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Kiral Diazadioksokaliks[2]aren[2]triazin Bazlı Organokatalizörün Nitrostirenler ile Antronun Enantiyoselektif Michael Tepkimesinde Kullanılması

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ÖZET

Kiral, stereoseçici ya da enantiyoseçici sentez olarak tanımlanan asimetrik sentez bir veya daha fazla stereojenik merkez bulunduran kiral bileşiklerin sentezlenmesini sağlayan organik sentez türüdür. Bir molekülün farklı enantiyomerleri genellikle birbirlerinden farklı biyolojik aktivite gösterdiklerinden dolayı, asimetrik sentez konusu ilaç kimyası ve organik kimyada oldukça önemli bir konudur. Kiral özellik göstermeyen bileşiklerden kiral bir bileşik sentezleme yöntemleri arasında en çok tercih edilen yöntemlerden biri kiral katalizör kullanımıdır. Bu çalışmada anthron ve farklı nitrostiren türevlerinin kullanıldığı asimetrik Michael tepkimesinde kullanılmak üzere literatürde bulunmayan bir kiral katalizör sentezlenmiştir. Öncelikle kiral katalizörün başlangıç maddesi olarak literatürde bulunan diazadioksookaliks[2]aren[2]triazin sentezlenmiştir. Sentezlenen başlangıç maddesi ile (*S*)-(+)-1-siklohekziletilamin tepkimeye sokularak enantiyoselektif tepkimede kiral katalizör olarak kullanılacak olan madde elde edilmiştir. Çalışma süresince yapılan tüm reaksiyonlar ince tabaka kromatografisi ile izlenmiş ve elde edilen maddeler kolon kromatografisi ile saflaştırılmıştır. Saflaştırılan ürünler FTIR, ^{1}H NMR ve ^{13}C NMR ile aydınlatılmış ve optik çevirme açıları ölçülmüştür. Sentezlenen katalizör asimetrik Michael reaksiyonunda denenmiş, yüksek verim ve yüksek enantiyoseçicilik elde edilmiştir (%95 verim ve %98 *ee*).

Chiral Diazadioxocalix[2]arene[2]triazine-Based Derivative as Organocatalyst for Enantioselective Michael Reaction of Nitrostyrenes with Anthrone

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ABSTRACT

Asymmetric synthesis, also known as chiral, enantioselective or stereoselective synthesis, is an organic synthesis which allows the formation of chiral compounds containing one or more stereogenic centers. Since different enantiomers of a molecule usually show different biological activity from each other, asymmetric synthesis is a very important topic in the pharmaceutical industry and organic chemistry. One of the most preferred methods to obtain a chiral compound from non-chiral compounds is the use of chiral catalysts. In this study, a chiral catalyst, which is not available in the literature, was synthesized for use in the asymmetric Michael reaction using anthrone and different nitrostyrene derivatives. First, diazadioxocalix[2]arene[2]triazine, which is available in the literature, was synthesized as the starting material of the chiral catalyst. (*S*)-(+)-1-cyclohexylethylamine was reacted with the synthesized starting material to obtain the substance to be used as a chiral catalyst in the enantioselective reaction. During the study, all reactions were monitored by thin layer chromatography and the obtained substances were purified by column chromatography. The structures of the purified products were elucidated by FTIR, ^{1}H NMR and ^{13}C NMR techniques and optical rotation angles were measured. The synthesized catalyst was tested in asymmetric Michael reaction and high yields and high enantioselectivity were obtained (95% yield and 98% *ee*).

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INTRODUCTION

Chiral compounds play an important role in biochemical systems, pharmaceuticals, organic synthesis and many chemical applications. These compounds are used in various analytical, synthetic and industrial applications due to their optically active properties [1-5]. The stereoselective synthesis of chiral substances is becoming increasingly important due to their applications in the pharmaceutical industry. Among the methods of obtaining a chiral compound from non-chiral compounds, the use of chiral catalysts has a number of advantages over other methods. The number of studies on the synthesis of chiral catalysts and their use in reactions is increasing day by day [6-10].

Chiral compounds can generally sythesized by four different strategies. The use of chiral catalysts and optical resolution are important among them. Optical resolution is realized by the consumption of only one enantiomer of a racemic compound by microorganisms or by converting it into a diastereoisomeric salt by interacting with a chemical containing a single enantiomer [11-12]. The use of a chiral catalyst has become one of the most preferred effective methods by researchers; it is a strategy to obtain predominantly a stereoisomer by acting on a reaction that normally yields products as racemic mixtures [13-14].

Since many biological systems contain amine, amino alcohol, carboxylic acid and amino acid groups, the enantiomeric recognition of these compounds is of particular importance. Such studies contribute to the understanding of the function of natural living systems and provide useful information for the design of asymmetric catalysis systems and new drugs [15-17].

In recent years, we have reported the synthesis of substituted calix[2]arene[2]triazine bearing various chiral subunits, their use as chiral organocatalysts in different stereoselective reactions and their catalytic activities [18-21].

