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Copper-Catalyzed Cascade Reactions of Substituted 4-Iodopyrazolecarbaldehydes with 1,2-Phenylenediamines and 2-Aminophenols

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Abstract: A new approach for the synthesis of novel annulated-pyrazoles is presented. This protocol includes an intermolecular condensation followed by a copper-mediated intramolecular C–N or C–O coupling reaction. The method is applied to a range of substituted 4-iodopyrazolecarbaldehydes which react with 1,2-phenylenediamines or 2-aminophenols to yield substituted 2,4- or 1,4-dihydrobenzo[*b*]pyrazolo[4,3-*e*][1,4]diazepines or substituted-2*H*- or 1*H*-benzo[*b*]pyrazolo[3,4-*f*][1,4]-oxazepines, respectively.

Keywords: C–N coupling; C–O coupling; copper; diazepines; oxazepines; pyrazoles

Compounds containing the pyrazole motif are of significant interest in medicinal, pharmaceutical and agricultural research due to their important biological activities.[1] Beside being the core unit of commercial drugs such as zometapin, sildenafil, celebrex and rimonabant, there are numerous pyrazoles that are ascribed with anti-inflammatory, anticancer, anti-HIV, antibacterial and cannabinoid receptor antagonist activities.[2] Primarily due to this reason, organic chemists are motivated to continuously develop strategies for producing new pyrazole-based compounds.[3] In this context the transition metal-promoted cross-coupling reactions have been of great value as they provide a robust route to install the desired substitution in pyrazoles. Surprisingly however, all transition metal-catalyzed cross-coupling reactions at 3-, 4- or 5-position result in C–C bond formation whereas the C–N coupling is restricted to the Ullman reaction leading to *N*-arylated pyrazoles.[4] Recently, we reported the synthesis of pyrazolo[4,3-*b*]pyridine-5-ones *via* the first copper-promoted intramolecular amidation in 4-iodopyrazole derivatives generated either from Morita–Baylis–Hillman (MBH) or Horner–Wadsworth–Emmon chemistry.[5] Although during this study the C–N coupling with allylamides was successful, we failed to achieve similar cross-coupling reactions with allylamines accessed *via* MBH chemistry. Nevertheless, we were keen to explore the copper-promoted cross-coupling of substituted 4-iodopyrazoles as it would allow access to intermediates suitable for generating novel annulated pyrazoles. Recently Reeves et al. reported the synthesis of several azole-annulated quinoxalines *via* copper-catalyzed annulation of 2-formylazoles with *o*-aminoiodoarenes whereas two identical papers by Cai et al. and Zhou et al. described the synthesis of aza-fused polycyclic quinolines through copper-catalyzed cascade reactions.[6] Based on these reports, we anticipated that treating 4-iodopyrazolecarbaldehydes with 1,2-phenylenediamine or 2-aminophenol in the presence of a copper catalyst may initiate a cascade reaction leading to the synthesis of novel annulated pyrazoles (Figure 1). To the best of our knowledge such a strategy for annulated pyrazoles has not been developed to date. In this update we disclose the results on the development of this methodology.

Initial feasibility of the approach was tested with 4-iodo-1,5-diphenyl-1*H*-pyrazole-3-carbaldehyde and 1,2-phenylenediamine employing some commonly used copper sources, ligands, bases and solvents. The results of the optimization study are illustrated in Table 1. To our delight the use of CuI as copper

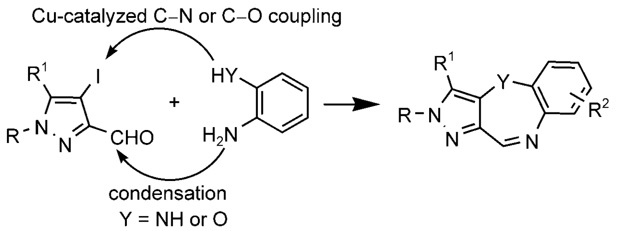
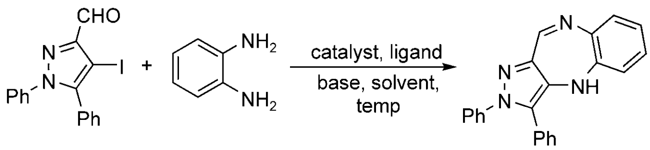


Figure 1. Cascade pathway to new annulated pyrazoles.

