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Supporting Information

Dirhodium Coordination Polymers for Asymmetric Cyclopropanation of Diazooxindoles with Olefins: Synthesis and Spectroscopic Analysis

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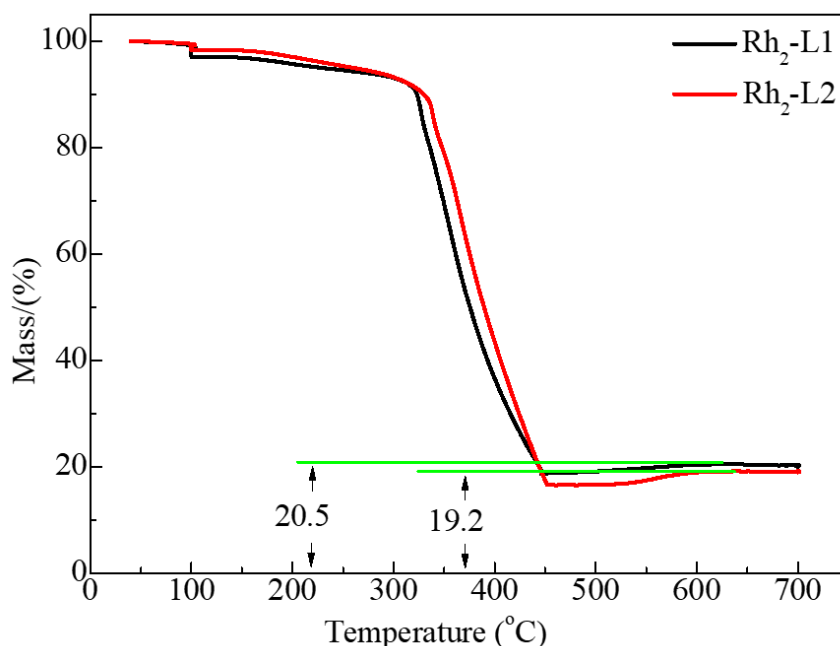
1. Thermogravimetric analysis

Fig. S1. TG spectra of Rh2-L1 and Rh2-L2 complex.

According to TG analysis, the mass of Rh_2-Ln (n=1, 2) slightly decreased at 100 °C. This indicates the presence of small amounts of solvent and water in the catalysts that are removed from the samples at a temperature of 100 °C, at which the samples are treated in the TG for 1 h. For both samples, the mass then decreases up to a temperature of ca. 450 °C, which refers to the complete decomposition of the organic ligand systems. The rise of the curve between 500 °C to 650 °C refers to the formation of rhodium (III) oxide at high temperature in oxygen atmosphere. The Rh contents of catalysts (Rh_2-Ln) (n=1-2) were determined following the procedure of Kaskel and co-workers.[1] Based on the residual mass at 650 °C, the rhodium (III) oxide contents of the samples are 20.5% and 19.2%, respectively.

It has to be noted that this analysis does not consider the weight loss due to removal of the solvent molecules at 100 °C. Assuming a weight loss of 4% due to solvent molecules the corrected rhodium (III) oxide contents of the samples are 21.4% and 20.0%. Since the catalysts were used as obtained in the catalytic reaction, and these corrected values do not significantly differ from the values calculated from the uncorrected residual mass at 650 °C, all Rh_2 contents in the manuscript are based on the non-corrected rhodium (III) oxide contents.

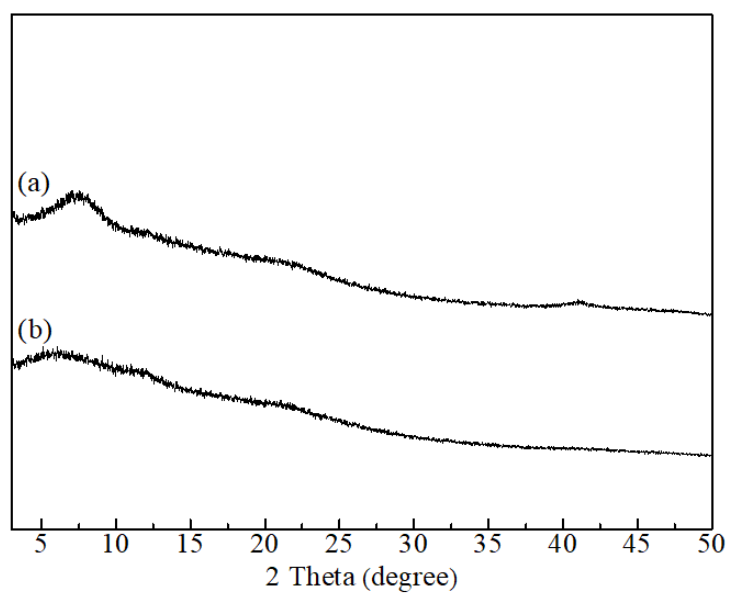## 2. XRD

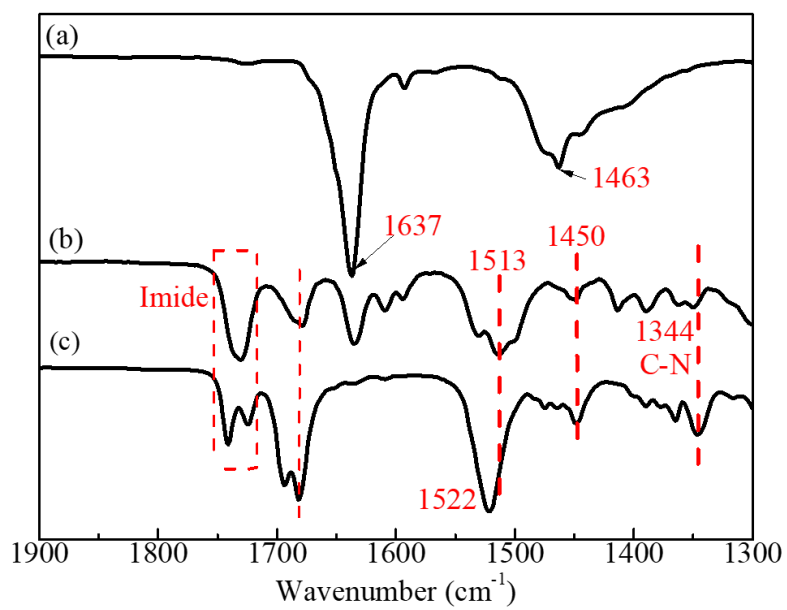**Fig. S2.** XRD patterns of the coordination polymers Rh_2-L1 (a) and Rh_2-L2 (b).

3. FT-IR

Fig. S3. FT-IR spectra of $Rh_2(TFA)_4$ (a), H_2L2 (b) and Rh_2-L2 (c) complex.

4. Quantitative Analysis of solid-state ¹⁹F NMR

The contents of fluorine in Rh$_2$-Ln (n=1, 2) polymers were calculated from solid-state ¹⁹F NMR measurements in which BaF$_2$ was employed as standard. The ¹⁹F signal for the trifluoroacetate groups in Rh$_2$-Ln (n=1, 2) polymers appear at around -74 ppm. Other signals in the ¹⁹F NMR spectra are attributed to BaF$_2$. The integral area of the NMR signal is proportional to the number of NMR active nuclei in the sample. Thus, the fluorine content in the Rh$_2$-Ln (n=1, 2) polymers were calculated according to the procedure described in the following. The initial amounts of samples for measuring ¹⁹F MAS NMR are shown in Table S1. First, a mixture of the coordination polymer Rh$_2$-L1 or Rh$_2$-L2, respectively, and BaF$_2$ as a standard was prepared. A specific amount of this mixture (called sample) was then filled in the rotor for measurements.

