Syntheses and Reactions of Halo- and Arylazo-Substituted 3-(3-(2-Naphthyl)acryloyl)tropolones: Formation of (Naphthalen-2-yl)Vinyl)-Substituted Heterocycle-Fused Troponoid Compounds

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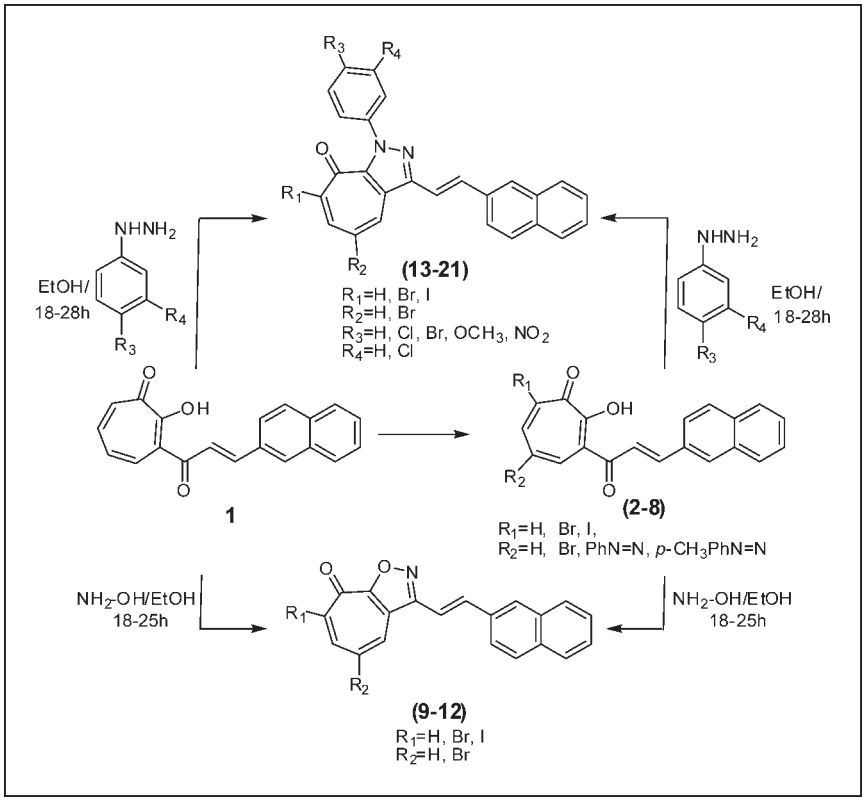

The starting substrate 3-(3-(2-naphthyl)acryloyl)tropolone (**1**) was achieved by the aldol condensation reaction of 3-acetyltropolone with 2-naphthaldehyde. Compound (**1**) reacted with bromine to give 7-bromo-(**2**) and 5,7-dibromo-3-(3-(2-naphthyl)acryloyl)tropolone (**3**) according to the amount of the brominated reagent. Iodination of **1** gave 7-iodo-3-(3-(2-naphthyl)acryloyl)tropolone (**4**). Azo-coupling reactions of **1**, **2**, and **4** gave 5-arylazo-3-(3-(2-naphthyl)acryloyl) tropolones (**5–8**). Compounds **1–4** reacted with hydroxyamine to give 3-[2-(2-naphthyl)vinyl]-8*H*-cyclohepta[*d*]isoxazol-8-ones (**9–12**). The reactions of **1–4** with phenylhydrazine and substituted phenylhydrazines gave 3-[2-(2-naphthyl)vinyl]-1-phenylcyclohepta[*c*]pyrazol-8(1*H*)-ones (**13–21**).

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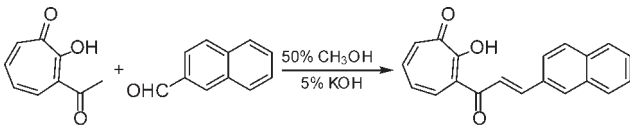
INTRODUCTION

Tropolone is an aromatic compound with a seven-membered ring, a metabolite of *Pseudomonas* sp.; the tropolone ring system represents the key structural element in a wide range of natural products, many of which are isolated from fungi [1] and higher plants [2]. Troponoids display various biological activities, such as pesticides [3], metals protease inhibition [4], and antifungal plant genetic disease genes [5]. Therefore, natural and synthetic tropolone derivatives have attracted considerable interest to organic chemists. The synthesis of substituted troponoids continues to be a considerable synthetic challenge. We have reported the electrophilic reactions of 3-acetyltropolone [6], 3-acetamidotropolone

Scheme 1



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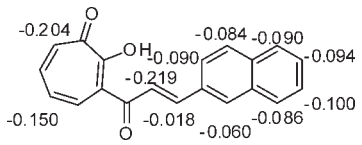


Figure 1. The calculated electronegativity of compound 1.

[7], 3-cinnamoyltropolone [8], 3-isopropenyltropolone [9], and 3-(2-quinolyl)tropolone [10], meanwhile various fused-heterocyclic troponoids have been prepared. In continuation of our interests in these compounds, we report the synthesis of 3-(3-(2-naphthyl)acryloyl)tropolone by the condensation of 3-acetyltropolone with 2-naphthaldehyde. 3-(3-(2-Naphthyl)acryloyl)tropolone possesses similar structure to 3-cinnamonytropolone and has three reactive parts for electrophilic reagents, two of which are seven-membered tropolone ring and a naphthalene ring and the third is a propenyl part between the two rings. Therefore, the reactions of 3-(3-(2-naphthyl)acryloyl)tropolone with electrophilic reagents are also expected to be interesting. On the other hand, the reactions with nucleophilic reagents are also of interest for participation of the tropolone ring, because chalcones reacted with hydroxylamine [11–14] and hydrazine [15–19] at the propenyl moiety to give diaryl-substituted isoxazolines and pyrazolines, respectively.

