### The Coupling-Isomerization Approach to Enimines and the First Sequential Three-Component Access to 2-Ethoxy Pyridines\*

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Dedicated to Dr. Hans-Ulrich Wagner on the occasion of his 65<sup>th</sup> birthday

The coupling-isomerization reaction (CIR) of electron-deficient halides 1 with N-[1-(hetero)arylprop-2-ynyl] tosyl amides 2 leads to the formation of N-tosyl enimines 3, in good to excellent yields. These electron deficient heterodienes are perfectly suited for Diels-Alder reactions with inverse electron demand. In the sense of a one-pot reaction a three-component CIR-cyclocondensation sequence of 1, 2a, and diethyl ketene acetal gives rise to the formation of 2-ethoxy 6-(p-anisyl)pyridines 4 in moderate to good yields.

Key words: Alkynes, Catalysis, Cross-Couplings, Cyclocondensation, Pyridines

Palladium-catalyzed cross-coupling reactions have considerably revolutionized synthetic methodology and the syntheses of complex natural and non-natural target molecules. In particular, the bimetallic, catalytic Sonogashira coupling has turned out to be a versatile and mild alkyne-to-alkyne transformation, *i.e.* a powerful tool for transforming a terminal alkyne into an internal one as a consequence of a sp-sp<sup>2</sup>-C,C-bond forming reaction [1]. Besides mild reaction conditions, an excellent compatibility with fragile functional groups dispenses with tedious protection-deprotection operations, and since hydrogen halide (scavenged by weak bases such as amines) is formed as the sole byproduct, the Sonogashira coupling displays a high degree of atom economy. As part of our program designed to develop new multicomponent methodologies initiated by transition metal catalyzed C,C-bond formation, we have recently discovered and developed an unusual mode of alkyne activation by a detouring outcome of the Sonogashira coupling, i.e. a coupling-isomerization reaction (CIR) [2]. Conceptually, the crosscoupling reaction of an electron deficient halide with a terminal alkyne not only activates the newly formed internal triple bond towards Michael-type additions but





also at the propargyl position, *e.g.* towards an alkyneallene isomerization (Scheme 1).

In particular, the Sonogashira coupling of electron poor halides with 1-(hetero)aryl propargyl alcohols furnishes chalcones in good to excellent yields. With this new enone synthesis in hand and based upon the inherent bifunctional electrophilicity of the *insitu* generated Michael acceptor, we have disclosed novel three- and four-component syntheses of pyrazolines [2], pyrimidines [3], benzothiazepines [4], pyrrols [5], furans, pyrindines and tetrahydroquinolines [6] in the sense of sequential one-pot reactions. Here we want to communicate our first findings on

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**3c** EWG- $\pi = p \cdot C_6 H_4 CN$ , (Het)Aryl =  $p \cdot C_6 H_4 OMe$ , 90 % **3d** EWG- $\pi = p \cdot C_6 H_4 CN$ , (Het)Aryl =  $p \cdot C_6 H_4 OPh$ , 94 % **3e** EWG- $\pi = p \cdot C_6 H_4 CF_3$ , (Het)Aryl =  $p \cdot C_6 H_4 OMe$ , quantitative **3f** EWG- $\pi = 2$ -pyridyl, (Het)Aryl =  $p \cdot C_6 H_4 OMe$ , quantitative **3g** EWG- $\pi = 2$ -pyrimidyl, (Het)Aryl =  $p \cdot C_6 H_4 OMe$ , quantitative

Scheme 2. CIR access to *N*-tosyl enimines **3** from propargyl *N*-tosyl amides **2**.

the extension of the CIR to *N*-propargyl tosyl amide substrates that opens a new access to *N*-tosyl enimines. This class of electron deficient heterodienes, substrates for Diels-Alder reactions with inverse electron demand, is perfectly suited for the development of three-component pyridine syntheses. In addition, we report first examples of CIR-cycloaddition sequences in a one-pot fashion.

We submitted electron deficient aromatic and heteroaromatic halides 1, and N-[1-(hetero)aryl-prop-2ynyl] tosyl amides 2 [7] to the reaction conditions of the CIR [2] in a boiling mixture of triethylamine and THF to give after trituration of the crude products in ethanol the N-tosyl enimines 3 in moderate to excellent yield as crystalline solids (Scheme 2) [8]. However, it should be mentioned that, due to the hydrolytic sensitivity of the enimine functionality, column chromatography often led to the isolation of the corresponding chalcones. Therefore, purification of the crude enimines is most efficiently achieved by recrystallization from ethanol or ethyl acetate/hexane mixtures.

According to <sup>1</sup>H NMR spectra of crude **3**, both *E*and *Z*-diastereomers with respect to the C=C bond are formed with an E/Z ratio ranging from 1:1 (**3g**) to 7:1 (**3f**) [9]. The *trans*-isomer is characterized by the appearance of doublets with large vicinal coupling constants ( $J_{trans} = \sim 16.0$  Hz) for the  $\alpha$ -olefinic methine resonances at  $\delta = 6.9 - 7.1$ . An E/Z isomerism of the imine bond was not observed. Recrystallized samples of **3** are considerably enriched with the *trans*-



Fig. 1. ORTEP plots of compounds 3a (top) and 3b (bottom).

isomer (E/Z = > 95 :< 5). The characteristic quaternary imine carbon resonances can be found in the <sup>13</sup>C NMR spectra between  $\delta = 168 - 175$ . Furthermore, the structure of *trans-3* is unambiguously supported by X-ray crystal structure analyses (Fig. 1, Table 1) of compounds **3a** and **3b** [10].

