Preparation of 2-(1-Phenyl-1*H*-pyrazol-5-yl)benzenesulfonamides from Polylithiated C(α),*N*-Phenylhydrazones and Methyl 2-(Aminosulfonyl)benzoate

Michelle A. Meierhoefer, S. Patrick Dunn, Laela M. Hajiaghamohseni, Matthew J. Walters, Mildred C. Embree, Sally P. Grant, Jennifer R. Downs, Jessica D. Townsend, Clyde R. Metz, and Charles F. Beam*

Department of Chemistry and Biochemistry
College of Charleston, Charleston, SC 29424

William T. Pennington and Donald G. VanDerveer

Department of Chemistry
Clemson University, Clemson, SC 29634

N. Dwight Camper

Department of Entomology Soils and Plant Sciences
Clemson University, Clemson, SC 29634

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Select C(α),*N*-phenylhydrazones were dilithiated in excess lithium diisopropylamide followed by condensation with methyl 2-(aminosulfonyl)benzoate and acid cyclization to afford new pyrazol-benzenesulfonamides, 2-(1-phenyl-1*H*-pyrazol-5-yl)benzenesulfonamides.

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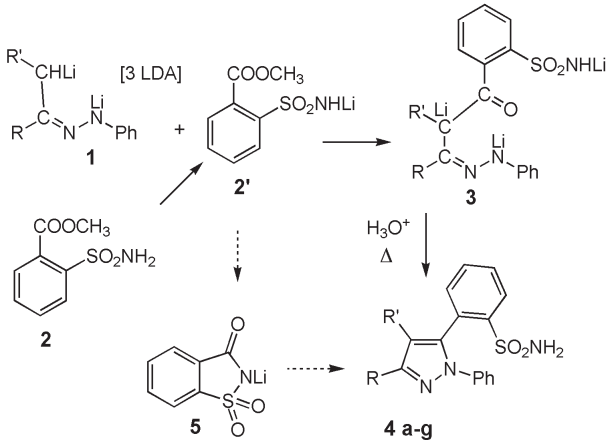
Methyl 2-(aminosulfonyl)benzoate is well documented for the preparation of important compounds, many of them heterocycles with potential for biological activity, and applications in agriculture. Many of the reactions involving this compound take advantage of the synthetic potential of the sulfonamide group. A major use for the carbomethoxy group has been for its reaction with the *ortho*-substituted sulfonamide to afford saccharin-related compounds [1-15].

A large group of heterocyclic compounds with biological and agricultural potential are substituted 1*H*-pyrazoles and related compounds [16]. Several reports deal with the benzenesulfonamide pendant group bonded to a 1*H*-pyrazole, or the substituted sulfonamide directly bonded to other azole rings. When the bonding of the substituted *ortho*-benzenesulfonamide is to the azole directly, or the sulfonamide is bonded to the azole [17], these materials are documented as herbicidal sulfonamides. When similar bonding of the sulfonamide has been in the *para* position of the phenyl group bonded to the azole, or when the sulfonamide is also directly bonded to the azole, the compounds have potential as chymase inhibitors [18].

Pyrazoles, especially 1*H*-pyrazoles, have been prepared by several key procedures, such as condensation-cyclization of β-dicarbonyl compounds with hydrazines, or 1,3-dipolar addition of nitrile imines with alkynes [16]. Our current synthetic emphasis has been on the condensation-cyclization of polylithiated C(α),*N*-hydrazones, such as acetophenone phenylhydrazone, with aromatic esters and related reagents [19-21]. A part of this developing study has been the condensation of these 1,4-dilithiated intermediates with challenging anionic electrophilic reagents, such as lithiated ethyl benzoylacetate [22], lithiated methyl salicylates [23], or lithiated ethyl oxanilate [24].

In two introductory reports, we have described the synthetic potential of (lithiated) methyl 2-(aminosulfonyl)benzoate with polylithiated nucleophiles, such as dilithiated β–diketones, or dilithiated *ortho*-toluic acids, for the



a. R = 3,4,5-$(CH_3O)_3C_6H_2$; R' = H
b. R = 3,4-$(CH_3O)_2C_6H_3$; R' = H
c. R = 4-$CH_3OC_6H_4$; R' = H
d. R = 4-$CH_3C_6H_4$; R' = H
e. R = C_6H_5; R' = H
f. R = $C_6H_5CH_2$; R' = C_6H_5
g. R = $C_{10}H_7$; R' = H

Figure 1. 2-(1-Phenyl-1*H*-pyrazol-5-yl)-benzenesulfonamides, **4a-g**.

preparation of new heterocyclic compounds, including 3-substituted 1,2-benzisothiazole-1,1-dioxides [25] and benzoisothiazolo[1,2-*b*][1,2]isoquinolin-11-one-1,1-dioxides [26].

