

Chapter 2

NHC-Catalyzed Annulations of Nitroalkenes

2.1 Introduction

As described in the previous chapter, the NHCs are powerful catalysts for the reaction of C–X (X = O, S, N) bonds, however the reactions of C–C unsaturated bonds catalyzed by NHC are far less developed. In 2006, Fu and coworkers [1] disclosed an NHC-catalyzed umpolung of Michael acceptors. Nucleophilic addition of the triazolium-derived carbene to the Michael acceptor gives the adduct **A**. The sequential proton shift forms a β -anion intermediate **B**. Therefore, the umpolung of Michael acceptors was realized by reversing the polarity of the β -carbon of the Michael acceptor from an acceptor to a donor (Fig. 2.1).

In 2011, Matsuoka and coworkers [2] expanded this method to the dimerization of methacrylates. Later on, a better substrate scope was realized by Glorius and coworkers [3] (Fig. 2.2).

Besides that, the NHC was also a suitable catalyst for Morita–Baylis–Hillman (MBH) reaction. In 2007, Ye and coworkers [4] found that the reaction of cyclic enones with a variety of *N*-tosylarylimines went well under the catalyst of stable NHC **1b**, giving the aza-MBH adduct in good to excellent yields (Fig. 2.3).

In 2011, Scheidt and coworkers [5] reported an NHC-catalyzed [3+2] annulation of nitrones and vinyl sulfone. The [3+2] annulation products were afforded in good yields with high diastereoselectivities in the presence of sodium *tert*-butoxide and 20 mol% of triazolium **cat. 5f** (Fig. 2.4).

1,3-Dipolar annulation reactions of nitrile oxides and alkynes are efficient approaches to obtain isoxazoles. In 2011, Vasam and coworkers [6] demonstrated the [3+2] annulation of nitrile oxides and alkynes catalyzed by NHC. In the presence of NHC **cat.1d**, a variety of nitrile oxides reacted well with the alkynes to provide the desired isoxazoles in good yields (Fig. 2.5).

Nitroalkenes, due to their high reactivity, have become one of the most powerful reagents to construct functionalized cyclic compounds [7–17]. We envision that the

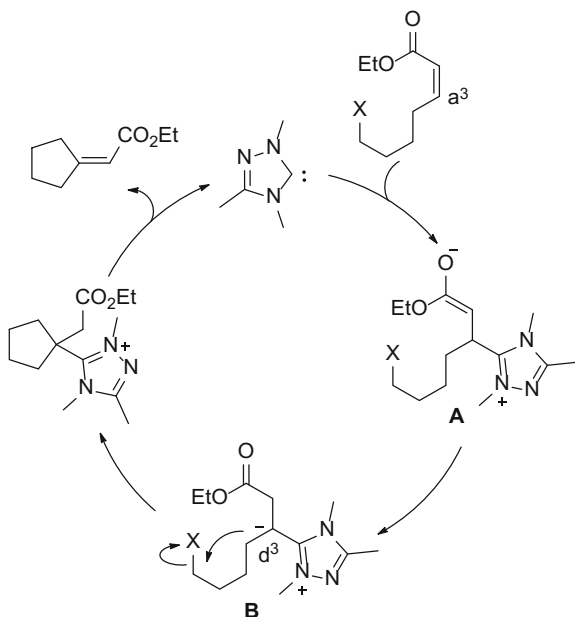
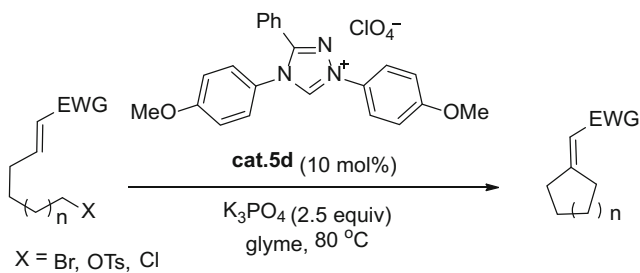


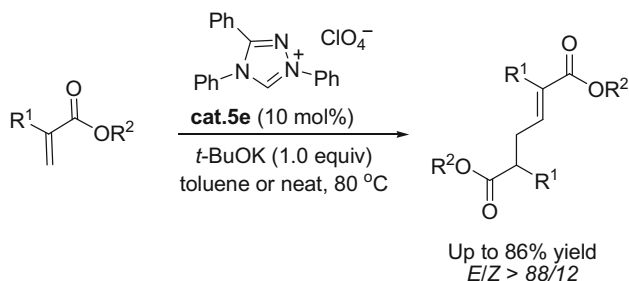
Fig. 2.1 NHC-catalyzed umpolung of Michael acceptors

NHC could attack nitroalkenes and finish the [4+2] annulation with oxodienes (Fig. 2.6).

2.2 Optimization of Conditions

Initially, we evaluated the model reaction of nitroalkene **2.1a** with oxodiene **2.2a** in the presence of various azolium salts. It was found that the use of imidazolium precatalyst **cat.1a** and triazolium precatalyst **cat.5e** gave no reaction (Table 2.1, entries 1 and 2). Gratifyingly, thioazolium **cat.8b–8c** showed reactivity for the reaction. And further solvent screening revealed that the reactions in toluene gave best yields of the desired product (entries 3–6, 9, and 10). It is necessary to note

Matsuoka's conditions:



Glorius' conditions: **cat.5e** (20 mol%), DBU (40 mol%),
1,4-dioxane, 80 °C

Fig. 2.2 NHC-catalyzed dimerization of Michael acceptors

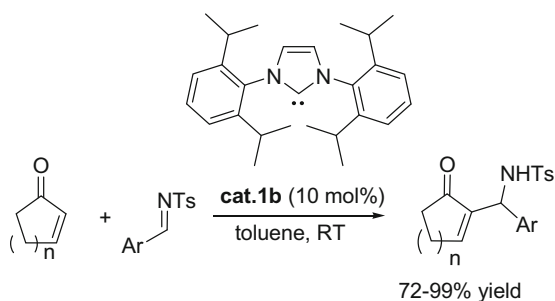


Fig. 2.3 NHC-catalyzed MBH reaction of cyclic enones

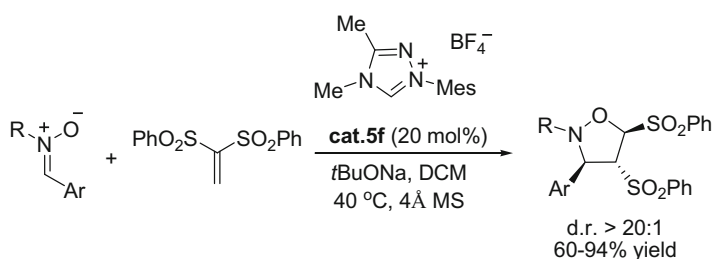


Fig. 2.4 NHC-catalyzed [3+2] annulation of vinyl sulfones with nitrones

that DABCO or PPh_3 offered no or little catalytic activity under current reaction conditions (entries 7 and 8). In the absence of catalyst, no reaction was observed (entry 11).

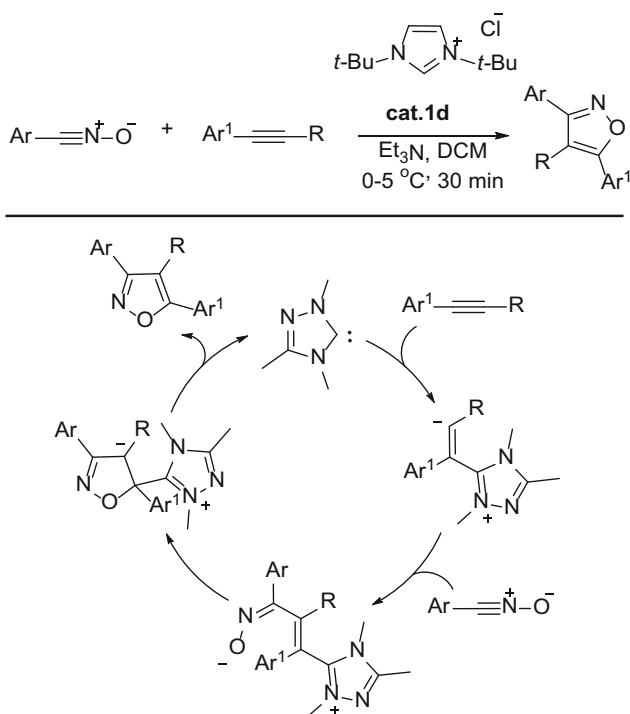


Fig. 2.5 NHC-catalyzed [3+2] annulation of alkynes

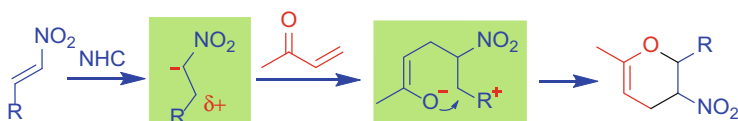
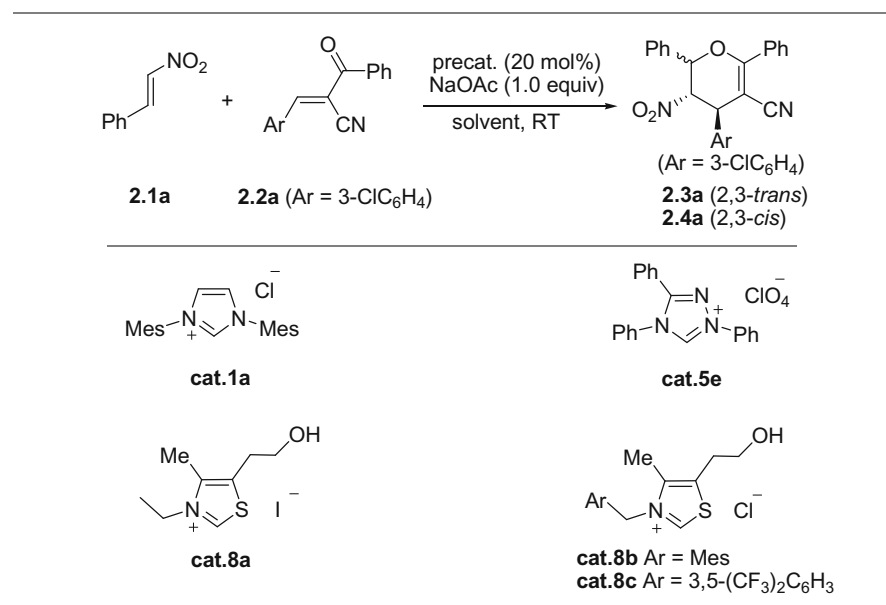


