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ARTICLE

Synthesis and Insecticidal Activity of Heptafluoroisopropyl-Containing Benzoylphenylurea Structures†

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Fourteen novel heptafluoroisopropyl-containing benzoylphenylureas were designed and synthesized. Their insecticidal activities against armyworm (*Pseudaletia separata* Walker) were examined and compared with the commercial product diflubenzuron. Three compounds (**IIi**, **IIj**, and **IIk**) showed excellent insecticidal effect, and their activity resembled that of diflubenzuron. Compound **IIi** also showed nearly the same insecticidal activity as novaluron on African cotton leafworm (*Spodoptera littoralis*). Furthermore, results from a field trial indicated that 5% EC **IIi** exhibited similar efficacy in comparison with chlorfluazuron and hexaflumuron against imported cabbage worm (*Pieris rapae* L.) and diamondback moth (*Plutella xylostella*), respectively.

KEYWORDS: Benzoylphenylureas; heptafluoroisopropyl; insecticidal activity

INTRODUCTION

Over the past three decades, benzoylphenylureas, an important class of potent insect growth regulators (IGRs) for which the mode of action is the inhibition of chitin formation in the cuticle of insects, have attracted worldwide attention due to their high selectivity, insecticidal activity, and low acute toxicity to mammals (*1*−*3*). Since the first commercial benzoylphenylurea, diflubenzuron, became available in 1973, there have been numerous reports and studies on the synthesis and bioassay of various benzoylphenylureas (*4*, *5*). Previous researchers have focused mainly on the substitutions at both the phenylamino nitrogen and the phenylamino ring (*6*, *7*). Up to now, more than 12 benzoylphenylureas have been launched into the market and used in crop protection such as novaluron, hexaflumuron, chlorfluazuron, and flucycloxuron. The introduction of a fluorine or polyfluorine atoms into organic molecules has become more mainstream, especially in the pharmaceutical and pesticide industries (*8*). Recently, heptafluoroisopropyl compounds are of interest to chemists owing to their unique properties, such as low polarizability, high lipophilicity, and electronegativity (*9*). Flubendiamide, a commercially successful example of the introduction of a heptafluoroisopropyl group to a bioactive compound, is a new class of insecticide with a novel mode of action on insect ryanodine receptors (*10*) (**Figure 1**).

Although benzoylphenylureas exhibit excellent activities against various insects, their lower solubility in polar solvents limits their further development. The solubility of diflubenzuron, flufenoxuron, and chlorfluazuron in acetone is only 6.5, 55, and 74 g/L (20 °C), respectively, whereas the solubility of novaluron, one of the most active chitin synthesis inhibitors developed by Makhteshim-Agan Ltd., can reach 199 g/L (20 °C) (*11*). Recently, Wang et al. have designed and synthesized two series of novel benzoylphenylurea derivatives by the replacement of the hydrogen on the nitrogen atom with carbamylosulfenyl or formate. They found that the target compounds had better solubility than the parent benzoylphenylurea in organic solvents and that the bioactivities against armyworm were good as compared to diflubenzuron (*12*). In our previous paper, our group has also concentrated on improving the solubility of this class of compound by replacing the aryl moiety with new heterocyclic rings (*13*). In this paper, a heptafluoroisopropyl group was introduced into the structure of the benzoylphenylurea by using 2-iodoheptafluopropane as the fluorinating reagent. A total of 14 new benzoylphenylureas containing a heptafluoroisopropyl group were synthesized, and field and laboratory evaluations of the active compound against different insects were performed.

MATERIALS AND METHODS

Instruments and Chemicals. Melting points were measured in an open capillary using a Büchi melting point B540 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 and 100 MHz, respectively) using TMS as internal standard. Gas chromatography (GC) was recorded on a HP 6890 Plus GC instrument, and HRMS data were obtained on a MicroMass GCT CA 055 instrument.

All of the reagents were purchased from commercial sources. Toluene and acetyl acetate were dried according to a standard method prior to use.

