Synthesis of Propyne Iminium Triflates By Vacuum Thermolysis of 3-Trifloxypropene Iminium Triflates: Scope and Some Limitations

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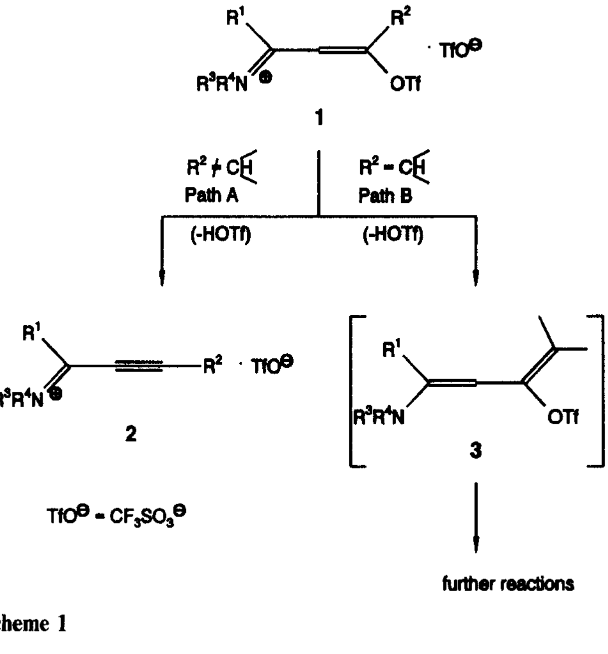
Vacuum thermolysis of various 3-trifloxypropene iminium triflates **1** leads to propyne iminium triflates **2** by β-elimination of triflic acid. In contrast, salt **1j** undergoes an intramolecular aromatic S_E reaction.

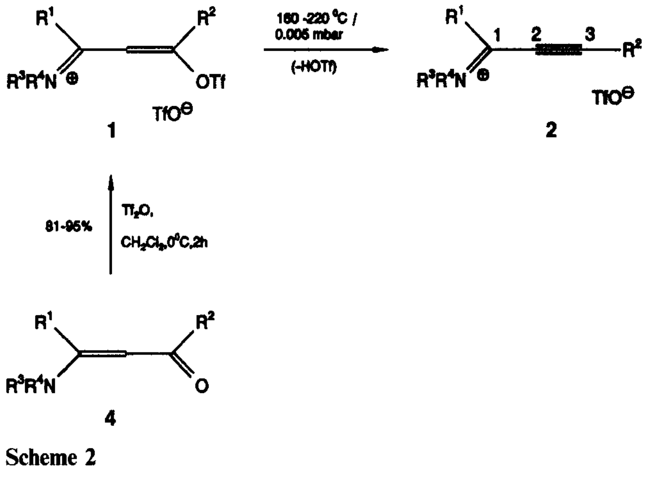
Propyne iminium triflates **2** are useful building blocks for cycloaddition reactions[1] and the synthesis of *N,N*-disubstituted aminoallenes, propargylamines, and 1- and 2-aminobutadienes.[2,3] They are readily obtained by elimination of triflic acid from (3-trifloxypropene) iminium salts **1**, where R^2 does not represent a methine, methylene, or methyl group (Scheme 1, path A). If R^2 is a CHR_2 substituent, however, base-assisted deprotonation occurs regioselectively at R^2 (path B). The dienamine **3** so formed (or a ionic form thereof) cannot be isolated, since it is consumed by fast subsequent reactions.[4]



Scheme 1

The transformation **1** → **2** can be carried out with the help of a tertiary amine (ethyldiisopropylamine, dimethylaminomethylpolystyrene) or by heating **1** in acetonitrile solution at 80 °C. For the three examples that we have studied earlier,[1] the effectiveness of each procedure depends strongly on the substrate.[1] In view of these complications and limitations, we required a method that made a broader range of salts **2** available in pure form and high yield. We report here, that the solvent-free vacuum thermolysis of 3-trifloxypropene iminium salts **1** is the method of choice for the synthesis of a variety of propyne iminium salts **2**, and we also report the limitations that we have encountered.

