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Synthesis, Crystal Structure, and Biological Activities of 2-Cyanoacrylates Containing Furan or Tetrahydrofuran Moieties

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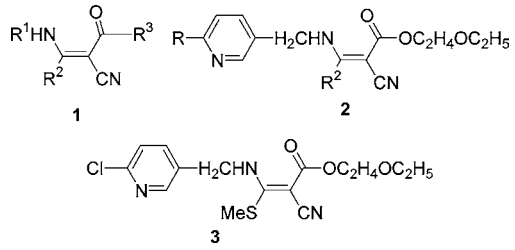
A series of novel cyanoacrylates containing furan or tetrahydrofuran moieties were synthesized, and their structures were characterized by ^{1}H NMR, elemental analysis, and single-crystal X-ray diffraction analysis. The herbicidal, plant growth regulatory, fungicidal, and antiviral activities of these cyanoacrylates were evaluated. The results of herbicidal activities showed that most of these cyanoacrylates exhibited higher herbicidal activities against dicotyledonous weeds than monocotyledonous weeds, and the compounds containing the tetrahydrofuran moiety gave higher herbicidal activities than corresponding furan analogues; (*Z*)-ethoxyethyl 2-cyano-3-isopropyl-3-(tetrahydrofuran-3-yl)methaneaminoacrylate showed excellent herbicidal activities against amaranth pigweed in postemergence treatment at a dose of 375 g/ha. At the same time, these cyanoacrylates had interesting plant growth regulatory activities, and some compounds stimulated radicle growth of cucumber, whereas some compounds had an inhibitory effect. These cyanoacrylates showed fungicidal activities as well.

KEYWORDS: Cyanoacrylates; furan; tetrahydrofuran; herbicidal activity; plant growth regulatory activity; fungicidal activity

INTRODUCTION

The herbicidal activity of cyanoacrylates **1** has attracted considerable attention for decades (*1*−*6*). These compounds are inhibitors of photosystem II (PSII) electron transport, and they inhibit the growth of weeds by disrupting photosynthetic electron transport at a common binding domain on the 32 kDa polypeptide (D1 protein) of the PSII reaction center. In recent years, we have been focusing on modifying the R^1 group and its effects on the herbicidal activity (*7*−*10*). Among these cyanoacrylates, cyanoacrylates **2** containing pyridyl exhibit high herbicidal activities, of which compound **3** has excellent herbicidal activity (*8*).



Bioisosterism is an effective way to optimize bioactive compounds (*11*). The development of neonicotinoids represents a successful example of bioisosterism. Neonicotinoids are a promising class of insecticides with excellent chemical and biological properties. The first successful member of this family is imidacloprid **4**, developed by Nihon Bayer Agrochem KK in 1991 (*12*). As a subclass chloronicotinyl compounds, nitenpyram **5** from Takada Chemical Industries (*13*), acetamiprid **6** from Nippon Soda (*14*), and thiacloprid **7** from Bayer CropScience (*15*) were brought to the market in 1995, 1996, and 2000, respectively. In the development of a novel insecticide, 2-chloro-5-thiazolyl compound **8**, named thiamethoxam, was developed by Novartis Crops Protection in 1998 (*16*, *17*). Another, clothianidin **9**, was introduced to the market by Bayer CropScience in 2002 (*18*). Dinotefuran **10** with a tetrahydro-3-furylmethyl group instead of an aromatic heterocyclic ring was developed by Mitsui Chemicals and was first registered in Japan in 2002 (*19*, *20*). 2-Chloro-5-thiazole and tetrahydro-3-furan are bioisosteric analogues of 2-chloro-5-pyridine. Encouraged by these reports, we developed an idea that the replacement of 2-chloro-5-pyridyl unit with 2-chlorothiazoyl or tetrahydro-3-furfuryl in **2** could improve their herbicidal activities.

In previous work, we have reported the syntheses of cyanoacrylates containing the 2-chloro-5-thiazoyl group and their excellent herbicidal activities (*9*). Herein, we report the synthesis of a series of novel cyanoacrylates containing furan or tetrahydrofuran moieties and their evaluation for herbicidal activities. Because cyanoacrylates have been shown to be important scaffolds with broad spectrum biological activities (*21*−*25*), these title compounds were also subjected to fungicidal, plant growth regularity, and antiviral assays.

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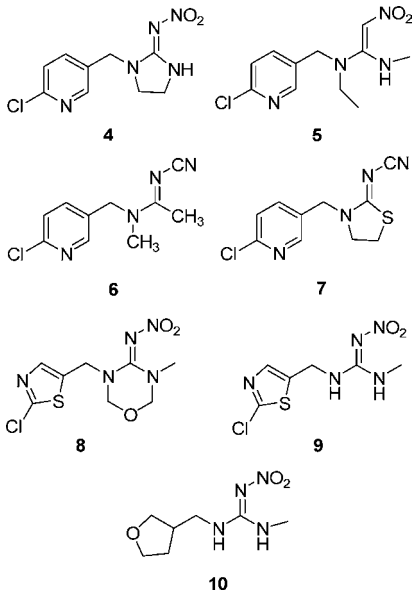
MATERIALS AND METHODS

Synthetic Procedures. The melting points of the products were determined on an X-4 binocular microscope (Beijing Tech Instrument Co., Beijing, China) and were not corrected. Proton NMR spectra were obtained at 300 MHz using a Bruker AC-P 300 spectrometer. Chemical shift values (δ) are given in ppm and were downfield from internal tetramethylsilane. Elemental analyses were determined on a Yanaca CHN Corder MT-3 elemental analyzer. The reagents were all analytically or chemically pure. All solvents and liquid reagents were dried in advance and distilled before use. 2-Cyano-3,3-(dimethylthio)acrylate **19a** and 2-cyano-3-alkyloxy-3-alkylacrylates **19b**−**e** were prepared according to the published procedure (*8*, *9*). (±)-(Tetrahydrofuran-2-yl)methanamine (**18**) was purchased from Acros.



