Supporting Information

Synthesis of Piperine-Based Ester Derivatives with Diverse Aromatic Rings and Their Agricultural Bioactivities against *Tetranychus cinnabarinus* Boisduval, *Aphis citricola* Van der Goot, and *Eriosoma lanigerum* Hausmann

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Contents

1. Characterization

Data for 6: Yield: 57%; white solid; mp 96-98 ºC; IR cm^{-1} (KBr): 3430, 3303, 3083, 2371, 1723, 1573, 1492, 1369, 951, 648, 539; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (d, J = 3.6 Hz, 1H), 7.83-7.85 (m, 2H), 6.90 (s, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.76-6.78 (m, 1H), 6.52-6.66 (m, 2H), 6.49 (d, J = 10.4 Hz, 1H), 5.98 (d, J = 2.0 Hz, 2H), 5.11 (s, 2H), 3.71 (s, 2H), 3.44 (t, J = 4.8 Hz, 2H), 1.63 (s, 4H), 1.44 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.18, 164.76, 150.65, 148.25, 148.18, 137.20, 137.18, 132.35, 130.77, 129.99, 122.86, 122.35, 121.67, 108.55, 105.59, 101.33, 67.56, 47.76, 42.53, 26.67, 25.82, 24.42.

Data for 7: Yield: 50%; orange solid; mp 179-180 ºC; IR cm^{-1} (KBr): 3304, 3084, 2940, 2860, 2375, 1702, 1594, 1492, 1449, 1264, 1134, 1027, 957, 817, 769, 613, 492; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.90 (s, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.54-6.63 (m, 2H), 6.44 (d, J = 6.0 Hz, 1H), 5.97 (s, 2H), 4.97 (s, 2H), 4.80 (s, 2H), 4.42 (s, 2H), 4.22 (s, 5H), 3.76 (s, 2H), 3.51 (s, 2H), 1.67 (s, 4H), 1.53 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.39, 148.19, 147.96, 136.15, 131.02, 130.65, 122.15, 122.10, 108.50, 105.58, 101.26, 71.45, 70.73, 70.16, 69.87, 65.74, 47.82, 42.47, 26.75, 25.92, 24.54.

Data for 8: Yield: 44%; colorless oil; IR cm^{-1} (KBr): 3049, 2937, 2865, 2351, 2186, 1732, 1594, 1491, 1445, 1359, 1250, 1142, 1032, 965, 923, 789, 728, 629, 533; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.77-7.79 (m, 1H), 7.46-7.54 (m, 2H), 7.39-7.42 (m, 2H), 6.83 (d, J = 1.2 Hz, 1H), 6.75-6.78 (m, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.35-6.46 (m, 2H), 6.15 (d, J = 10.0 Hz, 1H), 5.92 (s, 2H), 4.82 (s, 2H), 4.08 (s, 2H), 3.48 (s, 2H), 2.93 (s, 2H), 1.50 (s, 4H), 1.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.98, 167.14, 148.14, 147.94, 136.28, 133.81, 132.09, 130.99, 130.88, 130.66, 130.28, 128.66, 128.16, 128.10, 126.51, 125.86, 125.49, 123.81, 122.08, 121.75, 108.45, 105.48, 101.23, 66.66, 47.28, 42.15, 39.25, 26.39, 25.71, 24.34.

Data for 9: Yield: 56%; yellow oil; IR cm^{-1} (KBr): 3303, 3029, 2936, 2862, 2350, 1734, 1596, 1491, 1446, 1356, 1250, 1142, 1032, 968, 929, 807, 712, 610, 532; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28-7.34 (m, 5H), 6.87 (s, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.45-6.54 (m, 2H), 6.28 (d, J = 8.4 Hz, 1H), 5.95 (s, 2H), 4.83 (s, 2H), 3.64 (s, 4H), 3.22 (s, 2H), 1.59 (s, 4H), 1.40 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.08, 167.30, 148.21, 148.02, 136.47, 133.78, 131.22, 130.94, 130.80, 129.35, 128.65, 127.19, 122.18, 121.88, 108.51, 105.57, 101.29, 66.70, 47.57, 42.36, 41.44, 26.57, 25.81, 24.47.

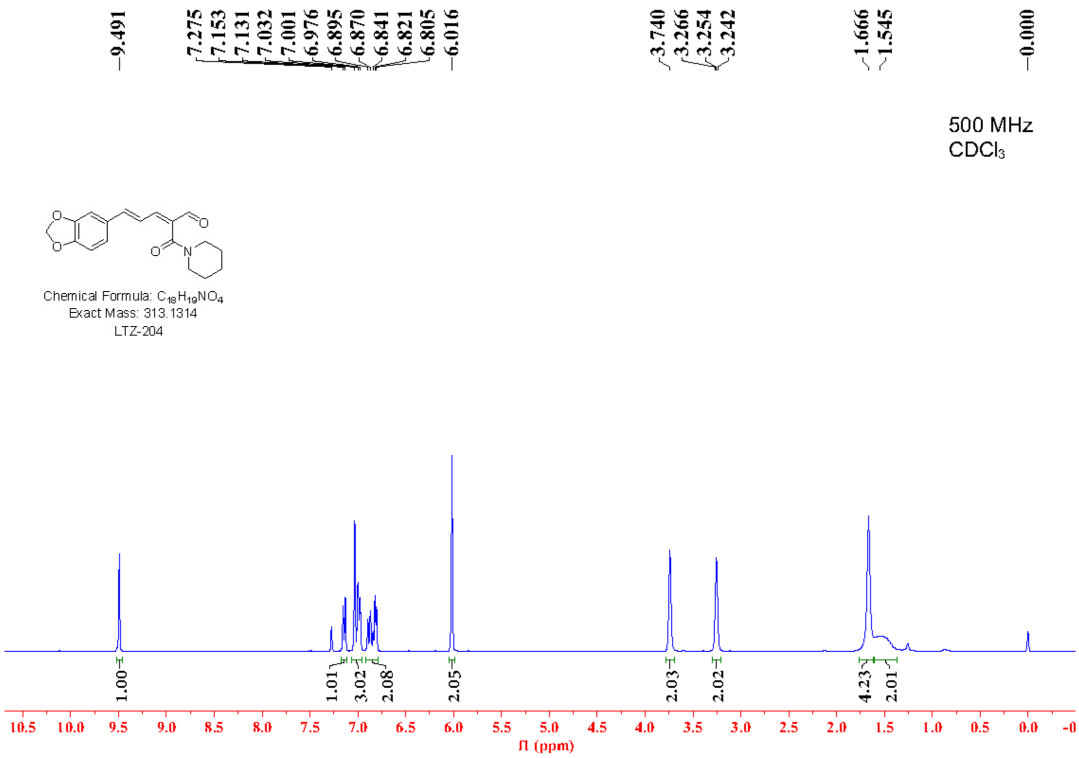
Data for 10: Yield: 54%; colorless oil; IR cm^{-1} (KBr): 3305, 2935, 2861, 2373, 2240, 1736, 1613, 1499, 1445, 1355, 1248, 1143, 1032, 967, 928, 806, 727, 607, 520; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (dd, J_1 = 8.4 Hz, J_2 = 5.6 Hz, 2H), 7.03 (t, J = 8.4 Hz, 2H), 6.88 (s, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.46-6.56 (m, 2H), 6.29 (d, J = 8.8 Hz, 1H), 5.96 (d, J = 2.0 Hz, 2H), 4.83 (s, 2H), 3.65 (s, 2H), 3.61 (s, 2H), 3.28 (t, J = 4.8 Hz, 2H), 1.61 (s, 4H), 1.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.92, 167.23, 163.28, 160.84, 148.20, 148.05, 136.60, 131.37, 130.96, 130.88, 130.86, 130.62, 129.50, 129.47, 122.22, 121.78, 115.57, 115.36, 108.50, 105.55, 101.28, 66.76, 47.61, 42.39, 40.47, 26.59, 25.78, 24.47.

Data for 11: Yield: 53%; colorless oil; IR cm^{-1} (KBr): 3303, 2936, 2865, 2420, 1735, 1588, 1491, 1446, 1357, 1249, 1146, 1031, 967, 930, 729, 522; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 1.2 Hz, 1H), 6.81-6.83 (m, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.45-6.55 (m, 2H), 6.27 (d, J = 8.8 Hz, 1H), 5.96 (s, 2H), 4.83 (s, 2H), 3.64 (s, 2H), 3.61 (s, 2H), 3.22-3.23 (m, 1H), 1.61 (s, 4H), 1.42 (t, J = 4.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.62, 167.20, 148.20, 148.05, 136.62, 133.19, 132.22, 131.37, 130.86, 130.75, 130.55, 128.76, 122.23, 121.77, 108.51, 105.56, 101.28, 66.82, 47.58, 42.39, 40.69, 26.58, 25.78, 24.46.

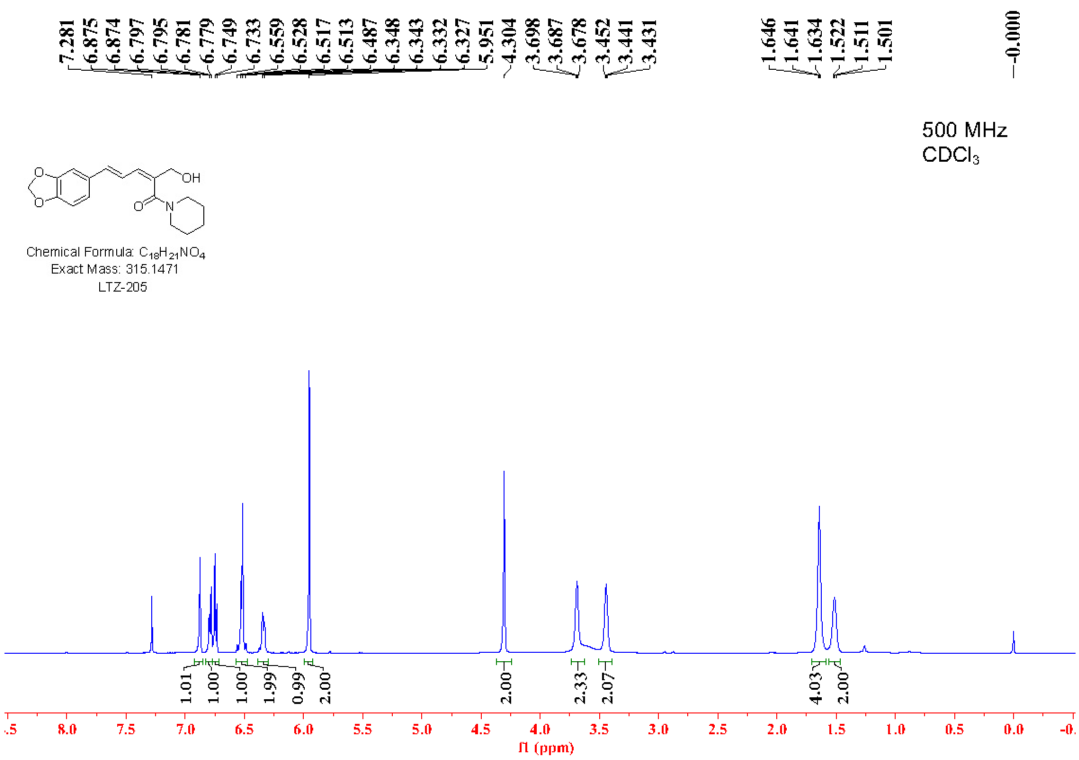
Data for 12: Yield: 44%; colorless oil; IR cm^{-1} (KBr): 3309, 2936, 2857, 2239, 1735, 1618, 1501, 1446, 1355, 1247, 1140, 1031, 968, 926, 808, 727, 606, 526; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.20 (d, J = 8.8 Hz, 2H), 6.87 (s, 1H), 6.86 (d, J = 8.4 Hz, 2H), 6.79-6.82 (m, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.45-6.54 (m, 2H), 6.26 (dd, J_1 = 6.8 Hz, J_2 = 3.2 Hz, 1H), 5.95 (s, 2H), 4.82 (s, 2H), 3.78 (s, 3H), 3.64 (s, 2H), 3.58 (s, 2H), 3.24 (s, 2H), 1.60 (s, 4H), 1.42 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.38, 167.28, 158.77, 148.18, 147.99, 136.41, 131.07, 130.92, 130.84, 130.36, 125.82, 122.15, 121.85, 114.02, 108.49, 105.54, 101.26, 66.53, 55.25, 47.57, 42.34, 40.50, 26.57, 25.79, 24.47.

