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Parallel Synthesis of Polystyrene Anchored Imine Sulfide Materials: Sorption and Metal Sensing Studies

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Abstract: In the present work we report the synthesis of a combinatorial library of 30 phenyl-ethyl based *N*-derivatives [nitro, amines and imines] bound to PS-thiophenol resin. The five step reaction sequence was characterized by ^{1}H NMR, MS and fluorescence spectroscopy of resin beads. The imines were screened for those that exhibited a large sorption capacity for Cu(II) and Pb(II) ions and those exhibiting a large fluorescence change upon the metal binding.
Keywords: Combinatorial library, solid phase, sensors, fluorescence.

Resumen. Se reporta la síntesis de una biblioteca combinatorial de 30 *N*-derivados fenil etilo (nitro, aminas e iminas) unidos a una resina PS-tiofenol. La secuencia de 5 pasos de reacción fue seguida por ^{1}H RMN, EM y espectroscopia de fluorescencia de la resina. Las iminas fueron monitoreadas para aquellas que mostraron gran capacidad de porción para iones Cu(II) y Pb(II) y aquellas que mostraron un gran cambio de fluorescencia por la unión al metal.
Palabras clave: Biblioteca combinatorial, fase sólida, sensors, fluorescencia.

Introduction

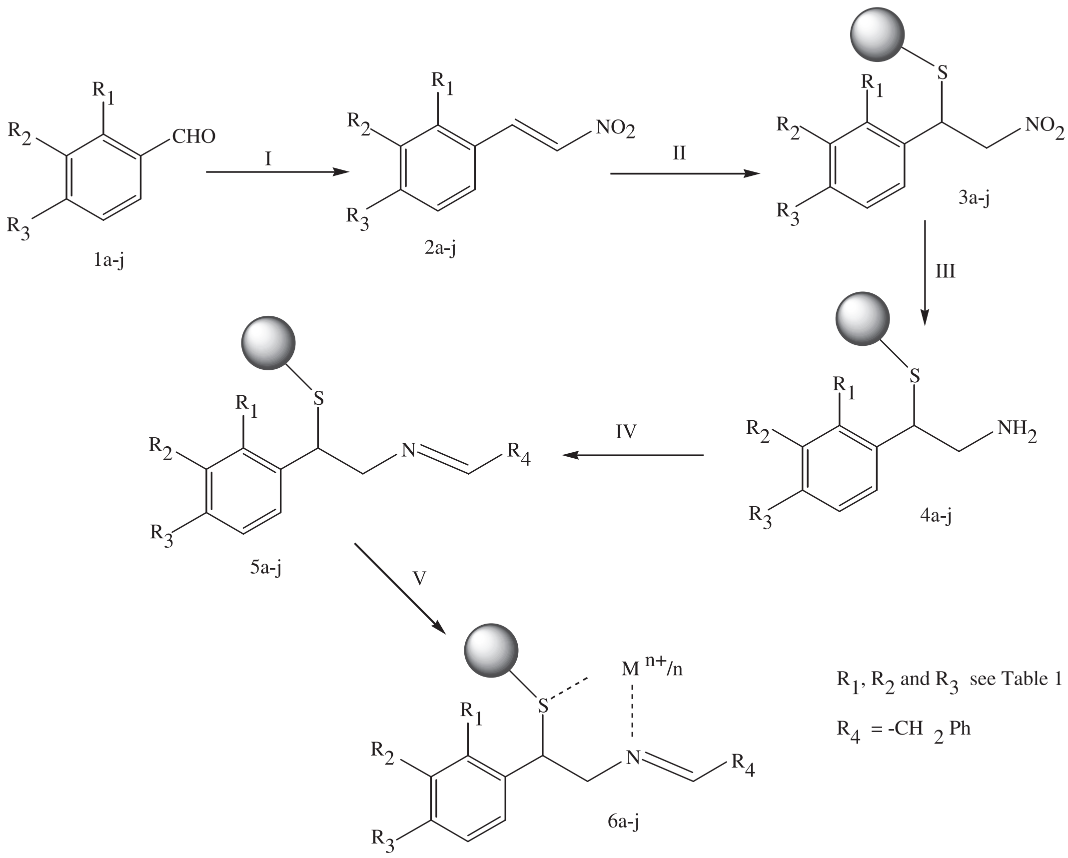
Recent progress in combinatorial chemistry has indeed provided an easy access to produce compounds which are screened, or tested, against biological targets as part of the drug discovery process. However, it is still a tough task to rationally design active recognition motifs having a proper receptor arrangement for metal ion binding and in the pursuit for new sensing candidates. In the field of combinatorial chemistry, solid phase organic synthesis (SPOS) is a rapidly growing research area [1-3]. The attractiveness of this technique lies in the possibility of conducting multistep reactions and to drive reactions to completion, which may increase the rate of investigations of new receptors and sorbent materials [1].

It is known that the selective interaction of transition and heavy metal cations may be achieved by chelating receptors. Ligands containing oxygen/sulfur and nitrogen donors have been of research interest because of the versatility of their steric and electronic properties, which can be modified by choosing the appropriate amine precursors and ring substituents [4]. The organic compounds known as imines, anils or Schiff's bases have the azomethine group (>C=N-) in their structure and are of great interest in chemistry and medicine [5]. For example, bidentate ligands containing imine groups have been used as modulators of electronic and structural properties of transition metal centers [6]. Additionally, imines have been attracting much attention because of their wide variety of applications in the field of electronics, opto-electronics and photonics [7]. Schiff bases are one of the most versatile and thorough ligands for recovery and complexation of metal ions; however, only a few Schiff bases have been immobilized to solid supports and used for metal ion removal and/or sensing studies [8, 9]. Our research group has been exploring the feasibility of using combinatorial chemistry to incorporate binding motifs into solid supports in order to prepare sorbent and/or sensing materials for metal ions [10-12]. Our objective is now the formation of Schiff base type chelating ligands with *S*- and *N*-donor groups attached to a polystyrene resin and the introduction of specific functionalities at the periphery of the coordinating imine moiety that may rise to develop sorbent/sensing tailored materials for metal ions. As a proof of the principle, Cu(II) and Pb(II), were selected as metal ions of environmental concern.

We describe for the first time the synthesis of a combinatorial library of thio-ether imine derivatives bound to PS-thiophenol resin as potential attached receptors for Cu(II) and Pb(II) ions. The materials display a suitable combination of donor atoms for metal complexation/sorption and π-conjugated systems for optical transduction. Starting from *o*-, *m*- and *p*-hydroxybenzaldehydes, a library of ten nitrolefins (**a-j**) were condensed to the PS-thiophenol resin (**Scheme 1**), which was subsequently reduced to the amine group to get a new library. Screening of the library members for their metal binding response was performed using fluorescence spectral changes and atomic absorption spectroscopy was used to evaluate their sorption capacity. The role of the substituents in the sensing properties is outlined.

