Supplementary material

Communication

Diethyl 2-((aryl(alkyl)amino)methylene)malonates: Unreported Mycelial Growth Inhibitors Against *Fusarium oxysporum*

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1. Physical and Spectroscopical data of DAMMs (1-5):

Diethyl 2-(((4-chlorophenyl)amino)methylene)malonate (**1**). White crystals, 80% yield. Melting point: 80-84 °C. Compound **1** was purified by PLC, positive to Dragendorff's reagent, soluble in dichloromethane, chloroform, and ethyl acetate, and insoluble in ethanol and water; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 10.99 (*d*, *J* = 13.4 Hz, 1H), 8.45 (*d*, *J* = 13.6 Hz, 1H), 7.35 – 7.31 (*m*, 2H), 7.08 – 7.05 (*m*, 2H), 4.27 (*dq*, *J* = 28.9, 7.1 Hz, 4H), 1.35 (*dt*, *J* = 24.8, 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 169.1, 165.7, 151.7, 138.1, 130.2, 130.0, 118.5 94.4, 60.7, 60.4, 14.5, 14.4. HRESIMS, positive mode, *m*/*z* $[M+Na]^+$ = 320.0624 (calcd. 320.0665), corresponding to the molecular formula $C_{14}H_{16}ClNO_4Na$.

Diethyl 2-(((2-nitrophenyl)amino)methylene)malonate (**2**). Yellow solid, 85% yield. Melting point: 100-102 °C. Compound **2** was purified by PLC, positive to Dragendorff's reagent, soluble in dichloromethane, chloroform, and ethyl acetate, and insoluble in ethanol and water; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 12.57 (*d*, *J* = 12.9 Hz, 1H), 8.53 (*d*, *J* = 13.0 Hz, 1H), 8.26 (*dd*, *J* = 8.4, 1.5 Hz, 1H), 7.71 – 7.66 (*m*, 1H), 7.50 (*d*, *J* = 8.2 Hz, 1H), 7.21 (*ddd*, *J* = 8.4, 7.3, 1.1 Hz, 1H), 4.34 (*dq*, *J* = 58.8, 7.1 Hz, 4H), 1.37 (*dt*, *J* = 23.2, 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 166.9, 165.8, 148.4, 137.2, 136.2, 136.0, 127.0, 123.5, 116.9, 99.6, 61.1, 60.9, 14.5, 14.5. HRESIMS, positive mode, *m*/*z* $[M+Na]^+$ = 331.0839 (calcd. 331.0906), corresponding to the molecular formula $C_{15}H_{18}N_2O_6Na$.

Diethyl 2-((cyclohexylamino)methylene)malonate (**3**). Brown solid, 90% yield. Melting point: 102-104 °C. Compound **3** was purified by PLC, positive to Dragendorff's reagent, soluble in dichloromethane, chloroform, and ethyl acetate, and insoluble in ethanol and water; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 9.24 (*s*, 1H), 8.05 (*d*, *J* = 14.3 Hz, 1H), 4.19 (*dq*, *J* = 27.1, 7.1 Hz, 4H), 3.25 – 3.17 (*m*, 1H), 1.94 (*dt*, *J* = 7.6, 3.9 Hz, 2H), 1.79 – 1.73 (*m*, 2H), 1.64 – 1.57 (*m*, 1H), 1.41 – 1.34 (*m*, 3H), 1.30 (*dt*, *J* = 27.2, 7.1 Hz, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 169.6, 166.5, 158.2, 89.2, 59.8, 59.6, 58.2, 34.0, 25.2, 24.6, 14.6, 14.5; HRESIMS, positive mode, *m*/*z* $[M+Na]^+$ = 292.1523 (calcd. 292.1524), corresponding to the molecular formula $C_{14}H_{23}NO_4Na$.

Diethyl 2-((naphthalen-1-ylamino)methylene)malonate (**4**). Purple solid, 74% yield. Melting point: 122-124 °C. Compound **4** was purified by PLC, positive to Dragendorff's reagent, ad soluble in dichloromethane, chloroform, and ethyl acetate, and insoluble in ethanol and water; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 11.78 (*d*, *J* = 13.1 Hz, 1H), 8.67 (*d*, *J* = 13.2 Hz, 1H), 8.04 (*d*, *J* = 8.5 Hz, 1H), 7.89 (*d*, *J* = 7.6 Hz, 1H), 7.70 (*d*, *J* = 8.2 Hz, 1H), 7.58 (*dddd*, *J* = 23.1, 8.0, 6.9, 1.2 Hz, 2H), 7.49 (*t*, *J* = 7.9 Hz, 1H), 7.36 (*d*, *J* = 7.5 Hz, 1H), 4.33 (*dq*, *J* = 56.9, 7.1 Hz, 4H), 1.38 (*dt*, *J* = 41.9, 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 169.7, 165.9 153.7, 135.7, 134.4, 128.8, 127.1, 126.9, 125.9, 125.7, 125.6, 120.8, 113.4, 94.5, 60.7, 60.3, 14.6, 14.5; HRESIMS, positive mode, *m*/*z* $[M+Na]^+$ = 336.1219 (calcd. 336.1211), corresponding to the molecular formula $C_{18}H_{19}NO_4Na$.

