

新型桃金娘烯醛基 2-酰基-1,2,4-三唑-3-硫酮化合物的合成及生物活性研究

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摘要 为了探寻新型的生物活性化合物,设计并合成了16个未见文献报道的桃金娘烯醛基 2-酰基-1,2,4-三唑-3-硫酮衍生物,通过 FTIR, NMR, ESI-MS 和元素分析确认了其结构。初步的离体抑菌和除草活性测试表明,部分目标化合物表现出良好的抑菌活性,在浓度为 50 mg/L 时,桃金娘烯醛基 2-对甲基苯甲酰基-1,2,4-三唑-3-硫酮(**7i**)对玉米小斑病菌和苹果轮纹病菌的相对抑菌率分别为 83.7%和 72.5%,桃金娘烯醛基 2-(3',5'-二甲苯甲酰基)-1,2,4-三唑-3-硫酮(**7j**)对苹果轮纹病菌的相对抑菌率为 72.5%(阳性对照百菌清对玉米小斑病菌和苹果轮纹病菌的相对抑菌率分别为 90.4%和 75.0%)。此外,绝大部分目标化合物对油菜胚根生长表现出优异的抑制活性,在浓度为 100 mg/L 时,有 15 个目标化合物的相对抑制率在 80.2%~99.1%之间,显示出比阳性对照丙炔氟草胺(相对抑制率为 63.0%)更好的除草活性。

关键词 桃金娘烯醛; α -蒎烯; 1,2,4-三唑-3-硫酮; 生物活性

Synthesis and Biological Activity of Novel Myrtenal-Derived 2-Acyl-1,2,4-triazole-3-thione Compounds

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Abstract Sixteen novel myrtenal-derived 2-acyl-1,2,4-triazole-3-thione compounds were designed and synthesized in search of new bioactive compounds. Their structures were confirmed by FTIR, NMR, ESI-MS and elemental analysis. The *in vitro* antifungal and herbicidal activities of the target compounds were preliminarily evaluated. Some target compounds exhibited favourable antifungal activity at 50 mg/L. Myrtenal-derived 2-(*p*-methylbenzoyl)-1,2,4-triazole-3-thione (**7i**) held 83.7% and 72.5% inhibition rates against corn southern leaf blight (*Bipolaris maydis*) and apple root spot (*Physalospora piricola*), respectively, and myrtenal-derived 2-(3',5'-dimethylbenzoyl)-1,2,4-triazole-3-thione (**7j**) had 72.5% inhibition rate against *P. piricola* (the positive control commercial fungicide chlorothalonil with growth inhibition rates of 90.4% and 75.0% against *B. maydis* and *P. piricola*, respectively). Besides, most of the target compounds displayed excellent herbicidal activity against the root-growth of rape (*Brassica campestris*). At 100 mg/L, 15 compounds held growth inhibition rates in the range of 80.2%~99.1%, exhibiting much better herbicidal activity than that of the commercial herbicide flumioxazin (positive control) with 63.0% growth inhibition rate.

Keywords myrtenal; α -pinene; 1,2,4-triazole-3-thione; biological activity

1 Introduction

Myrtenal, a natural bicyclic monoterpene compound bearing a α,β -unsaturated aldehyde group, is an ingredient in essential oils of medicinal plants such as *Artemisia*

douglasiana,^[1] *Lepidium meyenii*^[2] and *Ferula hermonis*.^[3] It can also be readily obtained by the selective oxidation reaction of α -pinene, which is a major constituent of the abundant and naturally renewable turpentine oil. Myrtenal associated with medicinal essential oils were widely investigated for its bioactive properties and found to display a

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broad spectrum of biological activities, such as black bean aphid repellent^[4] and bark beetle aggregation pheromone^[5,6] pesticide properties, as well as anticancer,^[7] antimicrobial,^[1] acetylcholinesterase inhibitory,^[8] and antimalarial^[9] pharmacological activities. Also, some myrtenal-derived amide and ester compounds were synthesized and found to present herbicidal, insecticidal, and mosquito repellent pesticide properties.^[10–12] Evidently, myrtenal deserves further study for agrochemical or pharmaceutical use based on its bioactive property and chemical reactivity.

On the other hand, 1,2,4-triazole derivatives were widely used in the fields of medicines and pesticides (e.g. the commercial fungicide triticonazole and herbicide carfentrazone-ethyl, Figure 1) because of their versatile biological properties, such as antifungal,^[13] antimicrobial,^[14] anti-inflammatory,^[15] antituberculosis,^[16] antitumor^[17] and herbicidal^[18] activities. It was worth noting that the 1,2,4-triazole-3-thione fungicide prothioconazole (Figure 1), a commercially available demethylase inhibitor, exhibited broader spectrum than other triazole fungicides. The investigation for its mode of action suggested that prothioconazole was a competitive inhibitor of substrate binding unlike other triazole fungicides such as epoxiconazole, tebuconazole and triadimenol, which

were the noncompetitive inhibitors. Additionally, an eventual metabolism to the desthio triazole compound within the fungus would lead to an active antifungal.^[19] In light of this new mode of antifungal action, 1,2,4-triazole-3-thione derivatives have attracted considerable interest in the research and development of agrochemicals in recent years. For example, some 1,2,4-triazole-3-thione derivatives were synthesized and found to show favorable fungicidal and herbicidal activities.^[20] In addition, amide derivatives play an important role in new pesticide discovery due to their unique biological properties.^[21] Our group has lately reported the synthesis of a series of myrtenal-derived 4-methyl-1,2,4-triazole-thioether derivatives and found that some target compounds exhibited excellent antifungal activity against *P. piricola*.^[22] In continuation of our interest in the bioactive properties of natural product-derived compounds,^[22–26] a series of myrtenal-derived 4-methyl-1,2,4-triazole-3-thione-amide compounds were designed and synthesized by integrating bioactive both 1,2,4-triazole-thione and amide moieties into the skeleton of myrtenal converted from α -pinene (Scheme 1). Structural characterization, antifungal and herbicidal evaluation of all the title compounds were carried out as well.

