	4458108	100.000

Peak#	Ret. Time	Height	Area	Area%
1	11.524	1753446	34364998	97.896
2	12.697	34544	738403	2.104
Total		1787990	35103401	100.000

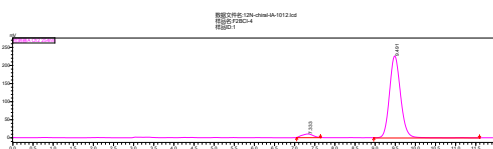
(aS)-1-(4-methoxyphenyl)-3-(1-(2-methoxyphenyl)naphthalen-2-yl)-1H-benzo[f]indole-4,9-dione (13)



Prepared according to the general procedure as deep dark yellow solid (22.6 mg, 42% yield) after silica gel chromatography (petroleum ether/ethyl acetate from 50:1 to 15:1). **R_f**: 0.06 (petroleum ether/ethyl acetate = 20:1). **MP** = 171.3–174.9. **¹H NMR (500 MHz, CDCl₃)** δ 8.18 – 8.14 (m, 1H), 8.07 – 8.04 (m, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.94 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.57 – 7.55 (m, 1H), 7.51 – 7.47 (m, 1H), 7.40 – 7.35 (m, 2H), 7.17 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.08 – 7.05 (m, 2H), 6.98 – 6.94 (m, 3H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.54 (d, *J* = 0.8 Hz, 1H), 3.86 (s, 3H), 3.52 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 180.8, 175.1, 159.7, 157.7, 135.2, 134.2, 134.0, 133.2, 133.1, 133.0, 132.7, 132.52, 132.46, 131.6, 130.3, 130.0, 128.9, 128.7, 128.6, 128.1, 127.0, 126.9, 126.7, 126.5, 126.2, 125.93, 125.89, 125.69, 125.66, 120.5, 114.0, 110.6, 55.5, 55.3. **HRMS (ESI)** *m/z* Calcd. for C₃₆H₂₅NNaO₄⁺ ([M+Na]⁺) = 558.1676, found: 558.1658. **[α]_D²⁵**; (MeOH, *c* = 0.1) = +115. **HPLC analysis** (Chiralpak IA, Hexane/Isopropanol (90/10), 1 mL/min, 30 °C, 254 nm) indicated 92% ee, *t*_{major} : 9.491 min, *t*_{min} : 7.333 min.

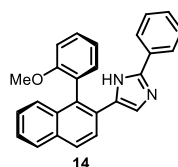


Peak#	Ret. Time	Height	Area	Area%
1	7.274	104022	1809495	50.201
2	9.485	91400	1795000	49.799
Total		195423	3604495	100.000



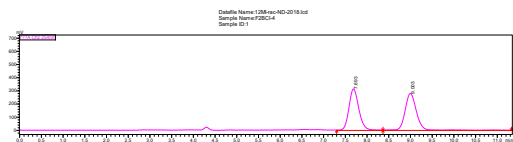
Peak#	Ret. Time	Height	Area	Area%
1	7.333	9589	180007	4.011
2	9.491	226117	4307587	95.989
Total		235706	4487595	100.000

(aS)-5-(1-(2-methoxyphenyl)naphthalen-2-yl)-2-phenyl-1H-imidazole (14)

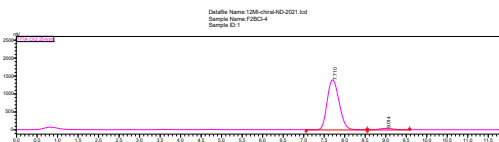


Prepared according to the general procedure as gray solid (29.6 mg, 79% yield) after silica gel chromatography (petroleum ether/ethyl acetate from 20:1 to 10:1). **R_f**: 0.27 (petroleum ether/ethyl acetate = 5:1). **MP** = 119.0–123.4 °C. **¹H NMR (500 MHz, DMSO)** δ 8.46 (d, *J* = 8.5 Hz, 1H), 8.03 – 7.90 (m, 4H), 7.59 – 7.53 (m, 1H), 7.49 – 7.42 (m, 3H), 7.40 – 7.34 (m, 2H), 7.31 – 7.24 (m, 2H),

7.19 – 7.14 (m, 1H), 7.14 – 7.09 (m, 1H), 5.87 (s, 1H), 3.58 (s, 3H). **¹³C NMR (126 MHz, DMSO)** δ 157.8, 145.2, 133.2, 132.4, 132.3, 131.8, 130.8, 130.1, 129.2, 128.72, 128.66, 128.2, 127.6, 126.5, 126.3, 126.2, 125.7, 125.4, 121.8, 112.4, 55.9. **HRMS (ESI)** m/z Calcd. for C₂₆H₂₁N₂O⁺ ([M+H]⁺) = 377.1648, found: 377.1628. **[α]_D²⁵** (MeOH, c = 0.1) = +90. **HPLC analysis** (Chiralpak ND, Hexane/Isopropanol (80/20), 1 mL/min, 30 °C, 254 nm) indicated 94% ee, t_{major} : 7.710 min, t_{min} : 9.014 min.



Peak#	Ret. Time	Height	Area	Area%
1	7.693	313221	4965106	49.503
2	9.003	278777	5064779	50.497
Total		591999	10029885	100.000



Peak#	Ret. Time	Height	Area	Area%
1	7.710	1385318	27968548	97.160
2	9.014	35514	817637	2.840
Total		1420832	28786185	100.000

4. X-ray Crystallographic Data

Crystals suitable for single crystal X-ray diffraction analysis were obtained by slow evaporation from a CHCl_3/n -hexane mixture for **3ag**.

Experimental

Single crystals of $\text{C}_{29}\text{H}_{20}\text{BrNO}_4$ [250829ha_z2590884_0m] were [3ag]. A suitable crystal was selected and [] on a **Bruker D8 VENTURE dual wavelength Mo/Cu** diffractometer. The crystal was kept at 193.00 K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [3ag]

Crystal Data for $\text{C}_{29}\text{H}_{20}\text{BrNO}_4$ ($M = 526.37$ g/mol): monoclinic, space group $P2_1$ (no. 4), $a = 21.3685(5)$ Å, $b = 9.2049(2)$ Å, $c = 24.2104(5)$ Å, $\beta = 90.6840(10)^\circ$, $V = 4761.72(18)$ Å³, $Z = 8$, $T = 193.00$ K, μ (CuK α) = 2.656 mm⁻¹, $D_{\text{calc}} = 1.468$ g/cm³, 169448 reflections measured ($4.136^\circ \leq 2\theta \leq 150.232^\circ$), 19540 unique ($R_{\text{int}} = 0.1107$, $R_{\text{sigma}} = 0.0517$) which were used in all calculations. The final R_1 was 0.0512 ($I > 2\sigma(I)$) and wR_2 was 0.1408 (all data).

Refinement model description

Number of restraints - 20, number of constraints - unknown.

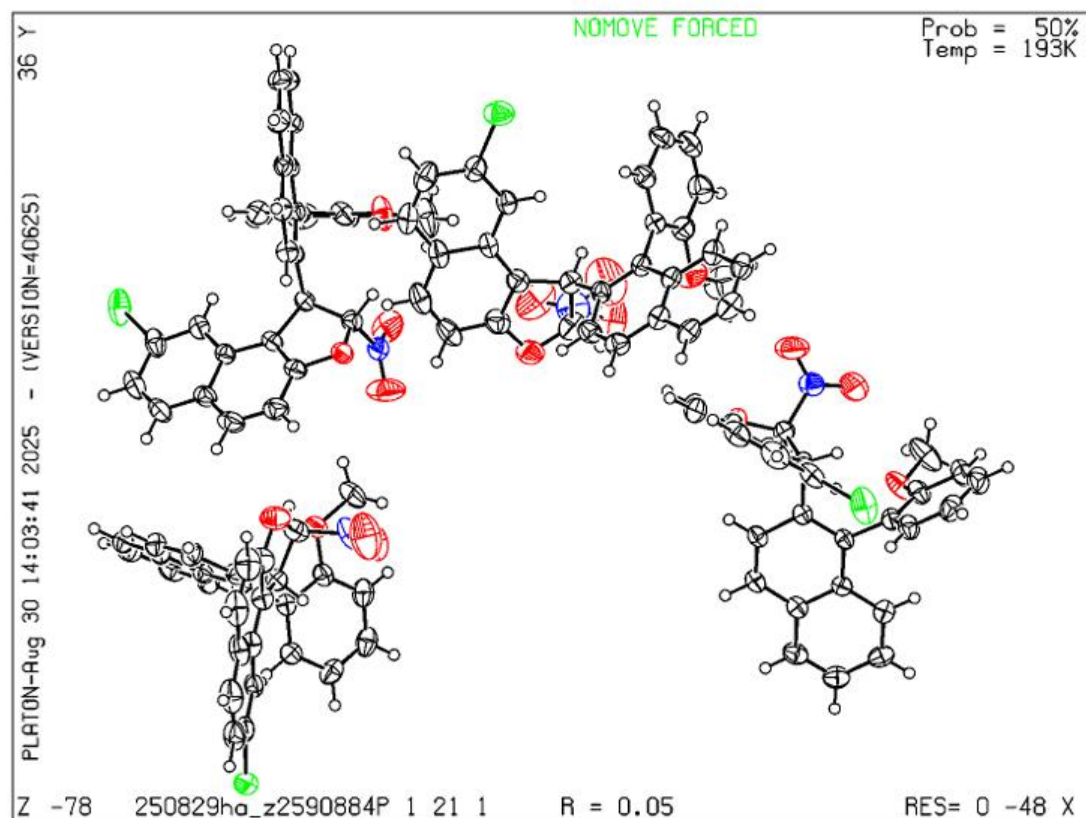


Figure S1. X-ray crystal structure of the product (CCDC 2484018).

Table 1 Crystal data and structure refinement for 3ag.

Identification code	3ag
Empirical formula	C ₂₉ H ₂₀ BrNO ₄
Formula weight	526.37
Temperature/K	193.00
Crystal system	monoclinic
Space group	P2 ₁
a/Å	21.3685(5)
b/Å	9.2049(2)
c/Å	24.2104(5)
α /°	90
β /°	90.6840(10)
γ /°	90
Volume/Å ³	4761.72(18)
Z	8
ρ_{calc} /g/cm ³	1.468
μ /mm ⁻¹	2.656
F(000)	2144.0
Crystal size/mm ³	0.13 × 0.12 × 0.1
Radiation	CuK α (λ = 1.54178)
2 Θ range for data collection/°	4.136 to 150.232
Index ranges	-26 ≤ h ≤ 26, -11 ≤ k ≤ 11, -25 ≤ l ≤ 30
Reflections collected	169448
Independent reflections	19540 [R_{int} = 0.1107, R_{sigma} = 0.0517]
Data/restraints/parameters	19540/20/1276
Goodness-of-fit on F ²	1.048
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0512, wR_2 = 0.1290
Final R indexes [all data]	R_1 = 0.0676, wR_2 = 0.1408
Largest diff. peak/hole / e Å ⁻³	0.71/-0.56
Flack parameter	0.020(6)

Table 2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å²×103) for 3ag. U_{eq} is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
Br1	-1394.7(4)	15454.3(8)	3508.7(3)	72.0(3)
O1	1754(2)	13300(6)	2340(2)	59.4(12)
O2	1831(4)	11519(9)	3168(3)	115(3)
O3	1208(3)	9982(8)	2806(3)	91.1(18)
O4	469(2)	9415(5)	1674.5(18)	50.7(11)
N1	1500(3)	11101(8)	2786(3)	65.9(17)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C1	-523(3)	15744(7)	3411(2)	52.3(16)
C2	-231(4)	16936(7)	3675(3)	62(2)
C3	389(4)	17193(7)	3584(3)	61(2)
C4	748(3)	16274(6)	3244(3)	49.9(16)
C5	1394(3)	16526(8)	3146(3)	58.3(19)
C6	1751(3)	15580(9)	2852(3)	60.7(18)
C7	1453(3)	14379(8)	2640(3)	48.8(15)
C8	825(3)	14110(6)	2689(2)	37.1(12)
C9	449(2)	15050(6)	2999(2)	37.3(11)
C10	-205(3)	14803(6)	3081(2)	38.3(12)
C11	667(3)	12734(6)	2379(2)	36.2(12)
C12	1342(3)	12145(7)	2310(3)	48.2(15)
C13	361(3)	12971(6)	1817(2)	34.0(11)
C14	589(3)	14096(6)	1472(2)	39.7(13)
C15	363(3)	14277(7)	949(2)	42.5(13)
C16	-102(3)	13346(6)	736(2)	36.9(12)
C17	-332(3)	13477(7)	177(2)	45.7(15)
C18	-772(3)	12544(8)	-22(2)	50.4(16)
C19	-1001(3)	11419(8)	310(2)	47.7(15)
C20	-801(3)	11270(7)	850(2)	39.7(12)
C21	-345(3)	12219(6)	1070(2)	34.0(11)
C22	-104(2)	12049(6)	1627(2)	31.5(11)
C23	-360(2)	10865(6)	1973(2)	31.9(11)
C24	-897(2)	11064(7)	2276(2)	37.2(12)
C25	-1159(3)	9907(8)	2560(2)	46.3(15)
C26	-888(3)	8574(7)	2538(3)	49.1(16)
C27	-343(3)	8342(7)	2244(3)	48.3(15)
C28	-78(3)	9498(6)	1969(2)	38.1(13)
C29	789(4)	8063(8)	1668(3)	68(2)
Br2	1466.4(4)	10065.9(8)	-1811.2(3)	65.7(2)
O5	2675.4(18)	8136(4)	1060.4(15)	39.6(9)
O6	1841(3)	6156(6)	1177(3)	100(2)
O7	2168(3)	4800(6)	533(2)	73.3(15)
O8	3371(2)	4040(5)	-182(2)	61.2(13)
N2	2204(2)	5867(6)	823(2)	45.8(12)
C30	1533(3)	10391(7)	-1041(3)	47.2(14)
C31	1202(3)	11582(7)	-810(3)	53.0(16)
C32	1261(3)	11844(7)	-253(3)	50.7(16)
C33	1635(3)	10983(6)	93(3)	41.1(13)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C34	1705(3)	11264(7)	664(3)	49.3(15)
C35	2050(3)	10376(7)	1002(2)	46.4(14)
C36	2332(2)	9173(6)	757(2)	36.8(12)
C37	2313(2)	8870(6)	210(2)	34.0(11)
C38	1955(2)	9771(6)	-154(2)	33.1(11)
C39	1905(2)	9514(6)	-721(2)	38.4(12)
C40	2685(2)	7498(6)	107(2)	31.3(11)
C41	2736(3)	6948(6)	701(2)	36.0(12)
C42	3333(2)	7746(6)	-122(2)	30.6(11)
C43	3725(3)	8820(6)	121(2)	36.8(12)
C44	4329(2)	9000(6)	-45(2)	36.2(12)
C45	4581(2)	8108(6)	-463(2)	34.0(11)
C46	5208(3)	8256(7)	-635(2)	41.5(13)
C47	5439(3)	7390(8)	-1041(2)	45.2(14)
C48	5064(3)	6315(7)	-1285(2)	43.2(13)
C49	4452(2)	6146(6)	-1133(2)	36.6(12)
C50	4193(2)	7035(6)	-715(2)	30.1(10)
C51	3563(2)	6864(5)	-543(2)	29.7(10)
C52	3145(2)	5820(6)	-837(2)	32.8(11)
C53	2830(3)	6256(7)	-1318(2)	42.1(13)
C54	2430(3)	5344(9)	-1602(3)	55.4(17)
C55	2339(3)	3950(8)	-1413(3)	55.4(18)
C56	2649(3)	3479(7)	-936(3)	51.6(16)
C57	3047(3)	4403(7)	-654(3)	42.2(13)
C58	3244(4)	2617(8)	34(4)	78(3)
Br3	6616.5(3)	5092.1(8)	1608.8(3)	62.5(2)
O9	3259.5(19)	4179(6)	2565.1(19)	57.7(12)
O10	3189(3)	2152(9)	1795(3)	100(2)
O11	3596(10)	498(16)	2238(9)	125(6)
O12	4432(2)	-174(5)	3286(2)	62.1(13)
N3	3363(3)	1747(9)	2248(3)	76(2)
C59	5766(3)	5579(6)	1600(2)	44.2(13)
C60	5570(4)	6777(7)	1283(3)	53.6(17)
C61	4963(4)	7236(7)	1305(3)	53.7(17)
C62	4529(3)	6515(7)	1642(2)	46.4(14)
C63	3903(3)	7017(8)	1687(3)	58.3(18)
C64	3471(3)	6301(8)	1991(3)	57.8(18)
C65	3660(3)	5034(8)	2259(2)	49.4(14)
C66	4257(3)	4522(7)	2256(2)	39.9(13)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C67	4718(2)	5262(6)	1948(2)	36.8(11)
C68	5349(2)	4820(6)	1929(2)	37.0(12)
C69	4294(3)	3157(7)	2604(2)	38.0(12)
C70	3578(3)	2890(8)	2675(3)	52.5(16)
C71	4606(3)	3355(6)	3162(2)	34.4(11)
C72	4399(3)	4495(7)	3510(2)	42.7(13)
C73	4632(3)	4671(7)	4031(2)	43.2(13)
C74	5091(3)	3718(6)	4244(2)	37.5(12)
C75	5325(3)	3858(7)	4798(2)	44.0(14)
C76	5757(3)	2900(8)	5000(2)	49.0(16)
C77	5974(3)	1760(7)	4671(2)	47.1(15)
C78	5756(3)	1598(7)	4133(2)	41.1(13)
C79	5309(3)	2565(6)	3912(2)	33.9(11)
C80	5057(3)	2397(6)	3360(2)	33.5(11)
C81	5301(2)	1185(6)	3019(2)	34.2(12)
C82	5865(3)	1301(7)	2741(2)	40.0(13)
C83	6114(3)	99(8)	2467(2)	49.5(16)
C84	5809(3)	-1191(8)	2477(3)	52.8(17)
C85	5248(4)	-1340(7)	2744(3)	56.0(17)
C86	4990(3)	-158(6)	3010(2)	42.3(13)
C87	4108(4)	-1537(9)	3303(4)	87(3)
Br4	3503.3(4)	371.6(8)	6843.5(3)	71.6(3)
O13	2329.9(19)	-1583(4)	3966.8(15)	41.5(9)
O14	3182(3)	-3552(6)	3905(3)	94(2)
O15	2789(3)	-4941(6)	4497(3)	85.2(17)
O16	1627(2)	-5732(5)	5265(2)	54.9(12)
N4	2782(2)	-3850(6)	4222(2)	46.4(12)
C88	3448(3)	705(7)	6075(3)	46.7(14)
C89	3786(3)	1876(7)	5846(3)	53.6(17)
C90	3740(3)	2140(7)	5287(3)	50.4(16)
C91	3357(3)	1275(7)	4942(3)	44.1(14)
C92	3307(3)	1532(7)	4368(3)	48.1(15)
C93	2967(3)	642(7)	4025(3)	48.7(15)
C94	2665(3)	-532(6)	4269(2)	38.6(12)
C95	2669(2)	-813(6)	4822(2)	34.3(11)
C96	3025(2)	76(6)	5184(2)	33.7(11)
C97	3073(3)	-174(6)	5755(2)	39.9(12)
C98	2300(2)	-2184(6)	4928(2)	32.5(11)
C99	2256(3)	-2755(6)	4332(2)	35.5(12)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
C100	1647(2)	-1982(6)	5147(2)	30.8(11)
C101	1240(2)	-945(6)	4892(2)	34.9(11)
C102	629(2)	-842(6)	5043(2)	35.7(12)
C103	377(2)	-1756(6)	5453(2)	33.1(11)
C104	-260(3)	-1684(7)	5604(2)	42.3(13)
C105	-490(3)	-2598(7)	5994(2)	45.0(14)
C106	-100(3)	-3638(7)	6251(2)	42.2(13)
C107	526(3)	-3722(6)	6120(2)	36.9(12)
C108	778(2)	-2786(6)	5712(2)	30.6(11)
C109	1422(2)	-2868(5)	5564(2)	29.8(10)
C110	1850(2)	-3854(6)	5878(2)	34.7(12)
C111	2166(3)	-3334(7)	6345(2)	41.9(13)
C112	2585(3)	-4182(8)	6638(3)	50.5(17)
C113	2688(3)	-5608(8)	6472(3)	52.7(17)
C114	2371(3)	-6145(7)	6017(3)	50.9(16)
C115	1955(2)	-5283(7)	5724(2)	40.6(13)
C116	1764(4)	-7150(8)	5065(4)	69(2)
O11A	3180(14)	622(19)	2495(7)	97(7)

Table 3 Anisotropic Displacement Parameters (Å²×10³) for 3ag. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Br1	75.5(5)	55.4(5)	85.9(5)	24.7(4)	40.0(4)	24.0(4)
O1	35(2)	73(3)	71(3)	-1(3)	8(2)	-2(2)
O2	127(6)	107(6)	108(5)	15(4)	-61(5)	5(5)
O3	103(5)	72(4)	98(4)	19(4)	-18(3)	15(4)
O4	54(3)	34(2)	64(3)	5.4(19)	19(2)	12(2)
N1	60(4)	52(4)	85(5)	4(3)	-27(3)	14(3)
C1	81(5)	36(3)	40(3)	10(3)	10(3)	19(3)
C2	110(7)	34(3)	41(3)	-3(3)	3(4)	20(4)
C3	102(6)	33(3)	48(4)	-8(3)	-19(4)	0(4)
C4	72(4)	28(3)	49(3)	-3(2)	-22(3)	0(3)
C5	61(4)	44(4)	69(4)	10(3)	-33(4)	-22(3)
C6	51(4)	60(5)	71(4)	9(4)	-23(3)	-17(4)
C7	38(3)	52(4)	57(4)	1(3)	-5(3)	-7(3)
C8	34(3)	36(3)	42(3)	0(2)	-6(2)	-4(2)
C9	46(3)	30(3)	36(3)	0(2)	-10(2)	-4(3)
C10	53(3)	27(3)	35(3)	2(2)	-2(2)	6(2)
C11	34(3)	34(3)	41(3)	0(2)	0(2)	-1(2)
C12	41(3)	51(4)	53(4)	-3(3)	1(3)	9(3)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C13	35(3)	26(3)	41(3)	0(2)	1(2)	0(2)
C14	43(3)	35(3)	41(3)	2(2)	3(2)	-5(2)
C15	48(3)	37(3)	43(3)	5(2)	5(3)	2(3)
C16	45(3)	34(3)	32(3)	2(2)	2(2)	7(2)
C17	53(4)	51(4)	33(3)	5(3)	4(3)	17(3)
C18	47(4)	68(4)	36(3)	-5(3)	-6(3)	20(3)
C19	42(3)	57(4)	44(3)	-10(3)	-9(3)	10(3)
C20	42(3)	38(3)	39(3)	-1(2)	-6(2)	2(3)
C21	39(3)	31(3)	32(3)	-3(2)	2(2)	8(2)
C22	36(3)	28(3)	30(3)	-1(2)	2(2)	0(2)
C23	31(3)	30(3)	34(3)	1(2)	-4(2)	-2(2)
C24	33(3)	41(3)	38(3)	0(2)	-3(2)	-1(2)
C25	35(3)	65(4)	39(3)	11(3)	-4(2)	-12(3)
C26	51(4)	48(4)	49(3)	14(3)	-10(3)	-16(3)
C27	57(4)	34(3)	54(4)	8(3)	-4(3)	-8(3)
C28	42(3)	31(3)	42(3)	1(2)	-1(2)	4(2)
C29	81(5)	43(4)	81(5)	-3(3)	10(4)	30(4)
Br2	86.0(5)	49.6(5)	60.8(4)	11.3(3)	-32.0(4)	-8.1(4)
O5	40(2)	40(2)	39(2)	-1.0(16)	0.5(16)	7.3(17)
O6	88(4)	54(3)	162(6)	-7(4)	81(4)	-8(3)
O7	87(4)	53(3)	80(3)	-3(3)	12(3)	-29(3)
O8	47(3)	43(3)	93(4)	27(2)	-25(2)	-12(2)
N2	41(3)	40(3)	56(3)	13(2)	9(2)	3(2)
C30	37(3)	37(3)	68(4)	15(3)	-14(3)	-6(3)
C31	43(4)	36(3)	80(5)	13(3)	-10(3)	4(3)
C32	38(3)	37(3)	77(5)	9(3)	3(3)	10(3)
C33	35(3)	29(3)	59(4)	1(2)	8(2)	1(2)
C34	43(3)	35(3)	70(4)	-8(3)	15(3)	2(3)
C35	48(3)	42(4)	50(3)	-7(3)	9(2)	1(3)
C36	29(3)	37(3)	44(3)	-2(2)	3(2)	3(2)
C37	28(3)	32(3)	42(3)	-1(2)	0(2)	5(2)
C38	31(3)	26(3)	42(3)	0(2)	3(2)	-1(2)
C39	32(3)	33(3)	49(3)	5(2)	-5(2)	-4(2)
C40	29(3)	31(3)	35(3)	-2(2)	-3(2)	1(2)
C41	31(3)	36(3)	41(3)	3(2)	-1(2)	0(2)
C42	27(3)	28(3)	36(3)	2(2)	-2(2)	1(2)
C43	34(3)	36(3)	41(3)	0(2)	-4(2)	-5(2)
C44	34(3)	33(3)	41(3)	2(2)	-5(2)	-5(2)
C45	28(3)	39(3)	35(3)	8(2)	-6(2)	-1(2)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C46	28(3)	53(4)	43(3)	6(3)	-4(2)	-8(3)
C47	35(3)	60(4)	41(3)	6(3)	4(2)	2(3)
C48	38(3)	52(4)	40(3)	3(3)	4(2)	6(3)
C49	34(3)	39(3)	37(3)	-1(2)	-1(2)	7(2)
C50	24(2)	31(3)	36(3)	7(2)	-3.2(19)	2(2)
C51	27(3)	25(3)	37(3)	4(2)	-3(2)	-1(2)
C52	28(3)	28(3)	42(3)	-5(2)	-1(2)	1(2)
C53	36(3)	47(3)	43(3)	0(3)	-5(2)	-4(3)
C54	43(3)	76(5)	47(3)	-4(3)	-6(2)	-11(4)
C55	45(4)	64(5)	57(4)	-19(3)	-3(3)	-13(3)
C56	43(4)	35(3)	76(5)	-13(3)	2(3)	-7(3)
C57	32(3)	33(3)	61(4)	-1(3)	-4(3)	-1(2)
C58	57(5)	48(4)	126(7)	40(5)	-33(5)	-17(4)
Br3	53.8(4)	52.5(5)	81.5(5)	-6.2(4)	19.2(3)	-6.9(4)
O9	37(2)	73(3)	64(3)	2(2)	3(2)	4(2)
O10	106(5)	135(6)	60(4)	-16(4)	-8(3)	-41(5)
O11	146(13)	78(9)	149(13)	-32(9)	-42(10)	-31(9)
O12	69(3)	42(3)	76(3)	-11(2)	28(2)	-20(2)
N3	63(4)	77(5)	87(5)	-7(4)	-20(4)	-19(4)
C59	61(4)	31(3)	41(3)	-3(2)	2(3)	-7(3)
C60	78(5)	40(4)	43(3)	1(3)	-1(3)	-18(3)
C61	74(5)	42(4)	45(4)	11(3)	-11(3)	-7(3)
C62	59(4)	36(3)	44(3)	3(2)	-16(3)	5(3)
C63	64(4)	53(4)	58(4)	8(3)	-24(3)	13(3)
C64	46(4)	61(5)	66(4)	1(3)	-19(3)	20(3)
C65	41(3)	61(4)	46(3)	-1(3)	-10(2)	6(3)
C66	38(3)	43(3)	38(3)	-3(2)	-7(2)	2(2)
C67	45(3)	28(3)	37(3)	0(2)	-11(2)	3(2)
C68	46(3)	27(3)	38(3)	-3(2)	-6(2)	0(2)
C69	36(3)	43(3)	35(3)	-2(2)	-5(2)	-3(2)
C70	50(4)	64(5)	44(3)	2(3)	-5(3)	-14(3)
C71	40(3)	29(3)	34(3)	0(2)	-1(2)	0(2)
C72	46(3)	39(3)	43(3)	-8(2)	-2(2)	5(3)
C73	48(3)	38(3)	44(3)	-9(2)	4(2)	-2(3)
C74	45(3)	35(3)	32(3)	-1(2)	-2(2)	-8(2)
C75	53(4)	50(4)	29(3)	-2(2)	0(2)	-11(3)
C76	48(4)	62(4)	37(3)	2(3)	-5(3)	-19(3)
C77	46(3)	52(4)	43(3)	7(3)	-8(3)	-7(3)
C78	48(3)	38(3)	37(3)	1(2)	-6(2)	-5(3)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C79	38(3)	33(3)	31(3)	2(2)	0(2)	-6(2)
C80	40(3)	27(3)	33(3)	-1(2)	0(2)	-3(2)
C81	34(3)	33(3)	36(3)	1(2)	-1(2)	2(2)
C82	38(3)	42(3)	40(3)	-1(2)	-8(2)	4(3)
C83	46(3)	65(5)	37(3)	-7(3)	-6(2)	25(3)
C84	65(4)	49(4)	45(3)	-9(3)	-11(3)	24(3)
C85	73(5)	39(4)	56(4)	-9(3)	-6(3)	4(3)
C86	52(3)	32(3)	43(3)	-3(2)	4(2)	-3(3)
C87	103(7)	45(4)	114(7)	-7(4)	30(6)	-35(5)
Br4	105.9(6)	50.7(5)	57.4(4)	-9.7(3)	-34.8(4)	4.0(4)
O13	47(2)	42(2)	36(2)	4.3(17)	-2.8(17)	-5.7(18)
O14	84(4)	60(4)	139(6)	11(4)	69(4)	9(3)
O15	105(4)	51(3)	101(4)	9(3)	33(3)	24(3)
O16	47(2)	39(2)	78(3)	-19(2)	-22(2)	12(2)
N4	48(3)	37(3)	54(3)	-7(2)	6(2)	-2(2)
C88	39(3)	35(3)	66(4)	-8(3)	-10(3)	8(3)
C89	43(4)	40(4)	78(5)	-12(3)	-12(3)	-5(3)
C90	38(3)	34(3)	79(5)	-4(3)	-1(3)	-3(3)
C91	33(3)	36(3)	63(4)	2(3)	5(3)	-2(2)
C92	49(4)	36(3)	60(4)	10(3)	10(3)	-5(3)
C93	53(4)	45(4)	48(3)	11(3)	8(3)	-2(3)
C94	38(3)	33(3)	44(3)	3(2)	4(2)	-7(2)
C95	30(3)	35(3)	38(3)	5(2)	-2(2)	-1(2)
C96	31(2)	28(3)	43(3)	1(2)	1.3(19)	0(2)
C97	39(3)	34(3)	47(3)	-4(2)	-6(2)	5(2)
C98	29(3)	33(3)	35(3)	5(2)	-4(2)	0(2)
C99	38(3)	33(3)	36(3)	-1(2)	3(2)	-1(2)
C100	29(3)	32(3)	32(3)	-1(2)	-4(2)	-1(2)
C101	34(3)	34(3)	37(3)	1(2)	-5(2)	6(2)
C102	33(3)	31(3)	43(3)	1(2)	-5(2)	4(2)
C103	30(3)	32(3)	38(3)	-3(2)	-6(2)	-1(2)
C104	32(3)	50(4)	45(3)	-6(3)	-5(2)	4(3)
C105	35(3)	53(4)	47(3)	-7(3)	0(2)	-3(3)
C106	35(3)	52(4)	40(3)	-5(3)	5(2)	-9(3)
C107	37(3)	38(3)	35(3)	0(2)	-4(2)	-5(2)
C108	29(3)	27(3)	36(3)	-3(2)	0(2)	-2(2)
C109	28(3)	24(2)	37(3)	0(2)	-3(2)	1(2)
C110	29(3)	33(3)	42(3)	7(2)	-2(2)	-2(2)
C111	38(3)	42(3)	46(3)	6(2)	-8(2)	1(3)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C112	40(3)	67(5)	45(3)	15(3)	-7(3)	-5(3)
C113	38(3)	61(4)	59(4)	19(3)	-9(3)	1(3)
C114	42(3)	36(3)	74(4)	12(3)	-3(3)	3(3)
C115	30(3)	39(3)	53(3)	1(3)	-9(2)	2(2)
C116	66(5)	38(4)	104(6)	-31(4)	-34(4)	15(3)
O11A	162(17)	51(8)	77(10)	-2(7)	-46(10)	-47(10)