Diethyl 2-((phenylamino)methylene)malonate (**5**). Brown solid, 96% yield. Melting point: 48-50 °C. Compound **5** was purified by PLC, positive to Dragendorff's reagent, soluble in dichloromethane, chloroform, and ethyl acetate, and insoluble in ethanol and water; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.00 (*d*, *J* = 13.6 Hz, 1H), 8.53 (*d*, *J* = 13.7 Hz, 1H), 7.39 – 7.35 (*m*, 2H), 7.17 – 7.12 (*m*, 3H), 4.28 (*dq*, *J* = 31.5, 7.1 Hz, 4H), 1.35 (*dt*, *J* = 26.4, 7.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 165.9, 152.1, 139.4, 130.0, 125.0, 117.3, 93.7, 60.5, 60.2, 14.6, 14.4; HRESIMS, positive mode, *m*/*z* $[M+Na]^+$ = 286.1046 (calcd. 286.1055), corresponding to the molecular formula $C_{14}H_{17}NO_4Na$.

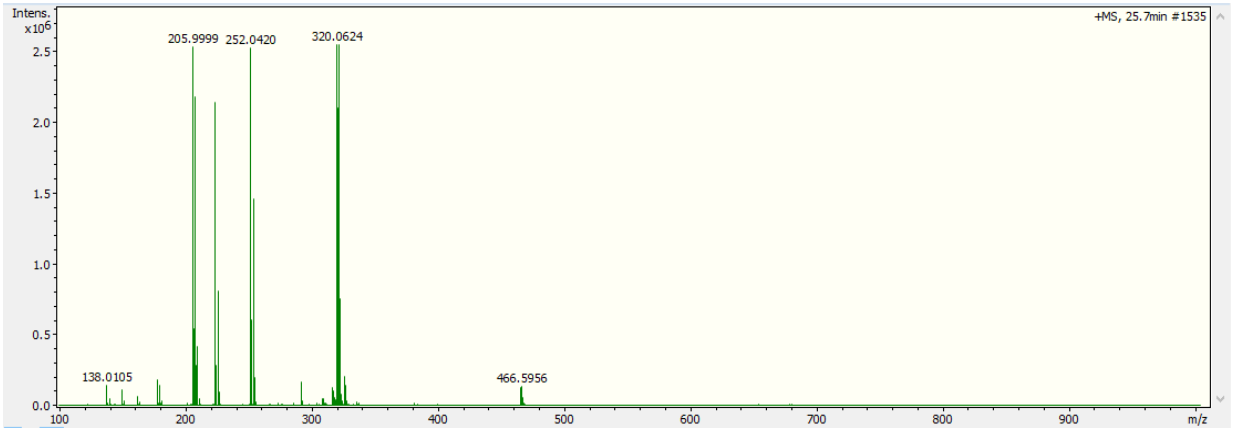


Figure S1. High-resolution mass spectra of compound **1**.

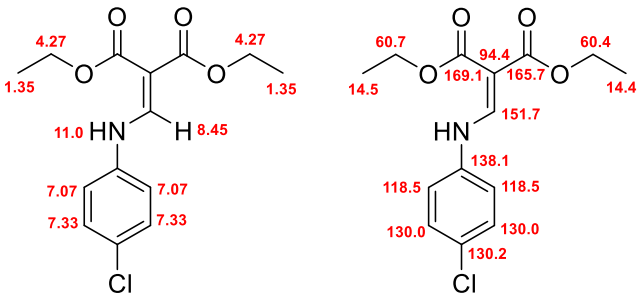


Figure S2. Assignments of ^{1}H and ^{13}C NMR chemical shifts of compound **1**.

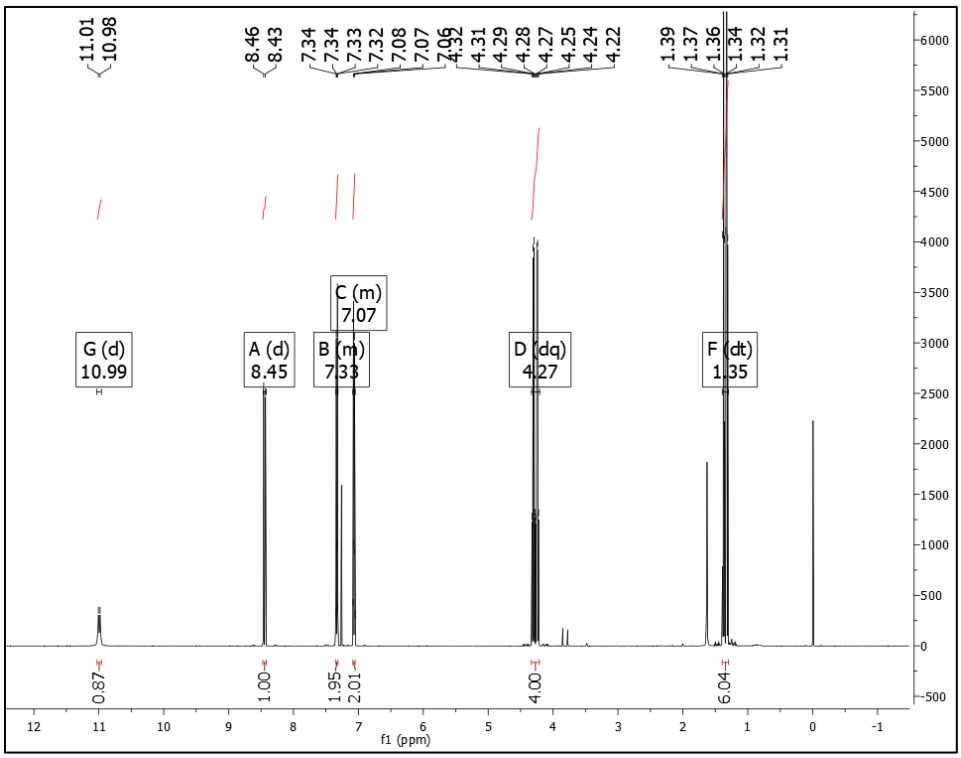


Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **1**.

