Synthesis and characterisations of boron nitride based propyl triethylenetetramine sulfonic acid catalyst

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Abstract

A simple and efficient procedure for the preparation of boron nitride bound *N*-propyl triethylenetetramine sulfonic acid (***BN-BPTETSA***) by the reaction of boron nitride bound *N*-propyl triethylenetetramine (3-TETANP BN) with chlorosulfonic acid in chloroform is described. The boron nitride (BN) nanomaterial was prepared by first activating BN with nitric acid under reflux for 24h. Thereafter trimethoxy -3-mercaptopropylchloride was added, refluxed for 24 h then an excess of triethylenetetramine was added in anhydrous xylene and the system was refluxed. After filtration and washing of the filter cake with xylene, chlorosulfonic acid was added drop-wise at 0 °C over a period of 3 h. Further filtration yielded a solid cake which was washed with ethanol and air died. The morphological properties of catalyst was characterized by FT-IR, XRD, TEM, SEM, BET and Raman spectroscopy techniques. The preparation of the catalyst is safe and demonstrates high catalytic activity for the synthesis of piperazinyl quinolinyl carbaldehyde derivatives. Furthermore, a small amount of catalyst was used, demonstrated good reusability and may have potential for industrial applications in the future.

Keywords: Boron nitride, mercaptopropyl chloride, Raman spectroscopy, solid acid catalyst, TETA.

Introduction

Boron nitride nano material (BNNs) and boron nitride nanotubes (BNNTs) have similar arrangements to carbon nanotubes. These materials are attracting increasing interest because of their better mechanical properties [**1**], chemical stability, electrical [**2-3**] and good thermal stability [**4**]. The BNNTs recently demonstrated good biocompatibility [**5**], and good interaction with macromolecules like proteins [**6**] and DNA [**7**]. These properties suggest BNNs may be promising nanovectors for some biological and biomedical applications [**8,9**]. Presently BNNs are functionalised mostly by physical approaches including hydrophobic or Van der Waals interactions [**10-11**]. In the biomedical applications of amphipathic dendrimers, they act as dispersing agents [**12**]; the aqueous dispersions of boron nitride nano tube coated with dendrimers is synthesised using R-mannose moieties [**13-14**]. Recently BNNs was chemically functionalised to new materials however some drawbacks became evident. The major issue is a lack of an easy and effective method to graft a suitable high density functional group on boron nitride (BN) to make it more chemically active, which could allow for further efficient nanotube modification [**15**]. Modification may occur either at N or B positions: The bonding on N sites has mainly been obtained by using amino group chemistry [**16**], but the achieved density of amino groups is rather low. The density of active N sites can be increased by exposure to NH_3 plasma, but surface damaging is a problem [**17**]. In fluorine (F)-doped BNNTs, F can be covalently linked to B, however the density of F is quite low [**18**]. Recently, BN was activated by oxidation in hydrogen peroxide under high temperature and pressure [**19**] and subsequently used as a starting material for further modification. However since the surface chemistry of BN is still in its infancy, effective surface functionalization remains a challenging.

In the present study, 3-chloropropyl-triethoxysilane was used as a silanising agent of BN surface. The 3-chloropropyl-triethoxysilane is important and applied in many research fields [**20**]. Literature on the synergistic effect of BN and graphene nano sheets, in 3D frame work, on the enhancement of thermal conductive properties of polymeric composites [**21**] and surface modification of BN by reduced graphene oxide for preparation of dielectric material with enhanced dielectric constant and well suppressed dielectric loss [**22**] are available. Also investigations on the core-shell structured BN polyphenylene sulfide composite film for high thermal conductivity with low filler concentration [**23**] are reported.

In our current study, we prepared a new composite material, in a 3 reaction step, which showed excellent catalytic activity for the synthesis of piperazinyl

quinolinyl derivatives in high yield. Furthermore, due to the small amount of catalyst used in the chemical transformation as well as its good reusability, there is good potential for its use in other named organic reactions, other than that we cite here-in, and some industrial applications in the future.

