DOI: 10.1002/ejoc.201001560

Ethyl 3- and 5-Triflyloxy-1*H*-pyrazole-4-carboxylates in the Synthesis of Condensed Pyrazoles by Pd-Catalysed Cross-Coupling Reactions

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Keywords: Heterocycles / Palladium / Cross coupling / Cyclization / NMR spectroscopy

The easily obtainable title compounds ethyl 5- and 3-triflyloxy-1*H*-pyrazole-4-carboxylates (**2** and **5**) have been used as precursors in Sonogashira-type cross-coupling reactions with various alkynes to obtain the corresponding 5- and 3-alkynyl-4-(ethoxycarbonyl)pyrazoles **3** and **6**. Cyclization of the latter *ortho*-difunctional synthons afforded different condensed pyrazoles such as pyrano[4,3-*c*]pyrazol-4(1*H*)-ones and -4(2*H*)-ones **7** and **10** as well as 1,5-dihydro- and 2,5-dihydro-4*H*-pyrazolo[4,3-*c*]pyridin-4-ones **9** and **12**, respectively. Suzuki coupling of triflate **2** with phenylboronic acids gave the corresponding 5-arylpyrazoles. Heating of 5-(3-chlorophenyl)-1-phenyl-1*H*-pyrazole-4-carboxylic acid (**16**) with trifluoromethanesulfonic acid led to the formation of the unexpected tetracyclic system **18**. Detailed NMR spectroscopic investigations were undertaken on all obtained products.

Introduction

Within the last three decades, transition-metal-mediated cross-coupling reactions have emerged as tools of great importance for C–X (X = C, O, N, S) bond formation.[1–4] Of these methods, those involving Pd^0 catalysis are of particularly special use for the synthesis of complex molecules due to their excellent selectivity and high functional-group compatibility. Thus, for instance, Sonogashira,[5,6] Suzuki,[7,8] Stille[9,10] and Heck[11] reactions have been widely used in the synthesis of natural products and biologically active compounds. In recent years the above-mentioned reactions have also been increasingly employed for the functionalization of heteroaromatics and for the construction of corresponding annulated systems.[12,13] For azoles, this has been documented in a number of studies.[14] These heteroarenes are found in many compounds of biological importance as well as in natural products.[15,16] Thus, the pyrazole (1,2-diazole) system is an important core structure in many pharmaceuticals, agrochemicals, dyes and complexing agents.[17–19] For the functionalization of pyrazoles by Suzuki,[20,21] Sonogashira[21,22] and Stille coupling reactions,[21] appropriate halopyrazoles have been mainly used as precursors. Recently, pyrazole triflates have also been employed in Suzuki coupling reactions.[20c,23] These reactive species are readily available from the corresponding pyrazolones (hydroxypyrazoles), which are frequently accessible from commercial sources. In contrast, the use of *O*-triflated pyrazoles in Sonogashira-type cross-coupling strategies is largely unexplored, but it is anticipated to be a powerful approach for the functionalization of such compounds, especially in the construction of fused systems containing pyrazole units. In this context, we herein report the cross-coupling (mainly Sonogashira) reactions of ethyl 3- and 5-triflyloxypyrazole-4-carboxylates and the subsequent synthesis of some annulated pyrazoles starting from the initially formed coupling products.

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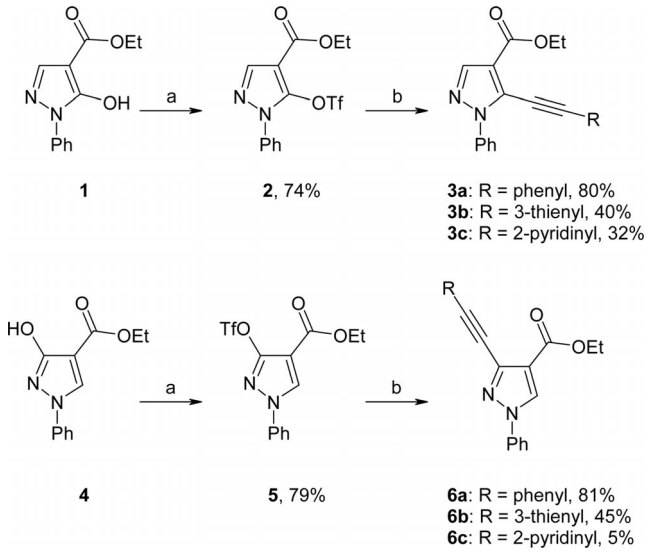
Results and Discussion

Synthesis

Triflates **2** and **5** represent the key compounds in the synthetic approach reported herein (Scheme 1). The general method for the preparation of *O*-triflates involves the treatment of hydroxylic substrates with triflic anhydride in the presence of non-nucleophilic tertiary amines or inorganic bases.[20c,20d,23,24] The triflate group was smoothly introduced at C-5 or C-3 of the pyrazole nucleus in high yields by the reaction of hydroxypyrazole **1** or **4** with triflic anhydride in the presence of triethylamine in dichloromethane to give 5- or 3-triflyloxy-1*H*-pyrazole-4-carboxylates **2** and **5** (Scheme 1). The formation of unwanted mixtures of *N*- and *O*-triflated products was not observed. The starting materials **1** and **4** are commercially available or easily obtainable through known procedures. Thus, reaction of diethyl ethoxymethylenemalonate with phenylhydrazine leads to **1**,[25] whereas treatment of diethyl ethoxymethylenemalonate with 2-acetyl-1-phenylhydrazine in the presence

of $POCl_3$ gives **4**.[25] Triflates **2** and **5** represent *ortho*-difunctional synthons with the OTf moiety as an ideal leaving group in Pd-catalysed cross-coupling reactions such as Suzuki[7,26] and Sonogashira[6] reactions. The corresponding ethyl 3- or 5-iodocarboxylates can be regarded as comparable synthons for Sonogashira reactions.[6,27] However, their synthesis seems less convenient and, for instance, requires the transformation of appropriate aminopyrazoles into the iodo derivatives by diazotization[28–30] as the direct introduction of iodo substituents into the pyrazole nucleus is preferred in the electron-rich 4-position.[31] In principle, the same is true for the corresponding ethyl bromopyrazolecarboxylates, which are also possible starting materials for Suzuki coupling reactions.

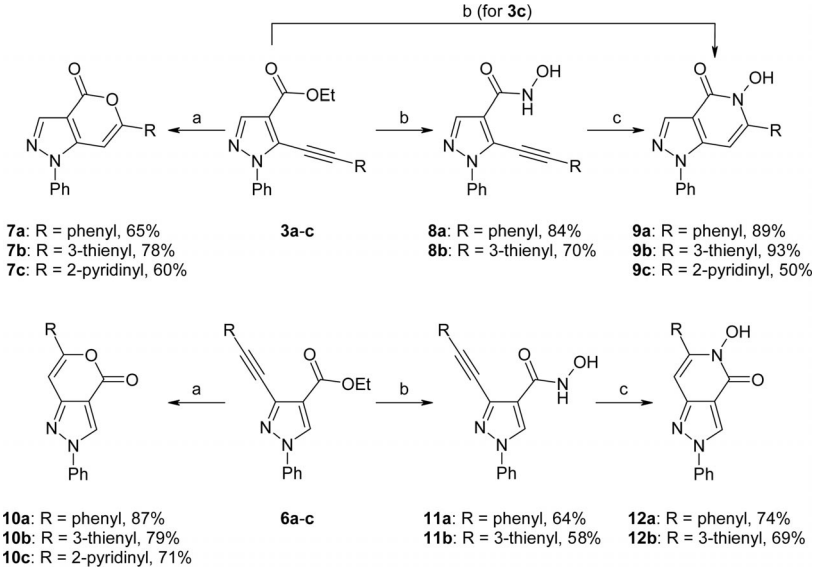


Scheme 1. Reagents and conditions: (a) Tf_2O, TEA, DCM, room temp., 1 h; (b) R–C≡CH, $[Pd(PPh_3)_2Cl_2]$, TEA, CuI, DMF, 55–80 °C, 2–24 h.

Triflate **2** smoothly underwent Sonogashira-type cross-coupling with ethynylbenzene (80% yield of coupling product **3a**). However, the reactions of **2** with 3-ethynylthiophene and 2-ethynylpyridine gave lower yields of the coupling products **3b** (40%) and **3c** (32%).

The OTf group in triflate **5** turned out to be less reactive than that in **2**, requiring longer reaction times and a higher temperature to obtain the corresponding coupling products **6a** and **6b** in comparable yields (**6a**: 81%; **6b**: 45%; Scheme 1). For some unknown reason, the yield of **6c** was very low (5%).

The 4,5- and 3,4-difunctionalized pyrazoles **3** and **6** are potential precursors of the corresponding annulated systems. This was demonstrated by the treatment of compounds **3** with polyphosphorus acid (PPA), which directly resulted in the formation of 1-phenylpyrano[4,3-*c*]pyrazol-4(1*H*)-ones **7a**–**c** (Scheme 2) in good yields by a 6-*endo*-dig ring-closing reaction.[32] The formation of a five-membered ring system (structure **X**, Figure 1) by 5-*exo*-dig cyclization can be ruled out on analysis of the NMR spectra of compounds **7** (see NMR Spectroscopic Investigations). The synthesis of related compounds has recently been reported to occur by the reaction of 5-iodo-1-methylpyrazole-4-carboxylic acid with different acetylenes under Pd/C/Cu catalysis.[30] Analogously, coupling products **6** were transformed into the corresponding 6-substituted 2-phenylpyrano[4,3-*c*]-pyrazol-4(2*H*)-ones **10a**–**c** in high yields. To obtain hydroxamic acids of type **8** and **11**, the esters **3a**–**c** and **6a**,**b** were treated with hydroxylamine. With **3a** and **3b** this yielded the appropriate products **8a** and **8b**, respectively. However, we did not isolate the expected hydroxamic acid upon treatment of **3c** with hydroxylamine, instead the cyclization product **9c** was obtained. The corresponding 5-hydroxy-1,5-dihydro-4*H*-pyrazolo[4,3-*c*]pyridin-4-ones **9a** and **9b** were achieved by reaction of **8a** and **8b** with triethylamine in methanol. Treatment of **6a** and **6b** with hydroxyl-



Scheme 2. Reagents and conditions: (a) PPA, 100 °C, 10 min; (b) $NH_2OH{\cdot}HCl$, NaOMe, reflux, 10 min; (c) TEA, MeOH, reflux, 2–24 h.

amine afforded the hydroxamic acids **11a** and **11b**, which were cyclized to **12a** and **12b** under the reaction conditions used for the synthesis of **9a** and **9b**. Investigations regarding the preparation of pyrazolopyridinones from *vic*-alkynyl/hydrazidopyrazoles and *vic*-alkynylpyrazole hydroxamic acids have been reported by Vasilevsky and Elguero.[33]

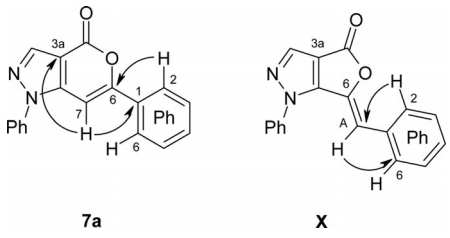
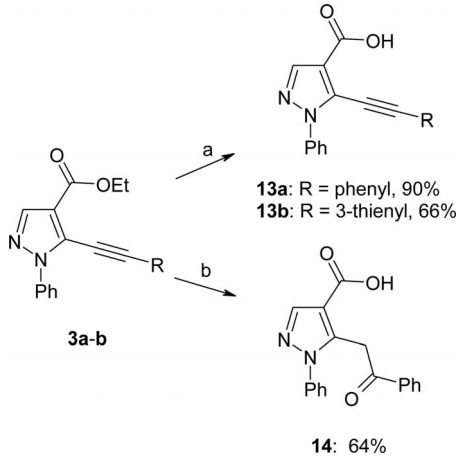


Figure 1. Proof of structure **7a** by diagnostic $^{13}C,^{1}H$ correlations (expected correlations for **7a** found; not found for **X**).

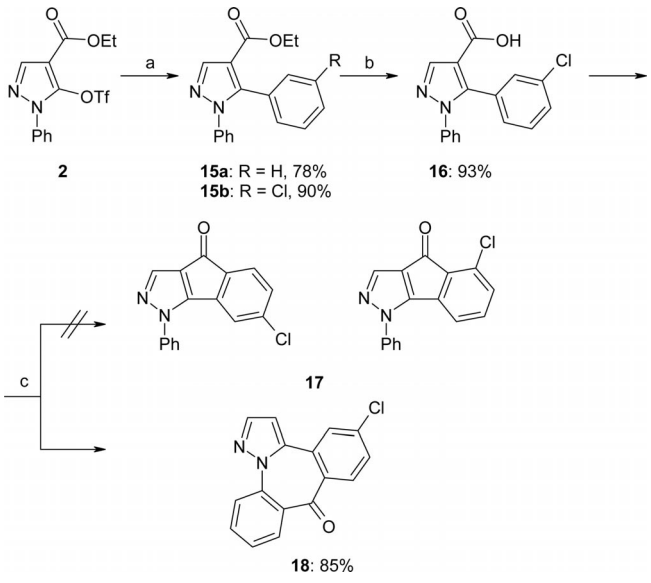
During the cyclization of **9** (and also **12**), in principle, the formation of a seven-membered ring, a 1*H*-pyrazolo[4,3-*d*][1,2]oxazepin-4(5*H*)-one system **Y** {or 2-phenyl-2*H*-pyrazolo[4,3-*d*][1,2]oxazepin-4(5*H*)-one system **Z**}, is also possible (see Figure 3). However, the NMR spectroscopic data (see NMR Spectroscopic Investigations) allowed the unambiguous assignment of structures **9** and **12**, respectively, to the cyclization products proposed above. Compounds **9** and **12** are interesting as they can be further functionalized at the OH group.

