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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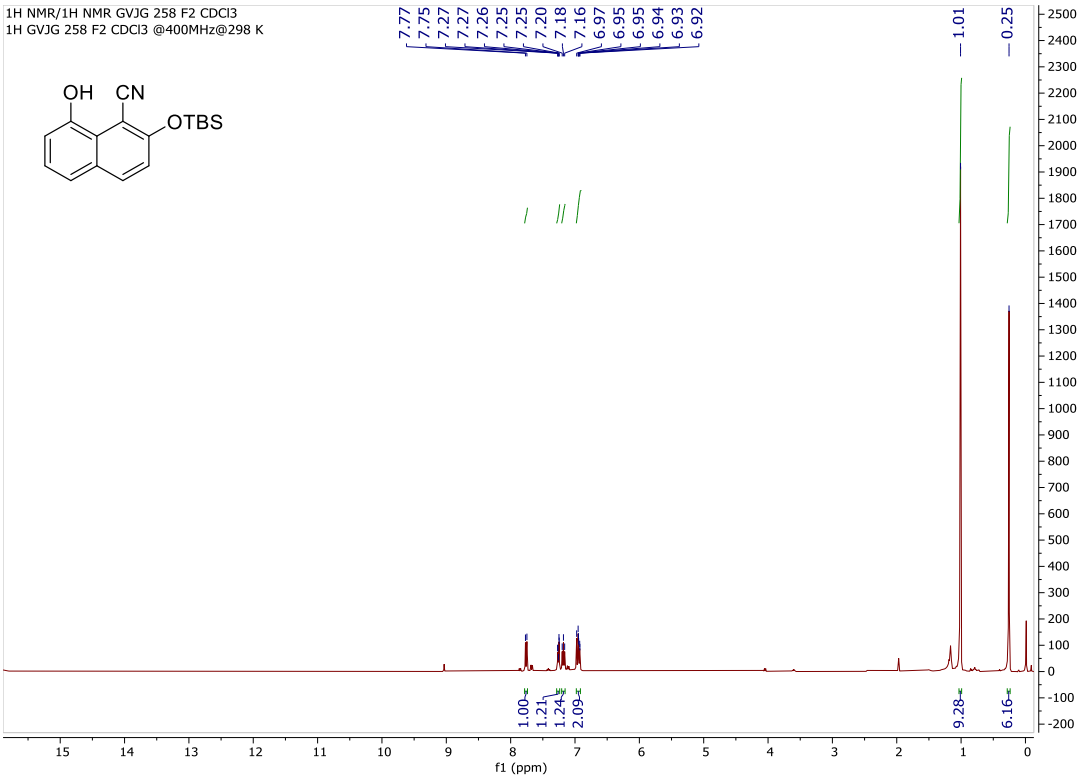

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of compound (**11**).

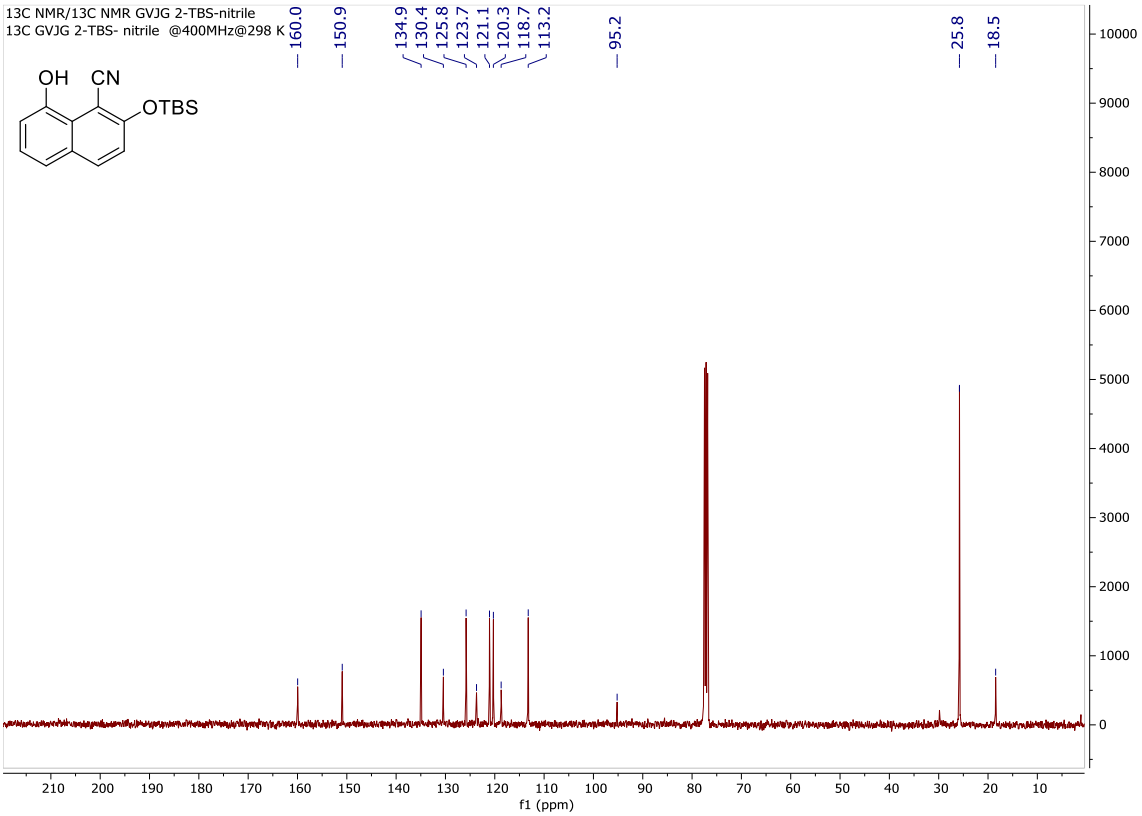

Figure S2. ^{13}C NMR (100.6 MHz, $CDCl_3$) of compound (**11**).

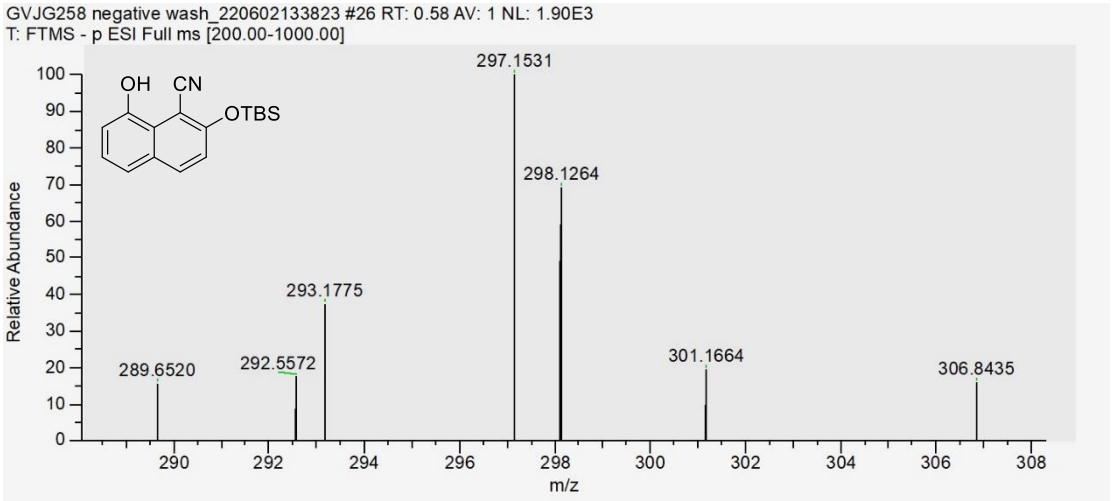

Figure S3. HRMS $[M+H]^+$ of compound (**11**) using 0.1% HCO_2H in MeOH as solvent.

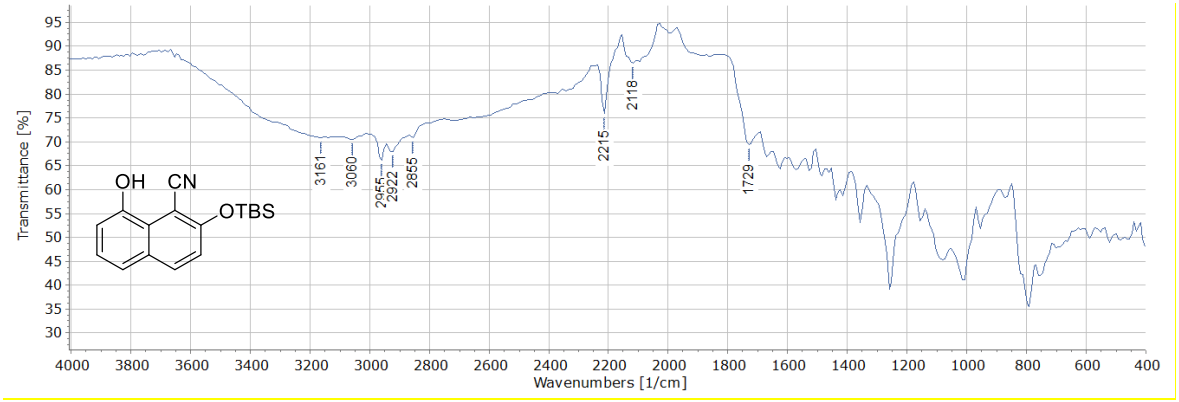

Figure S4. IR spectrum (solid) of compound (**11**).

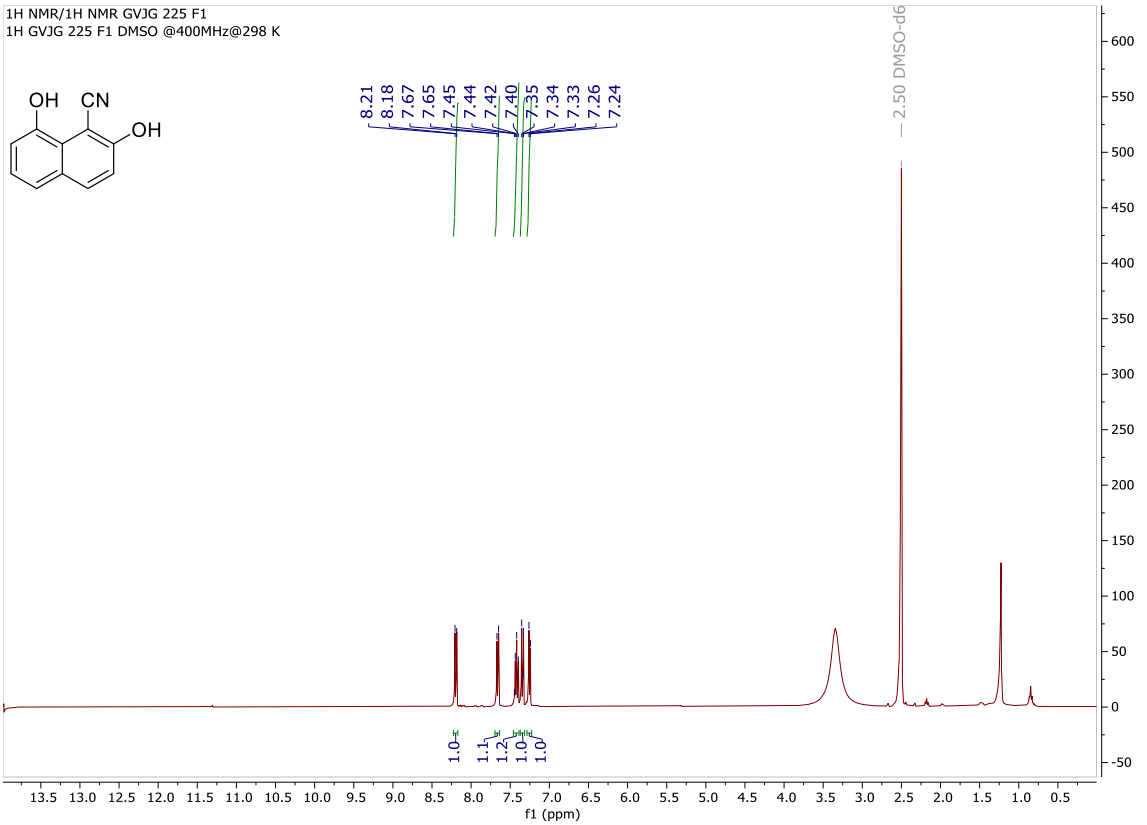

Figure S5. ^{1}H NMR (400 MHz, DMSO-d_6) of compound (**5**).

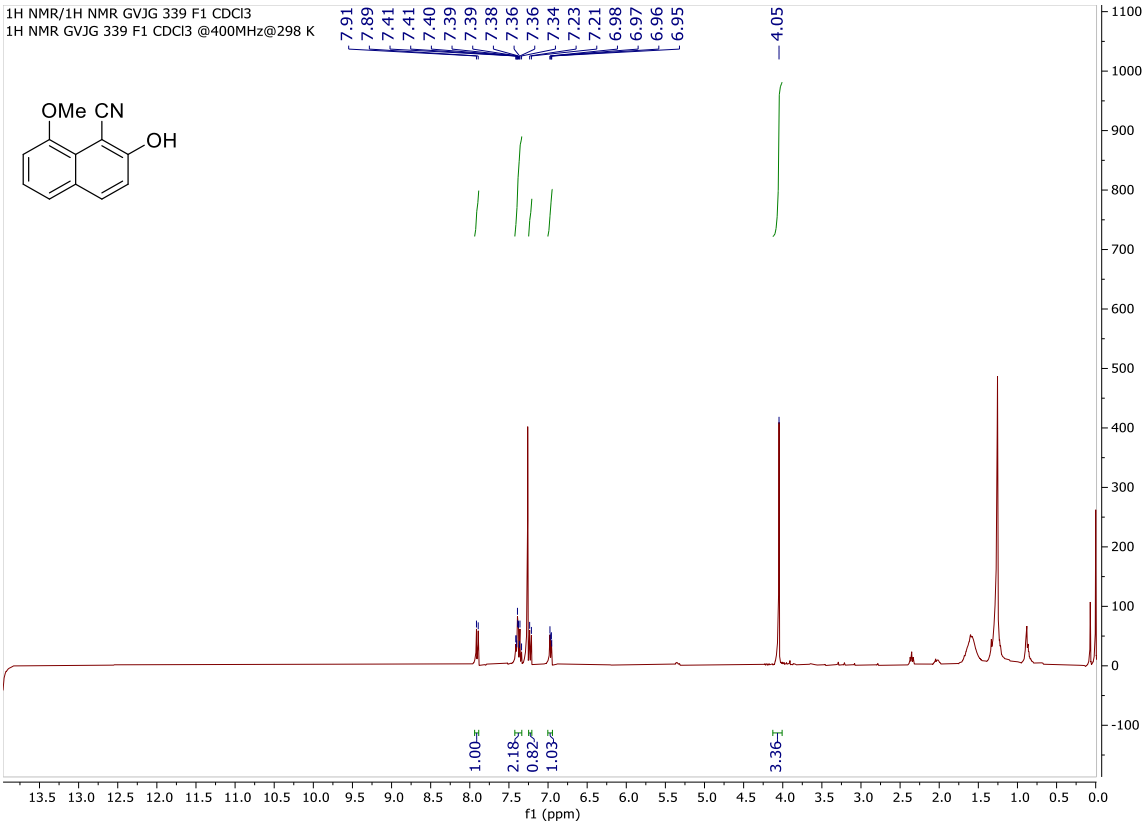

Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) of compound (**12**).

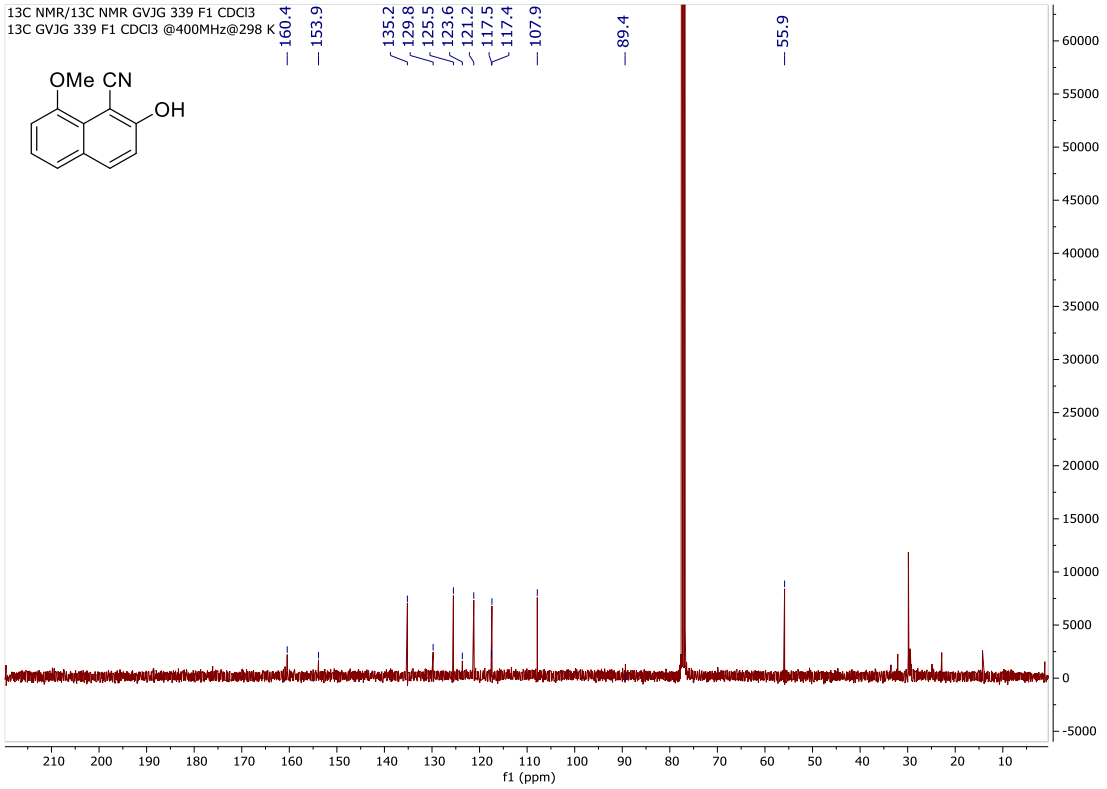

Figure S7. ^{13}C NMR (100.6 MHz, $CDCl_3$) of compound (**12**).

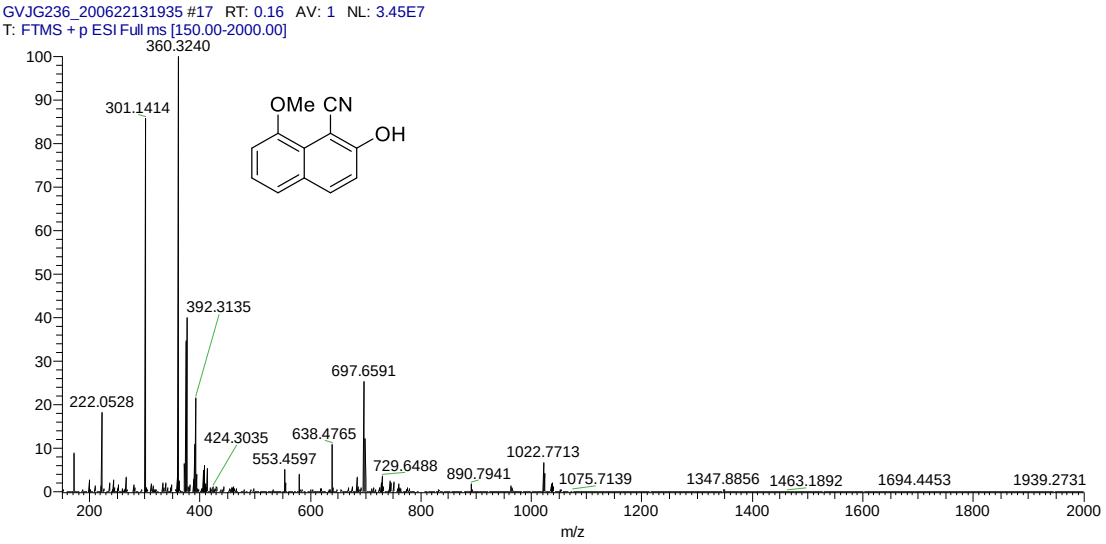

Figure S8. HRMS $[M+H]^+$ of compound (**12**) using 0.1% HCO_2H in MeOH as solvent.

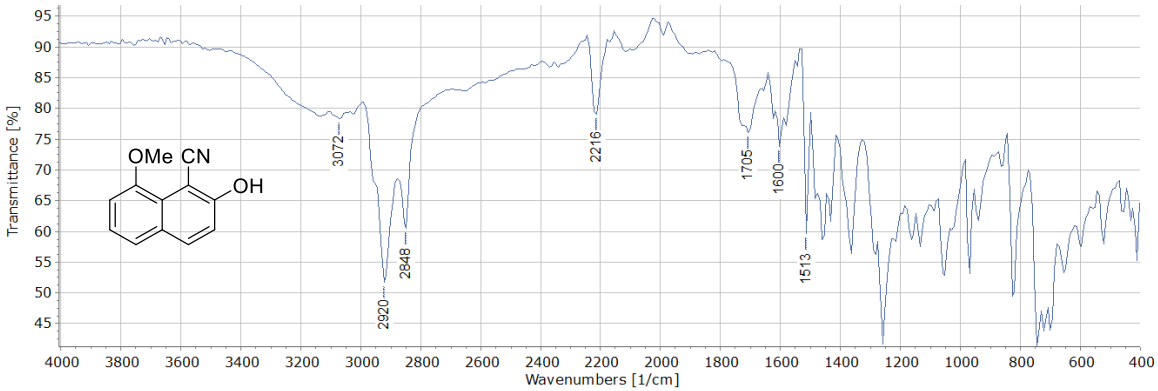

Figure S9. IR spectrum (solid) of compound (**12**).

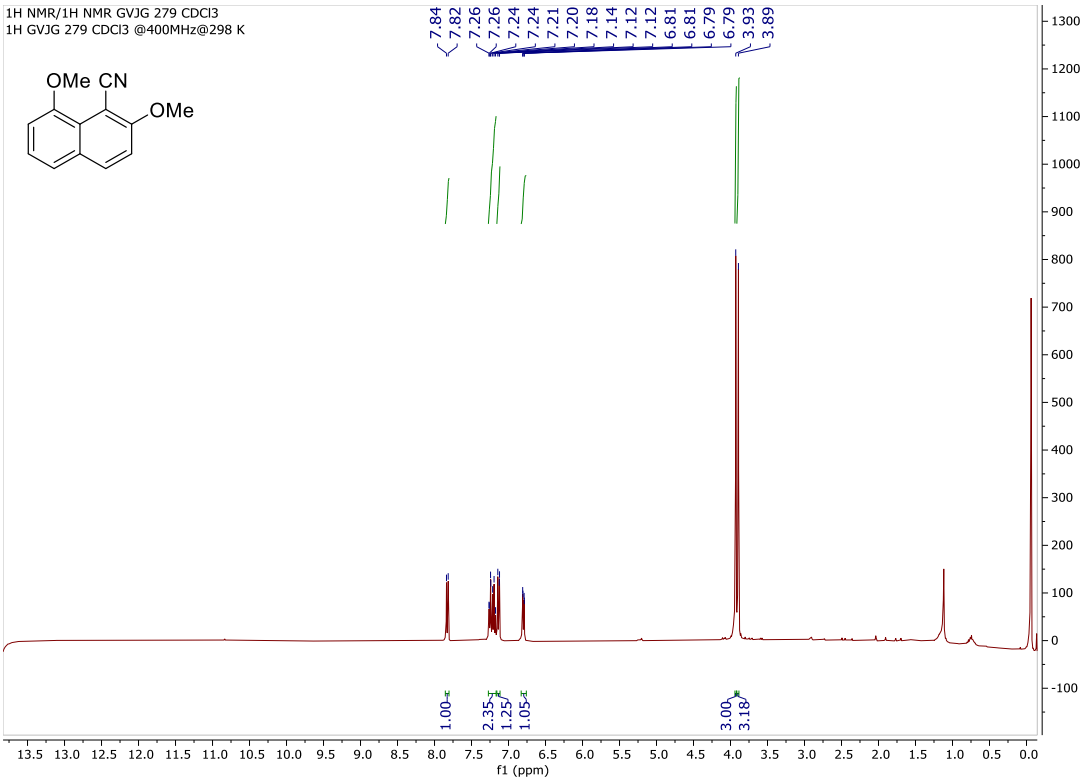

Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) of compound (**13**).