This article deals with the preparation of 3-(3-(2-naphthyl)acryloyl)tropolone as well as its electrophilic substitution reactions with halo and diazonium salts and the condensation reactions with hydroxylamine, phenylhydrazine, and substituted phenylhydrazines.

RESULTS AND DISCUSSION

The aldol condensation reactions of 3-acetyltropolone with substituted benzaldehydes [20] and heterocyclic aldehydes [21–23] have been reported. However, to our knowledge, the research of 3-acetyltropolone with 2-naphthaldehyde has never been performed, despite their important potential biological activities. Thus, we tried for the first time to study the preparation of 3-(3-(2-naphthyl)acryloyl)tropolone (**1**) from 3-acetyltropolone and 2-naphthaldehyde.

Scheme 1 outlines the aldol condensation reaction of 3-acetyltropolone with 2-naphthaldehyde using aqueous KOH (5%) as a catalyst and 50% methanol as solvent to furnish 3-(3-(2-naphthyl)acryloyl)tropolone (**1**) in 85.3% yield, mp 166–167°C. Its structure was established from the elemental analysis ($C_{20}H_{14}O_3$) and spectral data.

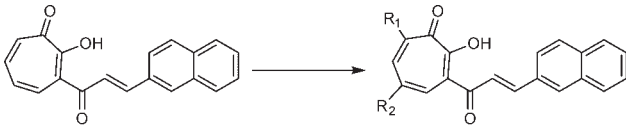
In its IR spectrum, an absorption band for the hydroxyl group was observed at 3190 cm^{-1}, and the two typical carbonyl absorption bands were observed at 1658 and 1613 cm^{-1}, respectively. The ^1H NMR spectrum showed a proton singlet at 7.98 (s, 1H) assignable to naphthalene H-1 and unresolved complex peaks at δ 7.14–7.86 for the protons of the aromatic ring and the exocyclic double bond. Moreover, the structure assigned for this reaction product was fully supported by its mass spectrum, which showed a molecular ion peak at 302 (M^+).

By theoretical calculation, the 5- and 7-position of the tropolone ring and the propenyl part have higher reactive activities than the naphthalene ring for electrophilic reagents, and their electronegativities are −0.150, −0.204, and −0.219, respectively, as shown in Figure 1.

To verify the calculated results, compound **1** was treated with some electrophilic reagents such as bromine, iodine, and diazonium salts. Thus, compound **1** was first subjected to react with bromine. When 3-(3-(2-naphthyl)acryloyl)tropolone (**1**) was reacted with bromine in acetic acid in a mole ratio of 1:1 or 1:2, the corresponding monosubstituted 7-bromo-3-(3-(2-naphthyl)acryloyl)tropolone (**2**) and disubstituted 5,7-dibromo-3-(3-(2-naphthyl)acryloyl)tropolone (**3**) were obtained in 67.7% and 73.2% yield, respectively (Scheme 2).

The structure of **2** was determined by the elemental analysis and spectral data. In the IR spectrum, an absorption band for the hydroxyl group was at 3180 cm^{-1}, and the two typical carbonyl absorption bands were observed at 1641 and 1601 cm^{-1}, respectively. The ^1H NMR spectrum showed a doublet at δ 8.50 (d, 1H, J = 8.5 Hz) assignable to tropolone H-4, a quartet at 7.76 (q, 1H, J = 10.0 Hz) attributable to tropolone H-5, a doublet at 8.18 (d, 1H, J = 10.0 Hz) for naphthalene H-6, a doublet at 7.99 (d, 1H, J = 6.3 Hz) for naphthalene H-1, and a triplet at 7.16 (t, 1H, J = 11.0 Hz) and a doublet at 7.26 (d, 1H, J = 15.6 Hz) for the proton of the carbon–carbon double bond, besides multiplet peaks at δ 7.50–7.56 and 7.83–7.87 for the

Scheme 2



1

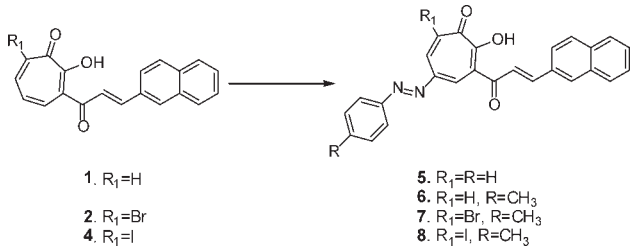
2. R_1=Br, R_2=H
3. R_1=R_2= Br
4. R_1=I, R_2=H

aromatic ring protons. It is worth mentioning that when compound **1** was treated with three equivalents of bromine, neither oxidative cyclization nor electrophilic addition reaction on carbon–carbon double bond occurred. Therefore, we concluded that the electrophilic reactivity of the 5- and 7-position of the tropolone ring were indeed higher than that of the naphthalene ring and of the propenyl part. The reaction of 3-(3-(2-naphthyl)acryloyl)tropolone (**1**) with excess iodine in the presence of potassium carbonate afforded only the monosubstituted compound 7-iodo-3-(3-(2-naphthyl)acryloyl)tropolone (**6**) in 51.9% yield. The reaction indicated that the 7-position of tropolone ring had the highest electrophilic activity, which is in agreement with the theoretically calculated results. In a similar method to compound **2**, the structures of **3** and **4** were also established from elemental analysis and spectral data. In addition, although the nitration of 3-acetyl, 3-acetamido, 3-cinnamoyl [6–8], and 3-(2-quinolyl)tropolone [10] gave 5-nitro- and/or 5,7-dinitro-substituted products, when 3-(3-(2-naphthyl)acryloyl)tropolone (**1**) was treated with concentrated or fuming nitric acid, any expected product was not observed. The reaction may proceed with an unknown mechanism that needs further investigation.

