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Chemoselectivity Switching in the Rhodium-Catalyzed Reactions of 4-Substituted-1-sulfonyl-1,2,3-triazoles with Allenols: Noticeable Differences between 4-Acyl- and 4-Aryl-Triazoles

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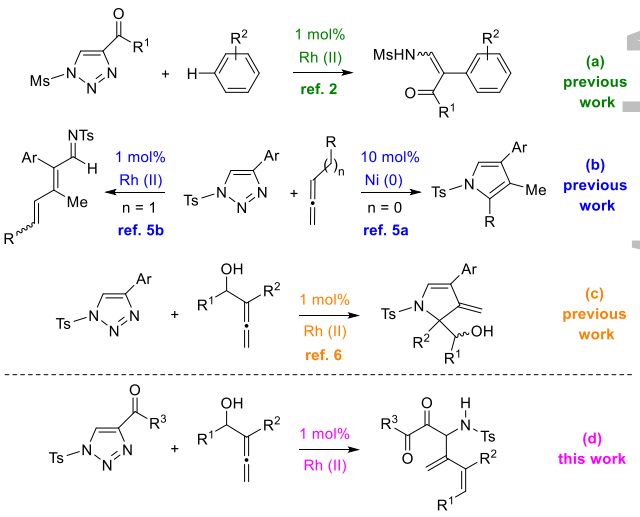
Abstract. Tunable chemoselectivity (*O*- versus *C*-attack) in the rhodium-catalyzed reactions of allenols with 4-substituted-1-sulfonyl-1,2,3-triazoles has been achieved through the replacement of the 4-aryl substituent by a 4-acetyl moiety.

Keywords: allenes; heterocycles; homogeneous catalysis; ketones; rhodium

1-Sulfonyl-1,2,3-triazole chemistry has merged as an excellent approach for the functionalization of unsaturated moieties and the construction of heterocyclic frameworks.[1] This strategy has been built through the use of 4-aryl-1-sulfonyl-1,2,3-triazoles as the source of α-imino metal-carbenes, which may be viewed as donor/acceptor carbenoids. At the end of 2017, Miura and Murakami unveiled the chemistry of acceptor/acceptor carbenoids, which were generated from 4-acyl-1-mesyl-1,2,3-triazoles, for the functionalization of aromatic C(sp^2)–H bonds (Scheme 1a).[2] Markedly contrasting results were obtained in comparison with donor/acceptor carbenoids.[3] On the other hand, dramatic growth in the synthetic utility of allenes has been noticed in the last decade.[4] Recently, Miura and Murakami have described the metal-catalyzed reaction of 4-aryl-1-tosyl-1,2,3-triazoles with simple allenes to form pyrroles or α,β,γ,δ-unsaturated imines (Scheme 1b),[5] while we reported the transannulation reaction of 4-aryl-1-tosyl-1,2,3-triazoles with allenols to give 2-pyrrolines (Scheme 1c).[6] Based on these results, we believed that allenols might also act as an *O*-containing nucleophiles able to trap acceptor/acceptor carbenoids. Herein, we describe an unprecedented *O*-attack/reorganization sequence between allenols and 4-acyl-1-tosyl-1,2,3-triazoles leading to 3-methylene-5,6-dioxo-hept-1-enyl-4-amine derivatives (Scheme 1d).



Scheme 1. Mode of reaction between 1-sulfonyl-1,2,3-triazoles and allenes: previous work and the present study.

Allenol **1a** was selected as model substrate. Initial experiments were performed through the reaction of **1a** with the previously described 1-[1-(methylsulfonyl)-1*H*-1,2,3-triazol-4-yl]ethan-1-one, but complex reaction mixtures were obtained. Nicely, 1-(1-tosyl-1*H*-1,2,3-triazol-4-yl)ethan-1-one **2**, which was easily prepared following the reported procedure for its methylsulfonyl counterpart,[2] was shown to be a promising reaction partner. The use of $Rh_2(Oct)_4$ as

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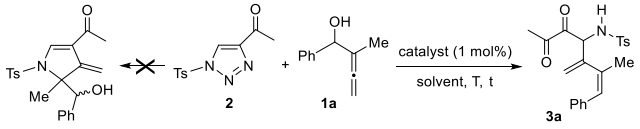
catalyst (1 mol%) and chloroform as solvent allowed the coupling between **1a** and **2** to progress at 65 °C and gave a reasonable 58% yield of product **3a** (Table 1, entry 3). The efficiency of the process could not be improved by moving to different metallic salts, solvents or reaction conditions. Adduct **3a** is a polydecorated molecule[7] bearing a 1,2-diketone functionality, a sulfonamide group, and a 1,3-diene moiety, which was obtained as single *Z* isomer at the newly formed double bond. Noteworthy, replacing an aryl group by an acetyl group in the metal-catalyzed reactions of 4-substituted-1-sulfonyl-1,2,3-triazoles with allenols **1** dramatically provokes a chemoselectivity switch (*O*- versus *C*-attack).[8]

