Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary data

Ru(II)-catalysed oxidative (4+2) annulation of chromene and coumarin carboxylic acids with alkynes/propargylic alcohols: Isolation of Ru(0) complexes

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Crystallographic data for compounds 5aa, 5ce, 5cj, 6aa and 7ab

Single crystal X-ray data for crystals of compounds **5aa, 5ce, 5cj, 6aa and 7ab** were collected on an X-ray diffractometer using Mo-Kα (λ = 0.71073 Å) radiation after mounting on glass fibers inside a brass pin in open air. The structures were solved by direct methods and refined by full matrix least squares method using standard procedures; absorption corrections were done using SADABS program, where applicable.[1] In general, all non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a Difference Fourier map and refined isotropically. CCDC numbers are 2213160-2213164.

ORTEPs and crystal data of* 5aa, 5ce, 5cj, 6aa and 7ab *(Figures* S1-S5*)

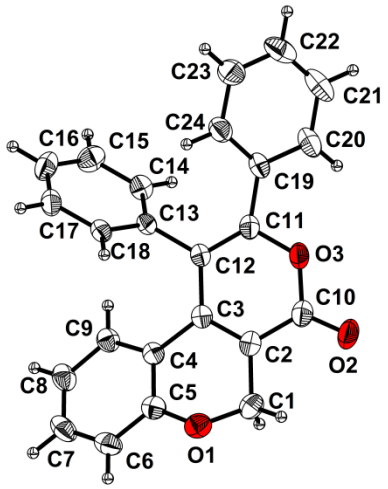


Figure S1. ORTEP view of compound **5aa** with 30% probability of ellipsoids. **Crystal data**: $C_{24}H_{16}O_3$, *M* = 352.37, Orthorhombic, Space group *Pna2 (1)*, *a* = 7.9771(3), *b* = 14.2651(6), *c* = 15.4453(7) Å, *V* = 1757.58(13) $Å^3$, *Z* = 4, μ = 0.087 mm^{-1}, data/restraints/parameters: 2973/1/245, R indices (I>2sigma(I): R1 = 0.0288, *w*R2 (all data) = 0.0747. Solvent for crystallization: EtOAc + hexane. CCDC No: 2213160.

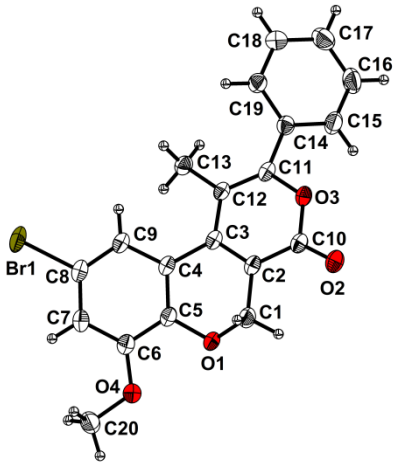


Figure S2. ORTEP view of compound **5ce** with 30% probability of ellipsoids. **Crystal data**: $C_{21}H_{15}BrClO_4$, M = 446.69, Monoclinic, Space group *P2(1)/c*, a = 16.4674(10), b = 7.5481(5), c = 16.6864(10) Å, V = 1837.3(2) Å^3, β = 117.646(2)^o, Z = 4, μ = 2.408 mm^{-1}, data/restraints/parameters: 3187/0/246, R indices (>2sigma(I): R1 = 0.0462, *w*R2 (all data) = 0.1320. Solvent for crystallization: DCM + hexane. CCDC No: 2213161.

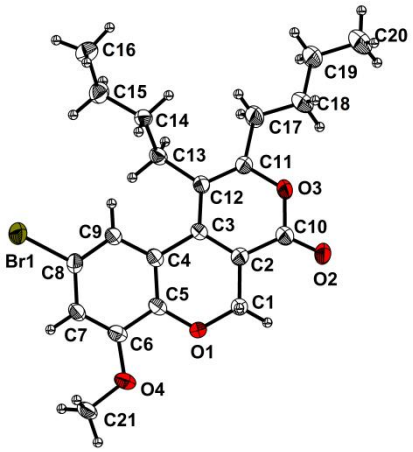


Figure S3. ORTEP view of compound **5cj** with 30% probability of ellipsoids. **Crystal data**: $C_{21}H_{25}BrO_4$, M = 421.32, Monoclinic, Space group *P 1 21 1*, a = 5.1663(2), b = 14.7442(5), c = 12.9318(5) Å, V = 974.41(6) Å^3, β = 98.432(4)^o, Z = 2, μ = 2.132 mm^{-1}, data/restraints/parameters: 2954/1/238, R indices (>2sigma(I)): R1 = 0.0544, *w*R2 (all data) = 0.1402. Solvent for crystallization: EtOAc + hexane. CCDC No: 2213162.

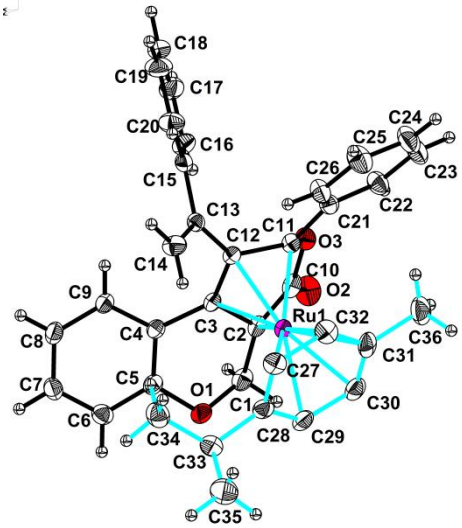


Figure S4. ORTEP view of compound **6aa** with 30% probability of ellipsoids. **Crystal data**: $C_{36}H_{32}O_3Ru$, M = 613.72, Monoclinic, Space group *P2(1)/c*, a = 18.2137(11) b = 9.1058(6) c = 17.3141(10) Å, V = 2781.2(3) Å^3, β = 104.407(2)^o Z = 4, μ = 0.600 mm^{-1}, data/restraints/parameters: 4886/0/364, R indices (>2sigma(I)): R1 = 0.0201, *w*R2 (all data) = 0.0543. Solvent for crystallization: EtOAc + hexane. CCDC No: 2213163.

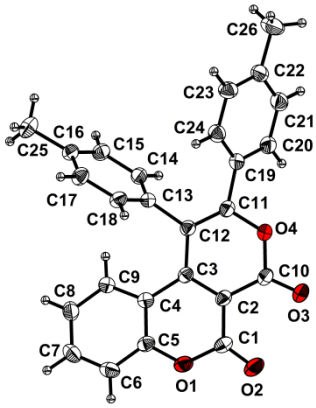


Figure S5. ORTEP view of compound **7ab** with 30% probability of ellipsoids. **Crystal data**: $C_{26}H_{18}O_4$, M = 394.40, Orthorhombic, Space group *Fdd2*, a = 52.655(4), b = 7.5681(4), c = 19.8301(12) Å, V = 7902.3(9) Å^3, Z = 16, μ = 0.089 mm^{-1}, data/restraints/parameters: 3261 /1/274, R indices (>2sigma(I)): R1 = 0.0339, *w*R2 (all data) = 0.0873. Solvent for crystallization: EtOAc + hexane. CCDC No: 2213164.