Synthesis of Furan-2-ylmethanamine (12). To a mixture of furfural (9.61 g, 0.10 mol) and hydroxylamine hydrochloride (8.69 g, 0.13 mol) in water (15 mL) was added dropwise sodium carbonate (6.63 g, 0.05 mol) in water (25 mL). Then, the mixture was heated to reflux for 1 h. After the mixture was cooled and filtered, 2-furfural oxime **11** was collected as a solid. The mother liquid was extracted by dichloromethane, and the extract was dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated to give another crop of compound **11**. Compound **11** was obtained (10.97 g, 98.8% yield), mp: 78−80 °C, which was used without further purification.

To a mixture of compound **11** (2.22 g, 20 mmol) and Raney Ni (1 g) in ethanol (20 mL), hydrogen was bubbled for 12 h. Then, the mixture was filtered and the solid was washed with ethanol (5 mL × 2). The filtrate was combined and dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to give furan-2-ylmethanamine (**12**) (27.5 g) as an oil in 60.0% yield, which was used in the next procedure without further purification.

Synthesis of 2,2,2-Trichloro-1-(4,5-dihydrofuran-3-yl)ethanone (13). A mixture of 2,3-dihydrofuran (2.10 g, 30 mmol) and pyridine (2.77 g, 35 mmol) in *n*-hexane (50 mL) was cooled to −15 °C. To the mixture, trichloroacetyl chloride (5.41 g, 30 mmol) in *n*-hexane (10 mL) was dropwise added and the mixture was stirred for 4 h at room temperature. Hydrochloric acid (10%, 25 mL) was then added to the mixture. The organic layer was washed successively with hydrochloric acid (10%, 50 mL), sodium carbonate (10%, 40 mL × 2), and water (40 mL). Then, the organic layer was dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated under reduced pressure to afford 2,2,2-trichloro-1-(4,5-dihydrofuran-3-yl)ethanone (**13**) as an orange oil (5.3 g, 82.1%); bp 90 °C/6 mm Hg. ^{1}H NMR ($CDCl_3$): δ 3.05 (t, $^3J_{HH}$ = 10 Hz, 2H), 4.66 (t, $^3J_{HH}$ = 10 Hz, 2H), 7.85 (s, 1H).

Synthesis of 2,2,2-Trichloro-1-(furan-3-yl)ethanone (14). A mixture of compound **13** (21.6 g, 0.1 mol), N-bromosuccinimide (17.8 g, 0.1 mol), and a catalytic amount of AIBN (0.49 g) in carbon tetrachloride (150 mL) was heated to reflux for 2 h. Then, the mixture was cooled and filtered, and the filtrate was washed with water (20 mL × 2). The organic layer was dried over anhydrous magnesium sulfate, filtered, and condensed under reduced pressure to give 2,2,2-trichloro-1-(furan-3-yl)ethanone (**14**) (27.5 g) in 100% yield as a brown oil, which was used without further purification. ^{1}H NMR ($CDCl_3$): δ 6.96 (s, 1H), 7.50 (s, 1H), 8.36 (s, 1H).

Synthesis of Furan-3-carboxamide (15). The reaction of compound **14** (0.95 g, 4.45 mmol) and ammonia (5 mL) was carried out in a sealed tube at 80 °C for 8 h. Then, the mixture was diluted with water and continuously extracted by dichloromethane for 4 h. The organic layer was dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure to give furan-3-carboxamide (**15**) as a solid (0.46 g, 93.0%); mp 175−176 °C. ^{1}H NMR ($CDCl_3$): δ 6.81 (s, 1H), 7.15 (s, 1H, NH), 7.62 (s, 1H, NH), 7.69 (s, 1H), 8.15 (s, 1H).

Synthesis of Furan-3-ylmethanamine (16). Under a nitrogen atmosphere, compound **15** was added in single portion to a mixture of lithium aluminum tetrahydride (0.41 g) in dry ether (50 mL), and the mixture was heated to reflux for 6 h. Then, water (2 mL) was dropwise added and 25% aqueous potassium hydroxide solution was then added dropwise until the solid in the mixture was dissolved. Then, the mixture was extracted by dichloromethane and the organic layer was dried over anhydrous magnesium sulfate. After the mixture was filtered, the filtrate was concentrated under reduced pressure to give furan-3-ylmethanamine (**16**) as a yellow oil (0.2 g, 69.4%), which was used without further purification. ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 2H, NH_2), 3.60 (s, 2H, CH_2), 6.27 (s, 1H), 7.24 (s, 1H), 7.27 (s, 1H).

Synthesis of (±)-(Tetrahydrofuran-3-yl)methanamine (17). Compound **16** (0.5 g, 5.1 mmol) and 5% Pd/C (0.2 g) in ethanol (10 mL) were hydrogenated at 100 atm and room temperature for 40 h. Then, the mixture was filtered and the solid was washed by ethanol (5 mL × 4). The filtrate was concentrated under reduced pressure to give (±)-(tetrahydrofuran-3-yl)methanamine (**17**) in 77.5% yield as a yellow oil .^{1}H NMR ($CDCl_3$): δ 1.53−1.64 (m, 2H), 1.99−2.10 (m, 1H), 2.23−2.37 (m, 1H), 2.71−2.73 (m, 1H), 3.48−3.53 (m, 1H), 3.71−3.79 (m, 1H), 3.83−3.91 (m, 2H), 4.83 (s, 2H).

General Synthetic Procedures for Target Compounds 20a−e, 21a−e, 22a−e, and 23a−e. A mixture of intermediate **19** (5 mmol) and **18** (or **12**, **16**, or **17**; 6 mmol) and ethanol (12 mL) was refluxed for 1−3 h and then evaporated under reduced pressure to give crude product. The product was purified by vacuum column chromatography on a silica gel.