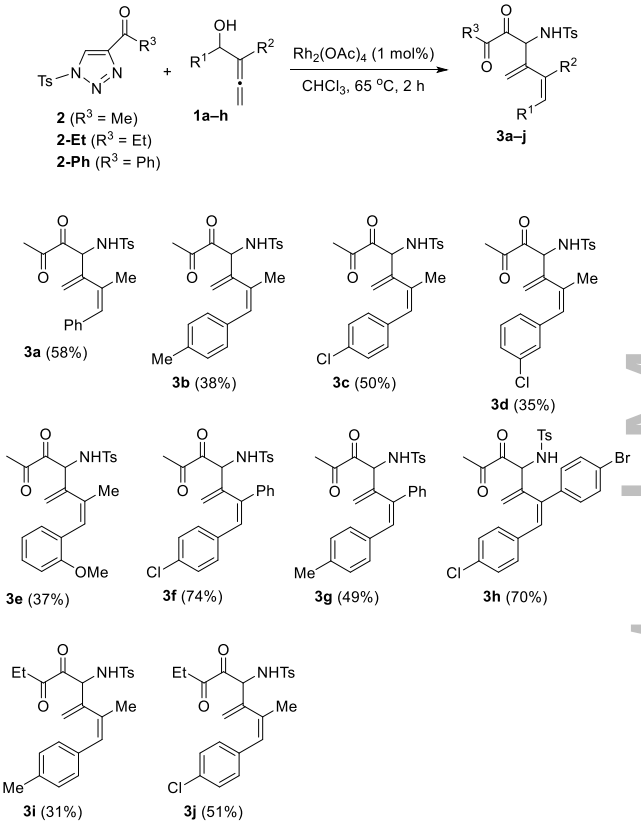
Table 1. Optimization of reaction conditions for the metal-catalyzed coupling of allenol **1a** with acyl-triazole **2**.[a], [b], [c]



Entry	Catalyst	Solvent	T (°C)	Time (h)	Yield (%)[d]
1	$Rh_2(OAc)$	$CHCl_3$	65	2	**3a** (17)
2	$Rh_2(Esp)_2$	$CHCl_3$	65	2	**3a** (30)
3	$Rh_2(Oct)_4$	$CHCl_3$	65	2	**3a** (58)
4	$Cu(OTf)_2$	toluene	70	3	–
5	$AgNTf_2$	toluene	70	4	–
6	$Rh_2(Oct)_4$	$CHCl_3$	20	24	**3a** (14)
7	$Rh_2(Oct)_4$	$CHCl_3$	40	6	**3a** (35)
8	$Rh_2(Oct)_4$	$CHCl_3$	65	3	**3a** (49)
9	$Rh_2(Oct)_4$	1,2-DCE	70	2	**3a** (45)
10	$Rh_2(Oct)_4$	toluene	70	8	**3a** (18)

[a] Reactions were carried out using **1a** (0.2 mmol), **2** (0.4 mmol), and the catalyst (0.002 mmol) in the corresponding solvent (0.15 M).
[b] OAc = acetate; Esp = (α,α,α′,α′-tetramethyl-1,3-benzenedipropionate); Oct = octanoate; 1,2-DCE = 1,2-dichloroethane.
[c] 1,2-DCE = 1,2-dichloroethane.
[d] Yield of pure, isolated product with correct analytical and spectral data.

Having in hand the optimized conditions, we then investigated the scope and generality of the transformation by modifying the substitution on the allenol substrate **1**. The observed results are depicted in Scheme 2. Almost all reactions progressed smoothly to provide the desired products **3a–h** in reasonable yields. Various substituents on the aromatic ring (R^1) of different electronic demand such as activating (methyl and methoxy) and weakly deactivating (chlorine) were well accommodated. Different substitution patterns were also tolerated, because when a substituent was placed either at the *ortho*, *meta*, and *para* positions of the phenyl ring, the corresponding products were formed in fair yields as single *Z* isomers. When the methyl group (R^2) of **1a** was replaced by an aryl group such as phenyl and 4-BrC_6H_4, the required polyfunctionalyzed adducts **3f–h** were efficiently obtained, without altering the total stereoselectivity. The single crystal XRD structure of adduct **3a** unambiguously confirmed its polyfunctional nature and stereochemistry (Figure 1).[9] Notably, the methylidene moiety survived under the reactions conditions and no isomerization towards the fully conjugated system occurred. Next, the scope of the reaction with respect to the 4-acyl-triazole reagent was explored using 1-(1-tosyl-1*H*-1,2,3-triazol-4-yl)propan-1-one **2-Et** and phenyl(1-tosyl-1*H*-1,2,3-triazol-4-yl)methanone **2-Ph**. Interestingly, triazole derivative **2-Et** was as rewarding as triazole **2**. As depicted in Scheme 2, the reactions of **2-Et** with allenols **1b** and **1c** worked well for the obtention of molecules of type **3**. Unfortunately, the Rh-catalyzed treatment of triazole **2-Ph** with allenols **1b** and **1c** resulted in complicated reaction mixtures and was non-productive for the preparation of adducts **3**.



