

Supporting Information

Naphtho[1,8-*de*][1,2]Oxazin-4-ol: Precursor to 1,2,8-Trisubstituted Naphthalenes and 1-Unsubstituted Naphtho[1,2-*d*]isoxazole 2-Oxide: A Novel Isomerization of the *N*-Oxide to Nitrile Oxide *en Route* to Isoxazol(in)es

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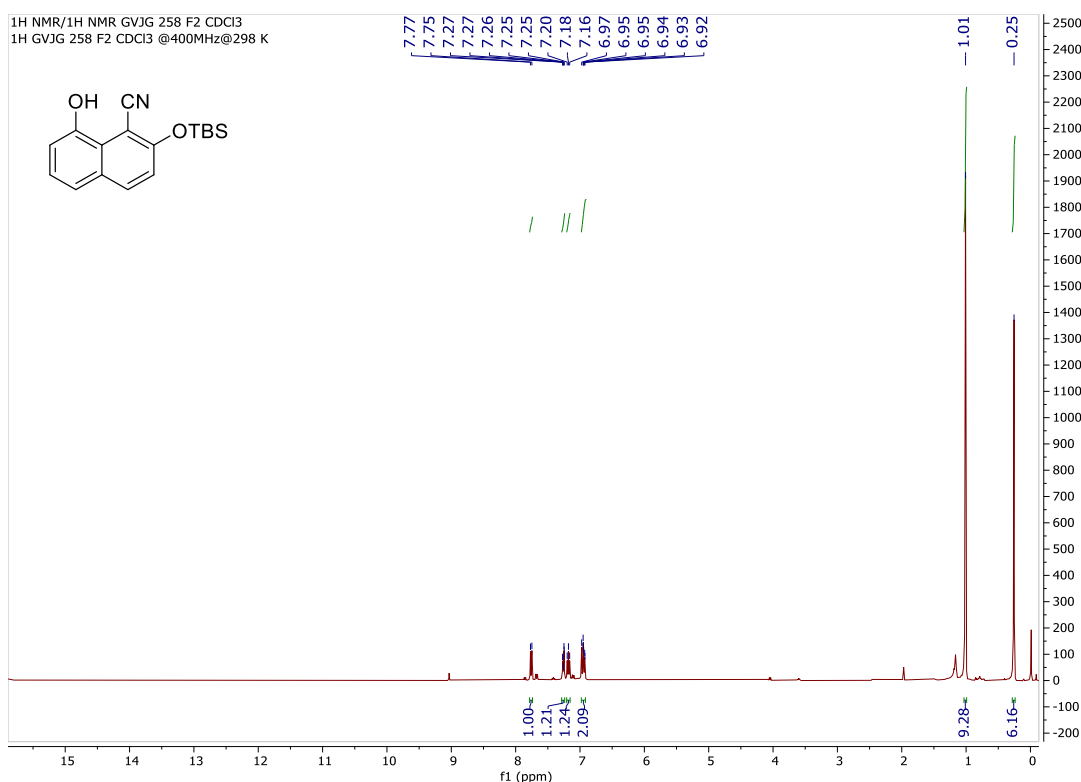


Figure S1. ^1H NMR (400 MHz, CDCl_3) of compound (**11**).

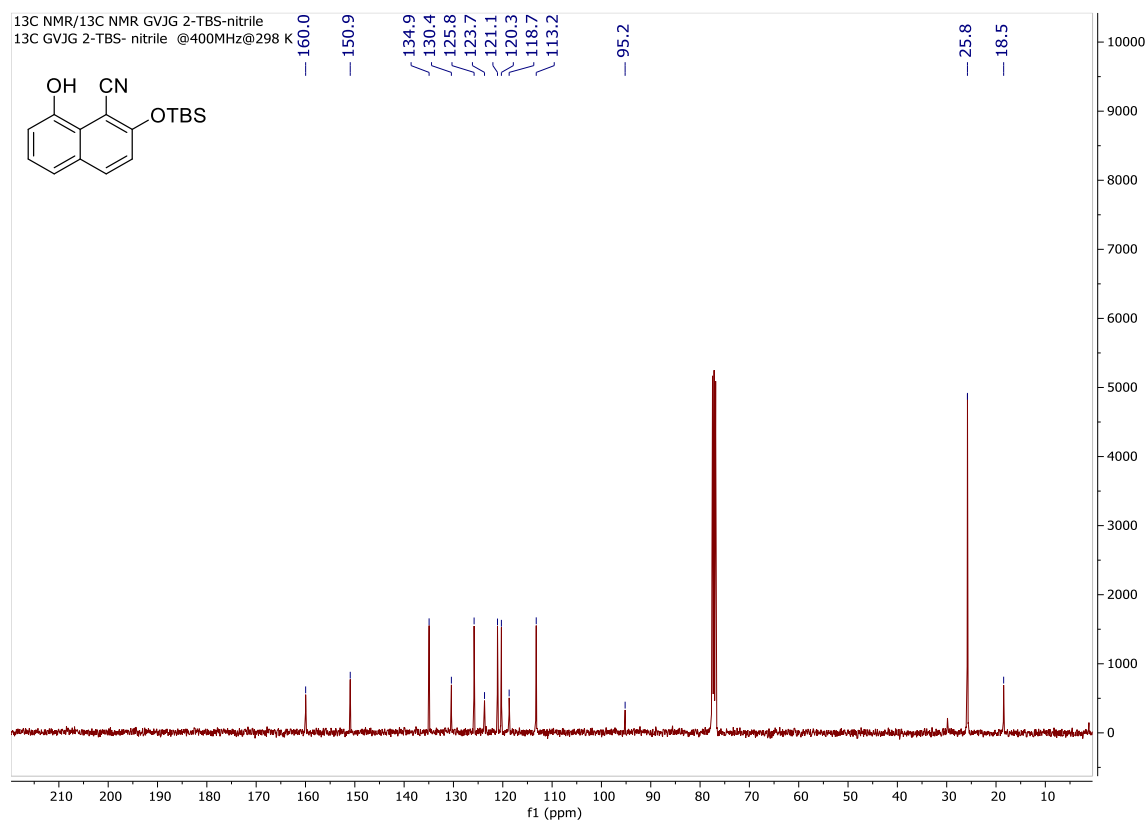


Figure S2. ^{13}C NMR (100.6 MHz, CDCl_3) of compound (**11**).

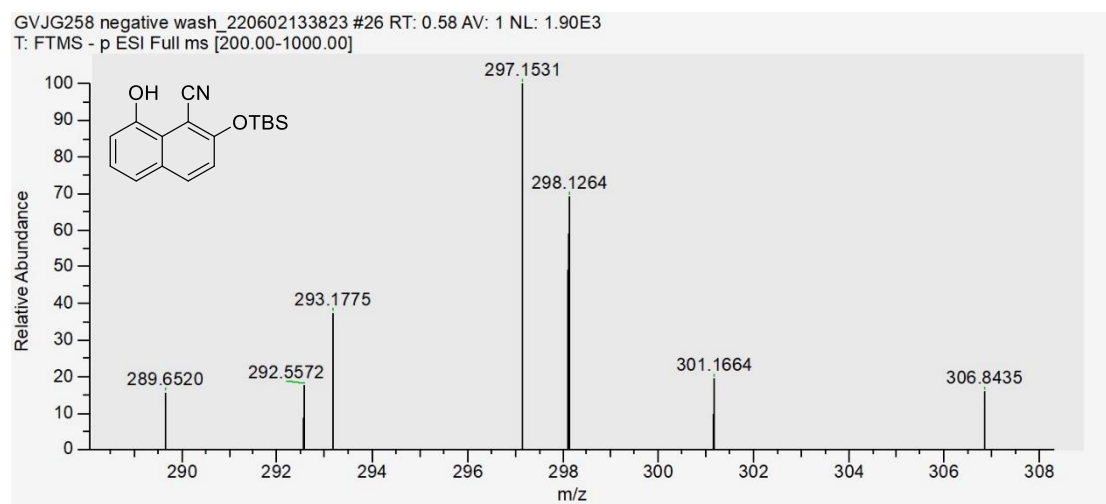


Figure S3. HRMS $[\text{M}+\text{H}]^+$ of compound (**11**) using 0.1% HCO_2H in MeOH as solvent.

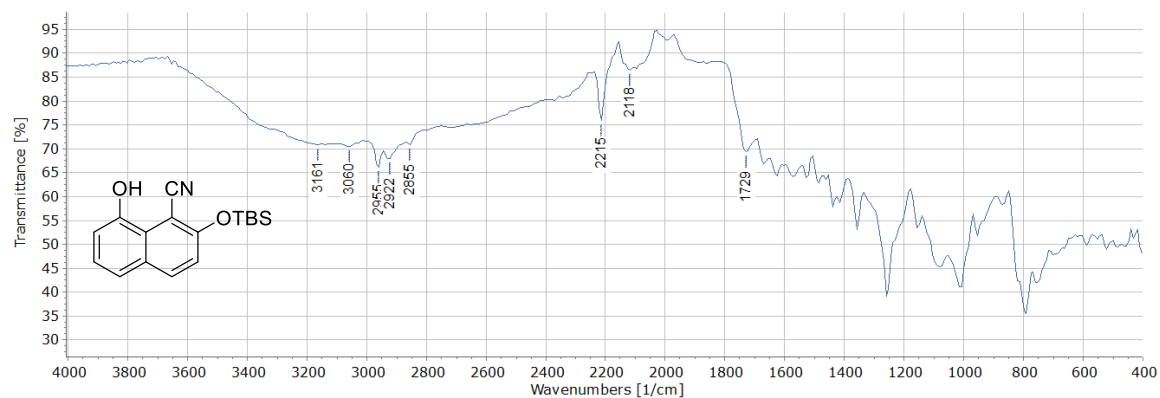


Figure S4. IR spectrum (solid) of compound (11).

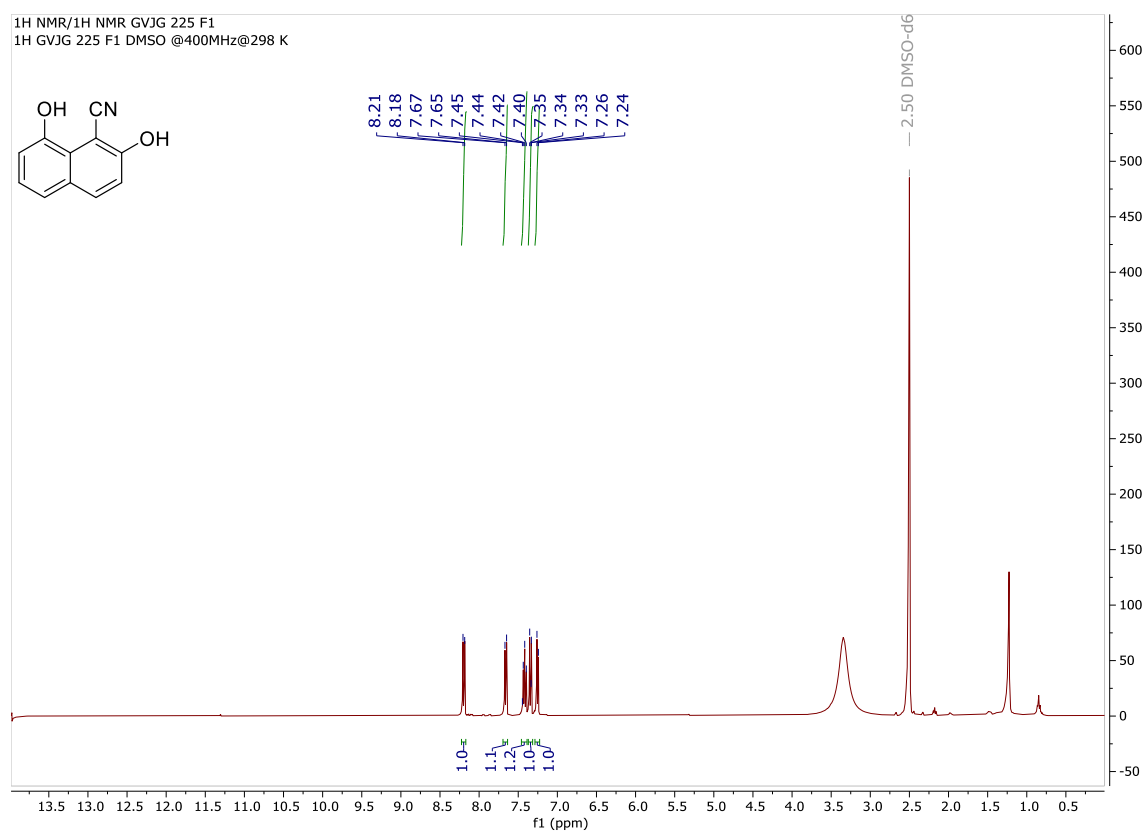


Figure S5. ¹H NMR (400 MHz, DMSO-*d*₆) of compound (5).

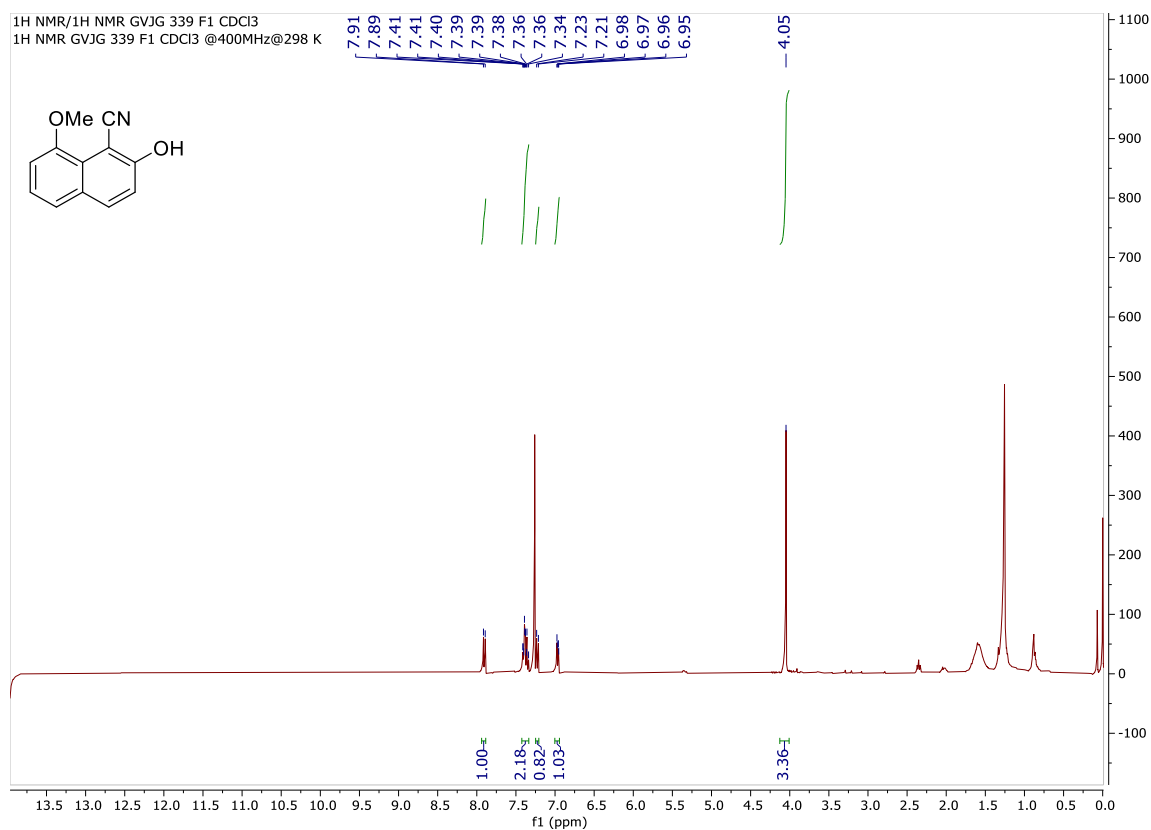


Figure S6. ^1H NMR (400 MHz, CDCl_3) of compound (12).

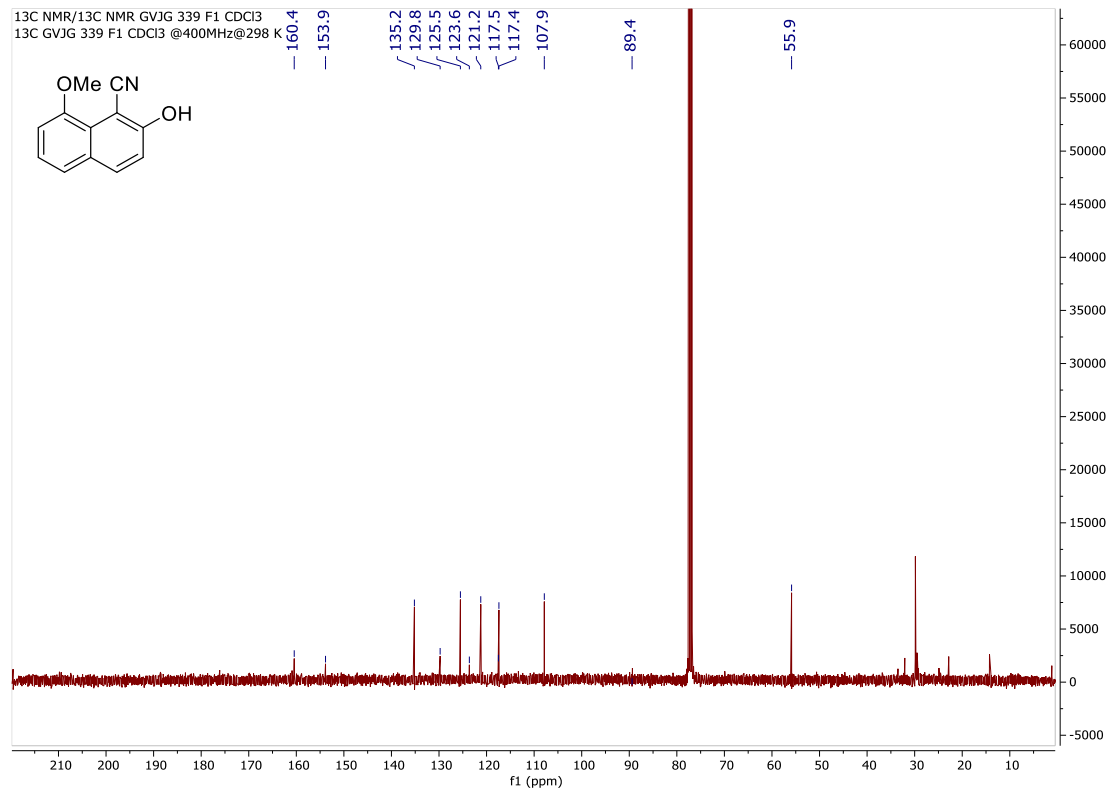


Figure S7. ^{13}C NMR (100.6 MHz, CDCl_3) of compound (12).

GVJG236_200622131935 #17 RT: 0.16 AV: 1 NL: 3.45E7
T: FTMS + p ESI Full ms [150.00-2000.00]

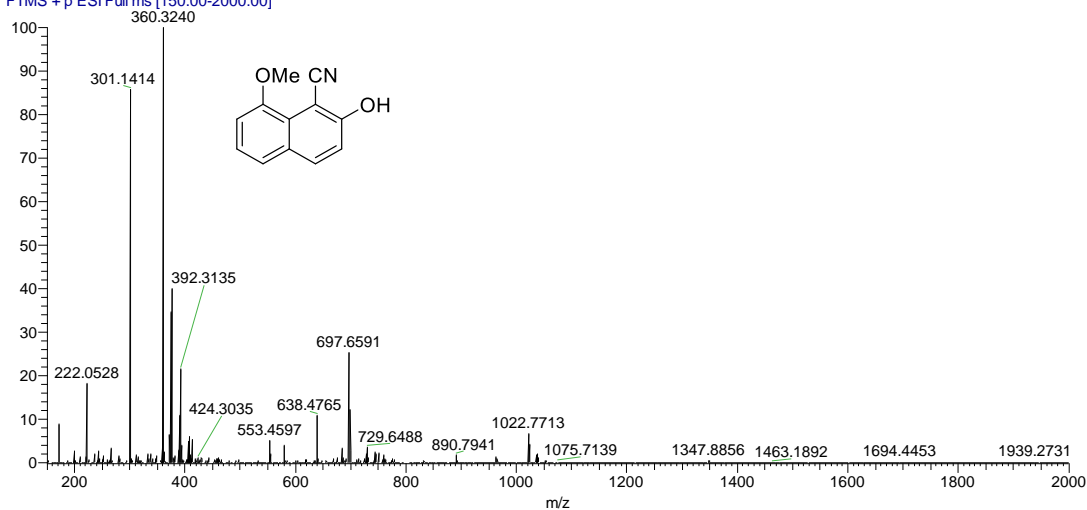


Figure S8. HRMS $[M+H]^+$ of compound (12) using 0.1% HCO_2H in MeOH as solvent.

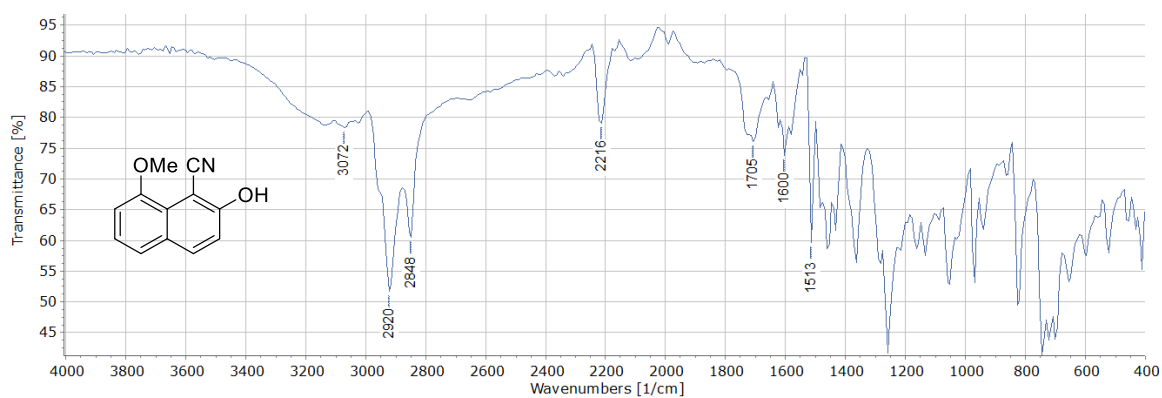


Figure S9. IR spectrum (solid) of compound (12).