Results and Discussion

The first phase of our study centered on the generation of a combinatorial library created according to the synthetic route outlined in Scheme 1, in which the solid support was a PS-thiophenol resin while ten benzaldehyde derivatives and three different substituents (Table 1) were used to impart diversity/selectivity. For the ultimate application as sensors, an imine group was used to allow for metal interaction.



Scheme 1. Solid phase organic synthesis of immobilized imines. Reagents and conditions: **I**) CH_3NO_2, AcOH, $AcONH_4$, **II**) PS-thiophenol, isopropylcyclohexylamine, CH_2Cl_2, **III**) $LiAlH_4$, THF, **IV**) RCHO, THF:DMSO (1:1), Na_2SO_4, **V**) $Pb(NO_3)_2$ or $Cu(NO_3)_2$ 10 mg/L

Table 1. Composition of intermediate and final library compounds (**1-5**)(**a-j**)

Compounds **1-5**	Substituents		
	R^1	R^2	R^3
a	H	H	OCH_2-ϕ
b	H	OCH_2ϕ	H
c	OCH_2ϕ	H	H
d	H	OCH_2ϕ	OCH_3
e	H	OCH_3	OCH_2ϕ
f	H	H	OCH_3
g	H	OCH_3	OCH_3
h	H	H	H
i	H	H	**A**
j	F	H	H

Seven hydroxybenzaldehydes were treated with methyl iodide or benzyl chloride in DMF in presence of K_2CO_3 to give the methyl and benzyl ethers **1a-g**, (Scheme 1, Table 1). Then, all benzaldehydes were condensed with nitromethane in the presence of ammonium acetate to give the nitro-olefins (**2a-j**) in excellent yields. Michael addition of PS-thiophenol resin with a catalytic amount of *N*-isopropylcyclohexylamine to each nitro-olefin was performed to obtain the supported compounds **3a-j.** This coupling reaction was simultaneously acting as a protective one and eventually, it was possible to remove the resin and recover the corresponding nitro-olefin. After exploring two methods for the nitro reduction, we found that the use of lithium aluminum hydride as the reducing agent (rt, THF) produced the desired amines **4a-j.** For compounds **1i, 2i** and **3i** R_3 = $-NO_2$, so that during the reduction step this group also suffered the redox process to give **4i**. The supported amines **4a-j** were finally treated with benzaldehyde to give the imines **5a-j**. Both amine groups in **4i** reacted to form the imine (**5i**).

Spectral characteristics of the fluorescents materials

As a complementary tool to the analytical techniques used in the characterization of the different products in Scheme 1 (see Experimental Section), we have used an efficient and fast technique to monitor the synthesis progress and the chemical changes on the solid phase. This approach is based in fluorescence measurements made directly on the solid phase [13]. In Figure 1, we can observe that immobilisation of **2i** ($-R_3 = -NO_2$) onto the PS-resin to render **3i** resulted in a red-shift of both the excitation and emission bands with a drastic decrease in the fluorescence intensity (Figure 1a). The nitrogen in nitro compounds is trigonally planar with electrons delocalized between the nitrogen and the two oxygen atoms in a 120º angle configuration. Although nitro groups are well known fluorescence quenchers due to both their electron inductively and mesomerically withdrawing properties [14, 15], the high fluorescence quantum yield of **2i** may be the result of an intramolecular charge delocalization between the aromatic ring (the donor) and the electron accepting groups, the nitro bonded to the ring and that in the branch, thus extending the conjugation length of the chromophore (Figure 2). The nitro group is forced to be in-plane with the benzene moiety and the enhancement of the rigidity of the molecule favored the radiational deactivation of the lowest singlet excited state. In **3i** the nitro-branch group may be twisted out of the conjugation chain, thus rendering the attached derivative noticeably less fluorescent than **2i** (Figure 1b). Fluorescence is restored upon reduction of the nitro groups to the corresponding amino-group (electron donor), **4i**. The high fluorescence quantum yield of **4i** may be the result of the amine groups, in particular to that bonded to the ring, with the lone pair electrons occupying a π-orbital. This is antisymmetric to the plane of the ring and can conjugate with the π-orbitals of the latter so that only π*-π transitions are expected (Figure 2).

The fluorescence properties of the bound nitro-olefins (**3a-3j**) also depended on the nature of the remaining substituent as well as on their relative positions in the benzene ring. In fact, taking **3h** as reference ($-R_1 = -R_2 = -R_3 = -H$), electron withdrawing substituents (e.g., $-NO_2$ and -F in **3i** and **3j**, respectively) caused a remarkable fluorescence quenching, while a marginal fluorescence increase was observed when the nitro-olefin beared a $-OCH_3$ electron donor group in R_3 position (**3f**) and an important fluorescence increase when the group $-OCH_3$ was in R_2 and R_3 positions, simultaneously (**3g**, Figure 3). The presence of $-OCH_2\phi$ groups, either the position, resulted in a fluorescence quenching effect (**3a-e**). The directive effect of substituents in the benzene ring follows the sequence: benzyl^3 methoxy>hydrogen. Based on this, one would expect the fluorescence intensity to follow the same trend. The low intensity of benzyl substituent could be explained by a preferred conformation where the two benzene rings are parallel to each other (Figure 4), suggesting a transfer of energy from one ring to another [16, 17].

On the other hand, there seems to be a correlation between the electron donating/acceptor properties of the substituents and the spectral characteristics of the derivatives. Taking **3h** as reference (see Table 2), the large spectral red-shifting observed for **3i** and **3j** may be due to the influence of electron withdrawal groups in position R_1 and R_3 of the ring system while the large spectral blue-shifting observed for the **3g** derivative could be explained by the presence of two donat-

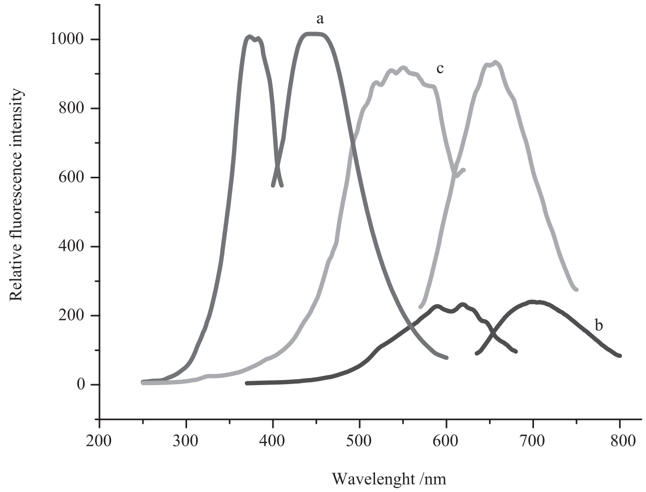


Fig. 1. Influence of the immobilisation process on the fluorescence spectra of **2i** (spectra **a** and **b**, before and after immobilization, respectively). Fluorescence enhancement upon reduction of the nitro groups in **3i** to yield **4i** (spectrum **c**).