2. [1]H NMR spectra of compounds

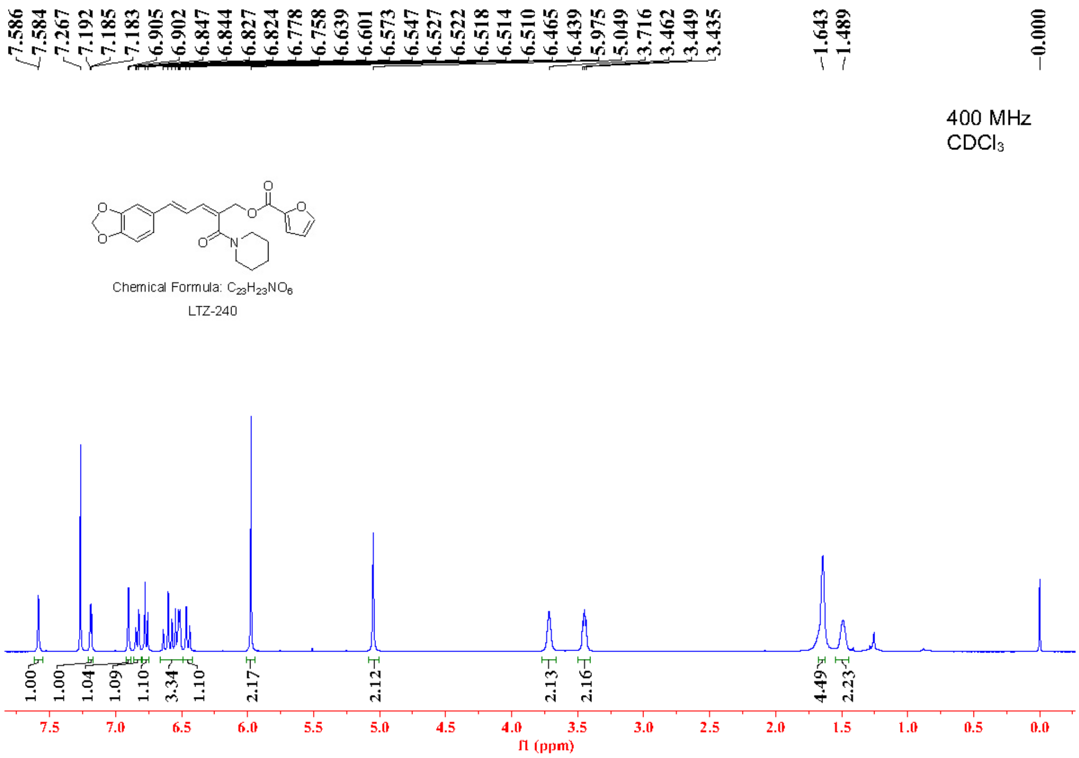
compound **2**



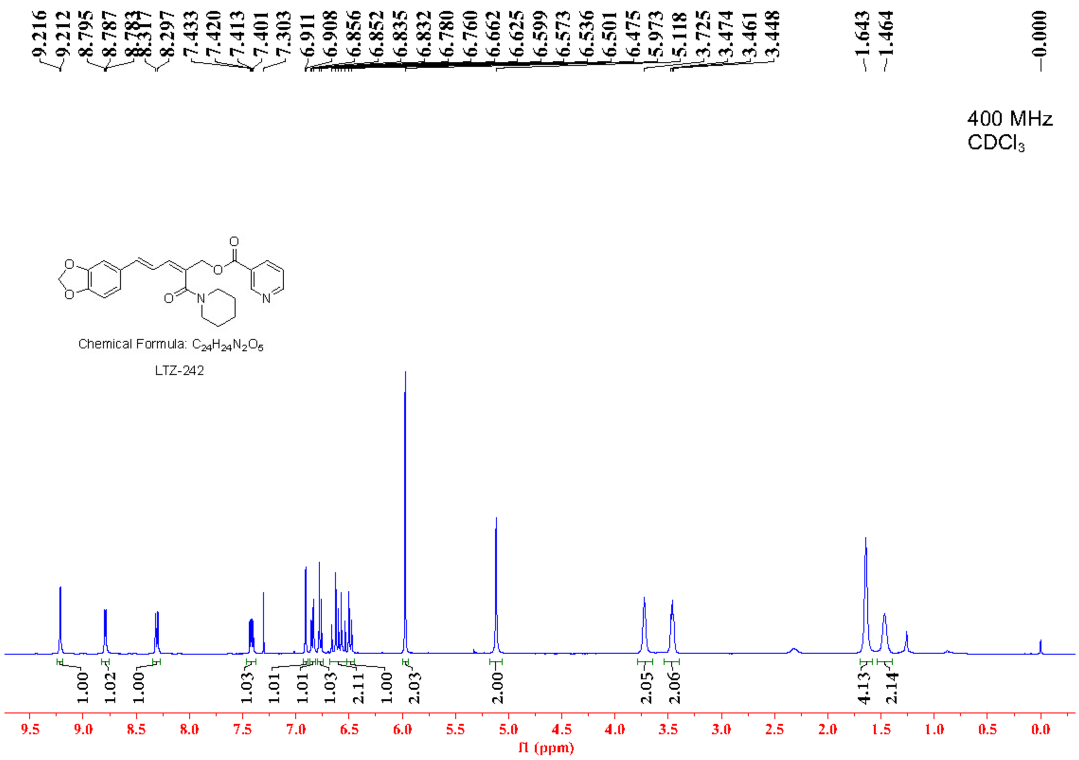
compound **3**



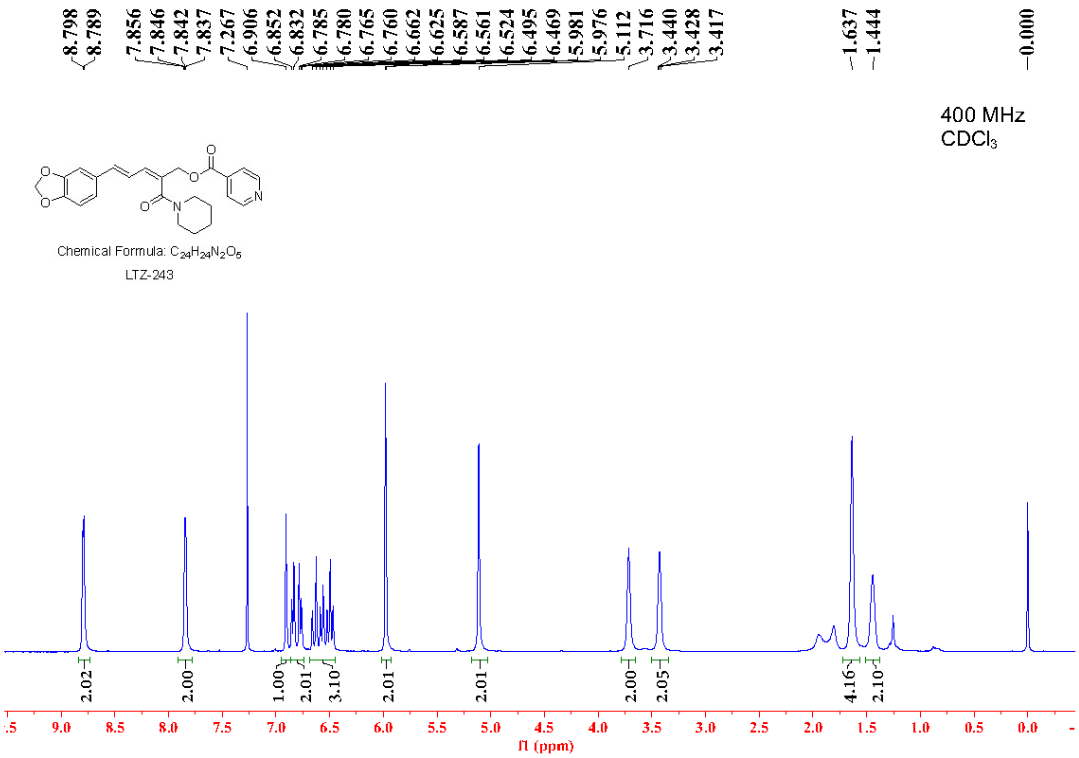
compound **4**



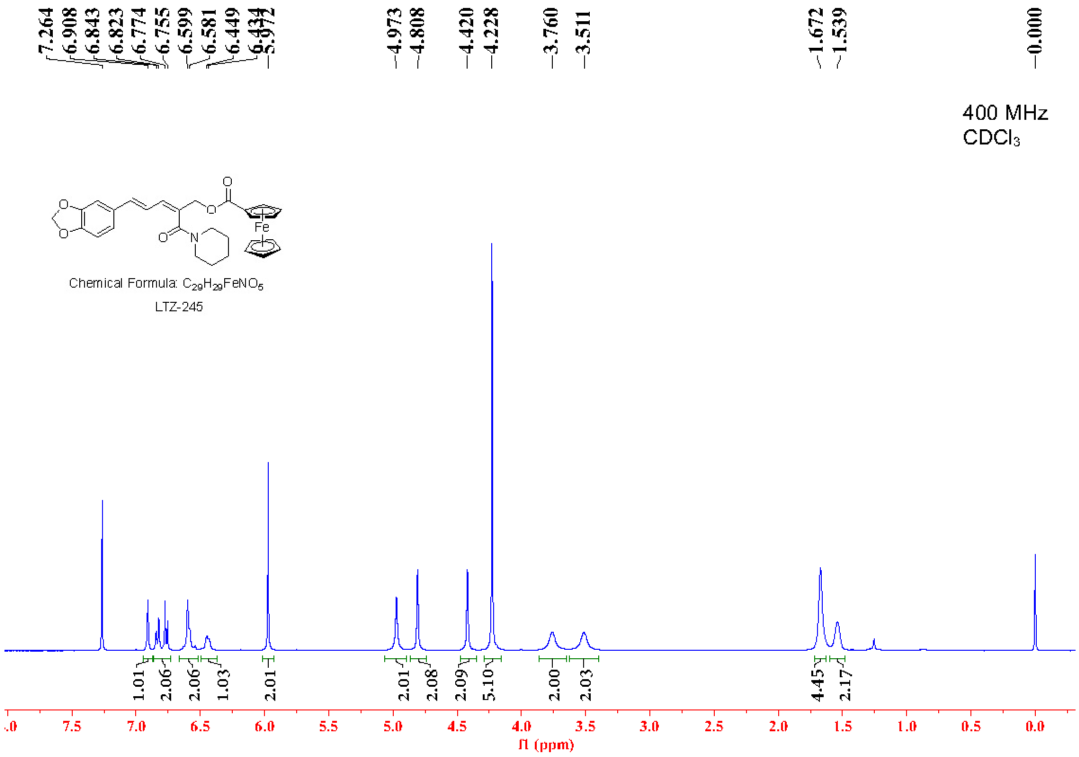
compound **5**



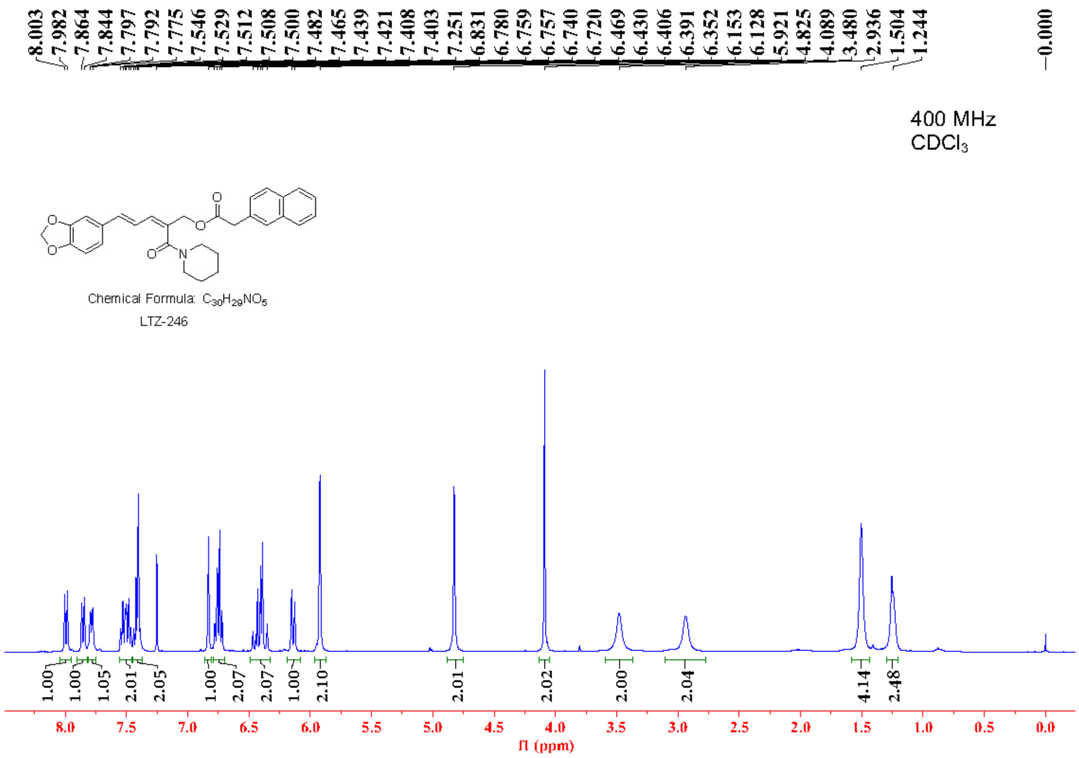
compound **6**



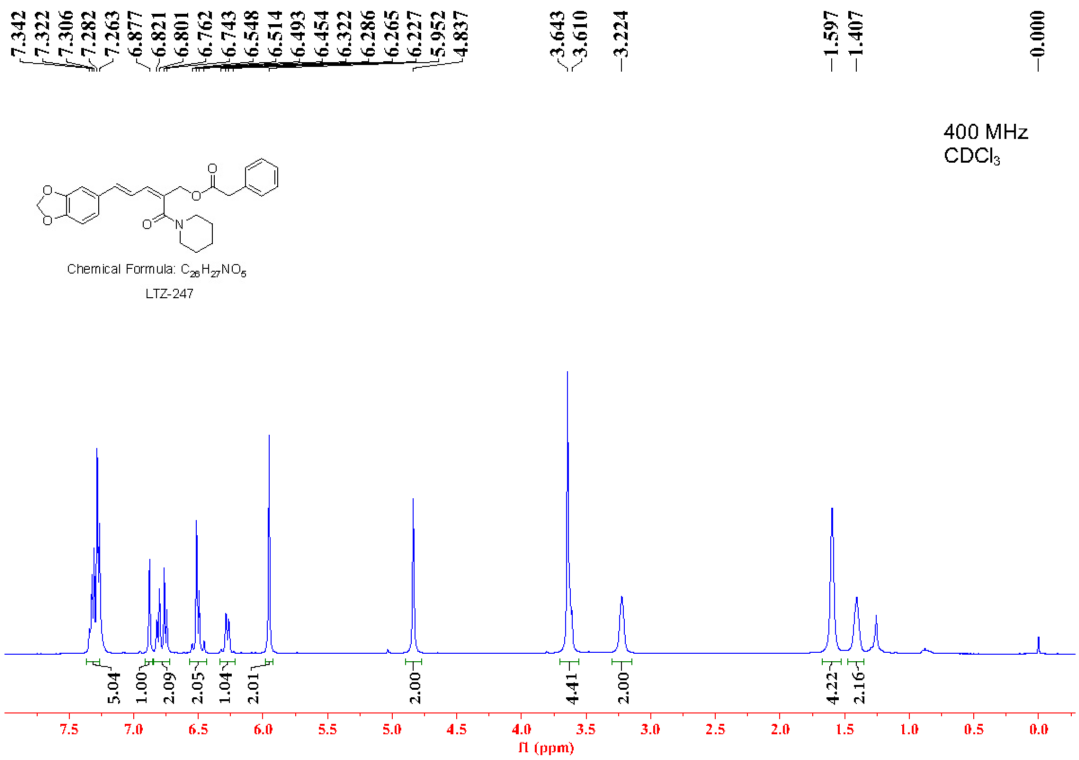
compound **7**



