

Regioselective Three-Component Synthesis of Highly Fluorescent 1,3,5-Trisubstituted Pyrazoles

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3,5-Disubstituted and 1,3,5-trisubstituted pyrazoles are readily synthesized from acyl chlorides, terminal alkynes, and hydrazines by a consecutive one-pot three-component Sonogashira coupling/Michael addition/cyclocondensation sequence in good to excellent yields. These pyrazoles are highly fluorescent, both in solution and in the solid state. Investigation of the electronic properties by UV/Vis and fluo-

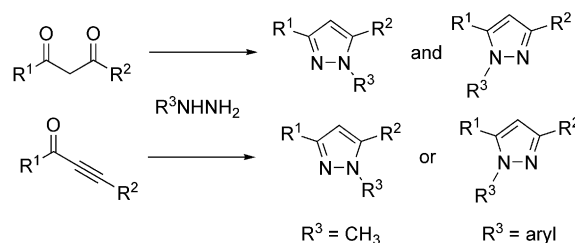
rescence spectroscopy and by DFT and ZINDO CI computations reveal that the excited state is highly polar and allows fine-tuning of the absorption and emission properties. X-ray structure analyses of 3,5-disubstituted pyrazoles reveal self-organization by hydrogen bonding and π -stacking.

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Introduction

Pyrazoles are five-membered heterocycles with two adjacent nitrogen atoms with a rich chemistry and numerous applications.^[1] A broad spectrum of biological activity, such as antihyperglycemic, analgesic, antiinflammatory, antipyretic, antibacterial and sedative-hypnotic activity has attracted considerable interest.^[2–4] In addition, several 3,5-diaryl-substituted pyrazoles also reversibly inhibit monoamine oxidase-A and monoamine oxidase-B.^[5] For crop protection 1,2-dialkyl-3,5-diphenylpyrazoles are known as potent herbicides.^[6] Furthermore, pyrazoles are omnipresent as ligands in coordination chemistry,^[7] as building blocks in heterocycle synthesis,^[8] as optical brighteners^[9] and UV stabilizers,^[10] as photoinduced electron-transfer systems,^[11] and as units in supramolecular entities.^[12] Hence, numerous methods for the synthesis of 1,3,5-substituted pyrazoles have been established.^[1,13] Among the most frequently used methods is the cyclocondensation of 1,3-dicarbonyl compounds, or equivalent 1,3-bis(electrophilic) reagents such as epoxy ketones, with hydrazines. However, for substituted hydrazines the product formation often results in mixtures of regioisomeric pyrazoles (Scheme 1).^[14] Alternatively, besides several regioselective methods^[15] substituted hydrazines can react with α,β -unsaturated ketones in a regioselective fashion to give pyrazolines, that can be oxidized to the corresponding pyrazoles.^[16] The direct conversion of hydrazines to pyrazoles can also be achieved by Michael addition/cyclocondensation to alkynones, a pro-

cess that has been known for more than a century.^[17] Neither the regioselectivity issue has been studied in detail, nor was the occurrence of mixtures of regioisomers reported.^[18] Despite of very few examples,^[19] the regioselective formation of *N*-substituted pyrazoles by the alkynone pathway has remained unexplored (Scheme 1). With respect to the interesting electronic properties of pyrazoles as fluorophores and the increasing quest for tailor-made functional π -electron systems by diversity-oriented strategies,^[20] as part of our program to develop multi-component syntheses of heterocycles,^[21] we have focused on one-pot syntheses of substituted pyrazoles. Here, we report on a concise, regioselective consecutive three-component synthesis of pyrazoles with a highly flexible substitution pattern and their absorption and emission properties.



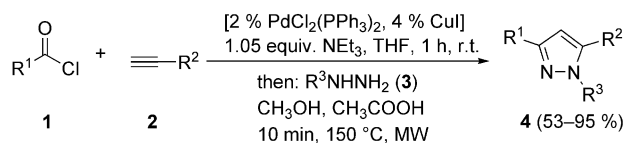
Scheme 1. Variable regioselectivity in pyrazole formation depending on 1,3-diketones and alkynones as C_3 building blocks.

Results and Discussion

Alkynones are easily accessible by Sonogashira coupling^[22] of acyl chlorides with terminal alkynes.^[23] Just recently, we reported that in THF as a solvent only 1 equiv. of triethylamine as the hydrochloric acid scavenging base

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proves to be most favorable for the successful coupling of even sensitive alkynes such as (trimethylsilyl)acetylene.^[24] In turn, the resulting alkynones are highly reactive and readily react in a one-pot fashion with all kinds of binucleophiles to give various heterocycles. Therefore, upon treating acyl chlorides **1** with terminal alkynes **2** under modified Sonogashira conditions at room temperature for 1 h to furnish the expected alkynones, subsequently, hydrazines **3**, methanol and glacial acetic acid were added to the reaction mixture and heated to give pyrazoles **4** (Scheme 2). Prior to screening the scope of this sequence, the pyrazole-forming



Scheme 2. One-pot three-component synthesis of pyrazoles **4**.

Michael addition/cyclocondensation step was optimized under conventional and microwave heating (Table 1). Best results for the formation of pyrazole **4b** were achieved after dielectric heating in the microwave cavity at 150 °C for 10 min in the presence of methanol and acetic acid (Table 1, Entry 6). Hence, in the sense of a consecutive one-pot process and with the optimized cyclocondensation conditions, the pyrazoles **4** were obtained in good to excellent yields,

Table 1. Optimization of the Michael addition/cyclocondensation step to give pyrazole **4b**.

Entry	Heating mode	<i>T</i> [°C]	<i>t</i>	Solvent	Yield
1	oil bath	80	3 d	CH ₃ OH	75%
2	MW	120	20 min	CH ₃ OH	74%
3	MW	120	10 min	CH ₃ OH	59%
4	MW	150	10 min	CH ₃ OH	80%
5	MW	150	15 min	CH ₃ OH	55%
6	MW	150	10 min	CH ₃ OH/CH ₃ CO ₂ H	82%

Table 2. One-pot three-component synthesis of pyrazoles **4**.

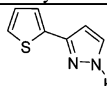
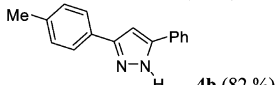
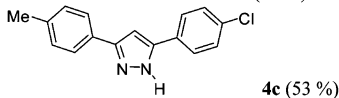
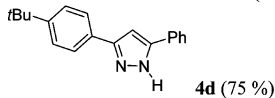
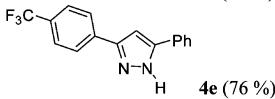
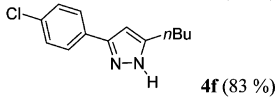
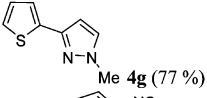
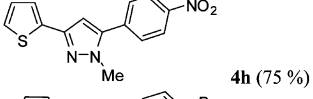
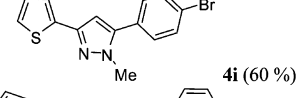
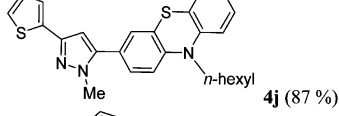
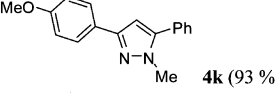
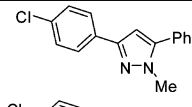
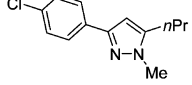
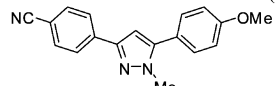
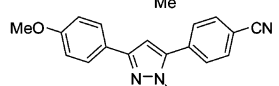
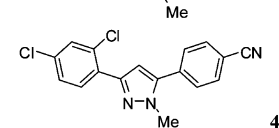
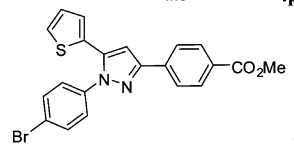
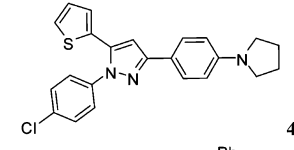
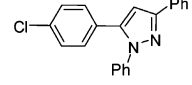
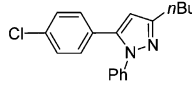
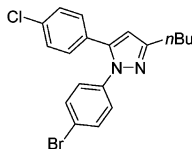
Entry	Acyl chloride 1	Alkyne 2	Hydrazine 3	Pyrazole 4 (yield)
1	1a : R ¹ = 2-thienyl	2a : R ² = SiMe ₃	3a : R ³ = H	 4a (94 %)
2	1b : R ¹ = 4-MeC ₆ H ₄	2b : R ² = Ph	3a	 4b (82 %)
3	1b	2c : R ² = 4-ClC ₆ H ₄	3a	 4c (53 %)
4	1c : R ¹ = 4- <i>t</i> BuC ₆ H ₄	2b	3a	 4d (75 %)
5	1d : R ¹ = 4-F ₃ CC ₆ H ₄	2b	3a	 4e (76 %)
6 ^[a]	1e : R ¹ = 4-ClC ₆ H ₄	2d : R ² = <i>n</i> Bu	3a	 4f (83 %)
7	1a	2a	3b : R ³ = CH ₃	 4g (77 %)
8	1a	2e : R ² = 4-O ₂ NC ₆ H ₄	3b	 4h (75 %)
9 ^a	1a	2f : R ² = 4-BrC ₆ H ₄	3b	 4i (60 %)
10	1a	2g : R ² = 10-hexylphenothiazin-3-yl	3b	 4j (87 %)
11 ^[a,b]	1f : R ¹ = 4-MeOC ₆ H ₄	2b	3b	 4k (93 %)

Table 2. (Continued)

