Synthesis and insecticidal activities of new pyrethroid acid oxime ester derivatives*

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Abstract A series of compounds containing oxime-ester linkage in place of the ester linkage in pyrethroid ester are designed and prepared. Bioassay data of insecticidal activities of these compounds on *Ostrinia nubilalis* (H.) and *Culex pipines* (L.) are presented. Among them 4-dimethyaminobenzaldehyde oxime ester of 2, 2, 3, 3-tetramethylcyclopropanecarboxylic acid and 4-dimethyamino benzaldehyde oxime ester of cyclopropanecarboxylic acid are found to be potent insecticide against *Ostrinia nubilalis* (H.). Structure-activity relationship of the compounds is discussed.

Keywords: pyrethroids, insecticides, oxime-ester, synthesis, structure-activity relationship.

Much attention has been paid to the structural modification of pyrethroids since Schechter and coworkers[1] reported the synthesis of allethrin in 1949. Various synthetic pyrethroids have been invented through retaining chrysanthemic acid as the acid moiety and modifying the alcohol moiety. These compounds, such as resmethrin[2], prallethrin[3], phenothrin[4] and cyphenothrin[5] have been commercially produced and have been in broad use as active ingredients, mainly for household insecticides. Then many pyrethroids having a chemically stable phenoxybenzyl group as the alcohol moiety with a modified acid moiety have been introduced. Pyrethroids, such as permethrin[6], cypermethrin[7], deltamethrin[7] and fenvalerate[8] have been used for agricultural purposes because of their chemical stability. Subsequent developments include some compounds produced by replacing the ester linkage with other linkages, examples being etofenprox[9], silafluofen[10] and flufenprox[11].

It is known that some oxime derivatives have biological activity, and typical examples of this can be found in pharmaceuticals and agrochemicals. For pyrethroids, compounds with oxime-ether linkage have been previously examined[12]. However, oxime-ester linkage of pyrethroids has got only limited attention. In our recent studies[13,14] for finding novel classes of insecticidal compounds relating to pyrethroid, we focused on pyrethroid acid oxime-ester derivatives. Amongst these compounds, a series of substituted benzaldehyde oxime esters of pyrethroid acids were selected. Through synthesis and biological assay against *Ostrinia nubilalis* H. and *Culex pipines* L., we have succeeded in finding novel pyrethroid acid oxime ester derivatives possessing insecticidal activity.

Herein we report the synthesis of novel substituted benzaldehyde oxime esters of pyrethroid acids and the insecticidal activity of these compounds, including detailed structure-activity relationships of the substitutents on the molecule and LC_{50} values for representative compounds.

1 Experimental methods

1.1 General experimental procedures

Melting points were measured with a Yanaco MP-500 apparatus and the thermometer was uncorrected. NMR spectra were recorded on a Bruker AC-P200 instrument using tetramethylsilane as an internal standard in deuterochloroform. Elemental analyses (CHN analyses) were carried out on a Yanaco MT-3 analyser.

1.2 Chemical synthesis

2, 2, 3, 3-tetramethylcyclopropanecarboxylic acid[15], 3-(2, 2-dichloroethenyl)-2, 2-dimethylcyclopropanecarboxylic acid[16] (*cis*/*trans* = 43/57), 3-

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(2,2-dibromo ethenyl)-2,2-dimethylcyclopropanecarboxylic acid[7] (*cis*/*trans* = 45/55), 2-(4-chloro phenyl)-3-methylbutyric acid[17], chrysanthemic acid[18](*cis*/*trans* = 40/60) were prepared according to the procedures in literature. Cyclopropanecarboxylic acid was obtained from Bayer A-G. Aromatic aldoximes were synthesized from the corresponding aldehydes as described in Ref. [19]. The synthetic pathways used to prepare the new oxime-ester derivatives are shown in Fig. 1.

Reaction of pyrethroid acids **I** with thionyl chloride produces acid chlorides **II**. A number of new pyrethroid acid oxime-ester derivatives **IV** were prepared by reacting the acid chlorides **II** with arometic aldoximes **III** in the presence of triethylamine.

Representative procedures are given below.

