Novel Synthesis of 2-Alkylquinolizinium-1-olates and Their 1,3-Dipolar Cycloaddition Reactions with Acetylenes

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Dedicated to Professor *Hans-Jürgen Hansen* on the occasion of his 75th birthday

Several 2-alkylquinolizinium-1-olates **9**, *i.e.*, heterobetaines, were prepared from ketone **11**, the latter being readily available either from pyridine-2-carbaldehyde *via* a *Grignard* reaction, followed by oxidation with MnO_2, or from 2-picolinic acid (= pyridine-2-carboxylic acid) *via* the corresponding *Weinreb* amide and subsequent *Grignard* reaction. Mesoionic heterobetaines such as quinolizinium derivatives have the potential to undergo cycloaddition reactions with double and triple bonds, *e.g.*, 1,3-dipolar cycloadditions or *Diels–Alder* reactions. We here report on the scope and limitations of cycloaddition reactions of 2-alkylquinolizinium-1-olates **9** with electron-poor acetylene derivatives. As main products of the reaction, 5-oxopyrrolo[2,1,5-*de*]quinolizines (='[2.3.3]cyclazin-5-ones') **19** were formed *via* a regioselective [2+3] cycloaddition, and cyclohexadienone derivatives, formed *via* a *Diels–Alder* reaction, were obtained as side products. The structures of 2-benzylquinolizinium-1-olate (**9a**) and two '[2.3.3]cyclazin-5-ones' **19i** and **19l** were established by X-ray crystallography.

1. Introduction. – Since the formulation of the concept of 1,3-dipolar cycloadditions ([2+3] cycloadditions) by *Huisgen* [1], this reaction type proved to be an indispensable tool for the synthesis of five-membered heterocycles [2]. Belonging to the pericyclic reactions, the special features of [2+3] cycloadditions such as chemo-, regio-, and stereoselectivity are nowadays well understood on the basis of the Frontier Molecular Orbital (FMO) theory [3], and the *Woodward–Hoffmann* [4] and *Dewar–Zimmerman* rules [5] allow reliable predictions of the reaction course and the structure of the products. But an increasing number of formal 1,3-dipolar cycloadditions is known, in which a non-concerted, two-step mechanism [6], *via* either a biradical [7] or a zwitterion [8] as the crucial intermediate, leads to the five-membered products.

An important group of 1,3-dipoles often used in [2+3] cycloadditions consists of azomethine ylides, which can be generated as reactive intermediates by various methods such as thermal and photochemical ring-opening of aziridines, deprotonation of iminium salts, desilylation of silylated amines and imines, base-catalyzed elimination

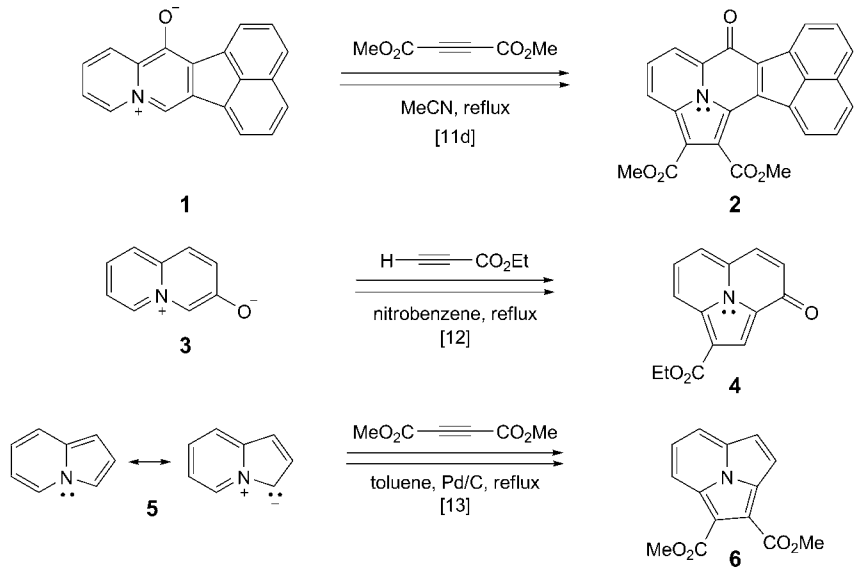
[1]) Part of the Ph.D. thesis of *A. G.*, Universität Zürich, 2001.

[2]) Part of the diploma thesis of *M. B.*, Universität Zürich, 1994.

of thiophenol from 2-(phenylsulfanyl)amines, thermal decarboxylation of 1,3-oxazolidin-5-ones, and dehydration of *N*-oxides of tertiary amines [9]. In addition, a series of relatively stable azomethine ylides has been described, in which the formal charges are stabilized by extended delocalization or electron-withdrawing substituents. Well-known examples are pyridinium, quinolinium, and isoquinolinium methanides, and mesoionic 1,3-oxazol-5-ones ('Münchnones') [10], which have also been used in [2 + 3] cycloadditions.

A less well-known group of stabilized azomethine ylides includes mesoionic quinolizinium-1-olates (*Scheme 1*). Although a few compounds of this group have been prepared [11], they were only scarcely investigated in dipolar cycloadditions. For example, *Pastor et al.* reported that **1** and dimethyl acetylenedicarboxylate (DMAD) reacted already at room temperature, and the '[2.3.3]cyclazin-5-one' (*Boekelheide* nomenclature) derivative **2**[3]) was isolated as the only product albeit in rather low yield [11d]. It is important to note that the initially formed [2 + 3] cycloadduct could not be isolated, and a spontaneous dehydrogenation occurred under the reaction conditions leading to the 'aromatized' product **2**. Analogous reactions were observed between quinolizinium-3-olate (**3**) and ethyl propiolate (= ethyl prop-2-ynoate) leading to **4** [12], and between the non-mesoionic pyrrolo[1,2-*a*]pyridine (**5**) and DMAD in refluxing toluene in the presence of Pd/C to yield **6** [13] (*Scheme 1*).

Scheme 1



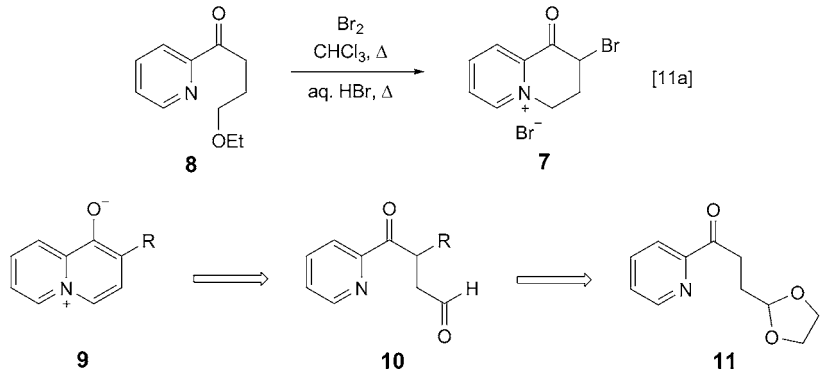
In the present study, we elaborated a new synthesis of 2-alkylquinolizinium-1-olates of type **9** and investigated their ability to undergo 1,3-dipolar cycloadditions with alkyl

[3]) The IUPAC (class) name of these compounds is pyrrolo[2,1,5-*de*]quinolizin-5-ones, and the semi-trivial name 8b-azaacenapthylen-5-one has also been used in the literature.

acetylenecarboxylates. As the cyclazine skeletons of type **2**, **4**, and **6** occur in quinolizinium alkaloids [14], these cycloadditions may be of interest as a synthetic tool for the preparation of these products.

2. Results and Discussion. – 2.1. *Synthesis of 2-Alkylquinolizinium-1-olates* **9**. In analogy to the synthesis of the quinolizinium derivative **7** *via* cyclization of **8** by *Fozard* and *Jones* [11a], our approach to **9** was based on the cyclization *via* formation of the C–N bond (*Scheme 2*). A suitable precursor is the aldehyde **10**, which after alkylation of **11**, can be generated *in situ* under acidic conditions.

Scheme 2



The known ketone **11** [15] was synthesized *via* two different routes, both involving a *Grignard* reaction (*Scheme 3*). Starting with 2-(2-bromoethyl)-1,3-dioxolane, the *Grignard* reagent **13** was prepared at 10°, followed by dropwise addition of pyridine-2-carbaldehyde (**12**; route *A*). When the reaction was complete, an aqueous solution of NH_4Cl was added. The crude alcohol was purified by column chromatography to yield **14** (29%), which was oxidized with MnO_2 to give ketone **11** in 82% yield. In the second approach (route *B*), the mixed anhydride of pyridine-2-carboxylic acid (**15**) and isobutyl chloroformate was formed *in situ*, and subsequent treatment with *N*,*O*-dimethylhydroxylamine gave the *Weinreb* amide **16** [16] in 75% yield. The following *Grignard* reaction with 1.5 equiv. of **13** led to **11** as white crystals in 79% yield. Route *A* has the disadvantage of a low overall yield (24%), but it has to be taken into account that the higher overall yield achieved *via* route *B* (59%) is connected with much higher costs of the starting materials.

The alkylation of **11** in the α-position to the C=O group was carried out by treatment with LDA ($LiN(i\text{-}Pr)_2$) at $-78°$ in THF/DMPU (1,3-dimethyltetrahydropyrimidin-2(1*H*)-one)[4]), followed by addition of various alkyl halogenides at the same temperature, to give the desired 2-alkylated products **17** (*Table 1*)[5]). After complete addition, the mixture was allowed to warm to room temperature and was then poured

[4]) The yields of the alkylation were much lower in the absence of DMPU.

[5]) The temperature of the mixture had to be kept below $-55°$, otherwise the yields decreased dramatically.

Scheme 3

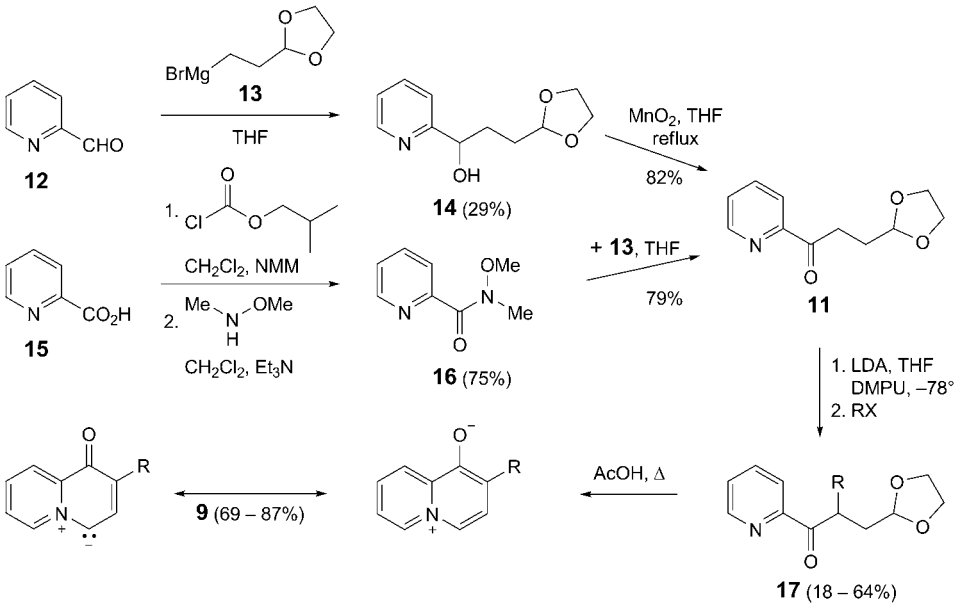


Table 1. *Formation of* **17** via *Alkylation of Ketone* **11** *and Cyclization to Give 2-Alkylquinolizinium-1-olates* **9**

R	**17**	Yield [%]	**9**	Yield [%]
Bn	**a**	63	**a**	87
Me	**b**	55	**b**	86
CH_2=CH–CH_2	**c**	64	**c**[a])	69
i-Pr	**d**	18	**d**	70
CH≡C–CH_2	**e**	64	**e**[b])	21
H	**11**		**f** [11b]	10

[a]) Prop-1-en-1-yl derivative. [b]) 2-[(1,3-Dioxolan-2-yl)methyl]-4-methylquinolizinium-1-olate.

into ice-water. The crude products were purified by column chromatography. With the exception of **17d**, the products were obtained in good yields.

For the cyclization, the respective ketones **17** were dissolved in glacial AcOH, and the solutions were heated to reflux for 12 h. Then, the excess AcOH was removed by azeotropic distillation with EtOH. The crude products were purified by chromatography and recrystallization to give **9a**–**9d** in 69–87% yield (*Table 1*). In the case of the allyl derivative **17c**, the ^{1}H- and ^{13}C-NMR spectra indicated that the formed quinolizinium-1-olate **9c** was the (*E*)-prop-1-en-1-yl derivative. The structures of the products **9**, which were obtained as yellow or orange solids, were determined on the basis of their analytical and spectroscopic data. They showed an intense UV absorption in the range of 361–416 nm and a bright yellow fluorescence, when solutions were

irradiated with UV light (λ 366 nm). In the ^{13}C-NMR spectra ($CDCl_3$), C(1)–O absorbed at 165.4 – 162.8 ppm, and the IR absorption ($CHCl_3$) of the C,O group was typically found at *ca.* 1550 cm^{-1}, *i.e.*, at much lower frequencies than the normal C=O groups[6]). Finally, the structure of **9a** was established by means of X-ray crystallography (*Fig. 1*). The crystal structure shows that the compound has the expected zwitterionic character: the C(1)–O bond is significantly longer (1.272(2) Å) than expected for C=O groups (*ca.* 1.20 Å).

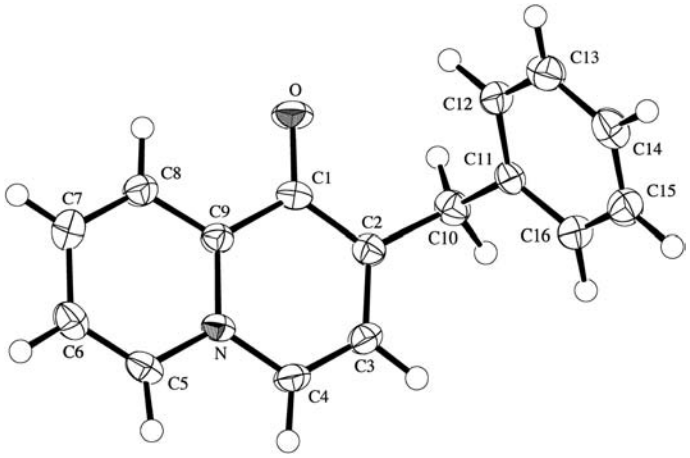


Fig. 1. *ORTEP Plot* [17] *of the molecular structure of* **9a** (50% probability ellipsoids; arbitrary numbering of the atoms)

We also tried to prepare the known parent compound **9f** [11b] *via* the acid-catalyzed cyclization of **11** under the conditions described above. The reaction was remarkably slower than that in the previous cases, and after 40 h in refluxing glacial AcOH and chromatographic workup, **9f** was obtained in only 10% yield. A possible explanation is the effect of a bulky substituent at the α-position on the conformation of the intermediate for the ring closure. Such a substituent may promote a conformation in which the acetal group is close to the pyridine N-atom, thereby favoring the cyclization.

