

An Exploration of the Effect of the Kleier Model and Carrier-Mediated Theory to Design Phloem-Mobile Pesticides Based on Researching the N-Alkylated Derivatives of Phenazine-1-Carboxylic Acid-Glycine

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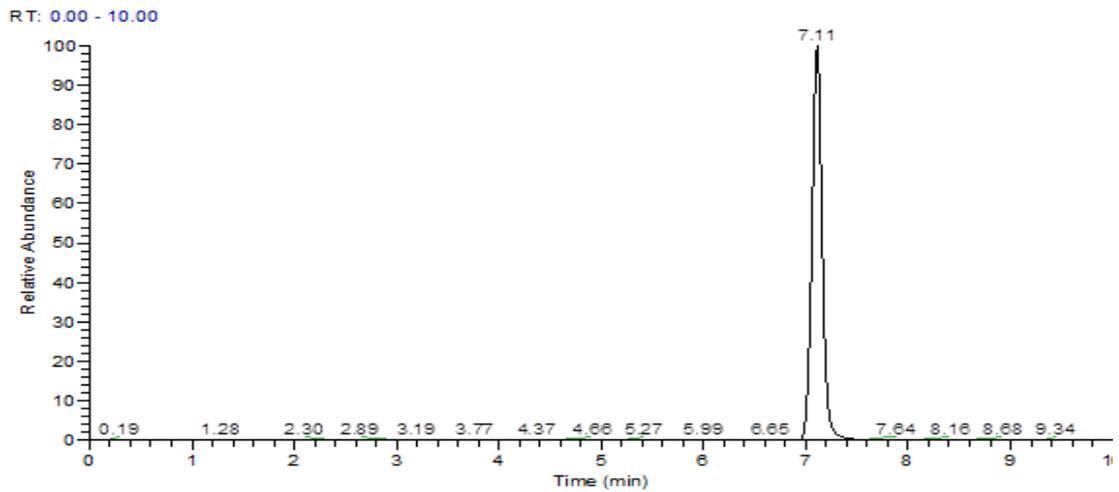
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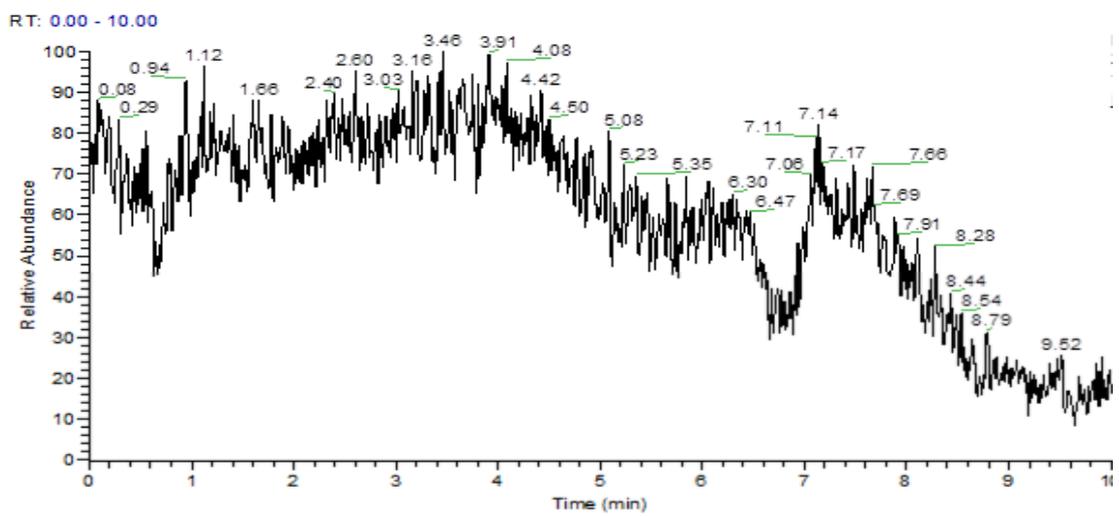
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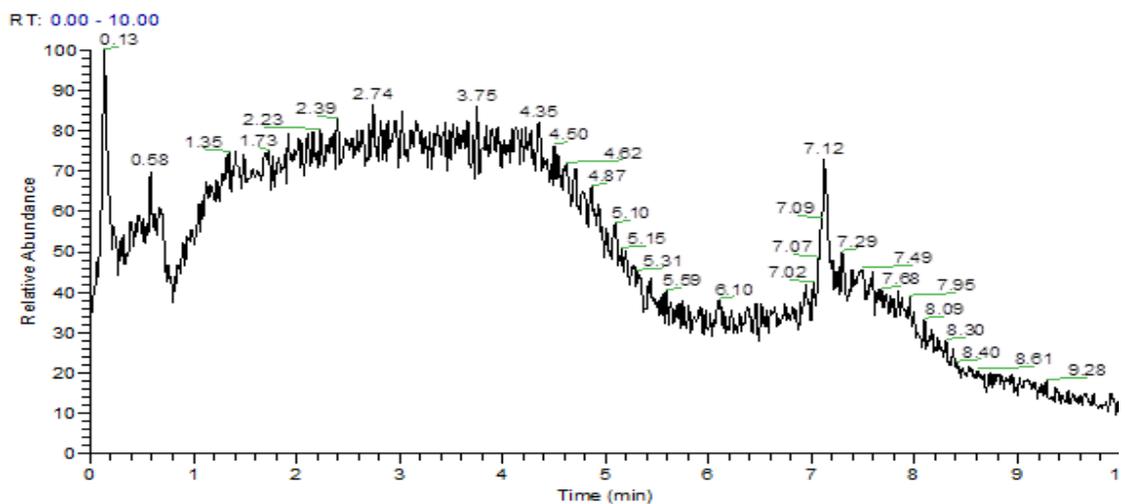
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3a-A

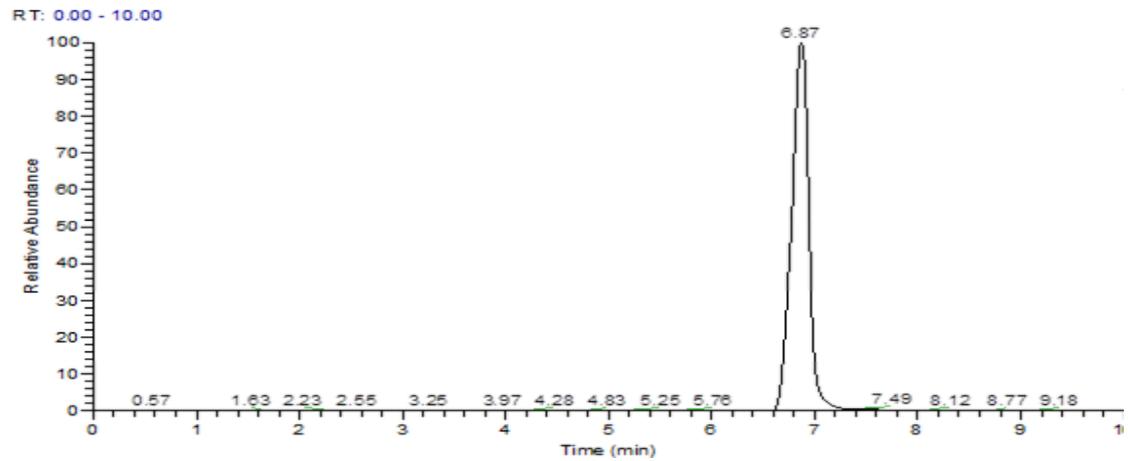


3a-B

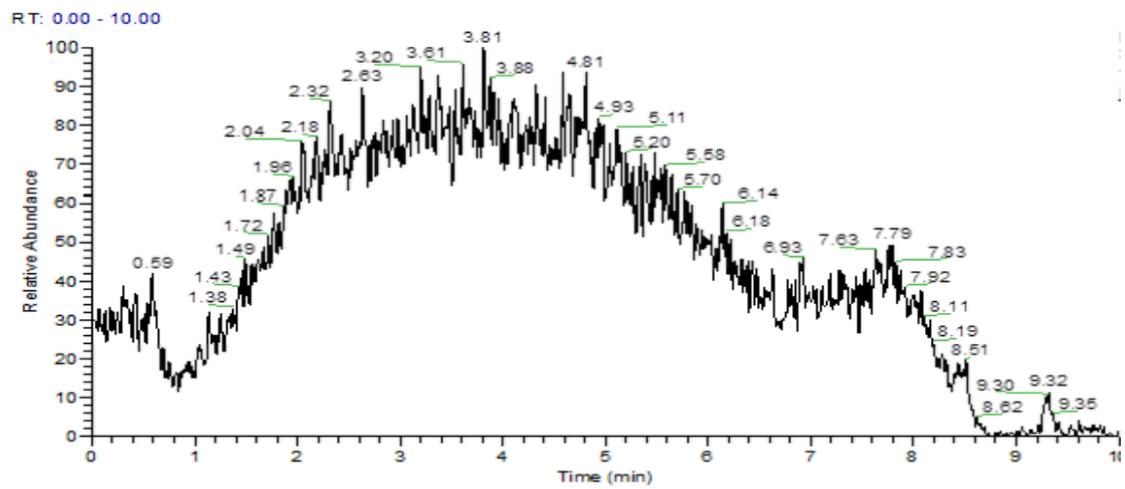


3a-C

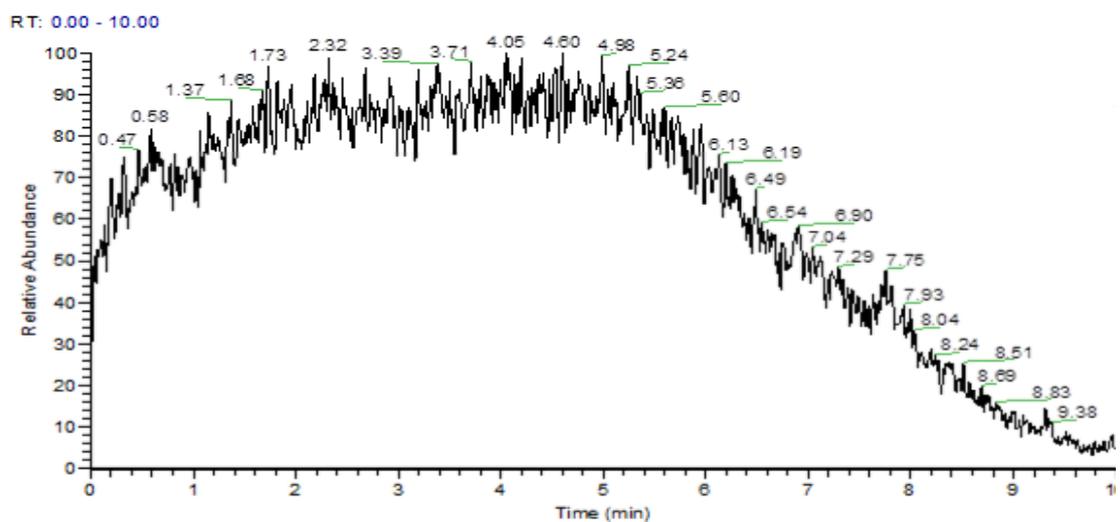
Figure S1. *R. communis* sap analysis by UHPLC-MS. **3a-A:** standard sample of **3a** (RT: 7.11 min); **3a-B:** control, the cotyledons were incubated in the standard medium; **3a-C:** treated set, the cotyledons were incubated in the same solution with **3a** at 0.2 mM concentration.



3g-A

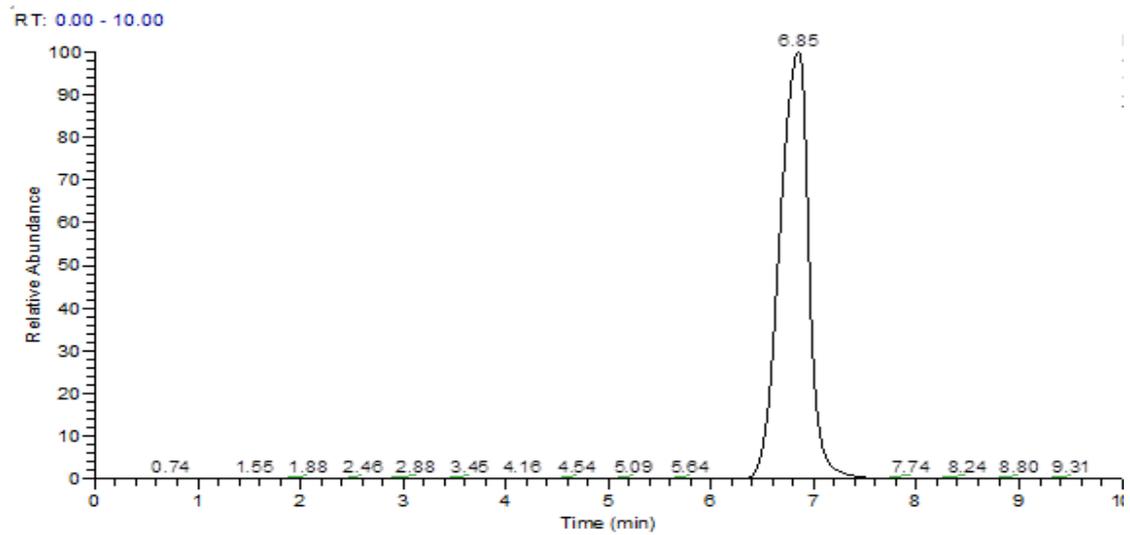


3g-B

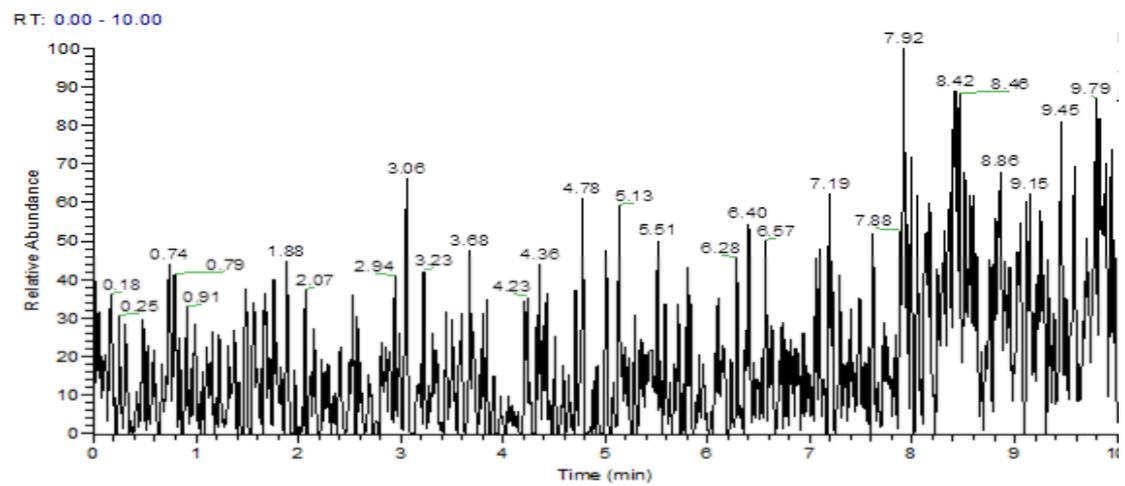


3g-C

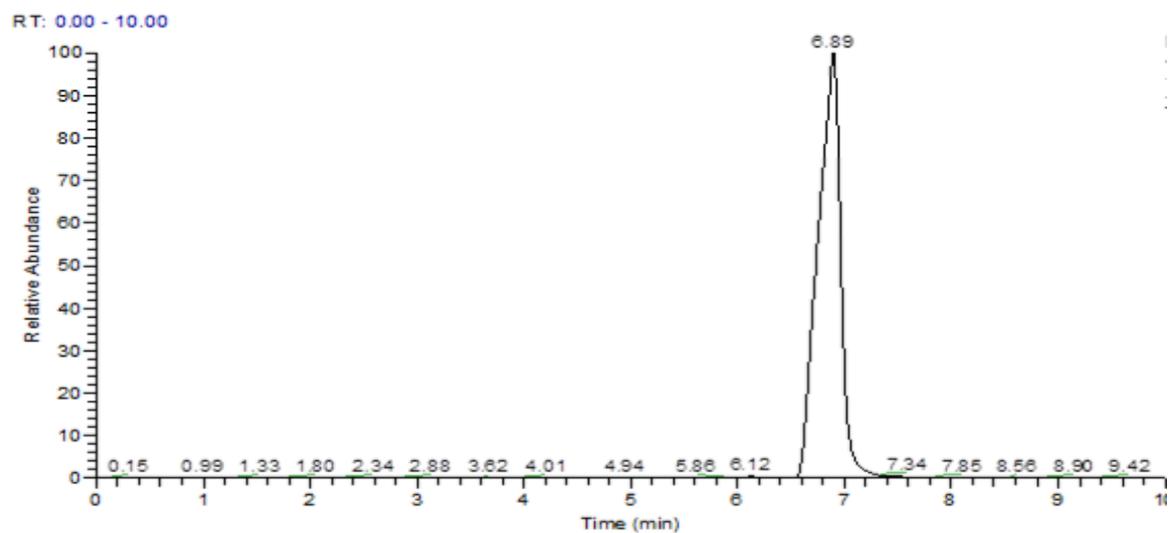
Figure S2. *R. communis* sap analysis by UHPLC-MS. **3g-A:** standard sample of **3g** (RT: 6.87 min); **3g-B:** control, the cotyledons were incubated in the standard medium; **3g-C:** treated set, the cotyledons were incubated in the same solution with **3g** at 0.2 mM concentration.