During the current study, Figure 1, several C(α),*N*-phenylhydrazones were dilithiated to **1** with excess lithium diisopropylamide (LDA), condensed with methyl 2-(aminosulfonyl)benzoate **2**, which was presumed to be at least monolithiated to **2'** [27], or cyclized to the lithiated saccharin salt **5** [28]. The *C*-acylated intermediates **3,** resulting from the condensation of **1** with **2**, were not quenched and isolated, but acid-cyclized directly with dilute hydrochloric acid to afford **4 a-g** in 50-93% yield. X-ray analysis of **4c** as well as spectral data for all compounds prepared were used to establish the fact that the substituted pyrazol-benzenesulfonamides **4a-g** were the products obtained and not the isomeric 1,2-benzisothiazole-1,1-dioxides (BIDs)**,** with phenylhydrazone pendant groups in the 3-position.

From the X-ray data, the molecular structure for **4c** is shown in Figure 2, the ORTEP diagram.

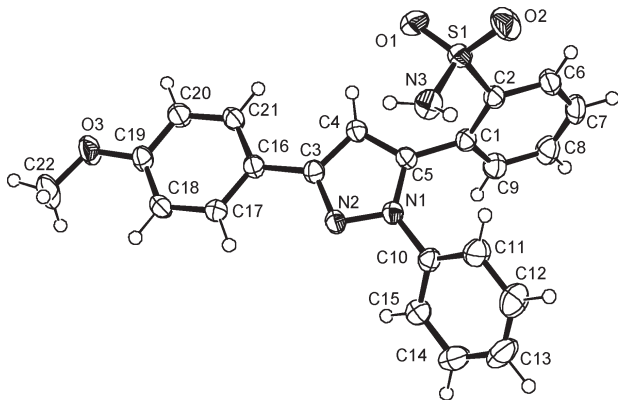


Figure 2. ORTEP diagram (50% ellipsoids for non-Hydrogen atoms) for $C_{22}H_{19}N_3O_3S$, **4c**.

We established that **4a-g** are pyrazoles and not the 3-substituted BIDs using gHMQC (gradient heteronuclear multiple quantum coherence experiment), ^{1}H NMR, ^{13}C NMR, and IR spectra. The ^{1}H absorptions at δ 7.01 for **4a**; δ 7.00 for **4b**, and δ 7.02 for **4d** were easily assigned to the C_4-H (1H) of each pyrazole ring, which was confirmed using the gHMQC data, in which the proton peaks displayed strong correlation to the ^{13}C NMR peaks for C4 at δ 107.3 for **4a,** δ 108.7 for **4b**, and δ 107.0 for **4d**. Further correlations occur for **4a** between the 3- and 5-methoxy protons (6H) and the carbons to which they are bonded (^{1}H, δ 3.93; ^{13}C, δ 56.1), and between the 4-methoxy protons (3H) and its bonding carbon (^{1}H, δ 3.88; ^{13}C, δ 60.8). A similar correlation in **4b** exists for the methoxy protons (3H) and carbon (^{1}H, δ 3.91; ^{13}C, δ 56.1) and for methoxy protons (3H) and carbon (^{1}H, δ 3.96; ^{13}C, δ 56.2); for **4d** for the methyl protons (3H) and carbon (^{1}H, δ 2.39; ^{13}C, δ 21.3).

