

Supporting Information

**Mechanochemical Cascaded C-N Cross-Coupling and Halogenation using *N*-Bromo-
and *N*-Chlorosuccinimide as Bifunctional Reagents**

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X-ray crystallography analysis

Procedure for preparing the crystal sample. In a 10 mL round bottom flask 20 mg of phenanthridinone derivatives (**3c**, **4a** and **2b**) was dissolved by using ethyl acetate and hexane mixture = 1:1 (6 mL). After that the solution was allowed for slow evaporation to obtain good quality of crystal.

Crystal measurement

The crystals data were collected with Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an INCOATEC micro source (Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$). SAINT¹ and SADABS² were used to integrate the intensities and to correct the absorption respectively. The structure was resolved by direct methods and refined on F² with SHELXL-97.³ ORTEP drawing of the compounds show ellipsoid contour at the 50% probability level.

Crystallographic data

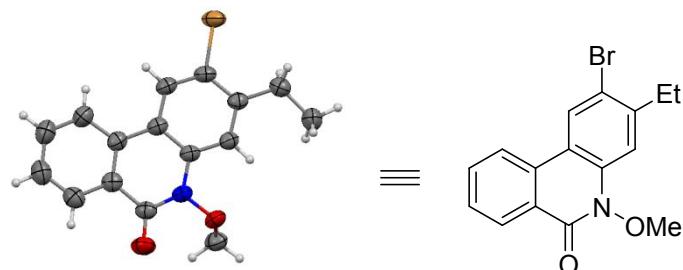


Figure S1. Crystal structure of **3c** (50% ellipsoid probability).

Table S1. Crystal data and structure refinement for **3c**.

CCDC No.	2074176
Empirical formula	C ₁₆ H ₁₄ BrNO ₂
Formula weight	332.19
Temperature/K	300.4(6)

Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	14.3679(2)
b/Å	5.86430(10)
c/Å	17.0577(3)
α/°	90
β/°	105.432(2)
γ/°	90
Volume/Å ³	1385.43(4)
Z	4
ρ _{calc} g/cm ³	1.593
μ/mm ⁻¹	4.050
F(000)	672.0
Crystal size/mm ³	0.2 × 0.18 × 0.18
Radiation	CuKα ($\lambda = 1.54184$)
2Θ range for data collection/°	10.762 to 150.756
Index ranges	-18 ≤ h ≤ 18, -7 ≤ k ≤ 6, -21 ≤ l ≤ 21
Reflections collected	20185
Independent reflections	2848 [R _{int} = 0.0446, R _{sigma} = 0.0225]
Data/restraints/parameters	2848/0/183
Goodness-of-fit on F ²	1.064
Final R indexes [I>=2σ (I)]	R ₁ = 0.0280, wR ₂ = 0.0757
Final R indexes [all data]	R ₁ = 0.0302, wR ₂ = 0.0774
Largest diff. peak/hole / e Å ⁻³	0.29/-0.51

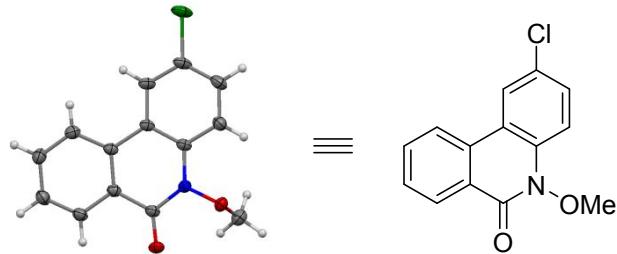


Figure S2. Crystal structure of **4a** (50% ellipsoid probability)

Table S2. Crystal data and structure refinement for **4a**

CCDC No.	2074177
Empirical formula	C ₁₄ H ₁₀ ClNO ₂
Formula weight	259.68
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	6.36750(10)
b/Å	11.9676(2)
c/Å	15.3511(3)
α/°	90
β/°	97.477(2)
γ/°	90
Volume/Å ³	1159.86(4)
Z	4
ρ _{calc} g/cm ³	1.487
μ/mm ⁻¹	2.858
F(000)	536.0
Crystal size/mm ³	0.2 × 0.18 × 0.18
Radiation	CuKα ($\lambda = 1.54184$)
2Θ range for data collection/°	9.4 to 160.926
Index ranges	-8 ≤ h ≤ 8, -10 ≤ k ≤ 15, -19 ≤ l ≤ 19
Reflections collected	18678

Independent reflections	2518 [$R_{\text{int}} = 0.0520$, $R_{\text{sigma}} = 0.0227$]
Data/restraints/parameters	2518/0/164
Goodness-of-fit on F^2	1.080
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0405$, $wR_2 = 0.1147$
Final R indexes [all data]	$R_1 = 0.0411$, $wR_2 = 0.1153$
Largest diff. peak/hole / e Å ⁻³	0.31/-0.35

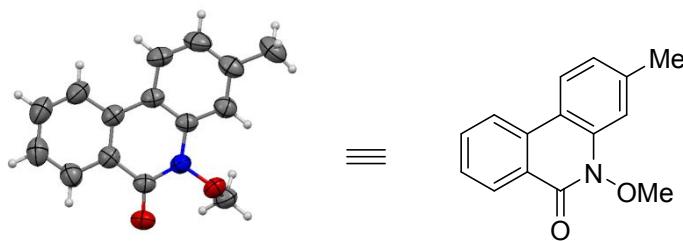


Figure S3. Crystal structure of **2b** (50% ellipsoid probability).

Table S3. Crystal data and structure refinement for **2b**. An identical structure to compound **2b** has been reported previously.⁴

CCDC No.	2074179
Empirical formula	C ₁₅ H ₁₃ NO ₂
Formula weight	239.26
Temperature/K	287(16)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	5.97070(10)
b/Å	15.8886(2)
c/Å	13.01240(10)
α/°	90
β/°	95.2120(10)
γ/°	90
Volume/Å ³	1229.33(3)

Z	4
ρ_{calc} g/cm ³	1.293
μ/mm^{-1}	0.696
F(000)	504.0
Crystal size/mm ³	0.2 × 0.18 × 0.18
Radiation	CuK α ($\lambda = 1.54184$)
2 Θ range for data collection/°	8.806 to 150.736
Index ranges	-7 ≤ h ≤ 7, -19 ≤ k ≤ 18, -16 ≤ l ≤ 15
Reflections collected	18686
Independent reflections	2522 [$R_{\text{int}} = 0.0341$, $R_{\text{sigma}} = 0.0179$]
Data/restraints/parameters	2522/0/165
Goodness-of-fit on F ²	1.084
Final R indexes [I >= 2σ (I)]	$R_1 = 0.0474$, $wR_2 = 0.1413$
Final R indexes [all data]	$R_1 = 0.0504$, $wR_2 = 0.1439$
Largest diff. peak/hole / e Å ⁻³	0.59/-0.18

References

- (1) SAINT+, Bruker AXS Inc., Madison, Wisconsin, USA, 1999 (Program for Reduction of Data collected on Bruker CCD Area Detector Diffractometer V. 6.02.)
- (2) Sheldrick, G. 1996.
- (3) Sheldrick, G., A short history of SHELX. *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.
- (4) Saha, R.; Sekar, G., Stable Pd-nanoparticles catalyzed domino CH activation/CN bond formation strategy: An access to phenanthridinones. *J. Catal.* **2018**, *366*, 176-188.

Calculation of environmental impact factor (E_{mw}) based on the molecular weight

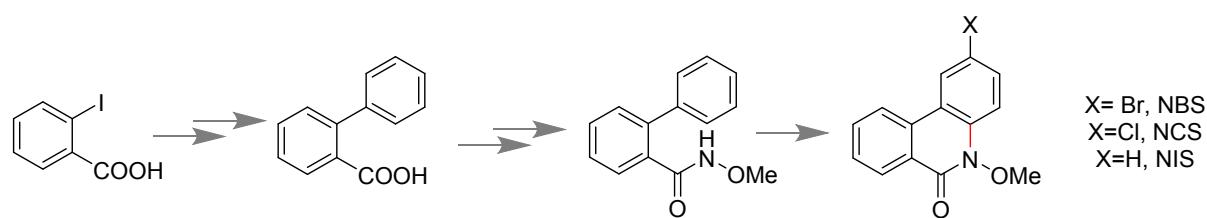
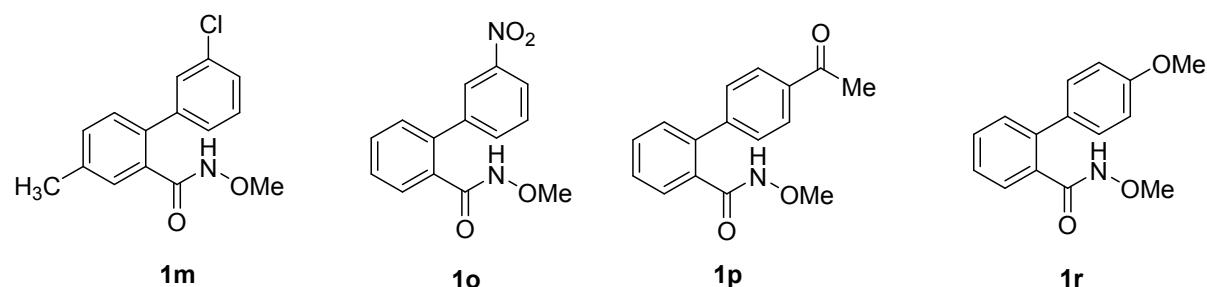


Table S4. E_{mw} -factors are calculated as mass of wastes (g) / mass of product (g).

Entry	Reagent	Product	E_{mw}
1	NBS	3a	3.83
2	NCS	4a	4.31
3	NIS	2a	4.50

Chart S1. Unsuccessful substrates for the chlorination and bromination reaction.



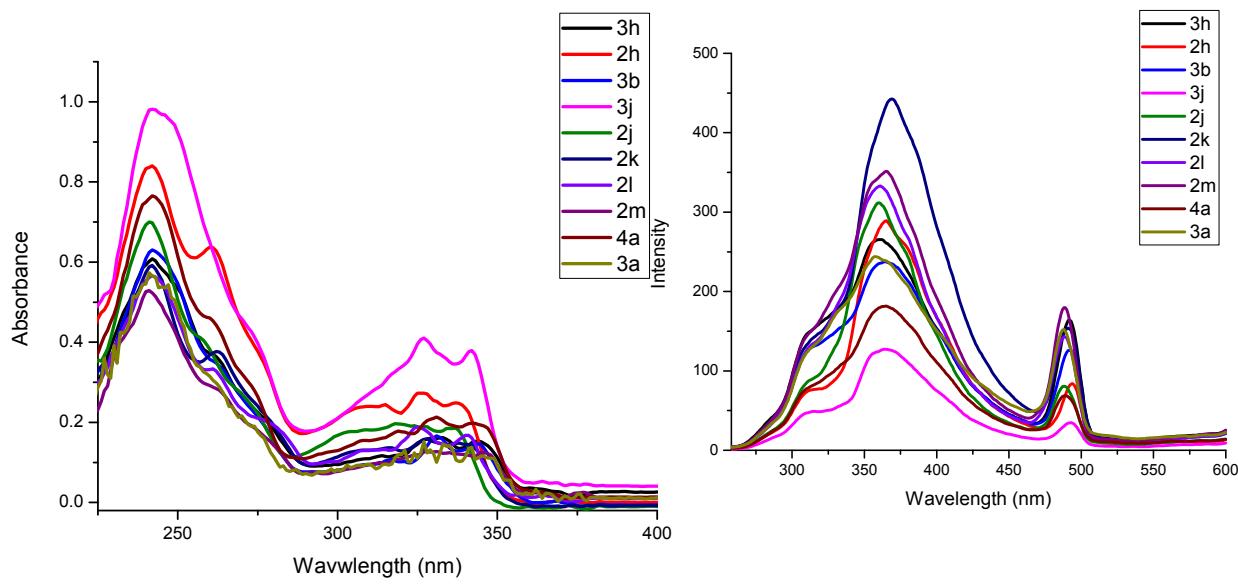


Figure S4. UV-Visible (left) and fluorescence (right, $\lambda_{\text{ex}} \sim 240$ nm) spectra of selected phenanthridinone derivatives (3×10^{-6} M in DCM).

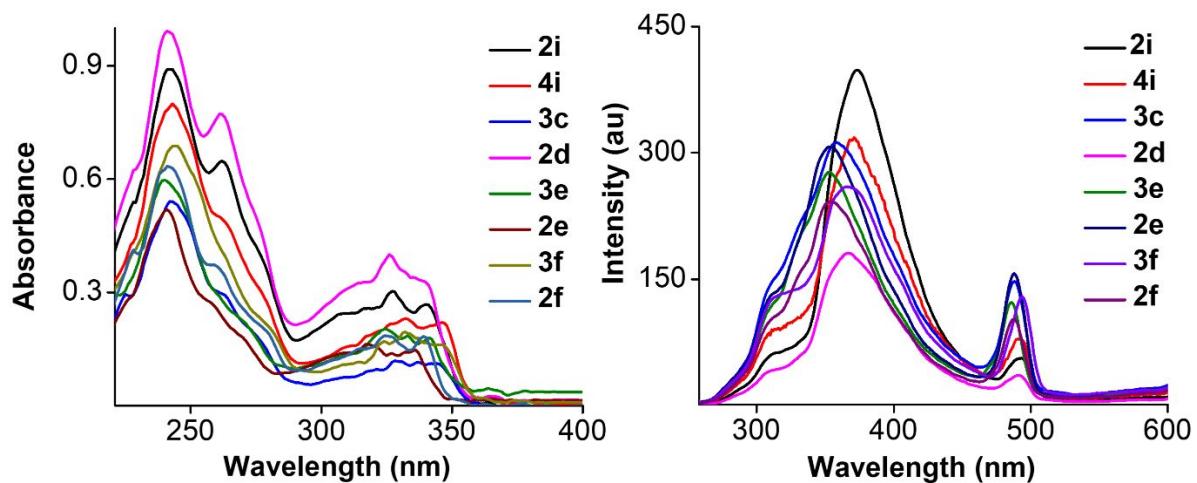


Figure S5. UV-Visible (left) and fluorescence (right, $\lambda_{\text{ex}} \sim 240$ nm) spectra of selected phenanthridinone derivatives (3×10^{-6} M in DCM).

NMR Spectra

¹H NMR (400 MHz, CDCl₃)

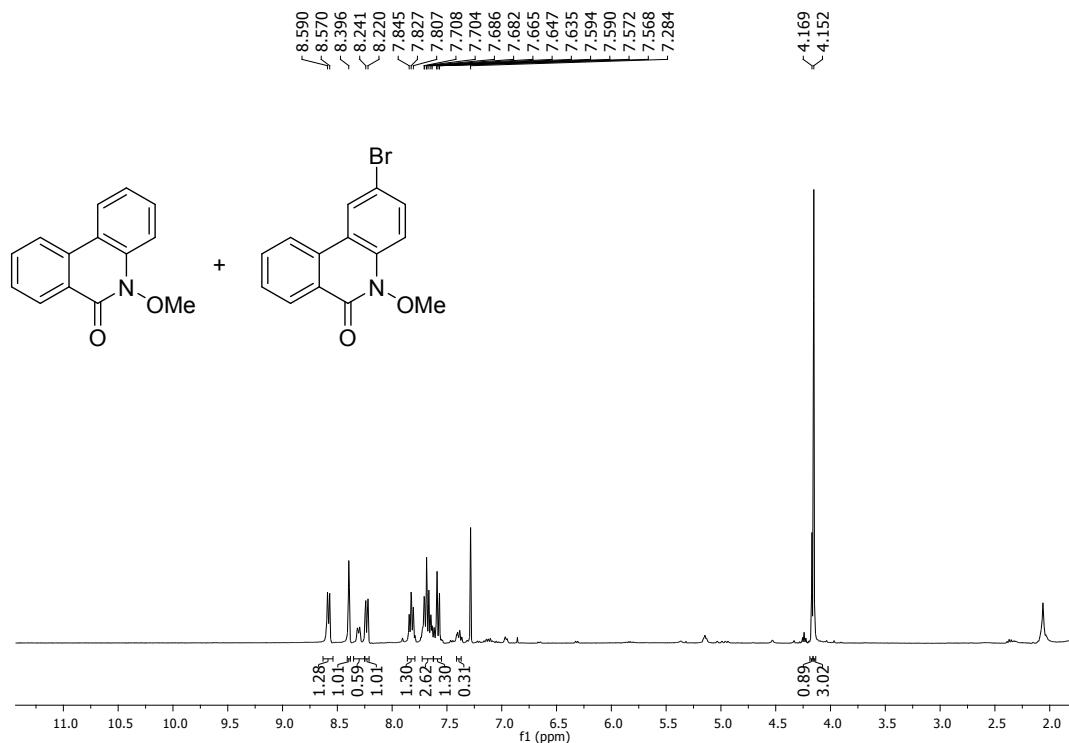


Figure S6. ¹H NMR spectrum of reaction mixture using 1 equiv of NBS

¹H NMR (400 MHz, CDCl₃)

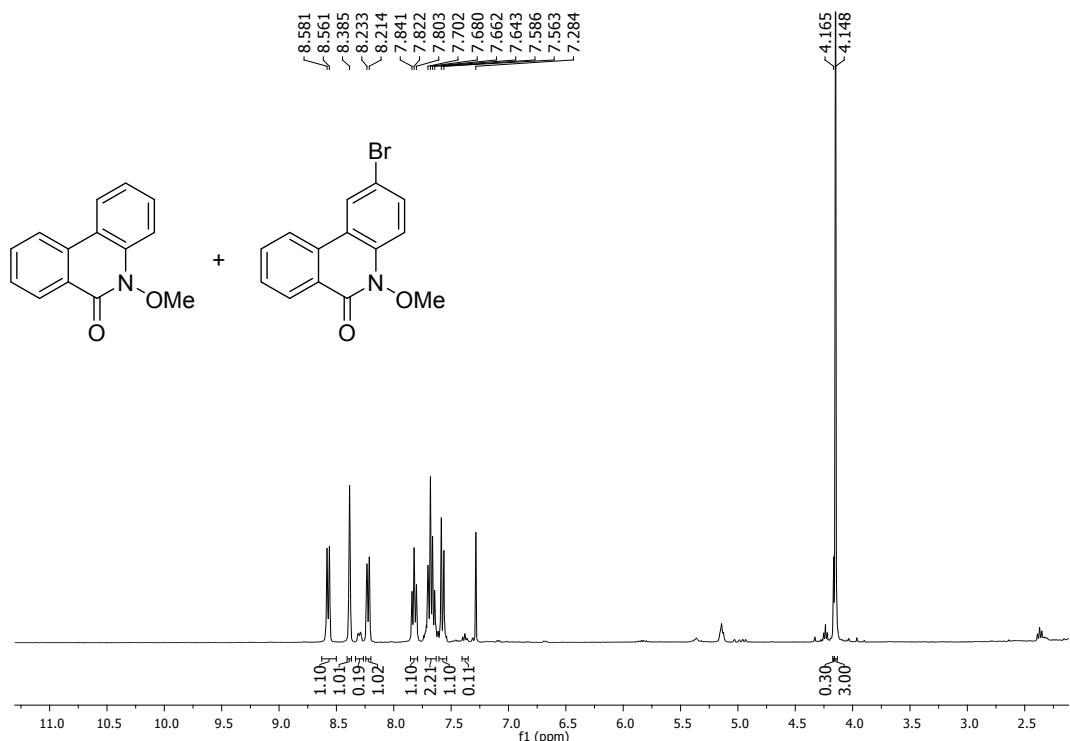


Figure S7. ¹H NMR spectrum of spectrum of reaction mixture using 1.5 equiv of NBS

¹H NMR (400 MHz, CDCl₃)

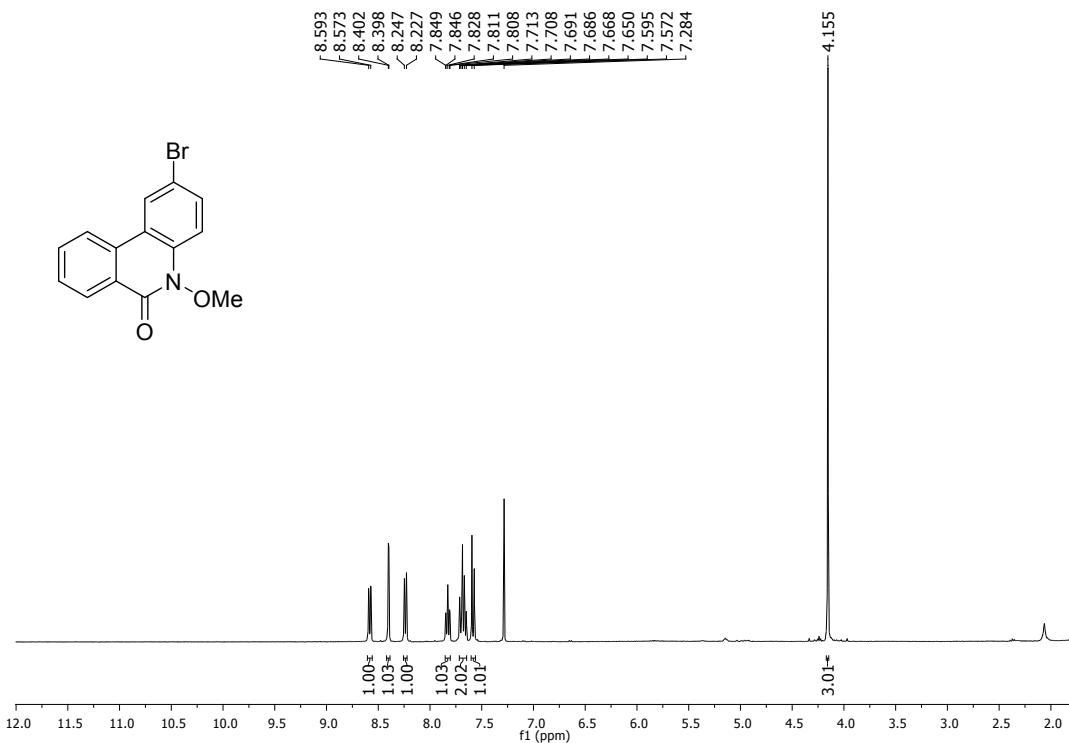


Figure S8. ¹H NMR spectrum of reaction mixture using 2 equiv of NBS

¹H NMR (400 MHz, CDCl₃)

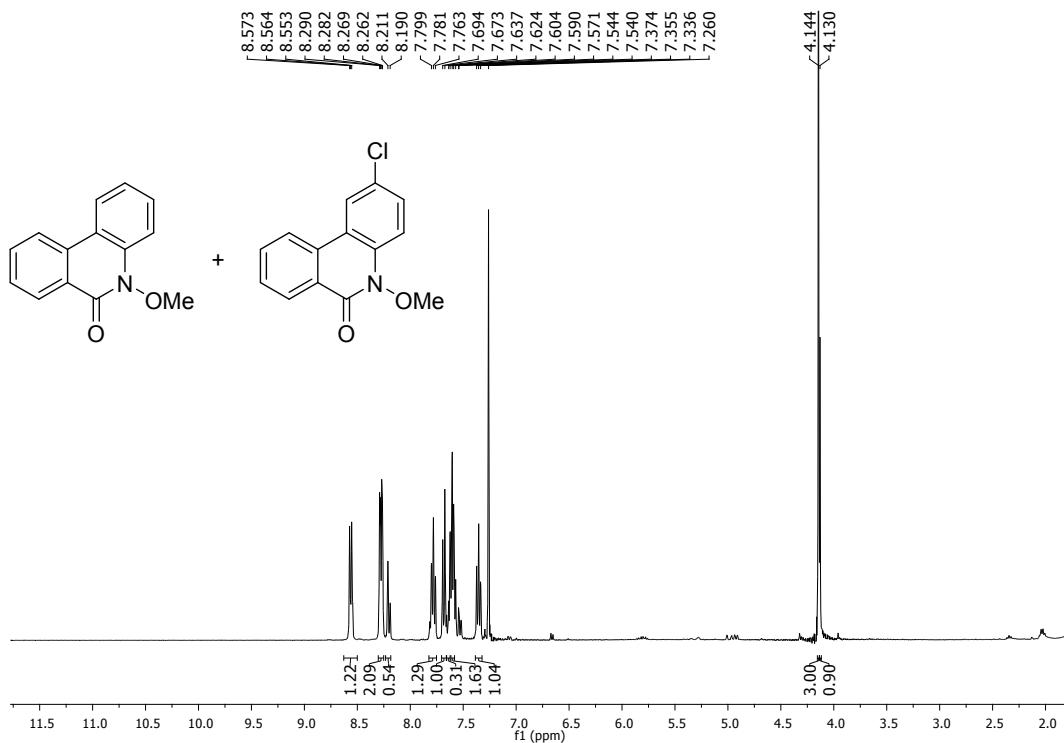


Figure S9. ¹H NMR spectrum of reaction mixture using 1 equiv of NCS

¹H NMR (400 MHz, CDCl₃)

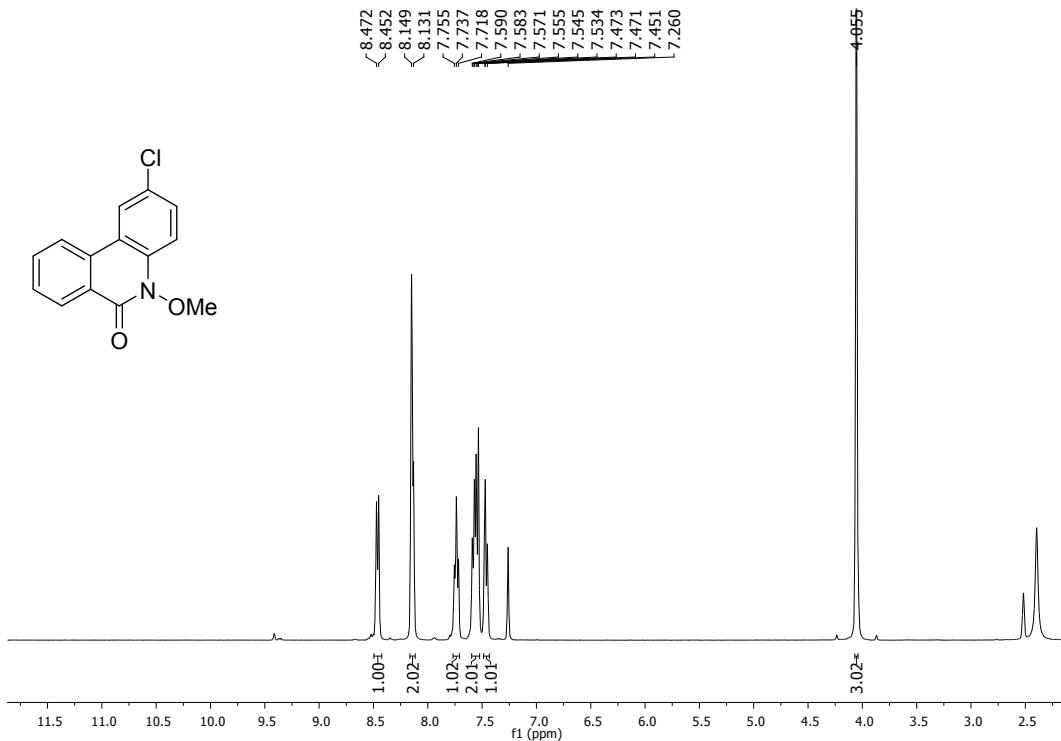


Figure S10. ¹H NMR spectrum of reaction mixture using 2 equiv of NCS

¹H NMR (400 MHz, CDCl₃)

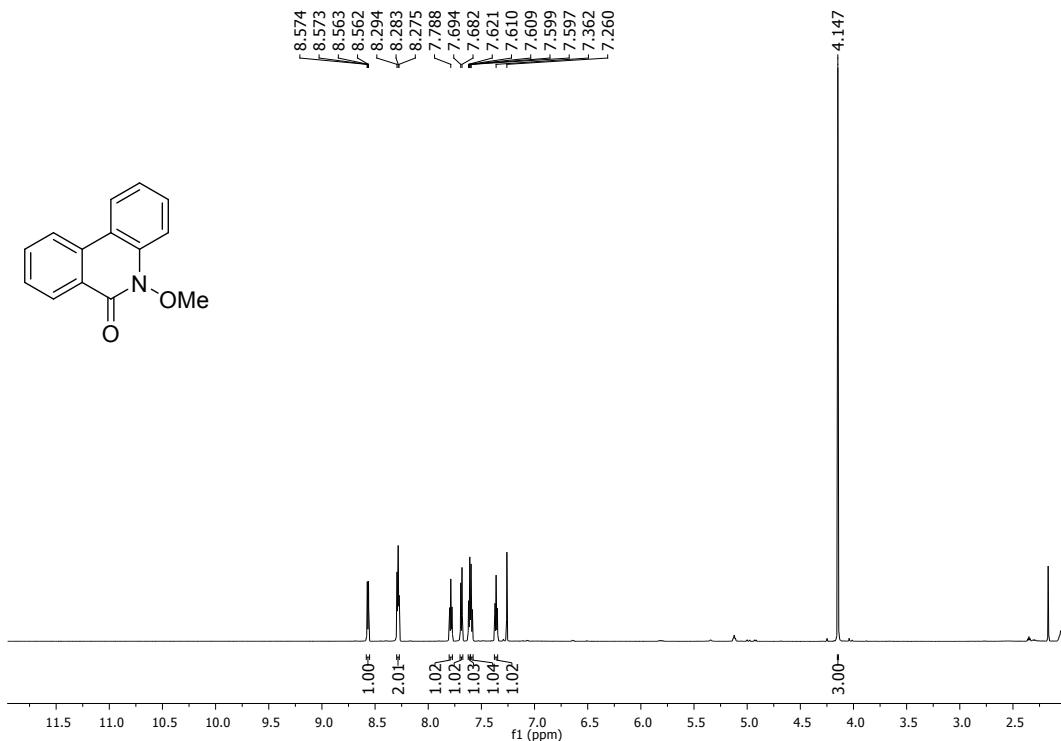


Figure S11. ¹H NMR spectrum of reaction mixture using 1 equiv of NIS

¹H NMR (400 MHz, CDCl₃)

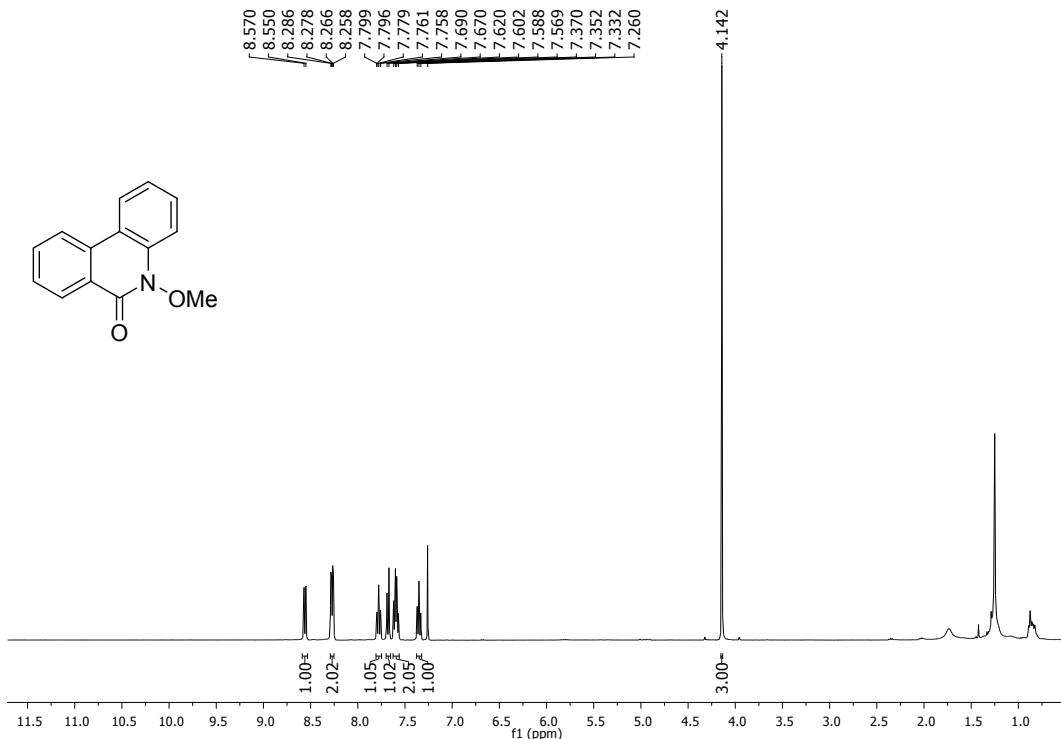


Figure S12. ¹H NMR spectrum of reaction mixture using 1.5 equiv of NCS

¹H NMR (400 MHz, CDCl₃)

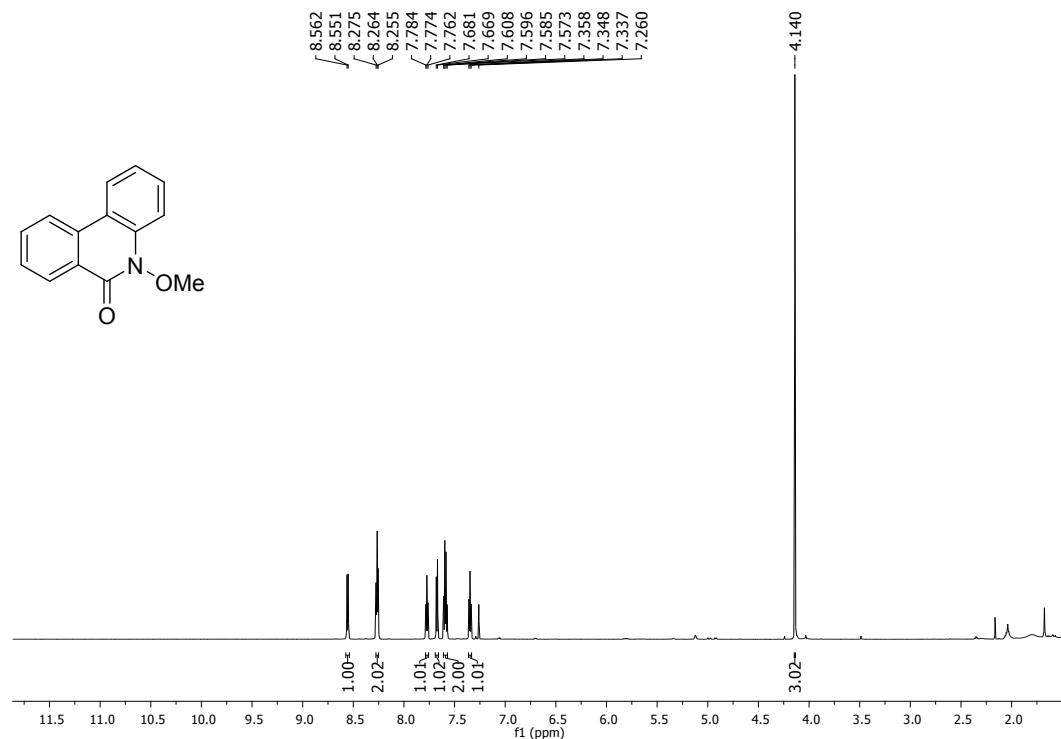


Figure S13. ¹H NMR spectrum of reaction mixture using 2 equiv of NIS

^1H NMR (400 MHz, CDCl_3)

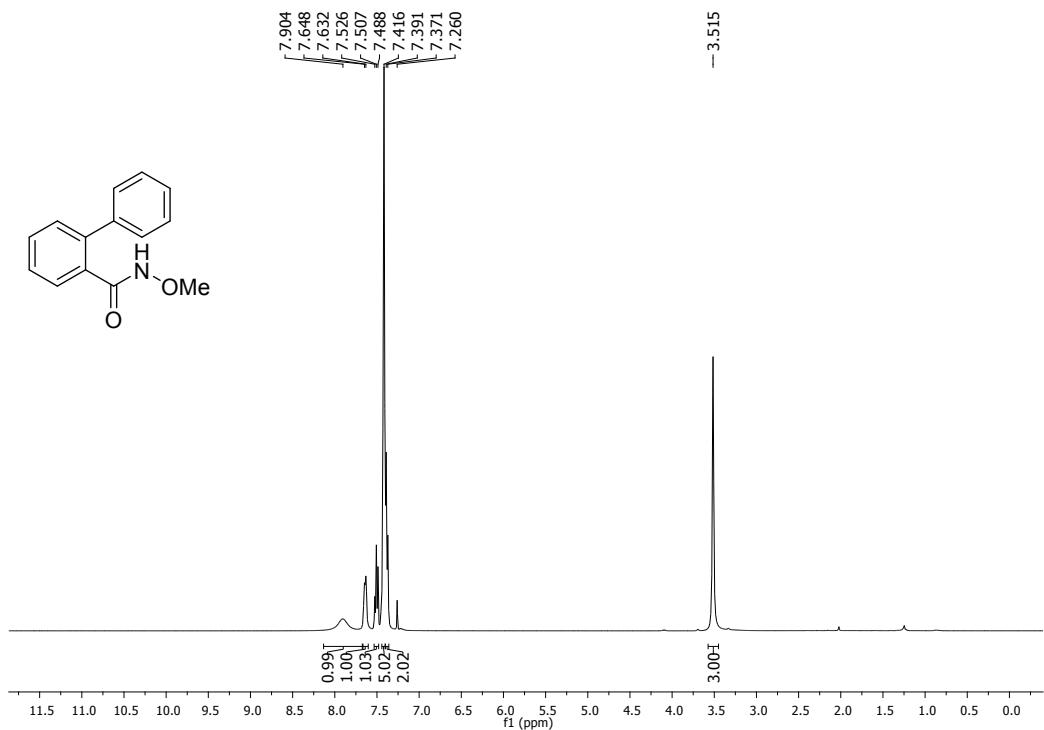


Figure S14. ^1H NMR spectrum of N-Methoxy-[1,1'-biphenyl]-2-carboxamide (**1a**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

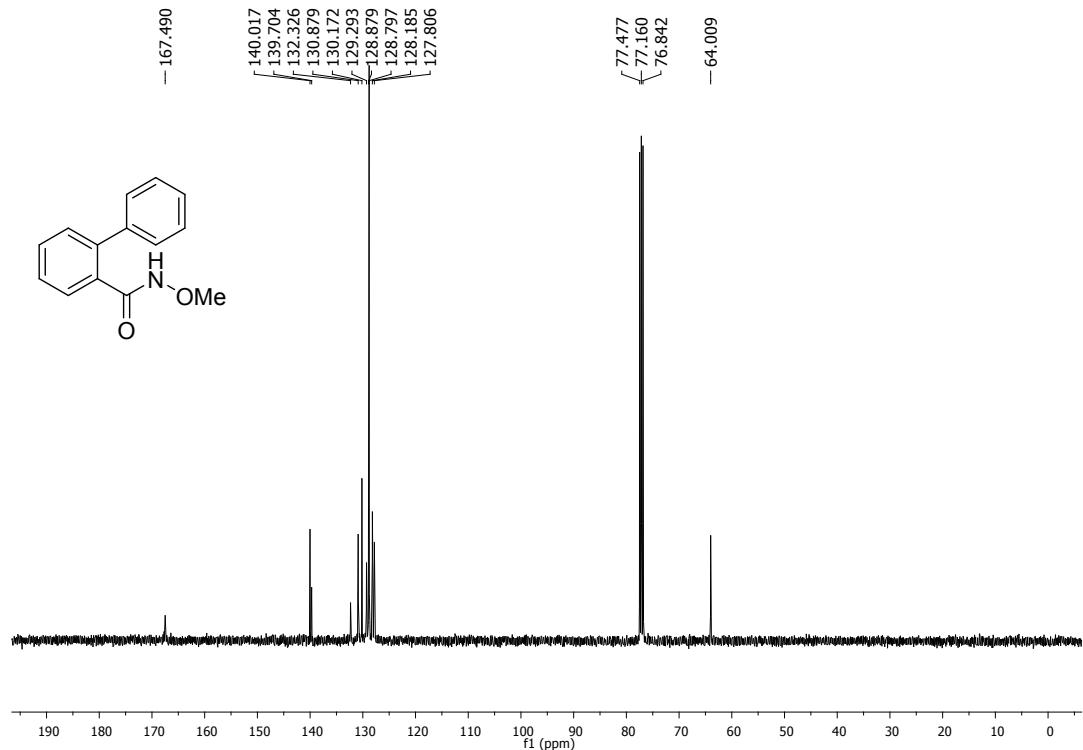


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of N-Methoxy-[1,1'-biphenyl]-2-carboxamide (**1a**)