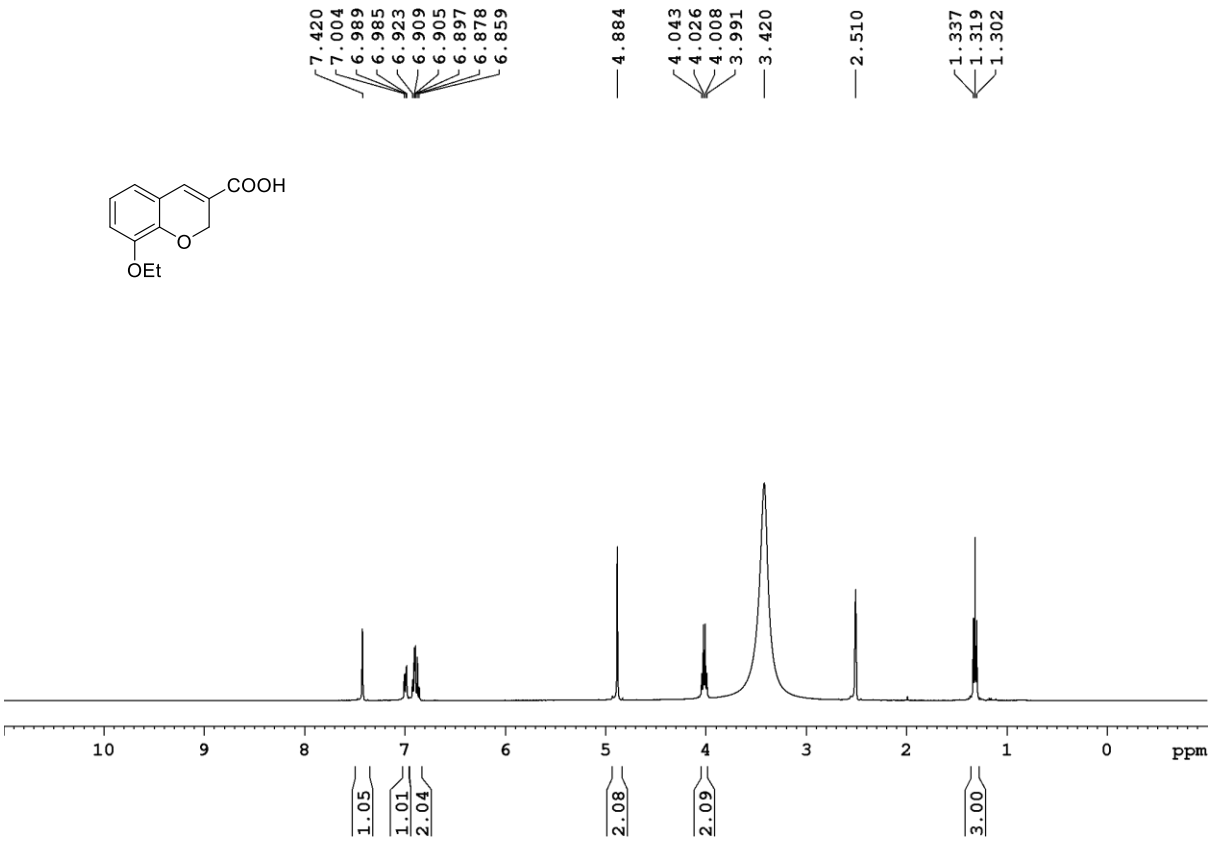


Figure S6. ^{1}H NMR spectrum of compound **1b**

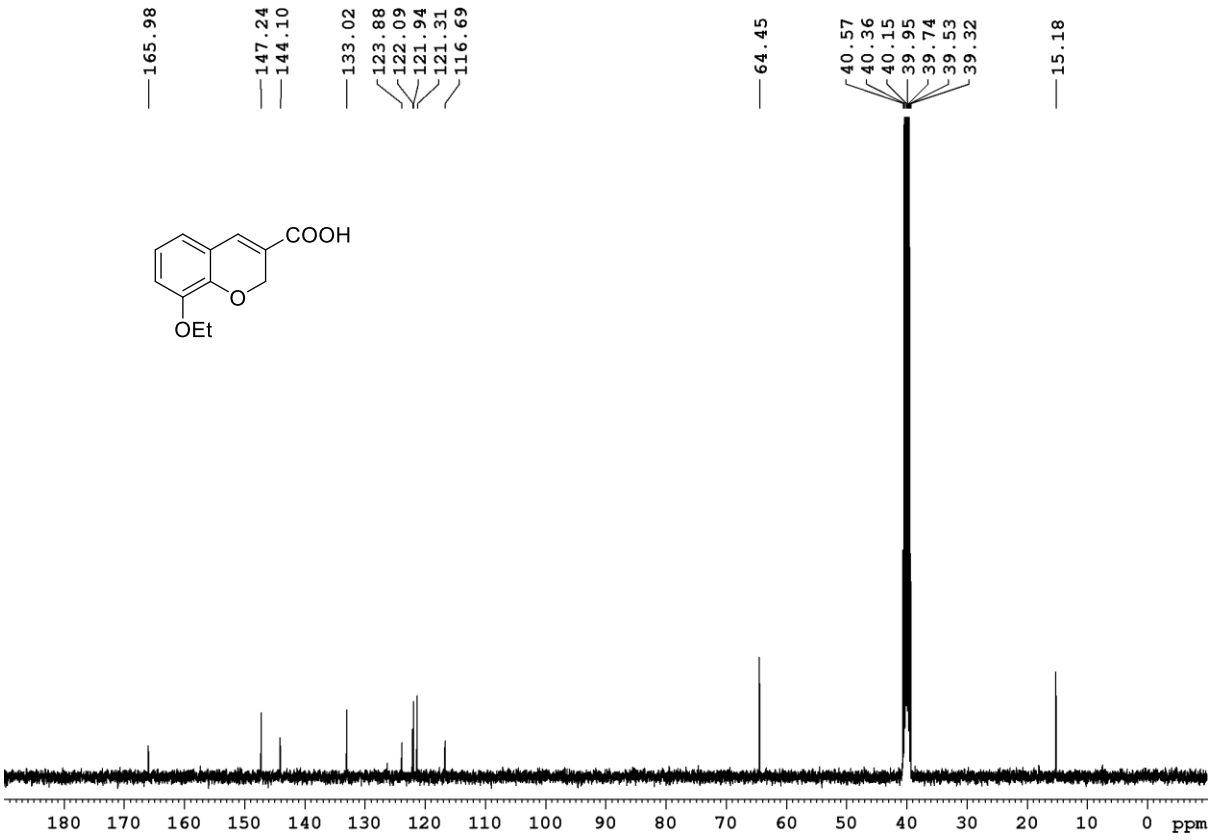


Figure S7. ^{13}C{^{1}H} NMR spectrum of compound **1b**

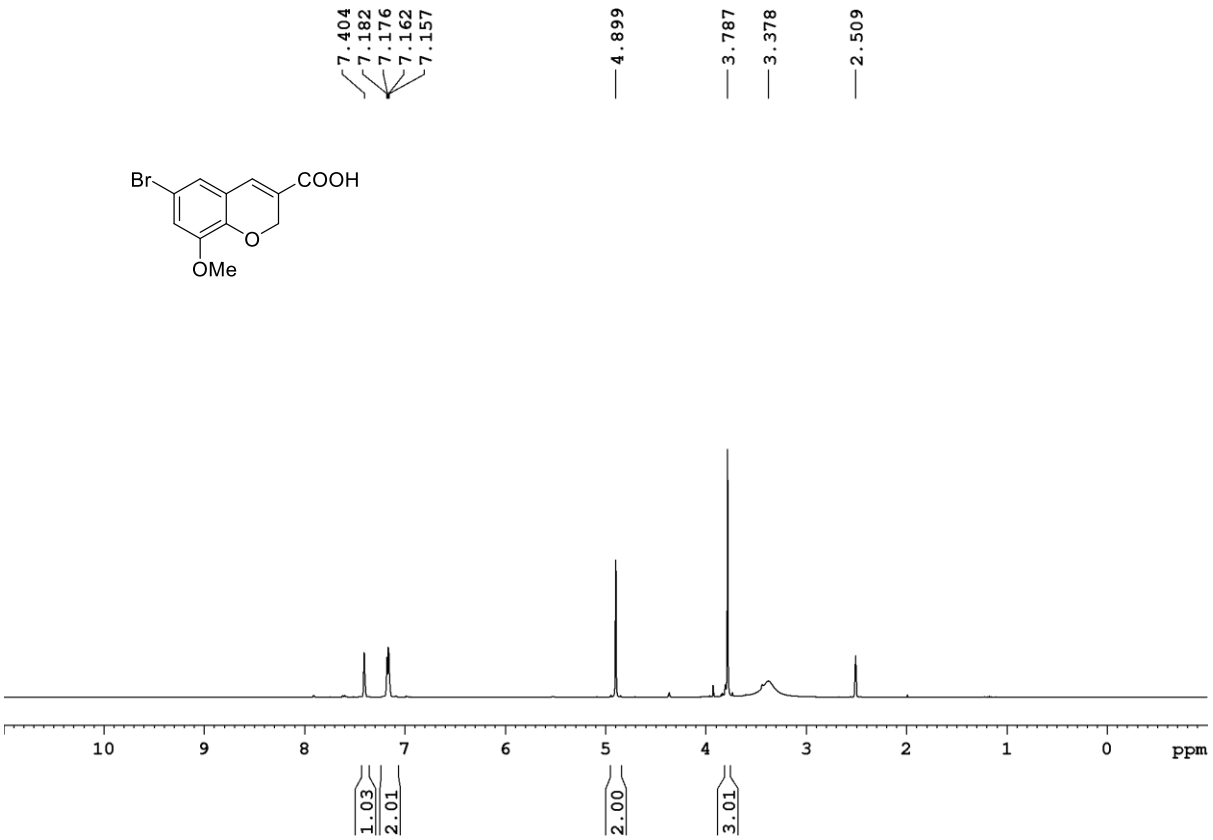


Figure S8. ^{1}H NMR spectrum of compound **1c**

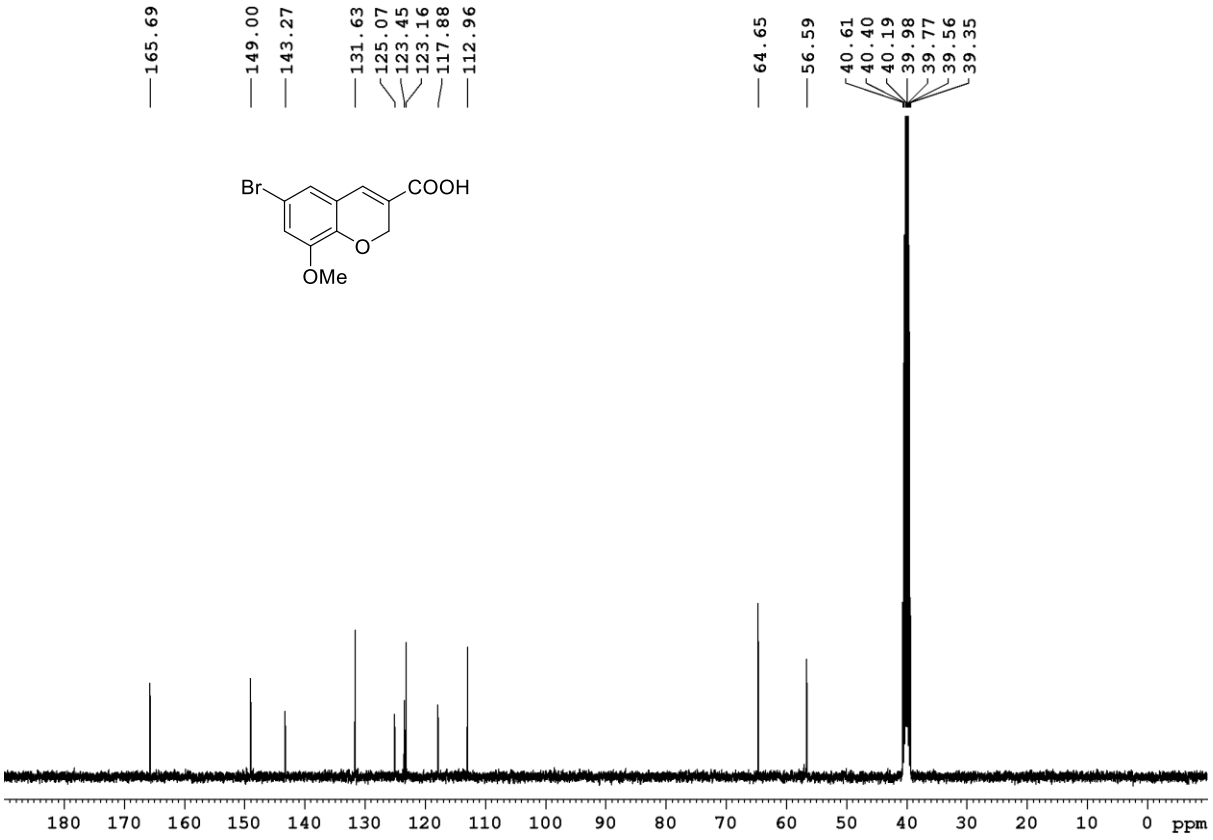


Figure S9. ^{13}C{^{1}H} NMR spectrum of compound **1c**

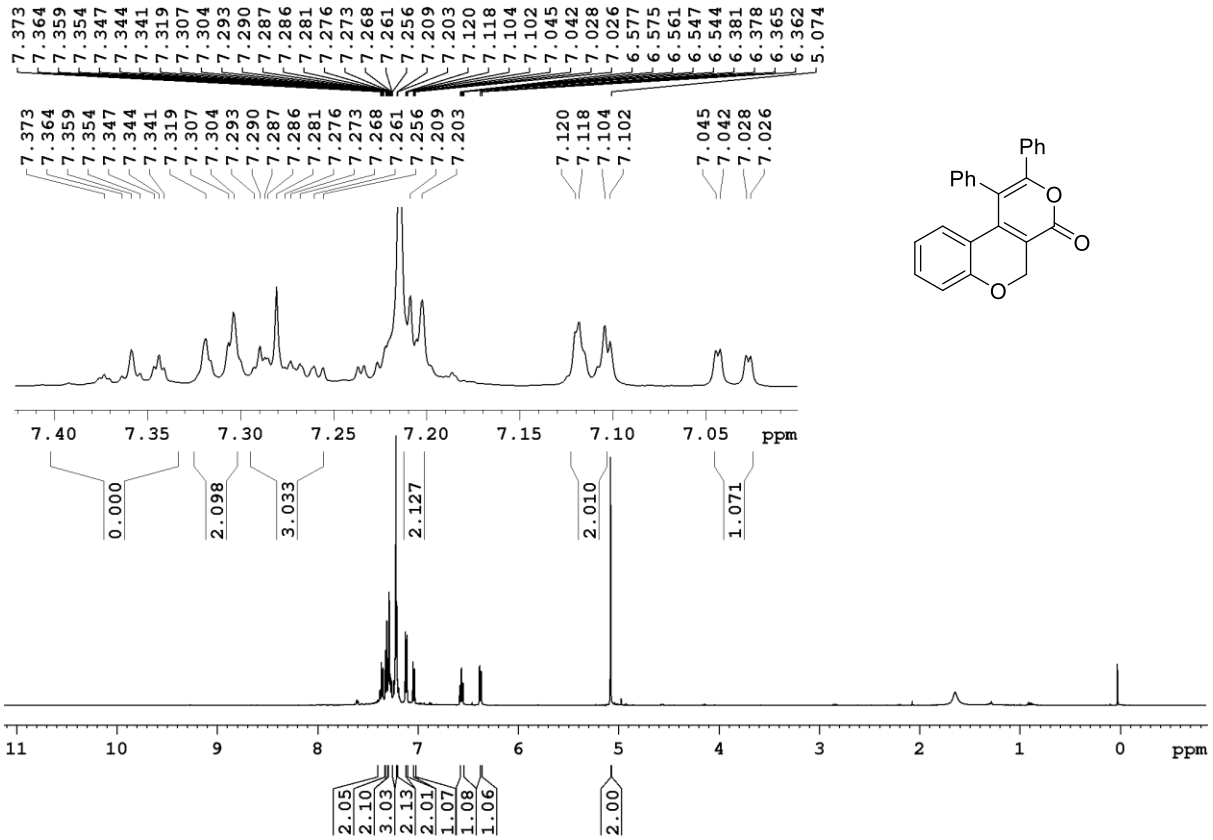


Figure S10. ^{1}H NMR spectrum of compound **5aa**

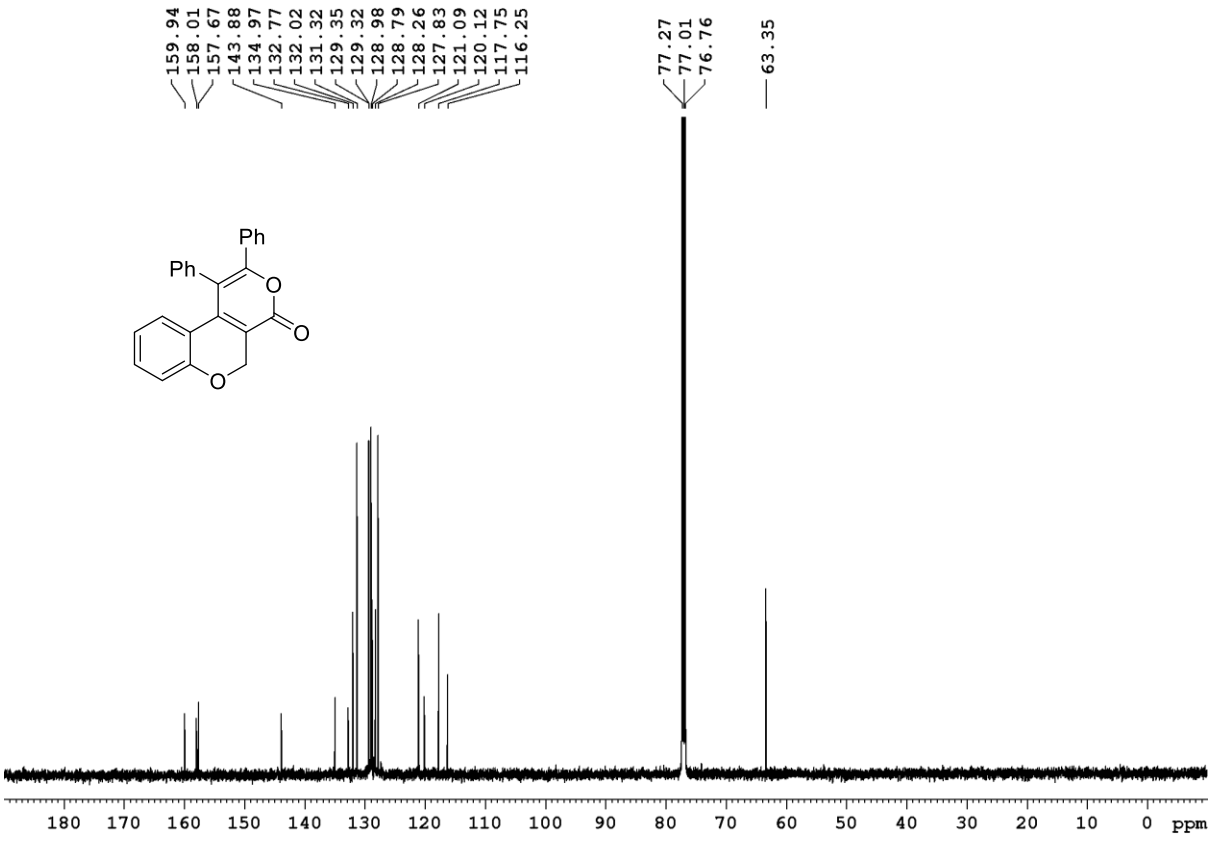


Figure S11. ^{13}C{^{1}H} NMR spectrum of compound **5aa**

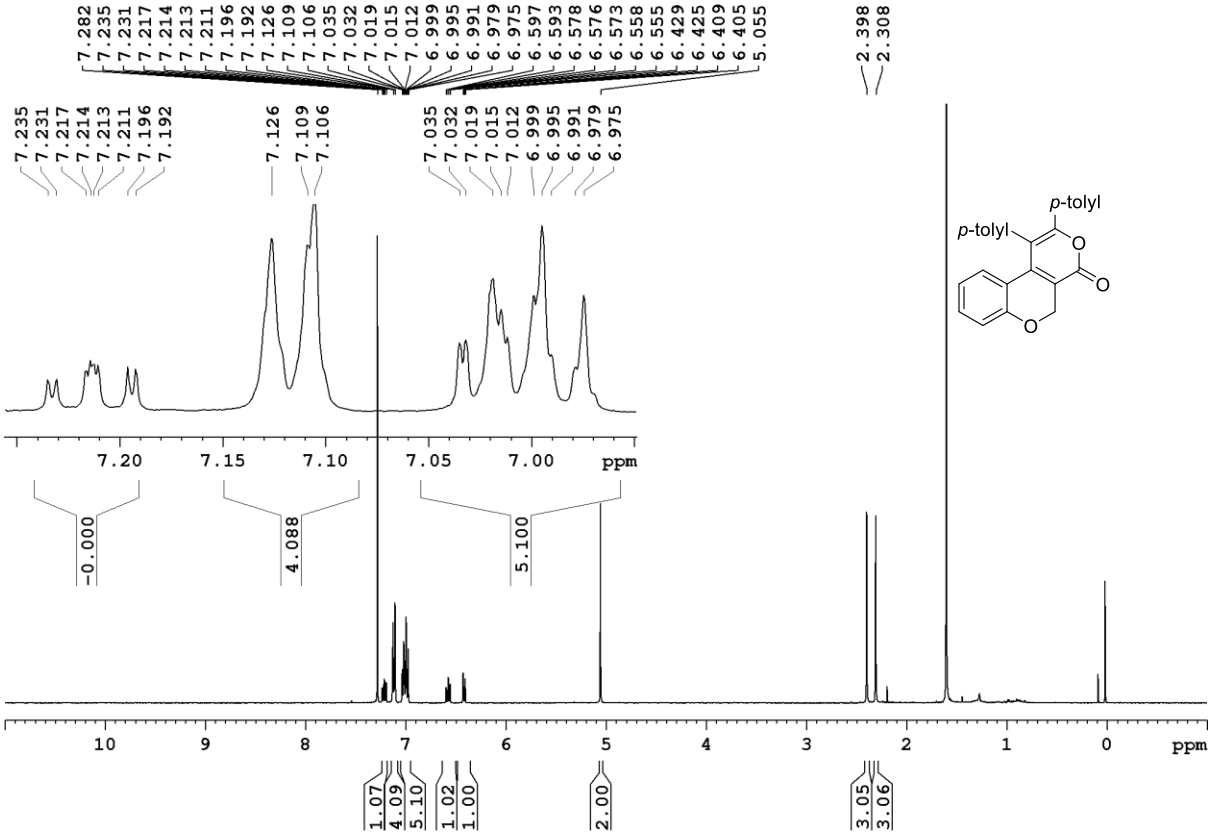


Figure S12. ^{1}H NMR spectrum of compound **5ab**

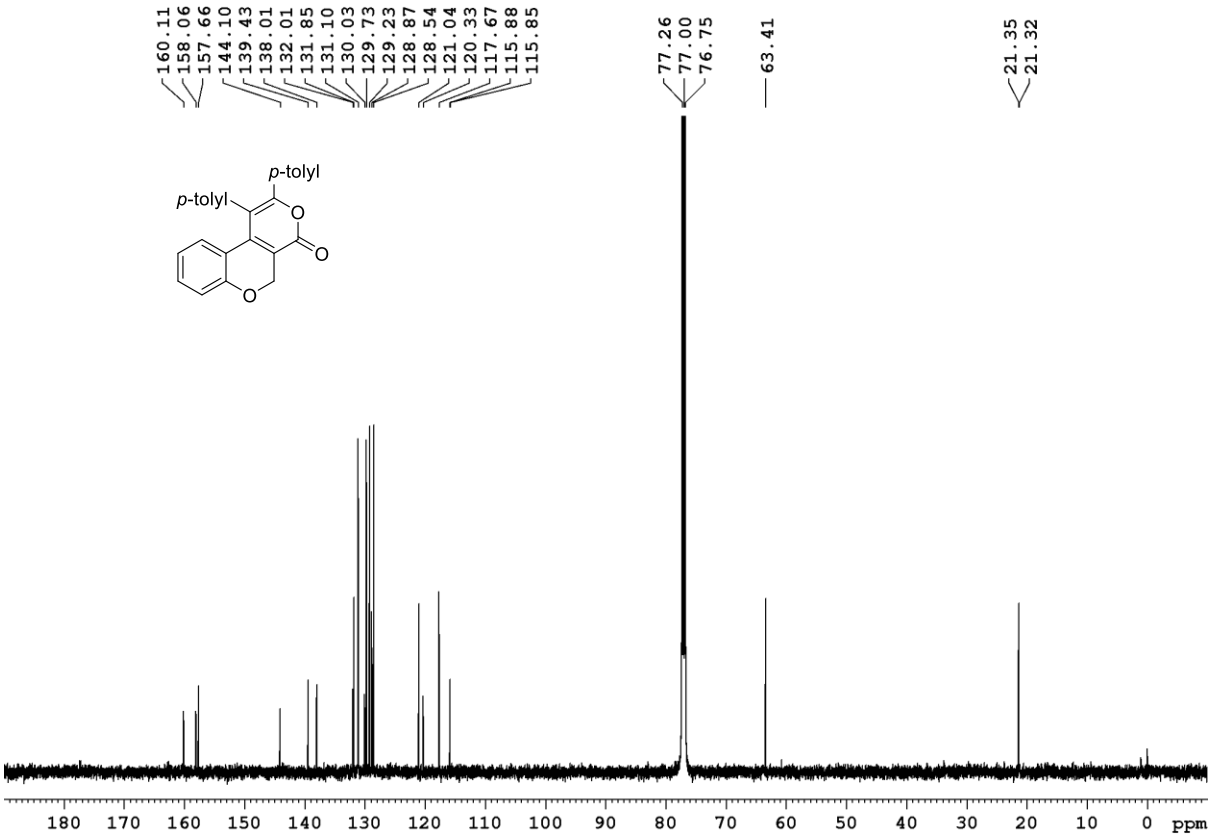


Figure S13. ^{13}C{^{1}H} NMR spectrum of compound **5ab**

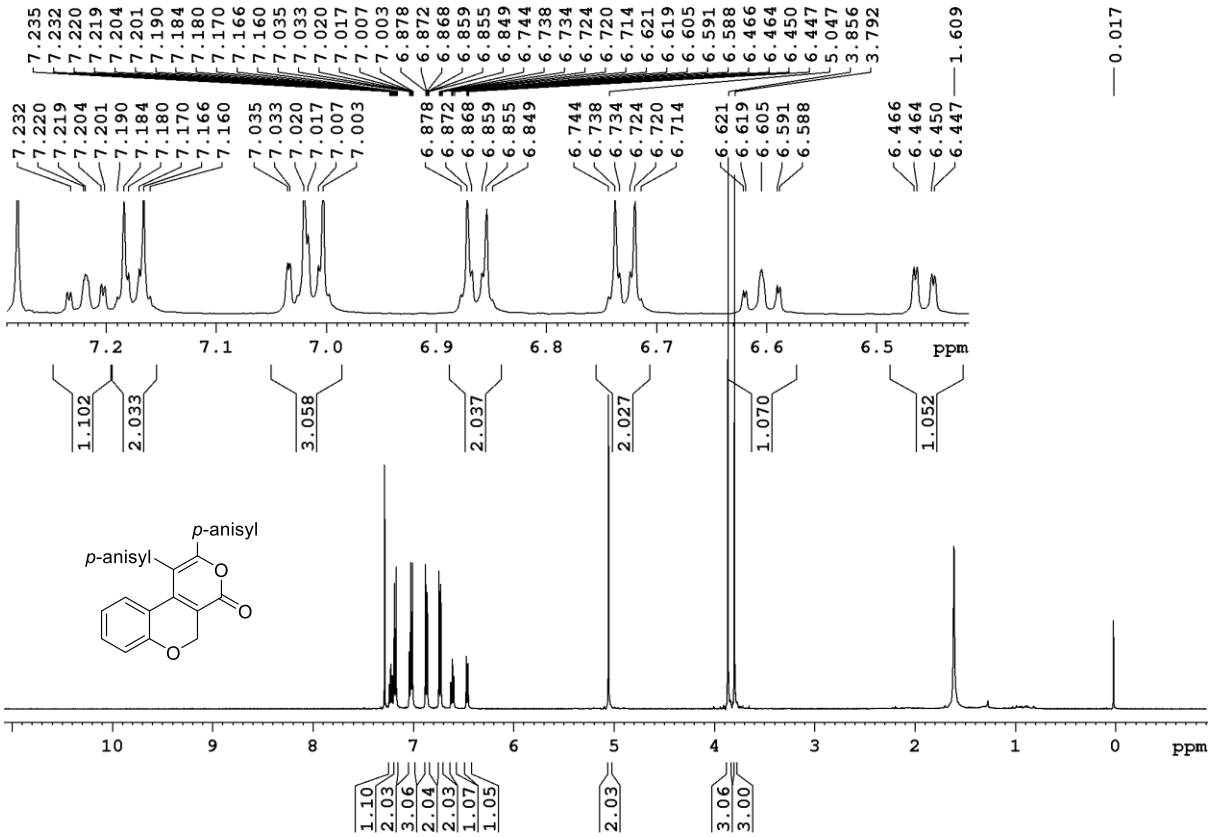


Figure S14. ^{1}H NMR spectrum of compound **5ac**

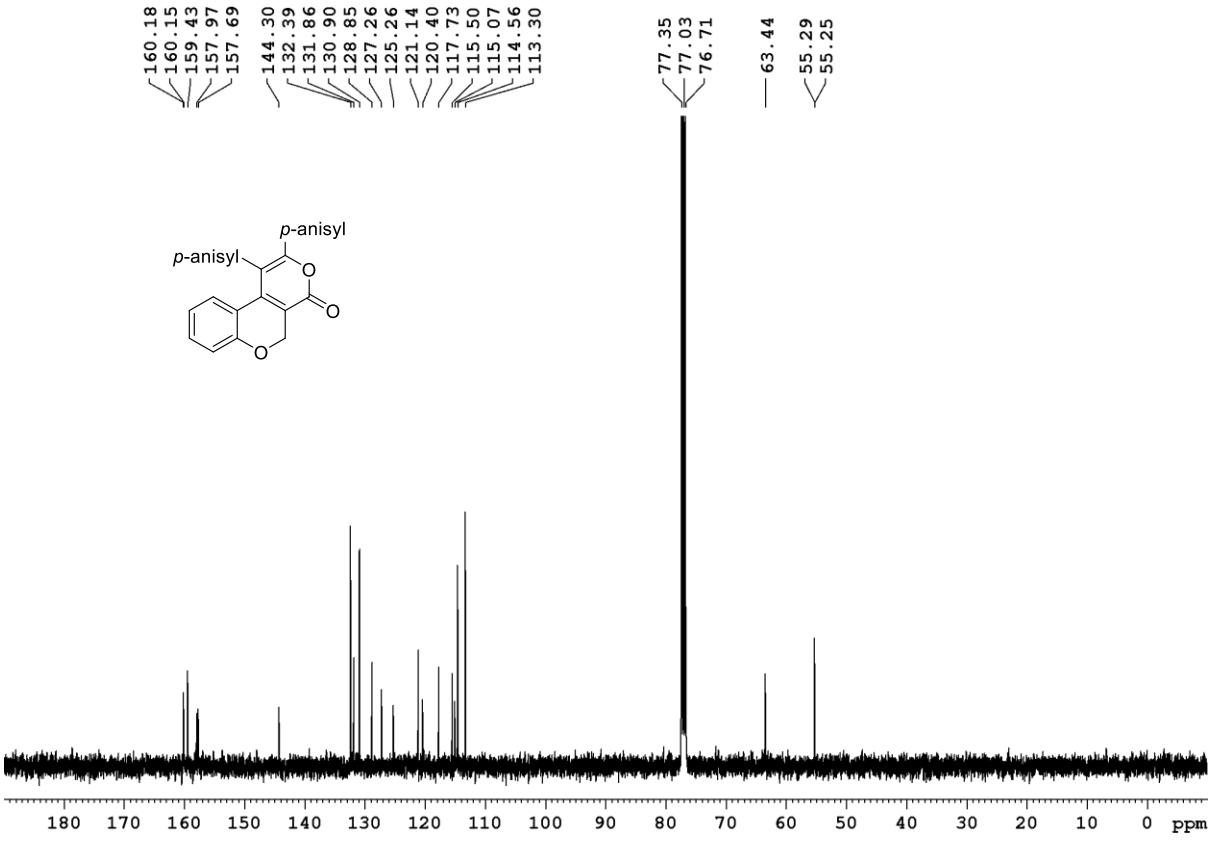


Figure S15. ^{13}C{^{1}H} NMR spectrum of compound **5ac**

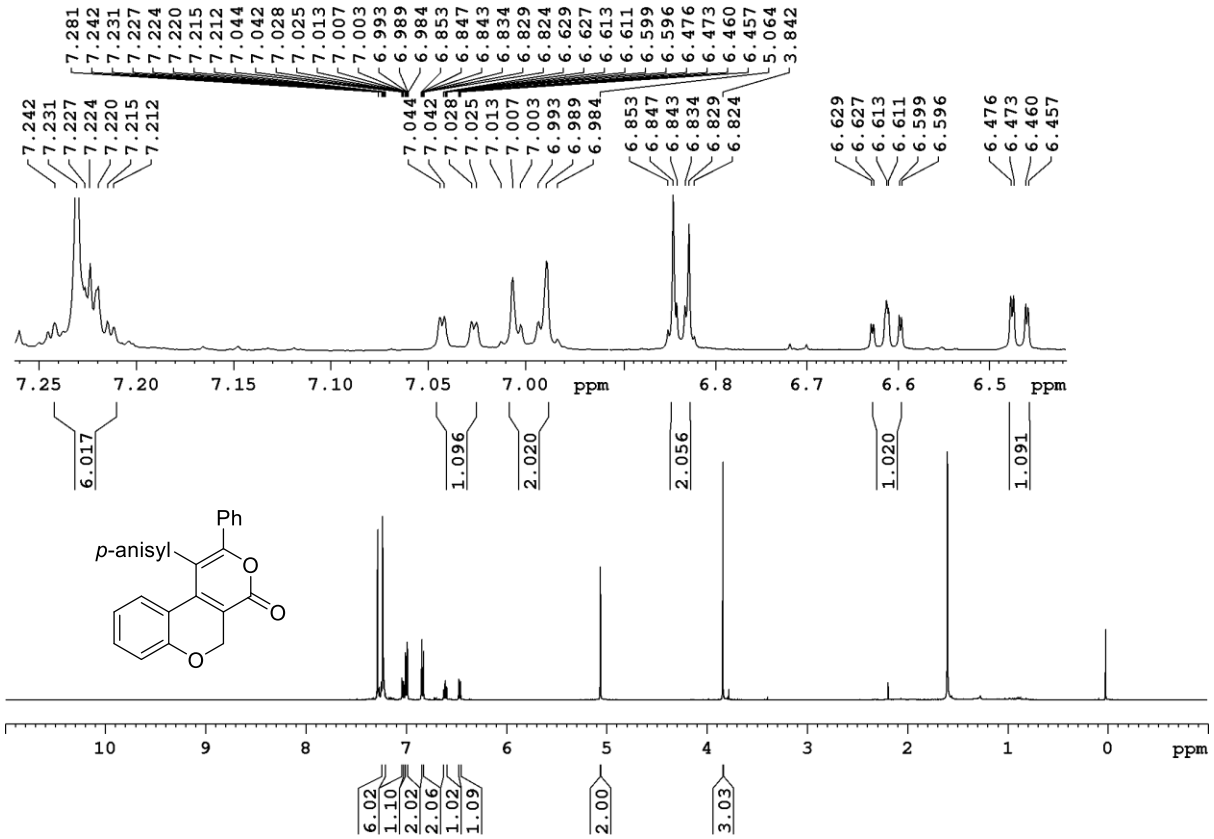


Figure S16. ^{1}H NMR spectrum of compound **5ad**

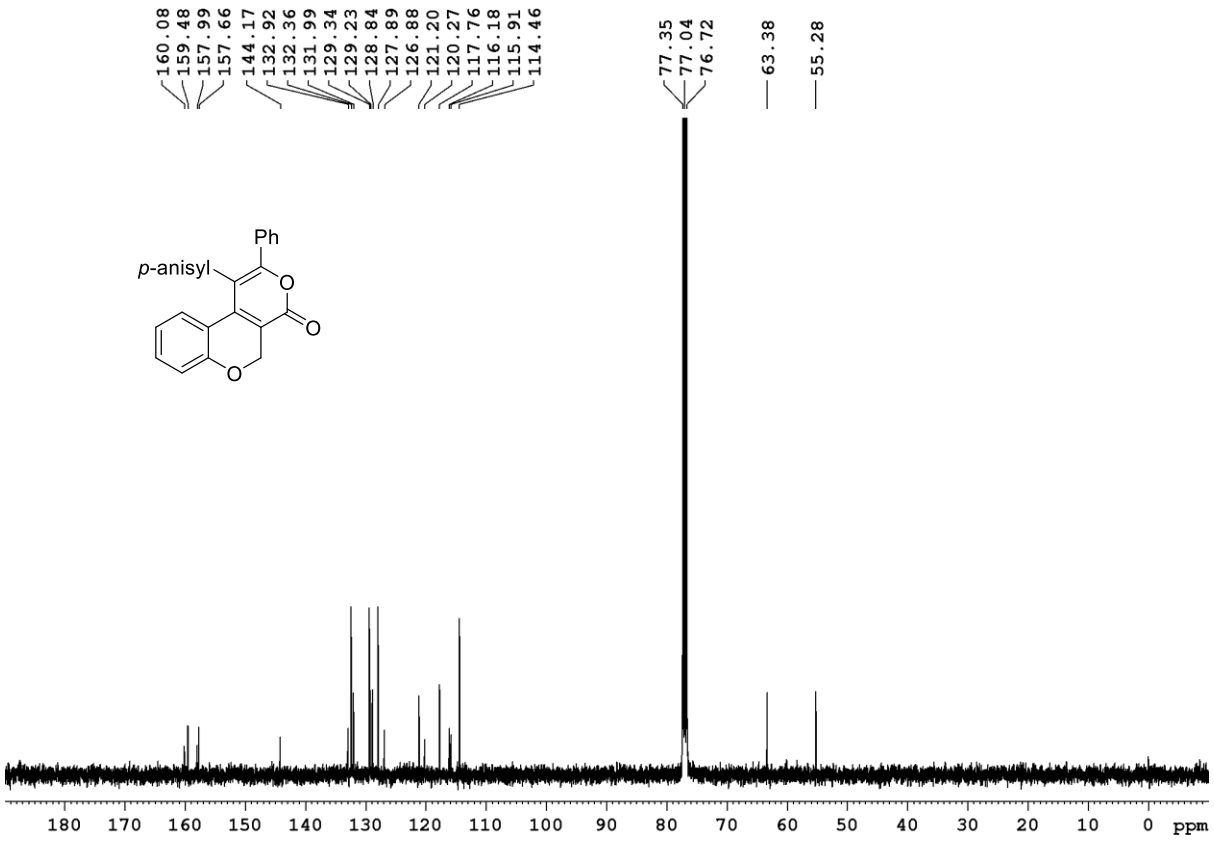


Figure S17. ^{13}C{^{1}H} NMR spectrum of compound **5ad**

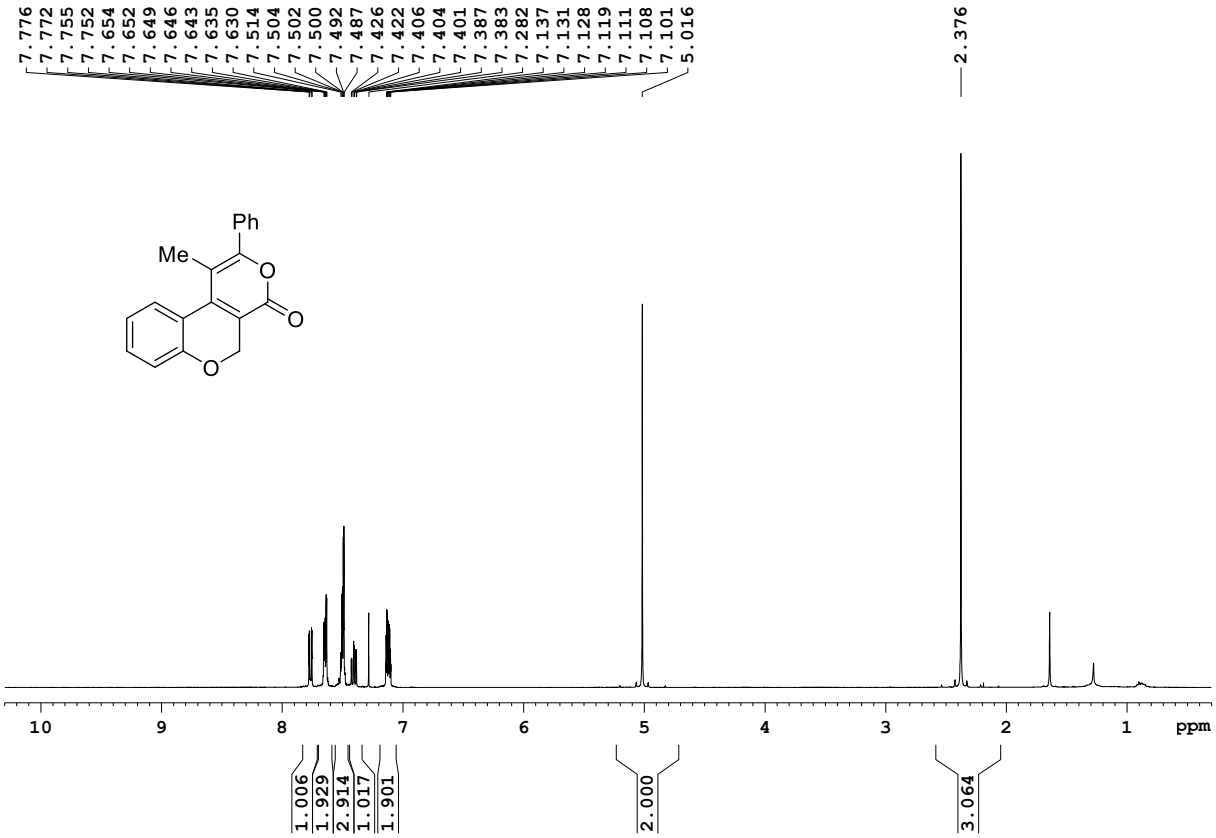


