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Divergent Selectivity in MgI_2-Mediated Ring Expansions of Methylenecyclopropyl Amides and Imides

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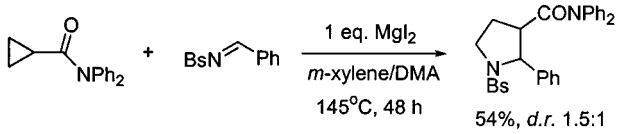
Abstract: We report a novel approach to prepare five- and six-membered heterocyclic compounds via a ring expansion of monoactivated methylenecyclopropanes (MCPs) with aldimines and aldehydes in the presence of MgI_2. Monoactivated MCPs behave as *homo*-Michael acceptors to afford bifunctional vinylogous enolates in the presence of MgI_2. The carbonyl moiety of the monoactivated MCP dramatically influences the reaction site in the dienolate with aryl aldimines and aldehydes as well as the size of the ring. Excellent divergent selectivity to five- vs. six-membered heterocycles is observed: α-alkylation/5-*exo-tet* cyclization (Z = NPh_2) vs. γ-alkylation/6-*exo-trig* cyclization (Z = 2-oxazolidone). Analogously, the reaction of the MCP imide with alkyl aldimines demonstrates the same selectivity by varing the size of electrophile or the reaction temperature. In addition, we observe the first example of the formation of the γ-alkylation adduct in the reaction of a vinylogous imide enolate with a carbonyl compound.

Introduction

Ring expansion reactions[1] of highly strained rings such as cyclopropanes constitute an efficient method for the construction of cyclic compounds. One useful approach to ring expansion involves the ring opening of a monoactivated or doubly-activated cyclopropane, which can act as a *homo*-Michael acceptor,[2] where the enolate or enol intermediate generated in situ acts as a nucleophile in a cyclization. Recently, Carreira and co-workers reported the ring expansion reaction of spiro[cyclopropane-1,3′-oxindole] with aldimines in the presence of catalytic MgI_2 which nicely illustrates this concept.[3] One example of a cyclopropanecarboxamide was disclosed as shown in Scheme 1.

In contrast, the most widely investigated reactions of methylenecyclopropanes (MCPs) are [3+2] cycloaddition processes.[4] We have examined the stereoselectivity in transition metal catalyzed intramolecular [3+2] cycloadditions of MCPs with alkynes and alkenes for the synthesis of five-membered carbocycles.[5] In addition, the double bond of MCPs has been used as a dienophile[6] in cycloaddition reactions and as an acceptor for reactive species such as radicals,[7] cations,[8] and metal

Scheme 1



intermediates[9] leading to ring opening or expansion. For instance, we studied a palladium-catalyzed hydrostannation of MCPs where ring opening was observed.[10]

A few reactions of MCPs activated by an electron withdrawing group have been reported. Nakamura and co-workers reported the thermal [3+2] cycloaddition reactions of highly activated methylenecyclopropanone derivatives with aldehydes and imines.[11] A thermally generated dipolar TMM (trimethylenemethane) was used as a reactive intermediate. The $TiCl_4$-mediated [3+2] cylcoaddition reactions of MCP ketones with allyltrimethylsilane were reported by Monti and co-workers[12] where the ketone, activated by $TiCl_4$, produced a zwitterionic reactive intermediate. Recently, Liu and co-workers described that the key step of the inactivation of crotonase is the ring opening of (methylene-cyclopropyl)formyl-CoA as *homo*-Michael acceptor.[13]

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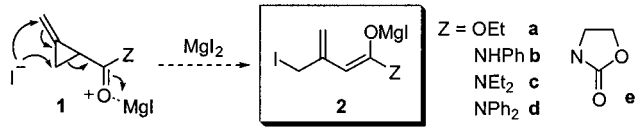
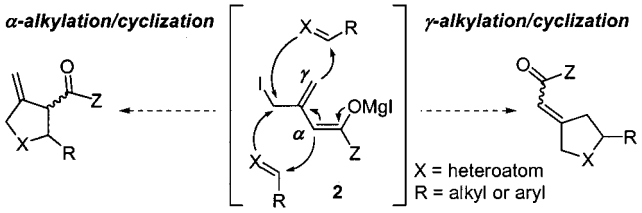
10.1021/ja011110o CCC: $22.00

