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# Pyrazoles and *C*-imidoylaziridines via [4+1]-annulation and [2+1]-cycloaddition of 1-azabuta-1,3-dienes with a synthetic equivalent of phthalimidonitrene

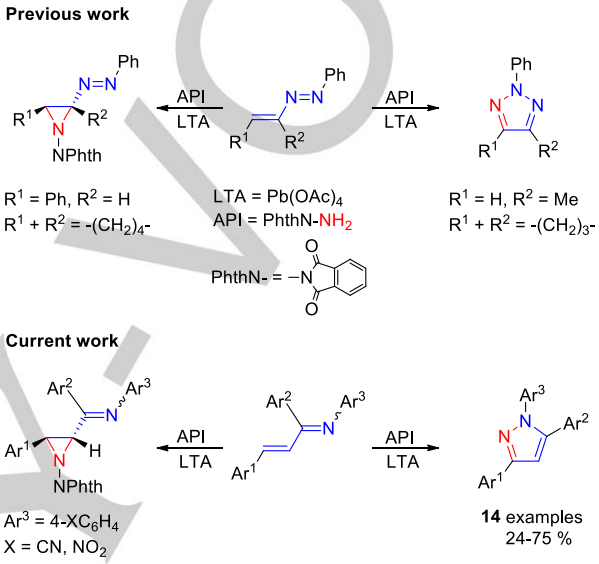
Aleksandr Stukalov,[a] Viktor V. Sokolov,[a] Vitalii V. Suslonov[b] and Mikhail A. Kuznetsov*[a]

This paper is dedicated to Prof. I. Kalvinsh (LIOS, Riga) on the occasion of his 70th birthday.

**Abstract:** Oxidative addition of *N*-aminophthalimide to 1,2,4-triaryl-1-azabuta-1,3-dienes leads, in most cases, to the regiodefined formation of 1,3,5-triarylpyrazoles via [4+1]-annulation in moderate to good yields. This transformation is supposed to proceed via a nitrenoid attack onto a lone pair of the imine nitrogen atom giving the vinyl-azomethine imine, followed by its 1,5-electrocyclization into pyrazoline and further aromatization into pyrazole. Rare examples of 2-imidoyl-1-phthalimidoaziridines that are formed via competitive [2+1]-cycloaddition onto the C=C bond were isolated in low yields for 1-azadienes with electron-deficient aryl substituents at the imine nitrogen atom.

## Introduction

A variety of nitrogen heterocycles can be conveniently prepared via readily accessible building blocks with a 1-azadiene (C=C–C=N) moiety. Such precursors are widely used in [4+2]-annulation reactions utilizing a multitude of partners such as alkenes, alkynes, allenes, isocyanates, carbonyl compounds, *etc.*, leading to six-membered nitrogen heterocycles.[1] [4+1]-Annulations of 1-azabuta-1,3-dienes with Fisher carbenes of chromium, *in situ* generated carbenes, sulfur ylides, allylcarbonates, isonitriles, rhodium vinylidenes lead to pyrrolines and pyrroles.[2] These diverse, well-known transformations add a one-carbon fragment to the C=C–C=N system. In contrast, reactions of 1-azadienes with aziridinating reagents are scarce and include only copper-catalyzed aziridination of *N*-substituted hydrazones of α,β-unsaturated aldehydes[3] as well as aminoaziridination of phthaloyl hydrazone of cinnamic aldehyde.[4] Because oxidative addition of *N*-aminophthalimide to C=C bonds is a convenient approach to *N*-phthalimidoaziridines with a different substitution pattern from that highlighted above,[5] we set about to explore if 2-imidoyl-1-phthalimidoaziridines could be prepared from 1,2,4-triaryl-1-azabuta-1,3-dienes (Scheme 1). Previously, we obtained azoaziridines and 2*H*-1,2,3-triazoles from conjugated azoalkenes (1,2-diazabuta-1,3-dienes) via *in situ* oxidation of *N*-aminophthalimide by lead tetraacetate.[6] Now we have unexpectedly found that it is mainly 1,3,5-triarylpyrazoles are formed from 1-azadienes instead of imidoylaziridines under similar conditions.




**Scheme 1.** Synthesis of 2*H*-1,2,3-triazoles and pyrazoles

Since pyrazoles find numerous applications as pharmaceuticals and for pest control, as dyes and ligands for transition metal catalysts or luminophores,[7] we studied this intriguing transformation in details, as reported below.

## Results and Discussion

Starting imines **1a-n** were obtained from chalcones and arylamines in good yields in the presence of $TiCl_4/Et_3N$[8] (Table 1) and were characterized by $^1H$, $^{13}C$ NMR and HRMS (ESI). According to the $^1H$ and $^{13}C$ NMR spectra, these α,β-unsaturated imines exist as mixtures of (*E*/*Z*)-isomers about the C=N bond in a ratio varying from 1.9:1 to 3.6:1. In most cases, these stereoisomers are configurationally stable at room temperature on the NMR time scale, with the exception of **1i** that shows broad signals in the $^1H$ NMR spectrum that transform into two sets of signals of (*E*/*Z*)-isomeric forms only at –20 °C. This is in accord with lower barriers of isomerization for *N*-arylimines with more electron-withdrawing substituents at the nitrogen atom.[9] Detailed spectroscopic analysis of the configurational assignment is given in the Supporting Information.

The oxidative addition of *N*-aminophthalimide to *N*-arylimines **1** led to pyrazoles **2** in good yields (Table 1), except for imines **1h,i** with electron withdrawing aryl groups on the nitrogen atom.

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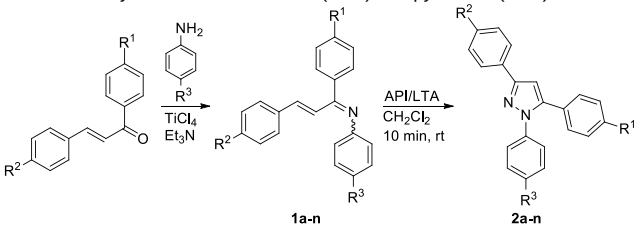
**Table 1.** Synthesis of 1-azadienes (**1a-n**) and pyrazoles (**2a-n**)

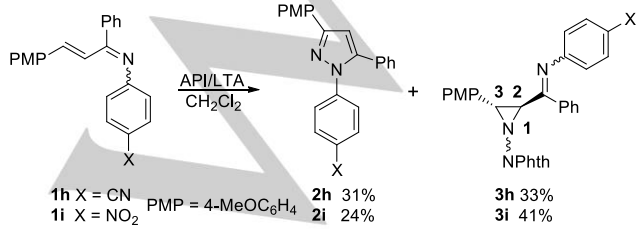



| **1** | Yield (%)[a] | $R^1$ | $R^2$ | $R^3$ | **2** | Yield (%)[a] |
|---|---|---|---|---|---|---|
| **1a** | 61 | H | H | Me | **2a** | 75 |
| **1b** | 91 | H | Me | OMe | **2b** | 72 |
| **1c** | 67 | H | Me | Cl | **2c** | 58 |
| **1d** | 56 | H | Me | Br | **2d** | 55 |
| **1e** | 66 | H | Me | $CO_2Me$ | **2e** | 46 |
| **1f** | 54 | H | OMe | Me | **2f** | 67 |
| **1g** | 53 | H | OMe | Cl | **2g** | 59 |
| **1h** | 67 | H | OMe | CN | **2h** | 31 |
| **1i** | 76 | H | OMe | $NO_2$ | **2i** | 24 |
| **1j** | 69 | H | Cl | OMe | **2j** | 68 |
| **1k** | 64 | H | Cl | Me | **2k** | 70 |
| **1l** | 77 | H | $NO_2$ | OMe | **2l** | 63 |
| **1m** | 88 | OMe | Me | OMe | **2m** | 54 |
| **1n** | 70 | $NO_2$ | Me | OMe | **2n** | 50 |

[a]Isolated yield.

The complete conversion of imines required a three-fold excess of *N*-aminophthalimide and lead tetraacetate. Reactions were completed in a few minutes at room temperature, and pyrazoles **2a-n** were isolated by column chromatography on silica gel. $^1$H NMR spectra and melting points of compounds **2a** and **2g** are in agreement with the literature data. All other pyrazoles are previously unknown and were characterized by $^1$H, $^{13}$C NMR and HRMS (ESI).

Classical synthesis of pyrazoles from hydrazines and 1,3-dicarbonyl compounds or their synthetic equivalents often yields mixtures of regioisomers.[7] In contrast, our [4+1]-annulation protocol provides pyrazoles with the arrangement of substituents unambiguously defined by the nature of the starting materials. Observed side products are anticipated imidoylaziridines, resulting from the [2+1]-addition of the nitrenoid onto the C=C bond. In most cases these compounds are too unstable during purification on silica gel and their formation can be proved by $^1$H NMR spectra of reaction mixtures. Nevertheless, we were able to isolate imidoylaziridines **3h,i** (Scheme 2) by avoiding chromatography and doing recrystallization of reaction mixtures (see ESI for details).

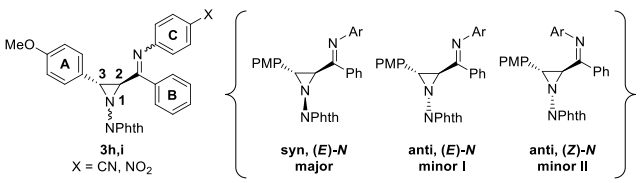



**Scheme 2.** Competitive formation of imidoylaziridines

Aziridines **3h,i** provide broad NMR signals at room temperature, but cooling their solutions down to –20 °C gives three sets of signals with the ratio 0.14/0.16/1.00 for **3h** and 0.13/0.13/1.00 for **3i**. *N*-Phthalimidoaziridines have high barrier of the pyramidal inversion of the aziridine nitrogen atom at room temperature producing two sets of NMR signals for two invertomers. Moreover, the coalescence of these signals does not usually occur even upon heating of their solutions up to the decomposition temperatures of aziridines.[10] Therefore, we speculate that the broadening of signals in NMR spectra of aziridines **3h,i** at room temperature is caused by the fast (*E/Z*)-isomerization about the C=N bond, similar to what is observed in the starting imines.