3-Trifloxypropene iminium triflates **1** are obtained from equimolar amounts of enaminones **4** and triflic anhydride.[5] Salts **1c–e** have been prepared now for the first time. Quantitative elimination of triflic acid from **1a–h** is achieved by vacuum thermolysis at 160–220 °C/0.005 mbar within 10–20 min (Scheme 2). The resulting propyne iminium triflates **2a–h** are usually obtained in high or even quantitative yield (Table 1) and can be purified easily by simple recrystallization.



Scheme 2

A comparison with the methods used earlier[1] (**1e** → **2e**: NEt *i*-Pr_2 as base, unseparable mixture of **2e** and HN^+Et *i*-$Pr_2 \cdot TfO^-$; **1g** → **2g**: MeCN, 80 °C, 11 h, 80%; **1h** → **2h**: dimethylaminomethylpolystyrene, 20 °C, 1 h, 76%) demonstrates the superiority of the solvent-free vacuum thermolysis. Furthermore, the case of **1f** → **2f** shows that even for $R^2 = CHR_2$ regioselective elimination of HOTf from the vinyl triflate moiety can occur, in contrast to the base-assisted deprotonation in solution (see Scheme 1).

In contrast, only unspecific decomposition is observed when **1i** is subjected to vacuum thermolysis at 160 °C. An IR spectrum of the product mixture does not reveal the presence of a $C\equiv C$ bond. It should be mentioned, however, that after thermolysis (130 °C) of **1i** in an equimolar amount of anthracene, the [4 + 2] cycloaddition product of the desired propyne iminium salt **2i** to anthracene is obtained in low yield.[6]

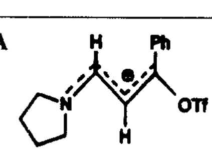
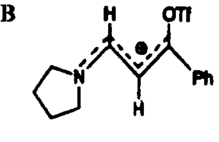
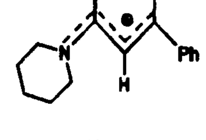
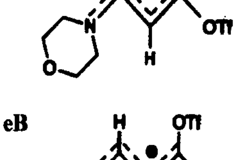
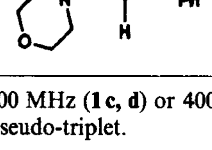
For the salts **1a–e,h** the ^1H and ^{13}C NMR spectra reveal the presence of a pair of diastereomers, whereas only one isomer is found for **1f,g** (Lit.[1,5] and Tables 2, 3). Arguments for the configurational assignment have been given.[5] In all cases, the *E* (1,2) configuration is found, whereas the diastereomeric pairs differ with respect to the configuration at the C-2–C-3 bond of the propene iminium unit.

In analogy to the well-known synthesis of alkenes by pyrolysis of carboxylic esters, the thermal elimination of triflic acid from **1** is likely to occur as a cyclic β-cis-elimination (Scheme 3). This requires the *E* (2,3) confi-

Table 1. Propyne Iminium Triflates **2** By Vacuum Pyrolysis of 3-Trifloxypropene Iminium Triflates **1**

1, 2	R^1	R^1	R^3	R^4	Reaction Temp. (°C)	Conditions Time (min)	Yield of **2** (%)
a	H	Ph	Me	Me	220	20	100
b	H	Ph	Me	Ph	160	15	88
c	H	Ph	$-(CH_2)_4-$		190	10	99
d	H	Ph	$-(CH_2)_5-$		220	15	100
e	H	Ph	$-(CH_2)_2O(CH_2)_2-$		190	15	97
f	Me	Me	$-(CH_2)_4-$		190	15	56
g	Me	Ph	$-(CH_2)_2O(CH_2)_2-$		180	15	100
h	Ph	Ph	$-(CH_2)_2O(CH_2)_2-$		220	20	100
i	H	Pr	Et	Et	160	20	0

Table 2. ^{1}H NMR data[a] and Diastereomer Ratios of 3-Trifloxypropene Iminium Triflates **1c–e**