Table 4 Bond Lengths for 3ag.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C1	1.900(7)	O9	C65	1.384(8)
O1	C7	1.392(8)	O9	C70	1.392(9)
O1	C12	1.383(8)	O10	N3	1.215(9)
O2	N1	1.220(9)	O11	N3	1.253(15)
O3	N1	1.206(9)	O12	C86	1.375(7)
O4	C28	1.378(7)	O12	C87	1.433(8)
O4	C29	1.421(8)	N3	C70	1.541(10)
N1	C12	1.534(9)	N3	O11A	1.259(16)
C1	C2	1.411(10)	C59	C60	1.405(9)
C1	C10	1.365(8)	C59	C68	1.391(8)
C2	C3	1.365(11)	C60	C61	1.365(10)
C3	C4	1.414(9)	C61	C62	1.409(9)
C4	C5	1.422(10)	C62	C63	1.419(9)
C4	C9	1.422(8)	C62	C67	1.427(8)
C5	C6	1.365(10)	C63	C64	1.360(10)
C6	C7	1.373(9)	C64	C65	1.392(9)
C7	C8	1.370(8)	C65	C66	1.361(8)
C8	C9	1.405(8)	C66	C67	1.416(8)
C8	C11	1.509(8)	C66	C69	1.515(8)
C9	C10	1.431(8)	C67	C68	1.409(7)
C11	C12	1.551(8)	C69	C70	1.559(8)
C11	C13	1.518(8)	C69	C71	1.510(7)
C13	C14	1.421(7)	C71	C72	1.420(8)
C13	C22	1.381(7)	C71	C80	1.387(8)
C14	C15	1.359(8)	C72	C73	1.360(8)
C15	C16	1.406(8)	C73	C74	1.409(8)
C16	C17	1.439(8)	C74	C75	1.432(7)
C16	C21	1.418(8)	C74	C79	1.414(8)
C17	C18	1.359(9)	C75	C76	1.365(9)
C18	C19	1.403(10)	C76	C77	1.401(9)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C19	C20	1.377(8)	C77	C78	1.385(8)
C20	C21	1.408(8)	C78	C79	1.406(8)
C21	C22	1.448(7)	C79	C80	1.444(7)
C22	C23	1.482(7)	C80	C81	1.486(7)
C23	C24	1.381(7)	C81	C82	1.393(8)
C23	C28	1.395(8)	C81	C86	1.403(8)
C24	C25	1.390(8)	C82	C83	1.398(8)
C25	C26	1.359(10)	C83	C84	1.353(10)
C26	C27	1.388(9)	C84	C85	1.376(10)
C27	C28	1.380(8)	C85	C86	1.382(9)
Br2	C30	1.891(6)	Br4	C88	1.887(7)
O5	C36	1.406(7)	O13	C94	1.405(7)
O5	C41	1.404(7)	O13	C99	1.405(6)
O6	N2	1.193(7)	O14	N4	1.188(7)
O7	N2	1.210(7)	O15	N4	1.205(7)
O8	C57	1.369(7)	O16	C115	1.370(7)
O8	C58	1.438(8)	O16	C116	1.424(8)
N2	C41	1.541(7)	N4	C99	1.536(7)
C30	C31	1.422(9)	C88	C89	1.415(9)
C30	C39	1.369(8)	C88	C97	1.373(8)
C31	C32	1.376(10)	C89	C90	1.376(10)
C32	C33	1.398(8)	C90	C91	1.410(9)
C33	C34	1.412(9)	C91	C92	1.413(9)
C33	C38	1.442(7)	C91	C96	1.440(7)
C34	C35	1.367(9)	C92	C93	1.369(9)
C35	C36	1.396(8)	C93	C94	1.393(8)
C36	C37	1.356(8)	C94	C95	1.364(7)
C37	C38	1.425(7)	C95	C96	1.413(7)
C37	C40	1.514(7)	C95	C98	1.513(7)
C38	C39	1.396(8)	C96	C97	1.405(7)
C40	C41	1.526(7)	C98	C99	1.537(7)
C40	C42	1.517(7)	C98	C100	1.510(7)
C42	C43	1.419(7)	C100	C101	1.425(7)
C42	C51	1.396(7)	C100	C109	1.390(7)
C43	C44	1.364(7)	C101	C102	1.364(7)
C44	C45	1.415(8)	C102	C103	1.411(7)
C45	C46	1.415(7)	C103	C104	1.416(7)
C45	C50	1.421(7)	C103	C108	1.420(7)
C46	C47	1.362(9)	C104	C105	1.362(9)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C47	C48	1.400(9)	C105	C106	1.409(9)
C48	C49	1.370(8)	C106	C107	1.380(8)
C49	C50	1.420(7)	C107	C108	1.422(7)
C50	C51	1.424(7)	C108	C109	1.428(7)
C51	C52	1.487(7)	C109	C110	1.490(7)
C52	C53	1.397(8)	C110	C111	1.394(8)
C52	C57	1.394(8)	C110	C115	1.386(8)
C53	C54	1.377(8)	C111	C112	1.378(8)
C54	C55	1.377(11)	C112	C113	1.392(10)
C55	C56	1.394(10)	C113	C114	1.378(10)
C56	C57	1.378(8)	C114	C115	1.382(8)
Br3	C59	1.871(6)			

Table 5 Bond Angles for 3ag.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	O1	C7	106.1(4)	C86	O12	C87	116.4(5)
C28	O4	C29	117.7(5)	O10	N3	O11	112.4(12)
O2	N1	C12	119.5(7)	O10	N3	C70	118.8(8)
O3	N1	O2	122.3(8)	O10	N3	O11A	126.0(10)
O3	N1	C12	117.1(6)	O11	N3	C70	121.6(9)
C2	C1	Br1	118.8(5)	O11A	N3	C70	109.6(9)
C10	C1	Br1	118.6(5)	C60	C59	Br3	118.6(5)
C10	C1	C2	122.6(7)	C68	C59	Br3	120.2(5)
C3	C2	C1	119.1(6)	C68	C59	C60	121.1(6)
C2	C3	C4	121.7(6)	C61	C60	C59	120.0(6)
C3	C4	C5	122.3(6)	C60	C61	C62	120.6(6)
C3	C4	C9	118.1(6)	C61	C62	C63	121.2(6)
C5	C4	C9	119.5(6)	C61	C62	C67	119.8(6)
C6	C5	C4	122.2(6)	C63	C62	C67	119.0(6)
C5	C6	C7	116.7(6)	C64	C63	C62	122.1(6)
C6	C7	O1	123.6(6)	C63	C64	C65	117.6(6)
C8	C7	O1	112.1(6)	O9	C65	C64	123.2(6)
C8	C7	C6	124.3(7)	C66	C65	O9	113.1(6)
C7	C8	C9	120.2(5)	C66	C65	C64	123.7(6)
C7	C8	C11	108.8(5)	C65	C66	C67	119.7(6)
C9	C8	C11	131.0(5)	C65	C66	C69	109.0(5)
C4	C9	C10	120.3(5)	C67	C66	C69	131.3(5)
C8	C9	C4	116.9(5)	C66	C67	C62	117.9(5)
C8	C9	C10	122.8(5)	C68	C67	C62	118.8(5)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	C10	C9	118.2(6)	C68	C67	C66	123.4(5)
C8	C11	C12	98.3(4)	C59	C68	C67	119.6(5)
C8	C11	C13	114.6(5)	C66	C69	C70	98.5(5)
C13	C11	C12	110.2(5)	C71	C69	C66	114.7(5)
O1	C12	N1	107.9(5)	C71	C69	C70	110.2(5)
O1	C12	C11	108.5(5)	O9	C70	N3	108.2(6)
N1	C12	C11	109.6(5)	O9	C70	C69	108.8(5)
C14	C13	C11	119.0(5)	N3	C70	C69	108.7(6)
C22	C13	C11	120.7(5)	C72	C71	C69	118.8(5)
C22	C13	C14	120.1(5)	C80	C71	C69	122.0(5)
C15	C14	C13	121.2(5)	C80	C71	C72	119.0(5)
C14	C15	C16	120.5(5)	C73	C72	C71	121.7(6)
C15	C16	C17	121.7(5)	C72	C73	C74	120.7(5)
C15	C16	C21	119.9(5)	C73	C74	C75	121.3(5)
C21	C16	C17	118.3(5)	C73	C74	C79	119.6(5)
C18	C17	C16	120.5(6)	C79	C74	C75	119.0(5)
C17	C18	C19	120.5(6)	C76	C75	C74	120.4(6)
C20	C19	C18	120.7(6)	C75	C76	C77	120.5(6)
C19	C20	C21	120.2(6)	C78	C77	C76	120.4(6)
C16	C21	C22	118.8(5)	C77	C78	C79	120.6(6)
C20	C21	C16	119.6(5)	C74	C79	C80	118.9(5)
C20	C21	C22	121.5(5)	C78	C79	C74	119.1(5)
C13	C22	C21	119.4(5)	C78	C79	C80	122.0(5)
C13	C22	C23	122.2(5)	C71	C80	C79	120.1(5)
C21	C22	C23	118.4(5)	C71	C80	C81	122.1(5)
C24	C23	C22	121.1(5)	C79	C80	C81	117.7(5)
C24	C23	C28	119.0(5)	C82	C81	C80	121.5(5)
C28	C23	C22	119.8(4)	C82	C81	C86	118.2(5)
C23	C24	C25	120.2(6)	C86	C81	C80	120.1(5)
C26	C25	C24	119.9(5)	C81	C82	C83	120.3(6)
C25	C26	C27	121.3(6)	C84	C83	C82	120.1(6)
C28	C27	C26	118.7(6)	C83	C84	C85	121.1(6)
O4	C28	C23	115.0(5)	C84	C85	C86	119.7(6)
O4	C28	C27	124.2(5)	O12	C86	C81	114.5(5)
C27	C28	C23	120.9(5)	O12	C86	C85	124.9(6)
C41	O5	C36	104.9(4)	C85	C86	C81	120.7(5)
C57	O8	C58	115.5(5)	C94	O13	C99	105.1(4)
O6	N2	O7	124.1(6)	C115	O16	C116	116.5(5)
O6	N2	C41	118.7(6)	O14	N4	O15	123.1(6)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O7	N2	C41	117.0(5)	O14	N4	C99	119.6(5)
C31	C30	Br2	118.5(4)	O15	N4	C99	117.0(5)
C39	C30	Br2	120.1(5)	C89	C88	Br4	119.0(5)
C39	C30	C31	121.3(6)	C97	C88	Br4	119.4(5)
C32	C31	C30	118.8(6)	C97	C88	C89	121.6(6)
C31	C32	C33	122.2(6)	C90	C89	C88	119.3(6)
C32	C33	C34	122.4(6)	C89	C90	C91	121.1(6)
C32	C33	C38	117.5(6)	C90	C91	C92	121.7(6)
C34	C33	C38	120.1(5)	C90	C91	C96	118.5(6)
C35	C34	C33	121.8(6)	C92	C91	C96	119.8(5)
C34	C35	C36	116.9(5)	C93	C92	C91	122.0(6)
C35	C36	O5	122.9(5)	C92	C93	C94	116.9(6)
C37	C36	O5	112.3(5)	C93	C94	O13	123.3(5)
C37	C36	C35	124.8(5)	C95	C94	O13	112.2(5)
C36	C37	C38	119.5(5)	C95	C94	C93	124.5(6)
C36	C37	C40	108.8(5)	C94	C95	C96	119.7(5)
C38	C37	C40	131.6(5)	C94	C95	C98	109.1(5)
C37	C38	C33	116.6(5)	C96	C95	C98	131.0(5)
C39	C38	C33	120.6(5)	C95	C96	C91	117.1(5)
C39	C38	C37	122.8(5)	C97	C96	C91	119.7(5)
C30	C39	C38	119.6(6)	C97	C96	C95	123.2(5)
C37	C40	C41	98.9(4)	C88	C97	C96	119.7(6)
C37	C40	C42	114.7(4)	C95	C98	C99	98.7(4)
C42	C40	C41	109.9(4)	C100	C98	C95	116.3(5)
O5	C41	N2	108.1(4)	C100	C98	C99	109.0(4)
O5	C41	C40	108.7(4)	O13	C99	N4	107.9(4)
C40	C41	N2	110.5(4)	O13	C99	C98	108.8(4)
C43	C42	C40	119.4(5)	N4	C99	C98	110.6(4)
C51	C42	C40	120.7(5)	C101	C100	C98	119.5(5)
C51	C42	C43	119.8(5)	C109	C100	C98	120.8(5)
C44	C43	C42	121.2(5)	C109	C100	C101	119.6(5)
C43	C44	C45	120.6(5)	C102	C101	C100	120.8(5)
C44	C45	C46	121.7(5)	C101	C102	C103	121.4(5)
C44	C45	C50	119.0(5)	C102	C103	C104	122.0(5)
C46	C45	C50	119.3(5)	C102	C103	C108	118.4(5)
C47	C46	C45	120.7(6)	C104	C103	C108	119.6(5)
C46	C47	C48	120.4(5)	C105	C104	C103	120.4(6)
C49	C48	C47	120.7(6)	C104	C105	C106	120.6(5)
C48	C49	C50	120.4(5)	C107	C106	C105	120.4(6)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C45	C50	C51	120.0(5)	C106	C107	C108	120.1(5)
C49	C50	C45	118.5(5)	C103	C108	C107	118.7(5)
C49	C50	C51	121.5(5)	C103	C108	C109	120.2(5)
C42	C51	C50	119.4(5)	C107	C108	C109	121.1(5)
C42	C51	C52	120.7(4)	C100	C109	C108	119.6(5)
C50	C51	C52	119.8(4)	C100	C109	C110	120.8(4)
C53	C52	C51	119.6(5)	C108	C109	C110	119.5(4)
C57	C52	C51	123.0(5)	C111	C110	C109	119.5(5)
C57	C52	C53	117.5(5)	C115	C110	C109	122.7(5)
C54	C53	C52	122.1(6)	C115	C110	C111	117.8(5)
C55	C54	C53	119.4(6)	C112	C111	C110	121.9(6)
C54	C55	C56	119.9(6)	C111	C112	C113	119.3(6)
C57	C56	C55	120.2(6)	C114	C113	C112	119.4(6)
O8	C57	C52	114.7(5)	C113	C114	C115	120.8(6)
O8	C57	C56	124.4(6)	O16	C115	C110	114.9(5)
C56	C57	C52	120.9(6)	O16	C115	C114	124.3(6)
C65	O9	C70	106.4(5)	C114	C115	C110	120.8(6)

Table 6 Torsion Angles for 3ag.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C1	C2	C3	-176.7(5)	Br3	C59	C68	C67	175.5(4)
Br1	C1	C10	C9	178.6(4)	O9	C65	C66	C67	178.4(5)
O1	C7	C8	C9	177.2(5)	O9	C65	C66	C69	-0.9(7)
O1	C7	C8	C11	-2.0(7)	O10	N3	C70	O9	28.8(9)
O2	N1	C12	O1	15.8(9)	O10	N3	C70	C69	-89.3(8)
O2	N1	C12	C11	-102.2(8)	O11	N3	C70	O9	177.0(16)
O3	N1	C12	O1	-176.1(7)	O11	N3	C70	C69	59.0(17)
O3	N1	C12	C11	66.0(8)	C59	C60	C61	C62	-0.2(10)
C1	C2	C3	C4	-1.7(10)	C60	C59	C68	C67	-0.4(8)
C2	C1	C10	C9	-0.4(8)	C60	C61	C62	C63	177.3(6)
C2	C3	C4	C5	-179.9(6)	C60	C61	C62	C67	-2.2(9)
C2	C3	C4	C9	-0.6(9)	C61	C62	C63	C64	177.2(7)
C3	C4	C5	C6	175.0(6)	C61	C62	C67	C66	-176.3(5)
C3	C4	C9	C8	-176.5(5)	C61	C62	C67	C68	3.4(8)
C3	C4	C9	C10	2.4(8)	C62	C63	C64	C65	-0.5(10)
C4	C5	C6	C7	1.7(10)	C62	C67	C68	C59	-2.0(8)
C4	C9	C10	C1	-2.0(8)	C63	C62	C67	C66	4.1(8)
C5	C4	C9	C8	2.9(8)	C63	C62	C67	C68	-176.2(5)
C5	C4	C9	C10	-178.2(5)	C63	C64	C65	O9	-177.6(6)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C5	C6	C7	O1	-178.6(6)	C63	C64	C65	C66	3.6(10)
C5	C6	C7	C8	2.4(10)	C64	C65	C66	C67	-2.6(9)
C6	C7	C8	C9	-3.7(10)	C64	C65	C66	C69	178.0(6)
C6	C7	C8	C11	177.1(6)	C65	O9	C70	N3	-97.8(6)
C7	O1	C12	N1	-94.4(6)	C65	O9	C70	C69	20.2(6)
C7	O1	C12	C11	24.3(7)	C65	C66	C67	C62	-1.3(8)
C7	C8	C9	C4	0.9(8)	C65	C66	C67	C68	179.0(5)
C7	C8	C9	C10	-178.0(5)	C65	C66	C69	C70	12.0(6)
C7	C8	C11	C12	15.2(6)	C65	C66	C69	C71	-105.0(6)
C7	C8	C11	C13	-101.6(6)	C66	C67	C68	C59	177.6(5)
C8	C9	C10	C1	176.9(5)	C66	C69	C70	O9	-19.5(6)
C8	C11	C12	O1	-24.0(6)	C66	C69	C70	N3	98.1(6)
C8	C11	C12	N1	93.5(6)	C66	C69	C71	C72	51.3(7)
C8	C11	C13	C14	41.3(7)	C66	C69	C71	C80	-133.4(6)
C8	C11	C13	C22	-143.1(5)	C67	C62	C63	C64	-3.2(10)
C9	C4	C5	C6	-4.3(10)	C67	C66	C69	C70	-167.3(6)
C9	C8	C11	C12	-163.9(6)	C67	C66	C69	C71	75.8(8)
C9	C8	C11	C13	79.3(8)	C68	C59	C60	C61	1.6(9)
C10	C1	C2	C3	2.2(9)	C69	C66	C67	C62	177.9(6)
C11	C8	C9	C4	179.9(6)	C69	C66	C67	C68	-1.8(9)
C11	C8	C9	C10	1.0(9)	C69	C71	C72	C73	175.5(5)
C11	C13	C14	C15	174.8(5)	C69	C71	C80	C79	-175.3(5)
C11	C13	C22	C21	-174.2(5)	C69	C71	C80	C81	5.2(8)
C11	C13	C22	C23	4.8(8)	C70	O9	C65	C64	168.7(6)
C12	O1	C7	C6	166.6(6)	C70	O9	C65	C66	-12.4(7)
C12	O1	C7	C8	-14.3(7)	C70	C69	C71	C72	-58.7(7)
C12	C11	C13	C14	-68.5(6)	C70	C69	C71	C80	116.6(6)
C12	C11	C13	C22	107.2(6)	C71	C69	C70	O9	100.8(6)
C13	C11	C12	O1	96.1(6)	C71	C69	C70	N3	-141.5(6)
C13	C11	C12	N1	-146.3(5)	C71	C72	C73	C74	0.1(9)
C13	C14	C15	C16	-0.2(9)	C71	C80	C81	C82	98.7(7)
C13	C22	C23	C24	95.1(6)	C71	C80	C81	C86	-87.0(7)
C13	C22	C23	C28	-88.7(7)	C72	C71	C80	C79	0.0(8)
C14	C13	C22	C21	1.4(8)	C72	C71	C80	C81	-179.5(5)
C14	C13	C22	C23	-179.6(5)	C72	C73	C74	C75	-177.9(6)
C14	C15	C16	C17	-177.5(5)	C72	C73	C74	C79	-0.3(9)
C14	C15	C16	C21	0.8(8)	C73	C74	C75	C76	178.2(6)
C15	C16	C17	C18	178.6(6)	C73	C74	C79	C78	-178.4(5)
C15	C16	C21	C20	-178.6(5)	C73	C74	C79	C80	0.3(8)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C15	C16	C21	C22	-0.3(8)	C74	C75	C76	C77	-0.5(9)
C16	C17	C18	C19	-1.3(9)	C74	C79	C80	C71	-0.1(8)
C16	C21	C22	C13	-0.8(7)	C74	C79	C80	C81	179.4(5)
C16	C21	C22	C23	-179.9(5)	C75	C74	C79	C78	-0.8(8)
C17	C16	C21	C20	-0.2(8)	C75	C74	C79	C80	177.9(5)
C17	C16	C21	C22	178.1(5)	C75	C76	C77	C78	0.5(9)
C17	C18	C19	C20	2.3(9)	C76	C77	C78	C79	-0.6(9)
C18	C19	C20	C21	-2.2(9)	C77	C78	C79	C74	0.7(8)
C19	C20	C21	C16	1.2(8)	C77	C78	C79	C80	-177.9(5)
C19	C20	C21	C22	-177.1(5)	C78	C79	C80	C71	178.5(5)
C20	C21	C22	C13	177.4(5)	C78	C79	C80	C81	-2.0(8)
C20	C21	C22	C23	-1.6(7)	C79	C74	C75	C76	0.7(8)
C21	C16	C17	C18	0.3(8)	C79	C80	C81	C82	-80.8(6)
C21	C22	C23	C24	-85.9(6)	C79	C80	C81	C86	93.5(6)
C21	C22	C23	C28	90.3(6)	C80	C71	C72	C73	0.0(9)
C22	C13	C14	C15	-0.9(8)	C80	C81	C82	C83	173.8(5)
C22	C23	C24	C25	174.6(5)	C80	C81	C86	O12	6.5(8)
C22	C23	C28	O4	6.3(8)	C80	C81	C86	C85	-172.8(5)
C22	C23	C28	C27	-173.7(5)	C81	C82	C83	C84	-0.8(9)
C23	C24	C25	C26	-0.2(8)	C82	C81	C86	O12	-179.0(5)
C24	C23	C28	O4	-177.4(5)	C82	C81	C86	C85	1.7(9)
C24	C23	C28	C27	2.6(8)	C82	C83	C84	C85	1.3(10)
C24	C25	C26	C27	1.1(9)	C83	C84	C85	C86	-0.3(10)
C25	C26	C27	C28	-0.2(9)	C84	C85	C86	O12	179.5(6)
C26	C27	C28	O4	178.3(5)	C84	C85	C86	C81	-1.3(10)
C26	C27	C28	C23	-1.7(9)	C86	C81	C82	C83	-0.7(8)
C28	C23	C24	C25	-1.6(8)	C87	O12	C86	C81	-178.0(7)
C29	O4	C28	C23	178.1(6)	C87	O12	C86	C85	1.3(10)
C29	O4	C28	C27	-1.9(9)	Br4	C88	C89	C90	-179.0(5)
Br2	C30	C31	C32	-178.5(5)	Br4	C88	C97	C96	179.4(4)
Br2	C30	C39	C38	179.5(4)	O13	C94	C95	C96	175.3(5)
O5	C36	C37	C38	176.6(5)	O13	C94	C95	C98	-0.4(6)
O5	C36	C37	C40	-0.8(6)	O14	N4	C99	O13	5.9(8)
O6	N2	C41	O5	0.0(8)	O14	N4	C99	C98	-113.0(7)
O6	N2	C41	C40	-118.8(7)	O15	N4	C99	O13	-179.3(6)
O7	N2	C41	O5	176.9(5)	O15	N4	C99	C98	61.8(7)
O7	N2	C41	C40	58.2(7)	C88	C89	C90	C91	0.8(9)
C30	C31	C32	C33	0.1(10)	C89	C88	C97	C96	0.6(9)
C31	C30	C39	C38	1.2(8)	C89	C90	C91	C92	-179.8(6)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C31	C32	C33	C34	178.8(6)	C89	C90	C91	C96	-1.7(9)
C31	C32	C33	C38	-1.1(9)	C90	C91	C92	C93	175.8(6)
C32	C33	C34	C35	177.1(6)	C90	C91	C96	C95	-176.9(5)
C32	C33	C38	C37	-177.5(5)	C90	C91	C96	C97	2.1(8)
C32	C33	C38	C39	2.2(8)	C91	C92	C93	C94	0.5(9)
C33	C34	C35	C36	0.0(9)	C91	C96	C97	C88	-1.6(8)
C33	C38	C39	C30	-2.2(8)	C92	C91	C96	C95	1.2(8)
C34	C33	C38	C37	2.5(8)	C92	C91	C96	C97	-179.8(5)
C34	C33	C38	C39	-177.8(5)	C92	C93	C94	O13	-176.2(6)
C34	C35	C36	O5	-177.0(5)	C92	C93	C94	C95	2.5(9)
C34	C35	C36	C37	3.5(9)	C93	C94	C95	C96	-3.5(9)
C35	C36	C37	C38	-3.9(9)	C93	C94	C95	C98	-179.2(5)
C35	C36	C37	C40	178.7(5)	C94	O13	C99	N4	-95.8(5)
C36	O5	C41	N2	-94.8(5)	C94	O13	C99	C98	24.2(6)
C36	O5	C41	C40	25.1(5)	C94	C95	C96	C91	1.5(8)
C36	C37	C38	C33	0.7(7)	C94	C95	C96	C97	-177.5(5)
C36	C37	C38	C39	-179.0(5)	C94	C95	C98	C99	14.0(6)
C36	C37	C40	C41	14.9(5)	C94	C95	C98	C100	-102.3(5)
C36	C37	C40	C42	-101.8(5)	C95	C96	C97	C88	177.3(5)
C37	C38	C39	C30	177.5(5)	C95	C98	C99	O13	-23.3(5)
C37	C40	C41	O5	-24.4(5)	C95	C98	C99	N4	95.0(5)
C37	C40	C41	N2	94.0(5)	C95	C98	C100	C101	46.9(7)
C37	C40	C42	C43	46.4(7)	C95	C98	C100	C109	-138.0(5)
C37	C40	C42	C51	-138.0(5)	C96	C91	C92	C93	-2.3(9)
C38	C33	C34	C35	-2.9(9)	C96	C95	C98	C99	-161.1(6)
C38	C37	C40	C41	-162.1(6)	C96	C95	C98	C100	82.6(7)
C38	C37	C40	C42	81.2(7)	C97	C88	C89	C90	-0.2(9)
C39	C30	C31	C32	-0.1(9)	C98	C95	C96	C91	176.2(5)
C40	C37	C38	C33	177.4(5)	C98	C95	C96	C97	-2.8(9)
C40	C37	C38	C39	-2.3(9)	C98	C100	C101	C102	173.3(5)
C40	C42	C43	C44	174.8(5)	C98	C100	C109	C108	-171.6(5)
C40	C42	C51	C50	-174.2(5)	C98	C100	C109	C110	11.2(8)
C40	C42	C51	C52	9.8(7)	C99	O13	C94	C93	163.8(5)
C41	O5	C36	C35	165.2(5)	C99	O13	C94	C95	-15.0(6)
C41	O5	C36	C37	-15.3(6)	C99	C98	C100	C101	-63.6(6)
C41	C40	C42	C43	-63.9(6)	C99	C98	C100	C109	111.5(5)
C41	C40	C42	C51	111.7(5)	C100	C98	C99	O13	98.5(5)
C42	C40	C41	O5	95.9(5)	C100	C98	C99	N4	-143.2(5)
C42	C40	C41	N2	-145.7(4)	C100	C101	C102	C103	-0.3(8)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C42	C43	C44	C45	-0.3(8)	C100	C109	C110	C111	87.6(7)
C42	C51	C52	C53	91.4(6)	C100	C109	C110	C115	-92.1(7)
C42	C51	C52	C57	-88.3(7)	C101	C100	C109	C108	3.5(8)
C43	C42	C51	C50	1.4(7)	C101	C100	C109	C110	-173.6(5)
C43	C42	C51	C52	-174.7(5)	C101	C102	C103	C104	-178.4(5)
C43	C44	C45	C46	-179.0(5)	C101	C102	C103	C108	0.7(8)
C43	C44	C45	C50	0.9(8)	C102	C103	C104	C105	178.9(5)
C44	C45	C46	C47	-179.7(5)	C102	C103	C108	C107	-179.3(5)
C44	C45	C50	C49	-179.9(5)	C102	C103	C108	C109	1.0(7)
C44	C45	C50	C51	-0.4(7)	C103	C104	C105	C106	-0.5(9)
C45	C46	C47	C48	-1.5(9)	C103	C108	C109	C100	-3.1(7)
C45	C50	C51	C42	-0.8(7)	C103	C108	C109	C110	174.1(5)
C45	C50	C51	C52	175.3(5)	C104	C103	C108	C107	-0.1(7)
C46	C45	C50	C49	0.0(7)	C104	C103	C108	C109	-179.9(5)
C46	C45	C50	C51	179.5(5)	C104	C105	C106	C107	1.5(9)
C46	C47	C48	C49	2.1(9)	C105	C106	C107	C108	-1.8(8)
C47	C48	C49	C50	-1.7(9)	C106	C107	C108	C103	1.1(8)
C48	C49	C50	C45	0.7(8)	C106	C107	C108	C109	-179.1(5)
C48	C49	C50	C51	-178.9(5)	C107	C108	C109	C100	177.2(5)
C49	C50	C51	C42	178.8(5)	C107	C108	C109	C110	-5.6(7)
C49	C50	C51	C52	-5.2(7)	C108	C103	C104	C105	-0.2(8)
C50	C45	C46	C47	0.4(8)	C108	C109	C110	C111	-89.6(6)
C50	C51	C52	C53	-84.6(6)	C108	C109	C110	C115	90.8(7)
C50	C51	C52	C57	95.7(6)	C109	C100	C101	C102	-1.9(8)
C51	C42	C43	C44	-0.8(8)	C109	C110	C111	C112	-177.6(5)
C51	C52	C53	C54	-178.9(5)	C109	C110	C115	O16	-0.9(8)
C51	C52	C57	O8	-0.5(8)	C109	C110	C115	C114	177.9(5)
C51	C52	C57	C56	179.1(5)	C110	C111	C112	C113	-1.3(9)
C52	C53	C54	C55	-0.7(10)	C111	C110	C115	O16	179.4(5)
C53	C52	C57	O8	179.8(5)	C111	C110	C115	C114	-1.7(8)
C53	C52	C57	C56	-0.7(8)	C111	C112	C113	C114	0.2(10)
C53	C54	C55	C56	0.3(10)	C112	C113	C114	C115	0.2(10)
C54	C55	C56	C57	-0.1(10)	C113	C114	C115	O16	179.4(6)
C55	C56	C57	O8	179.8(6)	C113	C114	C115	C110	0.6(10)
C55	C56	C57	C52	0.3(10)	C115	C110	C111	C112	2.1(9)
C57	C52	C53	C54	0.9(9)	C116	O16	C115	C110	174.5(6)
C58	O8	C57	C52	175.9(6)	C116	O16	C115	C114	-4.3(9)
C58	O8	C57	C56	-3.6(10)	O11A	N3	C70	O9	-126.5(17)
Br3	C59	C60	C61	-174.4(5)	O11A	N3	C70	C69	115.5(17)

Table 7 Hydrogen Atom Coordinates ($\text{\AA}\times 104$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 103$) for 3ag.

Atom	x	y	z	U(eq)
H2	-462.39	17550.79	3912.15	74
H3	582.99	18010.37	3753.25	74
H5	1582.94	17382.16	3290.39	70
H6	2185.07	15744.72	2796.43	73
H10	-412.3	14005.2	2909.29	46
H11	411.96	12064.47	2610.8	43
H12	1381.18	11636.31	1947.12	58
H14	904.4	14732.97	1608.63	48
H15	521.52	15039.34	725.71	51
H17	-174	14221.9	-54.81	55
H18	-926.79	12653.59	-389.42	60
H19	-1297.66	10752.56	161.35	57
H20	-970.26	10524.95	1074.57	48
H24	-1087.52	11995.81	2289.64	45
H25	-1527.43	10048.36	2768.74	56
H26	-1074.57	7784.71	2728.06	59
H27	-156.57	7405.91	2231.95	58
H29A	1161.83	8144.71	1439.24	102
H29B	511.34	7311.37	1515.86	102
H29C	913.35	7798.63	2046.15	102
H31	945.68	12184.45	-1037.05	64
H32	1039.33	12637.98	-97.7	61
H34	1506.39	12092.31	816.91	59
H35	2096.61	10569.42	1386.16	56
H39	2128.79	8733.94	-883.05	46
H40	2441.36	6802.33	-129.15	38
H41	3150.21	6467.43	762.15	43
H43	3564.81	9425.57	403.44	44
H44	4581.54	9729.69	122.42	43
H46	5469.65	8966.98	-466.89	50
H47	5857.98	7516.66	-1158.47	54
H48	5234.89	5695.98	-1558.09	52
H49	4199.63	5429.96	-1309.8	44
H53	2893.89	7212.48	-1453.47	51
H54	2217.88	5673.24	-1925.9	66
H55	2065.21	3310.78	-1607.12	67
H56	2586.23	2517.83	-804.94	62

Atom	x	y	z	U(eq)
H58A	3385.93	1879.78	-228.06	116
H58B	2793.46	2509.63	91.55	116
H58C	3467.24	2492.44	387.23	116
H60	5858.65	7267.06	1053.39	64
H61	4832.38	8048.66	1090.86	64
H63	3783.16	7879.29	1497.89	70
H64	3054.34	6652.91	2020.48	69
H68	5487.86	4008.39	2138.92	44
H69	4491.24	2344.21	2395.36	46
H70	3489.57	2547.54	3057.78	63
H72	4090.47	5152.62	3374.87	51
H73	4482.61	5443.57	4253.92	52
H75	5177.68	4622.65	5025.96	53
H76	5912.21	3006.73	5367.55	59
H77	6273.16	1094.75	4816.51	57
H78	5909.21	826.22	3912.39	49
H82	6082.93	2201.08	2737.5	48
H83	6496.09	186.49	2273.94	59
H84	5986.39	-2006.39	2295.86	63
H85	5039.55	-2251.45	2745.74	67
H87A	3964.97	-1798.2	2930.51	130
H87B	3747.05	-1453.8	3546.92	130
H87C	4391.97	-2290.18	3444.84	130
H89	4042.29	2474.48	6074.82	64
H90	3971.19	2918.12	5131.52	60
H92	3516.47	2346.49	4214.79	58
H93	2938.12	816.51	3638.71	58
H97	2847.01	-947.53	5918.58	48
H98	2544.58	-2868.76	5167.5	39
H99	1840.02	-3225.1	4267.41	43
H101	1396.82	-319.16	4614.34	42
H102	367.16	-140	4869.35	43
H104	-529.34	-993.33	5431.42	51
H105	-917.64	-2534.76	6094.34	54
H106	-268.25	-4284.3	6516.48	51
H107	788.71	-4407.01	6302.72	44
H111	2089.63	-2367.66	6464.16	50
H112	2800.61	-3797.03	6950.26	61
H113	2974.55	-6206.94	6670.25	63

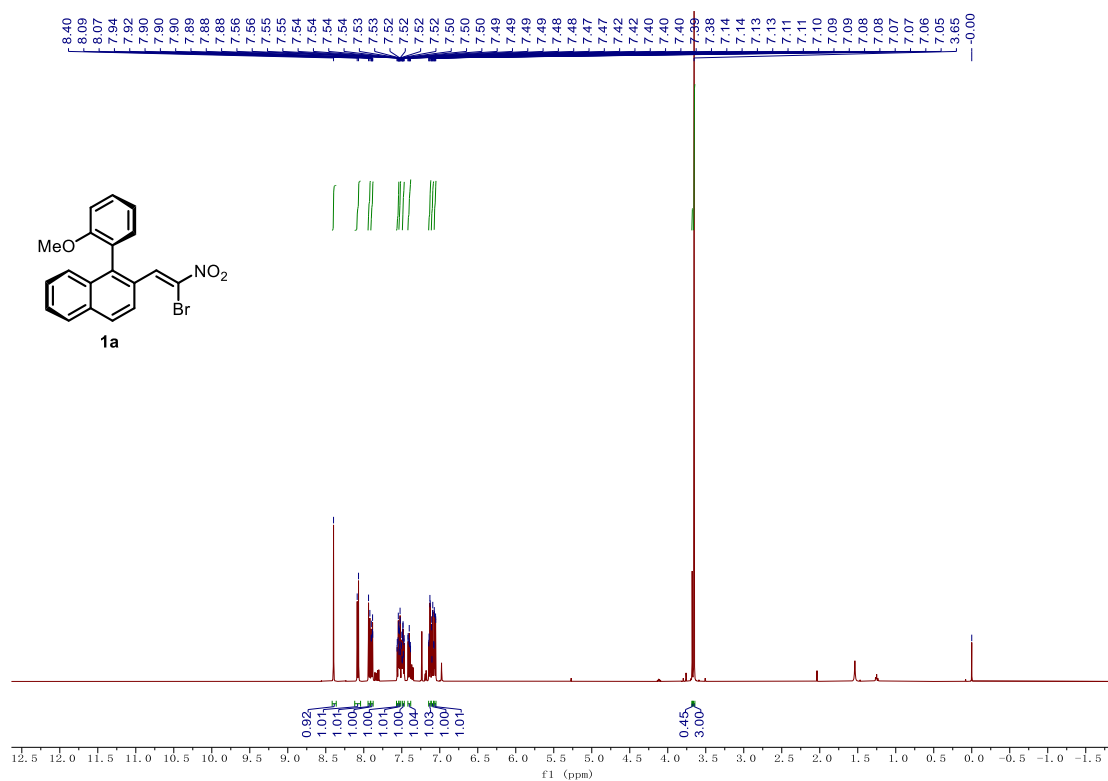
Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H114	2440.06	-7118.99	5902.83	61
H11A	1634.01	-7873.76	5337	104
H11B	2215.41	-7237	5003.95	104
H11C	1538.29	-7314.5	4715.84	104

Table 8 Atomic Occupancy for 3ag.