In this paper, the synthesis of a chiral diazadioxocalix[2]arene[2]triazine derivative from (S)-(+)-1-cyclohexylethylamine and its catalytic application in the Michael reaction between anthrone and various aromatic nitrostyrenes were described. To the best of the authors' knowledge, the catalytic application of the diazadioxocalix[2]arene[2]triazine derivative in the asymmetric Michael reaction of anthrone with various nitrostyrenes is reported for the first time.

MATERIALS AND METHODS

Synthesis and Use of Catalyst

Heteroatom bridged diazadioxocalix[2]arene[2]triazine was synthesized in according to the procedure published by Wang et al. [22-23].

Procedure for the Synthesis of 2

To the obtained solution of diazadioxocalix[2]arene[2]triazine (1) (0.5 mmol) in tetrahydrofuran (20 mL) was added the solution of (*S*)-(+)-1-cyclohexylethylamine (1.1 mmol) and N,N-Diisopropylethylamine (2.2 mmol) prepared in tetrahydrofuran (20 mL). The reaction mixture was refluxed for 28 h and then THF was removed. Finally, the product was purified by flash chromatography (Hexane/EtOAc).

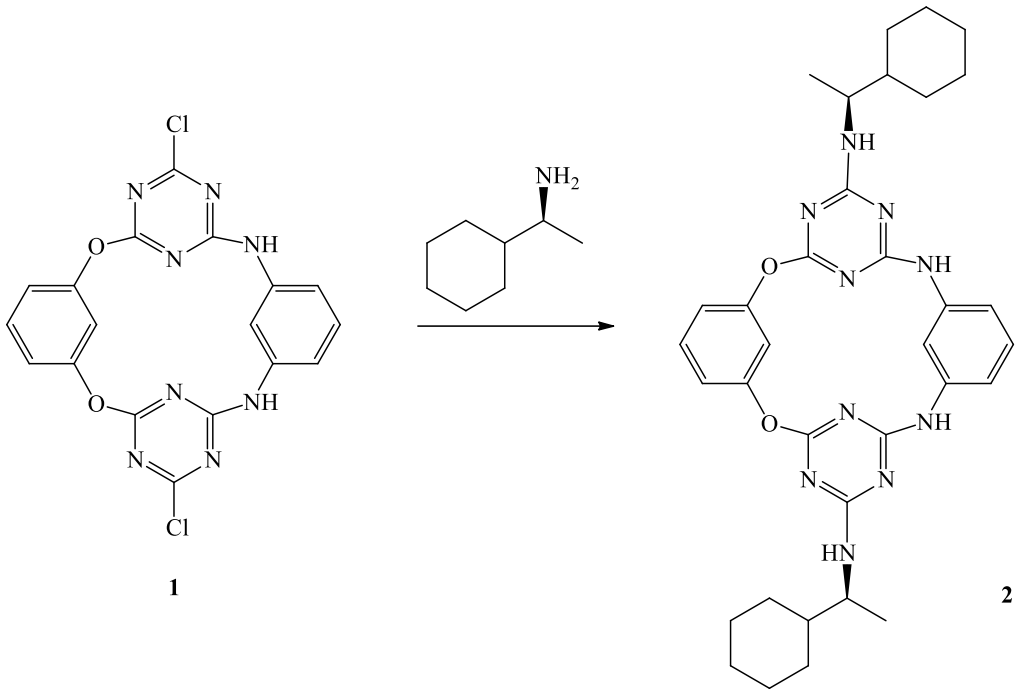


Figure 1. *The synthesis of chiral catalyst **2***

(**2**): Crystalline Solid; 74% yield; $[\alpha]_D^{25}$ =-14.45 (*c*=1.0, $CHCl_3$); mp.: 311-313 °C; FTIR (cm^{-1}): 3270, 2973, 1579, 1484, 1378; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94-7.78 (m, 4H, Ar***H***), 7.62-7.51 (m, 2H, Ar***H***), 7.43-7.35 (m, 2H, Ar***H***), 4.21–3.93 (m, 2H, methyl-C***H***-NH), 1.62–1.54 (m, 10H, cyclohexyl ***H***), 1.46 (d, *J*=7.8, 6H, methyl ***H***), 1.44–1.29 (m, 12H, cyclohexyl ***H***), NH-signals not found; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.72, 163. 20, 159.82, 157,93, 137.18, 132.13, 127.83, 118.53, 117.52, 110.10, 103.18, 59.35, 52.63, 40.92, 29.15, 25.85, 20.85; Anal. Calcd. for $C_{34}H_{42}N_{10}O_2$ (622.77): C, 65.57; H, 6.80; N, 22.49%. Found: C, 65.73; H, 6.61; N, 22.60%.

Procedure for 5a-5j

To a solution of nitrostyrene derivatives (**4a-j**) (0.4 mmol) and catalyst **2** (10% mol) in toluene (4 mL) was added anthrone (**3**) (0.48 mmol). The reactions were stirred at room temperature for a certain time and monitored by TLC. The completed reaction mixtures were concentrated. The residues were purified by column chromatography (**5a-j**). The obtained products were compared with the literature [24-25]. The *ee* of the pure products was determined by HPLC using chiral columns and compared with the reported data. Non-chiral catalysts were used for the preparation of racemic Michael products.