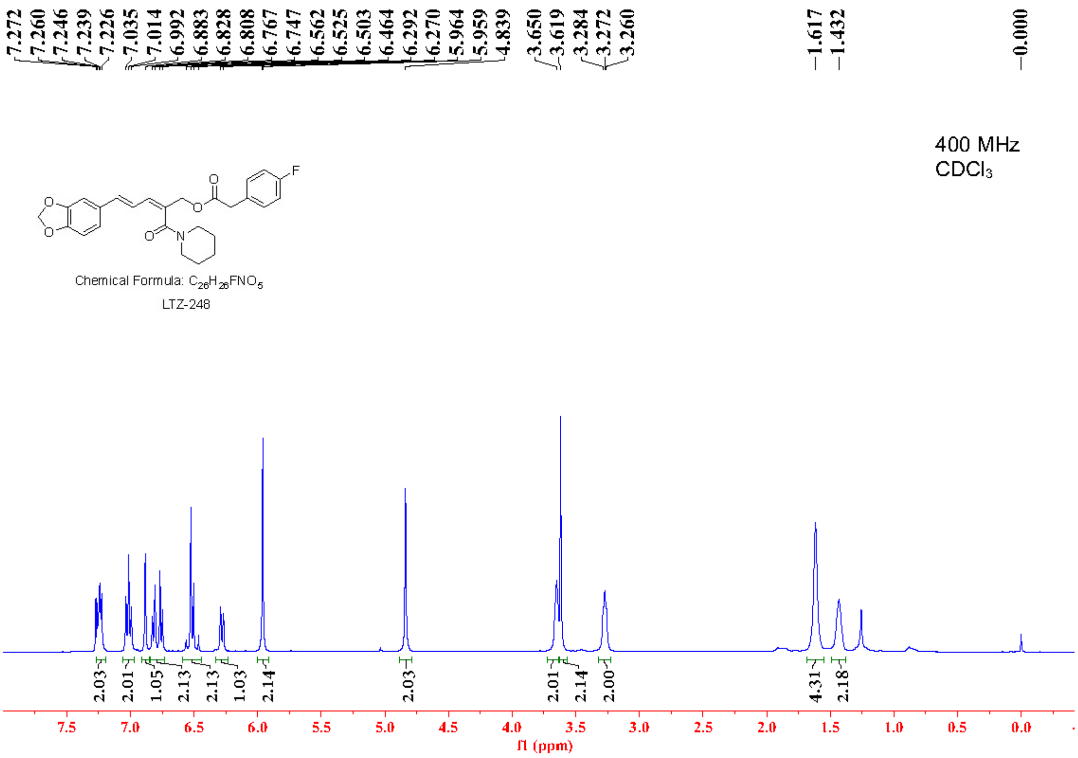
compound **8**



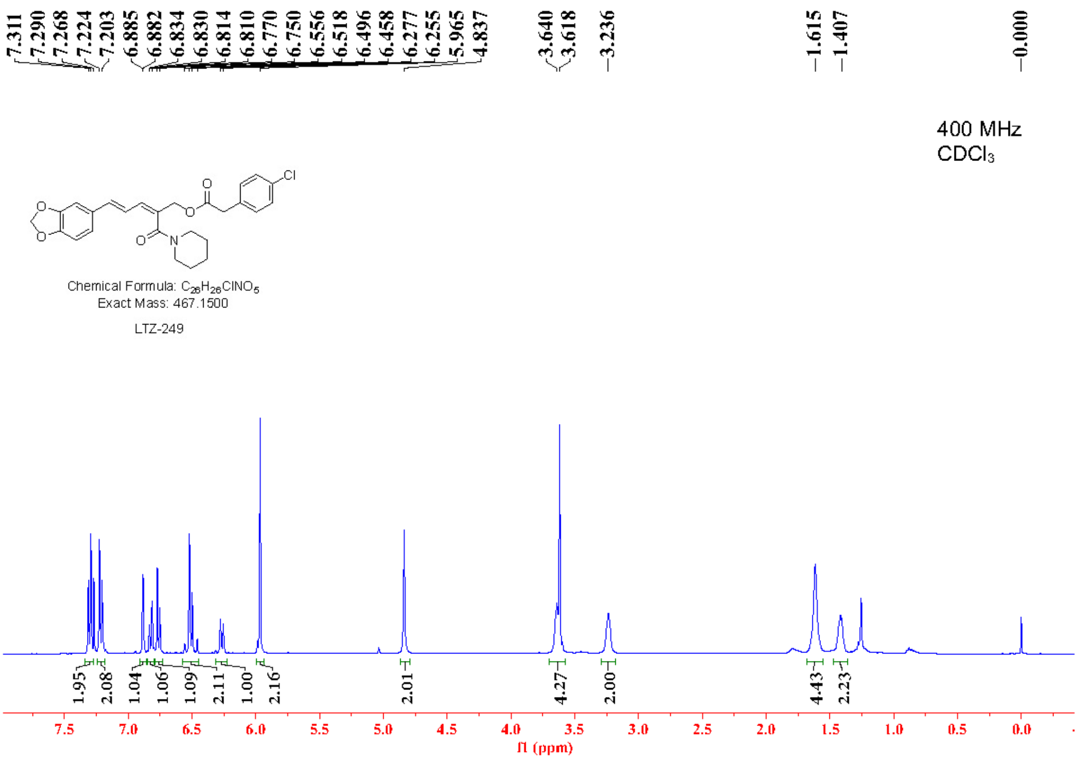
compound **9**



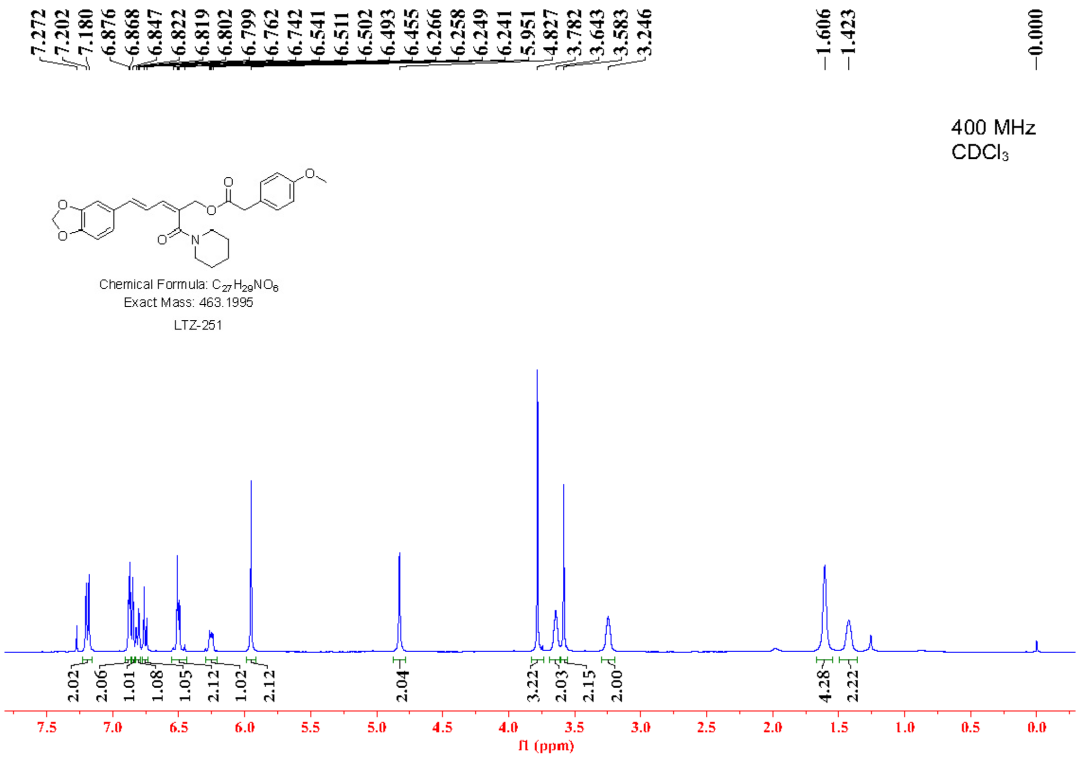
compound **10**



compound **11**



compound **12**


7.272
7.202
7.180
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6.847
6.822
6.819
6.802
6.799
6.762
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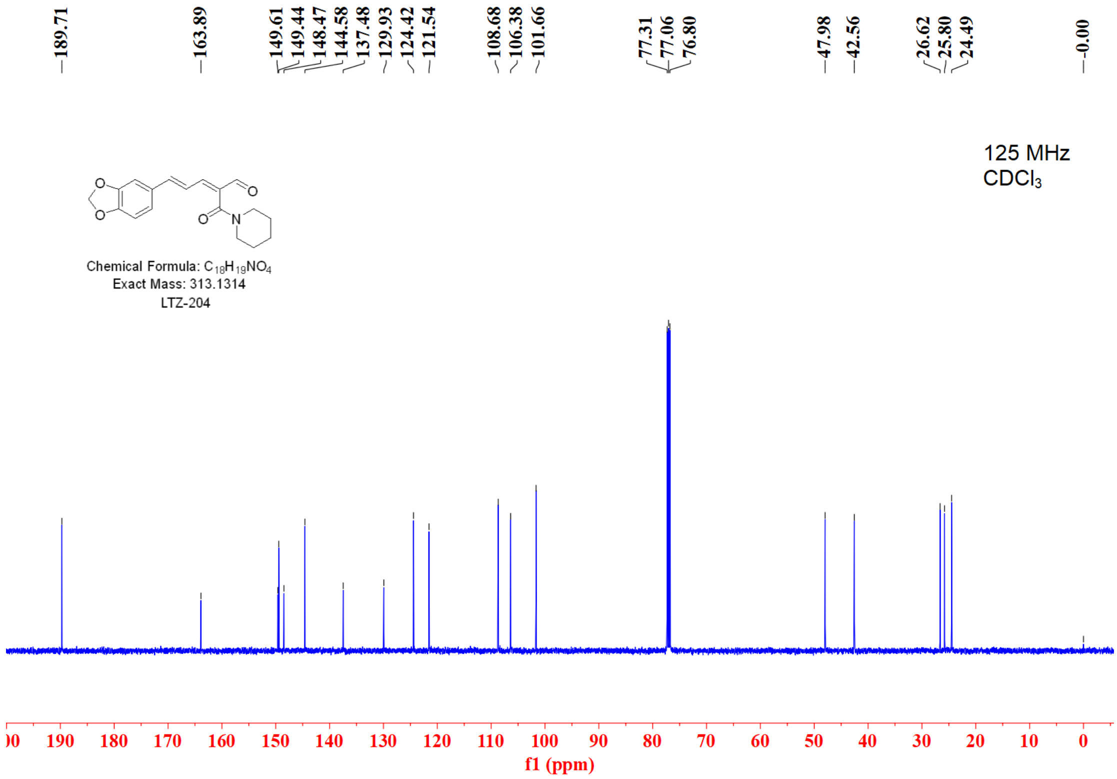
