A Triple-functionalised Metal Centre-Catalyzed Enantioselective Multicomponent Reactions

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1. Materials and Methods

All reactions and manipulations were carried out under an airatmosphere, in a flame-dried or oven-dried flask containing magnetic stir bar. All ^{1}H NMR, and ^{13}C NMR spectra were recorded using a Brucker 400 MHz spectrometer in $CDCl_3$.Tetramethylsilane (TMS) served as an internal standard (δ = 0) for ^{1}H NMR, and $CDCl_3$ was used as internal standard (δ = 77.0) for ^{13}C NMR. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). HRMS (ESI) Mass spectra were recorded on IonSpec FT-ICR mass spectrometer. Chiralpak AD-H, IA, OD-H, IC, chiral columns were purchased from Daicel Chemical Industries, LTD. For the React IR experiments, the reaction spectra were recorded using an IC 15 from Mettler Toledo AutoChem. Data manipulation was carried out using the ICIR software, version 4.3. The racemic standards used in HPLC studies were prepared according to the general procedure by using $[Rh(COD)Cl]_2$ and Cinchonine as catalyst.
Dichloromethane (DCM), 1, 2-dichloroethane (DCE) and toluene were distilled over calcium hydride. Solvents for the column chromatography were distilled before use. All reactions were carried out under an air atmosphere in glassware **L_1** and **L_7** were purchased from sigma-aldrich. **L_2-L_6** were prepared according to the literature.[1] Nitroacrylates were prepared according to literature.[2]

2. Experimental Procedures

General Procedure for Racemic Three-Component Reactions:

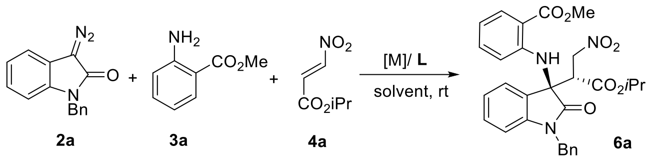
To a flask charged with 2 mol% $[Rh(COD)Cl]_2$, nitroacrylate (0.2 mmol) Cinchonine was added directly to the flask and stirred for another 30 minutes. Aromatic amine 2 (0.22 mmol) and diazooxindole 1 (0.22 mmol) in toluene (1 mL) were introduced by syringe pump over 1 hour at room temperature and the reaction solution was stirred for another 2 hours. After the completion of the reaction (monitored by TLC), the reaction mixture was filtrated and the filtrate was evaporated in vacuo to give the crude product. And then the crude product was purified by flash chromatography on silica gel (EtOAc/light petroleum ether = 1:20 ~ 1:5) to give the pure product.

General Procedure for Enantioselective Three-Component Reactions:

To a flask charged with 2 mol% $[Rh(COD)Cl]_2$ (1.97 mg, 0.0040 mmol, 2mol%), 4 mol% **L7** (7.93 mg, 0.01mmol, 5mol%) in toluene (1 ml) was stirred at 30^{0}C for 1h. Nitroacrylate (0.2mmol) was added directly to the flask and stirred for another 30 minutes. Aromatic amine **2** (0.22mmol) anddiazooxindole**1** (0.22mmol) in toluene (2 mL) were introduced by syringe pum pover 2 hours at room temperature and the reaction solution was stirred for another 1 hours. After the completion of the reaction (monitored by TLC), the reaction mixture was filtrated and the filtrate was evaporated in vacuo to give the crude product. And then the crude product was purified by flash chromatography on silica gel (EtOAc/light petroleum ether = 1:20 ~ 1:5) to give the pure product.

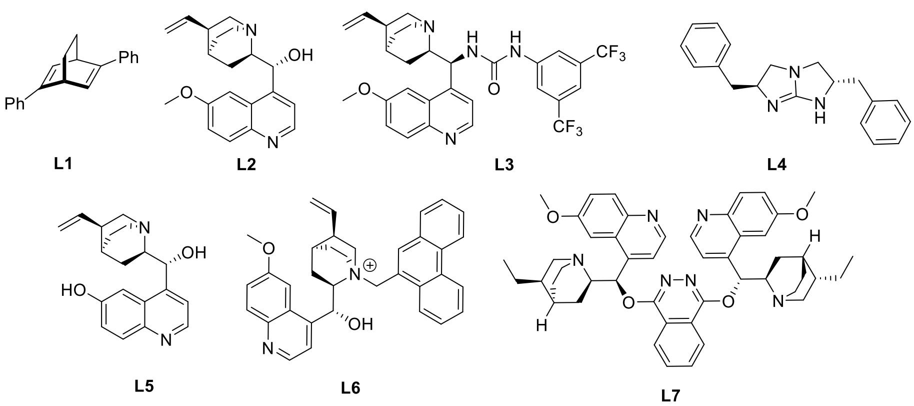
3.

Table S1 Optimisation of reaction conditions.[a]

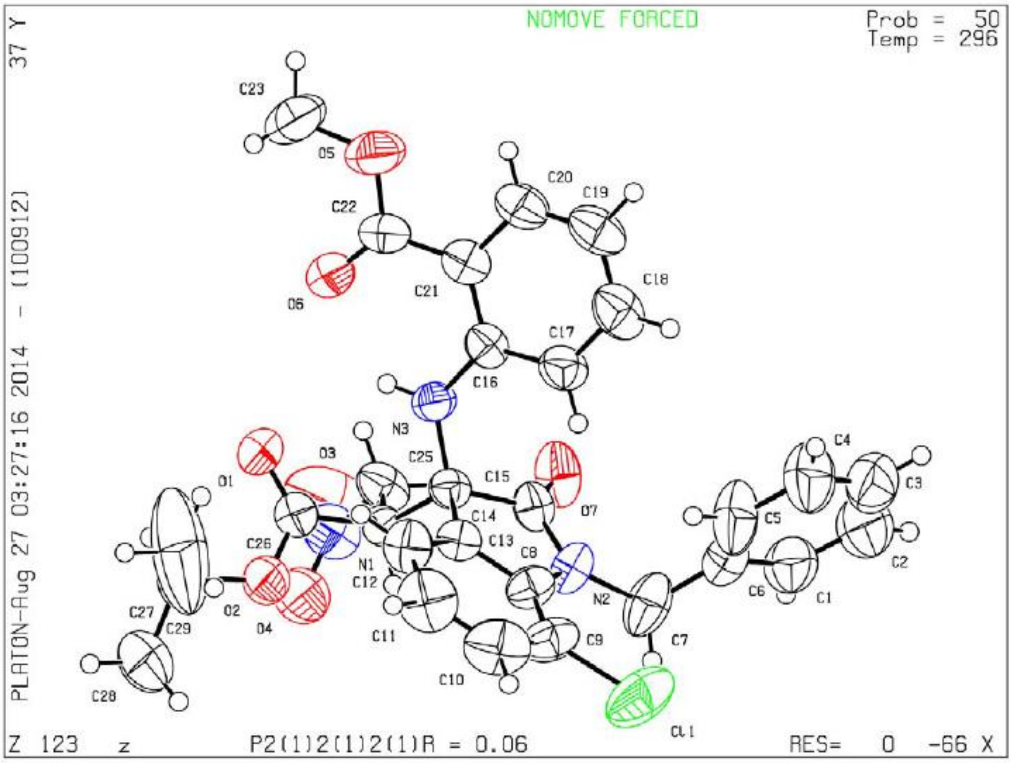


entry	L	[M]	solvent	yield (%)[b]	d.r.[c]	er (%)[d]
1	**L7**	$[Rh(COD)Cl]_2$	toluene	57	98:2	95:5
2	**L7**	$[Rh(COD)Cl]_2$	xylene	23	92:8	78:22
3	**L7**	$[Rh(COD)Cl]_2$	DCE	82	90:10	75:25
4	**L7**	$[Rh(COD)Cl]_2$	DCM	23	92:8	78:22
5	**L7**	$[Rh(COD)Cl]_2$	$CHCl_3$	76	95:5	88:12
6	**L7**	$[Rh(COD)Cl]_2$	THF	55	88:12	71:29

[a] Unless otherwise noted, all reactions were carried out on a 0.2 mmol scale with **2a**:**3a**:**4a**= 1.1:1.1:1.0.
[b] Yields of isolated products were determined afterpurification using column chromatography.
[c] Diastereomeric ratio (d.r.) was determined using ^{1}H NMR spectroscopy. [d] Determined using high-performance liquid chromatography (HPLC) analysis. [e] N.P.: no product. DCE = 1,2-dichloroethane; THF = tetrahydrofuran.



4.



Bond precision: C-C = 0.0080 A Wavelength=0.71073

Cell: a=8.6110(12) b=11.3415(15) c=28.819(4)
alpha=90 beta=90 gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	2814.5(7)	2814.5(7)
Space group	P 21 21 21	P2(1)2(1)2(
Hall group	P 2ac 2ab	?
Moiety formula	C29 H28 Cl N3 O7	?
Sum formula	C29 H28 Cl N3 O7	C29 H28 Cl N3 O7
Mr	565.99	565.99
Dx,g cm-3	1.336	1.336
Z	4	4
Mu (mm-1)	0.187	0.187
F000	1184.0	1184.0
F000'	1185.17	
h,k,lmax	10,13,34	10,13,34
Nref	4954[2836]	4955
Tmin,Tmax	0.967,0.987	0.919,0.987
Tmin'	0.918	

Correction method= MULTI-SCAN

Data completeness= 1.75/1.00 Theta(max)= 25.000

R(reflections)= 0.0564(2604) wR2(reflections)= 0.1486(4955)

S = 1.002 Npar= 361

Figure S1 The single crystal analysis for **6i**

5

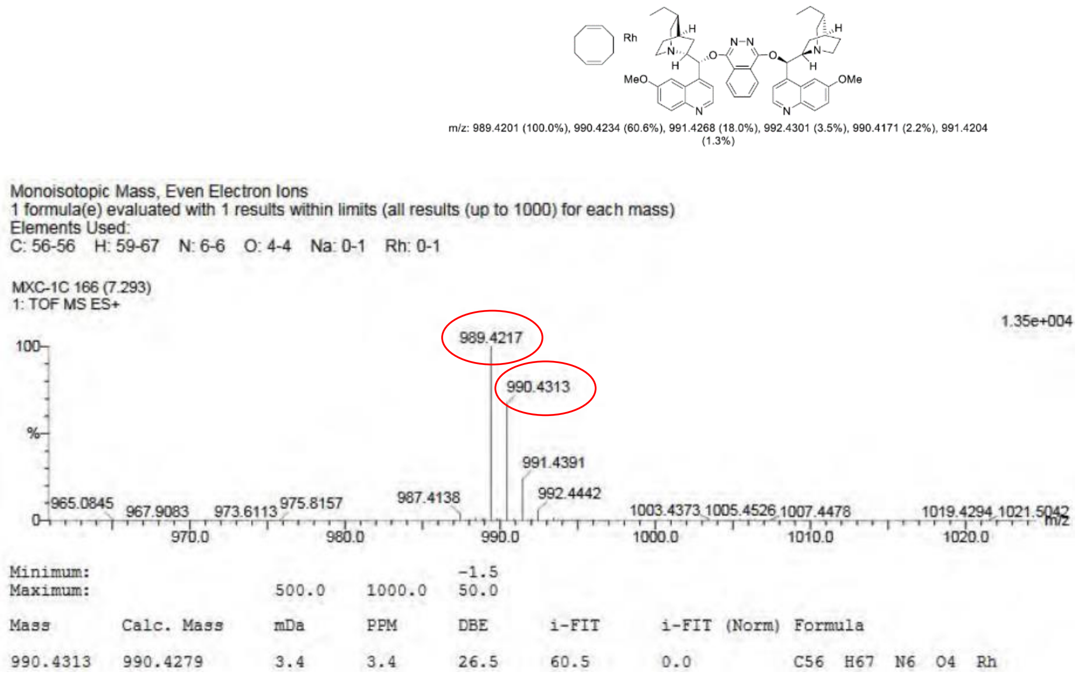


Figure S2 In situ analyze the reaction mixture to confirm the active catalyst in the three-component reaction

6.

The $[Rh(COD)Cl]_2$ was dissolved in $CDCl_3$, then different ratio of L_7 was added. The integration was detected by ^1H NMR.

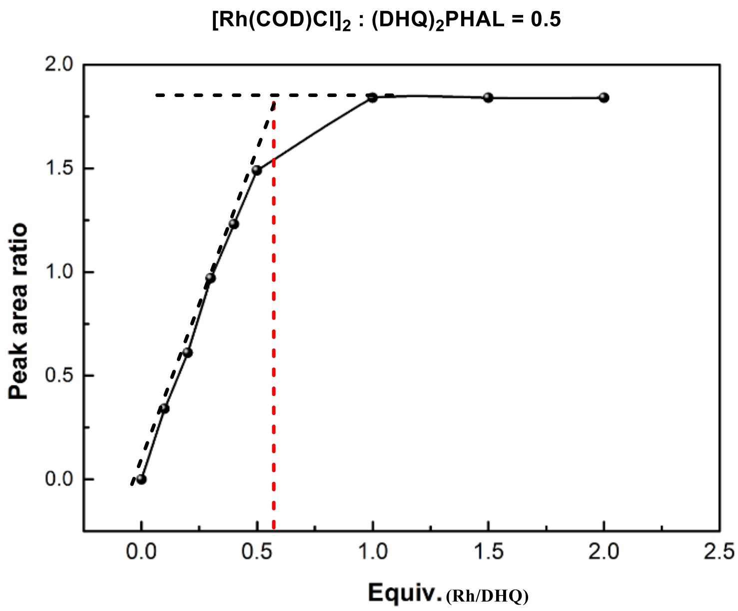


Figure S3 The ^1H spectra of **L7** with addition of $[Rh(COD)Cl]_2$

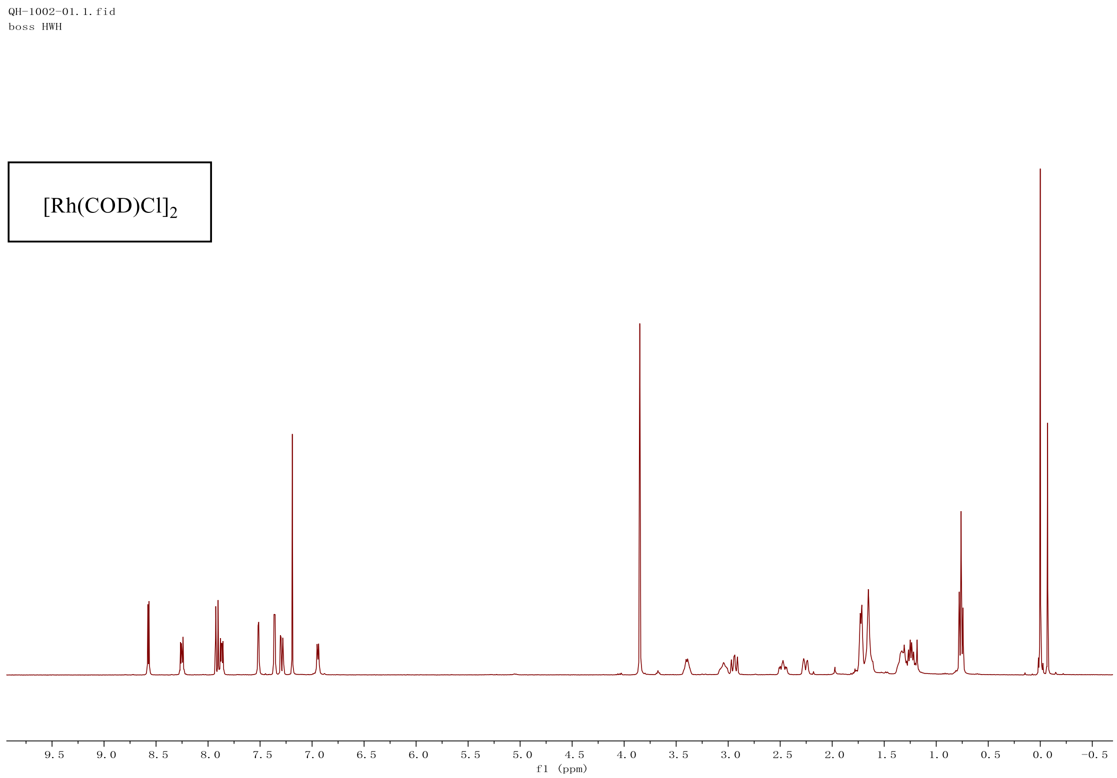


Figure S3-1 H NMR spectra of $[Rh(COD)Cl]_2$

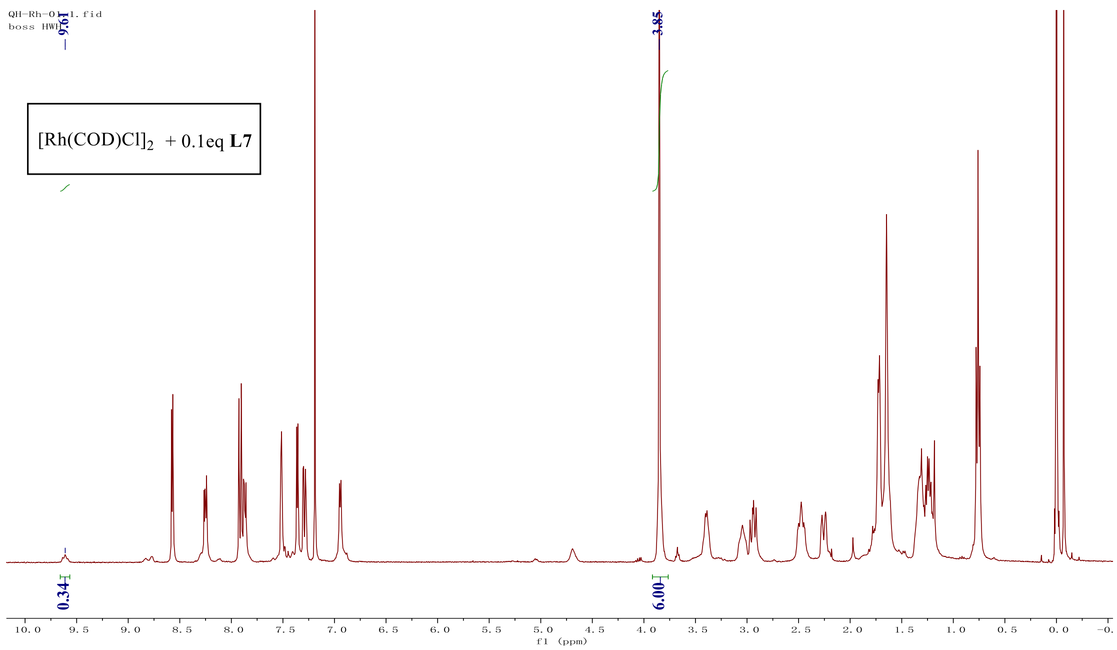


Figure S3-2^{1}H NMR spectra of $[Rh(COD)Cl]_2$ and 0.1 eq $(DHQ)_2$PHAL

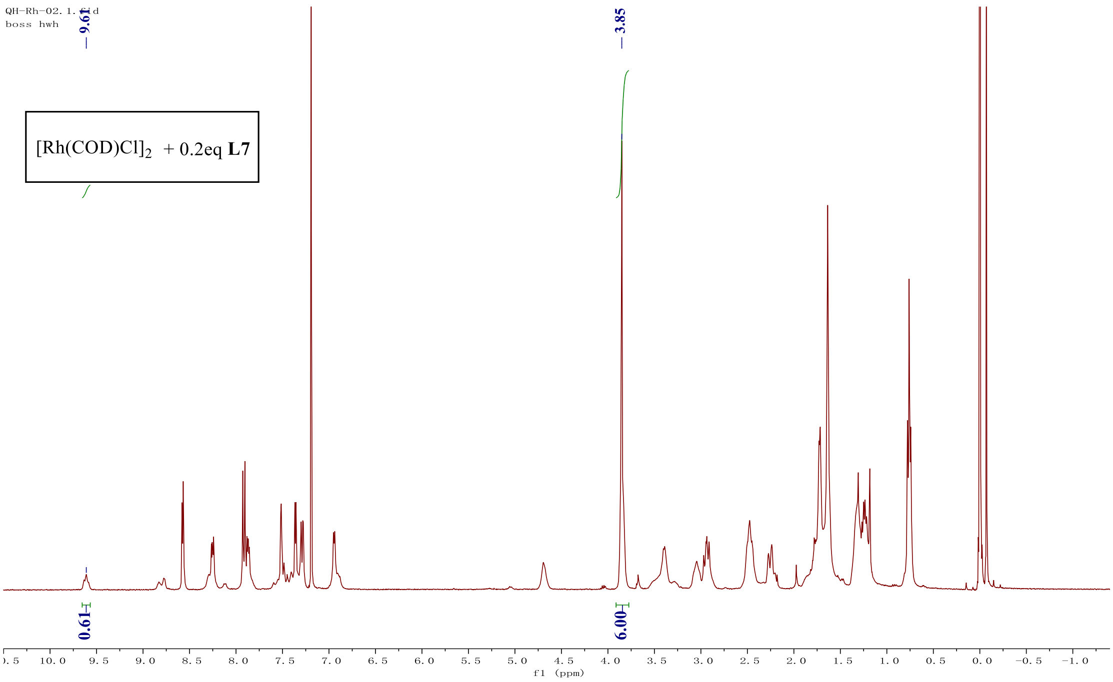


Figure S3-3 ^{1}H NMR spectra of $[Rh(COD)Cl]_2$ and 0.2 eq $(DHQ)_2$PHAL

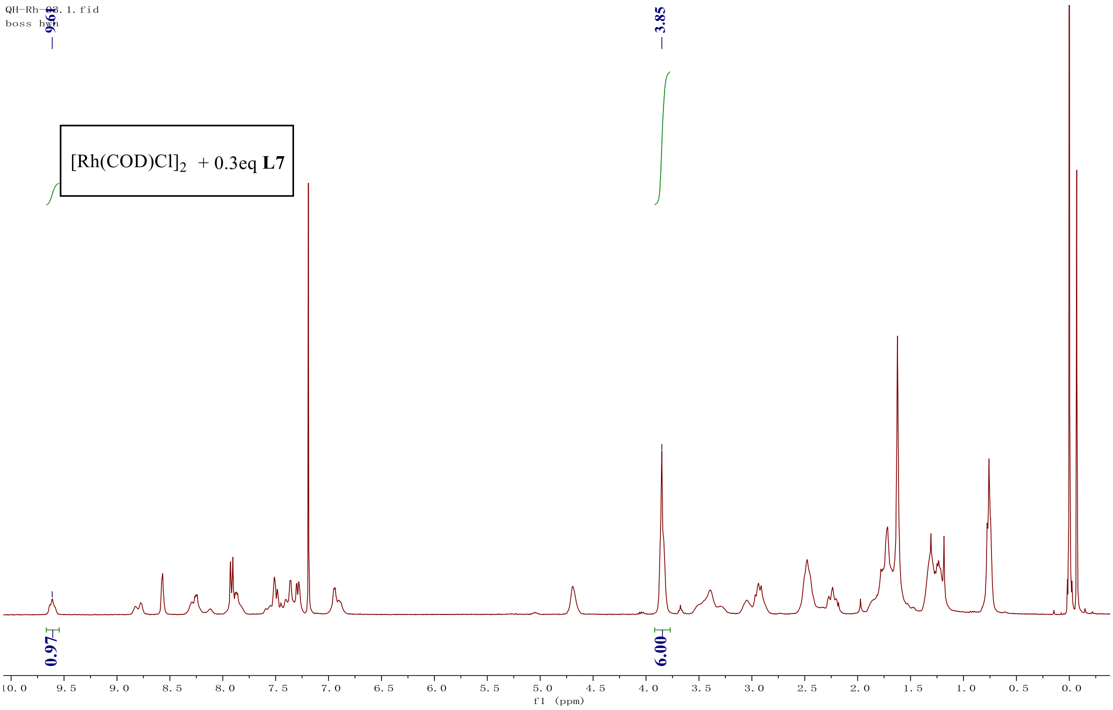


Figure S3-4 ^{1}H NMR spectra of $[Rh(COD)Cl]_2$ and 0.3eq $(DHQ)_2$PHAL

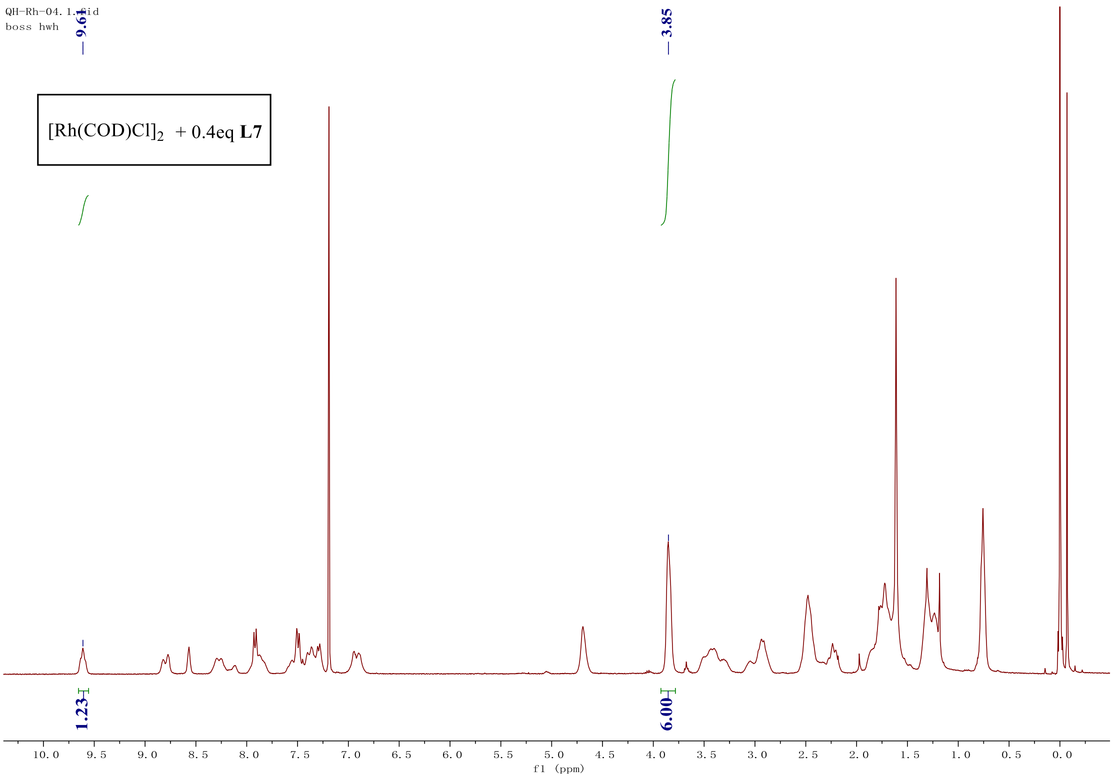


Figure S3-5 ^{1}H NMR spectra of [Rh(COD)Cl]$_2$ and 0.4eq (DHQ)$_2$PHAL

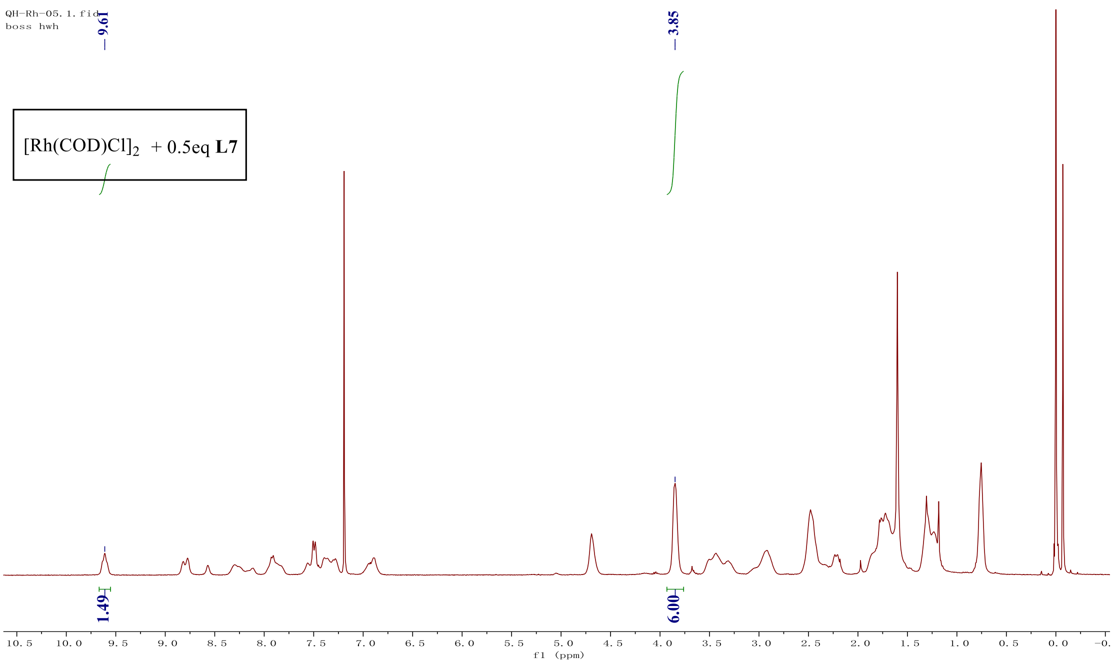


Figure S3-6 ^{1}H NMR spectra of [Rh(COD)Cl]$_2$ and 0.5eq (DHQ)$_2$PHAL

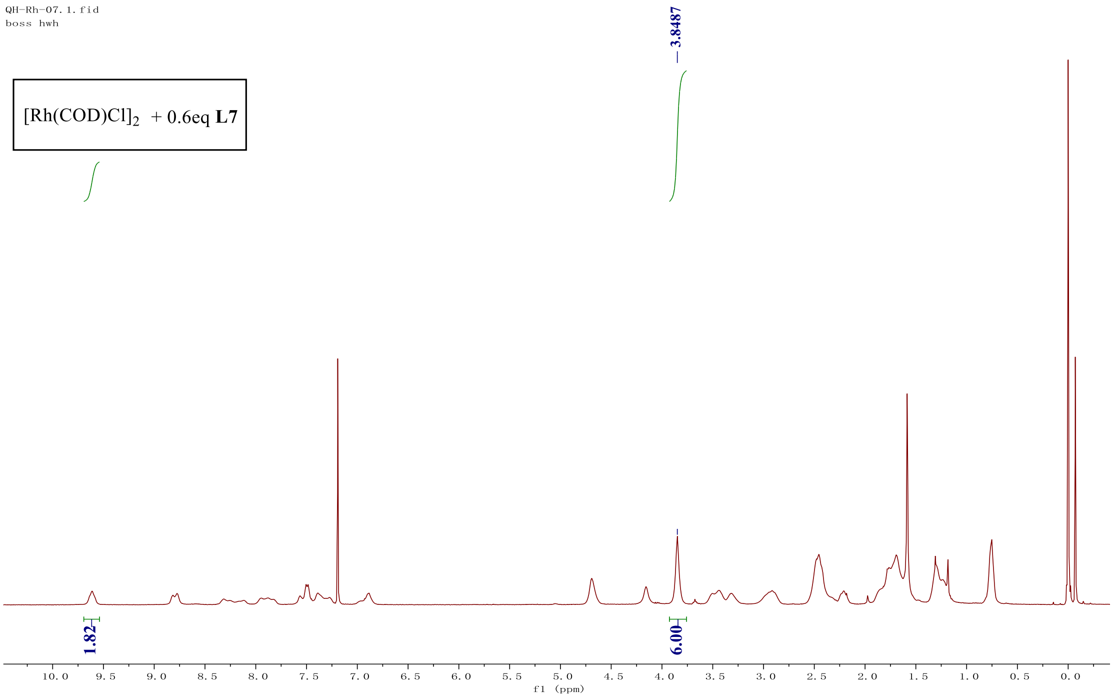


Figure S3-7 ^{1}H spectra of [Rh(COD)Cl]$_2$ and 0.6eq (DHQ)$_2$PHAL

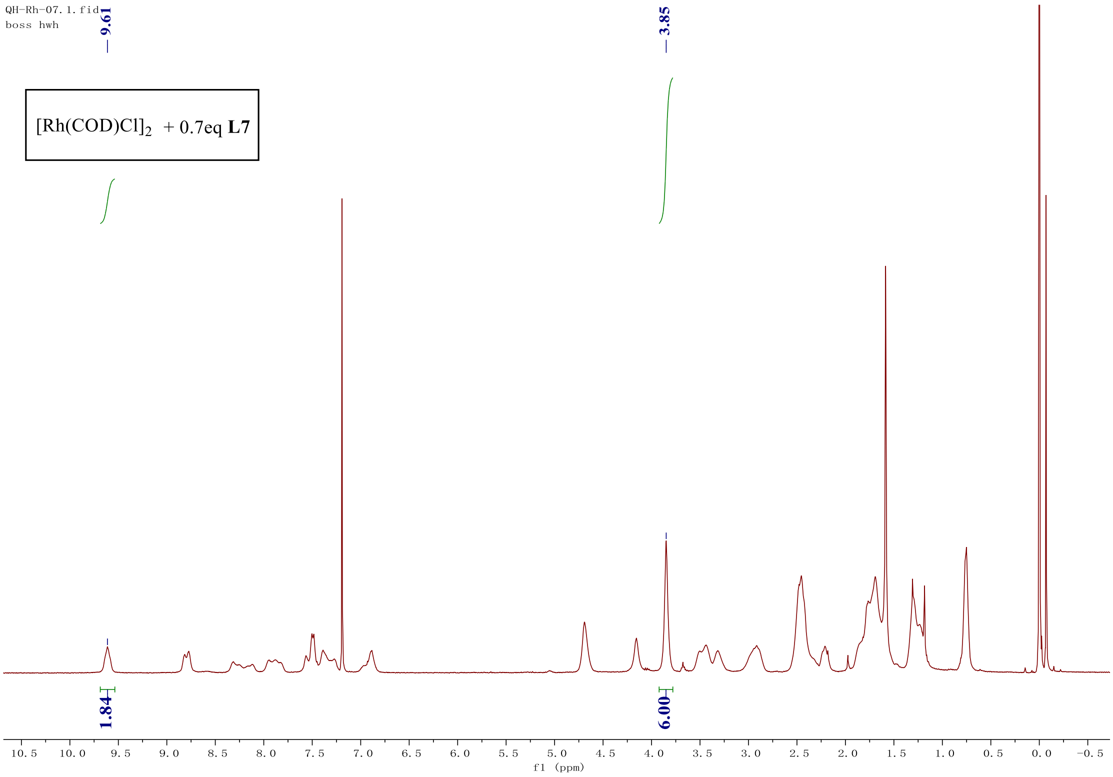


Figure S3-8 ^{1}H spectra of [Rh(COD)Cl]$_2$ and 0.7eq (DHQ)$_2$PHAL

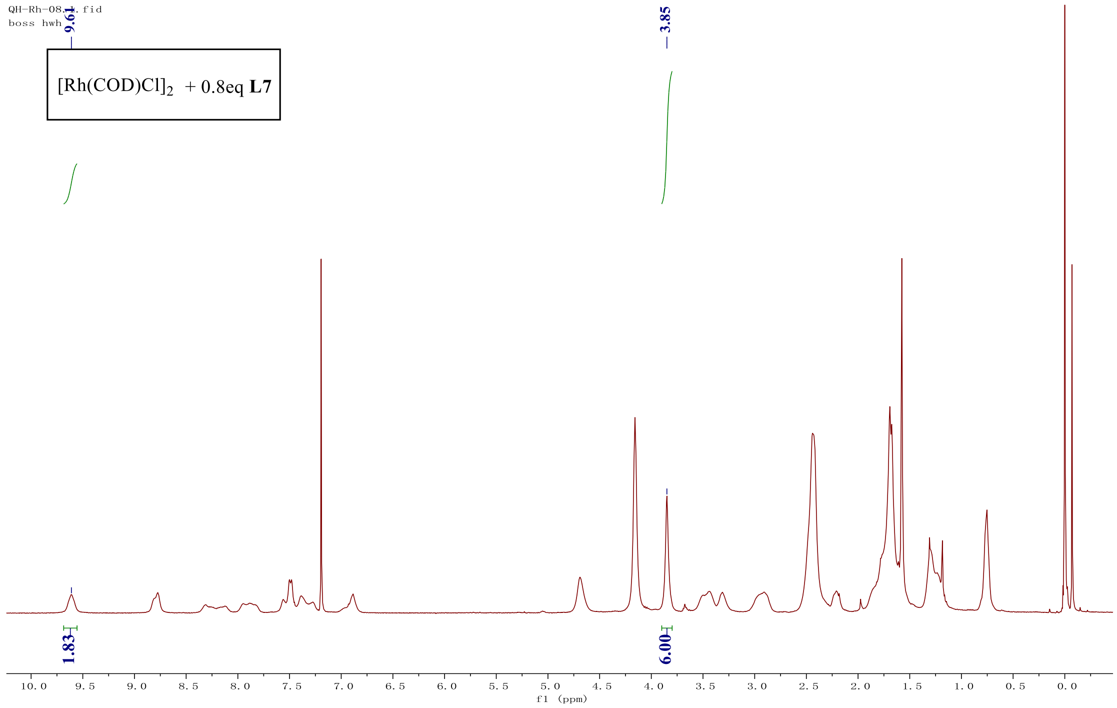


Figure S3-9 [1]H spectra of $[Rh(COD)Cl]_2$ and 0.7eq $(DHQ)_2PHAL$

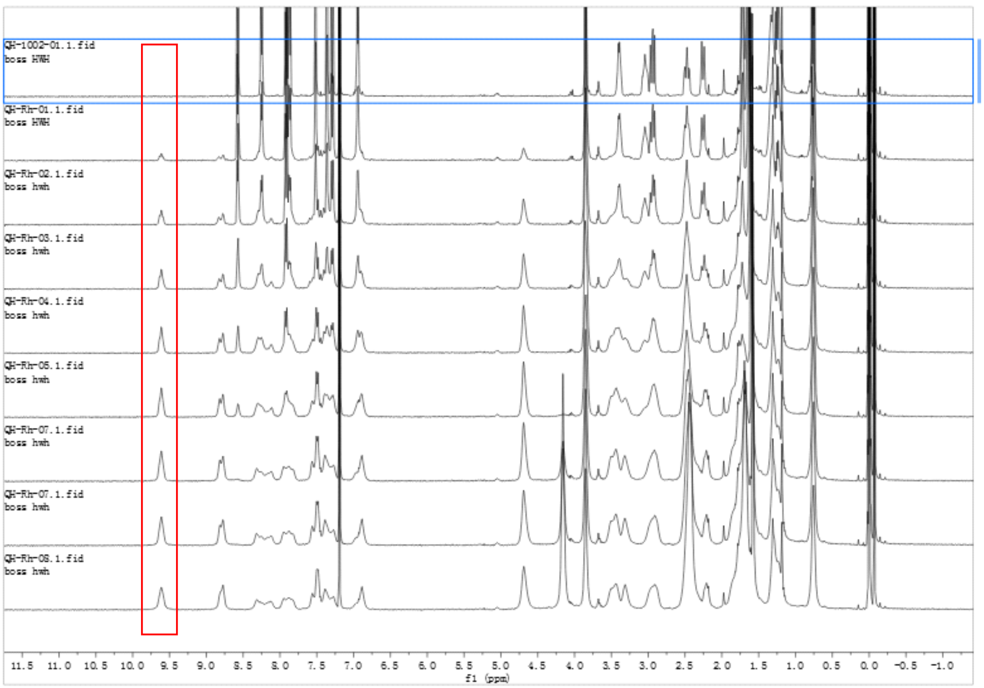


Figure S3-10 The combination of [1]HNMR spectra of the titration experiments

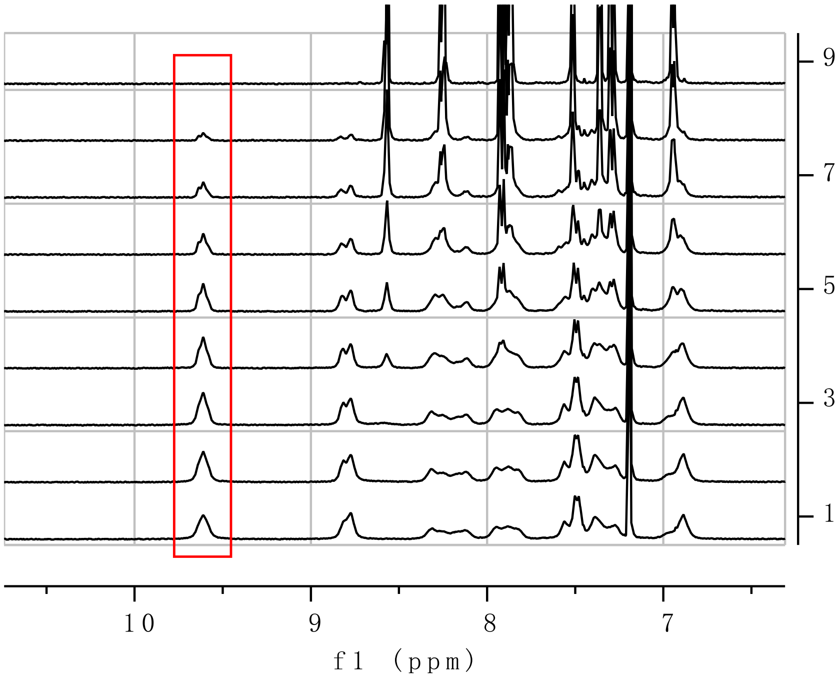


Figure S3-11 The expansion spectra of titration experiments

7.