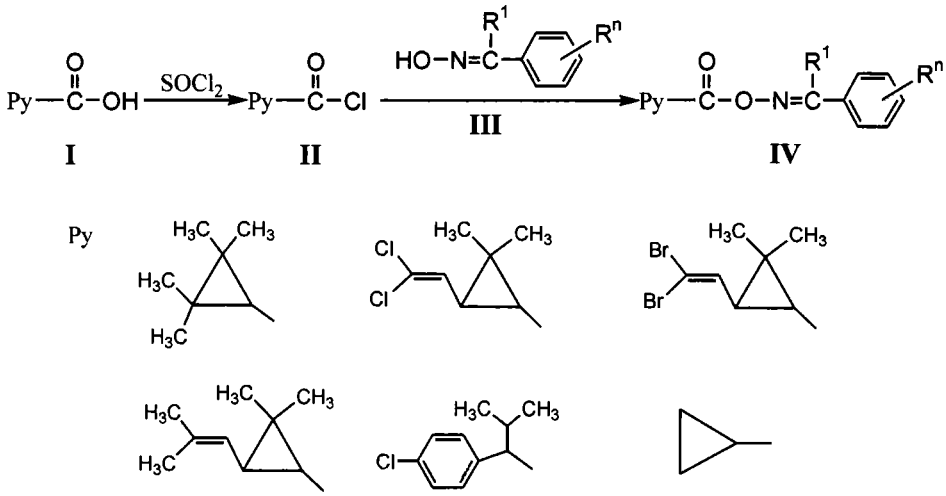


Fig. 1. Synthetic route to novel pyrethroid acid oxime ester derivatives.

1.2.1 General procedure for the preparation of aromatic aldoxime **III** Here (R^1 = H, R^n = 4-$(CH_3)_2N$ is an example. To a solution of 4-dimethylaminobenzaldehyde (1.80 g, 12.1 mmol) and $H_2NOH \cdot HCl$ (0.92 g, 13.3 mmol) in ethanol (10 mL), triethylamine (1.34 g, 13.3 mmol) was added dropwise at 0～5 ℃. The reaction was stirred for 2 h at this temperature. The mixture was concentrated in vacuum, diluted with water (20 mL) and extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine, dried over magnesium sulfate and evaporated in vacuum. The residue was recrystallized from 80% ethanol to give colorless needles (1.74 g, 87.9%), mp 144～146 ℃. ^{1}HNMR ($CDCl_3$): δ = 3.00 (s, 6H, $2CH_3$), 6.65～7.60 (dd, 4H, Ar), 8.20 (s, 1H, N=CH).

1.2.2 General procedure for the preparation of oxime-ester derivatives **IV** Acid chlorides **II** (4.2 mmol) in toluene (5 mL) was added dropwise to a solution of aromatic aldoximes **III** (3.5 mmol) and triethylamine (4.2 mmol) in toluene (10 mL) at 0～5 ℃. The reaction mixture was stirred at this temperature for 2～4 h when a thin layer chromatography analysis revealed the complete consumption of the starting material. Toluene (15 mL) was added to the resultant solution, washed with water (10 mL), 10% $NaHCO_3$ (10 mL) and brine. The organic layer was dried over magnesium sulfate and evaporated in vacuum. The residue obtained was recrystallized from petroleum ether (60～90 ℃) or separated by column chromatography to produce the required oxime esters (Compounds **1～30**, Tables 1, 2 and 3).

The physical, analytical and spectroscopic data for the synthetic oxime esters are reported in the Appendix.

1.3 Biological assays

Tests described below were repeated twice for each concentration. The insecticidal activity was expressed as indexes of 0 to 3, corresponding to 0, 1%～50%, 51%～99% and 100% mortality respectively.

1.3.1 Asiatic maize borer (*Ostrinia nubilalis* (Hubner)) Each compound was tested for its insecticidal activity against *O. nubilalis* at three dif-

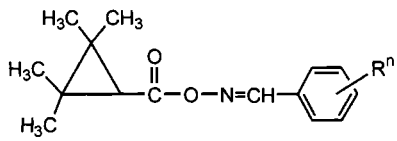
ferent concentrations (500, 250, 125 mg · L^{-1}). Maize stems were immersed in solutions for 20 s. Each treated stem was put into a glass tube (2 cm in diameter, 10 cm in length) with a small amount of water. After drying, instar larvae of *O. nubilalis* were released into each tube, which was kept at 25 ℃ with 50% relative humidity. Mortality was observed 24 h later, and 10 ~ 20 larvae were used for each treatment. A similar technique, with six concentrations, was used to determine LC_{50} values of selected compounds towards *O. nubilalis* (Tables 1~4).