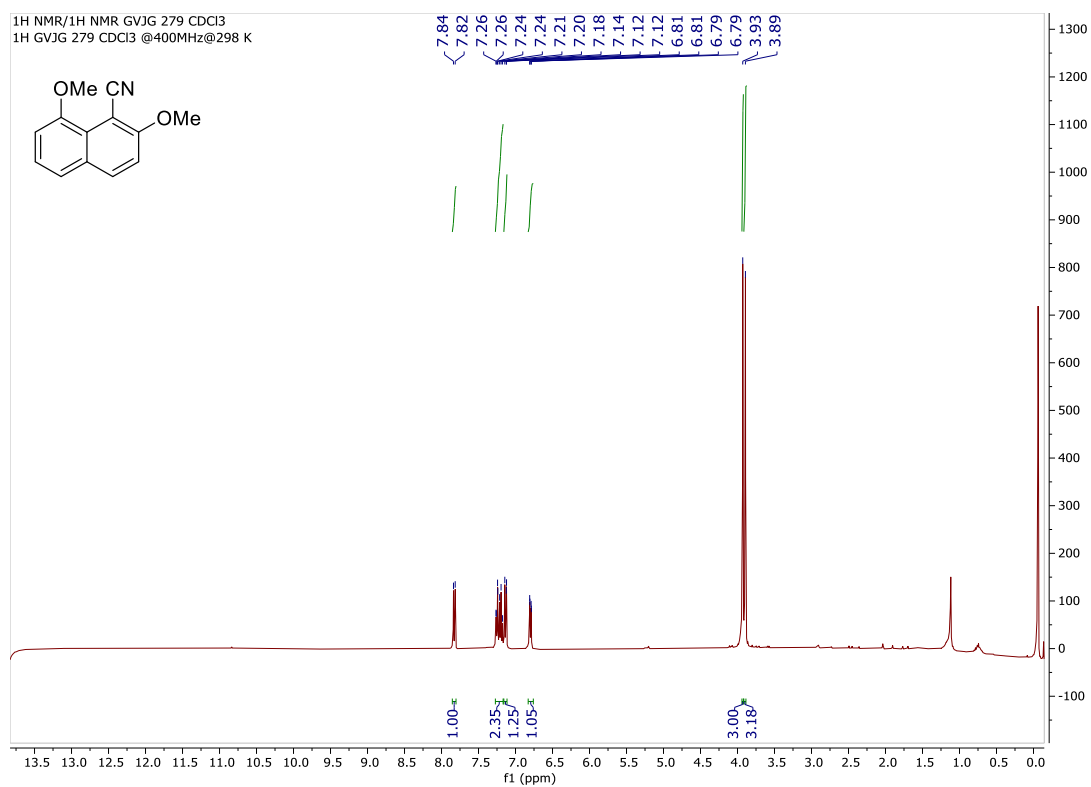


Figure S10. ¹H NMR (400 MHz, CDCl₃) of compound (13).

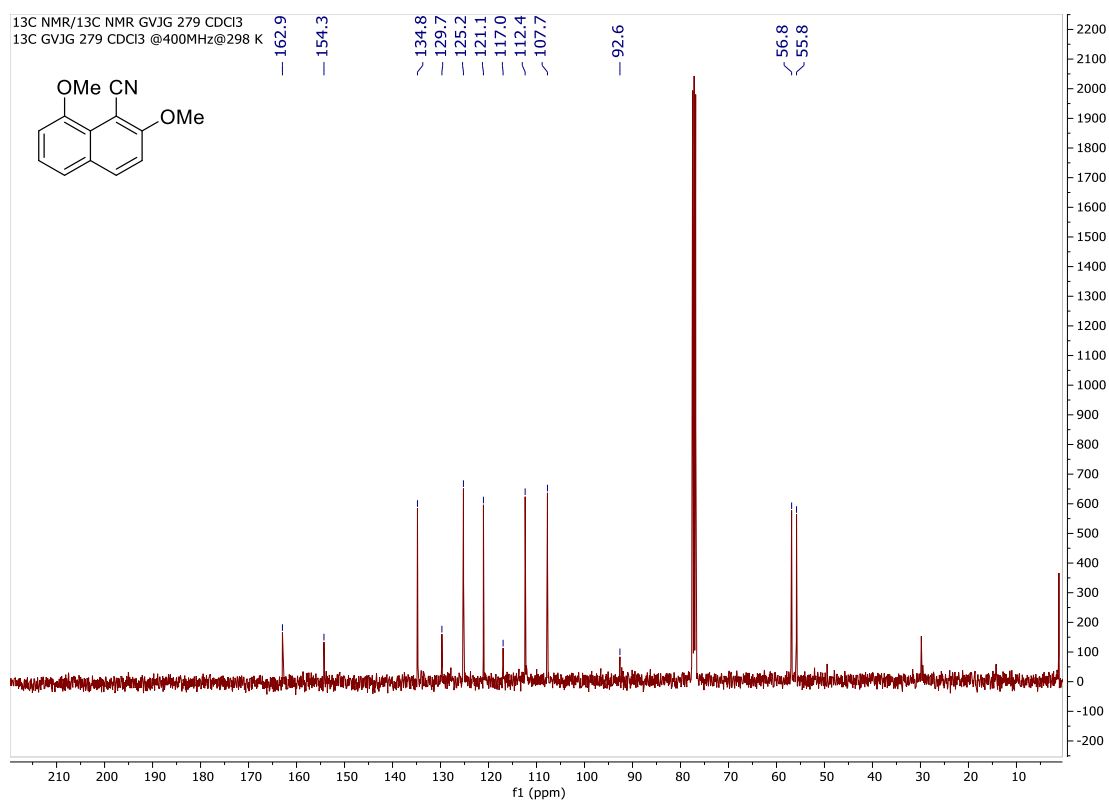


Figure S11. ¹³C NMR (400 MHz, CDCl₃) of compound (13).

GVJG279_230622120242 #81 RT: 1.17 AV: 1 NL: 1.33E7
T: FTMS + p ESI Full ms [150.00-400.00]

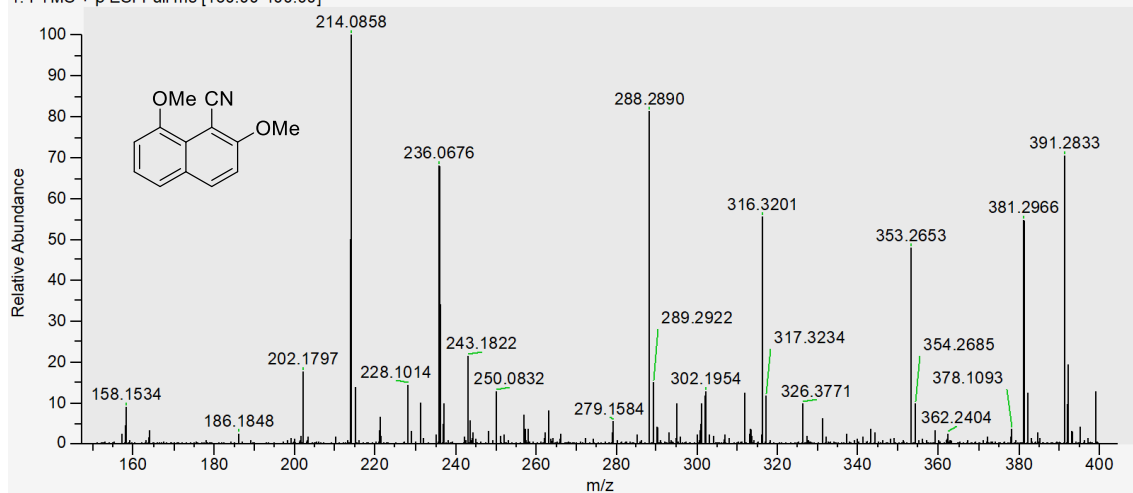


Figure S12. HRMS $[M+H]^+$ of compound (13) using 0.1% HCO_2H in MeOH as solvent.

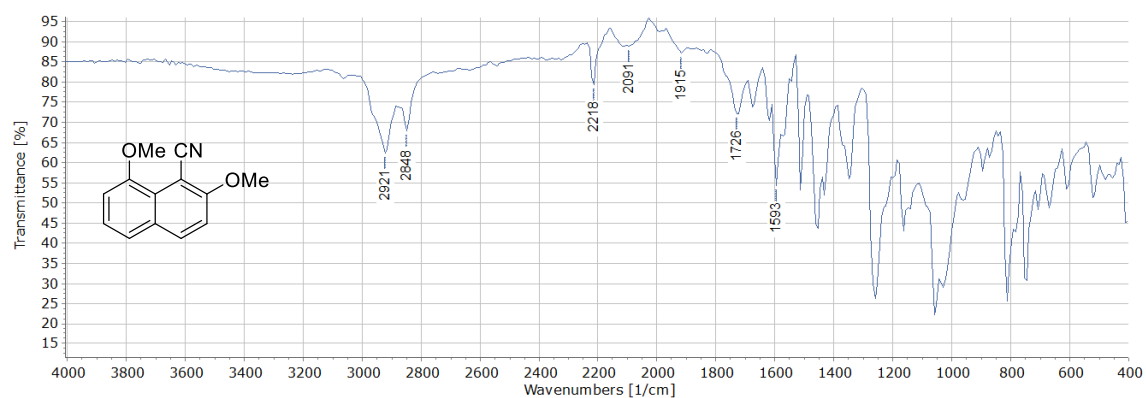


Figure S13. IR spectrum (solid) of compound (13).

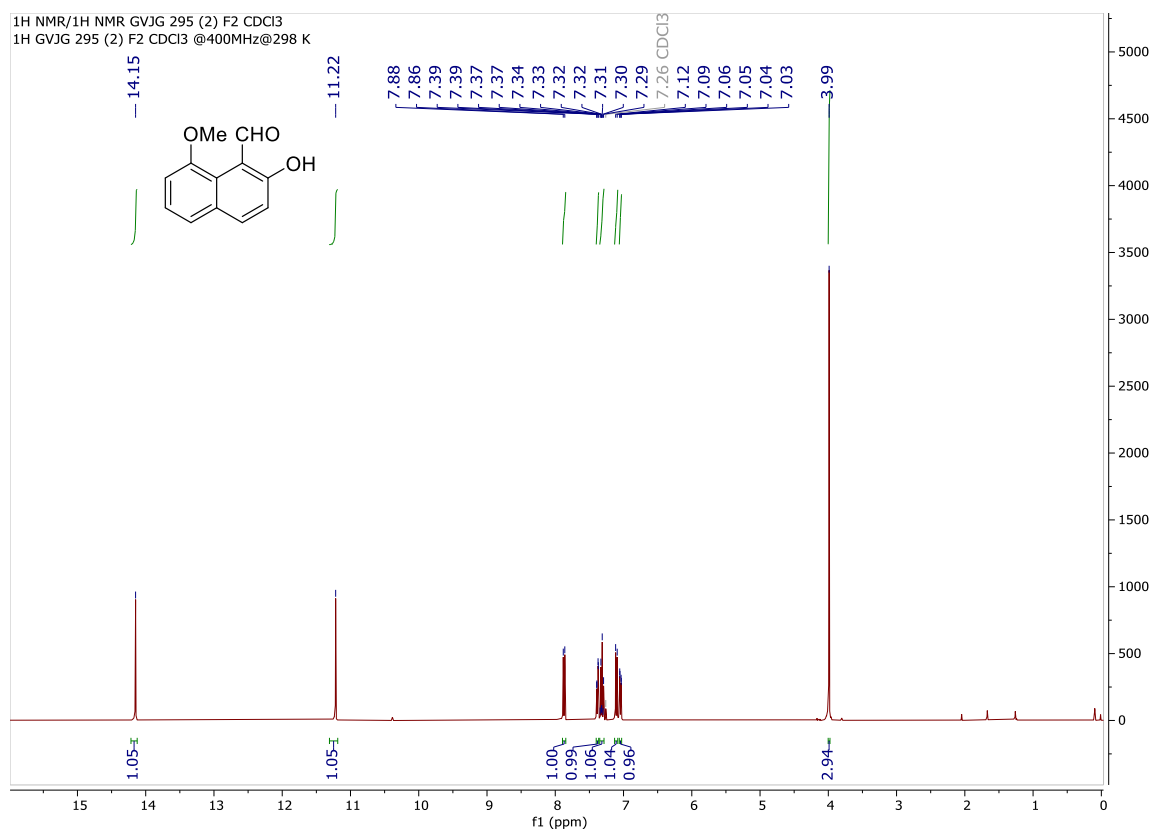


Figure S14. ^1H NMR (400 MHz, CDCl_3) of compound (14).

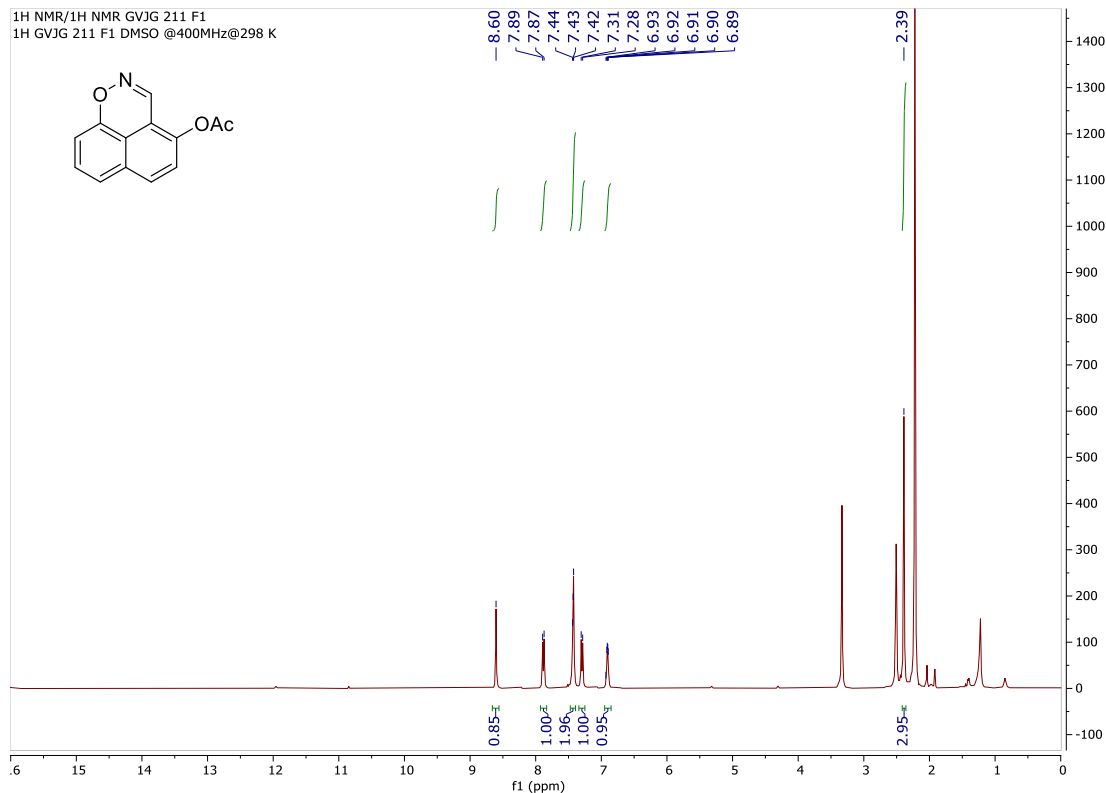


Figure S15. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) of compound (15).

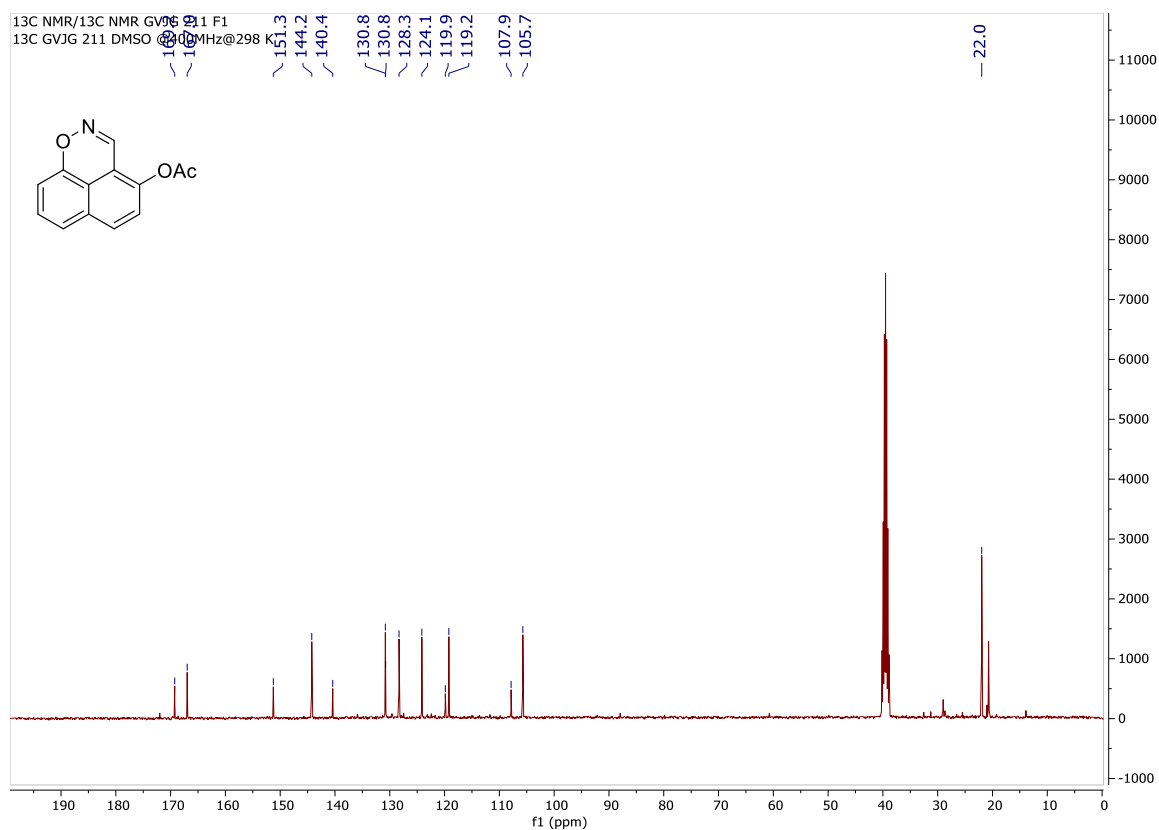


Figure S16. ^{13}C NMR (100.6 MHz, $\text{DMSO}-d_6$) of compound (15).

GVJG216_200617170358 #1 RT: 0.00 AV: 1 NL: 1.66E6
T: FTMS + p ESI Full ms [150.00-2000.00]

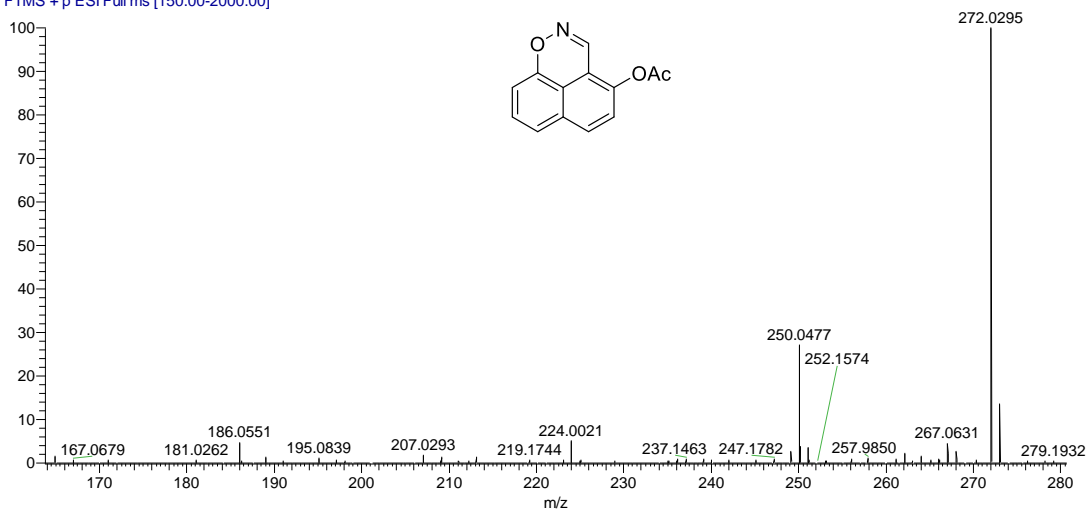


Figure S17. HRMS $[\text{M}+\text{H}]^+$ of compound (15) using 0.1% HCO_2H in MeOH as solvent.

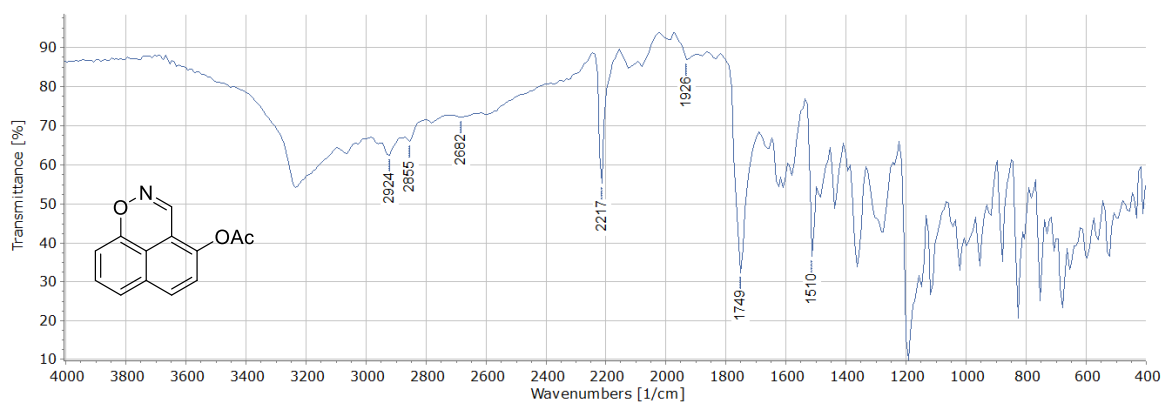


Figure S18. IR spectrum (solid) of compound (15).

