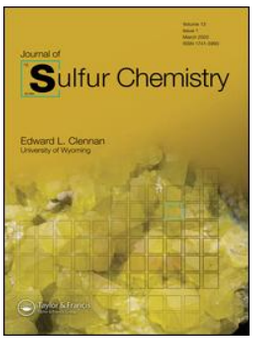

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Synthesis of novel quaternary ammonium salts from 1, 2-benzothiazine derivatives

Salman Gul, Maria Saleem, Munawar Ali Munawar, Hafiz Adnan Ahmad, Ejaz Ahmed, Robina Begum and Zahoor H. Farooqi

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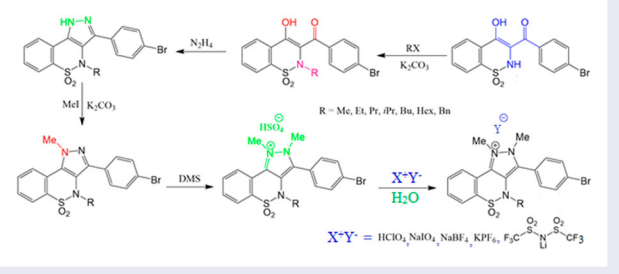
ABSTRACT

A series of novel 1,2-benzothiazine based quaternary ammonium salts were successfully prepared through different organic transformations. Products of all transformations and final salts were separated out and purified. The product yields were good to excellent for all transformations. Resultant 1,2-benzothiazine based cationic amphiphilic systems were stabilized using different counter anions. All final products were confirmed by ^{1}HNMR and ^{13}CNMR analyses. 1,2-benzothiazine based quaternary ammonium salts have a potential to be employed as a phase transfer catalyst for various reactions in future.



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KEYWORDS
Sulfur containing heterocyclic compounds; benzothiazine derivatives; quaternary ammonium salts

1. Introduction

Quaternary ammonium salts are ionic compounds that may be represented as $NR_4^+Y^-$, where R may be the same or different groups and Y^- is a replaceable counter anion. $NR_4^+Y^-$ system is a result of replacement of all four of the hydrogen atoms directly bonded to the nitrogen from $NH_4^+Y^-$ by aryl, alkyl or some other groups. The synthesis and characterization of quaternary ammonium compounds have gained much attention in the field of organic chemistry due to their potential use as versatile, nontoxic and cheap phase transfer catalyst in different organic reactions [1]. These compounds are used

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as a catalyst to initiate and to speed up various organic reactions like Williamson synthesis [2] and Michael addition [3]. It has also been found that quaternary ammonium salts are superior over other phase transfer catalytic systems like polyethylene glycol and crown ethers. They have phase transfer activity comparable to that of cryptands. Moreover, applications of cryptands, polyethylene glycol and crown ethers are limited, and their high concentration is needed to achieve their phase transfer activity. They are also known for their excellent antimicrobial abilities [4]. The synthesis of various quaternary ammonium compounds with different functionalities from various starting materials has been recently reviewed by various groups [5,6]. To the best of our knowledge, the synthesis and characterization of thiazine-based quaternary ammonium compounds have been rarely reported in the literature, and it needs to be explored for their versatile applications.

Thiazines are six-membered ring heterocyclic systems containing sulfur (S) and nitrogen (N) atoms in the same ring. When they are fused with the benzene ring, they produce bicyclic system containing N and S atoms in the same ring, which is known as benzothiazine. Different derivatives of benzothiazine have excellent microbial activities. Benzothiazines are known as antipsychotic drugs since last few decades [7]. Potent anticarcinogenic, antiinflammatory, fungicidal, herbicidal, antimicrobial and analgesic actions of benzothiazine derivatives has been widely reported in the literature [8–10]. Benzothiazine derivatives are also useful in antioxidant [11] and anticancer areas [12]. They are also used as precursors for the preparation of different organic compounds having anticorrosion [13] and antidiabetic activities [14].

Due to the aforementioned applications, the synthesis of benzothiazine derivatives has gained much attention in the last few decades [15]. It is very important to introduce new protocols for the synthesis of benzothiazine derivatives and quaternary ammonium salts.

In the present study, a series of compounds based on 1,2-benzothiazine nucleus were prepared using 4-bromoacetophenone as a starting material. Benzothiazene-based novel quaternary ammonium salts were synthesized by quaternization of 3-(4-bromophenyl)-1-methyl-1,4-dihydropyrazolo[4,3-*c*][1,2]benzothiazine 5,5-dioxide. Pyrazolium salts with different anions were obtained by replacement of HSO_4^- with new anion using suitable replacement salt.