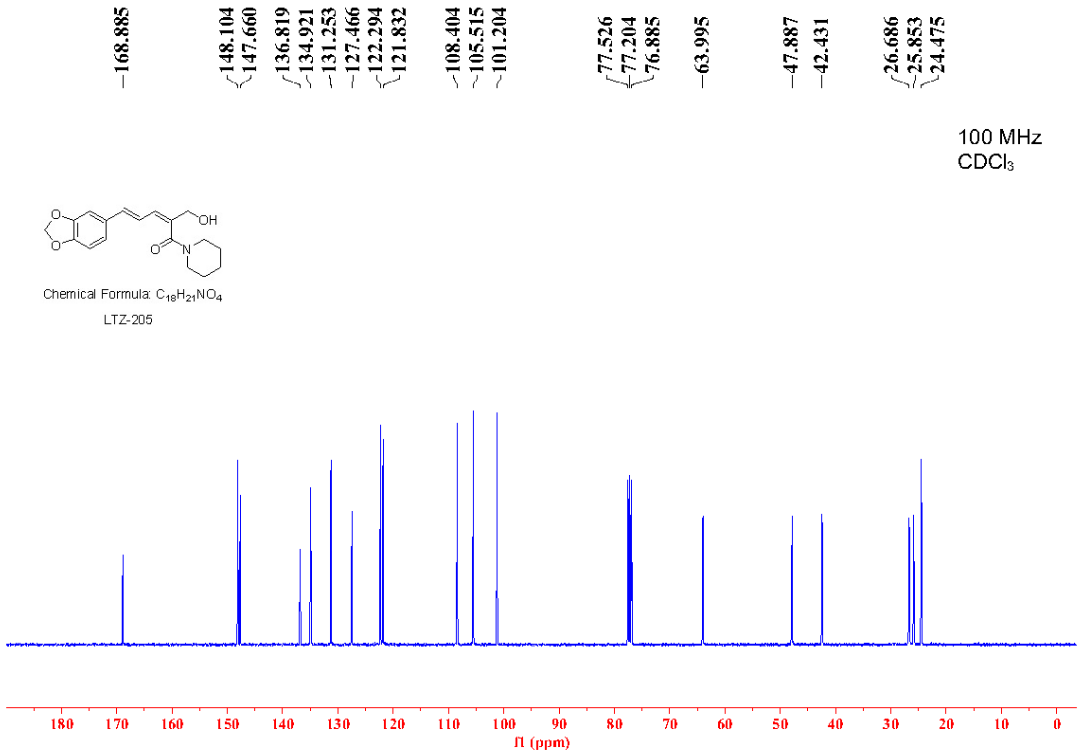
6.541
6.511
6.502
6.493
6.455
6.266
6.258
6.249
6.241
5.951
4.827
3.782
3.643
3.583
3.246
1.606
1.423
0.000
400 MHz
CDCl3
Chemical Formula: C27H29NO6
Exact Mass: 463.1995
LTZ-251
2.02
2.06
1.01
1.08
1.05
2.12
1.02
2.12
2.04
3.22
2.03
2.15
2.00
4.28
2.22
f1 (ppm)

3. ^{13}C NMR spectra of all compounds.