Table 1. Optimization of reaction conditions[a] with 1,2-phenylenediamine.



Entry	Catalyst	Ligand	Base	Solvent	Yield [%][b]
1	CuI	L-proline	K_3PO_4	DMSO	76
2	CuI	DMEDA	K_3PO_4	DMSO	24
3	CuI	L-proline	K_2CO_3	DMSO	37
4	CuI	L-proline	Cs_2CO_3	DMSO	28
5	CuI	L-proline	K_3PO_4	DMF	62
6	CuI	L-proline	K_3PO_4	toluene	13
7	CuI	L-proline	K_3PO_4	dioxane	41
8	CuCl	L-proline	K_3PO_4	DMSO	32
9	Cu_2O	L-proline	K_3PO_4	DMSO	17
10	CuI	–	K_3PO_4	DMSO	85
11	CuI	–	K_2CO_3	DMSO	65
12	CuI	–	Cs_2CO_3	DMSO	58

[a] *Reaction conditions:* 4-iodo-3-pyrazolecarbaldehyde (1.0 mmol), *o*-phenylenediamine (1.0 mmol), CuI (0.1 mmol), ligand (0.2 mmol), base (3.0 mmol), solvent (1.0 mL), 90 °C, 36 h.

[b] Isolated yields.

source, L-proline as ligand and K_3PO_4 as base led to the isolation of 76% of the desired product (Table 1, entry 1).[7] Changing the ligand to DMEDA was observed to be detrimental leading to a significant drop in the yields (Table 1, entry 2). Amongst the different bases, solvents and copper sources examined, K_3PO_4, DMSO and CuI, respectively, were found to be superior for this reaction. Later as a routine, we checked the reaction under copper-free or ligand-free conditions too. Although the copper-free conditions failed to induce a reaction, we were surprised to discover that reaction was successful under ligand-free conditions (Table 1, entrie 10–12). Indeed, the ligand-free reaction using K_3PO_4 furnished 85% of the required product whereas other evaluated bases although successful the furnished product in relatively lower yields. Hence the two most successful conditions of 10 mol% CuI, ligand-free or 20 mol% L-proline and 300 mol% K_3PO_4 in DMSO at 90 °C were simultaneously used for further investigation.

The scope of reaction was explored by using a combination of different 4-iodopyrazolecarbaldehydes and several 1,2-phenylenediamines (Table 2). It was satisfying to note that all substrates reacted smoothly to afford the required products and the yields were better in ligand-free conditions. Changing the substitution from phenyl to methyl at the 1-position did not affect the outcome of the reaction (Table 2, entry 14). Likewise the substitution pattern in the phenyl ring placed at C-5 or leaving it unsubstituted did not influence the formation of product. In general, the presence of a mild electron-withdrawing group on the 1,2-phenylenediamine resulted in relatively lower yields of the products as compared to unsubstituted 1,2-phenylenediamine or the one containing a mild electron-donating group. Thus this strategy proved to be a general and convenient route for the synthesis of substituted-2,4 or 1,4-dihydrobenzo[*b*]pyrazolo[4,3-*e*][1,4]-diazepines.

The second portion of this work involved the extension of the strategy to similar copper-catalyzed cascade reactions of 4-iodopyrazolecarbaldehydes with 2-aminophenol involving C–O coupling. It was satisfying to note that reacting 4-iodo-1,5-diphenyl-1*H*-pyrazole-3-carbaldehyde and 2-aminophenol in the presence of CuI and Cs_2CO_3 in toluene under ligand-free conditions successfully yielded 34% of the required product. However introduction of 1,10-phenanthroline as ligand, keeping all other conditions constant, improved the yield significantly (Table 3, entry 2).[8] A brief survey of reactions with different bases and solvents indicated Cs_2CO_3 and toluene to be superior for the purpose. Thus the optimal conditions of CuI (10 mol%), ligand 20 mol%, base 200 mol% in toluene at 90 °C for 24 h was employed for further screening.

With the optimized conditions in hand, we studied the generality of this method with various 4-iodo-pyrazolecarbaldehydes and different 2-aminophenols and the results are presented in Table 4. Although the nature of the 4-iodopyrazolecarbaldehydes did not have any effect on the yields, the substituents present on the 2-aminophenols influenced the formation of the final product. For example, the 2-aminophenols containing an electron-donating group such as methyl gave better yields as compared to the ones having an electron-withdrawing group such as chloro. However, the 2-aminophenol bearing a strong electron-withdrawing group such as nitro failed to react to yield the required product (Table 4, entry 6).