Compounds **3a**,**b** were readily hydrolysed to the corresponding pyrazole-4-carboxylic acids **13a**,**b** upon reaction with LiOH/H_2O in dioxane. Moreover, treatment of alkyne **3a** with hydrochloric acid led to compound **14**, which results from the addition of water to the triple bond followed by tautomerization of the thus formed enol to the corresponding ketone (Scheme 3).

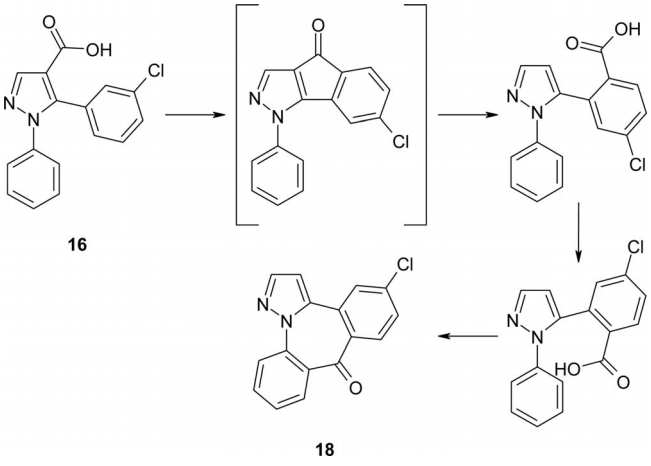


Scheme 3. Reagents and conditions: (a) LiOH, H_2O, dioxane, 60 °C, overnight; (b) 4 N HCl, dioxane, reflux, 3 d.

Triflate **2** not only is an appropriate starting material for Sonogashira reactions, but it can also be employed in Suzuki-type coupling reactions. This was demonstrated in brief by the reaction of **2** with phenylboronic acid under typical Suzuki conditions {[$Pd(PPh_3)_4$], K_3PO_4, KBr, dioxane}, which produced ethyl 1,5-diphenyl-1*H*-pyrazole-4-carboxylate (**15a**) in high yield (Scheme 4). Accordingly, **2** and (3-chlorophenyl)boronic acid gave **15b**, which was hydrolysed to the acid **16**. To obtain tricycle **17**, the latter was subjected to various cyclization conditions (H_2SO_4, PPA, $ClSO_3H$). Whereas in most of these attempts the starting material **16** remained unchanged, treatment of **16** with trifluoromethanesulfonic acid led to the formation of an unexpected product. On the basis of detailed NMR spectroscopic investigations, this compound was finally unequivocally assigned to the structure **18**. A possible explanation for the formation of **18** is given in Scheme 5: it includes a transfer of the COOH group from the pyrazole to the chlorophenyl system by a ring-closing/ring-opening process followed by a condensation reaction with the *N*-phenyl ring. The literature revealed only a few examples of related reactions with *N*-phenylpyrazoles.[34,35]



Scheme 4. Reagents and conditions: (a) arylboronic acid, [$Pd(PPh_3)_4$], K_3PO_4, KBr, dioxane, reflux, overnight; (b) HCl, H_2O, dioxane, reflux, 2 d; (c) TfOH, 165 °C, 4 d.



Scheme 5. Possible mechanistic explanation for the formation of **18**.

NMR Spectroscopic Investigations

The NMR spectroscopic data of all the compounds investigated in this study are given in the Exp. Sect. Unequivocal assignment of the signals was carried out by the combined application of standard NMR spectroscopic techniques such as ^{1}H-coupled ^{13}C NMR spectra, APT, HMQC, gs-HSQC, gs-HMBC, COSY, TOCSY, NOESY and NOE difference spectroscopy.[36] Moreover, in a few cases, experiments with selective excitation (DANTE) of certain ^{1}H resonances were performed, such as long-range INEPT[37] and 2D (δ,J) long-range INEPT;[38] the latter experiments were indispensable for the unambiguous mapping of long-range ^{13}C,^{1}H coupling constants. Reliable and unambiguously assigned chemical shift data such as those presented here can be considered as important and valuable reference material for NMR prediction programs, such as CSEARCH[39]/NMR PREDICT[40] and ACD/C + H predictor,[41] programs that have become very popular in the last few years, particularly for predicting ^{13}C NMR chemical shifts.

In the ^{13}C NMR spectra of the starting triflates **2** and **5**, the carbon atom of the trifluoromethyl group resonates as a quartet [$^1J(^{19}F,^{13}C) \approx 321$ Hz] at δ = 118.0 (**2**) and 118.6 ppm (**5**), respectively, whereas the corresponding ^{19}F shifts are located at δ = –73.8 (**2**) and –72.8 ppm (**5**). Coupling products **3a**–**c** exhibit very consistent signal sets related to the invariable part of the molecule; the same is true for their regioisomers **6a**–**c**. The alkyne C signals in compounds of type **3**, **6**, **8** and **11** can be easily discriminated on the basis of their coupling patterns. The alkyne C atom attached to the pyrazole system has no possibility of coupling with adjacent protons and hence appears as a singlet signal in the ^{1}H-coupled ^{13}C NMR spectrum and thus also lacks correlations in HMBC experiments. In contrast, the alkyne C atoms appended to the phenyl (series **a**), 3-thienyl (series **b**) or 2-pyridyl ring (series **c**) show couplings with protons of the latter (hetero)aromatic systems leading to multiplet signals in the ^{1}H-coupled ^{13}C NMR spectrum and to corresponding correlations in the HMBC spectra.

Switching from triflates **2** and **5** to the corresponding coupling products **3** and **6** results in a marked downfield shift for both pyrazole ^{15}N NMR resonances. Whereas compound **2** has δ = –171.6 ppm for pyrazole N-1 and δ = –82.3 ppm for pyrazole N-2, alkyne **3a**, as an example, exhibits chemical shifts of δ = –156.9 and –72.0 ppm for the corresponding pyrazole N atoms.

The 2-pyranone substructure in compound **7a** (and thus 6-*endo*-dig cyclization of precursor **6a**) unambiguously follows from the appearance of the correlations $^3J_{C\text{-}3a,7\text{-}H}$, $^3J_{PhC\text{-}1,7\text{-}H}$ and $^3J_{C\text{-}6,Ph2,6\text{-}H}$ in the HMBC spectra (also in ^{1}H-coupled ^{13}C NMR; Figure 1). With alternative structure **X** (resulting from 5-*exo*-dig cyclization) these correlations are not possible. Instead, for **X** the correlations $^3J_{PhC\text{-}2/6,alkene\text{-}H}$ and $^3J_{alkeneCH,Ph2,6\text{-}H}$ are expected; however, these were not observed (Figure 1). Analogously, structures **7b** and **7c** were unequivocally assigned. Proof of isomeric structures **10a**–**c** follows a similar approach.

In the ^{13}C NMR spectra of compounds **7**, the signals due to C-4 are located in the range between δ = 157.4 and 157.7 ppm, typical values for carbonyl C resonances in 2*H*-pyran-2-ones.[42] Another characteristic feature is the highly polarized double bond C-6=C-7 incorporated in the pyran system. Whereas C-6 (attached to the ring oxygen atom) resonates between δ = 154.9 (**7c**) and 158.6 ppm (**7a**), the ^{13}C chemical shift of C-7 is much smaller (δ = 90.0–92.4 ppm), as expected. The alkene 7-H chemical shifts in **7a** (δ = 7.03 ppm) and **7b** (δ = 6.86 ppm) are comparable; however, the corresponding 7-H signal in the pyridine derivative **7c** is markedly shifted downfield (δ = 7.81 ppm). A possible explanation for this phenomenon can be given on the basis of the following: form A of compound **7c** seems to be the less preferred conformer as here the lone-pairs of the ring oxygen atom and the pyridine N atom interact as an electrostatic obstacle (Figure 2). However, in the favoured form B the lone-pair of the pyridine N atom comes close to 7-H, which is influenced by the former (electrostatic field effect[43]) and thus experiences a considerable downfield shift. Similar effects can be observed, for instance, in 2,2′-bipyridine, in which 3-H (δ =8.50 ppm) has a much larger chemical shift than the corresponding 5-H (δ = 7.12 ppm; Figure 2). Even more pronounced effects appear in the rigid benzo[*h*]quinoline, the corresponding H atom resonating at δ = 9.30 ppm (shifts taken from ref.[44]; Figure 2). In contrast, a reverse situation is present in compound **9c**. Here the pyridine N atom is involved in an intramolecular hydrogen bond with the OH proton, promoting a conformation with 7-H and the pyridine N atom far apart (Figure 2). As a consequence, 7-H now shows a much smaller chemical shift (δ = 6.95 ppm) than 7-H in **7c**, being now in the same range as related chemical shifts for **7a**,**b**

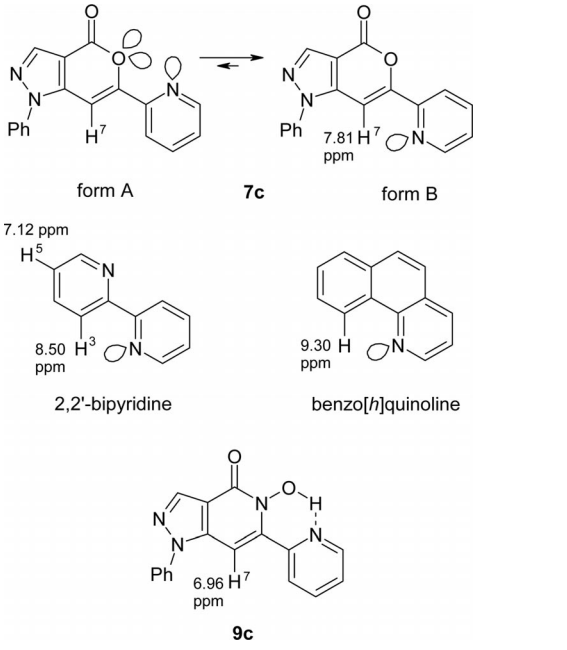


Figure 2. Influence of lone-pair effects on the ^{1}H NMR chemical shifts of **7c**, 2,2′-bipyridine, benzo[*h*]quinoline, and **9c** (all in $CDCl_3$).

and **9a**,**b**. The somewhat smaller ^{15}N chemical shift of N-5 (N–OH) in **9c** (δ = –178.9 ppm) relative to the corresponding shifts in **9a** (δ = –175.2 ppm) and **9b** (δ = –175.3 ppm) provides an additional hint for the presence of an intramolecular hydrogen bond in **9c**. Similar phenomena as found in series **7** were also observed with compounds **10a**–**c**.

As mentioned above in the Synthesis section, cyclization of alkynes **8** and **11** in principle can also lead to the formation of seven-membered ring systems of type **Y** and **Z**, respectively, by the addition of OH to the C≡C triple bond (Figure 3). However, these structures can be ruled out as the $^{15}N,^{1}H$ HMBC spectra of the cyclization products exhibit a clear correlation between the ring alkene H atom and the N–O nitrogen atom (N-5), which is only possible in the six-membered rings in structures **9** and **12** ($^{3}J_{N\text{-}5,H\text{-}7}$, Figure 3).

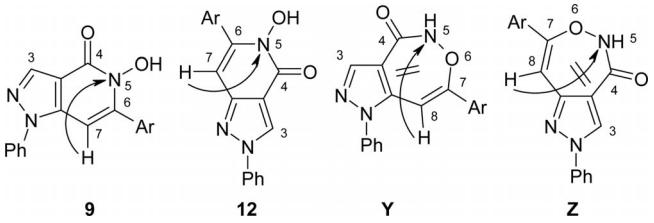


Figure 3. Proof of the structures **9** and **12** by $^{15}N,^{1}H$ HMBC correlations.

Careful NMR analysis permitted the elucidation of structure **18**, the formation of which had not been expected. Whereas the precursor substance **16** still shows the typical pattern of an *N*-phenyl system with joint signals of double intensity for 2,6-H, 3,5-H, C-2,6 and C-3,5, the symmetry of the *N*-Ph system is nullified in the spectra of **18**, leading to the conclusion that substitution must have occurred. Combined application of HSQC, HMBC, TOCSY, COSY and NOESY experiments finally enabled the unambiguous assignment of structure **18**.

Conclusions

We have demonstrated that the title compounds, triflates **2** and **5**, are suitable precursors for Sonogashira-type cross-coupling reactions. The resulting *ortho*-functionalized alkynylpyrazoles can be transformed into different condensed systems with a pyranopyrazole or pyrazolopyridine core. Moreover, the applicability of triflate **2** in Suzuki coupling reactions has been shown with two examples. Further investigations in this area are in progress and will be published elsewhere.

