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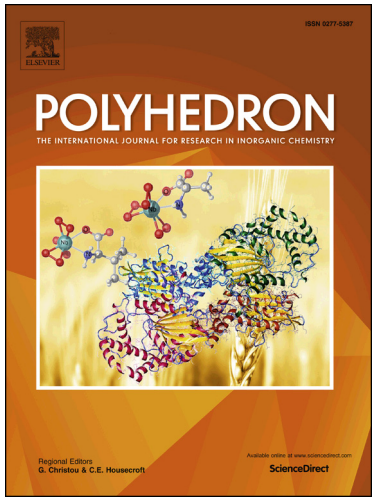

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The Bismarck Brown Y based functional polymer-bound palladium nanoparticles as a capable catalyst for the synthesis of *N*-arylsulfonyl cyanamides

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ABSTRACT

The 4-(benzyloxy)benzyl chloride polymer-bound (BBC-Polym) was functionalized with Bismarck Brown Y (BBY: 4,4'-(1*E*,1*E*')-1,3-phenylenebis(diazene-2,1-diyl)dibenzene-1,3-diamine (BBC-Polym@BBY), the corresponding novel nanoparticle Pd catalyst prepared by addition of $PdCl_2$ (BBC-Polym@BBY@Pd), and the catalyst used as an efficient heterogeneous catalyst for the synthesis of a range of *N*-arylsulfonyl cyanamides from the reaction of arylcyanamides with arylsulfonyl chloride at r.t. in EtOH. Recyclability of the catalyst, high yield, short reaction times, and easy work up are the attracting features of this protocol.

Keywords: BBC-Polymer bound, Bismarck Brown Y, palladium nanoparticles, aryl cyanamides, arylsulfonyl chloride, *N*-arylsulfonyl cyanamides

1. Introduction

Homogeneous and heterogeneous palladium catalyst have been extensively studied and used in diverse organic transformations. Homogeneous Pd nanoparticles have usually higher catalytic activity compared to their heterogeneous counterpart due to availability of all the catalytic active sites. However, workers prefer to use the heterogenized system to carry out organic synthesis since the work up is simpler and efficient. Immobilization of palladium nanoparticles on insoluble solid supported materials such as porous silica [1-4], alumina [5], and polymers [6] will produce desired heterogeneous catalysts. Also, mesoporous organic polymers carrying the organic functional groups at their surfaces are ideal to be bound to the active metals producing the heterogeneous catalysts as well [7-16]. In this respect, diversity-oriented organic syntheses were carried out by lots of workers. For example, several polystyrene anchored complexes were prepared and used as catalysts in functionalization of alkenes, namely for oxidative aminations, hydroaminations and several types of oxidations [17]. A series of chelating resin were synthesized by incorporating ethanolamine, 2-mercaptoethylamine, iminodiacetic acid, 8-quinolinol and anthranilic acid into chloromethylated polystyrene-divinyl benzene, and then they were treated with $FeCl_3{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $CoCl_2{\cdot}6H_2O$ and $NiCl_2{\cdot}6H_2O$ aqueous solution to form the metal complex on the surface. The obtained catalysts were then used for acetalization of carbonyl compounds [18]. A water-soluble polymer-bound Pd(0)-phosphine catalyst was synthesized and used for nucleophilic allylic substitution and in $sp\text{-}sp^2$ coupling reactions of aryl iodides with terminal alkynes

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[19]. Palladium acetate was used for the synthesis 2-phenyl pyridine via cyclization of aryl ketone with 1,3-diaminopropane [20]. The Pd catalyst was used for the Suzuki cross-coupling reaction to obtain the corresponding products in good to excellent yields [21]. The trans $[PdCl_2(PPh_3)_2]$ complex was applied as an efficient catalyst for the amination of aryl halides to afford primary amines and also in the catalytic Stille cross-coupling reaction with satisfactory results [22]. The Pd complexes were used in various C-C bond forming reactions, namely Suzuki–Miyaura, carbonylative Suzuki–Miyaura, asymmetric Heck-type coupling reactions and asymmetric conjugate addition of phenylboronic acid to heterocyclic acceptors [23]. The gallic acid-derived Pd(0) nanoparticles catalyst was applied for the Sonogashira reactions in ethanol under optimum thermal conditions [24]. A series of cationic allyl Pd complexes were applied in the asymmetric allylic substitution reaction of the benchmark substrate rac-3-acetoxy-1,3-diphenyl-1-propene with dimethyl malonate and benzylamine [25]. The Pd catalysts supported on hydrogen titanate nanotubes were tested in the Heck reaction between 4-bromobenzaldehyde or 4-bromostyrene and styrene [26]. The Pd(II) complexes catalyzed three-component coupling reaction of aldehydes, amines and phenylacetylenes under solvent free conditions in ionic liquid at 80 °C to give propargylamines in high yields [27]. Polycarbosilane was synthesized via the polycondensation of trichloromethylsilane and trimethoxyvinylsilane in the presence of sodium metal. Then, $Pd(OAc)_2$ was attached to the polycarbosilane and its catalytic activity investigated in the C–C coupling Heck reaction between aryl halides or vinyl halides and activated [28]. Also, A. Bhaumic and coworkers stabilized palladium nanoparticles at the surfaces of a hypercrosslinked porous polymer bearing carbazole and a,a'-dibromo-*p*-xylene monomeric units to obtain an efficient nanocatalyst which showed excellent catalytic activity towards formylation of amines by carbon dioxide fixation under mild reaction conditions [29]. In addition, A. Bhaumik and coworkers synthesized a new palladium grafted mesoporous organic polymer catalyst through the reaction of palladium(II) acetate with mesoporous poly-triallylamine in methanol. Then, the catalyst was used in the Heck coupling reactions between a series of aryl halides and alkenes to form the corresponding C–C coupling products in good yield using water as reaction medium [30].

N-Sulfonyl cyanamides (eg: *N*-cyano-*N*-tosyl-sulfonamide) are popular cyanamide derivatives with significant applications in synthetic chemistry [31]. Apparently, Tiemann was the first man who observed generation of the cyanamide type species from the reaction of amidoxime with aryl-sulfonyl-Cl [32]. Later, Chien and co-workers developed the reaction conditions and obtained the monosubstituted aryl-cyanamide from the corresponding aryl-amidoxime [33]. Presence of the sulfonyl group in the sulfonyl

