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SYNTHESIS AND REACTIVITY OF NOVEL 1*H*-ISOCHROMENO[3,4-*d*]IMIDAZOL-1-ONIUM SALTS

Bart I. Roman, Marie Guégan, Nils De Vos, Cedric Maton, and Christian V. Stevens*

Research group SynBioC, Department of Sustainable Organic Chemistry and Technology, Faculty of Bioscience Engineering, Coupure Links 653, B-9000 Ghent, Belgium. E-mail: Chris.Stevens@UGent.be

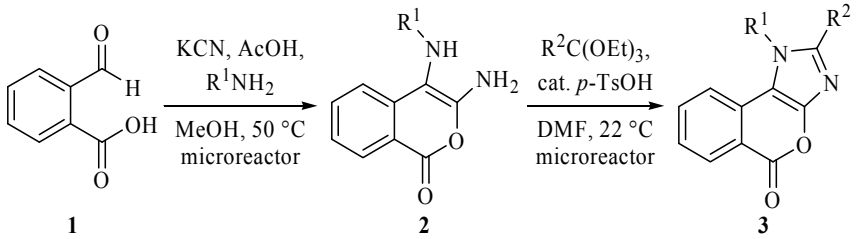
Abstract – A straightforward and convenient preparation of 25 novel imidazolium salts from the corresponding 1*H*-isochromeno[3,4-*d*]imidazolones is described, employing either a quaternization or a quaternization/anion metathesis strategy. The nature of the anion has a major influence on the melting point of these imidazolium salts (BF_4 > I, PF_6 > $N(Tf)_2$, $N(CN)_2$ > OTf).

INTRODUCTION

The synthesis of highly functionalized organic substances very often involves the intermediacy of polyfunctionalized compounds. Multicomponent reactions (MCRs) can offer efficient, short routes from readily accessible starting materials to such complex molecular scaffolds. Our research group has recently illustrated this rationale in the continuous flow synthesis of 3,4-diamino-1*H*-isochromen-1-ones **2** (Scheme 1).[1] Furthermore, we prepared the corresponding 1*H*-isochromeno[3,4-*d*]imidazol-1-ones **3** in one extra step.[2]

Having these imidazoles in hand, we were intrigued to investigate their conversion into imidazolium salts. Today, this class of compounds receives a tremendous amount of attention because of their application as ionic liquids. The latter non-volatile organic solvent surrogates may play a key role in green chemistry in the near future, although their supposed benignness recently became the topic of a lively debate.[3,4] Moreover, imidazolium salts are often used as precursors to stable N-heterocyclic carbenes (NHCs),[5] highly interesting species that show useful application in organocatalysis[6] or as ancillary ligands in various metal containing complex catalysts.[7] Such metal-NHC complexes also exhibit promising pharmacological

properties, which could render them useful as novel antibacterial and antitumor drugs.[8] The present paper provides an efficient protocol for the conversion of isochromeno[3,4-*d*]imidazol-1-ones into an array of corresponding imidazolium salts and evaluates the influence of the nature of the counter ion on the melting point of these substances.



Scheme 1. Continuous flow synthesis of isochromeno[3,4-*d*]imidazolones **3**

RESULTS AND DISCUSSION

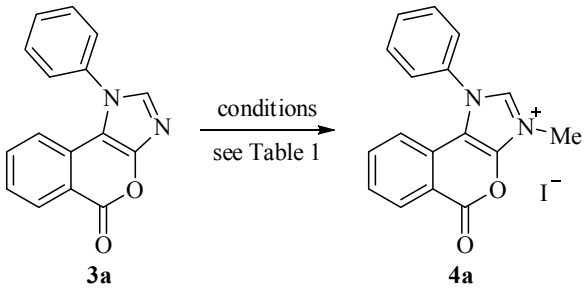
PREPARATION OF IMIDAZOLIUM HALIDES

The study of the potential of 1*H*-isochromeno[3,4-*d*]imidazol-1-ones to form imidazolium salts *via* alkylation of *N*(3) was initiated by the treatment of imidazole **3a** with methyl iodide as a model reaction (Scheme 2). An overview of the evaluated conditions and the corresponding yields of imidazolium salt **4a** is depicted in Table 1.

In an initial attempt, imidazole **3a** was treated with 4 equivalents of methyl iodide in acetonitrile at reflux temperature (Entry 1). After 2 h, imidazolium salt **4a** was obtained as a precipitate in a disappointing yield of 6%. Prolongation of the reaction time to 12 h did not significantly alter the reaction outcome (Entry 2). Since the solubility of the substrate in acetonitrile (MeCN) was particularly low, a subsequent trial was carried out in dimethylformamide (DMF, Entry 3). As this solvent was used to synthesize imidazole **3a** in a microreactor environment, solubility issues were obviously overcome in this manner. Furthermore, the transformation was carried out in a sealed vessel at 180 °C in an attempt to enhance the reaction rate and to avoid boil-off of methyl iodide. Under these conditions, precipitated crystals of imidazolium salt **4a** in a yield of 29% were obtained after 5 h. Isolation of further amounts of the salt from the mother liquor proved tedious.

Unfortunately, prolongation of the reaction time caused degradation (Entry 4). Though all starting material in the mother liquor was apparently consumed, the precipitated crystals of **4a** represented a mere yield of 12%. Moreover, removal of residual DMF from these crystals engendered a significant product loss. Subsequent attempts to alkylate imidazole **3a** with a large excess of *n*-butyl bromide or iodide (10 equiv) were somewhat more successful, but again DMF removal proved impractical. Clearly, the use of DMF as a solvent deemed problematic and was hence abandoned.

In a final attempt (Entry 5), the solvent was switched back to MeCN while maintaining the pressure vessel set-up. In order to avoid excessive pressure build-up of the more volatile acetonitrile, the reaction temperature was lowered to 150 °C. After 8 h of heating, the pressure vessel was stored at -15 °C. To our delight, this caused the formation of a copious amount of crystals, which were easily isolated by filtration. Furthermore, removal of solvent traces under a high vacuum atmosphere proved swift, and imidazolium salt **4a** was obtained in 75% yield. The mother liquor did not contain starting material, but isolation of further amounts of the desired salt from this mixture was uneconomical.



3a **4a**

Scheme 2. Model reaction for the synthesis of imidazolium salts *via* quaternization of *N*(3)

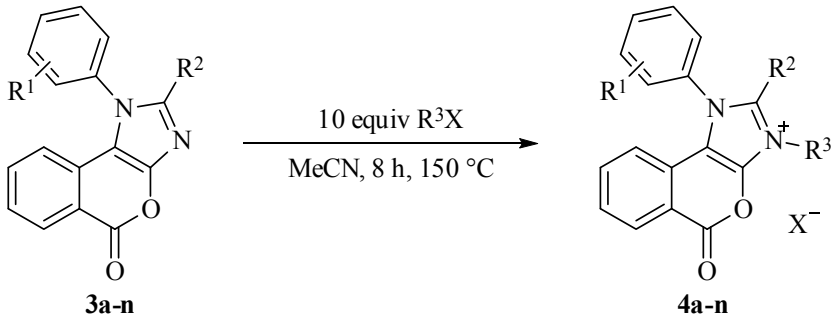
Table 1. Optimization of the model reaction presented in Scheme 2

Entry	Solvent	Equiv. MeI	Temp (°C)	Time (h)	Yield[a] (%)
1	MeCN	4	Δ	2	6
2	MeCN	4	Δ	12	10
3	DMF	4	180[b]	5	29
4	DMF	4	180[b]	24	12
5	MeCN	10	150[b]	8	75

[a]Spontaneous crystallization in the reaction medium occurred upon cooling.

[b]Reaction was carried out in a pressure vessel.

These optimized conditions were subsequently employed to prepare a library of imidazolium salts **4a-n**, the majority of which were obtained in good to excellent yields (Table 2). Only in the case of product **4c**, a prolonged reaction time of 24 h was required to obtain an acceptable yield. The discrepancy in yield between products **4c** and **4d** clearly indicates that, as could be expected, alkyl iodides are a better electrophilic partner in the reaction compared to the corresponding alkyl bromides. The somewhat lower yields reported for imidazolium salts **4b**, **4f** and **4k** are due to an extra recrystallization step in acetonitrile, required to obtain the pure substances.



Scheme 3. Synthesis of imidazolium salts **4a-n** under optimized conditions

Table 2. Yields and melting points of imidazolium salts **4a-n**

Product	R^1	R^2	R^3	X	Yield[a] (%)	MP (°C)
4a	H	H	Me	I	75	230
4b	H	H	Et	Br	40[b]	217
4c	H	H	*n*-Bu	Br	65[c]	221
4d	H	H	*n*-Bu	I	86	214
4e	3-Me	H	Me	I	94	200
4f	3-Me	H	*n*-Bu	I	37[b]	213
4g	4-F	H	Me	I	73	217
4h	4-F	H	*n*-Bu	I	71	220
4i	4-MeO	H	Me	I	95	227
4j	4-MeO	H	*n*-Bu	I	73	217
4k	4-Me	H	Me	I	67[b]	235
4l	4-Me	H	*n*-Bu	I	71	224
4m	3-MeO	H	*n*-Bu	I	74	215
4n	H	Me	Me	I	96	230

[a]Spontaneous crystallization yield in the reaction medium.

