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Chalcogen-Bond Catalysis: Telluronium-Catalyzed [4 + 2]-Cyclocondensation of (in situ Generated) Aryl Imines with Alkenes

Loïc Gros Lambert,^[a] Andres Padilla-Hernandez,^[a] Robin Weiss,^[a] Patrick Pale,^{*[a]} and Victor Mamane^{*[a]}

Abstract: In the chalcogen series, tellurium species exhibit the strongest chalcogen bonding (ChB) interaction with electron-rich atom. This property explains the renewed interest toward tellurium-based derivatives and their use in different applications, such as organocatalysis. In this context, the catalytic activity of telluronium salts in the Povarov reaction is presented herein. Different dienophiles, as well as imines of variable electronic nature, efficiently react in the presence of catalytic amount of either diarylmethyltelluronium or triaryltelluronium salts. Both catalysts could also readily perform the three-component Povarov reaction

starting from aldehyde, aniline and dihydrofuran. The reactivity of telluroniums towards imines and aldehydes was confirmed in the solid state by the ability of Te atom to interact through ChB with the oxygen carbonyl of acetone, and in solution with significant shift variations of the imine proton and of the tellurium atom in ¹H and ¹²⁵Te NMR spectroscopy. For the most active telluronium catalysts bearing CF₃ groups, association constants (*K*) with *N*-phenyl phenylmethanimine in the range 22–38 M⁻¹ were measured in dichloromethane.

Introduction

Chalcogen bond (ChB) is a non-covalent interaction, identified as such relatively recently, analog to the now more common halogen bond (XB).^[1] Both are due to attraction between a nucleophilic entity (Lewis base) and an electrophilic region, called σ -hole, present on a halogen or a chalcogen atom. Due to dissymmetric electron distribution around such atoms upon covalent bonding, the σ -hole region (blue area in Figure 1) is located at the antipode of the X– or Ch–R bond and spatially coincides with the LUMO orbital (σ^*) of the X– or Ch–R bond.^[2] In contrast to monovalent halogens, chalcogen atoms exhibit two σ -holes due to their divalent character (Figure 1).^[3]

Although comparable to hydrogen bond (HB) in term of strength, XB and ChB are highly directional in sharp contrast to HB. This interesting property has initiated over the last decade for XB^[4,5] and very recently for ChB their exploitation in crystal

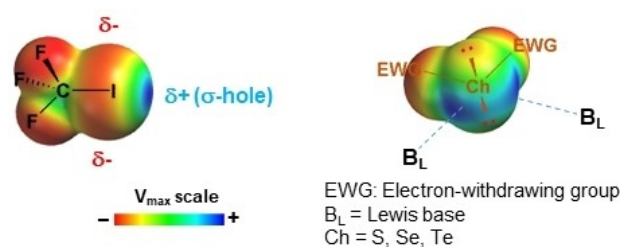


Figure 1. Location of σ -holes along covalent bond involving halogen or chalcogen.

engineering,^[6] supramolecular assemblies,^[7] anion recognition and transport tools,^[8] and even more recently in organocatalysis.^[4a,9] In the latter area, the high directionality of XB over HB has led to amazing developments. Combining this directionality to the presence of at least two σ -holes on chalcogen atom should allow even greater precision in 3D control. Organocatalysis based on ChB should thus be even more powerful.

As for XB, ChB strength depends on the polarizability of the chalcogen atom ($S < Se < Te$) and thus, chalcogen interactions involving tellurium are the strongest.^[8a,10] Tellurium derivatives are thus becoming the most promising for applications based on σ -hole interactions, with a few emerging in anion recognition^[9] and binding^[11] and in catalysis.^[12] Nevertheless, those applications remain scarce, especially in catalysis, in comparison to the lighter chalcogen-based derivatives.^[13]

Since we and others recently demonstrated that some tellurium and telluronium derivatives 1–4 indeed act as efficient

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catalysts in a few cases (Figure 2),^[12] we embarked on a program exploring the possibility and limit of such catalysts in organic synthesis.

To implement this goal, we reported here the synthesis of di- and triaryl telluronium derivatives **4–5** and their use as efficient catalysts in [4 + 2]-cycloadditions, namely the Povarov reaction (Scheme 1).^[14] While we were working on this reaction,^[15] Huber et al. reported that derivatives of type **2** were also efficient catalysts in the Povarov reaction between imines and 1,2-dihydrofuran.^[16]

This cycloaddition was selected for its synthetic interest, as it provides (hydro)quinoline derivatives. The latter is a common

structural motif in bioactive compounds, either natural or not, some having ended up as drugs (Figure 3), and as such have initiated various syntheses.^[17]