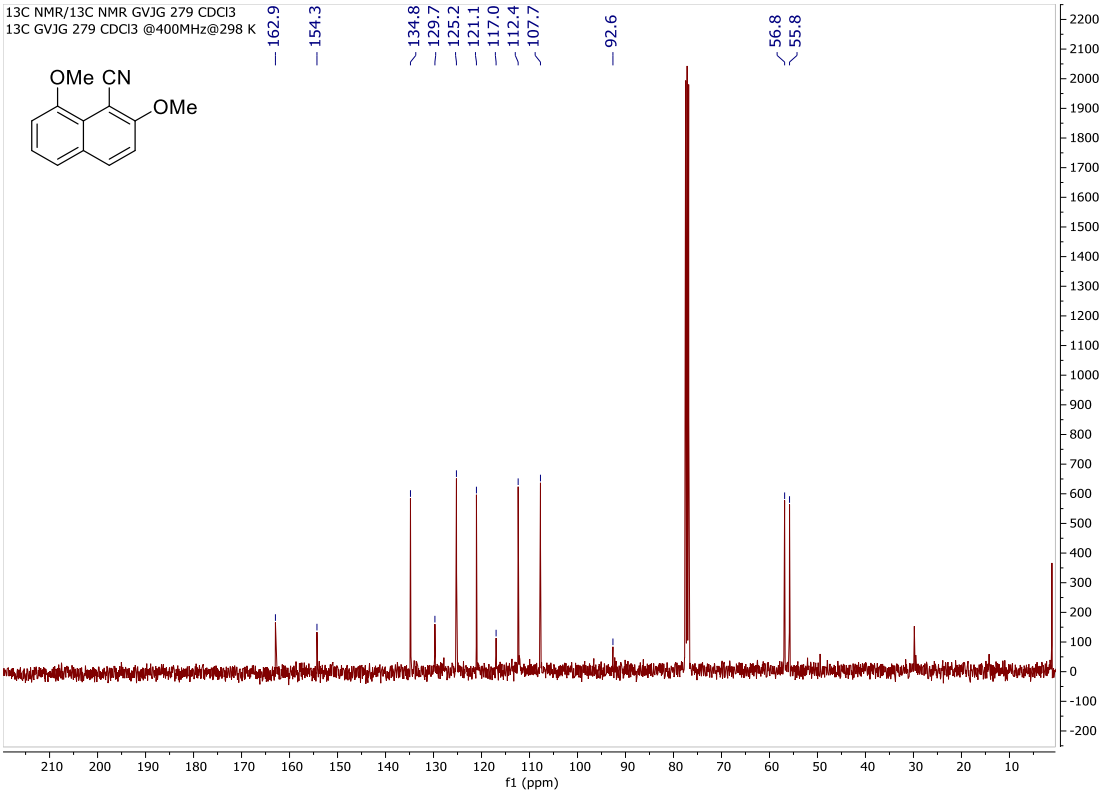

Figure S11. ^{13}C NMR (400 MHz, $CDCl_3$) of compound (**13**).

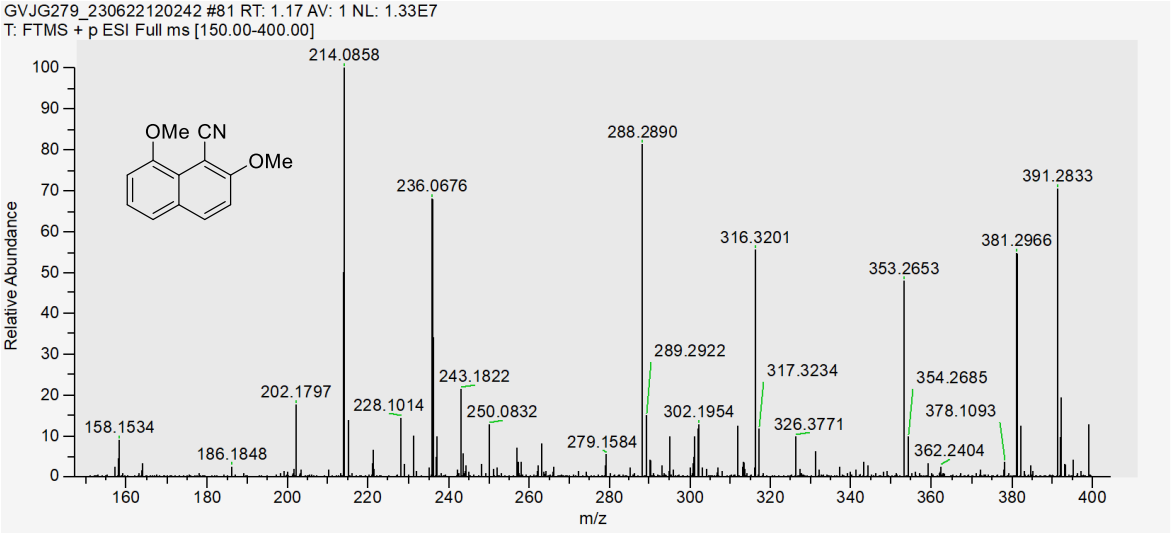

Figure S12. HRMS $[M+H]^+$ of compound (**13**) using 0.1% HCO_2H in MeOH as solvent.

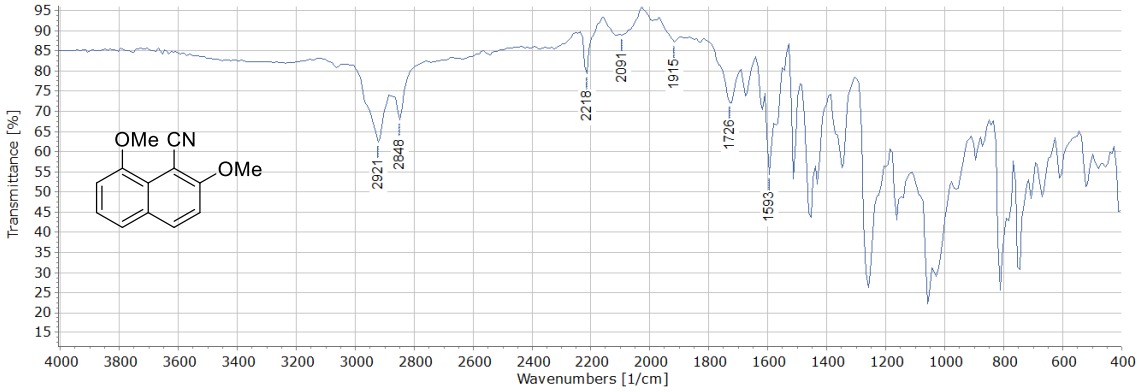

Figure S13. IR spectrum (solid) of compound (**13**).

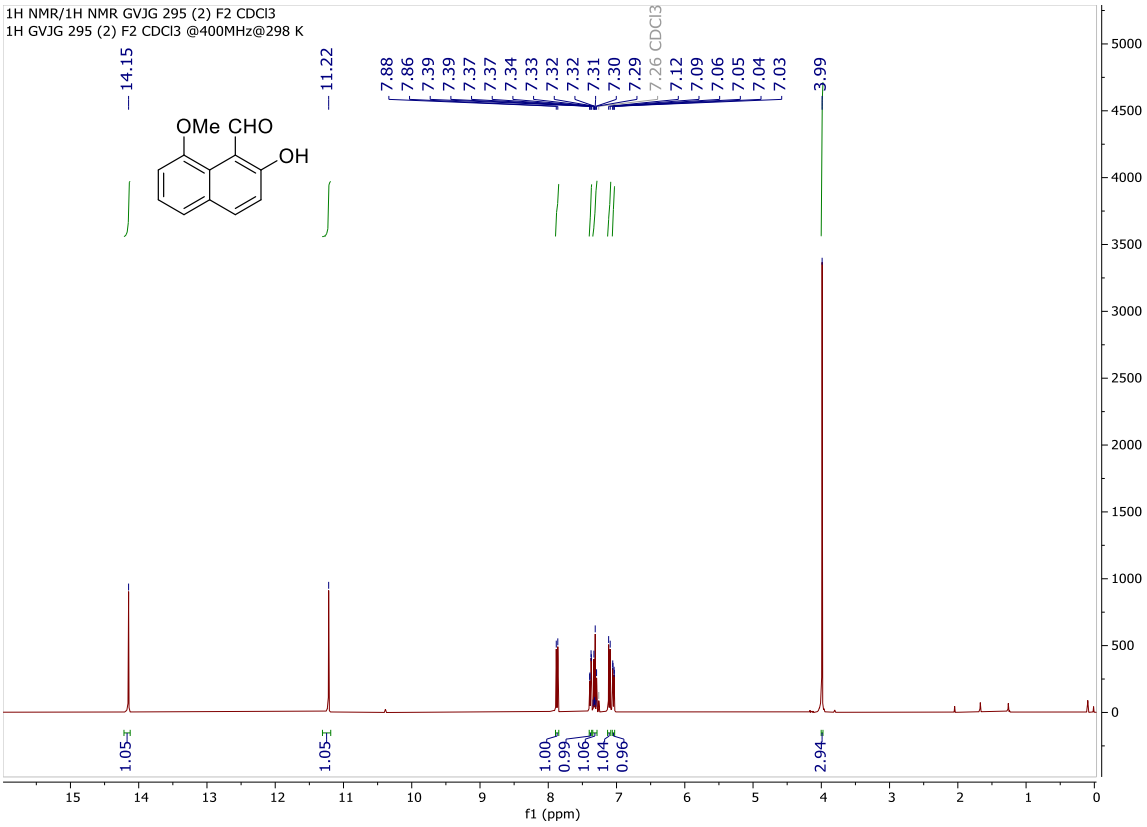

Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) of compound (**14**).

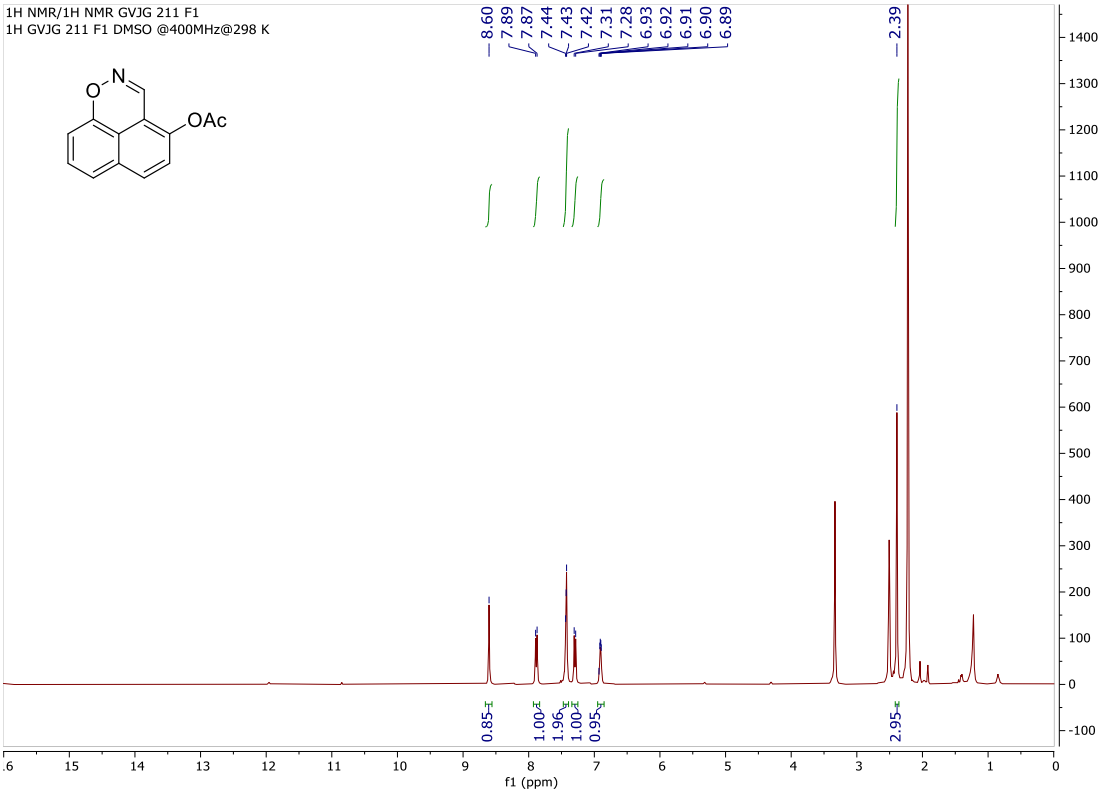

Figure S15. ^{1}H NMR (400 MHz, DMSO-d_6) of compound (**15**).

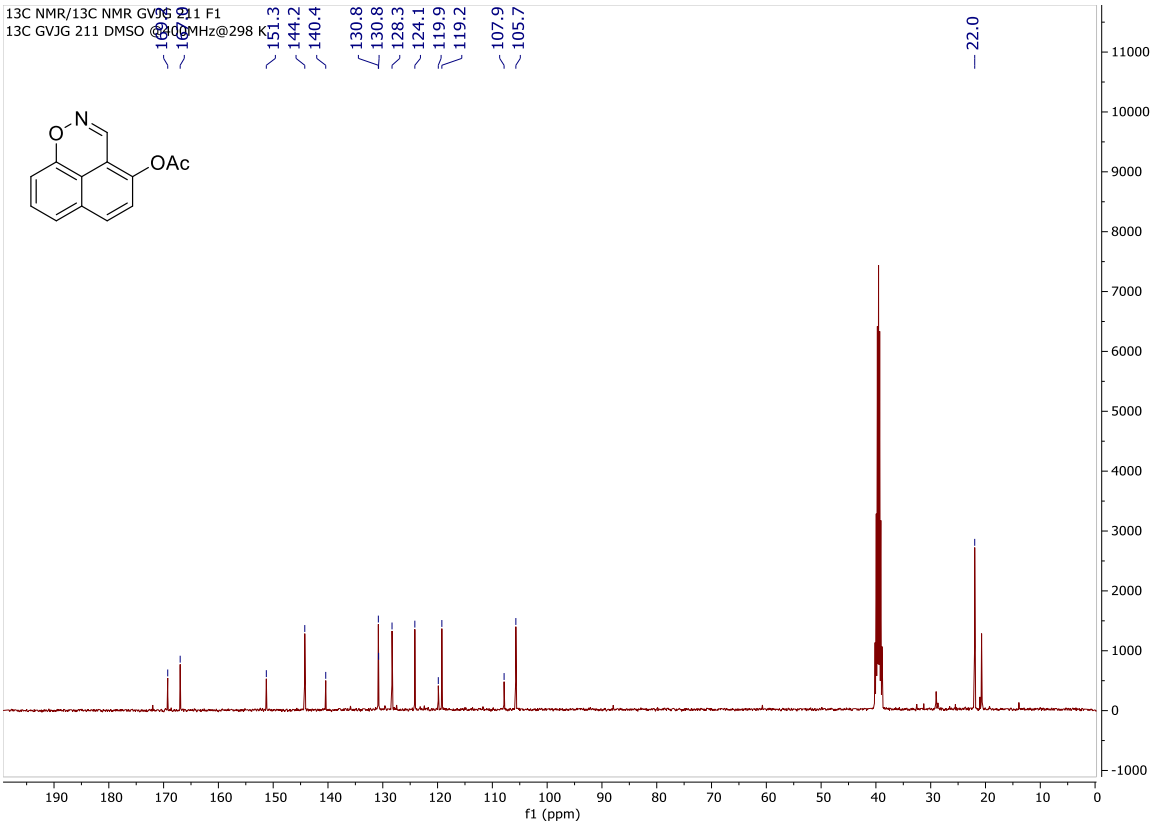

Figure S16. ^{13}C NMR (100.6 MHz, DMSO-d_6) of compound (**15**).

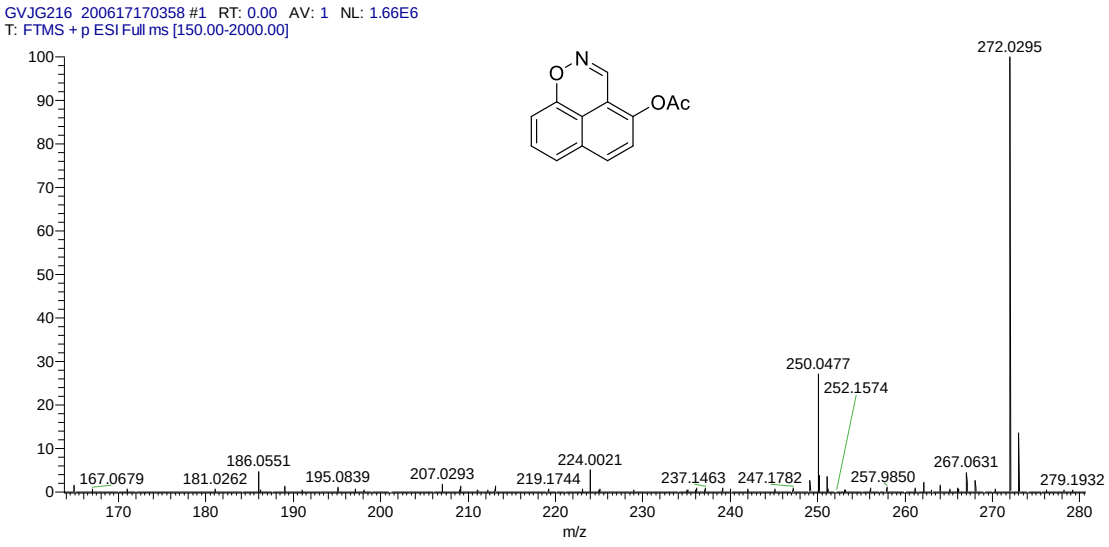

Figure S17. HRMS $[M+H]^+$ of compound (**15**) using 0.1% HCO_2H in MeOH as solvent.

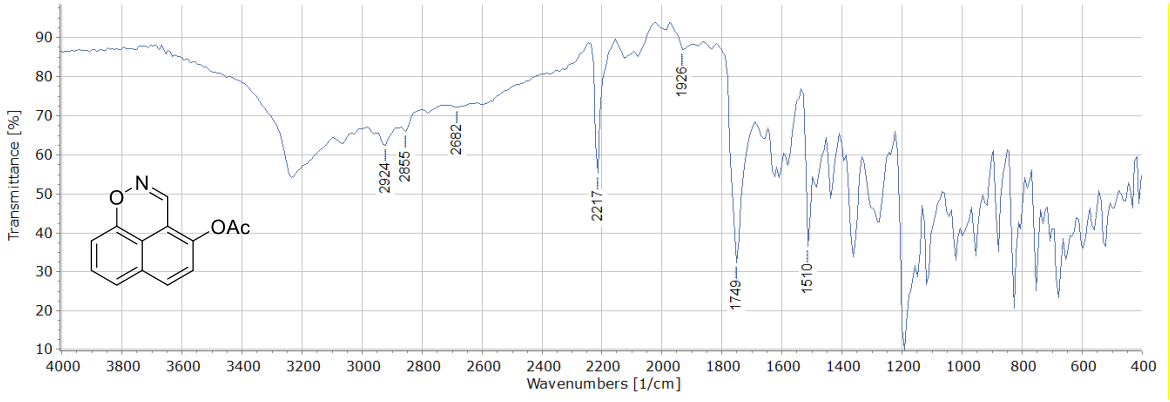

Figure S18. IR spectrum (solid) of compound (**15**).

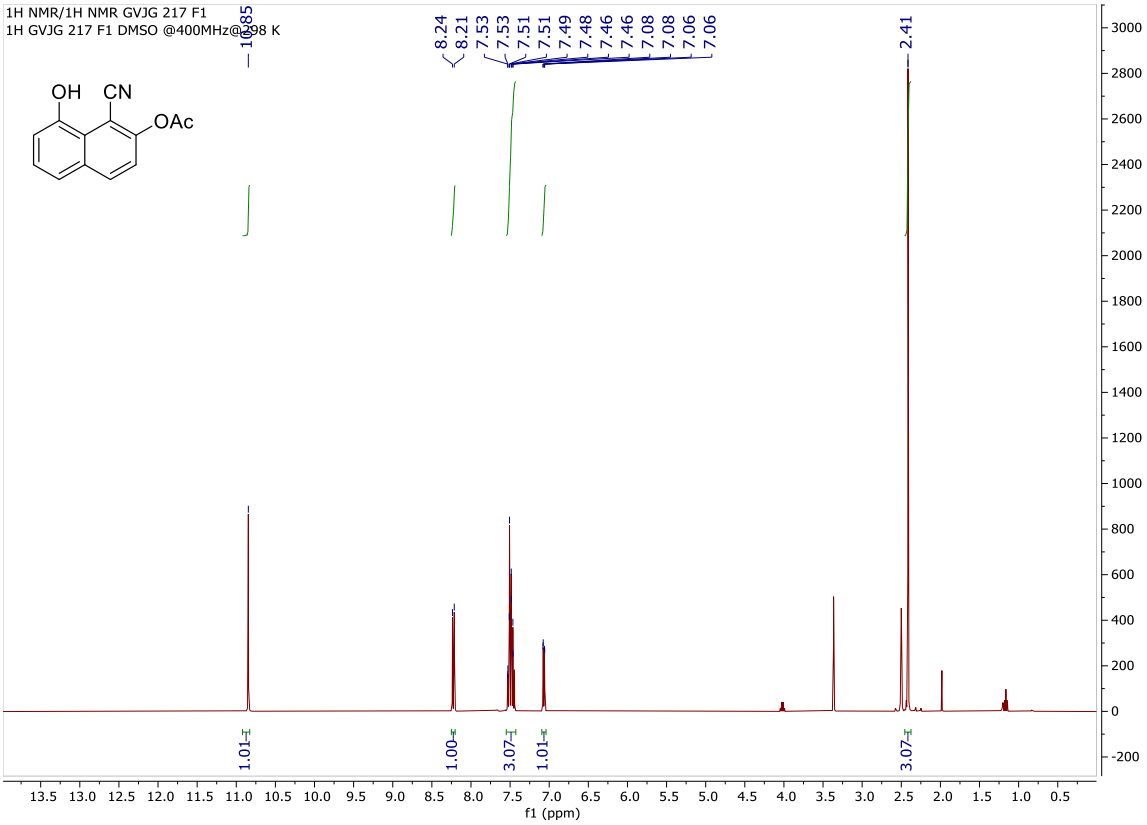

Figure S19. ^{1}H NMR (400 MHz, DMSO-d_6) of compound (**16**).

