

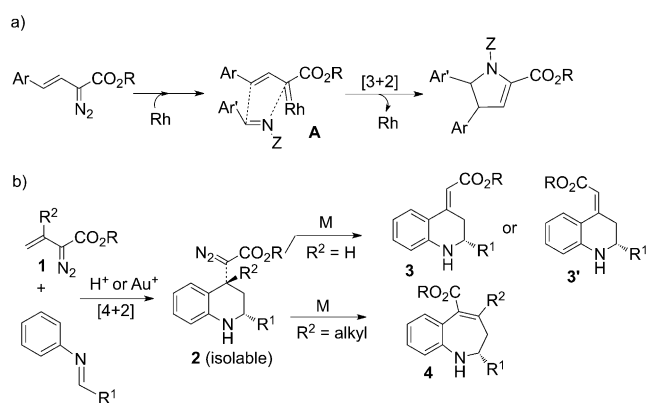
Synthetic Methods

Development of a Povarov Reaction/Carbene Generation Sequence for Alkenyldiazocarbonyl Compounds**

Appaso Mahadev Jadhav, Vinayak Vishnu Pagar, and Rai-Shung Liu*

Metal-catalyzed cycloadditions of alkenyldiazo reagents are useful tools to access carbo- and heterocycles.^[1] These diazo compounds are chemically sensitive toward both Brønsted or Lewis acids. Their reported cycloadditions rely heavily on the formation of metal carbenes to initiate regio- and stereo-selective [3+*n*] cycloadditions (*n* = 2–4) with suitable dipolarophiles.^[2–4] A noncarbene route was postulated for a few copper-catalyzed cycloadditions of these diazo species, but they resulted in complete diazo decomposition.^[3a,4a,5]

Doyle and co-workers reported^[4a] a [3+2] cycloaddition of the alkenylrhodium carbene **A** with imines to give dihydropyrroles (Scheme 1a). We proposed a cycloaddition



Scheme 1. Cycloaddition routes for alkenyldiazo species. a) Metal carbene routes (current pathways).^[2–4] b) Cycloaddition route (this work).

route with analogous reagents to secure their versatile diazo functionalities. Toward this objective, we developed an unprecedented cycloaddition route (Scheme 1b) involving an initial formal [4+2] cycloaddition (Povarov^[6,7] reaction) between the diazo species **1** and N-aryl imines to give isolable diazo-containing cycloadducts (**2**) stereoselectively. The subsequent formation of their metal carbenes allows efficient production of six- and seven-membered azacycles including

the tetrahydroquinoline derivatives **3** and **3'**, as well as the tetrahydro-1*H*-benzo[*b*]azepine species **4**.

Access to these frameworks are valuable for the preparation of several bioactive molecules including 2-phenyl-2,3-dihydroquinolone,^[8a] L-689,560,^[8b] torcetrapib,^[8c] martinellie acid,^[8d] OPC-31260,^[8e] OPC-51803,^[8f] and tetrapalone A (Figure 1).^[8g] Their specific biological functions have been well documented.^[8]

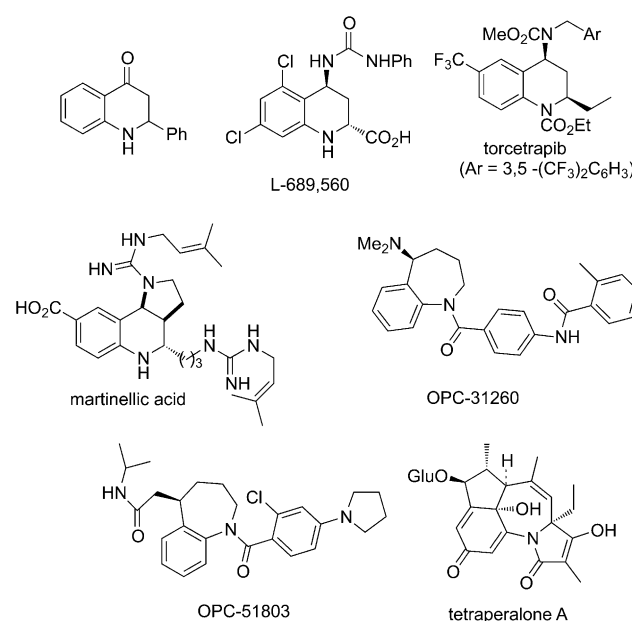


Figure 1. Accessible biologically active molecules.