Results and Discussion

Telluronium synthesis

To tune the tellurium σ -holes and thus enhance stronger interactions, triaryltelluronium derivatives carrying electron-withdrawing substituents or groups (EWG) **5b** were prepared and compared to those without such EWG **5a** and to the analogous methyldiaryltelluronium salts **4a–b** (Scheme 2). The latter were obtained in three steps from the corresponding diaryl ditellurides **7a–b**. While **7a** is commercially available, its trifluoromethyl analog **7b** has to be prepared from aryl bromide **6**.^[12e] Its metalation through halogen-lithium exchange in the presence of *t*-butyllithium provided an aryl metal species, which could then be converted to diaryl ditelluride **7b**^[18] by addition of tellurium powder at low temperature, ethanolsis and air oxidation. **7a–b** were then very efficiently converted to the corresponding diaryltellurides **8a–b** in the presence of powdered copper.^[19] Alkylation with methyl iodide in the presence of silver triflate gave the corresponding diarylmethyltelluronium triflate **4a–b**_{OTf} with excellent yields. Because

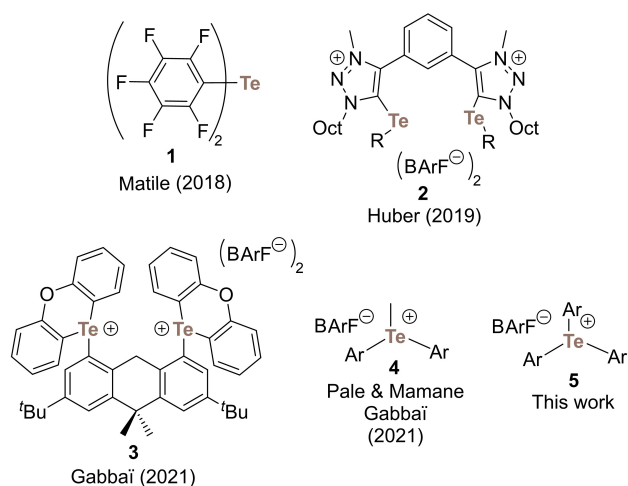
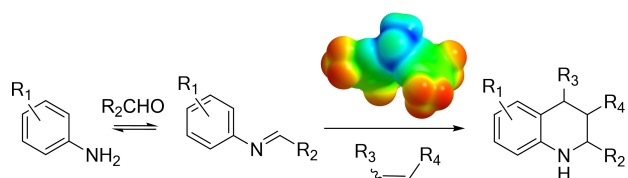


Figure 2. Few known ChB-based Te catalysts and the one proposed here.



Scheme 1. Telluronium-catalyzed Povarov reaction.

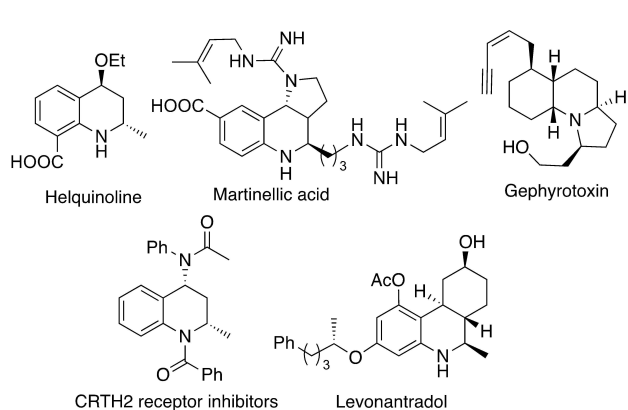
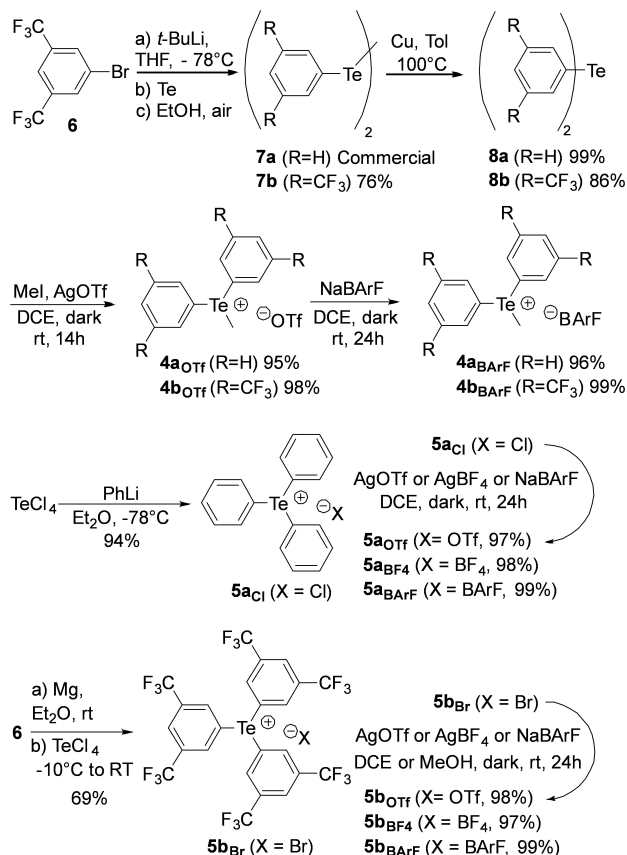


Figure 3. Selected examples of bioactive compounds containing a hydroquinoline motif.