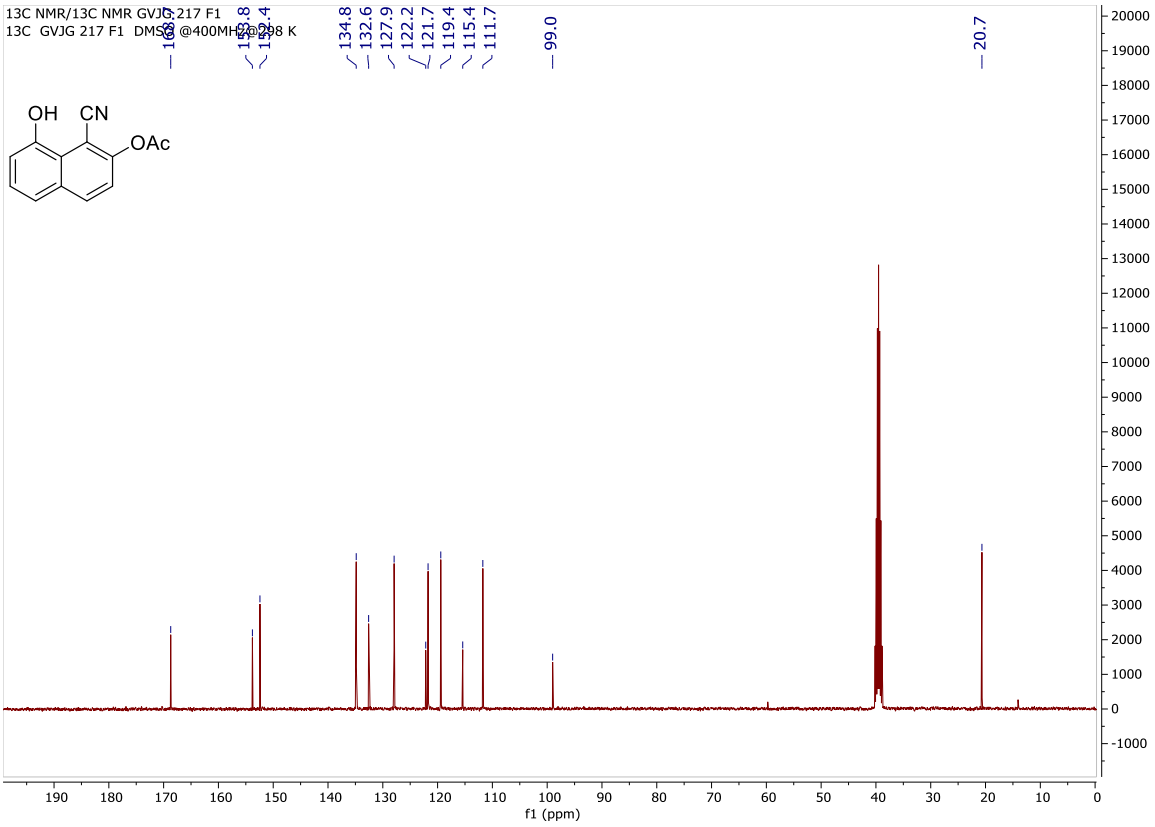

Figure S20. ^{13}C NMR (100.6 MHz, DMSO-d_6) of compound (**16**).

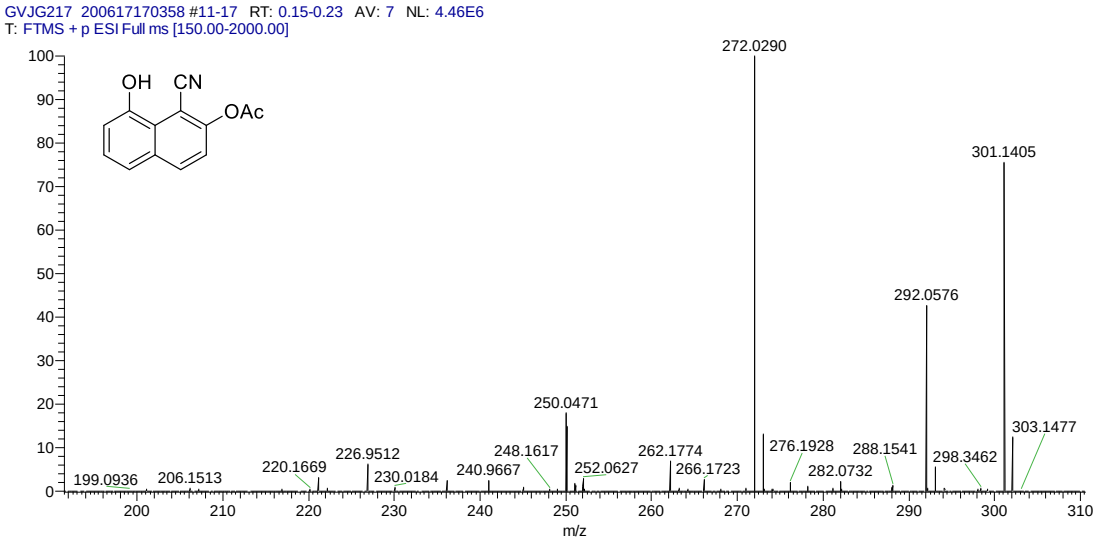

Figure S21. HRMS $[M+H]^+$ of compound (**16**) using 0.1% HCO_2H in MeOH as solvent.

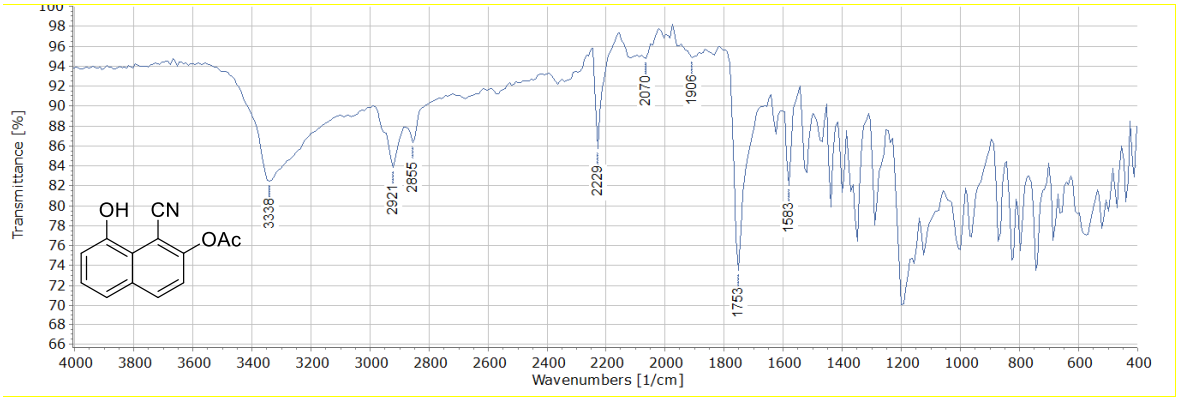

Figure S22. IR spectrum (solid) of compound (**16**).

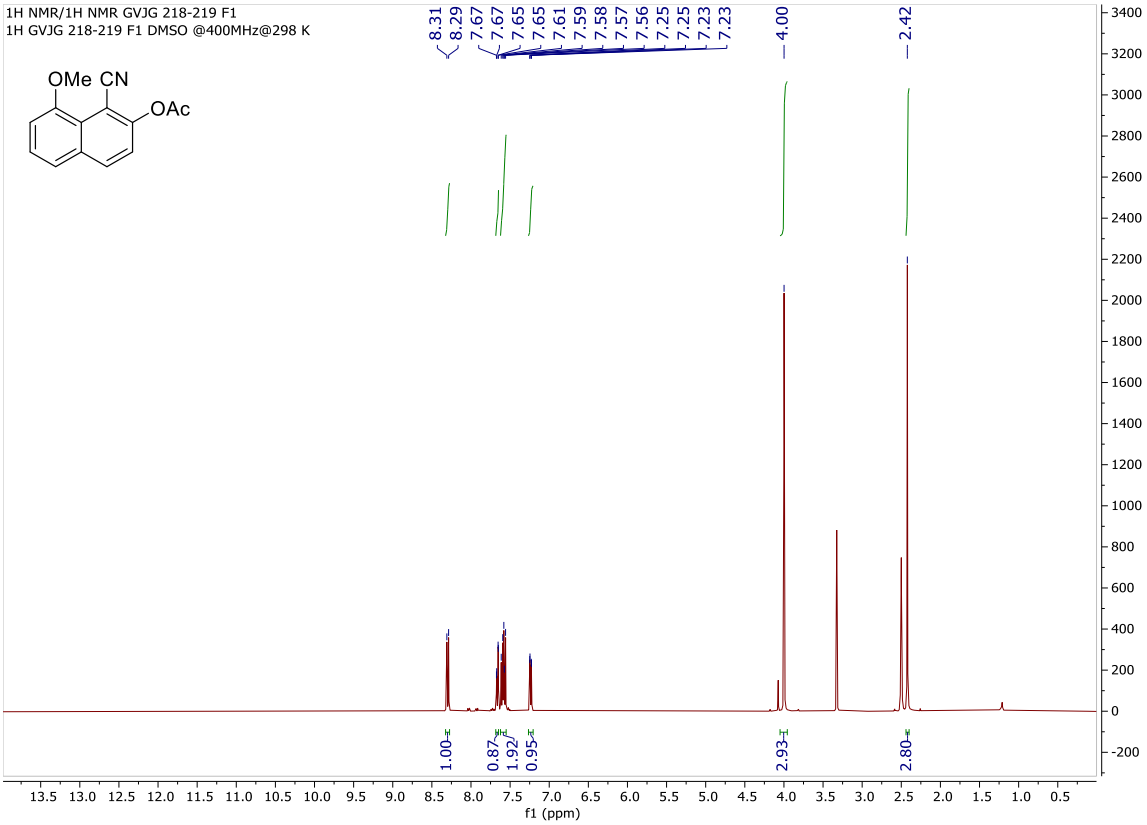

Figure S23. ^{1}H NMR (400 MHz, DMSO-d_6) of (**17**).

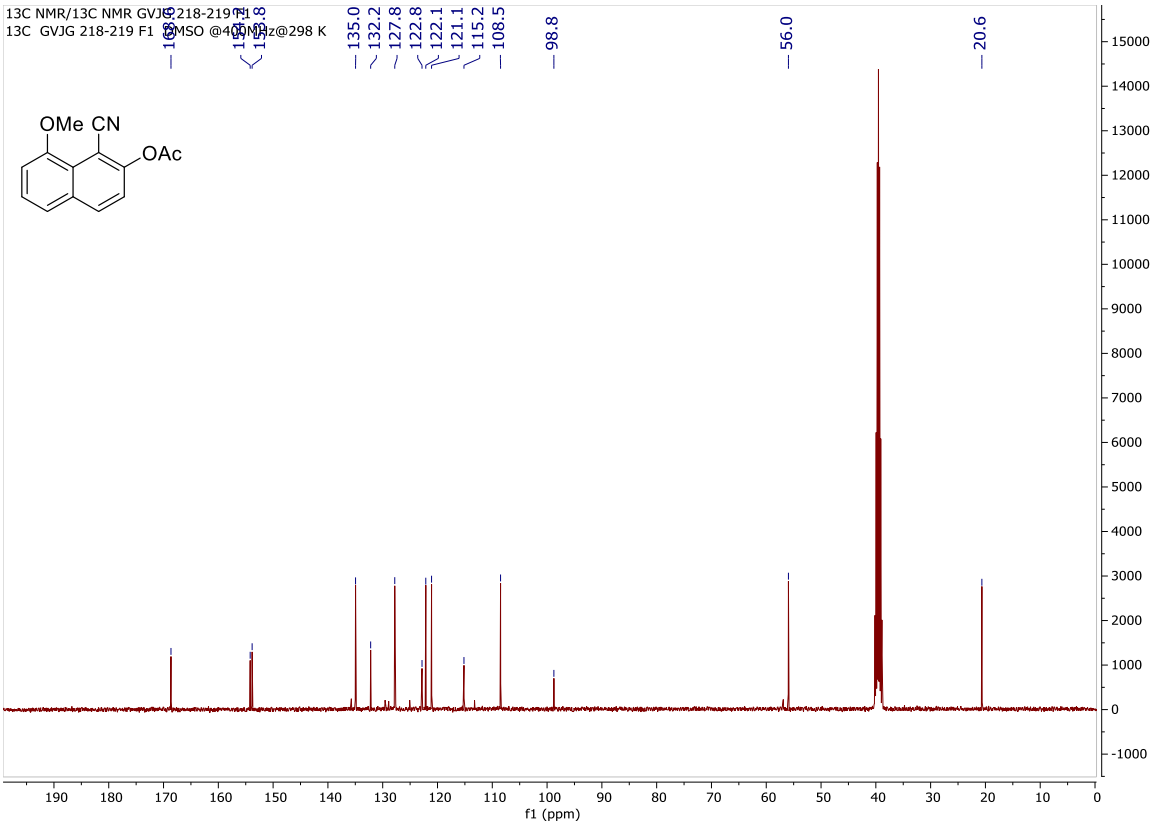

Figure S24. ^{13}C NMR (100.6 MHz, DMSO-d_6) of (**17**).

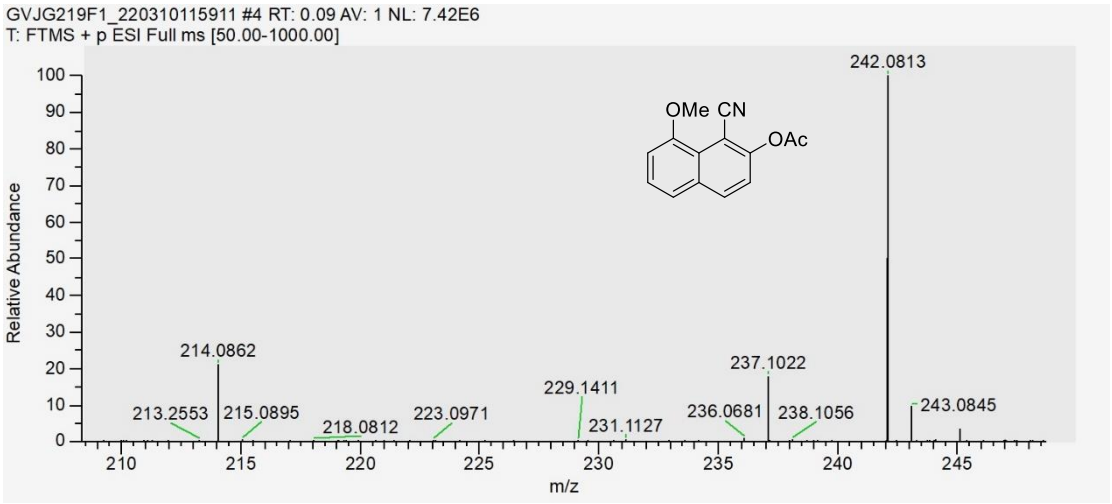

Figure S25. HRMS $[M+H]^+$ of compound (**17**) using 0.1% HCO_2H in MeOH as solvent.

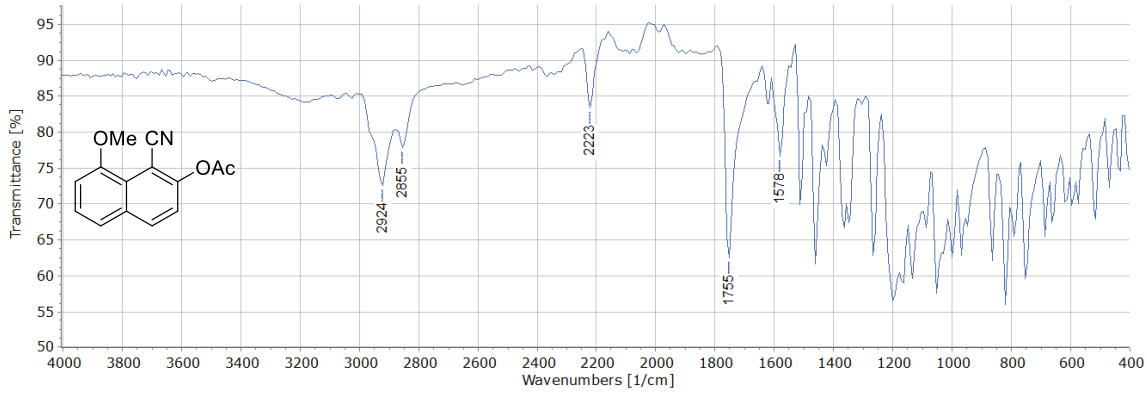

Figure S26. IR spectrum (solid) of (**17**)

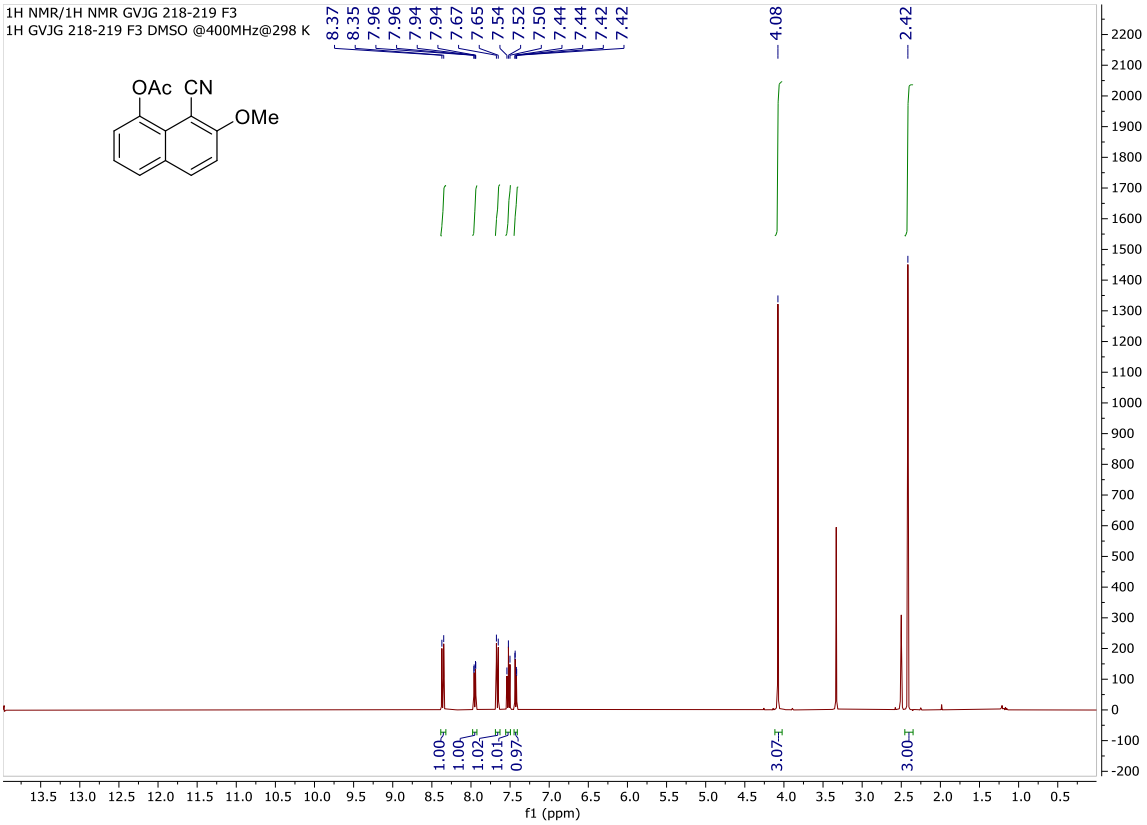

Figure S27. ^{1}H NMR (400 MHz, DMSO-d_6) of (**18**).

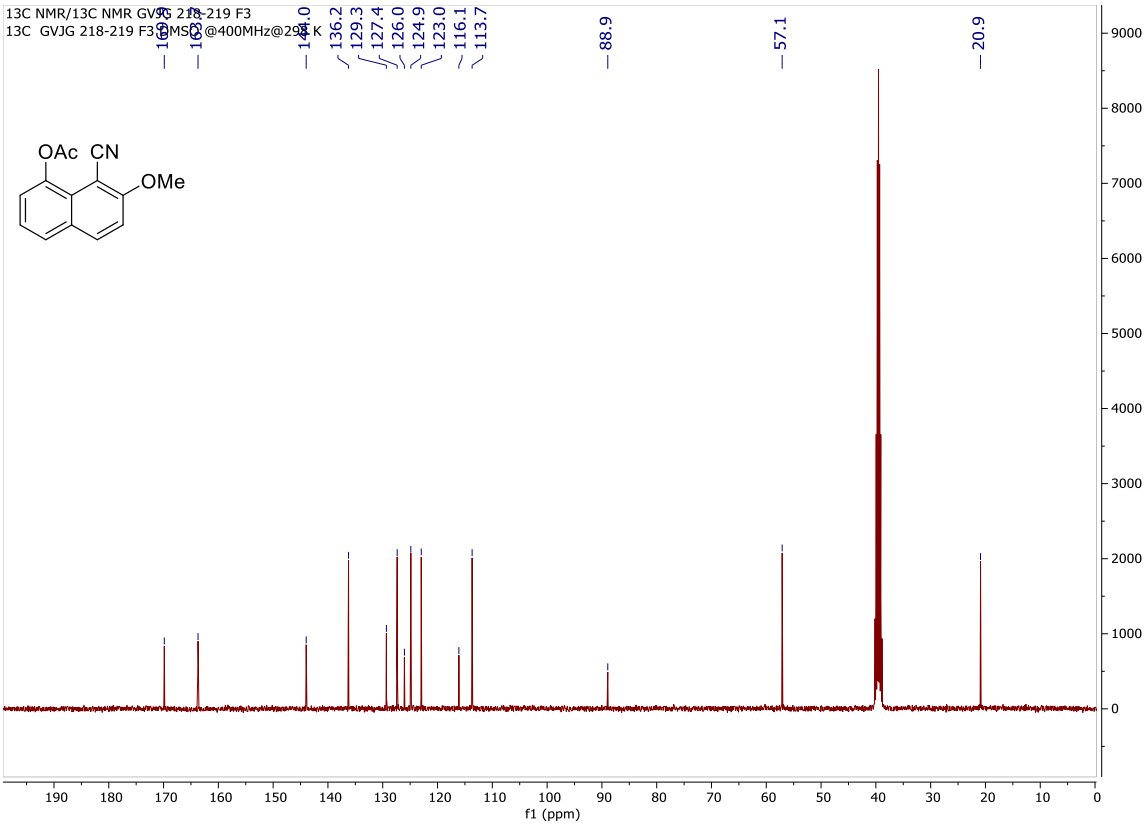

Figure S28. ^{13}C NMR (100.6 MHz, DMSO-d_6) of (**18**).