4a-A

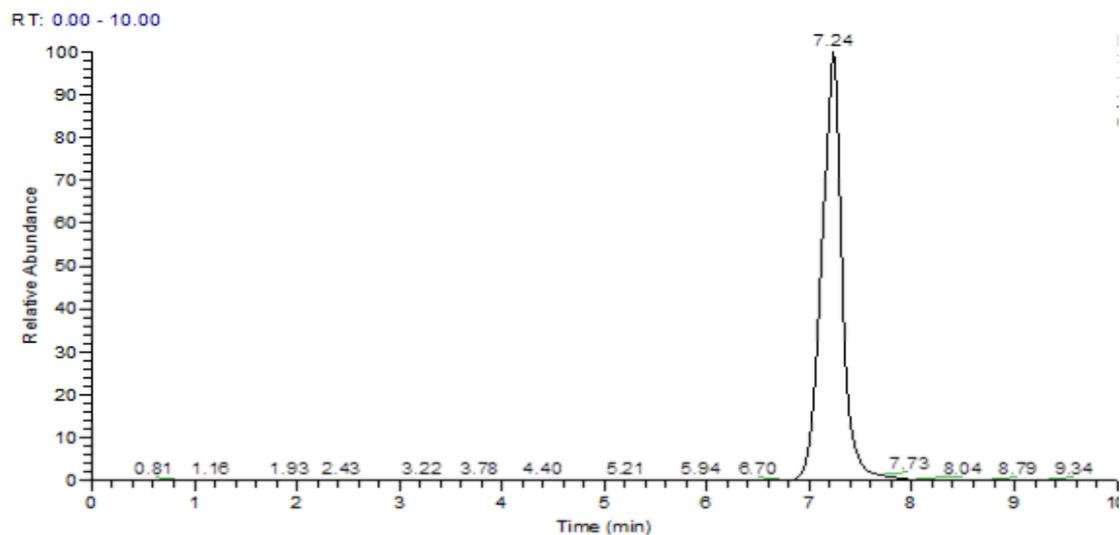


4a-B

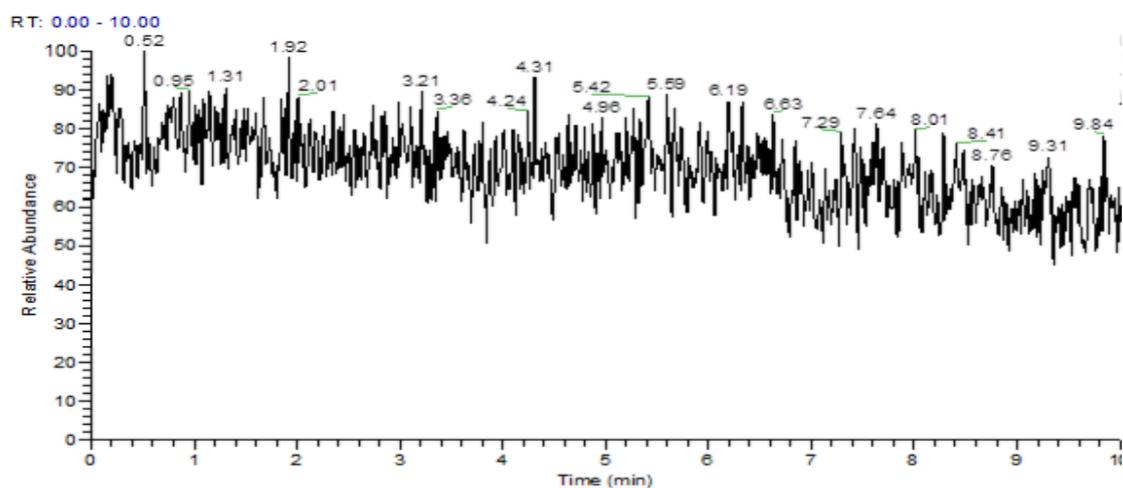


4a-C

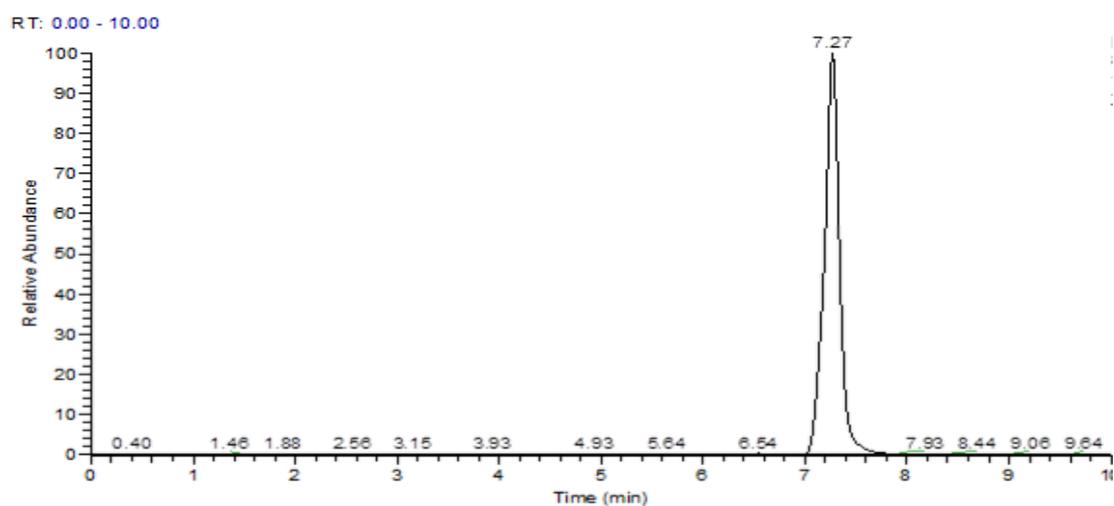
Figure S3. *R. communis* sap analysis by UHPLC-MS. **4a-A:** standard sample of **4a** (RT: 6.85 min); **4a-B:** control, the cotyledons were incubated in the standard medium; **4a-C:** treated set, the cotyledons were incubated in the same solution with **4a** (RT: 6.89 min) at 0.2 mM concentration.



4b-A

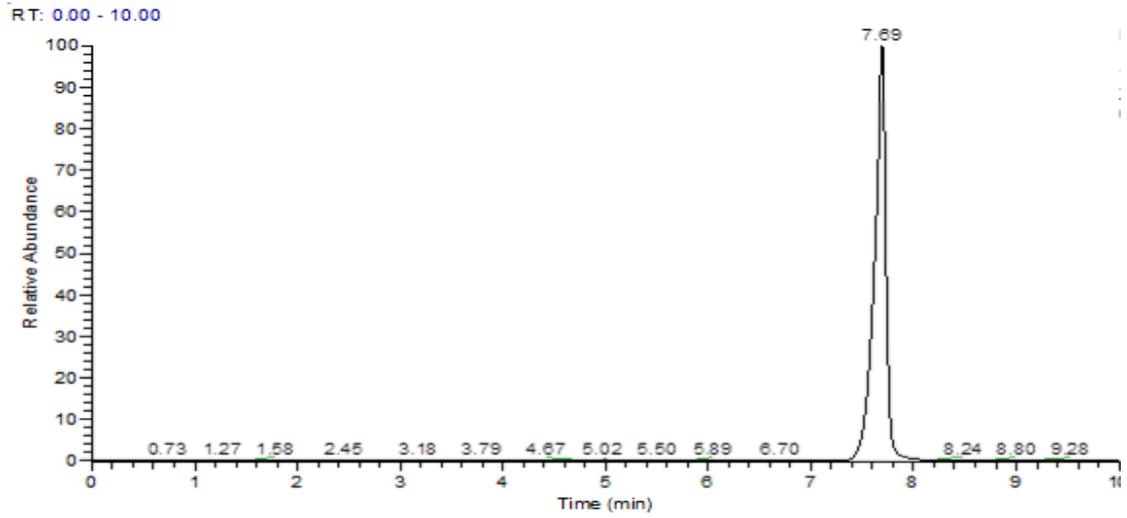


4b-B

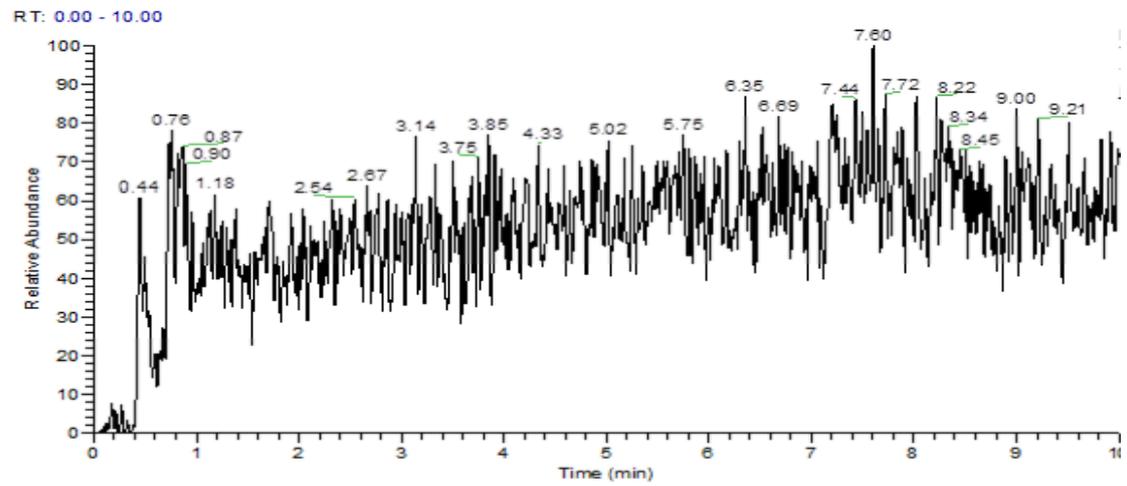


4b-C

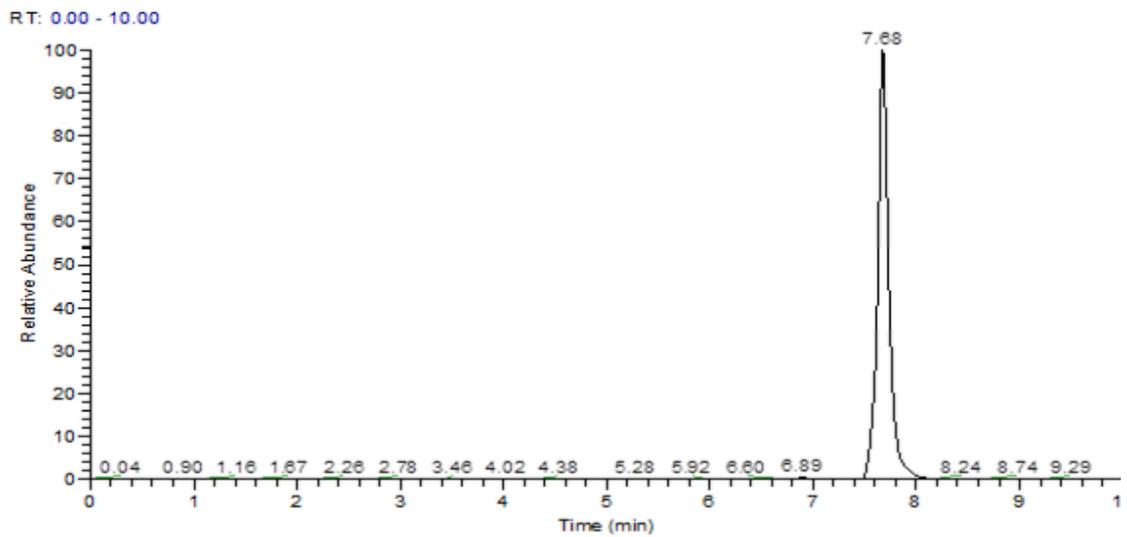
Figure S4. *R. communis* sap analysis by UHPLC-MS. **4b-A:** standard sample of **4b** (RT: 7.24 min); **4b-B:** control, the cotyledons were incubated in the standard medium; **4b-C:** treated set, the cotyledons were incubated in the same solution with **4b** (RT: 7.27 min) at 0.2 mM concentration.



4c-A

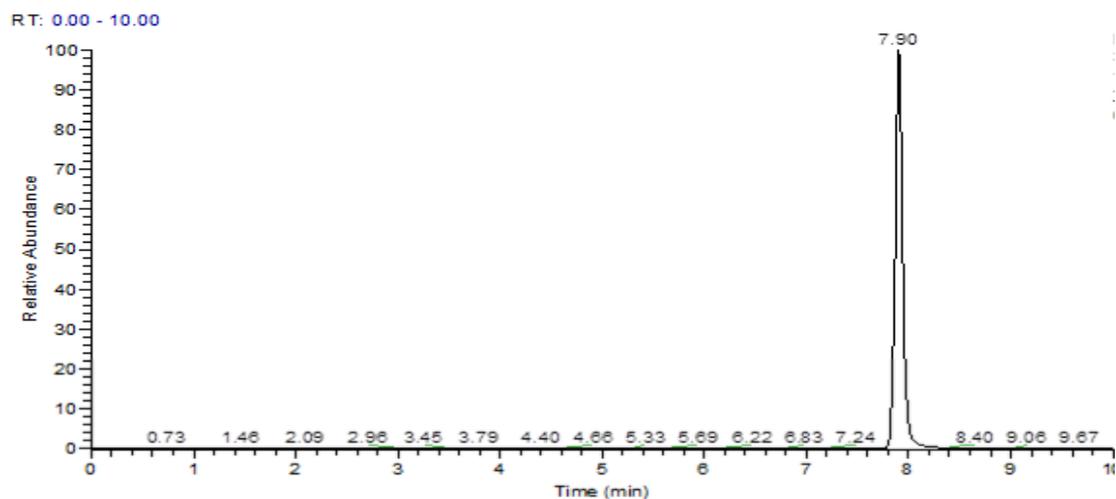


4c-B

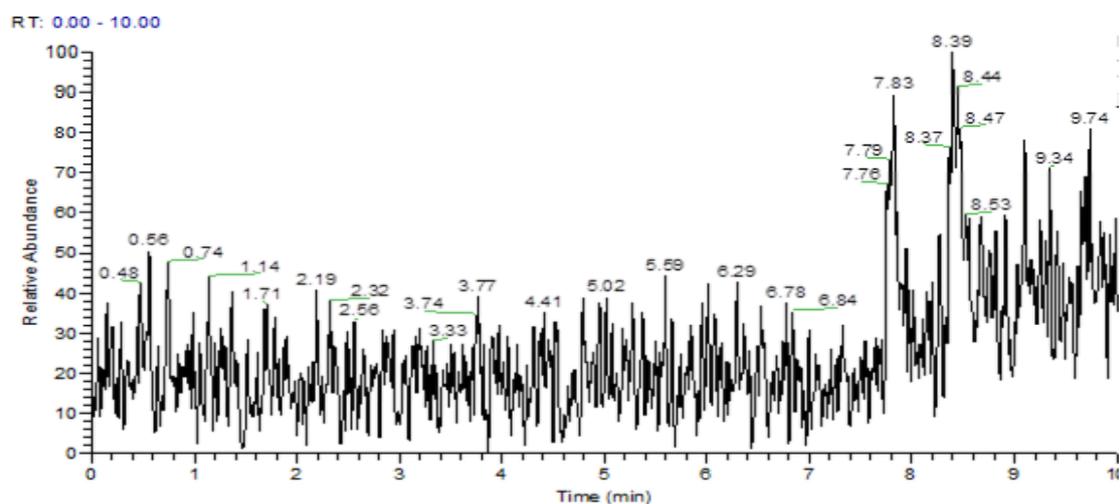


4c-C

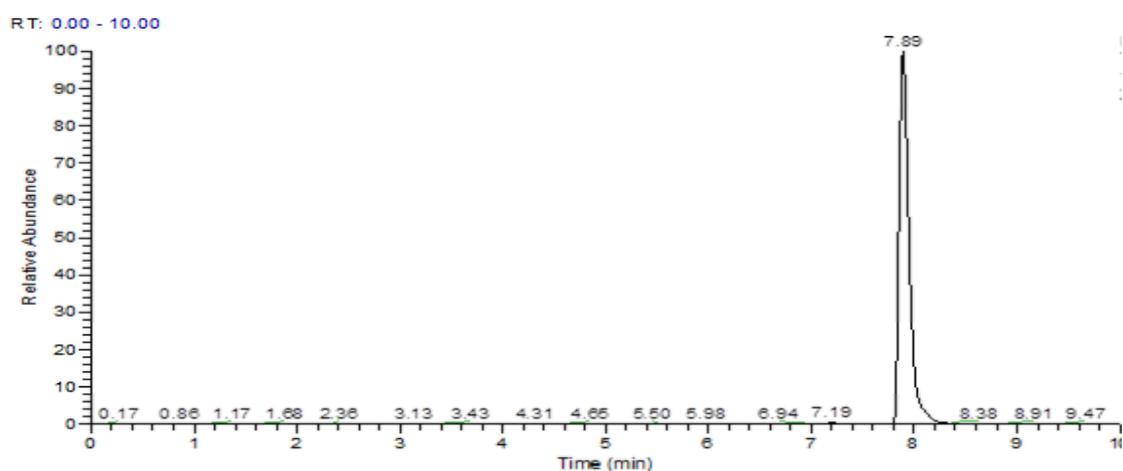
Figure S5. *R. communis* sap analysis by UHPLC-MS. **4c-A:** standard sample of **4c** (RT: 7.69 min); **4c-B:** control, the cotyledons were incubated in the standard medium; **4c-C:** treated set, the cotyledons were incubated in the same solution with **4c** (RT: 7.68 min) at 0.2 mM concentration.