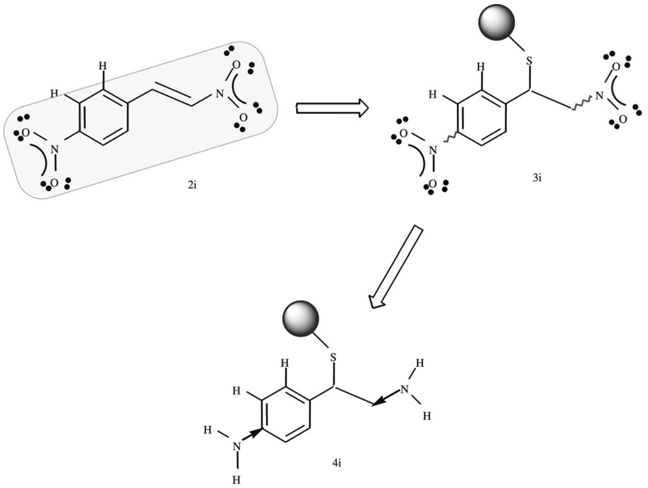


Fig. 2. Illustrating possible models of fluorescence quenching/enhancing in **2i, 3i** and **4i** library intermediates.

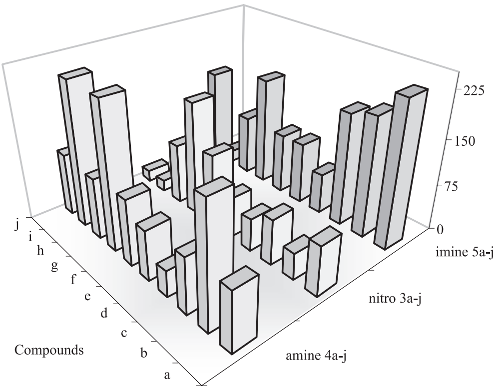


Fig. 3. Influence of ring substituents on the fluorescence intensity of immobilized nitro olefins **3a-j, 4a-j** amines and **5a-j** imines.

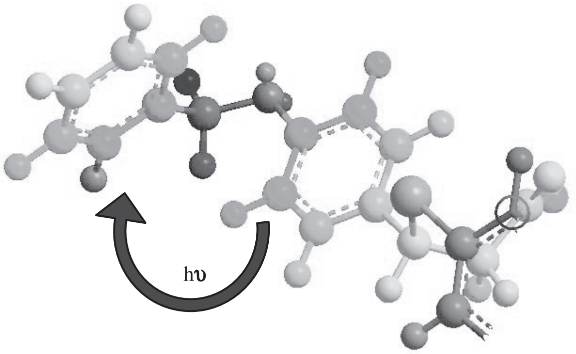


Fig. 4. Quenching by energy transfer between aromatic rings in **3a-e** library members.

Table 2. Spectral characteristics of **3a-j**, **4a-j** and **5a-j** libraries

Compounds	**3** (-NO$_2$)		**4** (-NH$_2$)		**5** (-N=C-Ph)	
	λ_{em}	I_f	λ_{em}	I_f	λ_{em}	I_f
a	530	266	540	364	530	580
b	530	144	540	740	540	480
c	530	246	520	340	525	445
d	530	175	555	163	560	161
e	530	218	555	310	560	248
f	561	390	555	412	560	246
g	460	615	535	900	515	440
h	555	330	544	380	545	245
i	650	61	555	896	660	50
j	650	54	535	388	530	376

ing groups in positions R$_2$ and R$_3$ (see Table 1). In Table 2, the influence of the nitro-reduction and the imine-reaction with introduction of the R$_4$ substituent on the fluorescence intensities of the different library members is shown. We can observe that the general trend is followed: nitro-compounds are less fluorescent than the corresponding amine- or imine- compounds. In Table 2 the spectral characteristics of these materials are summarized.

Binding properties towards Pb(II) and Cu(II) ions

In order to evaluate the binding properties of **3(a-j), 4(a-j)** and **5(a-j)** towards Pb(II) and Cu(II) ions, the array of materials was screened for its metal ion binding capacity by batch method, treating the above mentioned materials with the metal ions at room temperature and mild reaction conditions. The influence of pH on the sorption of Cu(II) and Pb(II) was studied by varying the pH of the mixture from 2 to 8, using buffer solutions. Typical sorption profiles for Cu(II) and Pb(II) by the **5g** library member are shown in Figure 5. Maximum Cu(II) and Pb(II) uptake happened at pH 7.5-8. Similar trends were observed for the rest of the **5a-j** library members. A pH 6 was selected in futher experiments as a compromise between a relatively high retention and prevention of metal ion hydrolysis at elevated pHs. At pH 6, Cu(II) and Pb(II) sorption percentages by the **5a-j** library members are gathered in Table 3. Focusing on these data, it appears that at pH 6, ca. 50% sorption of Pb(II) ions was achieved when using the **5g** library member while lower values were observed with the remaining materials. In the case of Cu(II) ions sorption values around 50% were obtained with **5g** and **5j** being the uptake of Cu(II) ions higher than that of Pb(II) with most of the remaining **5a-i** materials, thus indicating the higher affinity of Cu(II) ions by the chelating motif on the solid phases.

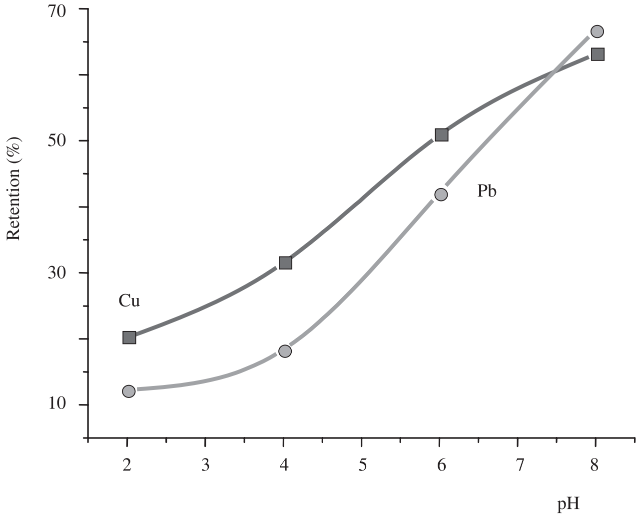


Fig. 5. pH influence on the Cu(II) and Pb(II) uptake using **5g** as sorbent.