Scheme 2. Di- and triaryltelluronium syntheses.

triflate anion is known to act as weak Lewis base towards several elements,^[20] the non-coordinating anion tetrakis[3,5-bis(trifluoromethyl)phenyl]borates (BARF) was also introduced to minimize any competition in solution. Anion metathesis readily occurred in the presence of sodium BARF salt and provided the telluronium BARF **4a–b**_{BARF} in very high yields. A shorter one- or two-step route was used for the preparation of the triaryltelluronium salts **5a–b**. Triphenyltelluronium chloride^[21] **5a**_{Cl} was directly obtained from addition of PhLi to TeCl₄. For the fluorinated aryl derivatives, addition of Mg turnings to **6** generated the Grignard reagent to which was added TeCl₄ at low temperature. Upon warming, the tellurate intermediate evolved to the corresponding triaryltelluronium bromide **5b**_{Br}. X-ray analysis revealed that the counter-ion was a bromine in this case. As for the above mentioned methyl diaryltelluroniums **4a–b**, anion metathesis could be applied to triaryltelluroniums **5a**_{Cl} and **5b**_{Br} with either AgOTf, AgBF₄ or NaBARF. The corresponding telluronium salts **5a–b**_{OTf}, **5a–b**_{BF₄} and **5a–b**_{BARF} were obtained in near quantitative yields.

Telluronium structures and interactions

To look for σ -hole interactions in the solid state, numerous attempts to get suitable crystals out of the diarylmethyl- or triaryltelluronium salts having coordinating ions were pursued. Among them, **5a**_{BF₄} and **5a**_{BARF} were successfully crystallized from a dichloromethane solution in the dark by slow diffusion of cyclohexane and their solid-state molecular structures were determined by single crystal X-ray diffraction (XRD) (See S III in S.I.). **5a**_{BF₄} structure exhibits close contacts between three fluorine atoms from one anion and three different tellurium atoms. Lengths and angles strongly suggest the presence of σ -hole interactions. Indeed, the Te...F distances $d_{\text{Te}\cdots\text{F}}$ are all below the sum of van der Waals radii and the C_{Ar}-Te-F angles are in the range 166–178°, showing the high linearity of the interaction. It is worth noticing that although dichloromethane molecule was found in the XRD structure, no interaction of the chlorine atoms with tellurium atom could be observed.

Due to these results, attempts to co-crystallize triaryltelluronium salts in the presence of Lewis bases were undertaken. Rewardingly, **5a**_{BF₄}, **5b**_{Br} and **5b**_{BARF} gave crystals from mixture of dichloromethane and acetone, and their XRD structures contained an acetone molecule in close contact with one σ -hole of the tellurium atom (Figure 4). In the crystal structure of adduct [**5a**_{BF₄}·CH₃COCH₃], the Te...O distance $d_{\text{Te}\cdots\text{O}}$ is 2.996 Å, far below the sum of van der Waals radii ($r_{\text{vdwTe}}=2.08$ Å, $r_{\text{vdwO}}=1.52$ Å, RR (reduction ratio) = $(r_{\text{vdwTe}} + r_{\text{vdwO}})/d_{\text{Te}\cdots\text{O}}=0.83$) and the C_{Ar}-Te-O angle (θ) is 177.0°. In agreement with the higher Te σ -hole activation in the trifluoromethylated telluronium **5b**, shorter $d_{\text{Te}\cdots\text{O}}$ values of 2.851 Å (RR=0.79) and 2.714 Å (RR=0.75) were noted in the crystal structures of [**5b**_{Br}·CH₃COCH₃] and [**5b**_{BARF}·CH₃COCH₃], respectively.

As expected from the lower coordinating ability of the BARF anion,^[20] the Te...O interaction in the BARF salt is much stronger than in the bromide one. The two geometrical parameters (RR < 1 and θ in the range 160–180°) confirm the Te...O ChB

