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Synthesis and Reactions of 1-Azo-2-azonia-allene Salts Derived from Pyridine Derivatives

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Summary. The 1-aza-2-azonia-allene salts prepared from 3-acetyl- or 3-benzoyl-pyridine *via* the corresponding hydrazone and α-chloroaryl-azo derivatives react with propionitrile to afford the corresponding 3-(3-pyridyl)-1,2,4-triazolium salts. The intramolecular cyclization products could be only isolated as the main products if the intermediate α-chlorophenyl-azo derivatives prepared from 4-benzoyl pyridine were treated with $SbCl_5$ in presence or absence of propionitrile. Also, only 3-methyl-1,2,3-triazolo[1,5-*a*]pyridinium salts were obtained by reaction of the cumulene prepared from 2-acetyl-pyridine with or without propionitrile in good yields. Treatment of 3-pyridylindazolium hexachloroantimonates and 3-methyl-1,2,3-triazolo[1,5-*a*]pyridinium salts with Na_2CO_3 gave 3-pyridylindazoles and 3-methyl-1,2,3-triazolo[1,5-*a*]pyridine.

Keywords. Cycloadditions; Hydrazones; Indazoles; Triazolium; Pyridines.

Synthese und Reaktionen von aus Pyridinderivaten abgleiteten 1-Azo-2-azoniumallensalzen

Zusammenfassung. Die 1-Aza-2-azoniasalze, die aus 3-Acetyl- oder 3-Benzoylpyridin über die entsprechenden Hydrazone und α-Chlorazoderivate dargestellt wurden, reagieren mit Propionitril zu den entsprechenden 3-(3-Pyridyl)-1,2,4-triazoliumsalzen. Intramolekulare Cyklisierungsprodukte konnten nur isoliert werden, wenn die intermediären α-Chlorphenylazoderivate aus Benzoylpyridin abgeleitet wurden und mit $SbCl_5$ mit oder ohne Propionitril umgesetzt wurden. Ebenso wurden im Fall der Reaktion des Cumulens aus 2-Acetylpyridin mit oder ohne Propionitril nur die 3-Methyl-1,2,3-triazolo[1,5-*a*]pyridiniumsalze in guten Ausbeuten erhalten. Behandlung von 3-Pyridylindazoliumhexachloroantimonaten mit Na_2CO_3 ergab 3-Pyridylindazole und 3-Methyl-1,2,3-triazolo[1,5-*a*]pyridine.

Introduction

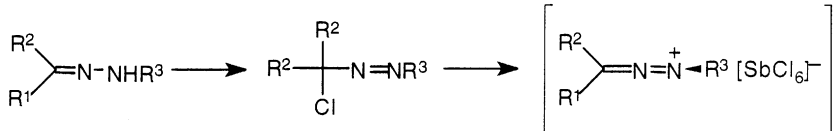
A series of studies have been directed towards the reaction of 1-aza-2-azonia-allene salts with multiple bonds [1–5]. These compounds, prepared from hydrazones with substituents such as methyl, phenyl, *etc*. have been postulated by *Jochims* as intermediates in the cycloaddition to many types of multiple bonds [3–11]. It seemed of interest to study the applicability of the cycloaddition protocol for heterocumulenes derived from the three isomeric acetyl- and benzoyl-pyridines. In the present study, the effect of the pyridyl ring in the heterocumulenes during the cycloaddition of compounds **3a–i** with nitriles will be investigated. The objective of such a study was to elucidate the site selectivity of this procedure with respect to

a synthetic method to obtain substituted triazolium and/or indazolium salts. Recently, some indazole derivatives have been reported as inhibitors of phosphodiesterase IV and tumor necrosis factor production [12]. This assessment prompted us to prepare derivatives of 3-pyridylindazole from 3-pyridyl-indazolium salts starting from azoazonia-allene salts to make them available for biological testing.

Results and Discussion

The synthesis of 3,4-dimethyl-3-pyridyl-4-yl-1-(2,4,6-trichlorophenyl)-3*H*-[1,2,4]-triazolium hexachloroantimonate from N-(1-pyridin-yl-ethylidene)-N′-(2,4,6-trichlorophenyl)-hydrazine (**1d**) and acetonitrile in the presence of a *Lewis* acid has been described previously [2]. The results of further experiments designed to explore the scope and the limitations of this procedure as a synthetic method for the formation of the pyridyl-triazolium salts **5a–b** and **8d** and the 3-pyridylindazoles **7** and **10e–g** are the subject of the present investigation. For this purpose a series of pyridyl hydrazones (**1a–i**) were synthesized by treatment of 2,4,6-trichlorophenylhydrazine, ethyl carbazate, and phenyl hydrazine with the pyridyl ketones 3-acetyl-pyridine, 3-benzoyl-pyridine, 4-acetyl-pyridine, 4-benzoyl-pyridine, or 2-acetyl-pyridine. Oxidation of **1a–i** by *tert*-butylhypochloride gave the geminal chloropyridyl-azo compounds **2a–i** in good yields (Scheme 1).

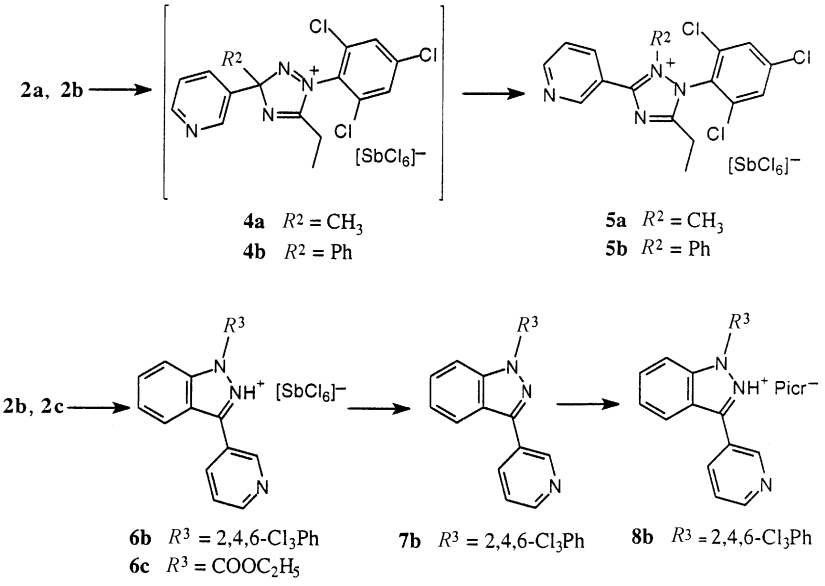
When **2a–i** were treated with the *Lewis* acid $SbCl_5$ at −60°C, they afforded the highly reactive 1-aza-2-azonia allene salts **3a–i**. It was found that it is possible to trap **3a**, **b** with nucleophiles such as propionitrile to obtain the triazolium salts **5** (Scheme 2). To rationalize the formation of **5a**, **b**, one has to assume the formation of intermediates **4a**, **b** which undergo a 1,2-shift of the substituent R^2. Treatment of **2b**, **c** with $SbCl_5$ in CH_2Cl_2 at −50°C induced an intramolecular cyclization to afford the 3-pyridyl-3-yl-1*H*-indazolium hexachloroantimonates **6b**, **c** in good yields. It is worth noting the complete regioselectivity of the cycloaddition, the