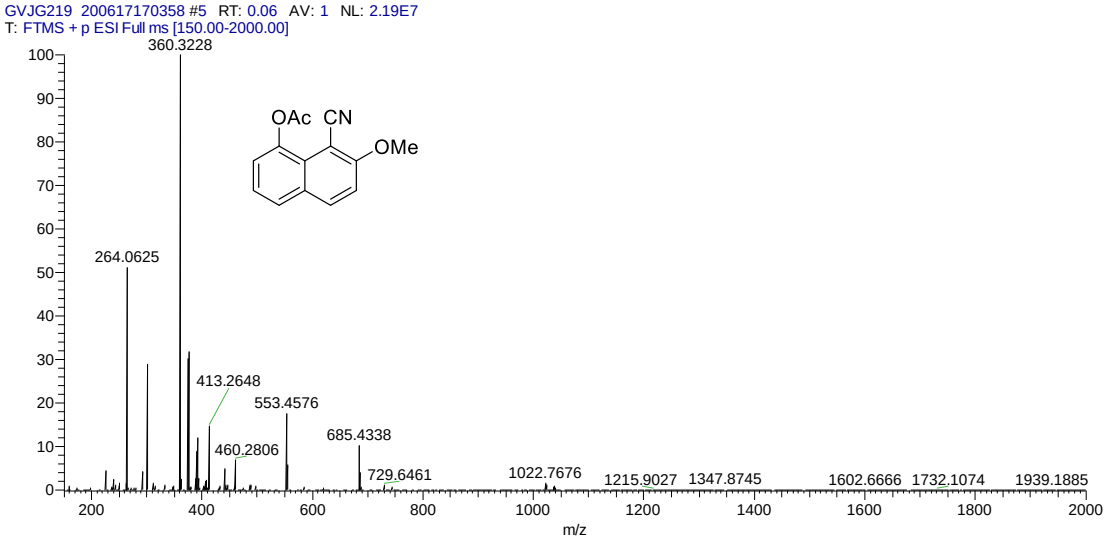

Figure S29. HRMS $[M+H]^+$ of compound (**18**) using 0.1% HCO_2H in MeOH as solvent.

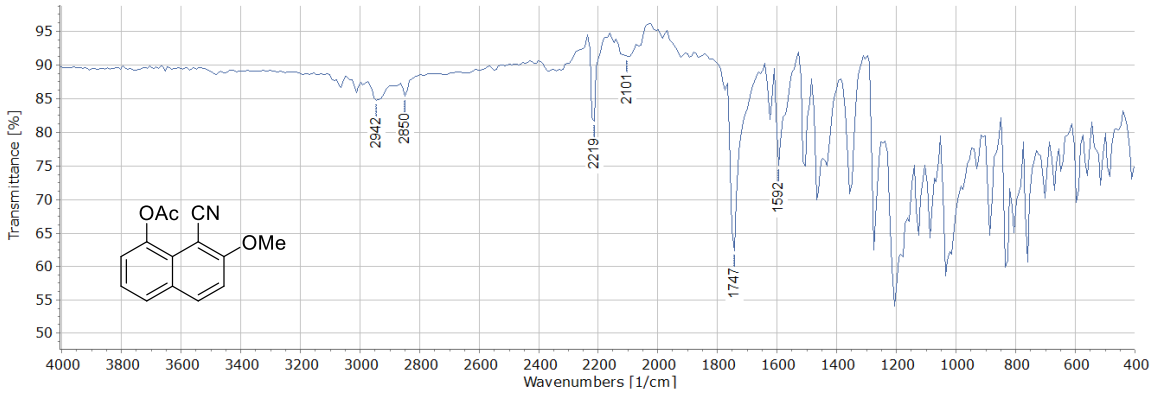

Figure S30. IR spectrum (solid) of (**18**).

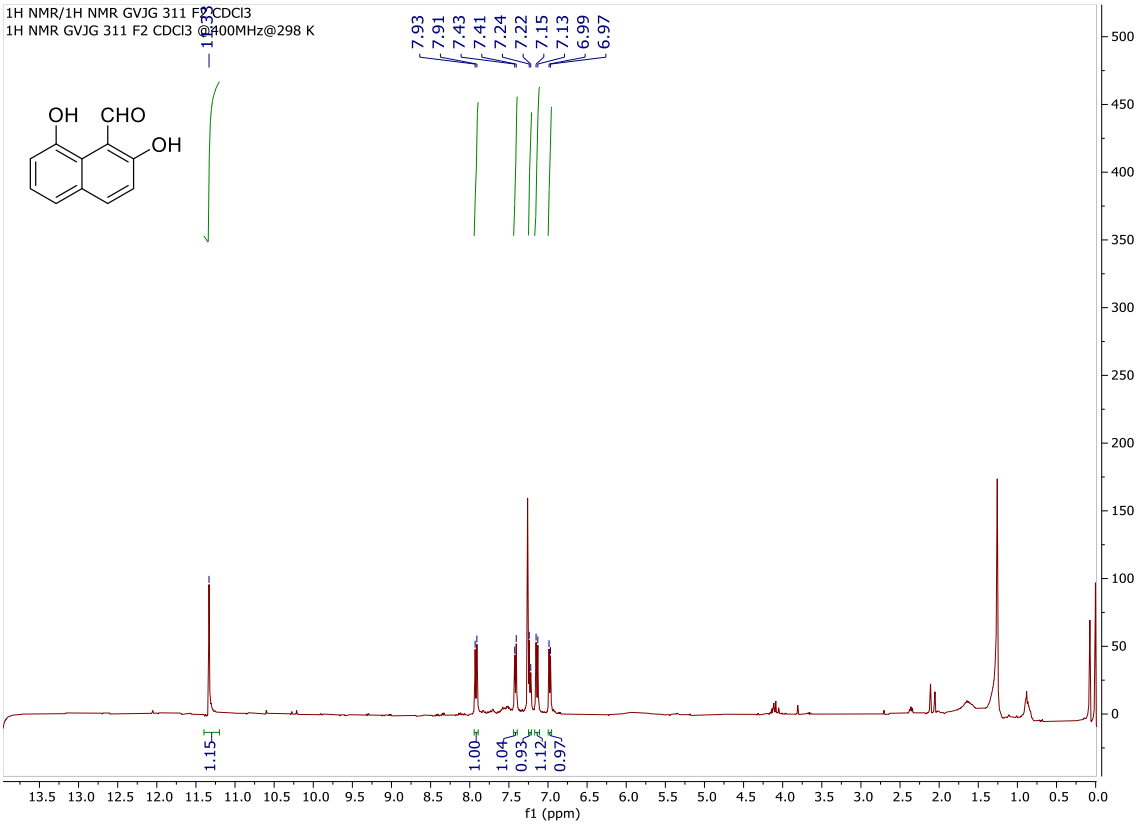

Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of (**19**).

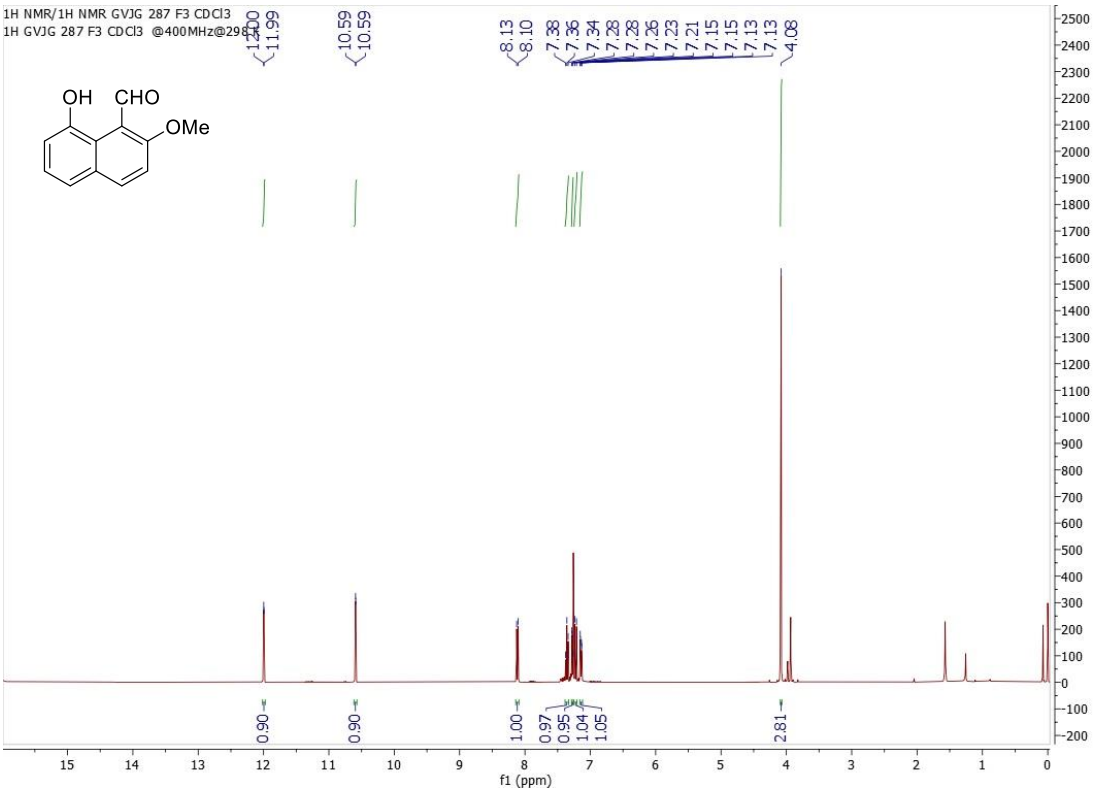

Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) of (**20**).

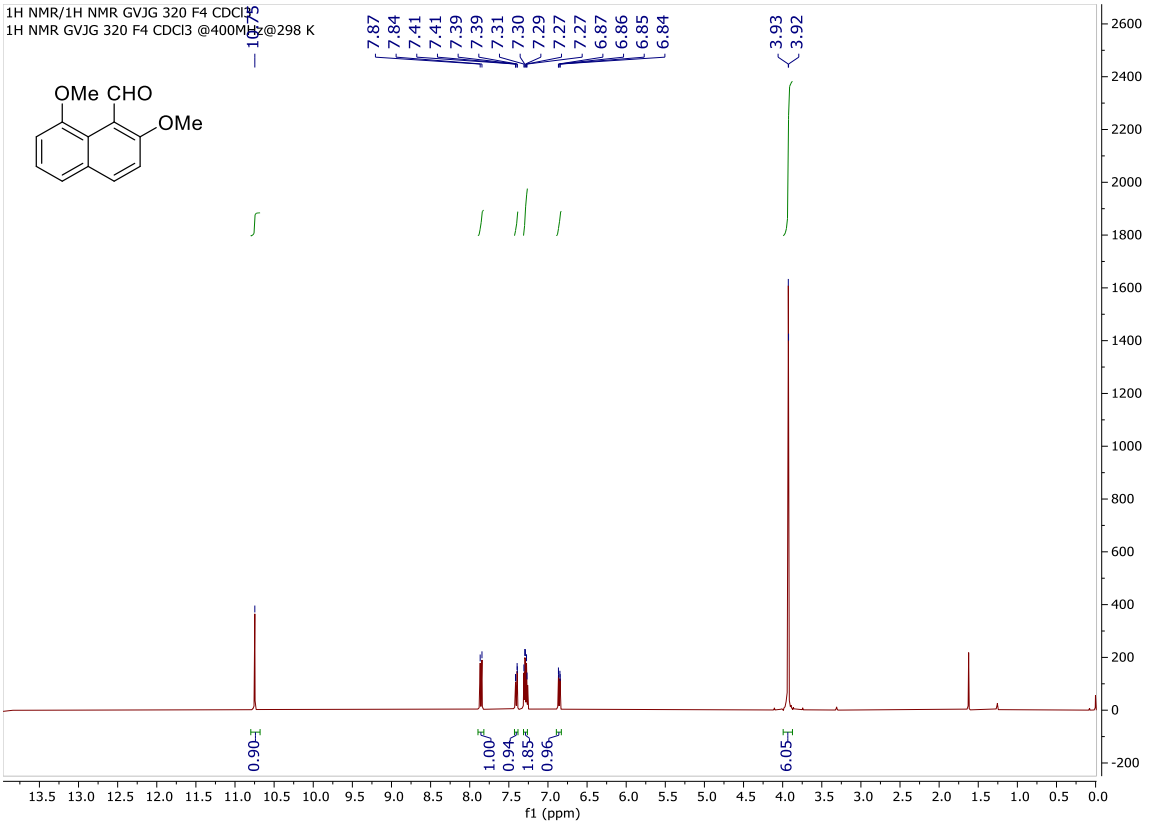

Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of (**21**).

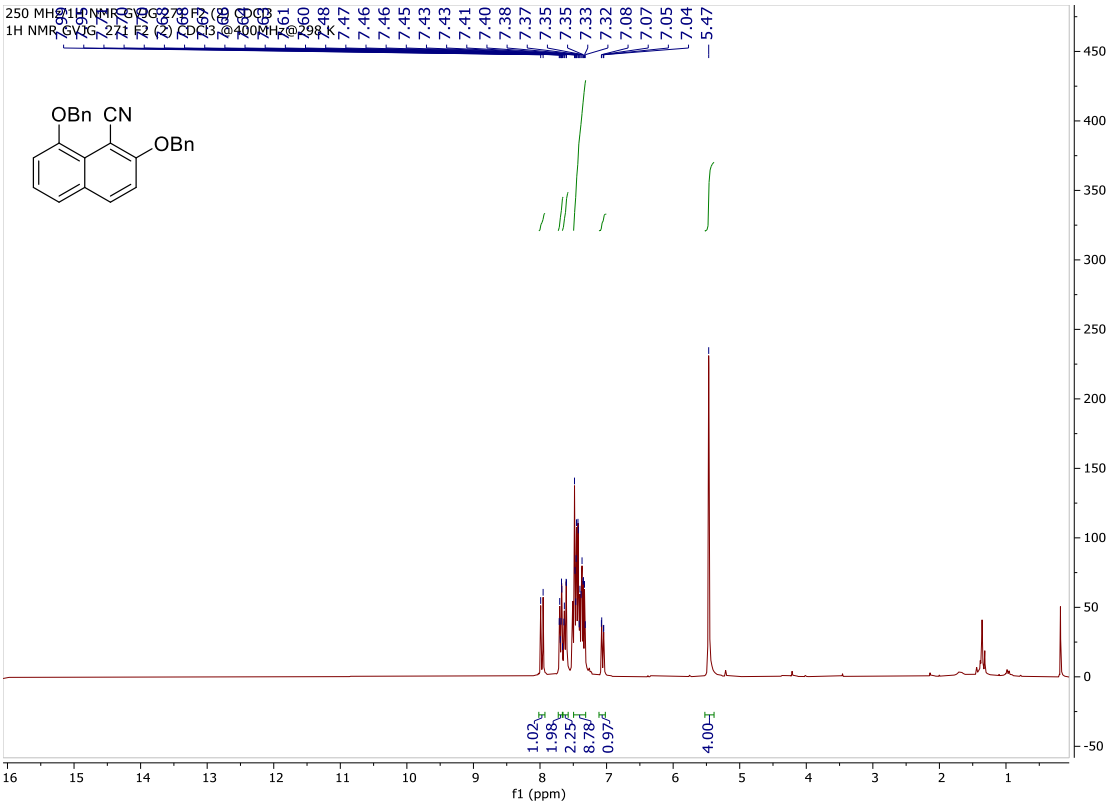

Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) of (**22**).

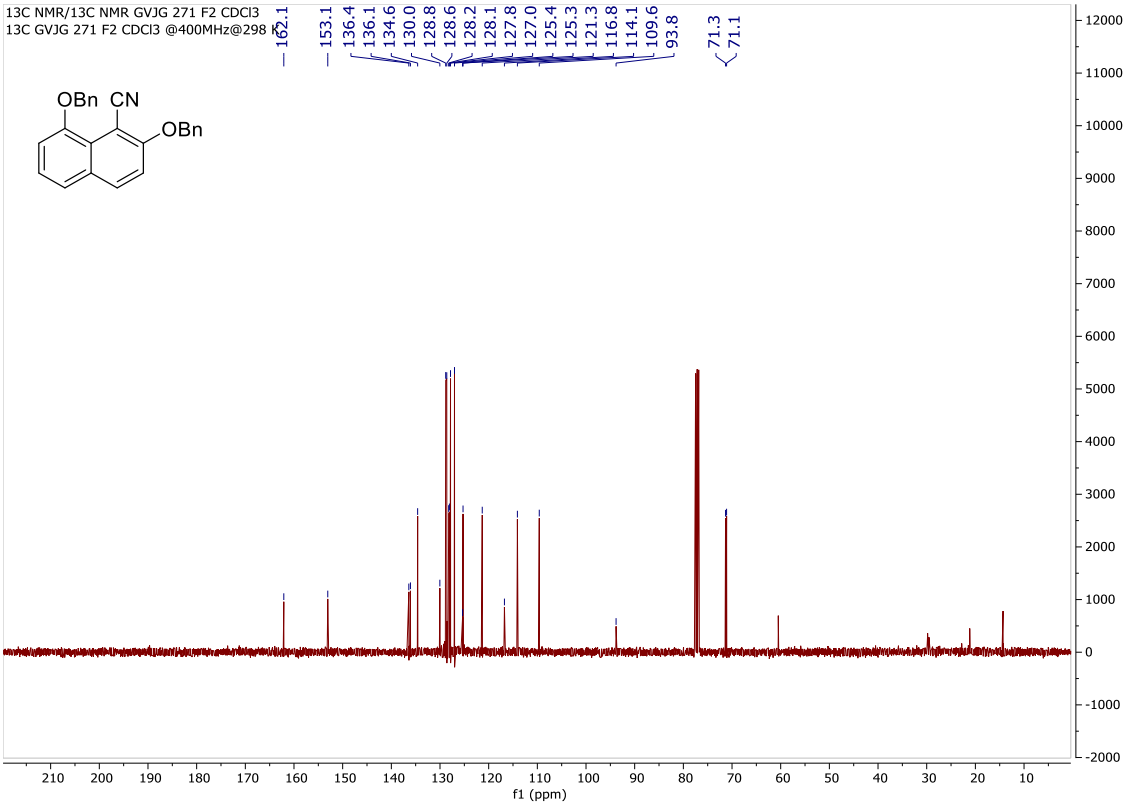

Figure S35. ^{13}C NMR (100.6 MHz, $CDCl_3$) of (**22**).

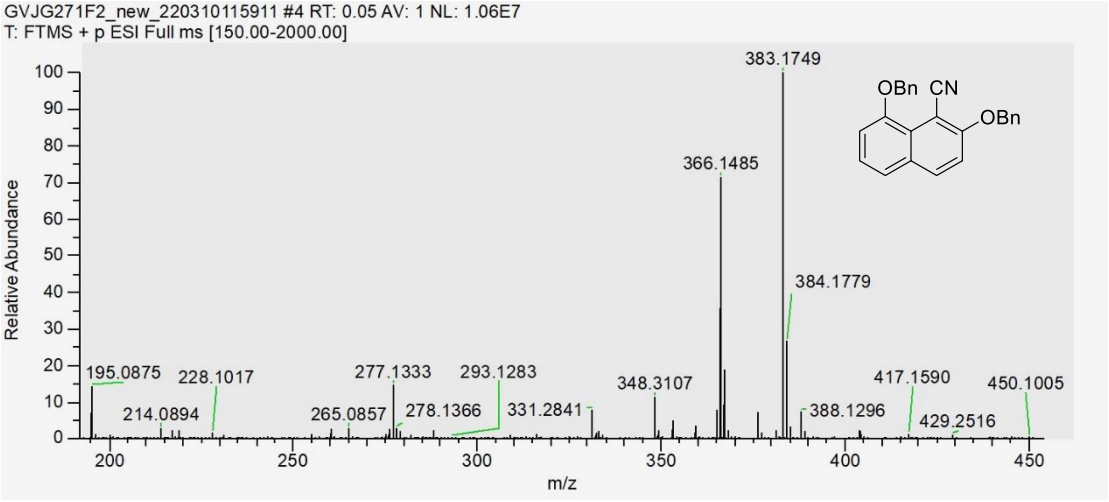

Figure S36. HRMS $[M+H]^+$ of compound (**22**) using 0.1% HCO_2H in MeOH as solvent.

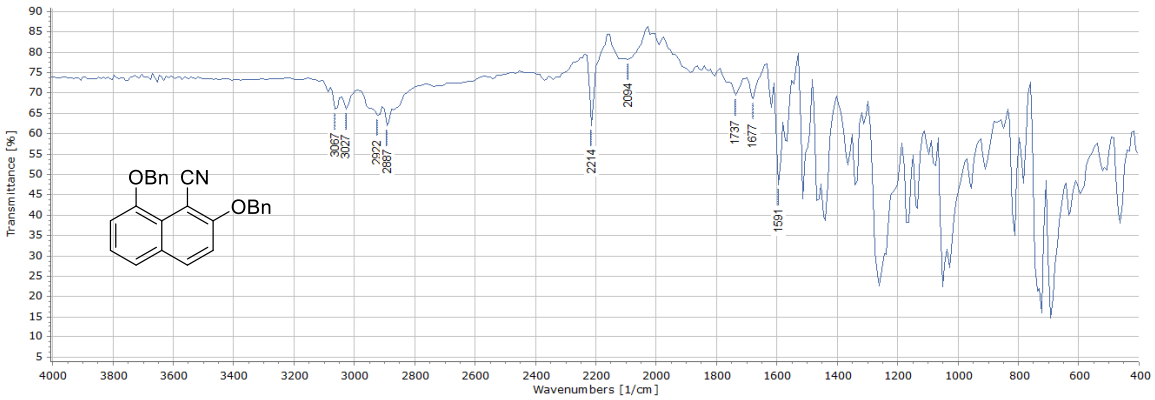

Figure S37. IR spectrum (solid) of (**22**).

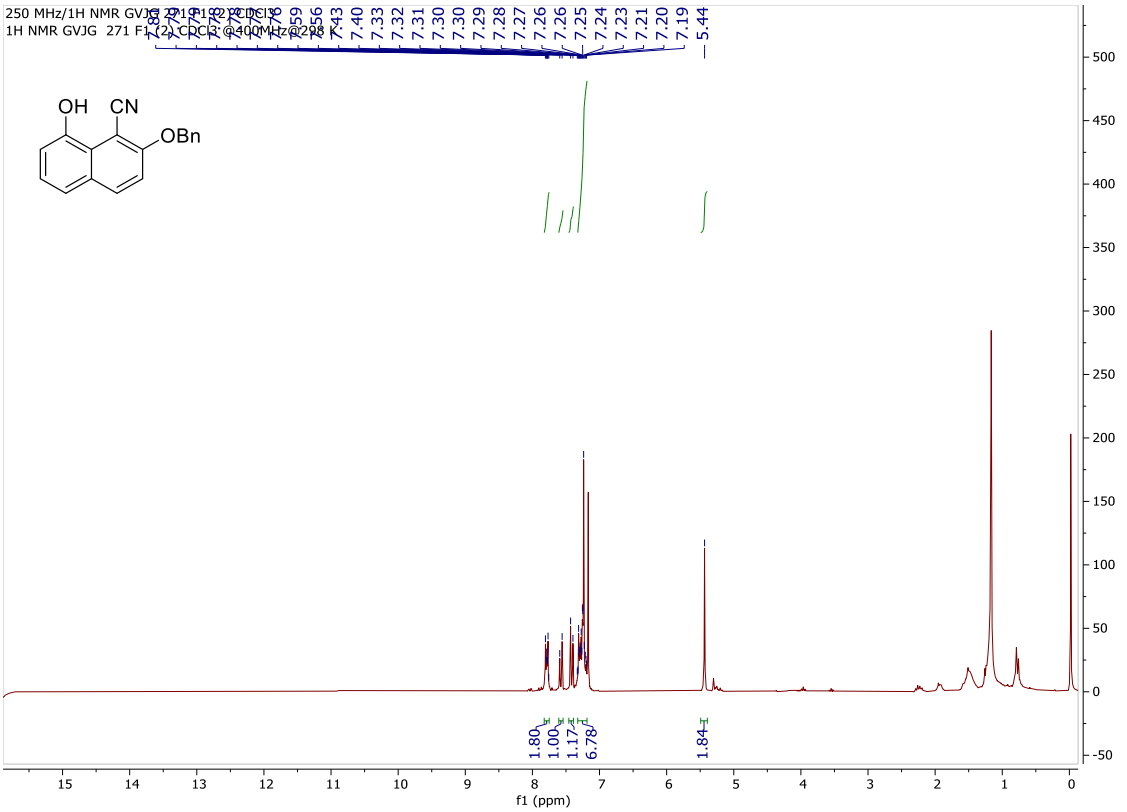

Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) of (**23**).

