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Development of Substituted Dihydrofurans and 1,2,3-NH-Triazoles through Lewis Base Catalyzed Cascade Condensation and Their Application in Synthesis of Chiral Triazole Derivatives through Mitsunobu Reaction

Tao Liao

**Thesis
Submitted to the Eberly College of Arts and Sciences
At
West Virginia University
In partial fulfillment of the requirements for the degree of
Master of Science
In Chemistry**

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**Keywords: Lewis Base Catalysis; Di-Hydrofuran; Chiral Triazole Derivative;
Mitsunobu Reaction**

Abstract

Synthesis of Dihydrofurans through Lewis Base Catalyzed One Pot Cascade Condensation

Tao Liao

A one-pot synthesis of substituted dihydrofurans was developed from a Lewis base catalyzed three-component cascade condensation with nitroalkenes, aldehydes and 1,3-dicarbonyl compounds. A large substrate scopes were prepared with excellent diastereoselectivity (trans product only) and excellent yield (up to 95%).

Synthesis of Chiral Triazole Derivatives through Mitsunobu Reaction

Tao Liao

Large substrate scope of chiral triazole derivatives were prepared through Mitsunobu reaction, this reaction gave excellent yields and complete stereochemistry inversion, making this strategy one practical approach for the synthesis of enantiomeric enriched triazole analogous. Interesting N-2 selectivity was observed even with the well know N-1 preferred benzotriazole, which may reveal an alternative strategy for the challenging N-2 functionalization.

DEDICATED TO
My family and parents

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Part I

Synthesis of Dihydrofurans through Lewis Base Catalyzed One-Pot Cascade Condensation

1. Introduction

1.1 Lewis base catalyzed reaction--organocatalysis

Since 2000, David Macmillan brought the term "organocatalysis" in chemistry¹, this area had been more and more focused as an important methodology in synthesis. Organocatalysts give many advantages, such as they don't contain metal, which really contributes to another highly focused area--"green chemistry", and by using chiral organocatalysis, it offers one approach to the chirality control in asymmetric synthesis.

Organocatalysts have been used in a long history, like Hajos-Parrish reaction developed in the 1970s. But current interest in organocatalysis is focused on asymmetric catalysis with chiral catalysts and this particular branch is called asymmetric organocatalysis or enantioselective organocatalysis. Most regular achiral organocatalysts are based on nitrogen like DABCO used in the Baylis-Hillman reaction, DMAP used in esterifications, piperidine used in the Knoevenagel condensation² and Thiazolium salts in the Stetter reaction (Scheme 1).

Scheme 1. Examples of Organocatalysis

Among those nitrogen-based organocatalysts, proline can easily activate carbonyl groups to form corresponding enamine or iminium cation³, and proline and other amines can also serve as Lewis base to interact with lone pair electron-acceptors, this interaction could enhance either the electrophilic or nucleophilic character of the bound species to catalyze the reaction. And at the end of reaction cycle, amines will be released and continue circling in reaction.

The diagram illustrates the catalytic cycle for a Lewis base (LB) in the formation of a cyclic acetal. The cycle involves the following steps:

- Initial State:** A carbonyl compound (R-C(=O)-LG) and a nucleophile (Nu) are present. The Lewis base (LB) is also present.
- Step 1:** The Lewis base (LB) attacks the carbonyl carbon of the carbonyl compound, forming a tetrahedral intermediate (R-C(O⁻)(LB)-LG).
- Step 2:** The tetrahedral intermediate collapses, regenerating the carbonyl compound (R-C(=O)-LG) and releasing the Lewis base (LB).
- Step 3:** The Lewis base (LB) attacks the carbonyl carbon of the nucleophile (Nu-C(=O)-R), forming a tetrahedral intermediate (Nu-C(O⁻)(LB)-R).
- Step 4:** The tetrahedral intermediate collapses, regenerating the nucleophile (Nu-C(=O)-R) and releasing the Lewis base (LB).
- Step 5:** The Lewis base (LB) attacks the carbonyl carbon of the carbonyl compound (R-C(=O)-LG), forming a tetrahedral intermediate (R-C(O⁻)(LB)-LG).
- Step 6:** The tetrahedral intermediate collapses, regenerating the carbonyl compound (R-C(=O)-LG) and releasing the Lewis base (LB).

The overall reaction scheme shows the catalytic cycle for the formation of a cyclic acetal, with the Lewis base (LB) acting as a catalyst.

A cascade reaction is a consecutive series of intramolecular organic reactions which often proceed via highly reactive intermediates. This type of reactions allows the organic synthesis of complex multinuclear molecules from a single acyclic precursor. The substrate contains many functional groups that take part in chemical transformations one at the time. The difference between cascade reaction and multi-component reaction is that the definition of cascade reaction includes the prerequisite intramolecular reactions.

Numerous examples of cascade reactions have been done, especially in alkyne chemistry, such as Banert cascade and polyolefin polycycloisomerizations. Usually alkyne cascade reactions are classified based on common features such as type of compound synthesized, like the spiro mode⁴ cascade (scheme 3A), the linear-fused mode⁵ cascade (scheme 3B), and the zipper mode⁶ cascade (scheme 3C). Other cascade reactions are included in Diels-Alder reactions, oxirane ring-opening reactions⁷ and Pauson-Khand reactions⁸.

Scheme 3. Examples of Cascade Reactions

1.3 Development synthesis of dihydrofuran

Furan and its derivatives are an important class of compounds in both chemical and biological research⁹. The synthesis of furan derivatives started from one century ago, and the most well-known approach is the Feist-Be´nary reaction¹⁰, and its recent modified “interrupted” Feist-Be´nary reaction¹¹ (Scheme 4A). Meanwhile, several methods were also reported focusing on the feasible cascade process to reach substituted dihydrofuran products with carbon substituents¹² (Scheme 4B). Tang and co-workers¹³ reported an enantioselective synthesis of dihydrofurans via formal [4 + 1] ylide annulation with excellent yields and enantioselectivity, although the substrate scope was limited (Scheme 4C). But previous studies by Ma, Liang, and Piras¹⁴ showed that the challenges in cis/trans diastereoselectivity and the competitive undesired cyclopropanation by-products in the Feist-Be´nary reaction. Therefore, there is a strong desire for new synthetic methods that allow the easy preparation of dihydrofurans (DHF) with good feasibility to assemble various substitution patterns, and more importantly, with controllable cis/trans diastereoselectivity.

Scheme 4. Different Approaches of Substituted Dihydrofuran

A) Feist-Benary reaction and "interrupted" Feist-Benary reaction

B) Other approaches for substituted dihydrofuran

C) formal [4 + 1] ylide annulation

2. Research Objective

2.1 Extension to amine activation of nitroalkene through nitrodiene intermediate

During the last couple of years, our group has been working on the development of cascade reactions through amine catalyzed nitroalkene activation¹⁵. The general process of this type of reaction mode started from the amine addition to the nitroalkene, giving the corresponding formal allylic nitro-carbanion (Scheme 5). The unexpected nitroalkene polymerization was avoided through the designated β -elimination, and sequential addition to proper electrophiles gave the highly functionalized products with high efficiency.

Scheme 5. Nitroalkene activation through nucleophilic addition

Recently, another interesting condensation strategy was revealed as an extension to the amine-catalyzed nitroalkene activation. By treating with the amine catalyst, which also served as Lewis base, nitroalkene could conduct nitro-aldol condensation with aldehyde, giving the nitro-diene. This highly reactive intermediate could then react with appropriate nucleophiles and precede a cascade process. For example, with the application of functional molecules possessing both nucleophiles and leaving groups (Nu-LG), such as another allylic nitro moiety, the above-mentioned strategy led to the formation of isoxazoline-N-oxide through an intramolecular S_N2 substitution¹⁶ (Scheme 6A). The successful one-pot synthesis of *NH*-1,2,3-triazole also suggested the similar reaction nature¹⁷ (Scheme 6B).

Scheme 6. Cascade reaction through nitrodiene intermediate

A) Formation of nitro-diene as active intermediate

B) Allylic nitro group as leaving group under mild conditions

Notably, it has been reported in the literature that nucleophilic substitution of the allylic nitro group usually required harsh conditions¹⁸, transition-metal assistance¹⁹, or strong Lewis acid activation²⁰. Thus, the effective substitution of allylic nitro group under mild conditions in our previous studies provided an appealing approach to further extend the cascade strategy for the stereoselective synthesis of complex building blocks. Combining these mechanistic discoveries, we postulated that the treatment of reactants with “di-nucleophile” moieties to the nitro-diene intermediate could lead to the facile synthesis of complex functionalized cyclic molecules in a “one-pot” fashion. Herein, we studied the proline catalyzed three-component condensation of nitroalkene, aldehyde and 1,3-dicarbonyl compound for the synthesis of substituted dihydrofurans with large substrate scope, good yields, and excellent diastereoselectivity.

2.2 Design of substituted Dihydrofurans synthesis

Encouraged by our previous success, we envisioned that 1,3-dicarbonyl compounds could be one of the feasible dinucleophiles to react with the nitrodiene intermediates and give the desired carbon-substituted dihydrofurans with different substitution patterns and high efficiency (Scheme 7).

Scheme 7. Proposed condensation of 1,3-diketone with nitrodiene

3. Results and Discussion

3.1 Reaction condition Optimization

To test our hypothesis, reactions between nitroalkene **1a**, aldehyde **2a** and cyclohexane-1,3-dione **3a** were investigated (Table 1).

Table 1. Reaction condition optimization^a

entry	Cat.	base(equiv.)	Sol.	Time (h)	Conv ⁿ . ^b (%)	Yield(%) ^c	
						4a	5a
1	Proline(20%)	-	DMSO	2	77	30	1
2	Proline(20%)	K ₂ CO ₃ (1.0)	DMSO	2	100	70 ^d	8
3	-	K ₂ CO ₃ (1.0)	DMSO	2	90	22	<5
4	Proline(20%)	K ₂ CO ₃ (0.5)	DMSO	2	100	80 ^d	<5
5	Proline(10%)	K ₂ CO ₃ (0.5)	DMSO	3	100	87 ^d	<5
6	Proline(5%)	K ₂ CO ₃ (0.5)	DMSO	4	100	87 ^d	<5
7	Proline(2%)	K ₂ CO ₃ (0.5)	DMSO	8	100	74 ^d	<5
8	Proline(5%)	K ₂ CO ₃ (0.5)	DMSO	4	100	91 ^e	<5
9	Proline(5%)	Other bases ^f	DMSO	4	100	<85 ^e	<5
10	Proline(5%)	K ₂ CO ₃ (0.5)	solvents ^g	4	100	<72	<5
11	PPh ₃ (20%)	K ₂ CO ₃ (0.5)	DMSO	3	100	26	18
12	Et ₃ N(20%)	K ₂ CO ₃ (0.5)	DMSO	8	100	37	<5
13	DMAP(20%)	K ₂ CO ₃ (0.5)	DMSO	8	100	30	21
14	Glycine(5%)	K ₂ CO ₃ (0.5)	DMSO	4	100	69 ^e	<5

^a **1a:2a:3a** = 1:1:1, concentration of **2a** is 0.15 M; yields determined by NMR with 1,3,5-trimethoxybenzene as internal standard. ^b Based on the nitroalkene **1a**. ^c NMR yield with 1,3,5-trimethoxybenzene as internal standard. ^d Isolated yields. ^e Isolated yield based on aldehyde, with the loading of **1a:2a:3a** = 1.2:1.0:1.1, concentration of **2a** is 0.15 M. ^f Other bases include Cs₂CO₃, NaOAc, NaOtBu, Et₃N and DIPEA. ^g Solvents include DCM, EtOAc, Acetone, Toluene and THF.

