Efficient and eco–friendly synthesis of fluorenone Azines by using sulphated titania acid catalyst

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ABSTRACT. Conjugated unsymmetrical azines have been synthesized in the presence of acid catalyst sulphated-titania (TiO_2-SO_4^{2-}) from fluorenone hydrazone with substituted aldehydes and acetophenones by using mortar and pestle. The scope of present synthetic route avoid in solvents, simple operating method and shorter reaction time. Special feature of synthetic method is recyclable catalyst for all in reactions.

1. INTRODUCTION

Now a day's interest, green chemistry has been proposed an innovative method for organic synthesis. The method should reduce the emission of volatile and baleful organic solvents and the use of perilous toxic chemicals [1]. In recent years synthesis of organic compound has been use catalyst such as hexaaquaaluminium (III) tetrafluoroborate [2], ionic liquids [3] and modified zirconia [4] etc. Diimines (azines) are most required compounds; they are undergoing interesting reactions and applications [5]. Azine compounds have been used in medicinal and materials relevant applications such as anti–bacterial drugs [6], anti–malarial drugs [7] anti–fungal drugs [8], drug development [9], tumor growth inhibitors [10], optoelectronics [11], NLO [12] materials , light-control devices [13], organic semiconductors [14], tunable molecular devices [15]. Azines form polymers, via Crisscross addition polymerization [16]. Azine compounds have been synthesized in various reaction conditions [17–19]. Interesting properties of donor–acceptor azines is its conjugation blockade [20] and are also used as paint drier accelerators [21]. Kononowicz and his co-workers have investigated azines and diazines with carbamate and ether moieties as functional groups which possess considerable H3 receptor antagonist activity and they are weak H2 and Hl receptor [22]. Bertolasi *et al*. have successfully synthesized keto–bile acid azines [23]. Sulphated titania, a stable solid acid has been found to act as a better catalyst with remarkable performance in an organic chemistry. Sulphated titania offers many special features in organic synthesis like Friedel–Crafts acylations and Beckmann rearrangements in solvent free condition [24], Friedel–Crafts benzylation [25], synthesis of fatty acids amide [26]. benzophenone azines [27], chalcones [28] and N–formylation of amines [29] and synthesis of pyrroles by clauson–kaas condensation under solvent-free conditions [30] etc. We are report herein, synthesis of fluorenone azines in the presence of sulphated titania acid catalyst through more efficacy such as efficient with operational simplicity which utilizes the approach of green chemistry.

2. EXPERIMENTAL
2.1. Reagents and instruments

All chemicals were purchased in analytical grade from Sigma–Aldrich, S.D. fine Chemicals, Spectrochem and Emplura. FT–IR spectra are recorded using an Avatar–330 FT–IR spectrophotometer using KBr pellets. ^{1}H and ^{13}C NMR spectra are recorded on a BRUKER AVANCE[III] 400 MHz instrument.

2.2. Preparation of 2–benzylidene–1– (9H–fluoren–9–ylidene)hydrazine (1)

Literature [31,27] is used in the preparation of fluorenone hydrazone and sulphated titania acid catalyst (TiO$_2$–SO$_4^{2-}$). To a mixture of fluorenone hydrazone (1 mmol) and benzaldehyde (1 mmol), 0.1 g of TiO$_2$–SO$_4^{2-}$ is added and the mixture is ground in a mortar with a pestle at room temperature for 45 seconds. Completion of the reaction is monitored by Thin Layer Chromatography (TLC). After the reaction is complete, ethyl acetate is added to the solidified crude and the insoluble catalyst is separated by filtration (Whatman No. 40). The solvent is evaporated to get the product. The crude sample is recrystallized from absolute ethanol. The structure of product obtained is confirmed by FT–IR, ^{1}H and ^{13}C NMR spectral analysis. Same experimental procedure is followed for the synthesis of azines **2–15**. Scheme 1 indicated synthetic routes of target azine compounds.