2. Results and discussions

Schematic illustration involving all steps of transformation along with necessary reaction conditions is shown in Scheme 1. The process was initiated by bromination of 4-bromoacetophenone (**a**) using *N*-bromosuccinimide (NBS) as a brominating agent to obtain product (**b**) with 95% yield. Purified (**b**) was dissolved in dried *N*,*N*-Dimethylformamide (DMF) and then heated with dried sodium saccharin (**c**) to obtain product (**d**) as a result of linkage between (**b**) and (**c**) through nitrogen of heterocyclic ring with 89% yield. Twenty-minute refluxing of (**d**) with sodium metal dissolved in dried methanol gives product (**e**) with 74% yield. Replacement of hydrogen atom bonded with nitrogen of heterocyclic ring with alkyl group (R = Me, Et, Pr, iPr, Bu, Bn) was carried out using suitable alkyl halide (alkyl bromide or alkyl iodide) in the presence of stepwise addition of K_2CO_3 base to obtain product (**f**) with different R groups having yield in the range of 94–96%. It is worth mentioning that the yield of the reaction product

(**f**) was found to be dependent on R and halide (X) groups of alkyl halide used. Base screening experiments revealed that the yield of (**f**) also depends on base used in the reaction. The yield of the product (**f**) was found to be highest in case of K_2CO_3 in comparison to other bases tested for the same purpose. Treating (**f**) with hydrazine (N_2H_4) in the presence of ethyl alcohol does not only reduce both carbonyl and phenolic groups but also creates N-N linkage in the form of a new 5-membered heterocyclic ring. The yield of resulting product (**g**) was found to be in the range of 81–83%. Replacement of hydrogen directly bonded to nitrogen by methyl group was carried out by refluxing of product (g) in the presence of MeOH and K_2CO_3 to obtain product (**h**) with the reasonable yield. Quaternization of 3-(4-bromophenyl)-1-methyl-1,4-dihydropyrazolo[4,3-*c*][1,2]benzothiazine 5,5-dioxide (**h**) was carried out by adding dimethyl sulfate (DMS) into stirred solution of any one of (**h**) in xylene at 60°C. The temperature was raised, and the process was further continued at 100°C for 6 h to obtain a series of quaternary ammonium salts based on benzothiazine compounds (**i**). The properties and applications of quaternary ammonium salt do not only depend on the structure of its cation but also depend on the type of counter anion. The surface and micellar properties of quaternary ammonium salts like their surface activity, solubility, aqueous stability and associative behavior depend on nature, size and geometry of counter ions. The effect of counter ions on properties and applications of quaternary ammonium salts has been widely reported in the literature [16–19]. Therefore, replacement of HSO_4^- with different anions was also carried out by treating (**h**) with the suitable source salt to obtain a variety of quaternary compounds to be used for different applications. The resulting products are shown in Scheme 1 (**i**). Proton NMR and Carbon-13 NMR data along with spectra for all prepared quaternary ammonium salts and their structures are given as supporting information.

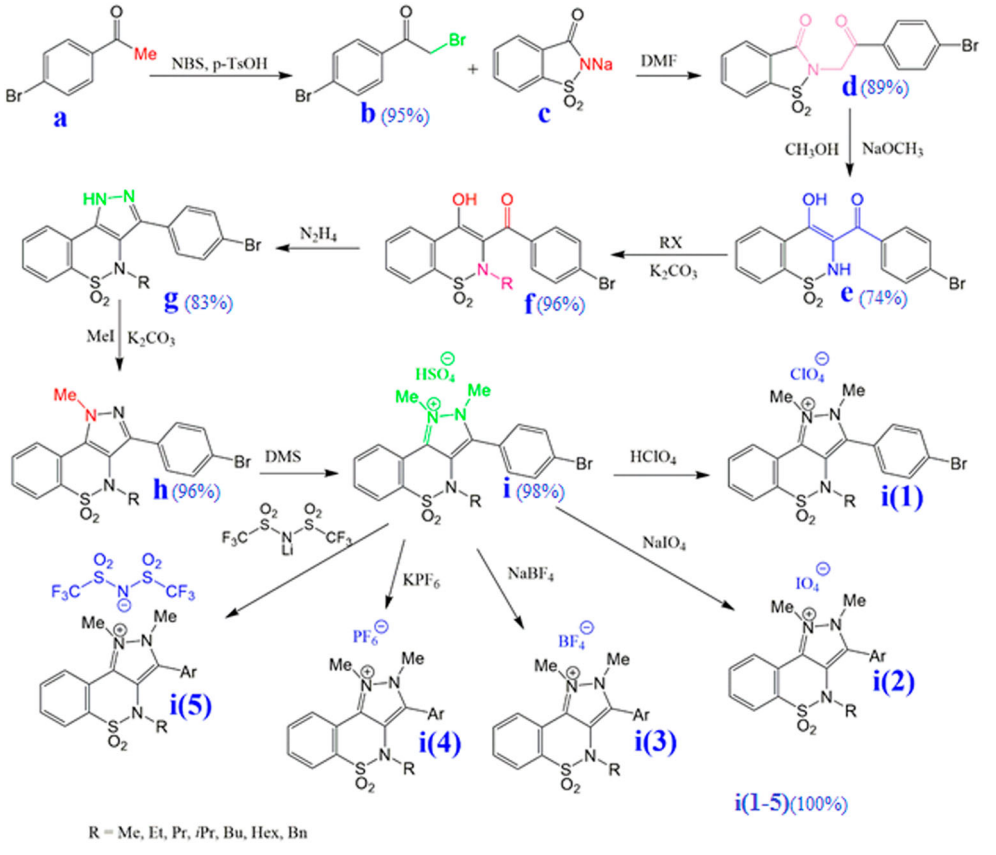
3. Conclusion

A series of quaternary ammonium salts was successfully prepared from benzothiazine derivatives by multi-step routs involving various organic transformations starting from 4-bromoacetophenone to final cationic amphiphilic salts having different anions. All steps involved in overall scheme of synthesis were facile with good to excellent yields. Medicinal, antimicrobial and catalytic applications of the synthesized cationic amphiphilic systems are in progress in our laboratory and will be reported shortly.