Table S1. Initial amounts of samples

Rh₂-L1		Rh₂-L2	
Masses (m) to prepare the mixtures of coordination polymer and BaF₂			
Rh₂-L1	0.0352 g	Rh₂-L2	0.0486 g
BaF₂	0.0232g	BaF₂	0.0100 g
Rh₂-L1+BaF₂	0.0584 g	Rh₂-L2+BaF₂	0.0586 g
Masses (m) to prepare rotors for NMR measurements			
Rotor+cap	0.5163 g	Rotor+cap	0.5163 g
Rotor+cap+sample	0.5348 g	Rotor+cap+sample	0.5367 g
sample	0.0185 g	sample	0.0204 g

<u>**Rh₂-L1:**</u>

The mass of BaF$_2$ in the sample is:

$$m_{\text{BaF}_2} = BaF_2 \; ratio \; (\%) \times m_{sample} = \frac{0.0232 \text{ g}}{0.0584 \text{ g}} \times 0.0185 \text{ g} = 0.0073 \text{ g}$$

The mass of fluorine in BaF$_2$ in the sample is:

$$m_{F(\text{BaF}_2)} = m_{\text{BaF}_2} \times \frac{2 \times M_F}{M_{BaF_2}} = 0.0073 \text{ g} \times \frac{2 \times 18.998 \text{ g·mol}^{-1}}{175.3238 \text{ g·mol}^{-1}} = 0.0016 \text{ g}$$

The mass of fluorine in Rh$_2$-L1 in the sample is:

$$\frac{Area_{F(\text{BaF}_2)}}{Area_{F(Rh_2-L1)}} = \frac{m_{F(\text{BaF}_2)}}{m_{F(Rh_2-L1)}} \rightarrow m_{F(Rh_2-L1)} = \frac{Area_{F(Rh_2-L1)}}{Area_{F(\text{BaF}_2)}} \times m_{F(\text{BaF}_2)}$$

$$m_{F(Rh_2-L1)} = \frac{1.664 \cdot 10^8}{5.307 \cdot 10^9} \times 0.0016 \text{ g} = 5.0 \cdot 10^{-5} \text{ g}$$

In the sample, the overall mass of Rh_2-L1 is:

$$m_{Rh_2-L1} = m_{sample} - m_{BaF_2} = 0.0185 \text{ g} - 0.0073 \text{ g} = 0.0112 \text{ g}$$
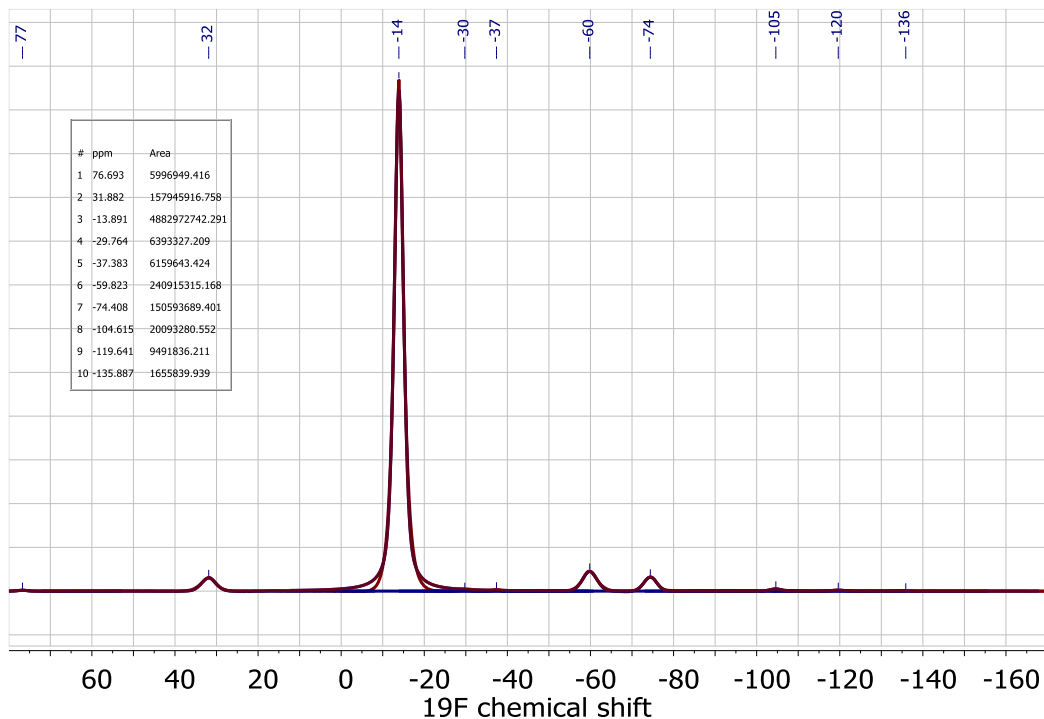
The fluorine ratio in Rh_2-L1 is:

$$\frac{m_{F(Rh_2-L1)}}{m_{Rh_2-L1}} \times 100\% = \frac{5.0 \times 10^{-5} \text{ g}}{0.0112 \text{ g}} \times 100\% \cong 0.45\%$$

The fluorine content in Rh_2-L1 is:

$$\text{Florine content (mol·g}^{-1}) = \frac{m_{F(Rh_2-L1)}}{m_{Rh_2-L1} \times M_F} = \frac{5.0 \times 10^{-5} \text{ g}}{0.0112 \text{ g} \times 18.998 \text{ g·mol}^{-1}}$$

$$\approx 2.4 \cdot 10^{-4} \text{ mol·g}^{-1}$$

Thus, the fluorine content in the Rh_2-L1 coordination polymer is 0.24 mmol/g and consequently the content of trifluoroacetate groups is 0.08 mmol/g since each trifluoroacetate group contains three fluorine atoms.


#	ppm	Area
1	76.693	5996949.416
2	31.882	157945916.758
3	-13.891	4882972742.291
4	-29.764	6393327.209
5	-37.383	6159643.424
6	-59.823	240915315.168
7	-74.408	150593689.401
8	-104.615	20093280.552
9	-119.641	9491836.211
10	-135.887	1655839.939

^{19}F MAS NMR of Rh_2-L1.

Taking the Rh_2 content for Rh_2-L1 into account (0.81 mmol/g), the Rh_2/TFA ratio is 0.81/0.08 = 10.1 for this catalyst. This means that only every 10th dirhodium unit contains one remaining TFA group, and thus overall, only $100 / (4 \cdot 10.1) \approx 2$ % of the TFA groups in the catalyst are preserved while 98% of the TFA groups are replaced during the formation process of the coordination polymer Rh_2-L1.

Rh_2-L2:

The analysis for Rh_2-L2 was performed in the same way. Thus, the content of fluorine in the Rh_2-L2 coordination polymer is 0.53 mmol/g and consequently the content of trifluoroacetate groups is 0.18 mmol/g.