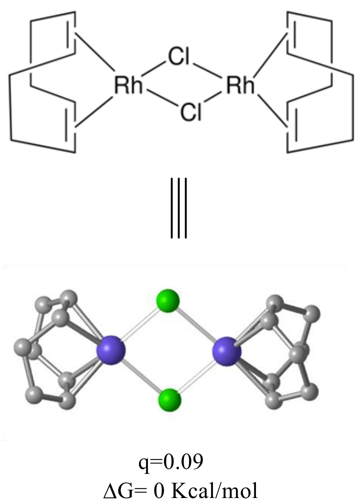


Figure S4 The DFT calculation of relative energies and the NPA charges of $[Rh(COD)Cl]_2$

8.

The [1]HNMR study interaction between $[Rh(COD)Cl]_2$, **L7**, and **4d**

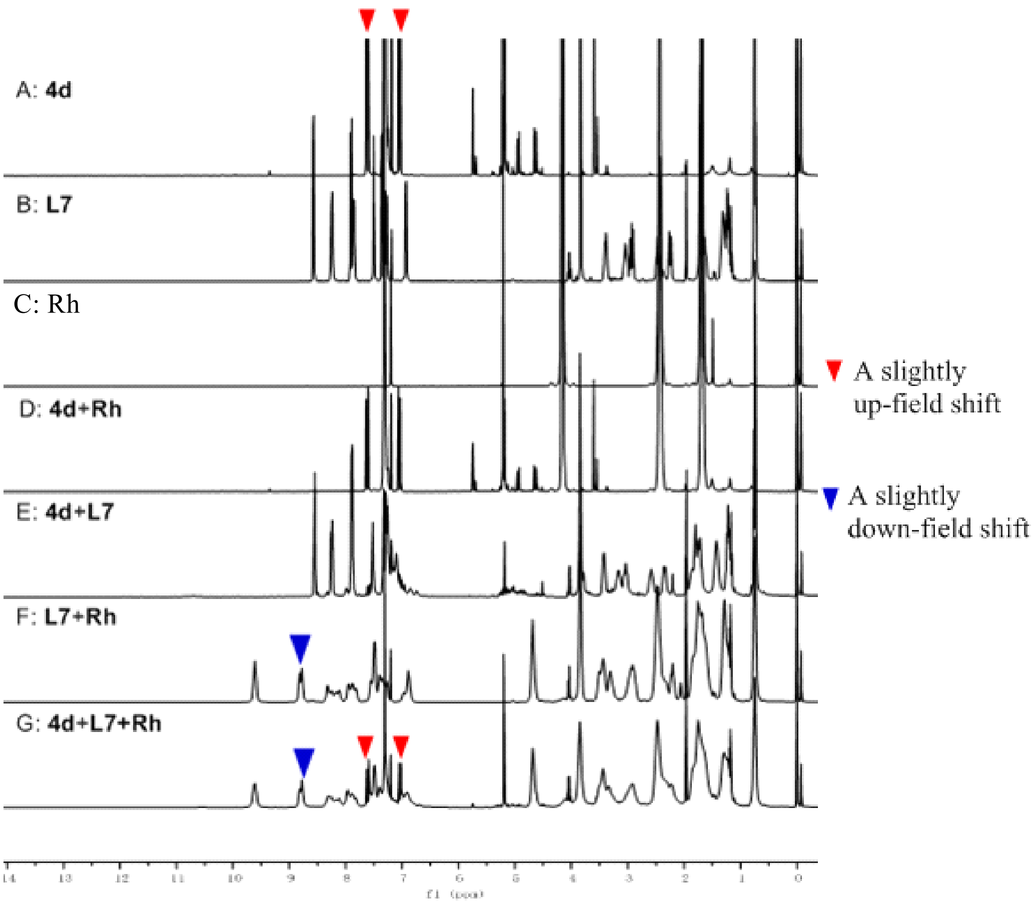


Figure S5 The ^{1}H NMR spectra of the mixture solution of **L7**, **4d** and $[Rh(COD)Cl]_2$ in $CDCl_3$

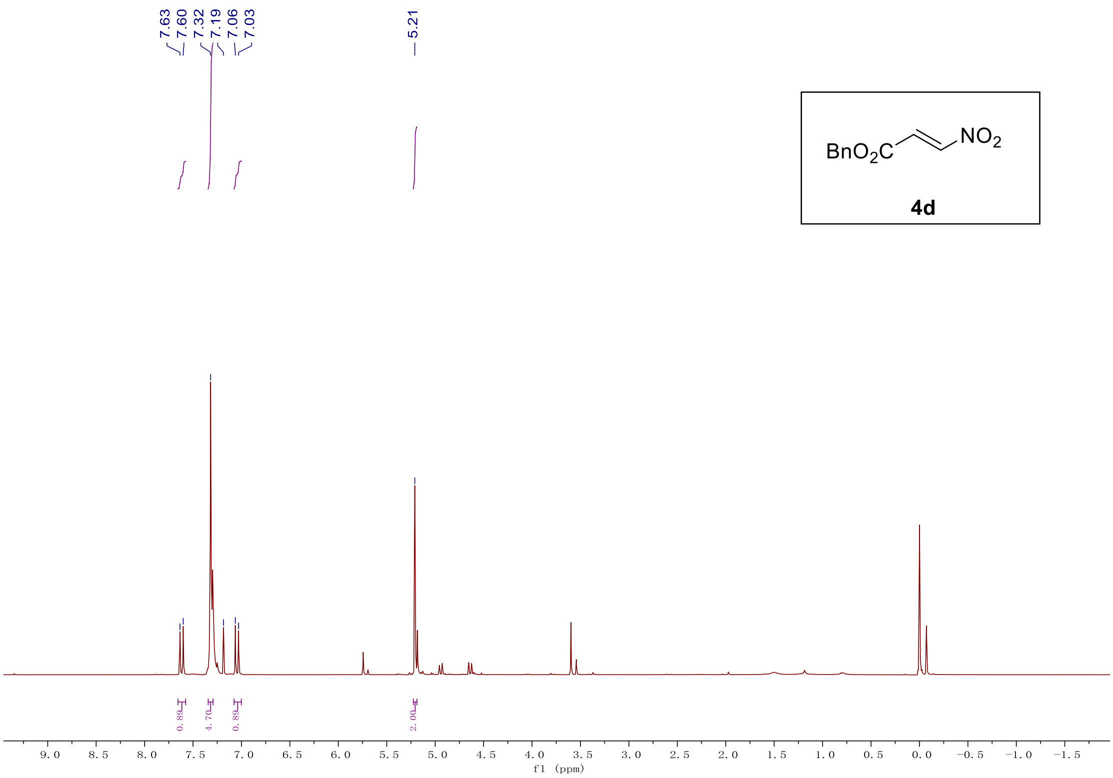


Figure S5-1 [1]HNMR spectrum of **4d**

The [1]H NMR Spectrum of **4d**: [1]H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 13.5 Hz, 1H), 7.32 (s, 5H), 7.05 (d, *J* = 13.5 Hz, 1H), 5.21 (s, 2H).

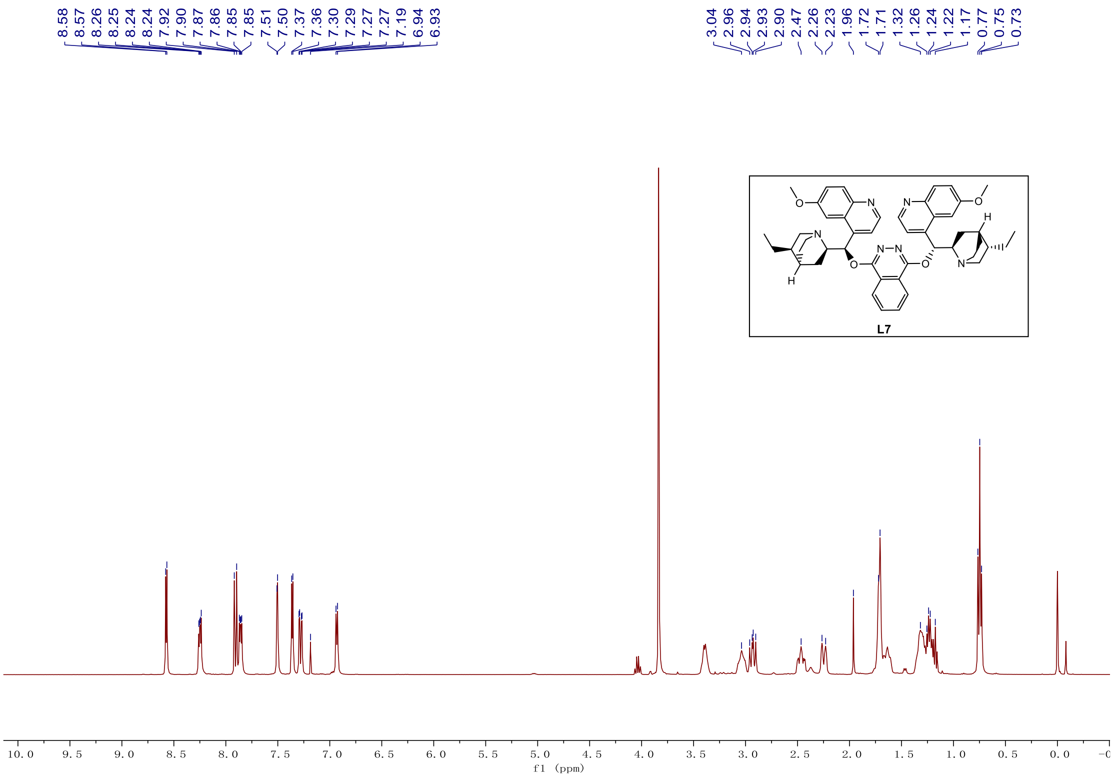


Figure S5-2 [1]HNMR spectrum of **L7**

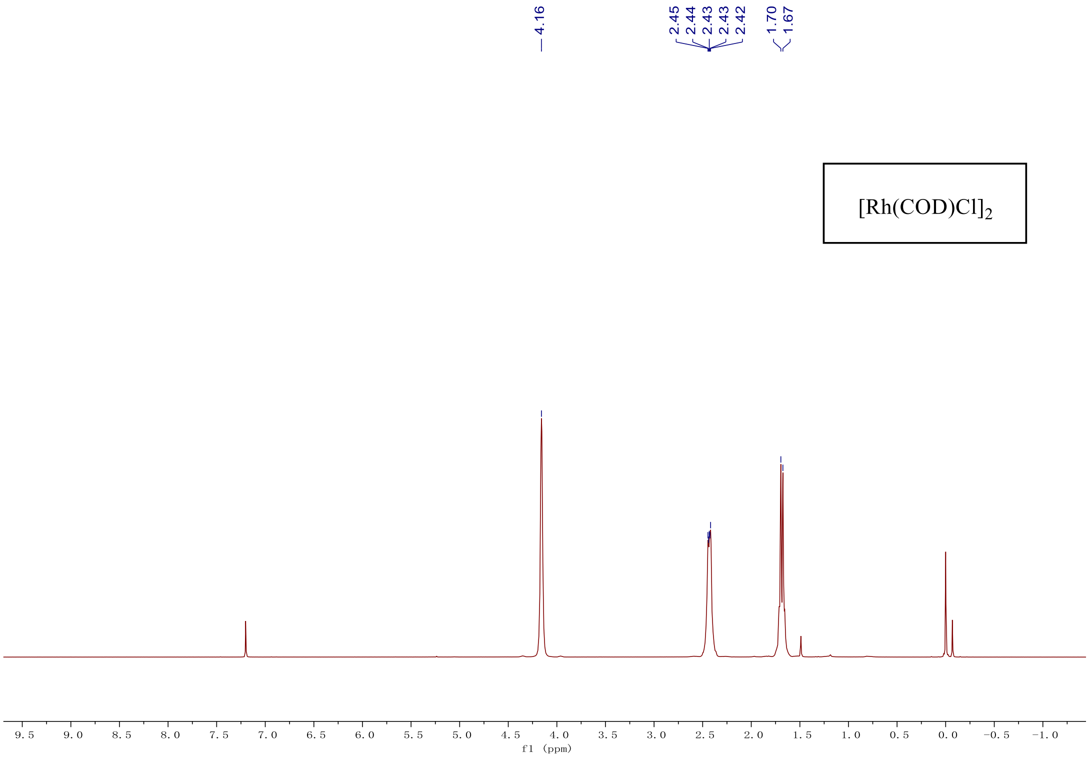


Figure S5-3 ^{1}HNMR spectrum of $[Rh(COD)Cl]_2$

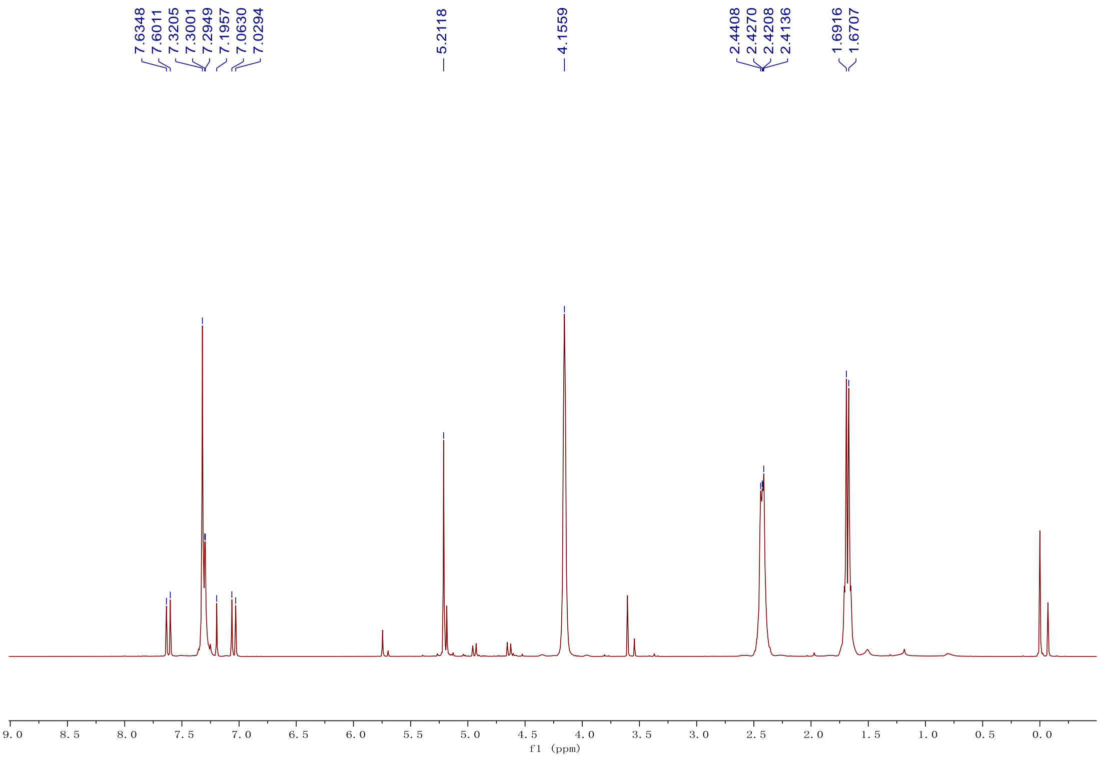


Figure S5-4 ^{1}HNMR spectrum of $[Rh(COD)Cl]_2$ and **4d**

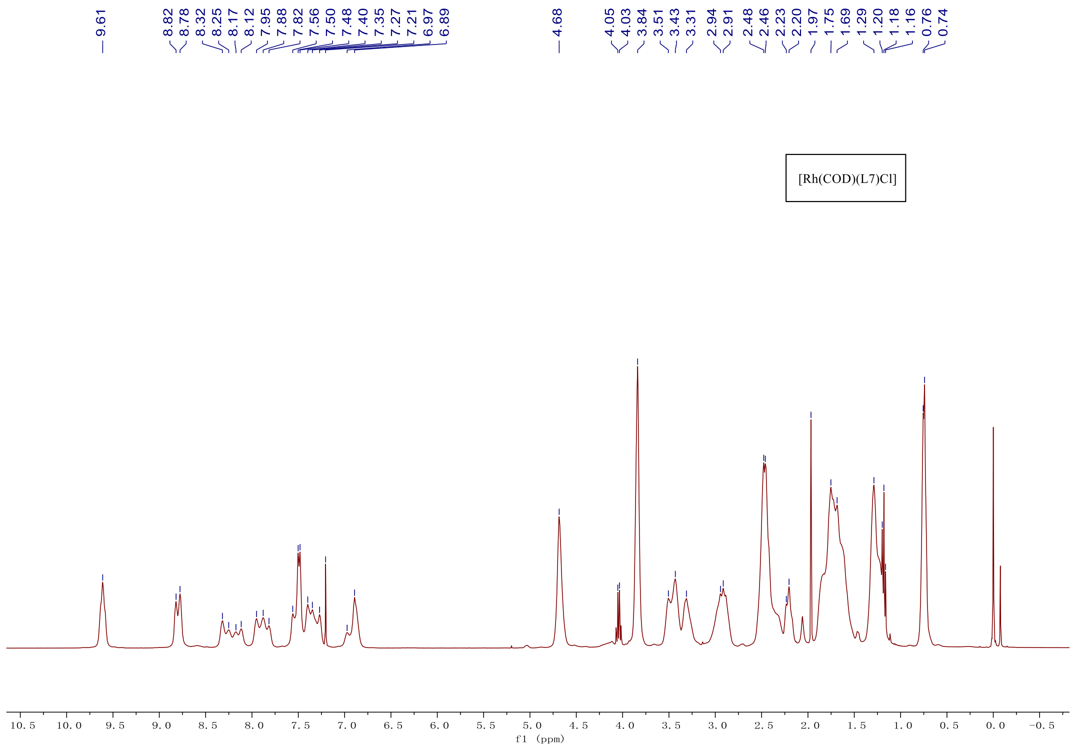


Figure S5-5 ^{1}HNMR spectrum of [Rh(COD)(L7)Cl]

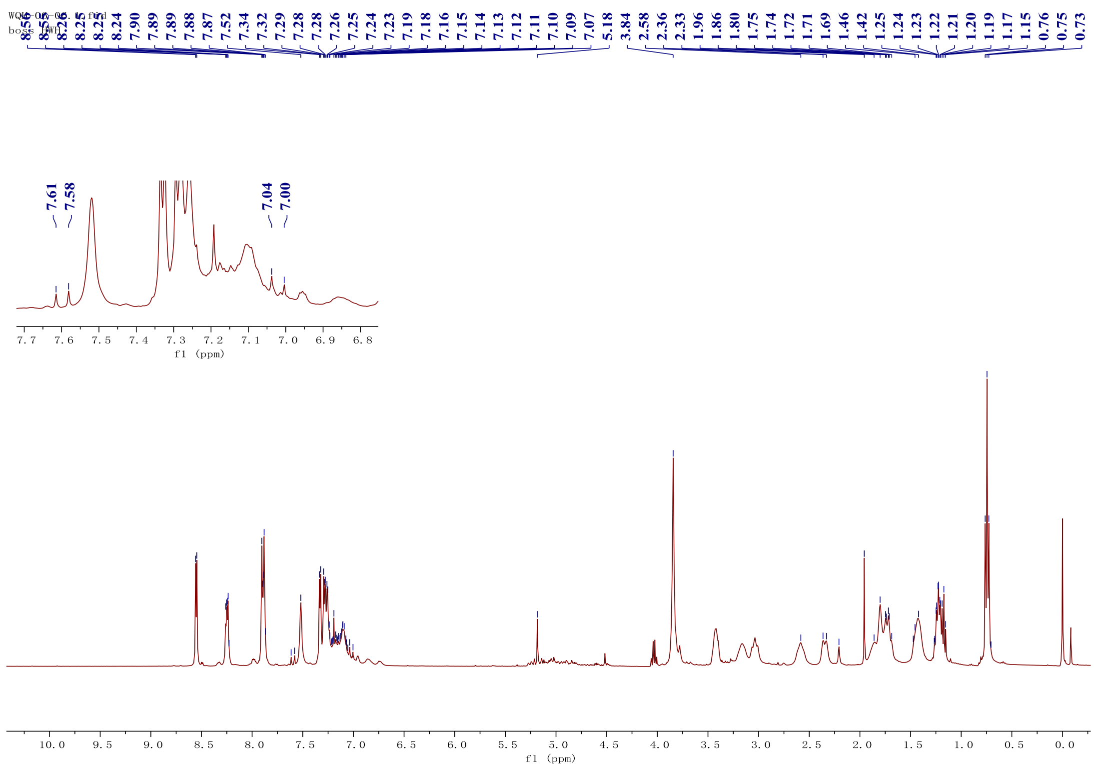


Figure S5-6 ^{1}HNMR spectrum of the mixture **L7** and **4d**

The ^{1}H NMR Spectroscopy of **4d** in the mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 13.5 Hz, 1H), 7.29 (s, 5H), 7.02 (d, *J* = 13.4 Hz, 2H), 5.18 (s, 2H).

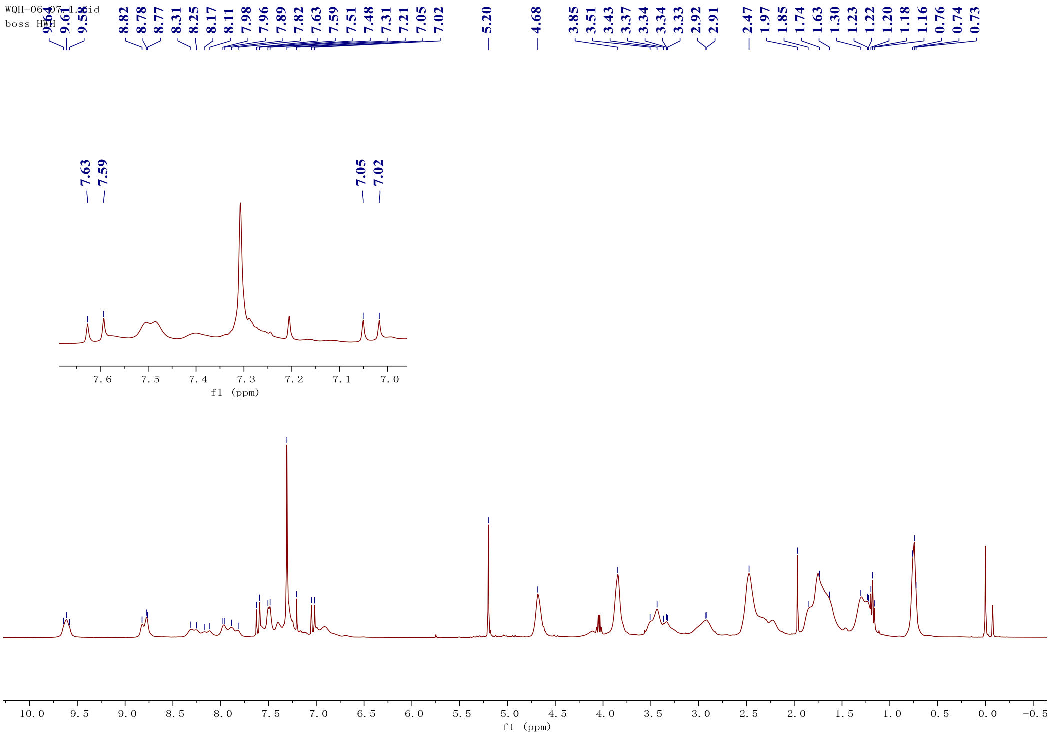


Figure S5-7 ^{1}HNMR spectrum of the mixture [Rh(L_7)COD]Cl and **4d**

The ^{1}H NMR Spectroscopy of **4d** in the mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 13.5 Hz, 1H), 7.29 (s, 5H), 7.02 (d, *J* = 13.4 Hz, 2H), 5.18 (s, 2H).

9.

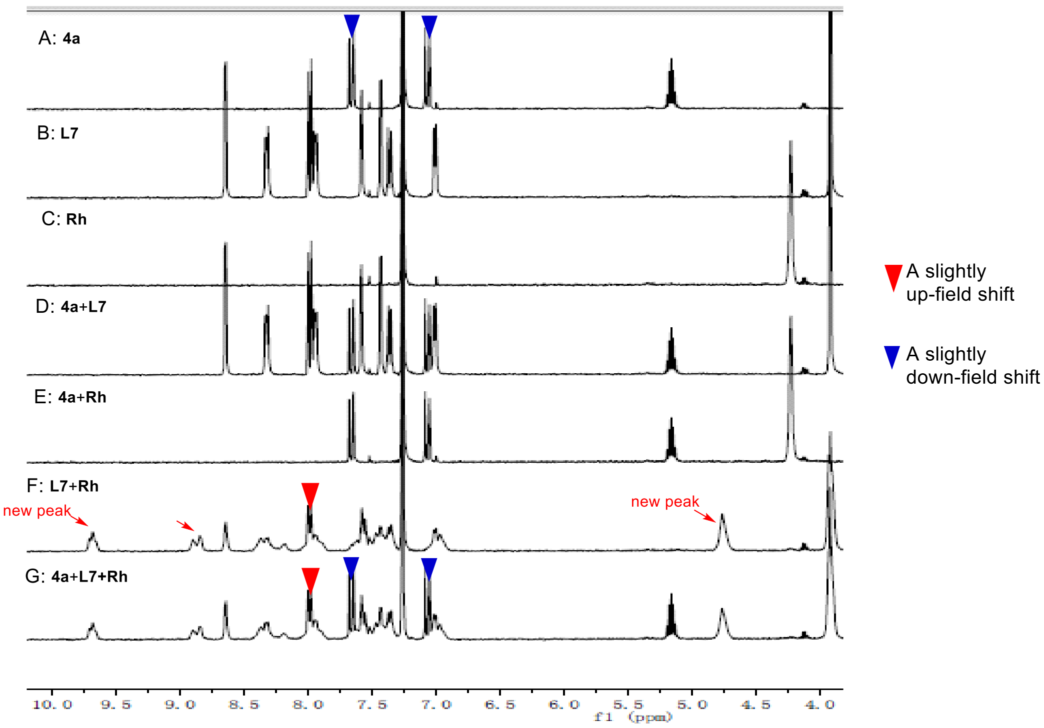


Figure S6 The ^{1}H NMR spectra of the mixture solution of **L7**, **4a** and $[Rh(COD)Cl]_2$ in $CDCl_3$.

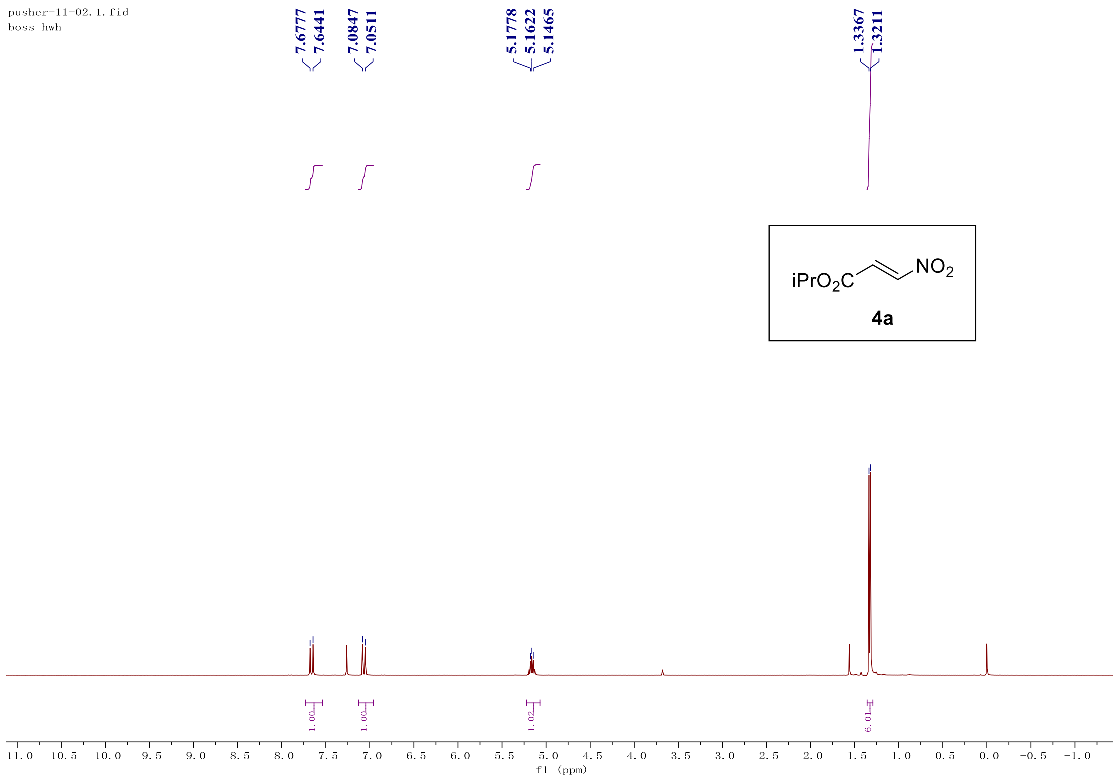


Figure S6-1 ^{1}HNMR spectrum of **4a**

The ^{1}H NMR Spectroscopy of **4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 13.4 Hz, 1H), 7.07 (d, J = 13.4 Hz, 1H), 5.22 – 5.07 (m, 1H), 1.33 (d, J = 6.3 Hz, 6H).

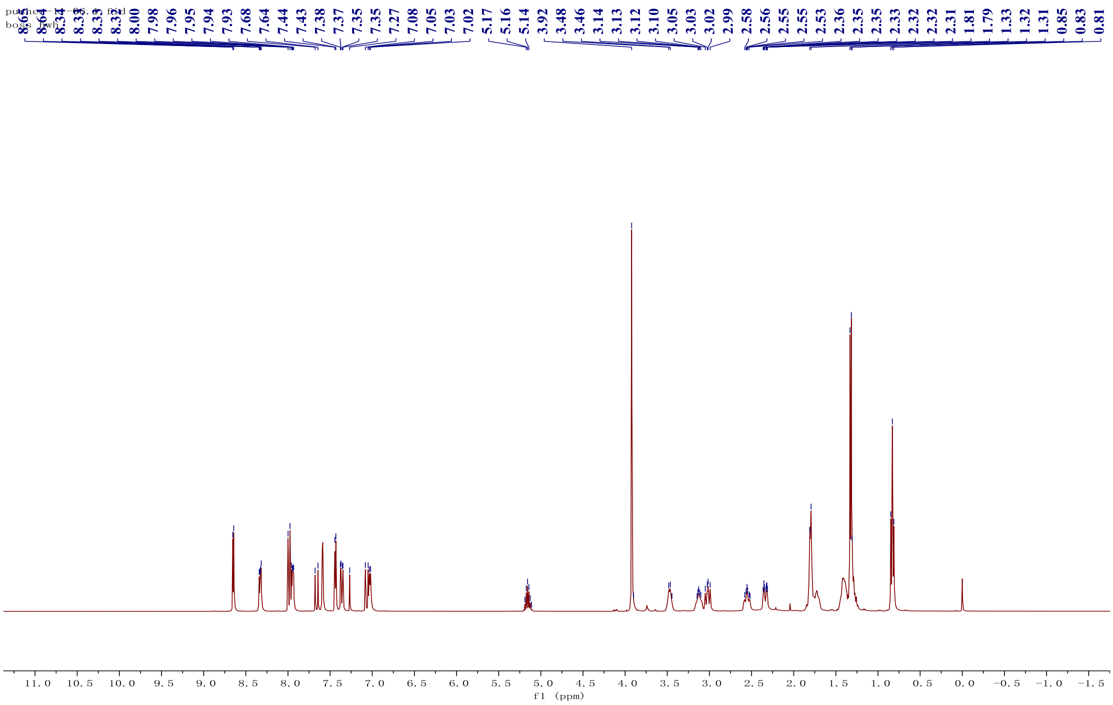


Figure S6-2 [1]HNMR spectrum of the mixture of **L7** and **4a**

The [1]H NMR Spectroscopy of 4a in the mixture:[1]H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 13.4 Hz, 1H), 7.07 (d, *J* = 13.5 Hz, 1H), 5.15 (m, *J* = 6.3 Hz, 1H), 1.32 (d, *J* = 6.2 Hz, 6H).

