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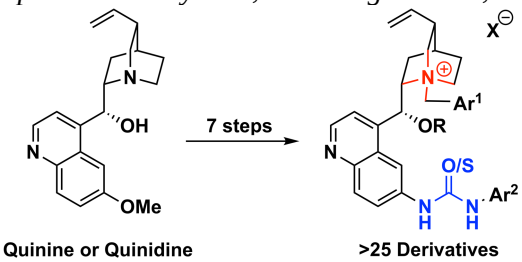

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ABSTRACT

A flexible and functional group tolerant synthesis route to access a structurally diverse collection of bifunctional 6'-(thio)-urea containing Cinchona alkaloid-based chiral quaternary ammonium salts has been developed. This route gives access to more than 25 different novel urea- and thiourea-containing ammonium salt derivatives, which were not accessible so far.

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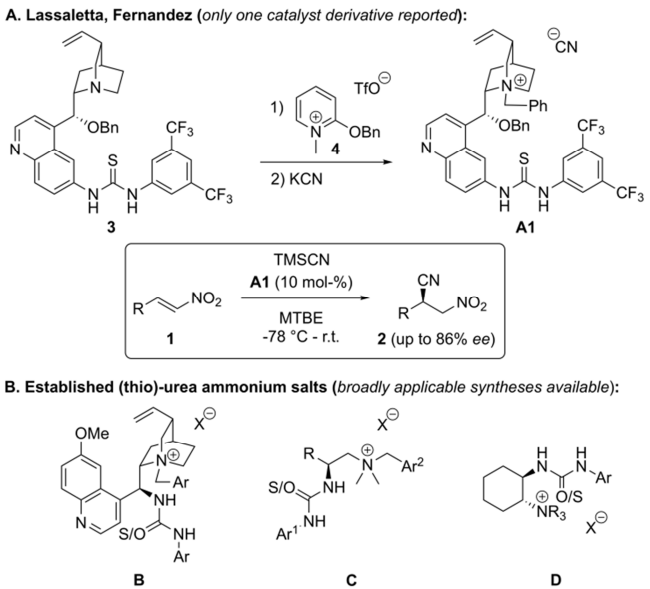
1. Introduction

Chiral quaternary ammonium salt phase-transfer catalysis has established itself as a unique and powerful asymmetric catalysis concept for more than four decades already.[1,2] Following the pioneering reports by the group of Wynberg[3] and a team of Merck scientist[4] in the late 1970's and early 1980's, the use of chiral Cinchona alkaloid ammonium salt catalysts became a heavily investigated topic. Spectacular contributions with respect to catalyst design and their applications by i.e. the groups of O'Donnell,[5] Lygo,[6] and Corey[7] established chiral Cinchona alkaloid-based ammonium salts as one of the privileged classes of non-covalently interacting asymmetric ion-pairing organocatalysts. Besides the use of Cinchona alkaloids as readily available naturally occurring chiral backbones, also the utilization of alternative chiral platforms for the development of a variety of other powerful ammonium salt phase-transfer catalysts has been reported over the course of the last two decades.[8]

Right from the seminal reports by Wynberg[3] and Merck scientists[4] it became obvious that the presence of an OH-group as an additional H-bonding unit besides the quaternary ammonium group can be beneficial to achieve high levels of enantioselectivities and good catalyst turnover. Thus, it comes as no surprise that especially the development of bifunctional ammonium salts became a topic of significant interest.[2] While OH-containing Cinchona ammonium salts and later on OH-containing Maruoka-type catalysts[9] have systematically been designed and are now routinely used in asymmetric catalysis,[10] the use of chiral ammonium salts with additional H-bonding donors, i.e. ureas or thioureas,[11] has a much shorter history.[2,12-17]

The first report describing the synthesis of a thiourea-containing chiral ammonium salt (again Cinchona alkaloid-based) and its use as a highly efficient organocatalysts was reported by the group of Fernandez and Lassaletta in 2010.[12] In this remarkable approach, they introduced the catalyst **A1** for asymmetric 1,4-additions of TMSCN to nitroalkenes **1** (Scheme 1A). Unfortunately however, only one catalyst derivative was accessed, which can be attributed to the rather demanding synthesis, which required the use of reagent **4** to achieve the quaternarization of the thiourea **3**, and no further applications of this catalyst have been reported since that. From 2012 on, several groups then independently reported the design and use of alternative bifunctional (thio)-urea containing ammonium salts (Scheme 1B). Dixon and Smith introduced the 9-substituted Cinchona salts **B**.[13] First only a few derivatives were reported, but later on very robust protocols to access libraries were developed and these catalysts are now frequently used for a variety of asymmetric target reactions.[14] Exploring other chiral backbones for their potential to access novel bifunctional ammonium salts, α-amino acids have been successfully employed by Zhao and co-workers first,[15] and have since then very frequently been used to access powerful and structurally diverse libraries of bifunctional ammonium salts **C** (the analogous quaternary phosphonium salts have been well-described either).[16,17]

In 2014, we introduced a modular and flexible protocol to access an easily tunable class of trans-cyclohexane-1,2-diamine-based ammonium salts **D**, and these catalysts have since then been used for numerous asymmetric applications as well.[18]



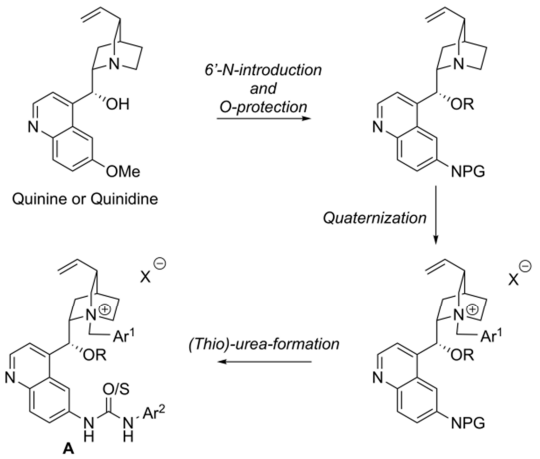
Scheme 1: Overview of the most-commonly described classes of (thio)-urea-containing chiral ammonium salt catalysts.

Based on the achievements made in syntheses and applications of (thio)-urea/ammonium salt hybrid systems so far, it is obvious that these catalysts have a very big potential for asymmetric non-covalent organocatalysis. Crucial for the success of catalyst classes **B**-**D** was the availability of robust and flexible syntheses routes that allowed for a fast and relatively simple catalyst optimization and fine-tuning for a given target reaction. Unfortunately however, this has so far not been achieved for the Cinchona catalysts **A**. Based on our general interest in the field, and considering our own experience with ammonium salts **D**,[18] we now targeted the development of a robust and flexible synthesis route to access a library of catalysts **A**. This route should first of all allow for the installation of ureas and thioureas. Both have been successfully reported for the other bifunctional systems in the past,[13-18] but it is also fair to say that for both, ureas and thioureas, in the majority of examples so far, the privileged 3,5-bis-CF_3-phenyl-derivatives outperformed other derivatives (exceptions were of course reported). The second major goal was to find a route that allows especially for high structural diversity on the ammonium side, as fine-tuning on this side was often very crucial for the more-established alternative systems **B**-**D**.[13-18]

2. Results and Discussion

As reported in the original paper by Fernandez and Lassaletta,[12] the installation of the quaternary ammonium group in the presence of the thiourea motive is a rather difficult task, and we observed the same challenges when we tried to synthesize catalysts **D** by first installing the (thio)-urea, followed by a final quaternization (interestingly however, this works well for catalysts **C**,[15-17] demonstrating that the structural features of the chiral backbone have a strong consequence for the required synthesis strategy). For hybrid salts **D** we succeeded in overcoming these obstacles by developing a flexible synthesis route where we first installed the ammonium group, followed by a final stage introduction of the H-bonding motive.[18] Interestingly, such a strategy was recently also successfully applied to the synthesis of a diverse library of catalysts **B**.[14e]

Accordingly, we now focused on the development of an analogous assembly procedure to overcome the existing limitations for the syntheses of Cinchona catalysts **A**. As outlined in Scheme 2, our plan was to introduce the protected 6'-N functionality first (starting from either quinine or quinidine), followed by quaternization of the quinuclidine ring next, and a final 6'-N-deprotection and (thio)-urea formation.

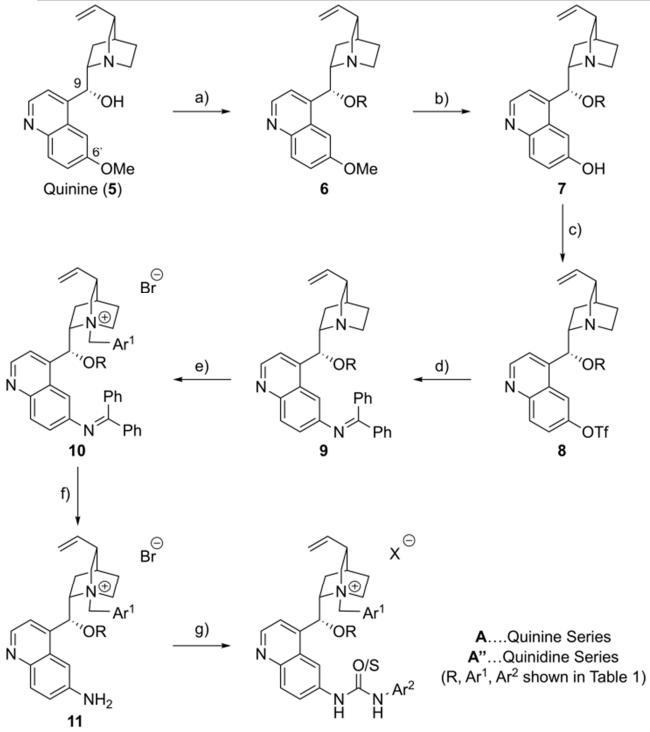


Scheme 2: Targeted general route to access bifunctional catalysts **A**.