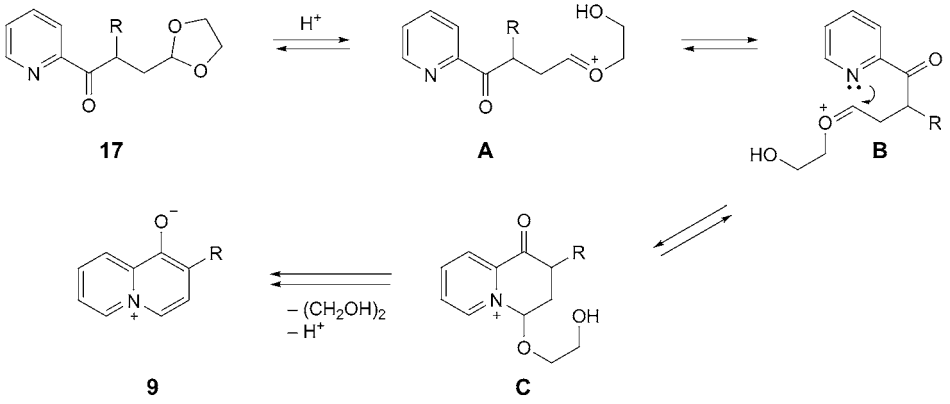
An unexpected result was obtained with the propargyl derivative **17e**. After 12 h in refluxing glacial AcOH, a complex mixture of products was formed. Following the progress of the reaction by TLC showed that a new product with a yellow fluorescence was present after *ca.* 2 h, but disappeared when the mixture was heated for a longer time. After azeotropic distillation of the excess AcOH with EtOH, column chromatography, and recrystallization, a yellow powder was isolated. Surprisingly, in the NMR spectra, all signals of the dioxolane ring were still present. Additionally, the ^{1}H-NMR spectrum showed the absorptions of a CH_2 group at 3.18 ppm (d, $J = 5.2$) and a Me signal at 2.63 ppm, and, in the ^{13}C-NMR spectrum, the signals of these groups were observed at 35.1 and 19.3 ppm, respectively. In the CI-MS (NH_3), the $[M+1]$

[6]) The C(1)–O group of the analogous mesoionic 8-(ethoxycarbonyl)acenaphtho[1,2-*b*]quinolizinium-1-olate absorbs at 1586 cm^{-1} (KBr) [11d].

peak appeared at *m*/*z* 246, *i.e.*, indicating the same mass as the starting material **17e**. The IR spectrum showed the characteristic band at 1551 cm^{-1}, suggesting the presence of a quinolizinium-1-olate. On the basis of these data, the structure **9e** was proposed for the product.

A reaction mechanism for the formation of **9** is proposed in *Scheme 4*. Under the acidic conditions, the dioxolane ring is opened to give intermediate **A**. A bulky substituent R may favor conformation **B**, which is suitable for the ring closure to give **C** *via* nucleophilic addition of the pyridine N-atom. Finally, elimination of ethyleneglycol and rearomatization yields the mesoionic product **9**.

Scheme 4



The formation of **9c** with a (*E*)-prop-1-en-1-yl side chain can be rationalized by a secondary isomerization of the initially formed 1-hydroxyquinolizidinium derivative **D** *via* the intermediate **E** (*Scheme 5*). In the case of the propargyl derivative **17e**, a protonation of the acetylenic group may lead to cation **F**, which is prone to undergo the ring closure to **G**. Aromatization of the latter *via* enolization and 1,3-H shift gives the isolated product **9e**. It is important to note that the acetal unit remains unreacted under the acidic reaction conditions, and the formal 6-*endo-dig* cyclization is the preferred ring closure.

2.2. *1,3-Dipolar Cycloadditions of* **9** *with Acetylenes.* As mentioned in the *Introduction*, quinolizinium-olates **1** and **3** can undergo 1,3-dipolar cycloadditions with electron-deficient acetylenes [11d][12]. Having in hand the quinolizinium-1-olates **9a**–**9f** (*Table 1*), we studied their reactions with acetylene dicarboxylates **18**. For this purpose, solutions of 1 equiv. of **9** and 2 equiv. of **18** in THF were stirred at room temperature. After *ca.* 30 min, **9** was completely consumed (TLC), and chromatographic workup gave the main product as an orange oil or powder (*Table 2*). On the basis of the analytical and spectroscopic data, the structure of 4-substituted [2.3.3]cyclazin-5-ones **19** (1,2-bis(alkoxycarbonyl)pyrrolo[2,1,5-*de*]quinolizinium-5-olates) was proposed (*Scheme 6*). For example, the IR spectrum ($CHCl_3$) of **19b** showed a strong band at 1584 cm^{-1}, and in the ^{13}C-NMR spectrum ($CDCl_3$), the C(5)–O group absorbed at 175.2 ppm, indicating a less pronounced dipolar character compared with **9a**. The CI-MS with $[M+1]^+$ at *m*/*z* 376 as well as the elemental analysis

Scheme 5

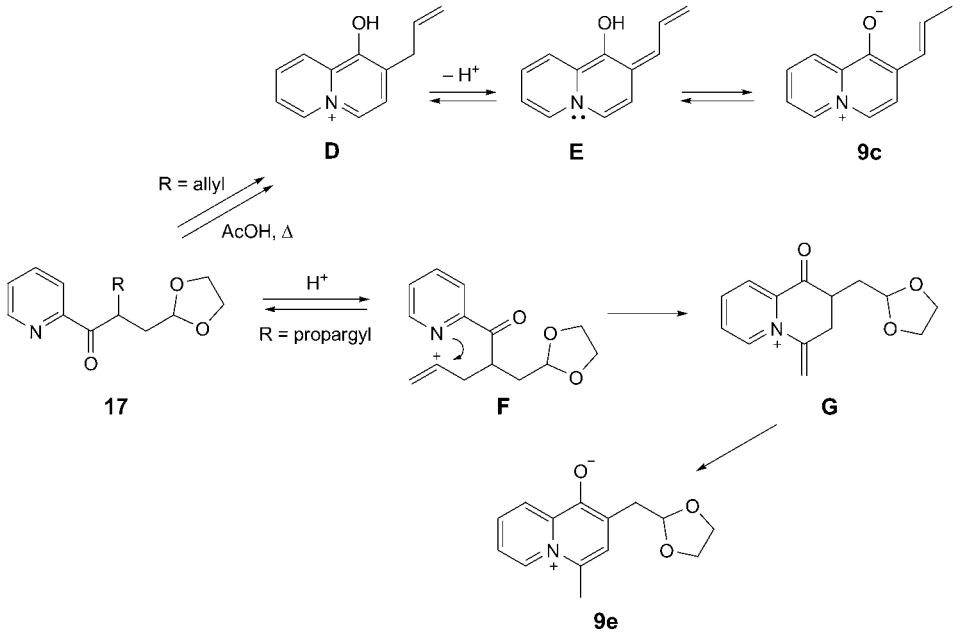


Table 2. *Formation of Compounds* **19** via *[2+3] Cycloaddition of* **9** *with Acetylene Dicarboxylates* **18a** and **18b**

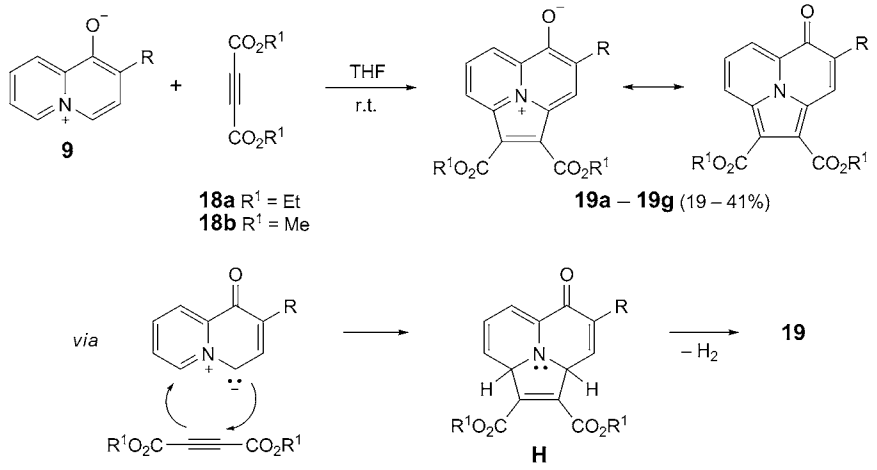
9	R	**18**	R^1	Procedure	**19**	Yield [%]	
a	Bn	**a**	Et	*A* [a])	**a**	36 (45[b]))	orange oil
		b	Me	*A*	**b**	40	orange powder, m.p. 169–170°
b	Me	**a**	Et	*A*	**c**	29	orange oil
		b	Me	*A*	**d**	39	orange powder, m.p. 148–149°
c	Me–CH=CH	**b**	Me	*A*	**e**	33	orange oil
d	i-Pr	**b**	Me	*A*	**f**	41	orange oil
f	H	**b**	Me	*A*	**g**	19	orange oil

[a]) Reaction in THF at room temperature. [b]) Reaction in toluene, 17 min reflux, 18 h at r.t.

supported this structure. Furthermore, **9a** exhibited an intense UV absorption at 473 nm ($\log \varepsilon = 4.01$, MeOH) and a bright yellow fluorescence.

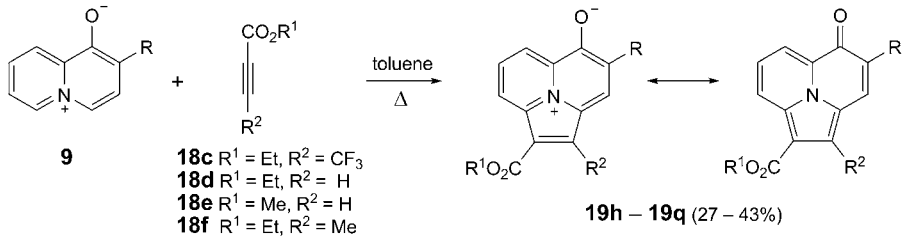
The formation of the products **19** can be rationalized by a [2+3] cycloaddition of **9** and **18** to give **H**, which spontaneously undergoes a dehydrogenation to yield the final product (*Scheme 6*). It is important to note that, in all experiments, the initially formed cycloadduct of type **H** could neither be isolated nor detected. This is in accordance with the results of the reaction **1** → **2** reported in [11d], whereas the reactions **3** → **4** [12] and **5** → **6** [13] (*Scheme 1*) have been carried out under dehydrogenation conditions.

Scheme 6



For the next series of reactions with **9**, unsymmetrical acetylenecarboxylates **18c** – **18f** were used. The reaction with ethyl 4,4,4-trifluorobut-2-ynoate (**18c**) occurred smoothly in THF at room temperature to yield a single product with the characteristic spectroscopic properties of compounds of type **19** in 43% yield (*Scheme 7*). The exact structure of **19l** was established by X-ray crystallography (*Fig. 2*, *b*).

Scheme 7



The C(1)–O bond length is 1.234(3) Å and is slightly longer than a normal C=O bond but shorter than the C,O bond in **9a** (1.272(2) Å), indicating a higher C=O bond character. On the other hand, the IR (1542 cm^{-1}) and ^{13}C-NMR spectra (175.8 ppm) point to a pronounced dipolar character of the C,O bond [18]. The molecule **19l** is highly planar with all ring atoms being within 0.05 Å of the mean plane. The C=C bonds are completely delocalized in the five-membered ring, but tend to be slightly more localized within the six-membered rings. This is in accordance with the observation that the C(1),C(2) bond of 8b-azaacenaphthylenium ions do not show olefinic character, *i.e.*, they do not undergo [2 + 4] cycloadditions with, *e.g.*, 1,3-diphenylisobenzofuran, in contrast to the isoelectronic acenaphthylene [12].

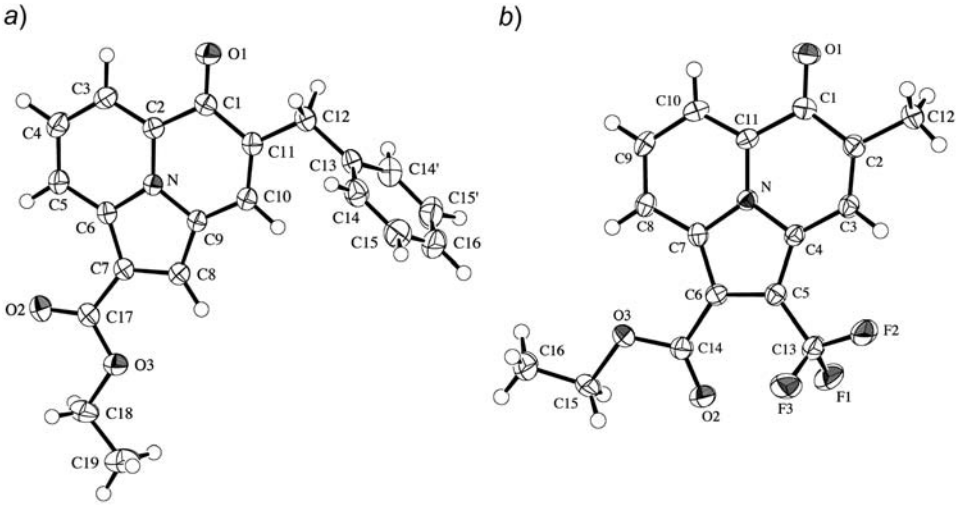


Fig. 2. *ORTEP Plots* [17] *of the molecular structures* a) *of* **19i** *and* b) *of* **19l** (50% probability ellipsoids; arbitrary numbering of the atoms)

Similar to **9a**, quinolizinium-1-olates **9b**–**9d** also reacted with **18c** in THF at room temperature to give the corresponding products **19** in a regioselective manner (*Table 3*). In contrast, the reactions of **9a** and **9b** with ethyl and methyl prop-2-ynoate (**18d** and **18e**, resp.) were sluggish at room temperature and, therefore, were carried out in boiling toluene. After 10–20 h, the corresponding products of type **19** were obtained in 27–29% yield, again as single regioisomers (*Table 3*).

Table 3. *Formation of Compounds* **19** via *[2+3] Cycloaddition Reaction of* **9** *with Unsymmetrical Acetylene Carboxylates* **18c**–**18f**

9	R	**18**	R^1	R^2	Procedure	**19**	Yield [%]
a	Bn	**c**	Et	CF_3	*A*[a])	**h**	43
		d	Et	H	*B*[b])	**i**	24
		e	Me	H	*B*	**j**	27
		f	Et	Me	*C*[c])	**k**	32
b	Me	**c**	Et	CF_3	*A*	**l**	41
		e	Me	H	*B*	**m**	29
		f	Et	Me	*C*	**n**	28
			Ac[d])	H	*C*	**o**	27
c	Me–CH=CH	**c**	Et	CF_3	*A*	**p**	33
d	i-Pr	**c**	Et	CF_3	*A*	**q**	36

[a]) Reaction in THF at room temperature. [b]) Reaction in boiling toluene. [c]) Reaction in toluene at 140° in a sealed tube. [d]) Ac instead of R^1O_2C in the formula **19h**–**19q** (*Scheme 7*); reaction with but-3-yn-2-one.

The product of the reaction of **9a** with **18d** was obtained as dark-yellow oil (27%), which crystallized as orange prisms after treatment with Et_2O. The most characteristic spectroscopic data were the IR absorption at 1577 cm^{-1} ($CHCl_3$), the ^{13}C-NMR signal

at 174.9 ppm, and the M^+ peak at *m/z* 331 in the EI-MS. The proposed structure **19i** was finally established by X-ray crystallography (*Fig. 2,a*). The molecule lies on a crystallographic mirror plane and is completely planar, except for the Ph ring, which is perpendicular to the mirror plane. The length of the C(1)–O bond is 1.241(2) Å, *i.e.*, in the same range as in the case of **19l**.