These results also suggest the important role of the aromatic ring substituents: the presence of -OCH$_3$ groups in *meta-* and *para-* positions seemed to favor the interaction between the metal ions and the binding positions (*S* and *N* atoms, Scheme 1) while the presence of bulky groups (e.g. –OCH$_2\Phi$) seemed to restrict the accessibility of the metal ions to the –S- and –*N*– binding sites.

Sensing properties towards Pb(II) and Cu(II) ions

Cu(II) and Pb(II) binding to **5a-j** materials was studied as a function of their fluorescence quenching/enhancement efficiency. These materials were contacted for 12h with the corresponding metal solution at pH 6, after which the solids were removed, packed into a conventional flow cell and the fluorescence spectra recorded. Fluorescence intensity and spectral characteristics of raw **5a-j** imines after their interaction with

Table 3. Pb(II) and Cu(II) sorption by **5a-j** library. pH 6.

Library member 5	% Sorption Pb(II)	Standard Deviation (σ)*	% Sorption Cu(II)	Standard Deviation (σ)*
a	32.0	0.14	39.0	0.05
b	30.4	0.10	38.2	0.03
c	30.8	0.08	40.1	0.05
d	36.2	0.10	44.3	0.06
e	30.4	0.11	36.8	0.05
f	16.0	0.03	26.0	0.06
g	**50.4**	0.21	**50.1**	0.10
h	28.8	0.05	35.2	0.05
i	32.0	0.13	40.5	0.06
j	29.3	0.09	**53.5**	0.10

Table 4. Spectral characteristics of **5a-j** library after reaction with Cu(II) and Pb(II). pH=6, 12 h, ultrasonic.

Material	[Cu(II)]		[Pb(II)]	
5	λ_{em}	I_f	λ_{em}	I_f
a	535	22	530	42
b	535	30	535	54
c	535	24	525	84
d	555	0	555	0
e	555	0	560	0
f	560	0	560	0
g	560	0	560	0
h	560	0	560	0
i	535	16	534	33
j	515	40	520	75

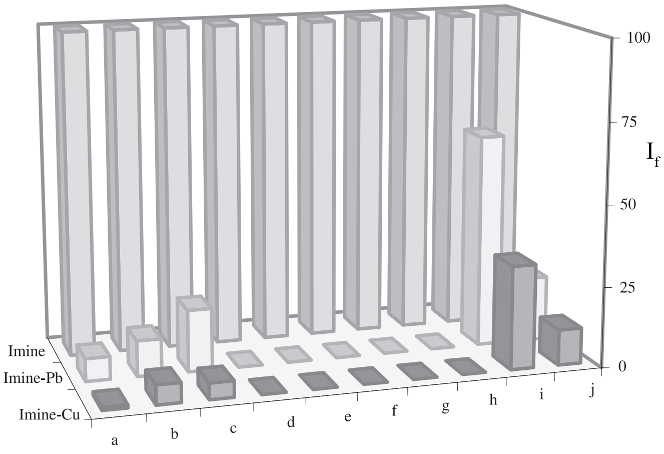


Fig. 6. Fluorescence intensity of raw **5a-j** imines after their interaction with Pb(II) and Cu(II) ions.

Cu(II) and Pb(II) are illustrated in Figure 6 and Table 4. As expected, the fluorescence of all materials was quenched by both metal ions, indicating a typical behavior of paramagnetic and heavy metals, respectively. The quenching of the fluorescence by paramagnetic metal ions, such as Cu(II) having unpaired d-electrons (d^9), is a well-known phenomenon. Quenching by Cu(II) ions may be explained by electron transfer and/or energy transfer to low-lying metal centred excited states might well account for explaining the efficient quenching of the singlet excited state of luminophors in **5a-j** materials. On the other hand, fluorescence quenching by closed-shell heavy metal ions, such as Pb(II), have been explained by non-fluorescent complex formation followed by rapid intersystem crossing. However, the quenching rates are, in these cases, much lower compared to those of paramagnetic metal ions, which evidences the efficient quenching of imines **5a-j** by Cu(II) compared to lower quenching by Pb(II) ions (see Figure 6).

Conclusions

Concluding, phenyl ethyl amines receptors bound to PS-thiophenol resins were synthesized. The fluorescence spectra of intermediates and products provided evidence for the progress of the ongoing structural changes, demonstrating the efficacy of the direct fluorescence measures on solid phase. The study of analytical potential of these materials reveals that resins of imine type (**5i, 5j**) present the best properties. The presence of $-OCH_3$ groups in *meta*- and *para*- positions seem to favor the interaction between the metal ions and the binding positions (S and N atoms) while the presence of bulky groups (e.g. $-OCH_2\Phi$) or competing binding groups (e.g.$-NH_2$) seem to restrict the accessibility of the metal ions to the *–S-* and *–N–* binding sites. Although our work solely describes measurements of copper and lead, application for immobilization and analysis of other metal ions can be envisaged. The results presented in this paper will undoubtedly form the foundations for future approaches capable of monitoring transition metal ions in real-time and real-space.

Experimental

Materials

The PS-thiophenol (1.54 mmol/g) resins were purchased from Argonaut. All other reagents, if not specified, were purchased from Aldrich. All other chemicals, buffers and solvents were of analytical reagent grade and were used without further purification. All aqueous solutions were prepared using deionized water. Standard solutions of Cu(II) and Pb(II) at different concentrations were prepared in the buffer solution.

Instrumentation

All fluorescence intensity measurements were made with a Shimadzu RF-5301 PC spectrometer which has a xenon discharge excitation source (pulse width at peak half-height < 10 μs). The 3 nm slit width for both excitation and emission intensities were used. Instrumental parameters and processing data are controlled by the Fluorescence Data manager software. A Hellma Model 176.52 flow cell (25 μL) was used. Beads were washed free of any starting materials and solvents and were packed into the flow-through cell. Measures of fluorescence intensity were obtained directly from the resin beads. pH measurements were made with an Orion Model 710A pH/ISE Meter. Lead and copper were estimated by Atomic Absorption spectrometer using a Varian Spectrometer AA-5 model with acetylene-air flame. Mass spectra were obtained on Agilent 1100 Series LC/MSD Trap 9. Combinatorial Chemistry was carried out in a Quest Reactor Argonaut model SLN-210. Melting points were determined on an Electrothermal 88629 apparatus. Infrared (IR) spectra were taken on a Perkin Elmer FT-IR 1600 spectrometer. ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian Mercury 200 MHz Spectrometer in $CDCl_3$ with TMS as internal standard.