Data for 20a. Yield, 90.1%; mp 67−69 °C. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.52−1.63 (m, 1H, THF), 1.88−2.10 (m, 3H), 2.66 (s, 3H, SCH_3), 3.54−3.64 (m, 3H), 3.70 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 3.75−3.84 (m, 2H, THF), 3.88−3.95 (m, 1H, THF), 4.02−4.10 (m, 1H, THF), 4.30 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 10.21 (s, 1H, NH). Anal. calcd for $C_{14}H_{22}N_2O_4S$: C, 53.48; H, 7.05; N, 8.91. Found: C, 53.44; H, 7.01; N, 8.95.

Data for 20b. Yield, 91.5%; mp 33−35 °C. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.53−1.65 (m, 1H, THF), 1.87−2.11 (m, 3H), 2.30 (s, 3H, CH_3), 3.29−3.37 (1H, THF), 3.48−3.61 (m, 3H), 3.69 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 3.76−3.83 (m, 1H, THF), 3.88−3.95 (m, 1H, THF), 4.01−4.10 (m, 1H, THF), 4.29 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 10.10 (s, 1H, NH). Anal. calcd for $C_{14}H_{22}N_2O_4$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.32; H, 7.80; N, 9.92.

Data for 20c. Yield, 76.3%; mp 34−36 °C. ^{1}H NMR ($CDCl_3$): δ 1.19−1.27 (m, 6H), 1.54−1.66 (m, 1H, THF), 1.90−2.11 (m, 3H), 2.62 (q, $^3J_{HH}$ = 8 Hz, 2H, CH_2), 3.30−3.39 (m, 1H, THF), 3.49−3.61 (m, 3H), 3.69 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 3.77−3.8 (m, 1H, THF), 3.89−3.97 (m, 1H, THF), 4.02−4.10 (m, 1H, THF), 4.27 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 10.07 (s, 1H, NH). Anal. calcd for $C_{15}H_{24}N_2O_4$: C, 60.79; H, 8.16; N, 9.45. Found: C, 60.81; H, 8.06; N, 9.35.

Data for 20d. Yield, 90.3%; mp 42−44 °C. ^{1}H NMR ($CDCl_3$): δ 1.06 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.19 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.53−1.69 (d, 4H), 1.94 (m, 2H, CH_2), 2.01−2.08 (m, 1H, THF), 2.54−2.59 (m, 2H), 3.29−3.36 (m, 1H), 3.47−3.53 (m, 1H, THF), 3.57 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 3.68 (t, $^3J_{HH}$ = 5 Hz, 2H), 3.77−3.83 (m, 1H, THF), 3.89−3.95 (m, 1H, THF), 4.02−4.08 (m, 1H, THF), 4.28

(t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 10.08 (s, 1H, NH). Anal. calcd for $C_{16}H_{26}N_2O_4$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.98; H, 8.36; N, 8.96.

Data for 20e. Yield, 80.6%; mp 46−47 °C. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.40 [d, 6H, $C(CH_3)_3$], 1.55−1.66 (m, 1H, THF), 1.90−2.11 (m, 3H), 3.17−3.26 (m, 1H), 3.37−3.35 (m, 1H, THF), 3.54−3.62 (m, 3H), 3.69 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 3.78−3.86 (m, 1H, THF), 3.90−3.97 (m, 1H, THF), 4.02−4.10 (m, 1H, THF), 4.29 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 10.43 (s, 1H, NH). Anal. calcd for $C_{16}H_{26}N_2O_4$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.89; H, 8.30; N, 8.95.

Data for 21a. Yield, 94.0%; mp 40−42 °C. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 2.67 (s, 3H, SCH_3), 3.57 (q, $^3J_{HH}$ = 7 Hz, 2H, OCH_2), 3.69 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 4.29 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 4.78 (d, $^3J_{HH}$ = 6 Hz, 2H, CH_2NH), 6.28−6.29 (m, 1H, furan), 6.34−6.36 (m, 1H, furan), 7.40 (m, 1H, furan), 10.24 (m, 1H, NH). Anal. calcd for $C_{14}H_{18}N_2O_4S$: C, 54.18; H, 5.85; N, 9.03. Found: 54.12; H, 5.90; N, 8.97.

Data for 21b. Yield, 76.8%; yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.20 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.57 (q, $^3J_{HH}$ = 7 Hz, 2H, OCH_2), 3.68 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 4.28 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 4.39 (d, $^3J_{HH}$ = 6 Hz, 2H, CH_2NH), 6.37 (s, 1H, furan), 7.41 (s, 1H, furan), 7.45 (s, 1H, furan), 10.15 (m, 1H, NH). Anal. calcd for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: 60.38; H, 6.55; N, 10.02.

Data for 21c. Yield, 72.0%; yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.20 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.29 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 2.71 (q, $^3J_{HH}$ = 7 Hz, 2H, CH_2), 3.56 (q, $^3J_{HH}$ = 7 Hz, 2H, OCH_2), 3.68 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 4.28 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 4.53 (d, $^3J_{HH}$ = 6 Hz, 2H, CH_2NH), 6.28−6.29 (m, 1H, furan), 6.35−6.36 (m, 1H, furan), 7.41 (m, 1H, furan), 10.09 (m, 1H, NH). Anal. calcd for $C_{15}H_{20}N_2O_4$: C, 61.63; H, 6.90; N, 9.58. Found: C, 61.58; H, 6.90; N, 9.66.

Data for 21d. Yield, 75.4%; yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.09 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.20 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.63−1.76 (m, 2H, CH_2), 2.65 (t, $^3J_{HH}$ = 7 Hz, 2H, CH_2), 3.56 (q, $^3J_{HH}$ = 7 Hz, 2H, OCH_2), 3.68 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 4.27 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 4.51 (d, $^3J_{HH}$ = 6 Hz, 2H, CH_2NH), 6.27−6.28 (m, 1H, furan), 6.35−6.36 (m, 1H, furan), 7.41 (m, 1H, furan), 10.12 (m, 1H, NH). Anal. calcd for $C_{16}H_{22}N_2O_4$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.70; H, 7.28; N, 9.11.

