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Review

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Nucleophilic rhodanine, thiazolidine-2,4-dione and thiazol-4(5*H*)-one substrates in asymmetric reactions

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Dedicated to Professor Choong Eui Song on the occasion of his 65th birthday

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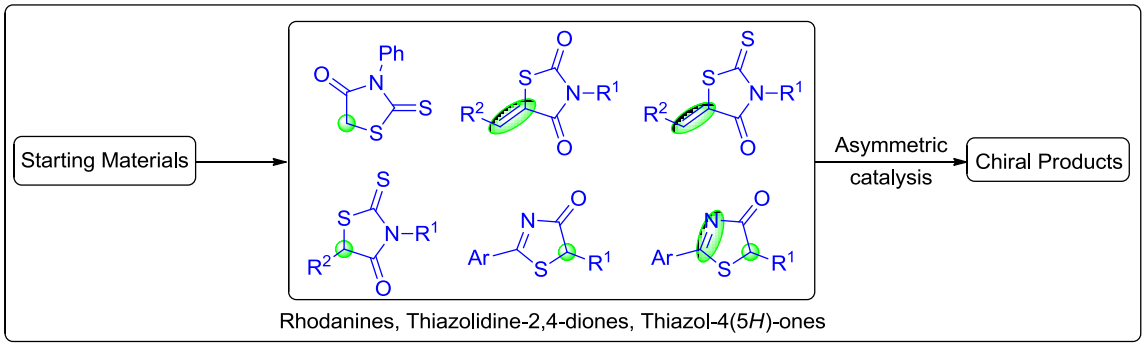
Abstract

Substituted rhodanines, thiazolidine-2,4-diones and thiazol-4(5*H*)-ones as nucleophilic substrates have attracted great attention in asymmetric reactions in the past six years due to their high impact in medicinal and pharmaceutical importance. The current review provides a cursory overview of the synthetic methods developed to access the rhodanine, thiazolidine-2,4-dione and thiazol-4(5*H*)-one substrates and a summary of their applications in catalytic asymmetric reactions to synthesize a broad range of differently substituted chiral derivatives of the corresponding substrates with tertiary/quaternary stereogenic centres.



Keywords: Rhodanines, thiazolidine-2,4-diones; thiazol-4(5*H*)-ones, asymmetric catalysis, metal catalysis, organocatalysis

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1. Introduction

Sulfur- and nitrogen-containing five- membered heterocyclic compounds such as rhodanines, thiazolidine-2,4-diones and thiazol-4(5*H*)-ones have become interesting target structures for drug development and discovery. Several compounds of these classes are in clinical trials for diabetic complications, type II *diabetes mellitus*, antibacterial, antiviral, antimalarial, antifungal, antitumour activities and inhibitors of pancreatic cholesterol esterase.[1-21] In particular, the rhodanine derivative epalrestat and the thiazolidine-2,4-dione derivatives rosiglitazone, troglitazone and pioglitazone are commercialized for the treatment of *diabetes mellitus* (Figure 1).[22-25] Rhodadynes (condensation product of rhodanine and carbonyl compounds), which inhibit the BCL-2 protein, are presently used in cancer therapy.[26] Rhodanines were also introduced into organic molecules to apply in the development of dye-sensitized solar cells / organic photovoltaic cells, which mainly promoted the absorption spectrum towards red-shift with high efficiency.[27-31]

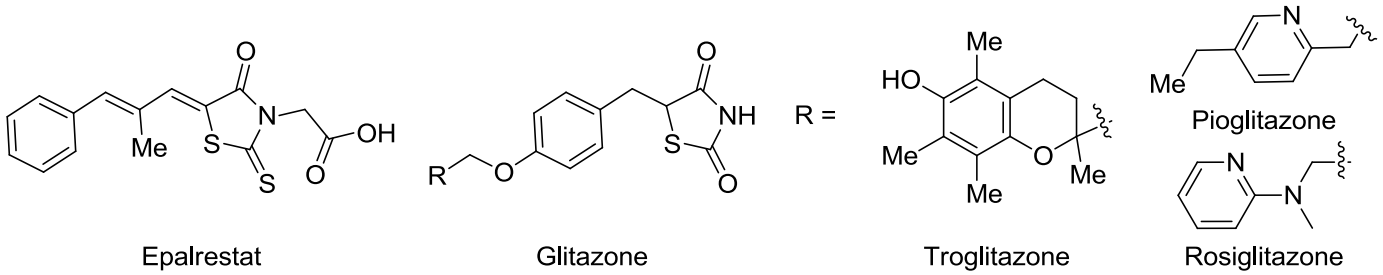


Figure 1. Commercialized drugs from the class of rhodanine and thiazolidine-2,4-dione.

In view of the importance of the rhodanines, thiazolidine-2,4-diones, thiazol-4(5*H*)-ones and their stereoisomers, in particular of their biological and pharmacological activities, several methods have been established for their facile synthesis. In this review, we summarize the development of enantioselective catalytic methods using rhodanine, thiazolidine-2,4-dione and thiazol-4(5*H*)-one as nucleophiles to synthesize

a wide range of their chiral derivatives. A systematic study of the published literature was organised, summarizing the nucleophiles, the synthetic procedures for accessing them, and their application under different asymmetric catalytic methods.

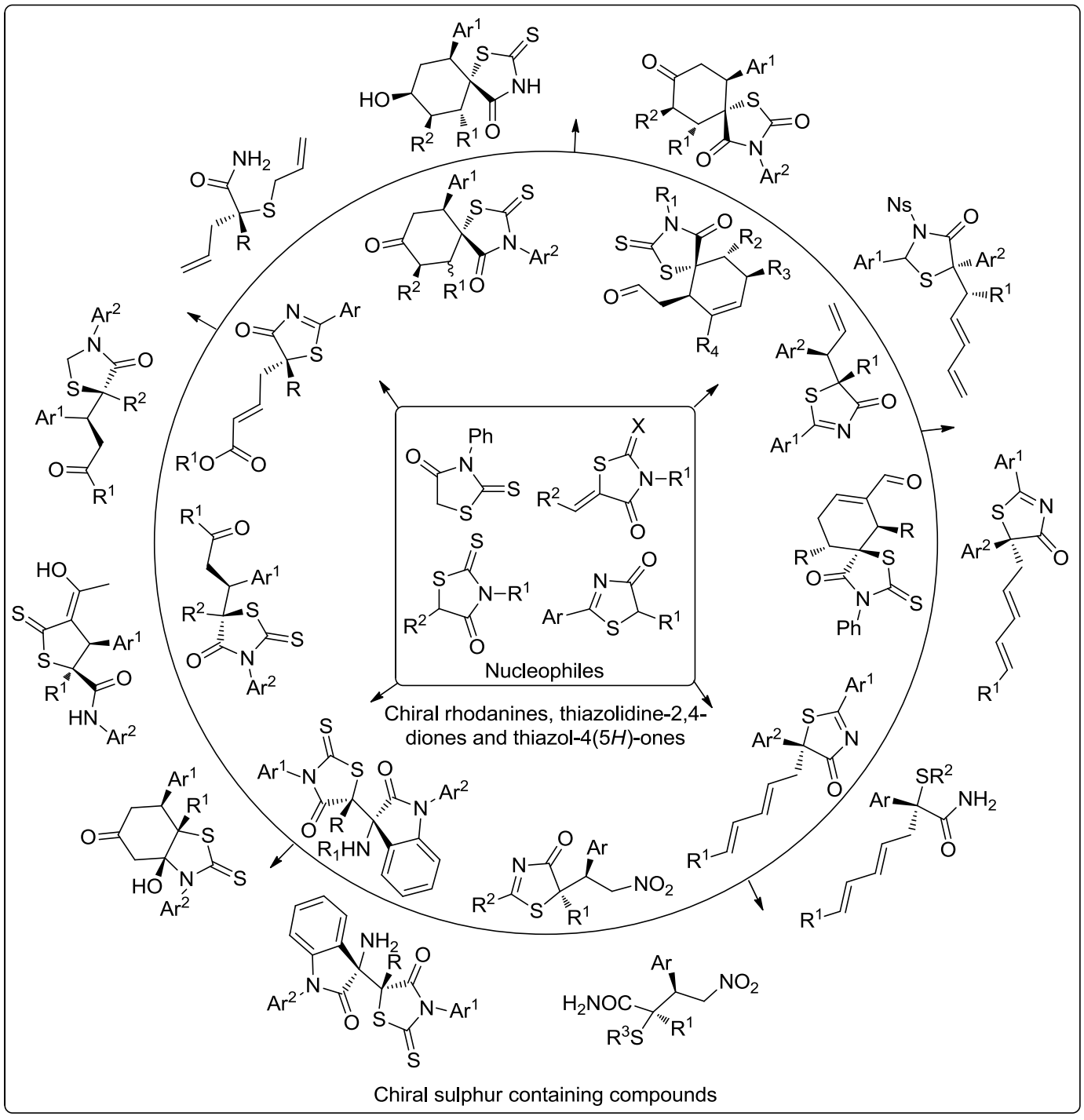


Figure 2. Versatile chiral rhodanines, thiazolidine-2,4-diones and thiazol-4(5*H*)-ones derivatives and diverse attractive chiral sulphur containing molecules derived from them.

2. Synthesis of the Nucleophiles

The nucleophiles used in the reported literatures are classified into the following five categories (Figure 3):

1. *N*-Substituted rhodanine substrates **1**
2. 5-Alkylidenethiazolidine-2,4-dione substrates **2**
3. 5-Alkylidenerhodanine substrates **3**
4. 5-Substituted rhodanine substrates **4**
5. Thiazol-4(5*H*)-one substrates **5**

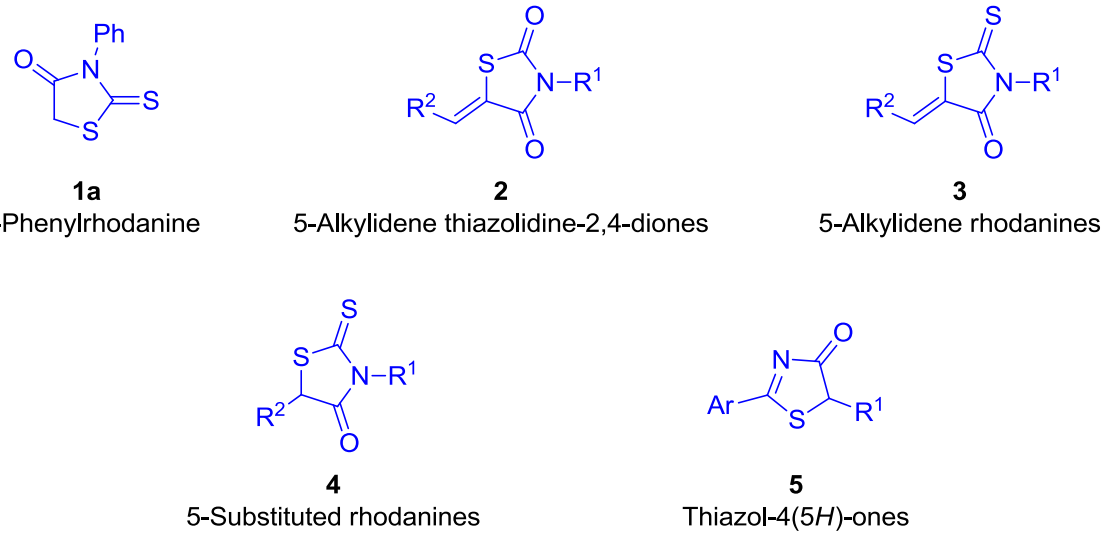
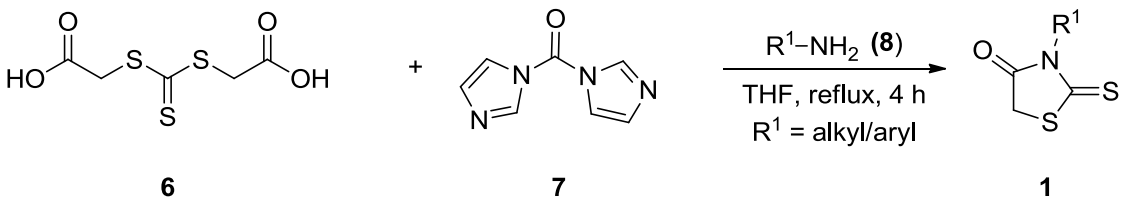


Figure 3. Varieties of rhodanines, thiazolidine-2,4-diones and thiazol-4(5*H*)-ones used as nucleophiles.

Rhodanine, thiazolidine-2,4-dione and their derivatives are synthesized by various well-known methods.[32-35] Rhodanine and thiazolidine-2,4-diones are commercially available and can easily be converted into their *N*-substituted derivatives through simple transformations.[36-44] However in this review, the methods employed for the preparation of these compounds as starting materials for further asymmetric reactions, are summarized in the sections below.

2.1. Synthesis of *N*- substituted rhodanines 1

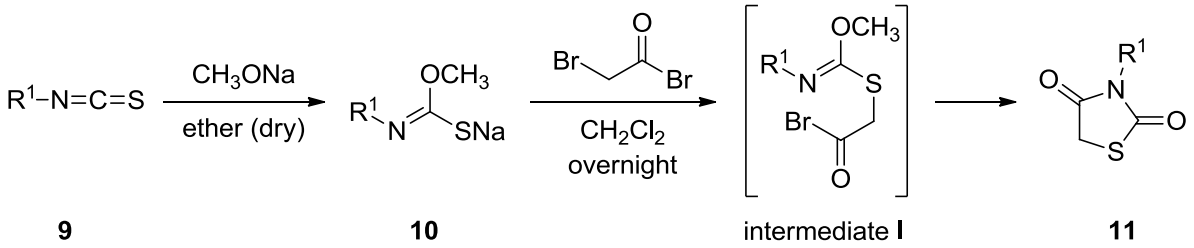
Harada *et al*. reported the direct synthesis of *N*-substituted rhodanines by the reaction of aliphatic/aromatic amines **8** with a stirred solution of bis(carboxymethyl)trithiocarbonate (**6**) and 1,1'-carbonyldiimidazole (**7**) in THF (Scheme 1).[45]



Scheme 1. *N*-Substituted rhodanines **1** from amine **8.**

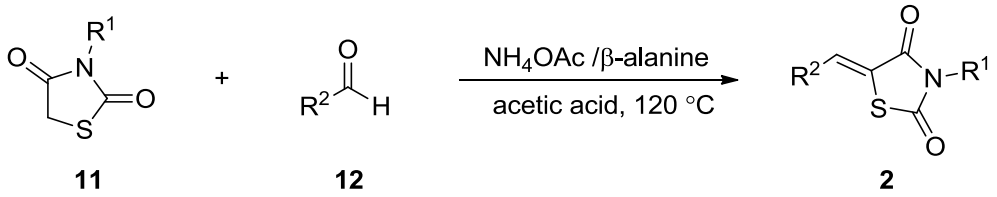
2.2. Synthesis of 5-alkylidenethiazolidine-2,4-diones 2

5-Alkylidenethiazolidine-2,4-dione **2** can easily be accessed through the synthesis of *N*-substituted thiazolidine-2,4-diones **11**. Initially, the sodium salts of *O*-methyl-*N*-substituted iminothiocarbonates **10** are prepared by the reaction of isothiocyanates **9** with sodium methoxide in dry ether, a method developed by Kristian and co-workers. The obtained products **10** were treated with bromoacetyl bromide in dichloromethane to obtain *N*-substituted thiazolidine-2,4-diones **11** through the intermediate **I** (Scheme 2).[46]



Scheme 2. *N*-Substituted thiazolidine-2,4-diones **11** from isothiocyanates **9.**

