Synthesis and Biological Activity of 3-Methyl-1*H*-pyrazole-4-carboxylic Ester Derivatives

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In search of novel pyrazole derivatives with bioactivity, a series of 3-methyl-1*H*-pyrazole-4-caboxylic ester derivatives were synthesized *via* α-oxoketene dithioacetals as starting material. The structures of all compounds prepared were confirmed by ^{1}H NMR, IR, MS and elemental analyses. Preliminary bioassays indicated that some compounds showed fungicidal activity against *wheat rust*, *phoma asparagi* and antiviral activity against *TMV*.

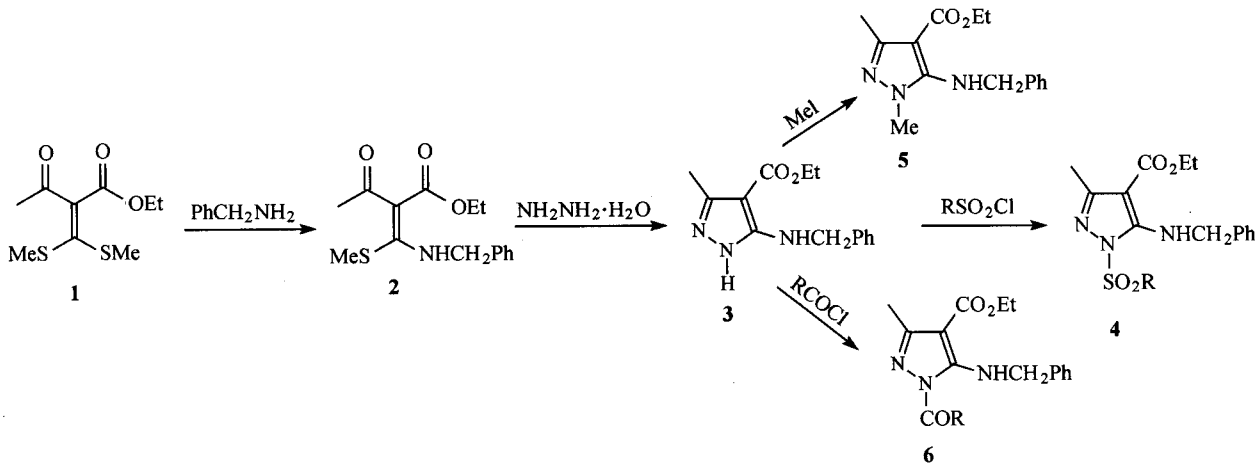
Keywords Pyrazole-4-carboxylic ester, synthesis, fungicidal activity, antiviral activity

Introduction

Pyrazole derivatives have been of continuing interests to scientist during the past two decades due to their diverse biological activities. Many pyrazole compounds exhibit excellent bioactivity. Some of them have been used as herbicides,[1] insecticides,[2] fungicides[3] and acaricides.[4] In previous works, we have synthesized many pyrazole derivatives with bioactivity.[5]

Sulfamide derivatives are a kind of important herbicide. If sulfonyls are introduced into pyrazole ring, sulfonyls may enhance biological activities. For example, 1-triazolesulfonyl-1*H*-pyrazoles possess excellent herbicidal activity.[6] As part of our ongoing program aimed at searching for agrochemicals, our interests in the pyrazole compounds containing sulfonyl led us to synthesize a novel series of 1-sulfonyl (methyl, formyl)-3-methyl-5-benzylamino (benzylthio, benzylsulfonyl)-1*H*-pyrazole-4-carboxylic esters.

Scheme 1



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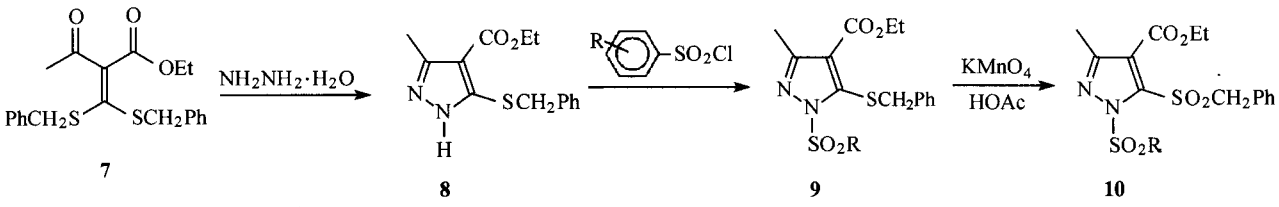
Scheme 2



7 8 9 10

Results and discussion

Synthesis

The α-oxoketene dithioacetals **1** reacted with benzyl amine to give α-oxoketene *N*, *S*-acetal **2**, which was cyclized in ethanol with hydrazine hydrate (80%) to give 3-methyl-5-benzylamino-1*H*-pyrazole-4-carboxylic ester **3**. Compound **3** was methylated, sulfonylated and formylated with iodomethane, sulfonyl chloride and formyl chloride to yield 1-methylpyrazole **5**, 1-sulfonylpyrazoles **4** and 1-formylpyrazoles **6**, respectively.