Experimental Section

General: Melting points were determined with a Reichert–Kofler hot-stage microscope. Mass spectra were obtained with Shimadzu QP 1000 (EI, 70 eV) and Finnigan MAT 8230 (EI, 70 eV, HRMS) instruments. IR spectra were recorded with a Perkin–Elmer FTIR 1605 spectrophotometer. Elemental analyses (C, H, and N) were performed at the Microanalytical Laboratory, University of Vienna, and the data are in good agreement (±0.4%) with calculated values. ^{1}H and ^{13}C NMR spectra were recorded with a Varian UnityPlus 300 spectrometer at 28 °C (299.95 MHz for ^{1}H, 75.43 MHz for ^{13}C) or Bruker Avance 500 spectrometer at 293 K (500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C). The centres of the solvent signals were used as internal standards and referenced to that of TMS with δ_H = 7.26 ($CDCl_3$) and 2.49 ppm ([D_6]DMSO) and δ_C = 77.0 ($CDCl_3$) and 39.5 ppm ([D_6]DMSO). ^{15}N (50.68 MHz, referenced to external nitromethane) and ^{19}F NMR spectra (470.56 MHz, absolute referencing by the Ξ ratio) were recorded with a Bruker Avance 500 instrument with a "directly" detecting broadband observe probe (BBFO). Digital resolutions were 0.25 Hz/data point in the ^{1}H NMR spectra and 0.4 Hz/data point in the ^{13}C NMR spectra. Th = thienyl. Systematic names were generated with the ACD/Name[45] program in accord with IUPAC recommendations and were checked manually.[46] For chromatographic separations, Kieselgel 60 (70–230 mesh, Merck) was used.

General Procedure for Pyrazole Triflation. Synthesis of Compounds 2 and 5: The appropriate hydroxypyrazole **1** or **4** (2.32 g, 10 mmol), triethylamine (1.62 mL, 12 mmol) and trifluoromethanesulfonic anhydride (1.77 mL, 10.5 mmol) were dissolved in dichloromethane (20 mL), and the mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water (30 mL) and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, washed with brine and dried with sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography (SiO_2, eluent ethyl acetate/light petroleum, 1:7 v/v).

Ethyl 1-Phenyl-5-{[(trifluoromethyl)sulfonyl]oxy}-1*H*-pyrazole-4-carboxylate (2): Yield: 2.696 g, 74%; colourless solid, m.p. 84 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.1 Hz, 3 H, CH_3), 4.39 (q, J = 7.1 Hz, 2 H, CH_2), 7.46–7.55 (m, 5 H, Ph-H), 8.09 (s, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 ($^{1}J_{CH3}$ = 127.4, $^{2}J_{CH3,OCH2}$ = 2.7 Hz, CH_3), 61.2 ($^{1}J_{OCH2}$ = 148.2, $^{2}J_{OCH2,CH3}$ = 4.4 Hz, CH_2), 106.3 ($^{2}J_{C\text{-}4,3\text{-}H}$ = 8.7 Hz, C-4), 118.0 (q, $^{1}J_{CF3}$ = 321.5 Hz, CF_3), 124.2 (Ph C-2,6), 129.48 (Ph C-3,5), 129.49 (Ph C-4), 136.0 (Ph C-1), 140.9 (C-5, $^{3}J_{C\text{-}5,3\text{-}H}$ = 5.8 Hz), 141.5 (C-3, $^{1}J_{C\text{-}3,3\text{-}H}$ = 195.5 Hz), 160.6 (C=O, $^{3}J_{CO,OCH2}$ = 3.2 Hz) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –171.6 (N-1), –82.3 (N-2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –73.8 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 1708 (C=O) cm^{-1}. MS: *m*/*z* (%) = 364 (7) $[M]^+$, 231 (34) $[M - SO_2CF_3]^+$, 185 (27), 157 (38), 91 (24), 77 (100), 53 (21), 51 (28). $C_{13}H_{11}F_3N_2O_5S$ (364.30): calcd. C 42.86, H 3.04, N 7.69; found C 42.99, H 2.79, N 7.59.

Ethyl 1-Phenyl-3-{[(trifluoromethyl)sulfonyl]oxy}-1*H*-pyrazole-4-carboxylate (5): Yield: 2.878 g, 79%; colourless solid, m.p. 103–105 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 (t, J = 7.2 Hz, 3 H, CH_3), 4.39 (q, J = 7.2 Hz, 2 H, CH_2), 7.40 (m, 1 H, Ph 4-H), 7.50 (m, 2 H, Ph 3,5-H), 7.65 (m, 2 H, Ph 2,6-H), 8.39 (s, 1 H, 5-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 ($^{1}J_{CH3}$ = 127.4, $^{2}J_{CH3,OCH2}$ = 2.7 Hz, CH_3), 61.3 ($^{1}J_{OCH2}$ = 148.2, $^{2}J_{OCH2,CH3}$ = 4.4 Hz, CH_2), 107.7 ($^{2}J_{C\text{-}4,5\text{-}H}$ = 6.3 Hz, C-4), 118.6 (q, $^{1}J_{CF3}$ = 321.0 Hz, CF_3), 119.3 (Ph C-2,6), 128.4 (Ph C-4), 129.8 (Ph C-3,5), 131.9 ($^{1}J_{C\text{-}5,5\text{-}H}$ = 194.4 Hz, C-5), 138.4 (Ph C-1), 151.8 ($^{3}J_{C\text{-}3,5\text{-}H}$ = 10.3 Hz, C-3), 160.3 ($^{3}J_{CO,OCH2}$ = 3.2, $^{3}J_{CO,5\text{-}H}$ = 0.8 Hz, C=O) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –173.4 (N-1), –94.8 (N-2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –72.8 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 1708 (C=O) cm^{-1}. MS: *m*/*z* (%) = 364 (39) $[M]^+$, 231 (100) $[M - SO_2CF_3]^+$, 77 (95), 69 (24), 53 (21), 51 (28). $C_{13}H_{11}F_3N_2O_5S$ (364.30): calcd. C 42.86, H 3.04, N 7.69; found C 42.97, H 2.90, N 7.62.

General Procedure for the Sonogashira Reaction. Synthesis of Compounds 3a–c and 6a–c: Triethylamine (2.08 mL, 15 mmol), the appropriate arylacetylene (phenyl, 3-thienyl or 2-pyridyl; 3.6 mmol),

$[Pd(PPh_3)_2Cl_2]$ (211 mg, 0.3 mmol) and CuI (114 mg, 0.6 mmol) were added to a solution of **2** or **5** (1.09 g, 3 mmol) in dry dimethylformamide (20 mL) under argon. The reaction mixture was stirred at 55 °C under argon for 2 h (for **5** at 80 °C for 24 h). The reaction mixture was poured into water (30 mL) and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, washed with brine and dried with sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography (SiO_2; eluent ethyl acetate/light petroleum, 1:7 v/v; for **6c** eluent ethyl acetate/light petroleum, 1:5 → 1:2 v/v).

Ethyl 1-Phenyl-5-(phenylethynyl)-1*H*-pyrazole-4-carboxylate (3a): Yield: 759 mg, 80%; colourless solid, m.p. 74 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (t, J = 7.1 Hz, 3 H, CH_3), 4.39 (q, J = 7.1 Hz, 2 H, CH_2), 7.37 (m, 3 H, CPh 3,4,5-H), 7.44 (m, 1 H, NPh 4-H), 7.46 (m, 2 H, CPh 2,6-H), 7.53 (m, 2 H, NPh 3,5-H), 7.81 (m, 2 H, NPh 2,6-H), 8.13 (s, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 ($^1J_{CH3}$ = 127.0, $^2J_{CH3,OCH2}$ = 2.7 Hz, CH_3), 60.5 ($^1J_{OCH2}$ = 147.6, $^2J_{OCH2,CH3}$ = 4.4 Hz, CH_2), 77.5 (*C*CPh), 100.7 ($^3J_{CCPh,CPh2,6-H}$ = 5.5 Hz, C*C*Ph), 118.2 ($^2J_{C-4,3-H}$ = 9.0 Hz, C-4), 121.7 (CPh C-1), 124.1 (NPh C-2,6), 127.2 ($^3J_{C-5,3-H}$ = 4.0 Hz, C-5), 128.45 (NPh C-4), 128.5 (CPh C-3,5), 128.9 (NPh C-3,5), 129.5 (CPh C-4), 131.6 (CPh C-2,6), 139.2 (NPh C-1), 141.9 ($^1J_{C-3,3-H}$ = 192.3 Hz, C-3), 162.3 ($^3J_{CO,OCH2}$ = 3.1, $^3J_{CO,3-H}$ < 1 Hz, C=O) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –156.9 (N-1), –72.0 (N-2) ppm. IR (KBr): $\tilde{\nu}$ = 1736 (C=O) cm^{-1}. MS: *m*/*z* (%) = 316 (17) $[M]^+$, 287 (25) $[M - CH_2CH_3]^+$, 271 (26) $[M - OCH_2CH_3]^+$, 97 (24), 83 (24), 77 (27), 71 (57), 69 (39), 57 (100), 56 (22), 55 (50), 43 (83), 41 (55). $C_{20}H_{16}N_2O_2$ (316.35): calcd. C 75.93, H 5.10, N 8.86; found C 76.03, H 4.94, N 8.66.

Ethyl 1-Phenyl-5-(3-thienylethynyl)-1*H*-pyrazole-4-carboxylate (3b): Yield: 387 mg, 40%; brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 (t, J = 7.1 Hz, 3 H, CH_3), 4.37 (q, J = 7.1 Hz, 2 H, CH_2), 7.13 (dd, $^3J_{Th4-H,Th5-H}$ = 5.0, $^4J_{Th2-H,Th4-H}$ = 1.2 Hz, 1 H, Th 4-H), 7.30 (dd, $^3J_{Th4-H,Th5-H}$ = 5.0, $^4J_{Th2-H,Th5-H}$ = 3.0 Hz, 1 H, Th 5-H), 7.42 (m, 1 H, Ph 4-H), 7.51 (m, 2 H, Ph 3,5-H), 7.55 (dd, $^4J_{Th2-H,Th5-H}$ = 3.0, $^4J_{Th2-H,Th4-H}$ = 1.2 Hz, 1 H, Th 2-H), 7.79 (m, 2 H, Ph 2,6-H), 8.11 (s, 1 H, 3-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 ($^1J_{CH3}$ = 127.0, $^2J_{CH3,OCH2}$ = 2.6 Hz, CH_3), 60.4 ($^1J_{OCH2}$ = 147.5, $^2J_{OCH2,CH3}$ = 4.4 Hz, CH_2), 77.1 (*C*CTh), 96.1 ($^3J_{CCTh,Th2-H}$ = 3.8, $^3J_{CCTh,Th4-H}$ = 2.1 Hz, C*C*Th), 118.1 ($^2J_{C-4,3-H}$ = 9.5 Hz, C-4), 120.8 ($^2J_{ThC-3,Th2-H}$ = 3.2, $^2J_{ThC-3,Th4-H}$ = 4.7, $^3J_{ThC-3,Th5-H}$ = 11.1 Hz, Th C-3), 124.0 (Ph C-2,6), 125.8 ($^1J_{ThC-5,5-H}$ = 188.1, $^2J_{ThC-5,4-H}$ = 7.1, $^3J_{ThC-5,Th2-H}$ = 5.6 Hz, Th C-5), 127.2 ($^3J_{C-5,3-H}$ = 4.2 Hz, C-5), 128.4 (Ph C-4), 128.9 (Ph C-3,5), 129.4 ($^1J_{ThC-4,Th4-H}$ = 172.3, $^2J_{ThC-4,Th5-H}$ = 4.6, $^3J_{ThC-4,Th2-H}$ = 8.4 Hz, Th C-4), 130.5 ($^1J_{ThC-2,Th2-H}$ = 188.6, $^3J_{ThC-2,Th4-H}$ = 8.4, $^3J_{ThC-2,Th5-H}$ = 4.6 Hz, Th C-2), 139.2 (Ph C-1), 141.9 ($^1J_{C-3,3-H}$ = 192.3 Hz, C-3), 162.3 ($^3J_{CO,OCH2}$ = 3.0 Hz, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1706 (C=O) cm^{-1}. MS: *m*/*z* (%) = 323 (20) $[M + H]^+$, 322 (100) $[M]^+$, 293 (93) $[M - CH_2CH_3]^+$, 277 (93) $[M - OCH_2CH_3]^+$, 111 (37), 77 (65), 51 (32). MS: calcd. for $[C_{18}H_{14}N_2O_2S + H]^+$ 323.0854; found 323.0853.