Even less reactive than **18d** and **18e** were ethyl but-2-ynoate (**18f**) and but-3-yn-2-one. In these cases, the reactions with **9a** and **9b** were performed in toluene in a sealed tube at 140°. After *ca.* 60 h, the expected products **19k**, **19n**, and **19o** were obtained in 27–31% yield (*Table 3*). Even under the most drastic conditions and with the most reactive acetylenes, no reaction of **9e** leading to products of type **19** could be observed, but decomposition occurred.

2.3. *Formation of Side Products.* In the reactions of quinolizinium-1-olates **9** with acetylenes described above, the formation of minor side products was observed, in addition to the desired compounds **19**. Therefore, some of the reactions were repeated aiming at the isolation and structure determination of some of the side products.

Repeated chromatography of the mixture of side products of the reaction of **9a** with **18a** in toluene (17 min reflux, 18 h at r.t.) furnished a pure substance as a yellow oil (*ca.* 8%). The CI-MS showed the $[M+1]^+$ peak at *m/z* 406, and both ^{1}H- and ^{13}C-NMR spectra indicated an adduct of **9a** and **18a**. Strong absorptions in the IR spectrum ($CHCl_3$) at 1753, 1714, and 1668 cm^{-1} evidenced the presence of three C=O groups, one of them exhibiting a ^{13}C-NMR signal at 194.4 ppm. In addition, the product was characterized by a UV absorption (EtOH) at 326 nm ($\log \varepsilon = 3.21$), typical for cyclohexa-2,4-dien-1-ones [19]. On the basis of these data, we proposed structure **20a** for this side product (*Scheme 8*)[7]). Analogous side products **20b**–**20d** were obtained from the reactions of **9a** with **18b** and **18d**, and of **9b** with **18b**. An additional side product, methyl 3-benzyl-2-hydroxy-6-(pyridin-2-yl)benzoate (**21**), could be isolated in the case of the reaction of **9a** with **18d**, whereas dimethyl 3-hydroxy-4-methylbenzene-1,2-dicarboxylate (**22**) was obtained from the reaction of **9b** and **18b**.

A mechanistic proposal for the formation of the identified side products is outlined in *Scheme 8*. The initial reaction step is a *Diels–Alder* addition to yield **I**, which undergoes a spontaneous rearrangement to give the cyclohexadienone **20**. In the case of $R^2 = H$, *i.e.*, the product of the reaction with methyl prop-2-ynoate, a second rearrangement could lead to 2-hydroxy-3-(pyridin-2-yl)benzoate **21**. The mechanism of the formation of **22** is not clear, and **I** as well as **20** may be the precursor. It is worth emphasizing that quinolizinium-1-olates **9** undergo [2+3] as well as [2+4] cycloadditions. There is only one other known example of a reaction occurring *via* similar dual pathways, which was described by *McEwen et al.* and by *Schmitt et al.* [20]. On treatment with HBF_4, the *Reissert* compound 2-benzoyl-1,2-dihydroisoquinoline-1-carbonitrile forms a reactive 1,3-oxazolium intermediate, which reacts with acetylenes and acrylates to give products *via* 1,3-dipolar cycloaddition and *Diels–Alder* reactions, respectively. On the other hand, [2+4] cycloadditions with aromatic *N*-heterocycles are well-known [21], including acridizinium salts [22] and a quinolizinium salt [23].

2.4. *Attempted 1,3-Dipolar Cycloadditions of* **9** *with Alkenes.* The attempted reaction of **9b** with electron-poor alkenes such as diethyl fumarate (**23a**), maleic

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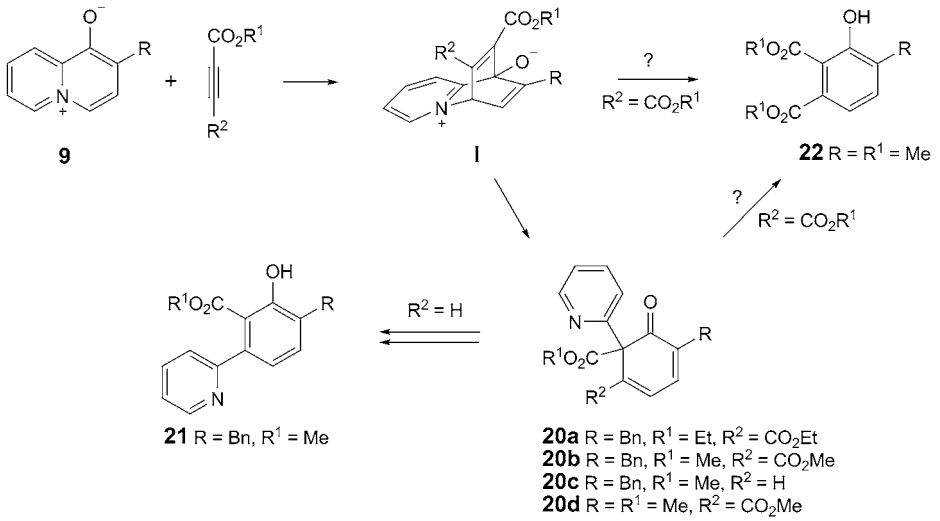
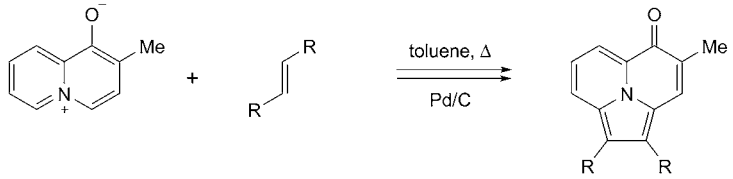
[7]) The same product **20a** was formed under the usual reaction conditions (THF, r.t.; TLC evidence).

Scheme 8



anhydride, *N*-phenylmaleimide, fumaronitrile (**23b**), *etc.*, in THF at room temperature failed. Even after several days, only starting materials could be detected (TLC). Heating of a mixture of **9b** and **23a** in toluene or mesitylene to reflux for some days led only to traces of product **19d**. The initially formed cycloadduct could not be detected. Therefore, mixtures of 1 equiv. of **9b**, 4 equiv. of **23a** or **23b**, and a small amount of Pd/C in toluene were heated to reflux for 4–5 d. After chromatographic workup, pyrrolo[2,1,5-*de*]quinolizinones **19d** and **19r**, respectively, were obtained in 8 and 14% yield (*Scheme 9*). With other C=C dipolarophiles, no analogous products were formed[8]).

Scheme 9



These results are in accordance with the observation of *Alvarez-Builla* and co-workers that only acetylenes undergo the 1,3-dipolar cycloaddition with quinolizinium-1-olates, but reactions with alkenes and isocyanates failed [11d]. In our hands, even thiobenzophenone and thiofluorenone, which are known as 'superdipolarophiles' [24], did not undergo the cycloaddition with **9**.

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[8]) At a higher temperature or after a longer reaction time, only decomposition of **9b** was observed.

3. Conclusions. – We reported on a new approach to mesoionic heterocycles of type **9**, *i.e.*, quinolizinium-1-olates, in reasonable yields, *via* a four-step synthesis with commercially available starting materials. The key intermediate, ketone **11**, was prepared *via* two different routes, both involving a *Grignard* reaction. The cyclization of the alkylated ketones **17** to give **9** was carried out under acidic conditions. In the case of the allyl derivative, a secondary isomerization was observed, whereas an unexpected cyclization occurred with the propargyl derivative.

The quinolizinium-1-olates **9** are stabilized, aromatic azomethine ylides, which reacted with electron-poor acetylenes to give '[2.3.3]cyclazin-5-ones' **19** in moderate yields as the result of a 1,3-dipolar cycloaddition, followed by a spontaneous dehydrogenation. Depending on the reactivity of the acetylene, the reaction was performed in THF at room temperature, in boiling toluene, or at higher temperature in a sealed tube. With unsymmetrical acetylenes as dipolarophiles, the cycloaddition occurred regioselectively, and only one regioisomer was obtained. Compared with the mesoionic 1,3-oxazol-5-ones ('Münchnones'), the reactivity of 2-alkylquinolizinium-1-olates **9** is much lower. In some cases, cyclohexa-2,4-dien-1-ones **20** and phenols **21** and **22** were isolated as minor products. Their formation was proposed to occur *via* a competitive [2 + 4] cycloaddition (*Diels–Alder* reaction) and subsequent rearrangements. The failure of the reactions with **9e** can be rationalized by steric hindrance of the cycloaddition step by the Me group at C(4) and by the impossibility of aromatization of the adduct.

The scope of the 1,3-dipolar cycloaddition of **9** is limited to reactions with acetylenes. With other dipolarophiles, such as electron-poor olefins or thioketones, no reaction was observed. Most likely, the aromatization of the initially formed cycloadducts to give '[2.3.3]cyclazin-5-ones' **19** is the driving force. Therefore, the reactions of **9** with fumaronitrile and ethyl fumarate as dipolarophiles, in the presence of Pd/C as dehydrating catalyst, led to the corresponding aromatized products, albeit in low yield.

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Experimental Part

1. *General*. TLC: *Merck 60 F_{254}* SiO_2-coated Al-plates, 0.2 mm; detection of the substances on the TLC plates under UV light (λ 254 nm) or with $KMnO_4$ soln. Prep. TLC: *Merck 60 F_{254}* SiO_2-coated glass-plates, 2 mm. Column chromatography (CC): *Merck* 60 SiO_2, 0.040–0.63 mm. M.p.: *Mettler-FP-5* instrument; uncorrected. UV/VIS Spectra: *Uvikon* instrument; in MeOH; λ_{max} in nm (log ε). IR Spectra: *Perkin–Elmer-1600* FT-IR spectrophotometer; in $CHCl_3$; cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker-AC-300* or *Bruker-ARX-300* instrument (at 300 and 75.5 MHz, resp.) or *Bruker-AMX 600* instrument (at 600 and 150 MHz, resp.), in $CDCl_3$; multiplicity of C-atoms from DEPT spectra; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. MS: *Finnigan MAT-90* (EI, 70 eV) or CI (NH_3 or isobutene)), *Finnigan SSQ-700* (EI and CI), or *Finnigan TSQ-700* (ESI) instrument; in *m*/*z* (rel. %). Elemental analyses were performed by the Mikroanalytisches Laboratorium des Organisch-chemischen Instituts der Universität Zürich (*Elementar Vario EL* instrument).

2. *Starting Materials.* All chemicals were commercially available (*Fluka*, *Aldrich*, and *Merck*). Solvents were purified as follows: hexane by distillation from CaH_2; AcOEt and CH_2Cl_2 by distillation from K_2CO_3 and storing over molecular sieves (4 Å); THF (*purum*, *Fluka*) and Et_2O, dried over Na and distilled; toluene (*p.a.*, *Merck*), stored over Na; MeOH (*p.a.*, *Merck*) and AcOH (*p.a.*, *Merck*) were directly used.

3. *Synthesis of 2-Alkylquinolizinium-1-olates* **9**. 3.1. *Synthesis of 3-(1,3-Dioxolan-2-yl)-1-(pyridin-2-yl)propan-1-one* (**11**). *Route A: 3-(1,3-Dioxolan-2-yl)-1-(pyridin-2-yl)propan-1-ol* (**14**). In a three-necked flask flushed with Ar and equipped with thermometer, mechanical stirrer, and dropping funnel, Mg pieces (2.34 g, 0.10 mol), THF (5 ml), an I_2 crystal, and 2-(2-bromoethyl)-1,3-dioxolane (2 ml) were mixed and intensively stirred. When the reaction started, the mixture was cooled to 10°, and a soln. of 2-(2-bromoethyl)-1,3-dioxolane (12 ml, 0.10 mmol) in 100 ml of dry THF was added dropwise, while keeping the temp. at 10°. After stirring for another 0.5 h, a soln. of *pyridine-2-carbaldehyde* (**12**; 10.5 ml, 0.11 mol) in THF (100 ml) was added within 0.5 h. Then, the temp. was allowed to increase to r.t., and the mixture was stirred for 19 h. The mixture was cooled with ice, hydrolyzed by addition of 20% aq. NH_4Cl soln. (100 ml), and extracted with Et_2O. The org. phase was washed with H_2O (200 ml) and brine (100 ml), dried ($MgSO_4$), and the solvent was evaporated. The crude product was purified by CC (AcOEt) to give **14** (6.02 g, 29%). Yellow oil. IR (film): 3370*w* (br.), 2947*m*, 2912*m*, 2871*m*, 1590*m*, 1568*m*, 1470*m*, 1406*m*, 1431*m*, 1305*w*, 1211*w*, 1179*w*, 1135*s*, 1105*m*, 1068*m*, 1027*s*, 997*m*, 970*m*, 941*m*, 748*m*, 703*w*. ^{1}H-NMR: 8.53 (*d*, *J* = 4.8, H–C(6) (Py)); 7.68 (*td*, *J* = 7.7, 1.7, H–C(4) (Py)); 7.30 (*d*, *J* = 7.8, H–C(3) (Py)); 7.19 (*dd*, *J* = 7.4, 5.0, H–C(5) (Py)); 4.91 (*t*, *J* = 4.4, OCHO); 4.80 (*t*, *J* = 7.0, H–C(1)); 4.38 (br. *s*, OH); 3.82–3.99 (*m*, OCH_2CH_2O); 1.97–2.04, 1.75–1.88 (2*m*, 2 CH_2). ^{13}C-NMR: 162.1 (*s*, C(2) (Py)); 148.2 (*d*, C(6) (Py)); 136.6 (*d*, C(4) (Py)); 122.2 (*d*, C(3) (Py)); 120.3 (*d*, C(5) (Py)); 104.3 (*d*, OCHO); 72.5 (*d*, C(1)), 64.9, 64.8 (2*t*, OCH_2CH_2O); 32.4, 29.5 (2*t*, 2 CH_2). CI-MS: 211 (11), 210 (100, $[M+1]^+$), 166 (5).

3-(1,3-Dioxolan-2-yl)-1-(pyridin-2-yl)propan-1-one (**11**) [15]. To a soln. of **14** (6.0 g, 29 mmol) in THF (70 ml) was added MnO_2 (36 g, 414 mmol), and the mixture was heated to reflux for 2 h. After cooling to r.t., filtration through *Celite* (Et_2O, 50 ml), and evaporation of the solvent, the product crystallized and was dried (h.v.): **11** (4.89 g, 82%). Pale yellow crystals. M.p. 65.9–66°. IR (KBr): 3062*w*, 2960*m*, 2939*m*, 2873*m*, 1690*s*, 1608*w*, 1580*s*, 1569*m*, 1480*w*, 1462*m*, 1439*s*, 1411*s*, 1397*s*, 1368*s*, 1354*s*, 1314*w*, 1299*m*, 1282*s*, 1247*m*, 1225*m*, 1203*m*, 1175*m*, 1131*s*, 1059*s*, 1022*s*, 987*s*, 958*s*, 931*s*, 881*s*, 808*m*, 789*m*, 760*s*, 704*w*, 663*m*, 612*s*. ^{1}H-NMR: 8.68 (*d*, *J* = 4.8, H–C(6) (Py)); 8.03 (*d*, *J* = 7.6, H–C(3) (Py)); 7.83 (*td*, *J* = 7.6, 1.4, H–C(4) (Py)); 7.46 (*dd*, *J* = 7.4, 5.2, H–C(5) (Py)); 5.03 (*t*, *J* = 4.3, OCHO); 4.00–3.80 (*m*, OCH_2CH_2O); 3.37 (*t*, *J* = 7.3, CH_2); 2.20–2.10 (*m*, CH_2). ^{13}C-NMR: 201.1 (*s*, C=O); 153.4 (*s*, C(2) (Py)); 148.9 (*d*, C(6) (Py)); 136.8 (*d*, C(4) (Py)); 126.9 (*d*, C(5) (Py)); 121.7 (*d*, C(3) (Py)); 103.6 (*d*, OCHO); 65.0 (*t*, OCH_2CH_2O); 31.9, 28.0 (2*t*, 2 CH_2). CI-MS: 209 (11), 208 (100, $[M+1]^+$). Anal. calc. for $C_{11}H_{13}NO_3$ (207.22): C 63.75, H 6.32, N 6.76; found: C 64.02, H 6.56, N 6.79.