The azo-coupling reaction of tropolone took place exclusively at the 5-position to give crystalline dyes. The reactions of 3-(3-(2-naphthyl)acryloyl)tropolone (**1**) with diazonium salts gave 5-arylazo-substituted 3-(3-(2-naphthyl)acryloyl)tropolones (**5** and **6**) in 47.8% and 76.2% yield, respectively. The compounds (**2**) and (**4**) were also reacted with *p*-toluidine diazonium salt to afford 7-bromo-3-(3-(2-naphthyl)acryloyl)-5-(*p*-tolyldiazenyl)tropolone (**7**) and 7-iodo-3-(3-(2-naphthyl)acryloyl)-5-(*p*-tolyldiazenyl)tropolone (**8**) in 28.5% and 20.9% yield, respectively. These structures were confirmed from the elemental analysis and spectral data (see Experimental section). For example, in the IR spectrum of compound **5**, an absorption band for the hydroxyl group was at 3185 cm^{-1}, for the tropolone carbonyl group was at 1648 cm^{-1}, and for the propenyl carbonyl group was at 1608 cm^{-1}. Its ^{1}H NMR spectrum showed peaks at δ 8.53 (d, 1H, J = 2.1 Hz) for tropolone H-4, at 8.31 (q, 1H, J = 2.2 Hz) for tropolone H-6, at 7.99 (s, 1H) for naphthalene H-1, at 7.74 (dd, 1H, J = 16.0, 2.2 Hz) for tropolone H-7, and an unresolved complex peaks at δ 7.73–7.93 and 7.34–7.59 for the protons of the aromatic ring and carbon–carbon double bond (Scheme 3).

As attacking site of nucleophilic reagents, chalcones have an enone moiety that connects two benzene rings. Thus, it has been reported that the chalcones reacted with hydroxylamine [11–14] and hydrazine [15–19] to afford diphenyl-substituted isoxazolines and pyrazolines, respectively. On the other hand, we found that 3-acetyl

Scheme 3

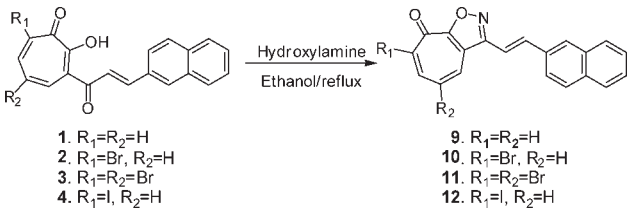


[6] and 3-cinnamoyltropolone [8] reacted with various nucleophilic reagents bearing two reactive sides to give a wide variety of heterocycle-fused troponoid compounds [24].

The reactions of 3-(3-(2-naphthyl)acryloyl)tropolone (**1**) with hydroxylamine in refluxing ethanol gave 3-[2-(2-naphthyl)vinyl]-8*H*-cyclohepta[*d*]isoxazol-8-one (**9**) in 47.7% yield. In the IR spectrum of **9**, the disappearance of characteristic hydroxyl and carbonyl absorption for tropolone and the carbonyl group in the side chain and the appearance of tropone carbonyl absorption at 1629 cm^{-1} were clear evidence for the formation of a new compound. Its ^{1}H NMR spectrum showed the absence of the hydroxy OH signal in addition to 7.12 (q, 1H, J = 8.5 Hz), 7.23 (d, 1H, J = 16.0 Hz) for carbon–carbon double bond protons, 7.29 (d, 1H, J = 12.6 Hz) for tropolone H-7, 7.44 (dd, 1H, J = 4.0, 8.2 Hz) for tropolone H-5, 7.77 (q, 1H, J = 16.5 Hz) for tropolone H-6, 7.98 (s, 1H) for naphthalene H-1, 8.21 (d, 1H, J = 4.5 Hz) for tropolone H-4, besides an unresolved complex peaks in the aromatic region at δ 7.51–7.54 and 7.85–7.90. The mass spectrum exhibited a molecular ion 299 (M^+), which matched the expected molecular weight for the corresponding compound **9**. The elemental analysis further supported the assigned structure. The vital characteristic structure of compound **9** could be authenticated by a simple method: when the compound was developed on thin layer chromatography (TLC) (silica gel: GF254, developing agent: ethyl acetate), there was only one main spot with no tailing, as well as giving a negative coloring test with iron (β) chloride in ethanol solution. In a similar way, the reactions of compounds **2**, **3**, and **4** with hydroxylamine also afforded the corresponding 5-substituted or 5,7-substituted 3-[2-(2-naphthyl)vinyl]-8*H*-cyclohepta[*d*]isoxazol-8-ones (**10–12**), and their structures were determined on the basis of a negative coloring test with iron (III) chloride and the elemental analysis as well as on spectral data (Scheme 4).

When a solution of 3-(3-(2-naphthyl)acryloyl)tropolone (**1**) and phenylhydrazine in ethanol was refluxed for 18 h, the 3-[2-(2-naphthyl)vinyl]-1-phenylcyclohepta[*c*]pyrazol-8(1*H*)-one (**13**) was isolated in 19.3% yield.