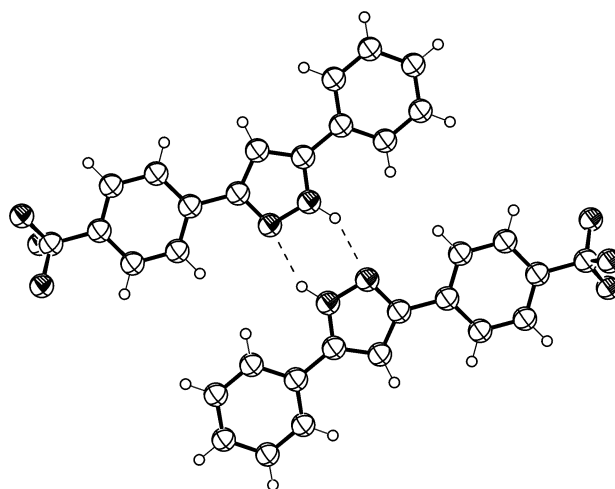
Entry	Acyl chloride 1	Alkyne 2	Hydrazine 3	Pyrazole 4 (yield)
12	1e	2b	3b	 4l (95 %)
13 ^[b]	1e	2h : R ² = <i>n</i> Pr	3b	 4m (95 %)
14	1g : R ¹ = 4-NCC ₆ H ₄	2i : R ² = 4-MeOC ₆ H ₄	3b	 4n (62 %)
15	1f	2j : R ² = 4-NCC ₆ H ₄	3b	 4o (58 %)
16	1h : R ¹ = 2,4-Cl ₂ C ₆ H ₃	2j	3b	 4p (59 %)
17	1a	2k : R ² = 4-MeO ₂ CC ₆ H ₄	3c : R ³ = 4-BrC ₆ H ₄	 4q (60 %)
18	1a	2l : R ² = 4-H ₈ C ₄ NC ₆ H ₄	3d : R ³ = 4-ClC ₆ H ₄	 4r (77 %)
19	1e	2b	3e : R ³ = Ph	 4s (81 %)
20	1e	2d	3e	 4t (67 %)
21	1e	2d	3c	 4u (70 %)

[a] *t*BuOH instead of CH₃OH. [b] Performed on a 10 mmol scale.

predominantly as colorless crystalline solids (Scheme 2, Table 2).

Three types of hydrazines were employed in the methodological studies, i.e. hydrazine (R³ = H, Table 2, Entries 1–6), methylhydrazine (R³ = Me, Table 2, Entries 7–16), and arylhydrazines (R³ = aryl, Table 2, Entries 17–21). In accordance with theory, in every case one of the two possible regioisomers, depending on the nature of the hydrazine substituent R³, was formed preferentially. Only traces of the other regioisomers could be detected (regioselectivity >98:<2). The structures and substitution patterns of pyrazoles **4** were unambiguously assigned by ¹H, ¹³C and 2D NMR spectroscopy, mass spectrometry and in addition by X-ray structure analysis of the pyrazoles **4c**, **4e** and **4l** (Figures 1, 2, and 3, Table 6).

As a consequence of 3,5-substitution (except for **4a** and **4g**), in the ¹H NMR spectra, only one resonance of the

Figure 1. Molecular structure and dimer formation of pyrazole **4e**.

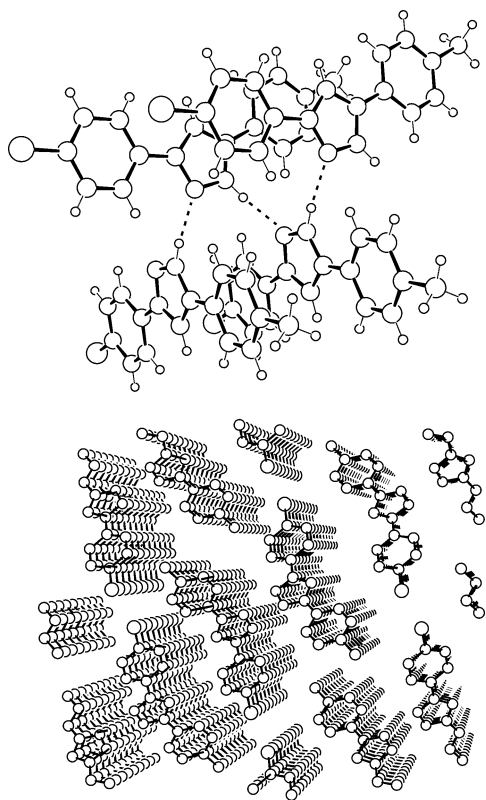


Figure 2. Bridging by hydrogen bonding and π -stacking in single crystals of **4c**.

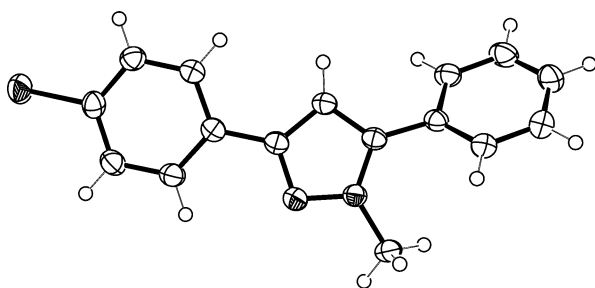


Figure 3. Molecular structure of pyrazole **4l**.

pyrazole core is found. These signals can be easily identified as sharp singlets. Depending on the nature of R^3 , the shifts of these signals may vary and are found between $\delta = 6.5$ and 6.7 ppm. The carbon resonances of the pyrazole core can be readily assigned. Evidently, the shifts of these resonances are even dependent on the electronic nature of R^3 . Signals for the methine nuclei C-4 can be determined at around at $\delta \approx 101$ – 105 ppm. With respect to the broad variation of R^1 and R^2 , the resonances of the two quaternary carbon nuclei of the pyrazole core appear between $\delta = 140$ and 150 ppm.

The solid-state structures of the pyrazoles were studied by single-crystal X-ray analyses.^[25] The 1*H*-pyrazoles **4c** and **4e** are organized in the crystal lattice by hydrogen bonding and π -stacking. Pyrazole **4e** forms layers constituted by hydrogen-bonded dimers (Figure 1). These hydro-

gen bonds (between donor and acceptor atoms) are 2.89 Å long. The distance between the layers of pyrazoles is found to be 3.43 Å. Interestingly, the strong π – π interactions are responsible for an almost perfect coplanarity of the 3,5-diarylpyrazole (distortion from planarity ca. 3°).

Pyrazole **4c** reveals another mode of self-organization by hydrogen bonding in the solid state (Figure 2). One pyrazole molecule bridges with two others leading to infinite chains by hydrogen bonding. Again, the hydrogen bonds are 2.89 Å long. In addition, π -stacking of the pyrazoles results in a columnar superstructure. The intermolecular distance of the π -stacked pyrazoles is 3.46 Å, i.e. within the same range as in graphite. The molecular entities are almost perfectly planar.

N-Substitution rules out the formation of hydrogen bonding and, hence, pyrazole **4l** will not form comparable supramolecular structures as observed in the previous crystal structures. The position of the methyl substituent is in perfect agreement with the Michael addition scenario where the most electron-rich nitrogen atom (adjacent to the methyl group) attacks the intermediate alkynone at the β -acetylene carbon center prior to cyclocondensation (Figure 3). Other than observed for the structure analyses of the 1*H*-pyrazoles **4c** and **4e** the aryl substituents in 3- and 5-position of **4l** are distorted from coplanarity by 11° (4-chlorophenyl) and 36° (phenyl) with respect to the central pyrazole ring.

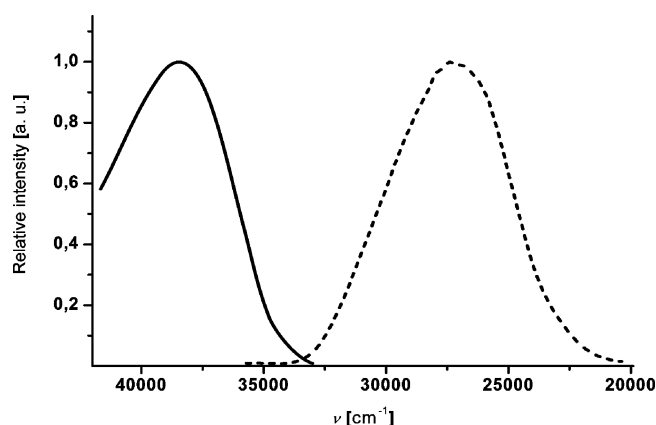
Pyrazoles are well known for interesting electronic properties.^[9,10] Therefore, our diversity-oriented approach to pyrazoles with variable substitution pattern allows a detailed investigation of the electronic properties by UV/Vis and fluorescence spectroscopy (Table 3). Expectedly, both absorption and emission properties are strongly effected by minute substituent variations or conformational biases. In solution, the absorption maxima $\lambda_{\text{max,abs}}$ of pyrazoles **4** are found in the near UV between 260 and 385 nm with molar extinction coefficients ϵ ranging from 5300 to 106000 L mol^{−1} cm^{−1}. Almost all compounds display considerable blue to green fluorescence with emission maxima between 320 and 380 nm. The fluorescence quantum yields were determined with *p*-terphenyl as a standard^[26] and vary between below 1% to 74% . Due to the large Stokes shifts ranging from 4200 to 12300 cm^{−1}, there is almost no overlap between absorption and emission bands of the pyrazoles **4** (Figure 4), a favorable effect for many applications as fluorescent dyes.^[27]

Large Stokes shifts for 3,5-diarylpyrazoles have been reported before^[28] and prompted us to study and scrutinize the electronic structure experimentally and computationally. Therefore, the UV/Vis absorption and emission spectra of compound **4k** were recorded in various solvents (Table 4). The absorption maximum $\lambda_{\text{max,abs}}$ is essentially independent of the solvent polarity, whereas the shortest-wavelength emission maximum $\lambda_{\text{max,em}}$ and the fluorescence quantum yield Φ_f reveal positive solvochromicity and high fluorescence efficiency in more polar solvents. The solid-state fluorescence is almost identical with the fluorescence in acetonitrile (Table 4, Entry 7).

Table 3. Selected electronic properties (UV/Vis and fluorescence data, fluorescence quantum yields Φ_f , and Stokes shifts $\Delta\tilde{\nu}$) of the pyrazoles **4** and **6**.