4d-A

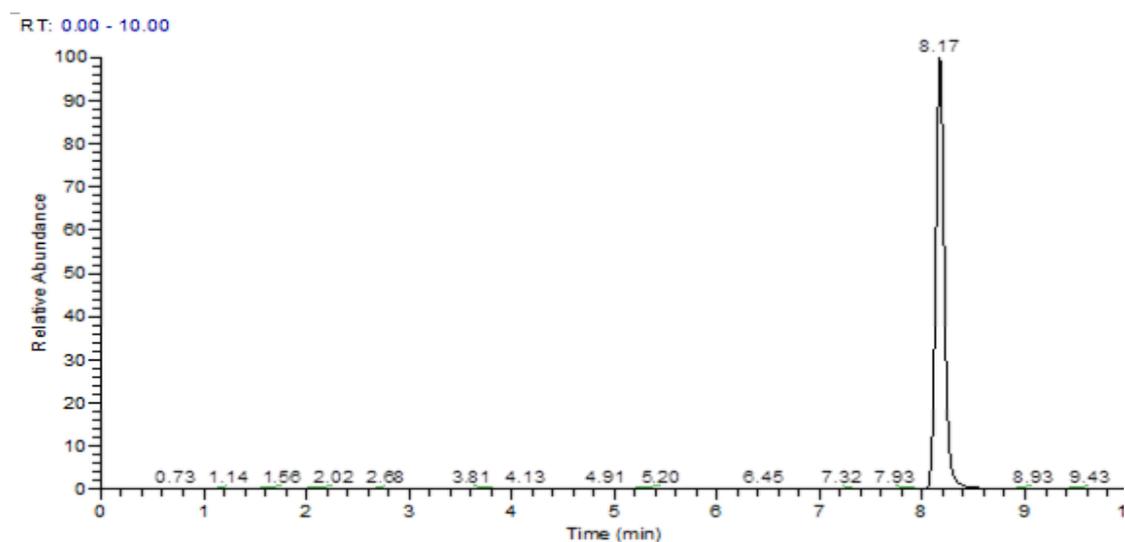


4d-B

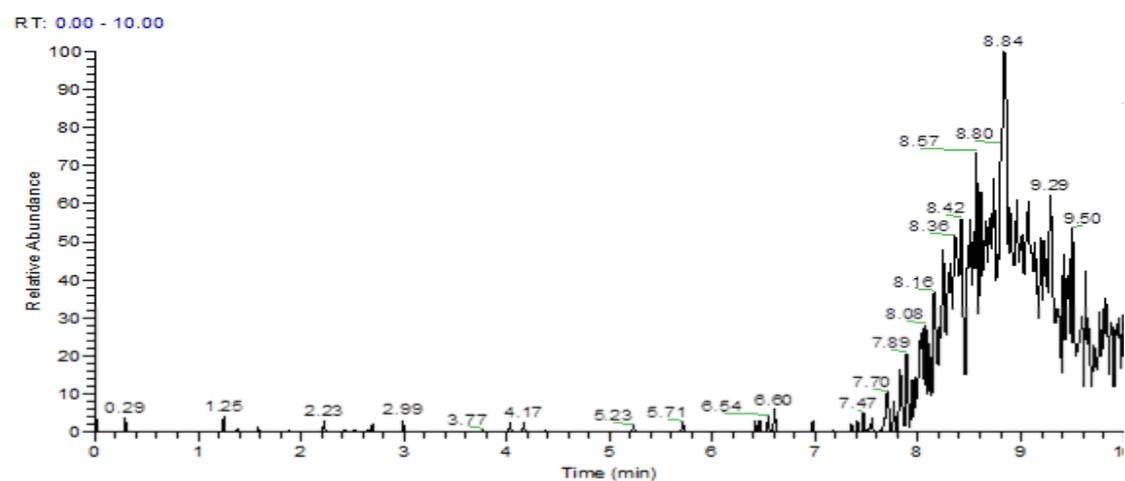


4d-C

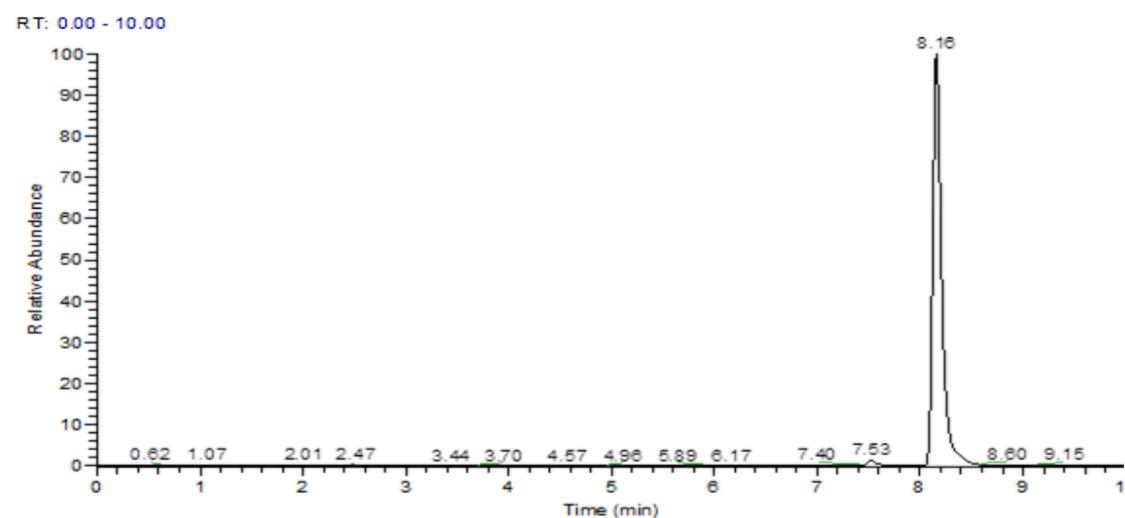
Figure S6. *R. communis* sap analysis by UHPLC-MS. **4d-A:** standard sample of **4d** (RT: 7.90 min); **4d-B:** control, the cotyledons were incubated in the standard medium; **4d-C:** treated set, the cotyledons were incubated in the same solution with **4d** (RT: 7.89 min) at 0.2 mM concentration.



4e-A

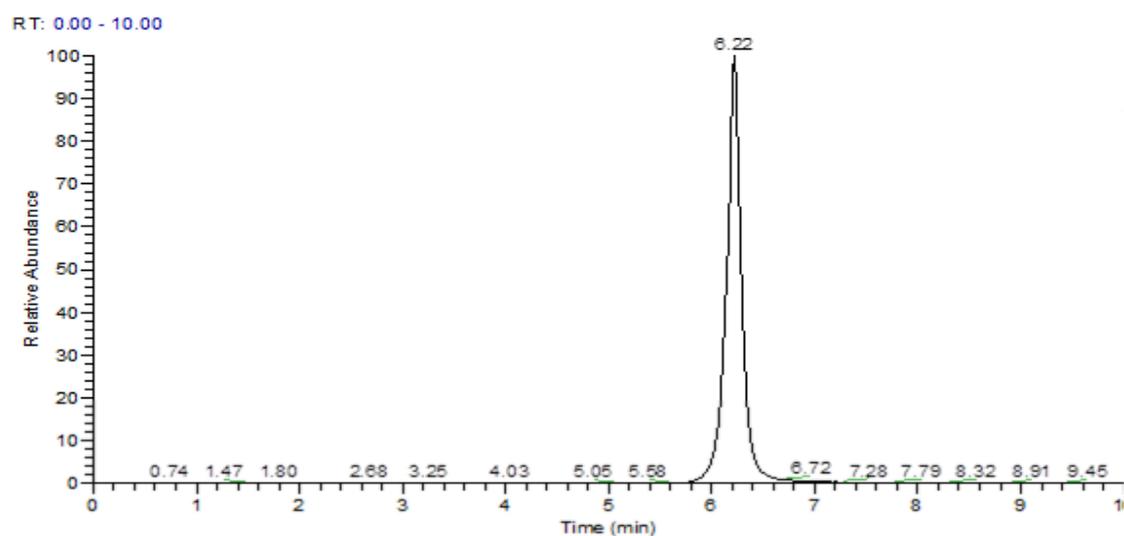


4e-B

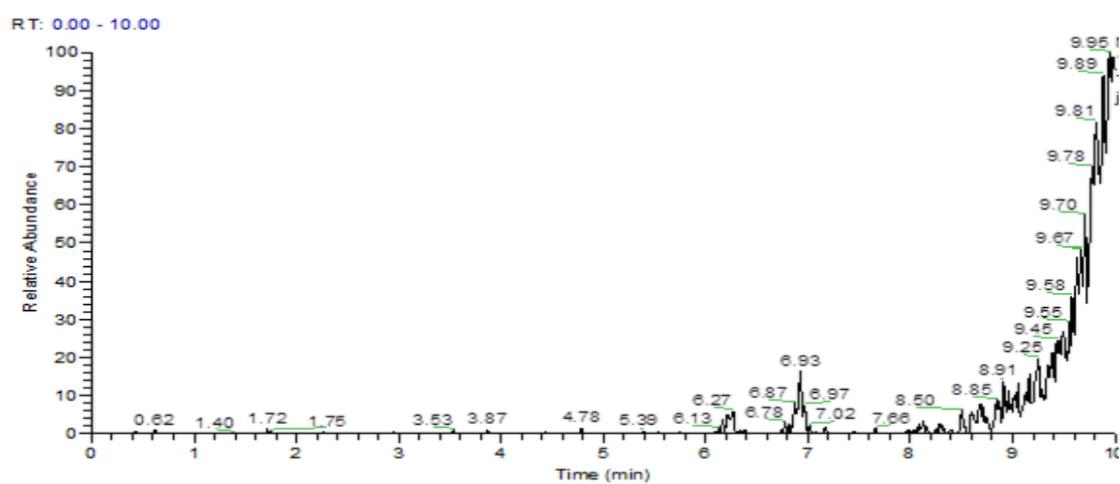


4e-C

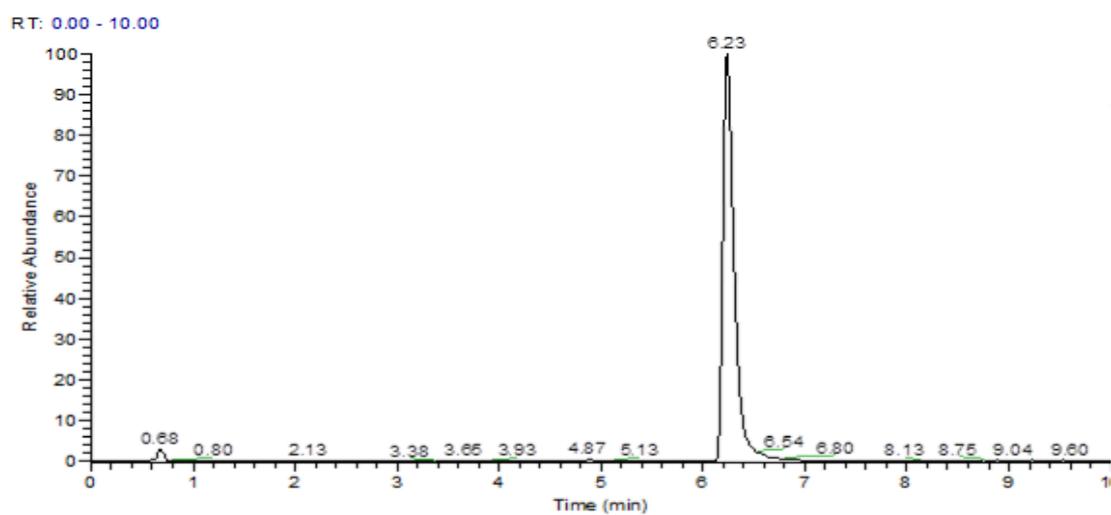
Figure S7. *R. communis* sap analysis by UHPLC-MS. **4e-A:** standard sample of **4e** (RT: 8.17 min); **4e-B:** control, the cotyledons were incubated in the standard medium; **4e-C:** treated set, the cotyledons were incubated in the same solution with **4e** (RT: 8.16 min) at 0.2 mM concentration.



4f-A

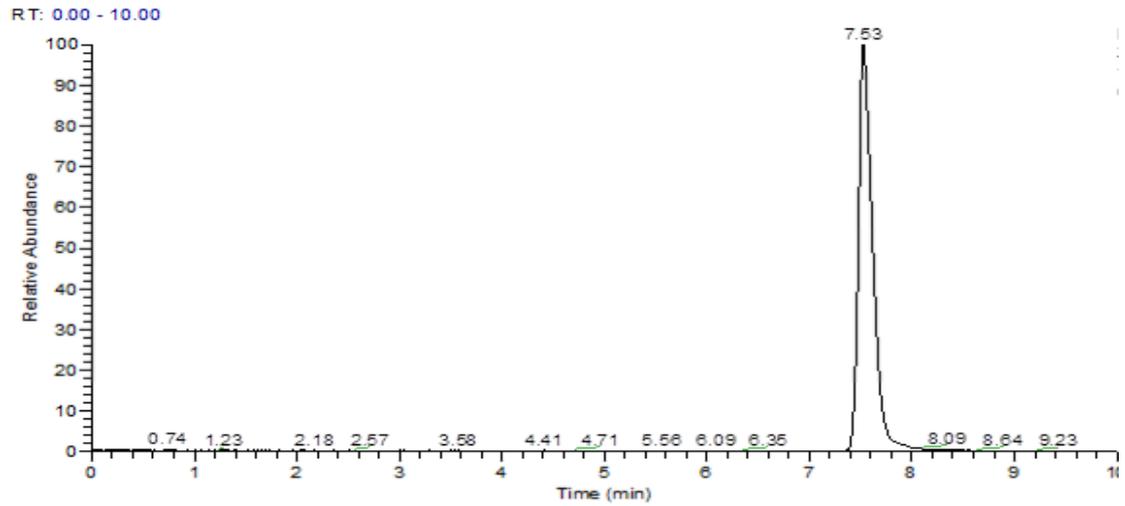


4f-B

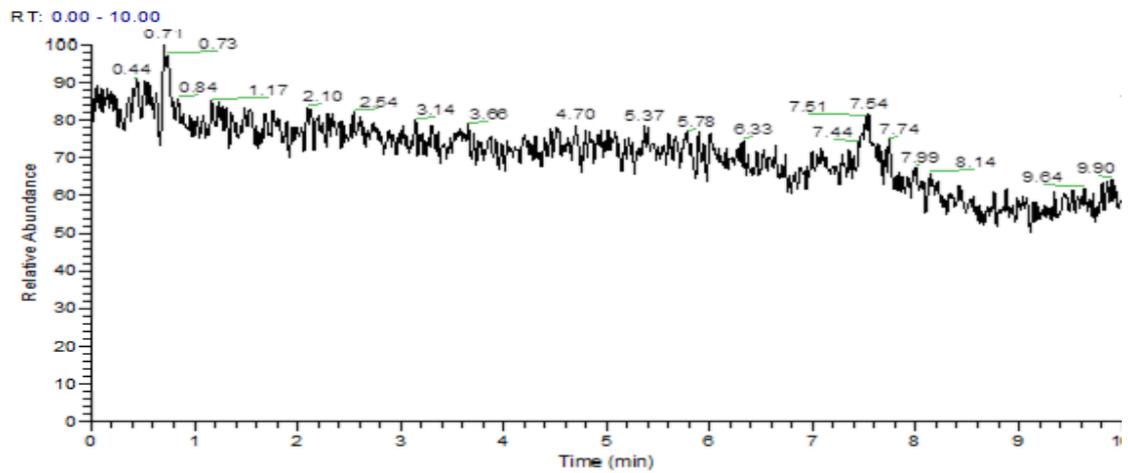


4f-C

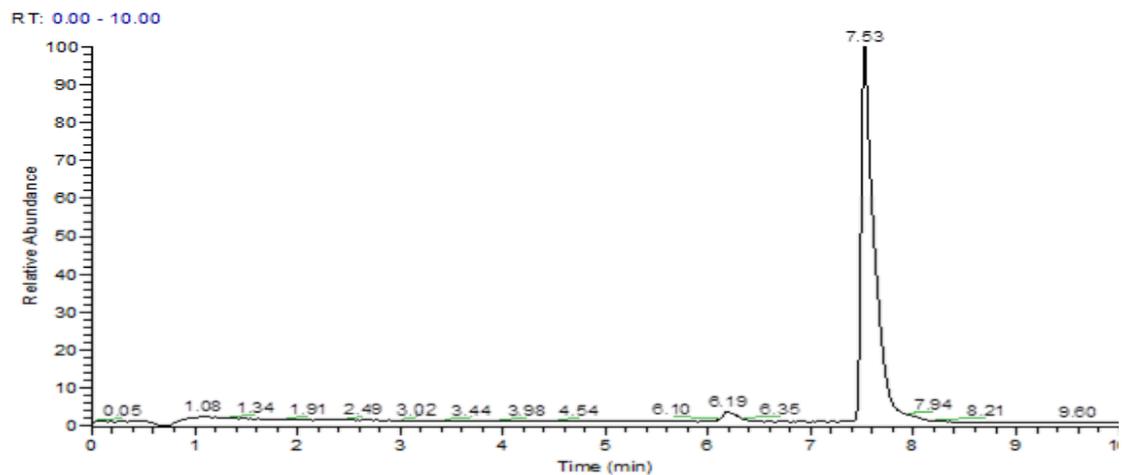
Figure S8. *R. communis* sap analysis by UHPLC-MS. **4f-A:** standard sample of **4f** (RT: 6.22 min); **4f-B:** control, the cotyledons were incubated in the standard medium; **4f-C:** treated set, the cotyledons were incubated in the same solution with **4f** (RT: 6.23 min) at 0.2 mM concentration.



