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Catalytic Activation of a Carbon–Chloride Bond by Dicationic Tellurium-Based Chalcogen Bond Donors

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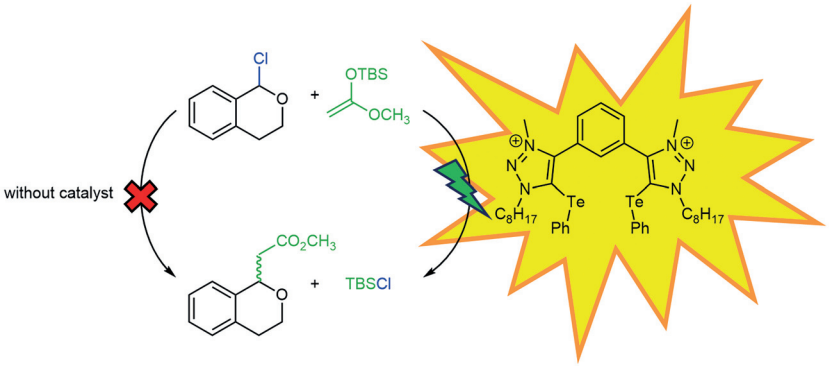

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Abstract Noncovalent interactions such as halogen bonding (XB) and chalcogen bonding (ChB) have gained increased interest over the last decade. Whereas XB-based organocatalysis has been studied in some detail by now, intermolecular ChB catalysis only emerged quite recently. Herein, bidentate cationic tellurium-based chalcogen bond donors are employed in the catalytic chloride abstraction of 1-chloroisochroman. While selenium-based ChB catalysts showed only minor activity in this given benchmark reaction, tellurium-based variants exhibited strong activity, with rate accelerations of up to 40 relative to non-chalogenated reference compounds. In general, the activity of the catalysts improved with weaker coordinating counterions, but tetrafluoroborate took part in a fluoride transfer side reaction. Catalyst stability was confirmed via a fluoro-tagged variant.

Key words chalcogen bonding, organocatalysis, halide abstraction, Lewis acids, intermolecular interactions, noncovalent interactions

Besides hydrogen bonding, the dominating noncovalent interaction in organocatalysis,[1] other interactions, such as anion-π,[2] halogen bonding (XB),[3] and chalcogen bonding (ChB),[4] have recently attracted more attention in this field of research. In contrast to halogen bonding, which has been employed in organocatalysis for about a decade now,[3a] chalcogen bonding has been far less studied in this regard.

This interaction between Lewis acidic chalcogen atoms in organic or inorganic molecules and Lewis bases can be rationalized by attractive contributions both from orbital interactions[5] (i.e., n → π* charge transfer)[6] and electrostatics. The latter is based on a region of positive electrostatic potential on the elongation of the R–Ch bond, the so called *σ-hole*.[7] Chalcogen bonds have the advantage that the binding strength can be fine-tuned by variation of the chalcogen (S < Se < Te). Also, the superior directionality of approximately 170° could be beneficial for high substrate selectivity.[5,7,8]

Several fascinating applications of chalcogen bonding in the solid state[9] are already known, along with its use in an intramolecular fashion in organic synthesis.[10] In the last years, Taylor,[11] Beer,[4b,12] and Matile[13] applied ChB in anion recognition as well as transport and thus described first intermolecular applications in solution.[14] In 2017, Matile reported the catalytic reduction of quinolines by sulfur-based ChB donors, which constitutes the first use of such species as noncovalent organocatalysts.[15] Subsequently, our group employed selenium-based ChB donors for the activation of carbon–halide bonds and in the above-mentioned quinoline reduction as benchmark.[16] Due to the weaker interaction of neutral substrates with ChB bond donors, the activation of such compounds is more challenging. Shortly after the first report of a carbonyl activation via Se-based ChB donors by Wang,[17] our group introduced the first cationic tellurium-based ChB organocatalysts and employed them in the activation of *trans*-β-nitrostyrene as well as *trans*-crotonophenone in (nitro)-Michael addition reactions.[18] These bidentate ChB donors are also expected to be the most active catalysts in halide abstraction reactions, but the use of Te-derived species in such reactions has so far been limited to the application of neutral polyfluorinated variants,[19] which are typically much weaker Lewis acids compared to (di)cationic ChB donors.

Herein, we now present the first carbon–halogen bond activation by cationic tellurium-based catalysts. Since this study is primarily meant to provide further data on the performance and structure-activity relationship of ChB donors

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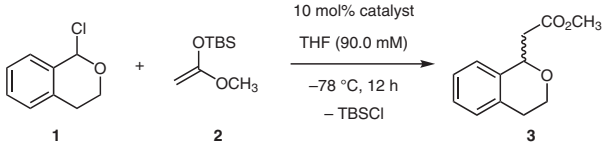
(also in comparison to HB and XB donors), we chose to use an often-employed benchmark reaction,[19,20] the nucleophilic substitution of 1-chloroisochroman (**1**) with a ketene silyl acetal **2** (Scheme 1). This reaction is ideal for this purpose since it features no background reaction and because it is immune to hidden acid catalysis.[20b,21]



Scheme 1 Benchmark reaction of the chloride abstraction involving 1-chloroisochroman (**1**) with catalytic amounts of chalcogen bond donor

Biographical Sketches

Tim Steinke, born 1993 in Eschwege, studied chemistry at the Ruhr-Universität Bochum (RUB) and received his Master's degree in 2019. Currently, he is a Ph.D. student in the group of Prof. Stefan M. Huber at the RUB. His research focuses on the synthesis and application of multidentate chalcogen bond donors in organic synthesis.

