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Introduction

Covalent organic frameworks (COFs) which possess either 2D or 3D polymeric structures with permanent porosity, are generally formed *via* covalent linkage between various organic moieties and these are widely explored as gas storage materials.¹ A bottom-up chemistry approach has been employed extensively to design similar types of microporous organic polymers like polymers of intrinsic microporosity (PIMs),² conjugated microporous polymers (CMPs)³ or porous organic polymers (POPs).⁴ These materials have found extensive application as heterogeneous catalysis for the synthesis of value added fine chemicals.⁵ The pore size and the surface area of the nanoporous materials are largely depended on the molecular length of the building blocks and the synthesis conditions.⁶ Further, these porous materials can be suitably modified through the incorporation of

Cu(II) anchored nitrogen-rich covalent imine network (Cu^{II}-CIN-1): an efficient and recyclable heterogeneous catalyst for the synthesis of organoselenides from aryl boronic acids in a green solvent⁺

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A new heterogeneous copper catalyst has been synthesized by immobilizing Cu(II) onto the surface of a nitrogen rich porous covalent imine network material CIN-1 and it was characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), EDAX, X-ray photoelectron spectroscopy (XPS), N₂ adsorption–desorption, UV-vis spectroscopy, Fourier transform infrared spectroscopy (FT-IR), thermogravimetric (TGA), and EPR spectroscopic analyses. The material has been successfully used to catalyze the cross-coupling reaction between aryl boronic acids and diphenyldiselenide to synthesize unsymmetrical organoselenides. Due to its high surface area and highly accessible catalytic sites, it shows good to excellent catalytic activity for the C–Se bond forming reaction, which was evident from the high TOF of the catalyst in this reaction. The catalyst was recycled for six repetitive runs without any appreciable loss of catalytic activity suggesting its potential usefulness in C–Se bond forming reaction.

multifaceted functionalities inside the framework.7 Synthesis of these functionalized porous materials is a very fast growing field of research as they have diverse applications in many frontline areas of energy, environment and biomedical research. Incorporation of nitrogen containing functional groups on the surface of porous materials often enhances their stability and catalytic activity. Jiang and co-worker have showed that nitrogen dopped carbon nanotubes (CNTs) can act as an excellent support for metal nanoparticles, which exhibited much better catalytic activity than pristine CNTs for the Heck cross-coupling reaction between iodobenzene and styrene.8 Nitrogen rich covalent triazine framework and magnetic nanomaterials grafted mesoporous polyaniline have been utilized as efficient catalytic supports.9 Recently we have developed a nitrogen rich porous covalent imine networkmaterial CIN-1 through the Schiff-base condensation reaction between 1,4-piperazinedicarbaldehyde and melamine, which was then used as efficient support for palladium to catalyze C-C cross-coupling reactions.¹⁰ With our continued interest in this field, now we have grafted copper at the surface of CIN-1 and explored its catalytic activity for the synthesis of a wide range of carbonheteroatom (C-Se) bond forming reaction.

Carbon–selenium bond forming reactions are of continued interest because of the synthesis of highly potent organoselenium compounds in biomedical research. These compounds possess antiviral, antimicrobial, antioxidant, antihypertensive, antitumor and anticancer activities.¹¹ They also

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[†] Electronic supplementary information (ESI) available: Details of characterisation (FTIR) of CIN-1 and Cu^{II}-CIN-1, ¹H NMR and ¹³C NMR spectral data of all products listed in Table 2. See DOI: 10.1039/c4ra08909j

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R = H, 2-NO₂, 4-CHO, 2-CHO, 4-CO₂Et, 4-Br, 3-CN, 4-OMe etc.

Scheme 1 $\,$ Cu $^{II}\text{-CIN-1}$ catalyzed phenyl selenylation of aryl boronic acids.

have important applications as catalysts¹² and material science.¹³ Hence several methods have been developed for the synthesis of organoselenium compounds. Various transition metals like Pd,14 Ni,15 Fe16 and Cu17 were employed to catalyze the C-Se bond forming reactions of aryl halides/boronic acids and selenol/PhSeNa/diphenyldiselenide for the synthesis of organoselenides. Among the various selenylating reagents, diphenyldiselenide is used because of its relatively higher stability and less toxicity. Synthesis of organoselenides from aryl halides is well-explored compared to boronic acids. Few catalytic systems of Cu^{17b,e-g,i,n} and only one catalytic system of each Fe16 and In18 were employed for the coupling between boronic acids and diphenyldiselenide. But most of the reactions used toxic or expensive ligands, hazardous solvents, microwave irradiation etc. which are not desired in the context of green chemistry.