Scheme 4



1. R_1=R_2=H
2. R_1=Br, R_2=H
3. R_1=R_2=Br
4. R_1=I, R_2=H

9. R_1=R_2=H
10. R_1=Br, R_2=H
11. R_1=R_2=Br
12. R_1=I, R_2=H

Its structure was confirmed from the elemental analysis ($C_{26}H_{18}N_2O$) and spectral data. The IR spectrum showed the absorption for tropone carbonyl group at 1630 cm^{-1}. Its ^1H NMR spectrum showed the absence of the hydroxy OH signal, and all the protons were observed at δ 6.86 (q, 1H, J = 8.4 Hz) for tropolone H-5, 7.94 (s, 1H) for naphthalene H-1, 6.99 (d, 1H, J = 12.5 Hz) for one proton of carbon–carbon double bond, 7.25–7.30 (m, 1H) for tropolone H-7, 7.44–7.52 (m, 8H), 7.77–7.87 (m, 6H) for the aromatic region and the other protons of carbon–carbon double bond. The compound (**1**) reacted with 4-nitro, 4-bromo, 4-chloro, 4-methoxy, and 3-chlorophenylhydrazines to give 3-(2-(2-naphthyl)vinyl)-1-(4-nitrophenyl)cyclohepta[*c*]pyrazol-8 (1*H*)-one (**14**), 1-(4-bromophenyl)-3-(2-(2-naphthyl)vinyl)cyclohepta[*c*]pyrazol-8(1*H*)-one (**15**), 1-(4-chlorophenyl)-3-(2-(2-naphthyl)vinyl)cyclohepta[*c*]pyrazol-8(1*H*) -one (**16**), 1-(4-methoxyphenyl)-3-(2-(2-naphthyl)vinyl)cyclohepta[*c*]pyrazol-8(1*H*)-one (**17**), and 1-(3-chlorophenyl)-3-(2-(2-naphthyl)vinyl)cyclohepta[*c*]-pyrazol-8(1*H*) -one (**18**) in 57.6%, 53.8%, 43.3%, 26.2%, and 41.2% yield, respectively. The electrophilic substitution products (**2–4**) reacted with phenylhydrazine and also gave the corresponding 1,8-dihydrocycloheptapyrazol-8-one derivatives (**19–21**). In conclusion, this investigation has demonstrated the synthesis of naphthalene-substituted tropolones and troponoids compounds (Scheme 5).

EXPERIMENTAL

The melting points were determined by using WRS-1B melting points apparatus. ^1H NMR was measured with a Varian Inova 500 NMR spectrometer at 500 MHz or a Varian Inova 400 NMR spectrometer at 400 MHz. The reported chemical shifts were against TMS. Mass spectra were determined using a MSD VL ESII spectrometer. Elemental analysis was performed using an Elementar Vario EL-III element analyzer.

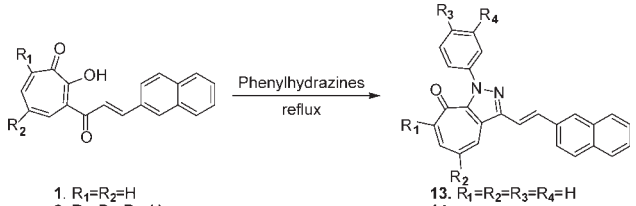
3-(3-(2-Naphthyl)acryloyl)tropolone (1). To a stirred solution of 3-acetyltropolone and 2-naphthaldehyde in 50% methanol, a solution of 5% KOH aqueous was added dropwise at room temperature. Having monitored by TLC, and after the reaction was completed, the mixture was acidified with 6*M* hydrochloric acid to precipitate yellow crystals. The crystals were collected and recrystallized from ethanol to give 3-(3-(2-naphthyl)acryloyl)tropolone (**1**) as yellow crystals, yield 85.3%; mp 166–167°C; IR (KBr): 3190 (OH), 1658 (C=O), 1613 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.14–7.86 (m, 12H, Ar-H and HC=CH), 7.98 (s, 1H, 2-NaphthH-1); ms: *m*/*z* 303 $(M+1)^+$. Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found: C, 79.30; H, 4.52.

7-Bromo-3-(3-(2-naphthyl)acryloyl)tropolone (2). To a stirred solution of 3-(3-(2-naphthyl) acryloyl)tropolone (0.302 g, 1 mmol) and sodium acetate (0.125 g) in acetic acid (50 mL), a solution of bromine (0.160 g, 1 mmol) in acetic acid (2 mL) was added dropwise at room temperature. After the reaction was completed, water (100 mL) was added. The precipitate was collected and recrystallized from ethyl acetate to give 7-bromo-3-(3-(2-naphthyl)acryloyl)tropolone as yellow crystals, yield 70.6%; mp 182–184°C; IR (KBr): 3180 (OH), 1641 (C=O), 1601 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.16 (t, 1H, —C=CH, J = 11.0 Hz), 7.26 (d, 1H, CH=C—, J = 15.6 Hz), 7.50–7.56 (m, 2H, Ar-H), 7.76 (q, 1H, tropolone H-5, J = 10.0 Hz), 7.83–7.87 (m, 4H, Ar-H), 7.99 (d, 1H, 2-NaphthH-1, J = 6.3 Hz), 8.18 (d, 1H, tropolone H-6, J = 10.0 Hz), 8.50 (d, 1H, tropolone H-4, J = 8.5 Hz); ms: *m*/*z* 381 $(M+1)^+$. Anal. Calcd. for $C_{20}H_{13}BrO_3$: C, 63.01; H, 3.44. Found: C, 62.97; H, 3.20.