Given two stereogenic centers in **3h,i** one would *a priori* expect four sets of signals of stereoisomers in low temperature NMR spectra. However, $^1$H NMR spectra of **3h,i** at –20°C feature three pairs of characteristic doublets assigned to the protons of the aziridine ring at δ 3.97(3.98) ($H^2$) and 4.80(4.80) ($H^3$) ppm for the major form of aziridines **3h(i)**, at 4.33(4.34) ($H^3$), 4.94(4.95) ($H^2$) ppm – for the first minor one and at 3.56(3.61) ($H^3$), 5.40(5.43) ($H^2$) ppm – for the second minor isomer. Values of the vicinal coupling constants $^3J$ = 5.2-5.8 Hz indicate the *trans*-arrangement of the protons in the aziridine ring[11] in all three forms of both compounds. It is consistent with the well-known retention of the configuration of the double bond in the oxidative aminoaziridination.[5] The signals of the aziridine carbon atoms in the $^{13}$C NMR spectra appear at δ 50.8(51.1) ($C^3$), 52.3(52.2) ($C^2$) ppm for the major form, at δ 47.2(47.2) ($C^2$), 52.8(53.0) ($C^3$) ppm – for the first minor one and at δ 42.6(42.8) ($C^2$), 51.7(51.7) ($C^3$) ppm – for the second minor isomer. The assignment of these signals was performed using COSY $^1$H-$^1$H, HMBC, HSQC $^1$H-$^{13}$C spectra of compound **3i**.

2D NOESY $^1$H-$^1$H spectrum of **3i** at –55 °C allows establishing the spatial structure of these stereoisomeric forms. The cross-peak between signals δ 6.48 ppm ($H^{oC}$) and 7.43-7.54 ppm ($H^{oA}$, $H^{oB}$) shows that the major form has (*E*)-configuration about the C=N bond. The orientation of the phthalimido substituent can be determined given that the latter deshields protons located *syn* in *N*-phthalimidoaziridines (and the lone pair of the endocyclic nitrogen atom, on the contrary, shields these protons).[11] Since the value of the chemical shift for the $H^2$ proton (3.98 ppm) in the major form (*syn*-, (*E*)-*N*) **3i** is far smaller and the value of the chemical shift for the $H^3$ proton (4.80 ppm) is far greater than the corresponding values in both minor forms (δ($H^2$) = 4.95 (*anti*-, (*E*)-*N*), 5.43 (*anti*-, (*Z*)-*N*) and δ($H^3$) = 4.34 (*anti*-, (*E*)-*N*), 3.61 (*anti*-, (*Z*)-*N*) ppm), the phthalimido substituent and $H^3$ proton are oriented *syn*- in the major form and *anti*- in both minor forms (the same for **3h**) (Scheme 3). As raising temperature from -55 °C to 25 °C hardly affects the shape of almost all signals of the major form (*syn*-, (*E*)-*N*) of **3i** in $^1$H spectrum, it is obvious that the (*E/Z*)-isomerization about the C=N bond is strongly inhibited or doesn't proceed at all in this form, most likely because of the steric hindrance.




**Scheme 3.** Stereoisomeric forms of aziridines **3h,i**

In order to determine the configuration about the C=N bond in minor isomers, which are easily convertible into each other, we used the observation that the *cis*-arrangement of the neighbouring aryl substituents causes their mutual shielding in $^1$H NMR spectrum. The *ortho*-protons of the phenyl ring B ($H^{oB}$) are most sensitive to this effect. For (*anti*, (*Z*)-*N*) isomer of **3h,i,** the signals of these *ortho*-protons appear at δ 8.03-8.10 ppm, while for (*anti*, (*E*)-*N*) they are shielded and appear as multiplets at 7.23-7.38 ppm. The fact that minor forms of **3h,i** have opposite configurations about the C=N bond follows from the room temperature $^1$H NMR spectra. The spectra of the starting imines feature the rapid isomerization of the C=N bond in the NMR time scale that causes broadening of signals in minor isomers with two signals of the OMe-group coalescing into one. In addition, at –20 °C the $^{13}$C NMR spectra of **3h,i** and at –55 °C the $^1$H NMR spectrum of the **3i** feature broadened signals of the phthalimido substituent. This indicates that another dynamic process, namely, rotation around the N–N bond is slowed down at these temperatures.

Finally, the structure of **3i** was confirmed by X-ray diffraction data, and it should be noted that its spatial arrangement in the solid state corresponds to the major form *(syn*-, (*E*)-*N*) in $CDCl_3$ solution (Figure 1).[12]

From the mechanistic standpoint, two things should be noted. First, oxidation of *N*-aminophthalimide with lead tetraacetate affords $CH_3COONHNPhth$, which is a synthetic equivalent of the phthalimidonitrene (nitrenoid), the most likely reactive species in the aziridination reaction.[13] Second, it was shown that *s-cis* conformation of the starting compound is preferable for aminoaziridination of α,β-unsaturated carbonyl compounds, and the nitrenoid attack on the double bond occurs from the side of the carbonyl group.

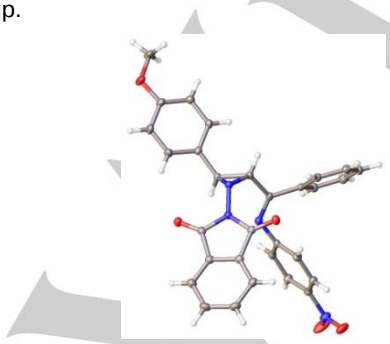


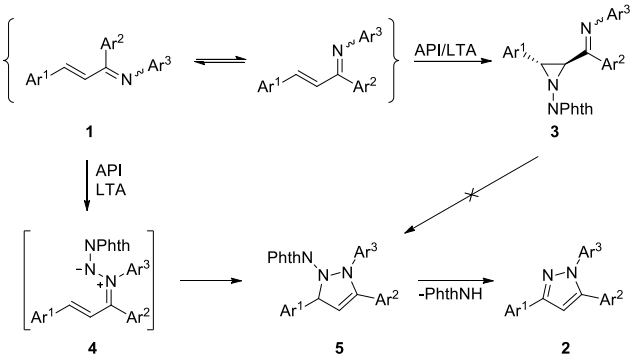
**Figure 1.** X-ray crystal structure of aziridine **3i**

This is due to the secondary orbital interactions between the C=O bonds of the phthalimido unit and the unsaturated substrate, which stabilize the transition state and are responsible for the preferable formation of the invertomer with the *syn*-phthalimido and carbonyl groups at low temperature. However, isomerization into a more stable *anti*-invertomer occurs when the temperature is increased.[11b]

In our case the secondary orbital interactions between the C=O bond of phthalimide and the C=N bond of the unsaturated imine appear to play the same role. As was already discussed, imines **1** exist as a mixture of (*E*/*Z*)-isomers with *s-trans* conformation (see ESI for details); however, the *s-cis* conformation, preferable for aminoaziridination, is easily reached *via* an almost free rotation around the single bond. At the same time, it's curious that for **3h,i** the invertomer with the *syn*-arrangement of the phthalimido and imidoyl substituents is the major species also at room temperature. It is easy to see (Fig. 1) that in this invertomer the imidoyl fragment becomes more compact with the *cis*-aryl rings at the C=N bond, so the (*E*/*Z*)-isomerization about the C=N bond doesn't occur.

Formation of pyrazoles **2** could be a result of an attack of the nitrenoid on the C=C bond followed by the isomerization of aziridines **3** into pyrazolines **5** including the C–N bond cleavage (note that the 1,3-sigmatropic shift is forbidden by the orbital symmetry) with the subsequent aromatization (Scheme 4). However, maintaining the reaction mixtures with aziridines for several hours didn't increase yields of the pyrazoles, and isolated imidoylaziridines **3h,i** didn't transform into pyrazoles **2h,i** under the reaction conditions either. Therefore we speculate that the pathway to pyrazoles **2** begins with an attack of the nitrenoid onto a lone pair of the imine nitrogen atom, giving the vinyl-azomethine imine **4** (Scheme 4) followed by its 1,5-electrocyclization into pyrazoline **5**, which gives the final **2** after elimination of the phthalimide.

The proposed mechanism assumes that reducing the nucleophility of the nitrogen atom makes it less reactive than the C=C bond, allowing the aziridination to take place.




**Scheme 4.** A plausible mechanism for the formation of pyrazoles **2**

This is in agreement with low yields of pyrazoles from imines **1h,i** possessing electron-poor aryl substituents at the nitrogen atom. This makes isolation of aziridines **3h,i** possible.

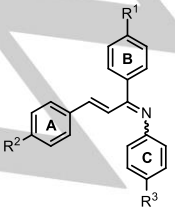
## Conclusions

We reported that the oxidative addition of the *N*-aminophthalimide to the 1,2,4-triaryl-1-azabuta-1,3-dienes in the most cases constitutes a convenient regiodefined method for the synthesis of the 1,3,5-triarylpyrazoles. This reaction is a rare example of a [4+1]-annulation reaction in which the formation of a weak N–N bond is followed by 1,5-electrocyclization of the vinyl-azomethine imine into a pyrazoline and its further aromatization into a pyrazole. Competing with this manifold is [2+1]-cycloaddition onto the C=C bond that gives imidoylaziridines.

## Experimental Section

**General:** NMR spectroscopic data were recorded on the Bruker Avance 400 spectrometer (400.13 MHz for $^1$H, 100.61 MHz for $^{13}$C, respectively) in $CDCl_3$ and DMSO-$d_6$. The signals are referenced to the residual solvent proton ($\delta$H = 7.26 and 2.50 ppm, respectively) and carbon signals ($\delta$C = 77.00 and 39.52 ppm, respectively). DEPT spectra were used for the assignment of carbon signals. Melting points were determined with a Stuart SMP30 instrument. High-resolution mass spectra were recorded with a Bruker Maxis HRMS-ESI-qTOF spectrometer (electrospray ionization mode). Column chromatography was performed on silica gel Merck 60. The composition of the reaction mixtures and fractions obtained after their separation as well as the purity of the isolated compounds were monitored by TLC on Alugram SIL G/UV$_{254}$ plates (Macherey-Nagel).

**General procedure for the preparation of imines 1a-n:** A solution of $TiCl_4$ in $CH_2Cl_2$ (5.0 mL, 1.0 M) was added dropwise to a stirred mixture of ketone (5 mmol), $Et_3N$ (3.5 mL, 2.5 g, 25 mmol) and arylamine (5 mmol) in dry $CH_2Cl_2$ (30 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for another 4 hours. Water (1 mL) was added, the resulting suspension filtered through Celite and the solid residue washed with $CH_2Cl_2$ (30 mL). The solution was washed with water (30 mL), the organic layer separated and the aqueous extracted with $CH_2Cl_2$ (2×15 mL). The combined organic layers were washed with water and brine and dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure and the residue purified by flash chromatography on silica gel (hexane/EtOAc). The obtained viscous oil was crystallized at about –20 °C from hexane/dichloromethane (10:1) (compounds **1c,d,g,i-n**) or petroleum ether/ethyl acetate (10:1) (compounds **1a,e,f**), the precipitate was quickly filtered and dried under reduced pressure. Compounds **1b,h** are viscous oils.




