Supporting information

Synthesis, insecticidal and fungicidal activities of methyl 2- (methoxyimino)-2-(2-((1-(N-nitrocarbamimidoyl)-2-hydrocarbylidenehydrazinyl)-methyl)phenyl)acetates

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Scheme 1. Preparation of title compounds

Synthesis procedure for Nitroaminoguanidine (8)

In a 1000 mL flask, a mixture of the nitroguanidine(7, 0.192 mol), water (250ml) was heated to 55 °C under stirring, 85% hydrazine hydrate (0.216 mol) was added dropwise to the mixture, the reaction was allowed to stir 15 minutes at 55°C. At this point, the solid was all dissolved in the water, then the solution was quickly cooled to about 20 °C, the balanced concentrated hydrochloric acid was added to the solution until PH=5~6. The crude product was precipitated from the solution. The precipitate was filtrated and washed with water, and the crude product was recrystallized from hot water to afford the compound 8.

Nitroaminoguanidine (8), white crystal, mp 134 - 136 °C, yield 70%. 1H NMR(DMSO-d6): δ: 9.33(s,1H), 8.27(s,1H), 7.56(s,1H), 4.69(s,2H).

General synthesis procedure for Intermediate (9-01~9-04, 9-07~9-23)

Method A: In a 250 mL flask, nitroaminoguanidine (8) (2.0 g,17 mmol) and glacial acetic acid (0.2 mL) were dissolved in menthol (100 mL), the mixture was heated at 50 °C, aldehyde (20 mmol) was added dropwise to the mixture, and the reaction was refluxed for 4 h. After completion, the solvent was removed under reduced pressure, and the resulting crude material was recrystallized using ethanol and petroleum ether (v/v, 3:1).

General synthesis procedure for Intermediate (9-05, 9-06)

Method B: In a 250 mL flask, nitroaminoguanidine (8) (2.0 g,17 mmol) and concentrated hydrochloric acid (0.2 mL) were dissolved in menthol (100 mL), the mixture was heated at 50 °C, ketone(20 mmol) was added dropwise to the mixture, and the mixture was refluxed for 6 h. After completion, the solvent was removed under reduced pressure, and the resulting crude material was recrystallized using methanol.

2-Butylidene-N-nitrohydrazinecarboximidamide(9-01): yellow solid, mp 100 - 102 °C, yield 80%. 1H NMR (300 MHz, DMSO-d6) δ 0.91 (t, 3H), 1.48 - 1.55 (m, 2H), 2.23 - 2.27 (m, 2H), 7.53 (t, 1H), 8.02 (brs, 1H), 8.64 (brs, 1H), 11.46 (brs, 1H).

2-(2-Methylpentylidene)-N-nitrohydrazinecarboximidamide(9-02): yellowish solid, mp 102 - 104 °C, yield 82%. 1H NMR (300 MHz, DMSO-d6) δ 0.88 (t, J = 6.90, 3H), 1.04 (d, J = 6.81, 3H), 1.24 - 1.48 (m, 4H), 2.38 - 2.51 (m, 1H), 7.43 (d, J = 5.97, 1H), 7.97 (brs, 1H), 8.65 (brs, 1H), 11.43 (s, 1H).

2-(2-Ethylbutylidene)-N-nitrohydrazinecarboximidamide(9-03): white solid, mp 134 - 136 °C, yield 75%. 1H NMR (300 MHz, DMSO-d6) δ 0.91 (t, 6H), 1.45 - 1.60 (m, 4H), 2.10 - 2.17 (m, 1H), 7.02 (brs, 1H), 7.55 (d, 1H), 8.76 (brs, 1H), 10.98 (brs, 1H).

2-Heptylidene-N-nitrohydrazinecarboximidamide(9-04): yellow solid, mp 93 - 95 °C, yield 70%. 1H NMR (300 MHz, DMSO-d6) δ 0.91(t, J = 1.62, 3H), 1.25 - 1.38 (m, 6H), 1.50 - 1.59 (m, 2H), 2.29 - 2.36 (m, 2H), 6.98 (brs, 1H), 7.70 (t, J = 5.46, 1H), 8.67 (brs, 1H), 10.81 (brs, 1H).

N-Nitro-2-(propan-2-ylidene)hydrazinecarboximidamide(9-05): white solid, mp 164 - 166 °C,
yield 80%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 1.92 (s, 3H), 1.99 (s, 3H), 7.99 (brs, 1H), 8.64 (brs, 1H), 10.76 (s, 1H).