With the *N*-tosyl enimines **3** that can be considered as electron deficient heterodienes in hand, the stage is set for the development of a one-pot CIR-cycloaddition sequence by combining CIR with a Diels-Alder reaction with inverse electron demand [11]. This concept was tested, after performing the CIR with the electron poor (hetero)aryl halides and the *N*-propargyl tosyl amide **2a**, by adding the electron rich diethyl ketene acetal to the reaction mixture; after reaction times of 24-48 h, the 2-ethoxy pyridines **4** were isolated in moderate to good yield as colorless to yellow crystals or as a light yellow oil (**4c**) (Scheme 3).

Mechanistically, the formation of 2-ethoxypyridines **4** can be rationalized by a [4+2] cycloaddition, either concerted or stepwise, of the transient

Compound	3a	3b	4b
Empirical formula	C <sub>23</sub> H <sub>20</sub> N <sub>2</sub> O <sub>5</sub> S	$C_{20}H_{16}N_2O_4S_2$	C <sub>23</sub> H <sub>23</sub> NO <sub>4</sub>
Formula weight	436.47	412.47	377.42
Temperature K	293(2)	293(2)	200(2)
Wavelength Å	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}2_{1}2_{1}$
Z	4	4	16
Unit cell dimensions	$a = 11.995(4)$ Å, $\alpha = 90^{\circ}$	$a = 14.2250(12)$ Å, $\alpha = 90^{\circ}$	$a = 13.9831(4)$ Å, $\alpha = 90^{\circ}$
	$b = 9.073(2)$ Å, $\beta = 105.90(2)^{\circ}$	$b = 20.025(2)$ Å, $\beta = 102.11(1)^{\circ}$	$b = 23.5154(7)$ Å, $\beta = 90^{\circ}$
	$c = 20.350(4)$ Å, $\gamma = 90^{\circ}$	$c = 6.930(2)$ Å, $\gamma = 90^{\circ}$	$c = 23.8147(7)$ Å, $\gamma = 90^{\circ}$
Volume Å <sup>3</sup>	2130.0(10)	1930.1(5)	7830.7(4)
Density (calculated) g/cm <sup>3</sup>	1.361	1.419	1.28
Absorption coefficient mm <sup>-1</sup>	0.190	0.305	0.09
Crystal size mm <sup>3</sup>	0.53  imes 0.37  imes 0.13	0.57  imes 0.30  imes 0.10	0.40 imes 0.30 imes 0.08
Theta range for data collection, deg.	2.33 to 23.98	2.51 to 23.97	1.7 to 22.0
Index ranges	$-13 \le h \le 13$	$-15 \le h \le 16$	$-14 \le h \le 14$
-	$0 \le k \le 10$	$-22 \le k \le 0$	$-24 \le k \le 24$
	$-23 \le l \le 0$	$-7 \leq l \leq 0$	$-25 \le l \le 25$
Reflections collected	3848	3283	51474
Independent reflections	3332 (R(int) = 0.0223)	3005 (R(int) = 0.0188)	9569 ( $R(int) = 0.0846$ )
Observed reflections	$3332 (I > 2\sigma(I))$	$3005 (I > 2\sigma(I))$	5890 ( $I > 2\sigma(I)$ )
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9962 and 0.8998	0.9981 and 0.9332	0.99 and 0.97
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3332 / 0 / 282	3005 / 0 / 254	9569 / 0 / 1009
Goodness-of-fit on $F^2$	1.093	1.058	1.06
Final <i>R</i> indices $(I > 2\sigma(I))$	R1 = 0.0547, wR2 = 0.1230	R1 = 0.0449, wR2 = 0.1088	R1 = 0.048, wR2 = 0.098
Largest diff. peak and hole $e^{A^{-3}}$	0.169 and -0.263	0.250 and -0.338	0.18 and -0.20

Table 1. Crystal data and structure refinements for 3a, 3b, and 4b.



Scheme 3. Three-component synthesis of 2-ethoxy pyridines **4** by CIR-cyclocondensation.

N-tosyl enimines **3** to furnish a tetrahydropyridine intermediate. However, the excellent leaving group

propensity of the *N*-tosyl group could lead to a base induced elimination giving rise to a dihydropyridine that rapidly eliminates ethanol with concomitant aromatization thereby concluding the formation of the aromatic pyridine core under these reaction conditions.

The structure of the 2-ethoxy-6-(p-anisyl)pyridines 4 is unambiguously supported by the expected appearance of the characteristic proton and carbon resonances and multiplicities. In particular, in the <sup>1</sup>H NMR spectra of 4 the diagnostic triplets for the ethoxy methyl proton signals at  $\delta = 1.35 - 1.46$  (J = 7.1 Hz) and the quartets for the ethoxy methylene protons at  $\delta =$ 4.39 - 4.53 (J = 7.1 Hz) are applied for the assignments of the 3-methine doublets of the newly formed pyridyl core at  $\delta = 6.73 - 7.05 (J = 1.3 \text{ Hz})$  by 2D-NOESY spectra, indicating clear cross-peaks as a consequence of spatial proximity. Most distinctly, the 5methine resonances couple to the 3-methine protons and, thus, also appear as doublets at  $\delta = 7.41 - 8.49$ (J = 1.3 Hz). Additionally, the mass spectrometric, IR spectroscopic, and combustion analytical data are in full agreement with the suggested molecular structure of the 2-ethoxy-pyridines 4. Furthermore, the structure



Fig. 2. ORTEP plot of compound 4b.

of **4** is corroborated by an X-ray crystal structure analysis of compound **4b** (Fig. 2, Table 1) [10].

In conclusion, we have demonstrated that the CIR can successfully extended to the synthesis of *N*-tosyl enimines starting from propargyl *N*-tosyl amides. These electron deficient heterodienes are perfectly suited as reaction partners in Diels-Alder reactions with inverse electron demand. Therefore, we could design a one-pot three-component synthesis of 2-ethoxy pyridines by CIR-cyclocondensation sequence. This novel consecutive pyridine synthesis not only enhances molecular and structural diversity in a combinatorial sense and potentially in solid phase applications, but it also allows a rapid construction of complex multicore heterocyclic arrays. Studies addressing CIR-cycloaddition sequences, their scope and limitations are currently underway.