General procedure for protection of phenol groups

To a solution of 2, 3 or 4-hydroxybenzaldehyde (5.0 g, 40 mmol), K_2CO_3 (6.8 g, 49.3 mmol) in dry DMF (20 mL), benzyl bromide (5.26 mL, 44 mmol) were added. The mixture was stirred for 3 h at RT after which the reaction mixture was quenched with water (50 mL). The organic phase was extracted with CH_2Cl_2 (3 × 20 mL) and dried over anhydrous sodium sulfate. The clear solution was concentrated under low pressure to get the solids **1a-j.** The crude products were chromatographed trough silica-gel with ethyl acetate and ethyl ether (1:1) to get pure solids.

4-Benzyloxy-benzaldehyde (1a): (Yield, 74.2%). Mp 71-74 ^{0}C. IR (KBr): 3024 (C-H), 2828, 2743 (C-H), 1687 ((C=O), 1600 (C=C), 1259, 1018 (C-O-C) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.85 (s, 1H, CH$\underline{O}$), 7.81(d, *J* = 8.8 Hz, 2H, Ar-H$_b$) 7.40-7.35 (m, 5H, Ar-H), 7.05 (d, *J* = 8.8 Hz, 2H, H$_c$) 5.11 (s, 2H, O-C$\underline{H}_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 190.8, 163.1, 136.0, 131.9, 130.7, 128.7, 128.3, 127.5, 115.1, 70.2. EIMS *m/z* [M$^+$] 212 (7), 91 (100).

3-Benzyloxy-benzaldehyde (1b): (Yield, 78.1%). Mp 57-60 ^{0}C. IR (KBr): 3071, 3030 (C=C-H); 2935(C-H); 2866), 2730 (CHO); 1694 ((C=O); 1592 (C=C); 1266, 1024 (C-O-C) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.78 (s,1H, CH$\underline{O}$), 7.46-6.91 (m, 8H, Ar-H), 5.12 (s, 2H, O-C$\underline{H}_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 192.0, 159.3, 137.8, 136.3, 136.1, 128.7, 128.5, 128.2, 127.5, 123.7, 122.2, 113.2, 70.2. EIMS *m/z* [M$^+$] 212 (9), 91 (100).

2-Benzyloxy-benzaldehyde (1c): (Yield, 73.9%). Mp 59-62 ^{0}C. IR (KBr): 3070, 3025 (C-H), 2863, 2760 (C-H), 1690 (C=O), 1598 (C=C), 1240, 1015 (C-O-C) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.53 (s,1H, C$\underline{H}$O), 7.82-6.93 (m, 9H, Ar-H), 5.10 (s, 2H, O-C$\underline{H}_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 189.6, 1601.0, 136.0, 135.9, 128,7, 128.3, 128.2, 127.7, 127.6, 127.2, 125.0, 120.9, 113.0, 70.3. EIMS *m/z* [M$^+$] 212 (9), 91 (100).

3-Benzyloxy-4-methoxy-benzaldehyde (1d): (Yield, 67.0%). Mp 61-64 ^{0}C. IR (KBr): 3025, 2929 (C=C-H), 2833 ($\underline{\text{C-H}}$O), 2730 ($\underline{\text{C-H}}$O), 1682 (C=O), 1587 (C=C), 1266, 1015 (C-O-C) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.78 (s, 1H, C$\underline{H}$O), 7.46-6.91 (m, 8H, Ar-H), 5.12 (s, 2H, O-C$\underline{H}_2$), 3.88 (s, 3H, O-C$\underline{H}_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 190.3, 154.6, 148.3, 135.9, 129.6, 128.3, 127.8, 126.6, 111.1, 110.5, 70.6, 56.0. EIMS *m/z* [M$^+$] 242 (11), 91 (100).

4-Benzyloxy-3-methoxy-benzaldehyde (1e): (Yield, 72.0%). Mp 62-65 ^{0}C. IR (KBr): 3063 (C=$\underline{\text{C-H}}$), 3030 (C=$\underline{\text{C-H}}$), 2936 (C-H), 2865 (O$\underline{\text{C-H}}$), 2740 (O$\underline{\text{C-H}}$), 1680 (C=O), 1586 ($\underline{\text{C=C}}$), 1268,1025 (C-O-C) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.79 (s,1H, C$\underline{H}$O), 7.40-7.33 (m, 8H, Ar-H), 5.18 (s, 2H, O-C$\underline{H}_2$), 3.87 (s, 3H, O-C$\underline{H}_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 190.8, 153.5, 149.9, 130.2, 128.6, 128.3, 128.1, 127.2, 126.5, 112.3, 109.3, 70.7, 55.9. EIMS *m/z* [M$^+$] 242 (14), 91 (100).

General procedure for derivatives of (E)-1-(2-nitrovinyl) benzene

To a solution of benzaldehyde (2.5 g, 23.6 mmol) in acetic acid (15 mL), ammonium acetate (1.9 g, 24.6 mmol) and nitromethane (6.56 mL, 7.39 g, 121.1 mmol) were added. The mixture was refluxed for 30 minutes at constant stirring and then cooled down. The solid formed was filtered under vacuum, washed with ethyl ether (2 × 20 mL) and re-dissolved in CH_2Cl_2 (20 mL). The solution was dried over anhydrous sodium sulfate. Finally, the organic phase was filtered and the excess of solvent was eliminated at reduced pressure to give a yellow solid 2.578 g (73.4%. yield).

(E)-1-((4-(2nitrovinyl)phenoxy)methyl)benzene (2a): (Yield, 75.2%). Mp 121-125 ^{0}C. IR (KBr): 3101, 3036 (C=C-

H); 2942, 2876 (C-H); 1624, 1598 (C=C); 1512, 1338 (C-NO$_2$); 1248, 1002 (C-O-C) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.96 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.50 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.48 (d, *J* = 8.0 Hz, 2H, H$_a$);7.46-7.36 (m, 5H, Ar-H); 7.02 (d, *J* = 8.0 Hz, 2 H, H$_b$); 5.11 (s, 2H, OCH$_2$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 162.1, 138.9, 136.0, 135.1, 131.2, 128.3, 127.5, 122.8, 115.8, 70.2. EIMS *m/z* [M^{+}] 255 (9), 91 (100).

(E)-1-((3-(2nitrovinyl)phenoxy)methyl)benzene (2b): (Yield, 70.3%). Mp 93-97 ^{0}C. IR (KBr): 3115, 3050 (C=C-H); 2934, 2876 (C-H); 1635, 1588 (C=C); 1497, 1338 (C-NO$_2$); 1237, 1010 (C-O-C) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.92 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.52 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.41-7.30 (m, 6H, Ar-H); 7.14-7.01 (m, 3H, Ar-H); 5.07 (s, 2H, OCH$_2$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 159.3, 139.0, 137.3, 136.3, 131.4, 130.7, 130.5, 128.7, 128.3, 127.6, 122.1, 118.8, 115.0, 70.2. EIMS *m/z* [M^{+}] 255 (15), 91 (100).