The competing side reactions for this three component condensation included the formation of isoxazoline **5a** and nitroalkene polymerization. To our delight, the desired DHF **4a** was formed when treating the three starting materials with proline, though the yield was low (30%, entry 1). Significant nitroalkene polymerization was observed in this case. Since one equivalent of HNO₂ would be generated in this process, various bases were added to balance the acidity of the overall reaction. With the application of 1.0 equiv of K₂CO₃, the yield of DHF was significantly improved (71%, entry 2). Notably, a much significantly lower yield was received when only K₂CO₃ was applied (22%, entry 3). These results were consistent with our previously reported proline-nitroalkene activation mechanism. Considering that strong basic conditions usually favored the undesired nitroalkene polymerization, the amount of K₂CO₃ was reduced to 0.5 equiv. Higher yield of **4a** was received as expected (80%, entry 4). Interestingly, decreasing the loading of proline resulted in better performance with only a slight increase in reaction time (entries 5-7). This could be explained by the relatively slower nitroalkene polymerization associated with the lower Lewis base loading. With this optimal condition, excellent yield of DHF **4a** was received as the single *trans* isomer, when slightly excess amounts (1.2 equiv) of nitroalkenes was applied (91%, entry 8). Different bases (such as DIPEA, Et₃N, and Cs₂CO₃) and various solvents have also been investigated, and K₂CO₃ (0.5 equiv) in DMSO was confirmed as the optimal choice. Different Lewis base catalysts, such as PPh₃ and DMAP, have also been applied to catalyze this reaction. However, much lower yields were obtained (entries 11-13) along with the formation of significant amounts of **5a**. These results highlighted the unique reaction nature of proline catalyzed nitroalkene activation in cascade syntheses.

3.2 Substrate scope

After the condition optimization, various nitroalkenes, aldehydes and 1,3-diketones/ β -keto-esters were then applied to investigate the reaction substrate scope. The results are shown in Table 2. The competing side reaction, homoisoxazoline-N-oxide formation, was also successfully diminished. And in addition, no *cis* diastereo-isomers or cyclopropanation products were observed.

Table 2. Substrate Scope of the One-Pot Dihydrofuran Synthesis^a

entr y	Nitroalkene	Aldehyde	Di-keto	Product	Yield(%)
4a					91

4b					82
4c					92
4d					81
4e					86
4f					94
4g					65
4h					93
4i					89

4q					85
4r					80
4s					85
4t					83
4u					75
4v					92

^a **1a:2a:3a** = 1.2:1.0:1.1, concentration of **2a** is 0.15 M; yields are isolated yields; only *trans* isomers were observed.

This new method worked for a great variety of substrates, giving the desired *trans* DHF in good to excellent yields. Both aromatic and aliphatic nitroalkene were suitable for this reaction, giving good diversity on the C-5 position. A large group of different aldehydes, including aromatic (with either electron donating groups or electron withdrawing groups), aliphatic and heterocyclic structures, were all suitable for this reaction, which provided an efficient strategy to introduce

different carbon-substitute groups on the C-4 position. The efficient assembly of readily available diverse groups on the C-4 and C-5 position made the reported method highly efficient for the preparation of functional substituted DHF that would be challenging to reach via other methods. The application of different 1,3-diketone and β -keto-esters further extended this method for easy introduction of various functional groups on C-2 and C-3 positions. In the case of β -keto-esters, good chemoselectivity was achieved, giving only the ketone cyclization products. This result gave advantage to selectively introduce different groups on either C-2 or C-3 positions through the reaction with corresponding dinucleophiles (i.e., **4u**). Notably, excellent diastereoselectivity was achieved in all cases, while only *trans* isomers were observed. Thus, with the great diversity, high efficiency and excellent diastereoselectivity, this method could be applied as a new general approach for the synthesis of various functional dihydrofuran building blocks.

4. Conclusions

In conclusion, a highly efficient cascade synthesis of dihydrofurans was developed through a proline catalyzed, one-pot three-component condensation of nitro alkenes, aldehydes and 1,3-diketone/ β -keto-esters. This reaction used readily available starting materials under mild conditions and gave the desired products in excellent yields, chemoselectivity, and diastereoselectivity. Substituted groups on all the four positions of furan could be readily controlled with the applications of corresponding starting materials. With the great atom efficiency and functional group tolerability, the reported methods would be of great interest for chemical and pharmaceutical researchers by providing a readily available compound library. In addition, the success of this method provided further strong support for the proposed secondary amine nucleophilic addition to nitroalkene. Further extension of this strategy with other plausible dinucleophiles for new transformations is being examined. An enantioselective version of DHF synthesis (<5% ee were observed with proline as catalyst in all cases) and application in natural product synthesis are also under investigation in our group.

Part II

Mitsunobu Reaction of 1,2,3-NH-Triazoles: Practical Synthesis of Chiral Triazole Derivatives

1. Introduction

1.1 Mitsunobu reaction

Discovered in 1967 by Oyo Mitsunobu, Mitsunobu reaction has received wide acceptance in organic chemistry due to its effectiveness and versatility. By using PPh_3 and DIAD/DEAD, this reaction converts an alcohol to several of functional groups²¹, and the alcohol undergoes an inversion of stereochemistry (Scheme 8).

Scheme 8. Mitsunobu Reaction

The mechanism has been well studied in last several years as shown here²² (Scheme 9). Triphenylphosphine and diisopropylazodicarboxylate (DIAD) quickly form a betaine intermediate, and alcohol can attack the betaine at phosphorus eventually forming oxyphosphonium ion, this ion undergoes $\text{S}_\text{N}2$ substitution to produce stereochemistry inversed product.

Scheme 9. Mechanism of Mitsunobu Reaction

In 1967, Mitsunobu reported the esterification through DEAD and PPh_3 condition (Scheme 10A), The ability to form carbon-oxygen ester bonds suggested that other types of C-O bonds could also be formed. The intermolecular formation of aliphatic ethers is unfortunately hindered by the

fact that the betaine intermediate is not basic enough to sufficiently deprotonate the weakly acidic hydroxyl group. However, formation of cyclic ethers via intramolecular condensation proceeds in good yields. Then in 1972, he reported the formation carbon- nitrogen bond through the same condition via alcohol and phthalimide²³ (Scheme 10B). And in 1981, he reported the reaction of ethyl cyanoacetate with (S)-(-)-ethyl 2-hydroxy-3-phenylpropionate, generating new C-C bond under Mitsunobu condition²⁴ (Scheme 10C).

Scheme 10. Various Mitsunobu Reactions

The Mitsunobu reaction has proven to be a useful, diverse and practical method for C-O, C-N and C-C bond formation, among other uses²⁴. Its mild reaction conditions and excellent stereoselectivity serves well in many purposes.

1.2 1,2,3-NH-triazoles

Since the recent discovery of the Cu-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC, “click-chemistry”, Scheme 11), the 1,2,3-triazole compounds have received much attention from scientists in various fields²⁵. Within the last several years, the importance of 1,2,3-triazole compounds has been continuously demonstrated in research fields such as material science²⁶ and chemical biology²⁷.

Scheme 11. Click Chemistry

Even though click chemistry gives high yield but there are some limitations.

1) Low reactivity with unsubstituted azides so we have to do deprotection to achieve NH-triazoles²⁸.

2) The preparation of substituted alkynes is challenging and has highly cost²⁹.

Therefore, an efficient synthesis of substituted 1,2,3-NH-triazoles is highly desirable. A couple of years ago, based on our previous study on amine catalyzed nitroalkene activation, our group developed one step cascade synthesis of 4,5-disubstituted-1,2,3-NH-triazoles³⁰ (Scheme 12).

Scheme 12. Cascade Synthesis of 1,2,3-NH-Triazoles

1.3 N-1, N-2 substituted 1,2,3-NH-triazoles

In the five-member ring of 1,2,3-NH-triazoles, with a strong dipole moment and high electron density on the nitrogens, the NH-triazoles are good nucleophiles, which will react with electrophiles under suitable conditions. However, among the reported examples, including acetylation and Michael addition, the N-1 substituted triazoles were the dominant products because the higher electron density associated with the two terminal N-1 and N-3 nitrogens than the internal N-2 nitrogen. Therefore, selective N-2 substitution remains a big challenge in triazole derivatization.

Our recent study successfully obtains N-2 substituted with specific C-substituted triazoles³¹, but it's still a big challenge for N-1 preferred triazoles, such benzotriazole to obtain N-2 substituted derivatives (Scheme 13).

Scheme 13. Challenges on 1,2,3-NH-Triazoles N-2 Substitution

2. Research Objective

2.1 Extended study of 1,2,3-triazole properties

In 2008, our group developed an amine-catalyzed three-component cascade reaction for the synthesis of 4,5-disubstituted-1,2,3-(NH)-triazoles. L-proline activated nitroalkene reacted with aldehyde could form nitro-diene as the intermediate. With the presence of NaN₃, nitro group served as leaving group to obtain 1,2,3-(NH)-triazole³⁰ (Scheme 14).

Scheme 14. Nitro-Diene Intermediate in 4,5-Substituted Triazoles

Various aryl aldehydes and β-alkyl nitroalkenes were suitable for this mild condition reaction to synthesize corresponding 4,5-disubstituted NH-triazoles. The modifications of the side chain can easily be carried out and used for further study (Scheme 15).

Scheme 15. Modification of 4,5-Substituted Triazoles

2.2 Synthesis of enantiomeric pure triazole analogous

Our group recently developed several effective strategies to introduce different functional groups on the triazole ring and applied the 1,2,3-triazoles as ligands to form new transition metal complexes. The interesting coordination ability of 1,2,3-triazoles and unique complex reactivity led to strong desire to prepare of enantiomeric pure triazole analogous. Considering the usually good stereoselectivity of Mitsunobu reaction, where complete inversion of alcohol stereogenic center occurred through SN2 mechanism, we wondered whether this condition could be applied for the introduction of chiral substitute groups on triazoles.

3. Results and Discussion

3.1 Screening of reaction condition

To verify our hypothesis, reaction between benzyl alcohol (**6a**) and benzotriazole (**7a**) was set up. As expected, the dehydration product **8a** was obtained in excellent yield. Screening conditions revealed THF as optimal solvent. The reaction results of benzotriazole with benzyl alcohol under different conditions are shown in Table 3.

Table 3. Screening of Reaction Condition between benzotriazole and benzyl alcohol^a

6a	7a		N2-8a	N1-8a
entry	solvent	N ₂ protection	Yield(%) ^b	
1	THF	No	97	
2	THF(dry)	Yes	98	
3	DMF	No	61	
4	DCE	No	81	
5	CH ₃ CN	No	75	
6	MeOH	No	68	

^a **6a:7a** = 1.0:1.1; ^b isolated yields.

All reagents had good solubility in most regular solvents, and these reactions went fast at room temperature, so oxygen in air almost had no influence, and trace water in solvent didn't really decrease yield. And due to the side reactions of triazoles with DIAD, we use alcohols as limiting reagents (Scheme 16).