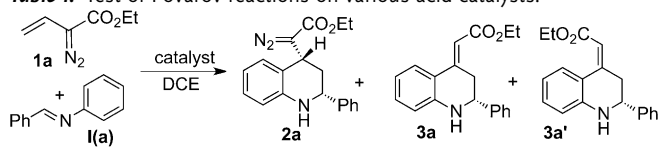
Shown in Table 1 are our efforts to realize a Povarov^[6,7] reaction between the *N*-benzylideneaniline [**I(a)**] and ethyl vinyl diazoacetate (**1a**) using various acid catalysts; the duration of reaction pertains to the complete consumption of **1a**. We selected **I(a)** as the target because of its great affinity toward metal coordination, possibly impeding diazo decomposition. As shown in entry 1, treatment of a 1,2-dichloroethane (DCE) solution of **1a** (1.0 equiv) and **I(a)** (1.1 equiv) with [Rh₂(OAc)₄] (2.5 mol %) at 28 °C (4 h) gave a complex mixture of products. Under the same reaction conditions, Cu(OTf)₂ (5 mol %, entry 2) gave the cycloadduct **2a** (18 %) together with the *E*- and *Z*-configured unsaturated esters **3a** (48 %) and **3a'** (27 %), respectively, and they were separable on a silica gel column. We sought to improve the chemoselectivity by using various gold catalysts (entries 3–5). [PPh₃AuCl]/AgNTf₂ gave the unsaturated esters **3a** and **3a'** in 55 and 30 % yields, respectively (entry 3). With [P(*t*Bu)₂(*o*-

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Table 1: Test of Povarov reactions on various acid catalysts.^[a]

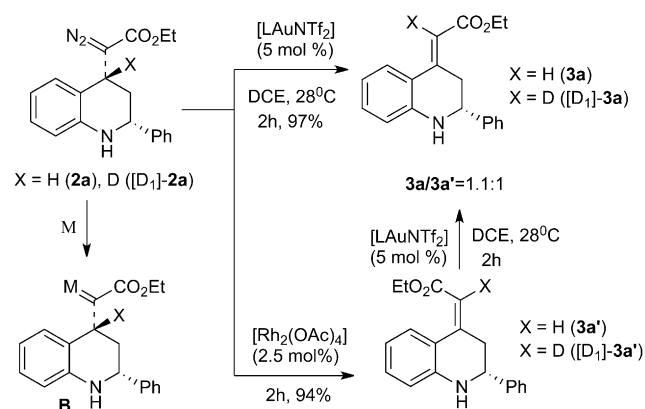


Entry	Catalyst (mol %)	T [°C]	t [h]	Yield [%] ^[b]		
				2a	3a	3a'
1	[Rh ₂ (OAc) ₄] (2.5)	28	4	—	—	— ^[c]
2	Cu(OTf) ₂ (5)	28	2	18	48	27
3	[PPh ₃ AuCl]/AgNTf ₂ (5)	28	2	—	55	30
4	[LAuCl]/AgNTf ₂ (5)	28	2	60	32	—
5	[LAuCl]/AgNTf ₂ (5)	60	4	—	84	—
6	[IPrAuCl]/AgNTf ₂ (5)	28	2	82	—	—
7	AgNTf ₂ (5)	28	2	—	—	—
8	HOTf (3)	28	0.2	95	—	—

[a] **1a** (1.0 equiv), **I(a)** (1.1 equiv), [**1a**] = 0.57 M. [b] Product yields are given for products isolated after purification using a silica gel column. [c] Complicated mixture of products. L = P(*t*Bu)₂(*o*-biphenyl), Tf = trifluoromethanesulfonyl.