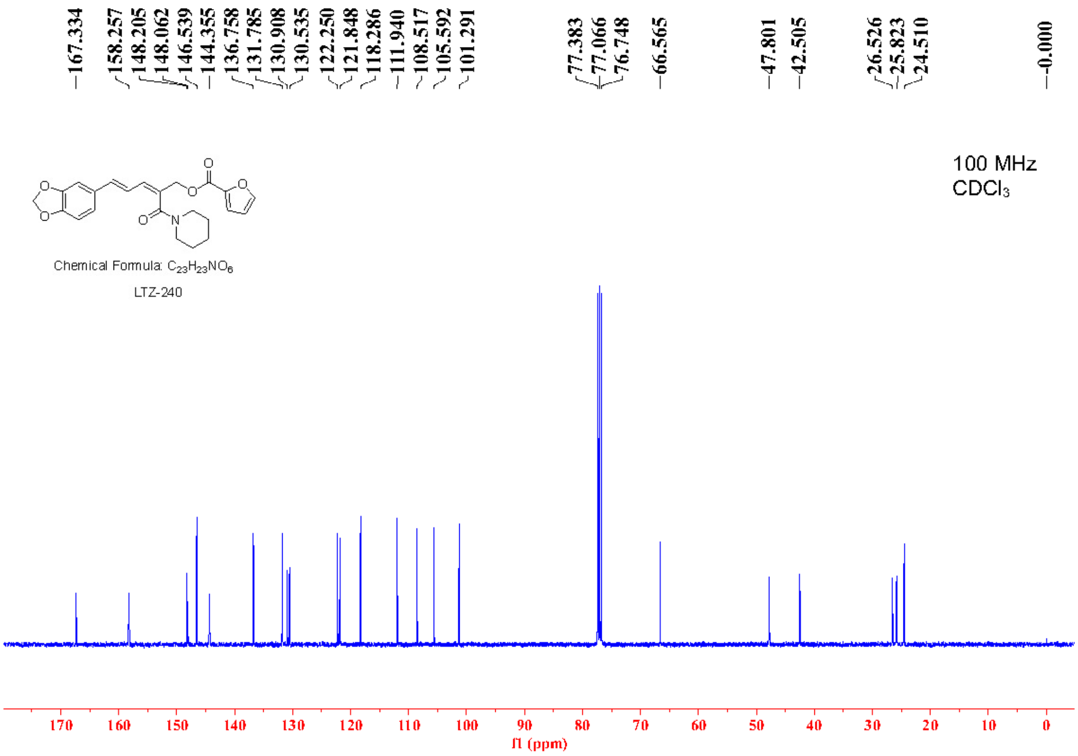
^{13}C NMR spectrum of compound **2**



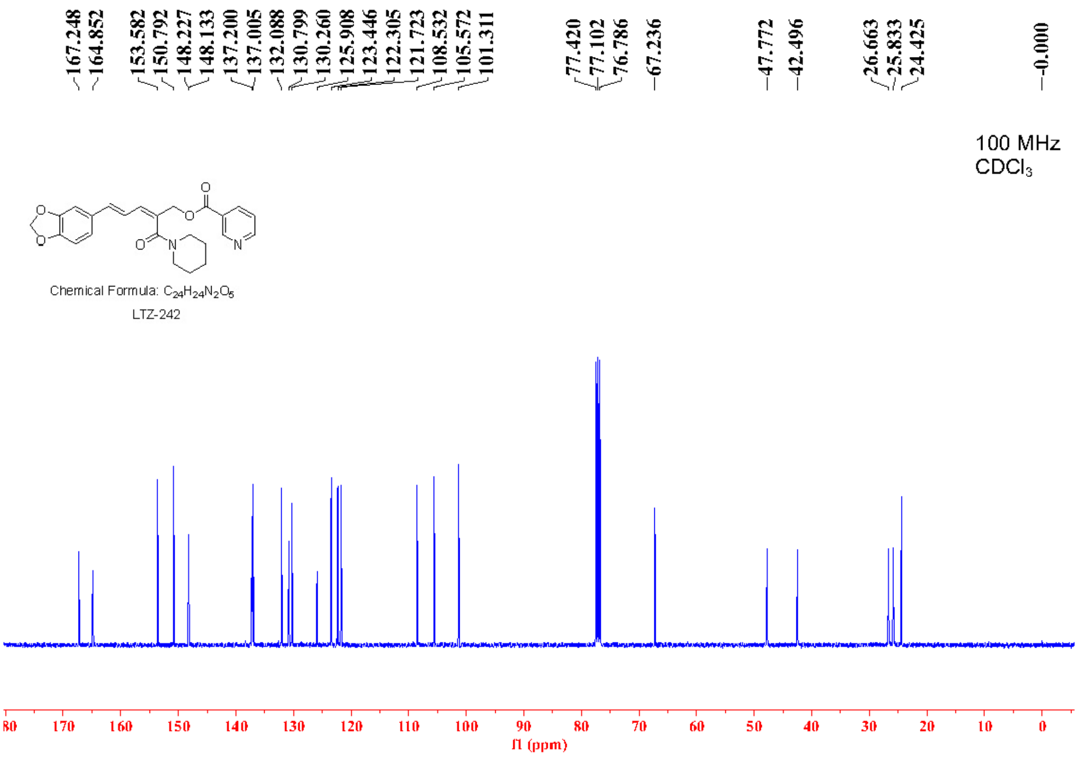
^{13}C NMR spectrum of compound **3**



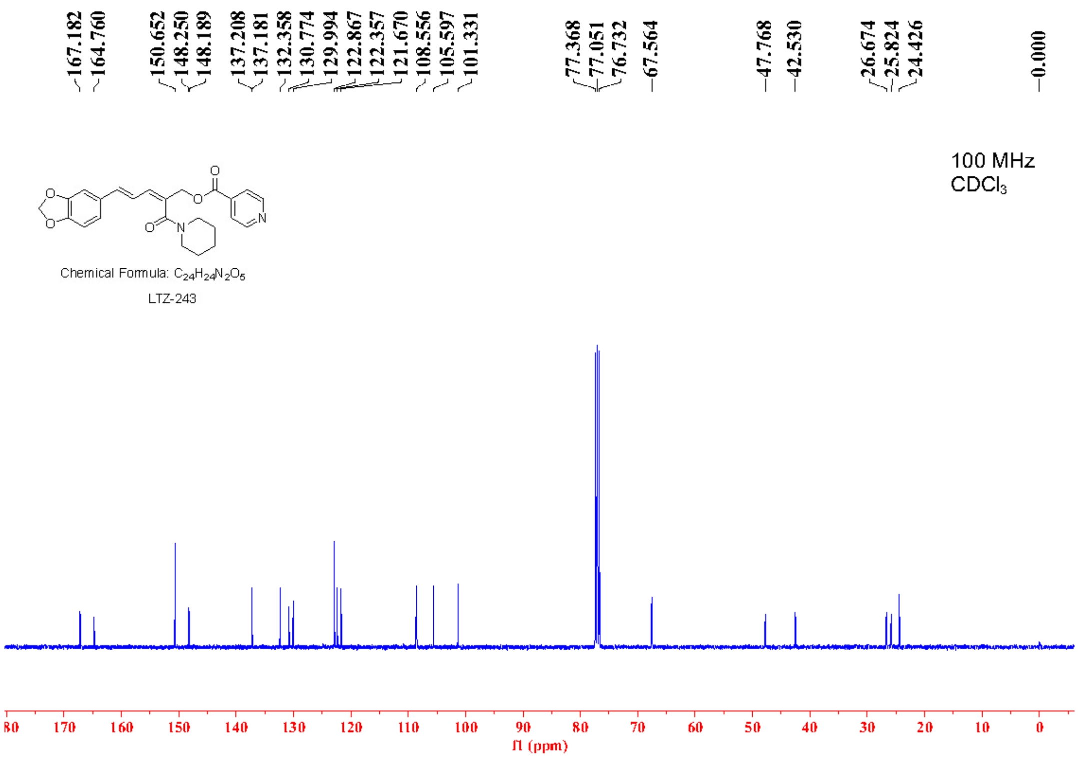
^{13}C NMR spectrum of compound **4**



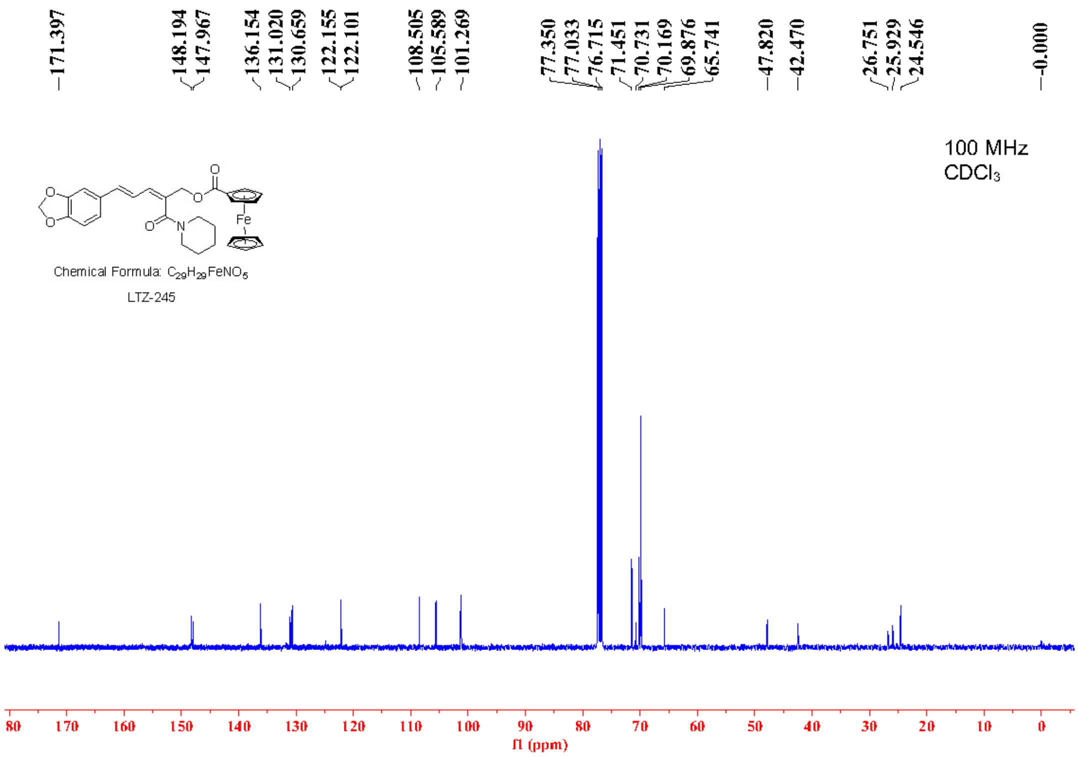
^{13}C NMR spectrum of compound **5**



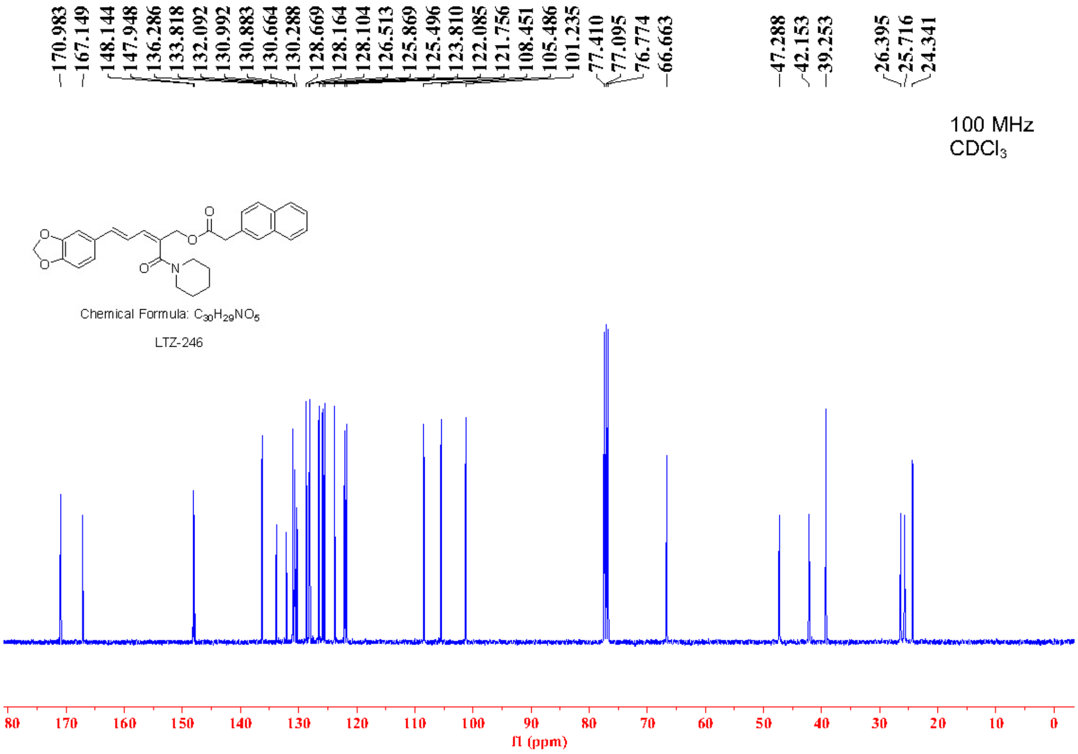
^{13}C NMR spectrum of compound **6**



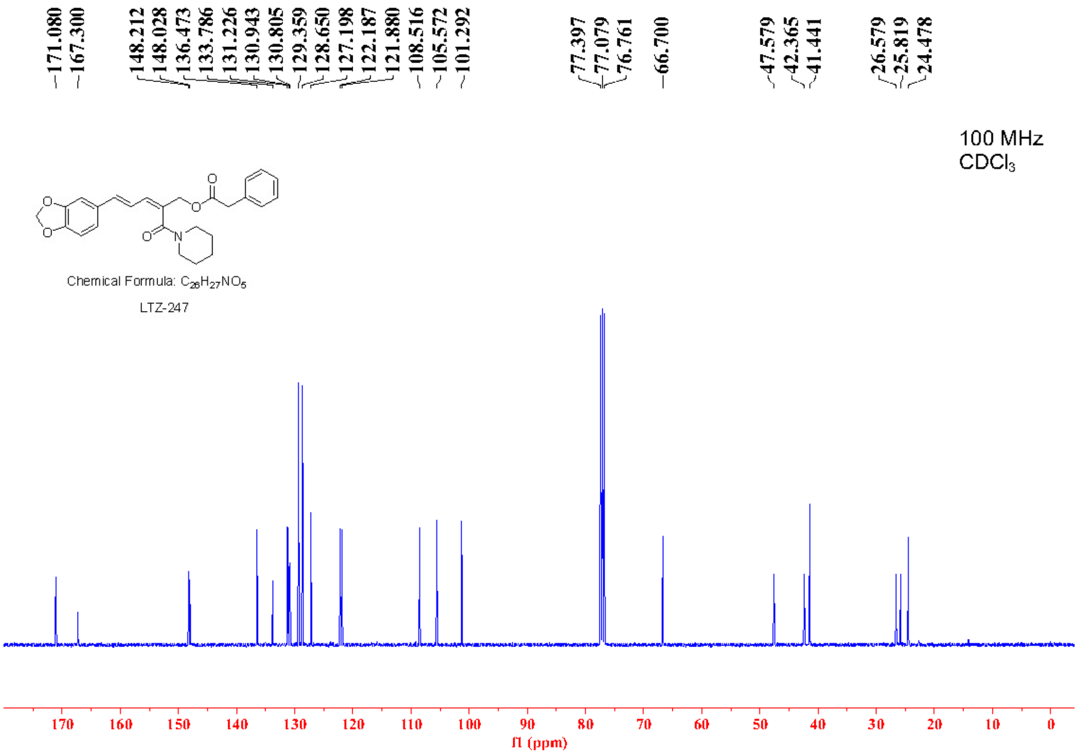