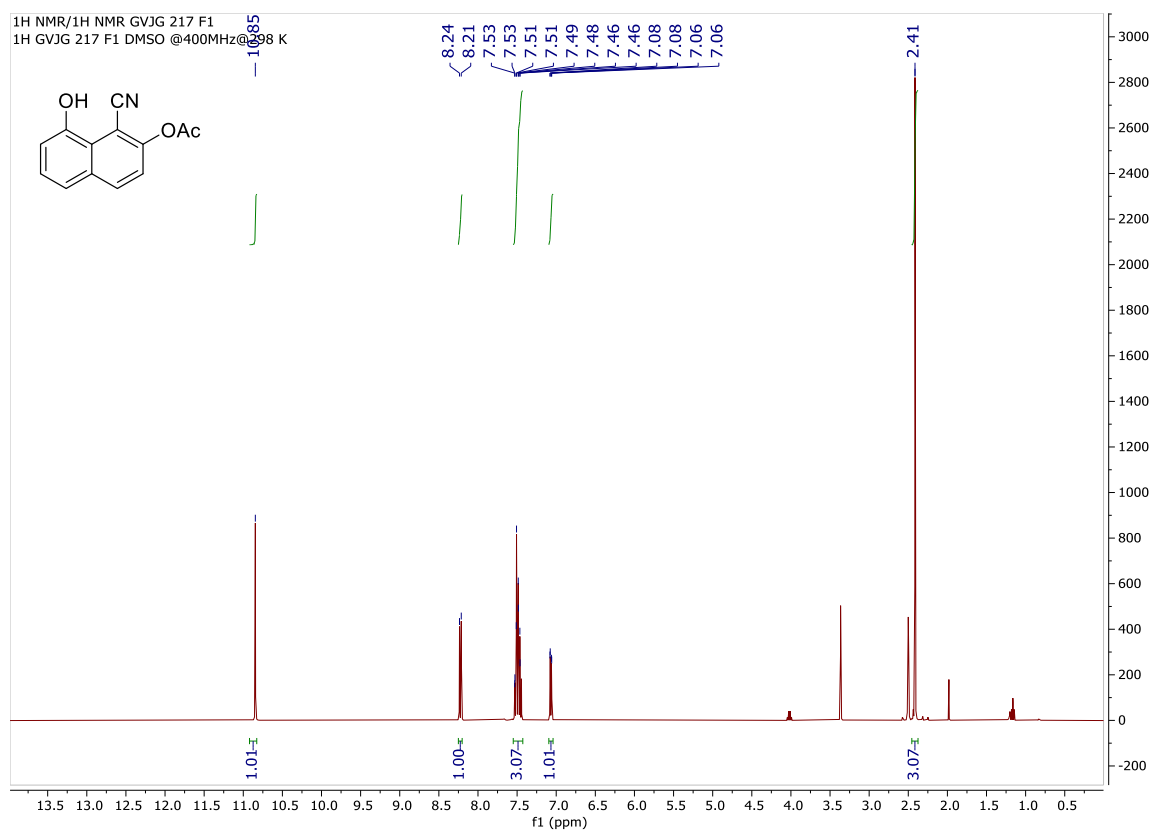


Figure S19. ¹H NMR (400 MHz, DMSO-*d*₆) of compound (16).

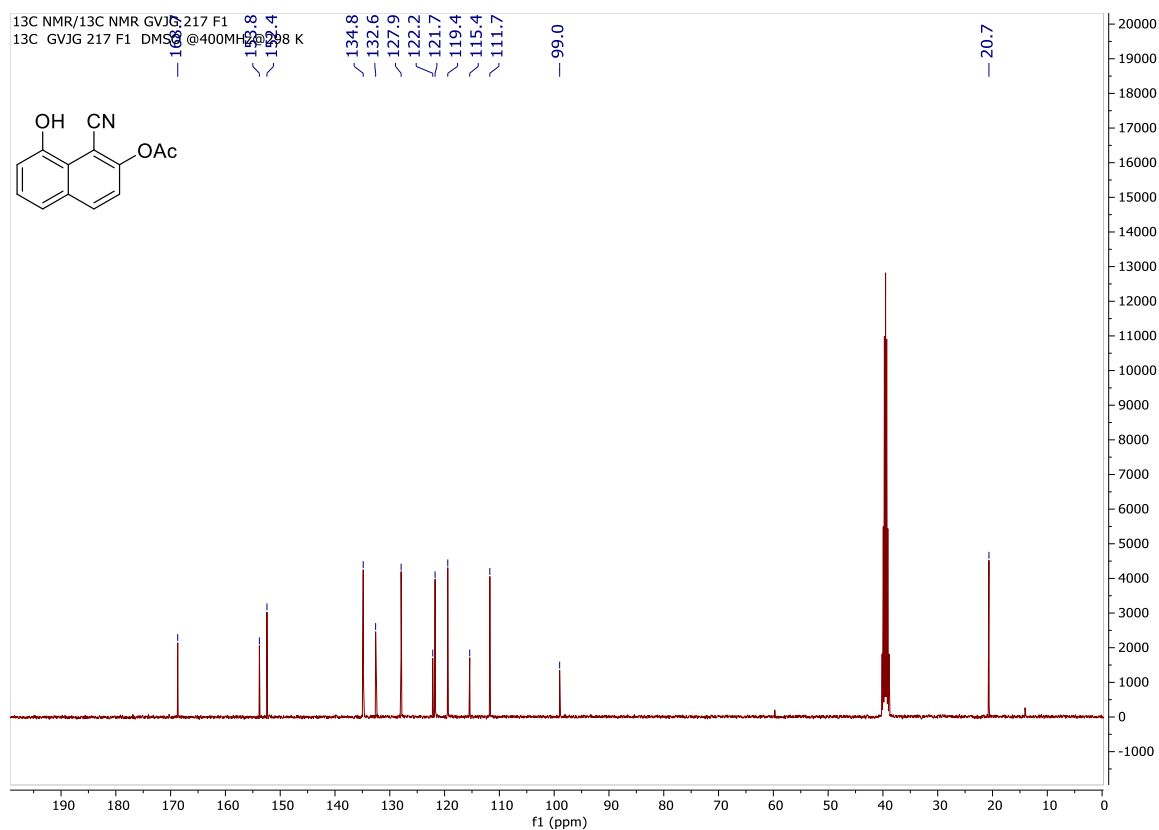


Figure S20. ^{13}C NMR (100.6 MHz, DMSO- d_6) of compound (16).

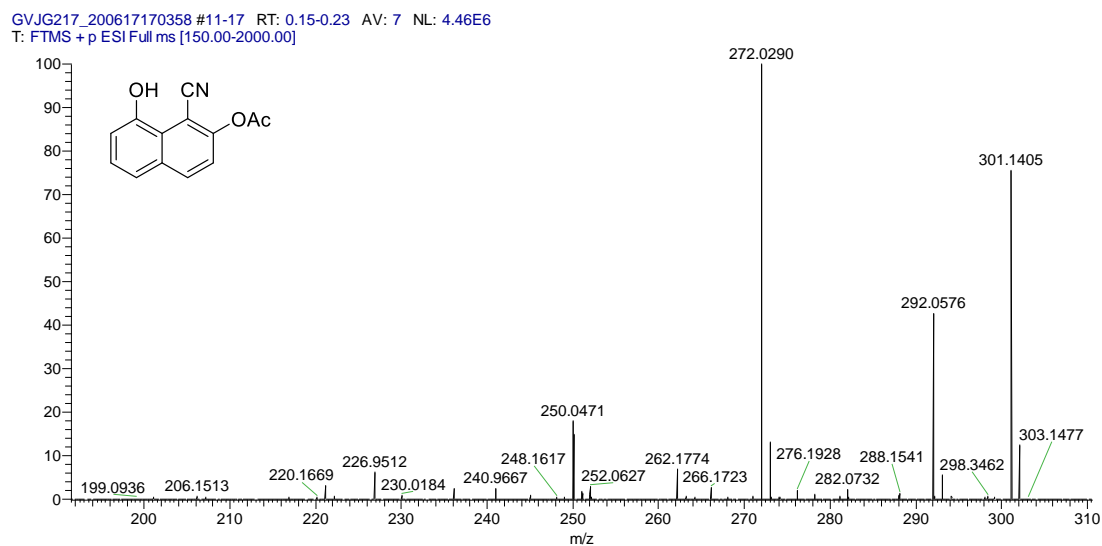


Figure S21. HRMS $[\text{M}+\text{H}]^+$ of compound (16) using 0.1% HCO_2H in MeOH as solvent.

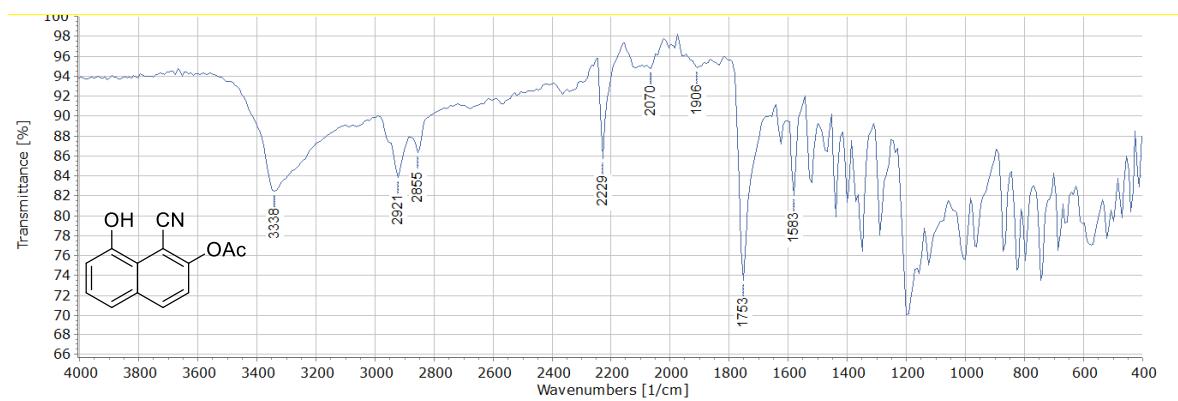


Figure S22. IR spectrum (solid) of compound (**16**).

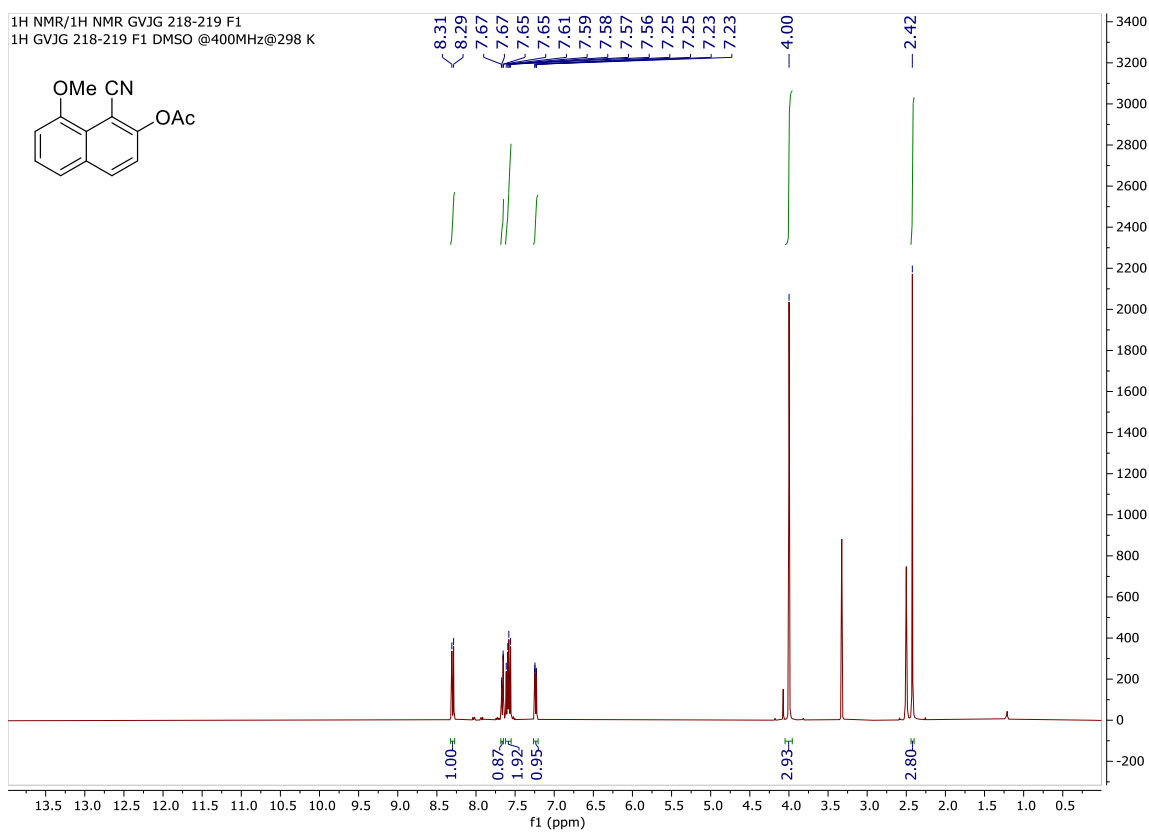


Figure S23. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) of (**17**).

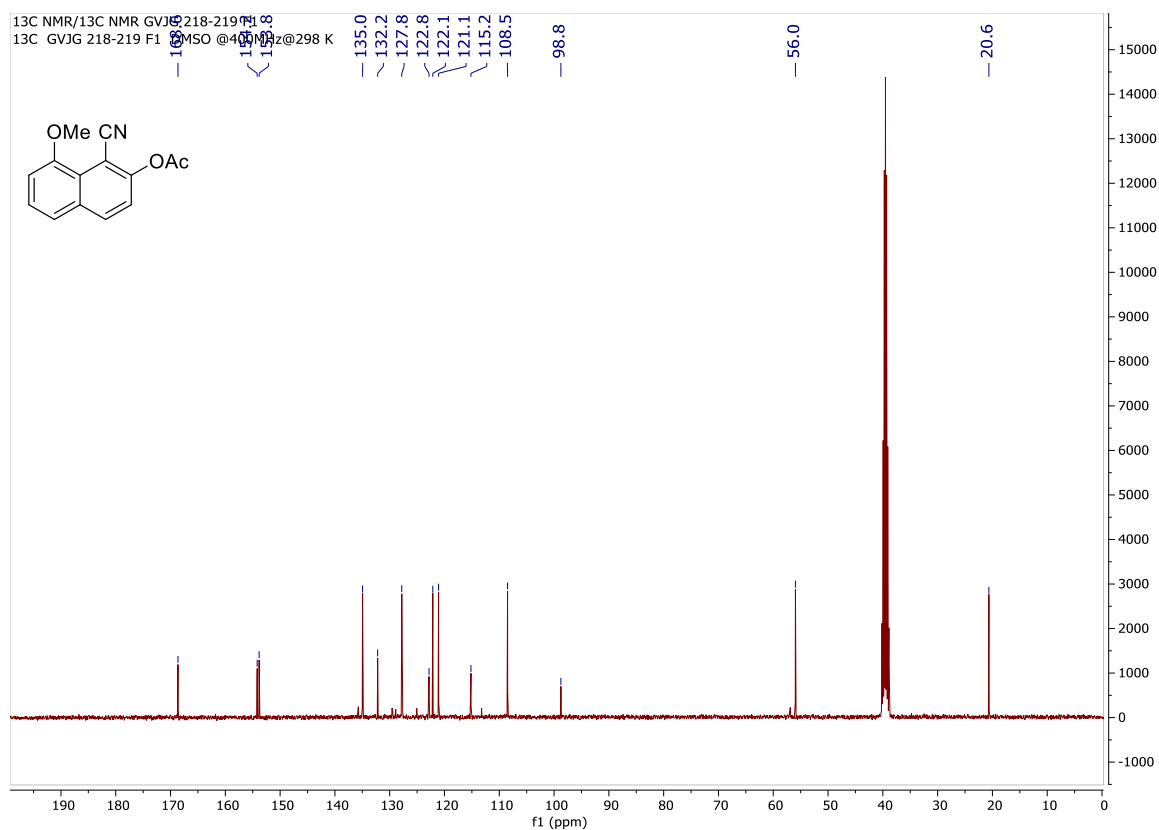


Figure S24. ^{13}C NMR (100.6 MHz, DMSO- d_6) of (17).

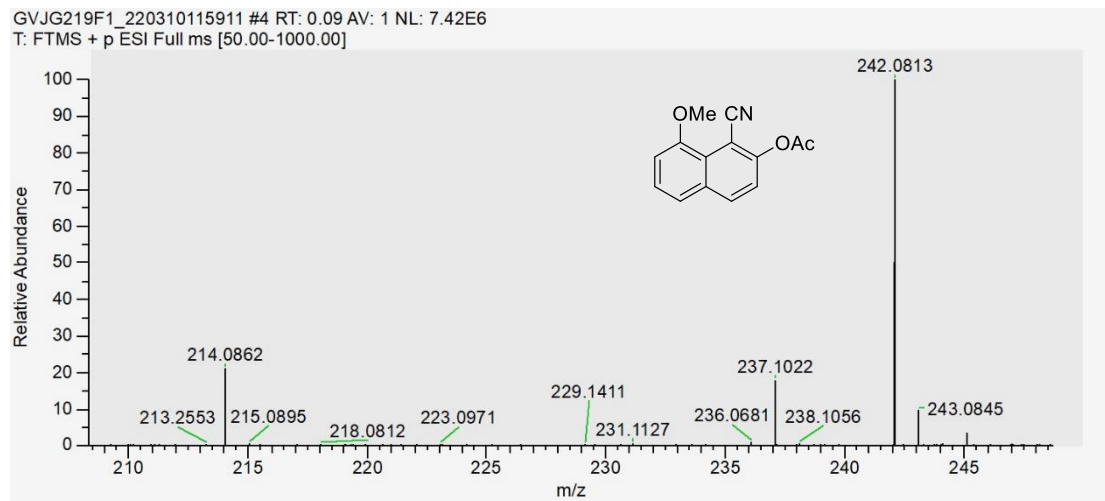


Figure S25. HRMS $[\text{M}+\text{H}]^+$ of compound (17) using 0.1% HCO_2H in MeOH as solvent.

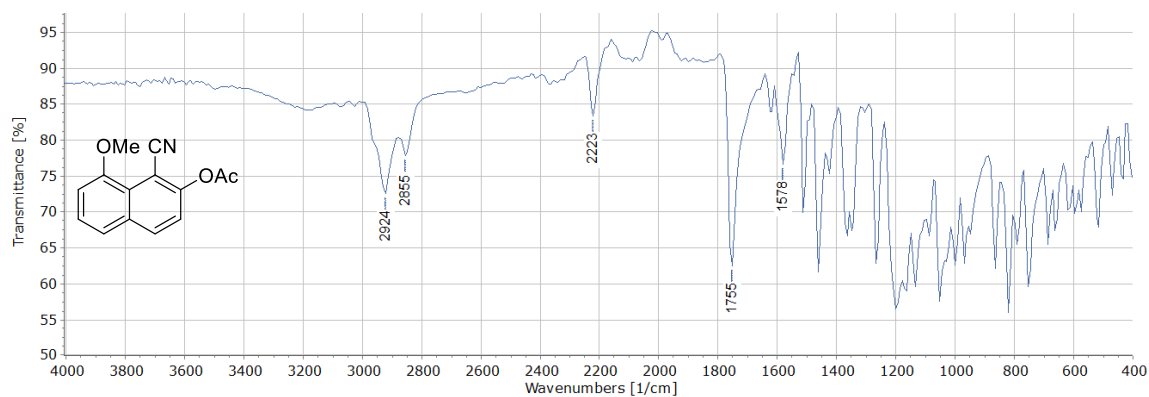


Figure S26. IR spectrum (solid) of **(17)**

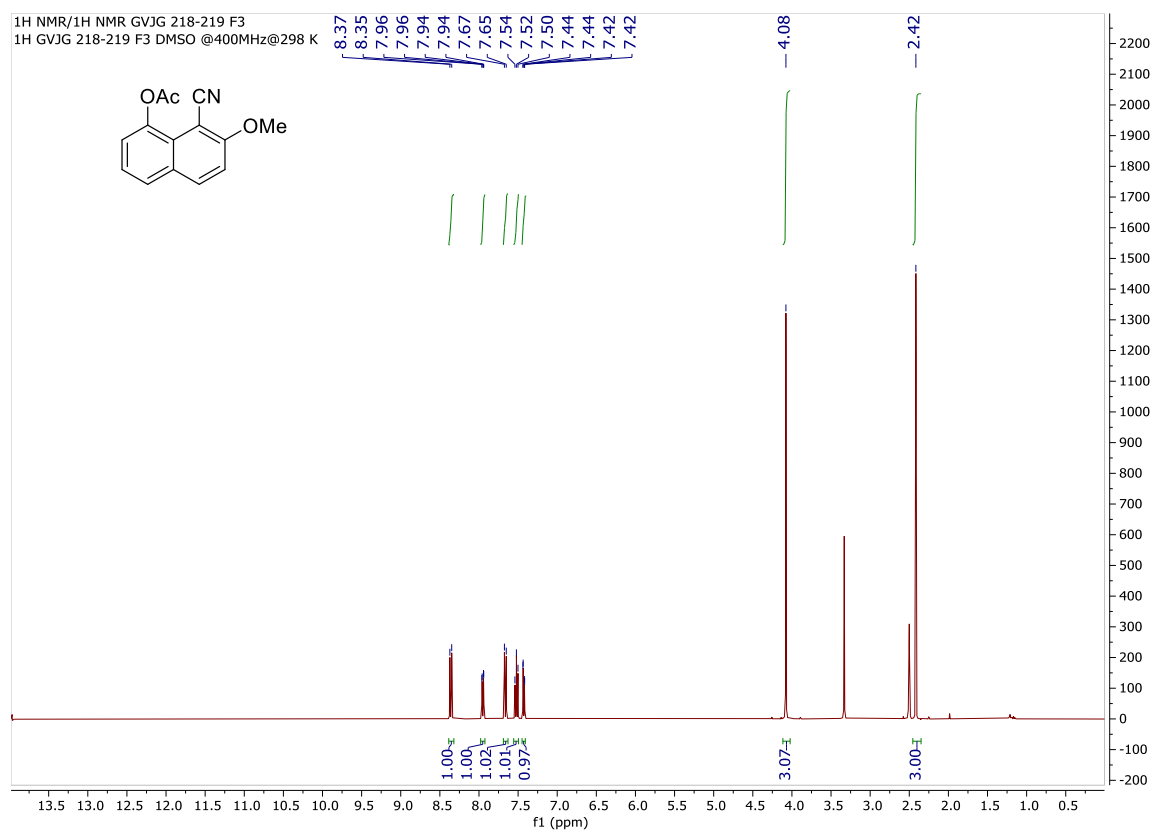


Figure S27. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) of **(18)**.

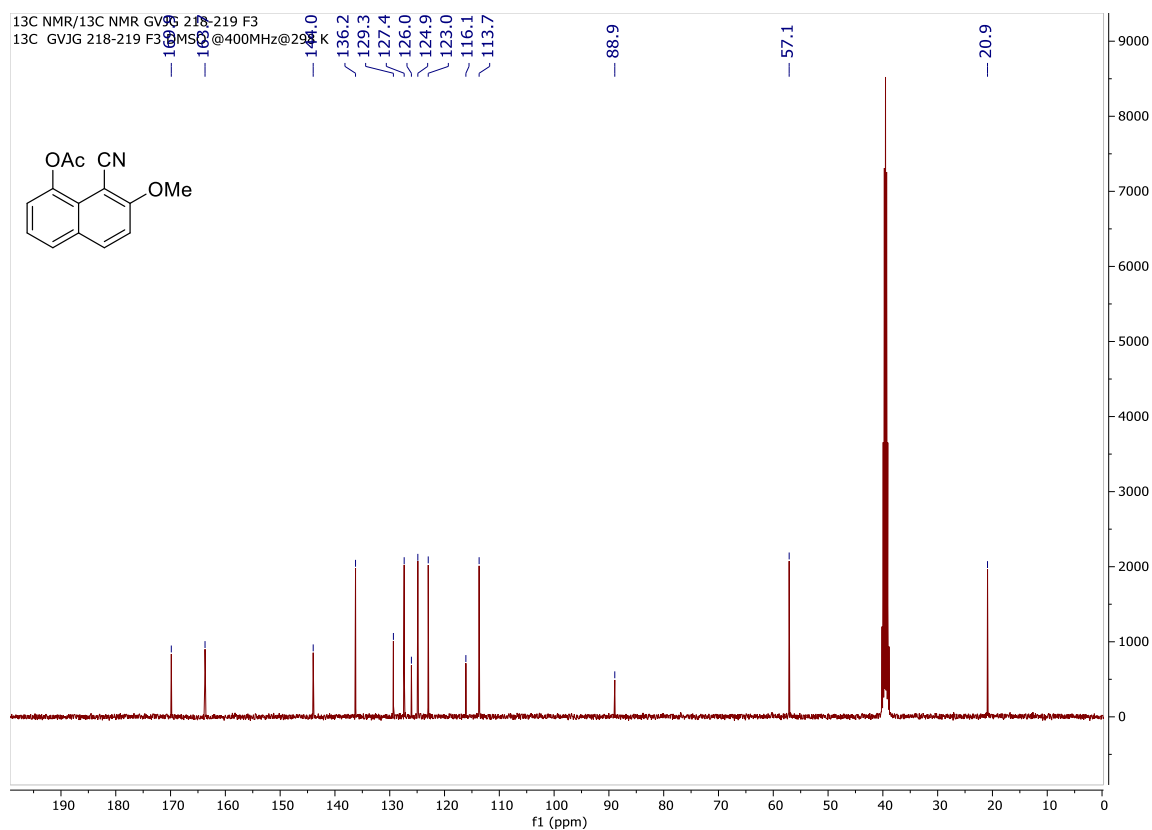


Figure S28. ^{13}C NMR (100.6 MHz, $\text{DMSO}-d_6$) of (18).