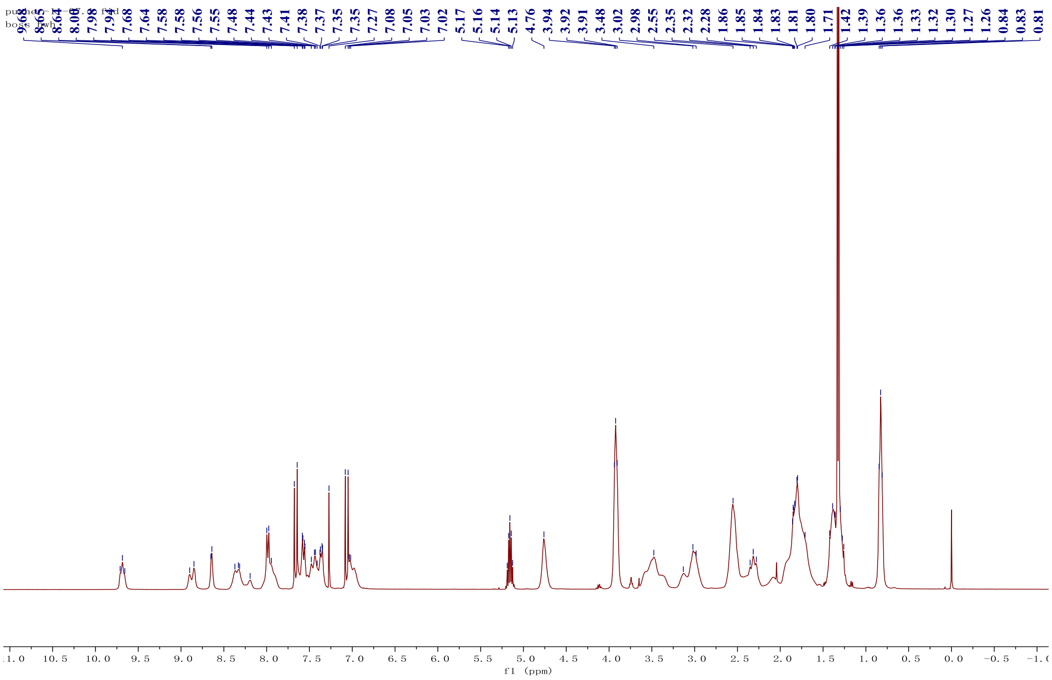


Figure S6-3 [1]HNMR spectrum of the mixture of [Rh(**L7**)COD]Cl and **4a**

10.

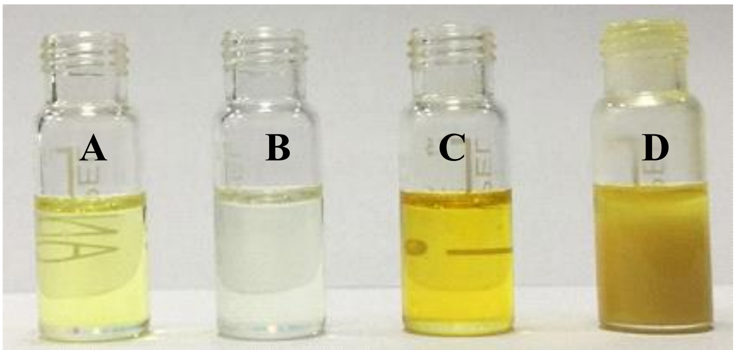


Figure S7 The photo of the precipitation from the mixture solution of Rh(COD)(**L7**)Cl and **4d.**
A: **4d**; B: **L7**; C: $[Rh(COD)Cl]_2$; D: Rh+**L7**+**4d**.

11.

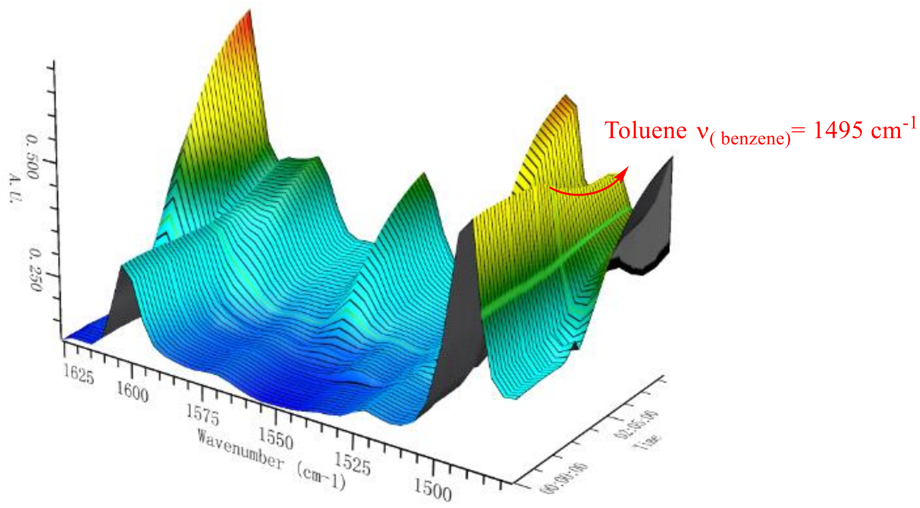


Figure S8 The operando IR spectra of solvent toluene in the reaction.

12.

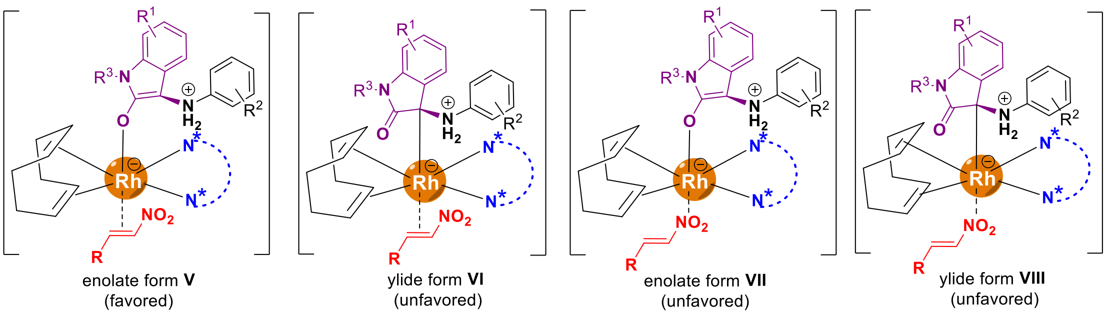
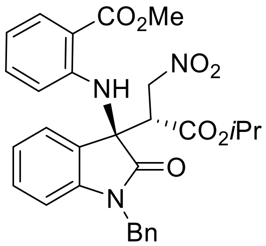


Figure S9 The proposed activation models by the multiple Rh^I center.

13. ^{1}H NMR, ^{13}C NMR data and HPLC data of compounds

Synthesis of methyl-2-(((*R*)-1-benzyl-3-((*S*)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate(6a).



(2*R*, 3*S*)-**6a**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 57% yield (60mg) as a white solid.

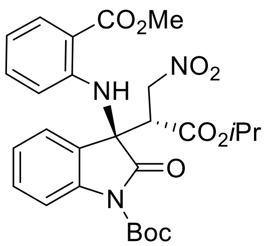
NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 7.90 (d, *J* = 9.8 Hz, 1H), 7.41 (d, *J* = 6.5 Hz, 2H), 7.33 (ddd, *J* = 16.5, 10.1, 4.8 Hz, 5H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.02 – 6.94 (m, 2H), 6.78 (d, *J* = 7.0 Hz, 1H), 6.57 (t, *J* = 7.5 Hz, 1H), 5.56 (d, *J* = 8.4 Hz, 1H), 5.35 – 5.16 (m, 4H), 3.92 (s, 3H), 3.55 (dd, *J* = 10.8, 3.2 Hz, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.88, 168.80, 168.37, 147.20, 141.38, 135.24, 134.11, 131.87, 130.22, 128.94, 128.31, 128.20, 126.63, 124.56, 123.30, 117.04, 112.95, 112.71, 110.13, 71.54, 70.47, 63.17, 51.98, 49.82, 44.69, 21.43, 21.41.

HRMS(ESI) Calcd for $C_{29}H_{29}N_3O_7$ $(M+Na)^+$:554.1093; Found: 554.1094.

95:5 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 = 41.59 min (minor), t_2 = 66.05 min (major).

Synthesis of tert-butyl(*R*)-3-((*S*)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-3-((2-(methoxycarbonyl)phenyl)amino)-2-oxoindoline-1-carboxylate (6b)



(2*R*, 3*S*)-**6b**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 45% yield (48mg) as a colorless solid.

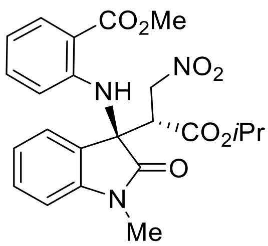
NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.93 – 7.84 (m, 2H), 7.38 – 7.33 (m, 1H), 7.10 – 7.06 (m, 2H), 6.98 (m, *J* = 18.7, 1.7 Hz, 1H), 6.57 (td, *J* = 7.6, 1.1 Hz, 1H), 5.84 – 5.79 (m, 1H), 5.16 – 5.10 (m, 1H), 5.06 – 4.90 (m, 3H), 3.85 (s, 3H), 3.72 (dt, *J* = 10.8, 2.3 Hz, 1H), 1.58 (s, 9H), 1.10 (d, *J* = 6.2 Hz, 3H), 0.98 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.76, 167.88, 166.81, 147.84, 145.83, 137.70, 133.41, 131.00, 129.61, 124.74, 124.03, 123.11, 116.43, 114.87, 112.02, 84.37, 70.32, 69.58, 51.04, 48.55, 27.07, 20.35, 20.17.

HRMS(ESI) Calcd. For $C_{27}H_{31}N_3O_9$ $(M+Na)^+$: 564.1985; Found: 564.1958.

83:17e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 =7.32 min (minor), t_2 = 8.12 min (major).

Synthesis of Methyl2-(((R)-3-((S)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-1-methyl-2-oxoindolin-3-yl)amino)benzoate (6c)



(2*R*,3*S*)-**6c**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 53% yield (48mg) as a white solid.

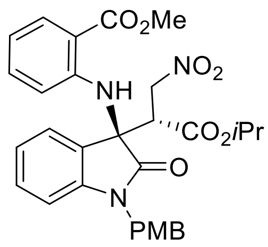
NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.97 – 7.83 (m, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.06 (m, 3H), 6.60 (t, *J* = 7.6 Hz, 1H), 5.69 (dd, *J* = 12.0, 8.4 Hz, 1H), 5.11 – 4.97 (m, 1H), 4.87 (ddd, *J* = 27.3, 13.8, 4.7 Hz, 2H), 3.92 (s, 3H), 3.88 (dd, *J* = 11.3, 3.2 Hz, 1H), 3.30 (s, 3H), 1.18 (d, *J* = 6.2 Hz, 3H), 0.94 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.12, 168.97, 168.46, 147.73, 142.76, 134.37, 131.83, 130.48, 126.26, 124.97, 123.50, 117.23, 112.71, 108.97, 72.28, 70.07, 63.22, 51.92, 51.02, 26.64, 21.34, 20.97.

HRMS(ESI) Calcd. for$C_{23}H_{25}N_3O_7$ $(M+Na)^+$: 478.1590; Found: 478.1609.

78:22 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 = 41.59 min (minor), t_2 = 66.05 min (major).

Synthesis of methyl2-(((*R*)-3-((*S*)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-1-(4-methoxybenzyl)-2-oxoindolin-3-yl)amino)benzoate (6d)



(2*R*, 3*S*)-**6d**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 45% yield (44.8mg) as a white solid.

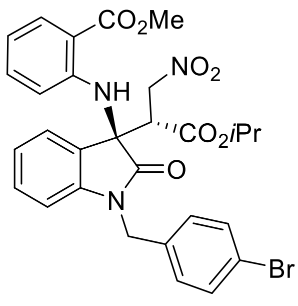
NMR Spectroscopy:^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.91 – 7.87 (m, 1H), 7.34 (dd, *J* = 8.7, 2.7 Hz, 3H), 7.28 (d, *J* = 3.3 Hz, 1H), 7.07 – 6.95 (m, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.88 – 6.83 (m, 2H), 6.79 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 6.58 (t, *J* = 7.5 Hz, 1H), 5.61 (d, *J* = 8.4 Hz, 1H), 5.08 – 4.97 (m, 2H), 4.93 – 4.83 (m, 2H), 4.71 (d, *J* = 15.1 Hz, 1H), 3.92 (s, 3H), 3.86 (dd, *J* = 11.2, 2.9 Hz, 1H), 3.79 (s, 3H), 1.20 (d, *J* = 6.4 Hz, 3H), 0.95 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.22, 168.91, 167.94, 159.45, 147.61, 141.94, 134.18, 131.81, 130.22, 129.69, 127.19, 126.33, 125.09, 123.37, 117.23, 114.22, 113.19, 109.99, 72.23, 70.17, 63.25, 55.31, 51.94, 50.89, 44.14, 21.43, 21.00.

HRMS (ESI) Calcd. For $C_{30}H_{31}N_3O_8(M+Na)^+$: 562.2189; Found: 562.2211.

84:16 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 = 32.00 min (minor), t_2 = 52.29 min (major).

Synthesis of Methyl-2-(((*R*)-1-(4-bromobenzyl)-3-((*S*)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate



(2*R*, 3*S*)-**6e**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 53% yield (64.5mg) as a white solid.

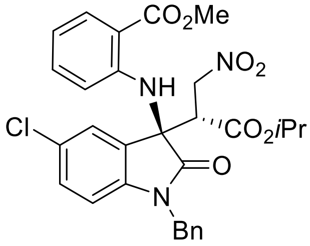
NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.25 (dt, *J* = 14.5, 7.5 Hz, 6H), 7.19 (s, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.81 – 6.70 (m, 2H), 6.55 (t, *J* = 7.6 Hz, 1H), 5.51 (d, *J* = 8.4 Hz, 1H), 5.03 (dd, *J* = 15.2, 12.2 Hz, 2H), 4.91 – 4.74 (m, 2H), 3.86 (s, 3H), 3.79 (dd, *J* = 11.3, 2.9 Hz, 1H), 1.12 (d, *J* = 6.3 Hz, 3H), 0.83 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.32, 167.93, 166.94, 146.52, 140.57, 133.13, 133.02, 132.63, 130.88, 129.30, 128.63, 125.35, 124.16, 122.61, 116.41, 111.99, 111.82, 108.80, 71.20, 69.16, 62.21, 59.38, 51.02, 49.89, 43.02, 28.68, 20.36, 20.05, 19.94, 13.18.

HRMS(ESI) Calcd. For $C_{29}H_{28}BrN_3O_7$ $(M+Na)^+$: 632.1024; Found: 632.1008.

70:30 e.r. HPLC (Chiral AD-H, λ=254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 =7.26 min (minor), t_2 = 11.33 min (major).

Synthesis of Methyl-2-(((*R*)-1-benzyl-5-chloro-3-((*S*)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate



(2*R*, 3*S*)-**6g**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 45% yield (59.8mg) as a white solid.

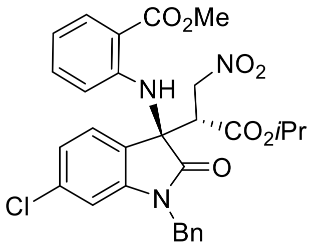
NMR Spectroscopy:^1H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.35 (m, 6H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.09 (d, *J* = 2.1 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.89 – 6.75 (m, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.43 (d, *J* = 8.4 Hz, 2H), 5.30 – 5.20 (m, 2H), 4.77 (d, *J* = 15.7 Hz, 1H), 3.96 (s, 3H), 3.91 – 3.85 (m, 1H), 1.19 (d, *J* = 6.3 Hz, 3H), 0.93 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.58, 168.81, 168.68, 146.78, 139.62, 134.74, 134.17, 132.02, 130.14, 129.07, 128.97, 128.94, 128.44, 128.32, 125.04, 117.28, 112.82, 112.50, 111.13, 71.34, 70.80, 63.04, 52.13, 49.47, 44.87, 29.71, 21.45.

HRMS (ESI) Calcd. For $C_{29}H_{28}ClN_3O_7$ $(M+Na)^+$: 588.1513; Found: 588.1539.

99:1 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 =20.46 min (minor), t_2 = 25.71 min (major).

Synthesis of Methyl-2-(((*R*)-1-benzyl-6-chloro-3-((*S*)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate



(2*R*, 3*S*)-**6h**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 71% yield (80.2mg) as a white solid.

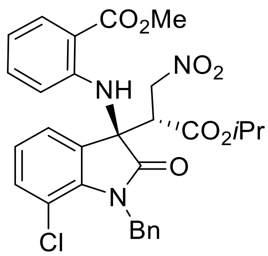
NMR Spectroscopy: ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.96 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.27 (m, 4H), 7.22 – 7.17 (m, 3H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.73 (t, *J* = 7.8 Hz, 1H), 6.52 (t, *J* = 7.5 Hz, 1H), 5.55 (d, *J* = 8.4 Hz, 1H), 5.10 – 4.93 (m, 2H), 4.86 – 4.79 (m, 2H), 3.85 (s, 3H), 3.82 – 3.76 (m, 1H), 1.13 (d, *J* = 6.3 Hz, 3H), 0.87 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.28, 167.91, 166.94, 146.55, 140.85, 134.12, 133.20, 130.81, 129.25, 127.85, 127.29, 127.12, 125.28, 124.06, 122.44, 116.26, 112.13, 111.73, 108.98, 71.20, 69.17, 62.23, 50.97, 49.85, 43.72, 20.38, 19.97.

HRMS(ESI) Calcd. For $C_{29}H_{28}ClN_3O_7$ $(M+Na)^+$: 588.1513; Found: 588.1539.

80:20 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min),t_1 = 17.26 min (minor), t_2 = 22.54 min (major).

Synthesis of Methyl-2-(((*R*)-1-benzyl-7-chloro-3-((*S*)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate



(2*R*, 3*S*)-**6i**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 56% yield (63.2mg) as an white solid.

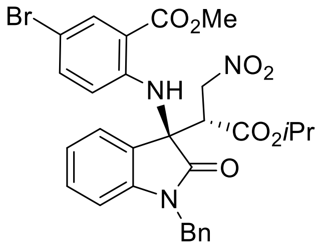
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.83 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.34 – 7.27 (m, 6H), 7.15 – 7.02 (m, 3H), 6.97 (d, *J* = 1.6 Hz, 1H), 6.81 – 6.73 (m, 1H), 6.56 (t, *J* = 7.5 Hz, 1H), 5.54 (d, *J* = 8.4 Hz, 1H), 5.06 – 4.99 (m, 1H), 4.86 – 4.79 (m, 2H), 4.65 (d, *J* = 15.3 Hz, 1H), 3.85 (s, 3H), 3.78 (dd, *J* = 11.3, 2.9 Hz, 1H), 1.13 (d, *J* = 6.3 Hz, 3H), 0.88 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.58, 167.77, 167.24, 145.70, 136.44, 135.60, 133.11, 131.89, 130.92, 128.85, 127.70, 126.83, 126.80, 123.05, 122.07, 116.26, 115.41, 111.83, 111.79, 70.33, 69.66, 61.73, 51.04, 48.82, 44.60, 28.68, 20.43.

HRMS(ESI) Calcd. For $C_{29}H_{28}ClN_3O_7$ $(M+Na)^+$: 588.1513; Found: 588.1539.

97:3 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1= 36.35 min (minor), t_2 = 49.04 min (major).

Synthesis of Methyl-2-(((*R*)-1-benzyl-7-chloro-3-((*S*)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)-5-bromobenzoate



(2*R*, 3*S*)-**6j**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 64% yield (77.9mg) as a white solid.

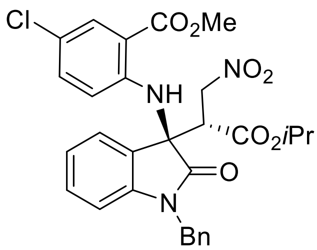
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.25 (dt, *J* = 12.1, 7.6 Hz, 6H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.75 (dd, *J* = 19.0, 7.9 Hz, 2H), 6.55 (t, *J* = 7.5 Hz, 1H), 5.51 (d, *J* = 8.4 Hz, 1H), 5.01 (d, *J* = 14.9 Hz, 2H), 4.87 (dd, *J* = 15.1, 2.5 Hz, 1H), 4.68 (d, *J* = 15.3 Hz, 1H), 4.05 (d, *J* = 7.2 Hz, 1H), 3.86 (s, 3H), 3.79 (dd, *J* = 11.2, 2.5 Hz, 1H), 1.12 (d, *J* = 6.2 Hz, 3H), 0.83 (d, *J* = 6.2 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.33, 167.95, 166.96, 146.53, 140.58, 133.14, 133.03, 132.64, 130.89, 129.32, 128.65, 128.02, 125.36, 124.17, 122.62, 116.42, 112.00, 111.83, 108.81, 71.21, 69.16, 62.22, 51.02, 49.90, 43.03, 20.36, 19.94.

HRMS(ESI) $C_{29}H_{28}BrN_3O_7$ Calcd. For $(M+Na)^+$: 632.1024; Found: 632.1008.

87:13 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 = 29.45 min (minor), t_2 = 35.24 min (major).

Synthesis of methyl2-(((*R*)-1-benzyl-7-chloro-3-((*S*)-1-isopropoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)-5-chlorobenzoate



(2*R*, 3*S*)-**6k**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 63% yield (71.2mg) as a white solid.

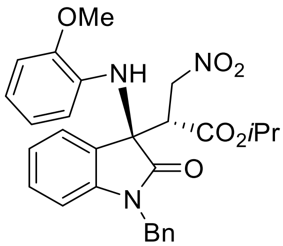
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.25 (dt, *J* = 12.1, 7.6 Hz, 6H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.75 (dd, *J* = 19.0, 7.9 Hz, 2H), 6.55 (t, *J* = 7.5 Hz, 1H), 5.51 (d, *J* = 8.4 Hz, 1H), 5.01 (d, *J* = 14.9 Hz, 2H), 4.87 (dd, *J* = 15.1, 2.5 Hz, 1H), 4.68 (d, *J* = 15.3 Hz, 1H), 4.05 (d, *J* = 7.2 Hz, 1H), 3.86 (s, 3H), 3.79 (dd, *J* = 11.2, 2.5 Hz, 1H), 1.12 (d, *J* = 6.2 Hz, 3H), 0.83 (d, *J* = 6.2 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.33, 167.95, 166.96, 146.53, 140.58, 133.14, 133.03, 132.64, 130.89, 129.32, 128.65, 128.02, 125.36, 124.17, 122.62, 116.42, 112.00, 111.83, 108.81, 71.21, 69.16, 62.22, 51.02, 49.90, 43.03, 20.36, 19.94.

HRMS(ESI) $C_{29}H_{27}Cl_2N_3O_7$ Calcd. For $(M^+Na)^+$, 588.1513; Found: 588.1539.

95:5 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 = 30.19 min (minor), t_2 = 36.63 min (major).

Synthesis of isopropyl (*S*)-2-((*R*)-1-benzyl-3-((2-methoxyphenyl)amino)-2-oxoindolin-3-yl)-3-nitropropanoate



(2*R*,3*S*)-**6l**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 61% yield (61.3mg) as a yellow soild.

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.24 – 7.17 (m, 6H), 7.12 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.91 (m, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.67 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.59 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.27 (td, *J* = 7.7, 1.4 Hz, 1H), 5.89 (s, 1H), 5.63 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.10 – 4.84 (m, 4H), 4.66 (d, *J* = 15.3 Hz, 1H), 3.82 (s, 3H), 3.70 (dd, *J* = 10.5, 3.6 Hz, 1H), 1.17 (s, 4H), 1.10 (d, *J* = 6.3 Hz, 3H).

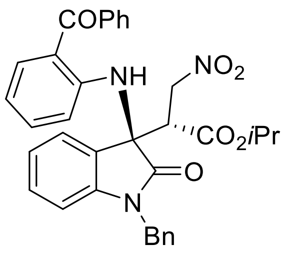
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.97, 167.27, 147.34, 141.19, 134.12, 132.87, 129.22, 127.85, 126.99, 126.95, 125.86, 123.40, 122.33, 119.69, 118.54, 112.53, 109.05, 108.95, 70.59, 69.49, 62.82, 54.70, 48.69, 43.50, 20.48, 20.37.

HRMS(ESI) $C_{28}H_{29}N_3O_6$ Calcd. For $(M+Na)^+$: 526.1954; Found: 526.1930.

86:14 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 = 14.94 min (minor), t_2 = 27.17 min (major).

Synthesis of

isopropyl (*S*)-2-((*R*)-3-((2-benzoylphenyl)amino)-1-benzyl-2-oxoindolin-3-yl)-3-nitropropanoate



(2*R*,3*S*)-**6m**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 54% yield (62.3mg) as a yellow soild.

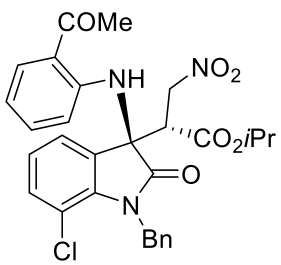
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 16.1, 7.8 Hz, 6H), 7.38 – 7.30 (m, 5H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.84 (t, *J* = 7.8 Hz, 1H), 6.57 (t, *J* = 7.5 Hz, 1H), 5.77 (d, *J* = 8.4 Hz, 1H), 5.20 – 5.06 (m, 2H), 4.89 – 4.71 (m, 2H), 3.91 (dd, *J* = 11.2, 2.9 Hz, 1H), 1.19 (d, *J* = 6.3 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.62, 174.14, 167.91, 147.93, 142.02, 139.67, 135.33, 135.17, 134.36, 131.37, 130.31, 129.50, 129.38, 128.96, 128.89, 128.30, 128.28, 128.14, 128.10, 128.06, 126.25, 125.18, 123.50, 120.38, 116.78, 113.99, 109.98, 72.22, 70.19, 63.36, 51.00, 44.78, 21.38, 20.98.

HRMS(ESI) $C_{28}H_{29}N_3O_6$Calcd. For $(M+Na)^+$: 600.2111; Found: 600.2151.

96:4 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 = 33.70 min (minor), t_2 = 67.23 min (major).

Synthesis of
Isopropyl-(*S*)-2-((*R*)-3-((2-acetylphenyl)amino)-1-benzyl-7-chloro-2-oxoindolin-3-yl)-3-nitropropa noa-te



(2*R*,3*S*)-**6n**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 56% yield (61.5mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.68 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.35 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 4H), 7.19 (d, *J* = 1.6 Hz, 1H), 6.95 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.89 (t, *J* =

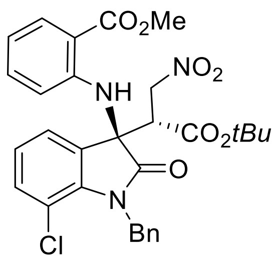
7.7 Hz, 1H), 6.75 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 6.54 (t, *J* = 7.6 Hz, 1H), 5.49 – 5.39 (m, 2H), 5.23 – 5.11 (m, 2H), 5.05 – 4.99 (m, 1H), 3.39 (dd, *J* = 10.5, 3.3 Hz, 1H), 2.56 (d, *J* = 1.6 Hz, 3H), 1.19 – 1.18 (m, 3H), 1.06 (d, *J* = 6.3 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.52, 174.57, 167.09, 145.68, 136.36, 135.57, 133.59, 131.90, 131.86, 128.79, 127.69, 126.83, 123.05, 122.10, 118.86, 115.83, 115.41, 112.19, 70.30, 69.69, 61.64, 48.74, 44.61, 26.99, 20.43, 20.41.

HRMS(ESI) $C_{29}H_{28}ClN_3O_6$ Calcd. For $(M+Na)^+$, 572.1564; Found: 572.1517.

95:5 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1= 19.62 min (minor), t_2 = 22.91 min (major).

Synthesis of Methyl2-(((*R*)-1-benzyl-3-((*S*)-1-(tert-butoxy)-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino) benzoate



(2*R*, 3*S*)-**6p**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 52% yield (56.68mg) as a white solid.

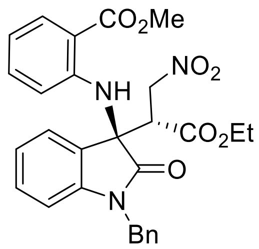
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.90 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.30 (t, *J* = 7.7 Hz, 5H), 7.14 – 7.07 (m, 1H), 7.03 – 6.95 (m, 1H), 6.86 – 6.80 (m, 1H), 6.60 (t, *J* = 7.6 Hz, 1H), 5.63 (d, *J* = 8.4 Hz, 1H), 5.42 (d, *J* = 9.8 Hz, 2H), 5.22 – 5.06 (m, 2H), 3.92 (s, 3H), 3.51 (dd, *J* = 10.7, 3.5 Hz, 1H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.66, 168.78, 167.12, 146.90, 138.30, 137.57, 136.70, 134.14, 132.84, 131.91, 129.98, 128.66, 127.76, 123.89, 123.54, 117.37, 116.32, 113.20, 112.89, 84.17, 71.60, 62.97, 52.01, 50.58, 45.60, 27.70.

HRMS (ESI) $C_{30}H_{30}ClN_3O_7$ Calcd. For $(M+Na)^+$: 602.1670; Found: 602.1680.

95:5 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min),t_1 = 27.64 min (minor), t_2 = 34.72 min (major).

Synthesis of methyl 2-(((*R*)-1-benzyl-3-((*S*)-1-ethoxy-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate



(2*R*, 3*S*)-**6q**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 52% yield (56.68mg) as a white solid.

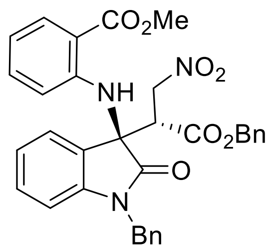
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.31 (d, *J* = 7.3 Hz, 1H), 7.87 – 7.82 (m, 1H), 7.22 (s, 3H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.92 – 6.87 (m, 2H), 6.70 (d, *J* = 7.7 Hz, 3H), 6.58 (t, *J* = 7.6 Hz, 1H), 5.48 (d, *J* = 8.4 Hz, 1H), 5.07 – 4.99 (m, 1H), 4.83 (s, 2H), 4.10 – 3.97 (m, 2H), 3.75 (s, 3H), 3.52 (dd, *J* = 10.6, 3.2 Hz, 1H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.24, 168.99, 168.54, 149.87, 142.83, 135.67, 134.59, 131.65, 129.33, 128.81, 128.31, 127.64, 126.50, 124.47, 123.12, 116.39, 112.76, 109.42, 72.05, 63.35, 62.22, 55.76, 51.62, 44.11, 29.69.

HRMS(ESI) $C_{28}H_{27}N_3O_7$ Calcd. for $(M+Na)^+$, 540.1747; Found: 540.1779.

95:5 e.r. HPLC (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 = 10.23 min (minor), t_2 = 13.02 min (major).

Synthesis ofmethyl-2-(((*R*)-1-benzyl-3-((*S*)-1-(benzyloxy)-3-nitro-1-oxopropan-2-yl)-2-oxoindolin-3-yl)amino)benzoate



(2*R*, 3*S*)-**6r**

Following the general procedure for the preparation of 3,3-disubstituted oxindoles. The title compound was obtained in 70% yield (81mg) as a white solid.

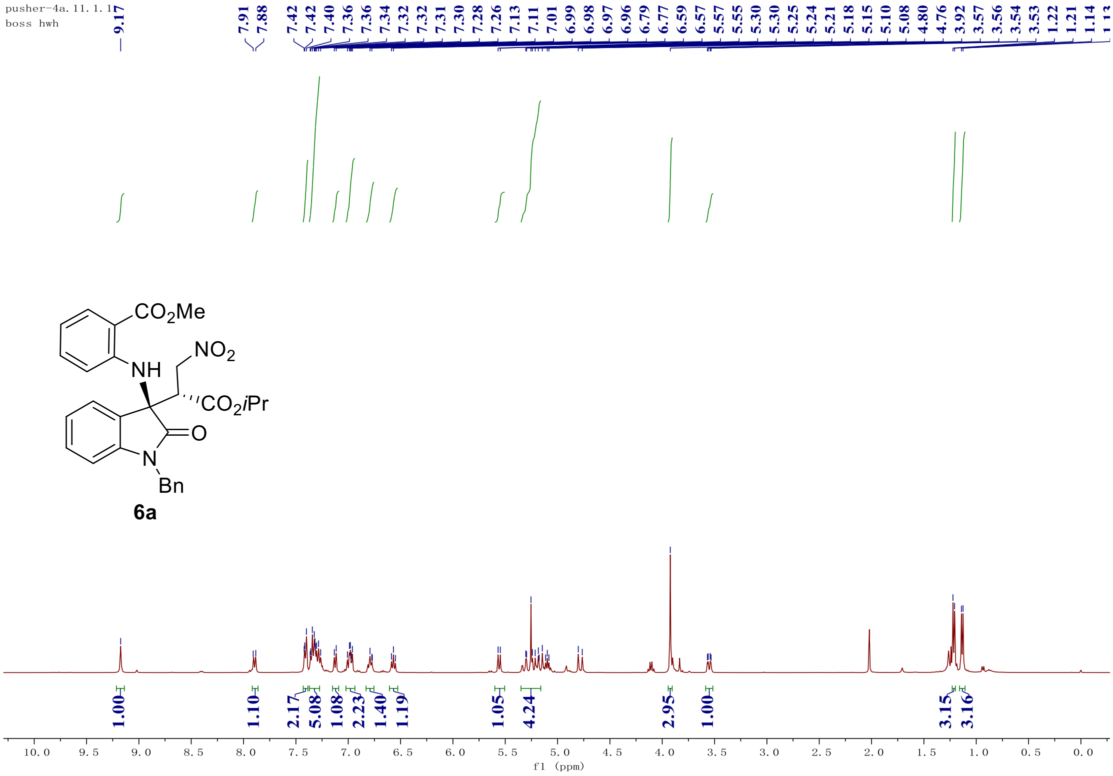
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.90 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.42 – 7.28 (m, 10H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.84 (m, 2H), 6.83 – 6.75 (m, 1H), 6.58 (t, *J* = 7.6 Hz, 1H), 5.54 (d, *J* = 8.4 Hz, 1H), 5.40 – 5.05 (m, 6H), 4.63 (d, *J* = 15.2 Hz, 1H), 3.92 (s, 3H), 3.68 (dd, *J* = 10.7, 3.1 Hz, 1H).

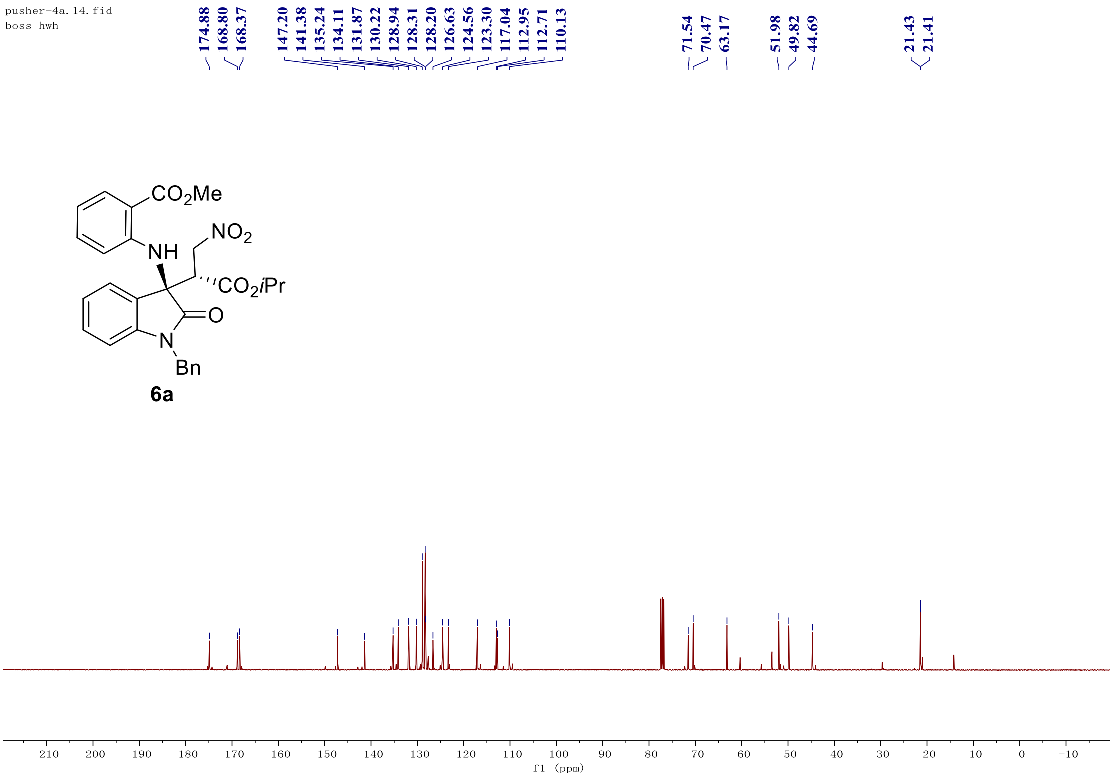
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.80, 169.01, 168.86, 147.12, 141.23, 135.14, 134.52, 134.16, 131.90, 130.20, 128.95, 128.91, 128.88, 128.60, 128.54, 128.33, 128.28, 128.22, 126.46, 124.32, 123.45, 117.13, 112.90, 112.72, 110.21, 71.31, 67.97, 63.12, 52.07, 49.58, 44.59.