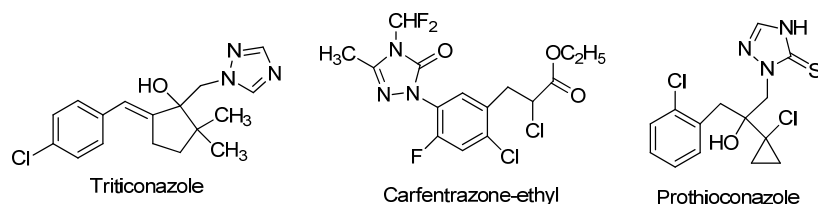
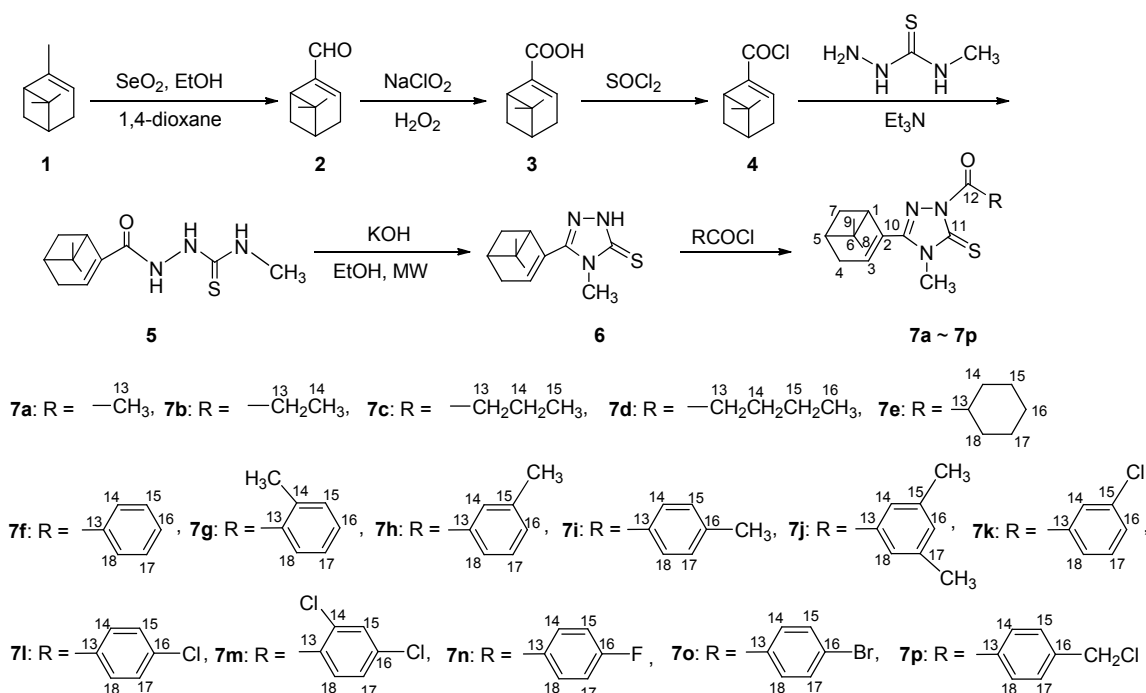


Figure 1 Some commercially available pesticides containing 1,2,4-triazole



Scheme 1 Synthetic route of myrtenal-derived 2-acyl-1,2,4-triazole-3-thiones 7a~7p

2 Results and discussion

2.1 Synthesis and characterization

As illustrated in Schemes 1, myrtenal (**2**) was prepared by allylic selective oxidation of α -pinene, and further oxidized and chlorinated to give myrtenyl chloride (**4**), which reacted with 4-methylthiosemicarbazide to afford 2-(6,6-dimethylbicyclo[3.1.1]hept-2-enecarbonyl)-*N*-methylhydrazinecarbothioamide (**5**). The cyclization reaction of intermediate **5** was performed under microwave irradiation to give intermediate **6**. In its IR spectrum, the signals of the stretching vibration for the amino group (N—H) at 3114 cm^{-1} and for the thione group (C=S) at 1099 cm^{-1} were observed, and the peak at 2600~2500 cm^{-1} for the mercapto group (SH) was not found, indicating that compound **6** was a thione rather than a thiol tautomeric form. Finally, 16 target compounds **7a**~**7p** were synthesized by the *N*-acylation reaction of intermediate **6** with different acyl chlorides.

The structures of the title compounds were characterized by IR, ^1H NMR, ^{13}C NMR, ESI-MS, and elemental analysis. In IR spectra, the strong absorption bands at 3000~2850 cm^{-1} were attributed to the stretching vibrations of the saturated C—H in the myrtenal moiety. The strong absorption bands at about 1700 cm^{-1} were assigned to the vibrations of C=O in the amide moiety. The weak absorption bands at about 1640 and 1100 cm^{-1} were due to the vibrations of C=N and C=S in the 1,2,4-triazole moiety, respectively. In the ^1H NMR, the olefinic protons of myrtenal scaffold showed signals at about δ 6.36, and the other protons bonded to the saturated carbons of the myrtenal

moiety displayed signals in the range of δ 0.92~2.70. The characteristic signals at about δ 3.60 were assigned to the methyl protons of the 1,2,4-triazole moiety. The ^{13}C NMR spectra of all the target compounds showed peaks for the olefinic carbons of the myrtenal-derived moiety at about δ 133.8 and 132.5, and the other saturated carbons displayed signals in the region of δ 21.1~44.5. For the 1,2,4-triazole moiety, the signals at about δ 170.8 and 151.7 were assigned to the carbons of C=S and C=N, respectively. The carbons of C=O and CH_3 bonded to the 1,2,4-triazole showed peaks at about δ 166.8 and 31.5, respectively. Their molecular weights and the C, H, and N element ratios were confirmed by ESI-MS and elemental analysis, respectively.

2.2 *In vitro* antifungal activity

The antifungal activity of the target compounds **7a**~**7p** was evaluated by *in vitro* method against corn southern leaf blight (*B. maydis*), apple root spot (*P. piricola*), fusarium wilt on cucumber (*F. oxysporum* f. sp. *cucumerinum*), watermelon anthracnose (*C. orbiculare*), rice sheath blight (*R. solani*), tomato early blight (*A. solani*), wheat scab (*G. zeae*), and speckle on peanut (*C. arachidicola*) at 50 mg/L. The results are listed in Table 1.