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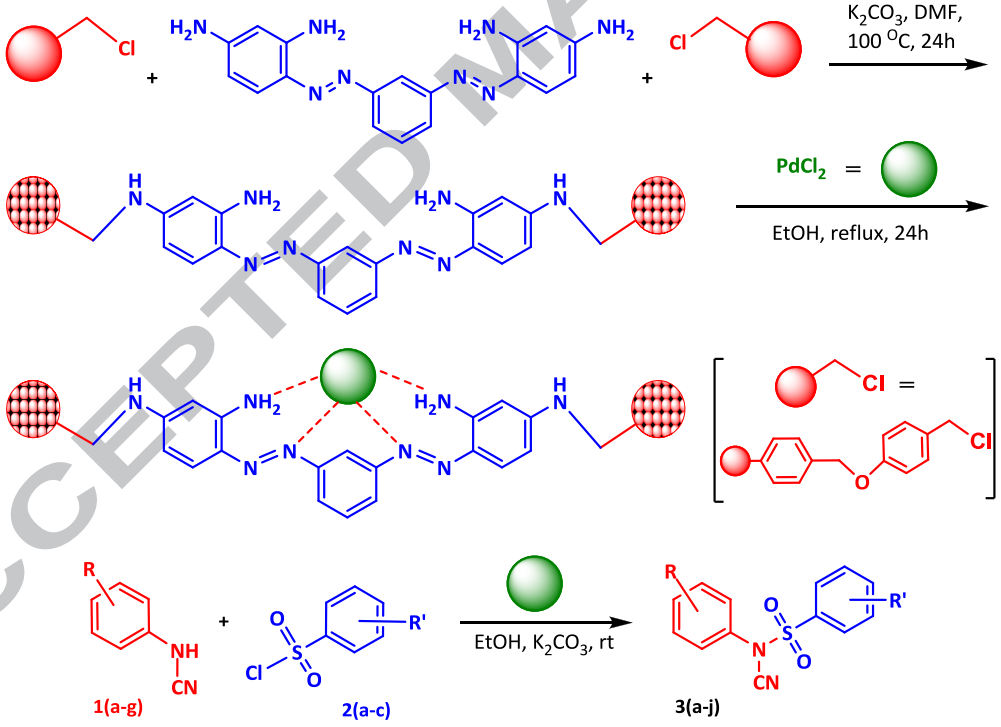
cyanamide compounds resulted different reactions of cyanamides such as the synthesis of heterocycles [34, 35], cyanation by reaction with Grignard reagents [36], generation of cyanamide anion [37], and the Lewis acid assisted aminocyanation [38]. A series of 1-sulfonyl-3-cyanoindole products were synthesized by CuI via the intramolecular aminocyanation of *N*-(2-ethynylphenyl)-*N*-sulfonyl-cyanamides by Chien and co-workers [39].

However, synthesis of *N*-arylsulfonyl cyanamides suffers from various disadvantages such as the low yields, long reaction times, the use of toxic organic solvents, reagents or catalysts, and tedious work-up. Therefore, it is desirable to develop an efficient and green method for preparation of *N*-arylsulfonyl cyanamides that reduce or eliminate the problems.

Herein, we intend to report preparation of a novel Pd nano-particle catalyst by reaction of the 4-(benzyloxy)benzyl chloride polymer-bound (BBC-Polym) with Bismarck Brown Y (BBY: 4,4'-(1*E*,1*E*')-1,3-phenylenebis(diazene-2,1-diyl)dibenzene-1,3-diamine) and complexation with $PdCl_2$. Then, the obtained Pd nano-catalyst was used for the synthesis of a range of *N*-arylsulfonyl cyanamides from the reaction of arylcyanamides with arylsulfonyl chloride at r.t. in ethanol as a green solvent (Scheme 1).



Scheme 1 Synthesis of BBC-Polym@BBY@Pd and *N*-arylsulfonyl cyanamides

2. Results and discussion

2.1. Synthesis and characterization of the Pd nano-catalyst

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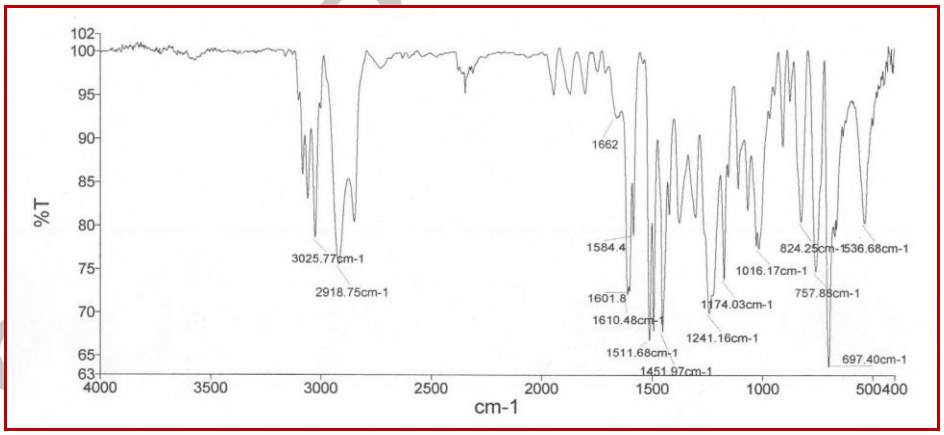
As far as we know and to the best of our knowledge, this is the first time which the Bismark Brown Y compound was used as a new ligand to form the Pd complex. The Pd nano-catalyst was prepared according to the synthesis procedure illustrated in Scheme 1. Formation of the catalyst was verified using the FT-IR, X-ray diffraction (XRD), dispersive X-ray spectroscopy (EDX), induced polarization measurement (ICP), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and thermogravimetric-differential thermal analysis (TG-DTA).

2.1.1. Characterization of the catalyst by the FT-IR spectroscopy

Figure 1 shows the four FT-IR spectra of **A**) BBC-Polym, **B**) BBY, **C**) BBC-Polym@BBY and **D**) BBC-Polym@BBY@Pd, and formation of BBC-Polym@BBY (Fig. 1, **C**) was confirmed by comparison of the three FT-IR spectra (Fig. 1, **A, B** & **C**). Disappearance of the C-Cl peak (751 cm^{-1}) confirms the formation of **C**. Formation of **D** was confirmed by comparison of the two **C** and **D** FT-IR spectra. Displacement of peaks to the lower frequencies confirm formation of the Pd complex since the peaks need less energy for vibrations during the complex formation. For example the stretching vibrations of the C=N bond (1672 cm^{-1}) in **C** was shifted to 1601 cm^{-1} in **D,** indicating the coordination of the nitrogen atom of the tetrazole ring to the manganese atom. This observation suggests that the ligand acts as a chelating agent coordinated via the nitrogen atom.