Experimental

Materials and methods

Chemicals were purchased from Merck, Sigma Aldrich. The reaction monitoring and purity of the product was accomplished by TLC. FTIR spectra were recorded in the range of 4000-400 cm^{-1} on a JASCO FT/IR-460 spectrophotometer using KBr pellets in functional group analysis. A Bruker D2 PHASER powder diffraction instrument; Cu Kα ray (wavelength λ = 0.154056 nm), was used to measure in a continuous step-scan mode: the minimum width of the stage 0.031°, equilibrium time of 256 seconds, the operating voltage to 30 kV with 10 mA identification for metal. Field-emission scanning electron microscopy (FESEM, Joel JSM 7600F) was employed to characterise the surface morphology. High Resolution-Transmission Electron Spectroscopy (HR-TEM) was used in particle size in catalyst. The BET gas sorption isotherms were measured at 77 K for N_2 and H_2, and 273 and 298 K for CO_2 using Micromeritics Auto pore 9500 system. Before recording gas sorption measurements, the sample was initially dehydrated at 423 K for 24 h under vacuum. Raman Spectroscopy was measured using the detector CCD (Triaxle) and the laser (He-Ne laser 632.8 nm) identification of metal and functional group.

Catalyst preparation

Synthesis of 3-triethylenetetramine-Npropyl boron nitride (3-TETANP BN)

To a mixture of chloropropyl boron nitride (15 g) in anhydrous xylene (150 ml), an excess of triethylenetetramine (20 ml) was added. The resulting mixture was refluxed with stirring for 24 h. The reaction mixture was then cooled to room temperature and filtered through a vacuum glass filter. The filter-cake was washed sequentially with xylene and a large excess of ethanol and dried under vacuum overnight at 80°C to give the desired product 3-TETANP BN (14 g).

Synthesis of BN-BPTETSA

To a magnetically stirred mixture of 3-TETANP BN (14g) in $CHCl_3$ (30 ml) was added chlorosulfonic acid (20 ml) in a drop-wise manner at 0°C over a period of 3 h. Upon completion of the reaction, the mixture was stirred for a further 3 h and then filtered. The filter-cake was washed with ethanol (50 ml) and dried at room temperature to afford the desired product, BN-BPTETSA, as a cream powder (15g) **(Scheme 1)**.

General procedure for the synthesis of substituted piperazin-1-yl quinolinyl carbaldehyde

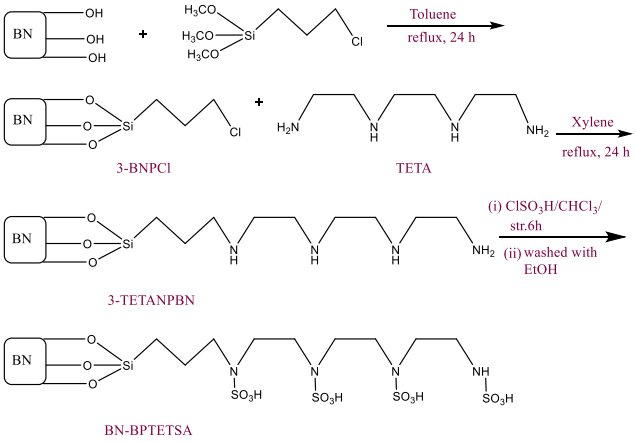
In order to synthesise methyl and ethyl piperazinyl-quinolinyl carbaldehyde derivatives, the starting compound 2-chloro-3-formyl quinoline (CFQ) (**1**) was prepared from acetanilide, DMF and $POCl_3$ by the Vilsmeir Haack reaction [**24-25**]. An aliquot (0.001 mol) of CFQ and BN-BPTETSA (0.002 mol) was added to 2 round bottom flasks and an excess of 1-methylpiperazine and 1-ethylpiperazine was added, separately to each of the 2 reaction vessels. The mixture was refluxed for 24 h at 170 °C; the reaction was monitored by TLC. After completion of the reaction, the reaction mass was cooled to room temperature and poured into water. It was then filtered, washed with water and dried. The crude product was purified by column chromatography using silica gel and a mobile phase of acetone and hexane (70:30) to produce a yellow powder.