Table 1

Crystallographic Data for $C_{22}H_{19}N_3O_3S$, **4c**

Crystal Dimensions (mm)	0.41 x 0.31 x 0.31
Space Group	P 2_1/c (#14)
a (Å)	11.469(2)
b (Å)	11.288(2)
c (Å)	16.198(3)
β	110.47(3)°
V (Å^3)	1964.5(7)
fw	405.46
Z	4
d_{calc} (g/cm^3)	1.371
μ (cm^{-1})	1.94
trans. factors	0.92-0.94
R_1 [a]	0.0391
wR_2 [b]	0.1001
Goodness of Fit	1.071

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2

Atomic Positional Parameters for $C_{22}H_{19}N_3O_3S$, **4c**

atom	x	y	z	U(eq)*
S(1)	0.97183(4)	0.23027(4)	0.06343(3)	0.0332(2)
O(1)	1.0284(1)	0.3402(1)	0.05464(9)	0.0431(3)
O(2)	1.0360(1)	0.1228(1)	0.0616(1)	0.0547(4)
O(3)	0.8672(1)	1.0290(1)	0.23493(9)	0.0491(4)
N(1)	0.6551(1)	0.3966(1)	0.08278(9)	0.0295(3)
N(2)	0.6657(1)	0.4992(1)	0.12909(9)	0.0315(3)
N(3)	0.9393(2)	0.2361(1)	0.1523(1)	0.0406(4)
C(1)	0.7276(2)	0.2999(1)	-0.0291(1)	0.0287(4)
C(2)	0.8255(2)	0.2220(1)	-0.0235(1)	0.0286(4)
C(3)	0.7540(2)	0.5610(1)	0.1119(1)	0.0285(3)
C(4)	0.8003(2)	0.4980(1)	0.0549(1)	0.0295(4)
C(5)	0.7349(2)	0.3937(1)	0.0368(1)	0.0276(3)
C(6)	0.8125(2)	0.1371(2)	-0.0885(1)	0.0374(4)
C(7)	0.7033(2)	0.1309(2)	-0.1604(1)	0.0432(5)
C(8)	0.6062(2)	0.2065(2)	-0.1668(1)	0.0431(5)
C(9)	0.6178(2)	0.2890(2)	-0.1011(1)	0.0375(4)
C(10)	0.5670(2)	0.3098(2)	0.0873(1)	0.0303(4)
C(11)	0.5971(2)	0.1905(2)	0.0937(1)	0.0432(5)
C(12)	0.5085(2)	0.1086(2)	0.0958(2)	0.0577(6)
C(13)	0.3918(2)	0.1450(2)	0.0919(2)	0.0558(6)
C(14)	0.3634(2)	0.2638(2)	0.0871(1)	0.0464(5)
C(15)	0.4508(2)	0.3470(2)	0.0848(1)	0.0367(4)
C(16)	0.7850(2)	0.6816(1)	0.1469(1)	0.0292(4)
C(17)	0.7350(2)	0.7285(2)	0.2068(1)	0.0337(4)
C(18)	0.7591(2)	0.8440(2)	0.2366(1)	0.0352(4)
C(19)	0.8351(2)	0.9147(2)	0.2076(1)	0.0332(4)
C(20)	0.8855(2)	0.8703(2)	0.1475(1)	0.0394(4)
C(21)	0.8608(2)	0.7548(2)	0.1183(1)	0.0360(4)
C(22)	0.8281(2)	1.0746(2)	0.3032(2)	0.0568(6)

*U(eq) defined as one third of the trace of the orthogonalized Uij tensor.

Table 3
Selected Bond Distances (Å) and Angles (E) for $C_{22}H_{19}N_3O_3S$, **4c**