Patrick Wonner, born in July 1991, studied chemistry at the Ruhr-Universität Bochum. He finished his bachelor's degree in the year 2014 and received his Master's degree in 2016. The master thesis was prepared in the group of S. M. Huber in the field of halogen bonding. Subsequently, he started his Ph.D. in the same group about the application of halogen and chalcogen bonding in organocatalysis and finished his research in April 2020 to receive his Ph.D.

Elric Engelage was born in Germany in 1990. He obtained his B.Sc. in Biochemistry from the Ruhr-Universität Bochum. For his master and doctoral studies in Chemistry he joined the workgroup of Prof. S. M. Huber, focusing on halogen bonding in solution, and serving as the group's crystallographer. After obtaining his doctoral degree in 2019 he transferred to the group of Prof. W. Sander.

Stefan M. Huber, born in 1977, studied chemistry at the Friedrich-Alexander-University Erlangen-Nuremberg and obtained his Ph.D. degree in 2007 with Prof. Robert Weiss. After postdoctoral stays at the University of Minnesota and the University of Geneva, he started his independent career at TU Munich in 2009. Since 2014, he is professor of organic chemistry at Ruhr-University Bochum.

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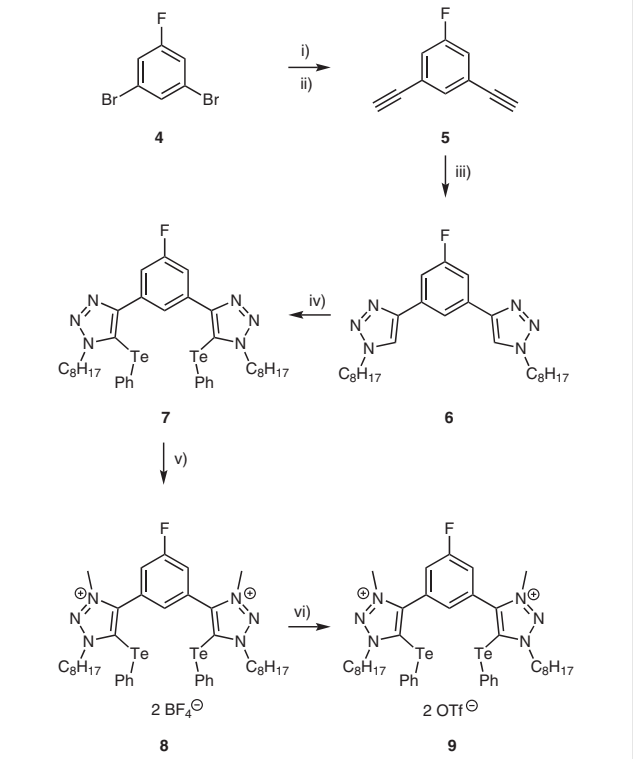
Previously, we had used the same reaction to introduce 1,3-bis(selenobenzimidazolium)benzene derivatives as ChB-based organocatalysts,[16b] these ChB donors were however susceptible to decomposition by dealkylation on the chalcogen center.[16a] Even though this is not feasible for the catalysts used in this study (like compound **14**, see Figure 2) due to the presence of a phenyl substituent, we nevertheless wanted to be able to check catalyst stability during the reaction. To this end, we synthesized fluorine-tagged variants like **8** and **9** (Scheme 2) which can easily be monitored by ^{19}F NMR spectroscopy. The synthetic route to these catalysts followed already known procedures (Scheme 2).[18] 1,3-Diethynyl-5-fluorobenzene is not commercially available and was therefore synthesized from the available 1,3-dibromo-3-fluorobenene by Sonogashira coupling with (trimethylsilyl)acetylene and subsequent deprotection.[22] The following steps involve a 1,3-dipolar cycloaddition reaction[23] of the alkyne moieties with azides to build up the triazole groups, and the formation of the chalcogen ether in basic media. The cationic catalysts were then obtained after methylation with Me_3OBF_4. Triflate salt **9** was obtained via anion exchange resin from **8**, as direct methylation with methyl trifluoromethanesulfonate led to impure compounds. Similarly, the non-fluorine-tagged catalysts **14**^{OTf} and **15**^{OTf} (see Figure 2) were also synthesized by ion exchange. To confirm the purity of the compounds and especially to rule out the presence of trifluoromethanesulfonic acid (HOTf), the recently proposed purity check by Franz et al. for halogen bond donors was employed.[24] Indeed, addition of triethylphosphine oxide to **14**^{OTf} showed a clear and sharp peak in the corresponding ^{31}P NMR spectrum. Residual HOTf would lead to a broad peak, which was confirmed by the addition of this acid, thus further validating the method.

First catalysis experiments were carried out with **14**^{BF4}. However, less than 5% yield of product **3** was obtained with 10 mol% of this catalyst after 12 h at –78 °C (Table 2, entry 2). Therefore, the corresponding triflate salt **14**^{OTf} was then tested, and with this catalyst, product **3** was obtained in 82% yield under the same conditions (Table 2, entry 3). To rule out other modes of activation except chalcogen bonding, several reference compounds were also studied in parallel, which included elemental tellurium and selenium, dichalcogenides **10**, neutral/non-alkylated ChB donors **11**, and non-chalcogenated variant **12**^{OTf} (Figure 1). All of these compounds showed only low or no activity (Table 1, entries 2–7), with hydrogen-bond donor **12**^{OTf} providing a mere yield of 9% (Table 1, entry 8). To exclude any innate activity of the counterions, their ammonium salts were also tested, but no formation of **3** was observed in any of these experiments (Table 1, entries 9–11). As compounds **14**^{OTf} and **15**^{OTf} are prepared by anion exchange chromatography, the Amberlyst resin used for this exchange was also employed in the reaction and again did not show any activity (Table 1, entry 12). The corresponding halogen-bond donor **13**^{OTf}, on the other hand, generated comparable yields to **14**^{OTf} (Table 1, entry 13).