4. Experimental

4.1. Preparation of 2-bromo-1-(4-bromorophenyl)ethanone

4-Bromoacetophenone (10 mmol) and *p*-toluenesulfonic acid (*p*-TsOH) (2.58 g, 15 mmol) were taken in acetonitrile (30 mL). During stirring, NBS (1.78, 10 mmol) was added slowly. Reaction mixture was refluxed for 2 h, and then solvent was evaporated on rotary. The residue was dissolved in dichloromethane, washed with 95 mL water, dried with $MgSO_4$ and solvent was removed by evaporation to achieve a product with the 95% yield.



Scheme 1. Schematic illustration involving all steps of organic transformations starting from 4-bromoacetophenone (a) to quaternary ammonium salts having different anions (i).

4.2. Preparation of 2-[2-(4′-bromophenyl)-2-oxoethyl]-1,2-benzisothiazol-3(2H)-one 1,1-dioxide

2-Bromo-1-(4′-bromophenyl)ethanone (15 mmol) was dissolved in dry DMF, and dried sodium saccharin (3.08 g, 15 mmol) was added to the heated mixture at 120°C for 3 h. When TLC showed that all 2-bromo-1-(4-bromophenyl)ethanone has converted to the product, then it was added to slightly acidic cold water to obtain white precipitates that were filtered and washed with excessive water and methanol to remove all impurities. Product purity was confirmed with the help of two-dimensional TLC, and the product was synthesized with the 89% yield.

4.3. Preparation of 3-(4′-bromobenzoyl)-4-hydroxy-2H-1,2-benzothiazine 1,1-dioxide

Sodium metal (4.83 g, 210 mmol) was dissolved in completely dried methanol (45 mL), and 2-[2-(4′-bromophenyl)-2-oxoethyl]-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide (30 mmol)

was added to reflux for 20 min. Then, reaction mixture was poured to slightly acidic ice-cold water, and yellow precipitates were formed that was filtered and recrystallized with methanol to have a pure product with the 74% yield.

4.4. Preparation of 2-alkyl-3-(4′-bromobenzoyl)-4-hydroxy-2H-1,2-benzothiazine 1,1-dioxide

3-(4′-bromobenzoyl)-4-hydroxy-*2H*-1,2-benzothiazine 1,1-dioxide (15 mmol) was dissolved in acetonitrile (50 mL), and alkyl bromide or iodide (15 mmol) was added. Potassium carbonate (2.07 g, 15 mmol) was taken and divided into three parts, where the first portion was added after 10 min stirring and remaining two installments were added with the time difference of 15 min during reflux of 2 hr. When the chromatographic analysis (TLC) showed that all amount of substrate has been converted to product, then the reaction mixture was poured into slightly acidic ice-cold water and pale yellow product was obtained in the form of precipitates that were filtered and dried at 70°C.

4.5. Preparation of 3-(4′-bromophenyl)-4-methyl-2,4-dihydropyrazolo[4,3-c][1,2] benzothiazine 5,5-dioxide

2-Alkyl-3-(4′-bromobenzoyl)-4-hydroxy-2H-1,2-benzothiazine 1,1-dioxide (7.5 mmol) and hydrazine monohydrate (2.91 mL, 60 mmol) were dissolved in ethanol, and the mixture was refluxed for 3 h. When reactants showed no spot on the TLC plate, then reaction contents were added to slightly acidic ice-cold water, and pH of the mixture was adjusted at 7–8 to precipitate out the required product. Then, white precipitates were subjected to filtration and drying to obtain pure product with 83% yield.

4.6. Preparation of 3-(4-bromophenyl)-1-methyl-1,4-dihydropyrazolo[4,3-c][1,2]benzothiazine 5,5-dioxide

3-(4′-Bromophenyl)-4-methyl-2,4-dihydropyrazolo[4,3-c][1,2] benzothiazine 5,5-dioxide (15 mmol) was taken in acetonitrile (50 mL), and CH_3I (15 mmol) was added. Potassium carbonate (2.07 g, 15 mmol) was taken and divided into three parts, where the first portion was added after 10 min stirring and remaining two installments were added with the time difference of 15 min during reflux of 2 h. When the TLC result showed that all amount of substrate has been converted to product, then the reaction mixture was poured into slightly acidic ice-cold water. The pure product was obtained by precipitation followed by filtration and drying at 70°C.