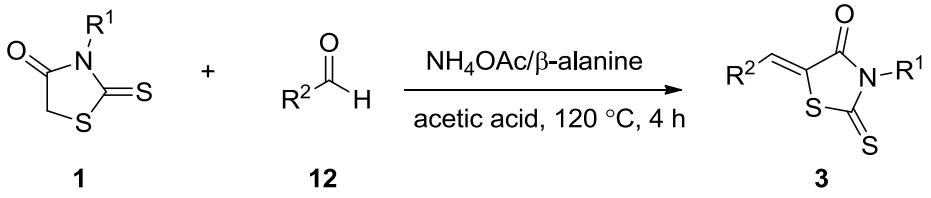
Deng *et al*.[47] performed the Knoevenagel-condensation of *N*-substituted thiazolidine-2,4-diones **11** with the aldehydes **12** in the presence of ammonium acetate or β-alanine in acetic acid to afford the desired 5-alkylidenethiazolidine-2,4-diones **2** following the procedure for the synthesis of rhodanine derivatives developed by Harada *et al*. (Scheme 3).[45]



Scheme 3. 5-Alkylidenethiazolidine-2,4-diones **2** from *N*-substituted thiazolidine-2,4-diones **11**

2.3. Synthesis of 5-alkylidenerhodanines 3

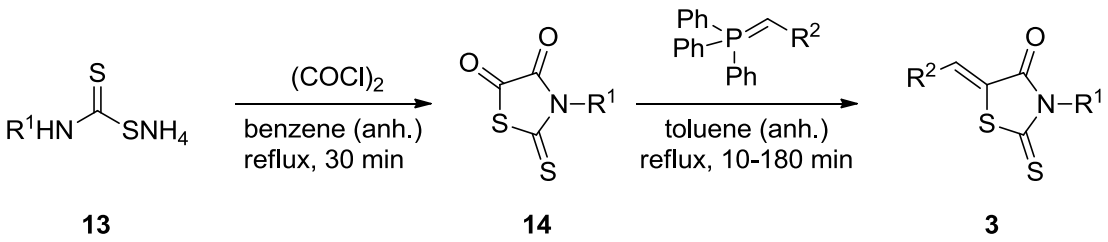
5-Alkylidenerhodanines **3** have been prepared by Knoevenagel condensations of *N*-substituted rhodanines **1** with aldehydes **12** in acetic acid in the presence of ammonium acetate or β-alanine as reported by Harada *et al*. (Scheme 4).[45]



Scheme 4. 5-Alkylidenerhodanines **3** from *N*- substituted rhodanines **1**

Alternatively, 5-alkylidenerhodanines **3** can be prepared through two-step reactions (Scheme 5). First, intermediates **14** were synthesized according to the method developed by Yurttaş *et al*. by the reaction of dry

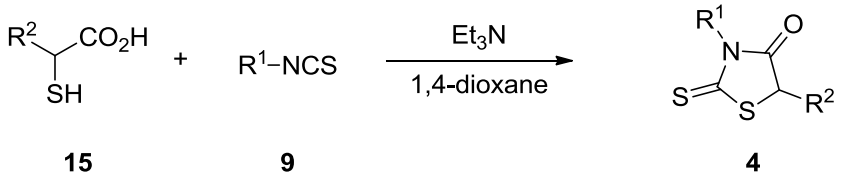
ammonium aryldithiocarbamates **13** with oxalyl chloride in anhydrous benzene. The intermediates **14** were then subjected to Wittig reaction conditions in anhydrous toluene to obtain desired 5-alkylidenerhodanines **3**.[48]



Scheme 5. 5-Alkylidenerhodanines **3** from ammonium *N*-aryldithiocarbamates **13**

2.4. Synthesis of 5-substituted rhodanines 4

Ye *et al*. reported the syntheses of 5-substituted rhodanines **4** by the reaction of an α-mercaptocarboxylic acid **15** with isothiocyanates **9** in 1,4-dioxane in the presence of triethylamine at 0 °C (Scheme 6).[49]

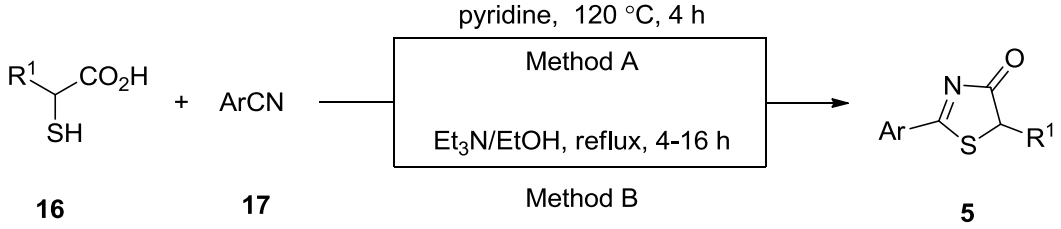


Scheme 6. 5-Substituted rhodanines **4** from α-mercaptocarboxylic acids **15.**

2.5. Synthesis of thiazol-4(5*H*)-ones 5

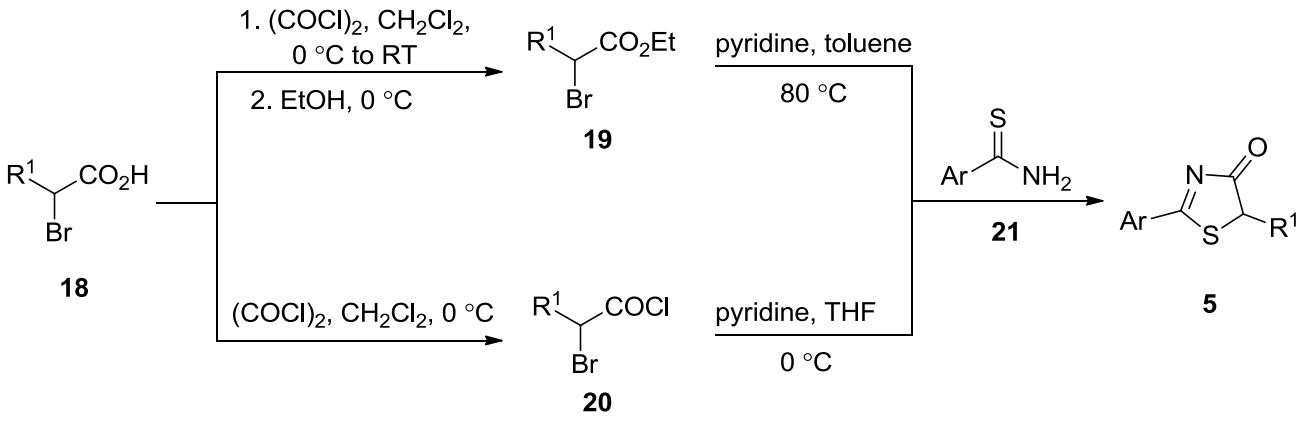
Thiazol-4(5*H*)-ones **5** were prepared through three different pathways, depending on the substituents.[50,51]

2.5.1. Path A. Thiazol-4(5*H*)-ones can be synthesized by treating α-mercaptocarboxylic acids **16** with carbonitriles **17** in the presence of either catalytic amount of pyridine or in the presence of triethylamine in ethanol under reflux condition (Scheme 7).



Scheme 7. Thiazol-4(5*H*)-ones **5** from α-mercaptocarboxylic acids **16.**

2.5.2. Path B. Alternatively, thiazol-4(5*H*)-ones **5** have been accessed by the coupling of arylthioamide **21** with ethyl 2-bromoester **19** or the acid chloride **20** in pyridine, which were prepared from the corresponding 2-bromoalkanoic acid **18** through well-established methods (Scheme 8).

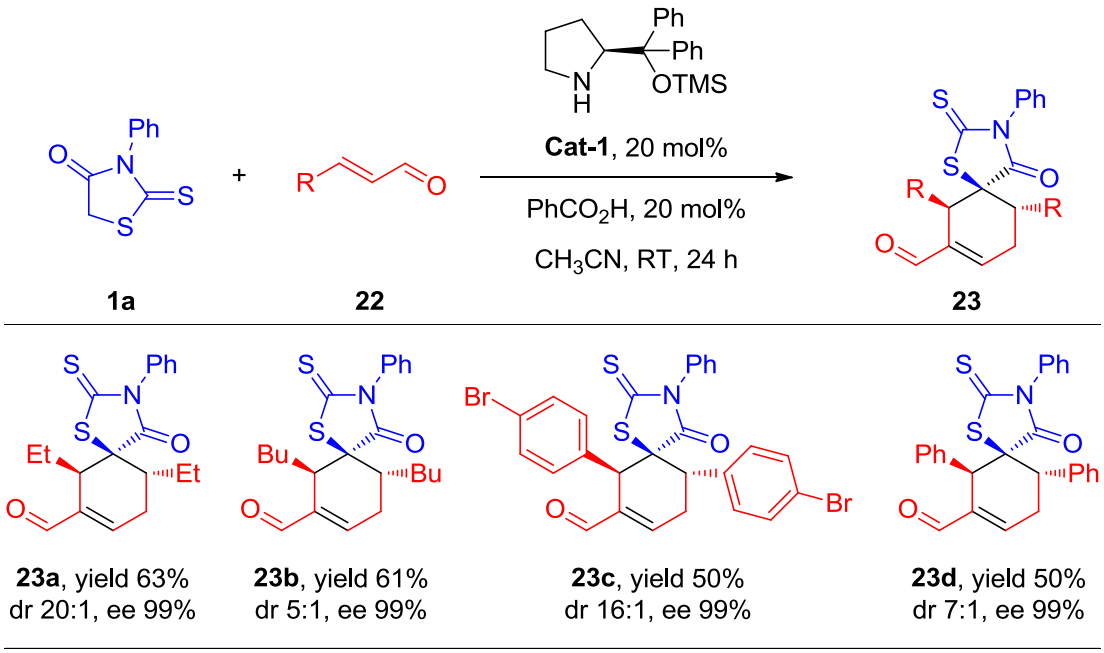


Scheme 8. Thiazol-4(5*H*)-ones **5** from 2-bromoalkanoic acid **18.**

3. Asymmetric Reactions of Rhodanines, Thiazolidine-2,4-diones, and Thiazol-4(5*H*)-ones

3.1. Asymmetric reactions of *N*-phenylrhodanine (1a)

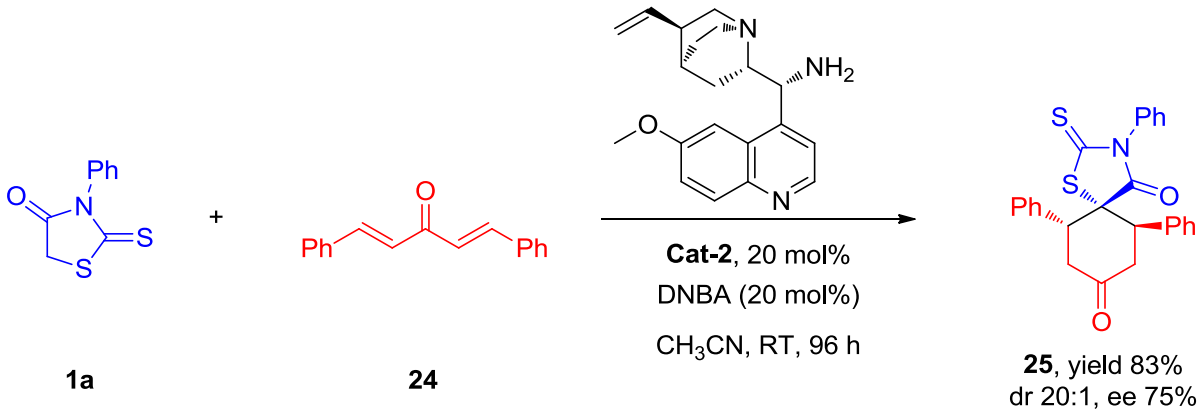
The first examples of an enantioselective organocatalytic Michael/Michael/aldol reaction of enals and the double Michael addition of aromatic dienones with bisnucleophile *N*-phenylrhodanine (**1a**) were reported in 2013 by Veselý *et al*. (Schemes 9, 10).[52]



Scheme 9. Michael Michael/Michael/Aldol reaction of *N*-phenylrhodanine (**1a**) with enals **22**

The Michael/Michael/aldol reaction of enals **22** with bisnucleophile *N*-phenylrhodanine (**1a**) occurs in presence of a proline-based catalyst **Cat-1** with good yields (up to 63%) and excellent stereoselectivities (dr up to 20:1 and ee up to 99%).

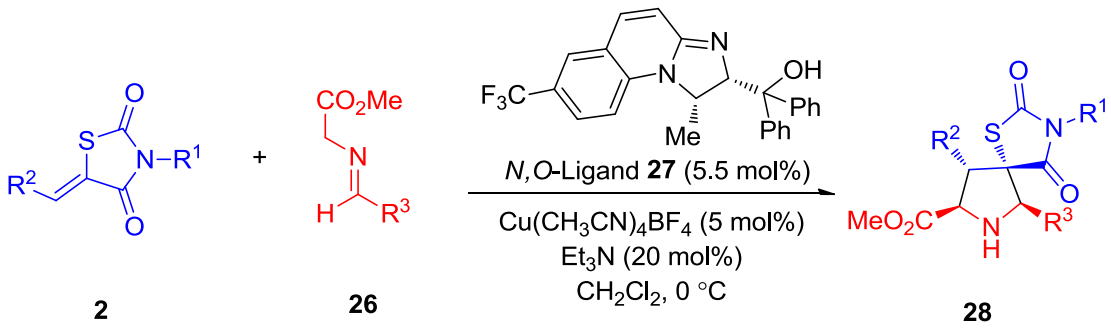
Furthermore, the double Michael addition between *trans*,*trans*-dibenzylideneacetone (**24**) and *N*-phenyl-rhodanine (**1a**) occurs in the presence of a cinchona-based primary-amine catalyst **Cat-2** in combination with the additive 2,4-dinitrobenzoic acid (DNBA) in acetonitrile to afford the best result in respect to yield (83%) and stereoselectivity (dr 20:1 and ee 75%).



Scheme 10. Michael addition of *N*-phenylrhodanine (**1a**) with *trans*,*trans*-dibenzylideneacetone (**24**).

3.2. Asymmetric reactions of 5-alkylidenethiazolidine-2,4-diones 2

In 2015, Deng and co-workers reported the asymmetric 1,3-dipolar cycloaddition of 5-alkylidenethiazolidine-2,4-diones **2** with azomethine ylides **26** using chiral *N*,*O*-ligand **27** in combination with $Cu(CH_3CN)_4BF_4$ (Scheme 11, Table 1).[47] The exo-spirocyclic pyrrolidine-thia(oxa)zolidinediones products **28** were obtained in high yields (up to 99%) with excellent levels of stereoselectivity (dr up to 99:1; ee up to 98%).