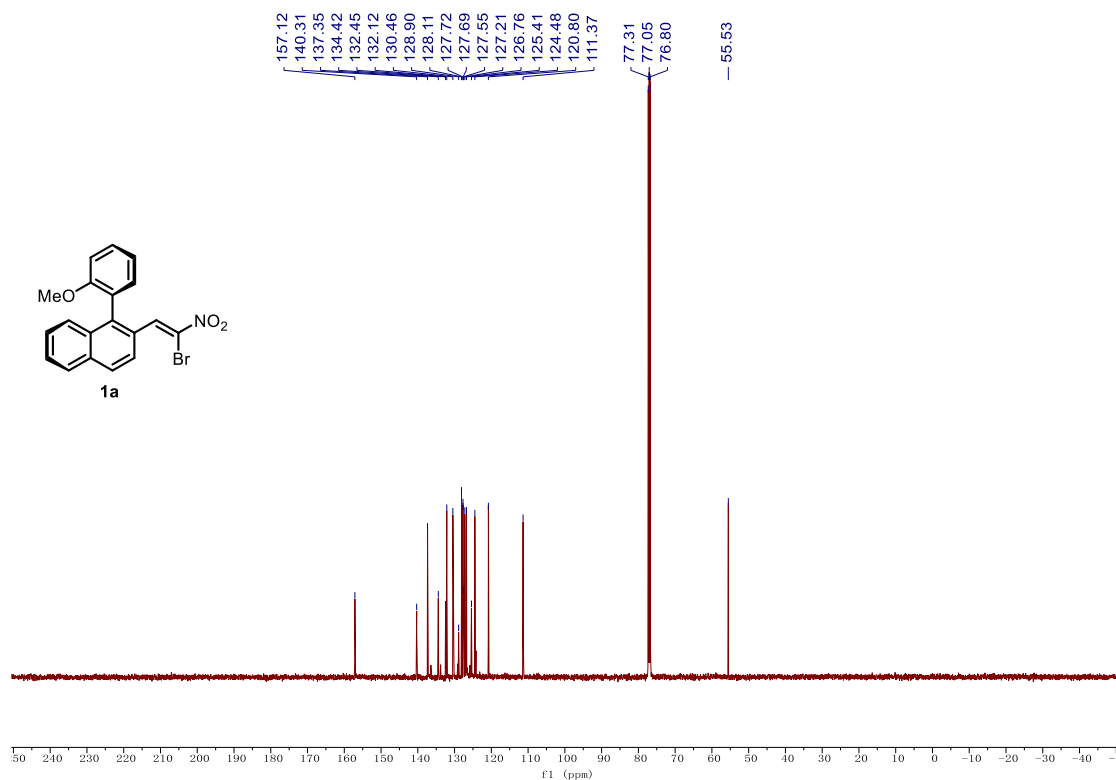
Atom	<i>Occupancy</i>	Atom	<i>Occupancy</i>	Atom	<i>Occupancy</i>
O11	0.59(3)	O11A	0.41(3)		

5. NMR spectra

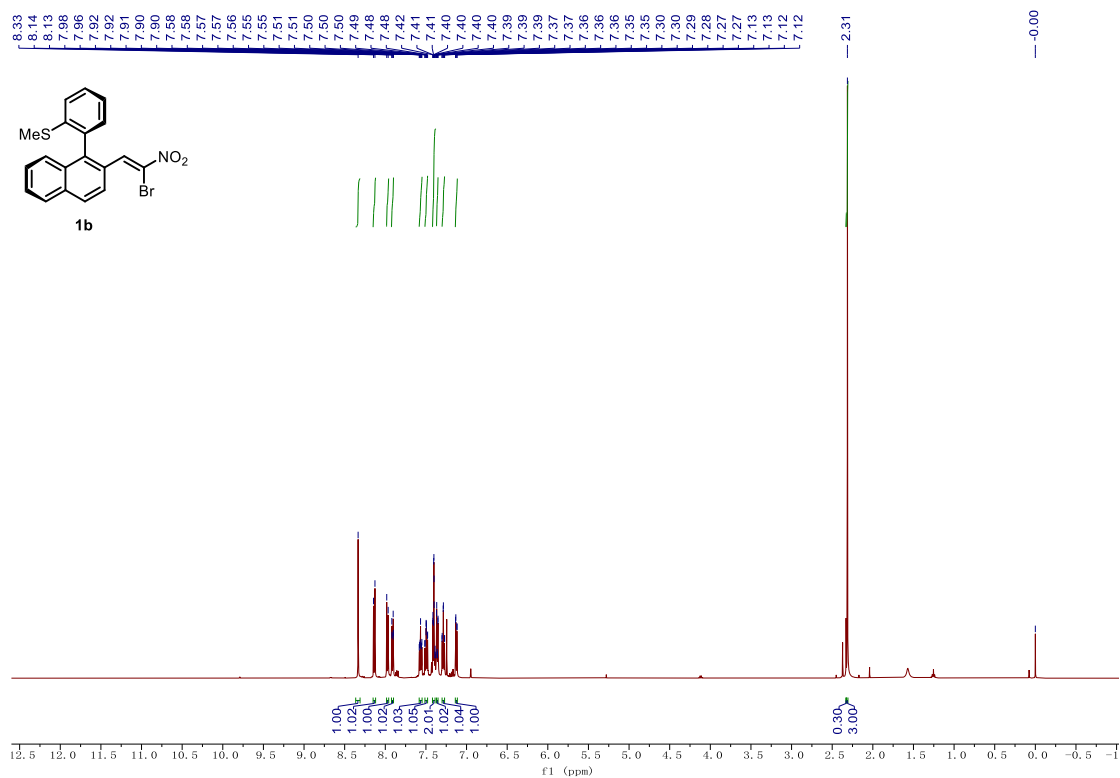
¹H NMR of 1a (500 MHz in CDCl₃):



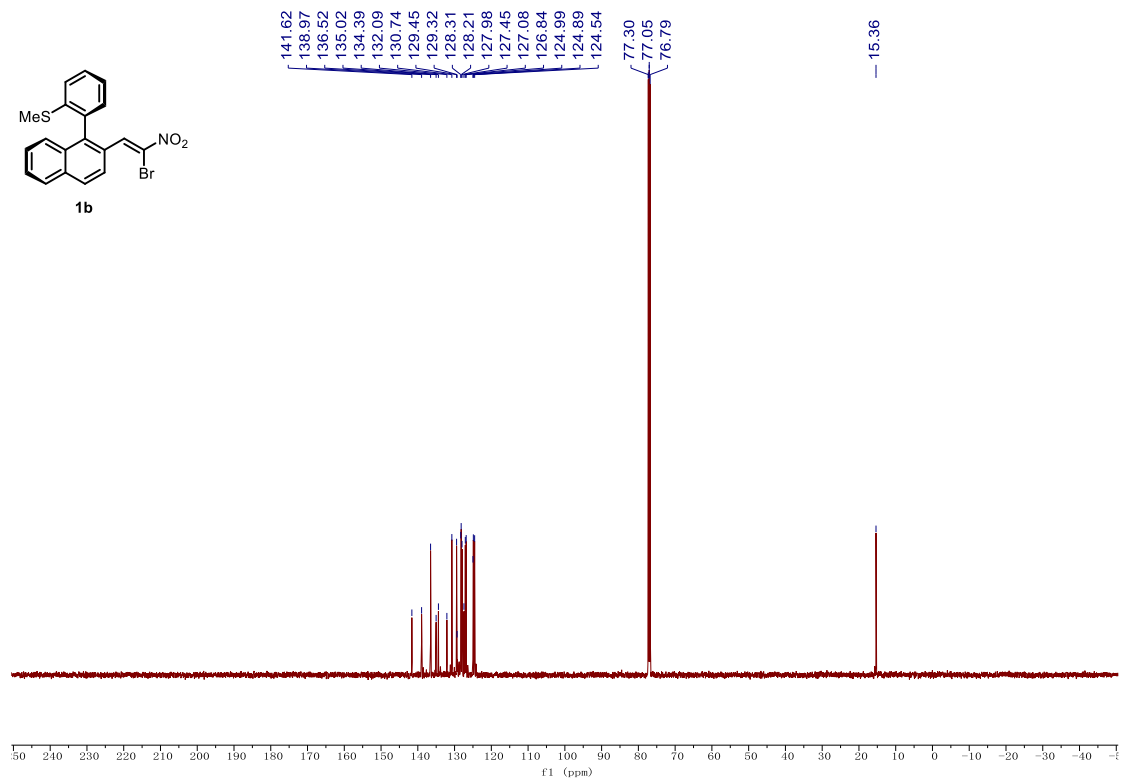
¹³C NMR of 1a (126 MHz in CDCl₃):



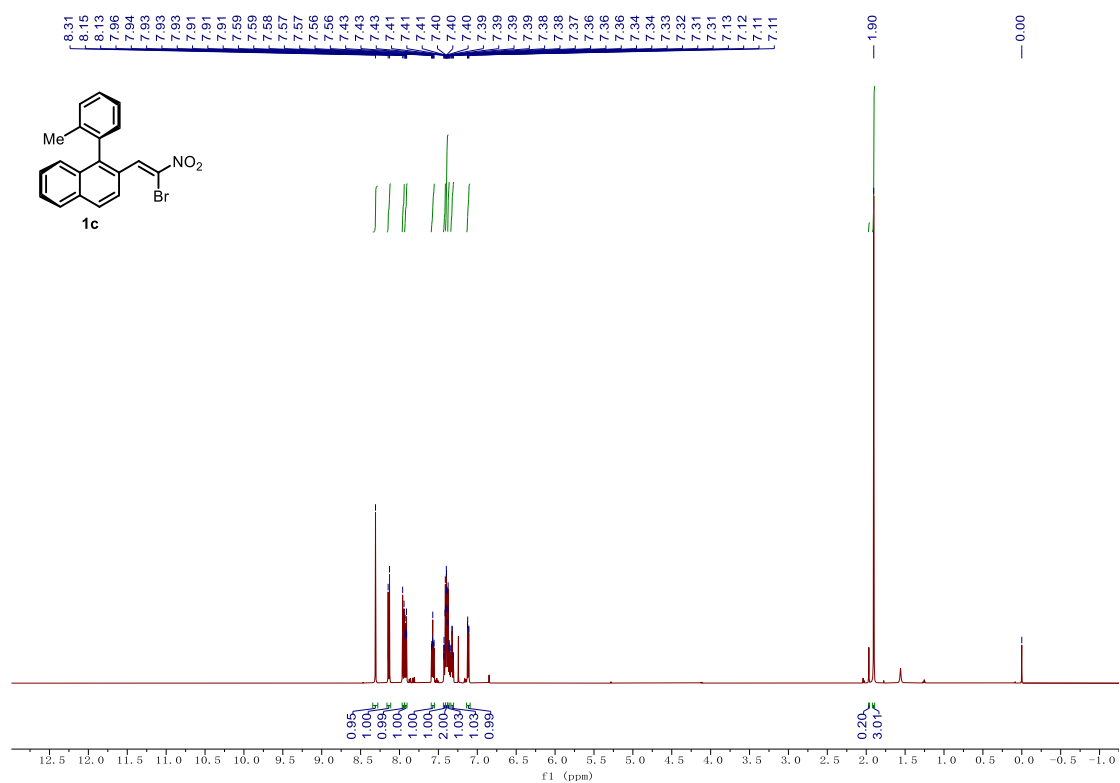
¹H NMR of 1b (500 MHz in CDCl₃):



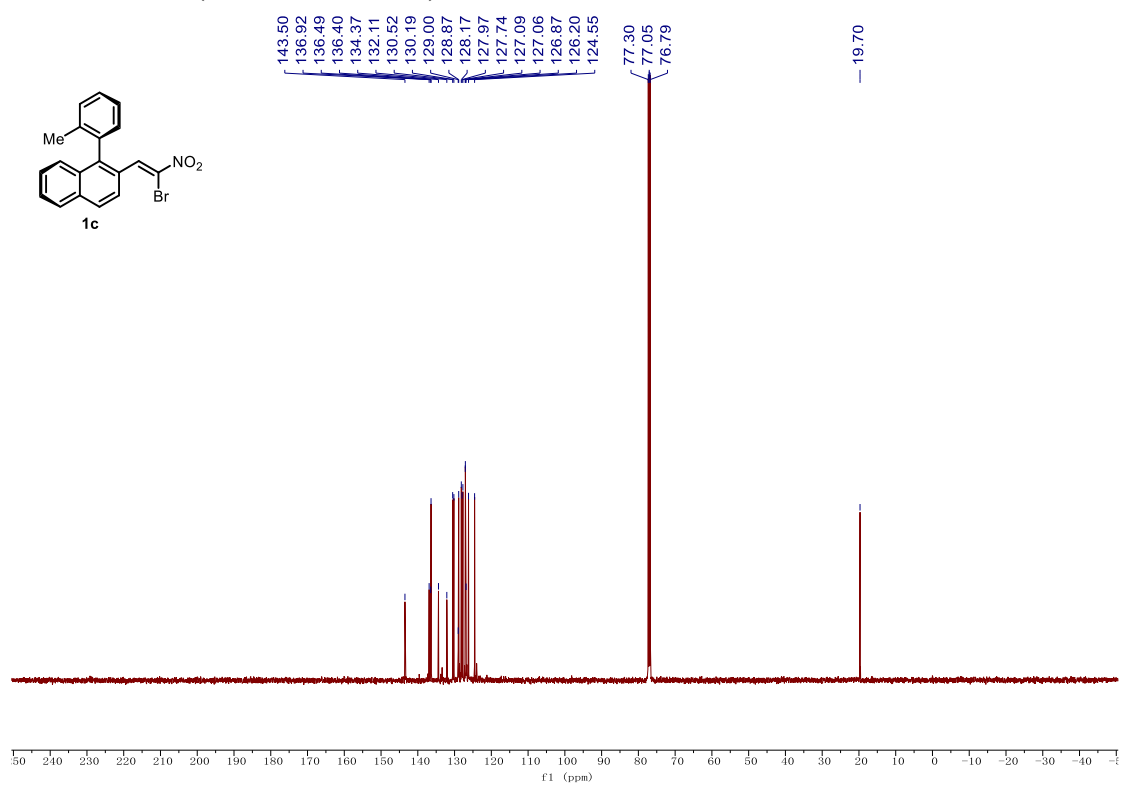
¹³C NMR of 1b (126 MHz in CDCl₃):



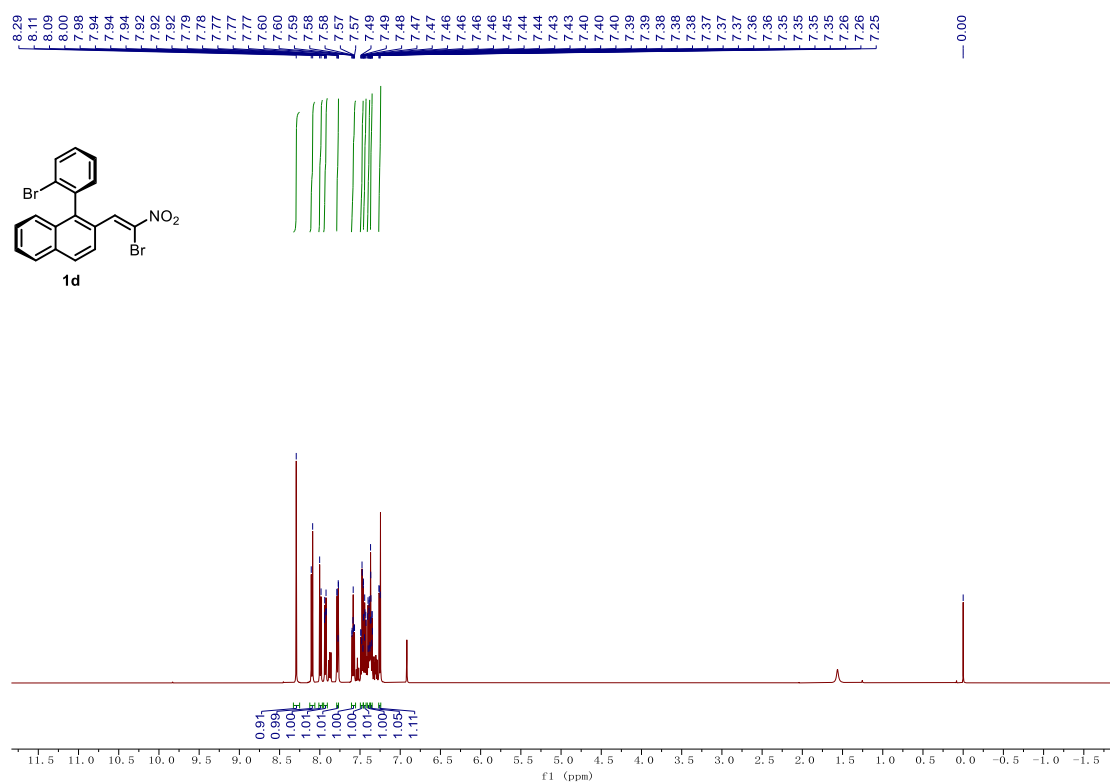
¹H NMR of 1c (500 MHz in CDCl₃):



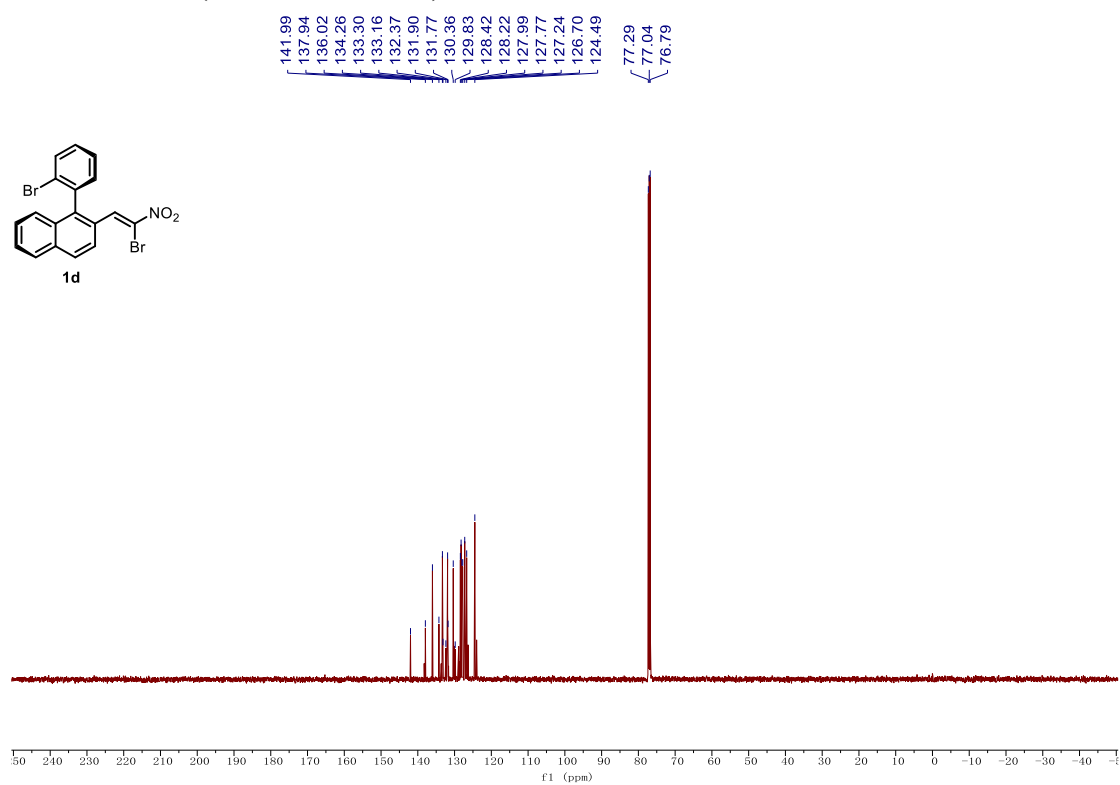
¹³C NMR of 1c (126 MHz in CDCl₃):



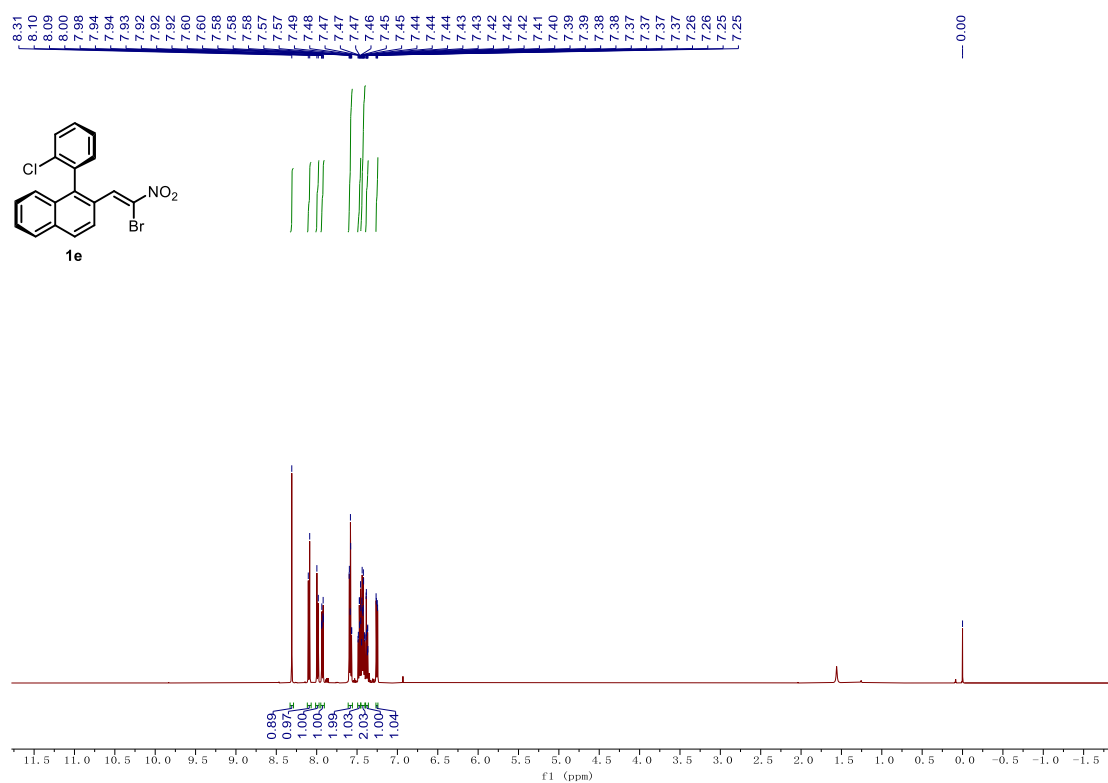
¹H NMR of 1d (500 MHz in CDCl₃):



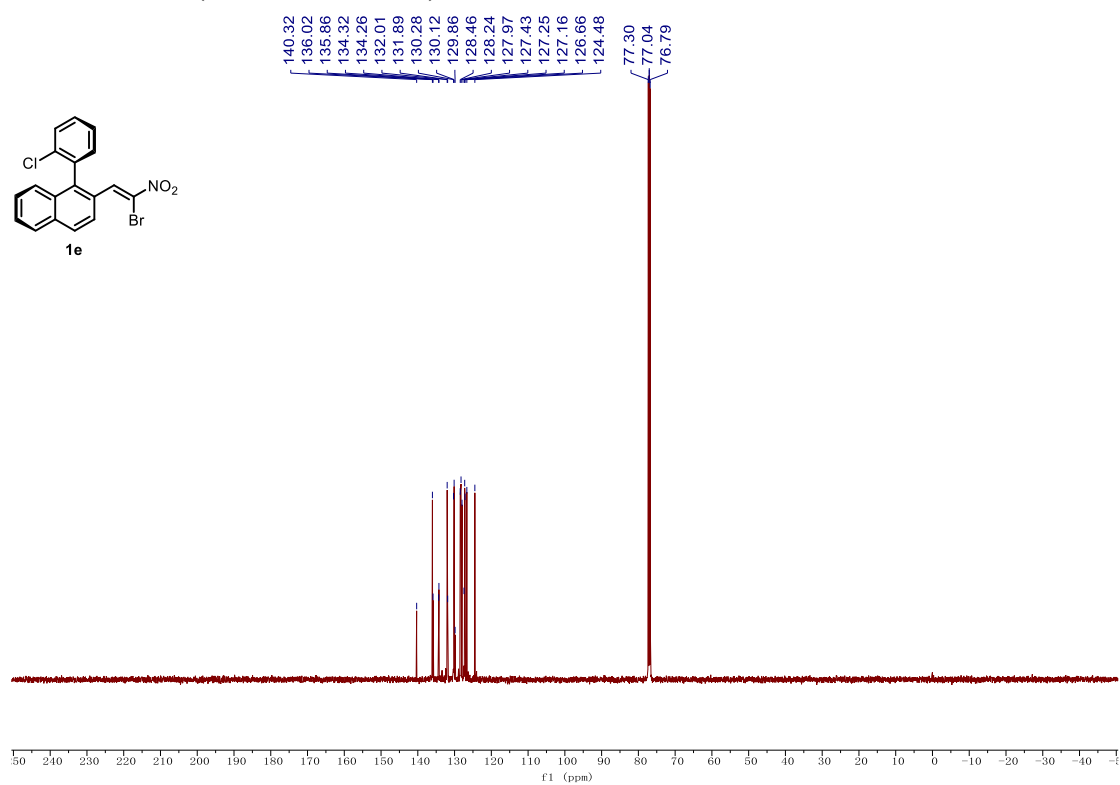
¹³C NMR of 1d (126 MHz in CDCl₃):



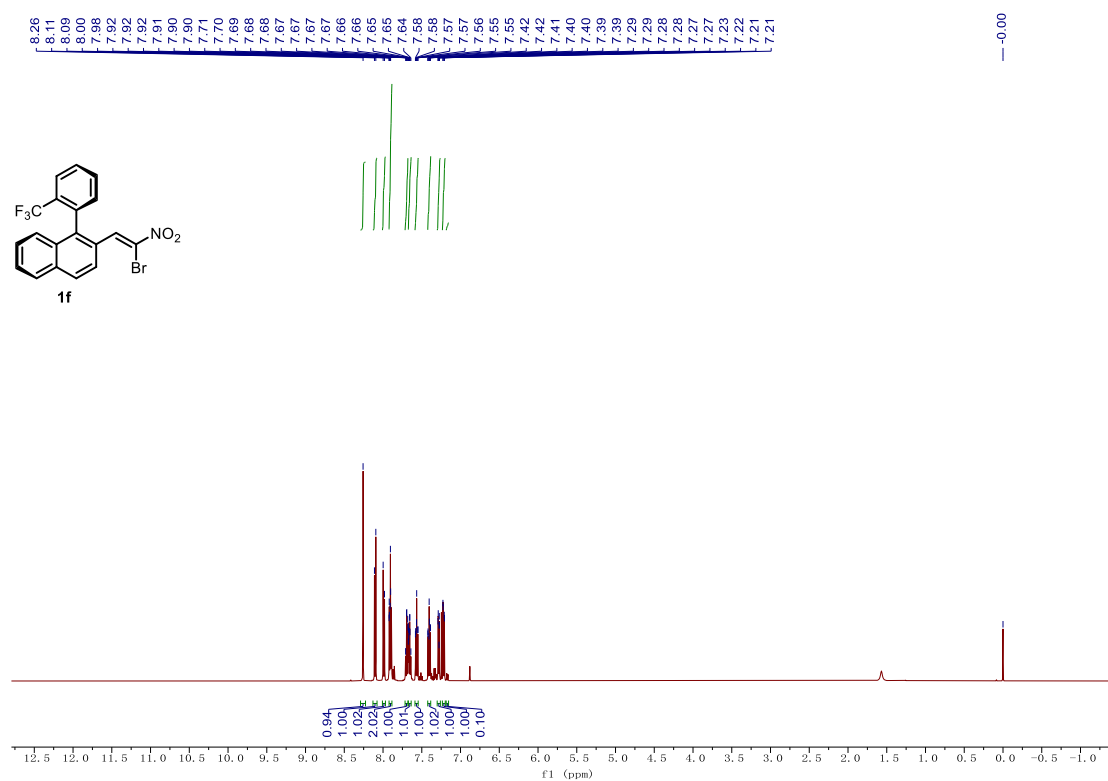
¹H NMR of 1e (500 MHz in CDCl₃):



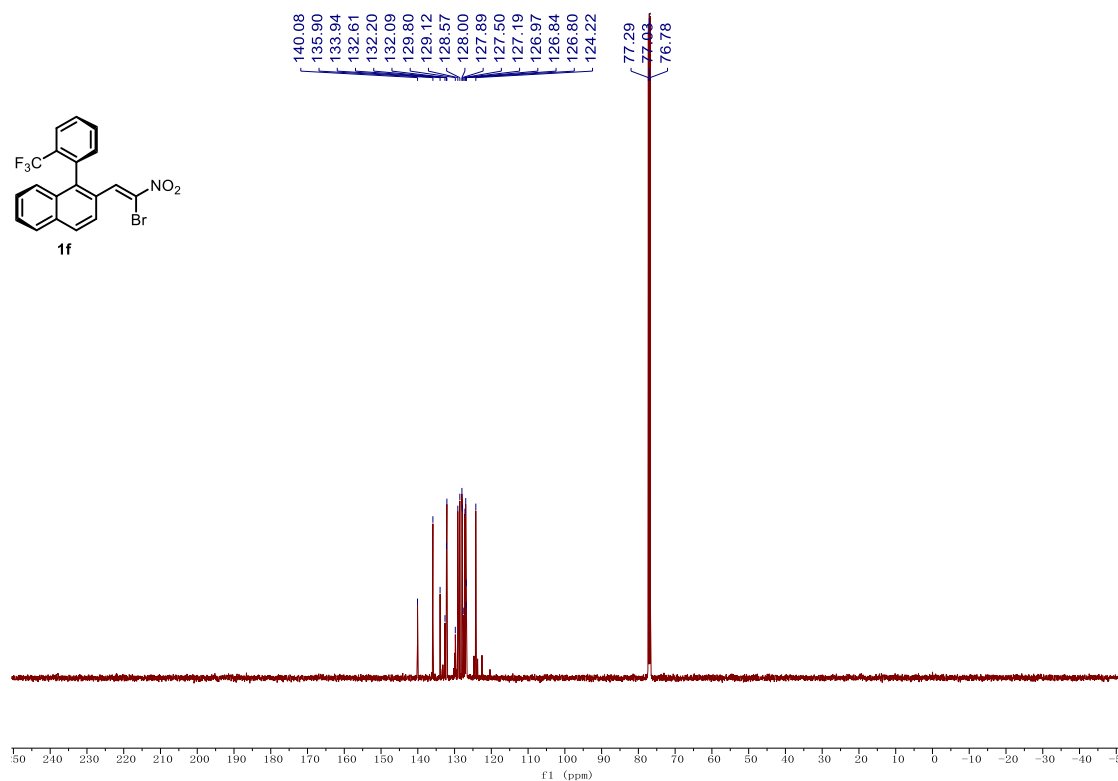
¹³C NMR of 1e (126 MHz in CDCl₃):



