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SYNTHESIS, CHARACTERIZATION, AND STRUCTURE OF SOME NEW SUBSTITUTED 5,6-FUSED RING PYRIDAZINES

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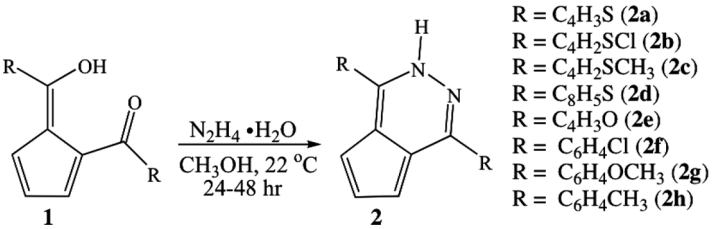
GRAPHICAL ABSTRACT



Abstract *Pyridazines are an important class of heterocyclic compounds as a result of their materials and commercial applications. The synthesis of 5,6-fused ring pyridazines* **2a–h** *from 1,2-diacylcyclopentadienes (fulvenes)* **1a–h** *is described herein. This route was quite general, and features an efficient and convenient two-step synthesis of a series of 5,6-fused ring 1,2-disubstituted pyridazines using enolized 1,2-disubstituted fulvenes in a methanolic solution of hydrazine. Full characterization of newly formed fulvene* **1e** *and pyridazines* **2a–h** *are reported. Single-crystal X-ray analysis confirms the molecular structure of pyridazine* **2f**, *which displayed the expected pyridazine fused to the cyclopentadienyl moiety. Adding to their real world capabilities in electronic devices, compounds* **2a–h** *display reasonably high stability in solution and in air at room temperature.*

Keywords Fulvenes; heterocyclic; NMR; pyridazines; X-ray crystallography

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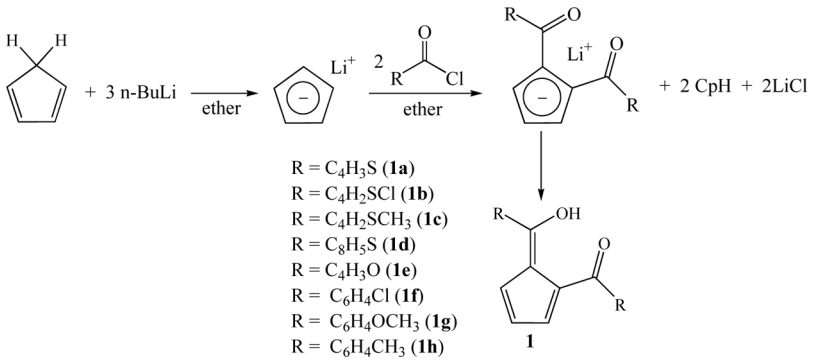
INTRODUCTION

Pyridazines, six-membered aromatic rings with two adjacent nitrogens, are promising candidates for a variety of materials and commercial applications. These novel heterocycles are structurally important components of several biologically active compounds and have been explored as α-helix mimetics.[1] Pyridazines have also been found to be efficient water oxidation catalysts when compared to dinuclear ruthenium complexes and have shown high efficiencies in catalytic water oxidation with turnover numbers of up to 700.[2] Additionally, pyridazines have been incorporated into iptycene frameworks,[3] compounds researched for polymer sensors,[4] gas absorption storage,[5] and host–guest chemistry.[6] Furthermore, they continue to serve as useful intermediates in the synthesis of several other classes of heterocycles.[7] For example, Boger and coworkers reported pyrrole synthesis when treating pyridazines to a solution of activated zinc in acetic acid.[8] Our current interests focus on the potential role of pyridazines in next-generation electronic devices that utilize organics as the semiconducting material. These molecular electronic materials possess several advantages over traditional inorganic semiconducting materials, including lower cost of production, higher processibility, and the ability to function on flexible substrates (so-called plastic electronics).[9–11] These compounds offer new materials suitable for a variety of real-world applications such as organic light-emitting diodes (OLEDs) and organic photovoltaic cells (OPVs).[12] Our recent efforts have been focused on the synthesis of a variety of 5,6-fused ring pyridazines. These fused heterocycles will serve as synthetic models and building blocks for potential organic or organometallic conducting polymers.

RESULTS AND DISCUSSION

The compounds presented herein were constructed from 1,2-diacylcyclopentadienes (fulvenes). Fulvenes 1,2-C_5H_3(COR)(COHR) **1a–h** were successfully synthesized using a modified procedure of Linn and Sharkey (Scheme 1).[13] Three molar equivalents of freshly cracked cyclopentadiene were added to a solution of two molar equivalents of ^{n}BuLi in dry ethyl ether in an ice bath. The suspension was stirred for

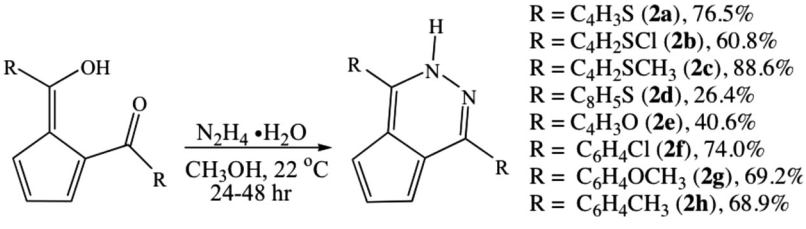


Scheme 1. Synthetic route to fulvenes **1a–h**.