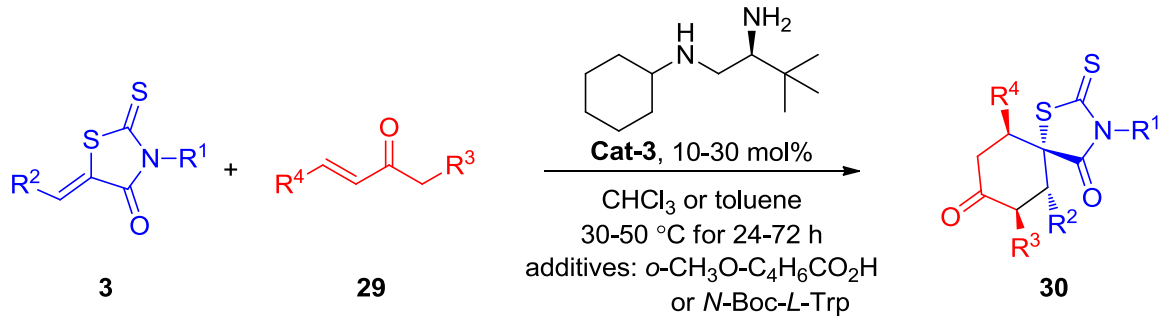
Scheme 11. Asymmetric 1,3-dipolar cycloaddition of 5-alkylidenethiazolidine-2,4-diones **2** with azomethine ylides **26.**

Table 1

Entry	R^1	R^2	R^3	Yield (%)	dr	ee (%)
1	Ph	Ph	*p*-ClC_6H_4	95	97:3	96
2	Ph	Ph	Ph	98	97:3	96
3	Ph	Ph	*o*-ClC_6H_4	80	87:13	90
4	Ph	Ph	*m*-ClC_6H_4	98	97:3	96
5	Ph	Ph	*p*-BrC_6H_4	98	97:3	97
6	Ph	Ph	*p*-$CF_3C_6H_4$	99	98:2	96
7	Ph	Ph	*o*-MeC_6H_4	95	86:14	89
8	Ph	Ph	*p*-MeC_6H_4	98	97:3	96
9	Ph	Ph	*p*-$MeOC_6H_4$	98	97:3	95
10	Ph	Ph	2-naphthyl	99	97:3	96
11	Ph	Ph	2-furyl	93	94:6	93
12	Ph	Ph	^{i}Bu	90	88:12	87
13	Ph	*p*-ClC_6H_4	*p*-ClC_6H_4	98	97:3	95
14	Ph	*m*-ClC_6H_4	*p*-ClC_6H_4	95	98:2	96
15	Ph	*p*-$MeOC_6H_4$	*p*-ClC_6H_4	90	99:1	96
16	Ph	2,6-$Me_2C_6H_3$	*p*-ClC_6H_4	40	88:12	95
17	*p*-BrC_6H_4	Ph	*p*-ClC_6H_4	98	98:2	98
18	*m*-BrC_6H_4	Ph	*p*-ClC_6H_4	99	97:3	94
19	*o*-BrC_6H_4	Ph	*p*-ClC_6H_4	98	98:2	95
20	*p*-$O_2NC_6H_4$	Ph	*p*-ClC_6H_4	99	97:3	97
21	*p*-$MeOC_6H_4$	Ph	*p*-ClC_6H_4	95	98:2	97
22	*m*-$MeOC_6H_4$	Ph	*p*-ClC_6H_4	98	98:2	96
23	2-furyl	Ph	*p*-ClC_6H_4	93	96:4	94
24	PhCH=CH	Ph	*p*-ClC_6H_4	85	96:4	94
25	CO_2Et	Ph	*p*-ClC_6H_4	85	80:20	89
26	H	Ph	*p*-ClC_6H_4	80	86:14	94
27	^{n}Pr	Ph	*p*-ClC_6H_4	80	97:3	95
28	Ph	Me	*p*-ClC_6H_4	98	98:2	94

3.3. Asymmetric reactions of 5-alkylidenerhodanines 3

The development of asymmetric reaction of 5-alkylidenerhodanines is known since 2012. The first report by Ye and co-workers was the asymmetric cascade reaction between acyclic α,β-unsaturated ketones **29** and 5-alkylidenerhodanines **3**.[53]



3 **29** **30**

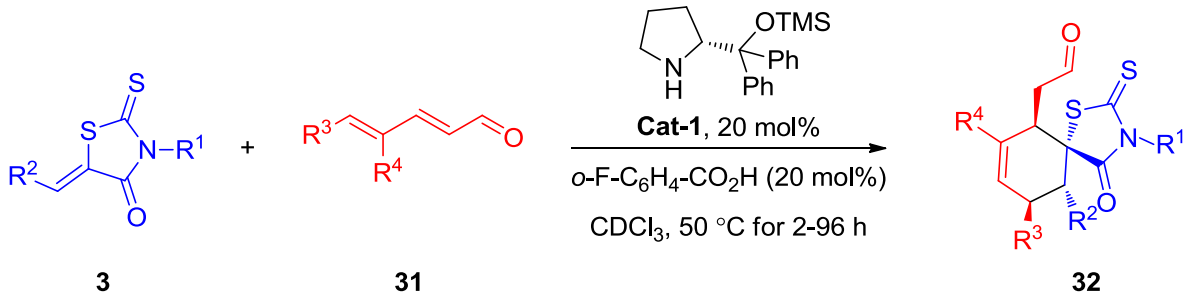
Scheme 12. Asymmetric cascade reaction of 5-alkylidenerhodanines **3** with α,β-unsaturated ketones **29.**

Table 2

Entry	R^1	R^2	R^3	R^4	Yield (%)	dr	ee (%)
1	Ph	CO_2Et	H	Ph	86	>20:1	98
2	Ph	CO_2Et	H	*o*-FC_6H_4	83	13:1	92
3	Ph	CO_2Et	H	*p*-BrC_6H_4	81	>20:1	87
4	Ph	CO_2Et	H	*o*-$MeOC_6H_4$	79	9:1	88
5	Ph	CO_2Et	H	*m*-MeC_6H_4	80	>20:1	98
6	Ph	CO_2Et	H	*p*-MeC_6H_4	80	>20:1	>99
7	Ph	CO_2Et	H	2-thienyl	90	18:1	90
8	Ph	CO_2Et	H	CO_2Et	35	>20:1	94
9	Ph	CO_2Et	cyclohexenone (29)		95	>20:1	0
10	Ph	Ph	H	Ph	70	>20:1	94
11	Ph	*p*-BrC_6H_4	H	Ph	94	>20:1	98
12	Ph	*p*-FC_6H_4	H	Ph	86	>20:1	95
13	Ph	*p*-$O_2NC_6H_4$	H	Ph	85	>20:1	98
14	Ph	*p*-$MeOC_6H_4$	H	Ph	68	>20:1	99
15	H	CO_2Et	H	Ph	90	9:1	99
16	H	CO_2Et	H	*m*-MeC_6H_4	77	8:1	89
17	$CH(CH_3)_2$	*p*-BrC_6H_4	H	Ph	88	>20:1	98
18	cyclohexyl	*p*-BrC_6H_4	H	Ph	87	>20:1	99
19	Ph	CO_2Et	Et	Ph	85	12:1	99
20	Ph	*p*-BrC_6H_4	Et	Ph	43	8:1	99
21	Ph	CO_2Et	Me	Ph	87	10:1	98
22	Ph	*p*-FC_6H_4	Me	Ph	83	7:1	93
23	H	CO_2Et	Me	Ph	78	8:1	97
24	H	CO_2Et	Me	2-furanyl	82	5:1	96

The reaction was promoted by a simple chiral diamine catalyst **Cat-3** to afford spirocyclohexanone-rhodanines **30** with multiple contiguous chiral centers with high stereoselectivities (up to >99% ee and >20:1 dr) (Scheme 12, Table 2). However, the enantioselectivity for the cascade reaction dropped to 0% ee when the reaction was performed in presence of cyclic α,β-unsaturated ketones (Table 2, entry 9).

In 2013, the same group further explored diphenylprolinol silyl ether **Cat-1**-catalyzed asymmetric Diels–Alder reaction between 2,4-dienals **31** and 5-alkylidenerhodanines **3** derivatives to access various spirocyclic compounds **32** with good yields (up to 98%) and excellent stereoselectivities (up to 99% ee and >19 : 1 dr). The reaction proceeded via trienamine intermediate, which is formed by the catalyst and the dienal substrate (Scheme 13, Table 3).[54]



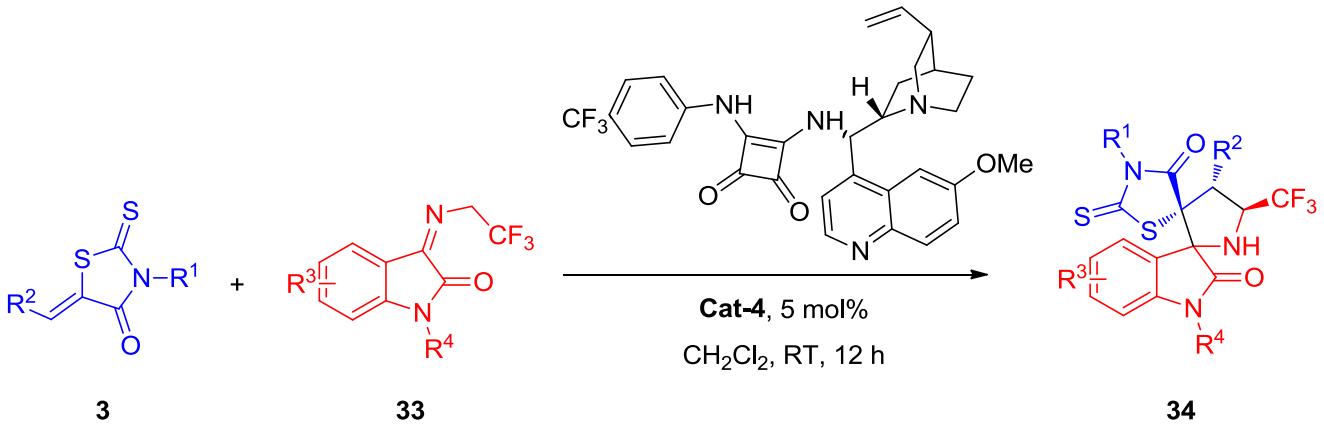
Scheme 13. Asymmetric Diels–Alder reaction between 5-alkylidenerhodanines **3** and 2,4-dienals **31.**

Table 3

Entry	R^1	R^2	R^3	R^4	Yield (%)	dr	ee (%)
1	cyclohexyl	*p*-BrC_6H_4	H	H	90	>19:1	94
2	Ph	*p*-FC_6H_4	H	H	82	10:1	93
3	Ph	*p*-$O_2NC_6H_4$	H	H	91	>19:1	90
4	Ph	Ph	H	H	84	>19:1	92
5	Ph	*p*-$MeOC_6H_4$	H	H	64	>19:1	91
6	Ph	*p*-$O_2NC_6H_4$	H	H	95	>19:1	92
7	Ph	CO_2Et	H	H	93	>19:1	94
8	Ph	*p*-BrC_6H_4	H	H	76	>19:1	93
9	cyclohexyl	Ph	H	H	88	>19:1	94
10	^{i}Pr	*p*-BrC_6H_4	H	H	89	>19:1	93
11	Ph	*p*-FC_6H_4	Me	Me	98	10:1	96
12	Ph	CO_2Et	Me	Me	91	>19:1	96
13	cyclohexyl	Ph	Me	Me	94	>19:1	97
14	cyclohexyl	*p*-BrC_6H_4	Me	Me	95	>19:1	97
15	Ph	*m*-$O_2NC_6H_4$	H	Et	98	>19:1	97
16	Ph	CO_2Et	H	Et	95	>19:1	97
17	cyclohexyl	*p*-BrC_6H_4	H	Et	93	>19:1	97
18	^{i}Pr	*p*-BrC_6H_4	H	Et	98	>19:1	97
19	Ph	CO_2Et	H	Ph	95	>19:1	99
20	^{i}Pr	*p*-BrC_6H_4	H	Ph	91	>19:1	99
21	Ph	*p*-BrC_6H_4	H	Ph	87	>19:1	99
22	Ph	*p*-$O_2NC_6H_4$	H	Ph	98	>19:1	99

Very recently, Du and co-workers reported a squaramide-catalyzed highly diastereo- and enantioselective domino Michael/Mannich [3 + 2] cycloaddition reaction between 5-alkylidenerhodanine derivatives **3** and *N*-

(2,2,2-trifluoroethyl)isatin ketimines **33** (Scheme 14, Table 4). The reaction proceeded smoothly to yield a broad range of CF_3-containing bispiro[oxindole-pyrrolidine-rhodanine]s **34** bearing four contiguous stereocenters, including two vicinal spiro-quaternary chiral centers, in good to excellent yields (up to 99%) and excellent stereoselectivities (up to >99% ee and >99:1 dr).[55] However, the reaction did not occur in the case substituents R^2 = Ph on the rhodanine derivative **3** (entry 4, Table 4).



Scheme 14. Asymmetric Michael/Mannich [3 + 2] cycloaddition reaction between 5-alkylidenerhodanines **3** and *N*-(2,2,2-trifluoroethyl)isatin ketimines **33.**

Table 4

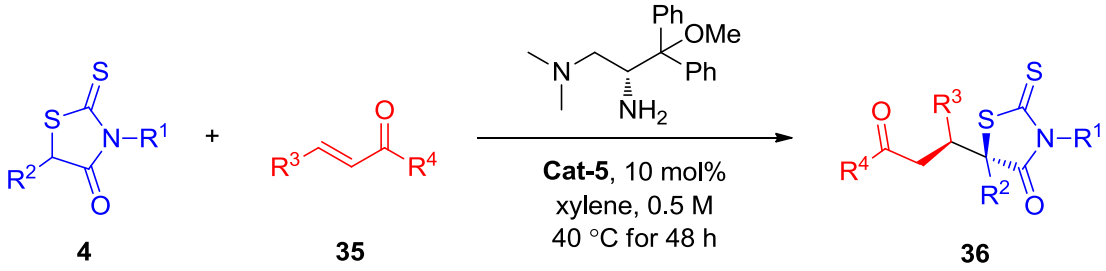
Entry	R^1	R^2	R^3	R^4	Yield (%)	dr	ee (%)
1	Ph	CO_2Et	H	Bn	99	99:1	96
2	Ph	Boc	H	Bn	96	99:1	93
3	Ph	CN	H	Bn	95	92:8	83
4	Ph	Ph	H	Bn		no reaction	
5	Bn	CO_2Et	H	Bn	85	99:1	97
6	cyclohexyl	CO_2Et	H	Bn	94	99:1	>99
7	Me	CO_2Et	H	Bn	93	98:2	95
8	^{n}Pr	CO_2Et	H	Bn	97	99:1	>99
9	H	CO_2Et	H	Bn	65	>99:1	57
10	*p*-MeC_6H_4	CO_2Et	H	Bn	97	99:1	90
11	*p*-$MeOC_6H_4$	CO_2Et	H	Bn	97	99:1	90
12	*p*-FC_6H_4	CO_2Et	H	Bn	90	98:2	91
13	*p*-ClC_6H_4	CO_2Et	H	Bn	98	99:1	90
14	*p*-BrC_6H_4	CO_2Et	H	Bn	99	98:2	91
15	Ph	CO_2Et	5-OMe	Bn	99	99:1	>99
16	Ph	CO_2Et	5-Me	Bn	99	99:1	93
17	Ph	CO_2Et	5,7-Me_2	Bn	80	97:3	98

Table 4. Continued

Entry	R^1	R^2	R^3	R^4	Yield (%)	dr	ee (%)
18	Ph	CO_2Et	5-F	Bn	98	95:5	80
19	Ph	CO_2Et	5-Cl	Bn	95	93:7	>99
20	Ph	CO_2Et	6-Cl	Bn	91	86:14	91
21	Ph	CO_2Et	5-Br	Bn	96	95:5	95
22	Ph	CO_2Et	H	H	85	97:3	86
23	Ph	CO_2Et	H	Me	92	99:1	89
24	Ph	CO_2Et	H	allyl	98	98:2	89
25	Ph	CO_2Et	H	*p*-$O_2NC_6H_4$	82	>99:1	90
26	Ph	CO_2Et	H	*p*-BrC_6H_4	87	98:2	92

3.4. Asymmetric reactions of 5-substituted rhodanines 4

The first report of direct diastereo- and enantioselective Michael addition using 5-substituted rhodanines **4** with α,β-unsaturated ketones **35** was reported by Ye *et al*. in 2012. The catalyst of choice was the chiral diamine **Cat-5**, which furnishes varieties of enantioenriched rhodanine derivatives **36** in high yields (up to 98%) with excellent diastereoselectivities (up to 99:1 dr) and enantioselectivities (up to >99% ee) (Scheme 15, Table 5).[49]



Scheme 15. Asymmetric Michael addition of substituted rhodanines **4** with α,β-unsaturated ketones **35.**