5,7-Dibromo-3-(3-(2-naphthyl)acryloyl)tropolone (3). To a stirred solution of sodium acetate and 3-(3-(2-naphthyl)acryloyl)tropolone (0.302 g,1 mmol) in acetic acid, a solution of bromine (0.320 g, 2 mmol) in acetic acid (2 mL) was added dropwise at room temperature. After completion, the mixture was poured into water (150 mL), and then the precipitate was collected and recrystallized from ethyl acetate to give 5,7-dibromo-3-(3-(2-naphthyl)acryloyl)tropolone as yellowish blue powder, yield 72.3%; mp 212–213°C; IR (KBr): 3185 (OH), 1647 (C=O), 1592 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.25 (d, 1H, —C=CH, J = 15.9 Hz), 7.50–7.56 (m, 2H, Ar-H), 7.71 (q, 1H, —C=CH, J = 1.6 Hz), 7.83–7.87 (m, 4H, Ar-H), 7.78 (d, 1H, tropolone H-6, J = 15.9 Hz), 7.99 (s, 1H, 2-NaphthH-1), 8.50 (d, 1H, tropolone H-4, J = 2.0 Hz); ms: *m*/*z* 461 $(M+1)^+$. Anal. Calcd. for $C_{20}H_{12}Br_2O_3$: C, 52.21; H, 2.63. Found: C, 52.01; H, 2.45.

7-Iodo-3-(3-(2-naphthyl)acryloyl)tropolone (4). To a stirred mixture of 3-(3-(2-naphthyl)acryloyl)tropolone (0.302 g,1 mmol) and potassium carbonate (0.305 g) in water (0.85 mL), a solution of iodine (0.325 g) and potassium iodide (0.325 g) in water (1.85 mL) was added in an ice water bath. After being stirred for 11.5 h, excess iodine was reduced with

Scheme 5



1. R_1=R_2=H
2. R_1=Br, R_2=H
3. R_1=R_2=Br
4. R_1=I, R_2=H

13. R_1=R_2=R_3=R_4=H
14. R_1=R_2=R_4=H, R_3=NO_2
15. R_1=R_2=R_4=H, R_3=Br
16. R_1=R_2=R_4=H, R_3=Cl
17. R_1=R_2=R_4=H, R_3=OCH_3
18. R_1=R_2=R_3=H, R_4=Cl
19. R_1=Br, R_2=R_3=R_4=H
20. R_1=R_2=Br, R_3=R_4=H
21. R_1=I, R_2=R_3=R_4=H

sodium hydrogen sulfite. The mixture was acidified with 6*M* hydrochloric acid (80 mL) to precipitate pale greenish crystals. The crystals were collected and recrystallized from ethyl acetate to give 7-iodo-3-(3-(2-naphthyl)acryloyl)tropolone as pale greenish crystals, yield 52.0%; mp 197–198°C; IR (KBr): 3179 (OH), 1670 (C=O), 1585 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.78 (t, 1H, CH=C—, J = 10.25 Hz), 7.29 (d, 1H, —C=CH, J = 15.9 Hz), 7.49–7.54 (m, 2H, Ar-H), 7.82–7.86 (m, 4H, Ar-H), 7.57 (dd, 1H, tropolone H-5, J = 7.5, 4.0 Hz), 7.75 (d, 1H, tropolone H-6, J = 10.2 Hz), 7.98 (s, 1H, 2-NaphthH-1), 8.49 (d, 1H, J = 10.0 Hz, tropolone H-4); ms: m/z 429 $(M+1)^+$. Anal. Calcd. for $C_{20}H_{13}IO_3$: C, 56.10; H, 3.06. Found: C, 56.14; H, 2.85.

3-(3-(2-Naphthyl)acryloyl)-5-(phenyldiazenyl)tropolone (5). To an ice-cooled stirred solution of compound **1** (0.302 g, 1 mmol) in pyridine (4 mL), arenediazonium chloride solution (2 mmol, 2 mL), prepared from aniline or *p*-toluidine, was added dropwise. After additional stirring for 2–3 h, the precipitate was collected and recrystallized from benzene or ethyl acetate to give product (**5**) as pale yellow crystals, yield 47.8%; mp 190–191°C; IR (KBr): 3185 (OH), 1648 (C=O), 1608 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.34–7.59 (m, 6H, Ar-H and CH=CH), 7.74 (dd, 1H, tropolone H-7, J = 16.0, 2.2 Hz), 7.73–7.93 (m, 7H, Ar-H), 7.99 (s, 1H, 2-NaphthH-1), 8.31 (q, 1H, tropolone H-6, J = 2.2 Hz), 8.53 (d, 1H, tropolone H-4, J = 2.1 Hz); ms: m/z 407 $(M+1)^+$. Anal. Calcd. for $C_{26}H_{18}N_2O_3$: C, 76.83; H, 4.46; N, 6.89. Found: C, 76.79; H, 4.29; N, 6.87.

3-(3-(2-Naphthyl)acryloyl)-5-(*p*-tolyldiazenyl)tropolone (6). The same experimental method as compound (**5**) was followed. This compound was obtained as deep red powder, yield 76.2%; mp 173–174°C; IR (KBr): 3203 (OH), 1673 (C=O), 1610 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.44 (s, 3H, CH_3), 7.30–7.58 (m, 6H, Ar-H and CH=CH), 7.73 (q, 1H, tropolone H-7, J = 1.5 Hz), 7.82–7.86 (m, 6H, Ar-H), 7.99 (s, 1H, 2-NaphthH-1), 8.28 (q, 1H, tropolone H-6, J = 2.1 Hz), 8.50 (d, 1H, tropolone H-4, J = 2.0 Hz); ms: m/z 421 $(M+1)^+$. Anal. Calcd. for $C_{27}H_{20}N_2O_3$: C, 77.13; H, 4.79; N, 6.66. Found: C, 77.11; H, 4.58; N, 6.53.