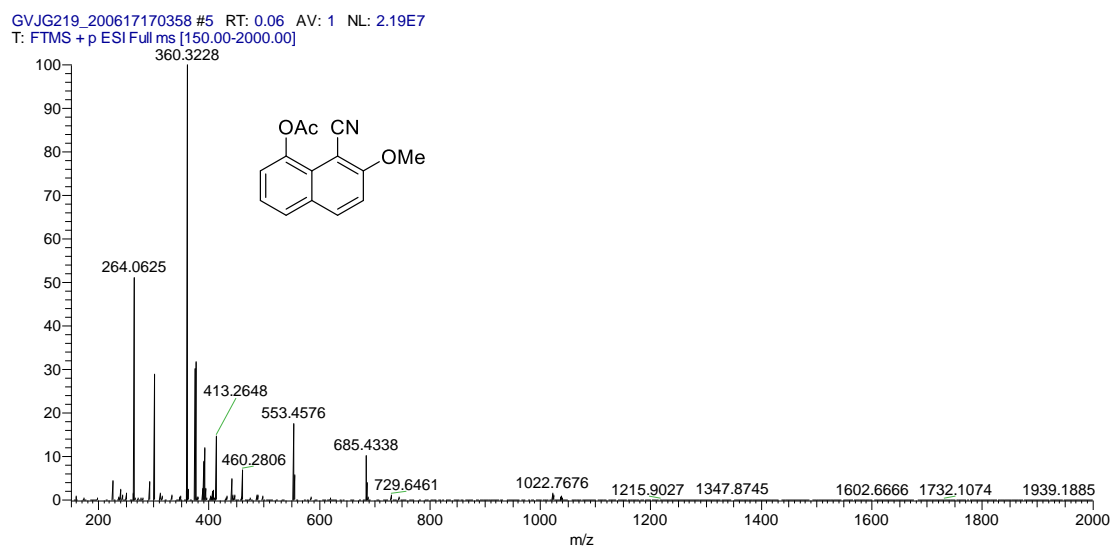


Figure S29. HRMS $[\text{M}+\text{H}]^+$ of compound (18) using 0.1% HCO_2H in MeOH as solvent.

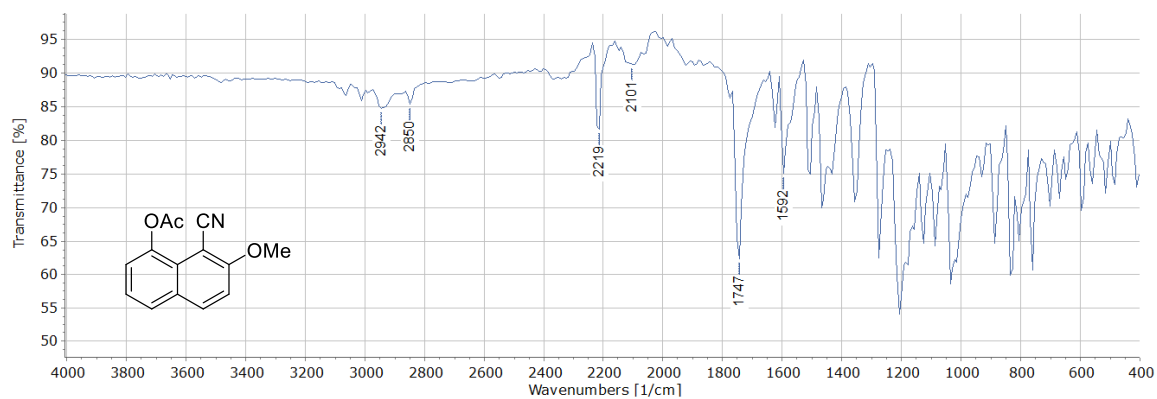


Figure S30. IR spectrum (solid) of (18).

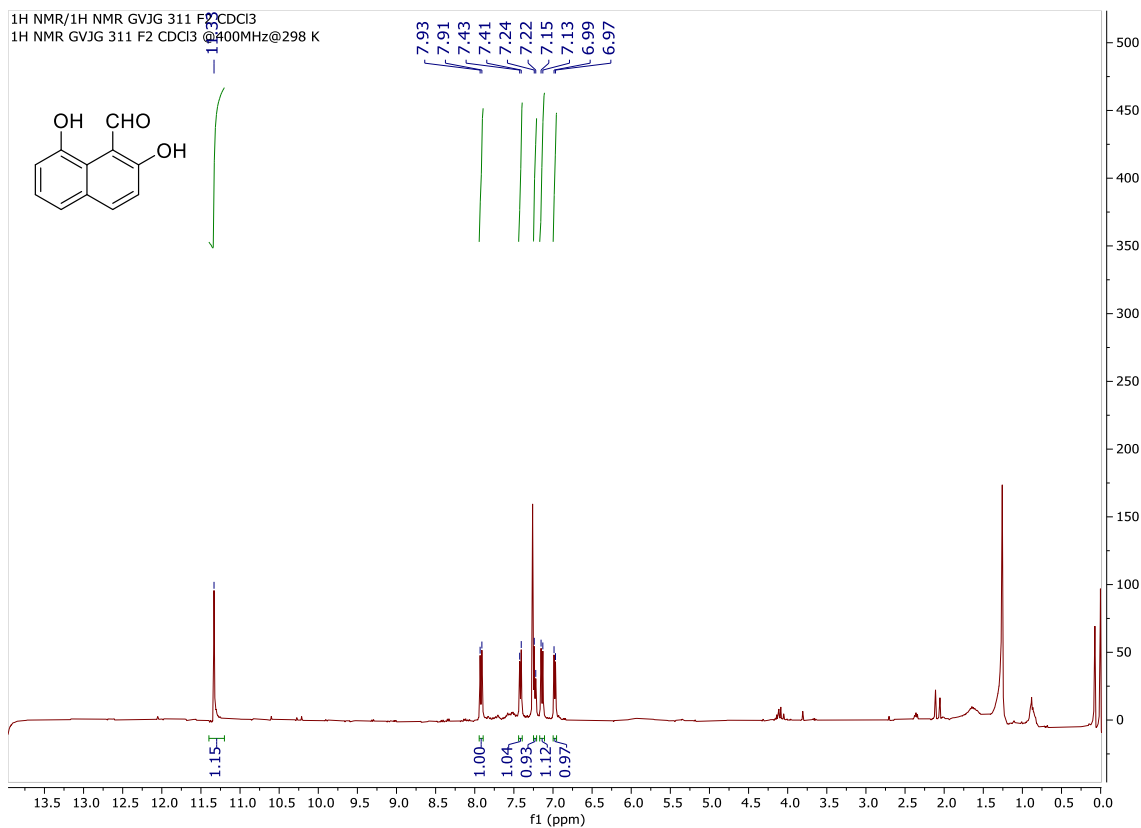


Figure S31. ¹H NMR (400 MHz, CDCl₃) of (19).

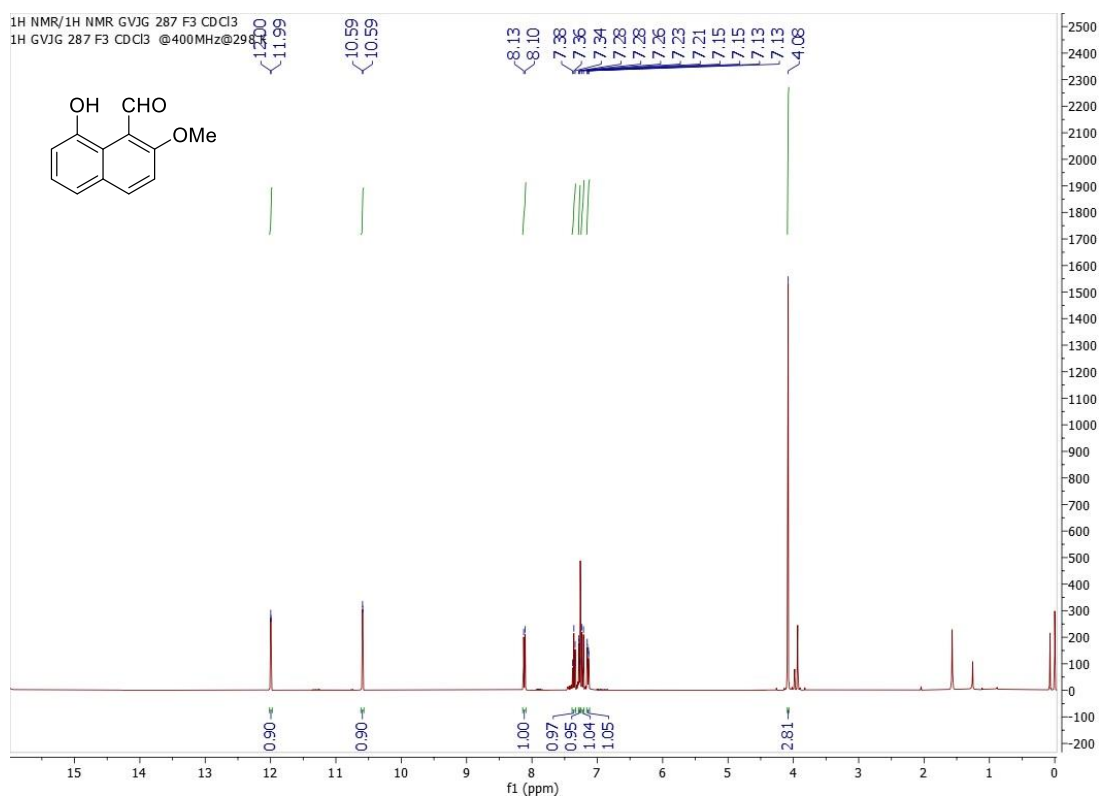


Figure S32. ^1H NMR (400 MHz, CDCl_3) of (20).

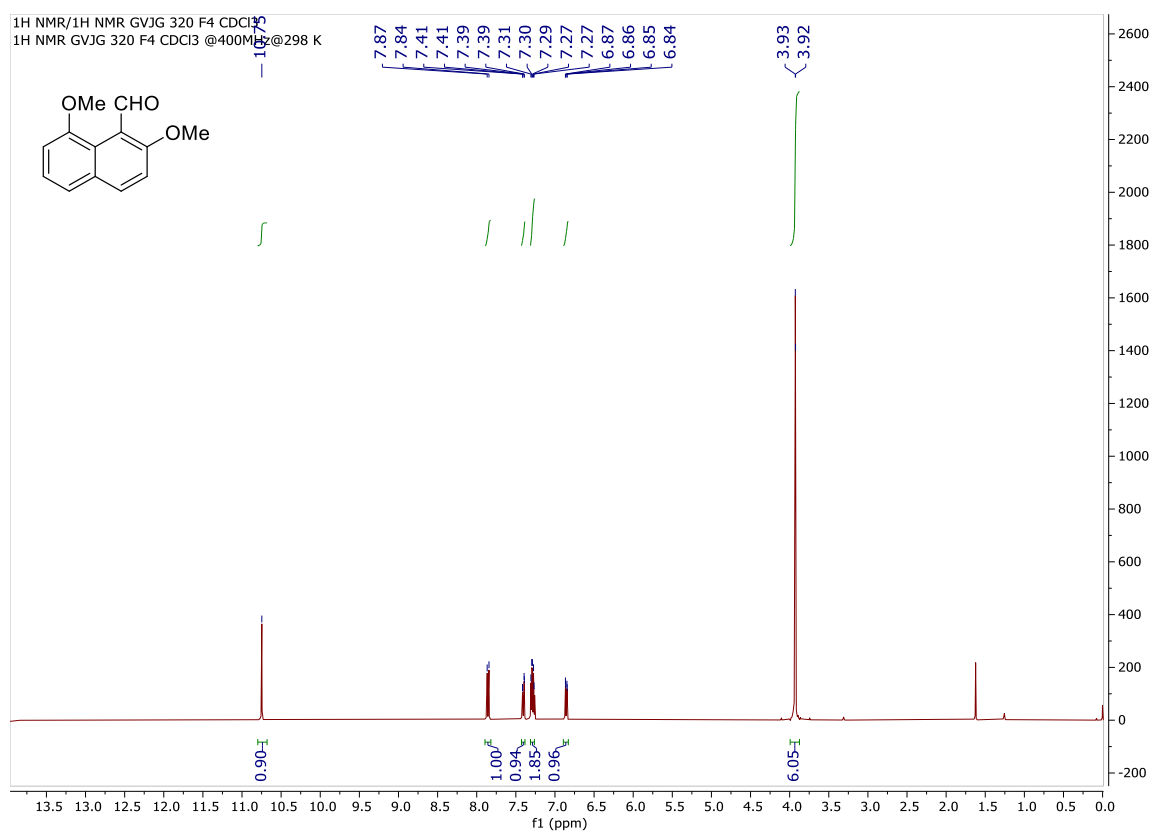


Figure S33. ^1H NMR (400 MHz, CDCl_3) of (21).

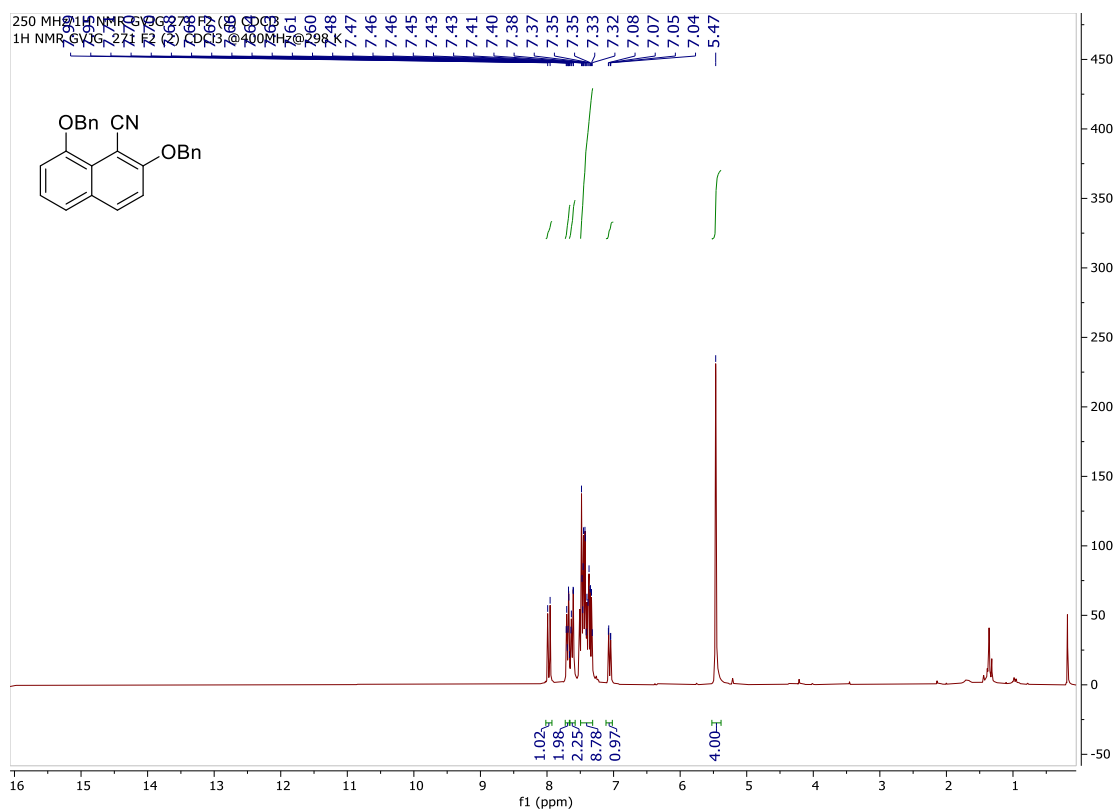


Figure S34. ¹H NMR (400 MHz, CDCl₃) of (22).

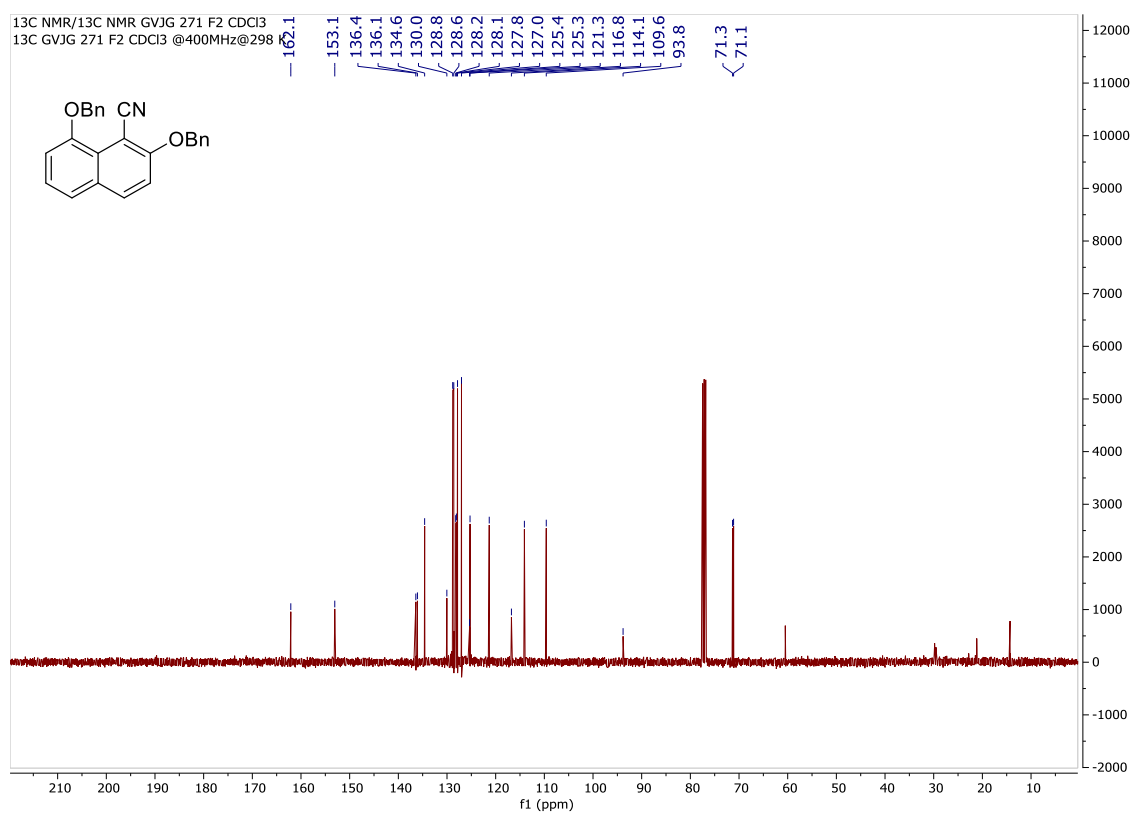


Figure S35. ¹³C NMR (100.6 MHz, CDCl₃) of (22).

GVJG271F2_new_220310115911 #4 RT: 0.05 AV: 1 NL: 1.06E7
T: FTMS + p ESI Full ms [150.00-2000.00]

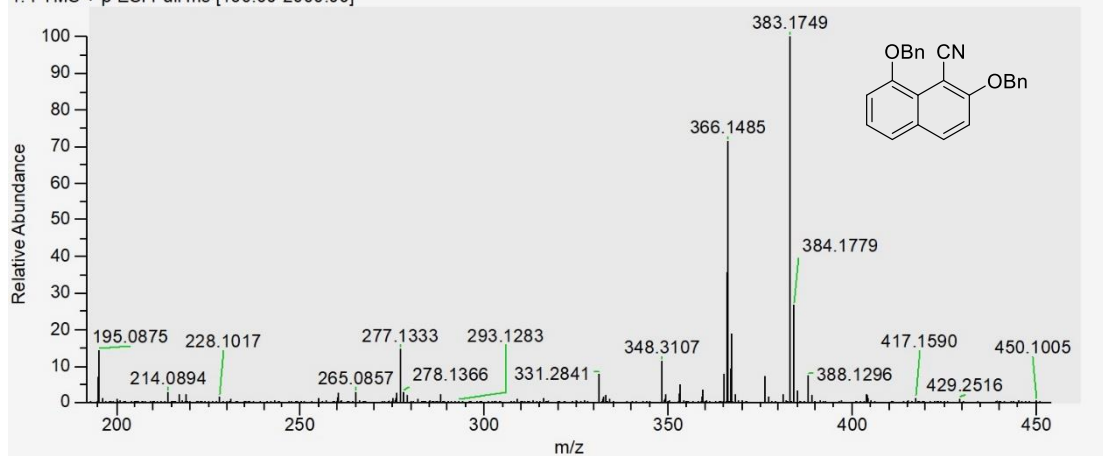


Figure S36. HRMS $[M+H]^+$ of compound (22) using 0.1% HCO_2H in MeOH as solvent.

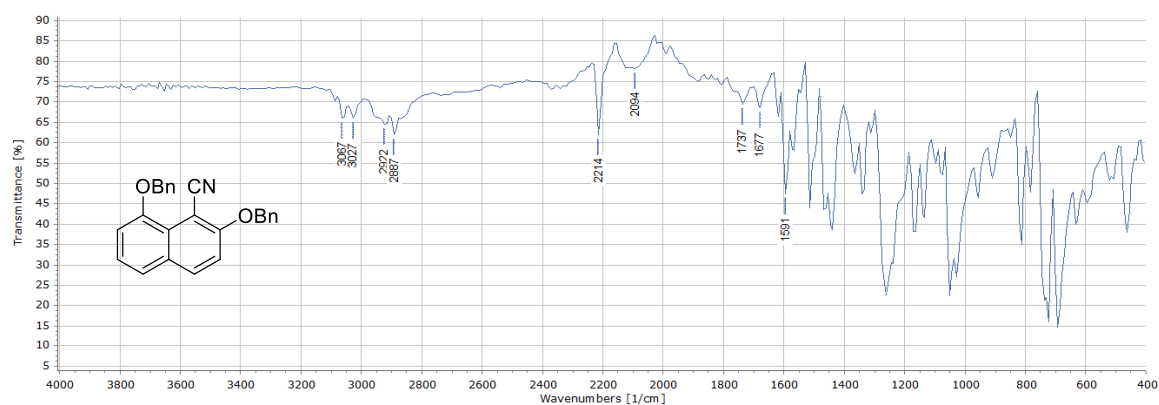


Figure S37. IR spectrum (solid) of (22).

