3-Trifloxypropene Iminium and Propyne Iminium Salts Derived from *N*-Allyl-, *N*-Homoallyl-, and *N*-Benzyl-Substituted Semicyclic Enaminones

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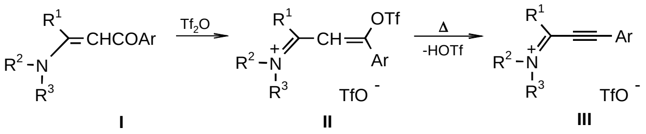
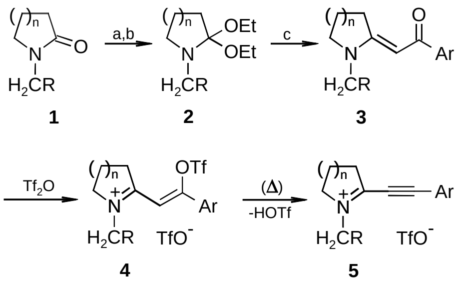
Abstract. The novel semicyclic enaminoketones **3a–n**, featuring *N*-allyl, *N*-homoallyl, *N*-benzyl, and *N*-4-chlorobenzyl substitution, have been prepared. Their reaction with triflic anhydride leads to 3-trifloxypropene iminium triflates **4** which are transformed into semicyclic propyne iminium triflates **5** by thermal *β*-elimination of triflic acid (HOTf). If a 4-chlorophenyl group is attached to the TfO-substituted carbon atom, salts **4** can be isolated (**4a**,**d**,**g**,**h**,**k**,**m**) and converted into propyne iminium triflates **5** at 120 °C. The presence of a 2-thienyl or 3-thienyl group adjacent to the trifloxy group prevents the isolation of **4** since HOTf elimination occurs already below room temperature. Thus, salts **5b**,**c**,**e**,**f**,**i**,**j**,**l**,**m**,**n** are obtained directly from enaminoketones **3** and triflic anhydride.

Propyne iminium salts have been recognized as useful synthetic building blocks in organic synthesis. Most importantly, they can be transformed into functionalized and highly substituted propargylamines, aminoallenes, and amino-1,3-butadienes [1–4]. In earlier papers [5–7], we have described that propyne iminium salts **III** are easily available by *O*-sulfonylation of enaminoketones **I** with triflic anhydride (Tf_2O), followed by elimination of triflic acid (HOTf) from the resulting 3-trifloxypropene iminium triflates **II** (Scheme 1). Elimination of HOTf from salts **II** is achieved by heating them in acetonitrile solution, by vacuum thermolysis, or with the help of tertiary amines.



Scheme 1

The enaminoketone route described above provides access to both acyclic and semicyclic propyne iminium salts **III**. In the acyclic salts, the NR^2R^3 moiety so far was either a dialkylamino, morpholino, pyrrolidino or piperidino group, whereas in the semicyclic salts, the iminium function was part of a five-, six-, or seven-membered ring and had an exocyclic methyl substituent [*i.e.* R^1–R^2 = $(CH_2)_n$, n = 3,4,5 and R^3 = Me]. For various synthetic studies with semicyclic 3-trifloxypropene iminium and propyne iminium salts, we had a need of derivatives in which a *π* system was incorporated in the exocyclic *N*-substituent. This is the case in *N*-allyl, *N*-homoallyl, and *N*-benzyl-substituted semicyclic iminium salts **II** and **III**. We describe here the synthesis and spectroscopic characterization of such salts.



1-5	n	R	Ar
a	1	$CH{=}CH_2$	4-chlorophenyl
b	1	$CH{=}CH_2$	2-thienyl
c	1	phenyl	2-thienyl
d	2	$CH{=}CH_2$	4-chlorophenyl
e	2	$CH{=}CH_2$	3-thienyl
f	2	$CH{=}CH_2$	2-thienyl
g	2	CH_2-$CH{=}CH_2$	4-chlorophenyl
h	2	4-chlorophenyl	4-chlorophenyl
i	2	4-chlorophenyl	3-thienyl
j	2	4-chlorophenyl	2-thienyl
k	2	phenyl	4-chlorophenyl
l	2	phenyl	2-thienyl
m	3	$CH{=}CH_2$	4-chlorophenyl
n	3	$CH{=}CH_2$	2-thienyl

Scheme 2 Conditions: a) $(MeO)_2SO_2$, 80 °C; b) NaOEt (2 equiv.); c) H_3C–CO–Ar, 80 °C

1436-9966/99/3410X-121 $ 17.50 + .50/0

Results

Semicyclic enaminoketones **3** (R = allyl, homoallyl, benzyl, 4-chlorobenzyl) were prepared, by analogy to a published procedure [8], in two steps from the corresponding *N*-alkyllactams **1**. The synthesis of the latter from their NH precursors and an alkyl halide has been described [9–13] except for 1-(4-chlorobenzyl)-2-piperidinone which was prepared analogously. *O*-Alkylation of **1a**–**n** with dimethyl sulfate followed by addition of NaOEt delivered lactam acetals **2**, which were condensed with an (het)aryl methyl ketone to give enaminoketones **3a**–**n** (Scheme 2 and Table 1).

Table 1 Yields, melting points, and elemental analyses of enaminoketones **3a**–**n**

Compound	Yield (%)	*m.p.* (°C)	Formula (g/mol)	Elemental Analysis Calcd./Found C	H	N
3a	79	76	$C_{15}H_{16}ClNO$	68.83	6.16	5.35
			(261.75)	68.80	6.14	5.44
3b	74	63	$C_{13}H_{15}NOS$	66.92	6.48	6.00
			(233.33)	67.10	6.58	5.96
3c	77	110–112	$C_{17}H_{17}NOS$	72.05	6.05	4.94
			(283.34)	71.86	5.79	4.73
3d	81	81	$C_{16}H_{18}ClNO$	69.69	6.58	5.08
			(275.78)	69.67	6.69	5.19
3e	69	35	$C_{14}H_{17}NOS$	67.98	6.93	5.66
			(247.36)	67.81	6.87	5.64
3f	74	53	$C_{14}H_{17}NOS$	67.98	6.93	5.66
			(247.36)	68.00	6.92	5.76
3g	78	84	$C_{17}H_{20}ClNO$	70.46	6.96	4.83
			(289.80)	70.29	6.78	4.75
3h	79	112	$C_{20}H_{14}Cl_2NO$	66.68	5.32	3.89
			(360.28)	66.68	5.28	3.95
3i	74	106–107	$C_{18}H_{18}ClNOS$	65.15	5.47	4.22
			(331.86)	65.01	5.69	4.52
3j	76	111–112	$C_{18}H_{18}ClNOS$	65.15	5.47	4.52
			(331.86)	65.08	5.49	4.29
3k	65	96-97	$C_{20}H_{20}ClNO$	73.72	6.19	4.30
			(325.84)	73.78	6.15	4.19
3l	87	110–111	$C_{18}H_{19}NOS$	72.69	6.44	4.71
			(297.41)	72.75	6.38	4.71
3m	66	59	$C_{17}H_{20}ClNO$	70.46	6.98	4.83
			(289.90)	70.31	7.08	4.84
3n	63	70	$C_{15}H_{19}NOS$	68.93	7.33	5.36
			(261.38)	68.61	7.38	5.27