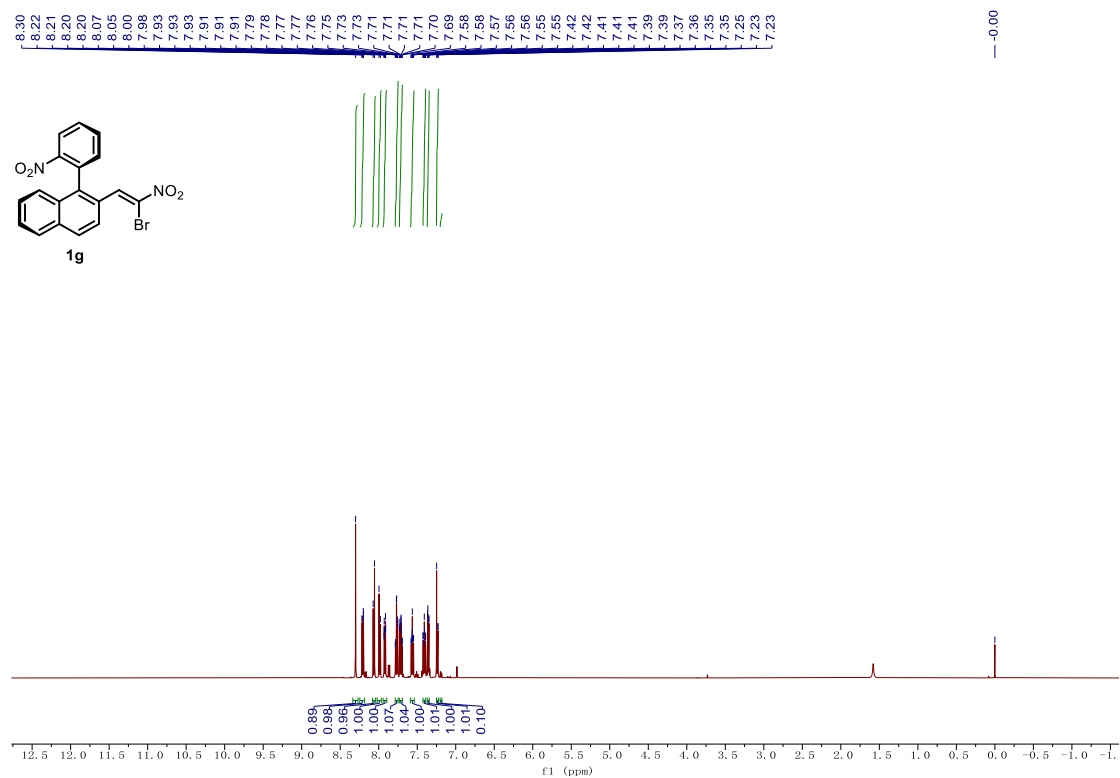
¹H NMR of 1f (500 MHz in CDCl₃):



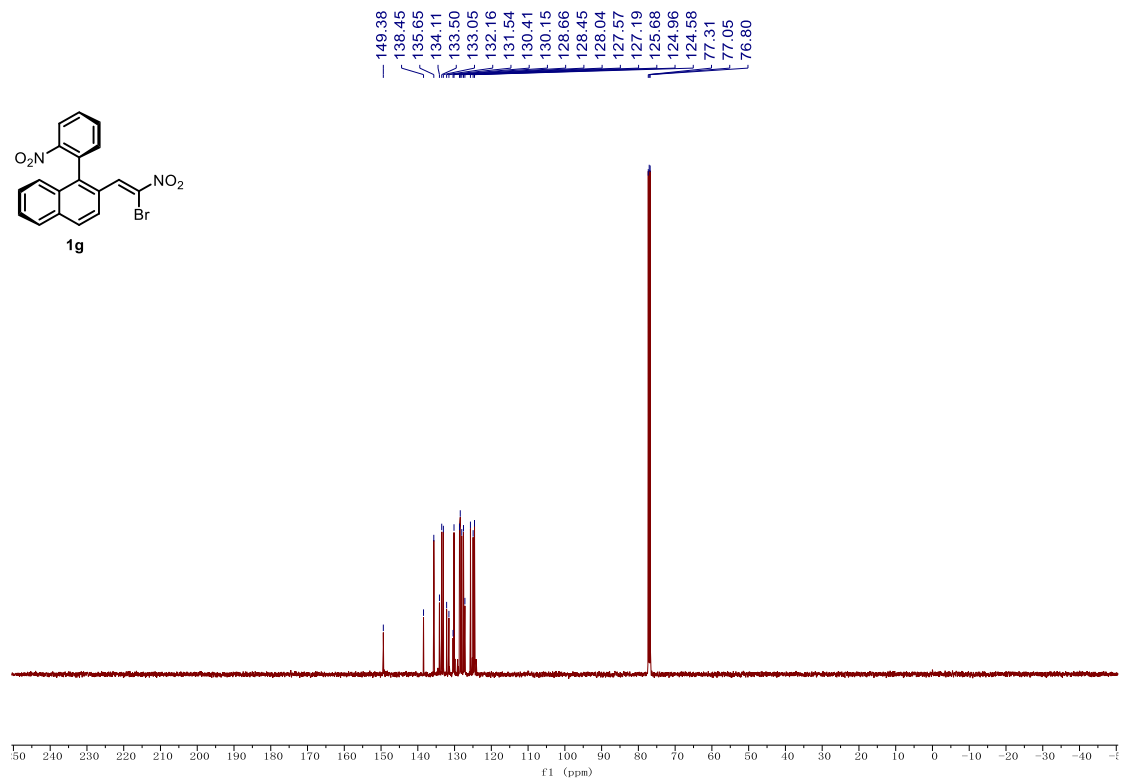
¹³C NMR of 1f (126 MHz in CDCl₃):



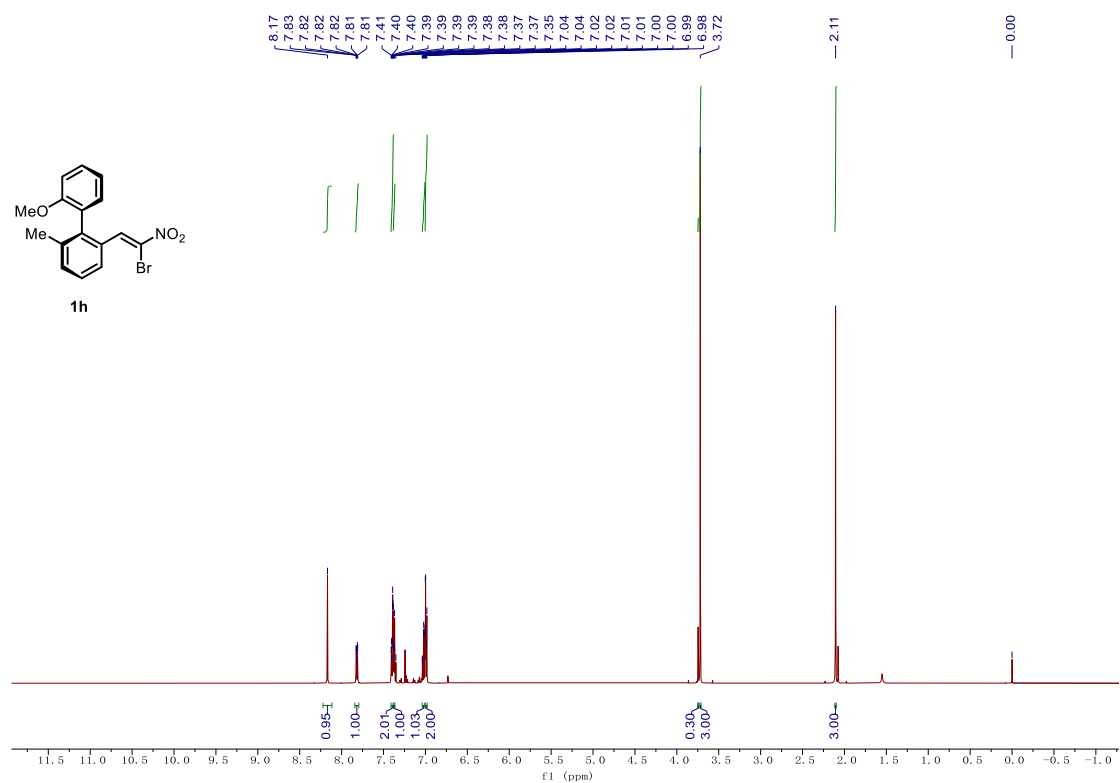
¹H NMR of 1g (500 MHz in CDCl₃):



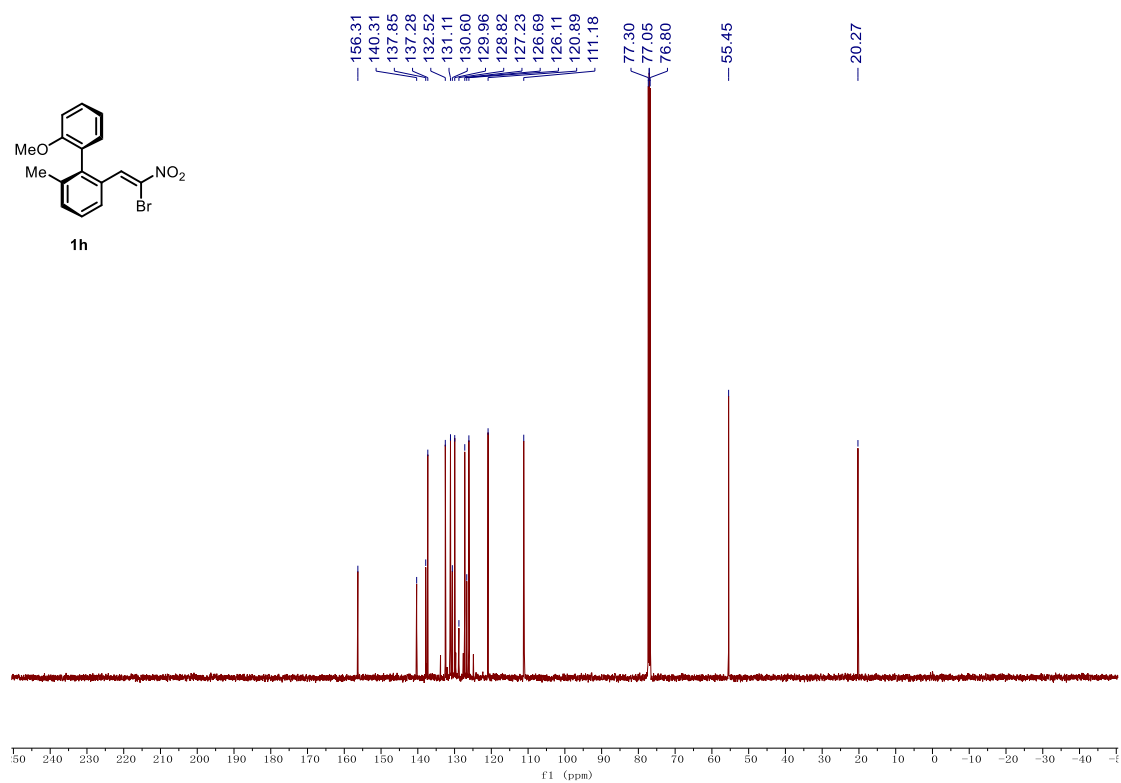
¹³C NMR of 1g (126 MHz in CDCl₃):



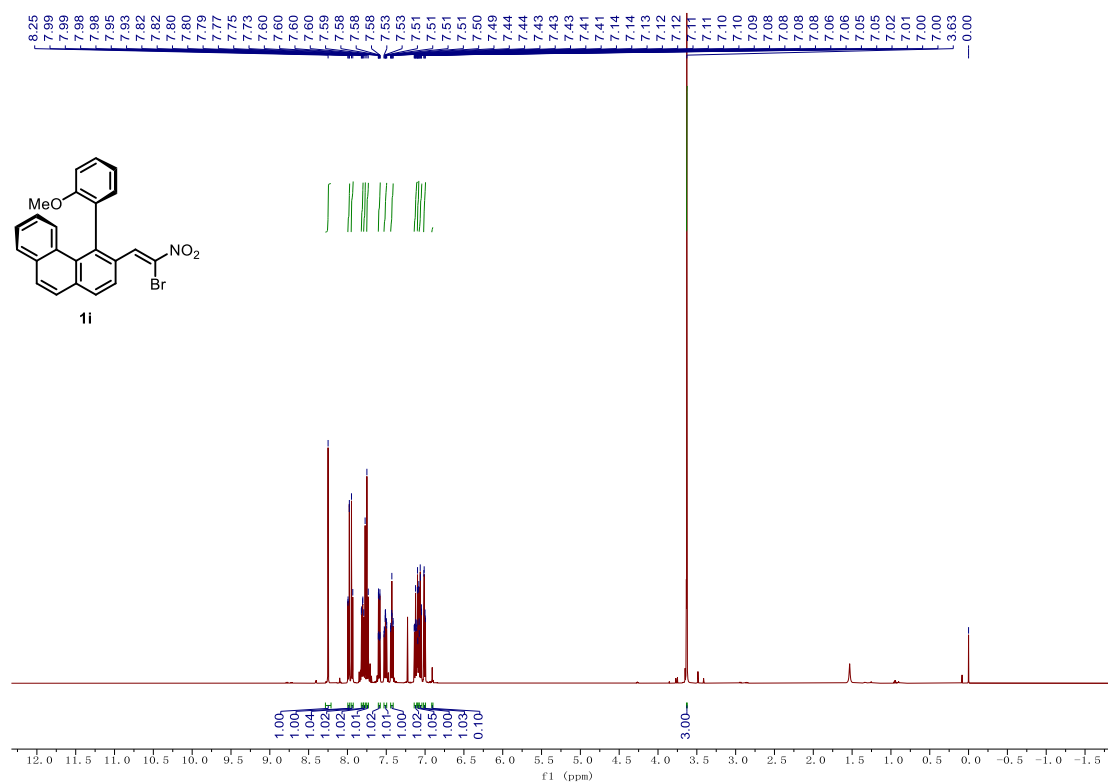
¹H NMR of 1h (500 MHz in CDCl₃):



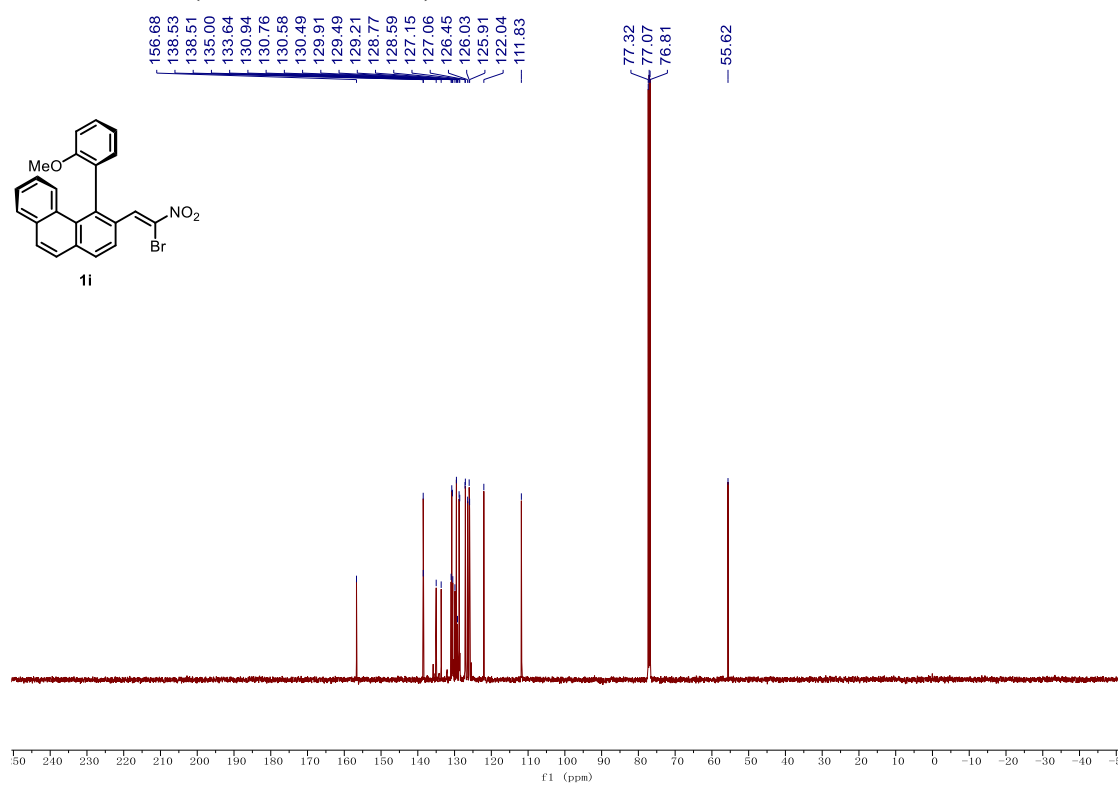
¹³C NMR of 1h (126 MHz in CDCl₃):



¹H NMR of 1i (500 MHz in CDCl₃):



¹³C NMR of 1i (126 MHz in CDCl₃):

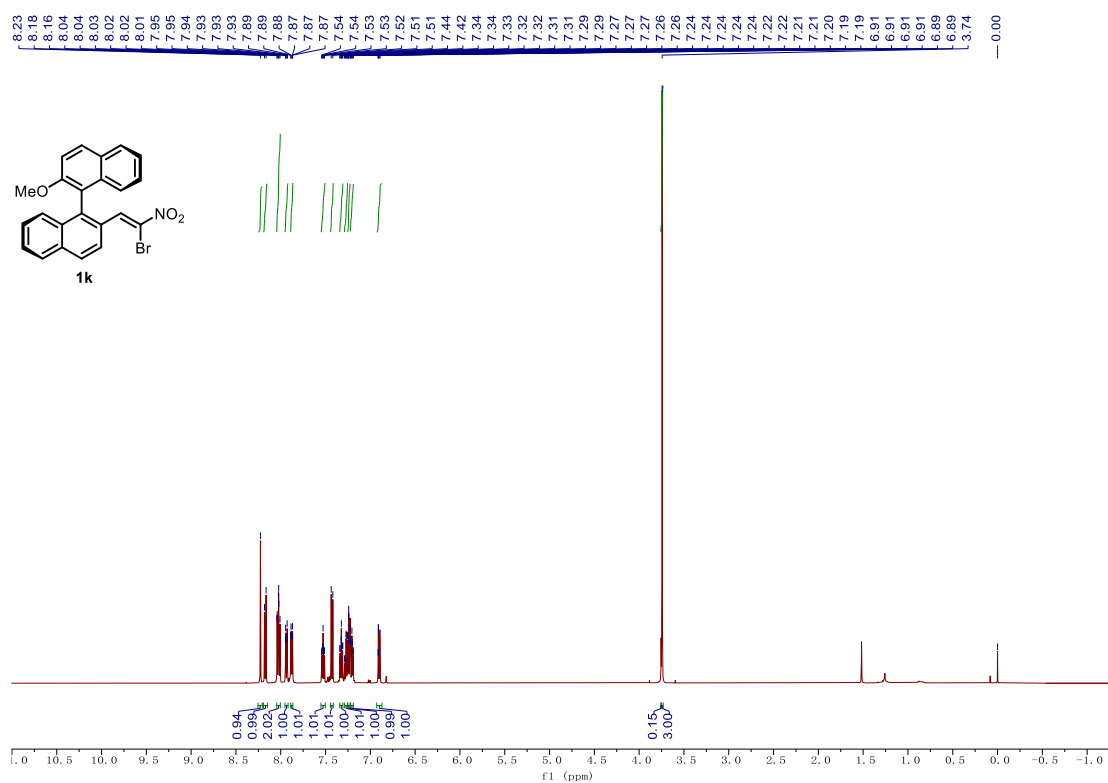


[illegible]

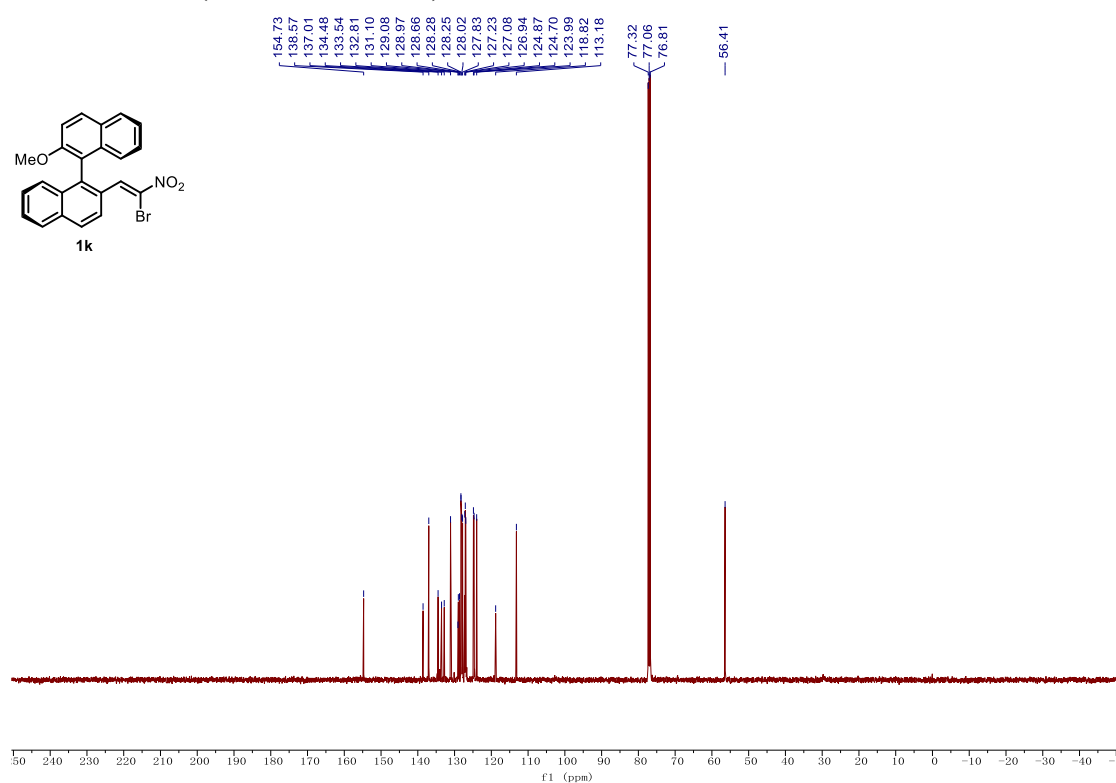
Chemical structure of **1j** is shown above the spectrum. The spectrum displays peaks corresponding to the carbon atoms in the molecule, with the following chemical shifts (ppm) labeled above the peaks:

Chemical Shift (ppm)
141.87
136.66
134.55
134.28
133.67
132.96
132.44
129.38
129.24
128.69
128.66
128.59
128.16
128.10
127.95
127.54
127.04
126.79
126.36
125.72
125.40
124.71
77.31
77.06
76.80

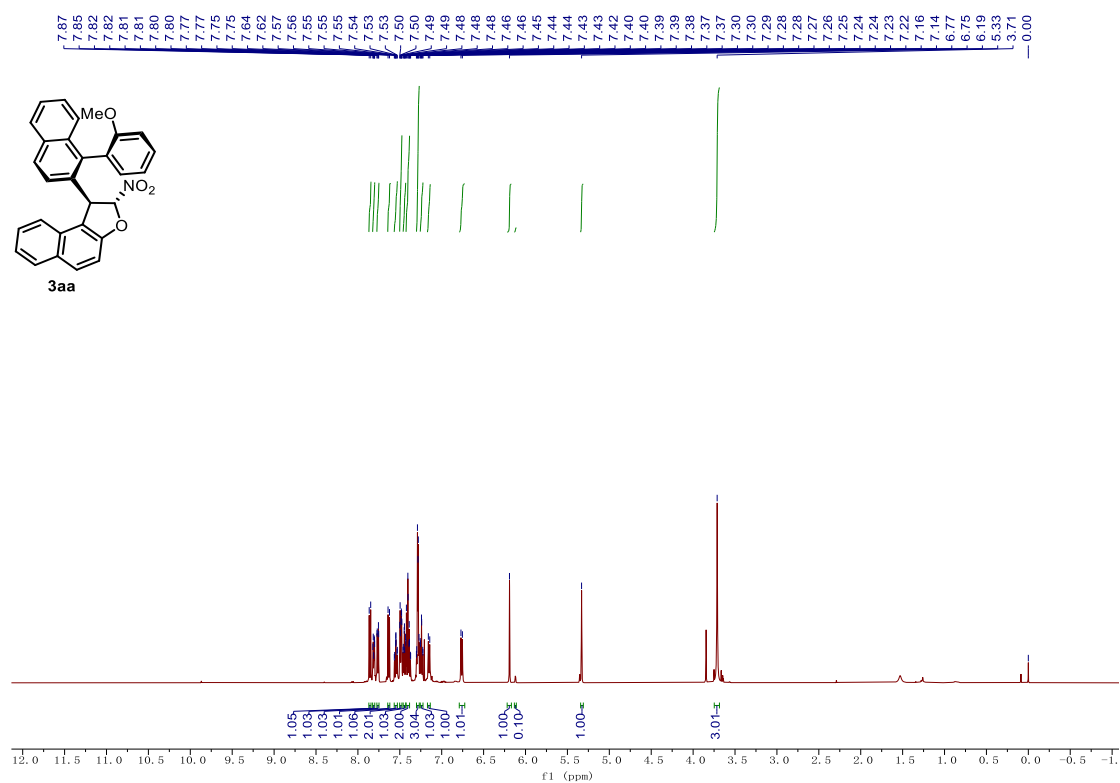
¹H NMR of 1k (500 MHz in CDCl₃):



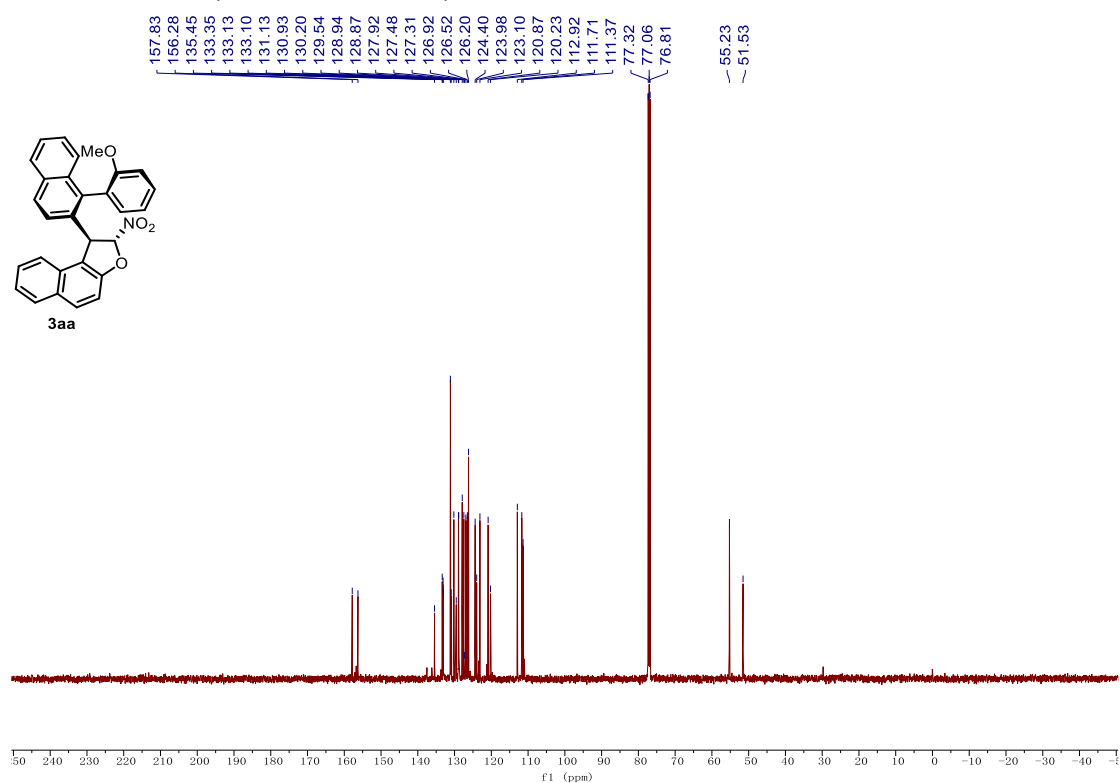
¹³C NMR of 1k (126 MHz in CDCl₃):



¹H NMR of 3aa (500 MHz in CDCl₃):



¹³C NMR of 3aa (126 MHz in CDCl₃):

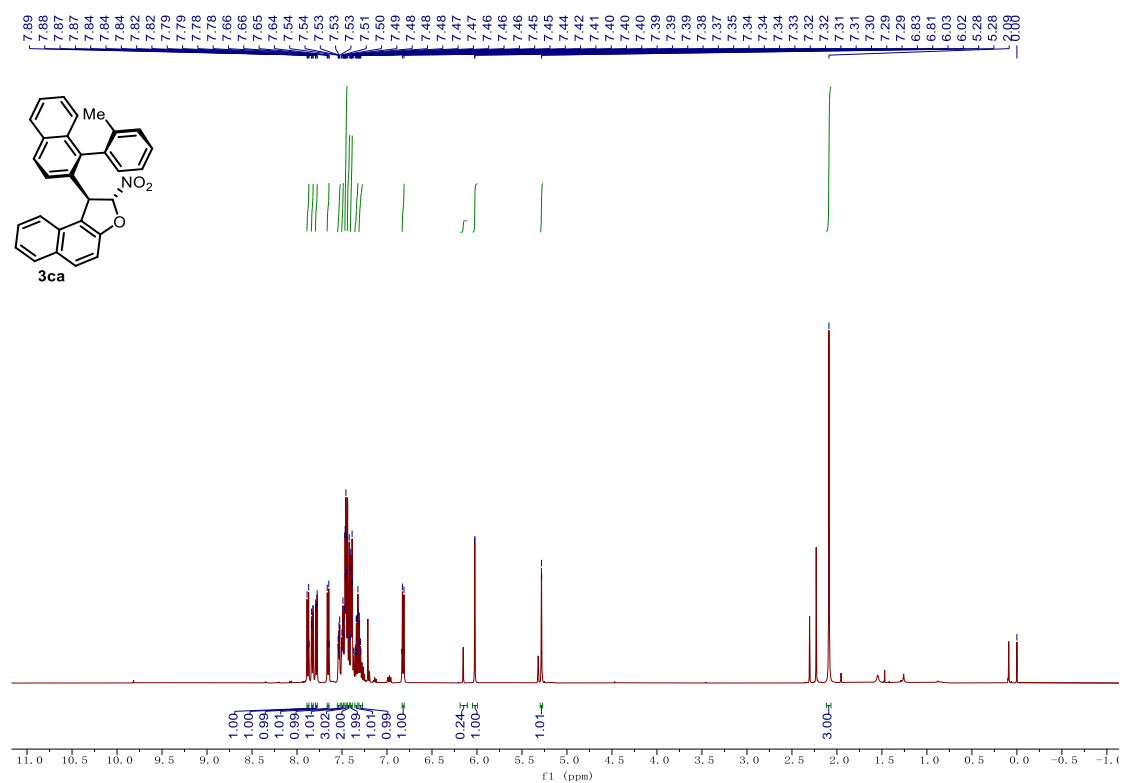


Chemical structure of **3ba** is shown. The ¹H NMR spectrum (CDCl₃) displays peaks from 0.00 to 7.90 ppm. Integration values are provided below the baseline: 1.04, 1.03, 1.00, 2.01, 2.01, 2.00, 2.07, 1.03, 1.05, 1.00, 1.00, 0.08, 1.03, and 3.00. A list of chemical shifts (δ) in ppm is shown at the top: 7.90, 7.78, 7.75, 7.74, 7.73, 7.70, 7.69, 7.68, 7.68, 7.58, 7.56, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.38, 7.38, 7.38, 7.37, 7.37, 7.36, 7.35, 7.35, 7.35, 7.34, 7.34, 7.33, 7.33, 7.33, 7.32, 7.32, 7.32, 7.31, 7.31, 7.26, 7.25, 7.24, 7.24, 7.23, 7.23, 7.22, 7.21, 7.21, 7.20, 7.20, 7.20, 6.67, 6.65, 6.40, 5.20, 5.19, and 0.00.