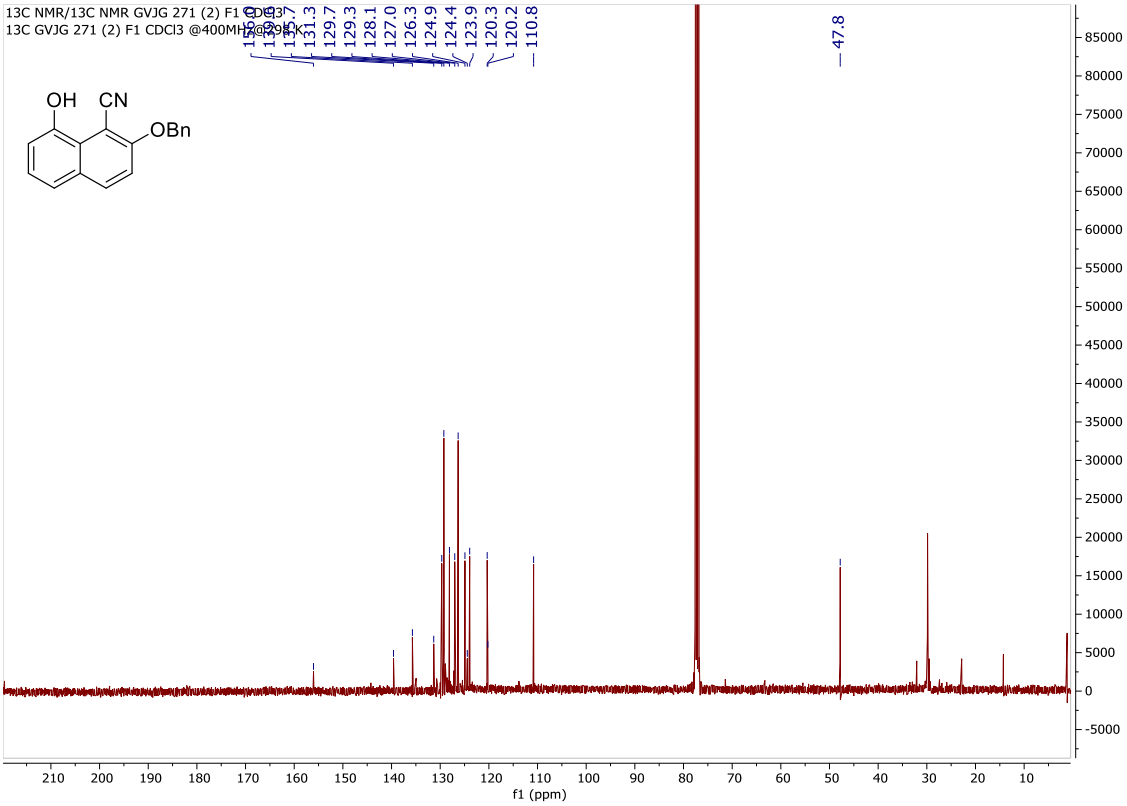

Figure S39. ^{13}C NMR (100.6 MHz, $CDCl_3$) of (**23**).

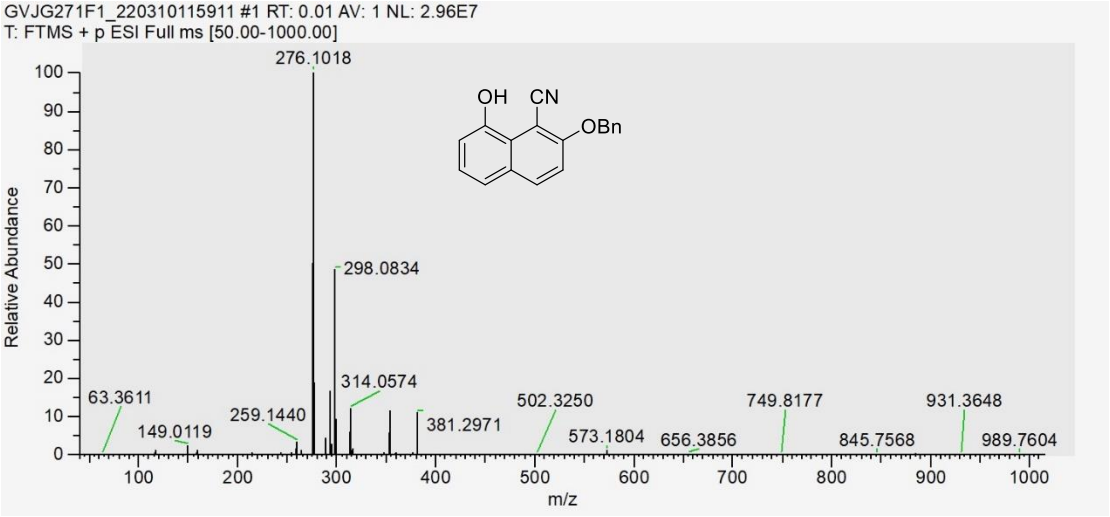

Figure S40. HRMS $[M+H]^+$ of compound (**23**) using 0.1% HCO_2H in MeOH as solvent.

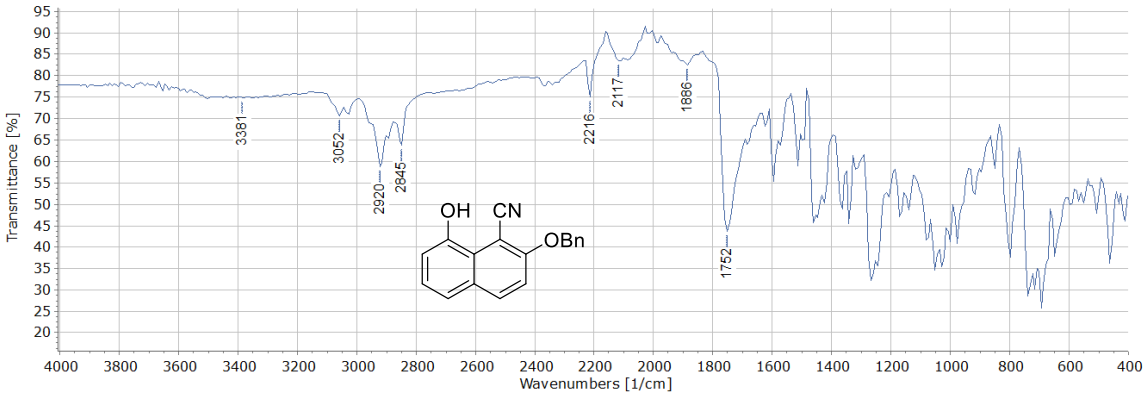

Figure S41. IR spectrum (solid) of (**23**).

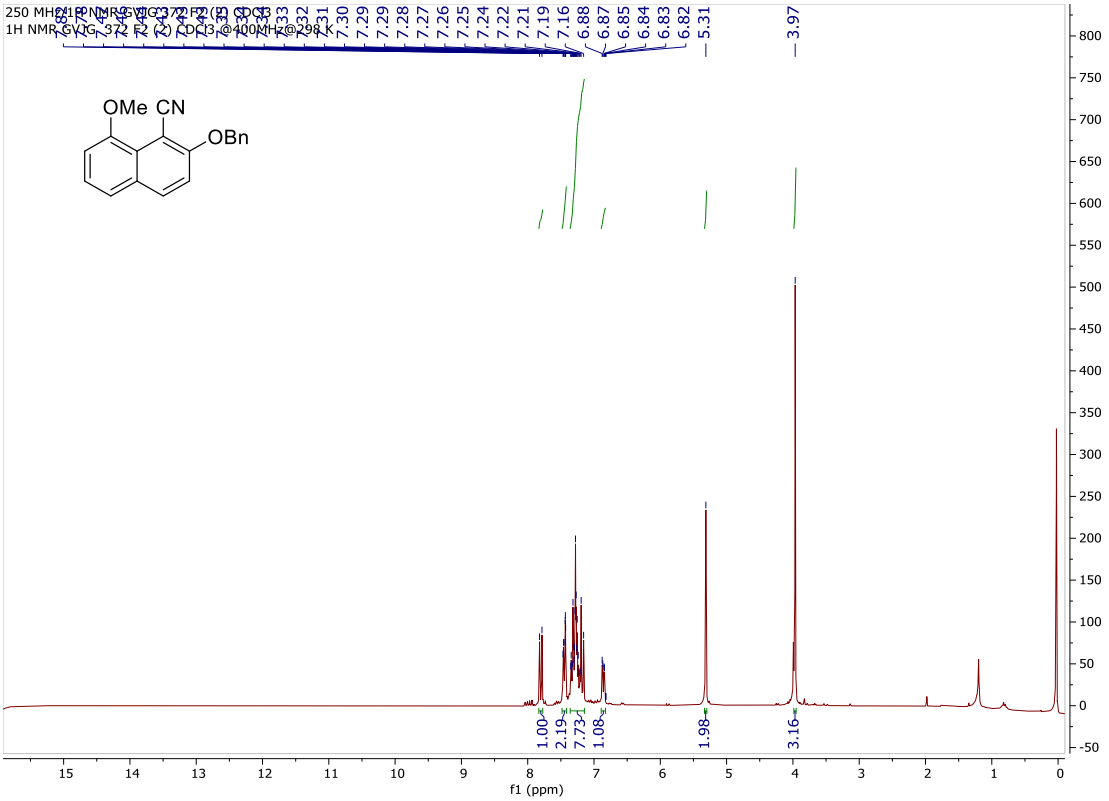

Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) of (**24**).

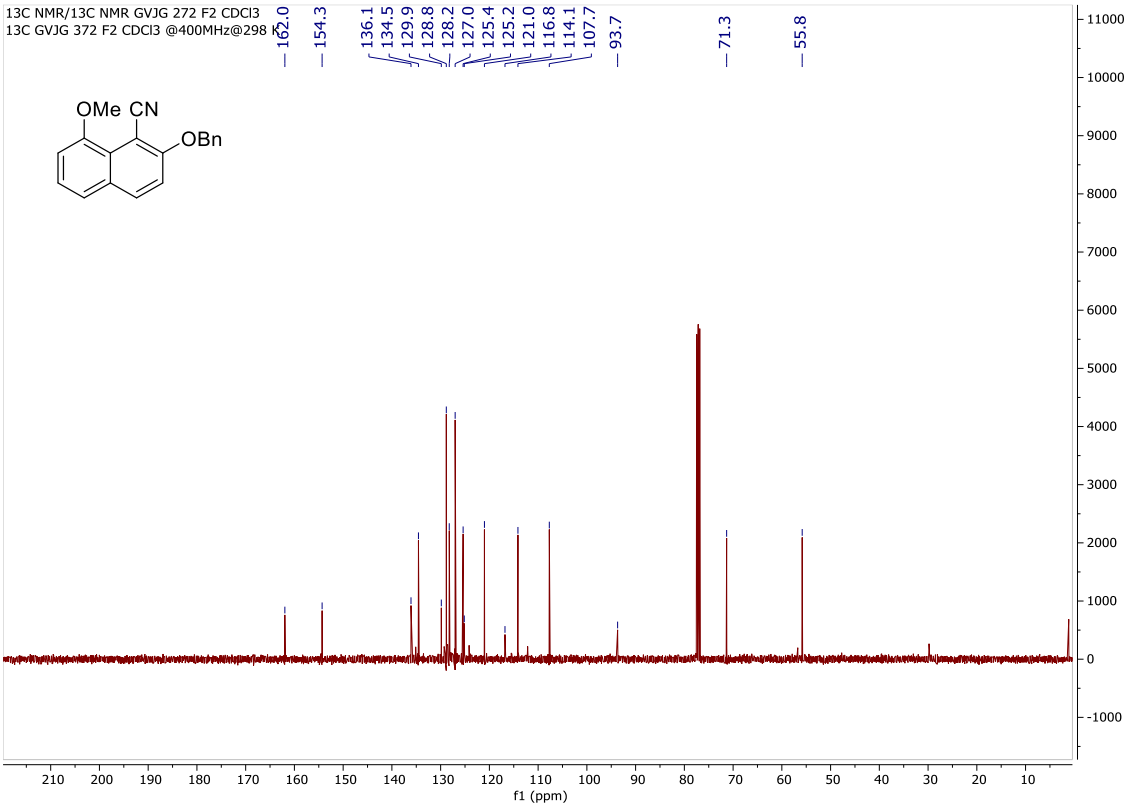

Figure S43. ^{13}C NMR (100.6 MHz, $CDCl_3$) of (**24**).

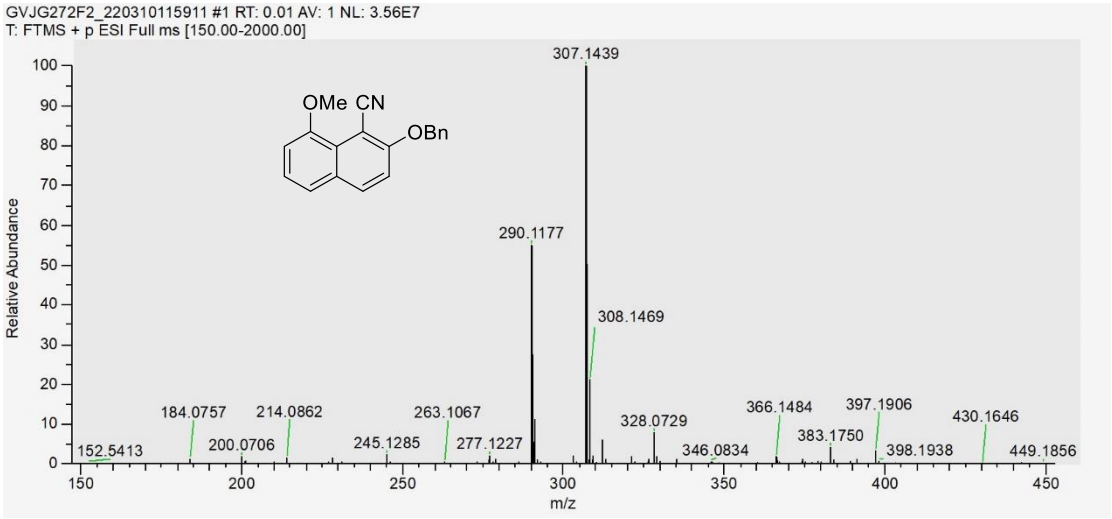

Figure S44. HRMS $[M+H]^+$ of compound (**24**) using 0.1% HCO_2H in MeOH as solvent.

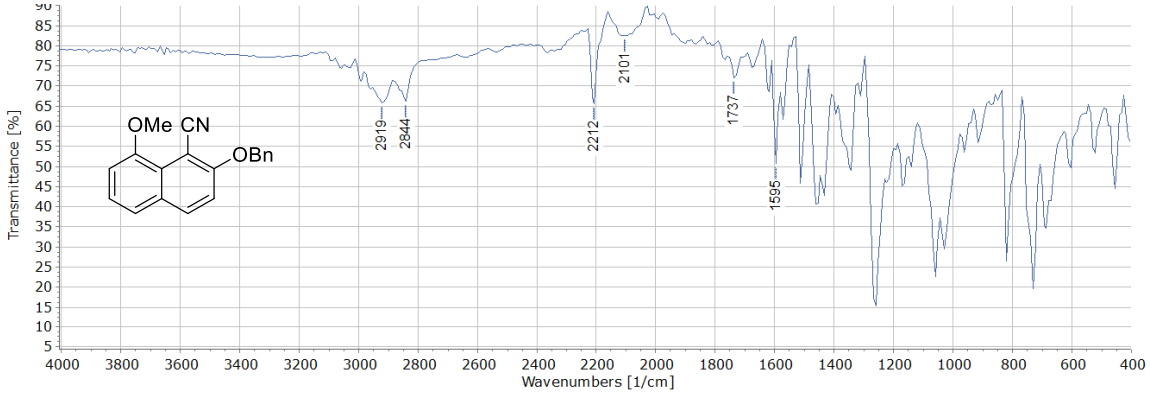

Figure S45. IR spectrum (solid state) of (**24**).

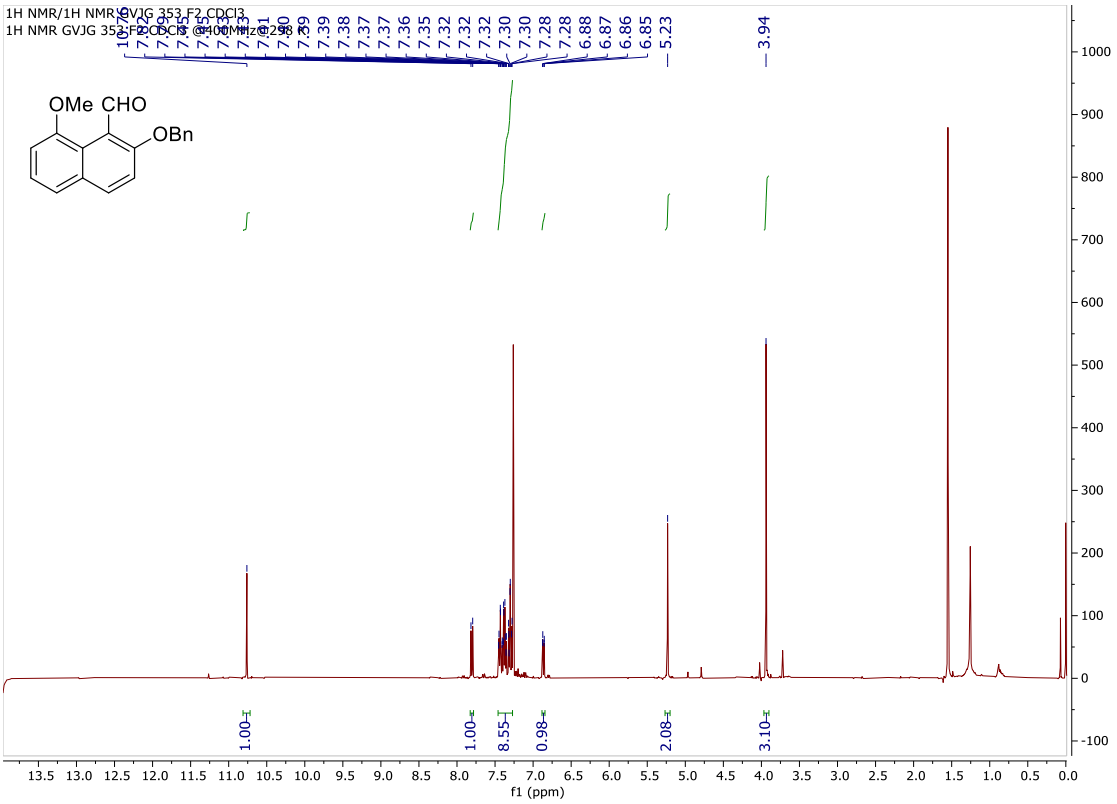

Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) of (**25**).

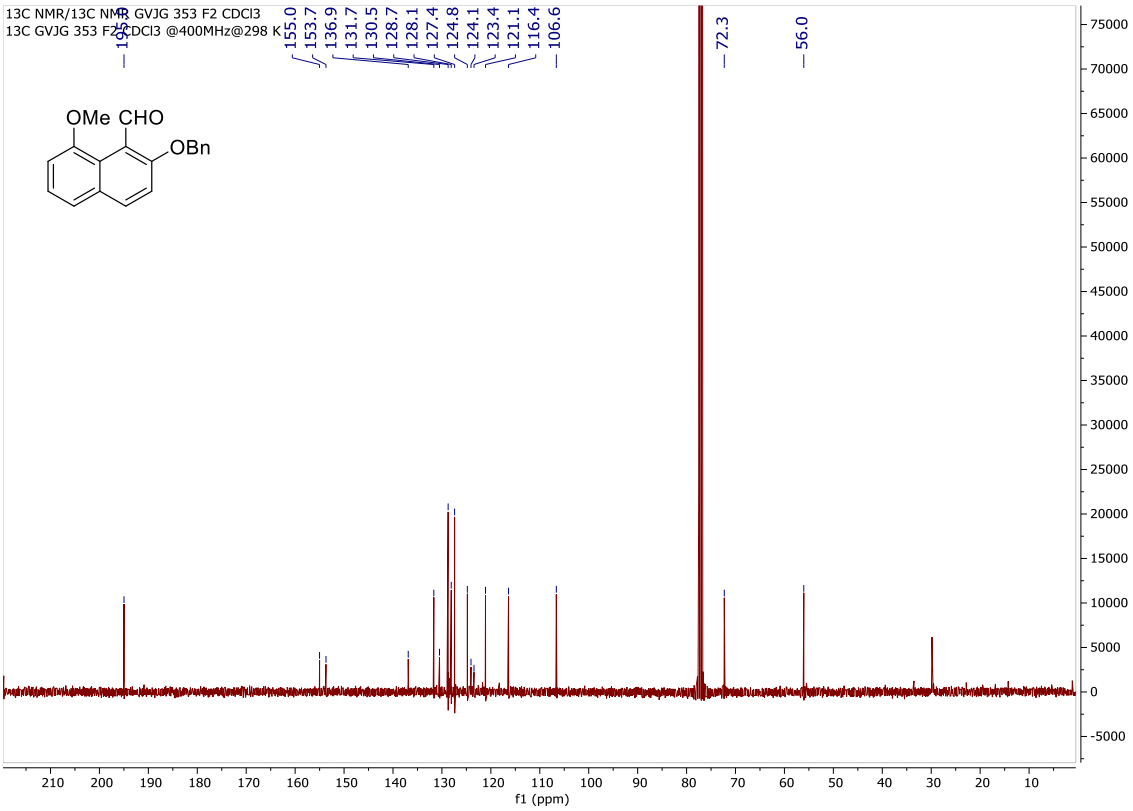

Figure S47. ^{13}C NMR [100.6 MHz, $CDCl_3$] of (**25**).

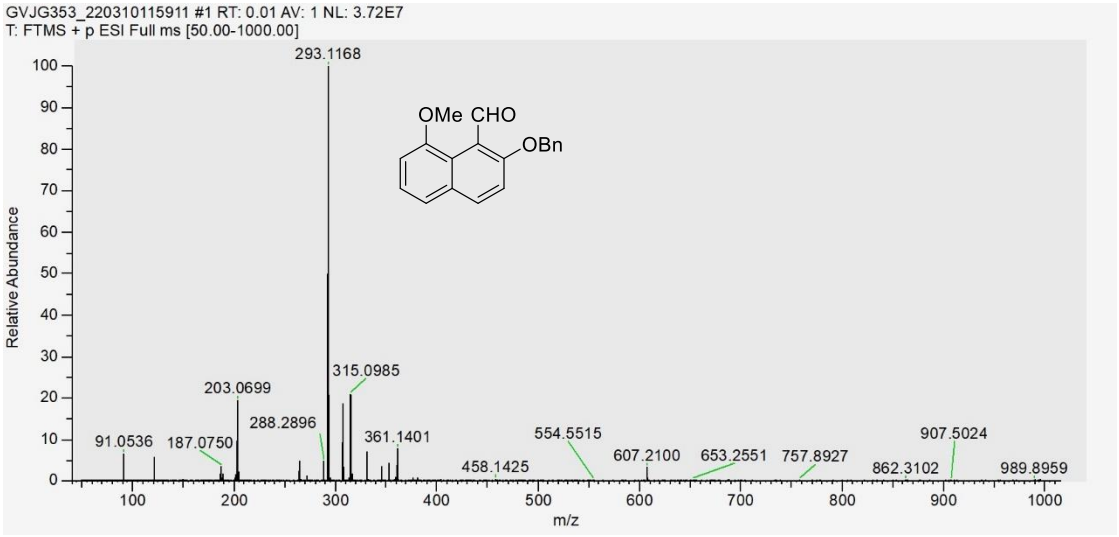

Figure S48. HRMS $[M+H]^+$ of compound (**25**) using 0.1% HCO_2H in MeOH as solvent.