Spectroscopic information: 2-(4-methylpiperazin-1-yl) quinoline-3-carbaldehyde (3)

The yield was 97 % (m.p 180 °C). IR (KBr): 2979, 2934, 2643, 2901, 2358, 2333, 1693, 1615, 1593, 1421, 1372, 1239, 952, 765, 512, 482 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): $CDCl_3$): δ 10.09 (1H, brs, CHO), 8.4 (1H, brs, Ar-H), 7.76 (1H, d, Ar-H, J = 8.48 Hz), 7.7 (1H, d, Ar-H, J = 7.36 Hz), 7.62 (1H, t, Ar-H, J =1.44 Hz), 7.31(1H, t, Ar-H, J =0.84Hz), 3.47 (4H, t, CH_2, J=5.4Hz), 2.6 (4H, t, CH_2, j=4.84 Hz),2.3 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190, 158, 149, 142, 132, 129, 127, 124, 123, 122, 54, 50, 45. TOF MS ES+ Calc. mass 256.1450, Found: 256.1449 Anal. Calc. For $C_{15}H_{17}N_3O$: C, 70.56; H, 6.71; N, 16.46; Found: C, 70.58; H, 6.72; N, 16.43. This compound was fully characterised by IR, ^{1}H-NMR, ^{13}C-NMR, TOF-MS and elemental analysis (**Fig. 3-5** in Supporting information).

Spectroscopic information: 2-(4-ethylpiperazin-1-yl) quinoline-3-carbaldehyde (4)

The yield was 97 % (m.p 220-222 °C). IR (KBr): 2979, 2934, 2643, 2901, 2358, 2333, 1693, 1615, 1593, 1421, 1372, 1239, 952, 765, 512, 482 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.16 (1H, brs, CHO), 8.47 (1H, brs, Ar-H), 7.82 (1H, d, J = 8.4 Hz, Ar-H), 7.76-7.79 (1H, dd, J = 1 Hz, Ar-H), 7.66-7.70 (1H, m, J =1.52 Hz, Ar-H), 7.34-7.38 (1H, m, J =1.04 Hz, Ar-H), 3.53-3.55 (4H, t, J= 4.84 Hz, CH_2), 2.66-2.69 (4H, t, J=4.92 Hz, CH_2), 2.49-2.54 (2H, q, J=7.28 Hz, CH_2), 1.13-1.16 (3H, t, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.27, 159, 149.35, 142.18, 132.41, 129.24, 127.56, 124.55, 123.98, 122.06, 52.70, 52.38, 51.04, 11.97. TOF MS ES+ Calc. mass 270.16, Found: 270.15 Anal. Calc. For $C_{16}H_{19}N_3O$: C, 71.35; H, 7.11; N, 15.60 %. Found: C, 71.37; H, 7.12; N, 15.62 %. This compound was fully characterised by IR, ^{1}H-NMR, ^{13}C-NMR, TOF-MS and elemental analysis (**Fig. 6-8** in Supporting information).



Scheme 1. The reaction scheme for the synthesis of BN-BPTETSA**.**

Results and discussion

The catalyst was synthesised in 3 steps. The first step was most important: the surface of BN was modified to carry OH groups which could react with the OH group in the silyl substrate **(Scheme 1)**. This was achieved by refluxing a mixture of BN and 65% nitric acid for 24h. After the usual work-up, the trimethoxy-3-mercaptochloropropyl substrate was added and refluxed. This reaction was followed by the addition of triethylenetetramine and the reaction mixture was refluxed followed by the addition of chlorosulfonic acid. The reaction was worked-up resulting in 15 g of a cream powder identified as a new catalyst. The catalyst was characterised completely by several technique.

Spectroscopic studies of catalyst

The FT-IR spectrum of pure and BN-BPTETSA (see **Fig. 1-2** in supplementary material) supplied some relevant information: in the case of BN, the absorption at 958, 1414, 2351 and 1645 cm^{-1} corresponds to the -OH stretching and bending vibrations of the adsorbed water. The spectrum of BN -BPTETSA is similar to BN however the absorption at 3243 cm^{-1} is flattened which can be attributed to the modification of BN. Also, the CH stretching vibrations of silylating agent was observed at 2954 cm^{-1} and the absorption at 1211 cm^{-1} is due to the Si-O stretching vibration. Furthermore, the absorptions at 1163 and 1141 cm^{-1} is due to the stretching mode of S=O in SO_3H.