1.3.2 Northern house mosquitos (*Culex pipines* (Linnaeus)) Instar larvae of *C. pipines* were immersed in a solution of the test compounds at two different concentrations (10, 2 mg · L^{-1}) for 20 s. The treated mosquitos were kept at 25 ℃ and 50% relative humidity during the test period. The mortality was observed 24 h after treatment (Tables 1~3).

2 Results and discussion

Table 1 contains data on a series of substituted benzaldehyde oxime esters of 2, 2, 3, 3-tetramethylcyclopropanecarboxylic acids, in which the 4-position on the phenyl group was replaced with various substituent and atoms.

Table 1. Biological activities of compounds **1~14** against *Ostrinia nubilalis* and *Culex pipines*



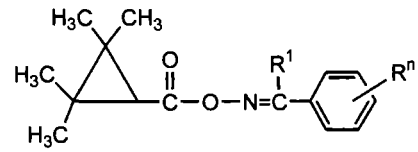
Compound No.	R^n	Activity rating (mg·L^{-1})				
		O. nubilalis			*C. pipines*	
		500	250	125	10	2
1	H	1	0	—	1	-
2	4-CH_3	1	0	—	1	0
3	4-$(CH_3)_2CH$	1	0	—	1	—
4	4-$(CH_3)_3C$	1	0	—	1	0
5	4-Cl	1	0	—	0	—
6	4-NO_2	0	—	—	1	—
7	4-$(CH_3)_2N$	3	3	3	2	1
8	4-$(CH_3CH_2)_2N$	2	1	1	3	3
9	4-CH_3O	1	0	—	1	0
10	4-CH_3CH_2O	1	0	—	0	—
11	4-$(CH_3)_2CHO$	1	0	—	1	0
12	4-OPh	1	0	—	0	—
13	3,4-OCH_2O	2	1	0	1	0
14	4-OCH_2Ph	1	0	—	1	0

— not tested.

A hydrogen atom at the 4-position (**1**) gave low activity against *O. nubilalis* and *C. pipines*. The introduction of alkyl groups at the 4-position on the phenyl ring, although not leading to complete inactivation, showed similarly low activity (**2~4**). In addition, the activity of compounds containing a chlorine atom (**5**) or a nitro group (**6**) as electron-withdrawing substituent was reduced or completely eliminated. The introduction of dialkylamino groups at 4-position drastically increased overall activity: compounds (**7**) showed 100% mortality at 125 mg · L^{-1} against *O. nubilalis* and compound (**8**) possessed 100% mortality at 2 mg · L^{-1} against *C. pipines*. However, replacement of dialkylamino groups with alkoxyl or phenoxyl groups (**9~14**) led to low activity.

Table 2 shows the effect of substitution at the 2- and 3-position of the phenyl group. Compounds **15**, **16** versus **7** exhibited low activity. In addition, when the substituent at the 4-position was a dimethylamino group, the introduction of substituent was unfavorable at the other positions of the aldoxime moiety (**17**, **18**, **19**, **20**).

Table 2. Biological activities of the examined compounds against *Ostrinia nubilalis* and *Culex pipines*



Compound No.	R^1	R^n	Activity (mg·L^{-1})				
			O. nubilalis			*C. pipines*	
			500	250	125	10	2
7	H	4-$(CH_3)_2N$	3	3	3	2	1
15	H	3-$(CH_3)_2N$	2	1	0	1	0
16	H	2-CH_3NH	2	1	0	1	0
17	H	2-Cl-4-$(CH_3)_2N$	1	0	—	2	1
18	H	3-Cl-4-$(CH_3)_2N$	1	0	—	1	0
19	Cl	3,5-Cl_2-4-$(CH_3)_2N$	1	0	—	1	0
20	CN	3,5-Cl_2-4-$(CH_3)_2N$	1	0	—	1	0

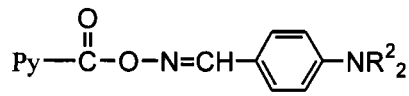
— not tested.