Enaminoketones **3** were fully characterized by NMR and IR spectroscopy (Table 2). In all cases, only one diastereomer was detected by NMR. Selective ROESY and NOESY experiments on **3c**,**h**–**l**, with irradiation at δ(=CH) showed an intensity enhancement for the exocyclic NCH_2 signal, which is indicative of the *E* configuration at the enaminic C=C bond. As the chemical shifts for the olefinic proton in all enaminoketones are very similar (δ = 5.57–5.79 ppm), the *E* configuration is also assumed for all other enaminoketones **3**.

The reaction of semicyclic enaminoketones **3a**,**d**,**g**,**h**,**k**,**m**, all of which have the electron-withdrawing 4-chlorophenyl substituent bonded to the carbonyl group, with triflic anhydride in CH_2Cl_2 yielded the 3-trifloxypropene iminium triflates **4** as colorless solids in high yields (Table 3). In order to avoid deprotonation of salt **4** by an excess of enaminoketone **3,** a solution of the latter in CH_2Cl_2 was added to Tf_2O in order to keep the stationary concentration of **3** low.

The constitution of salts **4** was indicated by an IR absorption at ν/cm^{-1} = 1413–1433 which is typical for the covalently bonded triflate group and represents the $\nu_{as}(SO_2)$ stretching vibration appearing at particularly high wavenumbers [14] due to the attachment of the electron-withdrawing CF_3 group. Furthermore, the ^{13}C NMR spectra show two quartets at δ/ppm = 119.1–120.1 (anionic triflate) and at δ/ppm = 121.9–122.2 (covalent triflate) (Table 4). The configuration of the salts **4h**,**k** was determined exemplarily by selective ROESY NMR experiments (Figure 1). In both salts, the propene iminium unit adopts the *Z, s-trans* configuration which was already established for related systems [7]. Due to the similar substitution pattern, the same geometry should also apply for all other salts **4**.

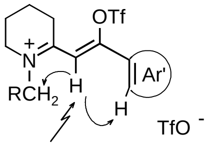


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Fig. 1 NOE ^1H signal intensity enhancement for 3-trifloxypropene iminium triflates **4**

In contrast to the results mentioned above, 3-trifloxypropene iminium triflates **4** with a thienyl ring adjacent to the trifloxy function could not be isolated. They eliminate HOTf already under the condition of their synthesis (*i.e.* at temperatures between –60 and 0 °C) to give propyne iminium salts **5**. Possible reasons for the acceleration of the β-elimination by electron-donating substituents at the trifloxy-substituted carbon atom have been discussed [7]. In those cases where HOTf elimination from **4** occurs already during the synthesis of **4**, fast addition of the enaminoketone **3** to Tf_2O is required. Otherwise, the eliminated triflic acid is trapped by unconsumed enaminoketone.

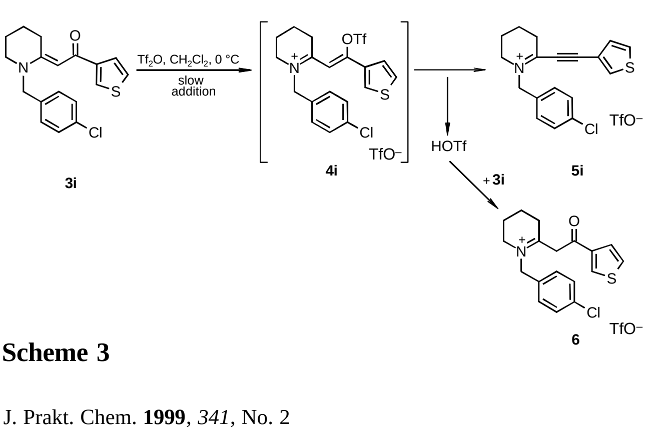
As an example, slow addition of **3i** during 90 minutes to Tf_2O in dichloromethane at 0 °C gave a mixture of propyne iminium salt **5i** (51%) and iminium salt **6** (12%) resulting from *C*-protonation of **3i** (Scheme 3).

Elimination of triflic acid from salts **4** bearing a 4-chlorophenyl substituent adjacent to the trifloxy function requires a higher thermal activation. All of these salts (**4a,d,g,h,k,m)** could be transformed in high yields into the propyne iminium salts **5** by heating them in acetonitrile solution at 120 °C for several hours (Table 5, Table 6).