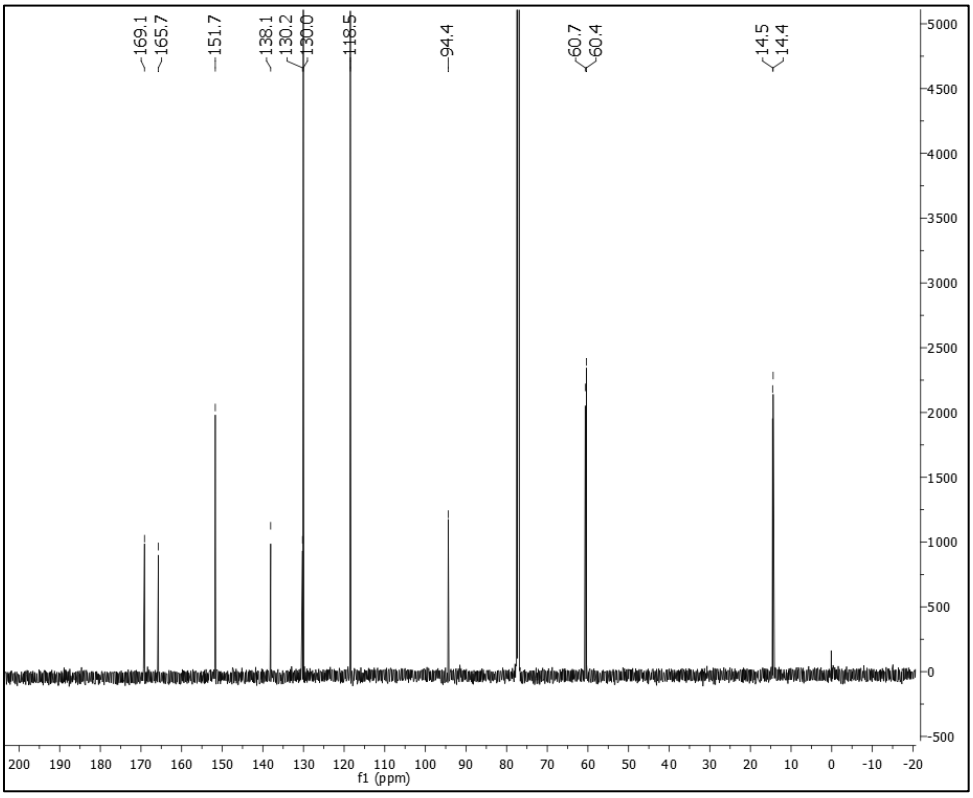


Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 125 MHz) of compound **1**.

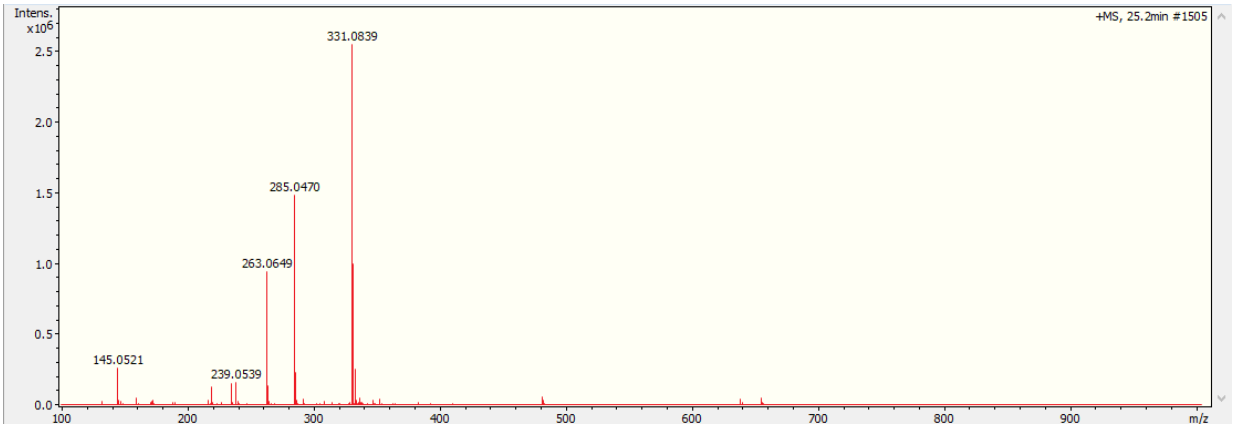


Figure S5. High-resolution mass spectra of compound **2**.

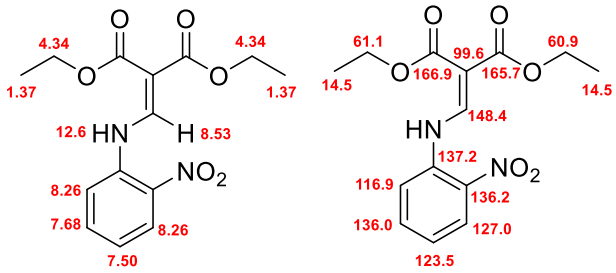


Figure S6. Assignments of ^{1}H and ^{13}C NMR chemical shifts of compound **2**.