Scheme 2 Synthesis of fluorine-tagged chalcogen bonding organocatalysts. *Reagents and conditions*: (i) $Me_3SiC{\equiv}CH$, $Pd(PPh_3)_4$, CuI, THF, Et_3N, 70 °C, 2 d; (ii) CsF, EtOH, r.t., 30 min; (iii) *n*-$C_8H_{17}N_3$, CuI, TBTA, THF, r.t., light exclusion, 3 d; (iv) *i*-Pr_2NH, *n*-BuLi, $(PhTe)_2$, THF, –78 °C → r.t., 18 h; (v) Me_3OBF_4, CH_2Cl_2, r.t., 18 h; (vi) Amberlyst® A26 (OH), HOTf, MeOH.

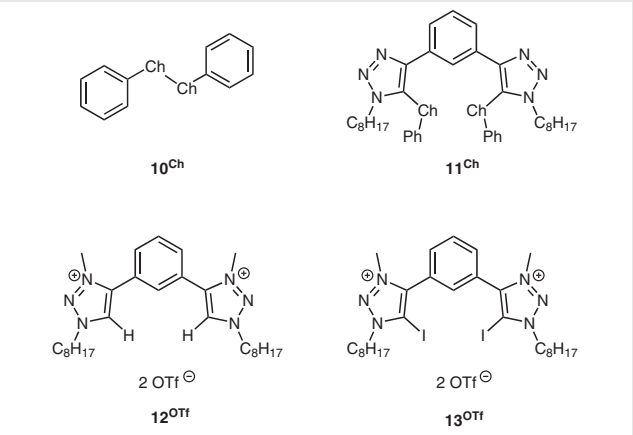


Figure 1 Selected reference compounds tested in the benchmark reaction to rule out activation based on other interactions than chalcogen bonding; Ch = Se, Te

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Table 1 NMR Yields of **3** in the Presence of the Activation Compounds after 12 h at –78 °C

Entry	Catalyst	mol%[a]	Yield (%) of **3**[b]
1	–	–	<5
2	Te	20	<5
3	Se	20	<5
4	**10**^{Te}	10	<5
5	**10**^{Se}	10	<5
6	**11**^{Te}	10	<5
7	**11**^{Se}	10	<5
8	**12**^{OTf}	10	9
9	Me_4NBF_4	20	<5
10	Et_4NOTf	20	<5
11	Me_4NBAr^F	20	8
12	Amberlyst[c]	20	<5
13	**13**^{OTf}	10	86

[a] Equivalents of catalyst with respect to **1**.
[b] ±5% measurement error assumed.
[c] Results for the used and unused Amberlyst are combined in this entry.

Similar performance was also observed for the fluorine-tagged variant **9**^{OTf} compared to its parent compound **14**^{OTf} (Table 2, entries 1 and 3). The stability of the former was then investigated by ^{19}F NMR spectroscopy of the reaction mixture after the reaction time of 12 h. The spectrum shows only the corresponding C_{arom}–F signal of the ChB donor and the signal for triflate. Addition of the pure catalysts to the mixture and repeating the ^{19}F experiment showed again only these two signals. Thus, decomposition of the catalyst can be ruled out and the combination of all these reference experiments clearly points to chalcogen bonding as the mode of action.

Table 2 NMR Yields of **3** in the Presence of the Activation Compounds after 12 h at –78 °C

Entry	Catalyst	mol%[a]	Yield (%) of **3**[b]
1	**9**^{OTf}	10	77
2	**14**^{BF4}	10	<5
3	**14**^{OTf}	10	82
4	**14**^{BArF4}	10	83
5	**15**^{BF4}	10	<5
6	**15**^{OTf}	10	6
7	**15**^{BArF4}	10	15
8	**16**^{OTf}	10	41

[a] Equivalents of catalyst with respect to **1**.
[b] ±5% measurement error assumed.

With these findings in hand, the influence of structural variations was investigated using the catalysts shown in Figure 2.

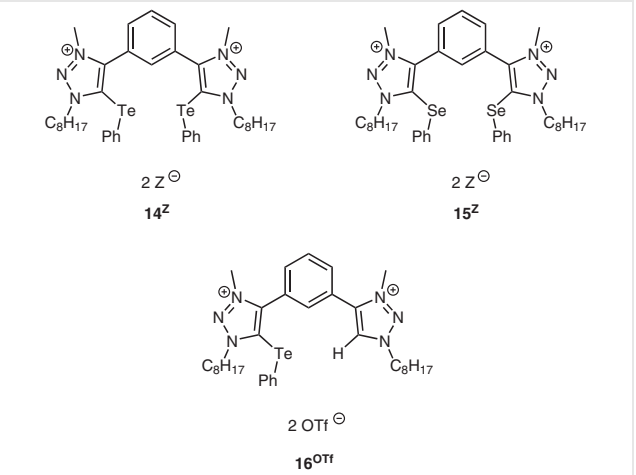

Figure 2 Tested chalcogen bond donors; Z = BF_4, OTf, BAr^F_4

Comparable activity as for **14**^{OTf} was observed for **14**^{BArF4} with 83% yield (Table 2, entry 4). Interestingly, a higher amount of diisochroman ether was formed when using BAr^F_4-containing catalysts, most likely due to increased hygroscopic properties. Since the similar yields induced by **14**^{BArF4} and **14**^{OTf} may at least be partially due to the fact that the reaction has already reached a plateau-like phase, additional kinetic measurements were performed to investigate the influence of the counterion more closely (see Figure 3). Here, a superior performance of **14**^{BArF4} was clearly observable: after 1 h, 31% of product was generated compared to 15% for **14**^{OTf}. This stronger acceleration, which is also reflected in the relative rate constants referenced to HB donor **12**^{OTf} (k_{rel} = 41 vs. k_{rel} = 20), is likely based on the weaker coordination of the BAr^F_4 counterion to the Lewis acidic chalcogen center. In addition, a kinetic profile of the reaction involving XB reference compound **13**^{OTf} was also taken and it demonstrated the even superior performance of structurally comparable XB donors in this reaction (k_{rel} = 60).