¹H NMR (400 MHz, CDCl₃)

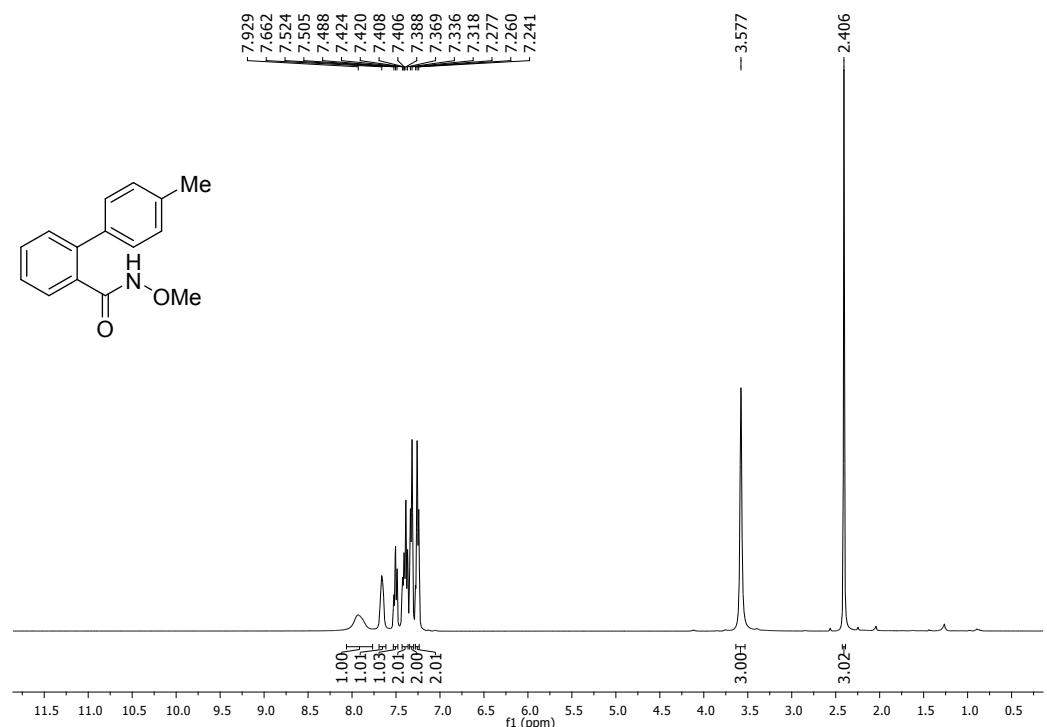


Figure S16. ¹H NMR spectrum of N-Methoxy-4'-methyl-[1,1'-biphenyl]-2-carboxamide (**1b**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

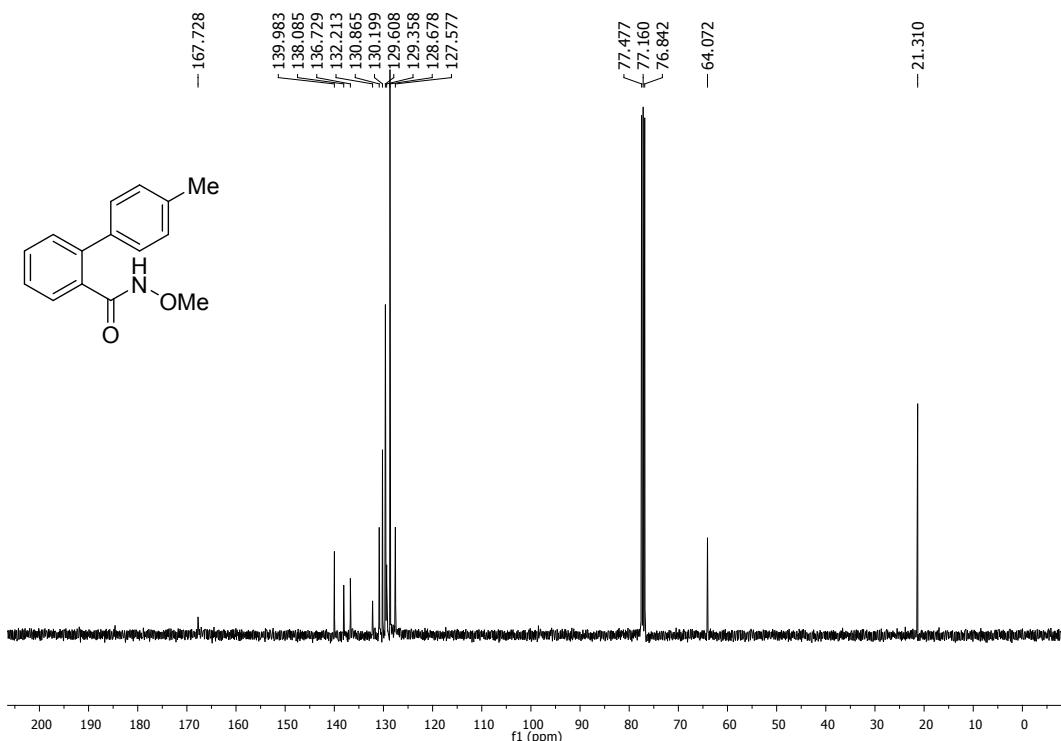


Figure S17. ¹³C{¹H} NMR spectrum of N-Methoxy-4'-methyl-[1,1'-biphenyl]-2-carboxamide (**1b**)

^1H NMR (400 MHz, CDCl_3)

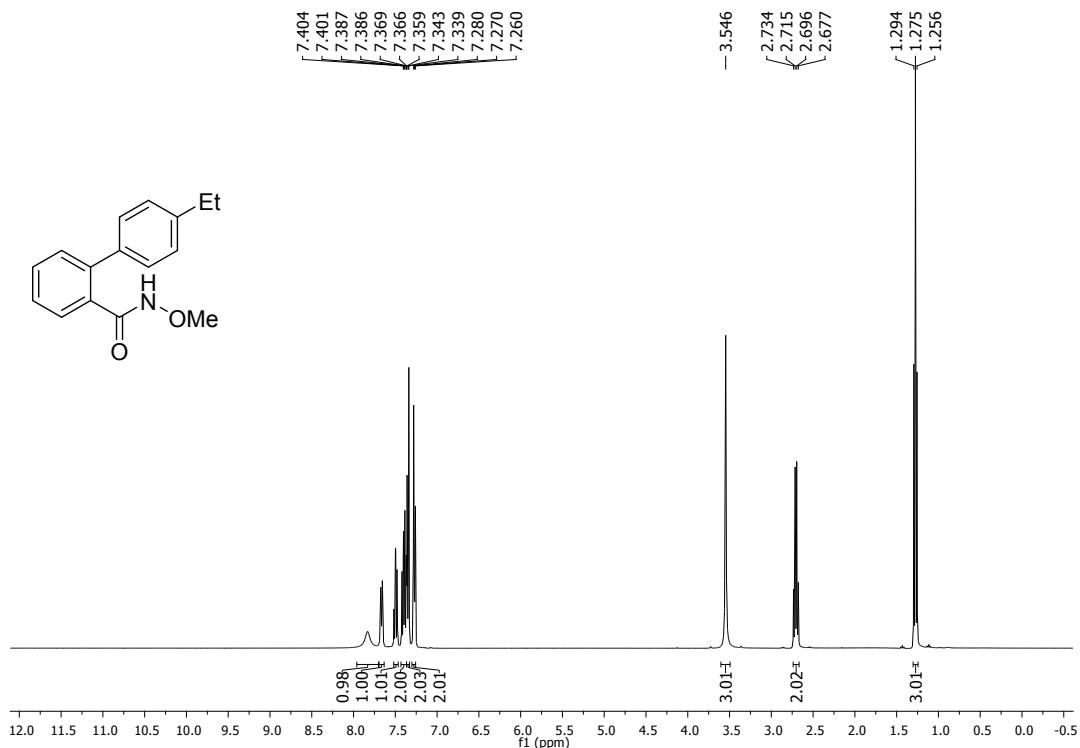


Figure S18. ^1H NMR spectrum of 4'-Ethyl-N-methoxy-[1,1'-biphenyl]-2-carboxamide (**1c**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

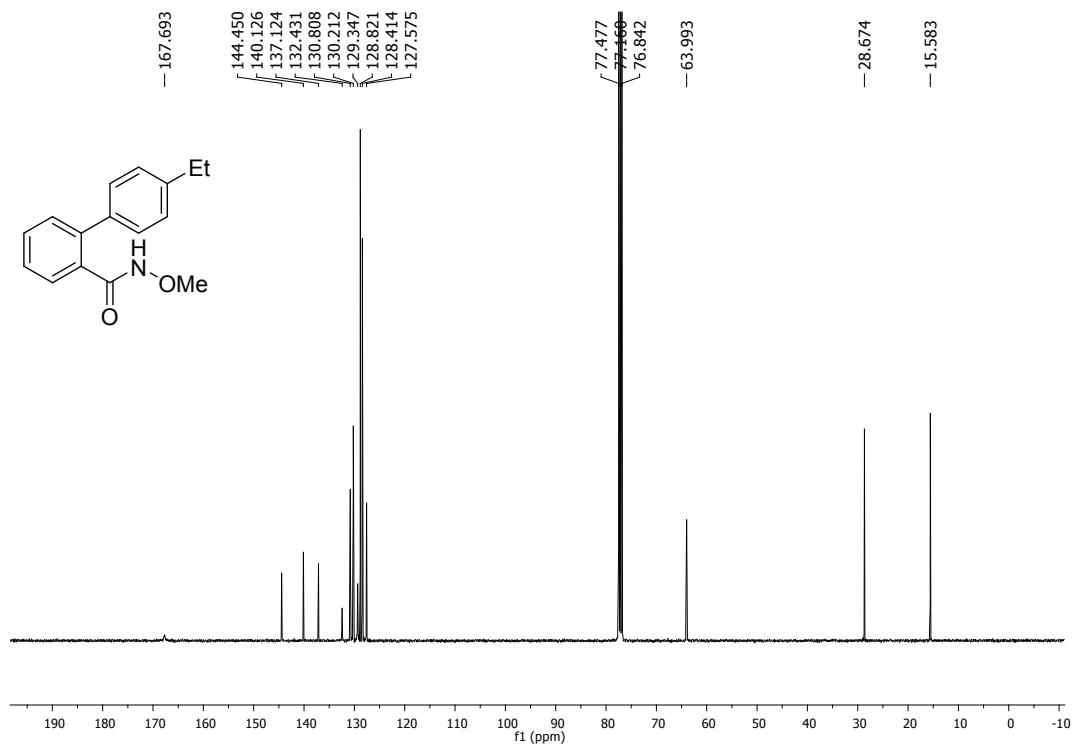


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4'-Ethyl-N-methoxy-[1,1'-biphenyl]-2-carboxamide (**1c**)

¹H NMR (400 MHz, CDCl₃)

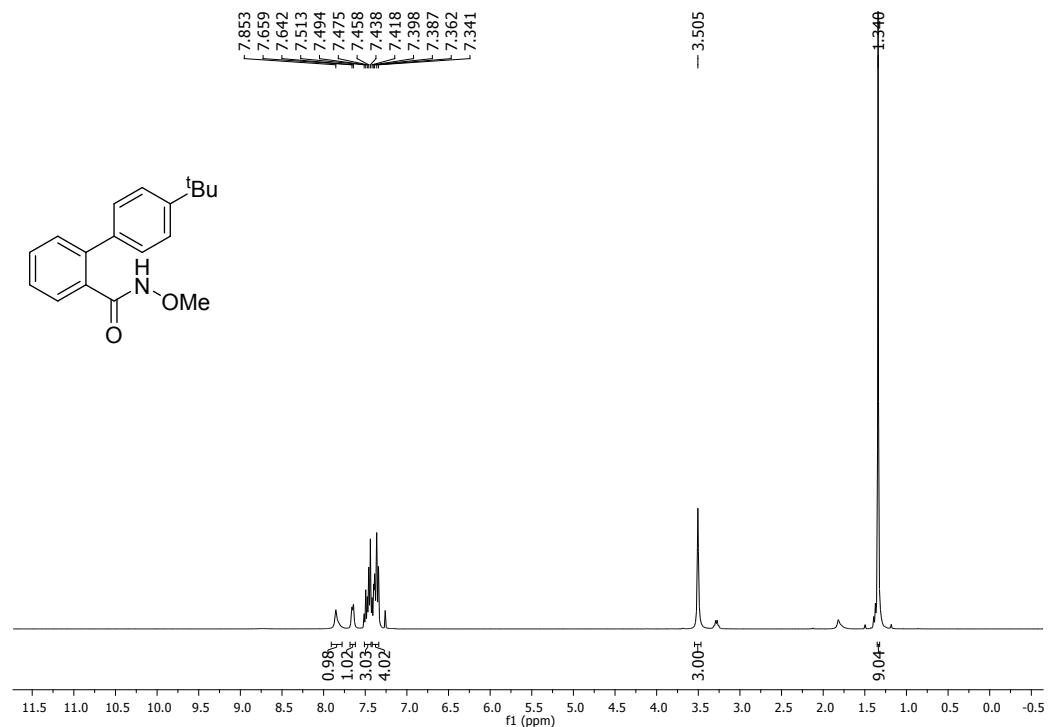


Figure S20. ¹H NMR spectrum of 4'-(Tert-butyl)-N-methoxy-[1,1'-biphenyl]-2-carboxamide (1d)

¹³C{¹H} NMR (100 MHz, CDCl₃)

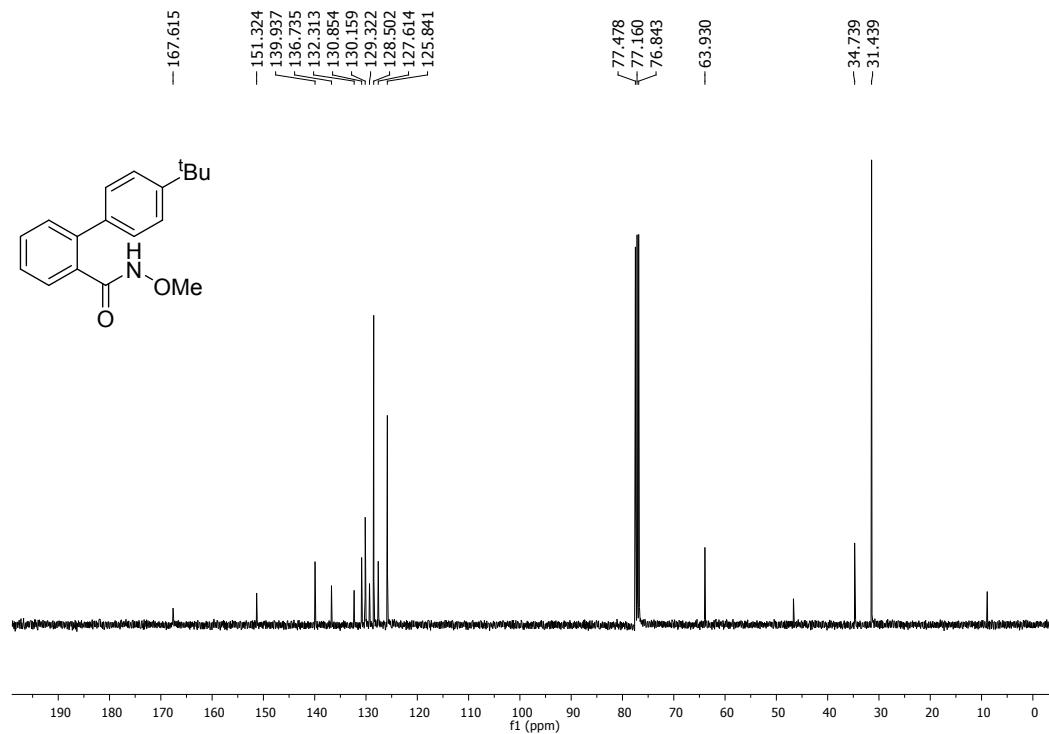


Figure S21. ¹³C{¹H} NMR spectrum of 4'-(Tert-butyl)-N-methoxy-[1,1'-biphenyl]-2-carboxamide (1d)

^1H NMR (400 MHz, CDCl_3)

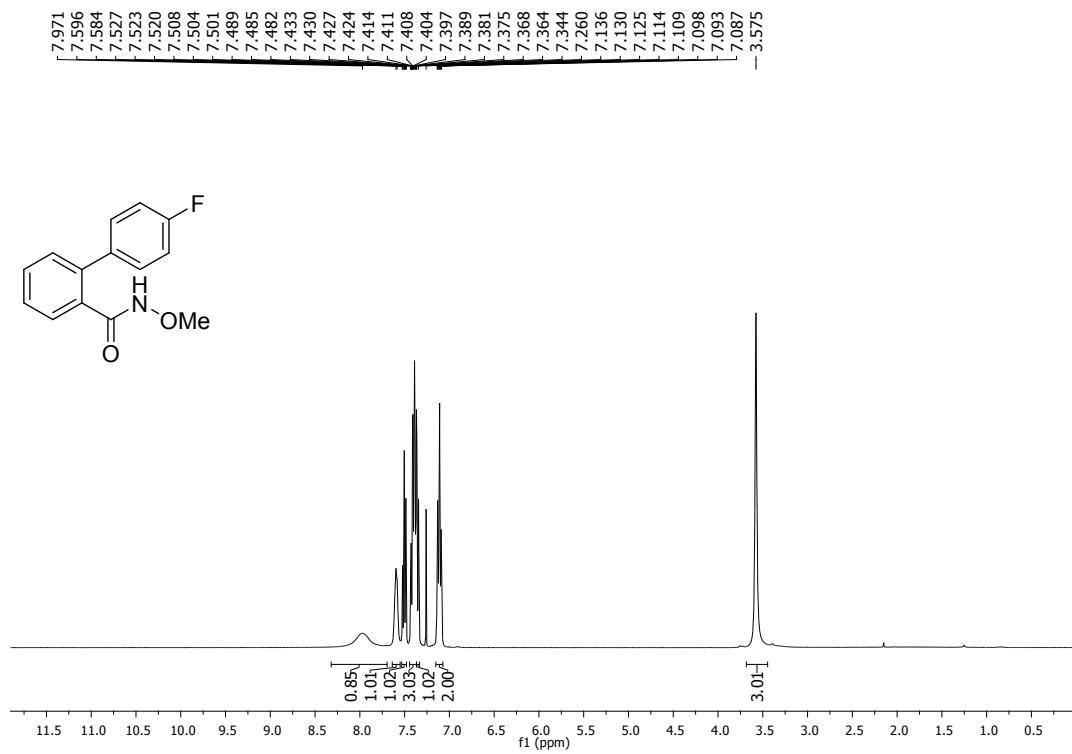


Figure S22. ^1H NMR spectrum of 4'-Fluoro-N-methoxy-[1,1'-biphenyl]-2-carboxamide (**1e**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

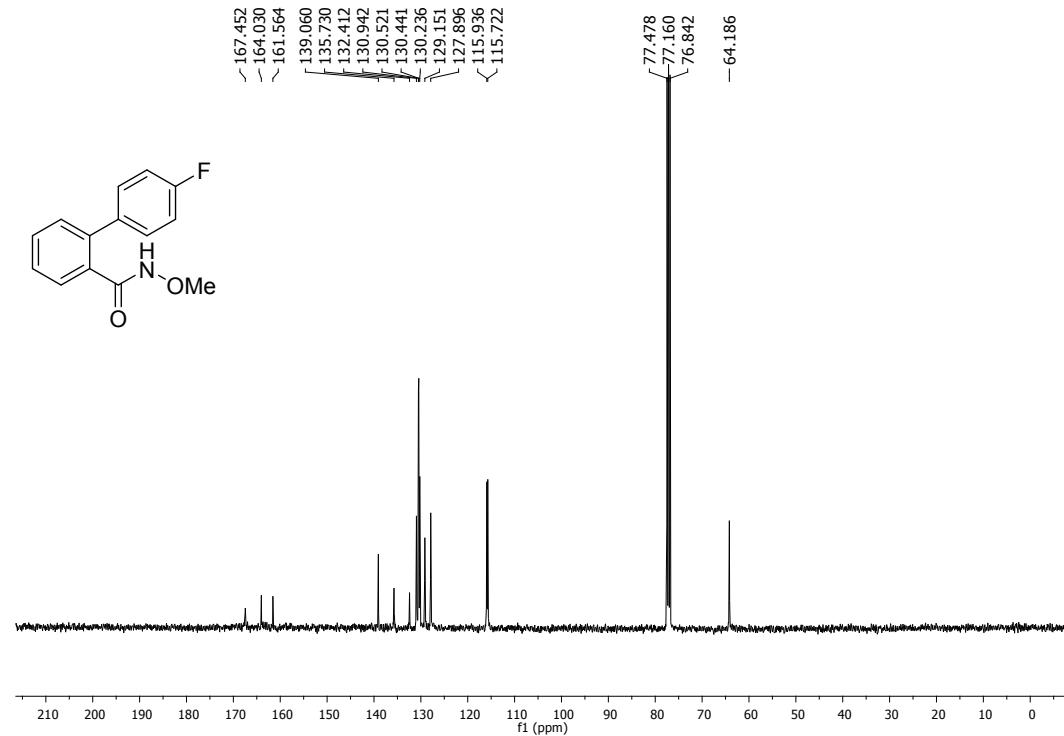


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4'-Fluoro-N-methoxy-[1,1'-biphenyl]-2-carboxamide (**1e**)

¹H NMR (400 MHz, CDCl₃)

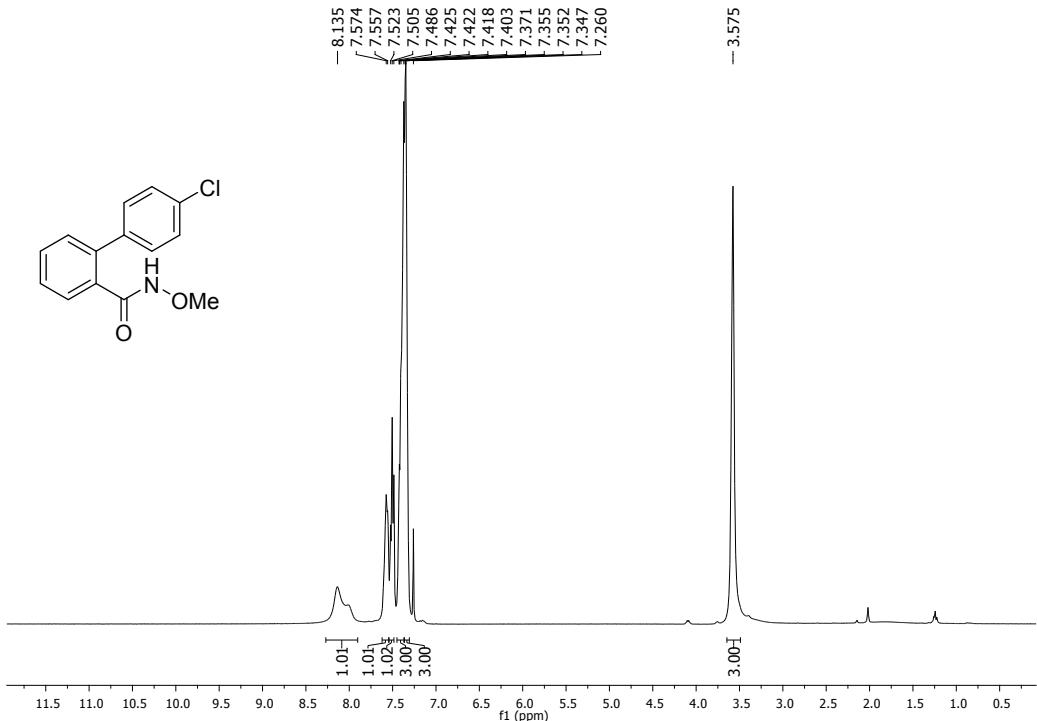


Figure S24. ¹H NMR spectrum of 4'-Chloro-N-methoxy-[1,1'-biphenyl]-2-carboxamide (**1f**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

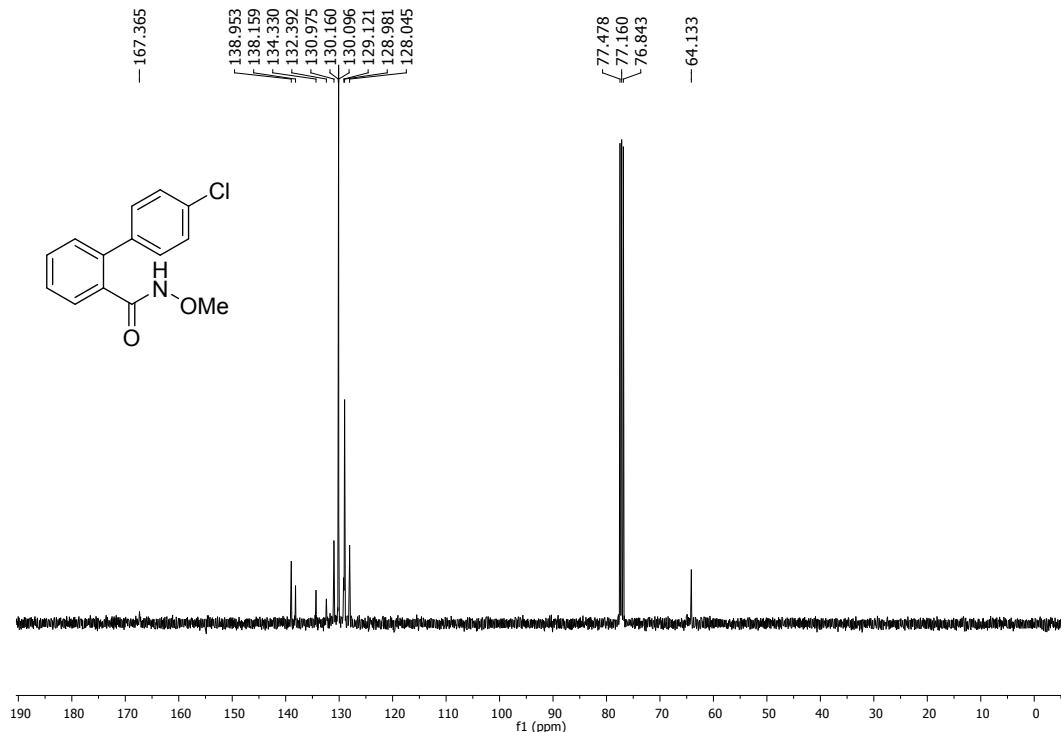


Figure S25. ¹³C{¹H} NMR spectrum of 4'-Chloro-N-methoxy-[1,1'-biphenyl]-2-carboxamide (**1f**)

¹H NMR (700 MHz, CDCl₃)

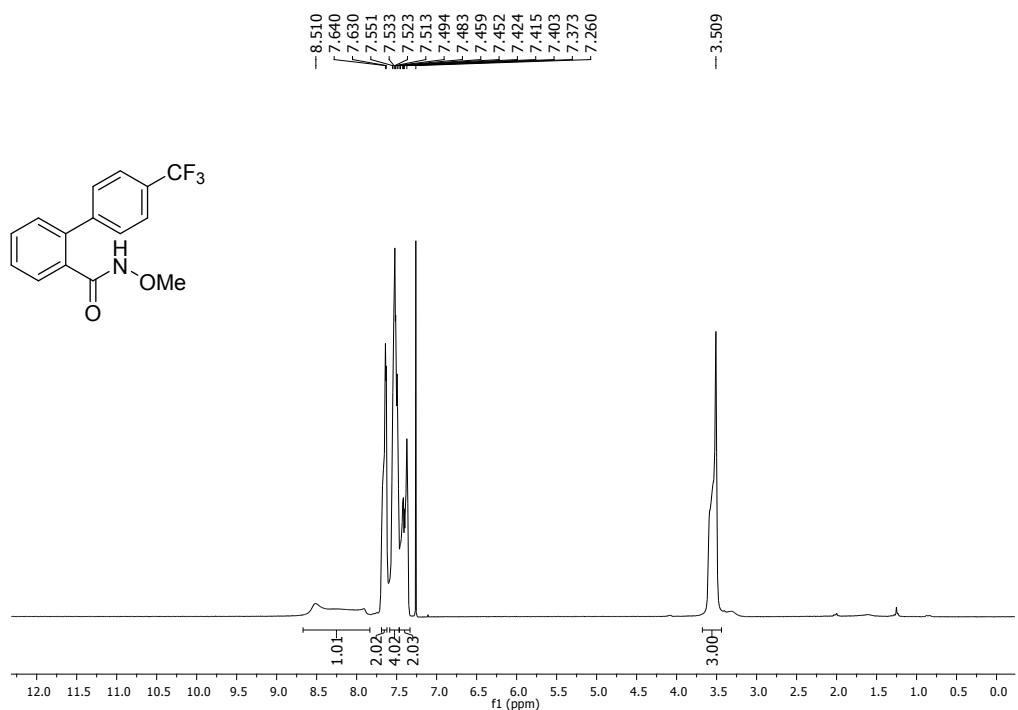


Figure S26. ¹H NMR spectrum of N-Methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (**1g**)

¹³C{¹H} NMR (175 MHz, CDCl₃)

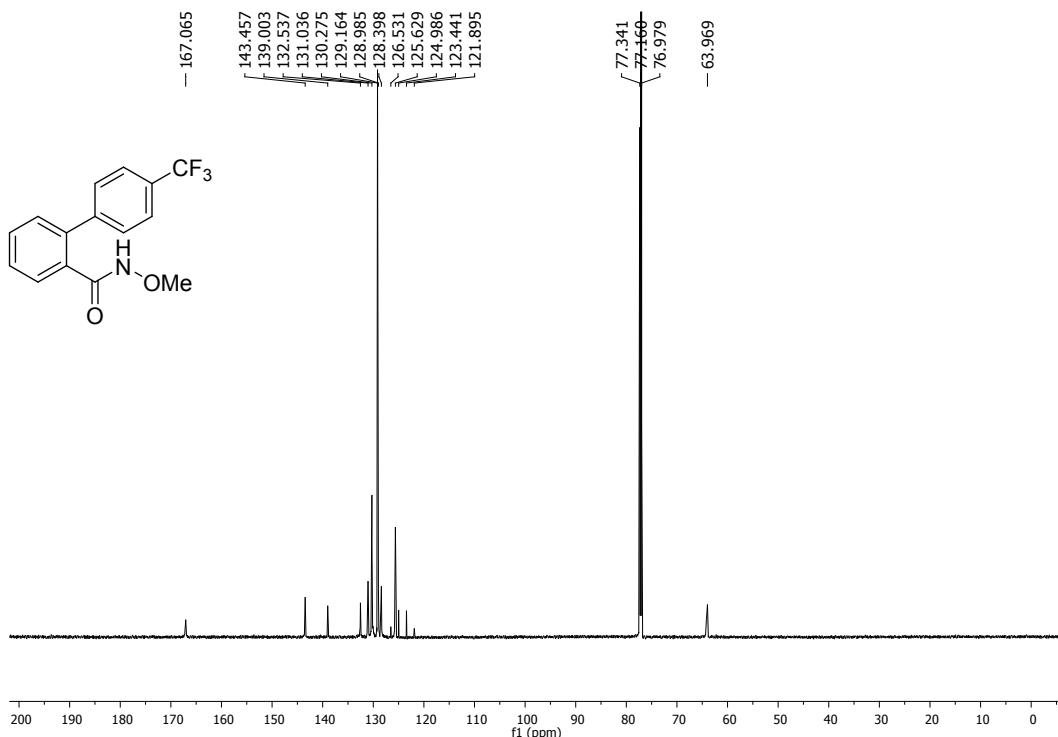


Figure S27. ¹³C{¹H} NMR spectrum of N-Methoxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (**1g**)

^1H NMR (400 MHz, CDCl_3)

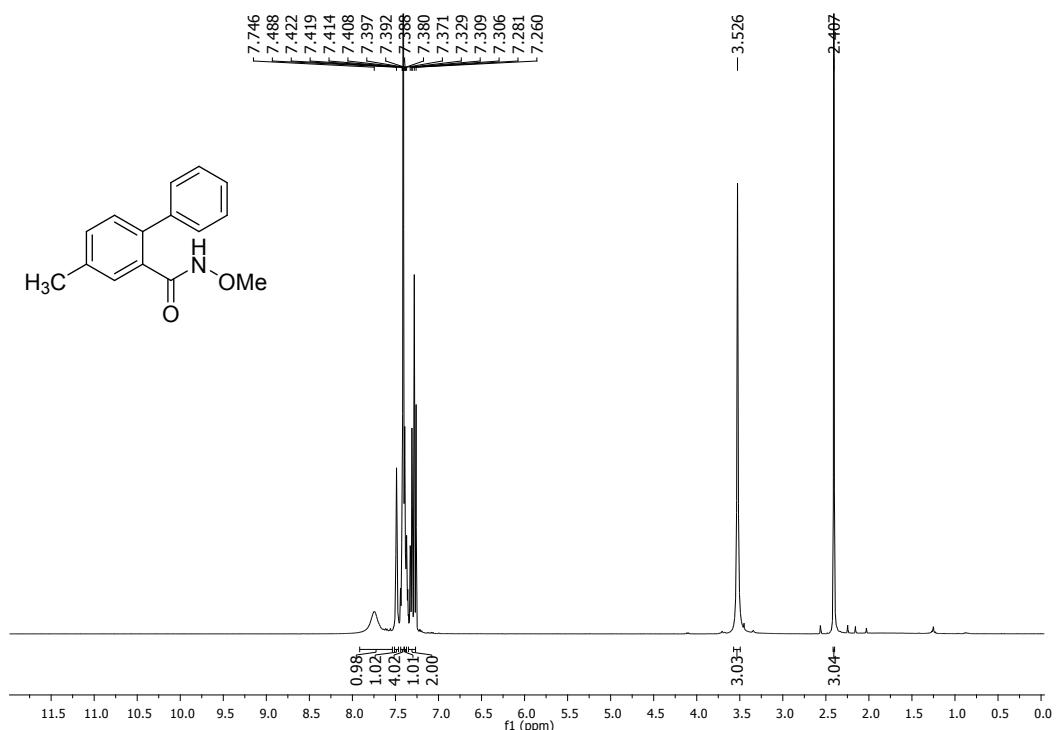


Figure S28. ^1H NMR spectrum of N-Methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1h**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

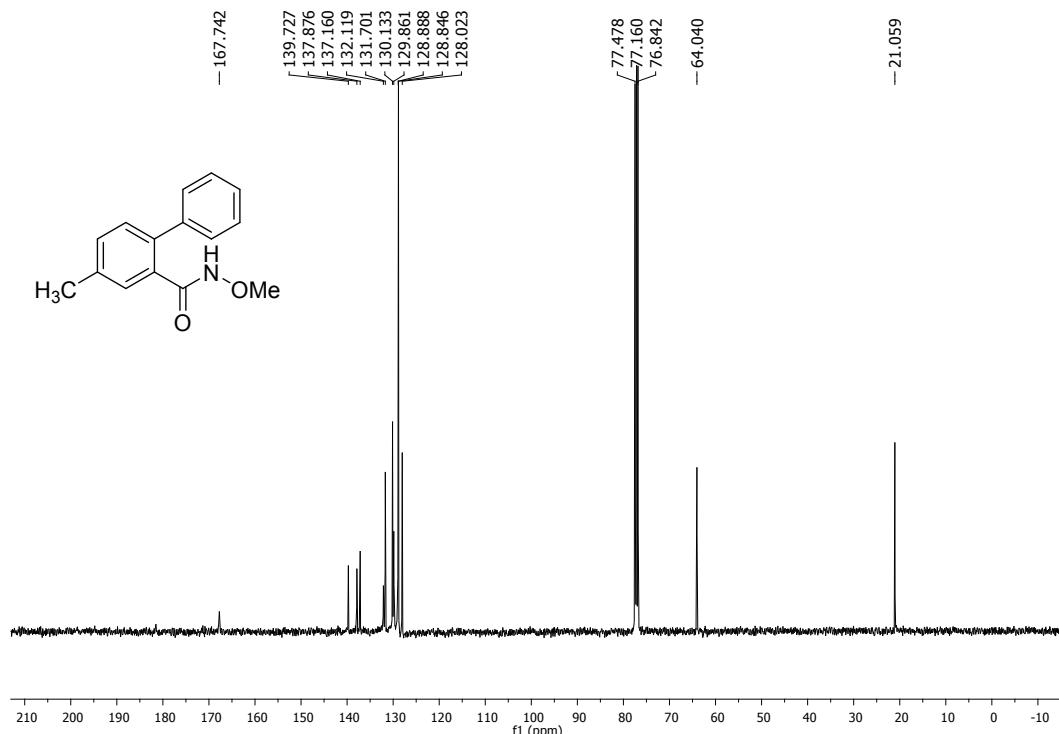


Figure S29. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of N-Methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1h**)

¹H NMR (400 MHz, CDCl₃)

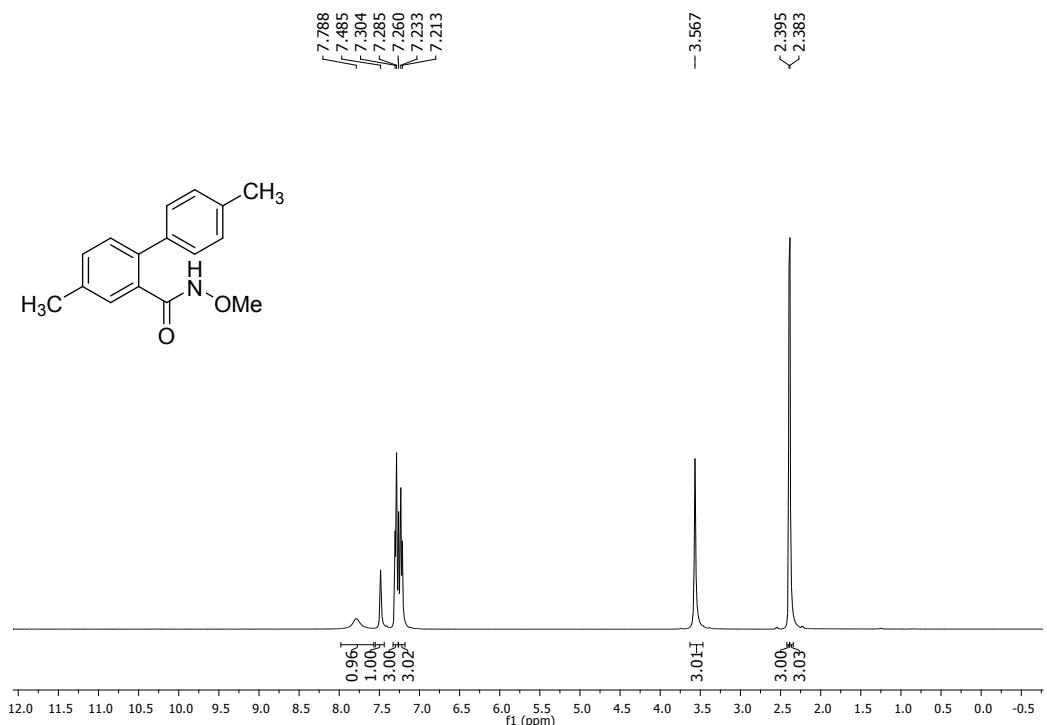


Figure S30. ¹H NMR spectrum of N-Methoxy-4,4'-dimethyl-[1,1'-biphenyl]-2-carboxamide (**1i**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