Scheme 2



Scheme 3



Inspired by the work of Carreira and Liu, we envisioned that monoactivated MCPs would be a *homo*-Michael acceptor. Thus, the ring opening of **1** could afford a *vinylogous* enolate intermediate **2** having both nucleophilic and electrophilic centers (Scheme 2). Enolate **2** could then undergo reaction with electrophiles such as aldehydes or aldimines at the α- or γ-site followed by a cyclization reaction, leading to two different regioisomeric five-membered heterocycles (Scheme 3). During the course of investigating the reaction of several monoactivated MCPs **1**, unexpected divergent selectivty to five- vs. six-membered heterocyclic compounds was observed depending on the nature of **Z**, the size of the electrophile, and the reaction temperature.

We now report the development of a novel tandem cyclization via a bifunctional vinylogous enolate intermediate generated in situ from a monoactivated MCP in the presence of MgI_2.

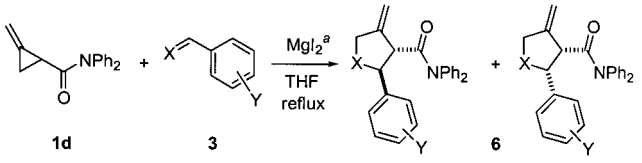
Results and Discussion

Reaction of MCP Amides. Our studies began with the reactions of several monoactivated MCP esters[14] **1a** and amides **1b**, **1c**, and **1d** with aryl aldimines in the presence of stoichiometric MgI_2. Initial attempts to react **1a**−**c** with **3e** in refluxing THF did not succeed. Ester **1a** did not react with MgI_2 whereas amides **1b** and **1c** gave complex mixtures even in the reactions with aryl aldehydes. In contrast the diphenyl amide **1d** reacted with **3e** to yield the methylenepyrrolidine **6e** in good yield as a mixture of diastereomers (Table 1). The formation of **6e** indicates a highly regioselective α-alkylation of the dienolate intermediate **2d** takes place. Reactions of the aldimines having a para-substituent yielded two diastereomers in good yields and modest to good stereoselectivities (entries 1, 2, and 4).

Significantly, in the case of aldimines bearing an ortho-substitutent (entries 7−10) only the trans diastereomers were obtained. Furthermore, it was found that the use of stoichiometric MgI_2 is not required since the reactions could also be carried out with 10−30 mol % of MgI_2 without any loss in yield (entries 3, 6, and 8−10). When 10 mol % MgI_2 was used, an increase in the reaction concentration to 0.2 M was required to ensure complete reaction (entry 6).

We also examined the reaction with aryl aldehydes under the same conditions. Reaction of **1d** with benzaldehyde gave

Table 1. Reactions between MCP Amide **1a** and Aryl Aldimines

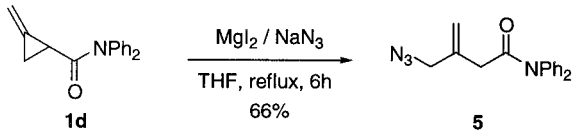


entry	3	X	Y	time (h)	6	yield (%)[b]	*d.r.* (trans:cis)
1	**a**	NTs[c]	4-CF_3	10	**a**	65	1.6:1
2	**b**	NTs	4-NO_2	6	**b**	57[d]	2.2:1
3	**c**	NTs	4-Br	10	**c**	85[d,e]	2.3:1
4	**d**	NTs	4-OMe	6	**d**	78	5.3:1
5	**e**	NBs[c]	H	6	**e**	81	4.1:1
6	**e**	NBs	H	15	**e**	76[f]	3.8:1
7	**f**	NTs	2-Br	6	**f**	71	>20:1[g]
8	**g**	NTs	2-CF_3	10	**g**	81[d,e]	>20:1[g]
9	**h**	NTs	2,4-dichloro	10	**h**	78[e]	>20:1[g]
10	**i**	NTs	2,4-dimethyl	10	**i**	82[e]	>20:1[g]