Similarly, 5-benzylthiopyrazole **8**, which was obtained *via* ring closure reaction of α-oxoketene dithioacetals **7** with hydrazine hydrate in ethanol, reacted with sulfonyl chloride to give 1-substituted benesulfonyl-5-benzylthiopyrazoles **9**. Treatment of **9** with $KMnO_4$/HOAc system afforded the corresponding 1, 5-disulfonylpyrazoles **10** in excellent yields.

Chemical properties

Among all compounds prepared, when 1-substituting groups of pyrazole rings were carbonyl, especially alkoxycarbonyl, carbonyl-nitrogen bonds were unstable. After recrystallized in ethanol, compounds **6** were transformed into **3**, but it was stable in other solvents. When the substituting groups were sulfonyl, sulfonyl-nitrogen bonds were more stable than carbonyl-nitrogen bonds. Compounds **4** could be recrystallized from ethanol. However, when **4** reacted with amine, only the compound **3** was obtained.

Biological activities

Fungicidal and antiviral activities of some compounds were tested *in vivo* at 500 ppm in greenhouse. The preliminary results were shown in Table 1, which showed the compounds **3** and **4** display inhibitory activities against *wheat rust* and *TMV*, respectively.

It was found from the Table 1 that the substituting groups of benzene ring of **4** have an important effect on their activities. **4c** had the best inhibitory activities against *wheat rust* and *TMV* among compounds **4**.

Table 1 The inhibition percentage of some products to *wheat rust* and *TMV*

Compd.	Concn. (ppm)	2	3	4a	4c	4e	4f
TMV	500	0	20	40	0	65	0
Wheat rust	500	20	80	10	40	90	0

In addition, it was found that compounds **5** and **6b** displayed good fungicidal activity against *phoma asparagi*. The *in vivo* inhibition rate of **5** and **6b** at 500 ppm was 93% and 86%, respectively.

Experimental

^1H NMR spectra were taken on a Bruker AC-P200 spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Elemental analyses were carried out on a Yanaco MT-3 instrument. Melting points were determined with a model Yanaco MP-500 apparatus and uncorrected. Mass spectra are recorded on a HP 5989 instrument (EI). IR spectra were obtained on a Shimadzu-435 spectrometer.

The reagents and solvents were available commercially. α-Oxoketene dithioacetals **1**, **7** and **8** were prepared according to the literatures.[7,8]

Synthesis of ethyl 2-(1′-benzylamino-1′-methylthiomethylene)-3-oxo-butanoic ester (**2**)

The benzyl amine (0.32 g, 3 mmol) was added dropwise to a solution of α-oxoketene dithioacetals **1** (0.7 g, 3 mmol) in ethanol (25 mL). The solution was stirred at room temperature about for 3 h. After removal ofsolvent, the residue was chromatographed on silica gel column eluting with ethyl acetate/petroleum ether (1/20) to give pure products **2** as a yellow liquid. yield

64%, ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.29 (t, J = 7.4, 3H), 2.17 (s, 3H), 2.35 (s, 3H), 4.23 (q, J = 7.2 Hz, 2H), 4.76 (s, 2H), 7.24—7.32 (m, 5H); IR (NaCl) ν: 3255, 3049, 1732, 1655, 1543, 1451, 1366, 1260 cm^{-1}; MS (70 eV) m/z(%): 293 (M^+, 4.6), 292 (18.3), 203 (3.8), 91 (100); Anal. calcd for $C_{15}H_{19}NO_3S$: C 61.41, H 6.53, N 4.77; found C 61.33, H 6.55, N 4.42.