#### **Experimental Section**

All reactions involving palladium-copper catalysis were performed in degassed oxygen free solvents under a nitrogen atmosphere using Schlenk and syringe techniques. Halogen compounds, tosyl amide, aldehydes, ethynylmagnesium bromide (1*M* in THF), (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>, and CuI were purchased reagent grade from ACROS, Aldrich, Fluka or Merck and used without further purification. Triethylamine, THF, and acetonitrile were dried and distilled according to standard procedures [12]. *N*-Tosyl imines were prepared in accordance with procedures described in the literature [12]. – Column chromatography: silica gel 60 (Merck, Darmstadt), mesh 70–230. TLC: silica gel plates (60 F<sub>254</sub> Merck, Darmstadt). Melting points (uncorrected values): Büchi Melting

Point B-540. – <sup>1</sup>H and <sup>13</sup>C NMR spectra: Bruker ARX 300, Varian VXR 400S CDCl<sub>3</sub> and  $[D_6]$ -DMSO. The assignments of quaternary C, CH, CH<sub>2</sub> and CH<sub>3</sub> have been made by using DEPT spectra. – IR: Perkin Elmer Lambda 3. – UV/vis: Perkin Elmer Models Lambda 16. MS: Finnigan MAT 90 and MAT 95 Q. – Elemental analyses were carried out in the Microanalytical Laboratories of the Department Chemie der Ludwigs-Maximilians-Universität München and the Organisch-Chemisches Institut der Universität Heidelberg.

#### N-[1-(hetero)aryl-prop-2-ynyl] tosyl amides 2

General procedure: To 1.3 equiv. of a 0.5 M solution of ethynyl magnesium bromide in THF at 0 °C (ice-water) 1.0 equiv. of a solution of the corresponding azomethine in THF (1.25 mmol/ml) was added dropwise within 15 min. After stirring of the suspension for 15 min at 0 °C the reaction mixture was stirred for 1 h at room temperature. After the reaction was complete according to TLC monitoring 120 ml of a saturated aqueous solution of NH<sub>4</sub>Cl was added to the reaction mixture and the aqueous phase was extracted three times with diethylether (3 × 100 ml). The combined organic layers were dried with anhydrous magnesium sulfate and after evaporation sufficiently pure (according to <sup>1</sup>H NMR spectra) *N*-[1-(hetero)aryl-prop-2-ynyl] tosyl amide **2** was isolated such that it could be recrystallized from ethanol in case of impurities.

#### *N*-[1-(4-Methoxyphenyl)-prop-2-ynyl]-4-methyl-benzenesulfonamide (**2a**)

According to the *GP* from the reaction of 10.1 g (34.5 mmol) of *N*-(4-methoxybenzylidene)-4-methyl-benzenesulfonamide [12] and 102 ml (52 mmol) of a 0.5 *M* solution of ethynyl magnesium bromide in 45 ml of THF, 7.3 g (89%) of **2a** were obtained as colorless crystals.

M. p. 124.5 - 125.5 °C. – IR (KBr): v = 3266, 2969, 2935, 2116, 1611, 1598, 1512, 1434, 1330, 1306, 1289, 1251, 1159, 1175, 1092, 1052, 970, 943, 922, 829, 815, 771, 703, 672, 574, 574, 548 cm<sup>-1</sup>. – <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 2.29$  (d, J = 2.3 Hz, 1 H), 2.41 (s, 3 H, TolMe), 3.76 (s, 3 H, OMe), 5.17 (d, J = 8.6 Hz, 1 H), 5.23 (dd, J = 2.2, 8.6 Hz, 1 H), 6.79 (d, J = 8.7 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.33 (d, J = 8.7 Hz, 2 H), 7.73 (d, J = 8.3 Hz, 2 H). – <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 21.5$ (CH3, TolMe), 48.4 (CH), 55.2 (CH3, OMe), 74.5 (CH), 80.6 (Cquat.), 113.9 (CH), 127.4 (CH), 128.4 (CH), 129.1 (Cquat.), 129.4 (CH), 137.3 (Cquat.), 143.4 (Cquat.), 159.6  $(C_{\text{quat.}})$ . – MS (70 eV, EI): m/z (%) = 315 (M<sup>+</sup>, 2), 159 (M<sup>+</sup>) - C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub> - H, 100), 145 (M<sup>+</sup> - C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub> - NH, 45), 91 (C<sub>7</sub>H<sub>7</sub>, 13). - C<sub>17</sub>H<sub>17</sub>NO<sub>3</sub>S (315.4): calcd. C 64.74 H 5.43, N 4.44, S 10.17; found C 64.76, H 5.47, N 4.38, S 10.08.

#### 4-Methyl-N-[1-(thien-2-yl)-prop-2-ynyl]-benzenesulfonamide (2b)

According to the *GP* from the reaction of 13.3 g (50.0 mmol) of 4-methyl-*N*-(thiophen-2-ylmethylene)-benzenesulfonamide [12] and 123 ml (63 mmol) of a 0.5 *M* solution of ethynyl magnesium bromide in 70 ml of THF, 13.7 g (94%) of **2b** were obtained as colorless crystals.

