Supplementary Materials

Synthesis of Novel Amino Acid-Fipronil Conjugates and Study on their Phloem Loading Mechanism

Qingqing Sheng¹², Xinxin Liu¹², Yun Xie¹², Fei Lin¹², Zhixiang Zhang¹², Chen Zhao¹² * and Hanhong Xu¹² *

¹ State Key Laboratory for Conservation and Utilization of Subtropical Agro-Bioresources, South China Agricultural University, Guangzhou 510642, China; shengqing277#163.com (Q.S.); 15913194557#163.com (X.L.); xieyun91#foxmail.com (Y.X.); resistanc@scau.edu.cn (F.L.); zdsys@scau.edu.cn (Z.Z.)
² Key Laboratory of Natural Pesticide and Chemical Biology, Ministry of Education, South China Agricultural University, Guangzhou 510642, China
* Correspondence: zhaoc@scau.edu.cn (C.Z.); hhxu@scau.edu.cn (H.X.); Tel.: +86-20-8528-5127 (H.X.)

Figures S1-S50. ¹H NMR and ¹³C NMR spectra of all compounds

Table S1. The fatality rates of 4a-l and fipronil against Plutella xylostella
Figure S1 $^1$H NMR spectra of 2 in DMSO-$d_6$.

Figure S2 $^{13}$C NMR spectra of 2 in DMSO-$d_6$. 
Figure S3 $^1$H NMR spectra of 3a in Chloroform-$d$.

Figure S4 $^{13}$C NMR spectra of 3a in Chloroform-$d$. 
Figure S5 $^1$H NMR spectra of 3b in Chloroform-$d$

Figure S6 $^{13}$C NMR spectra of 3b in Chloroform-$d$
Figure S7 ¹H NMR spectra of 3c in Chloroform-d

Figure S8 ¹³C NMR spectra of 3c in Chloroform-d
Figure S9 $^1$H NMR spectra of 3d in Chloroform-$d$

Figure S10 $^{13}$C NMR spectra of 3d in Chloroform-$d$
Figure S11 $^1$H NMR spectra of 3e in Chloroform-$d$

Figure S12 $^{13}$C NMR spectra of 3e in Chloroform-$d$
Figure S13 $^1$H NMR spectra of 3f in DMSO-$d_6$

Figure S14 $^{13}$C NMR spectra of 3f in DMSO-$d_6$
Figure S15 $^1$H NMR spectra of 3g in Chloroform-$d$

Figure S16 $^{13}$C NMR spectra of 3g in Chloroform-$d$
Figure S17 ¹H NMR spectra of 3h in Chloroform-"d

Figure S18 ¹³C NMR spectra of 3h in Chloroform-"d
Figure S19 $^1$H NMR spectra of 3i in Chloroform-$d$

Figure S20 $^{13}$C NMR spectra of 3i in Chloroform-$d$
**Figure S21** $^1$H NMR spectra of 3j in Chloroform-$d$

**Figure S22** $^{13}$C NMR spectra of 3j in Chloroform-$d$
Figure S23: 1H NMR spectra of 3k in Chloroform-d

Figure S24: 13C NMR spectra of 3k in Chloroform-d
Figure S25 $^1$H NMR spectra of 3l in Chloroform-$d$

Figure S26 $^{13}$C NMR spectra of 3l in Chloroform-$d$
Figure S27: $^1$H NMR spectra of 4a in Chloroform-$d$

Figure S28: $^{13}$C NMR spectra of 4a in Chloroform-$d$
Figure S29 $^1$H NMR spectra of 4b in DMSO-$d_6$

Figure S30 $^{13}$C NMR spectra of 4b in DMSO-$d_6$
Figure S31 $^1$H NMR spectra of 4c in DMSO-$d_6$

Figure S32 $^{13}$C NMR spectra of 4c in DMSO-$d_6$
Figure S33 $^1$H NMR spectra of 4d in DMSO-$d_6$

Figure S34 $^{13}$C NMR spectra of 4d in DMSO-$d_6$
Figure S35 $^1$H NMR spectra of 4e in Chloroform-$d$

Figure S36 $^{13}$C NMR spectra of 4e in Chloroform-$d$
Figure S37 $^1$H NMR spectra of 4f in DMSO-$d_6$

Figure S38 $^{13}$C NMR spectra of 4f in DMSO-$d_6$
Figure S39 $^1$H NMR spectra of 4g in DMSO-$d_6$

Figure S40 $^{13}$C NMR spectra of 4g in DMSO-$d_6$.
Figure S41 $^1$H NMR spectra of 4h in DMSO-$d_6$

Figure S42 $^{13}$C NMR spectra of 4h in DMSO-$d_6$
Figure S43 $^1$H NMR spectra of 4i in DMSO-$d_6$

Figure S44 $^{13}$C NMR spectra of 4i in DMSO-$d_6$
Figure S45 $^1$H NMR spectra of 4j in Chloroform-$d$

Figure S46 $^{13}$C NMR spectra of 4j in DMSO-$d_6$
Figure S47 $^1$H NMR spectra of 4k in DMSO-$d_6$

Figure S48 $^{13}$C NMR spectra of 4k in DMSO-$d_6$
Figure S49 $^1$H NMR spectra of 4l in DMSO-$d_6$

Figure S50 $^{13}$C NMR spectra of 4l in DMSO-$d_6$
Table S1. The fatality rates of 4a-l and fipronil against *Plutella xylostella*

<table>
<thead>
<tr>
<th>Compounds</th>
<th>12 h Fatality rate (%)</th>
<th>24 h Fatality rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>15.15</td>
<td>48.48</td>
</tr>
<tr>
<td>4b</td>
<td>32.26</td>
<td>80.65</td>
</tr>
<tr>
<td>4c</td>
<td>3.33</td>
<td>66.67</td>
</tr>
<tr>
<td>4d</td>
<td>6.06</td>
<td>84.85</td>
</tr>
<tr>
<td>4e</td>
<td>9.09</td>
<td>78.79</td>
</tr>
<tr>
<td>4f</td>
<td>8.11</td>
<td>40.54</td>
</tr>
<tr>
<td>4g</td>
<td>3.33</td>
<td>55.67</td>
</tr>
<tr>
<td>4h</td>
<td>0.00</td>
<td>32.26</td>
</tr>
<tr>
<td>4i</td>
<td>8.57</td>
<td>68.57</td>
</tr>
<tr>
<td>4j</td>
<td>0.00</td>
<td>12.50</td>
</tr>
<tr>
<td>4k</td>
<td>15.63</td>
<td>81.25</td>
</tr>
<tr>
<td>4l</td>
<td>46.67</td>
<td>86.67</td>
</tr>
<tr>
<td>Fipronil</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

*at the concentration of 100 mg/mL.