10 min, followed by dropwise addition of the appropriate acid chloride. A distinct color change was observed with addition of each acid chloride. For example, 1,2-$C_5H_3(COC_4H_3O)(COHC_4H_3O)$ (**1e**), prepared using 2-furoyl chloride, gave an immediate bright orange suspension. All reaction mixtures were allowed to warm to room temperature and were stirred for 45 min. The reactions were then hydrolyzed with dilute acetic acid, extracted with ethyl ether, dried over $MgSO_4$, filtered, and reduced to an oil or semisolid. Crude fulvenes **1a–h** were filtered through a silica plug (50:50 dichloromethane/hexane) and the solvent was reduced *in vacuo*. Any semisolids were triturated using cold hexane to afford solid fulvenes **1a–h**. Yields for the fulvenes were modest but reasonable (56–86%).[13–16] The newly reported furoyl fulvene, 1,2-$C_5H_3(COC_4H_3O)(COHC_4H_3O)$ (**1e**), was produced as a bright orange solid (10.5% yield) following elution through a silica plug. Lower than expected yields observed for **1e** were attributed to the majority of the product being retained on the silica plug. We are currently optimizing the isolation and purification methods for fulvene **1e**.

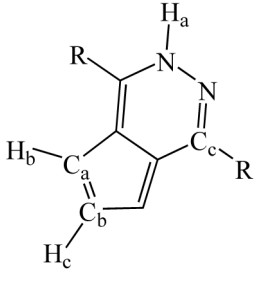
The structure of fulvene **1e** was confirmed by ^{1}H NMR, ^{13}C NMR, and infrared (IR) spectroscopy. The cyclopentadience (Cp) ring protons are observed as a triplet (CHC*H*CH) and doublet (C*H*CHC*H*) with chemical shifts of 6.07 and 8.15 ppm, respectively. The coupling constants for the Cp triplet and doublet are 4.0 Hz. The furoyl protons are observed as a doublet of doublets (6.62 ppm, $^3J_{AB} = 3.5$ Hz, $^3J_{AC} = 1.7$ Hz, CHC*H*CHO), a doublet (7.40 ppm, $^3J_{BC} = 3.5$ Hz, C*H*CHCHO), and a doublet (7.72 ppm, $^3J_{AB} = 1.7$ Hz, CHCHC*H*O). The Cp ring carbons for fulvene **1e**, CH*C*HCH and *C*HCH*C*H, are observed in their typical range and are found at 112.5 and 119.8 ppm, respectively. IR analysis confirmed the presence of the carbonyl functional group, with distinct stretching frequencies at 1530 and 1565 cm^{-1}. These stretches display a shift to lower energies as a result of the fulvene's enolized, delocalized structure when in solution, which matches with the corresponding values for fulvenes **1a–d,f–g**.[14–17] Analysis of **1e** by gas chromatography/mass spectrometry (GC/MS) also confirmed the structure or the furoyl fulvene **1e** ($M^+ = 254$).

The synthesis of the 5,6-fused ring pyridazines **2a–h** was accomplished by treating fulvenes 1,2-$C_5H_3(COR)(COHR)$ **1a–h** to a solution of excess hydrazine hydrate in methanol at room temperature (Scheme 2). Reaction times varied from 24–48 h, followed by a water quench and then ethyl ether extraction. Pyridazines **2a–h** were purified via silica plug and/or hexane trituration. Percentage yields for compounds **2a–h** ranged from 41% to 89%.



Scheme 2. Synthetic route for pyridazines **2a–h**.

Table 1. Selected ^{1}H and ^{13}C NMR data for **2a–h**



R = C_4H_3S (**2a**)
R = C_4H_2SCl (**2b**)
R = $C_4H_2SCH_3$ (**2c**)
R = C_8H_5S (**2d**)
R = C_4H_3O (**2e**)
R = C_6H_4Cl (**2f**)
R = $C_6H_4OCH_3$ (**2g**)
R = $C_6H_4CH_3$ (**2h**)

NMR nuclei	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**
H_a	11.2 (br s)	11.8 (br s)	11.3 (br s)	11.2 (br s)	11.2 (br s)	11.8 (br s)	12.1 (br s)	11.5 (br s)
H_b	7.84 (br s)	7.21 (d, $J = 3.5$ Hz)	7.37 (d, $J = 3.4$ Hz)	7.25 (d, $J = 4.0$ Hz)	7.25 (d, $J = 4.0$ Hz)	7.05 (d, $J = 3.45$ Hz)	7.07 (d, $J = 3.4$ Hz)	7.07 (d, $J = 4.0$ Hz)
H_c	7.21 (t, $J = 4.0$ Hz)	7.53 (t, $J = 3.5$ Hz)	7.61 (t, $J = 3.4$ Hz)	7.53 (t, $J = 4.0$ Hz)	7.53 (t, $J = 4.0$ Hz)	7.53 (t, $J = 3.45$ Hz)	7.54 (t, $J = 3.4$ Hz)	7.49 (t, $J = 4.0$ Hz)
C_a	109.5	109.5	109.7	108.5	109.5	109.3	114.3	108.9
C_b	119.8	119.5	120.2	112.4	120.3	120.3	120.2	120.4
C_c	139.4	141.2	144.1	144.3	136.5	136.5	146.9	141.2