General Synthesis. Synthesis procedures for the new chemicals are shown in **Scheme 1**. The key intermediates, heptafluoroisopropyl aniline derivatives, were prepared by modification of the method described in a patent (*14*). Aroyl isocyanates were synthesized from the corresponding aroyl amides according to the method in the literature (*15*). The target

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compounds were obtained by the reaction of heptafluoroisopropyl aniline with benzoyl isocyanates at room temperature in dried ethyl acetate (*16*).

General Procedure for the Synthesis of Heptafluoroisopropyl Aniline Derivatives I. Heptafluoroisopropyl iodide (1.3 mmol), tetrabutylammonium bromide (TBAB, 0.1 mmol), sodium bicarbonate (1.3 mmol), and sodium hydrosulfite (1.3 mmol) were added sequentially to a mixture of the arylamine (1 mmol) in diethyl ether and water. The mixture was stirred at room temperature until TLC monitoring showed that the reaction was complete (typically ca. 8−10 h). The mixture was diluted in water and extracted with ethyl acetate. The organic layer was washed successively with 2 N hydrochloric acid, 5% sodium carbonate, and a saturated salt solution, dried over anhydrous $MgSO_4$, and concentrated in vacuum, and the yellow crude product was purified by column chromatography on silica gel using a petroleum ether/ethyl acetate (4:1) mixture as eluent to afford the pure heptafluoroisopropylaniline.

General Procedure for the Synthesis of Target Compounds IIa−n. A solution of aroyl isocyanate (3 mmol) in 2 mL of dried ethyl acetate was added to a solution of 3 mmol heptafluoroisopropylaniline in 2 mL of dried ethyl acetate. After 5−7 h of stirring at room temperature, the mixture was filtered and washed with a small amount of petroleum ether and dried in a vacuum desiccator to give the desired compound without further purification.

N-(2,6-Difluorobenzoyl)-N′-(4-heptafluoroisopropylphenyl)urea ***IIa****:* yield, 85%; white solid; mp 213.5−215.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (2H, t, J=8.4 Hz, ArH), 7.57 (3H, d, J=8.8 Hz, ArH), 7.66 (2H, d, J = 8.4 Hz, ArH), 8.92 (1H, s, NH), 10.63 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.6, 120.3, 122.4, 126.6, 133.9, 139.4, 150.4, 158.8, 161.4, 162.1. HRMS Calcd for $C_{17}H_9F_9N_2O_2$ (M^+): 444.0520. Found: 444.0520.

N-(2,6-Difluorobenzoyl)-N′-(2-chloro-4-heptafluoroisopropylphenyl)urea ***IIb****:* yield, 80%; white solid; mp 191.2−193.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (2H, t, J=8.8 Hz, ArH), 7.54 (2H, t, J=7.2 Hz, ArH), 7.69 (1H, s, ArH), 8.19 (1H, s, NH), 8.53 (1H, d, J=8.8 Hz, ArH), 11.16 (1H, s, NH); ^{13}C NMR(100 MHz, $CDCl_3$) δ 112.5, 121.7, 123.8, 124.9, 127.4, 129.8, 133.7, 134.4, 150.2, 161.5. HRMS Calcd for $C_{17}H_8F_9Cl\,N_2O_2$ (M^+): 478.0131. Found: 478.0131.

N-(2,6-Difluorobenzoyl)-N′-(3-bromo-4-heptafluoroisopropylphenyl)urea ***IIc****:* yield, 80%; white solid; mp 183.7−185.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (2H, t, J=8.4 Hz, ArH), 7.17 (1H, t, J=8.0 Hz, ArH), 7.26 (1H, t, J=7.2 Hz, ArH), 7.51−7.58 (1H, m, ArH), 7.77 (1H, s, ArH), 9.93 (1H, s, NH), 10.57 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.2, 112.5, 118.8, 120.7, 123.1, 127.6, 130.1, 133.9, 151.1, 158.6, 161.2, 162.5. HRMS Calcd for $C_{17}H_8BrF_9N_2O_2$ (M^+): 521.9625. Found: 521.9625.