BBC-Polym **(A)**

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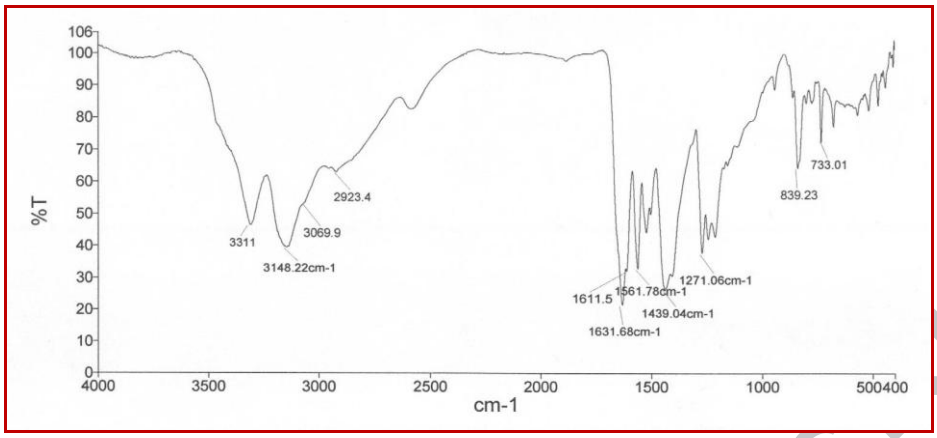
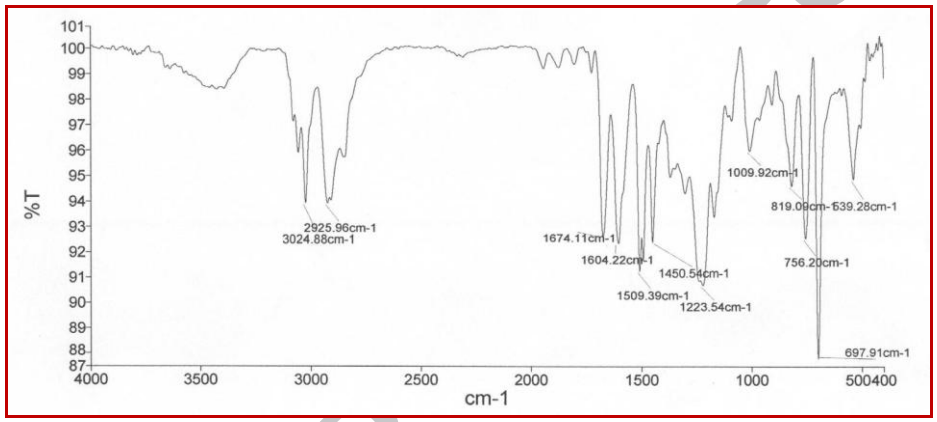
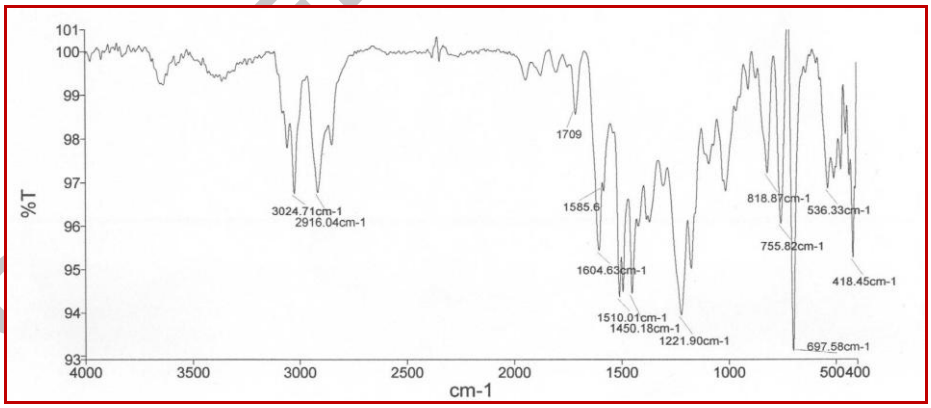


BBY **(B)**



BBC-Polym@BBY **(C)**



BBC-Polym@BBY@Pd **(D)**

Figure 1 The FT-IR spectra of: BBC-Polym **(A)**, BBY **(B),** BBC-Polym@BBY **(C)** and BBC-Polym@BBY@Pd **(D)**

2.1.2. Characterization of the catalyst by the XRD patterns

The crystalline phase and purity of the synthesized material was determined by the XRD patterns. The XRD pattern of the BBC-Polym@BBY@Pd novel heterogeneous nanoparticle catalyst is shown below

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(Figure 2). Appearance of the new peaks at 2θ=~20,~40,~47 and~70 are attributed to the Pd species [40].

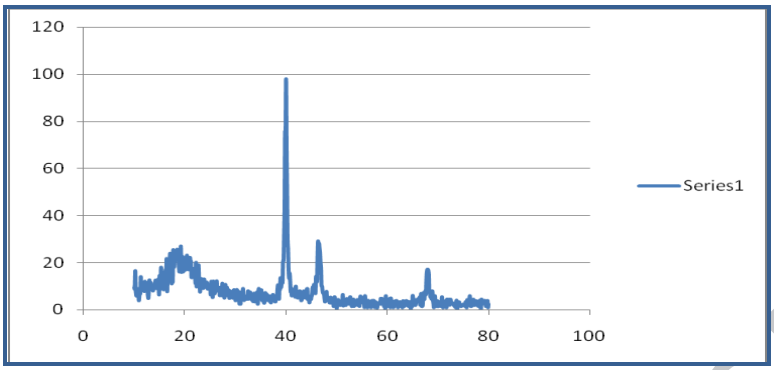

Figure 2 The XRD patterns of BBC-Polym@BBY@Pd

2.1.3. Characterization of the catalyst by the EDX analysis and ICP

The chemical composition of the Pd nano-catalyst was determined by the EDX analysis (Figure 3). The results confirm the presence of the anticipated elements in the structure of the catalyst, namely C (41.48 %), N (19.99 %), O (8.43 %), and Pd (30.12 %). The palladium content by the ICP measurement is about 12.9 %.

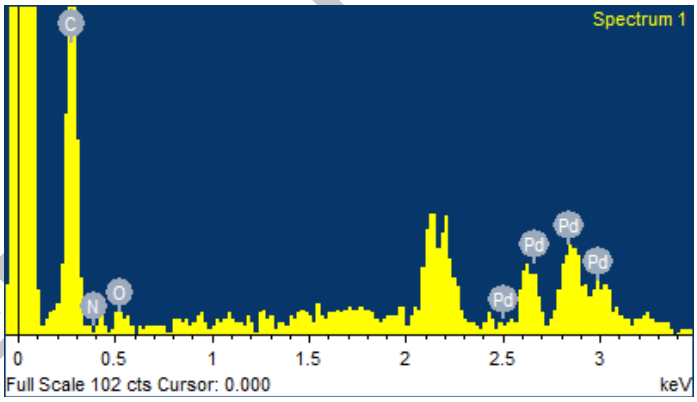

Figure 3 The EDX analysis of BBC-Polym@BBY@Pd

2.1.4. Characterization of the catalyst by the SEM and the TEM images

The morphology and the particle size of the Pd nano-catalyst were determined by the SEM and TEM images (Figures 4 & 5). According to these images, the sizes of the most Pd nano-catalyst particles are in the nanometer ranges (46.68, 70.31, 82.03, 84.45 and 93.75 nm).