S(1)-O(2)	1.425(1)	O(2)-S(1)-O(1)	118.76(9)
S(1)-O(1)	1.430(1)		
S(1)-N(3)	1.611(2)	O(2)-S(1)-N(3)	109.63(9)
S(1)-C(2)	1.777(2)	O(1)-S(1)-N(3)	107.99(8)
O(3)-C(19)	1.373(2)	O(2)-S(1)-C(2)	106.91(8)
O(3)-C(22)	1.427(2)	O(1)-S(1)-C(2)	107.59(8)
N(1)-N(2)	1.362(2)	N(3)-S(1)-C(2)	105.11(8)
N(1)-C(5)	1.368(2)	C(19)-O(3)-C(22)	117.9(2)
N(1)-C(10)	1.428(2)	N(2)-N(1)-C(5)	111.9(1)
N(2)-C(3)	1.337(2)	N(2)-N(1)-C(10)	118.9(1)
C(1)-C(9)	1.391(3)	C(5)-N(1)-C(10)	129.2(1)
C(1)-C(2)	1.404(2)	C(3)-N(2)-N(1)	104.9(1)
C(1)-C(5)	1.484(2)	C(9)-C(1)-C(2)	117.9(2)
C(2)-C(6)	1.393(2)	C(9)-C(1)-C(5)	118.2(2)
C(3)-C(4)	1.407(2)	C(2)-C(1)-C(5)	123.9(2)
C(3)-C(16)	1.470(2)	C(6)-C(2)-S(1)	117.2(1)
C(4)-C(5)	1.371(2)	C(1)-C(2)-S(1)	122.1(1)
C(6)-C(7)	1.382(3)	N(2)-C(3)-C(4)	111.1(1)
C(7)-C(8)	1.378(3)	N(2)-C(3)-C(16)	120.1(1)
C(8)-C(9)	1.386(3)	C(4)-C(3)-C(16)	128.7(2)
C(10)-C(11)	1.385(2)	C(5)-C(4)-C(3)	105.7(1)
C(10)-C(15)	1.384(2)		
C(11)-C(12)	1.383(3)	N(1)-C(5)-C(4)	106.4(1)
C(12)-C(13)	1.380(3)	N(1)-C(5)-C(1)	121.9(1)
C(13)-C(14)	1.375(3)	C(4)-C(5)-C(1)	130.9(2)
C(14)-C(15)	1.383(3)	C(15)-C(10)-N(1)	118.8(2)
C(16)-C(21)	1.391(2)	C(11)-C(10)-N(1)	120.5(2)
C(16)-C(17)	1.393(2)	C(21)-C(16)-C(17)	117.7(2)
C(17)-C(18)	1.384(2)	C(21)-C(16)-C(3)	121.1(2)
C(18)-C(19)	1.380(2)	C(17)-C(16)-C(3)	121.2(2)
C(19)-C(20)	1.387(2)	O(3)-C(19)-C(18)	124.3(2)
C(20)-C(21)	1.382(2)	O(3)-C(19)-C(20)	115.8(2)

Some of the mechanistic details for the condensation-cyclization may be described by the path illustrated in Figure 1. The straightforward Claisen-type path (**1** + **2'** → **3** → **4**) would be the *C*-acylation to **3** involving lithiated sulfonamide ester **2'** condensing with **1**, followed by acid cyclization of the *C*-acylated intermediate **3** to the desired pyrazole **4**. While the formation of saccharin salt **5** from **2'** may be considered to be an intermediate that would condense with **1** (**1** with **5**), we have not observed evidence for this happening. This path would result in additional intermediates (not illustrated) that would undergo protonation, hydrolysis followed by another cyclization to **4**. We observed that formation of lithiated saccharin **5** then saccharin directly from the lithiated ester sulfonamide **2'** under these reaction conditions was difficult. Also, an attempted condensation of the dilithiated phenylhydrazone **1** with lithiated saccharin **5** (from saccharin) followed by acid hydrolysis and cyclization did not give **4**.

The current procedure affords select examples for multigram preparation of **4 a-g**, that can be purified by recrystallization from common solvents. It is another indication of the potential for using methyl 2-(aminosulfonyl)benzoate **2** for Claisen-type condensation and subsequent cyclization in multiple anion-type systems. The unsubstituted sulfonamide group in **4** has potential for transformation into sulfonyl isocyanate, then sulfonyl urea and related compounds, many of which have agricultural potential. In addition, agricultural assays on the compounds reported here are being conducted.

EXPERIMENTAL

Melting points were obtained with a Mel-Temp II melting point apparatus in open capillary tubes and are uncorrected. Fourier Transform infrared spectra were obtained with a Nicolet Impact 410 FT-IR and a Mattson Genesis II FT-IR with Specac Golden Gate Accessory. Proton and C-13 magnetic resonance spectra were obtained with a Varian Associates Mercury Oxford 300 MHz nuclear magnetic resonance spectrometer, and chemical shifts are recorded in δ ppm downfield from an internal tetramethylsilane (TMS) standard.

Because the N-*H* protons are exchangeable with the solvent, their chemical shifts are subject to change. The proposed N-*H* protons for NH_2 (2H) were displayed at δ 4.93 in **4a**, δ 6.37 in **4b**, and δ 4.66 in **4d** but did not show a correlation to any carbons as expected. The IR displayed N-*H* peaks at 3315 cm^{-1}, 3230 cm^{-1} for **4a**; 3322 cm^{-1}, 3232 cm^{-1} **4b**; and 3414 cm^{-1} and 3328 cm^{-1} for **4d**.