Scheme 16. Side Reactions

3.2 Reactions between triazoles and achiral alcohols

After the condition optimization, various alcohols and NH-triazoles were then applied to investigate the reaction substrate scope. The results are shown in Table 4.

Table 4. Substrate Scope of the Triazole Mitsunobu Reactions

Entry	triazole	alcohol	product			
			N-2	Yield(%) ^a	N-1	Yield(%) ^a
8a				17		80
8b				29		50
8c				23		67
8d				20		75

8e				27		65
8f				26		64
8g				21		72
8h				25		69
8i				16		79
8j				30		42
8k				65		33
8l				59		20
8m				63		25

^a NMR yields.

In these reactions, benzotriazole still gave N-1 preferred products, but more hindered alcohol such tertiary alcohol, gave increased N-2 product. C-4 substituted triazoles had better N-2 selectivity and C4,C5-disubstituted triazole dominated N-2 product.

3.3 Stereoselectivity investigation

Encouraged by the good reactivity of NH-triazole under Mitsunobu reaction conditions, we investigated the stereoselectivity of this transformation. The *trans*-4-*tert*-butylcyclohexanol **9a** was applied to react with benzotriazole **7a**. As expected, excellent stereoselectivity was achieved with complete stereochemistry inversion (Scheme 17). The relative stereochemistry of *cis*-**10a-e** was confirmed by NMR analysis.

Scheme 17. Stereoselectivity Investigation

Then we set up several reactions with kinds of trans-alcohols and triazoles. The results are shown in Table 5.

Table 5. Substrate Scope of Stereoselectivity Investigation

Entr y	Triazoles	Alcohols	Products			
			N-2	Yield ^a (%)	N-1	Yield ^a (%)
10a				26		55
10b				25		64
10c				25		66
10d				70		24

^a NMR yields.

3.4 Synthesis of chiral triazoles

Due to the stereochemistry inversion, enantiomeric pure quinine **11** could react with benzotriazole **7a** to introduce chiral groups on triazoles (Scheme 18).

Scheme 18. Synthesis of Chiral Triazoles

3.4 N-2 selectivity

All these results above were exciting since it provided a practical approach for the preparation of enantiomeric 1,2,3-triazole derivatives. The N-1 and N-2 isomers were readily separable by column chromatography due to the large difference of polarity, which made them potential interesting novel ligands for asymmetric catalysis. However to our surprise, the N-1 and N-2 selectivity of these reactions were much lower than our previous reported alkylation reactions: the benzotriazole **7a** was known as “N-1-substitution-favored” triazole, where the reaction between **7a** and benzyl bromide gave exclusive N-1 alkylation product N1-**8a** with >95% isolated yield (Scheme 19).

Scheme 19. Alkylation of Benzotriazole

Moreover, in the synthesis of unsymmetrical bis-triazole, the alkylation of benzotriazole 7a gave excellent N-1 selectivity, but sequential Mitsunobu reaction yielded the unsymmetric N-2 isomers as major product in excellent yield (Scheme 20). This may provide a new approach to synthesize N-2 triazoles with those “N-1 substitution preferred” triazoles.

Scheme 20. Unsymmetrical Bis-Triazole

3.5 Possible future studies

In the future, several directions can be dug into for the novel triazole-quinine complex:

1) Reductive asymmetric amination through triazole-quinine-borane complex³² (Scheme 21);

Scheme 21. triazole-quinine-borane complex

2) Asymmetric triazole-Au catalyst³³ (Scheme 22);

Scheme 22. triazole-Au(I) catalyst

3) Design and synthesis of benzotriazole N-2 preferred derivatives.

4. Conclusion

In conclusion, we developed the Mitsunobu reactions between NH-triazole and alcohols as a practical strategy for 1,2,3-triazole functionalization under mild conditions. The reaction gave excellent stereoselectivity, which allowed asymmetric synthesis of enantiomeric pure triazole derivatives.

Part III

Experimental Section

General Methods and Materials:

Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. Air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. ^1H -NMR and ^{13}C -NMR spectra were recorded on Joel 270 MHz and Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.0 ppm) for ^{13}C .

. Melting points were measured on a Mel-Temp 1001D apparatus and uncorrected. HRMS were recorded on LTQFTUHRA spectrometer. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. Optical rotations were measured with a Jasco DIP-370 digital polarimeter in the solvent specified. High Pressure Liquid chromatography (HPLC) was performed on a SHIMADZU SPD-M20A (LC-20AB) chromatographs using a chiral column (50 cm) and guard column (5 cm) as noted for each compound.

The nitroalkene starting materials **1a-1v** were prepared according to reported procedures: 1) Ohta, H.; Kobayashi, N.; Ozaki, K. *J. Org. Chem.* **1989**, *54*, 1802-1804. 2) Matin, N. J. A.; Ozores, L.; List, B. *J. Am. Chem. Soc.* **2007**, *129*, 8976-8977. 3) Jang, Y. J.; Lin, W. W.; Shih, Y. K.; Liu, J. T.; Hwang, M. H.; Yao, C. F. *Tetrahedron*, **2003**, *59*, 4979-4992.

General Procedure for preparation of dihydrofuran (**4**)

The nitroalkene (202 mg, 1.2 mmol, 1.2 equiv.) was added to a DMSO solution of aldehyde (1.0 mmol, 1.0 equiv.), cyclohexane-1, 3-dione and L-Proline (6 mg, 0.05 mmol, 0.05 equiv.), with a concentration of 0.15 M for aldehyde. The reaction mixture was stirred for 5~10 minutes to have the clear solution; K_2CO_3 (69 mg, 0.5 mmol, 0.5 equiv.) was then added. The resulting reaction mixture was stirred at room temperature for 4 hours monitored by TLC. Upon the aldehyde was all consumed, the mixture was diluted with EtOAc (100 mL). The organic phase was washed by HCl solution (1.0 M), saturated NaHCO_3 (aq.) and brine and then dried over anhydrous Na_2SO_4 . The solvent

was removed under reduced pressure to give a residue. Flash silica gel chromatography was then applied to give the product.

General Procedure for Mitsunobu reactions of triazoles (8)

The benzyl alcohol (108 mg, 1.0 mmol, 1.0 equiv.) was added to a THF solution of benzotriazole (131mg, 1.1 mmol, 1.1 equiv.) and PPh₃ (328 mg, 1.25 mmol, 1.25 equiv.), with a concentration of 0.15 M for alcohol. The reaction mixture was stirred for 5 minutes to have the clear solution; DIAD (242 mg, 1.2 mmol, 1.2 equiv.) was then added. The resulting reaction mixture was stirred at room temperature for 3-5 hours monitored by TLC. Upon the alcohol was all consumed, the mixture was diluted with EtOAc (100 mL). The organic phase was washed by HCl solution (1.0 M), saturated NaHCO₃ (aq.) and brine and then dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure to give a residue. Flash silica gel chromatography was then applied to give the product.

Detailed screening conditions^a:

Entry	Cat.	Base(equiv)	Sol.	Time(h)	Conv. ^b (%)	Yield ^c (%)	
						4a	5a
1	Proline(20%)	-	DMSO	2	77	30	11
2	Proline(20%)	K ₂ CO ₃ (1.0)	DMSO	2	100	71 ^d	8
3	-	K ₂ CO ₃ (1.0)	DMSO	2	90	22	<5
4	Proline(20%)	K ₂ CO ₃ (0.5)	DMSO	2	100	80 ^d	<5
5	Proline(10%)	K ₂ CO ₃ (0.5)	DMSO	3	100	87 ^d	<5
6	Proline(5%)	K ₂ CO ₃ (0.5)	DMSO	4	100	87 ^d	<5
7	Proline(2%)	K ₂ CO ₃ (0.5)	DMSO	8	100	74 ^d	<5
8	Proline(5%)	K₂CO₃(0.5)	DMSO	4	100	91^e	<5
9	Proline(5%)	Cs ₂ CO ₃ (0.5)	DMSO	4	100	82 ^e	<5
10	Proline(5%)	NaOAc(1.0)	DMSO	4	86	71 ^e	8
11	Proline(5%)	NaOtBu(1.0)	DMSO	4	100	65 ^e	<5

12	Proline(5%)	Et ₃ N(1.0)	DMSO	4	93	85 ^e	<5
13	Proline(5%)	PIPEA(1.0)	DMSO	4	82	60 ^e	<5
14	Proline(5%)	NaOH(1.0)	DMSO	4	100	51 ^e	<5
15	Proline(5%)	K ₂ CO ₃ (0.5)	Acetone	4	75	32	<5
16	Proline(5%)	Et ₃ N(1.0)	DCM	4	56	42	<5
17	Proline(5%)	Et ₃ N(1.0)	EtOAc	4	63	40	<5
18	Proline(5%)	Et ₃ N(1.0)	Toluene	4	54	45	<5
19	Proline(5%)	Et ₃ N(1.0)	THF	4	68	61 ^e	<5
20	PPh ₃ (20%)	K ₂ CO ₃ (0.5)	DMSO	3	100	26	18
21	Et ₃ N(20%)	K ₂ CO ₃ (0.5)	DMSO	8	100	37	<5
22	DMAP(20%)	K ₂ CO ₃ (0.5)	DMSO	8	100	30	21
23	Glycine(5%)	K ₂ CO ₃ (0.5)	DMSO	4	100	69 ^e	<5

^a **1a:2a:3a** = 1:1:1, concentration of **2a** is 0.15 M; yields determined by NMR with 1,3,5-trimethoxybenzene as internal standard; ^b based on the nitroalkene **1a**. ^c NMR yield with 1,3,5-trimethoxybenzene as internal standard. ^d isolated yields. ^e isolated yield based on aldehyde, with the loading of **1a:2a:3a** = 1.2:1.0:1.1, concentration of **2a** is 0.15 M.

Compounds Characterization:

4a

2,3,6,7-tetrahydro-2-(1-phenylvinyl)-3-*p*-tolylbenzofuran-4(5*H*)-one

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 91%); ^1H NMR (600 MHz, CDCl_3) δ = 7.30 (t, J = 6.6 Hz, 3H), 7.27-7.25 (m, 2H), 7.04 (d, J = 7.8 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 5.42 (d, J = 5.4 Hz, 1H), 5.376 (s, 1H), 5.273 (s, 1H), 4.06 (d, J = 4.2 Hz, 1H), 2.67 (dt, J = 18.0 Hz, 10.8 Hz, 1H), 2.59-2.54 (m, 1H), 2.36-2.26 (m, 5H), 2.12-2.07 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 194.5, 176.8, 146.6, 139.2, 137.7, 136.4, 129.3, 128.4, 128.1, 127.2, 126.9, 116.4, 113.0, 93.8, 50.6, 36.8, 24.1, 21.7, 21.0; HRMS Calculated for $[\text{C}_{23}\text{H}_{22}\text{O}_2+\text{H}]^+$: 331.1692, Found: 331.1694.