3. SPECTRAL ANALYSIS DATA

(E)–1–benzylidene–2–(9H–fluoren–9–ylidene)hydrazine (1)
IR (KBr) (cm^{-1}): 1641 (C=N stretching), 3018 (Aromatic CH), 1086 (N–N); ^{1}H NMR (CDCl$_3$, 400 MHz) (δ, ppm): azomethine proton 8.56. (s, 1H), aromatic protons 7.23−8.46. ^{13}C NMR (CDCl$_3$, 100MHz, ppm) = 159.6 (azomethene carbon), 160.4 (imino carbon), ipso carbon signals at 142.5, 141.6, 136.8, 134.4, 133.7 other aromatic carbon signals at 119.9–131.7.

(E)–1–(9H-fluoren–9–ylidene)–2–(4–methylbenzylidene)hydrazine (2)
IR (KBr) (cm^{-1}): 1604 (C=N stretching), 3044 (CH), 3044 (N-N); ^{1}H NMR (CDCl$_3$, 400 MHz) (δ, ppm): azomethine proton 8.55 (s, 1H), methyl proton 2.44 (s, 3H), aromatic protons 7.31–8.50. ^{13}C NMR (CDCl$_3$, 100MHz, ppm) = 159.8 (azomethene carbon), 160.3 (imino carbon), 21.7 (methyl carbon) and other aromatic carbon signals 119.8–142.4.

(E)–1–(9H–fluoren–9–ylidene)–2–(4–methoxybenzylidene)hydrazine (3)
IR (KBr) (cm^{-1}): 1661 (C=N stretching), 3151 (CH), 1013 (N–N); ^{1}H NMR (CDCl$_3$, 400 MHz) (δ, ppm): azomethine proton 8.56 (s, 1H), methoxy 3.87 (s, 3H) proton aromatic protons 7.00–8.53. ^{13}C NMR (CDCl$_3$, 100MHz, ppm) = 160.4 (azomethene carbon), 160.1 (imino carbon), 55.4 (methoxy carbon) and other aromatic carbon signals 114.2–162.3.

(E)–1–(9H–fluoren–9–ylidene)–2–(4–(methylthio)benzylidene)hydrazine (4)
IR (KBr) (cm^{-1}): 1660 (C=N stretching), 3150 (CH), 1075 (N–N); ^{1}H NMR (CDCl$_3$, 400 MHz) (δ, ppm): azomethine proton 8.54 (s, 1H), thiomethyl 2.55 (s, 3H), aromatic protons 7.28–8.48. ^{13}C NMR (CDCl$_3$, 100MHz, ppm) = 159.5 (azomethene carbon), 160.4 (imino carbon), 15.1 (thiomethyl) and other aromatic carbon signals 119.88–143.35.

(E)–1–(4–bromobenzylidene)–2–(9H–fluoren–9–ylidene)hydrazine (5)
IR (KBr) (cm^{-1}): 1617 (C=N stretching), 3068 (CH), 1023 (N–N); ^{1}H NMR (CDCl$_3$, 400 MHz) (δ, ppm): azomethine proton 8.51 (s, 1H), aromatic protons 7.29–8.38. ^{13}C NMR (CDCl$_3$, 100MHz, ppm) = 158.2 (azomethene carbon), 160.4 (imino carbon) and other aromatic carbon signals 119.93–142.5.

(E)–1–(9H-fluoren–9–ylidene)–2–(4–fluorobenzylidene)hydrazine (6)
IR (KBr) (cm^{-1}): 1600 (C=N stretching), 3050 (CH), 1095 (N–N); ^{1}H NMR (CDCl$_3$, 400 MHz) (δ, ppm): azomethine proton 8.54 (s, 1H), aromatic protons 7.18–8.44. ^{13}C NMR (CDCl$_3$, 100MHz, ppm) = 159.5 (azomethene carbon), 160.4 (imino carbon) and other aromatic carbon signals at 116.13–165.9.

(E)–1–(9H–fluoren–9–ylidene)–2–(1–phenylethylidene)hydrazine (7)

IR (KBr) (cm^{-1}): 2919 (SP3 CH stretching), 3047 (Aromatic CH), 1025 (N–N); ^{1}H NMR CDCl$_3$, 400 MHz) (δ, ppm): methyl appeared at 2.42 (s, 3H), aromatic protons 7.17−8.01 (13 protons). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) = 15.1 (methyl carbon), 158.0 (imino carbon), 154.46 (CH$_3$–C=N) ipso carbon signals at 142.2, 141.3, 140.9, 137.8 and 136.8 other aromatic carbon signals 119.5–131.5.