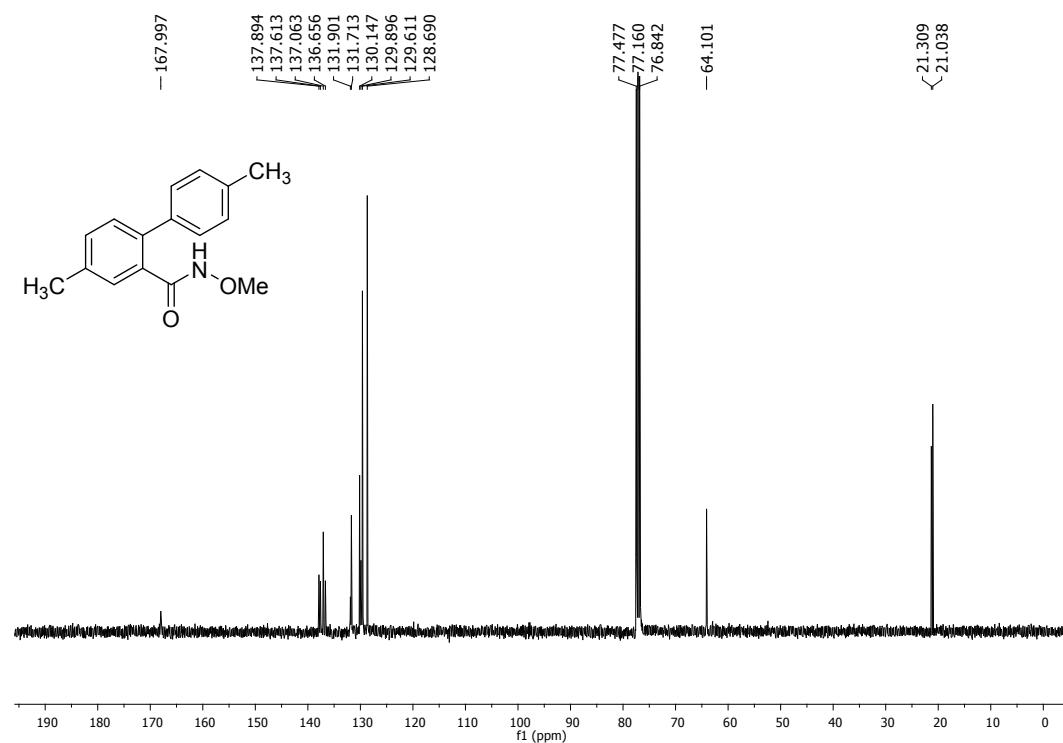


Figure S31. ¹³C{¹H} NMR spectrum of N-Methoxy-4,4'-dimethyl-[1,1'-biphenyl]-2-carboxamide (**1i**)

¹H NMR (400 MHz, CDCl₃)

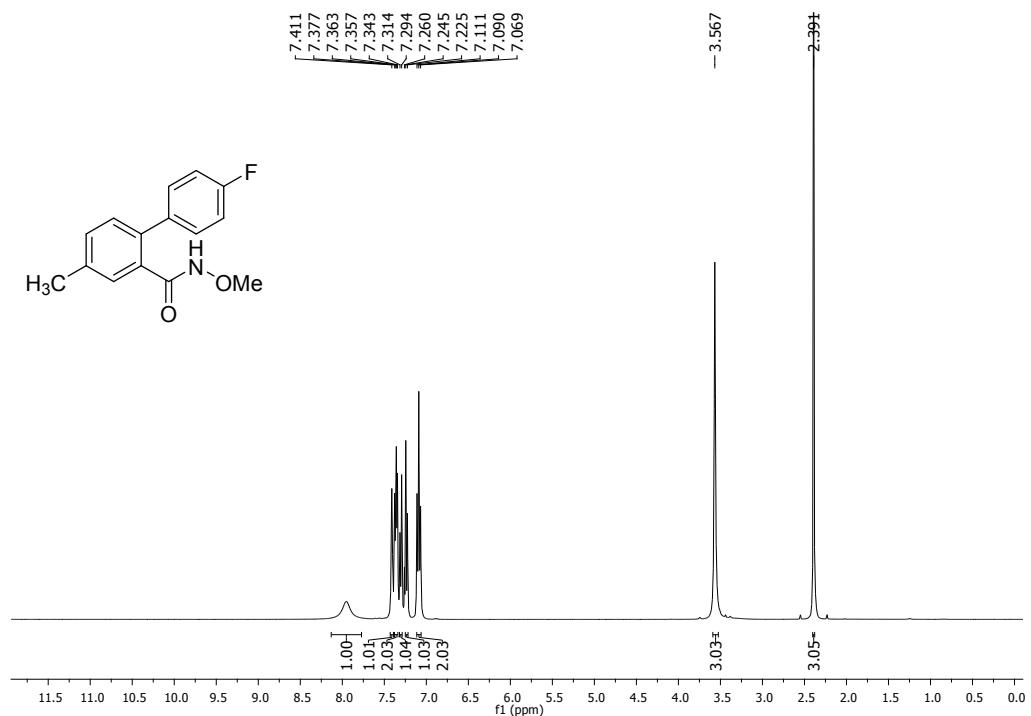


Figure S32. ¹H NMR spectrum of 4'-Fluoro-N-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1j**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

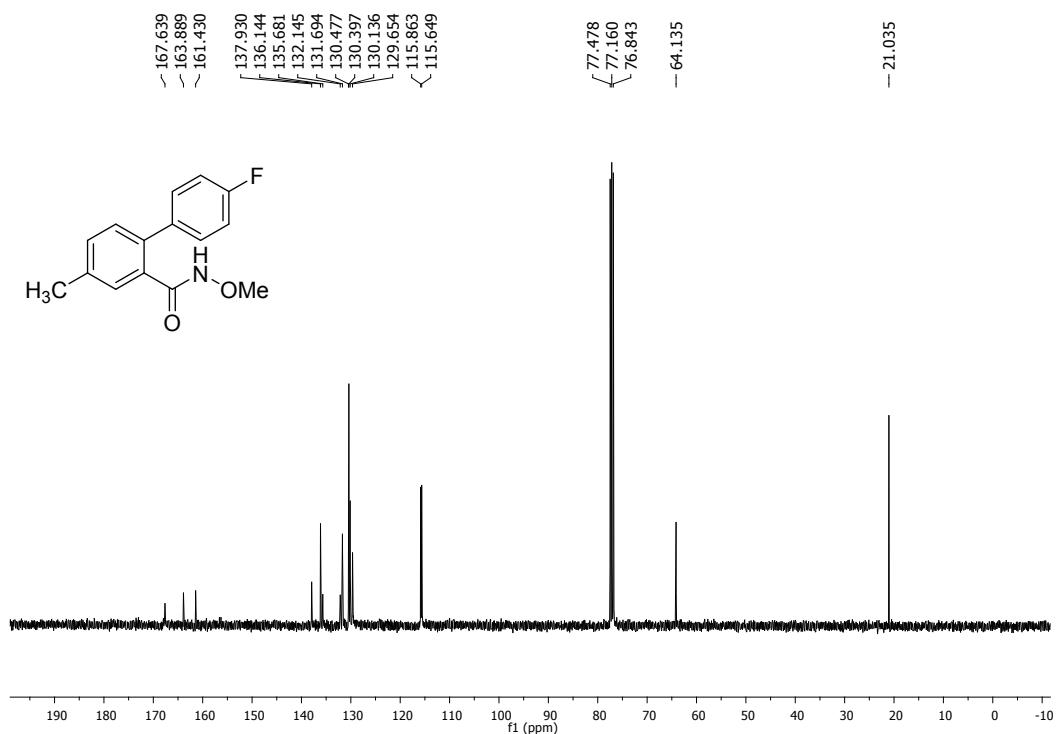


Figure S33. ¹³C{¹H}NMR spectrum of 4'-Fluoro-N-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1j**)

¹H NMR (400 MHz, CDCl₃)

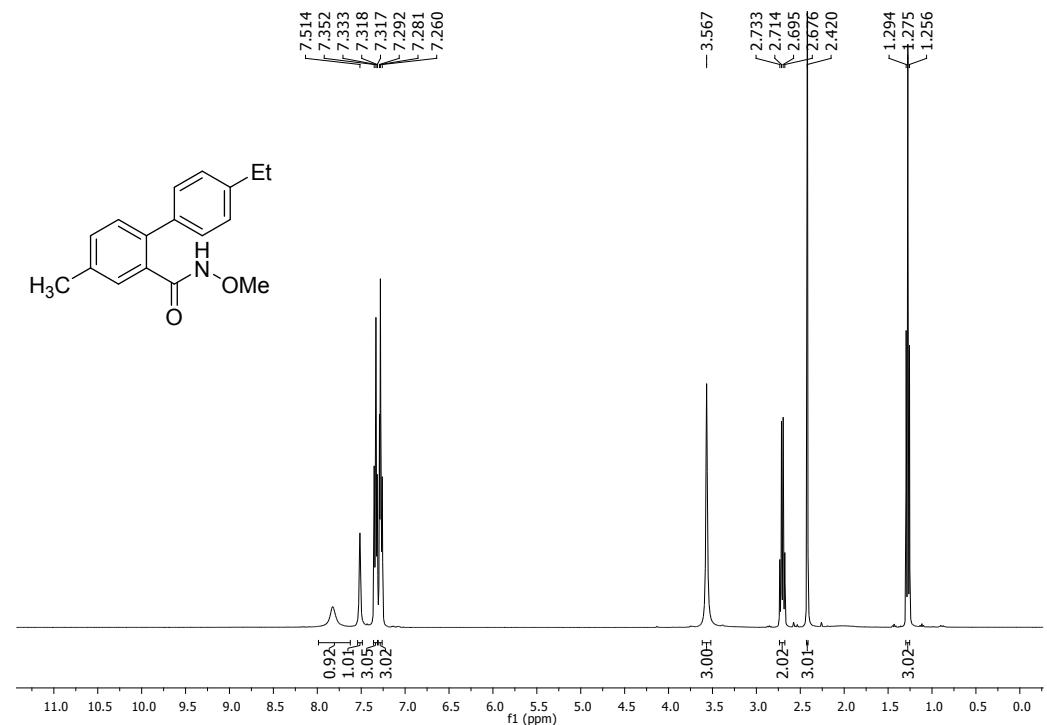


Figure S34. ¹H NMR spectrum of 4'-Ethyl-N-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1k**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

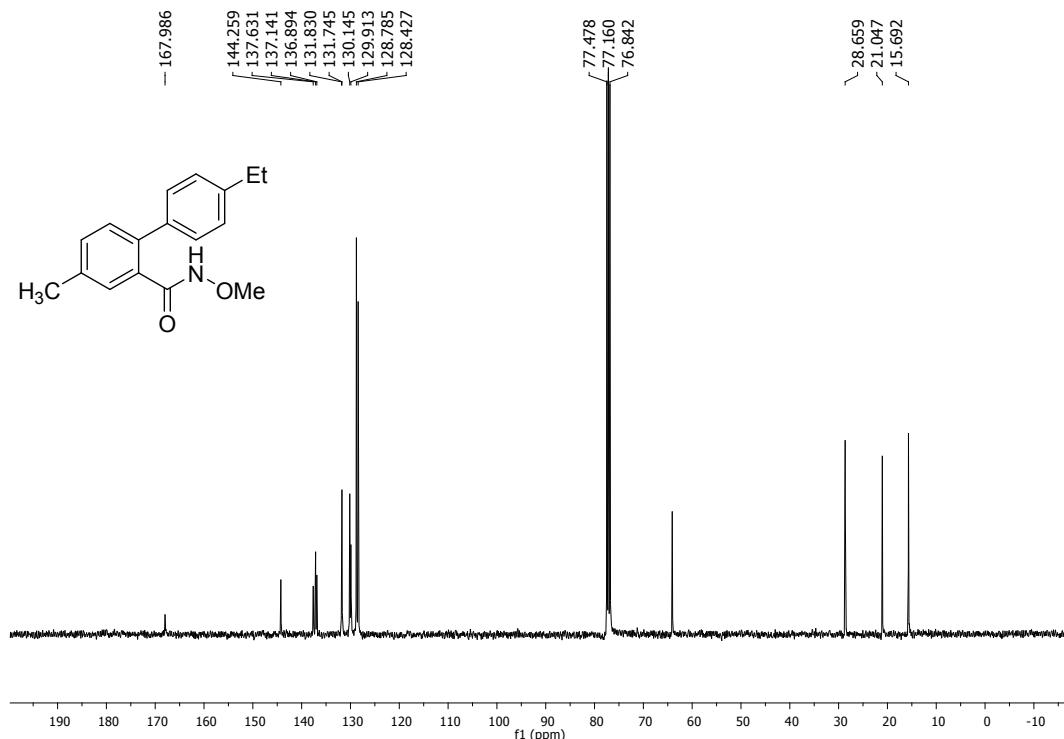


Figure S35. ¹³C{¹H} NMR spectrum of 4'-Ethyl-N-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1k**)

¹H NMR (400 MHz, CDCl₃)

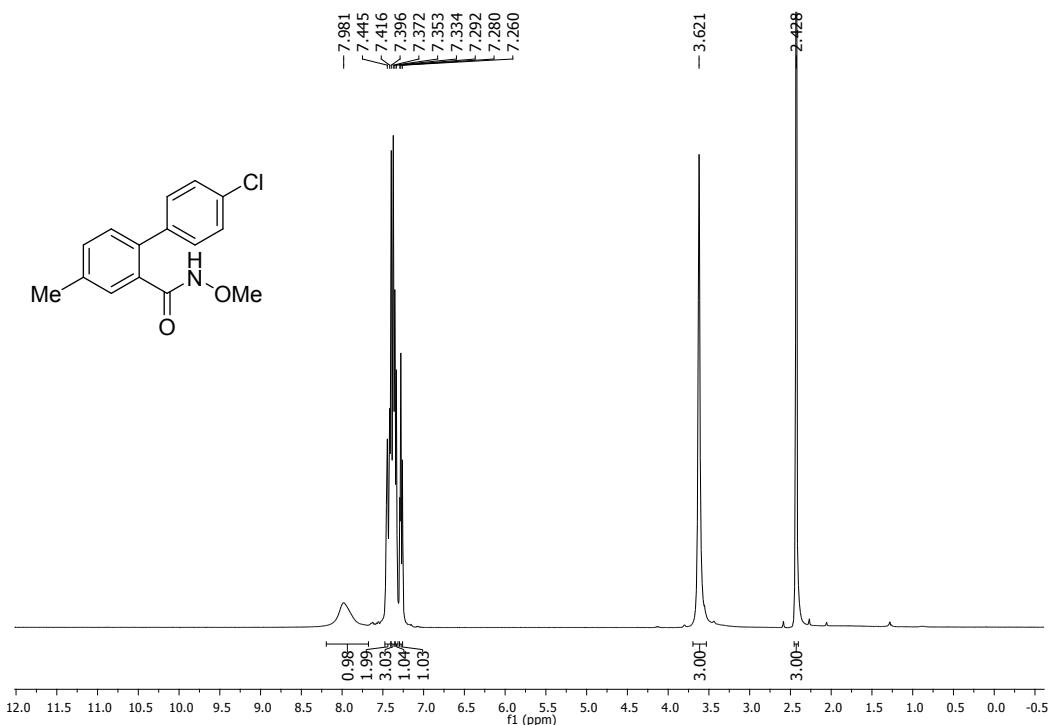


Figure S36. ¹H NMR spectrum of 4'-Chloro-N-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1l**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

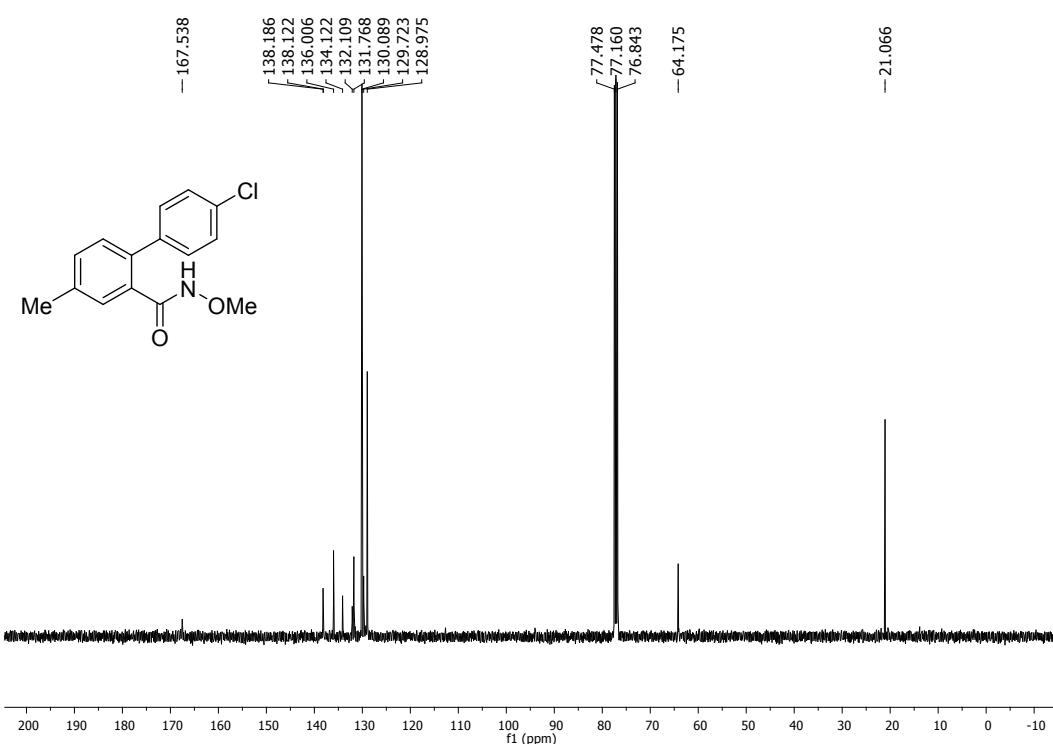


Figure S37. ¹³C{¹H} NMR spectrum of 4'-Chloro-N-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1l**)

¹H NMR (400 MHz, CDCl₃)

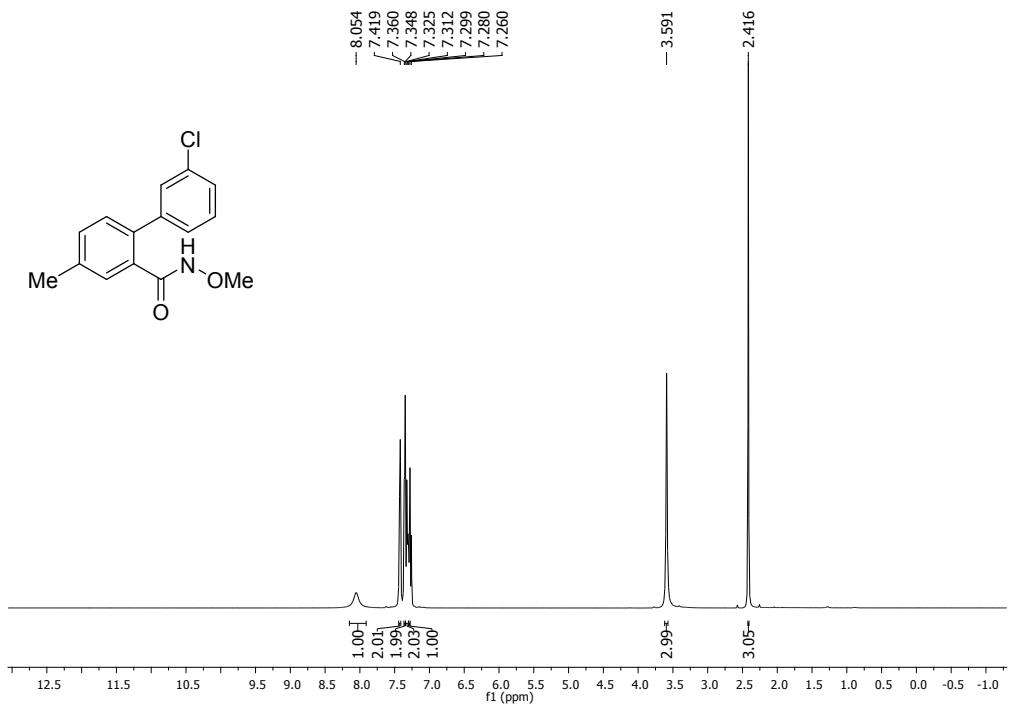


Figure S38. ¹H NMR spectrum of 3'-Chloro-N-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1m**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

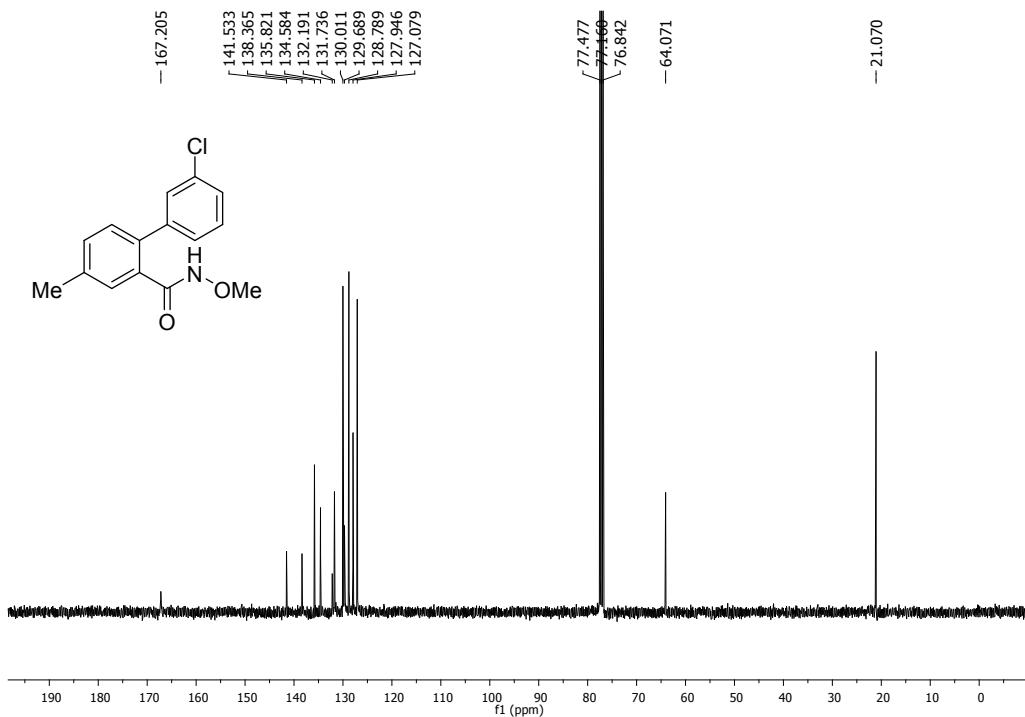


Figure S39. ¹³C{¹H} NMR spectrum of 3'-Chloro-N-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1m**)

¹H NMR (700 MHz, CDCl₃)

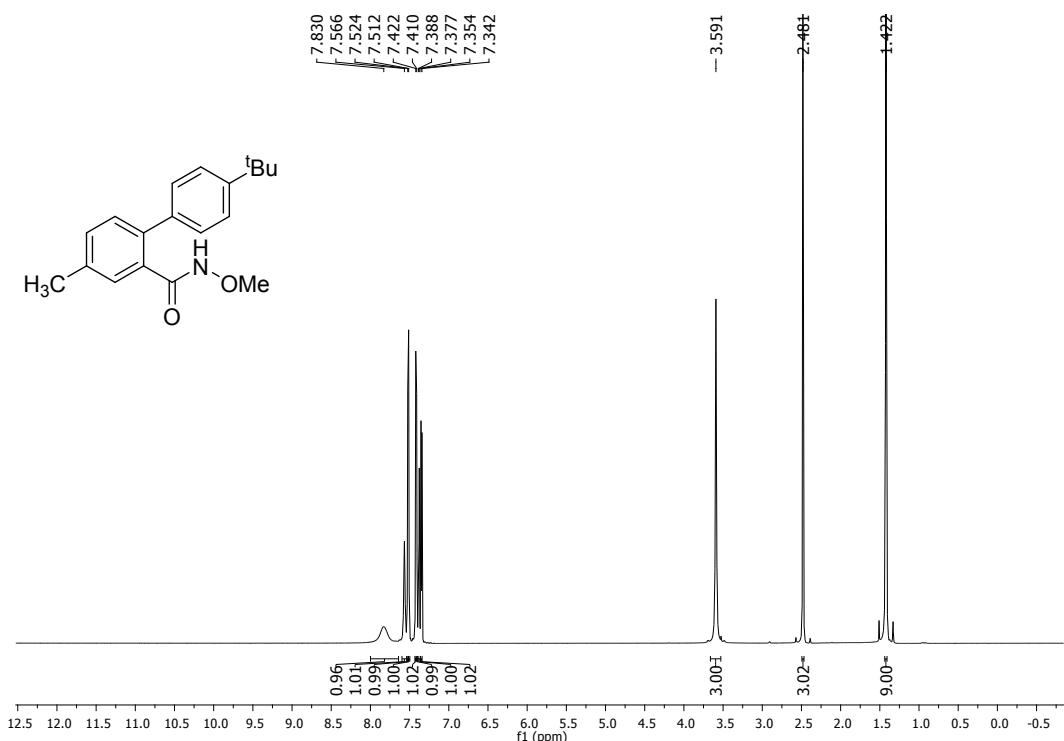


Figure S40. ¹H NMR spectrum of 4'-(Tert-butyl)-N-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1n**)

¹³C{¹H} NMR (175 MHz, CDCl₃)

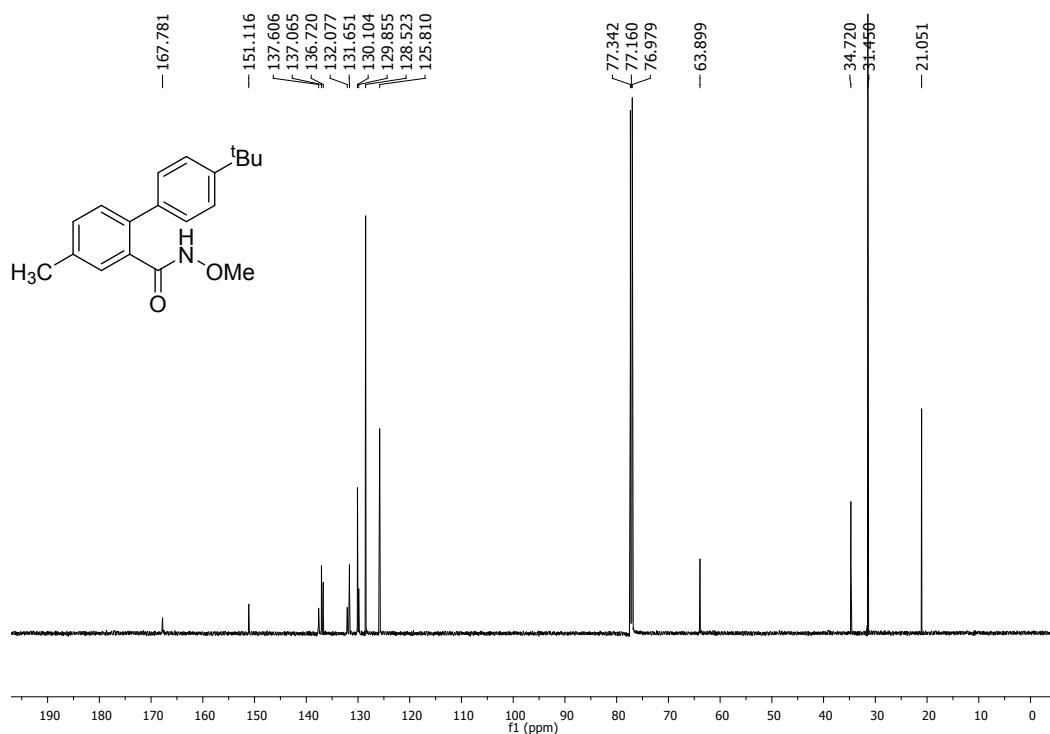


Figure S41. ¹³C{¹H} NMR spectrum of 4'-(Tert-butyl)-N-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxamide (**1n**)

^1H NMR (400 MHz, $\text{CDCl}_3 + \text{TFA-D}$)

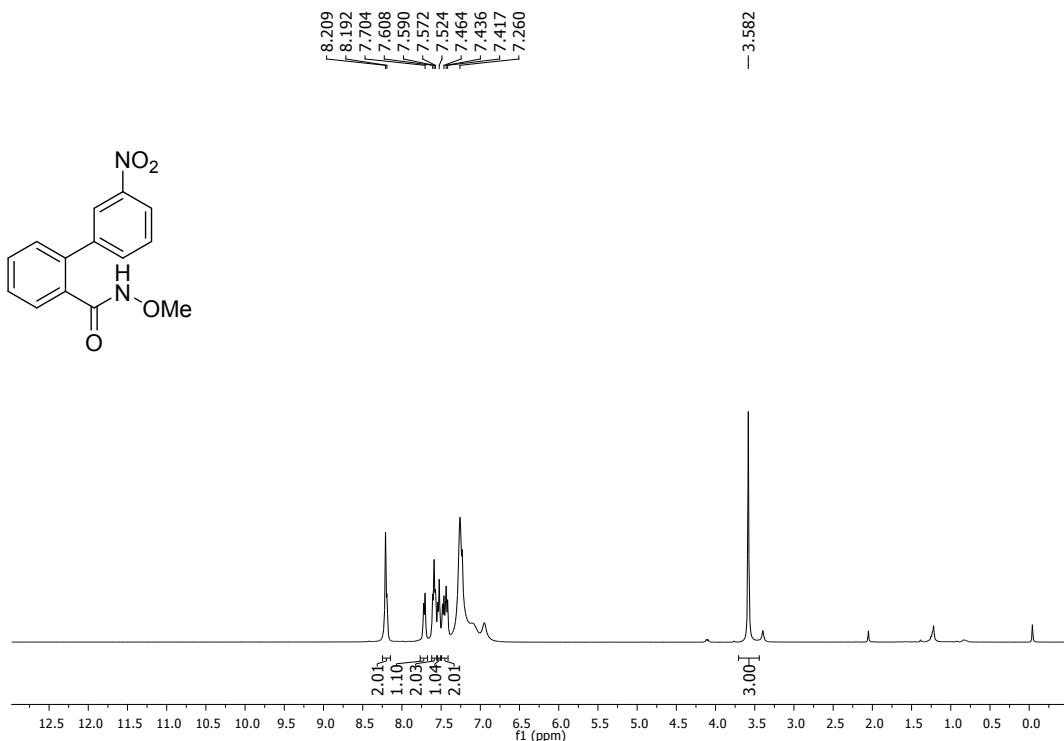


Figure S42. ^1H NMR spectrum of N-Methoxy-3'-nitro-[1,1'-biphenyl]-2-carboxamide (**1o**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{CDCl}_3 + \text{TFA-D}$)

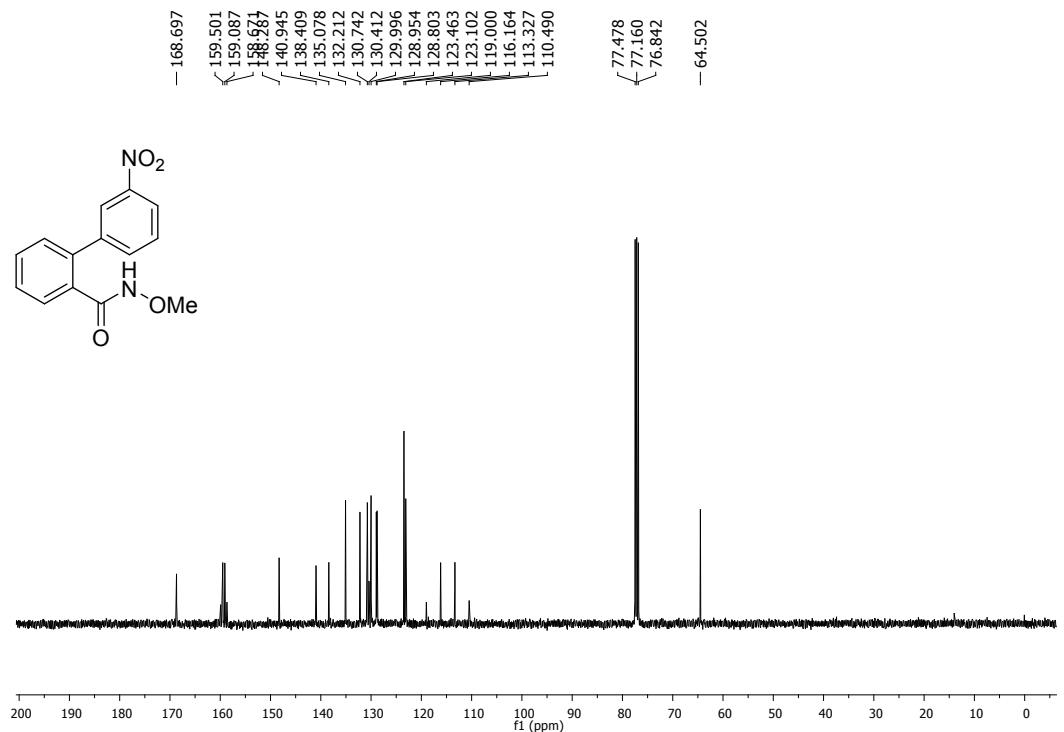


Figure S43. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of N-Methoxy-3'-nitro-[1,1'-biphenyl]-2-carboxamide (**1o**)

¹H NMR (400 MHz, CDCl₃)

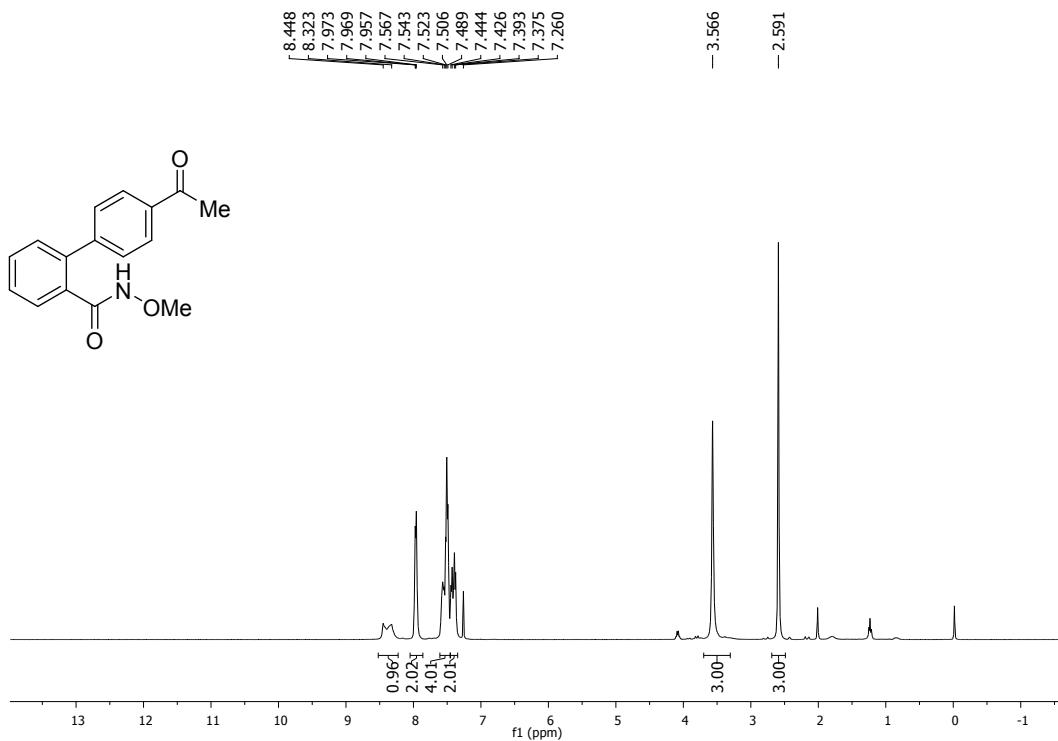


Figure S44. ^1H NMR spectrum of 4'-Acetyl-N-methoxy-[1,1'-biphenyl]-2-carboxamide (**1p**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

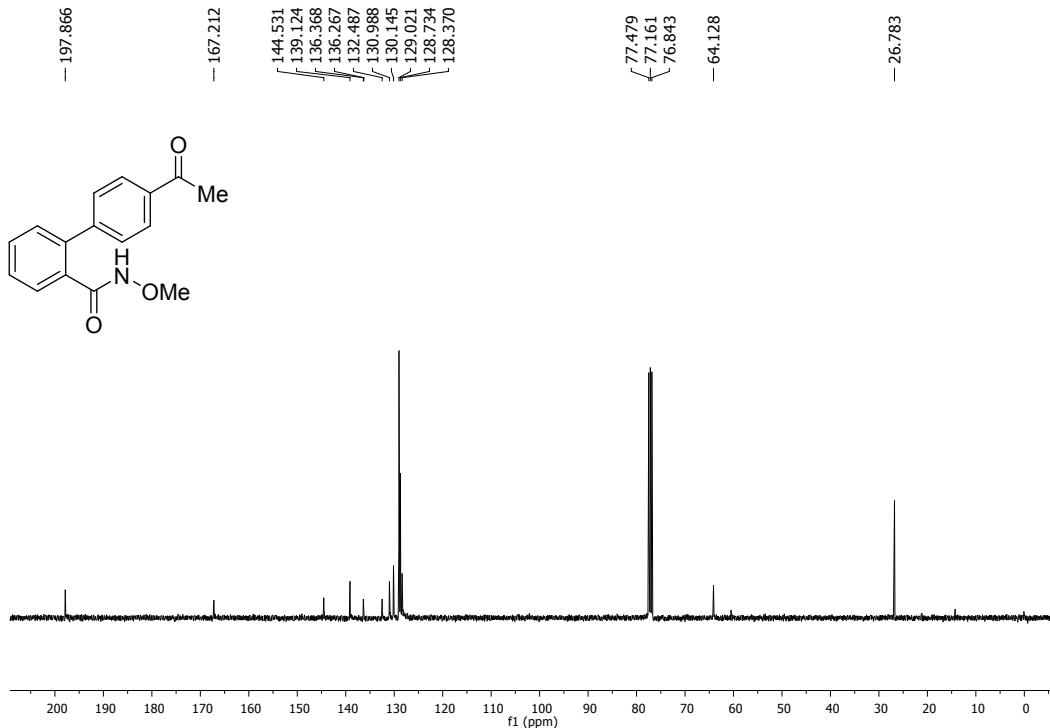


Figure S45. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of 4'-Acetyl-N-methoxy-[1,1'-biphenyl]-2-carboxamide (**1p**)