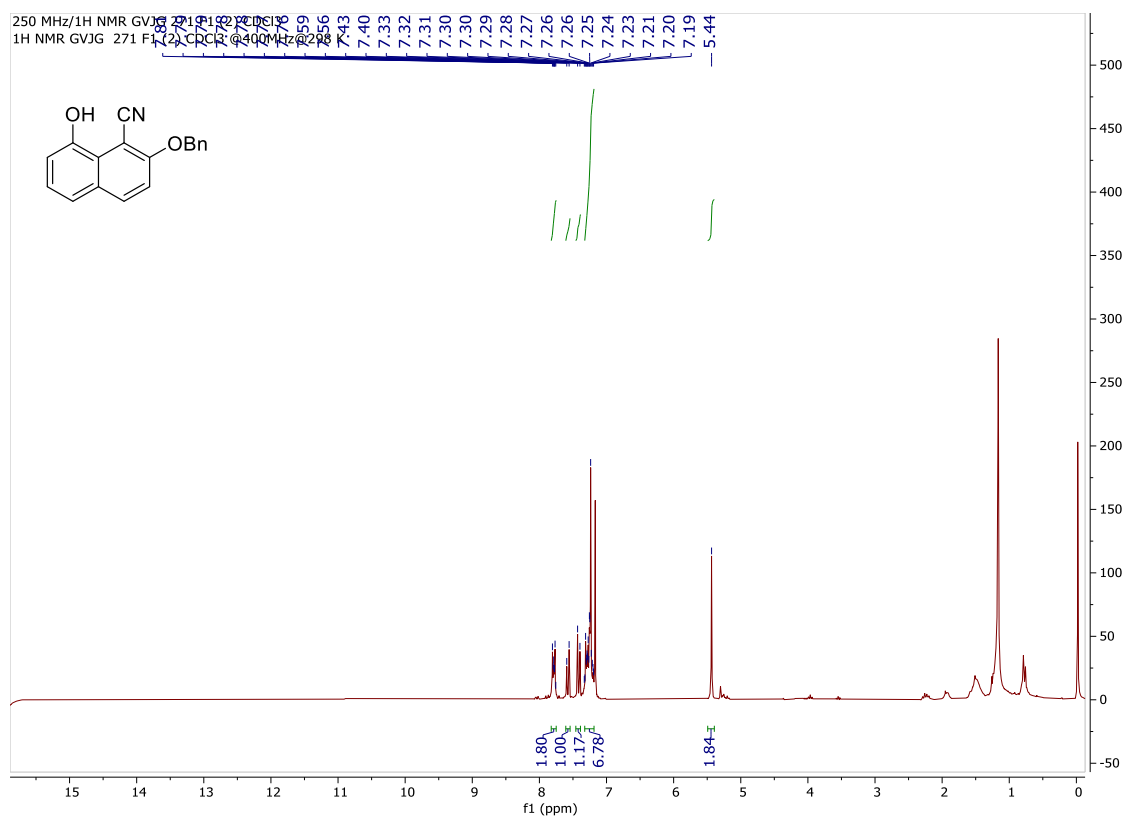


Figure S38. ¹H NMR (400 MHz, CDCl₃) of (23).

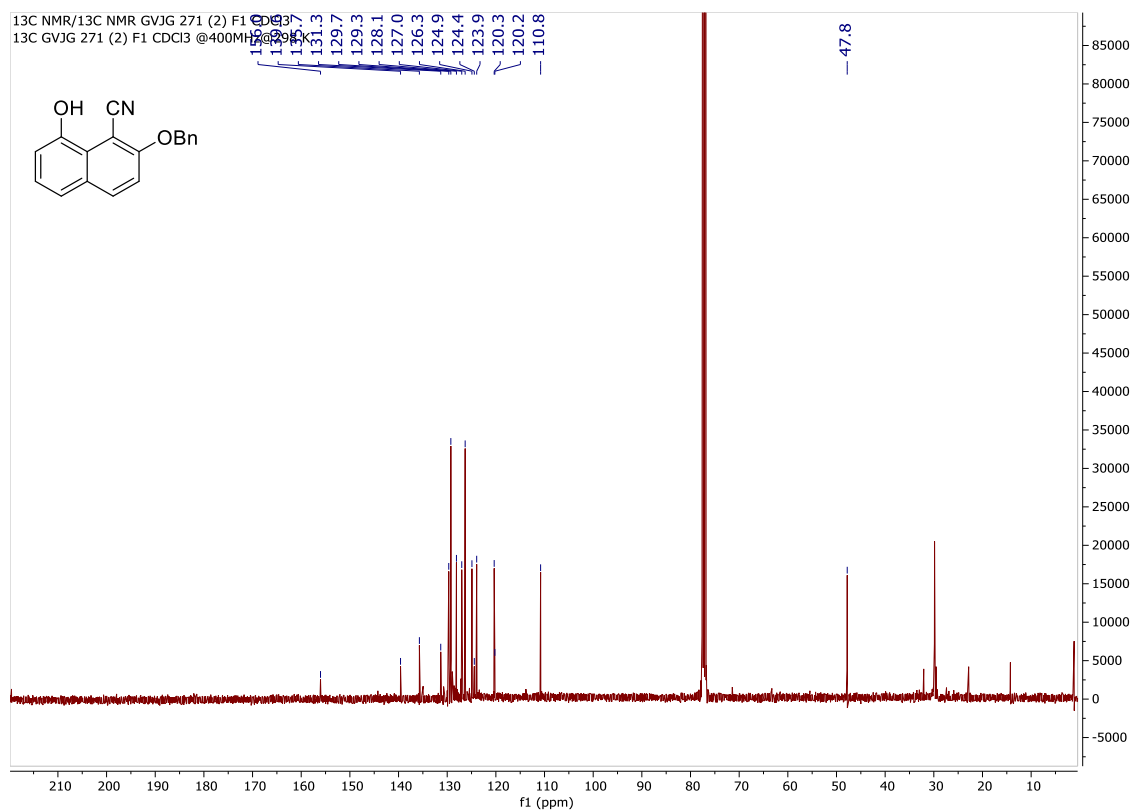


Figure S39. ¹³C NMR (100.6 MHz, CDCl₃) of (23).

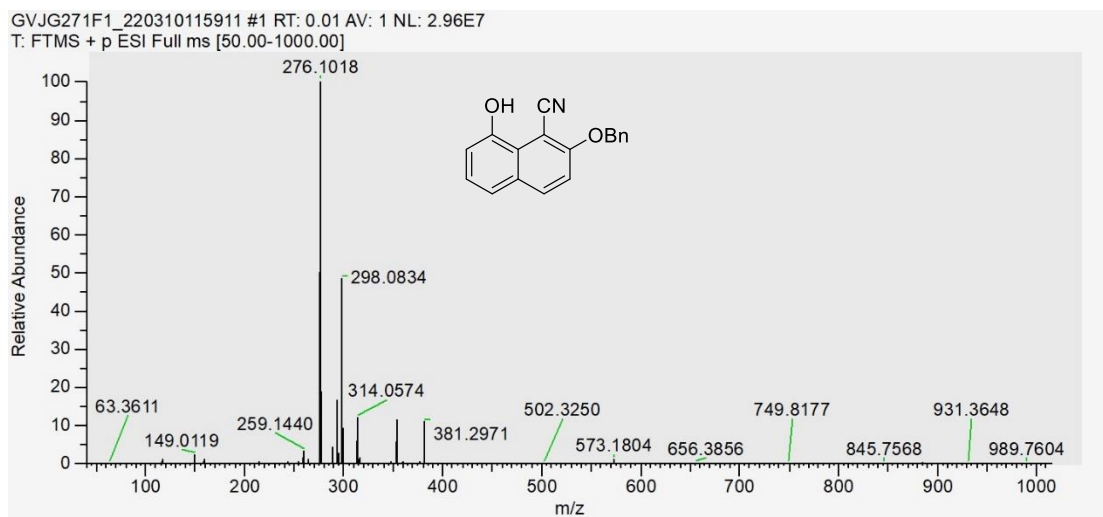


Figure S40. HRMS $[M+H]^+$ of compound (**23**) using 0.1% HCO_2H in MeOH as solvent.

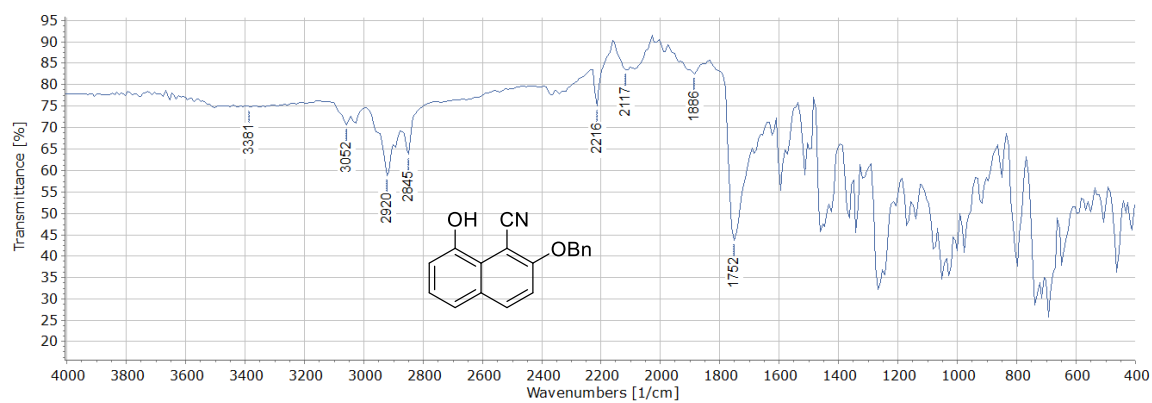


Figure S41. IR spectrum (solid) of (**23**).

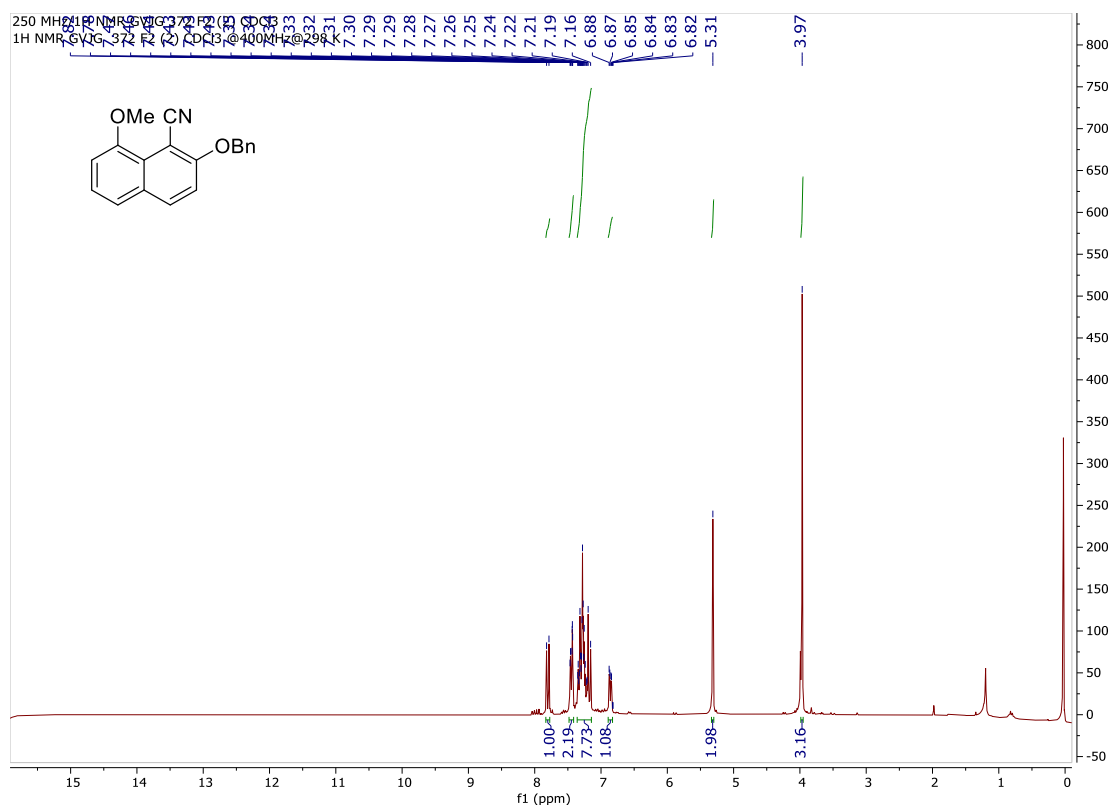


Figure S42. ¹H NMR (400 MHz, CDCl₃) of (24).

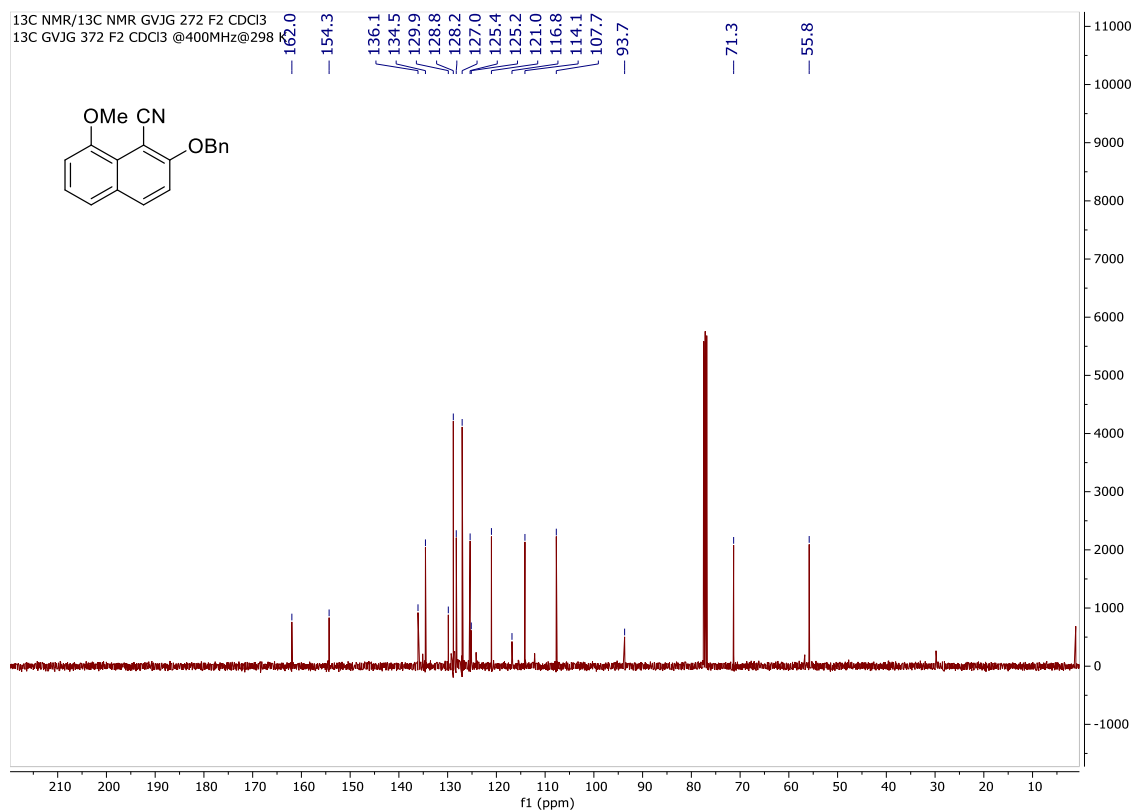


Figure S43. ¹³C NMR (100.6 MHz, CDCl₃) of (24).

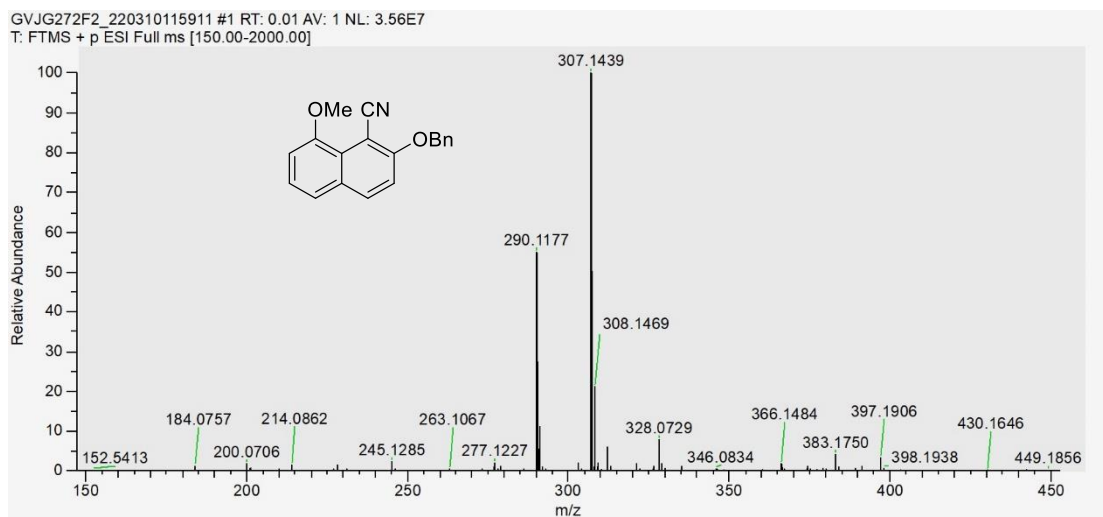


Figure S44. HRMS $[M+H]^+$ of compound (24) using 0.1% HCO_2H in MeOH as solvent.

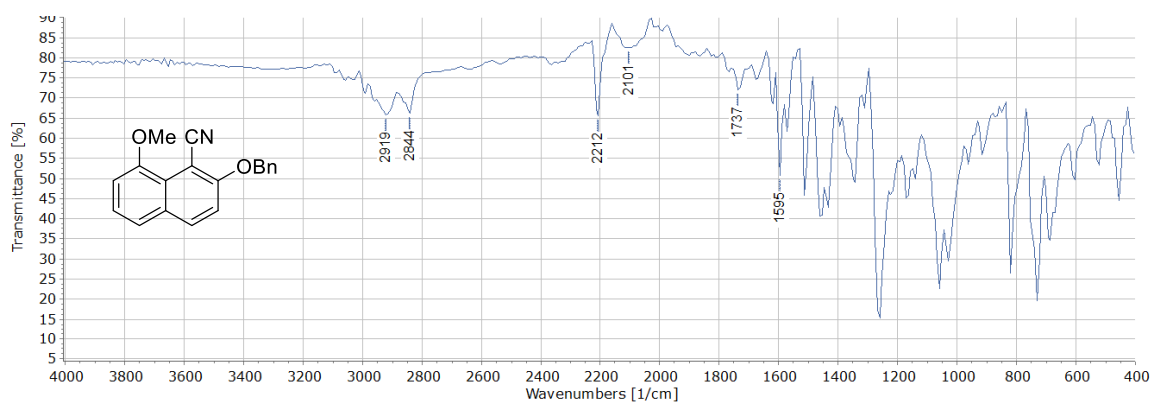


Figure S45. IR spectrum (solid state) of (24).

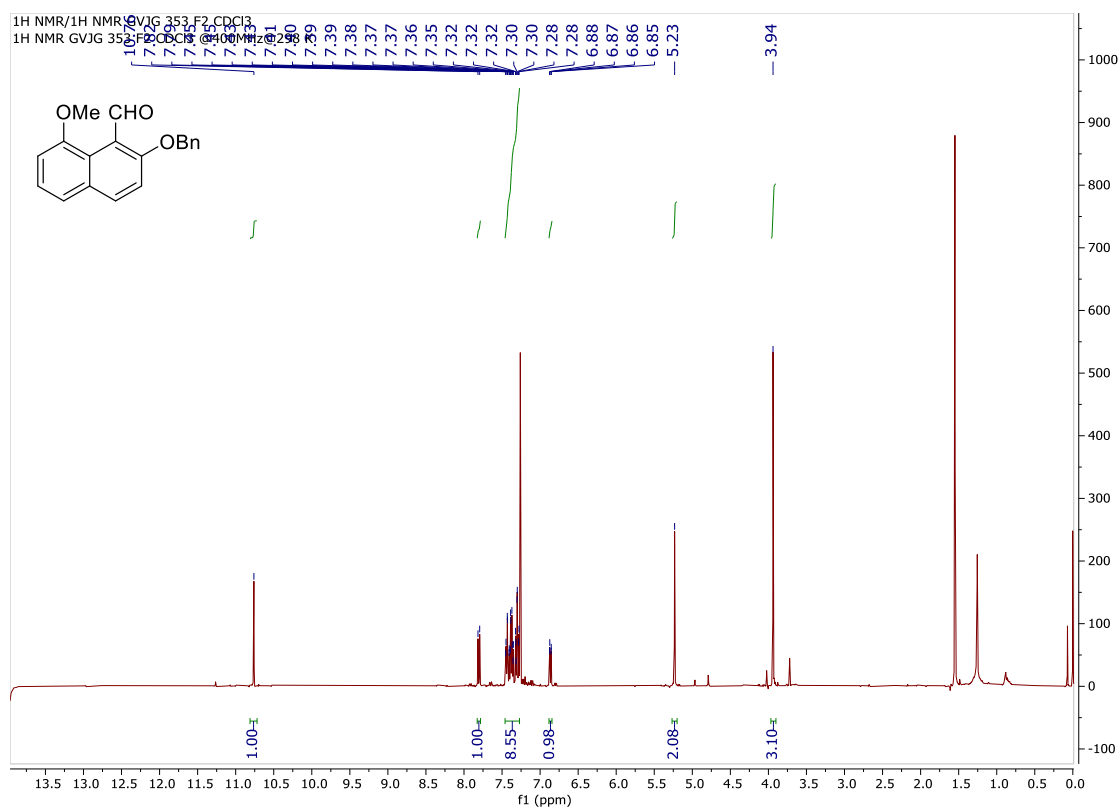


Figure S46. ¹H NMR (400 MHz, CDCl₃) of (25).