Taking the Rh_2 content for Rh_2-L2 into account (0.81 mmol/g), the Rh_2/TFA ratio is 0.76/0.18 = 4.2 for this catalyst. This means that only every 4th dirhodium unit contains one remaining TFA group, and thus overall, only $100 / (4 \cdot 4.2) \approx 6$ % of the TFA groups in the catalyst are preserved while 94% of the TFA groups are replaced during the formation process of the coordination polymer Rh_2-L2.
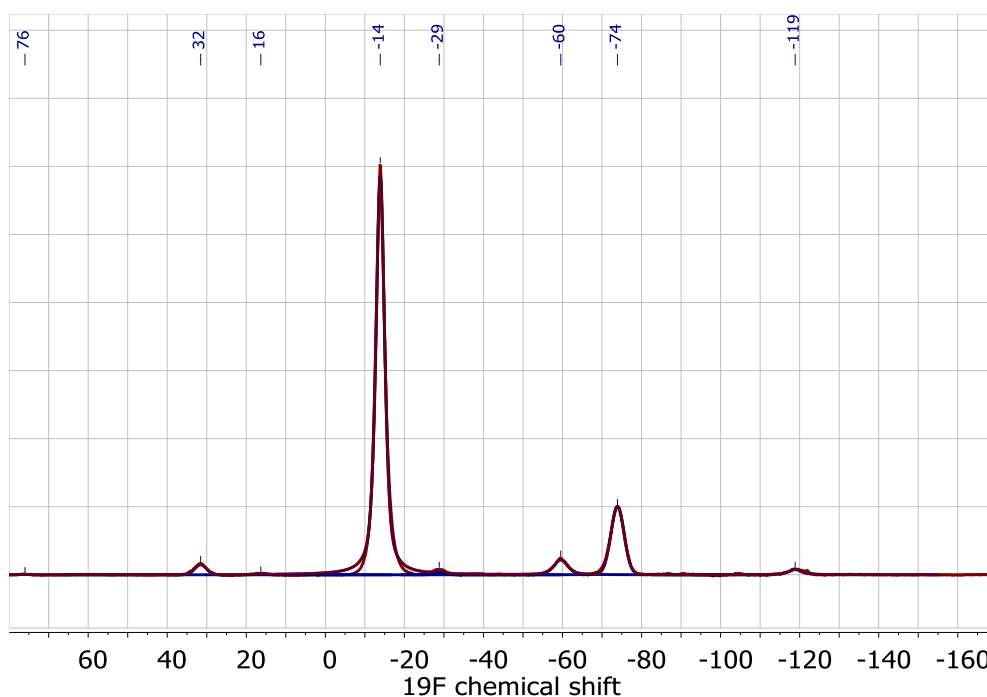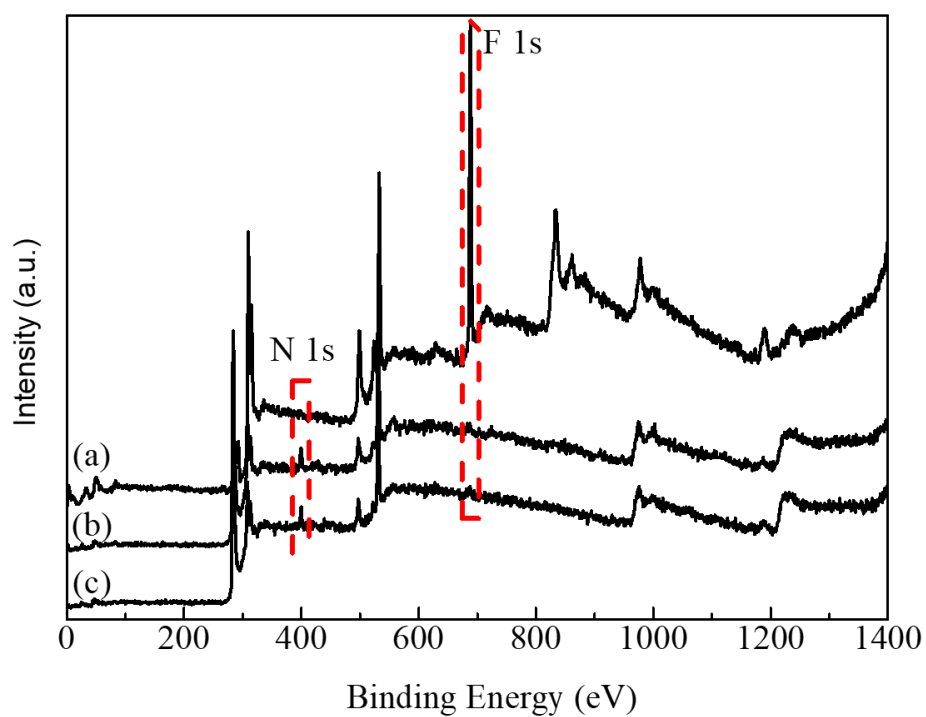

^{19}F MAS NMR of Rh_2-L2.

5. XPS

Fig. S4. XPS spectra of $Rh_2(TFA)_4$ (a), Rh_2-L1 (b) and Rh_2-L2 (c) complex in wide scan mode.

6. Calculation of turnover frequency (TOF)

The TOFs at certain reaction times (1.5 h and 3 h) for the Rh_2-L1 catalyst in each recycle run were calculated from the appropriate yields according to the procedure described in ref. [3]

$$TOF = n_{(3\text{- diazooxindole})} * yield / n_{(catalyst, exp)} / t,$$

Where t is the reaction time, $n_{(3\text{- diazooxindole})}$ is the amount of 3-diazooxindole used in the reaction, $n_{(catalyst, exp)}$ is the amount of dirhodium units calculated from the nominal concentration of the weighted samples.

$$n_{(catalyst, exp)} = n_{(catalyst)} * (Rh\% \text{ (nominal)} / Rh\% \text{ (TGA)})$$

Here $n_{(catalyst)}$ is the amount of Rh_2-L1, which was chosen as 3.75 μmol. Rh% (nominal) is the theoretical Rh content and Rh% (TGA) is the experimental Rh content in the dirhodium polymer, respectively.

Table S2. Calculation of the TOFs for Rh_2-L1 in each recycle run at 1.5 h and 3 h of reaction.

Time Cycle no.	1.5 h		3 h	
	Yield (%)	TOF (h^{-1})	Yield (%)	TOF (h^{-1})
1	65.9	17.4	95.0	12.5
2	65.4	17.2	95.0	12.5
3	63.5	16.7	93.0	12.2
4	60.6	16.0	95.0	12.5
5	61.9	16.3	89.0	11.7

7. Recycling tests

Table S3. Recycling test of Rh_2-L1 catalyst in the asymmetric cyclopropanation reaction between styrene and diazooxindole

Entry	Catalyst	Cycle no.	Temp. (°C)	Yield [a] (%)	dr [b]	ee [c] (%)
1	Rh_2-L1	1	0	95	88:12	13
2	Rh_2-L1	2	0	95	85:15	11
3	Rh_2-L1	3	0	93	84:16	11
4	Rh_2-L1	4	0	95	82:18	8
5	Rh_2-L1	5	0	89	82:18	7

Reaction conditions: styrene (0.75 mmol) and diazooxindole (0.15 mmol) in DCE (3 mL) were added to a two-necked round-bottom flask containing a magnetic stir bar under Ar atmosphere at 0 °C, followed by addition of Rh_2-L1(3.75 μmol) and stirred for 3 h.

[a] Overall yields of spiro-cyclopropyloxindoles. [b] The diastereomeric ratio (trans:cis) dr was determined by ^{1}H NMR of the reaction mixture. [c] The [ee] was analyzed for the trans-enantiomers. It was calculated from data determined by chiral HPLC analysis.

8. ICP-OES

The leaching test was prepared according to a previous described procedure.[2-3] In detail, the filtrated solution from the leaching test (3 mL) was collected for ICP-OES measurement to analyse the residual rhodium fraction. After the solvent was removed, the sample was heated at 650 °C for 4 h, and the residue was dissolved in 3 mL aqua regia at 50 °C for 24 h. Then, the sample was diluted with deionized water to obtain 25 mL solution of rhodium salts. The sample was analysed by the AZBA GmbH, Berlin.

Table S4. ICP-OES for leaching solution (Probe I)

Probenbezeichnung: **19-03106-001: Probe I**

Parameter	Methode	Einheit	BG	**Messwert**
Rhodium	DIN EN ISO 11885:2009-09	mg/l	0,05	< 0,05

The Rh content in the sample solution, determined by ICP-OES, was less than 0.05 ppm, i.e. below the detection threshold of the ICP-OES.