Table 2 ^{1}H and ^{13}C NMR and IR data of enaminoketones **3a–n**

Compound	^{1}H NMR a)	^{13}C NMR b)
3a	2.02 (quin, 2H), 3.41 (t, 2H), 3.45 (t, 2H), 3.91 (d, 2H), 5.18 (dd, ^{3}J = 17.2 Hz, ^{2}J = 1.2 Hz, 1H), 5.24 (dd, ^{3}J = 10.3 Hz, ^{2}J = 1.2 Hz, 1H), 5.67 (s, 1H), 5.78 (m_c, 1H), 7.33/7.80 (AA'BB', 4H)	20.6 (t), 33.7 (t), 48.9 (t), 52.5 (t), 86.1 (t), 117.6 (t), 128.0 (d, 2C), 128.5 (d, 2C), 130.2 (d), 136.0 (s), 140.2 (s), 167.2 (s), 185.9 (s)
3b	1.99 (quin, 2H), 3.38 (t, 2H), 3.42 (t, 2H), 3.90 (d, 2H), 5.14–5.28 (m, 2H), 5.65 (s, 1H), 5.78 (m_c, 1H), 7.03 (dd, ^{3}J = 5.0 Hz, ^{3}J = 1.1 Hz, 1H), 7.38 (dd, ^{3}J = 5.0 Hz, ^{4}J = 1.1 Hz, 1H), 7.53 (dd, ^{3}J = 3.8 Hz, ^{4}J = 1.1 Hz, 1H)	20.7 (t), 33.6 (t), 48.9 (t), 52.4 (t), 86.0 (d), 117.6 (t), 127.0 (d), 127.2 (d), 129.2 (d), 130.3 (d), 149.0 (s), 166.5 (s), 179.9 (s)
3c	1.99 (quin, 2 H), 3.24–3.48 (2 t, 4H), 4.48 (s, 2H), 5.79 (s, 1H), 6.99 (dd, 1H, ^{3}J = 5.0 Hz, ^{3}J = 3.7 Hz), 7.22 (m, 2H), 7.28 (m, 1H), 7.34 (t, 2H), 7.35 (dd, 1H), 7.46 (dd, ^{3}J = 3.7 Hz, ^{4}J = 1.2 Hz, ^{1}H)	20.8 (t), 33.6 (t), 50.2 (t), 52.6 (t), 86.3 (d), 127.1 (d, 2C), 127.2 (d), 127.3 (d), 127.6 (d), 128.8 (d, 2C), 129.3 (d), 135.4 (s), 149.1 (s), 167.0 (s), 180.1 (s)
3d	1.71 (m_c, 2H), 1.82 (m_c, 2H), 3.32 (t, 2H), 3.35 (t, 2H), 3.92 (d, 2H), 5.19 (d, ^{3}J = 17.2 Hz, 1H), 5.27 (d, ^{3}J = 10.4 Hz, 1H), 5.67 (s, 1H), 5.82 (m_c, 1H), 7.31/7.74 (AA'BB', 4H)	19.2 (t), 22.8 (t), 28.3 (t), 50.0 (t), 54.9 (t), 90.3 (t), 117.2 (t), 127.9 (d), 128.5 (d), 130.2 (d), 135.8 (s), 141.4 (s), 164.8 (s), 185.8 (s)
3e	1.69 (m_c, 2H), 1.78 (m_c, 2H), 3.28 (m_c, 2H), 3.33 (m_c, 2H), 3.90 (d, 2H), 5.19 (dd, ^{3}J = 10.3 Hz, ^{2}J = 1.3 Hz, 1H), 5.25 (dd, ^{3}J = 17.2 Hz, ^{2}J = 1.3 Hz, 1H), 5.65 (s, 1H), 5.81 (m_c, 1H), 7.21 (dd, ^{3}J = 5.0 Hz, ^{4}J = 3.0 Hz, 1H), 7.44 (dd, ^{3}J = 5.0 Hz, ^{4}J = 1.2 Hz, 1H), 7.75 (dd, ^{4}J = 3.0 Hz, ^{4}J = 1.2 Hz, 1H)	19.1 (t), 22.7 (t), 28.0 (t), 49.7 (t), 54.6 (t), 91.1 (t), 116.9 (t), 124.7 (d), 126.4 (d), 126.9 (d), 130.4 (t), 147.0 (s), 163.9 (s), 181.5 (s)
3f	1.69 (m_c, 2H), 1.79 (m_c, 2H), 3.31 (t, 2H), 3.34 (t, 2H), 3.92 (d, 2H), 5.21 (dd, ^{3}J = 17.2 Hz, ^{2}J = 1.3 Hz, 1H), 5.27 (dd, ^{3}J = 10.3 Hz, ^{2}J = 1.3 Hz, 1H), 5.70 (s, 1H), 5.83 (m_c, 1H), 7.01 (dd, ^{3}J = 4.8 Hz, ^{3}J = 3.8 Hz, 1H), 7.36 (dd, ^{3}J = 4.9 Hz, ^{4}J = 0.8 Hz, 1H), 7.47 (dd, ^{3}J = 3.8 Hz, ^{4}J = 0.8 Hz, 1H)	19.2 (t), 22.9 (t), 28.2 (t), 49.9 (t), 54.9 (t), 90.0 (d), 117.3 (t), 126.8 (d), 127.2 (d), 128.9 (d), 130.4 (d), 150.1 (s), 164.2 (s), 179.6 (s)
3g	1.68 (m_c, 2H), 1.79 (m_c, 2H), 2.44 (q, 2H), 3.29–3.42 (m, 6H), 5.08–5.16 (m, 2H), 5.66 (s, 1H), 5.81 (m_c, 1H), 7.33/7.76 (AA'BB', 4H)	19.0 (t), 22.7 (t), 28.1 (t), 29.9 (t), 50.4 (t), 52.0 (t), 89.7 (d), 117.3 (t), 128.0 (d, 2C), 128.4 (d, 2C), 134.3 (t), 135.7 (s), 141.6 (s), 164.6 (s), 185.6 (s)
3h	1.70 (quin, 2H), 1.80 (quin, 2H), 3.31–3.35 (m, 4H), 4.44 (s, 2H), 5.57 (s, 1H), 7.08/7.27 (AA'BB', 4H), 7.19/7.48 (AA'BB', 4H)	19.3 (t), 23.1 (t), 28.4 (t), 50.8 (t), 55.4 (t), 91.2 (d), 127.8 (d, 2C), 128.1 (d, 2C), 128.5 (d, 2C), 129.1 (d, 2C), 133.3 (s), 134.0 (s), 136.1 (s), 141.2 (s), 165.0 (s), 186.4 (s)
3i	1.67 (dt, 2H), 1.76 (dt, 2H), 3.27–3.33 (m, 4H), 4.41 (s, 2H), 5.54 (s, 1H), 7.07 (d, 3H), 7.20 (dd, ^{3}J = 5.0 Hz, ^{4}J = 0.5 Hz, 1H), 7.25 (d, 2H), 7.49 (d, ^{4}J = 3.0 Hz, ^{4}J = 1.2, 1H)	19.3 (t), 23.0 (t), 28.2 (t), 50.6 (t), 55.2 (t), 92.0 (d), 125.0 (d), 126.9 (d), 127.0 (d), 127.7 (d, 2 C), 129.0 (d, 2 C), 133.1 (s), 134.2 (s), 146.8 (s), 164.2 (s), 182.0 (s)
3j	1.64 (quin, 2H), 1.74 (quin, 2H), 3.26–3.31 (m, 4H), 4.40 (s, 2H), 5.58 (s, 1H), 6.85 (dd, 1H, ^{3}J = 4.9 Hz, ^{3}J = 3.7 Hz), 7.07/7.23 (AA'BB', 4H), 7.18 (dd, 1H, ^{3}J = 3.8 Hz, ^{4}J = 1.1 Hz), 7.23 (m, 1H)	19.1 (t), 22.9 (t), 28.1 (t), 50.6 (t), 55.2 (t), 90.7 (d), 126.9 (d), 127.3 (d), 127.7 (d, 2C), 128.9 (d, 2C), 129.2 (d), 133.0 (s), 134.1 (s), 149.7 (s), 164.2 (s), 179.7 (s)
3k	1.71 (quin, 2H), 1.78 (m_c, 2H), 3.33–3.36 (m, 4H), 4.47 (s, 2H), 5.61 (s, 1H), 7.14 (d, 2H), 7.17 (t, 1H), 7.29 (t, 2H), 7.16/7.47 (AA'BB', 4H)	19.3 (t), 23.0 (t), 28.4 (t), 50.8 (t), 56.0 (t), 91.2 (d), 126.4 (d, 2C), 127.5 (d), 128.0 (d, 2C), 128.5 (d, 2C), 128.9 (d, 2C), 135.5 (s), 135.9 (s), 141.3 (s), 165.1 (s), 186.2 (s)
3l	1.63–1.68 (m_c, 2H), 1.72–1.77 (m_c, 2H), 3.28–3.33 (m, 4H), 4.45 (s, 2H), 5.65 (s, 1H), 6.84 (dd,^{3}J = 5.0 Hz, ^{3}J = 3.7 Hz, 1H), 7.16 (d, 2H), 7.17–7.22 (m, 3H), 7.26 (t, 2H)	19.2 (t), 22.9 (t), 28.1 (t), 50.6 (t), 55.9 (t), 90.7 (d), 126.3 (d, 2 C), 126.8 (d), 127.2 (d), 127.4 (d), 128.8 (d, 2C), 129.1 (d), 135.6 (s), 150.0 (s), 164.5 (s), 179.8 (s)
3m	1.57–1.65 (m, 2H), 1.68–1.79 (m, 4H), 3.42–3.54 (m, 4H), 3.95 (m_c, 2H), 5.19 (dd, ^{3}J = 17.2 Hz, ^{2}J = 1.3 Hz, 1H), 5.25 (dd, ^{3}J = 10.4 Hz, ^{2}J = 1.3 Hz, 1H), 5.59 (s, 1H), 5.83 (m_c, 1H), 5.95 (s, 1H), 7.32/7.76 (AA'BB', 4H)	25.3 (t), 27.8 (2 t), 29.4 (t), 52.5 (t), 55.7 (t), 91.4 (d), 116.9 (t), 127.9 (d, 2C), 128.6 (d, 2C), 131.1 (d), 135.9 (s), 141.2 (s), 169.7 (s), 186.4 (s)
3n	1.53–1.61 (m, 2H), 1.63–1.75 (m, 2H), 3.42 (m_c, 2H), 3.45–3.53 (m, 2H), 3.94 (d, 2H), 5.17–5.26 (m, 2H), 5.62 (s, 1H), 5.83 (m_c, 1H), 7.00 (dd, ^{3}J = 5.0 Hz, ^{4}J = 3.7 Hz, 1H), 7.37 (dd, ^{3}J = 5.0 Hz, ^{4}J = 1.1 Hz, 1H), 7.48 (dd, ^{3}J = 3.7 Hz, ^{4}J = 1.1 Hz, 1H)	25.2 (t), 27.6 (t), 27.7 (t), 29.2 (t), 52.6 (t), 55.6 (t), 90.8 (d), 116.8 (t), 126.8 (d), 127.1 (d), 129.1 (d), 131.1 (t), 150.0 (s), 168.9 (s), 179.7 (s)