***N*-((2*E*)-1,3-Diphenylprop-2-en-1-ylidene)-4-methylaniline[14] (1a).** Pale yellow crystals, 0.906 g (61%), mp 90 °C (lit. 94-95 °C)[14]. According to the $^1$H NMR spectrum, imine **1a** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 2.7:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H, Me, minor); 2.39 (s, 3H, Me, major); 6.60 (d, *J* = 8.2 Hz, 2H, H$^{oC}$, minor); 6.83 (d, *J* = 16.4 Hz, 1H, H$^3$, minor); 6.87-7.01 (m, 4H, H$^{oC}$, H$^{2,3}$, major; 2H, H$^{mC}$, minor); 7.12-7.22 (m, 2H, H$^{mC}$, major; 2H, H$^{oB}$, minor); 7.27-7.40 (m, 5H, H$^A$, major; 7H, H$^{m,pB}$, H$^{m,pA}$, H$^2$, minor); 7.44-7.54 (m, 3H, H$^{m,pB}$, major; 2H, H$^{oA}$, minor); 7.71-7.79 (m, 2H, H$^{oB}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 20.8 (Me, minor); 20.9 (Me, major); 120.9 (C$^{oC}$, major); 121.1 (C$^{oC}$, minor); 122.1 (C$^2$, major); 127.5; 128.0; 128.3; 128.7; 128.9; 129.0; 129.1; 129.27; 129.33; 129.4; 129.7; 131.9; 132.8; 133.4; 135.7; 135.8; 135.9; 139.6 (C$^{iB}$, major); 140.9 (C$^3$, minor); 141.2; (C$^3$, major); 148.0 (C$^{iC}$, minor); 148.3 (C$^{iC}$, major); 166.9 (C=N, major); 168.5 (C=N, minor) ppm. Signals of the major and minor isomers partially overlap. HRMS (ESI), *m/z*: calcd for $C_{22}H_{19}N$ [M+H]$^+$ 298.1590, found 298.1586.

**4-Methoxy-*N*-((2*E*)-3-(4-methylphenyl)-1-phenylprop-2-en-1-ylidene)-aniline (1b).** Yellow oil, 1.487 g (91%). According to the $^1$H NMR spectrum, imine **1b** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 2.7:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3H, Me, major); 2.36 (s, 3H, Me, minor); 3.71 (s, 3H, OMe, minor); 3.85 (s, 3H, OMe, major); 6.59-6.70 (m, 4H, H$^{m,oC}$, minor); 6.79 (d, *J* = 16.3 Hz 1H, H$^3$, minor); 6.85-7.00 (m, 6H, H$^{m,oC}$, H$^{2,3}$, major); 7.09-7.19 (m, 2H, H$^{mA}$, major; 4H, H$^{mA}$, H$^{oB}$, minor); 7.20-7.28 (m, 2H, H$^{oA}$, major; 1H, H$^2$, minor; $CHCl_3$); 7.29-7.34 (m, 3H, H$^{m,pB}$, minor); 7.38 (d, *J* = 8.0 Hz, 2H, H$^{oA}$, minor); 7.42-7.53 (m, 3H, H$^{m,pB}$, major); 7.67-7.77 (m, 2H, H$^{oB}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.3 (Me, both isomers); 55.2 (OMe, minor); 55.4 (OMe, major); 113.6 (C$^{mC}$, minor); 114.0 (C$^{mC}$, major); 121.3 (C$^2$, major); 122.4 (C$^{oC}$, major); 122.8 (C$^{oC}$, minor); 127.38; 127.40; 128.1; 128.2; 129.0; 129.4; 129.5; 129.7; 131.0; 133.0; 133.2; 136.0 (C$^{iB}$, minor); 139.3; 139.6; 139.8; 140.7 (C$^3$, minor); 141.1 (C$^3$, major); 143.7 (C$^{iC}$, minor); 144.3 (C$^{iC}$, major); 155.9 (C$^{pC}$, minor); 156.5 (C$^{pC}$, major); 167.2 (C=N, major); 168.4 (C=N, minor) ppm. Signals of the major and minor isomers partially overlap. HRMS (ESI), *m/z*: calcd for $C_{23}H_{21}NO$ [M+H]$^+$ 328.1696, found 328.1697.

**4-Chloro-*N*-((2*E*)-3-(4-methylphenyl)-1-phenylprop-2-en-1-ylidene)-aniline (1c).** Pale yellow crystals, 1.110 g (67%), mp 89 °C. According to the $^1$H NMR spectrum, imine **1c** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 2.5:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3H, Me, major); 2.37 (s, 3H, Me, minor); 6.58-6.64 (m, 2H, H$^{oC}$, minor); 6.79-6.87 (m, 1H, =CH, major; 1H, H$^3$, minor); 6.88-6.97 (m, 3H, H$^{oC}$, =CH, major); 7.05-7.10 (m, 2H, H$^{mC}$, minor); 7.11-7.16 (m, 2H, H$^{mA}$, major; 2H, H$^{oB}$, minor); 7.18 (d, *J* = 8.1 Hz, 2H, H$^{mA}$, minor); 7.20-7.25 (m 2H, H$^{oA}$, major; 1H, H$^2$, minor); 7.29-7.36 (m, 2H, H$^{mC}$, major; 3H, H$^{m,pB}$, minor); 7.39 (d, *J* = 8.1 Hz, 2H, H$^{oA}$, minor); 7.45-7.55 (m, 3H, H$^{m,pB}$, major); 7.69-7.77 (m, 2H, H$^{oB}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.3 (Me, both isomers); 120.5 (C$^2$, major); 122.1 (C$^{oC}$, major); 122.5 (C$^{oC}$, minor); 127.50; 127.53; 128.2; 128.3; 128.4; 128.5 (C$^{pC}$, major); 128.6; 128.87; 128.91; 129.1 (C$^{pC}$, minor); 129.3; 129.54; 129.56; 130.0; 130.4; 132.7 (C$^{iA}$, major); 132.9 (C$^{iA}$, minor); 135.3 (C$^{iB}$, minor); 139.2; 139.7; 140.0; 141.9 (C$^3$, minor); 142.3 (C$^3$, major); 149.3 (C$^{iC}$, minor); 149.5 (C$^{iC}$, major); 167.9 (C=N, major); 169.7 (C=N, minor) ppm. HRMS (ESI), *m/z*: calcd for $C_{22}H_{18}ClN$ [M+H]$^+$ 332.1201, found 332.1191.

**4-Bromo-*N*-((2*E*)-3-(4-methylphenyl)-1-phenylprop-2-en-1-ylidene)-aniline (1d).** Pale yellow crystals, 1.051 g (56%), mp 99-100 °C. According to the $^1$H NMR spectrum, imine **1d** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 2.5:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3H, Me, major); 2.37 (s, 3H, Me, minor); 6.55 (d, *J* = 8.6 Hz, 2H, H$^{oC}$, minor); 6.78-6.89 (m, 3H, H$^{oC}$, =CH, major; 1H, H$^3$, minor); 6.93 (d, *J* = 16.4 Hz, 1H, =CH, major); 7.08-7.25 (m, 4H, H$^{m,oA}$, major; 7H, H$^{mA}$, H$^{oB}$, H$^{mC}$, H$^2$, minor); 7.28-7.34 (m, 3H, H$^{m,pB}$, minor); 7.38 (d, *J* = 8.0 Hz, 2H, H$^{oA}$, minor); 7.43-7.55 (m, 5H, H$^{m,pB}$, H$^{mC}$, major); 7.68-7.76 (m, 2H, H$^{oB}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.4 (Me, both isomers); 116.3 (C$^{pC}$, minor); 116.8 (C$^{pC}$, major); 120.5 (C$^2$, major); 122.6 (C$^{oC}$, major); 122.9 (C$^{oC}$, minor); 127.6; 128.2; 128.3; 128.6; 128.9; 129.3; 129.55; 129.57; 130.0; 130.4; 131.4; 131.9; 132.7

($C^{iA}$, major); 132.9 ($C^{iA}$, minor); 135.2 ($C^{iB}$, minor); 139.2; 139.7; 140.0; 142.0 ($C^{3}$, minor); 142.4 ($C^{3}$, major); 149.8 ($C^{iC}$, minor); 150.0 ($C^{iC}$, major); 167.9 (C=N, major); 169.6 (C=N, minor) ppm. Signals of the major and minor isomers partially overlap. HRMS (ESI), *m/z*: calcd for $C_{22}H_{18}BrN$ $[M+H]^+$ 376.0695, found 376.0698.

**4-(Methoxycarbonyl)-*N*-((2*E*)-3-(4-methylphenyl)-1-phenylprop-2-en-1-ylidene)aniline (1e).** Pale yellow crystals, 1.168 g (66%), mp 110 °C. According to the $^1$H NMR spectrum, imine **1e** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 2.5:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H, Me, major); 2.37 (s, 3H, Me, minor); 3.84 (s, 3H, $CO_2$Me, minor); 3.93 (s, 3H, $CO_2$Me, major); 6.70 (d, *J* = 8.4 Hz, 2H, $H^{oC}$, minor); 6.75 (d, *J* = 16.4 Hz, 1H, $H^2$, major); 6.86 (d, *J* = 16.3 Hz, 1H, $H^3$, minor); 6.94 (d, *J* = 16.4 Hz, 1H, $H^3$, major); 6.99 (d, *J* = 8.4 Hz, 2H, $H^{oC}$, major); 7.07-7.14 (m, 2H, $H^{mA}$, major; 2H, $H^{oB}$, minor); 7.15-7.31 (m, 2H, $H^{oA}$, major; 6H, $H^{mA}$, $H^{m,pB}$, $H^2$, minor; $CHCl_3$); 7.39 (d, *J* = 7.9 Hz, 2H, $H^{oA}$, minor); 7.44-7.56 (m, 3H, $H^{m,pB}$, major); 7.70-7.77 (m, 2H, $H^{oB}$, major); 7.81 (d, *J* = 8.4 Hz, 2H, $H^{mC}$, minor); 8.06 (d, *J* = 8.4 Hz, 2H, $H^{mC}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) of the (*E*)-isomer: δ = 21.4 (Me); 51.9 ($CO_2$Me); 120.3 ($C^2$); 120.3 ($C^{oC}$); 125.4 ($C^{pC}$); 127.56 ($C^{oA}$); 128.4 ($C^{mB}$); 129.3 ($C^{oB}$); 129.6 ($C^{mA}$); 130.1 ($C^{pB}$); 130.7 ($C^{mC}$); 132.6 ($C^{iA}$); 138.8 ($C^{iB}$); 140.1 ($C^{pA}$); 142.8 ($C^3$); 155.5 ($C^{iC}$); 167.0 ($CO_2$Me); 167.6 (C=N) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) of the (*Z*)-isomer: δ = 21.4 (Me); 51.8 ($CO_2$Me); 120.6 ($C^{oC}$); 124.7 ($C^{pC}$); 127.60 ($C^{oA}$); 128.1 ($C^{mB}$); 128.7 ($C^{pB}$); 128.8 ($C^{oB}$); 129.6 ($C^{mA}$); 130.0 ($C^2$); 130.2 ($C^{mC}$); 132.8 ($C^{iA}$); 135.1 ($C^{iB}$); 139.8 ($C^{pA}$); 142.4 ($C^3$); 155.3 ($C^{iC}$); 166.9 ($CO_2$Me); 169.6 (C=N) ppm. The assignment of signals was performed using 2D NMR including $^1$H-$^{13}$C and $^{15}$N-$^1$H HMBC, $^1$H-$^{13}$C HSQC spectra. HRMS (ESI), *m/z*: calcd for $C_{24}H_{21}NO_2$ $[M+H]^+$ 356.1645, found 356.1643.