N-Nitro-2-(pentan-3-ylidene)hydrazinecarboximidamide(9-06): white solid, mp 134 - 136°C, yield 75%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 0.91(t,6H), 1.45-1.60(m,4H), 2.10 -2.17 (m,1H), 7.02(brs,1H), 7.55(d,1H), 8.76 (brs,1H), 10.98(brs,1H)

2-(Furan-2-ylmethylene)-N-nitrohydrazinecarboximidamide(9-07): yellowish solid, mp 222 - 224°C, yield 87%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 6.67 - 7.88 (m, 3H), 8.08 (s, 1H), 8.18 (brs, 1H), 8.80 (brs, 1H), 11.83 (s, 1H).

2-Benzylidene-N-nitrohydrazinecarboximidamide(9-08): white solid, mp 195 - 197°C, yield 86%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 7.42 - 7.91 (m, 5H), 8.17 (s, 1H), 8.55 (brs, 1H), 8.84 (brs, 1H), 11.82 (s, 1H).

2-(4-Cyanobenzylidene)-N-nitrohydrazinecarboximidamide(9-09): yellowish solid, mp 244 - 246°C, yield 85%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 7.89 - 8.12 (m, 4H), 8.19 (s, 1H), 8.78 (brs, 1H), 12.00 (s, 1H).

2-(4-Chlorobenzylidene)-N-nitrohydrazinecarboximidamide(9-10): white solid, mp 186 - 188°C, yield 92%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 7.48 - 7.95 (m, 4H), 8.15 (s, 1H), 8.64 (brs, 1H), 8.87 (brs, 1H), 11.87 (s, 1H).

2-(2-Chlorobenzylidene)-N-nitrohydrazinecarboximidamide(9-11): white solid, mp 207 - 209°C, yield 90%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 7.38 - 8.42 (m, 4H), 8.57 (s, 1H), 8.69 (brs, 1H), 8.91 (brs, 1H), 11.97 (s, 1H).

2-(2,4-Dichlorobenzylidene)-N-nitrohydrazinecarboximidamide(9-12): yellowish solid, mp 228 - 230°C, yield 92%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 7.48 - 8.46 (m, 4H), 8.51 (s, 1H), 8.76 (brs, 1H), 8.94 (brs, 1H), 12.00 (s, 1H).

N-Nitro-2-(4-nitrobenzylidene)hydrazinecarboximidamide(9-13): yellow solid, mp 264 - 266°C, yield 95%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.15 - 8.29 (m, 5H), 8.82 (brs, 1H), 8.95 (brs, 1H), 12.05 (s, 1H).

N-Nitro-2-(3-nitrobenzylidene)hydrazinecarboximidamide(9-14): yellow solid, mp 256 - 258°C, yield 91%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 7.69 - 8.32 (m, 4H), 8.76 (brs, 1H), 8.89 (brs, 1H), 11.98 (s, 1H).

2-(4-(tert-Butyl)benzylidene)-N-nitrohydrazinecarboximidamide(9-15): white solid, mp 193 - 195°C, yield 89%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 1.30 (s, 9H), 7.46 (d, J = 8.43, 2H), 7.79 (d, J = 8.46, 2H), 8.14 (s, 1H), 8.50 (brs, 1H), 8.83 (brs, 1H), 11.80 (s, 1H).

2-(4-Methylbenzylidene)-N-nitrohydrazinecarboximidamide(9-16): white solid, mp 201 - 203°C, yield 84%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 2.34 (s, 3H), 7.24 - 7.78 (m, 4H), 8.13 (s, 1H), 8.50 (brs, 1H), 8.80 (brs, 1H), 11.77 (s, 1H).

2-(4-Methoxybenzylidene)-N-nitrohydrazinecarboximidamide(9-17): white solid, mp 202 - 204°C, yield 92%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 3.81 (s, 3H), 6.97 - 7.85 (m, 4H), 8.11 (s, 1H), 8.47 (brs, 1H), 8.78 (brs, 1H), 11.73 (s, 1H).

2-(3-Methoxybenzylidene)-N-nitrohydrazinecarboximidamide(9-18): white solid, mp 212 - 214°C, yield 90%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 3.80 (s, 3H), 6.98 - 7.52 (m, 4H), 8.13 (s, 1H), 8.67 (brs, 1H), 8.84 (brs, 1H), 11.83 (s, 1H).

