I. Copies of $^1$H and $^{13}$C NMR spectra

**Figure S1.** $^1$H NMR spectrum of 3-phenylprop-2-ynamide (1a) (DMSO-$d_6$, 400 MHz, 25 °C).

**Figure S2.** $^{13}$C NMR spectrum of 3-phenylprop-2-ynamide (1a) (DMSO-$d_6$, 100 MHz, 25 °C).
Figure S3. $^1$H NMR spectrum of 3-(2-chlorophenyl)prop-2-ynamide (1b) (DMSO-$d_6$, 400 MHz, 25 °C).

Figure S4. $^{13}$C NMR spectrum of 3-(2-chlorophenyl)prop-2-ynamide (1b) (DMSO-$d_6$, 100 MHz, 25 °C).
**Figure S5.** $^1$H NMR spectrum of 3-(4-chlorophenyl)prop-2-ynamide (1c) (DMSO-$d_6$, 400 MHz, 25 °C).

**Figure S6.** $^{13}$C NMR spectrum of 3-(4-chlorophenyl)prop-2-ynamide (1c) (DMSO-$d_6$, 100 MHz, 25 °C).
Figure S7. $^1$H NMR spectrum of 3-(4-bromophenyl)prop-2-ynamide (1d) (DMSO-$d_6$, 400 MHz, 25 °C).

Figure S8. $^{13}$C NMR spectrum of 3-(4-bromophenyl)prop-2-ynamide (1d) (DMSO-$d_6$, 400 MHz, 25 °C).
Figure S9. $^1$H NMR spectrum of 3-(4-nitrophenyl)prop-2-ynamide (1e) (DMSO-$d_6$, 400 MHz, 25 °C).

Figure S10. $^{13}$C NMR spectrum of 3-(4-nitrophenyl)prop-2-ynamide (1e) (DMSO-$d_6$, 100 MHz, 25 °C).
**Figure S11.** $^1$H NMR spectrum of 6-chloro-4-hydroxy-2-oxo-N-(3-phenylprop-2-ynoyl)-2H-pyran-3-carboxamide (5a) (CDCl$_3$, 400 MHz, 25 °C).

**Figure S12.** $^{13}$C NMR spectrum of 6-chloro-4-hydroxy-2-oxo-N-(3-phenylprop-2-ynoyl)-2H-pyran-3-carboxamide (5a) (CDCl$_3$, 400 MHz, 25 °C).
Figure S13. $^1$H NMR spectrum of 6-chloro-$N$-[3-(2-chlorophenyl)prop-2-ynoyl]-4-hydroxy-2-oxo-2H-pyran-3-carboxamide (5b) (CDCl$_3$, 400 MHz, 25 °C).

Figure S14. $^{13}$C NMR spectrum of 6-chloro-$N$-[3-(2-chlorophenyl)prop-2-ynoyl]-4-hydroxy-2-oxo-2H-pyran-3-carboxamide (5b) (CDCl$_3$, 100 MHz, 25 °C).
Figure S15. $^1$H NMR spectrum of 6-chloro-$N$-[3-(4-chlorophenyl)prop-2-ynoyl]-4-hydroxy-2-oxo-$2H$-pyran-3-carboxamide (5c) (CDCl$_3$, 400 MHz, 25 °C).

Figure S16. $^1$H NMR spectrum of 6-chloro-$N$-[3-(4-chlorophenyl)prop-2-ynoyl]-4-hydroxy-2-oxo-$2H$-pyran-3-carboxamide (5c) (DMF-$d_7$, 400 MHz, 25 °C).
Figure S17. $^{13}$C NMR spectrum of 6-chloro-$N$-[3-(4-chlorophenyl)prop-2-ynoyl]-4-hydroxy-2-oxo-$2H$-pyran-3-carboxamide (5c) (DMF-$d_7$, 100 MHz, 25 °C).

Figure S18. $^1$H NMR spectrum of 6-chloro-$N$-[3-(4-bromophenyl)prop-2-ynoyl]-4-hydroxy-2-oxo-$2H$-pyran-3-carboxamide (5d) (DMF-$d_7$, 400 MHz, 25 °C).
Figure S19. $^{13}$C NMR spectrum of 6-chloro-$N$-[3-(4-bromophenyl)prop-2-ynoyl]-4-hydroxy-2-oxo-2$H$-pyran-3-carboxamide (5d) (DMF-$d_7$, 100 MHz, 25 °C).