It was found that, at 50 mg/L, all the target compounds exhibited certain antifungal activity against the eight tested fungi. On the whole, the target compounds exhibited a noticeable antifungal activity against *B. maydis* and *P. piricola*. Also, compounds **7i** (R=*p*-methylphenyl) and **7j** (R=3,5-dimethylphenyl) showed a pronounced antifungal activity against all the eight tested fungi. Compared

Table 1 *In vitro* antifungal activity (inhibition rate/%) of the target compounds **7a**~**7p** at 50 mg/L^a

Compd.	<i>B. maydis</i>	<i>P. piricola</i>	<i>F. oxysporum</i> f. sp. <i>cucumerinum</i>	<i>C. orbiculare</i>	<i>R. solani</i>	<i>A. solani</i>	<i>G. zeae</i>	<i>C. arachidicola</i>
7a	52.1	41.3	15.0	45.3	41.4	41.3	46.4	21.1
7b	62.6	60.0	45.0	51.2	42.6	47.5	46.4	43.3
7c	57.4	53.8	45.0	33.5	44.9	47.5	49.4	32.2
7d	62.6	66.3	35.0	45.3	68.1	35.0	61.5	43.3
7e	57.7	57.5	62.3	56.2	29.0	36.9	25.2	44.4
7f	52.1	28.8	65.0	51.2	35.6	53.8	46.4	32.2
7g	20.5	16.3	35.0	15.9	21.6	53.8	28.2	21.1
7h	57.4	16.3	45.0	45.3	54.2	60.0	46.4	43.3
7i	83.7	72.5	60.0	57.1	35.6	60.0	46.4	54.4
7j	67.9	72.5	40.0	57.1	62.3	47.5	49.4	54.4
7k	57.4	22.5	45.0	45.3	39.1	41.3	22.1	21.1
7l	44.1	69.3	46.4	43.3	37.4	29.2	25.2	35.0
7m	37.3	65.9	39.5	38.2	32.6	33.1	31.2	41.3
7n	44.1	69.3	46.4	40.8	14.8	21.5	34.2	35.0
7o	35.0	52.4	39.5	43.3	41.0	29.2	29.7	25.6
7p	39.5	52.4	60.0	51.0	73.1	33.1	37.3	41.3
Myrtenal (2)	23.0	37.8	25.0	15.3	41.7	31.7	41.3	28.2
Chlorothalonil	90.4	75.0	100	91.3	96.1	73.1	73.9	73.3

^a Chlorothalonil, a current commercial fungicide, was used as a positive control. Values are the average of three replicates.

with that of the commercial fungicide chlorothalonil (positive control), compound **7i** (R = *p*-methylphenyl) with inhibition rates of 83.7% against *B. maydis* and 72.5% against *P. piricola*, and compound **7j** (R = 3,5-dimethylphenyl) with 72.5% inhibition rate against *P. piricola*, exhibited favourable antifungal activity (the commercial fungicide chlorothalonil with inhibition rates of 90.4% against *B. maydis* and 75.0% against *P. piricola*). Besides, some compounds displayed moderate activity in the range of 60%~80% inhibition rates, although their antifungal activities were inferior to that of the positive control. For example, compounds **7p** (R = *p*-chloromethylphenyl), **7d** (R = *n*-butyl), and **7j** (R = 3,5-dimethylphenyl) held 73.1%, 68.1%, and 62.3% inhibitory rates against *R. solani*, respectively, as well as compound **7f** (R = phenyl) had an inhibitory rate of 65.0% against *F. oxysporum* f. sp. *cucumerinum*. However, the title compounds showed weak activity against *C. arachidicola*.

Compared with that of myrtenal, most of the target compounds showed enhanced activities, indicating that the incorporation of 2-acyl-1,2,4-triazole-3-thione moiety into the myrtenal molecule was beneficial to the increase of antifungal activity. Preliminary structure-activity relationship (SAR) observation implied that these derivatives with alkyl and methylphenyl R groups, overall showed better antifungal activity. However, further SAR studies would be required to confirm this. Whether the mode of the action of the target compounds was similar to that of the triazolethione fungicide prothioconazole, however, need to be further studied.

2.3 Herbicidal activity

The herbicidal activities of the target compounds **7a**~**7p** were evaluated by the rape petri dish method and the barnyard grass beaker method against the root-growth of rape (*B. campestris*) and the seedling-growth of barnyard grass (*E. crusgalli*) at 10 and 100 mg/L, respectively. The results are listed in Table 2.

As shown in Table 2, the target compounds exhibited remarkable herbicidal activity against the root-growth of rape (*B. campestris*) as a whole. Among them, at 100 mg/L, fifteen target compounds displayed better herbicidal activity with 80.2%~99.1% inhibition rates than that of the commercial herbicidal flumioxazin (positive control) with an inhibition rate of 63.0%, in which up to twelve compounds held growth inhibition rates of over 90%. However, the title compounds showed extremely weak inhibition activity against the seedling-growth of barnyard grass (*E. crusgalli*). Compared with compounds **7h** (R = *m*-methylphenyl) and **7i** (R = *p*-methylphenyl), to our surprise, compound **7g** (R = *o*-methylphenyl) did not show growth inhibition activity against the root-growth of rape even in the different position of the methyl group on the benzene ring, implying that the contributory effect on different activity is not only R groups. Even though no reasonable explanation has been found so far, the difference

may inspire further investigations. And the target compounds showed outstanding herbicidal activity against the root-growth of rape in darkness instead of the seedling-growth of barnyard grass under light irradiation, indicating the mode of action differed from that of the phenyl triazolinone herbicide (e.g. carfentrazone-ethyl), which was the inhibition of protoporphyrinogen oxidase^[27].