4.7. Quaternization of 3-(4-bromophenyl)-1-methyl-1,4-dihydropyrazolo[4,3-c][1,2]benzothiazine 5,5-dioxide

DMS (0.21 mmol) was added in a stirred solution of title compound in xylene at 60°C. After dissolving DMS, the reaction mixture was further heated at 100°C for additional 6 h. After the completion of the reaction, the reaction mixture was cooled and the solvent was

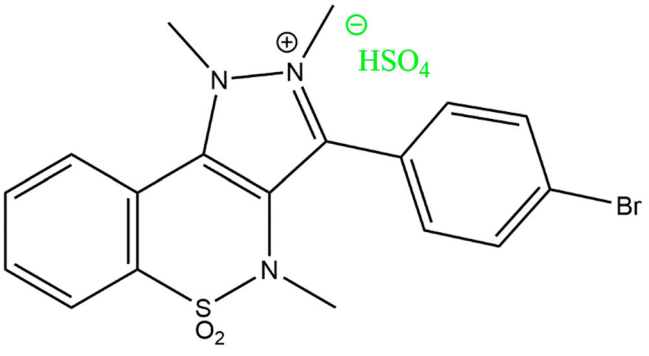
removed. The crude product was adsorbed on silica gel to carry out its purification using column chromatography.

4.8. General procedure for the replacement of anions

Separately prepared aqueous solution of anion replacement salt (0.6 mmol) and an aqueous solution of the earlier synthesized pyrazolium salt (0.5 mmol) immediately produced the precipitates on mixing at laboratory temperature. The precipitates were filtered and washed with ice-cold water followed by drying at room temperature. Almost in all reactions, quantitative yields were obtained during anion replacement.

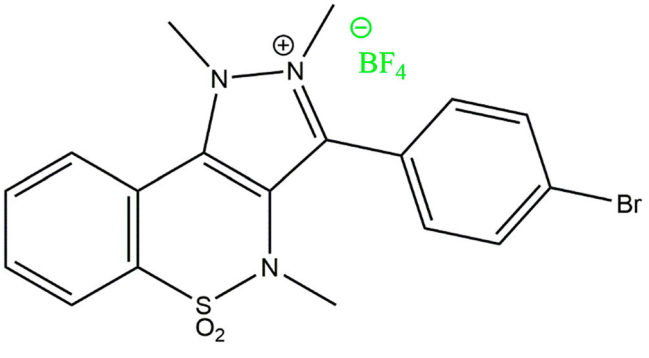
4.9. Characterization of products

The synthesized quaternary ammonium salts were separated, purified and characterized. ^{1}HNMR and ^{13}CNMR analyses were used for confirmation of the products. The NMR spectra of each product were recorded using dimethyl sulfoxide (DMSO) as a solvent. Chemical shift values are reported as δ (ppm).^{1}HNMR and ^{13}CNMR spectra of all products are given in supporting information, while data are presented as follows:



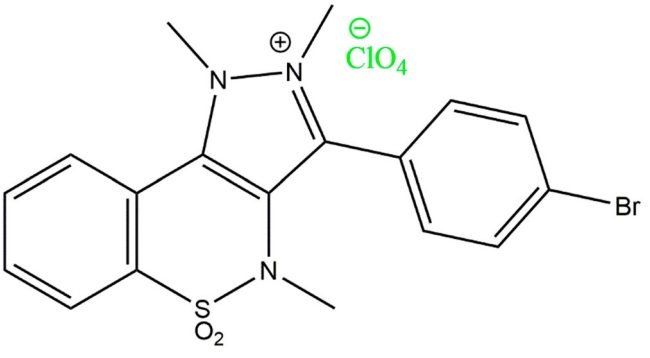
^{1}H NMR (600 MHz, DMSO) δ 8.38 (d, J = 7.9 Hz, 1H), 8.17 (d, J = 7.7 Hz, 1H), 8.09 (t, J = 7.8 Hz, 1H), 8.02 (t, J = 7.7 Hz, 1H), 7.97 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 4.53 (s, 3H), 4.09 (s, 3H), 2.77 (s, 3H).

^{13}C NMR (151 MHz, DMSO) δ 140.54, 134.63, 133.70, 133.44, 133.37, 132.27, 127.82, 126.27, 125.93, 123.59, 123.17, 120.89, 38.85, 37.96, 36.22.