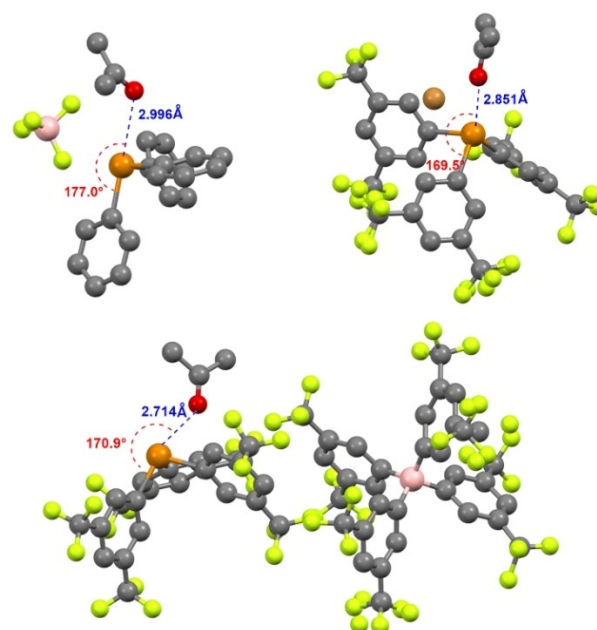


Figure 4. X-ray structures of the triaryltelluronium **5a**_{BF₄} (up, left), **5b**_{Br} (up, right) and **5b**_{BARF} (bottom) co-crystallized with acetone. Hydrogen atoms are omitted for clarity. Color code: carbon in gray, tellurium in orange, oxygen in red, boron in pink, fluorine in green, bromine in brown.

between telluroniums **5a/5b** and acetone. It is worth noting that in the structures of [**5a**_{BF₄}·CH₃COCH₃] and [**5b**_{Br}·CH₃COCH₃], the two other Te σ -holes respectively interact with BF₄[−] and Br[−] anions through strong Te...F and Te...Br ChBs leading to the formation of anion bridges between two telluronium-acetone adducts (See S III in S.I.).

These results in the solid state anticipate the fact that carbonyl groups and thus related imines can be activated in solution through ChB by telluronium catalysts. This was confirmed by conducting NMR experiments of a 1:1 CD₂Cl₂ mixture between the simplest non-functionalized imine, i.e. the *N*-phenyl phenylmethanimine, and telluroniums **4b**_{BARF} and **5b**_{BARF} (see S VII in S. I.). In ¹H NMR, the signal of the imine proton at 8.474 ppm was deshielded to 8.498 ppm and 8.480 ppm upon addition of **4b**_{BARF} and **5b**_{BARF}, respectively. Accordingly, variations were also observed in ¹²⁵Te NMR, with a shift from 655.08 ppm for **4b**_{BARF} to 663.77 ppm in the presence of imine ($\Delta\delta$ 8.69 ppm), and with a larger shift for **5b**_{BARF}, from 774.94 to 787.14 ppm in the presence of imine ($\Delta\delta$ 12.2 ppm). The capacity of telluroniums **4b**_{BARF} and **5b**_{BARF} to interact with *N*-phenyl phenylmethanimine could be compared by determining their association constants *K* through titration experiments (see Figures S7 and S8 in Supporting Information). Thus, the chemical shift variations for **4b**_{BARF} and **5b**_{BARF} upon addition of increasing amount of the imine were monitored by ¹²⁵Te NMR. The so-obtained *K* values revealed a slightly higher interaction of **4b**_{BARF} with the imine ($K(\mathbf{4b}_{\text{BARF}}/\text{imine})=38 \pm 5 \text{ M}^{-1}$) vs. $K(\mathbf{5b}_{\text{BARF}}/\text{imine})=22 \pm 4 \text{ M}^{-1}$).

It is worth noting that a slow decomposition of **4b**_{BARF} to the parent tellane **8b** occurred upon prolonged contact times as

evidenced by NMR. After 16 h at room temperature, ^{19}F NMR indicated the formation of about 50% of **8b**. Such decomposition could not be detected with **5b**_{BARF}.

Telluroniums as catalysts in Povarov reaction

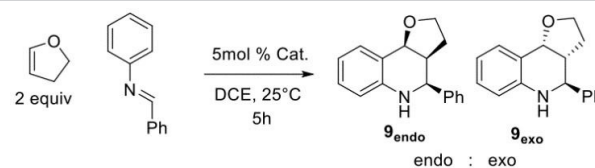
As expected from a ChB-driven reaction, a preliminary solvent survey revealed that coordinating or (Lewis) basic solvents hamper the Povarov reaction (See Table S1 in S.I.). Only the chlorinated solvents dichloromethane or 1,2-dichloroethane allowed the formation of the expected tetrahydroquinoline adducts. These results are in line with the absence of interaction between dichloromethane and telluronium in XRD structure, while clear interactions with co-crystallized acetone do exist in other XRD structures (see above).

The performances of the telluronium catalysts were first evaluated in the reaction between *N*-phenyl phenylmethanimine, and 2,3-dihydrofuran, known for its high activity in Povarov reaction (Table 1). While no reaction occurred without catalyst, even after 24 h (entry 1), the simple diphenylmethyltelluronium BARF **4a**_{BARF} was able to catalyze this model reaction at room temperature within a few hours (entry 2). Moderate conversion and yield were nevertheless observed after 5 h without significant selectivity for one or the other endo or exo stereoisomers. As expected, the trifluoromethylated analog **4b**_{BARF} proved more efficient and allowed to get **9** in high yield, but still without much selectivity (entry 3). The corresponding triflate **4b**_{OTf} provided similar results, but with a selectivity in favor of the endo isomer (entry 4). As noted from NMR studies, a small amount of tellane **8b** was observed at the end of the reaction. To attest that the reaction was only catalyzed by the telluronium, the catalytic activity of **8b** was also evaluated and no conversion was observed (entry 5).