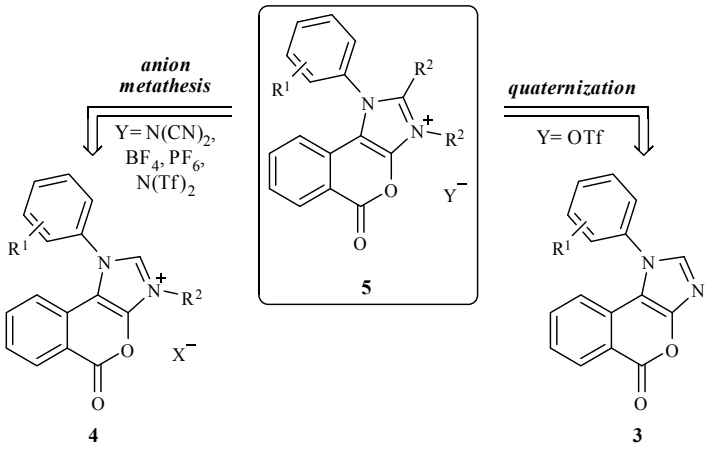
[b]An extra recrystallization step in MeCN was required.

[c]After a reaction time of 24 h.

As displayed in Table 2, halides **4a-n** possess relatively high melting points, which can appear surprising given the general opinion that larger imidazolium cations tend to produce relatively low melting points. However, the isochromenone moiety provides ample possibility for intermolecular interactions, thus increasing the melting points dramatically. Still, the alkyl chain length seems to bear no or very little

influence on the efficiency of ion packing, and thus on the melting point (comparing the values for compounds **4a** and **4d**, **4b** and **4c**, **4g** and **4h**, etc.)

It is well-accepted that simple halides generally inflict high melting points, while organic (e.g. triflate, tosylate) and larger inorganic (e.g. tetrafluoroborate, hexafluorophosphate) anions tend to give lower melting points. To investigate the validity of this rule for our isochromeno imidazolium salts, we prepared an array of salts **5**, possessing different anions Y^-, both *via* anion metathesis and a direct quaternization approach (Scheme 4).

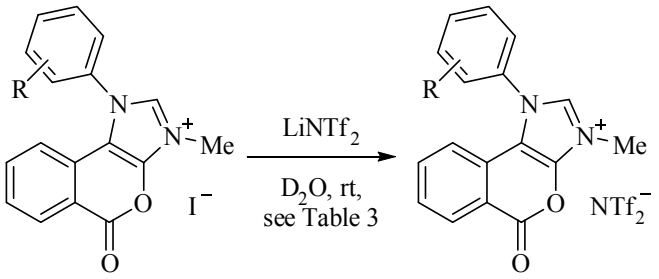


Scheme 4. Strategies for the preparation of 1*H*-isochromeno[3,4-*d*]imidazol-5-onium salts **5**

PREPARATION OF IMIDAZOLIUM SALTS *VIA* ANION METATHESIS

The investigation was started with the anion metathesis of imidazolium iodide **4a** *via* treatment with one equivalent of lithium bis(trifluoromethanesulfonyl)imide (lithium bistriflimide, $LiNTf_2$) at room temperature.[9] To facilitate analysis of the reaction mixture *via* ^1H NMR spectroscopy, D_2O was chosen as a solvent. During the course of the reaction a white precipitate formed, which was isolated *via* filtration. MS and ^{19}F NMR analyses confirmed that this was indeed the desired imidazolium bistriflimide **5a**, which was obtained in 58% yield (Scheme 5, Table 3). Moreover, no traces of imidazolium salts could be detected in the filtrate (D_2O phase). These results were confirmed by mass spectrometry and infrared spectroscopy.

In a similar manner, fluorinated analogue **5b** was obtained. The use of 2 equivalents of $LiNTf_2$ did not significantly augment the yield. In our opinion, the conversion to **5a** and **5b** is complete, but an appreciable amount of product is lost in the filtration step, given the small scale on which the experiments were conducted. This is evidenced by comparing the yields for entries 2 and 3 in Table 3.



4a-b **5a-b**

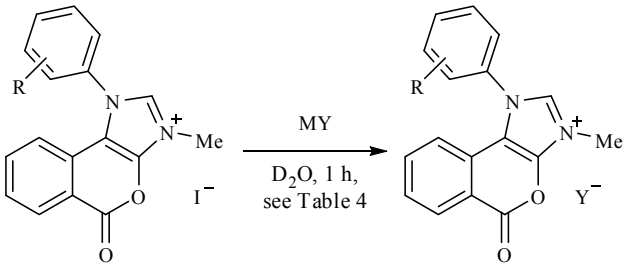
Scheme 5. Preparation of 1*H*-isochromeno[3,4-*d*]imidazol-5-onium bistriflimides **5a-b** *via* anion metathesis

Table 3. Synthetic conditions and yields of imidazolium salts **5a-b**

Entry	Product	R	Equiv $LiNTf_2$	Mass of **4** (mg)	Time (h)	Yield (%)
1	**5a**	H	1	100.0	1.17	58
2	**5b**	4-F	1	77.0	1	20
3	**5b**	4-F	2	107.4	1.5	48

Next, the preparation of the corresponding imidazolium dicyanamides *via* the same protocol was evaluated (Scheme 6, Table 4). Employing silver dicyanamide, however, a complex reaction mixture (Entry 1) or a sticky brown precipitate of different salts was formed (Entry 2). To our delight, utilizing $NaN(CN)_2$, the desired imidazolium dicyanamides were formed as a white precipitate in the reaction mixture, and could readily be isolated by filtration and thorough drying (Entries 3, 4). Indeed, the solubility of silver iodide in water is extremely low ($3x10^{-9}$ g.mL^{-1} at 20 °C) when compared to its lithium (1.51 g.mL^{-1}) or sodium counterparts (1.79 g.mL^{-1}).

Identical observations were made for the tetrafluoroborate salts (Entries 5-9). The yield of these imidazolium dicyanamides and tetrafluoroborates **5c-f** is moderate due to the small scale of the reaction set-up and the according respectable losses in the filtration step. This is apparent when comparing the yields of **5e** for Entries 7 and 8.



4 **5** [Y= $N(CN)_2$, BF_4]

Scheme 6. Preparation of 1*H*-isochromeno[3,4-*d*]imidazol-5-onium dicyanamides and tetrafluoroborates **5c-f** *via* anion metathesis

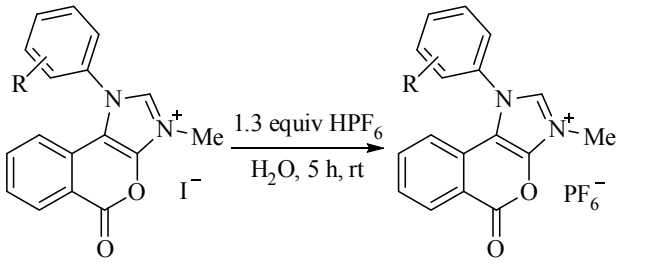
Table 4. Synthetic conditions and yields of imidazolium salts **5c-f**

Entry	Product	R^1	MY	Equiv MY	Temp. (°C)	Yield (%)
1	**5d**	4-F	$AgN(CN)_2$	1	r.t.	-
2	**5d**	4-F	$AgN(CN)_2$	1	80	-
3	**5d**	4-F	$NaN(CN)_2$	3	r.t.	47
4	**5c**	H	$NaN(CN)_2$	2	r.t.	62
5	**5e**	4-F	$AgBF_4$	1	r.t.	-
6	**5e**	4-F	$AgBF_4$	1	80	-
7	**5e**	4-F	$LiBF_4$	1	r.t.	51[a]
8	**5e**	4-F	$LiBF_4$	2	r.t.	65[b]
9	**5f**	H	$LiBF_4$	2	r.t.	44

[a]Reaction scale: 108 mg of starting material **4g**

[b]Reaction scale: 223 mg of starting material **4g**

Subsequently, we investigated the preparation of imidazolium hexafluorophosphates.[10] Treatment of the corresponding iodides with aqueous HPF_6 at room temperature yielded a white precipitate. Upon isolation *via* filtration, washing to neutrality of the residue and thorough drying, NMR and MS analyses proved that the desired salts **5g-h** were indeed obtained.



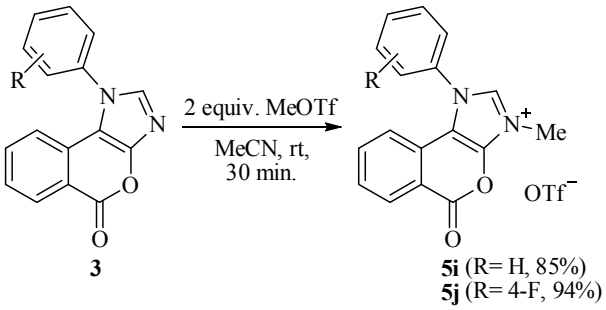
4 **5g** (R= H, 57%)
5h (R= 4-F, 40%)

Scheme 7. Preparation of 1*H*-isochromeno[3,4-*d*]imidazol-5-onium hexafluorophosphates **5g-h**

PREPARATION OF IMIDAZOLIUM SALTS *VIA* DIRECT ALKYLATION OF N(3)

Next, we wanted to evaluate the potential of methyl triflate in the direct alkylation of the imidazoles. Moreover, the inclusion of the triflate anion was also appealing in the light of our melting point study. Treatment of isochromeno imidazolones **3** with excess methyl triflate under dry conditions furnished the corresponding imidazolium triflates **5i-j** in a fast, exothermic reaction, while solvent and remaining alkylating reagent were easily removed by evaporation (Scheme 8). Oddly, these imidazolium triflates,

unlike all other salts obtained in this study, proved unstable in their pure solid state even when kept at -15 °C. It should also be noted that compounds **5c** and **5h** were unstable upon prolonged dissolution in DMSO-d_6, i.e. during the recording of their ^{13}C NMR spectra.