Compound	Absorption, ^[a] $\lambda_{\text{max,abs}}$ [nm] (ϵ [L mol ⁻¹ cm ⁻¹])	Emission, ^[b] $\lambda_{\text{max,em}}$ [nm] (Φ_f) ^[c]	Stokes shift $\Delta\tilde{\nu}$ ^[d] [cm ⁻¹]
4a	289 (4500), 273 (7600)	330 (< 0.01)	6300
4b	258 (95900)	331 (0.32)	8600
4c	283 (8200), 262 (20400)	331 (0.15)	8000
4d	283 (10700), 258 (36900),	323 (0.39)	7800
4e	259 (5300)	333 (0.74)	8600
4f	257 (38100)	320 (0.02)	7700
4g	273 (13500), 247 (10800),	348 (0.05)	7900
4h	334 (9200), 297 (20400), 286 (58800)	357 (< 0.01)	7000
4i	273 (54900), 260 (53300)	379 (< 0.01)	10200
4j	320 (18600), 269 (97200)	452 (0.01)	9100
4k	260 (52400)	369 (0.35)	11400
4l	280 (35200), 260 (87500)	331 (0.05)	8400
4m	262 (106400)	323 (0.02)	7200
4n	280 (49100)	392 (0.56)	10200
4o	278 (48600)	392 (0.10)	10500
4p	269 (24600)	383 (0.07)	11100
4q	348 (1300), 287 (44200).	383 (0.02)	8700
4r	385 (19100), 295 (98500)	460 (0.01)	4200
4s	293 (17400), 259 (50700)	382 (0.10)	12300
4t	263 (10500)	339 (0.09)	8500
4u	275 (34600)	341 (0.08)	7000
6	285 (7600)	382 (0.50)	8900

[a] Recorded in CH₂Cl₂ at $c = 10^{-3}$ M. [b] Recorded in CH₂Cl₂ at $c = 10^{-6}$ M. [c] Determined with *p*-terphenyl as a standard in cyclohexane, $\Phi_f = 0.82$. [d] $\Delta\tilde{\nu} = \lambda_{\text{max,abs}} - \lambda_{\text{max,em}}$ [cm⁻¹].

Figure 4. Normalized absorption (solid line) and emission (dotted line) spectra of pyrazole **4k** (recorded in CH₂Cl₂, 293 K).Table 4. Solvent dependence of the longest-wavelength absorption maximum $\lambda_{\text{max,abs}}$, the shortest-wavelength emission maximum $\lambda_{\text{max,em}}$, and the fluorescence quantum yields Φ_f of compound **4k**.

Entry	Solvent	Absorption, ^[a] $\lambda_{\text{max,abs}}$ [nm]	Emission, ^[b] $\lambda_{\text{max,em}}$ [nm]	Φ_f ^[c]
1	cyclohexane	259	337	0.10
2	CH ₂ Cl ₂	260	369	0.35
3	dioxane	260	358	0.09
4	THF	260	362	0.12
5	acetonitrile	259	377	0.64
6	ethanol	257	366	0.06
7	solid state	–	376	–

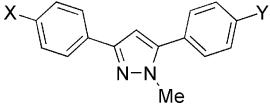
[a] Recorded at $c = 10^{-3}$ M. [b] Recorded at $c = 10^{-6}$ M. [c] Determined with *p*-terphenyl as standard in cyclohexane, $\Phi_f = 0.82$.

The polar nature of the excited state suggested to take a closer look at the electronic structure of selected pyrazoles. A pronounced absorptivity as reflected by large molar extinction coefficients ϵ can be accounted for by π – π^* transitions. Therefore, based upon the starting geometry extracted from the X-ray structure analysis of **4l**, calculations were carried out on the level of density functional theory (B3LYP/3-21+** functional^[29] for geometry optimization) as well as on a semi-empirical level (ZINDO CI^[30] after PM3 geometry optimization). To elucidate the influence of push-pull substitution on the electronic properties in the ground and the excited state (Table 3, compounds **4n** and **4o**) computations were carried out for the selected 3,5-diaryl-1-methylpyrazoles **4k**, **4n**, **4o**, and for the 3,5-diphenyl derivative (Table 5, Entry 1).

The λ_{max} values were either calculated from the computed HOMO–LUMO gap (DFT calculations) or produced by the ZINDO CI program (Table 5). Interestingly, the cheaper and faster semi-empirical ZINDO CI computation reproduces the experimental data for the more complex push-pull systems **4n** and **4o** better than the more expensive and slower DFT method. Thus, for computational high-throughput screening the ZINDO CI calculation can be considered as a valid tool.

Furthermore, the DFT-computed frontier orbitals of the push-pull systems **4n** (Figure 5) and **4o** (Figure 6) clearly show that the HOMO–LUMO transition is associated with significant charge transfer character. For system **4n** the charge transfer only occurs within the (*p*-cyanophenyl)pyrazolyl moiety whereas the *p*-methoxyphenyl substituent adopts an orthogonal orientation without orbital coefficients, suggesting the absence of *p*-electron interaction. In the system **4o** the charge transfer is characterized by a shift

Table 5. Comparison of experimentally (recorded in CH₂Cl₂, *T* = 293 K) and computationally (B3LYP/3-21+**) functional and ZINDO CI determined λ_{max} values of selected 3,5-diaryl-1-methylpyrazoles.



Entry	Substitution pattern	Experiment, $\lambda_{\text{max,exp.}}$ [nm]	DFT, $\lambda_{\text{max,calcd.}}$ [nm] ^[a]	ZINDO CI, $\lambda_{\text{max,calcd.}}$ [nm] ^[b]
1	X = Y = H	250 ^[31]	249	268
2	X = OCH ₃ , Y = H (4k)	260	268	268
3	X = CN, Y = OCH ₃ (4n)	280	265	287
4	X = OCH ₃ , Y = CN (4o)	278	333	284

[a] Calculated from the HOMO–LUMO gap of the DFT computation with the B3LYP/3-21+** functional. [b] ZINDO CI calculation after PM3 geometry optimization.

of electron density from the *p*-methoxyphenyl donor moiety in the HOMO to the *p*-cyanophenyl acceptor unit in the LUMO. Thus, in both cases, **4n** and **4o**, the origin of a pronounced positive solvochromicity of the emission as a consequence of a polar excited state is nicely rationalized. Expectedly, push-pull substitution causes a redshift in absorption and emission and can be successfully applied for fine-tuning of the fluorescence color of 1,3,5-trisubstituted pyrazoles. Yet, the pyrazole-inherent polarity has to be considered. Although, pyrazoles **4n** and **4o** are almost identical with respect to numerical absorption and emission, data the fluorescence efficiencies clearly deviate, revealing that the substitution pattern of **4n**, presumably as a consequence of a better overlap of HOMO and LUMO, leads to a more efficient fluorophore in comparison to **4o**.

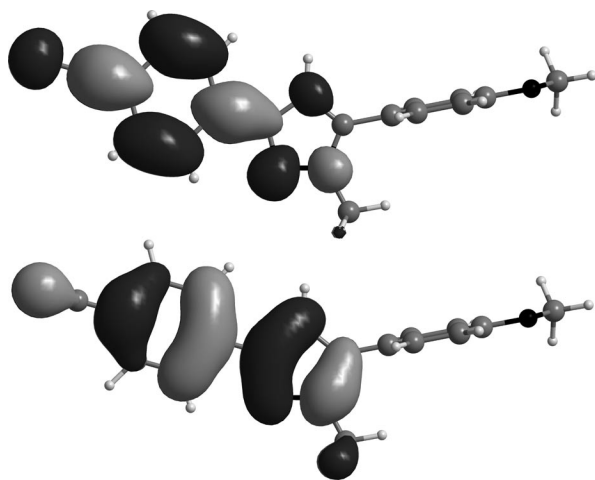


Figure 5. DFT-computed frontier orbitals of pyrazole **4n**, LUMO (top) and HOMO (bottom).

The three-component access to 1,3,5-trisubstituted fluorescent pyrazoles is a highly versatile diversity-oriented approach to fluorophores that can readily be fine-tuned by building-block diversity. Considering the mild reaction conditions of this three-component Sonogashira coupling/cyclocondensation sequence, the expansion to a four-component reaction as a level-two functionalization by addressing the Pd-catalyst system for a second time in the sense of a

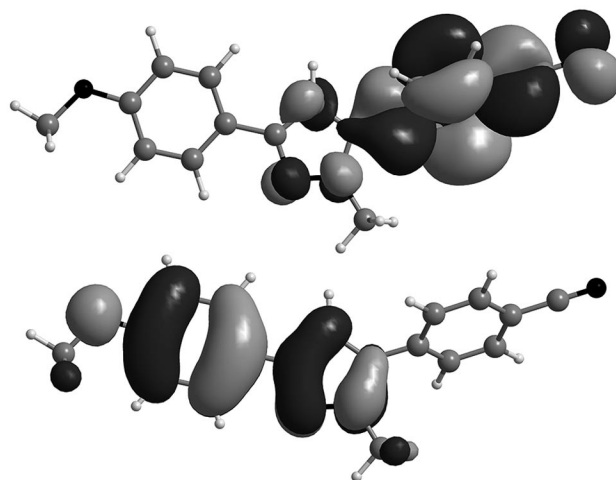
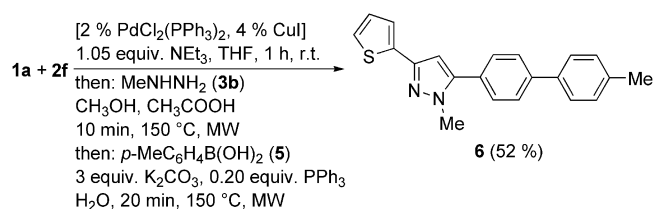


Figure 6. DFT-computed frontier orbitals of pyrazole **4o**, LUMO (top) and HOMO (bottom).

sequentially palladium-catalyzed process^[32] lies at hand. For instance, the Suzuki coupling has been shown to be highly compatible with Sonogashira catalyst systems and conditions.^[33]

Therefore, upon subsequent reaction of acyl chloride **1a**, (4-bromophenyl)acetylene (**2f**), and methylhydrazine (**3b**), according to the one-pot three-component synthesis of pyrazoles, the pyrazole **4i** bearing a bromo phenyl substituent is treated within the same reaction vessel without further catalyst addition and in the presence of 1.2 equiv. of *p*-tolylboronic acid (**5**), potassium carbonate and water under dielectric heating at 150 °C for 20 min to give the highly fluorescent biphenylpyrazole **6** in 52% yield (Scheme 3,



Scheme 3. One-pot four-component synthesis of pyrazole **6**.