Synthesis of ethyl 5-benzylamino-3-methyl-1H-pyrazol-4-carboxylic ester (**3**)

The hydrated hydrazine (50%) (0.3 g, 3 mmol) was added dropwise to a solution of α-oxoketene *N*, *S*-acetal **2** (0.88 g, 3 mmol) in ethanol (15 mL). The solution was stirred at room temperature for 3 h and then was refluxed for 1 h. The mixture was cooled and the separated solid was recrystallized from ethanol to give the pure products **3** as a white solid. yield 55%, m.p. 152—154℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.31 (t, J = 7.0 Hz, 3H), 2.38 (s, 3H), 4.25 (q, J = 7.0 Hz, 2H), 4.50 (s, 2H), 7.23—7.31 (m, 5H); IR (KBr) ν: 3374, 3075, 1662, 1608, 1533, 1494, 1443, 1135 cm^{-1}; MS (70 eV) m/z(%): 259 (M^+, 55), 258 (5), 212 (71), 91 (100); Anal. calcd for $C_{14}H_{17}N_3O_2$: C 64.85, H 6.61, N 16.21; found C 64.88, H 6.90, N 16.03.

General procedure for ethyl 5-benzylamino-3-menthyl-1-substituted sulfonyl pyrazole-4-carboxylic ester (**4**)

The substituted sulfonyl chloride (2 mmol) was added in portion to a mixture of sodium hydroxide (0.08 g, 2 mmol), the pyrazole **3** (0.39 g, 1.5 mmol) and $CHCl_3$ (5 mL) in sequence. The reaction mixture was stirred over night. After removal of solvent, the residue was washed with water and recrystallized from ethanol.

4a: R = *p*-$CH_3C_6H_4$, White solid, yield 79%, m.p. 145—147℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.29 (t, J = 7.0 Hz, 3H), 2.39 (s, 3H), 2.75 (s, 3H), 4.24 (q, J = 7.2 Hz, 2H), 4.47 (s, 2H), 7.20—7.76 (m, 9H); IR (KBr) ν: 3403, 3075, 2791, 1679, 1588, 1560, 1452, 1380, 1189, 1134 cm^{-1}; MS (70 eV) m/z(%): 413 (M^+, 17), 258 (15), 212 (67), 91 (100); Anal. calcd for $C_{21}H_{23}N_3O_4S$: C 61.00, H 5.61, N 10.16; found C 60.91, H 5.37, N 9.85.

4b: R = $C_6H_5CH_2$, White solid, yield 39%, m.p. 113—114℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.35 (t, J = 7.0 Hz, 3H), 2.55 (s, 3H), 4.28 (q, J = 7.0 Hz, 2H), 4.48 (s, 2H), 2.64 (s, 2H), 7.24—7.74 (m, 9H). IR (KBr) ν: 3407, 2922, 1662, 1670, 1585, 1536, 1367, 1170, 1146 cm^{-1}; MS (70 eV) m/z(%): 413 (M^+, 7), 302 (9), 258 (3), 212 (31), 91 (100); Anal. calcd for $C_{21}H_{23}N_3O_4S$: C 61.00, H 5.61, N 10.16; found C 61.04, H 5.84, N 9.82.

4c: R = *p*-FC_6H_4, White solid, yield 95%, m.p. 123—124℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.30 (t, J = 7.0 Hz, 3H), 2.75 (s, 3H), 4.26 (q, J = 7.0 Hz, 2H), 4.47 (s, 2H), 7.01—7.87 (m, 9H); IR (KBr) ν: 3401, 2974, 1683, 1589, 1544, 1375, 1190, 1137 cm^{-1}; MS (70 eV) m/z(%): 417 (M^+, 14), 258 (8), 212 (57), 91 (100); Anal. calcd for $C_{20}H_{20}FN_3O_4S$: C 57.54, H 4.83, N 10.07; found C 57.68, H 4.95, N 10.30.

4d: R = *p*-ClC_6H_4, White solid, yield 67%, m.p. 120—121℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.32 (t, J = 7.0 Hz, 3H), 2.78 (s, 3H), 4.30 (q, J = 7.0 Hz, 2H), 4.48 (s, 2H), 7.14—7.90 (m, 9H); IR (KBr) ν: 3402, 3074, 1682, 1589, 1544, 1392, 1188, 1136 cm^{-1}; MS (70 eV) m/z(%): 433 (M^+, 10), 258 (10), 212 (56), 91 (100); Anal. calcd for $C_{20}H_{20}ClN_3O_4S$: C 55.36, H 4.65, N 9.68; found C 55.25, H 4.77, N 9.53.