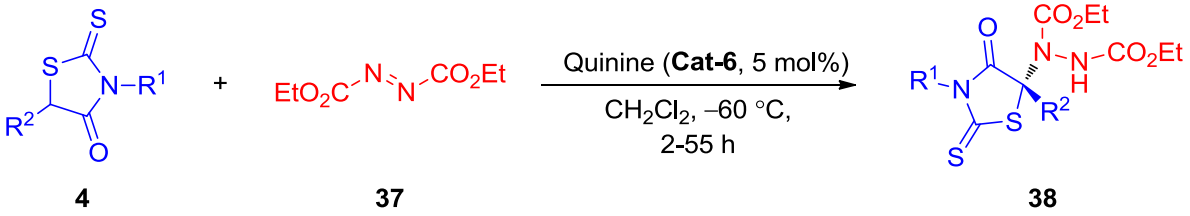
Table 5

Entry	R^1	R^2	R^3	R^4	Yield (%)	dr	ee (%)
1	Ph	Me	Ph	Me	95	99:1	96
2	Ph	Me	*p*-MeC_6H_4	Me	75	97:3	93
3	Ph	Me	*m*-$MeOC_6H_4$	Me	81	99:1	94
4	Ph	Me	*m*-BrC_6H_4	Me	92	99:1	93
5	Ph	Me	*p*-ClC_6H_4	Me	95	99:1	96
6	Ph	Me	*o*-$O_2NC_6H_4$	Me	89	99:1	95
7	Ph	Me	Naphthyl	Me	93	98:2	91
8	Ph	Me	2-thiophenyl	Me	96	97:3	98
9	Ph	Me	2-furanyl	Me	84	99:1	95
10	Ph	Me	Me	Me	64	95:5	80
11	Ph	Me	$PhCH_2CH_2$	Me	60	97:3	87

Table 5. Continued

Entry	R^1	R^2	R^3	R^4	Yield (%)	dr	ee (%)
12	Ph	Me	(*E*)-PhCH=CH	Me	83	93:7	96
13	^{i}Pr	Me	Ph	Me	97	99:1	90
14	Bn	Me	Ph	Me	94	98:2	95
15	*p*-$MeOC_6H_4$	Me	Ph	Me	98	99:1	96
16	Bn	Me	*p*-ClC_6H_4	Me	97	97:3	95
17	*p*-$MeOC_6H_4$	Me	*p*-BrC_6H_4	Me	96	99:1	95
18	Ph	Me	Ph	^{n}Pr	82	99:1	95
19	Ph	Et	Ph	Me	91	98:2	97
20	Ph	Et	Naphthyl	Me	96	99:1	91
21	Ph	Et	*p*-$O_2NC_6H_4$	Me	98	97:3	92
22	Ph	^{i}Pr	Ph	Me	68	93:7	71
23	Ph	Me	Ph	Ph	82	>30:1	92
24	Ph	Me	Ph	*p*-Br-C_6H_4	89	>30:1	93
25	Ph	Me	*p*-MeC_6H_4	Ph	93	>30:1	93
26	Ph	Me	cyclopentenone (**35**)		82	5:1	94
27	Ph	Me	cyclohexenone (**35**)		89	6:1	>99
28	Ph	Me	cycloheptenone (**35**)		93	1:1	>99

In 2014, Wang and co-workers reported a highly efficient quinine-catalyzed α-amination reaction between 5-substituted rhodanines **4** as nucleophiles with diethyl azodicarboxylate **37** (Scheme 16, Table 6). The method was applied to access a broad range of chiral *N,S*-acetals **38** in high yields (up to 99%) and excellent enantioselectivities (ee up to 96%). In addition, yield and selectivity for synthesis on gram scale were perfectly maintained for this method.[56]



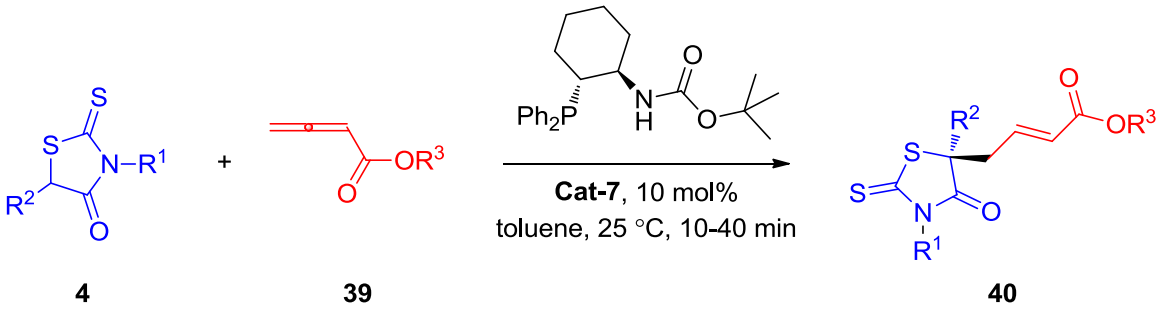
4 **37** **38**

Scheme 16. Asymmetric α-amination of 5-substituted rhodanines **4** with diethyl azodicarboxylate **37.**

Quite recently, Wu and co-workers have developed a chiral cyclohexane-based phosphine type catalyst **Cat-7** for enantioselective γ-additions of rhodanines **4** to allenoates **39** (Scheme 17, Table 7).[57] The method was very useful for the construction of chiral rhodanine derivatives **40** containing tertiary chiral carbon centers in good yields (up to 83%) and high enantioselectivities (up to 96%). However the method was unsuccessful for the γ-additions of benzyl penta-2,3-dienoate and benzyl but-2-ynoate electrophiles.

Table 6

Entry	R^1	R^2	Yield (%)	ee (%)	Entry	R^1	R^2	Yield (%)	ee (%)
1	Ph	Me	99	95	12	Ph	*o*-Cl-Bn	93	94
2	Ph	Et	95	96	13	Ph	3,4-Cl_2-Bn	90	95
3	Ph	*i*-Pr	99	91	14	Me	*p*-$MeOC_6H_4$	98	95
4	Ph	*n*-Bu	98	94	15	Me	*p*-MeC_6H_4	95	95
5	Ph	allyl	90	94	16	Me	*p*-FC_6H_4	99	94
6	Ph	$MeSCH_2CH_2$	92	94	17	Me	*p*-BrC_6H_4	96	94
7	Ph	Ph	91	81	18	Me	*p*-IC_6H_4	98	94
8	Ph	Bn	98	94	19	Me	*m*-MeC_6H_4	95	95
9	Ph	*o*-Me-Bn	96	89	20	Me	*m*-BrC_6H_4	96	93
10	Ph	*m*-Br-Bn	91	92	21	Me	3,5-$(CF_3)_2C_6H_3$	99	88
11	Ph	*p*-Me-Bn	97	95					

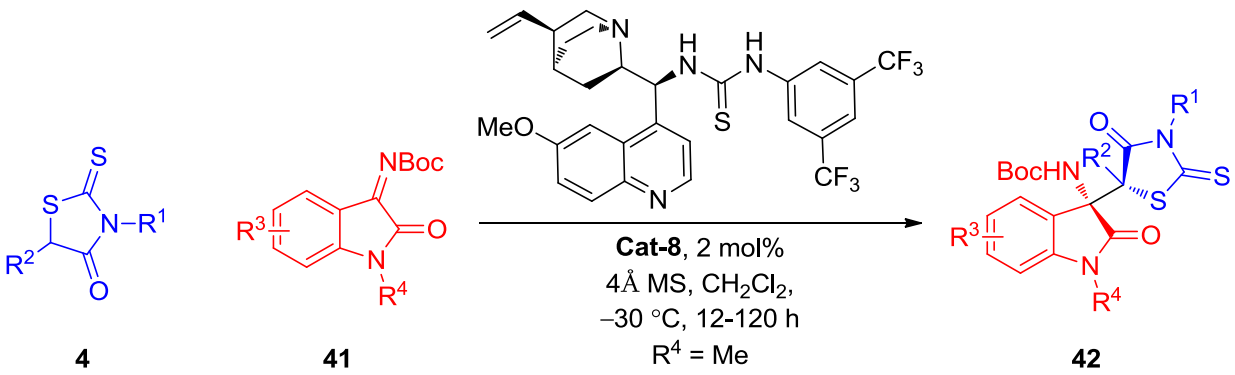


Scheme 17. Enantioselective γ-additions of rhodanines **4** to allenoates **39.**

The same group further developed quinine-based tertiary amine-thiourea catalyst **Cat-8** for the enantioselective Mannich reaction of rhodanines **4** with isatin derived ketimines **41** (Scheme 18, Table 8).[58] The reported reaction works well with 2 mol% catalyst loading to obtain 3,3-disubstituted oxindoles **42** with vicinal tetrasubstituted stereocenters with excellent yields (up to 99%), diastereoselectivities (up to 99:1) and high enantioselectivities (up to 97% ee). However, isopropyl substitution at 5-position of rhodanines **4** was found to be inactive for the enantioselective Mannich reaction under similar reaction conditions (Entry 9, Table 8). The result was explained with steric hindrance.

Table 7

Entry	R^1	R^2	R^3	Yield (%)	ee (%)	Entry	R^1	R^2	R^3	Yield (%)	ee (%)
1	Ph	Me	Bn	78	94	11	Ph	^{i}Pr	Bn	62	80
2	Bn	Me	Bn	79	92	12	Ph	^{n}Pr	Bn	72	86
3	*p*-$MeOC_6H_4$	Me	Bn	74	95	13	Ph	^{n}Bu	Bn	71	87
4	*p*-FC_6H_4	Me	Bn	83	89	14	Ph	^{t}Bu	Bn	61	79
5	*p*-ClC_6H_4	Me	Bn	82	90	15	Ph	Me	Ph	68	82
6	*p*-BrC_6H_4	Me	Bn	81	90	16	Ph	Me	$CHPh_2$	76	94
7	*p*-MeC_6H_4	Me	Bn	77	93	17	Ph	Me	9-fluorenyl	74	86
8	3,5-$(CF_3)_2C_6H_3$	Me	Bn	81	96	18	Ph	Me	5-dibenzo-cycloheptyl	77	93
9	Ph	Bn	Bn	76	91						
10	Ph	Et	Bn	75	93						



Scheme 18. Asymmetric Mannich reaction of rhodanines **4** with isatin-derived ketimines **41**.

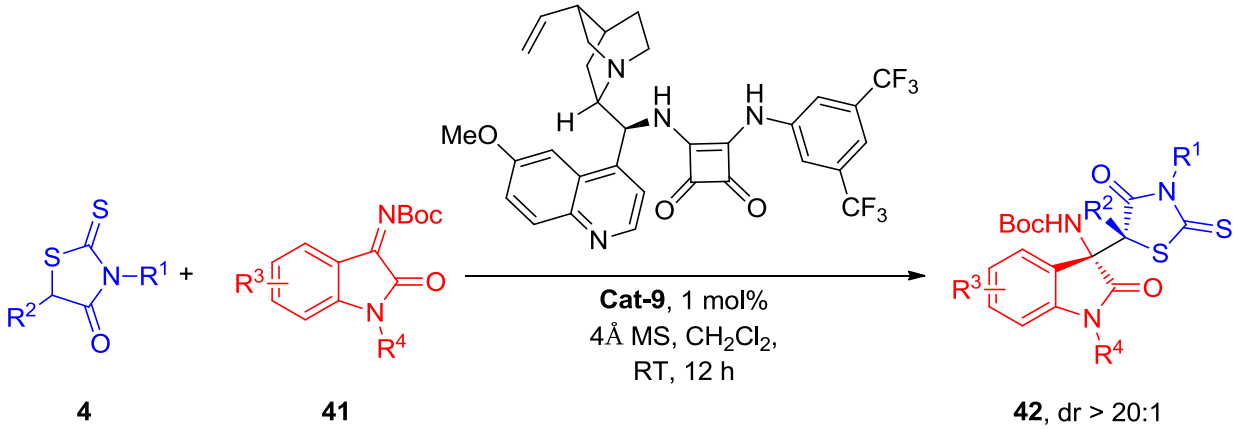
Table 8

Entry	R^1	R^2	R^3	Yield (%)	dr	ee (%)
1	Ph	Me	H	99	99:1	94
2	*p*-Br-C_6H_4	Me	H	99	99:1	94
3	*p*-MeO-C_6H_4	Me	H	91	99:1	93
4	Bn	Me	H	43	99:1	97
5	cyclohexyl	Me	H	53	98:2	90
6	Ph	Et	H	95	99:1	93
7	Ph	^{n}Pr	H	90	99:1	96
8	Ph	^{n}Bu	H	97	99:1	93
9	Ph	^{i}Pr	H	no reaction		
10	Ph	Bn	H	99	99:1	89

Table 8. Continued

Entry	R^1	R^2	R^3	Yield (%)	dr	ee (%)
11	Ph	Me	5-NO_2	99	99:1	36
12	Ph	Me	5-Br	99	98:2	74
13	Ph	Me	5-Me	98	99:1	93
14	Ph	Me	5-MeO	99	99:1	93
15	Ph	Me	6-F	99	99:1	94
16	Ph	Me	6-Cl	96	99:1	89
17	Ph	Me	6-Br	98	99:1	88
18	Ph	Me	6-MeO	95	99:1	96
19	Ph	Me	7-F	97	99:1	87
20	Ph	Me	7-Cl	99	99:1	84
21	Ph	Me	7-Br	99	99:1	81
22	Ph	Me	7-Me	98	99:1	90

Li and co-workers reported the same reactions of rhodanines **4** with isatin derived ketimines **41**. Interestingly, they observed an excellent reaction rate and stereoselectivity when the reaction was performed in presence of 1 mol% chiral squaramide catalyst **Cat-9** at room temperature (Scheme 19, Table 9).[59]



Scheme 19. Asymmetric Mannich reaction of rhodanines **4** with isatin-derived ketimines **41.**

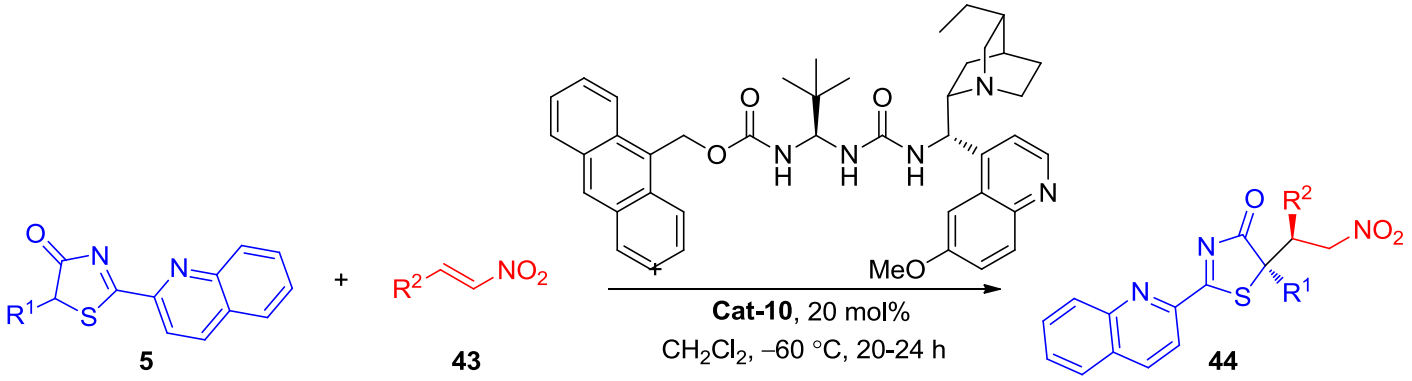
A variety of chiral 3-substituted-3-amino-2-oxindoles **42** containing two contiguous quaternary stereocenters were obtained in high yields (yield up to 96%) with excellent stereoselectivities (dr >20:1 and ee up to 98%).