Table 3). Interestingly, the combined yields of the two-step process, i.e. 60% for the formation of pyrazole **4i** and 70% for the Suzuki coupling of **4i** with **5** to give **6**, are lower than the yield of the four-component synthesis. Thus, with four new bonds and a ring formed in a one-pot fashion and an average yield of 85% per bond forming step this novel multi-component reaction is perfectly suited for the rapid assembly of complex structures with a pyrazole core.

Conclusions

A straightforward regioselective, microwave-assisted one-pot three-component synthesis of 1,3,5-substituted pyrazoles was developed in the sense of a consecutive coupling/cyclocondensation sequence. Furthermore, one example of an efficient four-component Sonogashira coupling/cyclocondensation/Suzuki coupling, a sequentially Pd-catalyzed process, giving rise to a biphenyl-substituted pyrazole could be demonstrated. Expectedly, most pyrazoles are blue to green light emitting fluorophores that were investigated by UV/Vis and emission spectroscopy as well as by computational methods. The rapid, diversity-oriented synthetic approach to fine-tunable fluorophores can be of considerable interest for the development of tailor-made emitters in OLED applications and fluorescence labelling of biomolecules, surfaces or mesoporous materials. 3,5-Di-substituted pyrazoles are highly intriguing building blocks

for crystal engineering as demonstrated by the well-balanced interplay of hydrogen bonding and π -stacking giving rise to supramolecular self-organization in crystal lattices. Studies addressing this methodology to enhance molecular diversity in biologically active, electronic and photonic targets are currently underway.

Experimental Section

General Considerations: All reactions involving water-sensitive compounds were carried out in flame-dried glassware under nitrogen unless stated otherwise. Reagents and catalysts were purchased reagent-grade and used without further purification. Solvents were dried by a solvent purification system. Flash column chromatography: silica gel 60, mesh 230–400. TLC: silica gel plates (60 F₂₅₄). ¹H, ¹³C, DEPT, NOESY, COSY, HMQC, and HMBC NMR spectra were recorded with a 500 MHz NMR spectrometer by using CDCl₃ as solvent unless stated otherwise. The assignments of quaternary C, CH, CH₂ and CH₃ were made on the basis of DEPT spectra. Mass spectra were recorded with a quadrupole spectrometer. The melting points are uncorrected. Elemental analyses were carried out in the microanalytical laboratory of the Pharmazeutisches Institut of the Heinrich-Heine-Universität Düsseldorf. Dielectric heating was performed in a single-mode microwave cavity producing continuous irradiation at 2450 MHz. For X-ray structure data of the pyrazoles **4c**, **4e** and **4i**, see Table 6.

General Procedure for the Synthesis of Pyrazoles 4 (GP): In a 10 mL microwave tube PdCl₂(PPh₃)₂ (15 mg, 0.02 mmol) and CuI (8 mg,

Table 6. Crystal data and structure refinement for **4c**, **4e** and **4i**.

Structure	4c	4e	4i
Empirical formula	C ₁₆ H ₁₃ ClN ₂	C ₁₆ H ₁₁ F ₃ N ₂	C ₁₆ H ₁₃ ClN ₂
Formula mass	268.73	288.27	268.73
Temperature [K]	200(2)	200(2)	200(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	4	4	4
<i>a</i> [Å]	15.111(2)	14.6850(2)	12.5736(13)
<i>a</i> [°]	90	90	90
<i>b</i> [Å]	4.8699(8)	5.8066(1)	7.2414(8)
<i>β</i> [°]	93.643(4)	98.766(1)	101.299(2)
<i>c</i> [Å]	17.599(3)	15.2535(2)	14.9816(16)
<i>γ</i> [°]	90	90	101.299(2)
Volume [Å ³]	1292.5(4)	1285.47(3)	1337.6(2)
Density (calcd.) [g/cm ³]	1.381	1.490	1.334
Absorption coefficient μ [mm ⁻¹]	0.281	0.120	0.272
Crystal shape	needle	polyhedron	polyhedron
Crystal size [mm]	1.87 × 0.08 × 0.06	0.58 × 0.22 × 0.20	0.39 × 0.23 × 0.16
Crystal colour	colorless	colorless	colorless
θ range for data collection [°]	1.72–28.31	1.79–27.49	1.94–28.31
Index ranges	−19 ≤ <i>h</i> ≤ 20, −6 ≤ <i>k</i> ≤ 6, −23 ≤ <i>l</i> ≤ 23	19 ≤ <i>h</i> ≤ 18, −7 ≤ <i>k</i> ≤ 7, −19 ≤ <i>l</i> ≤ 19	−16 ≤ <i>h</i> ≤ 16, −9 ≤ <i>k</i> ≤ 9, −19 ≤ <i>l</i> ≤ 19
Reflections collected	12800	12675	13547
Independent reflections	3213 [<i>R</i> (int) = 0.0354]	2946 [<i>R</i> (int) = 0.0549]	3326 [<i>R</i> (int) = 0.0297]
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	2821	2337	2976
Absorption correction	semi-empirical from equivalents		
Max./min. transmission	0.98/0.62	0.98/0.93	0.96/0.90
Refinement method	full-matrix least squares on <i>F</i> ²		
Data/restraints/parameters	3213/21/191	2946/0/198	3326/0/173
Goodness-of-fit on <i>F</i> ²	1.25	1.04	1.08
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.064, <i>wR</i> ₂ = 0.128	<i>R</i> ₁ = 0.045, <i>wR</i> ₂ = 0.109	<i>R</i> ₁ = 0.042, <i>wR</i> ₂ = 0.109
Largest difference peak/hole [e Å ⁻³]	0.27/−0.26	0.24/−0.27	0.29/−0.32

Table 7. Experimental details for the synthesis of pyrazoles 4.

Entry	Acyl chloride 1 [mg] ([mmol])	Alkyne 2 [mg] ([mmol])	Hydrazine 3 [mg] ([mmol])	Pyrazole 4 [mg] (yield [%])
1	147 (1.00) of 1a	99 (1.00) of 2a	56 (1.10) of 3a ^[a]	141 (94) of 4a
2	155 (1.00) of 1b	103 (1.00) of 2b	56 (1.10) of 3a ^[a]	191 (82) of 4b
3	155 (1.00) of 1b	137 (1.00) of 2c	56 (1.10) of 3a ^[a]	143 (53) of 4c
4	197 (1.00) of 1c	103 (1.00) of 2b	56 (1.10) of 3a ^[a]	207 (75) of 4d
5	209 (1.00) of 1d	103 (1.00) of 2b	56 (1.10) of 3a ^[a]	219 (76) of 4e
6	176 (1.00) of 1e	83 (1.00) of 2d	56 (1.10) of 3a ^[a]	194 (83) of 4f
7	147 (1.00) of 1a	99 (1.00) of 2a	51 (1.10) of 3b	127 (77) of 4g
8	147 (1.00) of 1a	148 (1.00) of 2e	51 (1.10) of 3b	215 (75) of 4h
9	147 (1.00) of 1a	192 (1.00) of 2f	51 (1.10) of 3b	180 (60) of 4i
10	147 (1.00) of 1a	308 (1.00) of 2g	51 (1.10) of 3b	386 (87) of 4j
11	1710 (10.0) of 1f	1030 (10.0) of 2b	510 (11.0) of 3b	1752 (93) of 4k
12	176 (1.00) of 1e	103 (1.00) of 2b	51 (1.10) of 3b	255 (95) of 4l
13	1760 (10.0) of 1e	690 (10.0) of 2h	510 (11.0) of 3b	2246 (95) of 4m
14	166 (1.00) of 1g	133 (1.00) of 2i	51 (1.10) of 3b	178 (62) of 4n
15	171 (1.00) of 1f	128 (1.00) of 2j	51 (1.10) of 3b	167 (58) of 4o
16	210 (1.00) of 1h	128 (1.00) of 2j	51 (1.10) of 3b	194 (59) of 4p
17	147 (1.00) of 1a	161 (1.00) of 2k	206 (1.10) of 3c	264 (60) of 4q
18	147 (1.00) of 1a	172 (1.00) of 2l	157 (1.10) of 3d	213 (77) of 4r
19	176 (1.00) of 1e	103 (1.00) of 2b	119 (1.10) of 3e	271 (81) of 4s
20	176 (1.00) of 1e	83 (1.00) of 2d	119 (1.10) of 3e	191 (67) of 4t
21	176 (1.00) of 1e	83 (1.00) of 2d	206 (1.10) of 3c	266 (70) of 4u

[a] As hydrazine monohydrate.

0.04 mmol) were dissolved in degassed THF (4 mL). Then, to this orange solution acyl chloride **1** (1.00 mmol), alkyne **2** (1.00 mmol), and triethylamine (1.05 mmol) were added. The reaction mixture was stirred at room temp for 1 h. Finally, hydrazine **3** (1.10 mmol) followed by methanol (0.5 mL) and glacial acetic acid (0.5 mL) were added to this suspension, and the reaction mixture was heated at 150 °C in the microwave cavity for 10 min. After cooling to room temp., the solvent was removed under reduced pressure, and the crude products were purified by silica gel flash column chromatography (hexane/ethyl acetate) to afford the analytically pure pyrazoles **4** (for experimental details, see Table 7).