Table 2 Herbicidal activity (growth inhibition rate/%) of the target compounds **7a**~**7p** at 10 and 100 mg/L^a

Compd.	<i>B. campestris</i>		<i>E. crusgalli</i>	
	10 mg/L	100 mg/L	10 mg/L	100 mg/L
7a	68.2	99.1	10.0	25.0
7b	69.1	96.1	0	10.0
7c	71.3	93.8	0	15.0
7d	71.4	94.0	0	0
7e	56.2	92.9	0	10.0
7f	63.5	93.2	0	10.0
7g	0	0	0	10.0
7h	72.6	91.0	0	0
7i	65.1	81.4	0	15.0
7j	57.6	83.6	0	30.0
7k	73.0	99.5	0	0
7l	72.5	95.8	0	0
7m	35.0	80.2	0	0
7n	68.4	92.6	15.0	20.0
7o	68.7	92.7	0	0
7p	68.7	90.4	0	25.0
Myrtenal (2)	0	20.4	0	5.0
Flumioxazin	57.8	63.0	95.1	97.5

^a Flumioxazin, a current commercial herbicide was used as a positive control values are the average of three replicates.

3 Conclusions

Sixteen novel myrtenal-derived 2-acyl-1,2,4-triazole-3-thione compounds were designed, synthesized, characterized, and preliminarily evaluated for their *in vitro* antifungal and herbicidal activities. Some target compounds exhibited favorable antifungal activity such as compound **7i** with inhibition rates of 83.7% against *B. maydis* and 72.5% against *P. piricola*, and compound **7j** with 72.5% inhibition rate against *P. piricola* (the commercial fungicide chlorothalonil with inhibition rates of 90.4% against *B. maydis* and 75.0% *P. piricola*). Besides, fifteen target compounds displayed excellent herbicidal activity with 80.2%~99.1% inhibition rates against the root-growth of rape (*B. campestris*), showing much better herbicidal activity than that of the commercial herbicidal flumioxazin with an inhibition rate of 63.0%. Among them, up to twelve compounds held growth inhibition rates of over 90%. Thus, these compounds can serve as new starting points for further studies.

4 Experimental section

4.1 General

Microwave irradiation-assisted synthesis was carried out

on an XO-SM50 ultrasonic microwave reaction system (Nanjing Xianou Instrument Manufacturing Co., Ltd., Nanjing, China). Melting points were determined on an MP420 automatic melting point apparatus (Hanon Instruments Co., Ltd., Jinan, China) and were not corrected. The GC analysis was conducted on an Agilent 6890 GC (Agilent Technologies Inc., Santa Clara, CA., USA) equipped with column HP-1 (30 m, 0.530 mm, 0.88 μ m) and FID. IR spectra were recorded on a Nicolet iS50 FT-IR spectrometer (Thermo Scientific Co., Ltd., Madison, WI., USA) (KBr pellet method). NMR spectra were recorded in a CDCl₃ solvent on a Bruker Avance III HD 600 MHz spectrometer (Bruker Co., Ltd., Zurich, Switzerland). MS spectra were obtained by means of the electrospray ionization (ESI) method on a TSQ Quantum Access MAX HPLC-MS instrument (Thermo Scientific Co., Ltd., Waltham, MA., USA). Elemental analyses were measured using a PE 2400 II elemental analyzer (Perkin-Elmer Instruments Co., Ltd., Waltham, MA, USA). α -Pinene (GC purity 98%) was provided by Wuzhou Pine Chemicals Co., Ltd. Wuzhou, Guangxi, China. Other reagents were purchased from commercial suppliers and used as received. Myrtenal (**2**), myrtenic acid (**3**), myrtenyl chloride (**4**) and 2-(6,6-dimethylbicyclo[3.1.1]hept-2-ene-carbonyl)-*N*-methylhydrazinecarbothioamide (**5**) were prepared according to our previous report.^[22]

4.2 Synthesis of 3-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-1*H*-1,2,4-triazole-5(4*H*)-thione (**6**)

Intermediate **5** (2.0 g, 6.5 mmol) and KOH (1.0 g) were mixed in anhydrous ethanol (30 mL). The mixture was placed in a program-controlled ultrasonic microwave reaction system, and irradiated under stirring at microwave power 100 W and temperature 79 °C for 1 h. Then, the reaction mixture was distilled under reduced pressure to remove ethanol. The crude product was purified by column chromatography on a silica gel column with a mixture of petroleum ether-ethyl acetate (*V* : *V* = 8 : 1) as an eluent to afford intermediate **6** as a colorless solid in 88% yield. m.p. 171.8~172.9 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 12.29 (br s, 1H, N-H), 6.25~6.26 (m, 1H, C³-H), 3.63 (s, 3H, N-CH₃), 2.71 (t, *J* = 5.6 Hz, 1H, C¹-H), 2.58~2.46 (m, 3H, C⁴-Ha, C⁷-H), 2.21~2.24 (m, 1H, C⁵-H), 1.36 (s, 3H, C⁸-H), 1.31 (d, *J* = 9.2 Hz, 1H, C⁴-Hb), 0.91 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 167.8, 151.7, 134.5, 130.0, 44.2, 40.2, 38.0, 32.5, 32.2, 31.4, 25.9, 21.0; IR (KBr) ν : 3114 (N-H), 3036 (=C-H), 2983, 2917 (C-H), 1629 (C=C), 1531 (C=N), 1484, 1341 (C-H), 1099 (C=S) cm⁻¹; MS (ESI) *m/z*: 235.85 ([*M*+*H*]⁺). Anal. calcd for C₁₂H₁₇N₃S: C 61.24, H 7.28, N 17.85; found C 61.22, H 7.27, N 17.81.

4.3 General procedure for synthesis of the target compounds **7a**~**7p**

Acyl chloride (1.5 mmol) was added dropwise into the stirred solution of intermediate **6** (0.4 g, 1.5 mmol) and potassium carbonate (0.5 g) in acetone (25 mL) at room temperature. Afterward, the mixture was refluxed at 60 °C

for 0.5 h. The reaction was quenched with water (10 mL), and ethyl acetate (20 mL) was added. The organic layer was separated, washed three times with water (10 mL each time), dried over anhydrous sodium sulfate, and distilled to remove the solvent. The resulting residue was purified by column chromatography on a silica gel column with a mixture of petroleum ether-ethyl acetate (*V* : *V* = 15 : 1) as an eluent to give the target products **7a**~**7p**.