Scheme 2. Synthesis of polydecorated compounds **3a–j**.

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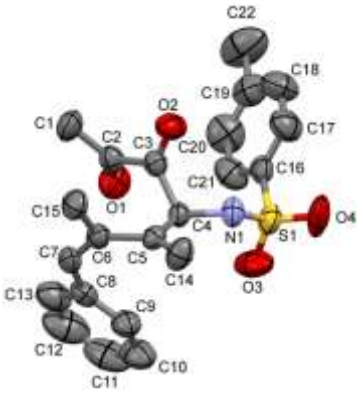
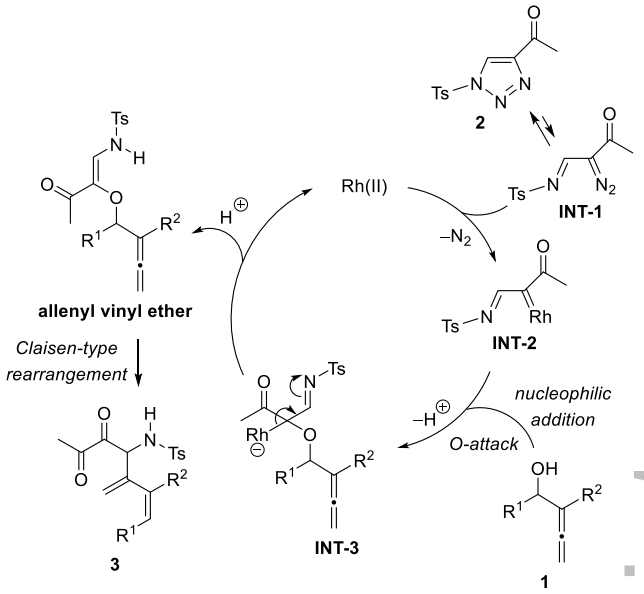


Figure 1. ORTEP drawing of (*Z*)-4-methyl-*N*-(2-methyl-3-methylene-5,6-dioxo-1-phenylhept-1-en-4-yl)benzenesulfonamide **3a**. Thermal ellipsoids shown at 50% probability.

A possible pathway for the rhodium-catalysed generation of polyfunctional compounds **3** is outlined in Scheme 3. Initially, the formation of an α-imino Rh(II)-carbenoid **INT-2** may be involved. **INT-2** should be formed by reaction of the $Rh_2(Oct)_4$ catalyst with 4-acetyl-1-tosyl-1,2,3-triazole **2** through its α-imino tautomer **INT-1**, with concurrent dinitrogen release, according to the general reaction mechanism proposed by Miura and Murakami.[2] Next, nucleophilic addition of the hydroxyl functionality of allenes **1** to rhodacarbenoid **INT-2** followed by deprotonation could lead to species **INT-3**. This path must be driven by the highly electrophilic character of the acceptor/acceptor rhodacarbenoid **INT-2**.[10] Species **INT-3** evolves into an allenyl vinyl ether intermediate after regeneration of the rhodium catalyst and concurrent protonation (Scheme 3). This allenyl vinyl ether intermediate may then undergo an allenic Claisen rearrangement to form 3-methylene-5,6-dioxo-hept-1-enyl-4-amine derivatives **3** (Scheme 3), which resembles that proposed by Miura and Murakami.[7b]



Scheme 3. Mechanistic explanation for the Rh(II)-catalyzed synthesis of polyfunctional compounds **3**.

Density Functional Theory (DFT) calculations at the dispersion-corrected PCM($CHCl_3$)-B3LYP-D3/def2-SVP level were carried out to gain more insight into mechanism involved in the transformation.[11] To this end, the reaction between the experimentally used substrates allenol **1a** and the Rh(II)-carbene **INT-2** was explored.

As shown in Figure 2, which gathers the corresponding free energies (computed at 298 K), the process begins with the formation of complex **INT-4**, where both reagents are linked by a hydrogen bond established between the OH group of the allenol and the nitrogen atom of the Rh(II)-carbenoid. **INT-4** is then readily transformed into **INT-5** by means of the insertion of the OH into the carbene carbon atom. This process is essentially barrierless, which is not surprising considering the highly exergonicity computed for this reaction step (ΔG_R = –45.9 kcal/mol). Indeed, relaxed scans from **INT-4** at different $C_{carbene}\cdots OH$ confirms the barrierless nature of this insertion reaction (see Figure 3). Release of the weakly bonded dirhodium catalyst in **INT-5** leads to zwitterion **INT-6** in an endergonic transformation (ΔG_R = 13.4 kcal/mol), which is compatible with the temperature required experimentally.[12] As a result of the abstraction of a proton from the OH-moeity by the imine, (*Z*)-allenyl vinyl ether **INT-6** is stereoselectively formed. Finally, **INT-6** can be directly converted into the observed dioxo-hept-1-enyl-4-amine **3a** through the transition state **TS** in a highly exergonic transformation (ΔG_R = –40.6 kcal/mol) and with a relatively low activation barrier of 15.2 kcal/mol. As depicted in Figure 2, this saddle-point is associated with the simultaneous C–O bond rupture and formation of the new C–C bond leading to the observed *Z*-dioxo-amine in a Claisen type [3,3]-sigmatropic rearrangement. Therefore, our calculations are fully consistent with our initial