Product	1-H	2-H	NR^3R^4	Ph	Ratio A : B
1cA 	8.35 (td) $^3J = 10.5$, $\lvert ^4J \rvert = 2.0$	6.87 (d) $^3J = 10.5$	2.03–2.26 (m, NCH_2CH_2) 4.05–4.25 (m, NCH_2)	7.54–7.95	1 : 6.8
1cB 	8.66 (td) $^3J = 10.5$, $\lvert ^4J \rvert = 2.0$	7.11 (d) $^3J = 10.5$			
1dB 	8.50 (d) $^3J = 10.4$	7.32 (d) $^3J = 10.4$	1.90–2.00 (m, NCH_2CH_2) 4.10, 4.14 ([b], NCH_2)	7.59–7.77 (m, 3H) 7.92 (d, 2H)	≈ 1 : 20
1eA 	8.19 (d) $^3J = 10.6$	7.06 (d) $^3J = 10.6$	3.75–4.22 (m, NCH_2, OCH_2)	7.56–7.95	1 : 1.9
1eB 	8.56 (d) $^3J = 10.5$	7.30 (d) $^3J = 10.5$			

[a] 200 MHz (**1c**, **d**) or 400 MHz (**1e**); CD_3CN/TMS, δ, J (Hz).
[b] Pseudo-triplet.

guration for the propene iminium salts **1**; but because of the reduced double-bond order of the charge-delocalized propene iminium cation, thermal $Z\,(2,3) \rightarrow E\,(2,3)$ isomerization can obviously occur under the reaction conditions, and the initial stereochemistry at this bond is of no relevance.

When salt **1j** is subjected to vacuum thermolysis, (indanylidene)morpholinium triflate **5** rather than a propyne iminium salt is obtained in high yield (Scheme 4). Deprotonation of this iminium salt yields 1-ethylidene-3-morpholinoindene (**6**). The E configuration of **6** was derived from an NOE experiment (see Experimental Part). Similar 1-alkylidene-3-aminoindenes have been prepared by a completely different method.[7]

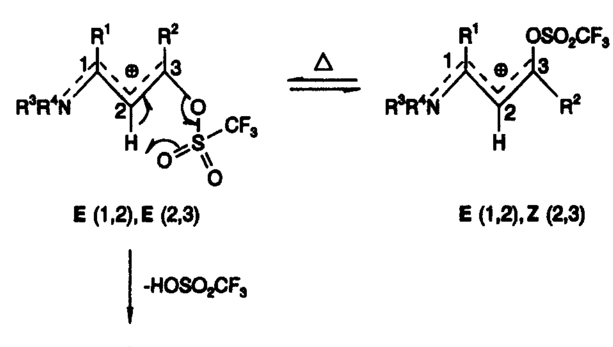
The formation of **5** can be rationalized as an intramolecular electrophilic aromatic substitution of **1j**, followed by elimination of triflic acid. This is the first example of an aromatic substitution reaction involving a 3-trifloxypropene iminium salt; in the meantime we have also found several intermolecular cases.[6] As far as the related 3-chloropropene iminium salts are concerned, a comparable cyclization has been reported for the dimethyl[3-

Table 3. ^{13}C NMR data[a] for **1c–e**

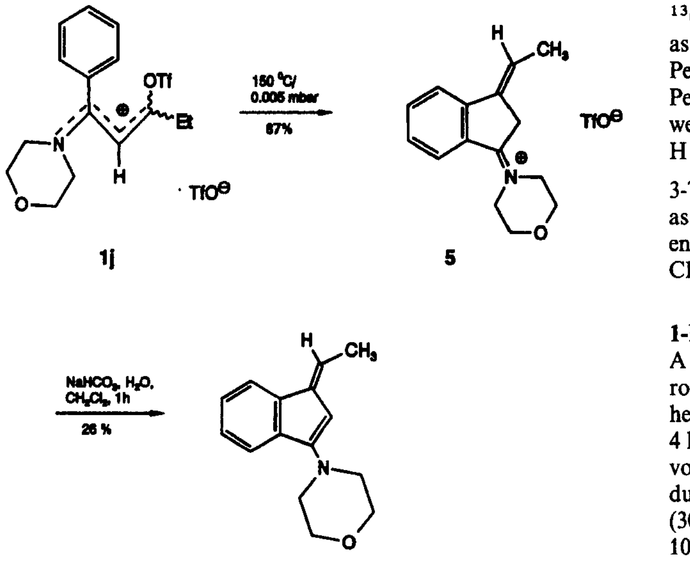
Product	C-1 (^1J)	C-2 (^1J)	C-3	NCH$_2$	Other Signals in NR^{3}R^4	CF$_3$[b] TfO$_{cov}$	CF$_3$[b] TfO$_{ion}$	Ph
1cA	162.9 (183.7)	113.7	167.2	54.4, 59.4	25.1 (NCH$_2$*C*H$_2$)	119.3	122.3	128.8–135.4
1cB	159.4 (184.9)	111.8 (169.3)	162.9	54.6, 59.8	24.9, 25.0			
1dB	160.6 (181.7)	109.9 (169.7)	164.0	54.0, 62.4	27.3, 27.9 (NCH$_2$*C*H$_2$) 23.0 (CH$_2$*C*H$_2$CH$_2$)	119.1	121.9	128.8 (d), 130.4 (s) 131.3 (d), 135.3 (d)
1eA	165.8 (197.4)	111.8 (170.2)	169.1	53.3, 60.1	66.5, 67.1 (OCH$_2$)	119.2	121.8	130.6 (d), 131.3 (s), 131.4 (d), 135.2 (d)
1eB	161.8 (183.4)	109.8 (167.2)	164.7	53.5, 60.6	67.0, 67.5 (OCH$_2$)			129.1 (d), 129.7 (d) 130.4 (s), 135.6 (d)