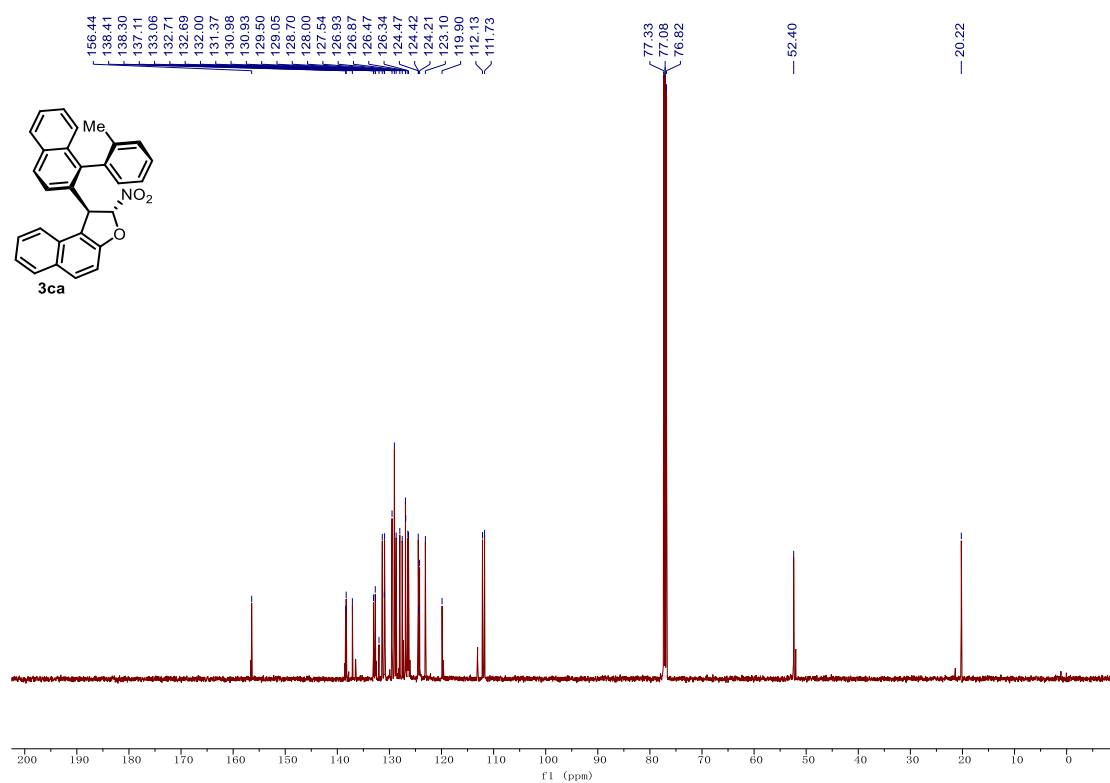
Chemical structure of **3ba** is shown in the top left. The ^{13}C NMR spectrum (CDCl₃) is displayed below, with the following chemical shifts (ppm) labeled on the left:

- 156.43
- 140.32
- 136.69
- 135.42
- 133.11
- 132.66
- 132.58
- 131.24
- 130.96
- 129.65
- 129.54
- 129.53
- 129.36
- 128.04
- 127.77
- 127.54
- 126.93
- 126.53
- 126.51
- 124.89
- 124.43
- 124.37
- 124.20
- 123.04
- 119.97
- 112.06
- 111.83
- 77.34
- 77.09
- 76.83
- 51.27
- 14.53

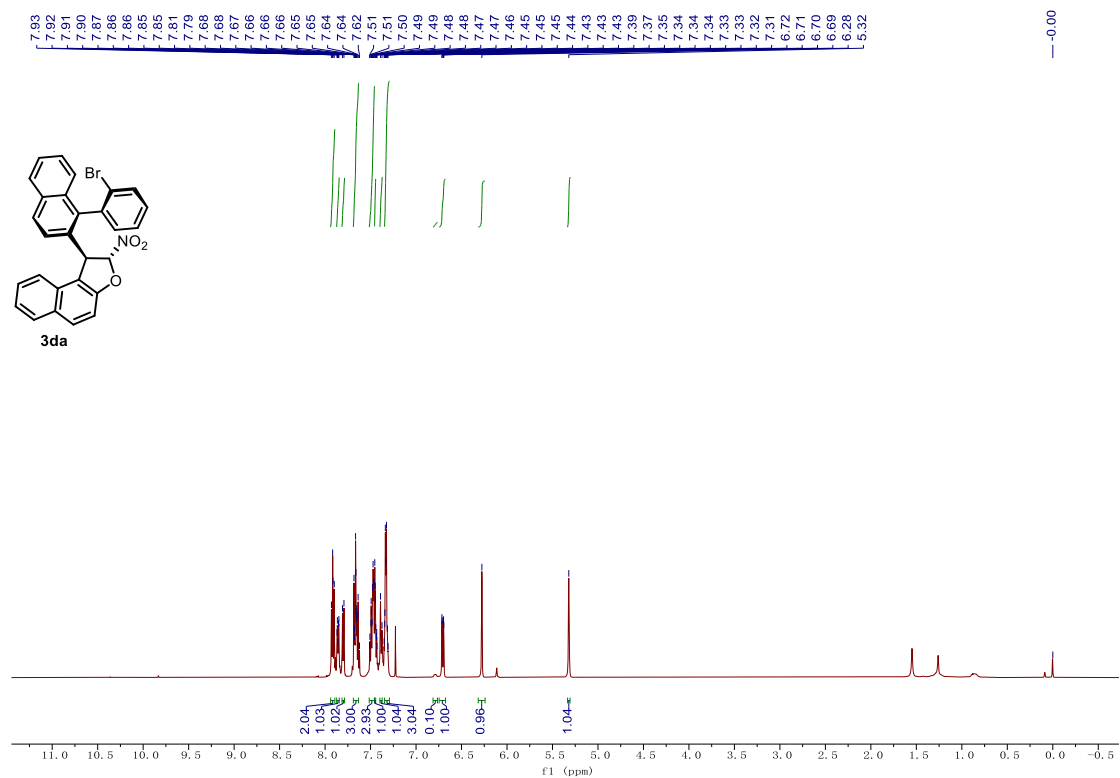
¹H NMR of 3ca (500 MHz in CDCl₃):



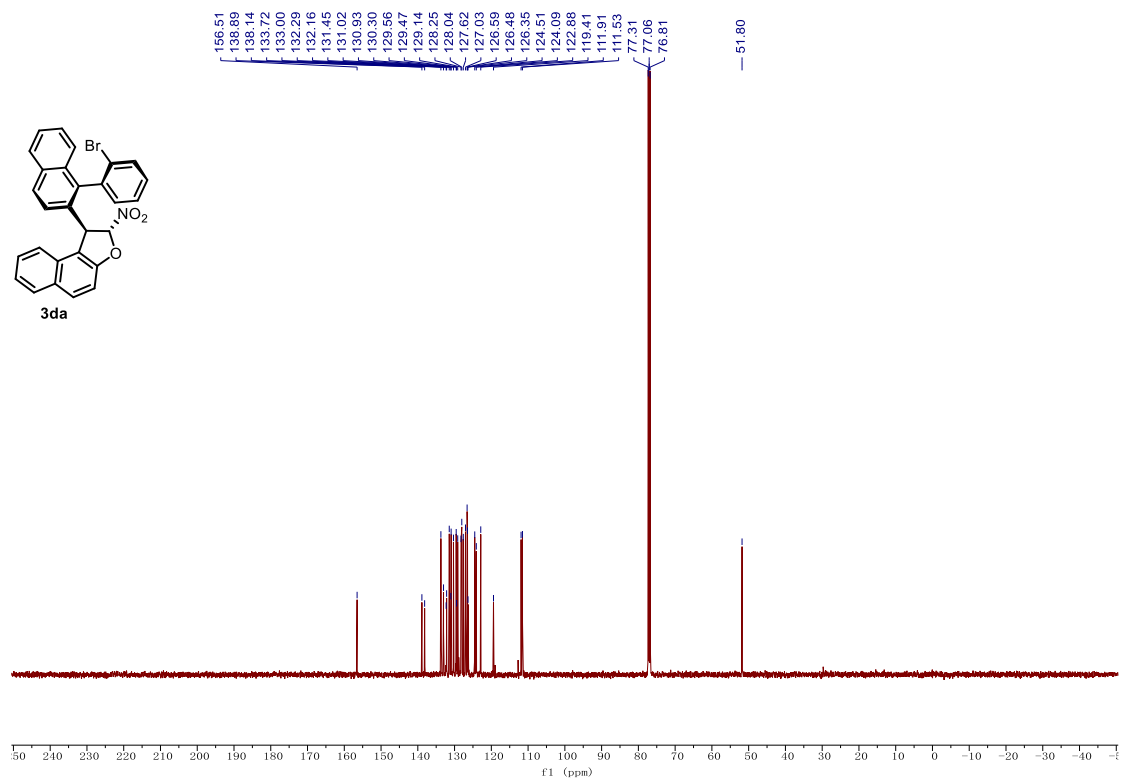
¹³C NMR of 3ca (126 MHz in CDCl₃):



¹H NMR of 3da (500 MHz in CDCl₃):



¹³C NMR of 3da (126 MHz in CDCl₃):

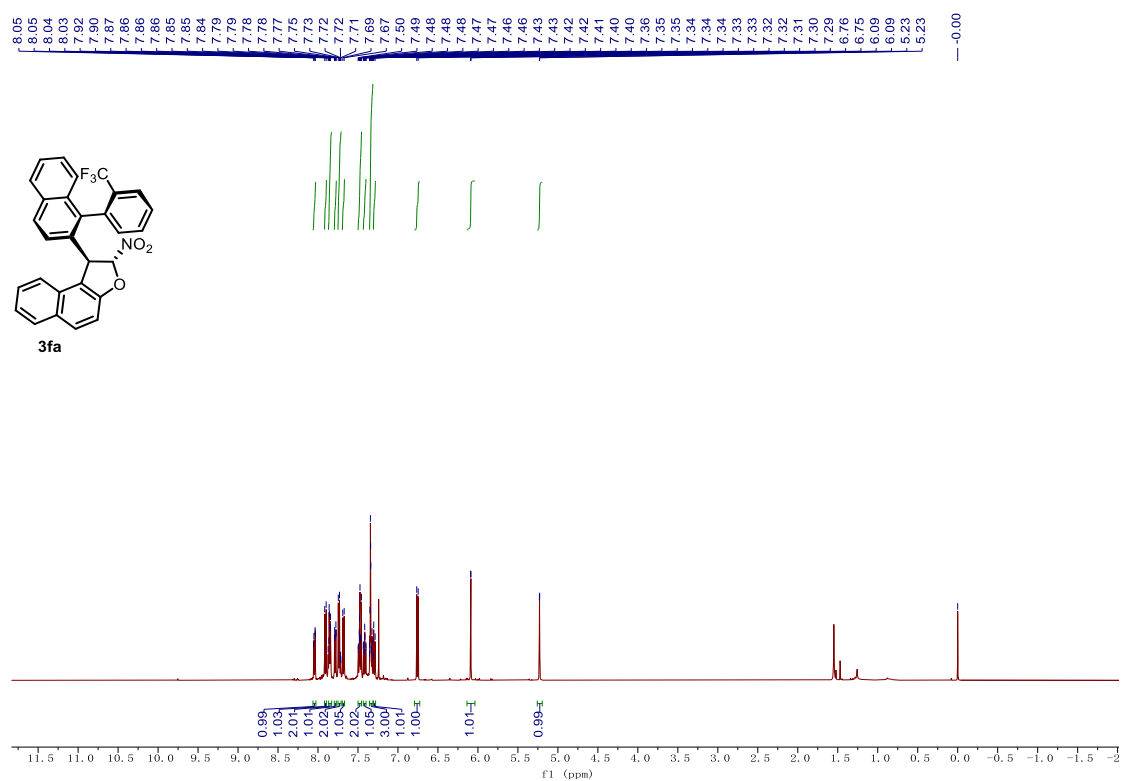


[illegible]

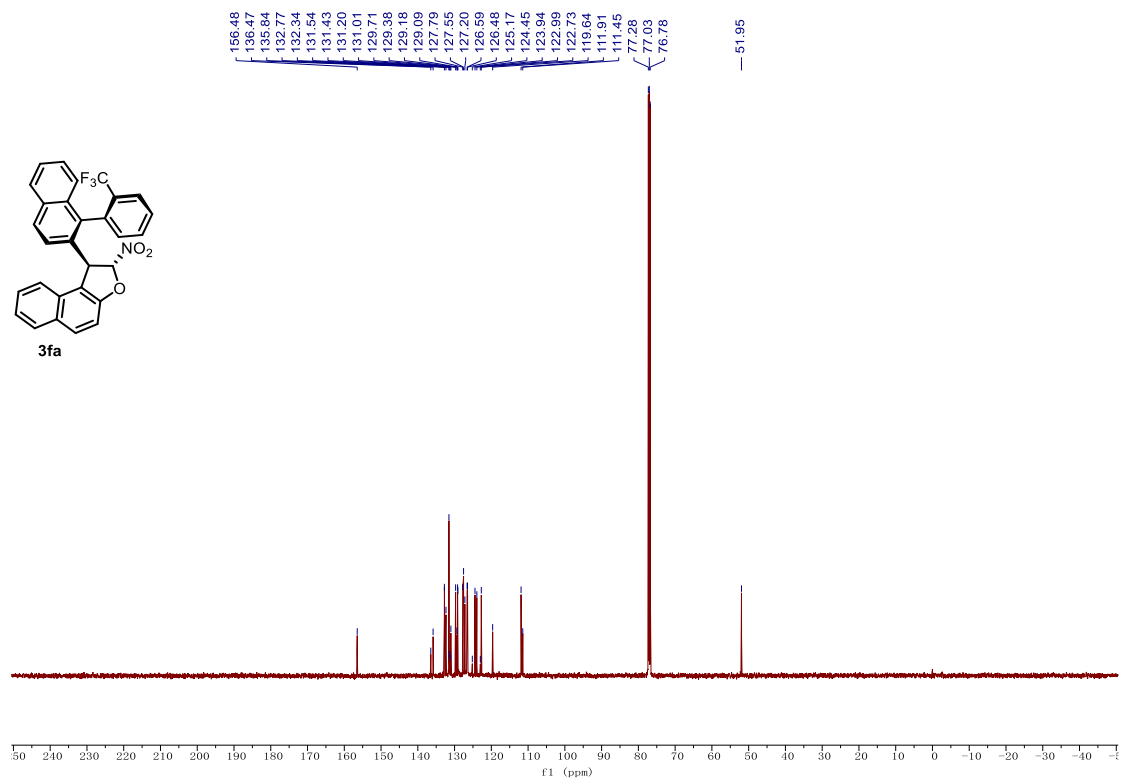
Chemical structure of **3ea** is shown above the ^{13}C NMR spectrum. The spectrum displays peaks corresponding to the structure, with the following chemical shifts (ppm) labeled:

- 156.49
- 136.84
- 136.33
- 135.73
- 133.00
- 132.57
- 132.40
- 131.42
- 130.99
- 130.95
- 130.56
- 130.18
- 128.56
- 128.45
- 128.11
- 125.03
- 124.80
- 124.60
- 127.01
- 126.56
- 126.36
- 124.49
- 124.05
- 122.86
- 119.38
- 111.87
- 111.73
- 77.28
- 77.03
- 76.78
- 51.82

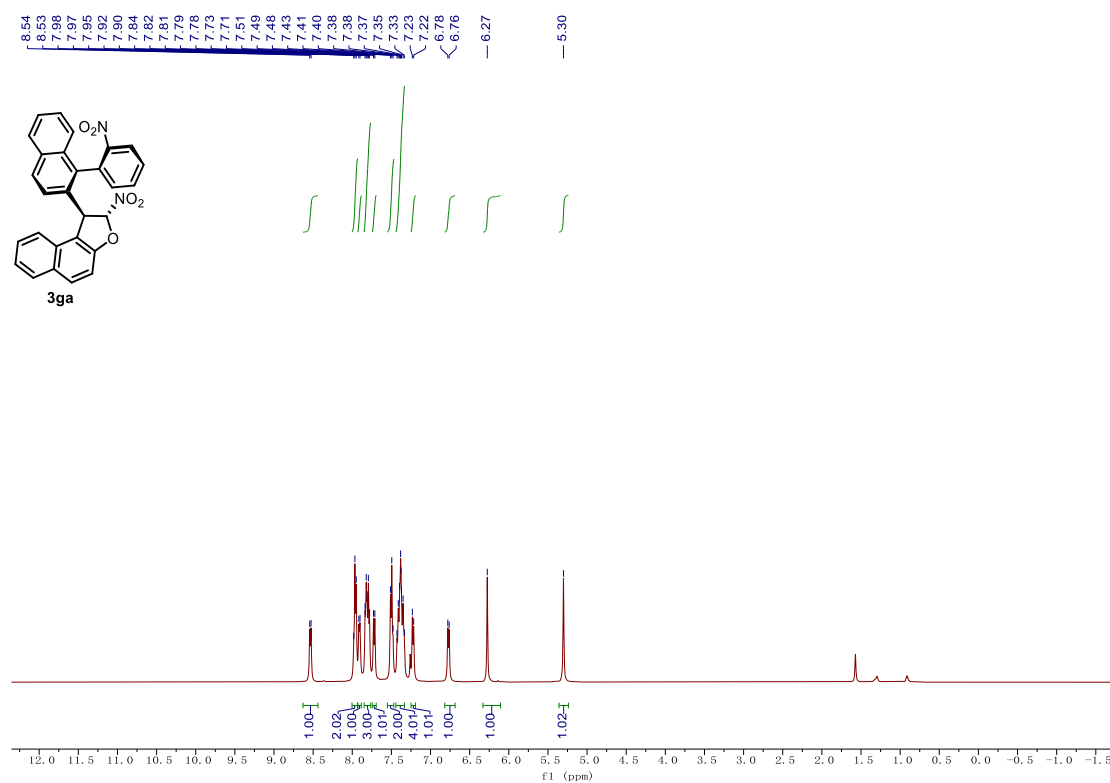
¹H NMR of 3fa (500 MHz in CDCl₃):



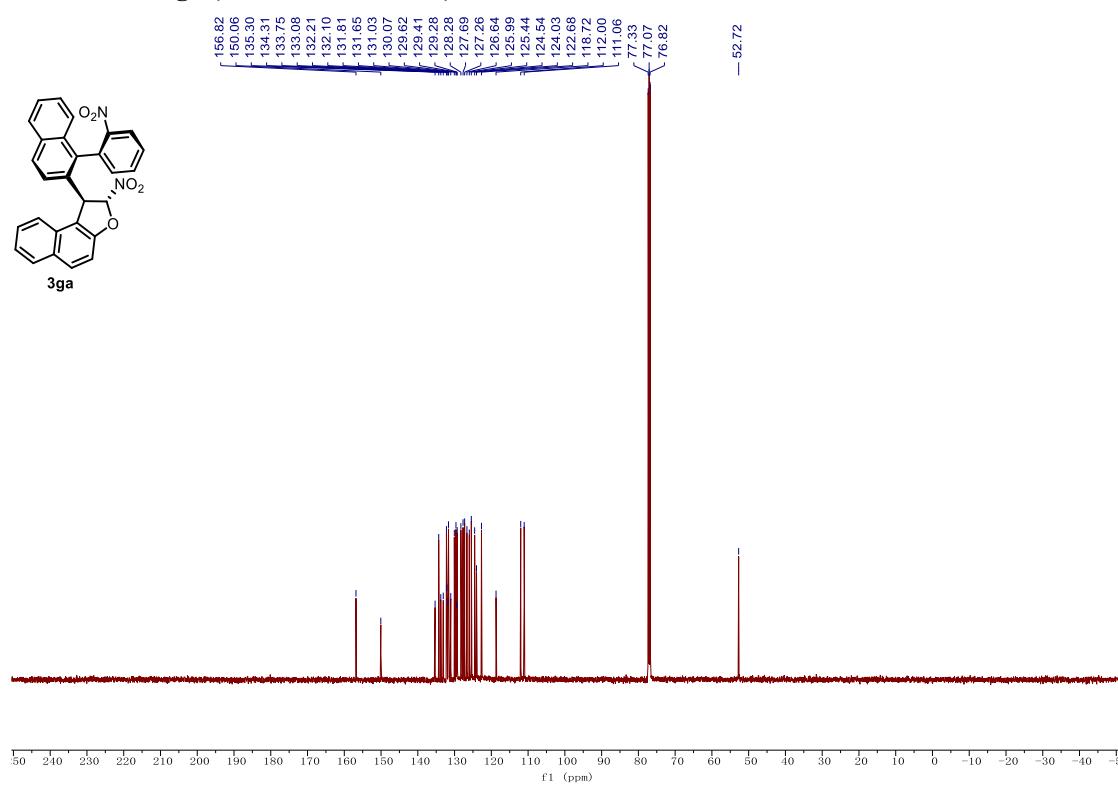
¹³C NMR of 3fa (126 MHz in CDCl₃):



¹H NMR of 3ga (500 MHz in CDCl₃):



¹³C NMR of 3ga (126 MHz in CDCl₃):



[illegible]

Chemical structure of 3ha: COc1ccc(cc1)[C@H]2c3ccccc3c4ccccc4O[C@@H]2C5=CC=C(C=C5)C

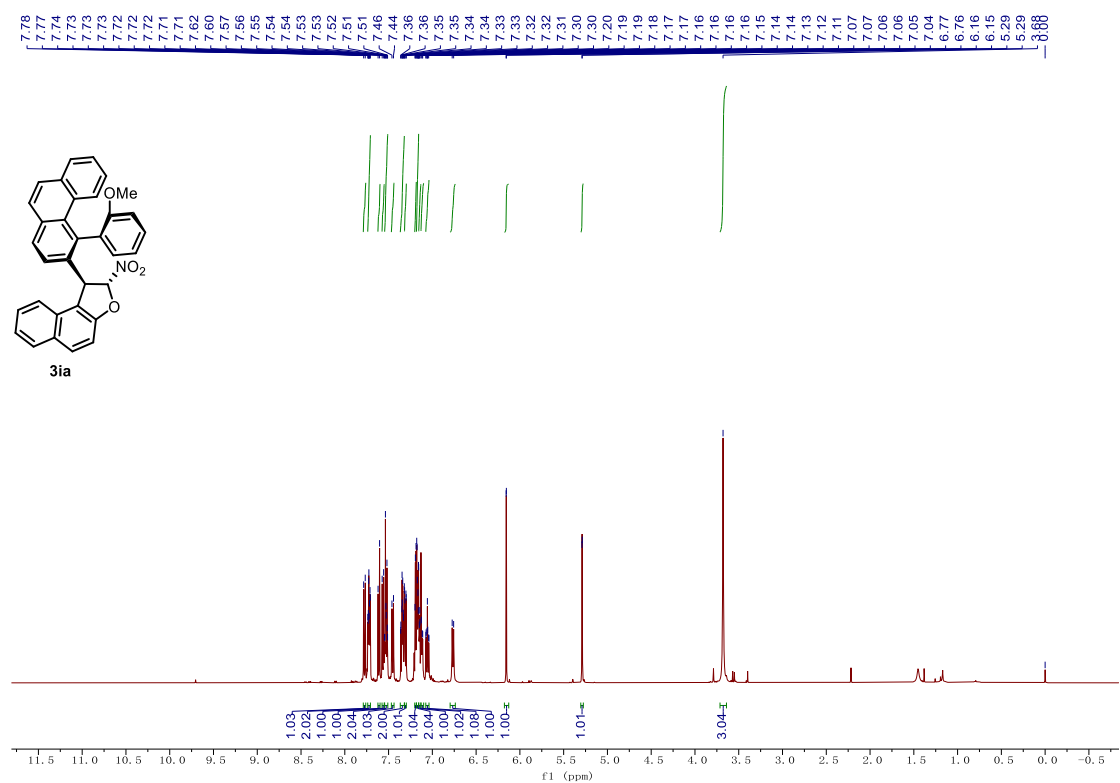
¹H NMR (CDCl₃):

- 7.73, 7.70, 7.68 ppm (m, 5H, aromatic)
- 5.51, 5.13 ppm (d, 2H, H-1, H-2)
- 20.81 ppm (s, 1H, H-3)

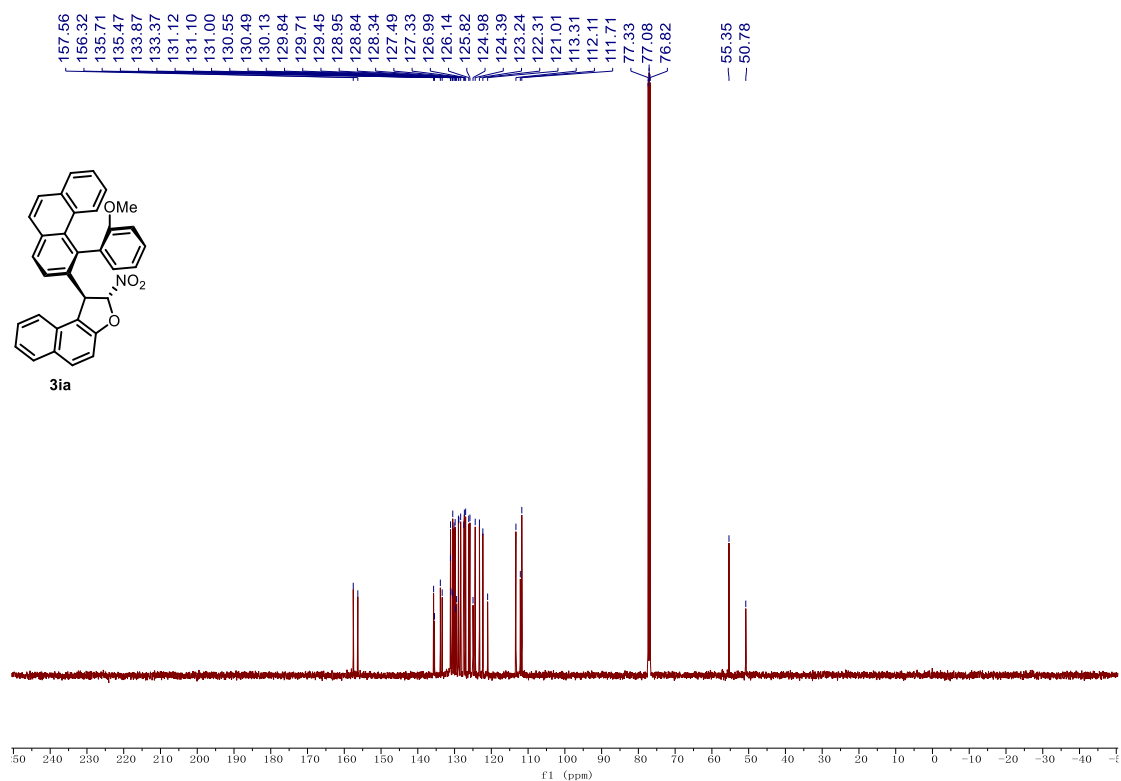
¹³C NMR (CDCl₃):

- 157.0, 156.3, 138.0, 137.8, 136.1, 130.9, 130.8, 129.9, 129.7, 128.9, 128.9, 128.0, 127.5, 127.4, 124.6, 124.3, 123.2, 121.6, 120.0, 112.8, 111.6, 111.3 ppm (aromatic and carbonyl)
- 77.3, 77.0, 76.8 ppm (solvent, CDCl₃)
- 55.1, 51.3 ppm (H-1, H-2)
- 20.8 ppm (H-3)

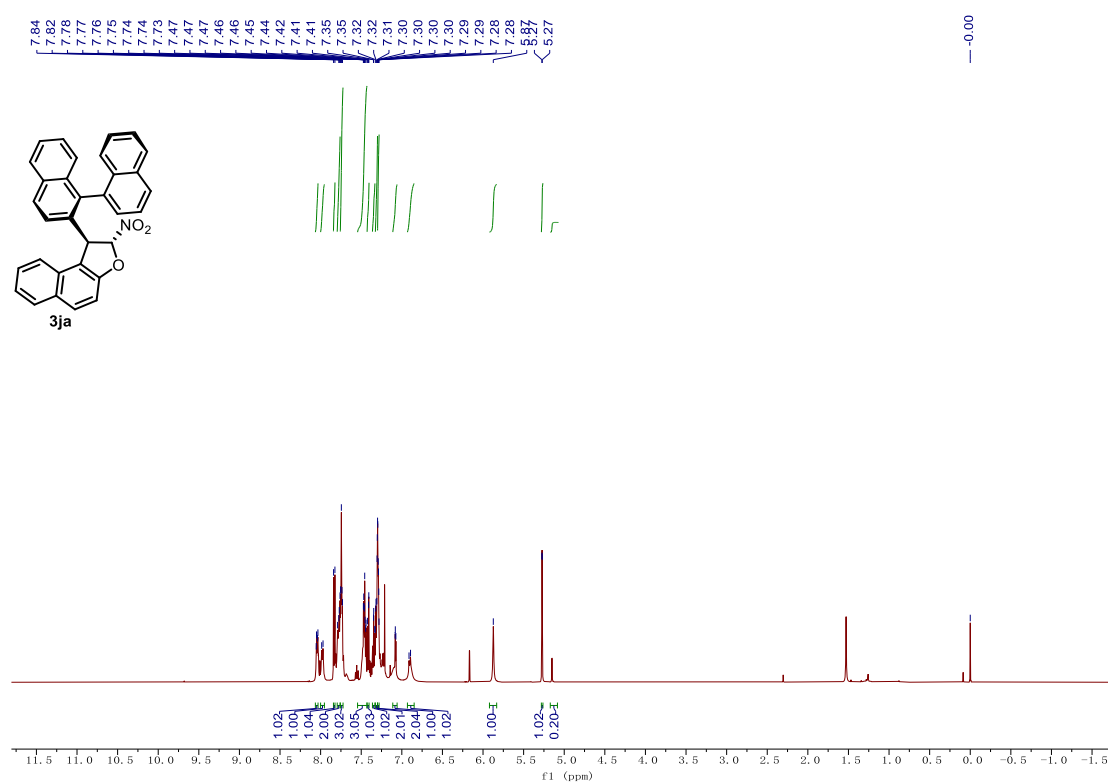
¹H NMR of 3ia (500 MHz in CDCl₃):



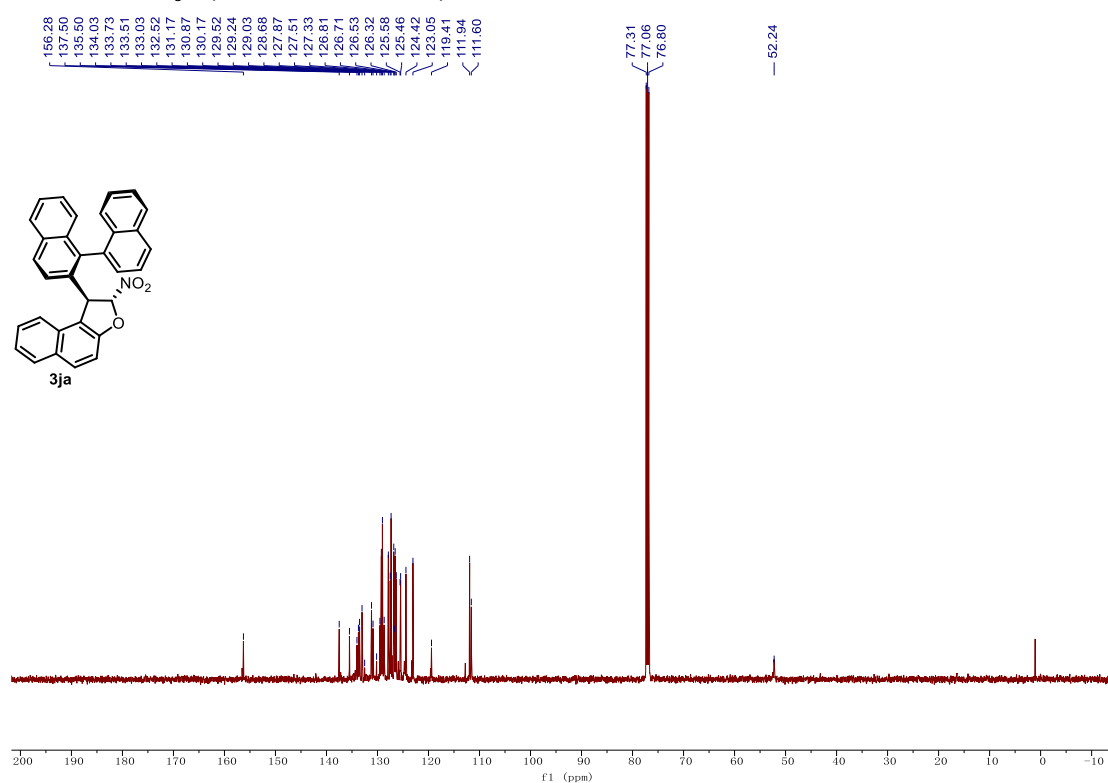
¹³C NMR of 3ia (126 MHz in CDCl₃):



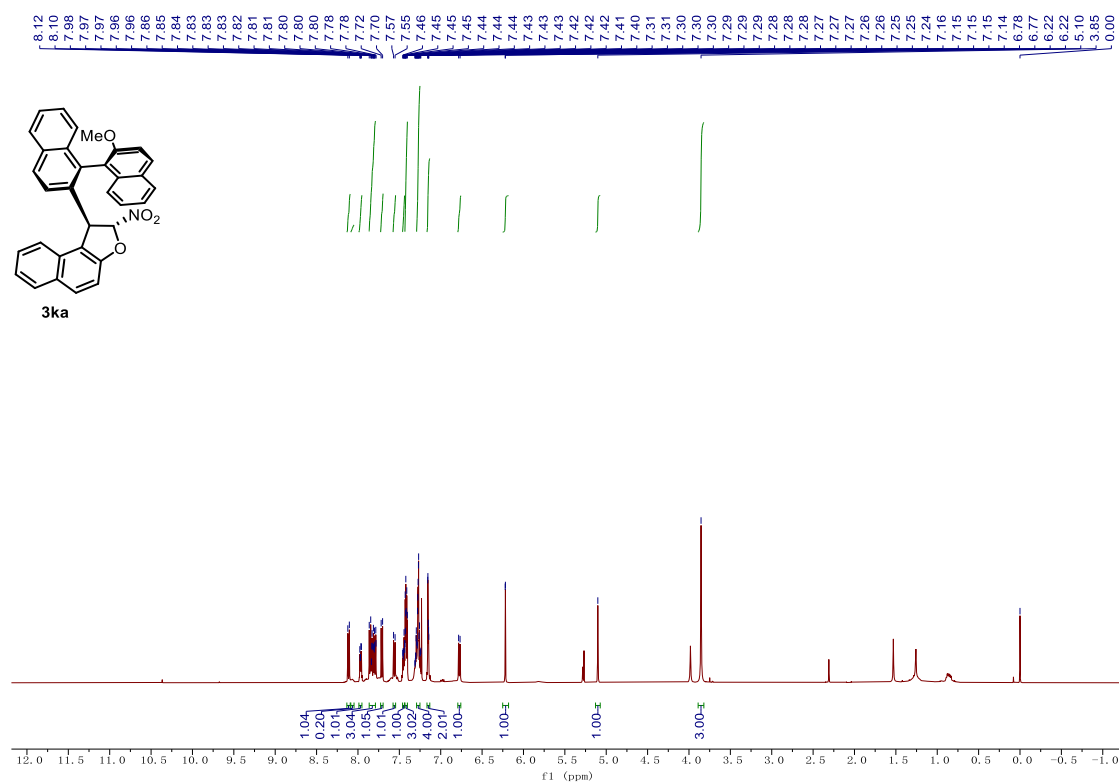
¹H NMR of 3ja (500 MHz in CDCl₃):