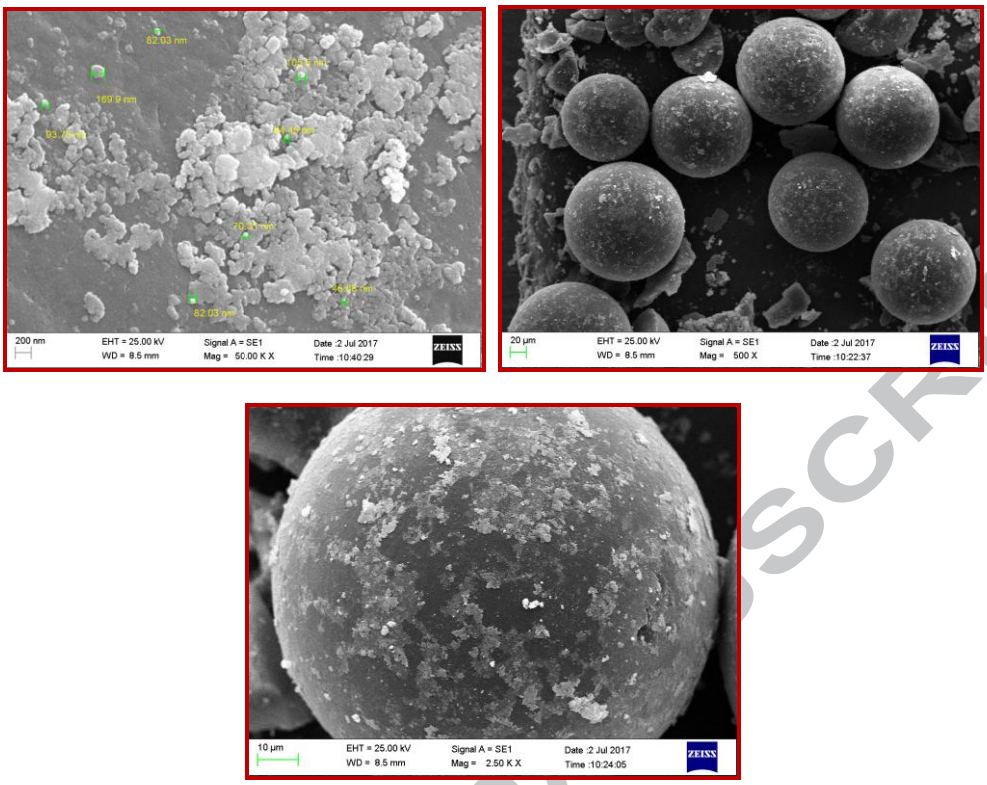

Figure 4 The SEM images of BBC-Polym@BBY@Pd

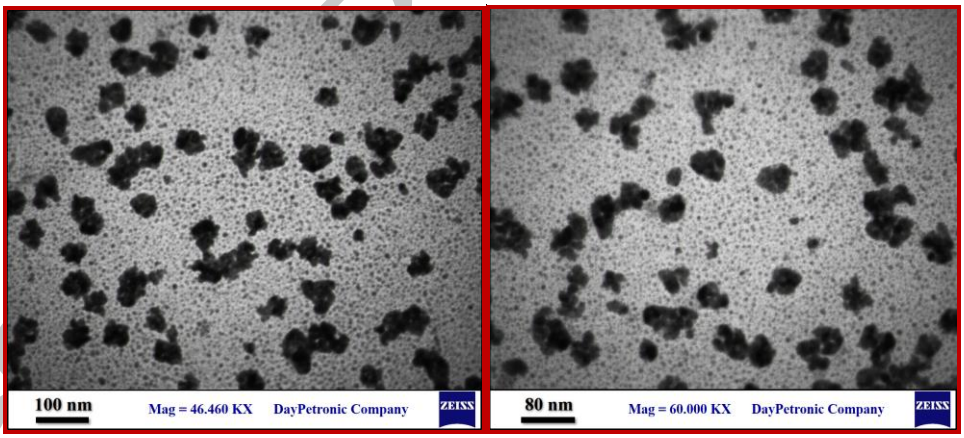

Figure 5 The TEM images of BBC-Polym@BBY@Pd

2.1.5. Characterization of the catalyst by the TG-DTA technique

The thermogravimetric analysis curves of the catalyst show the mass loss of the organic materials as they decompose upon heating (Figure 6). It can be observed that the catalyst shows about three weight loss steps in the temperature range of 300-430 °C. The initial weight loss at about 300 °C is probably due

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to the thermal decomposition of the complex, the second step at about 380 °C is probably due to the removal of the Bismarck ligand and the third weight loss at about 430 °C is related to the thermal decomposition of polymer-bound.

On the basis of these results, the well grafting of ligand groups is verified and indicated that the Pd catalyst has approximately a good thermal stability which is probably due to the strong interactions between the ligands, the polymer-bound and the Pd nano particles.

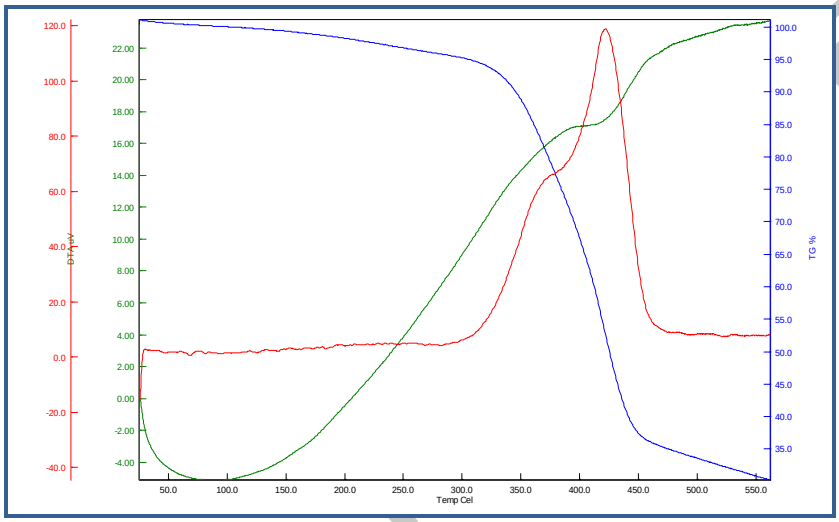
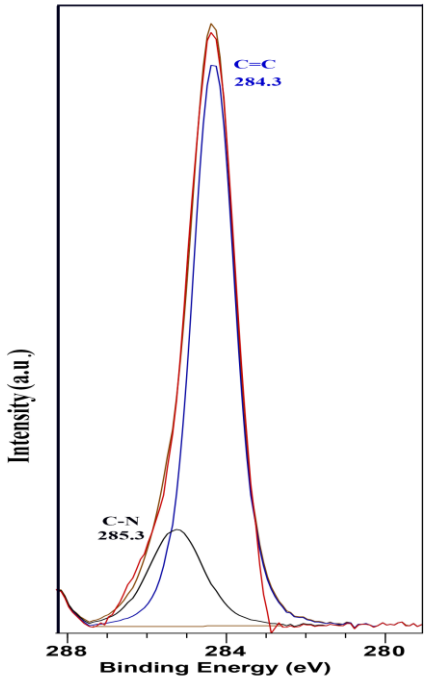
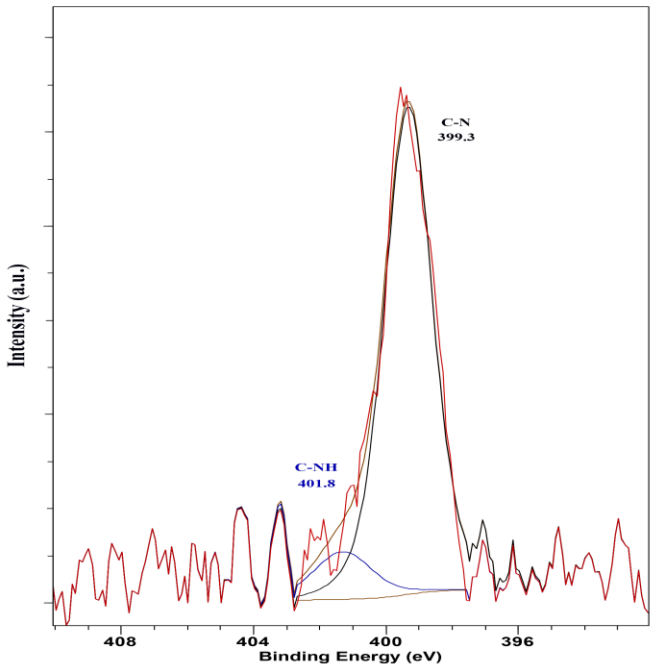