¹H NMR (400 MHz, CDCl₃)

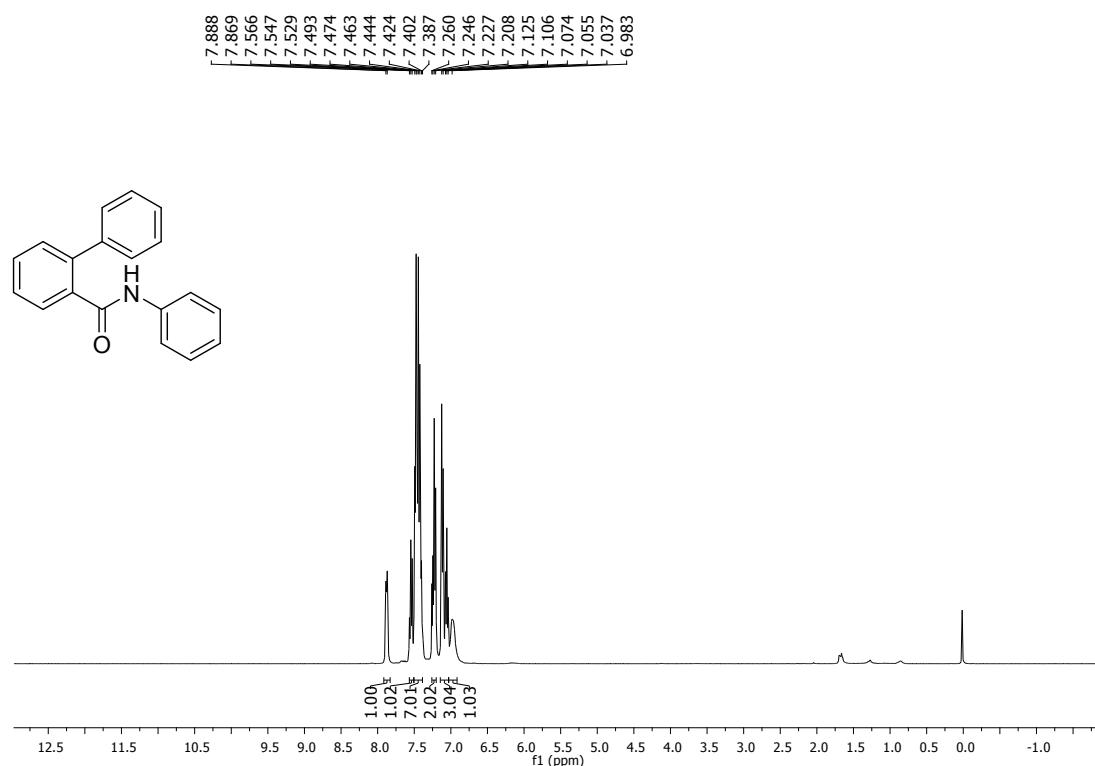


Figure S46. ¹H NMR spectrum of N-phenyl-[1,1'-biphenyl]-2-carboxamide (**1q**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

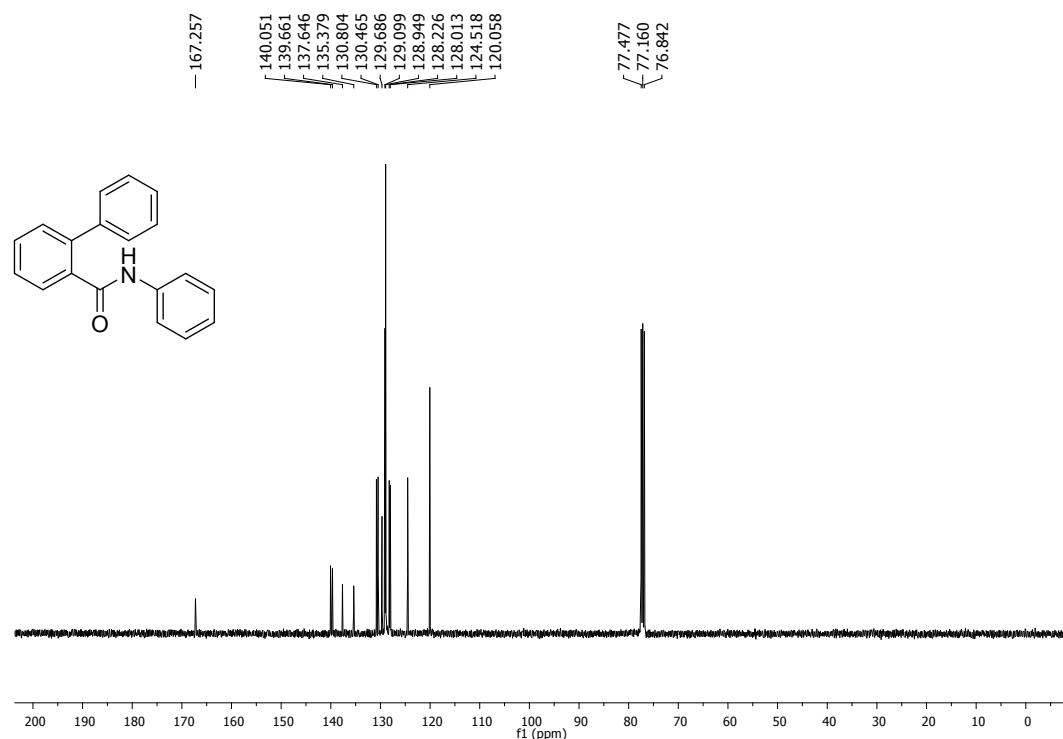


Figure S47. ¹³C{¹H} NMR spectrum of N-phenyl-[1,1'-biphenyl]-2-carboxamide (**1q**)

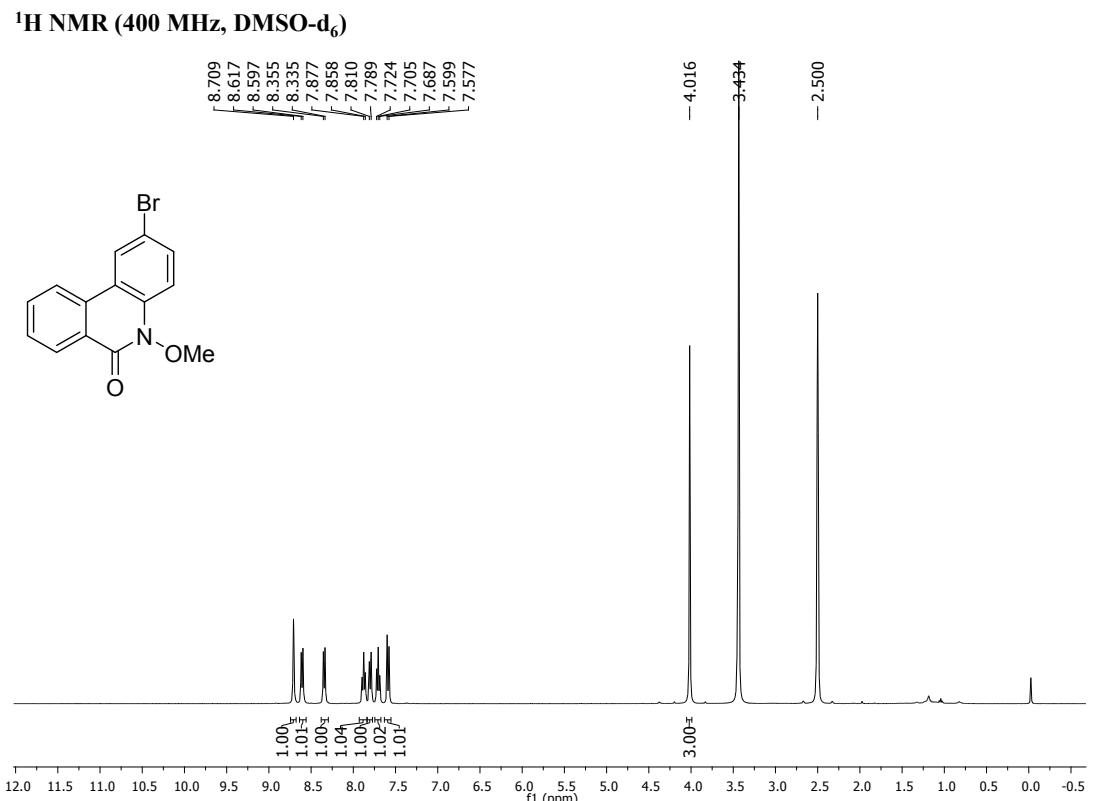


Figure S48. ^1H NMR spectrum of 2-Bromo-5-methoxyphenanthridin-6(5H)-one (**3a**)

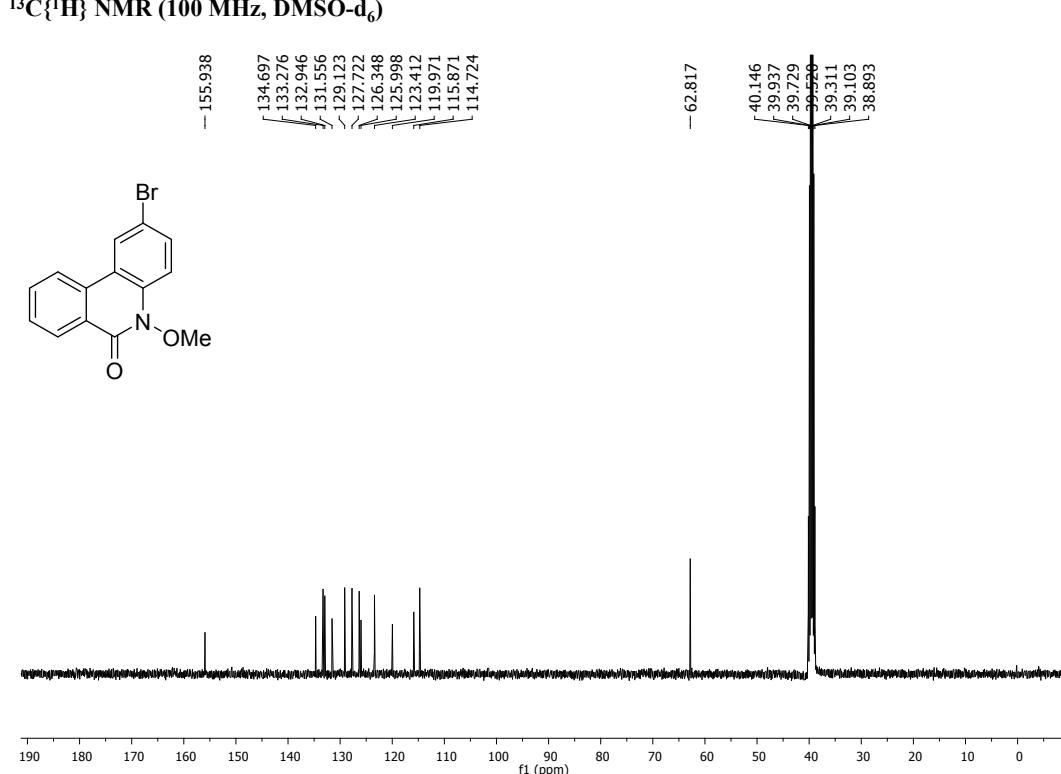


Figure S49. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of 2-Bromo-5-methoxyphenanthridin-6(5H)-one (**3a**)

¹H NMR (400 MHz, CDCl₃)

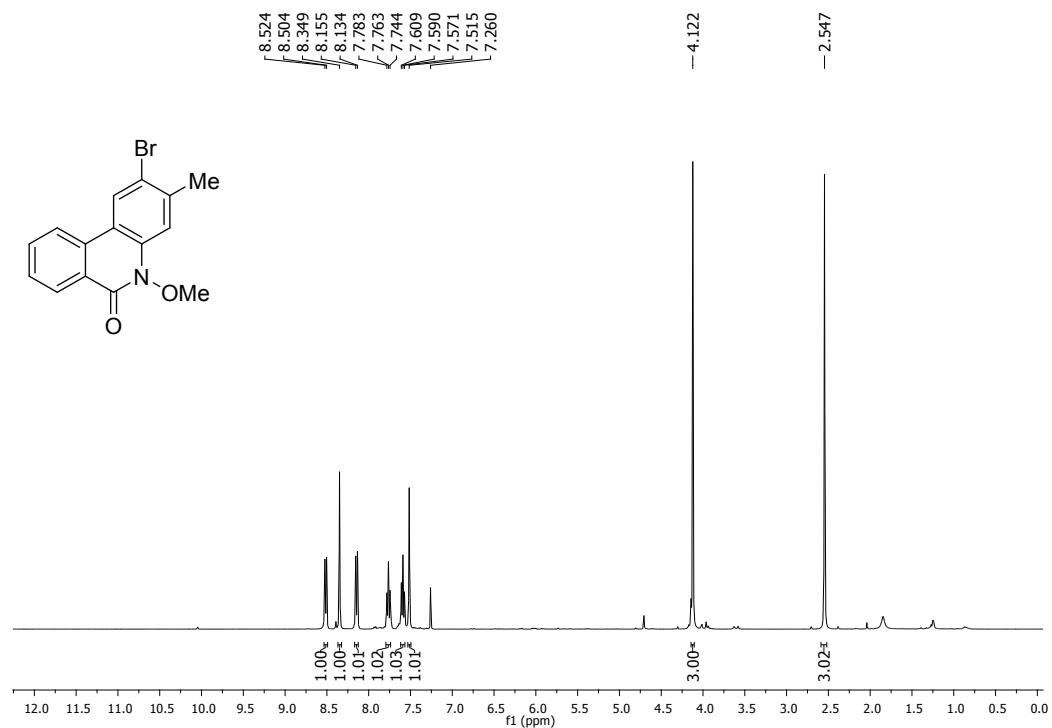


Figure S50. ¹H NMR spectrum of 2-Bromo-5-methoxy-3-methylphenanthridin-6(5H)-one (3b)

¹³C{¹H} NMR (100 MHz, CDCl₃)

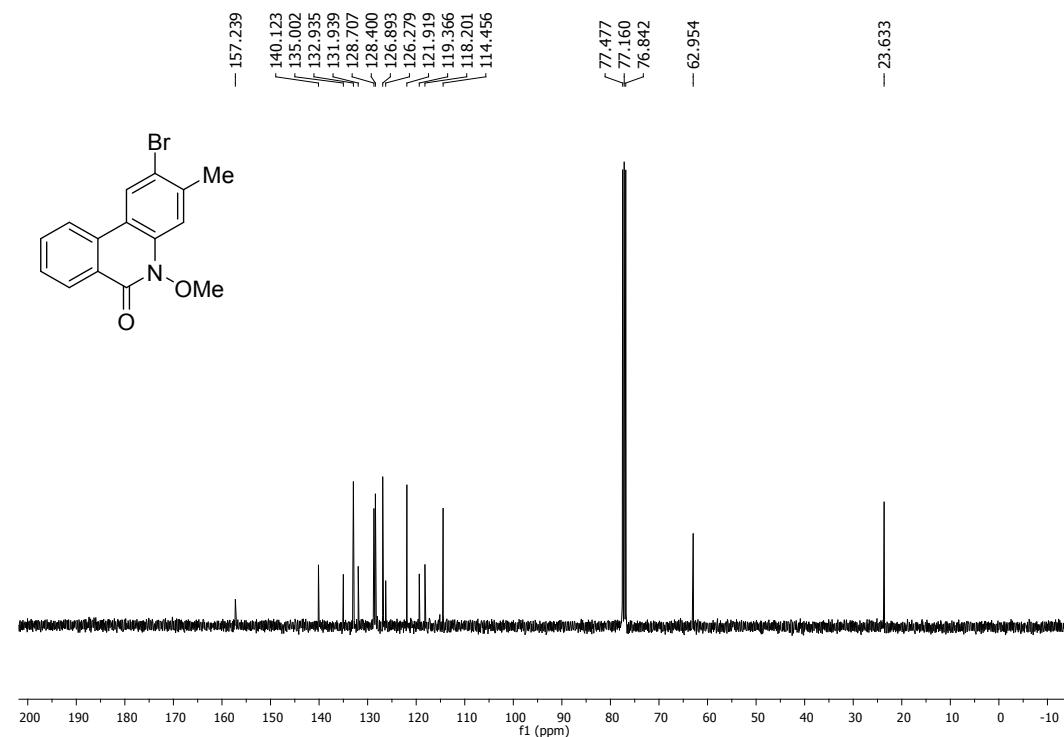


Figure S51. ¹³C{¹H} NMR spectrum of 2-Bromo-5-methoxy-3-methylphenanthridin-6(5H)-one (3b)

¹H NMR (400 MHz, CDCl₃)

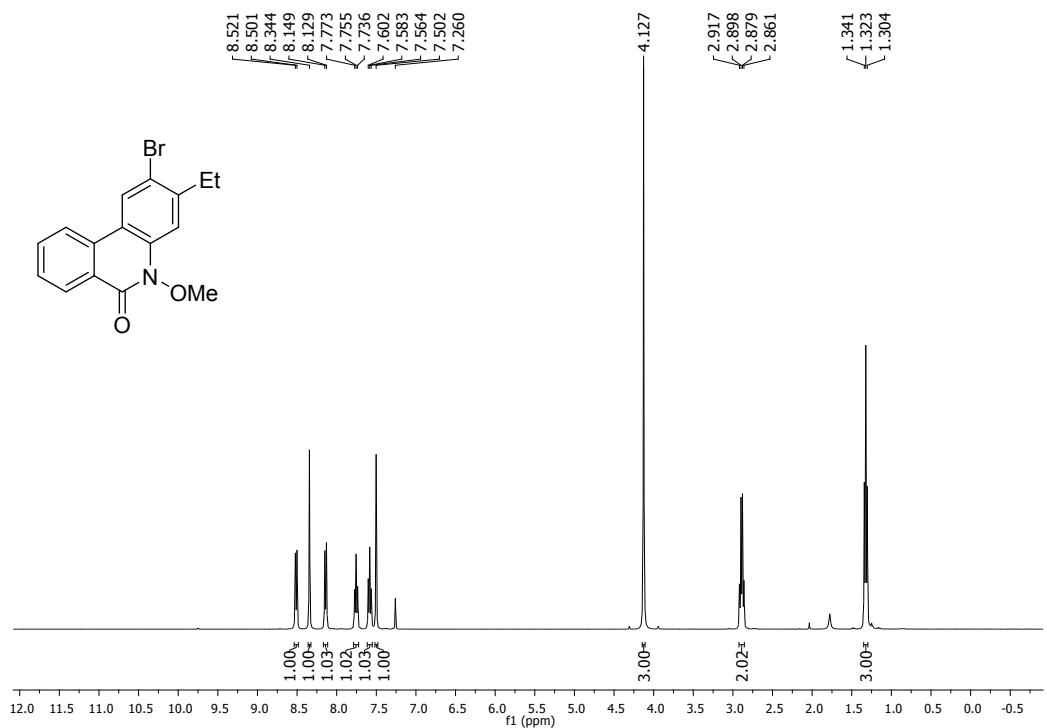


Figure S52. ¹H NMR spectrum of 2-Bromo-3-ethyl-5-methoxyphenanthridin-6(5H)-one (3c)

¹³C{¹H} NMR (100 MHz, CDCl₃)

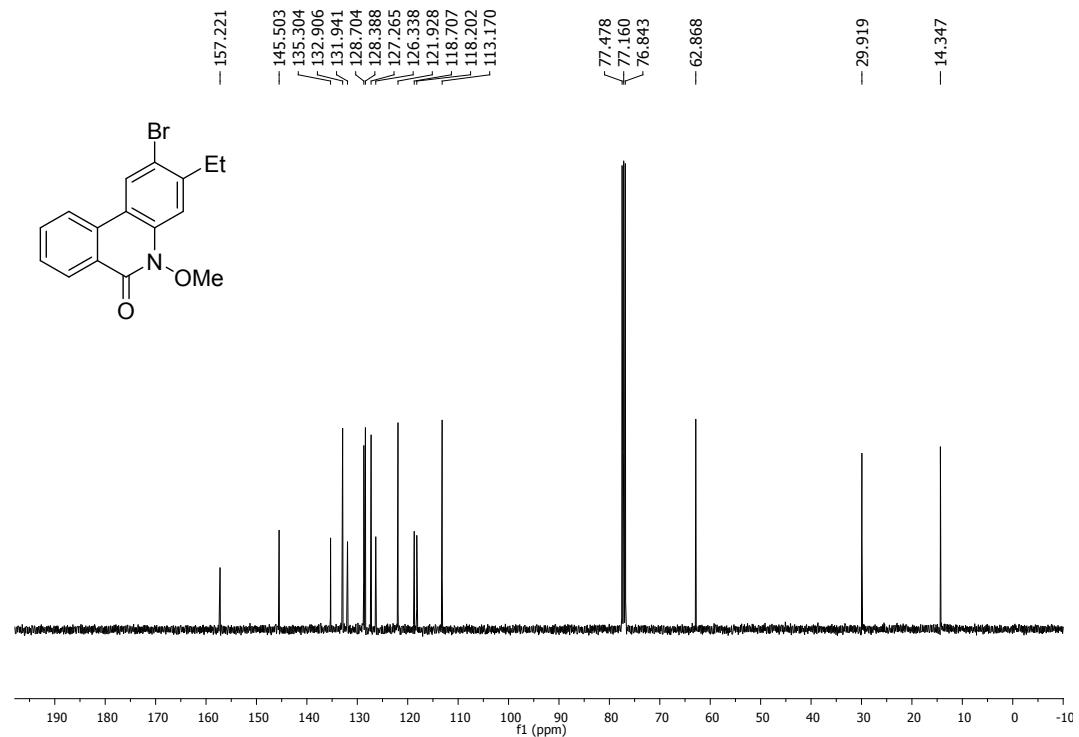


Figure S53. ¹³C{¹H} NMR spectrum of 2-Bromo-3-ethyl-5-methoxyphenanthridin-6(5H)-one (3c)

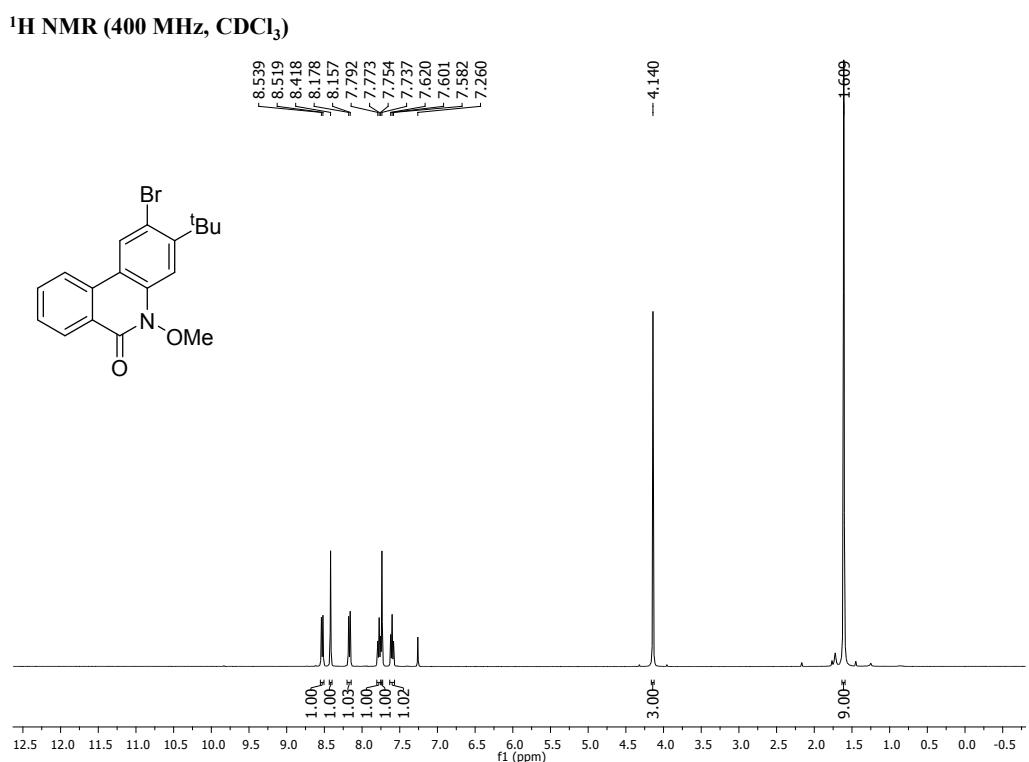


Figure S54. ^1H NMR spectrum of 2-Bromo-3-(tert-butyl)-5-methoxyphenanthridin-6(5H)-one (**3d**)

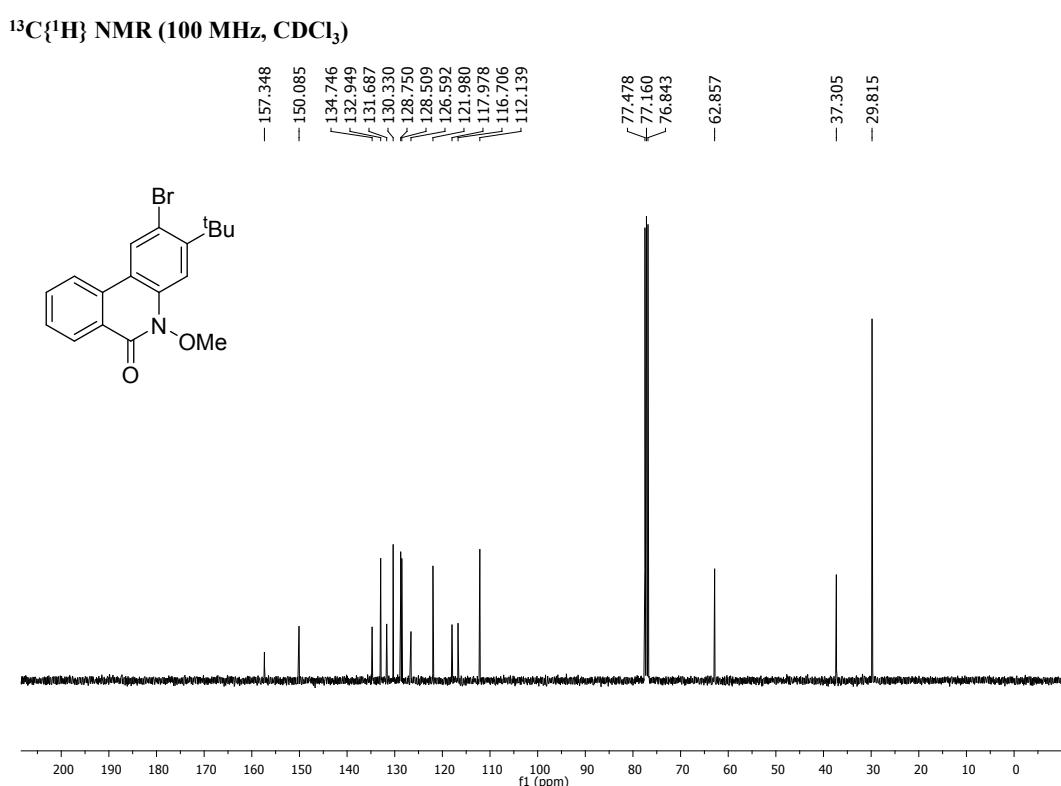


Figure S55. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of 2-Bromo-3-(tert-butyl)-5-methoxyphenanthridin-6(5H)-one (**3d**)

^1H NMR (400 MHz, DMSO-d₆)

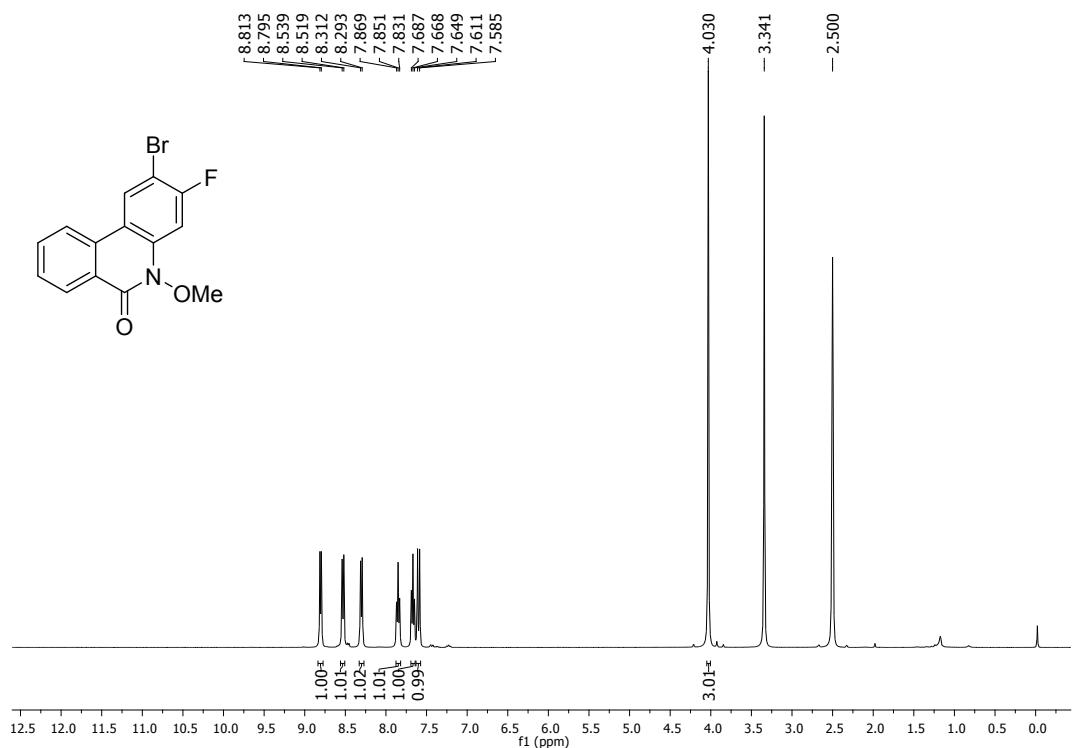


Figure S56. ^1H NMR spectrum of 2-Bromo-3-fluoro-5-methoxyphenanthridin-6(5H)-one (**3e**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-d₆)

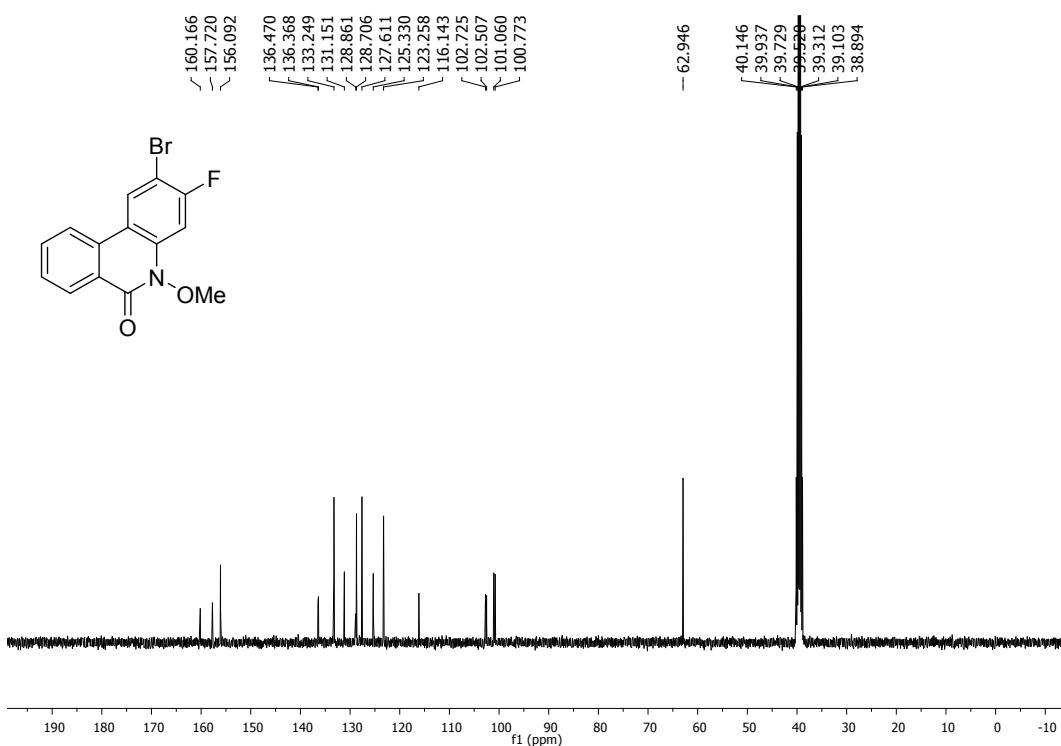


Figure S57. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-Bromo-3-fluoro-5-methoxyphenanthridin-6(5H)-one (**3e**)

¹H NMR (400 MHz, DMSO- d₆)

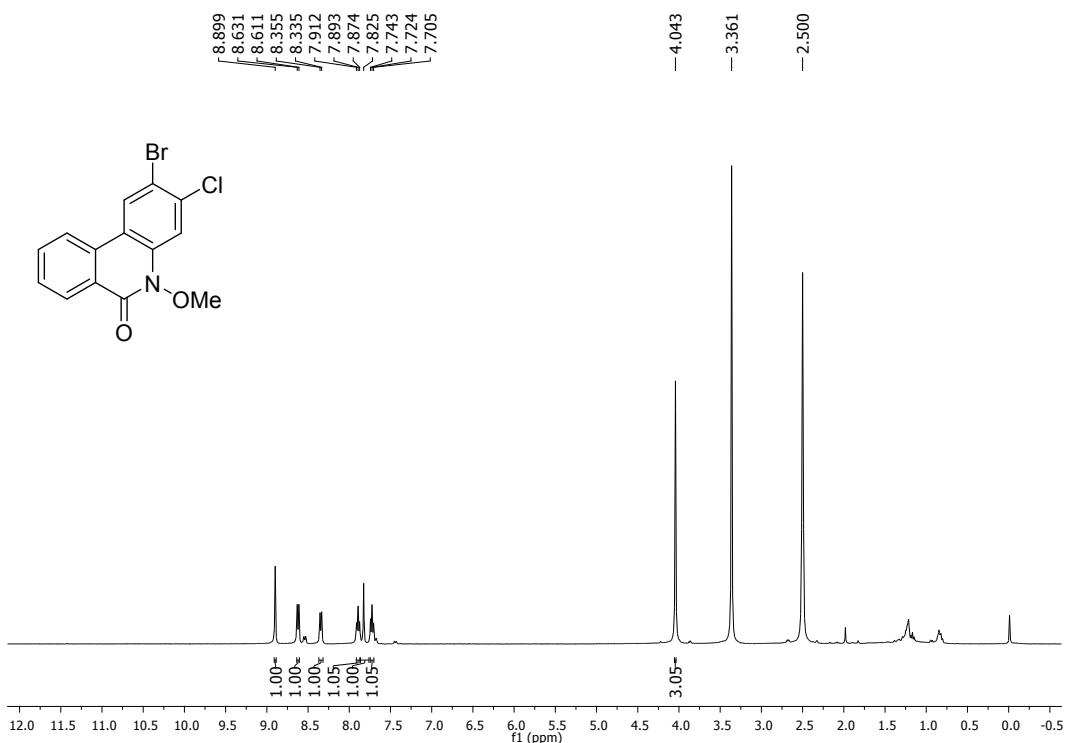


Figure S58. ¹H NMR spectrum of 2-Bromo-3-chloro-5-methoxyphenanthridin-6(5H)-one (**3f**)

¹³C{¹H} NMR (100 MHz, DMSO- d₆)

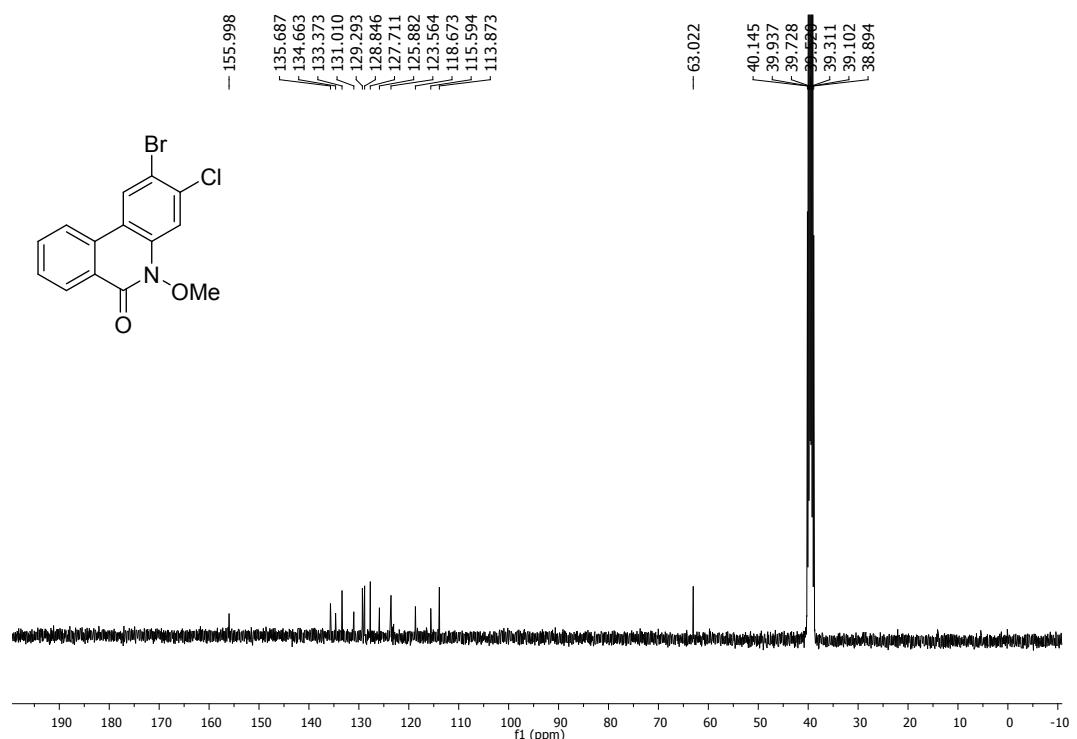


Figure S59. ¹³C{¹H} NMR spectrum of 2-Bromo-3-chloro-5-methoxyphenanthridin-6(5H)-one (**3f**)