Ethyl 1-Phenyl-5-(2-pyridylethynyl)-1*H*-pyrazole-4-carboxylate (3c): Yield: 305 mg, 32%; yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.1 Hz, 3 H, CH_3), 4.39 (q, J = 7.1 Hz, 2 H, CH_2), 7.28 (ddd, $^3J_{Pyr4-H,Pyr5-H}$ = 7.6, $^3J_{Pyr5-H,Pyr6-H}$ = 4.9, $^4J_{Pyr3-H,Pyr5-H}$ = 1.3 Hz, 1 H, Pyr 5-H), 7.43 (m, 1 H, Ph 4-H), 7.51 (m, $^3J_{Pyr3-H,Pyr4-H}$ = 7.8, $^4J_{Pyr3-H,Pyr5-H}$ = 1.3, $^5J_{Pyr3-H,Pyr6-H}$ = 1.0 Hz, 1 H, Pyr 3-H), 7.52 (m, 2 H, Ph 3,5-H), 7.68 (dt, $^3J_{Pyr3-H,Pyr4-H}$ = 7.8, $^3J_{Pyr4-H,Pyr5-H}$ = 7.6, $^4J_{Pyr4-H,Pyr6-H}$ = 1.8 Hz, 1 H, Pyr 4-H), 7.83 (m, 2 H, Ph 2,6-H), 8.13 (s, 1 H, 3-H), 8.63 (ddd, $^3J_{Pyr5-H,Pyr6-H}$ = 4.9, $^4J_{Pyr4-H,Pyr6-H}$ = 1.8, $^5J_{Pyr3-H,Pyr6-H}$ = 1.0 Hz, 1 H, Pyr 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 ($^1J_{CH3}$ = 127.1, $^2J_{CH3,OCH2}$ = 2.7 Hz, CH_3), 60.6 ($^1J_{OCH2}$ = 147.7, $^2J_{OCH2,CH3}$ = 4.4 Hz, CH_2), 77.2 (*C*CPyr), 99.4 ($^3J_{CCPyr,Pyr3-H}$ = 3.3 Hz, C*C*Pyr), 119.4 ($^2J_{C-4,3-H}$ = 8.9 Hz, C-4), 123.6 (Pyr C-5), 123.9 (Ph C-2,6), 126.3 ($^3J_{C-5,3-H}$ = 4.1 Hz, C-5), 127.7 ($^1J_{PyrC-3,Pyr3-H}$ = 167.4, $^3J_{PyrC-3,Pyr5-H}$ = 6.8, $^4J_{PyrC-3,Pyr6-H}$ = 1.7 Hz, Pyr C-3), 128.6 (Ph C-4), 129.1 (Ph C-3,5), 136.1 ($^1J_{PyrC-4,Pyr4-H}$ = 164.4, $^3J_{PyrC-4,Pyr6-H}$ = 6.3 Hz, Pyr C-4), 139.1 (Ph C-1), 141.9 ($^1J_{C-3,3-H}$ = 192.6 Hz, C-3), 142.2 (Pyr C-2), 150.4 ($^1J_{PyrC-6,Pyr6-H}$ = 188.1, $^2J_{PyrC-6,Pyr5-H}$ = 3.3, $^3J_{PyrC-6,Pyr4-H}$ = 7.1 Hz, Pyr C-6), 162.0 ($^3J_{CO,OCH2}$ = 3.1, $^3J_{CO,3-H}$ < 1 Hz, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1728 (C=O) cm^{-1}. MS: *m*/*z* (%) = 317 (36) $[M]^+$, 316 (38) $[M - H]^+$, 288 (66) $[M - CH_3CH_2]^+$, 277 (22), 272 (82) $[M - OCH_2CH_3]^+$, 262 (26), 245 (30), 244 (100) $[M - COOCH_2CH_3]^+$, 218 (23), 183 (24), 108 (24), 78 (29), 77 (64), 51 (34). MS: calcd. for $[C_{19}H_{15}N_3O_2 + H]^+$ 318.1243; found 318.1245.

Ethyl 1-Phenyl-3-(phenylethynyl)-1*H*-pyrazole-4-carboxylate (6a): Yield: 768 mg, 81%; colourless solid, m.p. 104–105 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (t, J = 7.2 Hz, 3 H, CH_3), 4.39 (q, J = 7.2 Hz, 2 H, CH_2), 7.37 (m, 4 H, NPh 4-H, CPh 3,4,5-H), 7.49 (m, 2 H, NPh 3,5-H), 7.64 (m, 2 H, CPh 2,6-H), 7.75 (m, 2 H, NPh 2,6-H), 8.44 (s, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 ($^1J_{CH3}$ = 127.0, $^2J_{CH3,OCH2}$ = 2.6 Hz, CH_3), 60.6 ($^1J_{OCH2}$ = 147.7, $^2J_{OCH2,CH3}$ = 4.4 Hz, CH_2), 80.6 (*C*CPh), 93.6 ($^3J_{CCPh,CPh2,6-H}$ = 5.6 Hz, C*C*Ph), 118.2 ($^2J_{C-4,5-H}$ = 6.4 Hz, C-4), 119.7 (NPh C-2,6), 122.5 (CPh C-1), 127.9 (NPh C-4), 128.3 (CPh C-3,5), 128.8 (CPh C-4), 129.6 (NPh C-3,5), 130.8 ($^1J_{C-5,5-H}$ = 192.5 Hz, C-5), 131.9 (CPh C-2,6), 137.0 ($^3J_{C-3,5-H}$ = 8.1 Hz, C-3), 139.0 (NPh C-1), 162.0 ($^3J_{CO,OCH2}$ = 3.0, $^3J_{CO,5-H}$ = 0.7 Hz, C=O) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –161.8 (N-1), –72.0 (N-2) ppm. IR (KBr): $\tilde{\nu}$ = 1693 (C=O) cm^{-1}. MS: *m*/*z* (%) = 317 (20) $[M + H]^+$, 316 (100) $[M]^+$, 288 (33), 287 (30) $[M - CH_2CH_3]^+$, 271 (30) $[M - OCH_2CH_3]^+$, 171 (34), 77 (51), 51 (27). $C_{20}H_{16}N_2O_2$ (316.35): calcd. C 75.93, H 5.10, N 8.86; found C 75.59, H 4.89, N 8.76.

Ethyl 1-Phenyl-3-(3-thienylethynyl)-1*H*-pyrazole-4-carboxylate (6b): Yield: 435 mg, 45%; brown solid, m.p. 130–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.1 Hz, 3 H, CH_3), 4.36 (q, J = 7.1 Hz, 2 H, CH_2), 7.26 (dd, $^3J_{Th4-H,Th5-H}$ = 5.0, $^4J_{Th2-H,Th4-H}$ = 1.2 Hz, 1 H, Th 4-H), 7.28 (dd, $^3J_{Th4-H,Th5-H}$ = 5.0, $^4J_{Th2-H,Th5-H}$ = 2.9 Hz, 1 H, Th 5-H), 7.33 (m, 1 H, Ph 4-H), 7.45 (m, 2 H, Ph 3,5-H), 7.63 (dd, $^4J_{Th2-H,Th5-H}$ = 2.9, $^4J_{Th2-H,Th4-H}$ = 1.2 Hz, 1 H, Th 2-H), 7.72 (m, 2 H, Ph 2,6-H), 8.41 (s, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 ($^1J_{CH3}$ = 127.0, $^2J_{CH3,OCH2}$ = 2.6 Hz, CH_3), 60.5 ($^1J_{OCH2}$ = 147.7, $^2J_{OCH2,CH3}$ = 4.4 Hz, CH_2), 80.2 (*C*CTh), 88.8 ($^3J_{CCTh,Th2-H}$ = 3.8, $^3J_{CCTh,Th4-H}$ = 2.2 Hz, C*C*Th), 117.9 ($^2J_{C-4,5-H}$ = 6.5 Hz, C-4), 119.5 (Ph C-2,6), 121.5 ($^2J_{ThC-3,Th2-H}$ = 3.2, $^2J_{ThC-3,Th4-H}$ = 5.4, $^3J_{ThC-3,Th5-H}$ = 10.5 Hz, Th C-3), 125.3 ($^1J_{ThC-5,Th5-H}$ = 187.4, $^2J_{ThC-5,Th4-H}$ = 7.3, $^3J_{ThC-5,Th2-H}$ = 5.9 Hz, Th C-5), 127.7 (Ph C-4), 129.5 (Ph C-3,5), 129.8 ($^1J_{ThC-4,Th4-H}$ = 171.7, $^2J_{ThC-4,Th5-H}$ = 4.7, $^3J_{ThC-4,Th2-H}$ = 8.4 Hz, Th C-4), 129.85 ($^1J_{ThC-2,Th2-H}$ = 188.0, $^3J_{ThC-2,Th4-H}$ = 8.3, $^3J_{ThC-2,Th5-H}$ = 5.1 Hz, Th C-2), 130.6 ($^1J_{C-5,5-H}$ = 192.5 Hz, C-5), 136.9 ($^3J_{C-3,5-H}$ = 8.1 Hz, C-3), 138.8 (Ph C-1), 161.9 (C=O) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –161.3 (N-1), –80.6 (N-2) ppm. IR (KBr): $\tilde{\nu}$ = 1691 (C=O) cm^{-1}. MS: *m*/*z* (%) = 323 (20) $[M + H]^+$, 322 (100) $[M]^+$, 294 (22), 293 (22) $[M - CH_2CH_3]^+$, 277 (28) $[M - OCH_2CH_3]^+$, 171 (32), 77 (42), 51 (23). $C_{18}H_{14}N_2O_2S$ (322.38): calcd. C 67.06, H 4.38, N 8.69; found C 67.23, H 4.37, N 8.43.

Ethyl 1-Phenyl-3-(2-pyridylethynyl)-1*H*-pyrazole-3-carboxylate (6c): Yield: 47 mg, 5%; brown solid, m.p. 108–110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 (t, J = 7.2 Hz, 3 H, CH_3), 4.38 (q, J = 7.2 Hz, 2 H, CH_2), 7.27 (ddd, $^3J_{Pyr4-H,Pyr5-H}$ = 7.4, $^3J_{Pyr5-H,Pyr6-H}$

= 4.9, $^4J_{Pyr3\text{-}H,Pyr5\text{-}H}$ = 1.4 Hz, 1 H, Pyr 5-H), 7.37 (m, 1 H, Ph 4-H), 7.49 (m, 2 H, Ph 3,5-H), 7.62 (m, $^3J_{Pyr3\text{-}H,Pyr4\text{-}H}$ = 8.0, $^4J_{Pyr3\text{-}H,Pyr5\text{-}H}$ = 1.4 Hz, 1 H, Pyr 3-H), 7.69 (dt, $^3J_{Pyr3\text{-}H,Pyr4\text{-}H}$ = 8.0, $^3J_{Pyr4\text{-}H,Pyr5\text{-}H}$ = 7.4, $^4J_{Pyr4\text{-}H,Pyr6\text{-}H}$ = 1.8 Hz, 1 H, Pyr 4-H), 7.74 (m, 2 H, Ph 2,6-H), 8.44 (s, 1 H, 5-H), 8.67 (d, $^3J_{Pyr5\text{-}H,Pyr6\text{-}H}$ = 4.9, $^4J_{Pyr4\text{-}H,Pyr6\text{-}H}$ = 1.8 Hz, 1 H, Pyr 6-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 ($^1J_{CH3}$ = 127.1, $^2J_{CH3,OCH2}$ = 2.6 Hz, CH_3), 60.7 ($^1J_{OCH2}$ = 147.7, $^2J_{OCH2,CH3}$ = 4.4 Hz, CH_2), 80.2 (*C*CPyr), 92.4 (C*C*Pyr), 118.7 ($^2J_{C\text{-}4,5\text{-}H}$ = 6.6 Hz, C-4), 119.6 (Ph C-2,6), 123.2 (Pyr C-5), 127.6 (Pyr C-3), 127.9 (Ph C-4), 129.6 (Ph C-3,5), 130.6 ($^1J_{C\text{-}5,5\text{-}H}$ = 192.8 Hz, C-5), 136.0 (Pyr C-4), 136.2 ($^3J_{C\text{-}3,5\text{-}H}$ = 8.1 Hz, C-3), 138.9 (Ph C-1), 142.9 (Pyr C-2), 150.1 (Pyr C-6), 161.8 ($^3J_{CO,OCH2}$ = 3.2 Hz, C=O) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –160.4 (N-1), –69.6 (N-2), –65.2 (Pyr N) ppm. IR (KBr): $\tilde{\nu}$ = 1696 (C=O) cm^{-1}. MS: *m*/*z* (%) = 317 (32) $[M]^+$, 272 (28) $[M - OCH_2CH_3]^+$, 245 (56), 244 (34), 140 (23), 77 (100), 57 (45), 55 (29), 51 (49), 43 (53). MS: calcd. for $[C_{19}H_{15}N_3O_2 + H]^+$ 318.1243; found 318.1240.

General Procedure for the Cyclization of 3a–c and 6a–c with PPA. Synthesis of Compounds 7a–c and 10a–c: An appropriate carboxylate (**3a**–**c**, **6a**–**b**; 158 mg, 0.5 mmol; for **6c** 0.16 mmol of starting material) and PPA (2 mL) were stirred at 100 °C for 10 min. Water (15 mL) was added to the reaction mixture, and the mixture was extracted with ethyl acetate (3 × 15 mL). The organic layers were combined, washed with brine and dried with sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography (SiO_2; eluent ethyl acetate/light petroleum, 1:5 v/v).