We started by carrying out the alkylation of the 9-OH group with benzylbromide, allylbromide and methyliodide following slightly adapted literature procedures[19] to obtain the 9-O-alkylated compounds **6** for both, the quinine and the quinidine series in yields higher than 87% (Scheme 3). The introduction of a free amino group in the 6'-position of the Cinchona skeleton starting from quinine or quinidine derivatives was very nicely developed by Hiemstra's group some years ago,[20] and in general their synthesis strategy to access the intermediate imines **9** was found to be rather straightforward and suited for our targeted route as well. First, the 6'-OMe group had to be demethylated, which was achieved by using NaSEt in DMF at elevated temperature (110 °C). This gave the cupreine and cupreidine derivatives **7**[21] in reliable yields of around 90% or higher. Using BBr_3 to facilitate the demethylation[22] was possible as well, but we found the NaSEt conditions somewhat more robust, especially with respect to the suppression of potential impurities that may interfere in the subsequent steps. Triflation of the 6'-OH group following Hiemstra's protocol[21] then gave the triflates **8** in satisfying yields. In general, conversion of **7** to the triflates **8** was found to be quantitative and it would be possible to employ crude **8** further, with purification on a later stage only. However, as the next three steps were then carried out without any purification step (as outlined below), it turned out to be beneficial with respect to the overall yield and also the easy of further purification to submit triflates **8** to silica gel column chromatography.

To install the amino group, these triflates were then subjected to a Pd-catalyzed Buchwald-Hartwig type coupling[23] with benzophenone imine giving the imines **9** (complete conversion of the triflates). Attempts to purify these imines by column chromatography always lead to a relatively fast imine hydrolysis and we originally thought that it will be most practical for the rest of the sequence to hydrolyze the imines **9** quantitatively (which is easily achieved upon treatment with citric acid) and introduce a more stable N-protecting group for the following quinuclidine quaternization. For catalysts **D** an N-Boc-protecting group was found to be best-suited for such a strategy.[18] In general, adapting this protecting group concept was possible herein as well, but the Boc-protection as well as the deprotection were found to be not straightforward in our first attempts (i.e. requiring tedious column chromatography purifications). Gratifyingly however, we realized that such a detour (requiring at least two additional chemical steps) was not necessary at all, as the benzophenone served well as a 6'-N-protecting group under neutral quaternization conditions. Thus, it was possible to carry out a direct and selective N-alkylation of the quinuclidine nitrogen by reacting imines **9** with various benzylic bromides (Table 1 contains the details of the groups that were successfully introduced). The quaternary ammonium salt imines **10** were then directly hydrolyzed with citric acid to access the novel 6'-NH_2-containing Cinchona ammonium salts **11**. These compounds were purified by column chromatography and could be obtained in isolated yields ranging from 33-85% over three steps. It should be noted that this procedure was not perfectly optimized for some of the lower yielding examples, but considering the straightforward procedure, avoiding any column chromatography purification on intermediates **9** and **10**, this approach reliably delivers reasonable quantities of differently substituted clean amines **11**. From a practical point of view, it was encouraging that the use of less clean intermediates for this sequence was still possible, as the column chromatographic purification of compounds **11** allows for the reliable removal of impurities originating from the early steps as well. Interestingly, the groups of Xie and Ma successfully used 9-NH_2-containing Cinchona alkaloid ammonium salts as asymmetric phase-transfer catalysts,[24] and given this interesting report the herein synthesized 6'-NH_2-Cinchona ammonium salts **11** may also be worth being tested in future asymmetric applications.

Finally, the last step that was necessary to achieve the main goal of these investigations was to couple the clean amines **11** with different iso(thio)cyanates. Considering the privileged role of 3,5-bis-CF_3-phenyl-based ureas and thioureas in asymmetric H-bonding catalysis in general,[25] and based on the fact that these groups were also the most generally used ones for the other chiral ammonium salt/H-bonding hybrid catalysts **B**-**D**, our main focus was clearly on the synthesis of catalysts **A** containing such a thiourea- or urea-group. However, we also demonstrated that some other (thio)-ureas can easily be introduced as well and considering this generality, we are confident that, in case other derivatives are necessary for a given reaction optimization, different iso(thio)cyanates should easily be introduced as well.



Scheme 3: Developed Synthesis route: a) RX (BnBr, allylbromide, MeI), KH or NaH in DMF or THF, r.t. (86-98%); b) NaSEt, DMF, 110 °C (> 90%); c) $PhNTf_2$, DMAP, CH_2Cl_2, r.t. (67-91%); d) $Ph_2C{=}NH$, $Pd(OAc)_2$, BINAP, Cs_2CO_3, THF, 65 °C; e) Ar^1CH_2Br, toluene, 65 °C; f) citric acid, H_2O/THF, r.t. (33-85% over three steps); g) Ar^2NCO/S, CH_2Cl_2, r.t. (37-91%).

Table 1 gives an overview of the ammonium salt derivatives that we synthesized so far (all compounds were isolated as the corresponding ammonium bromides). However, it should be pointed out that this is really just a representative first collection to demonstrate the generality of this flexible synthesis route. Overall this strategy works for different urea and thiourea groups Ar^2, allows to incorporate different ammonium substituents Ar^1 and different 9-O-alkyl groups R, and can be employed for both, quinine and quinidine-based hybrid catalysts **A** and **A''** straightforwardly.

Table 1. Hybrid ammonium salts accessed so far following the general route outlined in Scheme 2

Entry	Quinine Series	Quinidine Series	R	Ar^1	Ar^2	Counteranion X^-	(Thio)-Urea	Yield[a] (%)
1	**A1**	-	Bn-	Ph-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	56
2	**A2**	-	Bn-	Ph-	4-CH_3-C_6H_4-Ph-	Br^-	S	54
3	**A3**	-	Bn-	Ph-	Ph-	Br^-	S	59
4	**A4**	-	Bn-	Ph-	Ph-	Br^-	O	47
5	**A5**	-	Bn-	Ph-	3-NO_2-C_6H_4-	Br^-	O	64
6	**A6**	-	Bn-	Ph-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	O	46
7	**A7**	-	Bn-	4-CF_3-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	85
8	**A8**	-	Bn-	4-tBu-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	61
9	**A9**	-	Bn-	3-Ph-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	61
10	**A10**	-	Bn-	β-Np-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	37
11	**A11**	-	Allyl-	Ph-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	55
12	**A12**	-	Allyl-	4-CF_3-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	40
13	**A13**	-	Allyl-	4-tBu-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	38
14	**A14**	-	Allyl-	3-Ph-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	46
15	**A15**	-	Allyl-	3-MeO-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	71
16	**A16**	-	Allyl-	β-Np-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	46
17	**A17**	-	Me-	Ph-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	37
18	**A18**	-	Me-	Ph-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	O	46
19	**A19**	-	Me-	4-CF_3-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	42
20	**A20**	-	Me-	4-tBu-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	40
21	**A21**	-	Me-	3-Ph-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	91
22	**A22**	-	Me-	3-MeO-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	42
23	-	**A''23**	Bn-	Ph-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	43
24	-	**A''24**	Bn-	3-MeO-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	60
25	-	**A''25**	Bn-	4-CF_3-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	63
26	-	**A''26**	Allyl-	Ph-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	42
27	-	**A''27**	Me-	Ph-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	O	39
28	-	**A''28**	Me-	4-tBu-C_6H_4-	3,5-$(CF_3)_2$-C_6H_3-	Br^-	S	42

a) Isolated yield based on amine **11**.

3. Conclusion

A flexible synthesis route to access a structurally diverse collection of bifunctional 6'-(thio)-urea containing Cinchona alkaloid quaternary ammonium salt catalysts **A** (starting from quinine) and **A''** (quinidine-based) has been developed. This protocol allows to overcome the limitations of the previously reported original synthesis route[12] (which unfortunately delivered one derivative only). Key to success allowing for a flexible synthesis was to introduce the quaternary ammonium group first, followed by a final (thio)-urea introduction, which gave more than 20 derivatives straightforwardly.

4. Experimental section

General Information

^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded on a Bruker Avance III 300 MHz spectrometer with a broad band observe probe. All spectra were referenced on the solvent peak, the chemical shifts are given in ppm.

High resolution mass spectra for the final catalysts were obtained using an Agilent 6520 Q-TOF mass spectrometer with an ESI source and an Agilent G1607A coaxial sprayer or a Thermo Fisher Scientific LTQ Orbitrap XL with an Ion Max API Source. Mass spectra for the intermediates were obtained using an Agilent LC/MSD Trap SL. Analyses were made in the positive ionization mode if not otherwise stated.