PCA-Gly-A

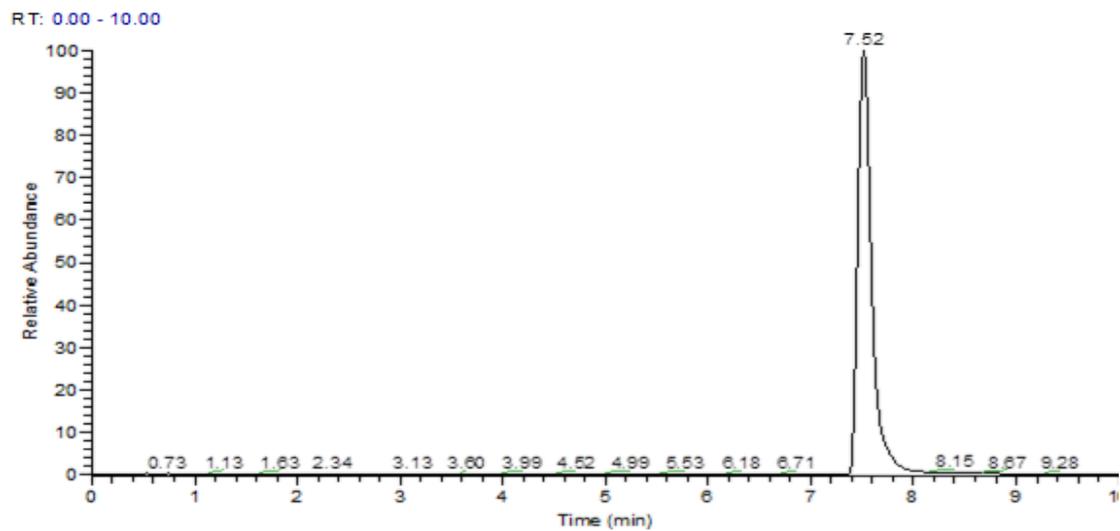


PCA-Gly-B

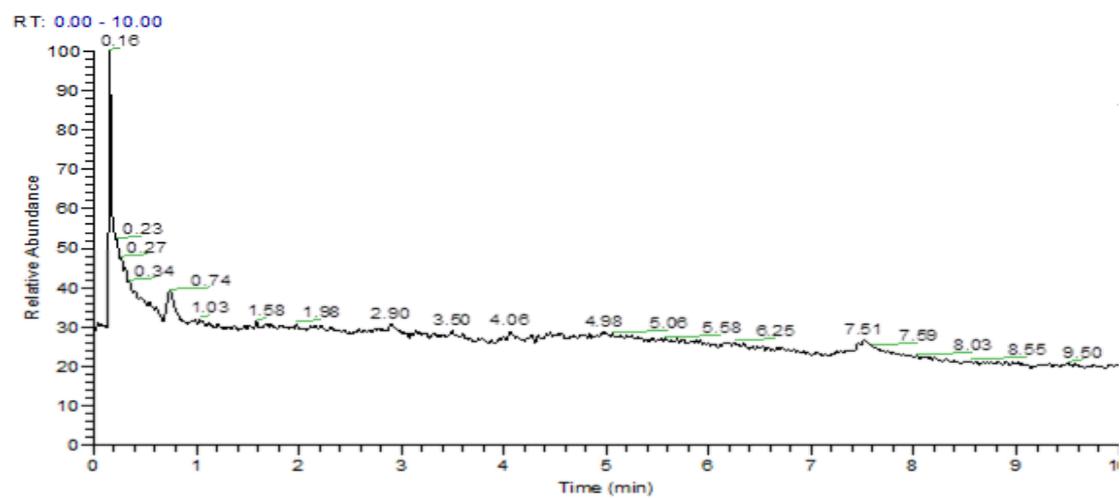


PCA-Gly-C

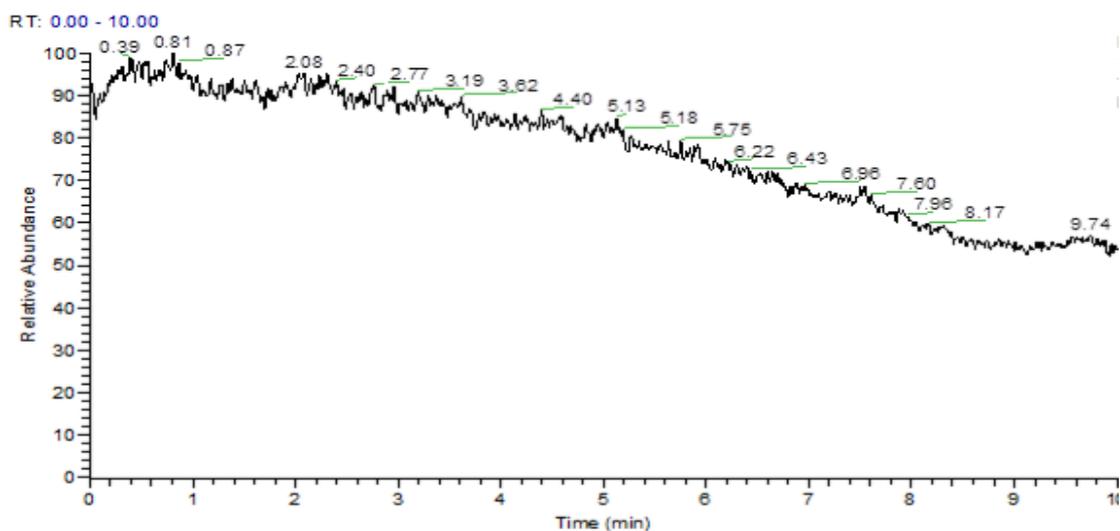
Figure S9. *R. communis* sap analysis by UHPLC-MS. **PCA-Gly-A:** standard sample of **PCA-Gly** (RT: 7.53 min); **PCA-Gly-B:** control, the cotyledons were incubated in the standard medium; **PCA-Gly-C:** treated set, the cotyledons were incubated in the same solution with **PCA-Gly** (RT: 7.53 min) at 0.2 mM concentration.



PCA-A



PCA-B



PCA-C

Figure S10. *R. communis* sap analysis by UHPLC-MS. **PCA-A:** standard sample of PCA (RT: 7.52 min); **PCA-B:** control, the cotyledons were incubated in the standard medium; **PCA-C:** treated set, the cotyledons were incubated in the same solution with PCA at 0.2 mM concentration.

Ethyl 2-(N-methylphenazine-1-carboxamido)acetate (3a) :

Yellow solid; yield: 86%; m.p. 115 – 117°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.33 – 8.21 (m, 3.00H, Phenazine-H), 7.94 – 7.79 (m, 4.09H, Phenazine-H), 5.00 (d, $J = 16.2$ Hz, 0.67H, COOCH_2), 4.32 (q, $J = 7.2$ Hz, 1.31H, N- CH_2), 4.11 – 4.00 (m, 1.34H, COOCH_2), 3.84 (d, $J = 19.8$ Hz, 0.71H, N- CH_2), 3.39 (s, 1.18H, N- CH_3), 2.89 (s, 1.95H, N- CH_3), 1.37 (t, $J = 7.2$ Hz, 1.94H, Methylene- CH_3), 1.11 (t, $J = 7.2$ Hz, 1.17H, Methylene- CH_3). HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 324.1343, found 324.1337.

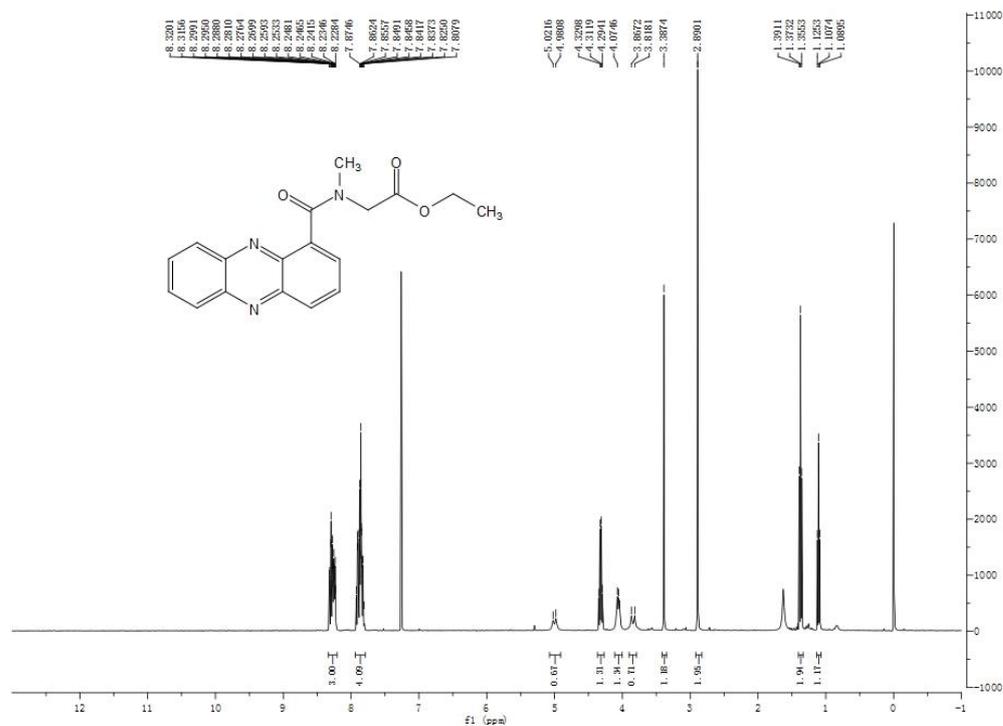


Figure S11. $^1\text{H-NMR}$ Spectrum of compound 3a

XYF-1_180911083612 #353 RT: 3.42 AV: 1 NL: 1.77E10
T: FTMS + p ESI Full ms [100.00-1500.00]

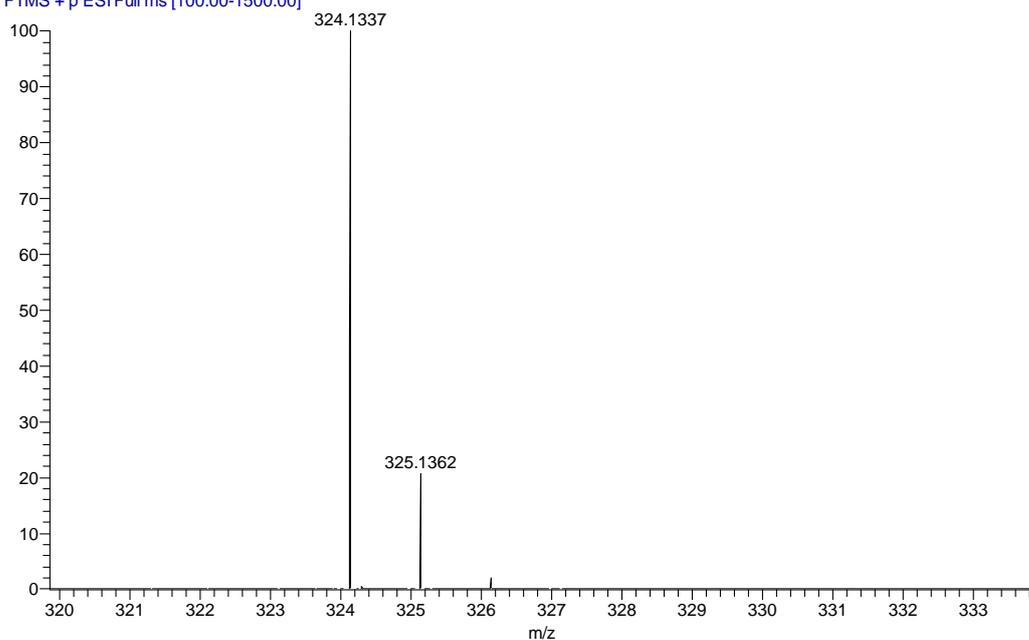


Figure S12. HRMS Spectrum of compound 3a

Ethyl 2-(N-ethylphenazine-1-carboxamido)acetate (**3b**) :

Yellow solid; yield: 76%; m.p. 133 – 135°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 – 8.18 (m, 3.00H, Phenazine-H), 7.92 – 7.79 (m, 4.04H, Phenazine-H), 4.88 (d, $J = 17.2$ Hz, 0.69H, N- CH_2 -Methyl), 4.33 (q, $J = 7.2$ Hz, 1.38H, N- CH_2), 4.17 – 3.98 (m, 1.72H, COOCH_2), 3.82 (s, 0.73H, N- CH_2), 3.65 (s, 0.38H, COOCH_2), 3.24 (dt, $J = 14.8, 7.2$ Hz, 1.36H, N- CH_2 -Methyl), 1.40 (dt, $J = 18.8, 7.2$ Hz, 3.08H, Methylene- CH_3), 1.07 (dt, $J = 24.2, 7.2$ Hz, 3.09H, N-Methylene- CH_3). HRMS calcd for $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 338.1499, found 338.1491.

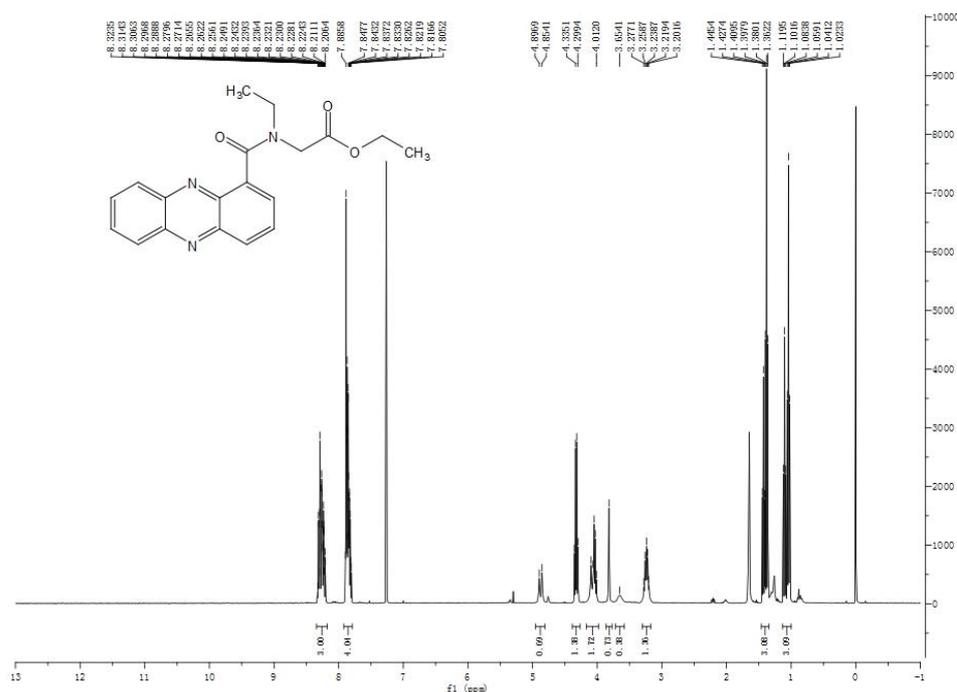


Figure S13. $^1\text{H-NMR}$ Spectrum of compound **3b**

XYF-2 #377 RT: 3.65 AV: 1 NL: 2.65E9
T: FTMS + p ESI Full ms [100.00-1500.00]

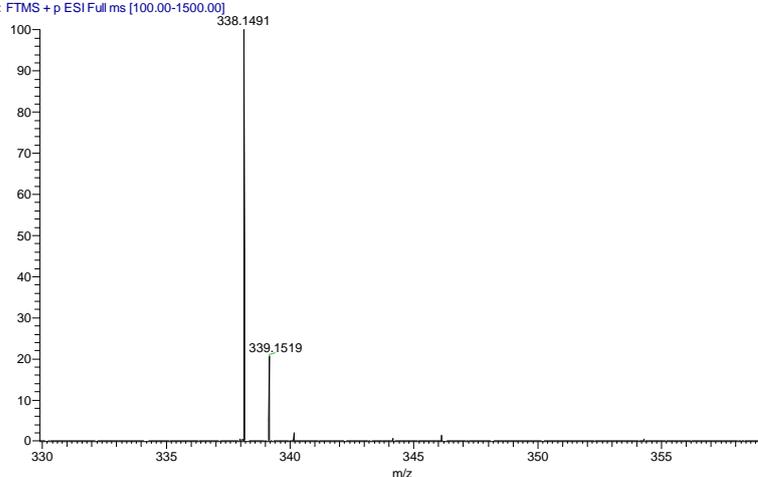


Figure S14. HRMS Spectrum of compound **3b**

Ethyl 2-(N-isopropylphenazine-1-carboxamido)acetate (**3c**) :

Yellow solid; yield: 73%; m.p. 131 – 132°C; ¹H NMR (400 MHz, CDCl₃) δ 8.33 – 8.22 (m, 3.09H, Phenazine-H), 7.89 – 7.82 (m, 4.05H, Phenazine-H), 4.64 (d, *J* = 16.8 Hz, 0.98H, N-CH), 4.33 (qd, *J* = 7.2, 1.8 Hz, 1.98H, COOCH₂), 3.96 (d, *J* = 16.8 Hz, 1.06H, N-CH₂), 3.77 – 3.72 (m, 1.02H, N-CH₂), 1.38 (t, *J* = 7.2 Hz, 2.80H, N-Methylene-CH₃), 1.15 – 1.05 (m, 6.00H, 2×CH₃). HRMS calcd for C₂₀H₁₉N₃O₃ [M+H]⁺: 352.1656, found 352.1648.