[a] Reactions were carried out in refluxing THF (0.05 M) with a stoichiometric amount of MgI_2 unless mentioned. [b] Isolated yield. [c] Ts = 4-toluenesulfonyl, Bs = benzenesulfonyl. [d] The relative stereochemistry for the major diastereomer was proven to be trans by X-ray crystallography. [e] The reactions were carried out with 30 mol % MgI_2. [f] The reaction was carried out with 10 mol % MgI_2 in 0.2 M THF. [g] Only one diastereomer was observed in the crude ^1H NMR.

an inseparable mixture of diastereomeric methylenetetrahydrofurans, which could not be identified. In the case of 2-bromobenzaldehyde, the minor diastereomer was contaminated with

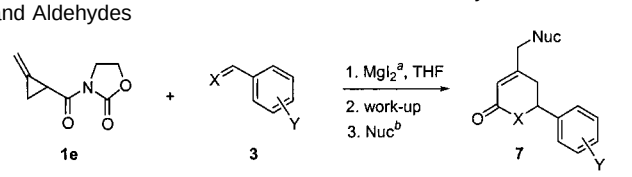
Scheme 4



an unknown byproduct, but the major diastereomer **4** (i.e. structure **6e** where X = O, see Supplementary Material) was isolated in 41% yield.

We attempted the ring opening reaction of **1d** with MgI_2 in the absence of electrophiles (Scheme 4). In refuxing THF, the dienolate intermediate **2d** was smoothly produced and then

Table 2. Reactions between MCP Imide **1e** and Aryl Aldimines and Aldehydes



entry	3	X	Y	method[c]	7	Nuc	yield (%)[d]
1	**c**	NTs	4-Br	A	**c**	N_3	78[e]
2	**c**	NTs	4-Br	B	**c′**	I	60[f]
3	**j**	NTs	H	A	**j**	N_3	81
4	**g**	NTs	2-CF_3	B	**g**	Ts	75
5	**i**	NTs	2,4-dimethyl	A	**i**	OAc	72
6	**k**	O	H	A	**k**	N_3	88
7	**l**	O	2-Br	A	**l**	SPh	67
8	**m**	O	4-NO_2	B	**m**	OAc	71
9	**n**	O	3,4-OCH_2O	A	**n**	Ts	65
10	**o**	O	2,4-dichloro	B	**o**	N_3	74

[a] Reactions were carried out using a stoichiometric amount of MgI_2 in THF (0.05 M). [b] The crude product was used for the next step without purification. [c] Method A: 0 °C to room temperature for 3 h. Method B: reflux for 1 h. [d] Isolated yield in two steps. [e] The structure of the product was identified by X-ray crystallography. [f] Compound **7c′** was isolated using silica flash chromatography and fully characterized by spectroscopic analysis, but it was not stable.

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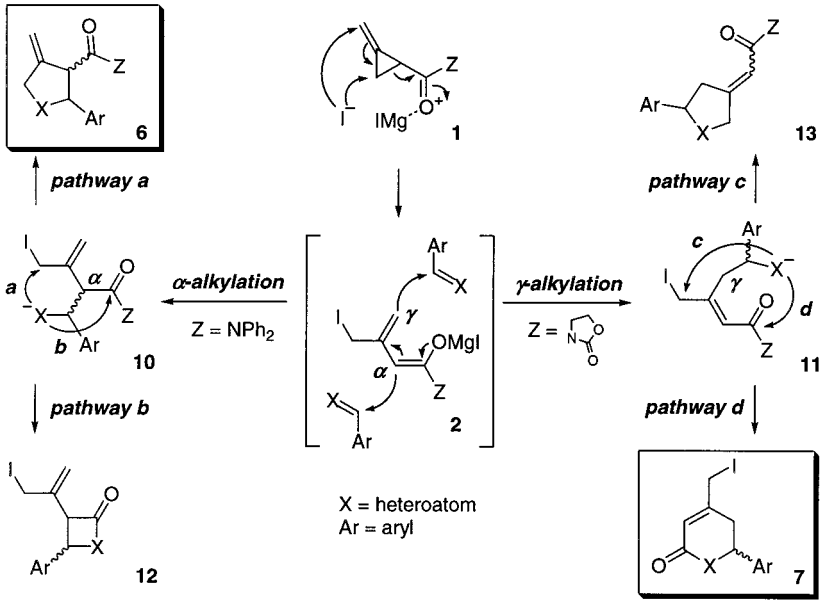
Scheme 5



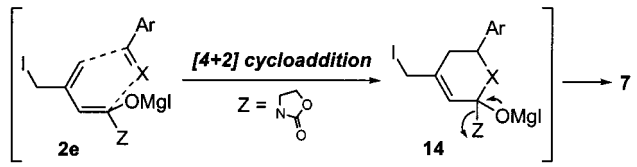
trapped with NaN_3 resulting in the isolation of the γ'-azido-β,γ-unsaturated amide **5** in 66% yield.