9. Diastereomeric ratio (dr)

The diastereomeric ratio (dr) was determined by crude ^{1}H NMR analysis. The ^{1}H signals of the two diastereoisomers show different chemical shift in the ^{1}H NMR spectra. For analysis the signal group at 3.37 ppm, which refers to *trans*-cyclopropyloxindole and the signal group at 3.19 ppm which refers to *cis*-cyclopropyloxindole were selected. The dr value was calculated from the integral area of each signal group of ^{1}H signals as dr = $area_{trans}$: $area_{cis}$.

Trans   *Cis*
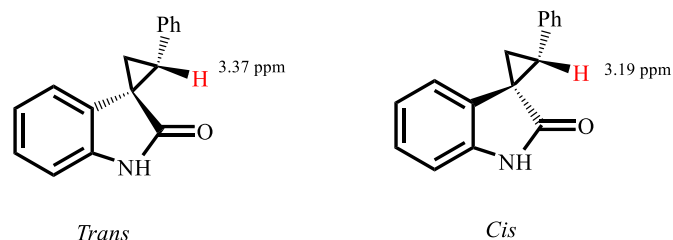
Rh$_2$-L1 as catalyst
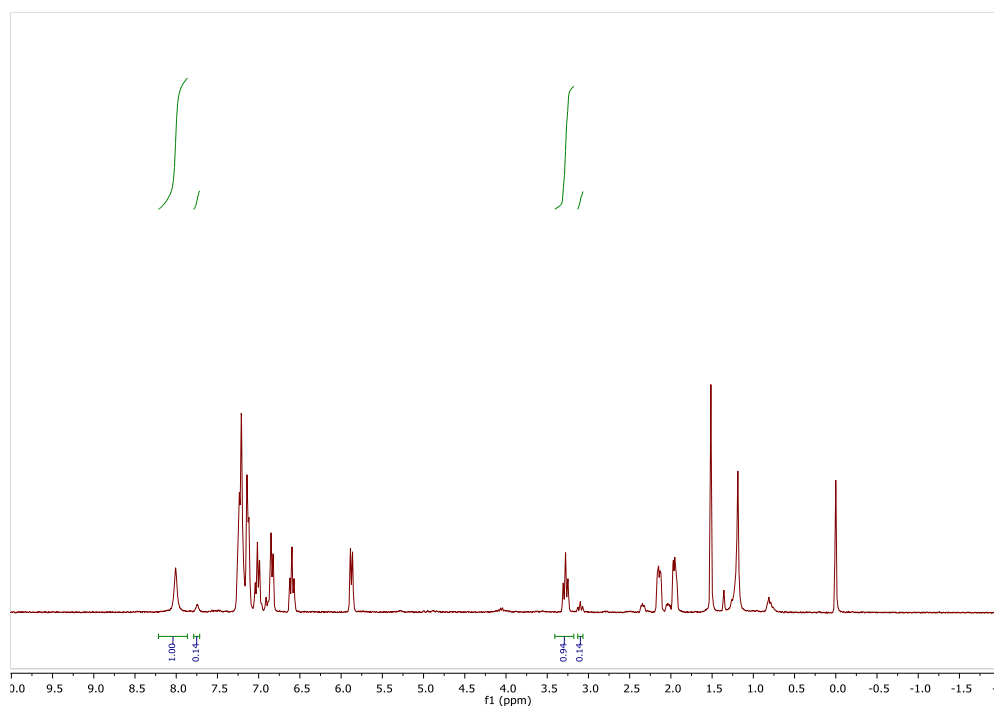
Rh₂-L2 as catalyst
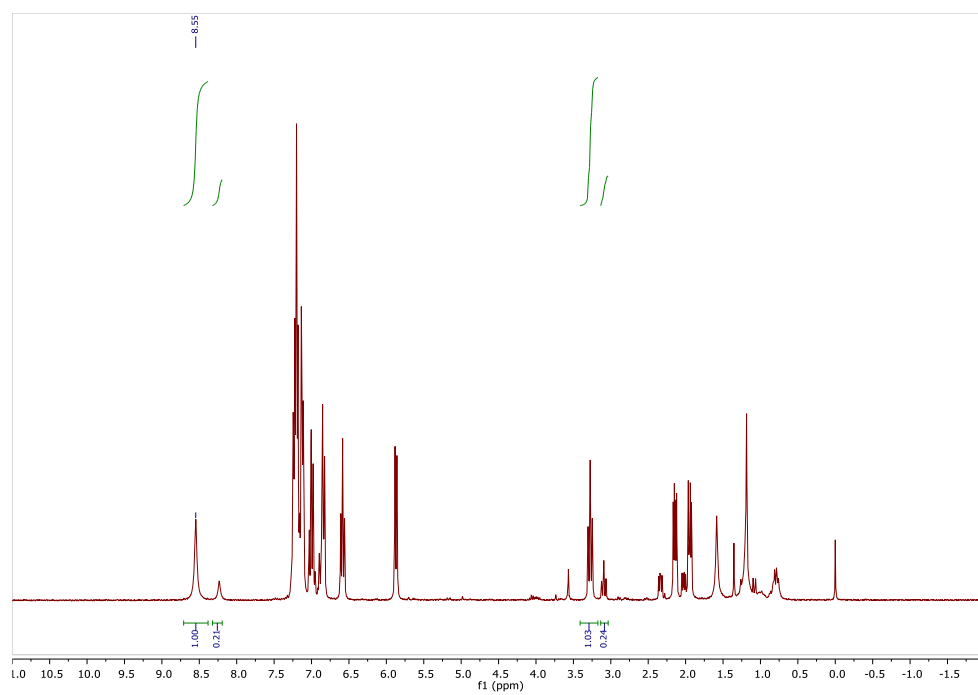
Rh₂(S-PTPA)₄ as catalyst
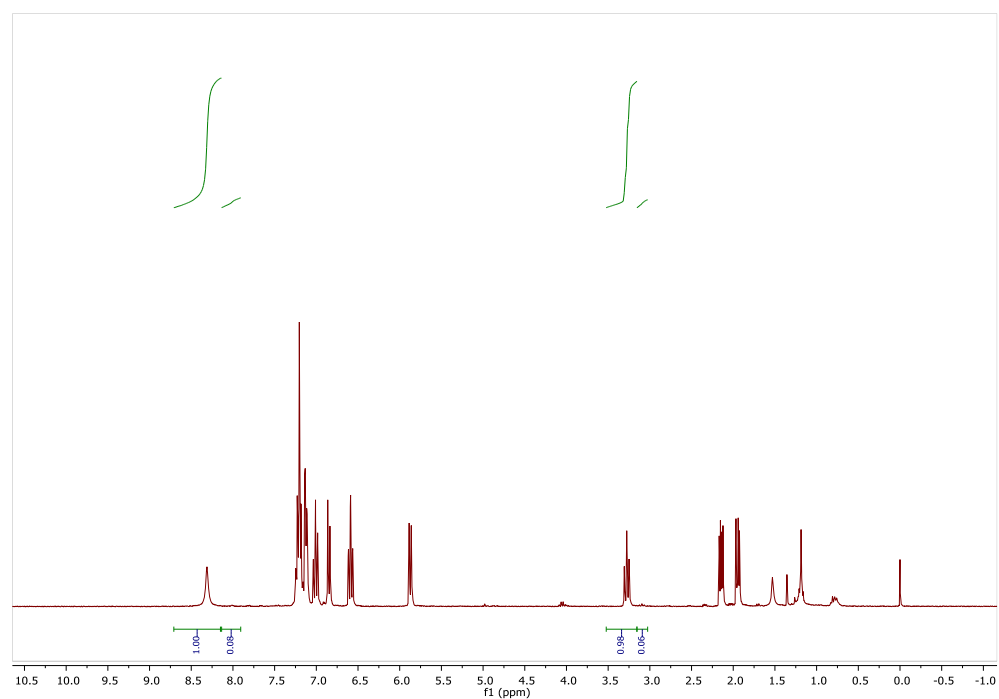
10.Enantiomeric excess (ee)