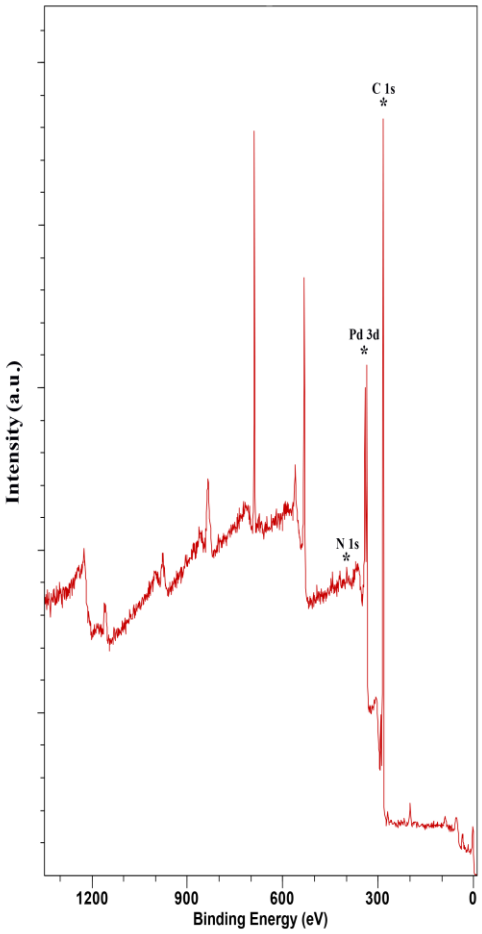
Figure 6 TG-DTA patterns of BBC-Polym@BBY@Pd in N_2 atmosphere

2.1.7. Characterization of the catalyst by the XPS analysis

The XPS analysis is used to investigate the elemental compositions and the surface chemistry of the BBC-Polym@BBY@Pd novel nano-magnetic heterogeneous catalyst (Fig. 7). The overall XPS spectrum of the Pd catalyst revealed that it is consisted of C, N, O and Pd elements. The high-resolution XPS spectrum of carbon peaks centered at 284.3, 285.3, 399.3, and 401.8 eV, correspond to carbon species of C=C, C–N, C-SN and C-NH, respectively. Also, the XPS spectrum of Pd peaks centered at 340.6, and 335.3 eV, correspond to $Pd^{2+}3d_{3/2}$ and $Pd^{2+}3d_{5/2}$, respectively [41-43].


C=C
284.3
C-N
285.3
Intensity (a.u.)
288
284
280
Binding Energy (eV)


C-N
399.3
C-NH
401.8
Intensity (a.u.)
408
404
400
396
Binding Energy (eV)


C 1s
Pd 3d
N 1s
Intensity (a.u.)
1200
900
600
300
0
Binding Energy (eV)

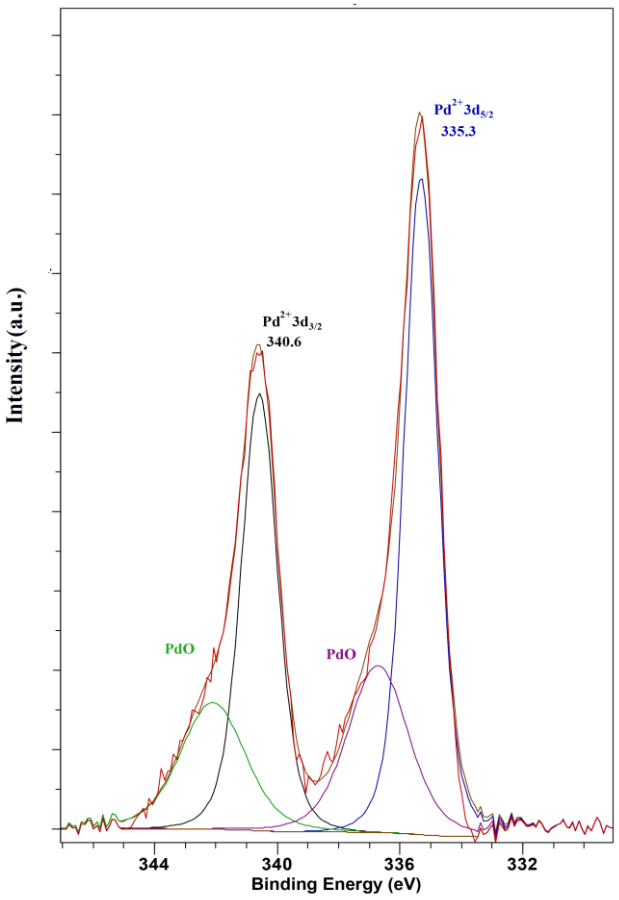

Pd2+3d5/2
335.3
Pd2+3d3/2
340.6
PdO
PdO
Intensity (a.u.)
344
340
336
332
Binding Energy (eV)

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Fig. 7 The XPS analysis of the BBC-Polym@BBY@Pd catalyst

2.2. Optimization of the reaction conditions

The catalyst activity was investigated in a model reaction [synthesis of *N*-(4-chlorophenyl)-*N*-cyano-4-methybenzenesulfonamide from the reaction of *N*-(4-chlorophenyl)cyanamide with 4-methylbenzene-1-sulfonyl chloride] under different conditions of temperature, amount of the catalyst and solvent. The best result was obtained with 30 mg of the Pd nano-particle catalyst in ethanol at r.t. (Table 1).

Table 1 Optimization of the reaction by BBC-Polym@BBY@Pd

Entry	Solvent	Amount of catalyst (mg)	Temperature (°C)	Time (min)	Yield (%)
1	EtOH	80	40	300	73
2	EtOH	80	60	300	76
3	EtOH	50	60	250	73
4	EtOH	**30**	**rt**	**250**	**90**
5	MeCN	30	rt	250	82
6	DMSO	30	rt	400	79
7	MeCN	30	reflux	200	81

Using less catalyst, at lower temperature, with a shorter reaction time, entry 4 is more active than an experiment using more than twice as much catalyst, at a higher temperature and longer reaction time (entry 5). One would expect the opposite for any one of those parameters, but by using more catalyst and higher temperature, the rate of the reverse reaction will probably be increased thereby reducing the net rate of the forward reaction. Incidentally, the use of more catalyst and higher temperature will probably increase the side reactions as well.