(E)-1-(9H-fluoren-9-ylidene)-2-(1-(p-tolyl)ethylidene)hydrazine (8)

IR (KBr) (cm^{-1}): 3192 (SP3 CH stretching), 2935 (Aromatic CH), 1034 (N–N); ^{1}H NMR CDCl$_3$, 400 MHz) (δ, ppm): methyl appeared at 2.44 and 2.40 (s, 3H), aromatic protons 7.17–7.44 (12 protons). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) = 21.4 and 15.0 (methyl carbon), 158.1 (imino carbon), 154.4 (CH$_3$–C=N) and other aromatic carbon signals 119.8–142.2.

(E)-1-(9H-fluoren-9-ylidene)-2-(1-(4-methoxyphenyl)ethylidene)hydrazine (9)

IR (KBr) (cm^{-1}): 3016 (SP3 CH stretching), 3149 (Aromatic CH), 1034 (N–N), 1226 SP3 (C–O); ^{1}H NMR CDCl$_3$, 400 MHz) (δ, ppm): methyl appeared at 2.41 (s, 3H), methoxy appeared at 3.88 (s, 3H) aromatic protons 6.99–7.98 (12 protons). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) = 14.9 (methyl carbon), 55.1 (methoxy), 161.2 (C–OCH$_3$) 158.2 (imino carbon), 154.7 (CH$_3$–C=N) and other aromatic carbon signals 113.9–142.2.

(E)-1-(9H-fluoren-9-ylidene)-2-(1-(4-isobutylphenyl)ethylidene)hydrazine (10)

IR (KBr) (cm^{-1}): 2921 (SP3 CH stretching), 3203 (Aromatic CH), 1011 (N–N); ^{1}H NMR CDCl$_3$, 400 MHz) (δ, ppm): methyl appeared at 0.96, 0.94 and 2.40 (s, 3H), CH proton appeared at 1.93 (m, 1H), CH$_2$ appeared at 2.55 (d, 2H), aromatic protons 7.19–8.05 (12 protons). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) = 14.8 (methyl carbon), 22.4–45.3 (isobuthyl carbons), 158.5 (imino carbon), 154.5 (CH$_3$–C=N) and other aromatic carbon signals 119.7–143.9.

(E)-1-(1-(4-bromophenyl)ethylidene)-2-(9H-fluoren-9-ylidene)hydrazine (11)

IR (KBr) (cm^{-1}): 2915 (SP3 CH stretching), 3064 (Aromatic CH), 1011 (N–N); ^{1}H NMR CDCl$_3$, 400 MHz) (δ, ppm): methyl appeared at 2.38 (s, 3H), aromatic protons 7.16–7.93 (12 protons). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) = 14.9 (methyl carbon), 157.2 (imino carbon), 154.6 (CH$_3$–C=N) other aromatic carbon signals 119.8–131.1.

(E)-1-(1-(4-chlorophenyl)ethylidene)-2-(9H-fluoren-9-ylidene)hydrazine (12)

IR (KBr) (cm^{-1}): 2920 (SP3 CH stretching), 3055 (Aromatic CH), 1006 (N–N); ^{1}H NMR CDCl$_3$, 400 MHz) (δ, ppm): methyl appeared at 2.39 (s, 3H), aromatic protons 7.17–7.94 (12 protons). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) = 14.9 (methyl carbon), 157.1 (imino carbon), 154.7 (CH$_3$–C=N) other aromatic carbon signals 119.8–131.1.

(E)-1-(9H-fluoren-9-ylidene)-2-(1-(4-fluorophenyl)ethylidene)hydrazine (13)

IR (KBr) (cm^{-1}): 2957 (SP3 CH stretching), 3065 (Aromatic CH), 1010 (N–N); ^{1}H NMR CDCl$_3$, 400 MHz) (δ, ppm): methyl appeared at 2.41 (s, 3H), aromatic protons 7.15–7.90 (12 protons). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) = 15.0 (methyl carbon), 157.7 (imino carbon), 154.7 (CH$_3$–C=N), C–F carbon signals 165.4 and 162.9 other aromatic carbon signals 115.5–145.6.