5a [24]**:** White solid, yield 95%; *ee* 95%, $[\alpha]_D^{25}$ = +25.0 (*c* 0.5, $CHCl_3$); mp.: 145°C-147°C; HPLC (AS-H); Hexane/ IPA: 90/10; 254 nm; 0.7 mL/min; t_R major: 16.55, minor: 19.45.

5b [25]**:** White solid, yield 85%; *ee* 93%, $[\alpha]_D^{25}$ = -4.5 (*c* 0.2, $CHCl_3$); mp.: 68°C-70°C; HPLC (OD-H); Hexane/ IPA: 70/30; 254 nm; 1.0 mL/min; t_R major: 15.25, minor: 18.02.

5c [25]**:** White solid, yield 93%; *ee* 89%, $[\alpha]_D^{25}$ = −8.7 (c 0.9, $CHCl_3$); mp.: 128°C-130°C; HPLC (AS-H); Hexane/ IPA: 80/20; 254 nm; 1.0 mL/min; t_R major: 11.75, minor: 14.72.

5d [25]**:** White solid, yield 92%; *ee* 96%, $[\alpha]_D^{25}$ = +6.7 (*c* 0.7, $CHCl_3$); mp.: 62°C-64°C; HPLC (AS-H); Hexane/ IPA: 80/20; 254 nm; 1.0 mL/min; t_R major: 10.55, minor: 13.25.

5e [25]**:** White solid, yield 93%; *ee* 98%, $[\alpha]_D^{25}$ = +33.7 (*c* 0.6, $CHCl_3$); mp.: 114°C-116°C;

HPLC (AS-H); Hexane/ IPA: 80/20; 254 nm; 1.0 mL/min; t_R major: 14.68, minor: 17.51.

5f [24]**:** White solid, yield 88%; *ee* 82%, $[\alpha]_D^{25}$ = +32.8 (*c* 0.5, $CHCl_3$); mp.: 173°C-171°C; HPLC (AS-H); Hexane/ IPA: 70/30; 254 nm; 1.0 mL/min; t_R major: 10.11, minor: 12.12.

5g [24]**:** White solid, yield 91%; *ee* 84%, $[\alpha]_D^{25}$ = +25.2 (*c* 0.5, $CHCl_3$); mp.: 166°C-168°C; HPLC (AS-H); Hexane/ IPA: 90/10; 254 nm; 1.0 mL/min; t_R major: 21.32, minor: 25.52.

5h [24]**:** White solid, yield 83%; *ee* 90%, $[\alpha]_D^{25}$ = +17.5 (*c* 0.7, $CHCl_3$); mp.: 117°C -118°C; HPLC (OD-H); Hexane/ IPA: 80/20; 254 nm; 1.0 mL/min; t_R major: 25.42, minor: 20.12.

5i [24]**:** White solid, yield 92%; *ee* 88%, $[\alpha]_D^{25}$ = +25.8 (*c* 0.6, $CHCl_3$); mp.: 157°C-159°C; HPLC (AS-H); Hexane/ IPA: 90/10; 254 nm; 1.0 mL/min; t_R major: 15.85, minor: 17.97.

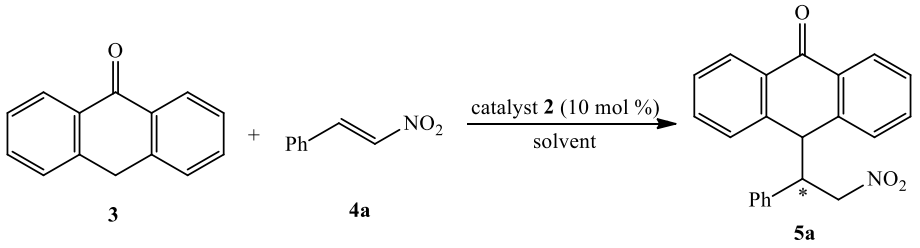
5j [24]**:** White solid, yield 90%; *ee* 89%, $[\alpha]_D^{25}$ = −14.7 (*c* 0.2, $CHCl_3$); mp.: 66°C-68°C; HPLC (OD-H); Hexane/ IPA: 80/20; 254 nm; 1.0 mL/min; t_R major: 12.84, minor: 16.02.

RESULTS AND DISCUSSION

In order to reach the target molecule, we first prepared diazadioxocalix[2]aren[2]triazine in specific steps using suitable starting materials [22-23]. To synthesize the target molecule, diazadioxocalix[2]aren[2]triazine (**1**), (*S*)-(+)-1-cyclohexylethylamine and N,N-Diisopropylethylamine (DIPEA) were reacted efficiently in THF at room temperature. As a result of this reaction, chiral **2** shown in Figure 1 was obtained. The obtained material was characterized by methods such as FTIR, ^{1}H NMR and ^{13}C NMR.