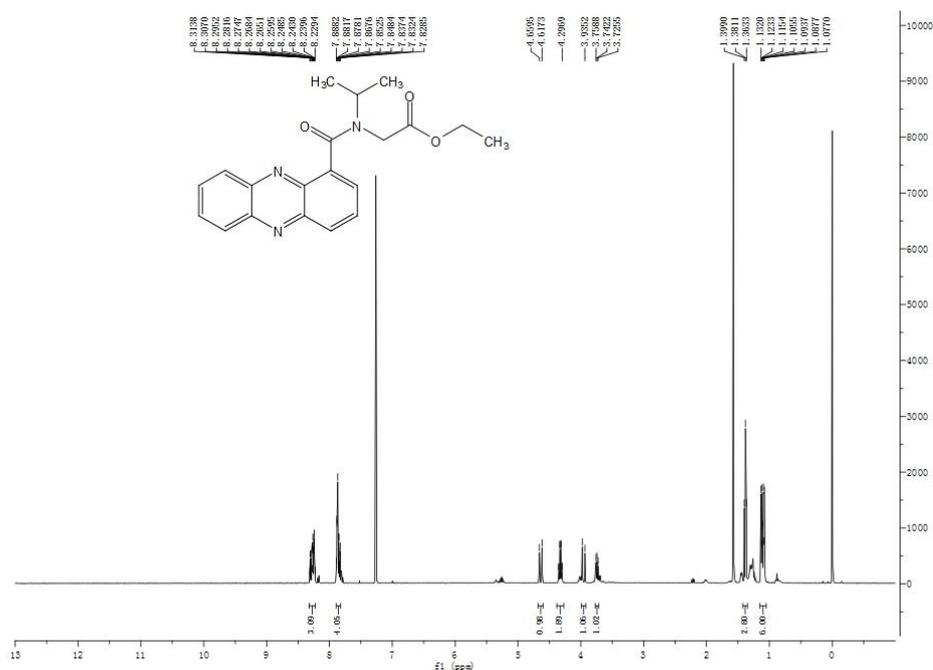


Figure S15. ¹H-NMR Spectrum of compound **3c**

XYF-3 #395 RT: 3.82 AV: 1 NL: 1.61E10
T: FTMS + p ESI Full ms [100.00-1500.00]

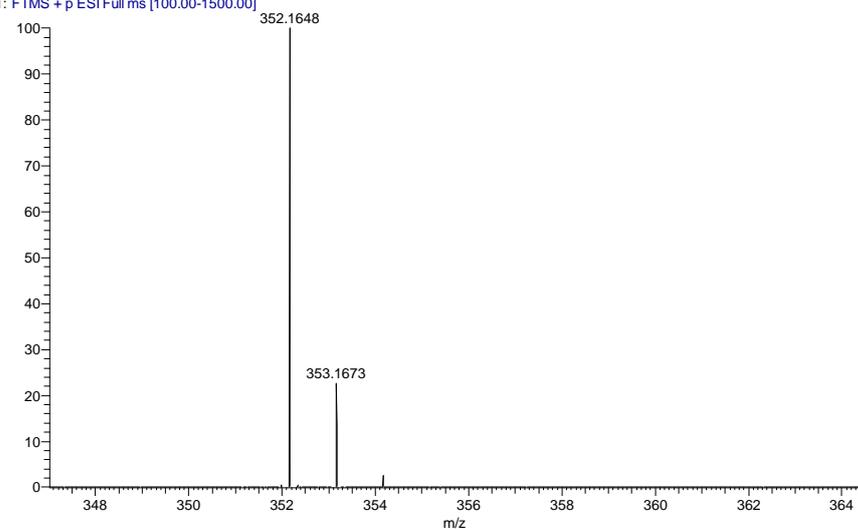


Figure S16. HRMS Spectrum of compound **3c**

Ethyl 2-(N-tert-butylphenazine-1-carboxamido)acetate (3d) :

Yellow solid; yield: 83%; m.p. 114 – 116°C; ¹H NMR (400 MHz, CDCl₃) δ 8.27 – 8.17 (m, 3.00H, Phenazine-H), 7.90 – 7.73 (m, 4.10H, Phenazine-H), 4.10 – 3.96 (m, 3.01H, COOCH₂, N-CH₂), 3.78 (d, *J* = 19.0 Hz, 1.03H, N-CH₂), 1.72 (s, 8.91H, 3×CH₃), 1.13 (t, *J* = 7.2 Hz, 3.02H, N-Methylene-CH₃). HRMS calcd for C₂₁H₂₃N₃O₃ [M+H]⁺: 366.1812, found 366.1808.

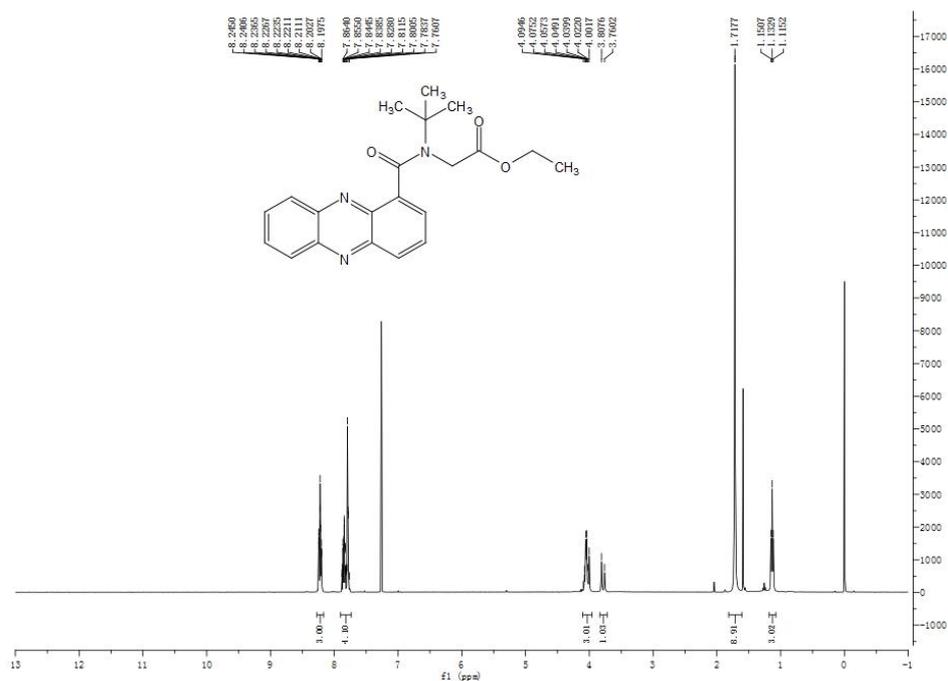


Figure S17. ¹H-NMR Spectrum of compound 3d

XYF-4 #421 RT: 4.10 AV: 1 NL: 1.00E8
T: FTMS + p ESI Full ms [100.00-1500.00]

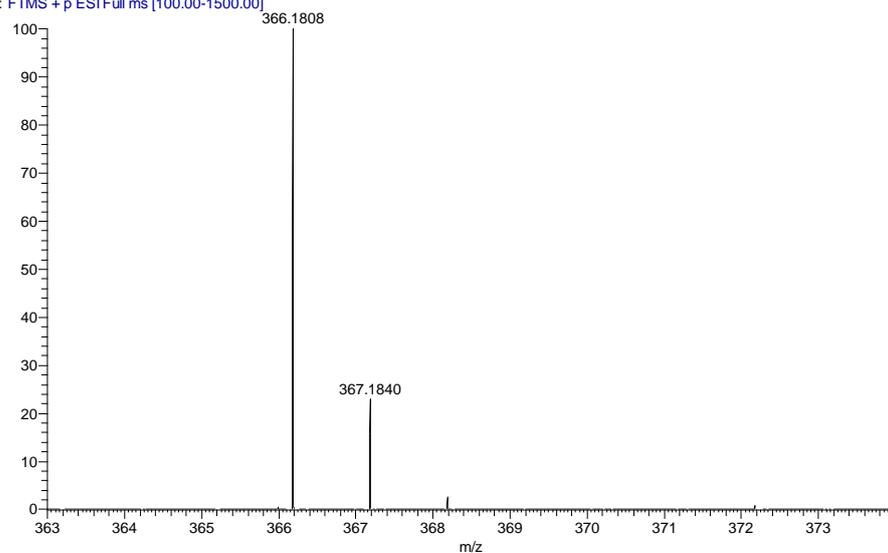


Figure S18. HRMS Spectrum of compound 3d

Ethyl 2-(N-benzylphenazine-1-carboxamido)acetate (3e) :

Yellow solid; yield: 85%; m.p. 138 – 140°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.38 – 8.20 (m, 3.10H, Phenazine-H), 7.98 – 7.82 (m, 4.00H, Phenazine-H), 7.74 (d, $J = 7.2$ Hz, 1.00H, Benzene-H), 7.50 (dd, $J = 13.2, 5.8$ Hz, 1.10H, Benzene-H), 7.37 (dd, $J = 17.2, 7.2$ Hz, 1.60H, Benzene-H), 7.25 – 7.15 (m, 1.49H, Benzene-H), 4.82 (d, $J = 17.4$ Hz, 0.70H, Benzene- CH_2), 4.35 (d, $J = 15.2$ Hz, 0.97H, COOCH_2), 4.29 (q, $J = 7.2$ Hz, 1.24H, Benzene- CH_2), 4.03 (q, $J = 7.2$ Hz, 1.11H, COOCH_2), 3.89 (d, $J = 17.2$ Hz, 0.71H, N- CH_2), 3.70 (d, $J = 16.8$ Hz, 1.37H, N- CH_2), 1.34 (t, $J = 7.2$ Hz, 1.57H, N-Methylene- CH_3), 1.09 (t, $J = 7.2$ Hz, 1.56H, N-Methylene- CH_3). HRMS calcd for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 400.1656, found 400.1647.

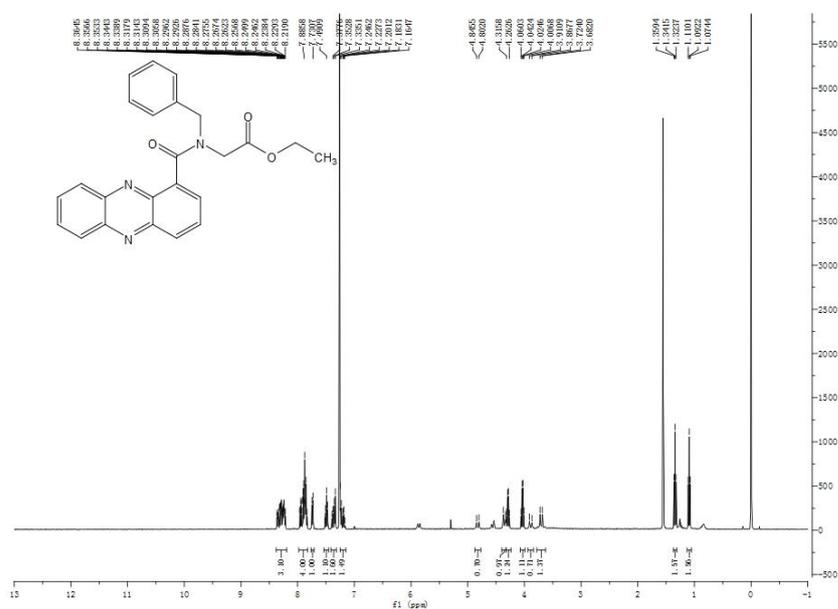


Figure S19. $^1\text{H-NMR}$ Spectrum of compound 3e

XYF-5 #433 RT: 4.21 AV: 1 NL: 4.74E9
T: FTMS + p ESI Full ms [100.00-1500.00]

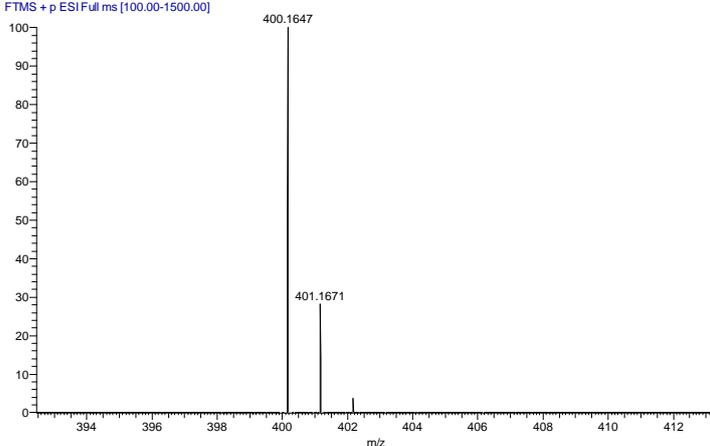


Figure S20. HRMS Spectrum of compound 3e

Diethyl 2,2'-((phenazine-1-carbonyl)azanediyl)diacetate (3f) :

Yellow solid; yield: 89%; m.p. 95 – 97°C; ¹H NMR (400 MHz, CDCl₃) δ 8.38 – 8.19 (m, 3.00H, Phenazine-H), 7.98 – 7.79 (m, 4.02H, Phenazine-H), 4.69 (s, 2.02H, N-CH₂), 4.32 (q, *J* = 7.2 Hz, 2.01H, N-CH₂), 3.96 (s, 4.02H, COOCH₂), 1.37 (t, *J* = 7.2 Hz, 3.00H, CH₃), 0.97 (t, *J* = 7.2 Hz, 3.00H, CH₃). HRMS calcd for C₂₁H₂₁N₃O₅ [M+H]⁺: 396.1554, found 396.1548.

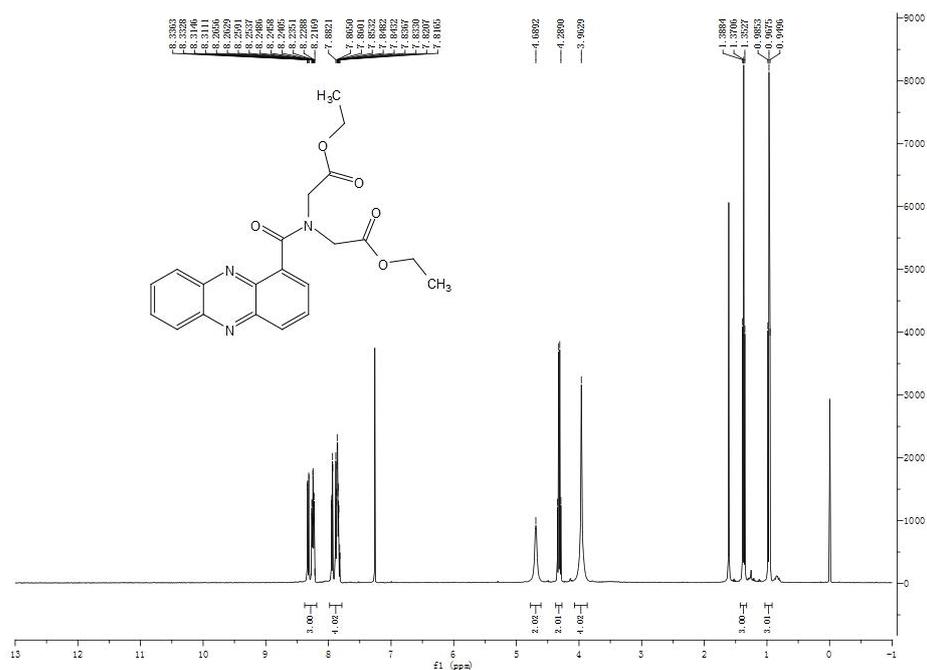


Figure S21. ¹H-NMR Spectrum of compound 3f

XYF-6 #387 RT: 3.76 AV: 1 NL: 6.00E8
T: FTMS + p ESI Full ms [100.00-1500.00]

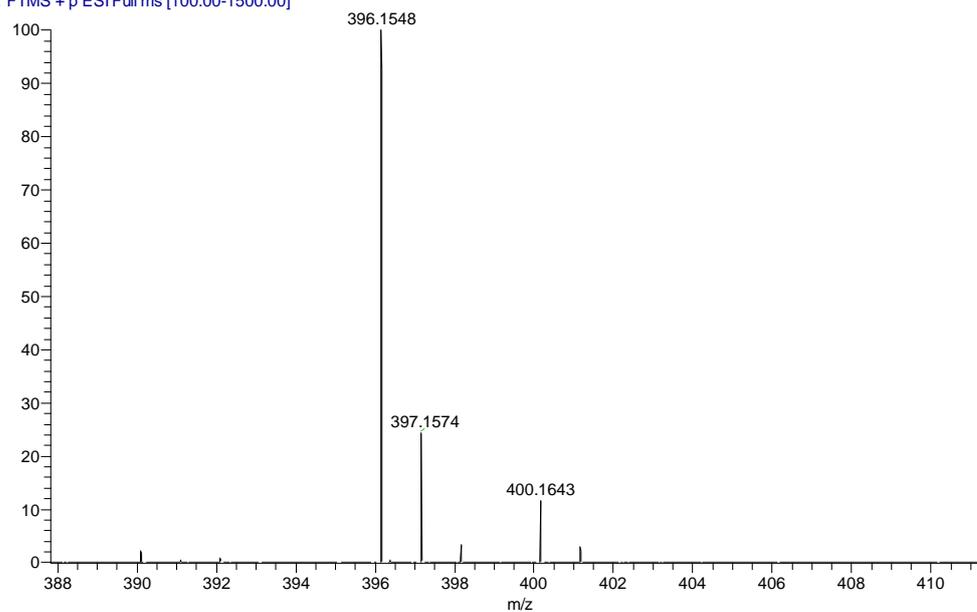


Figure S22. HRMS Spectrum of compound 3f

Methyl 2-(N-methylphenazine-1-carboxamido)acetate (3g) :

Yellow solid; yield: 90%; m.p. 123 – 125°C; ¹H NMR (400 MHz, CDCl₃) δ 8.33 – 8.21 (m, 3.00H, Phenazine-H), 7.94 – 7.80 (m, 4.08H, Phenazine-H), 4.99 (d, *J* = 17.2 Hz, 0.68H, COOCH₃), 4.11 (d, *J* = 16.2 Hz, 0.82H, N-CH₂), 3.87 (s, 2.31H, COOCH₃), 3.60 (s, 1.12H, N-CH₂), 3.39 (s, 1.02H, N-CH₃), 2.89 (s, 2.02H, N-CH₃). HRMS calcd for C₁₇H₁₅N₃O₃ [M+H]⁺: 310.1186, found 310.1180.