Reaction of MCP Imide. We reasoned that a more strongly activated MCP **1** could undergo the facile ring opening reaction under much milder conditions. MCP imide **1e** bearing a 2-oxazolidone reacted under the same conditions with aldimines **3** very quickly (entries 2 and 4, Table 2) and these reactions were rapid even at 0 °C (entries 1, 3, and 5). However, to our surprise, in contrast to the results with the diphenyl amide **1d**, the products obtained were exclusively six-membered heterocycles **7** bearing an allyl iodide and lacking the oxazolidone group. The reaction required a stoichiometric amount of MgI_2 in order to go to completion. The products **7** were isolated after functional group transformation because the iodo-substituted products were not stable to silica flash chromatography. In addition, reactions with aryl aldehydes furnished 5,6-dihydropyranones **7** in good yields in two steps (entries 6−10, Table 2).

The monoactivated MCPs **1** can potentially undergo the tandem cyclization leading to four possible cycloadducts: **6**, **7**, **12**, and **13** (Scheme 5). The reaction of the amide **1d** furnished only the five-membered heterocycles **6** via α-alkylation followed by 5-*exo-tet* cyclization pathway **a**, whereas the reaction of the imide **1e** proceeded via γ-alkylation followed by 6-*exo-trig* cyclization pathway **d** resulting in the exclusive formation of six-membered heterocycles **7**. Clearly, the substituent **Z** has a dramatic influence on the site of the alkylation and the eventual size of the ring formed. The facility of the tandem cyclizations can be attributed to the presence of a good leaving group: the allyl iodide in **10** or the oxazolidone[15] in **11**. We note that intermediate **11** having two potentially good leaving groups prefers 6-*exo-trig* cyclization (pathway **d**) to 5-*exo-tet* cyclization (pathway **c**).

More significantly, it is known that the reaction of vinylogous imide enolates with carbonyl compounds generally affords only the α-alkylation adduct.[16] To the best of our knowledge, *this is the first example of the γ-alkylation of a vinylogous imide enolate*.

Scheme 6



At this time we cannot completely exclude a concerted [4+2] *hetero*-Diels-Alder reaction pathway[17] to **7** (Scheme 6). Thus, the intermediate **2e** could react with an aldimine leading to a cycloadduct **14**, which would generate a six-membered heterocycle **7** via expulsion of the **Z** group.

To expand the scope of the reaction, we investigated the reaction with alkyl aldimines[18] (Table 3). Whereas **7** was the only product in the reactions with aryl aldimines (Table 2), the reaction of **1e** with alkyl aldimine **8p** furnished the methylenepyrrolidine **6p** as a major product (entry 1, Table 3) even in the presence of only 30 mol % MgI_2 (entry 2). Reaction with a more hindered imine such as **8q** led to a mixture of **6q** and **7q** in a ratio of ∼1:1 with a concomitant formation of **9q**[19] (entry 4). Reaction with the most hindered imine **8r** did not give any ring expanded products (entry 6). Significantly, in refluxing THF, **8q** and even **8p** furnished only six-membered pyridinones **7p** and **7q** in moderate yields (entries 3 and 5) while **8r** failed completely (entry 6). It appears these reactions are governed by the size of alkyl aldimines **8** and the reaction temperature.

(15) For example, it was easily removed from acyloxazolidinone in the presence of methoxymagnesium halide. See: Evans, D. A.; Morrissey, M. M.; Dorow, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 4346.