a) $CDCl_3$ as solvent, 500.14 MHz, δ values in ppm. b) Solvent $CDCl_3$, 125.77 MHz, δ values in ppm; signal multiplicities of proton-coupled spectra are given in parentheses.



Scheme 3

In summary, we have reported, for the first time, the preparation of 3-trifloxypropene iminium and proypne iminium salts with an exocyclic alkenyl or benzyl substituent at the nitrogen atom. As we will show in future papers, the presence of such substituents in the conjugated iminium salts offer opportunities for novel synthetic transformations.

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Table 3 Synthesis, melting points, and elemental analyses of 3-trifloxypropene iminium triflates **4**

Com-pound	Reaction Temp. (°C)	Yield (%)	*m.p.* (°C)	Formula (g/mol)	Elemental Analysis Calcd./Found		
					C	H	N
4a	– 60	85	71	$C_{17}H_{16}ClF_6NO_6S_2$ (543.90)	37.54 37.72	2.96 2.86	2.58 2.66
4d	– 60	87	72	$C_{18}H_{18}ClF_6NO_6S_2$ (557.91)	38.75 38.65	3.25 3.34	2.51 2.60
4g	– 60	91	70	$C_{19}H_{20}ClF_6NO_6S_2$ (571.93)	39.90 39.92	3.52 3.60	2.45 2.36
4h	– 5	88	122	$C_{22}H_{19}Cl_2F_6NO_6S_2$ (642.41)	41.13 41.11	2.98 3.10	2.18 2.30
4k	– 5	92	103	$C_{22}H_{20}ClF_6NO_6S_2$ (607.97)	43.46 43.58	3.32 3.41	2.30 2.46
4m	– 60	86	102	$C_{19}H_{20}ClF_6NO_6S_2$ (571.93)	39.90 39.85	3.52 3.45	2.45 2.36