Scheme 8. Preparation of 1*H*-isochromeno[3,4-*d*]imidazol-5-onium triflates **5i-j** *via* direct alkylation of *N*(2)

STUDY OF THE MELTING BEHAVIOR

Having an array of imidazolium salts in our hands, we were intrigued to evaluate the influence of the counter ion on their melting behaviour. Chart 1 provides an overview of the observed melting points. The high values recorded for the bistriflimides, dicyanamides, tetrafluoroborates, hexafluorophosphates and triflates are consonant with those already mentioned earlier for the imidazolium halides and can again be explained by the ample possibility for intermolecular interactions offered by the molecular skeleton. As a consequence, none of the synthesized salts can be used as an ionic liquid. Nevertheless, some interesting conclusions can be made from these data.

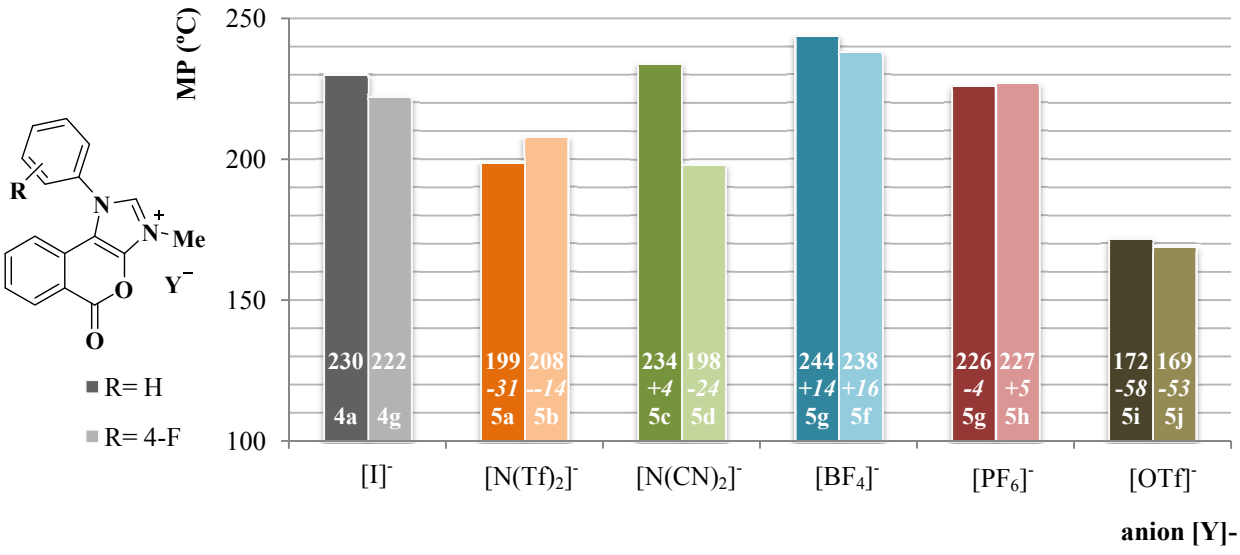


Chart 1. Overview of the melting points of the synthesized isochromeno imidazolium salts

Firstly, substitution of iodide for hexafluorophosphate does not alter the melting point. Moreover, the imidazolium tetrafluoroborates possess even higher melting points than the corresponding iodides. The latter observation can appear surprising when considering the popular, somewhat oversimplified rule stating that a reduction in the melting point can straightforwardly be obtained by increasing the size of the anion, or that of the cation. Indeed, this should reduce Coulombic attraction contributions to the lattice energy of the crystal, and increase the covalence of the ions. Yet, the contributions of anions and cations should not be considered separately, and simplistic predictions of melting point changes are thus questionable.[11-13] Our case supports this statement: the melting points of the hexafluorophosphate and tetrafluoroborate salts are higher than, or in the same range as those of the much smaller and less covalent iodide salts.

A moderate reduction in melting point (15-30 °C) can be observed for imidazolium bistriflimides and dicyanamides, while the largest difference was recorded for the triflates **5i** and **5j**. The latter salts melt at a temperature 58 °C to 53 °C lower than the corresponding iodides. These observations are in agreement with the general observation that highly fluorinated organic anions tend to give lower melting salts. In this context, the bistriflimide salts were also lower melting than the starting iodides. The most common explanation for this behaviour is the largely delocalized character of these anions due to the presence of the strongly electron-withdrawing CF_3-moiety.[14] The consequent weak coordination ability and absence of strong H-bonding contributes significantly to reduction of the melting point. An analogous *rationale* can be pursued for the dicyanamide anion, since the nitrile groups exhibits a similar, albeit weaker, electron withdrawing behavior.

CONCLUSIONS

A synthetic route was developed furnishing an entry to novel isochromeno imidazolonium salts. Starting from the straightforwardly obtainable 1*H*-isochromeno[3,4-*d*]imidazol-1-ones **3**, the corresponding imidazolium halides were prepared *via* a straightforward and convenient alkylation of the *N*(3) atom in a pressure vessel. Anion metathesis subsequently furnished the analogous tetrafluoroborates, hexafluorophosphates, bistriflimides and dicyanamides. The corresponding triflates were prepared upon treatment of the imidazolones with methyl triflate under mild conditions.

The imidazolium halide, tetrafluoroborate and hexafluorophosphate salts possess high melting points (MP~230 °C). With either bistriflimide or dicyanamide as a counter ion, lower melting salts were obtained (MP~200 °C). The largest reduction in melting point was recorded for the strongly delocalized triflate anion (MP~170 °C).

EXPERIMENTAL

All reagents were purchased from commercial sources (Aldrich, Acros) and used without further purification. Solvents were purchased from commercial sources (Aldrich) and employed as is. Crude reaction mixtures were analyzed on LC/MS/UV. Thin layer chromatography was carried out on silica gel 60F254 plates (Merck).

High resolution ^{1}H (300 MHz), ^{13}C (75 MHz), ^{31}P (121 MHz) and ^{19}F (282 MHz) magnetic resonance (NMR) spectra were recorded on a Jeol Eclipse+300 FT NMR spectrometer in deuterated solvents. Chemical shifts are reported using TMS and/or $CFCl_3$ as an internal reference, unless otherwise indicated. Peak assignments were obtained with the aid of DEPT, HSQC, HMBC and COSY spectra. Attenuated total reflection (ATR) IR spectra were recorded on a Perkin Elmer Spectrum BX spectrometer, equipped with a ZnSe-crystal, at room temperature. Low-resolution mass spectra were recorded on an Agilent 1100 series VL mass spectrometer (ES, 70 eV). Melting points were measured with a Büchi B-540 apparatus and are uncorrected.

SYNTHESIS OF IMIDAZOLIUM SALTS 4a-n

1*H*-Isochromeno[3,4-*d*]imidazolone **3** (0.5 mmol) and an appropriate alkyl halide (5 mmol, 10 equiv) were added to a 10 mL pressure vessel containing 2.5 ml of MeCN. The vessel was subsequently sealed and heated in an oil bath at 150 °C for 8 h, under continuous stirring. Next, the mixture was stored overnight at -15 °C to induce crystallization. Imidazolium salt **4** was isolated in crystalline form upon filtration and removal of residual solvent traces under a high vacuum atmosphere. In some cases, an extra recrystallization step in MeCN was necessary to obtain a sufficient degree of purity.

1-Phenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium iodide ***4a***

^{1}H NMR (DMSO-d_6, *300 MHz, ppm*): δ = 4.01 (s, 3H, CH_3); 6.80 (d, 1H, J = 7.70 Hz, H^9); 7.70 (td, 1H, J_{vic} = 7.7 Hz, J_{allyl} = 1.1 Hz, H^7); 7.79-7.78 (m, 6H, 6 x H_{ar}); 8.37 (d, 1H, J = 7.7 Hz, H^6); 9,70 (s, 1H, H^2); ^{13}C NMR (DMSO-d_6, *75 MHz, ppm*): δ = 32.45 (CH_3); 109.69 (C^{9b}); 118.36 (C^{5a}); 119.57 (C^9); 126.67 ($C^{2'}$, $C^{6'}$); 127.10 (C^{9a}); 129.49 (C^7); 130.73 ($C^{3'}$, $C^{5'}$); 132.03 ($C^{4'}$); 132.21 (C^6); 133.65 ($C^{1'}$); 134.88 (C^2); 136.56 (C^8); 140.44 (C^{3a}); 157.22 (C=O); IR (*ATR, cm^{-1}*): ν = 1760 (C=O); 1515 (C=C); MS (ES^+): m/z (%): 277.2 (M^+, 100); MP: 230.2-230.3 °C; Yield = 75%; pale yellow crystals; MW = 404.20.