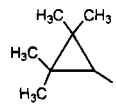
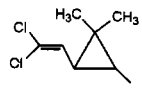
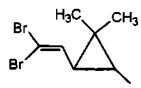
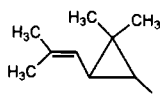
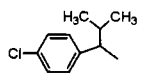
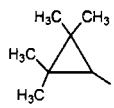
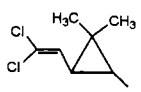
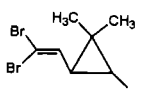
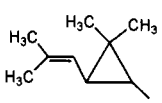
Although some compounds gave high activity against *O. nubilalis* and *C. pipines*, their structure-activity relationships are not clear. However, considering the results shown in Tables 1 and 2, dialkylamino group at the 4-position of the phenyl ring is required for the activity.

To examine the effect of the acid moiety, some pyrethroid acids were introduced. The results are shown in Table 3. It is interesting to note that most of the compounds listed in that table possess insectici-

dal activity against the two species. Compounds **7**, **23**, **24** and **25** gave the highest rating against *O. nubilalis*, while compounds **8** and **27** exhibited the highest rating against *C. pipines*. Replacement of the dimethylamino group at the 4-position of the phenyl ring with the diethylamino group showed a tendency to reduce activity against *O. nubilalis*. However, this replacement tended to increase activity against *C. pipines*.

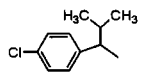
Table 3. Biological activities of oxime-esters of pyrethroid acids against *Ostrinia nubilalis* and *Culex pipines*



Compound No.	Py	R^2	Activity rating ($mg \cdot L^{-1}$)				
			O. nubilalis			*C. pipines*	
			500	250	125	10	2
7		CH_3	3	3	3	2	1
21[a)]		CH_3	3	3	2	2	0
22[a)]		CH_3	3	1	—	2	0
23[a)]		CH_3	3	3	3	2	0
24		CH_3	3	3	3	1	0
25		CH_3	3	3	3	2	0
8		CH_3CH_2	2	1	0	3	3
26[a)]		CH_3CH_2	2	1	0	2	0
27[a)]		CH_3CH_2	2	1	0	3	3
28[a)]		CH_3CH_2	2	1	0	2	1

To be continued

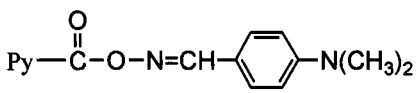
Continued

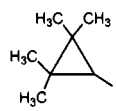
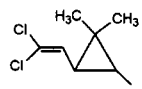
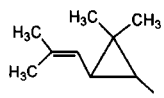
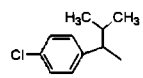
Compound No.	Py	R^2	Activity rating ($mg \cdot L^{-1}$)				
			O. nubilalis			*C. pipines*	
			500	250	125	10	2
29		CH_3CH_2	2	1	0	2	1
30		CH_3CH_2	1	0	—	3	2

a) The oxime esters were (1RS)-*cis*, *trans* isomeric mixtures. — not tested.

To assess in detail the insecticidal potential against *O. nubilalis*, compounds **7**, **21**, **23**, **24** and **25** were selected from the compounds showing high activities. The results in terms of LC_{50} values are shown in Table 4. Compounds **7** and **25** were the most active of those tested against *O. nubilalis*, with LC_{50} values of 7.7 and 6.6 $mg \cdot L^{-1}$, respectively.

Table 4. LC_{50} values of selected oxime-esters of pyrethroid acids against *Ostrinia nubilalis*



Compound No.	Py	LC_{50}($mg \cdot L^{-1}$)
7		7.7
21[a)]		19.0
23[a)]		14.5
24		11.0
25		6.6

a) The oxime esters were (1RS)-*cis*, *trans* isomeric mixtures.

As mentioned above, to obtain new insecticidal compounds, 30 derivatives of pyrethroid acid oxime-esters were synthesized. Among them, 4-dimethylamino benzaldehyde oxime ester of cyclopropanecarboxylic acid (**25**) was found to be potent insecticide against *O. nubilalis*.