Route B: N-*Methoxy*-N-*methylpyridine-2-carboxamide* (**16**). To a suspension of *pyridine-2-carboxylic acid* (**15**; 30.78 g, 0.25 mol) in CH_2Cl_2 (100 ml) at 0°, *N*-methylmorpholine (100 ml, 0.50 mol) was added dropwise. Then, the clear soln. was cooled to −10°, and isobutyl chloroformate (32.75 ml (0.25 mol) was added slowly, the mixture stirred for 0.5 h, and the precipitate was filtered off. In another flask, *N*,*O*-dimethylhydroxylamine hydrochloride (24.38 g, 0.25 mol) was suspended in CH_2Cl_2 (100 ml), Et_3N (40 ml, 0.5 mol) was added, and the formed $Et_3N \cdot HCl$ was filtered off. The soln. of the amine was added dropwise to the soln. of the mixed anhydride at −10°, and the mixture was stirred until no amine was left (TLC). The mixture was washed with 5% aq. Na_2CO_3 (3 × 100 ml) and brine (100 ml), and the org. phase was dried ($MgSO_4$). The crude product was distilled (bulb-to-bulb) to give **16** (31.87 g, 75%). Colorless oil. IR (film): 2936*m*, 1658*s*, 1586*s*, 1567*s*, 1439*s*, 1415*s*, 1384*s*, 1288*m*, 1226*m*, 1150*m*, 1073*m*, 1045*m*, 995*s*, 883*w*, 805*m*, 750*s*, 709*m*. ^{1}H-NMR: 8.62 (*d*, *J* = 4.8, 1 arom. H); 7.85–7.75 (*m*, 1 arom. H); 7.65 (br. *s*, 1 arom. H); 7.40–7.30 (*m*, 1 arom. H); 3.75 (br. *s*, MeO); 3.41 (br. *s*, MeN). ^{13}C-NMR: 153.0 (*s*, C(2) (Py)); 148.3 (*d*, C(6) (Py)); 136.6 (*d*, C(4) (Py)); 124.7 (*d*, C(5) (Py)); 123.1 (*d*, C(3) (Py)); 61.3 (*q*, MeO); 33.7 (br. *q*, MeN). CI-MS: 167 (100, $[M+1]^+$), 135 (20).

3-(1,3-Dioxolan-2-yl)-1-(pyridin-2-yl)propan-1-one (**11**). A soln. of **16** (16.6 g, 0.10 mol) in dry THF (120 ml) was cooled to −5°, and 1.5 equiv. of the *Grignard* reagent **13** were added dropwise. After complete addition, the mixture was stirred for 2 h at 0° and then hydrolyzed by addition of 3% HCl in EtOH (100 ml) at 0°. The mixture was poured into a mixture of brine and Et_2O/CH_2Cl_2 (1:1), the org. phase was separated and dried ($MgSO_4$), and the solvent was evaporated to give **11** (16.35 g, 79%).

3.2. *Alkylation of* **11** *to 2-Alkyl-3-(1,3-dioxolan-2-yl)-1-(pyridin-2-yl)propan-1-ones* **17**. *2-Benzyl-3-(1,3-dioxolan-2-yl)-1-(pyridin-2-yl)propan-1-one* (**17a**). A soln. of LDA (37 ml, 1.5M, 56 mmol) in dry THF (150 ml) was cooled to −78°, and a mixture of **11** (4.87 g, 23.5 mmol), dissolved in 1,3-

dimethyltetrahydropyrimidin-2(1*H*)-one (DMPU; 48.7 ml) was added, keeping the temp. below $-55°$. The mixture was stirred for 2–3 h, and a soln. of BnBr (3 ml, 17.8 mmol) in THF (40 ml) was added. The mixture was allowed to reach r.t. slowly and was stirred for 40 h. Then, H_2O (10 ml) was added, and the mixture was poured into ice water, extracted with Et_2O (3×100 ml), dried ($MgSO_4$), and evaporated. The crude product was separated by CC (hexane/AcOEt 4:1) to afford **17a** (4.4 g, 64%). Brownish oil. IR (film): 3055*w*, 3021*w*, 2920*m*, 2880*m*, 1690*s*, 1599*w*, 1580*m*, 1563*w*, 1491*w*, 1450*m*, 1432*m*, 1366*m*, 1227*m*, 1135*s*, 1024*m*, 992*s*, 975*s*, 943*m*, 877*w*, 850*w*, 793*m*, 746*s*, 698*s*, 616*s*. ^{1}H-NMR: 8.65 (*d*, $J = 4.7$, H–C(6) (Py)); 8.00 (*d*, $J = 7.6$, H–C(3) (Py)); 7.76 (*td*, $J = 7.6$, 1.5, H–C(4) (Py)); 7.35 (*ddd*, $J = 7.4$, 4.5, 1.2, H–C(5) (Py)); 7.30–7.00 (*m*, 5 arom. H); 4.87 (*t*, $J = 4.3$, OCHO); 4.75–4.60 (*m*, H–C(2)); 3.90–3.51 (*m*, OCH_2CH_2O); 3.10 (*dd*, $J = 13.6$, 6.6, 1 H, PhCH_2); 2.75 (*dd*, $J = 13.6$, 8.2, 1 H, PhCH_2); 2.35 (*ddd*, $J = 14.2$, 9.8, 4.4, 1 H–C(3)); 1.90 (*dt*, $J = 14.0$, 3.9, 1 H–C(3)). ^{13}C-NMR: 203.7 (*s*, C=O); 153.3 (*s*, C(2) (Py)); 148.8 (*d*, C(6) (Py)); 139.3 (*s*, C(1) (Ph)); 136.7 (*d*, C(4) (Py)); 129.2, 128.2 (2*d*, 4 arom. CH); 126.7 (*d*, C(5) (Py)); 126.1 (*d*, 1 arom. CH); 122.3 (*d*, C(3) (Py)); 103.0 (*d*, OCHO); 64.8, 64.6 (2*t*, OCH_2CH_2O); 40.9 (*d*, C(2)); 38.4 (*t*, PhCH_2); 34.9 (*t*, C(3)). CI-MS: 299 (15), 298 (100, $[M+1]^+$). Anal. calc. for $C_{18}H_{19}NO_3$ (297.34): C 72.71, H 6.44, N 4.71; found: C 72.68, H 6.59, N 4.88.

3-(1,3-Dioxolan-2-yl)-2-methyl-1-(pyridin-2-yl)propan-1-one (**17b**). As described for **17a**: LDA (56 ml, 2M, 112 mmol) in THF (150 ml), **11** (9.74 g, 47 mmol) in DMPU (97.4 ml), MeI (24 ml, 400 mmol) in THF (60 ml); 20 h. Yield: 5.70 g (55%). Brownish oil. IR (film): 3054*w*, 2969*m*, 2880*m*, 1697*s*, 1582*m*, 1568*m*, 1459*m*, 1435*m*, 1353*m*, 1266*m*, 1228*m*, 1143*s*, 1029*s*, 984*s*, 809*m*, 748*m*, 701*m*, 664*w*. ^{1}H-NMR: 8.69 (*d*, $J = 4.2$, H–C(6) (Py)); 8.05 (*d*, $J = 7.5$, H–C(3) (Py)); 7.83 (*td*, $J = 7.6$, 1.5, H–C(4) (Py)); 7.45 (*ddd*, $J = 7.6$, 4.5, 1.3, H–C(5) (Py)); 4.95 (*t*, $J = 4.9$, OCHO); 4.40–4.30 (*m*, H–C(2)); 4.00–3.70 (*m*, OCH_2CH_2O); 2.36 (*ddd*, $J = 14.0$, 9.4, 4.6, 1 H–C(3)); 1.96 (*dt*, $J = 14.0$, 4.6, 1 H–C(3)); 1.24 (*d*, $J = 6.9$, Me). ^{13}C-NMR: 204.5 (*s*, C=O); 152.9 (*s*, C(2) (Py)); 148.8 (*d*, C(6) (Py)); 136.7 (*d*, C(4) (Py)); 126.7 (*d*, C(5) (Py)); 122.3 (*d*, C(3) (Py)); 103.0 (*d*, OCHO); 64.7, 64.6 (2*t*, OCH_2CH_2O); 36.9 (*t*, C(3)); 34.3 (*d*, C(2)); 17.8 (*q*, Me). CI-MS: 223 (12), 222 (100, $[M+1]^+$), 208 (5). Anal. calc. for $C_{12}H_{15}NO_3$ (221.26): C 65.14, H 6.83; found: C 65.46, H 6.83.

2-[(1,3-Dioxolan-2-yl)methyl]-1-(pyridin-2-yl)pent-4-en-1-one (**17c**). As described for **17a**: LDA (28 ml, 2M, 56 mmol) in THF (100 ml), **11** (4.87 g, 23.5 mmol) in DMPU (48.7 ml), allyl bromide (10 ml, 100 mmol) in THF (40 ml); 25 h. Yield: 3.71 g (64%). Brown oil. IR (film): 2943*m*, 1668*s*, 1495*s*, 1446*s*, 1375*s*, 1285*s*, 1214*m*, 1132*s*, 1084*m*, 995*m*, 759*m*, 665*w*. ^{1}H-NMR: 8.69 (*d*, $J = 3.7$, H–C(6) (Py)); 8.04 (*d*, $J = 7.2$, H–C(3) (Py)); 7.82 (*td*, $J = 7.6$, 1.5, H–C(4) (Py)); 7.45 (*ddd*, $J = 7.5$, 4.5, 1.3, H–C(5) (Py)); 5.83–5.60 (*m*, CH_2=C*H*); 5.04, 4.99 (2*d*, $J = 1.5$, CH_2=CH); 4.92 (*t*, $J = 4.4$, OCHO); 4.50–4.40 (*m*, H–C(2)); 3.90–3.60 (*m*, OCH_2CH_2O); 2.57–2.47 (*m*, 1 H, CH_2=CH–CH_2); 2.40–2.16 (*m*, 1 H, CH_2=CH–CH_2), 1 H–C(3)); 1.94 (*dt*, $J = 14.0$, 4.0, 1 H–C(3)). ^{13}C-NMR: 203.7 (*s*, C=O); 153.4 (*s*, C(2) (Py)); 148.8 (*d*, C(6) (Py)); 136.8 (*d*, C(4) (Py)); 135.5 (*d*, CH_2=*C*H); 126.8 (*d*, C(5) (Py)); 122.3 (*d*, C(3) (Py)); 116.9 (*t*, *C*H_2=CH); 103.0 (*d*, OCHO); 64.9, 64.7 (2*t*, OCH_2CH_2O); 38.7 (*d*, C(2)); 36.8 (*t*, CH_2=CH–*C*H_2); 35.0 (*t*, C(3)). CI-MS: 249 (59), 248 (100, $[M+1]^+$), 208 (22), 129 (23). Anal. calc. for $C_{14}H_{17}NO_3$ (247.29): C 68.00, H 6.93, N 5.66; found: C 68.29, H 7.06, N 5.73.

2-[(1,3-Dioxolan-2-yl)methyl]-3-methyl-1-(pyridin-2-yl)butan-1-one (**17d**). As described for **17a**: LDA (28 ml, 2M, 56 mmol) in THF (100 ml), **11** (4.87 g, 23.5 mmol) in DMPU (48.7 ml), i-PrI (15 ml, 150 mmol) in THF (40 ml); 42 h. Yield: 1.04 g (18%). Brownish oil. IR (Film): 3054*w*, 2962*s*, 2876*s*, 1732*m*, 1693*s*, 1582*s*, 1568*m*, 1465*s*, 1435*s*, 1388*s*, 1371*s*, 1223*s*, 1140*s*, 1045*s*, 994*s*, 979*s*, 871*m*, 789*m*, 694*m*, 676*m*. ^{1}H-NMR: 8.69 (*d*, $J = 4.4$, H–C(6) (Py)); 8.06 (*d*, $J = 7.7$, H–C(3) (Py)); 7.82 (*td*, $J = 7.6$, 1.5, H–C(4) (Py)); 7.42 (*ddd*, $J = 7.5$, 4.5, 1.3, H–C(5) (Py)); 4.88 (*t*, $J = 4.1$, OCHO); 4.28–4.20 (*m*, H–C(2)); 3.70–3.50 (*m*, OCH_2CH_2O); 2.40 (*ddd*, $J = 13.9$, 11.3, 4.0, 1 H–C(3)); 2.04 (*sept.*, $J = 6.7$, Me_2CH); 1.90 (*dt*, $J = 13.8$, 3.8, 1 H–C(3)); 0.95, 0.89 (2*d*, $J = 6.8$, Me_2CH). ^{13}C-NMR: 204.4 (*s*, C=O); 154.1 (*s*, C(2) (Py)); 148.8 (*d*, C(6) (Py)); 136.8 (*d*, C(4) (Py)); 126.5 (*d*, C(5) (Py)); 122.2 (*d*, C(3) (Py)); 103.4 (*d*, OCHO); 64.9, 64.7 (2*t*, OCH_2CH_2O); 44.3 (*d*, C(2)); 32.4 (*t*, C(3)); 30.5 (*d*, Me_2CH); 20.9, 19.3 (2*q*, Me_2CH). CI-MS: 251 (19), 250 (100, $[M+1]^+$). Anal. calc. for $C_{14}H_{19}NO_3$ (249.31): C 67.45, H 7.68, N 5.62; found: C 67.81, H 7.60, N 5.49.