### (E)-1-(9H-fluoren-9-ylidene)-2-(1-(4-nitrophenyl)ethylidene)hydrazine (14)

IR (KBr) (cm^{-1}): 2922 (SP3 CH stretching), 3057 (Aromatic CH), 1009 (N–N) 1592 and 1339 (NO$_2$); ^{1}H NMR CDCl$_3$, 400 MHz) (δ, ppm): methyl appeared at 2.45 (s, 3H), aromatic protons 7.17–7.81 (12 protons). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) = 15.1 (methyl carbon), 156.1 (imino carbon), 154.6 (CH$_3$–C=N), other aromatic carbon signals 119.5–148.6.
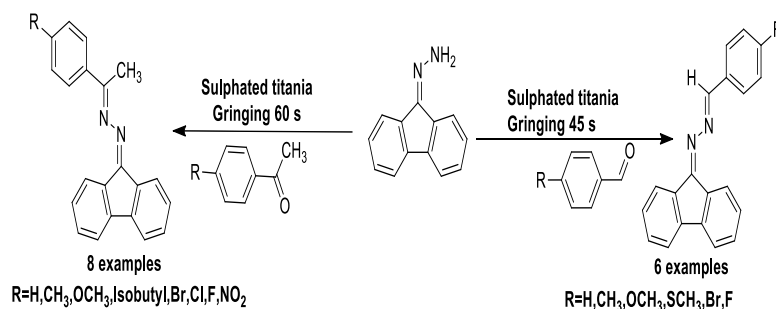
Scheme 1. Synthetic routes of target azine compounds.