3-(Thiophen-2-yl)-1H-pyrazole (4a): According to the GP, **4a** was obtained as a yellow oil.^[34] ¹H NMR (500 MHz, CDCl₃): δ = 6.44 (s, 1 H), 6.94–6.97 (m, 1 H), 7.15 (d, ³*J* = 5.0 Hz, 1 H), 7.24 (d, ³*J* = 3.4 Hz, 1 H), 7.52 (s, 1 H), 10.85 (br. s, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 102.6 (CH), 124.1 (CH), 124.5 (CH), 127.5 (CH), 131.4 (C_{quat}), 135.8 (CH), 145.6 (C_{quat}) ppm. EI MS (70 eV): *m/z* (%) = 150 (100) [M⁺], 123 (13), 122 (14), 121 (47), 96 (17), 78 (13), 69 (10), 45 (12), 39 (13). IR (KBr): $\tilde{\nu}$ = 2940 (m), 1645 (m), 1559 (w), 1505 (s), 1481 (m), 1418 (s), 1389 (s), 1329 (w), 1299 (w), 1276 (w), 1226 (s), 1048 (s), 942 (m), 914 (m), 847 (s), 759 (s), 705 (s), 644 (w), 612 (w) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 273 (7600), 289 (4500 L mol⁻¹ cm⁻¹) nm. Emission (CH₂Cl₂): λ_{max} (Stokes shift) = 330 (6300 cm⁻¹), 363 nm.

5-Phenyl-3-(*p*-tolyl)-1H-pyrazole (4b): According to the GP, **4b** was obtained as colorless crystals; m.p. 167 °C.^[13f] ¹H NMR (500 MHz, [D₆]DMSO): δ = 2.35 (s, 3 H), 7.25 (d, 2 H), 7.35 (t, 1 H), 7.48 (t, 2 H), 7.73 (d, 2 H), 7.85 (d, 2 H) ppm. ¹³C NMR (125 MHz, [D₆]DMSO): δ = 22.4 (CH₃), 99.6 (CH), 125.41 (2 CH), 125.46 (2 CH), 128.07 (CH), 129.14 (2 CH), 129.74 (2 CH), 137.51 (C_{quat}) ppm. EI MS (70 eV): *m/z* (%) = 235 (19), 234 (100) [M⁺], 233 (27), 167 (11), 149 (42). IR (KBr): $\tilde{\nu}$ = 2912 (m), 1656 (m), 1509 (s), 1476 (m), 1459 (s), 1269 (m), 1179 (m), 1076 (m), 974 (s), 819 (s), 757 (s), 684 (s), 511 (m) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 258 (95900 L mol⁻¹ cm⁻¹) nm. Emission (CH₂Cl₂): λ_{max} (Stokes shift) = 331 (8600 cm⁻¹), 360 nm.

5-(4-Chlorophenyl)-3-(*p*-tolyl)-1H-pyrazole (4c): According to the GP, **4c** was obtained as colorless crystals; m.p. 209 °C.^[5] ¹H NMR

(500 MHz, [D₆]acetone): δ = 2.36 (s, 3 H), 7.10 (s, 1 H), 7.28 (d, ³*J* = 8.1 Hz, 2 H), 7.46 (d, ³*J* = 8.6 Hz, 2 H), 7.75 (d, ³*J* = 8.1 Hz, 2 H), 7.97 (d, ³*J* = 8.6 Hz, 2 H) ppm. ¹³C NMR (125 MHz, [D₆]acetone): δ = 22.2 (CH₃), 99.8 (CH), 127.1 (2 CH), 128.7 (2 CH), 130.6 (2 CH), 131.3 (2 CH) ppm. EI MS (70 eV): *m/z* (%) = 270 (31) [³⁷Cl-M]⁺, 269 (21) [³⁵Cl¹³C-M]⁺, 268 (100) [³⁵Cl-M]⁺, 267 (14), 201 (15), 199 (16), 183 (10), 149 (13), 119 (12), 77 (22), 57 (15), 51 (12), 43 (16). IR (KBr): $\tilde{\nu}$ = 2920 (s), 1638 (m), 1507 (s), 1448 (s), 1385 (w), 1272 (s), 1174 (m), 1098 (s), 1059 (m), 1013 (m), 974 (s), 827 (s), 772 (w), 736 (w) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 262 (20400), 283 (8200 L mol⁻¹ cm⁻¹) nm. Emission (CH₂Cl₂): λ_{max} (Stokes shift) = 331 (8000 cm⁻¹) nm.

3-(4-*tert*-Butylphenyl)-5-phenyl-1H-pyrazole (4d): According to the GP, **4d** was obtained as colorless crystals; m.p. 142 °C. ¹H NMR (500 MHz, [D₆]acetone): δ = 1.34 (s, 9 H), 7.08 (s, 1 H), 7.30–7.35 (m, 1 H), 7.40–7.45 (m, 2 H), 7.49 (d, ³*J* = 8.6 Hz, 2 H), 7.82 (d, ³*J* = 8.6 Hz, 2 H), 7.88–7.92 (m, 2 H) ppm. ¹³C NMR (125 MHz, [D₆]acetone): δ = 32.5 (3 CH₃), 36.1 (C_{quat}), 101.0 (CH), 126.9 (2 CH), 127.1 (2 CH), 127.4 (2 CH), 129.5 (CH), 130.5 (2 CH), 152.5 (C_{quat}) ppm. EI MS (70 eV): *m/z* (%) = 277 (11), 276 (55) [M⁺], 262 (19), 261 (100), 161 (13), 149 (12), 117 (26), 72 (10), 71 (13), 57 (20), 43 (11). IR (KBr): $\tilde{\nu}$ = 1588 (w), 1506 (m), 1460 (s), 1363 (s), 1265 (s), 1173 (m), 1118 (m), 1072 (m), 1051 (w), 1026 (w), 967 (s), 909 (w), 834 (s), 797 (s), 764 (s), 739 (s), 689 (s), 650 (m), 552 (m), 515 (m) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 258 (36900), 283 (10700 L mol⁻¹ cm⁻¹) nm. Emission (CH₂Cl₂): λ_{max} (Stokes shift) = 323 (7800 cm⁻¹) nm. C₁₉H₂₀N₂ (276.4): calcd. C 82.57, H 7.29, N 10.14; found C 82.24, H 7.32, N 10.02.

5-Phenyl-3-[4-(trifluoromethyl)phenyl]-1H-pyrazole (4e): According to the GP, **4e** was obtained as colorless crystals; m.p. 226 °C.^[35] ¹H NMR (500 MHz, [D₆]acetone): δ = 2.36 (s, 3 H), 7.26 (s, 1 H), 7.30–7.40 (m, 1 H), 7.45–7.50 (m, 2 H), 7.78 (d, ³*J* = 8.1 Hz, 2 H), 7.87–7.91 (m, 2 H), 8.12 (d, ³*J* = 8.1 Hz, 2 H), 13.65 (br. s, [D₆]DMSO, 1 H) ppm. ¹³C NMR (125 MHz, [D₆]acetone): δ = 102.8 (CH), 127.2 (CH), 127.5 (q, ³*J*_{C-F} = 3.8 Hz, CH), 127.6 (CH), 130.2 (CH), 131.3 (CH) ppm. EI MS (70 eV): *m/z* (%) = 289 (20), 288 (100) [M⁺], 259 (13), 77 (10). IR (KBr): $\tilde{\nu}$ = 1619 (w), 1481 (w), 1325 (s), 1167 (m), 1155 (m), 1107 (m), 1067 (m), 1016 (w),

968 (m), 844 (m), 802 (m), 769 (s), 743 (w), 678 (w), 652 (w), 593 (w), 518 (m) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 259 (5300 $\text{L mol}^{-1} \text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 333 (8600 cm^{-1}), 358 nm.

5-Butyl-3-(4-chlorophenyl)-1H-pyrazole (4f): According to the GP, **4f** was obtained as colorless crystals; m.p. 65 °C. ^1H NMR (300 MHz, CDCl_3): δ = 0.69 (t, 3J = 7.3 Hz, 3 H), 1.10 (m, 2 H), 1.38 (q, 3J = 7.5 Hz, 2 H), 2.34 (t, 3J = 7.5 Hz, 2 H), 6.11 (s, 1 H), 7.11 (d, 3J = 8.5 Hz, 2 H), 7.45 (d, 3J = 8.5 Hz, 2 H), 11.24 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 13.7 (CH_3), 22.3 (CH_2), 25.9 (CH_2), 31.3 (CH_2), 100.9 (CH), 127.3 (2 CH), 128.8 (2 CH), 131.5 (C_{quat}), 133.4 (C_{quat}), 147.7 (C_{quat}), 149.4 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 236 (10) [$^{37}\text{Cl-M}$] $^+$, 234 (32) [$^{35}\text{Cl-M}$] $^+$, 194 (32), 192 (100), 157 (15). IR (KBr): $\tilde{\nu}$ = 2963 (s), 1655 (w), 1561 (w), 1509 (m), 1459 (w), 1262 (s), 1092 (s), 1030 (s), 801 (s), 509 (w) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 257 (38100 $\text{L mol}^{-1} \text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 320 (7700 cm^{-1}) nm. $\text{C}_{13}\text{H}_{15}\text{ClN}_2$ (234.7): calcd. C 66.52, H 6.44, N 11.93; found C 66.34, H 6.48, N 11.75.

1-Methyl-3-(thiophen-2-yl)-1H-pyrazole (4g): According to the GP, **4g** was obtained as a yellow oil.^[36] ^1H NMR (500 MHz, CDCl_3): δ = 3.98 (s, 3 H), 6.39 (d, 3J = 1.3 Hz, 1 H), 7.12 (t, 3J = 4.4 Hz, 1 H), 7.16 (d, 3J = 3.5 Hz, 1 H), 7.40 (d, 3J = 5.1 Hz, 1 H), 7.48 (d, 3J = 1.3 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 33.8 (CH_3), 106.7 (CH), 126.5 (CH), 126.8 (CH), 127.6 (CH), 131.3 (C_{quat}), 136.5 (C_{quat}), 138.4 (CH) ppm. EI MS (70 eV): m/z (%) = 165 (12), 164 (100) [M^+], 163 (21), 42 (15). IR (KBr): $\tilde{\nu}$ = 3104 (m), 2943 (m), 1647 (w), 1469 (m), 1416 (m), 1389 (s), 1275 (s), 1209 (s), 1060 (m), 1020 (m), 941 (s), 920 (w), 848 (s), 778 (s), 702 (s), 646 (s), 512 (w) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 247 (10800), 273 (13500 $\text{L mol}^{-1} \text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 348 (7900 cm^{-1}) nm.