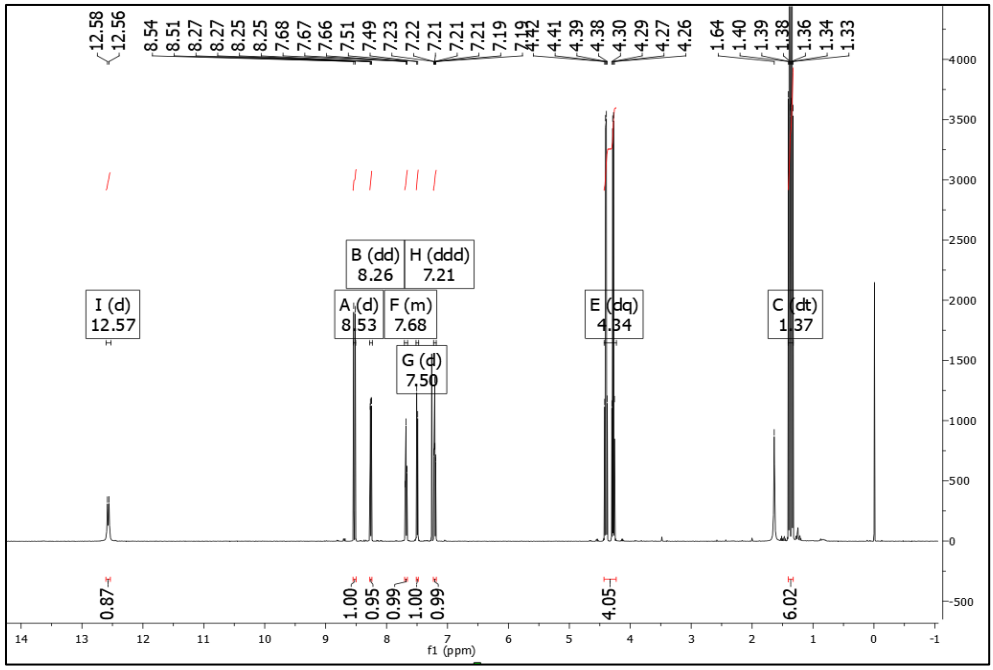


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **2**.

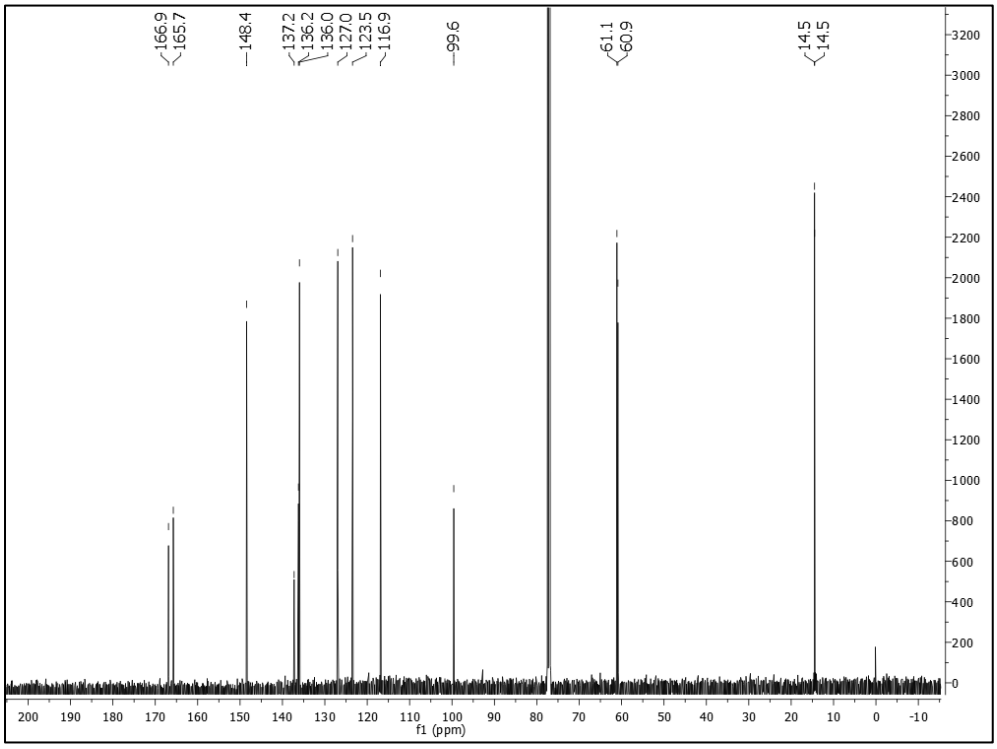


Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 125 MHz) of compound **2**.

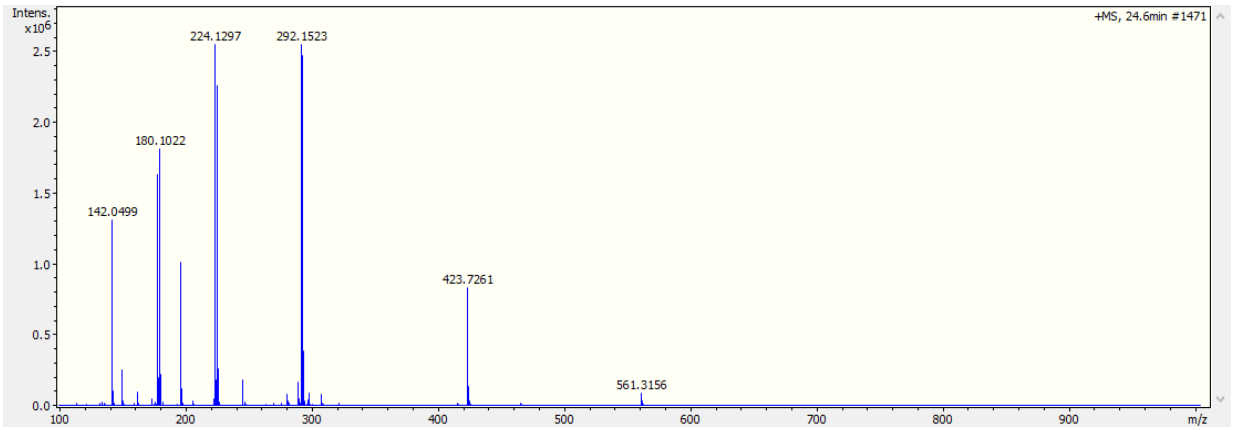


Figure S9. High-resolution mass spectra of compound **3**.