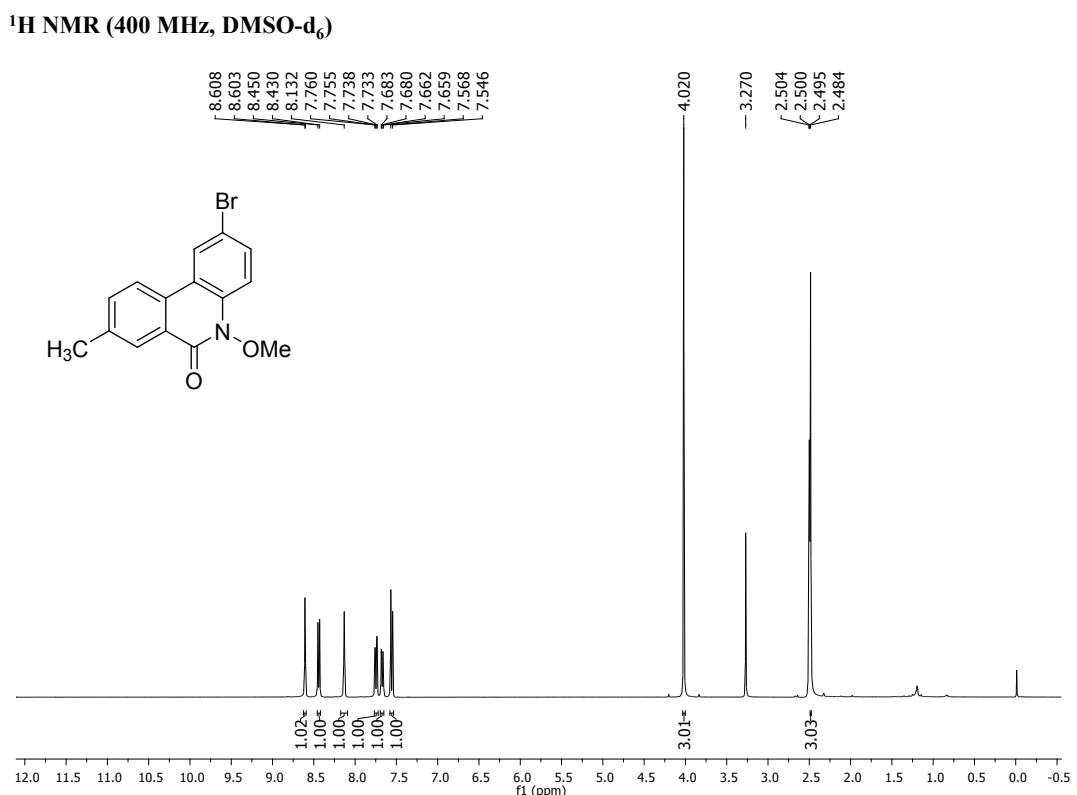


Figure S60. ^1H NMR spectrum of 2-Bromo-5-methoxy-8-methylphenanthridin-6(5H)-one (**3h**)

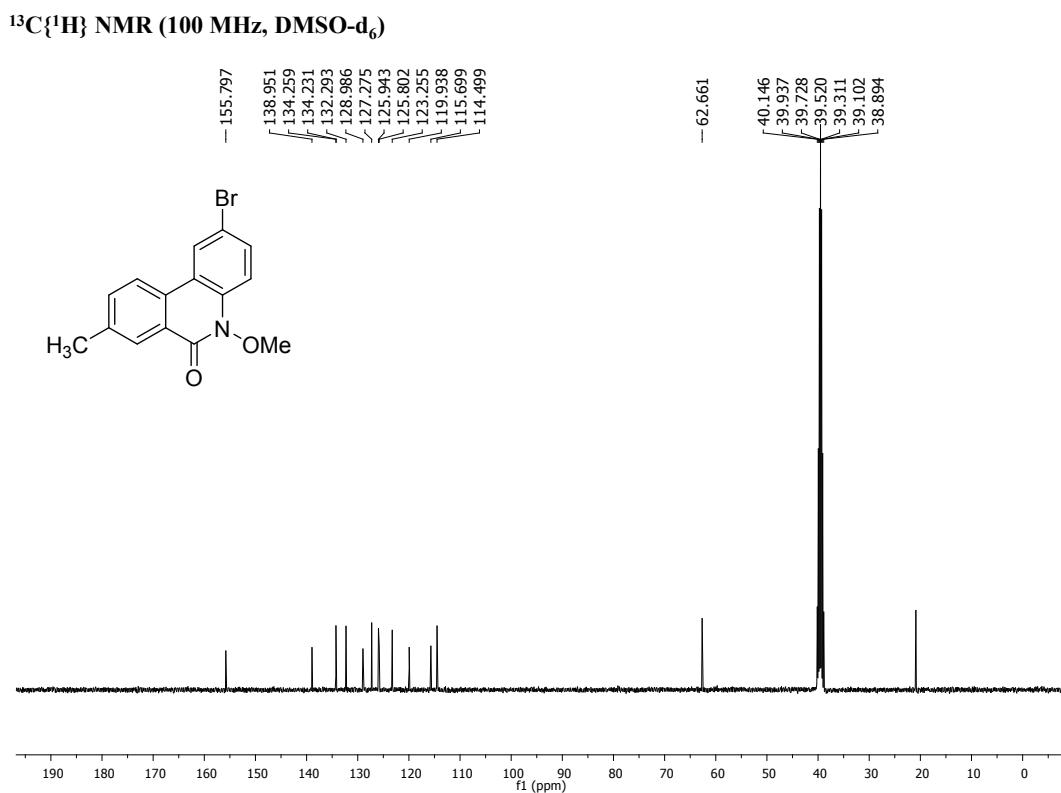


Figure S61. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of 2-Bromo-5-methoxy-8-methylphenanthridin-6(5H)-one (**3h**)

¹H NMR (400 MHz, CDCl₃ + DMSO-d₆)

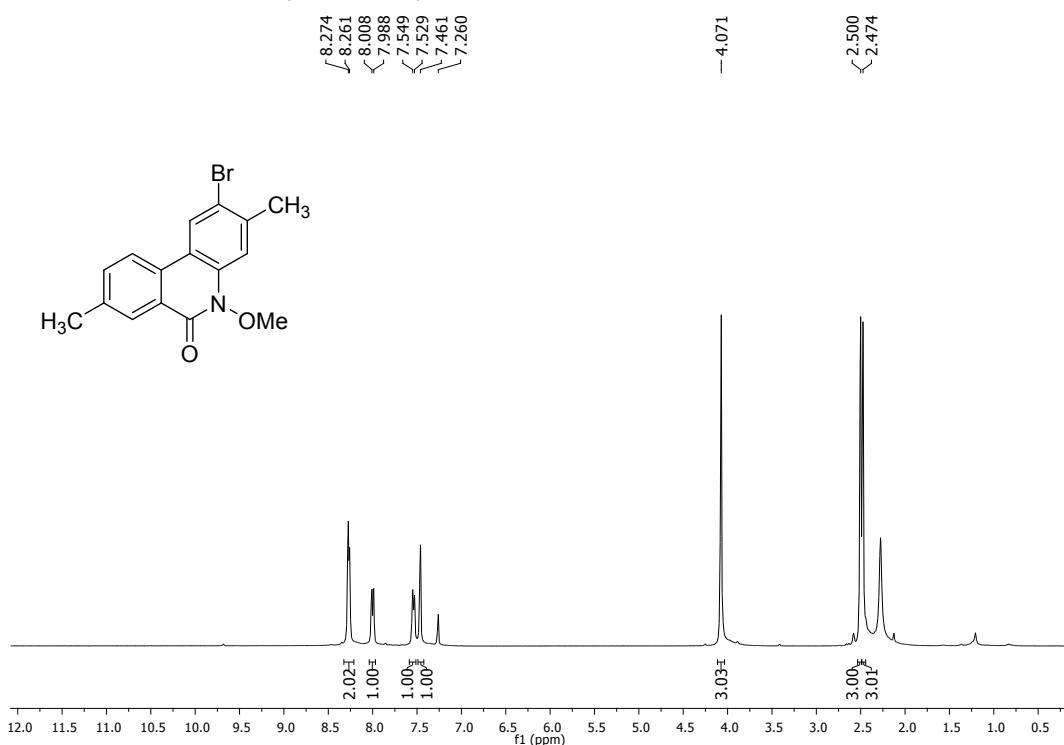


Figure S62. ¹H NMR spectrum of 2-Bromo-5-methoxy-3,8-dimethylphenanthridin-6(5H)-one (**3i**)

¹³C{¹H} NMR (100 MHz, CDCl₃ + DMSO-d₆)

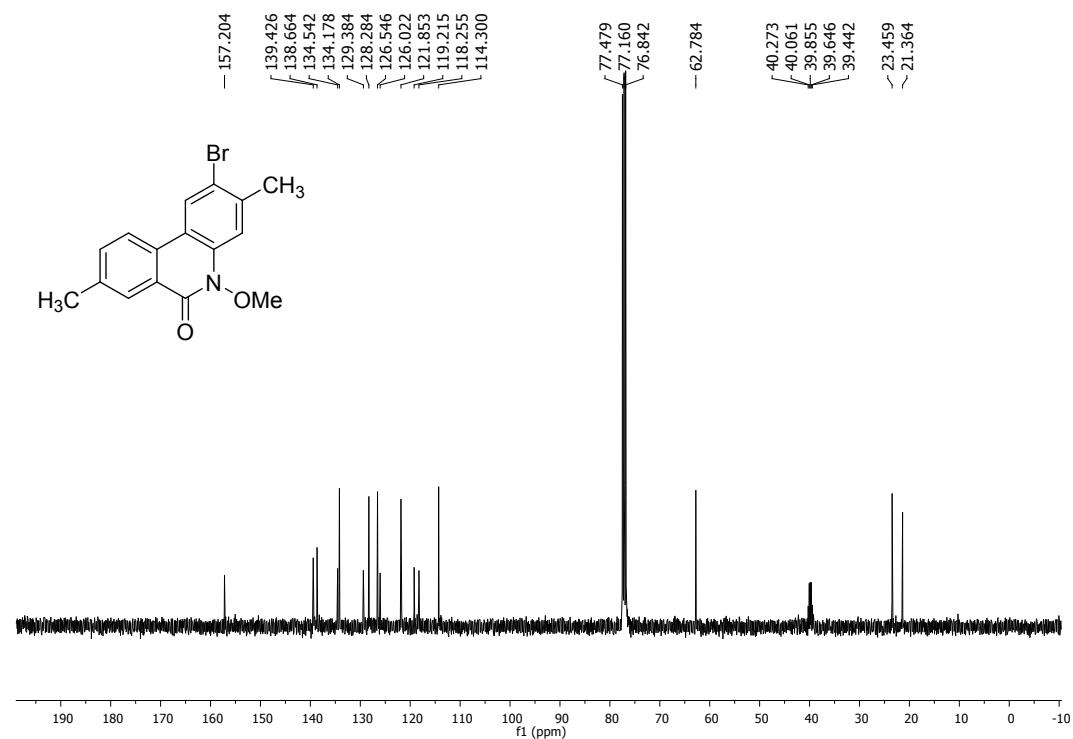


Figure S63. ¹³C{¹H} NMR spectrum of 2-Bromo-5-methoxy-3,8-dimethylphenanthridin-6(5H)-one (**3i**)

¹H NMR (400 MHz, CDCl₃ + DMSO-d₆)

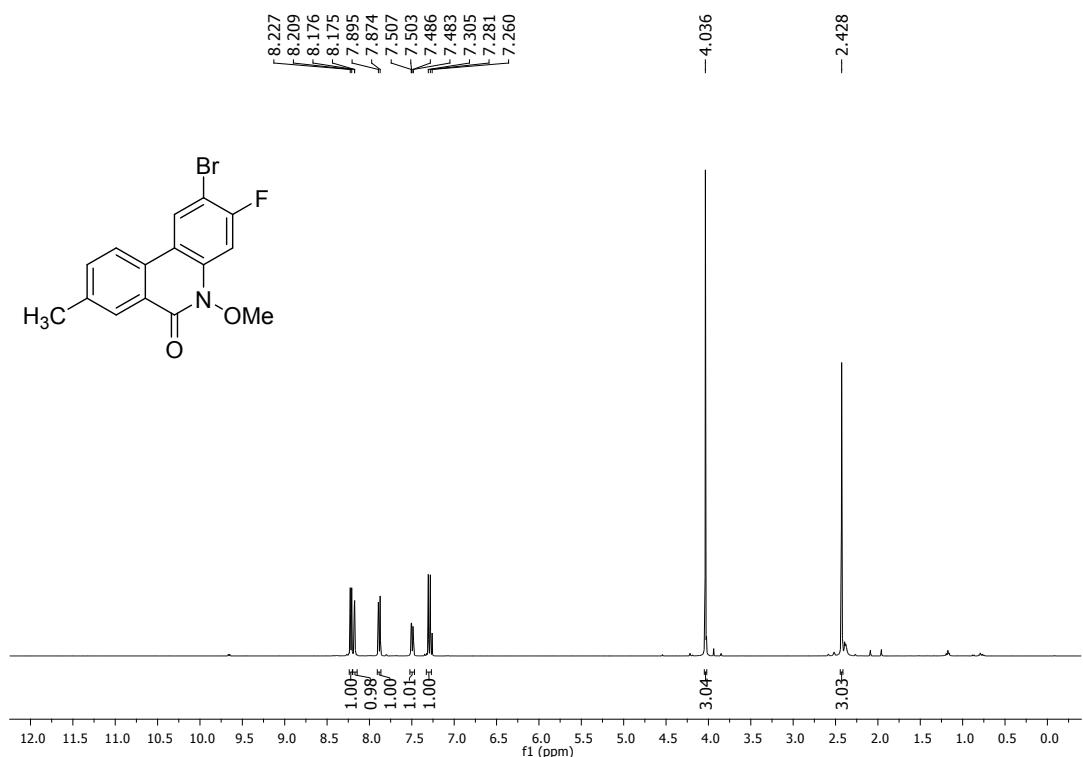


Figure S64. ¹H NMR spectrum of 2-Bromo-3-fluoro-5-methoxy-8-methylphenanthridin-6(5H)-one (**3j**)

¹³C{¹H} NMR (100 MHz, CDCl₃ + DMSO-d₆)

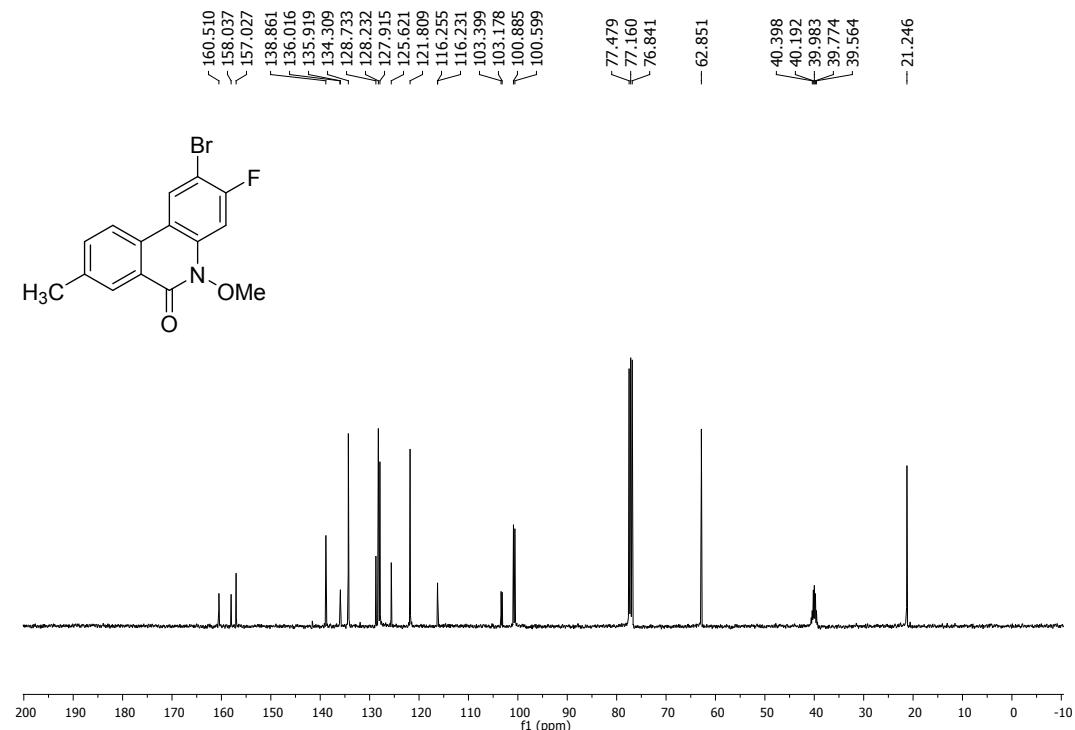


Figure S65. ¹³C{¹H} NMR spectrum of 2-Bromo-3-fluoro-5-methoxy-8-methylphenanthridin-6(5H)-one (**3j**)

¹H NMR (400 MHz, DMSO-d₆)

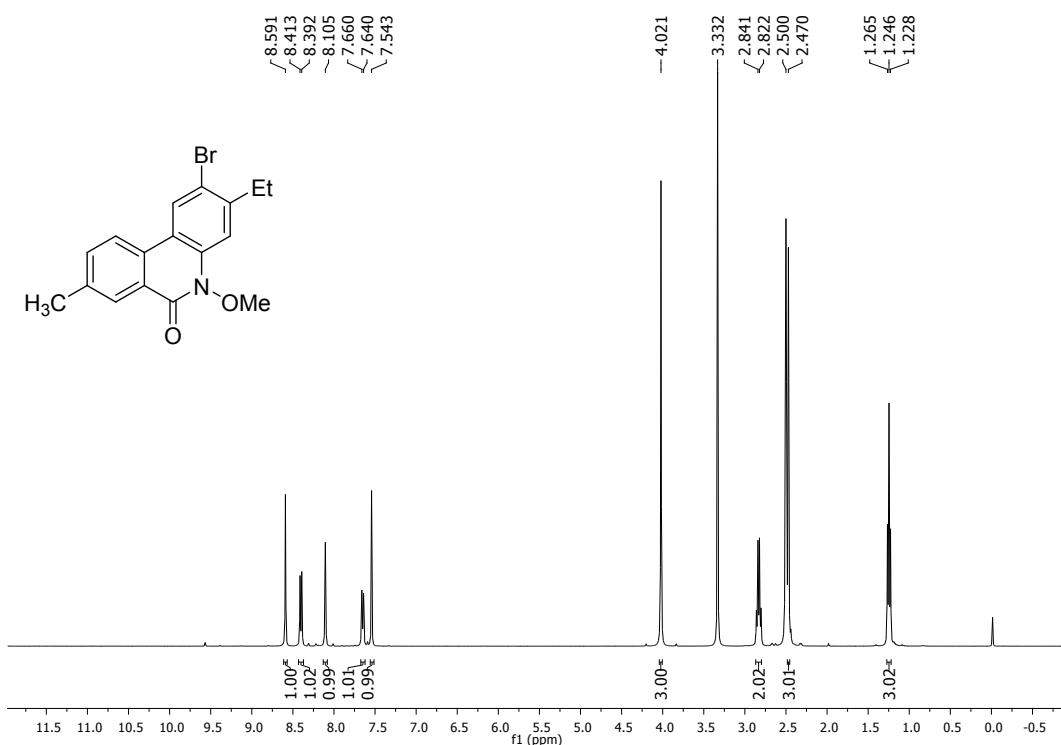


Figure S66. ^1H NMR spectrum of 2-Bromo-3-ethyl-5-methoxy-8-methylphenanthridin-6(5H)-one (**3k**)

¹³C{¹H} NMR (100 MHz, DMSO-d₆)

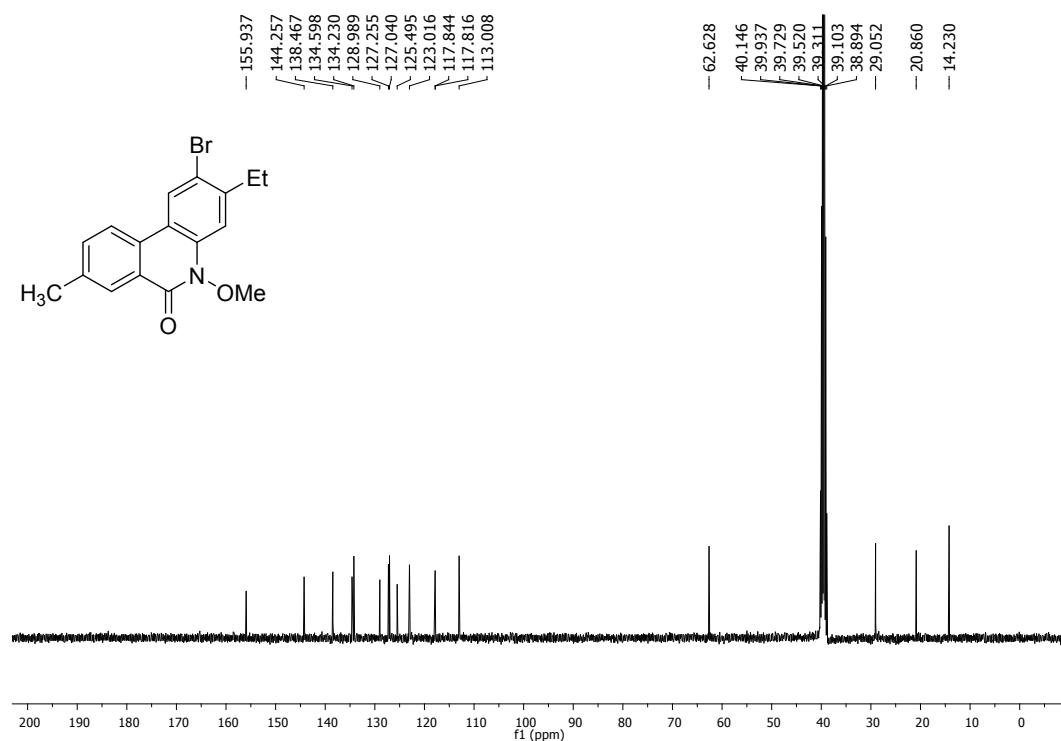


Figure S67. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of 2-Bromo-3-ethyl-5-methoxy-8-methylphenanthridin-6(5H)-one (**3k**)

¹H NMR (400 MHz, CDCl₃)

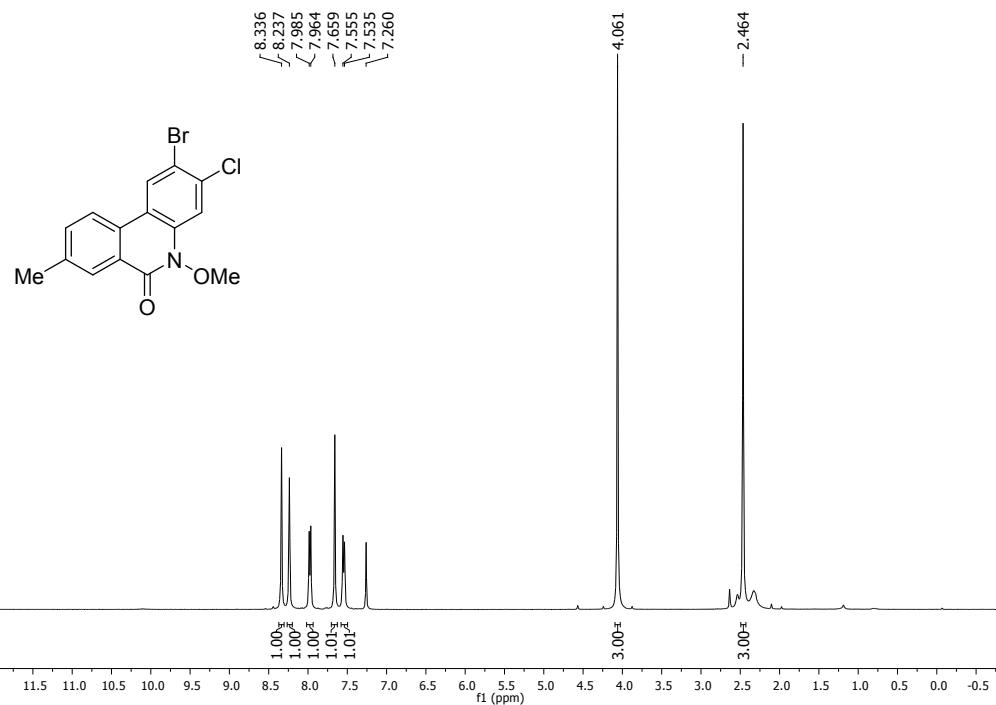


Figure S68. ¹H NMR spectrum of 2-Bromo-3-chloro-5-methoxy-8-methylphenanthridin-6(5H)-one (**3l**)

¹³C{¹H} NMR (100 MHz, CDCl₃ + DMSO-d₆)

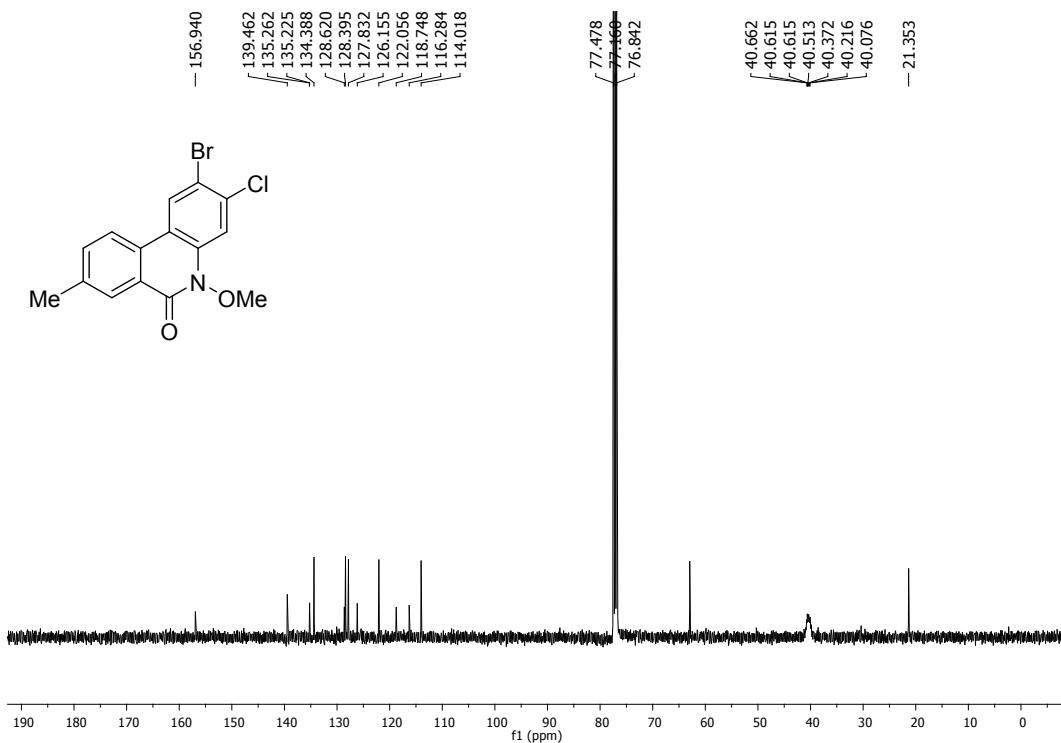


Figure S69. ¹³C{¹H} NMR spectrum of 2-Bromo-3-chloro-5-methoxy-8-methylphenanthridin-6(5H)-one (**3l**)

¹H NMR (700 MHz, CDCl₃)

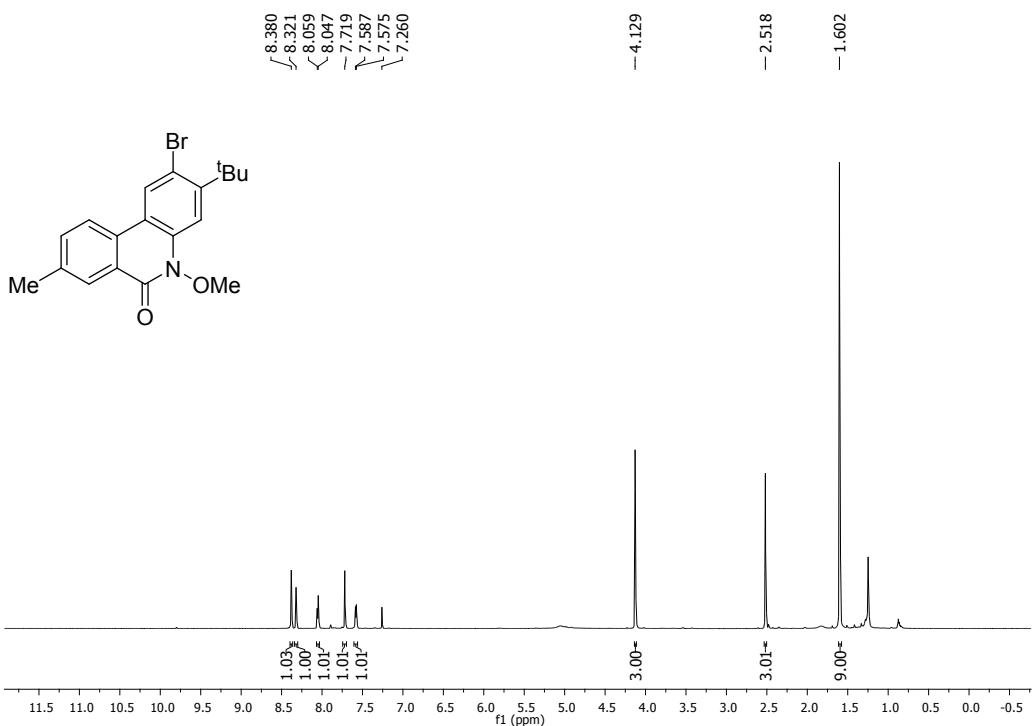


Figure S70. ¹H NMR spectrum of 2-Bromo-3-(tert-butyl)-5-methoxy-8-methylphenanthridin-6(5H)-one (**3n**)

¹³C{¹H} NMR (175 MHz, CDCl₃)

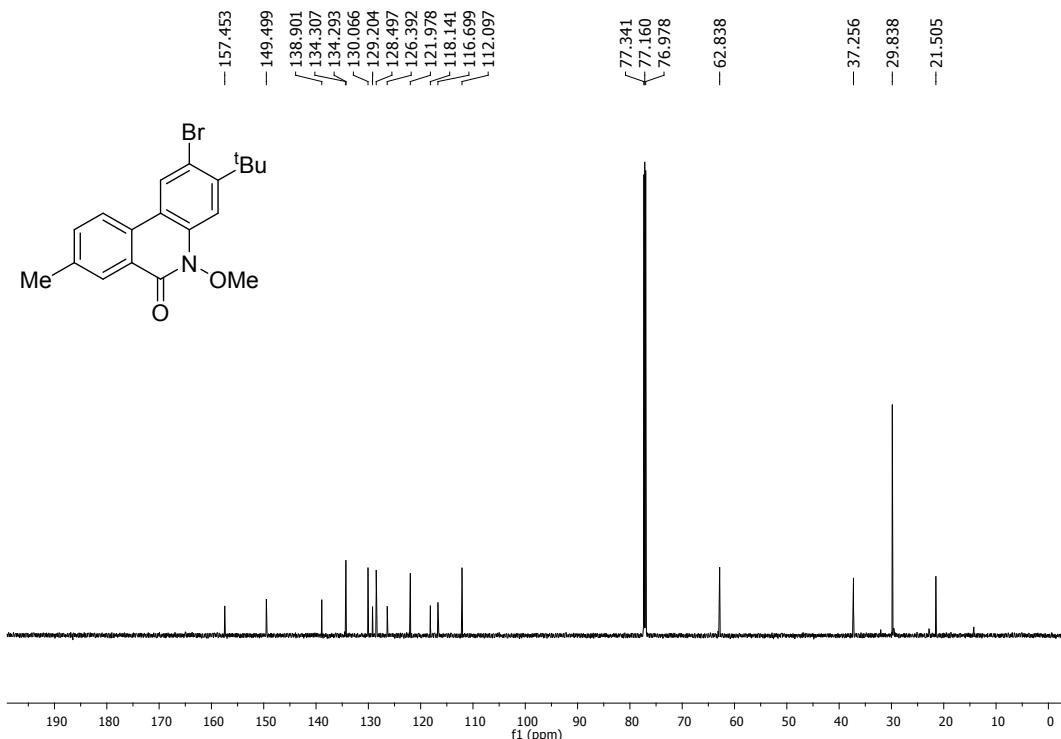


Figure S71. ¹³C{¹H} NMR spectrum of 2-Bromo-3-(tert-butyl)-5-methoxy-8-methylphenanthridin-6(5H)-one (**3n**)

¹H NMR (400 MHz, CDCl₃ + DMSO-d₆)

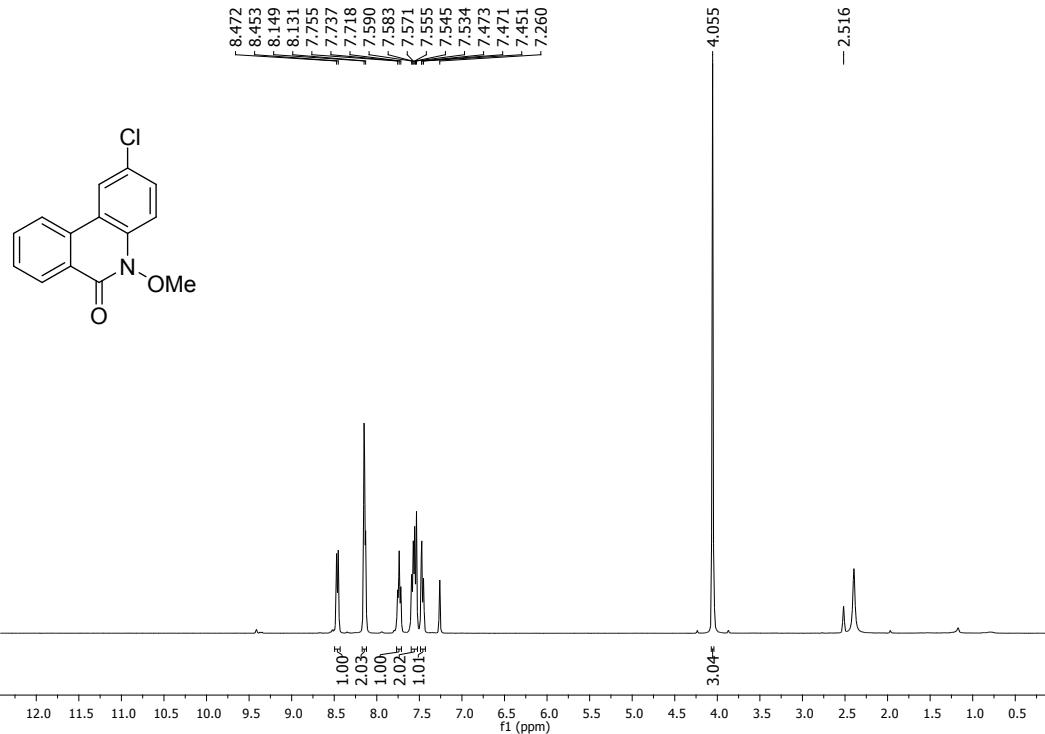


Figure S72. ¹H NMR spectrum of 2-Chloro-5-methoxyphenanthridin-6(5H)-one (4a)

¹³C{¹H} NMR (100 MHz, CDCl₃ + DMSO-d₆)

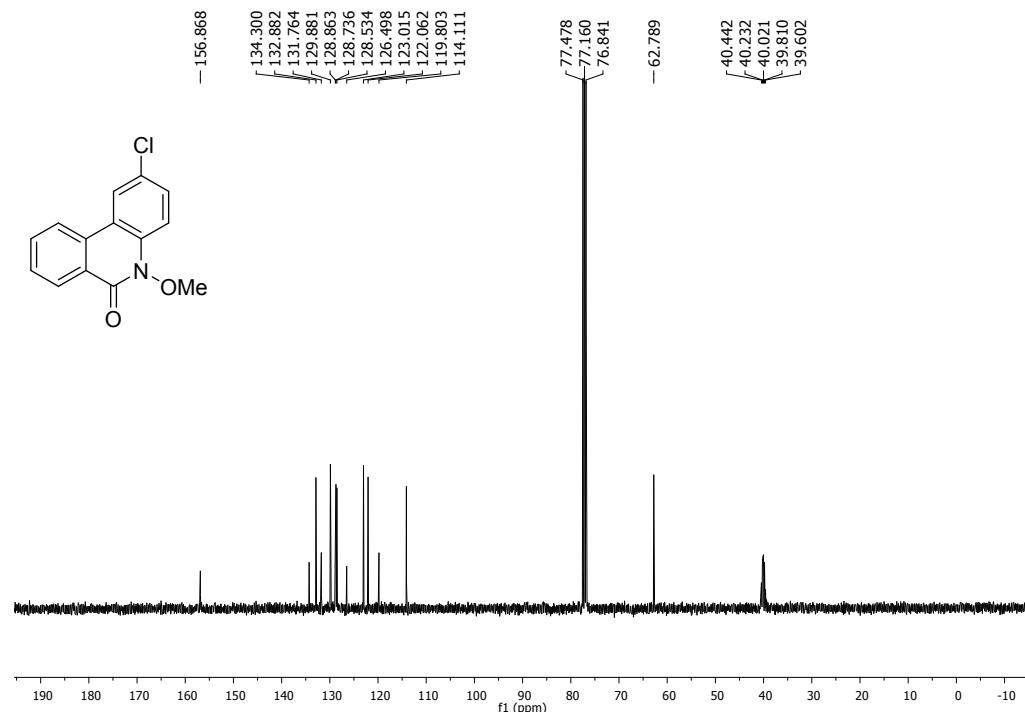


Figure S73. ¹³C{¹H} NMR spectrum of 2-Chloro-5-methoxyphenanthridin-6(5H)-one (4a)

¹H NMR (400 MHz, CDCl₃)

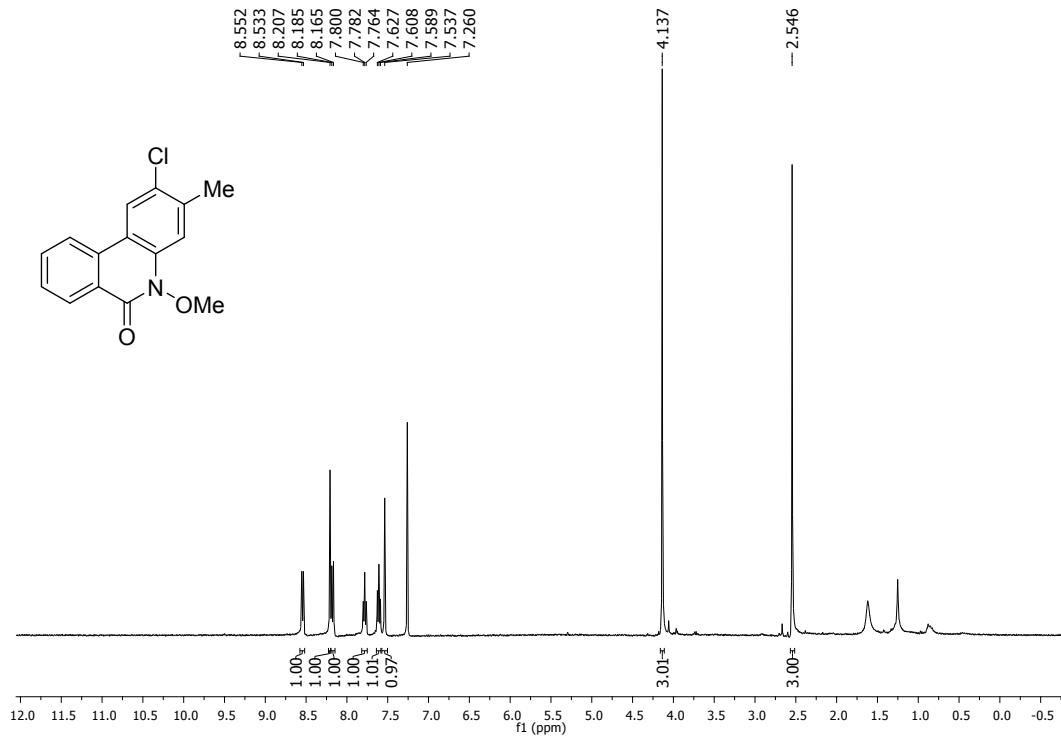


Figure S74. ¹H NMR spectrum of 2-Chloro-5-methoxy-3-methylphenanthridin-6(5H)-one (**4b**)