Preparative column chromatography was carried out using Davisil LC 60A 70-200 MICRON silica gel. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. THF and toluene were distilled over sodium under Ar atmosphere prior to use. All reactions were carried out under Argon.

General procedures for the 9-O-alkylation of quinine and quinidine (Syntheses of compounds **6***)*

Allylation and Benzylation: A solution of quinine/quinidine **5** in dry DMF (4 mL/mmol **5**) was treated with dry NaH (2.8 equiv.) and the resulting mixture was stirred at r.t. for 2 h. Benzyl chloride or allyl bromide (1.1 equiv.) were added and the resulting mixture was stirred at r.t. for 20 h. After extraction with brine and EtOAc the organic phase was dried over Na_2SO_4, filtrated and evaporated to dryness, giving 9-O-allylated or 9-O-benzylated compounds **6**[26] in > 87% yield and sufficient purity for the following steps.

Methylation: A solution of **5** in dry THF (3 mL/mmol **5**) was added slowly to a suspension of dry KH (3 equiv.) in dry THF (0.8 mL/mmol **5**) at 0 °C. The resulting mixture was first stirred at 0 °C for 30 min and then heated to 50 °C for 30 min. After cooling to 0 °C again, methyl iodide (1.05 equiv.) was added dropwise and the resulting mixture was stirred and allowed to warm to r.t. over night (12-14 h). After extraction with brine and EtOAc the organic phase was dried over Na_2SO_4, filtrated and evaporated to dryness, giving 9-O-methylated compounds **6**[26] in almost quantitative yield and sufficient purity for the following steps.

General procedure for the 6'-O-demethylation (Syntheses of compounds **7***)*

Sodium ethanolate (4.4 equiv) was weighed in a Young flask and a solution of **6** in dry DMF (6.3 mL/mmol **6**) was added. The flask was flushed with Ar, closed and heated to 110 °C for 5 days. Then, a saturated aq. solution of NH_4Cl was added and the mixture was extracted with EtOAc twice. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and evaporated to dryness to afford compounds **7**[26] in almost quantitative yield and sufficient purity for the following steps.

General procedure for the 6'-O-triflation (Syntheses of compounds **8***)*

Starting material **7** was dissolved in dry CH_2Cl_2 (15 mL/mmol **7**) and DMAP (0.2 equiv.) and $PhNTf_2$ (1.2 equiv.) were added and the mixture was stirred for 24 h. Then the solvent was evaporated and the remaining residue taken up in EtOAc, washed with brine, and the organic layer was dried over Na_2SO_4, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/MeOH = 20/1) to afford compounds **8**[26] in up to 90% yields.

General procedure for Buchwald-Hartwig reaction (Syntheses of compounds **9***)*

$Pd(OAc)_2$ (0.05 eq), racemic BINAP (0.1 equiv.) and Cs_2CO_3 (1.6 equiv.) were weighed into a Young flask and a solution of the triflate **8** in dry THF (10 mL/mmol **8**) and the benzophenone imine (Ph_2C=NH; 1.2 equiv.) were added. Subsequently, the flask was flushed with argon, closed and heated to 65-70 °C for 3-5 days. Then, the solution was cooled to r.t. and filtered through a pad of Celite. The filter cake was washed with CH_2Cl_2 and the filtrate was evaporated to obtain the imines **9**[26] that were used for the next step without further purification.

General quaternization procedure (Syntheses of compounds **10***)*

The crude imines **9** were dissolved in dry toluene (1.5 mL/mmol **9**) and the different benzyl bromides (1.05 equiv.) were added and the resulting mixture was stirred overnight at 65 °C. The solvent was evaporated and the crude products **10**[26] were used for the next step without further purification.

General N-deprotection procedure (Syntheses of compounds **11***)*

The crude imines **10** were dissolved in THF (6 mL/mmol **10**). Then, an aqueous solution of citric acid (10%, 13 mL/mmol **10**) was added and the resulting mixture was stirred overnight, followed by addition of a saturated solution of Na_2CO_3 (60 mL/mmol **10**). The mixture was extracted with CH_2Cl_2 and the combined organic phases were washed with brine, dried over Na_2SO_4, and evaporated to dryness. The crude products were purified by column chromatography (silica gel, CH_2Cl_2/MeOH/Et_2NH = 20/1/0.8 or CH_2Cl_2/2-PrOH = 10/1) and dried in vacuo to afford the pure amines **11**[26] in 33-85% yield (over three steps).

General procedure for the (thio)-urea formation (Syntheses of final ammonium salts **A***)*

The amines **11** were dissolved in CH_2Cl_2 (20 mL/mmol **11**) and the corresponding iso(thio)cyanates (1.2 equiv.) were added. The resulting mixture was stirred at r.t. overnight. The solvent was evaporated and the crude products were purified by column chromatography (silica gel, CH_2Cl_2 /MeOH = 20/1 to 10/1 or CH_2Cl_2 /2-PrOH = 10/1) to afford the ammonium salts **A**[26].

Details of (thio)-urea-containing ammonium salts ***A***

Ammonium salt **A1**: Obtained in 56% yield (585 mg) starting from 707 mg (1.23 mmol) of the corresponding amine **11c**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 12.08 (s, 1 H), 10.64 (s, 1 H), 8.92 (d, *J* = 4.4 Hz, 1 H), 8.63 (d, *J* = 9.0 Hz, 1 H), 8.42 (s, 1 H), 8.31 (s, 2 H), 8.10 (d, *J* = 9.0 Hz, 1 H), 7.61 (d, *J* = 4.3 Hz, 1 H), 7.56 (s, 1 H), 7.51-7.40 (m, 10 H), 6.18 (s, 1 H), 5.59-5.44 (m, 2 H), 5.31-5.25 (m, 1 H), 5.03-4.96 (m, 2 H), 4.44 (d, *J* = 11.8 Hz, 1 H), 4.26 (t, *J* = 9.4 Hz, 1 H), 4.13-3.93 (m, 3 H), 3.20-3.12 (m, 2 H), 2.56 (bs, 1 H), 2.19-2.03 (m, 3 H), 1.80-1.61 (m, 1 H), 1.46-1.38 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.1, 148.5, 146.0, 140.8, 139.3, 138.2, 135.8, 135.4, 133.7, 131.5, 131.0, 130.7, 129.7, 129.4, 126.5, 126.0, 125.1, 124.8, 123.4, 121.5, 119.2, 118.4, 117.6, 112.1, 72.2, 71.6, 67.1, 63.3, 60.4, 50.5, 37.5, 26.4, 25.0, 22.2; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.7; HRMS (ESI+): m/z calcd. for $C_{42}H_{39}F_6N_4OS$ $[M\text{-}Br]^+$: 761.2743, found: 761.2743.

Ammonium salt **A2**: Obtained in 54% yield (38 mg) starting from 57 mg (0.10 mmol) of the corresponding amine **11c**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.75 (s, 1 H), 9.50 (s, 1 H), 8.98 (d, *J* = 10.6 Hz, 1 H), 8.91 (d, *J* = 4.4 Hz, 1 H), 8.17 -8.13 (m, 2 H), 7.58-7.37 (m, 8 H), 7.20 (t, *J* = 7.7 Hz, 1 H), 6.95 (d, *J* = 7.3 Hz, 1 H), 6.10 (s, 1 H), 5.73 (d, *J* = 11.3 Hz, 1 H), 5.66-5.55 (m, 1 H), 5.41-5.29 (m, 2 H), 5.06-4.93 (m, 2 H), 4.43-4.28 (m, 3 H), 4.13 (bs, 1 H), 3.91 (d, *J* = 11.9 Hz, 1 H), 3.18-3.10 (m, 2 H), 2.54 (bs, 1 H), 2.33 (s, 3 H), 2.16-2.06 (m, 5 H), 1.78-1.71 (m, 1 H), 01.45-1.38 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.6, 147.6, 140.1, 138.8, 138.2, 135.9, 133.9, 130.8, 129.7, 129.4, 128.1, 127.8, 126.4, 126.1. 125.1, 122.1, 120.6, 119.2, 118.5, 117.1, 72.6, 71.7, 66.9, 60.4, 50.7, 49.9, 44.0, 42.3, 41.7, 37.6, 26.6, 25.0, 22.2, 21.4, 14.0;

HRMS (ESI+): m/z calcd. for $C_{41}H_{43}N_4OS$ $[M\text{-}Br]^+$: 639.3152, found: 639.3154.