4b

2,3,6,7-tetrahydro-3-(4-methoxyphenyl)-2-(1-phenylvinyl)benzofuran-4(5*H*)-one

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 82%); ^1H NMR (600 MHz, CDCl_3) δ = 7.30 (t, J = 6.6 Hz, 3H), 7.27-7.25 (m, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.77 (dd, J = 7.2 Hz, 1.8 Hz, 2H), 5.41 (d, J = 4.8 Hz, 1H), 5.37 (s, 1H), 5.27 (s, 1H), 4.05 (d, J = 4.2 Hz, 1H), 3.75 (s, 3H), 2.67 (dt, J = 18.0 Hz, 11.4 Hz, 1H), 2.60-2.54 (m, 1H), 2.37-2.26 (m, 2H), 2.12-2.08 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 194.6, 176.8, 158.5, 146.6, 137.7, 134.4, 128.4, 128.1, 128.0, 127.2, 116.4, 114.0, 112.9, 93.8, 55.2, 50.3, 36.8, 29.7, 24.1, 21.8; HRMS Calculated for $[\text{C}_{23}\text{H}_{22}\text{O}_3+\text{Na}]^+$: 369.1461, Found: 369.1462.

4c

2-(1-(4-chlorophenyl)vinyl)-2,3,6,7-tetrahydro-3-*p*-tolylbenzofuran-4(5*H*)-one

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 92%); ^1H NMR (600 MHz, CDCl_3) δ = 7.28-7.26 (m, 2H), 7.21-7.20 (m, 2H), 7.06 (d, J = 7.8 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 5.38 (d, J = 4.8 Hz, 1H), 5.37 (s, 1H), 5.29 (s, 1H), 4.03 (d, J = 4.2 Hz, 1H), 2.67

(dt, $J = 18.0$ Hz, 11.4 Hz, 1H), 2.58-2.53 (m, 1H), 2.37-2.26 (m, 5H), 2.12-2.08 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 194.5, 176.6, 145.5, 139.1, 136.6, 136.1, 134.1, 129.4, 128.6, 128.5, 126.9, 116.5, 113.7, 93.5, 50.7, 36.8, 24.1, 21.8, 21.2$. HRMS Calculated for $[\text{C}_{23}\text{H}_{21}\text{ClO}_2+\text{H}]^+$: 365.1303, Found: 365.1304.

4d

2,3,6,7-tetrahydro-2-(1-phenylvinyl)-3-(thiophen-2-yl)benzofuran-4(5H)-one

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 81%); ^1H NMR (600 MHz, CDCl_3) $\delta = 7.34$ -7.30 (m, 5H), 7.11 (dd, $J = 5.4$ Hz, 1.2 Hz, 1H), 6.86 (dd, $J = 4.8$ Hz, 3.6 Hz, 1H), 6.65 (dd, $J = 3.6$ Hz, 0.6 Hz, 1H), 5.52 (d, $J = 4.8$ Hz, 1H), 5.39 (s, 1H), 5.29 (s, 1H), 4.40 (d, $J = 4.2$ Hz, 1H), 2.67 (dt, $J = 18.0$ Hz, 11.4 Hz, 1H), 2.58-2.53 (m, 1H), 2.39 (dt, $J = 16.8$ Hz, 11.4 Hz, 1H), 2.33-2.28 (m, 1H), 2.13-2.06 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 194.5, 177.2, 146.1, 146.0, 137.5, 128.5, 128.3, 127.3, 127.0, 124.4, 124.0, 116.0, 113.3, 93.4, 46.0, 36.8, 29.7, 24.1, 21.6$; HRMS Calculated for $[\text{C}_{20}\text{H}_{18}\text{O}_2\text{S}+\text{H}]^+$: 323.1100, Found: 323.1091.

4e

1-(4,5-dihydro-2-methyl-5-(1-phenylvinyl)-4-*p*-tolylfuran-3-yl)ethanone

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 92%); ^1H NMR (600 MHz, CDCl_3) $\delta = 7.33$ -7.31 (m, 3H), 7.30-7.28 (m, 2H), 7.07 (d, $J = 7.8$ Hz, 2H), 6.89 (d, $J = 7.8$ Hz, 2H), 5.40 (s, 1H), 5.28 (d, $J = 5.4$ Hz, 1H), 5.27 (s, 1H), 4.02-4.01 (dd, $J = 4.8$ Hz, 1.2 Hz, 1H), 2.44 (d, $J = 1.8$ Hz, 3H), 2.31 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 195.3, 168.4, 146.6, 140.3, 137.7, 136.7, 129.5, 128.5, 128.1, 127.2, 127.2, 115.3, 112.7, 91.1, 54.7, 29.6, 21.0, 15.0$; HRMS Calculated for $[\text{C}_{22}\text{H}_{22}\text{O}_2+\text{H}]^+$: 319.1692, Found: 319.1694.

4f

1-(4,5-dihydro-2-methyl-4-(4-nitrophenyl)-5-(1-phenylvinyl)furan-3-yl)ethanone

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 94%); ^1H NMR (600 MHz, CDCl_3) $\delta = 8.12$ -8.10 (m, 2H), 7.35-7.31 (m, 3H), 7.24-7.22 (m, 2H), 7.15-7.13 (m, 2H), 5.41 (s, 1H), 5.30 (s, 1H), 5.28 (d, $J = 5.4$ Hz, 1H), 4.17 (d, $J = 5.4$ Hz, 1H), 2.48 (s, 3H),

1.95 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 193.6, 168.8, 150.8, 147.1, 146.1, 137.3, 128.7, 128.5, 128.2, 127.2, 124.0, 115.8, 113.0, 90.0, 54.9, 29.4, 15.2; HRMS Calculated for $[\text{C}_{21}\text{H}_{19}\text{NO}_4+\text{Na}]^+$: 372.1206, Found: 372.1208.

4g

1-(4,5-dihydro-2-methyl-5-(1-phenylvinyl)-4-propylfuran-3-yl)ethanone

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 65%); ^1H NMR (600 MHz, CDCl_3) δ = 7.33-7.29 (m, 5H), 5.24 (s, 1H), 5.19 (s, 1H), 5.10 (d, J = 3.6 Hz, 1H), 3.00-2.98 (m, 1H), 2.27 (d, J = 1.2 Hz, 3H), 2.16 (s, 3H), 1.55-1.42 (m, 2H), 1.26-1.20 (m, 1H), 1.12-1.08 (m, 1H), 0.8 (t, J = 14.4 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 194.3, 167.0, 147.5, 138.6, 128.4, 127.9, 127.3, 116.5, 112.9, 87.6, 47.8, 36.4, 29.2, 19.0, 15.3, 13.90. HRMS Calculated for $[\text{C}_{18}\text{H}_{22}\text{O}_2+\text{H}]^+$: 208.1692, Found: 208.1695.

4h

1-(4,5-dihydro-2-methyl-5-(1-phenylvinyl)-4-(pyridin-4-yl)furan-3-yl)ethanone

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 93%); ^1H NMR (600 MHz, CDCl_3) δ = 8.49 (dd, J = 4.8 Hz, 1.8 Hz, 2H), 7.34-7.32 (m, 3H), 7.25-7.23 (m, 2H), 6.92 (dd, J = 4.8 Hz, 1.8 Hz, 2H), 5.41 (s, 1H), 5.29 (dd, J = 1.8 Hz, 0.6 Hz, 1H), 5.27 (d, J = 5.4 Hz, 1H), 4.04 (d, J = 4.8 Hz, 1H), 2.46 (d, J = 1.2 Hz, 3H), 1.92 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 193.8, 169.0, 152.2, 150.2, 146.1, 137.4, 128.7, 128.4, 127.2, 122.5, 115.0, 113.0, 90.0, 54.4, 29.4, 15.2; HRMS Calculated for $[\text{C}_{20}\text{H}_{19}\text{NO}_2+\text{H}]^+$: 306.1489, Found: 306.1489.

4i

1-(4-(furan-2-yl)-4,5-dihydro-2-methyl-5-(1-phenylvinyl)furan-3-yl)ethanone

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 89%); ^1H NMR (600 MHz, CDCl_3) δ = 7.34-7.31 (m, 6H), 6.28 (dd, J = 3.0 Hz, 1.8 Hz, 1H), 5.97 (d, J = 3.6 Hz, 1H), 5.45 (dd, J = 5.4 Hz, 0.6 Hz, 1H), 5.44 (s, 1H), 5.30 (dd, J = 1.2 Hz, 0.6 Hz, 1H), 4.20 (d, J = 5.4 Hz, 1H), 2.39 (d, J = 1.2 Hz, 3H), 1.94 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 194.6, 168.9, 155.1, 146.0, 141.9, 137.4, 128.5, 128.2, 126.9, 113.2, 112.7, 110.5, 106.5, 87.6, 48.3, 29.1, 15.1; HRMS Calculated for $[\text{C}_{19}\text{H}_{18}\text{O}_3+\text{Na}]^+$: 317.1143, Found: 317.1139.

4j

methyl 4,5-dihydro-2-methyl-5-(1-phenylvinyl)-4-*p*-tolylfuran-3-carboxylate

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 89%); ^1H NMR (600 MHz, CDCl_3) δ = 7.31-7.26 (m, 5H), 7.05 (d, J = 7.8 Hz, 2H), 6.91 (dd, J = 6.6 Hz, 1.8 Hz, 2H), 5.39 (s, 1H), 5.31 (dd, J = 4.8 Hz, 0.6 Hz, 1H), 5.27 (d, J = 1.2 Hz, 1H), 3.98 (dd, J = 4.8 Hz, 1.2 Hz, 1H), 3.49 (s, 3H), 2.41 (d, J = 1.2 Hz, 3H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 168.2, 166.0, 146.7, 140.7, 137.8, 136.2, 129.2, 128.4, 128.0, 127.1, 127.0, 112.2, 106.3, 90.1, 53.8, 50.7, 21.0, 14.2; HRMS Calculated for $[\text{C}_{22}\text{H}_{22}\text{O}_3+\text{H}]^+$: 335.1642, Found: 335.1643.

4k

methyl 4-(4-fluorophenyl)-4,5-dihydro-2-methyl-5-(1-phenylvinyl)furan-3-carboxylate

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 90%); ^1H NMR (600 MHz, CDCl_3) δ = 7.31-7.30 (m, 3H), 7.26-7.24 (m, 2H), 6.98-6.91 (m, 4H), 5.40 (s, 1H), 5.39 (dd, J = 4.8 Hz, 0.6 Hz, 1H), 5.28 (d, J = 1.2 Hz, 1H), 4.00 (d, J = 4.8 Hz, 1H), 3.50 (d, J = 1.2 Hz, 3H), 2.41 (t, J = 2.4 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 168.5, 165.9, 162.6, 160.9, 146.5, 139.4, 139.4, 137.7, 128.7, 128.6, 128.5, 128.1, 127.1, 115.4, 115.2, 112.4, 106.2, 90.6, 53.6, 50.7, 14.3. HRMS Calculated for $[\text{C}_{21}\text{H}_{19}\text{FO}_3+\text{H}]^+$: 339.1391, Found: 339.1391.