1-Methyl-5-(4-nitrophenyl)-3-(thiophen-2-yl)-1H-pyrazole (4h): According to the GP, **4h** was obtained as yellow solid; m.p. 76 °C. ^1H NMR (500 MHz, CDCl_3): δ = 3.85 (s, 3 H), 6.53 (s, 1 H), 6.97–7.00 (m, 1 H), 7.18 (dd, 3J = 4.9 Hz, 4J = 1.0 Hz, 1 H), 7.26 (dd, 3J = 4.9 Hz, 4J = 1.0 Hz, 1 H), 7.55 (dd, 3J = 8.6 Hz, 2 H), 8.24 (d, 3J = 8.6 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 37.8 (CH_3), 104.1 (CH), 123.7 (CH), 124.0 (2 CH), 124.7 (CH), 127.5 (CH), 129.3 (2 CH), 135.8 (C_{quat}), 136.4 (C_{quat}), 142.7 (C_{quat}), 146.1 (C_{quat}), 147.5 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 182 (21), 167 (17), 111 (100), 39 (16). IR (KBr): $\tilde{\nu}$ = 2951 (m), 1651 (w), 1600 (w), 1520 (m), 1466 (s), 1341 (s), 1282 (m), 1126 (m), 1073 (w), 1050 (w), 854 (m), 741 (m), 714 (m) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 286 (58800), 297 (20400), 334 (9200 $\text{L mol}^{-1} \text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 357 (7000 cm^{-1}), 518 nm. $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$ (285.3): calcd. C 58.93, H 3.89, N 14.73; found C 58.84, H 3.99, N 14.53.

5-(4-Bromophenyl)-1-methyl-3-(thiophen-2-yl)-1H-pyrazole (4i): According to the GP, **4i** was obtained as yellow solid; m.p. 65 °C. ^1H NMR (500 MHz, CDCl_3): δ = 3.78 (s, 3 H), 6.41 (s, 1 H), 6.96 (dd, 3J = 4.9, 3J = 3.6 Hz, 1 H), 6.96 (dd, 3J = 4.9, 3J = 0.9 Hz, 1 H), 7.19–7.25 (m, 3 H), 7.50 (d, 3J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 37.4 (CH_3), 103.2 (CH), 123.0 (C_{quat}), 123.5 (CH), 124.4 (CH), 127.4 (CH), 129.1 (C_{quat}), 130.2 (2 CH), 131.9 (2 CH), 136.2 (C_{quat}), 143.8 (C_{quat}), 145.8 (C_{quat}) ppm. EI MS (70 eV): m/z (%) 321 (9) [$^{81}\text{Br}^{13}\text{C-M}$] $^+$, 320 (51) [$^{81}\text{Br-M}$] $^+$, 319 (13) [$^{79}\text{Br}^{13}\text{C-M}$] $^+$, 318 (47) [$^{79}\text{Br-M}$] $^+$, 240 (12), 217 (12), 168 (13), 161 (30), 121 (11), 117 (55), 111 (56), 90 (11), 89 (12), 85 (16), 83 (10), 71 (26), 57 (100), 55 (14), 43 (25), 41 (25), 39 (17). IR (KBr): $\tilde{\nu}$ = 2929 (m), 1655 (w), 1638 (w), 1597 (w), 1560 (w), 1479 (s), 1443 (m), 1390 (s), 1325 (w), 1284 (s), 1221 (w), 1167 (w), 1105 (w),

1067 (m), 1000 (s), 918 (w), 834 (s), 787 (s), 746 (w), 696 (s), 548 (m) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 260 (53300), 273 (54900 $\text{L mol}^{-1} \text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 362, 379 (10200 cm^{-1}), 404 nm. $\text{C}_{15}\text{H}_{11}\text{BrN}_2\text{S}$ (319.2): calcd. C 52.68, H 3.47, N 8.78; found C 52.70, H 3.54, N 8.68.

10-n-Hexyl-3-[1-methyl-3-(thiophen-2-yl)-1H-pyrazol-5-yl]-10H-pheno-thiazine (4j): According to the GP, **4j** was obtained as a yellow resin. ^1H NMR (500 MHz, $[\text{D}_6]\text{acetone}$): δ = 0.87 (t, 3J = 6.8 Hz, 3 H), 1.29–1.35 (m, 4 H), 1.45–1.53 (m, 2 H), 1.84 (q, 3J = 7.3 Hz, 2 H), 3.88 (s, 3 H), 4.00 (t, 3J = 7.8 Hz, 2 H), 6.63 (s, 1 H), 6.98 (dt, 3J = 7.5, 4J = 1.0 Hz, 1 H), 7.06–7.09 (m, 2 H), 7.14–7.25 (m, 3 H), 7.32 (d, 3J = 2.0 Hz, 1 H), 7.36–7.40 (m, 3 H) ppm. ^{13}C NMR (125 MHz, $[\text{D}_6]\text{acetone}$): δ = 14.4 (CH_3), 23.4 (CH_2), 27.3 (CH_2), 27.6 (CH_2), 32.3 (CH_2), 38.1 (CH_3), 48.0 (CH_2), 103.3 (CH), 116.6 (CH), 117.0 (CH), 123.8 (CH), 124.2 (CH), 125.0 (C_{quat}), 125.1 (CH), 125.6 (C_{quat}), 126.0 (C_{quat}), 128.0 (CH), 128.3 (CH), 128.8 (CH), 130.2 (CH), 132.8 (CH), 138.2 (C_{quat}), 144.7 (C_{quat}), 145.9 (C_{quat}), 146.3 (C_{quat}), 146.7 (C_{quat}) ppm. MALDI-TOF MS (matrix: dithranol): m/z = 445 [M^+]. IR (KBr): $\tilde{\nu}$ = 2921 (s), 2851 (s), 1605 (m), 1579 (m), 1460 (s), 1458 (s), 1398 (m), 1376 (m), 1331 (m), 1284 (s), 1244 (s), 1133 (m), 1072 (w), 1039 (w), 920 (s), 887 (m), 847 (m), 822 (m), 785 (s), 748 (s), 694 (s) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 269 (97200), 320 (18600 $\text{L mol}^{-1} \text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 356, 452 (9100 cm^{-1}), 504 nm. $\text{C}_{26}\text{H}_{27}\text{N}_3\text{S}_2$ (445.6): calcd. C 70.07, H 6.11, N 9.43; found C 69.74, H 6.17, N 9.23.

3-(4-Methoxyphenyl)-1-methyl-5-phenyl-1H-pyrazole (4k): According to the GP, **4k** was obtained as colorless crystals; m.p. 73 °C.^[7] ^1H NMR (500 MHz, CDCl_3): δ = 3.74 (s, 3 H), 3.81 (s, 3 H), 6.44 (s, 1 H), 6.85 (d, 3J = 8.9 Hz, 2 H), 7.30–7.37 (m, 5 H), 7.67 (d, 3J = 8.9 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 37.4 (CH_3), 55.2 (CH_3), 102.7 (CH), 114.0 (2 CH), 126.2 (C_{quat}), 126.7 (2 CH), 128.4 (CH), 128.6 (2 CH), 128.7 (2 CH), 130.0 (C_{quat}), 144.0 (C_{quat}), 150.3 (C_{quat}), 159.2 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 265 (18), 264 (100) [M^+], 249 (46), 221 (19), 152 (20), 116 (30), 115 (32), 89 (10), 77 (15), 73 (13), 43 (13). IR (KBr): $\tilde{\nu}$ = 3050 (s), 3017 (s), 2937 (s), 2839 (s), 1682 (w), 1646 (w), 1608 (s), 1578 (s), 1522 (s), 1486 (s), 1358 (s), 1291 (s), 1245 (m), 1176 (s), 1111 (s), 1025 (s), 958 (s), 919 (s), 829 (s), 792 (s), 765 (s), 967 (s), 670 (s), 602 (s), 566 (s), 525 (s) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 260 (52400 $\text{L mol}^{-1} \text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 347, 369 (11400 cm^{-1}) nm.

3-(4-Chlorophenyl)-1-methyl-5-phenyl-1H-pyrazole (4l): According to the GP, **4l** was obtained as colorless crystals; m.p. 95 °C.^[19] ^1H NMR (500 MHz, CDCl_3): δ = 3.93 (s, 3 H), 6.58 (s, 1 H), 7.38 (d, 3J = 8.5 Hz, 2 H), 7.43–7.51 (m, 5 H), 7.77 (d, 3J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 37.6 (CH_3), 103.1 (CH), 126.7 (2 CH), 128.6 (CH), 128.68 (2 CH), 128.71 (2 CH), 128.75 (2 CH), 130.4 (C_{quat}), 131.9 (C_{quat}), 133.2 (C_{quat}), 145.2 (C_{quat}), 149.3 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 271 (7) [$^{37}\text{Cl}^{13}\text{C-M}$] $^+$, 270 (35) [$^{37}\text{Cl-M}$] $^+$, 269 (23) [$^{35}\text{Cl}^{13}\text{C-M}$] $^+$, 268 (100) [$^{35}\text{Cl-M}$] $^+$, 267 (13), 234 (35), 233 (19), 219 (21), 218 (11), 118 (11), 117 (12), 89 (11), 77 (13), 71 (14), 57 (16), 55 (10), 43 (13). IR (KBr): $\tilde{\nu}$ = 2948 (s), 1605 (w), 1511 (w), 1484 (s), 1436 (s), 1363 (w), 1283 (m), 1235 (m), 1192 (m), 1087 (s), 1037 (w), 1011 (s), 958 (s), 836 (s), 797 (s), 770 (s), 754 (s), 701 (s), 673 (m), 566 (s), 511 (s) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 260 (87500), 280 (35200 $\text{L mol}^{-1} \text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 331 (8400 cm^{-1}) nm.