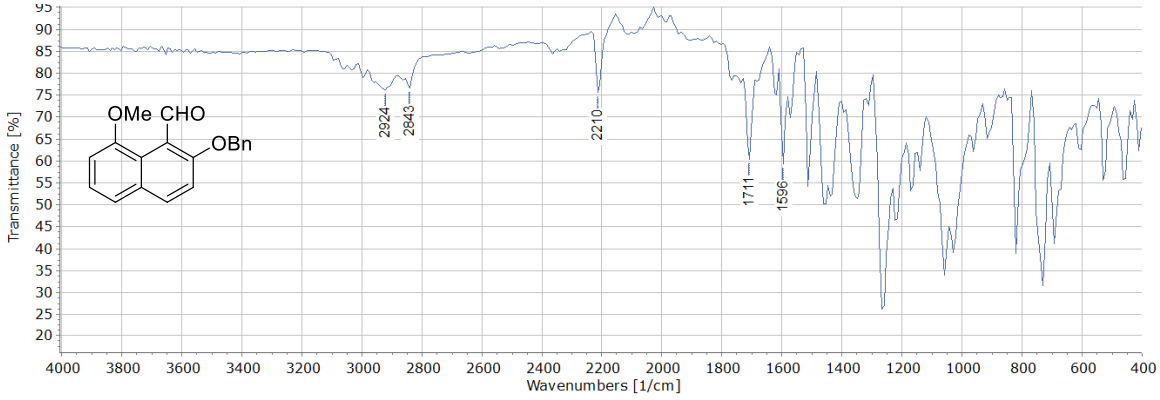

Figure S49. IR spectrum (solid state) of (**25**).

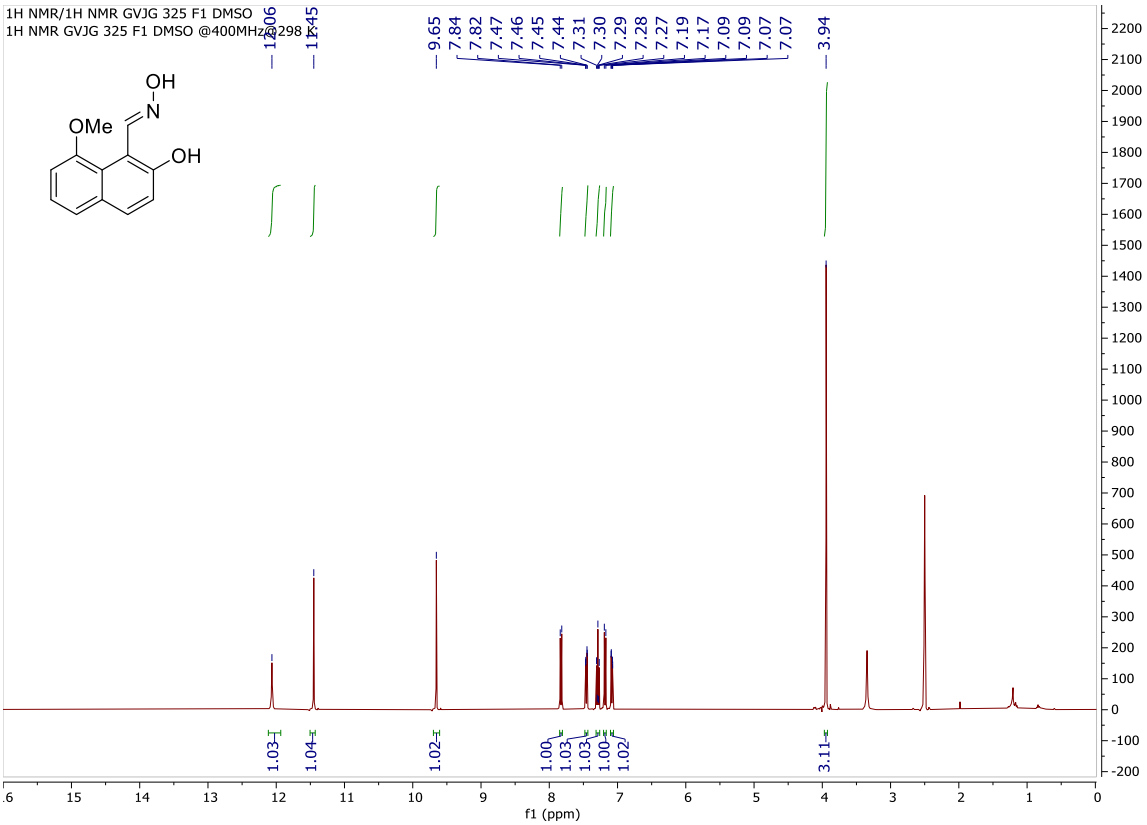

Figure S50. ^{1}H NMR (400 MHz, DMSO-d_6) of (**6**).

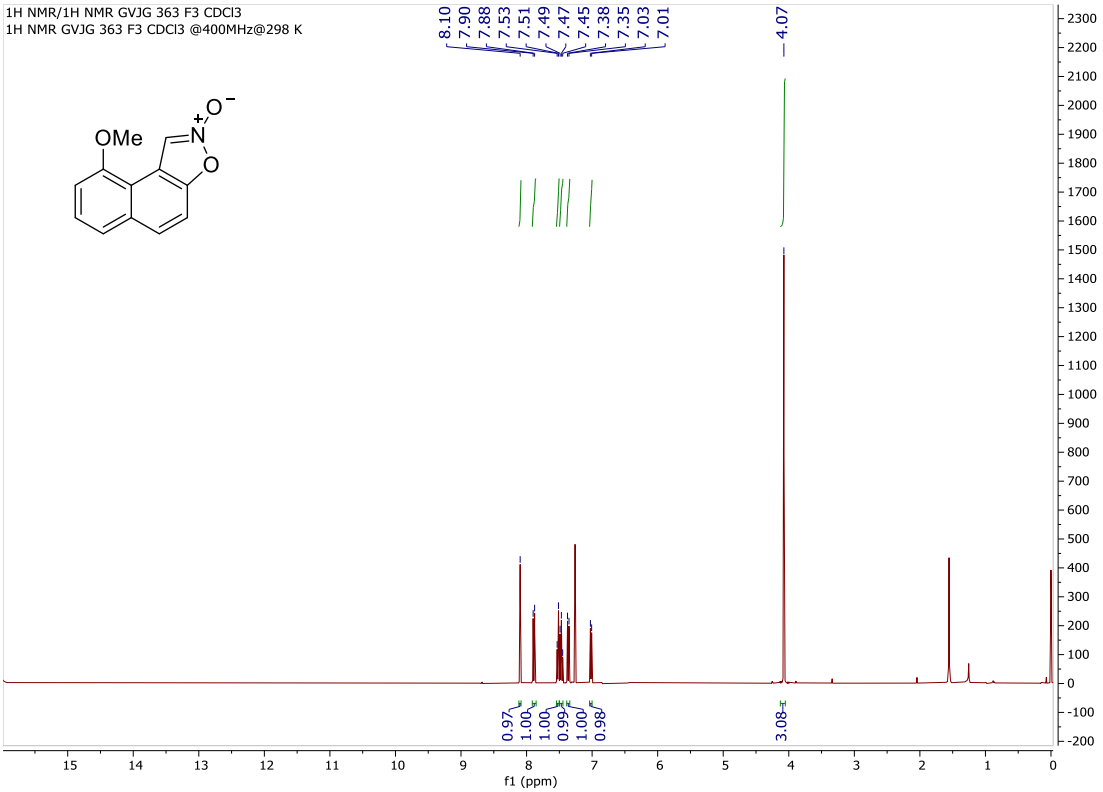

Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) of (**8**).

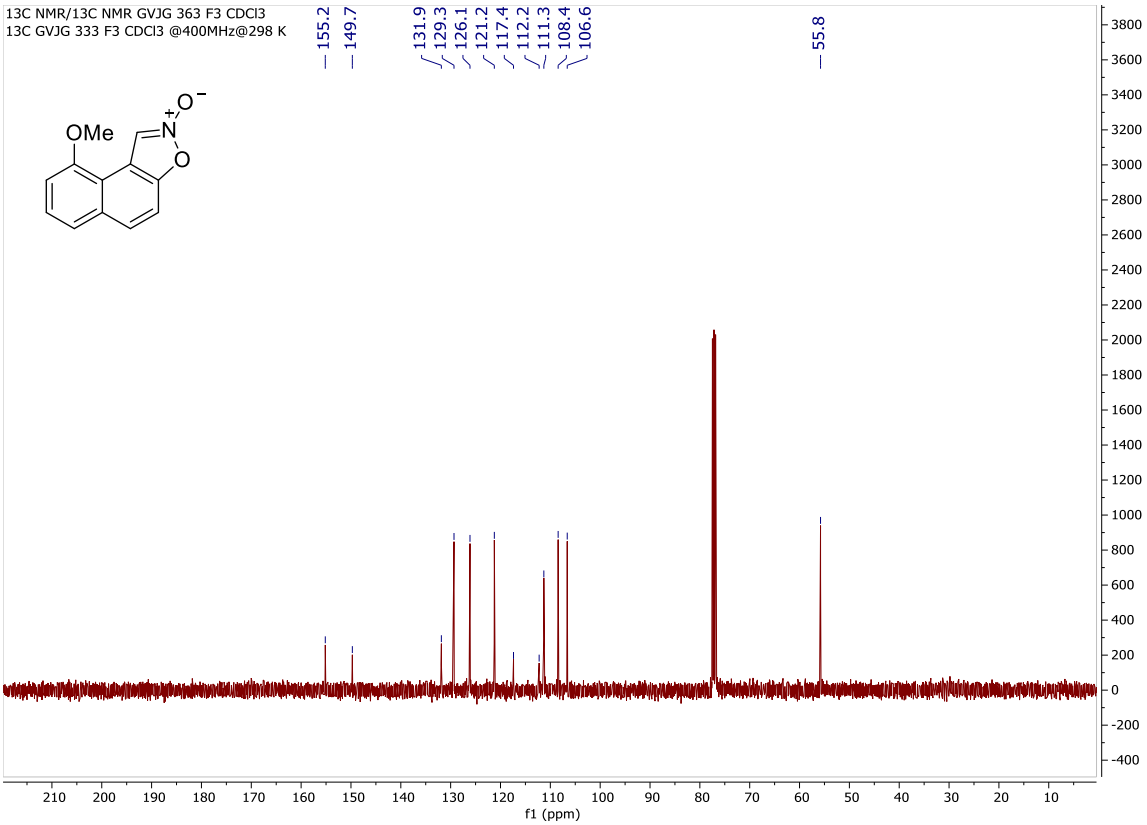

Figure S52. ^{13}C NMR [100.6 MHz, $CDCl_3$] of (**8**).

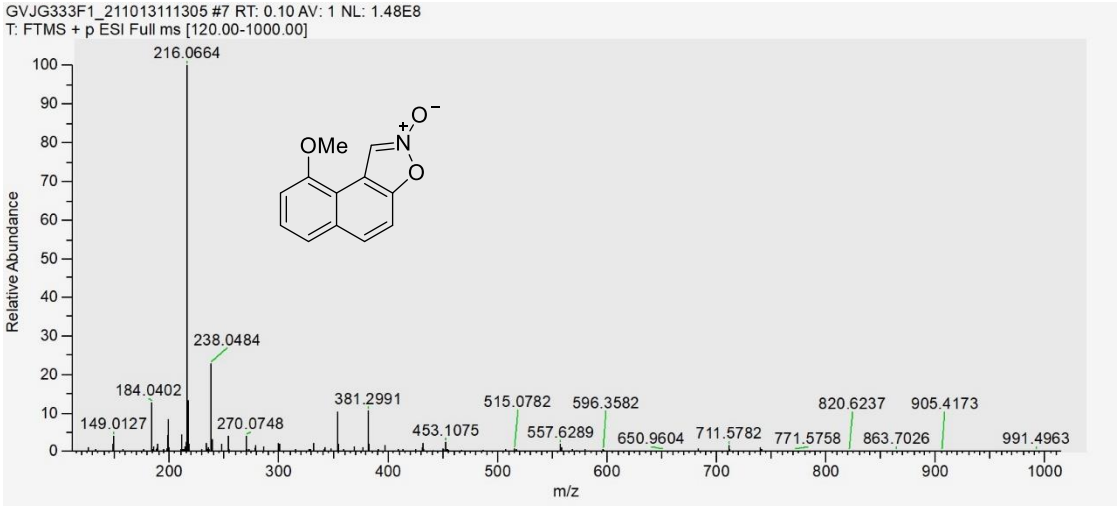

Figure S53. HRMS $[M+H]^+$ of compound (**8**) using 0.1% HCO_2H in MeOH as solvent.

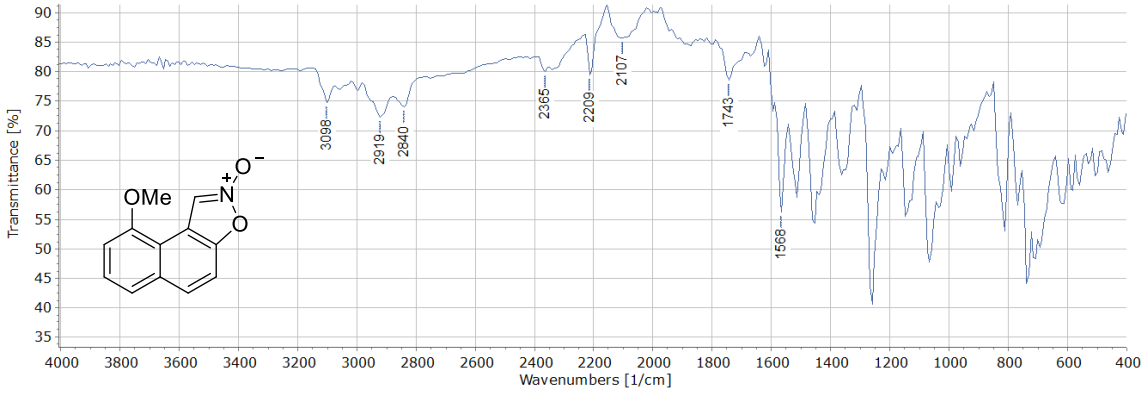

Figure S54. IR spectrum of (**8**).

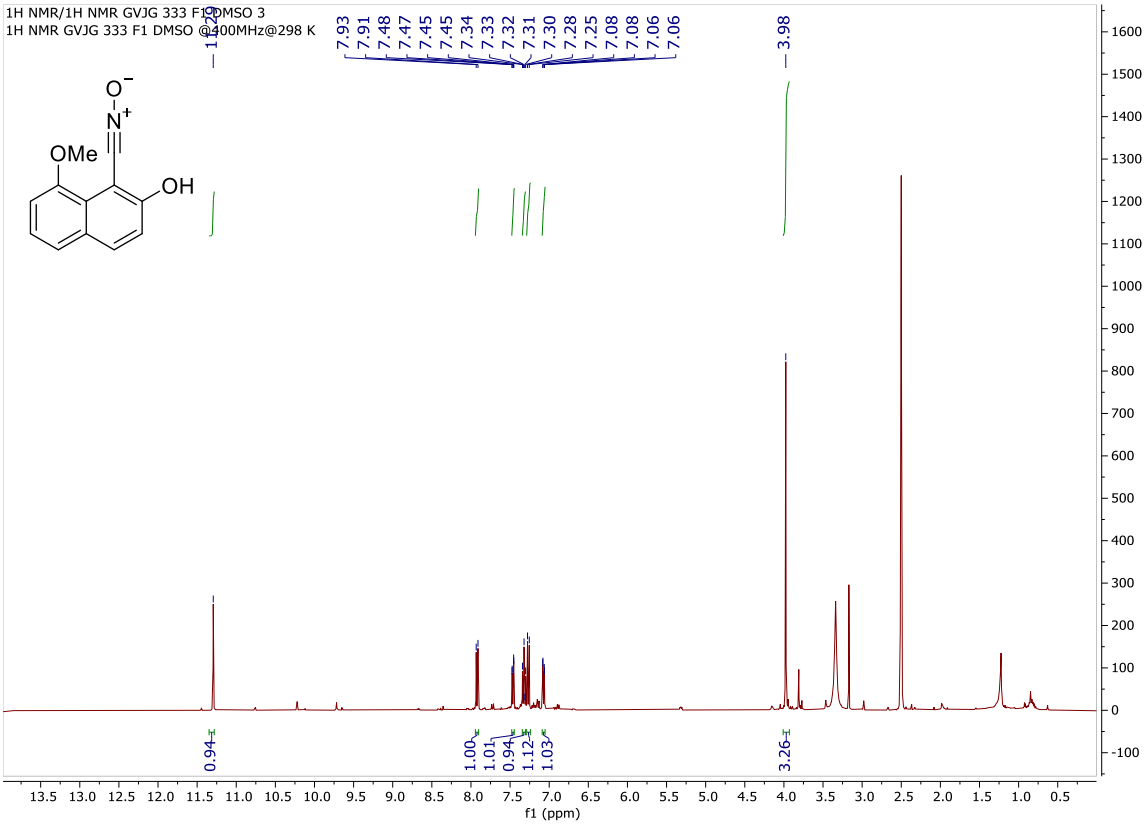

Figure S55. ^{1}H NMR (400 MHz, DMSO-d_6) of (**9**).

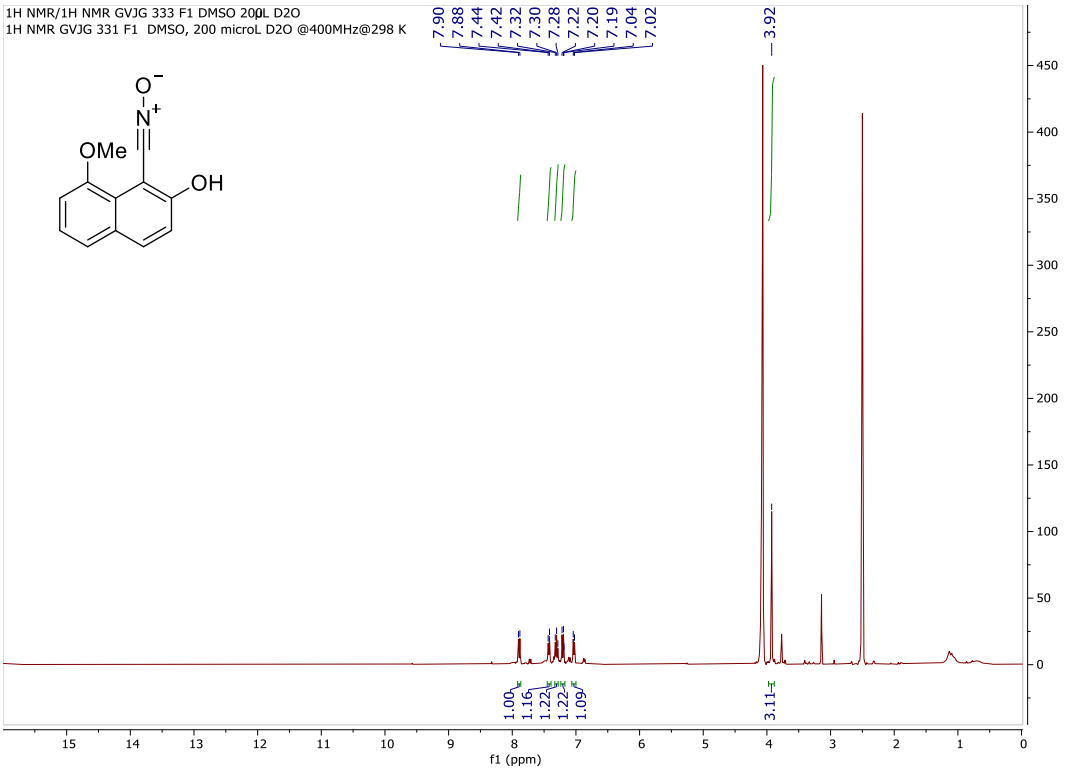

Figure S56. ^{1}H NMR (400 MHz, DMSO-d_6 + D_2O) of (**9**).

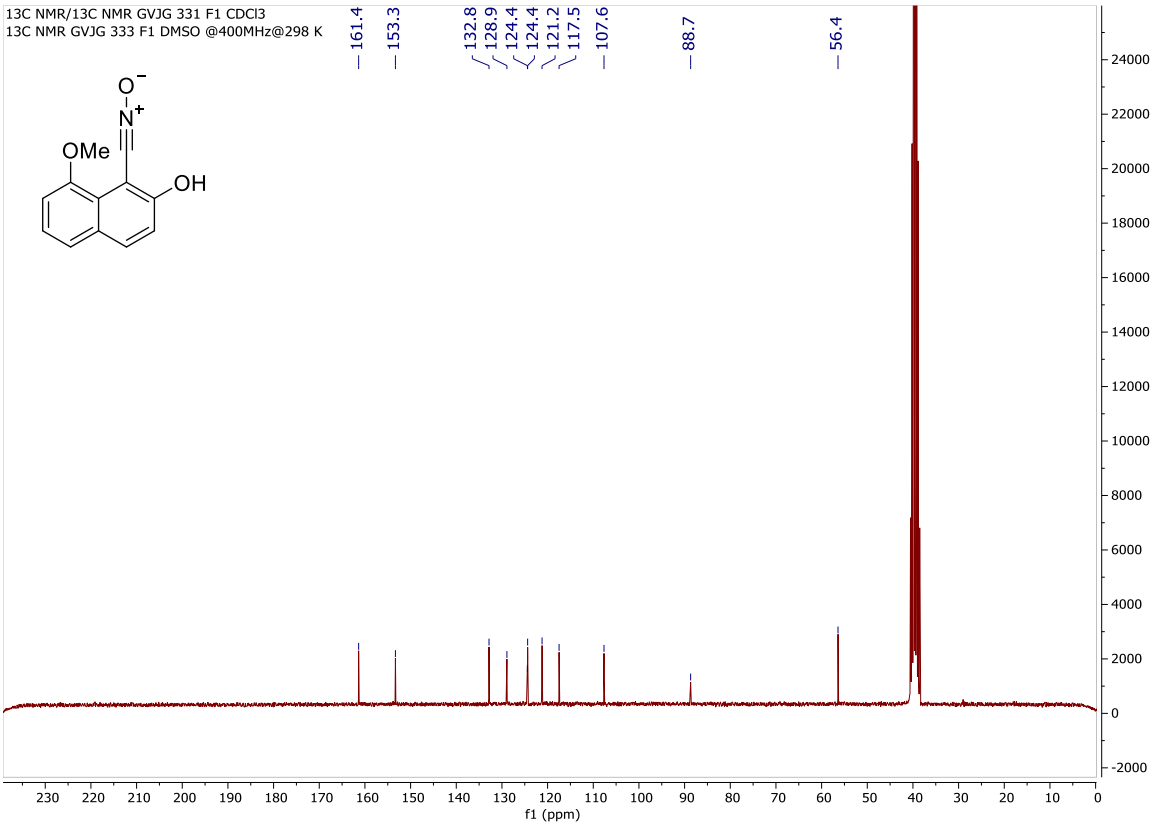

Figure S57. ^{13}C NMR [100.6 MHz, DMSO-d_6] of (**9**).