Also, in comparing polarity of the applied three solvents, a nice decrease in yield and reaction time is observed due to the decrease in the polarity of ethanol, acetonitrile and DMSO, respectively.

2.3. Synthesis of *N*-arylsulfonyl cyanamides (**3a-j**)

Applying the optimized results from the model reaction, various *N*-arylsulfonyl cyanamide derivatives were synthesized from the reaction of aryl cyanamides with arylsulfonyl chloride in ethanol at r.t. with good to excellent yields (Table 2).

Table 2 Synthesis of various *N*-arylsulfonyl cyanamides

Entry	Phenylcyanamide **1(a-g)**	Arylsulfonyl chloride **2(a-c)**	*N*-Arylsulfonyl cyanamide **3(a-j)**	Reaction time (min)	Yield (%)

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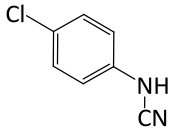
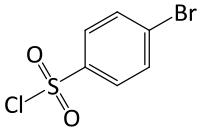
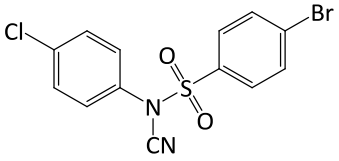
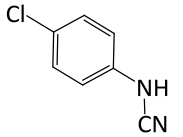
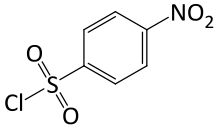
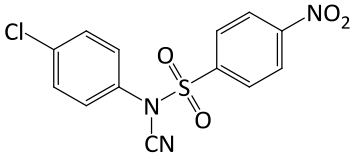
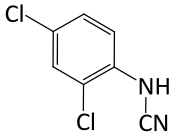
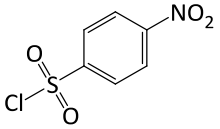
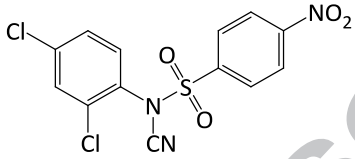
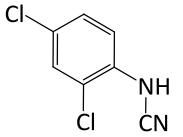
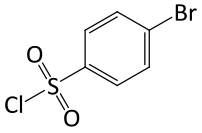
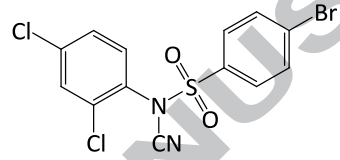
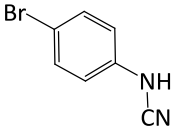
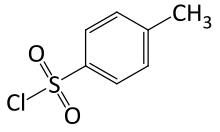
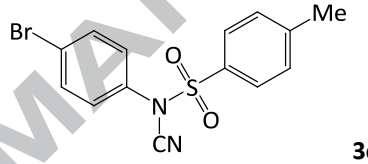
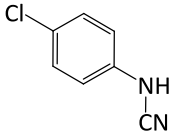
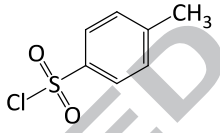
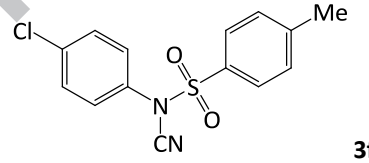
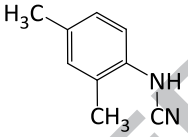
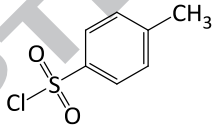
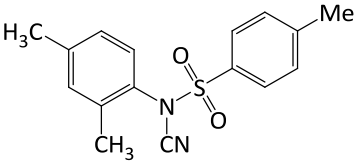
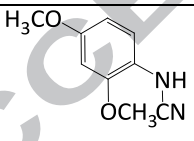
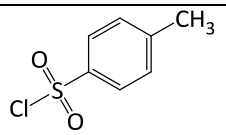
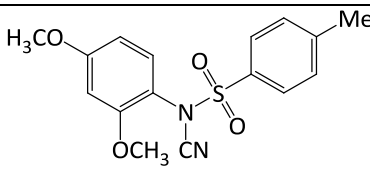
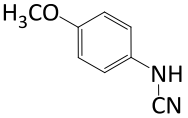
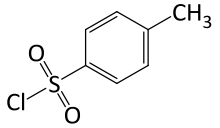
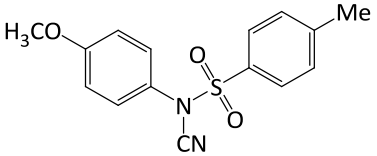
1	 **1a**	 **2a**	 **3a**	110	88
2	 **1a**	 **2b**	 **3b**	80	90
3	 **1b**	 **2b**	 **3c**	120	88
4	 **1b**	 **2a**	 **3d**	180	87
5	 **1c**	 **2c**	 **3e**	150	87
6	 **1a**	 **2c**	 **3f**	250	90
7	 **1d**	 **2c**	 **3g**	250	89
8	 **1e**	 **2c**	 **3h**	110	89
9	 **1f**	 **2c**	 **3i**	110	80

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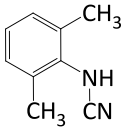
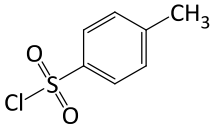
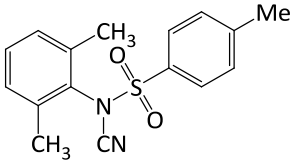
10	 **1g**	 **2c**	 **3j**	140	79

According to the Table 2, arylcyanamides with electron releasing groups (entry 9) and arylsulfonyl chlorides with electron withdrawing groups (entry 2) influence the course of the reaction, and the reaction need less time for completion. As we know, electron releasing groups will increase the electron density of the nitrogen nucleophilic center in arylcyanamides, and the electron withdrawing groups pull out the electron density of the sulfur electrophilic centers in arylsulfonyl chlorides, so the electrophilic center will become more positive, hence the nucleophilic attack will become easier.

2.4. Characterization of *N*-arylsulfonyl cyanamides

All known compounds were characterized by comparing their physical and spectroscopic data with those reported in the literature. The structures of all products were in agreement with their IR and NMR spectra. Disappearance of the strong N-H peak (about 3400 cm^{-1}) and appearance of the -C≡N (about 2230 cm^{-1}) and $–SO_2$ peaks (about 1380 & 1170 cm^{-1}) in all *N*-arylsulfonyl cyanamides confirm formation of products (Supporting Information).

4-Bromo-*N*-(4-chlorophenyl)-*N*-cyanobenzenesulfonamide (**2a**): M.p. 143-145 °C; FT-IR (KBr, cm^{-1}): (specified IR peaks (appearance of the -N(CN)-SO_2- peaks): 2234 (CN), 1393 and 1176 (SO_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.74 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C= 136.5, 133.7, 133.2, 132.6, 131.3, 130.3, 129.7, 127.7, 107.8(CN); Anal. Calcd for $C_{13}H_8BrClN_2O_2S$: C, 42.01; H, 2.17; N, 7.54. Found: C, 42.12; H, 2.28; N, 7.47.