4e: R = *p*-BrC_6H_4, White solid, yield 52%, m.p. 114—117℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.34 (t, J = 7.2 Hz, 3H), 2.78 (s, 3H), 4.28 (q, J = 7.2 Hz, 2H), 4.48 (s, 2H), 7.18—7.80 (m, 9H); IR (KBr) ν: 3402, 3076, 1679, 1588, 1543, 1387, 1190, 1133 cm^{-1}; MS (70 eV) m/z(%): 479 (M^+ (^{81}Br), 6), 477 (M^+ (^{79}Br), 5), 258 (10), 212 (57), 91 (100); Anal. calcd for $C_{20}H_{20}BrN_3O_4S$: C 50.22, H 4.21, N 8.53; found C 50.02, H 4.00, N 8.78.

4f: R = *p*-$NO_2C_6H_4$, Yellow solid, yield 63%, m.p. 138—139℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.35 (t, J = 7.1 Hz, 3H), 2.80 (s, 3H), 4.32 (q, J = 7.2 Hz, 2H), 4.48 (s, 2H), 7.21—8.28 (m, 9H); IR (KBr) ν: 3389, 2972, 1697, 1594, 1528, 1361, 1182, 1134 cm^{-1}; MS (70 eV) m/z(%): 444 (M^+, 9), 258 (8), 212 (53), 91 (100); Anal. calcd for $C_{20}H_{20}N_4O_6S$: C 54.05, H 4.53, N 12.61; found C 53.92, H 4.37, N 12.38.

4g: R = C_6H_5, White solid, yield 81%, m.p. 98—99℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.29 (t, J = 7.2 Hz, 3H), 2.76 (s, 3H), 4.24 (q, J = 7.2 Hz, 2H), 4.47 (s, 2H), 7.23—7.87 (m, 9H); IR (KBr) ν: 3402, 3016, 1684, 1589, 1558, 1361, 1184, 1137 cm^{-1}; MS (70 eV) m/z(%): 399 (M^+, 14), 258 (11), 212 (63), 91 (100); Anal. calcd for $C_{20}H_{21}N_3O_4S$: C 60.13, H 5.30, N 10.52; found C 59.86, H 5.36, N 10.67.

4h: R = 2, 4-$(NO_2)_2C_6H_4$, Red solid, yield 56%, m.p. 156—158℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.36 (t, J = 7.2 Hz, 3H), 2.81 (s, 3H), 4.33 (q, J = 7.0 Hz, 4H), 7.11—8.41 (m, 9H); IR (KBr) ν: 3381, 3092, 1691, 1605, 1547, 1357, 1183, 1138 cm^{-1}; MS (70 eV) m/z(%): 489 (M^+, 6), 258 (10), 212 (48), 91 (100); Anal. calcd for $C_{20}H_{19}N_5O_8S$: C 49.08, H 3.91, N 14.31; found C 49.16, H 3.97, N 14.31.

Synthesis of ethyl 5-benzylamino-1,3-dimethylpyrazole-4-carboxylic ester (**5**)

To a solution of pyrazole **3** (0.42 g, 1.7 mmol) in methanol (5 mL) was added sodium hydroxide (0.16 g, 4 mmol) and iodomethane (0.3 g, 2.1 mmol) in sequence. The reaction mixture was stirred over night and poured into water (15 mL). The oil residue was chromatographed on silica gel column eluting with ethyl acetate-petroleum ether to give pure products as white solid. 5: yield 62%, m.p. 65—70℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.32 (t, J = 7.0 Hz, 3H), 2.64 (s, 3H), 3.64 (s, 3H), 4.28 (q, J = 7.0 Hz, 2H), 4.50 (s, 2H), 7.20—7.42 (m, 5H); IR (NaCl) ν: 3474, 2920, 1662, 1561, 1436, 1083 cm^{-1}; MS (70 eV) m/z(%): 273 (M^+, 27), 244 (21), 226 (100), 199 (22), 148 (18), 122 (28); Anal. calcd for $C_{15}H_{19}N_3O_2$: C 50.22, H 4.21, N 8.78; found C 50.02, H 4.00, N 8.53.

General procedure for ethyl 5-benzylamino-3-menthyl-1-substituted formacylpyrazole-4-carboxylic ester (**6**)

The substituted formyl chloride (2 mmol) was added in portion to a mixture of sodium hydroxide (0.08 g, 2 mmol), the pyrazole **3** (0.39 g, 1.5 mmol) and $CHCl_3$ (5 mL) in sequence. The reaction mixture was stirred over night. After removal of solvent, the residue was washed with water and recrystallized from acetone-petroleum ether.