XRD and SEM images confirmed the crystallinity and purity of BN and BN-BPTETSA. The comparison of two XRD patterns of BN-BPTETSA are almost the same as those of BN thereby suggesting that the sulphate modification does not change BN (see **Fig. 1**).

The representative SEM images of BN and BN-BPTETSA (see **Fig. 2**) reveals an aggregation of cloud-like structures of small spherical-shaped particles. The SEM micrographs of BN-BPTETSA show some modifications with respect to BN such that the primary surface structure of BN has changed, however the cloud-like structure and small spherical-shaped particles still exists.

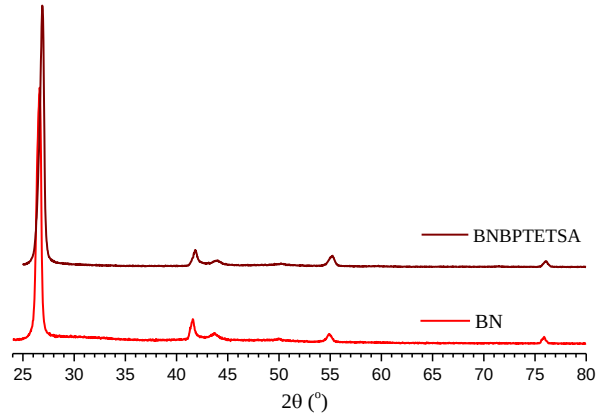


Fig 1. PXRD pattern of BN and BN –BPTETSA.

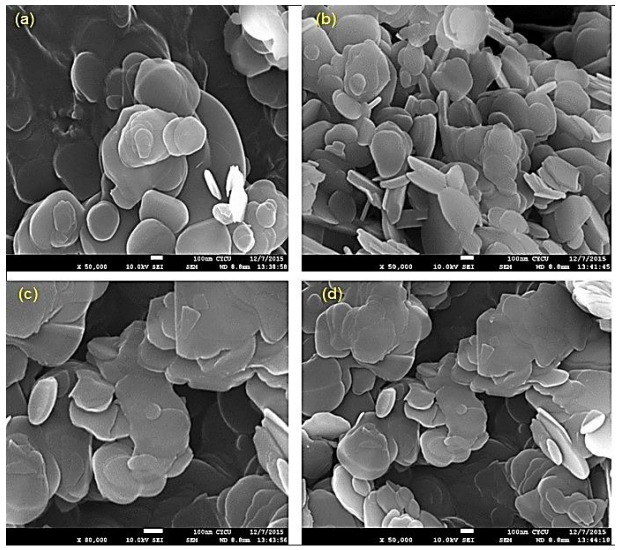


Fig 2. SEM image of BN (a, b) and BN-BPTETSA (c, d).

The catalyst were confirmed by EDS analysis (B, N, O, C, and S) for BN and BN-BPTETSA (see **Fig. 3**) EDS (energy-dispersive X-ray spectroscopy) confirms the presence of all the elements and the actual weight % is presented in **Table 1.**

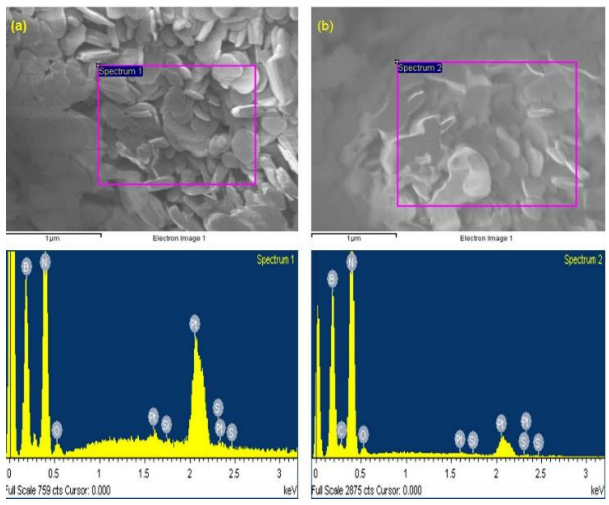


Fig 3. EDS analysis for BN image (a) and BN–BPTETSA image (b).

Table 1. The weight (%) analysis for BN and BN-BPTETSA.