1 **2** **3**

	R^1	R^2	R^3
1a–3a	3-pyridyl	CH_3	2,4,6-trichlorophenyl
1b–3b	3-pyridyl	Ph	2,4,6-trichlorophenyl
1c–3c	3-pyridyl	Ph	$COOC_2H_5$
1d–3d	4-pyridyl	CH_3	2,4,6-trichlorophenyl
1e–3e	4-pyridyl	Ph	2,4,6-trichlorophenyl
1f–3f	4-pyridyl	Ph	$COOC_2H_5$
1g–3g	4-pyridyl	Ph	Ph
1h–3h	2-pyridyl	CH_3	2,4,6-trichlorophenyl
1i–3i	2-pyridyl	CH_3	$COOC_2H_5$

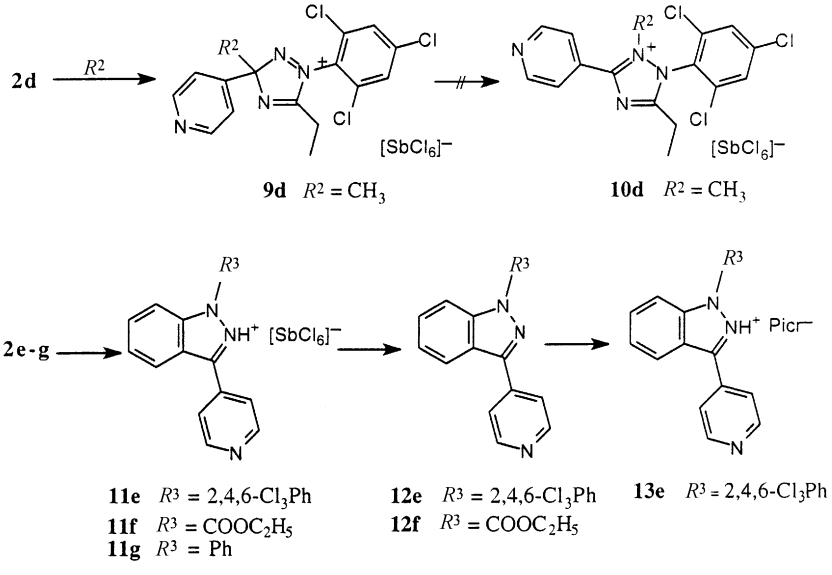
Scheme 1



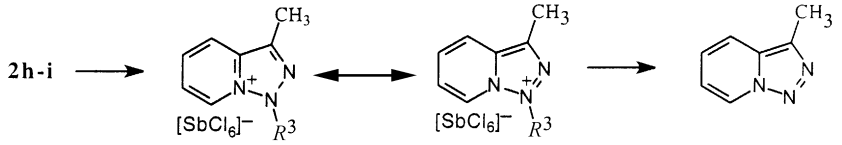
Scheme 2

complete site selectivity of the rearrangement, and the exclusive migration of phenyl. On the other hand, no condensation products from intramolecular cyclization at the carbon pyridine could be observed (Scheme 2).

The reaction of the cumulene **3d** with propionitrile afforded only the 3*H*-triazolium salt **9d** without migration of the methyl group from carbon to nitrogen (Scheme 3). The triazolium derivatives **9d** and **10d** can easily be distinguished by their ^{1}H NMR methyl reasonances which appear in the range of 2.3 to 2.6 ppm for **9d** and of 3.8 to 4.1 ppm for **10d**. This is in contrast to the results for 3-acetyl-



Scheme 3



14h R^3 = 2,4,6-Cl_3Ph
14i R^3 = $COOC_2H_5$

15

Scheme 4

pyridine. Also, the reaction of the cumulenes **3e–g** with or without propionitrile afforded only the indazolium salts **11e–g** *via* intramolecular cyclization. The expected triazolium salts did not form in contrast to cumulene **3b** prepared from 3-benzoyl-pyridine (Scheme 3).

Similarly, only the 3-methyl-1,2,3-triazolo[1,5]pyridinium salts **14h–i** were isolated when the cumulenes **3h–i** were treated with or without propionitrile, and no traces of the expected triazolium salts could be observed (Scheme 4).

In conclusion, only the cumulenes **3a**, **b** derived from 3-acetyl- or 3-benzoyl-pyridine show regioselectivity in the cycloaddition reaction with nitrile. This is in contrast to the cumulenes **3e–i** derived from 4-benzoyl- or 2-acetyl-pyridine.

Treatment of 3-pyridyl-indazolium salts **6b** and **11e–g** as well as the 3-methyl-1,2,3-triazolo[1,5]pyridinium salt **14i** with aqueous sodium carbonate yielded the 3-pyridyl-indazole derivatives **7b**, **12e–g**, and 3-methyl-1,2,3-triazolo[1,5]pyridine **15** in good yields. This method provides a possible starting point for the synthesis of many new indazole derivatives. Furthermore, treatment of indazoles **7b** or **12e** with picric acid afford the pure indazolium picrates **8b** or **13e**. The structures of all novel compounds were confirmed by their elemental and spectroscopic data.