The infrared spectra of catalyst **2** have been recorded and analyzed. The NH stretching modes of catalyst were observed in the region 3270 cm^{-1} and C-H stretches were observed in the region 2973 cm^{-1}. Additionally, the observed band at 1579 cm^{-1} in the FT-IR spectrum was assigned to the aromatic C=N and band at 1484 cm^{-1} was assigned to the aromatic C=C stretching modes.

Table 1. *Michael Addition Reaction **3** and **4a** with Catalyst **2** in Different Solvents*



3 **4a** **5a**

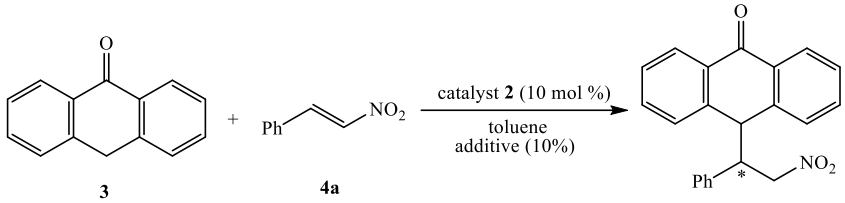
Entry[a]	Solvent	Time (d)	Yield (%)	*ee* (%)[b, c]
1	THF	4	91	91
2	Toluene	4	95	95
3	CH_3CN	2	93	89
4	CCl_4	4	90	87
5	1,4-dioxane	4	87	86
6	DMF	2	85	81
7	Et_2O	4	93	92
8	$CHCl_3$	4	92	92
9	Acetone	2	92	90
10	CH_2Cl_2	3	93	91
11	*i*-PrOH	2	88	89

[a] Conditions: **3** (0.48 mmol), **4** (0.40 mmol) and **2** (10 mol%) in solvents (4.0 mL). [b] Results were determined using HPLC. Configuration and retention time were determined by comparison with the literature data. [c] All products obtained in *R* configuration.

The obtained diazadioxocalix[2]arene[2]triazine-based compound was used as a catalyst in Michael addition, which is an enantioselective reaction, in order to learn the catalytic activity of catalyst

2. The reaction of *trans-β*-nitrostyrene with anthrone was shown in Table 1. The synthesized catalyst 2 was tested in this reaction, and the results obtained were reported in Table 1. Various solvents were tested to determine the most suitable solvent to be used in Michael addition. The highest yield and enantiomeric excess were obtained in the presence of toluene (entry 2).

Table 2. *Additive Effect for Michael Addition of **3** to **4a** Catalyzed by **2***



3 **4a** **5a**

Entry[a]	Additive	Time (d)	Yield (%)	*ee* (%)[b, c]
1	None	4	95	95
2	DMAP	4	93	89
3	AcOH	4	85	88
4	PhCOOH	4	84	90
5	Pyridine	4	92	88
6	*p*-TsOH	4	83	90

[a] Conditions: **3** (0.48 mmol), **4** (0.40 mmol), additive (10 mol%) and **2** (10 mol%) in toluene (4.0 mL). [b] Results were determined using HPLC. Configuration and retention time were determined by comparison with the literature data. [c] All products obtained in *R* configuration.

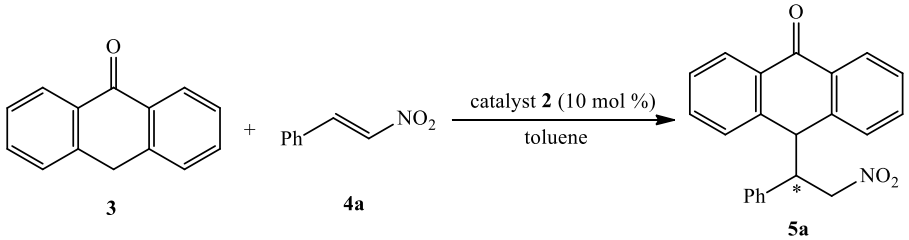
The same reaction was carried out at -20 ºC and 0ºC with toluene, as shown in Table 3. However, both the yield and enantiomeric excess were found to decrease. The experiments revealed that room temperature was the ideal temperature for this process (Table 3, entry 3).

We then added recycled catalyst **2** to the Michael addition and observed the results. The results obtained showed a decrease in yield and enantiomeric excess (Table 3, entry 4).

To investigate the effect of the amount of catalyst on the addition reaction, we added 15 mol% and 5 mol% catalyst to the reaction and observed the results. After these experiments, we decided that the optimum amount of catalyst was 10%. (Table 3, entries 5 and 6).

All our experimental studies have showed that catalyst containing bulky heteroatom bridged calixarene platform is highly effective on enantioselective addition reactions.