Combustion analyses were performed by Quantitative Technologies, Inc., P.O. Box 470, Whitehouse, NJ 08888.

Pyrazol-benzenesulfonamide **4c** was recrystallized from benzene. Single crystal X-ray measurements for crystals of **4c**, $C_{22}H_{19}N_3O_3S$, were collected on a Mercury CCD area detector coupled with a Rigaku AFC8 diffractometer with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. The data were collected at a temperature of 25 °C to a maximum 2 value of 25.10°. Data were collected in 0.50° oscillations in T with 45 s exposures (two identical scans were performed at each position to identify detector anomalies). A sweep of data was done using T oscillations from -90.0 to 90.0° at χ = 45.0° and ϕ = 0.0°; a second sweep was performed using T oscillations from -30.0 to 30.0° at χ = 45.0° and ϕ = 90.0°. The crystal-to-detector distance was 27.1 mm. The detector swing angle was 0.00°. Cell parameters and additional details of the data collection are reported in Table 1.

Of the 16765 reflections collected, 3493 were unique (R_{int} = 0.0448); equivalent reflections were merged. Data were collected, processed, and corrected for Lorentz-polarization and for absorption using CrystalClear (Rigaku) [29]. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Ideal hydrogen atom coordinates were calculated, and the hydrogen atoms were allowed to ride on the respective carbon atoms. The hydrogen atoms on N3 were located from a difference Fourier, and their coordinates were fixed. The temperature factors of all hydrogen atoms were varied isotropically. The final cycle of full-matrix least-squares refinement on F^2 converged with R_1 = 0.0391 (3177 observed reflections ($I > 2.00\sigma(I)$), wR_2 = 0.1001 (all data). The highest difference peak was 0.221 and the deepest hole was -0.333.

Structure solution, refinement, and the calculation of derived results were performed using the SHELXTL [30] package of computer programs. Neutral atom scattering factors were those

of Cromer and Waber [31], and the real and imaginary anomalous dispersion corrections were those of Cromer [32].

Atomic positional parameters are listed in Table 2 and selected bond distances and angles are listed in Table 3. The angles between the least squares planes of the heterocycle ring (with substituents bonded to N2, C3, and C5 of the pyrazole ring) and the *ortho*-benzenesulfonamide ring containing C1 and bonded to C5 of the pyrazole ring is 65.5°; the phenyl ring containing C10 and bonded to N1 of the pyrazole ring is 41.3°; and the *para*-methoxyphenyl ring containing C16 bonded to C3 of the pyrazole ring is 9.6°.

General Procedure for the Preparation of 2-(1-Phenyl-1*H*-pyrazol-5-yl)benzenesulfonamides (**4a-g**).

(Ratio of reagents – phenylhydrazone:LDA:ester - 1:5:1)

To a three-neck round-bottomed flask (*e.g*., 500 ml), equipped with a nitrogen inlet tube, a side-arm addition funnel (*e.g*., 125 ml), and a magnetic stir bar was added 49-50 ml of 1.6 *M n*-butyllithium (0.079 mol) in hexanes (0° under N_2). The flask was cooled in an ice water bath and 8.01 g (0.079 mol) of diisopropylamine (99.5% - Aldrich Chem. Co.), dissolved in 25-30 ml of dry THF (freshly distilled from sodium; benzophenone ketyl) was added from the addition funnel at a fast dropwise rate during a 5 min (0°, N_2) period. The solution was stirred for an additional 15-20 min, and then treated *via* the addition funnel, during 5 min, with phenylhydrazone [33] (0.015 mol) dissolved in 35-45 ml of THF. After 45-60 min, a solution of 3.47 g (0.0158 mol – 5% molar excess) of methyl 2-(aminosulfonyl)benzoate **2** dissolved in 25-35 ml of THF, was added, during 5 min, to the dilithiated intermediate, and the solution was stirred for 2-3 hr (0°, N_2). Finally, 100 ml of 3 *M* hydrochloric acid was added all at once, followed by an additional 100 ml of solvent grade THF, and the two-phase mixture was well-stirred and heated under reflux for approximately 45-60 min. At the end of this period, the mixture was poured into a large flask (*ca.* 1 or 2 liter) containing ice (*ca*., 100 g), followed by the addition of 100 ml of solvent grade ether. The mixture was then neutralized with solid sodium bicarbonate, and the layers separated. The aqueous layer was extracted with ether (2x75 ml), and the organic fractions were combined, not dried, filtered, evaporated, and recrystallized to afford product.