We speculate that, in the first step, a condensation reaction between the aldehyde and aniline occurs resulting in the formation of an imine. Subsequently the copper-promoted C–N or C–O cross-coupling reaction involving either the amino group of 1,2-phenyl-

Table 2. Scope and limitations.

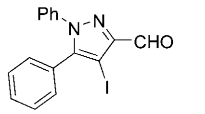
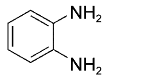
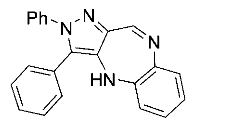
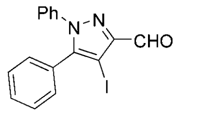
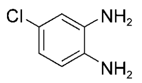
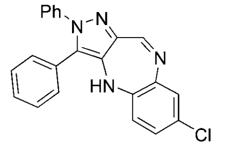
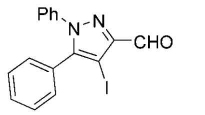
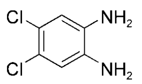
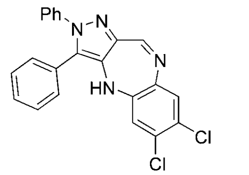
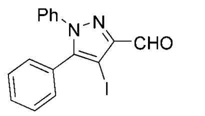
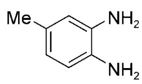
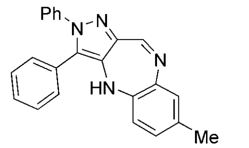
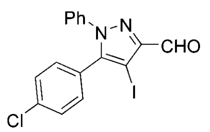
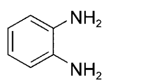
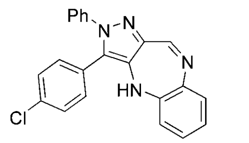
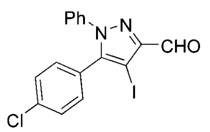
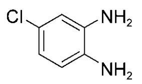
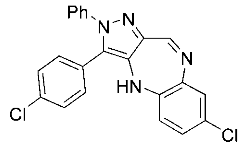
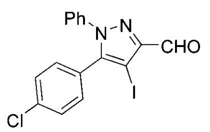
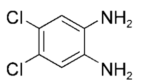
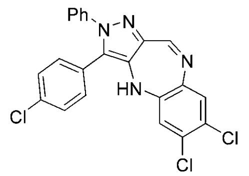
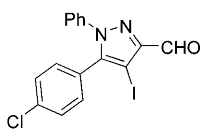
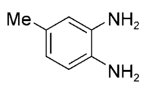
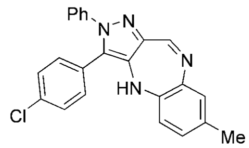
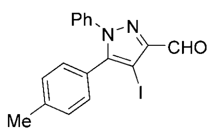
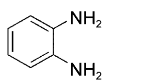
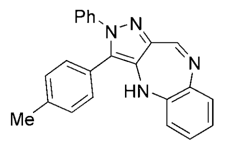
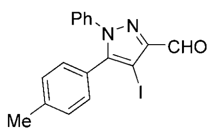
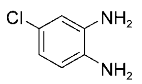
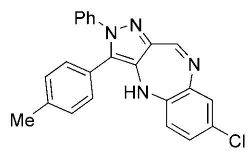
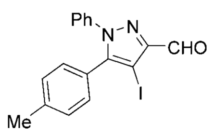
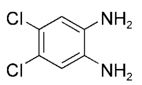
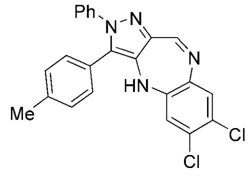
Entry	Aldehyde	1,2-Phenylenediamine	Product	Yield [%][a]
1				85/76
2				60/52
3				55/48
4				82/68
5				77/66
6				57/50
7				56/49
8				72/61
9				79/65
10				58/52
11				56/51

Table 2. (Continued)