Experimental

Melting points were measured on a Kofler hot stage microscope (Reichert, Vienna) and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 200 spectrometer at 200 MHz (^{1}H) and 50 MHz (^{13}C); chemical shifts are given in δ units relative to internal *TMS* at 295 K. IR spectra were obtained on a Biorad FT-IR-45 instrument. All experiments were carried out with exclusion of moisture. For all new compounds satisfactory elemental analyses were obtained.

Preparation of hydrazones **1**

A mixture of 100 mmol of ketone (3-acetyl-pyridine, 3-benzoyl-pyridine, 4-benzoyl-pyridine, or 2-acetyl-pyridine) and 100 mmol hydrazine in 70 ml methanol + 1 ml acetic acid was heated under reflux for 5 h. Evaporation of the solvent and crystallization of the residue afforded the pure hydrazone. N-(1-pyridin-4-yl-ethylidene)-N′-(2,4,6-trichlorophenyl)-hydrazine (**1d**) was prepared according to Ref. [2].

N-(1-Pyridin-3-yl-ethylidene)-N′-(2,4,6-trichlorophenyl)-hydrazine (**1a**; $C_{13}H_{10}Cl_3N_3$)

Prepared from 12.10 g 3-acetyl-pyridine (100 mmol) and 21.15 g 2,4,6-trichlorophenylhydrazine (100 mmol); crystallization from petrol ether (50–70°C) gave 29.85 g colourless fine crystals (95%);

m.p.: 86–90°C; IR (KBr): $\nu = 3350$ br, 2950 br, 1610, 1480, 1450 cm^{-1}; ^1H NMR ($CDCl_3$): 2.37 (s, CH_3), 7.38 (m, 3H, $H_{py+trichlorophenyl}$), 7.47 (s, NH), 8.13–8.19 (dd, $1H_{py}$), 8.56–8.59 (dd, $1H_{py}$), 8.97 (d, $1H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 21.38 (CH_3), 133.45, 135.87, 137.63, 138.53, 144.02, 144.42, 146.90, 152.53, 154.91, 157.09 (aryl, C=N) ppm.

N-(Phenyl-pyridin-3-yl-methylene)-N′-(2,4,6-trichlorophenyl)-hydrazine (**1b**; $C_{18}H_{12}Cl_3N_3$)

Prepared from 18.32 g 3-benzoyl-pyridine (100 mmol) and 21.15 g 2,4,6-trichlorophenyl-hydrazine (100 mmol); crystallization from methanol gave 3.48 g colourless fine crystals (89%); m.p.: 118–120°C; IR (KBr): $\nu = 3360$ br, 3130, 1620, 1580, 1520, 1490 cm^{-1}; ^1H NMR ($CDCl_3$): 7.29 (m, $5H_{ar}$), 7.47 (s, NH), 7.55–7.62 (m, $3H_{ar}$), 7.79 (dd, $1H_{py}$), 8.73 (d, H_{py}), 8.83 (s, $2H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 133.96, 135.78, 136.05, 137.23, 138.03, 138.47, 138.63, 139.82, 146.42, 146.74, 154.85, 159.26, 160.41 (aryl, C=N) ppm.

N-Ethoxycarbonyl-N′-(phenyl-pyridin-3-yl-methylene)-hydrazine (**1c**; $C_{15}H_{15}N_3O_2$)

Prepared from 18.32 g 3-benzoyl-pyridine (100 mmol) and 10.41 g ethyl carbazate (100 mmol); crystallization from petrol ether (50–70°C) gave 4.18 g colourless fine crystals (90%); m.p.: 72–74°C; IR (KBr): $\nu = 3350$, 3046, 2985, 1738, 1690, 1600, 1580, 1585, 1568, 1522 cm^{-1}; ^1H NMR ($CDCl_3$): 1.31 (t, $J = 7.1$ Hz, CH_3), 4.27 (q, $J = 7.1$ Hz, CH_2), 7.28–7.82 (m, $6H_{ar}$), 8.05 (d, $1H_{py}$), 8.35 (br, NH), 8.60–8.76 (m, $2H_{py}$) ppm.

N-(Phenyl-pyridin-4-yl-methylene)-N′-(2,4,6-trichlorophenyl)-hydrazine (**1e**; $C_{18}H_{12}Cl_3N_3$)

Prepared from 18.32 g 4-benzoyl-pyridine (100 mmol) and 21.15 g 2,4,6-trichlorophenyl-hydrazine (100 mmol); crystallization from ethanol gave 35.79 g colourless fine crystals (95%); m.p.: 140–145°C; IR (KBr): $\nu = 3360$, 3135, 1620, 1580, 1568, 1520 cm^{-1}; ^1H NMR ($CDCl_3$): 7.31–7.66 (m, $9H_{ar}$), 7.84 (s, NH), 8.55 (d, $2H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 129.99, 133.02, 135.42, 135.98, 137.25, 138.05, 138.21, 138.56, 139.60, 140.35, 145.87, 154.36, 154.98, 159.48, 161.03 (aryl, C=N) ppm.

N-Ethoxycarbonyl-N′-(phenyl-pyridin-4-yl-methylene)-hydrazine (**1f**; $C_{15}H_{15}N_3O_2$)

Prepared from 18.32 g 4-benzoyl-pyridine (100 mmol) and 10.41 g ethyl carbazate (100 mmol); crystallization from ethanol gave 20.75 g colourless fine crystals (77%); m.p.: 180°C; IR (KBr): $\nu = 3346$, 3133 br, 3046, 2986, 1739, 1689, 1599, 1585, 1522 cm^{-1}; ^1H NMR ($CDCl_3$): 1.32 (t, $J = 7.1$ Hz, CH_3), 4.27 (q, $J = 7.1$ Hz, CH_2), 7.22 (d, $2H_{ar}$), 7.36 (s, $3H_{ar}$), 7.53 (d, $2H_{py}$), 7.66 (s, NH), 8.86 (d, $2H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 24.04 (CH_3), 71.76 (CH_2), 131.55, 132.68, 136.82, 137.83, 139.49, 145.21, 149.72, 156.54, 157.71, 160.92, 162.00 (aryl, C=N) ppm.