Data for 21e. Yield, 78.3%; mp 27−29 °C. ^{1}H NMR ($CDCl_3$): δ 1.20 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.42 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3, CH_3), 3.57 (q, $^3J_{HH}$ = 7 Hz, 2H, OCH_2), 3.69 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 4.28 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 4.57 (d, $^3J_{HH}$ = 6 Hz, 2H, CH_2-NH), 6.27−6.28 (m, 1H, furan), 6.35−6.37 (m, 1H, furan), 7.41 (m, 1H, furan), 10.42 (m, 1H, NH). Anal. calcd for $C_{16}H_{22}N_2O_4$: C, 62.73; H, 7.24; N, 9.14. Found: C, 61.79; H, 7.19; N, 9.21.

Data for 22a. Yield, 90.8%; yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.58−1.69 (m, 1H, THF), 2.05−2.18 (m, 1H, THF), 2.46−2.60 (m, 1H, THF), 2.69 (s, 3H, SCH_3), 3.54−3.63 (m, 5H), 3.70 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 3.76−3.96 (m, 3H, THF), 4.30 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 10.13 (s, 1H, NH). Anal. calcd for $C_{14}H_{22}N_2O_4S$: C, 53.48; H, 7.05; N, 8.91. Found: C, 53.38; H, 6.98; N, 9.12.

Data for 22b. Yield, 83.9%; mp 26−28 °C. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.58−1.69 (m, 1H, THF), 2.10−2.21 (m, 1H, THF), 2.29 (s, 3H, CH_3), 2.49−2.59 (1H, THF), 3.28−3.41 (m, 2H, THF), 3.54−3.61 (m, 3H), 3.69 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 3.76−3.87 (m, 2H, THF), 3.90−3.97 (m, 1H, THF), 4.29 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 10.00 (s, 1H, NH). Anal. calcd for $C_{14}H_{22}N_2O_4$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.74; H, 7.71; N, 10.13.

Data for 22c. Yield, 72.0%; mp 35−36 °C. ^{1}H NMR ($CDCl_3$): δ 1.19−1.29 (m, 6H), 1.59−1.72 (m, 1H, THF), 2.10−2.22 (m, 1H, THF), 2.46−2.65 (m, 3H), 3.27−3.43 (m, 2H, THF), 3.54−3.61 (m, 3H), 3.69 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 3.76−3.87 (m, 2H, THF), 3.90−3.97 (m, 1H, THF), 4.28 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 9.94 (s, 1H, NH). Anal. calcd for $C_{15}H_{24}N_2O_4$: C, 60.79; H, 8.16; N, 9.45. Found: C, 60.93; H, 8.17; N, 9.54.

Data for 22d. Yield, 70.2%; mp 43−45 °C. ^{1}H NMR ($CDCl_3$): δ 1.08 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.21 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.59−1.73 (m, 3H), 2.10−2.21 (m, 1H, THF), 2.45−2.58 (m, 3H), 3.29−3.42 (m, 2H, THF), 3.53−3.61 (m, 3H), 3.69 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 3.76−3.87 (m, 2H, THF), 3.90−3.97 (m, 1H, THF), 4.28 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 9.97 (s, 1H, NH). Anal. calcd for $C_{16}H_{26}N_2O_4$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.81; H, 8.41; N, 9.19.

Data for 22e. Yield, 80.6%; mp 54−56 °C. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.40 [d, 6H, $C(CH_3)_3$], 1.59−1.70 (m, 1H, THF), 2.11−2.22 (m, 3H), 2.45−2.58 (m, 1H, THF), 3.17−3.26 (m, 1H, THF), 3.32−3.49 (m, 2H), 3.53−3.62 (m, 3H), 3.70 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 3.74−3.97 (m, 3H), 4.28 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 10.32 (s, 1H, NH). Anal. calcd for $C_{16}H_{26}N_2O_4$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.93; H, 8.29; N, 9.25.

Data for 23a. Yield, 91.9%; yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.20 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 2.70 (s, 3H, SCH_3), 3.57 (q, $^3J_{HH}$ = 7 Hz, 2H, OCH_2), 3.69 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 4.29 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 4.63 (d, $^3J_{HH}$ = 6 Hz, 2H, CH_2NH), 6.37 (s, 1H, furan), 7.42−7.43 (m, 2H, furan), 10.18 (m, 1H, NH). Anal. calcd for $C_{14}H_{18}N_2O_4S$: C, 54.18; H, 5.85; N, 9.03. Found: C, 53.91; H, 5.98; N, 8.92.

Data for 23b. Yield, 88.6%; yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.20 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.57 (q, $^3J_{HH}$ = 7 Hz, 2H, OCH_2), 3.68 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 4.28 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 4.39 (d, $^3J_{HH}$ = 6 Hz, 2H, CH_2NH), 6.37 (s, 1H, furan), 7.41 (s, 1H, furan), 7.44−7.45 (m, 1H, furan), 10.07 (m, 1H, NH). Anal. calcd for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.45; H, 6.52; N, 10.02.

Data for 23c. Yield, 69.0%; mp 42−43 °C. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.29 ($^3J_{HH}$ = 7 Hz, 3H, CH_3), 2.71 (q, $^3J_{HH}$ = 7 Hz, 2H, CH_2), 3.56 (q, $^3J_{HH}$ = 7 Hz, 2H, OCH_2), 3.68 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 4.28 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 4.41 (d, $^3J_{HH}$ = 6 Hz, 2H, CH_2NH), 6.37 (s, 1H, furan), 7.41 (s, 1H, furan), 7.44−7.45 (m, 1H, furan), 10.02 (m, 1H, NH). Anal. calcd for $C_{15}H_{20}N_2O_4$: C, 61.63; H, 6.90; N, 9.58. Found: C, 61.69; H, 6.92; N, 9.49.