2-[(1,3-Dioxolan-2-yl)methyl]-1-(pyridin-2-yl)pent-4-yn-1-one (**17e**). As described for **17a**: LDA (12 ml, 2M, 24 mmol) in THF (100 ml), **11** (2.0 g, 10 mmol) in DMPU (20 ml), propargyl bromide (7.4 ml, 11.4 mmol) in THF (25 ml); 20 h. Yield: 1.50 g (64%). Brown oil. IR (Film): 3280*m*, 3054*w*, 2887*m*,

2117*w*, 1697*s*, 1583*s*, 1568*m*, 1465*m*, 1436*s*, 1368*s*, 1269*m*, 1221*m*, 1140*s*, 1025*s*, 995*s*, 981*s*, 945*m*, 803*m*, 746*m*. ^{1}H-NMR: 8.68 (*d*, *J* = 4.8, H–C(6) (Py)); 8.06 (*d*, *J* = 7.8, H–C(3) (Py)); 7.84 (*td*, *J* = 7.7, 1.8, H–C(4) (Py)); 7.46 (*ddd*, *J* = 7.5, 4.8, 1.3, H–C(5) (Py)); 4.97 (*t*, *J* = 4.2, OCHO); 4.51–4.43 (*m*, H–C(2)); 3.90–3.65 (*m*, OCH_2CH_2O); 2.70–2.58 (*m*, $CH{\equiv}C{-}CH_2$); 2.41 (*ddd*, *J* = 14.3, 8.9, 4.3, 1 H–C(3)); 2.14 (*dt*, *J* = 14.3, 4.5, 1 H–C(3)); 1.95 (*t*, *J* = 2.7, CH≡). ^{13}C-NMR: 201.8 (*s*, C=O); 152.8 (*s*, C(2) (Py)); 148.7 (*d*, C(6) (Py)); 136.8 (*d*, C(4) Py); 126.8 (*d*, C(5) (Py)); 122.3 (*d*, C(3) (Py)); 102.7 (*d*, OCHO); 81.5 (*s*, CH≡*C*); 70.0 (*d*, *C*H≡C); 64.8, 64.5 (2*t*, OCH_2CH_2O); 38.7 (*d*, C(2)); 33.9 (*t*, C(3)); 21.2 (*t*, CH≡C–*C*H_2). CI-MS: 247 (14), 246 (100, $[M+1]^+$), 208 (7), 168 (6), 140 (20), 136 (7). Anal. calc. for $C_{14}H_{15}NO_3$ (245.28): C 68.56, H 6.16, N 5.71; found: C 68.33, H 6.16, N 5.52.

3.3. *Cyclization of* **17** *to 2-Alkylquinolizinium-1-olates* **9**. *2-Benzylquinolizinium-1-olate* (**9a**). A soln. of **17a** (4.40 g, 14.8 mmol) in glacial AcOH (130 ml) was heated to reflux for 12 h. The excess AcOH was removed by azeotropic distillation with EtOH, the residue was purified by CC (CH_2Cl_2/MeOH 12:1), and the product was dried (h.v., 80°) to give **9a** (3.01 g, 87%). Yellow powder. Recrystallization from EtOH/Et_2O gave yellow crystals. M.p.159–160°. UV (MeOH): 393 (3.65). IR ($CHCl_3$): 2960*m*, 1551*s*, 1512*m*, 1477*s*, 1462*s*, 1420*w*, 1356*w*, 1331*m*, 1310*w*, 1260*w*, 1187*w*, 1160*w*, 1136*w*, 1097*w*, 1026*w*, 698*w*, 659*w*. ^{1}H-NMR: 8.73 (*d*, *J* = 8.7, 1 arom. H); 8.22 (*d*, *J* = 6.8, 1 arom. H); 7.54 (*d*, *J* = 6.3, 1 arom. H); 7.40–7.16 (*m*, 7 arom. H); 7.12 (*d*, *J* = 6.3, 1 arom. H); 4.17 (*s*, Ph*C*H_2). ^{13}C-NMR: 164.1 (*s*, C(1)); 140.2, 138.1, 134.5 (3*s*, C(2), C(9a), C(1) Ph); 131.8, 129.4, 128.5, 126.2, 126.1, 125.5, 125.4, 121.4, 114.3 (9*d*, C(3)–C(9), 5 CH Ph); 36.1 (*t*, Ph*C*H_2). CI-MS: 237 (19), 236 (100, $[M+1]^+$). Anal. calc. for $C_{16}H_{13}NO$ (235.27): C 81.68, H 5.57, N 5.59; found: C 81.35, H 5.51, N 5.81.

Suitable crystals of **9a** for the X-ray crystal-structure determination were obtained by crystallization from THF/hexane.

2-Methylquinolizinium-1-olate (**9b**). As described for **9a**: **17b** (5.70 g, 25.7 mmol) in glacial AcOH (140 ml); 10 h. Yield: 3.54 g (86%). Yellow crystals. M.p. 149–150° (EtOH/Et_2O). UV (MeOH): 361 (3.86). IR ($CHCl_3$): 2966*w*, 2476*w*, 1763*w*, 1601*w*, 1555*s*, 1516*m*, 1478*s*, 1464*s*, 1417*m*, 1376*m*, 1349*m*, 1322*s*, 1269*m*, 1160*m*, 1141*w*, 1099*w*, 1050*w*, 1026*w*, 932*w*, 881*w*, 658*m*. ^{1}H-NMR: 8.69 (*d*, *J* = 8.7, 1 arom. H); 8.13 (*d*, *J* = 6.8, 1 arom. H); 7.48 (*d*, *J* = 6.1, 1 arom. H); 7.40–7.20 (*m*, 3 arom. H); 2.39 (*s*, Me). ^{13}C-NMR: 165.4 (*s*, C(1)); 132.1, 131.4 (2*s*, C(2), C(9a)); 126.4, 125.6, 125.4, 121.1, 113.4 (5*d*, C(3)–C(9)); 17.2 (*q*, Me). ESI-MS: 181 (20), 160 (100, $[M+1]^+$).

2-(Prop-1-en-1-yl)quinolizinium-1-olate (**9c**). As described for **9a**: **17c** (4.80 g, 19.4 mmol) in glacial AcOH (140 ml); 12 h. Yield: 2.50 g (69%). Yellow crystals. M.p. 129–130° (EtOH/Et_2O). UV (MeOH): 416 (4.05). IR ($CHCl_3$): 2964*m*, 1760*w*, 1549*s*, 1409*m*, 1470*s*, 1456*s*, 1422*m*, 1358*m*, 1328*s*, 1261*s*, 1139*m*, 1099*m*, 1026*m*, 813*m*, 658*m*. ^{1}H-NMR: 8.68 (*d*, *J* = 8.7, 1 arom. H); 8.18 (*d*, *J* = 6.8, 1 arom. H); 7.47 (*d*, *J* = 6.5, 1 arom. H); 7.40–7.15 (*m*, 3 arom. H); 6.95–6.73 (*m*, CH=CH); 1.94 (*d*, *J* = 5.4, Me). ^{13}C-NMR: 163.4 (*s*, C(1)); 139.1, 128.3 (2*s*, C(2), C(9a)); 132.0, 128.7, 126.6, 126.3, 125.4, 122.0, 120.9, 114.0 (8*d*, C(3)–C(9), CH=CH); 19.2 (*q*, Me). CI-MS: 186 (100, $[M+1]^+$), 170 (7).

2-(1-Methylethyl)quinolizinium-1-olate (**9d**). As described for **9a**: **17d** (1.0 g, 4.0 mmol) in glacial AcOH (75 ml); 12 h. Yield: 0.52 g (70%). Yellow crystals. M.p. 139–140° (EtOH/Et_2O). IR ($CHCl_3$): 2965*m*, 2872*m*, 2479*w*, 2361*w*, 1764*s*, 1639*m*, 1548*s*, 1512*m*, 1457*s*, 1421*s*, 1368*s*, 1337*s*, 1308*s*, 1288*m*, 1262*s*, 1164*s*, 1099*s*, 1014*s*, 924*m*, 894*m*, 867*m*, 806*s*, 658*m*, 629*m*. ^{1}H-NMR: 8.75 (*d*, *J* = 8.7, 1 arom. H); 8.11 (*d*, *J* = 6.8, 1 arom. H); 7.51 (*d*, *J* = 8.7, 1 arom. H); 7.4–7.3 (*m*, 2 arom. H); 7.25–7.20 (*m*, 1 arom. H); 3.68 (*sept.*, *J* = 6.9, Me_2CH); 1.27 (*d*, *J* = 6.9, *Me*$_2$CH). ^{13}C-NMR: 162.8 (*s*, C(1)); 141.7, 137.5 (2*s*, C(2), C(9a)); 131.9, 126.3, 125.1, 124.3, 121.1, 115.5 (6*d*, C(3)–C(9)); 26.7 (*d*, Me_2CH); 21.7 (*q*, *Me*$_2$CH). CI-MS: 189 (13), 188 (100, $[M+1]^+$).

2-[(1,3-Dioxolan-2-yl)methyl]-4-methylquinolizinium-1-olate (**9e**). As described for **9a**: **17e** (1.5 g, 6.1 mmol) in glacial AcOH (80 ml), 2.5 h. Yield: 0.30 g (21%). Yellow powder. IR ($CHCl_3$): 2963*m*, 1691*w*, 1612*w*, 1551*s*, 1508*w*, 1476*m*, 1448*m*, 1415*m*, 1327*w*, 1307*w*, 1261*s*, 1099*s*, 1013*s*, 806*s*, 658*w*. ^{1}H-NMR: 8.83–8.79 (*m*, 1 arom. H); 8.21–8.18 (*m*, 1 arom. H); 7.50–7.42 (*m*, 2 arom. H); 7.41 (*s*, H–C(3)); 5.31 (*t*, *J* = 5.2, OCHO); 4.10–3.70 (*m*, OCH_2CH_2O); 3.18 (*d*, *J* = 5.2, CH_2); 2.63 (*s*, Me). ^{13}C-NMR: 163.6 (*s*, C(1)); 138.3, 129.1 (2*s*, C(2), C(9a)); 128.8, 127.5, 125.6, 125.3, 121.9 (5*d*, C(3), C(6)–C(9)); 120.1 (*s*, C(4)); 102.4 (*d*, OCHO); 64.7, 64.5 (2*t*, OCH_2CH_2O); 35.1 (*t*, CH_2); 19.3 (*q*, Me). CI-MS: 278 (9), 262 (38, $[M+NH_3]^+$), 247 (14), 246 (100, $[M+1]^+$).

Quinolizinium-1-olate (**9f**) [11b]. As described for **9a**:**11** (1.0 g, 4.8 mmol) in glacial AcOH (75 ml); 40 h. Yield: 70 mg (10%). Brownish powder. M.p. 183–184°. IR ($CHCl_3$): 2924*m*, 2852*m*, 1568*s*, 1500*m*, 1471*m*, 1448*m*, 1453*m*, 1352*w*, 1310*w*, 1162*w*, 899*w*, 700*w*, 658*w*. ^{1}H-NMR: 8.69 (*d*, *J* = 8.6, 1 arom. H); 8.14 (*d*, *J* = 6.8, 1 arom. H); 7.39–7.44 (*m*, 2 arom. H); 7.29–7.33 (*m*, 2 arom. H); 6.96 (*d*, *J* = 8.7, 1 arom. H). ^{13}C-NMR: 163.9 (*s*, C(1)); 136.9 (*s*, C(9a)); 133.0, 128.1, 125.7, 124.4, 122.2, 118.9, 116.3 (7*d*, C(2)–C(9)). CI-MS: 147 (8), 146 (100, $[M+1]^+$).

4. *[2 + 3] Cycloadditions of* **9** *with Acetylenes. General Procedures. General Procedure 1* (*GP 1*). To a soln. of 1 equiv. of **9** in abs. THF (10 ml) under N_2, the respective acetylene derivative **18** (2 equiv.) was added, and the mixture was stirred at r.t., until **9** was consumed (TLC). The crude products were purified by CC (hexane/AcOEt 4:1 or 2:1) and, if necessary, followed by prep. TLC (hexane/AcOEt 1:1).

General Procedure 2 (*GP 2*). In toluene (10 ml) under N_2, 1 equiv. of **9** was suspended (sonification), and the respective acetylene **18** (2 equiv.) was added at r.t. Then, the mixture was heated to reflux, until **9** was consumed. The crude products were purified by CC (hexane/AcOEt 4:1 or 2:1) and, if necessary, followed by prep. TLC (hexane/AcOEt 1:1).

General Procedure 3 (*GP 3*). A mixture of **9** (1 equiv.), **18** (2 equiv.), and toluene (3–5 ml) in an evacuated and sealed tube was heated to 140° for 50–60 h. The crude products were purified by CC (hexane/AcOEt 4:1 or 2:1) and, if necessary, followed by prep. TLC (hexane/AcOEt 1:1).

4-Benzyl-1,2-bis(ethoxycarbonyl)-8b-azaacenaphthylenium-5-olate (=*1,2-Bis(ethoxycarbonyl)-4-(phenylmethyl)pyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19a**). According to *GP 1:* **9a** (120 mg, 0.51 mmol) and *diethyl acetylenedicarboxylate* (**18a**; 176 mg, 1.03 mmol). Yield: 76 mg (36%). Orange oil. IR ($CHCl_3$): 3001*m*, 2925*m*, 2854*w*, 1725*s*, 1710*s*, 1633*m*, 1582*s*, 1498*m*, 1474*s*, 1408*m*, 1383*m*, 1304*s*, 1273*s*, 1239*s*, 1215*s*, 1182*m*, 1143*m*, 1082*s*, 1051*w*, 1022*m*, 856*w*, 810*w*, 699*w*. ^{1}H-NMR: 8.76 (*d*, *J* = 8.6, H–C(6/8)); 8.55 (*d*, *J* = 7.6, H–C(8/6)); 7.93 (*s*, H–C(3)); 7.86 (*t*, *J* = 8.1, H–C(7)); 7.16–7.28 (*m*, 5 arom. H); 4.43–4.34 (*m*, 2 Me*CH*$_2$O); 4.05 (*s*, Ph*CH*$_2$); 1.37, 1.27 (2*t*, *J* = 7.1, 2 *Me*CH$_2$O). ^{13}C-NMR: 175.2 (*s*, C(5)); 163.5, 163.0 (2*s*, 2 EtO*CO*); 139.0, 138.6, 136.0, 132.0 (4*s*, C(4), C(5a), C(8a), C(1) Ph); 129.4, 128.7, 127.4, 126.6, 126.5, 124.6, 119.2 (7*d*, C(3), C(6), C(7), C(8), 5 CH (Ph)); 124.9, 119.8, 111.0 (3*s*, C(1), C(2), C(2a)); 62.0, 61.1 (2*t*, 2 Me*C*H$_2$O); 36.2 (*t*, Ph*C*H$_2$); 14.3, 14.1 (2*q*, 2 *Me*CH$_2$O). CI-MS: 405 (24), 404 (100, $[M+1]^+$), 298 (21).

4-Benzyl-1,2-bis(methoxycarbonyl)-8b-azaacenaphthylenium-5-olate (=*1,2-Bis(methoxycarbonyl)-4-(phenylmethyl)pyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19b**). According to *GP 1:* **9a** (120 mg, 0.51 mmol) and **18b** (150 mg, 1.06 mmol). Yield: 96 mg (40%). Orange powder. M.p. 169–170°. UV (MeOH): 473 (4.01). IR ($CHCl_3$): 3000*w*, 2954*w*, 1713*s*, 1636*w*, 1584*s*, 1499*m*, 1473*m*, 1442*m*, 1396*w*, 1307*s*, 1274*s*, 1240*s*, 1216*s*, 1177*m*, 1143*m*, 1087*s*, 1052*w*, 1000*w*, 940, 809*w*, 700*w*. ^{1}H-NMR: 8.79 (*d*, *J* = 8.3, H–C(6/8)); 8.59 (*d*, *J* = 7.5, H–C(8/6)); 8.05 (*s*, H–C(3)); 7.91 (*t*, *J* = 8.2, H–C(7)); 7.37–7.23 (*m*, 5 arom. H); 4.11 (*s*, Ph*CH*$_2$); 4.00 (*s*, 2 MeO). ^{13}C-NMR: 175.2 (*s*, C(5)); 164.0, 163.4 (2*s*, 2 MeO*CO*); 139.1, 138.7, 135.9, 132.1 (4*s*, C(4), C(5a), C(8a), C(1) Ph); 129.3, 128.6, 127.4, 126.5, 124.5, 119.9 (6*d*, C(3), C(6), C(7), C(8), 5 CH (Ph)); 126.6, 124.4, 110.6 (3*s*, C(1), C(2), C(2a)); 52.6, 52.2 (2*q*, 2 MeO); 36.3 (*t*, Ph*C*H$_2$). CI-MS: 377 (24), 376 (100, $[M+1]^+$), 362 (17), 288 (30). Anal. calc. for $C_{22}H_{17}NO_5$ (375.38): C 70.39, H 4.56, N 3.73; found: C 70.07, H 4.61, N 3.59.