1-(3-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)ethanone (**7a**): white powder, yield 73%. m.p. 119.8~120.5 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 6.37~6.36 (m, 1H, C³-H), 3.58 (s, 3H, N-CH₃), 2.74 (s, 3H, C¹³-H), 2.69 (t, *J* = 5.6 Hz, 1H, C¹-H), 2.61~2.50 (m, 3H, C⁴-Ha, C⁷-H), 2.27~2.22 (m, 1H, C⁵-H), 1.38 (s, 3H, C⁸-H), 1.35 (d, *J* = 9.2 Hz, 1H, C⁴-Hb), 0.94 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 169.6, 168.0, 150.8, 133.8, 132.4, 44.1, 40.1, 38.1, 32.6, 32.3, 31.5, 25.9, 25.0, 21.1; IR (KBr) ν : 2972, 2923, 2880, 1756, 1638, 1296, 1099 cm⁻¹; MS (ESI) *m/z*: 277.84 ([*M*+*H*]⁺). Anal. calcd for C₁₄H₁₉N₃OS: C 60.62, H 6.90, N 15.15; found C 60.59, H 6.88, N 15.14.

1-(3-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)propan-1-one (**7b**): white powder, yield 71%. m.p. 106.8~107.4 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 6.36~6.35 (m, 1H, C³-H), 3.59 (s, 3H, N-CH₃), 3.11 (q, *J* = 7.3 Hz, 2H, C¹³-H), 2.69 (t, *J* = 5.6 Hz, 1H, C¹-H), 2.60~2.49 (m, 3H, C⁴-Ha, C⁷-H), 2.26~2.24 (m, 1H, C⁵-H), 1.39 (s, 3H, C⁸-H), 1.35 (d, *J* = 9.6 Hz, 1H, C⁴-Hb), 1.26 (t, *J* = 7.3 Hz, 3H, C¹⁴-H), 0.94 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 171.7, 169.3, 150.7, 133.9, 132.2, 44.2, 40.1, 38.1, 32.6, 32.3, 31.5, 30.4, 25.9, 21.1, 8.2; IR (KBr) ν : 2985, 2920, 1755, 1640, 1288, 1098 cm⁻¹; MS (ESI) *m/z*: 291.85 ([*M*+*H*]⁺). Anal. calcd for C₁₅H₂₁N₃OS: C 61.82, H 7.26, N 14.42; found C 61.80, H 7.27, N 14.40.

1-(3-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)butan-1-one (**7c**): white powder, yield 63%. m.p. 81.8~82.6 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 6.36~6.35 (m, 1H, C³-H), 3.58 (s, 3H, N-CH₃), 3.09 (t, *J* = 7.3 Hz, 2H, H-13), 2.69 (t, *J* = 5.6 Hz, 1H, C¹-H), 2.61~2.49 (m, 3H, C⁴-Ha, C⁷-H), 2.26~2.24 (m, 1H, C⁵-H), 1.82~1.78 (m, 2H, C¹⁴-H), 1.39 (s, 3H, C⁸-H), 1.35 (d, *J* = 9.3 Hz, 1H, C⁴-Hb), 1.03 (t, *J* = 7.4 Hz, 3H, C¹⁵-H), 0.94 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.9, 169.3, 150.7, 133.9, 132.2, 44.2, 40.1, 38.5, 38.1, 32.6, 32.3, 31.5, 25.9, 21.1, 17.5, 13.6; IR (KBr) ν : 2954, 2924, 2879, 2828, 1748, 1639, 1299, 1082 cm⁻¹; MS (ESI) *m/z*: 305.84 ([*M*+*H*]⁺). Anal. calcd for C₁₆H₂₃N₃OS: C 62.92, H 7.59, N 13.76; found C 62.91, H 7.60, N 13.73.

1-(3-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)pentan-1-one (**7d**): white powder, yield 61%. m.p. 88.9~89.7 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 6.35~6.34 (m, 1H, C³-H), 3.58 (s, 3H, N-CH₃), 3.11 (t, *J* = 7.4 Hz, 2H, H-13), 2.68 (t, *J* = 5.6 Hz, 1H, C¹-H), 2.61~2.48 (m, 3H, C⁴-Ha, C⁷-H), 2.25~2.23 (m, 1H, C⁵-H), 1.77~1.72 (m, 2H, C¹⁴-H),

1.47~1.41 (m, 2H, C¹⁵-H), 1.38 (s, 3H, C⁸-H), 1.35 (d, $J=9.4$ Hz, 1H, C⁴-Hb), 0.95 (t, $J=7.3$ Hz, 3H, C¹⁶-H), 0.94 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 171.0, 169.3, 150.6, 133.9, 132.1, 44.2, 40.1, 38.1, 36.3, 32.6, 32.3, 31.5, 26.1, 25.9, 22.1, 21.1, 13.8; IR (KBr) ν : 2954, 2923, 2885, 1747, 1642, 1230, 1082 cm⁻¹; MS (ESI) m/z : 319.86 ([M+H]⁺). Anal. calcd for C₁₇H₂₅N₃OS: C 63.91, H 7.89, N 13.15; found C 63.91, H 7.90, N 13.14.

Cyclohexyl(3-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)-methanone (**7e**): white powder, yield 62%. m.p. 93.2~94.3 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 6.37~6.36 (m, 1H, C³-H), 3.70~3.65 (m, 1H, C¹³-H), 3.58 (s, 3H, N-CH₃), 2.68 (t, $J=5.4$ Hz, 1H, C¹-H), 2.61~2.48 (m, 3H, C⁴-Ha, C⁷-H), 2.25~2.24 (m, 1H, C⁵-H), 1.99~1.97 (m, 2H, C¹⁴-He, C¹⁸-He), 1.84~1.80 (m, 2H, C¹⁵-He, C¹⁷-He), 1.72~1.69 (m, 1H, C¹⁶-He), 1.59~1.52 (m, 2H, C¹⁴-Ha, C¹⁸-Ha), 1.39 (s, 3H, C⁸-H), 1.37~1.36 (m, 1H, C¹⁶-Ha), 1.35 (d, $J=9.1$ Hz, 1H, C⁴-Hb), 1.31~1.24 (m, 2H, C¹⁵-Ha, C¹⁷-Ha), 0.94 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 173.8, 169.4, 150.6, 133.9, 132.1, 44.2, 43.2, 40.1, 38.1, 32.6, 32.3, 31.5, 28.7, 25.9, 25.7, 25.3, 21.1; IR (KBr) ν : 2993, 2947, 2920, 2858, 1741, 1637, 1256, 1070 cm⁻¹; MS (ESI) m/z : 345.86 ([M+H]⁺). Anal. calcd for C₁₉H₂₇N₃OS: C 66.05, H 7.88, N 12.16; found C 66.05, H 7.87, N 12.17.