Figure S18. ^{1}H NMR spectrum of compound **5ae**

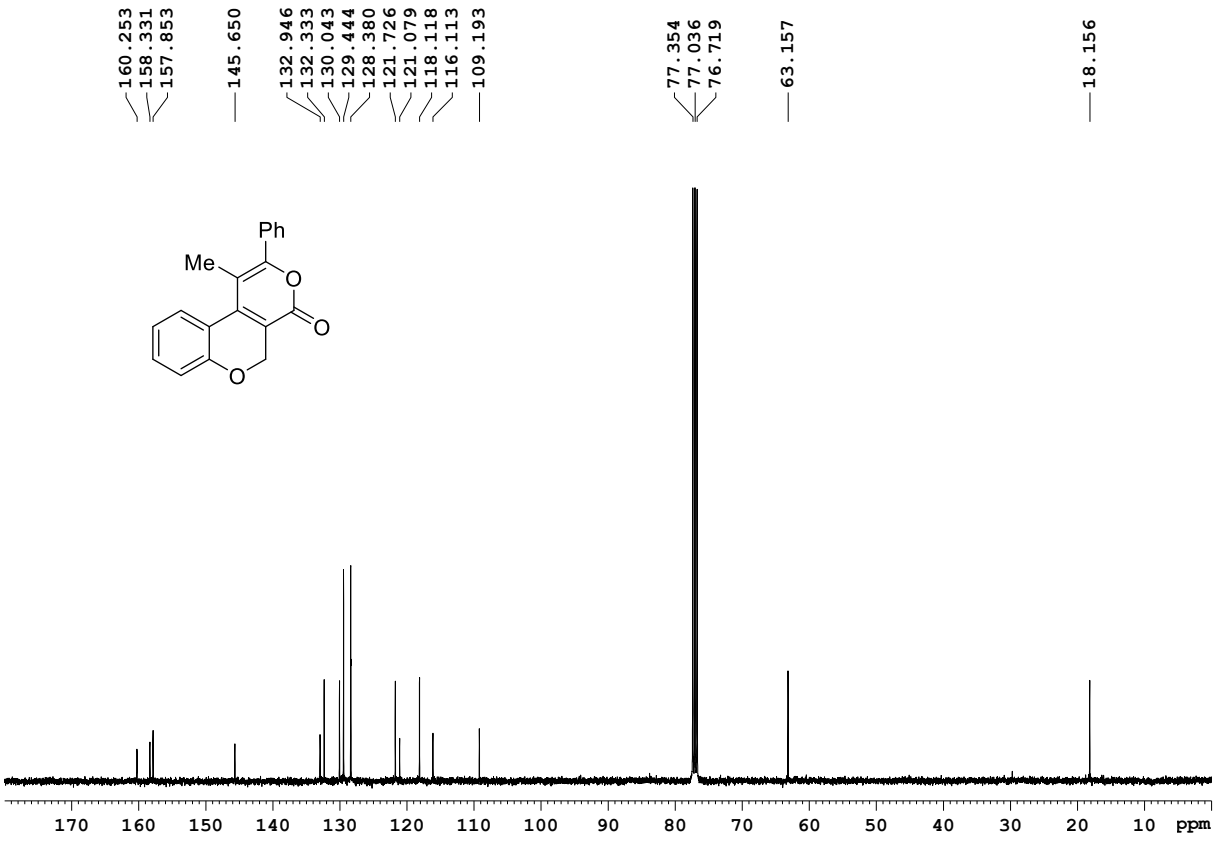


Figure S19. ^{13}C{^{1}H} NMR spectrum of compound **5ae**

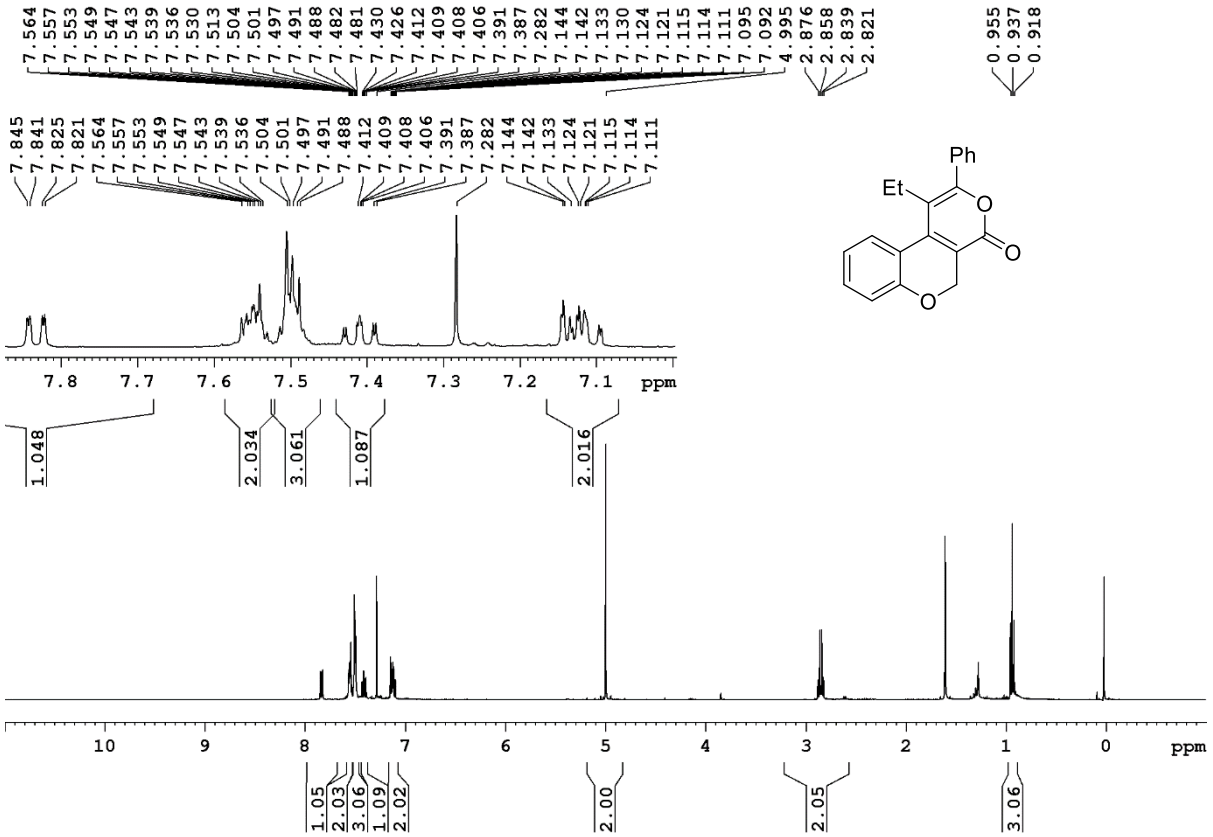


Figure S20. ^{1}H NMR spectrum of compound **5af**

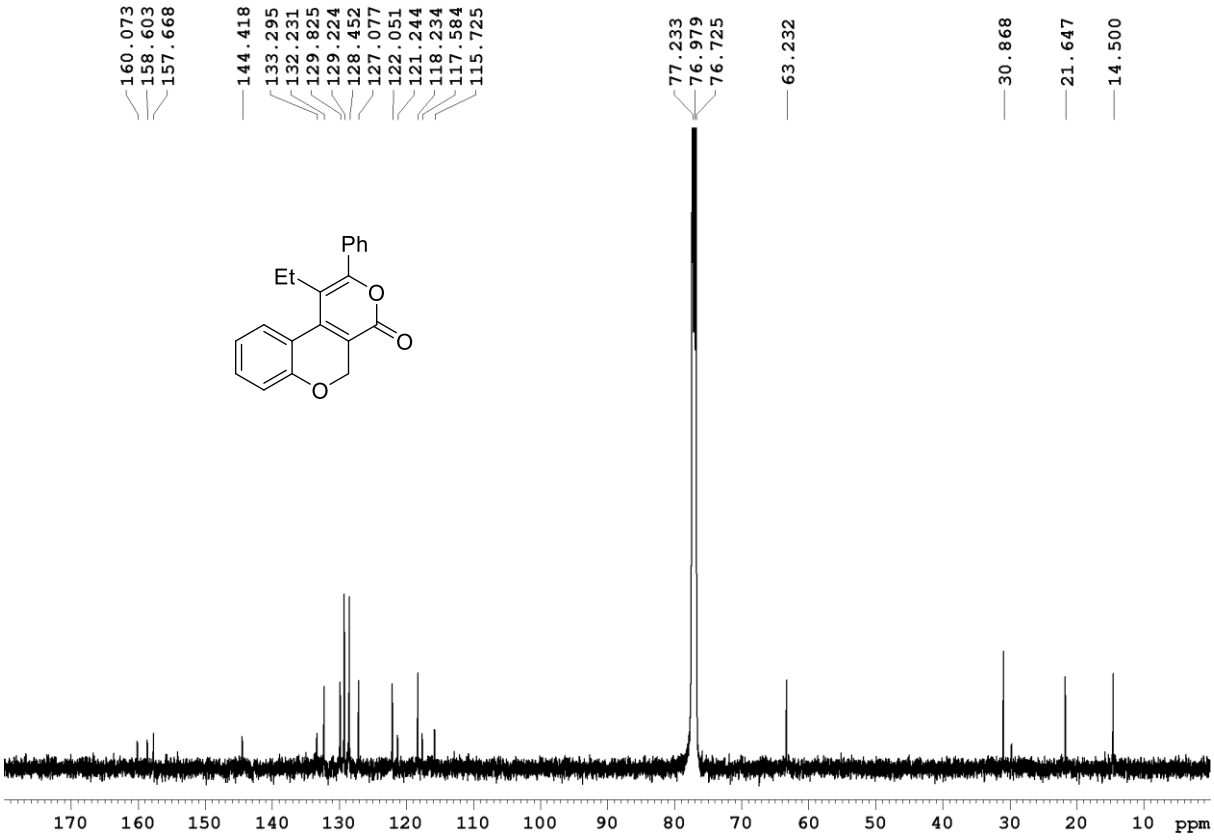


Figure S21. ^{13}C{^{1}H} NMR spectrum of compound **5af**

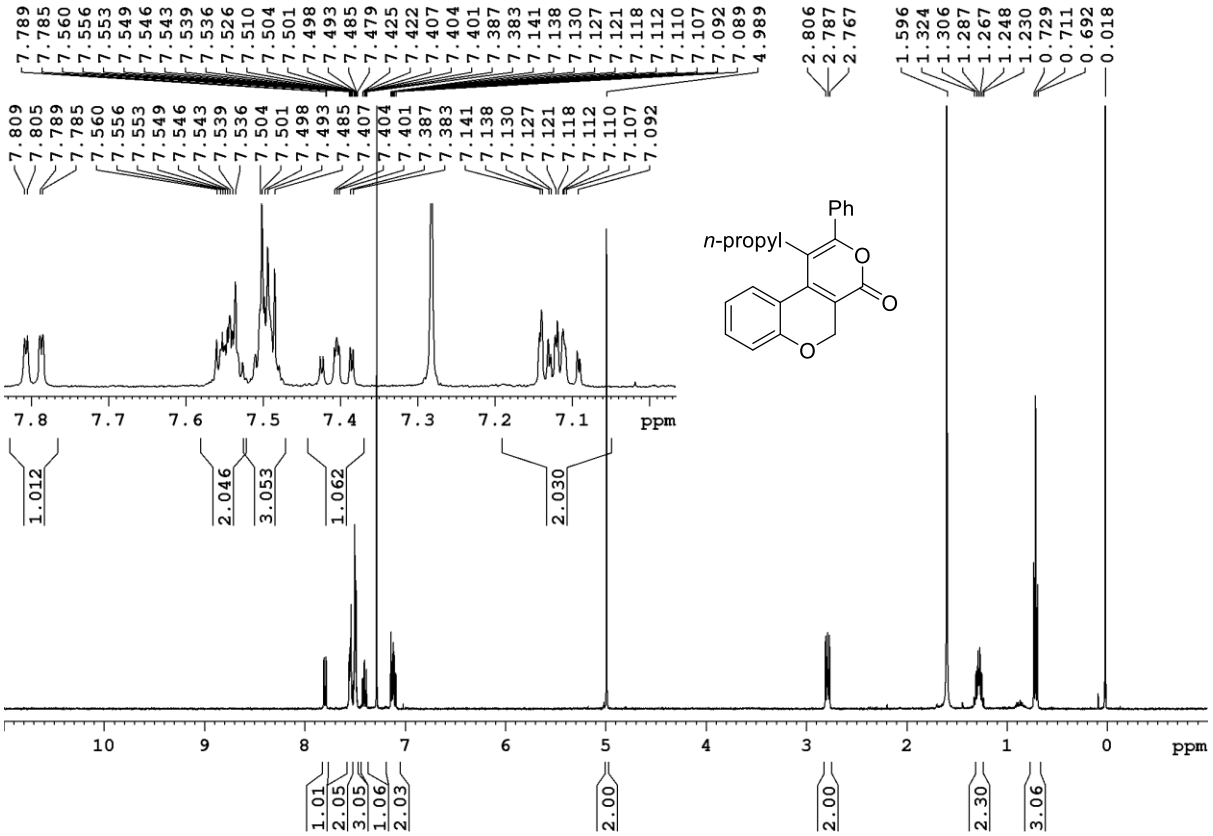


Figure S22. ^{1}H NMR spectrum of compound **5ag**

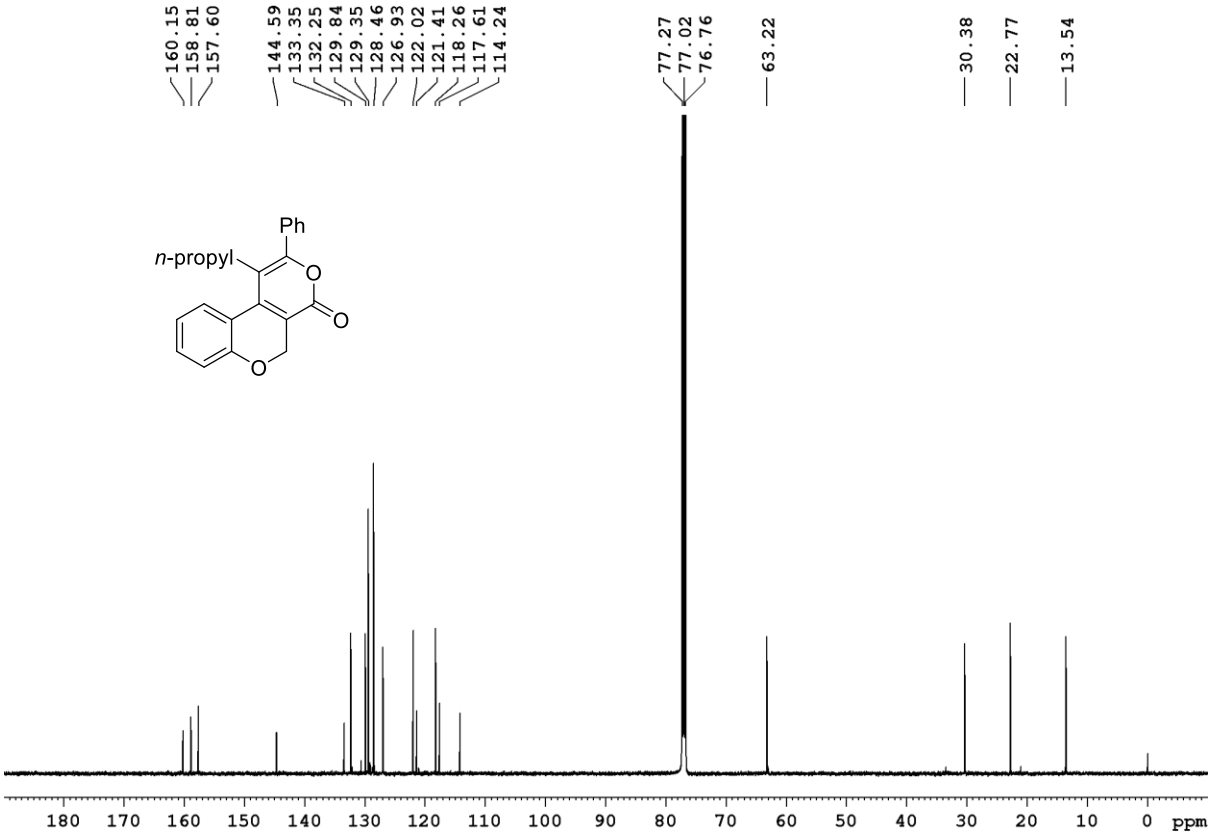


Figure S23. ^{13}C{^{1}H} NMR spectrum of compound **5ag**

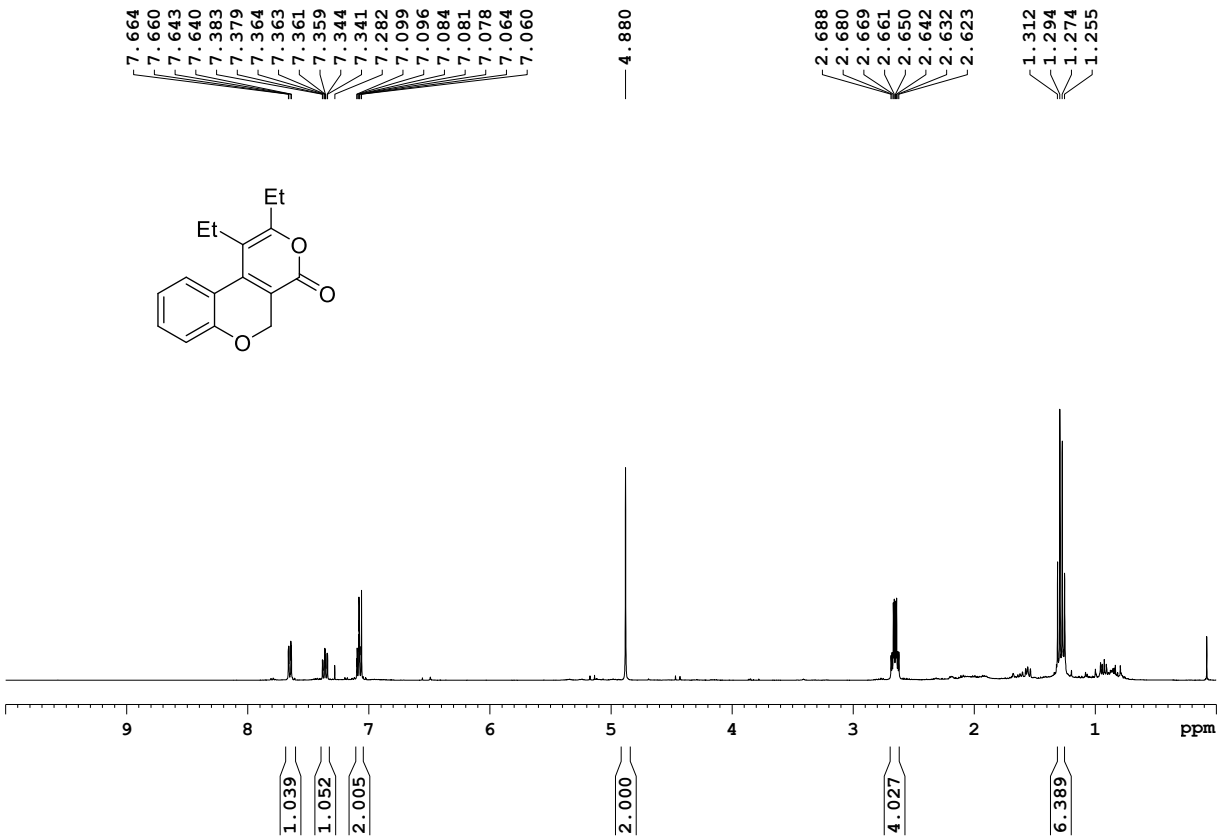


Figure S24. ^{1}H NMR spectrum of compound **5ah**

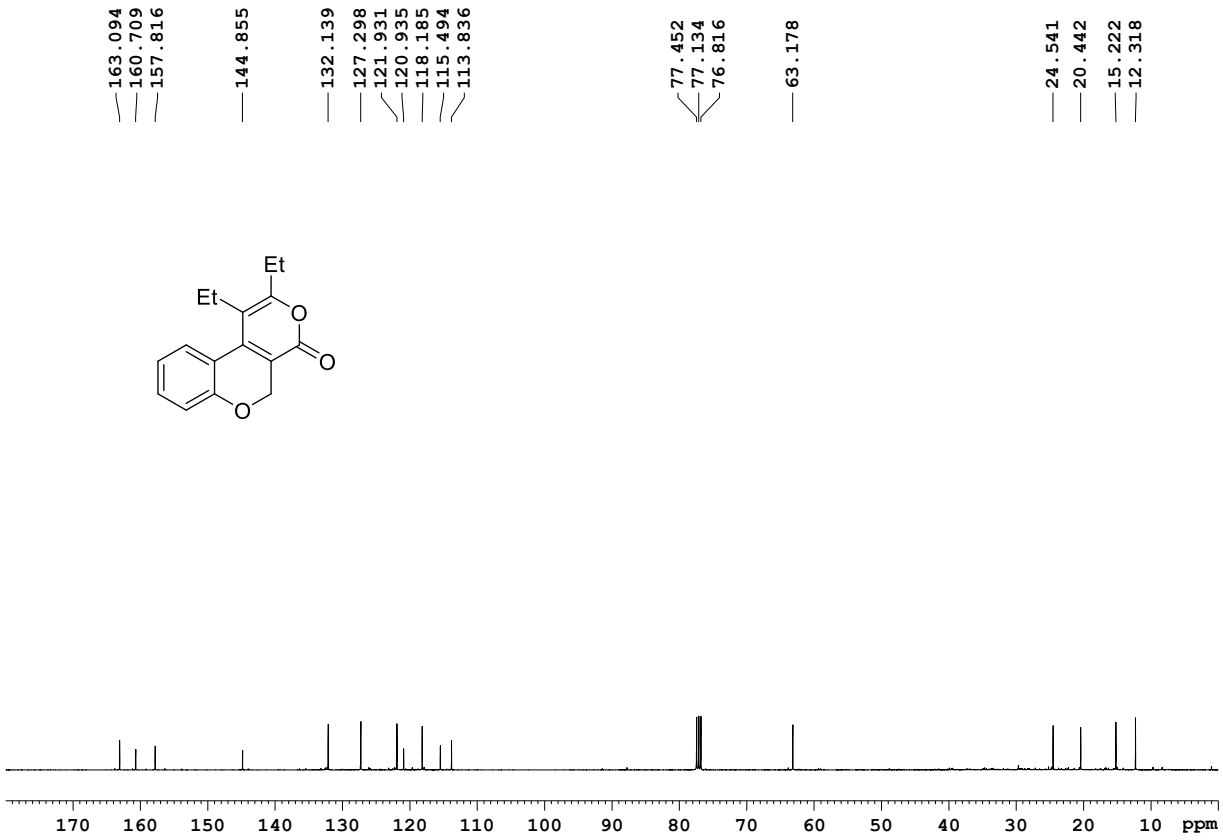


Figure S25. ^{3}C{^{1}H} NMR spectrum of compound **5ah**

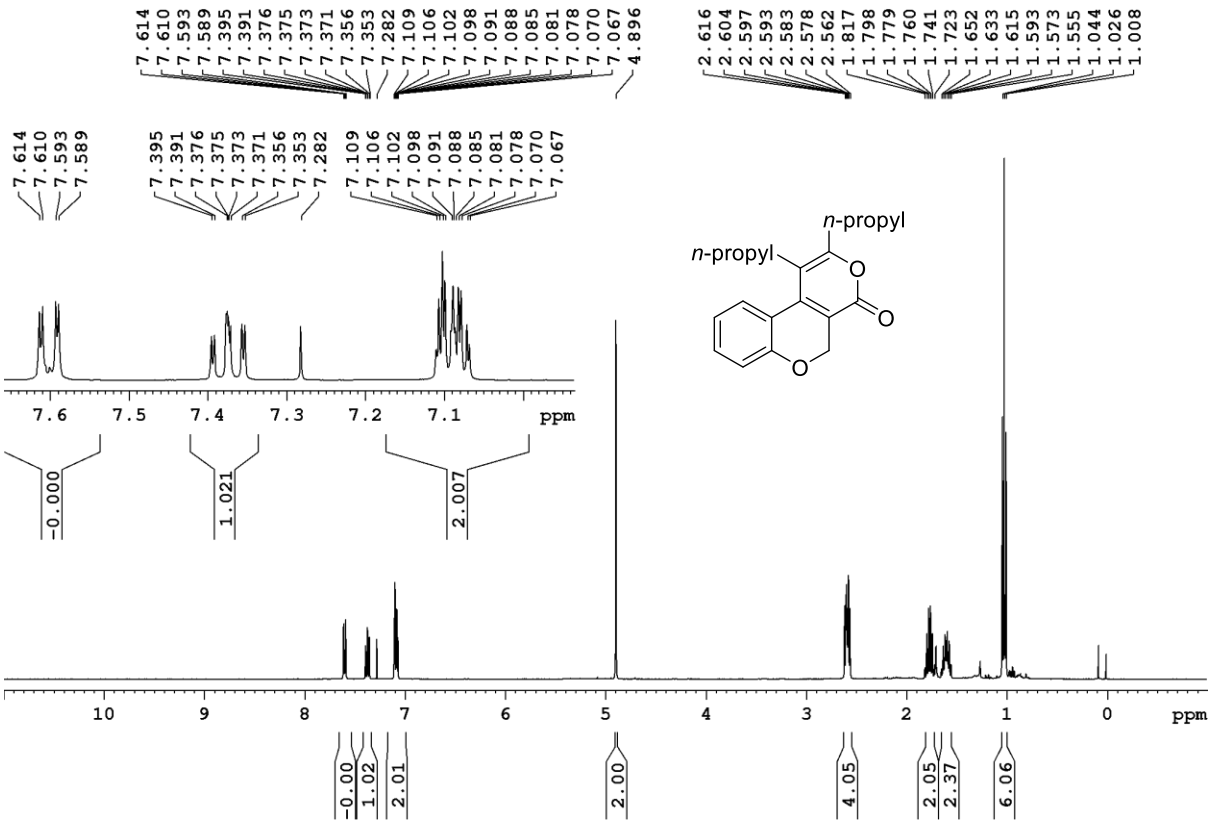


Figure S26. ^{1}H NMR spectrum of compound **5ai**

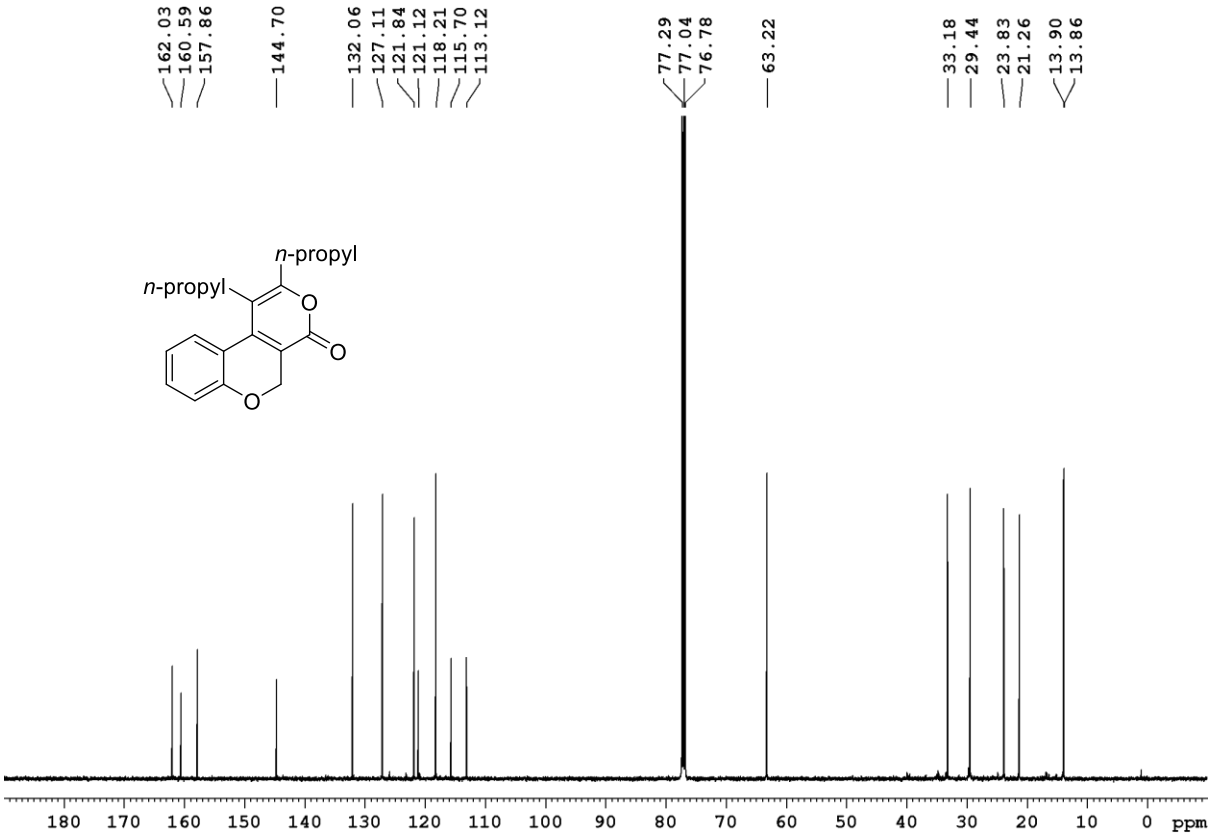


Figure S27. ^{13}C{^{1}H} NMR spectrum of compound **5ai**

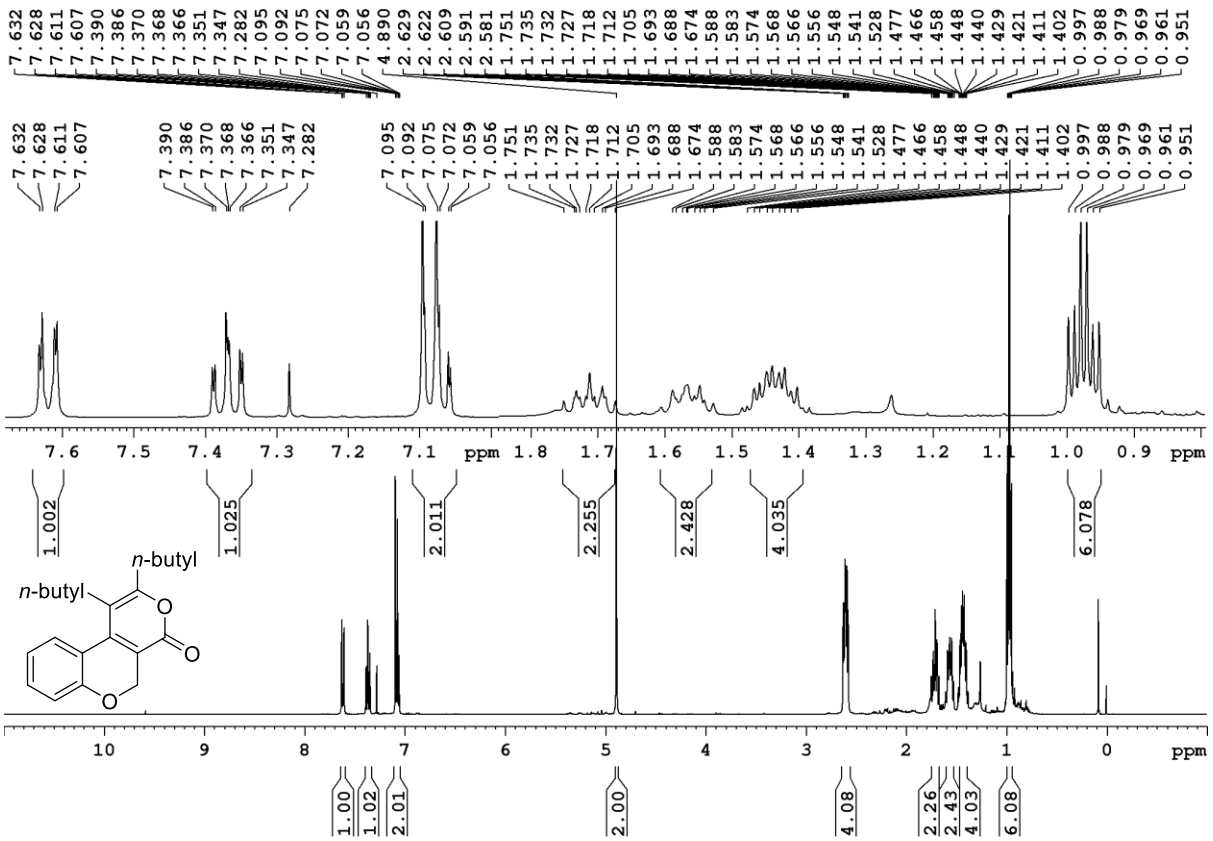


Figure S28. ^{1}H NMR spectrum of compound **5aj**

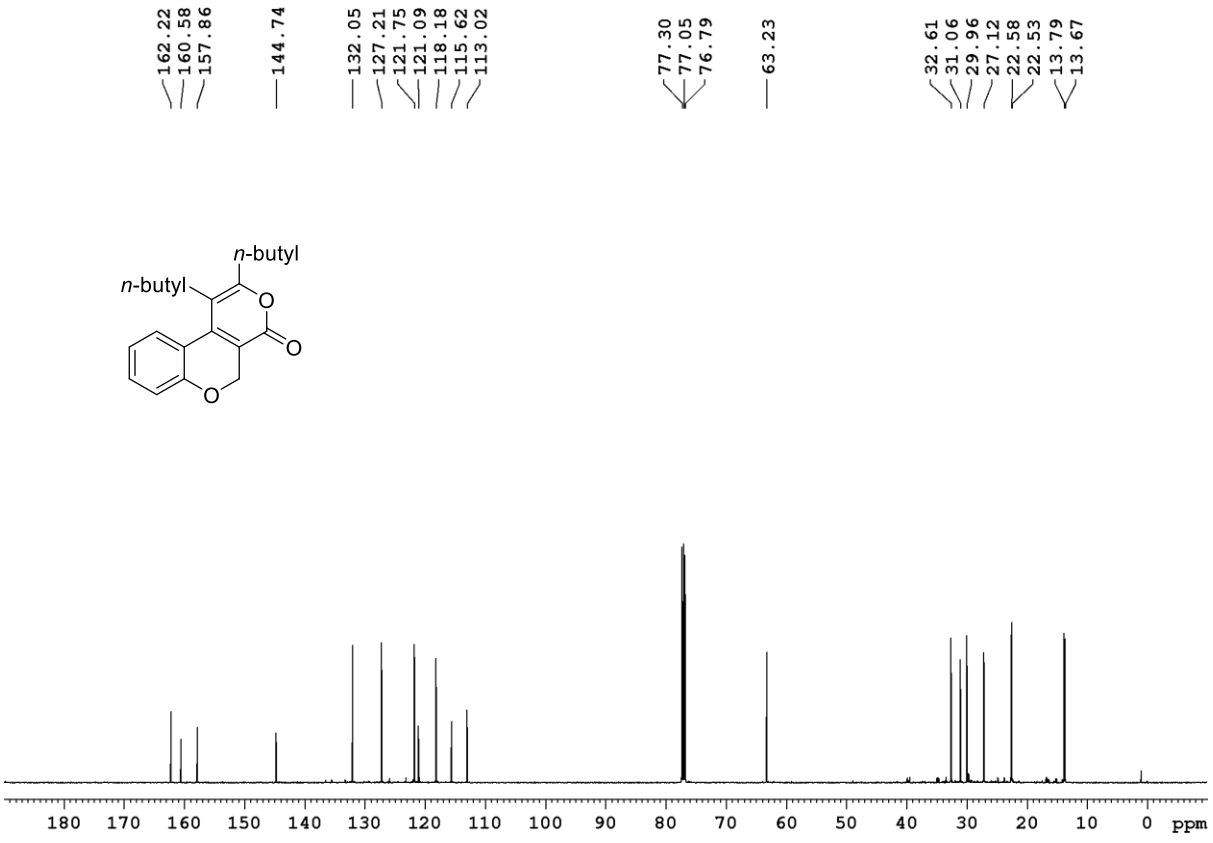


Figure S29. ^{13}C{^{1}H} NMR spectrum of compound **5aj**

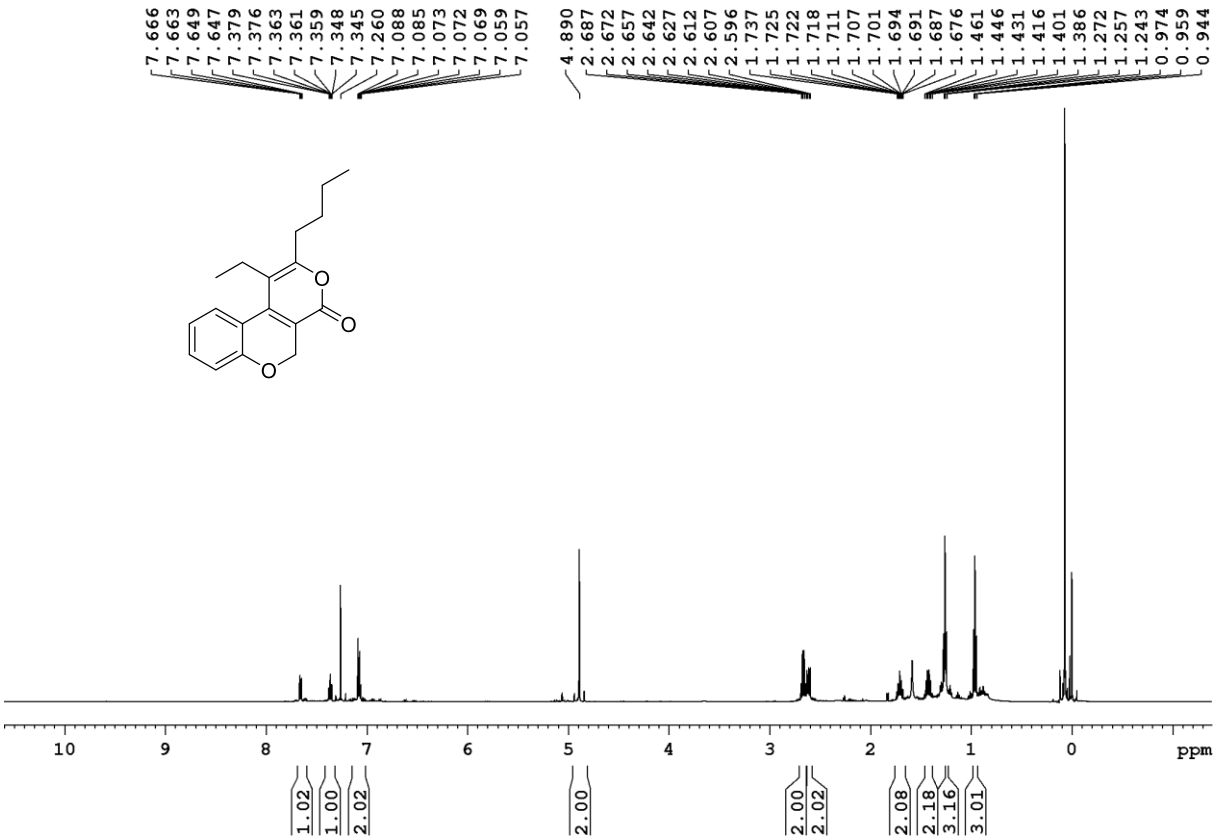


Figure S30. ^{1}H NMR spectrum of compound **5ak** (isomeric purity 95%)