Figure S20. $^1$H NMR spectrum of 4-hydroxy-5-methyl-2-(phenylethynyl)-6$H$-1,3-oxazin-6-one (8a) (DMSO-$d_6$, 400 MHz, 25 °C).
Figure S21. $^{13}$C NMR spectrum of 4-hydroxy-5-methyl-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8a) (DMSO-$d_6$, 100 MHz, 25 °C).

Figure S22. $^1$H NMR spectrum of 5-ethyl-4-hydroxy-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8b) (DMSO-$d_6$, 400 MHz, 25 °C).
Figure S23. $^{13}$C NMR spectrum of 5-ethyl-4-hydroxy-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8b) (DMSO-$d_6$, 100 MHz, 25 °C).

Figure S24. $^1$H NMR spectrum of 4-hydroxy-2-(phenylethynyl)-5-(propan-2-yl)-6H-1,3-oxazin-6-one (8c) (DMSO-$d_6$, 400 MHz, 25 °C).
**Figure S25.** $^{13}$C NMR spectrum of 4-hydroxy-2-(phenylethynyl)-5-(propan-2-yl)-6H-1,3-oxazin-6-one (8c) (DMSO-$d_6$, 100 MHz, 25 °C).

**Figure S26.** $^1$H NMR spectrum of 5-butyl-4-hydroxy-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8d) (DMSO-$d_6$, 400 MHz, 25 °C).
Figure S27. $^{13}$C NMR spectrum of 5-butyl-4-hydroxy-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8d) (DMSO-$d_6$, 100 MHz, 25 °C).

Figure S28. $^1$H NMR spectrum of 4-hydroxy-5-phenyl-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8e) (DMSO-$d_6$, 400 MHz, 25 °C).
Figure S29. $^{13}$C NMR spectrum of 4-hydroxy-5-phenyl-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8e) (DMSO-$d_6$, 100 MHz, 25 °C).

Figure S30. $^1$H NMR spectrum of 5-benzyl-4-hydroxy-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8f) (DMSO-$d_6$, 400 MHz, 25 °C).
Figure S31. $^{13}$C NMR spectrum of 5-benzyl-4-hydroxy-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8f) (DMSO-$d_6$, 100 MHz, 25 °C).

Figure S32. $^1$H NMR spectrum of 4-hydroxy-5-methyl-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8a) and its hydrolysis product (9a) (DMSO-$d_6$, 400 MHz, 25 °C): signals marked in red indicating the appearance of 9a after standing of 8a for one day in DMSO.
Figure S33. $^{13}$C NMR spectrum of 4-hydroxy-5-methyl-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8a) and its hydrolysis product (9a) (DMSO-$d_6$, 400 MHz, 25 °C): signals marked in red indicating the appearance of 9a after standing of 8a for one day in DMSO.

Figure S34. $^1$H NMR spectrum of 5-ethyl-4-hydroxy-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8b) and its hydrolysis product (9b) (DMSO-$d_6$, 400 MHz, 25 °C): signals marked in red indicating the appearance of 9b after standing of 8b for one day in DMSO.
Figure S35. $^{13}$C NMR spectrum of 5-ethyl-4-hydroxy-2-(phenylethynyl)-6-$H$-1,3-oxazin-6-one (8b) and its hydrolysis product (9b) (DMSO-$d_6$, 400 MHz, 25 °C): signals marked in red indicating the appearance of 9b after standing of 8b for one day in DMSO.

Figure S36. $^1$H NMR spectrum of 4-hydroxy-2-(phenylethynyl)-5-(propan-2-yl)-6-$H$-1,3-oxazin-6-one (8c) and its hydrolysis product (9c) (DMSO-$d_6$, 400 MHz, 25 °C): signals marked in red indicating the appearance of 9c after standing of 8c for one day in DMSO.
Figure S37. $^{13}$C NMR spectrum of 4-hydroxy-2-(phenylethynyl)-5-(propan-2-yl)-6H-1,3-oxazin-6-one (8c) and its hydrolysis product (9c) (DMSO-$d_6$ 400 MHz, 25 °C); signals marked in red indicating the appearance of 9c after standing of 8c for one day in DMSO.