Data for 23d. Yield, 52.5%; mp 67−69 °C. ^{1}H NMR ($CDCl_3$): δ 1.08 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.21 ($^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.64−1.77 (m, 2H), 2.62 (t, $^3J_{HH}$ = 7 Hz, 2H, CH_2), 3.57 (q, $^3J_{HH}$ = 7 Hz, 2H, OCH_2), 3.69 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 4.27 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 4.40 (d, $^3J_{HH}$ = 6 Hz, 2H, CH_2NH), 6.37 (m, 1H, furan), 7.41 (m, 1H, furan), 7.44−7.45 (m, 1H, furan), 10.04 (m, 1H, NH). Anal. calcd for $C_{16}H_{22}N_2O_4$: C, 62.73; H, 7.24; N, 9.14. Found: C, 61.67; H, 7.29; N, 8.98.

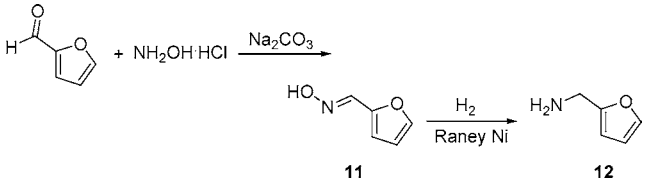
Data for 23e. Yield, 35.0%; yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.21 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.42 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 3.19−3.28 (m, 1H, THF), 3.57 (q, $^3J_{HH}$ = 7 Hz, 2H, OCH_2), 3.69 (t, $^3J_{HH}$ = 5 Hz, 2H, OCH_2), 4.27 (t, $^3J_{HH}$ = 5 Hz, 2H, CO_2CH_2), 4.46 (d, $^3J_{HH}$ = 6 Hz, 2H, CH_2NH), 6.37 (m, 1H, furan), 7.41 (m, 1H, furan), 7.44−7.45 (m, 1H, furan), 10.42 (m, 1H, NH). Anal. calcd for $C_{16}H_{22}N_2O_4$: C, 62.73; H, 7.24; N, 9.14. Found: C, 61.71; H, 7.22; N, 9.38.

X-ray Diffraction. The crystal structure of the compound **23b** was determined, and X-ray intensity data were recorded on a Bruker SMART 1000 CCD diffraction meter using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). In the range of 2.45° ≤ θ ≤ 21.06°, 3067 independent reflections were obtained. All calculations were refined anisotropically. All hydrogen atoms were located from a difference Fourier map and were placed at calculated positions and were included in the refinements in the riding mode with isotropic thermal parameters.

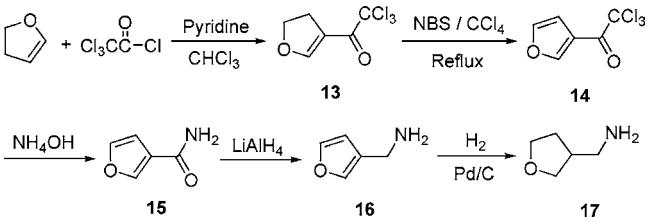
Herbicidal Activity Bioassay. The herbicidal activities of compounds **20a**−**e**, **21a**−**e**, **22a**−**e**, **23a**−**e**, and **3** were evaluated using a previously reported procedure (*7*−*9*).

Plant Material. Two dicotyledonous crops, rape (*Brassica napus* L.) and amaranth pigweed (*Amaranthus retroflexus*), and two monocotyledonous crops, alfalfa (*Medicago sativa* L.) and hairy crabgrass [*Digitaria sanguinalis* (L.) Scop.], were used to test the herbicidal activities of compounds. The seeds of amaranth pigweed were reproduced outdoors and stored at room temperature. Seeds of alfalfa and rape and hairy crabgrass were bought from the Institute of Crop, Tianjin Agriculture Science Academy.

Scheme 1



Scheme 2



Culture Method. The seeds were planted in 6 cm diameter plastic boxes containing artificial mixed soil. Before plant emergence, the boxes were covered with plastic film to retain moisture. Plants were grown in the green house. The fresh weight of the above ground tissues was measured 10 days after treatment. The inhibition percent was used to describe the control efficiency of the compounds.

Treatment. The dosage (activity ingredient) for each compound corresponded to 1.5 kg/ha. Purified compounds were dissolved in 100 μL of *N*,*N*-dimethylformamide with the addition of a little Tween 20 and then were sprayed using a laboratory belt sprayer delivering a 750 L/ha spray volume. Compounds were sprayed immediately after seed planting (preemergence treatment) or after the expansion of the first true leaf (postemergence treatment). The mixture of same amount of water, *N*,*N*-dimethylformamide, and Tween 20 was sprayed as the control. Each treatment was triplicated. The activity numbers represented the percent displaying herbicidal damage as compared to the control. The error of the experiments was 2%.

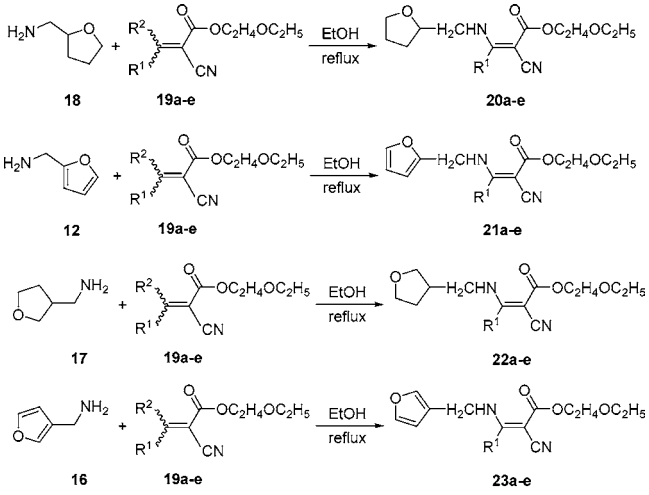
Plant Growth Regulatory Activity Assay. The plant growth regulatory activities of compounds **20a**−**e**, **21a**−**e**, **22a**−**e**, and **23a**−**e** were evaluated using previously reported procedures (*27*, *28*). Seeds of cucumber were incubated at 26 °C in the dark for 72 h, and 10 cotyledons were cut off. *N*,*N*-Dimethylformamide solutions of the test compounds were prepared at concentrations of 10 mg/L. The experiments were conducted in sterile Petri dishes (6 cm diameter) lined with a sheet of filter paper. To each dish was added 0.3 mL of the test solution, and the solvent was evaporated before addition of 3 mL of water, followed by the above cotyledons. Assays were carried out at 26 °C in the dark in an incubator for 5 days. The number of roots was counted, and the growth regulatory activities were evaluated. Controls were performed under the same conditions, using only water. Each treatment was performed in triplicate.