7-Bromo-3-(3-(2-naphthyl)acryloyl)-5-(*p*-tolyldiazenyl)tropolone (7). The same experimental method as compound (**5**) was followed. The compound was obtained as orange crystals, yield 38.5%; mp > 290°C; IR (KBr): 3210 (OH), 1673 (C=O), 1608 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.45 (s, 3H, —CH_3), 7.31–7.80 (m, 6H, Ar-H and CH=CH), 7.84–7.87 (m, 6H, Ar-H), 8.00 (s, 1H, 2-NaphthH-1), 8.38 (d, 1H, tropolone H-6, J = 2.0 Hz), 9.02 (d, 1H, tropolone H-4, J = 1.6 Hz); ms: m/z 499 $(M+1)^+$. Anal. Calcd. for $C_{27}H_{19}BrN_2O_3$: C, 64.94; H, 3.84; N, 5.61. Found: C, 64.89; H, 3.50; N, 5.65.

7-Iodo-3-(3-(2-naphthyl)acryloyl)-5-(*p*-tolyldiazenyl)tropolone (8). The same experimental method of compound (**7**) was followed. This compound was obtained as deep red crystals, yield 20.9%; mp > 290°C; IR (KBr): 3304 (OH), 1682 (C=O), 1617 (C=O) cm^{-1}; δ 2.45 (s, 3H, —CH_3), 7.30–7.55 (m, 3H, Ar-H and CH=C—), 7.75–7.87 (m, 9H, Ar-H and —C=CH), 8.00 (s, 1H, 2-NaphthH-1), 8.36 (d, 1H, tropolone H-6, J = 2.0 Hz), 9.26 (d, 1H, tropolone H-4, J = 1.6 Hz); ms: m/z 547 $(M+1)^+$. Anal. Calcd. for $C_{27}H_{19}IN_2O_3$: C, 59.35; H, 3.51; N, 5.13. Found: C, 59.38; H, 3.1 6; N, 5.10.

3-[2-(2-Naphthyl)vinyl]-8*H*-cyclohepta[*d*]isoxazol-8-one (9). A solution of 3-(3-(2-naphthyl)acryloyl)tropolone (0.151 g, 0.5 mmol) and hydroxylamine hydrochloride (0.071 g, 1 mmol) in ethanol (5 mL) was refluxed for 12 h. The precipitate was collected and recrystallized from acetic acid to give 3-[2-(2-naphthyl)vinyl]-8*H*-cyclohepta[*d*]isoxazol-8-one as pale brown powder, yield 47.7%; mp 252–253°C; IR (KBr): 1629 (C=O), 1573 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.12 (q, 1H, CH=C—, J = 8.5 Hz), 7.23 (d, 1H, —C=CH, J = 16.0 Hz), 7.51–7.54 (m, 2H, Ar-H), 7.29 (d, 1H, tropolone H-7, J = 12.6 Hz), 7.44 (dd, 1H, tropolone H-5, J = 4.0, 8.2 Hz), 7.77 (q, 1H, tropolone H-6, J = 16.5 Hz), 7.85–7.90 (m, 4H, Ar-H), 7.98 (s, 1H, 2-NaphthH-1), 8.21 (d, 1H, tropolone H-4, J = 4.5 Hz); ms: m/z 300 $(M+1)^+$. Anal. Calcd. for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.17; H, 4.01; N, 4.82.

7-Bromo-3-[2-(2-naphthyl)vinyl]-8*H*-cyclohepta[*d*]isoxazol-8-one (10). A solution of 7-bromo-3-(3-(2-naphthyl)acryloyl)tropolone (0.100 g) and hydroxylamine hydrochloride (0.036 g) in ethanol (5 mL) was refluxed for 20 h. The precipitate was collected and recrystallized from acetic acid to give 7-bromo-3-[2-(2-naphthyl)vinyl]-8*H*-cyclohepta[*d*]isoxazol-8-one as golden powder, yield 41.4%; mp 243–244°C; IR (KBr): 1670 (C=O), 1549 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.30–7.79 (m, 8H, Ar-H and CH=CH), 7.53 (q, 1H, tropolone H-5, J = 3.2 Hz), 7.88 (d, 1H, tropolone H-6, J = 6.8 Hz), 7.94 (s, 1H, 2-NaphthH-1), 8.41(d, 1H, tropolone H-4, J = 10.0 Hz); ms: m/z 378 $(M+1)^+$. Anal. Calcd. for $C_{20}H_{12}BrNO_2$: C, 63.51; H, 3.20; N, 3.70. Found: C, 63.33; H, 3.50; N, 3.59.

5,7-Dibromo-3-[2-(2-naphthyl)vinyl]-8*H*-cyclohepta[*d*]isoxazol-8-one (11). A solution of 5,7-dibromo-3-(3-(2-naphthyl)acryloyl)tropolone (0.100 g) and hydroxylamine hydrochloride (0.030 g) in ethanol (5 mL) was refluxed for 28 h. The precipitate was collected and recrystallized from ethyl acetate to give 5,7-dibromo-3-[2-(2-naphthyl)vinyl]-8*H*-cyclohepta[*d*]isoxazol-8-one as brown crystals, yield 60.7%; mp 196–197°C; IR (KBr): 1679 (C=O), 1560 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.89–7.24 (m, 8H, Ar-H and CH=CH), 7.78 (d, 1H, tropolone H-6, J = 12.7 Hz), 7.99 (s, 1H, 2-NaphthH-1), 8.51 (d, 1H, tropolone H-4, J = 1.5 Hz); ms: m/z 458 $(M+1)^+$. Anal. Calcd. for $C_{20}H_{11}Br_2NO_2$: C, 52.55; H, 2.43; N, 3.06. Found: C, 52.41; H, 3.39; N, 3.18.