Fig. 2.6 Reaction design

2.3 Substrate Scope

Under the optimized reaction conditions, we conducted the reactions of nitroalkene **2.1** with oxodiene **2.2**. As shown in Table 2.2, in the presence of precatalyst **cat.8b** (20 mol%). Both electron-rich (4-Me, 4-MeO) and electron-poor (4-Cl, 4-Br) *para*-substituted nitroalkenes were tolerated, giving the cycloadducts **2.3b–2.3f** in good yield with good diastereoselectivity. *meta*-Substituted aromatic nitroalkenes also worked well (**2.3g** and **2.3h**). Moreover, introducing a heterocyclic thienyl group on the nitroalkene gave the corresponding dihydropyran **2.3i** in 76% yield with a

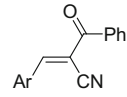
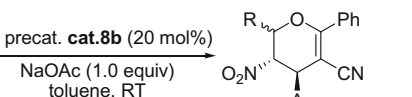
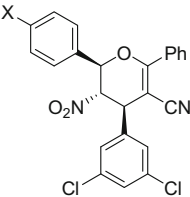
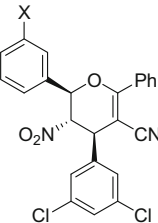
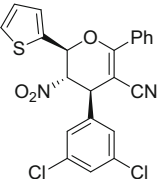
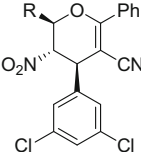
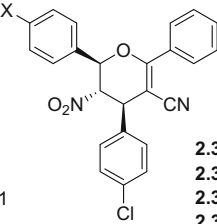
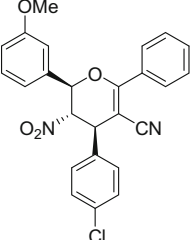
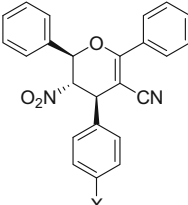
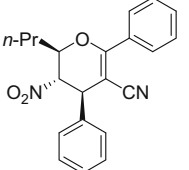
Table 2.1 Optimization of the reaction conditions

Entry	Cat	Solvent	Yield (%) ^a	2.3a:2.4a ^{b,c}
1	Cat.1a	DCM	Trace	/
2	Cat.5e	DCM	Trace	/
3	Cat.8a	DCM	Trace	/
4	Cat.8b	DCM	33	4:1
5	Cat.8c	DCM	84	1:2
6	Cat.8b	THF	55	5:1
7	DABCO ^d	THF	Trace	/
8	PPh ₃ ^d	THF	13	2:1
9	Cat.8b	Toluene	88	18:1
10	Cat.8c	Toluene	90	1:3
11	None	Toluene	NR	/

^aIsolated yield of the mixture of stereoisomers^bDetermined by ¹H NMR (300 MHz) of the raw product^cBeside **2.3a** and **2.4a**, another stereoisomer was also observed in the reaction mixture but not isolable^dNo base of NaOAc was added when DABCO or PPh₃ was used

diastereomeric ratio (d.r.) of 7:1. It is worth noting that good results were also obtained when β-alkyl nitroalkenes (R = cyclohexyl, *n*-butyl, *n*-propyl; cycloadducts **2.3j**, **2.3k** and **2.3l**) were employed. The α-cyano-β-aryl-α,β-unsaturated ketones were also varied. Different aryl groups (Ar = Ph, 4-ClC₆H₄, 4-BrC₆H₄)

Table 2.2 NHC-precursor **cat.8b** catalyzed [4+2] cycloadditions of nitroalkenes with oxodienes

 2.1	 2.2	 2.3 (2,3- <i>trans</i> , major)
Isolated yield, ^a followed by dr (<i>trans</i> / <i>cis</i>) of the reaction mixture ^b		
		
2.3b (X = H), 70%, dr = 7:1 ^c 2.3c (X = Me), 74%, dr = 9:1 2.3d (X = MeO), 72%, dr = 8:1 2.3e (X = Cl), 68%, dr = 6:1 2.3f (X = Br), 64%, dr = 5:1	2.3g (X = Cl), 70%, dr = 6:1 2.3h (X = MeO), 71%, dr = 6:1	2.3i , 76%, dr = 7:1
 2.3j (R = cyclohexyl), 50%, ^d dr = 3:1 2.3k (R = <i>n</i> -Bu), 72%, ^e dr = 5:1 2.3l (R = <i>n</i> -Pr), ^f 64%, dr = 6:1	 2.3m (X = H), 52%, dr = 7:1 ^c 2.3n (X = Me), 64%, dr = 5:1 2.3o (X = MeO), 55%, dr = 7:1 2.3p (X = Cl), 64%, dr = 4:1 2.3q (X = Br), 73%, dr = 6:1 ^c	
 2.3r , 76%, dr = 6:1	 2.3s , (X = H), 81%, ^f dr = 3:1 ^c 2.3t , (X = Br), 65%, dr = 5:1 ^c	 2.3u , 60%, dr = 4:1

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^aUnless otherwise noted, isolated yield of pure 2,3-*trans* isomer (**2.3**) is shown

^bDetermined by ¹H NMR spectroscopy (300 MHz)

^cAs well as the 2,3-*trans* (**2.3**) and 2,3-*cis* isomers (**2.4**), another stereoisomer was observed by ¹H NMR analysis of the reaction mixture, although it was not isolable

^dIsolated yield of a mixture of **2.3j** and **2.4j** (d.r. = 14:1)

^eIsolated yield of a mixture of **2.3k** and **2.4k** (d.r. = 7:1)

^fIsolated yield of the mixture of stereoisomers

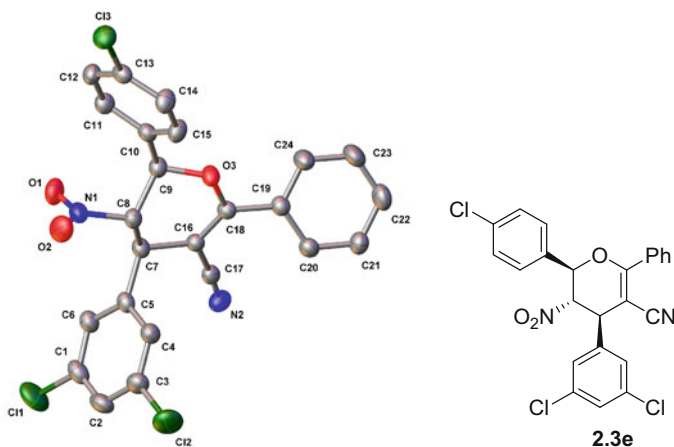


Fig. 2.7 X-ray structure of **2.3e**

were tolerable under current reaction conditions, giving the desired dihydropyrans **2.3m–2.3u** in good yield with moderate-to-good diastereoselectivity.

The structure of dihydropyrans **2.3e** was confirmed by the X-ray analysis of its crystal (Fig. 2.7).

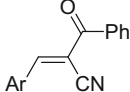
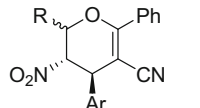
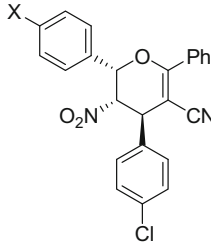
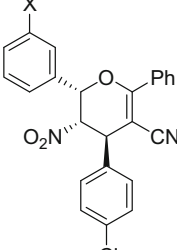
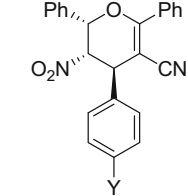
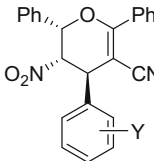
The synthesis of *cis*-cycloadduct **2.4** as the major product using NHC-precursor **cat.8c** was also investigated (Table 2.3). Both electron-donating and electron-withdrawing substituents at the *para* or *meta* positions of the β -phenyl group were well tolerated (**2.4m–2.4q**, **2.4r**, and **2.4v**). Moreover, the variation on the oxodienes was also investigated. Both *para* and *meta*-substituents on the aryl group of the oxodienes were well tolerated (**2.4s–2.4t** and **2.4a**). Much better diastereoselectivity was achieved when *ortho* chlorophenyl-substituted nitroalkenes were employed (**2.4w**).

The structure of dihydropyran **2.4s** was unambiguously established by the X-ray analysis of its crystal (Fig. 2.8).

2.4 Reduction of the Nitro Group of Dihydropyran

Some possible chemical transformations could be provided by the resulted highly functionalized dihydropyrans. For example, the nitro group in dihydropyrans **2.3** could be easily reduced by Zn/HCl, giving the corresponding 3-amino dihydropyrans **2.5** in good yield (Table 2.4).