N-(2,6-Difluorobenzoyl)-N′-(3-methyl-4-heptafluoroisopropylphenyl)urea ***IId****:* yield, 84%; white solid; mp 180.7−182.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (3H, s, CH_3), 7.04 (2H, t, J=8.0 Hz, ArH), 7.37 (1H, d, J= 8.8 Hz, ArH), 7.45 (1H, s, ArH), 7.49−7.56 (1H, m, ArH), 8.05 (1H, d, J= 8.8 Hz, ArH), 9.64 (1H, s, NH), 10.62 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 112.4, 119.2, 120.9, 121.9, 122.2, 124.1, 127.4, 128.3, 133.5, 138.0, 151.0, 158.7, 161.2, 162.4. HRMS Calcd for $C_{18}H_{11}F_9N_2O_2$ (M^+): 458.0677. Found: 458.0677.

N-(2,6-Difluorobenzoyl)-N′-(2-heptafluoroisopropyl-4-methylphenyl)urea ***IIe****:* yield, 81%; white solid; mp 177.6−178.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (3H, s, CH_3), 7.01 (2H, t, J=8.4 Hz, ArH), 7.32 (2H, t, J= 8.4 Hz, ArH), 7.45−7.52 (1H, m, ArH), 7.75 (1H, s, ArH), 9.02 (1H, s, NH), 10.60 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 112.2, 112.3, 127.4, 132.5, 151.4, 158.7, 161.2, 161.8. HRMS Calcd for $C_{18}H_{11}F_9N_2O_2$ (M^+): 458.0678. Found: 458.0677.

N-(2,6-Difluorobenzoyl)-N′-(2-heptafluoroisopropyl-4-methoxylphenyl)-urea ***IIf****:* yield, 85%; white solid; mp 173.9−175.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (3H, s, OCH_3), 6.96−7.03 (3H, m, ArH), 7.09 (1H, s, ArH), 7.42−7.49 (1H, m, ArH), 7.66 (1H, s, ArH), 9.32 (1H, s, NH), 10.44 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 112.1, 112.3, 116.4, 121.9, 133.2, 151.8, 158.7, 161.2, 161.9. HRMS Calcd for $C_{18}H_{11}F_9N_2O_3$ (M^+) 474.0612. Found: 474.0626.

N-(2,6-Difluorobenzoyl)-N′-(3-chloro-4-heptafluoroisopropylphenyl)urea ***IIg****:* yield, 75%; white solid; mp 197.9−199.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (2H, t, J = 8.4 Hz, ArH), 7.43 (1H, d, J = 8.8 Hz, ArH), 7.52−7.59 (2H, m, ArH), 7.82 (1H, s, ArH), 9.31 (1H, s, NH), 10.72 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.8, 112.6, 118.0, 123.9, 134.1, 140.0, 150.7, 158.7, 161.3, 162.4. HRMS Calcd for $C_{17}H_8F_9Cl\,N_2O_2$ (M^+): 478.0131. Found: 478.0131.

N-(2,6-Difluorobenzoyl)-N′-(2-heptafluoroisopropyl-4-bromophenyl)urea ***IIh****:* yield, 79%; white solid; mp 161.7−163.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98−7.03 (2H, m, ArH), 7.46−7.58 (1H, m, ArH), 7.60 (2H, d, J = 8.0 Hz, ArH), 7.83 (1H, s, ArH), 9.41 (1H, s, NH), 10.80 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.9, 112.3, 118.8, 119.1, 121.7, 122.0, 130.0, 133.4, 133.7, 134.6, 151.3, 158.7, 161.2, 161.9. HRMS Calcd for $C_{17}H_8\,BrF_9N_2O_2$ (M^+): 521.9625. Found: 521.9625.