Ammonium salt **A3**: Obtained in 59% yield (14.5 mg) starting from 20 mg (0.035 mmol) of the corresponding amine **11c**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.84 (s, 1 H), 9.60 (s, 1 H), 9.02 (dd, J_1 = 1.9 Hz, J_2 = 9.2 Hz, 1 H), 8.91 (d, J = 4.4 Hz, 1 H), 8.16 (d, J = 9.2 Hz, 1 H), 8.09 (d, J = 1.8 Hz, 1 H), 7.70 (d, J = 7.5 Hz, 2 H), 7.58 (d, J = 4.5 Hz, 1 H), 7.53-7.39 (m, 11 H), 7.32 (t, J = 7.6 Hz, 2 H), 6.10 (s, 1 H), 5.70 (d, J = 11.6 Hz, 1 H), 5.63-5.52 (m, 1 H), 5.36 (d, J = 17.2 Hz, 1 H), 5.05 (dd, J_1 = 1.2 Hz, J_2 = 10.4 Hz, 1 H), 4.96 (d, J = 11.9 Hz, 1 H), 4.44-4.28 (m, 3 H), 4.14-4.08 (m, 1 H), 3.89 (d, J = 11.7 Hz, 1 H), 3.18-3.10 (m, 2 H), 2.54 (bs, 1 H), 2.16-2.07 (m, 4 H), 1.46-1.38 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.8, 148.2, 146.0, 140.4, 139.1, 137.9, 135.9, 135.5, 134.0, 130.8, 130.4, 129.8, 129.4, 129.3, 128.4, 127.4, 126.4, 125.3, 124.9, 119.0, 118.7, 112.1, 72.6, 71.7, 66.6, 62.6, 60.3, 50.6, 37.6, 26.6, 25.1, 22.5; HRMS (ESI+): m/z calcd. for $C_{40}H_{41}N_4OS$ $[M\text{-}Br]^+$: 625.2996, found: 625.2999.

Ammonium salt **A4**: Obtained in 47% yield (11.2 mg) starting from 20 mg (0.035 mmol) of the corresponding amine **11c**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 10.65 (s, 1 H), 8.85 (d, J = 4.5 Hz, 1 H), 8.71 (dd, J_1 = 1.8 Hz, J_2 = 9.2 Hz, 1 H), 8.38 (s, 1 H), 8.12 (d, J = 9.3 Hz, 1 H), 7.91 (s, 1 H), 7.60-7.42 (m, 16 H), 6.08 (s, 1 H), 5.80 (d, J = 11.8 Hz, 1 H), 5.64-5.53 (m, 1 H), 5.42 (d, J = 17.5 Hz, 1 H), 5.07 (dd, J_1 = 1.2 Hz, J_2 = 10.3 Hz, 1 H), 4.95 (d, J = 11.7 Hz, 1 H), 4.43 (d, J = 11.8 Hz, 1 H), 4.37-4.31 (m, 1 H), 4.16-4.10 (m, 1 H), 4.03 (d, J = 11.7 Hz, 1 H), 3.21-3.13 (m, 2 H), 2.58 (bs, 1 H), 2.16-2.08 (m, 3 H), 1.77-1.71 (m, 1 H), 1.47-1.42 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 153.6, 147.3, 141.1, 139.6, 137.4, 135.9, 135.8, 134.2, 131.5, 130.9, 129.8, 129.7, 129.4, 128.8, 126.6, 125.5, 124.1, 122.5, 119.4, 119.1, 118.7, 106.9, 73.2, 72.0, 66.6, 62.8, 60.1, 50.6, 37.7, 26.6, 25.3, 22.6; HRMS (ESI+): m/z calcd. for $C_{40}H_{41}N_4O_2$ $[M\text{-}Br]^+$: 609.3224, found: 609.3224.

Ammonium salt **A5**: Obtained in 64% yield (16.5 mg) starting from 20 mg (0.035 mmol) of the corresponding amine **11c**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 10.59 (s, 1 H), 9.19 (s, 1 H), 8.83 (d, J = 4.4 Hz, 1 H), 8.49-8.47 (m, 1 H), 8.25 (d, J = 9.1 Hz, 1 H), 8.08 (s, 1 H), 7.95 (d, J = 9.2 Hz, 1 H), 7.72 (dd, J_1 = 1.4 Hz, J_2 = 8.1 Hz, 1 H), 7.60 (dd, J_1 = 1.2 Hz, J_2 = 8.1 Hz, 1 H), 7.55 (d, J = 5.0 Hz, 2 H), 7.50-7.48 (m, 5 H), 7.47-7.40 (m, 5 H), 6.31 (s, 1 H), 5.62-5.51 (m, 2 H), 5.35-5.28 (m, 1 H), 5.04 (dd, J_1 = 1.3 Hz, J_2 = 10.5 Hz, 1 H), 4.95 (d, J = 11.6 Hz, 1 H), 4.68 (d, J = 11.6 Hz, 1 H), 4.43 (d, J = 11.8 Hz, 1 H), 4.31 (t, J = 9.3 Hz, 1 H), 4.18-4.08 (m, 2 H), 3.29-3.14 (m, 2 H), 2.57 (bs, 1 H), 2.21-2.08 (m, 3 H), 1.50-1.42 (m, 1 H), 1.25-1.20 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 153.3, 148.6, 147.6, 145.1, 141.0, 139.9, 137.9, 136.0, 135.9, 134.1, 131.4, 130.9, 129.7, 129.5, 129.3, 129.2, 126.5, 125.4, 124.7, 123.7, 119.1, 118.5, 116.7, 113.3, 107.3, 72.9, 71.8, 67.2, 63.7, 60.2, 50.5, 37.7, 26.6, 25.2, 22.2; HRMS (ESI+): m/z calcd. for $C_{40}H_{40}N_5O_4$ $[M\text{-}Br]^+$: 654.3075, found: 654.3076.

Ammonium salt **A6**: Obtained in 46% yield (61 mg) starting from 89 mg (0.16 mmol) of the corresponding amine **11c**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 10.63 (s, 1 H), 8.96 (s, 1 H), 8.85 (d, J = 4.5 Hz, 1 H), 8.54 (d, J = 9.5 Hz, 1 H), 8.08 (d, J = 9.3 Hz, 1 H), 8.04 (s, 2 H), 7.94 (d, J = 1.7 Hz, 1 H), 7.58 (d, J = 4.5 Hz, 1 H), 7.53-7.39 (m, 11 H), 6.15 (s, 1 H), 5.64-5.52 (m, 2 H), 5.42-5.36 (m, 1 H), 5.04 (dd, J_1 = 10.3 Hz, J_2 = 1.1 Hz, 1 H), 4.95 (d, J = 11.7 Hz, 1 H), 4.46 (d, J = 11.7 Hz, 1 H), 4.31-4.26 (m, 2 H), 4.14-4.00 (m, 2 H), 3.25-3.13 (m, 2 H), 2.58 (bs, 1 H), 2.17-1.90 (m, 3 H), 1.78-1.67 (m, 1 H), 1.47-1.39 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 152.9, 147.6, 145.1, 141.0, 139.8, 137.6, 135.8, 135.5, 133.8, 132.0, 131.5, 130.8, 129.6, 129.5, 129.3, 129.1, 126.1, 125.3, 123.5, 121.6, 119.2, 118.4, 107.2, 72.9, 72.0, 66.5, 62.9, 60.1, 50.5, 37.5, 26.4, 25.0, 22.4; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{42}H_{39}F_6N_4O_2$ $[M\text{-}Br]^+$: 745.2972, found: 745.2975.

Ammonium salt **A7**: Obtained in 85% yield (124 mg) starting from 100 mg (0.16 mmol) of the corresponding amine **11n**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.66 (s, 1 H), 10.15 (s, 1 H), 8.93 (d, J = 4.5 Hz, 1 H), 8.70 (d, J = 9.0 Hz, 1 H), 8.30 (s, 1 H), 8.25 (s, 2 H), 8.07 (d, J = 9.4 Hz, 1 H), 7.70-7.41 (m, 11 H), 6.22 (s, 1 H), 5.71 (d, J = 12.0 Hz, 1 H), 5.57 (ddd, J_1 = 16.8 Hz, J_2 = 10.3 Hz, J_3 = 5.9 Hz, 1 H), 5.36-5.30 (m, 1 H), 5.06 (d, J = 10.3 Hz, 1 H), 5.00 (d, J = 12.0 Hz, 1 H), 4.46 (d, J = 11.8 Hz, 1 H), 4.32-4.16 (m, 3 H), 4.05 (d, J = 11.8 Hz, 1 H), 3.17-3.04 (m, 2 H), 2.58 (bs, 1 H), 2.25-2.05 (m, 2 H), 1.83-1.70 (m, 2 H), 1.47-1.41 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.2, 148.6, 146.0, 140.6, 139.3, 138.1, 135.5, 134.3, 131.5, 131.1, 130.6, 130.1, 129.7, 129.5, 126.7, 126.2, 124.9, 123.5, 121.6, 121.4, 119.3, 118.7, 117.8, 112.1, 72.3, 71.7, 67.2, 62.1, 60.5, 51.0, 37.5, 26.3, 24.9, 22.3; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8, -63.2; HRMS (ESI+): m/z calcd. for $C_{43}H_{38}F_9N_4OS$ $[M\text{-}Br]^+$: 829.2617, found: 829.2625.