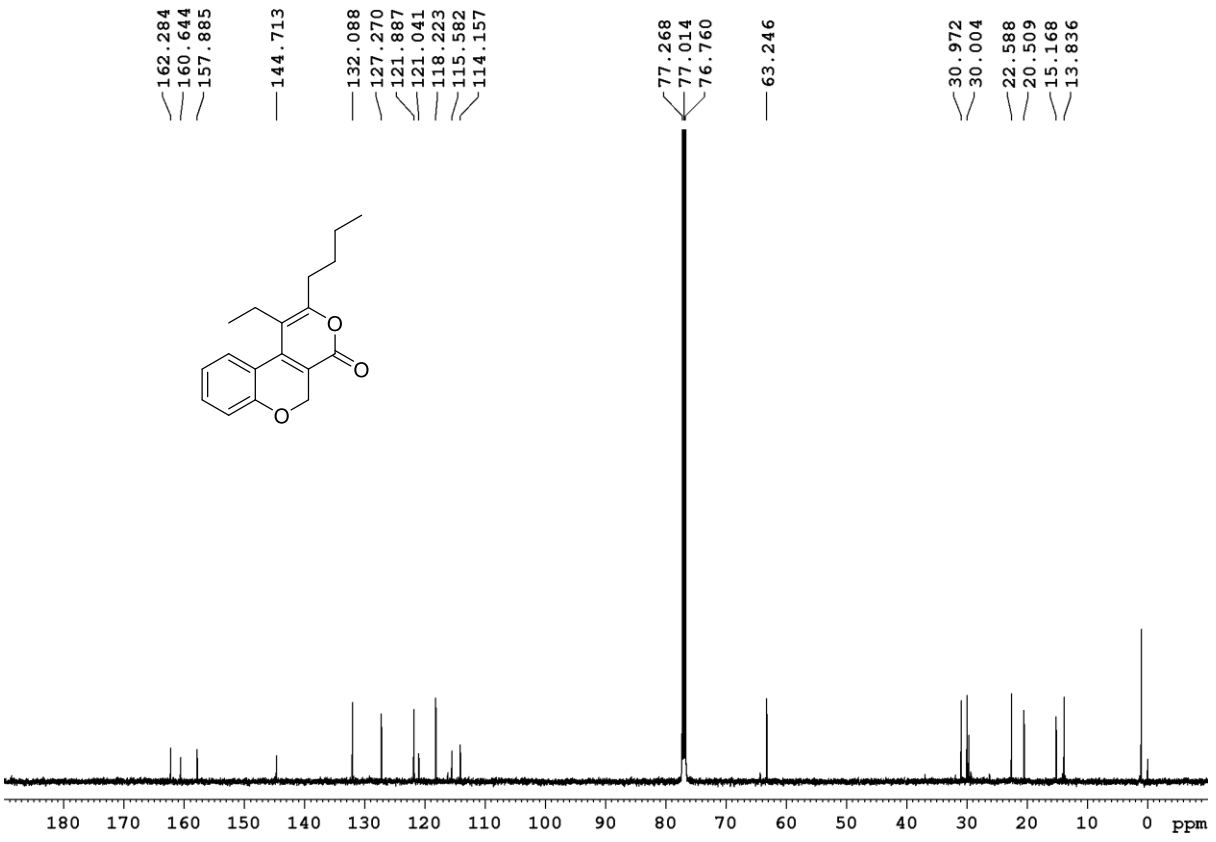


Figure S31. ^{13}C{^{1}H} NMR spectrum of compound **5ak**

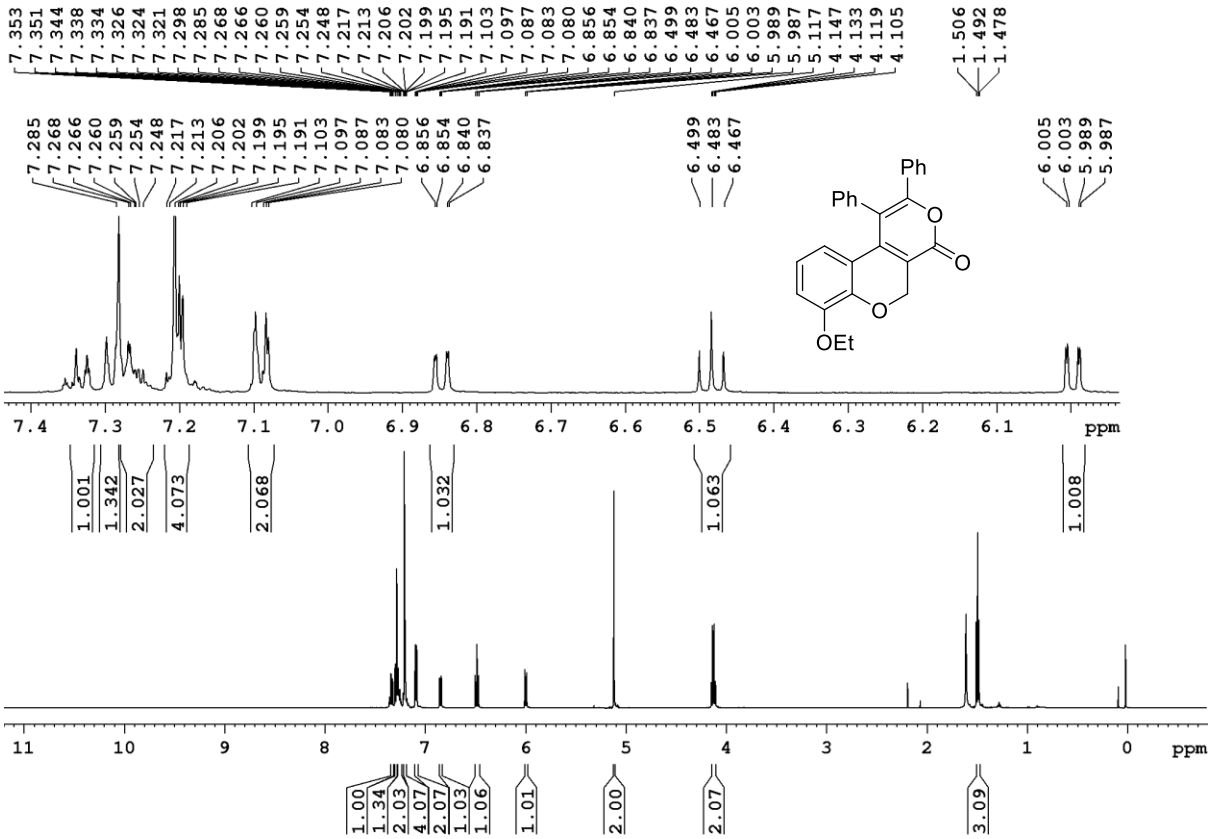


Figure S32. ^{1}H NMR spectrum of compound **5ba**

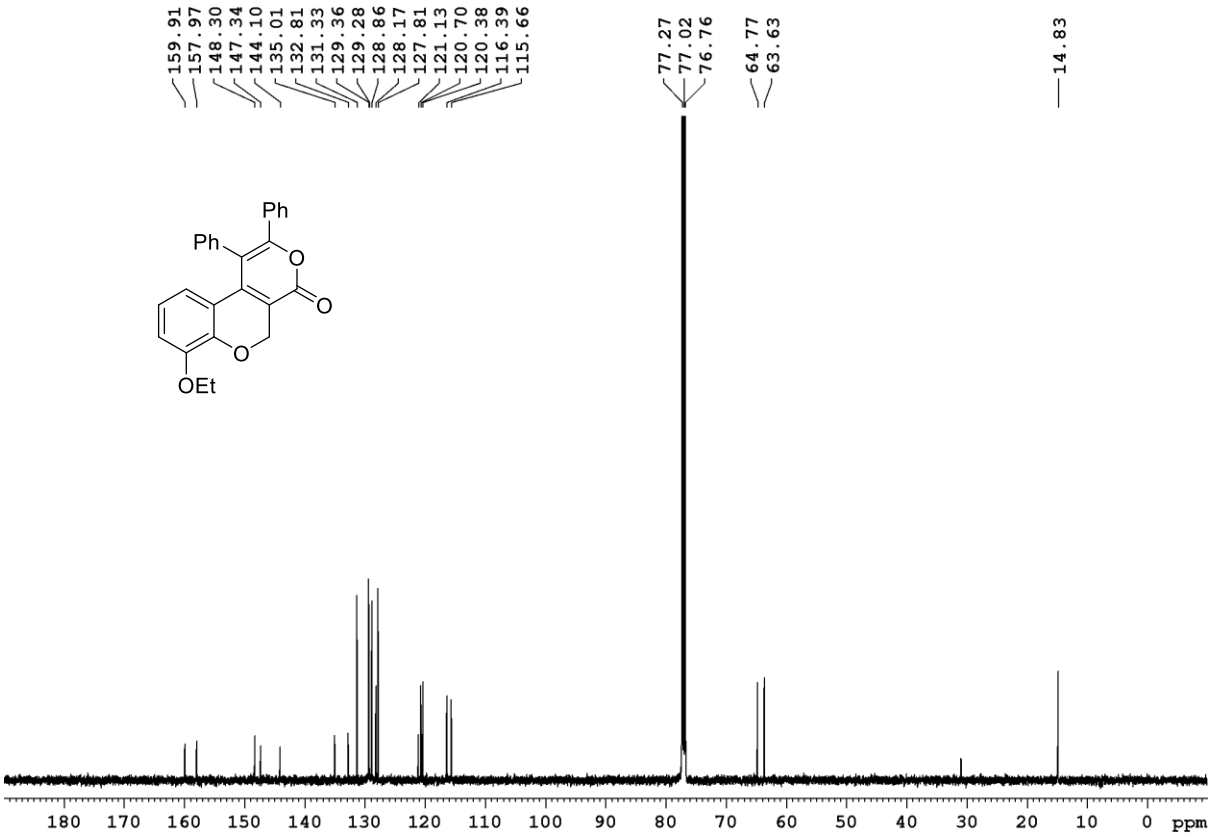


Figure S33. ^{13}C{^{1}H} NMR spectrum of compound **5ba**

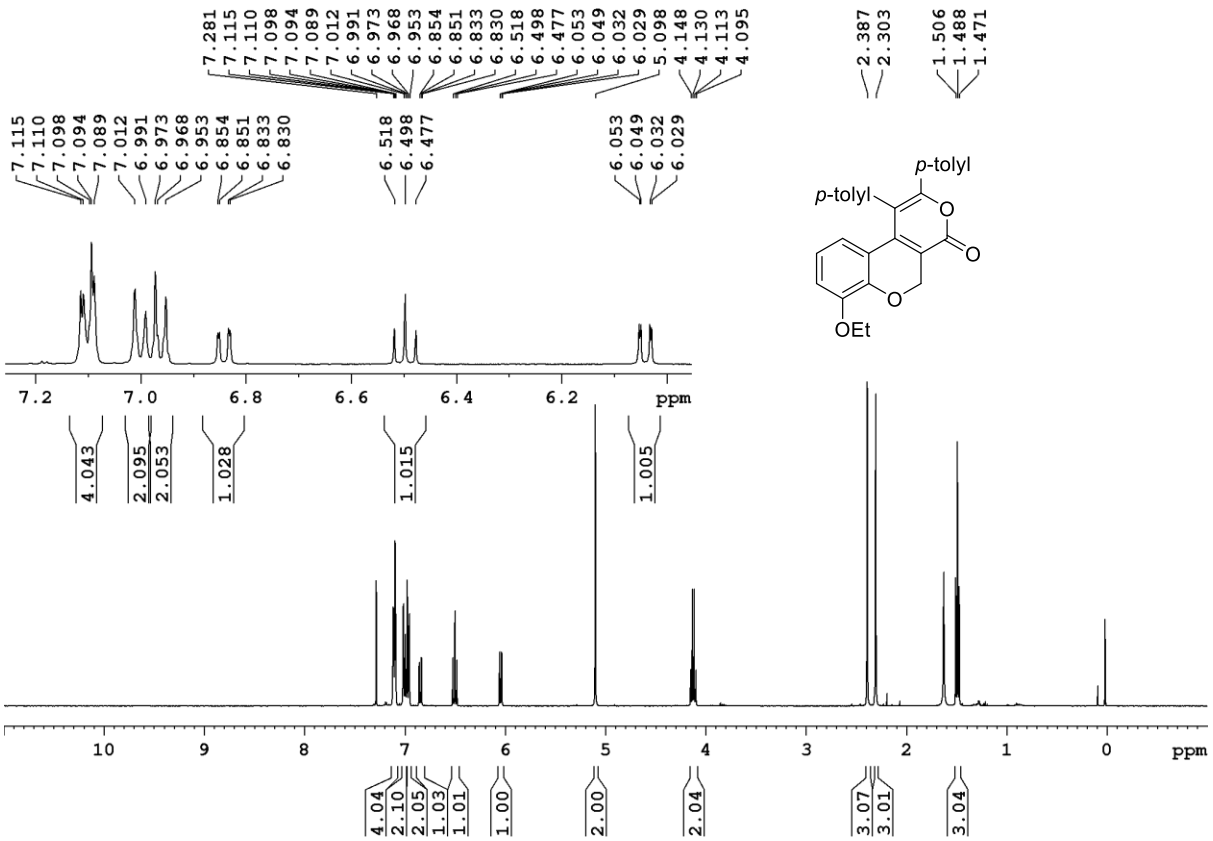


Figure S34. ^{1}H NMR spectrum of compound **5bb**

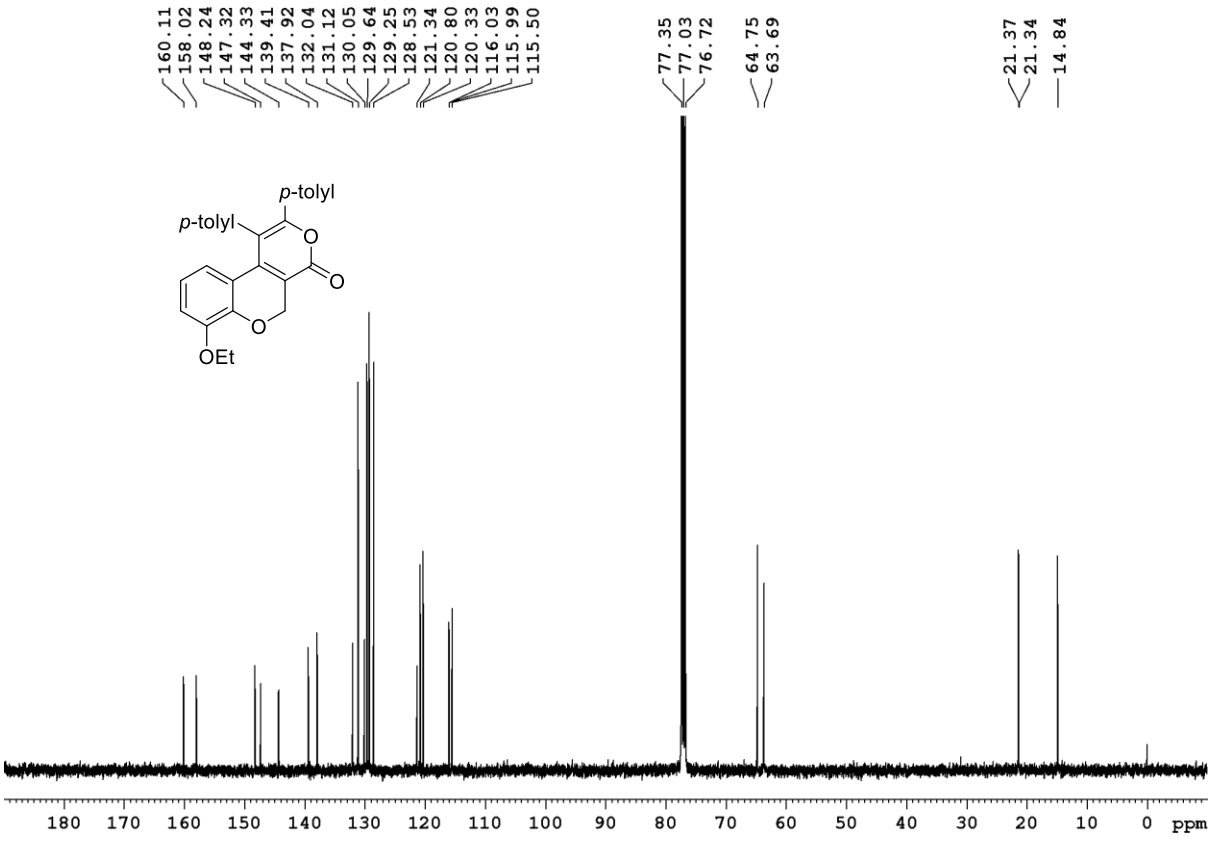


Figure S35. ^{13}C{^{1}H} NMR spectrum of compound **5bb**

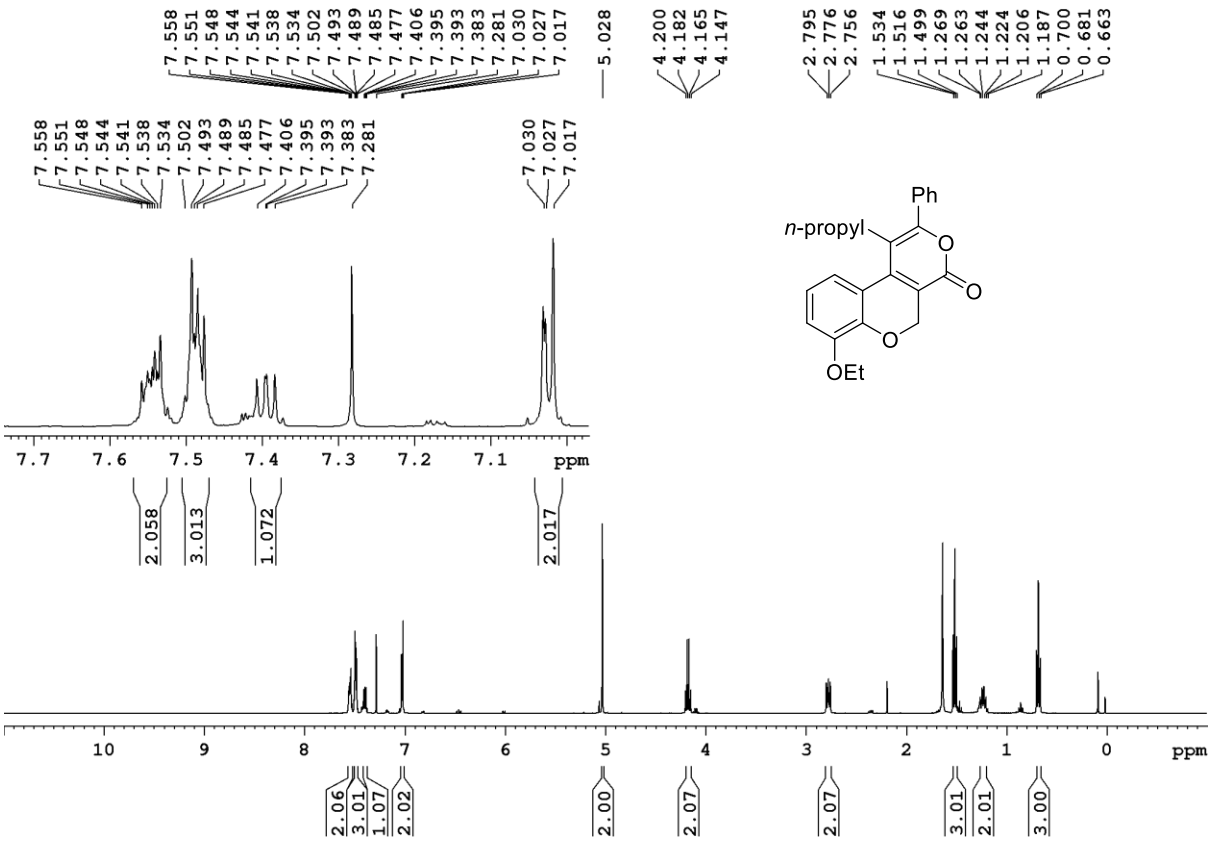


Figure S36. ^{1}H NMR spectrum of compound **5bg**

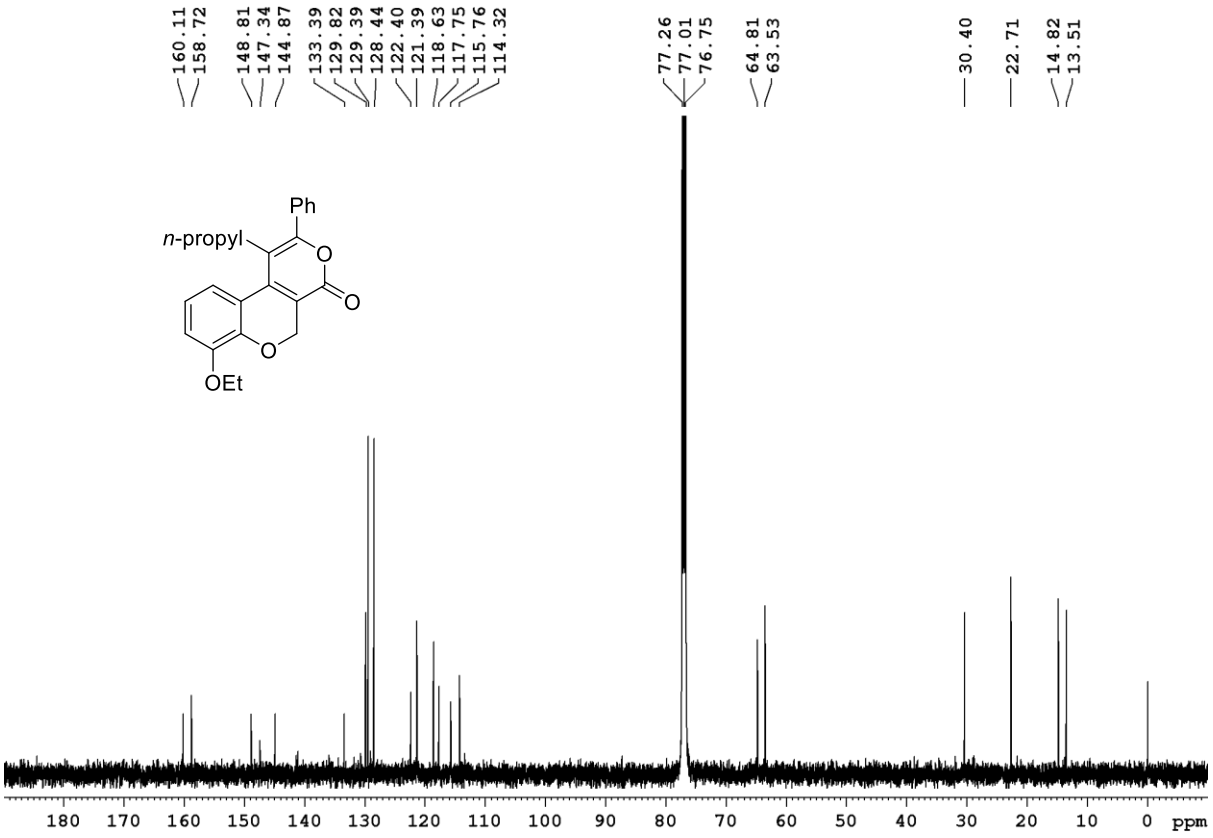


Figure S37. ^{13}C{^{1}H} NMR spectrum of compound **5bg**

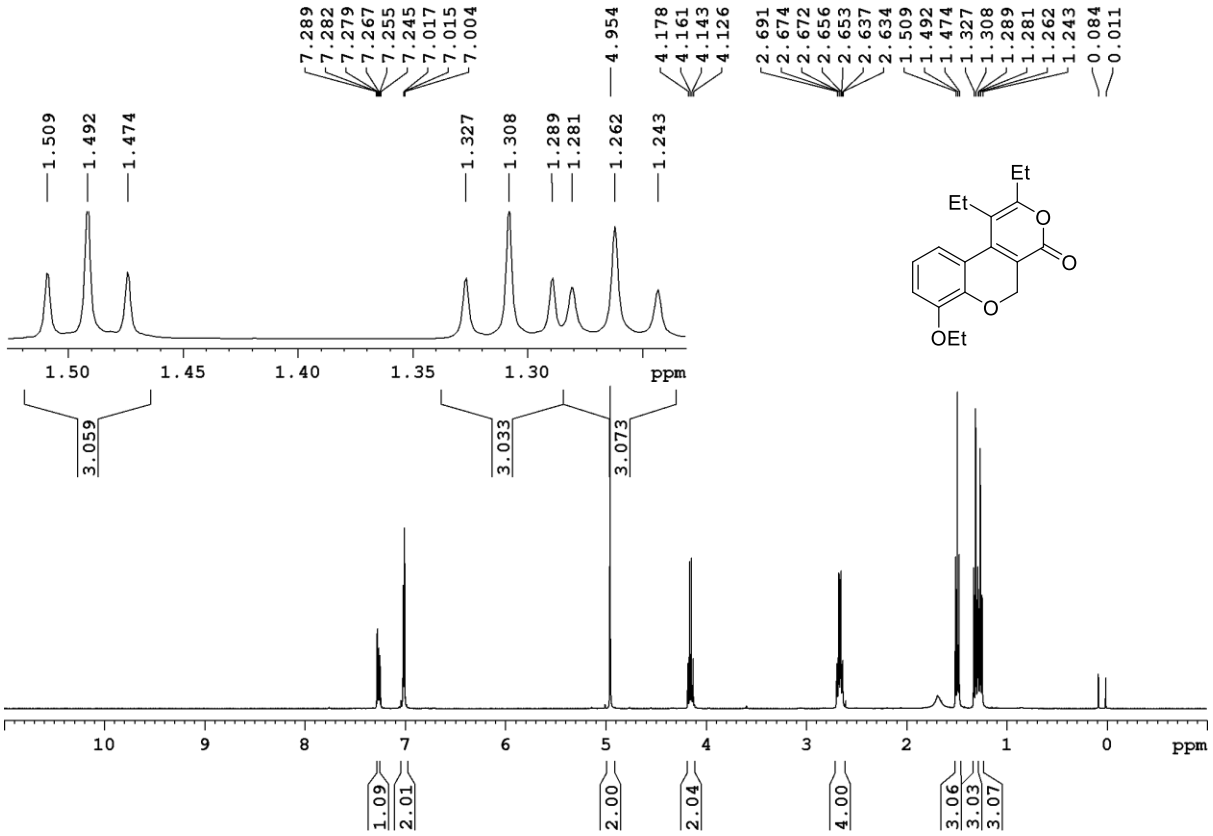


Figure S38. ^{1}H NMR spectrum of compound **5bh**

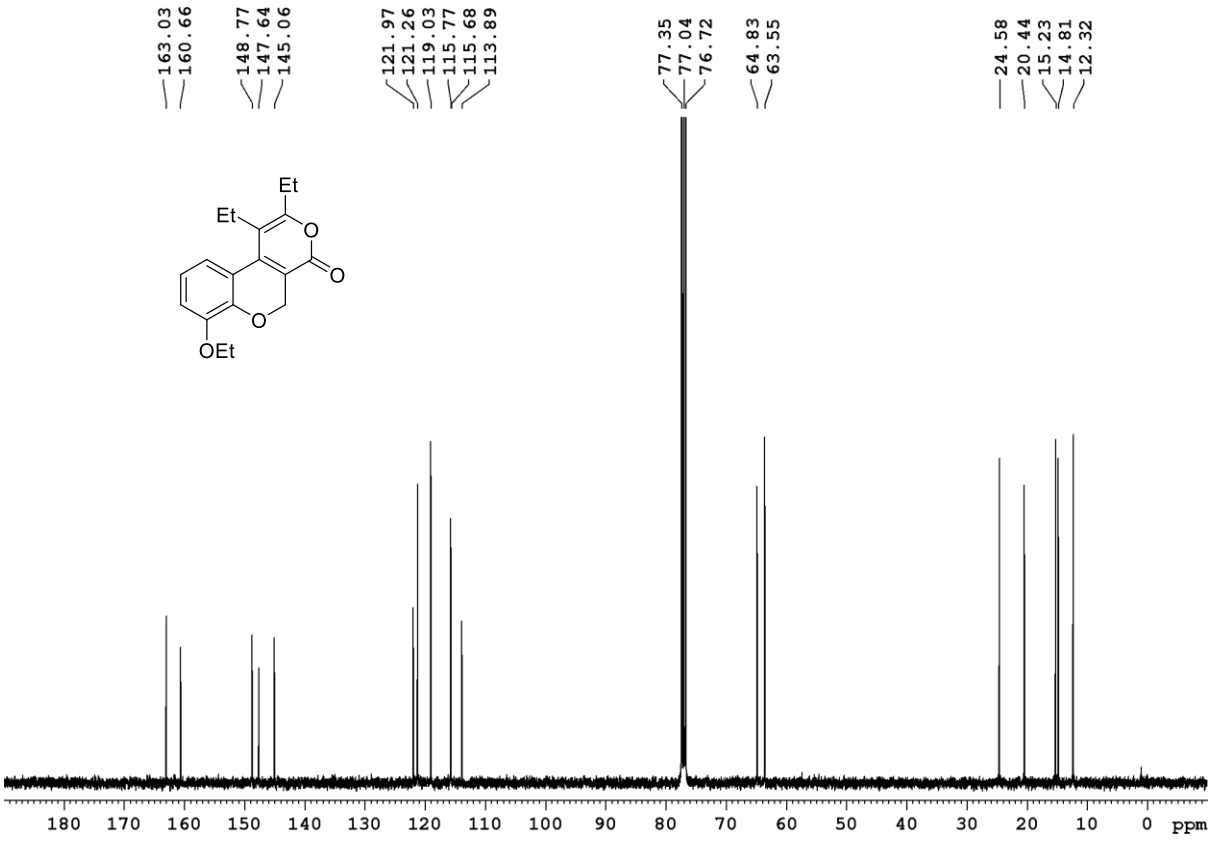


Figure S39. ^{13}C{^{1}H} NMR spectrum of compound **5bh**

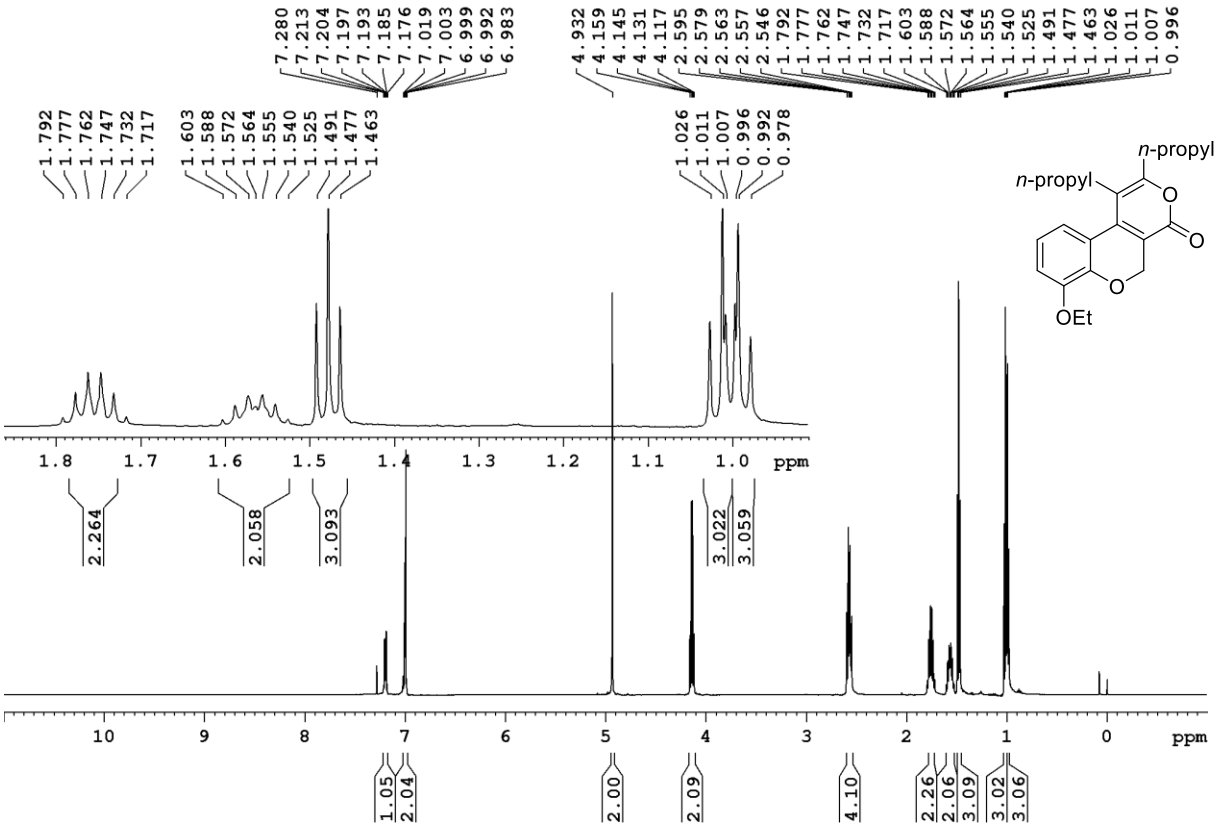


Figure S40. ^{1}H NMR spectrum of compound **5bi**

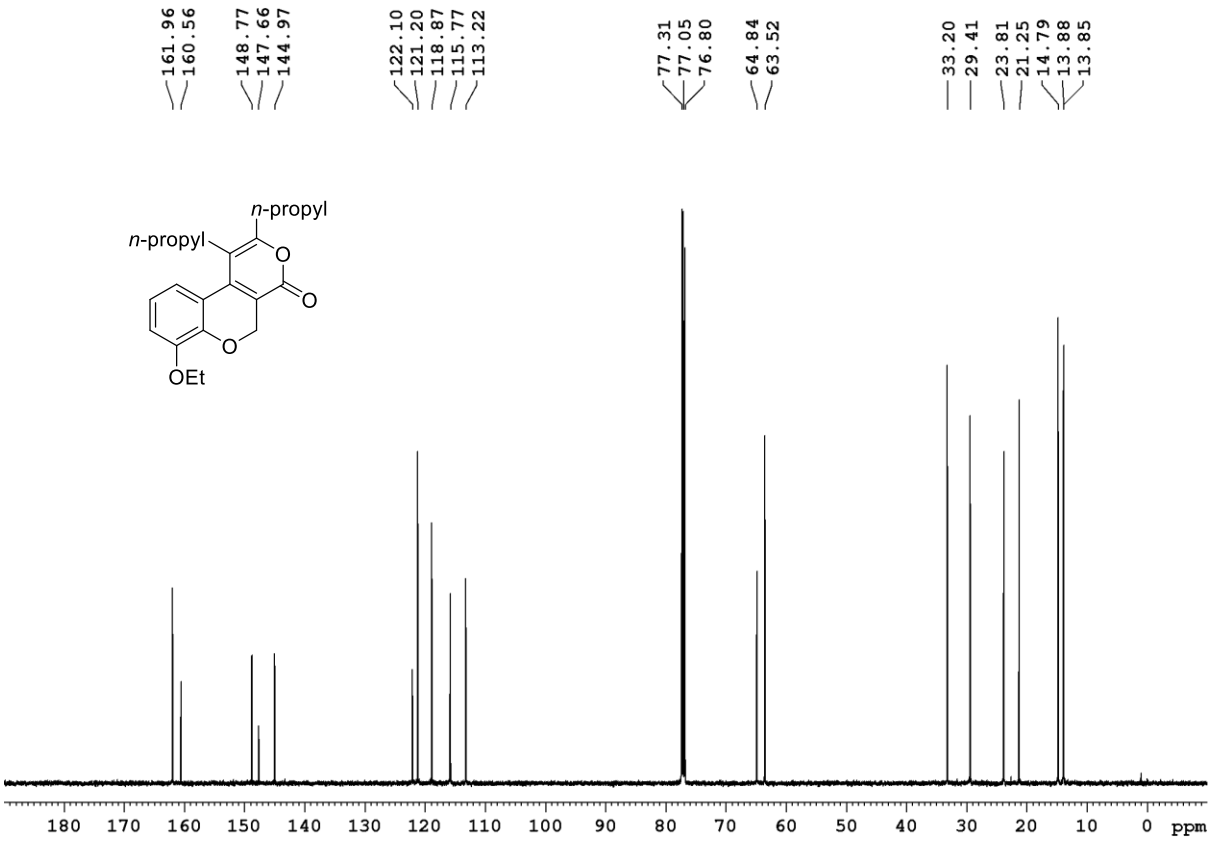


Figure S41. ^{13}C{^{1}H} NMR spectrum of compound **5bi**

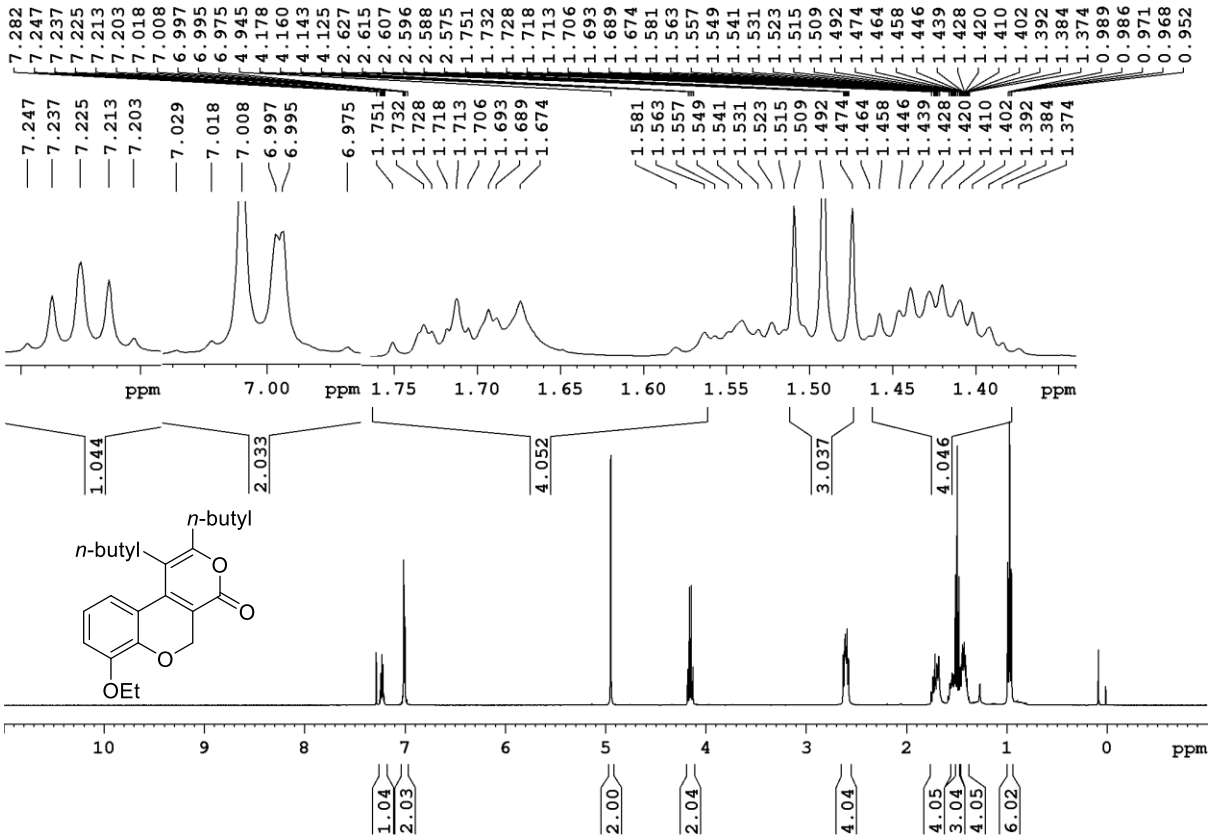


Figure S42. ^{1}H NMR spectrum of compound **5bj**

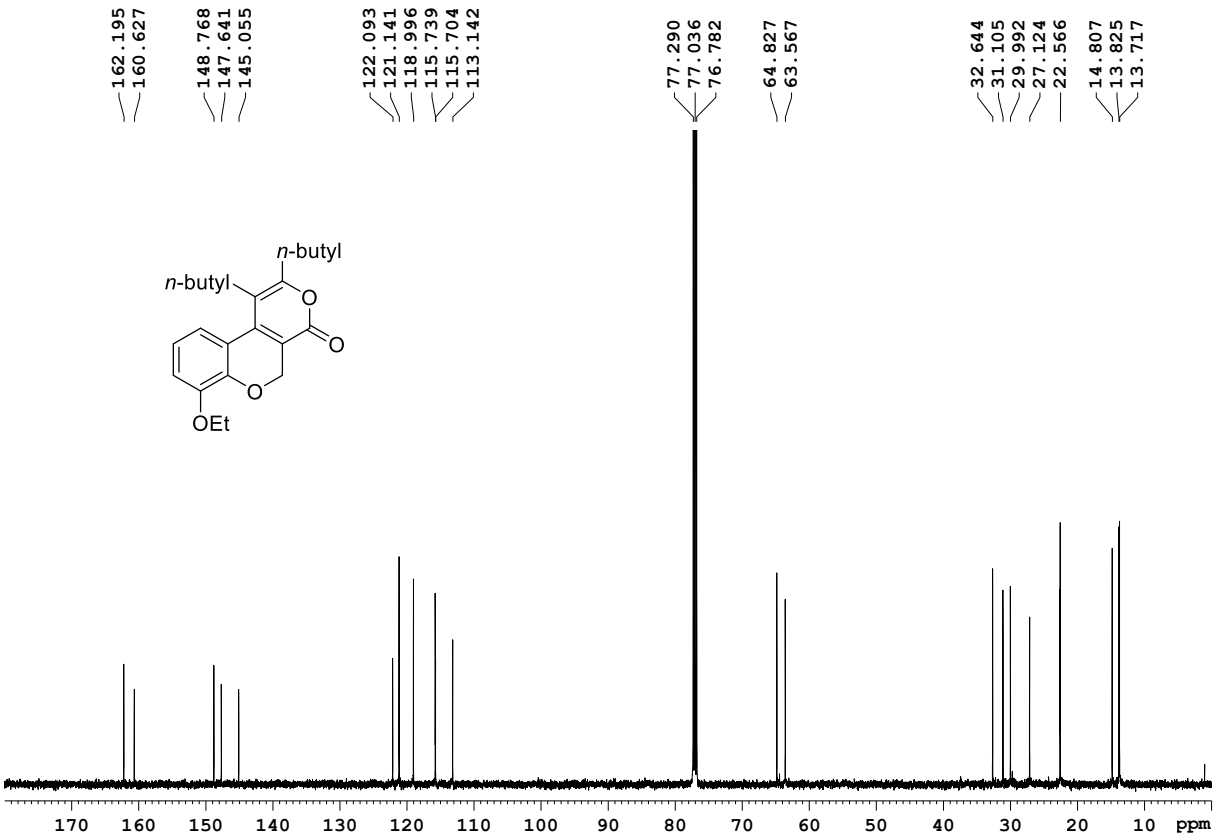


Figure S43. ^{13}C{^{1}H} NMR spectrum of compound **5bj**

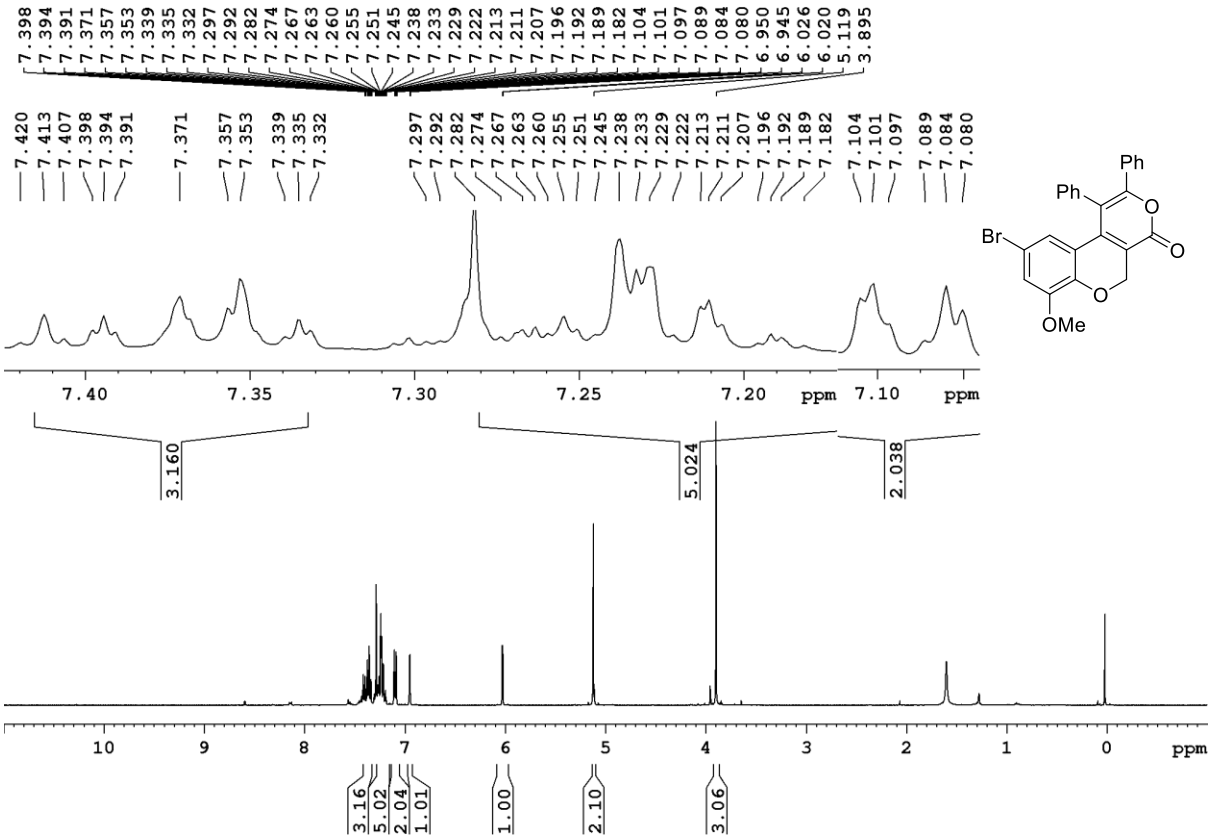


Figure S44. ^{1}H NMR spectrum of compound **5ca**

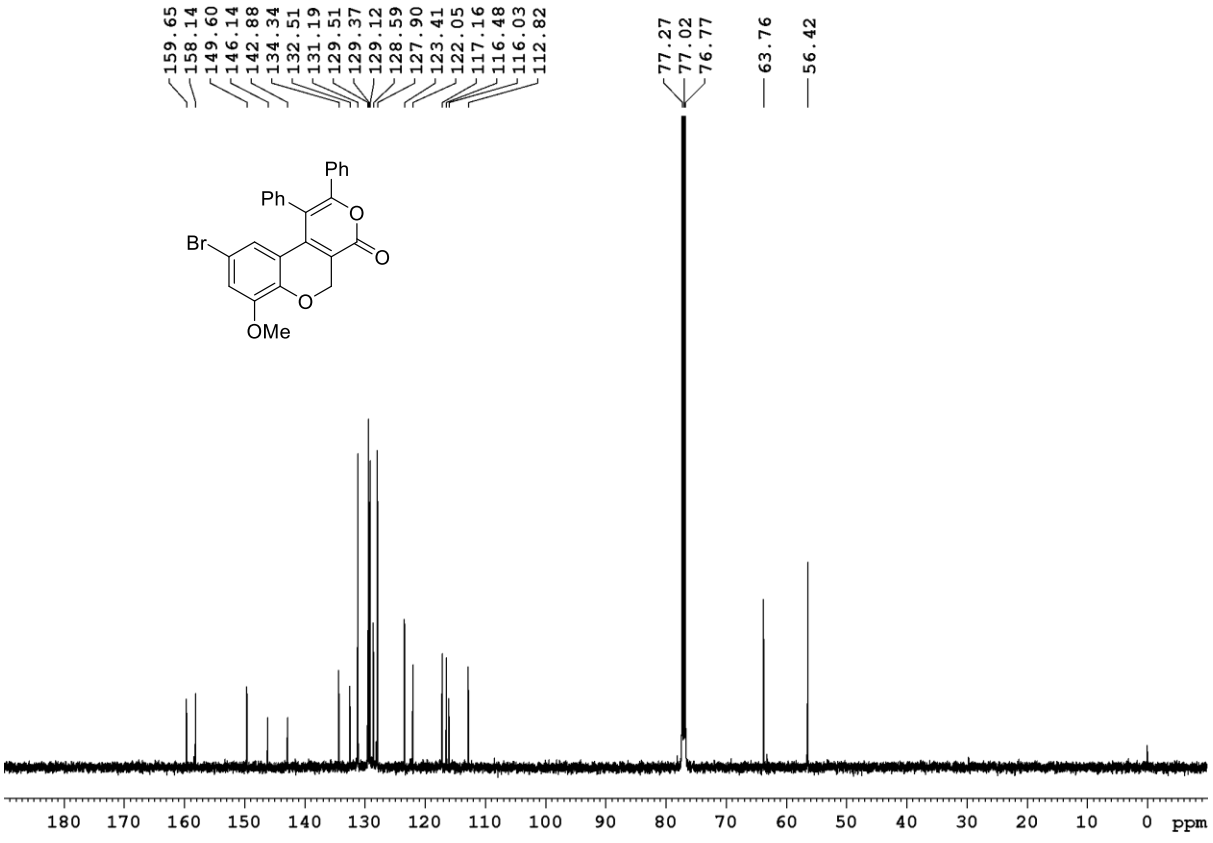


Figure S45. ^{13}C{^{1}H} NMR spectrum of compound **5ca**

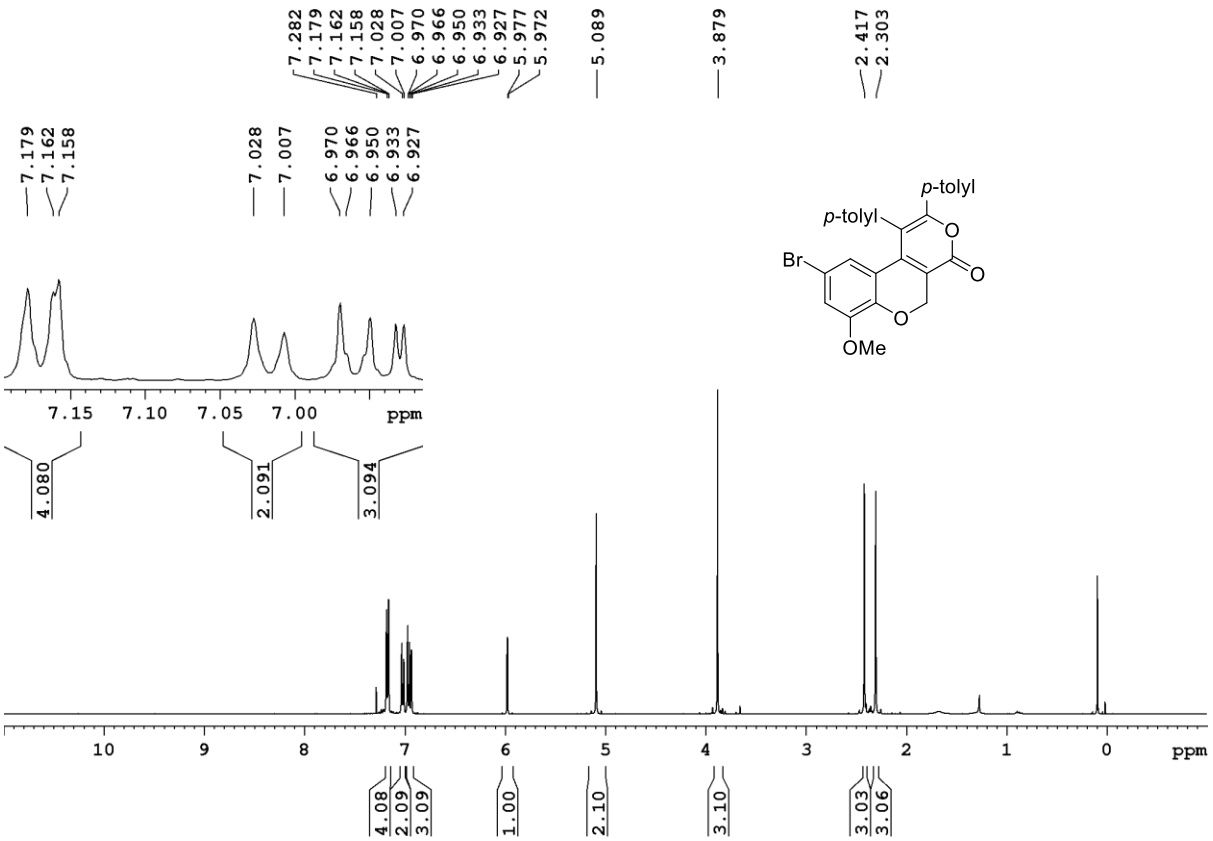
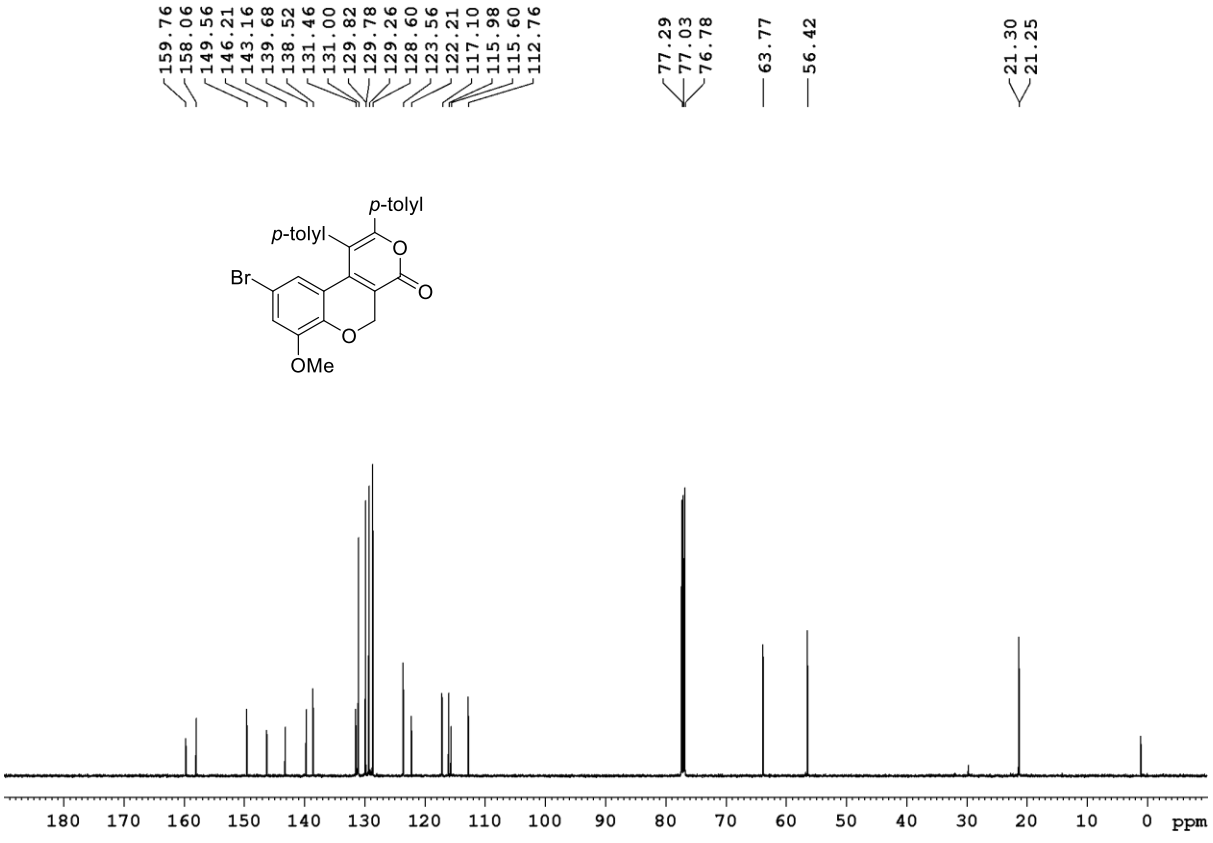