In the triaryltelluronium series, the triphenyltelluronium BARF salt **5a**_{BARF} only led to slow reactions at room temperature. Upon slight heating, it nevertheless proved as efficient as its diphenylmethyl analog **4a**_{BARF}, leading to similar results both in term of yields and selectivity (entry 6 vs. 2). The corresponding triflate **5a**_{OTf} afforded the expected adducts in similar yields but with a higher selectivity and without heating (entry 7 vs. 6). Under the same conditions, the tetrafluoroborate **5a**_{BF₄} exhibited a slightly lower reactivity, but induced a slightly higher selectivity in favor of the endo isomer (entry 8 vs. 7 vs. 6). Interestingly, the trifluoromethylated derivative **5b**_{BARF} exhibited a much higher efficacy as catalyst but with the same lack of selectivity (entry 9 vs. 6). Here again, shifting from BARF as counter-ion to triflate or tetrafluoroborate provided similar yields with better selectivity, especially with the triflate derivative **5b**_{OTf} (entry 9 vs. 10 vs. 11). This salt effect on the diastereoselectivity was also observed by Huber et al. but could not be clearly rationalized.^[16] The results in our hands did not allow to get more insight.

Subsequently, control experiments to assess the role of σ -hole interactions in the reaction were performed with the BARF catalyst **5b**_{BARF}. Known for its strong interaction with σ -holes, two equivalents of chloride salt (tetrabutylammonium chloride)

Table 1. Telluronium-catalyzed Povarov reaction starting from pre-formed imines: catalyst screening.^[a]



Entry	Telluronium structure	Catalyst	Yield (%) (endo:exo) ^[b]
1	-	None	0
2		4a _{BARF}	53 ^[c,d] (55:45)
3		4b _{BARF}	88 ^[d] (48:52)
4		4b _{OTf}	95 ^[d] (68:32)
5		8b	0
6		5a _{BARF}	49 ^[c,e] (49:51)
7		5a _{OTf}	47 ^[c] (68:32)
8		5a _{BF₄}	39 ^[c] (73:27)
9		5b _{BARF}	85 (45:55)
10		5b _{OTf}	98 (67:33)
11		5b _{BF₄}	92 (61:39)
12		5b _{BARF}	0 ^[f]
13		5b _{BARF}	84 ^[g] (48:52)

[a] Reaction conditions: imine (0.055 mmol), 2,3-dihydrofuran (0.110 mmol) in 1,2-DCE (0.4 mL) at 25 °C for 5 h; [b] Yield and endo/exo ratio were estimated by ^1H NMR by using 1,4-trimethylsilylbenzene as internal standard; [c] incomplete conversion; [d] Tellane **8a** or **8b** was observed at the end of the reaction; [e] reaction performed at 40 °C; [f] Addition of 10 mol% of tetrabutylammonium chloride; [g] Addition of 5 mol% of 2,6-ditertbutyl-4-methylpyridine.

were added relative to the telluronium salt. This presence totally suppressed the reaction (entry 12 vs. 9). To ensure that no acid trace could catalyze the reaction, another experiment was performed in the presence of a base, hindered to minimize competition for ChB. A stoichiometric amount of 2,6-ditertbutyl-4-methylpyridine relative to the telluronium salt was thus added and the cyclization proceeded as without it (entry 13 vs.

9). Both results clearly show the key role σ -hole interactions play in this reaction.

These results clearly highlight the higher reactivity and efficiency of catalysts carrying trifluoromethyl substituents, as expected. Yields were indeed improved in the methyldiaryltelluronium series (53 vs. 88–95% yield, entries 3–4 vs. 2) as well as in the triaryltelluronium series (39–49 vs. 85–98% yield, entries 6–8 vs. 9–11). Whatever the series, similar reactivity was observed (entry 2 vs. 6 and entries 3–4 vs. 9–11), despite the measured association constants slightly in favor of the methyldiaryltelluronium (see above). However, triaryltelluronium catalysts proved more stable than the methyldiaryltelluronium analogs (see above).

To go further towards synthetic applications, we then investigated the capacity and tolerance of these catalysts.