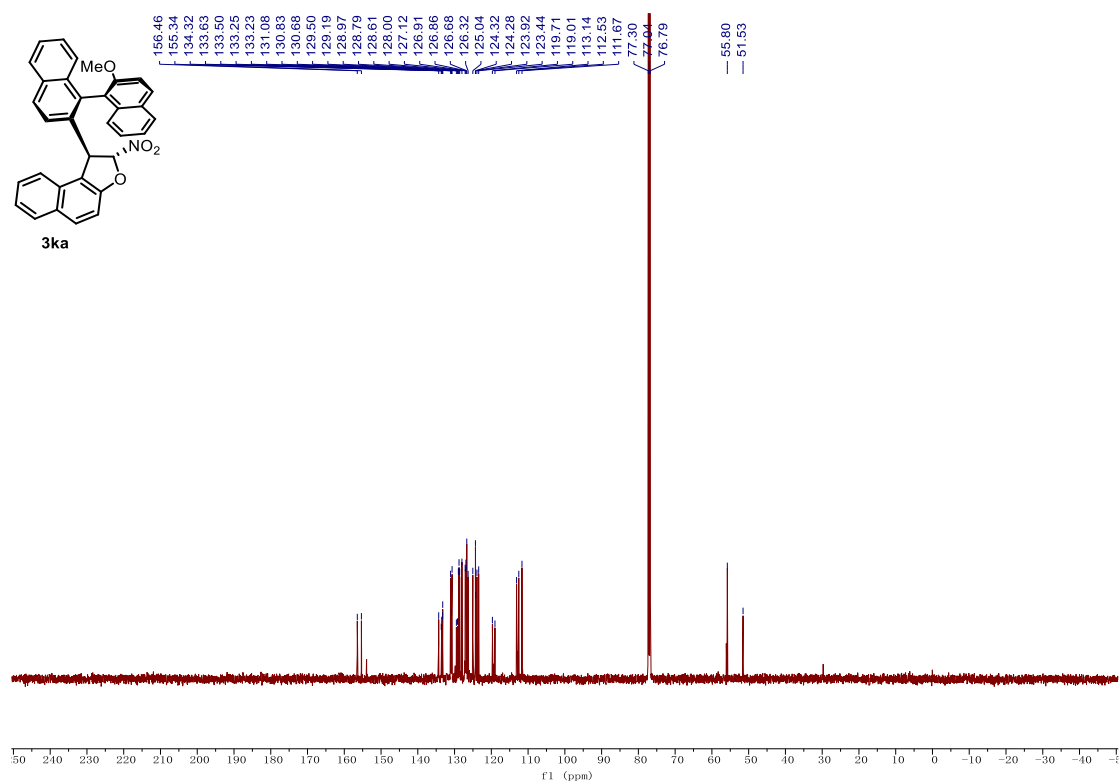
¹³C NMR of 3ja (126 MHz in CDCl₃):



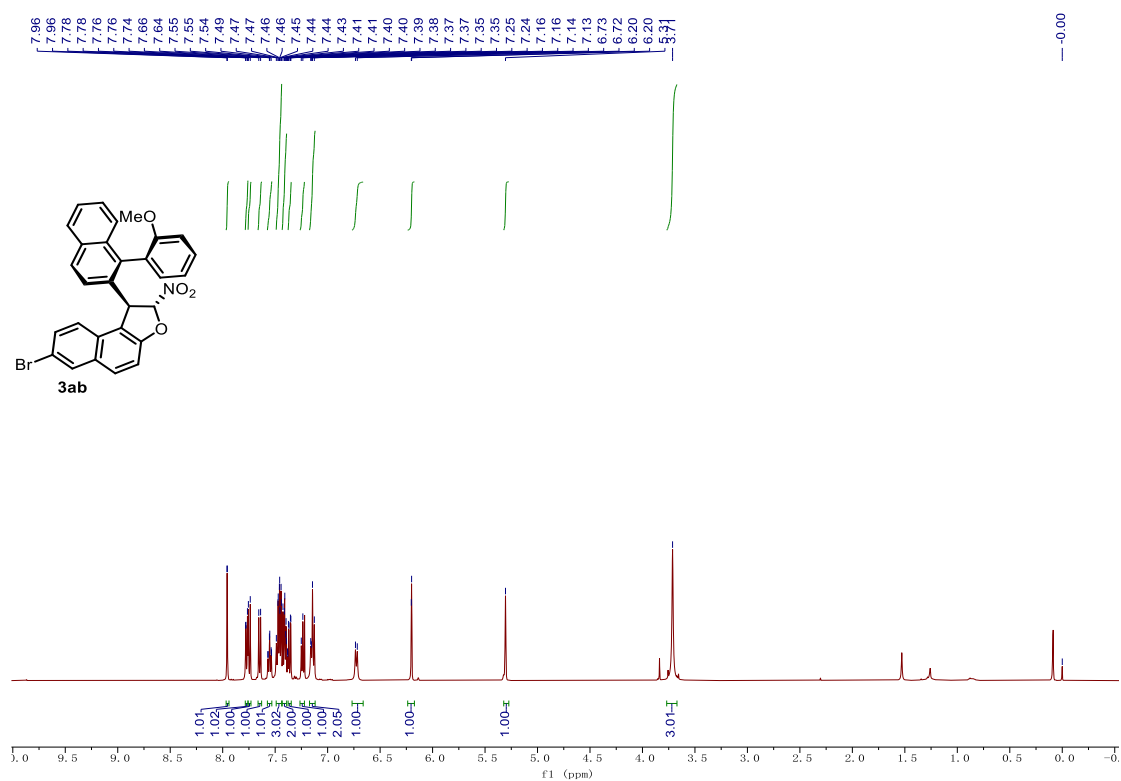
¹H NMR of 3ka (500 MHz in CDCl₃):



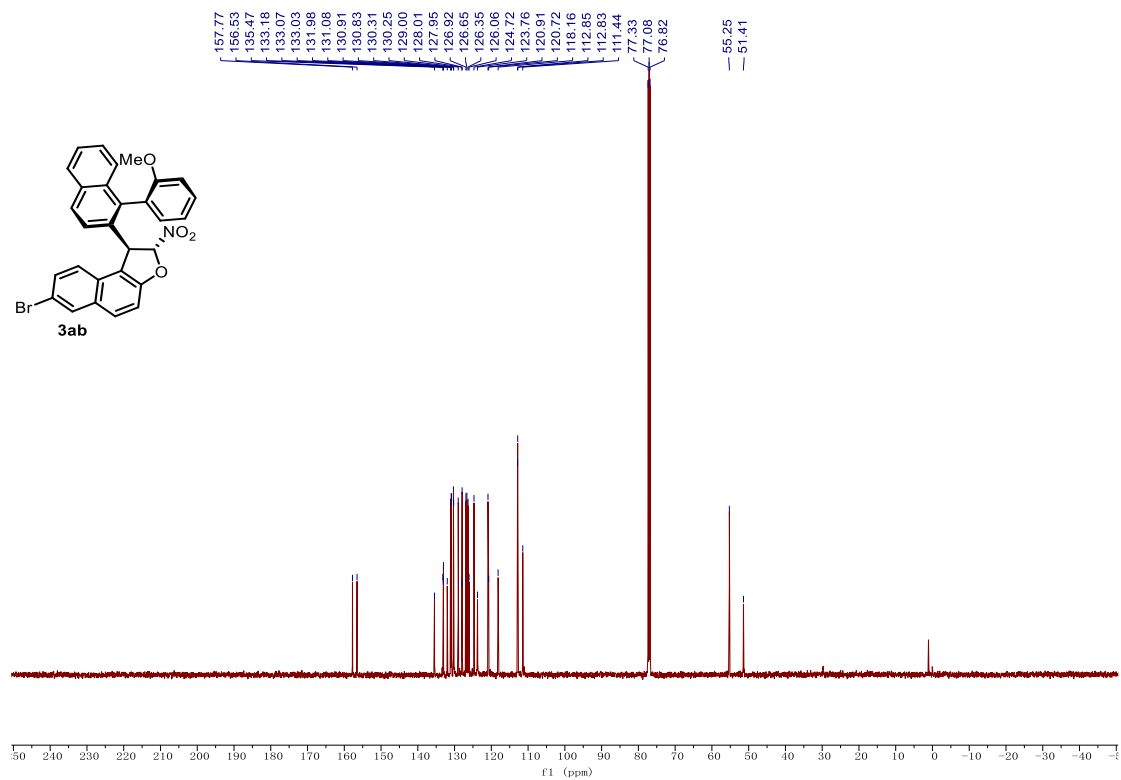
¹³C NMR of 3ka (126 MHz in CDCl₃):



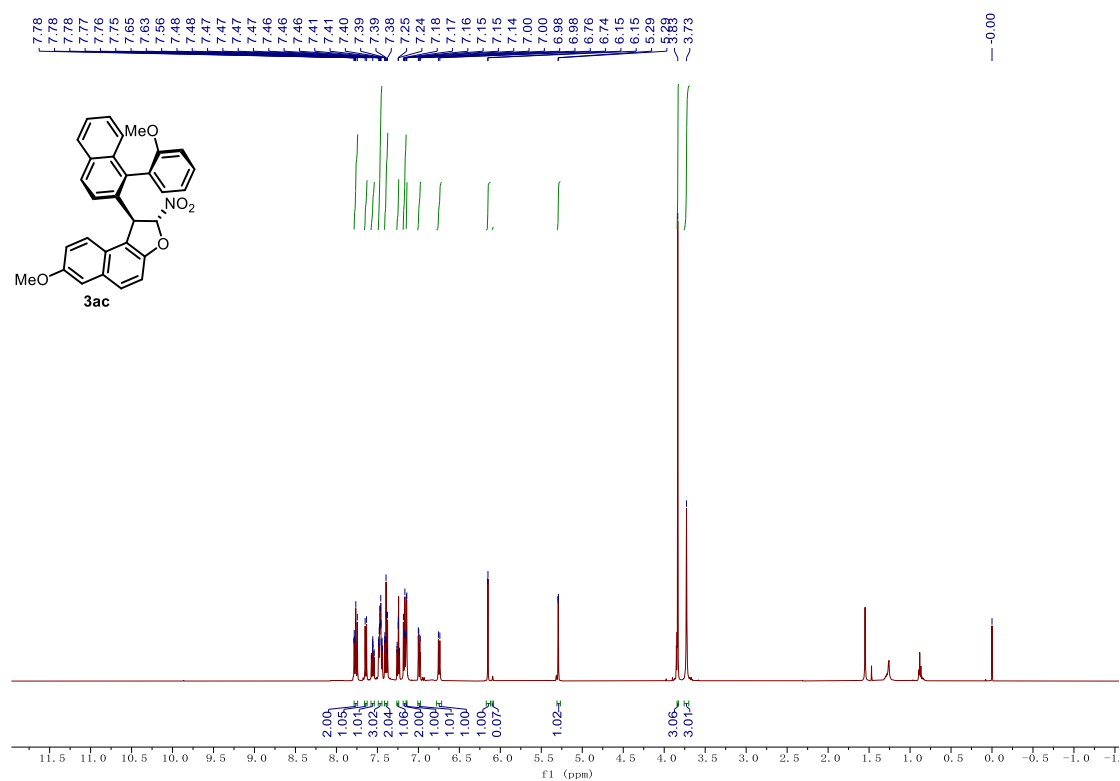
¹H NMR of 3ab (500 MHz in CDCl₃):



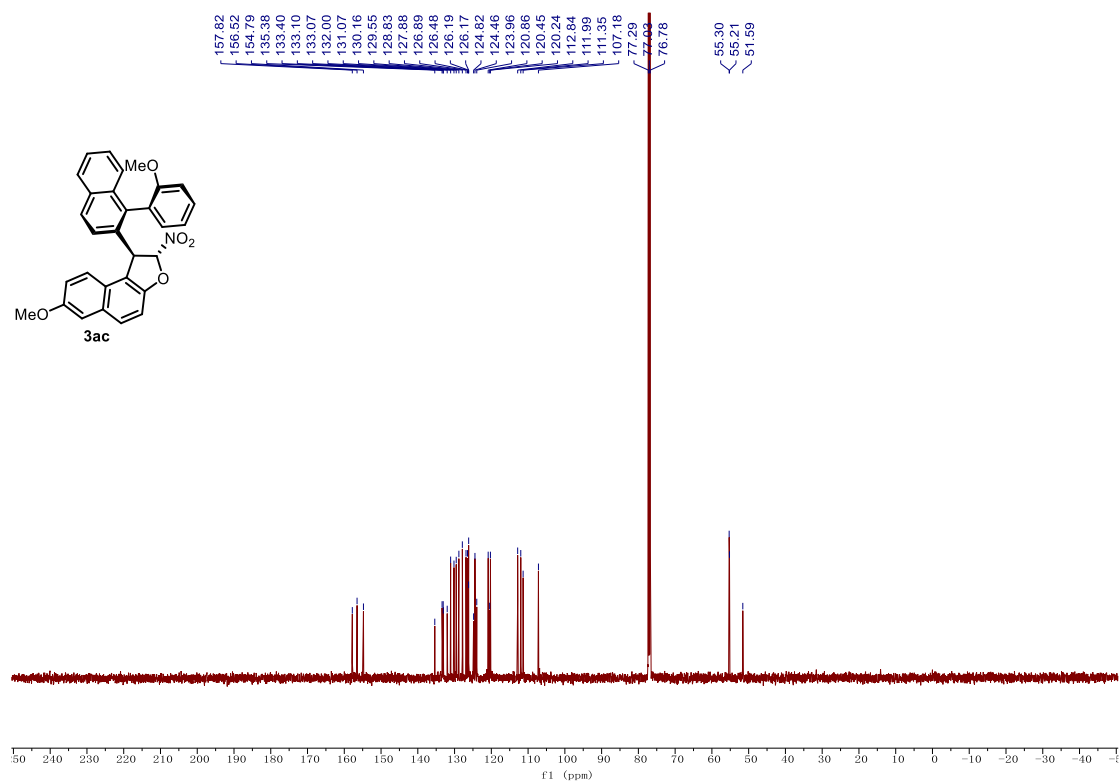
¹³C NMR of 3ab (126 MHz in CDCl₃):



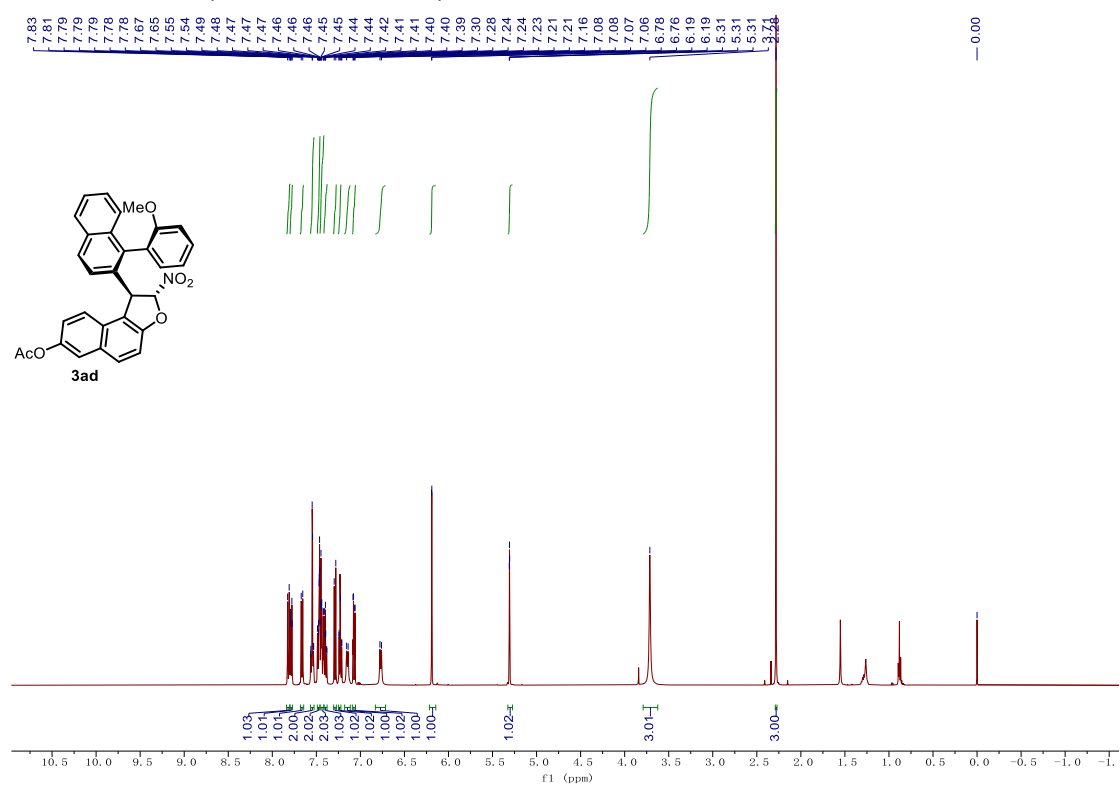
¹H NMR of 3ac (500 MHz in CDCl₃):



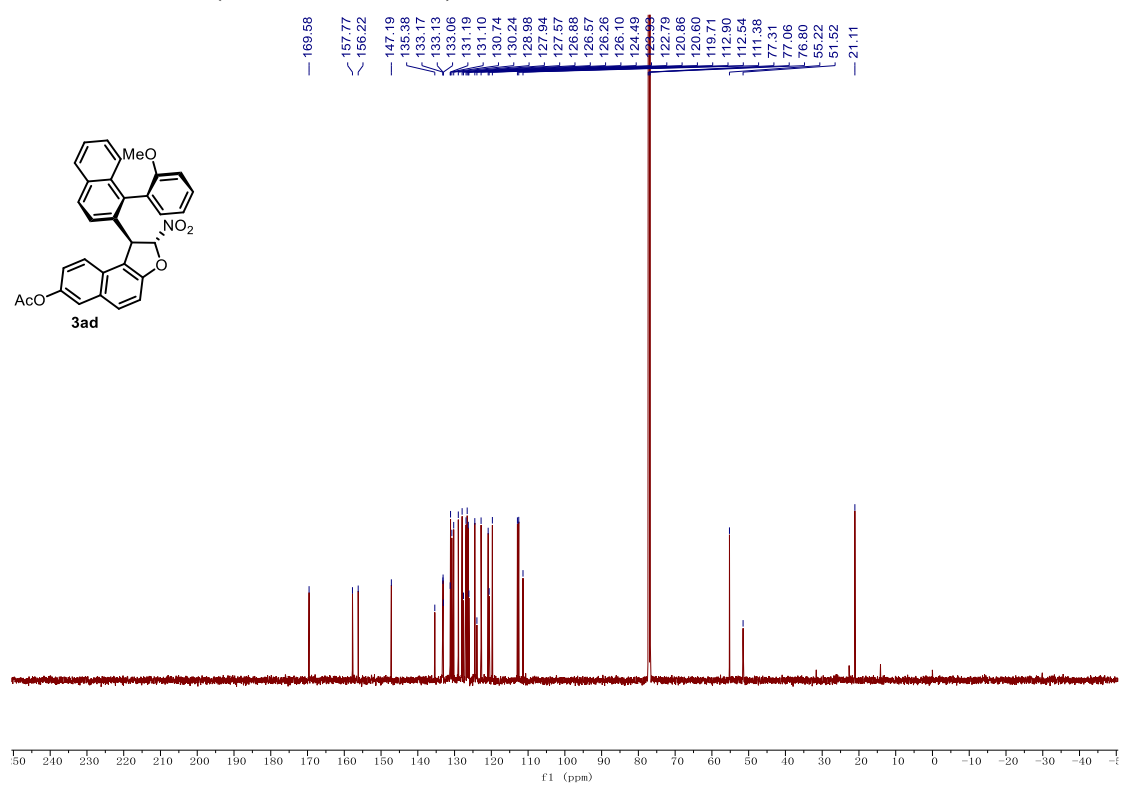
¹³C NMR of 3ac (126 MHz in CDCl₃):



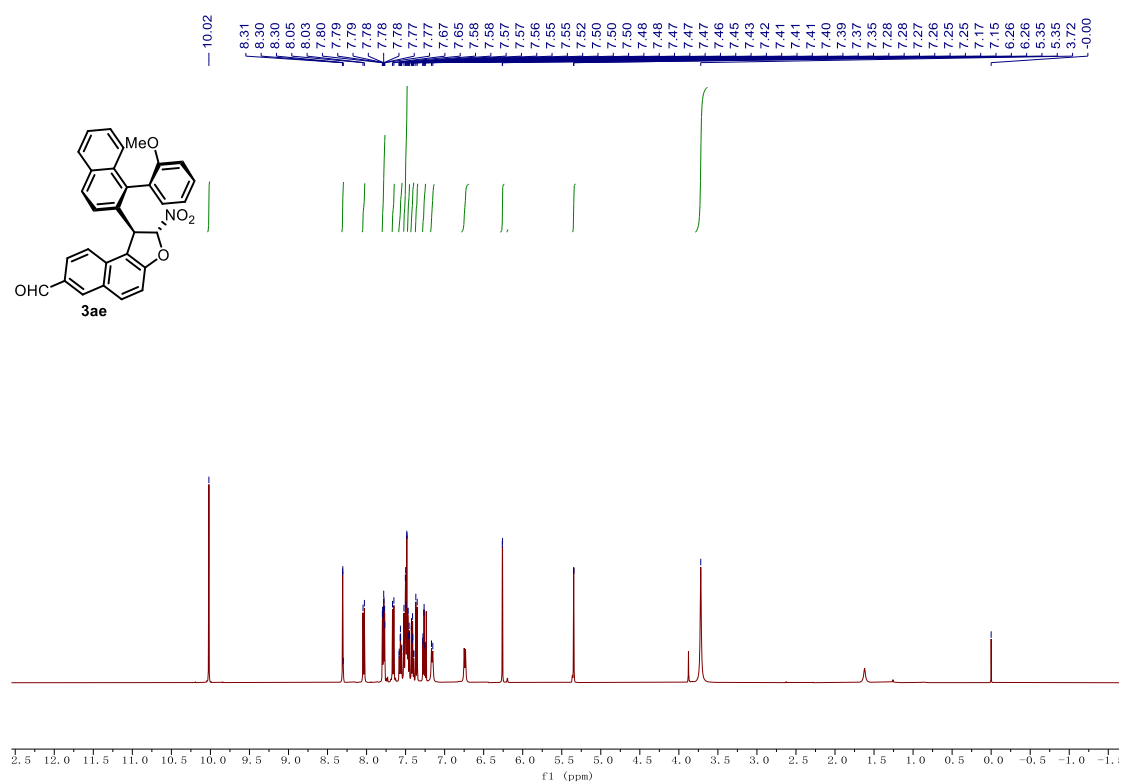
¹H NMR of 3ad (500 MHz in CDCl₃):



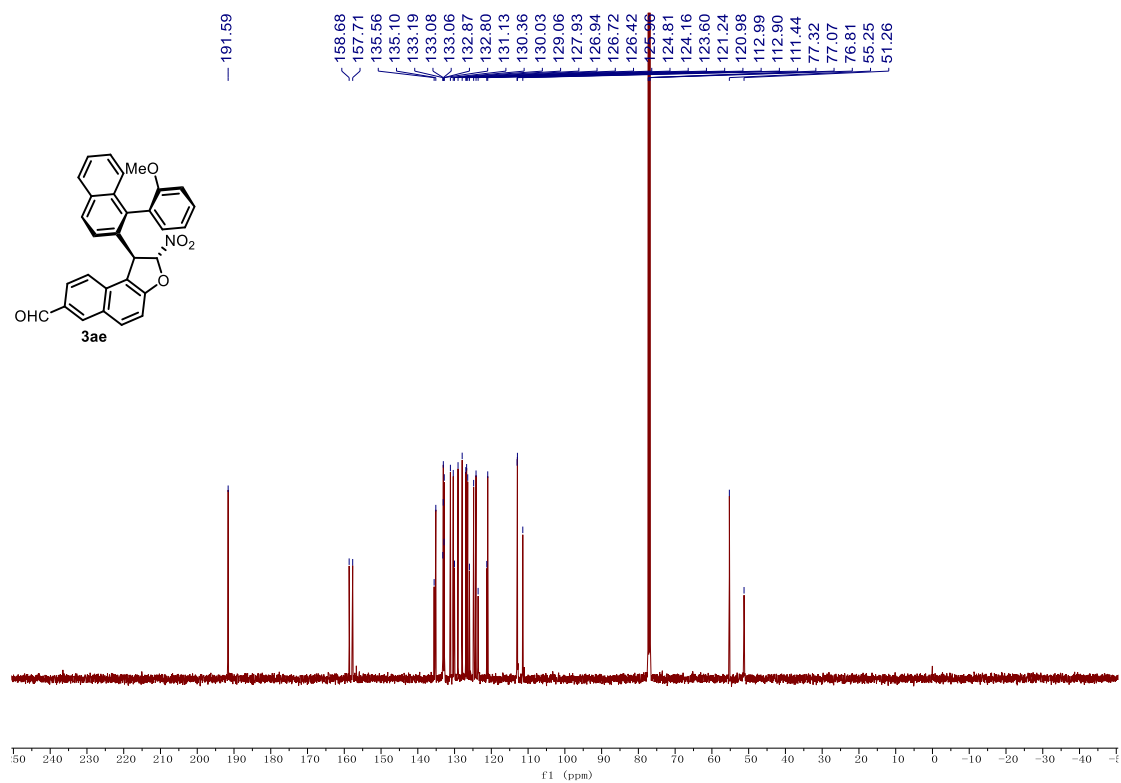
¹³C NMR of 3ad (126 MHz in CDCl₃):



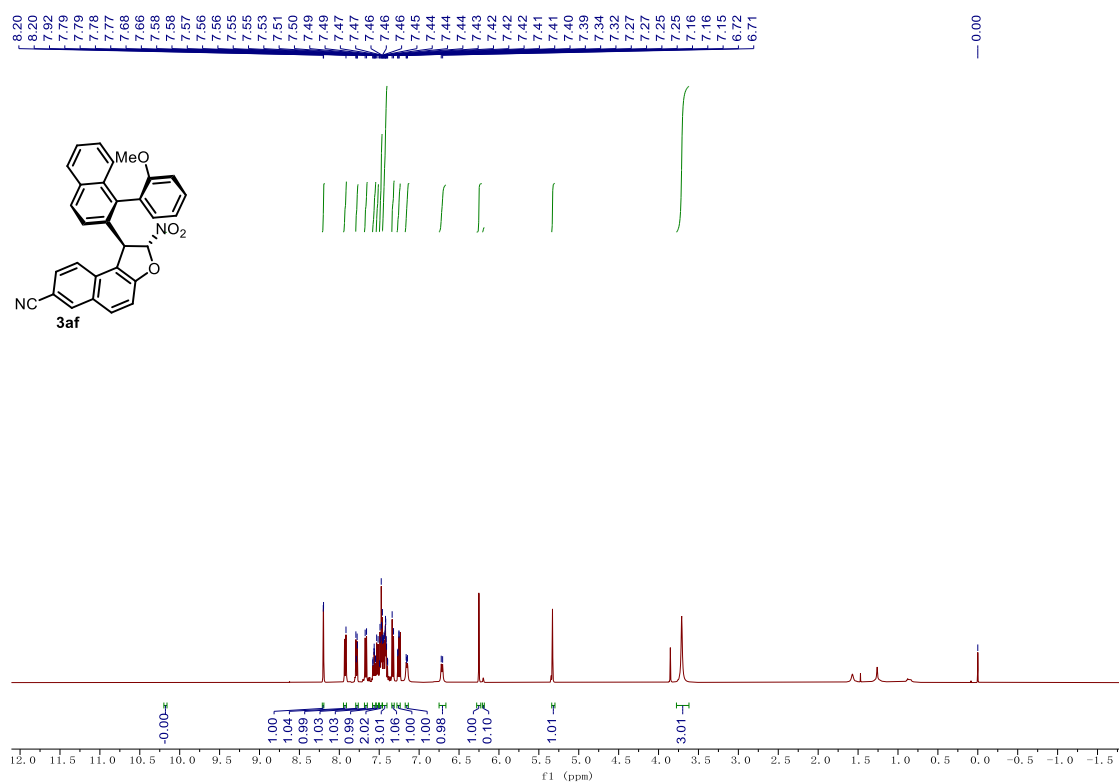
¹H NMR of 3ae (500 MHz in CDCl₃):



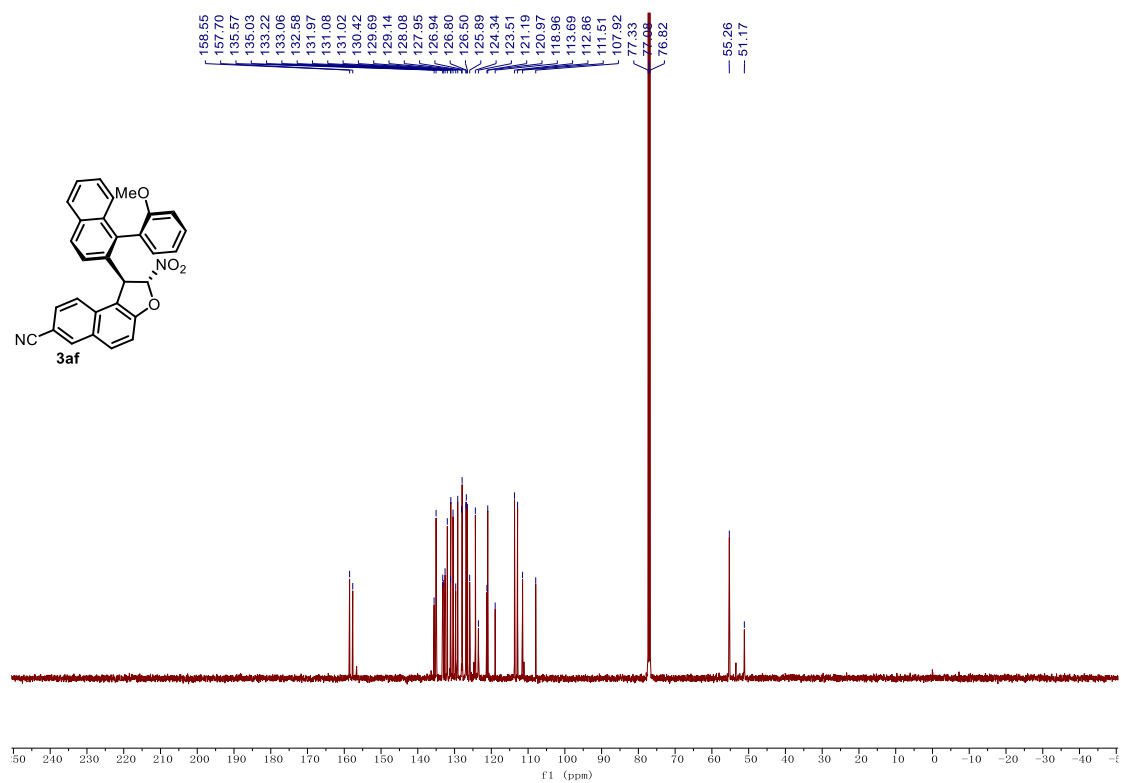
¹³C NMR of 3ae (126 MHz in CDCl₃):



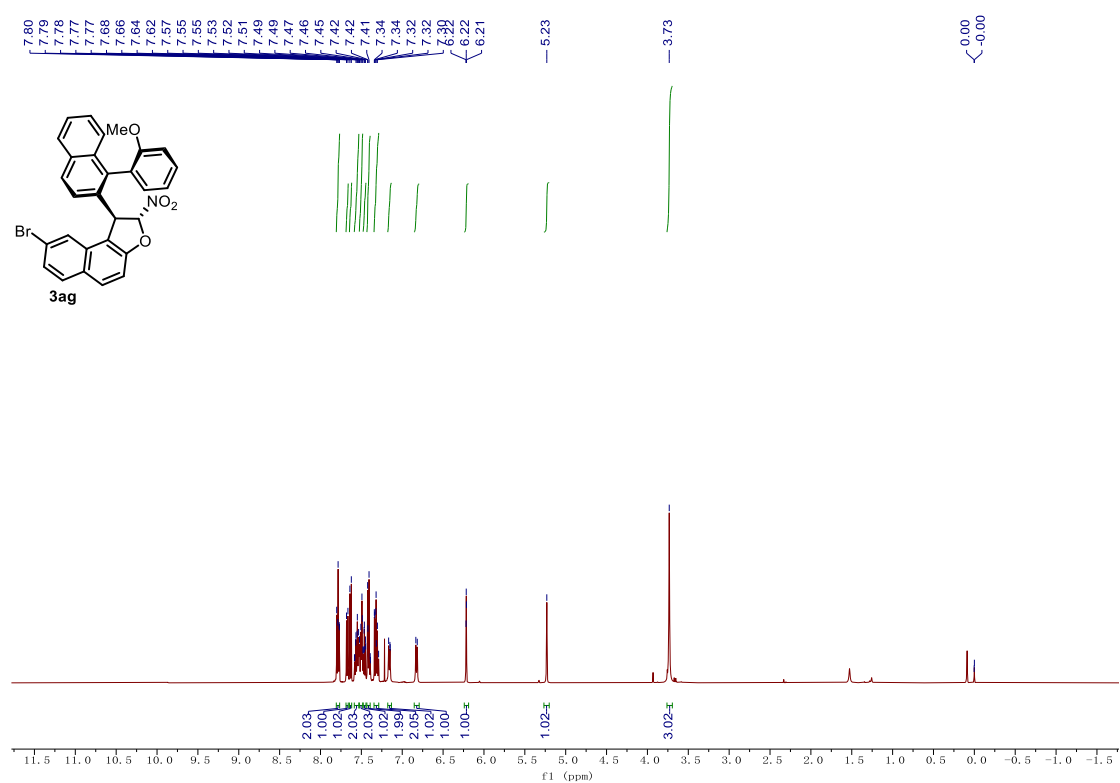
¹H NMR of 3af (500 MHz in CDCl₃):