3-(4-Chlorophenyl)-1-methyl-5-propyl-1H-pyrazole (4m): According to the GP, **4m** was obtained as colorless crystals; m.p. 54 °C. ^1H NMR (500 MHz, CDCl_3): δ = 1.02 (t, 3J = 7.3 Hz, 3 H), 1.70 (s, 3J = 7.5 Hz, 2 H), 2.57 (t, 3J = 7.6 Hz, 2 H), 3.81 (s, 3 H), 6.29 (s,

1 H), 7.33 (d, $^3J = 8.4$ Hz, 2 H), 7.69 (d, $^3J = 8.4$ Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 13.8$ (CH_3), 21.7 (CH_2), 27.6 (CH_2), 36.1 (CH_3), 101.5 (CH), 126.6 (2 CH), 128.6 (2 CH), 132.2 (C_{quat}), 132.9 (C_{quat}), 144.6 (C_{quat}), 148.8 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 237 (3) [$^{37}\text{Cl}^{13}\text{C-M}^+$], 236 (27) [$^{37}\text{Cl-M}^+$], 235 (10) [$^{35}\text{Cl}^{13}\text{C-M}^+$], 234 (70) [$^{35}\text{Cl-M}^+$], 208 (28), 207 (41), 206 (84), 205 (100), 218 (11), 127 (16). IR (KBr): $\tilde{\nu} = 2958$ (m), 1662 (m), 1599 (s), 1521 (s), 1461 (m), 1346 (s), 1109 (m), 1048 (m), 1011 (m), 855 (s), 765 (s), 713 (m), 696 (w) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 262 (106400 $\text{L mol}^{-1}\text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 323 (7200 cm^{-1}) nm. $\text{C}_{13}\text{H}_{15}\text{ClN}_2$ (234.7): calcd. C 66.52, H 6.44, N 11.93; found C 66.37, H 4.47, N 11.79.

4-[5-(4-Methoxyphenyl)-1-methyl-1H-pyrazol-3-yl]benzonitrile (4n): According to the GP, **4n** was obtained as light yellow solid; m.p. 143 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 3.87$ (s, 3 H), 3.92 (s, 3 H), 6.60 (s, 1 H), 7.01 (d, $^3J = 8.2$ Hz, 2 H), 7.38 (d, $^3J = 8.2$ Hz, 2 H), 7.68 (d, $^3J = 8.0$ Hz, 2 H), 7.92 (d, $^3J = 8.0$ Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 37.7$ (CH_3), 55.4 (CH_3), 103.5 (CH), 110.7 (C_{quat}), 114.2 (2 CH), 119.1 (C_{quat}), 122.4 (C_{quat}), 125.7 (2 CH), 130.0 (2 CH), 132.5 (2 CH), 137.9 (C_{quat}), 145.4 (C_{quat}), 148.3 (C_{quat}), 160.0 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 290 (21), 289 (100) [M^+], 274 (29), 45 (10). IR (KBr): $\tilde{\nu} = 2958$ (w), 2837 (w), 2224 (s), 1611 (m), 1560 (w), 1494 (s), 1447 (w), 1424 (w), 1363 (w), 1296 (m), 1278 (w), 1259 (s), 1176 (s), 1115 (w), 1039 (m), 1019 (w), 1001 (w), 958 (w), 841 (s), 826 (m), 788 (m), 611 (m), 552 (m), 513 (w) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 280 (49100 $\text{L mol}^{-1}\text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 392 (10200 cm^{-1}) nm.

4-[3-(4-Methoxyphenyl)-1-methyl-1H-pyrazol-5-yl]benzonitrile (4o): According to the GP, **4o** was obtained as light yellow solid; m.p. 120 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 3.88$ (s, 3 H), 3.92 (s, 3 H), 6.60 (s, 1 H), 7.01 (d, $^3J = 8.2$ Hz, 2 H), 7.38 (d, $^3J = 8.2$ Hz, 2 H), 7.68 (d, $^3J = 8.0$ Hz, 2 H), 7.92 (d, $^3J = 8.0$ Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 37.7$ (CH_3), 55.4 (CH_3), 103.5 (CH), 110.7 (C_{quat}), 114.2 (2 CH), 119.1 (C_{quat}), 122.4 (C_{quat}), 125.8 (2 CH), 130.0 (2 CH), 132.5 (2 CH), 137.9 (C_{quat}), 145.4 (C_{quat}), 148.4 (C_{quat}), 160.0 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 290 (22), 289 (100) [M^+], 274 (29). IR (KBr): $\tilde{\nu} = 2925$ (w), 2226 (s), 1647 (m), 1611 (s), 1492 (s), 1467 (w), 1449 (w), 1424 (w), 1360 (w), 1296 (m), 1254 (s), 1176 (s), 1112 (w), 1030 (m), 1001 (w), 958 (w), 847 (s), 828 (s), 769 (s), 712 (w), 676 (w), 613 (m), 568 (m), 548 (m), 510 (w) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 278 (48600 $\text{L mol}^{-1}\text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 392 (10500 cm^{-1}) nm.

4-[3-(2,4-Dichlorophenyl)-1-methyl-1H-pyrazol-5-yl]benzonitrile (4p): According to the GP, **4p** was obtained as colorless crystals; m.p. 164 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 3.98$ (s, 3 H), 6.92 (s, 1 H), 7.31 (dd, $^3J = 8.4$, $^4J = 2.1$ Hz, 1 H), 7.48 (d, $^4J = 2.1$ Hz, 1 H), 7.61 (d, $^3J = 8.5$ Hz, 1 H), 7.79 (d, $^3J = 8.5$ Hz, 2 H), 7.81 (d, $^3J = 8.4$ Hz, 1 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 38.0$ (CH_3), 108.0 (CH), 112.4 (C_{quat}), 118.3 (C_{quat}), 127.3 (CH), 128.4 (C_{quat}), 129.3 (2 CH), 130.1 (CH), 130.4 (C_{quat}), 131.1 (CH), 132.6 (2 CH), 134.1 (C_{quat}), 134.7 (C_{quat}), 142.4 (C_{quat}), 147.4 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 331 (11) [$^{37}\text{Cl},^{37}\text{Cl-M}^+$], 330 (15) [$^{37}\text{Cl},^{35}\text{Cl},^{13}\text{C-M}^+$], 329 (74) [$^{37}\text{Cl},^{35}\text{Cl-M}^+$], 328 (32) [$^{35}\text{Cl},^{35}\text{Cl},^{13}\text{C-M}^+$], 327 (100) [$^{35}\text{Cl},^{35}\text{Cl-M}^+$], 326 (13), 143 (19), 128 (13), 102 (15). IR (KBr): $\tilde{\nu} = 3056$ (w), 2360 (w), 2233 (s), 1612 (s), 1555 (w), 1482 (s), 1434 (s), 1376 (w), 1343 (w), 1277 (w), 1249 (w), 1190 (m), 1103 (m), 1055 (m), 1034 (m), 1007 (m), 959 (m), 847 (s), 834 (s), 797 (s), 719 (w), 690 (w), 572 (w), 555 (m), 516 (w) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 269 (24600 $\text{L mol}^{-1}\text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 383 (11100 cm^{-1}) nm.

Methyl 4-[1-(4-Bromophenyl)-5-(thiophen-2-yl)-1H-pyrazol-3-yl]benzoate (4q): According to the GP, **4q** was obtained as light yellow crystals; m.p. 123 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 3.82$ (s, 3 H), 6.78 (dd, $^3J = 3.6$, $^3J = 1.1$ Hz, 1 H), 6.80 (s, 1 H), 6.88 (dd, $^3J = 5.1$, $^3J = 3.6$ Hz, 1 H), 7.21–7.24 (sh, 3 H), 7.44 (d, $^3J = 8.7$ Hz, 2 H), 7.85 (d, $^3J = 8.5$ Hz, 2 H), 7.98 (d, $^3J = 8.5$ Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 52.0$ (CH_3), 105.9 (CH), 122.1 (C_{quat}), 125.5 (2 CH), 127.0 (CH), 127.3 (2 CH), 127.5 (CH), 127.7 (CH), 129.5 (C_{quat}), 130.0 (2 CH), 130.4 (C_{quat}), 132.1 (2 CH), 136.8 (C_{quat}), 138.3 (C_{quat}), 138.5 (C_{quat}), 151.0 (C_{quat}), 166.8 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 441 (29), 440 (100) [$^{81}\text{Br-M}^+$], 439 (35), 438 (92) [$^{79}\text{Br-M}^+$], 437 (11), 409 (13), 407 (12), 318 (21), 294 (46), 287 (17), 264 (10), 263 (40), 164 (11), 150 (11), 111 (66), 43 (33), 39 (11). IR (KBr): $\tilde{\nu} = 3108$ (w), 2956 (w), 1714 (s), 1612 (m), 1587 (w), 1492 (s), 1438 (m), 1408 (w), 1354 (w), 1310 (m), 1282 (s), 1197 (w), 1176 (m), 1107 (m), 1070 (m), 1012 (m), 957 (m), 926 (w), 861 (w), 849 (w), 829 (s), 773 (s), 706 (s), 595 (w), 535 (w), 519 (w) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 287 (44200), 348 (1300 $\text{L mol}^{-1}\text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 383 (8700 cm^{-1}) nm. $\text{C}_{21}\text{H}_{15}\text{BrN}_2\text{O}_2\text{S}$ (439.3): calcd. C 57.41, H 3.44, N 6.38; found C 57.39, H 3.49, N 6.32.