N-(2,6-Difluorobenzoyl)-N′-(2,6-dimethyl-4-heptafluoroisopropylphenyl)-urea ***IIi****:* yield, 95%; white solid; mp 203.6−206.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (6H, s, CH_3), 7.20 (3H, t, J=8.4 Hz, ArH), 7.34 (2H, s, ArH), 8.78 (1H, s, NH), 9.85 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8, 111.9, 112.6, 125.4, 133.7, 135.7, 136.4, 150.5, 158.8, 161.4, 162.0. HRMS Calcd for $C_{19}H_{13}F_9N_2O_2$(M^+): 472.0832. Found: 472.0833.

N-(2,6-Difluorobenzoyl)-N′-(2-fluoro-4-heptafluoroisopropylphenyl)urea ***IIj****:* yield, 85%; white solid; mp 199.8−202.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (2H, t, J=8.8 Hz, ArH), 7.35 (1H, d, J=8.8 Hz, ArH), 7.42 (1H, d, J=11.2 Hz, ArH), 7.55 (1H, s, ArH), 8.29 (1H, s, ArH), 9.11(1H, s, NH), 10.91(1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.6, 112.7, 113.2, 121.7, 122.1, 128.4, 133.9, 134.0, 151.1, 153.5, 158.9, 161.4, 161.9; MS (EI, 70 ev) m/z (%) = 462 (M^+, 30), 141 (100).

N-(2,6-Difluorobenzoyl)-N′-(2,6-difluoro-4-heptafluoroisopropylphenyl)-urea ***IIk****:* yield, 80%; white solid; mp: 197.3−198.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (2H, t, J=8.8 Hz, ArH), 7.27 (1H, d, J=8.0 Hz, ArH), 7.36 (1H, d, J=5.2 Hz, ArH), 7.47−7.52 (1H, m, ArH), 9.20(1H, s, NH), 10.05 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.1, 111.7, 112.6, 115.9, 116.2, 128.5, 133.8, 134.0, 150.4, 156.4, 158.9, 161.4, 162.1. HRMS Calcd for $C_{17}H_7F_{11}N_2O_2$ (M^+): 480.0332. Found: 480.0332.

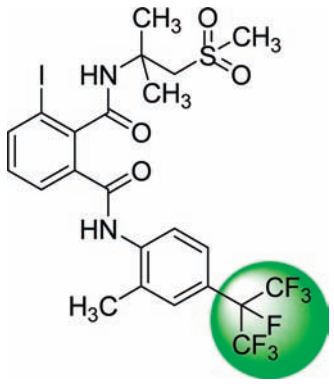


Figure 1. Structure of flubendiamide.

Scheme 1. General Synthetic Route for the Target Compounds

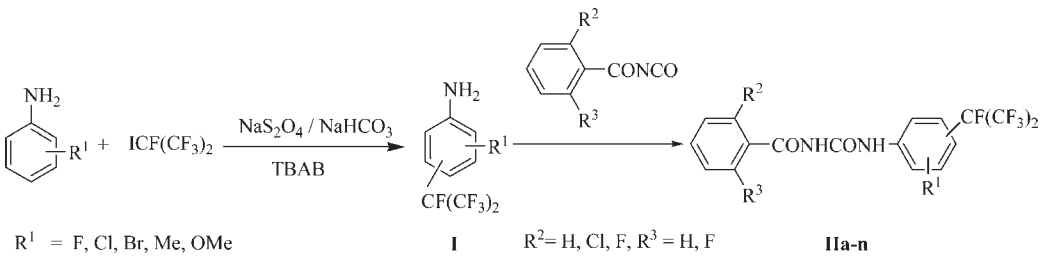
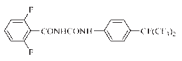
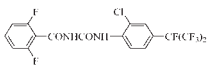
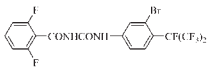
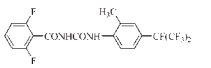
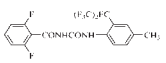
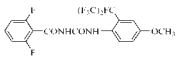
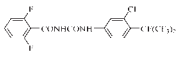
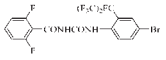
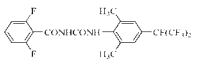
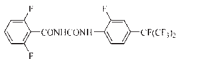
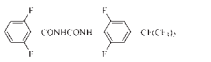
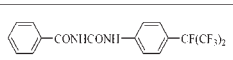
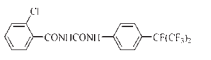
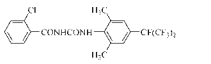
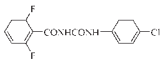