^{13}C NMR spectrum of compound **7**



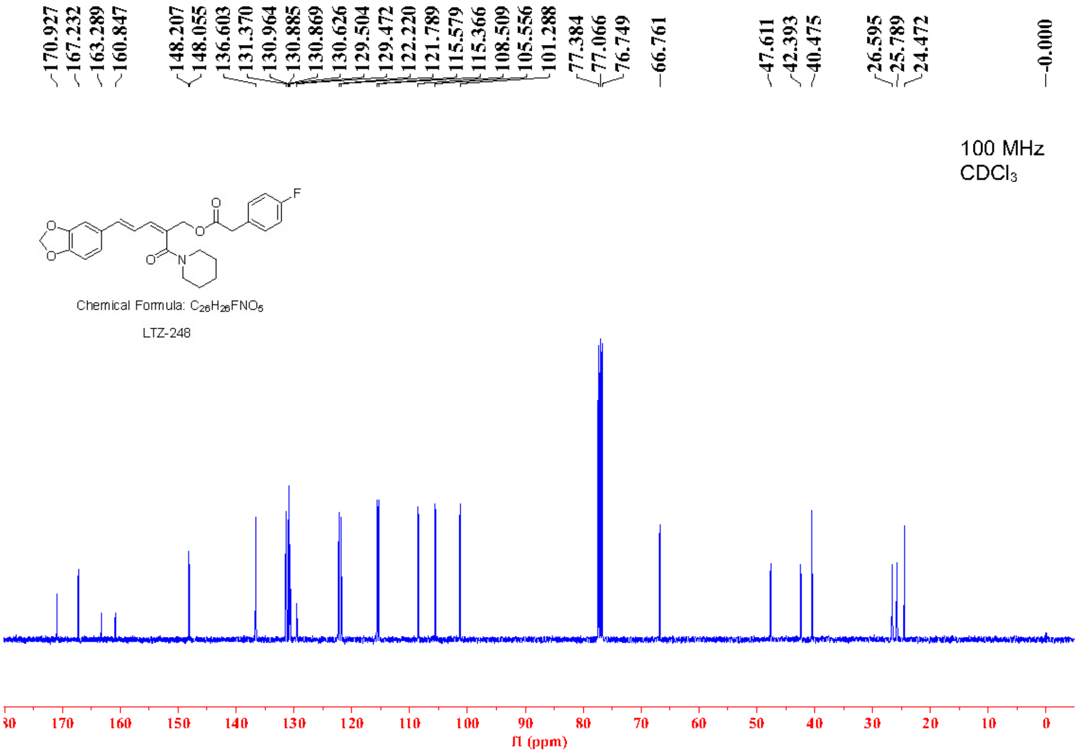
^{13}C NMR spectrum of compound **8**



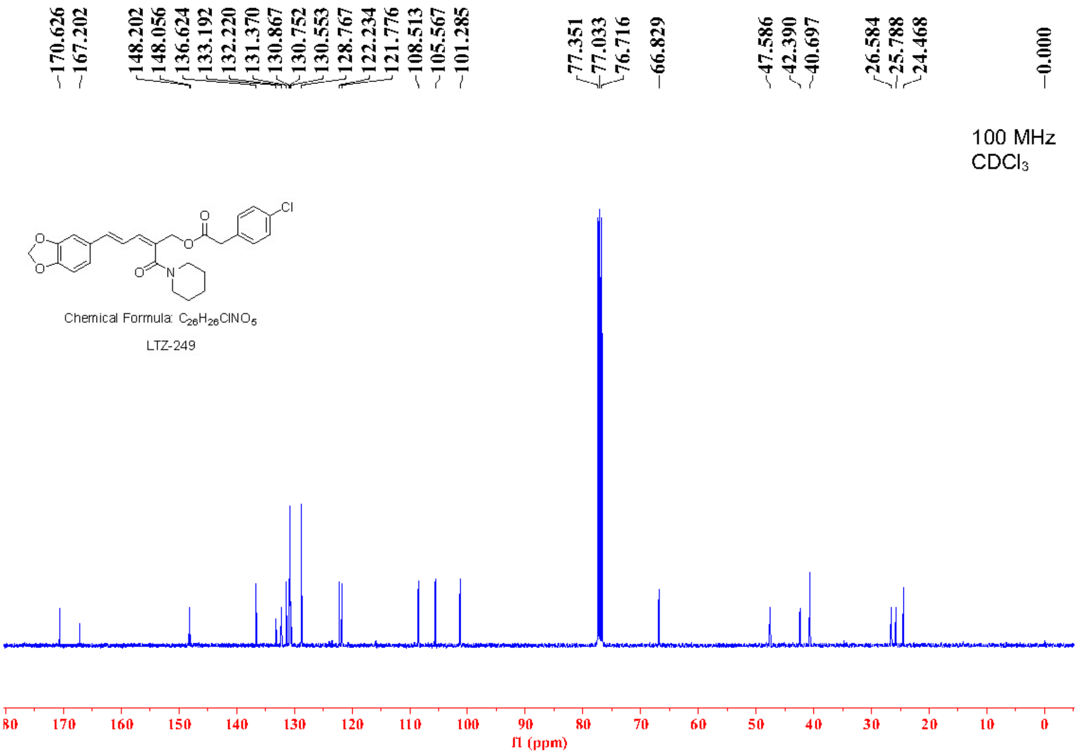
^{13}C NMR spectrum of compound **9**



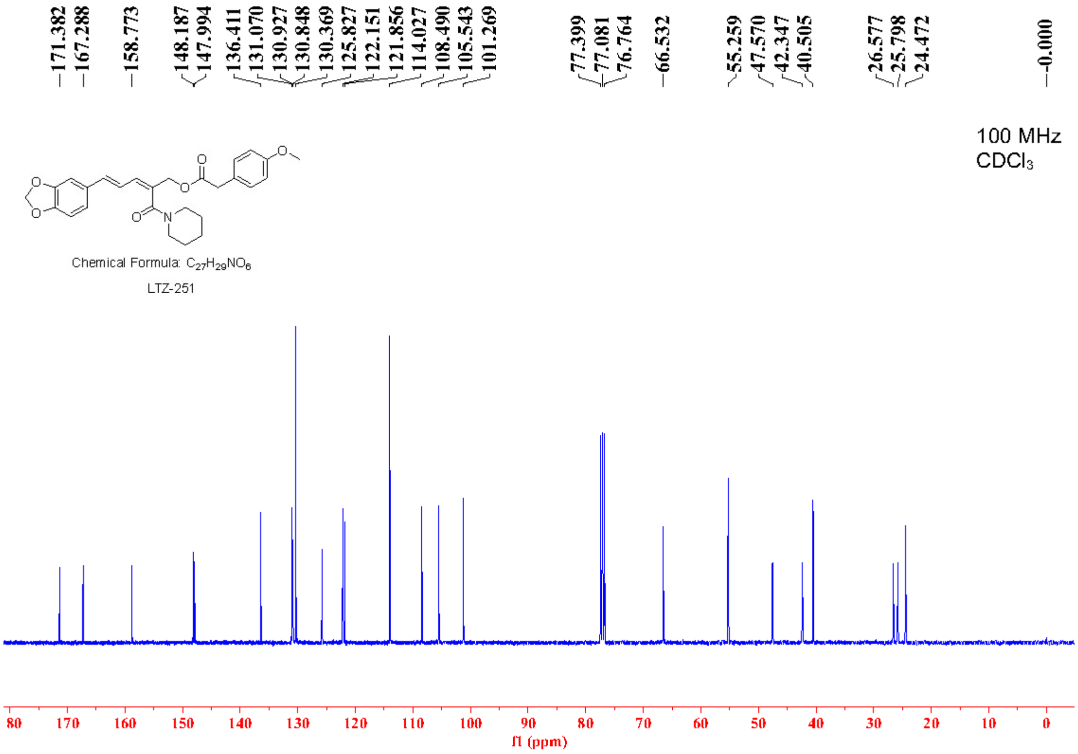
^{13}C NMR spectrum of compound **10**



^{13}C NMR spectrum of compound **11**



^{13}C NMR spectrum of compound 1**2**



4. Pictures of control effects against *T. cinnabarinus*