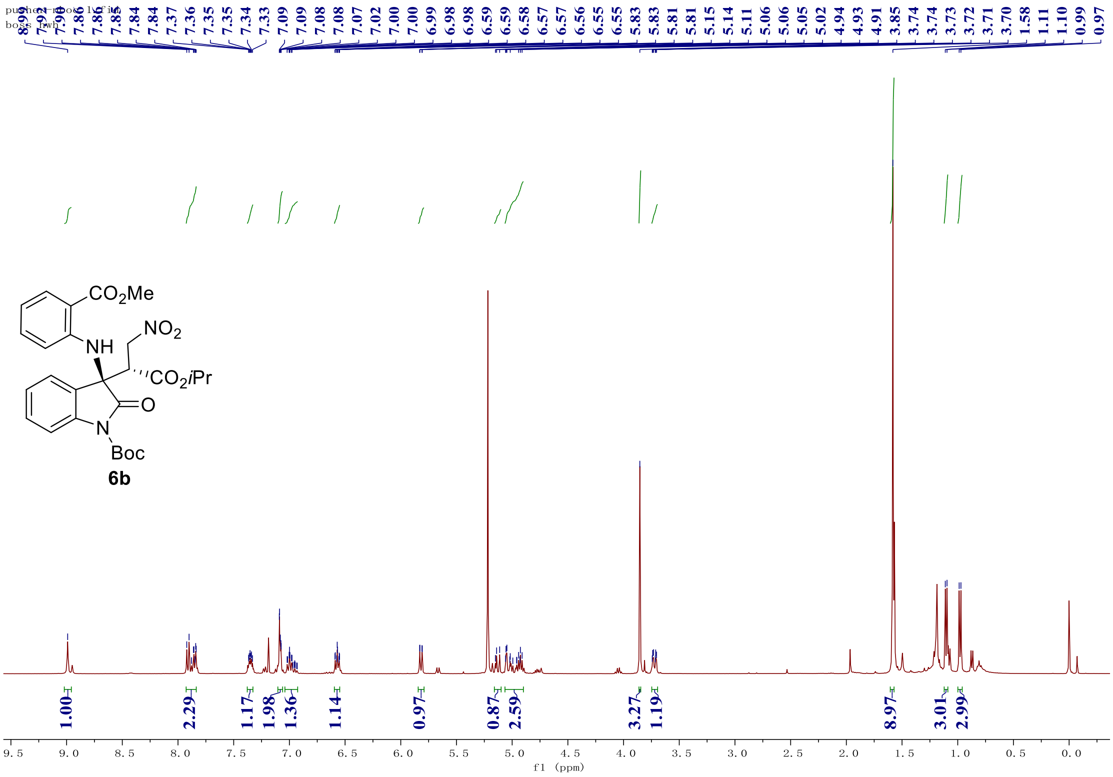
HRMS(ESI) $C_{33}H_{29}N_3O_7$Calcd. For $(M+Na)^+$: 602.1903; Found: 602.1860

86:14 e.r. HPLC (Chiral AD-H,λ = 254 nm, hexane/2-propanol = 20/1, Flow rate = 1.0 mL/min), t_1 = 37.44 min (minor), t_2 =55.37 min (major).

14. ^{1}H and ^{13}C NMR Spectra







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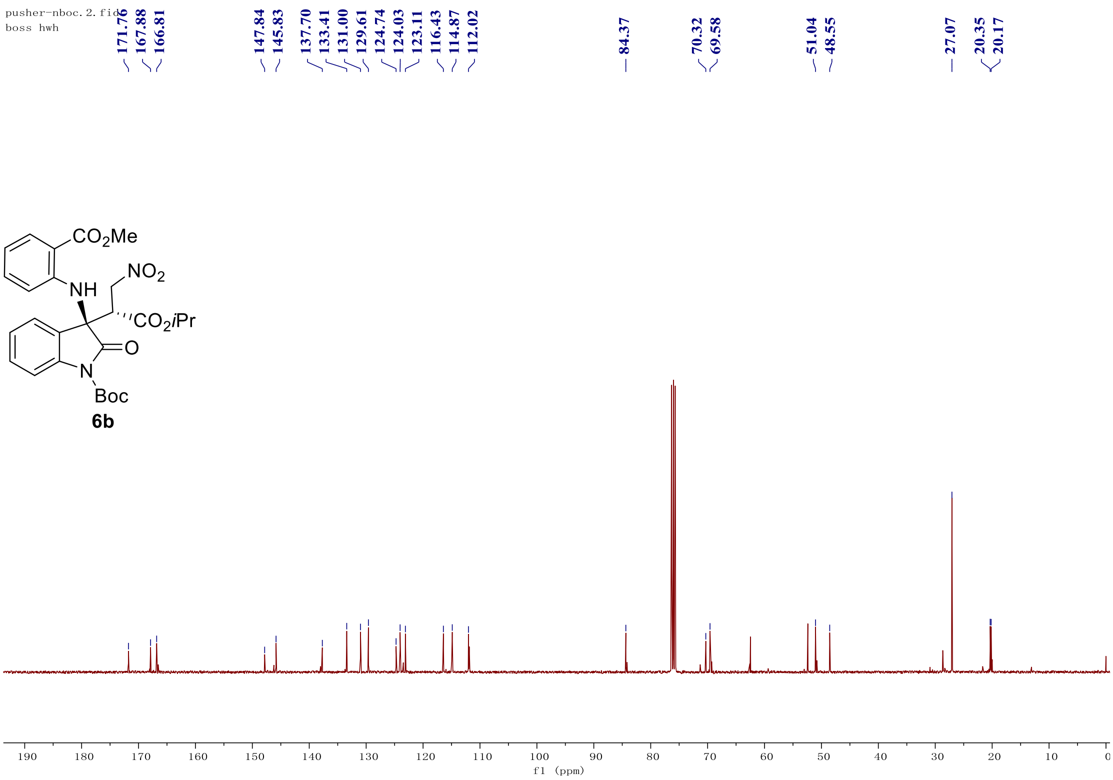
CO2Me
NO2
NH
CO2iPr
O
N
Boc
6b
1.00 2.29 1.17 1.98 1.36 1.14 0.97 0.87 2.59 3.27 1.19 8.97 3.01 2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



pusher-nboc.2.fid
boss hwh
171.76 167.88 166.81 147.84 145.83 137.70 133.41 131.00 129.61 124.74 124.03 123.11 116.43 114.87 112.02 84.37 70.32 69.58 51.04 48.55 27.07 20.35 20.17
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CO2iPr
O
N
Boc
6b
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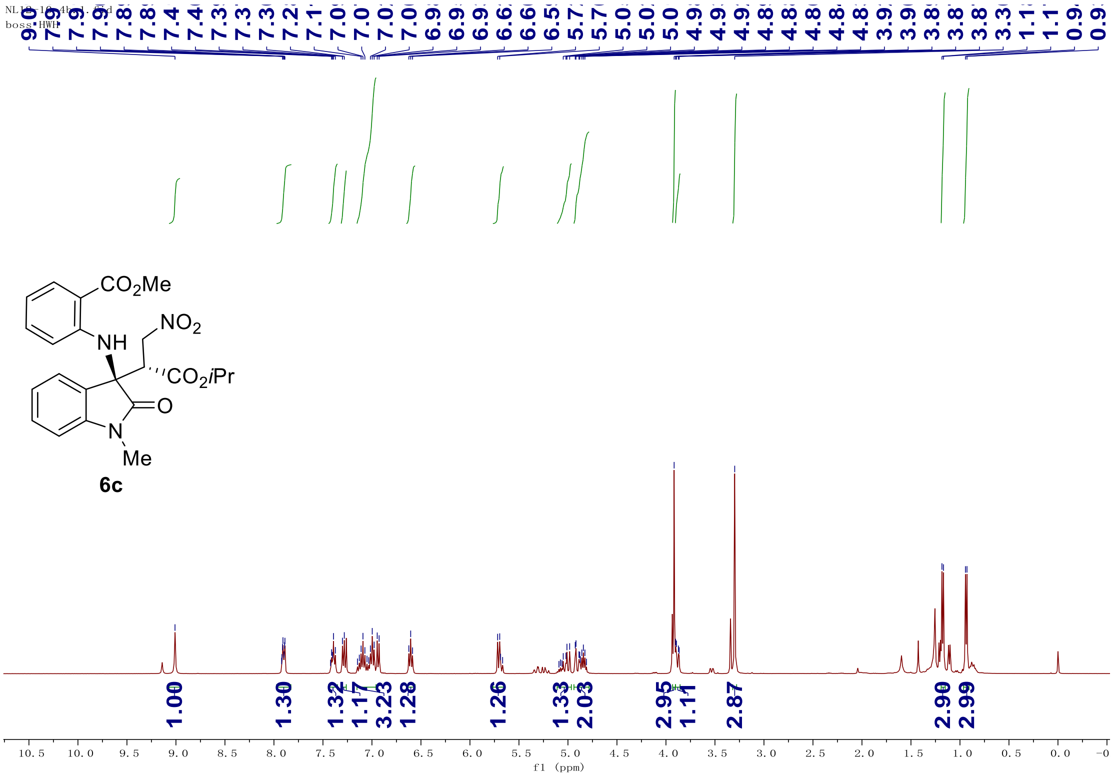
f1 (ppm)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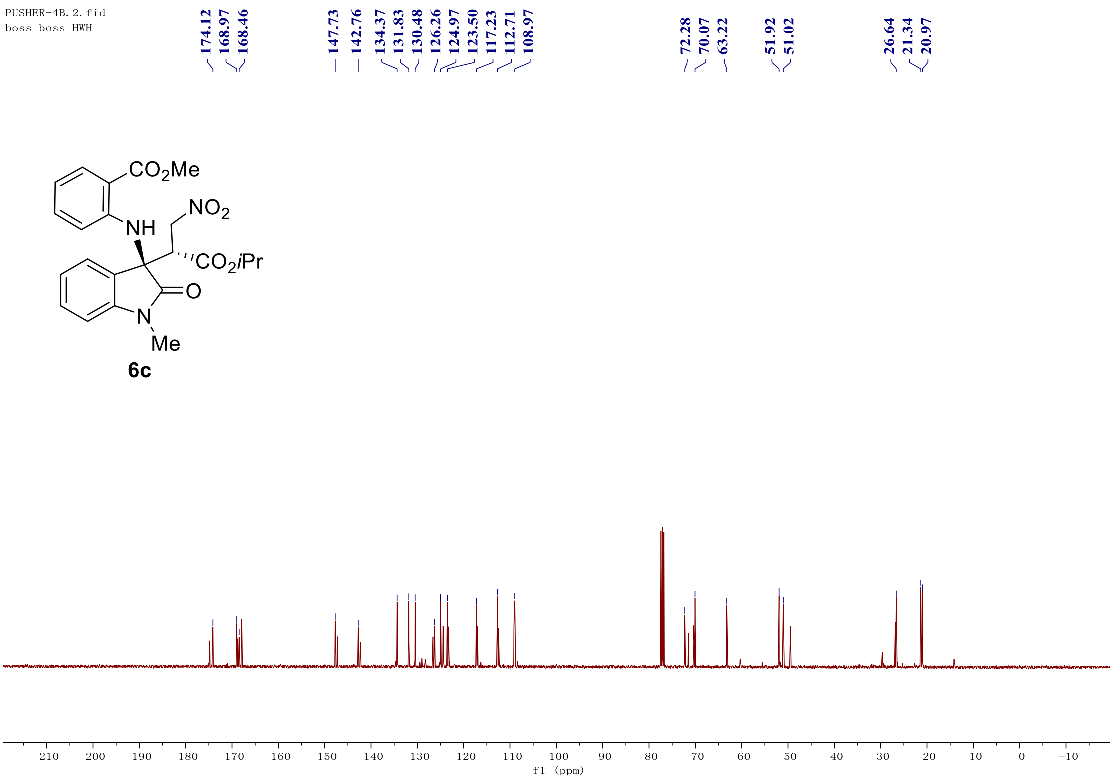
f1 (ppm)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117.23
112.71
108.97
72.28
70.07
63.22
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20.97
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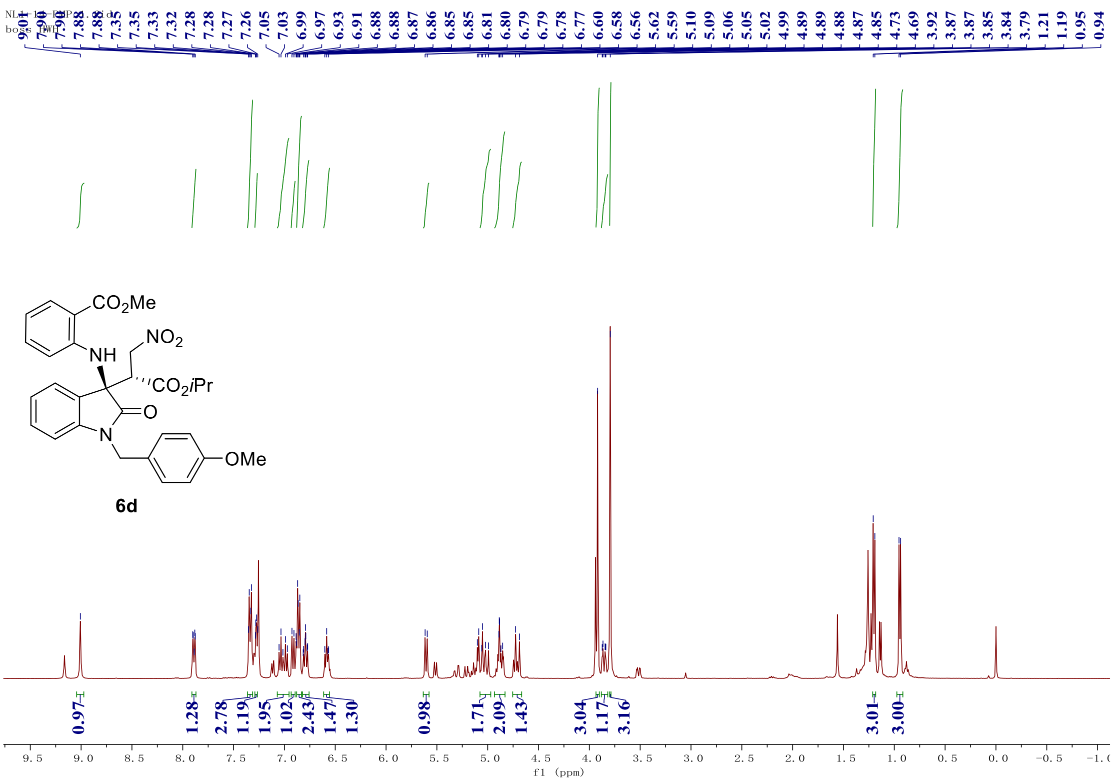
Me
6c
f1 (ppm)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O
N
OMe
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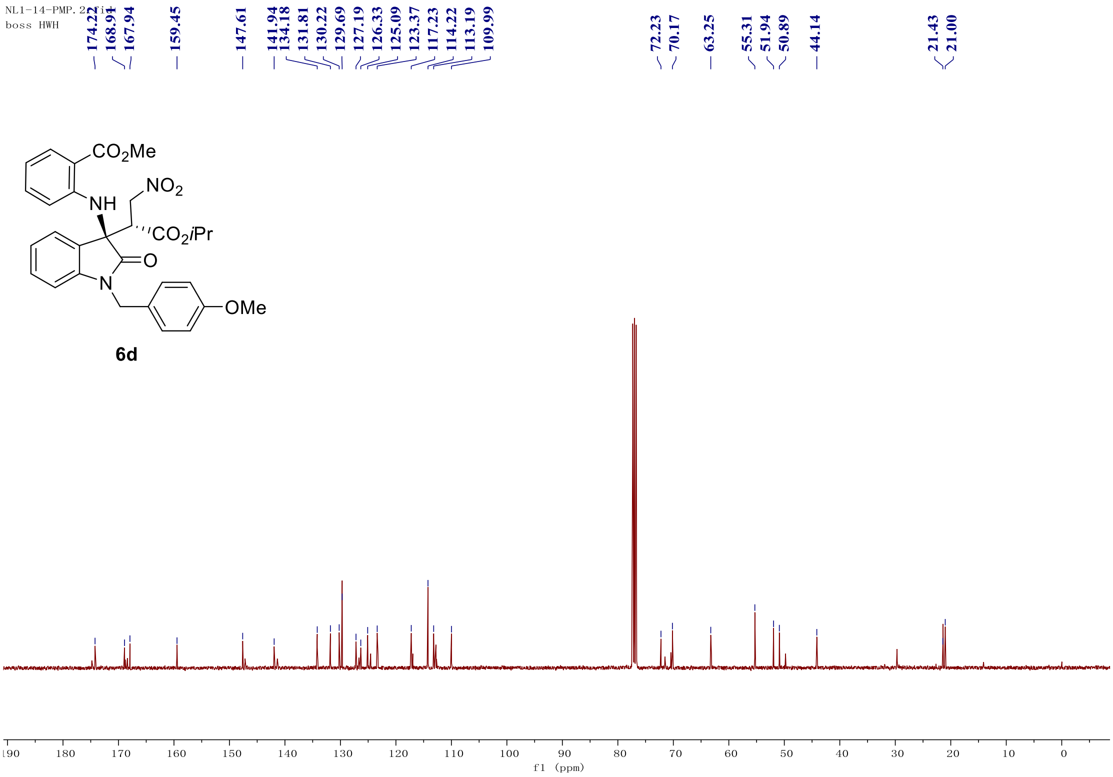
f1 (ppm)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126.33
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123.37
117.23
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113.19
109.99
72.23
70.17
63.25
55.31
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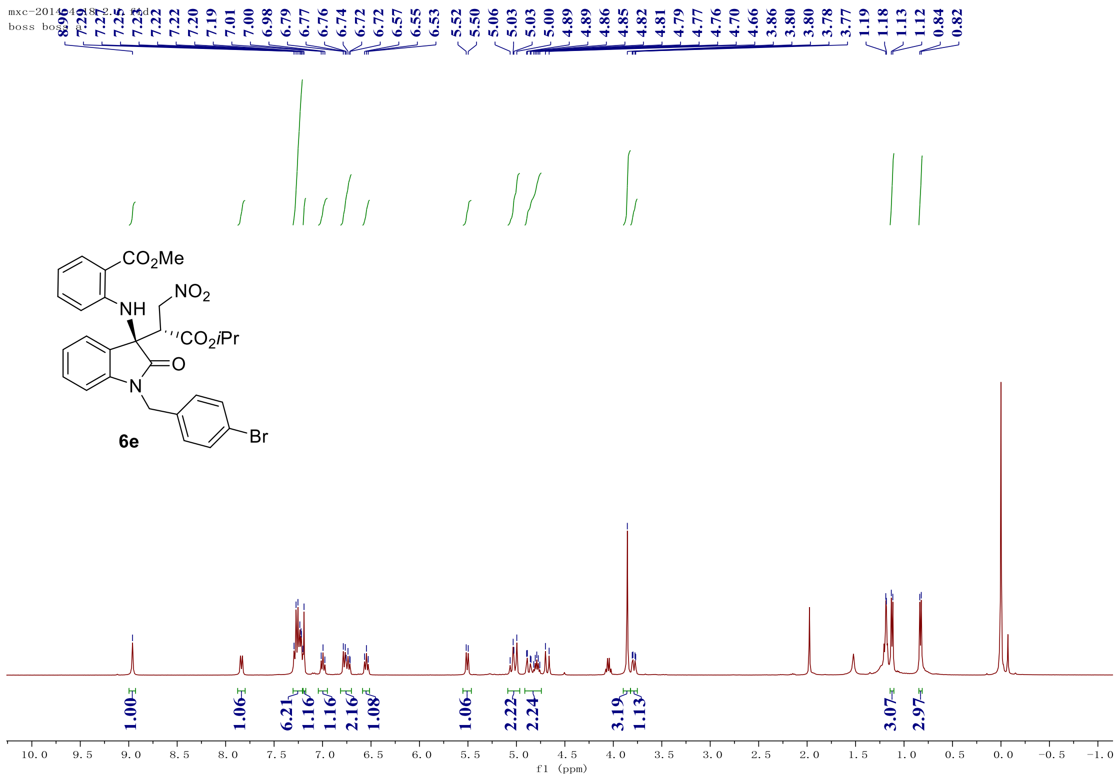
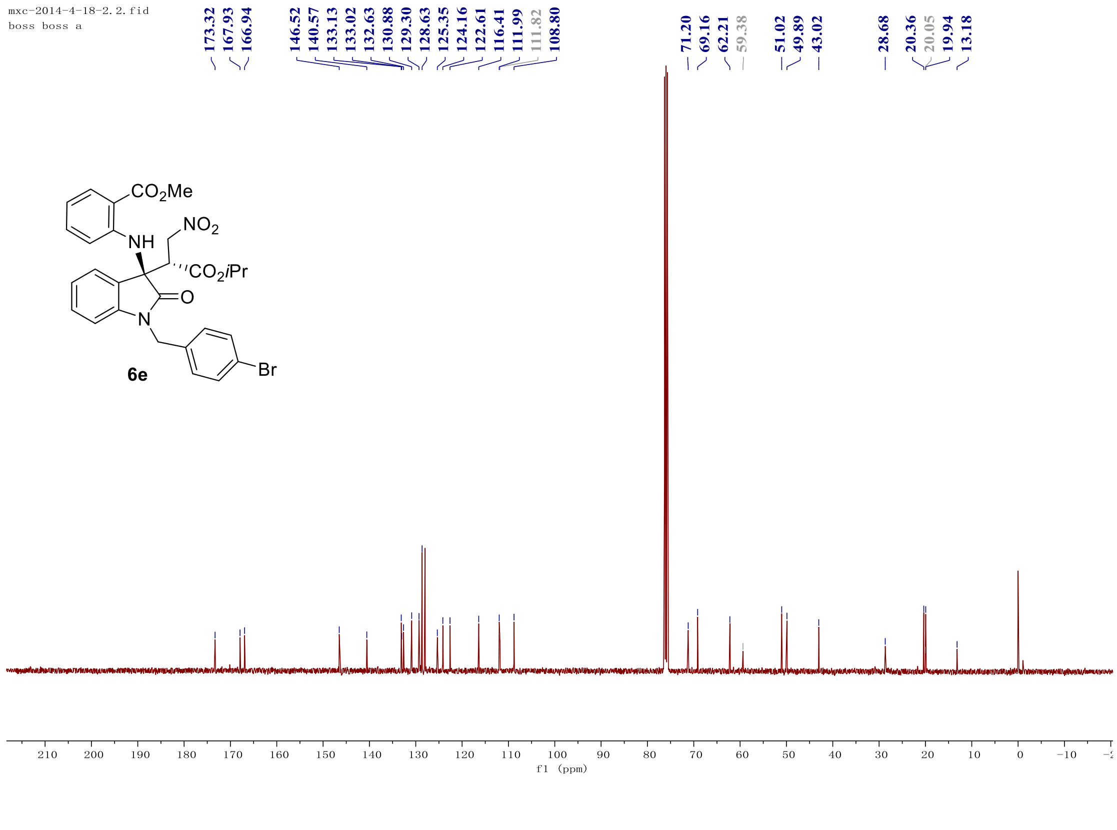
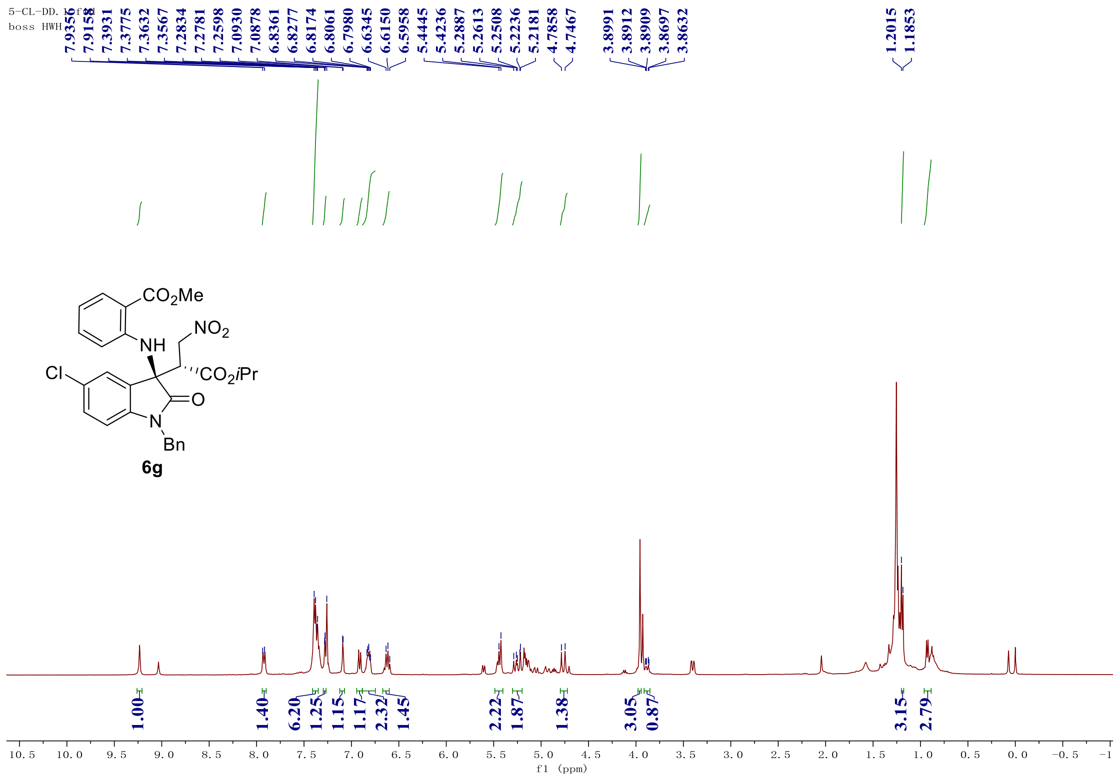
CO2iPr
O
N
OMe
6d
f1 (ppm)



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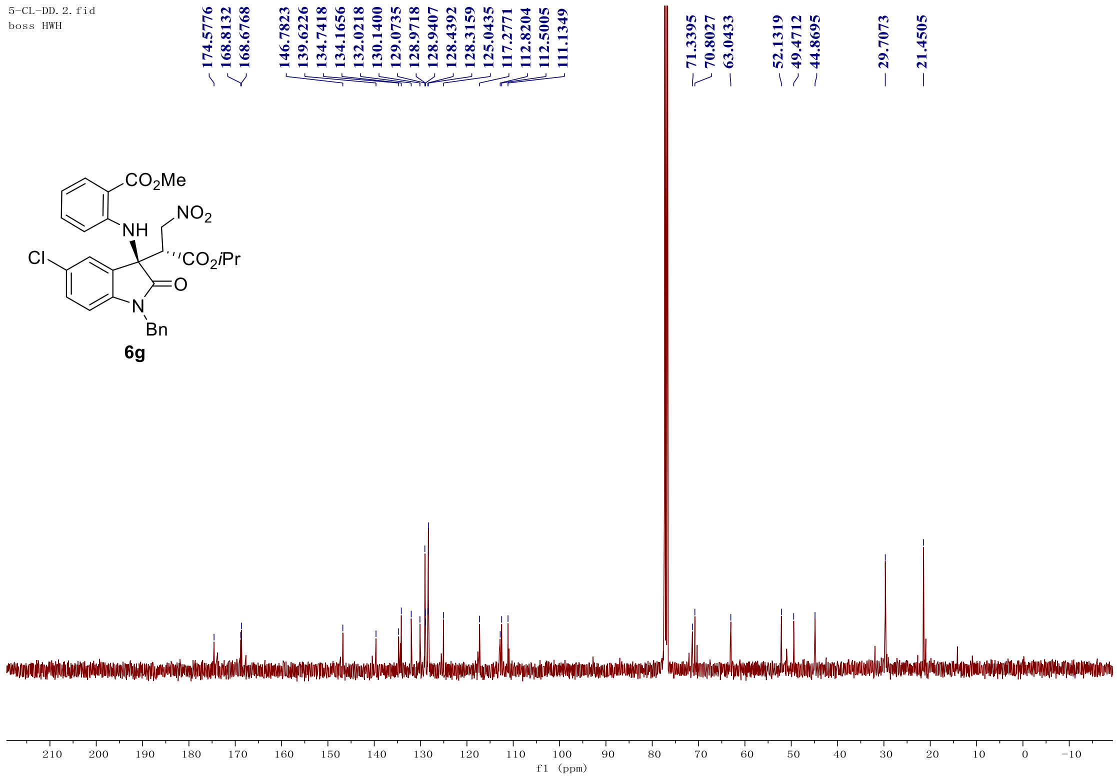
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128.4392
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63.0433
52.1319
49.4712
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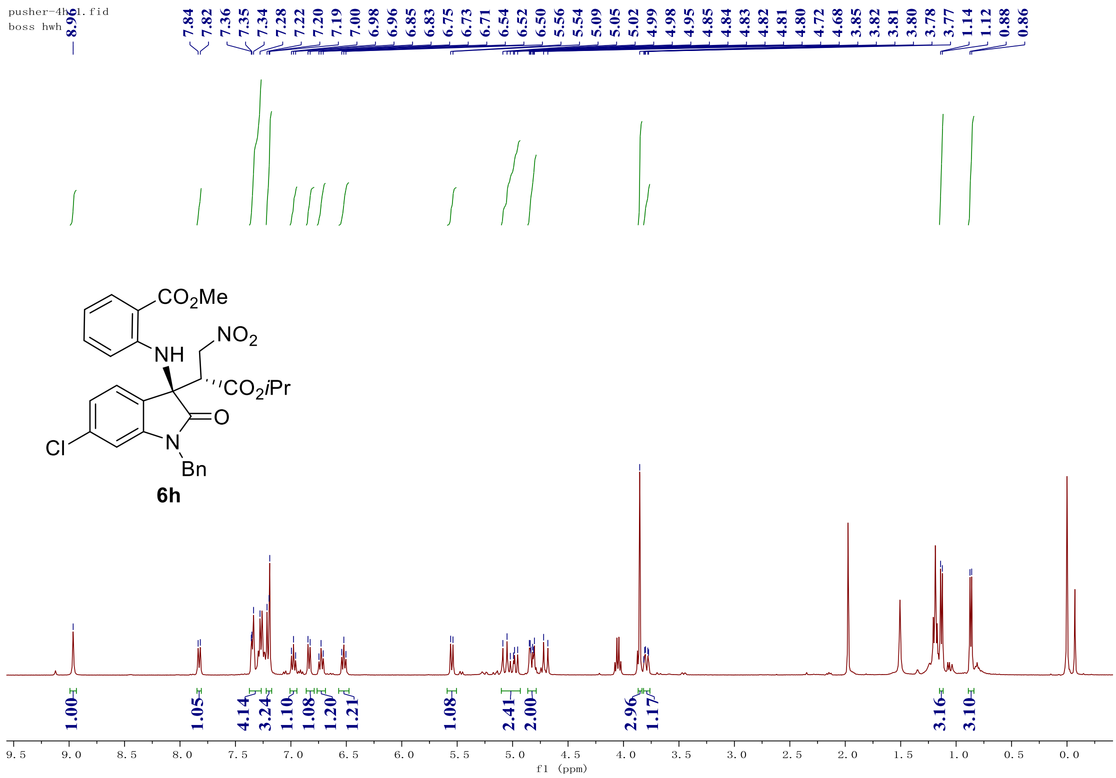
6g
f1 (ppm)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3.80
3.78
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NH
CO_2iPr
O
Cl
N
Bn
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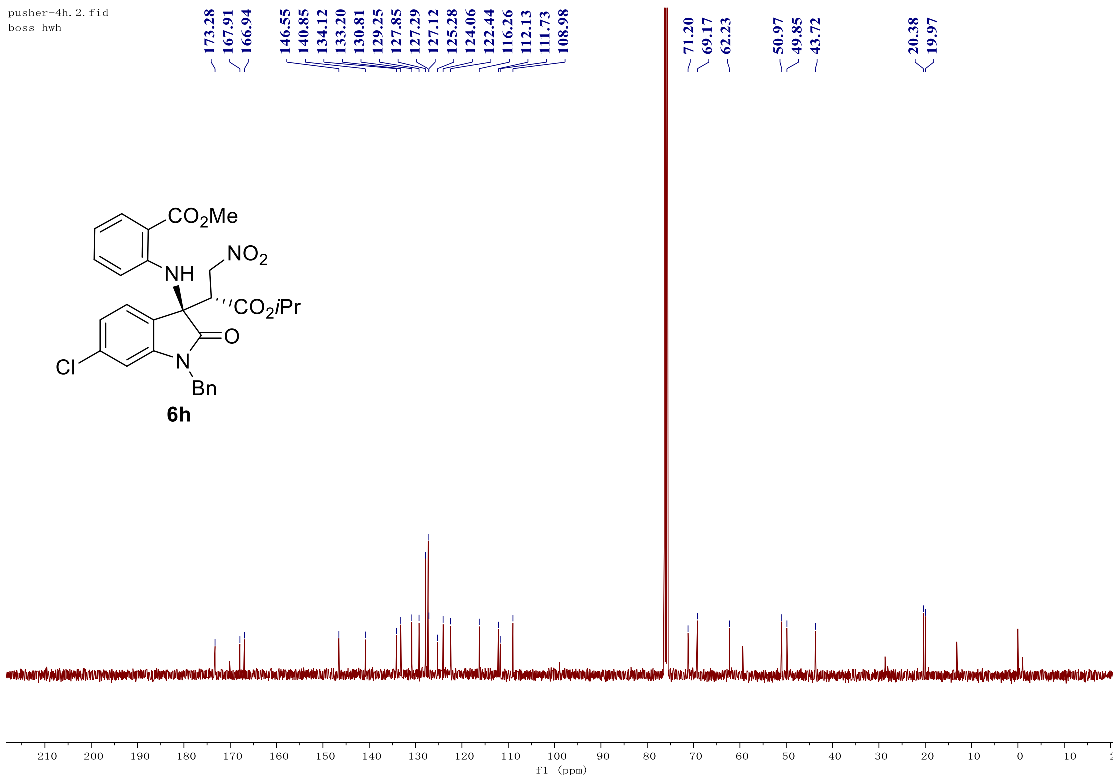
3.10
f1 (ppm)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127.85
127.29
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62.23
50.97
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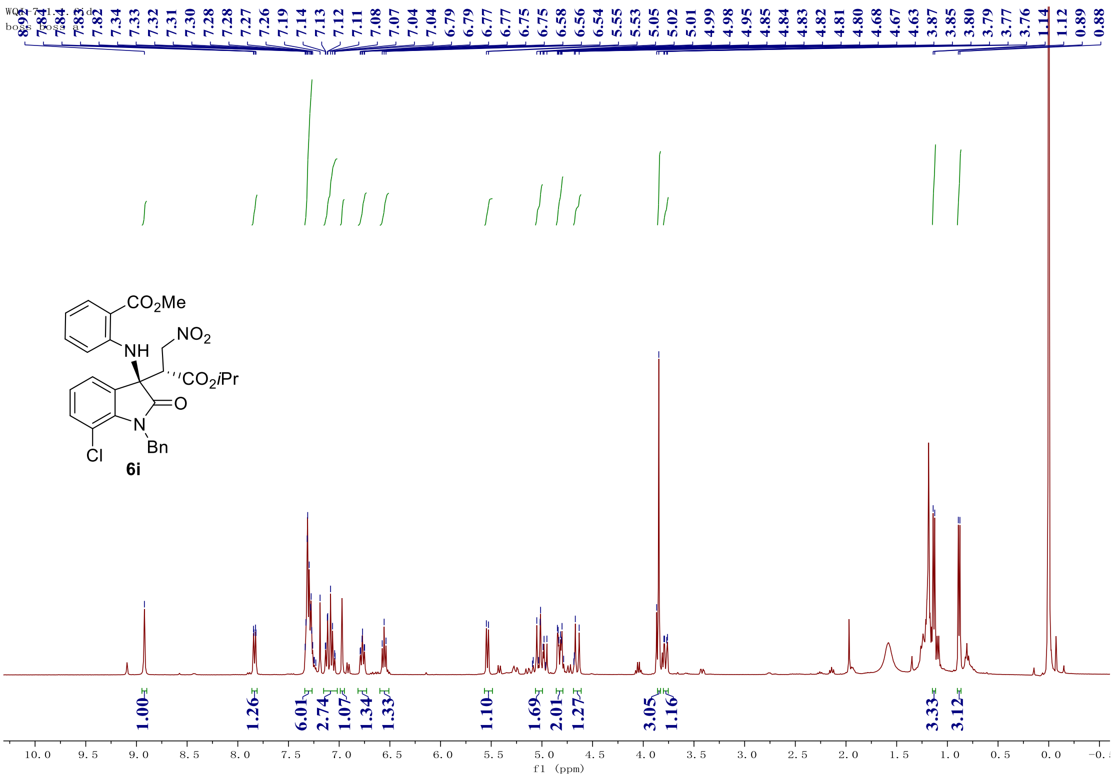
6h
f1 (ppm)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CO2Me
NH
NO2
CO2iPr
O
N
Bn
Cl
6i
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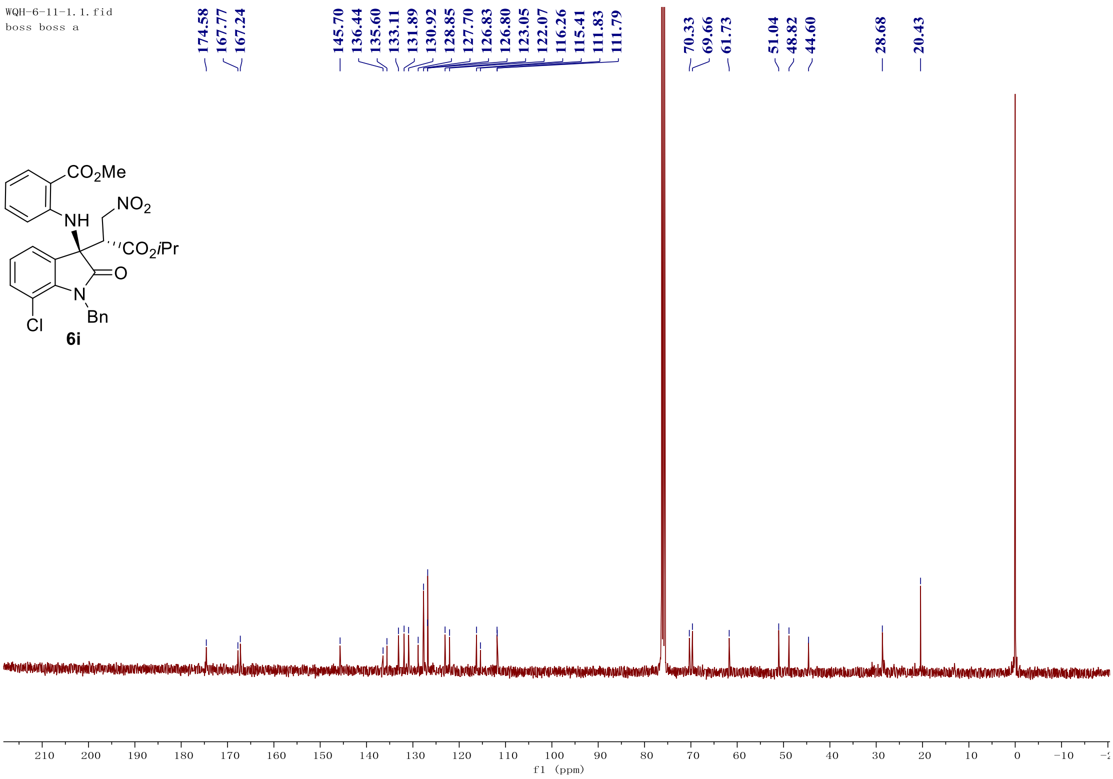
f1 (ppm)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O
N
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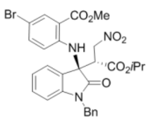
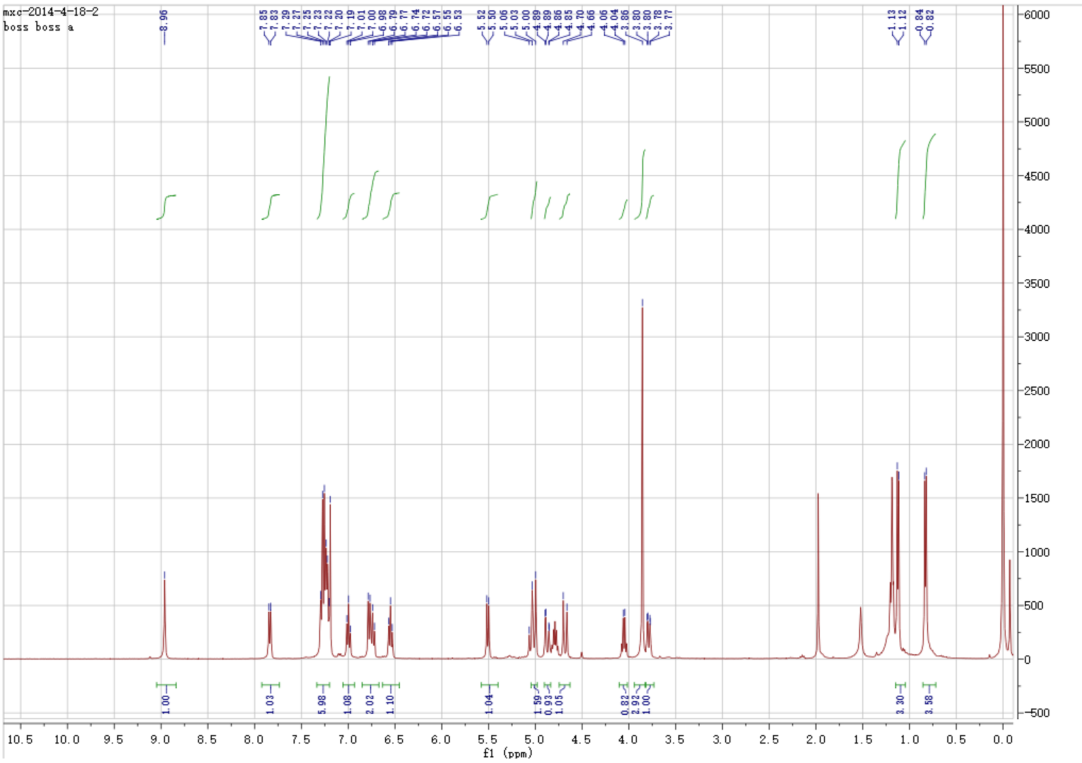
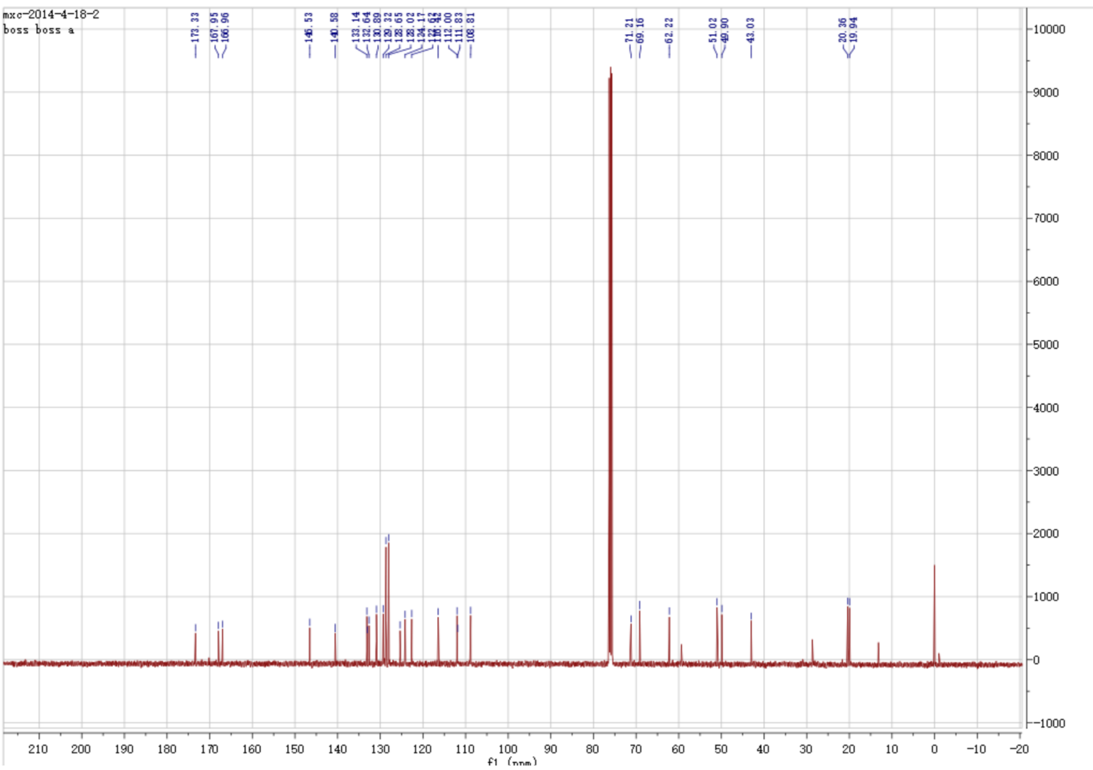
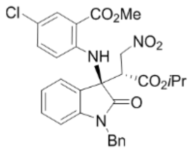
Cl
6i
f1 (ppm)