***N*-((2*E*)-3-(4-Methoxyphenyl)-1-phenylprop-2-en-1-ylidene)-4-methylaniline (1f).** Pale yellow crystals, 0.885 g (54%), mp 96 °C. According to the $^1$H NMR spectrum, imine **1f** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 2.9:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3H, Me, minor); 2.38 (s, 3H, Me, major); 3.80 (s, 3H, OMe, major); 3.83 (s, 3H, OMe, minor); 6.58 (d, *J* = 8.0 Hz, 2H, $H^{oC}$, minor); 6.77 (d, *J* = 16.3 Hz, 1H, $H^3$, minor); 6.80-6.94 (m, 6H, $H^{mA}$, $H^{oC}$, $H^{2,3}$, major; 4H, $H^{mA}$, $H^{mC}$, minor); 7.11-7.21 (m, 2H, $H^{mC}$, major; 3H, $H^{oB}$, $H^2$, minor); 7.23-7.33 (m, 2H, $H^{oA}$, major; 3H, $H^{m,pB}$, minor; $CHCl_3$); 7.43 (d, *J* = 8.7 Hz, 2H, $H^{oA}$, minor); 7.45-7.52 (m, 3H, $H^{m,pB}$, major); 7.68-7.77 (m, 2H, $H^{oB}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 20.8 (Me, minor); 20.9 (Me, major); 55.3 (OMe, both isomers); 114.2 ($C^{mA}$, both isomers); 119.9 ($C^{oC}$, minor); 120.9 ($C^{oC}$, major); 121.2 ($C^2$, major); 128.0; 128.19; 128.23; 128.5 ($C^{iA}$, major); 128.6 ($C^{iA}$, minor); 128.89; 128.93; 128.96; 129.00; 129.3; 129.4; 129.6; 129.8; 132.6 ($C^{pC}$, minor); 133.2 ($C^{pC}$, major); 135.9 ($C^{iB}$, minor); 139.8 ($C^{iB}$, major); 140.6 ($C^3$, minor); 141.0 ($C^3$, major); 148.1 ($C^{iC}$, minor); 148.5 ($C^{iC}$, major); 160.5 ($C^{pA}$, minor); 160.6 ($C^{pA}$, major); 167.3 (C=N, major); 168.8 (C=N, minor) ppm. Signals of the major and minor isomers partially overlap. HRMS (ESI), *m/z*: calcd for $C_{23}H_{21}NO$ $[M+H]^+$ 328.1696, found 328.1695.

**4-Chloro-*N*-((2*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-ylidene)-aniline (1g).** Yellow crystals, 0.926 g (53%), mp 89 °C. According to the $^1$H NMR spectrum, imine **1g** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 2.5:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3H, OMe, major); 3.83 (s, 3H, OMe, minor); 6.60 (d, *J* = 8.6 Hz, 2H, $H^{oC}$, minor); 6.74 (d, *J* = 16.3 Hz, 1H, =CH, major); 6.80 (d, *J* = 16.3 Hz, 1H, $H^3$, minor); 6.83-6.95 (m, 5H, $H^{mA}$, $H^{oC}$, =CH, major; 2H, $H^{mA}$, minor); 7.07 (d, *J* = 8.6 Hz, 2H, $H^{mC}$, minor); 7.09-7.19 (m, 3H, $H^{oB}$, $H^2$, minor); 7.22-7.37 (m, 4H, $H^{oA}$, $H^{mC}$, major; 3H, $H^{m,pB}$, minor; $CHCl_3$); 7.43 (d, *J* = 8.7 Hz, 2H, $H^{oA}$, minor); 7.45-7.55 (m, 3H, $H^{m,pB}$, major); 7.66-7.76 (m, 2H, $H^{oB}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.3 (OMe, both isomers); 114.26 ($C^{mA}$, minor); 114.29 ($C^{mA}$, major); 119.3 ($C^2$, major); 122.2 ($C^{oC}$, major); 122.5 ($C^{oC}$, minor); 128.1; 128.3; 128.4; 128.5; 128.88; 128.91; 129.0; 129.1; 129.2; 129.3; 129.9; 135.3 ($C^{iB}$, minor); 139.3 ($C^{iB}$, major); 141.6 ($C^3$, minor); 142.0 ($C^3$, major); 149.3 ($C^{iC}$, minor); 149.6 ($C^{iC}$, major); 160.7 ($C^{pA}$, minor); 160.9 ($C^{pA}$, major); 168.0 (C=N, major); 169.8 (C=N, minor) ppm. Signals of the major and minor isomers partially overlap. HRMS (ESI), *m/z*: calcd for $C_{22}H_{18}ClNO$ $[M+H]^+$ 348.1150, found 348.1159.

**4-Cyano-*N*-((2*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-ylidene)-aniline (1h).** Yellow oil, 1.127 g (67%). According to the $^1$H NMR spectrum, imine **1h** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 2.7:1 at -20 °C. $^1$H NMR (400 MHz, $CDCl_3$, 253 K): δ = 3.81 (s, 3H, OMe, major); 3.83 (s, 3H, OMe, minor); 6.58 (d, *J* = 16.2 Hz, 1H, $H^2$, major); 6.72 (d, *J* = 8.4 Hz, 2H, $H^{oC}$, minor); 6.79-6.88 (m, 2H, $H^{mA}$, major; 1H, $H^3$, minor); 6.90 (d, *J* = 8.7 Hz, 2H, $H^{mA}$, minor); 6.96 (d, *J* = 16.2 Hz, 1H, $H^3$, major); 7.02 (d, *J* = 8.4 Hz, 2H, $H^{oC}$, major); 7.06-7.11 (m, 2H, $H^{oB}$, minor); 7.13 (d, *J* = 16.3 Hz, 1H, $H^2$, minor); 7.23-7.36 (m, 2H, $H^{oA}$, major; 3H, $H^{m,pB}$, minor; $CHCl_3$); 7.40 (d, *J* = 8.4 Hz, 2H, $H^{mC}$, minor); 7.44 (d, *J* = 8.7 Hz, 2H, $H^{oA}$, minor); 7.47-7.58 (m, 3H, $H^{m,pB}$, major); 7.66 (d, *J* = 8.4 Hz, 2H, $H^{mC}$, major); 7.69-7.76 (m, 2H, $H^{oB}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.3 (OMe, both isomers); 105.8 ($C^{pC}$, minor); 106.4 ($C^{pC}$, major); 114.1 ($C^{mA}$, both isomers); 118.3 ($C^2$, major); 119.46 (C≡N, minor); 119.54 (C≡N, major); 121.3 ($C^{oC}$, major); 121.5 ($C^{oC}$, minor); 127.4; 127.6; 128.0; 128.2; 128.4; 128.7; 128.9; 129.2; 130.3 ($C^{pB}$, major); 132.6 ($C^{mC}$, minor); 133.1 ($C^{mC}$, major); 134.2 ($C^{iB}$, minor); 138.2 ($C^{iB}$, major); 143.1 ($C^3$, minor); 143.4 ($C^3$, major); 154.9 ($C^{iC}$, minor); 155.0 ($C^{iC}$, major); 160.6 ($C^{pA}$, minor); 160.8 ($C^{pA}$, major); 168.3 (C=N, major); 170.5 (C=N, minor) ppm. Signals of the major and minor isomers partially overlap. HRMS (ESI), *m/z*: calcd for $C_{23}H_{18}N_2O$ $[M+H]^+$ 339.1492, found 339.1484.

***N*-((2*E*)-3-(4-Methoxyphenyl)-1-phenylprop-2-en-1-ylidene)-4-nitroaniline (1i).** Orange crystals, 1.364 g (76%), mp 90 °C. According to the $^1$H NMR spectrum, imine **1i** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 2.7:1 at -20 °C. $^1$H NMR (400 MHz, $CDCl_3$, 253 K): δ = 3.81 (s, 3H, OMe, major); 3.84 (s, 3H, OMe, minor); 6.59 (d, *J* = 16.2 Hz, 1H, $H^2$, major); 6.74 (d, *J* = 8.9 Hz, 2H, $H^{oC}$, minor); 6.81-6.88 (m, 2H $H^{mA}$, major; 1H, $H^3$, minor); 6.90 (d, *J* = 8.7 Hz, 2H, $H^{mA}$, minor); 6.99 (d, *J* = 16.2 Hz, 1H, $H^3$, major); 7.05 (d, *J* = 8.8 Hz, 2H, $H^{oC}$, major); 7.09-7.18 (m, 3H, $H^{oB}$, $H^2$, minor); 7.23-7.36 (m, 2H, $H^{oA}$, major; 3H, $H^{m,pB}$, minor; $CHCl_3$); 7.45 (d, *J* = 8.7 Hz, 2H, $H^{oA}$, minor); 7.48-7.60 (m, 3H, $H^{m,pB}$, major); 7.66-7.80 (m, 2H, $H^{oB}$, major); 8.01 (d, *J* = 8.9 Hz, 2H, $H^{mC}$, minor); 8.27 (d, *J* = 8.8 Hz, 2H, $H^{mC}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.3 (OMe, both isomers); 114.1 ($C^{mA}$, both isomers); 118.2 ($C^2$, major); 120.9 ($C^{oC}$, major); 121.1 ($C^{oC}$, minor); 124.5 ($C^{mC}$, minor); 125.1 ($C^{mC}$, major); 127.3; 127.6; 127.8; 128.2; 128.5; 128.6; 129.0; 129.26; 129.30; 129.32; 130.4 ($C^{pB}$, major); 134.2 ($C^{iB}$, minor); 138.1 ($C^{iB}$ major); 142.8 ($C^{pC}$, minor); 143.4 ($C^3$, minor); 143.5 ($C^{pC}$, major); 143.9 ($C^3$, major); 157.12 ($C^{iC}$, minor); 157.14 ($C^{iC}$, major); 160.7 ($C^{pA}$, minor); 160.9 ($C^{pA}$, major); 168.4 (C=N, major); 170.6 (C=N, minor) ppm. HRMS (ESI), *m/z*: calcd for $C_{22}H_{18}N_2O_3$ $[M+H]^+$ 359.1390, found 359.1389.