M. p. 121–122 °C. – IR (KBr): v = 3269, 3118, 2940, 2122, 1596, 1493, 1432, 1330, 1290, 1229, 1165, 1092, 1058, 1039, 925, 815, 715, 673, 648, 587, 569, 550 cm<sup>-1</sup>. – <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 2.33$  (d, J = 2.3 Hz, 1 H), 2.42 (s, 3 H, Tol*Me*), 5.23 (d, J = 8.9 Hz, 1 H), 5.51 (d, J = 8.9 Hz, 1 H), 6.87–6.90 (m, 1 H), 7.08 (d, J = 3.5 Hz, 1 H), 7.22 (dd, J = 7.8 Hz, J = 1.2 Hz, 1 H), 7.28 (d, J = 8.2 Hz, 2 H), 7.77 (d, J = 8.4 Hz, 2 H). – <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 21.5$  (CH<sub>3</sub>, Tol*Me*), 44.8 (CH), 74.0 (CH), 80.0 (C<sub>quat</sub>.), 126.4 (CH), 126.5 (CH), 126.8 (CH), 127.4 (CH), 129.5 (CH), 137.1 (C<sub>quat</sub>.), 140.7 (C<sub>quat</sub>.), 143.7 (C<sub>quat</sub>.). – MS (70 eV, EI): m/z (%) = 291 (M<sup>+</sup>, 2), 155 (C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub>, 5), 136 (M<sup>+</sup> - C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub>, 100), 91 (C<sub>7</sub>H<sub>7</sub>, 21). – C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub>S<sub>2</sub> (291.4): calcd. C 57.71, H 4.50, N 4.81, S 22.01; found C 57.62, H 4.50, N 4.81, S 21.54.

#### 4-Methyl-N-[1-(4-phenoxyphenyl)-prop-2-ynyl]-benzenesulfonamide (2c)

According to the *GP* from the reaction of 2.73 g (7.77 mmol) of 4-methyl-N-(4-phenoxy-benzylidene)-benzenesulfonamide [12] and 19 ml (9.8 mmol) of a 0.5 *M* solution of ethynyl magnesium bromide in 10 ml of THF, 2.4 g (82%) of 2c were obtained as colorless crystals.

M. p. 96-97 °C. – IR (KBr): v = 3281, 3065, 2929, 2119, 1657, 1581, 1506, 1490, 1415, 1333, 1262, 1158, 1091, 1053, 963, 842, 813, 693, 669, 545  $\rm cm^{-1}.-^{1}H~\rm NMR$ (300 MHz, CDCl<sub>3</sub>):  $\delta = 2.31$  (d, J = 0.7 Hz, 1 H), 2.41 (s, 3H, TolMe), 5.27 (br, 2 H), 6.90 (d, J = 8.7 Hz, 2 H), 6.97 (dd, J = 0.8, 8.7 Hz, 2 H), 7.11 (t, J = 7.4 Hz, 1 H), 7.26 (d, J = 8.1 Hz, 2 H), 7.31 (dd, J = 0.8, 8.0, 2 H), 7.35 - 7.40 (m, 2 H), 7.75 (d, J = 8.3 Hz, 2 H). – <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 21.5$  (CH<sub>3</sub>, Tol*Me*), 48.4 (CH), 74.7 (CH), 80.4 (Cquat.), 118.6 (CH), 119.1 (CH), 123.6 (CH), 127.4 (CH), 128.7 (CH), 129.4 (CH), 129.8 (CH), 131.6 (Cquat.), 137.2 (Cquat.), 143.5 (Cquat.), 156.6 (Cquat.), 157.5 (Cquat.). - MS (70 eV, EI): m/z (%) = 377 (M<sup>+</sup>, 2), 222 (M<sup>+</sup> - C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub>, 80), 207 (M<sup>+</sup> - C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub> - NH, 28), 155 (C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub>, 7), 91 (C<sub>7</sub>H<sub>7</sub>, 44). - C<sub>22</sub>H<sub>19</sub>NO<sub>3</sub>S (377.5): calcd. C 70.01, H 5.07, N 3.71, S 8.49; found C 69.82, H 5.18, N 3.64, S 8.49.

#### General procedure for the enimine synthesis

A magnetically stirred solution of 1 equiv. of (het)aryl halide 1, 1.05 equiv. of propargyl N-tosyl amine 2, 14 mg (0.02 mmol) of Pd(PPh<sub>3</sub>)Cl<sub>2</sub>, and 2 mg (0.01 mmol) of CuI

in 4 ml of degassed triethylamine and 5 ml of THF under nitrogen was heated to reflux temperature for 24-48 h. After cooling to room temperature 30 ml of diethyl ether was added to the reaction mixture. After filtration the solvents were removed *in vacuo* and the residue was washed with ethanol to give the enimines **5**. Further purification could be achieved by recrystallization from ethanol or trituration with ethanol.

#### *N*-[1-(4-*Methoxyphenyl*)-3-(4-*nitrophenyl*)-allylidene]-4methyl-benzenesulfonamide (**3a**)

According to the *GP* the reaction of 473 mg (1.90 mmol) of 4-iodo-1-nitrobenzene (**1a**) and 631 mg (2.00 mmol) of **2a** furnished, after recrystallization from ethanol, 332 mg (40%) of **3a** as brown yellow crystals.

M. p. 148–150 °C. – IR (KBr): v = 3070, 2936, 1599, 1516, 1420, 1344, 1309, 1259, 1176, 1152, 1092, 1025, 958, 870, 847, 834, 823, 776, 755, 683, 665, 596, 568, 544 cm<sup>-1</sup>. – <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.42 (s, 3 H, TolMe), 3.87 (s, 3 H, OMe), 6.94 (d, J = 8.8 Hz, 2 H), 7.04 (d, J = 16.3 Hz, 1 H), 7.32 (d, J = 8.2 Hz, 2 H), 7.71 (d, J = 8.6 Hz, 2 H), 7.72 (d, J = 8.7 Hz, 2 H), 7.90 (d, J =8.3 Hz, 2 H), 8.03 (d, J = 16.3 Hz, 1 H), 8.24 (d, J = 8.7 Hz, 2 H).  $-{}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 21.5$  (CH<sub>3</sub>, Tol*Me*), 55.5 (CH<sub>3</sub>, OMe), 114.0 (CH), 124.1 (CH), 127.1 (CH), 128.8 (CH, br), 129.4 (CH), 130.9 (Cquat.), 132.5 (CH), 138.5 (Cquat.), 140.8 (Cquat.), 142.4 (CH), 143.6 (Cquat.), 148.5 (C<sub>quat.</sub>), 163.7 (C<sub>quat.</sub>), 175.2 (C<sub>quat.</sub>, C=N). - MS (70 eV, EI): m/z (%) = 436 (M<sup>+</sup>, 0.3), 280 (M<sup>+</sup> - C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub>, 100), 251 (M<sup>+</sup> - C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub> - NH -N, 71), 155 (C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub>, 5), 134  $(C_7H_4NO_2, 6), 91 (C_7H_7, 23). - C_{23}H_{20}N_2O_5S$  (436.5): calcd. C 63.29, H 4.62, N 6.42, S 7.35; found C 63.02, H 4.73, N 6.55, S 7.48.