¹³C{¹H} NMR (100 MHz, CDCl₃ + DMSO-d₆)

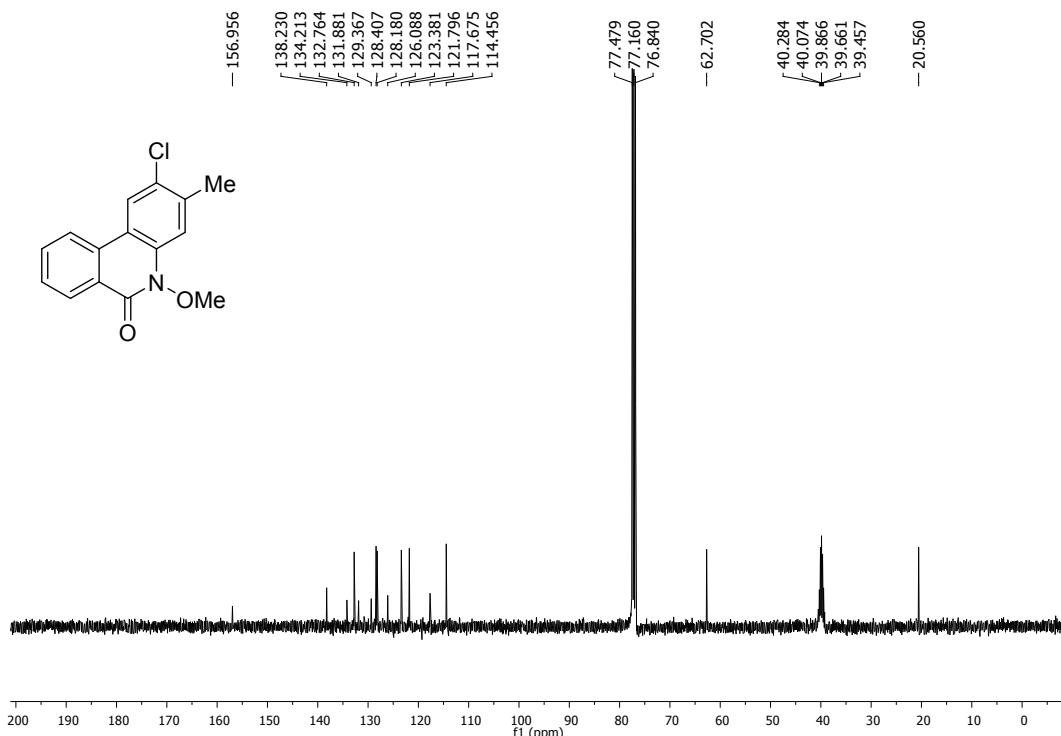


Figure S75. ¹³C{¹H} NMR spectrum of 2-Chloro-5-methoxy-3-methylphenanthridin-6(5H)-one (**4b**)

¹H NMR (400 MHz, CDCl₃ + DMSO-d₆)

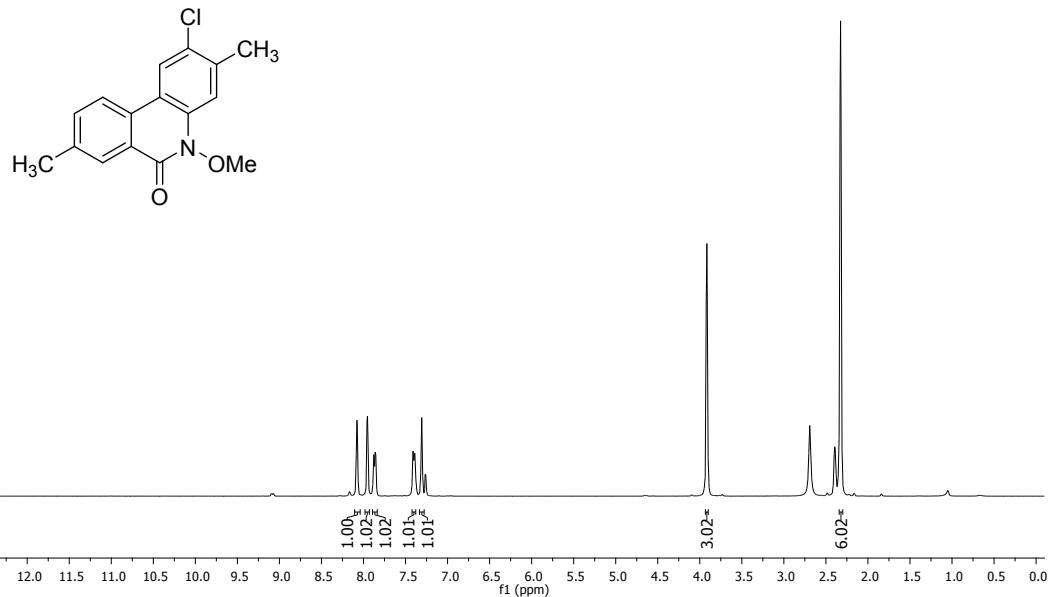


Figure S76. ¹H NMR spectrum of 2-Chloro-5-methoxy-3,8-dimethylphenanthridin-6(5H)-one (**4i**)

¹³C{¹H} NMR (100 MHz, CDCl₃ + DMSO-d₆)

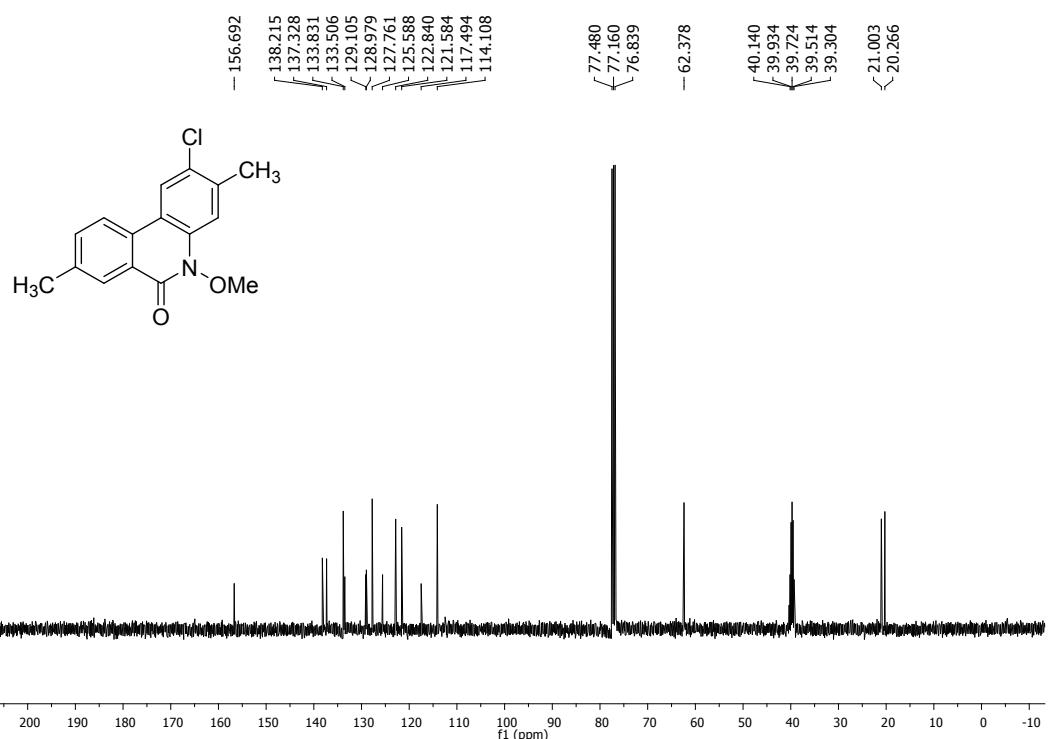


Figure S77. ¹³C{¹H} NMR spectrum of 2-Chloro-5-methoxy-3,8-dimethylphenanthridin-6(5H)-one (**4i**)

^1H NMR (400 MHz, CDCl_3)

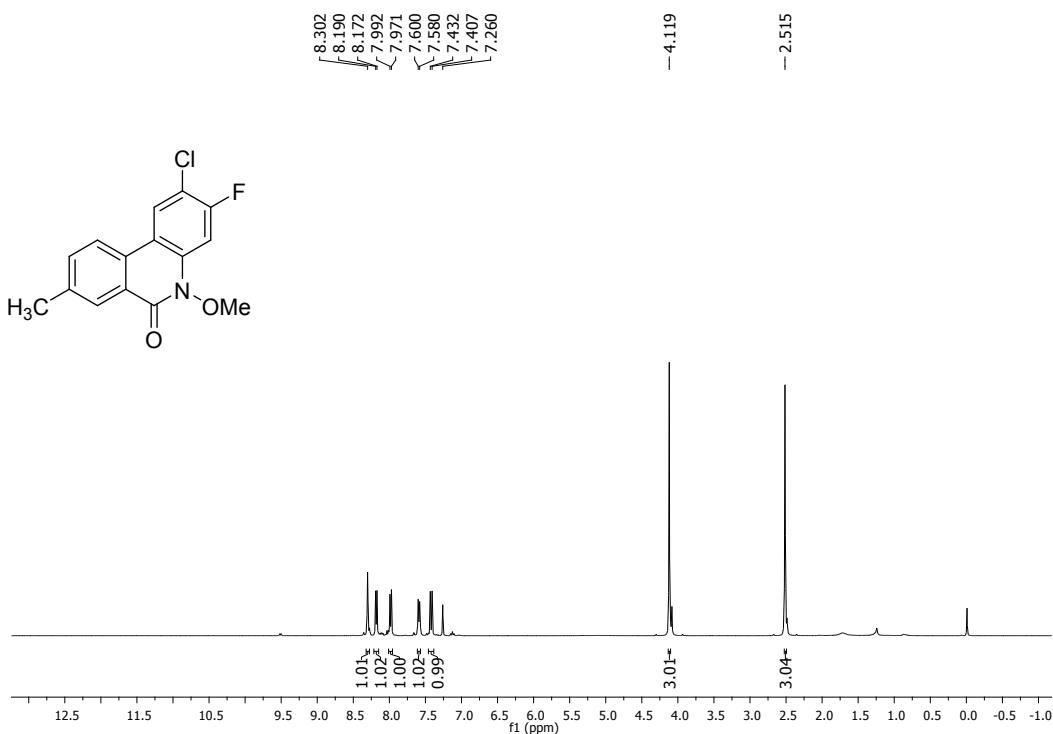


Figure S78. ^1H NMR spectrum of 2-Chloro-3-fluoro-5-methoxy-8-methylphenanthridin-6(5H)-one (**4j**)

$^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3)

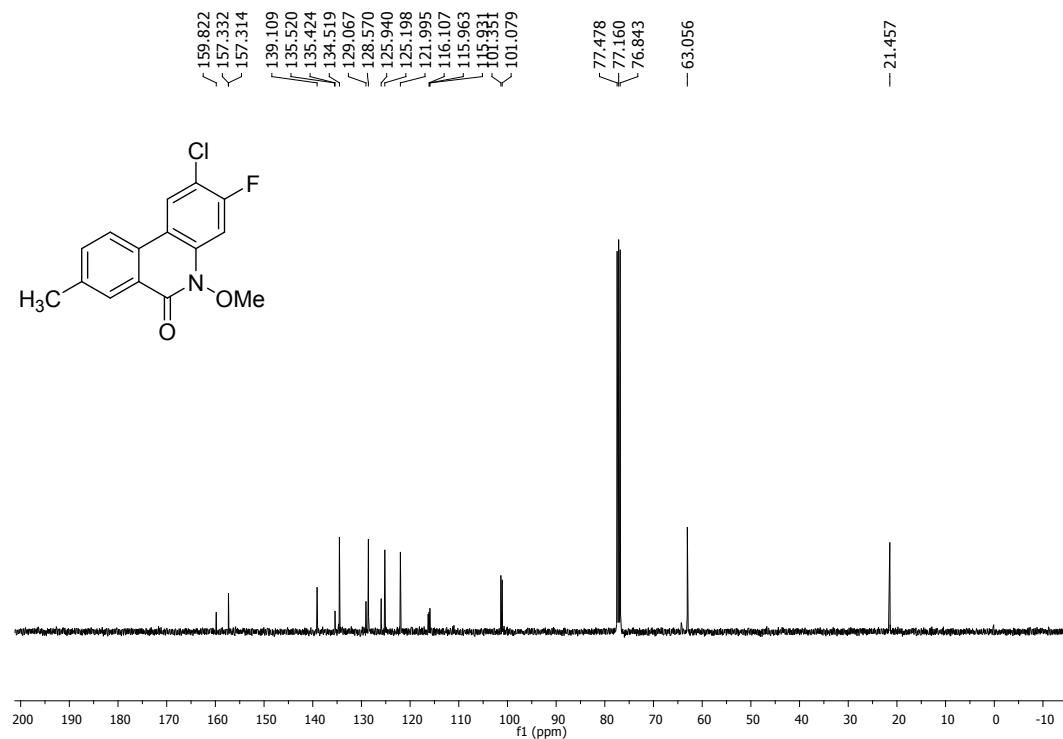


Figure S79. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-Chloro-3-fluoro-5-methoxy-8-methylphenanthridin-6(5H)-one (**4j**)

^1H NMR (400 MHz, $\text{CDCl}_3 + \text{DMSO-d}_6$)

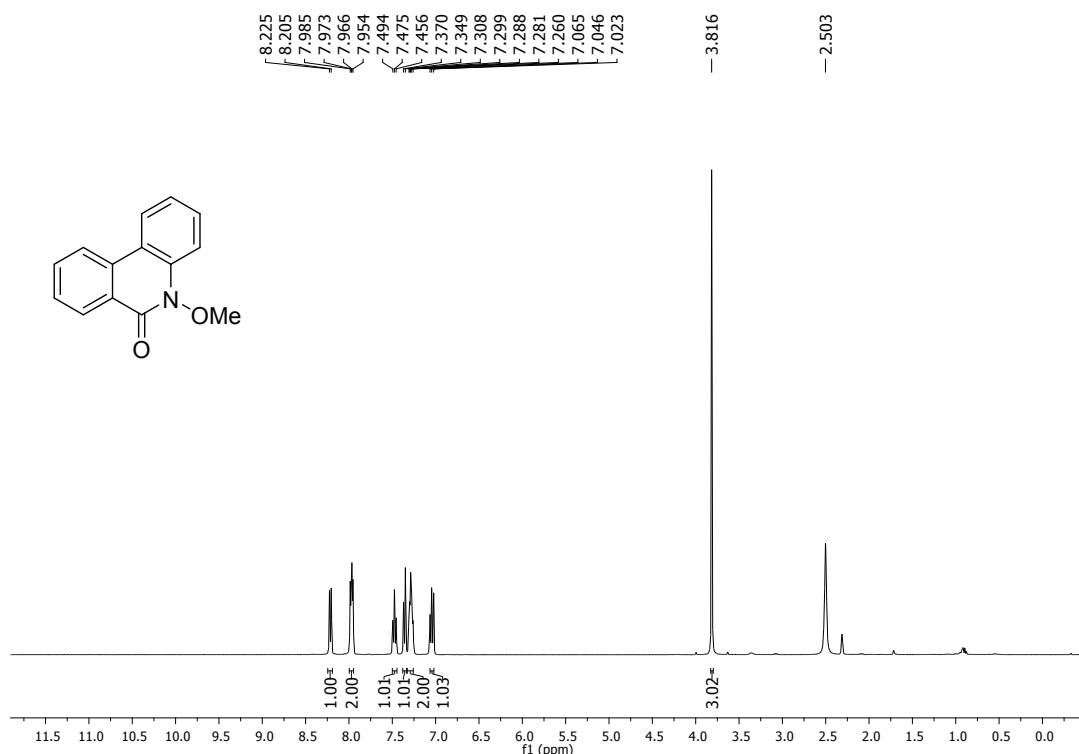


Figure S80. ^1H NMR spectrum of 5-Methoxyphenanthridin-6(5H)-one (**2a**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{CDCl}_3 + \text{DMSO-d}_6$)

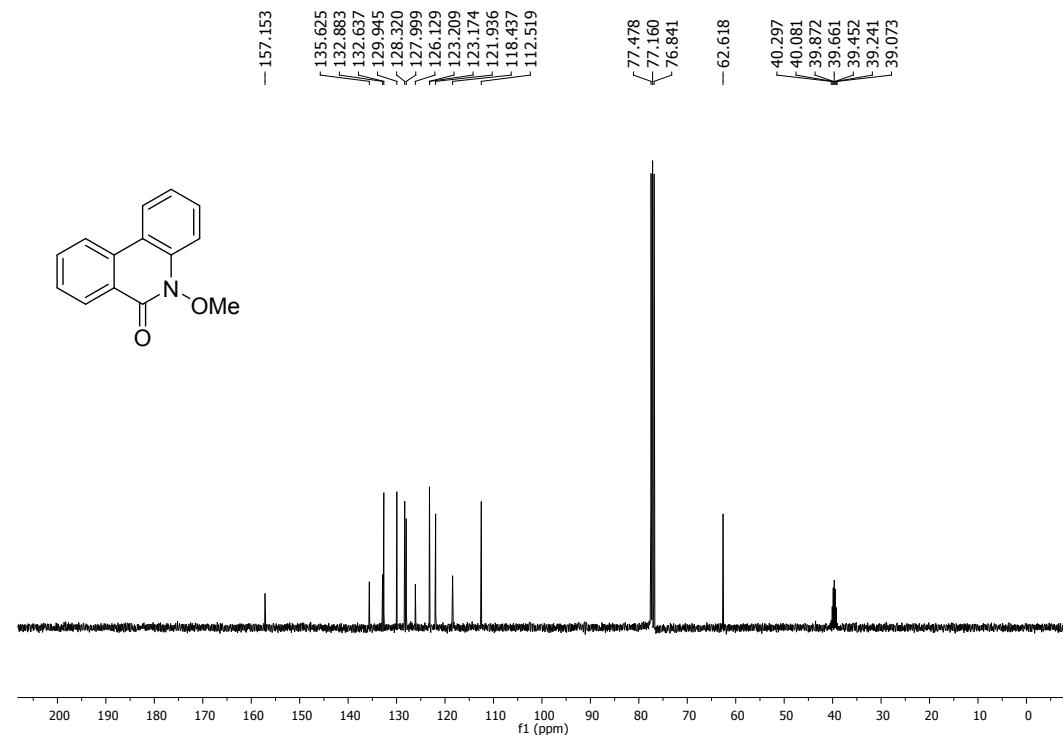


Figure S81. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5-Methoxyphenanthridin-6(5H)-one (**2a**)

¹H NMR (400 MHz, CDCl₃)

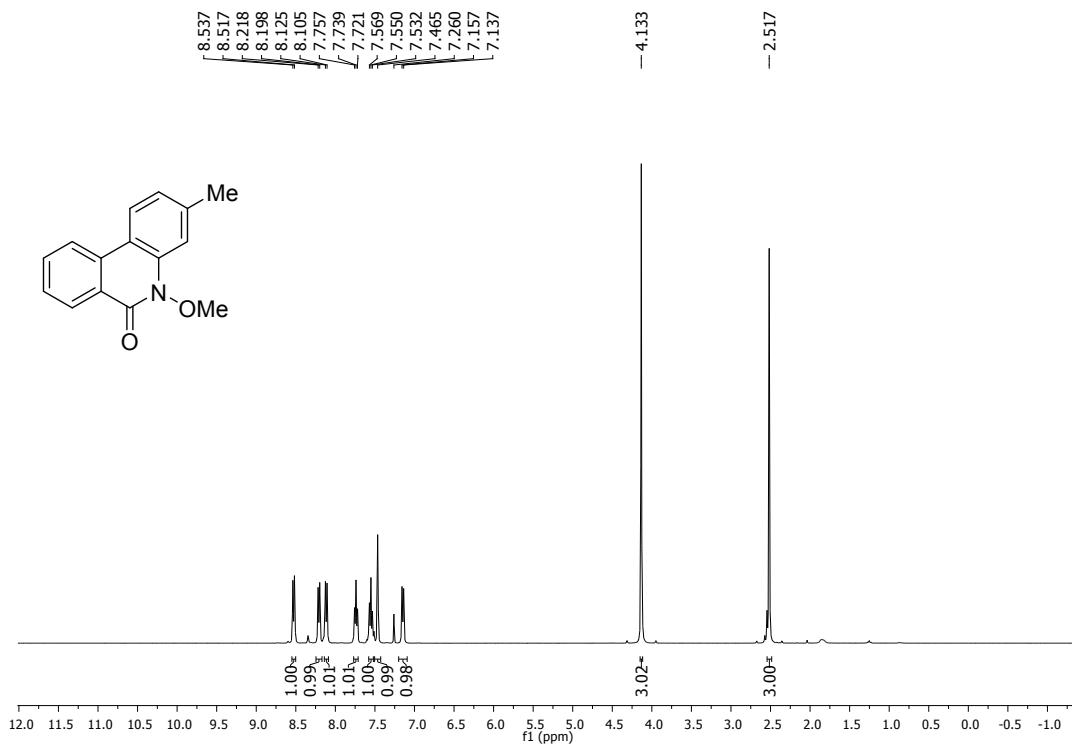


Figure S82. ¹H NMR spectrum of 5-Methoxy-3-methylphenanthridin-6(5H)-one (**2b**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

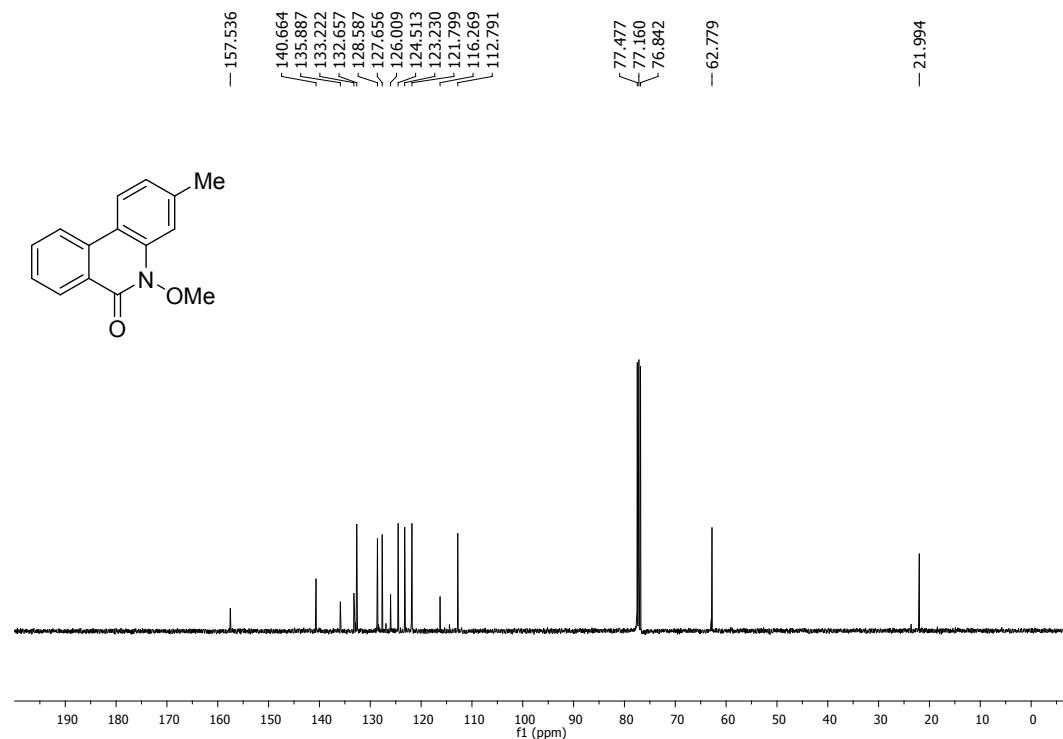


Figure S83. ¹³C{¹H} NMR spectrum of 5-Methoxy-3-methylphenanthridin-6(5H)-one (**2b**)

¹H NMR (400 MHz, CDCl₃)

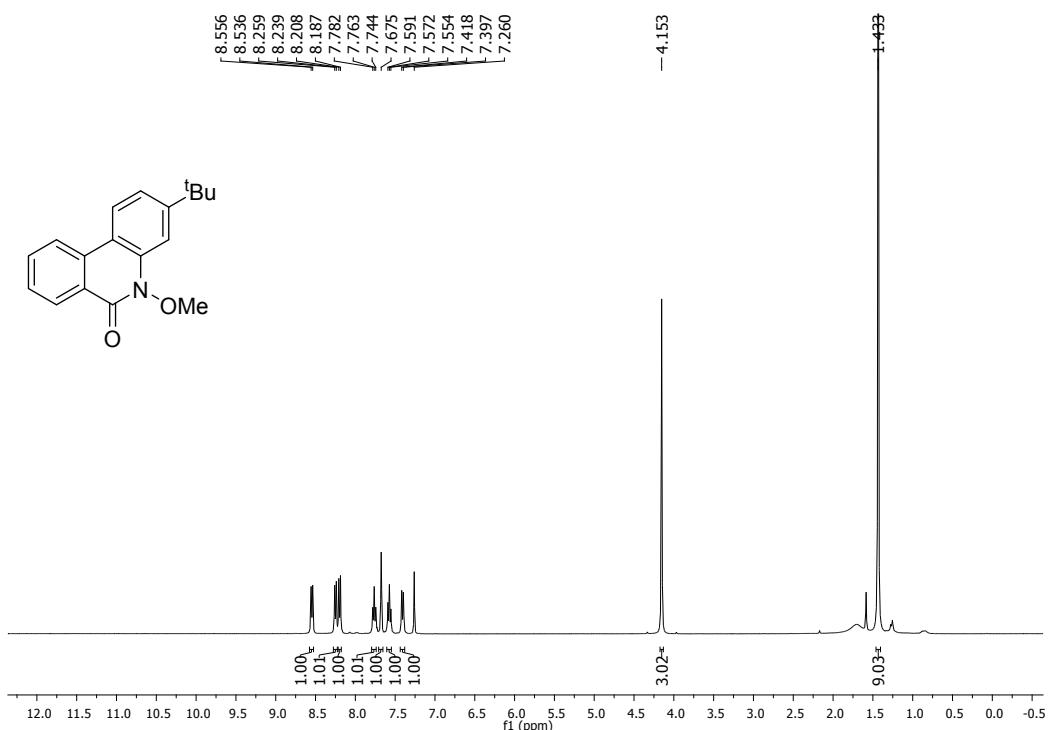


Figure S84. ¹H NMR spectrum of 3-(Tert-butyl)-5-methoxyphenanthridin-6(5H)-one (**2d**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

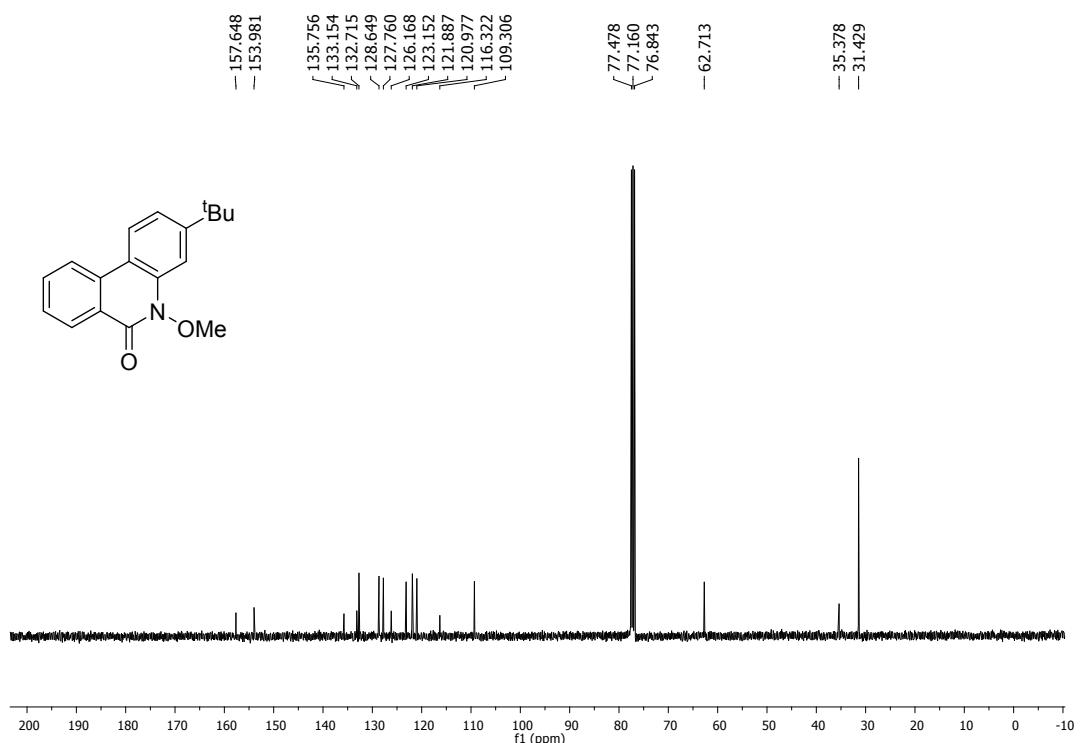


Figure S85. ¹³C{¹H} NMR spectrum of 3-(Tert-butyl)-5-methoxyphenanthridin-6(5H)-one (**2d**)

¹H NMR (400 MHz, CDCl₃)

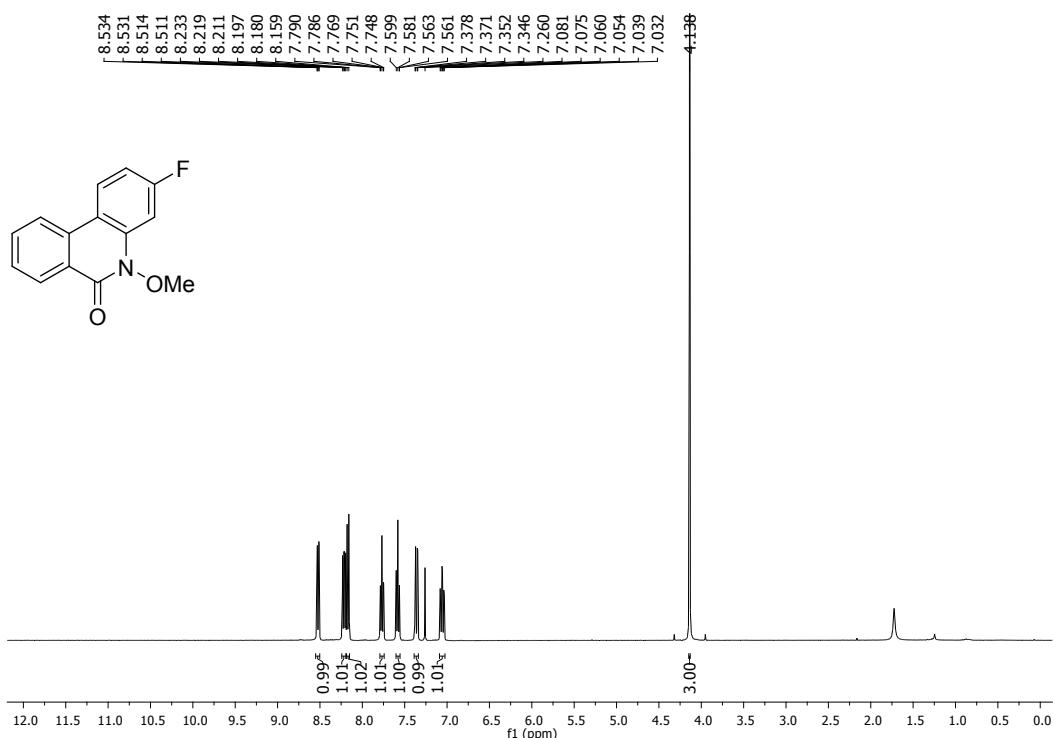


Figure S86. ¹H NMR spectrum of 3-Fluoro-5-methoxyphenanthridin-6(5H)-one (**2e**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

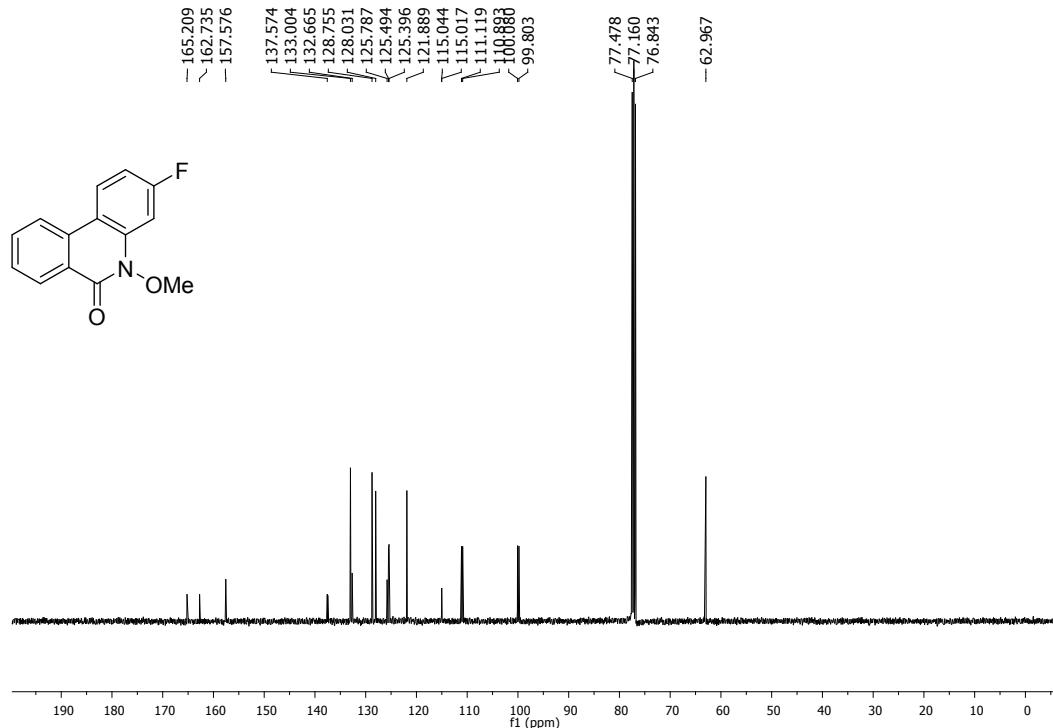


Figure S87. ¹³C{¹H} NMR spectrum of 3-Fluoro-5-methoxyphenanthridin-6(5H)-one (**2e**)

¹H NMR (400 MHz, CDCl₃ + DMSO-d₆)

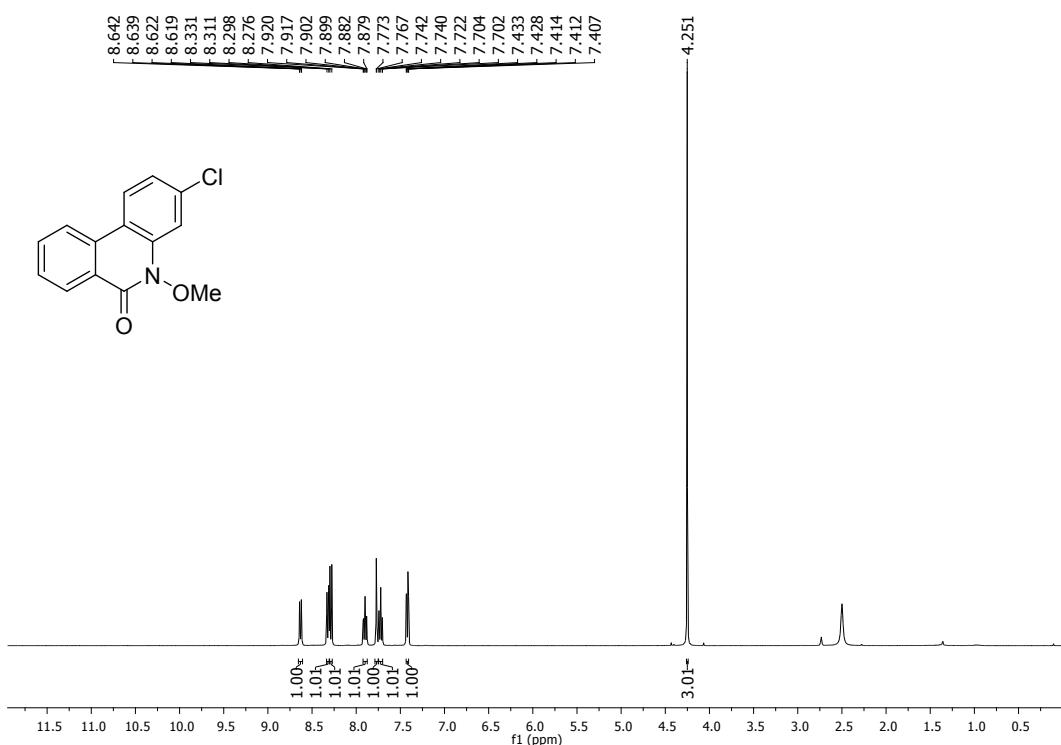


Figure S88. ^1H NMR spectrum of 3-Chloro-5-methoxyphenanthridin-6(5H)-one (**2f**)

¹³C{¹H} NMR (100 MHz, CDCl₃ + DMSO-d₆)

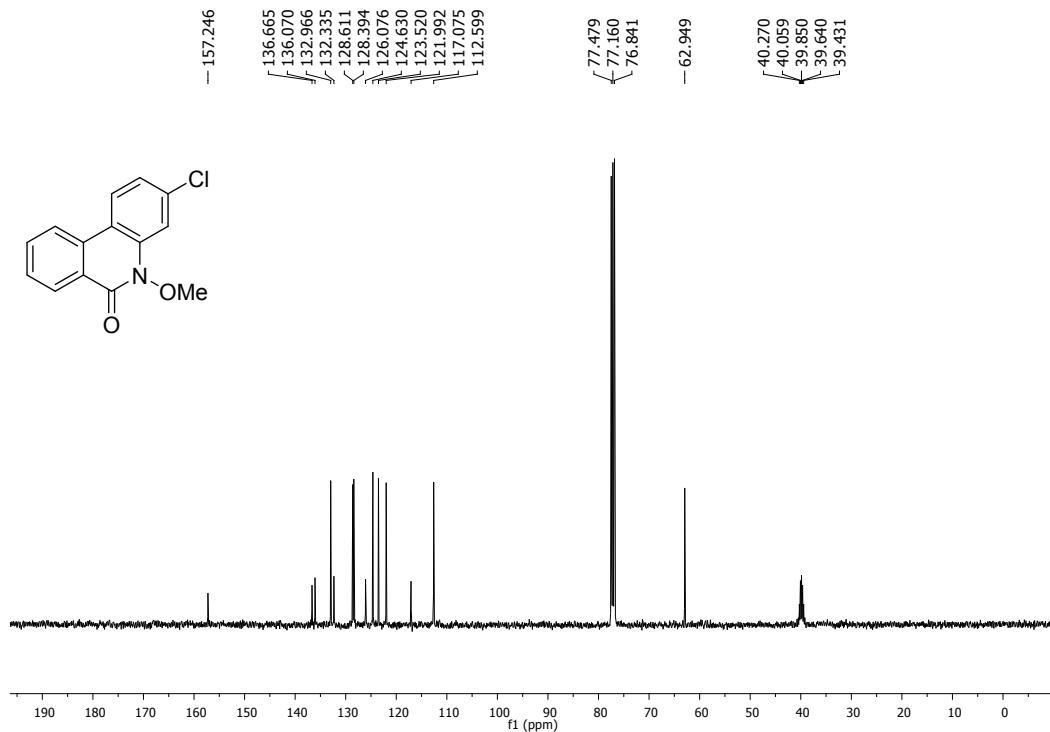


Figure S89. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of 3-Chloro-5-methoxyphenanthridin-6(5H)-one (**2f**)