Table 1. Larvicidal Activity against Oriental Armyworm of Compounds **IIa**−**n** and Diflubenzuron

Compd.	Structure	Concentration (mg/L)	Larvicidal activity (%)
IIa		31.25	100
		15.625	43.3
IIb		31.25	100
		15.625	20
IIc		31.25	100
		15.625	46.6
IId		31.25	100
		15.625	56.6
IIe		62.5	100
		31.25	93.3
IIf		62.5	100
		31.25	86.6
IIg		31.25	100
		15.625	86.6
IIh		31.25	100
		15.625	56.6
IIi		0.25	80.0
		0.125	50.0
IIj		0.25	100
		0.125	63.3
IIk		0.25	100
		0.125	62.7
III		12.5	100
		10	68.1
IIm		10	100
		5	66.9
IIn		50	100
		10	69.1
diflubenzuron		0.25	100
		0.125	69.5

N-Benzoyl-N′-(4-heptafluoroisopropylphenyl)urea ***III****:* yield, 90%; white solid; mp 221.7−223.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.61 (4H, m, ArH), 7.68 (1H, t, J = 7.2 Hz, ArH), 7.74 (2H, d, J = 8.4 Hz, ArH), 8.01 (2H, d, J = 7.2 Hz, ArH), 9.42 (1H, s, NH), 11.14 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.4, 122.3, 126.6, 127.8, 129.0, 131.8, 133.7, 139.8, 151.6, 168.5. HRMS Calcd for $C_{17}H_{11}F_7N_2O_2$ (M^+): 408.0703. Found: 408.0709.

N-(2-Chlorobenzoyl)-N′-(4-heptafluoroisopropylphenyl)urea ***IIm****:* yield, 85%; white solid; mp 202.3−204.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.43 (1H, m, ArH), 7.52 (2H, t, J = 2.0 Hz, ArH), 7.55 (2H, s, ArH), 7.66 (2H, s, ArH), 7.73 (1H, t, J = 2.4 Hz, ArH), 9.33 (1H, s, NH), 10.78 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.2, 122.1, 126.5, 127.3, 130.0, 131.3, 132.9, 139.6, 150.8, 167.9; MS (EI, 70 ev) m/z (%) 442 (M^+, 5), 139 (100).

N-(2-Chlorobenzoyl)-N′-(2,6-dimethyl-4-heptafluoroisopropylphenyl)-urea ***IIn****:* yield, 85%; white solid; mp 193.5−196.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (6H, s, CH_3), 7.34 (3H, s, ArH), 7.44 (2H, t, J = 2.4 Hz, ArH), 7.71 (1H, d, J = 7.2 Hz, ArH), 9.37 (1H, s, NH), 10.02 (1H, s, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 125.2, 125.4, 127.2, 130.1, 131.3, 132.6,135.8,136.3, 151.1, 168.0; MS (EI, 70 ev) m/z (%) 470 (M^+, 20), 315(100).

Biological Assay. *Larvicidal Activity against Armyworm* (*Pseudaletia separata Walker*). The larvicidal activities of the title compounds (**IIa**−**n**) against armyworm were evaluated according to the literature procedures (*17*). In leaf-dip bioassay, corn disks were dipped in insecticide solutions for 5 s and air-dried on filter paper; leaf disks dipped in water were used as controls. The dried leaf disks were then placed on a bed of agar in a small Petri dish (7 cm in diameter). Ten second-instar armyworm larvae were placed onto each treated leaf disk. Each Petri dish was then sealed with a ventilated lid and stored upside down. Mortality was assessed 7 days later. If necessary, mortality rates were corrected using Abbott's formula (*18*). To compare their activities, the commercial product diflubenzuron was tested under the same conditions. The tested concentrations of synthesized compounds against armyworm are in the range from 0.1 to 50 mg/L. The larvicidal activity of **IIa**−**n** against armyworm is summarized in **Table 1**.