	BN		BNBPTETSA.	
Element	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
B	38.58	52.93	41.54	49.8
N	41.73	44.12	49.8	44.75
O	1.67	1.54	1.26	1.04
C	-	-	4.54	4.56
S	-	-	0.12	0.05
pt	17.88	1.34	3.39	0.20

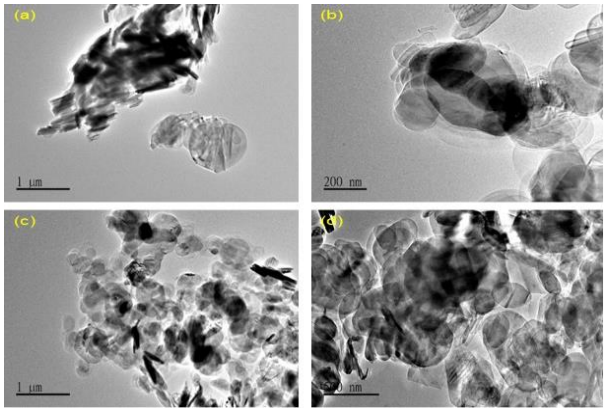


Fig 4. TEM image of BN (a, b) and BN-BPTETSA (c, d).

Field-emission scanning electron microscopy was employed to characterize the morphology. TEM image for different orientations was done to get the average crystallite size of, BN-BPTETSA. TEM images of BN and BN-BPTETSA are shown in (see **Fig. 4**) snapped at different place BN (a-1um, b-200 nm) BN-BPTETSA (c-1um, d-100 nm); shows the crystalline size of BN-BPTETSA which also show a BN-BPTETSA (1um for catalyst good mesoporous structures thereby suggesting a good surface for catalytic activity).

The porous properties of BN and BN-BPTETSA, analysed by N_2 gas adsorption measurements at 273K (see **Fig. 5)**, showed BN as a type-I adsorption isotherm which is characteristic of microporous material and the BET and Langmuir surface area of BN were calculated as 7 and 11 m^2/g, respectively. The N_2 adsorption isotherm of BN-BPTETSA also indicated a type-I adsorption isotherm however the BET and Langmuir surface area were calculated as 16 and 37 m^2/g, respectively.

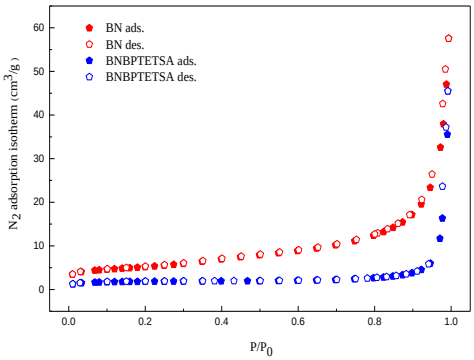


Fig 5. Adsorption and desorption isotherms of BN and BN-BPTETSA at 273K.

Further investigation of the structure of BN and BN-BPTETSA were investigated by Raman spectroscopy (see **Fig. 6**) which showed absorption signals at 600, 1300, 2000, 3000, and 3650 cm^{-1} for BN. The absorption signal of BN-BPTETSA showed absorptions signals at 600, 2000, 3000, 3650cm^{-1} with an additional signal at 3450 cm^{-1} indicating the acidic functional group.

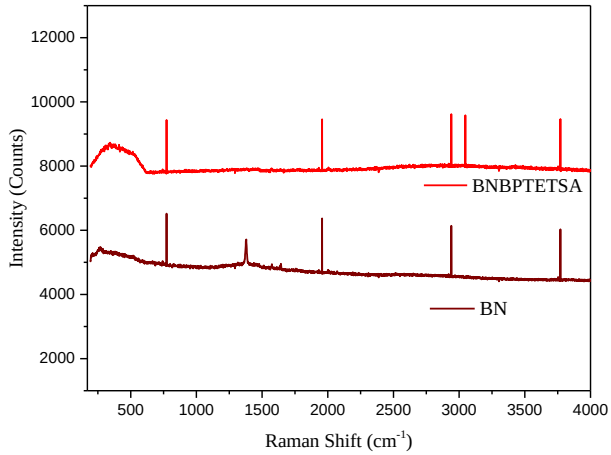
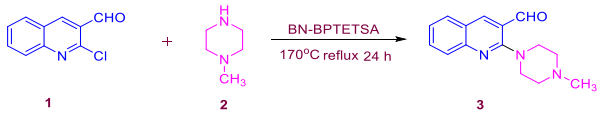


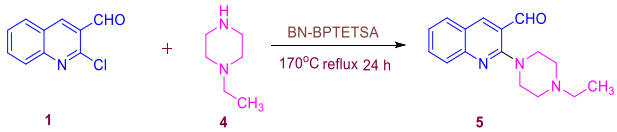
Fig 6. Raman Shift of BN and BN-BPTETSA.