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proposal described above (Scheme 3) based on the proposal by Miura and Murakami.[7b]

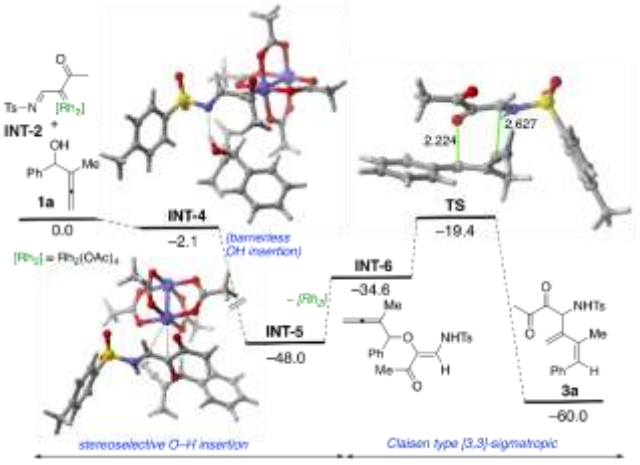

Figure 2. Computed profile for the transformation involving allenol **1a** and Rh(II)-carbene **INT-2**. Bond lengths and relative free energies (ΔG_{298}, computed at 298 K) are given in angstroms and kcal/mol, respectively. All data have been computed at the PCM($CHCl_3$)-B3LYP-D3/def2-SVP level.

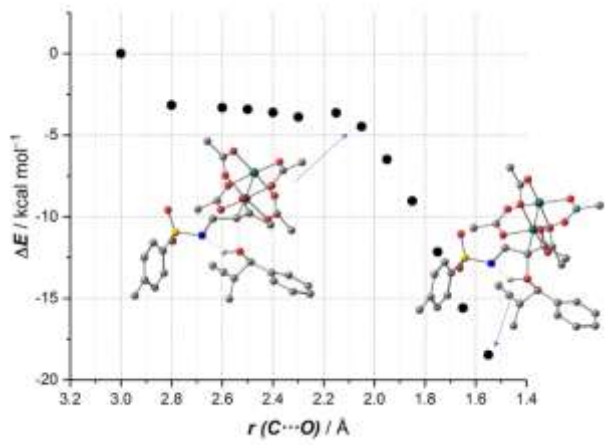

Figure 3. Relaxed scans modifying the key C···O distance for the **INT-4→INT-5** transformation. All data have been computed at the PCM($CHCl_3$)-B3LYP-D3/def2-SVP level.

In conclusion, we have developed a divergent outcome transformation of the rhodium-catalyzed reactions of allenols with 4-substituted-1-sulfonyl-1,2,3-triazoles, which has been accomplished through the replacement of the 4-aryl substituent by a 4-acetyl moiety. DFT calculations support the involvement of a Rh(II)-carbenoid produced from the reaction of the initial triazole and the dirhodium catalyst. This species is transformed, by reaction with the allenol, into an (*Z*)-allenyl vinyl ether intermediate which directly evolves into the observed reaction product through a Claisen type [3,3]-sigmatropic rearrangement.

Experimental Section

General methods: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance-300 or Bruker Avance AMX-700 spectrometers. NMR spectra were recorded in $CDCl_3$ or C_6D_6, except otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), $CDCl_3$ (^{13}C, 76.9 ppm) and C_6D_6 (^{13}C, 128.4 ppm). Low and high resolution mass spectra were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electrospray mode (ES) unless otherwise stated. IR spectra were recorded on a Bruker Tensor 27 spectrometer. X-Ray crystallographic data were collected on a Bruker Smart CCD difractomer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 Kv and 35 mA with an exposure of 30.18 s in ω. All commercially available compounds were used without further purification.

General procedure for the rhodium-catalyzed reactions of allenols 1a–h with acyl-triazole 2. Synthesis of 3-methylene-5,6-dioxo-hept-1-enyl-4-amine derivatives 3a–h.