Herein, we have developed a simple and green method for the synthesis of a series of organoselenides *via* C–Se bond forming cross-coupling reaction between aryl boronic acids and diphenyldiselenide catalyzed by Cu-loaded nitrogen rich CIN-1 (Cu^{II} -CIN-1) in PEG-600 solvent (Scheme 1).

Result and discussion

Synthesis and characterization of CIN-1

The covalent imine network (CIN-1) was synthesized by the reaction of piperazinedicarboxaldehyde with melamine under refluxing condition in DMSO at 180 $^{\circ}$ C under N₂ atmosphere. Then it was characterized by TEM and EDX analyses.

 Cu^{II} -CIN-1 was synthesized by immobilizing $Cu(OAc)_2$ onto the surface of CIN-1 material. $Cu(OAc)_2$ was added to a stirred suspension of CIN-1 in dry acetone at room temperature and then the stirring was continued for 48 h. The solid residue was then filtered and washed with acetone followed by drying at 80 °C to afford the Cu^{II} -CIN-1 catalyst. It was then characterized by the following analyses.

X-ray diffraction

Small angle powder XRD pattern of the sample Cu^{II}-CIN-1 is shown in Fig. 1. A broad peak is obtained at $2\theta = 20-25^{\circ}$ due to amorphous nature of imine network. This result agrees well with the small angle powder XRD pattern of the parent CIN-1 material.¹⁰ Some distinct sharp peaks observed at 2θ values with 10.28, 12.65, 25.1 degrees for Cu^{II}-CIN-1 could be assigned due to presence of crystalline features originated due to the binding of Cu(OAc)₂ at the pore surface.



Fig. 1 XRD analysis of Cu^{II}-CIN-1 material.

TEM analysis

TEM images of the as-synthesized CIN-1 material as well as for the Cu^{II}-CIN-1 material are shown in Fig. 2(a) and (b), respectively. There are some dark spots (shown in red circles) for the Cu^{II}-CIN-1 Fig. 2(b) material throughout the specimen grid, which can be attributed to the presence of Cu in the polymer framework. The EDX pattern of the Cu^{II}-CIN-1 material is shown



Fig. 2 TEM images of (a) CIN-1 and (b) Cu^{II}-CIN-1 material.

in the Fig. 3. Presence of C, N and Cu in the material is evident from this profile. It is to be noted that Cu is present in the specimen grid used for TEM analysis. But EPR and XPS analysis confirm the presence of Cu in the Cu^{II}-CIN-1 material as Cu(II) oxidation state (see below).

Thermal analysis

The quantitative determination of the organic content and the framework stability of the Cu^{II}-CIN-1 sample are obtained from the thermogravimetric analysis (TGA) under N2 flow. TGA curve of Cu^{II}-CIN-1material is shown in Fig. 4. The TGA of this material showed the first weight loss below 100 °C due to desorption of absorbed water. This was followed by a gradual decrease in the weight after 380 °C. Thus this thermal analysis data suggested that Cu^{II}-CIN-1 sample is stable up to 380 °C (Fig. 4).

250 300 350 400 mΤ



Electron paramagnetic resonance spectroscopy

To know the oxidation state of copper in the catalyst, we have carried out the EPR (Electron Paramagnetic Resonance)



Fig. 3 EDAX analysis of the Cu^{II}-CIN-1 material.



Fig. 4 The TGA plot of the Cu^{II}-CIN-1 material.



The XPS data of Cu^{II}-CIN-1 material. Fig. 6



Fig. 7 N₂ sorption analysis of CIN-1(a) and Cu^{II}-CIN-1(b).