6j



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CO2iPr
O
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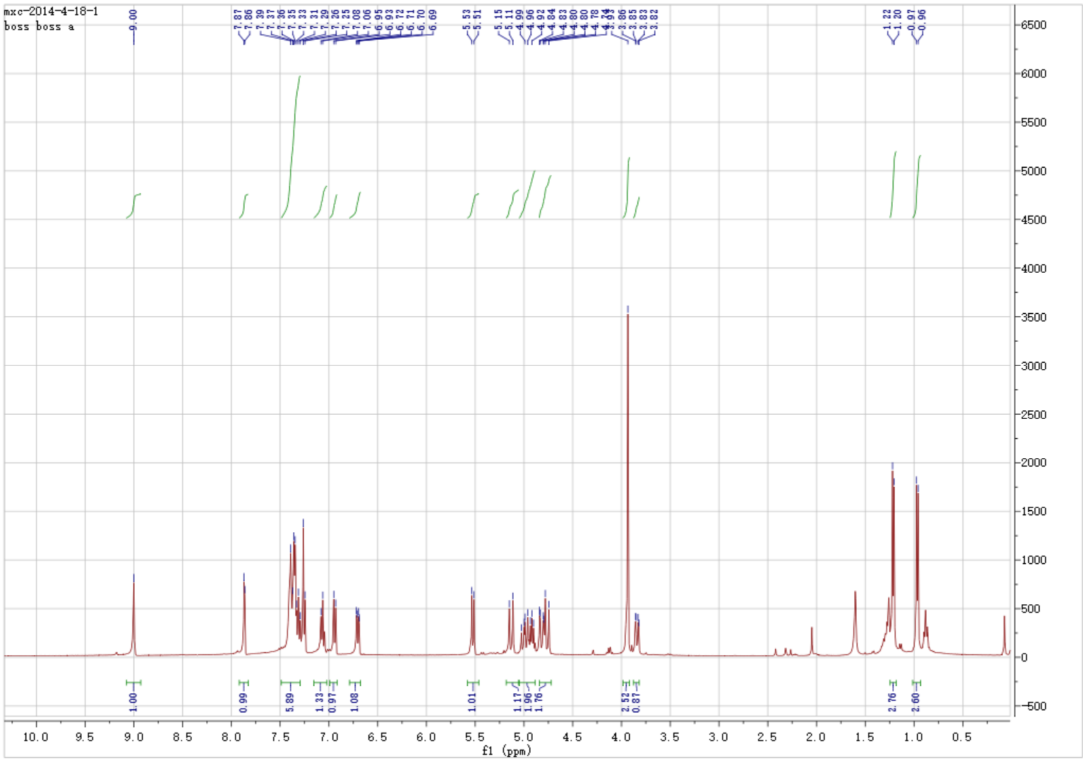
Bn

6k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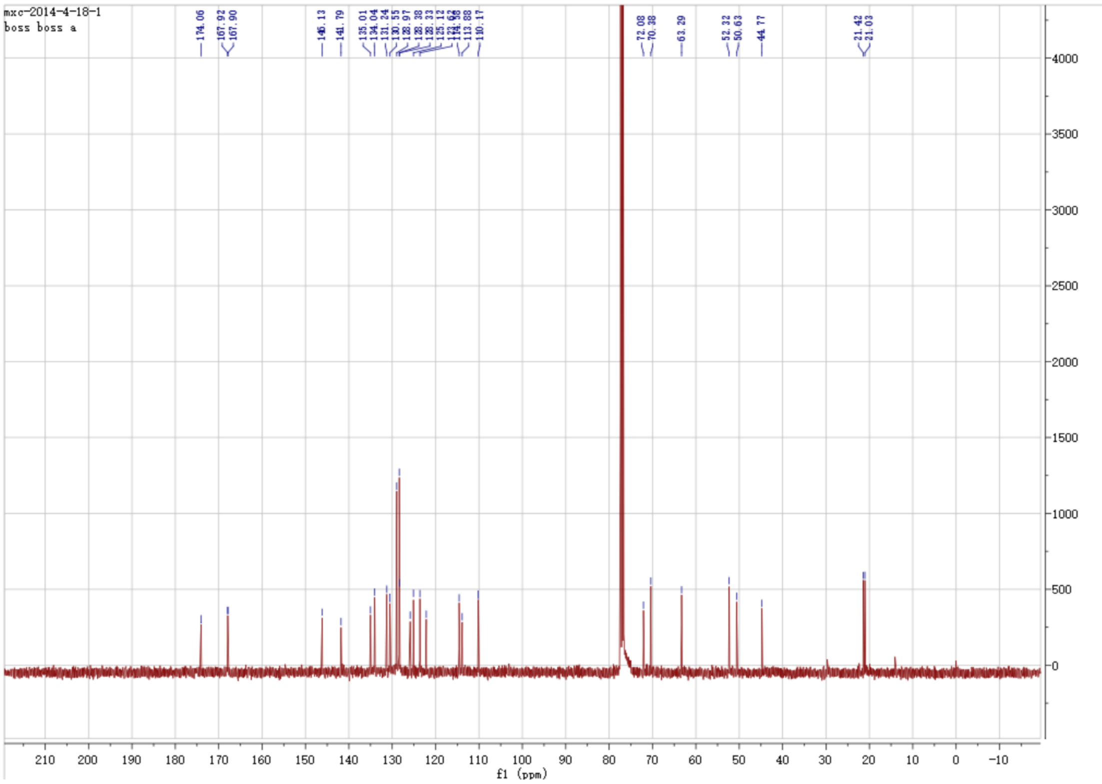
boss boss a
f1 (ppm)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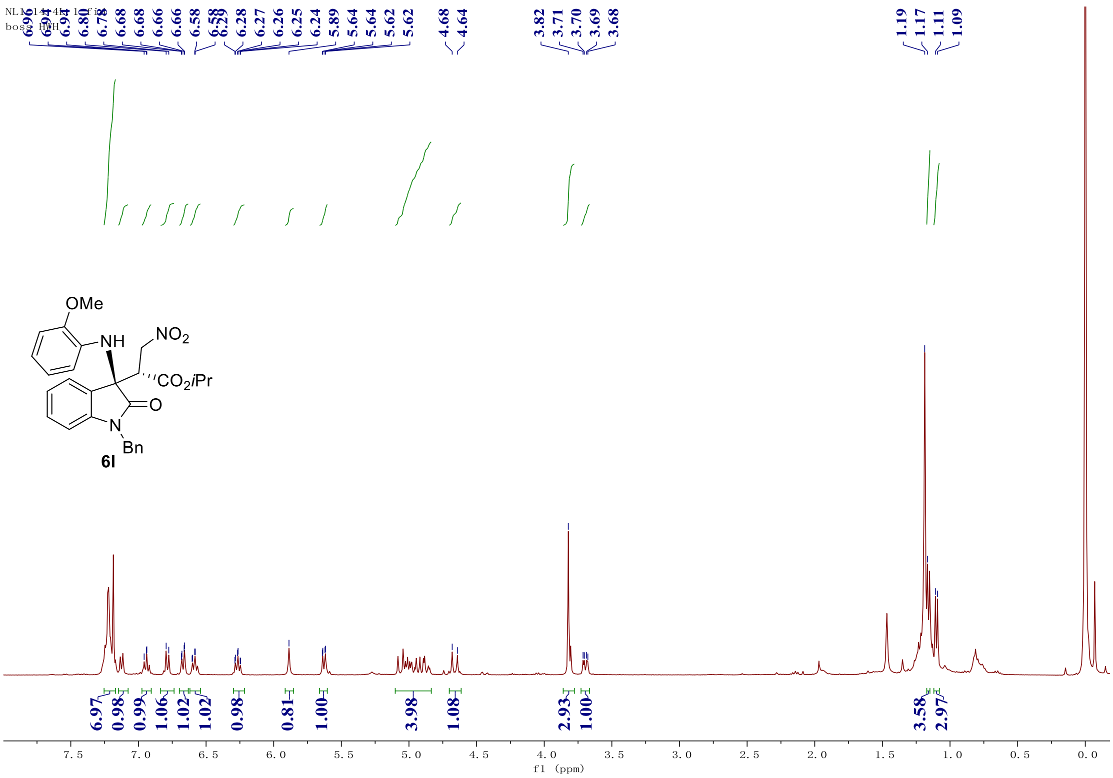
f1 (ppm)



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CO_2iPr
O
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Bn
6l
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0.99
1.06
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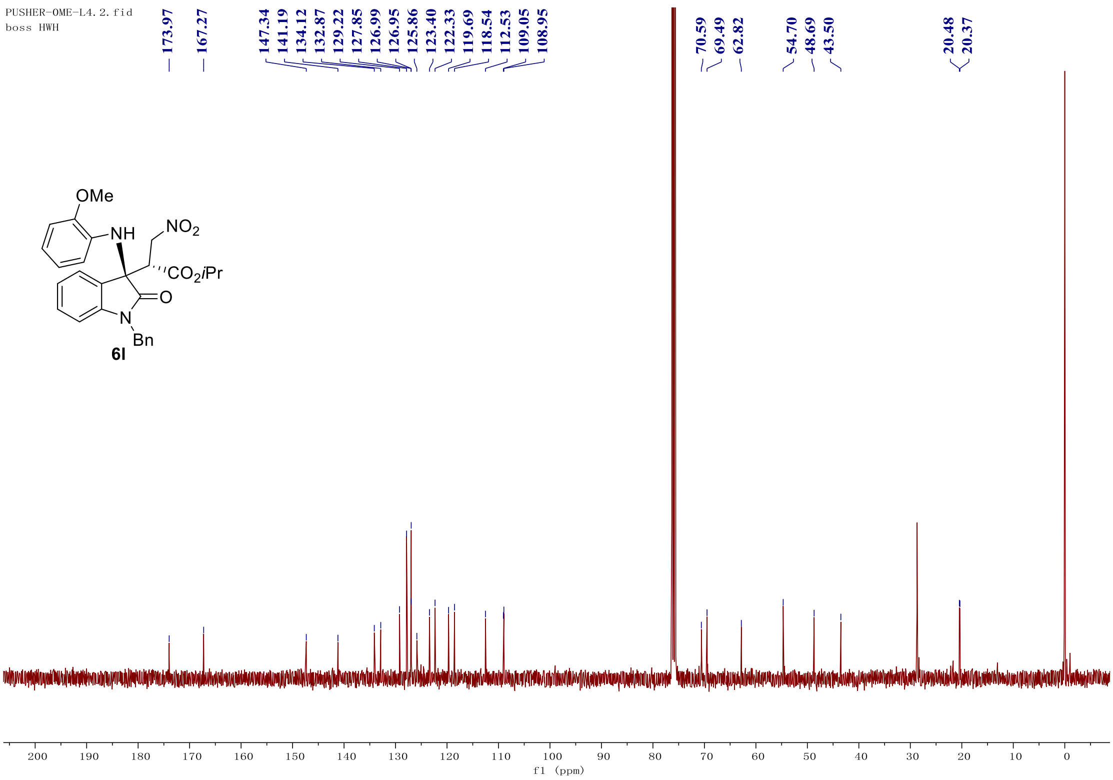
f1 (ppm)



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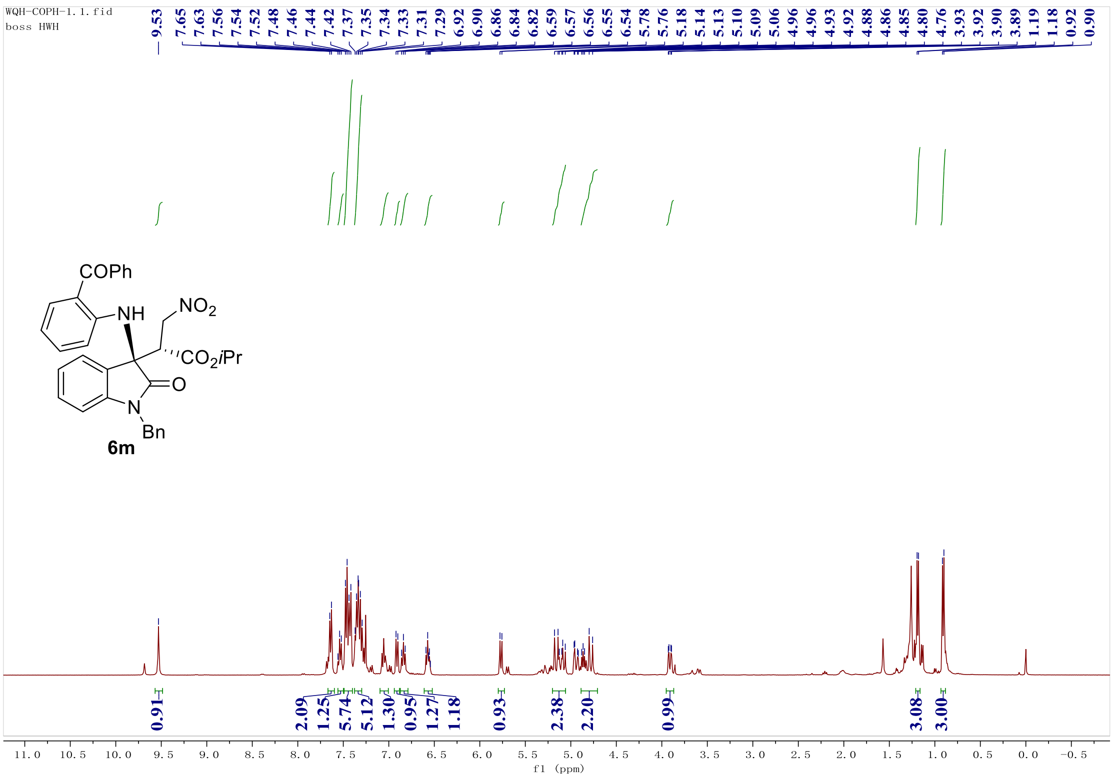
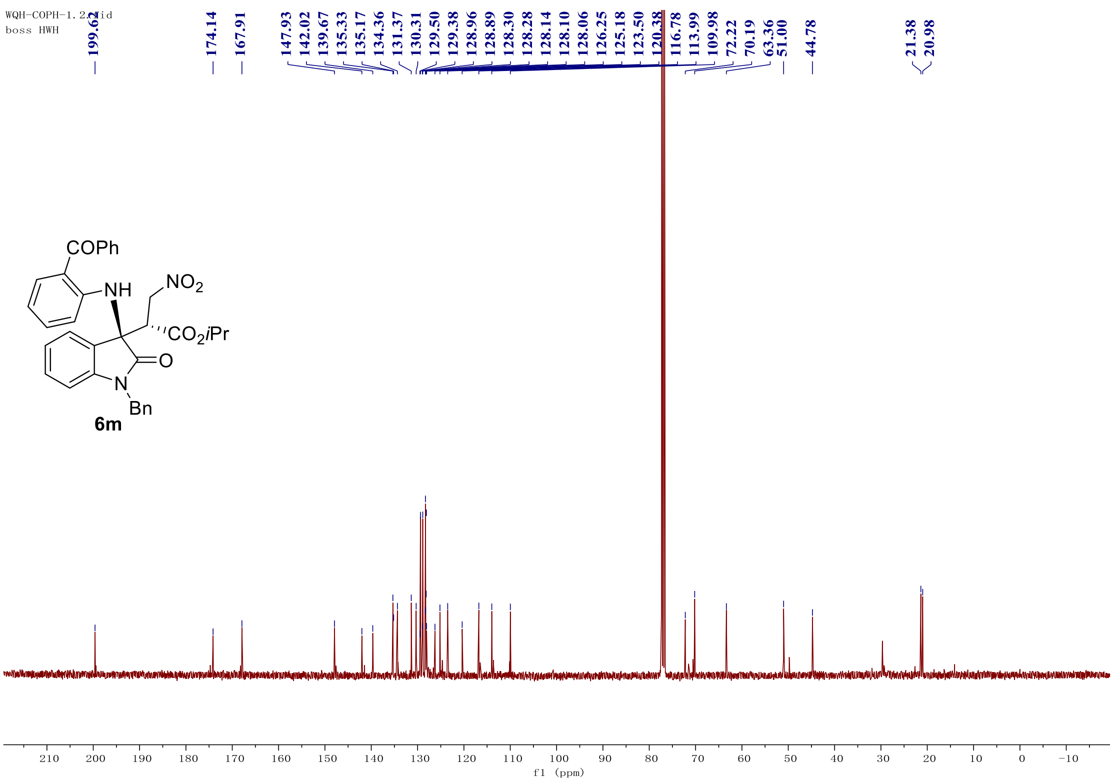
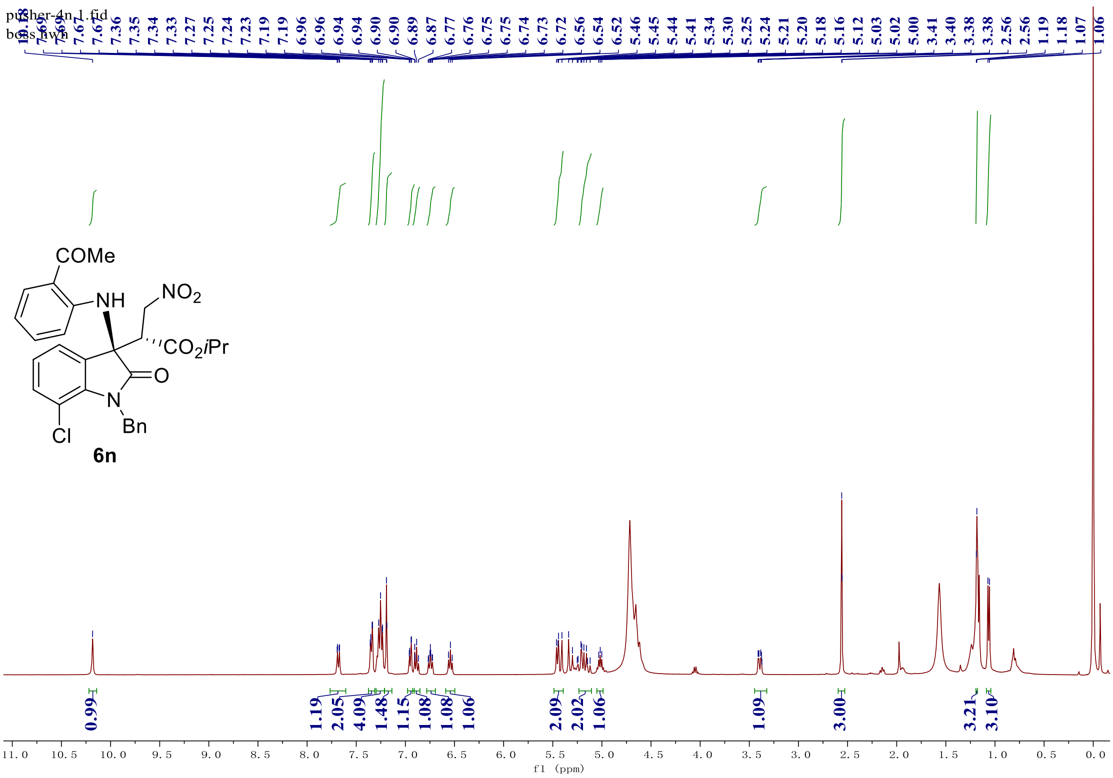
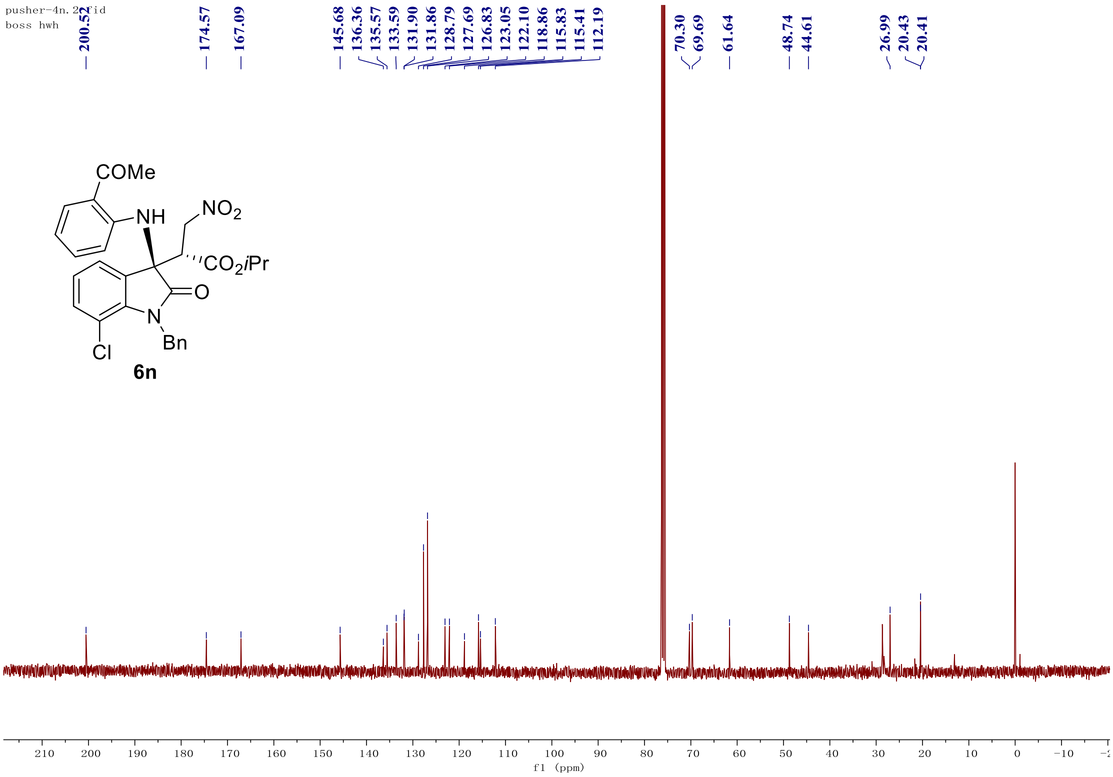
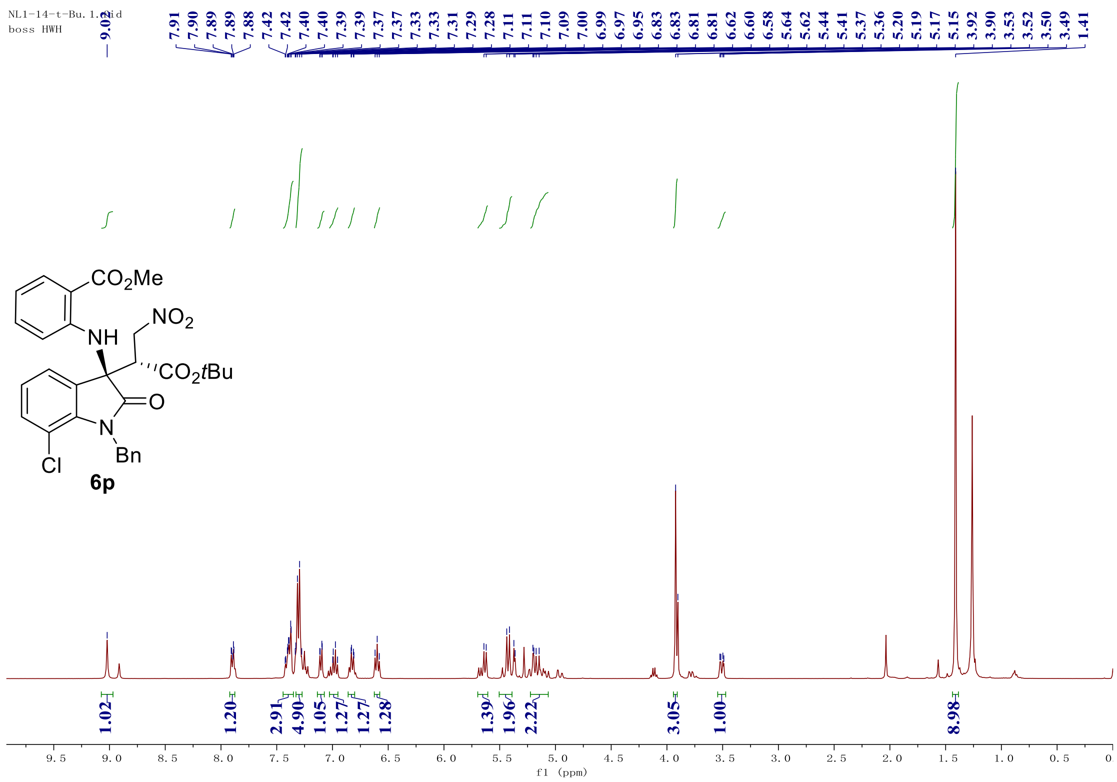
54.70
48.69
43.50
20.48
20.37
OMe
NH
NO_2
CO_2iPr
O
N
Bn
6l
f1 (ppm)

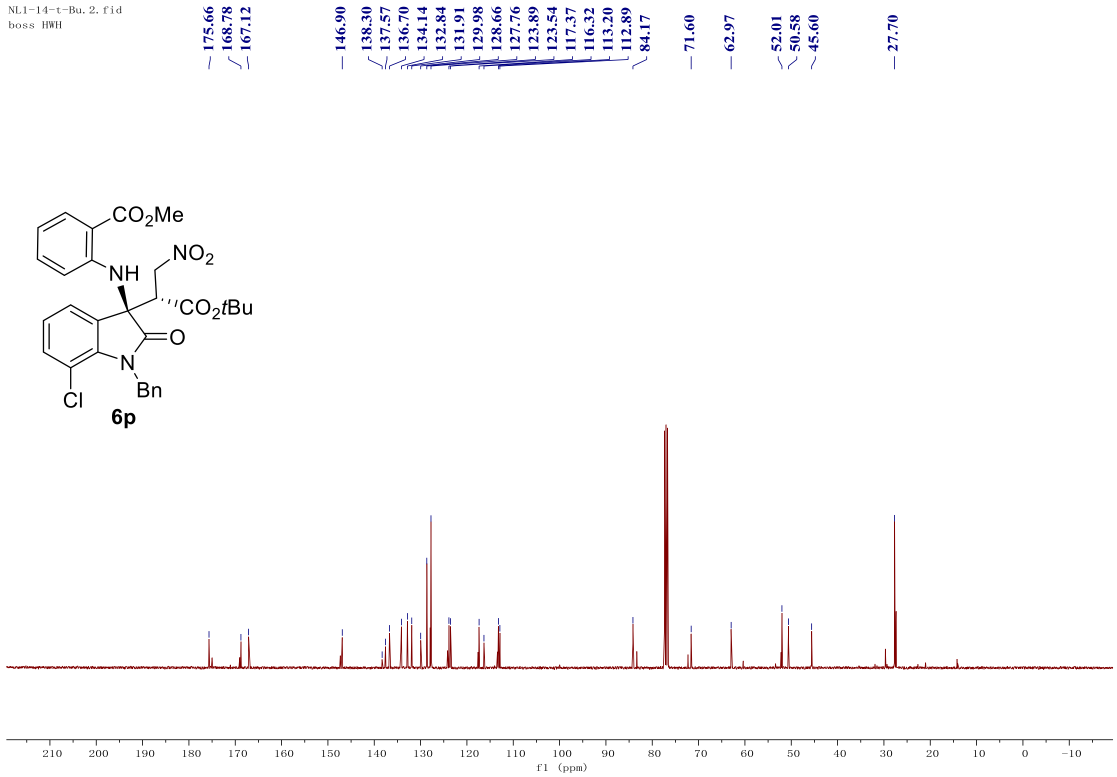

WQH-COPH-1.1.fid
boss HWH
COPh
NH
NO2
CO2iPr
O
N
Bn
6m
f1 (ppm)

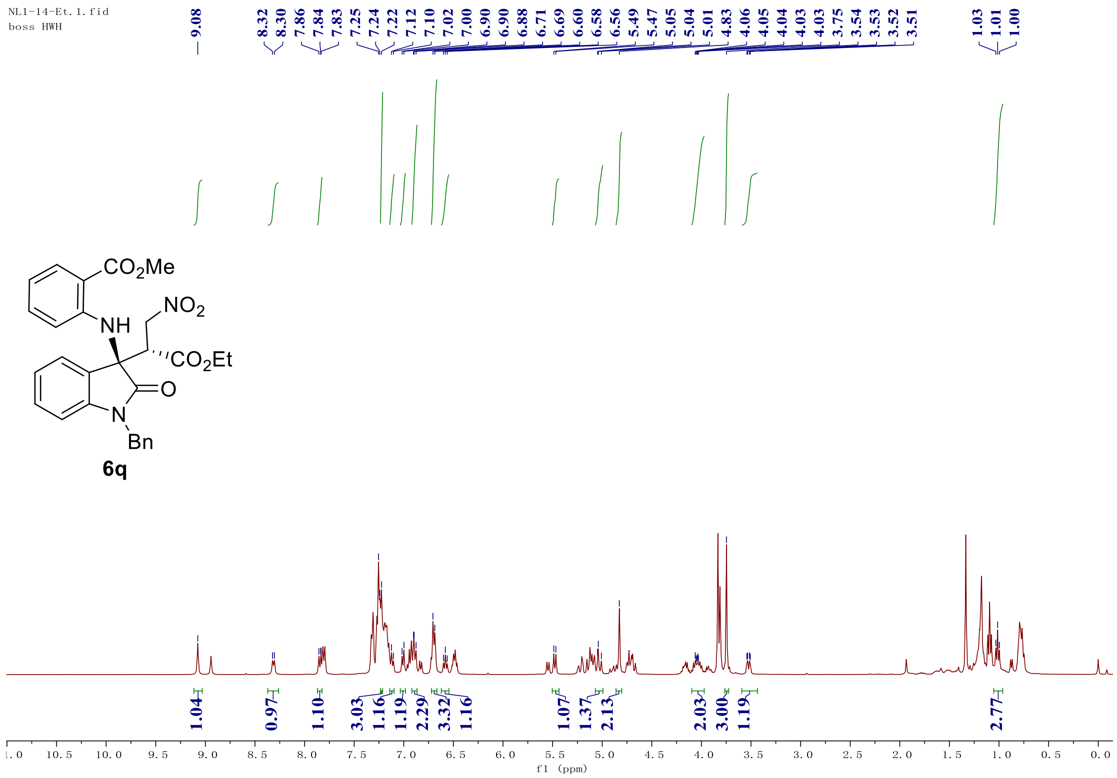

WQH-COPH-1.2.fid
boss HWH
COPh
NH
NO2
CO2iPr
O
N
Bn
6m
f1 (ppm)