[a] CD$_3$CN, δ, J (Hz).

[b] ^1J (C, F) = 319.9–320.9 Hz.



Scheme 3



Scheme 4

chloro-3-(3,4-dimethoxyphenyl)-2-methyl-2-propenylidene)]ammonium ion;[8] in that case, however, a more electron-rich phenyl ring was involved, and the iminium carbon atom functioned as the internal electrophilic center.

In summary, 3-trifloxypropene iminium triflates can be transformed into propyne iminium triflates conveniently by vacuum thermolysis, usually in high to quantitative yield. In the cases under study, this method proved superior to the same transformation using a tertiary amine as a base or solution thermolysis; some propyne iminium salts are accessible only by the new method. A limitation is encountered with the 1-phenyl-3-ethyl-substituted propene iminium salt **1j**, which undergoes an intramolecular aromatic substitution followed by HOTf elimination. However, this unexpected reaction pathway illustrates the highly electrophilic nature of 3-trifloxypropene iminium salts.

Melting points were determined in a copper block and are not calibrated. ^{1}H NMR spectra: Bruker AC 200 (200.1 MHz) and Bruker AMX 400 (400.1 MHz), TMS as internal standard. ^{13}C NMR spectra: Bruker AMX 400 (100.6 MHz), solvent signal as standard [δ (CDCl$_3$) = 77.0, δ (CD$_3$CN) = 118.2]. IR spectra: Perkin-Elmer infrared spectrophotometer 1310. Microanalyses: Perkin-Elmer EA 240 and EA 2400. Satisfactory elemental analyses were obtained for **1c–e**, **2a–h**, **4c–e**, **5**, and **6**: C ± 0.30 (**2e**: – 0.43), H ± 0.15, N ± 0.24.

3-Trifloxypropene iminium triflates **1a**,[1] **1b**,[5] **1f–h**[5] were prepared as described. The salts **1c–e** were obtained from the newly prepared enamino ketones **4c–e** and triflic anhydride [(CF$_3$SO$_2$)$_2$O] in CH$_2$Cl$_2$ according to the published procedure.[5]

1-Phenyl-3-pyrrolidino-2-propen-1-one (4c); Typical Procedure:[9]

A solution of acetophenone (25.23 g, 0.21 mol) and dimethoxy(pyrrolidino)methane[10] (29.91 g, 0.206 mmol) in MeOH (200 mL) was heated at 65 °C. The reaction mixture was then kept at reflux for 4 h (color change from yellow to black-red). The solvent and other volatile compounds were distilled off at ambient pressure. The product was precipitated by addition of low-boiling petroleum ether (300 mL); orange-colored powder (26.30 g, 64% yield), mp 104–106 °C.

IR (KBr): ν = 1630 (s, C=O), 1575 (s), 1535 cm^{-1} (s).