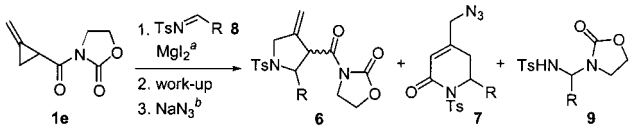
(16) For a general review for vinylogous aldol reaction, see: (a) Casiraghi, G.; Zanardi, F.; Appendino, G. *Chem. Rev.* **2000**, *100*, 1929. For examples of vinylogous imide enolates, see: (b) Evans, D. A.; Sjogren, E. B.; Bartroli, J.; Dow, R. L. *Tetrahedron Lett.* **1986**, *27*, 4957. (c) Black, W. C.; Giroux, A.; Greidanus, G. *Tetrahedron Lett.* **1996**, *37*, 4471.

(17) For a discussion of a stepwise vs. a cycloaddition mechanism, see a recent review of the vinylogous Mannich reaction: Bur, S. K.; Martin, S. F. *Tetrahedron* **2001**, *57*, 322

(18) Reactions of **1d** and **1e** with aliphatic aldehydes do not afford any products. In the case of **1d**, no reaction with alkyl aldimines occurred. In the presence of MgI_2, these electrophiles bearing an acidic proton appear not to be stable in refluxing THF.

(19) These products were not observed in the reactions in Table 2.

Table 3. Reactions between MCP Imide **1e** and Alkyl Aldimines



				yield (%)[d]		
entry	**8**	R	method[c]	**6** (trans:cis)	**7**	**9**
1	**p**	*n*-propyl	A	72 (6.2:1)	11	*e*
2	**p**	*n*-propyl	B	66 (4.5:1)	8	*e*
3	**p**	*n*-propyl	C	0	23	*e*
4	**q**	cyclohexyl	A	31 (>20:1)	34[f]	30[f]
5	**q**[g]	cyclohexyl	C	0	40	42
6	**r**	*t*-butyl	A or C	0	0	0

[a] Reactions were carried out with a stoichiometric amount of MgI_2 in THF (0.05 M). [b] The crude product was used for the next step without purification. [c] Method A: 0 °C to room temperature for 3 h. Method B: 30 mol % of MgI_2, room temperature for 7 h. Method C: reflux for 10 min. [d] Isolated yield in two steps. [e] Not determined. [f] The structure of the product was identified by X-ray crystallography. [g] Two equivalents of **8q** were used.

By controlling these two factors, it is possible to obtain two different heterocycles from the reactions of **1e** with alkyl aldimines **8**.

Conclusion

In conclusion, we have discovered a novel methodology to prepare five- and six-membered heterocyclic compounds via a tandem cyclization of monoactivated MCPs with aldimines or aldehydes in the presence of MgI_2. A key step is the in situ generation of an ambiphilic vinylogous enolate intermediate through the ring opening of a monoactivated MCP. In the reaction of monoactivated MCPs **1** with aryl aldimines and aldehydes, excellent divergent selectivity (five-membered vs. six-membered heterocycle) was achieved by changing the **Z** group in the carbonyl moiety of **1**. When the imide **1e** reacted with alkyl aldimines, depending on the size of the electrophile or the reaction temperature, the same divergent selectivity was observed. In both cases, the selectivity was attributed to the regioselective reaction of the dienolate **2** with electrophiles via α-alkylation/5-*exo*-*tet* cyclization or γ-alkylation/6-*exo*-*trig* cyclization. We also observed the first example of a vinylogous imide enolate **2e**, reacting at the γ-carbon with carbonyl compounds.

Experimental Section

General Procedures. All reactions were carried out in flame-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. All commercial materials were purchased from Sigma-Aldrich Co. and were used without further purification. Anhydrous magnesium iodide (MgI_2, ≥99%) was purchased from Fluka and stored in a glovebox under inert atmosphere. Weighing and transfer outside the glovebox were performed as quickly as possible to minimize air exposure. All reactions were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm) and treatment with acidic *p*-anisaldehyde or ceric ammonium nitrate stain followed by gentle heating. Purification of products was accomplished by flash chromatography using silica gel 60 (230−400 mesh) purchased from Silicycle Inc.

All ^{1}H and ^{13}C NMR spectra were recorded on Varian XL 400 and Varian Mercury 300 spectrometers. IR spectra were obtained on a Nicolet DX FT-IR spectrometer. High-resolution mass spectra were obtained on a VG70-250S (double focusing) mass spectrometer at 70 eV. Melting points were measured with a Fisher-Johns melting point apparatus.