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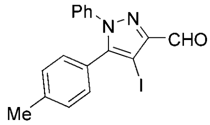
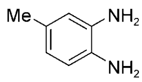
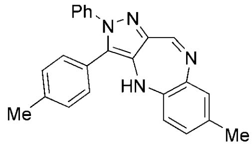
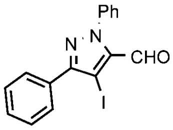
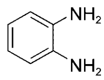
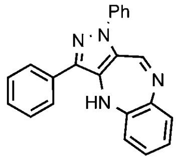
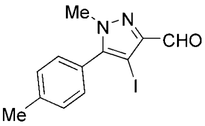
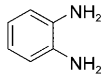
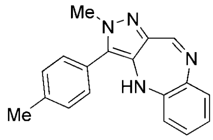
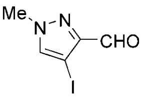
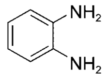
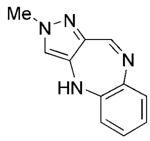
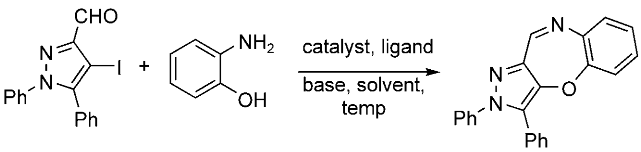
12				78/65
13				62/56
14				80/68
15				81/67

[a] Isolated yields for the product under ligand-free/L-proline-containing reaction conditions.

Table 3. Optimization of reaction conditions[a] with 2-aminophenol.



Entry	Catalyst	Ligand	Base	Solvent	Yield [%][b]
1	CuI		Cs_2CO_3	toluene	34
2	CuI	1,10-phenanthroline	Cs_2CO_3	toluene	72
3	CuI	1,10-phenanthroline	Cs_2CO_3	DMF	18
4	CuI	1,10-phenanthroline	Cs_2CO_3	dioxane	34
5	CuI	1,10-phenanthroline	K_2CO_3	toluene	0
6	CuI	1,10-phenanthroline	K_3PO_4	toluene	13
7	Cu_2O	1,10-phenanthroline	Cs_2CO_3	toluene	54
8	CuCl	1,10-phenanthroline	Cs_2CO_3	toluene	47

[a] *Reaction conditions:* 4-iodo-3-pyrazolecarbaldehyde (1.0 mmol), 2-amino phenol (1.0 mmol), CuI (0.1 mmol), ligand (0.2 mmol), base (2.0 mmol), solvent (1.0 mL), 90 °C, 24 h.
[b] Isolated yields.

enediamine or hydroxy group of 2-aminophenol takes place, respectively, leading to the intramolecularly cyclized product. In an effort to provide a rationale to this basis in a representative reaction the formyl group of 4-iodo-1,5-diphenyl-1*H*-pyrazole-3-carbaldehyde was transformed to acetal which was then independently reacted with 1,2-phenylenediamine and 2-aminophenol. Under both circumstances the reactions failed and the starting materials were recovered unreacted (Scheme 1). In view of this result, it is proposed that the imine formed as the first step in the process has *Z*-stereochemistry across the double bond which then undergoes the intramolecular cyclization *via* cross-coupling. All attempts to perform intermolecular C–N or C–O coupling reactions during this study were, however, unsuccessful.

In conclusion, we have developed an unprecedented strategy for the construction of substituted 2,4- or 1,4-dihydrobenzo[*b*]pyrazolo[4,3-*e*][1,4]diazepines or substituted 2*H*- or 1*H*-benzo[*b*]pyrazolo[3,4-*f*][1,4]-oxazepines *via* a copper-catalyzed cascade cyclization. We have demonstrated the scope of the strategy with a variety of reactants. This approach therefore updates the literature on the copper-catalyzed cross-cou-

Table 4. Scope and limitations.