$Rh_2(Oct)_4$ (2.3 mg, 0.003 mmol) and acyl-triazole **2** (159 mg, 0.6 mmol) were added to a stirred solution of the appropriate allenol **1** (0.3 mmol) in chloroform (2.0 mL). The reaction mixture was stirred at 65 ºC for 2 h, allowed to cool to rt, and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate (8:1) gave analytically pure compounds **3**. Spectroscopic and analytical data for compounds **3** follow.[13]

(*Z*)-4-Methyl-*N*-(2-methyl-3-methylene-5,6-dioxo-1-phenylhept-1-en-4-yl)benzenesulfonamide 3a. From 68 mg (0.427 mmol) of allenol **1a**, and after chromatography of the residue, gave compound **3a** (78 mg, 58%) as a green solid; mp 103–105 ºC; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.65 (d, 2H, *J* = 8.3 Hz, ArH), 7.23 (d, 2H, *J* = 7.3 Hz, ArH), 7.09 (t, 2H, *J* = 10.3 Hz, ArH), 6.98 (t, 1H, *J* = 7.3 Hz, ArH), 6.64 (d, 2H, *J* = 8.0 Hz, ArH), 6.10 (s, 1H, =CH), 5.72 (d, 1H, *J* = 9.8 Hz, CH-N*H*), 5.59 (d, 1H, *J* = 9.8 Hz, C*H*-NH), 5.03 (d, 1H, *J* = 1.2 Hz, C*H*H), 4.91 (s, 1H, CH*H*), 1.81 (d, 3H, *J* = 1.4 Hz, Me), 1.78 (s, 3H, Me), 1.64 (s, 3H, Ar); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 195.5 (C=O), 194.3 (C=O), 143.4, 143.2, 137.6, 137.1, 135.8, 129.7 (Ar, 2CH), 129.6 (=CH), 128.9 (Ar, 2CH), 128.5 (Ar, 2CH), 127,7 (Ar, 2CH), 127.3 (Ar, CH), 119.1 (=CH_2), 58.08 (CH-NH), 26.08 (Me), 23.4 (Me), 21.1 (Me); IR (C_6H_6, cm^{-1}): ν 3276, 1718, 1596, 1159; HRMS (ES): calcd for $C_{22}H_{24}NO_4S$ [*M* + H]$^+$: 398.14206; found: 398.14165.

(*Z*)-4-Methyl-*N*-(2-methyl-3-methylene-5,6-dioxo-1-(*p*-tolyl)hept-1-en-4-yl)benzenesulfonamide 3b. From 50 mg (0.315 mmol) of allenol **1b**, and after chromatography of the residue, gave compound **3b** (49 mg, 38%) as a yellow oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.67 (d, 2H, *J* = 8.3 Hz, ArH), 7.20 (s, 2H, ArH), 6.93 (d, 2H, *J* = 7.9 Hz, ArH), 6.65 (d, 2H, *J* = 8.0 Hz, ArH), 6.10 (s, 1H, =CH), 5.77 (d, 1H, *J* = 9.7 Hz, CH-N*H*), 5.65 (d, 1H, *J* = 9.8 Hz, C*H*-NH), 5.10 (d,1H, *J* = 1.2 Hz, C*H*H), 4.96 (s, 1H, CH*H*), 2.06 (s, 3H, Me), 1.81 (d, 3H, *J* = 1.4 Hz, Me), 1.79 (s, 3H, Me), 1.66 (s, 3H, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 195.5 (C=O), 194.4 (C=O), 143.4, 143.3, 137.7, 136.9, 134.9, 134.3,

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129.7 (Ar, 2CH), 129.6 (Ar, 2CH), 129.3 (=CH), 128.9 (Ar, 2CH), 127,4 (Ar. 2CH) 118.9 (=CH_2), 58.1 (CH-NH), 26.2 (Me), 23.4 (Me), 21.1 (Me), 21.1 (Me); IR (C_6H_6, cm^{-1}): ν 3272, 1718, 1600, 1160; HRMS (ES): calcd for $C_{23}H_{26}NO_4S$ [*M* + H]$^+$: 412.15771; found: 412.15969.

(*Z*)-*N*-(1-(4-Chlorophenyl)-2-methyl-3-methylene-5,6-dioxohept-1-en-4-yl)-4-methylbenzenesulfonamide 3c. From 72 mg (0.370 mmol) of allenol **1c**, and after chromatography of the residue, gave compound **3c** (78 mg, 50%) as a green solid; mp 106–108 ºC; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.67 (d, 2H, *J* = 8.3 Hz, ArH), 7.00 (m, 4H, ArH), 6.69 (d, 2H, *J* = 8.0 Hz, ArH), 5.94 (d, 1H, *J* = 1.0 Hz, =CH), 5.88 (d, 1H, *J* = 9.8 Hz, CH-N*H*), 5.61 (d, 1H, *J* = 9.8 Hz, C*H*-NH), 5.01 (d, 1H, *J* = 1.2 Hz, C*H*H), 4.85 (s, 1H, CH*H*), 1.84 (s, 3H, Me), 1.79 (d, 3H, *J* = 1.5 Hz, Me), 1.71 (s, 3H, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 195.6 (C=O), 194.3 (C=O), 143.6, 142.9, 137.3, 136.5, 135.5, 133.0, 130.2 (Ar, 2CH), 129.8 (Ar, 2CH), 128.7 (Ar, 2CH), 128.3 (=CH), 127.7 (Ar, 2CH), 119.1 (=CH_2), 57.9 (CH-NH), 26.0 (Me), 23.5 (Me), 21.1 (Me); IR (C_6H_6, cm^{-1}): ν 3276, 1717, 1595, 1159; HRMS (ES): calcd for $C_{22}H_{23}ClNO_4S$ [*M* + H]$^+$: 432.10308; found: 432.10452.