1-(4-Chlorophenyl)-3-[4-(pyrrolidin-1-yl)phenyl]-5-(thiophen-2-yl)-1H-pyrazole (4r): According to the GP, **4r** was obtained as a yellow resin. ^1H NMR (500 MHz, CDCl_3): $\delta = 2.02$ (d, $^3J = 6.6$ Hz, 4 H), 3.29 (t, $^3J = 6.6$ Hz, 4 H), 6.49 (d, $^3J = 8.8$ Hz, 2 H), 6.61 (s, 1 H), 7.07–7.11 (sh, 3 H), 7.26–7.41 (sh, 8 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 22.4$ (2 CH_2), 47.5 (2 CH_2), 104.2 (CH), 111.3 (2 CH), 116.3 (C_{quat}), 124.0 (CH), 124.7 (CH), 126.4 (2 CH), 127.4 (CH), 128.9 (2 CH), 129.6 (2 CH), 132.6 (C_{quat}), 136.4 (C_{quat}), 138.9 (C_{quat}), 145.3 (C_{quat}), 147.4 (C_{quat}), 147.7 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 408 (10), 407 (40) [$^{37}\text{Cl-M}^+$], 406 (35), 405 (100) [$^{35}\text{Cl-M}^+$], 404 (26), 167 (10), 149 (15), 57 (16), 43 (17). IR (KBr): $\tilde{\nu} = 2925$ (m), 2852 (s), 1612 (s), 1543 (w), 1496 (s), 1440 (w), 1375 (s), 1228 (w), 1184 (m), 1090 (m), 1013 (w), 971 (w), 917 (w), 832 (s), 791 (m), 702 (m) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 295 (98500), 385 (19100 $\text{L mol}^{-1}\text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 460 (4200 cm^{-1}) nm. $\text{C}_{23}\text{H}_{20}\text{ClN}_2\text{S}$ (405.9): calcd. C 68.05, H 4.97, N 10.35; found C 67.81, H 5.04, N 10.17.

5-(4-Chlorophenyl)-1,3-diphenyl-1H-pyrazole (4s): According to the GP, **4s** was obtained as colorless crystals; m.p. 69 °C. $^{[19]}$ ^1H NMR (500 MHz, CDCl_3): $\delta = 6.80$ (s, 1 H), 7.18 (dd, $^3J = 8.5$ Hz, 2 H), 7.22–7.44 (m, 10 H), 7.91 (d, $^3J = 8.5$ Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 105.2$ (CH), 125.2 (2 CH), 125.7 (2 CH), 127.6 (CH), 128.4 (CH), 128.6 (2 CH), 128.7 (2 CH), 128.9 (C_{quat}), 129.0 (2 CH), 129.9 (2 CH), 132.8 (C_{quat}), 134.3 (C_{quat}), 139.8 (C_{quat}), 143.1 (C_{quat}), 152.0 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 332 (37) [$^{37}\text{Cl-M}^+$], 331 (32) [$^{35}\text{Cl}^{13}\text{C-M}^+$], 330 (100) [$^{35}\text{Cl-M}^+$], 329 (41), 165 (13), 139 (24), 111 (11), 105 (15), 77 (39), 75 (11), 51 (13). IR (KBr): $\tilde{\nu} = 2926$ (w), 1597 (m), 1499 (s), 1458 (s), 1360 (m), 1275 (m), 1212 (w), 1176 (w), 1092 (s), 1014 (m), 971 (m), 912 (w), 834 (m), 801 (m), 765 (s), 693 (s), 597 (m), 536 (w) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 259 (50700), 293 (17400 $\text{L mol}^{-1}\text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 382 (12300 cm^{-1}) nm.

3-Butyl-5-(4-chlorophenyl)-1-phenyl-1H-pyrazole (4t): According to the GP, **4t** was obtained as a yellow oil. ^1H NMR (300 MHz, CDCl_3): $\delta = 0.98$ (t, $^3J = 7.3$ Hz, 3 H), 1.47 (m, 2 H), 1.74 (q, $^3J = 7.6$ Hz, 2 H), 2.74 (t, $^3J = 7.6$ Hz, 2 H), 6.33 (s, 1 H), 7.15 (d, $^3J = 8.6$ Hz, 2 H), 7.26 (d, $^3J = 8.6$ Hz, 2 H), 7.26–7.37 (m, 5 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 13.9$ (CH_3), 22.6 (CH_2), 28.0 (CH_2), 31.8 (CH_2), 106.8 (CH), 125.2 (CH), 127.2 (CH), 128.6 (CH), 128.9 (CH), 129.4 (C_{quat}), 129.8 (CH), 134.0 (C_{quat}), 140.0 (C_{quat}), 142.2 (C_{quat}), 154.4 (C_{quat}) ppm. EI MS (70 eV): m/z (%) =

312 (3) [$^{37}\text{Cl-M}$] $^+$, 310 (10) [$^{35}\text{Cl-M}$] $^+$, 281 (14), 270 (38), 268 (100). IR (KBr): $\tilde{\nu}$ = 2957 (m), 2941 (m), 2871 (m), 1599 (s), 1545 (w), 1504 (s), 1438 (m), 1400 (w), 1374 (m), 1192 (w), 1141 (w), 1092 (s), 1015 (s), 969 (s), 910 (w), 834 (s), 797 (m), 760 (s), 694 (s), 582 (m) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 263 (10500 $\text{L mol}^{-1} \text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 339 (8500 cm^{-1}) nm. $\text{C}_{19}\text{H}_{19}\text{ClN}_2$ (310.8): calcd. C 73.42, H 6.16, N 9.01; found C 73.11, H 6.21, N 8.86.

1-(4-Bromophenyl)-3-butyl-5-(4-chlorophenyl)-1H-pyrazole (4u): According to the GP, **4u** was obtained as colorless crystals; m.p. 83 °C. ^1H NMR (500 MHz, CDCl_3): δ = 0.90 (t, 3J = 7.5 Hz, 3 H), 1.36 (sext, 3J = 7.5 Hz, 2 H), 1.62 (q, 3J = 7.6 Hz, 2 H), 2.65 (t, 3J = 7.7 Hz, 2 H), 6.51 (s, 1 H), 7.34–7.38 (m, 4 H), 7.61 (d, 3J = 8.6 Hz, 2 H), 7.78 (d, 3J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 13.7 (CH₃), 22.3 (CH₂), 26.0 (CH₂), 30.8 (CH₂), 103.1 (CH), 121.6 (C_{quat}), 126.8 (2 CH), 126.9 (2 CH), 128.7 (2 CH), 131.6 (C_{quat}), 132.2 (2 CH), 133.5 (C_{quat}), 138.8 (C_{quat}), 145.6 (C_{quat}), 150.6 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 390 (18) [$^{81}\text{Br}^{35}\text{Cl-M}$], $^{79}\text{Br}^{37}\text{Cl-M}$] $^+$, 388 (11) [$^{79}\text{Br}^{35}\text{Cl-M}$] $^+$, 348 (32), 347 (10), 346 (25), 268 (12), 258 (13), 256 (18), 229 (20), 227 (27), 221 (19), 213 (10), 179 (16), 149 (18), 145 (12), 141 (32), 139 (100), 129 (12), 117 (20), 115 (23), 113 (17), 111 (46), 89 (13), 77 (20), 76 (14), 75 (26), 57 (26), 51 (11), 43 (15), 41 (18). IR (KBr): $\tilde{\nu}$ = 2959 (s), 2871 (s), 1655 (w), 1589 (w), 1492 (s), 1449 (m), 1361 (w), 1273 (m), 1091 (s), 1064 (s), 1007 (s), 956 (m), 832 (s), 776 (m), 586 (w), 513 (m) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 275 (34600 $\text{L mol}^{-1} \text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 327, 341 (7000 cm^{-1}), 358, 380 nm. $\text{C}_{19}\text{H}_{18}\text{BrClN}_2$ (389.7): calcd. C 58.56, H 4.66, N 7.19; found C 58.52, H 4.70, N 7.12.

1-Methyl-5-(4'-methylbiphenyl-4-yl)-3-(thiophen-2-yl)-1H-pyrazole (6): According to the GP after the generation of **4i**, boronic acid **5** (164 mg, 1.20 mmol), PPh_3 (53 mg, 0.20 mmol), K_2CO_3 (415 mg, 3.00 mmol), and water (1 mL) were added to the reaction mixture. This mixture was heated at 150 °C in the microwave cavity for 20 min. After cooling to room temp, the solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to afford analytically pure pyrazole **6** as colorless crystals; m.p. 119 °C. ^1H NMR (500 MHz, CDCl_3): δ = 2.33 (s, 3 H), 3.85 (s, 3 H), 6.46 (s, 1 H), 6.98 (dd, 3J = 4.9, 3J = 3.6 Hz, 1 H), 7.16 (dd, 3J = 3.6, 4J = 1.0 Hz, 1 H), 7.20 (d, 3J = 7.6 Hz, 2 H), 7.26 (dd, 3J = 4.9, 4J = 1.0 Hz, 1 H), 7.41 (d, 3J = 8.1 Hz, 2 H), 7.45 (d, 3J = 7.9 Hz, 2 H), 7.59 (d, 3J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 21.1 (CH₃), 37.6 (CH₃), 103.1 (CH), 123.4 (CH), 124.3 (CH), 126.9 (2 CH), 127.1 (2 CH), 127.4 (CH), 128.8 (C_{quat}), 129.0 (2 CH), 129.6 (2 CH), 136.6 (C_{quat}), 137.3 (C_{quat}), 137.6 (C_{quat}), 141.4 (C_{quat}), 144.8 (C_{quat}), 145.8 (C_{quat}) ppm. EI MS (70 eV): m/z (%) = 331 (24), 330 (100) [M] $^+$, 164 (15). IR (KBr): $\tilde{\nu}$ = 1655 (m), 1561 (w), 1514 (w), 1490 (s), 1440 (m), 1399 (m), 1285 (m), 1221 (m), 1181 (m), 1106 (w), 1048 (w), 1005 (m), 919 (m), 852 (s), 844 (m), 815 (s), 797 (s), 741 (w), 696 (s), 644 (w), 573 (m), 534 (m) cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 285 (7600 $\text{L mol}^{-1} \text{cm}^{-1}$) nm. Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 382 (8900 cm^{-1}) nm.

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