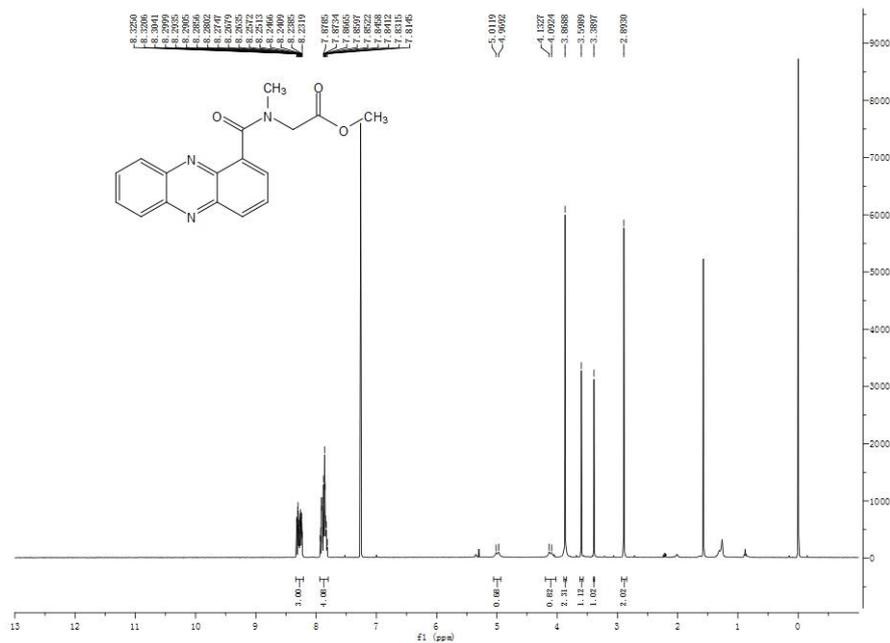


Figure S23. ¹H-NMR Spectrum of compound 3g

XYF-7 #343 RT: 3.32 AV: 1 NL: 1.71E10
T: FTMS + p ESI Full ms [100.00-1500.00]

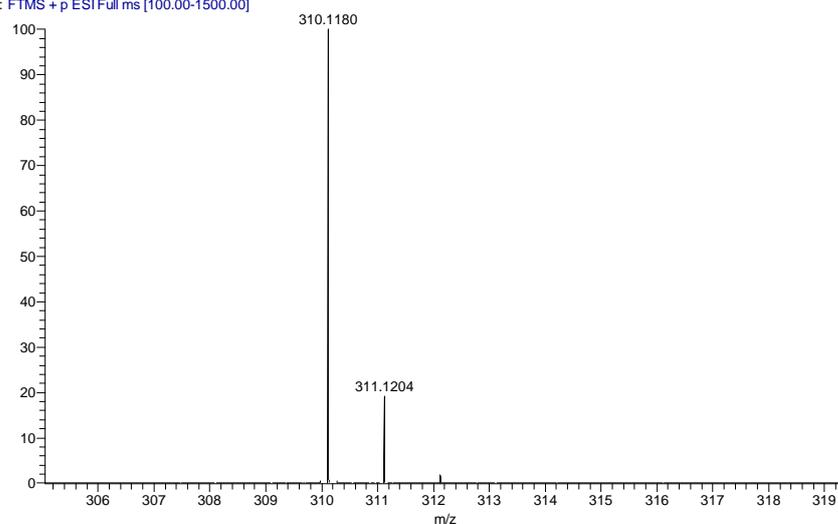


Figure S24. HRMS Spectrum of compound 3g

Methyl 2-(N-ethylphenazine-1-carboxamido)acetate (**3h**) :

Yellow solid; yield: 69%; m.p. 121 – 123°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 – 8.18 (m, 3.00H, Phenazine-H), 7.93 – 7.80 (m, 4.04H, Phenazine-H), 4.87 (d, $J = 17.2$ Hz, 0.71H, N- CH_2 -Methyl), 4.20 – 4.00 (m, 1.05H, N- CH_2), 3.86 (d, $J = 10.2$ Hz, 2.74H, COOCH_3), 3.68 (s, 0.31H, COOCH_3), 3.57 (s, 1.01H, N- CH_2), 3.24 (dt, $J = 14.6, 7.2$ Hz, 1.39H, N- CH_2 -Methyl), 1.42 (t, $J = 7.2$ Hz, 1.00H, N-Methylene- CH_3), 1.04 (t, $J = 7.2$ Hz, 2.09H, N-Methylene- CH_3). HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 324.1343, found 324.1338.

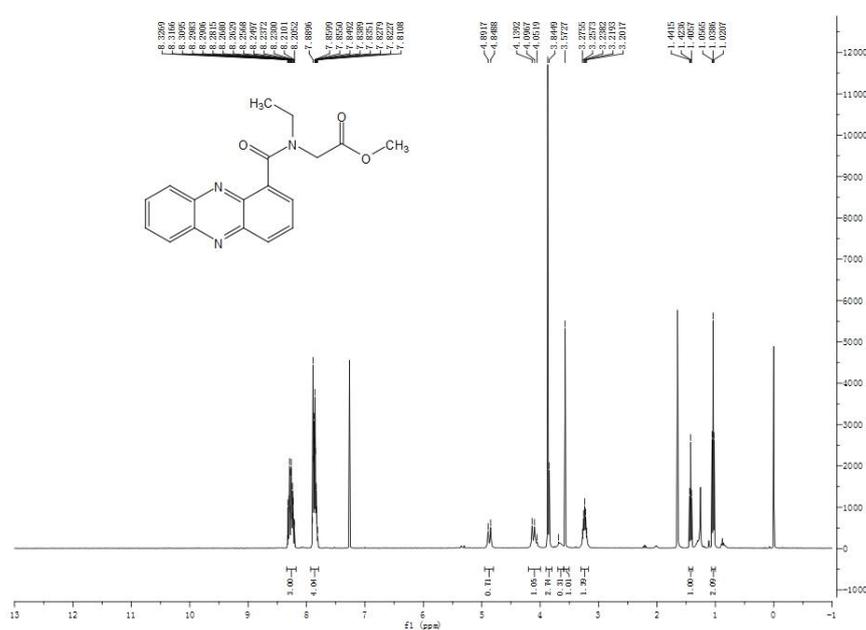


Figure S25. $^1\text{H-NMR}$ Spectrum of compound **3h**

XYF-8 #357 RT: 3.47 AV: 1 NL: 2.30E8
T: FTMS + p ESI Full ms [100.00-1500.00]

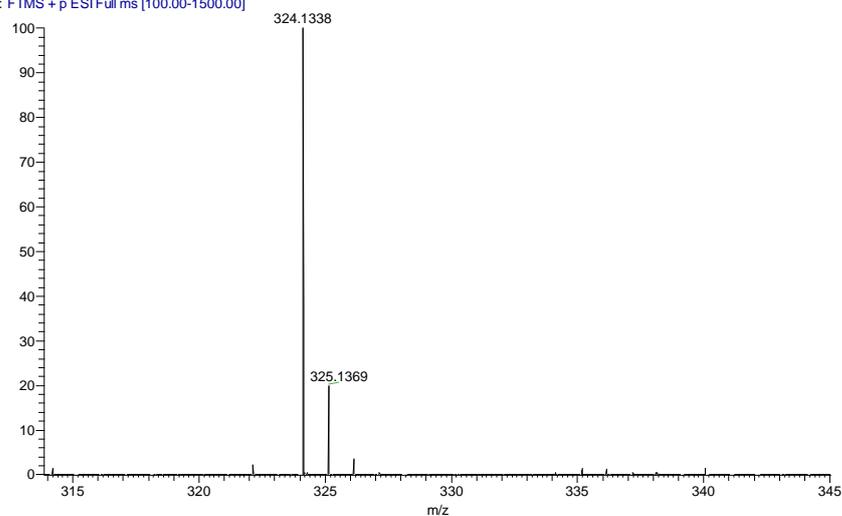


Figure S26. HRMS Spectrum of compound **3h**

Methyl 2-(N-isopropylphenazine-1-carboxamido)acetate (**3i**) :

Yellow solid; yield: 71%; m.p. 171 – 173°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.37 – 8.15 (m, 3.00H, Phenazine-H), 7.98 – 7.77 (m, 4.00H, Phenazine-H), 5.26 (d, $J = 6.6$ Hz, 0.27H, N-CH), 4.71 – 4.60 (m, 0.83H, N-CH), 4.07 – 3.95 (m, 0.88H, N-CH₂), 3.93 – 3.83 (m, 2.37H, COOCH₃), 3.82 – 3.69 (m, 1.27H, N-CH), 3.61 – 3.52 (m, 0.68H, COOCH₃), 1.45 (s, 0.74H, 2 \times CH₃), 1.30 (s, 0.86H, 2 \times CH₃), 1.14 (dd, $J = 9.8, 4.6$ Hz, 2.07H, 2 \times CH₃), 1.10 (dd, $J = 10.0, 4.8$ Hz, 2.42H, 2 \times CH₃) . HRMS calcd for $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 338.1499, found 338.1492.

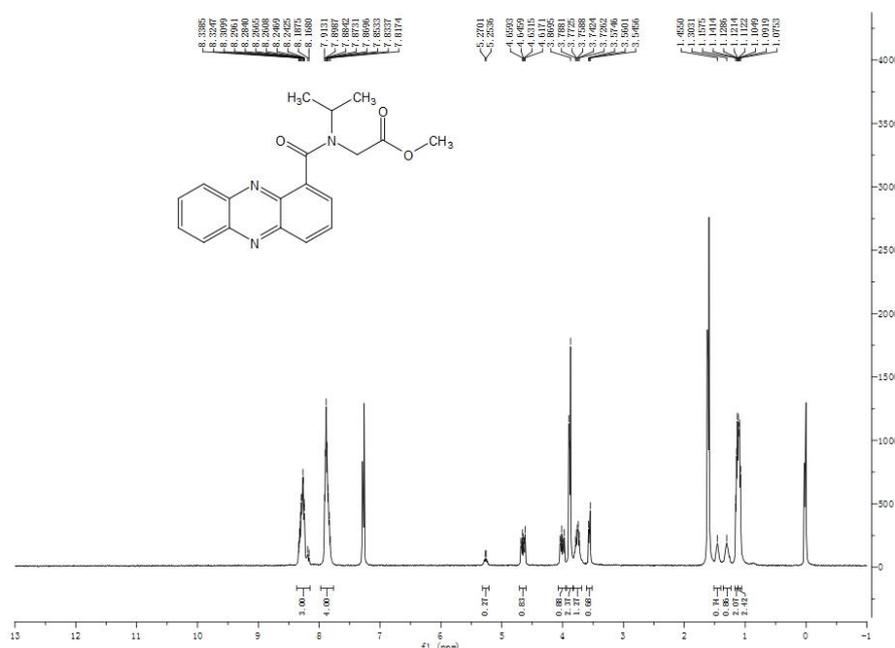


Figure S27. $^1\text{H-NMR}$ Spectrum of compound **3i**

XYF-9 #381 RT: 3.70 AV: 1 NL: 1.66E9
T: FTMS + p ESI Full ms [100.00-1500.00]

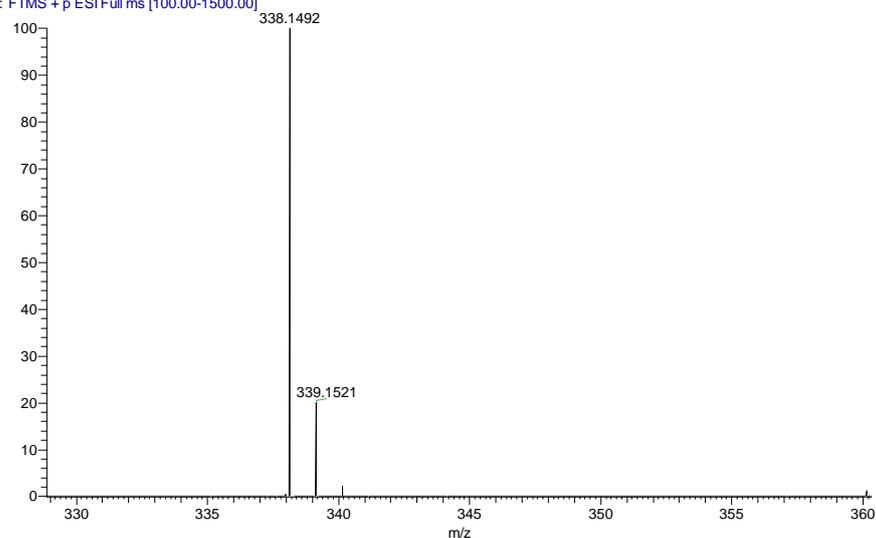


Figure S28. HRMS Spectrum of compound **3i**

Methyl 2-(N-(tert-butyl)phenazine-1-carboxamido)acetate (3j) :

Yellow solid; yield: 81%; m.p. 127 – 129°C; ¹H NMR (400 MHz, CDCl₃) δ 8.27 – 8.17 (m, 3.00H, Phenazine-H), 7.90 – 7.74 (m, 4.10H, Phenazine-H), 4.05 (d, *J* = 19.0 Hz, 1.00H, N-CH₂), 3.81 (d, *J* = 19.0 Hz, 1.03H, N-CH₂), 3.58 (s, 3.04H, COOCH₃), 1.71 (s, 8.88H, 3×CH₃). HRMS calcd for C₂₀H₂₁N₃O₃ [M+H]⁺: 352.1656, found 352.1647.

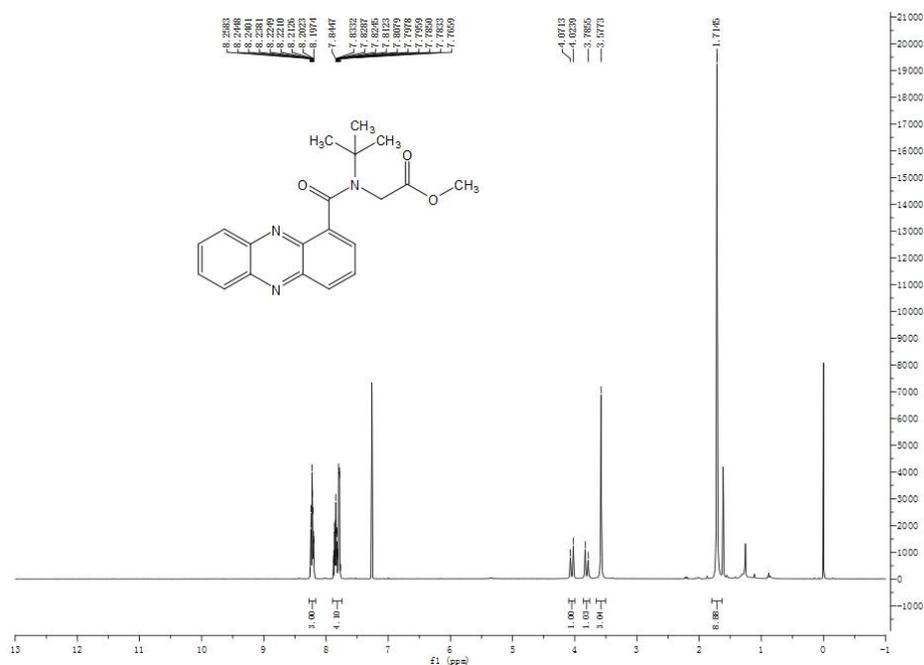


Figure S29. ¹H-NMR Spectrum of compound 3j

XYF-10 #417 RT: 4.06 AV: 1 NL: 3.68E9
T: FTMS + p ESI Full ms [100.00-1500.00]

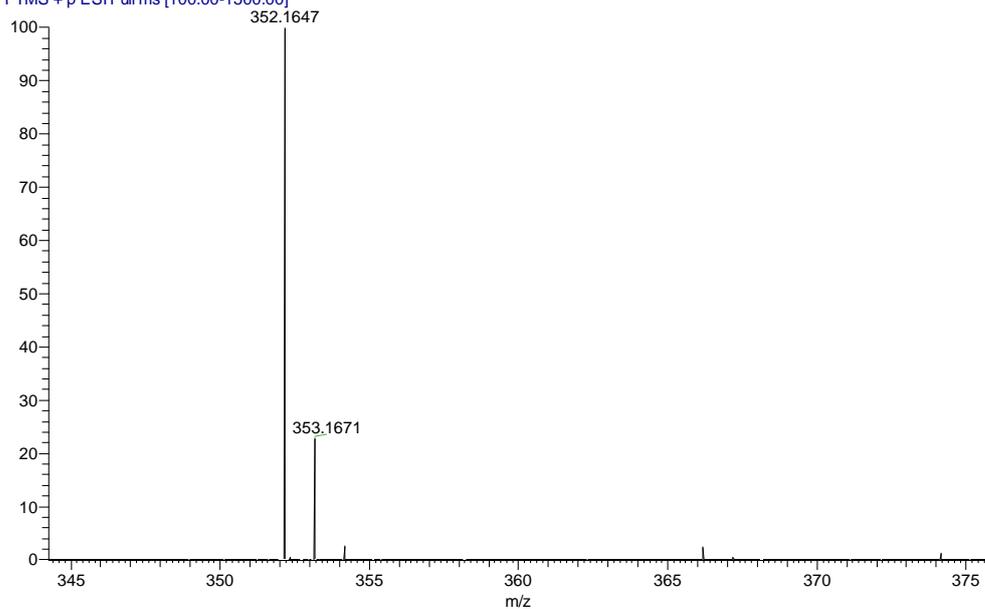


Figure S30. HRMS Spectrum of compound 3j

Methyl 2-(N-benzylphenazine-1-carboxamido)acetate (3k) :

Yellow solid; yield: 76%; m.p. 182 – 184°C; ¹H NMR (400 MHz, CDCl₃) δ 8.39 – 8.19 (m, 3.00H, Phenazine-H), 7.98 – 7.82 (m, 3.98H, Phenazine-H), 7.73 (d, *J* = 7.4 Hz, 0.93H, Benzene-H), 7.49 (t, *J* = 7.6 Hz, 0.98H, Benzene-H), 7.41 – 7.31 (m, 1.56H, Benzene-H), 7.26 – 7.16 (m, 1.48H, Benzene-H), 5.85 (d, *J* = 15.6 Hz, 0.51H, Benzene-CH₂), 4.81 (d, *J* = 17.2 Hz, 0.58H, Benzene-CH₂), 4.55 (d, *J* = 15.6 Hz, 0.60H, N-CH₂), 4.41 – 4.30 (m, 1.03H, Benzene-CH₂), 3.93 (d, *J* = 17.2 Hz, 0.59H, N-CH₂), 3.83 (s, 1.60H, COOCH₃), 3.73 (d, *J* = 15.6 Hz, 0.84H, N-CH₂), 3.57 (s, 1.40H, COOCH₃). HRMS calcd for C₂₃H₁₉N₃O₃ [M+H]⁺: 386.1499, found 386.1492.