1,2-Bis(ethoxycarbonyl)-4-methyl-8b-azaacenaphthylenium-5-olate (=*1,2-Bis(ethoxycarbonyl)-4-methylpyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19c**). According to *GP 1:* **9b** (160 mg, 1.0 mmol) and **18a** (349 mg, 2.05 mmol). Yield: 96 mg (29%). Orange oil. IR ($CHCl_3$): 3026*m*, 2986*m*, 1727*s*, 1638*m*, 1585*m*, 1501*m*, 1475*m*, 1444*m*, 1410*m*, 1377*m*, 1277*s*, 1241*s*, 1210*w*, 1191*m*, 1194*m*, 1089*s*, 1022*s*, 860*w*, 813*w*, 674*m*. ^{1}H-NMR: 8.77 (*dd*, *J* = 8.6, 0.9, H–C(6/8)); 8.55 (*dd*, *J* = 7.7, 1.0, H–C(8/6)); 8.15 (*d*-like, *J* = 0.9, H–C(3)); 7.86 (*t*, *J* = 7.9, H–C(7)); 4.47, 4.41 (2*q*, *J* = 7.2, 2 Me*CH*$_2$O); 2.33 (*d*, *J* = 0.9, Me); 1.41–1.38 (2*t*, *J* = 7.2, 2 *Me*CH$_2$O). ^{13}C-NMR: 175.8 (*s*, C(5)); 163.9, 163.0 (2*s*, 2 EtO*CO*); 135.9, 135.7, 131.4 (3*s*, C(4), C(5a), C(8a)); 127.3, 126.3, 124.4, 119.6 (4*d*, C(3), C(6), C(7), C(8)); 123.2, 118.5, 110.6 (3*s*, C(1), C(2), C(2a)); 62.1, 61.1 (2*t*, 2 Me*C*H$_2$O); 17.0 (*q*, Me); 14.4, 14.3 (2*q*, 2 *Me*CH$_2$O). EI-MS: 328 (19), 327 (100, M^+), 299 (9), 282 (12), 255 (10), 254 (22), 227 (14), 182 (12).

4-Methyl-1,2-bis(methoxycarbonyl)-8b-azaacenaphthylenium-5-olate (=*1,2-Bis(methoxycarbonyl)-4-methylpyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19d**).According to *GP 1:* **9b** (164 mg, 1.03 mmol) and **18b** (286 mg, 2.00 mmol). Yield: 117 mg (39%). Orange powder. M.p. 148–149°. IR ($CHCl_3$): 3030*w*, 3007*w*, 2955*m*, 1734*s*, 1636*s*, 1586*s*, 1499*m*, 1444*m*, 1396*w*, 1377*w*, 1300*s*, 1278*s*, 1243*s*, 1198*m*, 1179*m*,

1162*m*, 1143*m*, 1091*m*, 1021*w*, 1003*w*, 943*w*, 832*w*, 667*m*. ^{1}H-NMR: 8.60 (*dd*, *J* = 8.6, 0.9, H–C(6/8)); 8.38 (*dd*, *J* = 7.5, 1.0, H–C(8/6)); 8.06 (*d*-like, *J* = 0.9, H–C(3)); 7.78 (*t*, *J* = 7.7, H–C(7)); 4.06, 3.99 (2*s*, 2 MeO); 2.31 (*d*, *J* = 0.7, Me). ^{13}C-NMR: 175.5 (*s*, C(5)); 163.9, 163.2 (2*s*, 2 MeO*C*O); 135.9, 135.3, 131.1 (3*s*, C(4), C(5a), C(8a)); 127.1, 126.3, 124.2, 119.6 (4*d*, C(3), C(6), C(7), C(8)); 123.5, 119.6, 110.1 (3*s*, C(1), C(2), C(2a)); 52.9, 52.4 (2*q*, 2 MeO); 16.9 (*q*, Me). EI-MS: 300 (17), 299 (100, M^+), 285 (13), 284 (26), 268 (40), 254 (25), 253 (16), 252 (22), 238 (13), 182 (15), 181 (10), 167 (50), 113 (9), 43 (19). Anal. calc. for $C_{16}H_{13}NO_5$ (299.28): C 64.21, H 4.38, N 4.68; found: C 63.97, H 4.29, N 4.43.

1,2-Bis(methoxycarbonyl)-4-(prop-1-en-1-yl)-8b-azaacenaphthylenium-5-olate (=*1,2-Bis(methoxycarbonyl)-4-(prop-1-en-1-yl)pyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19e**). According to *GP 1:* **9c** (186 mg, 1.0 mmol) and **18b** (279 mg, 1.96 mmol). Yield: 108 mg (33%). Orange oil. IR ($CHCl_3$): 3008*m*, 2956*m*, 1730*s*, 1640*m*, 1591*s*, 1501*m*, 1476*m*, 1437*m*, 1396*m*, 1084*m*. ^{1}H-NMR: 8.72 (*dd*, *J* = 8.6, 1.0, H–C(6/8)); 8.55 (*dd*, *J* = 7.6, 1.1, H–C(8/6)); 8.20 (*s*, H–C(3)); 7.87 (*t*, *J* = 7.6, H–C(7)); 6.85 – 6.70 (*m*, CH=CH); 4.08, 4.00 (2*s*, 2 MeO); 1.98 (*d*, *J* = 5.3, Me). ^{13}C-NMR: 174.2 (*s*, C(5)); 164.2, 163.3 (2*s*, 2 MeO*C*O); 135.9, 133.7, 132.5 (3*s*, C(4), C(5a), C(8a)); 131.1, 126.6, 125.0, 124.5, 123.5, 120.1 (6*d*, C(3), C(6), C(7), C(8), CH=CH); 124.3, 119.6, 110.1 (3*s*, C(1), C(2), C(2a)); 52.9, 52.1 (2*q*, 2 MeO); 16.9 (*q*, Me). CI-MS: 327 (17), 326 (100, $[M+1]^+$).

1,2-Bis(methoxycarbonyl)-4-(1-methylethyl)-8b-azaacenaphthylenium-5-olate (=*1,2-Bis(methoxycarbonyl)-4-(1-methylethyl)pyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19f**). According to *GP 1:* **9d** (97 mg, 0.51 mmol) and **18b** (158 mg, 1.11 mmol). Yield: 68 mg (41%). Orange oil. IR ($CHCl_3$): 2994*m*, 2956*m*, 2872*m*, 1712*s*, 1637*s*, 1590*s*, 1495*m*, 1465*m*, 1397*m*, 1368*m*, 1354*m*, 1317*s*, 1148*s*, 1107*m*, 999*m*, 978*m*, 859*m*. ^{1}H-NMR: 8.79 (*dd*, *J* = 8.6, 1.0, H–C(6/8)); 8.59 (*dd*, *J* = 7.6, 1.1, H–C(8/6)); 8.13 (*s*, H–C(3)); 7.91 (*t*, *J* = 7.7, H–C(7)); 4.09, 4.02 (2*s*, 2 MeO); 3.52 (*sept.*, *J* = 6.8, Me_2CH); 1.32 (*d*, *J* = 6.9, Me_2CH). ^{13}C-NMR: 175.2 (*s*, C(5)); 164.5, 163.5 (2*s*, 2 MeO*C*O); 145.9, 135.7, 132.0 (3*s*, C(4), C(5a), C(8a)); 126.4, 124.4, 124.1, 119.8 (4*d*, C(3), C(6), C(7), C(8)); 120.0, 110.1 (2*s*, C(1), C(2), C(2a)); 53.0, 52.1 (2*q*, 2 MeO); 27.5 (*d*, Me_2CH); 21.6 (*q*, Me_2CH). CI-MS: 330 (5), 329 (19), 328 (100, $[M+1]^+$), 314 (17), 288 (9), 232 (5). Anal. calc. for $C_{18}H_{17}NO_5$ (327.34): C 66.05, H 5.23, N 4.28; found: C 65.74, H 5.18, N 4.46.

1,2-Bis(methoxycarbonyl)-8b-azaacenaphthylenium-5-olate (=*1,2-Bis(methoxycarbonyl)pyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19g**). According to *GP 1:* **9f** (70 mg, 0.48 mmol) and **18b** (76 mg, 0.55 mmol). Yield: 24 mg (19%). Orange oil. IR (KBr): 3072*w*, 2953*m*, 2924*m*, 2853*m*, 1719*s*, 1649*m*, 1606*m*, 1501*m*, 1468*m*, 1439*m*, 1395*m*, 1353*m*, 1344*m*, 1316*m*, 1277*s*, 1247*s*, 1149*m*, 1132*m*, 1096*m*, 1070*m*, 995*m*, 922*w*, 872*w*, 841*w*, 806*m*, 761*w*, 725*w*, 710*w*. ^{1}H-NMR: 8.85 (*d*, *J* = 8.6, H–C(6/8)); 8.60 (*d*, *J* = 7.6, H–C(8/6)); 8.30 (*d*, *J* = 9.9, H–C(3)); 7.97 (*t*, *J* = 8.1, H–C(7)); 7.16 (*d*, *J* = 9.9, H–C(4)); 4.07, 4.02 (2*s*, 2 MeO). ^{13}C-NMR: 176.1 (*s*, C(5)); 163.9, 163.3 (2*s*, 2 MeO*C*O); 136.4, 133.3 (2*s*, C(5a), C(8a)); 130.0, 127.2, 126.2, 125.0, 119.9 (5*d*, C(3), C(4), C(6), C(7), C(8)); 125.1, 120.2, 111.2 (3*s*, C(1), C(2), C(2a)); 53.0, 52.3 (2*q*, 2 MeO). CI-MS: 286 (100, $[M+1]^+$).

4-Benzyl-1-(ethoxycarbonyl)-2-(trifluoromethyl)-8b-azaacenaphthylenium-5-olate (=*4-Benzyl-1-(ethoxycarbonyl)-2-(trifluoromethyl)pyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19h**). According to *GP 1:* **9a** (59 mg, 0.25 mmol) and *ethyl 4,4,4-trifluorobut-2-ynoate* (**18c**, 87 mg, 0.51 mmol). Yield: 43 mg (43%). Orange oil. IR ($CHCl_3$): 3026*w*, 2962*m*, 2928*m*, 1738*s*, 1639*m*, 1593*s*, 1504*w*, 1475*m*, 1410*m*, 1386*m*, 1311*m*, 1261*s*, 1236*s*, 1151*m*, 1127*m*, 1085*s*, 1019*m*, 809*m*, 699*w*. ^{1}H-NMR: 9.00 (*dd*, *J* = 8.7, 0.9, H–C(6/8)); 8.64 (*dd*, *J* = 7.5, 1.0, H–C(8/6)); 8.14 (*s*, H–C(3)); 7.96 (*t*, *J* = 7.7, H–C(7)); 7.40 – 7.21 (*m*, 5 arom. H); 4.49 (*q*, *J* = 7.1, MeCH_2O); 4.12 (*s*, PhCH_2); 1.47 (*t*, *J* = 7.1, *Me*CH$_2$O). CI-MS: 401 (18), 400 (100, $[M+1]^+$).

4-Benzyl-1-(ethoxycarbonyl)-8b-azaacenaphthylenium-5-olate (=*4-Benzyl-1-(ethoxycarbonyl)pyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19i**). According to *GP 2:* **9a** (120 mg, 0.51 mmol) and *ethyl prop-2-ynoate* (**18d**; 101 mg, 1.03 mmol). Yield: 41 mg (24%). Yellow-orange powder. M.p. 140.3 – 141°. IR ($CHCl_3$): 3000*m*, 1700*s*, 1634*w*, 1577*s*, 1529*m*, 1513*m*, 1492*w*, 1450*m*, 1417*m*, 1384*m*, 1335*w*, 1304*s*, 1237*s*, 1220*s*, 1175*w*, 1149*s*, 1116*m*, 1074*s*, 1028*w*, 1017*w*, 960*w*, 915*w*, 863*w*, 810*w*, 699*w*, 658*w*. ^{1}H-NMR: 8.79 (*dd*, *J* = 8.4, 0.9, H–C(6/8)); 8.57 (*dd*, *J* = 7.7, 0.8, H–C(8/6)); 7.87 (*t*, *J* = 8.0, H–C(7)); 7.84, 7.72 (2*s*, H–C(2), H–C(3)); 7.29 – 7.17 (*m*, 5 arom. H); 4.39 (*q*, *J* = 7.1, MeCH_2O); 4.06 (*s*, PhCH_2); 1.38 (*t*, *J* = 7.1, *Me*CH$_2$O). ^{13}C-NMR: 174.9 (*s*, C(5)); 163.8 (*s*, Et*O*C*O*); 139.0, 137.6, 136.9, 132.2 (4*s*, C(4), C(5a), C(8a), C(1) (Ph)); 129.4, 128.2, 126.4, 125.9, 123.2, 122.2, 118.7 (7*d*, C(2), C(3), C(6), C(7), C(8), 5 CH

(Ph)); 120.2, 112.7 (2*s*, C(1), C(2a)); 60.5 (*t*, Me*C*H$_2$O); 36.0 (*t*, Ph*C*H$_2$); 14.4 (*q*, *Me*CH$_2$O). EI-MS: 332 (23), 331 (100, M^+), 330 (27), 303 (10), 302 (38), 286 (20), 258 (29), 257 (13), 228 (8), 169 (17), 69 (10). Anal. calc. for $C_{21}H_{17}NO_3$ (331.38): C 76.11, H 5.17, N 4.23; found: C 75.77, H 5.41, N 3.89.

Suitable crystals of **19i** for the X-ray crystal-structure determination were obtained by crystallization from EtOH/Et$_2$O.

4-Benzyl-1-(methoxycarbonyl)-8b-azaacenaphthylenium-5-olate (=*4-Benzyl-1-(methoxycarbonyl)-pyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19j**). According to *GP 2:* **9a** (120 mg, 0.51 mmol) and *methyl prop-2-ynoate* (**18e**; 97 mg, 1.15 mmol). Yield: 43.5 mg (27%). Yellow-orange powder. M.p. 146.5–147.7°. IR ($CHCl_3$): 3003*m*, 2954*w*, 1709*s*, 1633*w*, 1579*s*, 1531*m*, 1515*s*, 1494*w*, 1453*s*, 1435*s*, 1412*w*, 1391*m*, 1336*m*, 1304*s*, 1241*s*, 1150*s*, 1117*s*, 1080*s*, 1030*w*, 994*w*, 938*w*, 870*w*, 810*w*, 700*m*, 660*w*. ^{1}H-NMR: 8.87 (*d*, *J* = 8.3, H–C(6/8)); 8.64 (*d*, *J* = 7.6, H–C(8/6)); 7.97 (*t*, *J* = 8.2, H–C(7)); 7.89, 7.80 (2*s*, H–C(2), H–C(3)); 7.36–7.15 (*m*, 5 arom. H); 4.13 (*s*, PhCH_2); 4.00 (*s*, MeO). ^{13}C-NMR: 175.2 (*s*, C(5)); 164.5 (*s*, MeO*C*O); 139.3, 138.0, 137.3, 132.5 (4*s*, C(4), C(5a), C(8a), C(1) (Ph)); 129.7, 129.0, 128.5, 126.8, 126.3, 123.5, 122.4, 119.0 (8*d*, C(2), C(3), C(6), C(7), C(8), 5 CH (Ph)); 120.5, 112.6 (2*s*, C(1), C(2a)); 51.9 (*q*, MeO); 36.3 (*t*, Ph*C*H$_2$). CI-MS: 319 (18), 318 (100, $[M+1]^+$).