***N*-((2*E*)-3-(4-Chlorophenyl)-1-phenylprop-2-en-1-ylidene)-4-methoxyaniline[15] (1j).** Yellow crystals, 1.207 g (69%), mp 113 °C (lit. 113-115 °C)[15]. According to the $^1$H NMR spectrum, imine **1j** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 2.3:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.71 (s, 3H, OMe, minor); 3.85 (s, 3H, OMe, major); 6.60-6.70 (m, 4H, $H^{m,oC}$, minor); 6.75 (d, *J* = 16.3 Hz, 1H, $H^3$, minor); 6.86 (d, *J* = 16.4 Hz, 1H, $H^3$, major); 6.90-6.98 (m, 5H, $H^{m,oC}$, $H^2$, major); 7.10-7.17 (m, 2H, $H^{oB}$, minor); 7.20-7.35 (m, 4H, $H^{m,oA}$, major; 6H, $H^{m,pB}$, $H^{mA}$, $H^2$, minor; $CHCl_3$); 7.40 (d, *J* = 8.5 Hz, 2H, $H^{oA}$, minor); 7.43-7.53 (m, 3H, $H^{m,pB}$, major); 7.67-7.75 (m, 2H, $H^{oB}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) of the (*E*)-isomer: δ = 55.4 (OMe); 114.1 ($C^{mC}$); 122.4 ($C^{oC}$); 122.7 ($C^2$); 128.3 ($C^{mB}$); 128.5 ($C^{oA}$); 129.00 ($C^{mA}$); 129.3 ($C^{oB}$); 129.8 ($C^{pB}$); 134.3 ($C^{iA}$); 135.1 ($C^{pA}$); 139.5 ($C^{iB}$); 139.6 ($C^3$); 144.1 ($C^{iC}$); 156.6 ($C^{pC}$); 166.6 (C=N) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) of the (*Z*)-isomer: δ = 55.2 (OMe); 113.6 ($C^{mC}$); 122.8 ($C^{oC}$); 128.3 ($C^{mB}$); 128.4 ($C^{pB}$); 128.5 ($C^{oA}$); 128.9 ($C^{oB}$); 128.98 ($C^{mA}$); 132.6 ($C^2$); 134.5 ($C^{iA}$); 134.8 ($C^{pA}$); 135.7 ($C^{iB}$); 139.1 ($C^3$); 143.5 ($C^{iC}$); 156.1 ($C^{pC}$); 167.9 (C=N) ppm. The assignment of signals was performed using 2D NMR including $^1$H-$^{13}$C and $^{15}$N-$^1$H HMBC, $^1$H-$^{13}$C HSQC, and NOESY spectra. HRMS (ESI), *m/z*: calcd for $C_{22}H_{18}ClNO$ $[M+H]^+$ 348.1150, found 348.1142.

***N*-((2*E*)-3-(4-Chlorophenyl)-1-phenylprop-2-en-1-ylidene)-4-methylaniline[16] (1k).** Beige crystals, 1.059 g (64%), mp 116 °C (lit. 118-120 °C)[16]. According to the $^1$H NMR spectrum, imine **1k** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 2.5:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3H, Me, minor); 2.39 (s, 3H, Me,

major); 6.58 (d, *J* = 8.2 Hz, 2H, $H^{oC}$, minor); 6.76 (d, *J* = 16.4 Hz, 1H, $H^3$, minor); 6.83-6.96 (m, 4H, $H^{oC}$, $H^{2,3}$, major; 2H, $H^{mC}$, minor); 7.11-7.15 (m, 2H, $H^{oB}$, minor); 7.18 (d, *J* = 8.0 Hz, 2H, $H^{mC}$, major); 7.21-7.35 (m, 4H, $H^{m,oA}$, major; 6H, $H^{m,pB}$, $H^{mA}$, $H^2$, minor; $CHCl_3$); 7.40 (d, *J* = 8.6 Hz, 2H, $H^{oA}$, minor); 7.44-7.53 (m, 3H, $H^{m,pB}$, major); 7.68-7.76 (m, 2H, $H^{oB}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 20.8 (Me, minor); 20.9 (Me, major); 120.8 ($C^{oC}$, major); 121.1, 122.6 ($C^{oC}$, minor; $C^2$, major); 128.1; 128.3; 128.4; 128.6; 128.9; 128.96; 128.98; 129.3; 129.4; 129.8; 132.5; 133.0; 133.6; 134.3; 134.4; 134.9; 135.1; 135.6; 139.3 ($C^3$, minor); 139.4 ($C^{iB}$, major); 139.8 ($C^3$, major); 147.8 ($C^{iC}$, minor); 148.2 ($C^{iC}$, major); 166.6 (C=N, major); 168.2 (C=N, minor) ppm. Signals of the major and minor isomers partially overlap. HRMS (ESI), *m/z*: calcd for $C_{22}H_{18}ClN$ $[M+H]^+$ 332.1201, found 332.1207.

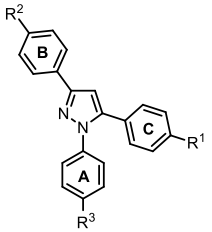
**4-Methoxy-*N*-((2*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-ylidene)-aniline (1l).** Orange crystals, 1.375 g (77%), mp 121 °C. According to the $^1$H NMR spectrum, imine **1l** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 1.9:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.72 (s, 3H, OMe, minor); 3.84 (s, 3H, OMe, major); 6.61-6.71 (m, 4H, $H^{m,oC}$, minor); 6.84 (d, *J* = 16.4 Hz, 1H, $H^3$, minor); 6.89-6.99 (m, 5H, $H^{m,oC}$, $H^3$, major); 7.10 (d, *J* = 16.5 Hz, 1H, $H^2$, major); 7.13-7.18 (m, 2H, $H^{oB}$, minor); 7.31-7.41 (m, 4H, $H^{m,pB}$, $H^2$, minor); 7.43-7.54 (m, 5H, $H^{oA}$, $H^{m,pB}$, major); 7.60 (d, *J* = 8.8 Hz, 2H, $H^{oA}$, minor); 7.68-7.76 (m, 2H, $H^{oB}$, major); 8.13-8.23 (m, 2H, $H^{mA}$, major; 2H, $H^{mA}$, minor) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.2 (OMe, minor); 55.4 (OMe, major); 113.7 ($C^{mC}$, minor); 114.1 ($C^{mC}$, major); 122.5 ($C^{oC}$, major); 123.0 ($C^{oC}$, minor); 124.1 ($C^{mA}$, both isomers); 126.2 ($C^2$, major); 127.8; 128.4; 128.7 ($C^{pB}$, minor); 128.8; 129.2; 130.1; 135.4 ($C^{iB}$, minor); 136.3; 137.3; 137.9 ($C^3$, major); 139.1 ($C^{iB}$, major); 142.1 ($C^{iA}$, major); 142.3 ($C^{iA}$, minor); 143.1 ($C^{iC}$, minor); 143.8 ($C^{iC}$, major); 147.6 ($C^{pA}$, minor); 147.8 ($C^{pA}$, major); 156.5 ($C^{pC}$, minor); 156.9 ($C^{pC}$, major); 165.8 (C=N, major); 167.0 (C=N, minor) ppm. Signals of the major and minor isomers partially overlap. HRMS (ESI), *m/z*: calcd for $C_{22}H_{18}N_2O_3$ $[M+H]^+$ 359.1390, found 359.1393.

**4-Methoxy-*N*-((2*E*)-1-(4-methoxyphenyl)-3-(4-methylphenyl)prop-2-en-1-ylidene)aniline (1m).** Yellow crystals, 1.572 g (88%), mp 123 °C. According to the $^1$H NMR spectrum, imine **1m** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 3.3:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3H, Me, major); 2.36 (s, 3H, Me, minor); 3.73 (s, 3H, OMe, minor); 3.81 (s, 3H, OMe, minor); 3.84 (s, 3H, OMe, major); 3.88 (s, 3H, OMe, major); 6.61-6.72 (m, 4H, $H^{m,oC}$, minor); 6.80-6.96 (m, 6H, $H^{m,oC}$, $H^{2,3}$, major; 3H, $H^{mB}$, $H^3$, minor); 6.98 (d, *J* = 8.7 Hz, 2H, $H^{mB}$, major); 7.08 (d, *J* = 8.6 Hz, 2H, $H^{oB}$, minor); 7.11-7.28 (m, 4H, $H^{m,oA}$, major; 3H, $H^{mA}$, $H^2$, minor; $CHCl_3$); 7.38 (d, *J* = 8.0 Hz, 2H, $H^{oA}$, minor); 7.71 (d, *J* = 8.7 Hz, 2H, $H^{oB}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.3 (Me, both isomers); 55.1 (OMe, minor); 55.2 (OMe, minor); 55.35 (OMe, major); 55.41 (OMe, major); 113.5, 113.60 ($C^{mB}$, $C^{mC}$, minor); 113.64, 114.0 ($C^{mB}$, $C^{mC}$, major); 121.8 ($C^2$, major); 122.6 ($C^{oC}$, major); 122.8 ($C^{oC}$, minor); 127.3; 127.4; 128.0; 129.5; 130.6; 130.9; 131.2 ($C^2$, minor); 132.3; 133.1; 133.2; 139.2 ($C^{pA}$, minor); 139.4 ($C^{pA}$, major); 140.4 ($C^3$, minor); 140.6 ($C^3$, major); 144.0 ($C^{iC}$, minor); 144.5 ($C^{iC}$, major); 155.8 ($C^{pC}$, minor); 156.3 ($C^{pC}$, major); 159.4 ($C^{pB}$, minor); 161.0 ($C^{pB}$, major); 166.4 (C=N, major); 168.0 (C=N, minor) ppm. Signals of the major and minor isomers partially overlap. HRMS (ESI), *m/z*: calcd for $C_{24}H_{23}NO_2$ $[M+H]^+$ 358.1802, found 358.1802.