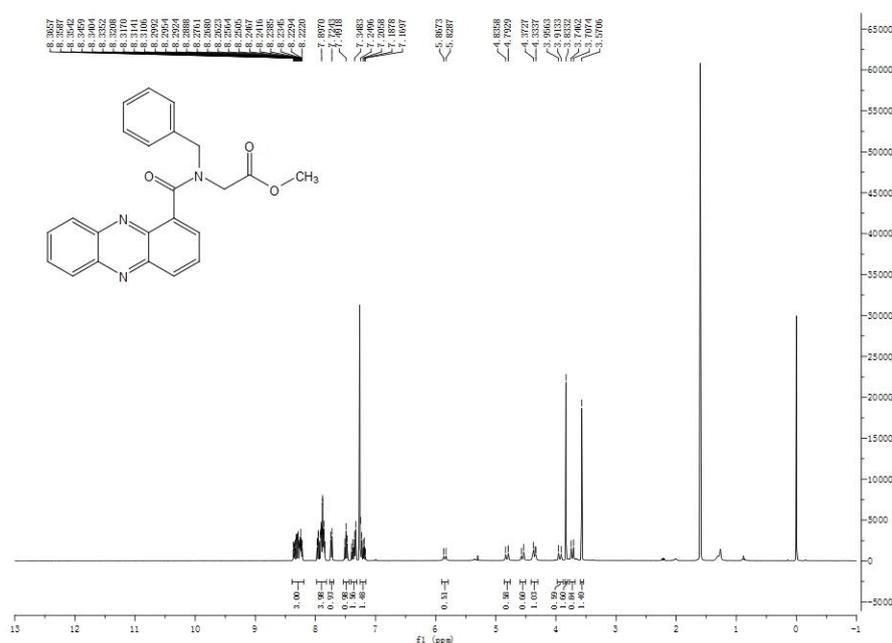


Figure S31. ¹H-NMR Spectrum of compound **3k**

XYF-11 #409 RT: 3.98 AV: 1 NL: 2.09E8
T: FTMS + p ESI Full ms [100.00-1500.00]

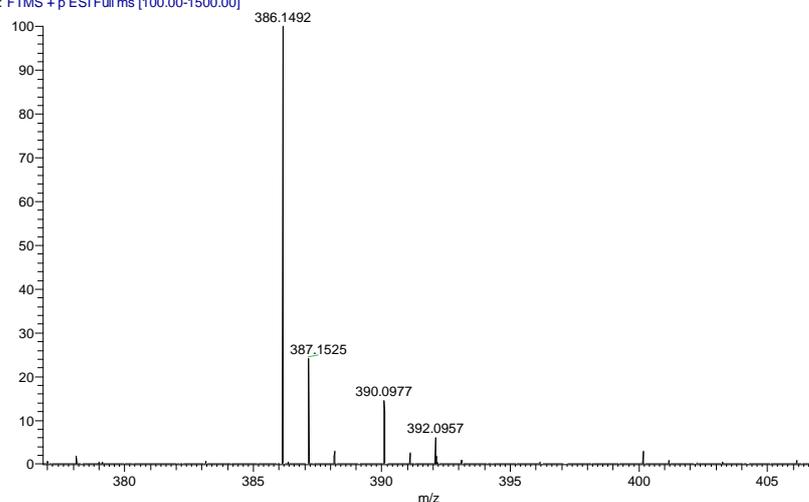


Figure S32. HRMS Spectrum of compound **3k**

Dimethyl 2,2'-((phenazine-1-carbonyl)azanediyl)diacetate (3l) :

Yellow solid; yield: 76%; m.p. 165 – 167°C; ¹H NMR (400 MHz, CDCl₃) δ 8.36 – 8.21 (m, 3.00H, Phenazine-H), 7.98 – 7.81 (m, 4.07H, Phenazine-H), 4.69 (s, 2.04H, N-CH₂), 3.99 (s, 2.01H, N-CH₂), 3.86 (s, 2.98H, COOCH₃), 3.49 (s, 3.00H, COOCH₃). HRMS calcd for C₁₉H₁₇N₃O₅ [M+H]⁺: 368.1241, found 368.1234.

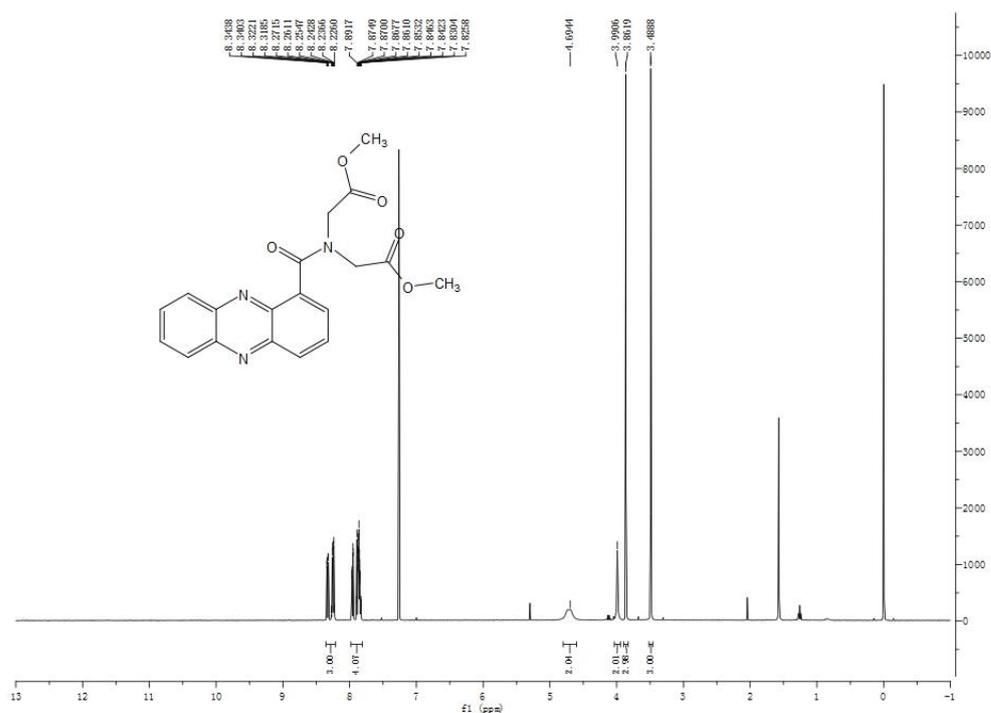


Figure S33. ¹H-NMR Spectrum of compound 3l

XYF-12 #353 RT: 3.43 AV: 1 NL: 1.70E9
T: FTMS + p ESIFull ms [100.00-1500.00]

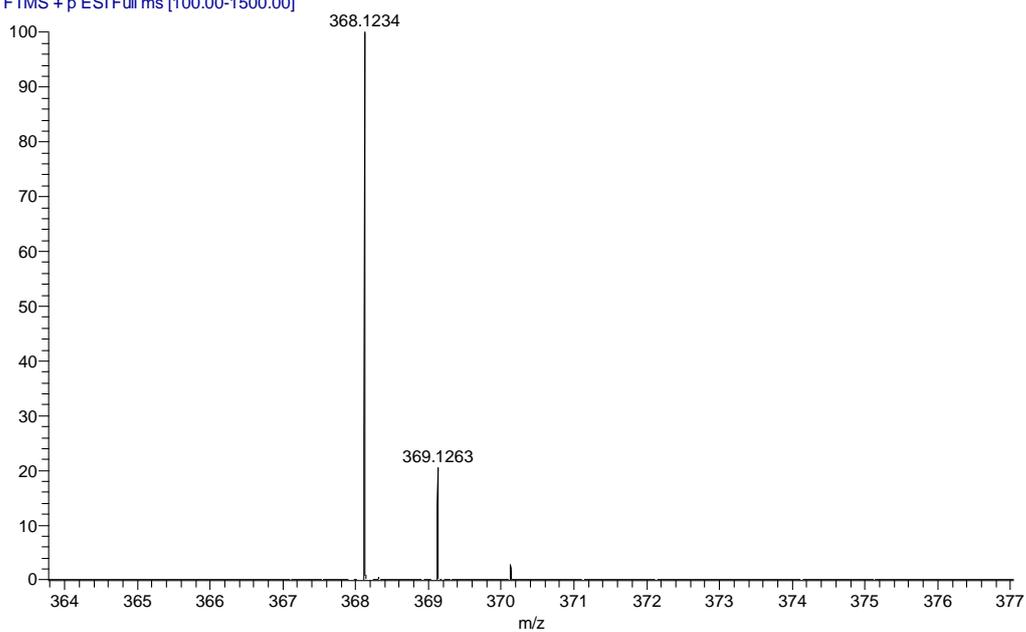


Figure S34. HRMS Spectrum of compound 3l

2-(N-methylphenazine-1-carboxamido)acetic acid (4a) :

Yellow solid; yield: 90%; m.p. 214 – 215°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.79 (s, 1.02H, COOH), 8.38 – 8.13 (m, 3.00H, Phenazine-H), 8.07 – 7.92 (m, 3.02H, Phenazine-H), 7.86 (dd, *J* = 6.8, 1.2 Hz, 0.57H, Phenazine-H), 7.78 (dd, *J* = 6.8, 1.2 Hz, 0.48H, Phenazine-H), 4.66 (d, *J* = 17.2 Hz, 0.61H, N-CH₂), 4.08 (d, *J* = 17.2 Hz, 0.62H, N-CH₂), 3.81 (d, *J* = 11.2 Hz, 0.83H, N-CH₂), 3.20 (s, 1.43H, N-CH₃), 2.77 (s, 1.65H, N-CH₃). HRMS calcd for C₁₆H₁₃N₃O₃ [M+H]⁺: 296.1030, found 296.1024.

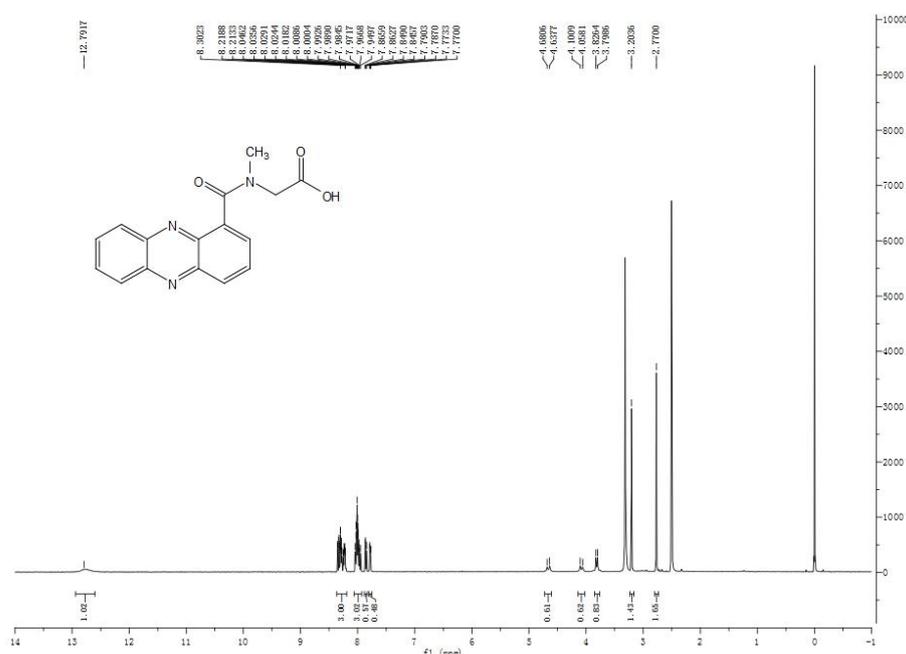


Figure S35. ¹H-NMR Spectrum of compound 4a

XYF-13 #265 RT: 2.57 AV: 1 NL: 2.99E8
T: FTMS + p ESI Full ms [100.00-1500.00]

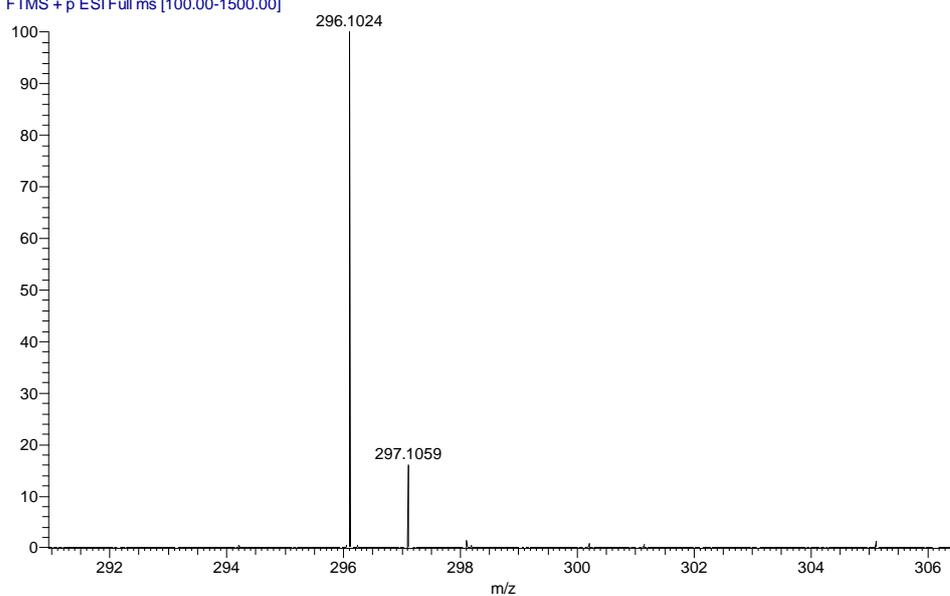


Figure S36. HRMS Spectrum of compound 4a

2-(N-ethylphenazine-1-carboxamido)acetic acid (**4b**) :

Yellow solid; yield: 91%; m.p. 119 – 121°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.69 (s, 1.02H, COOH), 8.38 – 8.15 (m, 3.00H, Phenazine-H), 8.07 – 7.75 (m, 4.08H, Phenazine-H), 4.55 (d, *J* = 17.2 Hz, 0.64H, N-CH₂-Methyl), 4.09 (d, *J* = 17.0 Hz, 0.64H, N-CH₂), 3.88 (d, *J* = 18.6 Hz, 0.76H, N-CH₂), 3.70 (d, *J* = 18.0 Hz, 0.43H, N-CH₂), 3.58 – 3.44 (m, 0.44H, N-CH₂), 3.12 (dt, *J* = 21.2, 7.2 Hz, 1.39H, N-CH₂-Methyl), 1.31 (t, *J* = 7.2 Hz, 1.16H, N-Methylene-CH₃), 0.94 (t, *J* = 7.0 Hz, 1.87H, N-Methylene-CH₃). HRMS calcd for C₁₇H₁₅N₃O₃ [M+H]⁺: 310.1186, found 310.1181.

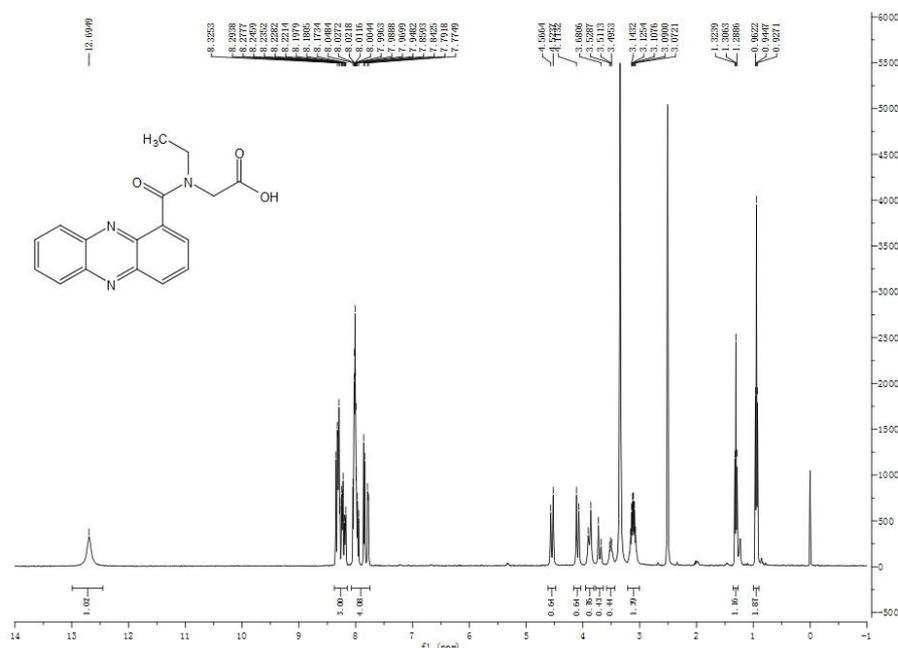


Figure S37. ¹H-NMR Spectrum of compound **4b**

XYF-14 #343 RT: 3.33 AV: 1 NL: 9.92E7
T: FTMS + p ESI Full ms [100.00-1500.00]

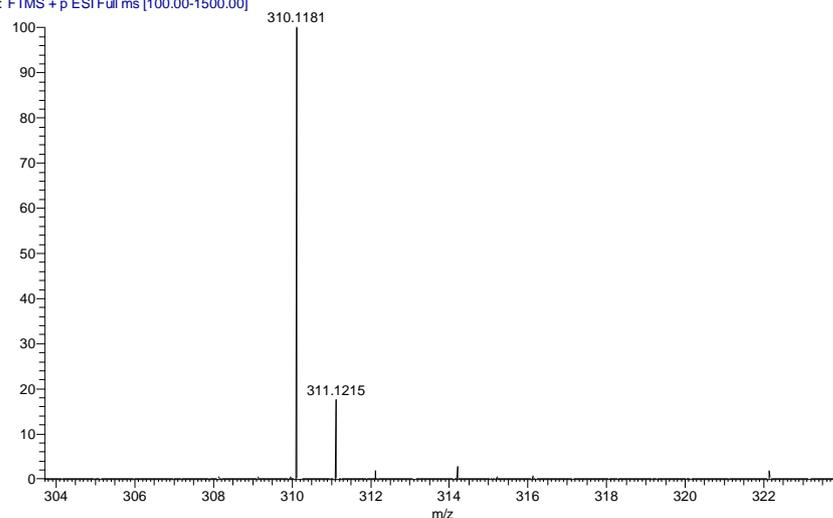


Figure S38. HRMS Spectrum of compound **4b**

2-(N-isopropylphenazine-1-carboxamido)acetic acid (**4c**) :

Yellow solid; yield: 89%; m.p. 230 – 232°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.57 (s, 1.00H, COOH), 8.36 – 8.10 (m, 2.98H, Phenazine-H), 8.07 – 7.73 (m, 4.00H, Phenazine-H), 4.98 (dt, *J* = 13.2, 6.4 Hz, 0.30H, N-CH), 4.31 (d, *J* = 17.0 Hz, 0.78H, N-CH), 4.04 (d, *J* = 17.0 Hz, 0.80H, N-CH₂), 3.90 (d, *J* = 18.8 Hz, 0.27H, N-CH₂), 3.58 (dt, *J* = 13.2, 6.6 Hz, 0.82H, N-CH₂), 3.47 (d, *J* = 19.2 Hz, 0.29H, N-CH₂), 1.29 (dd, *J* = 54.2, 6.6 Hz, 1.99H, 2×CH₃), 1.04 (d, *J* = 6.6 Hz, 2.09H, 2×CH₃), 1.01 (d, *J* = 6.6 Hz, 2.25H, 2×CH₃) . HRMS calcd for C₁₈H₁₇N₃O₃ [M+H]⁺: 324.1343, found 324.1339.