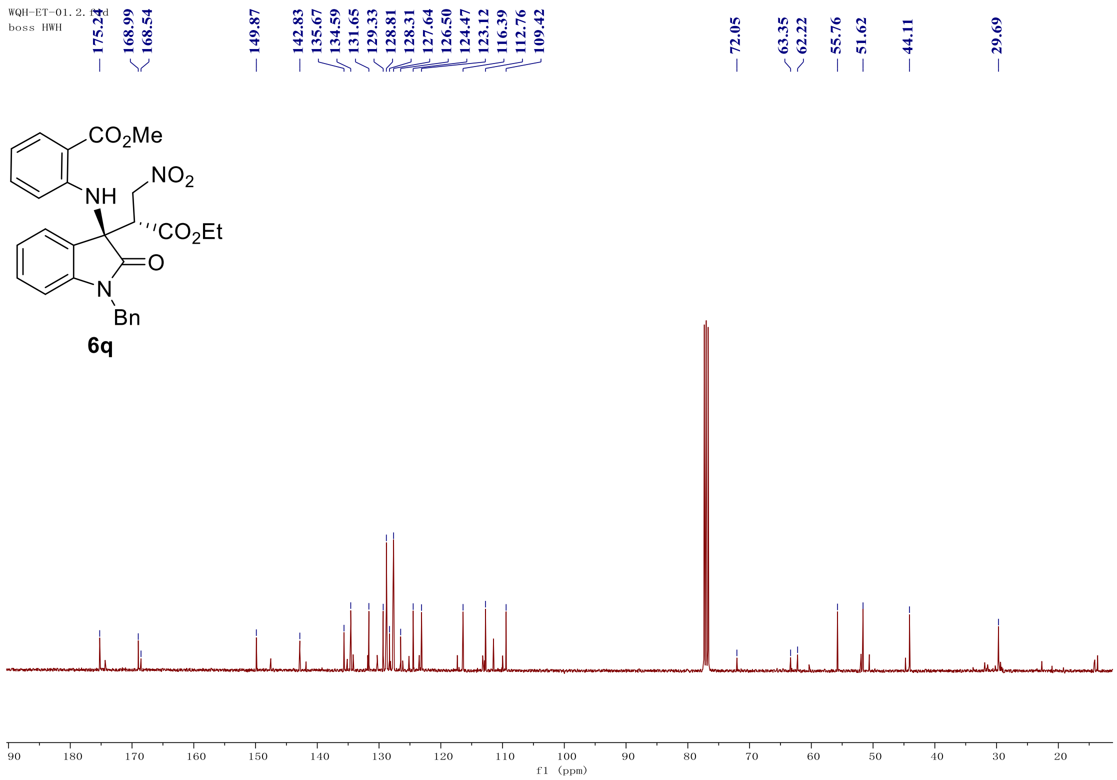



NL1-14-t-Bu.1.fid
boss HWH
9.03 7.91 7.90 7.89 7.89 7.88 7.42 7.42 7.40 7.40 7.39 7.39 7.37 7.37 7.33 7.33 7.31 7.29 7.28 7.11 7.11 7.10 7.09 7.00 6.99 6.97 6.95 6.83 6.83 6.81 6.81 6.62 6.60 6.58 5.64 5.62 5.44 5.41 5.37 5.36 5.20 5.19 5.17 5.15 3.92 3.90 3.53 3.52 3.50 3.49 1.41
CO2Me
NH
NO2
CO2tBu
O
N
Bn
Cl
6p
1.02 1.20 2.91 4.90 1.05 1.27 1.27 1.28 1.39 1.96 2.22 3.05 1.00 8.98
f1 (ppm)

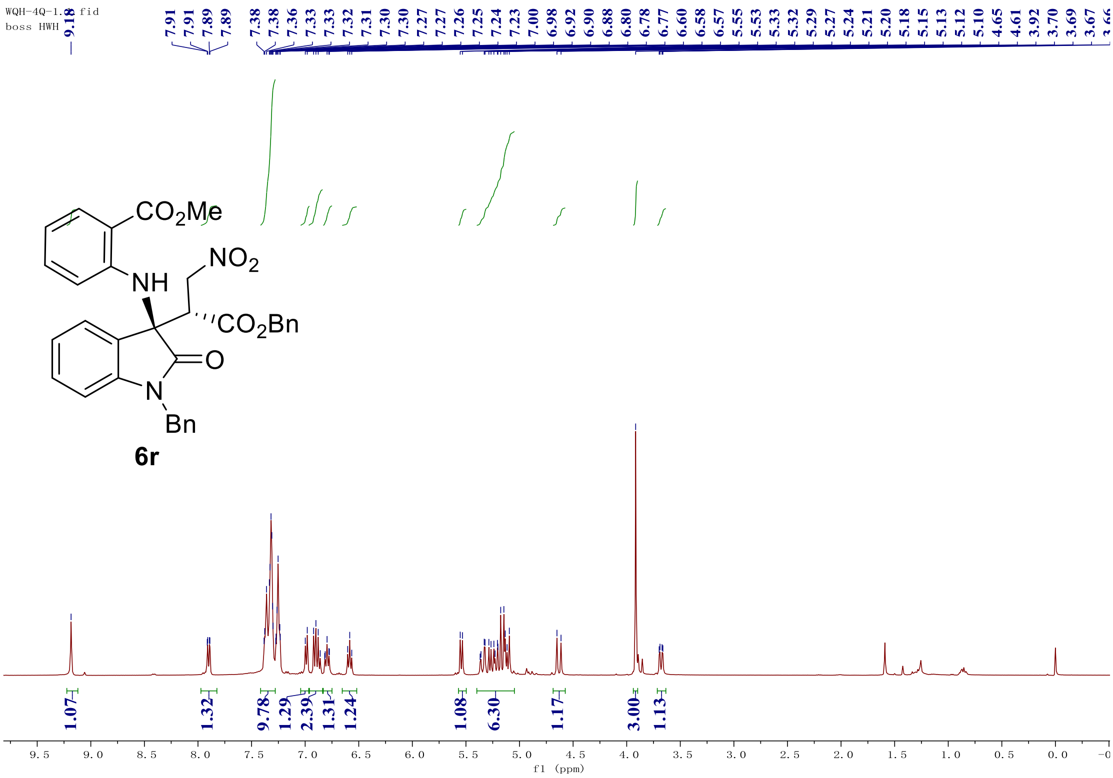

NL1-14-t-Bu.2.fid
boss HWH
175.66 168.78 167.12 146.90 138.30 137.57 136.70 134.14 132.84 131.91 129.98 128.66 127.76 123.89 123.54 117.37 116.32 113.20 112.89 84.17 71.60 62.97 52.01 50.58 45.60 27.70
CO2Me
NH
NO2
CO2tBu
O
N
Bn
Cl
6p
f1 (ppm)

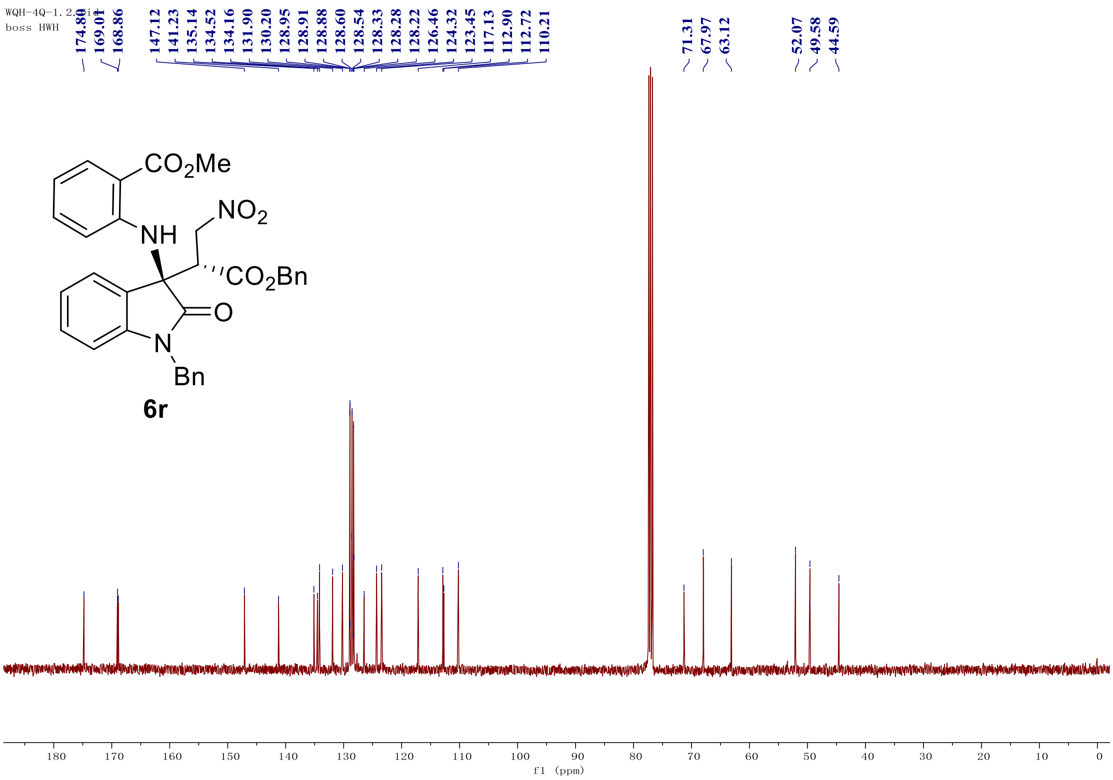

NL1-14-Et.1.fid
boss HWH
9.08
8.32
8.30
7.86
7.84
7.83
7.25
7.24
7.22
7.12
7.10
7.02
7.00
6.90
6.90
6.88
6.71
6.69
6.60
6.58
6.56
5.49
5.47
5.05
5.04
5.01
4.83
4.06
4.05
4.04
4.03
4.03
3.75
3.54
3.53
3.52
3.51
1.03
1.01
1.00
CO2Me
NO2
NH
CO2Et
O
N
Bn
1.04
0.97
1.10
3.03
1.16
1.19
2.29
3.32
1.16
1.07
1.37
2.13
2.03
3.00
1.19
2.77
f1 (ppm)

6q

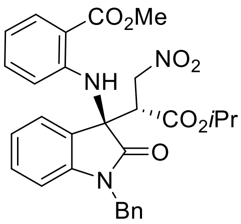

WQH-ET-01.2.fid
boss HWH
175.24
168.99
168.54
149.87
142.83
135.67
134.59
131.65
129.33
128.81
128.31
127.64
126.50
124.47
123.12
116.39
112.76
109.42
72.05
63.35
62.22
55.76
51.62
44.11
29.69
CO2Me
NO2
NH
CO2Et
O
N
Bn
f1 (ppm)

6q

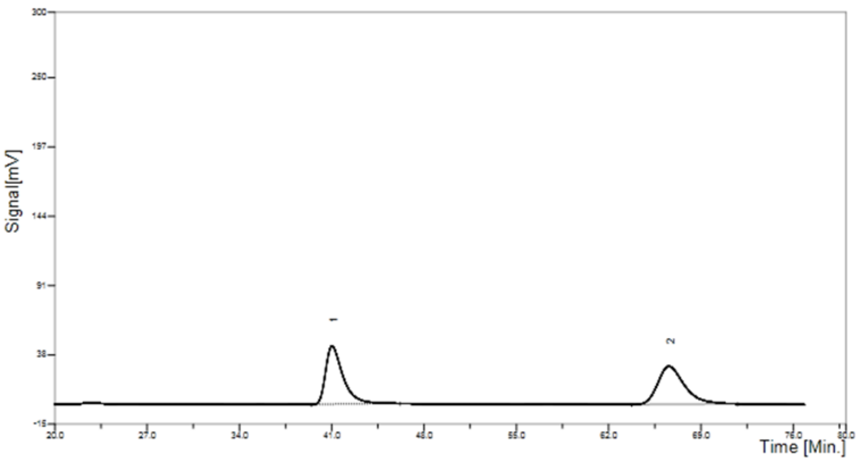

WQH-4Q-1.8 fid
boss HWH
9.18
7.91 7.91 7.89 7.89 7.38 7.38 7.36 7.33 7.33 7.32 7.31 7.30 7.30 7.27 7.27 7.26 7.25 7.24 7.23 7.00 6.98 6.92 6.90 6.88 6.80 6.78 6.77 6.60 6.58 6.57 5.55 5.53 5.33 5.32 5.29 5.27 5.24 5.21 5.20 5.18 5.15 5.13 5.12 5.10 4.65 4.61 3.92 3.70 3.69 3.67
CO2Me
NH
NO2
CO2Bn
O
N
Bn
6r
1.07 1.32 9.78 1.29 2.39 1.31 1.24 1.08 6.30 1.17 3.00 1.13
f1 (ppm)


WQH-4Q-1.2
boss HWH
174.80 169.01 168.86 147.12 141.23 135.14 134.52 134.16 131.90 130.20 128.95 128.91 128.88 128.60 128.54 128.33 128.28 128.22 126.46 124.32 123.45 117.13 112.90 112.72 110.21 71.31 67.97 63.12 52.07 49.58 44.59
CO2Me
NH
NO2
CO2Bn
O
N
Bn
6r
f1 (ppm)

15. HPLC Spectra



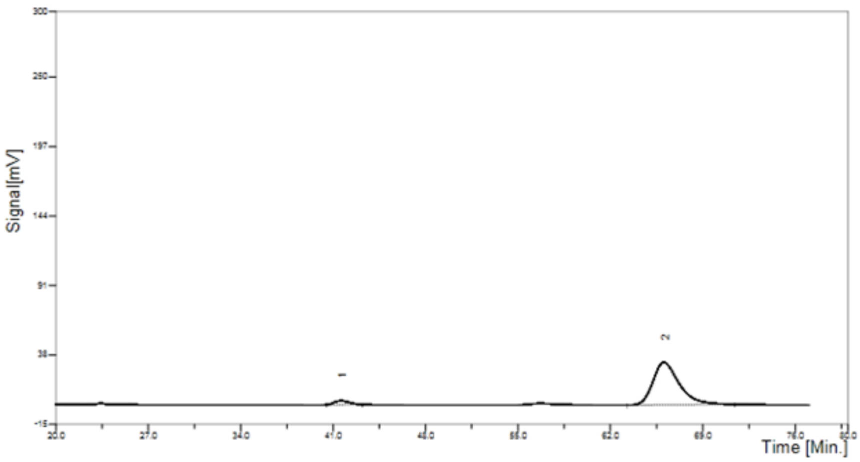
(2*R*, 3*S*)-**6a**



<Peak Results>

PDA ch1 256nm

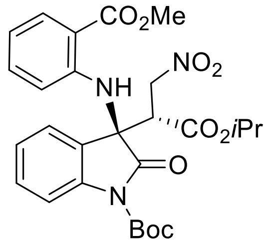
Index	Timie/min	Height/mV	Quanity(Mv.sec)	Area %/%
1	41.02667	44.44	4091.24	49.9518
2	66.57917	29.10	4099.14	50.0482



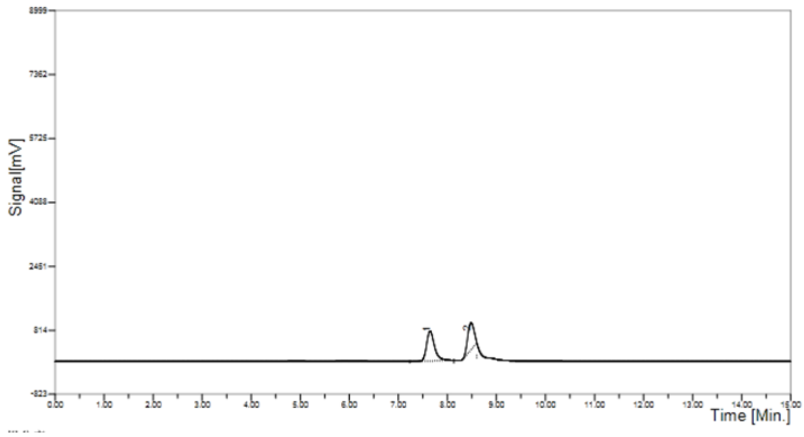
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	41.58917	3.04	253.63	4.9807
2	66.04958	32.43	4495.25	95.0193



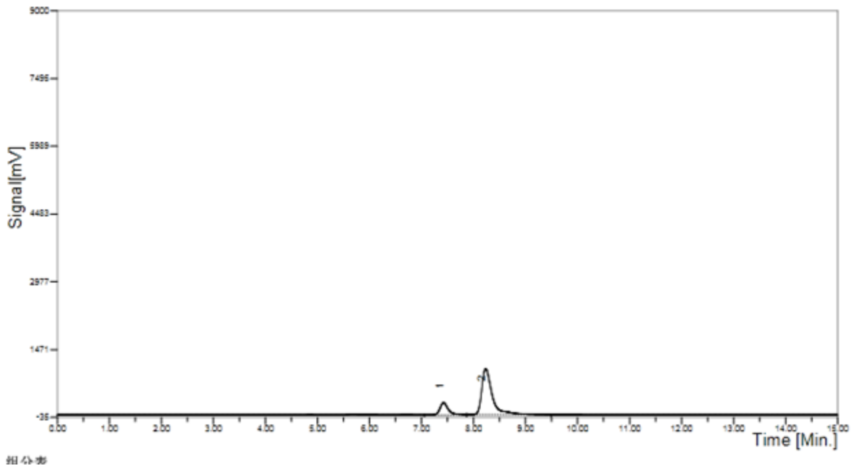
(2*R*,3*S*)-**6b**



<Peak Results>

PDA ch1 256nm

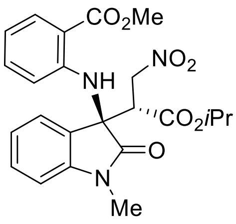
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	7.54497	769.12	8668.04	45.7889
2	8.36868	910.78	10262.38	54.2111



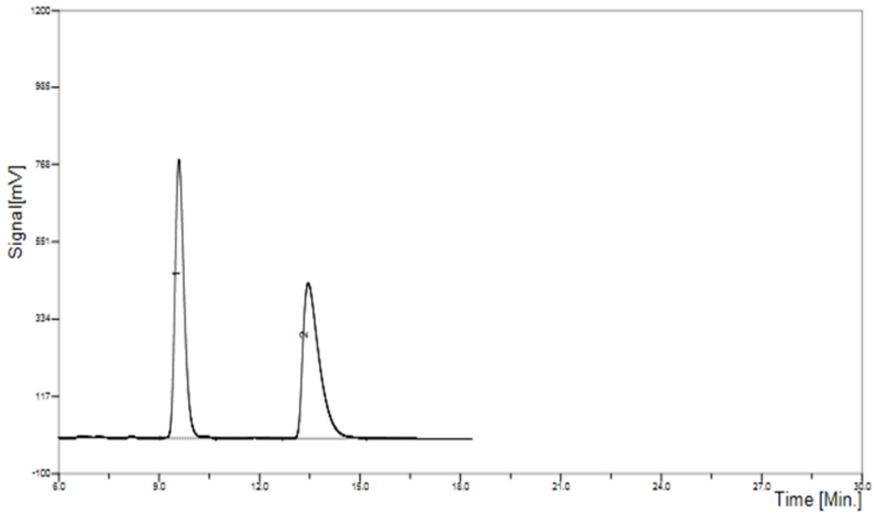
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	7.32383	268.55	2982.07	17.2794
2	8.12371	1027.06	14275.81	82.7206



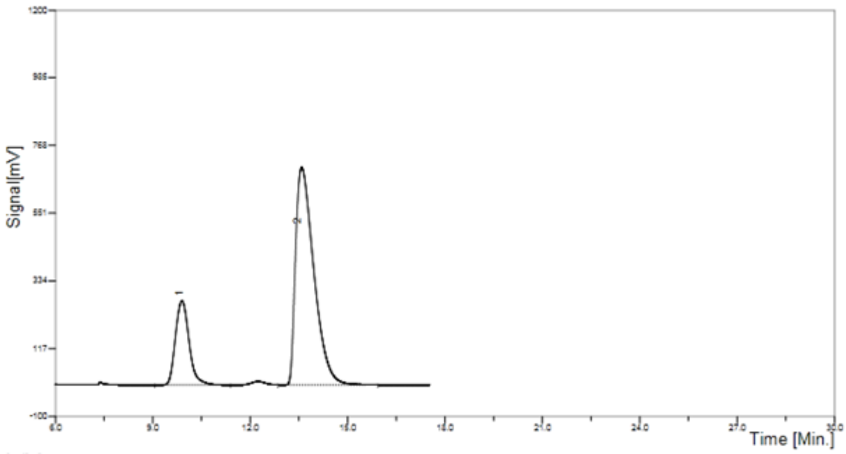
(2*R*,3*S*)-**6c**



<Peak Results>

PDA ch1 256nm

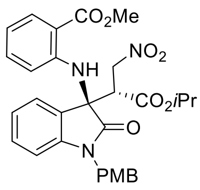
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	9.46039	779.97	14593.62	49.8947
2	13.27151	435.93	14655.21	50.1053



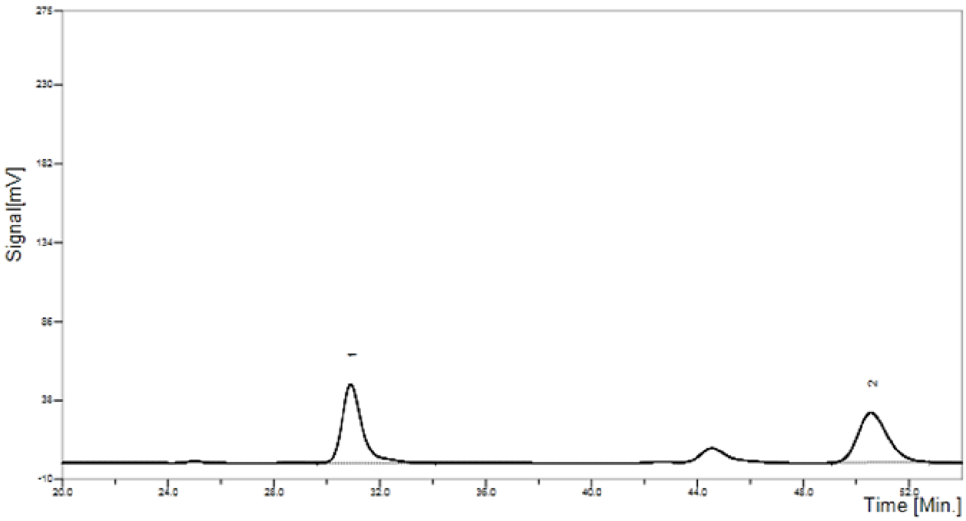
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	9.76374	269.22	7755.08	22.3111
2	13.40304	696.60	27003.75	77.6889



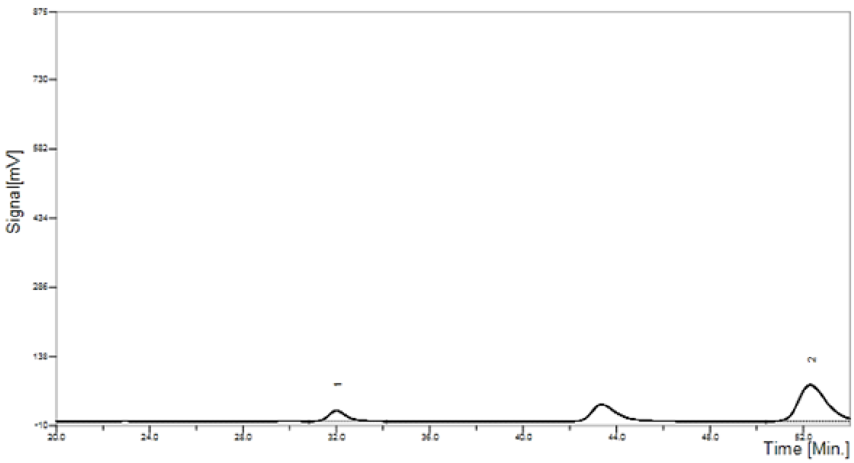
(2*R*,3*S*)-**6d**



<Peak Results>

PDA ch1 256nm

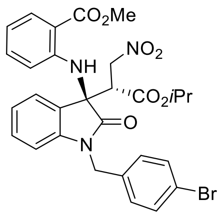
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	30.90083	48.01	2537.01	51.6082
2	50.55917	30.30	2378.89	48.3918



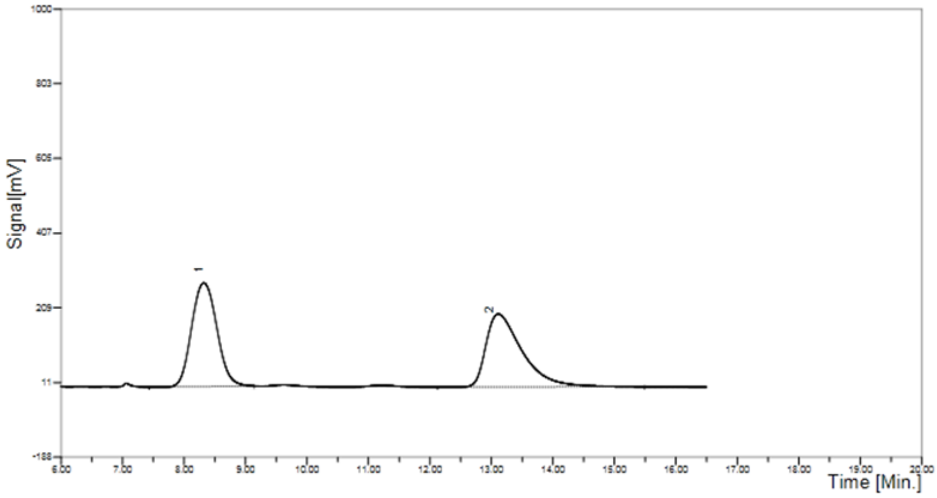
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	32.00500	22.91	1250.94	15.6284
2	52.29967	78.28	6752.30	84.3716



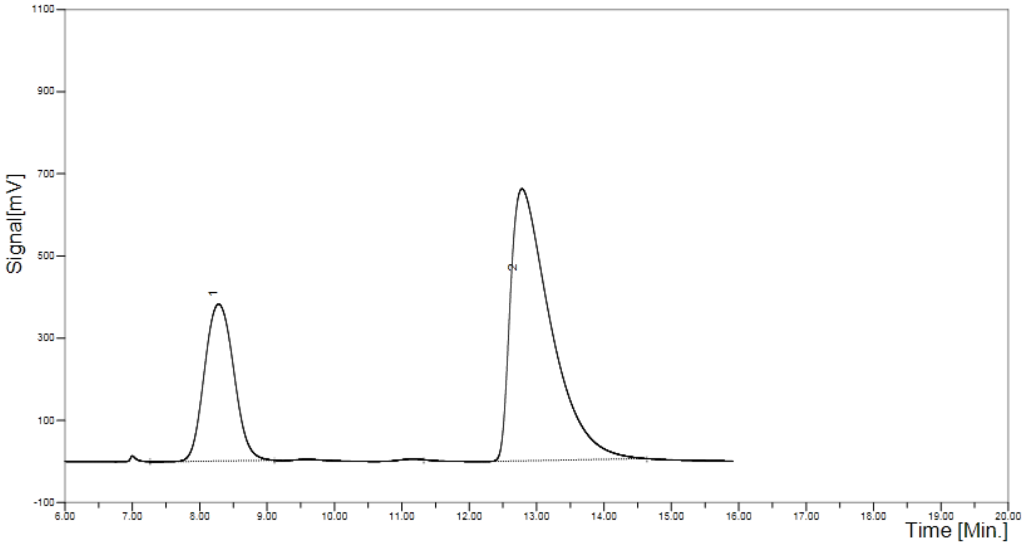
(2*R*, 3*S*)-**6e**



<Peak Results>

PDA ch1 256nm

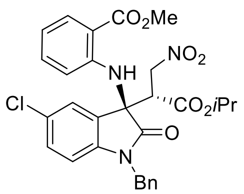
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	8.21084	274.87	7763.71	49.8909
2	12.93611	193.18	7797.67	50.1091



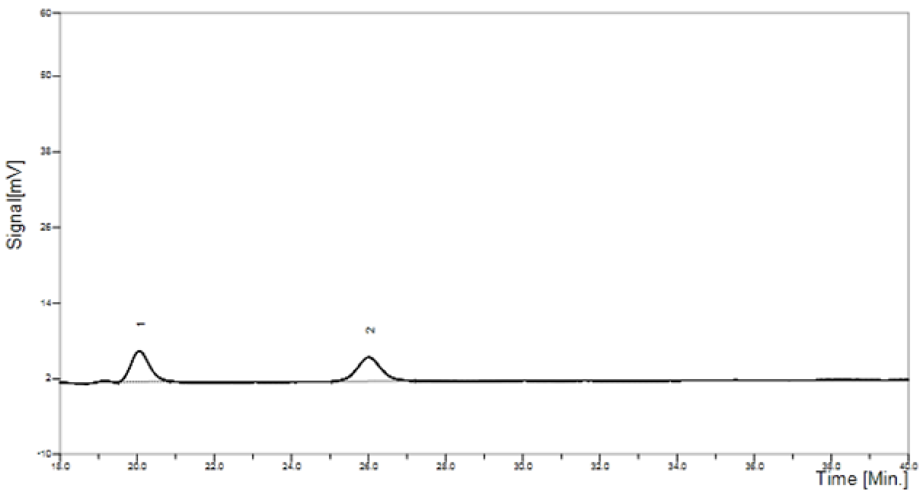
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	8.16974	382.13	11458.20	29.9167
2	12.61057	660.28	26842.12	70.0833



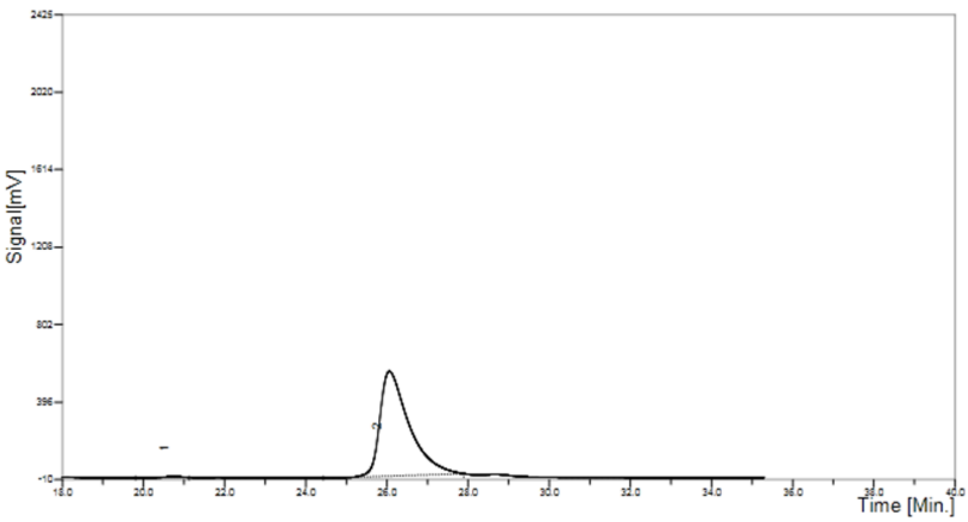
(2*R*, 3*S*)-**6g**



<Peak Results>

PDA ch1 256nm

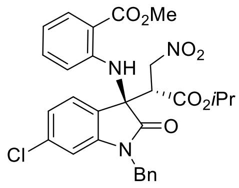
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	20.05583	4.85	160.72	49.7798
2	26.00167	3.77	162.14	50.2202



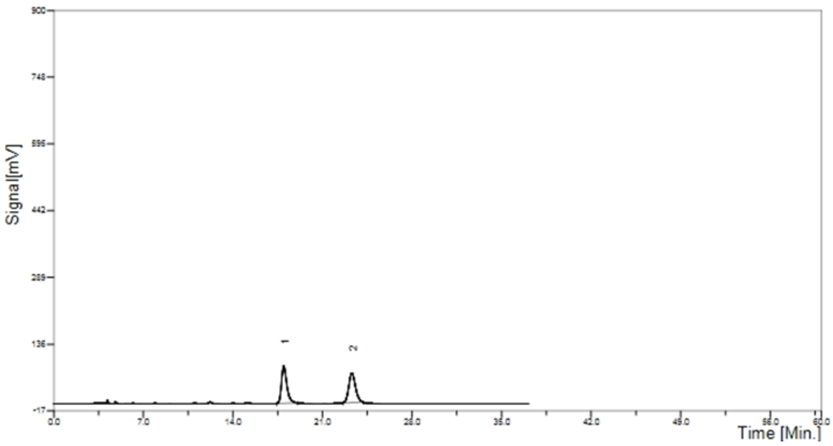
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	20.46833	6.66	199.50	0.7103
2	25.70863	551.93	27887.25	99.2897



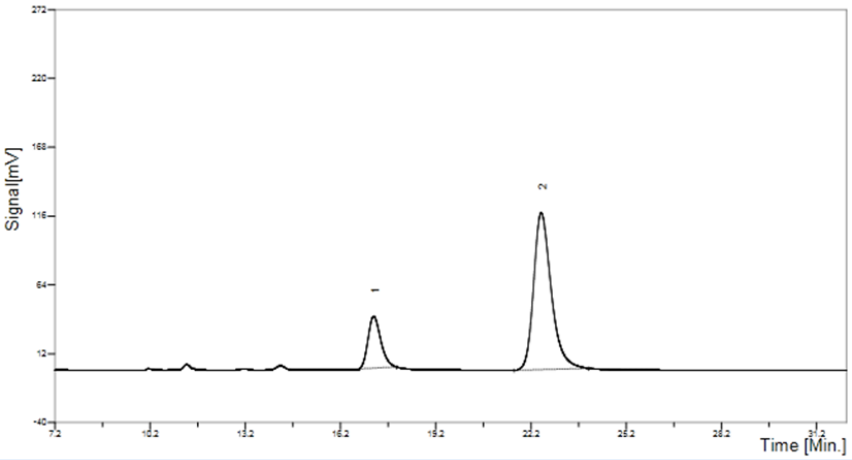
(2*R*, 3*S*)-**6h**



<Peak Results>

PDA ch1 256nm

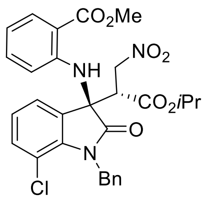
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	17.97250	85.05	2490.26	50.3468
2	23.29417	67.58	2455.95	49.6532



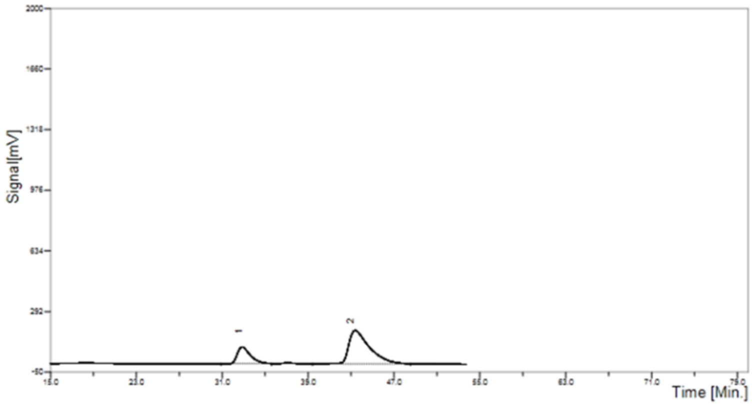
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	17.26833	39.20	1092.83	19.2783
2	22.54500	118.46	4575.89	80.7217