biphenyl)AuNTf₂] (entry 4), we obtained the desired **2a** as the major product (60 %) in addition to **3a** (32 %). With this gold catalyst in hot DCE (60 °C, 4 h), we obtained **3a** in 84 % yield. To our pleasure, the use of the less acidic [IPrAuNTf₂] (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) allowed efficient production of **2a** exclusively (entry 6). In a control experiment, AgNTf₂ alone gave a complex mixture of products in DCE (28 °C). Particularly appealing is HOTf (3 mol %), which gave **2a** stereoselectively (d.r. > 20:1) with a yield of up to 95 % after a short reaction time (entry 8).^[7] We postulate that the tetrahydroquinoline framework in **2a** is slightly basic and protects the diazo group from HOTf decomposition. The stereochemistry of **2a** is supported by the ¹H NOE data. The structure of **3a** was confirmed by X-ray diffraction.^[9]

The diazo-containing cycloadduct **2a** can be used in the stereoselective syntheses of **3a** and **3a'** via the carbene intermediate **B** (Scheme 2). The treatment of **2a** with [P(*t*Bu)₂(*o*-biphenyl)AuNTf₂] in DCE (28 °C, 2 h) gave **3a** in 97 % yield, whereas [Rh₂(OAc)₄] (2.5 mol %) gave only **3a'** in 94 % yield under the same reaction conditions. With deuterated [D₁]-**2a** (X = D), the same Au and Rh catalysts delivered

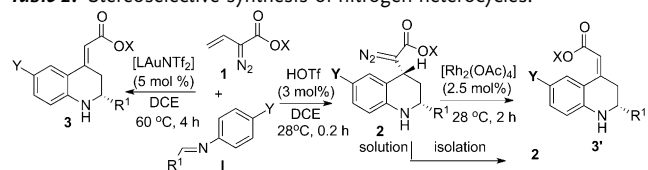


Scheme 2. Transformations into metal carbenes.

the *E*-configured ester [D₁]-**3a** and *Z*-configured ester [D₁]-**3a'**, respectively, with full deuterium content at their olefin positions. The treatment of **3a'** with [P(*t*Bu)₂(*o*-biphenyl)-AuNTf₂] in DCE (28 °C, 2 h) gave mixture of **3a** and **3a'** (1.1:1). We postulate that the 1,2-hydride shift proceeds stereoselectively for the Au and Rh carbenes **B**; the former favors *E*-alkene selectivity^[10] whereas the latter produces *Z* alkenes preferably.^[11]

We tested the reactions of the diazo reagents **1a–c** with various imines **I(a)–(i)** to generalize the stereoselective synthesis of the cycloadducts **2**, together with the *E*- and *Z*-esters **3** and **3'** (Table 2). We obtained the cycloadducts **2** and *E*-configured esters **3** directly from the starting reagents using

Table 2: Stereoselective synthesis of nitrogen heterocycles.



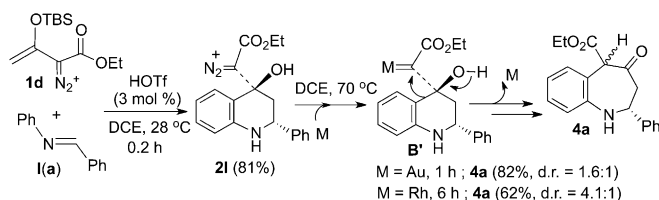
Entry	1 ^[a] (X)	I ^[b] (Y, R ¹)	Yield [%]		
			2 ^[c]	3 ^[d]	3' ^[e]
1	1a (Et)	I(b) (OMe, Ph)	2b : 83	3b : 77	3b' : 68
2	1a	I(c) (CF ₃ , Ph)	2c : 89	3c : 79	3c' : 72
3	1a	I(d) (Cl, Ph)	2d : 84	3d : 82	3d' : 67
4	1a	I(e) (H, 4-MeOC ₆ H ₄)	2e : 84	3e : 74	3e' : 73
5	1a	I(f) (H, 4-ClC ₆ H ₄)	2f : 89	3f : 75	3f' : 72
6	1a	I(g) (H, 2-furanyl)	2g : 86	3g : 76	3g' : 70
7	1a	I(h) (H, <i>n</i> Pr)	2h : 81	3h : 72	3h' : 60
8	1a	I(i) (H, CO ₂ Et)	2i : 84	3i : 74	3i' : 67
9	1b (<i>t</i> Bu)	I(a) (H, Ph)	2j : 89	3j : 86	3j' : 73
10	1c (Bn)	I(a)	2k : 84	3k : 85	3k' : 74