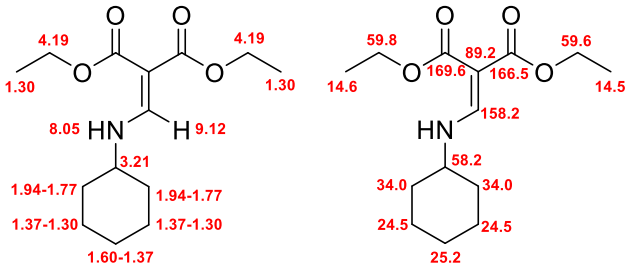


Figure S10. Assignments of ^{1}H and ^{13}C NMR chemical shifts of compound **3**.

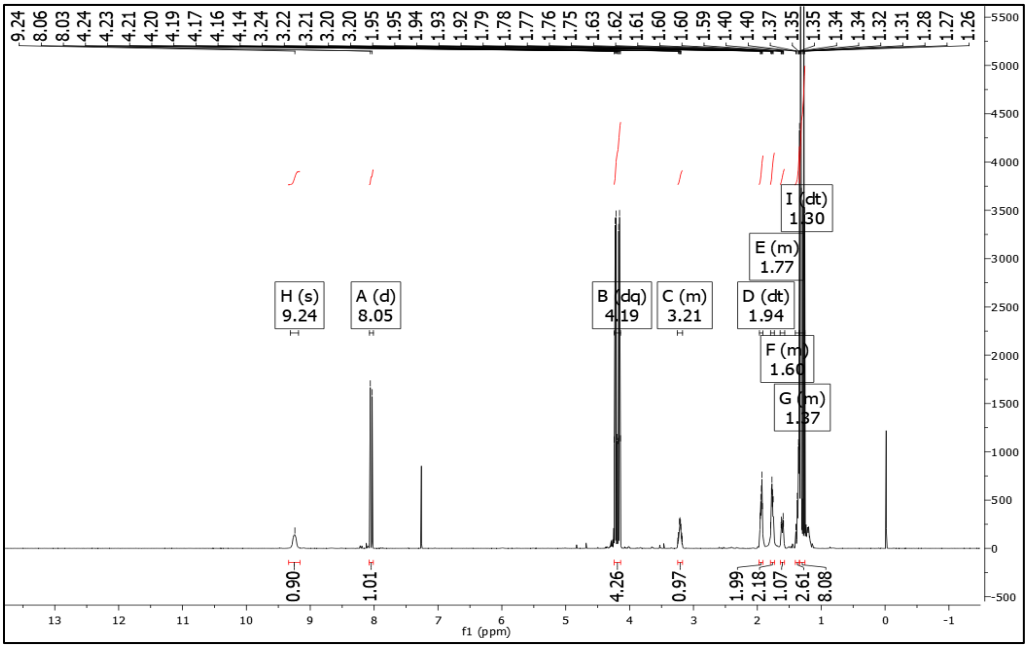


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **3**.

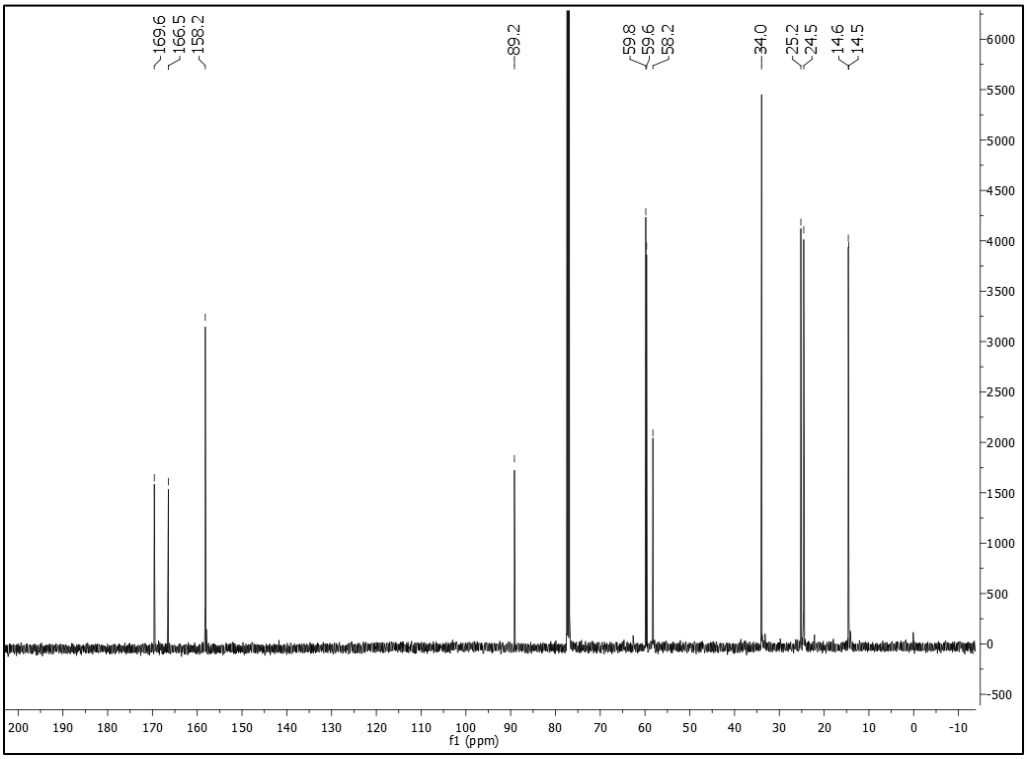


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 125 MHz) of compound **3**.