¹H NMR (700 MHz, CDCl₃)

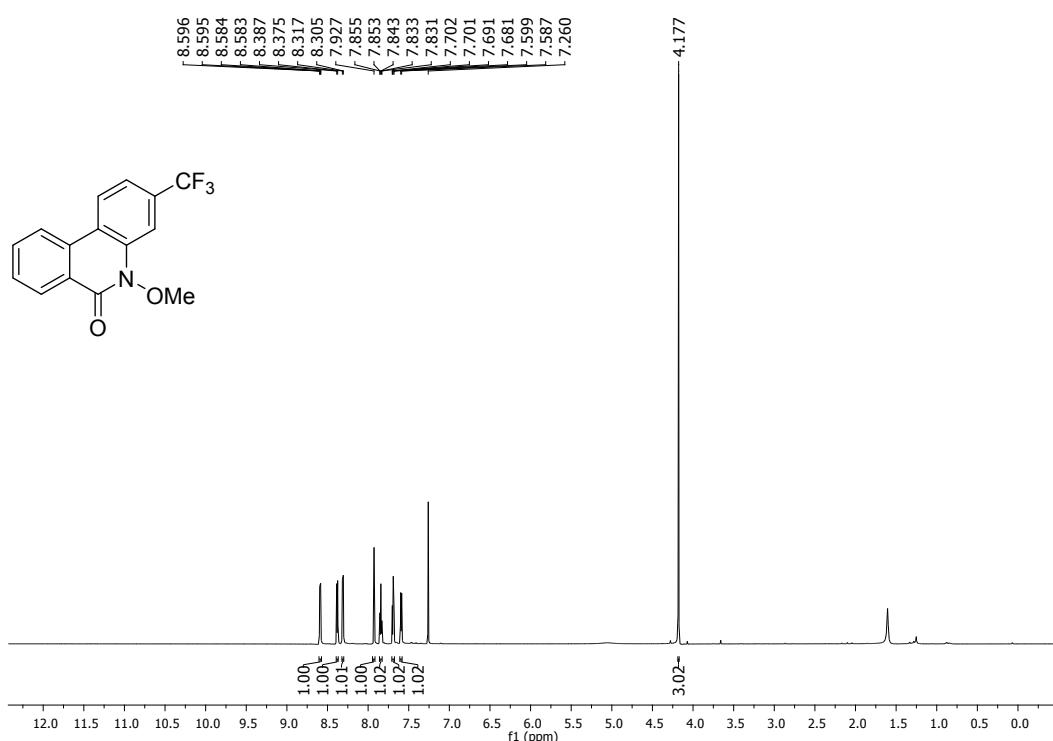


Figure S90. ¹H NMR spectrum of 5-Methoxy-3-(trifluoromethyl)phenanthridin-6(5H)-one (**2g**)

¹³C{¹H} NMR (175 MHz, CDCl₃)

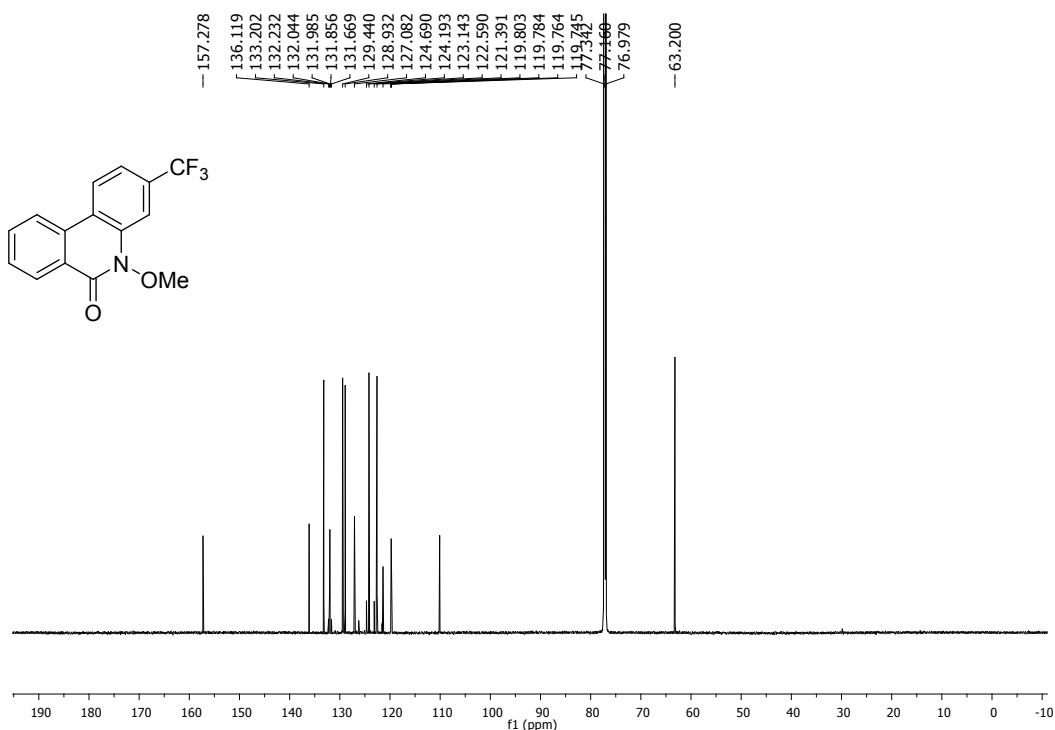


Figure S91. ¹³C{¹H} NMR spectrum of 5-Methoxy-3-(trifluoromethyl)phenanthridin-6(5H)-one (**2g**)

^1H NMR (400 MHz, DMSO-d₆)

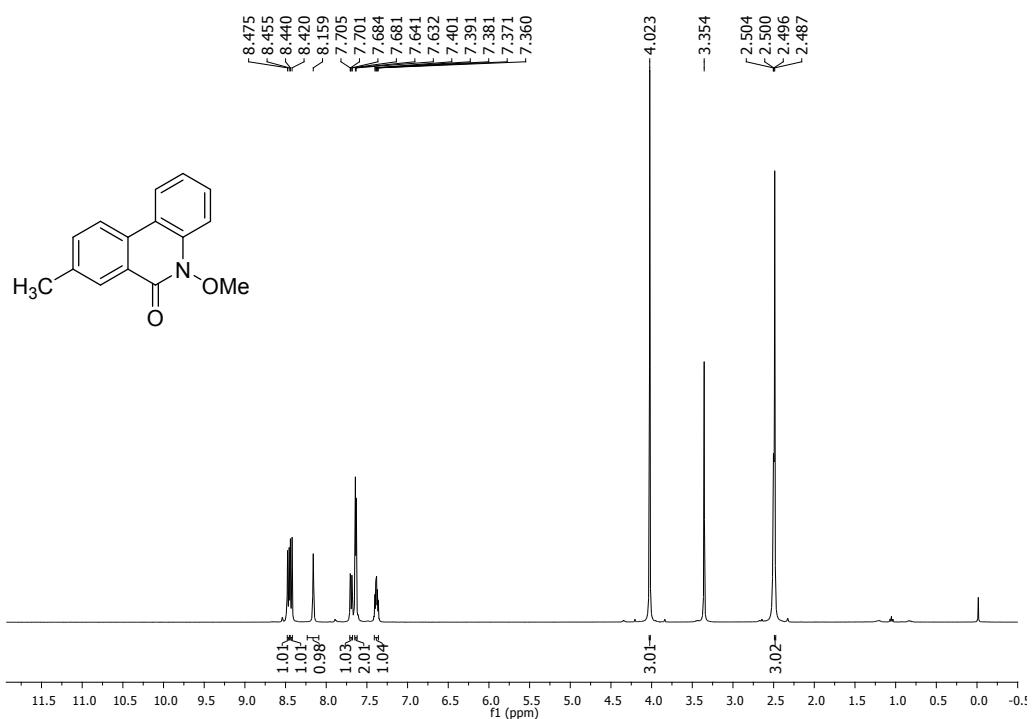


Figure S92. ^1H NMR spectrum of 5-Methoxy-8-methylphenanthridin-6(5H)-one (**2h**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-d₆)

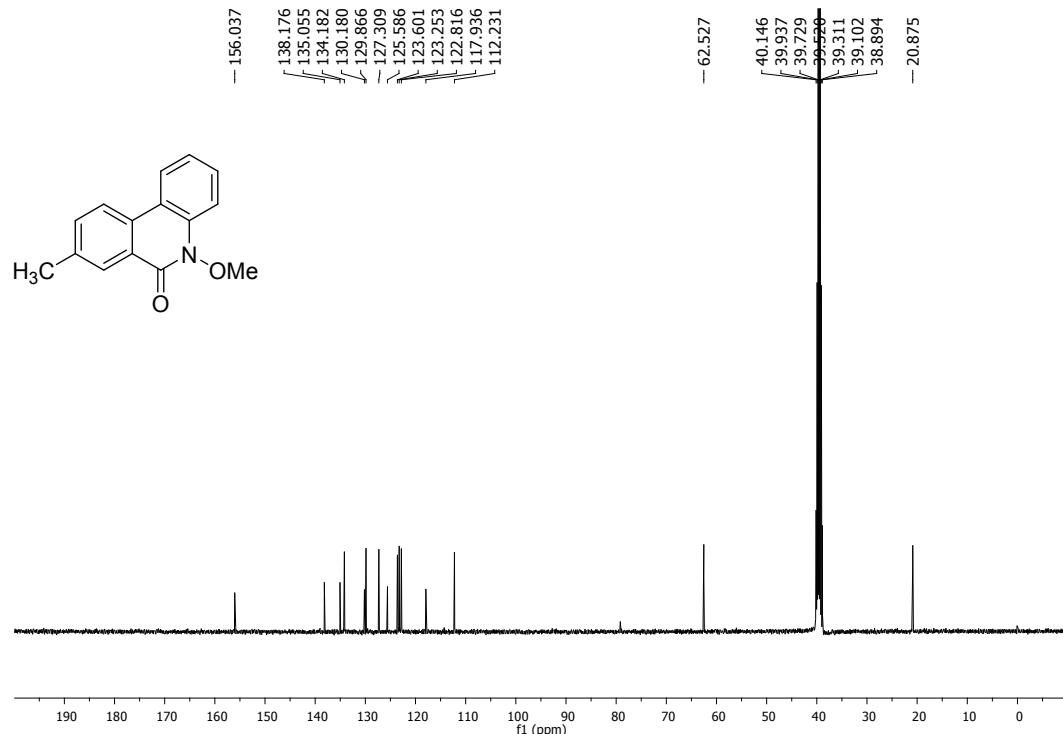


Figure S93. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5-Methoxy-8-methylphenanthridin-6(5H)-one (**2h**)

¹H NMR (400 MHz, CDCl₃)

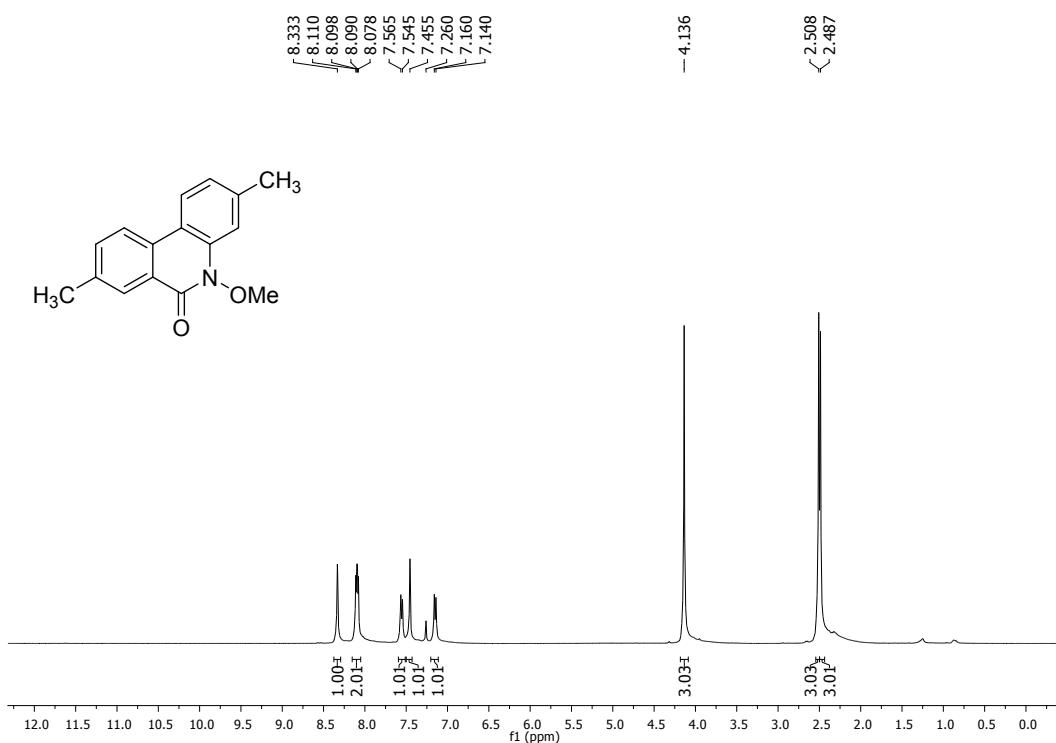


Figure S94. ¹H NMR spectrum of 5-Methoxy-3,8-dimethylphenanthridin-6(5H)-one (**2i**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

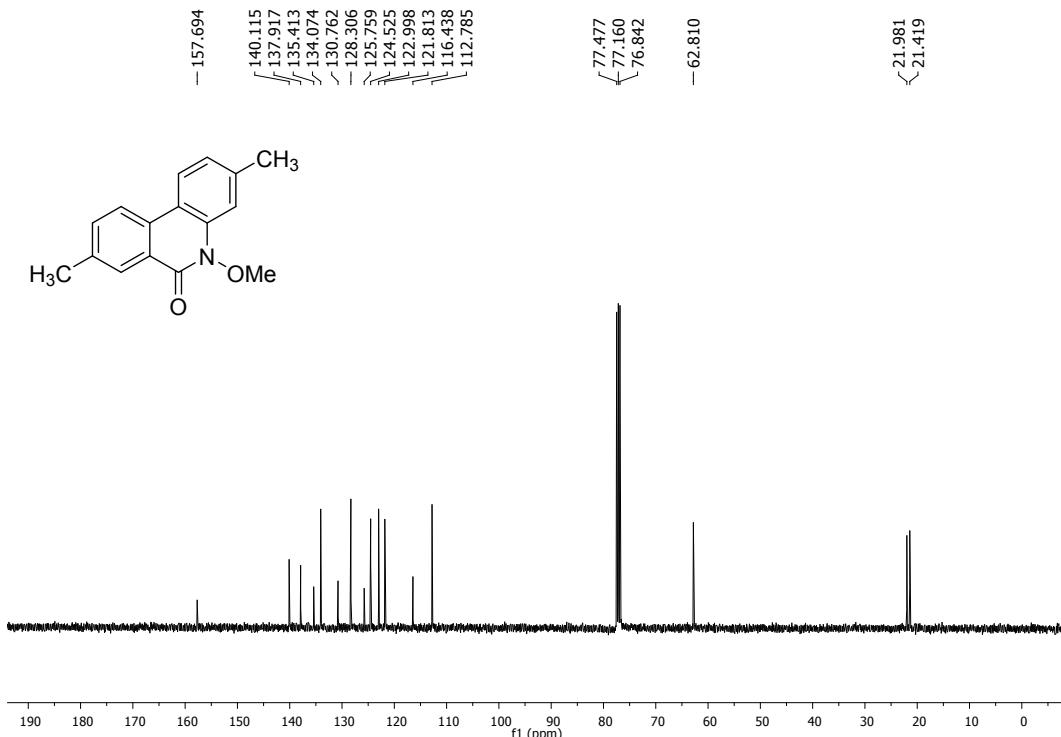


Figure S95. ¹³C{¹H} NMR spectrum of 5-Methoxy-3,8-dimethylphenanthridin-6(5H)-one (**2i**)

^1H NMR (400 MHz, DMSO- d_6)

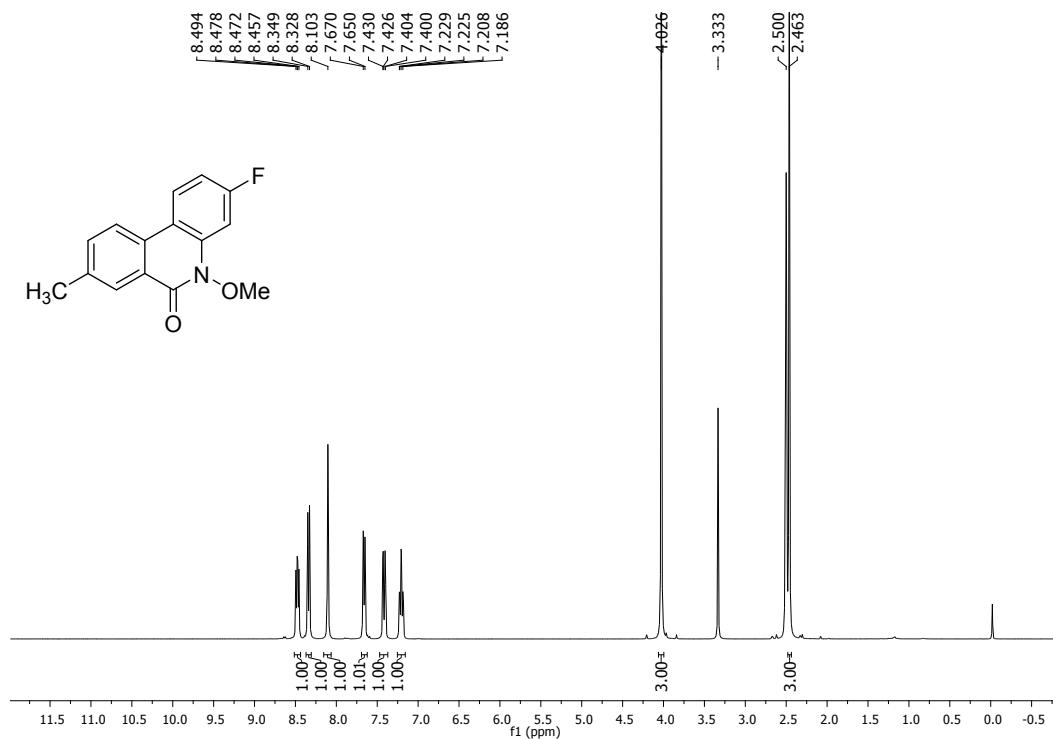


Figure S96. ^1H NMR spectrum 3-Fluoro-5-methoxy-8-methylphenanthridin-6(5H)-one (**2j**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6)

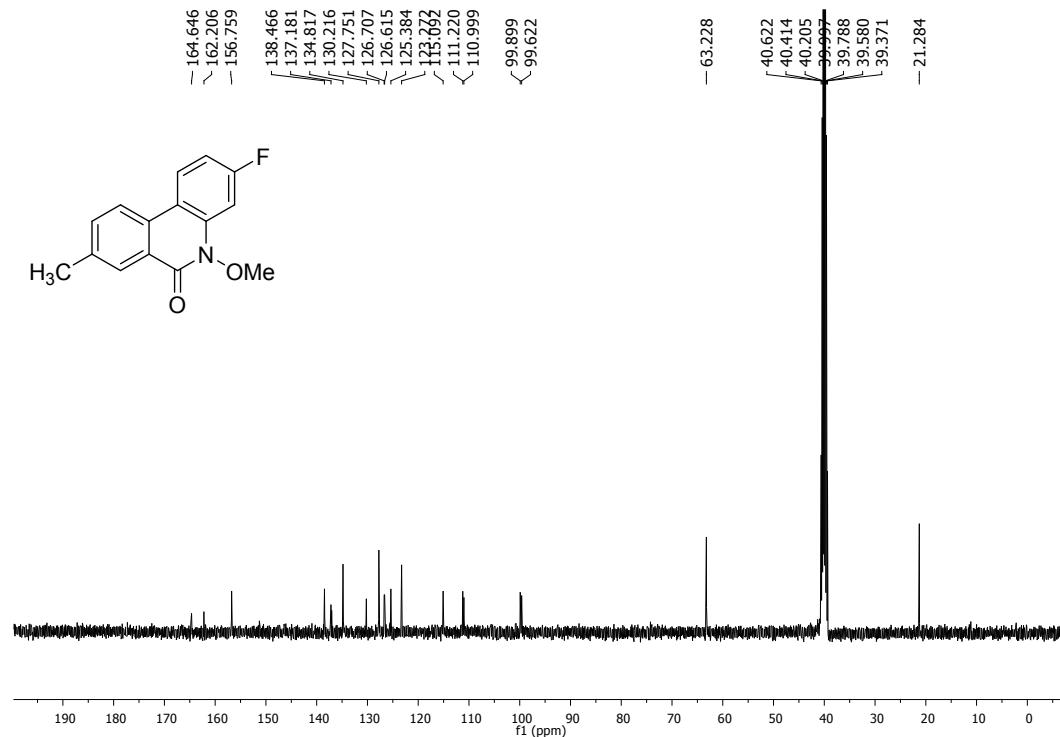


Figure S97. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum 3-Fluoro-5-methoxy-8-methylphenanthridin-6(5H)-one (**2j**)

^1H NMR (400 MHz, CDCl_3)

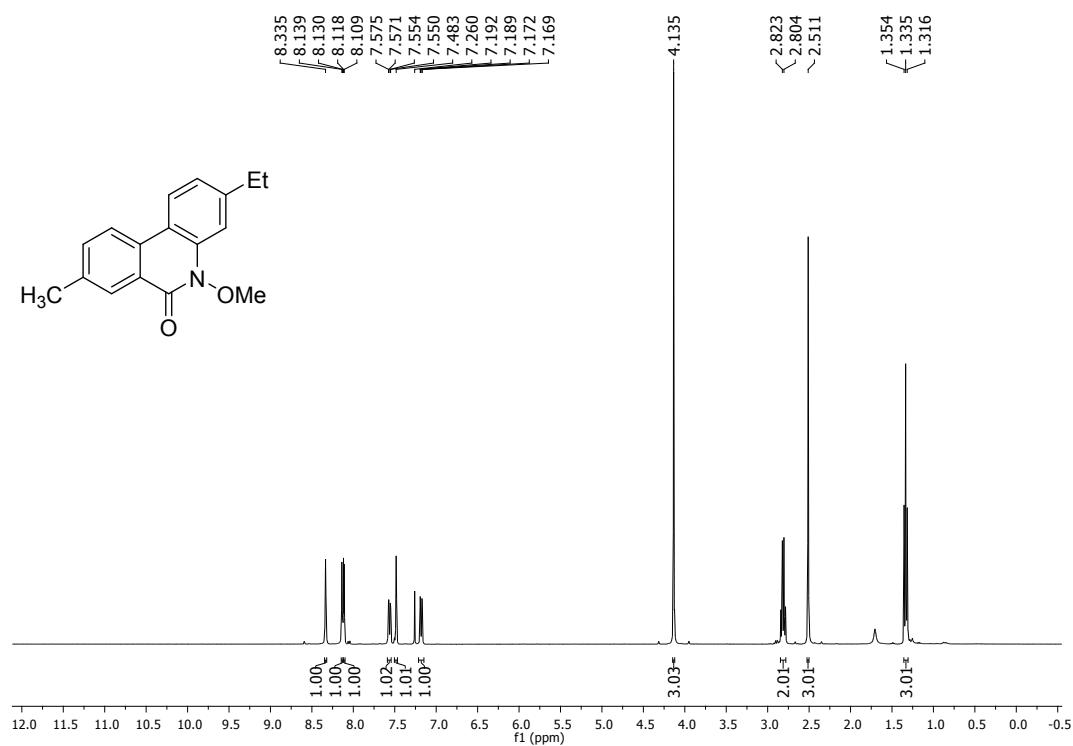


Figure S98. ^1H NMR spectrum of 3-Ethyl-5-methoxy-8-methylphenanthridin-6(5H)-one (**2k**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

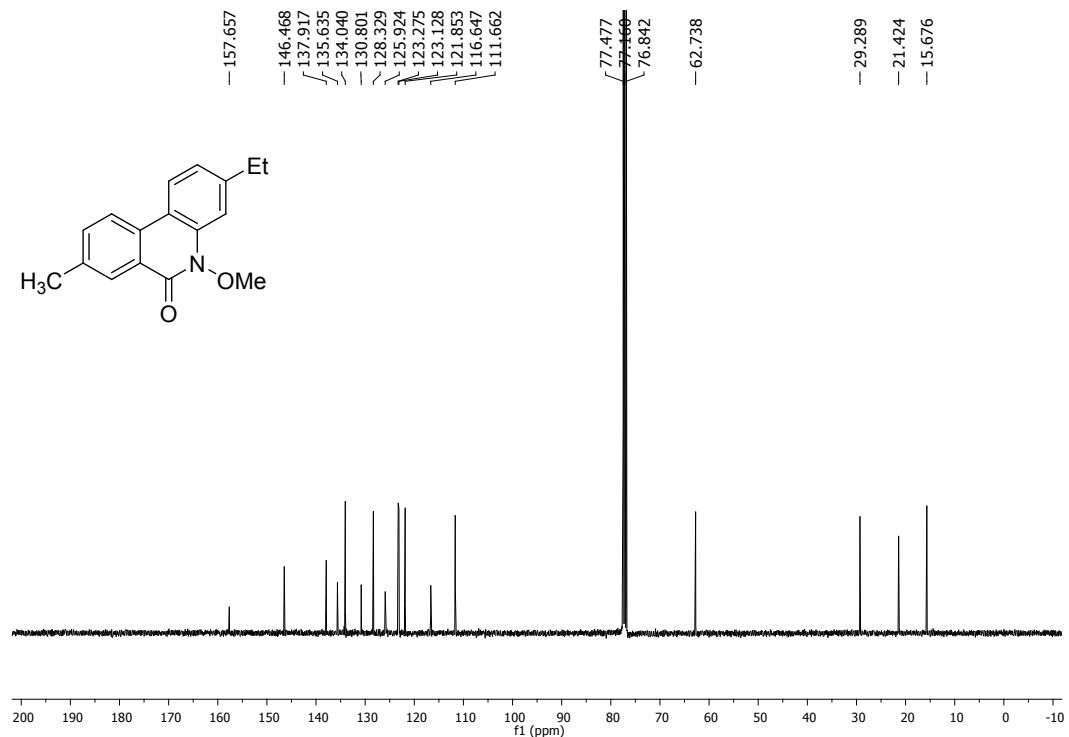


Figure S99. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 3-Ethyl-5-methoxy-8-methylphenanthridin-6(5H)-one (**2k**)

¹H NMR (400 MHz, CDCl₃ + DMSO-d₆)

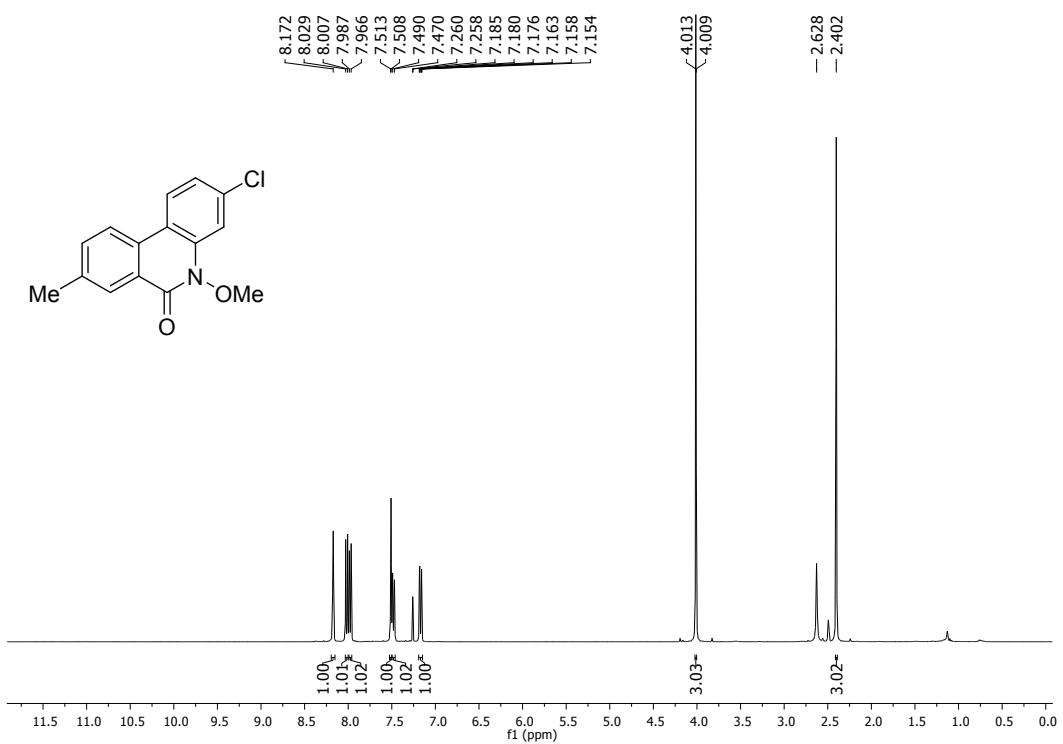


Figure S100. ^1H NMR spectrum of 3-Chloro-5-methoxy-8-methylphenanthridin-6(5H)-one (**2I**)

¹³C{¹H} NMR (100 MHz, CDCl₃ + DMSO-d₆)

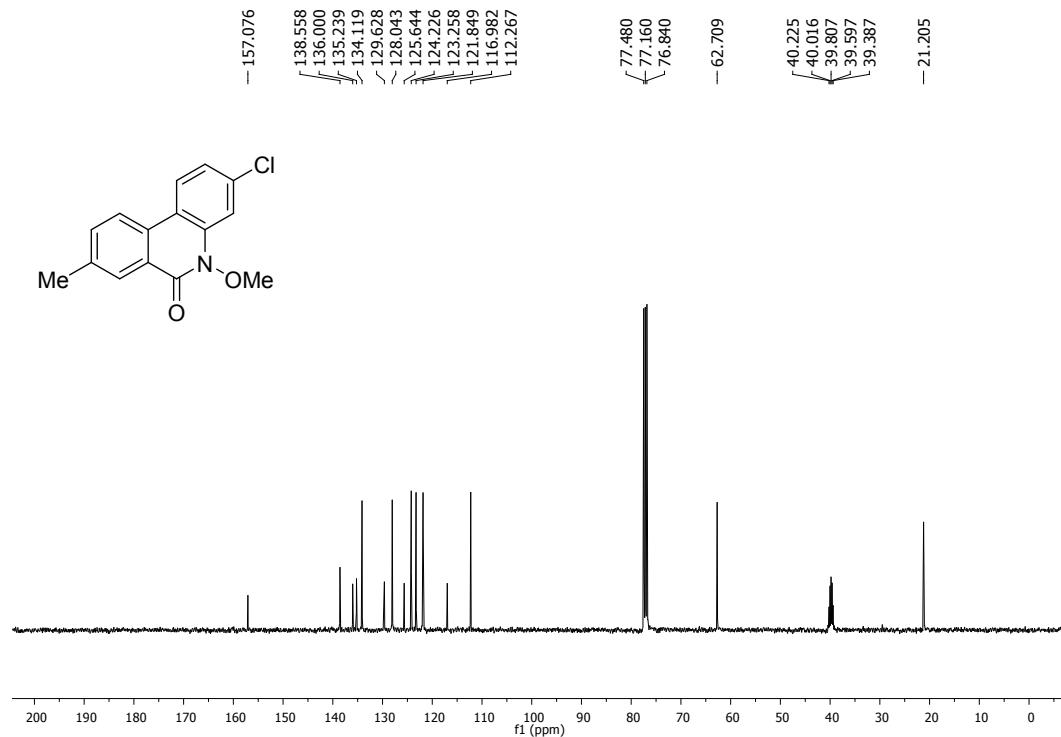


Figure S101. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of -Chloro-5-methoxy-8-methylphenanthridin-6(5H)-one (**2l**)

¹H NMR (400 MHz, DMSO-d₆)

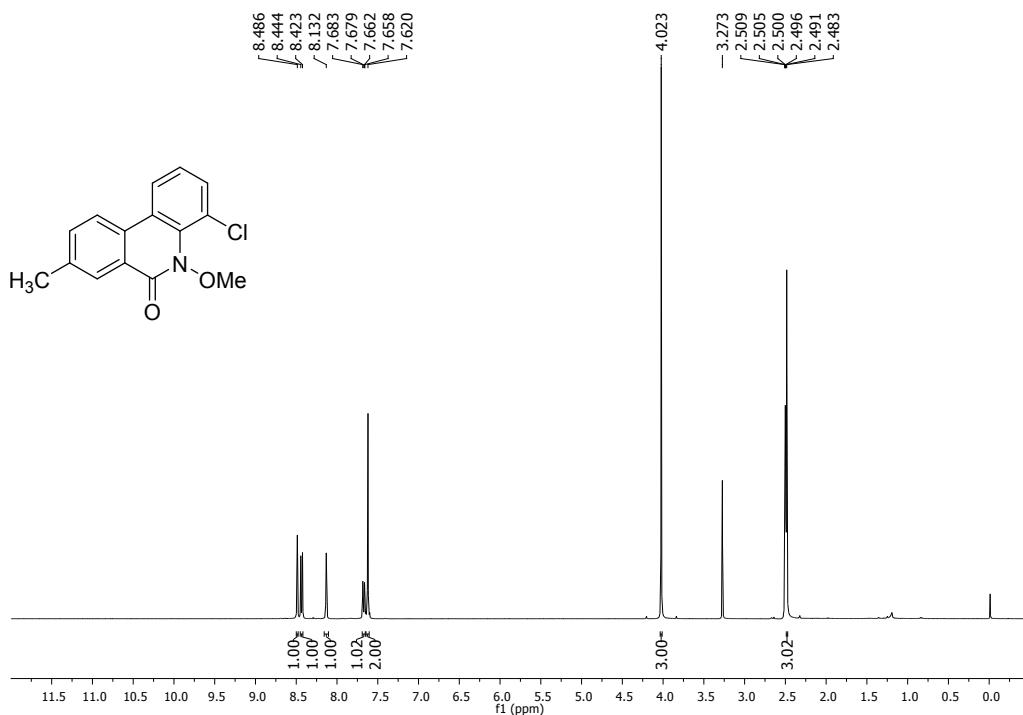


Figure S102. ¹H NMR spectrum of 4-Chloro-5-methoxy-8-methylphenanthridin-6(5H)-one (2m)

¹³C{¹H} NMR (100 MHz, DMSO-d₆)

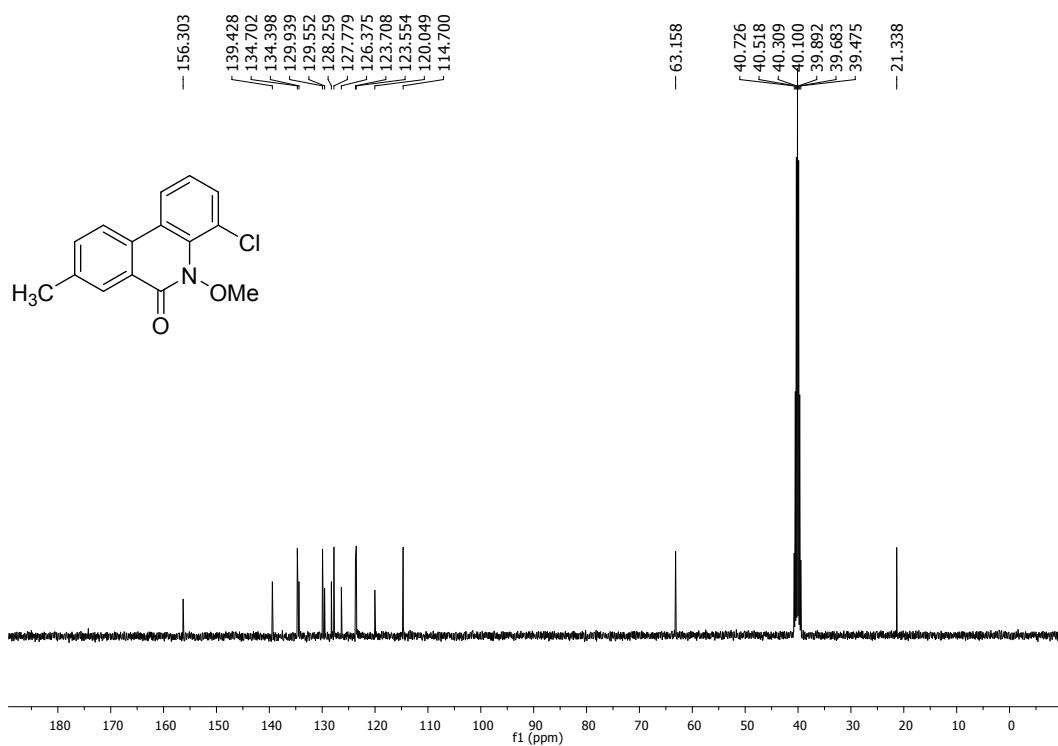


Figure S103. ¹³C{¹H} NMR spectrum of 4-Chloro-5-methoxy-8-methylphenanthridin-6(5H)-one (2m)

^1H NMR (400 MHz, CDCl_3)

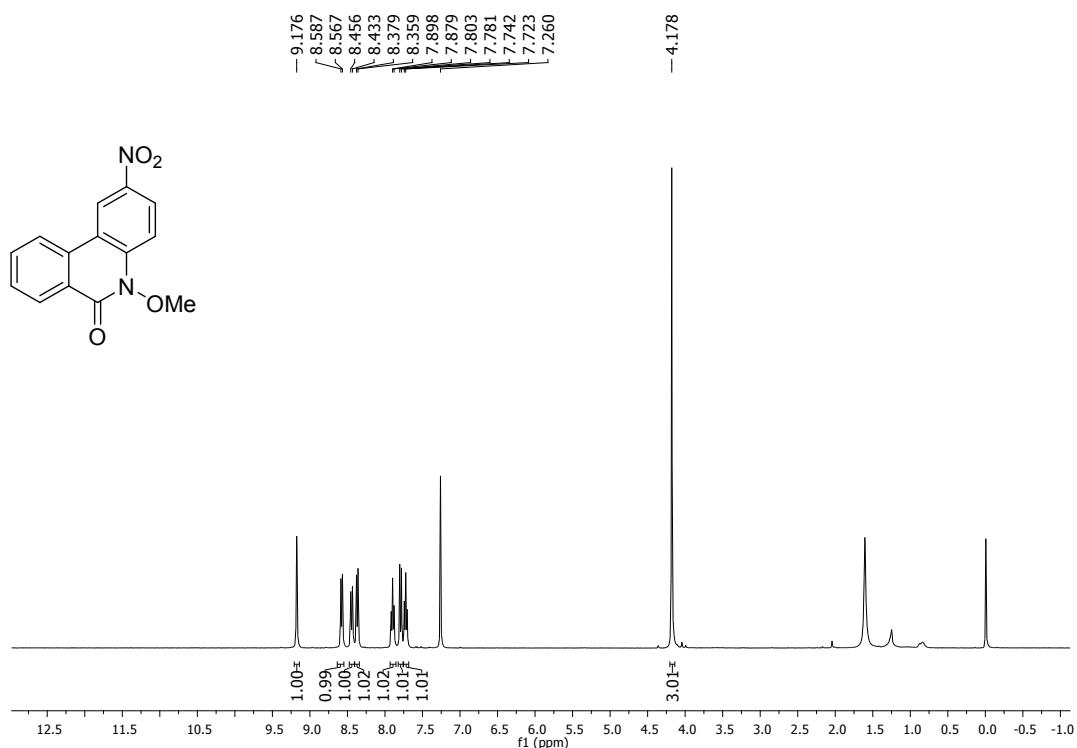


Figure S104. ^1H NMR spectrum of 5-Methoxy-2-nitrophenanthridin-6(5H)-one (**2o**)