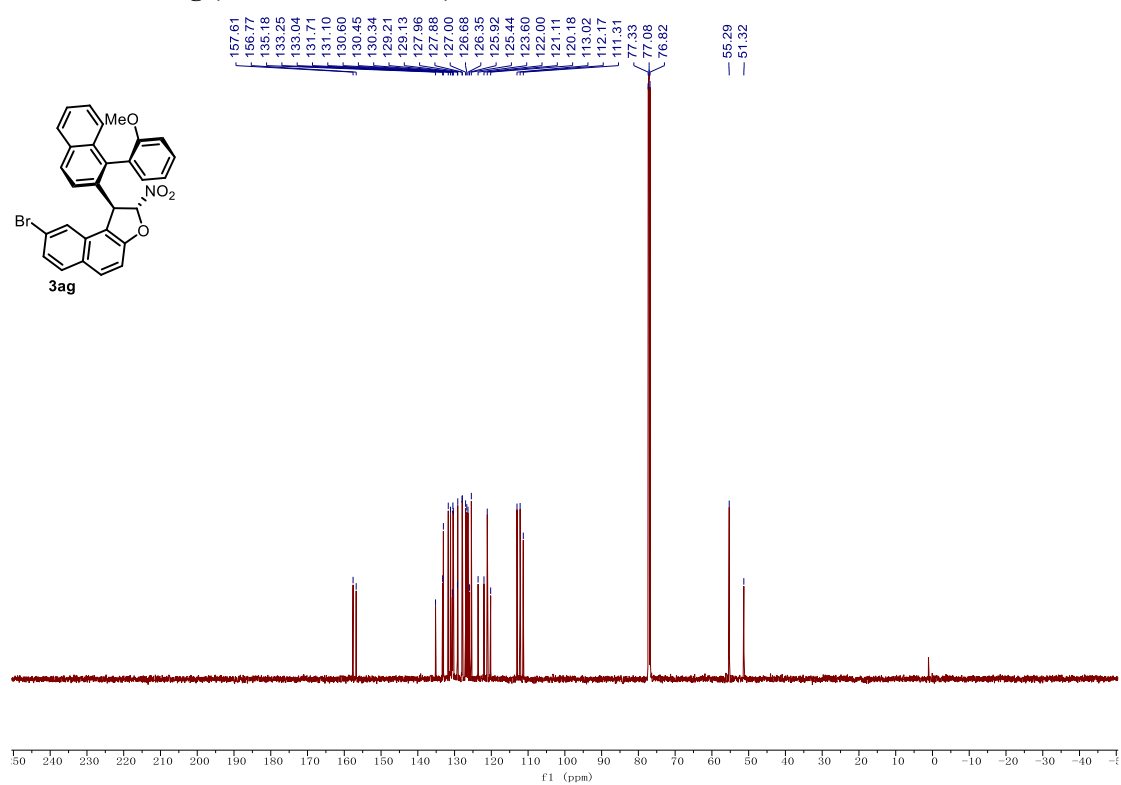
¹³C NMR of 3af (126 MHz in CDCl₃):



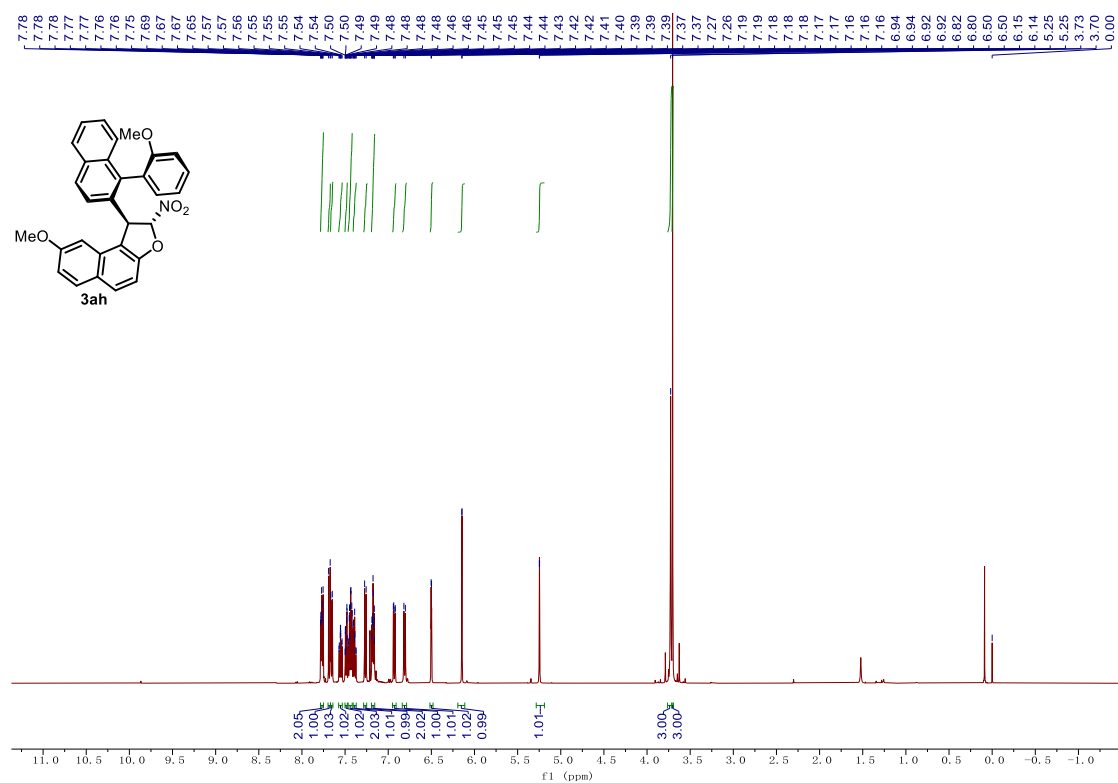
¹H NMR of 3ag (500 MHz in CDCl₃):



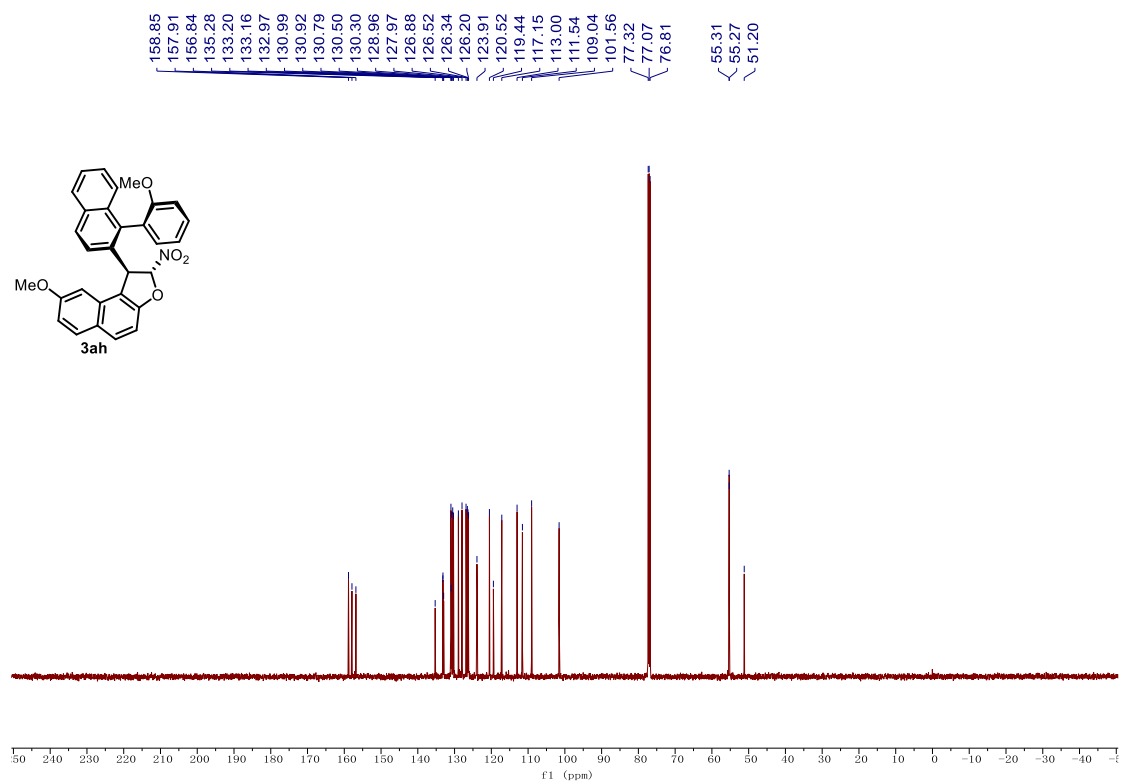
¹³C NMR of 3ag (126 MHz in CDCl₃):



¹H NMR of 3ah (500 MHz in CDCl₃):



¹³C NMR of 3ah (126 MHz in CDCl₃):



3ai

COc1ccc(cc1)[C@@H]2c3ccccc3O[C@H]2C(=O)OC4=CC=CC=C4C5=CC=CC=C5

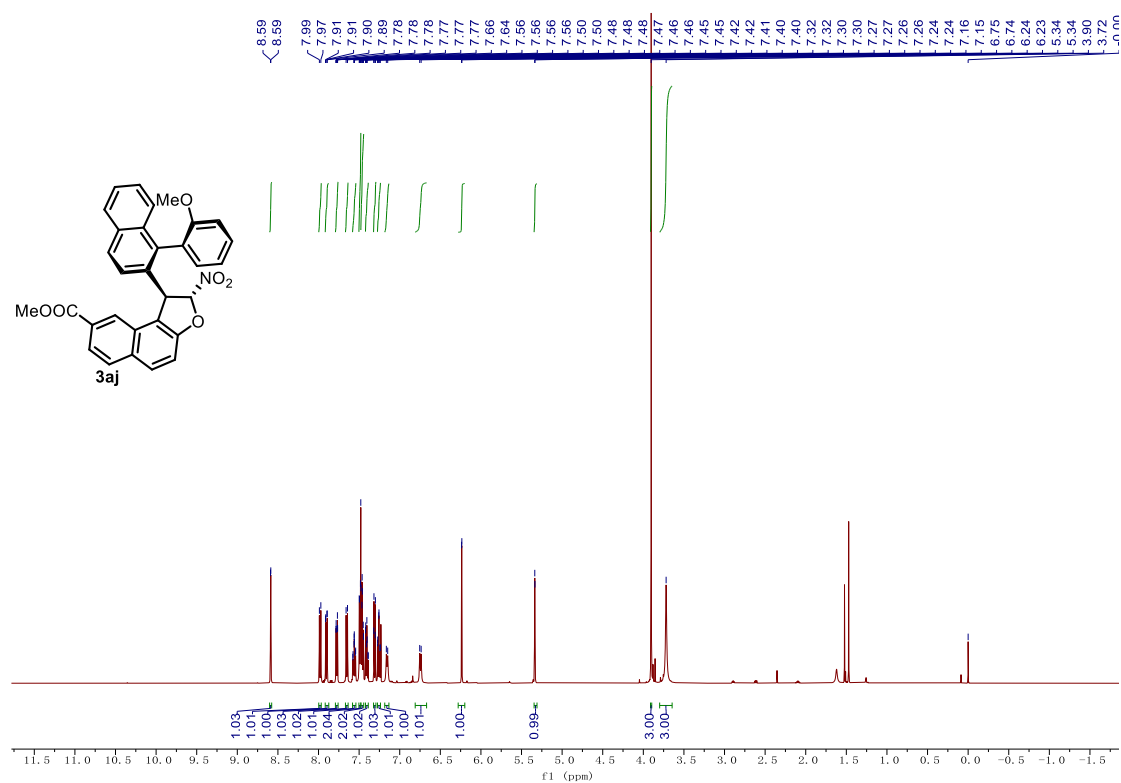
¹H NMR spectrum (CDCl₃) of compound **3ai**. The x-axis represents the chemical shift in ppm (f1), ranging from 12.0 to 0.0. The y-axis represents the intensity. The spectrum shows several peaks, with the following chemical shifts (ppm) and integrations (area) listed:

Chemical Shift (ppm)	Integration
7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.57, 1.56, 1.55, 1.54, 1.53, 1.52, 1.51, 1.50, 1.49, 1.48, 1.47, 1.46, 1.45, 1.44,	

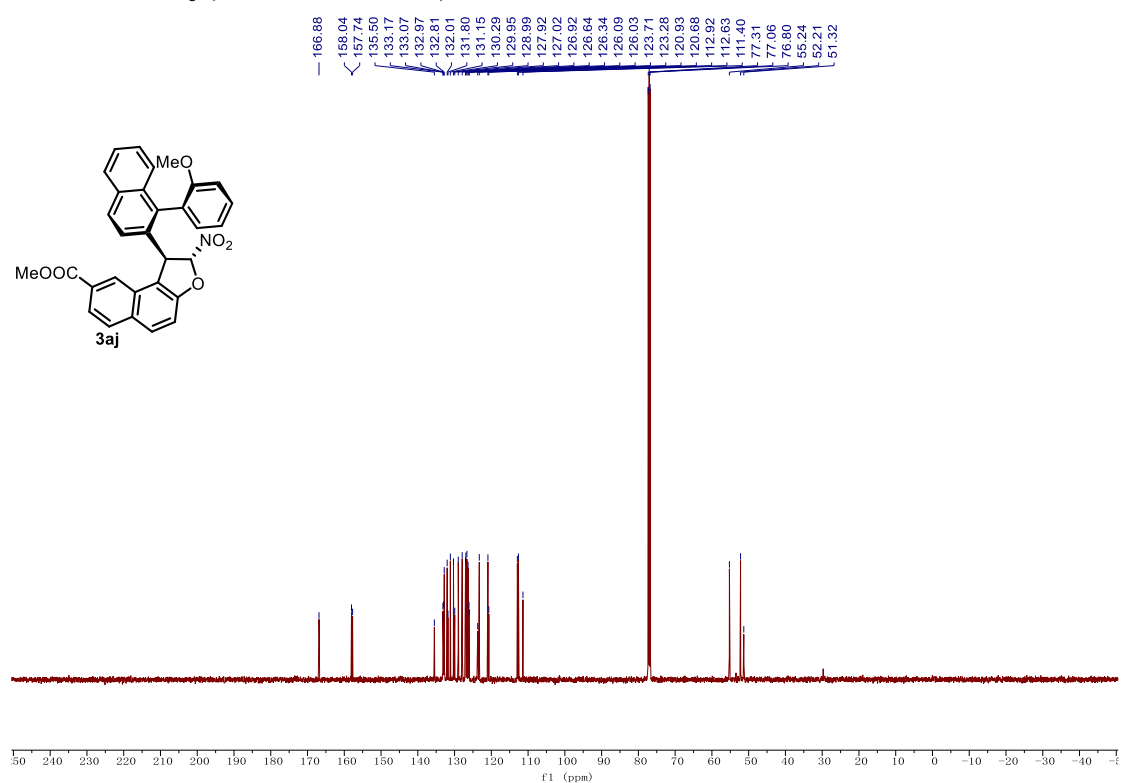
Chemical structure of **3ai** is shown above the spectrum. The spectrum displays peaks corresponding to the carbon atoms in the molecule, with the following chemical shifts (ppm) labeled above the peaks:

- 169.99
- 157.75
- 156.89
- 149.66
- 135.50
- 133.18
- 133.10
- 133.02
- 131.26
- 130.98
- 130.44
- 130.26
- 130.19
- 129.00
- 128.80
- 127.96
- 128.90
- 126.52
- 126.24
- 125.03
- 123.89
- 123.80
- 120.30
- 119.72
- 113.85
- 112.85
- 111.51
- 111.33
- 77.31
- 77.06
- 76.80
- 55.23
- 51.45
- 21.17

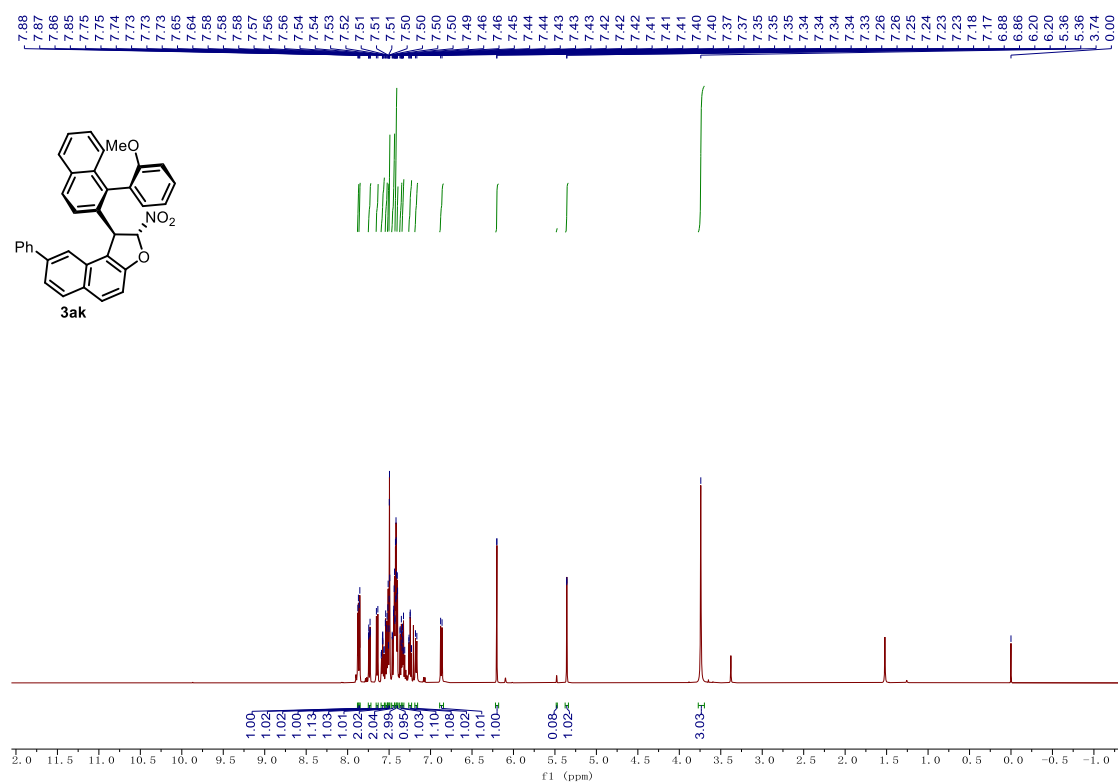
¹H NMR of 3aj (500 MHz in CDCl₃):



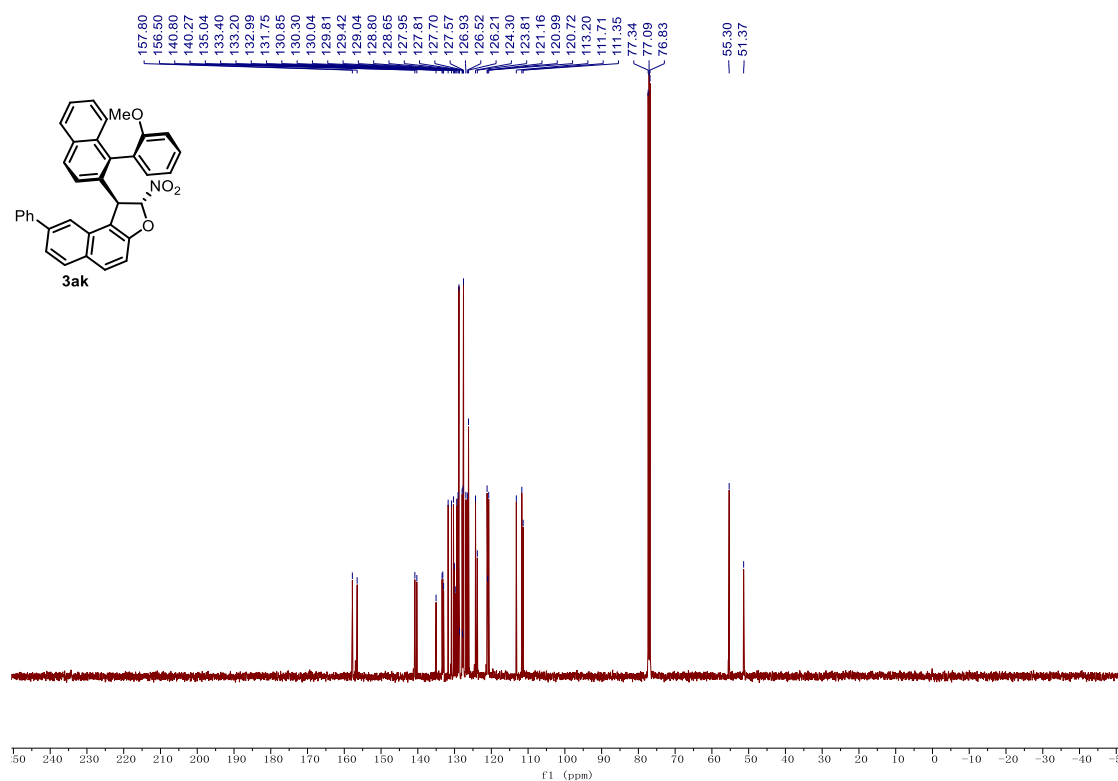
¹³C NMR of 3aj (126 MHz in CDCl₃):



¹H NMR of 3ak (500 MHz in CDCl₃):



¹³C NMR of 3ak (126 MHz in CDCl₃):



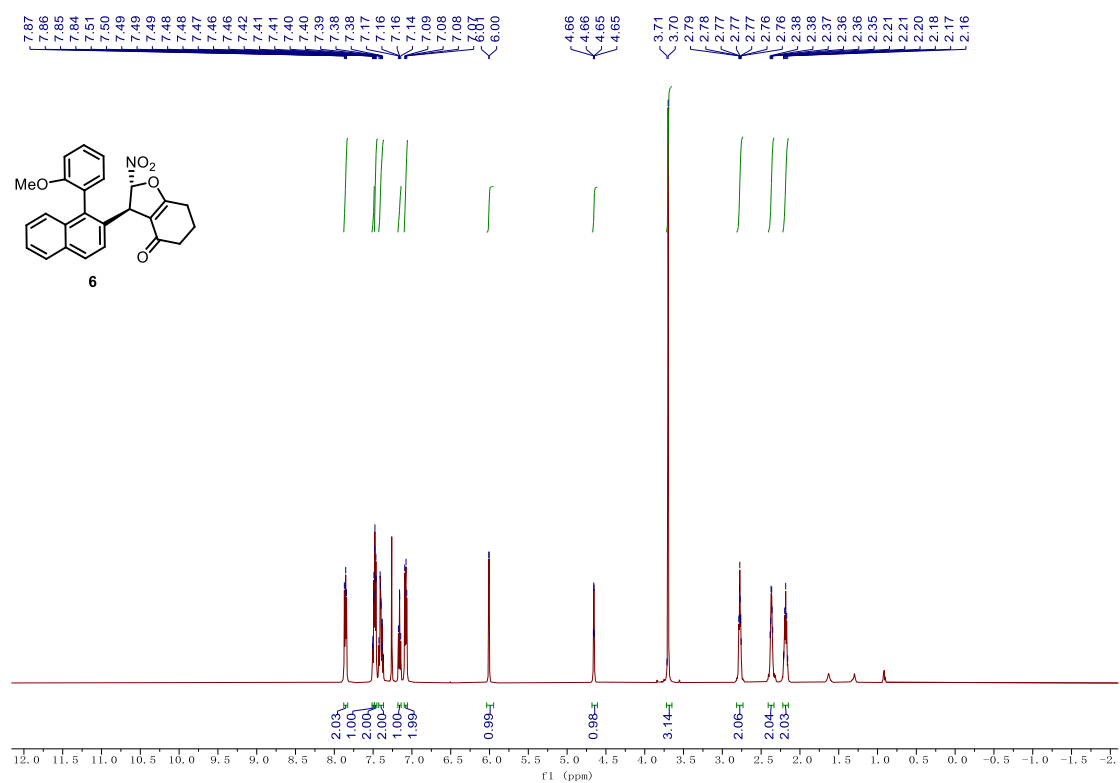
Chemical structure of **3aI** is shown above the spectrum.

¹H NMR spectrum (CDCl₃) of **3aI**. The x-axis represents the chemical shift in ppm, ranging from -1.0 to 11.5. The spectrum shows several multiplets in the aromatic region (6.5-8.1 ppm) and a singlet for the methoxy group (~3.8 ppm). Integration values are provided below the baseline, and a list of chemical shifts (delta) is shown on the right side of the spectrum.

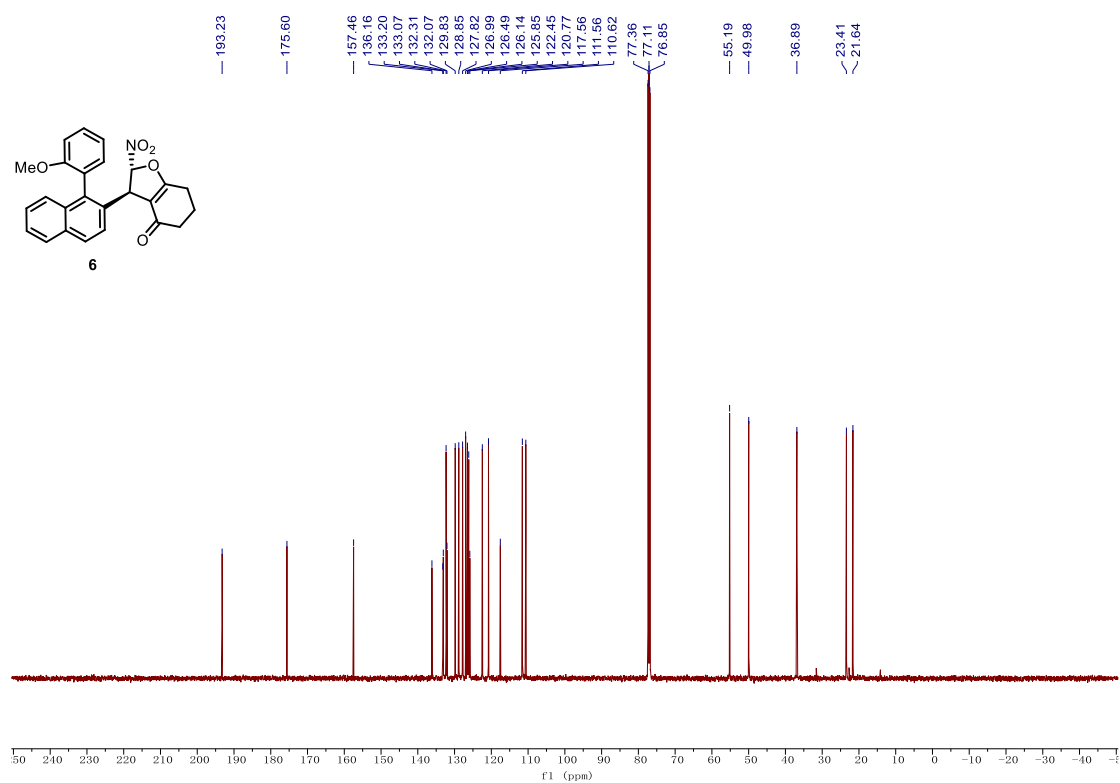
Chemical shifts (delta) listed on the right: 8.07, 7.81, 7.79, 7.77, 7.76, 7.75, 7.74, 7.69, 7.67, 7.56, 7.49, 7.48, 7.48, 7.48, 7.47, 7.47, 7.46, 7.46, 7.42, 7.42, 7.41, 7.33, 7.32, 7.31, 7.31, 7.30, 7.28, 7.24, 7.23, 7.22, 7.16, 6.80, 6.78, 6.25, 6.24, 5.40, 5.40, 5.40, 1.56, 0.00.

Integration values (from left to right): 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 2.00, 2.00, 2.02, 2.04, 1.00, 1.00, 1.00, 1.00, 3.02.

^1H NMR of 6 (500 MHz in CDCl_3):



^{13}C NMR of 6 (126 MHz in CDCl_3):

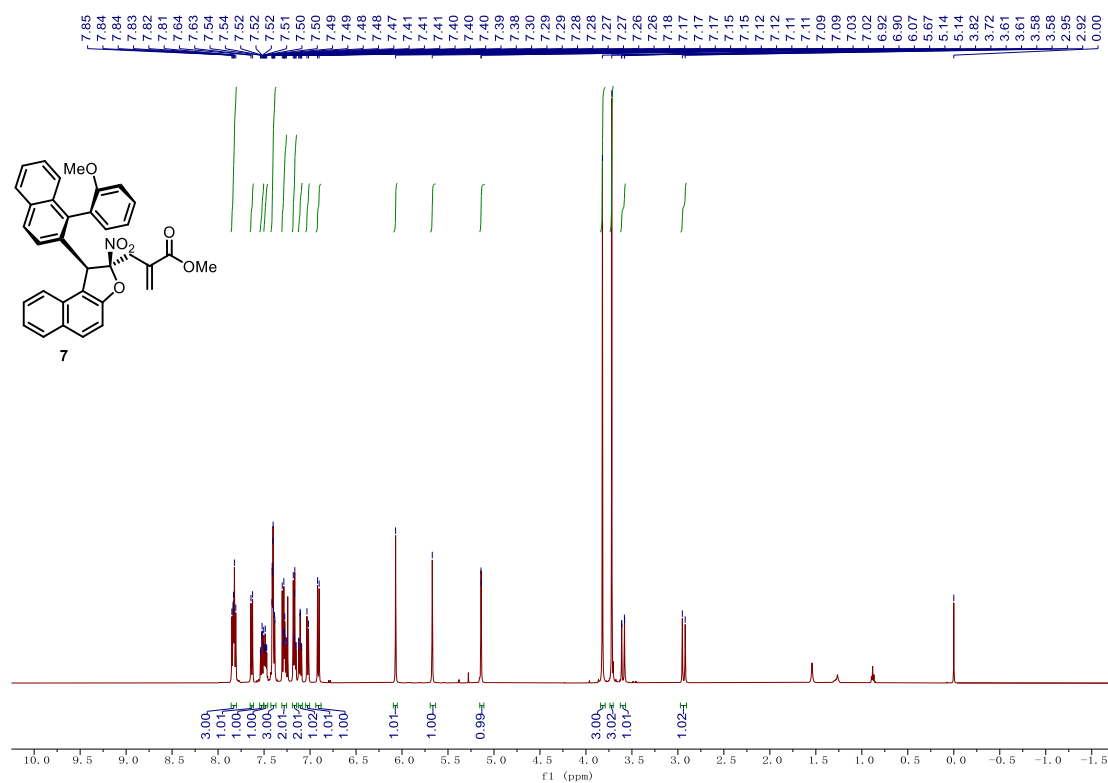


Chemical structure of **6'** is shown. The ^1H NMR spectrum (CDCl₃) displays the following chemical shifts (ppm) and integrations:

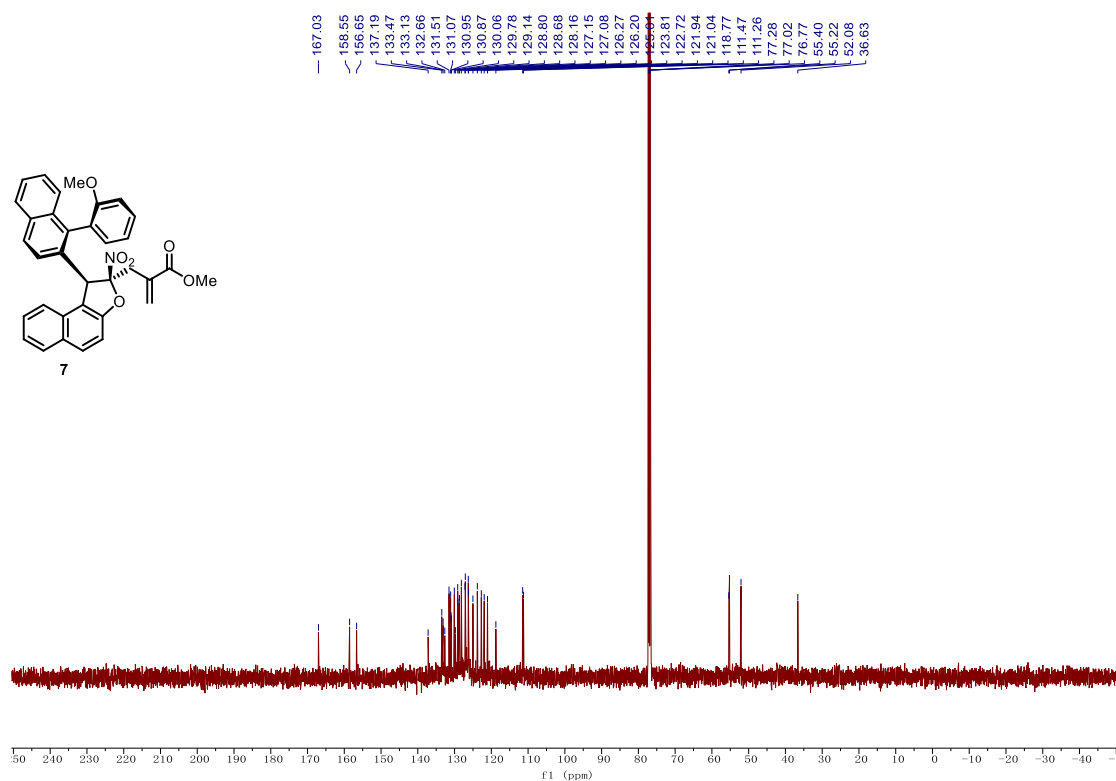
- Aromatic region (7.0–7.8 ppm): Multiple signals with integrations of 2.00, 2.01, 2.00, and 2.01.
- Methoxy group (3.78 ppm): Singlet with integration of 3.02.
- Methine proton (4.62 ppm): Singlet with integration of 1.01.
- Cyclopropane methylene (2.49–2.51 ppm): Doublet with integration of 2.02.
- Cyclopropane methyl groups (1.96–2.02 ppm): Multiple singlets with integrations of 1.02, 2.02, and 2.00.

Chemical structure of **6'** is shown. The ¹³C NMR spectrum (CDCl₃) shows the following chemical shifts (ppm): 193.18, 175.48, 157.35, 136.82, 133.44, 133.15, 132.72, 132.72, 131.94, 129.86, 128.79, 127.84, 126.58, 126.37, 126.12, 125.76, 120.42, 116.65, 111.28, 111.23, 77.31, 77.05, 76.80, 55.60, 52.20, 36.73, 23.24, and 21.27.