Table 2.3 NHC-precursor **cat.8c** catalyzed [4+2] cycloadditions of nitroalkenes with oxodienes

 2.1	 2.2	$\xrightarrow[\text{toluene, RT}]{\text{cat.8c (20 mol\%)}, \text{NaOAc (1.0 equiv)}}$	 2.4 (2,3-cis, major)
Isolated yield, ^a followed by dr (<i>cis</i> / <i>trans</i>) of the reaction mixture ^{b,c}			
 2.4m (X = H), 87%, dr = 3:1 2.4n (X = Me), 91%, dr = 3:1 2.4o (X = MeO), 85%, dr = 2:1 2.4p (X = Cl), 92%, dr = 2:1 2.4q (X = Br), 83%, dr = 2:1  2.4r (X = OMe), 90%, dr = 4:1 2.4v (X = Cl), 88%, dr = 2:1			
 2.4s (Y = H), 89%, dr = 5:1 2.4t (Y = Br), 93%, dr = 4:1  2.4a (Y = <i>m</i>-Cl), 90%, dr = 3:1 2.4w (Y = <i>o</i>-Cl), 44%, dr > 20:1			

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^aIsolated yield of mixture of diastereomers

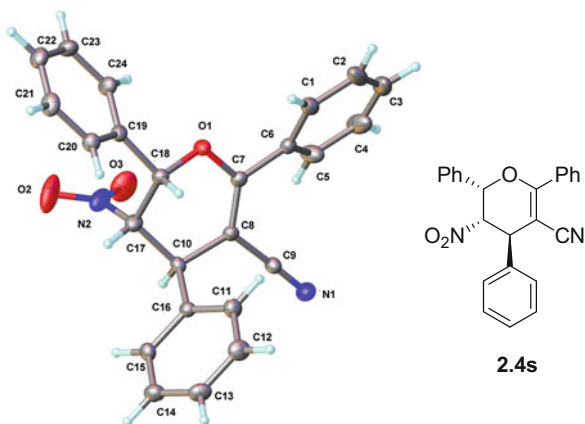
^bDetermined by ¹H NMR spectroscopy (300 MHz)

^cAs well as the 2,3-*trans* (**2.3**) and 2,3-*cis* isomers (**2.4**), another stereoisomer was observed by ¹H NMR analysis of the reaction mixture, although it was not isolable

2.5 Studies on the Enantioselectivity of the Annulation Process

We envisioned that a thiourea may be suitable catalyst to activate nitroalkenes. Therefore, a catalytic enantioselective variant of the annulation process was further studied with a series thioureas as co-catalysts. However, most of the thioureas have

Fig. 2.8 X-ray structure of **2.4s**



no catalytic effects and only gave trace of products. Thiourea **2.7d** could provide good yield but without enantioselectivity (Table 2.5).

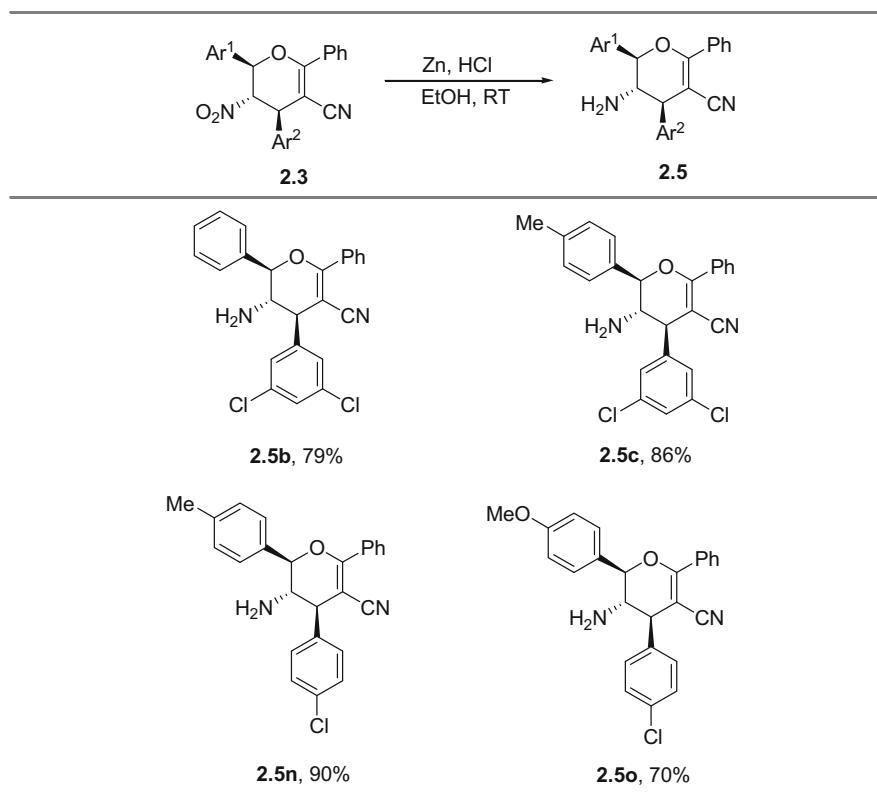
Although further optimization was extensively studied by a series of chiral NHCs, no more improvement could be achieved so far. Only chiral triazolium NHC **cat.2d** could catalyze the reaction, providing the desired dihydropyran **2.3b** in 24% yield with 29% ee (Table 2.6).

In order to improve the enantioselectivity, a series of additives and bases were also examined, but no further improvement was achieved (Table 2.7).

2.6 Mechanistic Studies

A plausible mechanism for the reaction is suggested in Fig. 2.9. Addition of the NHC catalyst to the nitroalkenes delivers the carbon anion intermediate **I**, this species could feasibly react with the electron-deficient oxodiene via Michael addition, providing adduct **II**. Intramolecular alkoxide attack at the carbonyl group leads to the desired dihydropyrans and regenerates the NHC catalyst.

The deuterium experiment was then carried out to investigate the mechanism. It was found that in the presence of NHC-precursor **cat.8b** (20 mol%), 1.0 equivalent of base, and D₂O, 19 and 14% deuteration of the α - and β -position of nitroalkene was observed. We proposed that the α -deuterium nitroalkenes were afforded via deuteration of adduct **I** followed by elimination. The acidity of the β -proton was enhanced by the addition of NHC to the β -position of nitroalkenes, and thus led to the β -deuterium nitroalkenes (Fig. 2.10).

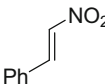
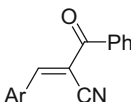
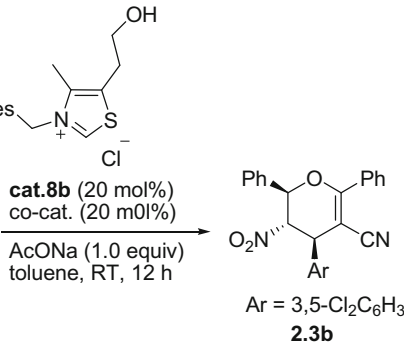
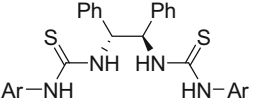
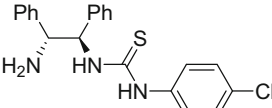
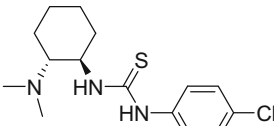
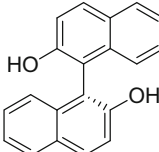
Table 2.4 Reduction of the nitro group of dihydropyran **2.3**

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2.7 Summary

In this chapter, *N*-heterocyclic carbene-catalyzed [4+2] annulation of nitroalkenes and oxodienes was developed, affording the corresponding dihydropyrans in good yield with good diastereoselectivity [18]. The reaction is possibly initiated by the addition of an *N*-heterocyclic carbene to nitroalkenes, which was revealed by deuteration experiments.

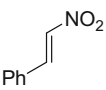
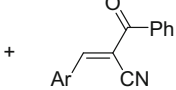
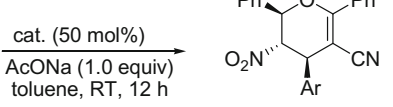
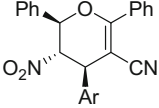
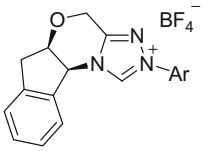
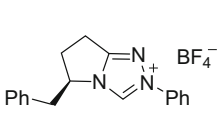
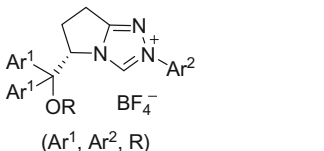
Table 2.5 Screening of co-catalysts

	+		 cat.8b (20 mol%) co-cat. (20 mol%) AcONa (1.0 equiv) toluene, RT, 12 h		
2.1a		2.2b			
co-cat.:					
 2.7a Ar = 4-ClC₆H₄ 2.7b Ar = 3,5-F₂C₆H₃			 2.7c		
 2.7d			 2.6		

Entry	Solvent	Co-cat.	Yield (%) ^a	2.3b:2.4b ^b	Ee ^c
1	Toluene	2.7a	Trace	/	/
2	Toluene	2.7b	Trace	/	/
3	Toluene	2.7c	Trace	/	/
4	Toluene	2.7d	76	7/1	0%
5	Toluene	2.6	Trace	/	/

^aIsolated yield of pure 2,3-*trans* isomer **2.3a**^bDetermined by ¹H NMR spectroscopy (300 MHz)^cDetermined by chiral-phase HPLC analysis

Table 2.6 Screening of chiral NHCs

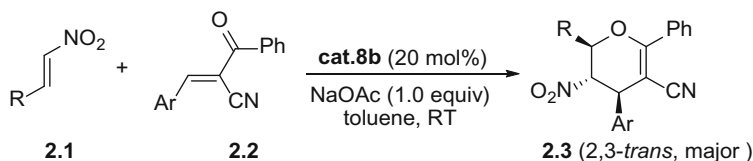
 2.1a	 2.2b	 cat. (50 mol%) AcONa (1.0 equiv) toluene, RT, 12 h  2.3b Ar = 3,5-Cl ₂ C ₆ H ₃
 cat.3c Ar = Ph, trace cat.3d Ar = Mes, trace	 cat.4d trace	 cat.6a (Ph, Ph, TBS), trace cat.2a (3,5-(CF ₃) ₂ C ₆ H ₃ , Ph, H), trace cat.2d (3,5-(CF ₃) ₂ C ₆ H ₃ , Bn, H) 24% yield, d.r. = 5/1, 29% ee cat.2e (Ph, Ph, H), trace cat.2f (3,5-(CF ₃) ₂ C ₆ H ₃ , Mes, H), trace

2.8 Experimental Part

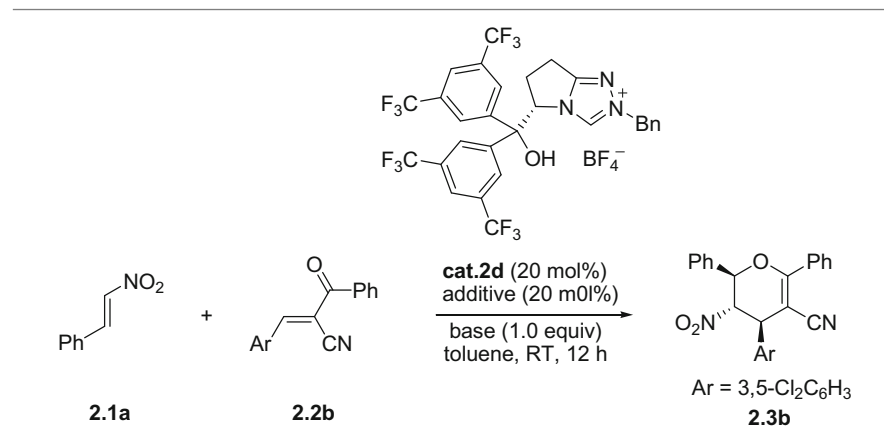
2.8.1 Materials

The nitroalkenes were prepared according to literature methods [19], purified by chromatography and recrystallization from ethanol. α -cyano- α,β -unsaturated ketones were prepared according to literature methods [20], purified by chromatography.