4-Benzyl-1-(ethoxycarbonyl)-2-methyl-8b-azaacenaphthylenium-5-olate (=*4-Benzyl-1-(ethoxycarbonyl)-2-methylpyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19k**). According to *GP 3:* **9a** (97 mg, 0.41 mmol) and *ethyl but-2-ynoate* (**18f**; 100 mg, 0.43 mmol). Yield: 23 mg (32%). Orange powder. M.p. 134.5–135°. IR ($CHCl_3$): 3007*w*, 2359*w*, 1698*m*, 1573*s*, 1530*w*, 1496*m*, 1480*m*, 1435*w*, 1405*w*, 1384*w*, 1354*w*, 1295*s*, 1261*s*, 1154*m*, 1086*s*, 1046*w*, 1015*w*, 810*m*, 688*w*. ^{1}H-NMR: 8.79 (*dd*, *J* = 8.4, 0.9, H–C(6/8)); 8.59 (*dd*, *J* = 7.7, 1.0, H–C(8/6)); 7.90 (*t*, *J* = 8.2, H–C(7)); 7.88 (*s*, H–C(3)); 7.40–7.20 (*m*, 5 arom. H); 4.48 (*q*, *J* = 7.2, MeCH_2O); 4.16 (*s*, PhCH_2); 2.79 (*s*, Me); 1.49 (*t*, *J* = 7.2, *Me*CH$_2$O). ^{13}C-NMR: 174.6 (*s*, C(5)); 164.5 (*s*, EtO*C*O); 139.3, 137.4, 136.4, 135.9, 131.9 (5*s*, C(2), C(4), C(5a), C(8a), C(1) (Ph)); 129.2, 128.6, 128.4, 126.3, 126.0, 122.3, 117.9 (7*d*, C(3), C(6), C(7), C(8), 5 CH (Ph)); 120.5, 110.3 (2*s*, C(1), C(2a)); 60.2 (*t*, Me*C*H$_2$O); 36.2 (*t*, Ph*C*H$_2$); 14.4 (*q*, *Me*CH$_2$O); 11.7 (*q*, Me). CI-MS: 347 (11), 346 (100, $[M+1]^+$).

1-(Ethoxycarbonyl)-4-methyl-2-(trifluoromethyl)-8b-azaacenaphthylenium-5-olate (=*1-(Ethoxycarbonyl)-4-methyl-2-(trifluoromethyl)pyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19l**). According to *GP 1:* **9b** (40 mg, 0.25 mmol) and **18c** (85 mg, 0.51 mmol). Yield: 33 mg (41%). Orange powder. IR ($CHCl_3$): 3019*m*, 1730*s*, 1640*m*, 1542*s*, 1504*m*, 1474*s*, 1443*m*, 1409*m*, 1378*m*, 1281*s*, 1239*s*, 1199*s*, 1151*s*, 1091*s*, 1025*m*, 899*w*, 815*m*, 665*w*. ^{1}H-NMR (600 MHz): 8.99 (*dd*, *J* = 8.6, 1.1, H–C(6/8)); 8.63 (*dd*, *J* = 7.5, 1.1, H–C(8/6)); 8.29 (*d*-like, *J* = 1.0, H–C(3)); 7.96 (*t*, *J* = 7.5, H–C(7)); 4.50 (*q*, *J* = 7.1, 2 MeCH_2O); 2.41 (*d*, *J* = 1.1, Me); 1.48 (*t*, *J* = 7.1, *Me*CH$_2$O). ^{13}C-NMR: 175.8 (*s*, C(5)); 162.3 (*s*, EtO*C*O); 147.4 (*q*, ^2J(C,F) = 29.5, C(2)); 138.6, 136.5, 131.6 (3*s*, C(4), C(5a), C(8a)); 127.5, 126.7, 125.1, 120.0 (4*d*, C(3), C(6), C(7), C(8)); 125.4 (*q*, ^1J(C,F) = 286.5, CF_3); 122.9, 118.4 (2*s*, C(1), C(2a)); 61.3 (*t*, Me*C*H$_2$O); 17.2 (*q*, Me); 14.1 (*q*, *Me*CH$_2$O). ^{19}F-NMR (600 MHz, $CDCl_3$; Cl_3CF as reference): −55 (*s*, CF_3). CI-MS: 325 (15), 324 (100, $[M+1]^+$), 323 (38).

Suitable crystals of **19l** for the X-ray crystal-structure determination were obtained by crystallization from AcOEt.

1-(Methoxycarbonyl)-4-methyl-8b-azaacenaphthylenium-5-olate (=*1-(Methoxycarbonyl)-4-methylpyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19m**). According to *GP 2:* **9b** (157 mg, 1.0 mmol) and **18e** (173 mg, 2.06 mmol). Yield: 71 mg (29%). Yellow powder. M.p. 137.5–138.9°. IR ($CHCl_3$): 3022*m*, 3007*s*, 2955*m*, 2927*m*, 1705*s*, 1635*m*, 1582*s*, 1530*s*, 1516*s*, 1488*m*, 1455*s*, 1435*s*, 1419*m*, 1390*s*, 1379*m*, 1343*m*, 1331*m*, 1305*s*, 1244*s*, 1195*m*, 1180*m*, 1150*s*, 1118*s*, 1085*s*, 1050*m*, 1019*m*, 972*m*, 944*w*, 935*w*, 904*m*, 871*w*, 815*m*, 609*m*. ^{1}H-NMR: 8.83 (*d*, *J* = 8.4, H–C(6/8)); 8.59 (*d*, *J* = 7.6, H–C(8/6)); 8.02 (*s*, H–C(3)); 7.00 (*t*, *J* = 7.4, H–C(7)); 4.01 (*s*, MeO); 2.39 (*s*, Me). ^{13}C-NMR: 175.8 (*s*, C(5)); 164.4 (*s*, MeO*C*O); 136.9, 134.6, 131.8 (3*s*, C(4), C(5a), C(8a)); 128.4, 125.9, 123.1, 121.6, 118.6 (5*d*, C(2), C(3), C(6), C(7), C(8)); 120.2, 112.1 (2*s*, C(1), C(2a)); 51.7 (*q*, MeO); 17.0 (*q*, Me). CI-MS: 242 (100, $[M+1]^+$). Anal. calc. for $C_{14}H_{11}NO_3$ (241.25): C 69.70, H 4.60, N 5.81; found: C 69.55, H 4.64, N 5.62.

1-(Ethoxycarbonyl)-2,4-dimethyl-8b-azaacenaphthylenium-5-olate (=*1-(Ethoxycarbonyl)-2,4-dimethylpyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19n**). According to *GP 3:* **9b** (80 mg, 0.50 mmol) and **18f** (131 mg, 1.2 mmol). Yield: 38 mg (28%). Orange powder. M.p. 150.6–151.8°. IR ($CHCl_3$): 3003*m*, 1703*s*, 1572*s*, 1530*m*, 1479*m*, 1434*m*, 1383*m*, 1292*s*, 1272*s*, 1239*s*, 1169*m*, 1153*m*, 1090*s*, 814*w*, 663*w*. ^{1}H-NMR: 8.70 (*dd*, *J* = 8.4, 1.0, H–C(6/8)); 8.48 (*dd*, *J* = 7.7, 1.0, H–C(8/6)); 7.99 (*d*-like, *J* = 0.9, H–C(3)); 7.80 (*t*,

J = 8.0, H–C(7)); 4.41 (q, J = 7.1, MeCH_2O); 2.78 (s, Me–C(2)); 2.34 (d, J = 0.8, Me–C(4)); 1.43 (t, J = 7.1, *Me*CH_2O). ^{13}C-NMR: 175.5 (s, C(5)); 164.6 (s, EtO*C*O); 137.3, 135.3, 133.3, 131.4 (4s, C(2), C(4), C(5a), C(8a)); 126.1, 125.7, 122.1, 117.7 (4d, C(3), C(6), C(7), C(8)); 120.3, 110.1 (2s, C(1), C(2a)); 60.2 (t, Me*C*H_2O); 17.1 (q, Me–C(4)); 14.5 (q, *Me*CH_2O); 11.6 (q, Me–C(2)). CI-MS: 271 (26), 270 (100, $[M+1]^+$). Anal. calc. for $C_{16}H_{15}NO_3$ (269.30): C 71.36, H 5.61, N 5.20; found: C 71.19, H 5.32, N 5.27.

1-Acetyl-4-methyl-8b-azaacenaphthylenium-5-olate (=*1-Acetyl-4-methylpyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19o**). According to *GP 3:* **9b** (80 mg, 0.50 mmol) and but-3-yn-2-one (102 mg, 1.5 mmol). Yield: 37 mg (27%). Orange oil. IR ($CHCl_3$): 3006*m*, 2954*m*, 1711*w*, 1602*s*, 1579*s*, 1536*m*, 1511*w*, 1386*m*, 1304*m*, 1150*m*, 1153*m*, 965*w*. ^{1}H-NMR: 9.05 (*dd*, J = 8.3, 0.6, H–C(6/8)); 8.61 (*dd*, J = 7.7, 1.0, H–C(8/6)); 8.02 (br. *s*, H–C(3)); 7.95 (*t*, J = 8.0, H–C(7)); 7.81 (*s*, H–C(2)); 2.69 (*s*, *Me*CO); 2.40 (*d*, J = 0.5, Me). ^{13}C-NMR: 193.5 (*s*, Me*C*O); 175.7 (*s*, C(5)); 136.3, 134.6, 131.5 (3*s*, C(4), C(5a), C(8a)); 128.3, 126.9, 124.2, 121.0, 118.9 (5*d*, C(2), C(3), C(6), C(7), C(8)); 120.3, 119.9 (2*s*, C(1), C(2a)); 16.9 (*q*, Me). CI-MS: 296 (9), 227 (15), 226 (100, $[M+1]^+$).

1-(Ethoxycarbonyl)-4-(prop-1-en-1-yl)-2-(trifluoromethyl)-8b-azaacenaphthylenium-5-olate (=*1-(Ethoxycarbonyl)-4-(prop-1-en-1-yl)-2-(trifluoromethyl)pyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19p**). According to *GP 1:* **9c** (102 mg, 0.55 mmol) and **18c** (224 mg, 1.35 mmol). Yield: 63 mg (33%). Orange oil. IR ($CHCl_3$): 3011*m*, 2956*m*, 1734*s*, 1640*m*, 1591*s*, 1504*m*, 1476*m*, 1443*m*, 1393*m*, 1238*s*, 1199*s*, 1152*s*, 1081*m*, 1025*m*, 899*w*, 815*m*, 667*w*. ^{1}H-NMR: 8.91 (*d*, J = 8.6, H–C(6/8); 8.56 (*dd*, J = 7.6, 0.9, H–C(8/6)); 8.27 (*s*, H–C(3)); 7.88 (*t*, J = 7.7, H–C(7)); 6.90 – 6.65 (*m*, CH=CH); 4.43 (*q*, MeCH_2O); 1.93 (*d*, J = 5.5, Me); 1.41 (*t*, J = 7.1, *Me*CH_2O). CI-MS: 352 (9), 351 (23), 350 (100, $[M+1]^+$), 276 (7).

1-(Ethoxycarbonyl)-4-(1-methylethyl)-2-(trifluoromethyl)-8b-azaacenaphthylenium-5-olate (=*1-(Ethoxycarbonyl)-4-(1-methylethyl)-2-(trifluoromethyl)pyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19q**). According to *GP 1:* **9d** (100 mg, 0.53 mmol) and **18c** (171 mg, 1.03 mmol). Yield: 67 mg (36%). IR ($CHCl_3$): 3011*m*, 1733*s*, 1641*m*, 1547*s*, 1504*m*, 1473*s*, 1453*m*, 1410*m*, 1378*m*, 1282*s*, 1237*s*, 1199*s*, 1161*s*, 1086*s*, 1023*s*, 812*m*, 695*m*. ^{1}H-NMR: 8.92 (*dd*, J = 8.6, 0.9, H–C(6/8)); 8.56 (*dd*, J = 7.5, 1.0, H–C(8/6)); 8.16 (*s*, H–C(3)); 7.89 (*t*, J = 7.6, H–C(7)); 4.43 (*q*, J = 7.1, MeCH_2O); 3.30 (*sept.*, J = 6.8, Me_2C*H*); 1.22 (*t*, J = 7.1, *Me*CH_2O); 1.10 (*d*, J = 6.8, Me_2CH). CI-MS: 353 (24), 352 (100, $[M+1]^+$).

5. *Isolation of Side Products, Diethyl 5-Benzyl-6-oxo-1-(pyridin-2-yl)cyclohexa-2,4-diene-1,2-dicarboxylate* (**20a**). A suspension of **9a** (300 mg, 1.27 mmol) and **18a** (607 mg, 3.57 mmol) in toluene (5 ml) was heated to reflux for 17 min and then stirred at r.t. for 18 h. Evaporation of the solvent and CC (hexane/AcOEt 3 : 1) of the residue gave **19a** (234 mg, 45%) and 138 mg of a brown oil. CC of the latter (CH_2Cl_2/hexane 3 : 1) yielded **20a** (42 mg, 8%). Dark yellow oil. UV (EtOH): 326 (3.21). IR ($CHCl_3$): 2984*m*, 2937*w*, 1753*s*, 1714*s*, 1668*s*, 1585*m*, 1496*w*, 1465*m*, 1432*m*, 1371*m*, 1274*s*, 1137*m*, 1099*m*, 1030*m*, 999*w*, 864*w*, 700*w*. ^{1}H-NMR: 8.34 (*ddd*, J = 4.8, 1.7, 0.6, H–C(6) (Py)); 7.88 (*d*, J = 8.2, H–C(3) (Py)); 7.63 (*td*, J = 7.8, 1.9, H–C(4) (Py)); 7.42 (*d*, J = 6.6, H–C(5) (Py)); 7.23 – 7.14 (*m*, 4 arom. H); 7.05 – 7.02 (*m*, 1 arom. H, H–C(3)); 6.74 (*dt*, J = 6.6, 1.4, H–C(4)); 4.24 – 4.13 (*m*, 2 MeCH_2O); 3.64 (*s*, PhCH_2); 1.19, 1.18 (2*t*, J = 7.1, 2 *Me*CH_2O). ^{13}C-NMR: 194.4 (*s*, C(6)); 167.4, 164.3 (2*s*, 2 EtO*C*O); 155.4 (*s*, C(2) (Py)); 148.0 (*d*, C(6) Pyr); 139.6 (*s*, C(1) (Ph)); 138.1, 137.7 (2*s*, C(2), C(5)); 136.6 (*d*, C(4) (Py)); 136.0 (*d*, *C*H=C); 129.0, 128.3 (2*d*, 4 CH (Ph)); 129.3, 126.3, 125.6, 123.0 (4*d*, 1 CH (Ph), C(3) (Py), C(5) (Py), *C*H=C); 69.0 (*s*, C(1)); 62.0, 61.0 (2*t*, 2 Me*C*H_2O); 35.2 (*t*, Ph*C*H_2); 13.9, 13.8 (2*q*, 2 *Me*CH_2O). CI-MS: 407 (23), 406 (100, $[M+1]^+$).