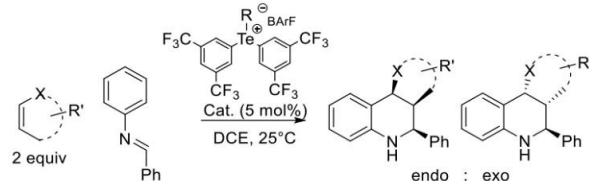
We first surveyed the dienophile partner. A series of variously substituted alkenes were thus reacted with the same non-functionalized *N*-phenyl phenylmethanimine (Table 2). For comparison purpose, both the trifluoromethylated methyldiphenyl- and triphenyltelluronium BARF salts, **4b**_{BARF} and **5b**_{BARF} respectively, were engaged as catalysts in reactions with the same dienophile. Since classical Povarov reactions usually involve electron-rich alkenes, especially enol ethers and conjugated dienes,^[14] we have engaged a representative panel of such dienophiles in our telluronium-catalyzed version (entries 1–8 and 9–10). Nevertheless, norbornene was also engaged as a few strained alkenes already proved reactive enough in classical Lewis acid-catalyzed Povarov reactions.^[22]


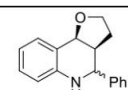


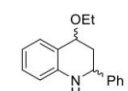


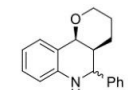


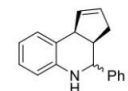


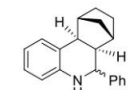

Enol ethers rapidly reacted with the methyldiaryltelluronium **4b**_{BARF} catalyst and very efficiently yielded the expected hydroquinolines (entries 1, 3 and 6) but with variable stereoselectivity. Indeed, the endo/exo ratio could be partly reversed (from 85:15, entry 3, to 35:65, entry 6) depending on the alkene size. The small ethoxyethene mostly provided the endo isomer, while the larger dihydropyran mostly gave the exo isomer (entry 3 vs. 6). In contrast, the triaryltelluronium **5b**_{BARF} required longer reaction times, except for dihydrofuran (entry 2 vs. 1). Dihydropyran could not be fully converted, even after 20 h (entries 7–8), while ethoxyethene was within the same time (entries 4–5). The same reversal in stereoselectivity was also observed with this catalyst (from 82:18, entries 4–5, to 35:65, entry 8).

Another catalyst activity difference was observed with conjugated and strained alkenes. In the presence of **4b**_{BARF}, cyclopentadiene provided the corresponding hydroquinoline, mostly as its endo isomer, within a few hours and in high yield (entry 9). However, a complex mixture was obtained in the presence of **5b**_{BARF} in which the expected hydroquinoline could barely be detected (entry 10). Similarly, norbornene readily reacted in the presence of **4b**_{BARF}, although longer reaction time was required (entries 11–12), while **5b**_{BARF} induced the norbornene polymerization (entry 13).

The very high exo-exo stereoselectivity of the latter reaction (entries 11–12) suggests the intervention of an asynchronous Diels-Alder type mechanism rather than a stepwise mechanism.^[22] The fact that a stereoselectivity change occurred with enol ethers, according to their size, corroborates such

Table 2. Telluronium-catalyzed Povarov reaction starting from pre-formed imines: screening of dienophiles.^[a]



Entry	Catalyst	Dienophile	Time (h)	Yield ^[b] (%)	Product Structure
1	4b _{BARF}		5	88 ^[c] (46:54)	
2	5b _{BARF}		5	85 (46:54)	9 _{endo} : 9 _{exo}
3	4b _{BARF}		5	94 (85:15)	
4	5b _{BARF}		5	48 ^[d] (82:18)	10 _{endo} : 10 _{exo}
5			20	80 (81:19)	
6	4b _{BARF}		5	92 (35:65)	
7	5b _{BARF}		5	26 ^[d,e]	11 _{endo} : 11 _{exo}
8			20	50 ^[d] (35:65)	
9	4b _{BARF}		5	91 ^[c] (74:26)	
10	5b _{BARF}		5	— ^[f]	12 _{endo} : 12 _{exo}
11	4b _{BARF}		5	60 ^[c,d] (5:95)	
12			24	79 ^[c] (5:95)	
13	5b _{BARF}		24	— ^[g]	13 _{exo-endo} : 13 _{exo-exo}

[a] Reaction conditions: imine (0.055 mmol), dienophile (0.110 mmol) in 1,2-DCE (0.4 mL) at 25 °C; [b] Yield and endo:exo ratio were estimated by ¹H NMR by using 1,4-trimethylsilylbenzene as internal standard; [c] Tellene **8b** was observed at the end of the reaction; [d] Incomplete conversion; [e] Endo:exo ratio could not be clearly determined; [f] Complex mixture; [g] Polymerization of the dienophile.

Diels-Alder type mechanism in which increasing steric interactions tend to shift the dienophile approach.

These results show that the methyldiaryltelluronium **4b**_{BARF} catalyst reacts similarly whatever the alkene (91 ± 3% yield), except for the hindered norbornene (entries 1,3,6,9 vs. 11), in contrast to the triaryltelluronium **5b**_{BARF} more sensitive to hindrance (entry 2 vs. 4 vs. 7 vs. 13), probably due to its larger size. Despite slower reactions with the latter catalyst, almost the same selectivity was achieved whatever the catalyst, at least in