Table 3. *Various Reaction Conditions for Michael Addition of **3** to **4a** Catalyzed by **2***



3 **4a** **5a**

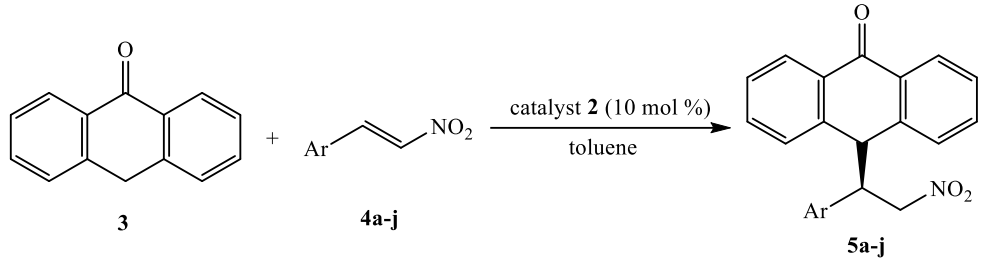
Entry[a]	Temp. (°C)	Time (d)	Yield (%)	*ee* (%)[b, c]
1	-20	5	82	86
2	0	4	85	88
3	r.t.	4	95	95
4[d]	r.t.	4	90	91
5[e]	r.t.	4	94	95
6[f]	r.t.	4	93	93

[a] Conditions: **3** (0.48 mmol), **4** (0.40 mmol) and **2** (10 mol%) in toluene (4.0 mL). [b] Results were determined using HPLC. Configuration and retention time were determined by comparison with the literature data. [c] All products obtained in *R* configuration. [d] Recycled catalyst was used in the reaction. [e] 15 mol% catalyst. [f] 5 mol% catalyst.

The results showed that the ideal conditions were toluene as a solvent, 10 mol% catalyst loading, room temperature, reaction time of four days and no additional additives.

The obtained chiral catalyst was used in the Michael reaction of anthrone with aromatic nitrostyrene derivatives under optimized conditions. In the experiments performed with the chiral catalyst **2**, Michael products (**5a-5j**) were obtained with high yield (83%-95%) and excellent enantioselectivity (82%-98%) (Table 4).

Table 4. *Asymmetric Michael Reaction of **3** to Various Aromatic Nitrostyrenes with Chiral Catalyst **2***



3 **4a-j** **5a-j**

Entry[a]	Ar	Time (d)	Product	Yield (%)	*ee* (%)[b, c]
1	C_6H_5	4	**5a**	95	95
2	2-NO_2-C_6H_4	3	**5b**	85	93
3	2-CH_3O-C_6H_4	3	**5c**	93	89
4	2-Br-C_6H_4	2	**5d**	92	96
5	3-Br-C_6H_4	2	**5e**	93	98
6	4-F-C_6H_4	4	**5f**	88	82
7	4-Cl-C_6H_4	4	**5g**	91	84
8	4- CH_3O-C_6H_4	3	**5h**	83	90
9	4-Me-C_6H_4	3	**5i**	92	88
10	2,4-Cl_2-C_6H_3	4	**5j**	90	89

[a] Conditions: **3** (0.48 mmol), **4a-j** (0.40 mmol) and **2** (10 mol%) in toluene (4.0 mL).[b] Results were determined using HPLC. Configuration and retention time were determined by comparison with the literature data. [c] All products obtained in *R* configuration.

DISCUSSION AND CONCLUSIONS

In conclusion, a novel chiral catalyst based on diazadioxocalix[2]arene[2]triazine for the asymmetric Michael addition of anthrone to various nitrostyrenes has been synthesized. The reaction provided the Michael adducts with high yield values (95%) and high enantioselectivity values (98%). According to the data obtained from the study, the chiral catalyst is a highly effective catalyst for the Michael reaction under catalytic asymmetric reaction conditions. Further investigation of this catalyst in other asymmetric reactions is currently on going in our laboratory.

Conflict of Interest

The authors have no conflicts of interest to disclose for this study.

Authorship Contribution Statement

Ü.Ö.: Methodology, Data Curation, Formal Analysis, **H.N.G.:** Conceptualization, Methodology, Investigation, Writing - Original Draft, **A.S.:** Supervision, Resources, Writing - Review & Editing

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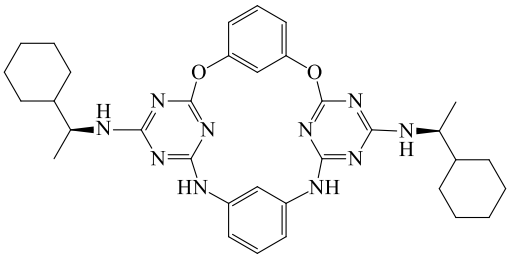
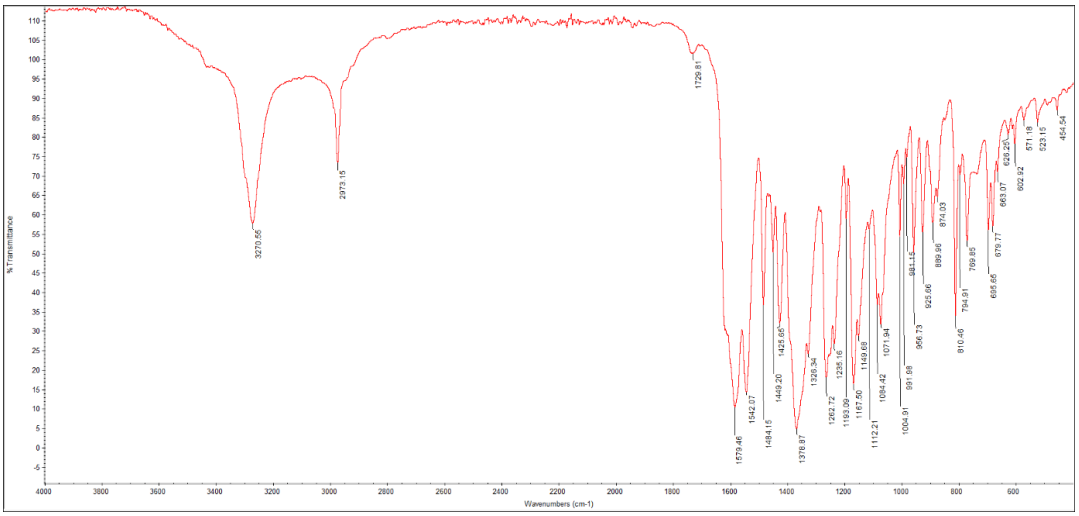
Supporting Information