At first glance, the low performance of **14**^{BF4} may seem puzzling in light of the yields generated by **14**^{OTf}, which should feature a more coordinating counterion. When the reaction was monitored by ^{19}F NMR spectroscopy, however, the reason for this inactivity became clear, as a new septet at –171.3 ppm was observed, which is characteristic of *tert*-butyldimethylsilyl fluoride.[25] Thus, apparently fluoride transfer from BF_4^- to the released TBS^+ moiety takes place, resulting in formation of the chloride salt of the catalyst, which is not catalytically active. This finding was corroborated by measurements involving catalyst **8**, which showed that a complete conversion of BF_4^- into BF_3 takes place under reaction conditions, again yielding no product.

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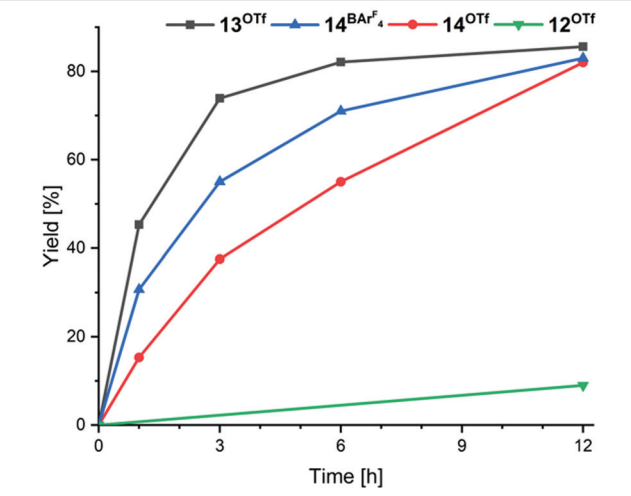

Figure 3 Kinetic plot of the chloride abstraction of **1** as yield versus time profile with ^{1}H NMR determined yields

Next, we tested the selenium-based analogues of our catalysts (Table 2, entries 5–7). It should be noted that the duration of the benchmark reaction was reduced by a factor of ten in this study compared to the experiments employing our previously reported bis(selenobenzimidazolium)-based ChB donors.[16b] The latter are also more preorganized than the core structures of the catalysts used herein. In accord with the observation of **14**^{BF4} not catalyzing the reaction, **15**^{BF4} also showed no activity (Table 2, entry 5). Triflate salt **15**^{OTf}, on the other hand, provided a slight yield of 6% (Table 2, entry 6). In this case, the less coordinating BAr^F_4 counterion leads to some improvement, as 15% yield was found for **15**^{BArF4} (Table 2, entry 7). Overall, still, all tested selenium-based ChB donors with the 1,3-bis(triazolium)benzene scaffold seem much less suitable for halide abstraction than their tellurium equivalents. The same low activity was already reported for structurally closely related 1,3-bis(imidazolium)benzene-based catalysts.[16b]

Furthermore, to determine the cooperative effect of the bidentate catalysts, monodentate analogue **16**^{OTf}, which features only one Lewis acidic tellurium center, was also applied in 10 mol% loading (Table 2, entry 8). Since hydrogen bond donor **12**^{OTf} showed little activity (Table 1, entry 8), it is reasonable to assume that the contribution of a potential additional hydrogen bond can be neglected. With compound **16**^{OTf}, a yield of 41% was observed, which is approximately half that obtained with **14**^{OTf}, and thus based on this orientating comparison, the cooperative effect does not seem very pronounced.

To obtain a better understanding of the possible geometry of a chloride complex of catalyst **14**, DFT calculations were carried out in parallel (using the M06-2X functional[26] with D3 dispersion corrections[27] and the triple-zeta TZVP basis set[28] as well as the intrinsic solvation model SMD18[29] with parameters for THF). In some contrast to the catalyst performances mentioned above, the resulting adduct (Figure 4) features two equally strong ChBs (with bond distances of 2.88 Å and angles of 164°).

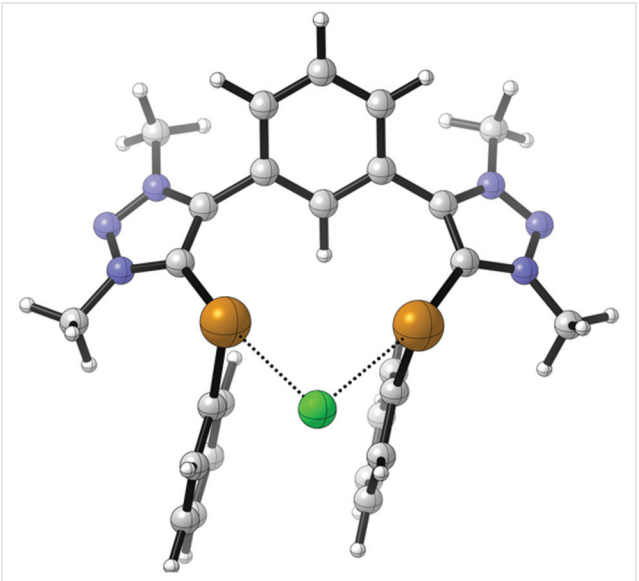

Figure 4 Calculated complex of **14** and chloride (Graphics by CYLview[30])

In conclusion, the catalytic activation of a carbon–halogen bond by bidentate and cationic tellurium-based chalcogen bond donors was presented. In line with expectations, selenium-based analogues were markedly less active while non-coordinating counterions increased the performance of the catalyst, with the exception of tetrafluoroborate, which led to fluoride transfer. Via several comparison experiments, including a stability check of a fluorine-tagged catalyst variant, the crucial role of chalcogen bonding was confirmed.