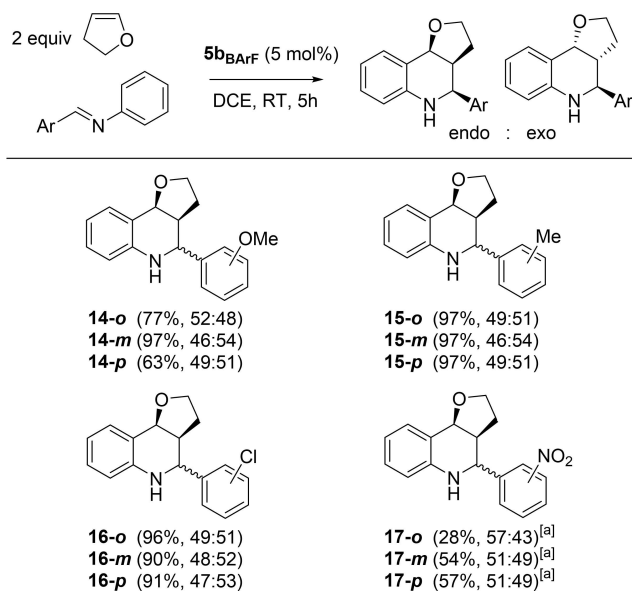
reaction with enol ethers (entries 4–5 vs. 3, 2 vs. 1 and 7–8 vs. 6).

It is worth mentioning that this telluronium-catalyzed Povarov reaction compared well with other versions catalyzed by more classical catalysts, which usually required either higher catalyst loading and/or longer reaction time and sometimes higher temperatures^[22,23] (See Table S2 in Supporting Information).

To further exemplify the present telluronium-catalyzed Povarov reaction and in attempts to shed light on the possible mechanisms,^[24] we prepared and investigated a series of imines carrying a *N*-phenyl group tuned with electron-withdrawing or donating substituents (EWG or EDG) at each *ortho*-, *meta*-, *para*-position (Scheme 3).

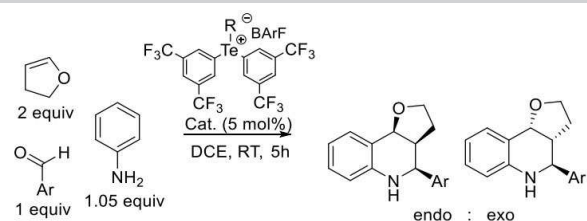
Submitted to the more electrophilic trifluoromethylated triphenyltelluronium BARF salt **5b**_{BARF}, these imines provided the expected hydroquinolines usually in high and nearly quantitative yields (see **14-m**, **15-o-m-p**, **16-o**). Except the strongly electron-withdrawing nitro group, which slowed the reaction (see **17-o-m-p**), no clear electronic effects seem to affect the reaction (see **16-o** vs. **15-o**). Nevertheless, and surprisingly, the *ortho*- and *para*-methoxy substituted derivatives were produced with lower yields than the *meta* isomer (see **14-o-p** vs. **14-m**) and than the methyl substituted derivatives (see **14-o-p** vs. **15-o-p**).

Looking for a truly multi-component one-pot reaction, we performed the same reactions starting from the imine precursors, i.e. aniline and benzaldehyde (Table 3). The latter in the presence of dihydrofuran and catalytic amount of methyl or aryl telluronium BARF salts gave the expected adducts usually in the same or similar yields and stereoselectivity compared to the reaction starting from pre-formed imines (entries 1–4 and 6).



Scheme 3. Telluronium-catalyzed Povarov reaction starting from pre-formed imines: screening of the imine. Reaction conditions: imine (0.055 mmol), 2,3-dihydrofuran (0.110 mmol) in 1,2-DCE (0.4 mL) at 25 °C; Yield and endo:exo ratio were estimated by ¹H NMR by using 1,4-trimethylsilylbenzene as internal standard; ^[a] Incomplete conversion.

Table 3. Telluronium-catalyzed Povarov reaction from in situ formed imines.



Entry	Catalyst	Ar	Yield ^[b] (%) (endo:exo)	Product
1	4b _{BARF}	C ₆ H ₅	80 ^[c] (49:51)	9
2	5b _{BARF}	C ₆ H ₅	84 (51:49)	9
3	5b _{BARF}	<i>p</i> -ClC ₆ H ₄	91 (51:49)	16-p
4	5b _{BARF}	<i>m</i> -ClC ₆ H ₄	80 (51:49)	16-m
5	5b _{BARF}	<i>o</i> -ClC ₆ H ₄	66 (53:47)	16-o
6	5b _{BARF}	<i>m</i> -MeC ₆ H ₄	98 (49:51)	15-m

[a] Reaction conditions: aldehyde (0.055 mmol), aniline (0.0558 mmol), 2,3-dihydrofuran (0.110 mmol) in 1,2-DCE (0.4 mL) at 25 °C; [b] Yield and endo:exo ratio were estimated by ¹H NMR by using 1,4-trimethylsilylbenzene as internal standard; [c] Tellane **8b** was observed at the end of the reaction.

However, the one-pot reaction with the *ortho*-chlorobenzaldehyde provided the adducts with a significantly lower yield, probably linked to the slower in situ imine formation (entry 5).