Figure S46. ^{1}H NMR spectrum of compound **5cb**



. **Figure S47.** ^{13}C{^{1}H} NMR spectrum of compound **5cb**

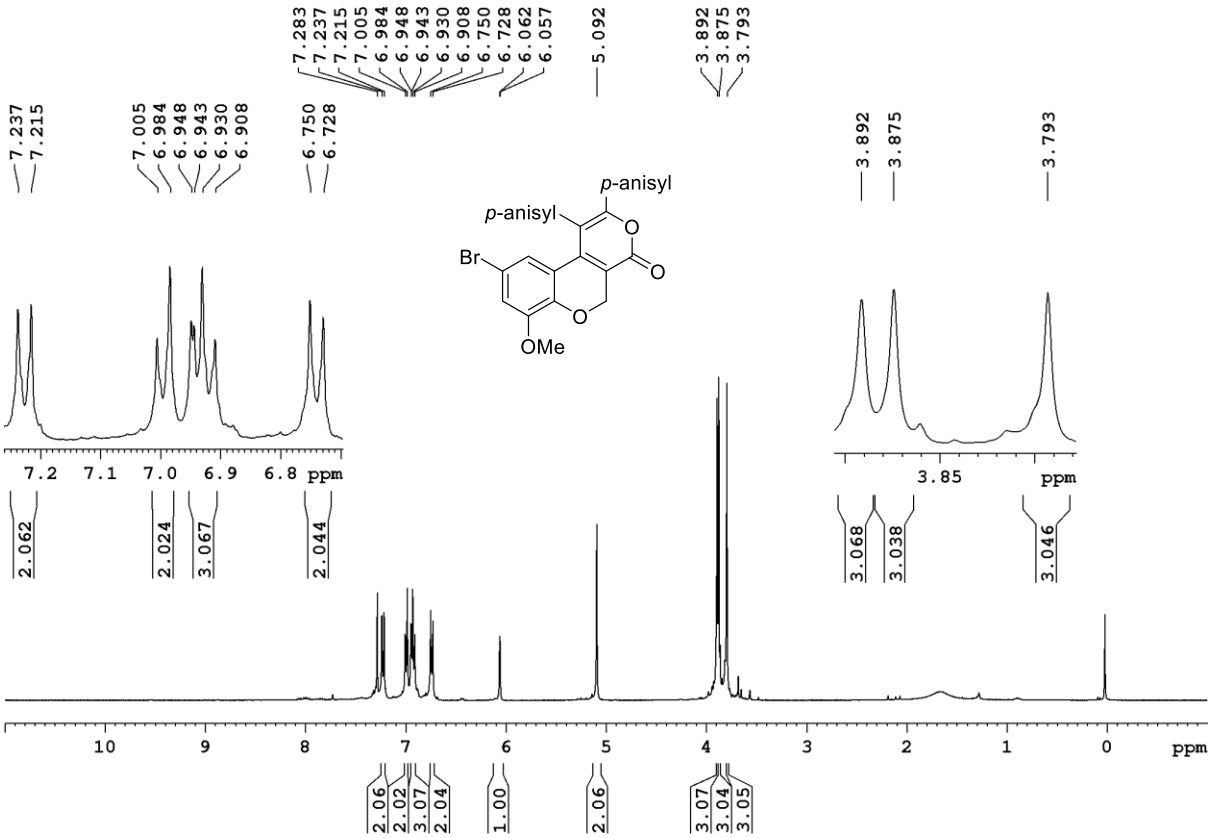


Figure S48. ^{1}H NMR spectrum of compound **5cc**

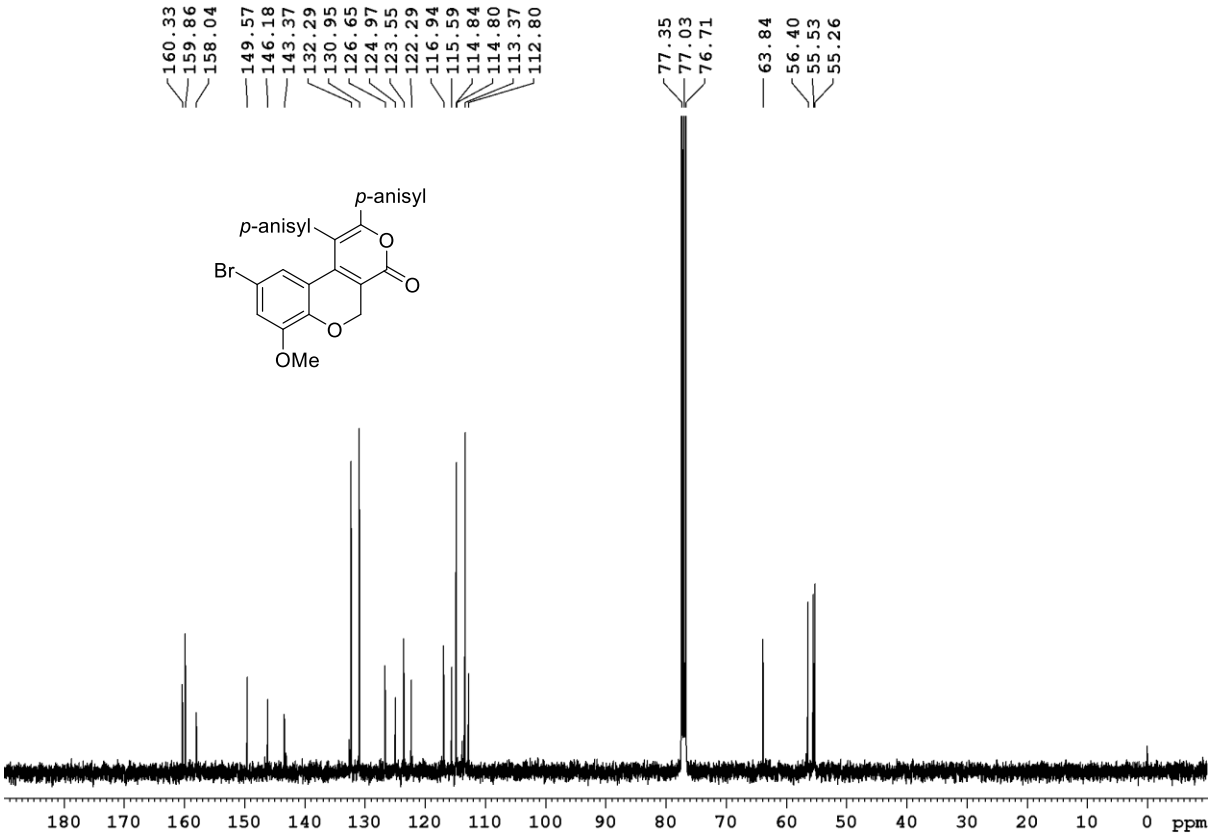


Figure S49. ^{13}C{^{1}H} NMR spectrum of compound **5cc**

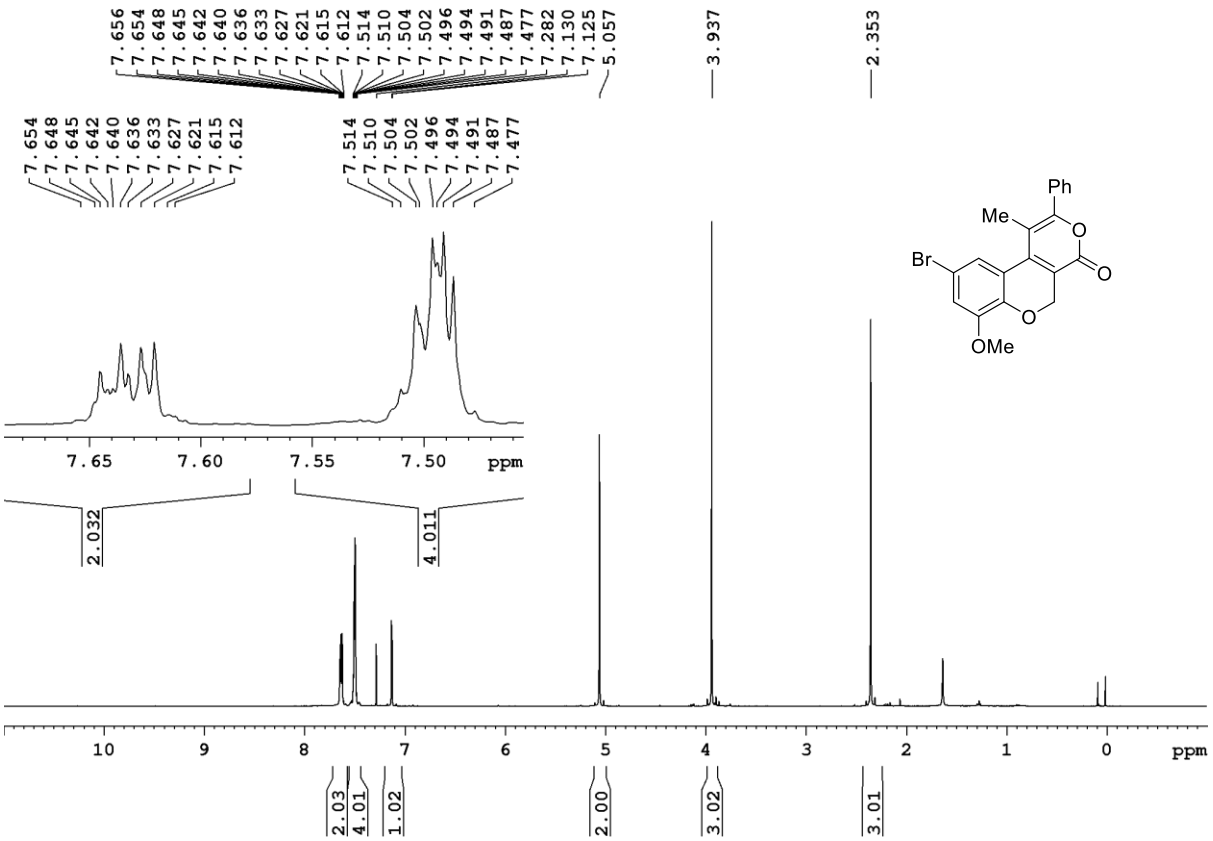


Figure S50. ^{1}H NMR spectrum of compound **5ce**

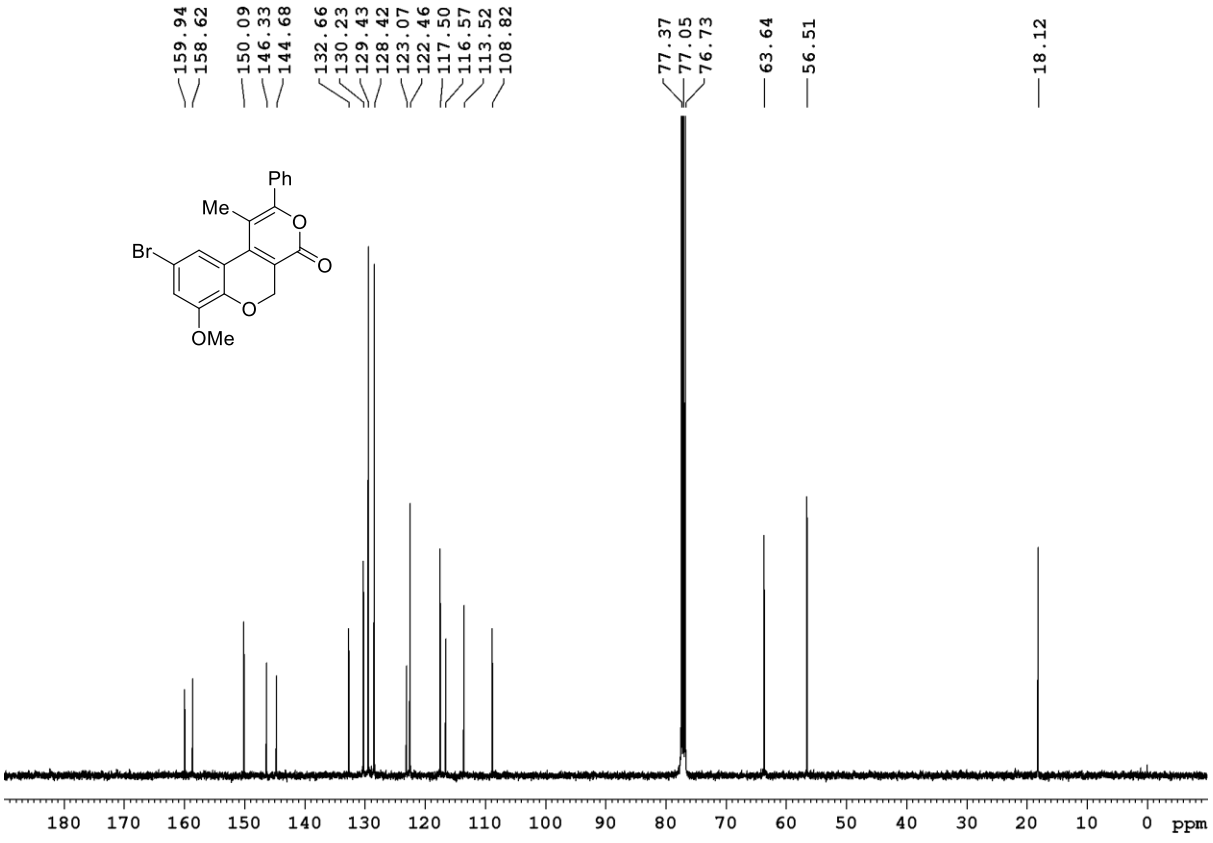


Figure S51. ^{13}C{^{1}H} NMR spectrum of compound **5ce**

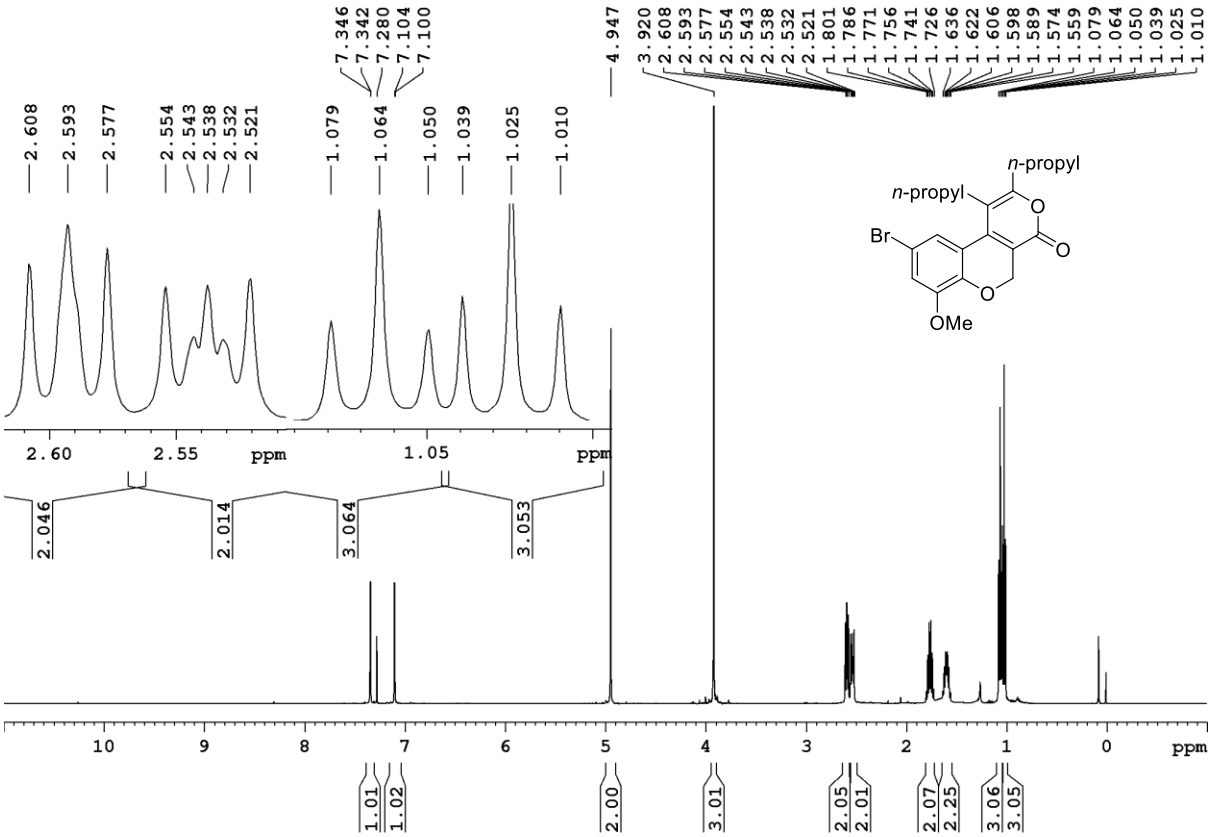


Figure S52. ^{1}H NMR spectrum of compound **5ci**

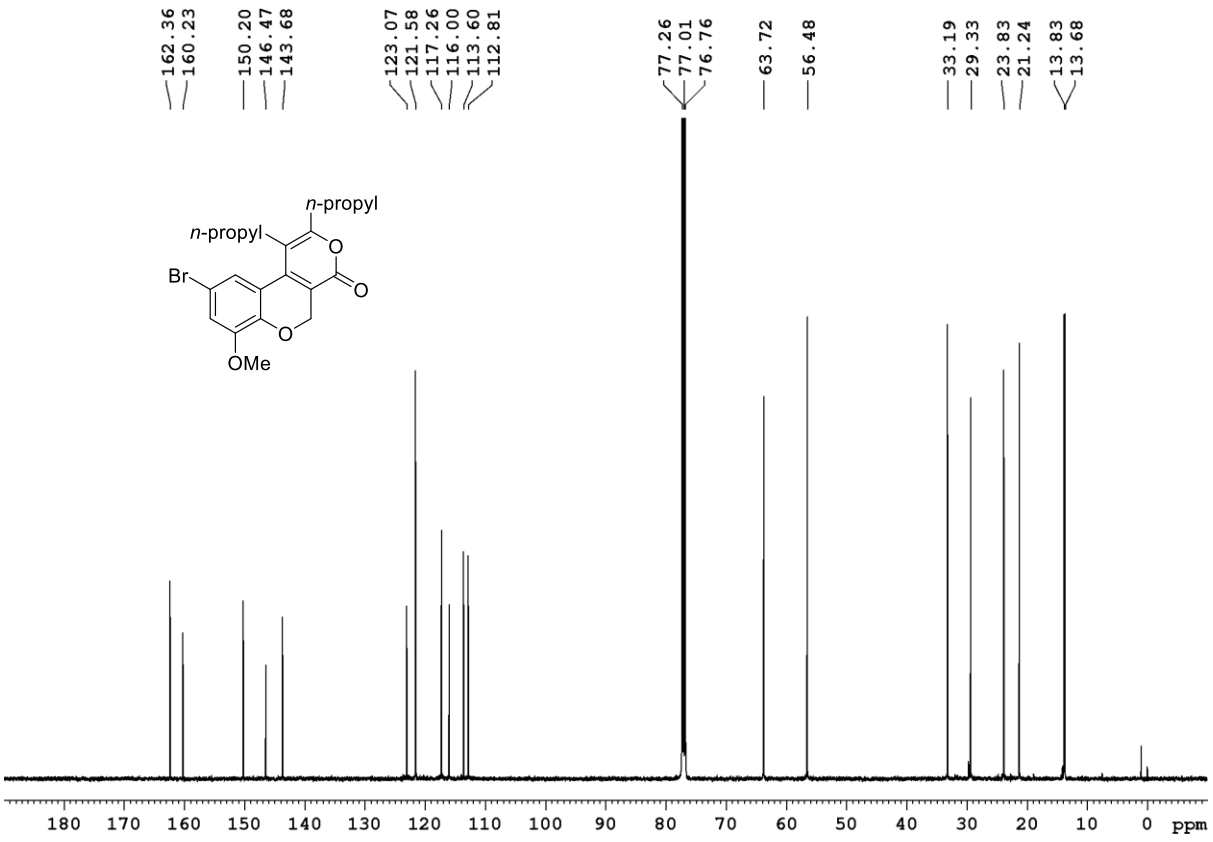


Figure S53. ^{13}C{^{1}H} NMR spectrum of compound **5ci**

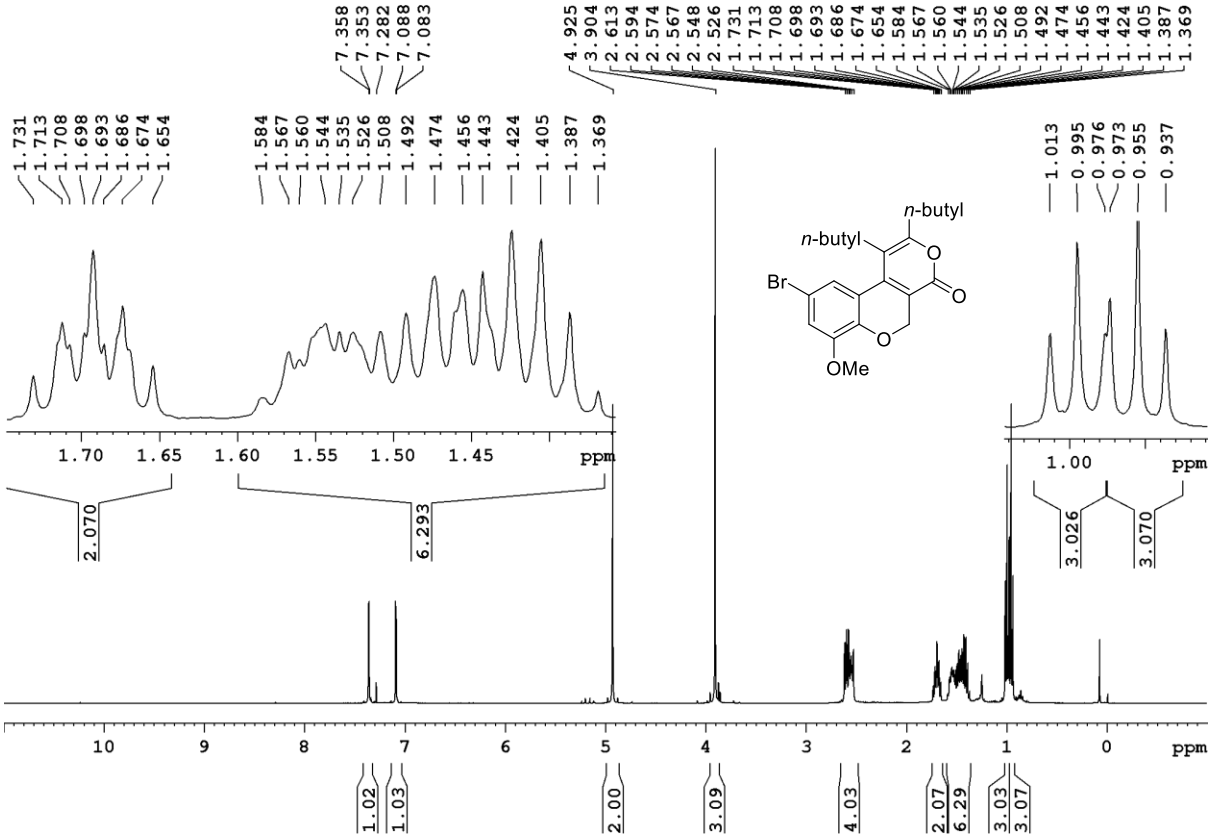


Figure S54. ^{1}H NMR spectrum of compound **5cj**

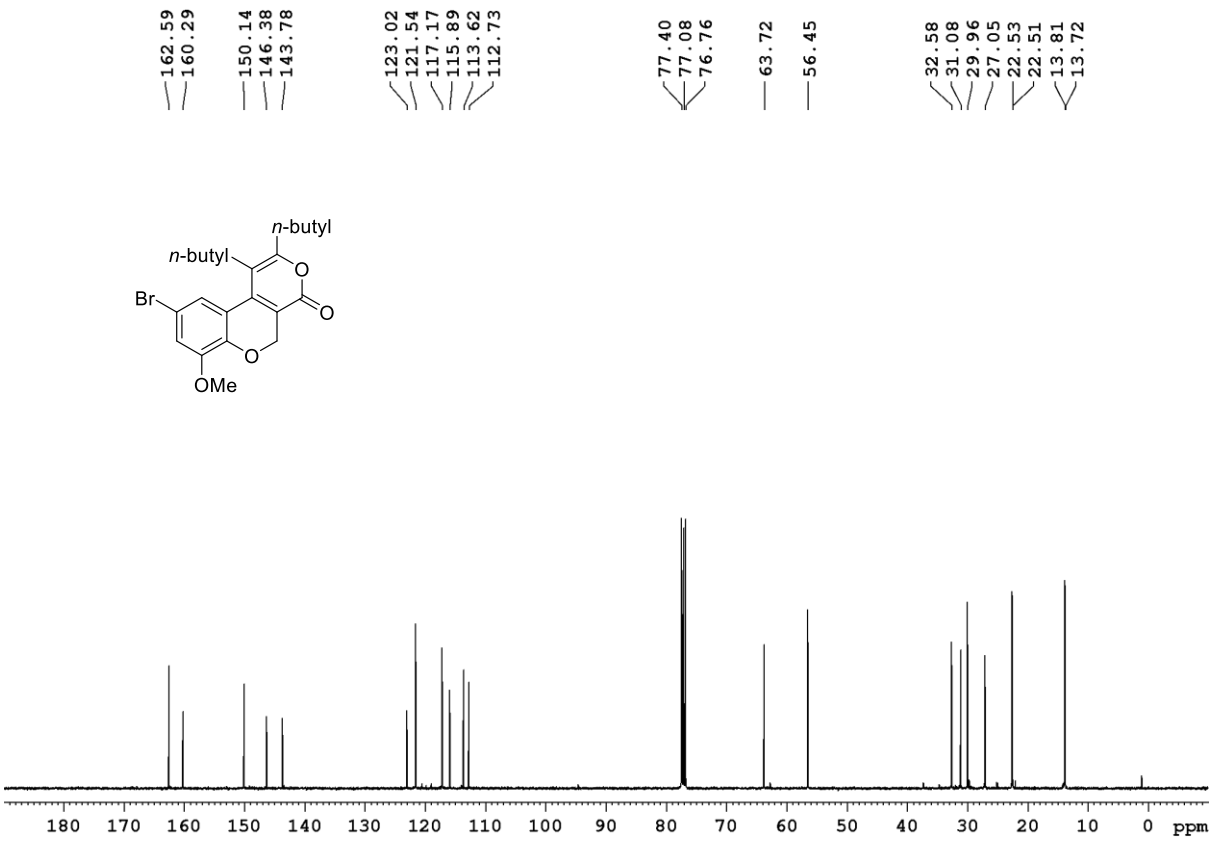


Figure S55. ^{13}C{^{1}H} NMR spectrum of compound **5cj**

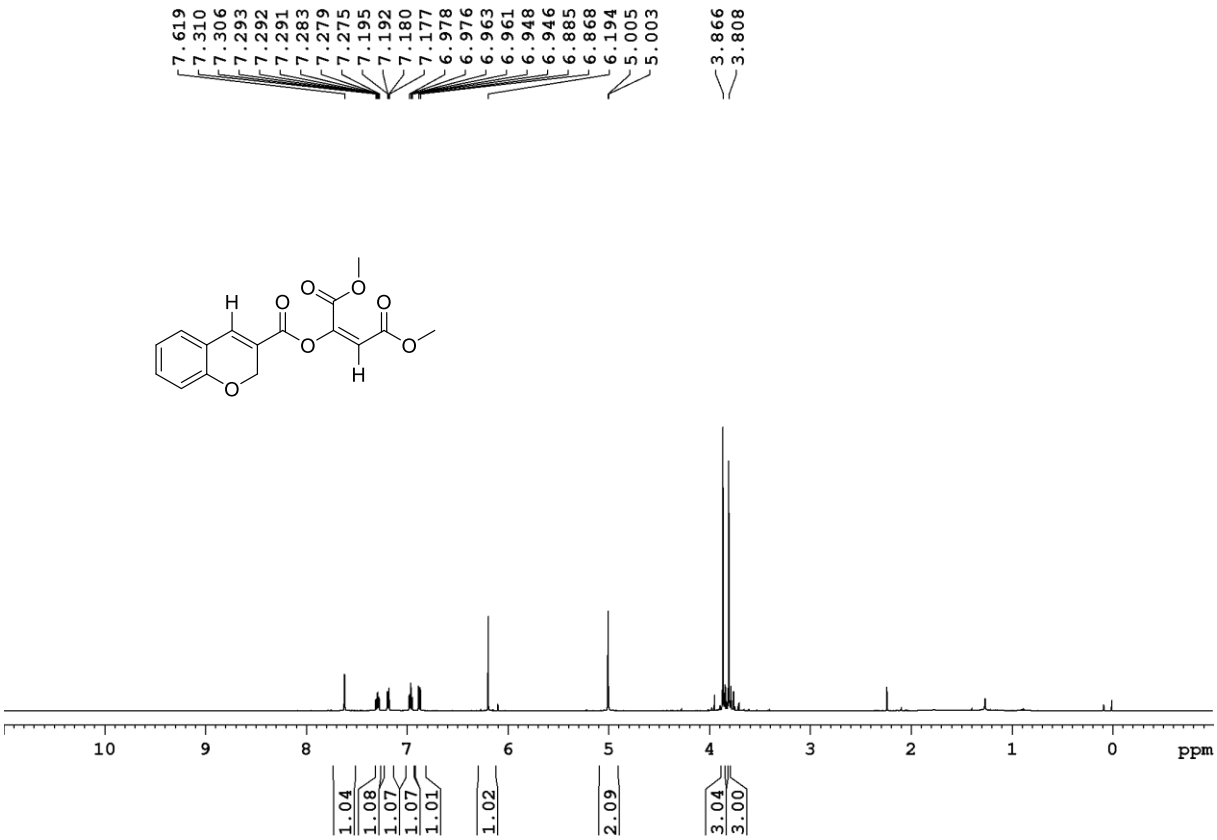


Figure S56. ^{1}H NMR spectrum of compound **5'al**

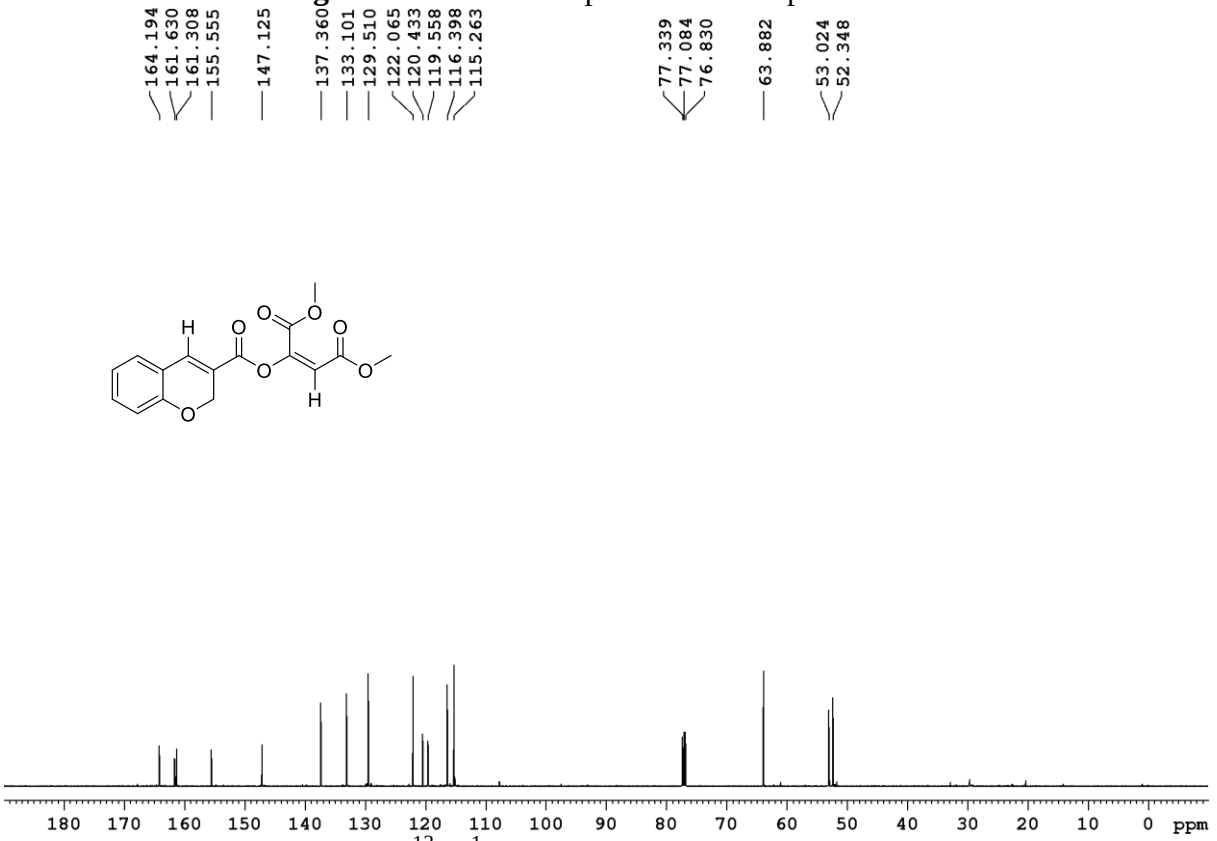


Figure S57. ^{13}C{^{1}H} NMR spectrum of compound **5'al**

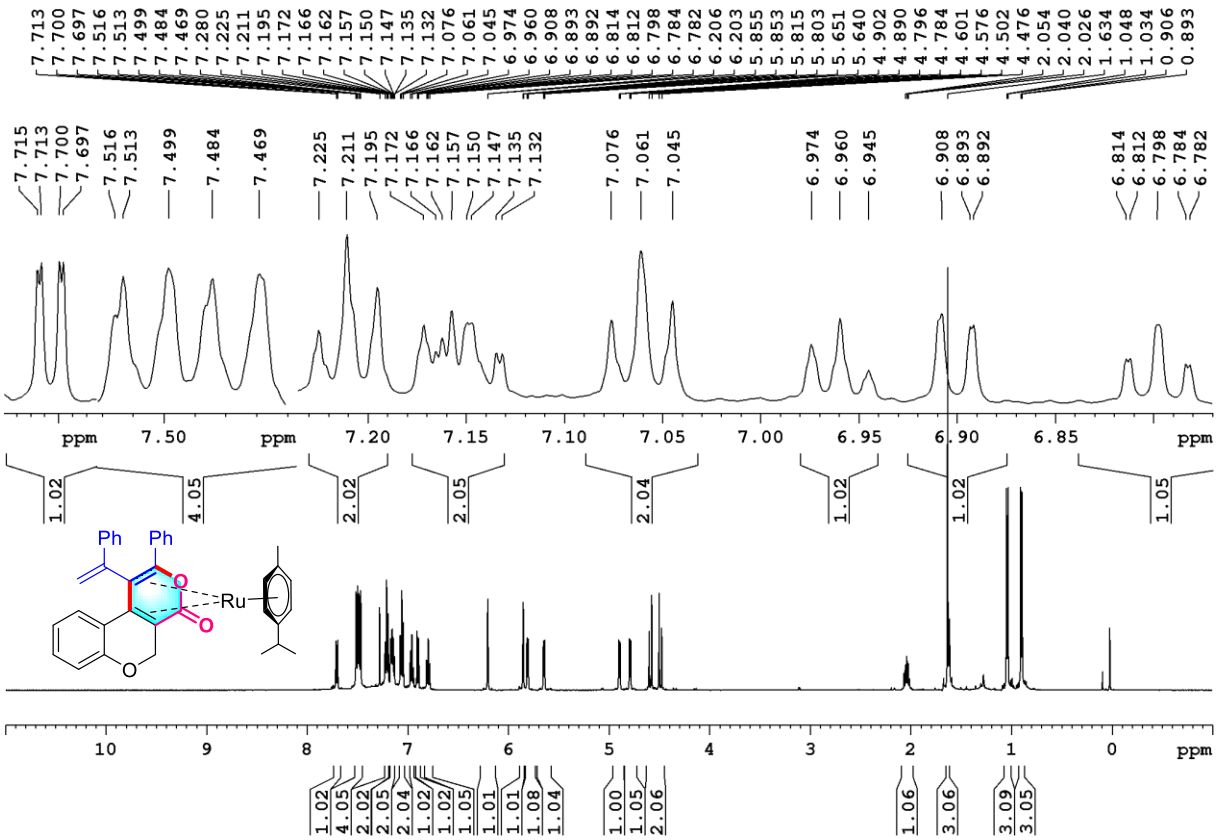