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Appendix: physical, analytical and spectroscopic data

Physical and elemental analytical data of compounds (**1**～**30**)

Compound No.	Formula	m.p.(℃)	Yield(%)	Elemental analysis(%, Calcd.)		
				C	H	N
1	$C_{15}H_{19}NO_2$	136～138	67.6	73.52(73.43)	7.83(7.80)	5.57(5.71)
2	$C_{16}H_{21}NO_2$	118～119	59.3	73.93(74.10)	8.14(8.16)	5.42(5.40)
3	$C_{18}H_{25}NO_2$	119～120	64.9	74.99(75.22)	8.72(8.77)	4.86(4.87)
4	$C_{19}H_{27}NO_2$	130～132	93.4	50.10(49.89)	4.97(5.04)	3.01(3.06)
5	$C_{15}H_{18}ClNO_2$	143～144	71.5	64.00(64.40)	6.62(6.48)	4.75(5.01)
6	$C_{15}H_{18}N_2O_4$	179～180	69.6	62.52(62.71)	5.36(5.26)	10.08(9.75)
7	$C_{17}H_{24}N_2O_2$	152～154	62.5	70.90(71.08)	8.10(8.38)	9.53(9.76)
8	$C_{19}H_{28}N_2O_2$	79～80	79.6	71.92(72.15)	8.64(8.86)	8.72(8.86)
9	$C_{16}H_{21}NO_3$	95～96	70.4	69.65(69.79)	7.84(7.69)	5.36(5.09)
10	$C_{17}H_{23}NO_3$	73～74	57.1	70.54(70.56)	7.93(8.01)	4.85(4.84)
11	$C_{18}H_{25}NO_3$	74～75	50.6	71.05(71.25)	8.27(8.31)	4.58(4.62)
12	$C_{21}H_{23}NO_3$	93～94	90.1	74.90(74.75)	6.62(6.87)	4.07(4.15)
13	$C_{16}H_{19}NO_4$	165～167	90.2	66.77(66.44)	6.75(6.57)	4.79(4.84)
14	$C_{22}H_{25}NO_3$	124～125	75.8	74.96(75.18)	7.08(7.17)	3.91(3.98)
15	$C_{17}H_{24}N_2O_2$	62～63	65.0	70.79(70.79)	8.20(8.38)	9.55(9.71)
16	$C_{16}H_{22}N_2O_2$	110～112	35.1	70.00(70.03)	8.10(8.08)	10.00(10.21)
17	$C_{17}H_{23}ClN_2O_2$	78～79	67.6	63.23(63.25)	7.12(7.18)	8.85(8.68)
18	$C_{17}H_{23}ClN_2O_2$	89～90	61.4	63.21(63.25)	7.35(7.18)	8.73(8.68)
19	$C_{17}H_{21}Cl_3N_2O_2$	110～111	40.5	52.01(52.13)	5.33(5.40)	7.20(7.15)
20	$C_{18}H_{21}Cl_2N_3O_2$	138～139	42.0	56.42(56.55)	5.34(5.54)	11.00(10.99)
21	$C_{17}H_{20}Cl_2N_2O_2$	101～106[a)]	84.0	57.30(57.46)	5.83(5.63)	7.43(7.88)
22	$C_{17}H_{20}Br_2N_2O_2$	128～135[a)]	74.0	46.03(46.06)	4.49(4.29)	6.32(6.32)
23	$C_{19}H_{26}N_2O_2$	66～76[a)]	68.3	72.60(72.60)	8.18(8.28)	8.61(8.92)
24	$C_{20}H_{23}ClN_2O_2$	108～109	71.5	67.00(66.95)	6.65(6.42)	7.80(7.86)
25	$C_{13}H_{16}N_2O_2$	108～110	81.0	66.86(67.24)	7.04(6.95)	11.97(12.07)
26	$C_{19}H_{24}Cl_2N_2O_2$	92～110[a)]	72.5	59.43(59.53)	6.06(6.31)	7.06(7.31)
27	$C_{19}H_{24}Br_2N_2O_2$	80～86[a)]	78.4	48.06(48.41)	5.20(4.88)	5.64(5.94)
28	$C_{21}H_{30}N_2O_2$	Viscous liquid[a)]	90.0	73.87(73.47)	9.03(9.04)	7.88(8.16)
29	$C_{22}H_{27}ClN_2O_2$	Viscous liquid	86.6	67.98(68.31)	6.72(6.99)	6.99(7.24)
30	$C_{15}H_{20}N_2O_2$	Viscous liquid	77.6	69.34(69.23)	7.54(7.69)	10.82(10.77)

a) The oxime esters were (1RS)-*cis*, *trans* isomeric mixtures.