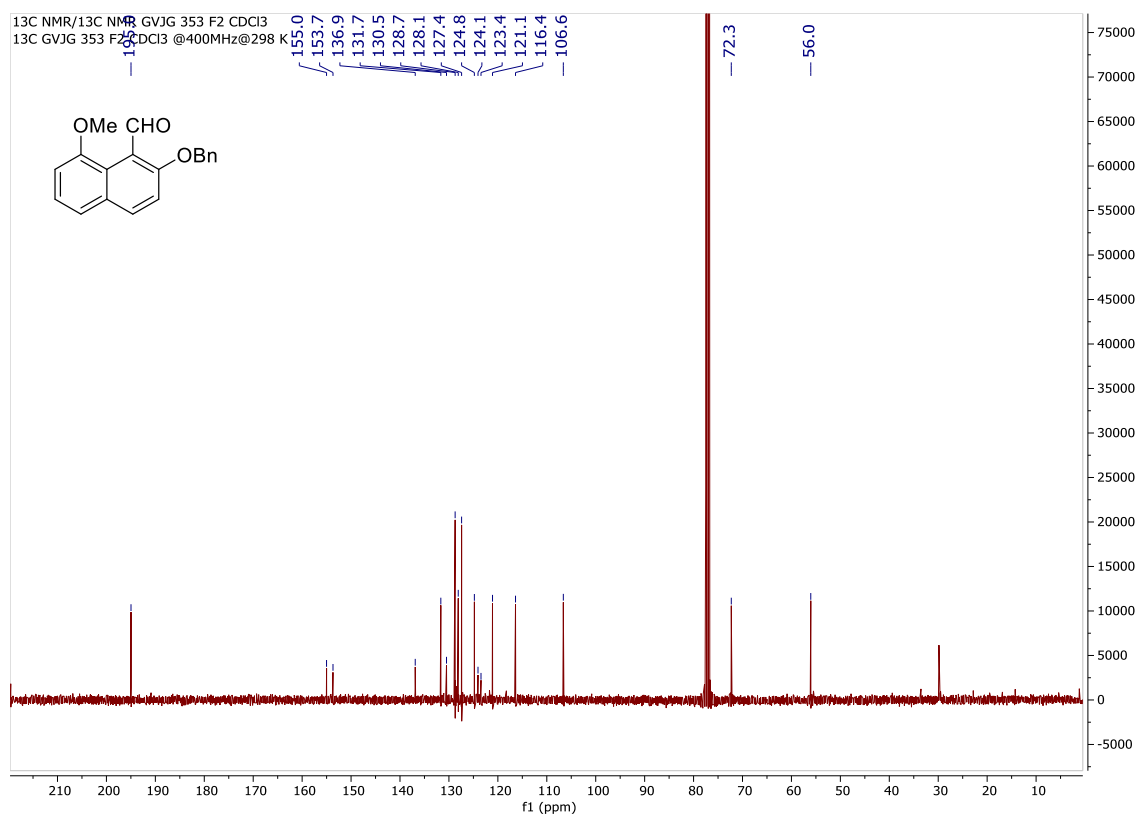


Figure S47. ¹³C NMR [100.6 MHz, CDCl₃] of (25).

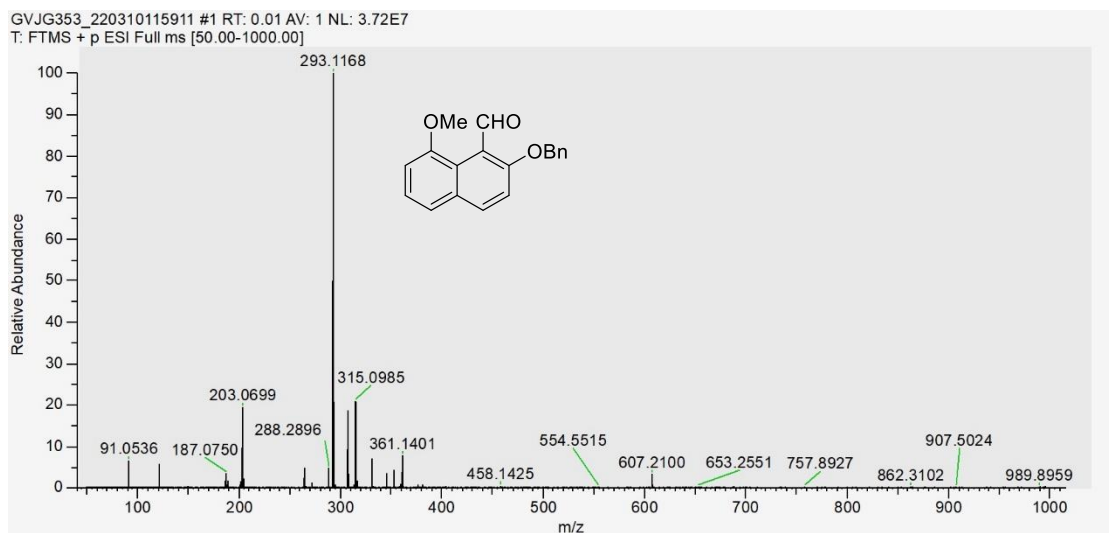


Figure S48. HRMS $[M+H]^+$ of compound (25) using 0.1% HCO_2H in MeOH as solvent.

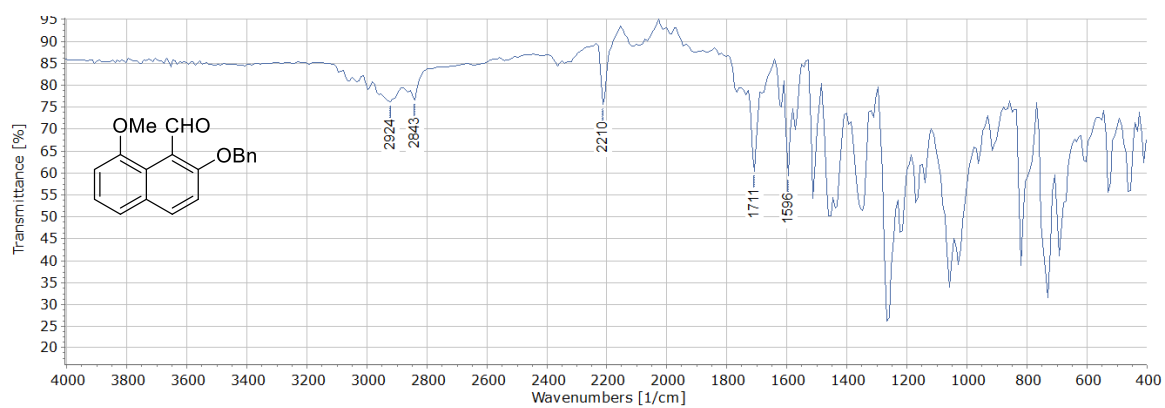


Figure S49. IR spectrum (solid state) of (25).

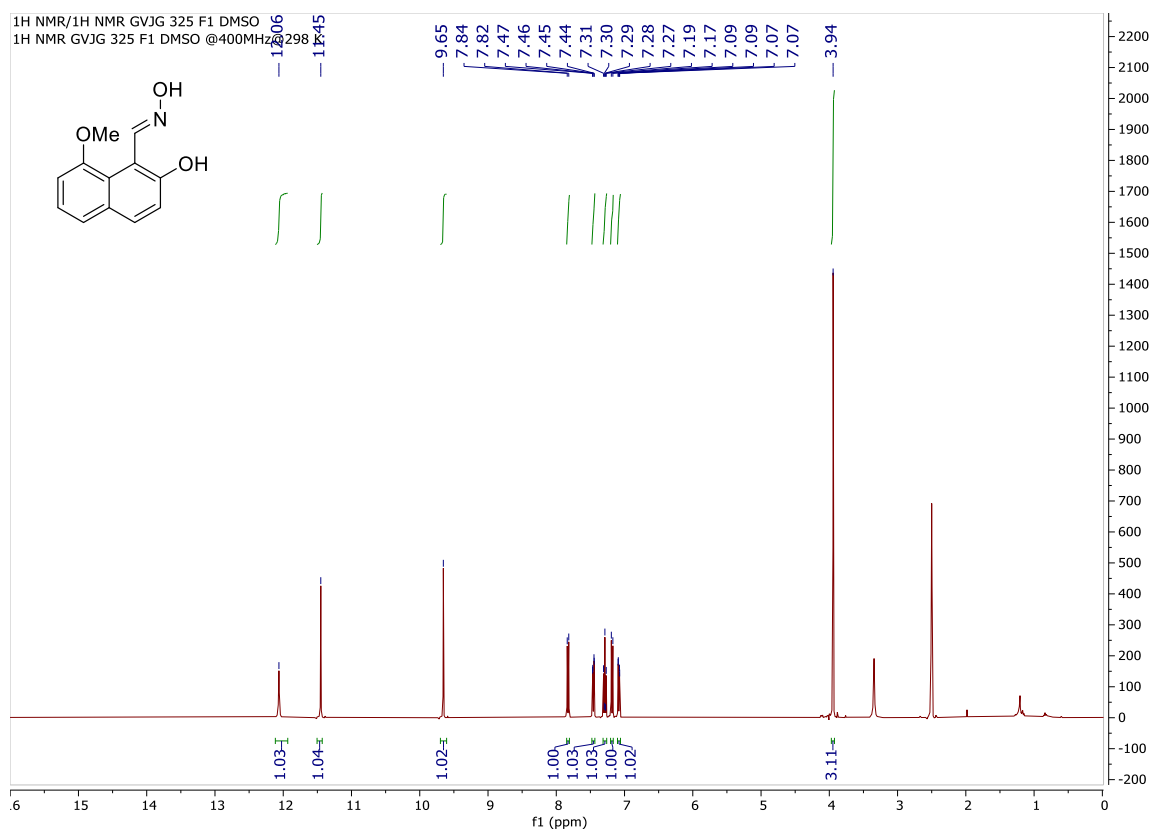


Figure S50. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) of (6).

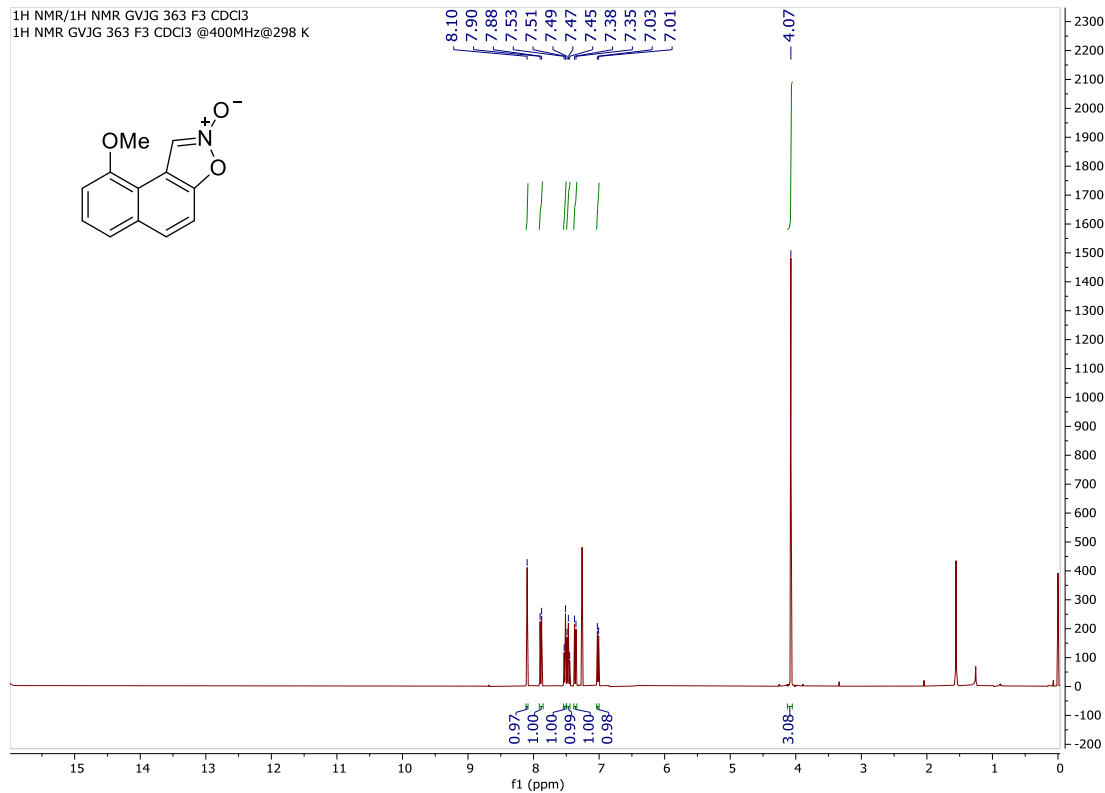


Figure S51. ^1H NMR (400 MHz, CDCl_3) of (8).

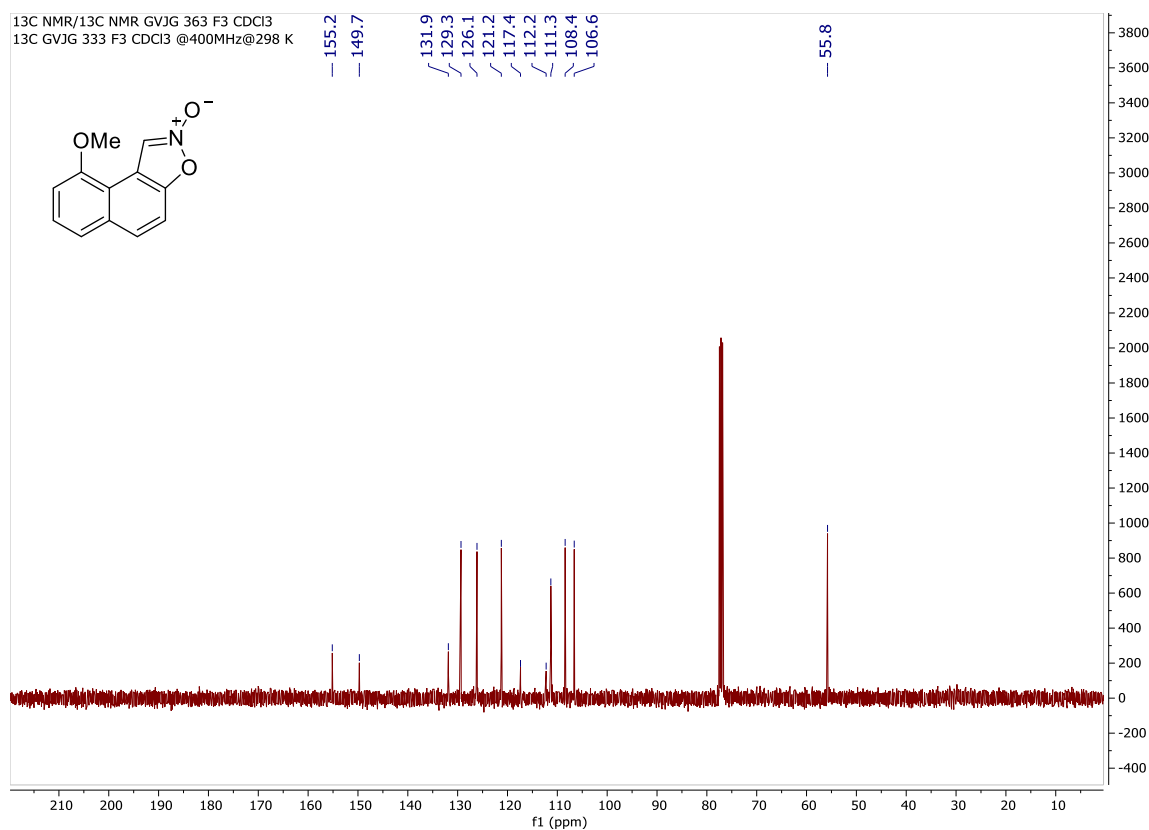


Figure S52. ^{13}C NMR [100.6 MHz, CDCl_3] of (8).

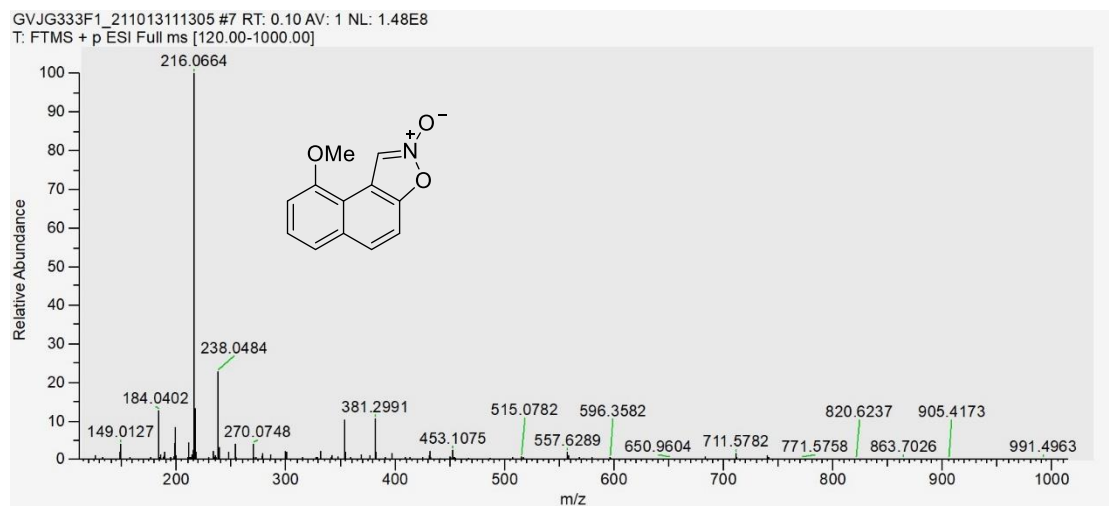


Figure S53. HRMS $[\text{M}+\text{H}]^+$ of compound (8) using 0.1% HCO_2H in MeOH as solvent.

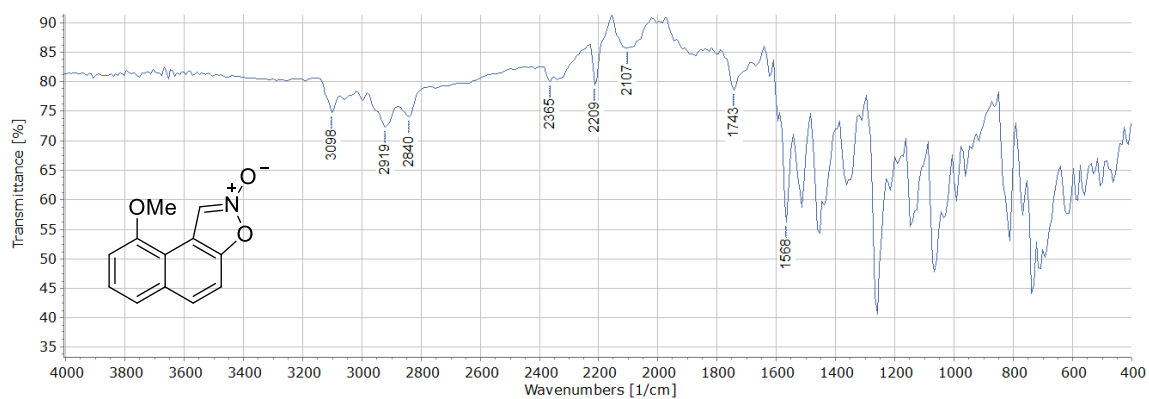


Figure S54. IR spectrum of (8).

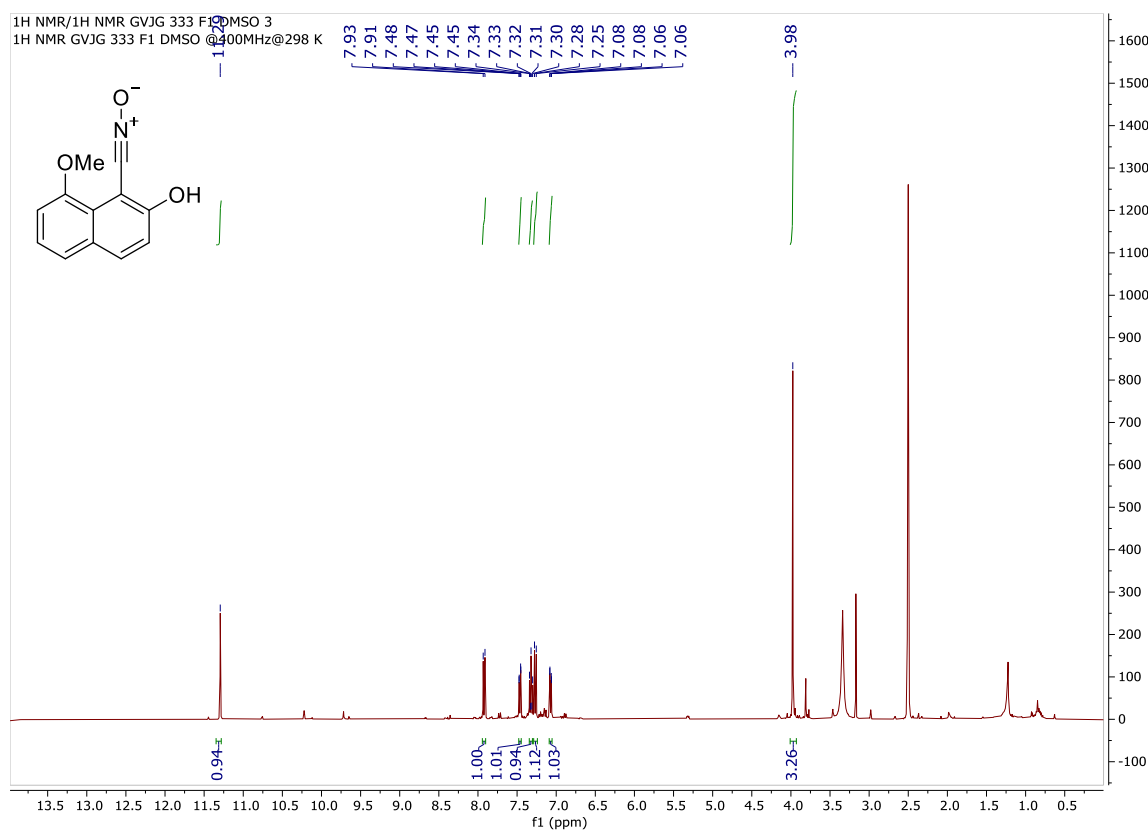


Figure S55. ¹H NMR (400 MHz, DMSO-*d*₆) of (9).