All chemicals were purchased from commercially available sources and used without further purification, if not stated otherwise. All reactions were carried out under argon atmosphere using standard Schlenk techniques, oven-dried or flame-dried glassware, and dry solvents. Dry CH_2Cl_2, Et_2O, and THF were received from a MBRAUN MB SPS-800. The solvents were distilled and dried over 4-Å molecular sieves and finally dried on an alox column. Other dry solvents were dried with flame-dried 4-Å molecular sieves. Residual water was determined by a Karl Fischer Titroline® 7500KF trace. Merck TLC aluminum sheets (silica gel 60, F254) were used for thin layer chromatography. Substances were detected by fluorescence under UV light (wavelength λ = 254 nm). Column chromatography was performed with silica gel (0.04–0.063 mm, Merck Si60) and distilled solvents. ^{1}H NMR spectra as well as ^{13}C were recorded with a Bruker AVIII 300 and a Bruker AVIII 400 spectrometer at r.t. ^{19}F NMR and ^{31}P NMR were recorded with a Bruker DPX-250 spectrometer at r.t. and were measured proton decoupled if not further noted. ESI-MS spectra were recorded with a Bruker Esquire 6000 with compounds dissolved in MeCN or MeOH. IR spectra were recorded with a Shimadzu IR

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Affinity-IS spectrophotometer. For stock solutions a Mettler Toledo XSR 105 Dual Range balance was used to weight starting material. TBTA = tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine.

Compounds **5**,[22] **11**^{Te},[18a] **11**^{Se},[18a] **12**^{OTf},[31] **13**^{OTf},[31] **14**^{BF4},[18a] **14**^{BArF4},[18a] **15**^{BF4},[18a] **15**^{BArF4}[18b] were synthesized according to literature procedures.

General Anion Exchange Procedure

The general procedure is modified from an already published procedure.[32] Amberlyst® A26 (OH) (1 g per 100 mg of the respective tetrafluoroborate salt) was suspended in MeOH (10 mL per g resin), carefully stirred and cooled to 0 °C. After 15 min, HOTf (20.0 mmol per g resin) was added dropwise over a period of 10 min. The mixture was carefully stirred for 30 min at 0 °C and then poured into a thin glass column and rinsed with MeOH until a neutral pH was obtained. Subsequently, the respective tetrafluoroborate salt dissolved in MeOH (0.05 M) was poured onto the column and rinsed slowly through the column. The collected solution was rinsed twice more through the column and finally the column was rinsed with MeOH (50 mL). The solvent was removed under reduced pressure and the residue dried under high vacuum to obtain the triflate salt.

1-Fluoro-3,5-bis(1-octyl-1*H*-1,2,3-triazol-4-yl)benzene (6)

An already published procedure was adapted for the synthesis of compound **6**.[31] In dry and degassed THF (62.5 mL, 20.0 mM), CuI (0.238 mg, 1.25 mmol, 0.10 equiv), and TBTA (0.663 g, 1.25 mmol, 0.10 equiv) were dissolved and stirred for 2 h at r.t. This mixture was added to a solution of 1,3-diethynyl-5-fluorobenzene (1.80 g, 12.5 mmol, 1.00 equiv) in dry and degassed THF (16.0 mL, 0.80 M). A solution of octyl azide (3.88 g, 25.0 mmol, 2.00 equiv) in dry and degassed THF (16 mL, 1.59 M) was slowly added over a period of 10 min. The resulting mixture was stirred at r.t. for 3 d under light exclusion. The solvent was removed under reduced pressure and the residual was taken up in EtOAc. The mixture was extracted with a basic aq EDTA solution (3 × 75 mL). The organic layer was extracted with water (2 × 100 mL) and brine (1 × 100 mL) and dried (Na_2SO_4). The solvent was removed under reduced pressure and the crude solid was purified by column chromatography (pentane/EtOAc 2:1; R_f = 0.55) to give the product as a pale yellow solid; yield: 4.97 g (10.9 mmol, 87%).

IR (ATR): 3146 (w), 2953 (m), 2918 (vs), 2853 (s), 1622 (w), 1604 (m), 1562 (w), 1470 (vs), 1427 (m), 1360 (m), 1346 (w), 1305 (w), 1227 (s), 1150 (s), 1082 (w), 1051 (m), 895 (vs), 858 (vs), 808 (vs), 791 (s), 754 (w), 721 (s), 677 (s), 654 (s), 536 (w), 496 (w), 448 (w), 410 cm^{-1} (w).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 (t, $^4J_{H-H}$ = 1.4 Hz, 1 H, C-C*H*-C), 7.84 (s, 2 H, $H_{triazole}$), 7.53 (dd, $^3J_{F-H}$ = 9.5 Hz, $^4J_{H-H}$ = 1.4 Hz, 2 H, C*H*-CF-C*H*), 4.42 (t, $^3J_{H-H}$ = 7.2 Hz, 4 H, $C_{triazole}$-CH_2-CH$_2$), 1.95 (q, $^3J_{H-H}$ = 7.3 Hz, 4 H, $C_{triazole}$-CH$_2$-CH_2), 1.29 (m, 20 H, H_{aliph}), 0.86 (m, 6 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6 (d, $^1J_{C-F}$ = 245.3 Hz, C_{arom}-F), 146.5 (d, $^4J_{C-F}$ = 2.9 Hz, CH-C-CH$_{arom}$-C-CH), 133.4 (d, $^3J_{C-F}$ = 9.1 Hz, *C*-$C_{triazole}$), 120.2 ($C_{triazole}$), 118.5 ($C_{triazole}$), 112.1 (d, $^2J_{C-F}$ = 23.3 Hz, C_{arom}F-*C*$_{arom}$H), 50.7 (C_{aliph}), 31.8 (C_{aliph}), 30.4 (C_{aliph}), 29.2 (C_{aliph}), 29.1 (C_{aliph}), 26.6 (C_{aliph}), 22.7 (C_{aliph}), 14.2 (C_{aliph}).