**4-Methoxy-*N*-((2*E*)-1-(4-nitrophenyl)-3-(4-methylphenyl)prop-2-en-1-ylidene)aniline (1n).** Orange crystals, 1.303 g (70%), mp 150-151 °C. According to the $^1$H NMR spectrum, imine **1n** exists as a mixture of *E*/*Z* isomers about the C=N bond in the ratio 3.3:1 at 23 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3H, Me, major); 2.37 (s, 3H, Me, minor); 3.71 (s, 3H, OMe, minor); 3.85 (s, 3H, OMe, major); 6.56-6.61 (m, 2H, $H^C$, minor); 6.63-6.70 (m, 3H, $H^C$, $H^3$, minor); 6.81 (d, *J* = 16.6 Hz, 1H, $H^3$, major); 6.91-7.01 (m, 5H, $H^{m,oC}$, $H^2$, major); 7.12-7.20 (m, 2H, $H^{mA}$, major; 2H, $H^{mA}$, minor); 7.22-7.28 (m, 2H, $H^{oA}$, major; 1H, $H^2$, minor; $CHCl_3$); 7.31-7.34 (m, 2H, $H^{oB}$, minor); 7.36 (d, *J* = 8.1 Hz, 2H, $H^{oA}$, minor); 7.86-7.92 (m, 2H, $H^{oB}$, major); 8.16-8.21 (m, 2H, $H^{mB}$, minor); 8.28-8.35 (m, 2H, $H^{mB}$, major) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.4 (Me, both isomers); 55.2 (OMe, minor); 55.4 (OMe, major); 113.9 ($C^{mC}$, minor); 114.2 ($C^{mC}$, major); 120.5 ($C^2$, major); 122.5 ($C^{oC}$, major); 123.46; 123.49 ($C^{mB}$, major); 127.5; 129.6; 130.00; 130.04; 130.3; 132.5 ($C^{iA}$, major); 132.6 ($C^{iA}$, minor); 139.9 ($C^{pA}$, minor); 140.2 ($C^{pA}$, major); 141.3 ($C^3$, minor); 141.6 ($C^3$, major); 142.96, 142.99 ($C^{iB}$, $C^{iC}$, minor); 143.5 ($C^{iC}$, major); 145.9 ($C^{iB}$, major); 147.5 ($C^{pB}$, minor); 148.5 ($C^{pB}$, major); 156.4 ($C^{pC}$, minor); 157.0 ($C^{pC}$, major); 165.0 (C=N, major); 166.2 (C=N, minor) ppm. Signals of the major and minor isomers partially overlap. HRMS (ESI), *m/z*: calcd for $C_{23}H_{20}N_2O_3$ $[M+H]^+$ 373.1547, found 373.1546.

**General procedure for the preparation of pyrazoles 2a-n:** *N*-Aminophthalimide (0.486 g, 3 mmol) was added to a stirred suspension of $K_2CO_3$ (2.5 g, 18 mmol) in a solution of imine **1a-n** (1 mmol) in dry $CH_2Cl_2$ (30 mL) at room temperature followed by addition of $Pb(OAc)_4$ (1.329 g, 3 mmol) in small portions within 5 min. Reaction mixture was stirred for 10 min and the inorganic precipitate was filtered off. The solid was washed with $CH_2Cl_2$ and combined filtrates concentrated under reduced pressure. The residue was purified by column chromatography (hexane/ethylacetate from 14:1 to 9:1) on silica gel. Aziridines **3h,i** could be obtained in addition to pyrazoles **2h,i** by avoiding column chromatography. (See General procedure for the preparation of pyrazoles, 2 mmol scale). The residue after solvent evaporation was grinded with 12 mL $Et_2O$/$CH_2Cl_2$/hexane 4:1:1. The precipitate was filtered and recrystallized from ethyl acetate with a little ethanol to give aziridines **3h,i**. The filtrate was evaporated under reduced pressure, and pyrazole **2h,i** was isolated by column chromatography on silica gel (hexane/ethyl acetate from 14:1 to 9:1).

**Possible transformation of imidoylaziridines 3h,i into pyrazoles 2h,i:** $Pb(OAc)_4$ (44 mg, 0.1 mmol) was added to a stirred suspension of $K_2CO_3$ (83 mg, 0.6 mmol) in solution of aziridine **3h,i** (0.1 mmol) and *N*-aminophthalimide (16 mg, 0.1 mmol) in dry $CH_2Cl_2$ (2 mL) at room temperature and the reaction mixture was kept for 2 hours. According to the TLC analysis, pyrazole **2h,i** did not form. According to $^1$H NMR spectra of the substances obtained after solvent removal, only starting aziridines **3h,i** and small amounts of unidentified impurities, but not pyrazoles **2h,i** were present in the reaction mixture.




**1-(4-Methylphenyl)-3,5-diphenylpyrazole[17] (2a).** Colorless crystals, 232 mg (75%), mp 107 °C (lit. 106-108 °C)[17]. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H, Me); 6.83 (s, 1H, $H^4$); 7.16 (d, *J* = 8.2 Hz, 2H, $H^{mA}$); 7.24-7.38 (m, 8H, $H^{oA}$, $H^{pB}$, $H^C$; $CHCl_3$); 7.40-7.48 (m, 2H, $H^{mB}$); 7.90-7.98 (m, 2H, $H^{oB}$) ppm.

**1-(4-Methoxyphenyl)-3-(4-methylphenyl)-5-phenylpyrazole (2b).** Cream crystals, 246 mg (72%), mp 160 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3H, Me); 3.82 (s, 3H, OMe); 6.79 (s, 1H, $H^4$); 6.87 (d, *J* = 8.8 Hz, 2H, $H^{mA}$); 7.20-7.36 (m, 9H, $H^{oA}$, $H^{mB}$, $H^C$; $CHCl_3$); 7.82 (d, *J* = 8.8 Hz 2H, $H^{oB}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.3 (Me); 55.5 (OMe); 104.5 ($C^4$); 114.1 ($C^{mA}$); 125.6, 126.7 ($C^{oB}$, $C^{oA}$); 128.1 ($C^{pC}$); 128.4; 128.7; 129.3; 130.3, 130.7 ($C^{iB}$, $C^{iC}$); 133.5 ($C^{iA}$); 137.6 ($C^{pB}$); 144.2 ($C^5$); 151.7 ($C^3$); 158.8 ($C^{pA}$) ppm. HRMS (ESI), *m/z*: calcd for $C_{23}H_{20}N_2O$ $[M+H]^+$ 341.1648, found 341.1636.

**1-(4-Chlorophenyl)-3-(4-methylphenyl)-5-phenylpyrazole (2c).** Yellow crystals, 201 mg (58%), mp 144 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H, Me); 6.79 (s, 1H, $H^4$); 7.23-7.32 (m, 8H, $H^A$, $H^{mB}$, $H^{oC}$; $CHCl_3$); 7.33-7.38 (m, 3H, $H^{m,pC}$); 7.81 (d, *J* = 8.1 Hz, 2H, $H^{oB}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.3 (Me); 105.4 ($C^4$); 125.7, 126.3 ($C^{oB}$, $C^{oA}$); 128.5 ($C^{pC}$); 128.6; 128.7; 129.0; 129.4; 130.0, 130.4 ($C^{iB}$, $C^{iC}$); 132.9 ($C^{pA}$); 137.9 ($C^{pB}$); 138.7 ($C^{iA}$); 144.3 ($C^5$); 152.3 ($C^3$) ppm. HRMS (ESI), *m/z*: calcd for $C_{22}H_{17}ClN_2$ $[M+H]^+$ 345.1153, found 345.1155.

**1-(4-Bromophenyl)-3-(4-methylphenyl)-5-phenylpyrazole (2d).** Beige crystals, 214 mg (55%), mp 154 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H, Me); 6.79 (s, 1H, $H^4$); 7.22-7.31 (m, 6H, $H^{oA}$, $H^{mB}$, $H^{oC}$; $CHCl_3$);

7.32-7.38 (m, 3H, $H^{m,pC}$); 7.43-7.49 (m, 2H, $H^{mA}$); 7.81 (d, *J* = 8.1 Hz, 2H, $H^{oB}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.3 (Me); 105.5 ($C^4$); 120.8 ($C^{pA}$); 125.7, 126.5 ($C^{oB}$, $C^{oA}$); 128.5 ($C^{pC}$); 128.6; 128.7; 129.4; 130.0, 130.4 ($C^{iB}$, $C^{iC}$); 132.0 ($C^{mA}$); 137.9 ($C^{pB}$); 139.2 ($C^{iA}$); 144.3 ($C^5$); 152.4 ($C^3$) ppm. HRMS (ESI), *m/z*: calcd for $C_{22}H_{17}BrN_2$ $[M+H]^+$ 389.0648, found 389.0639.

**1-(4-(Methoxycarbonyl)phenyl)-3-(4-methylphenyl)-5-phenylpyrazole (2e).** Colorless crystals, 169 mg (46%), mp 160 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H, Me); 3.91 (s, 3H, $CO_2$Me); 6.81 (s, 1H, $H^4$); 7.21-7.39 (m, 7H, $H^{mB}$, $H^C$; $CHCl_3$); 7.45 (d, *J* = 8.6 Hz, 2H, $H^{oA}$); 7.82 (d, *J* = 8.0 Hz, 2H, $H^{oB}$); 8.01 (d, *J* = 8.6 Hz, 2H, $H^{mA}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.3 (Me); 52.2 ($CO_2$Me); 106.1 ($C^4$); 124.4 ($C^{oA}$); 125.7 ($C^{oB}$); 128.4 ($C^{pA}$); 128.60 ($C^{pC}$); 128.64; 128.8; 129.4; 129.9 ($C^{iB}$); 130.3 ($C^{mA}$); 130.4 ($C^{iC}$); 138.1 ($C^{pB}$); 143.7 ($C^{iA}$); 144.5 ($C^5$); 152.7 ($C^3$); 166.4 ($CO_2$Me) ppm. HRMS (ESI), *m/z*: calcd for $C_{24}H_{20}N_2O_2$ $[M+H]^+$ 369.1598, found 369.1591.