Figure S58. ^{1}H NMR spectrum of compound **6aa**

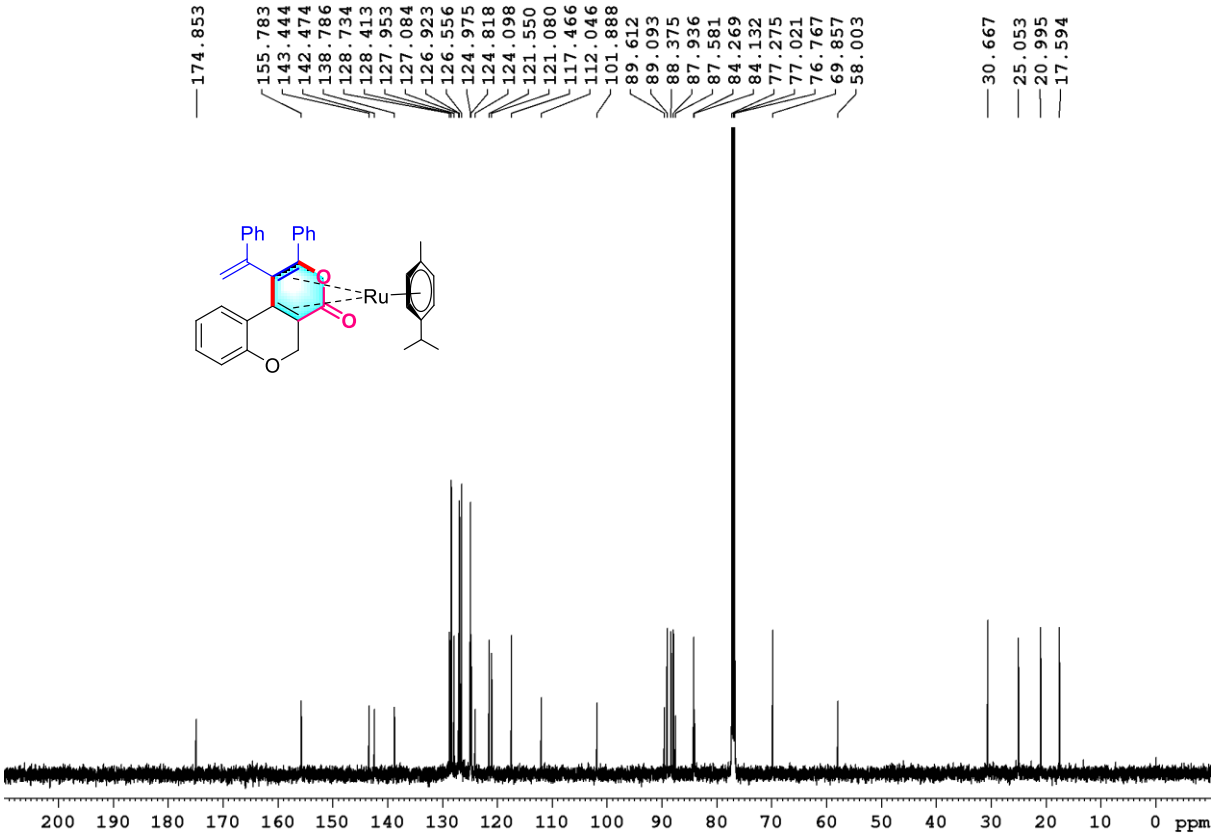


Figure S59. ^{13}C{^{1}H} NMR spectrum of compound **6aa**

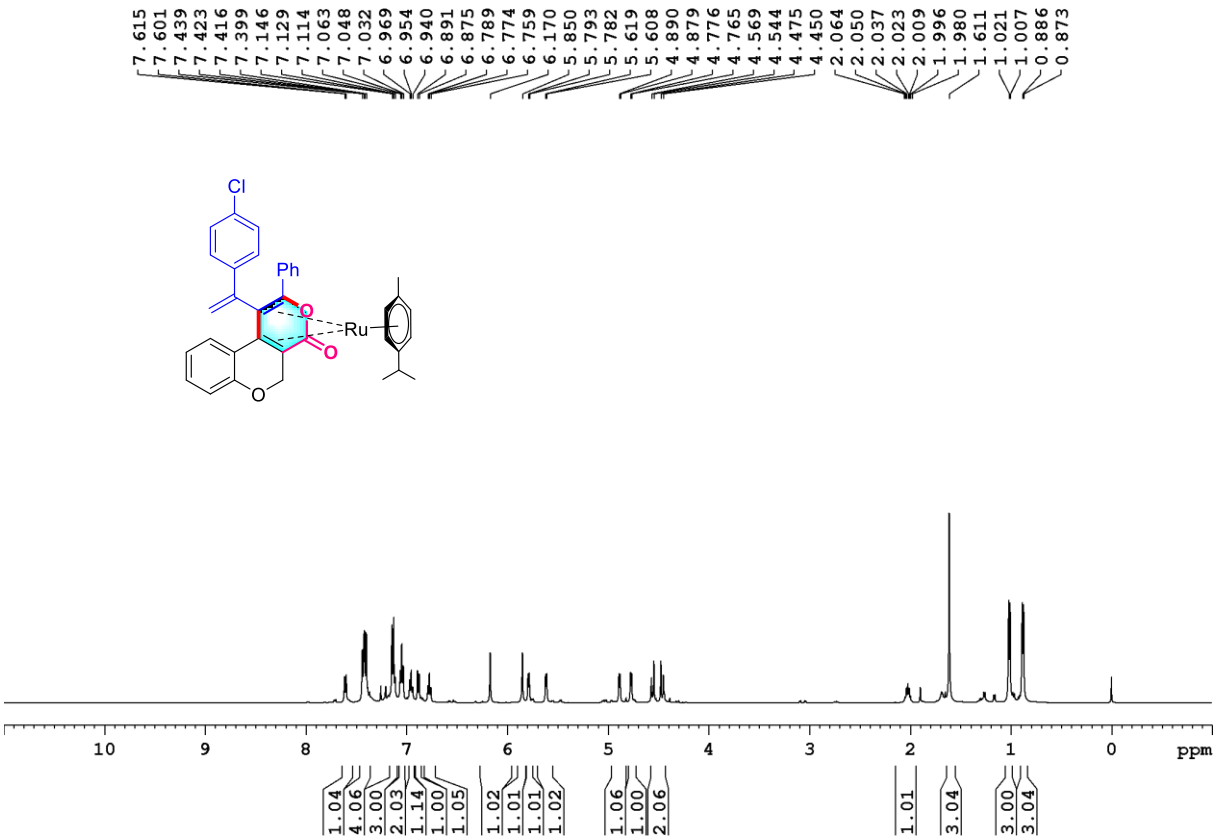


Figure S60. ^{1}H NMR spectrum of compound **6ab**

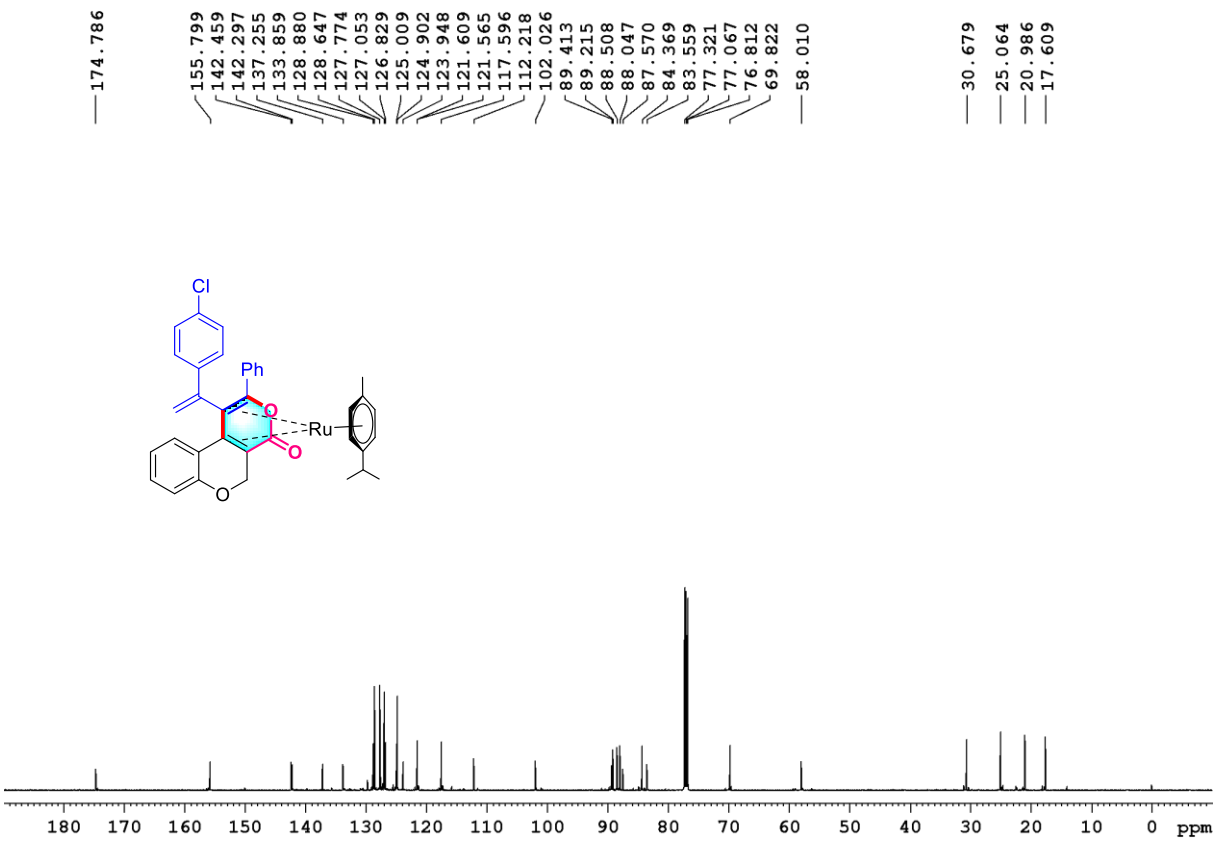


Figure S61. ^{13}C{^{1}H} NMR spectrum of compound **6ab**

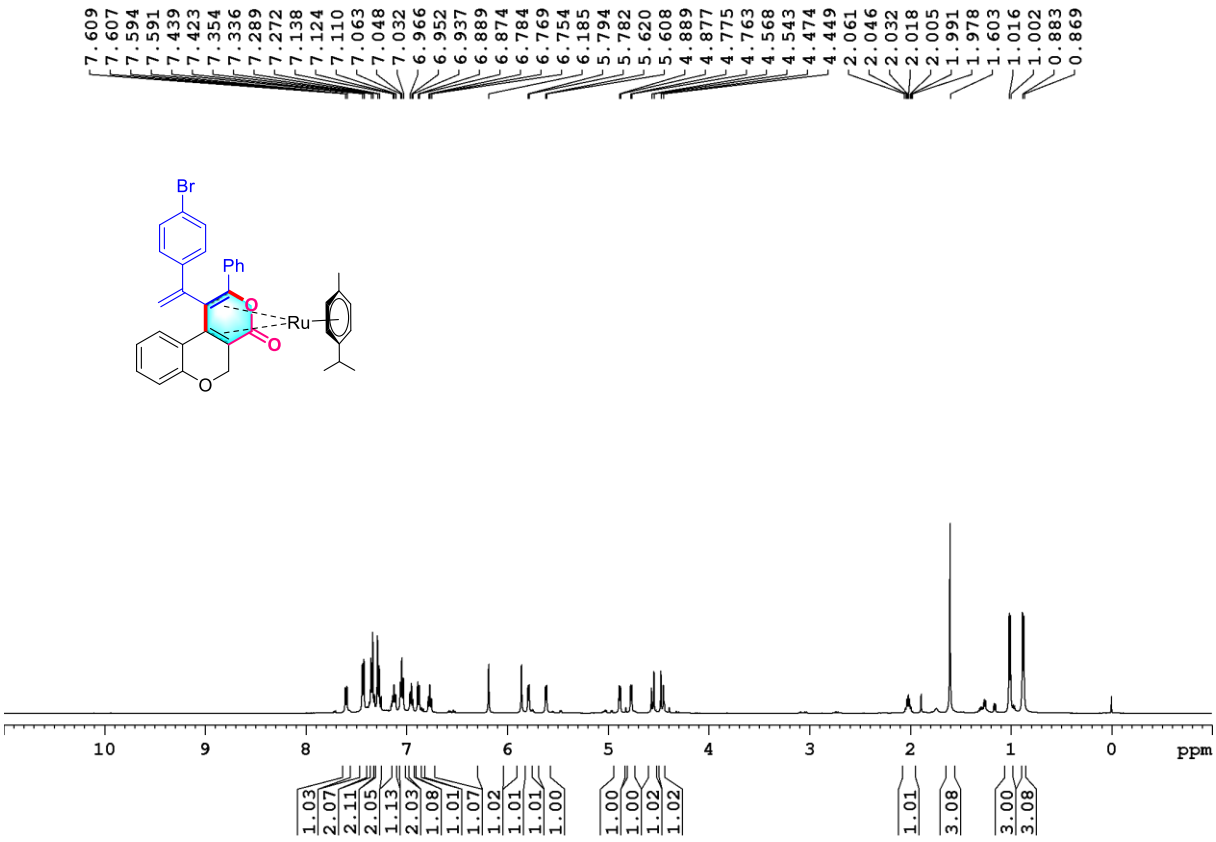


Figure S62. ^{1}H NMR spectrum of compound **6ac**

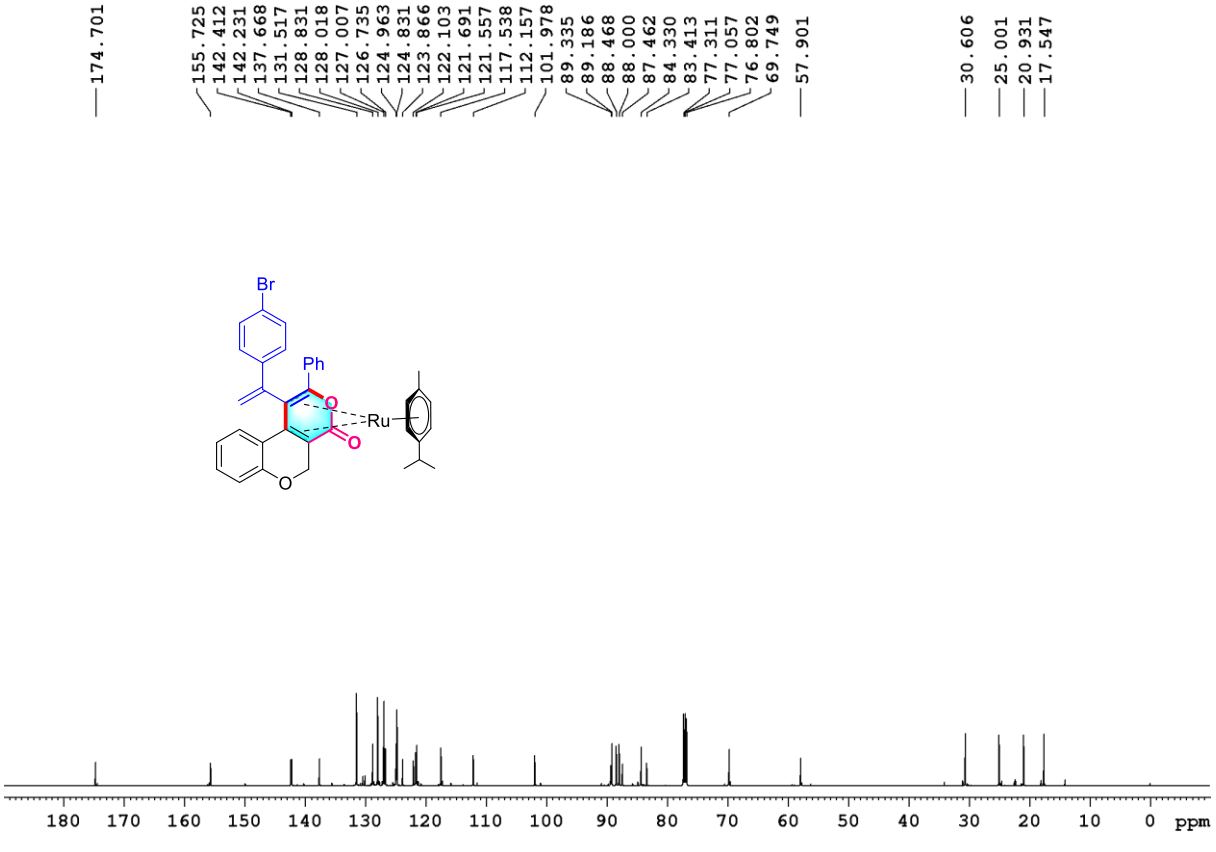


Figure S63. ^{13}C{^{1}H} NMR spectrum of compound **6ac**

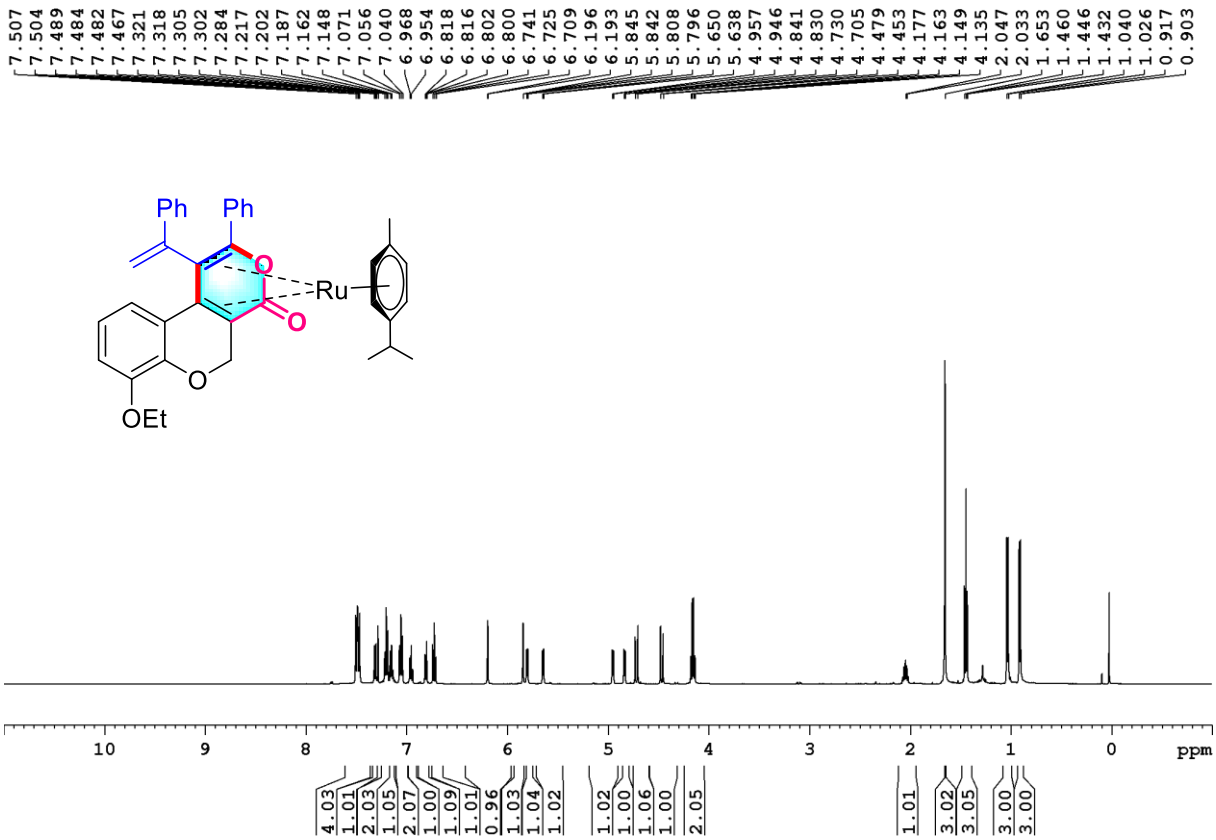


Figure S64. ^{1}H NMR spectrum of compound **6ba**

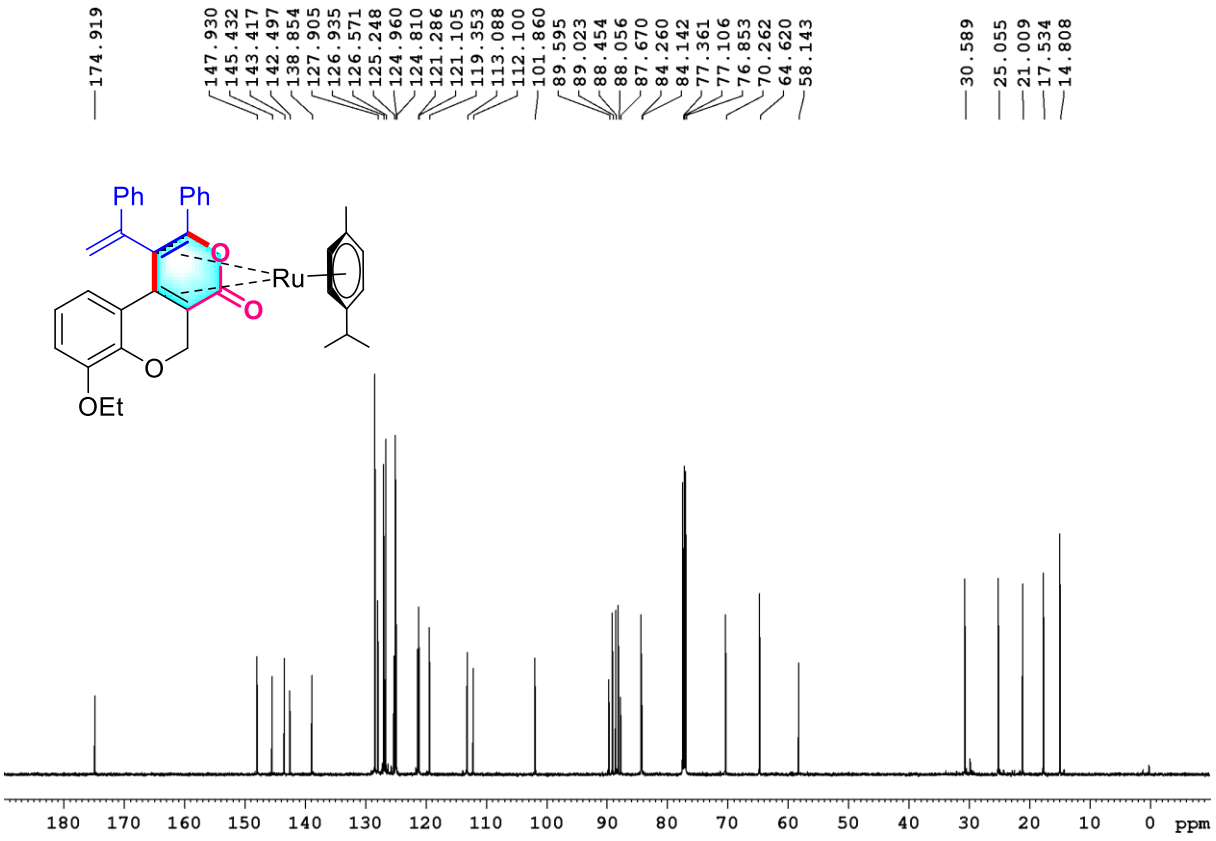


Figure S65. ^{13}C{^{1}H} NMR spectrum of compound **6ba**

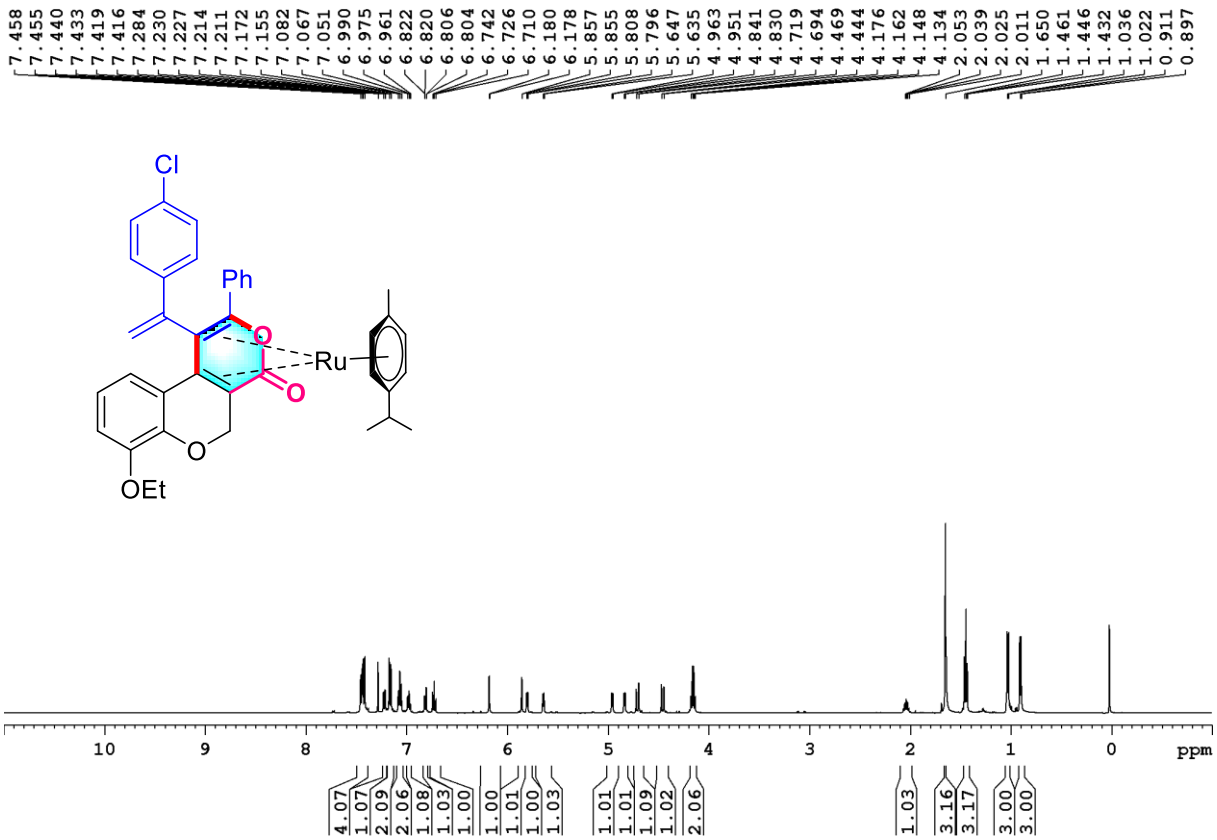


Figure S66. ^{1}H NMR spectrum of compound **6bb**

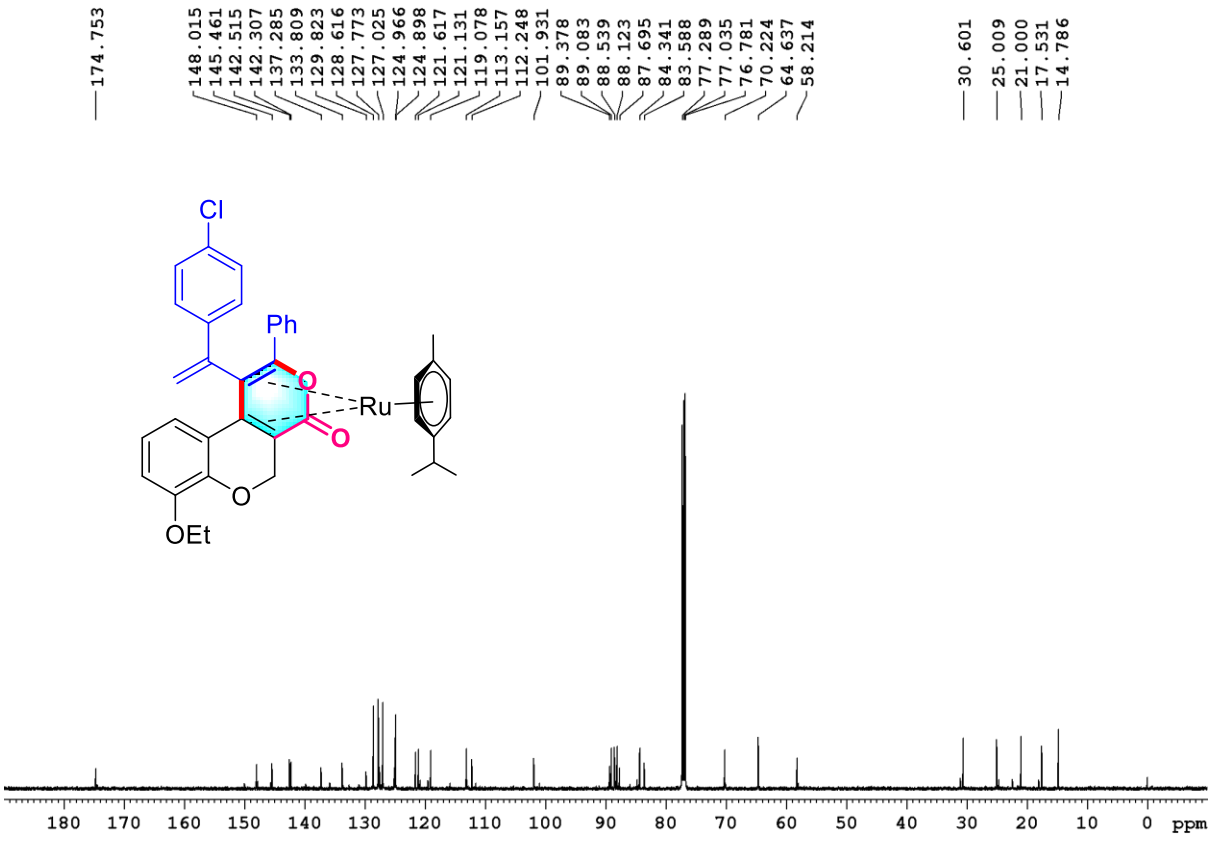


Figure S67. ^{13}C{^{1}H} NMR spectrum of compound **6bb**

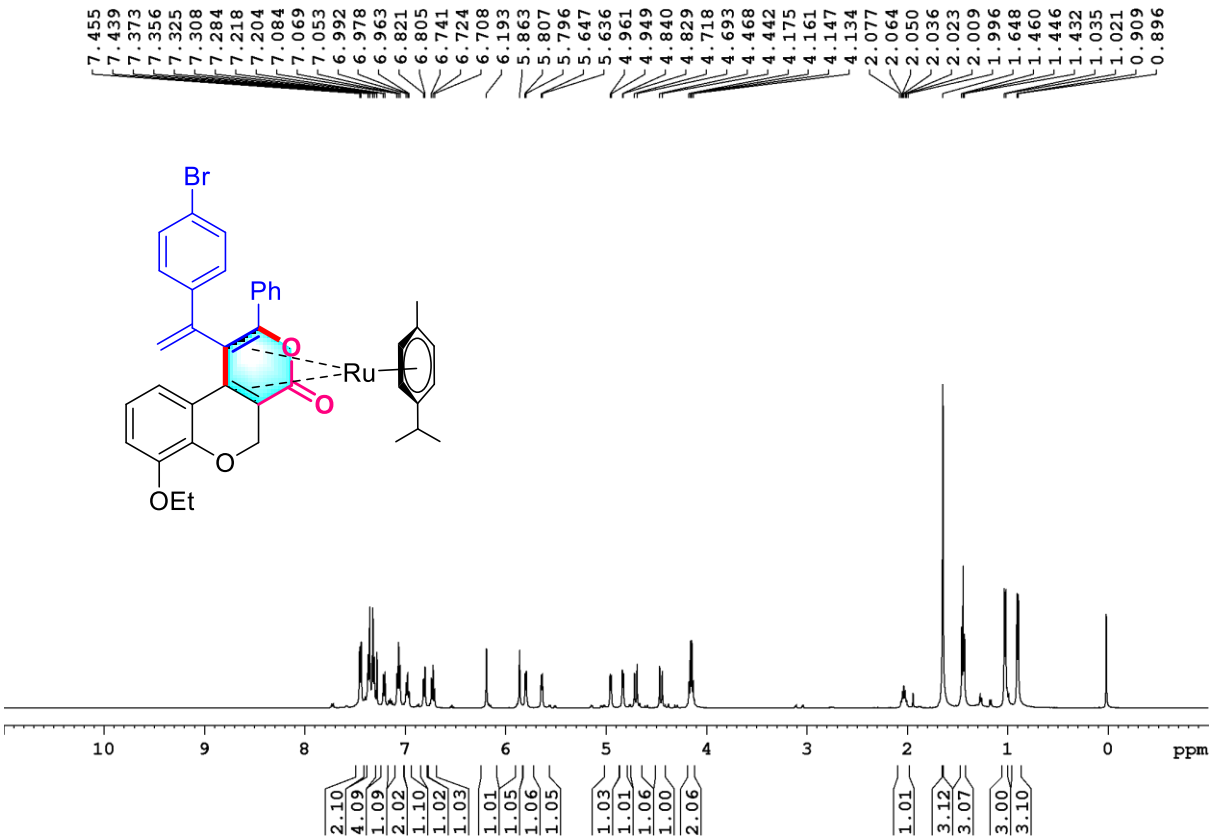


Figure S68. ^{1}H NMR spectrum of compound **6bc**

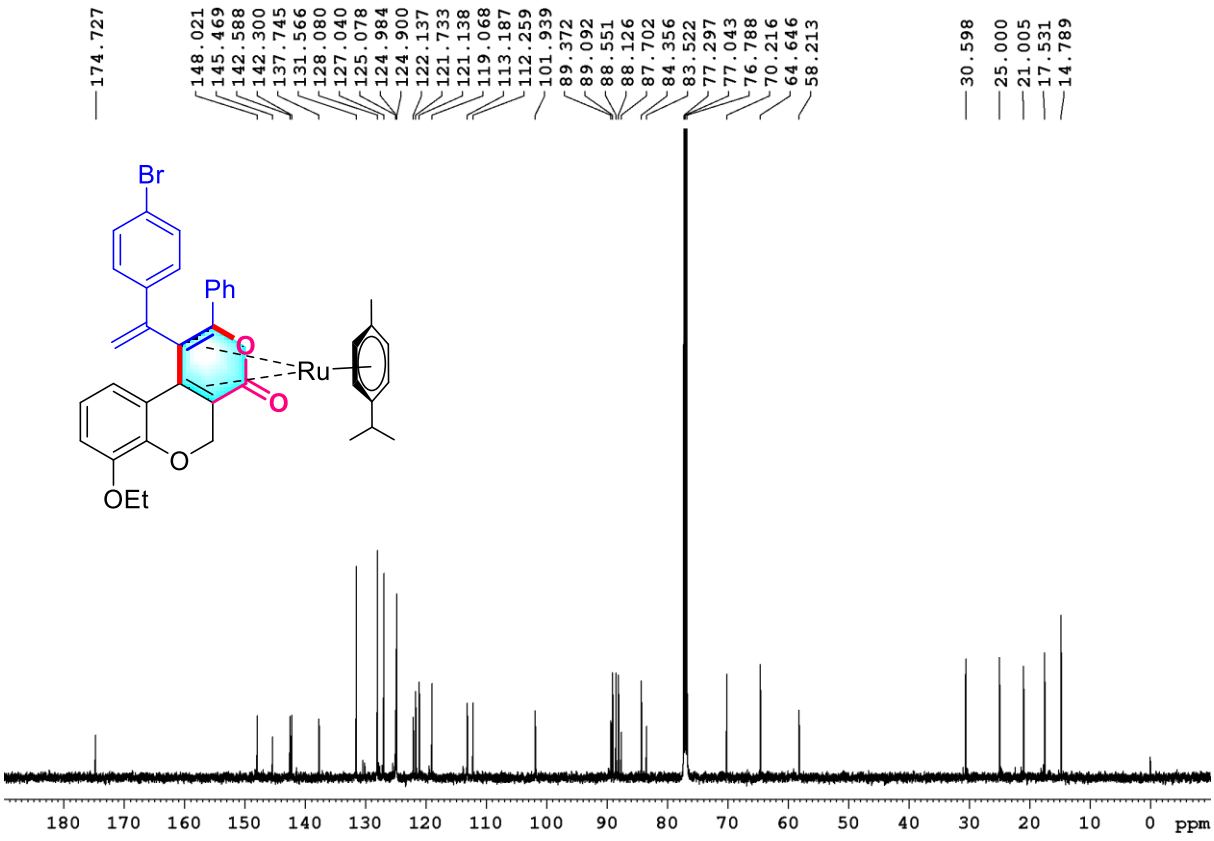


Figure S69. ^{13}C{^{1}H} NMR spectrum of compound **6bc**

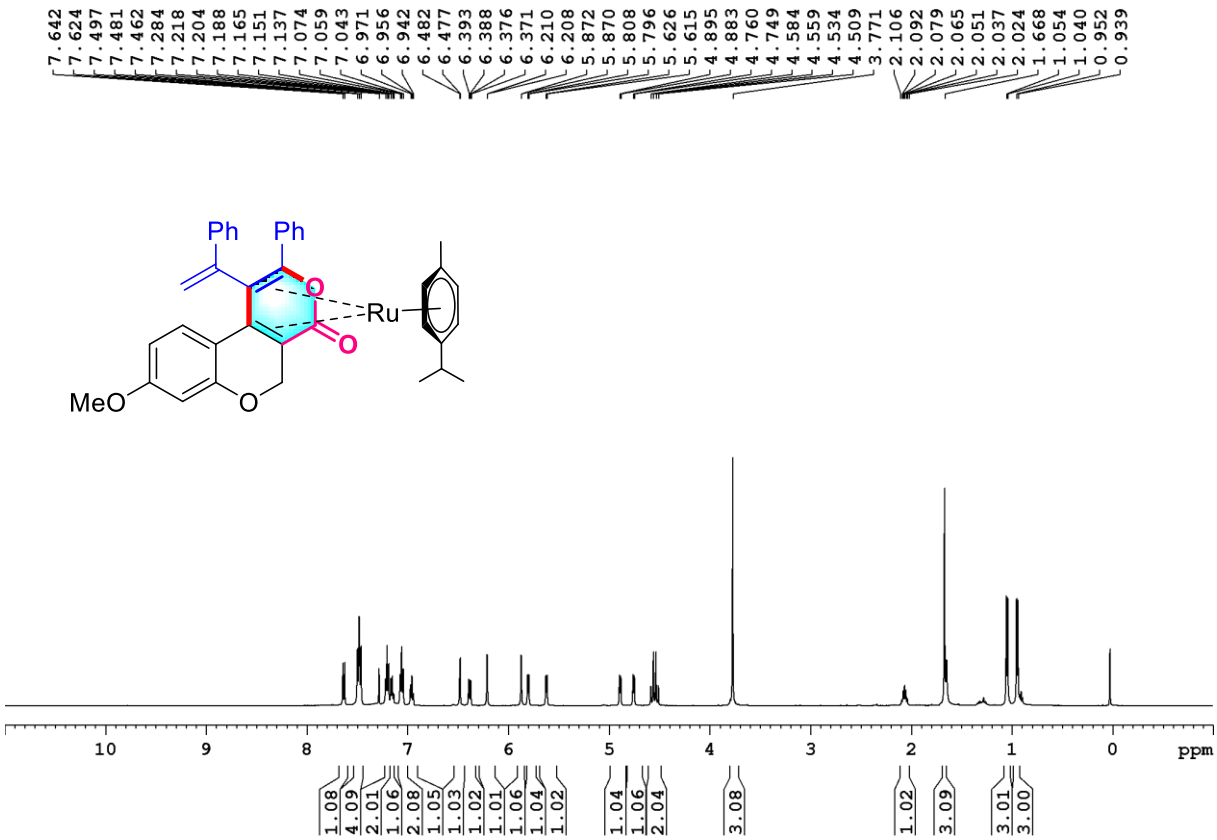