Larvicidal Activity against African Cotton Leafworm (*Spodoptera littoralis*). The larvicidal activities of one of the target compounds **IIi** and **III** (*N*-(2-chlorobenzoyl)-*N′*- (2,6-dimethylphenyl)-urea) against African cotton leafworm were also evaluated. Castor bean leaves treated with 0.25 or 0.5 mg of ai/L of each of the test formulations were exposed to third instars of *S. littoralis* (11 ± 1 mg) for 4 days of feeding; the larvae were exposed for an additional 4 days on untreated leaves. Larval mortality was determined at days 4 and 8. Larval weight gain (LWG) was determined at day 4. Average LWG in the untreated control was 111 ± 7 mg. The larvicidal activities of **IIi**, **III**, and novaluron against *S. littoralis* are listed in **Table 2**.

Table 2. Effect of **IIi** and **III** As Compared with the EC Novaluron Formulation on Third Instars of *Spodoptera littoralis*[a]

formulation and concn (mg of ai/L)	no. of L_3	larval mortality (% ± SEM) at 4 days	larval mortality (% ± SEM) at 8 days	LWG relative to control
0 (control)	50	6 ± 2a	10 ± 4a	100a
novaluron, 10 EC, 0.5	50	6 ± 2a	78 ± 12c	44 ± 6b
III, 0.25	50	8 ± 6ab	14 ± 5a	69 ± 11ab
III, 0.5	50	18 ± 7ab	22 ± 7ab	94 ± 10a
IIi, 0.25	50	8 ± 4ab	36 ± 12b	45 ± 9b
IIi, 0.5	50	18 ± 5b	78 ± 13c	31 ± 10b

[a] Data are averages ± SEM of four to five replicates of 10 larvae each. Within columns, means followed by the same letter do not differ significantly at $P = 0.05$.

RESULTS AND DISCUSSION

Synthesis. In the course of the preparation of heptafluoroisopropyl aniline derivatives, we found that the ratio of the starting materials, reaction temperature, and substituted groups on the aniline played important roles in determining yield and reaction time. The optimized conditions for the synthesis of heptafluoroisopropyl anilines were as follows. The molar ratio of the reactants (aromatic amines/heptafluoroisopropyl iodide/sodium bicarbonate/sodium hydrosulfite/TBAB) was 1:1.1−1.5:1.1−1.3:0.05−0.1; the range of reaction temperature was 10−20 °C. In addition, the substituted group on the benzene ring of aromatic amines had a great impact on the yields of reaction. The electron-donating substituents were more favorable for the reaction, and an excellent yield was obtained. However, aromatic amines containing electron-withdrawing groups yielded only 15−30% of the desired products with prolonged reaction time.

Generally, toluene is the most commonly used solvent for the synthesis of benzoylphenylureas. Other frequently used solvents are benzene, chloroform, dichloromethane, and tetrahydrofuran (*19*). Due to the low solubility of 2,6-difluorobenzoyl isocyanate in toluene, diethyl ether, and dichloromethane, when they were used as reaction solvents, it resulted in the crude product containing a minute quantity of unreacted 2,6-difluorobenzoyl isocyanate, and expensive, tedious, and time-consuming column chromatography was required. Considering the difference in solubility between 2,6-difluorobenzoyl isocyanate and product in the above-mentioned solvents, in this paper, we used dried ethyl acetate or acetone as both reaction and recrystallization solvent. As a result, the workup procedure became very simple, the solid products could be separated by filtration, washed with water and ethyl acetate or acetone, and vacuum-dried at room temperature. Recrystallization from ethyl acetate or acetone gave pure product. Compared with toluene as a solvent, the merits of ethyl acetate or acetone were low toxicity, high yields, simple workup, and cheap cost.