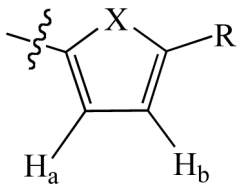
Table 2. Selected IR data for **2a–h**

Bond	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**
C=N	1592	1596	1592	1578	1612	1598	1573	1595
N–H	3171	3164	3059	3063	3120	3192	3057	3092

The structures for pyridazines **2a–h** were confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and are listed in Tables 1 and 2. The Cp ring protons C*H*CHC*H* are observed as a doublet and found in the range 7.05–7.84 ppm, whereas triplets are seen at 7.21–7.61 ppm corresponding to the CHC*H*CH proton. The C*H*CHC*H* and CHC*H*CH coupling constants are observed between $^{3}J = 3.4$–4.0 Hz. Amine protons for **2a–h** are observed highly downfield in the range of 11.2–12.1 ppm because of their delocalized nature in solution. The ^{13}C NMR spectrum for **2a–h** showed the disappearance of the carbonyl group (160.0–169.3 ppm) as observed in fulvenes **1a–h**. Instead, pyridazines **2a–h** show a characteristic C=N carbon signal ranging from 136.5 to 144.3 ppm. The Cp ring carbons, *C*HCH*C*H carbons, are seen in the narrow range of 108.5–114.3 ppm, whereas the CH*C*HCH signals are observed between 119.5 and 120.3 ppm. Pyridazine **2d** CH*C*HCH signal is found higher upfield at 112.4 ppm, presumably reflecting the greater delocalized nature of its C=N bond because of the larger conjugation of the benzo[*b*]thienyl groups. IR spectroscopy confirms the loss of carbonyl stretches and the appearance of C=N stretches seen between 1573 and 1612 cm^{-1} (Table 2). Secondary amine signals for **2a–h** are found between 3059 and 3192 cm^{-1}. GC/MS analysis confirms the structures of **2a–h**, with the expected parent ion peak for all cases except **2g**, which did not display an M^{+} peak (298, M^{+} – $HOCH_3$).

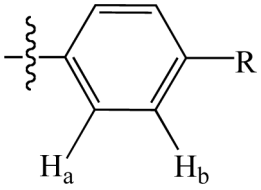
Comparison between the thienyl and furyl substituents in the pyridazines formed shows a relatively high degree of similarity in the chemical environment for each proton (Table 3). For example, the signals for the heterocylic substituents in **2a** and **2e** match very closely. Thienylic H_a (7.54 ppm) and furyl H_a (7.33 ppm)

Table 3. Selected ^{1}H data for **2a–c,e** substituents



Pyridazine **2** substituent	H_a	H_b
2a, X=S, R=H_c	7.54 (d, 1H, $^{3}J_{AB} = 4.55$ Hz)	7.68 (dd, 1H, $^{3}J_{AB} = 4.55$ Hz, $^{3}J_{AC} = 8.0$ Hz)
2b, X=S, R=Cl	7.03 (d, $J = 4.0$ Hz)	7.57 (d, $J = 4.0$ Hz)
2c, X=S, R=CH_3	7.62 (d, $J = 3.4$ Hz)	7.23 (d, $J = 3.4$ Hz)
2e, X=O, R=H	7.33 (d, 1H, $^{3}J_{AB} = 3.5$ Hz)	6.66 (dd, 1H, $^{3}J_{AB} = 3.5$ Hz, $^{3}J_{AC} = 1.7$ Hz)

Table 4. Selected selected ^{1}H data for **2f–h** substituents



Pyridazine **2** substituent	H_a	H_b
2f, R=Cl	7.81 (d, 1H, $^{3}J = 8.55$ Hz)	7.46 (d, 1H, $^{3}J = 8.55$ Hz)
2g, R=OCH_3	6.96 (d, 1H, $^{3}J = 8.6$ Hz)	7.85 (d, 1H, $^{3}J = 8.6$ Hz)
2h, R=CH_3	7.81 (d, 1H, $^{3}J = 8.0$ Hz)	7.29 (d, 1H, $^{3}J = 8.0$ Hz)

protons are both seen as doublets with coupling constants at $^{3}J_{AB} = 4.55$ and $^{3}J_{AB} = 3.5$ Hz respectively. Protons H_b for each case are observed as a doublet of doublets with chemical shifts 7.68 and 6.66 ppm, respectively. However, stronger coupling interactions were observed with the thienylic H_b, with its coupling constants at $^{3}J_{AB} = 4.55$ Hz and $^{3}J_{AC} = 8.0$ Hz. By comparison, the furylic H_b proton's coupling constants were $^{3}J_{AB} = 3.5$ Hz, $^{3}J_{AC} = 1.7$ Hz. For compounds **2b** and **c**, the thienylic protons H_a and H_b are seen as two doublets having coupling constants of $^{3}J = 3.4$ Hz and 4.0 Hz respectively and in observed ranges closely match those of the corresponding protons in **2a**.

With respect to the ^{1}H NMR signals of their aryl substituents, phenyl substituted pyridazines **2f–h** display similar chemical shifts and coupling constants (Table 4). The phenyl H_a protons for each case are seen in the range 6.96–7.81 ppm as a doublet with coupling constants ranging from 8.0 to 8.6 Hz. Phenyl H_b protons are also observed as a doublet from 7.29 to 7.85 ppm ($^{3}J = 8.0$–8.6 Hz).