Tosyl aryl aldimines and alkyl aldimines were prepared in moderate to good yields according to the known methods.[20] 2-Methylenecyclopropanecarboxylic acid ethyl ester (MCP ester, **1a**) and 2-methylenecyclopropanecarboxylic acid (MCP acid, **1z**) were prepared from 2-bromopropene.[21] MCP amides **1b**−**d** and MCP imide **1e** were prepared from **1z**.

Representative Procedure for the Synthesis of Methylenepyrrolidines from MCP Amide (1d) and Aryl Aldimines. To a solution of MCP amide **1d** (77.4 mg, 0.31 mmol) and aldimine **3d** (95.4 mg, 0.33 mmol) in THF (6 mL, 0.05 M) was added MgI_2 (86.2 mg, 0.31 mmol) rapidly under a positive nitrogen pressure. The reaction mixture was gently refluxed at 80 °C (oil bath temperature) for 6 h. The reaction mixture was then cooled to room temperature and quenched with a small portion of saturated aqueous Na_2SO_3 solution. The mixture was extracted with EtOAc (2 × 100 mL) and the combined organic phases were washed with H_2O (200 mL), brine (200 mL), dried over $MgSO_4$, filtered, and concentrated. Two diastereomers of **6d** (129 mg, 78%) were isolated by flash chromatography on silica gel (ethyl acetate: hexanes 1:5 → 1:3), which furnished the trans diastereomer (108 mg) as a white solid and the cis diastereomer as a colorless oil (21 mg).

***trans*-2-(4-Methoxyphenyl)-4-methylene-1-(4-toluenesulfonyl)pyrrolidine-3-carboxylic acid diphenylamide (6d):** white solid, mp 225−227 °C (ethyl acetate), R_f = 0.21 (silica gel, EtOAc:hexanes 1:3); IR ($CHCl_3$) ν_{max} (cm^{-1}) 3060, 2918, 2847, 1674, 1610, 1594, 1510, 1490, 1449, 1345, 1291, 1246, 1159, 1094, 1072, 1027, 843, 808, 752, 698; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61−7.56 (m, 2H), 7.32−7.05 (m, 10H), 7.09−6.96 (m, 2H), 6.89−6.83 (m, 2H), 6.74−6.61 (bs, 2H), 5.04 (dm, 1H, J = 2.19 Hz), 4.99 (dm, 1H, J = 2.19 Hz), 4.62 (d, 1H, J = 7.95 Hz), 4.25 (dm, 1H, J = 13.96 Hz), 4.00 (ddd, 1H, J = 13.96, 2.19, 2.19 Hz), 3.85 (s, 3H), 3.72 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 159.6, 144.0, 142.6, 132.8, 131.8, 129.8, 129.1, 128.5, 128.5, 128.4, 126.6, 126.3, 114.0, 108.5, 68.0, 58.1, 55.6, 54.6, 21.8; HRMS calcd for $C_{32}H_{30}N_2O_4S$ $(M)^+$ 538.1926, found 538.1914.

***cis*-2-(4-Methoxyphenyl)-4-methylene-1-(4-toluenesulfonyl)pyrrolidine-3-carboxylic acid diphenylamide (6d):** colorless oil, R_f = 0.42 (silica gel, EtOAc:hexanes 1:3); IR ($CHCl_3$) ν_{max} (cm^{-1}) 3305, 3061, 2924, 2832, 1650, 1611, 1592, 1512, 1489, 1447, 1386, 1337, 1321, 1269, 1249, 1154, 1090, 1032, 963, 906, 811, 761, 731, 700, 662; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48−7.42 (m, 2H), 7.34−7.13 (m, 6H), 7.06−6.92 (m, 6H), 6.77−6.71 (m, 2H), 6.66−6.52 (bs, 2H), 5.56 (s, 1H), 5.44 (d, 1H, J = 1.7 Hz), 4.78 (dd, 1H, J = 9.19, 3.70 Hz), 4.12 (d, 1H, J = 10.42 Hz), 3.94 (d, 1H, J = 3.57 Hz), 3.88 (d, 1H, J = 10.56 Hz), 3.80 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 159.2, 142.6, 141.8, 141.5, 140.8, 138.8, 131.2, 130.1, 129.2, 129.2, 128.7, 128.2, 128.1, 127.1, 127.0, 126.6, 118.8, 113.7, 56.6, 55.6, 52.5, 21.6, 8.8; HRMS calcd for $C_{32}H_{30}N_2O_4S$ $(M)^+$ 538.1926, found 538.1929.