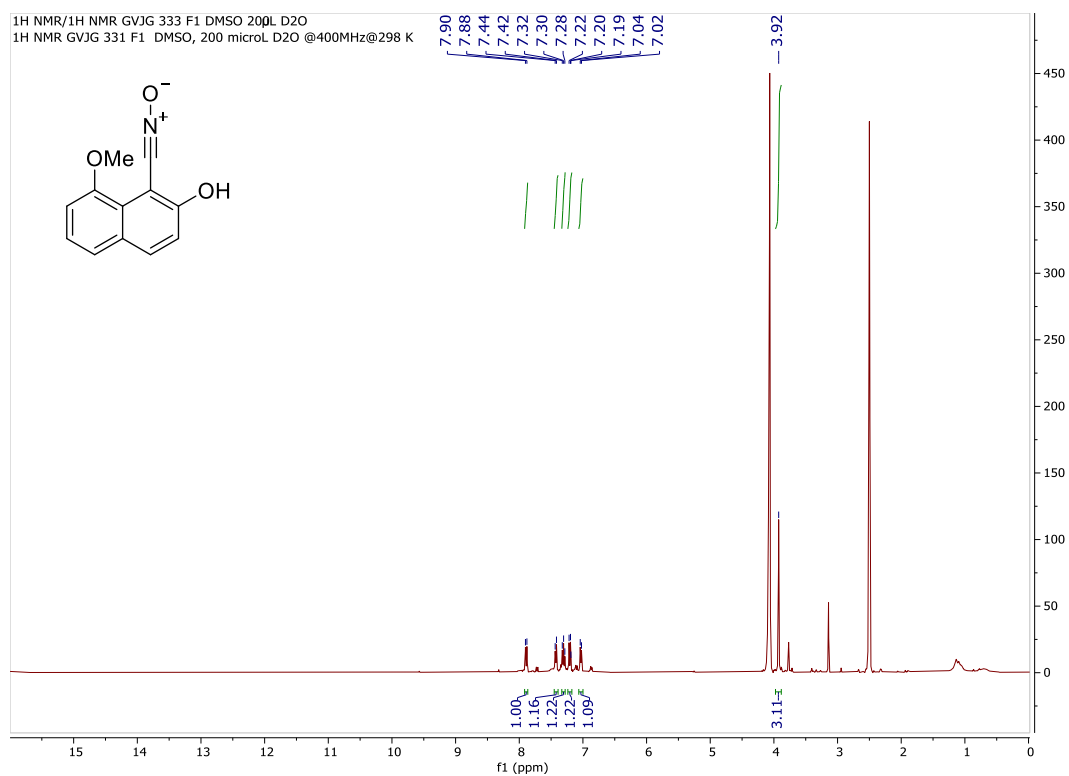


Figure S56. ¹H NMR (400 MHz, DMSO-*d*₆ + D₂O) of (**9**).

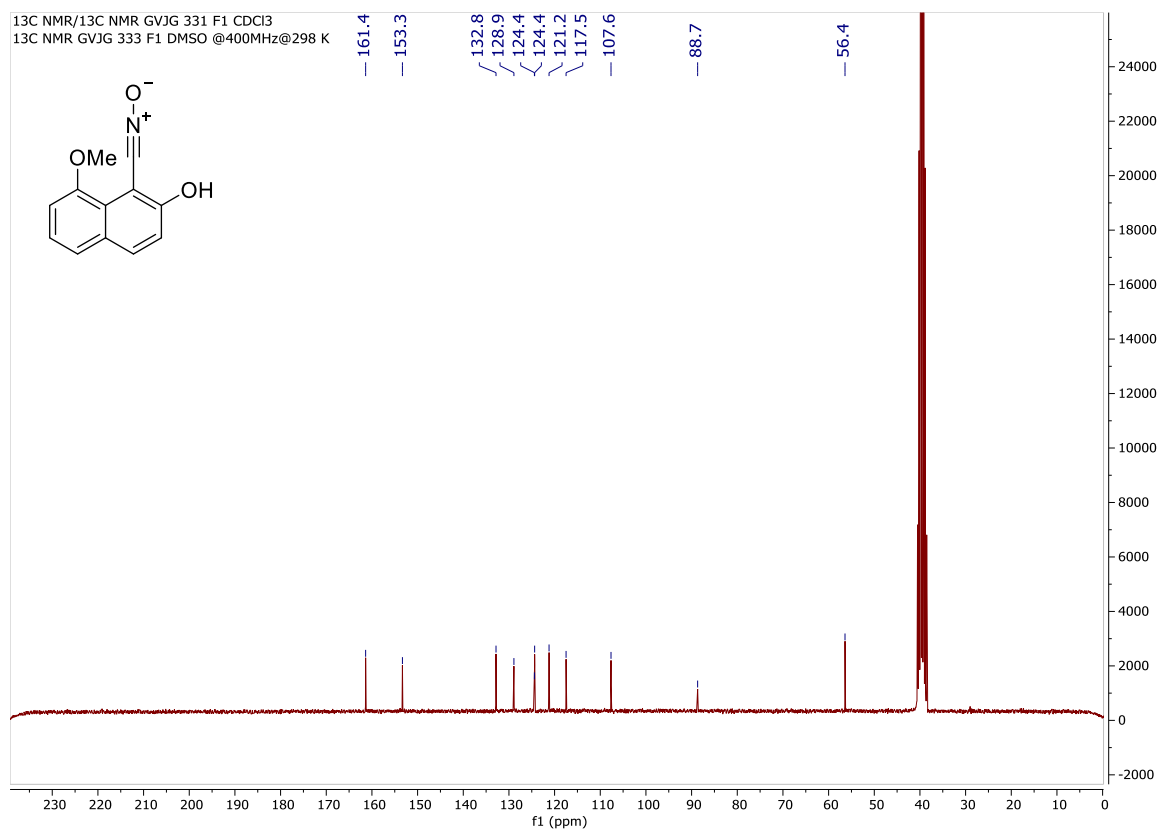


Figure S57. ¹³C NMR [100.6 MHz, DMSO-*d*₆] of (**9**).

GVJG333f1_9rt_210721103752 #37 RT: 0.52 AV: 1 NL: 1.33E7
T: FTMS + p ESI Full ms [200.00-500.00]

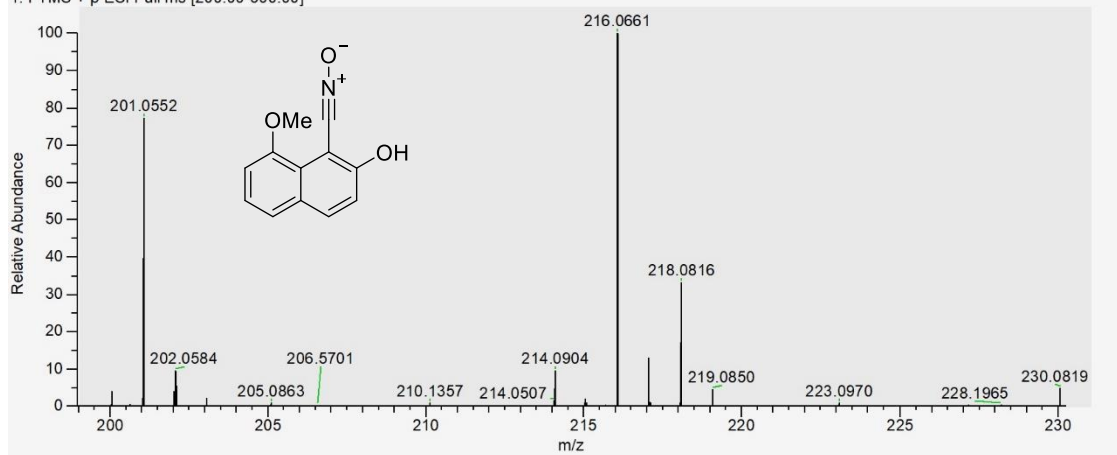


Figure S58. HRMS $[M+H]^+$ of compound (9) in DMSO- d_6 using 0.1% HCO₂H in MeOH as solvent.

1H NMR/1H NMR GVJG 333 F1 DMSO
1H NMR GVJG 333 F1 DMSO @400MHz@298 K

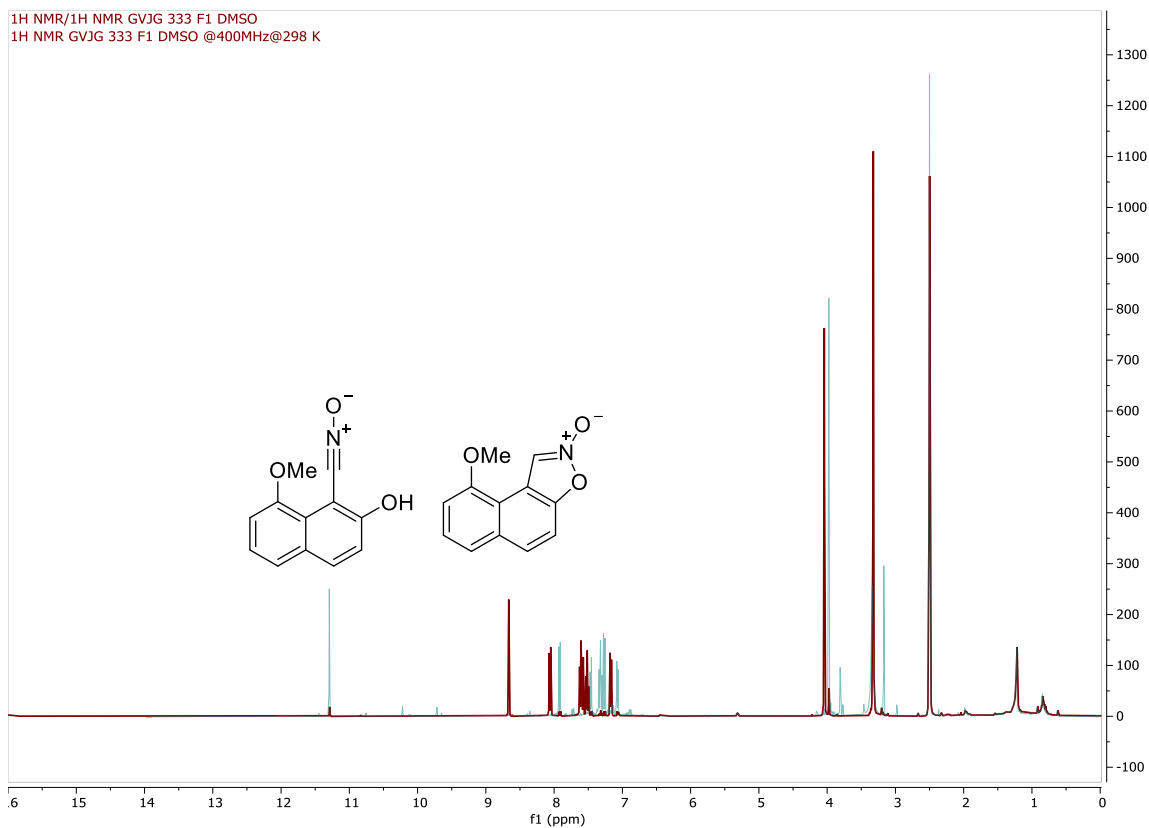


Figure S59. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) of nitrile oxide (**9**) and isoxazole-2-oxide (**8**), superimposed.

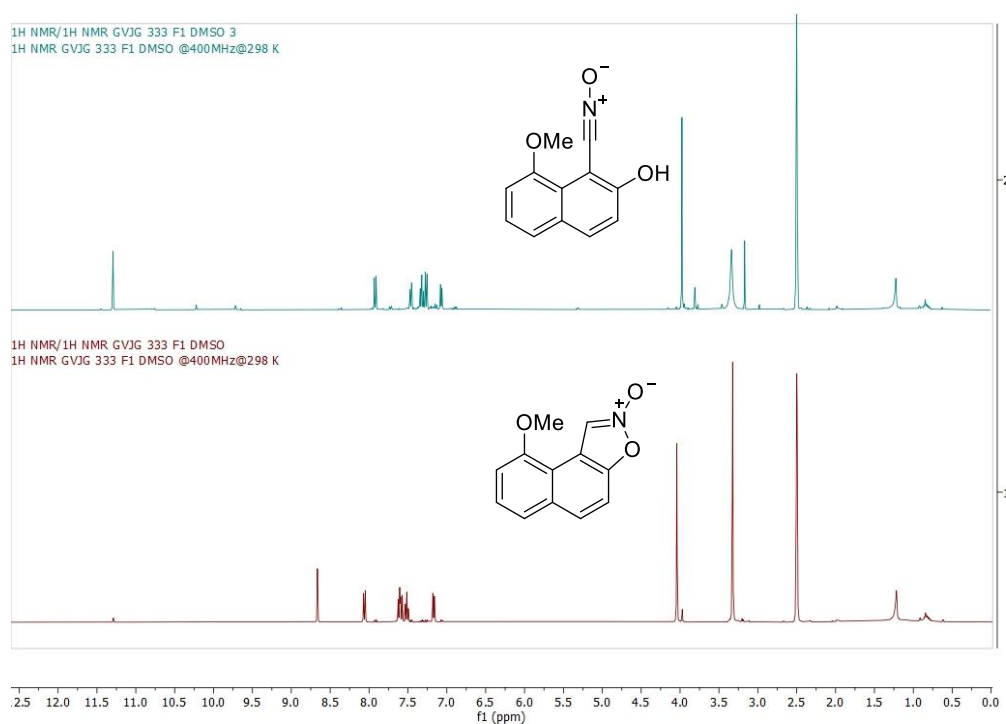


Figure S60. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) of nitrile oxide (**9**) and isoxazole-2-oxide (**8**), stacked.

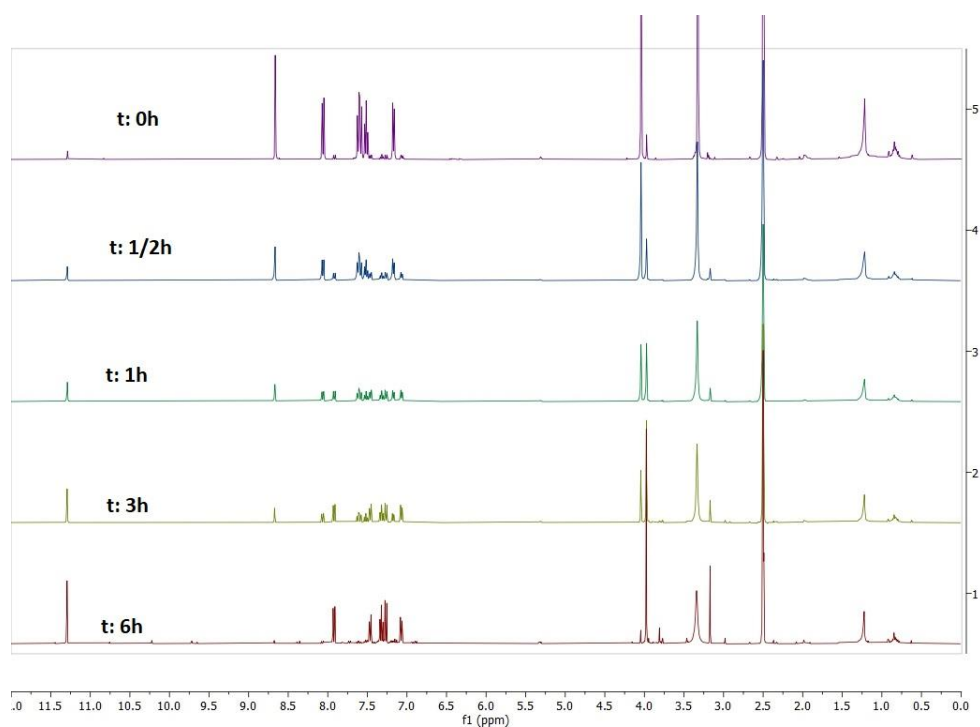


Figure S61. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) time-course experiment of the ring opening of isoxazole-2-oxide (**8**) (top spectra) to nitrile oxide (**9**) (bottom spectra).

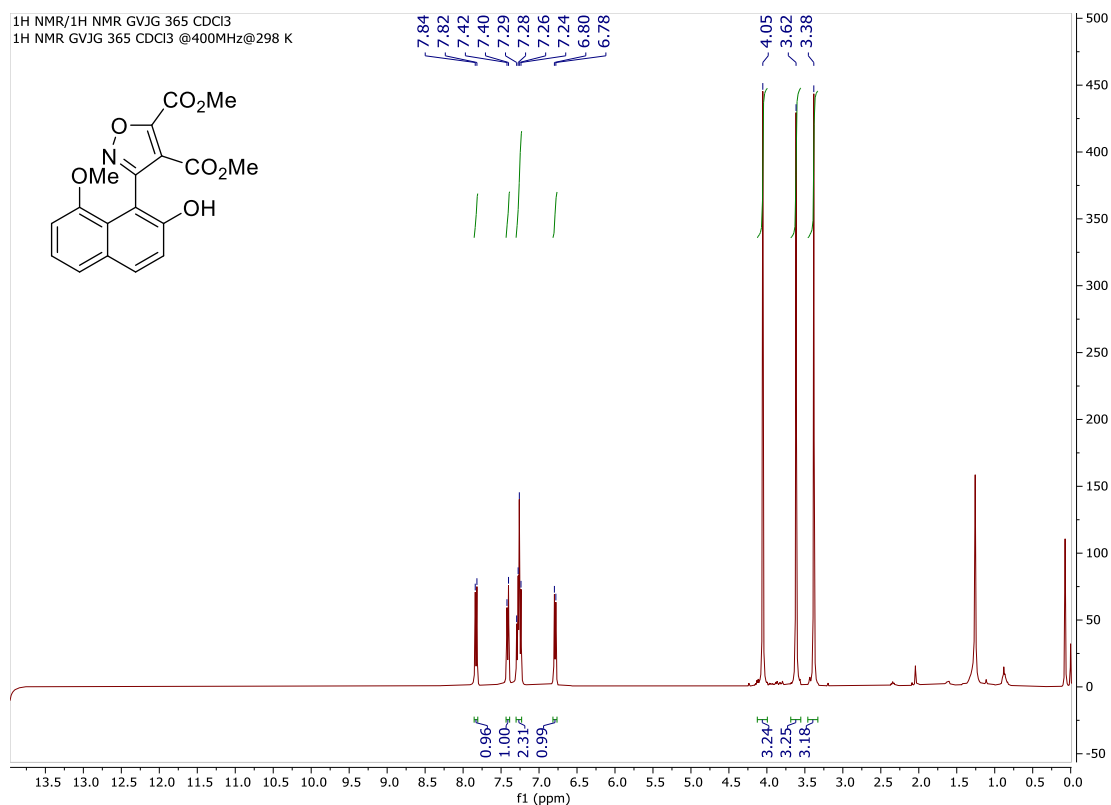


Figure S62. ¹H NMR (400 MHz, CDCl₃) of (10a).

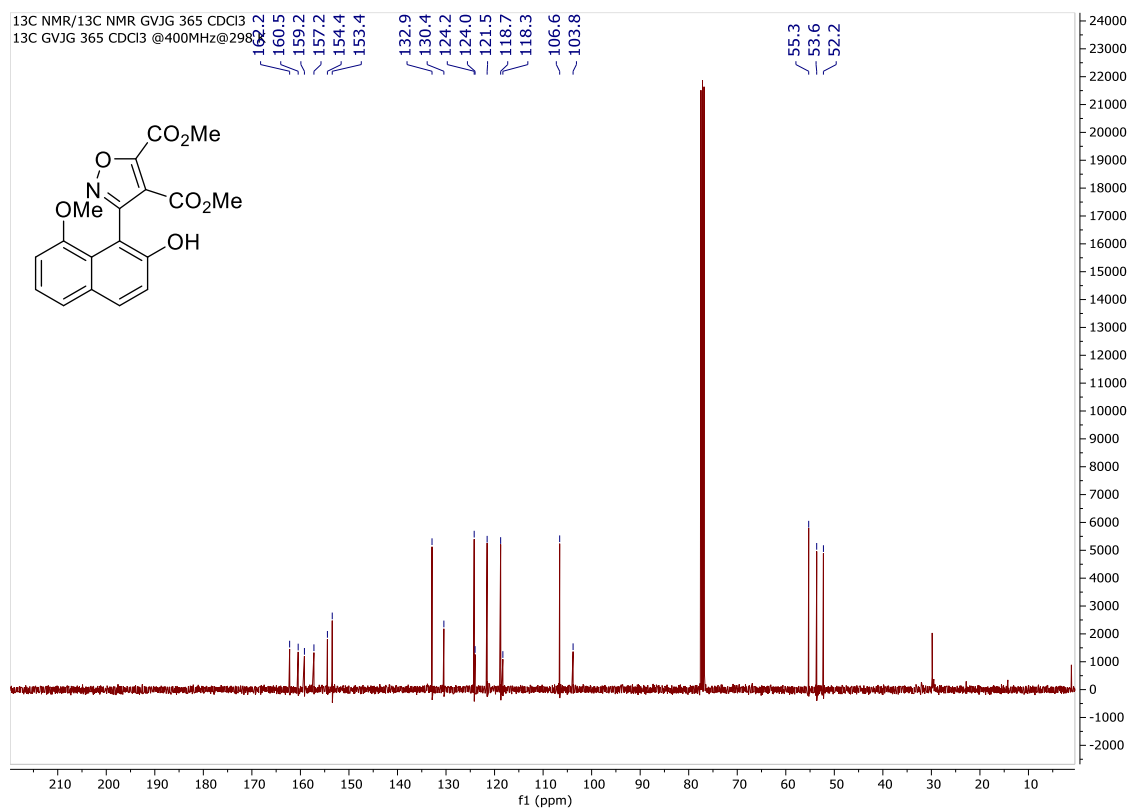


Figure S63. ¹³C NMR (100.6 MHz, CDCl₃) of (10a).

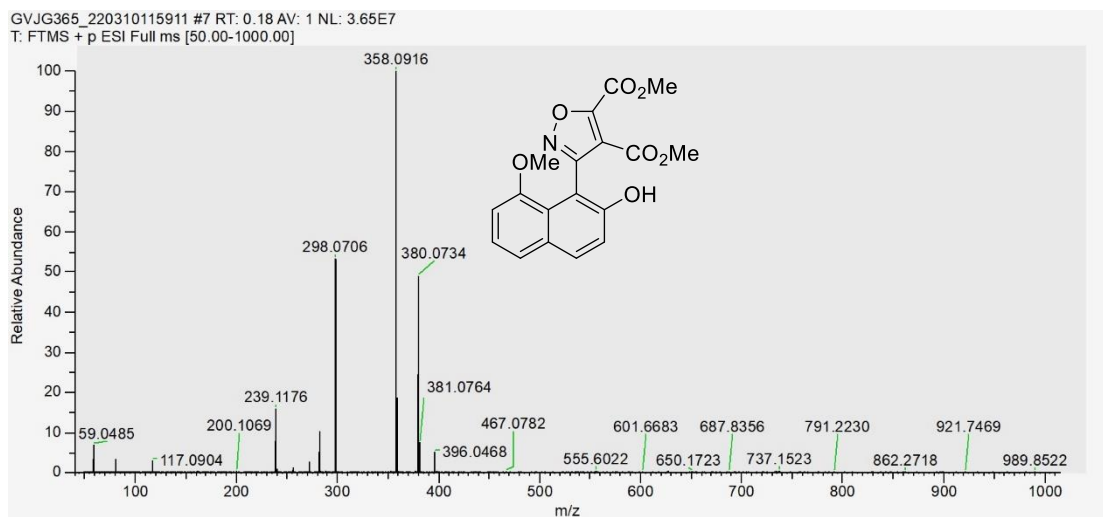


Figure S64. HRMS $[M+H]^+$ of compound **(10a)** using 0.1% HCO_2H in MeOH as solvent.