Table 4 ^{1}H and ^{13}C NMR data of 3-trifloxypropene iminium triflates **4**

Com-pound	^{1}H NMR ^{a})	^{13}C NMR ^{b})
4a	2.29 (quin, 2H), 3.51 (t, 2H), 4.17 (t, 2H), 4.56 (d, 2H), 5.43 (d, ^3J = 10.2 Hz, 1H), 5.47 (d, ^3J = 17.1 Hz, 1H), 6.91 (s, 1H), 7.55/7.73 (AA'BB', 4H)	20.0 (t), 39.0 (t), 54.7 (t), 60.6 (t), 109.8 (d), 119.1 (q, $J_{C,F}$ = 320.7), 122.1 (q, $J_{C,F}$ = 321.9 Hz), 123.1 (t), 128.9 (d), 130.5 (d, 2C), 130.7 (d, 2C), 140.2 (s), 159.3 (s), 179.3 (s)
4d	1.85–1.93 (m, 2H), 1.97–2.04 (m, 2H), 3.14 (m$_c$, 2H), 3.89 (m$_c$, 2H), 4.62 (d, 2H), 5.54 (d, ^3J = 10.2 Hz, 1H), 5.58 (d, 17.1 Hz, 1H), 5.96 (m$_c$, 1H), 7.08 (s, 1H), 7.58/7.75 (AA'BB', 4H)	17.4 (t), 21.1 (t), 33.8 (t), 54.1 (t), 62.4 (t), 114.8 (d), 119.2 (q, $J_{C,F}$ = 320.0 Hz), 122.2 (q, $J_{C,F}$ = 320.7 Hz), 124.7 (t), 128.5 (d), 129.8 (d, ^3J = 2C), 130.0 (s), 130.5 (d, 2C), 139.4 (s), 151.9 (s), 181.9 (s)
4g	1.84–1.91 (m, 2H), 1.96–2.02 (m, 2H), 2.62 (q, 2H), 3.11 (m$_c$, 2H), 3.92 (m$_c$, 2H), 4.04 (t, 2H), 5.19 (dd, ^3J = 10.2 Hz, ^2J = 1.5 Hz, 1H), 5.26 (dd, ^3J = 17.2 Hz, ^2J = 1.5 Hz, 1H), 5.84 (m$_c$, 1H), 7.02 (s, 1H), 7.59/7.75 (AA'BB', 4H)	17.4 (t), 21.1 (t), 31.7 (t), 33.7 (t), 54.6 (t), 59.3 (t), 114.7 (d), 119.2 (q, $J_{C,F}$ = 320.3 Hz), 119.9 (t), 122.0 (q, $J_{C,F}$ = 320.6 Hz), 129.9 (d, 2C), 130.1 (s), 130.5 (d, 2C), 133.7 (d), 139.5 (s), 152.0 (s), 181.5 (s)
4h	1.85–1.89 (m, 2H), 1.92–1.97 (m, 2H), 3.18–3.20 (m, 2H), 3.75–3.77 (t, 2H), 5.19 (s, 2H), 7.13 (t, 1H, ^4J = 1.6 Hz), 7.44/7.48 (AA'BB', 4H), 7.59/7.75 (AA'BB', 4H)	17.4 (t), 21.2 (t), 34.1 (t), 54.5 (t), 62.4 (t), 114.8 (d), 119.1 (q), 122.1 (q), 129.9 (d, 2C), 130.4 (d, 2C), 130.5 (s), 130.5 (d, 2C), 132.2 (d, 2C), 136.2 (s) 139.6 (s), 152.3 (s), 182.8 (s, C-6') ^{c})
4k	1.86–1.97 (m, 4H), 3.21 (t, 2H), 3.76 (t, 2H), 5.22 (s, 1H), 7.19 (s, 1H), 7.44–7.48 (m, 5H), 7.58/7.75 (AA'BB', 4H)	17.4 (t), 21.2 (t), 34.0 (t), 54.5 (t), 63.2 (t), 114.9 (d), 120.1 (q), 121.9 (q), 129.9 (d, 2C), 130.0 (d, 2C), 130.4 (3 d), 130.5 (d, 2C), 130.7 (s), 131.7 (s), 139.5 (s), 152.2 (s), 182.3 (s)
4m	1.78–1.96 (m, 6H), 3.29 (m$_c$, 2H), 4.15 (m$_c$, 2H), 4.66 (d, 2H), 5.55 (dd, ^3J = 10.2 Hz, ^2J = 1.0 Hz, 1H), 5.62 (dd, ^3J = 17.3 Hz, ^2J = 1.0 Hz, 1H), 5.96 (m$_c$, 1H), 7.30 (s, 1H), 7.58/7.79 (AA´BB', 4 H)	22.5 (t), 24.4 (t), 29.4 (t), 37.4 (t), 58.3 (t), 63.6 (t), 116.2 (d), 119.2 (q, $J_{C,F}$ = 320.3 Hz), 122.0 (q, $J_{C,F}$ = 320.1 Hz), 125.2 (t), 128.3 (d), 129.9 (d, 2 C), 130.2 (s), 130.5 (d, 2 C), 139.6 (s), 153.2 (s), 186.7 (s)

^{a}) CD_3CN as solvent, 500.14 MHz, δ values in ppm. ^{b}) Solvent CD_3CN, 125.77 MHz, δ values in ppm; signal multiplicities of proton-coupled spectra are given in parentheses. ^{c}) The signal of one carbon atom was not detected.

Experimental

The NMR spectra were taken on Bruker AMX 500 and AC 200 instruments. As the internal reference, Me_4Si was used for the proton spectra, and the solvent signal for the ^{13}C NMR spectra [δ ($CDCl_3$) = 77.0 ppm, δ (CD_3CN) = 1.3 ppm]. IR spectra were recorded on a Perkin Elmer IR 883 spectrometer. Microanalyses were carried out with analyzer systems Elementar Vario E1 and Heraeus CHN rapid. Melting points were determined in an apparatus after Dr. Tottoli (Buechi) and are not calibrated. Solvents were dried by established procedures. Triflic anhydride was distilled from phosphorus pentoxide prior to use. Column chromatography was performed under hydrostatic conditions (silica gel 60, Macherey-Nagel, 70–230 mesh). Dimethylaminomethyl-polystyrene was heated at 90 °C for 5 days to remove water. All reactions were carried out in oven-dried glassware and under argon. Lactams **1a**,**b**,**d**,**e**,**f**,**m**,**n** [9], **1g** [10,11], and **1c**,**j**–**l** [12, 13] were prepared by literature procedures.

1-(4-Chlorobenzyl)-1-piperidinone

A solution of 2-piperidinone (14.90 g, 0.15 mol) in toluene (60 ml) was added during 2 h to a suspension of sodium (3.40 g, 0.15 mol) in boiling toluene (300 ml), and the mixture was kept at reflux for 4 h. After addition of 4-chlorobenzyl chloride (24.2 g, 0.15 mol) in toluene (20 ml) at 20 °C, the mixture was refluxed again for 2 h. After cooling the precipitate was removed by centrifugation, and the solution was distilled to give the product at 143–148 °C/0.02 mbar as a colorless liquid; yield 22.15 g (66%). – IR (film): ν/cm^{-1}= 3083 (w), 3045 (m), 2946 (vs), 2865 (s), 1644 (vs), 1491 (vs), 1466 (s), 1446 (s), 1410 (s), 1350 (vs), 1284 (s), 1174 (s), 1090 (vs), 1015 (s). – ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ/ppm = 1.70–1.84 (m, 4H), 2.40–2.44 (m, 2H), 3.14–3.18 (m, 2H), 4.54 (s, 2H), 7.19/7.22 (AA'BB', 4H). – ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ/ppm = 20.6 (t), 22.6 (t), 31.9 (t), 46.9 (t), 48.9 (t), 128.1, 128.9, 132.5 (s), 135.5 (s), 169.3 (s).

$C_{12}H_{14}ClNO$	calcd.:	C 64.43	H 6.31	N 6.26
(223.70)	found:	C 64.10	H 6.56	N 6.32.