The structure of pyridazine **2f** was determined by X-ray crystallographic methods. The crystals for which data were collected were typical of others in the batch, which had been grown by slow evaporation from acetone at room temperature. These crystals were mounted on glass fibers with Paratone N oil. Data were collected at 90 K on a Nonius KappaCCD diffractometer. The main programs used were DENZO-SMN to obtain cell parameters and for data reduction, SCALEPACK for absorption correction, SHELXS-86 for structure solution, and SHELXL-93 for refinement.[18] Hydrogen atoms were placed in geometrically calculated positions. Crystal data and a summary of experimental details are given in Table 5.

Recrystallization of **2f** from hot acetone affords the pyridazine as yellow-orange block crystals (Fig. 1). Pyridazine **2f** crystallizes in a triclinic *P*-1 space group, with one molecule in the unit cell. The average Cp carbon–carbon bond lengths for **2f** are 1.4115(22) Å, and the average aromatic ring carbon–carbon bond lengths are 1.3927(10) Å. The N1–N2 bond length for the pyridazine portion of **2f** is 1.3586(15) Å. The *para*-chloro substitutents observed a carbon–chlorine bond length of 1.7437(13) Å and 1.7382(13) Å. X-ray analysis shows the phenyl rings are twisted out of the plane of the central pyridazine, with the [C13–C8–C7–N2] and [C19–C14–C1–N1] torsion angles at -36.92° and -39.73° respectively. One acetone solvent

Table 5. Crystal data and structure refinement for pyridazine **2f**

Empirical formula	$C_{22}H_{18}C_{12}N_2O$
Formula weight	397.28
Temperature	90.0(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	
a = 8.6250(1) Å	α = 97.9313(7)°
b = 9.8027(2) Å	β = 93.0136(7)°
c = 11.4677(2) Å	γ = 95.8685(7)°
Volume	953.08(3) Å^3
Z	2
Calculated density	1.384 Mg/m^3
Absorption coefficient	0.355 mm^{-1}
F(000)	412
Crystal size	0.20 × 0.15 × 0.15 mm
θ range for data collection	1.80 to 27.47°
Limiting indices	$-11 \le h \le 11$, $-12 \le k \le 12$, $-14 \le l \le 14$
Reflections collected/unique	21631/4346 [R(int) = 0.0195]
Completeness to θ = 27.47	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.949 and 0.932
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4346/0/246
Goodness of fit on F^2	1.014
Final R indices [I > 2 σ(I)]	R1 = 0.0322, wR2 = 0.0856
R indices (all data)	R1 = 0.0391, wR2 = 0.0908
Largest diff. peak and hole	0.383 and −0.278 e.Å^{-3}

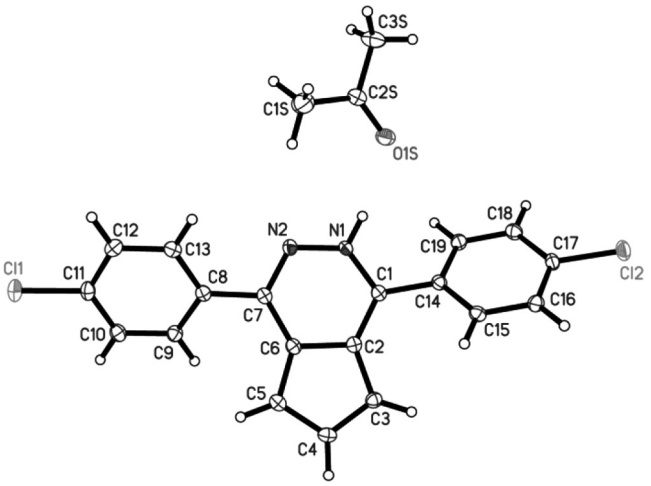


Figure 1. Molecular structure for pyridazine **2f**.

molecule co-crystallized with pyridazine **2f** and displayed a hydrogen bonding interaction between N1–H1 to O1. The calculated hydrogen bond (H1 . . . O1) distance is 2.00 Å.

EXPERIMENTAL

All reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere unless otherwise noted. NMR solvents $CDCl_3$ and dimethylsulfoxide (DMSO-d_6; Aldrich) were used without further purification. ^{n}BuLi, dicyclopentadiene, methanol, hydrazine hydrate, thienoyl chloride, 5-chlorothienoyl chloride, benzo[*b*]thienyl chloride, 2-furoyl chloride, *p*-chlorobenzoyl chloride, *p*-methoxybenzoyl chloride, and toluoyl chloride (Aldrich) were used without further purification. Fulvenes 1,2-$C_5H_3(COC_4H_3S)(COHC_4H_3S)$ (**1a**), 1,2-$C_5H_3(COC_4H_2SCl)(COHC_4H_2SCl)$ (**1b**), 1,2-$C_5H_3(COC_4H_2SCH_3)(COHC_4H_2SCH_3)$ (**1c**), $C_5H_3(COC_8H_5S)(COHC_8H_5S)$ (**1d**), 1,2-$C_5H_3(COC_6H_4Cl)(COHC_6H_4Cl)$ (**1f**), 1,2-$C_5H_3(COC_6H_4OCH_3)(COHC_6H_4OCH_3)$ (**1g**), and 1,2-$C_5H_3(COC_6H_4CH_3)(COHC_6H_4CH_3)$ (**1h**) were prepared according to the literature methods.[13–17] Ethyl ether was dried over sodium benzophenone ketyl.