^{19}F NMR (235 MHz, $CDCl_3$): δ = –112.3 (s, 1 F, C_{arom}-*F*).

MS (ESI): *m*/*z* (+) calcd for [M + Na]$^+$: 477.31; found: 477.23; *m*/*z* (+) calcd for [M + K]$^+$: 493.42; found: 493.06.

1-Fluoro-3,5-bis[1-octyl-5-(phenyltellanyl)-1*H*-1,2,3-triazol-4-yl]benzene (7)

An already published procedure was adapted for the synthesis of compound **7**.[18a] In a flame-dried Schlenk flask, *i*-Pr$_2$NH (1.02 mL, 0.735 g, 7.26 mmol, 2.20 equiv) was mixed with dry THF (33.0 mL, 0.10 M) and the mixture cooled to 0 °C. Afterwards, 2.5 M *n*-BuLi (3.17 mL, 7.92 mmol, 2.40 equiv) was added dropwise over a period of 15 min and the solution was stirred for 30 min at 0 °C. The solution was then cooled to –78 °C, stirred for 15 min and **6** (1.50 g, 3.30 mmol, 1.00 equiv) in THF (33.0 mL, 0.10 M) was added dropwise. The mixture was stirred for 3 h at –78 °C and subsequently diphenyl ditelluride (3.38 g, 8.25 mmol, 2.50 equiv) in dry THF (82.5 mL, 0.10 M) was added in one portion. The mixture was stirred and warmed to r.t. for 18 h. The solvent was removed under reduced pressure and the residue purified by column chromatography (pentane/EtOAc 3:1; R_f = 0.79) to give **7** as a yellow sticky oil; yield: 1.37 g (1.59 mmol, 48%).

IR (ATR): 3067 (w), 2922 (s), 2853 (s), 1734 (w), 1616 (w), 1591 (m), 1574 (m), 1474 (m), 1435 (m), 1319 (m), 1238 (m), 1121 (w), 1017 (m), 997 (m), 905 (m), 868 (m), 802 (m), 727 (vs), 689 (vs), 652 (w), 530 (w), 451 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45 (t, ^4J = 1.5 Hz, 1 H, C-C*H*-C), 7.73 (dd, ^3J = 9.7 Hz, ^4J = 1.5 Hz, 2 H, C*H*-CF-C*H*), 7.42–7.34 [m, 4 H, Te-C-(C*H*-CH)$_2$CH], 7.26–7.09 [m, 6 H, Te-C-(CH-C*H*)$_2$C*H*], 4.51 (d, ^3J = 7.5 Hz, 4 H, N-CH_2-CH$_2$), 1.79 (p, ^3J = 7.5 Hz, 4 H, N-CH$_2$-CH_2), 1.35–1.15 (m, 20 H, H_{aliph}), 0.93–0.82 (m, 3 H, CH$_2$-CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.73 (d, $^1J_{C-F}$ = 244.8 Hz, C_{arom}-F), 153.1 (d, $^4J_{C-F}$ = 2.8 Hz, CH-C-C*H*$_{arom}$-C-CH), 136.2 (C_{arom}), 133.7 (d, $^3J_{C-F}$ = 9.1 Hz, *C*-$C_{triazole}$), 130.2 (C_{arom}), 128.6 (C_{arom}), 123.9 (C_{arom}), 115.2 (d, $^2J_{C-F}$ = 23.2 Hz, C_{arom}F-*C*$_{arom}$H), 114.2 (C_{arom}), 102.6 (C_{arom}), 51.6 (C_{aliph}), 31.9 (C_{aliph}), 30.8 (C_{aliph}), 29.2 (C_{aliph}), 29.1 (C_{aliph}), 26.6 (C_{aliph}), 22.8 (C_{aliph}), 14.2 (C_{aliph}).

^{19}F NMR (235 MHz, $CDCl_3$): δ = –112.75 (s, 1 F, C_{arom}-*F*).

MS (ESI): *m*/*z* (+) calcd for [M + Na]$^+$: 885.02; found: 885.46.

4,4′-(1-Fluoro-3,5-phenylene)bis[3-methyl-1-octyl-5-(phenyltellanyl)-1*H*-1,2,3-triazol-3-ium] Tetrafluoroborate (8)

An already published procedure was adapted for the synthesis of compound **8**.[18a] Under inert gas atmosphere, compound **7** (0.344 g, 0.399 mmol, 1.00 equiv) was dissolved in dry CH_2Cl_2 (8.00 mL, 0.05 M). Subsequently, trimethyloxonium tetrafluoroborate (0.148 g, 0.997 mmol, 2.50 equiv) was added to the yellow solution and the mixture stirred at r.t. for 18 h. The solvent was removed under reduced pressure and the residue washed with Et_2O (3 × 30 mL) and pentane (3 × 30 mL) and dried under high vacuum to obtain **13** as a pale yellow sticky solid; yield: 0.373 g (0.350 mmol, 88%).