Fungicidal Activities Bioassay. The in vitro fungicidal activities of compounds **20a**−**e**, **21a**−**e**, **22a**−**e**, and **23a**−**e** against *Gibberella zeae*, *Alternaria solani*, *Physalospora piricola*, *Cercosporaa rachidicola*, and *Cladosporium cucumerinum* were tested by means of mycelium growth assays according to a previously reported method (*26*). The test solution (1 mL, 50 mg/L) was poured into sterile culture plates (9 cm diameter), and agar culture medium (9 mL) was added. Sterile water (1 mL) and agar culture medium (9 mL) were used as controls. The inocula, 4 mm in diameter, were removed from the margins of actively growing colonies of mycelium, placed in the centers of the above plates, and incubated at 26 °C. The diameter of the mycelium was measured for 72 h. Each treatment was performed in triplicate. The inhibition percent was used to describe the control efficiency of the compounds.

inhibition percent (%) =

(average hyphal diameter in the control − average hyphal diameter in the treatment)/ average hyphal diameter in the control

Scheme 3[a]



19a R^1 = MeS, R^2 = MeS; **19b** R^1 = Me, R^2 = OEt; **19c** R^1 = Et, R^2 = OMe; **19d** R^1 = Pr-*n*, R^2 = OMe; **19e** R^1 = Pr-*i*, R^2 = OMe

20, 21, 22, 23: a: R^1 = MeS, **b**: R^1 = Me, **c**: R^1 = Et, **d**: R^1 = Pr-*n*, **e**: R^1 = Pr-*i*

[a] Key: **19a**, R^1 = MeS and R^2 = MeS; **19b**, R^1 = Me and R^2 = OEt; **19c**, R^1 = Et and R^2 = OMe; **19d**, R^1 = Pr-*n* and R^2 = OMe; and **19e**, R^1 = Pr-*i* and R^2 = OMe. Compounds **20**–**23**: **a**, R^1 = Mes; **b**, R^1 = Me; **c**, R^1 = Et; **d**, R^1 = Pr-*n*; and **e**, R^1 = Pr-*i*.

Antiviral Biological Assay. The antiviral activities of the compounds against TMV (tobacco mosaic virus) were assayed by the conventional half-leaf method according to the reported method (*29*, *30*). A fresh leaf of the 5−6 growth stage of tobacco that had been inoculated by the juice-leaf rubbing method (the concentration of TMV was 5.88×10^{-2} μg/mL) was cut into two halves along the main vein. The two halves were immersed into the test solution and double distilled water for 20 min, respectively, and then cultured at 25 °C for 72 h. Each treatment was performed in triplicate. The in vitro inhibition ratio was calculated by comparing the average numbers of the viral inflammations on the two-half leaves according to eq 1.

$$Y = 100(\mathrm{CK} - \mathrm{A})/\mathrm{CK} \quad (1)$$

where Y is the antivirus inhibition ratio (in vitro) (%), CK is the average numbers of viral inflammations on control half leaf (in vitro), and A is the average numbers of viral inflammations on treatment half leaf (in vitro).

RESULTS AND DISCUSSION

Synthesis. Intermediate furan-2-ylmethanamine (**12**) was synthesized from furfural as shown in **Scheme 1**. Furfural was condensed with hydroxylamine hydrochloride to give 2-furfural oxime (**11**), and subsequent reduction using Raney Ni as a catalyst provided furan-2-ylmethanamine (**12**), which was used without further purification.

Furan-3-ylmethanamine (**16**) and (tetrahydrofuran-3-yl)-methanamine (**17**) were prepared from 2,3-dihydrofuran as shown in **Scheme 2**. 2,3-Dihydrofuran was reacted with trichloroacetyl chloride in the presence of pyridine to obtain 2,2,2-trichloro-1-(4,5-dihydrofuran-3-yl)ethanone (**13**) in 82.1% yield according to a reported procedure (*31*). The compound **13** was treated with N-bromosuccinimide to give 2,2,2-trichloro-1-(furan-3-yl)ethanone (**14**), and its reaction with ammonia yielded furan-3-carboxamide (**15**). The compound **15** was soluble in water; hence, a continuous extract from the aqueous layer was applied, and the yield was 93.0%, whereas the reported yield was 70% (*32*). The reduction of furan-3-carboxamide (**15**) using lithium aluminum tetrahydride provided furan-3-ylmetha-

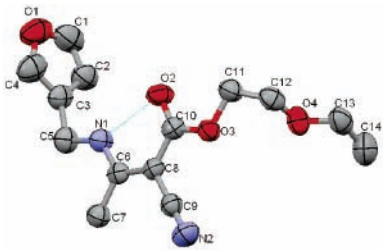


Figure 1. Molecular structure of compound **23b**.

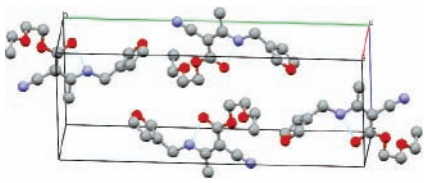


Figure 2. Packing diagram of compound **23b**.