Ammonium salt **A8**: Obtained in 61% yield (66 mg) starting from 75 mg (0.12 mmol) of the corresponding amine **11q**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.95 (s, 1 H), 10.56 (s, 1 H), 8.92 (d, J = 4.5 Hz, 1 H), 8.63 (d, J = 9.2 Hz, 1 H), 8.40 (s, 1 H), 8.32 (s, 2 H), 8.11 (d, J = 9.2 Hz, 1 H), 7.66-7.35 (m, 11 H), 6.15 (s, 1 H), 5.56-5.42 (m, 2 H), 5.30-5.25 (m, 1 H), 5.01 (d, J = 10.8 Hz, 1 H), 4.97 (d, J = 11.7 Hz, 1 H), 4.42 (d, J = 11.6 Hz, 1 H), 4.24-4.18 (m, 1 H), 4.17-3.99 (m, 2 H), 3.91 (d, J = 11.9 Hz, 1 H), 3.23-3.15 (m, 2 H), 2.57 (bs, 1 H), 2.20-2.06 (m, 3 H), 1.81-1.71 (m, 1 H), 1.46-1.38 (m, 1 H), 1.32 (s, 9 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.1, 154.4, 148.6, 146.0, 140.8, 139.2, 138.3, 135.9, 135.3, 133.3, 131.5, 131.0, 130.7, 129.6, 129.4, 126.6, 126.4, 125.1, 124.8, 123.5, 122.8, 121.5, 119.2, 118.4, 112.1, 72.2, 71.6, 67.0, 63.0, 60.4, 50.5, 37.5, 34.9, 31.1, 26.4, 25.0, 22.2; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.7; HRMS (ESI+): m/z calcd. for $C_{46}H_{47}F_6N_4OS$ $[M\text{-}Br]^+$: 817.3369, found: 817.3372.

Ammonium salt **A9**: Obtained in 61% yield (58 mg) starting from 77 mg (0.12 mmol) of the corresponding amine **11p**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.86 (s, 1 H), 10.28 (s, 1 H), 8.94 (d, J = 4.4 Hz, 1 H), 8.79 (d, J = 9.4 Hz, 1 H), 8.30 (s, 3 H), 8.12 (d, J = 9.2 Hz, 1 H), 7.72-7.39 (m, 16 H), 6.19 (s, 1 H), 5.66-5.51 (m, 2 H), 5.36-5.30 (m, 1 H), 5.06-4.97 (m, 2 H), 4.41 (d, J = 11.8 Hz, 1 H), 4.27-4.09 (m, 3 H), 4.03 (d, J = 11.7 Hz, 1 H), 3.29-3.16 (m, 2 H), 2.58 (bs, 1 H), 2.20-2.16 (m, 2 H), 1.80-1.71 (m, 2 H), 1.48-1.39 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.2, 148.6, 142.3, 140.7, 139.4, 138.2, 135.8, 135.4, 132.6, 132.2, 131.5, 131.1, 130.7, 129.9, 129.7, 129.5, 129.4, 129.1, 128.2, 127.2, 126.7, 126.6, 125.1, 124.9, 123.6, 121.5, 119.3, 118.5, 117.8, 112.0, 72.5, 71.8, 66.9, 63.0, 60.5, 50.7, 37.5, 26.4, 25.0, 22.4; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.7; HRMS (ESI+): m/z calcd. for $C_{48}H_{43}F_6N_4OS$ $[M\text{-}Br]^+$: 837.3056, found: 837.3061.

Ammonium salt **A10**: Obtained in 37% yield (26 mg) starting from 47 mg (0.08 mmol) of the corresponding amine **11o**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 12.03 (s, 1 H), 10.30 (s, 1 H), 8.96 (d, J = 4.5 Hz, 1 H), 8.90 (d, J = 9.2 Hz, 1 H), 8.32 (s, 2 H), 8.26 (s, 1 H), 8.18 (d, J = 9.5 Hz, 1 H), 7.94-7.45 (m, 15 H), 6.20 (s, 1 H), 5.72 (d, J = 11.0 Hz, 1 H), 5.58

(ddd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, J_3 = 5.9 Hz, 1 H), 5.40-5.34 (m, 1 H), 5.09-5.01 (m, 2 H), 4.44 (d, J = 11.7 Hz, 1 H), 4.39-4.29 (m, 2 H), 4.23-4.16 (m, 1 H), 4.10 (d, J = 11.7 Hz, 1 H), 3.27-3.18 (m, 2 H), 2.53 (bs, 1 H), 2.20-2.09 (m, 1 H), 1.74-1.60 (m, 2 H), 1.50-1.41 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.3, 148.5, 146.0, 140.7, 139.6, 138.1, 135.7, 135.5, 134.5, 133.8, 132.8, 131.6, 131.1, 130.7, 129.8, 129.5, 129.2, 128.4, 128.1, 127.8, 127.3, 126.8, 124.9, 123.7, 123.3, 121.5, 119.2, 118.6, 117.9, 112.0, 77.6, 71.8, 66.7, 63.1, 60.4, 50.6, 37.5, 29.7, 26.4, 25.1, 22.4; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.7; HRMS (ESI+): m/z calcd. for $C_{46}H_{41}F_6N_4OS$ $[M\text{-}Br]^+$: 811.2900, found: 811.2899.

Ammonium salt **A11**: Obtained in 55% yield (43 mg) starting from 53 mg (0.10 mmol) of the corresponding amine **11b**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 12.32 (s, 1 H), 10.43 (s, 1 H), 8.90-8.82 (m, 2 H), 8.45 (s, 1 H), 8.30 (s, 2 H), 8.14-8.07 (m, 1 H), 7.81-7.78 (m, 2 H), 7.58-7.50 (m, 5 H), 6.22 (s, 1 H), 6.18-6.07 (m, 1 H), 5.97 (d, J = 12.0 Hz, 1 H), 5.58 (ddd, J_1 = 16.6 Hz, J_2 = 10.2 Hz, J_3 = 5.3 Hz, 1 H), 5.48 (d, J = 5.8 Hz, 1 H), 5.43-5.37 (m, 2 H), 5.07 (d, J = 10.3 Hz, 1 H), 4.66 (d, J = 11.8 Hz, 1 H), 4.44-4.26 (m, 4 H), 4.11 (dd, J_1 = 12.3 Hz, J_2 = 6.8 Hz, 1 H), 3.43-3.36 (m, 1 H), 3.30-3.22 (m, 1 H), 2.63 (bs, 1 H), 2.21-2.07 (m, 3 H), 1.86-1.75 (m, 1 H), 1.42-1.37 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.2, 148.1, 145.2, 140.8, 139.5, 138.9, 135.7, 133.8, 132.3, 131.5, 131.1, 130.0, 129.6, 126.5, 126.3, 125.1, 124.7, 123.5, 121.5, 120.5, 118.8, 118.5, 112.1, 73.5, 70.5, 67.0, 64.0, 60.4, 50.9, 37.6, 26.5, 25.1, 22.4; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{38}H_{37}F_6N_4OS$ $[M\text{-}Br]^+$: 711.2587, found: 711.2587.

Ammonium salt **A12**: Obtained in 40% yield (17 mg) starting from 31 mg (0.05 mmol) of the corresponding amine **11j**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.81 (s, 1 H), 10.18 (s, 1 H), 8.88 (d, J = 4.6 Hz, 1 H), 8.70 (d, J = 8.9 Hz, 1 H), 8.34 (s, 1 H), 8.24 (s, 2 H), 8.02-7.47 (m, 7 H), 6.26 (s, 1 H), 6.21-6.06 (m, 2 H), 5.58 (ddd, J_1 = 17.1 Hz, J_2 = 10.6 Hz, J_3 = 6.2 Hz, 1 H), 5.49-5.36 (m, 3 H), 5.08 (dd, J_1 = 10.3 Hz, J_2 = 0.9 Hz, 1 H), 4.80 (d, J = 12.1 Hz, 1 H), 4.43-4.35 (m, 4 H), 4.16 (dd, J_1 = 12.8 Hz, J_2 = 6.8 Hz, 1 H), 3.56-3.19 (m, 2 H), 2.64 (bs, 1 H), 2.23-2.10 (m, 3 H), 1.88-1.78 (m, 1 H), 1.45-1.39 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.1, 148.5, 145.9, 140.6, 139.4, 137.9, 135.5, 134.4, 132.5, 132.3, 131.5, 131.1, 130.5, 130.4, 127.3, 126.5, 125.0, 124.6, 123.4, 121.4, 120.6, 118.8, 117.8, 112.1, 73.4, 70.4, 67.3, 62.9, 60.5, 51.3, 37.6, 26.4, 25.1, 22.4;^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8, -63.2; HRMS (ESI+): m/z calcd. for $C_{39}H_{36}F_9N_4OS$ $[M\text{-}Br]^+$: 779.2461, found: 779.2416.

Ammonium salt **A13**: Obtained in 38% yield (48 mg) starting from 84 mg (0.15 mmol) of the corresponding amine **11m**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 12.06 (s, 1 H), 10.48 (s, 1 H), 8.88 (d, J = 4.5 Hz, 1 H), 8.76 (d, J = 9.0 Hz, 1 H), 8.40 (s, 1 H), 8.33 (s, 2 H), 8.10 (d, J = 9.2 Hz, 1 H), 7.71-7.47 (m, 6 H), 6.18-6.06 (m, 2 H), 5.83 (d, J = 11.0 Hz, 1 H), 5.57 (ddd, J_1 = 17.0 Hz, J_2 = 10.6 Hz, J_3 = 5.9 Hz, 1 H), 5.46-5.33 (m, 3 H), 5.06 (dd, J_1 = 10.3 Hz, J_2 = 1.2 Hz, 1 H), 4.62 (d, J = 11.9 Hz, 1 H), 4.42-4.20 (m, 4 H), 4.04 (dd, J_1 = 12.7 Hz, J_2 = 7.1 Hz, 1 H), 3.44-3.26 (m, 2 H), 2.63 (bs, 1 H), 2.15-2.07 (m, 3 H), 1.88-1.78 (m, 1 H), 1.45-1.38 (m, 1 H), 1.35 (s, 9 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.2, 154.5, 148.4, 145.9, 140.8, 139.4, 138.1, 135.8, 133.5, 132.2, 131.5, 131.1, 130.6, 126.6, 126.4, 125.1, 124.7, 123.6, 123.0, 120.8, 118.8, 118.5, 112.0, 73.3, 70.5, 66.8, 63.5, 60.3, 50.8, 37.5, 34.9, 31.1, 26.5, 25.1, 22.4;^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{42}H_{45}F_6N_4OS$ $[M\text{-}Br]^+$: 767.3213, found: 767.3197.