7-Iodo-3-[2-(2-naphthyl)vinyl]-8*H*-cyclohepta[*d*]isoxazol-8-one (12). A solution of 7-iodo-3-(3-(2-naphthyl)acryloyl)tropolone (0.100 g) and hydroxylamine hydrochloride (0.032 g) in ethanol (5 mL) was refluxed for 24 h. The precipitate was collected and recrystallized from tetrahydrofuran to give 7-iodo-3-[2-(2-naphthyl)vinyl]-8*H*-cyclohepta[*d*]isoxazol-8-one as pale brown powder, yield 41.0%; mp 275°C decomposition; IR (KBr): 1692 (C=O), 1602 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.81–7.24 (m, 2H, CH=CH), 7.85–7.90 (m, 6H, Ar-H), 7.53 (q, 1H, tropolone H-5, J = 3.6 Hz), 7.78 (d, 1H, tropolone H-6, J = 8.4 Hz), 7.99 (s, 1H, 2-NaphthH-1), 8.76 (d, 1H, tropolone H-4, J = 9.2 Hz); ms: m/z 426 $(M+1)^+$. Anal. Calcd. for $C_{20}H_{12}INO_2$: C, 56.49; H, 2.84; N, 3.29. Found: C, 56.42; H, 2.61; N, 3.34.

Synthesis of 2-vinyl naphthalene heterocycle-fused tropono id compounds (13–18). A mixture of 3-(3-(2-naphthyl)acryloyl)tropolone (0.151 g, 0.5 mmol) and substituted phenylhydrazines (1 mmol) in ethanol (10 mL) was refluxed for 18–28 h. The precipitates were collected and recrystallized to give the products.

3-[2-(2-Naphthyl)vinyl]-1-phenylcyclohepta[c]pyrazol-8(1H)-one (13). This compound was obtained as golden needles, yield 19.3%; mp 193–194°C; IR (KBr): 1630 (C=O), 1600 (C=N)

cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.86 (q, 1H, tropolone H-5, J = 8.4 Hz), 6.99 (d, 1H, CH=C—, J = 12.5 Hz), 7.25–7.30 (m, 1H, tropolone H-7), 7.44–7.52 (m, 8H, Ar-H and CH=C—), 7.77–7.87 (m, 6H, Ar-H), 7.94 (s, 1H, 2-NaphthH-1); ms: m/z 375 $(M+1)^+$. Anal. Calcd. for $C_{26}H_{18}N_2O$: C, 83.40; H, 4.85; N, 7.48. Found: C, 83.17; H, 5.30; N, 7.45.

3-(2-(2-Naphthyl)vinyl)-1-(4-nitrophenyl)cyclohepta[c]pyrazol-8(1H)-one (14). This compound was obtained as brown powder, yield 57.6%; mp 280°C decomposition; IR (KBr): 1630 (C=O), 1604 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.95–7.10 (m, 2H, Ar-H and CH=C—), 7.43–7.51 (m, 4H, Ar-H and —C=CH), 7.66 (d, 2H, Ar-H, J = 9.2 Hz), 7.80–7.89 (m, 6H, Ar-H), 7.96 (s, 1H, 2-NaphthH-1), 8.37 (d, 2H, Ar-H, J = 9.2 Hz); ms: m/z 420 $(M+1)^+$. Anal. Calcd. for $C_{26}H_{17}N_3O_3$: C, 74.45; H, 4.09; N, 10.02. Found: C, 74.51; H, 4.38; N, 9.99.

1-(4-Bromophenyl)-3-(2-(2-naphthyl)vinyl)cyclohepta[c]pyrazol-8(1H)-one (15). This compound was obtained as yellow crystals, yield 53.8%; mp 284–285°C; IR (KBr): 1625 (C=O), 1576 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.91 (t, 1H, tropolone H-5, J = 5.6 Hz), 7.01 (d, 1H, CH=C—, J = 8.0 Hz), 7.26–7.64 (m, 8H, Ar-H and CH=C—), 7.77–7.86 (m, 6H, Ar-H), 7.95 (s, 1H, 2-NaphthH-1); ms: m/z 453 $(M+1)^+$. Anal. Calcd. for $C_{26}H_{17}BrN_2O$: C, 68.89; H, 3.78; N, 6.18. Found: C, 68.80; H, 3.87; N, 6.07.

1-(4-Chlorophenyl)-3-(2-(2-naphthyl)vinyl)cyclohepta[c]pyrazol-8(1H)-one (16). This compound was obtained as pale yellow crystals, yield 26.2%; mp 212–213°C; IR (KBr): 1652 (C=O), 1590 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.90–7.02 (m, 2H, Ar-H and —C=CH), 7.27 (d, 1H, tropolone H-7, J = 11.2 Hz), 7.39–7.50 (m, 7H, Ar-H and CH=C—), 7.77–7.88 (m, 6H, Ar-H), 7.94 (s, 1H, 2-NaphthH-1); ms: m/z 409 $(M+1)^+$. Anal. Calcd. for $C_{26}H_{17}ClN_2O$: C, 76.37; H, 4.19; N, 6.85. Found: C, 76.30; H, 3.95; N, 6.80.