(3-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)(phenyl)methanone (**7f**): white powder, yield 56%. m.p. 92.8~93.9 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.93 (d, $J=7.4$ Hz, 2H, C¹⁴-H, C¹⁸-H), 7.61 (t, $J=7.5$, 7.4 Hz, 1H, C¹⁶-H), 7.47 (t, $J=7.9$, 7.8 Hz, 2H, C¹⁵-H, C¹⁷-H), 6.37~6.36 (m, 1H, C³-H), 3.64 (s, 3H, N-CH₃), 2.66 (t, $J=5.6$ Hz, 1H, C¹-H), 2.58~2.48 (m, 3H, C⁴-Ha, C⁷-H), 2.24~2.21 (m, 1H, C⁵-H), 1.36 (s, 3H, C⁸-H), 1.35 (d, $J=9.3$ Hz, 1H, C⁴-Hb), 0.93 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.6, 166.2, 150.7, 133.9, 133.6, 132.1, 131.8, 131.2, 128.2, 44.1, 40.1, 38.1, 32.7, 32.3, 31.5, 25.9, 21.1; IR (KBr) ν : 2994, 2977, 2953, 2926, 1728, 1637, 1608, 1537, 1277, 1104 cm⁻¹; MS (ESI) m/z : 339.82 ([M+H]⁺). Anal. calcd for C₁₉H₂₁N₃OS: C 67.23, H 6.24, N 12.38; found C 67.24, H 6.24, N 12.36.

(3-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)(*o*-tolyl)methanone (**7g**): white powder, yield 60%. m.p. 168.9~169.7 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.42~7.40 (m, 2H, C¹⁶-H, C¹⁸-H), 7.27 (d, $J=3.6$ Hz, 1H, C¹⁵-H), 7.23 (t, $J=7.7$, 7.4 Hz, 1H, C¹⁷-H), 6.34~6.33 (m, 1H, C³-H), 3.59 (s, 3H, N-CH₃), 2.61 (t, $J=5.6$ Hz, 1H, C¹-H), 2.56~2.45 (m, 3H, C⁴-Ha, C⁷-H), 2.42 (s, 1H, Ar-CH₃), 2.22~2.20 (m, 1H, C⁵-H), 1.34 (s, 3H, C⁸-H), 1.31 (d, $J=9.3$ Hz, 1H, C⁴-Hb), 0.91 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.4, 167.0, 151.0, 138.1, 133.8, 132.8, 132.3, 131.5, 130.9, 129.3, 125.4, 44.0, 40.1, 38.1, 32.6, 32.3, 31.5, 25.9, 21.1, 20.1; IR (KBr) ν : 2953, 2916, 1726, 1642, 1548, 1278, 1102 cm⁻¹; MS (ESI) m/z : 353.81 ([M+H]⁺). Anal. calcd for C₂₀H₂₃N₃OS: C 67.96, H 6.56, N 11.89;

found C 67.95, H 6.57, N 11.90.

(3-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)(*m*-tolyl)methanone (**7h**): white powder, yield 60%. m.p. 109.2~111.3 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.75 (s, 1H, C¹⁴-H), 7.71 (d, $J=7.7$ Hz, 1H, C¹⁸-H), 7.42 (d, $J=7.6$ Hz, 1H, C¹⁶-H), 7.35 (t, $J=7.7$ Hz, 1H, C¹⁷-H), 6.36~6.35 (m, 1H, C³-H), 3.64 (s, 3H, N-CH₃), 2.67 (t, $J=5.5$ Hz, 1H, C¹-H), 2.59~2.47 (m, 3H, C⁴-Ha, C⁷-H), 2.41 (s, 3H, Ar-CH₃), 2.23~2.21 (m, 1H, C⁵-H), 1.36 (s, 3H, C⁸-H), 1.33 (d, $J=9.3$ Hz, 1H, C⁴-Hb), 0.93 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.5, 166.4, 150.6, 138.1, 134.4, 133.9, 132.0, 131.8, 131.7, 128.5, 128.0, 44.1, 40.1, 38.1, 32.7, 32.3, 31.5, 25.9, 21.3, 21.1; IR (KBr) ν : 2969, 2932, 1722, 1635, 1608, 1535, 1277, 1099 cm⁻¹; MS (ESI) m/z : 353.82 ([M+H]⁺). Anal. calcd for C₂₀H₂₃N₃OS: C 67.96, H 6.56, N 11.89; found C 67.97, H 6.56, N 11.88.

(3-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)(*p*-tolyl)methanone (**7i**): white powder, yield 55%. m.p. 111.9~112.5 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.85 (d, $J=8.2$ Hz, 2H, C¹⁴-H, C¹⁸-H), 7.27 (d, $J=8.1$ Hz, 2H, C¹⁵-H, C¹⁷-H), 6.36~6.35 (m, 1H, C³-H), 3.63 (s, 3H, N-CH₃), 2.67 (t, $J=5.4$ Hz, 1H, C¹-H), 2.58~2.47 (m, 3H, C⁴-Ha, C⁷-H), 2.43 (s, 3H, Ar-CH₃), 2.23~2.20 (m, 1H, C⁵-H), 1.36 (s, 3H, C⁸-H), 1.33 (d, $J=9.2$ Hz, 1H, C⁴-Hb), 0.93 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.4, 166.1, 150.6, 144.8, 133.9, 132.0, 131.5, 130.2, 129.0, 44.1, 40.1, 38.1, 32.7, 32.3, 31.5, 25.9, 21.8, 21.1; IR (KBr) ν : 2985, 2918, 1720, 1607, 1608, 1535, 1279, 1091 cm⁻¹; MS (ESI) m/z : 353.83 ([M+H]⁺). Anal. calcd for C₂₀H₂₃N₃OS: C 67.96, H 6.56, N 11.89; found C 67.98, H 6.55, N 11.87.