Table 9

Entry	R^1	R^2	R^3	R^4	Yield (%)	dr	ee (%)
1	Ph	Me	H	Bn	95	>20:1	96
2	Ph	Me	5-F	Bn	92	>20:1	96
3	Ph	Me	5-Cl	Bn	90	>20:1	94
4	Ph	Me	5-Br	Bn	93	>20:1	94
5	Ph	Me	5-Me	Bn	91	>20:1	96
6	Ph	Me	6-Cl	Bn	87	>20:1	90
7	Ph	Me	6-Br	Bn	92	>20:1	94
8	Ph	Me	7-F	Bn	94	>20:1	92
9	Ph	Me	7-Cl	Bn	83	>20:1	90
10	Ph	Me	H	allyl	93	>20:1	90
11	Ph	Me	H	Me	96	>20:1	93
12	Ph	Me	H	Ph	95	>20:1	82
13	*p*-ClC_6H_4	Me	H	Bn	92	>20:1	94
14	*p*-BrC_6H_4	Me	H	Bn	94	>20:1	94
15	*p*-MeC_6H_4	Me	H	Bn	90	>20:1	98
16	*m*-FC_6H_4	Me	H	Bn	95	>20:1	93
17	*o*-ClC_6H_4	Me	H	Bn	94	>20:1	94
18	*m*-MeC_6H_4	Me	H	Bn	95	>20:1	96
19	*o*-MeC_6H_4	Me	H	Bn	91	>20:1	96
20	Bn	Me	H	Bn	92	>20:1	98
21	Et	Me	H	Bn	81	>20:1	96
22	^{i}Pr	Me	H	Bn	86	>20:1	98
23	Ph	Et	H	Bn	92	>20:1	90
24	Ph	Bn	H	Bn	90	>20:1	96

3.5. Asymmetric reactions of thiazol-4(5*H*)-ones (5)

In 2013, Palomo's group developed the first catalytic Michael reaction of thiazol-4(5*H*)-ones **5** with aromatic and aliphatic nitroolefins **43** using a bifunctional Brønsted base catalyst **Cat-10** (Scheme 20, Table 10).[60] The method reflects the direct formation of a quaternary chiral carbon centre with high stereoselectivities (dr up to > 95:5 and ee up to 98%) and yields (up to 96%). However, comparitively low yields were observed in the reaction with aliphatic nitroolefins without affecting the stereoselectivities (entries 14-16).



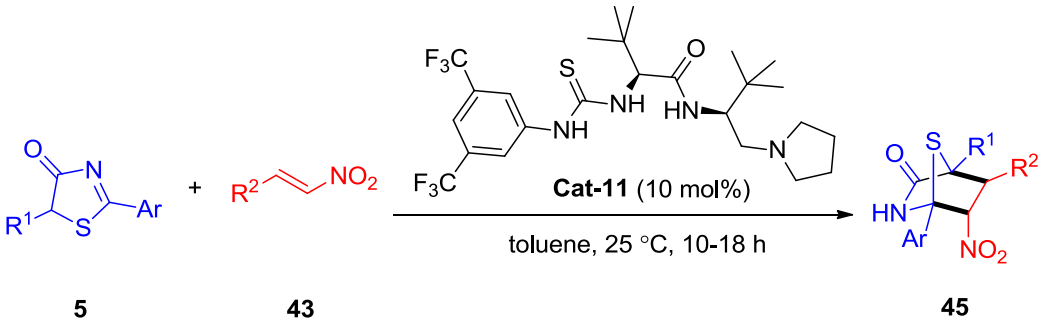
Scheme 20. Asymmetric Michael reaction of thiazol-4(5*H*)-ones **5** with nitroolefins **43.**

Table 10

Entry	R^1	R^2	Yield (%)	dr	ee (%)
1	Me	Ph	93	95:5	96
2	Me	*m*-MeC_6H_4	90	>95:5	91
3	Me	*p*-$MeOC_6H_4$	77	>95:5	92
4	Me	*m*-$MeOC_6H_4$	77	>95:5	94
5	Me	*p*-FC_6H_4	74	>95:5	90
6	Me	*p*-BrC_6H_4	79	>95:5	92
7	Me	*p*-ClC_6H_4	75	>95:5	92
8	Me	*p*-$O_2NC_6H_4$	68	>95:5	80
9	Me	*p*-NCC_6H_4	72	>95:5	86
10	Me	2-naphthyl	82	>92:8	94
11	Me	2-furyl	96	>92:8	91
12	Me	3-furyl	95	>92:8	89
13	Me	2-thienyl	93	>92:8	92
14	Me	*i*-Pr	47	>95:5	91
15	Me	*n*-Pr	42	>95:5	76
16	Me	cyclohexyl	40	>95:5	91
17	Et	Ph	95	>95:5	97
18	Et	*p*-MeC_6H_4	87	>95:5	91
19	Et	*p*-$MeOC_6H_4$	95	>95:5	97
20	Et	*p*-BrC_6H_4	81	>95:5	97
21	*n*-hexyl	Ph	96	>95:5	92
22	*n*-hexyl	*p*-MeC_6H_4	96	>95:5	98
23	Bn	Ph	90	>95:5	92

In 2016, Jiang and co-workers performed similar reactions of thiazol-4(5*H*)-ones **5** with sevaral electron-deficient alkenes **43**, **46**, **48** and **50** using a dipeptide-based multifunctional Brønsted base organocatalyst **Cat-11**.[61] They found the formation of several 1,4-sulfur-bridged piperidinone structural motifs **45**, **47**, **49** and **51** with various hetero-quaternary stereogenic centers through the asymmetric [4+2] annulation reaction. The

origin of enantio- and chemoselectivity were supported by density functional theory studies. Initially the substrates scope for the asymmetric [4+2] annulation reaction of thiazol-4(5*H*)-ones **5** were checked with nitroolefins **43** (Scheme 21, Table 11). The reactions proceeded well under the optimized reaction conditions with excellent diastereoselectivities (dr >20:1), enantioselectivities (ee up to 98%) with high yields (up to 89%).

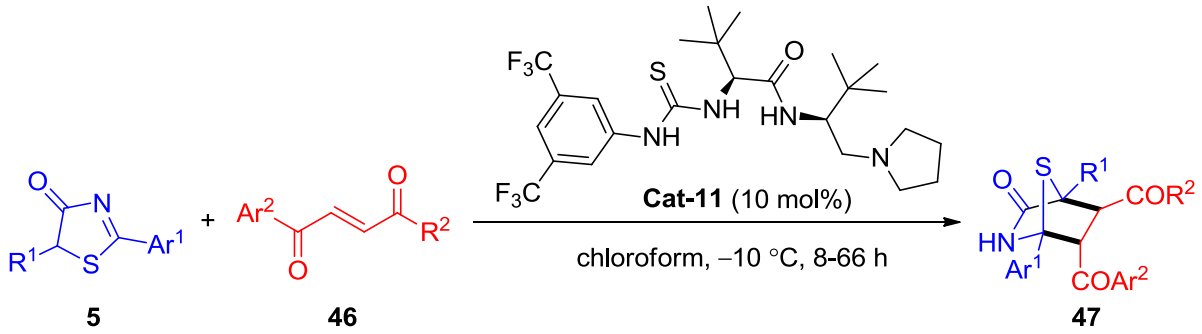


Scheme 21. Asymmetric [4+2] annulation reaction of thiazol-4(5*H*)-ones **5** with nitroolefins **43.**

Table 11

Entry	R^1	R^2	Ar	Yield (%)	dr	ee (%)
1	Me	Ph	2-quinolyl	83	>20:1	95
2	Me	*p*-FC_6H_4	2-quinolyl	78	>20:1	97
3	Me	*p*-BrC_6H_4	2-quinolyl	84	>20:1	96
4	Me	*p*-ClC_6H_4	2-quinolyl	89	>20:1	94
5	Me	*m*-ClC_6H_4	2-quinolyl	85	>20:1	92
6	Me	*o*-ClC_6H_4	2-quinolyl	82	>20:1	95
7	Me	*p*-MeC_6H_4	2-quinolyl	72	>20:1	95
8	Me	*m*-MeC_6H_4	2-quinolyl	76	>20:1	96
9	Me	*o*-MeC_6H_4	2-quinolyl	82	>20:1	93
10	Me	2-naphthyl	2-quinolyl	88	>20:1	95
11	Me	2-furanyl	2-quinolyl	76	>20:1	94
12	Me	cyclohexyl	2-quinolyl	41	>20:1	82
13	Et	Ph	2-quinolyl	55	>20:1	98
14	Me	Ph	*p*-BrC_6H_4	45	>20:1	90
15	Me	Ph	3-pyridinyl	76	>20:1	95

Next the substrate scope was extended by the coupling of thiazol-4(5*H*)-ones **5** with *trans*-4-oxo-4-arylbutenones **46** and *trans*-4-oxo-4-arylbutenoates **48** (Scheme 22 and 23, Table 12 and 13).

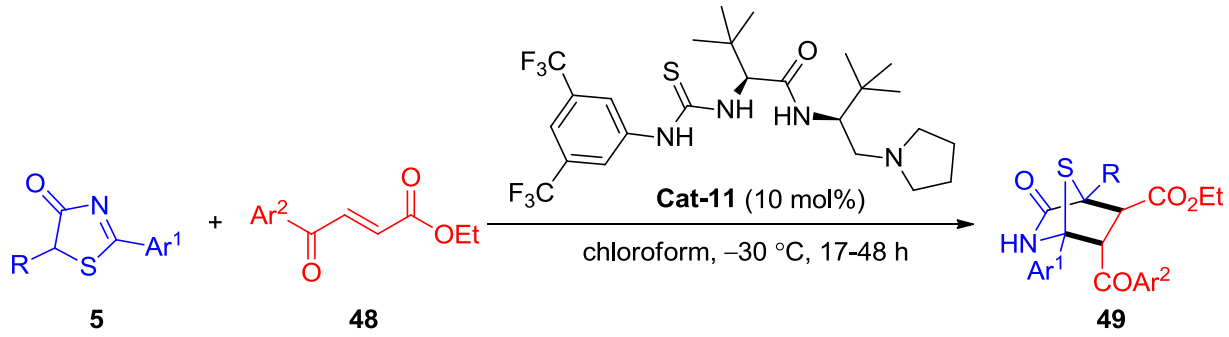


Scheme 22. Asymmetric [4+2] annulation of thiazol-4(5*H*)-ones **5** with trans-4-oxo-4-arylbutenones **46.**

Table 12

Entry	R^1	R^2	Ar^1	Ar^2	Yield (%)	dr	ee (%)
1	Me	Me	2-quinolyl	Ph	88	>20:1	98
2	Me	Me	2-quinolyl	*p*-CF_3-C_6H_4	90	>20:1	98
3	Me	Me	2-quinolyl	*p*-Br-C_6H_4	91	>20:1	99
4	Me	Me	2-quinolyl	*p*-Cl-C_6H_4	80	>20:1	97
5	Me	Me	2-quinolyl	3,4-$Cl_2C_6H_4$	95	>20:1	94
6	Me	Me	2-quinolyl	*p*-$MeOC_6H_4$	87	>20:1	97
7	Me	Me	2-quinolyl	*m*-$MeOC_6H_4$	82	>20:1	96
8	Me	Me	2-quinolyl	*o*-$MeOC_6H_4$	64	>20:1	94
9	Me	Me	2-quinolyl	2-thienyl	98	>20:1	99
10	Me	Me	2-quinolyl	2-furyl	92	>20:1	99
11	Me	Et	2-quinolyl	Ph	90	>20:1	97
12	Me	Me	2-pyridinyl	Ph	87	>20:1	98
13	Me	Me	3-pyridinyl	Ph	86	>20:1	98
14	Me	Me	2-thienyl	Ph	70	>20:1	99
15	Me	Me	2-furyl	Ph	75	>20:1	99
16	Me	Me	*p*-BrC_6H_4	Ph	54	>20:1	99
17	Et	Me	2-quinolyl	Ph	72	>20:1	97
18	Bn	Me	2-quinolyl	Ph	90	>20:1	98

The coupling reaction with *trans*-4-oxo-4-arylbutenones occurs in general at -10 °C whereas the reaction with *trans*-4-oxo-4-arylbutenoates proceeded preferably at -30 °C for the best results.



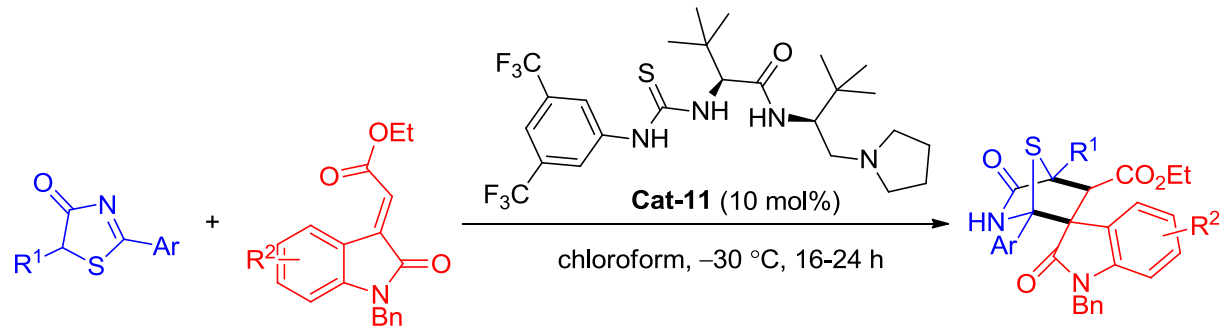
5 **48** **49**

Scheme 23. Asymmetric [4+2] annulation reaction of thiazol-4(5*H*)-ones **5** with *trans*-4-oxo-4-arylbutenoates **48.**

Table 13

Entry	R	Ar^1	Ar^2	Yield (%)	dr	ee (%)
1	Me	2-quinolyl	Ph	87	>20:1	95
2	Me	2-quinolyl	*p*-BrC_6H_4	87	>20:1	97
3	Me	2-quinolyl	3,4-$Cl_2C_6H_3$	96	>20:1	98
4	Me	2-quinolyl	*p*-$MeOC_6H_4$	90	>20:1	98
5	Me	2-quinolyl	2-thienyl	97	>20:1	99
6	Me	2-quinolyl	2-furyl	96	>20:1	98
7	Ph	2-quinolyl	Ph	67	>20:1	90
8	Me	2-pyridinyl	Ph	95	>20:1	97

Finally, the substrates scope of the reaction was elaborated using methyleneindolinones **50** (Scheme 24, Table 14). In this case, only one pair of diastereomers was obtained in high yields (up to 98%) and perfect enantioselectivities (>99%).



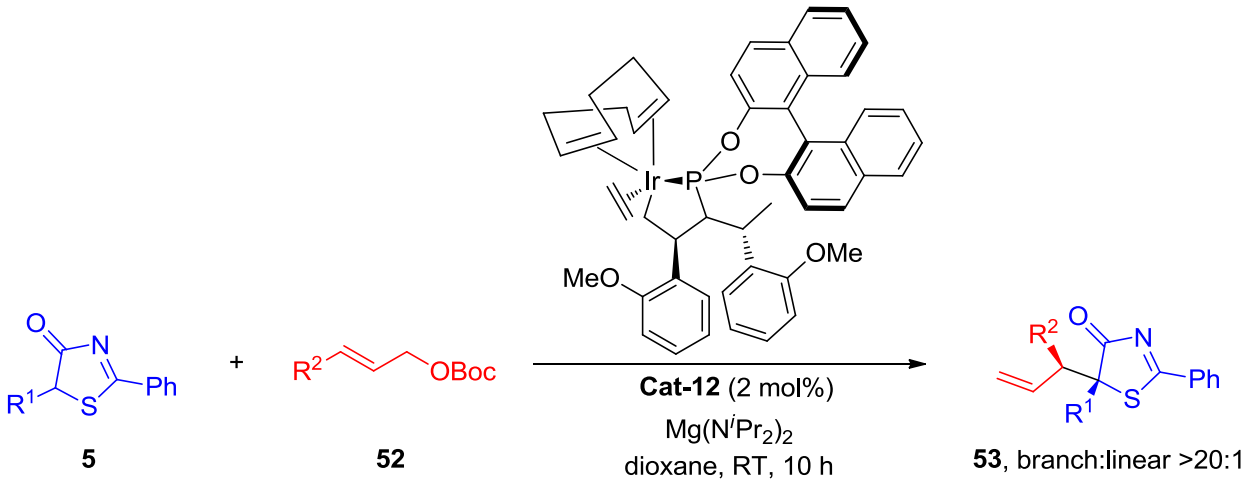
5 **50** **51**

Scheme 24. Asymmetric [4+2] annulation reaction of thiazol-4(5*H*)-ones **5** with methyleneindolinones **50.**

Table 14

Entry	R^1	Ar	R^2	Yield (%)	dr	ee (%)
1	Me	2-quinolyl	H	96	>20:1	95
2	Me	2-quinolyl	5-F	98	>20:1	94
3	Me	2-quinolyl	5-Cl	97	>20:1	92
4	Me	2-quinolyl	5-Br	98	>20:1	90
5	Me	2-quinolyl	5-Me	95	>20:1	>99
6	Me	2-quinolyl	5-OMe	98	>20:1	98
7	Ph	2-quinolyl	6-Cl	97	>20:1	>99
8	Me	2-quinolyl	6-OMe	94	>20:1	>99
9	Me	2-quinolyl	7-Cl	96	>20:1	93
10	Me	2-quinolyl	7-Me	97	>20:1	96
11	Me	*p*-Cl-C_6H_4	H	94	>20:1	90
12	Me	2-pyridinyl	H	96	>20:1	95
13	Et	2-quinolyl	H	87	>20:1	>99
14	Bn	2-quinolyl	H	84	>20:1	97

Stereoselective allylation of thiazol-4(5*H*)-ones **5** using a metallacyclic iridium complex **Cat-12** in combination with a non-nucleophilic base $Mg(N^iPr_2)_2$ was reported by Hartwig and co-workers in 2014 (Scheme 25, Table 15).[62] The reaction proceeded well through the formation of magnesium enolates to access enantioenriched allylation products which can readily be transformed to valuable tertiary thiols and thioethers with high yields (up to 96%), stereoselectivities (dr up to 13:1 and ee up to >99%) with excellent regio-selectivities (branched:linear >20:1).