Ammonium salt **A14**: Obtained in 46% yield (56 mg) starting from 81 mg (0.14 mmol) of the corresponding amine **11l**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.95 (s, 1 H), 10.17 (s, 1 H), 8.93-8.88 (m, 2 H), 8.31 (s, 3 H), 8.12 (d, J = 9.2 Hz, 1 H), 7.98 (s, 1 H), 7.86-7.77 (m, 2 H), 7.68-7.59 (m, 4 H), 7.52-7.42 (m, 4 H), 6.20-6.09 (m, 2 H), 6.05 (d, J = 11.9 Hz, 1 H), 5.60 (ddd, J_1 = 16.9 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1 H), 5.48-5.38 (m, 3 H), 5.08 (dd, J_1 = 10.6 Hz, J_2 = 0.8 Hz, 1 H), 4.69 (d, J = 11.9 Hz, 1 H), 4.49-4.30 (m, 4 H), 4.07 (dd, J_1 = 12.3 Hz, J_2 = 7.1 Hz, 1 H), 3.46-3.28 (m, 2 H), 2.64 (bs, 1 H), 2.20-2.08 (m, 3 H), 1.86-1.80 (m, 1 H), 1.46-1.35 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.3, 148.5, 146.0, 142.6, 140.7, 139.6, 139.4, 137.9, 135.7, 132.7, 132.3, 132.2, 131.6, 131.2, 130.6, 130.1, 129.7, 129.2, 128.3, 127.2, 126.8, 126.5, 125.1, 124.7, 123.7, 120.8, 118.8, 118.7, 111.9, 73.5, 70.5, 66.7, 63.5, 60.4, 51.0, 37.6, 26.5, 25.1, 22.6; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{44}H_{41}F_6N_4OS$ $[M\text{-}Br]^+$: 787.2900, found: 787.2902.

Ammonium salt **A15**: Obtained in 71% yield (47 mg) starting from 42 mg (0.09 mmol) of the corresponding amine **11i**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.72 (s, 1 H), 10.11 (s, 1 H), 8.88 (d, J = 4.5 Hz, 1 H), 8.80-8.77 (m, 1 H), 8.31-8.27 (m, 3 H), 8.08 (d, J = 9.2 Hz, 1 H), 7.58 (s, 1 H), 7.49-7.40 (m, 3 H), 7.29 (d, J = 8.0 Hz, 1 H), 7.06 (dd, J_1 = 8.2 Hz, J_2 = 2.1 Hz, 1 H), 6.16-6.04 (m, 2 H), 5.83 (d, J = 11.9 Hz, 1 H), 5.59 (ddd, J_1 = 16.7 Hz, J_2 = 10.2 Hz, J_3 = 5.8 Hz, 1 H), 5.45-5.36 (m, 3 H), 5.06 (d, J = 10.2 Hz, 1 H), 4.58 (d, J = 11.9 Hz, 1 H), 4.40-4.25 (m, 4 H), 4.03 (dd, J_1 = 12.5 Hz, J_2 = 7.2 Hz, 1 H), 3.87 (s, 3 H), 3.48-3.40 (m, 1 H), 3.35-3.27 (m, 1 H), 2.64 (bs, 1 H), 2.18-2.06 (m, 3 H), 1.86-1.76 (m, 1 H), 1.41-1.35 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.3, 160.2, 148.3, 145.5, 140.6, 139.4, 138.5, 135.8, 132.1, 132.0, 131.6, 131.1, 130.7, 130.6, 130.2, 128.7, 127.4, 126.7, 125.7, 125.1, 124.8, 123.8, 121.4, 120.8, 119.6, 119.0, 118.6, 117.8, 116.4, 112.1, 73.4, 70.5, 66.8, 63.5, 60.6, 51.1, 37.6, 26.4, 25.1, 22.5; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{39}H_{39}F_6N_4O_2S$ $[M\text{-}Br]^+$: 741.2692, found: 741.2695.

Ammonium salt **A16**: Obtained in 46% yield (23 mg) starting from 36 mg (0.06 mmol) of the corresponding amine **11k**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 12.11 (s, 1 H), 10.25 (s, 1 H), 8.95 (d, J = 9.1 Hz, 1 H), 8.90 (d, J = 4.5 Hz, 1 H), 8.32 (s, 2 H), 8.16-8.09 (m, 1 H), 8.05-7.84 (m, 6 H), 7.64-7.58 (m, 3 H), 7.52-7.47 (m, 1 H), 6.25-6.10 (m, 2 H), 5.61 (ddd, J_1 = 16.9 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1 H), 5.52-5.40 (m, 3 H), 5.10 (d, J = 10.2 Hz, 1 H), 4.78 (d, J = 11.8 Hz, 1 H), 4.53-4.35 (m, 4 H), 4.11 (dd, J_1 = 12.6 Hz, J_2 = 7.2 Hz, 1 H), 3.50-3.43 (m, 1 H), 3.36-3.29 (m, 1 H), 2.61 (bs, 1 H), 2.16-2.09 (m, 3 H), 1.81-1.70 (m, 2 H), 1.46-1.38 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.3, 148.4, 145.8, 140.7, 139.6, 138.3, 135.7, 134.6, 133.9, 132.9, 132.2, 131.6, 131.1, 130.1, 129.5, 128.6, 128.2, 127.8, 127.4, 126.7, 124.8, 123.8, 123.4, 121.5, 120.7, 118.9, 118.6, 117.9, 112.1, 73.6, 70.5, 66.7, 63.7, 60.5, 51.0, 37.6, 26.5, 25.2, 22.6; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{42}H_{39}F_6N_4OS$ $[M\text{-}Br]^+$: 761.2743, found: 761.2752.

Ammonium salt **A17**: Obtained in 37% yield (28 mg) starting from 50 mg (0.10 mmol) of the corresponding amine **11a**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.87 (s, 1 H), 10.25 (s, 1 H), 8.90 (d, J = 4.5 Hz, 1 H), 8.82 (d, J = 9.0 Hz, 1 H), 8.41 (s, 1 H), 8.30 (s, 2 H), 8.09 (d, J = 9.0 Hz, 1 H), 7.82-7.80 (m, 2 H), 7.58-7.46 (m, 5 H), 5.99-5.79 (m, 3 H), 5.33-5.19

(m, 2 H), 4.50-4.46 (m, 2 H), 4.36-4.30 (m, 1 H), 4.16-4.09 (m, 1 H), 3.63 (s, 3 H), 3.01-2.91 (m, 1 H), 2.53-2.45 (m, 1 H), 2.35-2.26 (m, 1 H), 1.96-1.80 (m, 3 H), 1.17-1.08 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.3, 148.5, 146.0, 140.7, 139.5, 137.5, 134.9, 133.8, 131.6, 131.1, 130.5, 129.6, 126.3, 126.1, 125.1, 124.8, 123.6, 118.7, 112.3, 67.1, 63.4, 57.6, 56.6, 54.4, 37.8, 27.0, 23.6, 21.7; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{36}H_{35}F_6N_4OS$ $[M\text{-}Br]^+$: 685.2430, found: 685.2433.

Ammonium salt **A18**: Obtained in 46% yield (38 mg) starting from 54 mg (0.10 mmol) of the corresponding amine **11a**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.02 (s, 1 H), 8.85-8.77 (m, 2H), 8.58 (d, *J* = 9.1 Hz, 1H), 8.11-7.95 (m, 4H), 7.91-7.78 (m, 2H), 7.59-7.46 (m, 3H), 7.46-7.37 (m, 2H), 6.00-5.78 (m, 3H), 5.28 (d, *J* = 10.5 Hz, 1H), 5.19 (d, *J* = 17.0 Hz, 1H), 4.62-4.42 (m, 2H), 4.36-4.26 (m, 1H), 4.14-4.02 (m, 1H), 3.62 (s, 3H), 3.67-3.52 (m, 4H), 3.04-2.91 (m, 1H), 2.52-2.40 (m, 1H), 2.36-2.22 (m, 1H), 2.04-1.78 (m, 3H), 1.17-1.01 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 153.0, 147.6, 145.0, 141.2, 140.2, 137.0, 135.0, 134.0, 131.9 (q, *J* = 33.3 Hz), 131.4, 131.1, 129.6, 126.4, 123.5 (q, *J* = 273 Hz), 123.0, 118.7, 118.6, 118.4, 115.2, 107.6, 77.4, 76.5, 67.1, 63.5, 57.6, 56.6,54.4,38.0, 27.2, 23.8, 21.7, 14.1; HRMS (ESI+): m/z calcd. for $C_{36}H_{35}F_6N_4O_2$ $[M\text{-}Br]^+$: 669.2659, found: 669.2642.