(*Z*)-*N*-(1-(3-Chlorophenyl)-2-methyl-3-methylene-5,6-dioxohept-1-en-4-yl)-4-methylbenzenesulfonamide 3d. From 78 mg (0.40 mmol) of allenol **1d**, and after chromatography of the residue, gave compound **3d** (58 mg, 35%) as a green oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.60 (d, 2H, *J* = 8.3 Hz, ArH), 7.17 (s, 1H, ArH), 7.02 (d, 1H, *J* = 7.7 Hz, ArH), 6.94 (d, 1H, *J* = 8.9 Hz, ArH), 6.80 (t, 1H, *J* = 7.8 Hz, ArH), 6.64 (d, 2H, *J* = 8.0 Hz, ArH), 5.89 (s, 1H, =CH), 5.58 (d, 1H, *J* = 10.0 Hz, CH-N*H*), 5.36 (d, 1H, *J* = 9.9 Hz, C*H*-NH), 4.85 (d, 1H, *J* = 1.2 Hz, CH*H*), 4.78 (s, 1H, CH*H*), 1.80 (s, 3H, Me), 1.77 (d, *J* = 1.5 Hz, 3H, Me), 1.68 (s, 3H, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 195.5 (C=O), 194.0 (C=O), 143.5, 142.8, 139.0, 137.6, 137.5, 134.4, 129.8 (Ar, 2CH), 129.0 (Ar, CH), 128.1 (Ar, CH), 127.8 (Ar, CH), 127.7 (Ar, CH), 127.3 (Ar, 2CH), 126.9 (Ar, CH), 119.4 (=CH_2), 58.0 (CH-NH), 25.8 (Me), 23.4 (Me), 21.1 (Me); IR (C_6H_6, cm^{-1}): ν 3273, 1718, 1596, 1160; HRMS (ES): calcd for $C_{22}H_{26}ClN_2O_4S$ [*M* + NH_4]$^+$: 449.12963; found: 449.13153.

(*Z*)-*N*-(1-(2-Methoxyphenyl)-2-methyl-3-methylene-5,6-dioxohept-1-en-4-yl)-4-methylbenzenesulfonamide 3e. From 72 mg (0.378 mmol) of allenol **1e**, and after chromatography of the residue, gave compound **3e** (61 mg, 37%) as a green oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.65 (d, 2H, *J* = 8.3 Hz, ArH), 7.32 (dd, 1H, *J* = 7.5, 1.1 Hz, ArH), 7.01 (t, 1H, *J* = 12.5 Hz, ArH), 6.80 (t, 1H, *J* = 7.4 Hz, ArH), 6.65 (d, 2H, *J* = 8.0 Hz, ArH), 6.50 (m, 2H, ArH + =CH), 5.64 (q, 2H, *J* = 4.3 Hz, C*H*-N*H*), 4.97 (s, 1H, C*H*H), 4.93 (s, 1H, CH*H*), 3.41 (s, 3H, OMe), 1.78 (s, 3H, Me), 1.77 (d, 3H, *J* = 1.5 Hz, Me), 1.73 (s, 3H, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 195.8 (C=O), 194.4 (C=O), 157.2, 143.2, 143.1, 137.9, 136.1, 130.4 (Ar, CH), 129.7 (Ar, 2CH), 128.8 (=CH), 127.3 (Ar, 2CH), 126.5, 125.8 (Ar, CH), 120.7 (Ar, CH), 119.2 (=CH_2), 110.9 (Ar, CH), 58.2 (CH-NH), 55.0 (OMe), 25.3 (Me), 23.5 (Me), 21.1 (Me); IR (C_6H_6, cm^{-1}): ν 3270, 1718, 1597, 1160; HRMS (ES): calcd for $C_{23}H_{26}NO_5S$ [*M* + H]$^+$: 428.15262; found: 428.15404.