#### 4-Methyl-N-[3-(4-nitrophenyl)-1-(thien-2-yl)-allylidene]benzene sulfonamide (**3b**)

According to the *GP* the reaction of 453 mg (1.80 mmol) of 4-iodo-1-nitrobenzene (**1a**) and 557 mg (1.90 mmol) of **2b** furnished, after recrystallization from ethanol, 368 mg (49%) of **3b** as light yellow crystals.

M. p. 180.7 – 181 °C. – IR (KBr): v = 3084, 2925, 1624, 1598, 1519, 1413, 1346, 1303, 1152, 1089, 979, 840, 785, 747, 668, 552, 536 cm<sup>-1</sup>. – <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 2.42$  (s, 3 H, Tol*Me*), 7.16 (t, J = 4.8 Hz, 1 H), 7.26 (d, J = 2.2 Hz, 1 H), 7.30–7.32 (m, 2 H), 7.69 (m, 2 H), 7.73 (d, J = 8.9 Hz, 2 H), 7.90 (d, J = 8.3 Hz, 2 H), 7.94 (d, J = 16.2 Hz, 1 H), 8.25 (d, J = 8.7 Hz, 2 H). – <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 21.5$  (CH<sub>3</sub>, Tol*Me*), 124.1 (CH), 126.1 (CH), 127.1 (CH), 128.5 (CH), 128.8 (CH), 129.4 (CH), 135.4 (CH), 135.6 (CH), 138.1 (C<sub>quat</sub>.), 140.6 (C<sub>quat</sub>.), 140.9 (C<sub>quat</sub>.), 141.8 (C<sub>quat</sub>.), 143.7 (CH), 148.5 (C<sub>quat</sub>.), 168.293 (C<sub>quat</sub>., *C*=N). – MS (70 eV, EI): m/z (%) = 412 (M<sup>+</sup>, 0.2), 317 (M<sup>+</sup> - C<sub>5</sub>H<sub>3</sub>S, 16), 256 (M<sup>+</sup> - C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub>, 100), 155 (C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub>, 9), 91 (C<sub>7</sub>H<sub>7</sub>, 21). - C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (412.5): calcd. C 58.24, H 3.91, N 6.79, S 15.55; found C 58.26, H 3.99, N 6.82, S 15.59.

# *N-[3-(4-Cyanophenyl)-1-(4-methoxyphenyl)-allylidene]-4-methyl-benzenesulfonamide* (**3c**)

According to the *GP* the reaction of 182 mg (1.00 mmol) of 4-bromobenzonitrile (**1b**) and 331 mg (1.05 mmol) of **2a** furnished, after recrystallization from ethanol, 375 mg (90%) of **3c** as light yellow crystals.

M. p. 129–132 °C. – IR (KBr): v = 3064, 2930, 2228, 1604, 1578, 1511, 1419, 1315, 1259, 1175, 1154, 1090, 1026, 836, 819, 781, 671, 548 cm<sup>-1</sup>. – <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 2.42$  (s, 3 H, Tol*Me*), 3.87 (s, 3 H, O*Me*), 6.94 (d, J = 8.8 Hz, 2 H), 7.04 (d, J = 16.3 Hz, 1 H), 7.32 (d, J = 16.3 Hz)8.2 Hz, 2 H), 7.71 (d, J = 8.6 Hz, 2 H), 7.72 (d, J = 8.7 Hz, 2 H), 7.90 (d, J = 8.3 Hz, 2 H), 8.03 (d, J = 16.1 Hz, 1 H), 8.24 (d, J = 8.7 Hz, 2 H). – <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 21.5 (CH<sub>3</sub>, TolMe), 55.5 (CH<sub>3</sub>, OMe), 114.0 (CH), 124.1 (CH), 127.1 (CH), 128.8 (CH), 129.4 (CH), 130.9 (Cquat.), 132.5 (CH), 138.5 (Cquat.), 140.8 (Cquat.), 142.4 (CH), 143.6 (Cquat.), 148.5 (Cquat.), 163.7 (Cquat.), 175.2 (Cquat., C=N). -MS (70 eV, EI): m/z (%) = 416 (M<sup>+</sup> +2H, 2), 261 (M<sup>+</sup> - C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub>, 100), 247 (M<sup>+</sup> - C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub> - NH, 12), 155  $(C_7H_7SO_2, 6), 91 (C_7H_7, 20). - C_{24}H_{20}N_2O_3S$  (416.5): calcd. C 69.21, H 4.84, N 6.73; found C 69.11, H 4.39, N 6.99.

#### *N-[3-(4-Cyanophenyl)-1-(4-phenoxyphenyl)-allylidene]-4methyl-benzenesulfonamide* (**3d**)

According to the *GP* the reaction of 182 mg (1.00 mmol) of 4-bromobenzonitrile (**1b**) and 396 mg (1.05 mmol) of **2c** furnished, after recrystallization from ethanol, 450 mg (94%) of **3d** as light yellow crystals.