Chiral Catalyst 2

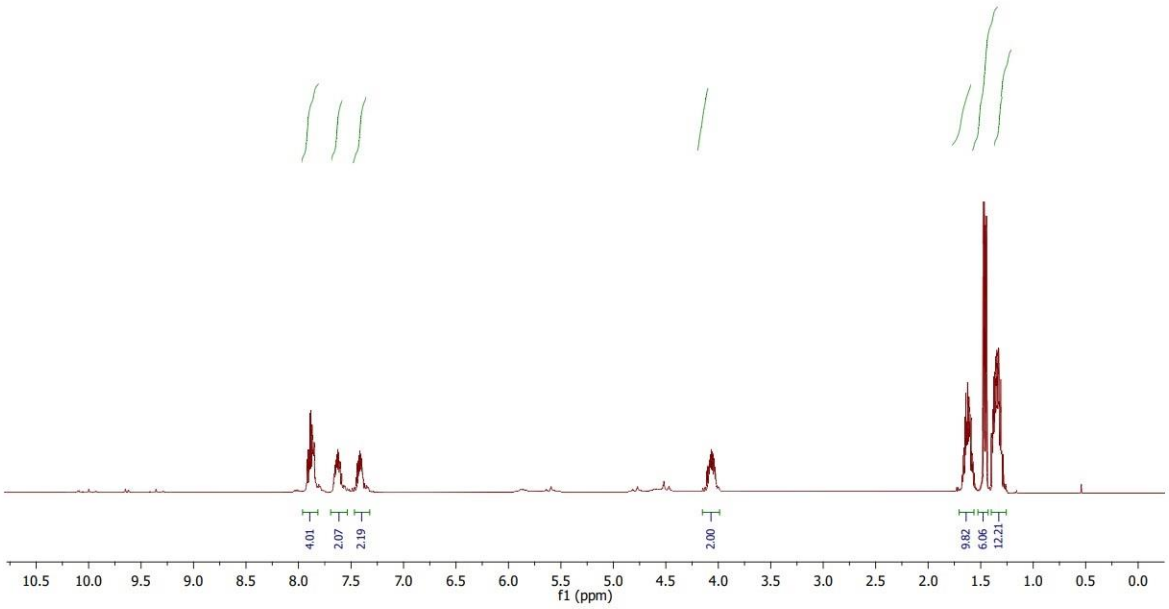


2

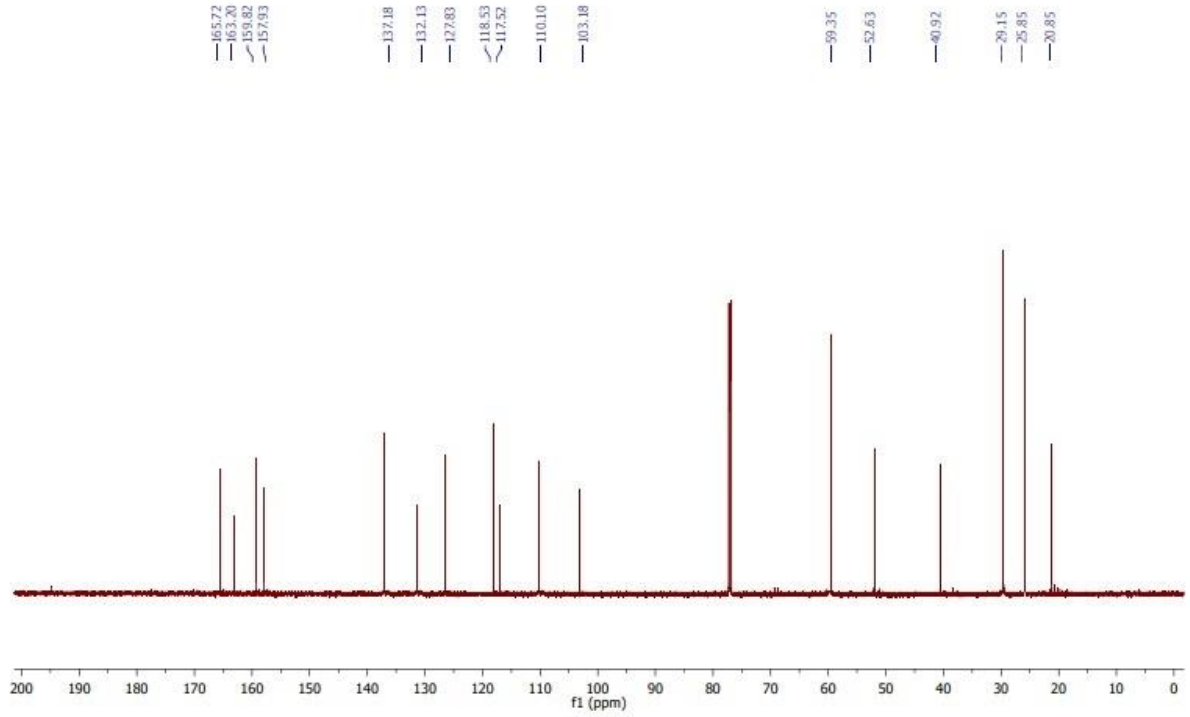
FT-IR spectra of catalyst 2



^{1}H NMR spectra of catalyst 2



^{13}C NMR spectra of catalyst 2



5a: (*R*)-10-(2-nitro-1-phenylethyl)anthracen-9(*10H*)-one [24]

FTIR (cm^{-1}): 1673, 1602, 1543, 1312, 928; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.65-7.54 (m, 2H), 7.51-7.42 (m, 4H), 7.12 (t, J = 7.8 Hz, 1H), 6.91 (t, J = 7.6 Hz, 2H), 6.00 (d, J = 7.8 Hz, 2H), 4.86 (dd, J = 13.0, 9.1 Hz, 1H), 4.58 (dd, J = 13.3, 7.3 Hz, 1H), 4.51 (d, J = 3.8 Hz, 1H), 4.08-4.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.5, 143.3, 138.7, 134.2, 133.6, 132.9, 132.7, 131.8, 128.8, 128.4, 128.3, 128.2, 128.0, 127.7, 126.7, 126.2, 75.4, 52.7, 46.9.

5b: (*R*)-10-(2-nitro-1-(2-nitrophenyl)ethyl)anthracen-9(*10H*)-one [25]

FTIR (cm^{-1}):1668, 1602, 1551, 1528, 1311, 934; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, J = 13.8, 7.7 Hz, 2H), 7.60-7.46 (m, 6H), 7.37-7.27 (m, 3H), 6.71-6.68 (m, 1H), 5.29 (dd, J = 13.8, 5.4 Hz, 1H), 5.12 (dd, J = 13.4, 10.3 Hz, 1H), 4.85 (d, J = 5.3 Hz, 1H), 4.77-4.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.1, 150.1, 140.8, 139.9, 134.2, 132.8, 132.3, 132.1, 131.8, 129.6, 129.3, 129.0, 128.8, 128,2, 127.7, 127.5, 126.3, 125.7, 124.9, 77.8, 46.5, 44.8.