Conclusion

The synthesis of telluronium salts and their catalytic activity in the Povarov reaction involving imines, or their components, and alkenes was reported. The ChB ability of the telluronium salts was first attested in the solid state by co-crystallization with acetone. The geometrical parameters of Te...O contacts (distances and angles) clearly correspond to a σ -hole based interaction. Moreover, the strength of the Te...O ChB could be correlated to the electron-withdrawing ability of Te substituents (*m,m*-(CF₃)₂-C₆H₃ vs. C₆H₅) and to the coordinating ability of the counter-ion (BARF vs. Br). In solution, addition of a stoichiometric amount of the telluronium BARF salts to the imine induced significant chemical shifts variations in ¹H and ¹²⁵Te NMR as a result of the Te...N ChB, allowing to determine association constants. Subsequently, the catalytic performances of the telluronium BARF salts and its generality were demonstrated through various Povarov reactions involving either different dienophiles or imines. Finally, a one-pot protocol for the

Povarov reaction was developed, starting from various aldehydes and aniline.

Further work to expand the scope of chemical functions that could be activated by the telluronium salts are underway in our group.

Experimental Section

General procedure for the Povarov reaction: In a 1 mL sealed tube containing the imine (0.055 mmol), catalyst (5 mol%) in 0.4 mL of freshly distilled and degassed 1,2-DCE was added the dienophile (0.110 mmol). The reaction mixture was shaken at 25 °C with a vortex. At the appropriate time, the standard (1,4-trimethylsilylbenzene, 200 μ L, 80 mM in acetone) was added to the reaction mixture. The solvent was removed under reduced pressure to remove volatile dienophile and solvent. Deuterated solvent was added and the resulting mixture was monitored by ^1H NMR.

X-Ray Diffraction: Single crystals of **5a_{BF4}** and **5a_{BAF}** were obtained by slow diffusion at 10 °C of cyclohexane into a solution of the telluronium in dichloromethane. Single crystals of [**5a_{BF4}**·CH₃COCH₃], [**5b_{Br}**·CH₃COCH₃] and [**5b_{BAF}**·CH₃COCH₃] were obtained by slow diffusion at 4 °C of cyclohexane into a solution of the telluronium in acetone. The crystals were placed in oil, and a single crystal was selected, mounted on a glass fiber and placed in a low-temperature N₂ stream. X-ray diffraction data collection was carried out on a Bruker PHOTON III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using Mo–K α radiation ($\lambda = 0.71073$ Å). The crystal-detector distance was 37 mm. The cell parameters were determined (APEX3 software)^[25] from reflections taken from 1 set of 180 frames at 1 s exposure. The structures were solved using the program SHELXT-2014.^[26] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F₂. A semi-empirical absorption correction was applied using SADABS in APEX3; transmission factors: $T_{\min}/T_{\max} = 0.7091/0.7456$ for **5a_{BF4}**; $T_{\min}/T_{\max} = 0.7264/0.7456$ for **5a_{BAF}**; $T_{\min}/T_{\max} = 0.6819/0.74650$ for [**5a_{BF4}**·CH₃COCH₃], $T_{\min}/T_{\max} = 0.6876/0.7460$ for [**5b_{Br}**·CH₃COCH₃] and $T_{\min}/T_{\max} = 0.7187/0.7456$ for [**5b_{BAF}**·CH₃COCH₃].

Deposition Numbers 2212565 (for **5a_{BF4}**), 2212566 (for **5a_{BAF}**), 2212567 (for [**5a_{BF4}**·CH₃COCH₃]), 2212568 (for [**5b_{Br}**·CH₃COCH₃]) and 2212569 (for [**5b_{BAF}**·CH₃COCH₃]) contain the supplementary crystallographic data for this paper. These data are provided by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: chalcogen bonds · cycloaddition · σ -holes · organocatalysis · tellurium

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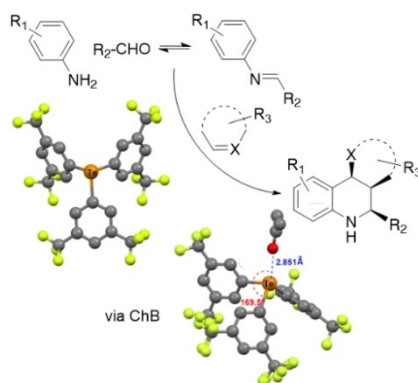
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RESEARCH ARTICLE

Telluronium salts bearing electron-withdrawing groups were prepared, and their ability to drive chalcogen bonds with ketones and imines was demonstrated in the solid state and in solution. These strong σ -hole bond donors were able to efficiently catalyze the Povarov reaction through chalcogen bond activation of imines and subsequent reaction with alkenes. The title reaction was found to be as efficient with pre-formed or in situ generated imines.



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Chalcogen-Bond Catalysis: Telluronium-Catalyzed [4+2]-Cyclocondensation of (in situ Generated) Aryl Imines with Alkenes