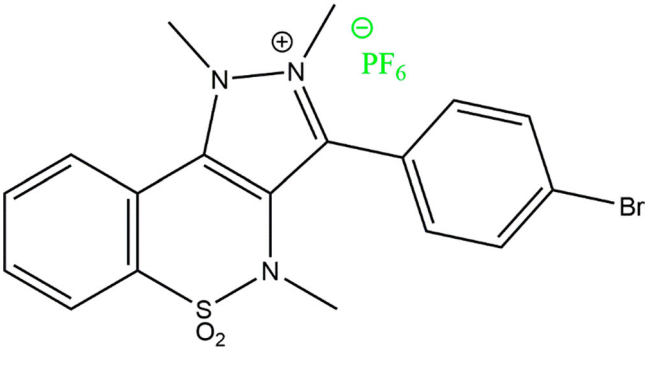
^{1}H NMR (400 MHz, DMSO) δ 8.39 (d, J = 7.8 Hz, 1H), 8.19 (d, J = 7.7 Hz, 1H), 8.10 (t, J = 7.8 Hz, 1H), 8.02 (d, J = 7.1 Hz, 1H), 7.99 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 4.52 (s, 3H), 4.08 (s, 3H), 2.78 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 140.66, 134.66, 133.74, 133.57, 133.44, 133.37, 132.16, 127.64, 126.36, 126.02, 123.65, 123.04, 120.76, 38.85, 37.96, 36.22.



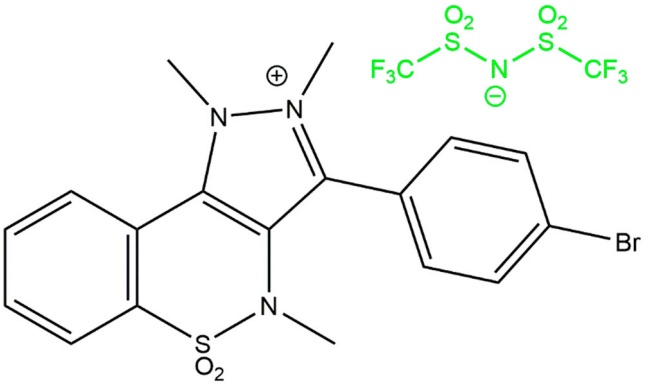
^{1}H NMR (400 MHz, DMSO) δ 8.38 (d, J = 7.7 Hz, 1H), 8.19 (d, J = 6.6 Hz, 1H), 8.10 (t, J = 7.1 Hz, 1H), 8.03 (t, J = 7.6 Hz, 1H), 7.99 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 4.52 (s, 3H), 4.08 (s, 3H), 2.78 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 140.66, 134.65, 133.75, 133.57, 133.44, 133.37, 132.16, 127.65, 126.36, 126.02, 123.65, 123.03, 120.77, 38.85, 37.98, 36.24.



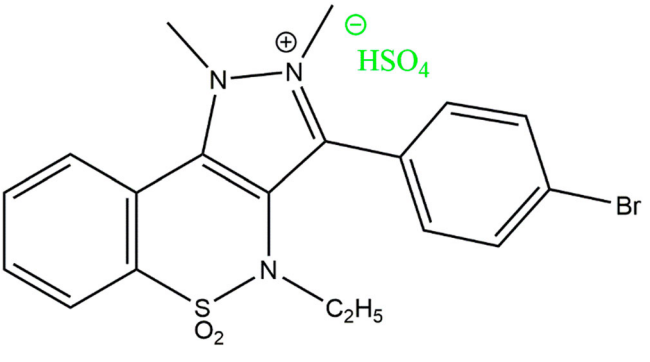
^{1}H NMR (400 MHz, DMSO) δ 8.39 (d, J = 7.7 Hz, 1H), 8.20 (d, J = 7.4 Hz, 1H), 8.10 (t, J = 7.5 Hz, 1H), 8.06–7.98 (m, 3H), 7.66 (d, J = 8.1 Hz, 2H), 4.52 (s, 3H), 4.09 (s, 3H), 2.79 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 140.67, 134.67, 133.73, 133.59, 133.46, 133.36, 132.15, 127.63, 126.38, 126.04, 123.64, 123.01, 120.75, 38.86, 37.98, 36.24.



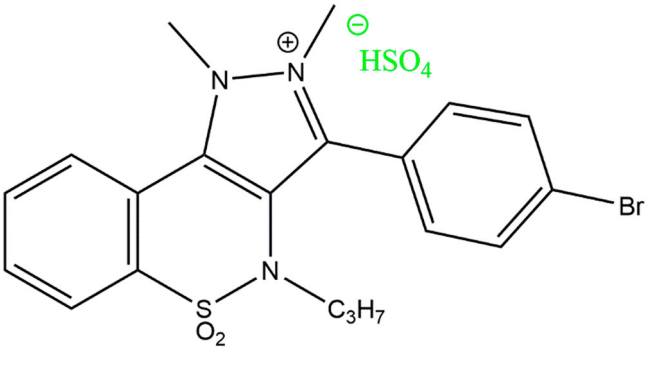
^{1}H NMR (400 MHz, DMSO) δ 8.39 (d, J = 7.7 Hz, 1H), 8.19 (d, J = 6.7 Hz, 1H), 8.10 (t, J = 7.1 Hz, 1H), 8.03 (t, J = 7.3 Hz, 1H), 7.99 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 4.52 (s, 3H), 4.08 (s, 3H), 2.78 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 140.67, 134.63, 133.74, 133.57, 133.44, 133.39, 132.14, 127.62, 126.38, 126.02, 123.65, 123.00, 121.55, 120.74, 38.82, 37.99, 36.25.