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

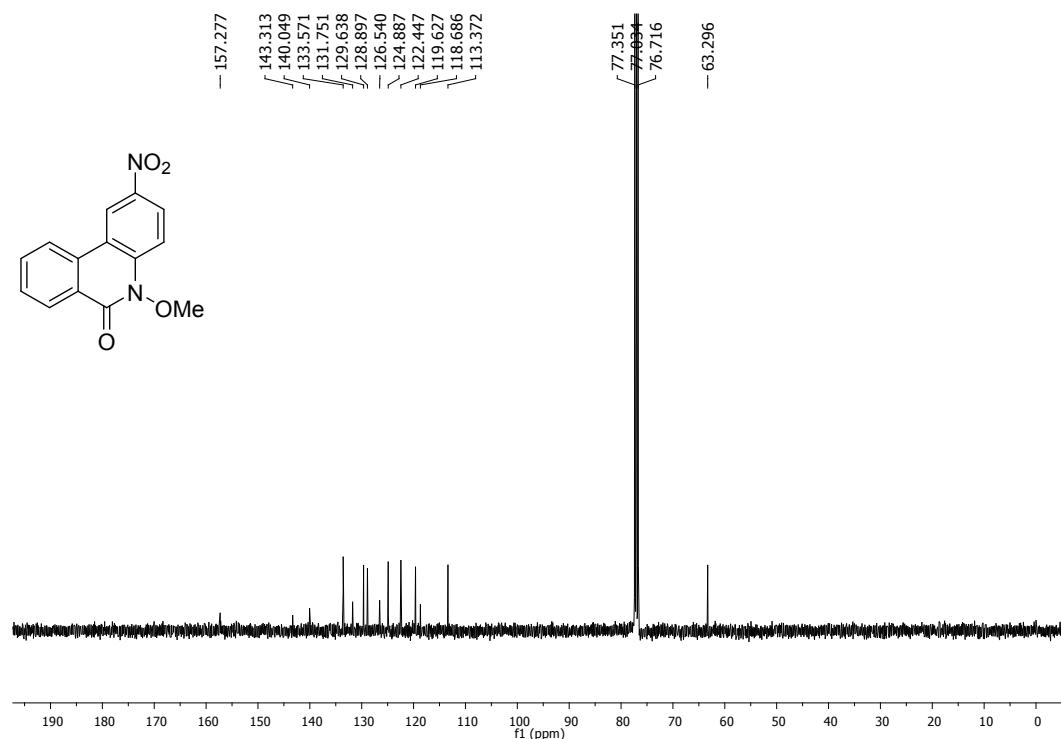


Figure S105. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5-Methoxy-2-nitrophenanthridin-6(5H)-one (**2o**)

¹H NMR (400 MHz, CDCl₃)

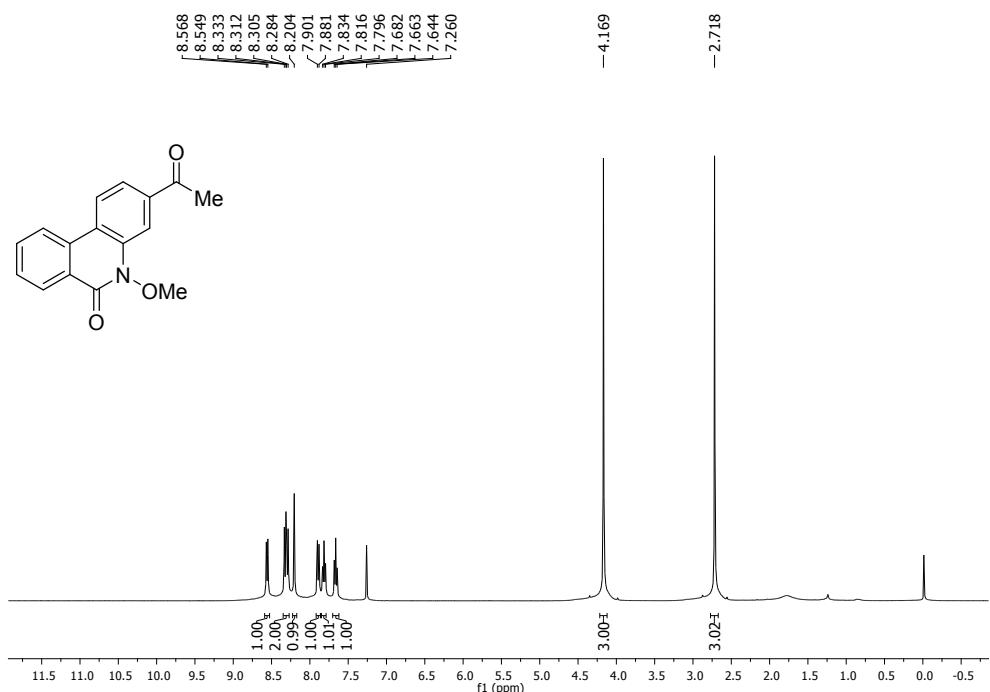


Figure S106. ¹H NMR spectrum of Methyl 5-methoxy-6-oxo-5,6-dihydrophenanthridine-3-carboxylate (**2p**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

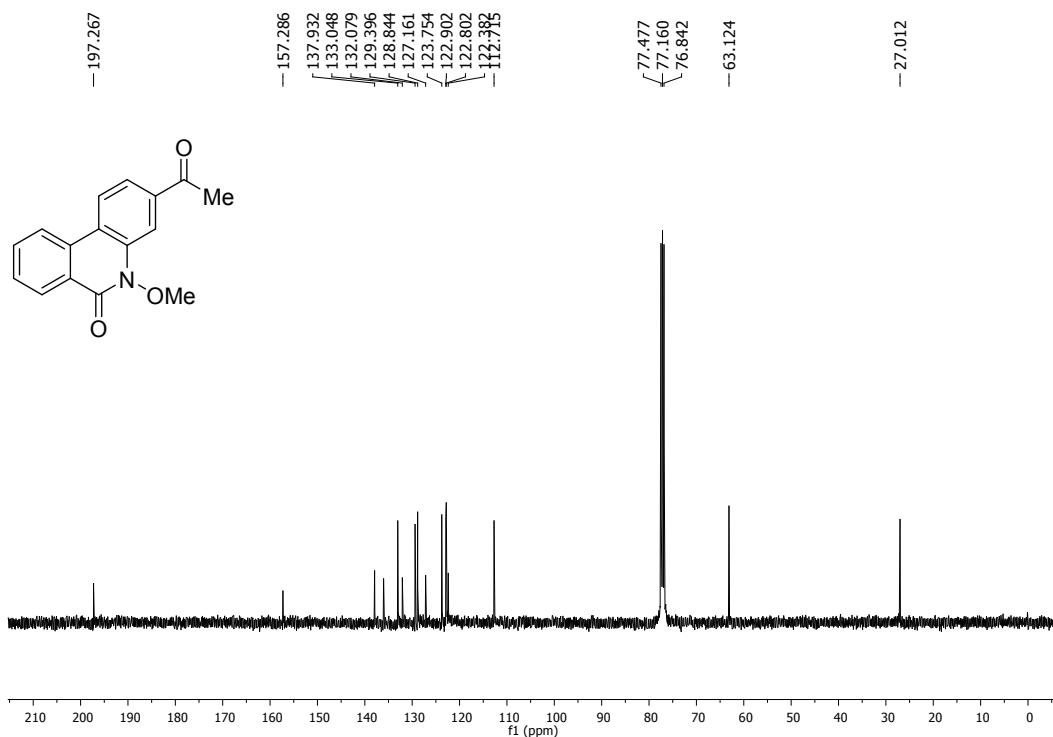


Figure S107. ¹³C{¹H} NMR spectrum of Methyl 5-methoxy-6-oxo-5,6-dihydrophenanthridine-3-carboxylate (**2p**)

¹H NMR (400 MHz, CDCl₃)

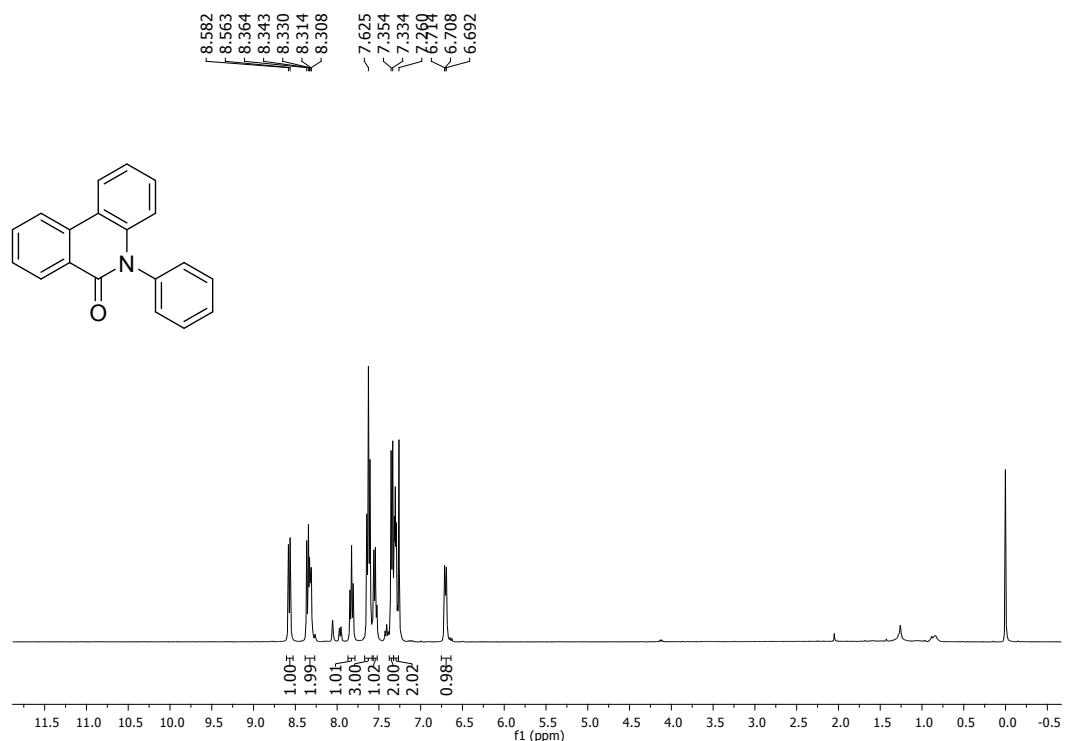


Figure S108. ¹H NMR spectrum of 5-Phenylphenanthridin-6(5H)-one (**2q**)

¹³C{¹H} NMR (100 MHz, CDCl₃)

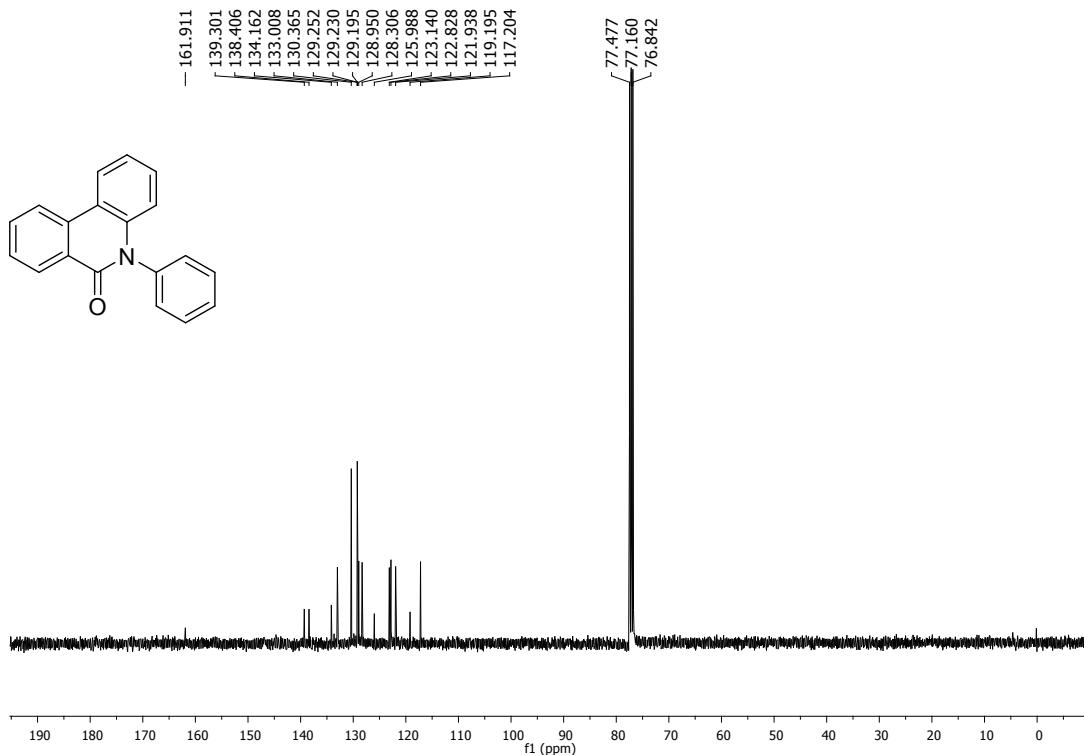


Figure S109. ¹³C{¹H} NMR spectrum of 5-Phenylphenanthridin-6(5H)-one (**2q**)

¹H NMR (700 MHz, CDCl₃)

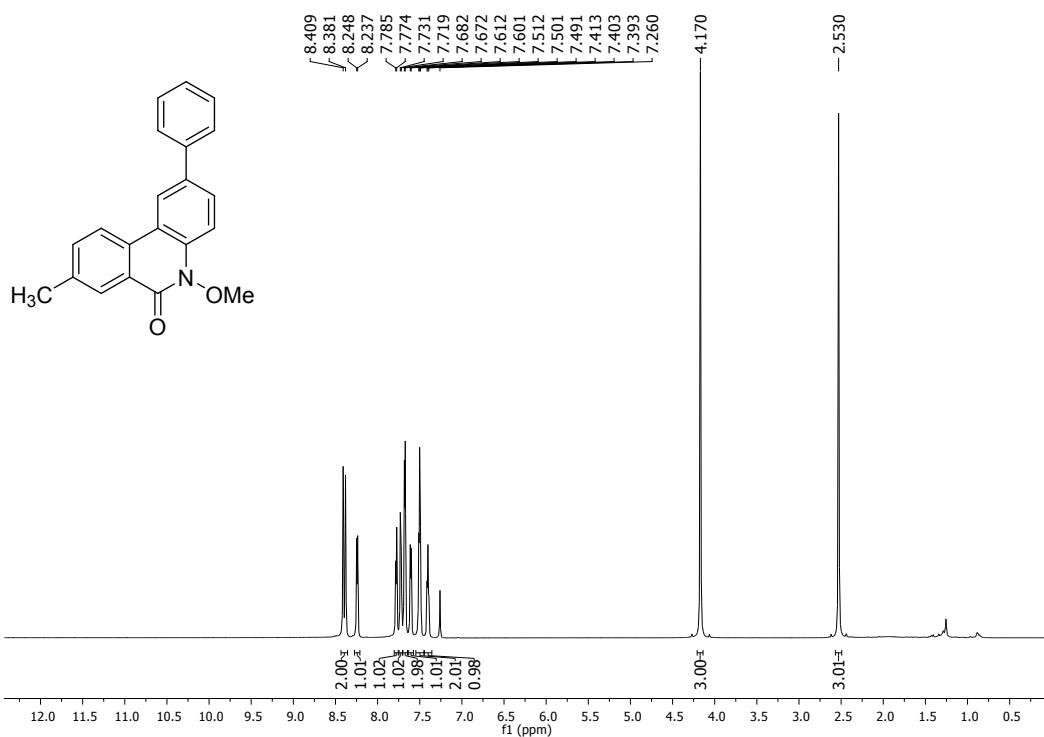


Figure S110. ¹H NMR spectrum of 5-Methoxy-8-methyl-2-phenylphenanthridin-6(5H)-one (5)

¹³C{¹H} NMR (175 MHz, CDCl₃)

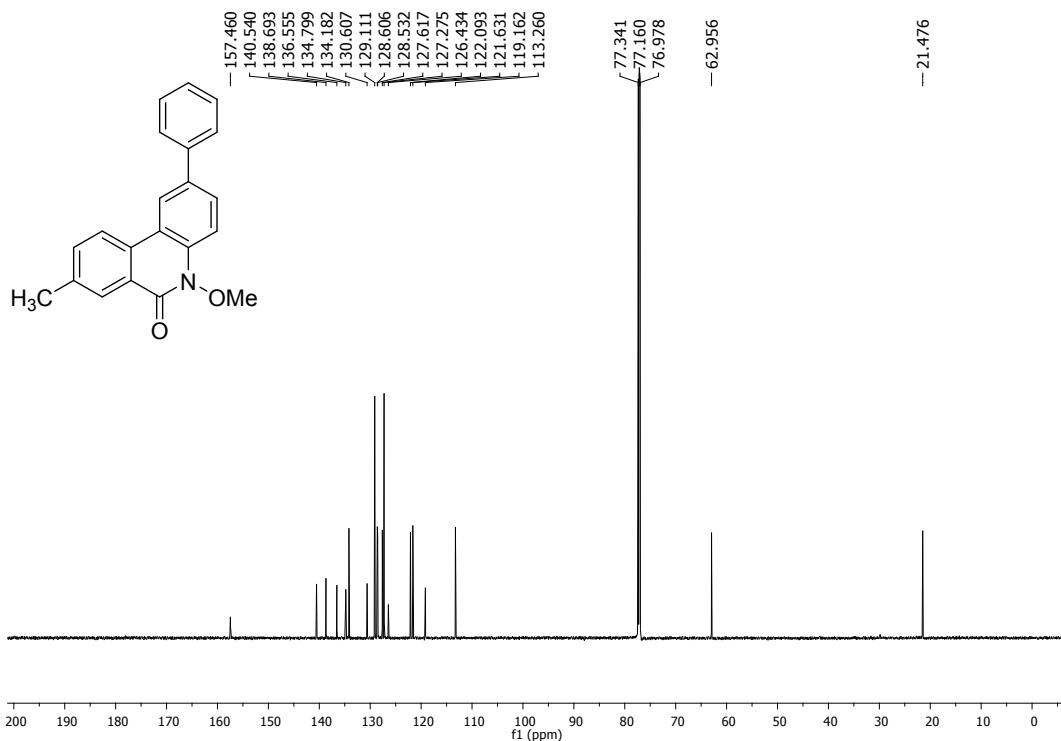


Figure S111. ¹³C{¹H} NMR spectrum of 5-Methoxy-8-methyl-2-phenylphenanthridin-6(5H)-one (5)

¹H NMR (700 MHz, CDCl₃)

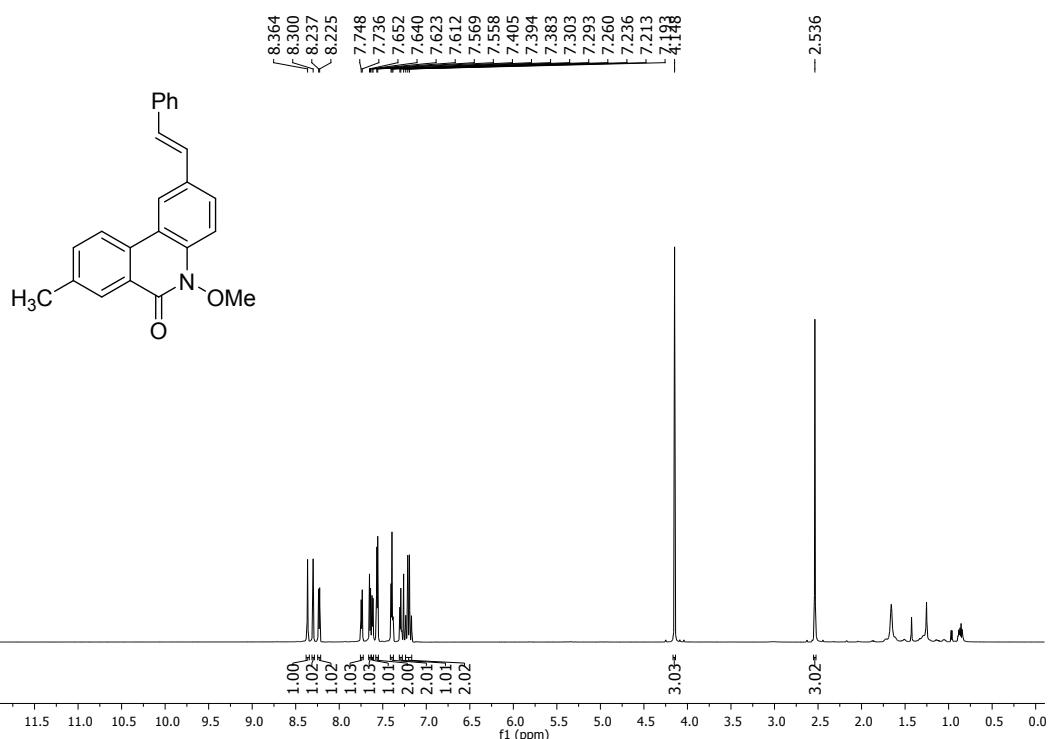


Figure S112. ¹H NMR spectrum of (E)-5-Methoxy-8-methyl-2-styrylphenanthridin-6(5H)-one (**6**)

¹³C{¹H} NMR (175 MHz, CDCl₃)

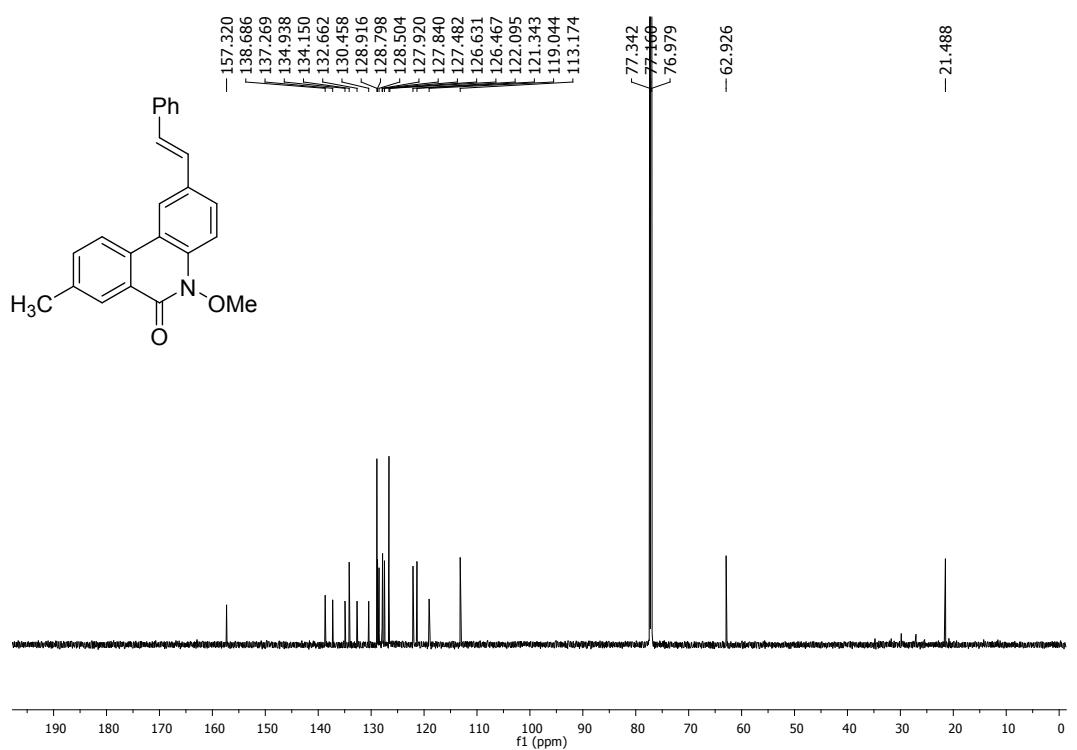


Figure S113. ¹³C{¹H} NMR spectrum of (E)-5-Methoxy-8-methyl-2-styrylphenanthridin-6(5H)-one (**6**)

^1H NMR (700 MHz, CDCl_3)

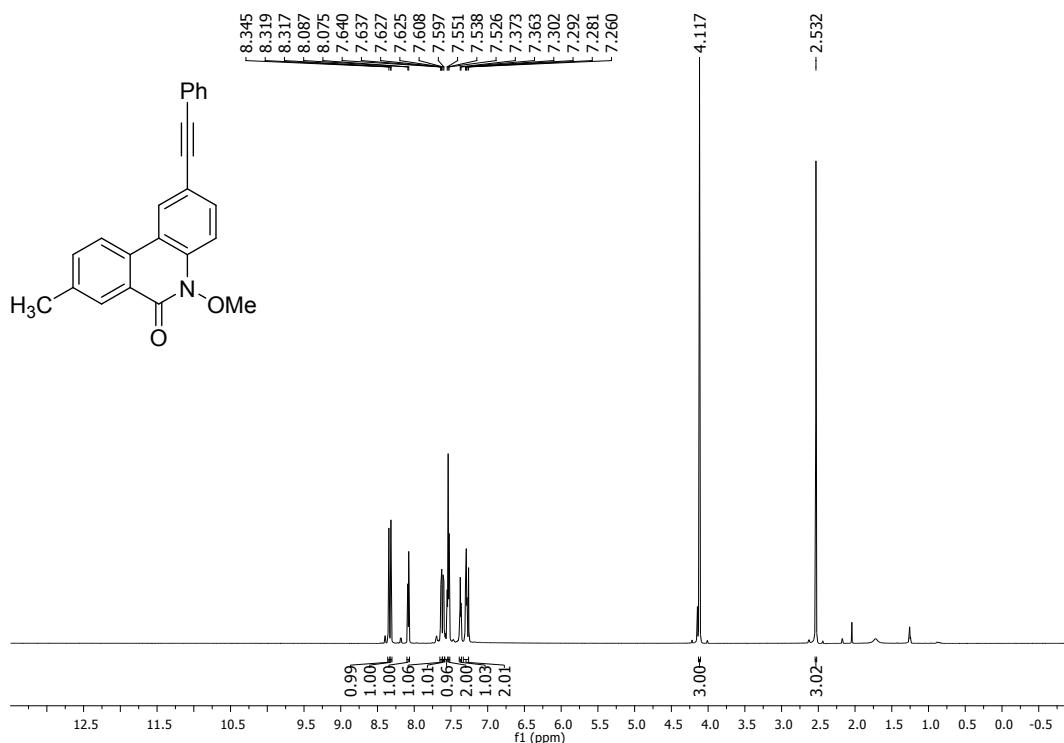


Figure S114. ^1H NMR spectrum of 5-Methoxy-8-methyl-2-(phenylethynyl)phenanthridin-6(5H)-one (7)

$^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3)

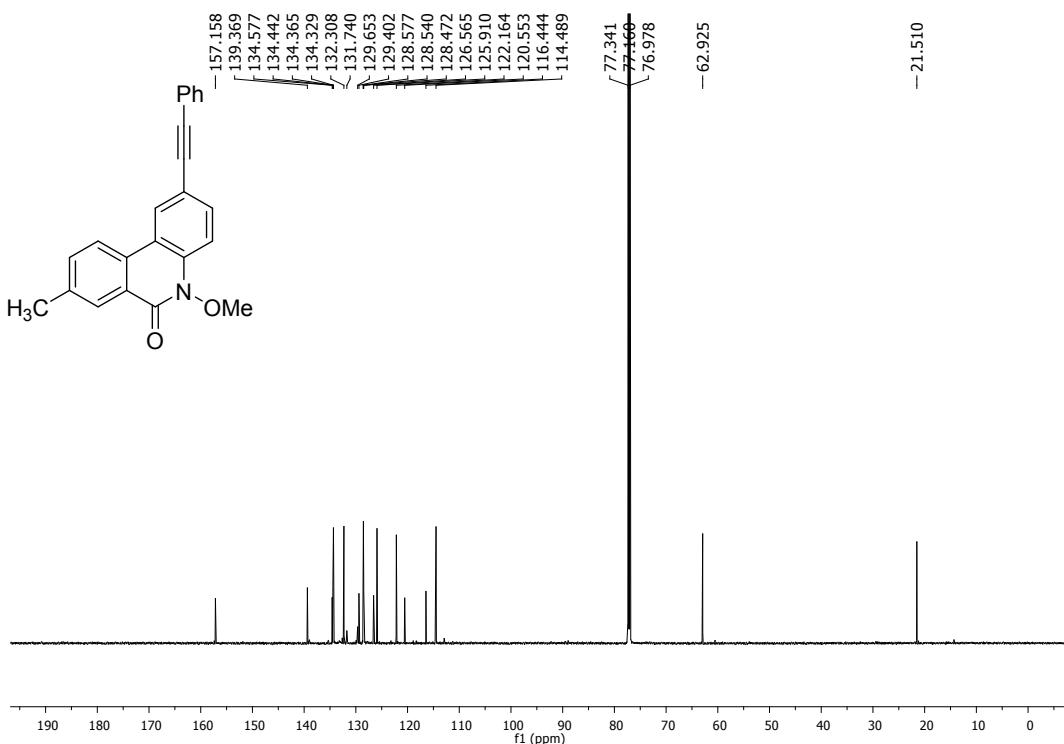


Figure S115. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5-Methoxy-8-methyl-2-(phenylethynyl)phenanthridin-6(5H)-one (7)

Display Report

Analysis Info

Analysis Name D:\Data\MAR-2021\NKS\16032021_PM_SKB_139_R.d
 Method Pos_tune_low.m
 Sample Name Tmix-131118
 Comment

Acquisition Date 3/16/2021 3:04:13 PM

 Operator Amit S.Sahu
 Instrument micrOTOF-Q II 10337

Acquisition Parameter

Source Type ESI	Ion Polarity Positive	Set Nebulizer 0.4 Bar
Focus Not active	Set Capillary 4500 V	Set Dry Heater 180 °C
Scan Begin 50 m/z	Set End Plate Offset -500 V	Set Dry Gas 4.0 l/min
Scan End 3000 m/z	Set Collision Cell RF 130.0 Vpp	Set Divert Valve Waste

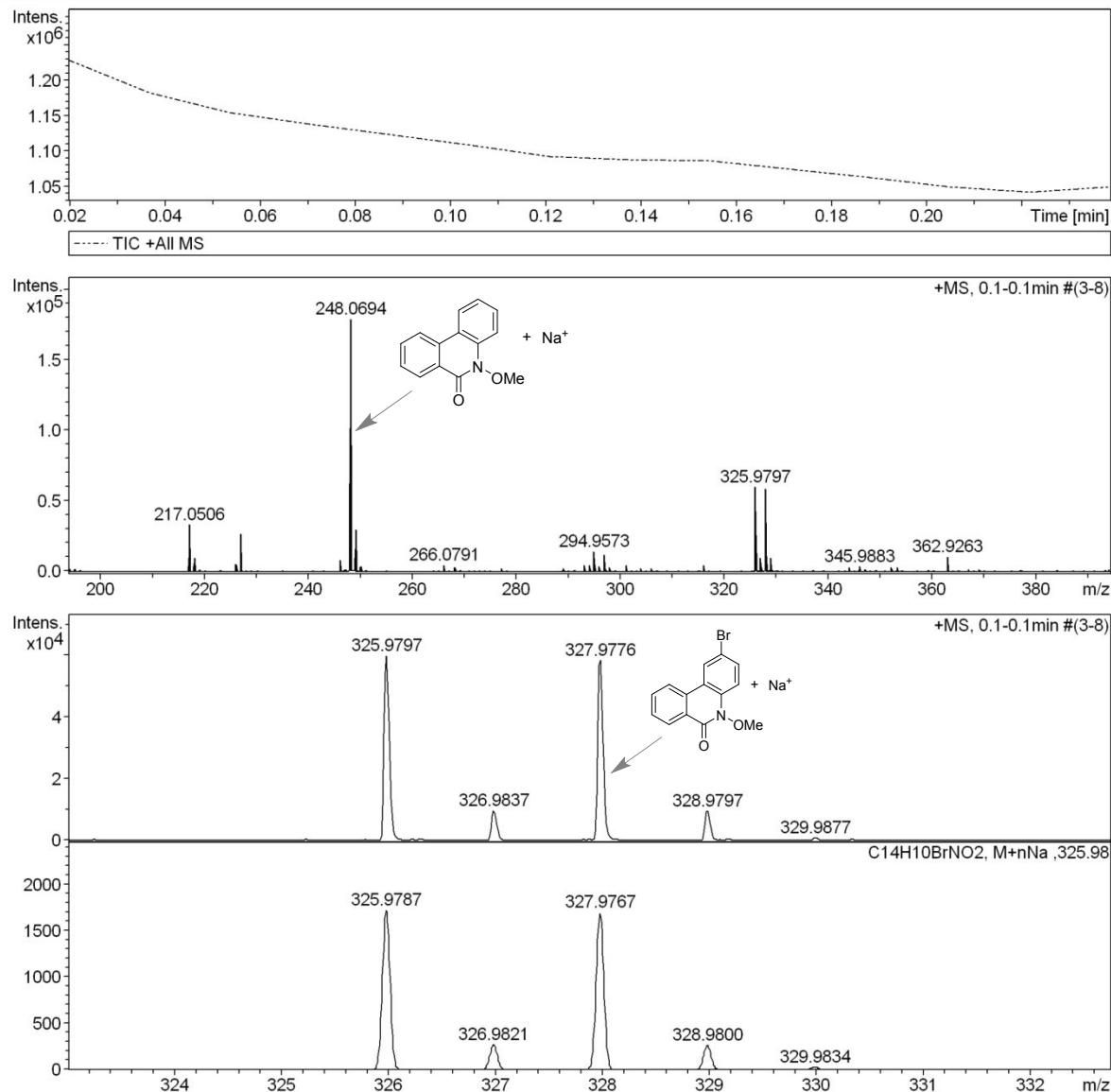


Figure S116. ESI-MS analysis of the reaction mixture using 2.0 equiv of NBS and **1a**.

Display Report

Analysis Info

Analysis Name	D:\Data\APR-2021\PM\13042021_PM_SKB_04_108.d	Acquisition Date	4/13/2021 3:11:51 PM
Method	Pos_tune_low.m	Operator	Amit S.Sahu
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

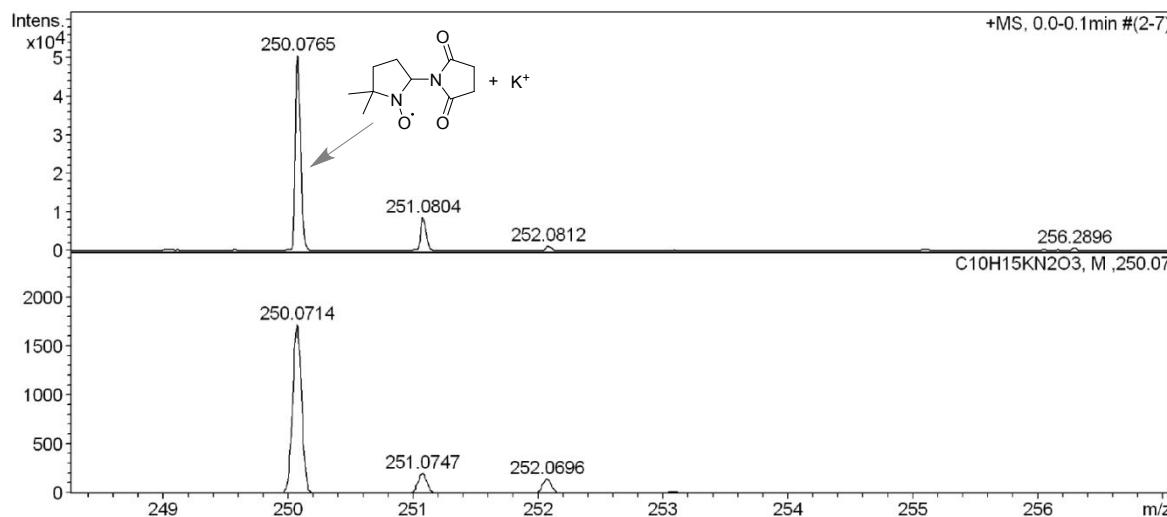
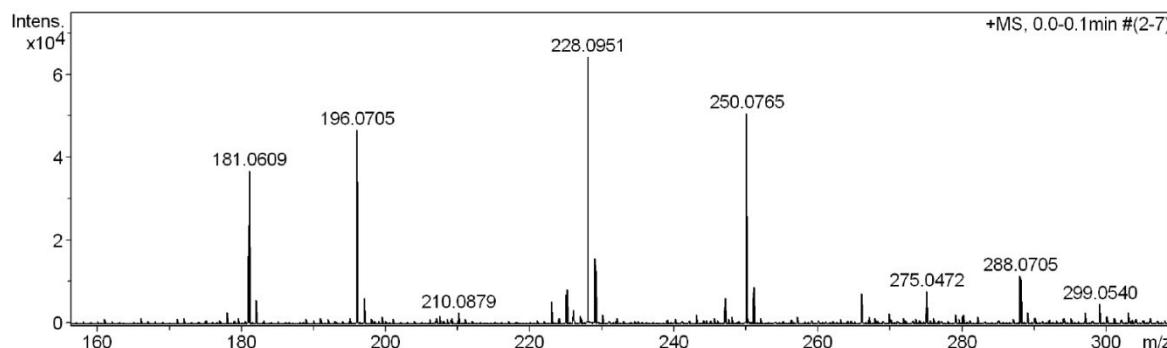
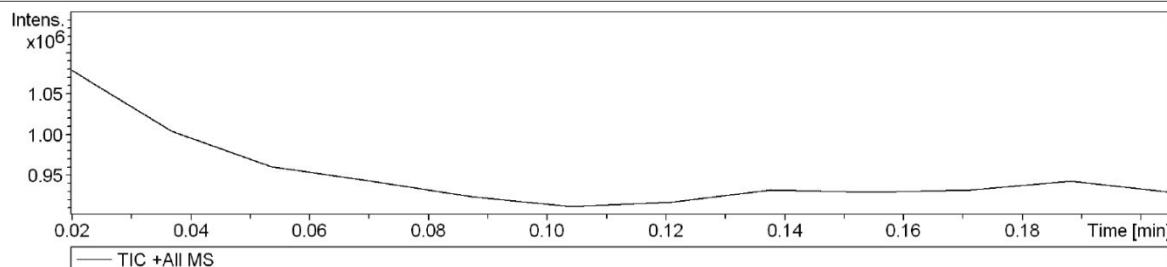


Figure S117. Experiment using DMPO under standard condition and the corresponding ESI-MS spectrum. The sample used for the EPR study.