1-Phenyl-3-ethyl-1H-isochromeno[3,4-d]imidazol-5-onium bromide ***4b***

^{1}H NMR (DMSO-d_6, *300 MHz, ppm*): δ = 1.60 (t, 3H, J = 7.3 Hz, CH_3); 4.43 (q, 2H, J = 7.3 Hz, NCH_2); 6.82 (d, 1H, J = 8.3 Hz, H^9); 7.67-7.89 (m, 7H, 7 x CH_{ar}); 8.38 (d, 1H, J = 7.7 Hz, H^6); 9.79 (s, 1H, H^2); ^{13}C NMR (DMSO-d_6, *75 MHz, ppm*): δ = 13.57 (CH_3); 41.76 (NCH_2); 109.69 ($C_{q,ar}$); 118.28 (CH_{ar}); 119.46 (CH_{ar}); 126.60 ($CH^{2'}{}_{ar}$); 126.96 ($C_{q,ar}$); 129.34 ($C_{q,ar}$); 130.53 ($CH^{3'}{}_{ar}$); 131.87 (CH_{ar}); 132.07 (CH_{ar}); 133.60 ($C_{q,ar}$); 134.05 (CH_{ar}); 136.44 ($C_{q,ar}$); 139.96 ($C_{q,ar}$); 157.77 (C=O); IR (*ATR, cm^{-1}*): ν = 1759 (C = O); 765;

MS (ES^+): m/z (%): 291.3 (M^+, 100); MP: 216.8-220.8 °C; Yield = 40%; white crystals; MW = 371.23.

1-Phenyl-3-butyl-1H-isochromeno[3,4-d]imidazol-5-onium bromide ***4c***

^{1}H NMR (DMSO-*d_6, 300 MHz, ppm*): δ = 0.97 (t, 3H, *J* = 7.4 Hz, CH_3); 1.46 (sextet, 2H, *J* = 7.4 Hz, $C\underline{H}_2$-CH_3); 1.96 (p, 2H, *J* = 7.4 Hz, NCH_2-$C\underline{H}_2$); 4.39 (t, 2H, *J* = 7.4 Hz, NCH_2); 6.82 (d, 1H, *J* = 7.7 Hz, H^9); 7.67-7.88 (m, 7H, 7x CH_{ar}); 8.38 (dd, 1H, J_{vic} = 7.7 Hz, J_{allyl} = 1.1 Hz, $CH^6{}_{ar}$); 9.80 (s, 1H, $CH^2{}_{ar}$); ^{13}C NMR (DMSO-*d_6, 75 MHz, ppm*): δ= 13.27 (CH_3); 18.81 (CH_2); 29.96 (CH_2); 46.06 (NCH_2); 109.82 (C^{9b}); 118.44 (C^{5a}); 119.46 (C^9); 126.65 ($C^{2'}$, $C^{6'}$); 127.05 (C^{9a}); 129.35 (C^7); 130.54 ($C^{3'}$, $C^{5'}$); 131.89 ($C^{4'}$); 132.02 (C^6); 133.61 ($C^{1'}$); 134.24 (C^2); 136.36 (C^8); 140.01 (C^{3a}); 157.83 (C=O); IR (*ATR, cm^{-1}*): ν = 2953 (CH=CH); 1766 (C=O); MS (ES^+): m/z (%): 319.2 (M^+, 100); MP: 220.6-222.7 °C; Yield = 65%; yellow crystals; MW = 399.28.

1-Phenyl-3-butyl-1H-isochromeno[3,4-d]imidazol-5-onium iodide ***4d***

^{1}H NMR (DMSO-*d_6, 300 MHz, ppm*): δ = 0.97 (t, 3H, *J* = 7,4 Hz, CH_3); 1.46 (sextet, 2H, *J* = 7.4 Hz, $C\underline{H}_2$-CH_3); 1.96 (p, 2H, *J* = 7.4 Hz, NCH_2-$C\underline{H}_2$); 4.39 (t, 2H, *J* = 7.4 Hz, NCH_2); 6.82 (d, 1H, *J* = 7.7 Hz, H^9); 7.71 (dxt, 1H, J_{vic} = 7.7 Hz, J_{allyl} = 1,1 Hz, H^7); 7.77-7.89 (m, 7H, 7 x CH_{ar}); 8.37 (dd, 1H, J_{vic} = 7.2 Hz, J_{allyl} = 1.1 Hz, H^6); 9.76 (s, 1H, H^2); ^{13}C NMR (DMSO-*d_6, 75 MHz, ppm*): δ = 13.37 (CH_3); 18.94 (CH_2); 29.99 (CH_2); 46.22 (N-CH_2); 110.03 (C^{9b}); 118.55 (C^{5a}); 119.57 (C^9); 126.75 ($C^{2'}$, $C^{6'}$); 127.16 (C^{9a}); 129.46 (C^7); 130.64 ($C^{3'}$, $C^{5'}$); 132.00 ($C^{4'}$); 132.12 (C^6); 133.71 ($C^{1'}$); 134.23 (C^2); 136.46 (C^8); 140.11 (C^{3a}); 157.92 (C=O); IR (*ATR, cm^{-1}*): ν = 1766 (C=O); MS (ES^+): m/z (%): 319.2 (M^+, 100); MP: 214.2-223.5 °C; Yield = 86%; gray crystals; MW = 446.28.

1-m-Methylphenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium iodide ***4e***

^{1}H NMR (DMSO-*d_6, 300 MHz, ppm*): δ = 2.48 (s, 3H, $C^{3'}$-CH_3); 4.01 (s, 3H, NCH_3); 6.86 (d, 1H, *J* = 8.0 Hz, H^9); 7.58-7.75 (m, 5H, 5 x H_{ar}); 7.85 (td, 1H, J_{vic} = 8.0 Hz, J_{allyl} = 1.7 Hz, H^8); 8.38 (dd, 1H, J_{vic} = 8.3 Hz, J_{allyl} = 1,1 Hz, H^6); 9.67 (s, 1H, H^2); ^{13}C NMR (DMSO-*d_6, 75 MHz, ppm*): δ = 20.86 (C_{ar}-$\underline{C}H_3$); 32.47 (NCH_3); 109.65 (C^{9b}); 118.35 (C^{5a}); 119.66 (C^9); 123.68 (CH_{ar}); 126.84 (CH_{ar}); 127.13 (C^{9a}); 129.48 (C^7); 130.47 ($C^{5'}$); 132.20, 132.58 (C^6, $C^{4'}$); 133.60 ($C^{1'}$); 134.78 (C^2); 136.61 (C^8); 140.43, 140.69 (C^{3a} en $C^{3'}$); 157.97 (C=O); MS (ES^+): m/z (%): 291.3 (M^+, 100); IR (*ATR, cm^{-1}*): ν = 1759 (C=O); 1517 (C=C); MP: 200.0-205.7 °C; Yield = 94%; yellow crystals; MW = 418.23.

1-m-Methylphenyl-3-butyl-1H-isochromeno[3,4-d]imidazol-5-onium iodide ***4f***

^{1}H NMR (DMSO-*d_6, 300 MHz, ppm*): δ = 0.94 (t, 3H, *J* = 7.1 Hz, CH_3); 1.42 (sextet, 2H, *J* = 7.1 Hz, $C\underline{H}_2$-CH_3); 1.94 (p, 2H, *J* = 7.1 Hz, NCH_2-$C\underline{H}_2$); 2.45 (s, 3H, C_{ar}-CH_3); 4.34 (t, 3H, *J* = 7.1 Hz, NCH_2); 6.83 (d, 1H, *J* = 8.3 Hz, H^9); 7.56-7.71 (m, 5H, 5 x CH_{ar}); 7.81 (td, 1H, J_{vic} = 7.8 Hz, J_{allyl} = 1.3 Hz, CH_{ar}); 8.34 (d, 1H, *J* = 7.7 Hz; H^6); 9.71 (s, 1H, H^2); ^{13}C NMR (DMSO-*d_6, 75 MHz, ppm*): δ = 13.40 (CH_3); 18.94 (CH_2); 20.83 (C_{ar}-$\underline{C}H_3$); 30.05 (CH_2); 46.21 (NCH_2); 109.92 (C^{9b}); 118.58 (C^{5a}); 119.68 (C^9); 123.74 (CH_{ar});

126.88 (CH_{ar}); 127.14 (C^{9a}); 129.50 (C^{7}); 130.41 ($C^{5'}$); 132.14 (C^{6}); 132.55 ($C^{4'}$); 133.65 ($C^{1'}$); 134.18 (C^{2}); 136.53 (C^{8}); 140.09 (C^{3a}); 140.64 ($C^{3'}$); 157.95 (C=O); IR (*ATR, cm^{-1}*): ν = 2956 (CH=CH); 1766 (C=O); MS (ES^+): m/z (%) : 333.3 (M^+, 100); MP: 213.2-214.2 °C; Yield = 37%; yellow crystals; MW = 460.31.