^{1}H NMR data of compounds (**1**～**30**)

Compound No.	^{1}H NMR (δ, $CDCl_3$)
1	1.22(s, 6H, $2CH_3$), 1.26(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 7.38～7.74 (m, 5H, Ar), 8.33(s, 1H, N=CH)
2	1.22(s, 6H, CH_3), 1.25(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 2.36(s, 3H, CH_3) 7.17～7.63(dd, 4H, Ar), 8.33(s, 1H, N=CH)
3	1.17～1.30(m, 19H, $6CH_3$, cyclopropane-H), 2.28(q, 1H, CH), 7.22～7.66(dd, 4H, Ar), 8.30(s, 1H, N=CH)
4	1.16～1.30(m, 22H, $7CH_3$, cyclopropane-H), 7.20～7.50(dd, 4H, Ar), 8.29(s, 1H, N=CH)
5	1.22(s, 6H, $2CH_3$), 1.25(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 7.34～7.68 (dd, 4H, Ar), 8.29(s, 1H, N=CH)
6	1.24(s, 6H, $2CH_3$), 1.27(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 7.89～8.24 (dd, 4H, Ar), 8.40(s, 1H, N=CH)

To be continued

Continued

Compound No.	^{1}H NMR (δ, $CDCl_3$)
7	1.21(s, 6H, $2CH_3$), 1.24(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 3.00(s, 6H, $2CH_3$), 6.65～7.60(dd, 4H, Ar), 8.22(s, 1H, N=CH)
8	1.13～1.30(m, 19H, $6CH_3$, cyclopropane-H), 3.36(bq, 4H, $2CH_2$), 6.63～7.57(dd, 4H, Ar), 8.19(s, 1H, N=CH)
9	1.24(s, 6H, $2CH_3$), 1.27(s, 1H, cyclopropane-H), 1.29(s, 6H, $2CH_3$), 3.82(s, 3H, CH_3), 6.87～7.67(dd, 4H, Ar), 8.27(s, 1H, N=CH)
10	1.21(s, 6H, $2CH_3$), 1.24(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 1.41(t, 3H, CH_3), 4.06(q, 2H, CH_2), 6.86～7.66(dd, 4H, Ar), 8.27(s, 1H, N=CH)
11	1.21～1.34(m, 19H, $6CH_3$, cyclopropane-H), 4.62(q, 1H, OCH), 6.84～7.66(dd, 4H, Ar), 8.25(s, 1H, N=CH)
12	1.21(s, 6H, $2CH_3$), 1.24(s, 1H, cyclopropane-H), 1.28(s, 6H, $2CH_3$), 7.00～7.36 (m, 9H, 2Ar), 8.28(s, 1H, N=CH)
13	1.21(s, 6H, $2CH_3$), 1.24(s, 1H, cyclopropane-H), 1.29(s, 6H, $2CH_3$), 5.99(s, 2H, OCH_2O), 6.81(d, 1H, Ar), 7.24(d, 1H, Ar), 7.34(s, 1H, Ar), 8.28(s, 1H, N=CH)
14	1.21(s, 6H, $2CH_3$), 1.24(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 5.08(s, 1H, OCH_2), 6.95～7.68(m, 9H, 2Ar), 8.40(s, 1H, N=CH)
15	1.22(s, 6H, $2CH_3$), 1.26(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 2.95(s, 6H, $2CH_3$), 6.80～7.30(m, 4H, Ar), 8.28(s, 1H, N=CH)
16	0.80(s, 1H, NH), 1.22～1.29(m, 13H, $4CH_3$, cyclopropane-H), 3.18(s, 3H, NCH_3), 7.20～7.90(dd, 4H, Ar), 8.25(s, 1H, N=CH)