2.8.2 [4+2] Annulation of Nitroalkenes with α -Cyano- α,β -Unsaturated Ketones Catalyzed by NHC-Precursor Cat.8b

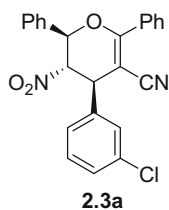


An oven-dried 50 mL Schlenk tube was charged with nitroalkenes **2.1** (0.4 mmol, 2.0 eq.), α -cyano- α,β -unsaturated ketones **2.2** (0.2 mmol, 1.0 eq.), **cat.8b** (0.04 mmol, 12 mg, 0.2 eq.), and AcONa (0.2 mmol, 16 mg, 1.0 eq.).

Table 2.7 Screening of additives and bases

Entry	Base	Additive	Yield (%)	2.3b:2.4b	Ee (%)
1	AcONa	LiBr	Trace	/	/
2	AcONa	AcOH	Trace	/	/
3	AcONa	PhOH	Trace	/	/
4	AcONa	Diphenyl thiourea	Trace	/	/
5	AcONa	Ti(OEt) ₄	Trace	/	/
6	AcONa	Zn(AcO) ₂	Trace	/	/
7	AcONa	Mg(<i>t</i> BuO) ₂	Trace	/	/
8	<i>t</i> BuOK	/	Trace	/	/
9	Cs ₂ CO ₃	/	Trace	/	/
10	DABCO	/	Trace	/	/
11	K ₂ CO ₃	/	Trace	/	/

To this mixture was added freshly distilled toluene (2 mL). The reaction mixture was stirred at room temperature until the full consumption of the α -cyano- α,β -unsaturated ketones (typically, 18 h). The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleumether/EtOAc as the eluent, typically 20:1-0:100) to furnish the corresponding cycloadduct.



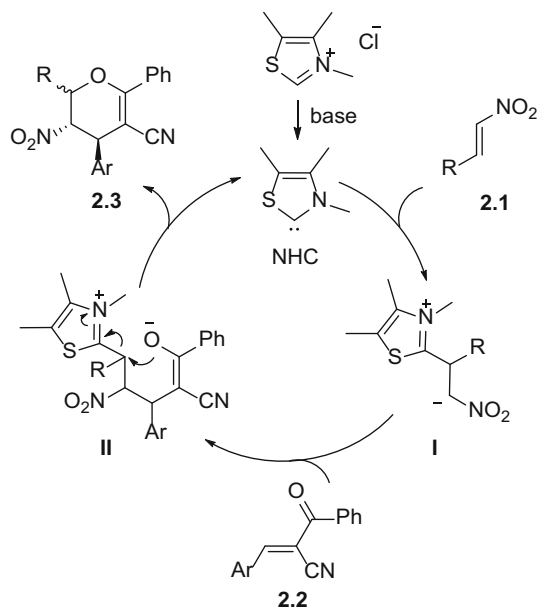


Fig. 2.9 Possible catalytic cycle. Reproduced from Ref. [18] by permission of John Wiley & Sons Ltd.

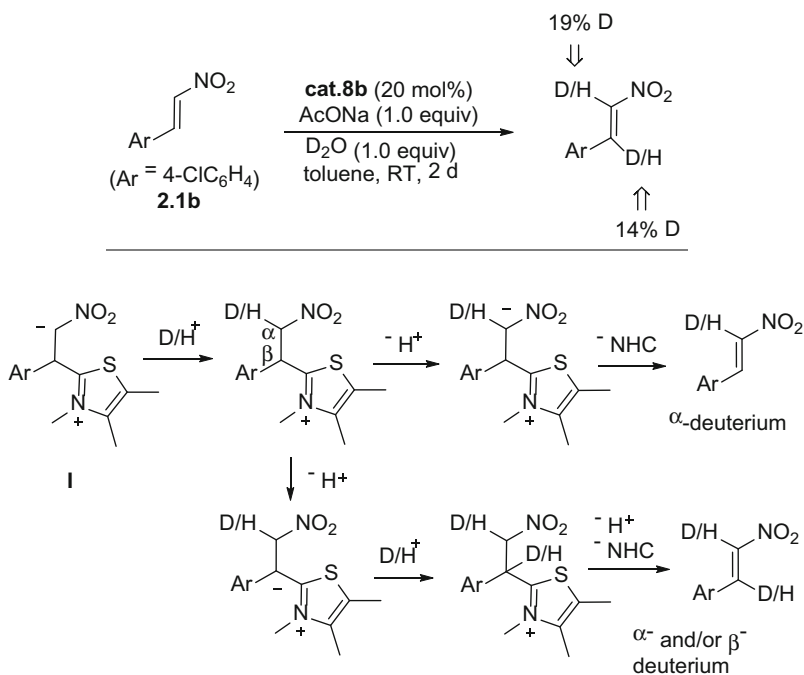
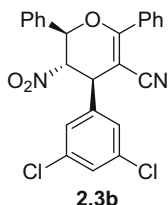


Fig. 2.10 Deuteration experiment. Reproduced from Ref. [18] by permission of John Wiley & Sons Ltd.

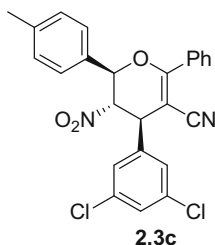
(2R*,3S*,4R*)-4-(3-chlorophenyl)-3-nitro-2,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 73 mg, 88%; yellow solid; mp 174–176 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, DMSO) δ 7.74 (d, J = 8.0 Hz, 3H), 7.65–7.61 (m, 2H), 7.56–7.44 (m, 9H), 5.85–5.83 (m, 2H), 4.78 (dd, J = 6.9, 3.6 Hz, 1H); ^{13}C NMR (75 MHz, DMSO) δ 165.4, 138.4, 133.7, 133.4, 131.6, 131.5, 130.9, 130.2, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 127.7, 117.7, 87.9, 86.6, 79.6, 45.8; IR (KBr) 2211, 1616, 1556, 1277, 1149, 778, 696; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 417.10005, found 417.09998.



(2R*,3S*,4R*)-4-(3,5-dichlorophenyl)-3-nitro-2,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile

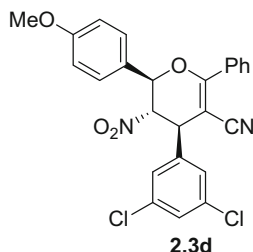
Yield: 63 mg, 70%; yellow solid; mp 211–213 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.83 (d, J = 7.1 Hz, 2H), 7.53–7.25 (m, 9H), 7.19 (d, J = 1.7 Hz, 2H), 5.45 (d, J = 9.7 Hz, 1H), 4.89 (t, J = 10.0 Hz, 1H), 4.58 (d, J = 10.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.5, 139.0, 136.4, 132.4, 132.3, 130.8, 130.8, 130.0, 129.4, 128.9, 128.6, 127.3, 126.6, 117.2, 90.3, 86.0, 80.4, 46.6; IR (KBr) 2360, 2210, 1622, 1556, 1297, 1161, 804, 694; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{17}\text{Cl}_2\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 451.06107, found 451.06161.



(2R*,3S*,4R*)-4-(3,5-dichlorophenyl)-3-nitro-6-phenyl-2-p-tolyl-3,4-dihydro-2H-pyran-5-carbonitrile

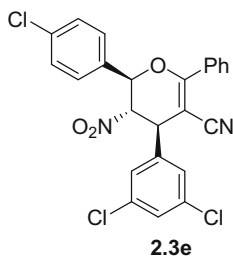
Yield: 68 mg, 74%; yellow solid; mp 238–240 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.82 (d, J = 7.1 Hz, 2H), 7.51–7.37 (m, 4H), 7.30–7.18 (m, 6H), 5.41 (d, J = 9.7 Hz, 1H), 4.89 (t, J = 9.9 Hz, 1H), 4.56 (d, J = 10.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.6, 140.9, 139.1, 136.3, 132.3, 130.9, 130.0, 129.8, 129.4, 128.8, 128.6, 127.3, 126.6,

117.3, 90.2, 85.9, 80.3, 46.6, 21.4; IR (KBr) 2360, 2211, 1557, 1273, 1151, 805, 694; HRMS (ESI) calcd for $C_{25}H_{19}Cl_2N_2O_3$ $[M+H]^+$ 465.07672, found 465.07685.



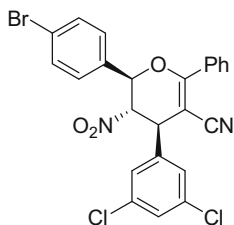
(2R*,3S*,4R*)-4-(3,5-dichlorophenyl)-2-(4-methoxyphenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 69 mg, 72%; yellow solid; mp 242–244 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 5:1); 1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 6.9 Hz, 2H), 7.52–7.25 (m, 6H), 7.19 (d, J = 1.8 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 5.39 (d, J = 9.7 Hz, 1H), 4.88 (t, J = 10.0 Hz, 1H), 4.56 (d, J = 10.2 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 161.3, 139.1, 136.3, 132.2, 130.9, 129.9, 128.9, 128.8, 128.6, 126.5, 124.2, 117.3, 114.7, 90.2, 85.9, 80.2, 55.5, 46.7; IR (KBr) 2210, 1613, 1557, 1516, 1250, 1150, 833, 694; HRMS (ESI) calcd for $C_{25}H_{19}Cl_2N_2O_4$ $[M+H]^+$ 481.07164, found 481.07241.