4. RESULT AND DISCUSSION

A number of synthetic strategies have been reported for the synthesis of conjugated azines under various conditions. In thermal method 0.01 M of (9H-fluoren-9-ylidene) hydrazine was dissolved in 20 ml of ethanol. 0.01 M of benzaldehyde is added and the reaction mixture is heated with stirring for 1.5 hours. The resulting solid is filtered, washed with water, dried and recrystallized from ethanol. Symmetrical azine is removed by column chromatography by using high baleful benzene and petether (yield 78%). The hydrazone and aldehyde (or) ketone reaction mixture ground in mortar blossomed out the unsymmetrical azines only in the presence of sulphated titania. Formation of all azines consumed less than 1 min of time with operational simplicity. The thermal method troubles are unable to be felt when using sulphated titania (low reaction time, high yield, undesired side product). These results mean using sulphated titania is an efficient method for synthesis of unsymmetrical azines. Yields are not much stricken by the substituents present in the aldehydes or ketones while using sulfated titania photo catalyst. Synthesized azine compounds are given in **Table 1**. Strong ring deactivating nitro benzaldehyde rejected itself to walk through reaction path, but the same nitro group in acetophenone underwent rapid change. This may be due to electron releasing methyl group in acetophenone moiety which will lower the electron withdrawing nature of nitro group than that in nitro benzaldehyde. Steric effect operate in azine formation using sulphated titania which concluded that benzophenone does not change in to product, aldehyde rapidly changed into azine when compared with acetophenone. 4–OH–benzaldehyde and 4–OH–acetophenone are impotent in azine formation because of strong interaction with TiO_2 surface and phenolic compounds to form a $\equiv$Ti–O–Ph. **Scheme 2** implies the protonation of hydrazone with acidic TiO_2–SO_4^{2-}. This protonated hydrazone (A) condenses with benzaldehyde initiating an intermediate (B) which on dehydration and deprotonation produces the product azine (C). Reusability of the catalyst is also examined, the catalytic activity slightly decreases in fourth run of the experiment. Actual environment of the acid sites of the sulfated titania is not known but Vega *et al.* [32] proposed a model of sulphated titania in **Scheme 3**.
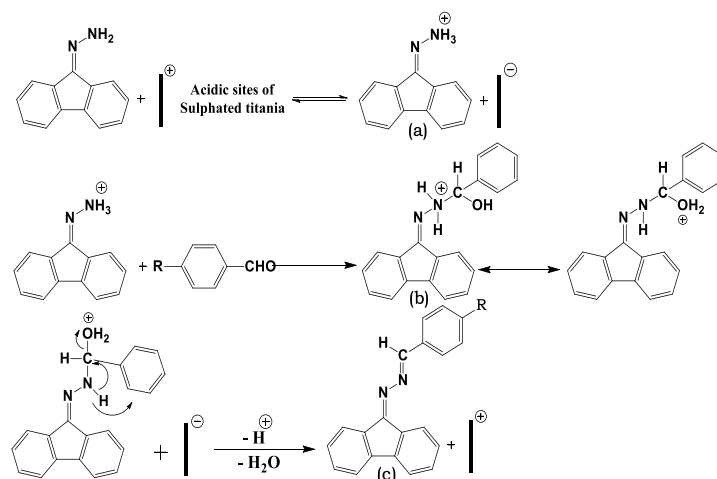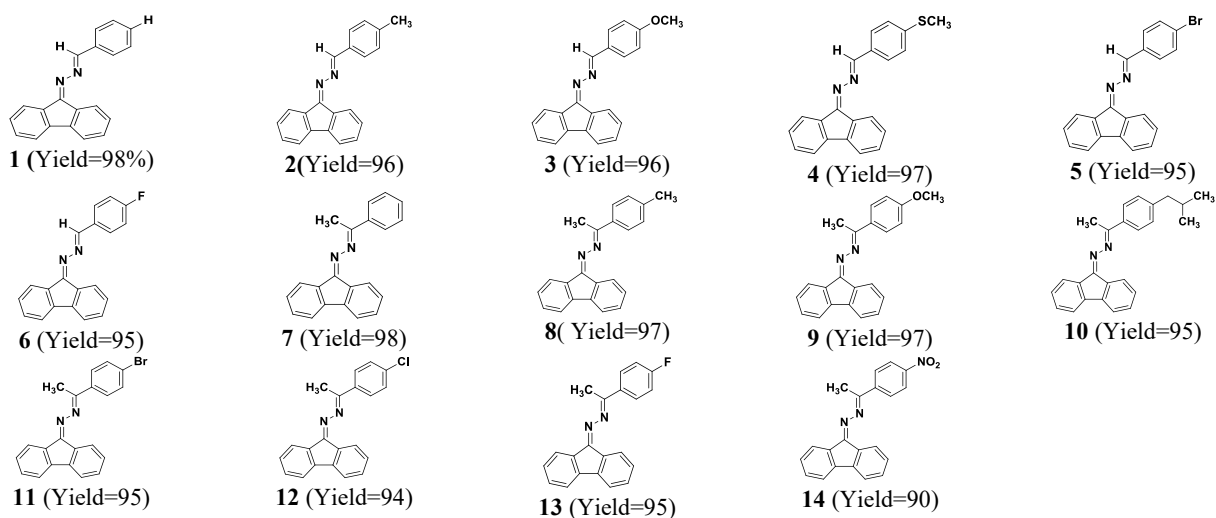
Scheme 2. Proposed mechanism of azine formation
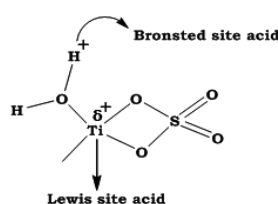
Scheme 3. Proposed structure of sulfated titania.

Table 1. Synthesis of unsymmetrical azine derivatives using sulfated titania under solvent free conditions.

1 (Yield=98%)   **2(**Yield=96)   **3 (**Yield=96)   **4 (**Yield=97)   **5 (**Yield=95)

6 (Yield=95)   **7 (**Yield=98)   **8(** Yield=97)   **9 (**Yield=97)   **10 (**Yield=95)

11 (Yield=95)   **12 (**Yield=94)   **13 (**Yield=95)   **14 (**Yield=90)

5. CONCLUSION

In synthesis of unsymmetrical azines in thermal method there are several disadvantages such as high reaction time, low yield, using baleful solvent synthesis and purification. Above mentioned defects cannot been seen when solid acid catalyst TiO_2-SO_4^{2-} is used. Benzaldehyde containing nitro group cannot change into product but *p*-nitro acetophenone undergoes a rapid change to form the product. Phenolic benzaldehyde and acetophenone interact with TiO_2 surface and hence it cannot change into product. Advantage of the catalyst is its reusability and high efficacy than thermal method.

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