5c: (*R*)-10-(1-(2-methoxyphenyl)-2-nitroethyl)anthracen-9(*10H*)-one [25]

FTIR (cm^{-1}): 1660, 1602, 1558, 1507, 1322, 927; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (m, J = 7.8 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.62-7.58 (t, J = 7.4 Hz, 2H), 7.50-7.40 (m, 4H), 7.13 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 6.53 (t, J = 7.4 Hz, 1H), 6.02 (d, J = 6.8 Hz, 1H), 4.43 (d, J = 5.7 Hz, 1H), 3.82 (s, 3H), 3.60 (m, 1H), 3.01 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.9, 156.8, 143.6, 141.3, 132.2, 131.8, 129.6, 129.3, 128.4, 128.1, 127.8, 126.6, 125.6, 124.5, 121.4, 120.6, 108.3, 75.3, 55.8, 46.2, 44.8.

5d: (*R*)-10-(1-(2-bromophenyl)-2-nitroethyl)anthracen-9(*10H*)-one [25]

FTIR (cm^{-1}): 1657, 1597, 1554, 1321, 936; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7,86 (d, J = 7.8 Hz, 1H); 7.65-7.52 (m, 5H), 7.37-7.30 (m, 2H), 7.14-7.11 (m, 2H), 6.62-6.59 (m, 1H), 5.14 (dd, J = 13.8,

5.5 Hz, 1H), 5.02-4.90 (m, 1H), 4.83 (d, *J* = 5.6 Hz, 1H), 4.00-3.96 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.4. 141.3, 139.6, 135.2, 133.3, 132.5, 132.3, 131.8, 130.1, 129.5, 129.0, 128.3, 127.6, 126.8, 126.1, 126.0, 76.9, 49.7, 45.2.