4l

methyl 4,5-dihydro-2-methyl-4-phenethyl-5-(1-phenylvinyl)furan-3-carboxylate

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 71%); ^1H NMR (600 MHz, CDCl_3) δ = 7.35-7.28 (m, 5H), 7.22-7.20 (m, 2H), 7.14-7.11 (m, 1H), 7.03 (dd, J = 8.4 Hz, 1.8 Hz, 2H), 5.27 (s, 1H), 5.23 (d, J = 2.4 Hz, 1H), 5.22 (d, J = 4.8 Hz, 1H), 3.64 (s, 3H), 3.04-3.00 (m, 1H), 2.55-2.50 (m, 1H), 2.39-2.34 (m, 1H), 2.28 (d, J = 1.2 Hz, 3H), 1.98-1.92 (m, 1H), 1.86-1.79 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ = 168.0, 166.2, 147.4, 141.8, 138.6, 128.4, 128.2, 128.2, 127.9, 127.3, 125.7, 113.1, 105.1, 87.7, 50.6, 47.4, 35.4, 32.0, 14.3; HRMS Calculated for $[\text{C}_{23}\text{H}_{24}\text{O}_3+\text{H}]^+$: 349.1798, Found: 349.1798.

4m

ethyl 4,5-dihydro-2-methyl-5-(1-phenylvinyl)-4-*p*-tolylfuran-3-carboxylate

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 86%); ^1H NMR (600 MHz, CDCl_3) δ = 7.32-7.28 (m, 5H), 7.07 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 1.8 Hz, 1H), 6.87 (s, 1H), 5.39 (s, 1H), 5.28 (d, J = 0.6 Hz, 1H), 5.27 (s, 1H), 4.01 (d, J = 4.8 Hz, 1H), 2.95-2.85 (m, 2H), 2.31 (s, 3H), 1.79 (s, 3H), 1.30 (t, J = 15.0 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 195.1, 173.1, 146.8, 140.4, 137.7, 136.7, 129.5, 128.4, 128.1, 127.2, 127.2, 114.2, 112.5, 90.8, 54.7, 29.6, 22.0, 21.0, 11.2. HRMS Calculated for $[\text{C}_{23}\text{H}_{24}\text{O}_3 + \text{H}]^+$: 349.1798, Found: 349.1798.

4n

1-(5-(1-(furan-2-yl)vinyl)-4,5-dihydro-2-methyl-4-*p*-tolylfuran-3-yl)ethanone

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 90%); ^1H NMR (600 MHz, CDCl_3) δ = 7.40 (d, J = 1.2 Hz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.37 (dd, J = 3.6 Hz, 1.8 Hz, 1H), 6.11 (d, J = 3.6 Hz, 1H), 5.65 (s, 1H), 5.13 (s, 1H), 5.13 (s, 1H), 4.16 (d, J = 4.2 Hz, 1H), 2.45 (d, J = 1.2 Hz, 3H), 2.34 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 195.3, 168.3, 150.9, 142.5, 140.3, 137.0, 136.2, 129.6, 127.5, 115.7, 111.2, 109.2, 107.3, 89.7, 55.5, 29.6, 21.1, 14.9; HRMS Calculated for $[\text{C}_{20}\text{H}_{20}\text{O}_3 + \text{Na}]^+$: 331.1305, Found: 331.1295.

4o

2-(1-(furan-2-yl)vinyl)-2,3,6,7-tetrahydro-3-(4-methoxyphenyl)benzofuran-4(5H)-one

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 83%); ^1H NMR (600 MHz, CDCl_3) δ = 7.38 (d, J = 1.8 Hz, 1H), 7.11 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 6.35 (dd, J = 3.6 Hz, 2.4 Hz, 1H), 6.07 (d, J = 3.6 Hz, 1H), 5.66 (s, 1H), 5.28 (d, J = 6.0 Hz, 1H), 5.15 (s, 1H), 4.20 (d, J = 5.4 Hz, 1H), 3.78 (s, 3H), 2.69-2.65 (m, 1H), 2.62-2.58 (m, 1H), 2.39-2.34 (m, 2H), 2.15-2.11 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 194.5, 176.6, 158.6,

150.8, 142.5, 136.0, 134.4, 128.3, 116.9, 114.2, 111.2, 109.5, 107.4, 92.2, 55.2, 51.0, 36.9, 24.0, 21.8. HRMS Calculated for $[C_{21}H_{20}O_4+H]^+$: 337.1434, Found: 337.1436.

4p

methyl 5-(1-(4-chlorophenyl)vinyl)-4,5-dihydro-2-methyl-4-(4-nitrophenyl)furan-3-carboxylate

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 95%); 1H NMR (600 MHz, $CDCl_3$) δ = 8.14-8.12 (m, 2H), 7.31-7.29 (m, 2H), 7.20-7.17 (m, 4H), 5.42 (s, 1H), 5.33 (d, J = 1.2 Hz, 1H), 5.27 (d, J = 6.0 Hz, 1H), 4.09 (dd, J = 5.4 Hz, 1.2 Hz, 1H), 3.51 (s, 3H), 2.43 (d, J = 1.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.2, 165.3, 150.9, 147.1, 145.0, 135.8, 134.4, 128.8, 128.4, 128.1, 123.9, 113.9, 105.7, 89.3, 54.3, 50.9, 14.3. HRMS Calculated for $[C_{21}H_{18}ClNO_5+H]^+$: 400.0946, Found: 400.0948.

4q

1-(4,5-dihydro-2-methyl-4-(4-nitrophenyl)-5-(prop-1-en-2-yl)furan-3-yl)ethanone

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 85%); 1H NMR (600 MHz, $CDCl_3$) δ = 8.19 (dd, J = 6.6 Hz, 1.8 Hz, 2H), 7.38 (dd, J = 6.6 Hz, 2.4 Hz, 2H), 4.94 (t, J = 2.4 Hz, 1H), 4.91 (d, J = 0.6 Hz, 1H), 4.73 (d, J = 6.0 Hz, 1H), 4.27 (dd, J = 6.0 Hz, 1.2 Hz, 1H), 2.42 (d, J = 1.2 Hz, 3H), 2.03 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.5, 169.1, 151.2, 147.1, 141.9, 128.2, 124.2, 115.9, 113.2, 92.8, 54.0, 29.4, 16.7, 15.2; HRMS Calculated for $[C_{16}H_{17}NO_4+H]^+$: 288.1230, Found: 288.1232.

4r

methyl 4,5-dihydro-2-methyl-5-(prop-1-en-2-yl)-4-(pyridin-4-yl)furan-3-carboxylate

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 80%); 1H NMR (600 MHz, $CDCl_3$) δ = 8.56 (b, 2H), 7.14 (d, J = 4.8 Hz, 2H), 4.91 (d, J = 1.2 Hz, 2H), 4.74 (d, J = 6.0 Hz, 1H), 4.06 (dd, J = 6.0 Hz, 1.2 Hz, 1H), 3.55 (s, 3H), 2.37 (d, J = 1.8 Hz, 3H), 1.78 (t, J = 1.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.7, 165.5, 152.7, 150.1, 142.2, 122.5, 112.9,

104.9, 92.7, 52.9, 50.8, 16.7, 14.2; HRMS Calculated for $[C_{15}H_{17}NO_3+H]^+$: 260.1281, Found: 260.1283.

4s

methyl 5-cyclohexenyl-4,5-dihydro-2-methyl-4-*p*-tolylfuran-3-carboxylate

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 85%); 1H NMR (600 MHz, $CDCl_3$) δ = 7.10 (d, J = 7.8 Hz, 2H), 7.07 (dd, J = 6.0 Hz, 1.8 Hz, 2H), 5.61 (s, 1H), 4.68 (d, J = 5.4 Hz, 1H), 4.04 (dd, J = 5.4 Hz, 1.2 Hz, 1H), 3.54 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H), 2.04-1.99 (m, 4H), 1.71-1.55 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.7, 166.2, 141.4, 136.1, 136.0, 129.2, 127.0, 124.6, 106.2, 94.7, 52.6, 50.6, 24.9, 22.8, 22.3, 22.3, 21.0, 14.2; HRMS Calculated for $[C_{20}H_{24}O_3+H]^+$: 313.1798, Found: 313.1799.

4t

1-(5-cyclohexenyl-4,5-dihydro-2-methyl-4-*p*-tolylfuran-3-yl)ethanone

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 83%); 1H NMR (600 MHz, $CDCl_3$) δ = 7.12 (d, J = 8.4 Hz, 2H), 7.07 (t, J = 7.8 Hz, 2H), 5.62 (s, 1H), 4.65 (d, J = 6.0 Hz, 1H), 4.09 (dd, J = 5.4 Hz, 0.6 Hz, 1H), 2.37 (d, J = 1.2 Hz, 3H), 2.32 (s, 3H), 2.04-1.98 (m, 4H), 1.88 (s, 3H), 1.71-1.57 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 195.2, 168.9, 140.9, 136.5, 135.6, 129.5, 127.2, 124.8, 115.4, 95.0, 53.4, 29.5, 24.8, 22.8, 22.2, 20.9, 14.9. HRMS Calculated for $[C_{20}H_{24}O_2+H]^+$: 297.1849, Found: 297.1850.

4u

ethyl 5-cyclohexenyl-4-(furan-2-yl)-4,5-dihydro-2-phenylfuran-3-carboxylate

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 75%); 1H NMR (600 MHz, $CDCl_3$) δ = 7.87-7.85 (m, 2H), 7.44-7.38 (m, 3H), 7.35 (dd, J = 1.8 Hz, 0.6 Hz, 1H), 6.32 (dd, J = 3.0 Hz, 1.8 Hz, 1H), 6.15 (d, J = 3.0 Hz, 1H), 5.77 (d, J = 0.6 Hz, 1H), 4.99 (d, J = 6.0 Hz, 1H), 4.45 (d, J = 6.6 Hz, 1H), 4.11-4.05 (m, 1H), 4.02-3.97 (m, 1H), 2.12-2.07 (m, 4H),

1.72-1.57 (m, 4H), 1.07 (t, $J = 14.4$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 166.0, 164.7, 156.0, 141.5, 135.7, 130.5, 129.8, 129.4, 127.6, 124.9, 110.4, 105.7, 103.7, 90.1, 59.6, 48.2, 24.9, 22.9, 22.3, 14.0$; HRMS Calculated for $[\text{C}_{23}\text{H}_{24}\text{O}_4+\text{Na}]^+$: 387.1567, Found: 387.1555.

4v

2-cyclohexenyl-2,3,6,7-tetrahydro-3-*p*-tolylbenzofuran-4(5*H*)-one

Purified by flash chromatography (hexane-EtOAc) as colorless oil (yield: 92%); ^1H NMR (600 MHz, CDCl_3) $\delta = 7.10$ (d, $J = 8.4$ Hz, 2H), 7.05 (t, $J = 8.4$ Hz, 2H), 5.66 (s, 1H), 4.83 (d, $J = 5.4$ Hz, 1H), 4.11 (d, $J = 5.4$ Hz, 1H), 2.62-2.49 (m, 2H), 2.39-2.28 (m, 5H), 2.11-2.04 (m, 4H), 1.98 (d, $J = 1.2$ Hz, 2H), 1.73-1.55 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 194.5, 177.3, 139.7, 136.3, 135.4, 129.3, 127.0, 125.5, 116.5, 97.7, 49.2, 36.8, 24.9, 24.0, 22.7, 22.2, 21.8, 21.0$; HRMS Calculated for $[\text{C}_{21}\text{H}_{24}\text{O}_2+\text{H}]^+$: 309.1849, Found: 309.1850.