Table 5 Synthesis, yields, melting points, and elemental analyses of propyne iminium salts **5**

Compound	Reaction Conditions (°C/h)	Yield (%)	*m.p.* (°C)	Formula (g/mol)	Elemental Analysis Calcd./Found C	H	N
5a	120/5	85 a)	79	$C_{16}H_{15}ClF_3NO_3S$ (393.81)	48.80 48.90	3.84 3.78	3.56 3.59
5b	60/0.25	77 b)	68	$C_{14}H_{14}F_3NO_3S_2$ (365.38)	46.02 45.70	3.86 3.94	3.83 3.72
5c	–10/0.5	54 b)	101	$C_{18}H_{16}F_3NO_3S_2$ (415.46)	52.03 52.07	3.88 3.89	3.37 3.44
5d	120/1	88 a)	122	$C_{17}H_{17}ClF_3NO_3S$ (407.84)	50.07 49.93	4.20 4.20	3.43 3.45
5e	–60/0.5	69 b)	76	$C_{15}H_{16}F_3NO_3S_2$ (379.41)	47.49 47.52	4.25 4.25	3.69 3.79
5f	60/0.25	80 b)	58	$C_{15}H_{16}F_3NO_3S_2$ (379.41)	47.49 47.21	4.25 4.45	3.69 3.64
5g	120/0.5	93 a)	109	$C_{18}H_{19}ClF_3NO_3S$ (421.86)	51.25 51.40	4.54 4.62	3.32 3.36
5h	120/2.5	93 a)	114	$C_{21}H_{18}Cl_2F_3NO_3S$ (492.34)	51.23 51.11	3.68 3.73	2.84 3.06
5i	–15/0.5	58 b)	105–107	$C_{19}H_{17}ClF_3NO_3S_2$ (463.92)	49.19 48.90	3.69 3.78	3.02 3.09
5j	–15/0.5	57 b)	112	$C_{19}H_{17}ClF_3NO_3S_2$ (463.92)	49.19 49.11	3.69 3.64	3.02 3.06
5k	120/2.5	91 a) c)	103–105	$C_{21}H_{19}ClF_3NO_3S$ (457.89)	55.09 54.83	4.18 4.21	3.06 2.96
5l	–15/0.5	61 b)	110–111	$C_{19}H_{18}F_3NO_3S_2$ (429.47)	53.14 52.94	4.22 4.25	3.26 3.58
5m	120/1	84 a)	88	$C_{18}H_{19}ClF_3NO_3S$ (421.86)	51.25 51.16	4.54 4.62	3.32 3.43
5n	–60/0.5	80 b)	79	$C_{16}H_{18}F_3NO_3S_2$ (393.44)	48.85 48.76	4.61 4.69	3.56 3.54

a) Yields are based on salts **4**. b) Yields are based on enaminoketones **3**. c) A similar yield was obtained by bulb-to-bulb distillation (170 °C, 0.002 mbar, 8 min).

Synthesis of Enaminoketones 3

The following procedure, carried out in analogy to a published method [8], is typical. For yields and physical data, see Table 1; for NMR data, see Table 2.

2-(1-Allyltetrahydro-1H-2-pyrrolylidene)-1-(4-chlorophenyl)-1-ethanone (**3a**)

A two-phase mixture of 1-allylpyrrolidin-2-one (**1a**) (25.2 g, 0.20 mol) and of dimethyl sulfate (26.5 g, 0.21 mol) was heated at 80 °C for 12 h. After cooling, the homogeneous oil was washed with ether (50 ml), and residual solvent was removed *in vacuo*. The residue was slowly added to a solution of NaOEt [from sodium (9.2 g) in ethanol (200 ml)]. After 2 h, the precipitate was filtered off with suction under argon, the solvent was evaporated, and the residue was destilled at 82 °C/10 mbar to give 1-allyl-2,2-diethoxypyrrolidine (**2a**, yield 31.9 g, 0.16 mol), which was used immediately. A mixture of this acetal (31.9 g, 0.16 mol) and of 4-chloroacetophenone (27.3 g, 0.175 mol) was heated at 80 °C for 8 h. The solvent was removed *in vacuo*, and from the remaining dark oil, **3a** was obtained as a yellow powder by crystallization with CH_2Cl_2-petroleum ether (*b.p.* 40–60 °C). – IR (KBr): ν/cm^{-1} = 3051 (w), 2963 (w), 1612 (s), 1581 (s), 1551 (s), 1482 (m), 1417 (m), 1352 (m), 1297 (m), 1217 (m), 1176 (m), 1109 (m), 1091 (m), 1009 (m).

Synthesis of 3-Trifloxypropene Iminium Triflates 4

The following procedure is typical. For yields and physical data, see Table 3; for NMR data, see Table 4.

1-Allyl-5-{2-(4-chlorophenyl)-2-[(trifluoromethyl)sulfonyloxy]-1-ethenyl}-3,4-dihydro-2H-pyrrolium Trifluoromethanesulfonate (**4a**)

A solution of enaminoketone **3a** (8.60 g, 35.6 mmol) in CH_2Cl_2 (50 ml) was added dropwise to a cooled (–60 °C) solution of triflic anhydride [15] (6.50 ml, 39.6 mmol) in CH_2Cl_2 (100 ml). After stirring for 30 min, the red-brown solution was concentrated by partial evaporation of the solvent *in vacuo*. Addition of diethyl ether yielded **4a** as a pale-yellow solid, which was purified further by redissolving in CH_2Cl_2 and precipitation with diethyl ether as a colorless powder; yield 16.46 g (85%). – IR (KBr): ν/cm^{-1} = 3098 (w), 3044 (w), 1643 (s), 1593 (m), 1431 (s), 1376 (m), 1282 (s), 1254 (vs), 1228 (s), 1163 (m), 1094 (m), 1031 (s), 1017 (m), 991 (m).

Synthesis of Propyne Iminium Triflates 5a,d,g,h,m

The following procedure is typical. For yields and physical data, see Table 5; for NMR data, see Table 6.

1-Allyl-5-[2-(4-chlorophenyl)-1-ethynyl]-3,4-dihydro-2H-pyrrolium Trifluoromethanesulfonate (**5a**)

A solution of **4a** (5.4 g, 10 mmol) in CH_3CN (15 ml) was placed in a thick-walled Schlenk tube; the tube was closed and immersed in an oil bath. The solution was heated with stirring at 120 °C for 5 h. After concentration of the solution to half its volume and cooling at –30 °C, the product was precipitated by addition of diethyl ether. The supernatant solution was decanted, and the solid residue was washed with diethyl ether (3 × 50 ml) to afford **5a** as orange-yellow crys-