^{1}H and ^{13}C NMR spectra were recorded on a JEOL 500-MHz NMR spectrometer at ca. 22 °C and were referenced to residual solvent peaks. All ^{13}C NMR spectra were listed as decoupled. IR spectra were recorded on a Spectrum One Fourier transform (FT)–IR spectrometer. Electron ionization (EI) mass spectra were recorded at 70 eV on a Varian Saturn GC/MS. Melting points were taken on a standard Mel-Temp apparatus. X-ray diffraction data were collected at 90 K on a Nonius KappaCCD diffractometer at the University of Kentucky X-ray Crystallographic Laboratories. Elemental analysis were performed at Western Kentucky University's Advanced Materials Institute.

Synthesis of 1,2-$C_5H_3(COC_4H_3O)(COHC_4H_3O)$ (1d)

Freshly cracked cyclopentadiene (3.14 mL, 2.51 g, 38.1 mmol) was added dropwise to a cooled solution (0 °C) of n-butyllithium (16.2 mL of 2.50 M, 23.4 g, 40.5 mmol) in ethyl ether (120 mL). A white precipitate of cyclopentadienyllithium was formed immediately. The suspension was stirred for 10 min, and 2-furoyl chloride (2.48 mL, 3.29 g, 25.2 mmol) was added dropwise. A bright orange color formed immediately. The solution was stirred for 45 min at room temperature. The reaction mixture was hydrolyzed with dilute (3%) acetic acid (100 mL). The organic layer was separated, and the aqueous layer was extracted twice more with ethyl ether (2×10 mL). The combined ethyl ether extracts were dried ($MgSO_4$) and removed under reduced pressure to leave a red oil. The oil was eluted through a silica plug (50:50 dichloromethane/hexane) to give an orange solution. The organic solution was removed under reduced pressure to leave an orange semisolid. The solid was triturated with hexane (2×10 mL) to leave a bright orange solid (337 mg, 1.33 mmol, 10.5%). Mp: 109–110 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.07 (t, 1H, $^3J = 4$ Hz, Hz, CHC*H*CH), 6.62 (dd, 1H, $^3J_{AB} = 3.5$ Hz, $^3J_{AC} = 1.7$ Hz CHC*H*CHO), 7.40 (d, 1H, $^3J_{BC} = 3.5$ Hz, C*H*CHCHO), 7.72 (d, 1H, $^3J_{AB} = 1.7$ Hz, CHCHC*H*O), 8.15 (d, 1H, $^3J = 4$ Hz, C*H*CHC*H*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 83.8

(CH*C*CO), 112.5 (CH*C*HCH), 119.8 (*C*HCH*C*H), 123.5 (*C*CO), 124.1, 139.3, 146.9 (Fr), 152.0 (O*C*CO), 169.3 (*C*O). IR (KBr, cm^{-1}): 1530, 1565 ($CO C_4H_3O$), 3076, 3115, 3134, 3143 (C−H). MS: m/z 254 (M^+), 186 ($M^+ - C_4H_4O$), 119 ($M^+ - 2C_4H_4O$). Anal. calcd. for $C_{15}H_{10}O_2$: C, 70.86; H, 3.96. Found: C, 67.56; H, 3.56.

Synthesis of 1,2-$C_5H_3(CC_4H_3SNH)(CC_4H_3SN)$ (2a)

1,2-$C_5H_3(COC_4H_3S)(COHC_4H_3S)$ (**1a**, 164 mg, 0.573 mmol) was dissolved in 50 mL of methanol in a 200-mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 48 h. Water (20 mL) was added to the reaction, and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3×10 mL), and the organic layers were collected, dried ($MgSO_4$), and filtered. The volatiles were removed *in vacuo*, and the crude product was triturated with cold hexane to give 1,2-$C_5H_3(CC_4H_3SNH)(CC_4H_3SN)$ (**2a**, 124 mg, 0.439 mmol, 76.5%) as a red powder. Mp: 131–134 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.21 (t, 1H, $^3J = 4.0$ Hz, CHC*H*CH), 7.29 (d, 1H, $^3J_{BC} = 4.55$ Hz, CHCHC*H*S), 7.54 (d, 1H, $^3J_{AB} = 4.55$ Hz, Hz, C*H*CHCHS), 7.68 (dd, 1H, $^3J_{AB} = 4.55$ Hz, $^3J_{AC} = 8.0$ Hz CHC*H*CHS), 7.84 (br s, 1H, C*H*CHC*H*), 11.2 (br s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 109.5 (*C*HCH*C*H), 119.8 (CH*C*HCH), 123.2 (NC*C*CH), 127.9, 128.1, 128.6, 132.7, 133.1, 134.0 (Tp) 139.4 (CHCH*C*N). IR (KBr, cm^{-1}): 1592 (*CN*), 3064, 3095 (C−H), 3171 (N−H). MS: m/z 282 (M^+). Anal. calcd. for $C_{15}H_{10}N_2S_2$: C, 63.80; H, 3.57. Found: C, 63.14; H, 3.92.