8a-N2

2-benzyl-2H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as yellow oil (yield: 17%); ^1H NMR (600 MHz, CDCl_3) $\delta = 7.87$ -7.85 (m, 2H), 7.42-7.40 (m, 2H), 7.36-7.30 (m, 5H), 5.87 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 144.9, 134.9, 129.1, 128.8, 128.6, 126.6, 118.4, 60.6$.

8a-N1

1-benzyl-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 80%); ^1H NMR (600 MHz, CDCl_3) $\delta = 8.05$ -8.03 (m, 1H), 7.38-7.24 (m, 8H), 5.82 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 146.6, 135.0, 133.0, 129.2, 128.7, 127.8, 127.6, 124.1, 120.3, 109.9, 52.6$.

8b-N2

2-(2,2-dimethyl-1-phenylpropyl)-2H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 29%); ^1H NMR (600 MHz, CDCl_3) $\delta = 7.90$ -7.88 (m, 2H), 7.75 (d, $J = 7.2$ Hz, 2H), 7.37-7.34 (m, 2H), 7.33-7.29 (m, 3H), 5.82 (s, 1H), 1.10 (s, 9H).

8b-N1

1-(2,2-dimethyl-1-phenylpropyl)-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 50%); ^1H NMR (600 MHz, CDCl_3) δ = 8.05 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 7.2 Hz, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.43 (t, J = 15.6 Hz, 1H), 7.34-7.27 (m, 4H), 5.43 (s, 1H), 1.15 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3): δ = 136.5, 129.5, 128.0, 127.9, 127.0, 123.7, 119.9, 109.4, 72.6, 37.2, 27.6.

8c-N2

2-(1-phenylallyl)-2H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 23%); ^1H NMR (600 MHz, CDCl_3) δ = 7.88-7.86 (m, 2H), 7.39-7.36 (m, 4H), 7.30-7.28 (m, 2H), 7.25-7.22 (m, 1H), 6.76 (d, J = 16.2 Hz, 1H), 6.56-6.51 (m, 1H), 5.48-5.47 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 144.8, 136.0, 135.5, 128.8, 128.5, 127.0, 126.6, 122.2, 118.3, 58.8.

8c-N1

1-(1-phenylallyl)-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 67%); ^1H NMR (600 MHz, CDCl_3) δ = 8.07-8.06 (m, 1H), 7.56-7.54 (m, 1H), 7.45-7.43 (m, 1H), 7.36-7.32 (m, 3H), 7.30-7.27 (m, 2H), 7.25-7.23 (m, 1H), 6.66 (d, J = 15.6 Hz, 1H), 6.40-6.36 (m, 1H), 5.43-5.42 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 146.5, 135.8, 134.7, 133.1, 128.9, 128.6, 127.6, 126.9, 124.2, 122.4, 120.3, 110.0, 50.8.

8d-N2

2-(1-phenylethyl)-2H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 20%); ^1H NMR (600 MHz, CDCl_3) δ = 7.86-7.85 (m, 2H), 7.40-7.38 (m, 2H), 7.36-7.24 (m, 5H), 6.16-6.12 (m, 1H), 2.14 (d, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 144.4, 140.4, 129.0, 128.5, 126.8, 126.4, 118.4, 66.4, 21.6.

8d-N1

1-(1-phenylethyl)-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 75%); ^1H NMR (600 MHz, CDCl_3) δ = 8.03-8.02 (m, 1H), 7.32-7.22 (m, 8H), 6.04-6.00 (m, 1H), 2.15 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 146.7, 140.4, 132.7, 129.1, 128.4, 127.2, 126.5, 124.0, 120.2, 110.4, 59.3, 21.4.

8e-N2

2-(2-methoxybenzyl)-2H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 27%); ^1H NMR (600 MHz, CDCl_3) δ = 7.87-7.85 (m, 2H), 7.36-7.34 (m, 2H), 7.31-7.28 (m, 1H), 7.11-7.09 (m, 1H), 6.91-6.89 (m, 2H), 5.94 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 157.3, 144.7, 130.1, 129.9, 126.4, 123.5, 121.0, 118.4, 111.0, 55.8, 55.2.

8e-N1

1-(2-methoxybenzyl)-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 65%); ^1H NMR (600 MHz, CDCl_3) δ = 8.06-8.04 (m, 1H), 7.49-7.47 (m, 1H), 7.42-7.40 (m, 1H), 7.35-7.32 (m, 1H), 7.30-7.27 (m, 1H), 7.08-7.06 (m, 1H), 6.92-6.87 (m, 2H), 5.87 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 156.9, 146.1, 133.1, 129.8, 129.4, 127.1, 123.7, 123.2, 120.9, 119.9, 110.6, 110.0, 55.4, 46.8.

8f-N2

2-(2,3-dihydro-1H-inden-1-yl)-2H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 26%); ^1H NMR (600 MHz, CDCl_3) δ = 7.87-7.84 (m, 2H), 7.36-7.34 (m, 3H), 7.30 (t, J = 15.0 Hz, 1H), 7.20-7.15 (m, 2H), 6.49-6.46 (m, 1H), 3.47-3.42 (m, 1H), 3.12-3.07 (m, 1H), 2.90-2.83 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 144.6, 144.2, 140.7, 129.3, 127.2, 126.4, 125.4, 125.0, 118.4, 71.5, 33.0, 31.2.

8f-N1

1-(2,3-dihydro-1H-inden-1-yl)-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 64%); ^1H NMR (600 MHz, CDCl_3) δ = 8.05-8.04 (m, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.34-7.23 (m, 3H), 7.14 (t, J = 15.0 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 6.92-6.90 (m, 1H), 6.63 (t, J = 15.0 Hz, 1H), 3.33-3.28 (m, 1H), 3.16-3.10 (m, 1H), 2.88-2.83 (m, 1H), 2.56-2.50 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ = 147.0, 143.7, 139.5, 131.9, 129.3, 127.4, 127.2, 125.5, 125.0, 124.0, 120.4, 110.6, 65.1, 32.8, 31.0.

8g-N2

2-allyl-2H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as yellow oil (yield: 21%); ^1H NMR (600 MHz, CDCl_3) δ = 7.86-7.85 (m, 2H), 7.37-7.35 (m, 2H), 6.21-6.17 (m, 1H), 5.39-5.36 (m, 2H), 5.33-5.32 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 144.7, 131.3, 126.6, 120.4, 118.2, 59.1.

8g-N1

1-allyl-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 72%); ^1H NMR (600 MHz, CDCl_3) δ = 8.03 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.46-7.42 (m, 1H), 7.35-7.32 (m, 1H), 6.07-6.00 (m, 1H), 5.31-5.28 (m, 1H), 5.28-5.24 (m, 2H), 5.22-5.21 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ = 146.4, 133.1, 131.4, 127.5, 124.1, 120.2, 119.4, 109.9, 51.0.

8h-N2

(E)-2-(pent-3-en-2-yl)-2H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 25%); ^1H NMR (600 MHz, CDCl_3) δ = 7.88-7.86 (m, 2H), 7.38-7.35 (m, 2H), 5.92-5.88 (m, 1H), 5.82-5.78 (m, 1H), 5.52-5.49 (m, 1H), 1.82 (d, J = 6.6 Hz, 3H), 1.74-1.72 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 144.3, 130.4, 129.4, 126.3, 118.3, 64.9, 21.3, 17.9.

8h-N1

(E)-1-(pent-3-en-2-yl)-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 69%); ^1H NMR (600 MHz, CDCl_3) δ = 8.04 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.43-7.40 (m, 1H), 7.34-7.31 (m, 1H), 5.83-5.73 (m, 1H), 5.75-5.70 (m, 1H), 5.48-5.46 (m, 1H), 1.82 (d, J = 7.2 Hz, 3H), 1.70 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 146.6, 132.4, 130.2, 128.8, 127.0, 123.9, 120.2, 110.4, 57.6, 20.3, 17.8.

8i-N2

2-(prop-2-ynyl)-2H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as yellow oil (yield: 16%); ^1H NMR (600 MHz, CDCl_3) δ = 7.88-7.87 (m, 2H), 7.40-7.38 (m, 2H), 5.52 (d, J = 3.0 Hz, 2H), 2.61 (t, J = 4.5 Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ = 144.9, 127.0, 118.4, 75.9, 75.4, 46.2.

8i-N1

1-(prop-2-ynyl)-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 79%); ^1H NMR (600 MHz, CDCl_3) δ = 8.04-8.03 (m, 1H), 7.69-7.67 (m, 1H), 7.49 (t, J = 15.6 Hz, 1H), 7.36 (t, J = 15.6 Hz, 1H), 5.42 (d, J = 2.4 Hz, 2H), 2.48 (d, J = 4.8 Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ = 146.6, 132.7, 127.9, 124.4, 120.3, 110.0, 75.5, 75.3, 38.2.

8j-N2

2-(2-methylbut-3-yn-2-yl)-2H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 30%); ^1H NMR (600 MHz, CDCl_3) δ = 7.92-7.90 (m, 2H), 7.40-7.38 (m, 2H), 2.70 (s, 1H), 2.13 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ = 144.4, 126.7, 118.5, 73.4, 30.7.

8j-N1

1-(2-methylbut-3-yn-2-yl)-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 42%); ^1H NMR (600 MHz, CDCl_3) δ = 8.08-8.07 (m, 1H), 8.03-8.01 (m, 1H), 7.49-7.47 (m, 1H), 7.39-7.36 (m, 1H), 2.67 (s, 1H), 2.13 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ = 132.1, 127.0, 124.0, 120.3, 112.4, 84.2, 73.7, 56.1, 30.1.

8k-N2

2-benzyl-4-phenyl-2H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 65%); ^1H NMR (600 MHz, CDCl_3) δ = 7.88 (s, 1H), 7.82-7.80 (m, 2H), 7.44-7.42 (m, 2H), 7.37-7.32 (m, 6H), 5.64 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 148.0, 135.3, 131.4, 130.4, 128.8, 128.7, 128.4, 128.2, 127.9, 125.9, 58.7.

8k-N1

1-benzyl-4-phenyl-1H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 33%); ^1H NMR (600 MHz, CDCl_3) δ = 7.81-7.80 (m, 2H), 7.66 (s, 1H), 7.41-7.37 (m, 5H), 7.32-7.30 (m, 3H), 5.58 (s, 2H).

8l-N2

2-(2,2-dimethyl-1-phenylpropyl)-4-phenyl-2H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 59%); ^1H NMR (600 MHz, CDCl_3) δ = 7.85 (s, 1H), 7.84-7.82 (m, 2H), 7.69-7.68 (m, 2H), 7.42-7.41 (m, 2H), 7.35-7.32 (m, 3H), 7.31-7.29 (m, 1H), 5.56 (s, 1H), 1.08 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3): δ = 146.9, 136.3, 130.7, 130.1, 129.5, 128.8, 128.2, 127.7, 125.9, 78.8, 36.8, 27.1.

8l-N1

1-(2,2-dimethyl-1-phenylpropyl)-4-phenyl-1H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 20%); ^1H NMR (600 MHz, CDCl_3) δ = 7.85 (s, 1H), 7.84-7.82 (m, 2H), 7.59-7.58 (m, 2H), 7.42-7.39 (m, 2H), 7.36-7.31 (m, 4H), 5.30 (s, 1H), 1.10 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3): δ = 136.3, 130.7, 129.3, 128.8, 128.1, 128.0, 125.6, 75.8, 36.6, 27.5.