Ammonium salt **A19**: Obtained in 42% yield (8 mg) starting from 12 mg (0.05 mmol) of the corresponding amine **11e**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.15 (s, 1 H), 9.92 (s, 1H), 8.92 (d, *J* = 4.5 Hz, 1H), 8.79 (dd, J_1 = 9.3 Hz, J_2 = 1.6 Hz, 1H), 8.27 (s, 2H), 8.18 (d, *J* = 1.3 Hz, 1H), 8.10 (d, *J* = 9.3 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.48 (d, *J* = 4.5 Hz, 1H), 6.02-5.79 (m, 3H), 5.34 (d, *J* = 10.4 Hz, 1H), 5.24 (d, *J* = 17.1 Hz, 1H), 4.58-4.44 (m, 2H), 4.37-4.25 (m, 1H), 4.24-4.13 (m, 1H), 3.63 (s, 3H), 3.59-3.47 (m, 1H), 2.99-2.86 (m, 1H), 2.58-2.45 (m, 1H), 2.39-2.27 (m, 1H), 2.08-1.87 (m, 3H), 1.22-1.11 (m, 1H); HRMS (ESI+): m/z calcd. for $C_{37}H_{34}F_9N_4OS$ $[M\text{-}Br]^+$: 753.2304, found: 753.2301.

Ammonium salt **A20**: Obtained in 40% yield (42 mg) starting from 70 mg (0.13 mmol) of the corresponding amine **11h**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.92 (s, 1 H), 10.37 (s, 1 H), 8.90 (d, *J* = 4.4 Hz, 1 H), 8.83 (d, *J* = 9.2 Hz, 1 H), 8.40 (s, 1 H), 8.33 (s, 2 H), 8.12 (d, *J* = 9.1 Hz, 1 H), 7.72 (d, *J* = 8.3 Hz, 2 H), 7.62-7.46 (m, 4 H), 5.96-5.82 (m, 2 H), 5.73 (d, *J* = 11.6 Hz, 1 H), 5.32 (d, *J* = 10.6 Hz, 1 H), 5.27-5.14 (m, 2 H), 4.42 (d, *J* = 11.6 Hz, 1 H), 4.33-4.26 (m, 1 H), 4.13-4.02 (m, 1 H), 3.61 (s, 3 H), 3.59-3.54 (m, 1 H), 3.00-2.92 (m, 1 H), 2.52-2.45 (m, 1 H), 2.36-2.28 (m, 1 H), 2.01-1.78 (m, 4 H), 1.35 (s, 9 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.4, 154.6, 148.5, 146.0, 140.8, 139.5, 137.6, 135.4, 135.0, 133.5, 131.5, 131.1, 130.5, 126.6, 126.5, 126.2, 125.6, 124.8, 123.7, 122.9, 118.6, 67.0, 63.2, 57.5, 56.6, 54.3, 37.8, 34.9, 31.3, 27.1, 23.6, 21.6; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{40}H_{43}F_6N_4OS$ $[M\text{-}Br]^+$: 741.3056, found: 741.3062.

Ammonium salt **A21**: Obtained in 91% yield (61 mg) starting from 47 mg (0.08 mmol) of the corresponding amine **11g**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.79 (s, 1 H), 10.08 (s, 1 H), 8.98 (d, *J* = 9.5 Hz, 1 H), 8.92 (d, *J* = 4.5 Hz, 1 H), 8.31-8.29 (m, 2 H), 8.16 (d, *J* = 9.1 Hz, 1 H), 7.88-7.40 (m, 13 H), 5.97-5.84 (m, 3 H), 5.34-5.19 (m, 2 H),4.64-4.60 (m, 1 H), 4.51 (d, *J* = 11.8 Hz, 1 H), 4.37-4.31 (m, 1 H), 4.17-4.10 (m, 1 H), 3.63 (s, 3 H), 3.39-3.26 (m, 1 H), 3.11-2.99 (m, 1 H), 2.52-2.44 (m, 1 H), 2.36-2.27 (m, 1 H), 2.02-1.88 (m, 3 H), 1.18-1.11 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.6, 148.5, 146.0, 140.7, 139.7, 139.4, 134.9, 133.7, 132.7, 132.3, 131.6, 131.2, 130.5, 130.1, 129.8, 129.7, 129.5, 129.3, 129.2, 128.9, 128.3, 127.2, 126.7, 123.8, 118.7, 112.8, 67.0, 63.2, 57.6, 56.7, 54.4, 37.9, 27.1, 23.6, 21.8; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{42}H_{39}F_6N_4OS$ $[M\text{-}Br]^+$: 761.2734, found: 761.2750.

Ammonium salt **A22**: Obtained in 42% yield (33 mg) starting from 54 mg (0.10 mmol) of the corresponding amine **11d**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.69 (s, 1 H), 10.11 (s, 1 H), 8.93-8.87, (m, 2 H), 8.32-8.28 (m, 2 H), 8.13 (d, *J* = 9.2 Hz, 1 H), 7.60 (s, 1 H), 7.51-7.42 (m, 4 H), 7.32 (d, *J* = 7.7 Hz, 1 H), 7.10-7.06 (m, 1 H), 5.94-5.83 (m, 2 H), 5.71 (d, *J* = 12.2 Hz, 1 H), 5.32 (d, *J* = 10.9 Hz, 1 H), 5.25-5.19 (m, 1 H), 4.57-4.50 (m, 1 H), 4.42 (d, *J* = 11.9 Hz, 1 H), 4.32-4.26 (m, 1 H), 4.13-4.06 (m, 1 H), 3.89 (s, 3 H), 3.63-3.54 (m, 4 H), 3.06-2.95 (m, 1 H), 2.52-2.45 (m, 1 H), 2.34-2.26 (m, 1 H), 2.05-1.90 (m, 3 H), 1.18-1.08 (1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.6, 160.4, 148.5, 146.0, 140.7, 139.6, 137.5, 134.9, 131.6, 131.2, 130.6, 127.4, 126.8, 125.8, 124.9, 123.9, 121.5, 119.5, 118.6, 117.9, 116.6, 112.5, 67.0, 63.3, 57.5, 56.8, 55.9, 54.5, 37.8, 27.0, 23.6, 21.7; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{37}H_{37}F_6N_4O_2S$ $[M\text{-}Br]^+$: 715.2536, found: 715.2537.

Ammonium salt **A''23**: Obtained in 43% yield (79 mg) starting from 97.4 mg (0.17 mmol) of the corresponding amine **11''c**. 11.79 (s, 1 H), 10.04 (s, 1 H), 8.94 (d, *J* = 4.5 Hz, 1 H), 8.86 (dd, J_1 = 9.4 Hz, J_2 = 2.2 Hz, 1 H), 8.32 (d, *J* = 2.0 Hz, 1 H), 8.30 (s, 2 H), 8.14 (d, *J* = 9.3 Hz, 1 H), 7.62 (d, *J* = 4.5 Hz, 1 H), 7.59 (s, 1 H), 7.54-7.42 (m, 10 H), 6.19 (s, 1 H), 5.87 (ddd, J_1 = 17.3 Hz, J_2 = 10.6 Hz, J_3 = 6.9 Hz, 1 H), 5.55 (d, *J* = 11.9 Hz, 1 H), 5.29 (d, *J* = 10.2 Hz, 1 H), 5.13 (d, *J* = 17.4 Hz, 1 H), 4.98 (d, *J* = 11.9 Hz, 1 H), 4.59-4.51 (m, 1 H), 4.44 (d, *J* = 11.7 Hz, 1 H), 4.31-4.25 (m, 1 H), 4.12-3.99 (m, 2 H), 3.37 (t, *J* = 11.1 Hz, 1 H), 2.93-2.83 (m, 1 H), 2.48-2.35 (m, 2 H), 1.96-1.75 (m, 3 H), 1.59-1.39 (m, 1 H), 1.47-1.39 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.9, 148.8, 146.5, 141.0, 139.6, 138.1, 135.6, 135.2, 133.8, 131.6, 131.2,130.8, 129.8, 129.6, 129.3, 127.8, 126.2, 123.9, 123.5, 119.2, 118.6, 113.1, 77.4, 73.3, 72.2, 67.0, 62.8, 56.9, 54.1, 53.6, 37.8, 32.2, 27.2, 23.7, 21.9, 14.2 HRMS (ESI+): m/z calcd. for $C_{42}H_{39}F_6N_4OS$ $[M\text{-}Br]^+$: 761.2743, found: 761.2751.