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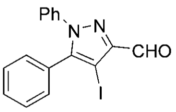
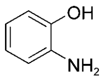
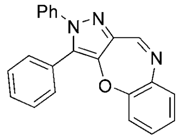
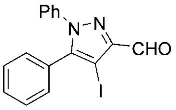
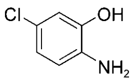
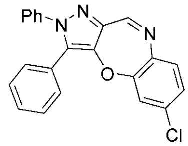
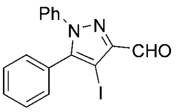
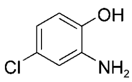
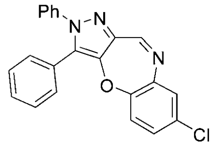
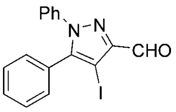
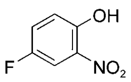
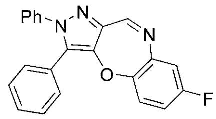
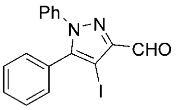
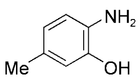
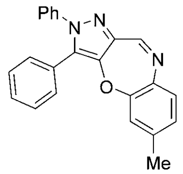
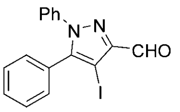
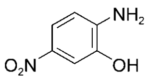
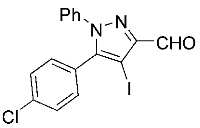
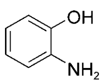
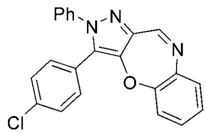
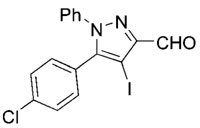
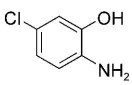
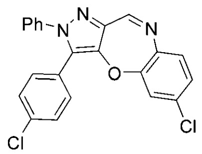
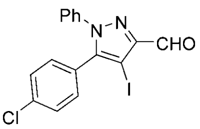
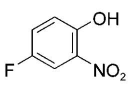
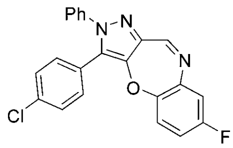
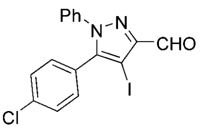
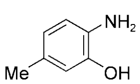
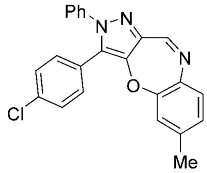
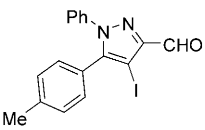
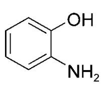
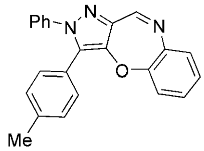
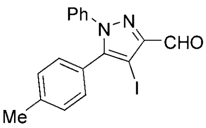
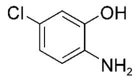
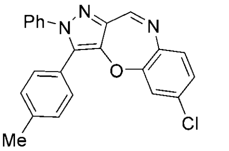
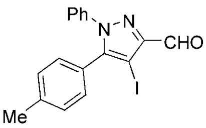
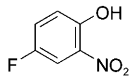
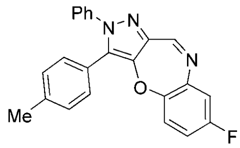
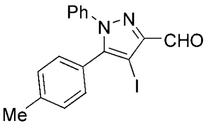
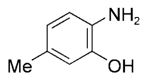
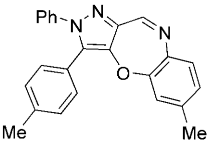
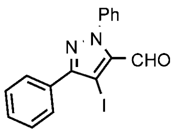
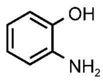
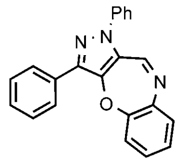
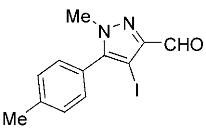
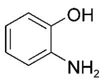
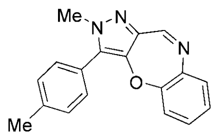
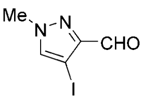
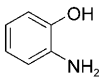
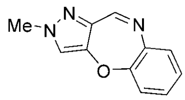
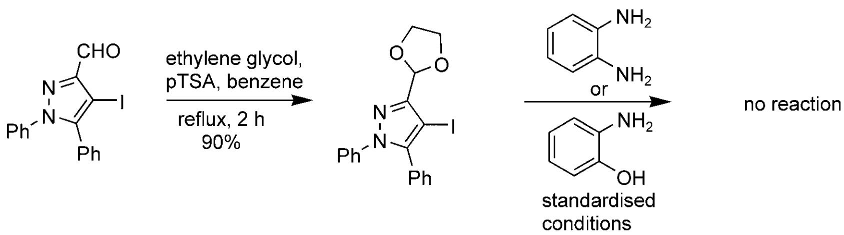
1				72
2				59
3				60
4				57
5				70
6			no reaction	
7				64
8				57
9				56
10				69
11				70

Table 4. (Continued)

Entry	Aldehyde	2-Aminophenol	Product	Yield [%][a]
12				60
13				57
14				74
15				61
16				61
17				63

[a] Isolated yields.