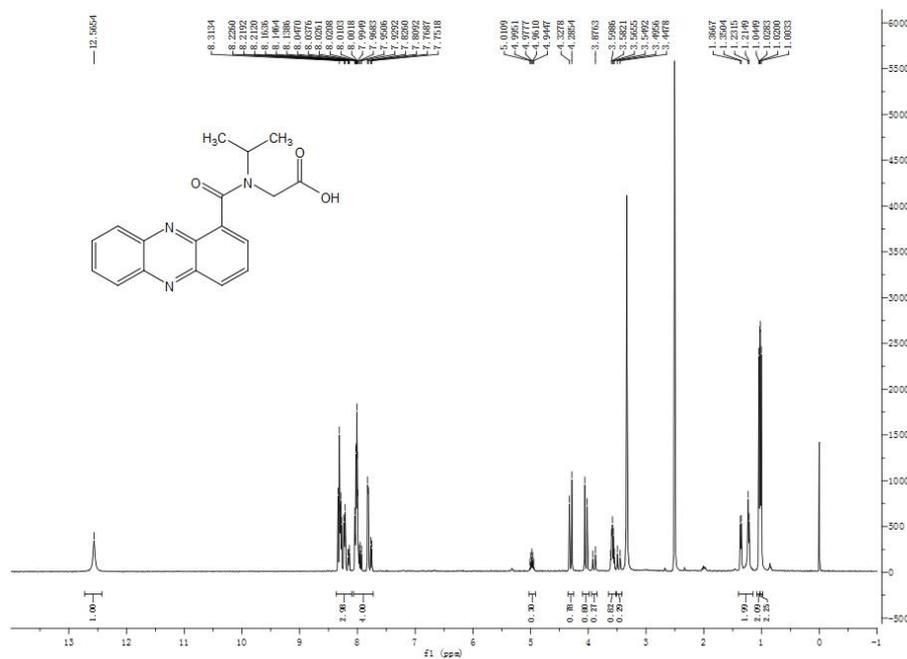


Figure S39. ¹H-NMR Spectrum of compound **4c**

XYF-15 #321 RT: 3.11 AV: 1 NL: 2.10E8
T: FTMS + p ESI Full ms [100.00-1500.00]

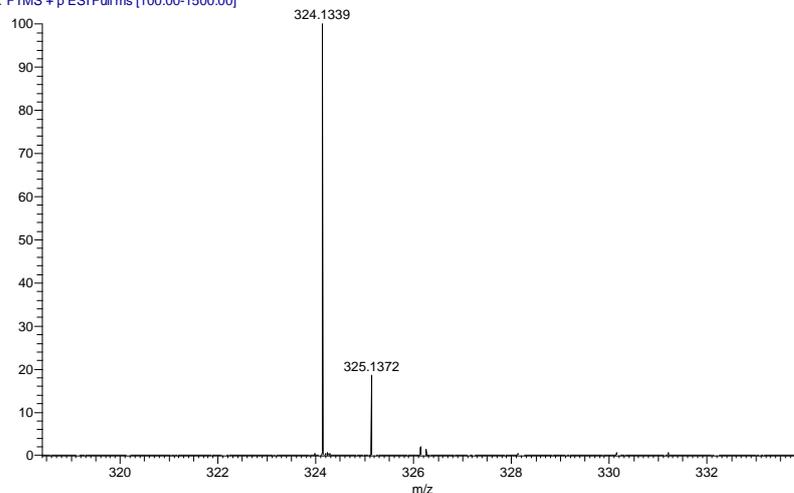


Figure S40. HRMS Spectrum of compound **4c**

2-(N-(tert-butyl)phenazine-1-carboxamido)acetic acid (4d) :

Yellow solid; yield: 92%; m.p. 213 – 214°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.56 (s, 1.02H, COOH), 8.32 – 8.11 (m, 3.00H, Phenazine-H), 8.05 – 7.89 (m, 3.00H, Phenazine-H), 7.70 (d, *J* = 6.7 Hz, 0.97H, Phenazine-H), 4.05 (d, *J* = 19.2 Hz, 1.02H, N-CH₂), 3.62 (d, *J* = 19.2 Hz, 1.02H, N-CH₂), 1.63 (s, 8.66H, 3×CH₃). HRMS calcd for C₁₉H₁₉N₃O₃ [M+H]⁺: 338.1499, found 338.1491.

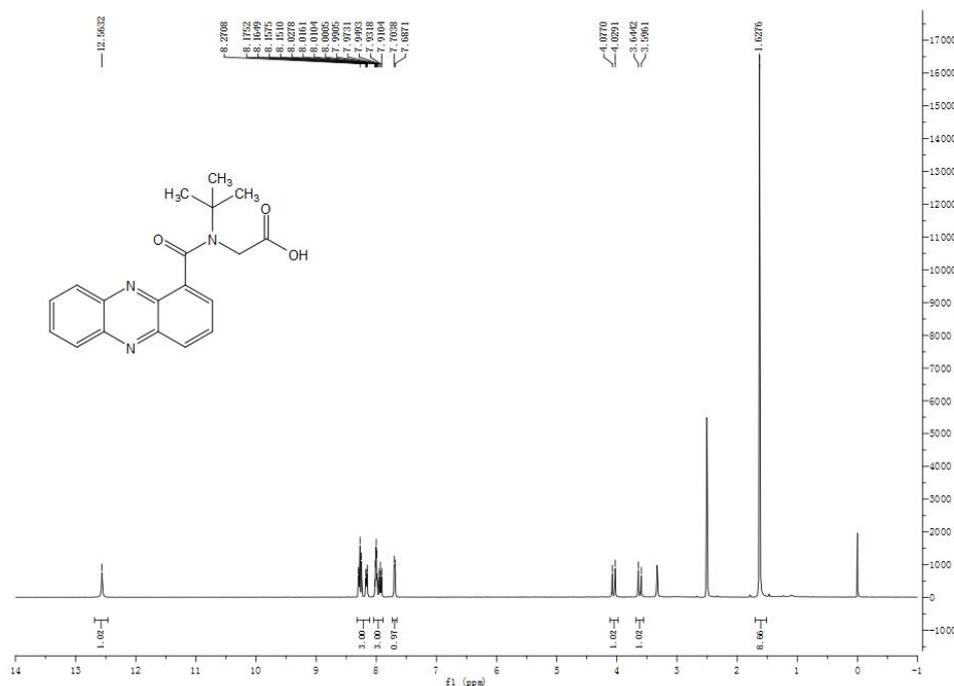


Figure S41. ¹H-NMR Spectrum of compound 4d

XYF-16 #325 RT: 3.15 AV: 1 NL: 8.51E8
T: FTMS + p ESI Full ms [100.00-1500.00]

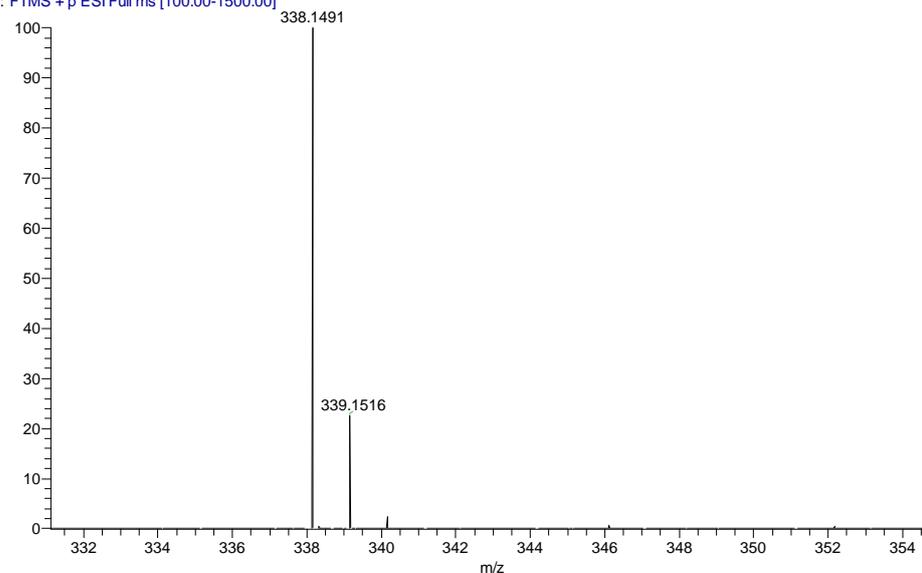


Figure S42. HRMS Spectrum of compound 4d

2-(N-benzylphenazine-1-carboxamido)acetic acid (4e) :

Yellow solid; yield: 87%; m.p. 152 – 154°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.76 (s, 0.96H, COOH), 8.37 – 8.20 (m, 3.00H, Phenazine-H), 8.11 – 7.95 (m, 3.03H, Phenazine-H), 7.87 (ddd, *J* = 17.8, 6.8, 1.2 Hz, 1.02H, Phenazine-H), 7.77 (d, *J* = 7.2 Hz, 1.25H, Benzene-H), 7.54 (t, *J* = 7.6 Hz, 1.30H, Benzene-H), 7.38 (t, *J* = 7.4 Hz, 0.68H, Benzene-H), 7.29 (d, *J* = 7.4 Hz, 0.72H, Benzene-H), 7.20 (t, *J* = 7.4 Hz, 0.74H, Benzene-H), 7.11 (t, *J* = 7.2 Hz, 0.38H, Benzene-H), 4.57 – 4.21 (m, 2.01H, Benzene-CH₂), 3.69 (dt, *J* = 41.2, 17.4 Hz, 2.04H, N-CH₂). HRMS calcd for C₂₂H₁₇N₃O₃ [M+H]⁺: 372.1343, found 372.1336.

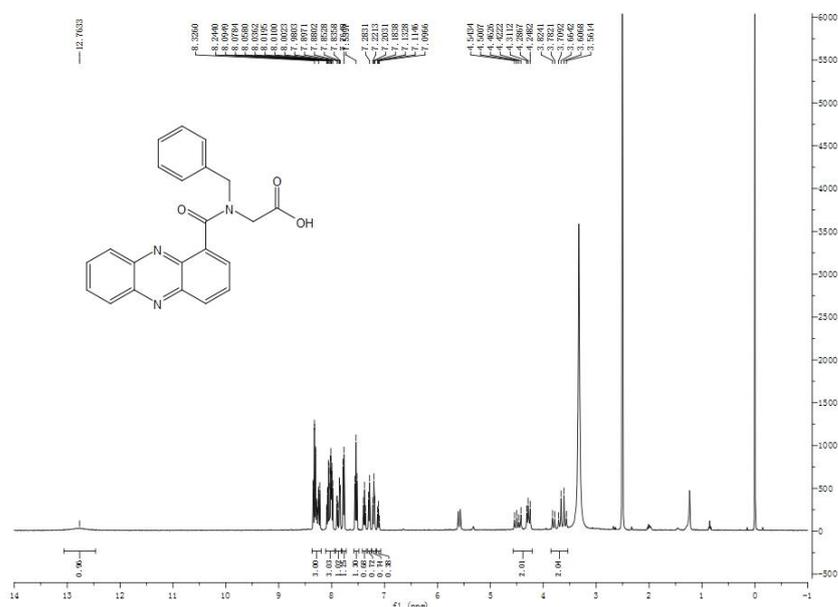


Figure S43. ¹H-NMR Spectrum of compound 4e

XYF-17 #321 RT: 3.11 AV: 1 NL: 3.16E9
T: FTMS + p ESI Full ms [100.00-1500.00]

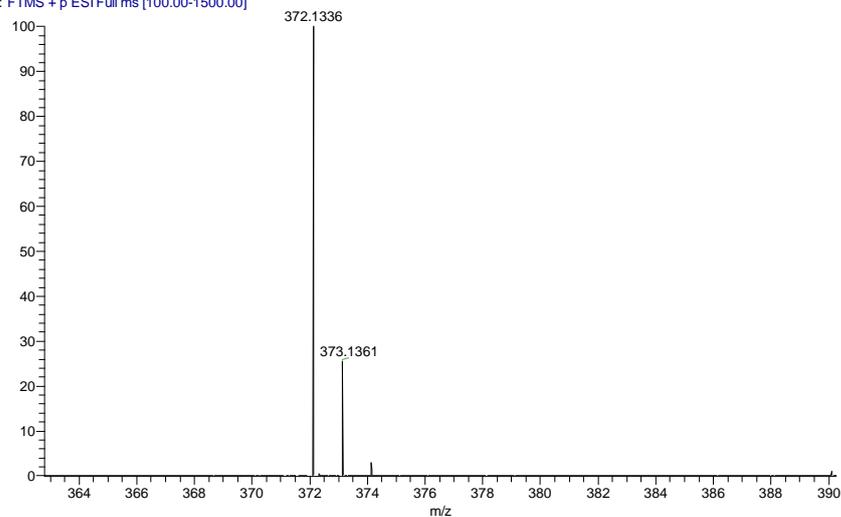


Figure S44. HRMS Spectrum of compound 4e

2,2'-((phenazine-1-carbonyl)azanediyldiacetic acid (4f) :

Yellow solid; yield: 90%; m.p. 224 – 226°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.75 (s, 2.02H, COOH), 8.48 – 8.36 (m, 2.03H, Phenazine-H), 8.29 (s, 1.00H, Phenazine-H), 8.16 – 8.04 (m, 3.00H, Phenazine-H), 7.94 (d, *J* = 5.8 Hz, 1.00H, Phenazine-H), 4.50 (s, 2.01H, N-CH₂), 3.96 (s, 2.03H, N-CH₂). HRMS calcd for C₁₇H₁₃N₃O₅ [M+H]⁺: 340.0928, found 340.0922.

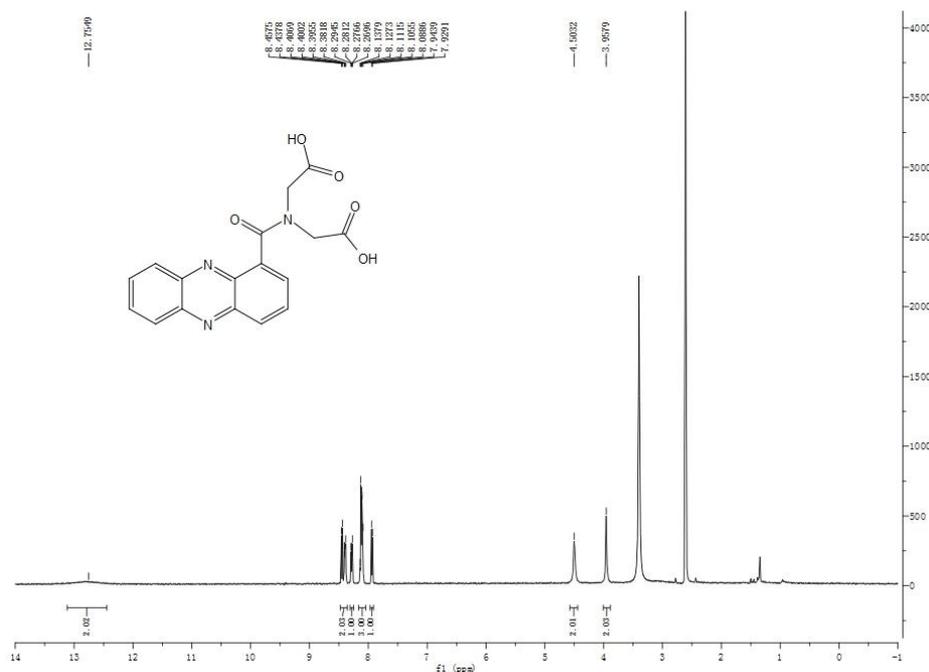


Figure S45. ¹H-NMR Spectrum of compound 4f

XYF-18 #231 RT: 2.23 AV: 1 NL: 6.65E9
T: FTMS + p ESI Full ms [100.00-1500.00]

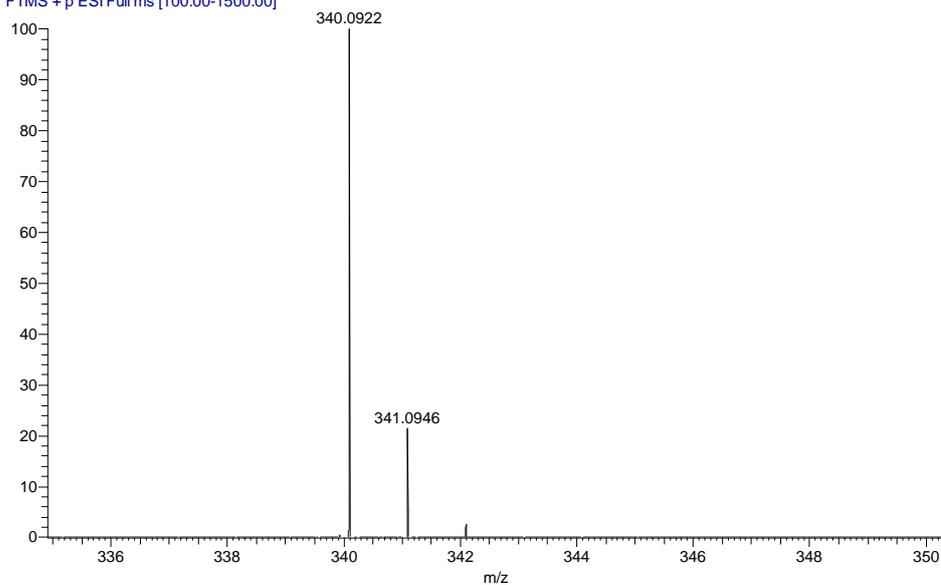


Figure S46. HRMS Spectrum of compound 4f