(3-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)(3,5-dimethylphenyl)methanone (**7j**): white powder, yield 69%. m.p. 118.6~119.5 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.53 (s, 2H, C¹⁴-H, C¹⁸-H), 7.23 (s, 1H, C¹⁶-H), 6.36~6.35 (m, 1H, C³-H), 3.64 (s, 3H, N-CH₃), 2.67 (t, $J=5.6$ Hz, 1H, C¹-H), 2.59~2.47 (m, 3H, C⁴-Ha, C⁷-H), 2.36 (s, 6H, Ar-CH₃), 2.24~2.21 (m, 1H, C⁵-H), 1.36 (s, 3H, C⁸-H), 1.33 (d, $J=9.2$ Hz, 1H, C⁴-Hb), 0.93 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.5, 166.6, 150.6, 137.9, 135.5, 133.9, 131.9, 129.0, 127.9, 44.1, 40.1, 38.1, 32.7, 32.3, 31.4, 25.9, 21.2, 21.1; IR (KBr) ν : 2985, 2951, 2924, 1720, 1645, 1607, 1451, 1265, 1104 cm⁻¹; MS (ESI) m/z : 367.83 ([M+H]⁺). Anal. calcd for C₂₁H₂₅N₃OS: C 68.63, H 6.86, N 11.43; found C 68.60, H 6.83, N 11.42.

(*m*-Chlorophenyl)(3-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)methanone (**7k**): yellow powder, yield 62%. m.p. 87.3~88.2 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.91 (s, 1H, C¹⁴-H), 7.82 (d, $J=8.1$ Hz, 1H, C¹⁸-H), 7.57 (d, $J=8.0$ Hz, 1H, C¹⁶-H), 7.41 (t, $J=7.9$ Hz, 1H, C¹⁷-H), 6.38~6.37 (m, 1H, C³-H), 3.63 (s, 3H, N-CH₃), 2.65 (t, $J=5.5$ Hz, 1H, C¹-H), 2.59~2.49 (m, 3H, C⁴-Ha, C⁷-H), 2.24~2.23 (m, 1H, C⁵-H), 1.36 (s, 3H, C⁸-H), 1.33 (d, $J=9.2$ Hz,

1H, C⁴-Hb), 0.93 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.7, 164.9, 150.9, 134.2, 133.8, 133.6, 133.3, 132.4, 131.1, 129.5, 129.2, 44.1, 40.1, 38.1, 32.7, 32.4, 31.4, 25.9, 21.1; IR (KBr) ν : 2988, 2953, 1717, 1640, 1271, 1108 cm⁻¹; MS (ESI) m/z : 373.74 ([M+H]⁺). Anal. calcd for C₁₉H₂₀ClN₃OS: C 61.03, H 5.39, N 11.24; found C 61.00, H 5.37, N 11.22.

(*p*-Chlorophenyl)(3-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)methanone (**7l**): yellow powder, yield 64%. m.p. 109.6~110.7 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.89 (d, J =8.7 Hz, 2H, C¹⁴-H, C¹⁸-H), 7.44 (d, J =8.7 Hz, 2H, C¹⁵-H, C¹⁷-H), 6.37~6.36 (m, 1H, C³-H), 3.63 (s, 3H, N-CH₃), 2.64 (t, J =5.6 Hz, 1H, C¹-H), 2.59~2.48 (m, 3H, C⁴-Ha, C⁷-H), 2.25~2.23 (m, 1H, C⁵-H), 1.36 (s, 3H, C⁸-H), 1.33 (d, J =9.2 Hz, 1H, C⁴-Hb), 0.93 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.6, 165.2, 150.8, 140.0, 133.8, 132.6, 132.3, 130.2, 128.6, 44.1, 40.1, 38.1, 32.7, 32.3, 31.5, 25.9, 21.1; IR (KBr) ν : 2971, 2951, 2932, 1720, 1639, 1279, 1093 cm⁻¹; MS (ESI) m/z : 373.75 ([M+H]⁺). Anal. calcd for C₁₉H₂₀ClN₃OS: C 61.03, H 5.39, N 11.24; found C 61.02, H 5.40, N 11.25.

(2,4-Dichlorophenyl)(3-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)methanone (**7m**): yellow powder, yield 66%. m.p. 122.1~122.9 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.44 (d, J =1.9 Hz, 1H, C¹⁵-H), 7.42 (d, J =8.3 Hz, 1H, C¹⁷-H), 7.35 (dd, J =8.3, 1.9 Hz, 1H, C¹⁸-H), 6.36~6.35 (m, 1H, C³-H), 3.57 (s, 3H, N-CH₃), 2.60 (t, J =5.5 Hz, 1H, C¹-H), 2.58~2.49 (m, 3H, C⁴-Ha, C⁷-H), 2.23~2.21 (m, 1H, C⁵-H), 1.35 (s, 3H, C⁸-H), 1.32 (d, J =9.1 Hz, 1H, C⁴-Hb), 0.91 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.4, 163.6, 151.7, 137.6, 133.6, 133.0, 132.9, 132.4, 130.6, 129.8, 127.3, 44.0, 40.1, 38.1, 32.6, 32.3, 31.5, 25.9, 21.1; IR (KBr) ν : 2955, 2930, 2830, 1732, 1647, 1267, 1108 cm⁻¹; MS (ESI) m/z : 407.73 ([M+H]⁺). Anal. calcd for C₁₉H₁₉Cl₂N₃OS: C 55.88, H 4.69, N 10.29; found C 55.86, H 4.70, N 10.27.