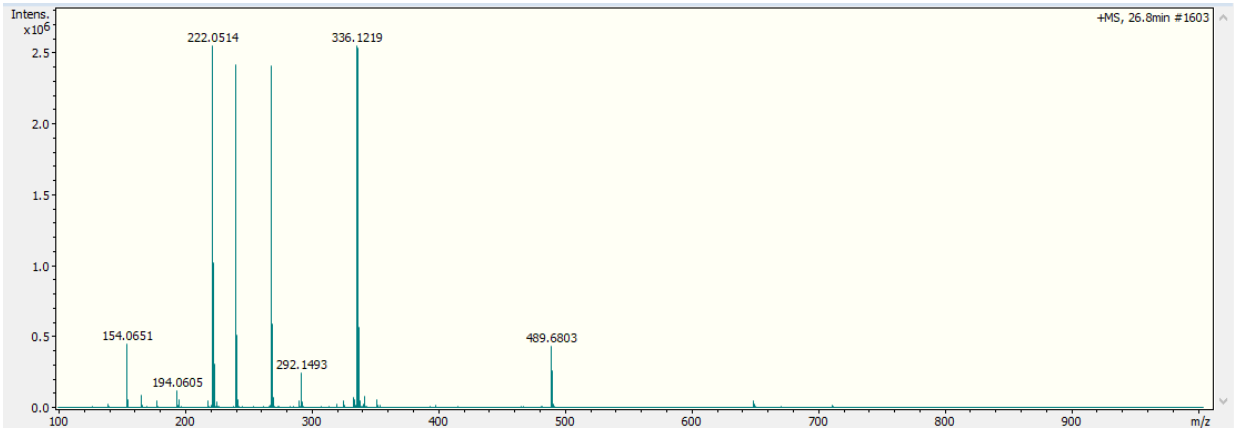


Figure S13. High-resolution mass spectra of compound **4**.

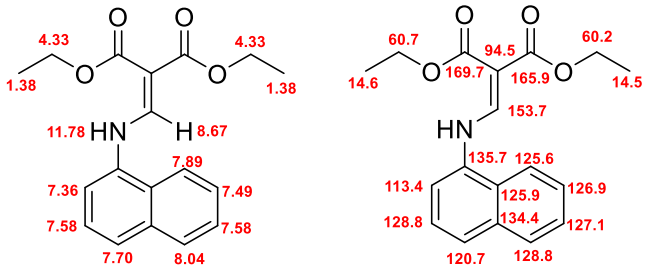


Figure S14. Assignments of ^{1}H and ^{13}C NMR chemical shifts of compound **4**.

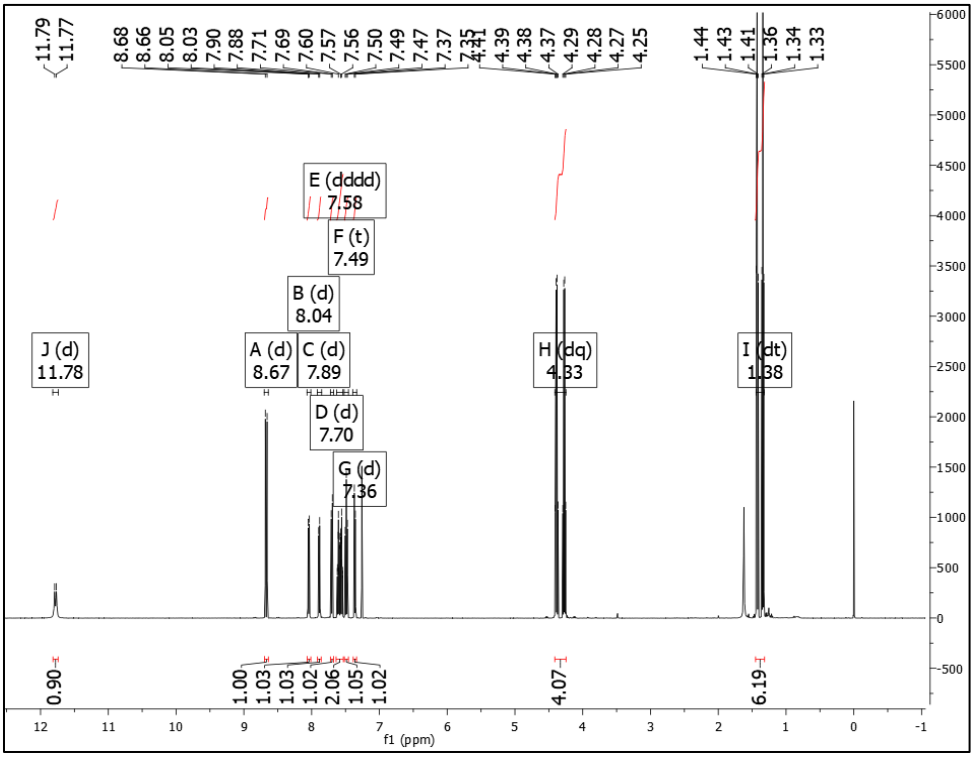


Figure S15. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **4**.