M. p. 137.5 – 138.5 °C. – IR (KBr): v = 3060, 2920, 2228, 1605, 1622, 1585, 1533, 1502, 1488, 1320, 1305, 1247, 1198, 1168, 1154, 1093, 1020, 972, 867, 814, 787, 694, 674, 574, 540 cm<sup>-1</sup>. – <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.42 (s, 3 H, TolMe), 6.99 (d, J = 8.6 Hz, 2 H), 7.03 (d, J = 16.2 Hz, 1 H), 7.07 (d, J = 8.0 Hz, 2 H), 7.18–7.25 (m, 1 H), 7.32 (d, J = 8.2 Hz, 2 H), 7.37 - 7.42 (m, 2 H), 7.64 - 7.71 (m, 6 H), 7.91 (d, J = 8.2 Hz, 2 H), 8.02 (d, J = 9.0 Hz, 1 H). – <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 21.5$  (CH<sub>3</sub>, Tol*Me*), 117.3 (CH, br), 118.3 (C<sub>quat.</sub>), 120.2 (CH), 124.8 (CH), 126.2 (Cquat.), 127.1 (CH), 128.7 (CH), 129.5 (CH), 130.1 (CH), 130.1 (Cquat.), 132.4 (CH), 132.6 (CH), 138.4 (Cquat.), 138.8 (Cquat.), 143.6 (CH), 155.2 (Cquat.), 162.1 (Cquat.), 175.2  $(C_{quat.}, C=N). - MS (70 \text{ eV}, \text{EI}); m/z (\%) = 478 (M^+, 1), 323$ (M<sup>+</sup> - C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub>, 100), 231 (C<sub>7</sub>H<sub>8</sub><sup>+</sup>, 25), 155 (C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub>, 3), 91 (C<sub>7</sub>H<sub>7</sub>, 8). - C<sub>29</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>S (478.6): calcd. C 72.78, H 4.63, N 5.85; found C 72.70, H 4.76, N 5.75.

*N-[1-(4-Methoxyphenyl)-3-(4-trifluoromethylphenyl)allylidene]-4-methyl-benzenesulfonamide* (**3e**) [9]

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>), mixture of two isomers (*trans/cis* = 4 : 1):  $\delta$  = 2.24 (s, 3 H, Tol*Me*), 3.69 (s, 3 H, O*Me*), 6.76–6.84 (m, 1 H), 6.87 (d, *J* = 16.2 Hz, 1 H), 7.03–7.22 (m, 2 H), 7.47–7.67 (m, 6 H), 7.76–7.79 (m, 2 H), 7.87–7.93 (m, 2 H).

#### *N*-[1-(4-Methoxyphenyl)-3-(pyridin-2-yl)-allylidene]-4methyl-benzenesulfonamide (**3f**) [9]

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>), mixture of two isomers (*trans/cis* = 7 : 1):  $\delta$  = 2.29 (s, 3 H, Tol*Me*), 3.73 (s, 3 H, O*Me*), 6.80 – 6.88 (m, 2 H), 6.87 (d, *J* = 16.0 Hz, 1 H), 7.07 – 7.20 (m, 4 H), 7.40 (d, *J* = 7.6 Hz, 1 H), 7.58 – 7.68 (m, 6 H), 7.76 – 7.79 (m, 3 H), 7.80 (dt, *J* = 1.7, 8.4 Hz, 1 H), 7.98 – 8.19 (m, 1H), 8.55 (d, *J* = 4.8 Hz, 1 H).

#### *N*-[1-(4-Methoxy-phenyl)-3-pyrimidin-2-yl-allylidene]-4methyl-benzenesulfonamide (**3g**) [9]

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>), mixture of two isomers (*trans/cis* = 1 : 1):  $\delta$  = 2.21 (s, 3 H, Tol*Me*), 3.71 (s, 3 H, O*Me*), 6.78–6.88 (m, 3 H), 7.01–7.23 (m, 4 H), 7.57–7.69 (m, 2 H), 7.78 (d, *J* = 6.0 Hz, 1 H), 7.73 (dt, *J* = 2.0, 7.0 Hz, *J* = 2 Hz, 1 H), 8.64–8.67 (m, 2 H).

#### General procedure for the synthesis of 2-ethoxy-6-p-anisylpyridines

A magnetically stirred solution of 1 equiv. of (het)aryl halide 1, 1.05 equiv. of propargyl N-tosyl amine 2, 14 mg (0.02 mmol) of Pd(PPh<sub>3</sub>)Cl<sub>2</sub>, and 2 mg (0.01 mmol) of CuI in 4 ml of degassed triethylamine and 5 ml of THF or toluene under nitrogen was heated to reflux temperature for 24-48 h. After cooling to room temperature a solution of 4 mmol of diethyl ketene acetal in 5 ml of THF or acetonitrile were added and the reaction mixture was heated to reflux temperature for 24-48 h. After cooling to room temperature 40 ml of ethyl acetate and 40 ml of water were added and stirring was continued for 5 to 10 min. The aqueous layer was extracted with ethyl acetate  $(4 \times 15 \text{ ml})$  and the combined organic phases were dried with magnesium sulfate. After evaporation of the solvents in vacuo the residue was chromatographed on silica gel (hexane/ethyl acetate 4:1 or 1:1) and recrystallized from ethanol or pentane/chloroform (1:1) to give the analytically pure pyridine derivatives 4.

# *4-[2-Ethoxy-6-(4-methoxyphenyl)-pyridin-4-yl]-benzonitrile* (**4**a)

According to the *GP* the reaction of 182 mg (1.00 mmol) of 4-bromobenzonitrile (**1b**), 331 mg (1.05 mmol) of **2a**,

and 470 mg (4.00 mmol) of diethyl ketene acetal in acetonitrile furnished, after chromatography on silica gel (hexane/ethyl acetate, 4:1) and recrystallization from ethanol, 188 mg (57%) of **4a** as yellow crystals.