N-Phenyl-N′-(phenyl-pyridin-4-yl-methylene)-hydrazine (**1g**; $C_{18}H_{15}N_3$)

Prepared from 18.32 g 4-benzoyl-pyridine (100 mmol) and 10.81 g phenylhydrazine (100 mmol) after heating for 15 min; crystallization from $CHCl_3$/MeOH gave 24.00 g yellowish white fine crystals (88%); m.p.: 192–196°C; IR (KBr): $\nu = 3352$ br, 3133, 3040, 1620, 1580, 1518 cm^{-1}; ^1H NMR ($CDCl_3$): 6.92 (t, $1H_{ar}$), 7.10 (d, $2H_{ar}$), 7.30 (m, $4H_{ar}$), 7.48 (d, $2H_{py}$), 7.56 (m, $3H_{ar}$), 7.84 (s, NH), 8.49 (d, $2H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 123.00, 130.01, 130.97, 138.65, 138.93, 139.52, 139.72, 140.41, 150.05, 153.03, 156.38, 157.73, 161.01 (aryl, C=N) ppm.

N-(1-Pyridin-2-yl-ethylidene)-N′-(2,4,6-trichlorophenyl)-hydrazine (**1h**; $C_{13}H_{10}Cl_3N_3$)

Prepared from 12.10 g 2-acetyl-pyridine (100 mmol) and 21.15 g 2,4,6-trichlorophenyl-hydrazine (100 mmol); yellow orange oil which slowly solidifies at −15°C; crystallization from petrol ether

(50–70°C) gave 28.35 g fine crystals (90%); m.p.: 54°C; IR (KBr): $\nu = 3350$ br, 3135, 3040, 1618, 1579, 1567, 1490 cm^{-1}; ^1H NMR ($CDCl_3$): 2.50 (s, CH_3), 7.23 (t, $1H_{py}$), 7.38 (s, $2H_{trichlorophenyl}$), 7.63 (s, NH), 7.68 (t, $1H_{py}$), 8.15 (d, $1H_{py}$), 8.60 (d, $1H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 19.65 (CH_3), 129.74, 132.18, 132.57, 135.50, 137.04, 138.51, 145.71, 147.06, 157.04, 157.93, 165.34 (aryl, C=N) ppm.

N-Ethoxycarbonyl-N′-(1-pyridin-2-yl-ethylidene)-hydrazine (**1i**; $C_{10}H_{13}N_3O_2$)

Prepared from 12.10 g 2-acetyl-pyridine (100 mmol) and 10.41 g ethyl carbazate (100 mmol); crystallization from ethylacetate/petrol ether (50–70°C) gave 24.18 g colourless fine crystals (90%); m.p.: 110–112°C; IR (KBr): $\nu = 3355$, 3133, 2985, 2905, 1740, 1690, 1600, 1567, 1518 cm^{-1}; ^1H NMR ($CDCl_3$): 1.34 (t, $J = 7.1$ Hz, CH_3), 2.38 (s, 3H, CH_3), 4.33 (q, $J = 7.1$ Hz, CH_2), 7.22 (t, $1H_{py}$), 7.75 (t, $1H_{py}$), 8.10 (s, NH), 8.20 (d, $1H_{py}$), 8.64 (d, $1H_{py}$) ppm.

Preparation of α-chloroaryl-azo compounds **2**

The reaction was carried out in the dark. 13.03 g *tert*-butylhypochlorite (120 mmol) were added dropwise to a cold (−10°C) solution of 100 mmol hydrazones **1a–i** in 120 ml $CHCl_3$. The mixture was stirred for 3 h at 0°C. Evaporation of the solvent afforded the orange-yellow compounds **2**. In most cases, the oil thus obtained was used without further purification. 1-Chloro-1-pyridin-4-yl-ethyl-(2,4,6-trichlorophenyl)-diazene (**2d**) was prepared according to Ref. [2].

1-Chloro-1-pyridin-4-yl-ethyl-(2,4,6-trichlorophenyl)-diazene (**2a;** $C_{13}H_9Cl_4N_3$)

Prepared from 3.14 g **1a** (10 mmol); yield: 3.30 g (95%) as a yellow oil; ^1H NMR ($CDCl_3$): 2.38 (s, CH_3), 7.44 (s, $2H_{trichlorophenyl}$), 7.45 (m, $1H_{py}$), 8.06 (tt, $1H_{py}$), 8.66 (dd, $1H_{py}$), 8.97 (d, $1H_{py}$) ppm. ^{13}C NMR ($CDCl_3$): 39.31 (CH_3), 103.47 (CCl), 133.29, 135.43, 136.70, 138.63, 143.84, 145.36, 146.34, 154.69, 156.58, 158.55 (aryl) ppm.

Chloro-phenyl-pyridin-3-yl-methyl-(2,4,6-trichlorophenyl)-diazene (**2b**; $C_{18}H_{11}Cl_4N_3$)

Prepared from 3.76 g **1b** (10 mmol); yield: 4.00 g (98%) as an orange oil; ^1H NMR ($CDCl_3$): 7.27–7.50 (m, $7H_{ar}$), 8.07 (dd, $1H_{py}$), 8.65 (dd, $1H_{py}$), 8.95 (d, $2H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 105.30 (CCl), 136.38, 136.75, 137.15, 137.33, 137.44, 137.97, 138.24, 138.71, 139.61, 145.06, 146.83, 150.26, 150.77, 151.64, 154.87 (aryl) ppm.

Chloro-phenyl-pyridin-3-yl-methyl-ethoxycarbonyl-diazene (**2c**: $C_{15}H_{14}ClN_3O_2$)

Prepared from 2.69 g **1c** (10 mmol); yield: 2.40 g (80%) as a reddish oil which solidified at −15°C; IR (CCl_4): $\nu = 3025$, 2985, 1750, 1610, 1580, 1500 cm^{-1}.

Chloro-phenyl-pyridin-4-yl-methyl-(2,4,6-trichlorophenyl)-diazene (**2e**; $C_{18}H_{11}Cl_4N_3$)

Prepared from 3.76 g **1e** (10 mmol); yield: 4.05 g (99%) as a brown oil; ^1H NMR ($CDCl_3$): 7.40 (s, $5H_{ph}$), 7.56–7.59 (m, 4H, H_{py} and $H_{trichlorophenyl}$), 8.69 (d, $2H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 108.37 (CCl), 132.57, 135.39, 136.89, 137.76, 138.20, 138.66, 138.59, 139.71, 143.99, 148.65, 154.86, 159.35, 159.88 (aryl) ppm.