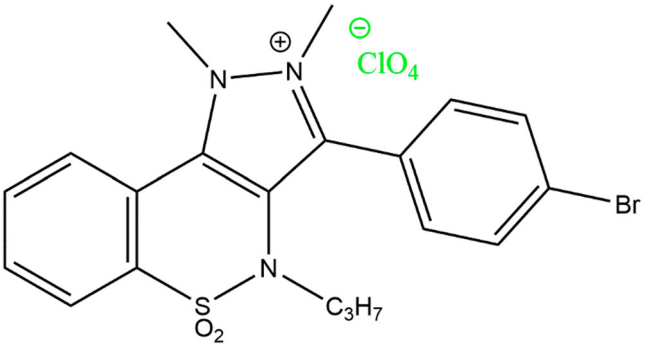
^{1}H NMR (600 MHz, DMSO) δ 8.38 (d, J = 7.9 Hz, 1H), 8.16 (d, J = 7.8 Hz, 1H), 8.07 (t, J = 7.3 Hz, 1H), 8.02 (t, J = 7.6 Hz, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 4.52 (s, 3H), 4.09 (s, 1H), 3.23 (q, J = 7.1 Hz, 1H), 0.53 (t, J = 7.1 Hz, 1H).

^{13}C NMR (151 MHz, DMSO) δ 140.66, 135.55, 134.66, 134.50, 133.54, 133.45, 132.16, 127.76, 126.30, 125.08, 123.31, 121.66, 120.78, 47.81, 37.95, 36.19, 12.23.



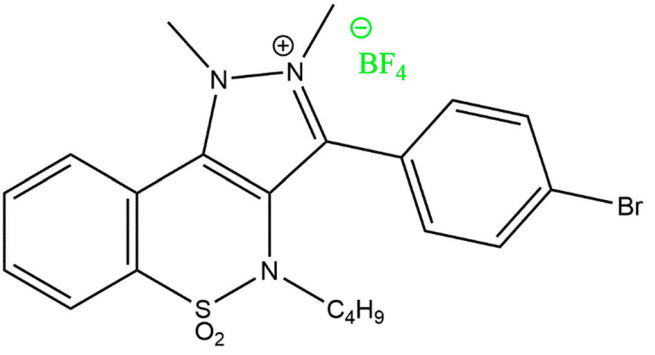
^{1}H NMR (600 MHz, DMSO) δ 8.38 (d, J = 7.9 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H), 8.08 (t, J = 8.4 Hz, 1H), 8.02 (t, J = 7.7 Hz, 1H), 7.99 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 4.52 (s, 3H), 4.07 (s, 3H), 3.15–3.12 (m, 2H), 1.00–0.90 (m, 2H), 0.35 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, DMSO) δ 140.32, 135.21, 134.46, 134.23, 133.49, 133.46, 132.21, 127.67, 126.31, 125.12, 123.37, 121.89, 120.67, 53.42, 53.26, 37.96, 36.13, 20.23, 10.81.



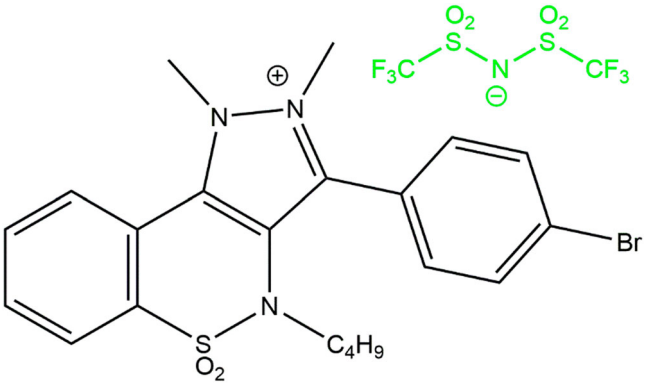
^{1}H NMR (400 MHz, DMSO) δ 8.38 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 6.8 Hz, 1H), 8.10–7.96 (m, 4H), 7.63 (d, J = 8.4 Hz, 2H), 4.53 (s, 3H), 4.08 (s, 3H), 3.16–3.12 (m, 2H), 1.01–0.92 (m, 2H), 0.36 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 140.36, 135.22, 134.46, 134.29, 133.47, 132.17, 127.64, 126.31, 125.10, 123.35, 121.92, 120.67, 53.45, 37.94, 36.11, 20.20, 10.80.