1-p-Fluorophenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium iodide ***4g***

^{1}H NMR (DMSO-*d_6, 300 MHz, ppm*): δ = 4.01 (s, 3H, NCH_3); 6.85 (d, 1H, *J* =7.7 Hz, H^9); 7.63-7.97 (m, 6H, 6 x CH_{ar}); 8.38 (d, 1H, *J* =7.7 Hz, H^6); 9.69 (s, 1H, H^2); ^{13}C NMR (DMSO-*d_6, 75 MHz, ppm*): δ = 32.34 (N-CH_3); 109.79 (C^{9b}); 117.53 (CH_{ar}); 117.84 (CH_{ar}); 117.89 (CH_{ar}); 119.63 (C^9); 126.92 (C^{9a}); 129.18 (C^7); 129.36 (d, *J* = 8.1 Hz, C_{ar}); 129.80 (d, *J* = 2.3 Hz, C_{ar}); 132.10 (C^6); 136.59 (C^8); 140.09 (C^{3a}); 157.80 (C=O); 161.72 ($C^{4'}$); IR (*ATR, cm^{-1}*): ν = 2981 (CH=CH); 1748 (C=O); 1514 (C=C); MS (ES^+): m/z (%): 295.2 (M^+, 100); MP: 221-222 °C; Yield = 73%; yellow crystals; MW = 422.19.

1-p-Fluorophenyl-3-butyl-1H-isochromeno[3,4-d]imidazol-5-onium iodide ***4h***

^{1}H-NMR (DMSO-*d_6, 300 MHz, ppm*): δ = 0.97 (t, 3H, *J* = 7.2 Hz, CH_3); 1.46 (sextet, 2H, *J* = 7.2 Hz, $C\underline{H}_2$-CH_3); 1.97 (p, 2H, *J* = 7.2 Hz, NCH_2-$C\underline{H}_2$); 4.39 (t, 2H, *J* = 7.2 Hz, NCH_2); 6.86 (d, 1H, *J* =7.2 Hz, H^9); 7.64-7.98 (m, 6H, 6 x CH_{ar}); 8.38 (dd, 1H, J_{vic} = 7.7 Hz, J_{allyl} = 1.1 Hz, H^6); 9.77 (s, 1H, H^2); ^{13}C-NMR (DMSO-*d_6, 75 MHz, ppm*): δ = 13.27 (CH_3); 18.81 (CH_2); 29.94 (CH_2); 46.13 (NCH_2); 110.10 (C^{9b}); 117.47 (CH_{ar}); 117.78 (CH_{ar}); 118.40 (C^{5a}); 119.64 (C^9); 126.97 (C^{9a}); 129.28 (C^7); 129.41 (CH_{ar}); 129.88 (d, *J* = 3.5 Hz, C_{ar}); 132.05 (C^6); 134.45 (C_{ar}); 136.53 (C^8); 139.87 (C^{3a}); 157.80 (C=O); 161.78 ($C^{4'}$); IR (*ATR, cm^{-1}*): ν = 2999 (CH=CH); 1753 (C=O); 1515 (C=C); MS (ES^+): m/z (%): 337.2 (M^+, 100); MS (ES^-): 591.0; 127.2 (I^-); MP: 219.8-221.5 °C; Yield = 71%; yellow crystals; MW = 464.27.

1-p-Methoxyphenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium iodide ***4i***

^{1}H-NMR (DMSO-*d_6, 300 MHz, ppm*): δ = 3.93 (s, 3H, OCH_3); 4.00 (s, 3H, NCH_3); 6.86 (d, 1H, *J* = 7.7 Hz, H^9); 7.33 (~dt, 2H, J_{vic} = 8.8 Hz, J_{allyl} = 2.8 Hz, $H^{2'}$, $H^{6'}$); 7.68-7.89 (m, 4H, 4 x CH_{ar}); 8.37 (dd, 1H, J_{vic} = 8.3 Hz, J_{allyl} = 1.1 Hz, H^6); 9.67 (s, 1H, H^2); ^{13}C-NMR (DMSO-*d_6, 75 MHz, ppm*): δ = 32.29 (N-CH_3); 55.82 (OCH_3); 109.82 (C^{9b}); 115.55 ($C^{2'}$, $C^{6'}$); 118.21 (C^{5a}); 119.49 (C^9); 125,95 ($C^{1'}$); 127.12 (C^{9a}); 127.98 ($C^{3'}$, $C^{5'}$); 129.32 (C^7); 132.04 (C^6); 134.88 (C^2); 136.50 (C^8); 140.16 (C^{3a}); 157.86 (C=O); 161.27 ($C^{4'}$); IR (*ATR, cm^{-1}*): ν = 3030 (CH=CH); 1762 (C=O); 1513 (C=C); MS (ES^+): m/z (%): 307.3 (M^+, 100); MP: 226.5-233.1 °C; Yield = 95%, yellow crystals; MW = 434.23.

1-p-Methoxyphenyl-3-butyl-1H-isochromeno[3,4-d]imidazol-5-onium iodide ***4j***

^{1}H-NMR (DMSO-*d_6, 300 MHz, ppm*): δ = 0.97 (t, 3H, *J* = 7.3 Hz, CH_3), 1.46 (sextet, 2H, *J* = 7.3 Hz, $C\underline{H}_2$-CH_3), 1.96 (p, 2H, *J* = 7,3 Hz, NCH_2-$C\underline{H}_2$), 3.93 (s, 3H, OCH_3), 4.38 (t, 2H, *J* = 7.3 Hz, NCH_2), 6.88 (d, 1H, *J* =8.3 Hz, H^9), 7.33 (~dt, 2H, J_{vic} = 9.4 Hz, J_{allyl} = 2.8 Hz, $H^{2'}$, $H^{6'}$), 7.67-7.99 (m, 4H, 4 x CH_{ar}), 8.37 (d, 1H, *J* = 7.7 Hz, CH^6_{ar}), 9.72 (d, 1H, *J* = 1.7 Hz, H^2); ^{13}C-NMR (DMSO-*d_6, 75 MHz, ppm*): δ = 13.25 (CH_3), 18.83 (CH_2), 29.97 (CH_2), 46.03 (NCH_2), 55.82 (OCH_3), 110.01 (C^{9b}), 115.49 ($C^{2'}$, $C^{6'}$), 118.42 (C^{5a}),

119.50 (C^9), 126.01 ($C^{1'}$), 127.15 (C^{9a}), 128.05 ($C^{3'}$, $C^{5'}$), 129.32 (C^7), 131.98 (C^6), 134.27 (C^2), 136.42 (C^8), 139.82 (C^{3a}), 157.86 (C=O), 161.23 ($C^{4'}$); IR (*ATR, cm^{-1}*): ν = 1752 (C=O), 1514 (C=C); MS (ES^+): m/z (%): 349.2 (M^+, 100); MP: 216.9-219.5 °C; Yield = 73%; yellow crystals; MW = 476.31.

1-p-Methylphenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium iodide ***4k***

^{1}H NMR (DMSO-*d$_6$, 300 MHz, ppm*): δ = 2.51 (s, 3H, $CH_3C^{4'}$), 4.01 (s, 3H, NCH_3), 6.86 (d, 1H, *J* = 7.7 Hz, H^9), 7.58-7.74 (m, 5H, 5 x CH_{ar}), 7.85 (t, 1H, *J* = 7.4 Hz, CH_{ar}), 8.38 (d, 1H, *J* = 7.7 Hz, H^6), 9.65 (s, 1H, H^2); ^{13}C NMR (DMSO-*d$_6$, 75 MHz, ppm*): δ = 20.86 ($\underline{C}H_3C_{q,ar}$), 32.29 (NCH_3), 109.56 (C^{9b}), 118.24 (C^{5a}), 119.47 (C^9), 126.27 ($C^{2'}$, $C^{6'}$), 127.05 (C^{9a}), 129.35 (C^7), 130.94 ($C^{3'}$, $C^{5'}$), 131.03 ($C^{1'}$), 132.07 (C^6), 134.74 (C^2), 136.45 (C^8), 140.30 (C^{3a}), 141.92 ($C^{4'}$), 157.83 (C=O); IR (*ATR, cm^{-1}*): ν = 1766 (C=O), 1516 (C=C); MS (ES^+): m/z (%): 291.3 (M^+, 100); MP: 234.8-241.7 °C; Yield = 67%, yellow crystals; MW = 418.23.

1-p-Methylphenyl-3-butyl-1H-isochromeno[3,4-d]imidazol-5-onium iodide ***4l***

^{1}H-NMR (DMSO-*d$_6$, 300 MHz, ppm*): δ = 0.97 (t, 3H, *J* = 7.4 Hz, CH_3), 1.46 (sextet, 2H, *J* = 7.4 Hz, $C\underline{H}_2$-CH_3), 1.96 (p, 2H, *J* = 7.4 Hz, NCH_2-$C\underline{H}_2$), 2.52 (s, 3H, $CH_3C^{4'}$), 4.38 (t, 2H, *J* = 7.4 Hz, NCH_2), 6.86 (d, 1H, *J* =8.0 Hz, H^9), 7.62 (d; 2H, *J* = 8.3 Hz, $H^{3'}$ en $H^{5'}$), 7.70 (td, 1H, J_{vic} = 8.0 Hz, J_{allyl} = 1.1 Hz, H^7), 7.74 (d, 2H, *J* = 8.3 Hz, $H^{2'}$ en $H^{6'}$), 7.85 (td, 1H, J_{vic} = 7.8 Hz, J_{allyl} = 1.1 Hz, H^8), 8.37 (d, 1H, *J* = 8.0 Hz, H^6), 9.75 (s, 1H, H^2); ^{13}C-NMR (DMSO-*d$_6$, 75 MHz, ppm*): δ = 13.27 (CH_3), 18.84 (CH_2), 20.87 ($C^{4'}$-$\underline{C}H_3$); 29.94 (CH_2); 46.09 (NCH_2); 109.95 (C^{9b}); 118.43 (C^{5a}); 119.49 (C^9); 126.36 ($C^{2'}$, $C^{6'}$), 127.11 (C^{9a}), 129.32 (C^7), 130.86 ($C^{3'}$, $C^{5'}$), 131.11 ($C^{1'}$), 131.99 (C^6), 134.10 (C^2), 136.37 (C^8), 139.96 (C^{3a}), 141.89 ($C^{4'}$), 157.83 (C=O); IR (*ATR, cm^{-1}*): ν = 1752 (C=O), 1517 (C=C); MS (ES^+): m/z (%): 333.3 (M^+, 100); MP: 224.3-227.8 °C; Yield = 71%; yellow crystals; MW = 460.31.