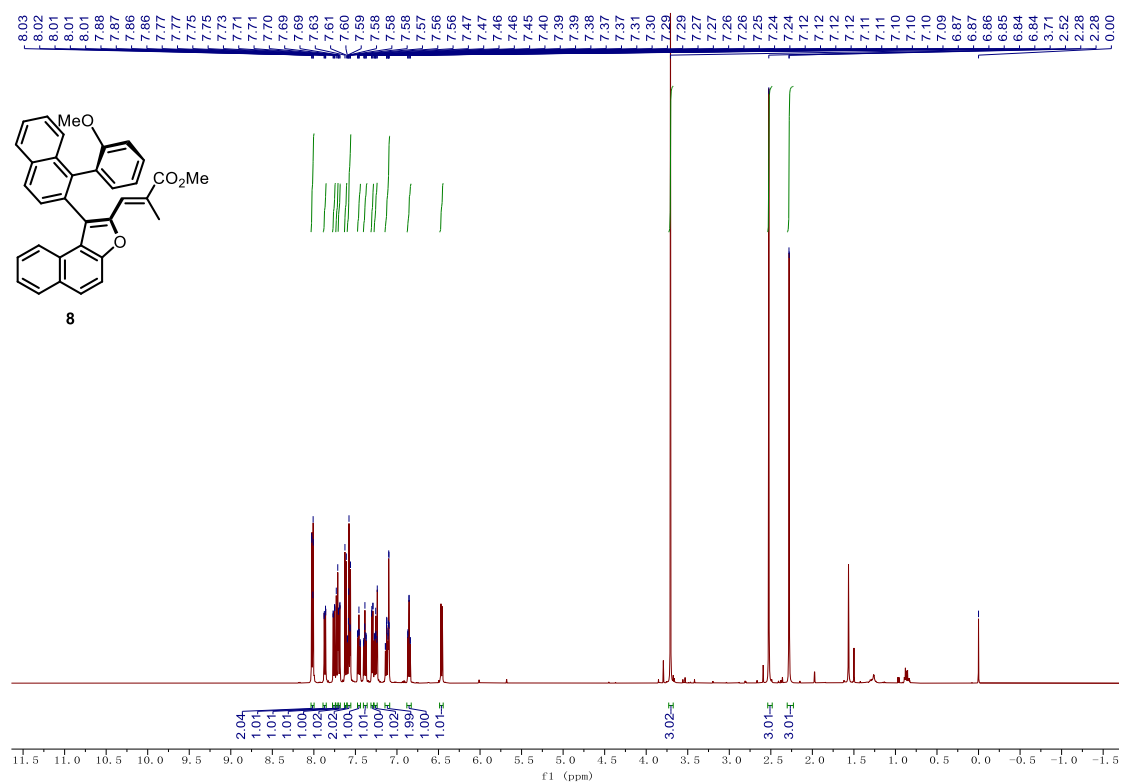
¹H NMR of 7 (500 MHz in CDCl₃):



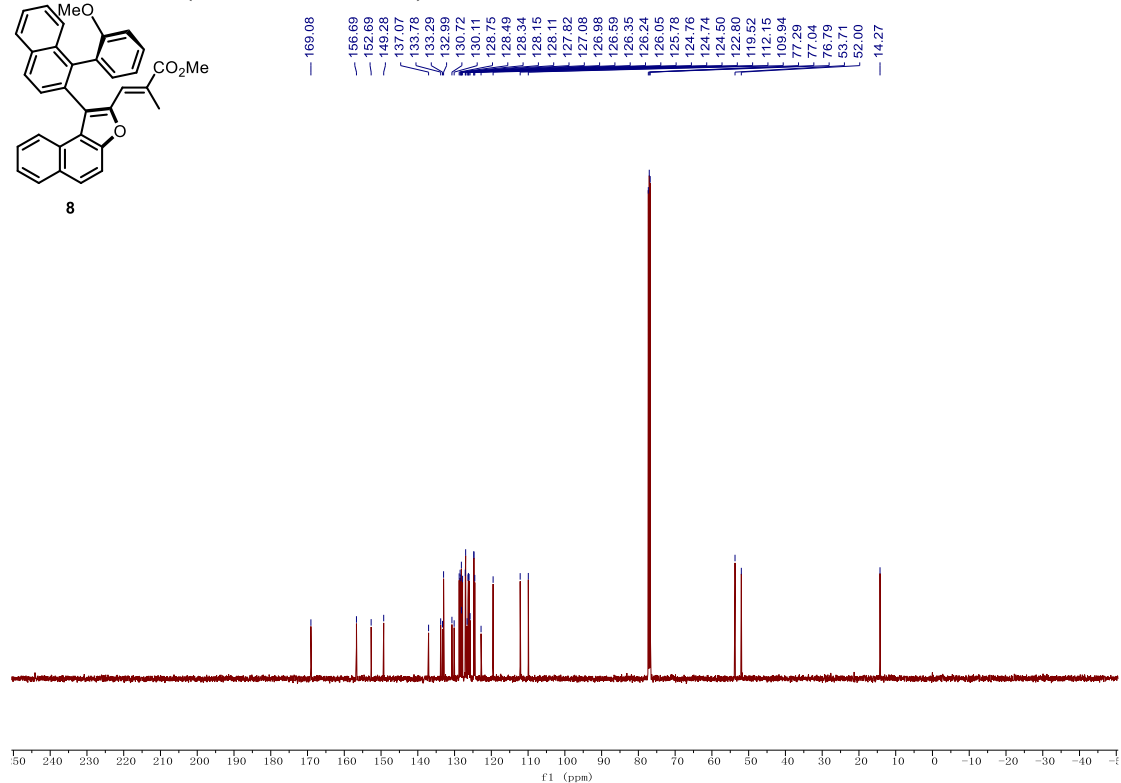
¹³C NMR of 7 (126 MHz in CDCl₃):



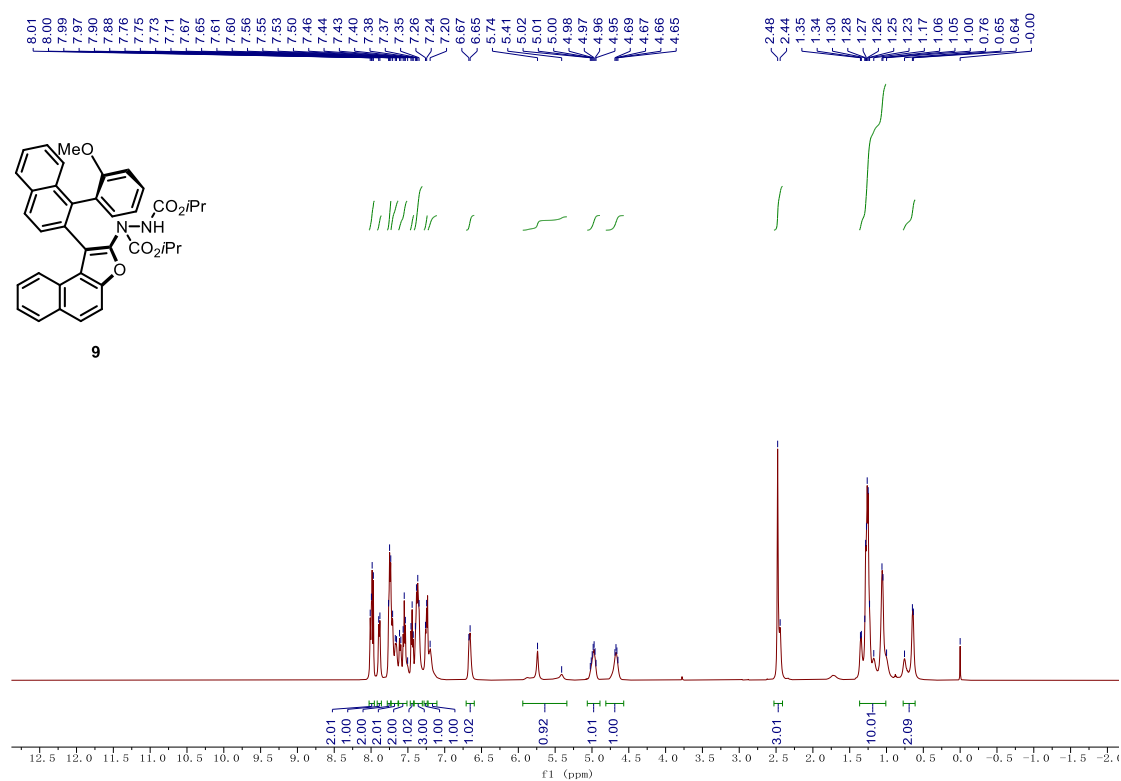
¹H NMR of 8 (500 MHz in CDCl₃):



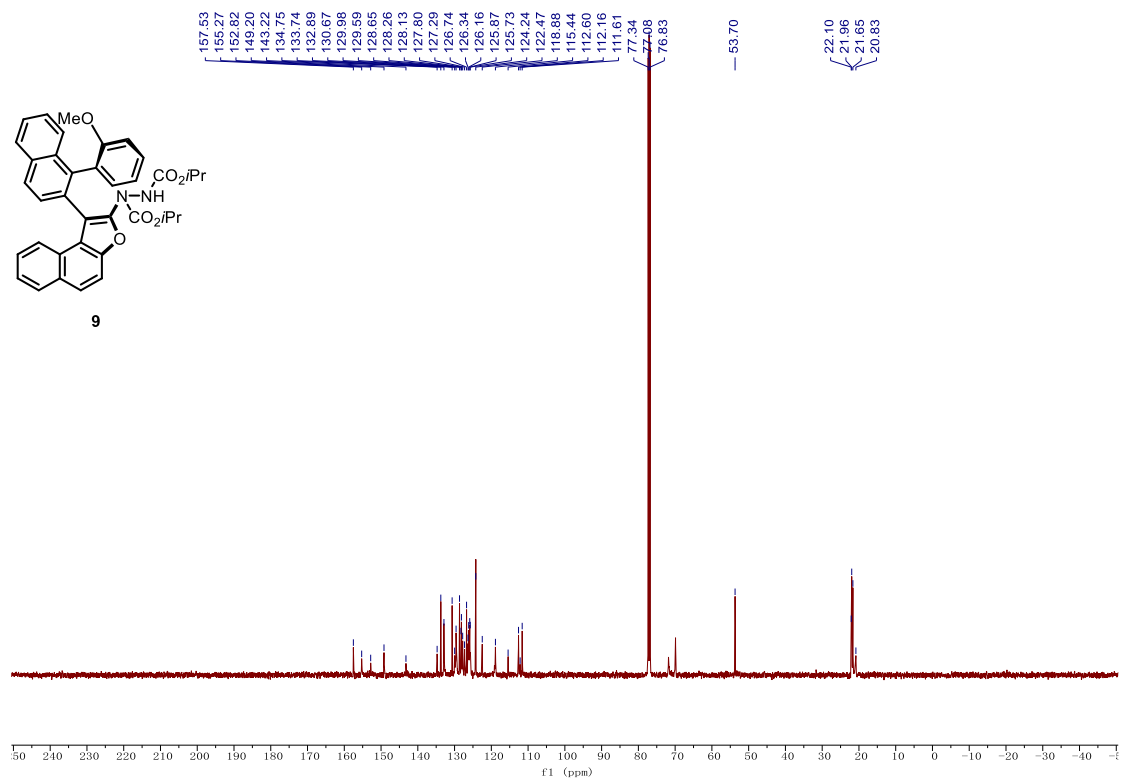
¹³C NMR of 8 (126 MHz in CDCl₃):



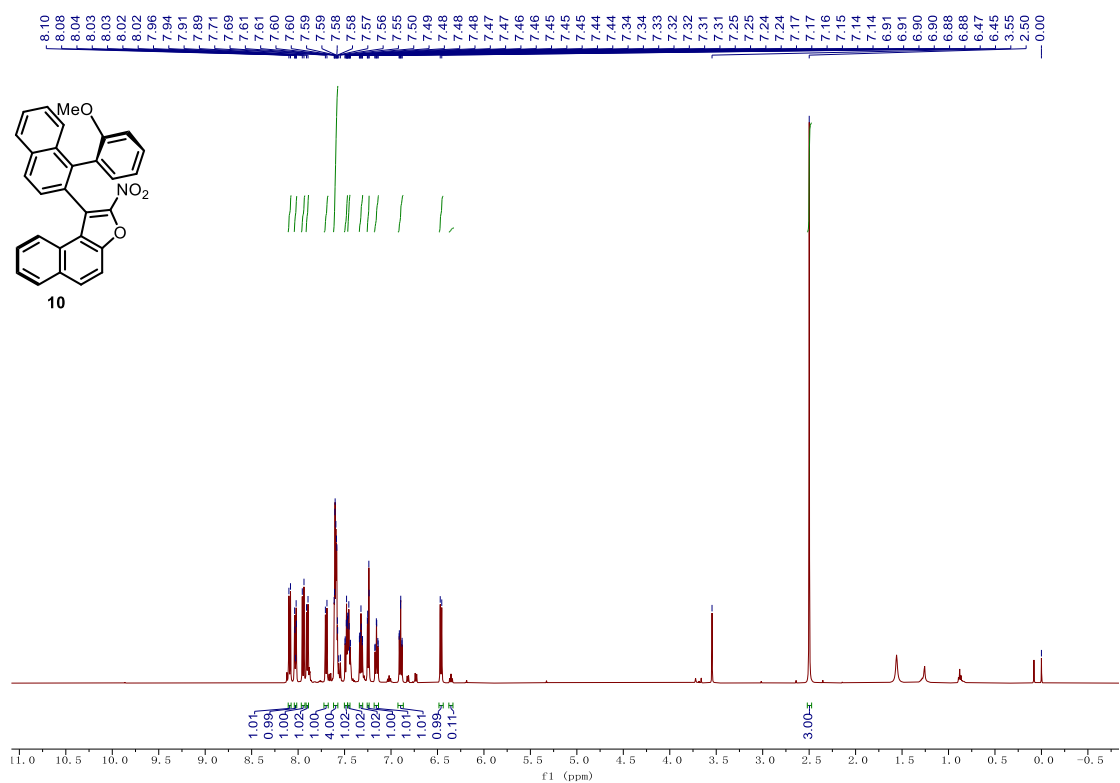
¹H NMR of 9 (500 MHz in CDCl₃):



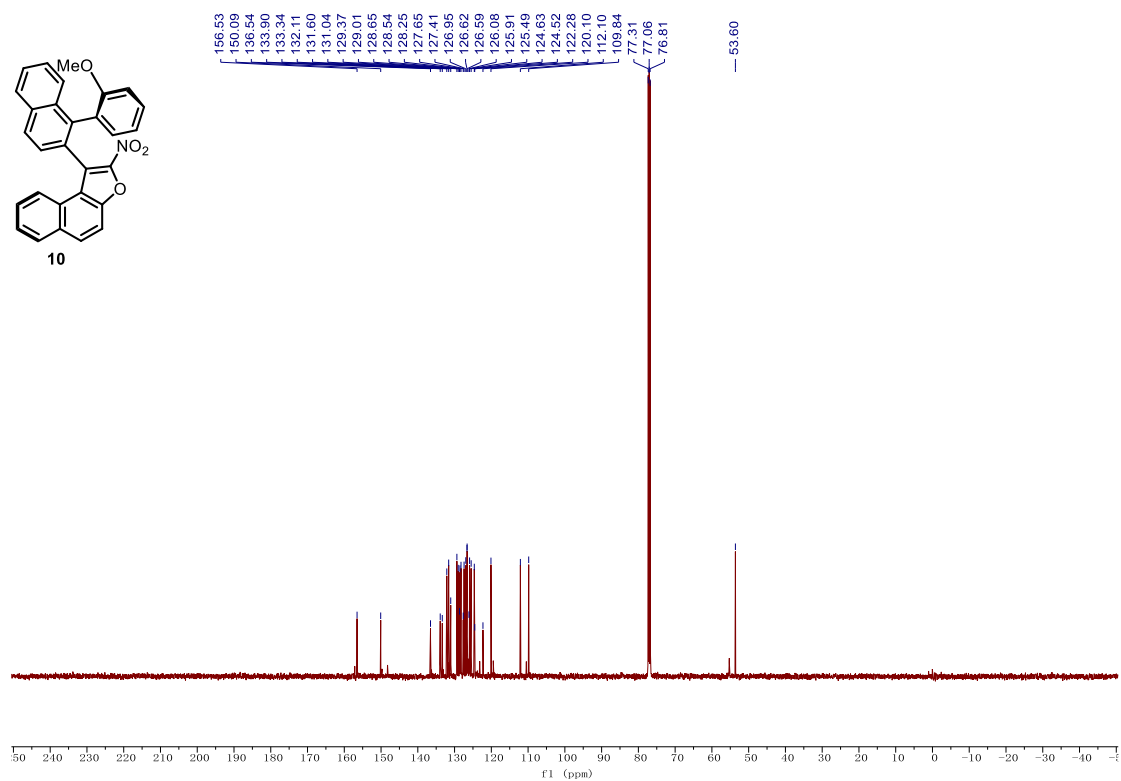
¹³C NMR of 9 (126 MHz in CDCl₃):



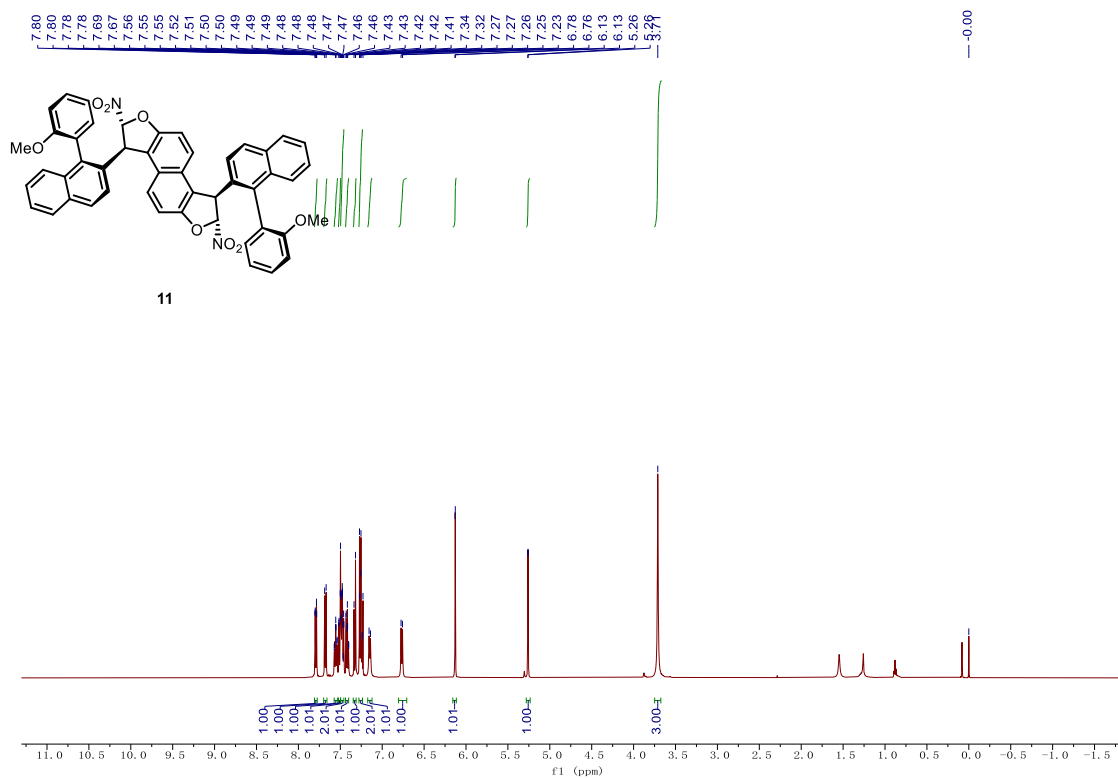
¹H NMR of 10 (500 MHz in CDCl₃):



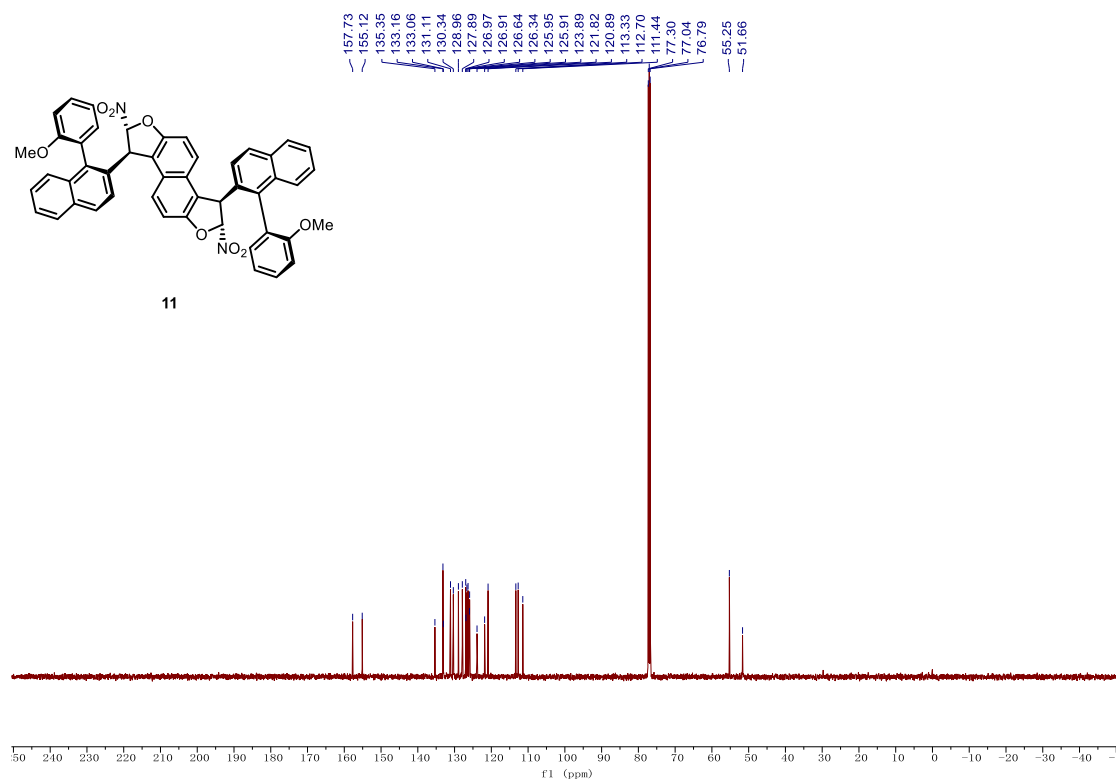
¹³C NMR of 10 (126 MHz in CDCl₃):



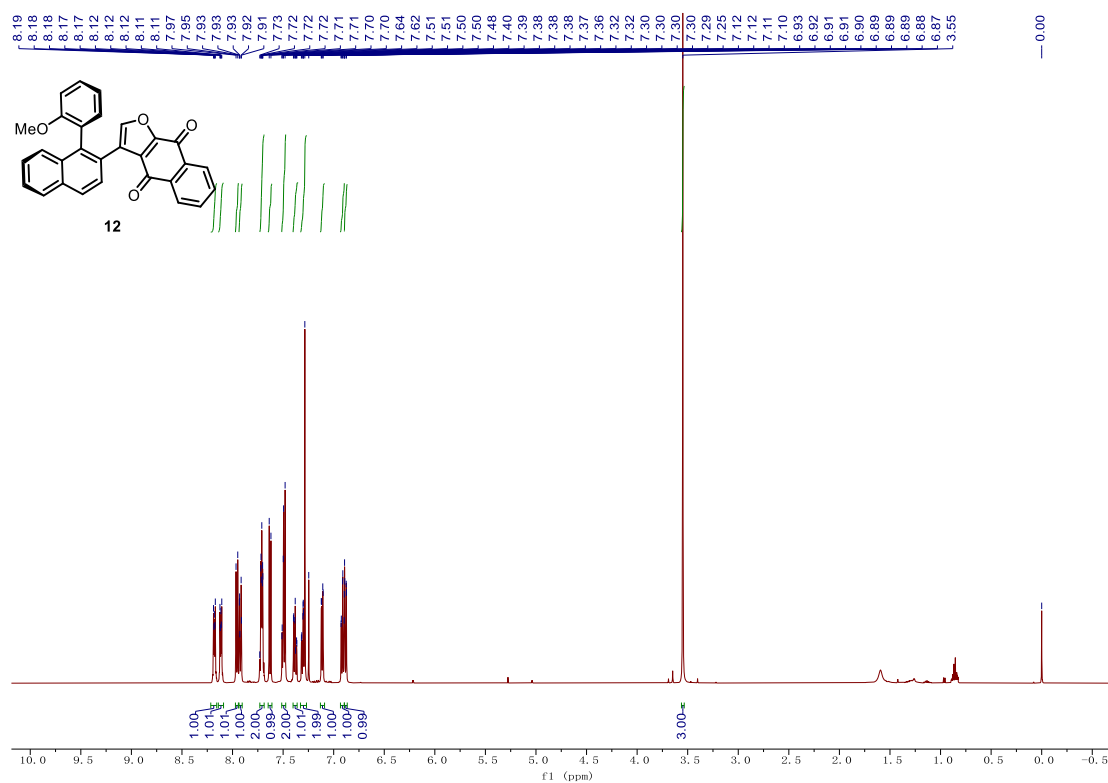
¹H NMR of 11 (500 MHz in CDCl₃):



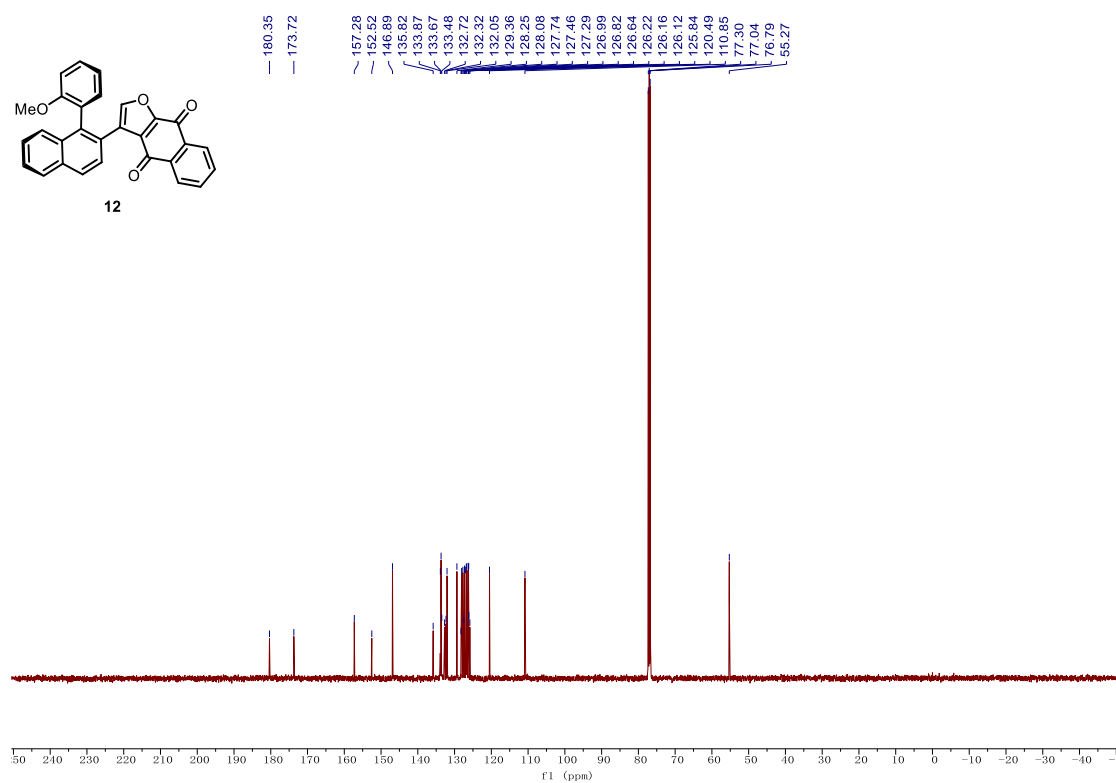
¹³C NMR of 11 (126 MHz in CDCl₃):



^1H NMR of 12 (500 MHz in CDCl_3):



^{13}C NMR of 12 (126 MHz in CDCl_3):



Chemical structure of compound **13** is shown in the top left. The ¹H NMR spectrum (CDCl₃) is displayed below, with the x-axis labeled f1 (ppm) ranging from 12.0 to -0.5. The spectrum shows several multiplets in the aromatic region (6.5-8.1 ppm) and two singlets in the aliphatic region (3.4-3.8 ppm). Integration values are provided below the baseline, and a list of peak chemical shifts is on the right.

Chemical structure of **13**: COc1ccc(cc1)N2C(=O)c3ccccc3C(=O)C2=Cc4ccc5cc(OC)ccc5c4

¹H NMR spectrum (CDCl₃) data:

- Chemical shifts (ppm): 8.13, 8.12, 8.12, 8.11, 8.04, 8.04, 8.03, 8.03, 8.02, 8.02, 7.99, 7.99, 7.92, 7.92, 7.91, 7.91, 7.90, 7.90, 7.80, 7.80, 7.78, 7.78, 7.64, 7.64, 7.63, 7.63, 7.62, 7.62, 7.61, 7.61, 7.60, 7.60, 7.54, 7.54, 7.53, 7.53, 7.48, 7.48, 7.47, 7.47, 7.46, 7.46, 7.45, 7.45, 7.37, 7.37, 7.37, 7.36, 7.36, 7.35, 7.35, 7.34, 7.34, 7.34, 7.34, 7.34, 7.34, 7.32, 7.32, 7.15, 7.15, 7.13, 7.13, 7.13, 7.13, 7.04, 7.04, 7.03, 7.03, 7.03, 7.03, 6.99, 6.99, 6.99, 6.99, 6.93, 6.93, 6.93, 6.92, 6.92, 6.91, 6.91, 6.90, 6.90, 6.89, 6.89, 6.51, 6.51, 3.84, 3.84, 3.83, 3.83, 3.49, 3.49, 0.00.
- Integration values: 1.02, 1.00, 1.01, 1.02, 1.00, 2.02, 1.01, 1.01, 1.01, 2.01, 1.03, 2.02, 3.01, 1.01, 1.00, 3.02, 3.00.

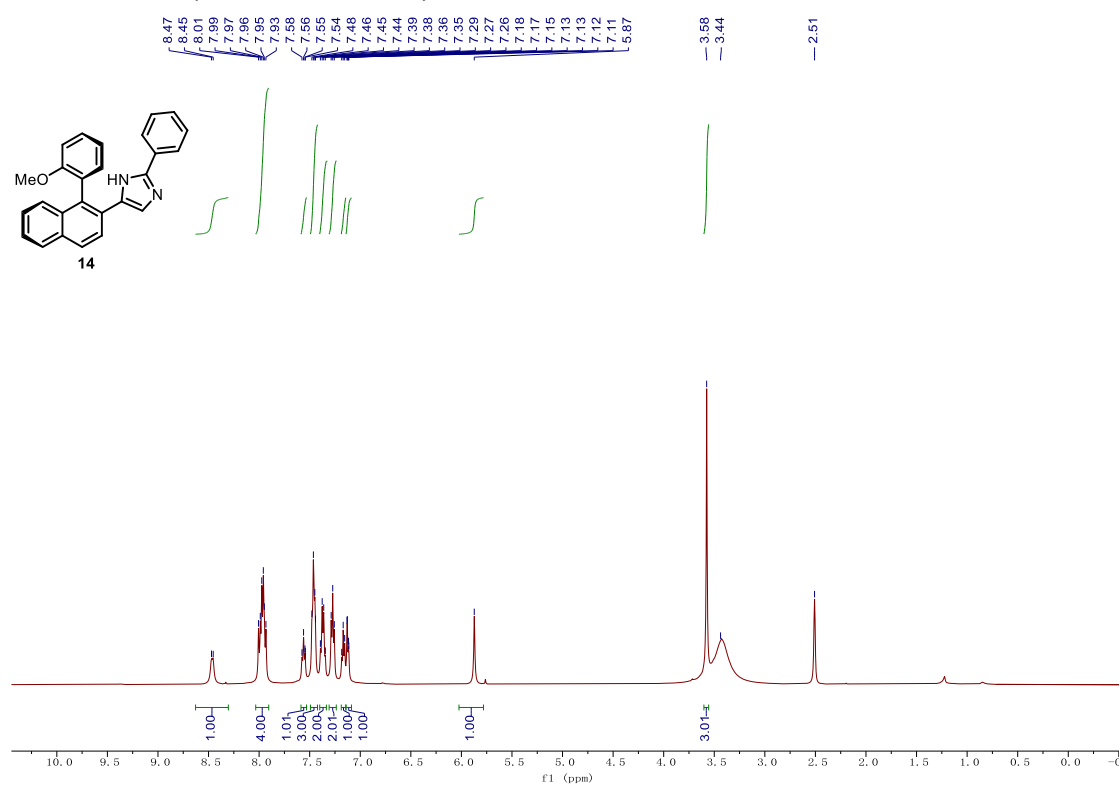
Chemical structure of compound **13** is shown. The structure is a complex polycyclic molecule featuring a naphthalene system, a benzimidazole core, and a methoxy-substituted phenyl ring.

¹³C NMR spectrum (CDCl₃) of compound **13** is displayed. The x-axis represents the chemical shift in ppm, ranging from -5 to 180.79. The spectrum shows several peaks corresponding to the carbon atoms in the molecule, with a prominent solvent peak at 77.10 ppm.

Key peaks (ppm) labeled on the spectrum include:

- 180.79, 175.14, 159.70, 157.69, 135.23, 134.21, 133.99, 133.23, 133.11, 132.96, 132.72, 132.52, 132.45, 131.60, 130.28, 130.02, 128.88, 128.74, 128.55, 128.10, 126.97, 126.87, 126.74, 126.54, 126.23, 125.93, 125.89, 125.69, 125.66, 120.51, 118.11, 110.81, 77.10, 76.84, 55.54, 55.32.

¹H NMR of 14 (500 MHz in CDCl₃):



¹³C NMR of 14 (126 MHz in CDCl₃):