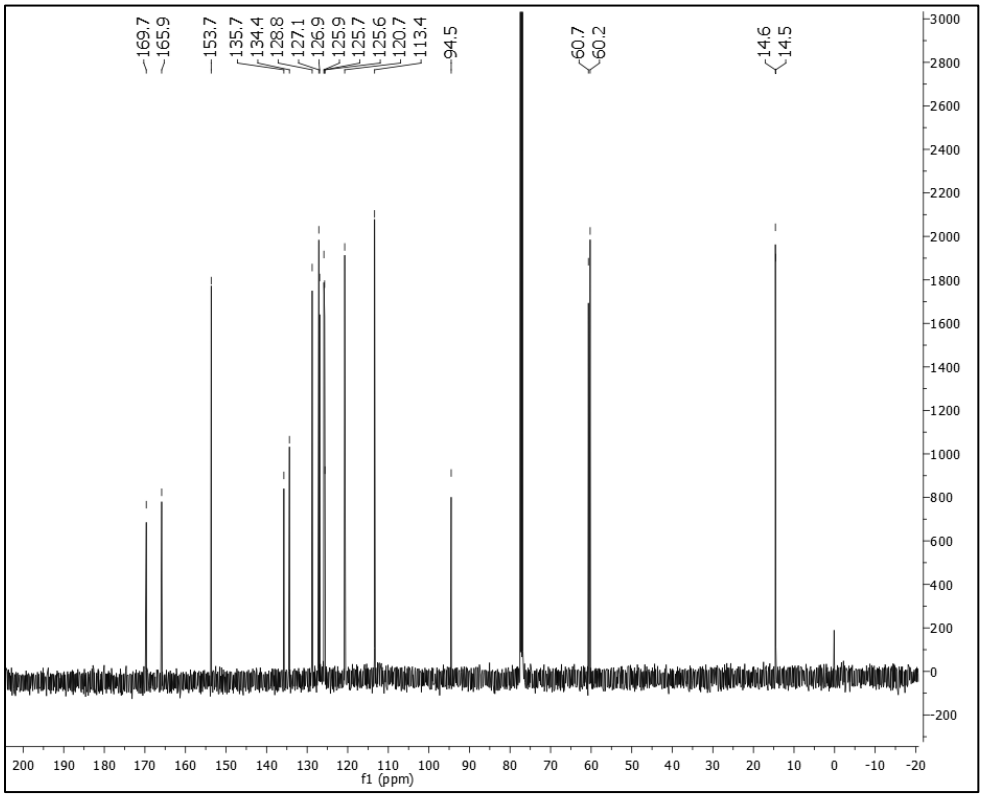


Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 125 MHz) of compound **4**.

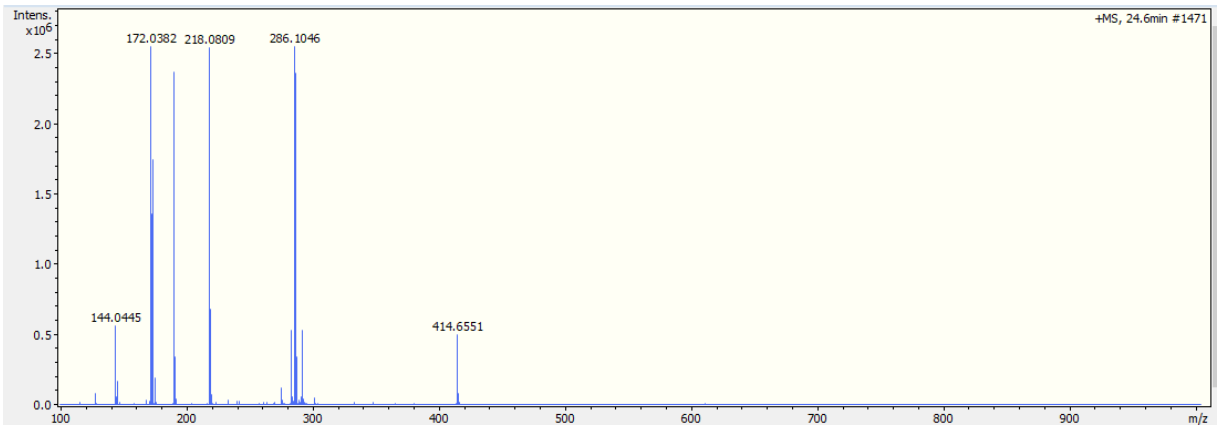


Figure S17. High-resolution mass spectra of compound **5**.

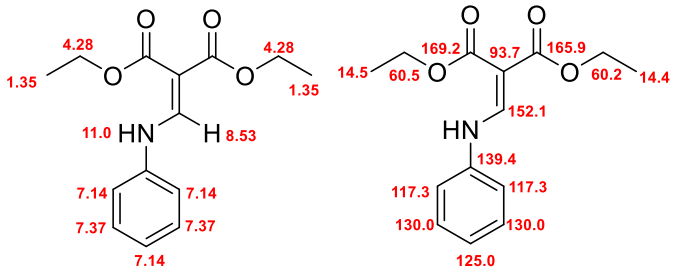


Figure S18. Assignments of ^{1}H and ^{13}C NMR chemical shifts of compound **5**.