1,6-Diphenylpyrano[4,3-*c*]pyrazol-4(1*H*)-one (7a): Yield: 94 mg, 65%; colourless solid, m.p. 133–134.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03 (s, 1 H, 7-H), 7.45 (m, 3 H, CPh 3,4,5-H), 7.50 (m, 1 H, NPh 4-H), 7.61 (m, 2 H, NPh 2,6-H), 7.62 (m, 2 H, NPh 3,5-H), 7.86 (m, 2 H, CPh 2,6-H), 8.31 (s, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 90.5 ($^1J_{C\text{-}7,7\text{-}H}$ = 172.3 Hz, C-7), 107.5 ($^2J_{C\text{-}3a,3\text{-}H}$ = 9.7, $^3J_{C\text{-}3a,7\text{-}H}$ = 4.3 Hz, C-3a), 123.7 (NPh C-2,6), 125.9 (CPh C-2,6), 128.7 (NPh C-4), 128.9 (CPh C-3,5), 129.8 (NPh C-3,5), 130.8 (CPh C-4), 131.6 (CPh C-1), 138.4 (NPh C-1), 139.4 ($^1J_{C\text{-}3,3\text{-}H}$ = 194.2 Hz, C-3), 144.2 ($^3J_{C\text{-}7a,3\text{-}H}$ = 3.2, $^2J_{C\text{-}7a,7\text{-}H}$ < 1 Hz, C-7a), 157.7 (C-4), 158.6 ($^2J_{C\text{-}6,7\text{-}H}$ = 4.5, $^3J_{C\text{-}6,CPh2,6\text{-}H}$ = 4.5 Hz, C-6) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –174.0 (N-1), –66.5 (N-2) ppm. IR (KBr): $\tilde{\nu}$ = 1752 (C=O) cm^{-1}. MS: *m*/*z* (%) = 288 (64) $[M]^+$, 260 (28) $[M - CO]^+$, 105 (91), 77 (100), 57 (31), 51 (44). $C_{18}H_{12}N_2O_2$ (288.30): calcd. C 74.99, H 4.20, N 9.72; found C 74.77, H 4.00, N 9.60.

1-Phenyl-6-(3-thienyl)pyrano[4,3-*c*]pyrazol-4(1*H*)-one (7b): Yield: 115 mg, 78%; colourless solid, m.p. 192–195 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.86 (s, 1 H, 7-H), 7.39 (m 1 H, Th 5-H), 7.40 (m, 1 H, Th 4-H), 7.50 (m, 1 H, Ph 4-H), 7.60 (m, 4 H, Ph 2,3,5,6-H), 7.95 (dd, $^4J_{Th2\text{-}H,Th5\text{-}H}$ = 2.6, $^4J_{Th2\text{-}H,Th4\text{-}H}$ = 1.8 Hz, 1 H, Th 2-H), 8.29 (s, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 90.0 ($^1J_{C\text{-}7,7\text{-}H}$ = 172.5 Hz, C-7), 107.3 ($^2J_{C\text{-}3a,3\text{-}H}$ = 9.8, $^3J_{C\text{-}3a,7\text{-}H}$ = 4.5 Hz, C-3a), 123.6 (Ph C-2,6), 124.4 ($^1J_{ThC\text{-}4,Th4\text{-}H}$ = 168.8, $^2J_{ThC\text{-}4,Th5\text{-}H}$ = 4.6, $^3J_{ThC\text{-}4,Th2\text{-}H}$ = 8.4 Hz, Th C-4), 125.9 ($^1J_{ThC\text{-}2,Th2\text{-}H}$ = 187.7, $^3J_{ThC\text{-}2,Th4\text{-}H}$ = 7.2, $^3J_{ThC\text{-}2,Th5\text{-}H}$ = 5.8 Hz, Th C-2), 127.2 ($^1J_{ThC\text{-}5,Th5\text{-}H}$ = 187.4, $^2J_{ThC\text{-}5,Th4\text{-}H}$ = 6.2, $^3J_{ThC\text{-}5,Th2\text{-}H}$ = 6.2 Hz, Th C-5), 128.7 (Ph C-4), 129.8 (Ph C-3,5), 133.8 (Th C-3), 138.4 (Ph C-1), 139.5 ($^1J_{C\text{-}3,3\text{-}H}$ = 194.2 Hz, C-3), 144.2 ($^3J_{C\text{-}7a,3\text{-}H}$ = 3.2, $^2J_{C\text{-}7a,7\text{-}H}$ < 1 Hz, C-7a), 154.9 (C-6), 157.6 (C-4) ppm. IR (KBr): $\tilde{\nu}$ = 1748 (C=O) cm^{-1}. MS: *m*/*z* (%) = 294 (100) $[M]^+$, 266 (49) $[M - CO]^+$, 261 (29), 237 (20), 211 (21), 111 (56), 83 (29), 77 (69), 51 (51). $C_{16}H_{10}N_2O_2S$ (294.33) ·0.3H_2O: calcd. C 64.12, H 3.56, N 9.35; found C 64.17, H 3.26, N 9.35.

1-Phenyl-6-(2-pyridyl)pyrano[4,3-*c*]pyrazol-4(1*H*)-one (7c): Yield: 87 mg, 60%; colourless solid, m.p. 209–210 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (ddd, $^3J_{Pyr4\text{-}H,Pyr5\text{-}H}$ = 7.6, $^3J_{Pyr5\text{-}H,Pyr6\text{-}H}$ = 4.7, $^4J_{Pyr3\text{-}H,Pyr5\text{-}H}$ = 1.2 Hz, 1 H, Pyr 5-H), 7.49 (m, 1 H, Ph 4-H), 7.59 (m, 2 H, Ph 3,5-H), 7.66 (m, 2 H, Ph 2,6-H), 7.81 (d, $^5J_{7\text{-}H,3\text{-}H}$ = 0.9 Hz, 1 H, 7-H), 7.84 (ddd, $^3J_{Pyr3\text{-}H,Pyr4\text{-}H}$ = 8.0, $^3J_{Pyr4\text{-}H,Pyr5\text{-}H}$ = 7.6, $^4J_{Pyr4\text{-}H,Pyr6\text{-}H}$ = 1.8 Hz, 1 H, Pyr 4-H), 8.09 (ddd, $^3J_{Pyr3\text{-}H,Pyr4\text{-}H}$ = 8.0, $^4J_{Pyr3\text{-}H,Pyr5\text{-}H}$ = 1.2, $^5J_{Pyr3\text{-}H,Pyr6\text{-}H}$ = 1.2 Hz, 1 H, Pyr 3-H), 8.34 (d, $^5J_{7\text{-}H,3\text{-}H}$ = 0.9 Hz, 1 H, 3-H), 8.63 (ddd, $^3J_{Pyr5\text{-}H,Pyr6\text{-}H}$ = 4.7, $^4J_{Pyr4\text{-}H,Pyr6\text{-}H}$ = 1.8, $^5J_{Pyr3\text{-}H,Pyr6\text{-}H}$ = 1.2 Hz, 1 H, Pyr 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 92.4 ($^1J_{C\text{-}7,7\text{-}H}$ = 177.4 Hz, C-7), 108.3 ($^2J_{C\text{-}3a,3\text{-}H}$ = 9.7, $^3J_{C\text{-}3a,7\text{-}H}$ = 4.7 Hz, C-3a), 120.8 (Pyr C-3), 123.7 (Ph C-2,6), 124.9 (Pyr C-5), 128.7 (Ph C-4), 129.8 (Ph C-3,5), 137.2 (Pyr C-4), 138.3 (Ph C-1), 139.5 ($^1J_{C\text{-}3,3\text{-}H}$ = 194.4 Hz, C-3), 144.0 ($^3J_{C\text{-}7a,3\text{-}H}$ = 3.2 Hz, C-7a), 149.0 (Pyr C-2), 149.6 (Pyr C-6), 156.9 (C-6), 157.4 (C-4) ppm. IR (KBr): $\tilde{\nu}$ = 1768 (C=O) cm^{-1}. MS: *m*/*z* (%) = 289 (100) $[M]^+$, 261 (38) $[M - CO]^+$, 211 (45), 183 (23), 106 (51), 78 (66), 77 (62), 51 (57). $C_{17}H_{11}N_3O_2$ (289.30) ·0.4H_2O: calcd. C 69.07, H 3.81, N 13.95; found C 68.87, H 4.01, N 14.17.

2,6-Diphenylpyrano[4,3-*c*]pyrazol-4(2*H*)-one (10a): Yield: 125 mg, 87%; colourless solid, m.p. 219–220 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11 (s, 1 H, 7-H), 7.45 (m, 4 H, NPh 4-H, CPh 3,4,5-H), 7.54 (m, 2 H, NPh 3,5-H), 7.78 (m, 2 H, NPh 2,6-H), 7.88 (m, 2 H, CPh 2,6-H), 8.63 (s, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 94.9 ($^1J_{C\text{-}7,7\text{-}H}$ = 170.4 Hz, C-7), 109.2 ($^2J_{C\text{-}3a,3\text{-}H}$ = 6.9, $^3J_{C\text{-}3a,7\text{-}H}$ = 4.8 Hz, C-3a), 120.2 (NPh C-2,6), 125.5 (CPh C-2,6), 128.5 ($^1J_{C\text{-}3,3\text{-}H}$ = 193.9 Hz, C-3), 128.5 (NPh C-4), 128.8 (CPh C-3,5), 129.8 (NPh C-3,5), 130.0 (CPh C-4), 132.1 (CPh C-1), 139.1 (NPh C-1), 152.3 ($^3J_{C\text{-}7a,3\text{-}H}$ = 6.9 Hz, C-7a), 156.8 (C-6), 158.6 (C-4) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –152.5 (N-2), –92.6 (N-1) ppm. IR (KBr): $\tilde{\nu}$ = 1735 (C=O) cm^{-1}. MS: *m*/*z* (%) = 288 (100) $[M]^+$, 260 (44) $[M - CO]^+$, 231 (31), 77 (42), 51 (25). $C_{18}H_{12}N_2O_2$ (288.30) ·0.2H_2O: calcd. C 74.06, H 4.28, N 9.60; found C 74.09, H 3.92, N 9.56.

2-Phenyl-6-(3-thienyl)pyrano[4,3-*c*]pyrazol-4(2*H*)-one (10b): Yield: 116 mg, 79%; light-brown solid, m.p. 198–199 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.94 (s, 1 H, 7-H), 7.39 (dd, $^3J_{Th4\text{-}H,Th5\text{-}H}$ = 5.1, $^4J_{Th2\text{-}H,Th5\text{-}H}$ = 3.0 Hz, 1 H, Th 5-H), 7.42 (m, 1 H, Ph 4-H), 7.42 (dd, $^3J_{Th4\text{-}H,Th5\text{-}H}$ = 5.1, $^4J_{Th2\text{-}H,Th4\text{-}H}$ = 1.3 Hz, 1 H, Th 4-H), 7.53 (m, 2 H, Ph 3,5-H), 7.76 (m, 2 H, Ph 2,6-H), 7.87 (dd, $^4J_{Th2\text{-}H,Th5\text{-}H}$ = 3.0, $^4J_{Th2\text{-}H,Th4\text{-}H}$ = 1.3 Hz, 1 H, Th 2-H), 8.61 (s, 1 H, 3-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 94.4 ($^1J_{C\text{-}7,7\text{-}H}$ = 170.6 Hz, C-7), 109.1 ($^2J_{C\text{-}3a,3\text{-}H}$ = 6.9, $^3J_{C\text{-}3a,7\text{-}H}$ = 4.9 Hz, C-3a), 120.2 (Ph C-2,6), 124.36 ($^1J_{ThC\text{-}2,Th2\text{-}H}$ = 187.4, $^3J_{ThC\text{-}2,Th4\text{-}H}$ = 8.2, $^3J_{ThC\text{-}2,Th5\text{-}H}$ = 5.0 Hz, Th C-2), 124.43 ($^1J_{ThC\text{-}4,Th4\text{-}H}$ = 168.8, $^2J_{ThC\text{-}4,Th5\text{-}H}$ = 4.7, $^3J_{ThC\text{-}4,Th2\text{-}H}$ = 8.4 Hz, Th C-4), 126.9 ($^1J_{ThC\text{-}5,Th5\text{-}H}$ = 187.1, $^2J_{ThC\text{-}5,Th4\text{-}H}$ = 6.2, $^3J_{ThC\text{-}5,Th2\text{-}H}$ = 6.2 Hz, Th C-5), 128.45 (Ph C-4), 128.55 ($^1J_{C\text{-}3,3\text{-}H}$ = 193.9 Hz, C-3), 129.8 (Ph C-3,5), 134.3 ($^2J_{ThC\text{-}3,Th2\text{-}H}$ = 2.7, $^2J_{ThC\text{-}3,Th4\text{-}H}$ = 4.9, $^3J_{ThC\text{-}3,Th5\text{-}H}$ = 9.6, $^3J_{ThC\text{-}3,7\text{-}H}$ = 2.9 Hz, Th C-3), 139.1 (Ph C-1), 152.2 ($^3J_{C\text{-}7a,3\text{-}H}$ = 6.7 Hz, C-7a), 153.3 ($^2J_{C\text{-}6,7\text{-}H}$ = 6.1, $^3J_{C\text{-}6,Th2\text{-}H}$ = 2.9, $^3J_{C\text{-}6,Th4\text{-}H}$ = 1.1 Hz, C-6), 158.4 (C-4) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –152.8 (N-2), –93.1 (N-1) ppm. IR (KBr): $\tilde{\nu}$ = 1741 (C=O) cm^{-1}. MS: *m*/*z* (%) = 294 (90) $[M]^+$, 266 (75) $[M - CO]^+$, 237 (74), 111 (28), 77 (100), 51 (47). $C_{16}H_{10}N_2O_2S$ (294.33): calcd. C 65.29, H 3.42, N 9.52; found C 65.47, H 3.52, N 9.12.