1-m-Methoxyphenyl-3-butyl-1H-isochromeno[3,4-d]imidazol-5-onium jodide ***4m***

^{1}H-NMR (DMSO-*d$_6$, 300 MHz, ppm*): δ = 0.98 (t, 3H, *J* = 7.2 Hz, CH_3), 1.47 (sextet, 2H, *J* = 7.2 Hz, $C\underline{H}_2$-CH_3), 1.97 (p, 2H, *J* = 7.2 Hz, NCH_2-$C\underline{H}_2$), 3.87 (s, 3H, OCH_3), 4.39 (t, 2H, *J* = 7.2 Hz, NCH_2), 6.92 (d, 1H, *J* = 7.7 Hz, H^9), 7.42 (d, 2H, *J* = 7.7 Hz, 2 x CH_{ar}), 7.52 (d, 1H, *J* = 1.7 Hz, $CH^{2'}{}_{ar}$), 7.67-7.77 (m, 2H, 2 x CH_{ar}), 7,87 (t, 1H, *J* = 7.4 Hz, CH_{ar}), 8.38 (d, 1H, *J* = 7.7 Hz, $CH^6{}_{ar}$), 9.79 (d, 1H, *J* = 2.2 Hz, $CH^2{}_{ar}$); ^{13}C-NMR (DMSO-*d$_6$, 75 MHz, ppm*): δ = 13.27 (CH_3), 18.84 (CH_2), 29.94 (CH_2), 46.13 (NCH_2), 55.90 (OCH_3), 109.89 (C^{9b}), 112.31 ($C^{2'}$), 117.61 (CH_{ar}), 118.39 (C_{ar}), 118.47 (C_{ar}), 119.69 (C^9), 127.03 (C^{9a}), 129.37 (C^7), 131.41 ($C^{5'}$), 131.98 (C^6), 134.13 (C^2), 134.53 ($C^{1'}$), 136.44 (C^8), 139.89 (C^{3a}), 157.80 (C=O), 160.19 ($C^{3'}$); IR (*ATR, cm^{-1}*): ν = 1765 (C=O); MS (ES^+): m/z (%): 349.2 (M^+, 100); MP: 214.6-218.9 °C; Yield = 74%; yellow crystals; MW = 476.31.

1-Phenyl-2-methyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium iodide ***4n***

^{1}H-NMR (DMSO-*d$_6$, 300 MHz, ppm*): δ = 2.57 (s, 3H, C_{ar}-CH_3), 3.95 (s, 3H, NCH_3), 6.50 (d, 1H, *J* = 7.7 Hz, H^9), 7,65 (t, 1H, *J* = 7.4 Hz, CH_{ar}), 7.73-7.92 (m, 6H, 6 x CH_{ar}), 8.36 (d, 1H, *J* = 7.7 Hz, H^6); ^{13}C-NMR

(DMSO-*d_6, 75 MHz, ppm*): δ= 10.38 (C_{ar}-$\underline{C}H_3$), 30.90 (NCH_3), 108.55 ($C_{q,ar}$), 118.08 ($C_{q,ar}$), 118.75 (CH_{ar}), 127.01 ($C_{q,ar}$), 127.30 ($CH^{2'}{}_{ar}$), 128.86 ($C_{q,ar}$), 131.00 ($CH^{3'}{}_{ar}$), 132.10 (CH_{ar}), 132.69 (CH_{ar}), 136.42 (CH_{ar}), 139.64 ($C_{q,ar}$), 143.99 ($C_{q,ar}$), 157.79 (C=O); IR (*ATR, cm^{-1}*): ν = 1761 (C=O), MS (ES^+): m/z (%): 291.3 (M^+, 100); MP: 230.4-239.1 °C; Yield = 96%; yellow crystals; MW = 418.23.

SYNTHESIS OF IMIDAZOLIUM BISTRIFLIMIDES 5a-b.

A solution of **4a** or **4g** (100 mg) and $LiNTf_2$ (2 equiv) in water (3 mL) was stirred at room temperature for 1 h, during which time a white precipitate of **5a** or **5b**, respectively, formed. This precipitate was isolated by filtration, washed with water (3 x 2 mL) and dried under vacuum for 1 h.

*1-Phenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium bistriflimide **5a***

^{1}H-NMR (DMSO-*d_6, 300 MHz, ppm*): δ= 2.49 (s, DMSO), 3.36 (s, H_2O), 4.00 (s, 3H, NMe), 6.80 (d, 1H, J_{vic} = 8.3 Hz, H^9), 7.70 (t, 1H, H^7), 7.77-7.86 (m, 6H, $H^{3'}$, $H^{5'}$, $H^{2'}$, $H^{6'}$, H^8, H^4), 8.37 (d, 1H, J_{vic} = 8.3 Hz, H^6), 9.67 (s, 1H, H^2); ^{13}C-NMR (DMSO-*d_6, 75 MHz, ppm*): δ= 32.43 (NMe), 39.54 (DMSO-*d_6*), 109.67 (C^{9b}), 118.39 (C^{5a}), 119.59 (C^9), 126.68 ($C^{2'}$, $C^{6'}$), 127.09 (C^{9a}), 129.52 (C^7), 130.75 ($C^{3'}$, $C^{5'}$), 132.05 ($C^{4'}$), 132.23 (C^6), 133.65 ($C^{1'}$), 134.91 (C^2), 136.59 (C^8), 140.45 (C^{3a}), 157.93 (C=O), no CF_3 peak visible; ^{19}F-NMR (DMSO-*d_6, 292 MHz, ppm*): δ= (-)78.60 (s, 6F, CF_3); IR (*ATR, cm^{-1}*): ν = 1134.44 (C-F), 1196.67 (C-O), 1517.23 (C=C), 1655.44 (C=N), 1759.78 (C=O), 3152.20 (=C-H); MS (*ES^+*): m/z (%): 277.3 (M^+, 100), 278.3 ($[M+1]^+$, 19); MS (*ES^-*): m/z (%): 280.0 ($[N(Tf)_2]^-$, 100), 281 ($[N(Tf)_2]^-$, 5), 282 ($[N(Tf)_2]^-$, 10), 582.8 (7); MP: 198-200 °C; Yield = 58%; beige powder; MW = 557.44.

*1-p-Fluorophenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium bistriflimide **5b***

^{1}H-NMR (DMSO-*d_6*, 300 MHz, ppm): δ= 2.51 (s, DMSO), 3.37 (s, H_2O), 4.01 (s, 3H, NMe), 6.84 (d, 1H, J_{vic} = 7.7 Hz, H^9), 7.68 (t, 2H, $H^{3'}$, $H^{5'}$), 7.71 (t, 1H, H^7), 7.85 (t, 1H, J_{vic} = 7.7 Hz, H^8) 7.92 (dd, 2H, $J_{H\text{-}F}$ = 5.0Hz, J_{vic} = 8.8 Hz, $H^{2'}$, $H^{6'}$), 8.38 (d, 1H, J_{vic} = 8.3 Hz, H^6), 9.68 (s, 1H, H^2); ^{13}C-NMR (DMSO-*d_6*, 75 MHz, ppm): δ= 32.35 (NMe), 39.52 (DMSO-*d_6*), 109.81 (C^{9b}), 116.73 (q, 2C, $J_{C\text{-}F}$ = 333.4 Hz, CF_3), 117.69 (d, $J_{C\text{-}F}$ = 24.2 Hz, $C^{3'}$, $C^{5'}$), 118.22 (C^{5a}), 119.64 (C^9), 126.94 (C^{9a}), 129.27 (d, $J_{C\text{-}F}$ = 10.4 Hz, $C^{2'}$, $C^{6'}$), 129.43 (C^7), 129.82 (d, $J_{C\text{-}F}$ = 3.5 Hz, $C^{1'}$), 132.11 (C^6), 135.04 (C^2), 136.59 (C^8), 140.22 (C^{3a}), 157.81 (C^5=O), 163.42 (d, $J_{C\text{-}F}$ = 249.2 Hz, $C^{4'}$); ^{19}F-NMR (DMSO-*d_6*, 292 MHz, ppm): δ= (-)107.9-(-)107.8 (m), (-)78.61 (s, 6F, CF_3); IR (ATR, cm^{-1}): ν = 1191.51 (C-F), 1211.48 (C-O), 1514.22 (C=C), 1656.90 (C=N), 1746.22 (C=O), 3133.83 (=C-H); MS (ES^+): m/z (%): 295.3 (M^+, 100), 296.3 ($[M+1]^+$, 19); MS (ES^-): m/z (%): 280.0 ($[N(Tf)_2]^-$, 100), 282 ($[N(Tf)_2]^-$, 10), 548.8 (7); MP: 201-205 °C; Yield = 48%; beige powder; MW = 575.43.