Representative Procedure for the Synthesis of Dihydropyridinones and Dihydropyranones from MCP Imide (1e) and Aryl Aldimines and Aldehydes. To a solution of MCP imide **1e** (42 mg, 0.25 mmol) and aldimine **3c** (91 mg, 0.27 mmol) in THF (5 mL, 0.05 M) was added MgI_2 (75.1 mg, 0.27 mmol) rapidly at 0 °C under a positive nitrogen pressure. The reaction mixture was allowed to warm to room temperature for 3 h. The reaction mixture was then quenched with small portion of saturated aqueous Na_2SO_3 solution. The mixture was extracted with EtOAc (2 × 100 mL) and the combined organic phases were washed with H_2O (200 mL) and brine (200 mL), dried over $MgSO_4$, filtered, and concentrated. The resulting product was used directly in the next step. The crude product was dissolved in acetone (3 mL) followed by the addition of sodium azide (81 mg, 1.25 mmol).

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The reaction mixture was stirred at room temperature for 16 h. The mixture was extracted with EtOAc (2 × 50 mL), washed with brine (100 mL), dried over $MgSO_4$, filtered, and concentrated. Flash chromatography on silica gel (ethyl acetate:hexanes 1:5 → 1:3) furnished the product **7c** (81 mg, 78%) as a colorless oil.

4-Azidomethyl-6-(4-bromophenyl)-1-(4-toluenesulfonyl)-5,6-dihydro-1*H*-pyridin-2-one (7c): $R_f = 0.15$ (silica gel, EtOAc:hexanes 1:5); IR ($CHCl_3$) ν_{max} (cm^{-1}) 3064, 2978, 2106, 1775,1686, 1647, 1597, 1488, 1350, 1290, 1227, 1166, 1117, 1085, 1007, 958, 908, 848, 813, 703, 679; ^1H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, 2H, $J = 8.1$ Hz), 7.39 (d, 2H, $J = 8.4$ Hz), 7.21 (d, 2H, $J = 8.1$ Hz), 6.97 (d, 2H, $J = 8.4$ Hz), 5.96 (m, 2H), 3.85 (d, 1H, $J = 15.9$ Hz), 3.71 (d, 1H, $J = 16.2$ Hz), 3.19 (ddt, 1H, $J = 17.4$, 6.9, 1.2 Hz), 2.54 (dd, 1H, $J = 17.7$, 1.2 Hz), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 148.9, 145.3, 138.3, 135.5, 132.0, 129.5, 129.2, 128.2, 122.4, 121.3, 56.9, 54.2, 34.6, 21.8; HRMS calcd for $C_{19}H_{17}BrN_4O_3S$ $(M)^+$ 461.0283, found 461.0266.

4-Azidomethyl-6-phenyl-5,6-dihydro-pyran-2-one (7k). 7k was prepared as above using benzaldehyde **3k** instead of aldimine **3c** in 88% as a colorless oil. $R_f = 0.43$ (silica gel, EtOAc:hexanes 1:3); IR ($CHCl_3$) ν_{max} (cm^{-1}) 3064, 3036, 2917, 2098, 1717, 1496, 1454, 1423, 1377, 1346, 1265, 1244, 1132, 1066, 1017, 849, 758, 695; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45−7.33 (m, 5H), 6.15 (dm, 1H, $J = 1.8$ Hz), 5.45 (dd, 1H, $J = 11.7$, 4.2 Hz), 4.06 (s, 2H), 2.69 (ddt, 1H, $J = 17.7$, 11.4, 1.2 Hz), 2.55 (dd, 1H, $J = 17.7$, 4.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 152.9, 138.2, 129.0, 128.9, 126.2, 117.7, 78.9, 54.3, 33.4; HRMS calcd for $C_{12}H_{11}N_3O_2$ $(M)^+$ 229.0851, found 229.0853.

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Supporting Information Available: Details of all experimental procedures and analytical data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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