2-Phenyl-6-(2-pyridyl)pyrano[4,3-*c*]pyrazol-4(2*H*)-one (10c): Yield: 33 mg, 71%; light-brown solid, m.p. 205–206 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (ddd, $^3J_{Pyr4\text{-}H,Pyr5\text{-}H}$ = 7.6, $^3J_{Pyr5\text{-}H,Pyr6\text{-}H}$ = 4.7, $^4J_{Pyr3\text{-}H,Pyr5\text{-}H}$ = 1.1 Hz, 1 H, Pyr 5-H), 7.43 (m, 1 H, Ph 4-H), 7.54 (m, 2 H, Ph 3,5-H), 7.80 (m, 2 H, Ph 2,6-H),

7.81 (ddd, $^3J_{Pyr3\text{-}H,Pyr4\text{-}H}$ = 8.0, $^3J_{Pyr4\text{-}H,Pyr5\text{-}H}$ = 7.6, $^4J_{Pyr4\text{-}H,Pyr6\text{-}H}$ = 1.8 Hz, 1 H, Pyr 4-H), 7.84 (d, $^5J_{3\text{-}H,7\text{-}H}$ = 0.9 Hz, 1 H, 7-H), 8.01 (td, $^3J_{Pyr3\text{-}H,Pyr4\text{-}H}$ = 8.0, $^4J_{Pyr3\text{-}H,Pyr5\text{-}H}$ = 1.1, $^5J_{Pyr3\text{-}H,Pyr6\text{-}H}$ = 0.9 Hz, 1 H, Pyr 3-H), 8.66 (d, $^5J_{3\text{-}H,7\text{-}H}$ = 0.9 Hz, 1 H, 3-H), 8.67 (ddd, $^3J_{Pyr5\text{-}H,Pyr6\text{-}H}$ = 4.7, $^4J_{Pyr4\text{-}H,Pyr6\text{-}H}$ = 1.8, $^5J_{Pyr3\text{-}H,Pyr6\text{-}H}$ = 0.9 Hz, 1 H, Pyr 6-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 97.2 ($^1J_{C\text{-}7,7\text{-}H}$ = 175.5 Hz, C-7), 109.8 ($^2J_{C\text{-}3a,3\text{-}H}$ = 6.8, $^3J_{C\text{-}3a,7\text{-}H}$ = 5.1 Hz, C-3a), 120.1 (Pyr C-3), 120.4 (Ph C-2,6), 124.3 (Pyr C-5), 128.6 (Ph C-4), 128.7 ($^1J_{C\text{-}3,3\text{-}H}$ = 194.2 Hz, C-3), 129.8 (Ph C-3,5), 137.0 ($^1J_{PyrC\text{-}4,Pyr4\text{-}H}$ = 164.2, $^3J_{PyrC\text{-}4,Pyr6\text{-}H}$ = 6.2 Hz, Pyr C-4), 139.2 (Ph C-1), 149.68 (Pyr C-2), 149.74 ($^1J_{PyrC\text{-}6,Pyr6\text{-}H}$ = 179.4, $^2J_{PyrC\text{-}6,Pyr5\text{-}H}$ = 3.4, $^3J_{PyrC\text{-}6,Pyr4\text{-}H}$ = 7.0 Hz, Pyr C-6), 152.0 ($^3J_{C\text{-}7a,3\text{-}H}$ = 6.7 Hz, C-7a), 155.4 (C-6), 158.4 (C-4) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –151.5 (N-2), –78.4 (PyrN) ppm; N-1 signal not found (by HMBC). IR (KBr): $\tilde{\nu}$ = 1735 (C=O) cm^{-1}. MS: *m*/*z* (%) = 289 (89) [M]$^+$, 261 (90) [M – CO]$^+$, 211 (32), 78 (40), 77 (100), 57 (21), 51 (68). MS: calcd. for [$C_{17}H_{11}N_3O_2$ + H]$^+$ 290.0930; found 290.0933.

General Procedure for the Synthesis of Hydroxamic Acids 8a,b and 11a,b: Hydroxylamine hydrochloride (130 mg, 2.6 mmol) was added to a solution of Na (133 mg, 5.8 mmol) in absolute methanol (5 mL) under argon. An appropriate carboxylate (**3a**,**b**, **6a**,**b**; 1 mmol) was added to the prepared solution. The reaction mixture was heated at reflux for 10 min. Methanol was distilled off under reduced pressure, the residue was dissolved in water, and acetic acid was added (pH = 5–6). The precipitate was filtered off and recrystallized from ethanol for **8a**,**b** and from toluene for **11a**,**b**.

***N*-Hydroxy-1-phenyl-5-(phenylethynyl)-1*H*-pyrazole-4-carboxamide (8a):** Yield: 255 mg, 84%; colourless solid, m.p. 158–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (m, 1 H, NPh 4-H), 7.42 (m, 2 H, CPh 3,5-H), 7.43 (m, 1 H, CPh 4-H), 7.48 (m, 2 H, CPh 2,6-H), 7.52 (m, 2 H, NPh 3,5-H), 7.77 (m, 2 H, NPh 2,6-H), 8.20 (s, 1 H, 3-H), 8.87 (br. s, 1 H, OH), 9.36 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 76.9 (*C*CPh), 102.5 (C*C*Ph), 118.1 ($^2J_{C\text{-}4,3\text{-}H}$ = 8.8 Hz, C-4), 120.3 (CPh C-1), 122.7 ($^3J_{C\text{-}5,3\text{-}H}$ = 4.0 Hz, C-5), 123.8 (NPh C-2,6), 128.6 (NPh C-4), 128.8 (CPh C-3,5), 129.0 (NPh C-3,5), 130.3 (CPh C-4), 131.7 (CPh C-2,6), 139.0 (NPh C-1), 141.3 ($^1J_{C\text{-}3,3\text{-}H}$ = 193.2 Hz, C-3), 161.1 (C=O) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –218.2 (NH), –157.2 (N-1), –69.9 (N-2) ppm. IR (KBr): $\tilde{\nu}$ = 3390–3076 (OH, NH), 1644 (C=O) cm^{-1}. MS: *m*/*z* (%) = 303 (11) [M]$^+$, 271 (58) [M – NHOH]$^+$, 259 (51) [M – CNHOH]$^+$, 204 (40), 128 (31), 102 (21), 94 (23), 77 (100), 57 (29), 55 (30), 51 (66). $C_{18}H_{13}N_3O_2$ (303.32) ·0.2H_2O: calcd. C 70.44, H 4.40, N 13.69; found C 70.55, H 4.37, N 13.80.

***N*-Hydroxy-1-phenyl-5-(3-thienylethynyl)-1*H*-pyrazole-4-carboxamide (8b):** Yield: 217 mg, 70%; colourless solid, m.p. 170 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17 (d, $^3J_{Th4\text{-}H,Th5\text{-}H}$ = 4.9 Hz, 1 H, Th 4-H), 7.37 (dd, $^3J_{Th4\text{-}H,Th5\text{-}H}$ = 4.9, $^4J_{Th2\text{-}H,Th5\text{-}H}$ = 2.9 Hz, 1 H, Th 5-H), 7.44 (m, 1 H, Ph 4-H), 7.51 (m, 2 H, Ph 3,5-H), 7.64 (d, $^4J_{Th2\text{-}H,Th5\text{-}H}$ = 2.9 Hz, 1 H, Th 2-H), 7.76 (m, 2 H, Ph 2,6-H), 8.20 (s, 1 H, 3-H), 9.30 (br. s, 2 H, NH, OH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 76.6 (*C*CTh), 97.9 (C*C*Th), 117.9 ($^2J_{C\text{-}4,3\text{-}H}$ = 9.0 Hz, C-4), 119.3 (Th C-3), 122.6 (C-5), 123.8 (Ph C-2,6), 126.5 (Th C-5), 128.7 (Ph C-4), 129.1 (Ph C-3,5), 129.3 (Th C-4), 131.7 (Th C-2), 139.0 (Ph C-1), 141.3 ($^1J_{C\text{-}3,3\text{-}H}$ = 193.1 Hz, C-3), 161.0 (C=O) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –157.2 (N-1), –70.0 (N-2) ppm. IR (KBr): $\tilde{\nu}$ = 3380–3200 (OH, NH), 1620 (C=O) cm^{-1}. MS: *m*/*z* (%) = 309 (23) [M]$^+$, 278 (27) [M – NOH]$^+$, 277 (100) [M – NHOH]$^+$, 265 (77) [M – CNHOH]$^+$, 210 (30), 77 (48), 51 (29). $C_{16}H_{11}N_3O_2S$ (309.35) ·0.8H_2O: calcd. C 59.36, H 3.92, N 12.98; found C 59.52, H 3.61, N 12.61.

***N*-Hydroxy-1-phenyl-3-(phenylethynyl)-1*H*-pyrazole-4-carboxamide (11a):** Yield: 194 mg, 64%; colourless solid, m.p. 169–171 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.40 (m, 1 H, NPh 4-H), 7.45 (m, 3 H, CPh 3,4,5-H), 7.55 (m, 2 H, NPh 3,5-H), 7.59 (m, 2 H, CPh 2,6-H), 7.86 (m, 2 H, NPh 2,6-H), 8.89 (s, 1 H, 5-H), 10.05 (br. s, 2 H, NH, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 81.5 (*C*CPh), 92.4 (C*C*Ph), 119.0 (NPh C-2,6), 119.7 (C-4), 121.8 (CPh C-1), 127.5 (NPh C-4), 128.8 (CPh C-3,5), 128.8 ($^1J_{C\text{-}5,5\text{-}H}$ = 193.5 Hz, C-5), 129.2 (CPh C-4), 129.7 (NPh C-3,5), 131.4 (CPh C-2,6), 134.4 (C-3), 138.7 (NPh C-1), 159.1 (C=O) ppm. ^{15}N NMR (50 MHz, [D$_6$]DMSO): δ = –162.3 (N-1) ppm; N-2 signal not found (by HMBC). IR (KBr): $\tilde{\nu}$ = 3388 (NH, OH), 1656 (C=O) cm^{-1}. MS: *m*/*z* (%) = 303 (3) [M]$^+$, 259 (100) [M – CNHOH]$^+$, 131 (36), 104 (69), 77 (39), 51 (26). $C_{18}H_{13}N_3O_2$ (303.32) ·0.2H_2O: calcd. C 70.44, H 4.40, N 13.69; found C 70.54, H 4.12, N 13.46.

***N*-Hydroxy-1-phenyl-3-(3-thienylethynyl)-1*H*-pyrazole-4-carboxamide (11b):** Yield: 179 mg, 58%; brown solid, m.p. 168–169 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.28 (dd, $^3J_{Th4\text{-}H,Th5\text{-}H}$ = 4.9, $^4J_{Th2\text{-}H,Th4\text{-}H}$ = 1.0 Hz, 1 H, Th 4-H), 7.39 (m, 1 H, Ph 4-H), 7.55 (m, 2 H, Ph 3,5-H), 7.67 (dd, $^3J_{Th4\text{-}H,Th5\text{-}H}$ = 4.9, $^4J_{Th2\text{-}H,Th5\text{-}H}$ = 2.9 Hz, 1 H, Th 5-H), 7.84 (m, 2 H, Ph 2,6-H), 7.94 (m, $^4J_{Th2\text{-}H,Th5\text{-}H}$ = 2.9, $^4J_{Th2\text{-}H,Th4\text{-}H}$ = 1.0 Hz, 1 H, Th 2-H), 8.86 (s, 1 H, 5-H), 9.13 and 10.80 (NH, OH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 80.7 (*C*CTh), 88.0 (C*C*Th), 118.9 (Ph C-2,6), 119.3 (C-4), 120.6 (Th C-3), 127.1 (Th C-5), 127.5 (Ph C-4), 128.7 (C-5), 129.5 (Th C-4), 129.7 (Ph C-3,5), 130.7 (Th C-2), 134.4 (C-3), 138.6 (Ph C-1), 159.2 (C=O) ppm. ^{15}N NMR (50 MHz, [D$_6$]DMSO): δ = –161.9 (N-1) ppm; N-2 signal not found (by HMBC). MS: *m*/*z* (%) = 309 (27) [M]$^+$, 277 (26) [M – NHOH]$^+$, 265 (100) [M – CNHOH]$^+$, 131 (47), 104 (93), 77 (60), 51 (41). IR (KBr): $\tilde{\nu}$ = 3681–3400, 3375 (NH, OH), 1676 (C=O) cm^{-1}. $C_{16}H_{11}N_3O_2S$ (309.35) ·0.25H_2O: calcd. C 61.23, H 3.69, N 13.39; found C 61.20, H 3.42, N 13.04.

General Procedure for the Cyclization of Hydroxamic Acids 8 and 11. Synthesis of Compounds 9a,b and 12a,b: The appropriate hydroxamic acid (**8a**,**b**, **11a**,**b**; 0.25 mmol), triethylamine (0.64 mL) and methanol (2 mL) were heated at reflux for 2 h (for **11a**,**b** the reaction time was 24 h). The solvent was distilled off, and the residue was recrystallized from dichloromethane (**9a**,**b**) or purified by column chromatography (SiO_2; eluent dichloromethane/methanol, 100:1 v/v; **12a**,**b**).