Chloro-phenyl-pyridin-4-yl-methyl-ethoxycarbonyl-diazene (**2f**; $C_{15}H_{14}ClN_3O_2$)

Prepared from 2.69 g **1f** (10 mmol); yield: 2.50 g (83%) as a brown oil which solidified at −15°C; ^{1}H NMR ($CDCl_3$): 1.44 (t, $J = 7.1$ Hz, CH_3), 4.48 (q, $J = 7.1$ Hz, CH_2), 7.38 (s, $5H_{ar}$), 7.50 (d, $2H_{ar}$), 7.55 (m, $2H_{ar}$), 8.67 (d, $2H_{py}$) ppm.

Chloro-phenyl-pyridin-4-yl-methyl-phenyl-diazene (**2g**; $C_{18}H_{14}ClN_3$)

Prepared from 2.73 g **1g** (10 mmol); yield: 2.65 g (85%) as a orange red oil; ^{1}H NMR ($CDCl_3$): 7.36–7.56 (m, $10H_{ar}$), 7.81–7.91 (d, $2H_{py}$), 8.64 (d, $2H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 107.15 (CCl), 132.47, 132.57, 133.09, 134.38, 137.47, 138.20, 138.63, 138.88, 139.17, 144.78, 149.97, 158.57, 158.94 (aryl) ppm.

1-Chloro-1-pyridin-2-yl-ethyl-(2,4,6-trichlorophenyl)-diazene (**2h**; $C_{13}H_9Cl_4N_3$)

Prepared from 3.14 g **1h** (10 mmol); yield: 3.47 g (100%) as a yellow oil which solidified to give a yellow powder; m.p.: 75°C; ^{1}H NMR ($CDCl_3$): 2.46 (s, CH_3), 7.29 (t, $1H_{py}$), 7.42 (s, $2H_{trichlorophenyl}$), 7.72 (d, $1H_{py}$), 7.76 (t, $1H_{py}$), 8.70 (d, $1H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 37.31 (CH_3), 105.75 (CCl), 132.26, 135.44, 136.58, 138.51, 140.07, 143.44, 146.49, 158.59, 167.24 (aryl) ppm.

1-Chloro-1-pyridin-2-yl-ethyl-ethoxycarbonyl-diazene (**2i**; $C_{10}H_{12}ClN_3O_2$)

Prepared from 2.07 g **1i** (10 mmol); yield: 1.90 g (79%) as a yellow oil; ^{1}H NMR ($CDCl_3$): 1.36 (t, $J = 7.1$ Hz, CH_3), 2.27 (s, CH_3), 4.39 (q, $J = 7.1$ Hz, CH_2), 7.20 (t, $1H_{py}$), 7.32 (d, $1H_{py}$), 7.64 (t, $1H_{py}$), 8.59 (d, $2H_{py}$) ppm.

Reactions of the α-chloroarylazo compounds with propionitrile and formation of [1,2,4]triazolium hexachloroantimonates **5a–b** *and* **9b**

A solution of 2.99 g $SbCl_5$ (10 mmol) in 10 ml CH_2Cl_2 was added dropwise to a cold (−60°C) solution of 10 mmol of the α-chloroarylazo compound and 15 mmol nitrile in 25 ml CH_2Cl_2. The mixture was stirred at −60°C for 2 h, then at 0°C for 1 h, and finally at room temperature for 15 min. The solvent was evaporated under reduced pressure, and the remaining salt was purified by crystallization.

5-Ethyl-2-methyl-3-pyridyl-3-yl-1-(2,4,6-trichlorophenyl)-1H-[1,2,4]triazolium hexachloroantimonate (**5a**; $C_{16}H_{14}Cl_9N_4Sb$)

Prepared from 3.49 g **2a** (10 mmol), 2.99 g $SbCl_5$ (10 mmol), and 0.83 g propionitrile (15 mmol); the residue was crystallized at −20°C from acetonitrile/ether to yield 5.73 g colourless fine crystals (82%); m.p.: 188–193°C; IR (KBr): $\nu = 3077$, 2942, 1635, 1567, 1560, 1507, 1488, 1460, 1389, 1379 cm^{-1}; ^{1}H NMR (*DMSO*-d_6): 1.30 (t, $J = 7.5$ Hz, CH_3), 2.84 (q, $J = 7.5$ Hz, CH_2), 4.05 (s, NCH_3), 7.75 (dd, $1H_{py}$), 8.35 (s, $2H_{trichlorophenyl}$), 8.50 (dd, $1H_{py}$), 8.94 (dd, $1H_{py}$), 9.25 (d, $1H_{py}$) ppm; ^{13}C NMR (*DMSO*-d_6): 20.55 (CH_3), 29.52 (CH_2), 46.13 (NCH_3), 130.46, 132.91, 134.19, 135.43, 140.80, 145.51, 147.96, 150.79, 159.99, 163.61, 167.40, 173.89 (aryl, C=N) ppm.

5-Ethyl-2-phenyl-3-pyridyl-3-yl-1-(2,4,6-trichlorophenyl)-1H-[1,2,4]triazolium hexachloroantimonate (**5b**; $C_{21}H_{16}Cl_9N_4Sb$)

Prepared from 4.11 g **2b** (10 mmol), 2.99 g $SbCl_5$ (10 mmol), and 0.83 g propionitrile (15 mmol); the residue was crystallized at −20°C from acetonitrile/ether to yield 4.21 g colourless fine crystals

(55%); m.p.: 206–208°C; IR (KBr): $\nu = 3078$, 2974, 1637, 1567, 1558, 1507, 1488, 1458, 1433, 1389, 1379 cm^{-1}; ^1H NMR (*DMSO*-d_6): 1.41 (t, CH_3), 2.97 (q, CH_2), 7.40–7.62 (m, $4H_{ar}$), 7.66 (d, $2H_{ar}$), 7.81 (dd, $1H_{ar}$), 8.15 (s, $2H_{ar}$), 8.79 (s, $2H_{ar}$) ppm; ^1H NMR (CD_3CN): 1.46 (t, $J = 7.5$ Hz, CH_3), 2.96 (q, $J = 7.5$ Hz, CH_2), 7.64–7.66 (s, $4H_{ar}$), 7.76 (m, $1H_{ar}$), 7.78 (s, $2H_{ar}$), 8.20 (m, $1H_{ar}$), 8.50 (d, $1H_{ar}$), 8.96 (s, d, $2H_{ar}$) ppm; ^{13}C NMR (*DMSO*-d_6): 20.59 (CH_3), 29.73 (CH_2), 130.23, 133.18, 133.50, 134.05, 137.25, 139.99, 140.33, 144.20, 145.60, 147.66, 150.70, 159.84, 163.66, 167.65, 174.97 (aryl, C=N) ppm.