6a: R = C_6H_4, White solid, yield 35%, m.p. 163—166℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.36 (t, J = 7.0 Hz, 3H), 2.87 (s, 3H), 4.33 (q, J = 7.1 Hz, 2H), 4.41 (s, 2H), 7.23—7.89 (m, 10H); Anal. calcd for $C_{21}H_{21}N_3O_3$: C 69.41, H 5.82, N 11.56; found C 69.86, H 5.63, N 11.42.

6b: R = OC_2H_5, White solid, yield 76%, m.p. 60—61℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.32 (t, J = 7.0, 3H), 1.44 (t, J = 7.0, 3H), 2.81 (s, 3H), 4.28 (q, J = 7.0, 2H), 4.46 (q, J = 7.0, 2H) 4.60 (s, 2H), 7.24—7.34(m, 5H); IR (KBr) ν: 3409, 3042, 1733, 1689, 1597, 1565, 1389, 1343, 1262, 1135 cm^{-1}; MS (70 eV) m/z(%): 331 (M^+, 43), 258 (4), 240 (12), 212 (63), 91 (100); Anal. calcd for $C_{17}H_{21}N_3O_4$: C 61.62, H 6.39, N 12.68; found C 61.58, H 6.41, N 12.92

General procedure for ethyl 5-benzylthio-3-menthyl-1-substituted sulfonylpyrazole-4-carboxylic ester (**9**)

To a solution of pyrazole **8** (1.66 g, 6 mmol) in $CHCl_3$ (20 mL) was added sodium hydroxide (0.28 g, 7 mmol) and sulfonyl chloride (7 mmol) insequence. The reaction mixture was stirred over night. After removal of solvent, the residue was washed with water and recrystallized from ethanol.

9a: R = C_6H_5, White solid, yield 64%, m.p. 113—114℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.30 (t, J = 7.2 Hz, 3H), 2.80 (s, 3H), 4.25 (q, J = 7.1, 2H), 4.27 (s, 2H), 7.24—7.89 (m, 11H); IR (KBr) ν: 3383, 1699, 1605, 1549, 1411, 1383, 1254, 1186, 1135 cm^{-1}; MS (70 eV) m/z(%): 416 (M^+, 3), 275 (19), 229 (14), 135 (100), 91 (75); Anal. calcd for $C_{20}H_{20}N_2O_4S_2$: C 57.67, H 4.84, N 6.73; found C 57.68, H 4.83, N 6.73.

9b: R = p-$CH_3C_6H_4$, White solid, yield 69%, m.p. 96—97℃; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.30 (t, J = 7.2 Hz, 3H), 2.41 (s, 3H), 2.79 (s, 3H), 4.24 (q, J = 7.4 Hz, 2H), 4.26 (s, 2H), 7.24—7.78 (m, 10H); IR (KBr) ν: 3402, 2981, 1714, 1552, 1422, 1389, 1272, 1187, 1131 cm^{-1}; MS (70 eV) m/z (%): 430 (M^+, 1.8), 275 (18.1), 229 (12.6), 135 (100), 91 (85.1); Anal. calcd for $C_{21}H_{22}N_2O_4S_2$: C 58.58, H 5.15, N 6.51;

found C 58.37, H 4.89, N 6.46.

9c: R = *p*-FC_6H_4, White solid, yield 63%, m.p. 105—107℃; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.31 (t, J = 7.0 Hz, 3H), 2.80 (s, 3H), 4.25 (s, 2H), 4.28 (q, J = 6.8 Hz, 2H), 7.12—7.89 (m, 10H) IR (KBr) ν: 3407, 2970, 1697, 1587, 1490, 1382, 1289, 1190, 1153 cm^{-1}; MS (70 eV) m/z(%): 434 (M^+, 2.4), 275 (17.1), 229 (14.8), 135 (100), 91 (79.4); Anal. calcd for $C_{20}H_{19}FN_2O_4S_2$: C 55.28, H 4.41, N 6.45; found C 55.12, H 4.20, N 6.48.