Fig. 8 The DRS-UV-visible absorption spectrum of CIN-1 (a) and $\mbox{Cu}^{II}-\mbox{CIN-1}$ material.

spectroscopic analysis for the fresh catalyst for the solid state at room temperature (Fig. 5). The four hyperfine lines of the corresponding spectrum were obtained due to the coupling of the unpaired electron of copper with its nucleus which indicates the presence of copper in its +2 oxidation state in Cu^{II} -CIN-1 catalyst.

X-ray photoelectron spectroscopy (XPS)

The XPS spectrum of the Cu^{II}-CIN-1 catalyst is shown in Fig. 6. The binding energy values 935.6 and 955.8 eV corresponding to the spin orbit splitting components of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ in the +2 oxidation state of copper agrees well with the reported

 Table 1
 Optimization of reaction conditions^a

literature values.¹⁹ There is also a satellite peak present in the XPS spectrum, which is a feature of $2p \rightarrow 3d$ satellite peak of Cu in +2 oxidation state. For pure and uniform Cu²⁺ ions, the intensity ratio of the satellite to the 2p3/2 peak is ordinarily 0.5. For our Cu^{II}-CIN-1 sample the ratio is 0.51 which further reveals that pure Cu(II) specie is present in the sample. Based on the XPS results, the Cu species in the Cu^{II}-CIN-1 is found to be in the +2 oxidation state.

N₂ adsorption-desorption

 $\rm N_2$ sorption analysis revealed the porous nature of CIN-1 and Cu^{II}-CIN-1 materials (Fig. 7). Calculated BET surface area of CIN-1 and Cu^{II}-CIN-1 materials are 605 and 550 m² g⁻¹ respectively. Pore size distribution plots obtained by using NLDFT model suggested the peak pore widths of 1.37 and 1.12 nm, respectively for CIN-1 and Cu^{II}-CIN-1. Respective pore volumes are 0.21 cm³ g⁻¹ and 0.19 cm³ g⁻¹. The decrease in surface area, pore size as well as pore volume reflect the successful loading of bivalent Cu(II) over CIN-1 material.

FT-IR spectroscopy

FT-IR spectrum of Cu^{II}-CIN-1 shows stretching frequencies for imine (C==N) at 1630, 1193 cm⁻¹. The distinct bands related to quadrant (1551 cm⁻¹) and semicircle stretching (1477 cm⁻¹) indicates presence of the triazine ring in the spectrum of CIN-1 material.⁹ Details assignments of FT-IR peaks are given in ESI (Fig. S1†).

UV-vis DRS analysis

The UV-vis absorption spectrum of the CIN-1 and Cu^{II}-CIN-1 catalyst were recorded in diffuse reflectance mode as a BaSO₄



Entry	Base	Solvent	Temp (°c)	Time (h)	$\operatorname{Yield}^{b}(\%)$
1	Cs ₂ CO ₃	DMF	120	10	76
2	Cs_2CO_3	DMSO	120	10	78
3	Cs_2CO_3	PEG-600	120	10	88
4	Cs_2CO_3	H_2O	80	10	—
5	Cs_2CO_3	Toluene	110	10	_
6	Cs_2CO_3	THF	60	10	—
7	K ₂ CO ₃	PEG-600	120	10	88
8	K ₂ CO ₃	PEG-600	100	10	88
9	K ₂ CO ₃	PEG-600	80	10	88
10	K_2CO_3	PEG-600	70	10	78
11	K ₂ CO ₃	PEG-600	80	8	88
12	K_2CO_3	PEG-600	80	6	71
13 ^c	K ₂ CO ₂	PEG-600	80	8	67

^{*a*} Reaction conditions: 4-methoxy phenylboronic acid (1 mmol),diphenyldiselenide (0.5 mmol), K₂CO₃ (1.5 mmol), Cu^{II}-CIN (0.1 mol% of Cu), PEG-600 (5 ml). ^{*b*} Yields refer to those of isolater pure products. ^{*c*} 0.05 mol% of Cu was used.