5-Ethyl-3-methyl-3-pyridyl-4-yl-1-(2,4,6-trichlorophenyl)-1H-[1,2,4]triazolium hexachloroantimonate (**9d**; $C_{16}H_{14}Cl_9N_4Sb$)

Prepared from 3.49 g **2d** (10 mmol), 2.99 g $SbCl_5$ (10 mmol), and 0.83 g propionitrile (15 mmol); the residue was crystallized at −20°C from acetonitrile and ether to yield 4.55 g faint yellow fine crystals (65%); m.p.: 222°C; IR (KBr): $\nu = 3077$, 2972, 1615, 1560, 1550, 1531, 1485, 1450, 1390 cm^{-1}; ^1H NMR (*DMSO*-d_6): 1.38 (t, $J = 7.5$ Hz, CH_3), 2.39 (s, CH_3), 2.88 (q, $J = 7.5$ Hz, CH_2), 7.96 (d, $2H_{py}$), 8.35 (s, $2H_{trichlorophenyl}$), 9.12 (d, $2H_{py}$) ppm.

General procedure for the preparation of 3-pyridyl-1H-indazolium salts **6b**, **c** *and* **11e–g**

A solution of 2.99 g $SbCl_5$ (10 mmol) in 10 ml CH_2Cl_2 was added dropwise to a solution of 10 mmol α-chlorophenyl-azo derivatives **2** in 25 ml CH_2Cl_2 at −50°C. The mixture was stirred for 1 h at −50°C, then for 1 h at 0°C, and for 15 min at room temperature. The solvent was evaporated and the residue was crystallized to give the pure indazolium derivatives.

3-Pyridyl-3-yl-1-(2,4,6-trichlorophenyl)-1H-indazolium hexachloroantimonate (**6b**; $C_{18}H_{11}Cl_9N_3Sb$)

Prepared from 4.11 g **2b** (10 mmol) and 2.99 g $SbCl_5$ (10 mmol); the residue was crystallized at −20°C from acetonitrile/ether to yield fine crystals (4.40 g, 62%); m.p.: 217–220°C; IR (KBr): $\nu = 3278$, 3168, 3083, 1631, 1598, 1574, 1553, 1525, 1511, 1488, 1453 cm^{-1}; ^1H NMR (*DMSO*-d_6): 7.40–7.59 (m, $3H_{ar}$), 8.05 (d, $1H_{ar}$), 8.09 (s, $2H_{trichlorophenyl}$), 8.31 (d, $1H_{ar}$), 8.88 (d, $1H_{ar}$), 8.99 (d, $1H_{ar}$), 9.46 (s, $1H_{ar}$), 11.50 (br, NH) ppm; ^1H NMR (CD_3CN): 7.37 (d, $1H_{ar}$), 7.52–7.66 (m, $2H_{ar}$), 7.85 (s, $2H_{trichlorophenyl}$), 8.22 (d, $2H_{ar}$), 8.75 (t, $1H_{ar}$), 9.24–9.35 (m, $2H_{ar}$), 13.50 (br, NH) ppm; ^{13}C NMR (*DMSO*-d_6): 120.94, 130.74, 131.21, 133.45, 136.87, 138.66, 139.46, 140.53, 142.48, 145.22, 146.33, 151.02, 151.11, 151.75, 152.26, 153.80 (aryl, C=N) ppm; ^{13}C NMR (CD_3CN): 120.22, 130.05, 130.57, 133.55, 137.78, 138.39, 139.06, 141.82, 142.74, 145.18, 146.58, 149.05, 149.48, 150.02, 151.83, 154.46 (aryl, C=N) ppm.

1-Ethoxycarbonyl-3-pyridyl-3-yl-1H-indazolium hexachloroantimonate (**6c**; $C_{15}H_{14}Cl_6N_3O_2Sb$)

Prepared from 3.03 g **2c** (10 mmol) and 2.99 g $SbCl_5$ (10 mmol); the residue was crystallized at −20°C from acetonitrile/ether to yield 2.10 g fine crystals (35%); m.p.: 94–97°C; IR (KBr): $\nu = 3246$, 3088, 3062, 2983, 1740, 1671, 1654, 1635, 1599, 1577, 1559, 1541, 1497 cm^{-1}; ^1H NMR (CD_3CN): 1.23 (t, $J = 7.1$ Hz, CH_3), 4.18 (q, $J = 7.1$ Hz, CH_2), 7.34–7.87 (m, $5H_{ar}$), 8.65–9.03 (m, $3H_{ar}$), 12.78 (br, NH) ppm.

3-Pyridyl-4-yl-1-(2,4,6-trichlorophenyl)-1H-indazolium hexachloroantimonate (**11e**; $C_{18}H_{11}Cl_9N_3Sb$)

Prepared from 4.11 g **2e** (10 mmol), with or without propionitrile (15 mmol), and 2.99 g $SbCl_5$ (10 mmol); the residue was crystallized at −20°C from acetonitrile to yield 5.00 g fine crystals

(71%); m.p.: 217–222°C; IR (KBr): $\nu = 3277$, 3166, 3083, 1632, 1598, 1574, 1553, 1525, 1511, 1487 cm^{-1}; ^1H NMR (*DMSO*-d_6): 7.47–7.60 (m, $3H_{ar}$), 8.11 (s, $2H_{trichlorophenyl}$), 8.43 (d, $1H_{ar}$), 8.65 (d, $2H_{ar}$), 8.96–9.00 (d, $2H_{ar}$), 11.50 (br, NH) ppm; ^1H NMR (CD_3CN): 7.20 (d, $1H_{ar}$), 7.40–7.69 (m, $2H_{ar}$), 7.86 (s, $2H_{trichlorophenyl}$), 8.34–8.38 (d, $1H_{ar}$), 8.69–8.83 (m, $4H_{ar}$), 13.00 (br, NH) ppm; ^{13}C NMR (CD_3CN): 120.53, 130.36, 131.23, 133.68, 134.37, 135.44, 138.52, 139.12, 142.10, 145.01, 146.79, 150.00, 151.32, 152.19, 161.01 (aryl, C=N) ppm.