The enantiomeric excess (ee) was determined by chiral HPLC with a Reprosil chiral OM-R column [35% MeCN in water + 0.1% TFA, 1.0 mL/min, 45 min];

t_R (major enantiomer) = 35.2 min; t_R (minor enantiomer) = 36.6 min. The ee% was calculated according to Eq. S1.
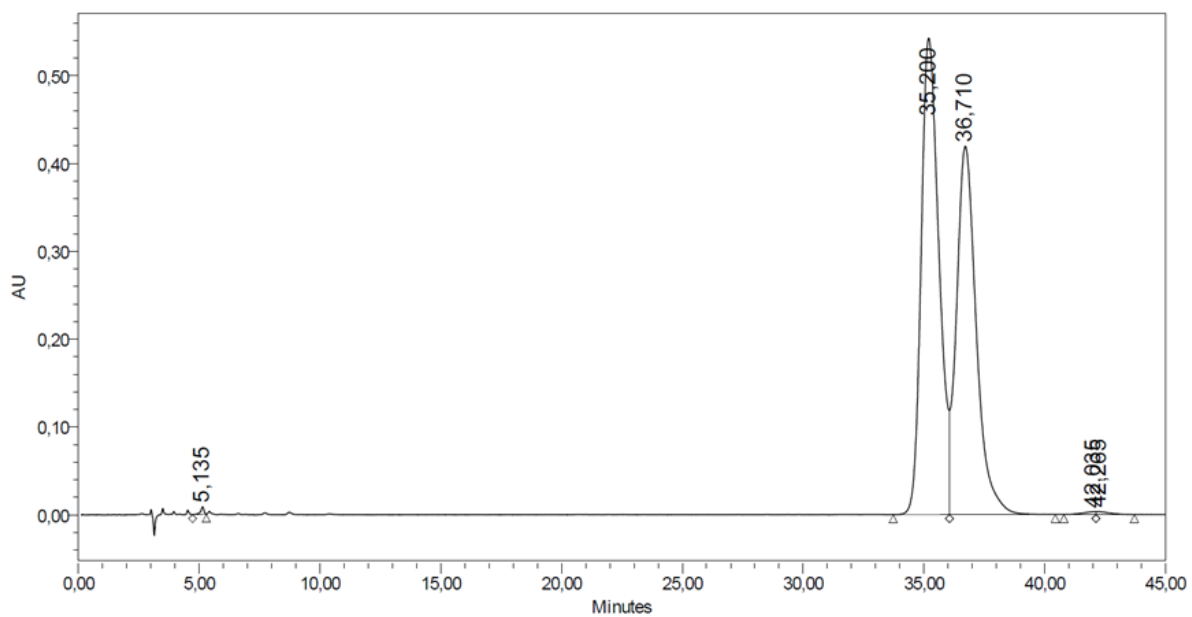
$$ee\% = \frac{Area_{major} - Area_{minor}}{Area_{major} + Area_{minor}} \times 100\% \qquad \text{Eq. S1}$$

Rh$_2$-L1 as catalyst
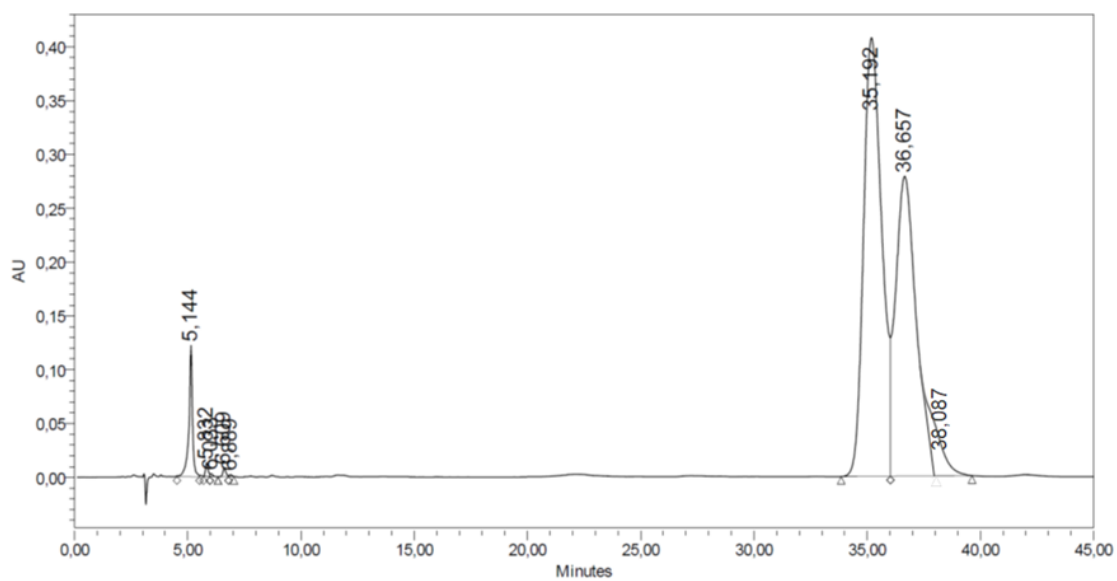
	RT	Area	%Area	Height
1	5,144	1330163	3,02	122186
2	5,832	107948	0,24	12874
3	6,033	24543	0,06	2957
4	6,609	78126	0,18	8266
5	6,889	16043	0,04	1801
6	35,192	22745371	51,61	407670
7	36,657	17589465	39,91	278686
8	38,087	2183891	4,95	63095

Rh₂-L2 as catalyst

	RT	Area	%Area	Height
1	5,135	77639	0,15	8610
2	35,200	27608781	53,15	542552
3	36,710	24030527	46,26	419393
4	42,035	110083	0,21	3058
5	42,265	122011	0,23	3186

Rh₂(S-PTPA)₄ as catalyst
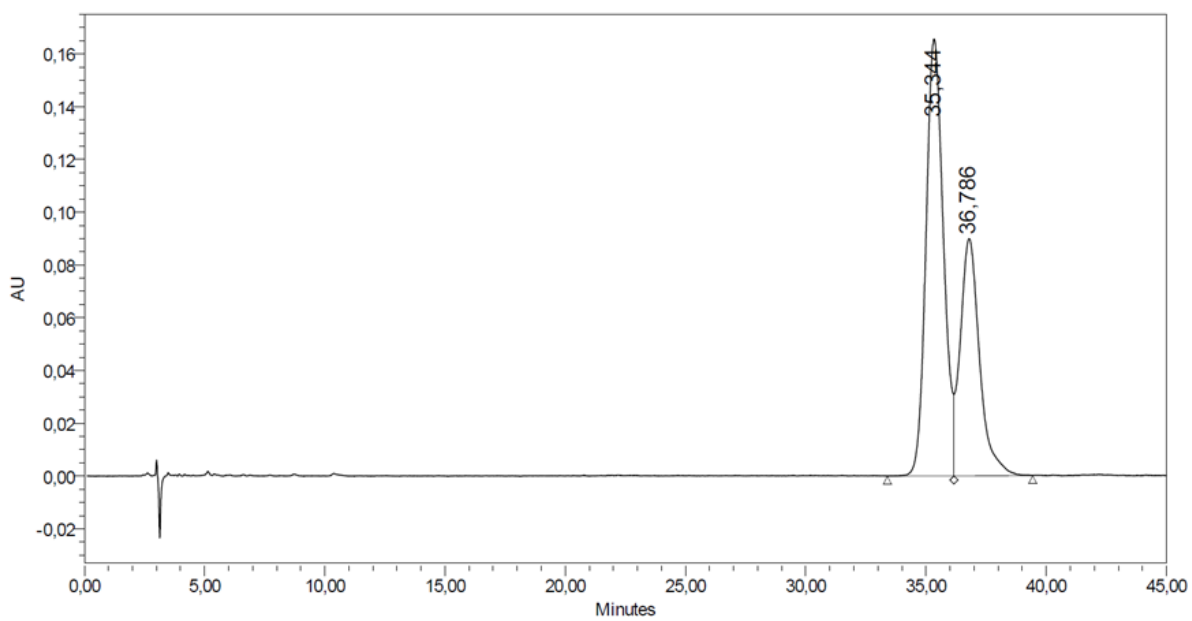
	RT	Area	%Area	Height
1	35,344	8431743	62,82	165627
2	36,786	4990325	37,18	89940