Table 6 ^{1}H and ^{13}C NMR data of propyne iminium triflates **5a**–**n**

Compound	^{1}H NMR a)	^{13}C NMR b)
5a	2.37 (quin, 2H), 3.39 (t, 2H), 4.22 (t, 2H), 4.66 (d, 2H), 5.51 (dd, $^{3}J = 10.2$ Hz, $^{2}J = 1.0$ Hz, 1H), 5.57 (dd, $^{3}J = 17.1$ Hz, $^{2}J = 1.0$ Hz, 1H), 5.98 (m_c, 1H), 7.56/7.78 (AA'BB', 4H)	20.1 (t), 40.9 (t), 56.1 (t), 59.7 (t), 79.5 (s), 116.7 (s), 117.7 (s), 122.2 (q, $J_{C,F} = 321.1$ Hz), 123.7 (t), 128.9 (d), 130.7 (d, 2C), 136.3 (d, 2C), 140.3 (s), 169.4 (s)
5b	2.35 (quin, 2H), 3.35 (t, 2H), 4.18 (t, 2H), 4.59 (d, 2H), 5.49 (dd, $^{3}J = 10.2$ Hz, $^{2}J = 1.0$ Hz, 1H), 5.55 (dd, $^{3}J = 17.1$ Hz, $^{2}J = 1.0$ Hz, 1H), 5.97 (m_c, 1H), 7.28 (dd, $^{3}J = 5.0$ Hz, $^{3}J = 3.8$ Hz, 1H), 7.86 (dd, $^{3}J = 3.8$ Hz, $^{4}J = 1.2$ Hz, 1H), 7.99 (dd, $^{3}J = 5.0$ Hz, $^{4}J = 1.2$ Hz, 1H)	20.3 (t), 40.6 (t), 55.8 (t), 59.5 (t), 84.2 (s), 112.9 (s), 118.4 (s), 123.5 (t), 129.1 (d), 130.2 (d), 138.4 (d), 141.7 (d), 168.5 (s) c)
5c	2.27 (quin, 2H), 3.36 (t, 2H), 4.07 (t, 2H), 5.17 (s, 2H), 7.28 (dd, $^{3}J = 5.0$ Hz, $^{3}J = 3.9$ Hz, 1H), 7.46 (m, 5H), 7.88 (dd, $^{3}J = 3.9$ Hz, $^{4}J = 1.0$ Hz, 1H), 7.99 (dd, $^{3}J = 5.0$ Hz, $^{4}J = 0.6$ Hz, 1H)	20.2 (t), 40.6 (t), 57.2 (t), 59.4 (t), 84.5 (s), 113.3 (s), 118.0 (s), 122.1 (q, $J_{C,F} = 320.3$ Hz), 130.2 (d), 130.3 (4 d), 130.5 (d), 132.3 (s), 138.6 (d), 141.9 (d), 168.6 (s)
5d	1.83–1.90 (m, 2H), 1.97–2.04 (m, 2H), 3.10 (m_c, 2H), 3.83 (m_c, 2H), 4.74 (d, 2H), 5.49–5.59 (m, 2H), 6.01 (m_c, 1H), 7.55/7.73 (AA'BB', 4H)	17.4 (t), 21.3 (t), 35.0 (t), 53.2 (t), 63.1 (t), 83.3 (s), 113.7 (s), 117.9 (s), 121.8 (q, $J_{C,F} = 320.3$ Hz), 123.3 (t), 129.2 (d), 130.6 (d, 2C), 136.1 (d, 2 C), 139.9 (s), 167.9 (s)
5e	1.80–2.04 (m, 4H), 3.06 (m_c, 2H), 3.80 (m_c, 2H), 4.69 (d, 2H), 5.47–5.57 (m, 2H), 5.99 (m_c, 1H), 7.39 (dd, $^{3}J = 5.1$ Hz, $^{4}J = 1.1$ Hz, 1H), 7.60 (dd, $^{3}J = 5.1$ Hz, $^{4}J = 2.9$ Hz, 1H), 8.23 (dd, $^{4}J = 2.9$ Hz, $^{4}J = 1.1$ Hz, 1H)	17.5 (t), 21.3 (t), 34.9 (t), 53.0 (t), 62.8 (t), 83.2 (s), 111.2 (s), 118.5 (s), 123.2 (t), 129.1 (d), 129.3 (d), 131.1 (d), 139.4 (d), 167.8 (s) c)
5f	1.81–1.87 (m, 2H), 1.92–2.02 (m, 2H), 3.06 (m_c, 2H), 3.80 (m_c, 2H), 4.66 (d, 2H), 5.47–5.56 (m, 2H), 5.99 (m_c, 1H), 7.26 (dd, $^{3}J = 5.1$ Hz, $^{3}J = 3.8$ Hz, 1H), 7.81 (dd, $^{3}J = 5.1$ Hz, $^{4}J = 1.2$ Hz, 1H), 7.95 (dd, $^{3}J = 3.8$ Hz, $^{4}J = 1.2$ Hz, 1H)	18.1 (t), 22.0 (t), 35.2 (t), 53.6 (t), 63.5 (t), 88.3 (s), 110.5 (s), 119.1 (s), 122.8 (q, $J_{C,F} = 321.2$ Hz), 123.7 (t), 129.9 (d), 130.7 (d), 138.3 (d), 141.7 (s), 167.7 (s)
5g	1.77–1.86 (m, 2H), 1.90–2.00 (m, 2H), 2.63 (q, 2H), 3.05 (m_c, 2H), 3.83 (m_c, 2H), 4.15 (t, 2H), 5.16 (d, $^{3}J = 10.2$ Hz, 1H), 5.23 (d, $^{3}J = 17.1$ Hz, 1H), 5.87 (m_c, 1H), 7.55/7.71 (AA'BB', 4 H)	17.4 (t), 21.2 (t), 32.2 (t), 34.8 (t), 53.6 (t), 60.3 (t), 83.3 (s), 113.6 (s), 118.0 (s), 119.6 (t), 130.6 (d, 2C), 134.0 (d), 136.0 (d, 2C), 139.9 (s), 167.5 (s), c)
5h	1.82–1.85 (m, 2H), 1.90–1.95 (m, 2H), 3.15 (t, 2H), 3.71–3.74 (m, 2H), 5.31 (s, 2H), 7.47 (s, br, 4H), 7.54/7.73 (AA'BB', 4H)	17.4 (t), 21.3 (t), 35.4 (t), 53.1 (t), 63.3 (t), 83.7 (s), 114.3 (s), 117.8 (s), 122.2 (q), 130.3 (d, 2C), 130.6 (d, 2C), 131.4 (s), 131.8 (d, 2C), 135.9 (s), 136.2 (d, 2C), 140.2 (s), 168.6 (s)
5i	1.80–1.85 (m, 2H), 1.90–1.94 (m, 2H), 3.12 (t, 2H), 3.71 (m, 2H), 5.28 (s, 2H), 7.39 (dd, 1H), 7.45–7.49 (m, 4H), 7.59 (dd, 1H), 8.23 (dd, 1H)	17.5 (t), 21.3 (t), 35.2 (t), 53.0 (t), 63.1 (t), 83.7 (s), 111.9 (s), 118.3 (s), 122.2 (q), 129.2 (d), 130.3 (d, 2C), 131.1 (d), 131.6 (s), 131.8 (d, 2C), 136.0 (s), 139.8 (d), 168.5 (s)
5j	1.81–1.85 (m, 2H), 1.90–1.94 (m, 2H), 3.12 (t, 2H), 3.73 (t, 2H), 5.25 (s, 2H), 7.24 (dd, $^{3}J = 5.1$ Hz, $^{3}J = 3.8$ Hz, 1H), 7.46 (s, br, 4H), 7.80 (dd, $^{3}J = 3.8$ Hz, $^{4}J = 1.1$ Hz, 1H), 7.94 (dd, $^{3}J = 5.1$ Hz, $^{4}J = 1.1$ Hz, 1H)	17.5 (t), 21.4 (t), 34.9 (t), 53.1 (t), 63.1 (t), 88.2 (s), 110.6 (s), 118.3 (s), 122.2 (q), 130.1 (d), 130.3 (d, 2C), 131.7 (d, 2C), 131.7 (s), 135.8 (s), 138.1 (d), 141.4 (d), 167.8 (s)
5k	1.82–1.87 (m, 2H), 1.91–1.95 (m, 2H), 3.17 (t, 2H), 3.75 (m, 2H), 5.36 (s, 2H), 7.42–7.50 (m, 5H). 7.51/7.72 (AA'BB', 4H)	17.5 (t), 21.3 (t), 35.3 (t), 53.1 (t), 64.1 (t), 83.8 (s), 113.8 (s), 117.8 (s), 122.2 (q), 129.9 (d, 2C), 130.3 (d, 2C), 130.4 (d), 130.5 (d, 2C), 132.6 (s), 136.1 (d, 2C), 139.9 (s) 168.2 (s)
5l	1.81–1.86 (m, 2H), 1.91–1.96 (m, 2H), 3.12 (t, 2H), 3.75 (t, 2H), 5.28 (s, 2H), 7.25 (dd, $^{3}J = 5.1$ Hz, $^{3}J = 3.8$ Hz, 1H), 7.45–7.48 (m, 5H), 7.81 (dd, $^{3}J = 3.8$ Hz, $^{4}J = 0.9$ Hz, 1H), 7.94 (dd, $^{3}J = 5.1$ Hz, $^{4}J = 0.9$ Hz, 1H)	17.5 (t), 21.4 (t), 34.8 (t), 53.0 (t), 63.9 (t), 88.2 (s), 110.2 (s), 118.3 (s), 122.2 (q), 129.9 (d, 2C), 130.1 (d), 130.3 (d, 2C), 130.4 (d), 132.9 (s), 138.0 (d), 141.3 (d), 167.4 (s)
5m	1.73–1.91 (m, 6H), 3.23 (m_c, 2H), 4.08 (m_c, 2H), 4.78 (d, 2H), 5.50 (d, $^{3}J = 10.3$ Hz, 1H), 5.57 (d, $^{3}J = 17.0$ Hz, 1H), 5.98 (m_c, 1H), 7.53/7.74 (AA'BB', 4H)	22.5 (t), 24.8 (t), 29.5 (t), 38.7 (t), 57.4 (t), 64.6 (t), 85.4 (s), 117.0 (s), 117.9 (s), 122.2 (q, $J_{C,F} = 320.7$ Hz), 123.9 (t), 129.0 (d), 130.6 (d, 2C), 136.4 (d, 2C), 140.3 (s), 172.5 (s)
5n	1.58–1.88 (m, 6H), 3.18 (m_c, 2H); 4.05 (m_c, 2H), 4.71 (d, 2H), 5.47 (dd, $^{3}J = 10.2$ Hz, $^{2}J = 0.9$ Hz, 1H), 5.54 (dd, $^{3}J = 17.1$ Hz, $^{2}J = 1.0$ Hz, 1H), 5.95 (m_c, 1H), 7.26 (dd, $^{3}J = 5.0$ Hz, $^{3}J = 3.8$ Hz, 1H), 7.85 (dd, $^{3}J = 3.8$ Hz, $^{4}J = 1.1$ Hz, 1H), 8.00 (dd, $^{3}J = 5.0$ Hz, $^{4}J = 1.1$ Hz, 1H)	22.8 (t), 25.0 (t), 29.6 (t), 38.3 (t), 57.2 (t), 64.3 (t), 90.1 (s), 113.2 (s), 118.6 (s), 123.6 (t), 129.2 (d), 130.3 (d), 138.8 (d), 141.9 (s), 171.4 (s) c)