M. p. 97-98 °C. – IR (KBr): v = 3065, 2973, 2227(C≡N), 1602, 1545, 1515, 1425, 1380, 1342, 1296, 1260, 1260, 1176, 1037, 830, 586, 516 cm<sup>-1</sup>. – <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 1.46$  (t, J = 7.3 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 3.86 (s, 3 H, OMe), 4.53 (q, J = 7.1 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 6.77 (d, J = 1.1 Hz, 1 H), 6.98 (d, J = 8.9 Hz, 2 H), 7.41 (d, J = 1.1 Hz, 1 H), 7.70-7.76 (m, 4 H), 8.02 (d, J = 8.8 Hz, 2 H). –  $^{13}\text{C}$  NMR (CDCl\_3, 75 MHz):  $\delta$  = 14.7 (CH\_3), 55.4 (CH<sub>3</sub>, OMe), 61.9 (CH<sub>2</sub>, OCH<sub>2</sub>CH<sub>3</sub>), 106.5 (CH), 110.4 (CH), 112.5 (Cquart.), 114.1 (CH), 118.6 (Cquart.), 127.8 (CH), 128.1 (CH), 131.4 (Cquart.), 132.7 (CH), 143.5 (Cquart.), 149.9 (Cquart.), 155.5 (Cquart.), 160.7 (Cquart.), 164.2 (C<sub>quart.</sub>). – MS (70 eV, EI): m/z (%) = 330.1 (M<sup>+</sup>, 43), 315  $(M^+ - CH_3, 100), 302 (M^+ - C_2H_4, 30). - C_{21}H_{18}N_2O_2$ (330.4): calcd. C 76.34, H 5.49, N 8.48; found C 76.25, H 5.47, N 8.39.

# 4-[2-Ethoxy-6-(4-methoxyphenyl)-pyridin-4-yl]-benzoic acid ethyl ester (**4b**)

According to the *GP* the reaction of 229 mg (1.00 mmol) of ethyl 4-bromobenzoate (**1f**), 331 mg (1.05 mmol) of **2a**, and 470 mg (4.00 mmol) of diethyl ketene acetal in toluene furnished, after chromatography on silica gel (hexane/ethyl acetate, 5:1) and recrystallization from ethanol, 94 mg (25%) of **4b** as colorless crystals.

M. p. 96 °C. – UV/vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}(\lg \varepsilon) = 272$  (4.62), 322 (4.00). – IR (KBr): v = 2979, 1715, 1605, 1549, 1516, 1427, 1342, 1278, 1253, 1241, 1208, 1183, 1105, 834, 774, 587 cm<sup>-1</sup>. – <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 1.30$  (t, J = 7 Hz, 3 H, CH<sub>3</sub>), 1.34 (t, J = 7 Hz, 3 H, CH<sub>3</sub>), 3.76 (s, 3 H, OMe), 4.27 (q, J = 7 Hz, 2 H), 4.40 (q, J = 7 Hz, 2 H), 6.73 (d, J = 1.25 Hz, 1 H), 6.87 – 6.93 (m, 2 H), 7.37 (d, J = 1.0 Hz, 1 H), 7.59 - 7.62 (m, 2 H), 7.91 - 7.97 (m, 2 H), 8.01-8.07 (m, 2 H). - <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta = 14.3$  (CH<sub>3</sub>), 14.7 (CH<sub>3</sub>), 55.3 (CH<sub>3</sub>, OMe), 61.07 (CH<sub>2</sub>, OCH<sub>2</sub>CH<sub>3</sub>), 61.67 (CH<sub>2</sub>, OCH<sub>2</sub>CH<sub>3</sub>), 106.5 (CH), 110.5 (CH), 114.0 (CH), 125.9 (CH), 128.0 (CH), 130.1 (CH), 130.6 (Cquat.), 131.6 (Cquat.), 143.2 (Cquat.), 150.7 (Cquat.), 155.1 (Cquat.), 160.5 (Cquat.), 164.1 (Cquat.), 166.2 (Cquat.). -MS (70 eV, EI): m/z (%) = 377 (M<sup>+</sup>, 72), 362 (M<sup>+</sup> - CH<sub>3</sub>, 100), 348.9 ( $M^+$  -  $C_2H_4$ , 42). -  $C_{23}H_{23}NO_4$  (377.4): calcd. C 73.19, H 6.14, N 3.71; found C 73.18, H 6.09, N 3.82.

#### 2-Ethoxy-6-(4-methoxyphenyl)-4-(4-trifluoromethylphenyl)pyridine (**4c**)

According to the *GP* the reaction of 272 mg (1.00 mmol) of 4-iodobenzotrifluoride (**1e**), 331 mg (1.05 mmol) of **2a**, and 470 mg (4.00 mmol) of diethyl ketene acetal in toluene

furnished, after chromatography on silica gel (hexane/ethyl acetate, 1:1) and recrystallization from ethanol, 111 mg (30%) of **4c** as a light yellow oil.