8m-N2

2-(2,3-dihydro-1H-inden-1-yl)-4-phenyl-2H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 63%); ^1H NMR (600 MHz, CDCl_3) δ = 7.86 (s, 1H), 7.81-7.80 (m, 2H), 7.43-7.41 (m, 2H), 7.36-7.33 (m, 2H), 7.32-7.29 (m, 1H), 7.26-7.24 (m, 1H), 7.21-7.19 (m, 1H), 6.24-6.22 (m, 1H), 3.39-3.34 (m, 1H), 3.08-3.02 (m, 1H), 2.81-2.73 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 147.5, 143.7, 140.7, 131.0, 130.5, 128.7, 128.2, 126.8, 125.9, 125.0, 124.7, 69.6, 32.2, 30.8.

8m-N1

1-(2,3-dihydro-1H-inden-1-yl)-4-phenyl-1H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 25%); ^1H NMR (600 MHz, CDCl_3) δ = 7.79-7.77 (m, 2H), 7.48 (s, 1H), 7.40-7.35 (m, 4H), 7.32-7.21 (m, 3H), 6.30-6.28 (m, 1H), 3.25-3.20 (m, 1H), 3.10-3.04 (m, 1H), 2.89-2.83 (m, 1H), 2.45-2.39 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ = 147.9, 143.9, 139.8, 130.7, 129.4, 128.8, 128.1, 127.4, 125.7, 125.3, 124.9, 117.6, 65.5, 34.2, 30.4.

8m-N2

2-benzyl-4-(4-chlorophenyl)-2H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 64%); ^1H NMR (600 MHz, CDCl_3) δ = 7.83 (s, 1H), 7.71-7.69 (m, 2H), 7.38-7.31 (m, 7H), 5.61 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 147.2, 135.4, 134.4, 131.6, 129.3, 129.1, 129.0, 128.6, 128.2, 127.4, 59.0.

8o-N2

4-(4-chlorophenyl)-2-(2-methylbut-3-yn-2-yl)-2H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 62%); ^1H NMR (600 MHz, CDCl_3) δ = 7.86 (s, 1H), 7.75-7.74 (m, 2H), 7.40-7.38 (m, 2H), 2.58 (s, 1H), 2.00 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ = 146.9, 134.4, 131.2, 129.3, 129.2, 127.5, 84.8, 72.5, 59.9, 30.1.

8p-N2

2-(2,3-dihydro-1H-inden-1-yl)-4-(4-methoxyphenyl)-2H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 61%); ^1H NMR (600 MHz, CDCl_3) δ = 7.82 (s, 1H), 7.71-7.70 (m, 2H), 7.38-7.36 (m, 2H), 7.34 (d, J = 7.8 Hz, 1H), 7.29 (t, J = 14.4 Hz, 1H), 7.24-7.18 (m, 2H), 6.20 (t, J = 13.8 Hz, 1H), 3.36-3.32 (m, 1H), 3.06-3.02 (m, 1H), 2.77-2.73 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 146.8, 144.0, 140.9, 134.3, 131.2, 129.3, 129.2, 129.1, 127.4, 127.1, 125.3, 124.9, 70.0, 32.4, 31.0.

8q-N2

2-(2,3-dihydro-1H-inden-1-yl)-4-(4-methoxyphenyl)-2H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 65%); ^1H NMR (600 MHz, CDCl_3) δ = 7.77 (s, 1H), 7.72-7.70 (m, 2H), 7.34-7.17 (m, 4H), 6.96-6.93 (m, 1H), 6.20 (t, J = 13.8 Hz, 1H), 3.82 (s, 3H), 3.37-3.32 (m, 1H), 3.06-3.01 (m, 1H), 2.78-2.71 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 159.7, 147.4, 143.7, 140.8, 130.5, 128.7, 127.2, 126.7, 125.0, 124.6, 123.3, 114.2, 69.5, 55.2, 32.2, 30.7.

8r-N2

2-benzyl-4-phenyl-5-(1-phenylvinyl)-2H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 85%); ^1H NMR (600 MHz, CDCl_3) δ = 7.60-7.59 (m, 2H), 7.42 (d, J = 7.8 Hz, 2H), 7.38-7.33 (m, 6H), 7.25-7.21 (m, 5H), 5.85 (d, J = 1.6 Hz, 1H), 5.64 (s, 2H), 5.54 (s, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ =

145.7, 144.6, 139.4, 138.8, 135.3, 130.5, 128.7, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.6, 126.8, 118.5, 58.7.

8r-N1

1-benzyl-4-phenyl-5-(1-phenylvinyl)-1H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 11%); ^1H NMR (600 MHz, CDCl_3) δ = 7.81-7.79 (m, 2H), 7.30-7.22 (m, 6H), 7.20-7.17 (m, 5H), 7.08-7.07 (m, 2H), 6.04 (s, 1H), 5.29 (s, 2H), 5.27 (s, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ = 145.2, 136.8, 136.1, 135.1, 133.0, 130.8, 128.9, 128.5, 128.5, 128.1, 127.8, 127.7, 126.5, 126.1, 121.2, 92.7, 52.2.

10a-N1

1-((1s,4s)-4-tert-butylcyclohexyl)-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 55%); ^1H NMR (600 MHz, CDCl_3) δ = 8.07-8.06 (m, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.46-7.43 (m, 1H), 7.36-7.34 (m, 1H), 4.91-4.89 (m, 1H), 2.53-2.51 (m, 2H), 2.02-1.96 (m, 2H), 1.73-1.65 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3): δ = 146.0, 133.1, 126.8, 123.8, 120.2, 110.1, 54.2, 47.8, 32.9, 30.9, 27.7, 22.5.

10b-N2

2-((1R,2S)-2-methylcyclohexyl)-2H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 25%); ^1H NMR (600 MHz, CDCl_3) δ = 7.88-7.86 (m, 2H), 7.36-7.34 (m, 2H), 2.57-2.56 (m, 1H), 2.43-2.37 (m, 1H), 2.16-2.11 (m, 1H), 2.08-2.05 (m, 1H), 1.88-1.85 (m, 1H), 1.76-1.65 (m, 2H), 1.54-1.47 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 143.8, 125.8, 118.0, 67.9, 34.8, 30.8, 26.7, 24.1, 21.2, 13.5.

10b-N1

1-((1R,2S)-2-methylcyclohexyl)-1H-benzo[d][1,2,3]triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 64%); ^1H NMR (600 MHz, CDCl_3) δ = 8.06 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.46-7.43 (m, 1H), 7.36-7.33 (m, 1H), 4.83-4.80 (m, 1H), 2.54-2.49 (m, 1H), 2.40 (br, 1H), 2.08-2.07 (m, 2H), 1.91-1.87 (m, 1H), 1.77-1.70 (m, 2H), 1.57-1.53 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 145.7, 133.2, 126.7, 123.6, 120.1, 109.7, 60.8, 34.2, 30.9, 27.0, 24.4, 21.4, 14.0.

10c-N2**2-((1R,2S)-2-methylcyclopentyl)-2H-benzo[d][1,2,3]triazole**

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 25%); ^1H NMR (600 MHz, CDCl_3) δ = 7.87-7.84 (m, 2H), 7.34-7.32 (m, 2H), 5.30-5.27 (m, 1H), 2.61-2.55 (m, 1H), 2.47-2.42 (m, 1H), 2.40-2.34 (m, 1H), 2.21-2.17 (m, 1H), 1.93-1.88 (m, 1H), 1.80-1.71 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 143.8, 125.8, 117.9, 70.8, 40.5, 32.5, 31.5, 23.6, 13.8.

10c-N1**1-((1R,2S)-2-methylcyclopentyl)-1H-benzo[d][1,2,3]triazole**

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 66%); ^1H NMR (600 MHz, CDCl_3) δ = 8.06 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.46-7.44 (m, 1H), 7.36-7.33 (m, 1H), 5.10-5.07 (m, 1H), 2.68-2.63 (m, 1H), 2.51-2.46 (m, 1H), 2.43-2.38 (m, 1H), 2.24-2.20 (m, 1H), 1.98-1.94 (m, 1H), 1.83-1.74 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ = 170.9, 126.8, 123.6, 119.9, 109.6, 89.3, 62.9, 39.8, 32.6, 31.0, 23.3, 14.3.

10d-N2**2-((1R,2S)-2-methylcyclohexyl)-4-phenyl-2H-1,2,3-triazole**

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 70%); ^1H NMR (600 MHz, CDCl_3) δ = 7.83 (s, 1H), 7.82-7.80 (m, 2H), 7.44-7.41 (m, 2H), 7.34-7.32 (m, 1H), 4.72-4.69 (m, 1H), 2.45-2.41 (m, 1H), 2.30-2.25 (m, 1H), 2.04-2.00 (m, 2H), 1.84-1.80 (m, 1H), 1.68-1.62 (m, 2H), 1.51-1.45 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 146.7, 130.9, 129.9, 128.7, 128.0, 125.8, 66.1, 34.5, 30.5, 26.8, 23.9, 21.5, 13.9.

10d-N1

1-((1R,2S)-2-methylcyclohexyl)-4-phenyl-1H-1,2,3-triazole

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 24%); ^1H NMR (600 MHz, CDCl_3) δ = 7.85-7.84 (m, 2H), 7.75 (s, 1H), 7.43-7.41 (m, 2H), 7.33-7.30 (m, 1H), 4.71-4.68 (m, 1H), 2.46-2.44 (m, 1H), 2.16-2.10 (m, 1H), 2.03-1.95 (m, 2H), 1.75-1.70 (m, 2H), 1.68-1.59 (m, 1H), 1.56-1.48 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 130.9, 128.8, 127.9, 125.6, 118.5, 62.4, 34.2, 30.8, 26.5, 24.6, 20.7, 13.1.

10e-N2**2-((1R,2S)-2-methylcyclopentyl)-4-phenyl-2H-1,2,3-triazole**

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 72%); ^1H NMR (600 MHz, CDCl_3) δ = 7.82 (s, 1H), 7.81-7.79 (m, 2H), 7.44-7.41 (m, 2H), 7.35-7.35 (m, 1H), 5.06-5.02 (m, 1H), 2.48-2.43 (m, 1H), 2.38-2.33 (m, 1H), 2.32-2.26 (m, 1H), 2.16-2.12 (m, 1H), 1.90-1.86 (m, 1H), 1.74-1.68 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ = 146.8, 130.9, 130.1, 128.8, 128.1, 125.8, 69.3, 40.3, 32.4, 31.1, 23.5, 14.1.

10e-N1**1-((1R,2S)-2-methylcyclopentyl)-4-phenyl-1H-1,2,3-triazole**

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 19%); ^1H NMR (600 MHz, CDCl_3) δ = 7.86-7.84 (m, 2H), 7.68 (s, 1H), 7.44-7.41 (m, 2H), 7.36-7.31 (m, 1H), 4.98-4.94 (m, 1H), 2.42-2.34 (m, 2H), 2.32-2.26 (m, 1H), 2.14-2.08 (m, 1H), 1.99-1.94 (m, 1H), 1.84-1.77 (m, 1H), 1.61-1.54 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ = 147.1, 130.9, 129.0, 128.8, 128.0, 125.6, 119.3, 65.4, 39.4, 32.1, 31.2, 22.9, 14.2.