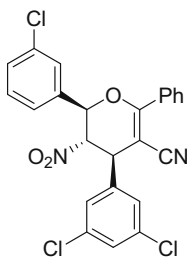
(2R*,3S*,4R*)-2-(4-chlorophenyl)-4-(3,5-dichlorophenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 66 mg, 68%; yellow solid; mp 227–230 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 5:1); 1H NMR (300 MHz, $CDCl_3$) δ 7.83–7.80 (m, 2H), 7.54–7.25 (m, 8H), 7.18 (d, J = 1.7 Hz, 2H), 5.43 (d, J = 9.7 Hz, 1H), 4.85 (t, J = 10.0 Hz, 1H), 4.56 (d, J = 10.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 138.7, 136.9, 136.4, 132.4, 130.9, 130.6, 130.0, 129.7, 128.9, 128.7, 128.6, 126.5, 117.1, 90.1, 86.2, 79.7, 46.6; IR (KBr) 2212, 1616, 1557, 1272, 1151, 830, 694; HRMS (ESI) calcd for $C_{24}H_{16}Cl_3N_2O_3$ $[M+H]^+$ 485.02210, found 485.02224.

**2.3f**

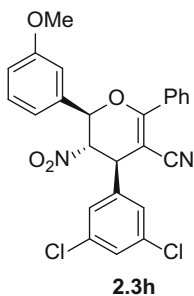
(2R*,3S*,4R*)-2-(4-bromophenyl)-4-(3,5-dichlorophenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 68 mg, 64%; yellow solid; mp 230–233 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.81 (d, J = 7.5 Hz, 2H), 7.57–7.39 (m, 6H), 7.28–7.25 (m, 2H), 7.18 (d, J = 1.6 Hz, 2H), 5.42 (d, J = 9.7 Hz, 1H), 4.84 (t, J = 10.0 Hz, 1H), 4.55 (d, J = 10.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.3, 138.7, 136.4, 132.6, 132.4, 131.4, 130.6, 130.0, 128.9, 128.6, 126.5, 125.1, 117.1, 90.0, 86.2, 79.7, 46.5; IR (KBr) 2359, 2212, 1617, 1557, 1264, 1151, 805, 695; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{16}\text{BrCl}_2\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 528.97159, found 528.97161.

**2.3g**

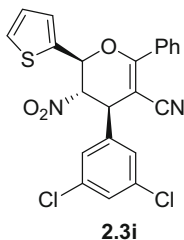
(2R*,3S*,4R*)-2-(3-chlorophenyl)-4-(3,5-dichlorophenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 67 mg, 70%; yellow solid; mp 191–193 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.82 (d, J = 7.2 Hz, 2H), 7.55–7.35 (m, 7H), 7.26 (d, J = 5.7 Hz, 1H), 7.19 (d, J = 1.5 Hz, 2H), 5.43 (d, J = 9.7 Hz, 1H), 4.86 (t, J = 10.0 Hz, 1H), 4.56 (d, J = 10.2 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.3, 138.7, 136.5, 135.4, 134.4, 132.4, 131.0, 130.6, 130.6, 130.0, 128.9, 128.6, 127.4, 126.5, 125.6, 117.0, 90.0, 86.3, 79.5, 46.5; IR (KBr) 2212, 1610, 1557, 1301, 1151, 862, 805, 694; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{16}\text{Cl}_3\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 485.02210, found 485.02232.



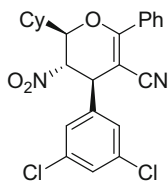
(2R*,3S*,4R*)-4-(3,5-dichlorophenyl)-2-(3-methoxyphenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 68 mg, 71%; yellow solid; mp 224–226 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.83 (d, J = 7.2 Hz, 2H), 7.53–7.43 (m, 3H), 7.38–7.25 (m, 2H), 7.19 (d, J = 1.5 Hz, 2H), 6.97–6.91 (m, 3H), 5.42 (d, J = 9.6 Hz, 1H), 4.88 (t, J = 9.9 Hz, 1H), 4.56 (d, J = 10.2 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.5, 160.2, 139.0, 136.4, 133.8, 132.3, 130.8, 130.5, 129.9, 128.9, 128.6, 126.6, 119.5, 117.2, 116.0, 113.1, 90.2, 86.0, 80.2, 55.5, 46.6; IR (KBr) 2211, 1611, 1557, 1274, 1149, 862, 774, 695; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{19}\text{Cl}_2\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 481.07164, found 481.07206.



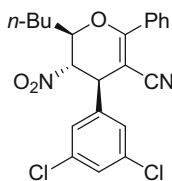
(2R*,3S*,4R*)-4-(3,5-dichlorophenyl)-3-nitro-6-phenyl-2-(thiophen-2-yl)-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 69 mg, 76%; yellow solid; mp 218–220 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.84 (d, J = 7.5 Hz, 2H), 7.54–7.39 (m, 5H), 7.19–7.15 (m, 3H), 7.04–7.01 (m, 1H), 5.79 (d, J = 9.6 Hz, 1H), 4.92 (t, J = 9.9 Hz, 1H), 4.54 (d, J = 10.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.1, 138.8, 136.4, 134.2, 132.4, 130.6, 130.0, 128.9, 128.8, 128.6, 128.5, 127.5, 126.6, 117.1, 90.4, 86.2, 76.3, 46.7; IR (KBr) 2359, 2214, 1558, 1276, 1149, 807, 697; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{15}\text{Cl}_2\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 457.01749, found 457.01795.

**2.3j**

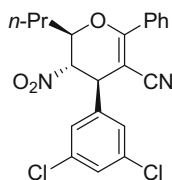
(2R*,3S*,4R*)-2-cyclohexyl-4-(3,5-dichlorophenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 46 mg, 50%; **2.3j/2.4j** = 14/1, yellow solid; R_f = 0.5 (**2.3j**), R_f = 0.51 (**4j**) (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ (**2.3j**) 7.79 (dd, J = 8.1, 1.5 Hz, 2H), 7.55–7.47 (m, 3H), 7.40 (t, J = 1.8 Hz, 1H), 7.15 (d, J = 1.8 Hz, 2H), 4.81 (t, J = 10.0 Hz, 1H), 4.42 (d, J = 10.2 Hz, 1H), 4.35 (d, J = 10.0 Hz, 1H), 1.82–1.62 (m, 7H), 1.33–1.18 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ (**2.3j**) 166.4, 139.4, 136.4, 132.2, 131.2, 129.9, 128.9, 128.4, 126.6, 117.4, 86.2, 85.5, 81.7, 46.5, 38.3, 29.8, 26.3, 26.0, 25.8, 25.1; IR (KBr) 2210, 1619, 1556, 1282, 1162, 805, 694; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{23}\text{Cl}_2\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 457.10802, found 457.10883.

**2.3k**

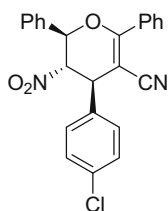
(2R*,3S*,4R*)-2-butyl-4-(3,5-dichlorophenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 62 mg, 72%; **2.3k/2.4k** = 7/1; yellow solid; R_f = 0.5 (**2.3k** and **2.4k**) (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ (**2.3k**) 7.79 (d, J = 6.9 Hz, 2H), 7.54–7.46 (m, 3H), 7.39 (s, 1H), 7.15 (d, J = 1.6 Hz, 2H), 4.65 (t, J = 9.9 Hz, 1H), 4.50–4.38 (m, 2H), 1.78–1.68 (m, 3H), 1.43–1.37 (m, 3H), 0.94 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ (**2.3k**) 166.1, 139.3, 136.3, 132.2, 131.1, 129.8, 128.9, 128.4, 126.6, 117.3, 88.8, 85.7, 77.9, 46.1, 30.6, 26.4, 22.3, 13.9; IR (KBr) 2354, 2210, 1616, 1556, 1281, 1162, 805, 693; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{Cl}_2\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 431.09237, found 431.09312.

**2.3l**

(2R*,3S*,4R*)-4-(3,5-dichlorophenyl)-3-nitro-6-phenyl-2-propyl-3,4-dihydro-2H-pyran-5-carbonitrile

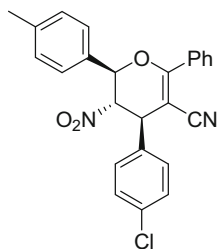
Yield: 53 mg, 64%; **2.3l/2.4l** = 5/1; yellow solid; R_f = 0.6 (**2.3l** and **2.4l**) (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ (**2.3l**) 7.79 (d, J = 6.9 Hz, 2H), 7.55–7.46 (m, 3H), 7.39 (s, 1H), 7.15 (d, J = 1.6 Hz, 2H), 4.64 (t, J = 9.9 Hz, 1H), 4.68–4.39 (m, 2H), 1.78–1.67 (m, 2H), 1.62–1.53 (m, 2H), 1.00 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ (**2.3l**) 166.1, 139.3, 136.4, 132.2, 131.1, 129.8, 128.9, 128.4, 126.6, 117.3, 88.8, 85.7, 77.7, 46.1, 32.9, 17.9, 13.7; IR (KBr) 2213, 1616, 1556, 1306, 1189, 735, 697; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 417.07672, found 417.07700.



2.3m

(2R*,3S*,4R*)-4-(4-chlorophenyl)-3-nitro-2,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 44 mg, 52%; yellow solid; mp 223–225 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.84–7.81 (m, 2H), 7.52–7.39 (m, 10H), 7.27–7.25 (m, 2H), 5.46 (d, J = 9.8 Hz, 1H), 4.88 (t, J = 10.1 Hz, 1H), 4.62 (d, J = 10.3 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.1, 135.5, 134.0, 132.7, 132.1, 131.1, 130.7, 130.1, 129.3, 128.8, 128.6, 127.4, 117.5, 90.8, 87.0, 80.5, 46.8; IR (KBr) 2359, 2210, 1616, 1557, 1275, 1150, 835, 694; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 417.10005, found 417.09991.