Scheme 1.

pling in pyrazoles and offers an opportunity to construct new fused benzazepines and benzoxepines with other heterocyclic systems too.

Experimental Section

General Procedure for Pyrazole-Annulated Benzodiazepines as Exemplified for the Synthesis of 2,3-Diphenyl-2,4-dihydropyrazolo[4,3-*b*][1,5]benzodiazepine

To a solution of 4-iodo-1,5-diphenyl-1*H*-pyrazole-3-carbaldehyde (200 mg, 0.53 mmol) in DMSO (4 mL), K_3PO_4 (339 mg, 1.60 mmol) and CuI (10 mg, 0.053 mmol) were added and the reaction mixture was heated at 90 °C for 36 h under a nitrogen atmosphere. Thereafter, water (50 mL) and ethyl acetate (25 mL) were added and the reaction mass was pass through a Celite bed and the layers were separated. The aqueous layer was further extracted with ethyl acetate (2×20 mL) and the collected organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum. Column chromatography of the crude product over silica gel furnished the pure 2,3-diphenyl-2,4-dihydropyrazolo[4,3-*b*][1,5]benzodiazepine as a yellow solid (ethyl acetate/hexanes, 1:5); yield: 153 mg (85%).

2,3-Diphenyl-2,4-dihydropyrazolo[4,3-*b*][1,5]benzodiazepine (Table 2, entry 1): mp 248–249 °C; R_f = 0.54 (hexanes: EtOAc, 70:30, v/v); IR (KBr): ν_{max} = 3443 (NH) cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.37 (m, 14 H), 7.84 (s, 1 H), 10.13 (brs, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ = 106.6, 122.0, 125.2, 127.7, 128.3, 128.6, 129.4, 139.4, 144.0, 144.4, 146.3; ESI-MS: *m/z* = 337 [M+H]$^+$; DART-HR-MS: *m/z* = 337.1450, calcd. for $C_{22}H_{17}N_4$ [MH]$^+$: 337.1453.

General Procedure for Pyrazole-Annulated Benzoxazepines as Exemplified for the Synthesis of 2,3-Diphenyl-2*H*-pyrazolo[4,3-*b*][1,5]benzoxazepine

To a solution of 4-iodo-1,5-diphenyl-1*H*-pyrazole-3-carbaldehyde (200 mg, 0.53 mmol) in toluene (10 mL), Cs_2CO_3 (348 mg, 1.07 mmol), CuI (10 mg, 0.053 mmol) and 1,10-phenanthroline (19 mg, 0.107 mmol) were added and the reaction mixture was heated at 90 °C for 24 h under a nitrogen atmosphere. Thereafter, water and ethyl acetate were added and the reaction mass was pass through a Celite bed and the layers were separated. The aqueous layer was further extracted with ethyl acetate (2×20 mL) and the collected organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum. Column chromatography of the crude product over silica gel furnished the pure 2,3-diphenyl-2*H*-pyrazolo[4,3-*b*][1,5]benzoxazepine as a white solid (ethyl acetate/hexanes, 1:20); yield: 130 mg (72%).

2,3-Diphenyl-2*H*-pyrazolo[4,3-*b*][1,5]benzoxazepine (Table 4, entry 1): Mp 169–170 °C; R_f = 0.34 (hexanes: EtOAc, 90:10, v/v); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.26–7.29 (m, 13 H), 7.64 (dd, J = 3.2 and 5.9 Hz, 1 H), 7.81 (dd, J = 3.2 and 5.9 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 108.5, 111.1, 120.3, 124.8, 125.5, 125.8, 128.5, 128.8, 129.0, 129.2, 129.7, 139.7, 141.4, 141.9, 145.2, 150.7, 158.3; ESI-MS: *m/z* = 338 [M+H]$^+$; DART-HR-MS: *m/z* = 338.1302, calcd. for $C_{22}H_{16}N_3O$ [MH]$^+$: 338.1293.

Supporting Information

Characterization data for the remaining products and copies of ^{1}H and ^{13}C NMR spectra are available in the Supporting Information.

Acknowledgements

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