12-N2**(2S,4S,8R)-2-((S)-(2H-benzo[d][1,2,3]triazol-2-yl)(6-methoxyquinolin-4-yl)methyl)-8-vinylquinuclidine**

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 30%); ^1H NMR (600 MHz, CDCl_3) δ = 8.83 (d, J = 4.8 Hz, 1H), 8.01 (d, J = 9.0 Hz, 1H), 7.84 (d, J = 4.2 Hz, 1H), 7.82-7.79 (m, 2H), 7.77 (s, 1H), 7.37-7.35 (m, 1H), 7.31-7.28 (m, 2H), 6.75 (d, J = 11.4 Hz, 1H), 5.98-5.93 (m, 1H), 5.12-5.08 (m, 2H), 4.45 (d, J = 8.4 Hz, 1H), 4.02 (s, 3H), 3.56-3.51 (m,

1H), 3.16-3.12 (m, 1H), 2.84 (d, $J = 14.4$ Hz, 1H), 2.78-2.73 (m, 1H), 2.32-2.31 (m, 1H), 1.90 (t, $J = 22.8$ Hz, 1H), 1.76 (d, $J = 3.0$ Hz, 1H), 1.69-1.58 (m, 2H), 0.95-0.92 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 158.4, 148.1, 147.7, 147.0, 144.9, 144.1, 141.4, 139.0, 128.3, 126.2, 121.9, 121.8, 118.3, 118.1, 114.7, 101.1, 101.0, 58.6, 55.8, 41.1, 39.3, 27.8, 27.7, 26.8$.

12-N1

(2S,4S,8R)-2-((S)-(1H-benzo[d][1,2,3]triazol-1-yl)(6-methoxyquinolin-4-yl)methyl)-8-vinylquinuclidine

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 58%); ^1H NMR (600 MHz, CDCl_3) $\delta = 8.85$ (d, $J = 4.8$ Hz, 1H), 8.00-7.97 (m, 2H), 7.72 (d, $J = 4.2$ Hz, 1H), 7.67 (d, $J = 2.4$ Hz, 1H), 7.4 (d, $J = 8.4$ Hz, 1H), 7.34-7.32 (m, 1H), 7.31-7.29 (m, 1H), 7.24-7.22 (m, 1H), 6.71 (d, $J = 11.4$ Hz, 1H), 5.99-5.93 (m, 1H), 5.12-5.08 (m, 2H), 3.95 (s, 3H), 3.50-3.46 (m, 1H), 3.09-3.05 (m, 1H), 2.74-2.65 (m, 2H), 2.31 (d, $J = 3.0$ Hz, 1H), 2.04-2.03 (m, 1H), 1.82 (t, $J = 2.4$ Hz, 1H), 1.69-1.64 (m, 1H), 1.61-1.56 (m, 1H), 1.07-1.03 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 158.5, 147.1, 146.3, 145.1, 141.5, 138.2, 132.2, 132.0, 128.4, 127.2, 123.6, 122.2, 120.4, 114.7, 109.7, 101.0, 56.4, 55.9, 55.8, 41.0, 39.2, 27.8, 27.7, 26.8$.

13-N2

1,2'-(ethane-1,2-diyl)bis(1H-benzo[d][1,2,3]triazole)

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 65%); ^1H NMR (600 MHz, CDCl_3) $\delta = 7.93$ -7.92 (m, 1H), 7.70-7.67 (m, 2H), 7.28-7.26 (m, 2H), 7.20-7.18 (m, 2H), 7.06-7.05 (m, 1H), 5.29-5.23 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 145.7, 144.6, 133.1, 127.5, 126.7, 123.9, 120.0, 117.9, 108.5, 55.4, 47.2$.

13-N1

1,2-di(1H-benzo[d][1,2,3]triazol-1-yl)ethane

Purified by flash chromatography (hexane-EtOAc) as white solid (yield: 20%); ^1H NMR

(600 MHz, CDCl₃) δ = 7.87-7.86 (m, 2H), 7.17-7.14 (m, 4H), 6.85-6.83 (m, 2H), 5.22 (s, 2H);
¹³C NMR (150 MHz, CDCl₃): δ = 145.6, 133.2, 127.7, 124.0, 119.7, 107.9, 47.6.

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^1H -NMR and ^{13}C -NMR Spectra

4l

4u

iao-1-282-1A-C
Pulse Sequence: zgpg30

Exp: 1-282-18-1
 Archive directory: /export/home/vmr1/vmr/sys/data
 Sample directory:
 File: PROTON
 Pulse Sequence: zgpg30

tao-1-282-18-C
Pulse Sequence: zgpg30

160-2-47-18-H
 Archive directory: /export/home/merl/vmr/sys/data
 Sample directory:
 Pulse Sequence: szpu1

tao-1-28i-28-H
Archive directory: /export/home/vmr1/vmrasy/data
Sample directory:
File: tao101
Pulse Sequence: zgpg30

tsa-1-28f-28-C
Pulse Sequence: t2pu1

tao-1-282-3A-H
 Archive directory: /export/home/vmar1/vmarsys/data
 Sample directory:
 Pulse Sequence: zgpg1

86-N2

tao-1-262-3a-c
Pulse Sequence: zgpg30

teo-1-22-3D-H
Archive directory: /export/home/vmar1/vmarsys/data
Sample directory:
File: PROTON
Pulse Sequence: zgpg30

tau-1-282-30-C
Pulse Sequence: zgpg30

ts01-202-44-C
Pulse Sequence: zgpg30

Lab-1-282-40-H
Archive directory: /export/home/vmr1/umersys/data
Sample directory: /export/home/vmr1/umersys/data
File: 8d-N1
Pulse sequence: zgpg30

120-1-20-40-C
Pulse Sequence: zgpg30

t400-1-181-6A-H
Archive directory: /export/home/vmr1/vmr/sys/data
File: t400-1-181-6A-H
File: PROTON
Pulse Sequence: zgpg30

66-N2

tao-1-282-6A-C
Pulse Sequence: szpu1

160-2-36-25-H *160-1-282-6B*
Archive directory: /export/home/vmr1/vmr/sy5/441A
Scan 1 of 1
File: proton
Pulse Sequence: zgpg30

tao-2-36-28-C
Pulse Sequence: szpu1

tao-1-282-5A-C
Pulse Sequence: szpul

tao-1-282-SC-C
Pulse Sequence: szpu1

8g-N2

tao-1-282-7A-C
Pulse Sequence: szpu1

tau-1-282-7C-H
Archive directory: /export/home/vnmr1/vnmrjs/data
Sample directory: /export/home/vnmr1/vnmrjs/data
Sample name: tau-1-282-7C-H
Pulse sequence: zgpg30

tao-1-282-7-C-C
Pulse Sequence: szpu1

8h-N2

tao-1-282-8A-C
Pulse Sequence: szpu1

tao-1-282-88-C
Pulse Sequence: szpu1

1ao-1-282-3d-H
Archive directory: /export/home/vmr1/vmr/svs/data
Sample directory: /export/home/vmr1/vmr/svs/data
File: 2821001
Pulse Sequence: szpul

tao-1-282-9A-C
Pulse Sequence: szpu1

140-1-282-38-H
Archive directory: /export/home/vmart/vnmrsys/data
File: 140-1-282-38-H
File: PROTON
Pulse Sequence: zgpg30

100-585-1-001
b12e 2ednauce: 22bnj

tao-1-282-10A-C
Pulse Sequence: szpu1

tao-1-282-100-C
Pulse Sequence: szpu1

tao-2-45-A-H
 Archive directory: /export/home/vnmr1/vnmr.sys/data
 Sample directory:
 File: PROTON
 Pulse Sequence: szpu1

tau-2-45-A-C
Pulse Sequence: szpu]

tao-2-45-B-H
 Archive directory: /export/home/vmr1/vmr/sys/data
 Sample directory:
 File: PROTON
 Pulse Sequence: s2pu1

tao-2-47-2A-H
 Archive directory: /export/home/vmr1/vmr/sys/data
 Sample directory:
 File: PROT0N
 Pulse Sequence: szpul

tao-2-47-28-H
Archive directory: /export/home/vnmr1/vnmr.sys/data
Sample directory:
File: PROTON
Pulse Sequence: zgpg30

tao-2-17-2b-C
Pulse Sequence: szpul

8m-N2

tao-2-50-2A-H
Archive directory: /export/home/vmr1/vmr sys/data
Sample directory: /export/home/vmr1/vmr sys/data
File: PROTON
Pulse Sequence: szpu1

tao-2-50-28-H
Archive directory: /export/home/vmrl/vmr/sys/data
Sample directory: /export/home/vmrl/vmr/sys/data
File: PROTON
Pulse Sequence: szpu1

8n-N2

tao-1-286-1A-H
 Archive directory: /export/home/vmrl/vmrsys/data
 Sample directory:
 File: PROTON
 Pulse Sequence: szpu1

tao-1-286-4a-H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: zgpg30

tao-1-236-4a-c
Pulse Sequence: szpu1

tao-1-286-2A-H
 Archive directory: /export/home/vnmr1/vnmr-sys/data
 Sample directory:
 File: PROTON
 Pulse Sequence: szpul

tao-1-286-2A-C
Pulse Sequence: szpu1

tao-1-267-2a-h
 Archive directory: /export/home/vnmr1/vnmr-sys/data
 Sample directory:
 File: PROTON
 Pulse Sequence: szpu1

tao-2-39-H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pu1

8f-N2

tao-2-39-C
Pulse Sequence: szpu1

8f-N2

tao-2-39-C-H
Archive directory: /export/home/vnmr1/vnmr/sy/data
Sample directory:
File: PROTON
Pulse Sequence: zgpg30

tao-2-39-C-C
Pulse Sequence: szpu1

8f=N1

tao-1-282-118-C
Pulse Sequence: szpu1

tao-2-35-A-H
Archive directory: /export/home/vmm1/vmrsgs/data
Sample directory:
File: tao235
Pulse Sequence: zgpg30

10b-N2

10b-N2

tao-2-35-A-C
Pulse Sequence: zgpg30

tao-2-35-8-H
Archive directory: /export/home/vnmr1/vnmrjys/data
Sample directory:
File: ta0208
Pulse Sequence: zgpg30

10b-N1

1a0-2-35-B-C
Pulse Sequence: s2pul

1a0-2-34-A-H
Archive directory: /export/home/vmar1/vmarsj/data
Sample directory:
File: 1A0101
Pulse sequence: zgpg30

106-N2

106-N2

tau-2-34-A-C
Pulse Sequence: s2pu1

1a0-2-34-8-FH
Archive directory: /export/home/vmr1/vmr/svs/data
Sample directory:
File: 1a0120
Pulse Sequence: zgpg30

106-N1

1a0-2-34-B-C
Pulse Sequence: s2pu1

tao-1-238-1-C
Pulse Sequence: szpu1

N2-12

tao-1-298-2-H
Archive directory: /export/home/vmr1/vmr/sys/data
Sample directory:
File: PROTON
Pulse Sequence: zgpg30

tao-1-298-2-C
Pulse Sequence: szpu1

tao-1-299-1A-H
Archive directory: /export/home/vmr1/vmr.sys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pu1

tao-1-239-1A-C
Pulse Sequence: szpu1

N1-13

tao-1-239-1b-H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pu1

tao-1-299-18-C
Pulse Sequence: szpul

N1-13