[a] **1** (1.0 equiv). [b] Imine (1.1 equiv), [substrate] = 0.57 M. [c] For reaction using HOTf. Yields are given for product isolated after purification using a silica gel column. [d] For reaction using [LAuNTf₂]. Yields are given for product isolated after purification using a silica gel column. [e] For reaction using H⁺/Rh. Yields are given for product isolated after purification using a silica gel column. L = P(*t*Bu)₂(*o*-biphenyl).

HOTf (3 mol %) and [P(*t*Bu)₂(*o*-biphenyl)AuNTf₂] (5 mol %) respectively, under the optimum reaction conditions detailed in entries 5 and 8 of Table 1. Production of the *Z*-configured esters **3'** relies on an initial treatment of the reagents with HOTf (3 mol %), and subsequent addition of [Rh₂(OAc)₄] (2.5 mol %) to the same DCE solution. The three reactions worked well for the imines **I(b)–(d)** bearing *para*-methoxy, *para*-trifluoromethyl, and *para*-chloro substituents, respectively, on their aniline moieties. The resulting products **2b–d**, **3b–d**, and **3b'–d'** were obtained with satisfactory yields (entries 1–3). For **I(e),(f)** bearing 4-MeOC₆H₄ and 4-ClC₆H₄, respectively, the corresponding products **2e,f**, **3e,f**, and **3e',f'** were obtained with yields greater than 72 % (entries 4 and 5). These catalytic reactions can be used for the imines **I(g)–(i)** bearing 2-furanyl, *n*-propyl, and ester groups, respectively, thus giving the desired compounds **2g–i**, **3g–i**, and **3g'–i'** in reasonable yields (entries 6–8). We tested the reactions on the α -diazo esters **1b,c**, thus producing the expected cycloadducts **2j,k** by using HOTf as the catalyst. We obtained the *E*- (**3j,k**)

and *Z*-configured (**3j'**, **k'**) esters using the Au and Rh catalysts, respectively (entries 9 and 10).

To expand the scope of the diazo substrates, we examined the HOTf-catalyzed cycloaddition of the β -substituted diazoester **1d** with **I(a)** in DCE (28 °C, 0.2 h), thus giving the desired cycloadduct **2l** (d.r. > 20:1) in 81 % yield (Scheme 3).



Scheme 3. Reactions of the 2-substituted alkenyldiazo species **1d**. TBS = *tert*-butyldimethylsilyl.

Interestingly, the treatment of the cycloadduct **2l** with $[P(tBu)_2(o\text{-biphenyl})AuNTf_2]$ in hot DCE (70 °C, 1 h) gave the seven-membered azacycle **4a** in 82 % yield, albeit with low diastereoselectivity (d.r. = 1.6:1). $[Rh_2(OAc)_4]$ gave the same azacycle with a better d.r. value (4.1:1), but a decreased yield (62 %).