9d: R = *p*-ClC_6H_4, White solid, yield 89%, m.p. 105—106℃; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.31 (t, J = 7.2 Hz, 3H), 2.79 (s, 3H), 4.26 (s, 2H), 4.27 (q, J = 6.8 Hz, 2H), 7.24—7.78 (m, 10H); IR (KBr) ν: 3398, 2956, 1707, 1552, 1440, 1394, 1268, 1186, 1127 cm^{-1}; MS (70 eV) m/z(%): 450 (M^+, 3), 275 (46), 229 (36), 135 (100), 91 (87); Anal. calcd for $C_{20}H_{19}ClN_2O_4S_2$: C 53.27, H 4.25, N 6.21; found C 53.24, H 4.21, N 6.12.

9e: R = *o*-$NO_2CH_3C_6H_4$, White solid, yield 42%, m.p. 129—131℃; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.33 (t, J = 7.2 Hz, 3H), 2.88 (s, 3H), 4.10 (s, 2H), 4.29 (q, J = 7.1 Hz, 2H), 7.18—8.30 (m, 10H); IR (KBr) ν: 3398, 3085, 1721, 1558, 1437, 1386, 1271, 1186, 1132 cm^{-1}; MS (70 eV) m/z(%): 461 (M^+, 1), 275 (20), 229 (11), 135 (88), 91 (100); Anal. calcd for $C_{20}H_{19}N_3O_6S_2$: C 52.05, H 4.15, N 9.10; found C 51.97, H 4.18, N 9.11.

General procedure for ethyl 5-benzylsulfonyl-3-menthyl-1-substituted sulfonylpyrazole-4-carboxylic ester (**10**)

The pyrazloe **9** (1.9 mmol) and potassium permanganate (0.8 g, 5 mmol) was added to a acetic acid-water mixed solvent (3:1, 15 mL). The reaction mixture was stirred over night and a saturated sodium bisulfite solution (40 mL) was added until the purple disappeared. The separated solid was washed with water and recrystallized from ethanol.

10a: R = C_6H_5, White solid, yield 93%, m.p. 133—135℃; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.35 (t, J = 7.2 Hz, 3H), 2.80 (s, 3H), 4.34 (q, J = 7.2 Hz, 2H), 4.76 (s, 2H), 7.24—7.88 (m, 11H); IR (KBr) ν: 3387, 2968, 1734, 1446, 1420, 1331, 1255, 1188, 1139 cm^{-1}; MS (70 eV) m/z (%): 448 (M^+, 3), 91 (100); Anal. calcd for $C_{20}H_{20}N_2O_6S_2$: C 53.56, H 4.49, N 6.25; found C 53.40, H 4.41, N 6.28.

10b: R = *p*-$CH_3C_6H_4$, White solid, yield 83%, m.p. 159—161℃; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.35 (t, J = 7.2 Hz, 3H), 2.45 (s, 3H), 2.80 (s, 3H), 4.34 (q, J = 7.3 Hz, 2H), 4.76 (s, 2H), 7.24—7.86 (m, 10H); IR (KBr) ν: 3391, 3022, 1716, 1442, 1386, 1333, 1253, 1193, 1130 cm^{-1}; MS (70eV) m/z(%): 462 (M^+, 2), 91 (100); Anal. calcd for $C_{21}H_{22}N_2O_6S_2$: C 54.53, H 4.79, N 6.06; found C 54.45, H 4.61, N 6.07.

10c: R = *p*-FC_6H_4, White solid, yield 93%, m.p. 170—173℃; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.36 (t, J = 7.1 Hz, 3H), 2.81 (s, 3H), 4.36 (q, J = 7.1 Hz, 2H), 4.75 (s, 2H), 7.20—7.97 (m, 10H); IR (KBr) ν: 3390, 2969, 1718, 1488, 1441, 1378, 1332, 1253, 1195, 1131 cm^{-1}; MS (70 eV) m/z(%): 466 (M^+, 2), 91 (100); Anal. calcd for $C_{20}H_{19}FN_2O_6S_2$: C 51.49, H 4.11, N 6.00; found C 51.40, H 4.13, N 5.98.

10d: R = *p*-ClC_6H_4, White solid, yield 95%, m.p. 187—189℃; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.37 (t, J = 7.2 Hz, 3H), 2.80 (s, 3H) 4.36 (q, J = 7.2 Hz, 2H), 4.75 (s, 2H), 7.24—7.89 (m, 10H); IR (KBr) ν: 3398, 2973, 1717, 1441, 1391, 1333, 1254, 1192, 1130 cm^{-1}; MS (70 eV) m/z (%): 482 (M^+, 1), 91 (100); Anal. calcd for $C_{20}H_{19}ClN_2O_6S_2$: C 49.74, H 3.97, N 5.80; found C 49.60, H 3.88, N 5.7

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