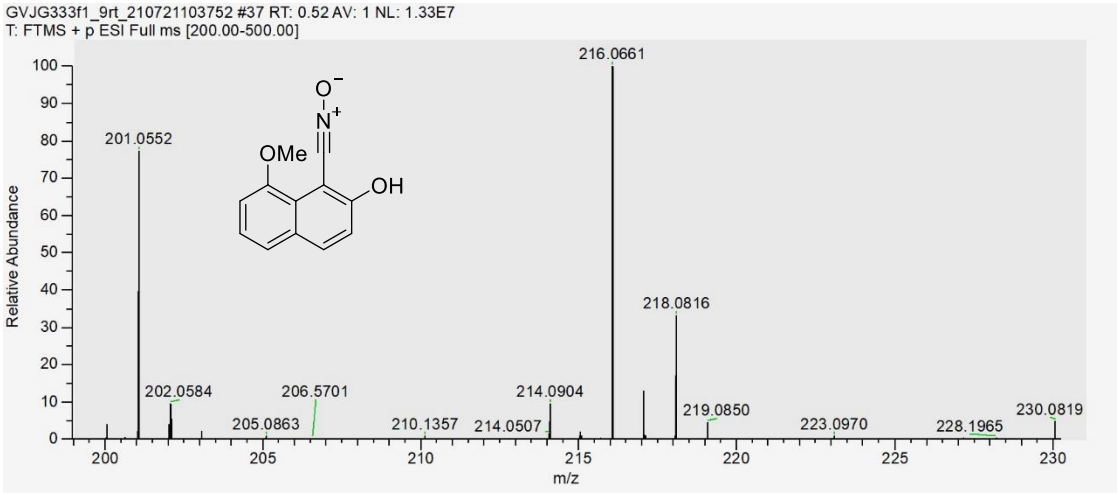

Figure S58. HRMS $[M+H]^+$ of compound (**9**) in DMSO-d_6 using 0.1% HCO_2H in MeOH as solvent.

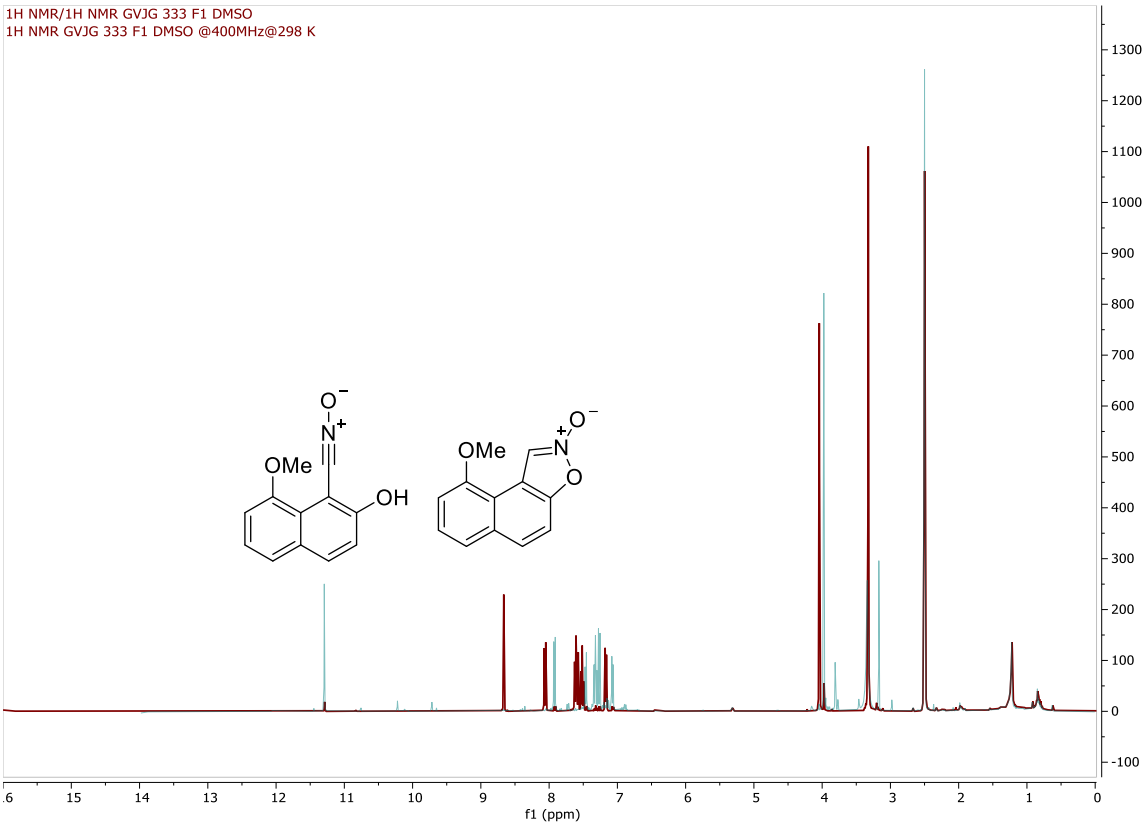

Figure S59. ^{1}H NMR (400 MHz, DMSO-d_6) of nitrile oxide (**9**) and isoxazole-2-oxide (**8**), superimposed.

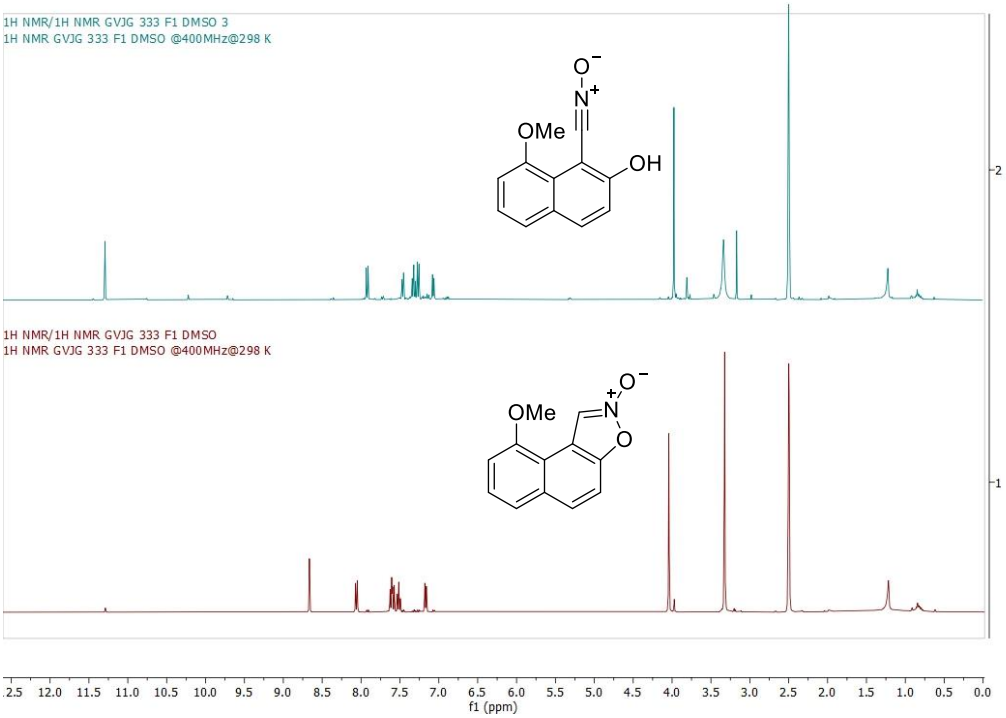

Figure S60. ^{1}H NMR (400 MHz, DMSO-d_6) of nitrile oxide (**9**) and isoxazole-2-oxide (**8**), stacked.

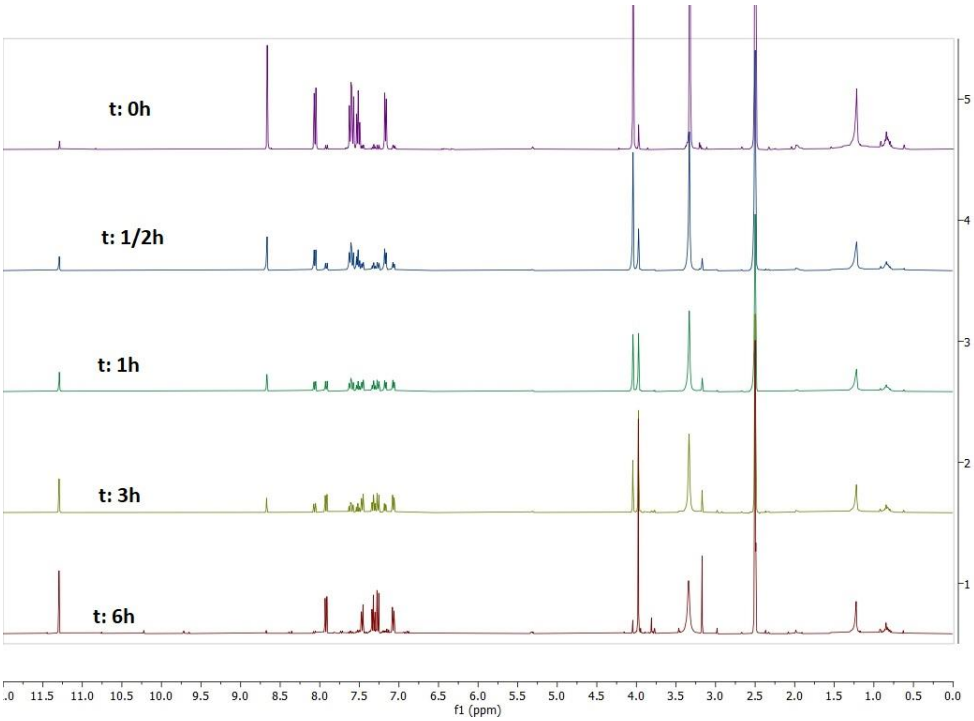

Figure S61. ^{1}H NMR (400 MHz, DMSO-d_6) time-course experiment of the ring opening of isoxazole-2-oxide (**8**) (top spectra) to nitrile oxide (**9**) (bottom spectra).

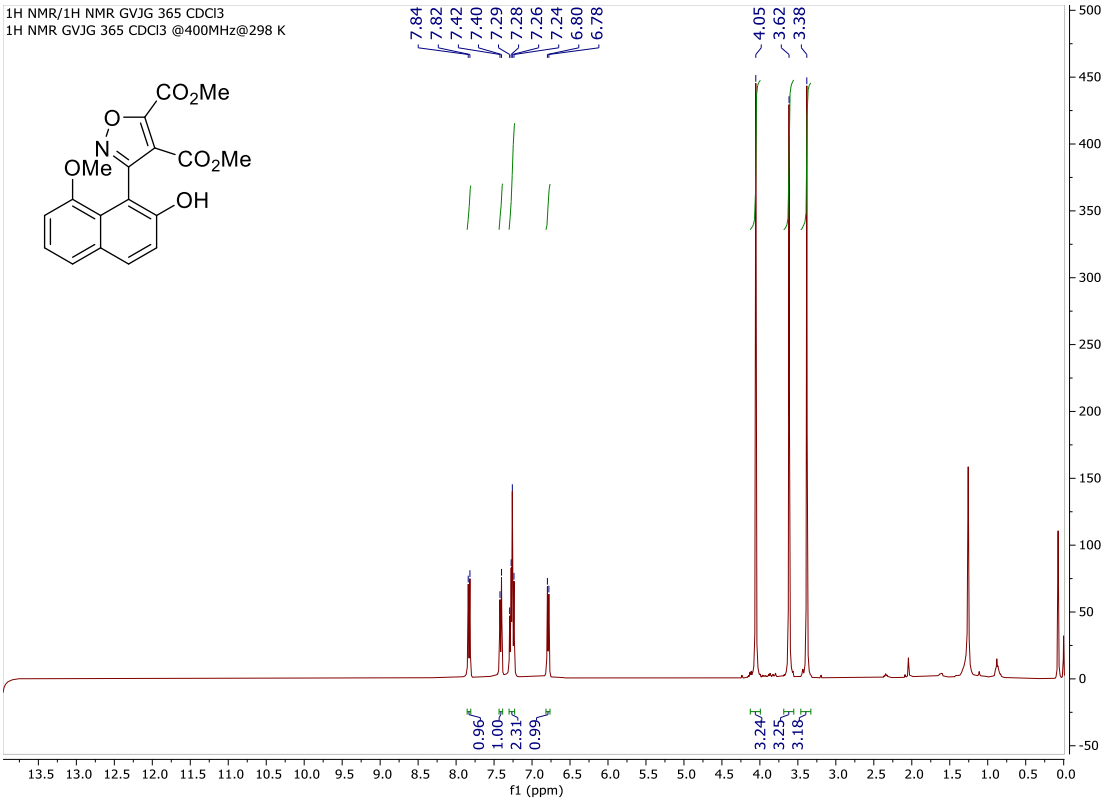

Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) of (**10a**).

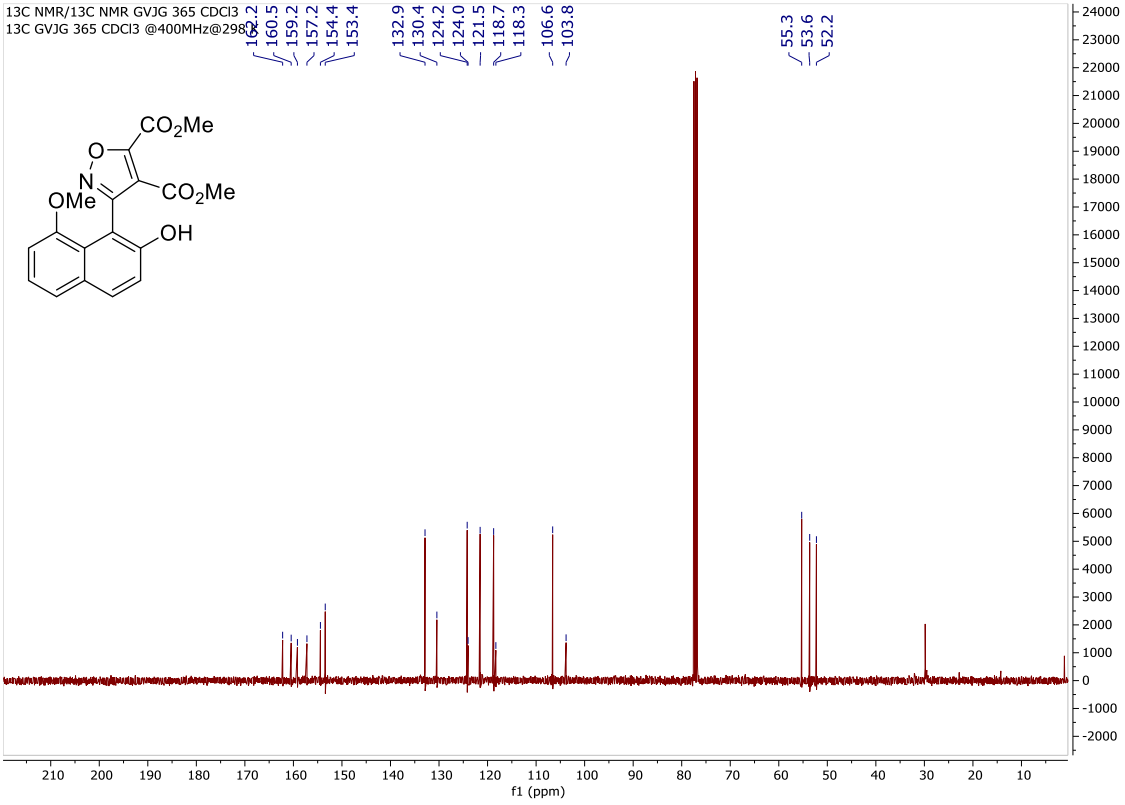

Figure S63. ^{13}C NMR (100.6 MHz, $CDCl_3$) of (**10a**).

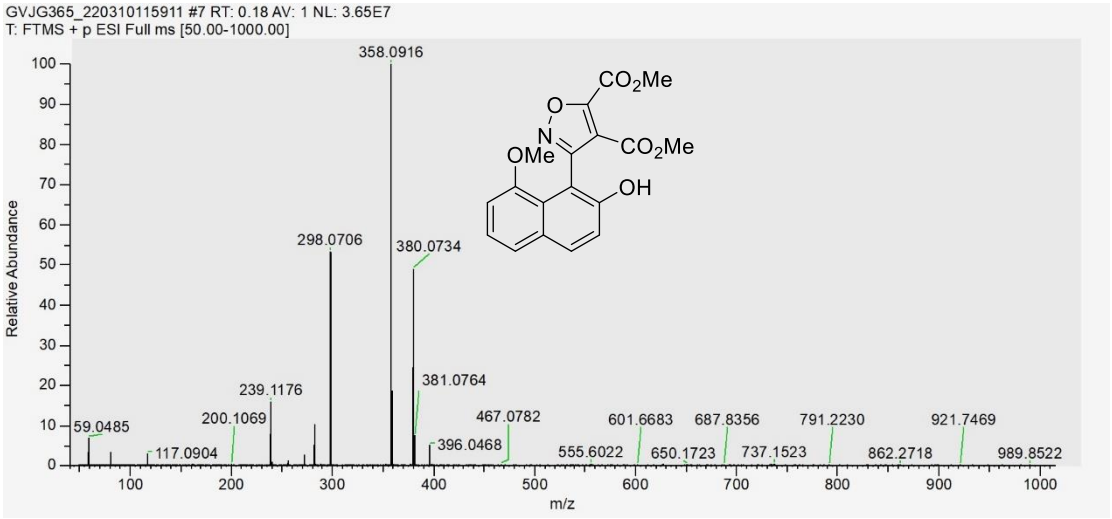

Figure S64. HRMS $[M+H]^+$ of compound (**10a**) using 0.1% HCO_2H in MeOH as solvent.

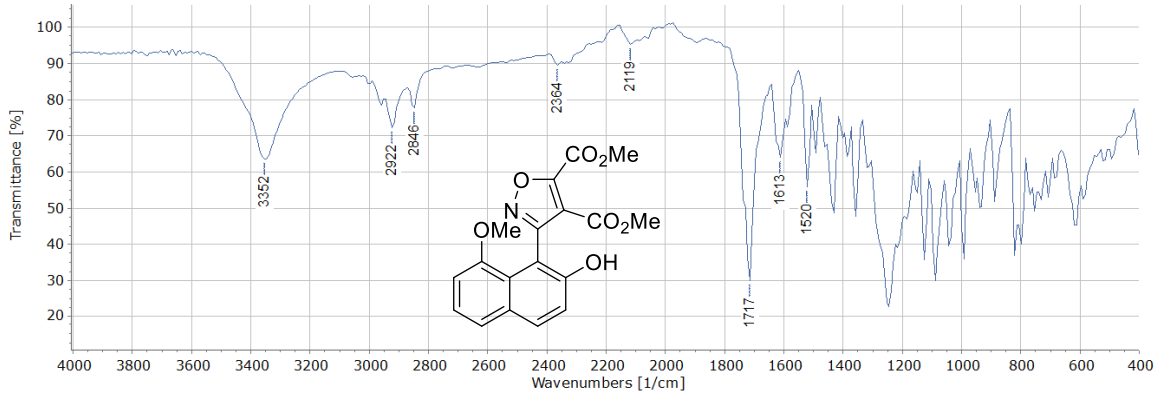

Figure S65. IR spectrum (solid) of (**10a**).

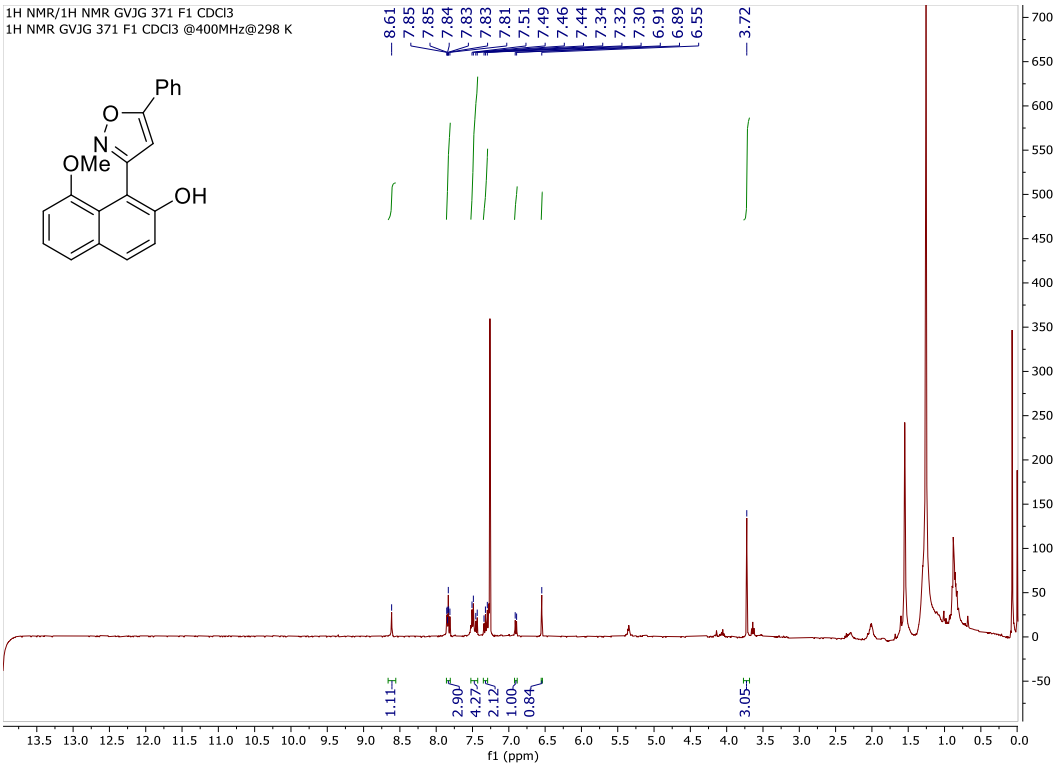

Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) of (**10b**).