1-Ethoxycarbonyl-3-pyridyl-4-yl-1H-indazolium hexachloroantimonate (**11f**; $C_{15}H_{14}Cl_6N_3O_2Sb$)

Prepared from 3.03 g **2f** (10 mmol) and 2.99 g $SbCl_5$ (10 mmol); the residue was crystallized at −20°C from acetonitrile/ether to yield 2.30 g fine crystals (38%); m.p.: 203°C; IR (KBr): $\nu = 3126$, 3062, 2984, 1740, 1642, 1605, 1579, 1541, 1510, 1489 cm^{-1}; ^1H NMR (CD_3CN): 1.29 (t, $J = 7.1$ Hz, CH_3), 4.24 (q, $J = 7.1$ Hz, CH_2), 7.35–7.69 (m, $4H_{ar}$), 8.03 (d, $2H_{ar}$), 8.57 (t, $2H_{ar}$), 12.80 (br, NH) ppm.

1-Phenyl-3-pyridyl-4-yl-1H-indazolium hexachloroantimonate (**11g**; $C_{18}H_{14}Cl_6N_3Sb$)

From 3.07 g **2g** (10 mmol), with or without propionitrile (15 mmol), and 2.99 g $SbCl_5$ (10 mmol); the residue was crystallized at −20°C from acetonitrile and ether to yield 3.00 g greenish yellow fine crystals (48%); m.p.: 215–220°C; IR (KBr): $\nu = 3196$, 3096, 3080, 2923, 2255 (w), 1635, 1595, 1560, 1525, 1507, 1497 cm^{-1}; ^1H NMR (*DMSO*-d_6): 7.54–7.92 (m, $8H_{ar}$), 8.45 (d, $1H_{ar}$), 8.67 (d, $2H_{ar}$), 8.96 (d, $2H_{ar}$) ppm; ^{13}C NMR (*DMSO*-d_6): 121.84, 127.59, 131.09, 132.41, 134.10, 134.41, 134.50, 135.01, 138.31, 138.53, 139.13, 139.96, 148.62, 150.44, 158.10 (aryl, C=N) ppm.

3-Methyl-1-(2,4,6-trichlorophenyl)-1,2,3-triazolo[1,5-a]pyridinium hexachloroantimonate (**14h**; $C_{13}H_9Cl_9N_3Sb$)

Prepared from 3.49 g **2h** (10 mmol), with or without propionitrile (15 mmol), and 2.99 g $SbCl_5$ (10 mmol) as described for **6b**; the residue was crystallized from acetonitrile to yield 6.00 g faint yellow prisms (91%); m.p.: 185–188°C; IR (KBr): $\nu = 3095$, 3030, 1625, 1576, 1556, 1485, 1432, 1378 cm^{-1}; ^1H NMR (CD_3CN): 2.89 (s, CH_3), 7.95 (s, $2H_{trichlorophenyl}$), 8.07 (t, $1H_{py}$), 8.39 (t, $1H_{py}$), 8.59 (d, $1H_{py}$), 8.81 (d, $1H_{py}$) ppm; ^{13}C NMR (CD_3CN): 20.12 (CH_3), 131.33, 134.20, 134.92, 135.48, 140.18, 145.77, 146.25, 150.70, 153.94 (aryl, C=N) ppm; ^{13}C NMR (CH_2Cl_2): 21.34 (CH_3), 131.41, 134.49, 135.89, 140.45, 145.09, 146.33, 146.44, 152.02, 153.14 (aryl, C=N) ppm.

1-Ethoxycarbonyl-3-methyl-1,2,3-triazolo[1,5-a]pyridinium hexachloroantimonate (**14i**; $C_{10}H_{12}Cl_6N_3O_2Sb$)

Prepared from 2.41 g **2i** (10 mmol), with or without propionitrile (15 mmol), and 2.99 g $SbCl_5$ (10 mmol) as described for **6b**; the residue was crystallized from acetonitrile and ether to yield 3.90 g faint brown crystals (72%); m.p.: 80–82°C; IR (KBr): $\nu = 3092$, 3030, 2942, 1809 (w), 1709, 1620, 1607, 1528, 1460, 1376 cm^{-1}; ^1H NMR (*DMSO*-d_6): 1.57 (t, $J = 7.1$ Hz, CH_3), 2.59 (s, 3H, CH_3), 4.95 (q, $J = 7.1$ Hz, CH_2), 6.71 (t, $1H_{py}$), 6.79 (t, $1H_{py}$), 7.24 (d, $1H_{py}$), 7.49 (d, $1H_{py}$) ppm.

General procedure for the hydrolysis of **6** *and* **14** *and the formation of 1H-indazole derivatives* **7b** *and* **12e–g**

A solution of 4.0 g Na_2CO_3 in 15 ml water was added dropwise at room temperature to a solution of 10 mmol indazolium salts **6b** or **11e–g** in 15 ml $CHCl_3$. The mixture was stirred for 30 min and then extracted with 2×20 ml $CHCl_3$. The combined organic extracts were dried over anhydrous Na_2SO_4

and the solvent was evaporated. The residue was purified by column chromatography on silica using a mixture of $CHCl_3/CH_3OH = 20/1$ as eluent, the solvent was evaporated, and the residue was crystallized to give pure indazole derivatives **7b** and **12e–g**.

3-Pyridyl-3-yl-1-(2,4,6-trichlorophenyl)-1H-indazole (**7b**; $C_{18}H_{10}Cl_3N_3$)

Prepared from 7.10 g **6b** (10 mmol); yield: 2.63 g (71%) as brownish oil which solidified at −20°C and crystallized from aqueous ethanol to give faint fine crystals; m.p.: 138–142°C; IR (KBr): $\nu = 3075$, 3032, 1631, 1601, 1573, 1552, 1523, 1510, 1491 cm^{-1}; ^1H NMR ($CDCl_3$): 7.10 (d, $1H_{ar}$), 7.28–7.46 (m, $3H_{ar}$), 7.53 (s, $2H_{trichlorophenyl}$), 8.04 (d, $1H_{ar}$), 8.32 (tt, $1H_{ar}$), 9.34 (d, $1H_{ar}$), 9.60 (s, $1H_{ar}$) ppm; ^{13}C NMR ($CDCl_3$): 119.61, 130.62, 131.27, 132.31, 133.57, 137.43, 137.83, 138.59, 138.92, 142.80, 144.97, 145.85, 145.98, 151.46, 157.65, 158.47 (aryl, C=N) ppm.