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disk due to its solubility limitations in common organic solvents. The UV spectra of the extracted CIN-1 (a) and Cu^{II} -CIN-1 (b) are given in Fig. 8. In both case peaks in between 200–350

nm is due to the π - π * transition of the conjugated system present in the covalent imine network. In the case of the Culoaded sample a small hump at around 305-340 nm is

Table 2 Ci	u ^{II} -CIN-1 catalyzed	cross-coupling between	aryl boronics	and diphenyl	diselenide ^a
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R [−] B(OH) ₂ + (PhSe) ₂								
Entry	R	Product	Time (h)	$\mathrm{Yield}^{b}\left(\%\right)$	Ref.			
1		Se	8	88	17g			
2	СНО	Se CHO	9	82	17n			
3	онс	OHC	9	83	17a			
4	EtO ₂ C	EtO ₂ C	10	80	17m			
5	CN	CN Se	9	88	18b			
6	CF ₃	CF ₃	9	84	17g			
7	NO ₂	NO ₂ Se	10	85	17g			
8	Br	Br	10	79	17g			
9	MeO	MeO	8	88	17g			
10		Se	10	85	17b			
11	OMe	OMe	10	79	17m			
12	MeON	MeON	10	85	_			

 a Reaction conditions: boronic acid (1 mmol), diphenyl diselenide (0.5 mmol), K₂CO₃ (1.5 mmol), Cu^{II}-CIN (0.1 mol% of Cu), PEG-600(5 ml). b Yields refer to those of isolater pure products.

present can be attributed due to LMCT. In addition to this, a broad absorption band in between 600–800 nm is observed. This could be attributed to the d-d transition of Cu^{+2} ion.²⁰

Catalytic activity

To optimise the reaction conditions, a series of experiments were carried out with the variation of base, solvent, temperature and time for a representative reaction between 4-methoxy phenyl boronic acid and diphenyldiselenide in presence of 0.1 mol% of Cu in Cu^{II}-CIN-1. The results are summarized in Table 1. Among various solvents like DMF, DMSO, PEG-600, H₂O, toluene and THF, PEG-600 was found to be the best (Table 1, entries 1–7). Both the carbonate base, *i.e.* Cs_2CO_3 and K₂CO₃ showed equal activity for the selenylation reaction. But K_2CO_3 being cheaper and milder than Cs_2CO_3 , it was considered as the choice of base. The best result in terms of yield and time was obtained by carrying out the reaction in PEG-600, in presence of K₂CO₃ at 80 °C for 8 h (Table 1, entry 11). It was also observed that with the decrease of catalyst loading from 0.1 mol% of copper, yield of product also decreases (Table 1, entry 13).

Several diversely substituted aryl boronic acids were subjected for the selenylation reaction using diphenyldiselenide to synthesize a library of organoselenides under the standardised reaction conditions. The results are tabulated in Table 2. Both electron-donating and electron-withdrawing group substituted aryl boronic acids underwent phenyl selenylation reaction smoothly. Various electron withdrawing substituents like CHO, CO_2Et , CN, CF_3 and NO_2 were compatible (Table 2, entries 2–7).

Base-sensitive functionalities (CO₂Et, CN) were remained intact under the mild basic reaction conditions (Table 2, entries 4 and 5). Halide containing aryl boronic acid, *i.e.* 4-bromophenyl boronic acid produced halide containing organoselenide (Table 2, entry 8). Electron donating group *i.e.*, OMe containing aryl boronic acids were also reacted with diphenyldiselenide without any difficulties (Table 2, entry 9, 10 and 12). Two napthyl boronic acids produced two analogous of 5-LOX (Lipoxygenase) inhibitor^{11e} after phenyl selenylation (Table 2, entries 10 and 11). Heteroaryl substituted boronic acid *i.e.*



Fig. 9 EPR spectrum of used Cu^{II}-CIN-1 catalyst.

2-methoxypyridine-5-boronic acid upon phenyl selenylation produced heteroaryl-aryl selenide (Table 2, entry 12).

To know the oxidation state of copper after the reaction in Cu^{II} -CIN-1, we have performed EPR (Electron Paramagnetic Resonance) spectroscopic analysis of the used catalyst in its solid state at room temperature (Fig. 9), which also showed similar type of spectrum with the fresh catalyst (Fig. 5). Hence, it is evident that the oxidation state of copper remains unchanged after the reaction.