17	1.21(s, 6H, $2CH_3$), 1.26(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 3.00(s, 6H, $2CH_3$), 6.65(d, 1H, Ar), 6.66 (s, 1H, Ar), 7.95(d, 1H, Ar), 8.22(s, 1H, N=CH)
18	1.22(s, 6H, $2CH_3$), 1.24(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 2.88(s, 6H, $2CH_3$), 7.03～7.74(m, 4H, Ar), 8.21(s, 1H, N=CH)
19	1.22(s, 6H, $2CH_3$), 1.24(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 2.91(s, 6H, $2CH_3$), 7.87(s, 2H, Ar)
20	1.22(s, 6H, $2CH_3$), 1.24(s, 1H, cyclopropane-H), 1.30(s, 6H, $2CH_3$), 2.94(s, 6H, $2CH_3$), 7.82(s, 2H, Ar)
21	1.22～1.34(m, 6H, $2CH_3$), 1.60～2.10(m, 2H, cyclopropane-H), 3.00(s, 6H, $2CH_3$), 5.75(d, trans-1H, CH=C), 6.28(d, cis-1H, CH=C), 6.65(d, 2H, Ar), 7.57(d, 2H, Ar), 8.22(s, 1H, N=CH)
22	1.27～1.32(m, 6H, $2CH_3$), 1.69～2.04(m, 2H, cyclopropane-H), 3.01(s, 6H, $2CH_3$), 6.09(d, trans-1H, CH=C), 6.66(d, cis-1H, CH=C), 6.84(d, 2H, Ar), 7.57(d, 2H, Ar), 8.23(s, 1H, N=CH)
23	1.14～1.70(m, 13H, $4CH_3$, cyclopropane-H), 2.24(m, 1H, cyclopropane-H), 3.01(s, 6H, $2CH_3$), 4.99(d, 1H, CH=C), 6.82～7.67(m, 4H, Ar), 8.24(s, 1H, N=CH)
24	1.07(d, 6H, $2CH_3$), 2.30～2.50(m, 1H, CH), 3.00(s, 6H, $2CH_3$), 3.12(d, 1H, CH), 6.59～7.42(m, 8H, 2Ar), 8.24(s, 1H, N=CH)
25	0.80～1.07(m, 4H, cyclopropane-H), 1.70～1.85(m, 1H, cyclopropane-H), 3.00(s, 6H, $2CH_3$), 6.65～7.60(dd, 4H, Ar), 8.24(s, 1H, N=CH)
26	1.12～1.34(m, 12H, $4CH_3$), 1.73(d, 1H, cyclopropane-H), 2.41(q, 1H, cyclopropane-H), 3.37(q, 4H, $2CH_2$), 5.63 (d, trans-1H, CH=C), 6.30(d, cis-1H, CH=C), 6.68(d, 2H, Ar), 7.54(d, 2H, Ar), 8.21(s, 1H, N=CH)
27	1.13～1.34(m, 12H, $4CH_3$), 1.73(d, 1H, cyclopropane-H), 2.25(q, 1H, cyclopropane-H), 3.38(q, 4H, $2CH_2$), 6.05 (d, trans-1H, CH=C), 6.61(d, cis-1H, CH=C), 6.84(d, 2H, Ar), 7.56(d, 2H, Ar), 8.23(s, 1H, N=CH)
28	1.12～1.69(m, 19H, $6CH_3$, cyclopropane-H), 2.28(m, 1H, cyclopropane-H), 3.38(q, 4H, $2CH_2$), 4.89(d, 1H, CH=C), 6.56-7.40(m, 4H, Ar), 8.21(s, 1H, N=CH)
29	0.84～1.18(m, 13H, $4CH_3$, CH), 2.44(m, 1H, CH), 3.35(q, 4H, $2CH_2$), 6.60～7.53(m, 8H, Ar), 8.15(s, 1H, N=CH)
30	0.89～1.19(m, 10H, $2CH_3$, $2CH_2$), 1.72(m, 1H, cyclopropane-H), 3.36(q, 4H, $2CH_2$), 6.85(d, 2H, Ar), 7.55(d, 2H, Ar), 8.22(s, 1H, N=CH)