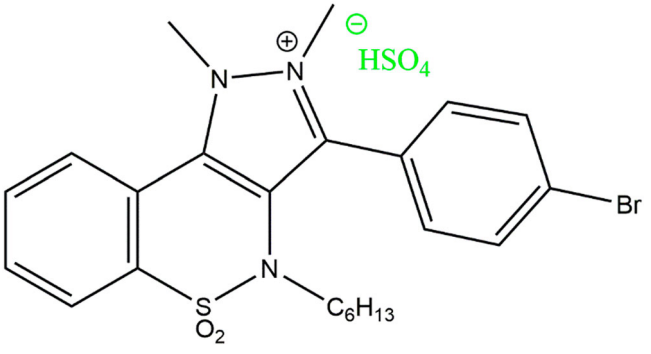
^{1}H NMR (400 MHz, DMSO) δ 8.39 (d, J = 7.6 Hz, 1H), 8.18 (d, J = 7.4 Hz, 1H), 8.11–7.99 (m, 4H), 7.63 (d, J = 7.9 Hz, 2H), 4.52 (s, 3H), 4.07 (s, 3H), 3.17 (t, J = 6.9 Hz, 2H), 0.92–0.89 (m, 2H), 0.80–0.75 (m, 2H), 0.50 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 140.37, 135.13, 134.49, 134.21, 133.52, 133.47, 132.20, 127.62, 126.34, 125.14, 123.36, 122.01, 120.64, 51.67, 37.94, 36.12, 28.88, 19.19, 13.45.



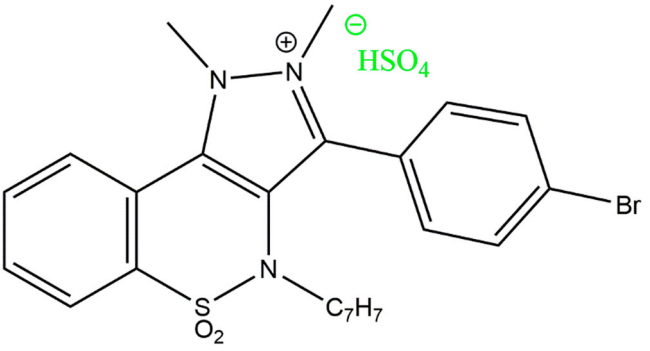
^{1}H NMR (400 MHz, DMSO) δ 8.39 (d, J = 7.8 Hz, 1H), 8.18 (d, J = 7.1 Hz, 1H), 8.11–7.99 (m, 4H), 7.63 (d, J = 8.4 Hz, 2H), 4.52 (s, 3H), 4.07 (s, 3H), 3.17 (t, J = 7.3 Hz, 2H), 0.94–0.87 (m, 2H), 0.83–0.74 (m, 2H), 0.50 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 140.40, 135.16, 134.46, 134.23, 133.53, 133.47, 132.18, 127.59, 126.36, 125.15, 123.33, 122.03, 121.55, 120.62, 118.35, 51.64, 37.97, 36.14, 28.91, 19.18, 13.43.



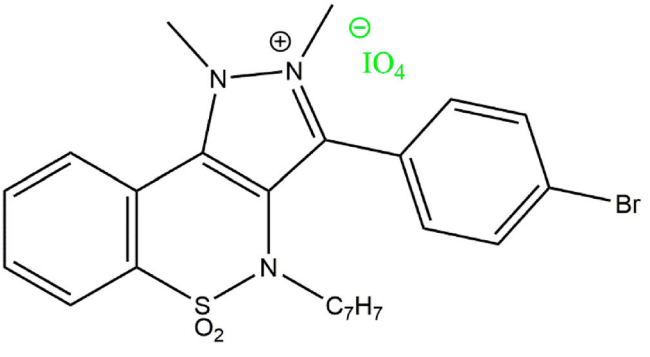
^{1}H NMR (600 MHz, DMSO) δ 8.38 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 7.7 Hz, 1H), 8.08 (t, J = 7.8 Hz, 1H), 8.02 (d, J = 15.2 Hz, 1H), 7.99 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 7.7 Hz, 2H), 4.51 (s, 3H), 4.07 (s, 3H), 3.15 (t, J = 7.3 Hz, 2H), 0.98–0.91 (m, 4H), 0.84–0.79 (m, 2H), 0.74–0.68 (m, 5H).

^{13}C NMR (151 MHz, DMSO) δ 139.94, 134.54, 133.96, 133.71, 132.98, 132.94, 131.77, 127.17, 125.87, 124.75, 122.90, 121.67, 120.19, 51.62, 37.45, 35.65, 30.34, 26.66, 25.19, 21.69, 13.67.

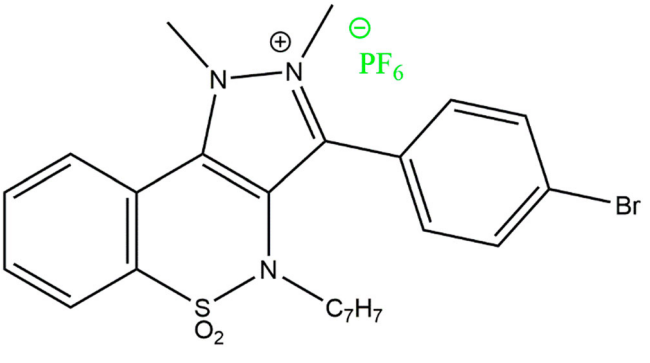


^{1}H NMR (600 MHz, DMSO) δ 8.15 (d, J = 6.9 Hz, 1H), 8.08 (dd, J = 6.9, 1.8 Hz, 1H), 7.96–7.91 (m, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.94 (t, J = 7.6 Hz, 2H), 6.72 (d, J = 7.4 Hz, 2H), 4.45 (s, 3H), 4.32 (s, 2H), 4.06 (s, 3H).