Synthesis of 1,2-$C_5H_3(CC_4H_2SClNH)(CC_4H_2SClN)$ (2b)

1,2-$C_5H_3(COC_4H_2SCl)(COHC_4H_2SCl)$ (**1b**, 100 mg, 0.394 mmol) was dissolved in 50 mL of methanol in a 200-mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 48 h. Water (20 mL) was added to the reaction, and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3×10 mL), and the organic layers were collected, dried ($MgSO_4$), and filtered. The volatiles were removed *in vacuo*, and the crude product was triturated with cold hexane to give 1,2-$C_5H_3(CC_4H_2SClNH)(CC_4H_2SClN)$ (**2b**, 60.5 mg, 0.173 mmol, 60.8%) as an orange-red powder. Mp: 146–148 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.03 (d, 1H, $^3J = 4.0$ Hz, ClCCHC*H*), 7.21 (d, 1H, $^3J = 3.5$ Hz, C*H*CHC*H*), 7.53 (t, 1H, $^3J = 3.5$ Hz, CHC*H*CH), 7.57 (d, 1H, $^3J = 4.0$ Hz, ClCC*H*CH), 11.8 (br s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 109.5 (*C*HCH*C*H), 119.5 (CH*C*HCH), 127.3, 127.5, 133.8, 139.9 (Tp) 141.2 (CHCH*C*N). IR (KBr, cm^{-1}): 1596 (*CN*), 3054 (C−H), 3164 (N−H). MS: m/z 350 (M^+), 315 (M^+ – Cl). Anal. calcd. for $C_{15}H_8Cl_2N_2S_2$: C, 51.29; H, 2.30. Found: C, 56.03; H, 4.01.

Synthesis of 1,2-$C_5H_3(CC_4H_2SCH_3NH)(CC_4H_2SCH_3N)$ (2c)

1,2-$C_5H_3(COC_4H_2S\ CH_3)(COHC_4H_2SCH_3)$ (**1c**, 329 mg, 1.05 mmol) was dissolved in 50 mL of methanol in a 200-mL round-bottom flask. An excess of

hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 48 h. Water (20 mL) was added to the reaction, and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3×10 mL), and the organic layers were collected, dried ($MgSO_4$), and filtered. The volatiles were removed *in vacuo*, and the crude product was triturated with cold hexane to give 1,2-$C_5H_3(CC_4H_2SClNH)(CC_4H_2SClN)$ (**2c**, 288 mg, 0.928 mmol, 88.6%) as an orange powder. Mp: 146–148 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.58 (s, 3H, CH_3), 6.67 (d, 2H, $^3J = 4.0$ Hz, C*H*CHC*H*), 7.23 (d, 1H, $^3J = 3.4$ Hz, CHC*H*CCH$_3$), 7.48 (t, 1H, $^3J = 4.0$ Hz, CHC*H*CH), 7.62 (d, 1H, $^3J = 3.4$ Hz, C*H*CHCCH$_3$), 11.3 (br s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 15.6 (CH_3), 109.2 (*C*HCH*C*H), 119.4 (CH*C*HCH), 126.5, 128.2, 132.4 (Tp) 143.6 (CHCH*C*N). IR (KBr, cm^{-1}): 1592 (*CN*), 2855, 2959 (C−H), 3059 (N−H). MS: m/z 310 (M^+). Anal. calcd. for $C_{17}H_{14}N_2S_2$: C, 65.77; H, 4.55. Found: C, 62.65; H, 5.25.

Synthesis of 1,2-$C_5H_3(CC_8H_5SNH)(CC_8H_5SN)$ (2d)

1,2-$C_5H_3(COC_8H_5S)(COHC_8H_5S)$ (**1d**, 257 mg, 0.665 mmol) was dissolved in 50 mL of methanol in a 200-mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 48 h. Water (20 mL) was added to the reaction, and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3×10 mL), and the organic layers were collected, dried ($MgSO_4$), and filtered. The volatiles were removed *in vacuo*, and the crude product was triturated with cold hexane to give 1,2-$C_5H_3(CC_8H_5SNH)(CC_8H_5SN)$ (**2d**, 60.0 mg, 0.157 mmol, 26.4%) a purple powder. Mp: 168–172 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.66 (dd, 1H, $^3J_{AB} = 3.5$ Hz, $^3J_{AC} = 1.7$ Hz, Tp), 7.25 (d, 1H, $^3J = 4$ Hz, C*H*CHCH), 7.33 (d, 1H, $^3J = 4$ Hz, CHCHC*H*), 7.53 (t, 1H, $^3J = 4$ Hz, CHC*H*CH), 7.66 (m, 2H, Tp), 11/.2 (br s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 108.5 (*C*HCH*C*H), 112.4 (CH*C*HCH), 112.7 (NC*C*CH), 112.6, 118.0, 133.2 (Tp) 144.3 (CHCH*C*N). IR (KBr, cm^{-1}): 1578 (*CN*), 3006 (C−H), 3063 (N−H). MS: m/z 382 (M^+). Anal. calcd. for $C_{25}H_{14}N_2S_2$: C, 72.22; H, 3.69. Found: C, 65.74; H, 4.72.

Synthesis of 1,2-$C_5H_3(CC_4H_3ONH)(CC_4H_3ON)$ (2e)

1,2-$C_5H_3(COC_4H_3O)(COHC_4H_3O)$ (**1e**, 100 mg, 0.394 mmol) was dissolved in 50 mL of methanol in a 200-mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 48 h. Water (20 mL) was added to the reaction, and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3×10 mL), and the organic layers were collected, dried ($MgSO_4$), and filtered. The volatiles were removed *in vacuo*, and the crude product was triturated with cold hexane to give 1,2-$C_5H_3(CC_4H_3ONH)(CC_4H_3ON)$ (**2e**, 40.0 mg, 0.160 mmol, 40.6%) as a red powder. Mp: 146–148 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.66 (dd, 1H, $^3J_{AB} = 3.5$ Hz, $^3J_{AC} = 1.7$ Hz CHC*H*CHO), 7.25 (d, 1H, $^3J = 4.0$ Hz, C*H*CHCH), 7.33 (d, 1H, $^3J = 3.5$ Hz, C*H*CHCHO), 7.53 (t, 1H, $^3J = 4.0$ Hz, CHC*H*CH), 7.66 (m, 2H, Fr), 11.2 (br s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 108.5