**3-(4-Methoxyphenyl)-1-(4-methylphenyl)-5-phenylpyrazole (2f).** Colorless crystals, 228 mg (67%), mp 119 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3H, Me); 3.86 (s, 3H, OMe); 6.75 (s, 1H, $H^4$); 6.97 (d, *J* = 8.7 Hz, 2H, $H^{mB}$); 7.14 (d, *J* = 8.2 Hz, 2H, $H^{mA}$); 7.21-7.36 (m, 7H, $H^{oA}$, $H^C$; $CHCl_3$); 7.86 (d, *J* = 8.7 Hz, 2H, $H^{oB}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.1 (Me); 55.3 (OMe); 104.5 ($C^4$); 114.0 ($C^{mB}$); 125.1 ($C^{oA}$); 126.0 ($C^{iB}$); 127.0; 128.1 ($C^{pC}$); 128.4; 128.7; 129.4; 130.8 ($C^{iC}$); 137.2, 137.8 ($C^{iA}$, $C^{pA}$); 144.2 ($C^5$); 151.6 ($C^3$); 159.5 ($C^{pB}$) ppm. HRMS (ESI), *m/z*: calcd for $C_{23}H_{20}N_2O$ $[M+H]^+$ 341.1648, found 341.1645.

**1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-5-phenylpyrazole[18] (2g).** Colorless crystals, 214 mg (59%), mp 123-124 °C (lit. 124-125 °C)[18]. $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3H, OMe); 6.75 (s, 1H, $H^4$); 6.97 (d, *J* = 8.7 Hz, 2H, $H^{mB}$); 7.25-7.32 (m, 6H, $H^A$, $H^{oC}$; $CHCl_3$); 7.33-7.38 (m, 3H, $H^{m,pC}$); 7.84 (d, *J* = 8.7 Hz, 2H, $H^{oB}$) ppm.

**1-(4-Cyanophenyl)-3-(4-methoxyphenyl)-5-phenylpyrazole (2h).** Cream crystals, 218 mg (31%) (2 mmol scale), mp 132-133 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3H, OMe); 6.77 (s, 1H, $H^4$); 6.95-7.01 (m, 2H, $H^{mB}$); 7.27-7.32 (m, 2H, $H^{oC}$); 7.35-7.43 (m, 3H, $H^{m,pC}$); 7.46-7.51 (m, 2H, $H^{oA}$); 7.57-7.63 (m, 2H, $H^{mA}$); 7.81-7.88 (m, 2H, $H^{oB}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.3 (OMe); 106.5 ($C^4$); 110.1 ($C^{pA}$); 114.1 ($C^{mB}$); 118.3 (C≡N); 124.6 ($C^{oA}$); 125.1 ($C^{iB}$); 127.1; 128.76; 128.82; 128.9 ($C^{pC}$); 130.2 ($C^{iC}$); 132.8 ($C^{mA}$); 143.4 ($C^{iA}$); 144.6 ($C^5$); 152.9 ($C^3$); 160.0 ($C^{pB}$) ppm. HRMS (ESI), *m/z*: calcd for $C_{23}H_{17}N_3O$ $[M+H]^+$ 352.1444, found 352.1444.

**1-(4-Nitrophenyl)-3-(4-methoxyphenyl)-5-phenylpyrazole (2i).** Yellow crystals, 179 mg (24%) (2 mmol scale), mp 134-135 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3H, OMe); 6.79 (s, 1H, $H^4$); 6.99 (d, *J* = 8.8 Hz, 2H, $H^{mB}$); 7.28-7.34 (m, 2H, $H^{oC}$); 7.36-7.45 (m, 3H, $H^{m,pC}$); 7.50-7.57 (m, 2H, $H^{oA}$); 7.86 (d, *J* = 8.8 Hz, 2H, $H^{oB}$); 8.14-8.22 (m, 2H, $H^{mA}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.3 (OMe); 106.9 ($C^4$); 114.2 ($C^{mB}$); 124.3, 124.4 ($C^{mA}$, $C^{oA}$); 125.0 ($C^{iB}$); 127.2; 128.8; 128.9; 129.0 ($C^{pC}$); 130.2 ($C^{iC}$); 144.8, 145.0 ($C^5$, $C^{iA}$); 145.6 ($C^{pA}$); 153.1 ($C^3$); 160.0 ($C^{pB}$) ppm. HRMS (ESI), *m/z*: calcd for $C_{22}H_{17}N_3O_3$ $[M+Na]^+$ 394.1162, found 394.1157.

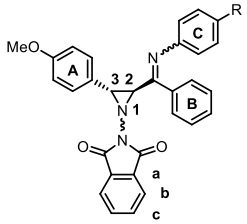
**3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-5-phenylpyrazole (2j).** Cream crystals, 245 mg (68%), mp 174 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3H, OMe); 6.78 (s, 1H, $H^4$); 6.84-6.91 (m, 2H, $H^{mA}$); 7.24-7.35 (m, 7H, $H^{oA}$, $H^C$; $CHCl_3$); 7.36-7.42 (m, 2H, $H^{mB}$); 7.82-7.88 (m, 2H, $H^{oB}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.5 (OMe); 104.5 ($C^4$); 114.1 ($C^{mA}$); 126.7, 127.0 ($C^{oB}$, $C^{oA}$); 128.3 ($C^{pC}$); 128.5; 128.7; 128.8; 130.4 ($C^{iC}$); 131.7 ($C^{iB}$); 133.3, 133.6 ($C^{iA}$, $C^{pB}$); 144.5 ($C^5$); 150.5 ($C^3$); 158.9 ($C^{pA}$) ppm. HRMS (ESI), *m/z*: calcd for $C_{22}H_{17}ClN_2O$ $[M+H]^+$ 361.1102, found 361.1108.

**3-(4-Chlorophenyl)-1-(4-methylphenyl)-5-phenylpyrazole (2k).** Colorless crystals, 242 mg (70%), mp 160 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H, Me); 6.78 (s, 1H, $H^4$); 7.15 (d, *J* = 8.2 Hz, 2H, $H^{mA}$); 7.21-7.36 (m, 7H, $H^{oA}$, $H^C$; $CHCl_3$); 7.40 (d, *J* = 8.5 Hz, 2H, $H^{mB}$); 7.86 (d, *J* = 8.5 Hz, 2H, $H^{oB}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.1 (Me); 104.8 ($C^4$); 125.1 ($C^{oA}$); 127.0 ($C^{oB}$); 128.3 ($C^{pC}$); 128.5; 128.7; 128.8; 129.5 ($C^{mA}$); 130.5 ($C^{iC}$); 131.7 ($C^{iB}$); 133.6 ($C^{pB}$); 137.5, 137.6 ($C^{iA}$, $C^{pA}$); 144.5 ($C^5$); 150.6 ($C^3$) ppm. HRMS (ESI), *m/z*: calcd for $C_{22}H_{17}ClN_2$ $[M+H]^+$ 345.1153, found 345.1158.

**3-(4-Nitrophenyl)-1-(4-methoxyphenyl)-5-phenylpyrazole (2l).** Colorless crystals, 234 mg (63%), mp 146 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3H, OMe); 6.85-6.93 (m, 3H, $H^4$, $H^{mA}$); 7.24-7.37 (m, 7H, $H^{oA}$, $H^C$; $CHCl_3$); 8.07 (d, *J* = 8.9 Hz, 2H, $H^{oB}$); 8.28 (d, *J* = 8.9 Hz, 2H, $H^{mB}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.5 (OMe); 105.3 ($C^4$); 114.2 ($C^{mA}$); 124.1 ($C^{mB}$); 126.1, 126.6 ($C^{oB}$, $C^{oA}$); 128.5 ($C^{pC}$); 128.6; 128.7; 130.0 ($C^{iC}$); 133.0 ($C^{iA}$); 139.5 ($C^{iB}$); 145.0 ($C^5$); 147.2 ($C^{pB}$); 149.2 ($C^3$); 159.2 ($C^{pA}$) ppm. HRMS (ESI), *m/z*: calcd for $C_{22}H_{17}N_3O_3$ $[M+H]^+$ 372.1343, found 372.1341.

**1,5-Bis(4-methoxyphenyl)-3-(4-methylphenyl)pyrazole (2m).** Beige crystals, 201 mg (54%), mp 119 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3H, Me); 3.81 (s, 3H, OMe); 3.82 (s, 3H, OMe); 6.72 (s, 1H, $H^4$); 6.81-6.91 (m, 4H, $H^{mA}$, $H^{mC}$); 7.17-7.25 (m, 4H, $H^{mB}$, $H^{oC}$); 7.27-7.32 (m, 2H, $H^{oA}$); 7.81 (d, *J* = 8.1 Hz, 2H, $H^{oB}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.3 (Me); 55.2 (OMe); 55.4 (OMe); 103.9 ($C^4$); 113.8, 114.0 ($C^{mA}$, $C^{mC}$); 123.1 ($C^{iC}$); 125.6 ($C^{oA}$); 126.7 ($C^{oB}$); 129.3, 129.9 ($C^{mB}$, $C^{oC}$); 130.4 ($C^{iB}$); 133.6 ($C^{iA}$); 137.5 ($C^{pB}$); 144.0 ($C^5$); 151.5 ($C^3$); 158.7, 159.4 ($C^{pA}$, $C^{pC}$) ppm. HRMS (ESI), *m/z*: calcd for $C_{24}H_{22}N_2O_2$ $[M+H]^+$ 371.1754, found 371.1749.

**1-(4-Methoxyphenyl)-3-(4-methylphenyl)-5-(4-nitrophenyl)pyrazole (2n).** Beige crystals, 193 mg (50%), mp 183 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H, Me); 3.84 (s, 3H, OMe); 6.87-6.94 (m, 3H, $H^4$, $H^{mA}$); 7.21-7.30 (m, 4H, $H^{oA}$, $H^{mB}$; $CHCl_3$); 7.39-7.46 (m, 2H, $H^{oC}$); 7.80 (d *J* = 8.1 Hz, 2H, $H^{oB}$); 8.13-8.20 (m, 2H, $H^{mC}$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.3 (Me); 55.5 (OMe); 105.5 ($C^4$); 114.4 ($C^{mA}$); 123.7 ($C^{mC}$); 125.7 ($C^{oA}$); 126.9 ($C^{oB}$); 129.1, 129.4 ($C^{mB}$, $C^{oC}$); 129.7 ($C^{iB}$); 132.8 ($C^{iA}$); 136.8 ($C^{iC}$); 138.1 ($C^{pB}$); 141.8 ($C^5$); 147.1 ($C^{pC}$); 152.1 ($C^3$); 159.3 ($C^{pA}$) ppm. HRMS (ESI), *m/z*: calcd for $C_{23}H_{19}N_3O_3$ $[M+H]^+$ 386.1499, found 386.1501.