These Povarov reactions are amenable to the β -substituted diazoesters **1e–j** using HOTf as a catalyst (3 mol %), and the resulting cycloadducts **2m–s** were produced with a diastereoselectivity of greater than 4:1 (Table 3). We also obtained the seven-membered azacycles **4b–h** in a one-pot operation involving treatment of the cycloadducts **2** in situ with $[P(tBu)_2(o\text{-biphenyl})AuNTf_2]$ (5 mol %) in DCE (28 °C, 1 h). For the methyl-substituted diazo species **1e**, cycloaddition with **I(a)** and **I(l)** gave the corresponding cycloadducts **2m** and **2n** stereoselectively (d.r. > 20:1), and the seven-membered azacycles **4b** and **4c** were obtained in 67–76 % yields (entries 1 and 2). The stereochemistry of **2m** was determined by X-ray diffraction.^[9] Excellent diastereoselectivity was also obtained for the cycloadducts **2o** and **2p**, which were derived from the diazo substrates **1f** and **1g**, respec-

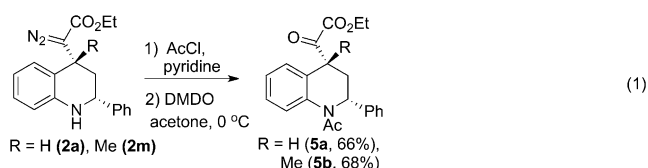
Table 3: [4+2] cycloadditions and ring expansions.

Entry	1 ^[a] (R^2)	I ^[b]	2 ^[c]	Yield [%]	4 ^[d]
1	1e (Me)	I(a)	2m : 82 (d.r. > 20:1)		4b : 76
2	1e	I(l)	2n : 72 (d.r. > 20:1)		4c : 67
3	1f (Cy)	I(a)	2o : 80 (d.r. > 20:1)		4d : 75
4	1g (Bn)	I(a)	2p : 83 (d.r. > 20:1)		4e : 76
5	1h (<i>n</i> Bu)	I(a)	2q : 86 (d.r. = 4:1)		4f : 73
6	1i (3-methylbutyl)	I(a)	2r : 88 (d.r. = 4.4:1)		4g : 67
7	1j (3-methyl-3-butenyl)	I(a)	2s : 88 (d.r. = 4.4:1)		4h : 82

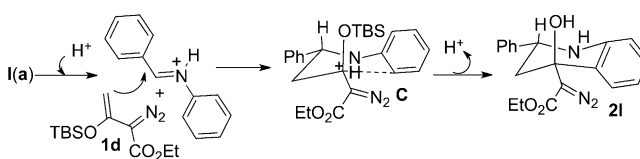
[a] **1** (1.0 equiv). [b] Imine (1.1 equiv), [substrate] = 0.57 M. [c] For reaction using HOTf. Yields are given for product isolated after purification using a silica gel column. [d] For reaction using H^+/Au . Yields are given for product isolated after purification using a silica gel column.

tively (entries 3 and 4). The seven-membered azacycles **4d** and **4e** were also produced in good yields (75–76 %). For the remaining diazoesters **1h–j** (entries 5–7), we obtained two diastereomeric products (d.r. = 4:1–4.4:1) for compounds **2q** ($R^2 = n\text{-butyl}$), **2r**, and **2s** which were separable on a silica gel column. Gold carbene generation in situ for these isomeric mixtures gave the seven-membered azacycles **4f–h** in 67–82 % yields. The molecular structure of **4f** was confirmed by X-ray diffraction.^[9]

Equation (1) highlights the functionalization of the diazo group of **2a** and **2m**. Dimethyldioxirane (DMDO)^[12] oxidation of the acetyl derivatives of these two azacycles in cold THF (0 °C) gave the α -keto esters **5a** and **5b** in 66 and 68 %, yields respectively.