Dimethyl 5-Benzyl-6-oxo-1-(pyridin-2-yl)cyclohexa-2,4-diene-1,2-dicarboxylate (**20b**). A suspension of **9a** (300 mg, 1.27 mmol) and **18b** (650 mg, 4.57 mmol) in toluene (5 ml) was heated to reflux for 2 h and then stirred at r.t. for 10 h. Evaporation of the solvent and CC (hexane/AcOEt/CH_2Cl_2, 3 ×) of the residue gave **19b** (160 mg, 33%) and 110 mg of a brown oil. CC of the latter (CH_2Cl_2/hexane 3 : 1) yielded **20b** (29 mg, 6%). Yellow oil. IR ($CHCl_3$): 2983*m*, 1754*s*, 1711*s*, 1667*s*, 1582*m*, 1489*w*, 1432*m*, 1368*m*, 1275*s*, 1137*m*, 1099*m*, 1031*m*, 995*w*, 864*w*, 698*w*. ^{1}H-NMR: 8.34 (*d*, J = 4.1, H–C(6) (Py)); 7.83 (*d*, J = 8.0, H–C(3) (Py)); 7.63 (*td*, J = 7.8, 1.7, H–C(4) (Py)); 7.40 (*d*, J = 6.6, H–C(5) (Py)); 7.29 – 7.15 (*m*, 4 arom. H); 7.05 – 7.02 (*m*, 1 arom. H, H–C(3)); 6.70 (*dt*, J = 6.4, 1.4, H–C(4)); 3.73 (*s*, 2 MeO); 3.64 (*s*, PhCH_2). ^{13}C-NMR: 194.5 (*s*, C(6)); 168.0, 165.0 (2*s*, 2 MeO*C*O); 155.2 (*s*, C(2) (Py)); 148.2 (*d*, C(6) (Py)); 140.0 (*s*, C(1) (Ph)); 137.6 (*s*, C(2), C(5)); 136.5 (*d*, C(4) (Py)); 136.3 (*d*, *C*H=C); 129.1, 128.5 (2*d*, 4 CH (Ph)); 129.7, 126.5, 125.7, 123.2 (4*d*, 1 CH (Ph), C(3) (Py), C(5) (Py), *C*H=C); 69.0 (*s*, C(2)); 53.1, 52.2 (2*q*, 2 MeO); 35.3 (*t*, Ph*C*H_2). CI-MS: 379 (20), 378 (89, $[M+1]^+$).

Methyl 5-Benzyl-6-oxo-1-(pyridin-2-yl)cyclohexa-2,4-diene-1-carboxylate (**20c**). A mixture of **9a** (242 mg, 1.03 mmol) and **18e** (174 mg, 2.07 mmol) in toluene (10 ml) was heated to reflux for 30 min. Evaporation of the solvent and CC (hexane/AcOEt/CH_2Cl_2) of the residue gave **19j** (74 mg, 23%), **20c** (9 mg, 3%) as a yellow oil, and *methyl 3-benzyl-2-hydroxy-6-(pyridin-2-yl)benzoate* (**21**; 3 mg, 1%).

Data of **20c**. IR ($CHCl_3$): 3005*w*, 2956*w*, 1740*s*, 1664*m*, 1645*m*, 1588*m*, 1495*w*, 1467*m*, 1453m, 1431*s*, 1396*w*, 1370*m*, 1220*br*, 1175*m*, 1076*w*, 1030*w*, 1017*w*, 993*w*, 700*w*. ^{1}H-NMR: 8.53 (*d*, *J* = 3.7, H–C(6) (Py)); 7.64 (*td*, *J* = 7.7, 1.9, H–C(4) (Py)); 7.32–7.16 (*m*, 7 arom. H); 6.71 (*dd*, *J* = 9.5, 0.9, H–C(2) or H–C(4)); 6.65 (*dd*, *J* = 6.6, 1.1, H–C(4) or H–C(2)); 6.39 (*dd*, *J* = 9.5, 6.2, H–C(3)); 3.74 (*s*, MeO); 3.69, 3.61 (2*d*, *J* = 17.2, PhCH_2). ^{13}C-NMR: 195.1 (*s*, C(6)); 169.0 (*s*, MeO*C*O); 157.1 (*s*, C(2) (Py)); 149.1 (*d*, C(6) (Py)); 138.5 (*s*, C(1) (Ph)); 138.0, 137.4, 136.7 (3*d*, C(4) (Py), C(2), C(4)); 136.5 (*s*, C(5)); 129.3, 128.4, 126.3, 123.8, 122.9, 122.5 (6*d*, C(3), C(3) (Py), C(5) (Py), 5 CH (Ph)); 69.1 (*s*, C(1)); 53.4 (*q*, MeO); 35.1 (*t*, Ph*C*H_2). CI-MS: 321 (15), 320 (100, $[M+1]^+$), 262 (21), 261 (25).

Data of **21**. IR ($CHCl_3$): 3001*w*, 2963*w*, 1726*m*, 1673*m*, 1599*s*, 1495*m*, 1435*s*, 1374*m*, 1272*m*, 1240*m*, 1216*s*, 1091*w*, 993*w*, 960*w*, 827*w*, 699*w*. ^{1}H-NMR: 10.71 (br. *s*, OH); 8.60 (*dd*, *J* = 4.2, 0.7, H–C(6) (Py)); 7.74 (*td*, *J* = 7.8, 1.8, H–C(4) (Py)); 7.40–7.10 (*m*, 8 arom. H); 6.85 (*d*, *J* = 7.7, 1 arom. H); 4.06 (*s*, PhCH_2); 3.45 (*s*, MeO). ^{13}C-NMR: 171.2 (*s*, MeO*C*O); 160.0, 158.9 (2*s*, C(2) (Py), C–OH); 148.4 (*d*, C(6) (Py)); 141.2, 140.0, 129.9, 111.8 (4*s*, 4 arom. C)); 136.0, 134.2, 128.9, 128.3, 126.0, 122.7, 121.6, 121.2 (8*d*, C(4) (Py), C(3) (Py), C(5) (Py), 7 arom. CH); 51.8 (*q*, MeO); 35.5 (*t*, Ph*C*H_2). CI-MS: 641 (11), 640 (37), 639 (82, $[2M+1]^+$), 322 (12), 321 (23), 320 (100, $[M+1]^+$).

Dimethyl 5-Methyl-6-oxo-1-(pyridin-2-yl)cyclohexa-2,4-diene-1,2-dicarboxylate (**20d**). A soln. of **9b** (300 mg, 1.9 mmol) and **18b** (675 mg, 4.75 mmol) in THF (10 ml) was stirred at r.t. for 1 h. Evaporation of the solvent, CC and prep. TLC of the residue gave **19d** (213 mg, 38%), **20d** (21 mg, 5%) as a yellow oil, and *dimethyl 3-hydroxy-4-methylbenzene-1,2-dicarboxylate* (**22**; 22 mg, 4%).

Data of **20d**. IR ($CHCl_3$): 3391*w*, 3030*m*, 2953*m*, 2926*w*, 2848*w*, 2456*w*, 2359*w*, 1758*s*, 1718*s*, 1667*s*, 1584*m*, 1572*m*, 1499*w*, 1464*m*, 1437*s*, 1380*m*, 1370*m*, 1350*m*, 1283*s*, 1248*s*, 1138*s*, 1104*m*, 1075*w*, 1057*w*, 1037*w*, 1016*w*, 997*w*, 899*w*, 869*w*, 694*w*, 657*w*, 640*w*, 614*w*. ^{1}H-NMR: 8.29 (*ddd*, *J* = 4.8, 1.8, 1.1, H–C(6) (Py)); 7.90 (*d*, *J* = 8.2, H–C(3) (Py)); 7.63 (*td*, *J* = 7.7, 1.7, H–C(4) (Py)); 7.35 (*d*, *J* = 6.5, H–C(3)); 7.12 (*dt*, *J* = 6.4, 1.0, H–C(5) (Py)); 6.88 (*dd*, *J* = 6.5, 1.5, H–C(4)); 3.67 (*s*, 2 MeO); 1.86 (*d*, *J* = 1.4, Me). ^{13}C-NMR: 195.4 (*s*, C(6)); 169.1, 165.3 (2*s*, 2 MeO*C*O); 155.9 (*s*, C(2) (Py)); 149.0 (*d*, C(6) (Py)); 137.5, 136.8 (2*s*, C(2), C(5)); 135.9, 134.2, 130.1, 123.0, 120.6 (5*d*, C(4) (Py), C(3) (Py), C(5) (Py)), C(3), C(4)); 63.4 (*s*, C(1)); 51.6, 50.7 (2*q*, MeO); 16.8 (*q*, Me). CI-MS: 303 (17), 302 (100, $[M+1]^+$), 206 (23), 188 (10).

Data of **22**. IR ($CHCl_3$): 3446 *m* (br.), 2955*m*, 2361*w*, 1733*s*, 1677*s*, 1584*m*, 1436*s*, 1417*m*, 1282*s*, 1201*s*, 1156*s*, 1076*m*, 1031*m*, 1004*m*, 916*w*, 875*m*, 835*m*, 802*m*, 756*m*, 734*m*. ^{1}H-NMR: 10.69 (*s*, OH); 7.26 (*d*, *J* = 7.4, 1 arom. H); 6.82 (*d*, *J* = 7.5, 1 arom. H); 3.84, 3.80 (2*s*, 2 MeO); 2.21 (*s*, Me). ^{13}C-NMR: 167.0 (*s*, MeO*C*O); 159.1 (*s*, C–OH); 134.8, 122.1 (2*d*, 2 arom. CH); 130.1, 128.9, 118.8 (3*s*, 3 arom. C); 50.6, 50.0 (2*q*, 2 MeO); 11.9 (*q*, Me). CI-MS: 226 (10), 225 (100, $[M+1]^+$), 195 (10), 193 (19).

6. *Attempted [2+3] Cycloadditions of* **9** *to Alkenes.* A mixture of **9b** (50 mg, 0.31 mmol), *fumaronitrile* (100 mg, 1.28 mmol), and a small amount of Pd/C in toluene (10 ml) was heated to reflux for 4 d[9]). Then, the mixture was filtered through *Celite* and the solvent was evaporated. The crude product and starting materials were separated by CC to give *1,2-Dicyano-4-methyl-8b-azaacenaphthylenium-5-olate* (=*1,2-Dicyano-4-methylpyrrolo[2,1,5*-de*]quinolizinium-5-olate*; **19r**, 11 mg, 14%). ^{1}H-NMR: 8.56 (*dd*, *J* = 7.5, 1.0, H–C(6/8)); 8.38 (*dd*, *J* = 8.7, 0.9, H–C(8/6)); 8.04 (*s*, H–C(3)); 7.96 (*t*, *J* = 7.5, H–C(7)); 2.36 (*s*, Me). EI-MS: 235 (7), 234 (16), 233 (100, M^+), 232 (27), 205 (10), 204 (55), 203 (7), 169 (47), 150 (11), 147 (12), 119 (11), 100 (6), 69 (29).

The analogous reaction of **9b**, *dimethyl fumarate*, and Pd/C in toluene gave **9d** (7.5 mg, 8%). All attempts with other dipolarophiles (*e.g.*, dimethyl maleate, *N*-phenylmaleimide, tetracyanoethene, thiobenzophenone, thiofluorenone, *etc.*) were unsuccessful.

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[9]) In the absence of Pd/C, only traces of **19r** could be detected.

7. *X-Ray Crystal-Structure Determination of* **9a**, **19i**, *and* **19l** (*Table 4* and *Figs. 1* and *2*)[10]). All measurements were performed on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_α radiation (λ 0.71069 Å) and a 12-kW rotating anode generator. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1* and *2*. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Equivalent reflections were merged. Each structure was solved by direct methods using SHELXS-86 [25], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were located in difference electron-density maps, and their positions were allowed to refine together with

Table 4. *Crystallographic Data of Compounds* **9a**, **19i**, *and* **19l**

	9a	**19i**	**19l**
Crystallized from	THF/hexane	EtOH/Et_2O	AcOEt
Empirical formula	$C_{16}H_{13}NO$	$C_{21}H_{17}NO_3$	$C_{16}H_{12}F_3NO_3$
Formula weight	235.28	331.37	323.27
Crystal color, habit	yellow, prism	orange, prism	orange, prism
Crystal dimensions [mm]	$0.22 \times 0.38 \times 0.43$	$0.25 \times 0.30 \times 0.52$	$0.30 \times 0.35 \times 0.48$
Temp. [K]	173(1)	173(1)	173(1)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	*C*2/*m*	$P2_1/n$
Z	8	4	4
Reflections for cell determination	25	25	25
2θ Range for cell determination [°]	36–40	38–40	39–40
Unit cell parameters:			
a [Å]	24.982(2)	20.015(5)	6.760(6)
b [Å]	13.317(1)	6.764(7)	12.410(4)
c [Å]	7.171(1)	13.684(3)	16.610(4)
β [°]	90	114.60(1)	97.64(4)
V [Å^3]	2385.6(4)	1684(2)	1381(1)
D_x [g cm^{-3}]	1.310	1.307	1.555
μ(MoK_α) [mm^{-1}]	0.0818	0.0880	0.134
Scan type	ω	$\omega-2\theta$	$\omega/2\theta$
2θ(max) [°]	60	60	55
Total reflections measured	4683	2715	3594
Symmetry-independent reflections	3480	2646	3171
Reflections used in refinement [$I>2\theta(I)$][a])	2062	1845	2471
Parameters refined	216	187	257
Final $R(F)$	0.0443	0.0445	0.0560
$wR(F)$	0.0375	0.0421	0.0625
Weighting parameter [a][b])	0.005	0.005	0.005
Goodness-of-fit	1.487	2.539	3.263
Secondary extinction coefficient	$2.3(3) \times 10^{-7}$	2.01×10^{-7}	5.80×10^{-7}
Final Δ_{max}	0.0004	0.0002	0.0006
$\Delta\rho$(max; min) [e Å^{-3}]	0.26; −0.21	0.29; −0.21	0.31; −0.30

[a]) [$I>3\sigma(I)$ reflections] for **19i**. [b]) $w^{-1}=\sigma^2(F_o)+(pF_o)^2$.

[10]) CCDC-863882–863884 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* http://www.ccdc.cam.ac.uk/data_request/cif.

individual isotropic displacement parameters. The refinement of each structure was carried out on F using full-matrix least-squares procedures [26], which minimized the function $\Sigma w(|F_o|-|F_c|)^2$. A correction for secondary extinction was applied in each case. Neutral atom-scattering factors for non-H-atoms were taken from [27a], and the scattering factors for H-atoms were taken from [28]. Anomalous dispersion effects were included in F_c [29]; the values for f' and f'' were those of [27b]. The values of the mass attenuation coefficients are those of [27c]. All calculations were performed using the TEXSAN crystallographic software package [30].

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