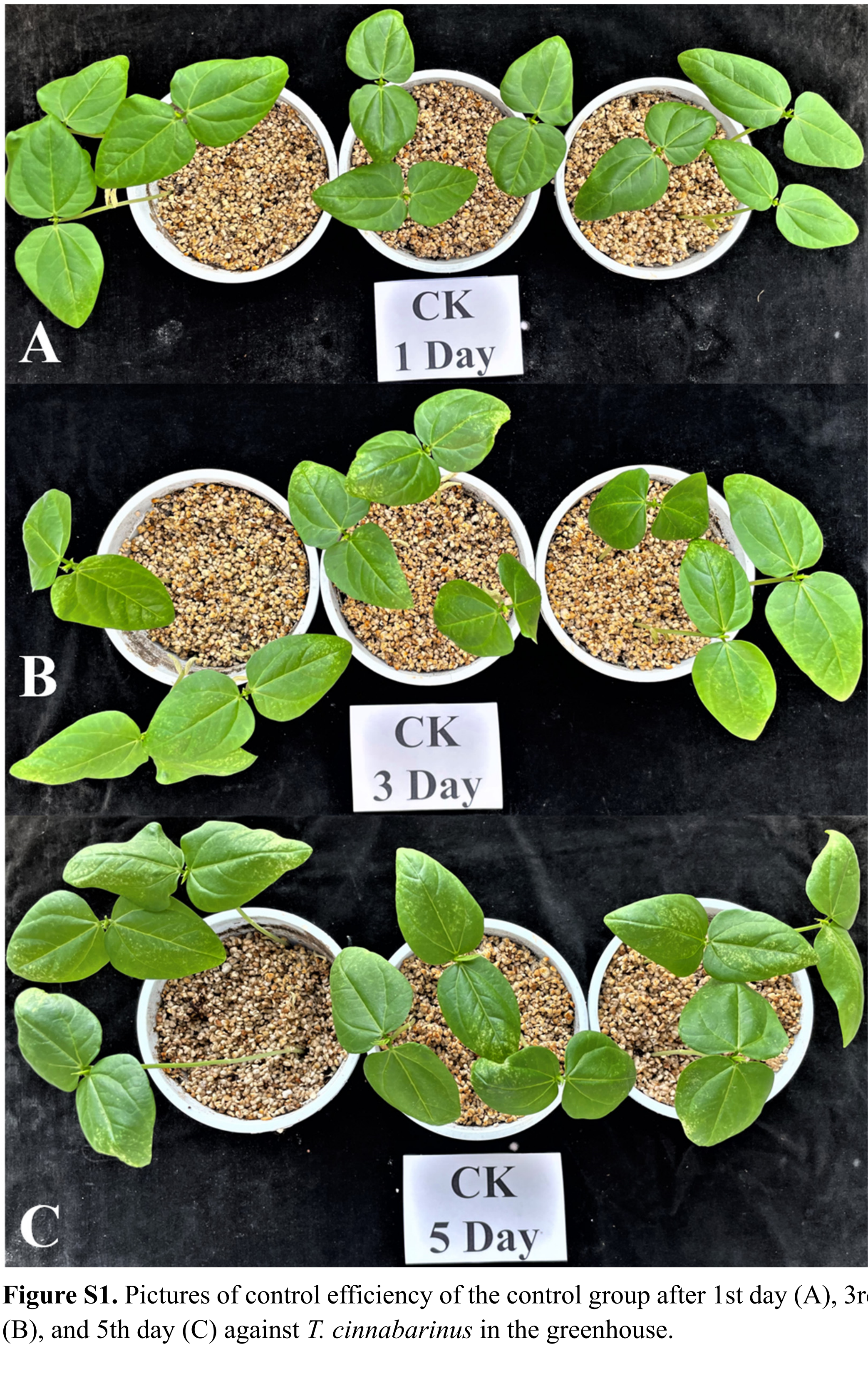


Figure S1. Pictures of control efficiency of the control group after 1st day (A), 3rd day (B), and 5th day (C) against *T. cinnabarinus* in the greenhouse.

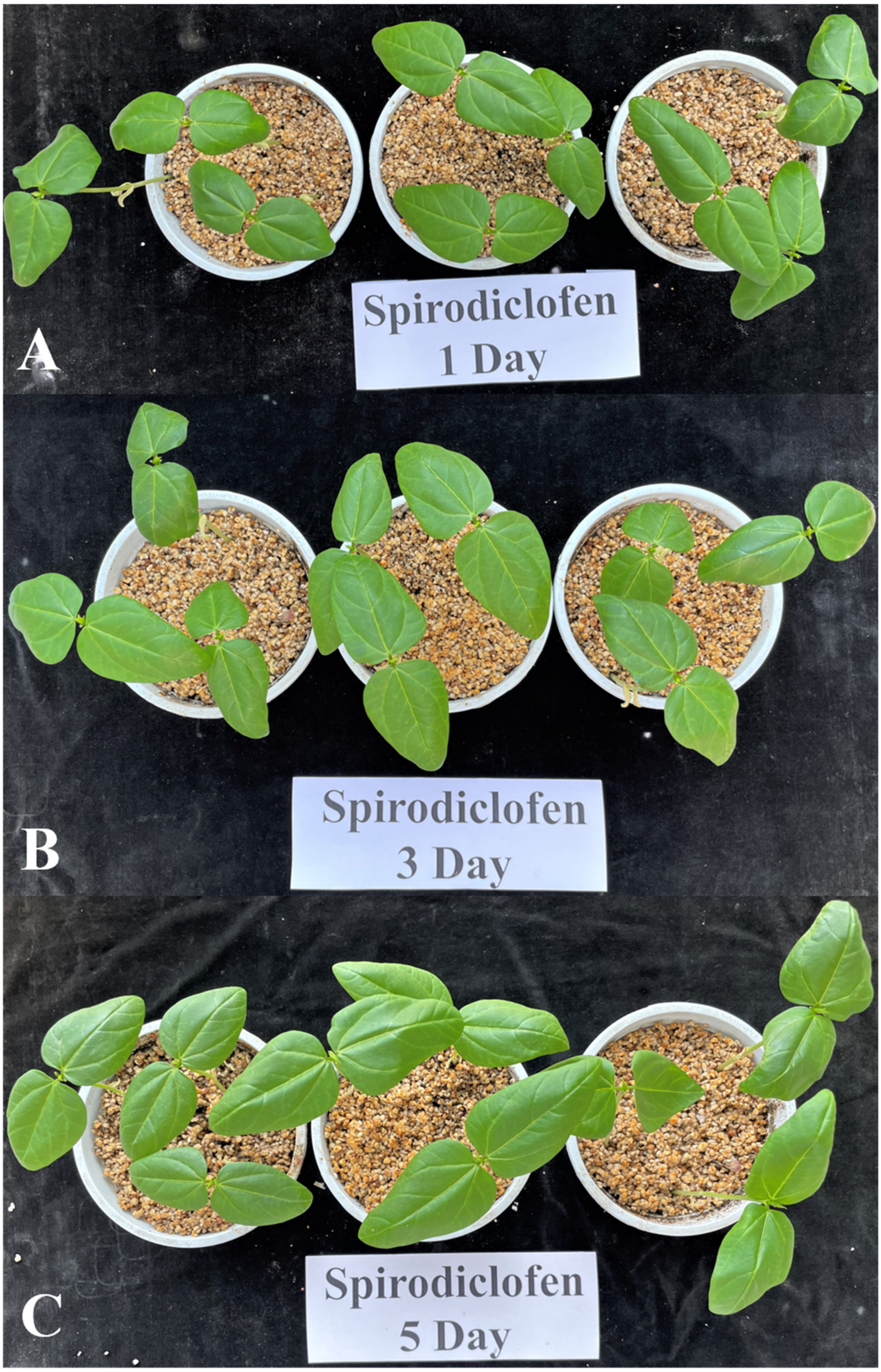


Figure S2. Pictures of control efficiency of positive control group spirodiclofen after 1st day (A), 3rd day (B), and 5th day (C) against *T. cinnabarinus* in the greenhouse.