N-(4-Chlorophenyl)-*N*-cyano-4-nitrobenzenesulfonamide (**2b**): M.p. 178-181 °C; FT-IR (KBr, cm^{-1}): (specified IR peaks (appearance of the -N(CN)-SO_2- peaks): 2243 (CN), 1387 and 1187 (SO_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.45 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ_C= 151.6(C-NO_2), 140.1, 137.1, 132.1, 130.6, 129.8, 127.7, 125.0, 107.4(CN); Anal. Calcd for $C_{13}H_8ClN_3O_4S$: C, 46.23; H, 2.39; N, 12.44. Found: C, 46.31; H, 2.28; N, 12.31.

N-Cyano-*N*-(2,4-dichlorophenyl)-4-nitrobenzenesulfonamide (**2c**): M.p. 153-156 °C; FT-IR (KBr, cm^{-1}): (specified IR peaks (appearance of the -N(CN)-SO_2- peaks): 2236 (CN), 1350 and 1189 (SO_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.47 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 2.8

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Hz, 1H), 7.09-7.06 (dd, *J* = 2.8 Hz, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 151.7 (C-NO_2), 139.9, 135.6, 134.5, 132.7, 131.8, 129.8, 128.2, 125.2, 125.1, 106.9 (CN); Anal. Calcd for $C_{13}H_7Cl_2N_3O_4S$: C, 41.95; H, 1.90; N, 11.29. Found: C, 42.06; H, 1.83; N, 11.35.

4-Bromo-*N*-cyano-*N*-(2,4-dichlorophenyl)benzenesulfonamide (**2d**): M.p. 193-196 °C; FT-IR (KBr, cm^{-1}): (specified IR peaks (appearance of the -N(CN)-SO_2- peaks): 2235 (CN), 1384 and 1178 (SO_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 7.77 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.08-7.05 (dd, *J* = 2.8 Hz, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C= 135.1, 134.2, 133.5, 133.4, 133.2, 132.6, 131.6, 129.7, 128.2, 125.3, 107.5 (CN); Anal. Calcd for $C_{13}H_7BrCl_2N_2O_2S$: C, 38.45; H, 1.74; N, 6.90. Found: C, 38.56; H, 1.83; N, 6.79.

N-(4-Bromophenyl)-*N*-cyano-4-methylbenzenesulfonamide (**2e**): M.p. 145-146 °C; FT-IR (KBr, cm^{-1}): (specified IR peaks (appearance of the -N(CN)-SO_2- peaks): 2232 (CN), 1388 and 1182 (SO_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 7.66 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 2.50 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C= 147.1, 133.5, 133.1, 131.9, 130.4, 128.4, 127.9, 124.3, 108.3 (CN), 21.9(CH_3); Anal. Calcd for $C_{14}H_{11}N_2O_2BrS$: C, 47.88; H, 3.16; N, 7.98. Found: C, 47.82; H, 3.20; N, 7.94.

N-(4-Chlorophenyl)-*N*-cyano-4-methylbenzenesulfonamide (**2f**): M.p. 140-144 °C; FT-IR (KBr, cm^{-1}): (specified IR peaks (appearance of the -N(CN)-SO_2- peaks): 2233 (CN), 1388 and 1173 (SO_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 7.64 (d, *J* = 8.4 Hz, 2H), 7.38-7.35 (dd, *J* = 2.0 Hz, *J* = 2.4 Hz, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 2.49 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 147.1, 136.2, 132.9, 131.8, 130.4, 130.1, 128.4, 127.7, 108.3 (CN), 21.9(CH_3); Anal. Calcd for $C_{14}H_{11}ClN_2O_2S$: C, 54.81; H, 3.61; N, 9.13. Found: C, 47.92; H, 3.73; N, 9.04.

N-Cyano-*N*-(2,4-dimehylphenyl)-4-methylbenzenesulfonamide (**2g**): M.p. 104-106 °C; FT-IR (KBr, cm^{-1}): (specified IR peaks (appearance of the -N(CN)-SO_2- peaks): 2224 (CN), 1383, 1120 (SO_2); ^{1}H NMR (400 MHz, $CDCl_3$): δH= 7.74 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 2.53 (s, 3H), 2.35 (s, 3H), 2.18 (s, 3H, *o*-CH3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C= 146.7, 141.2, 137.4, 133.3, 132.6, 130.3, 128.5, 128.1, 127.9, 108.5 (CN), 21.8(CH_3), 21.2(CH_3), 17.5(CH_3); Anal. Calcd for $C_{16}H_{16}N_2O_2S$: C, 63.98; H, 5.37; N, 9.33. Found: C, 64.05; H, 5.42; N, 9.42.

N-Cyano-*N*-(2,4-dimethoxyphenyl)-4-methylbenzenesulfonamide (**2h**): M.p. 132-134 °C; FT-IR (KBr, cm^{-1}): (specified IR peaks (appearance of the -N(CN)-SO_2- peaks): 2231 (CN), 1375 and 1178 (SO_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 7.69 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 1H), 6.51-6.48 (dd, *J* = 2.8 Hz, *J* = 2.4 Hz, 1H), 6.34 (d, *J* = 2.8 Hz, 1H), 3.83 (s, 3H, *p*-OCH_3), 3.42 (s, 3H, *o*-OCH_3), 2.49

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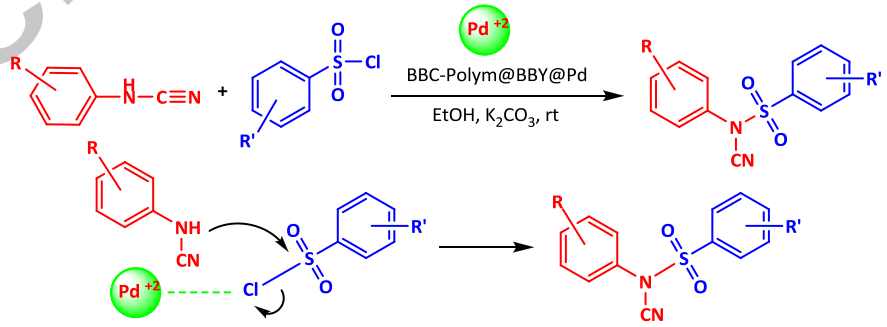
(s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 162.6 (C-OMe), 156.2 (C-OMe), 146.0, 133.7, 131.5, 129.7, 128.6, 114.7 (CN), 108.5, 104.9, 99.2, 55.7 (*p*-OCH_3), 55.3 (*o*-OCH_3), 21.8 (*p*-CH_3); Anal. Calcd for $C_{16}H_{16}N_2O_4S$: C, 57.82; H, 4.85; N, 8.43. Found: C, 57.86; H, 4.90; N, 8.49.