5-Hydroxy-1,6-diphenyl-1,5-dihydro-4*H*-pyrazolo[4,3-*c*]pyridin-4-one (9a): Yield: 67 mg, 89%; colourless solid, m.p. 190–192 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.64 (s, 1 H, 7-H), 7.30–7.77 (br. s, 1 H, OH), 7.42 (m, 1 H, NPh 4-H), 7.48 (m, 3 H, CPh 3,4,5-H), 7.53 (m, 2 H, NPh 3,5-H), 7.63 (m, 2 H, NPh 2,6-H), 7.66 (m, 2 H, CPh 2,6-H), 8.40 (s, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 92.5 ($^1J_{C\text{-}7,7\text{-}H}$ = 173.9 Hz, C-7), 111.9 ($^2J_{C\text{-}3a,3\text{-}H}$ = 9.7, $^3J_{C\text{-}3a,7\text{-}H}$ = 5.3 Hz, C-3a), 123.3 (NPh C-2,6), 128.0 (NPh C-4), 128.3 (CPh C-3,5), 129.2 (CPh C-2,6), 129.6 (NPh C-3,5), 129.8 (CPh C-4), 132.3 (CPh C-1), 137.2 ($^1J_{C\text{-}3,3\text{-}H}$ = 193.9 Hz, C-3), 138.9 (NPh C-1), 141.0 ($^3J_{C\text{-}7a,3\text{-}H}$ = 3.1 Hz, C-7a), 142.3 (C-6), 154.4 (C-4) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –179.2 (N-1), –175.2 (N-5), –66.6 (N-2) ppm. IR (KBr): $\tilde{\nu}$ = 3420 (NH), 1648 (C=O) cm^{-1}. MS: *m*/*z* (%) = 303 (44) [M]$^+$, 287 (31), 111 (27), 97 (41), 95 (28), 85 (37), 83 (38), 77 (44), 69 (50), 57 (100), 51 (21). $C_{18}H_{13}N_3O_2$ (303.32) ·0.6H_2O: calcd. C 68.82, H 4.56, N 13.38; found C 68.91, H 4.18, N 12.99.

5-Hydroxy-1-phenyl-6-(3-thienyl)-1,5-dihydro-4*H*-pyrazolo[4,3-*c*]pyridin-4-one (9b): Yield: 72 mg, 93%; colourless solid, m.p. 167–169 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.76 (s, 1 H, 7-H), 7.42 (m, 1 H, Th 5-H), 7.44 (m, 1 H, Ph 4-H), 7.49 (m, 1 H, Th 4-H), 7.55 (m, 2 H, Ph 3,5-H), 7.63 (m, 2 H, Ph 2,6-H), 7.87 (m, 1 H, Th 2-H), 8.38 (s, 1 H, 3-H), 10.50 (br. s, 1 H, OH) ppm. ^{13}C NMR

(125 MHz, $CDCl_3$): δ = 91.4 ($^1J_{C\text{-}7,7\text{-}H}$ = 173.4 Hz, C-7), 111.6 (C-3a), 123.3 (Ph C-2,6), 125.8 ($^1J_{ThC\text{-}5,Th5\text{-}H}$ = 187.2, $^2J_{ThC\text{-}5,Th4\text{-}H}$ = 6.2, $^3J_{ThC\text{-}5,Th2\text{-}H}$ = 6.2 Hz, Th C-5), 127.4 ($^1J_{ThC\text{-}2,Th2\text{-}H}$ = 187.7, $^3J_{ThC\text{-}2,Th4\text{-}H}$ = 8.4, $^3J_{ThC\text{-}2,Th5\text{-}H}$ = 4.6 Hz, Th C-2), 128.0 (Ph C-4), 128.1 ($^1J_{ThC\text{-}4,Th4\text{-}H}$ = 170.8, $^2J_{ThC\text{-}4,Th5\text{-}H}$ = 4.5, $^3J_{ThC\text{-}4,Th2\text{-}H}$ = 8.4 Hz, Th C-4), 129.7 (Ph C-3,5), 132.2 (Th C-3), 137.2 ($^1J_{C\text{-}3,3\text{-}H}$ = 193.9 Hz, C-3), 137.3 (C-6), 138.8 (Ph C-1), 141.0 (C-7a), 154.3 (C-4) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –179.5 (N-1), –175.3 (N-5), –66.3 (N-2) ppm. IR (KBr): $\tilde{\nu}$ = 3424 (NH), 1652 (C=O) cm^{-1}. MS: *m*/*z* (%) = 309 (77) $[M]^+$, 293 (25), 289 (20), 248 (48), 111 (34), 97 (30), 96 (21), 95 (21), 78 (26), 77 (100), 69 (62), 57 (74), 51 (83). $C_{16}H_{11}N_3O_2S$ (309.35) ·0.3H_2O: calcd. C 61.06, H 3.71, N 13.35; found C 60.78, H 3.33, N 13.25.

5-Hydroxy-2,6-diphenyl-2,5-dihydro-4*H*-pyrazolo[4,3-*c*]pyridin-4-one (12a): Yield: 56 mg, 74%; red solid, m.p. 93–95 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 6.55 (s, 1 H, 7-H), 7.42 (m, 1 H, NPh 4-H), 7.45 (m, 3 H, CPh 3,4,5-H), 7.56 (m, 2 H, NPh 3,5-H), 7.58 (m, 2 H, CPh 2,6-H), 8.05 (m, 2 H, NPh 2,6-H), 9.45 (s, 1 H, 3-H), 10.84 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 97.0 ($^1J_{C\text{-}7,7\text{-}H}$ = 171.8 Hz, C-7), 114.4 ($^2J_{C\text{-}3a,3\text{-}H}$ = 6.3, $^3J_{C\text{-}3a,7\text{-}H}$ = 6.3 Hz, C-3a), 119.8 (NPh C-2,6), 127.6 ($^1J_{C\text{-}3,3\text{-}H}$ = 196.2 Hz, C-3), 127.8 (NPh C-4), 128.0 (CPh C-3,5), 128.7 (CPh C-4), 129.1 (CPh C-2,6), 129.7 (NPh C-3,5), 133.9 (CPh C-1), 139.1 (NPh C-1), 145.1 (C-6), 149.2 ($^3J_{C\text{-}7a,3\text{-}H}$ = 6.7 Hz, C-7a), 156.0 (C-4) ppm. ^{15}N NMR (50 MHz, [D$_6$]DMSO): δ = –184.7 (N-5), –152.5 (N-2), –96.2 (N-1) ppm. IR (KBr): $\tilde{\nu}$ = 3675–3281 (OH), 1646 (C=O) cm^{-1}. MS: *m*/*z* (%) = 303 (45) $[M]^+$, 211 (33), 105 (52), 77 (100), 51 (39). MS: calcd. for $[C_{18}H_{13}N_3O_2 + H]^+$ 304.1086; found 304.1090.

5-Hydroxy-2-phenyl-6-(3-thienyl)-2,5-dihydro-4*H*-pyrazolo[4,3-*c*]pyridin-4-one (12b): Yield: 53 mg, 69%; red solid, m.p. 82–84 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 6.72 (s, 1 H, 7-H), 7.42 (m, 1 H, Ph 4-H), 7.46 (m, 1 H, Th 4-H), 7.56 (m, 2 H, Ph 3,5-H), 7.62 (m, 1 H, Th 5-H), 7.93 (m, 1 H, Th 2-H), 8.05 (m, 2 H, Ph 2,6-H), 9.42 (s, 1 H, 3-H), 10.93 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 96.3 ($^1J_{C\text{-}7,7\text{-}H}$ = 172.1 Hz, C-7), 114.2 ($^2J_{C\text{-}3a,3\text{-}H}$ = 6.3, $^3J_{C\text{-}3a,7\text{-}H}$ = 6.3 Hz, C-3a), 119.7 (Ph C-2,6), 125.6 (Th C-5), 126.3 (Th C-2), 127.5 ($^1J_{C\text{-}3,3\text{-}H}$ = 196.2 Hz, C-3), 127.8 (Ph C-4), 128.7 (Th C-4), 129.6 (Ph C-3,5), 133.9 (Th C-3), 139.1 (Ph C-1), 140.3 (C-6), 149.2 ($^3J_{C\text{-}7a,3\text{-}H}$ = 6.7 Hz, C-7a), 156.0 (C-4) ppm. ^{15}N NMR (50 MHz, [D$_6$]DMSO): δ = –184.7 (N-5), –152.5 (N-2) ppm; N-1 signal not found (by HMBC). IR (KBr): $\tilde{\nu}$ = 3628–3170 (OH), 1642 (C=O) cm^{-1}. MS: *m*/*z* (%) = 309 (22) $[M]^+$, 121 (27), 77 (100), 69 (23), 57 (46), 51 (61), 35 (32). MS: calcd. for $[C_{16}H_{11}N_3O_2S + H]^+$ 310.0650; found 310.0654.

5-Hydroxy-1-phenyl-6-(2-pyridyl)-1,5-dihydro-4*H*-pyrazolo[4,3-*c*]pyridin-4-one (9c): Hydroxylamine hydrochloride (65 mg, 1.3 mmol) was added to a solution of Na (67 mg, 2.9 mmol) in dry methanol (3 mL) under argon. Ethyl 1-phenyl-5-(2-pyridylethynyl)-1*H*-pyrazole-4-carboxylate (**3c**; 159 mg, 0.5 mmol) was added to the prepared solution. The reaction mixture was heated at reflux for 10 min. Methanol was distilled off under reduced pressure, the residue was dissolved in water (15 mL) and acetic acid was added (pH = 5–6). The mixture was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, washed with brine and dried with sodium sulfate. The solvent was evaporated, and the product was recrystallized from dichloromethane. Yield: 76 mg, 50%; colourless solid, m.p. 95–97 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.96 (s, 1 H, 7-H), 7.39 (m, 1 H, Pyr 5-H), 7.41 (m, 1 H, Ph 4-H), 7.53 (m, 2 H, Ph 3,5-H), 7.67 (m, 2 H, Ph 2,6-H), 7.84 (m, 1 H, Pyr 4-H), 7.89 (d, $^3J_{Pyr3\text{-}H,Pyr4\text{-}H}$ = 7.8 Hz, 1 H, Pyr 3-H), 8.30 (s, 1 H, 3-H), 8.65 (d, $^3J_{Pyr5\text{-}H,Pyr6\text{-}H}$ = 4.6 Hz, 1 H, Pyr 6-H), 11.25 (br. s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 93.7 ($^1J_{C\text{-}7,7\text{-}H}$ = 175.0 Hz, C-7), 113.1 (C-3a), 123.4 (Ph C-2,6), 124.3 (Pyr C-5), 125.1 (Pyr C-3), 128.1 (Ph C-4), 129.7 (Ph C-3,5), 137.0 (Pyr C-4), 137.3 ($^1J_{C\text{-}3,3\text{-}H}$ = 193.8 Hz, C-3), 138.7 (Ph C-1), 140.6 (C-7a), 140.9 (C-6), 149.0 (Pyr C-6), 150.2 (Pyr C-2), 154.7 (C-4) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –178.9 (N-5), –177.8 (N-1), –65.5 (N-2) ppm. IR (KBr): $\tilde{\nu}$ = 3418 (NH), 1662 (C=O) cm^{-1}. MS: *m*/*z* (%) = 304 (88) $[M]^+$, 288 (23), 211 (28), 137 (44), 109 (25), 97 (24), 96 (52), 79 (33), 78 (72), 77 (100), 67 (69), 55 (69), 51 (92). $C_{17}H_{12}N_4O_2$ (304.31) ·0.2H_2O: calcd. C 66.31, H 4.06, N 18.20; found C 66.39, H 3.87, N 17.92.

General Procedure for Ester Hydrolysis. Synthesis of 13a,b: A solution of LiOH (17 mg, 0.7 mmol) in water (2 mL) was added to a solution of the appropriate ester (**3a**,**b**; 0.5 mmol) in dioxane (8 mL), and the mixture was stirred at 60 °C overnight. The reaction mixture was neutralized with 2 N HCl (to pH = 7), and then the solvent was evaporated. Water was added, and the mixture was exhaustively extracted with ethyl acetate. The organic layers were combined, washed with brine and dried with sodium sulfate. The product was recrystallized from dichloromethane.

1-Phenyl-5-(phenylethynyl)-1*H*-pyrazole-4-carboxylic Acid (13a): Yield: 130 mg, 90%; colourless solid, m.p. 184–187 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (m, 2 H, CPh 3,5-H), 7.38 (m, 1 H, CPh 4-H), 7.46 (m, 1 H, NPh 4-H), 7.48 (m, 2 H, CPh 2,6-H), 7.55 (m, 2 H, NPh 3,5-H), 7.84 (m, 2 H, NPh 2,6-H), 8.21 (s, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 77.2 (*C*CPh), 101.6 ($^3J_{CCPh,CPh2,6\text{-}H}$ = 5.3 Hz, C*C*Ph), 117.2 ($^2J_{C\text{-}4,3\text{-}H}$ = 8.9 Hz, C-4), 121.6 (CPh C-1), 124.1 (NPh C-2,6), 128.1 ($^3J_{C\text{-}5,3\text{-}H}$ = 4.0 Hz, C-5), 128.5 (CPh C-3,5), 128.6 (NPh C-4), 129.0 (NPh C-3,5), 129.6 (CPh C-4), 131.8 (CPh C-2,6), 139.1 (NPh C-1), 142.6 ($^1J_{C\text{-}3,3\text{-}H}$ = 192.8 Hz, C-3), 167.5 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3430 (OH), 1678 (C=O) cm^{-1}. MS: *m*/*z* (%) = 289 (21) $[M + H]^+$, 288 (100) $[M]^+$, 287 (21) $[M – H]^+$, 260 (34) $[M – CO]^+$, 211 (24), 184 (29), 105 (93), 77 (86), 51 (34). $C_{18}H_{12}N_2O_2$ (288.31) ·0.3H_2O: calcd. C 73.61, H 4.32, N 9.54; found C 73.80, H 3.96, N 9.42.