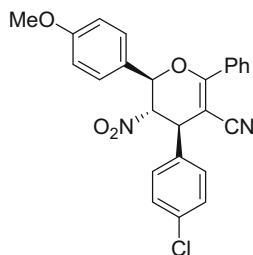


2.3n

(2R*,3S*,4R*)-4-(4-chlorophenyl)-3-nitro-6-phenyl-2-p-tolyl-3,4-dihydro-2H-pyran-5-carbonitrile

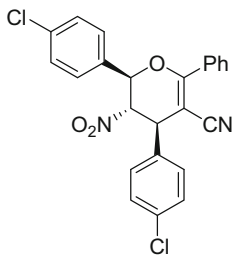
Yield: 55 mg, 64%; yellow solid; mp 197–199 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.82 (d, J = 7.1 Hz, 2H),

7.50–7.37 (m, 5H), 7.29–7.19 (m, 6H), 5.41 (d, $J = 9.8$ Hz, 1H), 4.88 (t, $J = 10.1$ Hz, 1H), 4.59 (d, $J = 10.4$ Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.2, 140.8, 135.4, 134.1, 132.1, 131.1, 130.0, 130.0, 129.7, 129.3, 128.8, 128.6, 127.3, 117.5, 90.7, 86.9, 80.4, 46.8, 21.4; IR (KBr) 2359, 2211, 1615, 1557, 1274, 1149, 818, 695; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 431.11570, found 431.11616.

**2.3o**

(2R*,3S*,4R*)-4-(4-chlorophenyl)-2-(4-methoxyphenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

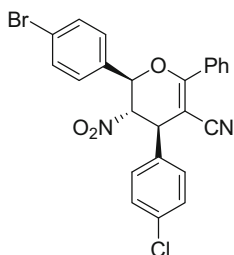
Yield: 52 mg, 58%; yellow solid; mp 194–196 °C; $R_f = 0.33$ (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.81 (dd, $J = 8.2, 1.2$ Hz, 2H), 7.50–7.23 (m, 9H), 6.91 (d, $J = 8.7$ Hz, 2H), 5.40 (d, $J = 9.8$ Hz, 1H), 4.87 (t, $J = 10.1$ Hz, 1H), 4.58 (d, $J = 10.4$ Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.3, 161.3, 135.4, 134.1, 132.1, 131.1, 130.0, 129.3, 128.9, 128.8, 128.6, 124.5, 117.6, 114.7, 90.7, 86.8, 80.3, 55.5, 46.9; IR (KBr) 2210, 1614, 1556, 1252, 1178, 1148, 737, 698; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 447.11061, found 447.11091.

**2.3p**

(2R*,3S*,4R*)-2,4-bis(4-chlorophenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 58 mg, 64%; yellow solid; mp 189–191 °C; $R_f = 0.33$ (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.82–7.80 (m, 2H), 7.53–7.32 (m, 9H), 7.26–7.23 (m, 2H), 5.44 (d, $J = 9.8$ Hz, 1H), 4.84 (t, $J = 10.1$ Hz, 1H), 4.59 (d, $J = 10.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.9, 136.8, 135.5,

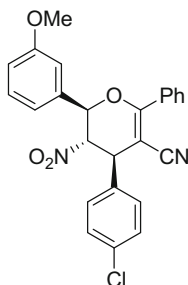
133.8, 132.2, 131.2, 130.9, 130.1, 129.6, 129.3, 128.9, 128.7, 128.5, 117.3, 90.6, 87.2, 79.7, 46.7; IR (KBr) 2360, 2211, 1616, 1557, 1272, 1149, 827, 696; HRMS (ESI) calcd for $C_{24}H_{17}Cl_2N_2O_3$ $[M+H]^+$ 451.06107, found 451.06121.



2.3q

(2R*,3S*,4R*)-2-(4-bromophenyl)-4-(4-chlorophenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 72 mg, 73%; yellow solid; mp 194–196 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 5:1); 1H NMR (300 MHz, $CDCl_3$) δ 7.82–7.79 (m, 2H), 7.55–7.37 (m, 7H), 7.27–7.22 (m, 4H), 5.41 (d, J = 9.8 Hz, 1H), 4.84 (t, J = 10.1 Hz, 1H), 4.58 (d, J = 10.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 135.5, 133.7, 132.5, 132.2, 131.7, 130.8, 130.0, 129.3, 128.9, 128.8, 128.5, 125.0, 117.3, 90.5, 87.1, 79.7, 46.7; IR (KBr) 2360, 2211, 1617, 1557, 1271, 1149, 824, 695; HRMS (ESI) calcd for $C_{24}H_{17}BrClN_2O_3$ $[M+H]^+$ 495.01056, found 495.01025.

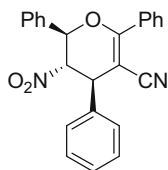


2.3r

(2R*,3S*,4R*)-4-(4-chlorophenyl)-2-(3-methoxyphenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

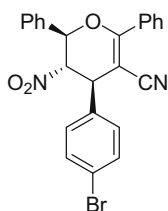
Yield: 69 mg, 76%; yellow solid; mp 192–194 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 5:1); 1H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 7.6 Hz, 2H), 7.52–7.24 (m, 8H), 6.97–6.92 (m, 3H), 5.42 (d, J = 9.8 Hz, 1H), 4.87 (t, J = 10.1 Hz, 1H), 4.60 (d, J = 10.3 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 160.2, 135.5, 134.1, 134.0, 132.1, 131.1, 130.5, 130.1, 129.3, 128.8, 128.6, 119.6, 117.5, 115.8, 113.2, 90.7, 87.0, 80.4, 55.5, 46.8; IR (KBr) 2359, 2210, 1614,

1557, 1273, 1151, 778, 697; HRMS (ESI) calcd for $C_{25}H_{20}ClN_2O_4$ $[M+H]^+$ 447.11061, found 447.11115.

**2.3s**

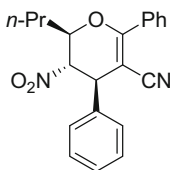
(2R*,3S*,4R*)-3-nitro-2,4,6-triphenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 62 mg, 81%; **2.3s/2.4s** = 3/1; yellow solid. A small amount of **2.3s** was obtained by careful recrystallization. Analytical data for **2.3s**: mp 238–240 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 5:1); 1H NMR (300 MHz, DMSO) δ 7.73 (d, J = 6.8 Hz, 2H), 7.63–7.39 (m, 13H), 5.83 (d, J = 9.7 Hz, 1H), 5.71 (t, J = 10.0 Hz, 1H), 4.70 (d, J = 10.2 Hz, 1H); ^{13}C NMR (75 MHz, DMSO) δ 165.2, 136.0, 133.4, 131.7, 131.5, 130.2, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 117.8, 88.5, 87.3, 79.8, 46.5; IR (KBr) 2211, 1617, 1556, 1273, 1148, 773, 697. HRMS (ESI) calcd for $C_{24}H_{19}N_2O_3$ $[M+H]^+$ 383.13902, found 383.13993.

**2.3t**

(2R*,3S*,4R*)-4-(4-bromophenyl)-3-nitro-2,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile

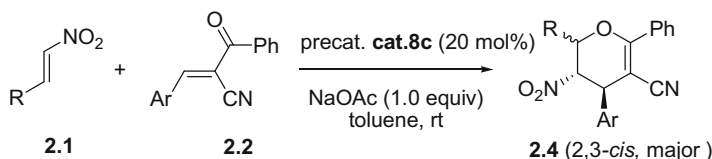
Yield: 60 mg, 65%; yellow solid; mp 220–222 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 5:1); 1H NMR (300 MHz, $CDCl_3$) δ 7.84–7.81 (m, 2H), 7.57–7.39 (m, 10H), 7.19 (dd, J = 8.8, 2.2 Hz, 2H), 5.45 (d, J = 9.8 Hz, 1H), 4.88 (t, J = 10.1 Hz, 1H), 4.60 (d, J = 10.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 134.6, 133.0, 132.7, 132.1, 131.1, 130.7, 129.6, 129.3, 128.8, 128.6, 127.4, 123.6, 117.5, 90.7, 86.9, 80.5, 46.9; IR (KBr) 2210, 1616, 1556, 1276, 1149, 830, 696; HRMS (ESI) calcd for $C_{24}H_{18}BrN_2O_3$ $[M+H]^+$ 461.04953, found 461.05042.

**2.3u**

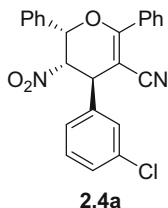
(2R*,3S*,4R*)-3-nitro-4,6-diphenyl-2-propyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 42 mg, 60%; yellow solid; mp 173–175 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.80 (dd, J = 8.0, 1.4 Hz, 2H), 7.51–7.37 (m, 6H), 7.26 (dd, J = 7.4, 1.5 Hz, 2H), 4.69 (t, J = 9.9 Hz, 1H), 4.53–4.42 (m, 2H), 1.81–1.52 (m, 4H), 0.99 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.3, 135.9, 131.8, 131.5, 129.7, 129.3, 128.8, 128.4, 127.9, 117.7, 89.6, 87.2, 77.7, 46.7, 33.0, 17.9, 13.7; IR (KBr) 2359, 2209, 1616, 1556, 1306, 1159, 761, 697; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 349.15467, found 349.15506.

**2.8.3 [4+2] Annulation of Nitroalkenes
with α -Cyano- α,β -Unsaturated Ketones
Catalyzed by NHC-Precursor Cat.8c**

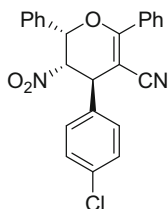


An oven-dried 50 mL Schlenk tube was charged with nitroalkenes **2.1** (0.4 mmol, 2.0 eq.), α -cyano α,β -unsaturated ketones **2.2** (0.2 mmol, 1.0 eq.), **cat.8c** (16 mg, 0.04 mol, 0.2 eq.), and AcONa (0.2 mmol, 16 mg, 1.0 eq.). To this mixture was added freshly distilled toluene (2 mL). The reaction mixture was stirred at room temperature until the full consumption of the α -cyano α,β -unsaturated ketones (typically, 18 h). The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent, typically 20:1-0:100) to furnish the corresponding cycloadduct as a mixture of *trans*- and *cis* isomers.