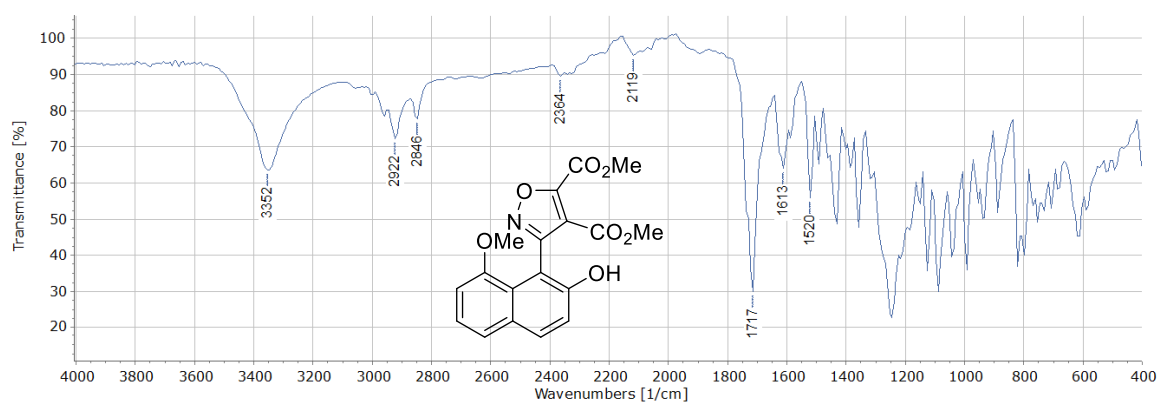


Figure S65. IR spectrum (solid) of **(10a)**.

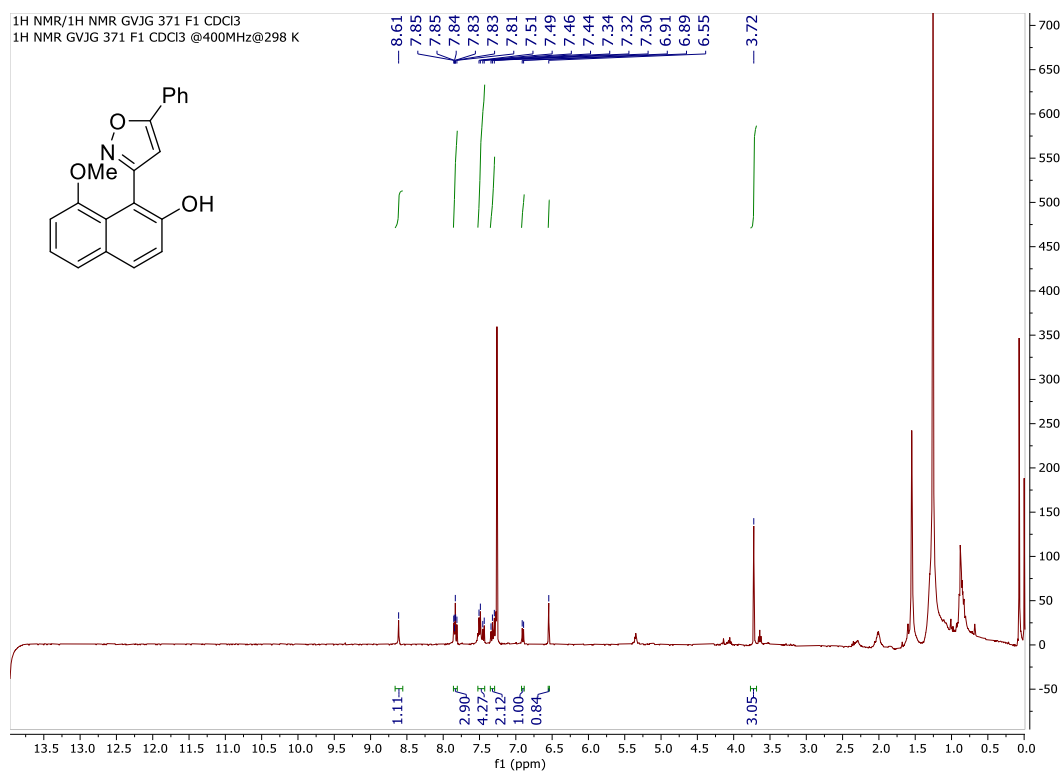


Figure S66. ¹H NMR (400 MHz, CDCl₃) of **(10b)**.

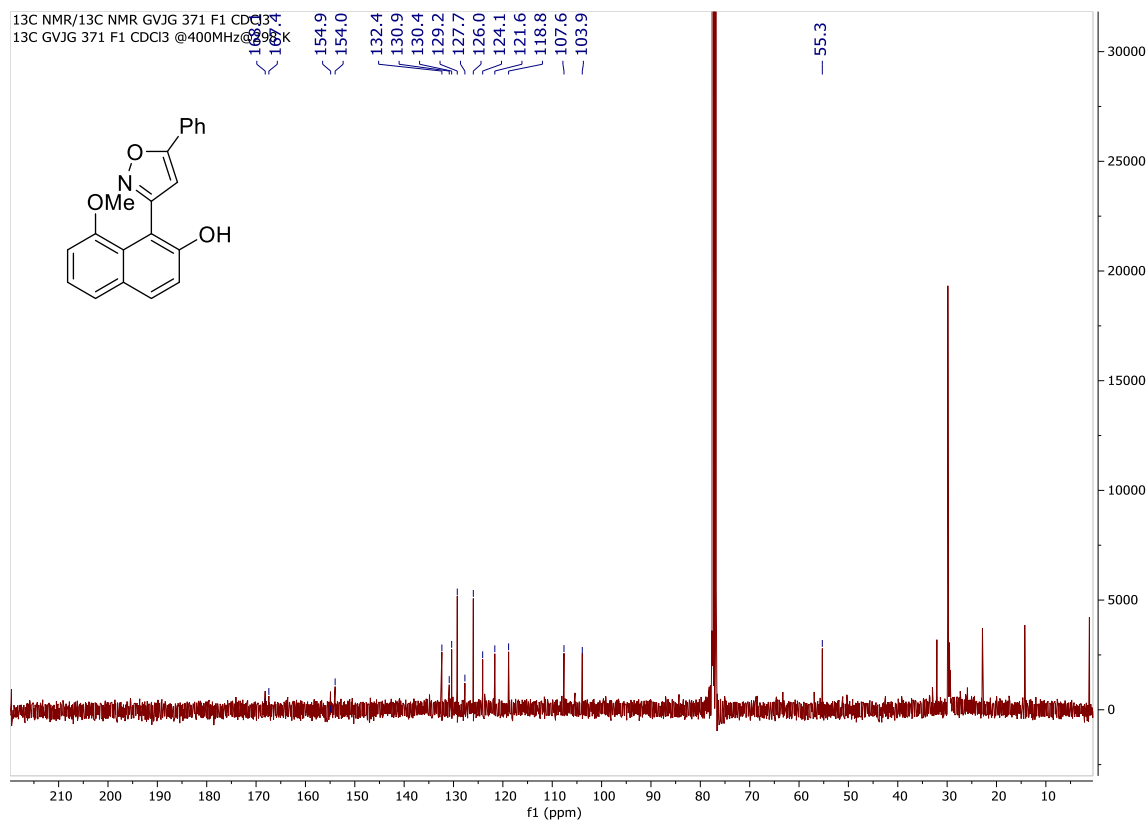


Figure S67. ¹³C NMR (100.6 MHz, CDCl₃) of **(10b)**.

GVJG371_220720112325 #2 RT: 0.02 AV: 1 NL: 1.47E7
T: FTMS + p ESI Full ms [50.00-1000.00]

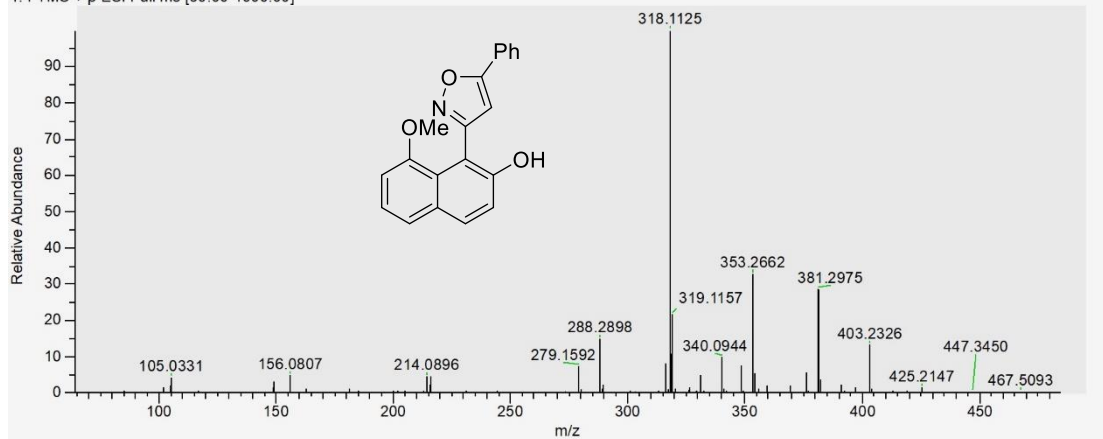


Figure S68. HRMS $[M+H]^+$ of compound (10b) using 0.1% HCO_2H in MeOH as solvent.

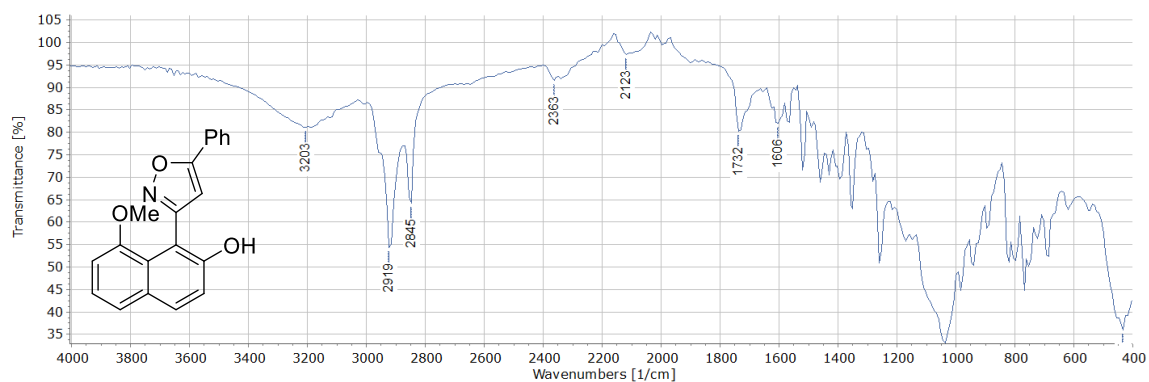


Figure S69. IR spectrum (solid) of (10b).

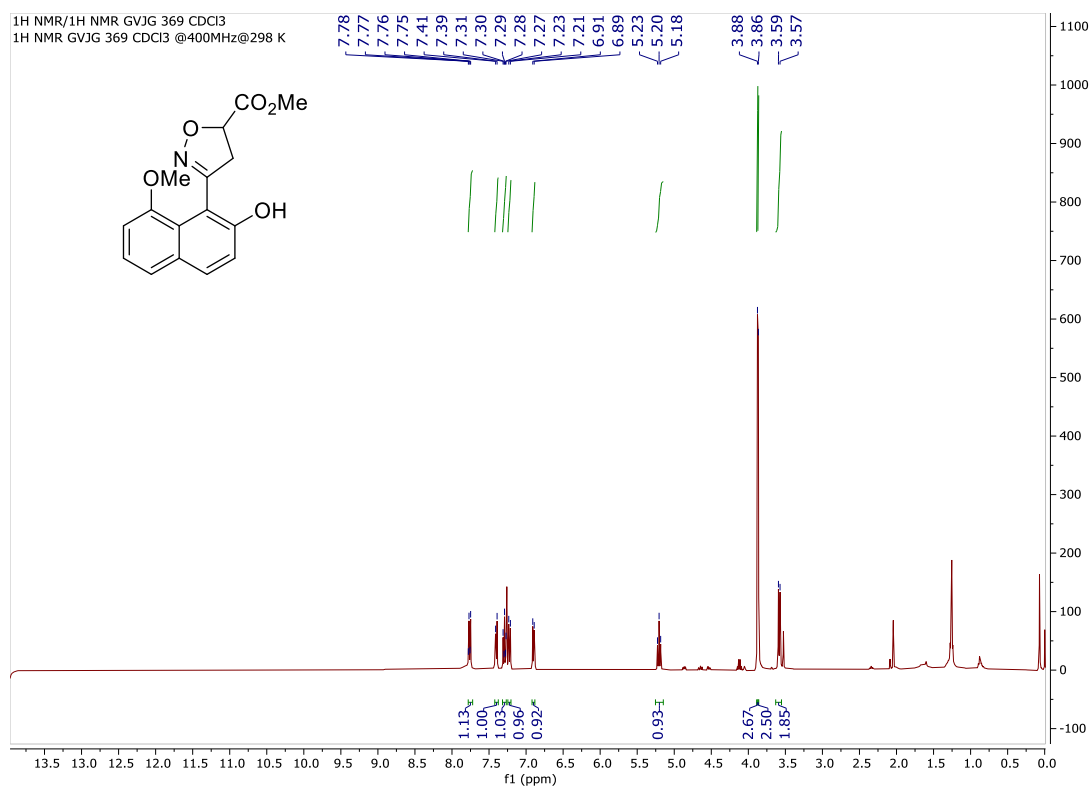


Figure S70. ¹H NMR (400 MHz, CDCl₃) of **(10c)**.

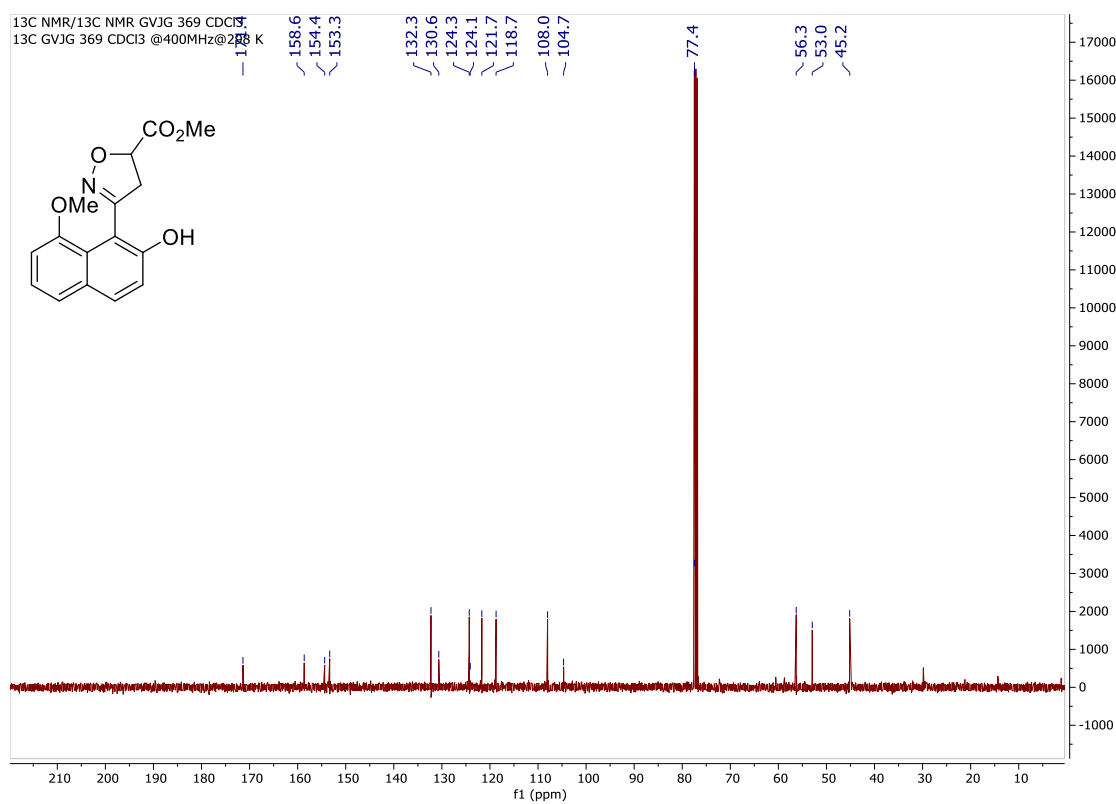


Figure S71. ¹³C NMR (100.6 MHz, CDCl₃) of **(10c)**.

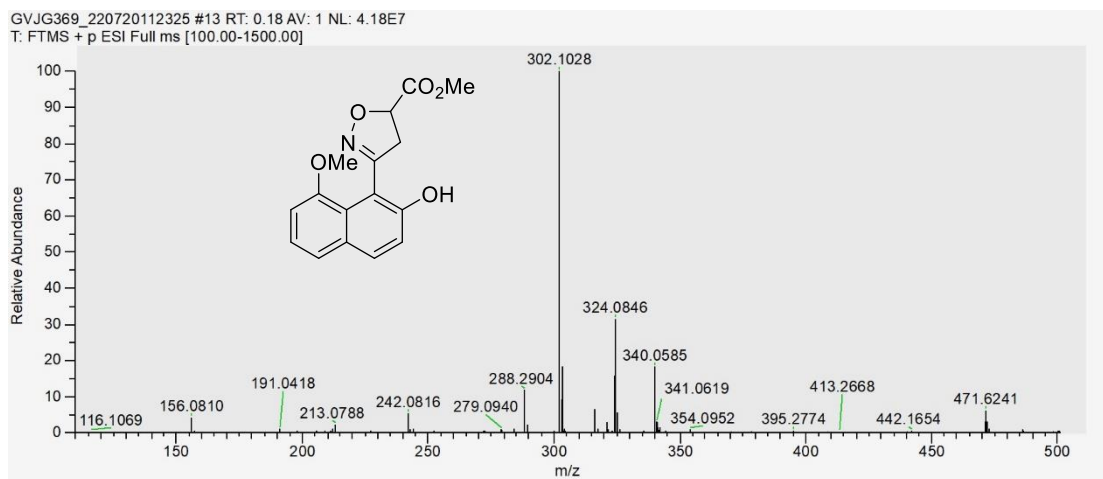


Figure S72. HRMS $[M+H]^+$ of compound (**10c**) using 0.1% HCO_2H in MeOH as solvent.

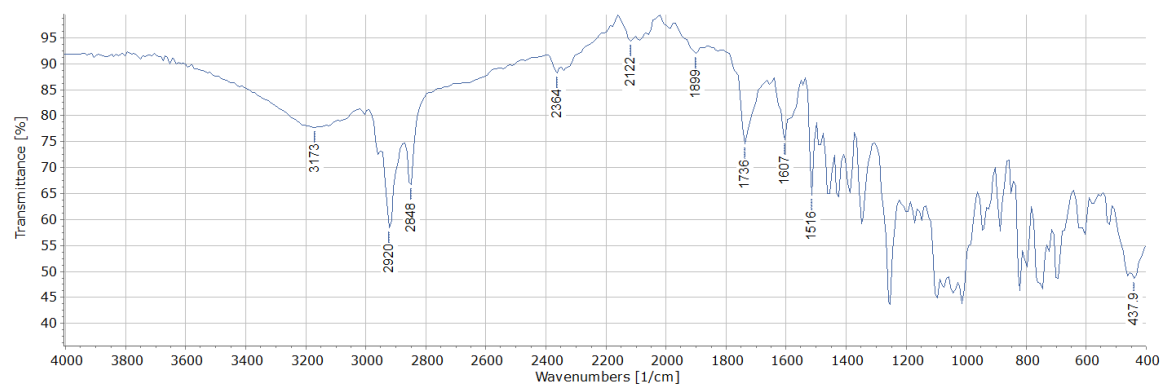
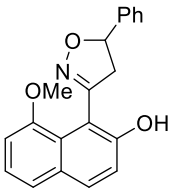
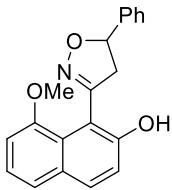


Figure S73. IR spectrum (solid) of (**10c**).



GVJG370_220720112325 #4 RT: 0.05 AV: 1 NL: 1.73E8
T: FTMS + p ESI Full ms [50.00-1000.00]

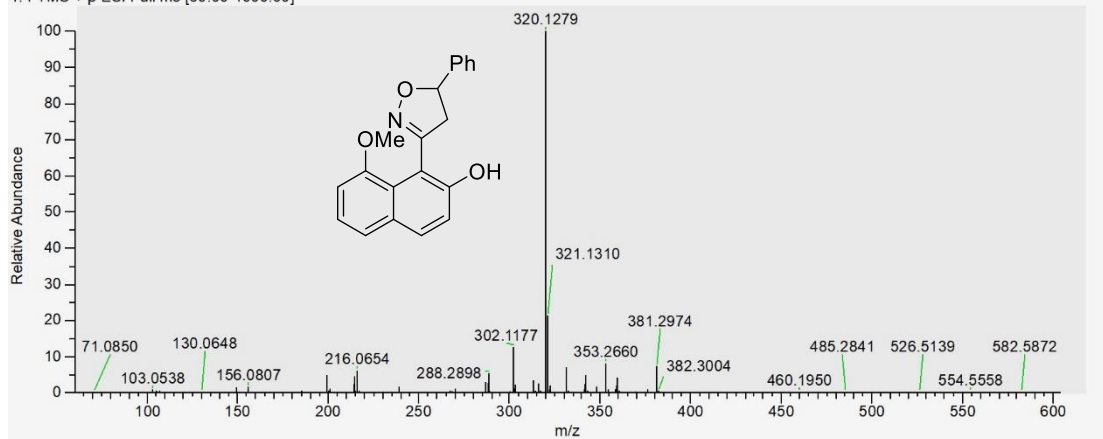


Figure S76. HRMS $[M+H]^+$ of compound (**10d**) using 0.1% HCO_2H in MeOH as solvent.

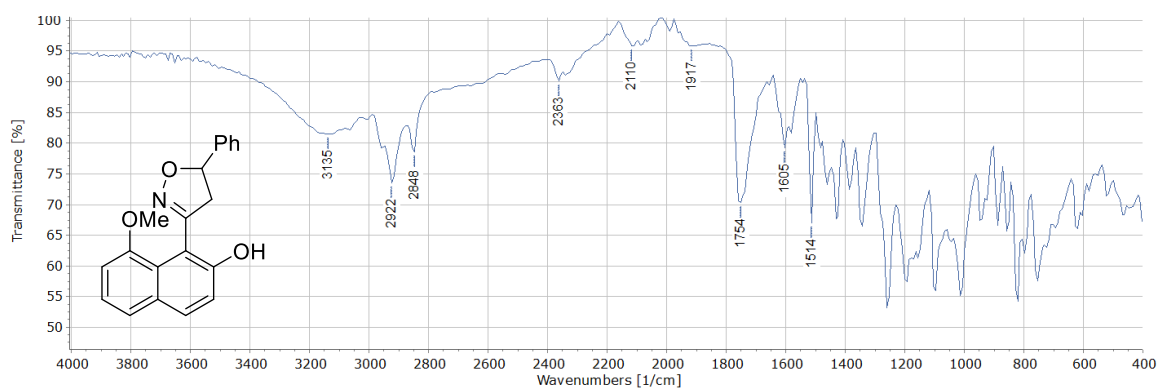


Figure S77. IR spectrum (solid) of (**10d**).