Bioassay. Laboratory bioassay tests indicated that most of the target compounds exhibited considerable larvicidal activities against armyworm (**Table 1**). We examined the effect of substituent groups attached to the benzene ring on the biological activity. Similar to the literature, the basic 2,6-difluoro configuration in the benzoylurea moiety is critical to the activity (*20*); for example, compound **IIi** is more active than compound **IIn**. It is found that exchanging the heptafluoroisopropyl-containing phenylamino ring in benzoylphenylurea with various substituent groups can retain the insecticidal activity irrespective of electronic effects (electron-donating or -withdrawing substituents). Among the 14 compounds, **IIi**, **IIj**, and **IIk** are the most active compounds (**Table 1**). Their larvicidal activities against armyworm at 0.125 mg/L are 50, 63, and 63%, respectively, which is almost as active as diflubenzuron (69.5% at the same concentration). Compound **III**, *N*-(2-chlorobenzoyl)-*N*′-(2,6-dimethylphenyl)-urea, exhibited weaker activity compared to the corresponding heptafluoroisopropyl-containing benzoylphenylurea (**IIi**). This indicated that the introduction of heptafluoroisopropyl to benzene is favorable to the activity.

Larval mortalities of compounds **IIi** and **III** and novaluron against *S. littoralis* are listed in **Table 2**. Results show that **IIi** resembles in its toxicity that of the novaluron (Rimon EC) formulation. At a concentration of 0.5 mg of ai, both **IIi** and Rimon EC formulation resulted in a similar mortality and larval weight gain inhibition. On the other hand, **III** at a concentration of 0.5 mg of ai/L has only slight effect on larval mortality. It should be mentioned that the formulations of the new **IIi** and **III** have been made in our laboratory.

IIi and **III** formulations have no effect on *Bemisia tabaci* nymphs, resulting in a similar percentage of pupation as in the untreated control, which indicates that **IIi** and **III** have no appreciable effect by contact. On the other hand, novaluron resulted at 0.3 mg of ai/L in a strong suppression of pupation.

In addition, field evaluations of compound **IIi** against diamondback moth *Plutella xylostella* (L.), imported cabbage worm *Pieris rapae* (L.), and rice leaf roller *Cnaphalocrocis medinalis* Guenee were performed. The results in field experiments indicated that 5% **IIi** EC at 37.5 g of ai/ha exhibited excellent control against diamondback moth before third-instar larvae, and the control efficacy reached >92% after 7 days of trial, which was almost equivalent to the contrasting insecticide, 5% hexaflumuron EC. The imported cabbage worm was also effectively controlled by 5% **IIi** EC at 7 days after application of 2000 diluent 5% EC and as good as 5% Atabron (chlorfluazuron) EC. When applied at 25 g of ai/ha in field plot trials, the efficacy of 5% **IIi** EC was slightly inferior to 5% EC Atabron against rice leaf roller before third-instar larvae at 10 days after application.

Conclusions. In summary, a series of novel benzoylphenylureas containing a heptafluoroisopropyl group were designed and synthesized. These new benzoylphenylureas were soluble in most organic solvents; for example, the solubility of compound **IIi** in acetone is around 120 g/L at 25 °C, better than that of the corresponding parent compounds diflubenzuron. The larvicidal activities against armyworm of these new benzoylphenyureas were evaluated. The bioassay results showed that most compounds exhibited considerable larvicidal activities against armyworm, and some of them are good as compared to diflubenzuron. Particularly, compound **IIi** and novaluron displayed similar larvicidal activities against *S. littoralis*. Furthermore, results from field trials indicated that 5% EC **IIi** exhibited similar efficacy comparable with that of hexaflumuron against diamondback moth and similar efficacy to that of reference chlorfluazuron against imported cabbage worm.

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