IR (ATR): 3075 (w), 2926 (m), 2855 (m), 1603 (w), 1574 (w), 1547 (w), 1460 (w), 1435 (m), 1328 (m), 1287 (w), 1182 (w), 1047 (vs), 1030 (vs), 995 (vs), 932 (s), 887 (m), 849 (m), 732 (s), 689 (s), 654 (m), 600 (w), 519 (m), 453 cm^{-1} (m).

^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 7.87 (t, ^4J = 1.2 Hz, 2 H, C-C*H*-C), 7.56 (dd, ^3J = 8.5 Hz, ^3J = 1.3 Hz, 2 H, C*H*-CF-C*H*), 7.47 [dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 4 H, Te-C-(C*H*-CH)$_2$CH], 7.31–7.16 [m, 6 H, Te-C-(CH-C*H*)$_2$C*H*], 4.59 (d, ^3J = 7.5 Hz, 4 H, N-CH_2-CH$_2$), 4.19 (s, 6 H, N-CH_3), 1.87 (d, ^3J = 7.7 Hz, 4 H, N-CH$_2$-CH_2), 1.40–1.15 (m, 20 H, H_{aliph}), 0.94–0.83 (m, 6 H, CH$_2$-CH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 162.29 (d, $^1J_{C-F}$ = 251.8 Hz, C_{arom}-F), 147.7 (d, $^4J_{C-F}$ = 2.4 Hz, CH-C-C*H*$_{arom}$-C-CH), 137.8 (C_{arom}), 130.8 (C_{arom}), 129.7 (C_{arom}), 129.0 (C_{arom}), 127.0 (d, $^3J_{C-F}$ = 9.4 Hz, *C*-$C_{triazole}$), 121.7 (d,

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$^2J_{C-F}$ = 24.2 Hz, $C_{arom}F$-$C_{arom}H$), 114.2 (C_{arom}), 112.1 (C_{arom}), 55.6 (C_{aliph}), 39.1 (C_{aliph}), 31.8 (C_{aliph}), 29.3 (C_{aliph}), 29.0 (C_{aliph}), 28.9 (C_{aliph}), 26.36 (C_{aliph}), 22.7 (C_{aliph}), 14.2 (C_{aliph}).

^{19}F NMR (235.6 MHz, $CDCl_3$): δ = –107.1 (s, 1 F, C_{arom}-*F*), –152.6 (d, 8 F, BF_4).

MS (ESI): *m*/*z* (+) calcd for $[M - BF_4]^+$: 978.91; found: 979.33; *m*/*z* (–) calcd for $[BF_4]^-$: 86.80; found: 86.79.

4,4′-(1-Fluoro-3,5-phenylene)bis[3-methyl-1-octyl-5-(phenyltellanyl)-1*H*-1,2,3-triazol-3-ium] Triflate (8)

Compound **9** was synthesized according to the general anion exchange procedure using Amberlyst® A26 (OH) (3.40 g), MeOH (34 mL), and compound **8** (0.336 g, 0.316 mmol) dissolved in MeOH (6.32 mL) to give **9** as a pale yellow sticky solid; yield: 0.333 g (0.280 mmol, 89%).

IR (ATR): 3059 (w), 2926 (m), 2857 (w), 1603 (w), 1574 (w), 1547 (w), 1460 (w), 1435 (w), 1246 (vs), 1223 (vs), 1152 (vs), 1026 (vs), 997 (m), 932 (m), 885 (w), 851 (w), 733 (s), 689 (s), 656 (w), 635 (vs), 573 (m), 515 (vs), 453 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (t, ^4J = 1.3 Hz, 1 H, C-*CH*-C), 7.68 (dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 2 H, *CH*-CF-*CH*), 7.49 [dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 4 H, Te-C-(*CH*-CH)$_2$-CH], 7.31–7.14 [m, 6 H, Te-C-(CH-*CH*)$_2$-*CH*], 4.63 (t, ^3J = 7.8 Hz, 4 H, N-*CH*$_2$-CH$_2$), 4.23 (s, 6 H, N-*CH*$_3$), 1.87 (q, ^3J = 8.0 Hz, 4 H, N-CH$_2$-*CH*$_2$), 1.37–1.18 (m, 20 H, H_{aliph}), 0.86 (m, ^3J = 7.0 Hz, 6 H, CH$_2$-*CH*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.3 (d, $^1J_{C-F}$ = 252.4 Hz, *C*$_{arom}$-F), 147.5 (d, ^4J = 2.4 Hz, CH-C-*CH*$_{arom}$-C-CH), 137.7 (C_{arom}), 130.6 (C_{arom}), 129.6 (C_{arom}), 129.3 (C_{arom}), 126.9 (d, $^3J_{C-F}$ = 9.4 Hz, -*C*-$C_{triazole}$), 121.69 (d, $^2J_{C-F}$ = 23.8 Hz, $C_{arom}F$-*C*$_{arom}$H), 122.2 (q, $^1J_{C-F}$ = 321.9 Hz, F_3C-SO_3), 115.1 (C_{arom}), 112.8 (C_{arom}), 55.6 (C_{aliph}), 33.2 (C_{aliph}), 31.8 (C_{aliph}), 29.3 (C_{aliph}), 28.9 (C_{aliph}), 28.8 (C_{aliph}), 26.3 (C_{aliph}), 22.6 (C_{aliph}), 14.1 (C_{aliph}).