Application of the catalyst in the nucleophilic addition-elimination reactions

In a preliminary study to synthesize **3 and 5 (Scheme 2 and 3)** ethanol was used as the solvent. The nucleophilic addition-elimination reactions of **1** and 1-methyl piperazinyl **2,** as the template reaction, was carried out in the presence of different quantity of catalyst (0.02, 0.05, 0.07 g): **3** was produced and subsequently characterized by IR, ^{1}H-NMR, ^{13}C-NMR, TOF-MS and elemental analysis. It was found that increasing the quantity of the catalyst beyond 0.05 g did not increase the yield noticeably hence we selected this quantity as optimum for all subsequent reactions. The choice of an appropriate reaction medium is crucial for successful synthesis. Hence to accelerate the nucleophilic addition-elimination reactions, various solvents such as ethanol, methanol, acetonitrile, dichloromethane and toluene, were examined and were shown to have varying impact on the yield of **3**. The best yield (97%) was obtained in a solvent free system (**Table 2** entries 6).



Scheme 2. Synthesis of 2-(4-methylpiperazin-1-yl) quinoline-3-carbaldehyde.



Scheme 3. Synthesis of 2-(4-ethylpiperazin-1-yl) quinoline-3-carbaldehyde.

Moderate yield were observed when catalyst and solvents such as ethanol and acetonitrile were used under reflux for 24h (**Table 2** entries 1-3). The yield decreased and longer reaction time were required with catalyst and solvent such as DCM, methanol and toluene (**Table 2** entries 2, 4, 5). Consequently, BN-BPTETSA catalyst was used for all subsequent reactions (**Table 2**).

Table 2. A comparison of the reaction of a solvent/solvent-free system using BN-BPTETSA for the synthesis of **4**.

Entry	Catalyst	Solvent	Temp (^{0}C)	Time (h)	Yield
1	BN-BPTETSA	EtOH	Reflux	24	80
2	BN-BPTETSA	MeOH	Reflux	24	75
3	BN-BPTETSA	CH_3CN	Reflux	24	85
4	BN-BPTETSA	DCM	Reflux	24	70
5	BN-BPTETSA	Toluene	Reflux	24	77
6	BN-BPTETSA	Neat	170	24	97

The re-usability potential of BN-BPTETSA was also investigated in the model reaction to synthesize **3**: briefly, the solid was rinsed with refluxed at 170 ˚C solvent free conditions and taken for subsequent reactions. We found that the catalyst could be re-used five times with an overall loss of 5% catalytic activity and concluded that it is an important benefit if commercial application is required.

The synthesis (**Scheme 2 and 3)** of piperazinyl-quinolinyl derivatives **3 and 5**, using BN-BPTETSA, were undertaken in a reflux system for a reaction time of 24h at 170^{0}C. The yield of the products were 97%. Compounds **3 and 5** were characterized by IR, ^{1}H NMR, ^{13}C NMR, MS-TOF (the Figures showing all characterization data are presented in Supporting Information).

Conclusion

In summary, a novel boron nitride-based based propyl triethylenetetramine sulfonic acid catalyst was prepared and fully characterised. The method is simple and safe whilst the catalyst demonstrated only 5 % loss in catalytic activity after five cycles of re-use thereby making it cost-effective. The composite material was used for the subsequent synthesis of methyl and ethyl piperazinyl-quinolinyl carbaldehyde derivatives. This reaction is relatively fast, safe, and environmentally friendly and gives high yields. Furthermore the one pot reaction used in this study gives rise to a new type of methyl and ethyl piperazinyl-quinolinyl carbaldehyde which have suitable functionality for a host of chemical transformation towards possibly better biological applications.

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