2-(3-(3,4,5-Trimethoxyphenyl)-1-phenyl-1*H*-pyrazol-5-yl))benzenesulfonamide (**4a**).

This compound was obtained as pale yellow crystals, mp. 172-174° (methanol/toluene) in 50 % yield (3.49 g) using the general procedure from the condensation-cyclization of dilithiated 3',4',5'-trimethoxyacetophenone phenylhydrazone and ester sulfonamide **2**; IR 3315, 3230 cm^{-1}; ^1H NMR (deuteriochloroform): δ (ppm) 4.00 (s, 3H), 4.06 (s, 6H), 4.93 (s, 2H), 7.14 (s, 1H), 7.26-7.64 (m, 10H), and 8.28 (d, 1H); ^{13}C NMR (deuteriochloroform): δ (ppm) 56.1, 60.8, 102.7, 107.3, 124.0, 127.0, 127.6, 127.8, 128.4, 128.5, 129.0, 131.8, 132.7, 137.8, 139.0, 139.6, 141.0, 151.2, and 153.0.

Anal. Calcd for $C_{24}H_{23}N_3O_5S$: C, 61.92; H, 4.98; N, 9.03. Found: C, 61.80; H, 4.77; N, 8.92.

2-(3-(3,4-Dimethoxyphenyl)-1-phenyl-1*H*-pyrazol-5-yl))benzenesulfonamide (**4b**).

This compound was obtained as off-white crystals, mp 206-208° (ethanol/benzene) in 71 % yield (4.63 g) using the general procedure from the condensation-cyclization of dilithiated 3',4'-dimethoxyacetophenone phenylhydrazone and ester sulfonamide **2**; IR: 3322, 3232 cm^{-1}; ^1H NMR (deuteriochloroform /DMSO-d_6): δ (ppm) 3.91 (s, 3H), 3.83 (s, 3H), 6.37 (s, 2H), 7.00 (s, 1H), 7.02-7.05, 7.15-7.17, 7.24-7.48, 7.57-7.63, 8.04-8.07 (m, 12H); ^{13}C NMR (deuteriochloroform /DMSO-d_6): δ (ppm) 56.1, 56.2, 108.7, 109.7, 112.6, 118.9, 125.0, 126.4, 127.7, 127.9, 129.3, 129.4, 129.6, 130.0, 132.1, 133.6, 140.3, 141.2, 143.9, 149.5, 149.6, and 151.0.

Anal. Calcd for $C_{23}H_{21}N_3O_4S$: C, 63.43; H, 4.86; N, 9.65. Found: C, 63.17; H, 4.99; N, 9.29.

2-(3-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazol-5-yl))benzenesulfonamide (**4c**).

This compound was obtained as pale yellow crystals, mp 212-214° (methanol/toluene) in 80 % yield (4.86 g) using the general procedure from the condensation-cyclization of dilithiated 4'-methoxyacetophenone phenylhydrazone and ester sulfonamide **2**; IR (paraffin oil): 3394, 3263 cm^{-1}; ^1H NMR (DMSO-d_6): δ (ppm) 3.80 (s, 3H, OCH_3), 7.02-7.05, 7.15-7.64, 7.86-7.89, 8.08-8.10 (m, 16H); ^{13}C NMR (DMSO-d_6): δ (ppm) 55.2, 107.4, 114.1, 124.3, 125.5, 126.8, 127.0, 127.3, 128.7, 128.8, 129.3, 131.5, 133.0, 139.7, 140.5, 143.3, 150.2, and 159.2.

Anal. Calcd for $C_{22}H_{19}N_3O_3S$: C, 65.17; H, 4.72; N, 10.36. Found: C, 64.91; H, 4.66; N, 10.27.

2-(3-(4-Methylphenyl)-1-phenyl-1*H*-pyrazol-5-yl))benzenesulfonamide (**4d**).