Figure S70. ^{1}H NMR spectrum of compound **6da**

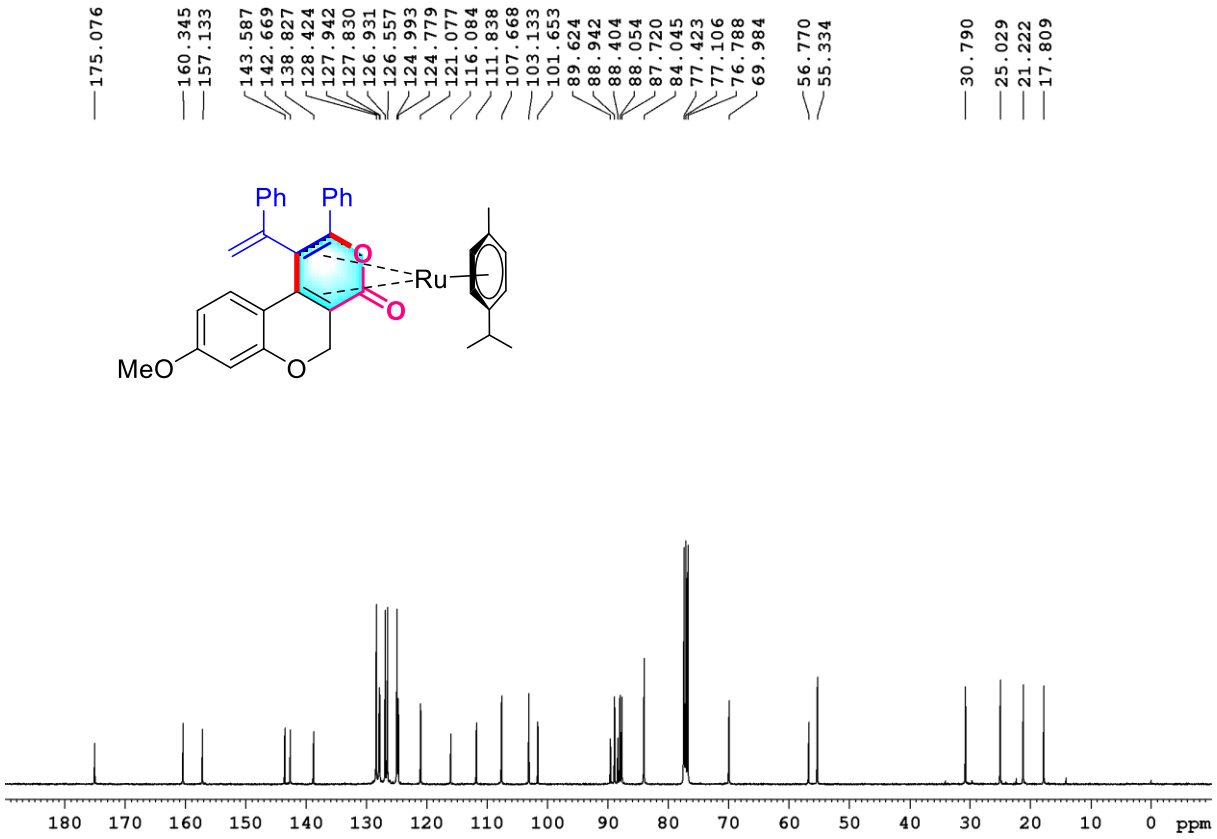


Figure S71. ^{13}C{^{1}H} NMR spectrum of compound **6da**

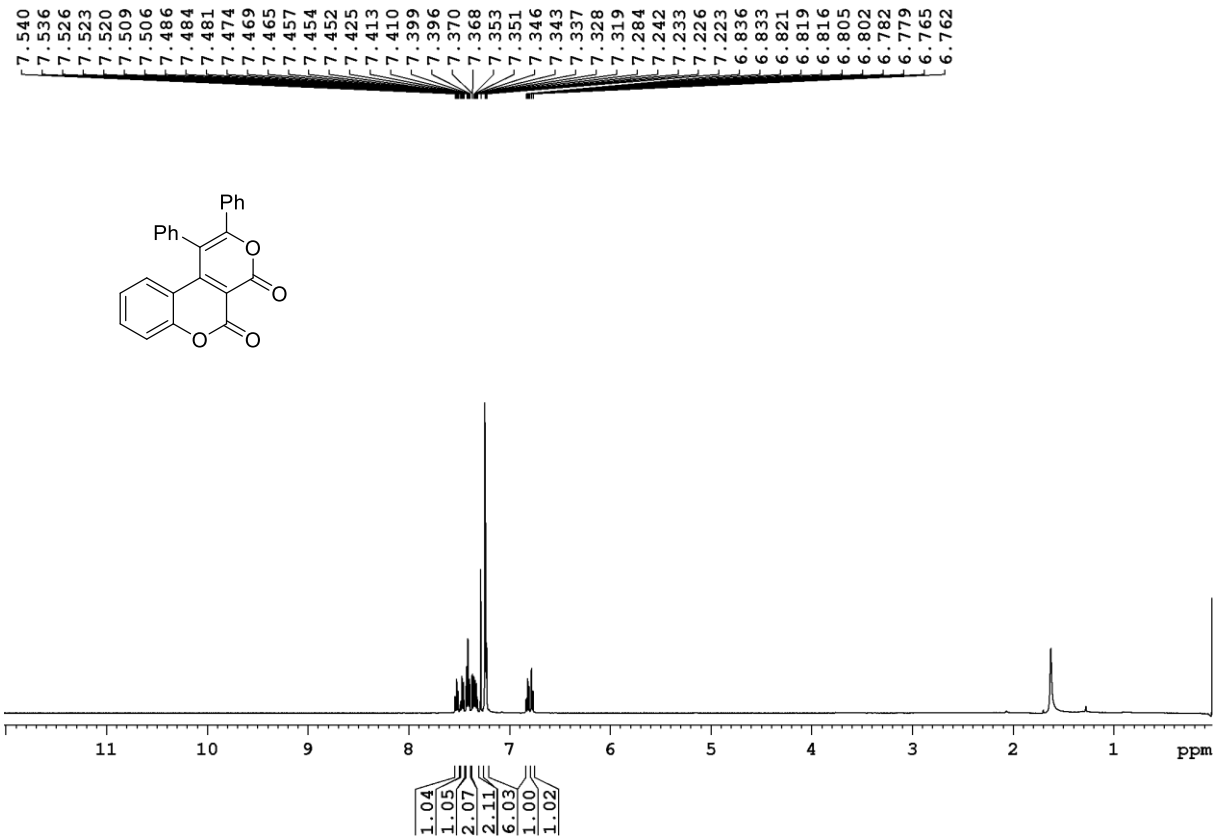


Figure S72. ^{1}H NMR spectrum of compound **7aa**

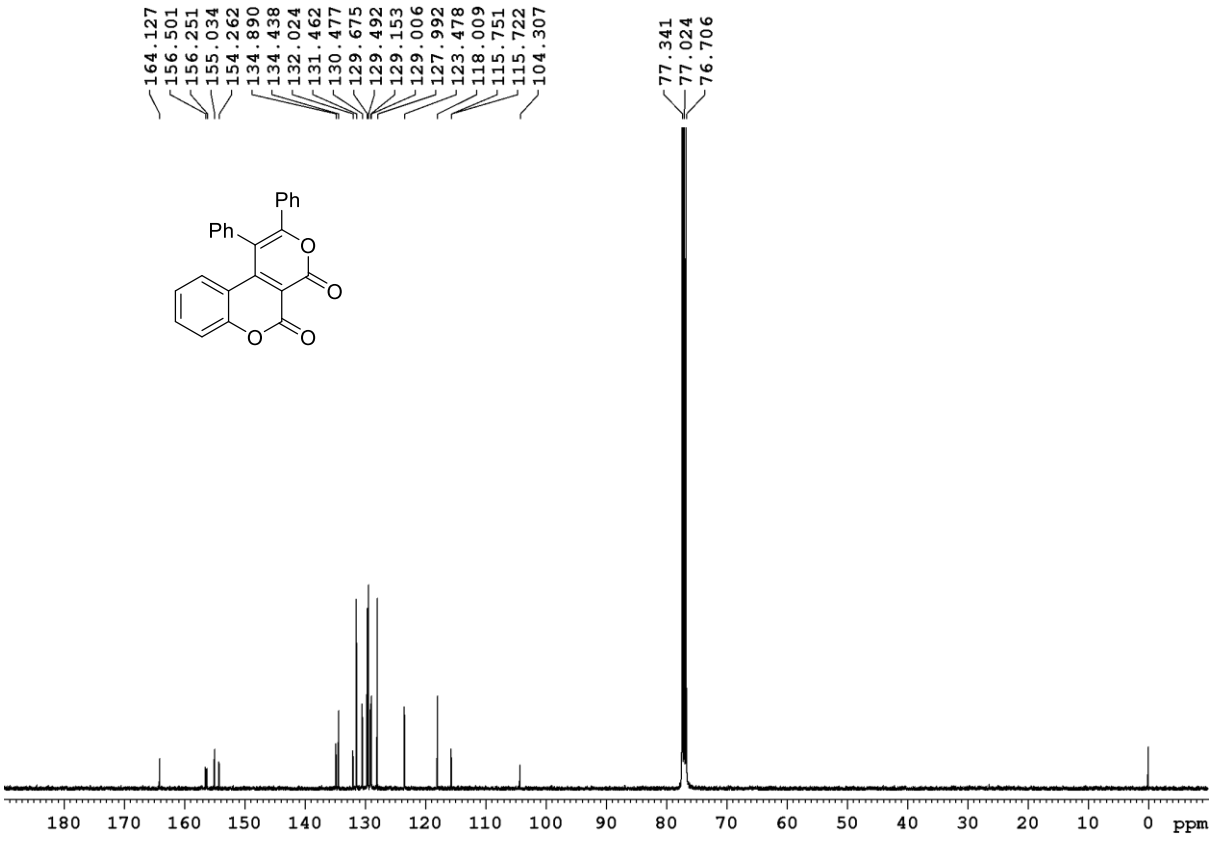


Figure S73. ^{13}C{^{1}H} NMR spectrum of compound **7aa**

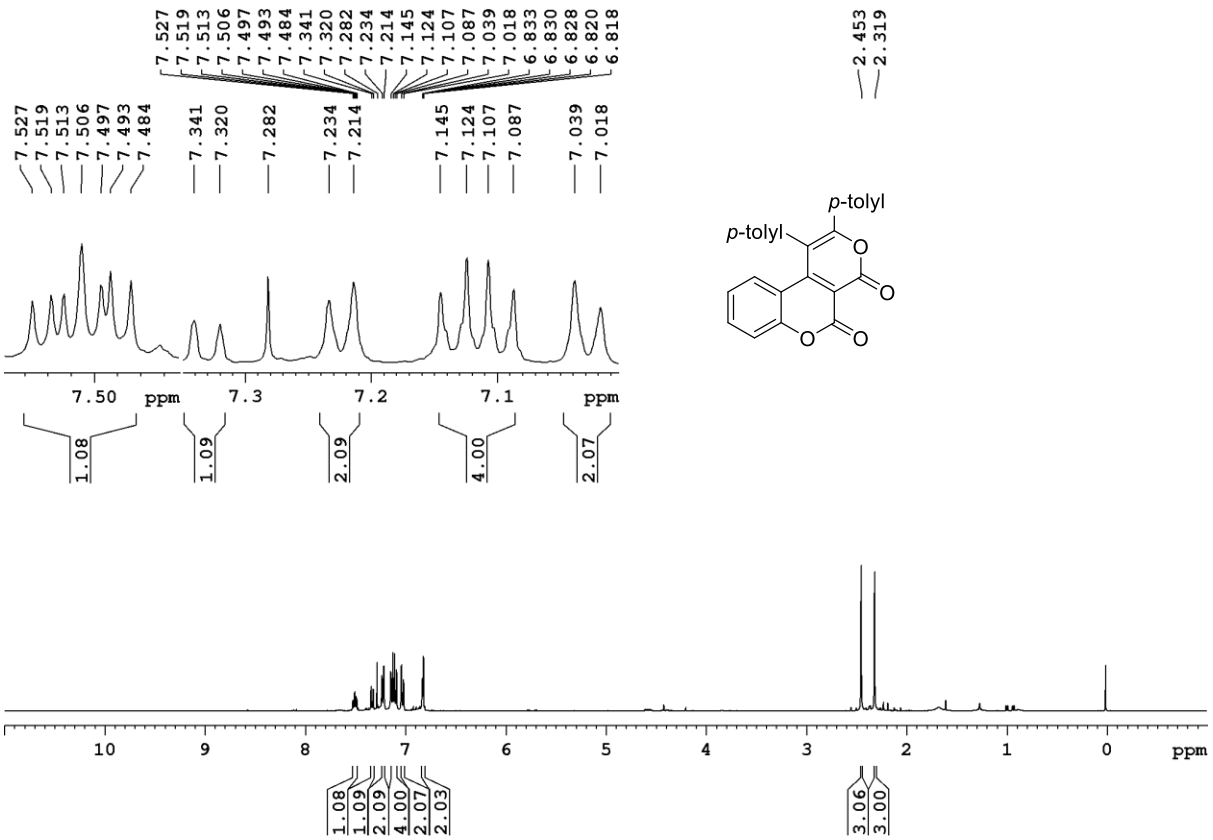


Figure S74. ^{1}H NMR spectrum of compound **7ab**

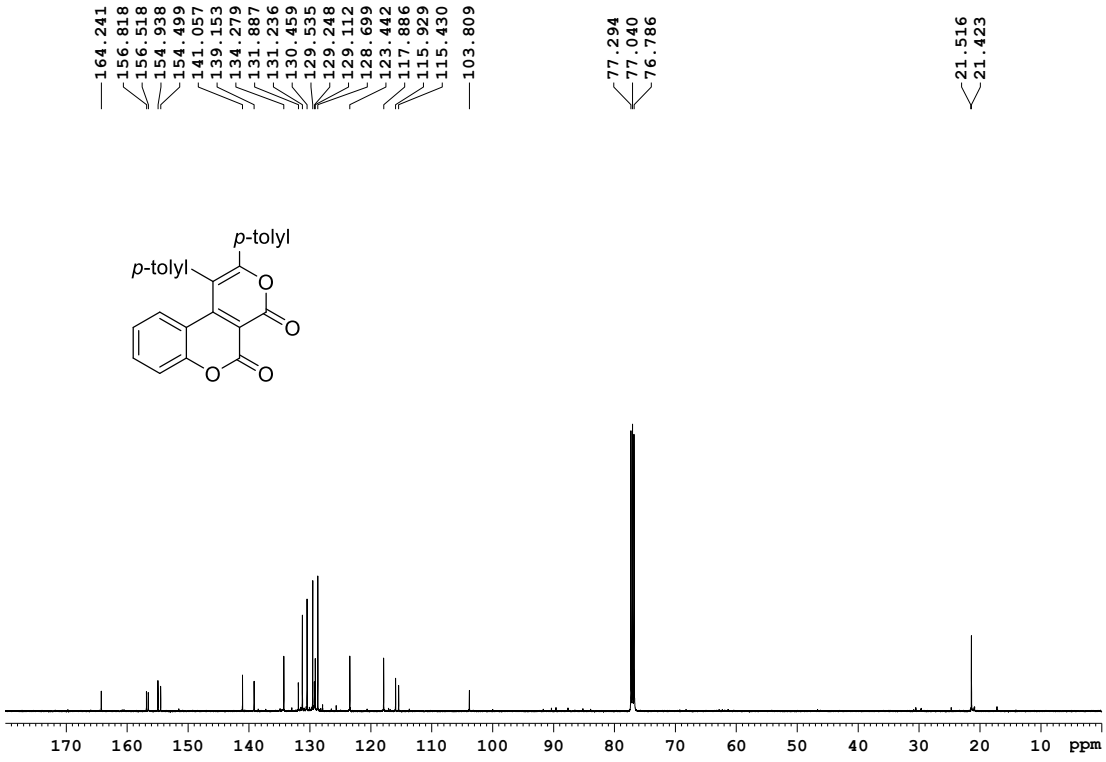


Figure S75. ^{13}C{^{1}H} NMR spectrum of compound **7ab**

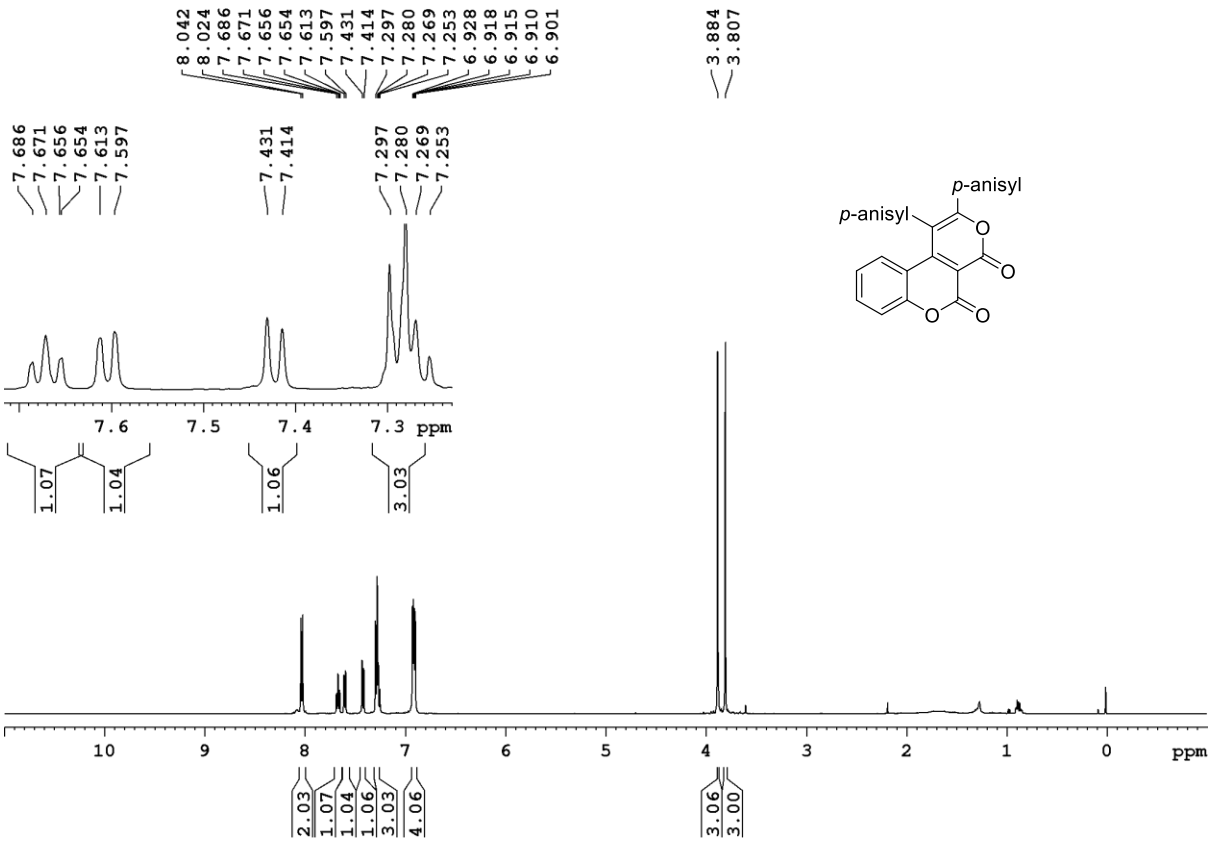


Figure S76. ^{1}H NMR spectrum of compound **7ac**

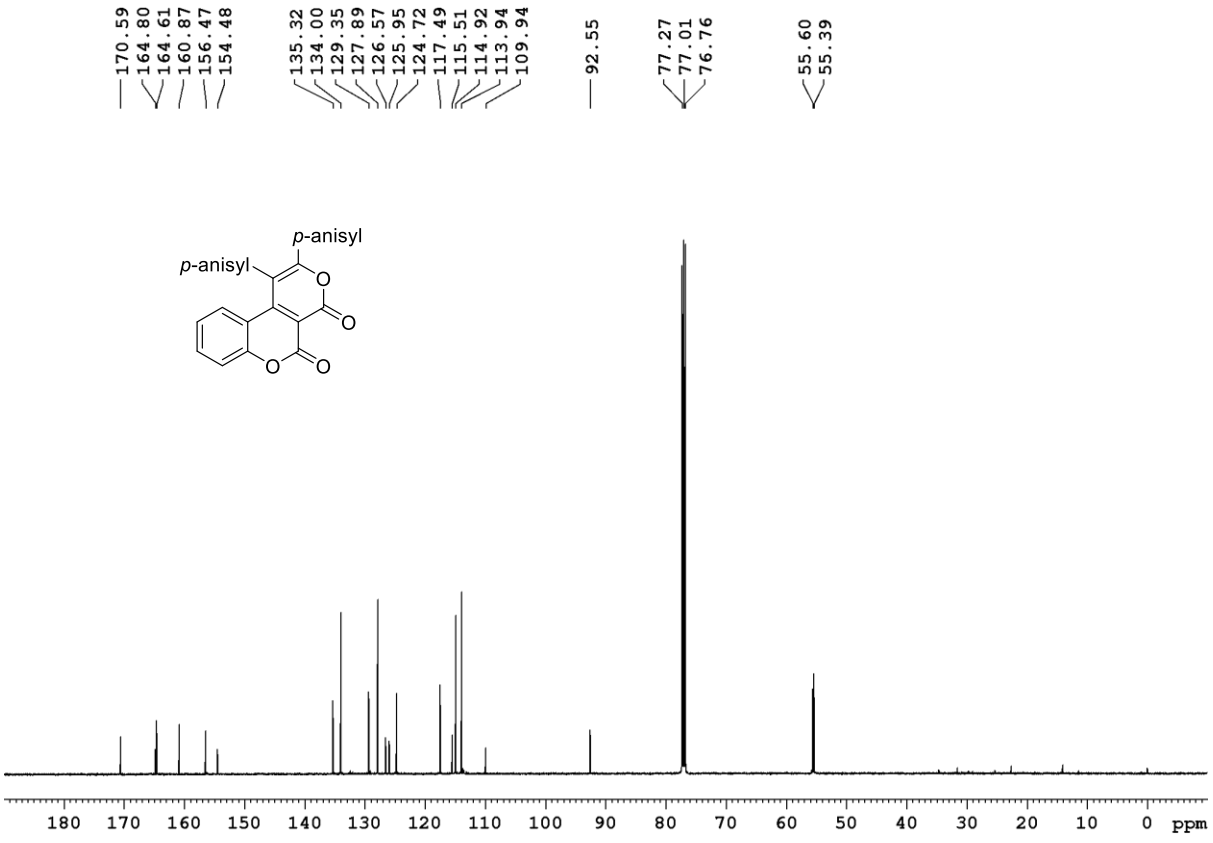


Figure S77. ^{13}C{^{1}H} NMR spectrum of compound **7ac**

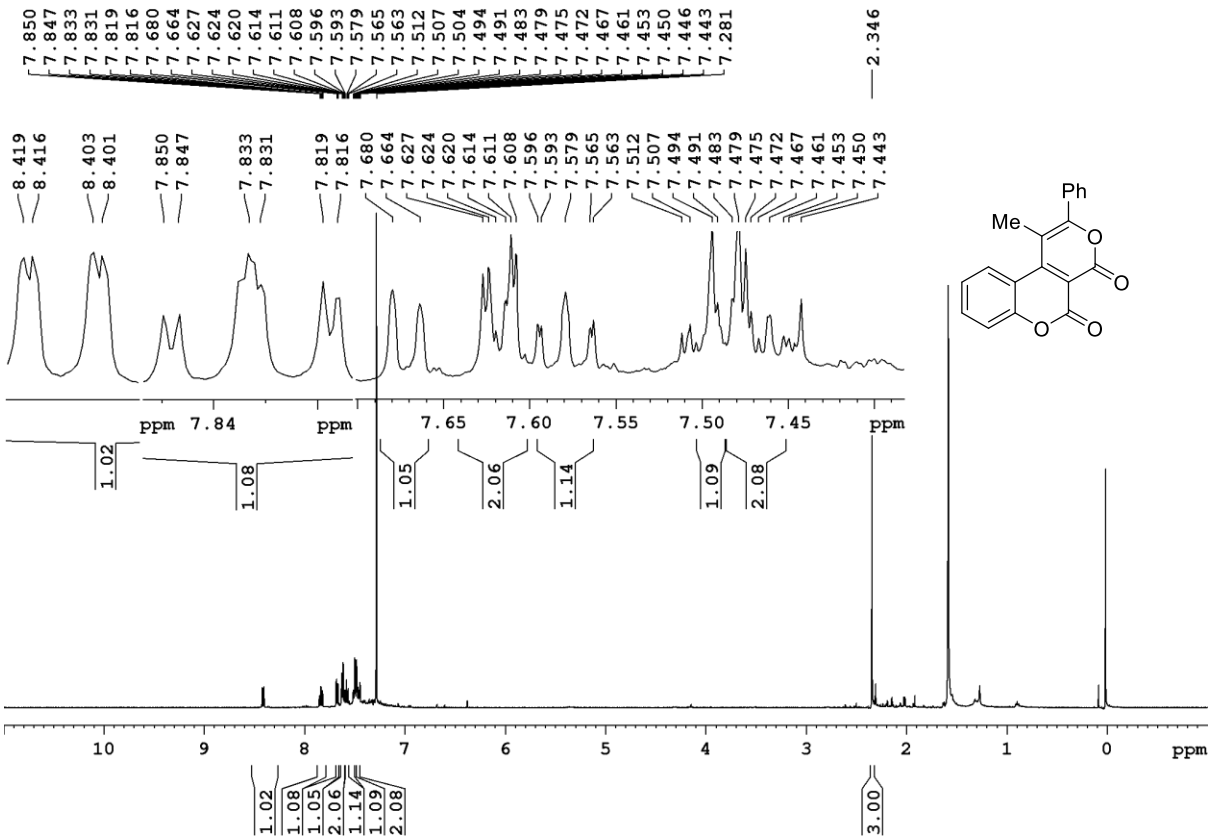


Figure S78. ^{1}H NMR spectrum of compound **7ae**

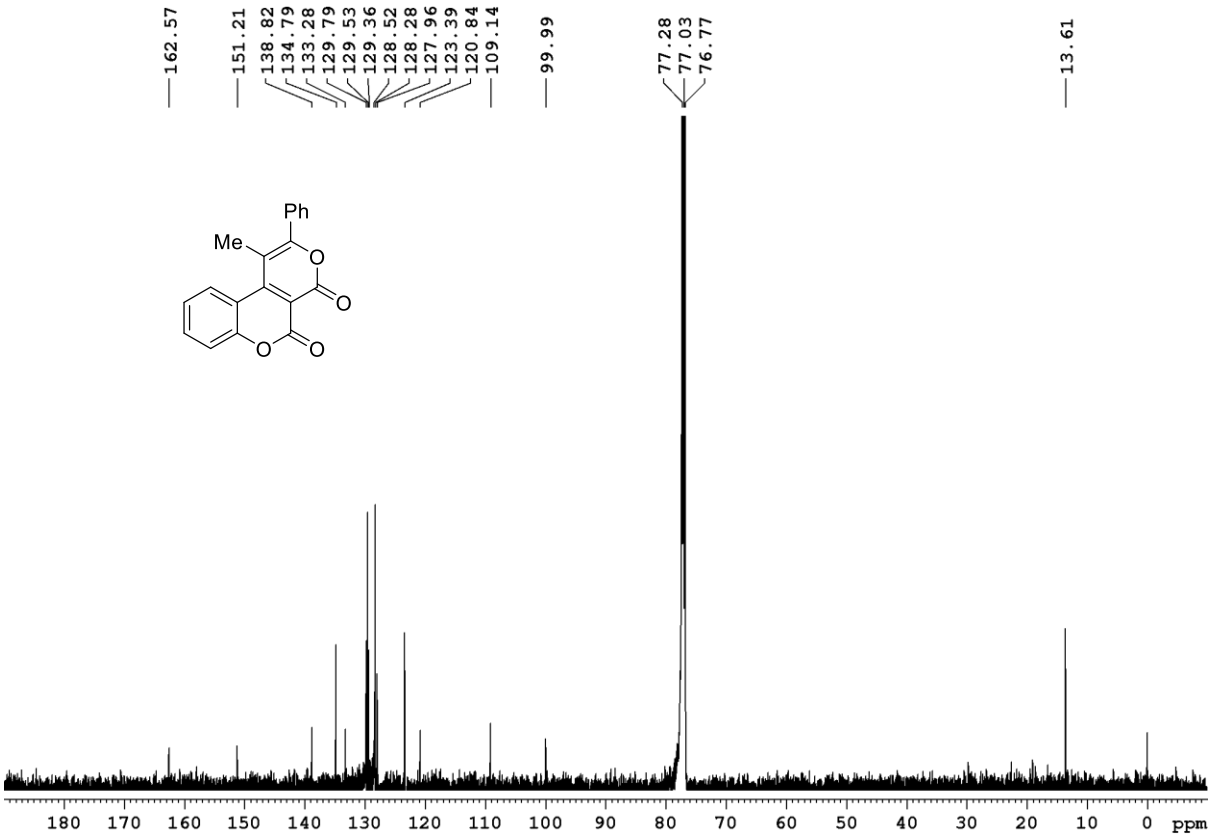


Figure S79. ^{13}C{^{1}H} NMR spectrum of compound **7ae**

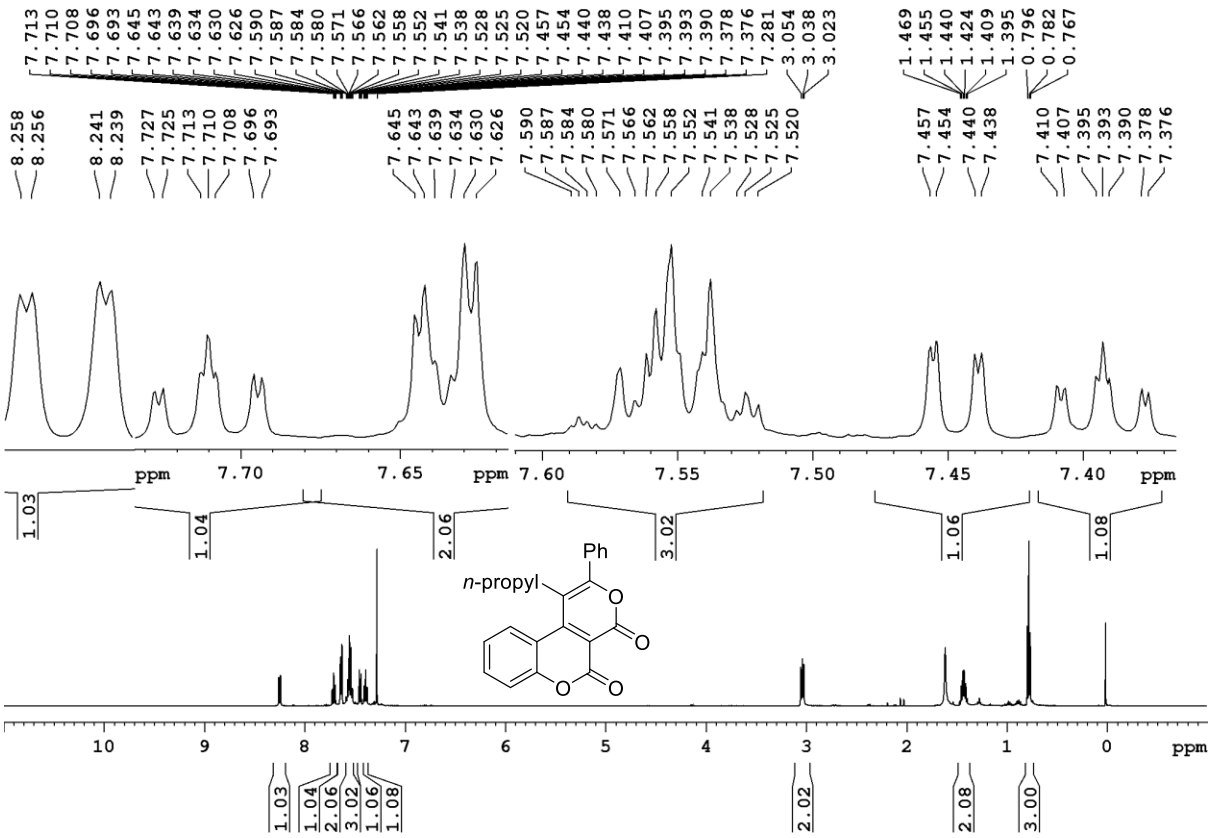


Figure S80. ^{1}H NMR spectrum of compound **7ag**

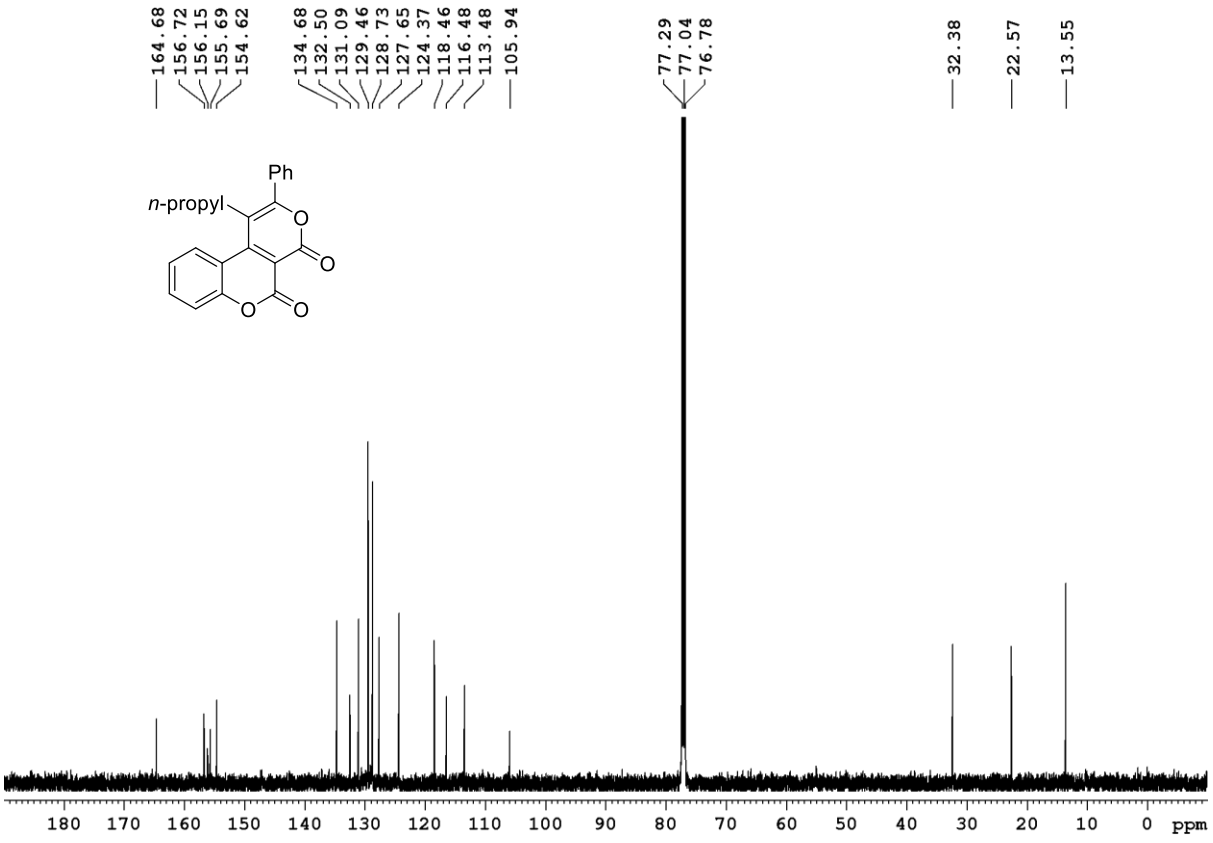


Figure S81. ^{13}C{^{1}H} NMR spectrum of compound **7ag**

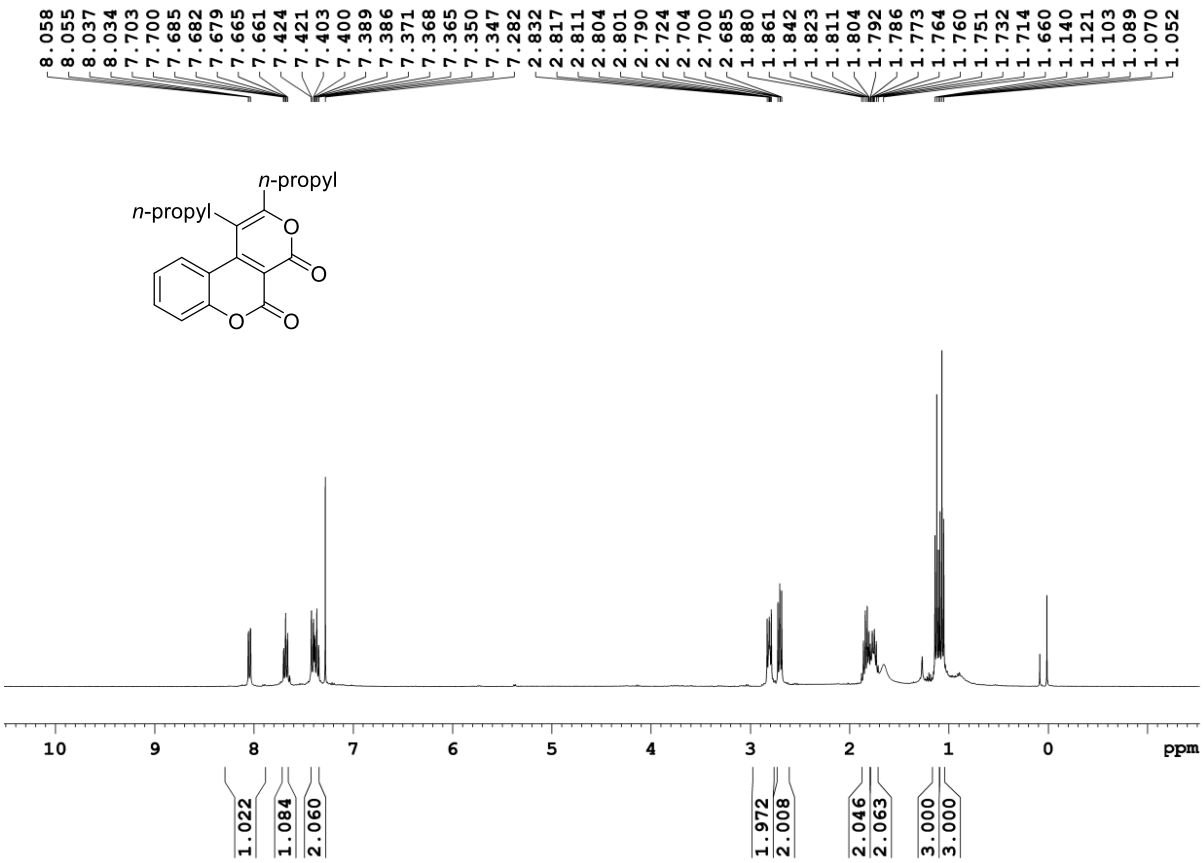