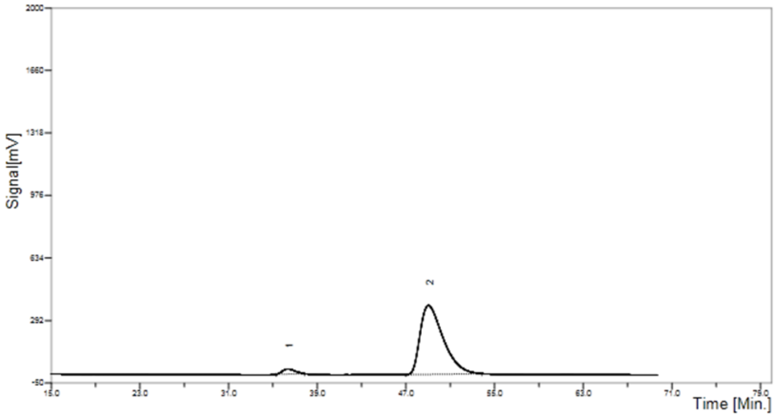
(2*R*, 3*S*)-**6i**



<Peak Results>

PDA ch1 256nm

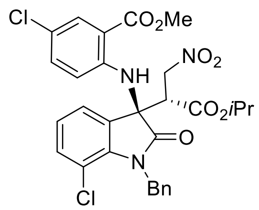
Index	Timie/min	Height/mAU	Area %/%
1	32.41261	95.32	24.2292
2	42.80688	188.10	75.7708



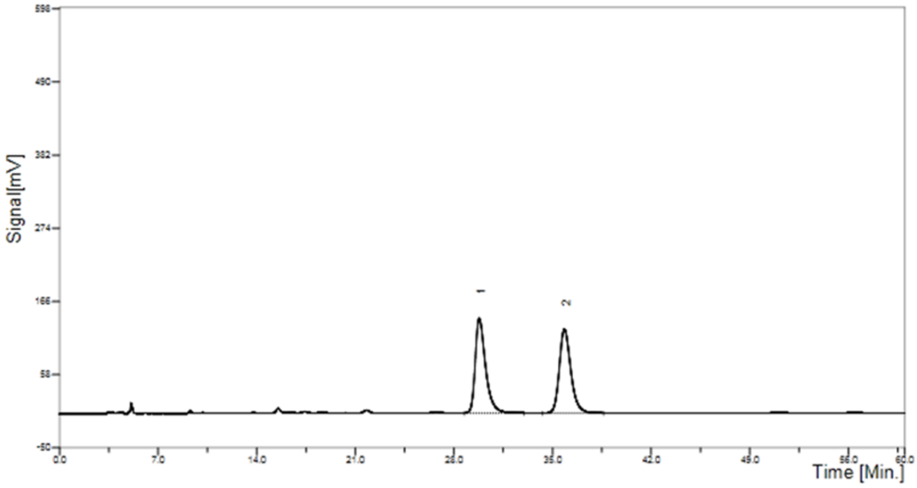
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Area %/%
1	36.34917	27.90	3.8623
2	49.03583	377.35	96.1377



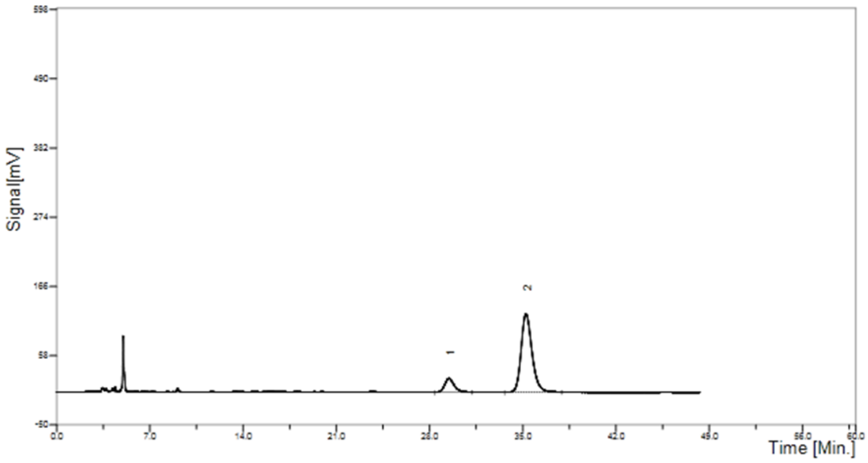
(2*R*, 3*S*)-**6j**



<Peak Results>

PDA ch1 256nm

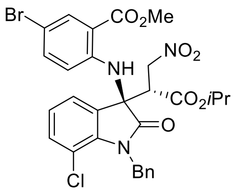
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	29.80250	139.53	7119.88	50.3273
2	35.84500	123.80	7027.57	49.6748



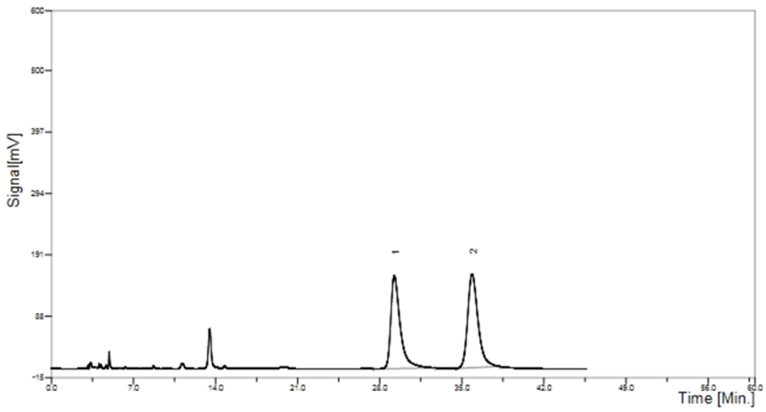
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	29.45417	21.42	1063.95	13.2485
2	35.24083	122.85	6966.74	86.7515



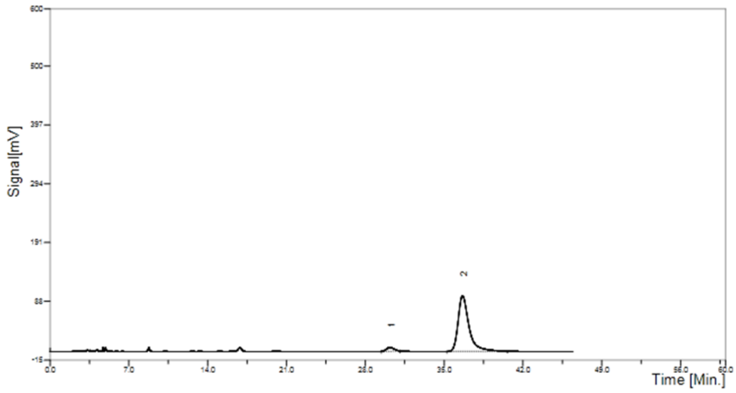
(2*R*, 3*S*)-**6k**



<Peak Results>

PDA ch1 256nm

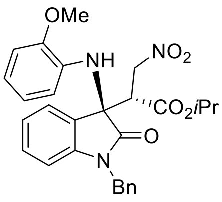
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	29.24250	156.02	8742.94	47.5152
2	35.87500	156.90	9567.36	52.4848



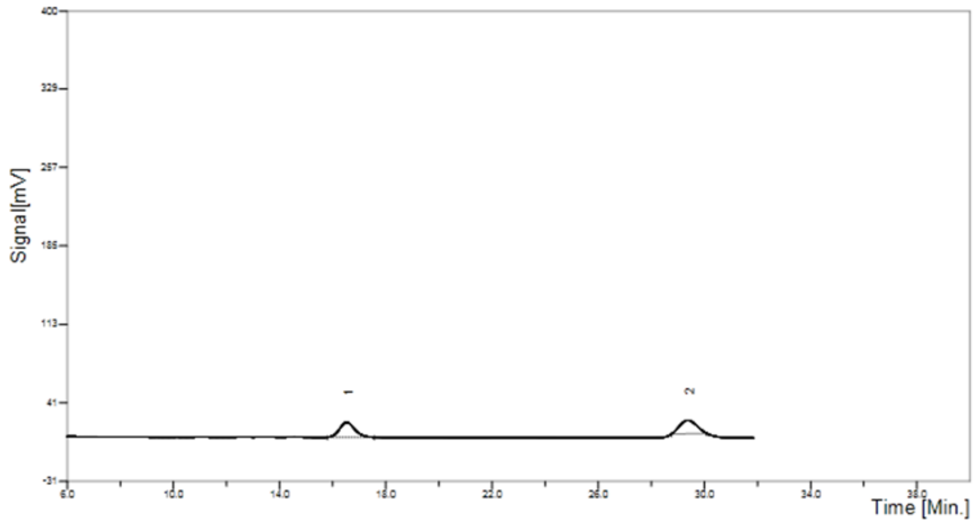
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	30.19417	6.77	316.47	4.5893
2	36.63333	97.80	6579.40	95.4107



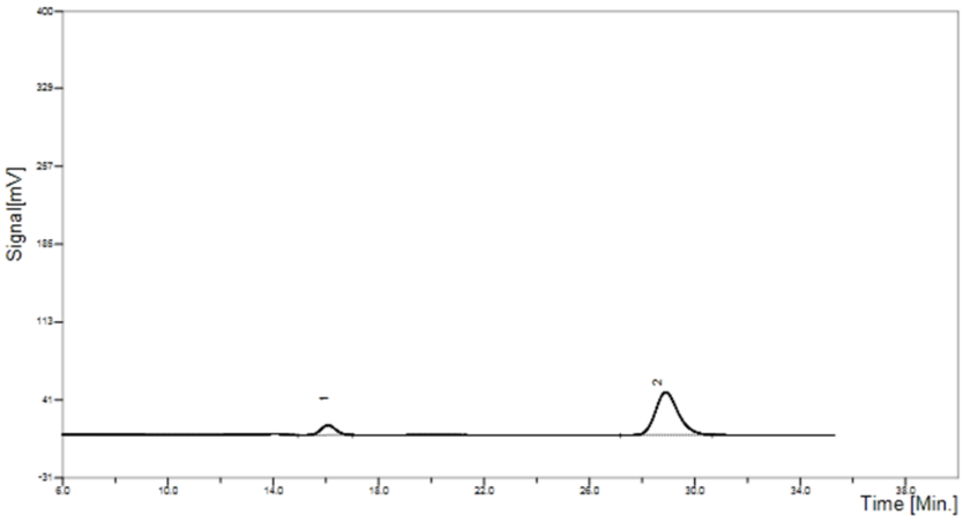
(2*R*,3*S*)-**6l**



<Peak Results>

PDA ch1 256nm

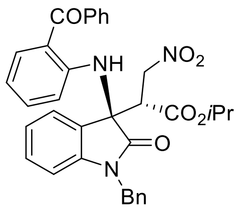
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	16.30578	13.74	545.78	36.6554
2	28.98376	16.09	943.17	63.3446



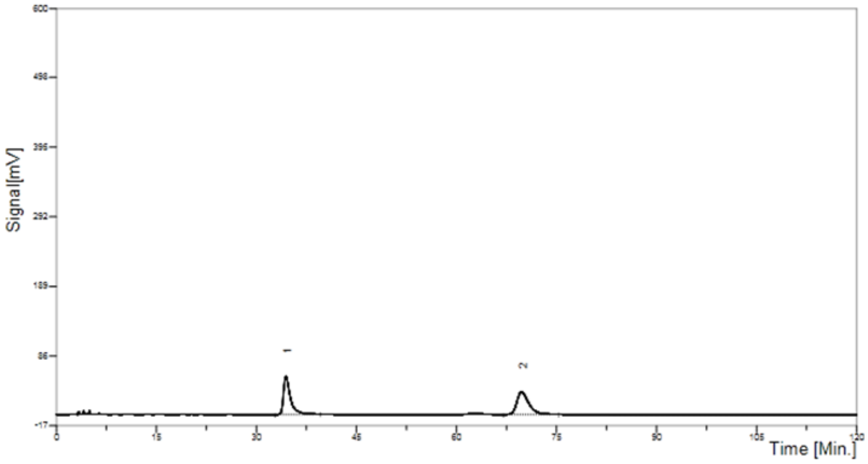
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	14.94	9.38	374.89	13.6230
2	27.17	39.82	2377.00	86.3770



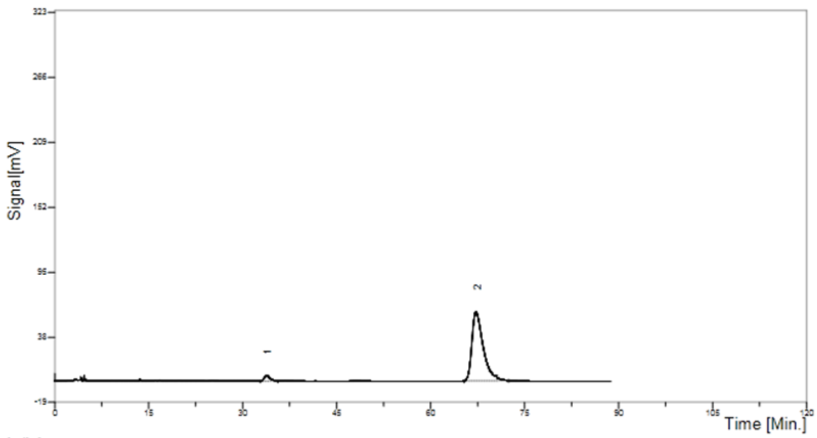
(2*R*,3*S*)-**6m**



<Peak Results>

PDA ch1 256nm

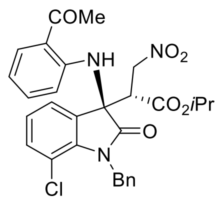
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	34.41917	56.34	4210.63	49.6716
2	69.75833	33.52	4175.12	50.3284



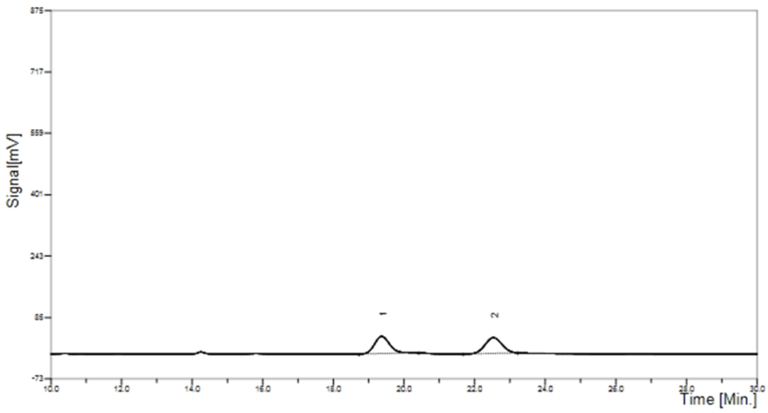
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	33.70583	4.40	295.82	3.7585
2	67.22750	60.62	7574.87	96.2415



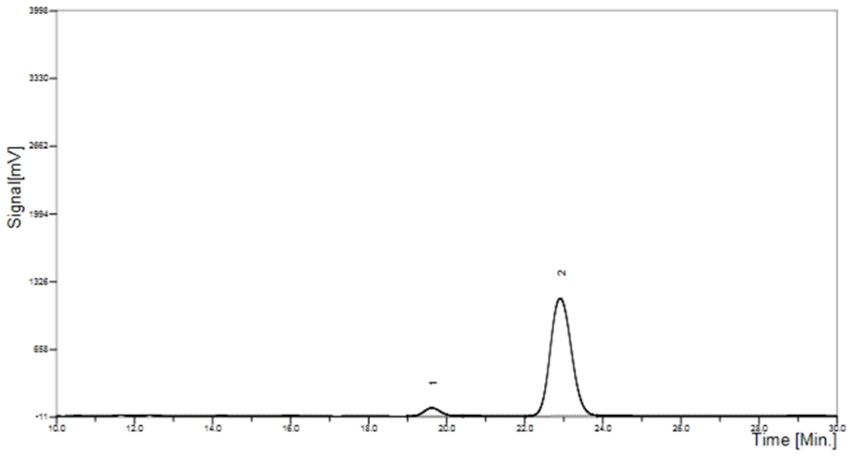
(2*R*,3*S*)-**6n**



<Peak Results>

PDA ch1 256nm

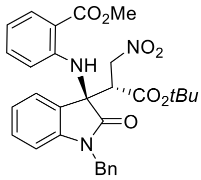
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	19.36917	44.12	1327.30	49.6114
2	22.53167	40.46	1348.10	50.3886



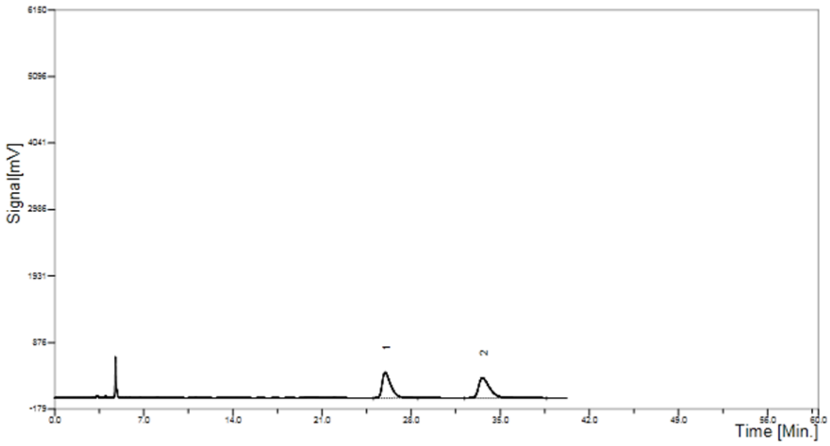
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	19.61583	80.52	2349.89	5.1533
2	1160.18	1160.18	43249.44	94.8467



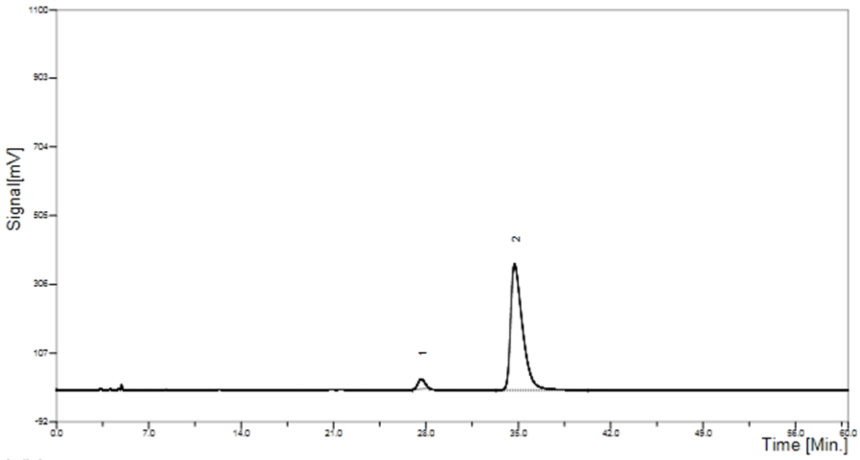
(2*R*, 3*S*)-**6p**



<Peak Results>

PDA ch1 256nm

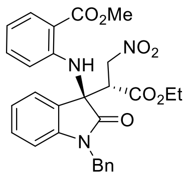
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	25.96000	404.41	19112.65	49.6131
2	33.60583	320.75	19410.74	50.3869



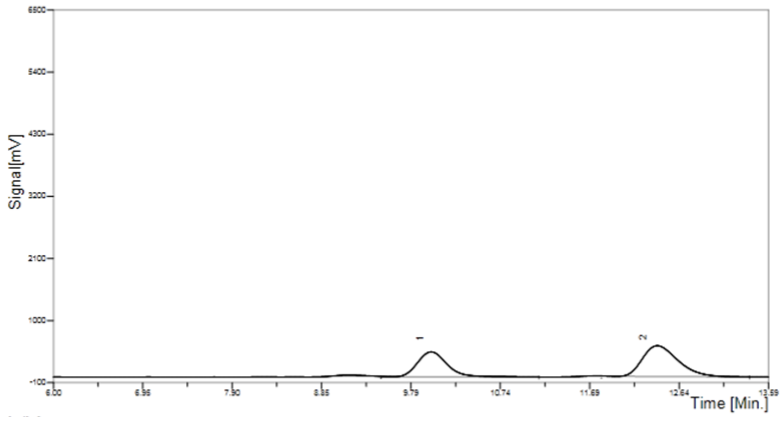
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	27.64750	28.78	1065.07	4.4393
2	34.72000	365.01	22926.74	95.5607



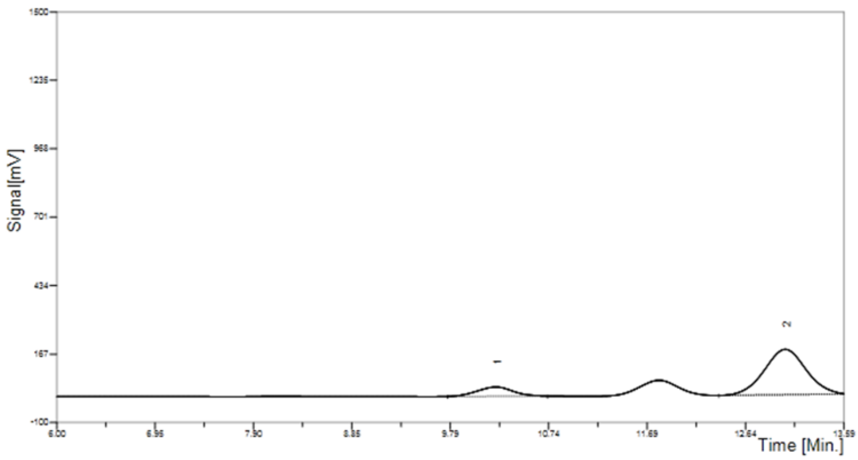
(2*R*, 3*S*)-**6q**



<Peak Results>

PDA ch1 256nm

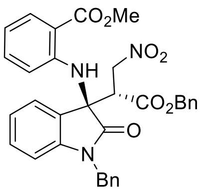
Index	Timie/min	Height/mAU	Area %/%
1	9.87472	441.84	40.2992
2	12.24146	545.30	59.7008



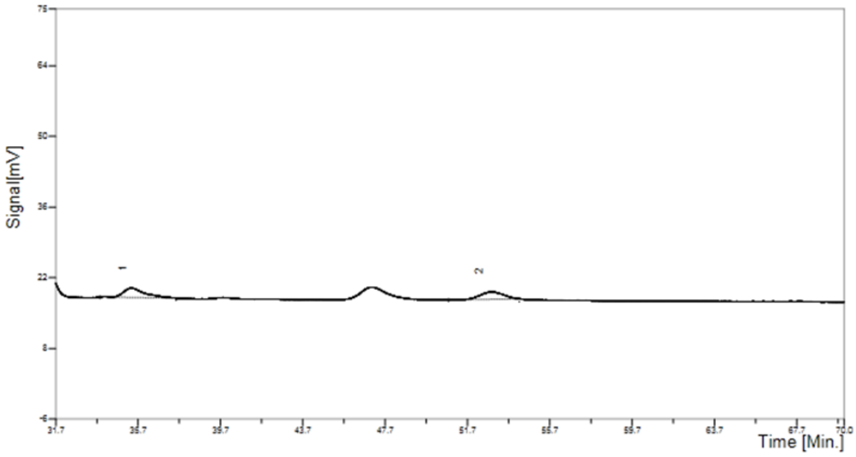
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Area %/%
1	10.23417	36.03	14.7723
2	13.02417	177.08	85.2277



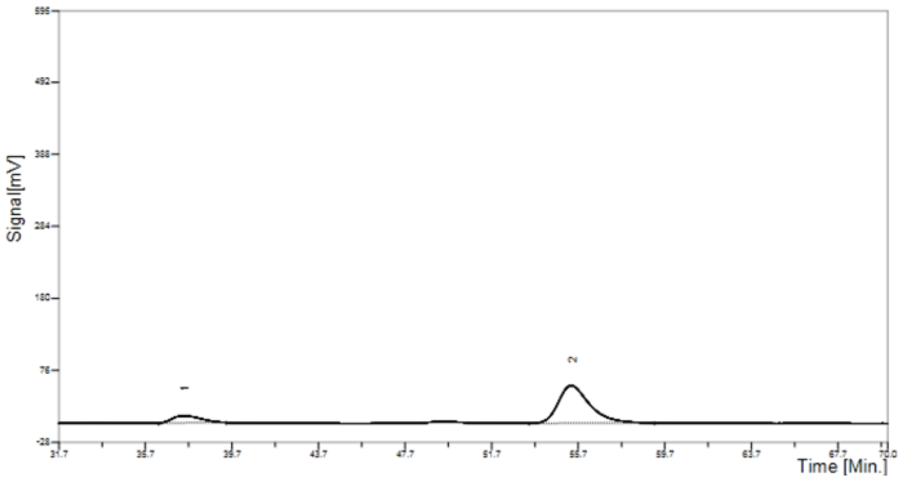
(2*R*, 3*S*)-**6r**



<Peak Results>

PDA ch1 256nm

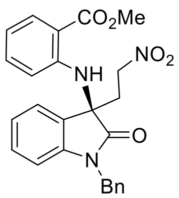
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	34.87389	1.81	133.18	49.8967
2	52.17767	1.56	133.74	50.1033



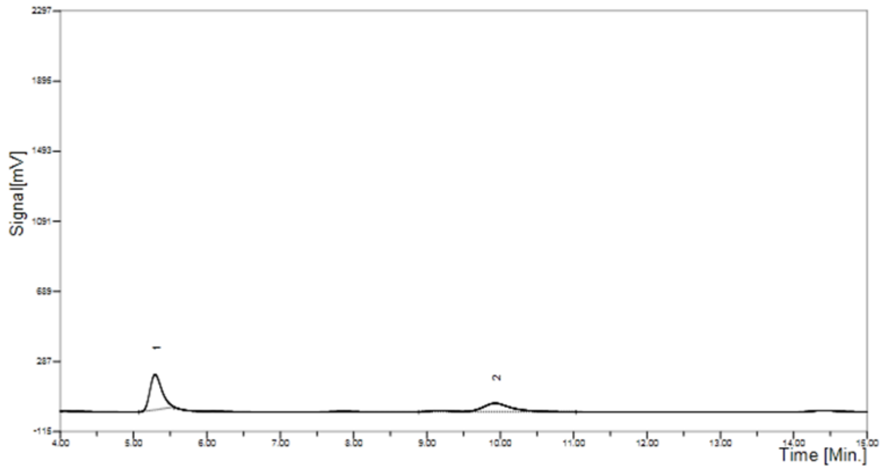
<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	37.4433	10.04	925.00	14.4250
2	55.37083	54.25	5487.51	85.5750



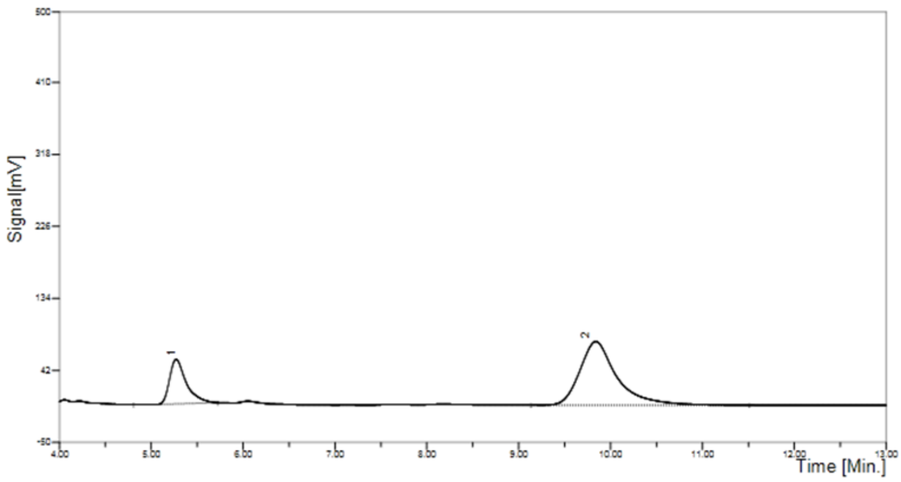
(2*R*, 3*S*)-**6s**



<Peak Results>

PDA ch1 256nm

Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	5.29417	201.83	2260.32	60.1951
2	9.92570	49.31	39.8049	39.8049



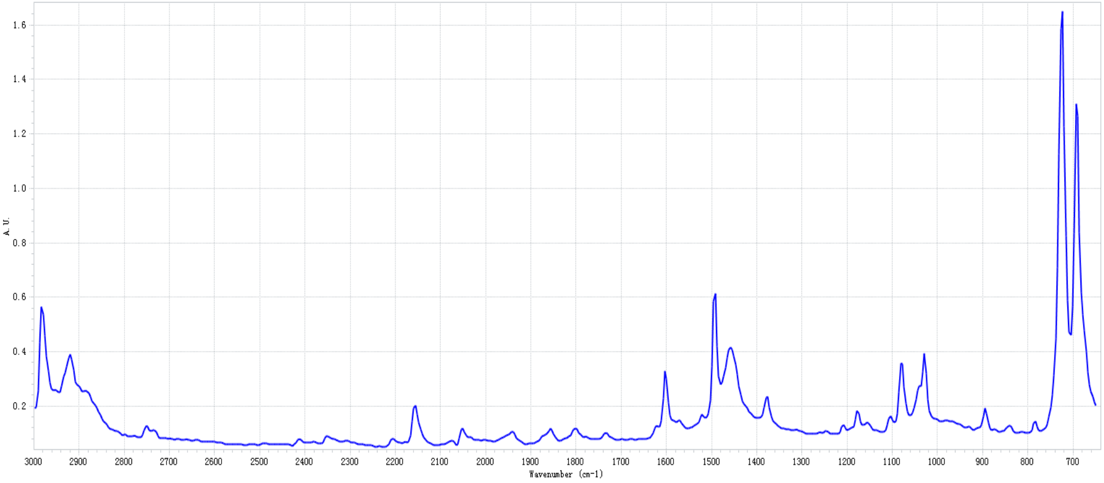
<Peak Results>

PDA ch1 256nm

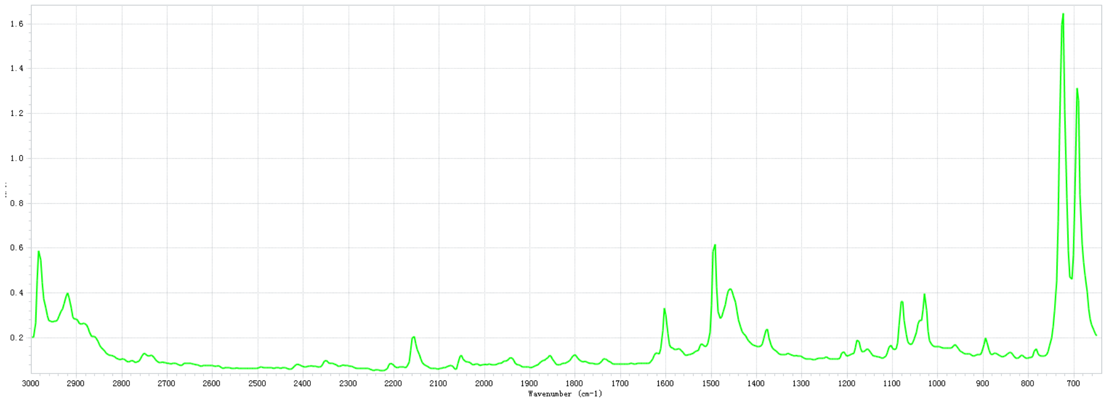
Index	Timie/min	Height/mAU	Quanity/Area	Area %/%
1	5.19960	56.92	709.23	24.0826
2	9.70619	81.03	2235.75	75.9174

16. IR Data and Spectra

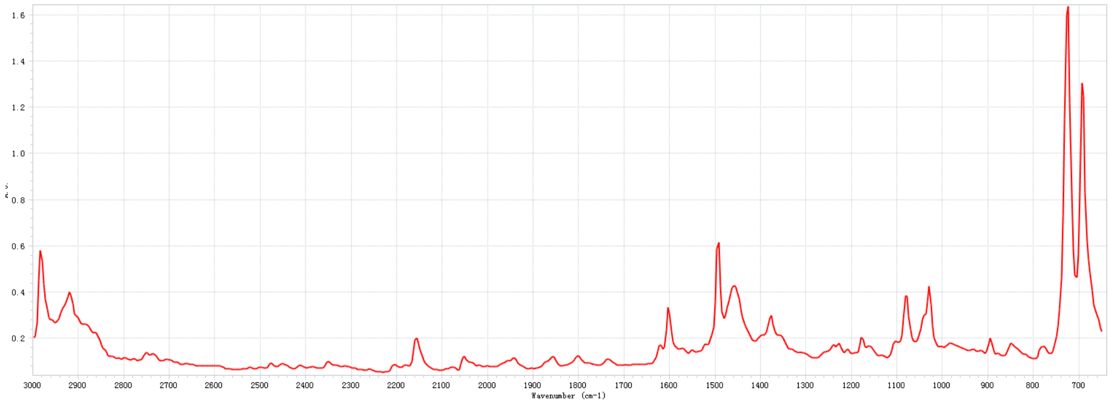
1) The IR Spectra of toluene



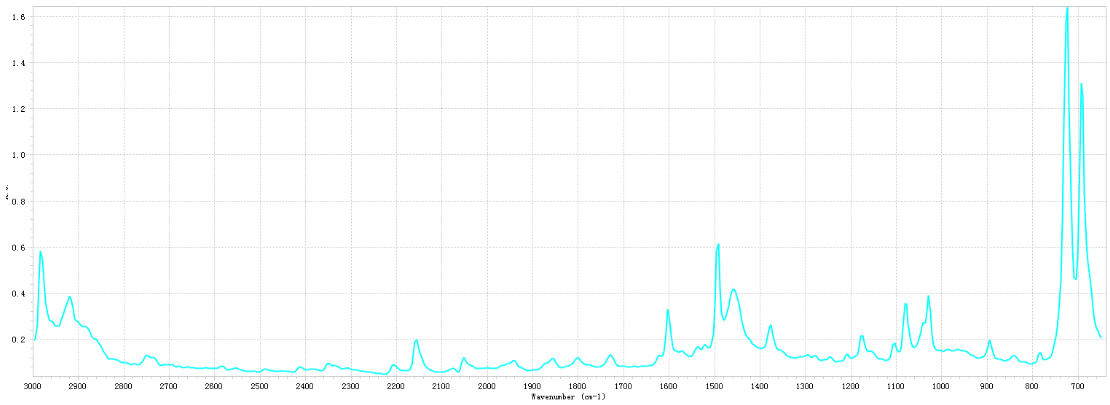
①The IR Spectra of $[Rh(COD)CL]_2$ (dissolved in toluene)



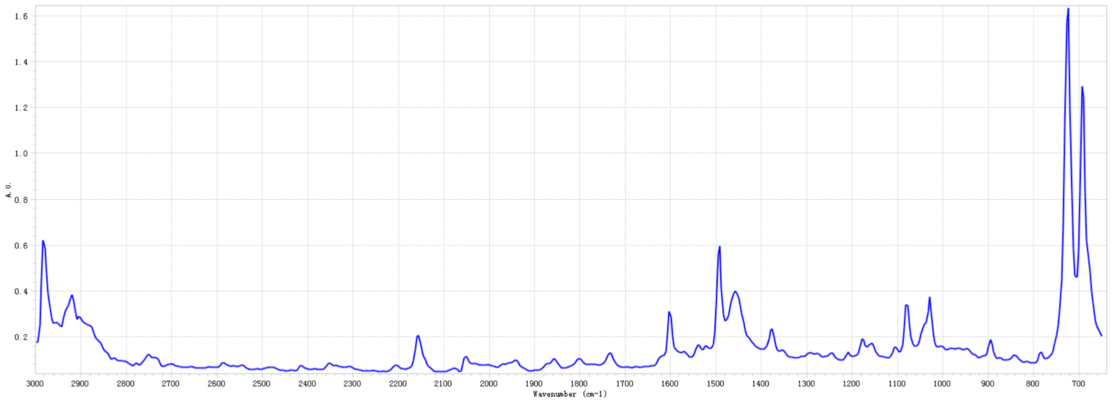
②The IR Spectra of **L7** (dissolved in toluene)



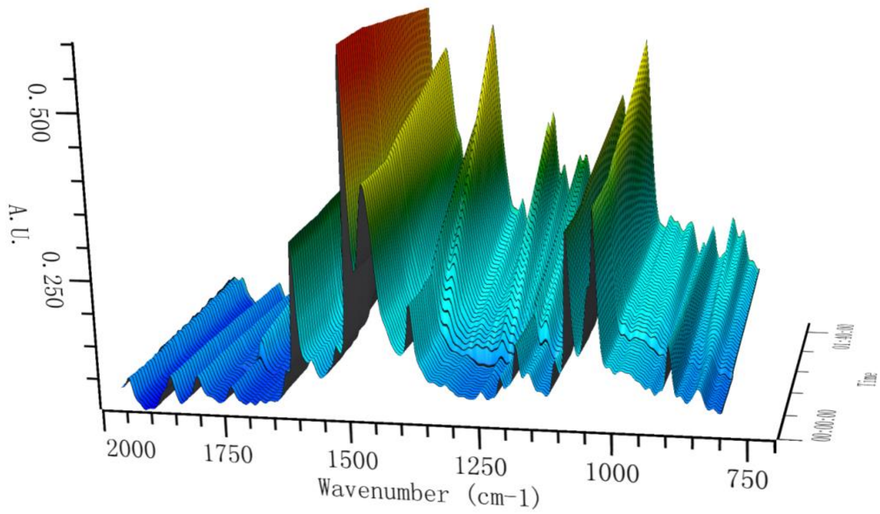
③ The IR Spectra of **4a** (dissolved in toluene)