2-benzyloxy-β-nitroestyrene (2c): (Yield, 57.7%). Mp 71-75 ^{0}C. IR (KBr): 3152, 3065, 3028 (C=C-H); 2942, 2884 (C-H); 1626, 1598 (C=C); 1508, 1327 (C-NO$_2$); 1241, 999 (C-O-C) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.17 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.83 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.46-7.36 (m, 7H, Ar-H); 7.04-6.99 (m, 2H, Ar-H); 5.19 (s, 2H, OCH$_2$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 158.5, 138.3, 135.8, 135.4, 133.4, 132.4, 128.9, 128.7, 128.5, 127.7, 127.4, 121.4, 119.4, 112.8, 70.7. EIMS *m/z* [M^{+}] 255 (4), 118 (26), 91 (100).

3-benzyloxy-4-methoxy-β-nitroestyrene (2d): (Yield, 76.1%). Mp 128-132 ^{0}C. IR (KBr): 3106, 3028 (C=C-H); 2936, 2886 (C-H); 1624, 1595 (C=C); 1510, 1333 (C-NO$_2$); 1265, 1003 (C-O-C) cm^{-1}. ^{1}H RMN (200 MHz, CDCl$_3$): δ 7.90 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.43 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.44-7.31 (m, 5H, Ar-H); 7.19 (dd, *J* = 8.4, 1.6 Hz, 1H, H$_b$); 7.03 (d, *J* = 1.6 Hz, 1H, H$_a$); 6.92 (d, *J* =8.4 Hz, 1H, H$_h$); 5.07 (s, 2H, OCH$_2$); 3.07 (s, 3H, OCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 153.8, 148.6, 139.3, 136.3, 135.1, 128.7, 128.6, 128.3, 127.3, 124.9, 122.7, 113.2, 111.8, 71.2, 56.1. EIMS *m/z* [M^{+}] 285 (6), 91 (100).

4-benzyloxy-3-methoxy-β-nitroestyrene (2e): (Yield, 71.6%). Mp 122-125 ^{0}C. IR (KBr): 3106, 3049, 3000 (C=C-H); 2943, 2872 (C-H); 1631, 1595 (C=C); 1510, 1333 (C-NO$_2$); 1262, 1028 (C-O-C) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.94 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.51 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.45-7.25 (m, 5H, Ar-H); 7.10 (dd, *J* = 8.2, 2.2 Hz, 1H, H$_a$); 7.02 (d, *J* = 2.2 Hz, 1H, H$_b$); 6.91 (d, *J* = 8.6 Hz, 1H, H$_h$); 5.21 (s, 2H, OCH$_2$); 3.92 (s, 3H, OCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 151.9, 150.0, 139.3, 136.1, 135.2, 128.7, 128.2, 127.2, 124.4, 123.1, 113.4, 110.8, 70.9, 56.1. EIMS *m/z* [M^{+}] 285 (8), 91 (100).

4-methoxy-β-nitroestyrene (2f): (Yield, 37.9%). Mp 85-88 ^{0}C. IR (KBr): 3112 (C=C-H); 2941, 2901, 2839 (C-H); 1622, 1602 (C=C); 1514, 1327 (C-NO$_2$); 1252, 1031 (C-O-C) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.97 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.51 (d, *J* = 13.6 Hz, 1H, CH=C-NO$_2$); 7.45 (d, *J* = 9.0 Hz, 2H, H$_a$); 6.95 (d *J* = 9.0 Hz, 2H, Ar-H$_b$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 163.0, 139.1, 135.0, 131.2, 122.6, 114.9, 55.5. EIMS *m/z* [M^{+}] 179 (53), 132 (100).

3,4-dimethoxy-β-nitroestyrene (2g): (Yield, 69.3%). Mp 140-144 ^{0}C. IR (KBr): 3126, 3044, 3003 (C=C-H); 2948, 2839 (C-H); 1626, 1595 (C=C); 1514, 1340 (C-NO$_2$); 1269, 1017 (C-O-C) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.98 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.54 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$); 7.18 (dd, *J* = 8.2, 2.2 Hz, 1H, H$_a$); 7.01 (d, *J* = 2.2 Hz, 1H, H$_e$); 6.93 (d, *J* = 8.4 Hz, 1H, H$_b$); 3.94 (s, 6H, OCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 152.9, 149.6, 139.3, 135.2, 124.6, 122.8, 111.4, 110.3, 56.1, 56.0. EIMS *m/z* [M^{+}] 209 (100).

β-nitroestyrene (2h): (Yield, 74.0%). Mp 55-58 ^{0}C. IR (KBr): 3106, 3035 (C=C-H); 2964 (C-C-H); 1627, 1602 (C=C); 1514, 1340 (C-NO$_2$) cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.99 (d, *J* = 13.6 Hz, 1H, CH=CH-NO$_2$), 7.58 (d, *J* = 13.6 Hz, 1H, , CH=CH-NO$_2$), 7.56-7.43 (m, 5H, Ar-H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 139.1, 137.1, 132.2, 130.1, 129.4, 129.2. EIMS *m/z* [M^{+}] 149 (46), 77 (100).

4-nitro-β-nitroestyrene (2i): (Yield, 92.1%). Mp 193-197 ^{0}C. IR (KBr): 3112, 3058 (C=C-H); 1636, 1602 (C=C); 1531, 1340 (C-NO$_2$) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.28 (d, *J* = 8.8 Hz, 2H, H$_b$); 8.18 (s, 2H, CH=CH-NO$_2$); 8.03 (d, *J* = 8.8 Hz, 2H, H$_{a;}$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 148.9, 140.7, 136.6, 136.6, 130.5, 124.0. EIMS *m/z* [M^{+}] 194 (100).

2-fluor-β-nitroestyrene (2j): (Yield, 74.7%). Mp 55-57 ^{0}C. IR (KBr): 3160, 3051 (C=C-H); 2962, 2928 (C-H); 1636 (C=C); 1507, 1347 (C-NO$_2$), 1211 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.05 (d, *J* = 13.8 Hz, 1H, CH=CH-NO$_2$), 7.73 (d, *J* = 13.8 Hz, 1H, CH=CH-NO$_2$), 7.55-7.44 (m, 2H, H$_{a,e}$), 7.28-7.14 (m, 2H, Hb,f). ^{13}C NMR (50 MHz, CDCl$_3$): δ 164.4, 159.3, 139.49, 139.2, 133.8, 133.6, 132.5, 131.4, 131.4, 125.1, 125.0, 118.6, 118.3, 116.9, 116.4. EIMS *m/z* [M^{+}] 167 (11), 91 (100).