This compound was obtained as pale yellow crystals, mp 201-204° (ethanol) in 93 % yield (5.43 g) using the general procedure from the condensation-cyclization of dilithiated 4'-methylacetophenone phenylhydrazone and ester sulfonamide **2**; IR 3414, 3328 cm^{-1}; ^1H NMR (deuteriochloroform): δ (ppm) 2.38 (s, 3H), 4.66 (s broad, 2H), 7.01(s, 1H), 7.13-7.47 (m, 10H), 7.80 (d, 2H), and 8.11 (d apparent, 1H); ^{13}C NMR (deuteriochloroform): δ (ppm) 21.3, 107.2, 123.8, 125.4, 126.9, 127.6 128.5, 128.9, 129.0, 129.2 [2], 131.8, 132.7, 137.7, 139.1, 139.3, 141.0, and 151.4.

Anal. Calcd for $C_{22}H_{19}N_3O_2S$: C, 67.85; H, 4.92; N, 10.79. Found: C, 67.74; H, 4.84; N, 10.77.

2-(1,3-Diphenyl-1*H*-pyrazol-5-yl)benzenesulfonamide (**4e**).

This compound was obtained as off-white crystals, mp 173-174° (ethanol) in 73 % yield (4.11 g) using the general procedure from the condensation-cyclization of dilithiated acetophenone phenylhydrazone and ester sulfonamide **2**; IR (paraffin oil): 3360, 3256 cm^{-1}; ^1H NMR (DMSO-d_6): δ (ppm) 7.14-7.64, 7.95-7.98, 8.09-8.12 (m, 17H); ^{13}C NMR (DMSO-d_6): δ (ppm) 108.5, 125.1, 126.2, 127.9, 128.0, 128.7, 129.2, 129.4, 129.5, 130.1, 132.2, 133.5, 133.6, 140.3, 141.4, 144.0, and 151.0.

Anal. Calcd for $C_{21}H_{17}N_3O_2S$: C, 67.18; H, 4.56; N, 11.19. Found: C, 66.98; H, 4.58; N, 11.09.

2-(1,4-Diphenyl-3-phenylmethyl-1*H*-pyrazol-5-yl)benzenesulfonamide (**4f**).

This compound was obtained as white crystals, mp 220-222° (ethanol/toluene) in 51 % yield (3.56 g) using the general procedure from the condensation-cyclization of dilithiated 1,3-diphenylacetone phenylhydrazone and ester sulfonamide **2**; IR (paraffin oil): 3394, 3174 cm^{-1}; ^1H NMR (DMSO-d_6): δ (ppm) 4.04 (s, 2H), 7.06-7.26, 7.48-7.57, 7.86-7.89 (m, 21H); ^{13}C NMR (DMSO-d_6): δ (ppm) 32.9, 123.2, 124.7, 126.6, 127.1, 127.3, 128.3, 128.6, 128.8 (2), 128.9, 129.11, 129.14, 130.2, 132.0, 133.3, 134.8, 138.2, 140.4, 140.8, 144.6, and 149.1.

Anal. Calcd for $C_{28}H_{23}N_3O_2S$: C, 72.24; H, 4.98; N, 9.03. Found: C, 72.03; H, 4.99; N, 8.89.

2-(3-(2-Naphthyl)-1*H*-pyrazol-5-yl)benzenesulfonamide (**4g**).

This compound was obtained as white crystals, mp 155-158° (benzene/hexane) in 65 % yield (4.25 g) using the general procedure from the condensation-cyclization of dilithiated 2'-acetonaphthone phenylhydrazone and ester sulfonamide **2**; IR (paraffin oil): 3391, 3192 cm^{-1}; ^1H NMR (deuteriochloroform): δ (ppm) 7.19-7.62, 7.80-8.18 (m); ^{13}C NMR (deuteriochloroform): δ (ppm) 108.2, 124.2, 124.6, 124.9, 126.3, 126.6, 127.7, 128.0, 128.3, 128.5, 128.7, 129.2, 129.6, 130.1, 132.4, 133.4, 133.6, 133.78, 139.8, 140.4, 141.7, and 152.1.

Anal. Calcd for $C_{25}H_{19}N_3O_2S \cdot 3/4H_2O$ [34]: C, 68.40; H, 4.71; N, 9.57. Found: C, 68.68; H, 4.91; N, 9.06.

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