3-Pyridyl-4-yl-1-(2,4,6-trichlorophenyl)-1H-indazole (**12e**; $C_{18}H_{10}Cl_3N_3$)

From 7.10 g **11e** (10 mmol); yield: 2.85 g (76%) as brownish solid which crystallized from aqueous ethanol to give fine crystals; m.p.: 154–156°C; IR (KBr): $\nu = 3076$, 3030, 1632, 1601, 1573, 1552, 1524, 1510, 1491 cm^{-1}; ^1H NMR ($CDCl_3$): 7.17 (d, $1H_{ar}$), 7.38–7.57 (m, $2H_{ar}$), 7.60 (s, $2H_{trichlorophenyl}$), 8.05 (d, $2H_{py}$), 8.15 (d, $1H_{ar}$), 8.79 (d, $2H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 119.80, 130.53, 131.33, 131.63, 132.69, 137.52, 138.22, 138.62, 139.70, 142.68, 145.77, 146.20, 151.15, 151.65, 153.40, 158.80 (aryl, C=N) ppm.

1-Ethoxycarbonyl-3-pyridyl-4-yl-1H-indazole (**12f**; $C_{15}H_{13}N_3O_2$)

Prepared from 6.03 g **11f** (10 mmol); yield: 0.80 g (30%) as brownish solid which crystallized from ethanol to give yellowish white crystals; m.p.: 150–158°C; IR (KBr): $\nu = 3126$, 3062, 2984, 1740, 1642, 1602, 1578, 1512, 1486 cm^{-1}; ^1H NMR ($CDCl_3$): 1.32 (t, $J = 7.1$ Hz, CH_3), 4.27 (q, $J = 7.1$ Hz, CH_2), 7.23–8.01 (m, $6H_{ar}$), 8.56 (d, $2H_{py}$) ppm.

1-Phenyl-3-pyridyl-4-yl-1H-indazole (**12g**; $C_{18}H_{13}N_3$)

Prepared from 6.07 g **11g** (10 mmol); yield: 1.35 g (50%) as brownish solid which crystallized from aqueous ethanol to give fine crystals; m.p.: 72–75°C; IR (KBr): $\nu = 3152$, 3075, 3032, 1630, 1600, 1574, 1552, 1524, 1490 cm^{-1}; ^1H NMR ($CDCl_3$): 7.36–7.60 (m, $5H_{ar}$), 7.78 (m, $3H_{ar}$), 7.98 (d, $2H_{ar}$), 7.98 (d, $1H_{ar}$), 8.76 (d, $2H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 120.43, 120.67, 130.58, 130.72, 131.33, 132.32, 132.46, 132.83, 137.02, 137.30, 139.16, 139.30, 150.13, 159.82 (aryl, C=N) ppm.

3-Methyl-1,2,3-triazolo[1,5-a]pyridine (**15**; $C_7H_7N_3$)

Prepared from 5.41 g **14i** (10 mmol) as described for **7b**; the residue was crystallized from benzene and petrol ether (50–70°C) to yield 1.10 g colourless needles (82%); m.p.: 83–85°C [13]; faint deep blue fluorescence under ultraviolet light; ^1H NMR ($CDCl_3$): 2.64 (s, CH_3), 6.91 (t, $1H_{py}$), 7.15 (t, $1H_{py}$), 7.61 (d, $1H_{py}$), 8.64 (d, $1H_{py}$) ppm; ^{13}C NMR ($CDCl_3$): 19.47 (CH_3), 126.24, 127.50, 134.32, 134.94, 135.45, 143.18 (pyridyl, C=C) ppm.

Formation of the 1H-indazolium picrates **8b** *and* **13e**

A solution of 0.28 g picric acid (1.2 mmol) in 3 ml ethanol was added dropwise to a solution of 3-pyridyl-indazole derivatives **7b** and **12e** (1 mmol) in 3 ml ethanol at room temperature. Yellow

crystals precipitated at once; filtering afforded a yellow powder which was recrystallized from ethanol.

3-Pyridyl-3-yl-1-(2,4,6-trichlorophenyl)-1H-indazolium picrate (**8b**; $C_{24}H_{13}Cl_3N_6O_7$)

Prepared from 0.37 g **7b** (1 mmol); yield: 0.54 g (90%) as yellow fine crystals; m.p.: 182–198°C; ^{1}H NMR ($CDCl_3$): 7.21 (d, $1H_{ar}$), 7.52 (m, $2H_{ar}$), 7.63 (s, $2H_{trichlorophenyl}$), 8.04 (t, $1H_{ar}$), 8.15 (d, $1H_{ar}$), 8.89 (d, $1H_{ar}$), 9.01 (d, $1H_{ar}$), 9.02 (s, $2H_{trinitrophenyl}$), 9.58 (s, $1H_{py}$) ppm.

3-Pyridyl-4-yl-1-(2,4,6-trichlorophenyl)-1H-indazolium picrate (**13e**; $C_{24}H_{13}Cl_3N_6O_7$)

Prepared from 0.37 g **12e** (1 mmol); yield: 0.56 g (92%) as yellow fine crystals; m.p.: 188–194°C; ^{1}H NMR ($CDCl_3$): 7.25 (d, $1H_{ar}$), 7.56 (m, $2H_{ar}$), 7.65 (s, $2H_{trichlorophenyl}$), 8.19 (d, $1H_{ar}$), 8.61 (d, $2H_{ar}$), 8.95 (d, $2H_{ar}$), 8.99 (s, $2H_{trinitrophenyl}$) ppm; ^{13}C NMR ($CDCl_3$): 110.99, 120.19, 121.69, 132.60, 142.86, 126.62, 128.78, 129.22, 129.25, 132.36, 135.81, 137.45, 140.37, 141.45, 142.55, 149.90, 161.44 (aryl, C=N) ppm.

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