Table 1. Hydrogen Bonds for Compound **23b**

bond	length (Å) or degree (°)
N(1)–H	0.860
H···O(2)	1.942
N(1)···O(2)	2.638
<N(1)–H···O(2)	137.13

Table 2. Selected Bond Lengths (Å) and Torsion Angles (°) of Compound **23b**

selected bond	lengths (Å)	selected bond	lengths (Å)	selected torsion angles	torsion angles (°)
C1–C2	1.330(4)	C6–C8	1.398(3)	N1–C6–C8–C10	–2.2(3)
C2–C3	1.418(3)	C6–C7	1.492(3)	N1–C6–C8–C9	–179.07(18)
C3–C4	1.339(3)	C8–C9	1.419(3)	C6–C8–C10–O2	5.5(3)
C4–O1	1.349(3)	C8–C10	1.438(3)	C6–C8–C10–O3	–174.03(17)
O1–C1	1.365(4)	C10–O2	1.222(2)	C9–C8–C10–O2	–177.5(2)
N1–C6	1.316(2)	C10–O3	1.342(2)	C9–C8–C10–O3	2.9(3)

namine (**16**) in 69.4% yield, and further reduction using Pd/C gave (tetrahydrofuran-3-yl)methanamine in 77.5% yield (**17**).

Intermediates **19** were reacted with **12** or **16**−**18** in refluxing absolute ethanol to give the target compounds **20**−**23** in good yields (**Scheme 3**). All of these target compounds were confirmed by ^{1}H NMR and elemental analysis.

Crystal Structure Analysis. Compound **23b** was recrystallized from ethyl acetate/petroleum ether to give colorless crystals suitable for X-ray single-crystal diffraction with the following crystallographic parameters: $a = 7.5899(16)$ Å, $b = 21.892(5)$ Å, $c = 9.352(2)$ Å, $\alpha = 90.00°$, $\beta = 106.485(4)°$, $\gamma = 90.00°$, $\mu = 0.092$, $V = 1490.1(6)$ Å^3, the fact that there are four molecules in the unit cell and the space group $P2_1/n$, $z = 4$, $D_x = 1.241$ mg/m^3, $F(000) = 592$, $T = 294(2)$ K, $2.45° \leq \theta \leq 21.06°$; and the final R factor, $R_1 = 0.0438$ and $\omega R_2 = 0.0979$.

It could be seen from the X-ray single-crystal analysis that amino and carbonyl are of the same side of the vinyl, and there existed an intramolecular hydrogen bond between the nitrogen atom and the oxygen of the carbonyl (**Figure 1** and **Table 1**). Selected bond lengths are listed in **Table 2**. The bond length of C(6)−C(8) (1.398 Å) is longer than normal C═C (1.34 Å), C(6)−C(7) (1.492 Å), and C(8)−C(9) (1.419 Å), the bond length of C(8)−C(10) (1.438 Å) is shorter than normal C−C (1.54 Å), the bond length of C(10)−O(2) (1.222 Å) is shorter than normal C═O (1.34 Å), the bond length of C(10)−O(3) (1.342 Å) is shorter than normal single C−O (1.44 Å), and the bond length of C(6)−N(1) (1.316 Å) bond is shorter than the normal C−N single bond (1.49 Å), which suggest that the electron density is localized among N(1)−C(6)−C(8)−C(10)−O(2) and O(3). Considering the additional hydrogen bond, the atoms H(1)−N(1)−C(6)−C(8)−C(10)−O(2) are close to planar, and the deviations from the least-squares plane through the atoms are all less than or equal to 0.027 nm. For the furan rings [O(1), C(1), C(2), C(3), and C(4)], the deviations from the least-squares plane through the ring atoms are smaller than 0.002 nm. The dihedral angle between the two planes is 76.3°, which is reasonable considering the sp^3 configuration of C(11).

Table 3. Herbicidal Activities of Compounds **20**–**23** and **3** (1.5 kg/ha, Percent Inhibition, %)

	postemergence treatment				preemergence treatment			
	rape	amaranth pigweed	alfalfa	hairy crabgrass	rape	amaranth pigweed	alfalfa	hairy crabgrass
20a	47.5	37.8	23.4	0	0	9.5	21.8	35.7
20b	57.9	36.4	28.7	7.1	8.5	0	11.3	5.7
20c	63.7	46.1	22.2	0	7.4	8.4	3.0	0
20d	36.3	16.4	19.2	0	0	0	15.0	0
20e	97.2	100	60.5	100	80.0	3.2	20.3	40.0
21a	22.9	30.2	18.6	13.1	20.7	10.5	0	37.8
21b	20.1	32.3	5.4	17.2	8.5	3.2	12.0	42.1
21c	47.9	22.6	35.9	27.3	16.3	9.5	0	12.1
21d	22.9	31.6	12.6	1.0	30.7	0	0	22.8
21e	56.3	41.9	26.3	0	3.3	6.3	4.5	37.8
22a	50.5	43.3	4.2	0	0	22.1	0	5.7
22b	52.3	29.5	5.4	0	0	12.6	7.5	31.4
22c	68.0	51.6	25.7	11.1	34.1	4.2	6.0	0
22d	58.8	8.1	11.4	1.0	0	9.5	0	0
22e	88.2	37.8	41.3	57.6	0	12.6	2.3	0
23a	30.8	28.8	31.1	5.1	0	8.4	16.5	0
23b	49.8	37.1	20.4	0	0	21.1	6.8	22.8
23c	33.8	23.3	0	0	0	11.6	2.3	0.
23d	25.2	14.3	31.1	0	0	0	4.5	35.7
23e	51.9	27.4	13.2	0	0	22.1	10.5	33.6
3	100	100	41.3	89.9	68.9	13.7	1.5	18.6

Table 4. Herbicidal Activities of Compounds **20e** and **3** (Percent Inhibition, %)

		postemergence treatment		
compd	rate (g/ha)	rape	amaranth pigweed	hairy crabgrass
20e	750	70.2	100	67.9
	375	65.0	100	32.1
3	750	100	100	
	375	100	92.3	