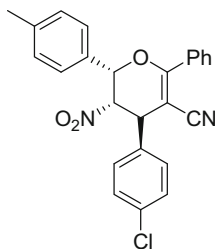
(2S*,3S*,4R*)-4-(3-chlorophenyl)-3-nitro-2,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Total yield: 74 mg, 90%; **2.4a/2.3a** = 3/1; yellow solid. A small amount of **2.4a** was obtained by recrystallization. Analytical data for **2.4a**: R_f = 0.4 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, DMSO) δ 7.91 (dd, J = 7.4, 2.1 Hz, 2H), 7.79 (s, 1H), 7.62–7.59 (m, 3H), 7.53–7.49 (m, 3H), 7.38 (d, J = 1.6 Hz, 5H), 5.75 (d, J = 2.0 Hz, 1H), 5.55 (d, J = 1.3 Hz, 1H), 4.85 (s, 1H); ^{13}C NMR (75 MHz, DMSO) δ 165.6, 140.5, 134.1, 133.7, 132.1, 131.4, 130.8, 129.2, 128.7, 128.6, 128.5, 128.2, 127.8, 125.6, 118.8, 85.8, 84.0, 73.6, 41.7. IR (KBr) 2210, 1622, 1556, 1156, 776, 696; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 417.10005, found 417.10039.

**2.4m**

(2S*,3S*,4R*)-4-(4-chlorophenyl)-3-nitro-2,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile

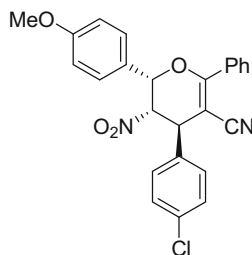
Total yield: 73 mg, 87%; **2.4 m/2.3 m** = 3/1; yellow solid. A small amount of **2.4 m** was obtained by careful chromatograph. Analytical data for **2.4 m**: mp 176–178 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.95–7.93 (m, 2H), 7.53–7.46 (m, 5H), 7.39–7.37 (m, 5H), 7.25–7.23 (m, 2H), 5.35 (d, J = 2.3 Hz, 1H), 5.01 (t, J = 2.2 Hz, 1H), 4.38 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.5, 136.4, 135.4, 133.3, 131.9, 131.8, 130.2, 129.9, 129.7, 129.2, 128.8, 128.5, 125.7, 118.5, 87.2, 83.4, 74.0, 43.6; IR (KBr) 2210, 1624, 1555, 1298, 1159, 828, 697; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 417.10005, found 417.09975.

**2.4n**

(2S*,3S*,4R*)-4-(4-chlorophenyl)-3-nitro-6-phenyl-2-(p-tolyl)-3,4-dihydro-2H-pyran-5-carbonitrile

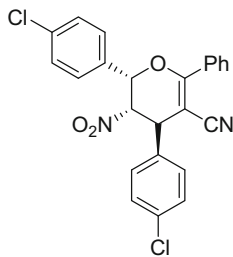
Total yield: 78 mg, 91%; **2.4n/2.3n** = 3/1; yellow solid. A small amount of **2.4n** was obtained by careful chromatograph. Analytical data for **2.4n**: mp 159–161 °C;

$R_f = 0.35$ (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.93 (dd, $J = 7.9, 1.5$ Hz, 2H), 7.52–7.45 (m, 5H), 7.37 (d, $J = 8.5$ Hz, 2H), 7.14 (dd, $J = 19.6, 8.2$ Hz, 4H), 5.33 (d, $J = 2.3$ Hz, 1H), 4.98 (t, $J = 2.4$ Hz, 1H), 4.36 (d, $J = 1.5$ Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.5, 139.7, 136.4, 135.3, 131.9, 131.8, 130.3, 130.1, 129.9, 129.8, 128.8, 128.5, 125.6, 118.6, 87.3, 83.4, 74.1, 43.5, 21.3; IR (KBr) 2210, 1624, 1555, 1298, 1159, 830, 696; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 431.11570, found 431.11618.

**2.4o**

(2S*,3S*,4R*)-4-(4-chlorophenyl)-2-(4-methoxyphenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

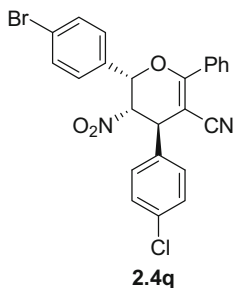
Total yield: 75 mg, 85%; **2.4o/2.3o** = 2/1; yellow solid. A small amount of **2.4o** was obtained by careful chromatograph. Analytical data for **2.4o**: mp 179–181 °C; $R_f = 0.35$ (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.94–7.91 (m, 2H), 7.55–7.45 (m, 5H), 7.37 (d, $J = 8.5$ Hz, 2H), 7.15 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 5.31 (d, $J = 2.5$ Hz, 1H), 4.97 (t, $J = 2.3$ Hz, 1H), 4.36 (d, $J = 1.6$ Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.6, 160.6, 136.4, 135.3, 131.9, 131.8, 130.1, 129.9, 128.8, 128.5, 127.1, 125.2, 118.6, 114.6, 87.3, 83.4, 74.0, 55.5, 43.5; IR (KBr) 2210, 1615, 1555, 1254, 1159, 826, 772, 696; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 447.11061, found 447.11062.

**2.4p**

(2S*,3S*,4R*)-2,4-bis(4-chlorophenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

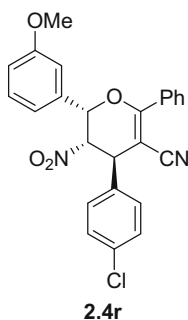
Total yield: 83 mg, 92%; **2.4p/2.3p** = 2/1; yellow solid. A small amount of **2.4p** was obtained by careful chromatograph. Analytical data for **2.4p**: mp 174–176 °C;

$R_f = 0.35$ (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.93–7.91 (m, 2H), 7.57–7.46 (m, 5H), 7.39–7.34 (m, 4H), 7.18 (d, $J = 8.5$ Hz, 2H), 5.31 (d, $J = 2.2$ Hz, 1H), 4.97 (t, $J = 2.1$ Hz, 1H), 4.40 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.3, 136.2, 135.7, 135.5, 132.0, 131.9, 131.6, 130.3, 129.8, 129.4, 128.9, 128.4, 127.1, 118.3, 87.0, 83.5, 73.4, 43.5; IR (KBr) 2210, 1624, 1555, 1298, 1159, 830, 696; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{17}\text{Cl}_2\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 451.06107, found 451.06127.



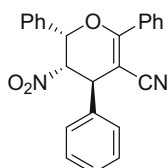
(2S*,3S*,4R*)-2-(4-bromophenyl)-4-(4-chlorophenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Total yield: 82 mg, 83%; **2.4q/2.3q** = 2/1; yellow solid. A small amount of **2.4q** was obtained by careful chromatograph. Analytical data for **2.4q**: mp 186–188 °C; $R_f = 0.42$ (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.93–7.90 (m, 2H), 7.56–7.46 (m, 7H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 5.29 (d, $J = 1.8$ Hz, 1H), 4.97 (d, $J = 1.8$ Hz, 1H), 4.40 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.3, 136.2, 135.5, 132.4, 132.4, 132.0, 131.6, 130.2, 129.8, 128.9, 128.4, 127.3, 123.9, 118.3, 86.9, 83.5, 73.4, 43.5; IR (KBr) 2210, 1620, 1555, 1297, 1158, 826, 695; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{17}\text{BrClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 495.01056, found 495.01076.



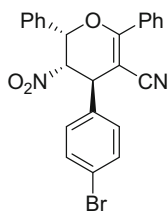
(2S*,3S*,4R*)-4-(4-chlorophenyl)-2-(3-methoxyphenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Total yield: 80 mg, 90%; **2.4r/2.3r** = 4/1; yellow solid. A small amount of **2.4r** was obtained by careful chromatograph. Analytical data for **2.4r**: mp 154–156 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.94 (dd, J = 8.0, 1.6 Hz, 2H), 7.55–7.45 (m, 5H), 7.36 (d, J = 8.5 Hz, 2H), 7.28–7.25 (m, 1H), 6.91–6.88 (m, 1H), 6.80–6.78 (m, 2H), 5.30 (d, J = 2.2 Hz, 1H), 5.00 (t, J = 2.1 Hz, 1H), 4.37 (d, J = 0.9 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.4, 160.1, 136.4, 135.4, 134.8, 131.9, 130.3, 130.2, 129.9, 128.8, 128.5, 118.5, 117.8, 114.6, 111.8, 87.2, 83.4, 73.8, 55.5, 43.5; IR (KBr) 2210, 1613, 1555, 1293, 1151, 772, 694; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 447.11061, found 447.11061.

**2.4s**

(2S*,3S*,4R*)-3-nitro-2,4,6-triphenyl-3,4-dihydro-2H-pyran-5-carbonitrile

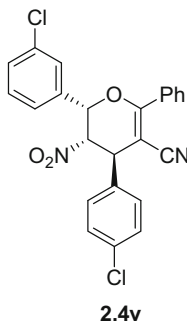
Total yield: 68 mg, 89%; **2.4s/2.3s** = 5/1; yellow solid. A small amount of **2.4s** was obtained by careful recrystallization. Analytical data for **2.4s**: R_f = 0.5 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.96 (dd, J = 7.8, 1.6 Hz, 2H), 7.53–7.35 (m, 11H), 7.25 (s, 2H), 5.38 (d, J = 2.1 Hz, 1H), 5.10 (t, J = 2.1 Hz, 1H), 4.42 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.3, 138.0, 133.6, 132.0, 131.7, 129.9, 129.6, 129.4, 129.2, 129.1, 128.8, 128.5, 125.7, 118.8, 87.5, 83.7, 73.8, 44.3; IR (KBr) 2210, 1623, 1556, 1290, 1152, 769, 698. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 383.13902, found 383.13918.