UV/vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}(\lg \varepsilon) = 260 \text{ nm } (4.40), 290$ (4.00), 296 (3.98), 322 (4.05), 348 (3.36). – IR (KBr): v = 2981, 2932, 1607, 1551, 1515, 1428, 1381, 1342, 1326, 1252, 1207, 1177, 1127, 1068, 1036, 1017, 830 cm<sup>-1</sup>. – <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 1.37$  (t, J = 7.0 Hz, 3 H, CH<sub>3</sub>), 3.8 (s, 3 H, OMe), 4.43 (q, J = 7.0 Hz, 2 H), 6.74 (d, J = 1.3 Hz, 1 H), 6.91 – 6.96 (m, 2 H), 7.40 (d, J = 1.3 Hz, 1 H), 7.94 – 8.00 (m, 2 H). – <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta = 14.72$  (CH<sub>3</sub>), 55.36 (CH<sub>3</sub>, OMe), 61.78 (CH<sub>2</sub>, OCH<sub>2</sub>CH<sub>3</sub>), 106.6 (CH), 110.6 (CH), 114.0 (CH), 125.86 (CH), 125.91 (CH), 127.4 (CH), 128.1 (CH), 131.6 (CH), 150.4 (C<sub>quat.</sub>), 155.3 (C<sub>quat.</sub>), 160.5 (C<sub>quat.</sub>), 164.2 (C<sub>quat.</sub>). – HRMS-EI (70 eV, m/z) (C<sub>21</sub>H<sub>18</sub>F<sub>3</sub>NO<sub>2</sub>): calcd. 373.1281; found 373.1303.

#### 2'-Ethoxy-6'-(4-methoxyphenyl)-[2,4']bipyridinyl (4d)

According to the *GP* the reaction of 158 mg (1.00 mmol) of 2-bromo pyridine (**1d**), 331 mg (1.05 mmol) of **2a**, and 470 mg (4.00 mmol) of diethyl ketene acetal in toluene furnished, after chromatography on silica gel (hexane/ethyl acetate, 1:1) and recrystallization from ethanol, 199 mg (65 %) of **4d** as yellow crystals.

M. p. 98.5 °C. – UV/vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}(\lg \varepsilon) = 254$  nm (4.25), 264 (4.39), 290 (4.12), 328 (4.03). – IR (KBr): v =2970, 2935, 2895, 1611, 1588, 1577, 1555, 1516, 1473, 1432, 1416, 1383, 1343, 1297, 1255, 1215, 1205, 1178, 1040, 833, 785 cm<sup>-1</sup>. – <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 1.38 (t, J = 7.3, 3 H, CH<sub>3</sub>), 3.73 (s, 3 H, OMe), 4.39 (q, J = 7.0 Hz, 2 H), 6.85 – 6.91 (m, 2 H), 7.05 (d, J = 1.3 Hz, 1 H), 7.15-7.23 (m, 1 H), 7.64-7.67 (m, 2 H), 7.83 (d, J = 1.3 Hz, 1 H), 7.96-8.02 (m, 2 H), 8.6 (dt, J = 1.3, 4.5 Hz, 1 H).  $-{}^{13}$ C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta = 14.8$  (CH<sub>3</sub>), 55.3 (CH<sub>3</sub>, OMe), 61.7 (CH<sub>2</sub>, OCH<sub>2</sub>CH<sub>3</sub>), 106.0 (CH), 110.1 (CH), 113.9 (CH), 121.1 (CH), 123.6 (CH), 128.2 (CH), 131.1 (C<sub>quat.</sub>), 137.1 (CH), 149.8 (CH), 155.2 (C<sub>quat.</sub>), 155.3  $(C_{quat.})$ , 160.4  $(C_{quat.})$ , 164.3  $(C_{quat.})$ . – MS (70 eV, EI): m/z(%) = 306.2 (M<sup>+</sup>, 90), 291 (M<sup>+</sup> - CH<sub>3</sub>, 100), 278 (M<sup>+</sup> - $C_2H_4$ , 30), 247 (M<sup>+</sup> - CH<sub>3</sub>, -  $C_2H_5O$ , 12). -  $C_{19}H_{18}N_2O_2$ (306.4): calcd. C 74.49, H 5.92, N 9.14; found C 73.96, H 5.91, N 8.93.

# 2-[2-*Ethoxy*-6-(4-*methoxyphenyl*)-*pyridin*-4-*yl*]-*pyrimidine* (**4e**)

According to the *GP* the reaction of 160 mg (1.00 mmol) of 2-bromopyrimidine (1e), 331 mg (1.05 mmol) of 2a, and 470 mg (4.00 mmol) of diethyl ketene acetal in toluene furnished, after chromatography on silica gel (hexane/ethyl acetate, 1:1) and recrystallization from ethanol, 141 mg (46%) of **4e** as colorless crystals.

M. p. 120.9 °C. – UV/vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}(\lg \varepsilon) = 272$  nm (4.62), 322 (4.00). – IR (KBr): v = 2979, 1715, 1605, 1549, 1516, 1427, 1342, 1278, 1253, 1241, 1208, 1183, 1105, 834, 774 cm<sup>-1</sup>. – <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 1.27 - 1.35$  (m, 3 H, CH<sub>3</sub>), 3.77 (s, 3 H), 4.36 (q, J = 7.2 Hz, 2 H), 7.28 (t, J = 4.9 Hz, 1 H), 7.44 – 7.53 (m, 3 H), 8.13 – 8.15 (m, 2 H), 8.49 (s, 1 H), 8.83 (d, J = 4.9 Hz, 2 H). – <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta = 14.8$  (CH<sub>3</sub>), 55.4 (CH<sub>3</sub>, OMe), 61.9 (CH<sub>2</sub>, OCH<sub>2</sub>CH<sub>3</sub>), 107.2 (CH), 110.6 (CH), 113.9 (CH), 128.2 (CH), 131.8 (Cquat.), 155.2 (Cquat.), 157.3 (Cquat.), 160.4 (Cquat.), 164.5 (Cquat.). – MS (70 eV, EI): m/z (%) = 307

 $(M^{+},\,57),\,291$   $(M^{+}$  -  $CH_{3},\,100),\,279$   $(M^{+}$  -  $C_{2}H_{4},\,34).$  –  $C_{18}H_{17}N_{3}O_{2}$  (307.4): calcd. C 70.34, H 5.58, N 13.67; found C 70.12, H 5.50, N 13.66.

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- [10] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-229839 (3a), CCDC-229838 (3b), and CCDC-229868 (4b). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).
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