a) CD_3CN as solvent, 500.14 MHz, δ values in ppm. b) Solvent CD_3CN, 125.77 MHz, δ values in ppm; signal multiplicities of proton-coupled spectra are given in parentheses. c) $CF_3SO_3^-$ not found.

tals; yield 3.11 g (79%). – IR (KBr): ν/cm^{-1} = 3060 (w), 2968 (w), 2207 (s), 1648 (s), 1586 (s) 1461 (m), 1387 (s), 1276 (vs), 1174 (s), 1100 (m), 1090 (s), 1030 (vs).

Synthesis of Propyne Iminium Triflates 5b,f

1-Allyl-5-[2-(2-thienyl)-1-ethynyl]-3,4-dihydro-2H-pyrrolium Trifluoromethanesulfonate (**5b**); Typical Procedure

A solution of enaminoketone **3b** (7.0 g, 30 mmol) in CH_2Cl_2 (50 ml) was added dropwise during 20 min to a cooled (–60 °C) solution of triflic anhydride (5.54 ml, 33 mmol) in CH_2Cl_2 (100 ml). After removing the solvent *in vacuo*, the dark oil was dissolved in CH_3CN and placed in a thick-walled Schlenk tube. After 15 minutes at 60 °C, the elimination of HOTf was complete. The solution was concentrated to half its volume, and diethyl ether was added. After stirring at 0 °C, **5b** could be isolated as a dark solid which was triturated with diethyl ether (3 × 50 ml), then dissolved in CH_3CN and precipitated with diethyl ether to give a yellow powder; yield 8.44 g (77%). – IR (KBr): ν/cm^{-1} = 3071 (w), 2189 (s), 1628 (m), 1508 (m), 1439 (m), 1321 (m), 1260 (s), 1222 (m), 1150 (m), 1048 (m), 1030 (s). See Table 6 for NMR data.

Synthesis of Propyne Iminium Triflates 5c,e,i,j,l

1-Benzyl-5-[2-(2-thienyl)-1-ethynyl]-3,4-dihydro-2H-pyrrolium Trifluoromethanesulfonate (**5c**); Typical Procedure

A solution of enaminoketone **3c** (8.5 g, 30 mmol) in CH_2Cl_2 (60 ml) was added dropwise to a cooled (–10 °C) solution of triflic anhydride (5.54 ml, 33 mmol) in CH_2Cl_2 (100 ml). After stirring at room temperature for 1 h, the solvent was removed *in vacuo*. The brown solution was concentrated to half its volume, and diethyl ether was added. After stirring at 0 °C, **5c** was isolated as a dark solid, triturated with diethyl ether (3×50 ml), dissolved in CH_3CN and precipitated with diethyl ether to give a yellow solid; yield 6.73 g (54%). – IR (KBr): ν/cm^{-1} = 3075 (w), 2186 (s), 1631 (m), 1260 (s), 1148 (s, sh), 1029 (s). See Table 6 for NMR data.

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