**2.4t**

(2S*,3S*,4R*)-4-(4-bromophenyl)-3-nitro-2,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile

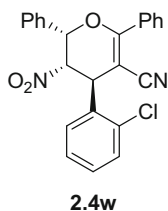
Total yield: 85 mg, 93%; **2.4t/2.3t** = 4/1; yellow solid. A small amount of **2.4t** was obtained by careful chromatograph. Analytical data for **2.4t**: mp 170–172 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 7.94 (d, J = 6.6 Hz, 2H), 7.63–7.05 (m, 5H), 7.38–7.22 (m, 7H), 5.35 (d, J = 1.9 Hz, 1H), 5.01 (d, J = 1.8 Hz, 1H), 4.36 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3)

δ 166.5, 136.9, 133.3, 133.1, 131.9, 131.8, 130.2, 129.7, 129.1, 128.8, 128.5, 125.6, 123.5, 118.5, 87.1, 83.3, 74.0, 43.6; IR (KBr) 2210, 1624, 1555, 1298, 1159, 824, 696; HRMS (ESI) calcd for $C_{24}H_{18}BrN_2O_3$ $[M+H]^+$ 461.04953, found 461.04928.



(2S*,3S*,4R*)-2-(3-chlorophenyl)-4-(4-chlorophenyl)-3-nitro-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

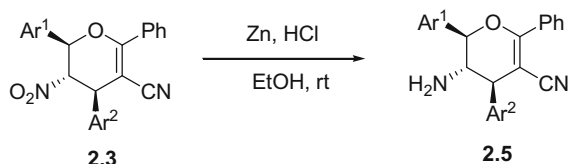
Total yield: 79 mg, 88%; **2.4v**/**2.3v** = 2/1; yellow solid. A small amount of **2.4v** was obtained by careful chromatograph. Analytical data for **2.4v**: mp 100–102 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 5:1); 1H NMR (300 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.0, 1.4 Hz, 2H), 7.57–7.47 (m, 5H), 7.39–7.23 (m, 5H), 7.13 (d, J = 7.3 Hz, 1H), 5.29 (s, 1H), 4.99 (dd, J = 2.3, 1.6 Hz, 1H), 4.42 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 136.1, 135.5, 135.4, 135.2, 132.0, 131.6, 130.5, 130.3, 129.8, 128.9, 128.5, 125.9, 123.8, 118.3, 86.9, 83.6, 73.1, 43.6; IR (KBr) 2210, 1556, 1298, 1151, 831, 694; HRMS (ESI) calcd for $C_{24}H_{17}Cl_2N_2O_3$ $[M+H]^+$ 451.06107, found 451.06113.



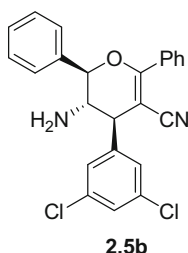
(2S*,3S*,4R*)-4-(2-chlorophenyl)-3-nitro-2,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 37 mg, 44%; white solid; mp 158–160 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 5:1); 1H NMR (300 MHz, $CDCl_3$) δ 7.97–7.94 (m, 2H), 7.57–7.47 (m, 5H), 7.43–7.35 (m, 5H), 7.24–7.21 (m, 2H), 5.26 (d, J = 1.8 Hz, 1H), 5.04 (dd, J = 2.4, 1.1 Hz, 1H), 4.84 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 134.8, 134.2, 133.4, 131.9, 131.8, 131.0, 130.6, 130.3, 129.6, 129.1, 128.8, 128.5, 128.1, 125.7, 118.6, 85.5, 83.0, 74.1, 41.8; IR (KBr) 2359, 2210, 1622, 1555, 1295, 1156, 856, 695; HRMS (ESI) calcd for $C_{24}H_{18}ClN_2O_3$ $[M+H]^+$ 417.10005, found 417.10029.

2.8.4 Reduction of the Nitro Group of 2.3

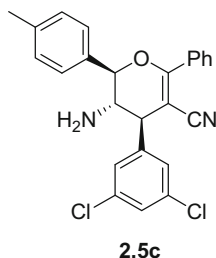


Typical procedure: To a stirred solution of **2.3c** (128 mg, 0.28 mmol) in EtOH (4 mL) was added zinc powder (330 mg, 18.0 eq.) and 1.5 mL of 6 M HCl (aq.). The resulting reaction mixture was stirred at room temperature for 1.0 h. followed by the filtration through Celite with washing by ether. The solvent was removed in vacuo. NaOH (15%) was added to the above mixture until pH 10. The aqueous layer was extracted with ether, the combined organic layer was washed with brine, dried (MgSO₄), and concentrated to give the products **2.5c**.



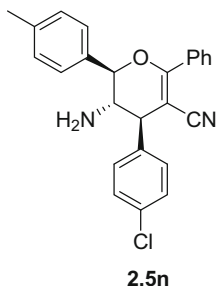
(2R*,3S*,4R*)-3-amino-4-(3,5-dichlorophenyl)-2,6-diphenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 79%; yellow solid; mp 181–183 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 1:1); ¹H NMR (300 MHz, CDCl₃) δ 7.82 (dd, J = 8.1, 1.5 Hz, 2H), 7.47–7.35 (m, 9H), 7.28 (d, J = 1.8 Hz, 2H), 4.86 (d, J = 9.5 Hz, 1H), 3.60 (d, J = 9.5 Hz, 1H), 3.23 (t, J = 9.5 Hz, 1H), 0.93 (br, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 166.8, 143.0, 135.9, 132.1, 131.6, 129.7, 129.2, 128.8, 128.6, 128.5, 127.8, 127.1, 118.9, 86.7, 84.6, 56.3, 49.9; IR (KBr) 2359, 2207, 1613, 1587, 1270, 1156, 801, 698; HRMS (ESI) calcd for C₂₄H₁₉Cl₂N₂O [M+H]⁺ 421.08690, found 421.08717.



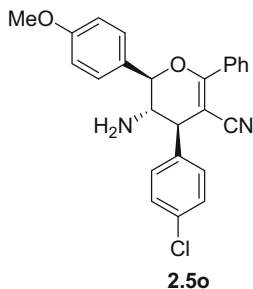
(2R*,3S*,4R*)-3-amino-4-(3,5-dichlorophenyl)-6-phenyl-2-(p-tolyl)-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 86%; yellow solid; mp 100–102 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 1:1); ^1H NMR (300 MHz, CDCl_3) δ 7.82–7.79 (m, 2H), 7.45–7.20 (m, 10H), 4.82 (d, J = 9.5 Hz, 1H), 3.57 (d, J = 9.5 Hz, 1H), 3.22 (t, J = 9.5 Hz, 1H), 2.37 (s, 3H), 0.98 (br, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.7, 143.1, 139.6, 135.8, 132.9, 132.1, 131.4, 129.7, 128.6, 128.5, 128.5, 127.7, 127.1, 118.9, 86.5, 84.6, 56.1, 50.0, 21.3; IR (KBr) 2360, 2207, 1613, 1567, 1269, 1156, 803, 696; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{21}\text{Cl}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 435.10255, found 435.10376.



(2R*,3S*,4R*)-3-amino-4-(4-chlorophenyl)-6-phenyl-2-(p-tolyl)-3,4-dihydro-2H-pyran-5-carbonitrile

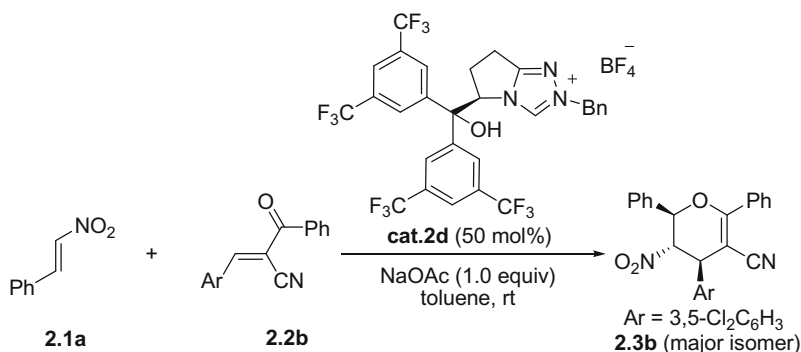
Yield: 90%; yellow solid; mp 169–171 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 1:1); ^1H NMR (300 MHz, CDCl_3) δ 7.81 (dd, J = 7.9, 1.3 Hz, 2H), 7.45–7.31 (m, 9H), 7.24 (d, J = 7.8 Hz, 2H), 4.85 (d, J = 9.5 Hz, 1H), 3.62 (d, J = 9.5 Hz, 1H), 3.23 (t, J = 9.5 Hz, 1H), 2.37 (s, 3H), 0.96 (br, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.4, 139.6, 137.9, 134.2, 133.3, 132.4, 131.3, 129.9, 129.8, 129.6, 128.8, 128.5, 127.7, 119.2, 87.4, 84.6, 56.3, 49.8, 21.4; IR (KBr) 2359, 2206, 1613, 1516, 1274, 1154, 816, 697; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{22}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 401.14152, found 401.14203.



(2R*,3S*,4R*)-3-amino-4-(4-chlorophenyl)-2-(4-methoxyphenyl)-6-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

Yield: 70%; yellow solid; mp 180–182 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 1:1); ^1H NMR (300 MHz, CDCl_3) δ 7.73 (dd, J = 8.0, 1.5 Hz, 2H), 7.38–7.25 (m, 9H), 6.88 (d, J = 8.7 Hz, 2H), 4.77 (d, J = 9.5 Hz, 1H), 3.75 (s, 3H), 3.55 (d, J = 9.5 Hz, 1H), 3.16 (t, J = 9.5 Hz, 1H), 1.18 (br, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.4, 160.6, 138.0, 134.2, 132.5, 131.3, 129.9, 129.6, 129.1, 128.5, 128.5, 128.2, 119.2, 114.5, 87.4, 84.4, 56.3, 55.5, 49.8; IR (KBr) 23580, 2206, 1613, 1515, 1277, 1153, 829, 698; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{22}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 417.13643, found 417.13700.

2.8.5 Recation Catalyzed by Chiral NHC-Precursor Cat.2d



The reaction was carried out as the same procedure in Table 2.1: Yield: 24%; HPLC analysis: 29% ee. [Daicel CHIRALPAK AD-H column; 20 °C; 0.8 mL/min; solvent system: isopropanol/hexanes = 8:92; retention times: 13.5 min (minor), 14.9 min (major)].

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