Figure S82. ^{1}H NMR spectrum of compound **7ai**

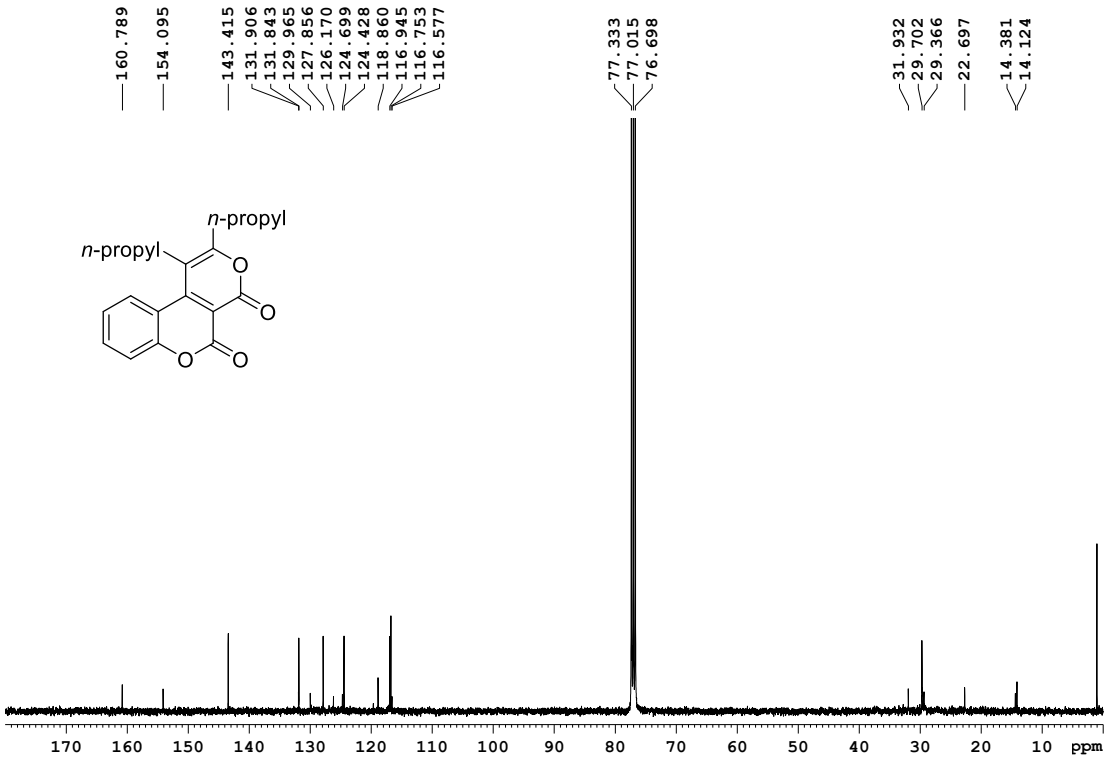


Figure S83. ^{13}C{^{1}H} NMR spectrum of compound **7ai**

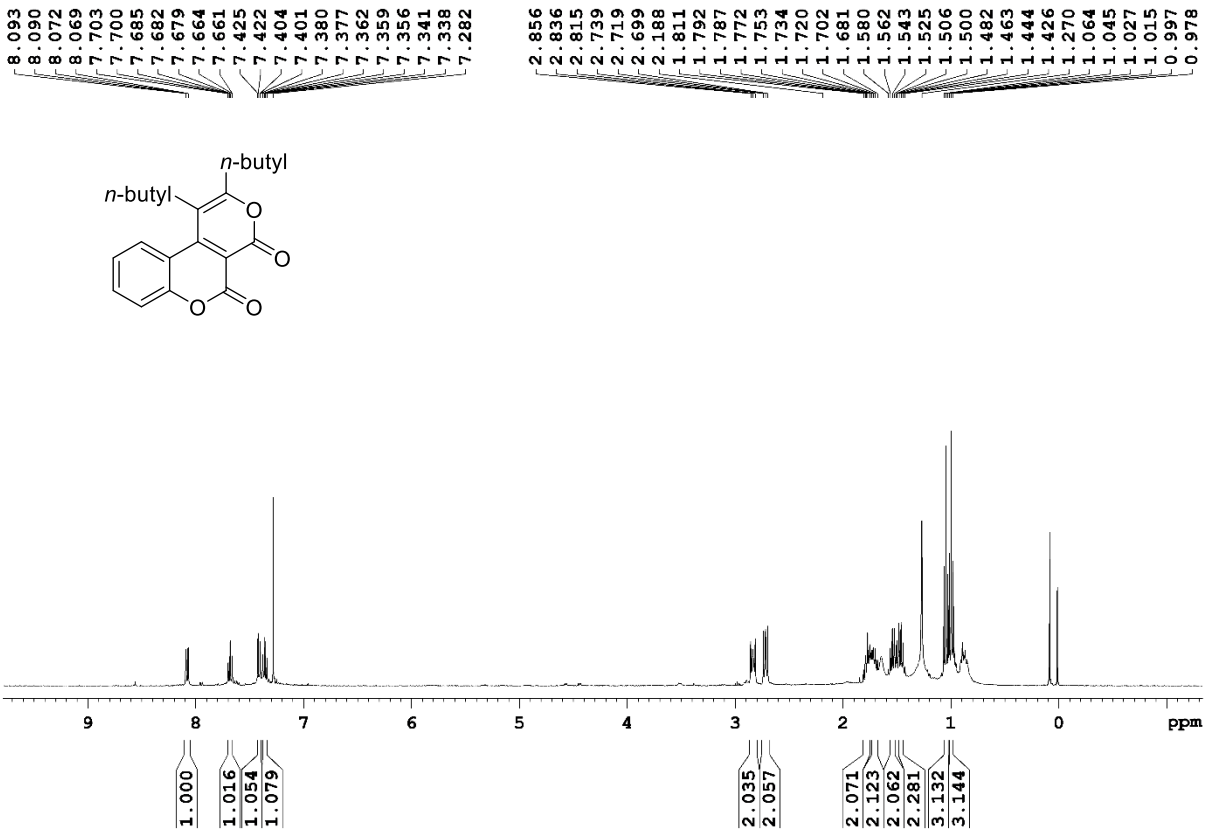


Figure S84. ^{1}H NMR spectrum of compound **7aj**

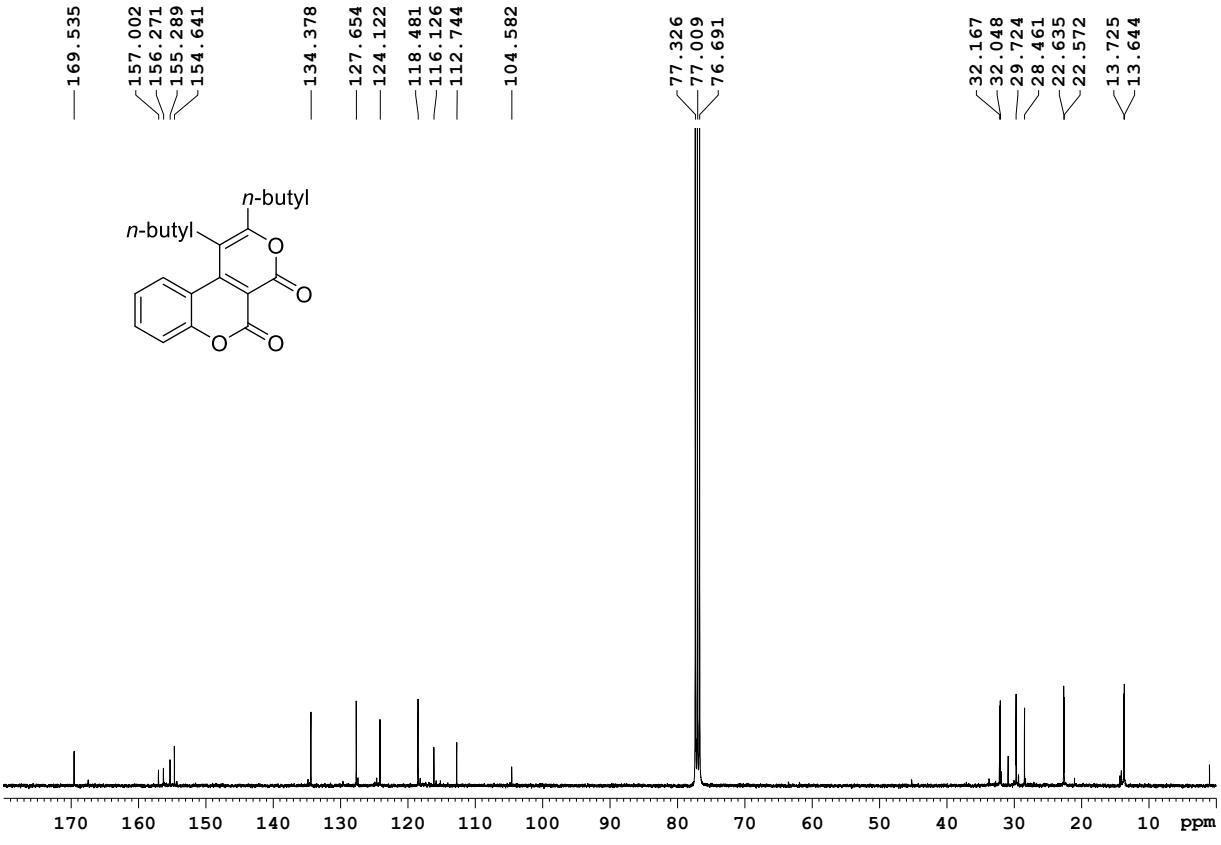


Figure S85. ^{13}C{^{1}H} NMR spectrum of compound **7aj**

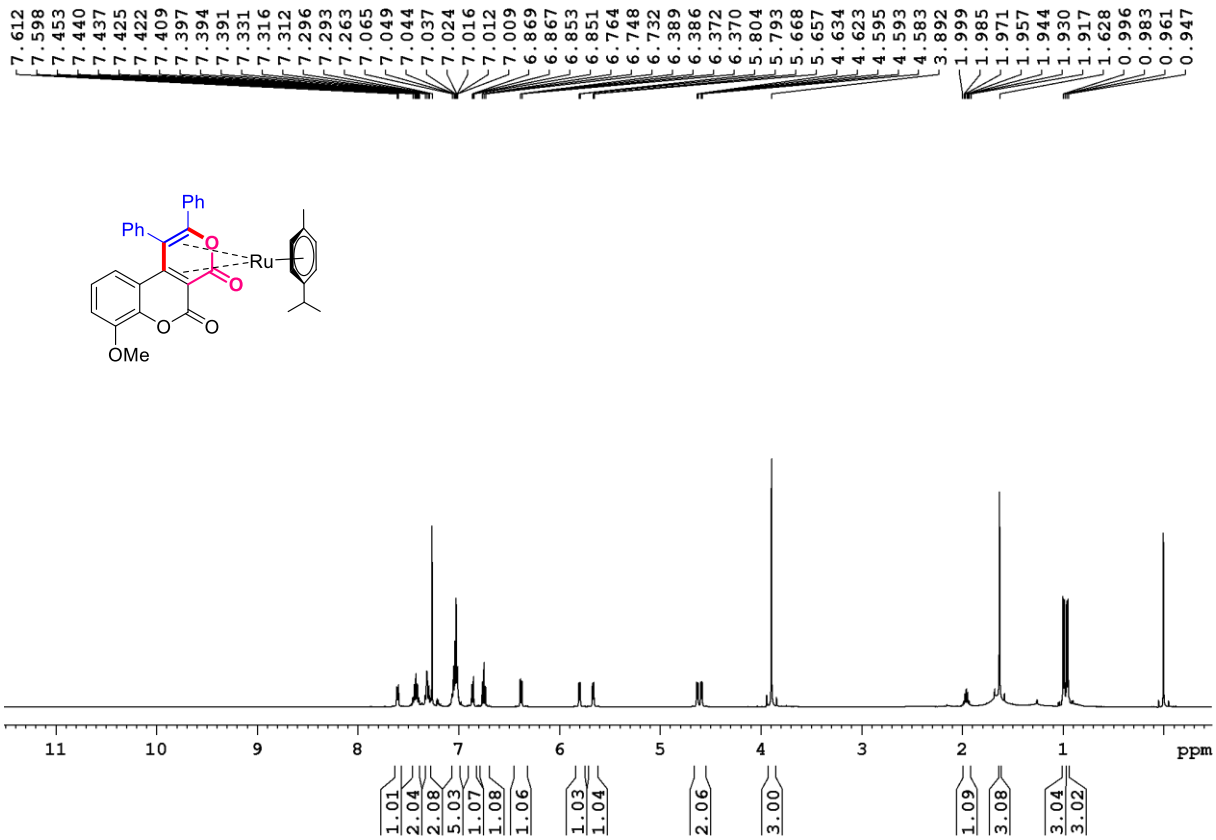


Figure S86. ^{1}H NMR spectrum of compound **7'ba**

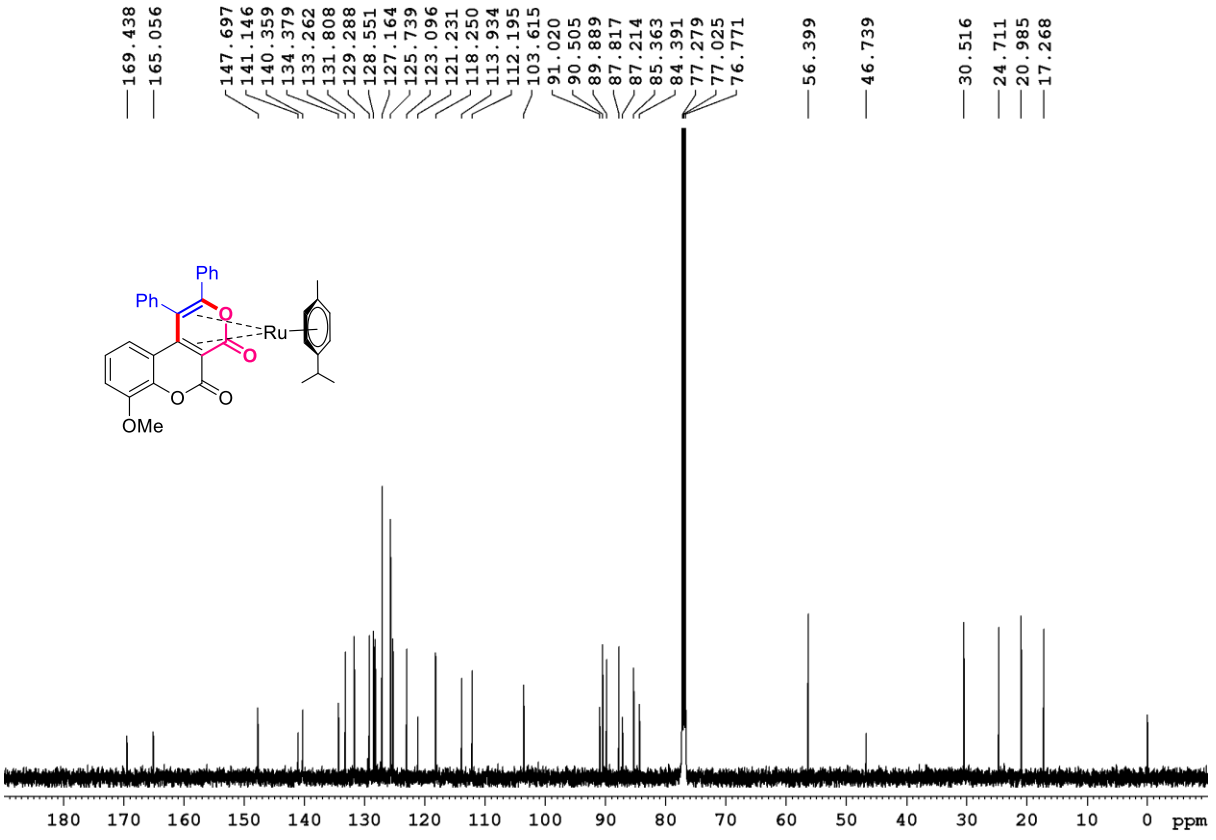


Figure S87. ^{13}C{^{1}H} NMR spectrum of compound **7'ba**

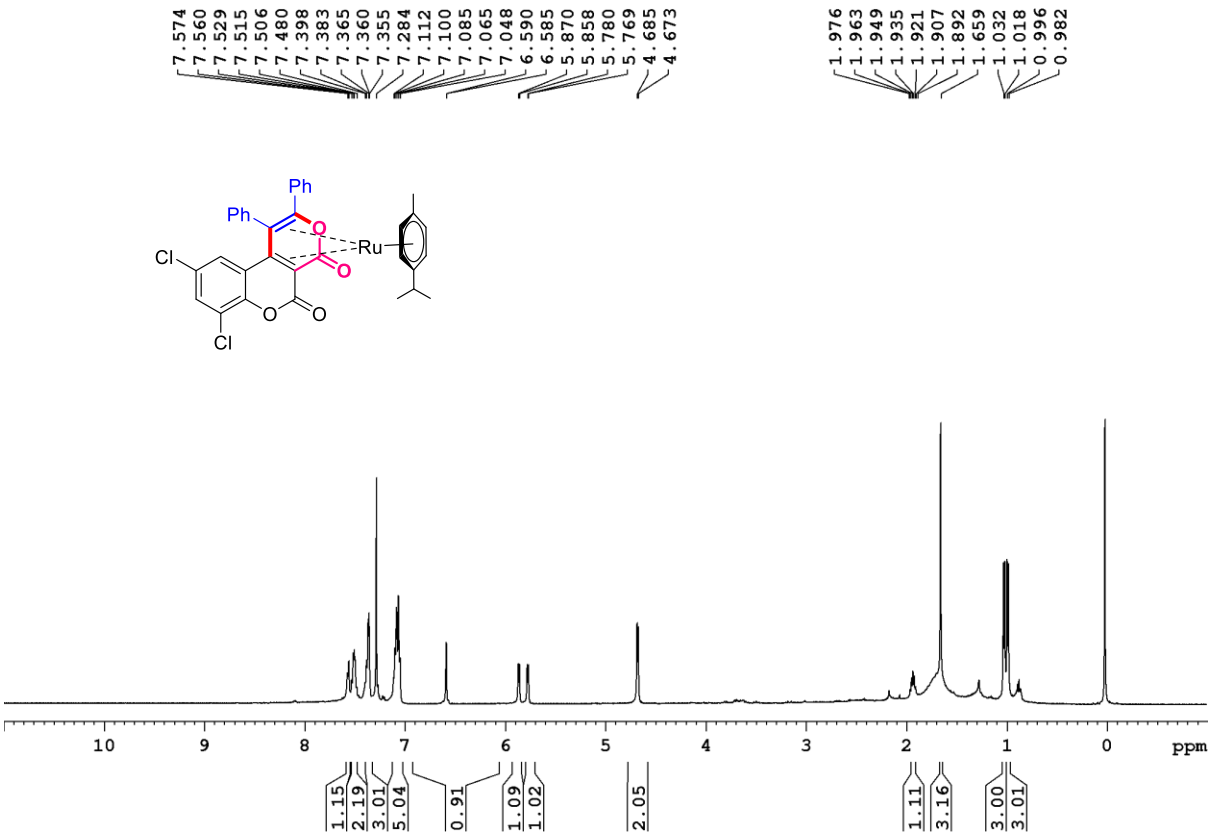


Figure S88. ^{1}H NMR spectrum of compound **7'ca**

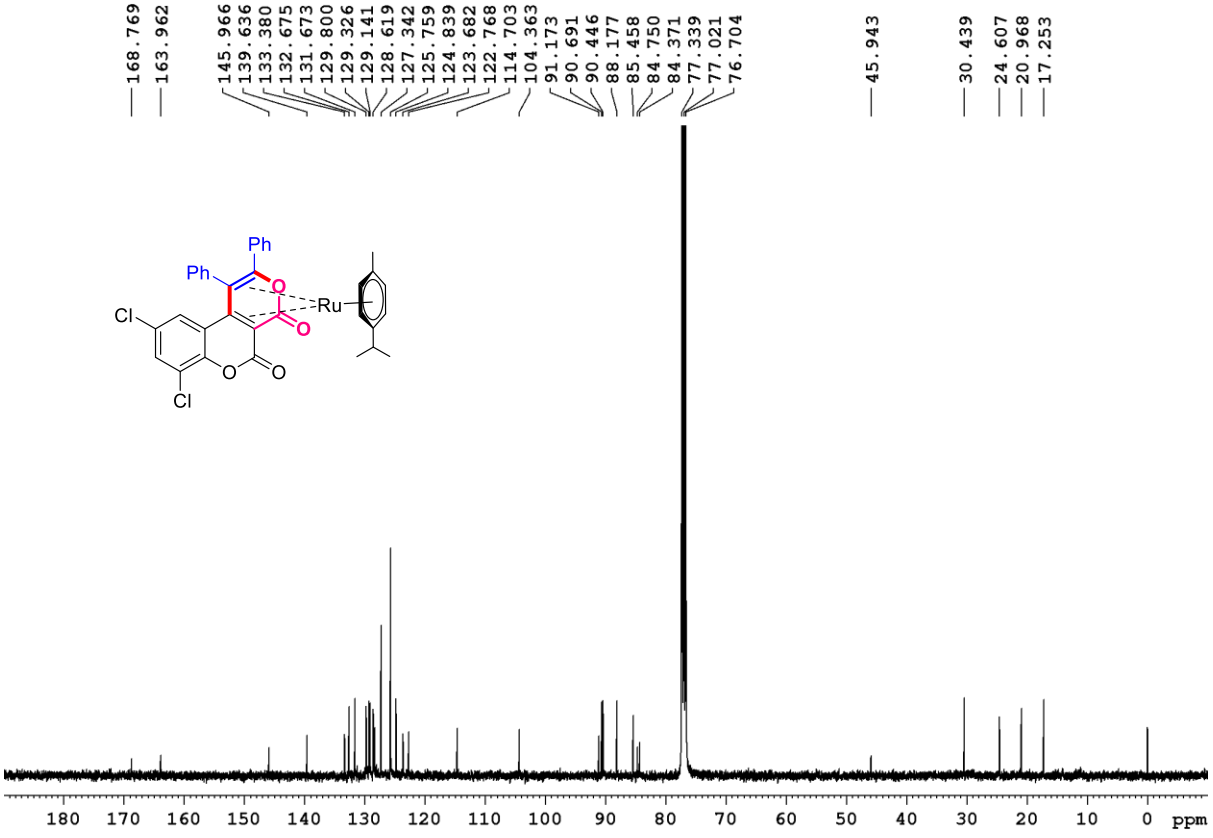


Figure S89. ^{13}C{^{1}H} NMR spectrum of compound **7'ca**

REFERENCE

(1) (a) Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption Correction*, University of Gottingen, Germany, **1996**. (b) Sheldrick, G. M. SHELX-97-*A program for crystal structure solution and refinement*, University of Gottingen, **1997**. (c) Sheldrick, G. M. *SHELXTL NT Crystal Structure Analysis Package*, Bruker AXS, Analytical X-ray System, WI, USA, **1999**, version 5.10].