(*C*HCH*C*H), 112.4 (CH*C*HCH), 112.7 (NC*C*CH), 112.6, 118.0, 133.2 (Fr) 144.3 (CHCH*C*N). IR (KBr, cm^{-1}): 1612 (*CN*), 2958 (C−H), 3120 (N−H). MS: *m/z* 250 (M^+), 221 (M^+– CHO), 193 ($M^+ - C_2H_2O_2$). Anal. calcd. for $C_{15}H_{10}N_2O_2$: C, 71.99; H, 4.03. Found: C, 74.32; H, 6.30.

Synthesis of 1,2-$C_5H_3(CC_6H_4ClNH)(CC_6H_4ClN)$ (2f)

1,2-$C_5H_3(COC_6H_4Cl)(COHC_6H_4Cl)$ (**1f**, 256 mg, 0.766 mmol) was dissolved in 50 mL of methanol in a 200-mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 24 h. Water (20 mL) was added to the reaction, and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3×10 mL), and the organic layers were collected, dried ($MgSO_4$), and filtered. The volatiles were removed *in vacuo*, and the crude product was triturated with cold hexane to give 1,2-$C_5H_3(CC_6H_4ClNH)(CC_6H_4ClN)$ (**2f**, 186 mg, 0.548 mmol, 74.0%) as a yellow-orange powder. Mp: 218–222 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.05 (d, 1H, $^3J = 3.45$ Hz, C*H*CHC*H*), 7.46 (d, 1H, $^3J = 8.55$ Hz, C*H*CHCCl), 7.54 (t, 1H, $^3J = 3.45$ Hz, CHC*H*CH), 7.81 (d, 1H, $^3J = 8.55$ Hz, CHC*H*CCl), 11.8 (br s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 109.2 (*C*HCH*C*H), 120.3 (CH*C*HCH), 129.4, 128.9, 133.4 (Ph) 136.5 (CHCH*C*N). IR (KBr, cm^{-1}): 1598 (*CN*), 3047 (C−H), 2931, 2965 (CH_3), 3192 (N−H). MS: *m/z* 338 (M^+), 302 (M^+ – Cl). Anal. calcd. for $C_{19}H_{12}N_2Cl_2$: C, 67.27; H, 3.57. Found: C, 67.56; H, 3.56.

Synthesis of 1,2-$C_5H_3(CC_6H_4OCH_3NH)(CC_6H_4OCH_3N)$ (2g)

1,2-$C_5H_3(COC_6H_4OCH_3)(COHC_6H_4OCH_3)$ (**1g**, 383 mg, 1.15 mmol) was dissolved in 50 mL of methanol in a 200-mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution was stirred 24 h. Water (20 mL) was added to the reaction, and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3×10 mL), and the organic layers were collected, dried ($MgSO_4$), and filtered. The volatiles were removed *in vacuo*, and the crude product was triturated with cold hexane to give 1,2-$C_5H_3(CC_6H_4OCH_3NH)(CC_6H_4OCH_3N)$ (**2g**, 262 mg, 0.793 mmol, 69.2%) as a yellow solid. Mp: 180–184 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 3.90 (s, 3H, CH_3), 6.96 (d, 1H, $^3J = 8.6$ Hz, OCHC*H*), 7.07 (d, 1H, $^3J = 3.4$ Hz, C*H*CHC*H*), 7.54 (t, 1H, $^3J = 3.4$ Hz, CHC*H*CH), 7.85 (d, 1H, $^3J = 8.6$ Hz, OCC*H*CH), 12.1 (br s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 55.4 (O*C*H$_3$), 108.8 (*C*HCH*C*H), 114.3 (CH*C*HCH), 120.2 (*C*CN), 130.0, 131.9 (Ph) 161.0 (CHCH*C*N). IR (KBr, cm^{-1}): 1573 (*CN*), 2934, 2963 (CH_3), 3057 (N−H). MS: *m/z* 298 ($M^+ - HOCH_3$), 239 ($M^+ - C_6H_4OCH_3$). Anal. calcd. for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49. Found: C, 74.32; H, 6.30.

Synthesis of 1,2-$C_5H_3(CC_6H_4CH_3NH)(CC_6H_4CH_3N)$ (2h)

1,2-$C_5H_3(COC_6H_4CH_3)(COHC_6H_4CH_3)$ (**1h**, 369 mg, 1.22 mmol) was dissolved in 50 mL of methanol in a 200-mL round-bottom flask. An excess of hydrazine hydrate (1.00 mL, 1.03 g, 20.6 mmol) was added to the solution. The solution