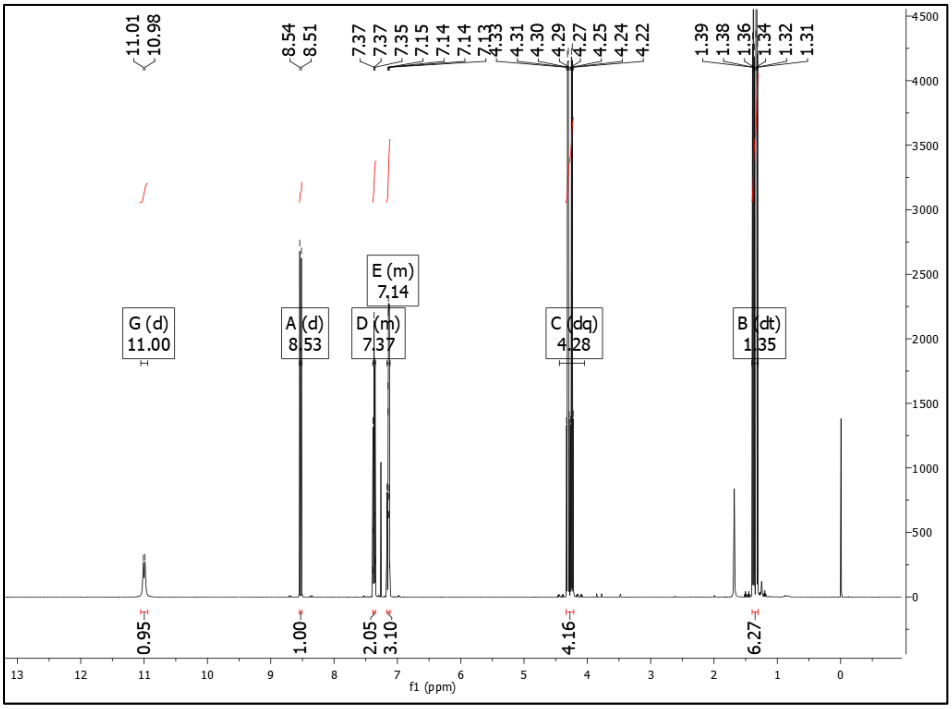


Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **5**.

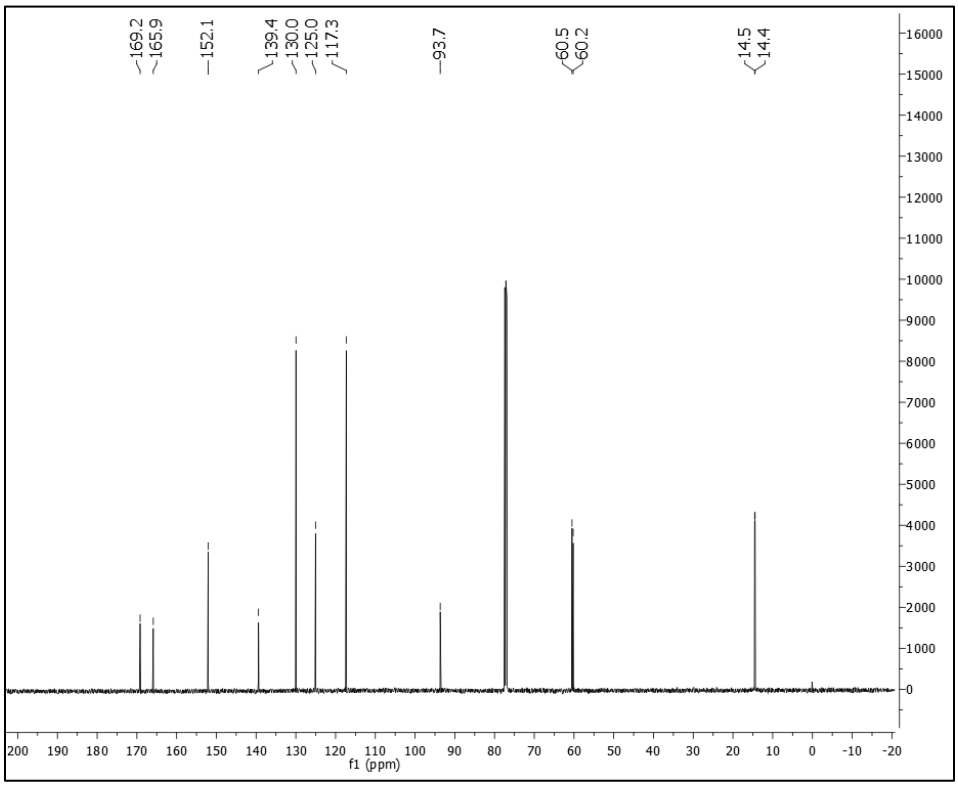
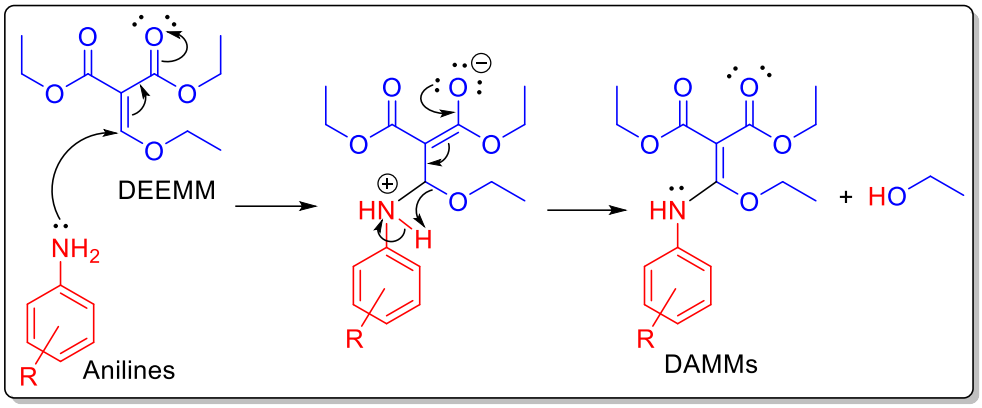


Figure S20. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of compound **5**.



Scheme S1. Reaction mechanism to produce DAMMs