Ammonium salt **A''24**: Obtained in 60% yield (57 mg) starting from 67 mg (0.11 mmol) of the corresponding amine **11''r**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.85 (s, 1 H), 10.16 (s, 1 H), 8.93 (d, *J* = 4.5 Hz, 1 H), 8.84 (dd, J_1 = 9.3 Hz, J_2 = 1.5 Hz, 1 H), 8.28 (s, 2 H), 8.26 (d, *J* = 2.0 Hz, 1 H), 8.14 (d, *J* = 9.1 Hz, 1 H), 7.62 (d, *J* = 4.5 Hz, 1 H), 7.58 (s, 1 H), 7.52-7.33 (m, 7 H), 7.16 (bs, 1 H), 7.01 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.15 (s, 1 H), 5.87 (ddd, J_1 = 17.2 Hz, J_2 = 10.3 Hz, J_3 = 6.8 Hz, 1 H), 5.40 (d, *J* = 11.8 Hz, 1 H), 5.29 (d, *J* = 10.0 Hz, 1 H), 5.13 (d, *J* = 17.2 Hz, 1 H), 4.98 (d, *J* = 11.3 Hz, 1 H), 4.50-4.40 (m, 2 H), 4.22 (t, *J* = 9.6 Hz, 1 H), 4.09-4.02 (m, 1 H), 3.93 (d, *J* = 11.7 Hz, 1 H), 3.84 (s, 3 H), 3.45 (t, *J* = 11.2 Hz, 1 H), 2.97-2.86 (m, 1 H), 2.48-2.35 (m, 2 H), 1.99-1.84 (m, 3 H), 1.22-1.12 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.4, 160.1, 148.5, 146.1, 140.7, 139.5, 137.9, 135.3, 131.1, 129.6, 129.2, 127.3, 126.8, 125.7, 124.9, 123.8, 121.5, 119.4, 119.0, 118.4, 116.4, 112.2, 73.0, 71.9, 66.9, 62.5, 56.8, 55.8, 54.0, 37.6, 26.9, 23.6, 21.7; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{43}H_{41}F_6N_4O_2S$ $[M\text{-}Br]^+$: 791.2849, found: 791.2852.

Ammonium salt **A''25**: Obtained in 63% yield (75 mg) starting from 83 mg (0.13 mmol) of the corresponding amine **11''n**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 11.71 (s, 1 H), 10.11 (s, 1 H), 8.93 (d, *J* = 4.5 Hz, 1 H), 8.78 (d, *J* = 8.9 Hz, 1

H), 8.31 (s, 1 H), 8.26 (s, 2 H), 8.08 (d, *J* = 9.1 Hz, 1 H), 7.78-7.41 (m, 12 H), 6.25 (s, 1 H), 5.88 (ddd, J_1 = 17.4 Hz, J_2 = 10.6 Hz, J_3 = 7.0 Hz, 1 H), 5.63 (d, *J* = 11.9 Hz, 1 H), 5.31 (d, *J* = 10.6 Hz, 1 H), 5.15 (d, *J* = 17.2 Hz, 1 H), 5.01 (d, *J* = 11.8 Hz, 1 H), 4.56-4.45 (m, 2 H), 4.31-4.25 (m, 1 H), 4.15-4.08 (m, 1 H), 4.03 (d, *J* = 11.7 Hz, 1 H), 3.31-3.24 (m, 1 H), 2.88-2.78 (m, 1 H), 2.49-2.38 (m, 2 H), 2.01-1.84 (m, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.2, 148.6, 146.0, 140.6, 139.4, 137.8, 135.5, 137.8, 135.5, 134.8, 134.3, 131.0, 129.7, 129.1, 126.5, 126.3, 124.9, 123.5, 119.0, 118.7, 117.8, 112.3, 73.0, 71.9, 67.2, 61.7, 56.8, 54.2, 37.6, 29.7, 26.9, 23.5, 21.6; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8, -63.2; HRMS (ESI+): m/z calcd. for $C_{43}H_{38}F_9N_4OS$ $[M\text{-}Br]^+$: 829.2617, found: 829.2618.

Ammonium salt **A''26**: Obtained in 42% yield (204 mg) starting from 320 mg (0.61 mmol) of the corresponding amine **11''b**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 12.07 (s, 1 H), 10.57 (s, 1 H), 8.85 (d, *J* = 4.5 Hz, 1 H), 8.62 (d, *J* = 8.9 Hz, 1 H), 8.53 (bs, 1 H), 8.26 (s, 2 H), 8.0 (d, *J* = 9.1 Hz, 1 H), 7.75-7.72 (m, 2 H), 7.55-7.47 (m, 5 H), 6.23-6.06 (m, 2 H), 5.89 (ddd, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 7.2 Hz, 1 H), 5.75 (d, *J* = 11.9 Hz, 1 H), 5.50-5.42 (m, 2 H), 5.31 (d, *J* = 10.4 Hz, 1 H), 5.21 (d, *J* = 17.3 Hz, 1 H), 4.58 (d, *J* = 11.9 Hz, 1 H), 4.41-4.32 (m, 3 H), 4.21-4.11 (m, 2 H), 3.58 (t, *J* = 11.3 Hz, 1 H), 3.00-2.90 (m, 1 H), 2.52-2.43 (m, 1 H), 2.39-2.30 (m, 1 H), 2.02 (bs, 1 H), 1.94-1.84 (m, 2 H), 1.17-1.08 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 179.1, 148.4, 145.6, 140.7, 139.3, 138.2, 134.9, 133.7, 132.3, 131.9, 131.4, 131.1, 131.0, 130.4, 129.6, 126.2, 126.1, 125.1, 124.6, 121.5, 120.3, 118.6, 112.4, 73.9, 70.6, 67.2, 63.6, 56.8, 54.3, 37.8, 27.0, 23.6, 21.6; ^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ / ppm = -62.8; HRMS (ESI+): m/z calcd. for $C_{38}H_{37}F_6N_4OS$ $[M\text{-}Br]^+$: 711.2587, found: 711.2588.

Ammonium salt **A''27**: Obtained in 39% yield (30 mg) starting from 49 mg (0.1 mmol) of the corresponding amine **11''a**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm = 10.28 (s, 1 H), 9.01 (s, 1H), 8.94 (d, *J* = 4.4 Hz, 1H), 8.94 (d, *J* = 4.4 Hz, 1H), 8.57 (d, *J* = 9.1 Hz, 1H), 8.11-8.02 (m, 3H), 7.93-7.88 (m, 1H), 7.85-7.78 (m, 2H), 7.55-7.49 (m, 3H), 7.45-7.40 (m, 2H), 5.93 (d, *J* = 1.3 Hz, 1H), 5.79 (d, *J* = 11.5 Hz, 1H), 5.65 – 5.51 (m, 1H), 5.44 – 5.34 (m, 1H), 5.07 (dd, J_1 = 10.5 Hz, J_2 = 1.3 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.37-4.18 (m, 3H), 3.62 (s, 3H), 3.46-3.34 (m, 1H), 3.34-3.23 (m, 1H), 2.68-2.57 (m, 1H), 2.21-1.95 (m, 3H), 1.85-1.69 (m, 1H), 1.43-1.31 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 153.1, 147.7, 145.1, 141.3, 140.0, 135.9, 134.1, 131.9 (q, *J* = 33 Hz), 131.4, 131.1, 129.7, 126.4, 125.4, 123.6, 123.5 (q, *J* = 273 Hz), 118.9, 118.5, 115.4, 107.7, 77.4, 76.3, 66.9, 64.0, 60.3, 57.5, 50.9, 37.8, 26.6, 25.5, 25.3, 22.6, 14.3; HRMS (ESI+): m/z calcd. for $C_{36}H_{35}F_6N_4O_2$ $[M\text{-}Br]^+$: 669.2659, found: 669.2650.

Ammonium salt **A''28**: Obtained in 42% yield (15 mg) starting from 25 mg (0.05 mmol) of the corresponding amine **11''h**. ^{1}H-NMR (300 MHz, $CDCl_3$, 298.0 K): δ / ppm =10.81 (bs, 1H), 10.47 (s, 1H), 8.90 (d, *J* = 4.5 Hz, 1H), 8.79-8.72 (m, 1H), 8.37-8.31 (m, 3H), 8.12 (d, *J* = 9.2 Hz, 1H), 7.75-7.68 (m, 2H), 7.60 (s, 1H), 7.58-7.52 (m, 2H), 7.45 (d, *J* = 4.4 Hz, 1H), 5.77 (d, *J* =12.0 Hz, 1H), 5.94 (d, *J* = 1.9 Hz, 1H), 5.64-5.50 (m, 1H), 5.39-5.30 (m, 1H), 5.06 (d, J_1 = 10.4 Hz, J_2 = 1.4 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.36-4.15 (m, 3H), 3.60 (s, 3H), 3.50-3.38 (m, 1H), 3.33-3.21 (m, 1H), 2.68-2.58 (m, 1H), 2.20-2.01 (m, 3H), 1.88-1.75 (m, 1H), 1.35 (s, 9H), 1.45-1.33 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ / ppm = 180.2, 154.9, 148.9, 146.5, 141.0, 139.4, 136.0, 133.7, 131.9, 131.6 (q, *J* = 33.2 Hz), 131.4, 130.6, 128.4, 126.8, 125.2, 124.0, 123.4 (q, *J* = 271 Hz), 123.4, 123.0, 119.2, 118.3, 113.6, 77.4, 76.6, 67.1, 61.0, 57.5, 51.0, 37.9, 35.2, 31.3, 26.8, 22.8, 14.4; HRMS (ESI+): m/z calcd. for $C_{40}H_{43}F_6N_4OS$ $[M\text{-}Br]^+$: 741.3056, found: 741.3047.

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26. The online supporting information contains further analytical details.
27.

Supplementary Material

The supporting information contains the analytical details of the intermediates and copies of the NMR spectra of the final ammonium salts.

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