(1-(4-(metoxy)phenyl)-2-nitroethyl)-sulfane: To a solution of tiophenol (4mL) in CH$_2$Cl$_2$ (20 mL), 4-methoxy-β-nitroestyrene (3.0 g, 16.79 mmol) was added. The mixture was cooled at 0^{0}C and 4 drops of isopropylcyclohexylamine were added. After the addition, the mixture was stirred at RT for 1 h. The organic phase was washed with water (3 × 70 mL), a solution of hydrochloride acid (3 × 70 mL) and finally water (3 × 70mL).The organic phase was dried over anhydrous Na$_2$SO$_4$ and the excess of solvent was eliminated at reduced pressure to get a white solid (3.97g, 82%). Mp. 96^{0}C. IR (KBr): 3070, 3020, 3021, 2920, 2890, 1610 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.30 (s, 5H, Ar-H), 7.10 (d, 2H, J=8 Hz, Ar-H), 6.70 (d, 2H, J = 8 Hz, Ar-H), 4.80 (m, 3H, HC-CH$_2$), 3.70 (s, 3H, CH$_3$-O). EIMS *m/z* [M^{+}] 289 (31).132 (100).

General procedure for coupling of nitroolefins to solid phase (3a-j)

The PS-thiophenol resin (200 mg, 0.274 mmol) was swollen in CH_2Cl_2 (15mL) and the nitro-olefins (0.548 mmol) and 4 drops of isopropylcyclohexylamine were added. The mixture was stirred at RT for 30 min. The resins were filtered and washed with CH_2Cl_2 (3´25 mL), H_2O (3´25 mL), MeOH (3´25 mL) and CH_2Cl_2 (3´25 mL). The solids were dried under reduced pressure. The MS data were obtained to follow the general method to liberate the products (nitroolefins).

PS-(1-(4-(benzyloxy)phenyl)-2-nitroethyl)-sulfane (3a): (Yield, 95%). IR (KBr): 3420 (N-H), 3051, 3021 (C=C-H); 2920, 2870 (C-H); 1670 (N-C=O), 1607, (C=C); 1558, 1373 (NO_2); 1247, 1020 (C-O-C) cm^{-1}. FI 266 au, E_{em}= 680 nm, (E_{ex}=465 nm). EIMS *m/z* [M$^+$] 255 (9), 91 (100).

PS-(1-(3-(benzyloxy)phenyl)-2-nitroethyl)-sulfane (3b): (Yield, 92%). IR (KBr): 3417 (N-H), 3061, 3023 (C=C-H); 2920, 2870 (C-H); 1671 (N-C=O), 1598, (C=C); 1551, 1365 (NO_2); 1265, 1021 (C-O-C) cm^{-1}. FI 140 au, E_{em}= 530 nm, (E_{ex}=465 nm). EIMS *m/z* [M$^+$] 255(M$^+$, 15), 91(100).

PS-(1-(2-(benzyloxy)phenyl)-2-nitroethyl)-sulfane *(*3c): (Yield, 95%). IR(KBr): 3408 (N-H), 3051, 3023 (C=C-H); 2910, 2845 (C-H); 1659 (N-C=O), 1593, (C=C); 1547, 1369 (NO_2); 1229, 1014 (C-O-C) cm^{-1}. FI 246 au, E_{em}= 530 nm, (E_{ex}=465 nm). EIMS *m/z* [M$^+$] 255 (4), 118 (26), 91 (100).

PS-(1-(3-(benzyloxy)-4-metoxyphenyl)-2-nitroethyl)-sulfane (3d): (Yield, 92%). IR (KBr): 3408 (N-H), 3056, 3032 (C=C-H); 2920, 2850 (C-H); 1668 (N-C=O), 1603, (C=C); 1555, 1365 (NO_2); 1257, 1019 (C-O-C) cm^{-1}. FI 175 au, E_{em}= 530 nm, (E_{ex}=465 nm). EIMS *m/z* [M$^+$] 285 (6), 91 (100).

PS-(1-(4-(benzyloxy)-3-metoxyphenyl)-2-nitroethyl)-sulfane (3e): (Yield, 96%). IR (KBr): 3412 (N-H), 3055, 3009 (C=C-H); 2917, 2844 (C-H); 1674 (N-C=O), 1600, (C=C); 1555, 1371 (NO_2); 1261, 1018 (C-O-C) cm^{-1}. FI 178 au, E_{em}= 530 nm, (E_{ex}=465 nm). EIMS *m/z* [M$^+$] 285 (8), 91 (100).

PS-(1-(3,4-dimetoxy)phenyl)-2-nitroethyl)-sulfane (3f): (Yield, 92%). IR (KBr): 3420 (N-H), 3057, 3013 (C=C-H); 2922, 2845 (C-H); 1678 (N-C=O), 1595, (C=C); 1559, 1355 (NO_2); 1260, 1018 (C-O-C) cm^{-1}. FI 615 au, E_{em}= 460 nm, (E_{ex}=395 nm). EIMS *m/z* [M$^+$] 209 (100).

PS-(1-(2-(fluor)phenyl)-2-nitroethyl)-sulfane (3g): (Yield, 96%). IR (KBr): 3418 (N-H), 3057, 3022 (C=C-H); 2925, 2845 (C-H); 1674 (N-C=O), 1602, (C=C); 1555, 1366 (NO_2); cm^{-1}. FI 54 au, E_{em}= 625 nm, (E_{ex}=550 nm). EIMS *m/z* [M$^+$] 167 (11), 91 (100).

PS-(1-(4-(metoxy)phenyl)-2-nitroethyl)-sulfane (3h): (Yield, 90%). IR (KBr): 3419 (N-H), 3047, 3024 (C=C-H); 2921, 2901 (C-H); 1683 (N-C=O), 1610, (C=C); 1560, 1370 (NO_2); 1254, 1028 (C-O-C) cm^{-1}. FI 390 au, E_{em}= 530 nm, (E_{ex}=465 nm). EIMS *m/z* [M$^+$] 179 (53), 132 (100).

PS-(1-(phenyl)-2-nitroethyl)-sulfane (3i): (Yield, 94%). IR (KBr): 3411 (N-H), 3047, 3021 (C=C-H); 2909, 2848 (C-H); 1671 (N-C=O), 1602, (C=C); 1552, 1359 (NO_2); 1269, 1017 (C-O-C) cm^{-1}. FI 330 au, E_{em}= 530 nm, (E_{ex}=465 nm). EIMS *m/z* [M$^+$] 149 (46), 77 (100).