(*Z*)-*N*-(1-(4-Chlorophenyl)-3-methylene-5,6-dioxo-2-phenylhept-1-en-4-yl)-4-methylbenzenesulfonamide 3f. From 60 mg (0.234 mmol) of allenol **1f**, and after chromatography of the residue, gave compound **3f** (85 mg, 74%) as a yellow oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.58 (d, 2H, *J* = 8.3 Hz, ArH), 7.23 (d, 2H, *J* = 8.5 Hz, ArH), 7.09 (m, 4H, ArH), 7.01 (m, 3H), 6.61 (d, 2H, *J* = 8.0 Hz, ArH), 6.45 (s, 1H, =CH), 5.78 (d, 1H, *J* = 9.8 Hz, CH-N*H*), 5.69 (d, 1H, *J* = 9.8 Hz, C*H*-NH), 5.46 (d, 1H, *J* = 1.2 Hz, C*H*H), 5.05 (s, 1H, CH*H*), 1.81 (s, 3H, Me), 1.51 (s, 3H, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 194.8 (C=O), 194.4 (C=O), 143.5, 140.4, 140.1, 139.9, 137.3, 135.1, 133.8, 130.9 (Ar, 2CH), 130.5 (Ar, 2CH), 129.8 (Ar, 2CH), 128.9 (Ar, 2CH), 128,1 (Ar, CH), 128.0 (=CH), 127.7 (Ar, 2CH), 127.4 (Ar, 2CH),121.6 (=CH_2), 58.9 (CH-NH), 23.1 (Me), 21.1 (Me); IR (C_6H_6, cm^{-1}): ν 3263, 1719, 1596, 1159; HRMS (ES): calcd for $C_{27}H_{28}ClN_2O_4S$ [*M* + NH_4]$^+$: 511.14528; found: 511.14537.

(*Z*)-4-Methyl-*N*-(3-methylene-5,6-dioxo-2-phenyl-1-(*p*-tolyl)hept-1-en-4-yl)benzenesulfonamide 3g. From 66 mg (0.279 mmol) of allenol **1g**, and after chromatography of the residue, gave compound **3g** (64 mg, 49%) as a yellow oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.58 (d, 2H. *J* = 8.2 Hz, ArH), 7.44 (d, 2H, *J* = 8.1 Hz, ArH), 7.19 (s, 1H, ArH), 7.02 (dd, 6H, *J* = 9.5, 7.9 Hz, ArH), 6.66 (s, 1H, =CH), 6.58 (d, 2H, *J* = 8.1 Hz, ArH), 5.82 (d, 1H, *J* = 9.8 Hz, CH-N*H*), 5.59 (d, 1H, *J* = 9.8 Hz, C*H*-NH), 5.52 (d, 1H, *J* = 1.1 Hz, C*H*H), 5.17 (s, 1H, CH*H*), 2.09 (s, 3H, Me), 1.77 (s, 3H, Me), 1.50 (s, 3H, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 194.8 (C=O), 194.7 (C=O), 143.2, 140.7, 140.5, 138.4, 137.9, 137.5, 133.8, 131.9 (Ar, 2CH), 129.7 (Ar, 2CH), 129.6 (Ar, 2CH), 129.5 (Ar, 2CH), 128.8 (=CH), 128.3 (Ar, CH), 127.7 (Ar, 2CH), 127.6 (Ar, 2CH), 121.4 (=CH_2), 59.2 (CH-NH), 23.1 (Me), 21.2 (Me), 21.0 (Me); IR (C_6H_6, cm^{-1}): ν 3279, 1718, 1598, 1159; HRMS (ES): calcd for $C_{28}H_{31}N_2O_4S$ [*M* + NH_4]$^+$: 491.19990; found: 491.19980.

(*Z*)-*N*-(2-(4-Bromophenyl)-1-(4-chlorophenyl)-3-methylene-5,6-dioxohept-1-en-4-yl)-4-methylbenzenesulfonamide 3h. From 64 mg (0.19 mmol) of allenol **1h**, and after chromatography of the residue, gave compound **3h** (69 mg, 70%) as a yellow oil; ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC) δ: 7.54 (d, 2H, *J* = 8.3 Hz, ArH), 7.19 (dd, 4H, *J* = 5.8, 2.8 Hz, ArH), 7.09 (m, 2H, ArH), 6.85 (m, 2H), 6.65 (d, 2H, *J* = 8.0 Hz, ArH), 6.34 (s, 1H, =CH), 5.87 (d, 1H, *J* = 9.6 Hz, N*H*-CH), 5.50 (d, *J* = 9.6 Hz, NH-C*H*), 5.37 (d, 1H, *J* = 1.4 Hz, C*H*H), 5.00 (d, 1H, *J* = 1.0 Hz, CH*H*), 1.88 (s, 3H, Me), 1.61 (s, 3H, Me); ^{13}C-NMR (75 MHz, C_6D_6, 25 ºC) δ: 195.1 (C=O), 194.5 (C=O), 143.7, 139.9, 139.1, 138.9, 136.9, 134.7, 133.9, 131.9 (Ar, 2CH), 130.9 (Ar, 2CH), 130.8 (=CH), 129.8 (Ar, 2CH), 129.2 (Ar, 2CH), 128.9 (Ar, 2CH), 127.65 (Ar, 2CH), 122.7, 122.0 (=CH_2), 58.7 (CH-NH), 23.2 (Me), 21.2 (Me); IR (C_6H_6, cm^{-1}): ν 3264, 1718, 2280, 1596, 1159; HRMS (ES): calcd for $C_{27}H_{27}BrClN_2O_4S$ [*M* + NH_4]$^+$: 591.05379; found: 591.05528.