Figure S38. $^1$H NMR spectrum of 5-butyl-4-hydroxy-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8d) and its hydrolysis product (9d) (DMSO-$d_6$ 400 MHz, 25 °C); signals marked in red indicating the appearance of 9d after standing of 8d for one day in DMSO.
Figure S39. $^{13}$C NMR spectrum of 5-butyl-4-hydroxy-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8d) and its hydrolysis product (9d) (DMSO-$d_6$, 400 MHz, 25 °C): signals marked in red indicating the appearance of 9d after standing of 8d for one day in DMSO.

Figure S40. $^1$H NMR spectrum of 5-benzyl-4-hydroxy-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8f) and its hydrolysis product (9f) (DMSO-$d_6$, 400 MHz, 25 °C): signals marked in red indicating the appearance of 9f after standing of 8f for one day in DMSO.
**Figure S41.** $^{13}$C NMR spectrum of 5-benzyl-4-hydroxy-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8f) and its hydrolysis product (9f) (DMSO-$d_6$, 400 MHz, 25 °C): signals marked in red indicating the appearance of 9f after standing of 8f for one day in DMSO.

**Figure S42.** $^1$H NMR spectrum of 4-hydroxy-5-phenyl-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8e) and 3-phenyl-N-(phenylacetyl)prop-2-ynamide (10) (DMSO-$d_6$, 400 MHz, 25 °C): signals marked in red indicating the appearance of 10 after standing of 8e for one day in DMSO.
**Figure S43.** $^{13}$C NMR spectrum of 4-hydroxy-5-phenyl-2-(phenylethynyl)-6H-1,3-oxazin-6-one (8e) and 3-phenyl-N-(phenylacetyl)prop-2-ynamide (10) (DMSO-$d_6$, 400 MHz, 25 °C): signals marked in red indicating the appearance of 10 after standing of 8e for one day in DMSO.

**Figure S44.** $^1$H NMR spectrum of 3-phenyl-N-(phenylacetyl)prop-2-ynamide (10) (DMSO-$d_6$, 400 MHz, 25 °C).
Figure S45. $^{13}$C NMR spectrum of 3-phenyl-$N$-(phenylacetyl)prop-2-ynamide (10) (DMSO-$d_6$, 100 MHz, 25 °C).

Figure S46. $^1$H NMR spectrum of 3-\{[(2Z)-3-Chloro-3-phenylprop-2-enoyl]amino\}-2,2-dimethyl-3-oxopropanoic acid (12a) (DMSO-$d_6$, 400 MHz, 25 °C).
Figure S47. $^{13}$C NMR spectrum of 3-\{(2Z)-3-Chloro-3-phenylprop-2-enoyl\}amino)-2,2-dimethyl-3-oxopropanoic acid (12a) (DMSO-$d_6$, 100 MHz, 25 °C).

Figure S48. $^1$H NMR spectrum of 3-\{(2Z)-3-Chloro-3-(4-chlorophenyl)prop-2-enoyl\}amino)-2,2-dimethyl-3-oxopropanoic acid (12b) (DMSO-$d_6$, 400 MHz, 25 °C).
**Figure S49.** $^{13}$C NMR spectrum of 3-*((2Z)-3-Chloro-3-(4-chlorophenyl)prop-2-enoyl)amino)-2,2-dimethyl-3-oxopropanoic acid (12b) (DMSO-$d_6$, 100 MHz, 25 °C).

**Figure S50.** $^1$H NMR spectrum of (2Z)-3-Chloro-$N$-(2-methylpropanoyl)-3-phenyl-prop-2-enamide (13a) (DMSO-$d_6$, 400 MHz, 25 °C).
Figure S51. $^{13}$C NMR spectrum of (2Z)-3-Chloro-N-(2-methylpropanoyl)-3-phenyl-prop-2-enamide (13a) (DMSO-$d_6$, 100 MHz, 25 °C).

Figure S52. $^1$H NMR spectrum of (2Z)-3-Chloro-3-(4-chlorophenyl)-N-(2-methyl-propanoyl)prop-2-enamide (13b) (CD$_3$CN, 400 MHz, 25 °C).
Figure S53. $^{13}$C NMR spectrum of (2Z)-3-Chloro-3-((4-chlorophenyl)-N-(2-methyl-propanoyl)prop-2-enamide (13b) (CD$_3$CN, 100 MHz, 25 °C).