^{1}H NMR (CDCl$_3$, 200 MHz): Two isomers were observed (1 : 1 ratio, rotamers at the C-2–C-3 bond); δ = 1.8–2.1 (m, 4 H, CH$_2$), 2.75–3.6 (m, 4 H, NCH$_2$), 5.67/5.70 (d, J = 12.4/12.4 Hz, H-2), 7.78/7.99 (d, J = 12.4/12.4 Hz, H-3), 7.37–7.5 and 7.87–7.92 (m, Ph).

1-Phenyl-3-piperidino-2-propen-1-one (**4d**):

From acetophenone and diethoxy(piperidino)methane[11] in boiling EtOH; yield: 68%; yellow needles, mp 78–79 °C.

IR (KBr): ν = 1630 (s, C=O), 1580 (s), 1505–1545 cm^{-1} (br, s).

Table 4. Spectral Data for Propyne Iminium Triflates **2a–f**

Product	IR[a], ν (C≡C), ν (C≡N) (cm^{-1})	^{1}H NMR (CD_3CN/TMS)[b] δ, J (Hz)	^{13}C NMR (CD_3CN), δ, J (Hz) C-1	C-2	C-3	CF_3[c]	Other Signals
2a	2195, 1655–1630 (br)	3.77 (s, NMe_2), 7.51–7.79 (m, Ph), 8.36 (s, 1-H)	155.1 $^1J = 191.7$	81.6	118.6*[d]	121.6	45.4/49.1 (NMe_2), 118.9* (s), 130.0 (d), 134.3 (d), 134.6 (d)
2b	2190, 1605	4.23 (s, NMe), 7.53–7.78 (m, 8 H, Ph), 7.87–7.89 (m, 2 H, Ph), 8.62 (s, 1-H)	154.8 $^1J = 194.9$	84.1	118.8	121.9	46.3 (NMe), 118.8 (ipso-C at C-3), 123.4–135.3 (C-arom.), 143.4 (N-C-arom.)
2c	2190, 1640	2.09–2.18 (m, NCH_2CH_2), 4.19–4.22 (m, NCH_2), 7.52–7.93 (m, Ph), 8.41 (t, $\lvert ^4J \rvert = 2.1$, 1-H)	151.1 $^1J = 195.0$	82.6	118.8*[d]	121.1	24.8/25.4 (NCH_2CH_2), 56.7/58.7 (NCH_2), 119.0* (s), 129.1 (d), 134.4 (d), 134.7 (d)
2d	2190, 1635	1.80 (m_c, $CH_2CH_2CH_2$), 1.97 (m_c, NCH_2CH_2), 4.12/4.26 ([e], NCH_2), 7.53–7.95 (m, Ph), 8.38 (s, 1-H)	151.9 $^1J = 195.2$	81.1	118.8	122.7	22.6 ($CH_2CH_2CH_2$), 27.1/27.4 (NCH_2CH_2), 55.9/60.0 (NCH_2), 118.8 (s), 130.3/133.7/134.6 (all d)
2e	2190, 1630	4.0 (m_c, NCH_2), 4.18/4.32 (m_c, OCH_2), 7.52–7.84 (m, Ph), 8.45 (s, 1-H)	153.0 $^1J = 194.0$	81.2	120.1*[d]	121.7	54.9/58.4 (NCH_2), 66.8/67.0 (OCH_2), 118.8* (s), 130.1 (d), 134.5 (d), 134.9 (d)
2f	2220, 1630	2.06–2.18 (m, NCH_2CH_2), 2.29 (s, Me), 2.48 (s, Me), 3.92/4.05 ([e], NCH_2)	162.7	75.9	116.5 $^2J = 11.3$	121.8	5.3 (3-Me), 24.7/25.3 (NCH_2CH_2), 24.9 (1-Me), 54.7/58.2 (NCH_2)

[a] KBr pellet (**2a–e**) or Nujol suspension (**2f**).

[b] Recorded at 200.1 MHz (**2a,c,e**) or 400.1 MHz (**2b,d,f**).

[c] ^1J (C,F) = 320.7–322.9 Hz.

[d] Signals marked with "*" may be interchanged.