2-(2-Methoxybenzylidene)-N-nitrohydrazinecarboximidamide(9-19): white solid, mp 191 - 193°C, yield 88%. $^1$H NMR (300 MHz, DMSO-$d_6$) δ 3.85 (s, 3H), 6.98 - 8.20 (m, 4H), 8.52 (s, 1H), 8.52 (brs, 1H), 8.82 (brs, 1H), 11.77 (s, 1H).
2-(Benzo[d][1,3]dioxol-5-ylmethylene)-N-nitrohydrazinecarboximidamide (9-20): yellowish solid, mp 220 - 222°C, yield 88%. ¹H NMR (300 MHz, DMSO-d₆) δ 6.09 (s, 2H), 6.95 - 7.75 (m, 3H), 8.07 (s, 1H), 8.56 (brs, 1H), 8.80 (brs, 1H), 11.72 (s, 1H).

N-Nitro-2-(3-phenoxymethylidene)hydrazinecarboximidamide (9-21): white solid, mp 211 - 213°C, yield 90%. ¹H NMR (300 MHz, DMSO-d₆) δ 7.00 - 7.74 (m, 9H), 8.16 (s, 1H), 8.65 (brs, 1H), 8.84 (brs, 1H), 11.85 (s, 1H).

2-(3-Hydroxybenzylidene)-N-nitrohydrazinecarboximidamide (9-22): white solid, mp 210 - 212°C, yield 90%. ¹H NMR (300 MHz, DMSO-d₆) δ 6.84 - 7.29 (m, 4H), 7.40 (s, 1H), 8.08 (brs, 1H), 8.19 (brs, 1H), 9.60 (s, 1H), 11.77 (s, 1H).

2-(2-Hydroxybenzyldiene)-N-nitrohydrazinecarboximidamide (9-23): yellow solid, mp > 300°C, yield 89%. ¹H NMR (300 MHz, DMSO-d₆) δ 6.82 – 8.04 (m, 4H), 8.47 (s, 1H), 8.78 (brs, 2H), 10.02 (s, 1H), 11.87 (s, 1H).
The NMR and HRMS spectrum of the title compounds (6-01~6-23):

6-01

MW 378.1652
MW 402.1288
MW 412.1495

[Chemical structure image]

[Graphical representation of the molecule]

[Graphical representation of the mass spectrum]

[Graphical representation of another mass spectrum]
MW 468.2121

[Chemical structure and graph]

[Graph of NMR spectrum]

[Table of NMR data]

- **Title**: 袁小勇C谱
- **Comment**: 13C NMR of YN34
- **Origin**: UXNMR, Bruker Analytische Messtechnik GmbH
- **Owner**: root
- **Site**: Spectrometer dpx300
- **Solvent**: DMSO
- **Temperature**: 298.2
- **Pulse Sequence**: zgdc30
- **Experiment**: 1D
- **Number of Scans**: 596
- **Receiver Gain**: 9216
- **Relaxation Delay**: 1.5000
- **Pulse Width**: 12.0000
- **Acquisition Time**: 1.4451
- **Acquisition Date**: 2014-12-26T07:19:14
- **Modification Date**: 2014-12-26T07:48:20
- **Spectrometer Frequency**: 75.47
- **Spectral Width**: 22675.7
- **Lowest Frequency**: -3808.6
- **Nucleus**: 13C
- **Acquired Size**: 32768
- **Spectral Size**: 65536
(E)-methyl 2-(2-(bromomethyl)phenyl)-2-(methoxyimino)acetate

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{Br} &
\end{align*}
\]

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 7.59 – 7.50 (m, 1H), 7.49 – 7.34 (m, 2H), 7.26 – 7.14 (m, 1H), 4.45 (s, 2H), 3.96 (s, 3H), 3.76 (s, 3H).

$^1$H NMR date of (E)-methyl 2-(2-(bromomethyl)phenyl)-2-(methoxyimino)acetate in References 19:

$^1$H NMR (600 MHz, CDCl$_3$): 3.86 (3H, s, -COOMe), 4.04 (3H, s, N-OCH$_3$), 4.31 (2H, s, -CH$_2$-), 7.13 (1H, dd, $J_1$ = 7.8 Hz, $J_2$ = 1.2 Hz, 3-ArH), 7.35-7.40 (2H, m, Ar-H), 7.46 (1H, dd, $J_1$ = 7.8 Hz, $J_2$ = 0.6 Hz, 6-ArH).