**4-{[[*rel*-(2*S*,3*R*)-1-(1,3-Dioxo-1,5-dihydro-2*H*-isoindol-2-yl)-3-(4-methoxyphenyl)-aziridin-2-yl](phenyl)methylene]amino}benzonitrile (3h).** Pale yellow crystals, 328 mg (33%), mp 164 °C. According to the $^1$H NMR spectrum at -20 °C it exists as a mixture of three forms in the ratio of 1:0.16:0.14. $^1$H NMR (400 MHz, $CDCl_3$, 253 K): δ = 3.56 (d, *J* = 5.8 Hz, 1H, $H^3$, minor II); 3.69 (s, 3H, OMe, minor II); 3.72 (s, 3H, OMe, minor I); 3.81 (s, 3H, OMe, major); 3.97 (d, *J* = 5.2 Hz, 1H, $H^2$, major); 4.34 (d, *J* = 5.4 Hz, 1H, $H^3$, minor I); 4.80 (d, *J* = 5.2 Hz, 1H, $H^3$, major); 4.94 (d, *J* = 5.4 Hz, 1H, $H^2$, minor I); 5.40 (d, *J* = 5.8 Hz, 1H, $H^2$, minor II); 6.45 (d, *J* = 8.5 Hz, 2H, $H^{oC}$, major); 6.68 (d, *J* = 8.7 Hz, 2H, $H^{mA}$, minor II); 6.77 (d, *J* = 8.7 Hz, 2H, $H^{mA}$, minor I); 6.81 (d, *J* = 8.5 Hz, 2H, $H^{oC}$, minor I); 6.90-6.98 (m, 2H, $H^{mA}$, major; 2H, $H^{oA}$, minor II); 7.02 (d, *J* = 8.5 Hz, 2H, $H^{oC}$, minor II); 7.23-7.37 (m, 5H, $H^{m,pB}$, $H^{mC}$, major; 4H, $H^{oA}$, $H^{oB}$, minor I; $CHCl_3$); 7.41-7.53 (m, 4H, $H^{oA}$, $H^{oB}$, major; 10H, $H^{m,pB}$, $H^{mC}$, minor I and II); 7.58-7.73 (m, 4H, PhthN, major, 8H, PhthN, minor I and II); 8.05-8.10 (m, 2H, $H^{oB}$, minor II) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$, 253 K): δ = 42.6 ($C^2$, minor II); 47.2 ($C^2$, minor I); 50.8 ($C^3$, major); 51.7 ($C^3$, minor II); 52.3 ($C^2$, major); 52.8 ($C^3$, minor I); 55.06, 55.08 (OMe, minor I and II); 55.2 (OMe, major); 106.07 ($C^{pC}$, major); 106.14, 106.4 ($C^{pC}$, minor I and II); 113.5, 113.6 ($C^{mA}$, minor I and II); 113.8 ($C^{mA}$, major); 119.1 (C≡N, major); 119.9 ($C^{oC}$, minor); 120.1 (C≡N, minor I or II); 120.6 ($C^{oC}$, major); 121.2 ($C^{oC}$, minor); 121.3 (C≡N, minor I or II); 122.8 ($C^b$, br); 123.0; 127.1 ($C^{iA}$, major); 128.2; 128.3; 128.4; 128.50; 128.52; 129.1; 129.5 ($C^a$, br); 129.8 ($C^{pB}$, major); 130.1; 130.2; 130.6; 131.4; 132.78 ($C^{mC}$, major); 132.85 ($C^{mC}$, minor); 134.1 ($C^c$, minor); 134.16 ($C^c$, major); 134.24 ($C^c$, minor); 134.3 ($C^{iB}$, minor); 135.4 ($C^{iB}$, major); 135.6 ($C^{iB}$, minor); 153.5 ($C^{iC}$, major); 153.9, 154.3 ($C^{iC}$, minor I and II); 159.4 ($C^{pA}$, major); 159.7,

159.8 ($C^{pA}$, minor I and II); 164.0 (C=N, major); 164.2 (C=N, minor II); 165.2 (CON, br, all forms); 167.4 (C=N, minor I) ppm. Signals of the major and minor isomers partially overlap. HRMS (ESI), *m/z*: calcd for $C_{31}H_{22}N_4O_3$ $[M+H]^+$ 499.1765, found 499.1745.

***N*-[[*rel*-(2*S*,3*R*)-1-(1,3-Dioxo-1,5-dihydro-2*H*-isoindol-2-yl)-3-(4-methoxyphenyl)-aziridin-2-yl](phenyl)methylene]-4-nitroaniline (3i).** Pale yellow crystals, 425 mg (41%), mp 164 °C. According to the $^1$H NMR spectrum at -20 °C it exists as a mixture of three forms in the ratio of 1:0.13:0.13. $^1$H NMR (400 MHz, $CDCl_3$, 253 K): δ = 3.61 (d, *J* = 5.8 Hz, 1H, $H^3$, minor II); 3.69 (s, 3H, OMe, minor II); 3.74 (s, 3H, OMe, minor I); 3.83 (s, 3H, OMe, major); 3.98 (d, *J* = 5.2 Hz, 1H, $H^2$, major); 4.34 (d, *J* = 5.4 Hz, 1H, $H^3$, minor I); 4.80 (d, *J* = 5.2 Hz, 1H, $H^3$, major); 4.95 (d, *J* = 5.4 Hz, 1H, $H^2$, minor I); 5.43 (d, *J* = 5.8 Hz, 1H, $H^2$, minor II); 6.48 (d, *J* = 8.9 Hz, 2H, $H^{oC}$, major); 6.67 (d, *J* = 8.6 Hz, 2H, $H^{mA}$, minor II); 6.78 (d, *J* = 8.6 Hz, 2H, $H^{mA}$, minor I); 6.85 (d, *J* = 8.8 Hz, 2H, $H^{oC}$, minor I); 6.94 (d, *J* = 8.6 Hz, 2H, $H^{mA}$, major); 6.99 (d, *J* = 8.6 Hz, 2H, $H^{oA}$, minor II); 7.05 (d, *J* = 8.8 Hz, 2H, $H^{oC}$, minor II); 7.27-7.38 (m, 3H, $H^{m,pB}$, major, 4H, $H^{oA}$, $H^{oB}$, minor I); 7.43-7.54 (m, 4H, $H^{oA}$, $H^{oB}$, major, 6H, $H^{m,pB}$, minor I and II); 7.59-7.74 (m, 4H, PhthN, major, 8H, PhthN, minor I and II); 7.87 (d, *J* = 8.9 Hz, 2H, $H^{mC}$, major); 8.03-8.10 (m, 6H, $H^{oB}$, minor II, $H^{mC}$, minor I and II) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$, 253 K): δ = 42.8 ($C^2$, minor II); 47.2 ($C^2$, minor I); 51.1 ($C^3$, major); 51.7 ($C^3$, minor II); 52.2 ($C^2$, major); 53.0 ($C^3$, minor I); 55.11, 55.14 (OMe, minor I and II); 55.3 (OMe, major); 113.5 ($C^{mA}$, minor I); 113.7 ($C^{mA}$, minor II); 113.9 ($C^{mA}$, major); 119.6 ($C^{oC}$, minor II); 120.1 ($C^{iA}$, minor II); 120.2 ($C^{oC}$, major), 120.8 ($C^{oC}$, minor I); 121.3 ($C^{iA}$, minor I); 122.8 ($C^b$, br); 123.1 ($C^b$); 124.6 ($C^{mC}$, minor I or II); 124.7 ($C^{mC}$, major); 124.8 ($C^{mC}$, minor I or II); 127.1 ($C^{iA}$, major); 128.2 ($C^{oB}$, minor II); 128.4 ($C^{oA}$, major); 128.45 ($C^{mB}$, major); 128.53; 128.55; 128.6; 129.2 ($C^{oB}$, major); 129.6 ($C^a$, br, all forms); 130.1 ($C^{pB}$, major); 130.2 ($C^{oA}$, minor II); 130.3; 130.6 ($C^{oA}$, minor I); 131.6 ($C^{pB}$, minor II); 134.2 ($C^c$, minor I or II or both); 134.3 ($C^c$, major); 135.37 ($C^{iB}$, major); 135.42 ($C^{iB}$, minor I or II or both); 143.0 ($C^{pC}$, major); 143.2 ($C^{pC}$, minor II), 143.3 ($C^{pC}$, minor I); 155.6 ($C^{iC}$, major); 156.0, 156.5 ($C^{iC}$, minor I and II); 159.5 ($C^{pA}$, major); 159.8, 159.9 ($C^{pA}$, minor I and II); 163.9 (C=N, minor II); 164.4 (C=N, major); 165.2 (CON, br, all forms); 167.7 (C=N, minor I) ppm. Signals of the major and minor isomers partially overlap. The assignment of signals was performed using 2D NMR including $^1$H-$^{13}$C HSQC, HMBC, $^1$H-$^1$H COSY and NOESY spectra. HRMS (ESI), *m/z*: calcd for $C_{30}H_{22}N_4O_5$ $[M+Na]^+$ 541.1482, found 541.1474.

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[12] CCDC 1515644 contains the supplementary crystallographic data for this paper (**3i**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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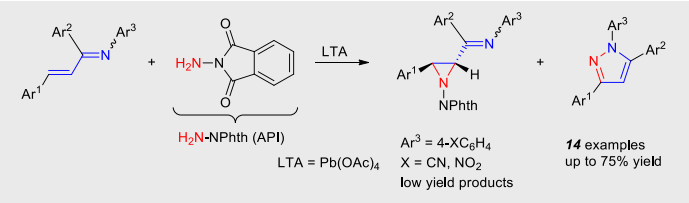


Oxidative addition of *N*-aminophthalimide to 1,2,4-triaryl-1-azabuta-1,3-dienes leads, in most cases, to the regiodefined formation of 1,3,5-triarylpyrazoles via [4+1]-annulation in moderate to good yields. Rare examples of 2-imidoyl-1-phthalimidoaziridines that are formed via competitive [2+1]-cycloaddition onto the C=C bond were isolated in low yields for 1-azadienes with electron-deficient aryl substituents at the imine nitrogen atom.

**Cycloaddition, [4+1]-Annulation**

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**Pyrazoles and *C*-imidoylaziridines via [4+1]-annulation and [2+1]-cycloaddition of 1-azabuta-1,3-dienes with a synthetic equivalent of phthalimidonitrene**