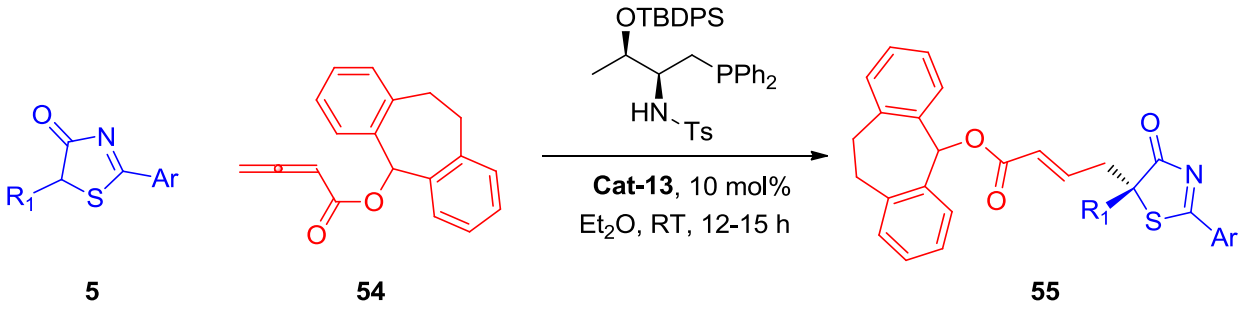
Scheme 25. Asymmetric allylation of thiazol-4(5H)-ones **5**.

In 2015, Lu and co-workers reported a modular pathway to access a wide range of chiral thiazolones containing tertiary chiral centers through the phosphine-catalyzed highly enantioselective γ-addition of thiazol-4(5*H*)-ones **5** to allenoate **54** (Scheme 26, Table 16).[51] Several substituted thiazol-4(5*H*)-ones were

easily converted to the corresponding chiral thiazolone derivatives **55** bearing sulfur heteroatom-containing tertiary chiral centers in high yields and excellent enantioselectivities (yield up to 97% and ee up to 95%).

Table 15

Entry	R^1	R^2	Yield (%)	dr	ee (%)
1	Me	Ph	88	10.4	99
2	Me	*p*-FC_6H_4	92	10:1	>99
3	Me	*p*-ClC_6H_4	94	10:1	>99
4	Me	*m*-BrC_6H_4	92	12:1	>99
5	Me	*p*-$CF_3C_6H_4$	81	11:1	>99
6	Me	*p*-MeC_6H_4	96	9:1	98
7	Me	*p*-$MeOC_6H_4$	85	10:1	>99
8	Me	2-naphthyl	84	8:1	>99
9	Me	3,4-$Cl_2C_6H_3$	82	13:1	>99
10	Me	*N*-Boc-3-indolyl	90	7:1	98
11	Me	2-furyl	82	5:1	>99
12	Et	Ph	81	9:1	99
13	Bn	Ph	79	4:1	98
14	$CH_2CH_2SCH_3$	Ph	75	7:1	>99

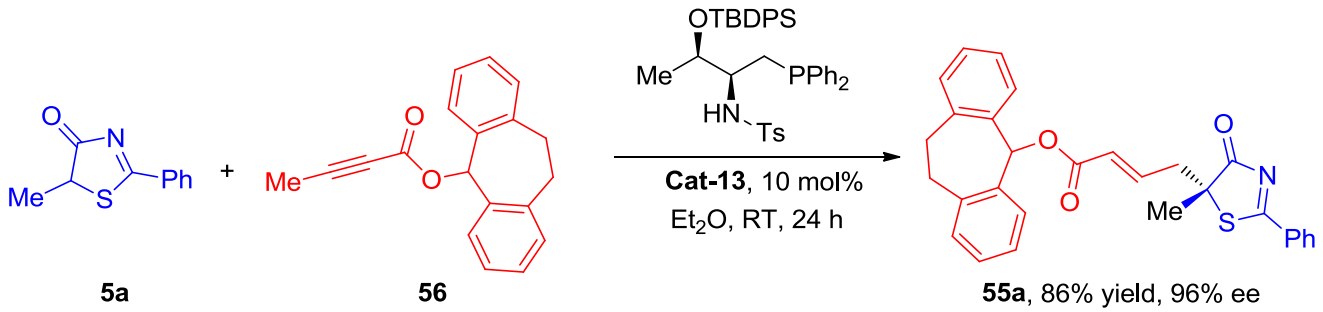


Scheme 26. Enantioselective γ-additions of thiazol-4(5*H*)-ones **5** to allenoate **54.**

Table 16

Entry	R^1	Ar	Yield (%)	ee (%)	Entry	R^1	Ar	Yield (%)	ee (%)
1	Me	Ph	97	95	4	^{i}Pr	Ph	92	92
2	Et	Ph	95	94	5	^{n}Bu	Ph	94	94
3	^{n}Pr	Ph	97	94	6	^{i}Bu	Ph	89	88
7	*n*-C_6H_{13}	Ph	96	94	10	*n*-$C_{10}H_{21}$	Ph	86	93
8	$CH(CH_2)_5$	Ph	95	93	11	Bn	Ph	90	92
9	$(CH_2)_2SCH_3$	Ph	93	90	12	Me	2-naphthyl	96	89

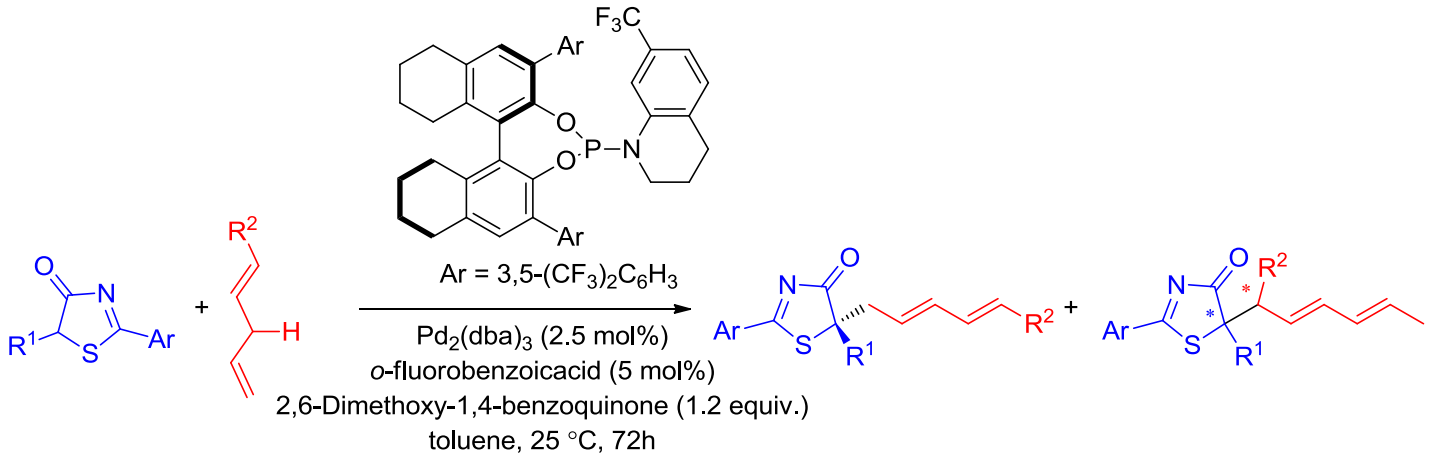
Interestingly, the thiazole substrate reacts with the alkynoate substrate **56** to afford the same product **55a** with similar chemical yields and enantioselectivities (86% yield and 95% ee) after 24h (Scheme 26). The mechanism of the catalyst-substrate interactions and product formation were further investigated through DFT calculations.



5a **56** **55a**, 86% yield, 96% ee

Scheme 27. Enantioselective γ-additions of thiazol-4(5*H*)-one **5a** to alkynoate **56.**

In 2018, Gong and co-workers developed the palladium-based enantioselective allylic C–H alkylation in combination with an optimized chiral phosphoramide ligand (Scheme 28, Table 17).[63] When 1,4-pentadienes **57** were used in the enantioselective allylic C–H alkylation of thiazol-4(5*H*)-ones **5**, a competition of linear and branched products were observed (linear products are formed predominantly). A wide range of chiral substituted thiazol-4(5*H*)-one products (major product **58**) bearing a quaternary stereogenic centre were obtained in high yields, regio- (linear products predominate over branched products) and stereoselectivities (dr up to >20:1 and ee up to 93%).



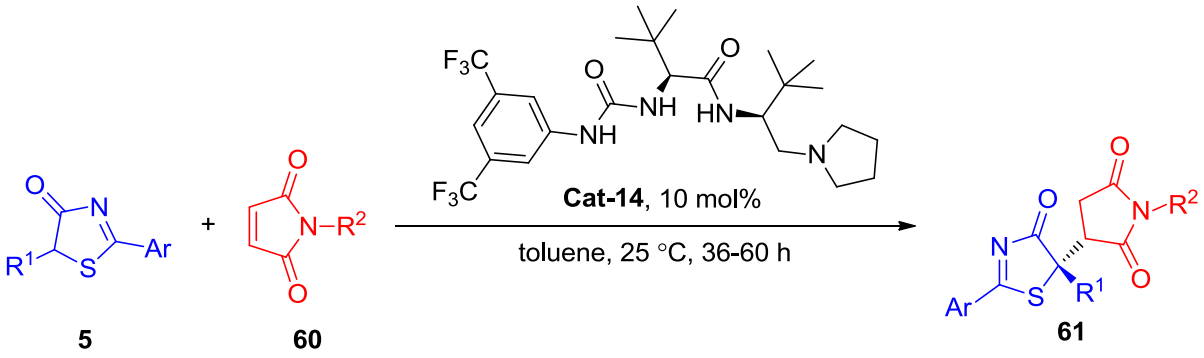
5 **57** **58** **59**

Scheme 28. Asymmetric allylic C-H alkylation of thiazol-4(5*H*)-ones **5** with 1,4-pentadienes **57**

Table 17

Entry	R^1	Ar	R^2	Yield (%)	**58**:**59**	dr	ee (%)
1	Bn	Ph	*n*-C_6H_{13}	95	20:1	>20:1	90
2	*p*-$FC_6H_4CH_2$	Ph	*n*-C_6H_{13}	56	38:1	>20:1	56
3	*m*-$MeOC_6H_4CH_2$	Ph	*n*-C_6H_{13}	91	17:1	>20:1	84
4	*p*-$CNC_6H_4CH_2$	Ph	*n*-C_6H_{13}	93	23:1	>20:1	93
5	2-$C_{10}H_7CH_2$	Ph	*n*-C_6H_{13}	37	14:1	>20:1	90
6	*o*-$ClC_6H_4CH_2$	Ph	*n*-C_6H_{13}	89	13:1	>20:1	89
7	*m*-$ClC_6H_4CH_2$	Ph	*n*-C_6H_{13}	90	12:1	>20:1	91
8	*p*-$ClC_6H_4CH_2$	Ph	*n*-C_6H_{13}	87	12:1	>20:1	87
9	*m*-$MeC_6H_4CH_2$	Ph	*n*-C_6H_{13}	43	10:1	>20:1	85
10	*o*-$MeC_6H_4CH_2$	Ph	*n*-C_6H_{13}	52	19:1	>20:1	86
11	*p*-$MeC_6H_4CH_2$	Ph	*n*-C_6H_{13}	66	11:1	>20:1	87
12	*m*-$BrC_6H_4CH_2$	Ph	*n*-C_6H_{13}	89	15:1	>20:1	89
13	*o*-$BrC_6H_4CH_2$	Ph	*n*-C_6H_{13}	66	13:1	>20:1	88
14	*p*-$BrC_6H_4CH_2$	Ph	*n*-C_6H_{13}	92	20:1	>20:1	91
15	H	Ph	*n*-C_6H_{13}	94	30:1	>20:1	83
16	*p*-$NCC_6H_4CH_2$	Ph	Me	95	20:1	>20:1	92
17	*p*-$NCC_6H_4CH_2$	Ph	*n*-Pr	91	23:1	>20:1	91
18	*p*-$NCC_6H_4CH_2$	Ph	*n*-C_9H_{17}	90	38:1	>20:1	93
18	*p*-$NCC_6H_4CH_2$	Ph	$Ph(CH_2)_2$	91	20:1	>20:1	93
19	*p*-$NCC_6H_4CH_2$	Ph	$Cl(CH_2)_2$	81	21:1	>20:1	89
20	*p*-$NCC_6H_4CH_2$	Ph	cyclohexyl	94	34:1	>20:1	83
21	*p*-$NCC_6H_4CH_2$	Ph	Ph	81	24:1	>20:1	90
22	*p*-$NCC_6H_4CH_2$	Ph	*p*-MeC_6H_4	54	22:1	>20:1	91
.23	*p*-$NCC_6H_4CH_2$	Ph	*p*-$MeOC_6H_4$	50	17:1	>20:1	92
24	*p*-$NCC_6H_4CH_2$	Ph	*m*-ClC_6H_4	86	40:1	>20:1	93
25	*p*-$NCC_6H_4CH_2$	Ph	H	73	5:1	>20:1	84
26	*p*-$NCCC_6H_4CH_2$	Ph	$EtO_2C(CH_2)_2$	99	11:1	>20:1	84
27	*p*-$NCCC_6H_4CH_2$	Ph	$BnNHCO(CH_2)_2$	79	10:1	>20:1	83
28	*p*-$NCC_6H_4CH_2$	Ph	$TsO(CH_2)_2$	92	16:1	>20:1	90
29	Ph	Ph	Me	90	11:1	5:1	87
30	Ph	*m*-MeC_6H_4	Me	70	10:1	6:1	91
31	Ph	*p*-BrC_6H_4	Me	87	13:1	4:1	88
32	Ph	*p*-FC_6H_4	Me	80	10:1	5:1	88
33	Ph	Ph	H	92	-	13:1	89
34	Ph	*m*-MeC_6H_4	*n*-Bu	57	10:1	3:1	91
35	Ph	*m*-MeC_6H_4	*n*-Pr	75	10:1	9:1	91

Stereoselective 1,4-conjugate addition process of thiazol-4(5*H*)-ones **5** with *N*-maleimides **60** or 1,4-naphthoquinones **62** were developed by Jiang and co-workers in 2016 based on a dipeptide-derived tertiary amine catalyst **Cat-14**.[64]