5e: (*R*)-10-(1-(3-bromophenyl)-2-nitroethyl)anthracen-9(*10H*)-one [25]

FTIR (cm^{-1}): 1662, 1659, 1549, 1315, 935; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.70-7.64 (m, 2H), 7.59-7.42 (m, 4H), 7.29 (d, *J* = 8.8 Hz, 1H), 6.55 (m, 2H), 5.56 (m, 1H), 4.86 (d, *J* = 6.6 Hz, 1H), 4.60-4.56 (m, 1H), 3.57 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.2, 142.6, 139.3, 135.6, 134.8, 133.7, 133.2, 132.8, 131.8, 131.5, 129.5, 128.7, 128.4, 128.3, 128.2, 127.4, 127.1, 126.8, 121.8, 76.2, 54.0, 46.8.

5f: (*R*)-10-(1-(4-fluorophenyl)-2-nitroethyl)anthracen-9(*10H*)-one [24]

FTIR (cm^{-1}): 1655, 1601, 1547, 1512, 1333, 932; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.4 Hz, 1H), 7.70-7.66 (m, 2H), 7.54-7.42 (m, 4H), 6.71 (t, *J* = 8.6 Hz, 2H), 5.95 (dd, *J* = 8.6, 5.4 Hz, 2H), 4.88 (dd, *J* = 13.2, 9.2 Hz, 1H), 4.58 (dd, *J* = 13.1, 7.4 Hz, 1H), 4.45 (d, *J* = 3.7 Hz, 1H), 4.05-4.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.6, 161.7, 142.3, 138.7, 134.4, 133.4, 132.6, 131.8, 131.1, 129.4, 128.8, 128.4, 128.2, 128.0, 127.8, 127.5, 127.2, 115.3, 114.6, 75.6, 53.7, 47.3.

5g: (*R*)-10-(1-(4-chlorophenyl)-2-nitroethyl)anthracen-9(*10H*)-one [24]

FTIR (cm^{-1}): 1657, 1612, 1551, 1326, 932; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.66-7.60 (m, 2H), 7.56-7.42 (m, 4H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.02 (d, *J* = 8.6 Hz, 2H), 4.66 (d, *J* = 6.8 Hz, 1H), 4.48 (d, *J* = 3.4 Hz, 1H), 4.02 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.7, 141.6, 138.3, 134.5, 134.2, 133.2, 132.7, 132.4, 131.8, 130.2, 128.5, 128.2, 128.0, 127.8, 127.5, 127.3, 127.0, 126.7, 75.4, 52.4, 46.8.

5h: (*R*)-10-(1-(4-methoxyphenyl)-2-nitroethyl)anthracen-9(*10H*)-one [24]

FTIR (cm^{-1}): 1671, 1585, 1557, 1502, 1312, 931; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.4 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.66-7.59 (m, 2H), 7.52-7.40 (m, 4H), 6.48 (d, *J* = 8.6 Hz, 2H), 6.06 (d, *J* = 8.7 Hz, 2H), 4.75 (dd, *J* = 13.2, 8.9 Hz, 1H), 4.55 (dd, *J* = 13.3, 7.6 Hz, 1H), 4.38 (d, *J* = 3.7 Hz, 1H), 3.99-3.96 (m, 1H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.7, 161.2, 141.6, 139.2, 134.6, 133.8, 132.7, 132.5, 129.5, 128.4, 128.3, 128.0, 127.9, 127.6, 127.1, 125.3, 114.2, 76.8, 54.8, 52.3, 46.8.

5i: (*R*)-10-(2-nitro-1-(*p*-tolyl)ethyl)anthracen-9(*10H*)-one [24]

FTIR (cm^{-1}): 1658, 1596, 1547, 1322, 930; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.4 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.60-7.56 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.42-7.32 (m, 2H), 6.73 (d, *J* = 7.8 Hz, 2H), 6.01 (d, *J* = 8.0 Hz, 2H), 4.85 (dd, *J* = 13.2, 8.7 Hz, 1H), 4.58 (td, *J* = 6.8, 6.5 Hz, 1H), 3.91 (d, *J* = 6.8 Hz, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.8, 142.2, 139.5, 138.3, 134.5, 133.7, 132.5, 132.3, 129.8, 128.6, 128.5, 128.2, 127.6, 127.3, 126.5, 126.1, 75.7, 54.1, 46.8, 21.9.

5j: (*R*)-10-(1-(2,4-dichlorophenyl)-2-nitroethyl)anthracen-9(*10H*)-one [24]

FTIR (cm^{-1}): 1672, 1592, 1552, 1323, 931; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (t, *J* = 7.6 Hz, 2H), 7.61 (s, 2H), 7.60-7.42 (m, 4H), 6.98 (d, *J* = 7.1 Hz, 1H), 6.79 (d, *J* = 6.8 Hz, 1H), 6.22 (d, *J* = 8.6 Hz, 1H), 4.67-4.58 (m, 2H), 4.38-4.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.5, 140.1, 138.8, 136.2, 134.7, 133.7, 133.3, 132.9, 132.4, 131.6, 130.4, 129.7, 128.7, 128.5, 128.2, 127.8, 127.3, 127.2, 126.4, 73.2, 47.0, 43.0.