11. Liquid NMR Spectra

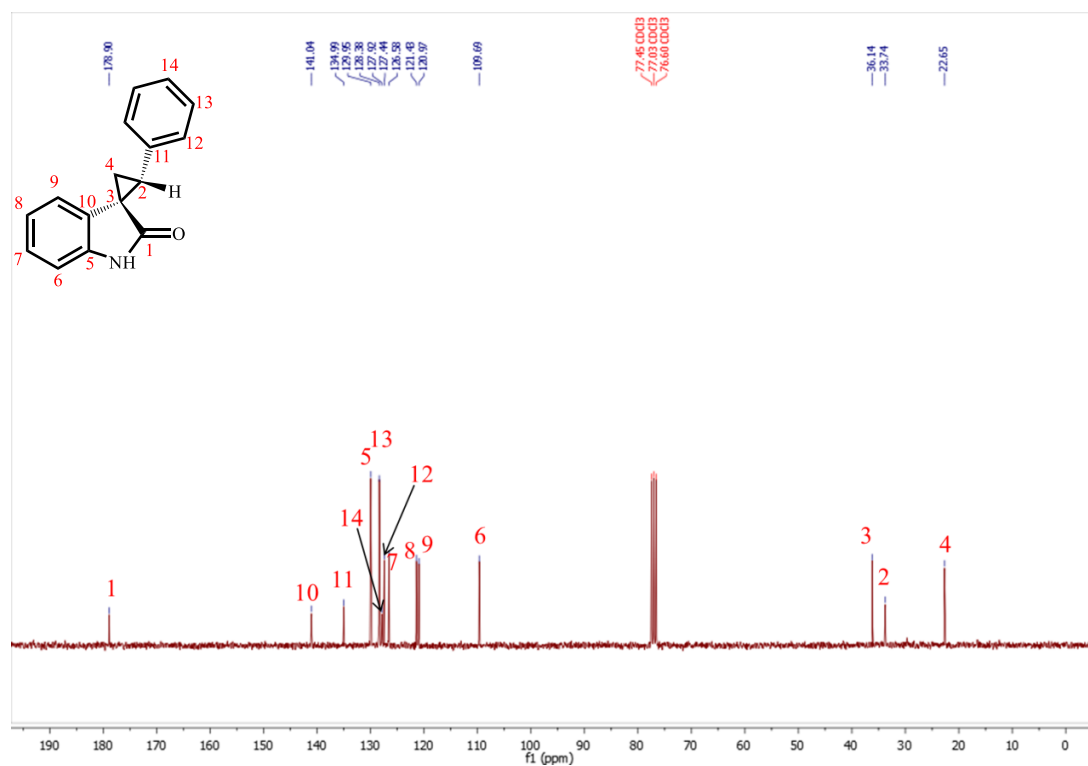## 3-Diazooxindole (CDCl₃ as solvent)
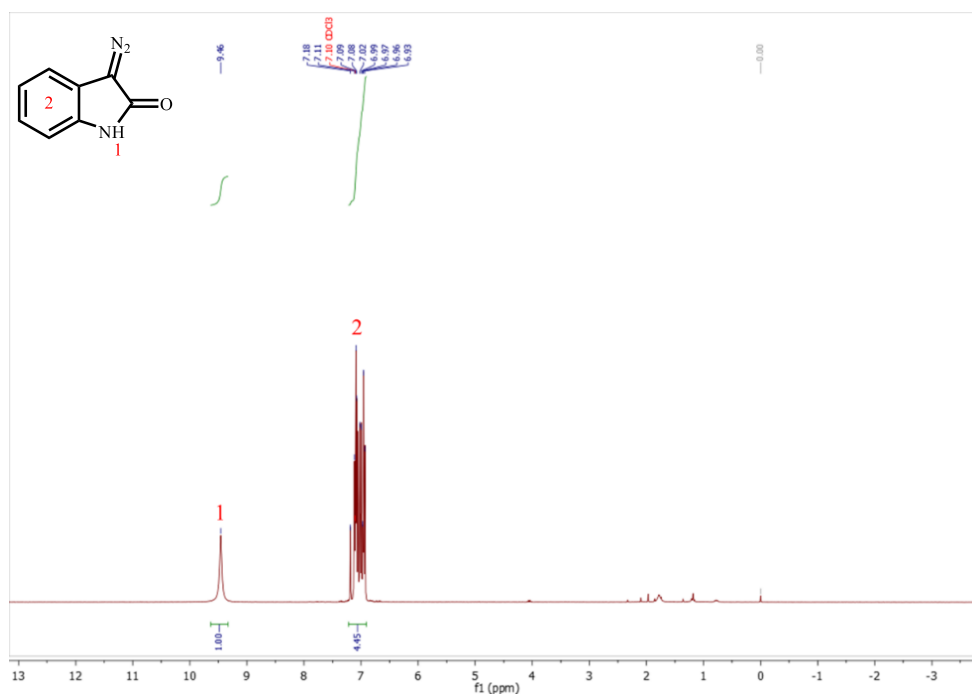
¹H NMR spectrum of 3-diazooxindole
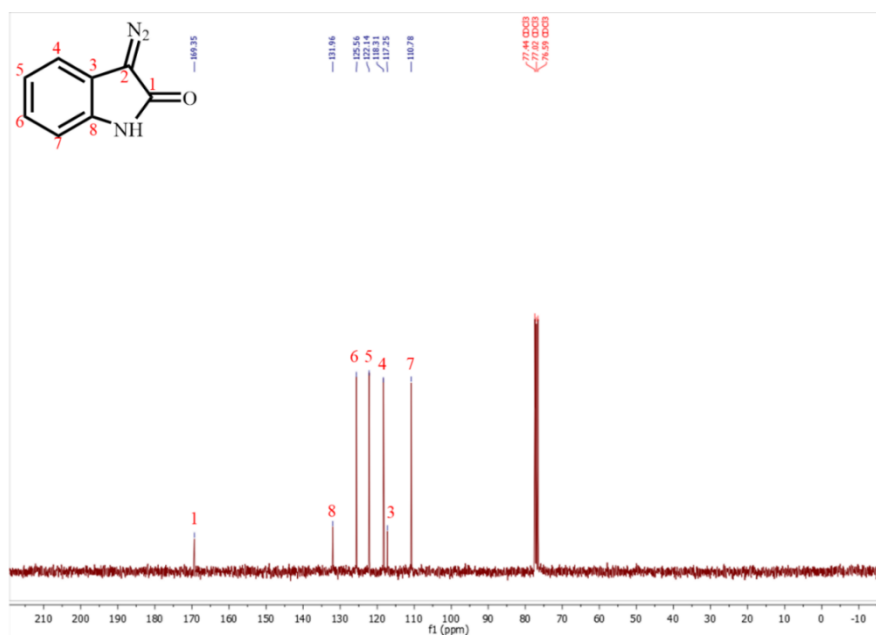
¹³C NMR spectrum of 3-diazooxindole