Herbicidal Activities. In our previous work, the cyanoacrylate structure modified by the replacement of phenyl with pyridyl and thiazole showed good herbicidal activities (*8*, *9*). To further amplify the interaction of these cyanoacrylates with the lipophilic binding domain, pyridyl was replaced by tetrahydrofuran or furan heterocycles in 2-cyanoacrylates, and their herbicidal activities were evaluated (**Table 3**). Most of the compounds **20a**−**e**, **21a**−**e**, **22a**−**e**, and **23a**−**e** showed greater herbicidal activities in postemergence treatment than in preemergence treatment. In postemergence treatment, most of the compounds exhibited higher herbicidal activities against dicotyledonous weeds (rape and amaranth pigweed) than monocotyledon weeds (alfalfa and hairy crabgrass), especially rape. The structure−activity relationship according to herbicidal activities against rape in the postemergence treatment showed that the compounds containing tetrahydrofuran moiety, whether 2- or 3-substituted, gave higher herbicidal activities than corresponding furan analogues. (*Z*)-Ethoxyethyl 2-cyano-3-isopropyl-3-(tetrahydro-

Table 5. Plant Growth Regulatory Activities (10 mg/L), Fungicidal Activities (50 mg/L), and Antiviral Activities (100 mg/L) of Compounds **20**–**23** and **3**

	fungicidal activities						
	G. zeae	*A. solani*	*C. rachidicola*	*P. piricola*	*C. cucumerinum*	plant growth regulatory activities	antiviral activities (TMV)
20a	40.0	0	4.5	17.9	34.2	–0.6	
20b	10.0	0	9.1	44.6	13.2	–6.6	7.5
20c	20.0	10.7	22.7	37.5	15.8	2.4	13.2
20d	23.3	0	4.5	32.1	10.5	8.4	0
20e	33.3	14.3	18.2	28.6	0	32.5	7.2
21a	36.7	25.0	22.7	16.1	15.8	14.4	
21b	46.7	0	22.7	44.6	21.1	–0.6	
21c	20.0	0	27.3	35.7	21.1	11.4	13.3
21d	30.0	10.7	9.1	3.6	13.2	14.4	
21e	23.3	17.9	22.7	37.5	13.2	2.4	0
22a	0	21.4	27.3	25.0	21.1	–9.6	
22b	0	35.7	27.3	12.5	18.4	–6.6	
22c	20.0	17.9	9.1	39.3	7.9	41.5	7.2
22d	0	10.7	27.3	41.1	21.1	5.4	9.4
22e	0	0	9.1	17.9	5.3	14.4	4.9
23a	36.7	3.6	9.1	12.5	13.2	14.4	8.0
23b	33.3	0	13.6	44.6	36.8	–18.6	
23c	33.3	10.7	4.5	35.7	26.3	23.4	
23d	16.7	25.0	31.8	12.5	21.1	–6.6	0
23e	0	25.0	22.7	30.4	13.2	11.4	
3	6.7	7.1	22.7	21.4	0	–3.6	18.3

furan-3-yl)methaneaminoacrylate (**20e**) exhibited excellent herbicidal activities against amaranth pigweed and hairy crabgrass in postemergence treatment. (*Z*)-Ethoxyethyl 2-cyano-3-methylthio-3-(2-chloro-5-pyridyl)methaneaminoacrylate (**3**) was prepared for comparison of herbicidal activity. This comparison (**Tables 3** and **4**) clearly showed that the compound **20e** had a higher level of herbicidal activities against amaranth pigweed and hairy crabgrass in postemergence treatment than compound **3**. In particular, compound **20e** showed excellent herbicidal activities against amaranth pigweed in postemergence treatment even at a dose of 375 g/ha.

Plant Growth Regulatory Activities. The plant growth regulatory activities of compounds **20a**−**e**, **21a**−**e**, **22a**−**e**, **23a**−**e**, and **3** were evaluated, and their effects on the radicle growth of cucumber were shown in **Table 5**. Interestingly, some compounds, such as **20e** and **22c**, stimulated radicle growth of cucumber, whereas other compounds, such as **23b**, had an inhibitory effect: Compounds **20e** and **22c** gave 32.5 and 41.5% promotion, respectively, and compound **23b** gave 18.6% inhibition.

Fungicidal Activities. The in vitro fungicidal activities of compounds **20a**−**e**, **21a**−**e**, **22a**−**e**, **23a**−**e**, and **3** against *G. zeae*, *A. solani*, *P. piricola*, *C. rachidicola*, and *C. cucumerinum* were evaluated by means of mycelium growth assays. The screening data (**Table 5**) revealed that some compounds showed fungicidal activities. For example, compounds **20a** and **21b** exhibited 40 and 46.7% inhibition effect against mycelial growth of *G. zeae*, respectively, and compounds **20b**, **21b**, and **23b** gave 44.6% inhibition against *P. piricola*. No structure−activity relationship was apparent.

Antiviral Activities. The antiviral activities of some target compounds against TMV were evaluated by the conventional half-leaf method. To our disappointment, the compounds showed low antiviral activities as shown in **Table 5**.

In summary, a series of novel cyanoacrylates containing furan or tetrahydrofuran moieties were synthesized, and their structures were characterized by ^{1}H NMR, elemental analysis, and single-crystal X-ray diffraction analysis. The herbicidal, plant growth regulatory, fungicidal, and antiviral activities of these cyanoacrylates were evaluated. The results of herbicidal activities showed that most of these cyanoacrylates exhibited higher herbicidal activities against dicotyledonous weeds than monocotyledonous weeds, and the compounds containing the tetrahydrofuran moiety gave higher herbicidal activities than corresponding furan analogues; (*Z*)-ethoxyethyl 2-cyano-3-isopropyl-3-(tetrahydrofuran-3-yl)methaneaminoacrylate showed excellent herbicidal activities against amaranth pigweed in postemergence treatment even at a dose of 375 g/ha. At the same time, these cyanoacrylates had interesting plant growth regulatory activities, and some compounds stimulated radicle growth of cucumber, whereas some compounds had an inhibitory effect. These cyanoacrylates showed fungicidal activities as well.

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