[e] Pseudo-triplet.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.60–1.70 (m, 6 H, CH_2), 3.30–3.45 (m, 4 H, NCH_2), 5.81 (d, J = 12.5 Hz, H-2), 7.77 (d, J = 12.5 Hz, H-3), 7.36–7.45 (m, 3 H) and 7.86–7.91 (m, 2 H).

3-Morpholino-1-phenyl-2-propen-1-one (**4e**):

From acetophenone and diethoxy(morpholino)methane[11] in boiling EtOH; yield: 67 %; yellow needles, mp 60–64 °C.

IR (KBr): ν = 1625 (s, C=O), 1570 (s), 1500–1540 cm^{-1} (br, s).

^{1}H NMR ($CDCl_3$, 200 MHz): Two isomers were observed (1.3 : 1, rotamers at the C-2–C-3 bond); δ = 2.87 and 3.04 (unresolved m, NCH_2, both isomers), 3.33 and 3.69 (m, OCH_2, both isomers), 5.69 (major)/5.87 (minor) (d, J = 12.5/12.6 Hz, H-2), 7.70 (minor)/7.77 (major) (d, J = 12.6/12.5 Hz, H-3), 7.3–7.5 (m, 3 H) and 7.85–7.95 (m, 2 H).

N-[3-Phenyl-3-(trifluoromethylsulfonyloxy)-2-propenylidene]-pyrrolidinium Trifluoromethanesulfonate (1c):

From **4c** and triflic anhydride; yield: 81 %, beige powder, mp 158–162 °C.

IR (KBr): ν = 1655 (s), 1620 (s), 1420 (s, covalent OTf), 1280, 1250, 1230, 1220, 1150, 1130, 1030 cm^{-1} (all s, CF_3SO_3).

E/*Z* ratio and NMR data: See Tables 2 and 3.

N-[3-Phenyl-3-(trifluoromethylsulfonyloxy)-2-propenylidene]-piperidinium Trifluoromethanesulfonate (1d):

From **4d** and triflic anhydride; yield: 95 %, colorless powder, mp 163–164 °C.

IR (KBr): ν = 1655 (s), 1610 (s), 1415 (s, covalent OTf); 1295–1215 (br), 1165–1125 (br), 1030 cm^{-1} (all s, CF_3SO_3).

E/*Z* ratio and NMR data: See Tables 2 and 3.

4-[3-Phenyl-3-(trifluoromethylsulfonyloxy)-2-propenylidene]-morpholinium Trifluoromethanesulfonate (1e):

From **4e** and triflic anhydride; yield: 86 %, pale-yellow powder, mp 160–161 °C.

IR (KBr): ν = 1645 (s), 1620 (s), 1580 (m), 1405 (s, covalent OTf), 1290–1225 (vs, br), 1160–1130 (s, br), 1030 cm^{-1} (CF_3SO_3).

E/*Z* ratio and NMR data: See Tables 2 and 3.

Vacuum Pyrolysis of 3-Trifloxypropene Iminium Trifluoromethanesulfonates (Triflates) 1a–h: General Procedure:

Salt **1** (0.21–9.05 mmol) was heated in a Kugelrohr distillation apparatus at 0.005 mbar; for reaction temperature and duration see Table 1. The residual viscous brown oil was allowed to cool to r. t. and triturated with Et_2O (3 × 5–50 mL); thereby, the product separated as a solid. The purification was done by one of the following methods. Method A: The product was dissolved in CH_2Cl_2 and allowed to crystallize at – 78 °C. Still at this temperature, the mother liquor was pipetted off, and the remaining beige powdery product was washed with Et_2O and dried at 0.005 mbar. Method B: The crude product was recrystallized by dissolving in CH_2Cl_2 and precipitation with Et_2O.

(3-Phenyl-2-propynylidene)dimethylammonium Triflate (**2a**):

Method A, mp 69 °C.

Methylphenyl(3-phenyl-2-propynylidene)ammonium Triflate (**2b**):

Method B, mp 131 °C. Since the product is very moisture sensitive, the workup is done under an inert gas atmosphere.

1-(3-Phenyl-2-propynylidene)pyrrolidinium Triflate (**2c**):

Method B, mp 91 °C.

1-(3-Phenyl-2-propynylidene)piperidinium Triflate (**2d**):

Method B, mp 110 °C.