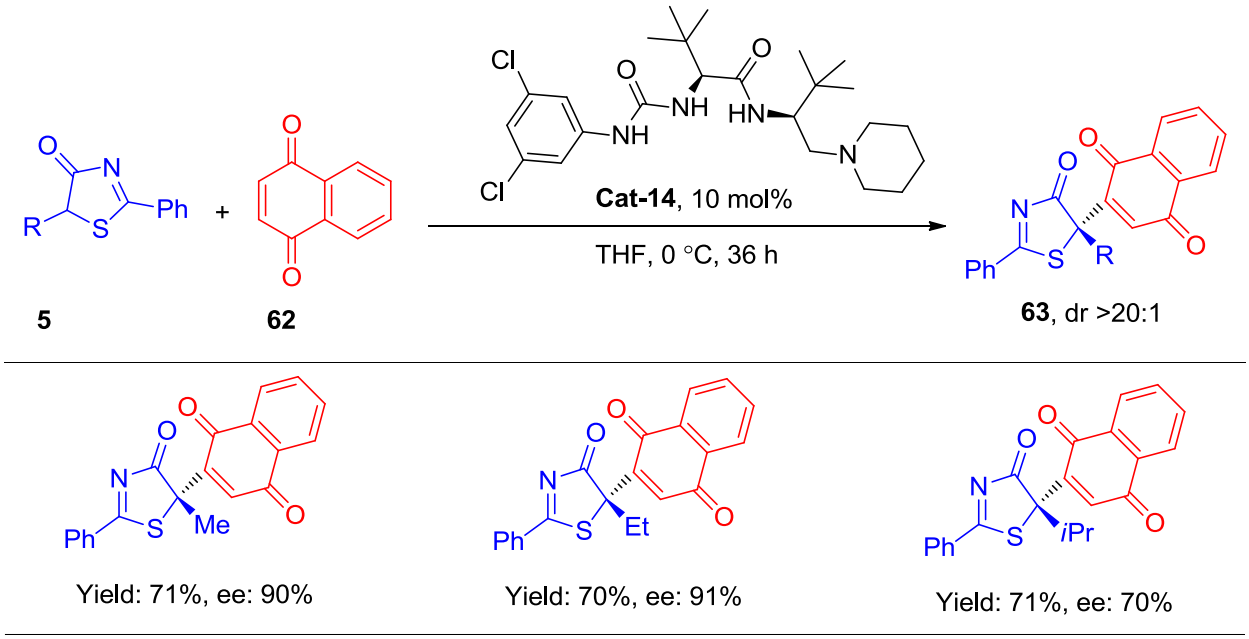


Scheme 29. Asymmetric 1,4-conjugate addition of thiazol-4(5*H*)-ones **5** with maleimides **60.**

A series of valuable heterocyclic compounds **61** and **63**, derived from the *N*-maleimides **60** or 1,4-naphthoquinones **62** were obtained with excellent enantio-/disastereo-selectivities (up to 99% ee, dr >20:1) and yields (up to 97%) (Scheme 29, Table 18 & Scheme 30). The absolute configuration of one substrate was determined trough X-ray crystallographic analysis, and the configuration of other substrates of 61 were determined by analogy.

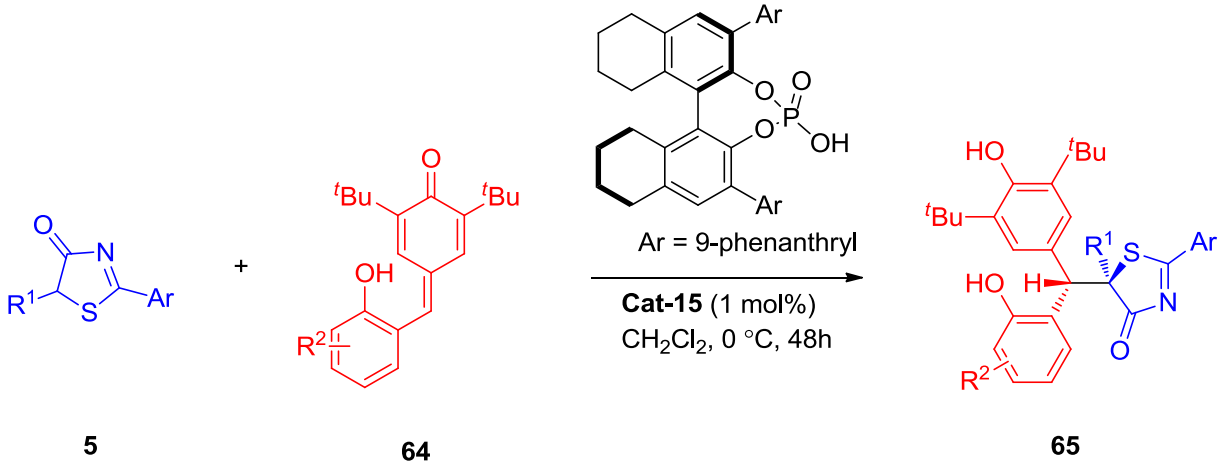
Table 18

Entry	R^1	Ar	R^2	Yield (%)	dr	ee (%)
1	Me	Ph	Ph	96	>20:1	97
2	Me	Ph	*p*-FC_6H_4	97	>20:1	97
3	Me	Ph	*p*-ClC_6H_4	89	>20:1	98
4	Me	Ph	*m*-BrC_6H_4	95	>20:1	99
5	Me	Ph	3,5-$F_2C_6H_3$	92	>20:1	98
6	Me	Ph	*m*-ClC_6H_4	93	>20:1	98
7	Me	Ph	*m*-BrC_6H_4	97	>20:1	97
8	Me	Ph	*p*-MeC_6H_4	96	>20:1	98
9	Me	Ph	*m*-MeC_6H_4	95	>20:1	99
10	Me	Ph	*o*-MeC_6H_4	92	>20:1	97
11	Me	Ph	*p*-$MeOC_6H_4$	93	>20:1	98
12	Me	Ph	*m*-$MeOC_6H_4$	84	>20:1	94
13	Me	Ph	Bn	90	>20:1	98
14	Me	Ph	Me	91	>20:1	97
15	Et	Ph	Ph	87	>20:1	97
16	^{i}Pr	Ph	Ph	93	>20:1	95
17	Bn	Ph	Ph	92	>20:1	97
18	Me	2-quinolyl	Ph	82	>20:1	96



Scheme 30. Asymmetric 1,4-conjugate addition of thiazol-4(5*H*)-ones **5** with 1,4-naphthoquinones **62.**

In 2018, Li and co-workers reported diastereodivergent asymmetric reactions of thiazol-4(5*H*)-ones **5** with *p*-quinone methides and *o*-quinone methides catalyzed by two pseudoenantiomeric catalysts.[65] A wide range of adducts possessing vicinal sulfur-functionalized quaternary and tertiary stereocenters were obtained in high yields with excellent stereoselectivities (Schemes 31-33).



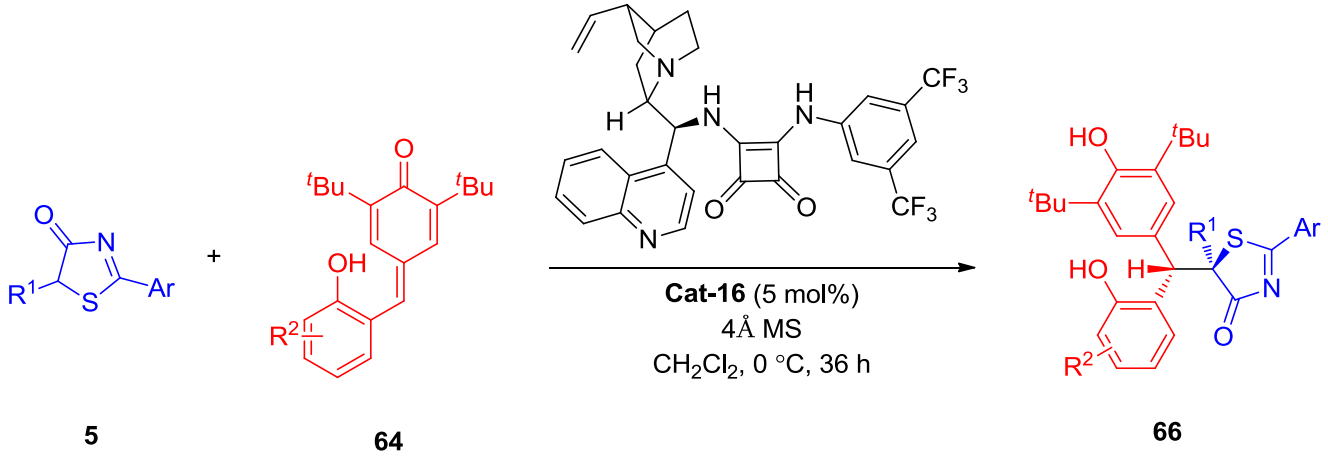
Scheme 31. Asymmetric reactions of thiazol-4(5*H*)-ones **5** with *p*-quinone methides **64.**

The reaction of thiazol-4(5*H*)-ones **5** with *p*-quinone methides **64** were first carried out in presence of a naphthol-based phosphoric acid catalyst **Cat-15** to obtain the substituted thiazol-4(5*H*)-ones adducts **65** with very high yield (up to 97%), enantioselectivity (ee up to >99%) and excellent diastereoselctivity (dr >20:1) (Scheme 31, Table 19).

Table 19

Entry	R^1	Ar	R^2	Yield (%)	dr	ee (%)
1	Me	Ph	H	94	>20:1	96
2	Me	Ph	4-F	90	>20:1	90
3	Me	Ph	4-Cl	89	>20:1	86
4	Me	Ph	4-Me	83	>20:1	92
5	Me	Ph	5-Br	93	>20:1	96
6	Me	Ph	6-MeO	85	>20:1	94
7	Me	*p*-FC_6H_4	H	95	>20:1	94
8	Me	*p*-ClC_6H_4	H	97	>20:1	92
9	Me	*p*-MeC_6H_4	H	93	>20:1	90
10	Me	*m*-FC_6H_4	H	94	>20:1	96
11	Me	*m*-BrC_6H_4	H	93	>20:1	96
12	Me	*m*-$MeOC_6H_4$	H	94	>20:1	94
13	Me	*o*-FC_6H_4	H	84	>20:1	96
14	Me	2-thienyl	H	93	>20:1	80
15	Me	2-pyridinyl	H	94	>20:1	98
16	Et	2-pyridinyl	H	88	>20:1	94
17	^{n}Pr	2-pyridinyl	H	85	>20:1	88
18	Me	3-pyridinyl	H	85	>20:1	>99
19	Bn	Ph	H	83	>20:1	82

However, when the same reactions were performed in the presence of a squaramide catalyst **Cat-16**, the diastereoisomers of the products **65**, *i.e.* **66**, were obtained (Scheme 32, Table 20) with high yields and stereoselectivities (yield up to 99%, dr up to >20:1, ee up to 99% for **66**).



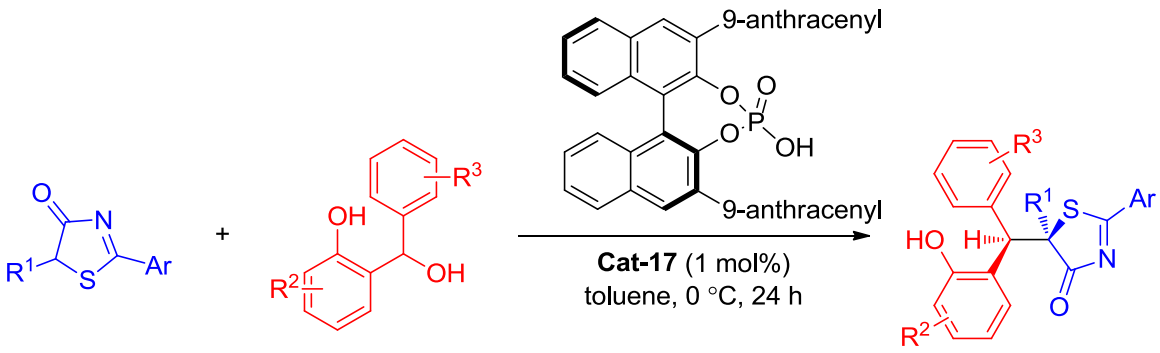
5 **64** **66**

Scheme 32. Asymmetric reactions of *p*-quinone methides **64** with thiazol-4(5*H*)-ones **5.**

Table 20

Entry	R^1	Ar	R^2	Yield (%)	dr	ee (%)
1	Me	Ph	H	83	15:1	92
2	Me	Ph	5-OMe	98	>20:1	88
3	Me	Ph	4-Me	84	>20:1	92
4	Me	Ph	4-Br	76	>20:1	96
5	Me	Ph	6-MeO	93	>20:1	99
6	Bn	Ph	H	87	6:1	78
7	Me	*p*-FC_6H_4	H	81	>20:1	92
8	Me	*p*-ClC_6H_4	H	85	11:1	98
9	Me	*p*-MeC_6H_4	H	88	13:1	94
10	Me	*o*-FC_6H_4	H	87	15:1	86
11	Me	*m*-BrC_6H_4	H	86	>20:1	88
12	Me	2-thienyl	H	86	11:1	86
13	Me	2-pyridinyl	H	99	>20:1	98
14	Et	2-pyridinyl	H	83	18:1	92
15	Me	3-pyridinyl	H	86	12:1	88

Next, the method was applied to the reaction of substituted thiazol-4(5*H*)-ones **5** with *o*-hydroxybenzyl alcohols **67** in presence of a binaphthol-based phosphoric acid catalyst. The reaction proceeded through the *o*-quinone methides intermediates (Scheme 33, Table 21). The adducts **68** were obtained in high yields and stereoselectivities (yield up to 95%, dr up to >20:1, ee up to 99%).



5 **67** **68**

Scheme 33. Asymmetric reactions of *o*-hydroxybenzyl alcohols **67** with thiazol-4(5*H*)-ones **5.**

Table 21

Entry	R^1	Ar	R^2	R^3	Yield (%)	dr	ee (%)
1	Me	Ph	H	4-MeO	87	19:1	98
2	Me	Ph	4-Br	4-MeO	81	10:1	89
3	Me	Ph	4-Me	4-MeO	87	13:1	94
4	Me	Ph	H	H	95	>20:1	96
5	Me	Ph	H	4-F	84	13:1	86
6	Me	Ph	H	4-Cl	94	17:1	94
7	Me	Ph	H	3-Me	84	18:1	92
8	Me	Ph	H	2-Me	82	17:1	94
9	Me	*p*-FC_6H_4	H	4-MeO	84	13:1	95
10	Me	*p*-ClC_6H_4	H	4-MeO	89	>20:1	99
11	Me	*m*-BrC_6H_4	H	4-MeO	86	>20:1	96
12	Me	*m*-$MeOC_6H_4$	H	4-MeO	83	14:1	95
13	Me	*o*-FC_6H_4	H	4-MeO	90	16:1	86
14	Me	2-pyridinyl	H	4-MeO	76	15:1	92
15	Bn	Ph	H	4-MeO	88	9:1	80

Conclusions

Substituted chiral rhodanines, thiazolidine-2,4-diones and thiazol-4(5*H*)-ones are the growing group of chiral compounds. Catalysis has made enormous strides in the last few years on asymmetric reactions of rhodanines, thiazolidine-2,4-diones and thiazol-4(5*H*)-ones, which in turn can further enlighten the design of new reactions using these nucleophile substrates. In this review, we have shown the development of catalytic enantioselective methods using rhodanine, thiazolidine-2,4-dione and thiazol-4(5*H*)-one as nucleophile to synthesize a wide range of chiral derivatives including synthetic procedures used to access the nucleophiles themselves. There are still several challenges, such as catalytic asymmetric reactions of fluorinated representatives of these classes, or reactions in aqueous media for further derivatization, which need to be addressed.