(*Z*)-4-Methyl-*N*-(2-methyl-3-methylene-5,6-dioxo-1-(*p*-tolyl)oct-1-en-4-yl)benzenesulfonamide 3i. From 30 mg (0.172 mmol) of allenol **1b**, and after chromatography of the residue, gave compound **3i** (22 mg, 31%) as a yellow oil;

^{1}H-NMR (700 MHz, C_6D_6, 25 ºC) δ: 7.63 (d, 2H, *J* = 8.1 Hz, ArH), 7.17 (d, 2H, *J* = 8.0 Hz , ArH), 6.92 (d, 2H, *J* = 7.9 Hz, ArH), 6.61 (d, 2H, *J* = 7.9 Hz, ArH), 6.09 (s, 1H, =CH), 5.76 (d, 1H, *J* = 9.8 Hz, CH-N*H*), 5.41 (d, 1H, *J* = 9.7 Hz, C*H*-NH), 5.07 (s, 1H, =C*H*H), 4.94 (s, 1H, =CH*H*), 2.23 (m, 1H, CH*H*), 2.05 (s, 3H, Me), 1.97 (m, 1H, C*H*H), 1.80 (m, 3H, Me), 1.76 (s, 3H, Me), 0.67 (t, 3H, *J* = 7.2 Hz, Me); ^{13}C-NMR (175 MHz, C_6D_6, 25 ºC) δ: 198.2 (C=O), 194.5 (C=O), 143.4, 143.2, 137.7, 136.9, 134.9, 134.3, 129.7 (Ar, 2CH), 129.6 (Ar, 2CH), 129.3 (=CH), 129.0 (Ar, 2CH), 127,7 (Ar, 2CH), 118.9 (=CH_2), 58.4 (CH-NH), 29.9 (CH_2), 26.2 (Me), 21.1 (Me), 21.0 (Me), 6.7 (Me); IR (C_6H_6, cm^{-1}): ν 3662, 2923, 1721, 1164; HRMS (ES): calcd for $C_{24}H_{28}NO_4S$ [*M* + H]$^+$: 426.17336; found: 426.17256.

(*Z*)-*N*-(1-(4-Chlorophenyl)-2-methyl-3-methylene-5,6-dioxooct-1-en-4-yl)-4-methylbenzenesulfonamide 3j. From 30 mg (0.154 mmol) of allenol **1c** and after chromatography of the residue, gave compound **3j** (35 mg, 51%) as a yellow oil; ^{1}H-NMR (700 MHz, C_6D_6, 25 ºC) δ: 7.62 (d, 2H, *J* = 8.2 Hz, ArH), 7.03 (d, 2H, *J* = 8.5 Hz , ArH), 6.98 (d, 2H, *J* = 8.5 Hz, ArH), 6.64 (d, 2H, *J* = 8.0 Hz, ArH), 5.91 (s, 1H, =CH), 5.60 (d, 1H, *J* = 9.9 Hz, CH-N*H*), 5.56 (d, 1H, *J* = 9.9 Hz, C*H*-NH), 4.96 (s, 1H, =C*H*H), 4.82 (s, 1H, =CH*H*), 2.26 (m, 1H, CH*H*), 2.03 (m, 1H, C*H*H), 1.80 (s, 3H, Me), 1.77 (d, 3H, *J* = 1.4 Hz, Me), 0.68 (t, 3H, *J* = 7.2 Hz, Me); ^{13}C-NMR (175 MHz, C_6D_6, 25 ºC) δ: 198.3 (C=O), 194.4 (C=O), 143.5, 143.0, 137.4, 136.6, 135.5, 133.0, 130.2 (Ar, 2CH), 129.8 (Ar, 2CH), 128.7 (=CH), 128.4 (Ar, 2CH), 127,7 (Ar, 2CH), 119.1 (=CH_2), 58.1 (CH-NH), 30.0 (CH_2), 26.1 (Me), 21.1 (Me), 6.7 (Me); IR (C_6H_6, cm^{-1}): ν 3272, 1721, 1598, 1163; HRMS (ES): calcd for $C_{23}H_{28}ClN_2O_4S$ [*M* + NH_4]$^+$: 463.14528; found: 463.14539.

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[13] Experimental procedures as well as full spectroscopic and analytical data for compounds not included in this Experimental Section are described in the Supporting Information. It contains computational details, experimental procedures, characterization data, and copies of NMR spectra for all new compounds.

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UPDATES

Chemoselectivity Switching in the Rhodium-Catalyzed Reactions of 4-Substituted-1-sulfonyl-1,2,3-triazoles with Allenols: Noticeable Differences between 4-Acyl- and 4-Aryl-Triazoles

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