4-(3-Phenyl-2-propynylidene)morpholinium Triflate (**2e**):

Method B, mp 120 °C.

(1-Methyl-2-butynylidene)pyrrolidinium Triflate (**2f**):

Method A, mp 74 °C.

4-(1-Methyl-3-phenyl-2-propynylidene)morpholinium Triflate (**2g**):

Method B, mp 133 °C (Lit.[1] 136 °C).

4-(1,3-Diphenyl-2-propynylidene)morpholinium Triflate (**2h**):

Method B, recrystallization from MeCN/Et_2O, mp 127 °C (Lit.[1] 127 °C).

See Table 4 for spectroscopic data.

4-[(*E*)-3-Ethylidene-1-indanylidene]morpholinium Trifluoromethanesulfonate (5):

Salt **1j**[5] (3.09 g, 5.85 mmol) was kept for 20 min at 150 °C/0.005 mbar in a Kugelrohr distillation apparatus. The resulting oil was allowed to reach r.t. and triturated with Et_2O (3×20 mL). The remaining solid product was recrystallized twice from CH_2Cl_2/Et_2O, then from MeCN/Et_2O; 1.72 g (87 %) of a yellow powder, mp 224 °C.

IR (KBr): ν = 1635 (s, C=C), 1590 (s, C=N); 1260 (vs, br), 1220 (s), 1145 (s), 1110 (s), 1030 cm^{-1} (vs).

^1H NMR ($CD_3CN/CDCl_3$ 1:1, 400 MHz): δ = 1.97 (d, ^3J = 7.2 Hz, Me), 3.96 (br s, CH_2), 4.0–4.1 (m, 4 H, NCH_2), 4.12 and 4.47 (each pseudo-t, OCH_2), 6.63 (qt, ^3J = 7.2 Hz, ^4J = 1.8 Hz), 7.53 (m_c, 1 H), 7.81 (m_c, 1 H), 7.99 (d, 4-H), 8.15 (d, 7-H).

^{13}C NMR ($CD_3CN/CDCl_3$, 100.6 MHz): δ = 13.8 (Me), 36.9 (C-2), 51.9 (NCH_2), 53.8 (NCH_2), 64.4 (OCH_2), 64.7 (OCH_2), 120.3 (q, J = 321.5 Hz, CF_3), 121.0 (d), 122.9 (d), 128.1 (d), 128.3 (d), 129.3 (s), 130.8 (s), 136.6 (d), 152.7 (s), 180.7 (s, C-1).

1-(*E*)-Ethylidene-3-morpholinoindene (6):

The two-phase system consisting of a solution of iminium salt **5** (1.50 g, 4.43 mmol) in CH_2Cl_2 (15 mL) and sat. aq $NaHCO_3$ (5 mL) was vigorously stirred for 1 h. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2×10 mL). The combined organic phases were dried ($MgSO_4$), and the solvent was replaced by Et_2O (5 mL). On cooling at 2 °C, **6** was obtained as a yellow powder; yield 0.26 g (26 %); mp 64–65 °C. The product should be stored in an inert gas atmosphere in the dark.

IR (KBr): ν = 1630 (w), 1575 cm^{-1} (s).

^1H NMR ($CDCl_3$, 400 MHz): δ = 2.07 (d, ^3J = 7.4 Hz, Me), 3.16 (pseudo-t, 4 H, NCH_2), 3.83 (pseudo-t, 4 H, OCH_2), 5.89 (s, 2-H), 6.31 (q, ^3J = 7.4, $\underline{CH}$=Me), 7.14–7.21 (m, 2 H), 7.27 (mc, 1 H), 7.53 (mc, 1 H). The *E* configuration was derived from an NOE experiment: On saturation of the signal at δ = 6.31, the intensity of the signal at δ = 7.53 increased by 8 %, whereas no effect was observed on saturation of the Me signal.

^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.2 (Me), 50.7 (NCH_2), 66.5 (OCH_2), 102.4 (^1J = 166.0 Hz, ^3J = 9.0 Hz, C-2), 119.3 (d), 120.1 (d), 125.1 (d), 126.1 (d), 128.7 (d), 137.7 (^2J = 7.0 Hz, C-1), 138.1 (s), 138.7 (s), 153.9 (C-3).

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