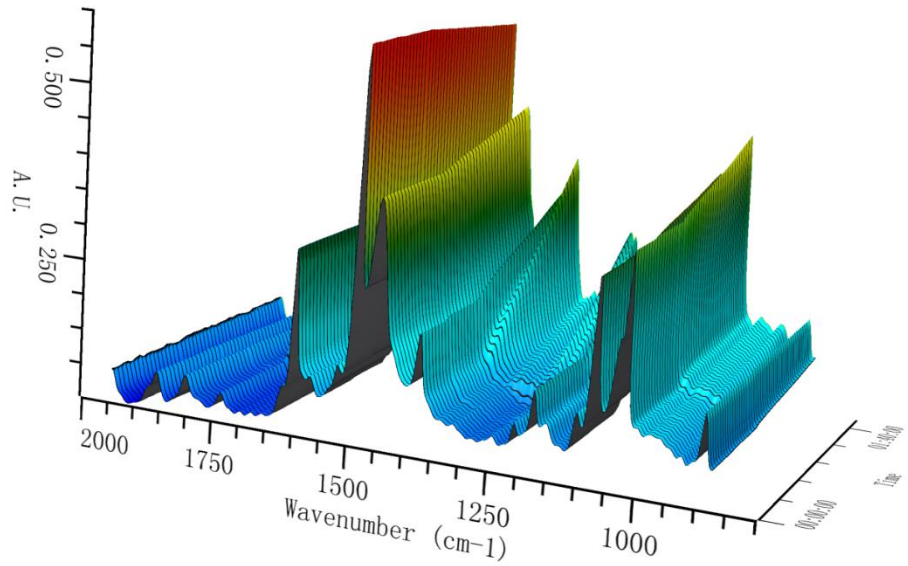
④ The IR Spectra of **4d** (dissolved in toluene)



⑤ The full Spectra of Figure 4B



⑥ The full Spectra of Figure 4C

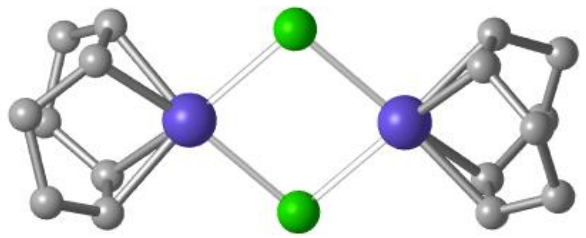


17. Computational Methods

All the calculations were carried out with the Gaussian 09 software program.[3] Geometry optimization and energy calculations were employed with B3LYP functional.[4] The LANL2DZ basis set[5] with ECP was used for Rhodiumand the 6-31G(d) basis set was used for all other atoms. And this is referred to as B1.Frequency analysis was handled at the same level to obtain the thermodynamic energy corrections. With the optimized geometries, single point energies were calculated in toluenesolvent using M06-2X [6]/SDD[7]-6-311G(d) level referred as B2 using SMD solvation model.[8] Natural bond orbital(NBO) analysis provided Natural population analysis charges. [7]

Coordinates of the Optimized Structures

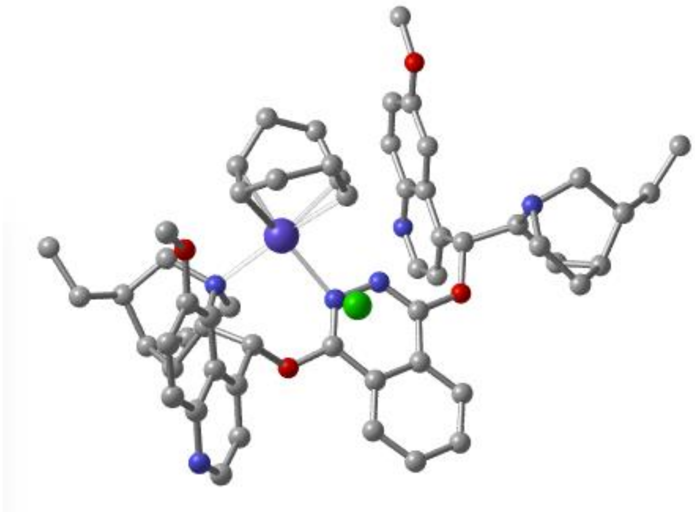
①$[Rh(COD)Cl]_2$



Elements	X	Y	Z

C	-3.37025400	1.38862300	0.63420200
C	-3.24154000	-1.42081400	0.77078600
C	-3.37018500	-1.38877100	-0.63373100
C	-3.24230600	1.42070000	-0.77039900
H	-2.83452300	2.15695400	1.18909300
H	-2.63103400	-2.22165200	1.18646400
H	-2.83441300	-2.15686000	-1.18891300
H	-2.63231900	2.22178200	-1.18637200
C	-4.51530500	0.70717600	1.37834400
C	-4.16650100	0.74633700	-1.76794500
C	-4.16549000	-0.74673200	1.76875700
C	-4.51576000	-0.70765100	-1.37735400
H	-5.08150000	-1.34178300	1.91205000
H	-3.65093900	-0.74155600	2.73646100
H	-4.74539900	1.27869100	2.28446000
H	-5.42328800	0.73464400	0.76615000
H	-5.08272300	1.34115600	-1.91085700
H	-3.65236700	0.74128100	-2.73587200
H	-4.74609500	-1.27923800	-2.28336100
H	-5.42346000	-0.73535700	-0.76475300
C	3.37006100	-1.38833700	0.63483000
C	3.24170600	1.42124200	0.77018100
C	3.37043900	1.38840700	-0.63430100
C	3.24210700	-1.42120200	-0.76975800
H	2.83438800	-2.15640800	1.19013900
H	2.63128900	2.22238600	1.18538700
H	2.83476400	2.15630700	-1.18984500
H	2.63213100	-2.22248700	-1.18534600
C	4.51521500	-0.70659900	1.37859600
C	4.16621600	-0.74729700	-1.76769500
C	4.16524500	0.74733100	1.76864000
C	4.51585200	0.70673900	-1.37767200
H	5.08117300	1.34242900	1.91230600
H	3.65023100	0.74228500	2.73610800
H	4.74552600	-1.27783800	2.28483200
H	5.42309000	-0.73412500	0.76625400
H	5.08228100	-1.34234200	-1.91070100
H	3.65182000	-0.74242600	-2.73549000
H	4.74626400	1.27791900	-2.28391700
H	5.42358700	0.73449800	-0.76512700
Rh	-1.85351600	0.00018600	-0.00011600
Rh	1.85356100	-0.00009500	-0.00013600
Cl	-0.00000200	1.72975200	-0.00120400
Cl	0.00014700	-1.72959200	-0.00060100

②The proposed model **4a**



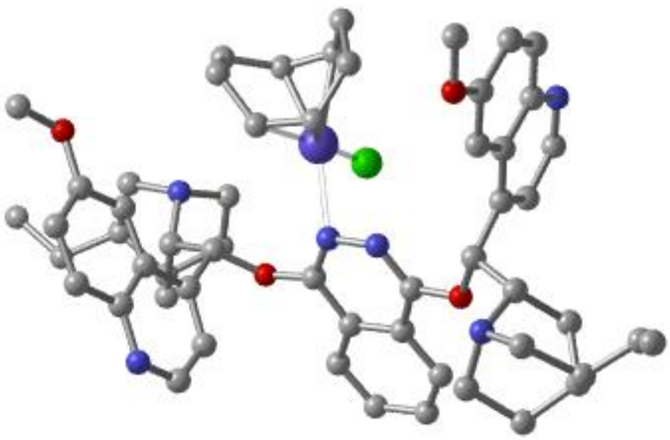
Elements	X	Y	Z
C	-0.91910300	-1.48610300	-1.27322100
N	-0.23298200	-0.43267300	-0.86567600
N	1.13146800	-0.51825100	-0.75473800
C	1.75725400	-1.61388700	-1.06814400
C	1.11310300	-2.80411600	-1.54917400
C	1.79093300	-3.98651800	-1.90451200
C	1.06466700	-5.08228000	-2.33563100
C	-0.34133000	-5.02114100	-2.40890100
C	-1.01617200	-3.86350700	-2.06665000
C	-0.29159000	-2.73268900	-1.63942700
H	2.87148100	-4.02383400	-1.83104800
H	1.57903600	-5.99945200	-2.60833300
H	-0.90121100	-5.89601300	-2.72662200
H	-2.09669300	-3.82265500	-2.08995100
O	3.10573300	-1.68673400	-0.95706200
C	3.83164800	-0.56015800	-0.42151400
N	4.65424200	2.37450500	-3.54907500
C	4.36924700	1.11957100	-3.82139900
C	4.08599800	0.13563200	-2.84110500
C	4.09951900	0.46984400	-1.50554800
C	4.41064600	1.82624100	-1.15653600
C	4.46403800	2.30463500	0.17485800
C	4.75595000	3.63280500	0.44239600
C	5.01860000	4.53553200	-0.62005700

C	4.97732200	4.08719400	-1.92226200
C	4.67655300	2.73778200	-2.23227300
O	4.76440200	3.98915300	1.76069100
C	5.11010800	5.32098900	2.10779000
H	3.22598500	-0.11795500	0.37107400
H	4.35579800	0.84191300	-4.87528900
H	3.85035700	-0.87677500	-3.15090200
H	4.28077000	1.64946400	1.01954000
H	5.25046500	5.57494900	-0.41758900
H	5.17510500	4.75784300	-2.75257600
H	5.07471800	5.36207900	3.19792800
H	6.12253500	5.57806100	1.76969900
H	4.39673300	6.04767600	1.69699300
N	4.92653800	-1.46556600	1.63820400
C	5.14322900	-1.06849200	0.22946500
C	5.89903000	-2.17907200	-0.56621400
C	6.27713100	-3.29937400	0.42776400
C	7.11155200	-2.73723100	1.60645300
C	6.24662000	-1.61412400	2.27690700
C	4.20927500	-2.75335300	1.74455500
C	4.97326900	-3.89205600	0.99966900
C	8.51760900	-2.26102000	1.20387100
C	9.41548300	-1.93426300	2.40428600
H	6.84989500	-4.07747000	-0.09246700
H	6.78850100	-1.76400300	-1.05256100
H	5.27107400	-2.59861600	-1.35856900
H	7.24346300	-3.55986300	2.32524000
H	6.07971800	-1.82160200	3.33970700
H	6.75780600	-0.64464800	2.21625400
H	4.11100600	-2.97620600	2.81229300
H	3.19622700	-2.63083700	1.35776800
H	5.20237200	-4.72219500	1.67947900
H	4.36120200	-4.30358500	0.18813400
H	8.44101300	-1.37477100	0.55814000
H	9.00089000	-3.04023700	0.59738600
H	10.40860300	-1.60389000	2.07899500
H	9.54940800	-2.81432900	3.04548400
H	8.98940100	-1.13644200	3.02427600
H	5.78516000	-0.18298900	0.28704000
O	-2.23036600	-1.40022500	-1.58708500
C	-3.21187400	-0.84659400	-0.67966700
N	-6.64807900	-3.53913600	-0.46079400
C	-5.79665000	-3.56820600	-1.46263800
C	-4.65796700	-2.73143100	-1.56327900

C	-4.37276900	-1.82540400	-0.56476600
C	-5.25752600	-1.77624200	0.56199100
C	-5.07416300	-0.91912100	1.67055500
C	-5.97543300	-0.90696400	2.72099500
C	-7.10379600	-1.76644700	2.70418400
C	-7.29393800	-2.62086100	1.64085500
C	-6.39086800	-2.65754800	0.54958000
O	-5.70116200	-0.03389000	3.73538100
C	-6.50160600	-0.07602000	4.90534200
H	-2.72130900	-0.75268800	0.29687200
H	-6.00770300	-4.28026100	-2.26058300
H	-4.02187900	-2.80399000	-2.43798900
H	-4.19534300	-0.29328000	1.75187300
H	-7.81217000	-1.76571900	3.52493900
H	-8.14243800	-3.29697200	1.60866100
H	-6.06316700	0.65033300	5.59233800
H	-7.54224000	0.20890300	4.69868400
H	-6.48433800	-1.06959000	5.37150900
N	-2.68413300	1.58938000	-1.27985700
C	-3.73483700	0.50814600	-1.19654900
C	-4.52604900	0.45096200	-2.52742500
C	-4.35653800	1.79181300	-3.26725700
C	-4.55478100	2.98210900	-2.30417800
C	-3.42623900	2.89190300	-1.22466800
C	-1.95930800	1.56132400	-2.60033900
C	-2.91279500	1.85491300	-3.78873100
C	-5.97326100	3.07867100	-1.71061500
C	-6.24780600	4.40607700	-0.99227300
H	-5.06841000	1.86066800	-4.09801300
H	-5.57730300	0.23036000	-2.32163700
H	-4.15304200	-0.35986000	-3.16351200
H	-4.38985500	3.90006700	-2.88617900
H	-2.68556200	3.68404900	-1.36028800
H	-3.84341300	2.99720300	-0.22022200
H	-1.15476300	2.29861600	-2.53048900
H	-1.49583400	0.58562800	-2.70221400
H	-2.70852600	2.84030600	-4.22510300
H	-2.75813000	1.11388700	-4.58146400
H	-6.15564900	2.24670200	-1.01745700
H	-6.69958100	2.95888800	-2.52632700
H	-7.26995600	4.43552600	-0.59941900
H	-6.12719100	5.25612200	-1.67508500
H	-5.56844300	4.56285700	-0.14566900
H	-4.41221800	0.84710800	-0.40668800

C	0.24630700	0.73424200	1.98343300
C	-2.25879600	2.04742100	1.92333300
C	-1.54592000	3.15256500	1.41927600
C	0.86904000	1.72643700	1.22438300
H	0.42439900	-0.30791000	1.73377800
H	-3.30046000	1.95218300	1.61032500
H	-2.08027500	3.82357700	0.75295000
H	1.54248100	1.38846700	0.44269200
C	-0.42498800	0.94674300	3.32879600
C	0.98578400	3.19560400	1.57473200
C	-1.93014700	1.25248100	3.17269700
C	-0.33590500	3.78365200	2.10239400
H	-2.32014800	1.77607100	4.06072200
H	-2.45614200	0.29541700	3.11038000
H	-0.32260800	0.02235600	3.90435800
H	0.08406100	1.73867300	3.88989300
H	1.80699100	3.35583000	2.29037500
H	1.27491100	3.72916000	0.66169100
H	-0.35034800	4.86573800	1.92503900
H	-0.41262700	3.65580500	3.18686900
Rh	-1.06890800	1.33153600	0.29106000
Cl	-1.39155900	-2.28256500	1.70656900

③The proposed model **4b**



Elements	X	Y	Z

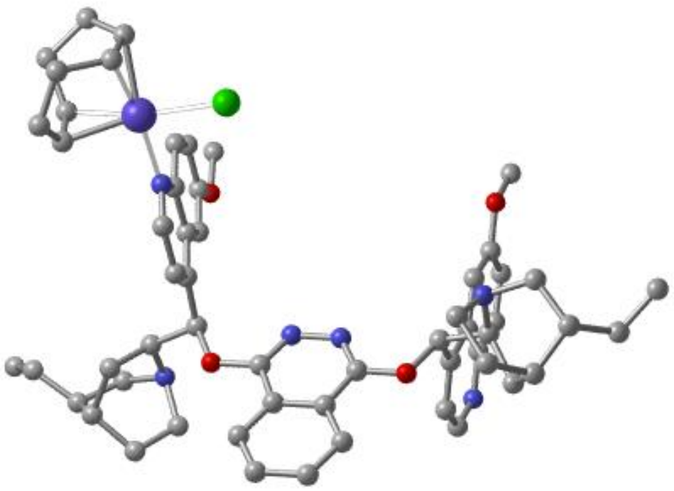
C	1.07465500	1.72458700	-0.56931800
N	0.37243000	0.62712700	-0.38305100
N	-0.99916100	0.68114800	-0.31272800
C	-1.61640700	1.80319300	-0.54406800
C	-0.95204800	3.03726900	-0.87130100
C	-1.62042100	4.24184200	-1.16827800
C	-0.88445600	5.37924300	-1.44989300
C	0.52470700	5.33976900	-1.43933200
C	1.19397400	4.16547500	-1.14474900
C	0.45889000	2.99500800	-0.85916100
H	-2.70407600	4.26017300	-1.17474000
H	-1.39460700	6.30963300	-1.68243600
H	1.08919000	6.23924900	-1.66772100
H	2.27659700	4.12503200	-1.14800500
O	-2.96462300	1.87322500	-0.47021500
C	-3.71846400	0.70013800	-0.08675000
N	-4.40231600	-1.93602500	-3.49924100
C	-4.04583600	-0.67896400	-3.64643100
C	-3.80284600	0.21039800	-2.56890900
C	-3.92528400	-0.22932700	-1.27099000
C	-4.30377800	-1.59710900	-1.05758800
C	-4.46172400	-2.18565400	0.22086400
C	-4.83416100	-3.51434800	0.35373000
C	-5.06361600	-4.31061500	-0.79748500
C	-4.91120900	-3.75763100	-2.05013300
C	-4.53257700	-2.40308800	-2.22234100
O	-4.95798000	-3.97658100	1.63221900
C	-5.33363400	-5.32913700	1.83618400
H	-3.15778700	0.18756000	0.69819500
H	-3.93674400	-0.31930900	-4.66870400
H	-3.50924100	1.23244600	-2.78066600
H	-4.29386600	-1.61985600	1.13089700
H	-5.35448900	-5.35040800	-0.70154700
H	-5.07813000	-4.34590600	-2.94699600
H	-5.36669600	-5.46812900	2.91839600
H	-6.32475600	-5.54390100	1.41498300
H	-4.60056600	-6.02433900	1.40604900
N	-4.95023100	1.58003800	1.92566800
C	-5.06913100	1.16215800	0.51007000
C	-5.83716400	2.22745700	-0.32965500
C	-6.45681800	3.24433200	0.65416600
C	-7.28912500	2.52774500	1.74794800
C	-6.30533300	1.57138400	2.51003300

C	-4.39849600	2.94337700	2.05572000
C	-5.30317000	3.99797100	1.34499300
C	-8.53674300	1.81045000	1.20265100
C	-9.48817300	1.32096400	2.30184900
H	-7.09529300	3.94946000	0.10764400
H	-6.60319300	1.74943500	-0.94890400
H	-5.16327300	2.75572900	-1.01246400
H	-7.64114300	3.30325300	2.44446400
H	-6.21251500	1.85512700	3.56443300
H	-6.67363500	0.53818200	2.48903900
H	-4.31067900	3.15562400	3.12707500
H	-3.38898800	2.94956200	1.64280500
H	-5.70474300	4.72357000	2.06373700
H	-4.72939500	4.56837700	0.60342800
H	-8.23449000	0.95733800	0.57909000
H	-9.08146400	2.49595800	0.53790100
H	-10.36462600	0.82162800	1.87346500
H	-9.84645500	2.15838300	2.91358500
H	-8.99877400	0.60656800	2.97464400
H	-5.67267800	0.24941300	0.54273900
O	2.42150300	1.74191800	-0.53729100
C	3.18359500	0.83580600	0.29870900
N	2.68314700	1.85746000	4.52659700
C	2.37918100	2.69587600	3.56093900
C	2.51661600	2.40552300	2.18022700
C	2.98944400	1.17741900	1.77172200
C	3.34853200	0.23283700	2.79291800
C	3.87384400	-1.05439700	2.52816100
C	4.19570400	-1.92125300	3.56051700
C	4.00878000	-1.52788800	4.90994900
C	3.50564800	-0.27663800	5.18977200
C	3.16637500	0.63437000	4.15894700
O	4.68609200	-3.13949300	3.18622700
C	5.02757600	-4.08060700	4.19287400
H	2.85289200	-0.18539900	0.08631000
H	1.99952800	3.67136000	3.86422200
H	2.24225900	3.16350300	1.45612300
H	4.04229100	-1.39628500	1.51352600
H	4.25735000	-2.20099400	5.72235200
H	3.35489200	0.05128800	6.21338500
H	5.38689700	-4.96414900	3.66251300
H	5.82492500	-3.70312700	4.84620500
H	4.15765100	-4.35505500	4.80365200
N	5.03474800	0.08238400	-1.24047000

C	4.68140400	0.94142900	-0.09078300
C	5.21738900	2.39540500	-0.27776200
C	6.08384500	2.42035600	-1.55486200
C	7.20687900	1.35495000	-1.48882800
C	6.50581200	-0.03172400	-1.27549300
C	4.57966300	0.65934000	-2.52646700
C	5.17194800	2.08502500	-2.75092200
C	8.28863500	1.65735500	-0.43775800
C	9.50929200	0.73316900	-0.53412900
H	6.52755600	3.41612600	-1.68097500
H	5.79089600	2.70814600	0.60164800
H	4.39699800	3.11091400	-0.39231200
H	7.70263300	1.35315100	-2.47092000
H	6.76393000	-0.73403100	-2.07560600
H	6.83104100	-0.48761100	-0.33123000
H	4.90585900	-0.02934800	-3.31339900
H	3.49006500	0.66499400	-2.55357800
H	5.74470600	2.13262500	-3.68573800
H	4.36809600	2.82728900	-2.83094300
H	7.85930700	1.58450700	0.57166200
H	8.61969100	2.69935100	-0.55379400
H	10.25923600	0.98621700	0.22408000
H	9.98803900	0.81533700	-1.51789500
H	9.23500100	-0.31837400	-0.38766100
H	5.20702500	0.49335000	0.75823300
C	0.76562500	-3.20136000	-2.41379400
C	-0.16309900	-2.52503600	0.17116700
C	1.19167500	-2.47915300	0.54023700
C	2.10346700	-2.88665100	-2.11792200
H	0.40696600	-2.90396900	-3.39632700
H	-0.83326500	-1.82611300	0.67027200
H	1.46010600	-1.76062600	1.31131900
H	2.66767800	-2.38728300	-2.90327500
C	-0.05581600	-4.26792900	-1.69770100
C	2.94868700	-3.47846200	-1.00690000
C	-0.86394700	-3.68123200	-0.51828300
C	2.18540200	-3.61864400	0.32997100
H	-1.11180100	-4.46966200	0.21104500
H	-1.81970300	-3.30513000	-0.89633200
H	-0.74912800	-4.72324000	-2.41400200
H	0.60017200	-5.07608100	-1.35552900
H	3.36965900	-4.44909800	-1.31738200
H	3.80076400	-2.80282400	-0.86630300
H	2.90534400	-3.63010300	1.15562900

H	1.66201800	-4.58006400	0.37470400
Rh	0.85550500	-1.34290700	-1.30417600
Cl	1.00460700	-0.07557500	-3.36818200

④ The proposed model **4c**



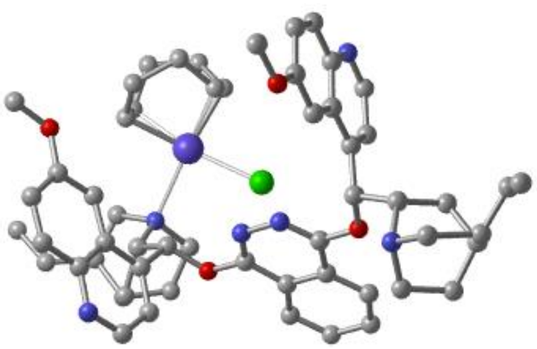
Elements	X	Y	Z
C	-3.03010100	-0.96058100	-1.44475600
N	-2.30514200	-0.85961100	-0.36570600
N	-1.04798200	-1.39452600	-0.33936200
C	-0.58516300	-2.02340200	-1.38114800
C	-1.30679000	-2.19229600	-2.61447100
C	-0.80571300	-2.86781600	-3.74728900
C	-1.58654300	-2.96718900	-4.88479800
C	-2.87743400	-2.39918000	-4.92067800
C	-3.38431300	-1.73428400	-3.81852500
C	-2.60165600	-1.62327500	-2.64999200
H	0.18733000	-3.30154300	-3.71150900
H	-1.20419700	-3.48623400	-5.75927600
H	-3.47692000	-2.48592600	-5.82251400
H	-4.37522000	-1.29478600	-3.83746900
O	0.65680600	-2.58020500	-1.34306100
C	1.43021900	-2.42842100	-0.13414400
N	3.71946500	1.27299000	-0.22965700
C	3.21279500	0.73521800	-1.32715200
C	2.44636100	-0.44782200	-1.32810300

C	2.18300600	-1.10836700	-0.14930100
C	2.67854700	-0.53356800	1.06686500
C	2.44306500	-1.09606900	2.34311100
C	2.92478700	-0.48998100	3.49198400
C	3.66715700	0.71453700	3.39981000
C	3.91548600	1.27758500	2.16799300
C	3.44320000	0.67663600	0.97791600
O	2.63659800	-1.11521300	4.66604300
C	3.04542200	-0.51145200	5.88468500
H	0.74024700	-2.45046500	0.71065900
H	3.42025000	1.25327400	-2.25768200
H	2.06890600	-0.82898100	-2.26949500
H	1.86596700	-2.00628800	2.45830500
H	4.03386700	1.20764300	4.29249700
H	4.46288300	2.21112600	2.08198100
H	2.68358800	-1.16981000	6.67627300
H	4.13850800	-0.43361600	5.95260500
H	2.60146600	0.48419300	6.01148500
N	1.74340700	-4.80043500	0.62087900
C	2.40047000	-3.62855000	0.00081500
C	3.15250500	-4.02738300	-1.30636000
C	3.13380900	-5.56806000	-1.41137400
C	3.69806000	-6.22172700	-0.12450200
C	2.79874500	-5.73036500	1.06353400
C	0.86813900	-5.51002500	-0.33312900
C	1.66704900	-6.01408700	-1.57628100
C	5.19733400	-5.95726800	0.09805500
C	5.80647200	-6.80745400	1.22017300
H	3.72558900	-5.88828800	-2.27798100
H	4.17773600	-3.64213000	-1.29399900
H	2.66345000	-3.60496600	-2.19012700
H	3.57519200	-7.30926400	-0.23684300
H	2.30900400	-6.57197600	1.56590600
H	3.40268600	-5.21468200	1.82079000
H	0.41234400	-6.34577600	0.20930200
H	0.05857000	-4.84126000	-0.62860000
H	1.61338900	-7.10660500	-1.66411800
H	1.25047000	-5.59732300	-2.50189800
H	5.35885400	-4.89333600	0.32238700
H	5.73957500	-6.15768800	-0.83705800
H	6.87369000	-6.59208800	1.34560900
H	5.70525700	-7.87781300	1.00177000
H	5.31755700	-6.61969000	2.18361800
H	3.13895600	-3.30299700	0.74134400

O	-4.27301800	-0.42108100	-1.48175700
C	-4.76892600	0.23373900	-0.29003500
N	-6.39515800	-2.69299700	2.51505500
C	-6.24596600	-2.95373800	1.23472400
C	-5.70956900	-2.04012200	0.29382000
C	-5.29885100	-0.79045700	0.70102500
C	-5.43358800	-0.46029600	2.09052800
C	-5.04739600	0.78127200	2.64865400
C	-5.20873100	1.03520700	4.00140000
C	-5.76725400	0.04730500	4.85278200
C	-6.14581200	-1.16930200	4.32967200
C	-5.99529300	-1.46198900	2.95180600
O	-4.80350700	2.26489300	4.43194900
C	-4.91330800	2.57826100	5.81045900
H	-3.94003900	0.78853800	0.15258500
H	-6.56593500	-3.94003100	0.89853600
H	-5.61941800	-2.33582300	-0.74586800
H	-4.60755300	1.56406800	2.04077400
H	-5.89552100	0.23949700	5.91191700
H	-6.57226900	-1.94312200	4.96023300
H	-4.51936500	3.59070900	5.91678500
H	-5.95749800	2.56077400	6.15048400
H	-4.32023400	1.89380500	6.43142500
N	-5.30563600	2.51865400	-1.19696700
C	-5.86681800	1.24419600	-0.69620900
C	-6.95693500	0.69081200	-1.66291700
C	-7.27285100	1.79227200	-2.69884600
C	-7.62379300	3.13105000	-2.00142900
C	-6.37461600	3.53324800	-1.14063600
C	-4.84263600	2.40857000	-2.59449900
C	-6.00908300	2.01307000	-3.55401300
C	-8.93174600	3.08176200	-1.19205000
C	-9.40940900	4.46203000	-0.72313000
H	-8.10970600	1.47712400	-3.33472400
H	-7.85251400	0.39622600	-1.10578400
H	-6.60433800	-0.20318500	-2.18870600
H	-7.76352600	3.87968900	-2.79552000
H	-5.94714500	4.48316500	-1.48048200
H	-6.65495200	3.66791900	-0.08841000
H	-4.41457900	3.37850800	-2.87055400
H	-4.03457900	1.67747100	-2.63500500
H	-6.19140900	2.79722100	-4.29996600
H	-5.76591200	1.09671000	-4.10716200
H	-8.80608300	2.42672500	-0.31860600

H	-9.71769200	2.62161100	-1.80797200
H	-10.34476800	4.38668500	-0.15692300
H	-9.58813800	5.12704000	-1.57729800
H	-8.67077000	4.94881500	-0.07508400
H	-6.34699300	1.50864900	0.25217300
C	6.80538100	2.06239400	0.00846400
C	6.08879800	4.81620200	0.08813700
C	6.04362200	4.73533000	-1.30699800
C	6.50270200	1.93742900	-1.36227100
H	6.56864100	1.20638000	0.63901500
H	5.36058000	5.47112100	0.56147000
H	5.27030100	5.31806900	-1.80185000
H	6.07518900	0.98600200	-1.68040000
C	7.84964200	3.02126000	0.57694800
C	7.10847800	2.74745700	-2.49463300
C	7.24364300	4.38799400	0.97333100
C	7.19625300	4.25853900	-2.18274300
H	8.02503800	5.16493100	0.98961700
H	6.86183500	4.32310200	1.99914500
H	8.31336000	2.56581600	1.45986500
H	8.66024700	3.15732700	-0.14766100
H	8.10050500	2.35306800	-2.76939400
H	6.47090200	2.60527200	-3.37562900
H	7.18687300	4.82069800	-3.12357700
H	8.15107500	4.49487700	-1.70066800
Rh	4.92564500	3.06204600	-0.43888300
Cl	2.90238500	4.35005900	-0.29845700

⑤The proposed model **4d**



Elements	X	Y	Z
C	0.30924000	2.06160300	0.55305300
N	-0.28207300	0.92664300	0.78885900
N	-1.61203800	0.78128500	0.51274500
C	-2.28520800	1.78650700	0.02964200
C	-1.73127800	3.09109600	-0.22025800
C	-2.46783700	4.18882600	-0.71299300
C	-1.83625100	5.40343500	-0.90967100
C	-0.46283400	5.55139200	-0.62364100
C	0.27429200	4.48370400	-0.14507200
C	-0.35336600	3.23806100	0.06088300
H	-3.52202100	4.06476000	-0.93390800
H	-2.39995100	6.25095000	-1.28972700
H	0.01879300	6.51167300	-0.78600000
H	1.33139600	4.58819200	0.07115600
O	-3.60501200	1.64101700	-0.25995200
C	-4.21567000	0.35572100	-0.01508900
N	-3.29260600	-2.46239800	-3.22455100
C	-3.17452900	-1.16083600	-3.37601900
C	-3.45408000	-0.21183100	-2.36097800
C	-3.86832500	-0.63255200	-1.11775300
C	-4.00426600	-2.04417800	-0.89920900
C	-4.41289200	-2.61779900	0.32857800
C	-4.52936200	-3.99108300	0.47041300
C	-4.23810200	-4.84975700	-0.62009800
C	-3.83337100	-4.31140500	-1.82196200
C	-3.70350400	-2.91220600	-2.00147800
O	-4.93303500	-4.43491700	1.69803700
C	-5.05736400	-5.83033500	1.91179900
H	-3.84150700	-0.01473700	0.94155100
H	-2.84074700	-0.81223300	-4.35290000
H	-3.32287400	0.84399800	-2.56971300
H	-4.63910500	-2.00319700	1.19282100
H	-4.32771100	-5.92516700	-0.51652500
H	-3.60141000	-4.94655800	-2.67126000
H	-5.38171100	-5.94487800	2.94796400
H	-5.80857300	-6.27960100	1.24819500
H	-4.09976400	-6.35059700	1.77521400
N	-6.14943100	1.02930800	1.44868600
C	-5.74496900	0.55170900	0.10593400

C	-6.39522100	1.41523700	-1.01704800
C	-7.45095500	2.33088600	-0.35883300
C	-8.44460600	1.50963900	0.50157100
C	-7.59443200	0.77623100	1.59767100
C	-5.91170200	2.47675300	1.61699700
C	-6.71054700	3.31444200	0.56938300
C	-9.33096700	0.55725400	-0.31991900
C	-10.48076800	-0.05631000	0.48942600
H	-8.00044800	2.88220900	-1.13212800
H	-6.84404100	0.77552400	-1.78431400
H	-5.64730100	2.03787400	-1.51922600
H	-9.11413200	2.23012500	0.99480100
H	-7.88531600	1.09519600	2.60507100
H	-7.75136500	-0.30864300	1.54872300
H	-6.20944200	2.73617200	2.63933300
H	-4.84039600	2.66426600	1.53593300
H	-7.42918200	3.98236400	1.06153900
H	-6.03567500	3.94882300	-0.01927700
H	-8.71760500	-0.24985900	-0.74424700
H	-9.74920200	1.10525300	-1.17627800
H	-11.08672500	-0.72817400	-0.12918300
H	-11.14417900	0.72325300	0.88442300
H	-10.11121500	-0.63821800	1.34228600
H	-6.15229300	-0.46290100	0.04165100
O	1.64283700	2.18700700	0.79712400
C	2.35542500	1.00019500	1.17824000
N	1.92726600	0.33265600	5.48728400
C	1.65900100	1.48659400	4.91598800
C	1.76802700	1.73071100	3.52520800
C	2.16764000	0.72607200	2.67105400
C	2.44453700	-0.55783500	3.24503900
C	2.83197100	-1.69049600	2.49275600
C	3.09739400	-2.90283800	3.10786800
C	2.98072700	-3.03015500	4.51536100
C	2.59361600	-1.94272300	5.26670100
C	2.31334200	-0.68916900	4.66878400
O	3.46686000	-3.92768400	2.28226200
C	3.69844600	-5.20941300	2.84511200
H	1.96668300	0.16641600	0.58617200
H	1.34173500	2.29406900	5.57558400
H	1.52917000	2.71484700	3.13852300
H	2.90648700	-1.64061900	1.41387700
H	3.18597800	-3.97537200	5.00457500
H	2.48805100	-2.01474300	6.34457800

H	3.95009600	-5.86110600	2.00641900
H	4.53634700	-5.19628500	3.55466400
H	2.80410400	-5.59853700	3.34893000
N	4.22302900	1.24187500	-0.60375800
C	3.85605500	1.19901400	0.86346400
C	4.48451300	2.40649900	1.61472700
C	5.55179800	3.06299600	0.72400800
C	6.53445600	2.00645600	0.18003800
C	5.69854100	0.99310500	-0.66684700
C	3.98445200	2.60699500	-1.18574100
C	4.82836900	3.69837200	-0.47225400
C	7.38634500	1.32899100	1.26977200
C	8.53377200	0.47815000	0.71084800
H	6.09907300	3.82545700	1.29149600
H	4.90449100	2.07025100	2.56755500
H	3.71596700	3.14883300	1.85310800
H	7.22935800	2.52531900	-0.49579600
H	5.97864400	1.04123300	-1.72197800
H	5.87798000	-0.02894600	-0.32252800
H	4.23192300	2.53680300	-2.24751900
H	2.91943700	2.80206500	-1.12690400
H	5.55672100	4.14220900	-1.16245300
H	4.17877900	4.51249500	-0.12795400
H	6.74964600	0.70450500	1.91161600
H	7.80564500	2.10737400	1.92238000
H	9.11788300	0.02437200	1.51914800
H	9.21699900	1.08726100	0.10612900
H	8.16741100	-0.33691400	0.07482900
H	4.32724000	0.28099600	1.22751000
C	1.81790000	-1.86985100	-2.88464600
C	4.07547000	-2.05949500	-1.20959800
C	4.81333600	-1.67505600	-2.34398400
C	2.52115900	-1.24480800	-3.92838200
H	0.81856200	-1.49192100	-2.68357600
H	4.48098000	-1.77393900	-0.23801900
H	5.71656200	-1.09569800	-2.17776100
H	1.99707500	-0.45308700	-4.45779700
C	2.12725400	-3.26156700	-2.34734900
C	3.73780800	-1.79288800	-4.64439800
C	3.10399500	-3.22601300	-1.15091800
C	4.77269000	-2.40892300	-3.68109700
H	3.65636000	-4.17627300	-1.07346600
H	2.53060100	-3.14375600	-0.22321900
H	1.19053000	-3.73411200	-2.03264700

H	2.52576800	-3.88775200	-3.15355200
H	3.43548600	-2.52334100	-5.41202000
H	4.20319200	-0.95911500	-5.18330600
H	5.76634600	-2.36922500	-4.14269700
H	4.56108100	-3.47068600	-3.51493800
Rh	3.10932800	-0.32750500	-2.06328500
Cl	1.38343100	1.30688400	-2.54601200

18. Supplementary References

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