^{19}F NMR (235 MHz, $CDCl_3$): δ = –78.9 (s, 6 F, *CF*$_3$SO$_3$), –106.9 (s, 1 F, C_{arom}-*F*).

MS (ESI): *m*/*z* (+) calcd for $[M - OTf]^+$: 1041.17; found: 1041.11; *m*/*z* (+) calcd for $[M - C_6H_5]^+$: 1112.12; found: 1112.71; *m*/*z* (–) calcd [OTf]$^-$: 149.06; found 148.66.

4,4′-(1,3-Phenylene)bis[3-methyl-1-octyl-5-(phenyltellanyl)-1*H*-1,2,3-triazol-3-ium] Triflate (14^{OTf})

Compound **14**^{OTf} was synthesized according to the general anion exchange procedure using Amberlyst® A26 (OH) (4.00 g), MeOH (40 mL), and compound **14**^{BF4} (0.400 g, 0.382 mmol) dissolved in MeOH (7.64 mL) to give **14**^{OTf} as a pale yellow sticky solid; yield: 0.295 g (0.251 mmol, 66%). The spectroscopy data confirm the product **14**^{OTf}.[18a]

4,4′-(1,3-Phenylene)bis[3-methyl-1-octyl-5-(phenylselanyl)-1*H*-1,2,3-triazol-3-ium] Triflate (15^{OTf})

Compound **15**^{OTf} was synthesized according to the general anion exchange procedure using Amberlyst® A26 (OH) (4.00 g), MeOH (40 mL), and compound **15**^{BF4} (0.400 g, 0.421 mmol) dissolved in MeOH (8.42 mL) to give **15**^{OTf} as a pale yellow sticky solid; yield: 0.290 g (0.270 mmol, 64%). The spectroscopy data confirm the product **15**^{OTf}.[18b]

5-(Phenyltellanyl)-4,4′-(1,3-phenylene)bis(3-methyl-1-octyl-1*H*-1,2,3-triazol-3-ium) Triflate (16^{OTf})

Compound **16**^{OTf} was synthesized according to the general anion exchange procedure using Amberlyst® A26 (OH) (2.50 g), MeOH (25 mL), and tetrafluoroborate salt (0.250 g, 0.296 mmol) dissolved in MeOH (5.92 mL) to give **16**^{OTf} as a pale yellow sticky solid; yield: 0.205 g (0.213 mmol, 72%).

IR (ATR): 3078 (w), 2955 (w), 2926 (m), 2857 (w), 1572 (w), 1466 (w), 1437 (w), 1252 (vs), 1223 (vs), 1152 (vs), 1028 (vs), 997 (w), 916 (w), 837 (w), 808 (w), 754 (w), 737 (m), 691 (m), 635 (vs), 573 (m), 517 (vs), 455 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.00 (s, 1 H, $H_{triazole}$), 8.16 (d, ^4J = 1.4 Hz, 1 H, C-*CH*-C), 8.03 (dt, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 1 H, C-CH-CH-*CH*-C), 7.80 (dt, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1 H, C-*CH*-CH-CH-C), 7.68 (t, ^3J = 7.8 Hz, 1 H, C-CH-*CH*-CH-C), 7.47 [dt, ^3J = 6.9 Hz, ^4J = 1.4 Hz, 2 H, Te-C-(*CH*-CH)$_2$CH], 7.31–7.13 [m, 4 H, Te-C-(CH-*CH*)$_2$*CH*], 4.65 (t, ^3J = 7.7 Hz, 2 H, $C_{triaz.H}$-*CH*$_2$-CH$_2$), 4.60 (t, ^3J = 7.5 Hz, 2 H, $C_{triaz.TePh}$-*CH*$_2$-CH$_2$), 4.35 (s, 3 H, $N_{triaz.H}$-*CH*$_3$), 4.19 (s, 3 H, $N_{triaz.TePh}$-*CH*$_3$), 2.08 (q, ^3J = 7.5 Hz, 2 H, $C_{triaz.H}$-CH$_2$-*CH*$_2$), 1.91 (p, ^3J = 7.7 Hz, 2 H, $C_{triaz.TePh}$-CH$_2$-*CH*$_2$), 1.49–1.18 (m, 20 H, H_{aliph}), 0.94–0.82 (m, 6 H, CH$_2$-*CH*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.5 (C_{arom}), 142.1 (C_{arom}), 138.9 (C_{arom}), 138.3 (C_{arom}), 133.8 (C_{arom}), 132.8 (C_{arom}), 131.8 (C_{arom}), 131.0 (C_{arom}), 130.6 (C_{arom}), 130.5 (C_{arom}), 129.7 (C_{arom}), 125.4 (C_{arom}), 123.5 (C_{arom}), 121.84 (q, $^1J_{C-F}$ = 319.6 Hz, F_3C-SO_3), 115.2 (C_{arom}), 112.7 (C_{arom}), 55.6 (C_{aliph}), 54.6 (C_{aliph}), 39.4 (C_{aliph}), 39.1 (C_{aliph}), 31.8 (C_{aliph}), 29.4 (C_{aliph}), 29.3 (C_{aliph}), 29.0 (C_{aliph}), 28.9 (C_{aliph}), 26.4 (C_{aliph}), 26.3 (C_{aliph}), 22.7 (C_{aliph}), 14.2 (C_{aliph}).

^{19}F NMR (235 MHz, $CDCl_3$): δ = –78.5 (s, *CF*$_3$SO$_3$).

MS (ESI): *m*/*z* (+) calcd for $[M - OTf]^+$: 821.16; found: 820.92; *m*/*z* (–) calcd for [OTf]$^-$: 149.06; found: 148.67.

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Supporting Information

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