N-Cyano-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (**2i**): M.p. 114-116 °C; FT-IR (KBr, cm^{-1}) (specified IR peaks (appearance of the -N(CN)-SO_2- peaks): 2232 (CN), 1383 and 1179 (SO_2); ^1H NMR (90 MHz, $CDCl_3$) δ_H = 7.61 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 106.7, 146.7, 132.2, 130.2, 128.5, 128.4, 126.8, 114.9, 108.9, 55.6, 21.9; Anal. Calcd for $C_{15}H_{14}N_2O_3S$: C, 59.59; H, 4.67; N, 9.27. Found: C, 59.65; H, 4.72; N, 9.23.

N-Cyano-*N*-(2,6-dimethylphenyl)-4-methylbenzenesulfonamide (**2j**): M.p. 135-137 °C; FT-IR (KBr, cm^{-1}) (specified IR peaks (appearance of the -N(CN)-SO_2- peaks): 2220 (CN), 1381 and 1190 (SO_2); ^1H NMR (90 MHz, $CDCl_3$) δ_H = 7.81 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.18-7.07 (m,3H), 2.49 (s, 3H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 156.8, 145.9, 145.6, 143.0, 137.2, 131.8, 130.3, 129.8, 129.4, 128.6, 115.9, 109.8, 103.2, 21.7, 17.7; Anal. Calcd for $C_{16}H_{16}N_2O_2S$: C, 63.98; H, 5.37; N, 9.33. Found: C, 64.04; H, 5.42; N, 9.27.

2.5. The plausible mechanism

On the basis of the above described experiments, we would like to propose the plausible mechanism for the synthesis of various *N*-arylsulfonyl cyanamide derivatives from the reaction of arylcyanamides with arylsulfonyl chloride at r.t. in ethanol by the Pd nano-catalyst is shown below (Scheme 2). The mechanism is probably due to the Lewis acidity of the Pd nano-catalyst by attaching to the surface of the chlorine group to facilitate the nucleophilic attack of the nitrogen atom of arylcyanamide to form the final product.



Scheme 2 Suggested mechanism for the synthesis of *N*-arylsulfonyl cyanamides

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2.6. Reusability of the Pd catalyst

The reusability of BBC-Polym@BBY@Pd was investigated with the model reaction [synthesis of *N*-(4-chlorophenyl)-*N*-cyano-4-methybenzenesulfonamide from the reaction of *N*-(4-chlorophenyl)cyanamide with 4-methyl- benzene-1-sulfonyl chloride] to find the capability of the catalyst. Therefore, the catalyst was separated by filtration after the first run, washed with ethanol, dried under vacuum and reused for the next successive runs under the same conditions. Consequently, we found that the Pd catalyst is an efficient, capable and reusable catalyst even after five runs (90, 87, 83, 79 and 76%, respectively).

3. Experimental

3.1. General methods

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. The NMR spectra were recorded in DMSO or $CDCl_3$. ^{1}HNMR and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 400 and 300 MHz instruments. The chemical shifts are reported in parts per million relative to TMS as an internal standard and *J* values are given in hertz. FT-IR (KBr) spectra were recorded on a Perkine Elmer 781 spectrophotometer. Melting points were taken in open capillary tubes with a BUCHI 510 melting point apparatus and are uncorrected. Elemental analysis was performed using Heraeus CHNeO-Rapid analyzer. The ICP measurements for the metal content evaluation were performed using a Perkin-Elmer ICP/6500. TLC was performed on silica gel polygram SIL G/UV 254 plates. The TEM images were recorded on a Zeiss-EM10C-80 KV transmission electron microscope, and the SEM images were recorded on a Philips XL-30 scanning electron microscope. The XRD measurements were done by a Bruker D8 Advance powder diffractometer, using Cu Kα (λ=1.54 A°) as the incident radiation. Magnetic measurements were carried out at r.t. using an Iranian Meghnatis Daghigh Kavir Co Vibrating Sample Magnetometer (VSM).

3.2. Catalyst preparation

3.2.1. Synthesis of BBC-Polym@BBY

The mixture of BBC-Polym (0.465 g, 2 mmol) and BBY (0.419 g, 1.0 mmol) was stirred in H_2O (60 ml). Then, K_2CO_3 (0.138 g, 1.0 mmol) was added and the mixture was reflux for 24 h. The polymer-anchored ligand was filtered out and the purple color solid washed thoroughly with water and dried under vacuo.

3.2.2. Synthesis of BBC-Polym@BBY@Pd

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$PdCl_2$ (0.425 g, 2.46 mmol) was dispersed in ethanol (50 ml), BBC-Polym@BBY (1.0 g, 1.23 mmol) added and the mixture refluxed for 24 h. Then, the mixture was filtered off and the obtained gray solid catalyst washed with ethanol (3 x 10 ml) and air-dried (Scheme 1).

3.3. Synthesis of *N*-arylsulfonyl cyanamides

Arylcyanamide (1.0 mmol), the requisite arylsulfonyl chloride (1.0 mmol), K_2CO_3 (1.0 mmol) and the Pd nano-particle catalyst (30 mg) were mixed in ethanol (15 ml), stirred at r.t. and completion of the reaction monitored with TLC. Then, acetone (20 ml) was added, the Pd catalyst was filtered, the filtrate concentrated and the solvent removed in *vacuo*. The obtained *N*-arylsulfonyl cyanamide recrystallized in ethanol and characterized by comparing its physical and spectroscopic data with the reported literature (Scheme 1).

4. Conclusion

In conclusion, a novel Pd nano-catalyst was successfully prepared by functionalization of the 4-(benzyloxy)benzyl chloride polymer-bound (BBC-Polym) with the Bismarck Brown Y ligand (4,4'-(1*E*,1*E*')-1,3-phenylenebis(diazene-2,1-diyl)dibenzene-1,3-diamine, BBC-Polym@BBY), the corresponding novel Pd catalyst prepared by addition of $PdCl_2$ (BBC-Polym@BBY@Pd), and the catalyst used as an efficient heterogeneous catalyst for the synthesis of a range of *N*-arylsulfonyl cyanamides from the reaction of arylcyanamides with arylsulfonyl chloride at r.t. in ethanol.

Recyclability of the catalyst, high yield, short reaction times, and easy work up are the attracting features of this protocol.

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Supplementary data

Supporting information for this article is available online at http://dx.doi.org/.....

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The Bismarck Brown Y based functional polymer-bound palladium nanoparticles as a capable catalyst for the synthesis of *N*-arylsulfonyl cyanamides

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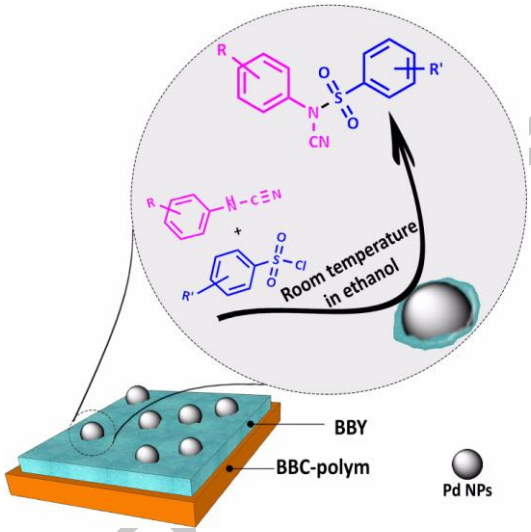

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