Scheme 4 depicts a plausible path to rationalize the stereochemical course of the resulting cycloadducts, a path involving the initial reaction of HOTf with **1d**.^[7] According to

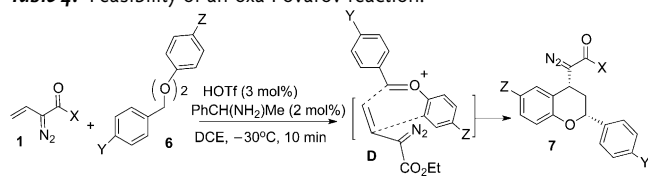


Scheme 4. A plausible model for stereochemistry.

a preferable stepwise mechanism,^[6b] the formation of an initial C–C bond generates the chairlike transition-state **C** which has the small hydrogen and OTBS substituents in axial positions, thus generating the cycloadduct **2l** with the observed stereochemistry. For other less polarized alkenyldiazo species, including **1a–c** and **1e–j**, the cycloadditions likely proceed in a concerted endo fashion.^[6c–e]

Inspired by our success in the preceding Povarov reactions catalyzed with triflic acid, we investigated accessing diazo-containing oxacycles by an unprecedented oxa-Povarov reaction via the postulated benzylidene(phenyl)oxonium **D** (Table 4). Treatment of an equimolar mixture of ethyl vinyl-diazoacetate (**1a**; 0.57 M) and (diphenoxy)methylbenzene (**6a**) with HOTf (3 mol %) in cold DCE (–30 °C, 10 min) led to the rapid decomposition of **6a** into phenol and benzaldehyde. After some optimization, we found that the presence of α -phenylethylamine (2 mol %) in this triflic acid system delivered the desired diazo-containing oxacycle **7a** as a single diastereomer in 75 % yield (entry 1). The role of this primary amine is to decrease the acidity of the reaction medium. The stereochemistry of **7a** was confirmed by ¹H NOE and NMR data. This oxa-Povarov reaction worked well for the acetals **6b–e** to give the desired oxacycles **7b–**

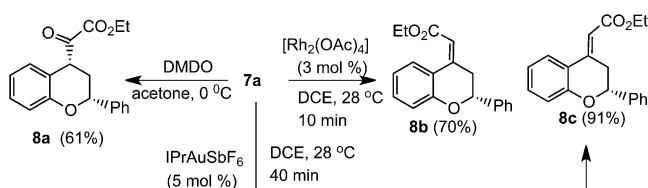
Table 4: Feasibility of an oxa-Povarov reaction.



Entry	1 ^[a] (X)	6 ^[b] (Y, Z)	7: Yield [%] ^[c]
1	1a (OEt)	6a (H, H)	7a: 75
2	1a	6b (H, OMe)	7b: 77
3	1a	6c (H, Cl)	7c: 72
4	1a	6d (Me, H)	7d: 69
5	1a	6e (Cl, H)	7e: 56
6	1b (OtBu)	6a	7f: 74
7	1k (Ph)	6a	7g: 76
8	1l (nPr)	6a	7h: 68

[a] 1a (0.57 M). [b] Acetal (1.1 equiv). [c] Yields are given for product isolated after purification using a silica gel column.

e stereoselectively (entries 2–5). The generality of this unprecedented cycloaddition is again manifested with its applicability to various alkenyldiazo compounds (**1b,k** and **1l**), thus giving the cycloadducts **7f–h** in 68–76% yields (entries 6–8). Using our methods discussed above, the compound **7a** was converted into the dicarbonyl species **8a**, and the *Z*- and *E*-configured esters **8b** and **8c**, respectively, with 61–91% yields (Scheme 5).



Scheme 5. Chemical functionalization of diazo compound **7a**.

Reported catalytic cycloadditions on alkenyldiazo reagents are inevitably accompanied by a diazo decomposition. We have developed a HOTf-catalyzed Povarov reaction for these diazo species to give diazo-containing cycloadducts stereoselectively. The resulting cycloadducts provide access to various six- and seven-membered azacycles, by either the generation of metal carbenes or the functionalization of the diazo group. Our preliminary results also reveal the feasibility of oxa-Povarov reactions, which are unknown in the literature. Future work will be focused on the asymmetric versions of these new reactions.

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- [9] CCDC 905645 (**2m**), CCDC 905646 (**3a**), and CCDC 905647 (**4f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Full details are provided in the Supporting Information.
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