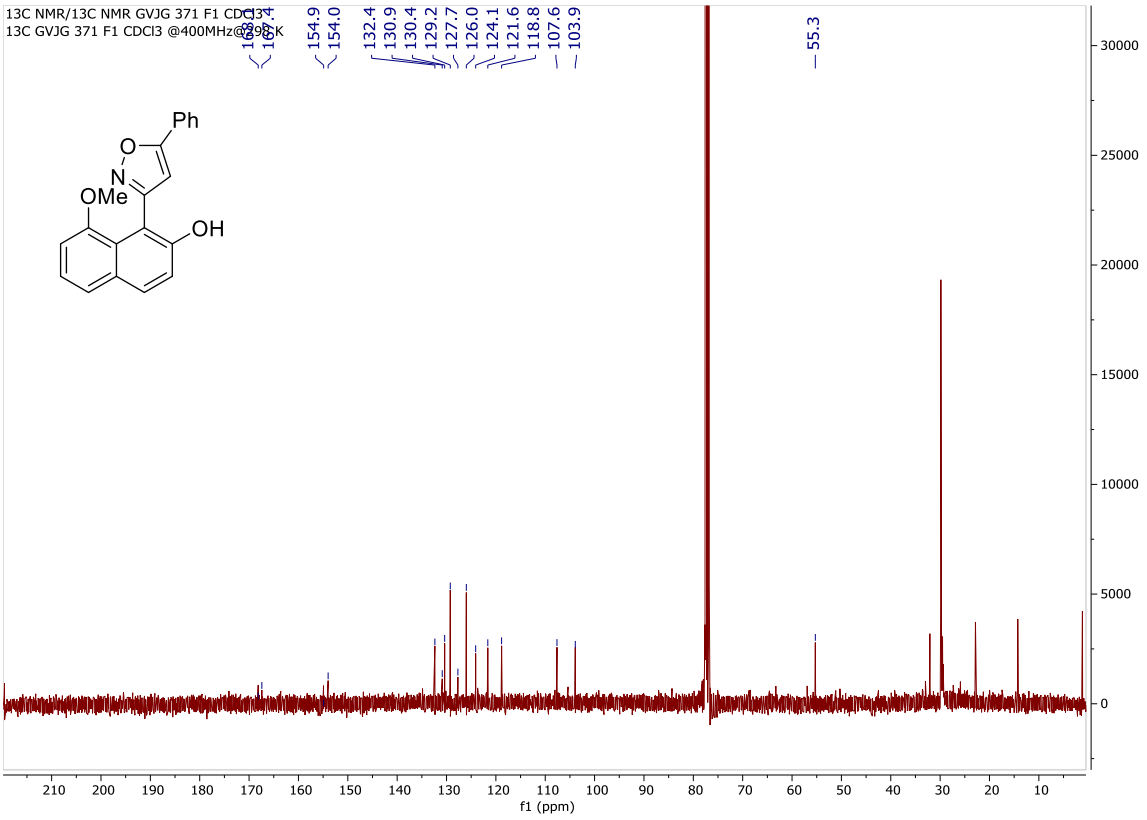

Figure S67. ^{13}C NMR (100.6 MHz, $CDCl_3$) of (**10b**).

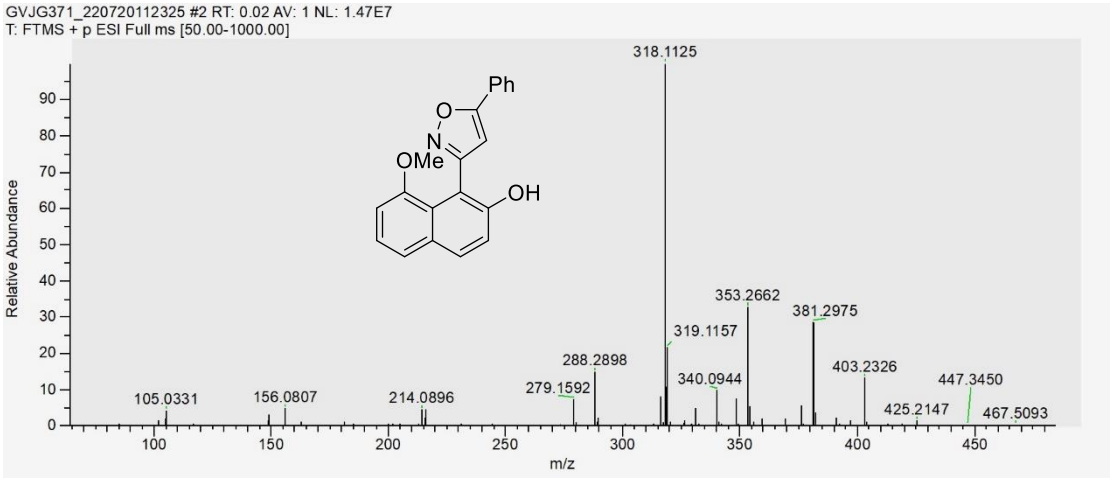

Figure S68. HRMS $[M+H]^+$ of compound (**10b**) using 0.1% HCO_2H in MeOH as solvent.

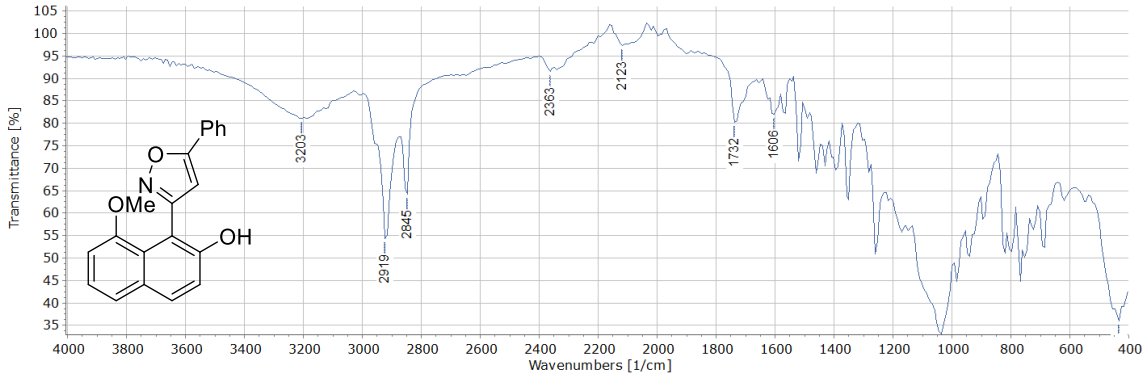

Figure S69. IR spectrum (solid) of (**10b**).

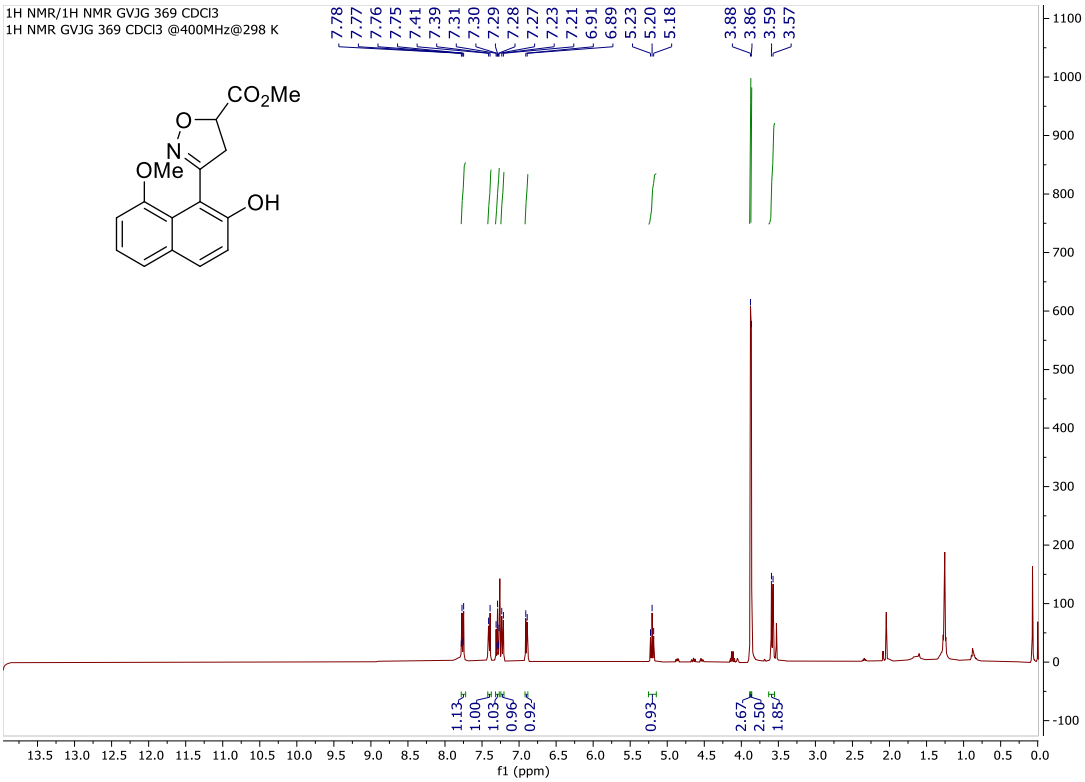

Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) of (**10c**).

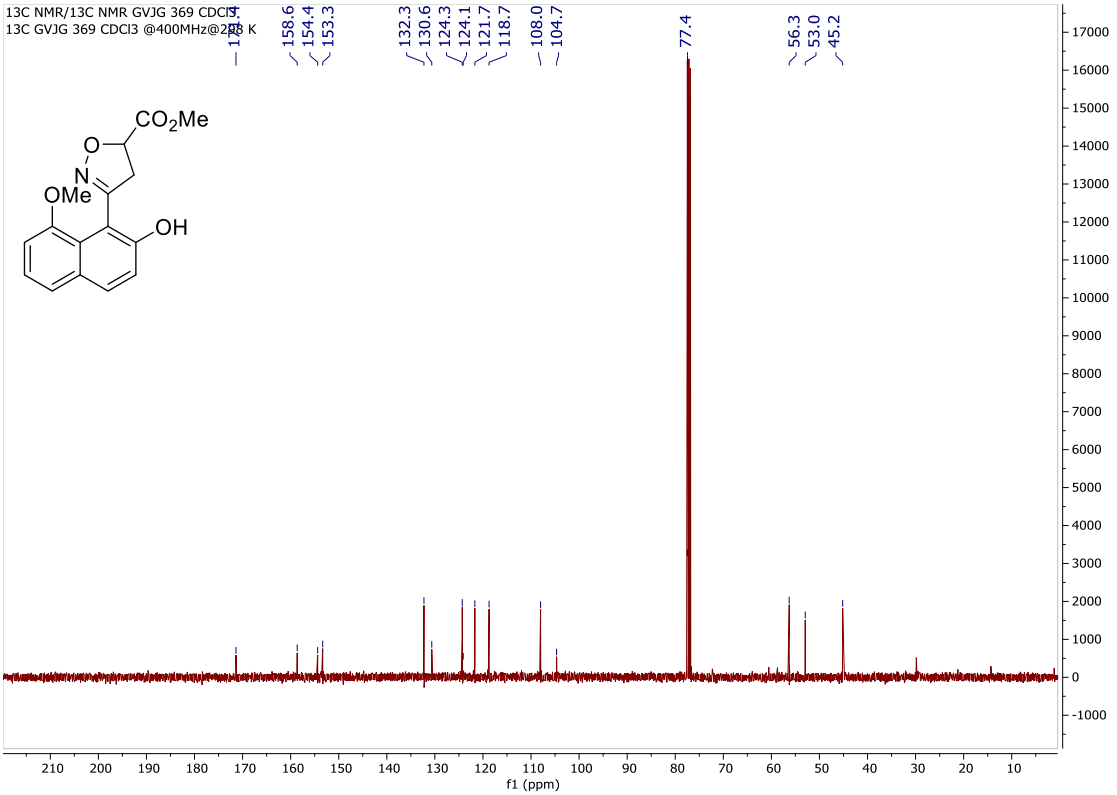

Figure S71. ^{13}C NMR (100.6 MHz, $CDCl_3$) of (**10c**).

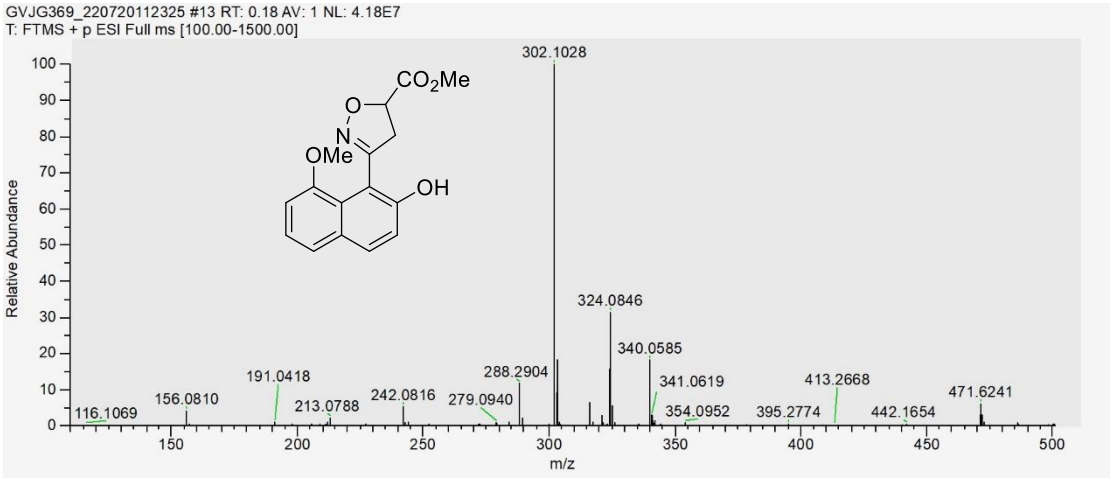

Figure S72. HRMS $[M+H]^+$ of compound (**10c**) using 0.1% HCO_2H in MeOH as solvent.

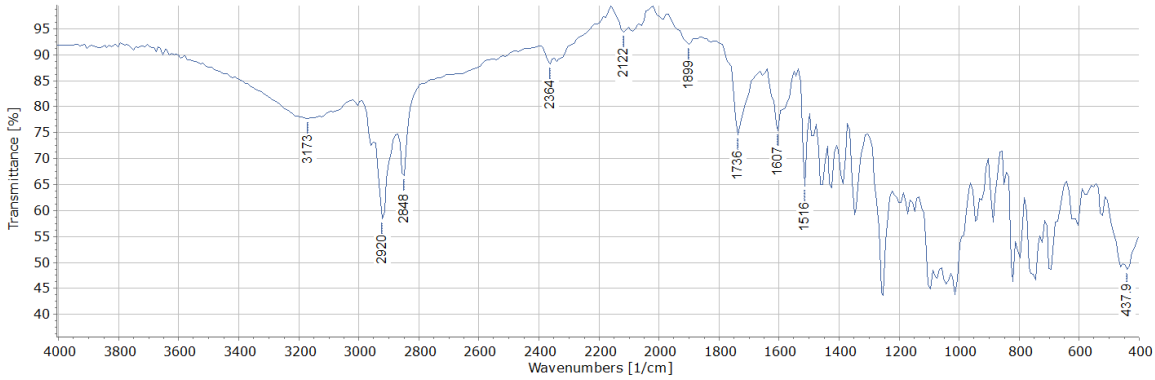

Figure S73. IR spectrum (solid) of (**10c**).

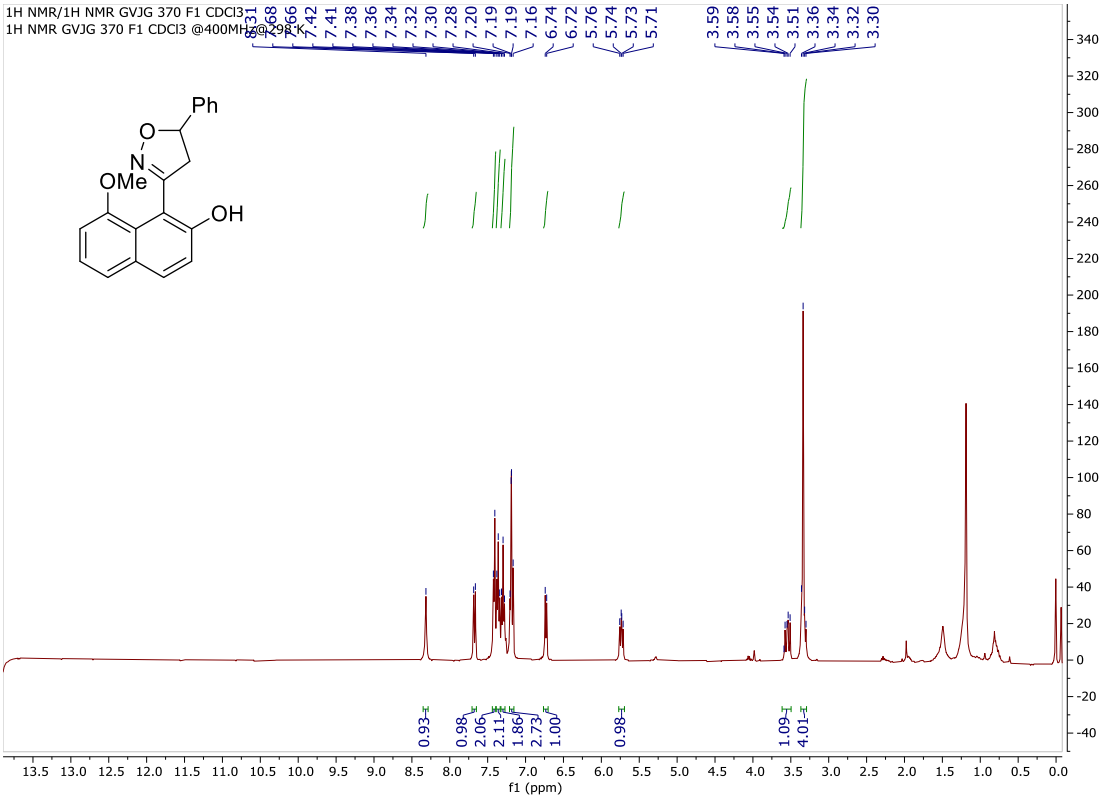

Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) of (**10d**).

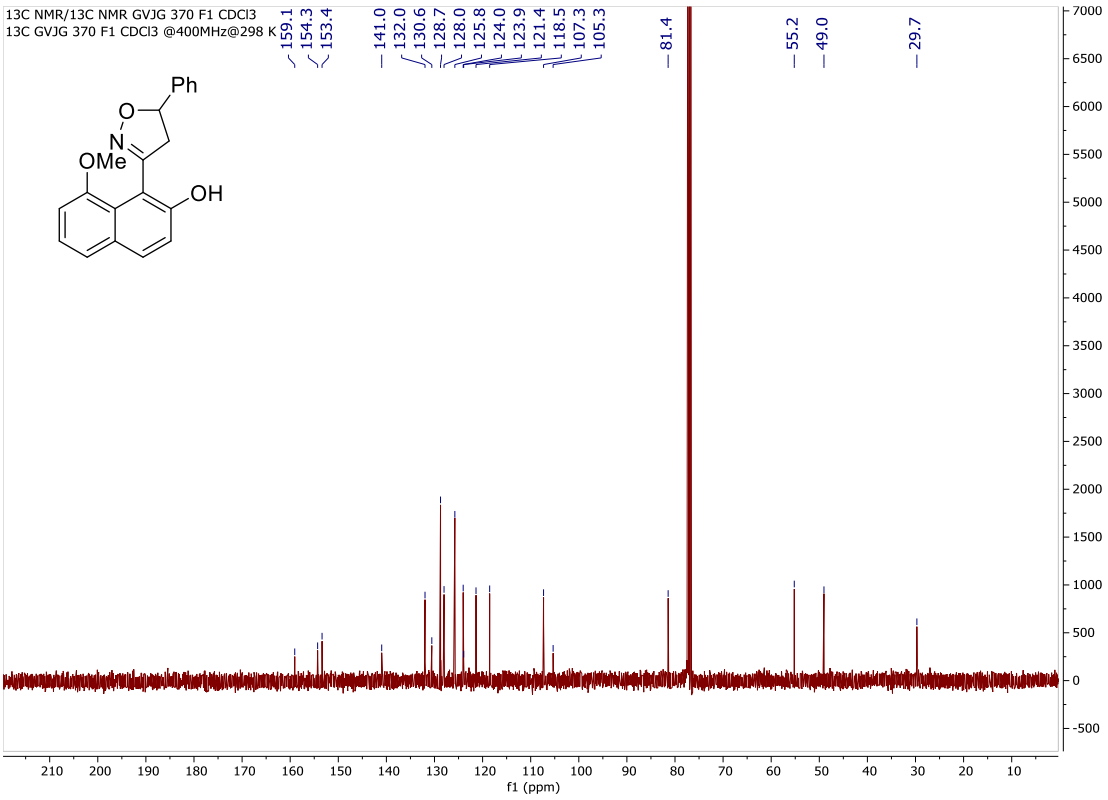

Figure S75. ^{13}C NMR (100.6 MHz, $CDCl_3$) of (**10d**).

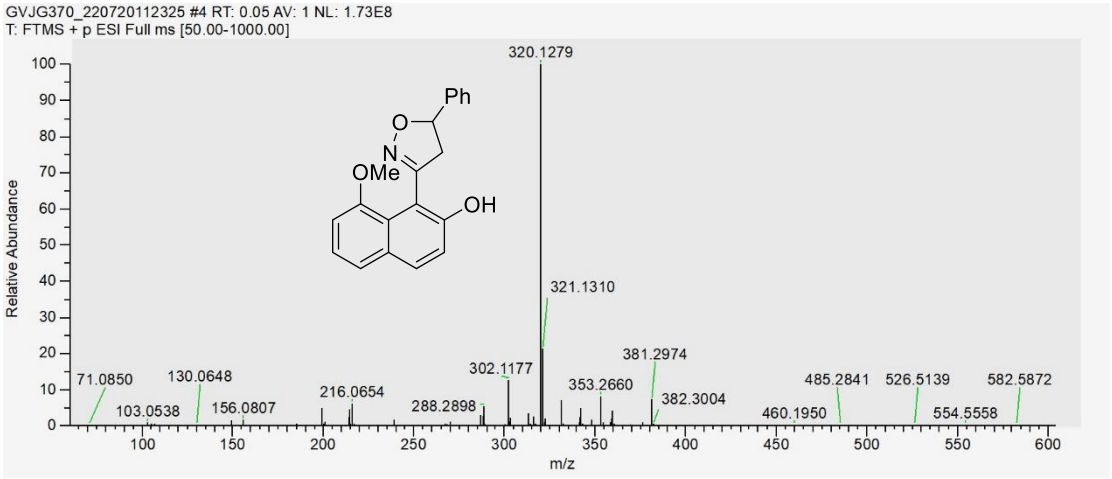

Figure S76. HRMS $[M+H]^+$ of compound (**10d**) using 0.1% HCO_2H in MeOH as solvent.

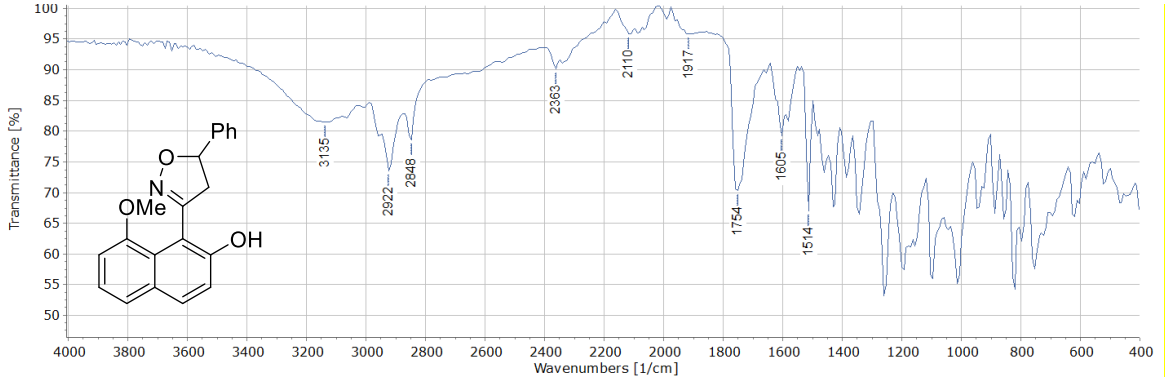

Figure S77. IR spectrum (solid) of (**10d**).