Recycling of catalyst

For a heterogeneous catalyst, it is important to examine its ease of separation from the reaction mixture, recoverability and reusability. The reusability of the Cu^{II} -CIN-1 catalyst was investigated for the representative C–Se cross coupling reaction between 4-methoxy phenylboronic acid and diphenyldiselenide (Table 2, entry 9). After the first cycle of the reaction, catalyst was recovered by simple filtration through a sintered glass-bed (G-4) and washed with ethanol followed by acetone which was then dried in an oven at 100 °C. The performance of the recycledcatalyst for the representative reaction was tested with time (h) upto six successive runs and the corresponding kinetic plots are shown in Fig. 10. These plots clearly suggest that the catalytic efficacy of the recovered catalyst remained almost the same after six reaction cycles.

Heterogeneity test

To examine whether copper was being leached out from the solid support to the solution, a typical test was performed in C–Se cross coupling reaction between 4-methoxy phenyl-boronicacid and diphenyldiselenide (Table 2, entry 9) with our supported Cu^{II}-CIN-1 catalyst. For the various proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture after 6 h and the filtrate was allowed to react



Fig. 10 Kinetic plot of recycling test of catalyst (Cu^{II} -CIN-1) in the C–Se cross coupling reaction between 4-methoxy phenylboronic acid and diphenyldiselenide.

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up to the completion of the reaction (8 h). In this case no change in conversion was observed, which suggests that the catalyst is heterogeneous in nature. No evidence for leaching of copper or decomposition of the complex catalyst was observed during the catalytic reaction. It was noticed that after filtration of the catalyst from the reaction mixture, reaction do not proceed further. Atomic absorption spectrometric analysis of the supernatant solution of the reaction mixture thus collected by filtration also confirmed the absence of copper ions (below detection limit of AAS) in the liquid phase. Thus, results of the above test suggested that Cu was not being leached out from the solid catalyst during the reactions.

Conclusions

In conclusion, we have developed an easy and green procedure for the phenylselenylation of arylboronic acids catalysed by a newly synthesized heterogeneous Cu(II) catalyst supported on nitrogen rich porous covalent imine network (Cu^{II} -CIN-1) in PEG-600 solvent. The catalyst provides few advantages for the selenylation reaction, like ligand-free protocol, mild reaction conditions, efficient phenylselenylation using very low copper content (0.1 mol%), high TOF of the catalyst, reaction at PEG-600 which is a green solvent, general applicability, high yields of products and recyclability of the catalyst for six runs without any appreciable loss of activity. To the best of our knowledge, we are not aware of such green selenylation of aryl boronic acids using an efficient and highly recyclable copper catalyst and this will make an important addition to the existing procedures.

Experimental section

Materials

Melamine, 1,4-piparazine dicarbaldehyde and all boronic acids were purchased from Sigma-Aldrich. Diphenyldiselenide was purchased from Merck, Germany. Copper acetate $(Cu(OAc)_2)$, potassium carbonate (K_2CO_3) were purchased from Merck, India. All other reagents and solvents were purchased from commercial sources and were used without further purification. Solvents were dried and distilled through standard procedure.

Physical measurements

Powder X-ray diffraction (XRD) patterns of different samples were analyzed with a Bruker D8 Advance X-ray diffractometer using Ni-filtered Cu K α ($\lambda = 0.15406$ nm) radiation. Transmission electron microscopic (TEM) images of the porous polymer were obtained using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. The copper content of the samples was measured by Varian AA240 atomic absorption spectrophotometer (AAS). Nitrogen adsorption/desorption isotherms of were obtained by using a Quantachrome Autosorb 1C surface area analyzer at 77 K. Prior to gas adsorption, samples were degassed for 4 h at 393 K under high vacuum. UV-visible diffuse reflectance spectra were recorded on a Shimadzu UV 2401 PC coupled with an integrating sphere attachment. BaSO₄ was used as background standard. Thermogravimetric

analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. The EPR (electron paramagnetic resonance) spectra were recorded for the solid sample at room temperature using a JES-FA200ESR spectrometer (JEOL).¹H NMR spectra were recorded on a Bruker 300 MHz, 400 MHz and 500 MHz spectrometers.