was stirred 24 h. Water (20 mL) was added to the reaction, and an orange precipitate formed immediately. The aqueous suspension was washed with ethyl ether (3×10 mL), and the organic layers were collected, dried ($MgSO_4$), and filtered. The volatiles were removed *in vacuo*, and the crude product was triturated with cold hexane to give 1,2-$C_5H_3(CC_6H_4CH_3NH)(CC_6H_4\ CH_3N)$ (**2h**, 250 mg, 0.838 mmol, 68.9%) as a red powder. Mp: 182–186 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.46 (s, 3H, CH_3), 7.07 (d, 1H, $^3J = 4.0$ Hz, C*H*CHC*H*), 7.29 (d, 1H, $^3J = 8.0$ Hz, CH_3C*H*CH), 7.49 (t, 1H, $^3J = 4.0$ Hz, CHC*H*CH), 7.81 (d, 1H, $^3J = 8.0$ Hz, CH_3CHC*H*), 11.5 (br s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 108.9 (*C*HCH*C*H), 120.4 (CH*C*HCH), 128.5, 129.0, 129.7, 130.0, 132.2 (Ph) 141.2 (CHCH*C*N). IR (KBr, cm^{-1}): 1595 (*CN*), 3031 (C−H), 2918 (CH_3), 3092 (N−H). MS: m/z 298 (M^+), 283 ($M^+ - CH_3$), 207 ($M^+ - C_6H_4CH_3$). Anal. calcd. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08. Found: C, 81.62; H, 6.55.

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REFERENCES

1. Volonterio, A.; Moisan, L.; Rebek Jr., J. Synthesis of pyridazine-based scaffolds as a-helix mimetics. *Org. Lett.* **2007**, *9*, 3733–3736.
2. Xu, Y.; Akermark, T.; Gyollai, V.; Zou, D.; Eriksson, L.; Duan, L.; Zhang, R.; Akermark, B.; Sun, L. A new dinuclear ruthenium complex as an efficient water oxidation catalyst. *Inorg. Chem.* **2009**, *48*, 2717–2719.
3. Bouffard, J.; Eaton, R. F.; Muller, P.; Swager, T. M. Iptycene-derived pyridazines and phthalazines. *J. Org. Chem.* **2007**, *72*, 10166–10180.
4. Yang, J. S.; Swager, T. M. Porous shape persistent fluorescent polymer films: An approach to TNT senory materials. *J. Am. Chem. Soc.* **1998**, *120*, 5321–5322.
5. Ghanem, B. S.; Msayib, K. J.; McKeown, N. B.; Harris, K. D. M.; Pan, Z.; Budd, P. M.; Butler, A.; Selbie, J.; Book, D.; Walton, A. A triptycene-based polymer of intrinsic microposity that displays enhanced surface area and hydrogen adsorption. *Chem. Commun.* **2007**, 67–69.
6. Han, T.; Zong, Q. S.; Chen, C. F. Complexation of triptycene-based cylindrical macrotricyclic polyether toward diquaternary salts: Ion-controlled binding and release of the guests. *J. Org. Chem.* **2007**, *72*, 3108–3111.
7. Ellis, G. P. In *Synthesis of Fused Heterocycles*; John Wiley and Sons Inc.: New York, 1987; pp. 226–239.
8. Boger, D. L.; Coleman, R. S.; Panek, J. S.; Yohannes, D. Thermal cycloaddition of dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate with electron-rich olefins: 1,2-Diazine and

pyrrole introduction: Preparation of octamethylporphin (OMP). *J. Org. Chem.* **1984**, *49*, 4405–4409.
9. *Inorganic and Organometallic Polymers II: Advanced Materials and Intermediates*; P. Wisian-Neilson, H. R. Allcock, and K. J. Wynne (Eds.); ACS Symposium Series 572; Division of Polymer Chemistry, Inc.: Denver, CO, 1994; pp. 442–497.
10. Wright, M. E.; Sigman, M. S. Organometallic nonlinear optical polymers. *Macromolecules* **1992**, *25*, 6050–6054.
11. Zotti, G.; Zecchin, S.; Shiavon, G. Conductivity in redox modified conducting polymers. *Chem. Mater.* **1995**, 2309–2315.
12. *Inorganic and Organometallic Polymers II: Advanced Materials and Intermediates*; P. Wisian-Neilson, H. R. Allcock, and K. J. Wynne (Eds.); ACS Symposium Series 572; Division of Polymer Chemistry, Inc.: Denver, CO, 1994; pp. 442–497.
13. Linn, W. J.; Sharkey, W. H. Benzoylation of cyclopentadienyllithium. *J. Am. Chem. Soc.* **1957**, *79*, 4970–4972.
14. Snyder, C. A. The synthesis, characterization, and structure of some cyclopenta[*c*]thiophenes and their manganese complexes. Ph.D. thesis, Department of Chemistry, University of Kentucky, Lexington, KY, 2005.
15. Tice, N. C. The synthesis, structure, and reactivity of some organometallic-fused heterocycles. Ph.D. thesis, Department of Chemistry, University of Kentucky, Lexington, KY, 2006.
16. Wallace, C. E.; Selegue, J. P.; Carrillo, A. Synthesis and characterization of a 1,2-dibenzoylruthenocene and a derived pyridazine. *Organometallics* **1998**, *17*, 3390–3393.
17. Snyder, C. A.; Selegue, J. P.; Tice, N. C.; Wallace, C. E.; Blankenbuehler, M. T.; Parkin, S.; Allen, K. D. E. Synthesis, characterization, and structure of cyclopenta[*c*]thiophenes and their manganese complexes. *J. Am. Chem. Soc.* **2005**, *127*, 15010–15011.
18. Otwinowski, Z.; Minor, W. *Macromolecular Crystallography, Part A, of Methods in Enzymology*; C. W. Carter Jr. and R. M. Sweet, (Eds.); vol. 276, Academic Press: New York, 1997.