SYNTHESIS OF IMIDAZOLIUM DICYANAMIDES 5c-d.

A solution of **4a** or **4g** (100 mg) and $NaN(CN)_2$ (3 equiv) in water (3 mL) was stirred at room temperature for 1 h, during which time a white precipitate of **5c** or **5d**, respectively, formed. This precipitate was

isolated by filtration, washed with water (3 x 2 mL) and dried under vacuum for 1 h.

1-Phenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium dicyanamide ***5c***

^{1}H-NMR (DMSO-d_6, *300 MHz, ppm*): δ = 2.50 (s, DMSO), 3.35 (s, H_2O), 4.01 (s, 3H, NMe), 6.81 (d, 1H, J_{vic} = 7.7 Hz, H^9), 7.71 (t, 1H, H7), 7.78-7.88 (m, 6H, $H^{3'}$, $H^{5'}$, $H^{2'}$, $H^{6'}$, H^8, H^4), 8.38 (d, 1H, J_{vic} = 8.3 Hz, H^6), 9.70 (s, 1H, H^2); ^{13}C-NMR (DMSO-d_6, *75 MHz, ppm*): δ = 32.40 (NMe), 39.42 (DMSO-d_6), 109.64 (C^{9b}), 117.32 (CN), 118.21 (C^{5a}), 119.43 (C^9), 126.56 ($C^{2'}$, $C^{6'}$), 127.00 (C^{9a}), 129.34 (C^7), 130.57 ($C^{3'}$, $C^{5'}$), 131.89 ($C^{4'}$), 132.07 (C^6), 133.52 ($C^{1'}$), 134.73 (C^2), 136.41 (C^8), 140.31 (C^{3a}), 157.80 (C=O); IR (*ATR, cm^{-1}*): ν = 1192, 1213 (C-O), 1498, 1519 (C=C), 1598, 1742 (C=O), 2189 (CN); MS (*ES$^+$*): m/z (%): 277.3 (M^+, 100), 278.3 ($[M+1]^+$, 19); MP: 233.5-234.5 °C; Yield = 62%; off-white powder; MW = 343.34. The product proved unstable upon prolonged dissolution in DMSO-d_6. Hence, breakdown was observed in the ^{13}C NMR spectrum.

1-p-Fluorophenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium dicyanamide ***5d***

^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): δ = 2.50 (s, DMSO), 3.36 (s, H_2O), 4.01 (s, 3H, NMe), 6.85 (d, 1H, J_{vic} = 7.7 Hz, H^9), 7.64-7.77 (m, 3H, $H^{3'}$, $H^{5'}$, H^7), 7.80-7.98 (m, 3H, $H^{2'}$, $H^{6'}$, H^8), 8.38 (d, 1H, J_{vic} = 8.3 Hz, H^6), 9.69 (s, 1H, H^2); ^{13}C-NMR (DMSO-d_6, *75 MHz, ppm*): δ = 32.44 (NMe), 39.52 (DMSO-d_6), 109.90 (C^{9b}), 117.81 (d, J_{C-F} = 23.1Hz, $C^{3'}$, $C^{5'}$), 118.32 (C^{5a}), 119.05 (CN), 119.76 (C^9), 127.01 (C^{9a}),129.36 (d, J_{C-F} = 9.2Hz, $C^{2'}$, $C^{6'}$), 129.53 (C^7), 129.92 (d, J_{C-F} =2.31Hz, $C^{1'}$), 132.22 ($C^{6)}$, 135.17 (C^2), 136.71 (C^8), 140.33 (C^{3a}), 157.92 (C^5=O), 163.53 (d, J_{C-F} = 249.2Hz, $C^{4'}$); ^{19}F-NMR (DMSO-d_6, 292 MHz, ppm): δ = (-)107.79-(-)107.91(m); IR (ATR, cm^{-1}): ν = 1158.00 (C-F), 1217.88 (C-O), 1516.97 (C=C), 1650.48 (C=N), 1746.73 (C=O), 2135.02 (CN), 3113.68 (=C-H); MS (ES$^+$): m/z (%): 295.3 (M^+, 100), 296.3 ($[M+1]^+$, 22); MP: 197-199 °C; Yield = 47%; white powder; MW = 361.33.

SYNTHESIS OF IMIDAZOLIUM TETRAFLUOROBORATES 5e-f.

A solution of **4a** or **4g** (200 mg) and $LiBF_4$ (2 equiv) in water (6 mL) was stirred at room temperature for 1 h, during which time a white precipitate of **5e** or **5f**, respectively, formed. This precipitate was isolated by filtration, washed with water (3 x 4 mL) and dried under vacuum for 1 h.

1-Phenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium tetrafluoroborate ***5e***

^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): δ = 2.50 (s, DMSO), 3.39 (s, H_2O), 4.02 (s, 3H, NMe), 6.82 (d, 1H, J_{vic} = 7.7 Hz, H^9), 7.69 (t, 1H, H^7), 7.77-7.87 (m, 6H, $H^{3'}$, $H^{5'}$, $H^{2'}$, H6', H^8, H^4), 8.38 (d, 1H, J_{vic} = 7.7 Hz, H^6), 9.68 (s, 1H, H^2); ^{13}C-NMR (DMSO-d_6, *75 MHz, ppm*): δ = 32.38 (NMe), 39.53 (DMSO-d_6), 110.21 (C^{9b}), 118.39 (C^{5a}), 119.59 (C^9), 126.66 ($C^{2'}$, $C^{6'}$), 127.09 (C^{9a}), 129.52 (C^7), 130.76 ($C^{3'}$, $C^{5'}$), 132.05 ($C^{4'}$), 132.24 (C^6), 133.66 ($C^{1'}$), 134.91 (C^2), 136.57 (C^8), 140.45 (C^{3a}), 157.95 (C^5=O); ^{19}F-NMR (DMSO-d_6, 292 MHz, ppm): δ = (-)71.91(s), (-)148.18 (s, $[^{11}BF_4]^-$), (-)148.13 (s, $[^{10}BF_4]^-$); IR (ATR, cm^{-1}): ν = 1049.44 (C-F), 1220.95 (C-O), 1508.96 (C=C), 1643.38(C=N), 1759.53 (C=O), 3080.44 (=C-H); MS (ES$^+$): m/z

(%): 277.3 (M^+, 100), 278.3 ([M+1]$^+$, 19); MS (ES-): m/z (%): 86.3 ([$^{10}BF_4$]$^-$, 30), 87.3 ([$^{11}BF_4$]$^-$, 100), 197 (69); MP: 242-245 °C; Yield = 44%; beige powder; MW = 364.10.

1-p-Fluorophenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium tetrafluoroborate ***5f***

^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): δ = 2.50 (s, DMSO), 3.38 (s, H_2O), 4.02 (s, 3H, NMe), 6.86 (d, 1H, J_{vic} = 7.7 Hz, $H^{9)}$, 7.61-7.76 (m, 3H, $H^{3'}$, $H^{5'}$, H^7), 7.81-7.94 (m, 3H, $H^{2'}$, $H^{6'}$, H^8), 8.38 (d, 1H, J_{vic} = 7.7 Hz, H^6), 9.66 (s, 1H, H^2); ^{13}C-NMR (DMSO-d_6, *75 MHz, ppm*): δ = 32.39 (NMe), 39.52 (DMSO-d_6), 109.86 (C^{9b}), 117.82 (d, J_{C-F} = 24.2Hz, $C^{3'}$, $C^{5'}$), 118.33 (C^{5a}), 119.75 (C^9), 127.02 (C^{9a}), 129.36 (d, J_{C-F} = 9.2 Hz, $C^{2'}$, $C^{6'}$), 129.54 (C^7), 129.94 (d, J_{C-F} = 2.3Hz, $C^{1')}$, 132.21 (C^6), 135.16 (C^2), 136.70 (C^8), 140.34 (C^{3a}), 157.93 (C^5=O), 163.56 (d, J_{C-F} = 249.2Hz, $C^{4'}$); ^{19}F-NMR (DMSO-d_6, 292 MHz, ppm): δ = (-)107.4-(-)107.6 (m), (-)148.08 (s, [$^{11}BF_4$]$^-$), (-)148.02 (s, [$^{10}BF_4$]$^-$); IR (ATR, cm^{-1}): ν = 1059.77 (C-F), 1214.65 (C-O), 1511.36 (C=C), 1651.92 (C=N), 1757.10 (C=O), 3126.61 (=C-H); MS (ES+): m/z (%): 295.3 (M^+, 100), 296.3 ([M+1]$^+$, 22); MS (ES-): m/z (%): 86.3 ([$^{10}BF_4$]$^-$, 22), 87.3 ([$^{11}BF_4$]$^-$, 92), 468 (57), 469.0 (100); MP: 237-239 °C; Yield = 65%; beige powder; MW = 382.09.

SYNTHESIS OF IMIDAZOLIUM HEXAFLUOROPHOSPHATES 5g-h.