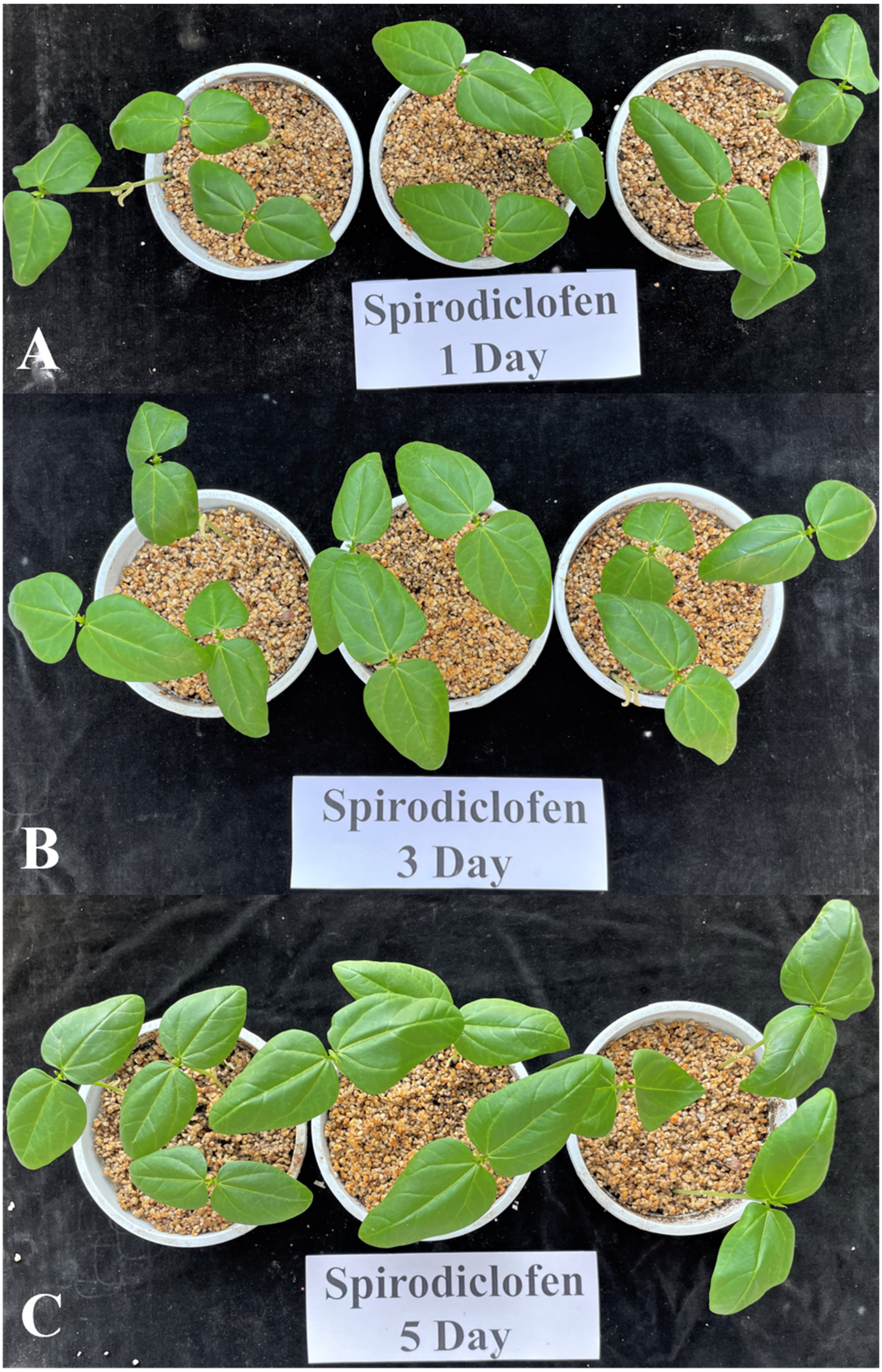


Figure S3. Pictures of control efficiency of piperine (**1**) after 1st day (A), 3rd day (B), and 5th day (C) against *T. cinnabarinus* in the greenhouse.

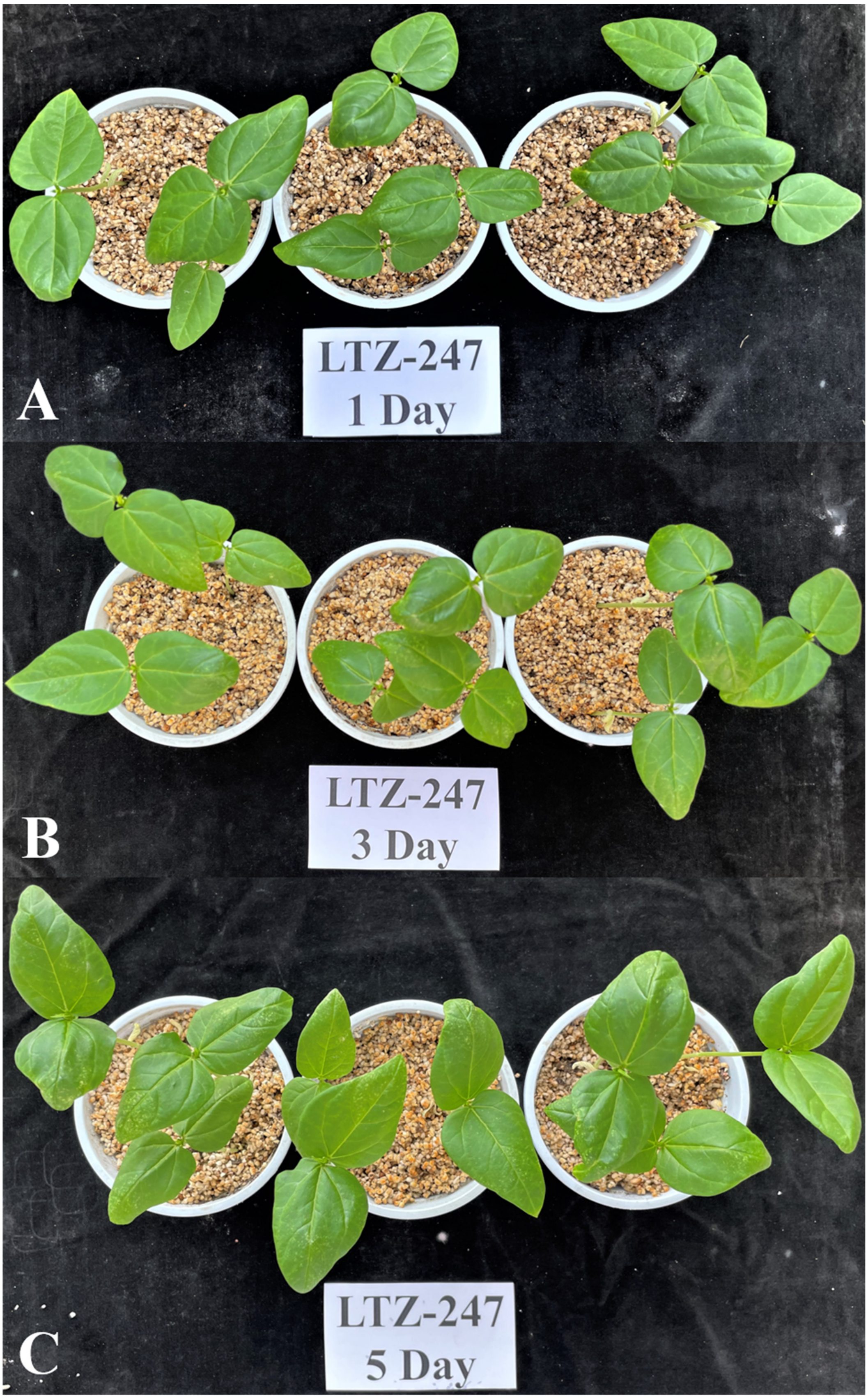


Figure S4. Pictures of control efficiency of compound **9** (LTZ-247) after 1st day (A), 3rd day (B), and 5th day (C) against *T. cinnabarinus* in the greenhouse.

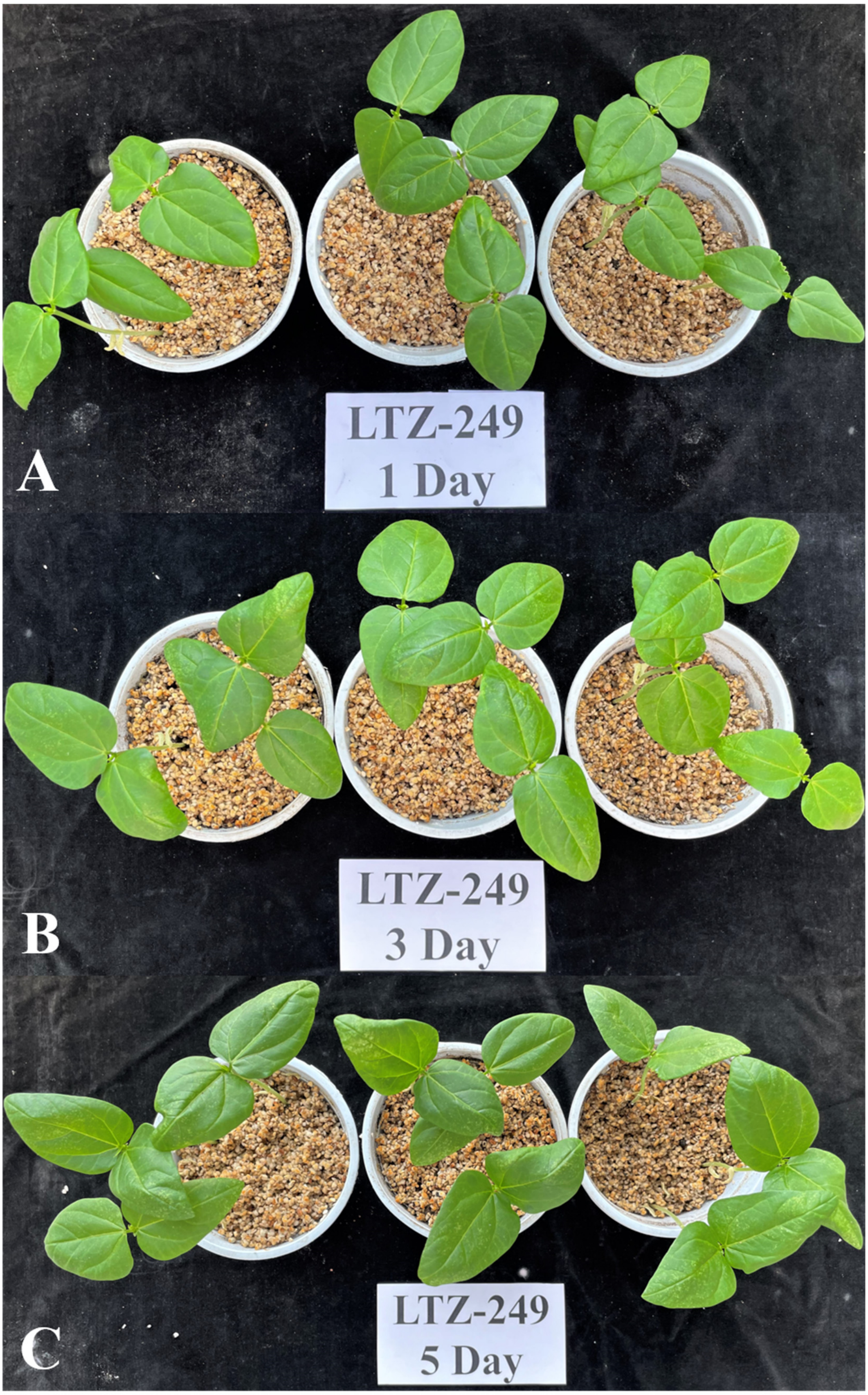


Figure S5. Pictures of control efficiency of compound **11** (LTZ-249) after 1st day (A), 3rd day (B), and 5th day (C) against *T. cinnabarinus* in the greenhouse.