Preparation of the catalyst

Synthesis of covalent imine network material CIN-1. Piparazinedicarbaldehyde (169 mg, 1.19 mmol) and melamine (100 mg, 0.79 mmol) were stirred with dimethyl sulfoxide (12 ml) in a round bottom flask fitted with a reflux condenser, at 453 K for 72 h in dry N₂ atmosphere. After cooling to room temperature, the white precipitate was filtered over a Buchner funnel and washed using dry ethanol, excess dry acetone, THF and dichloromethane sequentially. Finally the white solid product was dried under vacuum to obtain solvent free powder (257 mg, 95.5% yield) CIN-1material.⁹

Synthesis of the Cu^{II}-CIN-1 catalyst. CIN-1 (250 mg) and copper acetate (15 mg) were added to dry acetone (20 ml). Then it was stirred at room temperature (298–300 K) for 48 h. When light green coloured solid appeared, it was then filtered through G-4 sintered glass crucible and washed with acetone (4×5 mL) to remove any trace amount of unreacted Cu(OAc)₂. Then it was dried in the oven at 353 K for overnight to provide an easy flowing light green powder. This CIN-1 supported Cu catalyst Cu^{II}-CIN-1 (Cu content = 0.42 wt%, determined by AAS) was used for all the C-Se cross coupling reactions.

Experimental for carbon–selenium cross coupling reaction of 4-methoxy phenylboronic acid with diphenyldiselenide catalyzed by Cu^{II}-CIN-1 catalyst (Table 2, entry 9)

To a solution of 4-methoxy phenylboronic acid (152 mg, 1 mmol) and diphenyldiselenide (156 mg, 0.5 mmol) in 10 ml PEG-600, K₂CO₃ (207 mg, 1.5 mmol) and Cu^{II}-CIN-1 catalyst (20 mg, 0.1 mol%) were added. The mixture was stirred at 80 °C for 8 h. The progress of the reactions was monitored by TLC. After the reaction the catalyst was filtered through a sintered glass bed (G-4) and washed with water followed by acetone and dried in oven. The filtrate was extracted three times with ethyl acetate $(3 \times 20 \text{ ml})$ and washed with water. The organic layers were combined and dried with anhydrous Na2SO4. Then the solvent was evaporated to dryness under vacuum. The residue was then purified by column chromatography on silica gel to provide the desired product as a pale yellow liquid (134 mg, yield 88%); TOF $= 110 \text{ h}^{-1}$; IR (neat) 3065, 2922, 2831, 1576, 1470, 1280 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.82 (s, 3H), 6.86 (d, J = 7 Hz, 2H), 7.18–7.21 (m, 3H), 7.32 (d, J = 7 Hz, 2 Hz); ¹³C NMR (125 MHz, $CDCl_3$) δ 55.4, 115.3 (2C), 120.2, 126.6, 129.4 (2C), 131.1 (2C), 133.4 (2C), 136.6 (2C), 159.8. These spectroscopic data (IR, ¹H NMR, and ¹³C NMR) are in good agreement with those of the authentic compounds reported earlier. This procedure was followed for all the reactions in Table 2. Most of these products are known in literature and these are identified by a comparison of their spectroscopic data with those previously reported (see references in Table 2). The product which is not reported earlier was characterized by its ¹H NMR and ¹³C NMR spectroscopic data and elemental analysis, which is provided below.

2-Methoxy-5-phenylselanyl-pyridine (Table 2, entry 12). Light yellow liquid (85%); IR (neat) 3025, 2927, 1731, 1563, 1463, 1412, 1379, 1187, 1032 cm⁻¹;¹H NMR (400 MHz, CDCl₃) δ 3.94 (s, 3H), 6.70 (d, J = 7 Hz, 1H), 7.20–7.24 (m, 3H), 7.34–7.36 (m, 2H), 7.73 (dd, $J_1 = 8.4$, $J_2 = 5.2$, 1H), 8.37 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 53.7, 112.2, 118.0, 127.0, 129.4 (2C), 131.4 (2C), 132.1, 145.3, 152.4, 164.1. Anal. calcd for C₁₂H₁₁NOSe: C, 54.56; H, 4.20; N, 5.30%. Found: C, 54.50; H, 4.24; N, 5.33%.

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