1-Phenyl-5-(3-thienylethynyl)-1*H*-pyrazole-4-carboxylic Acid (13b): Yield: 97 mg, 66%; colourless solid, m.p. 182–185 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (d, $^3J_{Th4\text{-}H,Th5\text{-}H}$ = 4.9 Hz, 1 H, Th 4-H), 7.24 (m, 1 H, Th 5-H), 7.44 (m, 1 H, Ph 4-H), 7.49 (m, 2 H, Ph 3,5-H), 7.53 (d, $^4J_{Th2\text{-}H,Th5\text{-}H}$ = 2.8 Hz, 1 H, Th 2-H), 7.75 (m, 2 H, Ph 2,6-H), 8.14 (s, 1 H, 3-H), 9.62 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 77.2 (*C*CTh), 96.9 (C*C*Th), 117.7 (C-4), 120.7 (Th C-3), 124.0 (Ph C-2,6), 125.7 (Th C-5), 127.9 (C-5), 128.5 (Ph C-4), 128.8 (Ph C-3,5), 129.5 (Th C-4), 130.8 (Th C-2), 139.1 (Ph C-1), 142.6 ($^1J_{C\text{-}3,3\text{-}H}$ = 192.5 Hz, C-3), 167.7 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3430 (OH), 1686 (C=O) cm^{-1}. MS: *m*/*z* (%) = 294 (100) $[M]^+$, 266 (38), 261 (23), 111 (43), 77 (34), 51 (21). $C_{16}H_{10}N_2O_2S$ (294.33) ·0.2H_2O: calcd. C 64.50, H 3.52, N 9.40; found C 64.27, H 3.46, N 9.28.

5-(2-Oxo-2-phenylethyl)-1-phenyl-1*H*-pyrazole-4-carboxylic Acid (14): A solution of ethyl 1-phenyl-5-(phenylethynyl)-1*H*-pyrazole-4-carboxylate (**3a**; 151 mg, 0.5 mmol), 4 N HCl (3 mL) and dioxane (6 mL) was heated at reflux for 3 d. The solvent was evaporated, water (15 mL) was added, and the mixture was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, washed with brine and dried with sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography (SiO_2; eluent dichloromethane/methanol, 100:5 v/v). Yield: 98 mg, 64%; colourless solid, m.p. 183–185 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.64 (s, 2 H, CH_2), 7.42 (m, 5 H, NPh-H), 7.44 (m, 2 H, CPh 3,5-H), 7.58 (m, 1 H, CPh 4-H), 7.92 (m, 2 H, CPh 2,6-H), 8.15 (s, 1 H, 3-H), 7.00–11.00 (br. s, 1 H, OH) ppm. ^{13}C NMR

(75 MHz, $CDCl_3$): δ = 36.1 ($^1J_{CH2}$ = 129.0 Hz, CH_2), 113.1 (C-4), 125.7 (NPh C-2,6), 128.2 (CPh C-2,6), 128.7 (CPh C-3,5), 129.2 (NPh C-4), 129.4 (NPh C-3,5), 133.5 (CPh C-4), 136.1 (CPh C-1), 138.4 (NPh C-1), 141.9 (C-5), 142.5 ($^1J_{C\text{-}3,3\text{-}H}$ = 191.2 Hz, C-3), 168.4 (*C*OOH), 194.3 (CH_2*C*O) ppm. IR (KBr): $\tilde{\nu}$ = 3422 (OH), 1666 (C=O) cm^{-1}. MS: *m*/*z* (%) = 306 (0.3) $[M]^+$, 184 (67), 105 (100), 77 (59). $C_{18}H_{14}N_2O_3$ (306.32): calcd. C 70.58, H 4.61, N 9.15; found C 70.20, H 6.60, N 9.10.

General Procedure for the Suzuki Reaction. Synthesis of 15a,b: Anhydrous K_3PO_4 (1.27 g, 6 mmol), arylboronic acid (6 mmol), $[Pd(PPh_3)_4]$ (277 mg, 0.24 mmol) and KBr (393 mg, 3.3 mmol) were added to a solution of ethyl 1-phenyl-5{[(trifluoromethyl)sulfonyl]-oxy}-1*H*-pyrazole-4-carboxylate (**2**; 1.092 g, 3 mmol) in 1,4-dioxane (20 mL) under argon. After heating at reflux under argon overnight, the mixture was diluted with water (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried with sodium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2; eluent ethyl acetate/light petroleum, 1:8 v/v, for **15b** eluent ethyl acetate/hexane, 1:10 v/v).

Ethyl 1,5-Diphenyl-1*H*-pyrazole-4-carboxylate (15a): Yield: 683 mg, 78%; m.p. 120–122 °C (ref.[47] m.p. 120 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.21 (q, *J* = 7.2 Hz, 2 H, CH_2), 7.20 (m, 2 H, NPh 2,6-H), 7.27 (m, 2 H, NPh 3,5-H), 7.29 (m, 3 H, CPh 2,6-H, NPh 4-H), 7.34 (m, 1 H, CPh 4-H), 7.35 (m, 2 H, CPh 3,5-H), 8.19 (s, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 ($^1J_{CH3}$ = 127.0, $^2J_{CH3,OCH2}$ = 2.6 Hz, CH_3), 60.0 ($^1J_{OCH2}$ = 147.4, $^2J_{OCH2,CH3}$ = 4.4 Hz, CH_2), 113.9 ($^2J_{C\text{-}4,3\text{-}H}$ = 8.9 Hz, C-4), 125.3 (NPh C-2,6), 127.8 (NPh C-4), 128.0 (CPh C-3,5), 128.8 (NPh C-3,5), 128.9 (CPh C-1), 129.0 (CPh C-4), 130.5 (CPh C-2,6), 139.2 (NPh C-1), 142.4 ($^1J_{C\text{-}3,3\text{-}H}$ = 190.9 Hz, C-3), 145.4 (C-5), 162.9 ($^3J_{CO,OCH2}$ = 3.1 Hz, C=O) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –160.5 (N-1), –76.0 (N-2) ppm.

Ethyl 5-(3-Chlorophenyl)-1-phenyl-1*H*-pyrazole-4-carboxylate (15b): Yield: 883 mg, 90%; colourless solid, m.p. 97–98 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.1 Hz, 3 H, CH_3), 4.22 (q, *J* = 7.1 Hz, 2 H, CH_2), 7.11 (m, 1 H, CPh 6-H), 7.20 (m, 2 H, NPh 2,6-H), 7.25 (m, 1 H, CPh 5-H), 7.31 (m, 3 H, NPh 3,4,5-H), 7.34 (m, 1 H, CPh 2-H), 7.35 (m, 1 H, CPh 4-H), 8.19 (s, 1 H, 3-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 ($^1J_{CH3}$ = 127.0, $^2J_{CH3,OCH2}$ = 2.6 Hz, CH_3), 60.2 ($^1J_{OCH2}$ = 147.5, $^2J_{OCH2,CH3}$ = 4.4 Hz, CH_2), 114.2 ($^2J_{C\text{-}4,3\text{-}H}$ = 8.8 Hz, C-4), 125.3 (NPh C-2,6), 128.2 (NPh C-4), 128.7 (CPh C-6), 129.0 (NPh C-3,5), 129.21 (CPh C-5), 129.24 (CPh C-4), 130.6 (CPh C-1), 130.7 (CPh C-2), 133.8 (CPh C-3), 138.8 (NPh C-1), 142.5 ($^1J_{C\text{-}3,3\text{-}H}$ = 191.3 Hz, C-3), 143.6 (C-5), 162.7 ($^3J_{CO,OCH2}$ = 3.0 Hz, C=O) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –160.4 (N-1), –74.8 (N-2) ppm. IR (KBr): $\tilde{\nu}$ = 1716 (C=O) cm^{-1}. MS: *m*/*z* (%) = 328/326 (2/7) $[M]^+$, 256/254 (34/100) $[M - COOEt + H]^+$, 222 (28), 218 (25), 152 (22), 109 (26), 95 (29), 77 (47), 51 (41). $C_{18}H_{15}ClN_2O_2$ (326.78): calcd. C 66.16, H 4.63, N 8.57; found C 66.16, H 4.66, N 8.21.

5-(3-Chlorophenyl)-1-phenyl-1*H*-pyrazole-4-carboxylic Acid (16): A solution of ethyl 5-(3-chlorophenyl)-1-phenyl-1*H*-pyrazole-4-carboxylate (**15b**; 978 mg, 3 mmol), 4 N HCl (15 mL) and dioxane (30 mL) was heated at reflux for 2 d. The solvent was evaporated, water (20 mL) was added, and the mixture was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, washed with brine and dried with sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography (SiO_2; eluent dichloromethane/methanol, 100:2 v/v). Yield: 831 mg, 93%; colourless solid, m.p. 174–175 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14 (m, 1 H, CPh 6-H), 7.19 (m, 2 H, NPh 2,6-H), 7.25 (m, 1 H, CPh 5-H), 7.30 (m, 1 H, CPh 2-H), 7.31 (m, 3 H, NPh 3,4,5-H), 7.35 (m, 1 H, CPh 4-H), 8.23 (s, 1 H, 3-H), 7.00–9.20 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 113.2 ($^2J_{C\text{-}4,3\text{-}H}$ = 8.9 Hz, C-4), 125.4 (NPh C-2,6), 128.4 (NPh C-4), 128.7 (CPh C-6), 129.0 (NPh C-3,5), 129.3 (CPh C-5), 129.5 (CPh C-4), 130.2 (CPh C-1), 130.5 (CPh C-2), 134.0 (CPh C-3), 138.7 (NPh C-1), 143.2 ($^1J_{C\text{-}3,3\text{-}H}$ = 192.0 Hz, C-3), 144.5 (C-5), 167.6 (C=O) ppm. ^{15}N NMR (50 MHz, $CDCl_3$): δ = –159.2 (N-1), –74.1 (N-2) ppm. IR (KBr): $\tilde{\nu}$ = 3430 (OH), 1674 (C=O) cm^{-1}. MS: *m*/*z* (%) = 300/298 (33/100) $[M]^+$, 299 (31), 279 (46), 281 (28), 279 (32), 253 (28), 122 (23), 77 (80), 51 (61). $C_{16}H_{11}ClN_2O_2$ (298.72): calcd. C 64.33, H 3.71, N 9.38; found C 64.70, H 3.80, N 9.40.

5-Chloro-8*H*-dibenzo[*c*,*f*]pyrazolo[1,5-*a*]azepin-8-one (18): 5-(3-Chlorophenyl)-1-phenyl-1*H*-pyrazole-4-carboxylic acid (**16**; 73 mg, 0.25 mmol) and trifluoromethanesulfonic acid (2 mL) were stirred at 165 °C for 4 d. Water (10 mL) was added to the reaction mixture, and the mixture was extracted with diethyl ether (2 × 10 mL). The organic layers were combined, washed with brine and dried with sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography (SiO_2; eluent ethyl acetate/light petroleum, 1:7 v/v). Yield: 60 mg, 85%; colourless solid, m.p. 198–199 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.82 (d, $^3J_{2\text{-}H,3\text{-}H}$ = 2.0 Hz, 1 H, 3-H), 7.44 (m, $^3J_{9\text{-}H,10\text{-}H}$ = 7.8, $^3J_{10\text{-}H,11\text{-}H}$ = 7.4 Hz, 1 H, 10-H), 7.47 (m, $^3J_{6\text{-}H,7\text{-}H}$ = 8.3, $^4J_{4\text{-}H,6\text{-}H}$ = 2.0 Hz, 1 H, 6-H), 7.69 (m, $^3J_{11\text{-}H,12\text{-}H}$ = 8.3, $^3J_{10\text{-}H,11\text{-}H}$ = 7.4 Hz, 1 H, 11-H), 7.75 (d, $^4J_{4\text{-}H,6\text{-}H}$ = 2.0 Hz, 1 H, 4-H), 7.82 (d, $^3J_{2\text{-}H,3\text{-}H}$ = 2.0 Hz, 1 H, 2-H), 7.83 (m, $^3J_{9\text{-}H,10\text{-}H}$ = 7.8 Hz, 1 H, 9-H), 7.86 (d, $^3J_{6\text{-}H,7\text{-}H}$ = 8.3 Hz, 1 H, 7-H), 8.14 (d, $^3J_{11\text{-}H,12\text{-}H}$ = 8.3 Hz, 1 H, 12-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 108.8 (C-3), 123.3 (C-12), 127.3 (C-10), 127.8 (C-4), 128.4 (C-3b), 129.4 (C-6), 129.7 (C-9), 130.8 (C-7), 132.0 (C-8a), 133.7 (C-11), 136.7 (C-5), 137.5 (C-12a), 139.0 (C-7a), 140.6 (C-3a), 141.1 (C-2), 192.4 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 1654 (C=O) cm^{-1}. MS: *m*/*z* = 283/281 (27/82) $[M]^+$, 257/255 (35/100). $C_{16}H_9ClN_2O$ (280.71) ·0.15H_2O: calcd. C 67.81, H 3.31, N 9.88; found C 67.81, H 3.15, N 9.83. MS: calcd. for $[C_{16}H_9ClN_2O]^+$ 280.0403; found 280.0409.

Acknowledgments

We are grateful to Dr. L. Jirovetz for recording the mass spectra.

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Received: November 18, 2010
Published Online: February 23, 2011