(3-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)(*p*-fluorophenyl)methanone (**7n**): white powder, yield 71%. m.p. 103.1~104.2 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 8.00~7.98 (m, 2H, C¹⁴-H, C¹⁸-H), 7.15 (t, J =8.5 Hz, 2H, C¹⁵-H, C¹⁷-H), 6.37~6.36 (m, 1H, C³-H), 3.64 (s, 3H, N-CH₃), 2.65 (t, J =5.5 Hz, 1H, C¹-H), 2.59~2.48 (m, 3H, C⁴-Ha, C⁷-H), 2.25~2.22 (m, 1H, C⁵-H), 1.36 (s, 3H, C⁸-H), 1.33 (d, J =9.2 Hz, 1H, C⁴-Hb), 0.93 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.6, 166.8, 165.0, 150.8, 134.1, 133.8, 132.3, 128.0, 115.6, 44.1, 40.1, 38.1, 32.7, 32.3, 31.5, 25.9, 21.1; IR (KBr) ν : 2975, 2922, 1723, 1641, 1277, 1101 cm⁻¹; MS (ESI) m/z : 357.80 ([M+H]⁺). Anal. calcd for C₁₉H₂₀FN₃OS: C 63.84, H 5.64, N 11.76; found C 63.83, H 5.64, N 11.74.

(*p*-Bromophenyl)(3-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)methanone (**7o**): yellow powder, yield 60%. m.p. 112.6~113.7 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.81 (d,

J =8.7 Hz, 2H, C¹⁴-H, C¹⁸-H), 7.61 (d, J =8.7 Hz, 2H, C¹⁵-H, C¹⁷-H), 6.37~6.36 (m, 1H, C³-H), 3.63 (s, 3H, N-CH₃), 2.64 (t, J =5.5 Hz, 1H, C¹-H), 2.59~2.48 (m, 3H, C⁴-Ha, C⁷-H), 2.25~2.22 (m, 1H, C⁵-H), 1.36 (s, 3H, C⁸-H), 1.33 (d, J =9.1 Hz, 1H, C⁴-Hb), 0.92 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.6, 165.4, 150.8, 133.8, 132.7, 132.4, 131.5, 130.7, 128.7, 44.1, 40.1, 38.1, 32.7, 32.4, 31.5, 25.9, 21.1; IR (KBr) ν : 2992, 2959, 2926, 1721, 1642, 1278, 1102 cm⁻¹; MS (ESI) m/z : 417.68, 419.66 ([M+H]⁺). Anal. calcd for C₁₉H₂₀BrN₃OS: C 54.55, H 4.82, N 10.04; found C 54.57, H 4.81, N 10.02.

(*p*-Chloromethylphenyl)(3-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl)methanone (**7p**): yellow powder, yield 51%. m.p. 136.4~137.6 °C; ¹H NMR (CDCl₃, 600 MHz) δ : 7.93 (d, J =8.4 Hz, 2H, C¹⁴-H, C¹⁸-H), 7.49 (d, J =8.4 Hz, 2H, C¹⁵-H, C¹⁷-H), 6.37~6.36 (m, 1H, C³-H), 4.64 (s, 2H, -CH₂Cl), 3.63 (s, 3H, N-CH₃), 2.65 (t, J =5.5 Hz, 1H, C¹-H), 2.59~2.48 (m, 3H, C⁴-Ha, C⁷-H), 2.24~2.22 (m, 1H, C⁵-H), 1.36 (s, 3H, C⁸-H), 1.33 (d, J =9.2 Hz, 1H, C⁴-Hb), 0.93 (s, 3H, C⁹-H); ¹³C NMR (CDCl₃, 150 MHz) δ : 170.6, 165.6, 150.8, 142.8, 133.8, 132.3, 131.8, 131.6, 128.2, 45.3, 44.1, 40.1, 38.1, 32.7, 32.3, 31.5, 25.9, 21.1; IR (KBr) ν : 2981, 2938, 1721, 1639, 1275, 1102 cm⁻¹; MS (ESI) m/z : 387.79 ([M+H]⁺). Anal. calcd for C₂₀H₂₂ClN₃OS: C 61.92, H 5.72, N 10.83; found C 61.91, H 5.73, N 10.80.

4.4 *In vitro* antifungal activity test

This test was performed according to the literature.^[28] The tested compound was dissolved in acetone. Sorporl-144 (200 mg/L) emulsifier was added to dilute the solution to 500 mg/L. Then, 1 mL solution of the tested compound was poured into a culture plate, and then 9 mL of Potato-Sugar-Agar (PSA) culture medium was added to obtain flats containing 50 mg/L the test compound. A bacterium tray of 5-mm diameter cut along the external edge of the mycelium was transferred to the flat containing the tested compound and put in equilateral triangular style in triplicate. Later, the culture plate was cultured at (24±1) °C and the expanded diameter of the bacterium tray was measured after 48 h and compared with that treated with aseptic distilled water to calculate the relative inhibition percentage. The current commercial fungicide chlorothalonil was used as a positive control.

4.5 Herbicidal activity test

4.5.1 Inhibition of the root-growth of rape (*B. campestris*)

This test was carried out according to the literature.^[28] The compounds to be tested were made into emulsions by using Tween-80 as emulsifying agent to aid dissolution at concentrations of 10 and 100 mg/L. Groups of 15 seeds of rape (*B. campestris*) were placed on a 5.6-cm filter paper that was in 6-cm Petri dishes containing 2 mL of compound solutions. Equal volume of distilled water was used as control. Petri dishes were placed in darkness at (28±1) °C for 72 h. The radicle lengths of seedlings were

measured. All experiments had three replicates. The inhibition percent of average length to control was used to describe the activity of compounds. And the current commercial herbicide flumioxazin was used as a positive control.

4.5.2 Inhibition of the seedling growth of barnyard grass (*E. crusgalli*)

This test was performed according to the literature.^[28] The compounds to be evaluated were made into emulsions by using TW-80 as emulsifying agent to aid dissolution, at concentrations of 10 and 100 mg/L. Groups of 10 germinated seeds of barnyard grass (*E. crusgalli*) were placed on a filter paper that was in a 50 mL beaker containing 6 mL of compound solutions. Equal volume of distilled water was used as control. Beakers were placed at (28±1) °C (3000 lux) for 72 h. The heights of seedlings were measured. All experiments had three replicates. The inhibition percent of average height to control was used to describe the activity of compounds, and the current commercial herbicide flumioxazin was used as a positive control.

Supporting Information The ¹H NMR, ¹³C NMR, ESI-MS, and IR spectra for the synthesized compounds. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn>.

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