1-(4-Methoxyphenyl)-3-(2-(2-naphthyl)vinyl)cyclohepta[c]pyrazol-8(1H)-one (17). This compound was obtained as golden powder, yield 43.3%; mp 277–278°C; IR (KBr): 1660 (C=O), 1587 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.89 (s, 3H, —OCH_3), 6.86 (q, 1H, tropolone H-5, J = 10.0 Hz), 7.01 (d, 1H, tropolone H-7, J = 4.8 Hz), 7.37–7.50 (m, 7H, Ar-H and CH=CH), 7.77–7.85 (m, 7H, Ar-H), 7.94 (s, 1H, 2-NaphthH-1); ms: m/z 405 $(M+1)^+$. Anal. Calcd. for $C_{27}H_{20}N_2O_2$: C, 80.18; H, 4.98; N, 6.93. Found: C, 80.11; H, 4.73; N, 6.94.

1-(3-Chlorophenyl)-3-(2-(2-naphthyl)vinyl)cyclohepta[c]pyrazol-8(1H)-one (18). This compound was obtained as golden crystals, yield 41.2%; mp 247°C decomposition; IR (KBr): 1639 (C=O), 1574 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.91 (q, 1H, tropolone H-5, J = 10.0 Hz), 7.02 (d, 1H, —C=CH, J = 12.8 Hz), 7.35–7.52 (m, 8H, Ar-H and CH=C—), 7.77–7.84 (m, 6H, Ar-H), 7.95 (s, 1H, 2-NaphthH-1); ms: m/z 409 $(M+1)^+$. Anal. Calcd. for $C_{26}H_{17}ClN_2O$: C, 76.37; H, 4.19; N, 6.85. Found: C, 76.25; H, 4.50; N, 6.90.

7-Bromo-3-[2-(2-naphthyl)vinyl]-1-phenylcyclohepta[c]pyrazol-8(1H)-one (19). A mixture of 7-bromo-3-(3-(2-naphthyl)acryloyl)tropolone (0.100 g) and phenylhydrazine hydrochloride (0.056 g) in absolute ethanol (5 mL) was refluxed for 19 h. The precipitate was collected and recrystallized from ethyl acetate to give 7-bromo-3-[2-(2-naphthyl)vinyl]-1-phenylcyclohepta[c]pyrazol-8(1H)-one as yellow crystals, yield 29.0%; mp 288–289°C; IR (KBr): 1644 (C=O), 1589 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.75 (q, 1H, tropolone H-5, J = 9.6 Hz), 7.47–7.52 (m, 6H, Ar-H and CH=CH), 7.81–7.90 (m, 7H, Ar-H), 7.94 (s, 1H, 2-NaphthH-1), 8.28 (d, 1H, tropolone H-6, J = 6.8 Hz), 8.51 (d, 1H, tropolone H-4, J = 8.0 Hz); ms: m/z 453 $(M+1)^+$. Anal. Calcd. for $C_{26}H_{17}BrN_2O$: C, 68.89; H, 3.78; N, 6.18. Found: C, 68.70; H, 3.47; N, 6.07.

5,7-Dibromo-3-[2-(2-naphthyl)vinyl]-1-phenylcyclohepta[c]pyrazol-8(1H)-one (20). A mixture of 5,7-dibromo-3-(3-(2-naphthyl)acryloyl)tropolone (0.100 g) and phenylhydrazine hydrochloride (0.048 g) in absolute ethanol (5 mL) was refluxed for 22 h. The precipitate was collected and recrystallized from ethyl acetate to give 5,7-dibromo-3-[2-(2-naphthyl)-vinyl]-1-phenylcyclohepta[c] pyrazol-8(1H)-one as orange crystals, yield 35.0%; mp > 290°C; IR (KBr): 1656 (C=O), 1591 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.26–7.53 (m, 5H, Ar-H and CH=CH), 7.80–7.87 (m, 8H, Ar-H), 7.95 (s, 1H, 2-NaphthH-1), 8.16 (d, 1H, tropolone H-6, J = 1.6 Hz), 8.52 (d, 1H, tropolone H-4, J = 1.6 Hz); ms: m/z 533 $(M+1)^+$. Anal. Calcd. for $C_{26}H_{16}Br_2N_2O$: C, 58.67; H, 3.03; N, 5.26. Found: C, 58.63; H, 3.29; N, 5.33.

7-Iodo-3-[2-(2-naphthyl)vinyl]-1-phenylcyclohepta[c]pyrazol-8(1H)-one (21). A mixture of 7-iodo-3-(3-(2-naphthyl)acryloyl)tropolone (0.100 g) and phenylhydrazine hydrochloride (0.051 g) in absolute ethanol (5 mL) was refluxed for 47 h. The precipitate was collected and recrystallized from ethyl acetate to give 7-iodo-3-[2-(2-naphthyl)vinyl]-1-phenylcyclohepta[c]pyrazol-8(1H)-one as yellowish blue powder, yield 24.0%; mp >290°C; IR (KBr): 1635 (C=O), 1581 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.60 (t, 1H, tropolone-5, J = 10.0 Hz), 7.41–7.43 (m, 2H, CH=CH), 7.43–7.52 (m, 5H, Ar-H), 7.79–7.88 (m, 6H, Ar-H), 7.87 (d, 1H, tropolone H-6, J = 2.4 Hz), 7.94 (s, 1H, 2-NaphthH-1), 8.63 (d, 1H, tropolone-4, J = 9.6 Hz); ms: m/z 501 $(M+1)^+$. Anal. Calcd. for $C_{26}H_{17}IN_2O$: C, 62.41; H, 3.42; N, 5.60. Found: C, 62.32; H, 3.64; N, 5.71.

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