PS-(1-(4-(nitro)phenyl)-2-nitroethyl)-sulfane (3j): (Yield, 95 %). IR (KBr): 3409 (N-H), 3112, 3022 (C=C-H); 2916, 2845 (C-H); 1678 (N-C=O), 1599, (C=C); 1559, 1339 (NO_2); cm^{-1}. FI 61 au, E_{em}= 650 nm, (E_{ex}=465 nm). EIMS *m/z* [M$^+$] 194(M$^+$, 100).

General Methods for reduction of nitro group

Method A (LiAlH$_4$)

The supported nitrolefins **5a-j** (200 mg, 0.274 mmol) were swollen during 15 minutes in dried THF (15 mL) and cooled to 3 ^{0}C. A solution of $LiAlH_4$ (1mL, 1 mol/L) in diethyl ether was then added. The mixture was filtered and another 1 mL of $LiAlH_4$ was added and kept for 24 h at RT. The resins were filtered and washed with THF (3 × 25 mL). THF:HCl (10%) in proportion 9:1 (3 × 25 mL), THF:TEA 9:1 (3 × 25 mL) and diisopropylethylamine (3 × 10 mL). Finally, the solids were dried under reduced pressure.

Method B (Zn/HCl)

The supported nitrolefins **5a-j** (200 mg, 0.274 mmol) were swollen during 15 min in CH_2Cl_2 (15 mL) and AcOH (2 mL) and powder Zn (141 mg, 2.15 mmol) were added. Then, concentrated HCl (2 mL) was added dropwise and the solution was stirred overnight at RT. The resin was filtered and washed with CH_2Cl_2 (3 × 25 mL), H_2O (3 × 25 mL), MeOH (3 × 25 mL) and CH_2Cl_2 (3 × 25 mL). The solids were dried under reduced pressure. The resulting reduction materials were used for the next step.

Synthesis of Imines:

The supported amines **6a-j** (200 mg, 0.24 mmol) were swollen during 15 min in THF:DMSO 4:1 (15 mL) and benzaldehyde (127 mg, 1.2 mmol) and sodium sulfate anhydrous (1.0 g, 7 mmol) was added. The solution was stirred overnight at RT**.** The resins were filtered and washed with THF (3 × 25 mL), H_2O (3 × 25 mL), MeOH (3 × 25 mL) and CH_2Cl_2 (3 × 25 mL). The solids were dried under reduced pressure.

7a: (Yield 92%). IR (KBr): 3419 (N-H), 3056, 3021 (C=C-H); 2920, 2870 (C-H); 1681 (C=N), 1654 (N-C=O), 1600, (C=C); 1247 (C-O-C) cm^{-1}. FI 580 au, E_{em}=540 nm, (E_{ex}=465 nm).

7b: (Yield 90%). IR (KBr): 3417 (N-H), 3054, 3023 (C=C-H); 2922, 2866 (C-H); 1681 (C=N), 1658 (N-C=O), 1598, (C=C); 1265 (C-O-C) cm^{-1}. FI 480 au, E_{em}=540 nm, (E_{ex}=465 nm).

7c: (Yield 89%). IR (KBr): 3418 (N-H), 3051, 3023 (C=C-H); 2920, 2845 (C-H); 1685 (C=N), 1659 (N-C=O), 1593, (C=C); 1229 (C-O-C) cm^{-1}. FI 445 au, E_{em}= 525 nm, (E_{ex}= 465 nm).

7d: (Yield 90%). IR (KBr): 3418 (N-H), 3056, 3022 (C=C-H); 2921, 2850 (C-H); 1682 (C=N), 1655 (N-C=O), 1603, (C=C); 1257 (C-O-C) cm^{-1}. FI 161 au, E_{em}= 560 nm, (E_{ex}= 465 nm).

7e: (Yield 90%). IR (KBr): 3417 (N-H), 3055, 3019 (C=C-H); 2916, 2843 (C-H); 11682 (C=N), 1654 (N-C=O), 1600, (C=C); 1262 (C-O-C) cm^{-1}. FI 248 au, E_{em}= 560 nm, (E_{ex}=465 nm).

7f: (Yield 92%). IR (KBr): 3419 (N-H), 3054, 3020 (C=C-H); 2921, 2846 (C-H); 1683 (C=N), 1653 (N-C=O), 1610, (C=C); 1250 (C-O-C) cm^{-1}. FI 246 au, E_{em}= 560 nm, (E_{ex}=465 nm).

7g: (Yield 94%). IR (KBr): 3420 (N-H), 3057, 3017 (C=C-H); 2920, 2845 (C-H); 1681 (C=N), 1658 (N-C=O), 1598, (C=C); 1250 (C-O-C) cm^{-1}. FI 440 au, E_{em}= 515 nm, (E_{ex}=465 nm).

7h: (Yield 88%). IR (KBr): 3417 (N-H), 3057, 3023 (C=C-H); 2920, 2848 (C-H); 1681 (C=N), 1656 (N-C=O), 1599 (C=C) cm^{-1}. FI 245 au, E_{em}= 545 nm, (E_{ex}=465 nm).

7i: (Yield 90%). IR (KBr): 3420 (N-H), 3122, 3022 (C=C-H); 2916 (C-H); 1680 (C=N), 1658 (N-C=O), 1599, (C=C) cm^{-1}. FI 20 au, E_{em}= 560 nm, (E_{ex}=465 nm).

7j: (Yield 89%). IR (KBr): 3418 (N-H), 3057, 3022 (C=C-H); 2922, 2845 (C-H); 1680 (C=N), 1654 (N-C=O), 1600 (C=C) cm^{-1}. FI 580 au, E_{em}= 376 nm, (E_{ex}=465 nm).

General Method for liberate the products from the resin:

The supported sulfanes **3a-j** (200 mg), were swollen during 15 min in THF:H_2O 4:1 (5 mL) and then a solution of potassium periodate (280 mg, 1.23 mmol) in water (1 mL) was added. The mixtures were refluxed during 18 h. The resins were filtered and washed with THF (3 × 25 mL), H_2O (3 × 25 mL), MeOH (3 × 25 mL) and CH_2Cl_2 (3 × 25 mL). Dry toluene and sodium carbonate (1.5 g, 14 mmol) was added the solids and the mixtures were refluxed over night. The mixtures were filtered and washed with CH_2Cl_2 (3 × 5 mL). The aliquots were combined and the excess of solvent was eliminated under reduced pressure to get the products. The crudes were redisolved in methanol (1 mL) and analyzed by EIMS.

General Method for evaluate sorption percentage

50 mg of the corresponding material were incubated with the different metal stock solutions (10 mL, 25 mg L^{-1}) at different pHs. The reaction mixture was subjected to ultrasonic shaking for 12 h after which the concentration of copper and lead in the supernatant was determined by atomic absorption spectroscopy.

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