Note: Only 7 signals are obtained in the ¹³C NMR spectrum which is in good agreement with the literature. [4]
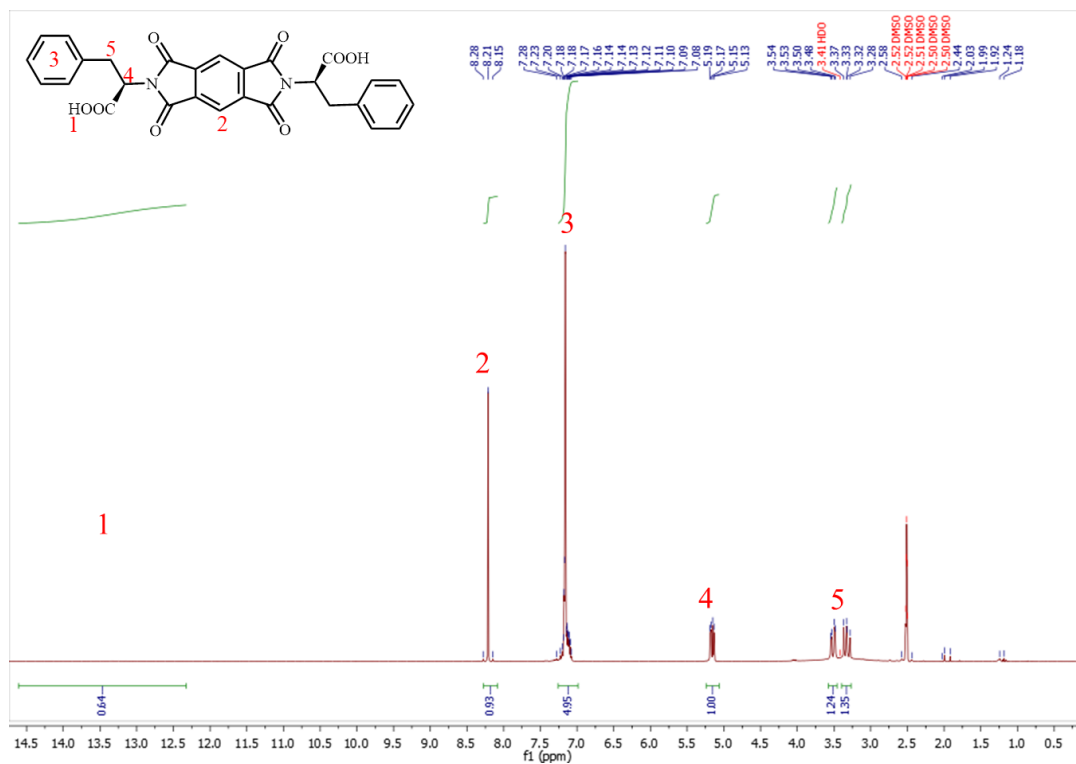
Trans-cyclopropyloxindol (CDCl₃ as solvent)
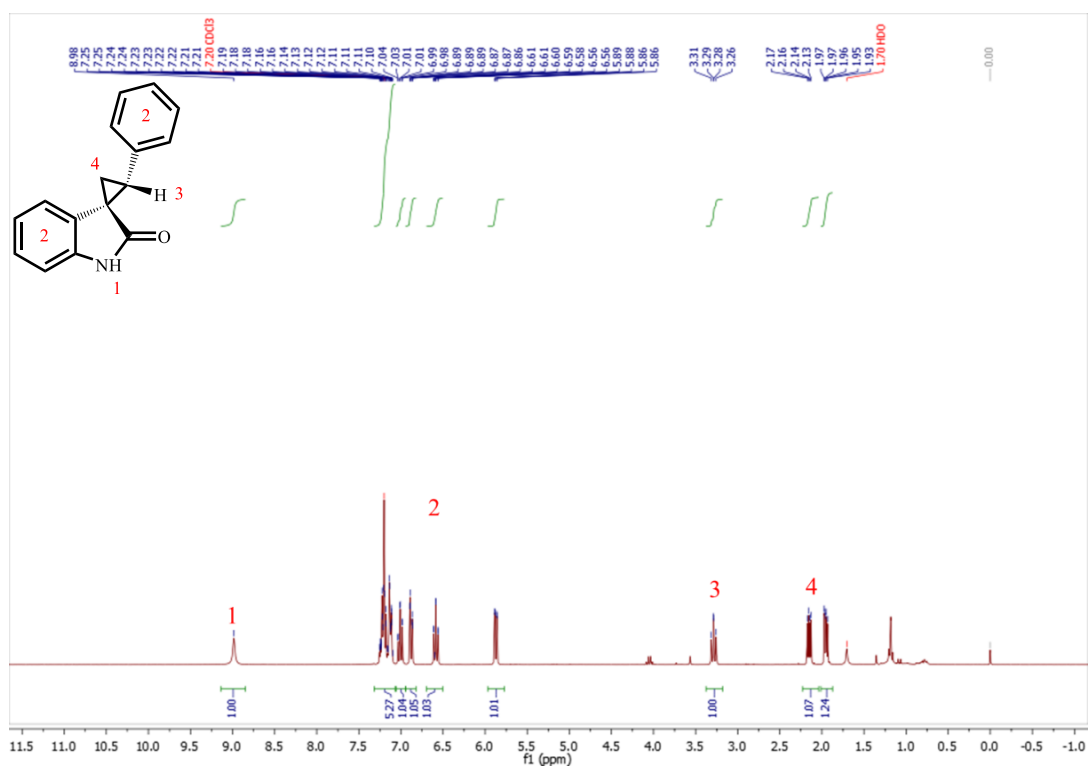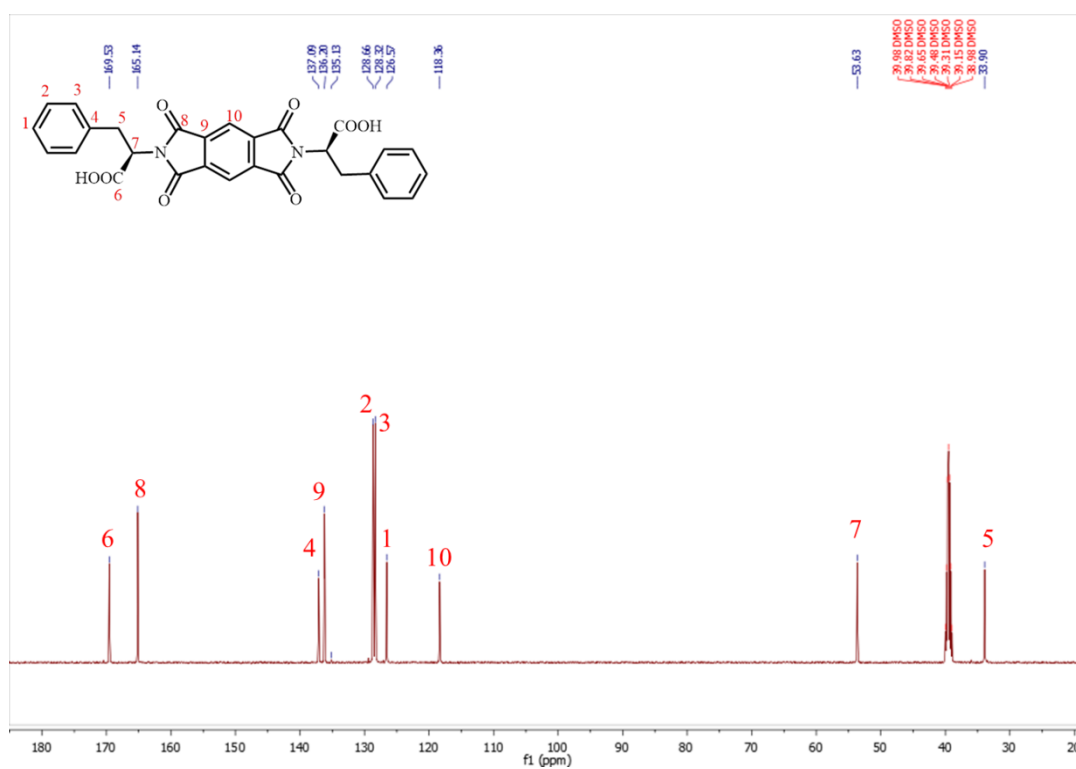