Hexafluorophosphoric acid (65 wt% in water, 1.3 equiv, ~0.1 mL) was added to a suspension of **4a** or **4g** (0.5 mmol) in water (5 mL). The resulting mixture was stirred at room temperature for 8 h, during which time a precipitate of **5g** or **5h**, respectively, formed. This precipitate was isolated by filtration, washed with water until neutral, and dried under vacuum for 1 h.

1-Phenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium hexafluorophosphate ***5g***

^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): δ = 2.50 (s, DMSO), 3.36 (s, H_2O), 4.01 (s, 3H, NMe), 6.81 (d, 1H, J_{vic} = 7.8 Hz, H^9), 7.71 (t, 1H, J_{vic} = 7.8 Hz, H^7), 7.77-7.91 (m, 6H, $H^{3'}$, $H^{5'}$, $H^{2'}$, $H^{6'}$,H^8, $H^{4'}$), 8.38 (d, 1H, J_{vic} = 7.8 Hz, H^6), 9.69 (s, 1H, H^2); ^{13}C-NMR (DMSO-d_6, *75 MHz, ppm*): δ = 32.31 (NMe), 39.41 (DMSO-d_6), 109.56 (C^{9b}), 118.24 (C^{5a}), 119.46 (C^9), 126.54 ($C^{2'}$, $C^{6'}$), 126.98 (C^{9a}), 129.37 (C^7), 130.60 ($C^{3'}$, $C^{5'}$), 131.92 ($C^{4'}$), 132.08 (C^6), 133.53 ($C^{1'}$), 134.76 (C^2), 136.44 (C^8), 140.32 (C^{3a}), 157.81 (C^5=O); ^{19}F-NMR (DMSO-d_6, 292 MHz, ppm): δ = (-)70.40 (d, J_{P-F} = 710.3 Hz, [PF_6]$^-$); IR (ATR, cm^{-1}): ν = 835.05, 1214.41 (C-O), 1520.75 (C=C), 1657.33 (C=N), 1742.69 (C=O), 3152.20 (=C-H); MS (ES+): m/z (%): 277.3 (M+, 100), 278.3 ([M+1]+, 19); MS (ES-): m/z (%): 127.0 (I-, 13), 145.0 ([PF_6]$^-$, 100), 293.3 (16), 313.0 (59); MP: 224-227 °C; Yield = 57%; white powder; MW = 422.26.

1-p-Fluorophenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium hexafluorophosphate ***5h***

^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): δ = 2.50 (s, DMSO), 3.35 (s, H_2O), 4.01 (s, 3H, NMe), 6.86 (d, 1H, J_{vic} = 8.3Hz, H^9), 7.64-7.75 (m, 3H, $H^{3'}$, $H^{5'}$, H^7), 7.82-7.92 (m, 3H, $H^{2'}$, $H^{6'}$, H^8), 8.39 (d, 1H, J_{vic} = 8.3Hz, H^6), 9.65 (s, 1H, H^2); ^{13}C-NMR (DMSO-d_6, *75 MHz, ppm*): δ = 32.28 (NMe), 39.45 (DMSO-d_6), 109.75 (C^{9b}), 117.73 (d, J_{C-F} = 23.1 Hz, $C^{3'}$, $C^{5'}$), 118.24 (C^{5a}), 119.69 (C^9), 126.92 (C^{9a}), 129.24 (d, J_{C-F} = 9.2Hz,

$C^{2'}$, $C^{6'}$), 129.46 (C^7), 129.82 (d, J_{C-F} = 2.3 Hz, C1'), 132.15 (C^6), 135.12 (C^2), 136.62 (C^8), 140.25 (C^{3a}), 157.80 (C^5=O), 163.48 (d, J_{C-F} = 250.3 Hz, $C^{4'}$); ^{19}F-NMR (DMSO-d_6, 292 MHz, ppm): δ = (-)70.01 (d, J_{P-F} = 718.2 Hz, $[PF_6]^-$), (-)107.85-(-)107.88 (m); IR (ATR, cm^{-1}): ν = 835.05, 1220.23 (C-O),1320.26 (C-F), 1517.99 (C=C), 1660.90 (C=N), 1746.28 (C=O), 3156.01 (=C-H); MS (ES^+): m/z (%): 295.0 (M^+, 100), 296.3 ($[M+1]^+$, 18); MS (ES^-): m/z (%): 145.0 ($[PF_6]^-$, 100), 280.0 (35), 313.0 (18); MP: 226-228 °C; Yield = 40%; white powder; MW = 440.25. The product proved unstable upon prolonged dissolution in DMSO. Hence, breakdown was observed in the ^{13}C NMR spectrum.

SYNTHESIS OF IMIDAZOLIUM TRIFLATES 5i-j.

1*H*-Isochromeno[3,4-*d*]imidazol-1-one **3a** or **3b** (1 mmol), methyl triflate (2 equiv) and MeCN (5.5 mL) were quickly added to a flame-dried round bottom flask equipped with a stirring bar. The resulting mixture was kept under an N_2 atmosphere and stirred at room temperature for 30 min. Reaction progress was monitored using TLC. The desired imidazolium triflates **5i** or **5j** were obtained *via* evaporation of the solvent and excess alkylating agent. Finally, the obtained salts were dried under vacuum for 1 h. If impurities should be present, the product can be recrystallized from acetonitrile at -15 °C.

*1-Phenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium triflate **5i***

^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): δ = 2.50 (s, DMSO), 3.46 (s, H_2O), 4.01 (s, 3H, NMe), 6.81 (d, 1H, J_{vic} = 7.7 Hz, H^9), 7.70 (t, 1H, H^7), 7.79-7.88 (m, 6H, $H^{3'}$, $H^{5'}$, $H^{2'}$, $H^{6'}$,H^8, $H^{4'}$), 8.38 (d, 1H, J_{vic} = 7.7 Hz, H^6), 9.67 (s, 1H, H^2); ^{13}C-NMR (DMSO-d_6, *75 MHz, ppm*): δ = 32.38 (NMe), 39.41 (DMSO-d_6), 109.69 (C^{9b}), 118.43 (C^{5a}), 119.62 (C^9), 121.20 (q, J_{C-F} = 321.9, CF_3), 126.70 (C2', $C^{6'}$), 127.13 (C^{9a}), 129.48 (C^7), 130.75 ($C^{3'}$, $C^{5'}$), 132.06 ($C^{4'}$), 132.23 (C^6), 133.71 ($C^{1'}$), 134.92 (C^2), 136.55 (C^8), 140.50 (C^{3a}), 157.97 (C^5=O); ^{19}F-NMR (DMSO-d_6, 292 MHz, ppm): δ = 77.64 (s, 3F, CF_3); IR (ATR, cm^{-1}): ν = 1143.45 (C-F), 1258.59 (C-O), 1517.42 (C=C), 1647.93 (C=N), 1758.54 (C=O), 3043.88 (=C-H); MS (ES^+): m/z (%): 277.3 (M^+, 100), 278.3 ($[M+1]^+$, 21); MS (ES-): m/z (%): 149.0 ($[OTf]^-$, 100), 151 (6), 316.0 (18), 321.0 (6), 575.0 (6); MP: 170-173 °C; Yield = 85%; brown powder; MW = 426.37.

*1-p-Fluorophenyl-3-methyl-1H-isochromeno[3,4-d]imidazol-5-onium triflate **5j***

^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): δ = 2.50 (s, DMSO), 3.38 (s, H_2O), 4.02 (s, 3H, NMe), 6.86 (d, 1H, J_{vic} = 8.3 Hz, H^9), 7.63-7.74 (m, 3H, $H^{3'}$, $H^{5'}$, H^7), 7.81-7.92 (m, 3H, $H^{2'}$, $H^{6'}$, H^8), 8.38 (d, 1H, J_{vic} = 7.7 Hz, H^6), 9.65 (s, 1H, H^2); ^{13}C-NMR (DMSO-d_6, 75 MHz, ppm): δ = 32.54 (NMe), 39.52 (DMSO-d_6), 110.26 (C^{9b}), 118.03 (d, J_{C-F} = 23.1 Hz, $C^{3'}$, $C^{5'}$), 118.61 (C^{5a}), 119.96 (C^9), 120.89 (q, J_{C-F} = 321.9 Hz, CF_3), 127.36 (C^{9a}), 129.59 (d, J_{C-F} = 9.2Hz, $C^{2'}$, $C^{6'}$), 130.26 (d, J_{C-F} = 2.3 Hz, $C^{1'}$), 130.63 (C^7), 132.38 (C^6), 135.33 (C^2), 136.80 (C^8), 140.70 (C^{3a}), 158.25 (C^5=O), 163.89 (d, J_{C-F} = 249.2 Hz, $C^{4'}$); ^{19}F-NMR (DMSO-d_6, 292 MHz, ppm): δ = (-)107.94-(-)107.82 (m), (-)77.69 (s, 3F, CF_3); IR (ATR, cm^{-1}): ν = 1028.61 (C-F), 1245.02 (C-O), 1509.37 (C=C), 1650.80 (C=N), 1759.04 (C=O), 3045.96 (=C-H): MS

(ES+): m/z (%): 295.0 (M+, 100), 296.3 ([M+1]+, 18); MS (ES-): m/z (%): 149.0 ([OTf]$^-$, 100), 321.0 (20), 593.0 (50); MP: 167-170 °C; Yield = 94%; brown powder; MW = 444.36.

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