^{13}C NMR (151 MHz, DMSO) δ 137.95, 135.22, 134.87, 134.29, 133.31, 133.27, 132.06, 128.91, 128.39, 127.47, 126.28, 125.45, 122.97, 120.57, 55.74, 37.95, 36.34.

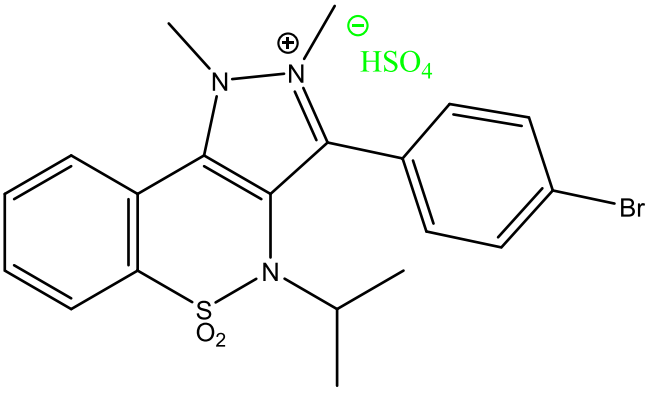


^{1}H NMR (400 MHz, DMSO) δ 8.14 (d, J = 6.6 Hz, 1H), 8.11–8.06 (m, 1H), 7.98–7.91 (m, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 6.94 (t, J = 7.6 Hz, 2H), 6.71 (d, J = 7.4 Hz, 2H), 4.44 (s, 1H), 4.33 (s, 1H), 4.06 (s, 1H).
^{13}C NMR (101 MHz, DMSO) δ 141.08, 135.26, 134.92, 134.29, 133.34, 132.81, 132.00, 128.91, 128.50, 128.38, 127.41, 126.31, 125.46, 122.93, 121.72, 120.54, 55.72, 37.93, 36.32.



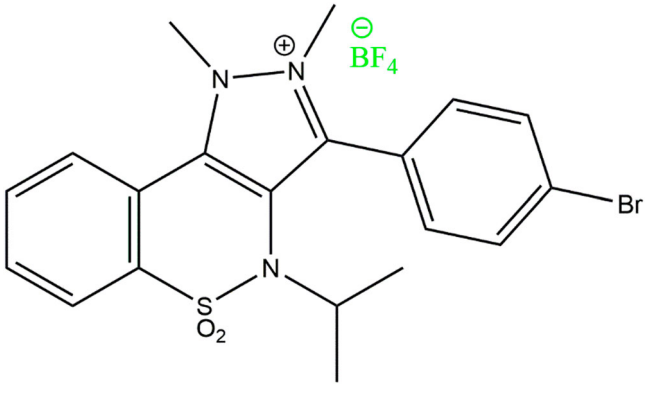
^{1}H NMR (600 MHz, DMSO) δ 8.15 (d, J = 7.1 Hz, 1H), 8.09 (d, J = 7.4 Hz, 1H), 7.97–7.90 (m, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.06 (t, J = 7.3 Hz, 1H), 6.94 (t, J = 7.5 Hz, 2H), 6.72 (d, J = 7.4 Hz, 2H), 4.45 (s, 3H), 4.33 (s, 2H), 4.07 (s, 3H).

^{13}C NMR (151 MHz, DMSO) δ 141.06, 135.25, 134.90, 134.29, 133.32, 132.89, 132.05, 128.91, 128.48, 128.39, 127.47, 126.30, 125.46, 122.99, 121.77, 120.57, 55.74, 37.99, 36.38.



^{1}H NMR (400 MHz, DMSO) δ 8.36 (d, J = 7.8 Hz, 1H), 8.15 (d, J = 7.7 Hz, 1H), 8.06 (t, J = 7.2 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 4.51 (s, 3H), 4.13 (s, 3H), 3.90–3.84 (m, 1H), 0.57 (d, J = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, DMSO) δ 142.23, 136.75, 136.03, 134.54, 133.61, 133.33, 132.44 128.00, 126.13, 125.31, 124.15, 121.01, 120.04, 57.46, 37.77, 36.23, 20.16.



^{1}H NMR (600 MHz, DMSO) δ 8.37 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 7.6 Hz, 1H), 8.07 (t, J = 7.6 Hz, 1H), 8.03–7.99 (m, 3H), 7.64 (d, J = 8.3 Hz, 2H), 4.49 (s, 3H), 4.11 (s, 3H), 3.91–3.86 (m, 1H), 0.58 (d, J = 6.7 Hz, 6H).

^{13}C NMR (151 MHz, DMSO) δ 142.33, 136.75, 136.07, 134.58, 133.69, 133.40, 132.38, 127.88, 126.20, 125.38, 124.05, 120.93, 120.13, 57.45, 37.77, 36.23, 20.14.

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Disclosure statement

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