¹H NMR spectrum of cyclopropyoxindol
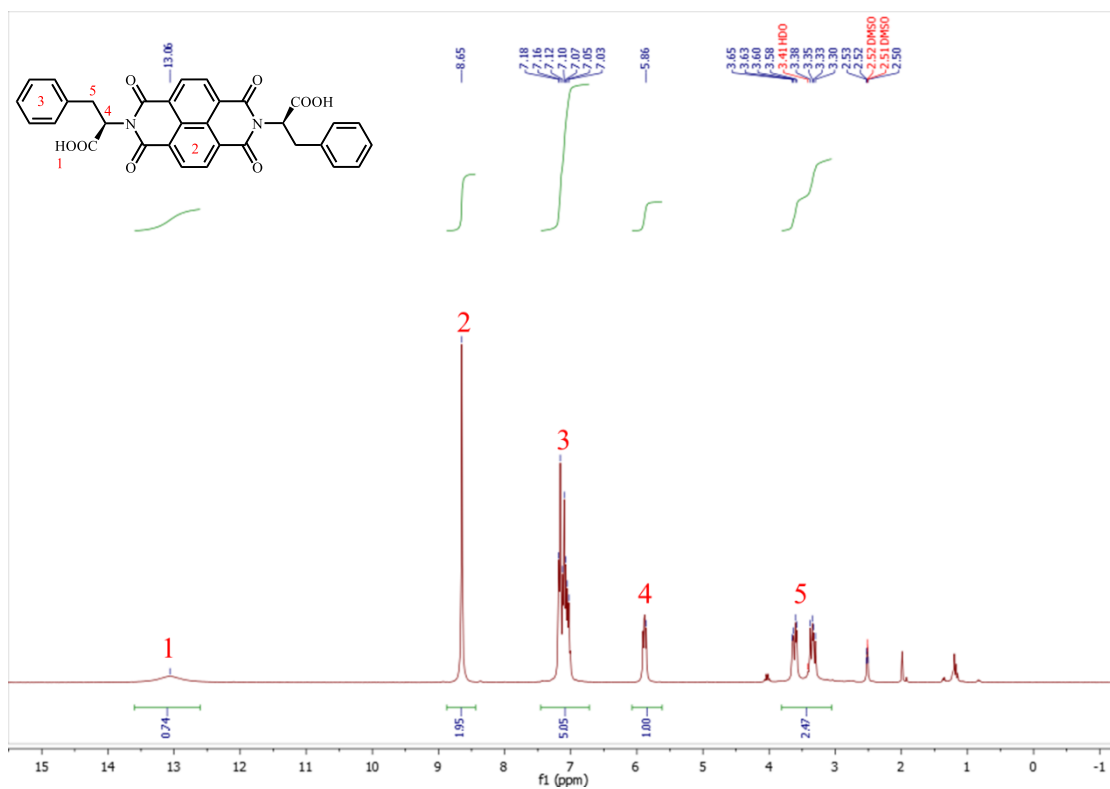

¹³C NMR spectrum of cyclopropyoxindol

Chiral ligands (DMSO-d$_6$ as solvent)

^{1}H NMR spectrum of H$_2$L1

^{13}C NMR spectrum of H$_2$L1

^{1}H NMR spectrum of H$_2$L2
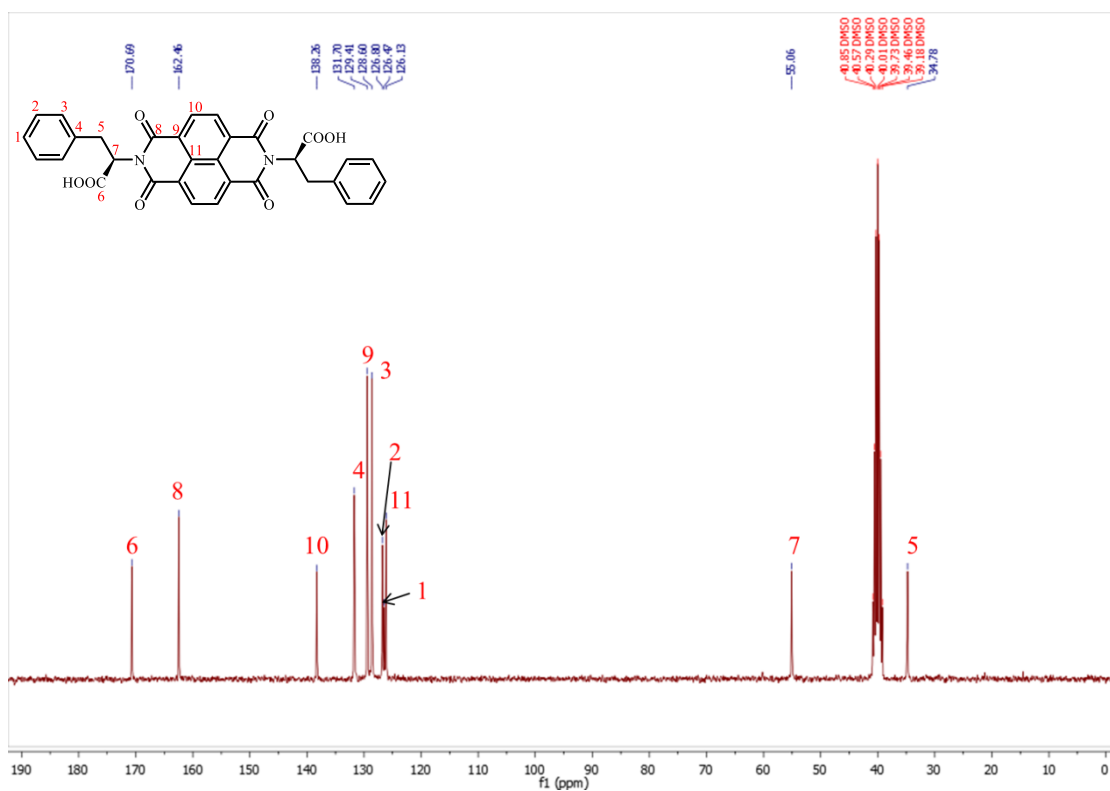
^{13}C NMR spectrum of H$_2$L2

References

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2.   Liu, J.; Fasel, C.; Braga-Groszewicz, P.; Rothermel, N.; Thankamony, A. S. L.; Sauer, G.; Xu, Y.; Gutmann, T.; Buntkowsky, G., Heterogeneous self-supported dirhodium (ii) catalysts with high catalytic efficiency in cyclopropanation–a structural study. *Catal. Sci. Tech.* **2016,** *6*, 7830-7840.

3.   Liu, J.; Xu, Y.; Groszewicz, P. B.; Brodrecht, M.; Fasel, C.; Hofmann, K.; Tan, X.; Gutmann, T.; Buntkowsky, G., Novel dirhodium coordination polymers: the impact of side chains on cyclopropanation. *Catal. Sci. Tech.* **2018,** *8*, 5190-5200.

4. Ošeka, M.; Kimm, M.; Kaabel, S.; Järving, I.; Rissanen, K.; Kanger, T., Asymmetric Organocatalytic Wittig [2,3]-Rearrangement of Oxindoles. *Org. Lett.* **2016**, *18*, 1358-1361.