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References

1. Brown, C. F. *Chem. Rev.* **1961**, *61*, 463-521.

http://dx.doi.org/10.1021/cr60213a002
2. Singh, S. P.; Parmar, S. S.; Raman, K.; Steinberg, V. I. *Chem. Rev.* **1981**, *81*, 175-203. http://dx.doi.org/10.1021/cr00042a003
3. Lesyk, R. B.; Zimenkovsky, B. S. *Curr. Org. Chem.* **2004**, *8*, 1547-1577. https://doi.org/10.2174/1385272043369773
4. Grummt, U. V.; Weiss, D.; Birckner, E.; Beckert, R. *J. Phys. Chem. A* **2007**, *111*, 1104- 1110. http://dx.doi.org/10.1021/jp0672003
5. Sortino, M.; Delgado, P.; Juárez, S.; Quiroga, J.; Abonía, R.; Insuasty, B.; Nogueras, M.; Rodero, L.; Garibotto, F. M.; Enriz, R. D.; Zacchino, S. A. *Bioorg. Med. Chem.* **2007**, *15*, 484-494. https://doi.org/10.1016/j.bmc.2006.09.038
6. Murugan, R.; Anbazhagan, S.; Narayanan, S. S. *Eur. J. Med. Chem.* **2009**, *44*, 3272-3279. https://doi.org/10.1016/j.ejmech.2009.03.035
7. Tomasič, T.; Masič, L. P. *Curr. Med. Chem.* **2009**, *16*, 1596-1629. http://dx.doi.org/10.2174/092986709788186200
8. Véniant, M. M.; Hale, C.; Hungate, R. W.; Gahm, K.; Emery, M. G.; Jona, J.; Joseph, S.; Adams,J.; Hague, A.; Moniz, G.; Zhang, J.; Bartberger, M. D.; Li, V.; Syed, R.; Jordan, S.; Komorowski, R.; Chen, M. M.; Cupples, R.; Kim, K. W.; St Jean, D. J.; Johansson, L.; Henriksson, M. A.; Williams, M.; Vallgårda, J.; Fotsch, C.; Wang, M. J. *J. Med. Chem.* **2010**, *53*, 4481-4487. http://dx.doi.org/10.1021/jm100242d
9. Tomašić, T.; Zidar, N.; Mueller-Premru, M.; Kikelj, D.; Mašić, L. P. *Eur. J. Med. Chem.* **2010**, *45*, 1667-1672.
10. https://doi.org/10.1016/j.ejmech.2009.12.030
11. Tomašić, T.; Zidar, N.; Kovač, A.; Turk, S.; Simćić, M.; Blanot, D.; Mueller-Premru, M.; Filipić, M.; Grdadolnik, S. G.; Zega, A.; Anderluh, M.; Gobec, S.; Kikelj, D.; Mašić, L. P. *ChemMedChem*, **2010**, *5*, 286-295.
12. https://doi.org/10.1002/cmdc.200900449
13. Ono, M.; Hayashi, S.; Matsumura, K.; Kimura, H.; Okamoto, Y.; Ihara, M.; Takahashi, R.; Mori, H.; Saji, H. *ACS Chem. Neurosci.* **2011**, *2*, 269-275. http://dx.doi.org/10.1021/cn200002t
14. Heng, S.; Tieu, W.; Hautmann, S.; Kuan, K.; Sejer Pedersen, D.; Pietsch, M.; Gütschow, M.; Abell, A. D. *Bioorg. Med. Chem.* **2011**, *19*, 7453-7463. https://doi.org/10.1016/j.bmc.2011.10.042
15. Ma, L. A.; Xie, C. F.; Ma, Y. H.; Liu, J. A.; Xiang, M. L.; Ye, X.; Zheng, H.; Chen, Z. Z.; Xu, Q. Y.; Chen, T.; Chen, J. Y.; Yang, J. C.; Qiu, N.; Wang, G. C.; Liang, X. L.; Peng, A. H.; Yang, S. Y.; Wei, Y. Q.; Chen, L. J. *J. Med. Chem.* **2011**, *54*, 2060-2068. http://dx.doi.org/10.1021/jm1011534
16. Mendgen, T.; Steuer, C.; Klein, C. D. *J. Med. Chem.* **2012**, *55*, 743-753. http://dx.doi.org/10.1021/jm201243p
17. Jain, A. K.; Vaidya, A.; Ravichandran, V.; Kashaw, S. K.; Agrawal, R. K. *Bioorg. Med. Chem.* **2012**, *20*, 3378-3395. https://doi.org/10.1016/j.bmc.2012.03.069
18. Jain, V. S.; Vora, D. K.; Ramaa, C. S. *Bioorg. Med. Chem.* **2013**, *21*, 1599-1620. https://doi.org/10.1016/j.bmc.2013.01.029
19. Khalil, N. A.; Ahmed, E. M.; El-Nassan, H. B. *Med. Chem. Res.* **2013**, *22*, 1021-1027. https://doi.org/10.1007/s00044-012-0098-7

20. Bhatti, R. S.; Shah, S.; Suresh, P.; Krishan, P.; Sandhu, J. S. *Int. J. Med. Chem.* **2013**, *2013*, 1-16. http://dx.doi.org/10.1155/2013/793260
21. Desai, N. C.; Pandit, U. P.; Dodiya, A. *Expert Opin. Ther. Pat.* **2015**, 25, 479-488. https://doi.org/10.1517/13543776.2014.1001738
22. Naim, M. J.; Alam, M. J.; Ahmad, S.; Nawaz, F.; Shrivastava, N.; Sahu, M.; Alam, O. *Eur. J. Med. Chem.* **2017**, *129*, 218-250. https://doi.org/10.1016/j.ejmech.2017.02.031
23. Kaminskyy, D.; Kryshchyshyn, A.; Lesyk, R. *Eur. J. Med. Chem.* **2017**, *140*, 542-594. https://doi.org/10.1016/j.ejmech.2017.09.031
24. Saltiel, A. R.; Olefsky, J. M. *Diabetes* **1996**, *45*, 1661-1669. https://doi.org/10.2337/diab.45.12.1661
25. Krische, D. *Western J. Med.* **2000**, *173*, 54-57.
26. Ramirez, M. A.; Borja, N. L. *Pharmacotherapy* **2008**, *28*, 646-655. https://doi.org/10.1592/phco.28.5.646
27. Zhou, C.; Tang, C.; Chang, E.; Ge, M.; Lin, S.; Cilne, E.; Tan, C. P.; Yue, F.; Zhou, Y. P.; Eiermann, G. J.; Petrov, A.; Salituro, G.; Meinke, P.; Mosley, R.; Akiyama, T. E.; Einstein, M.; Kumar, S.; Berger, J.; Howard, A. D.; Thornberry, N.; Mills S. G.; Yang, L. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 1298-1301. https://doi.org/10.1016/j.bmcl.2009.10.052
28. Lugovskoy, A. A.; Degterev, A. I.; Fahmy, A. F.; Zhou, P.; Gross, J. D.; Yuan, J.; Wagner, G. *J. Am. Chem. Soc.* **2002**, *124*, 1234-1240. http://dx.doi.org/10.1021/ja011239y
29. Wadsworth, A.; Moser, M.; Marks, A.; Little, M. S.; Gasparini, N.; Brabec, C. J.; Baran, D.; McCulloch, I. *Chem. Soc. Rev.* **2019**, *48*, 1596-1625. http://dx.doi.org/10.1039/C7CS00892A
30. Marinado, T.; Hagberg, D. P.; Hedlund, M.; Edvinsson, T.; Johansson, E. M. J.; Boschloo, G.; Rensmo, H.; Brinck, T.; Sun, L.; Hagfeldt, A. *Phys. Chem. Chem. Phys.* **2009**, *11*, 133-141. http://dx.doi.org/10.1039/B812154K
31. Li, Z.; He, G.; Wan, X.; Liu, Y.; Zhou, J.; Long, G.; Zuo, Y.; Zhang, M.; Chen, Y. *Adv. Energy Mater.* **2012**, *2*, 74-77. https://doi.org/10.1002/aenm.201100572
32. Meyer, T.; Ogermann, D.; Pankrath, A.; Kleinermanns, K.; Müller, T. J. J. *J. Org. Chem.* **2012**, *77*, 3704-3715. http://dx.doi.org/10.1021/jo202608w
33. Holliday, S.; Ashraf, R. S.; Nielsen, C. B.; Kirkus, M.; Röhr, J. A.; Tan, C.-H.; Collado-Fregoso, E.; Knall, A.-C.; Durrant, J. R.; Nelson, J.; McCulloch, I. *J. Am. Chem. Soc.* **2015**, *137*, 898-904. http://dx.doi.org/10.1021/ja5110602
34. C. E. Redemann, R. N. Icke, G. A. Alles, *Org. Synth.* **1947**, *27*, 73-75. http://dx.doi.org/10.15227/orgsyn.027.0073
35. Sucheta; Tahlan S.; Prabhakar, K. V. *Chem. Cent. J.* **2017**, *11*, 130-158 https://doi.org/10.1186/s13065-017-0357-2
36. Gabillet, S.; Lecerclé, D.; Loreau, O.; Carboni, M.; Dézard,S.; Gomis, J. M.; Taran, F. *Org. Lett.* **2007**, *9*, 3925-3927. http://dx.doi.org/10.1021/ol701563e
37. Alizadeh, A.; Rostamnia, S.; Zohreh, N.; Hosseinpour, R. *Tetrahedron Lett.* **2009**, *50*, 1533-1535.

https://doi.org/10.1016/j.tetlet.2008.12.107
38. Khodair, A. I. *J. Heterocycl. Chem.* **2002**, *39*, 1153-1160. https://doi.org/10.1002/jhet.5570390607
39. Radi, M.; Botta, L.; Casaluce, G.; Bernardini, M.; Botta, M. *J. Comb. Chem.* **2010**, *12*, 200-205. http://dx.doi.org/10.1021/cc9001789
40. Dhara, K.; Paladhi, S.; Midya, G. C.; Dash, J. *Org. Biomol. Chem.* **2011**, *9*, 3801-3807. http://dx.doi.org/10.1039/C0OB01248C
41. Hassanabadi, A.; Mosslemin, M. H.; Anary-Abbasinejad, M.; Kalantarinejad, A.; Shirazi, M. J. *Eur.-J. Chem.* **2012**, *9*, 2074-2078. https://doi.org/10.1155/2012/786024
42. Shah, S.; Singh, B. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 5388-5391. https://doi.org/10.1016/j.bmcl.2012.07.049
43. Paladhi, S.; Chauan, A.; Dhara, K.; Tiwari, A. K.; Dash, J. *Green Chem.* **2012**, *14*, 2990-2995. http://dx.doi.org/10.1039/C2GC35819K
44. Paladhi, S.; Bhati, M.; Panda, D.; Dash, J. *J. Org. Chem.* **2014**, *79*, 1473-1480. http://dx.doi.org/10.1021/jo402515d
45. Kotha, S.; Sreevani, G. *Eur. J. Org. Chem.* **2018**, 5935-5941. https://doi.org/10.1002/ejoc.201800775
46. Shinde, D. N.; Trivedi, R.; Krishna, J. V. S.; Giribabu, L.; Sridhar, B.; Khursade, P. S.; Prakasham, R. S. *New J. Chem.* **2018**,*42*, 12587-12594. http://dx.doi.org/10.1039/C8NJ01598H
47. Harada, K.; Kubo, H.; Abe, J.; Haneta, M.; Conception, A.; Inoue, S.; Okada, S.; Nishioka, K. *Bioorg. Med. Chem.* **2012**, *20*, 3242-3254. https://doi.org/10.1016/j.bmc.2012.03.052
48. Imrich, J.; Bernat, J.; Kristian, P.; Busova, T.; Hocova, S. *Collect. Czech. Chem. Commun.* **1996**, *61*, 432-436. https://doi.org/10.1135/cccc19960432
49. Yang, W.-L.; Tang, F.-F.; He, F.-S.; Li, C.-Y.; Yu, X.; Deng, W.-P. *Org. Lett.* **2015**, *17*, 4822-4825. http://dx.doi.org/10.1021/acs.orglett.5b02387
50. Üngören, Ş. H.; Albayrak, S.; Günay, A.;Yurtseven, L.; Yurttas, N. *Tetrahedron* **2015**, *71*, 4312-4323. https://doi.org/10.1016/j.tet.2015.04.069
51. Yu, F.; Hu, H.; Gu, X.; Ye, J. *Org. Lett.* **2012**, *14*, 2038-2041. https://doi.org/10.1021/ol300489q
52. Kerdesky, F. A. J.; Holms, J. H.; Moore, J. L.; Bell, R. L.; Dyer, R. D.; Carter, G. W.; Brooks, D. W. *J. Med. Chem.* **1991**, *34*, 2158-2165. http://dx.doi.org/10.1021/jm00111a035
53. Wang, T.; Yu, Z.; Hoon, D. L.; Huang, K.-W.; Lan, Y.; Lu, Y. *Chem. Sci.* **2015**, *6*, 4912-4922. http://dx.doi.org/10.1039/C5SC01614B
54. Géant, P.-Y.; Urban, M.; Remeš, M.; Císařová, I.; Veselý, J. *Eur. J. Org. Chem.* **2013**, *2013*, 7979-7988. https://doi.org/10.1002/ejoc.201300931
55. Wu, W.; Huang, H.; Yuan, X.; Zhu, K.; Ye, J. *Chem. Commun.* **2012**, *48*, 9180-9182. http://dx.doi.org/10.1039/C2CC34321E
56. Zhu, K.; Huang, H.; Wu, W.; Wei, Y.; Ye, J. *Chem. Commun.* **2013**, *49*, 2157-2159. http://dx.doi.org/10.1039/C3CC00023K
57. Song, Y.-X.; Du, D.-M. *J. Org. Chem.* **2018**, *83*, 9278-9290.

http://dx.doi.org/10.1021/acs.joc.8b01245
58. Zhang, H.; Wang, B.; Cui, L.; Li, Y.; Qu, J.; Song, Y. *Org. Biomol. Chem.* **2014**, *12*, 9097-9100. http://dx.doi.org/10.1039/C4OB01921K
59. Kang, T.-C.; Wu, L.-P.; Sha, F.; Wu, X.-Y. *Tetrahedron* **2018**, *74*, 1017-1023. https://doi.org/10.1016/j.tet.2017.12.050
60. Xu, H.; Kang, T.-C.; Sha, F.; Wu, X.-Y. *Org. Biomol. Chem.* **2018**,*16*, 5780-5787. http://dx.doi.org/10.1039/C8OB01524D
61. Huang, Q.; Zhang, L.; Cheng, Y.; Li, P.; Li, W. *Adv. Synth. Catal.* **2018**, *360*, 3266-3270. https://doi.org/10.1002/adsc.201800642
62. Diosdado, S.; Etxabe, J.; Izquierdo, J.; Landa, A.; Mielgo, A.; Olaizola, I.; López, R.; Palomo, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 11846-11851. http://dx.doi.org/10.1002/anie.201305644
63. Zhu, B.; Qiu, S.; Li, J.; Coote, M. L.; Lee, R.; Jiang, Z. *Chem. Sci.* **2016**, *7*, 6060-6067. http://dx.doi.org/10.1039/C6SC02039A
64. Chen, W.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 377-382. http://dx.doi.org/10.1021/ja410650e
65. Wang, T.-C.; Han, Z.-Y.; Wang, P.-S.; Lin, H.-C.; Luo, S.-W.; Gong, L.-Z. *Org. Lett.* **2018**, *20*, 4740−4744. http://dx.doi.org/10.1021/acs.orglett.8b01697
66. Li, J.; Qiu, S.; Ye, X.; Zhu, B.; Liu, H.; Jiang, Z. *J. Org. Chem.* **2016**, *81*, 11916−11923. http://dx.doi.org/10.1021/acs.joc.6b02384
67. Zhang, L.; Yuan, H.; Lin, W.; Cheng, Y.; Li, P.; Li, W. *Org. Lett.* **2018**, *20*, 4970-4974. http://dx.doi.org/10.1021/acs.orglett.8b02088

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