Electronic Supplementary Information

(3 + 3) Annulation of acetoxy allenoates with with enolisable carbonyl substrates leading to fused pyrans

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(1) X-ray data collection, solution, refinement and the ORTEPs/Crystal Data of 3ah, 4an, 6aa and 8al

X-ray data collection, solution, refinement and the ORTEPs/crystal data: Single crystal X-ray data for crystals of compounds **3ah, 4an, 6aa** and **8al** were collected on an X-ray diffractometer using Mo-K_α (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 S34 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. The solvent/s of crystallization for all the products was ethyl acetate-hexane (ca 4:1 v/v). CCDC numbers are 2257153-2257156.

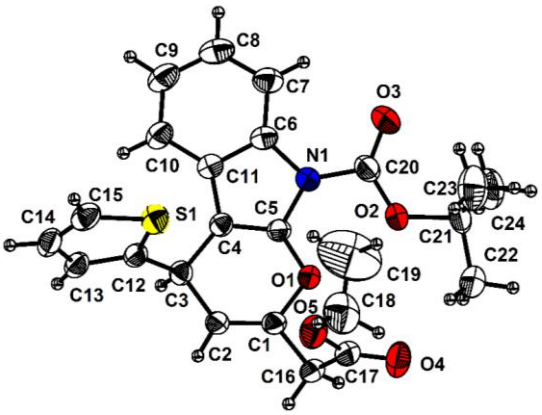

Figure S1. ORTEP view of **3ah** with 30% probability of ellipsoids. ***Crystal data:*** $C_{24}H_{25}NO_5S$, M = 439.51, Triclinic, Space group *P-1*, a = 10.3479(3), b = 10.5057(3), c = 11.7663(3) Å, α = 93.409(2), β = 114.609(3), γ = 95.175(2)^o, V = 1151.55(6) Å^3, Z = 2, μ = 0.175 mm^{-1}, data/restraints/parameters: 4815/0/284, R indices (I> 2sigma(I)): R1 = 0.0656, wR2 (all data) = 0.2083. CCDC No: 2257153.

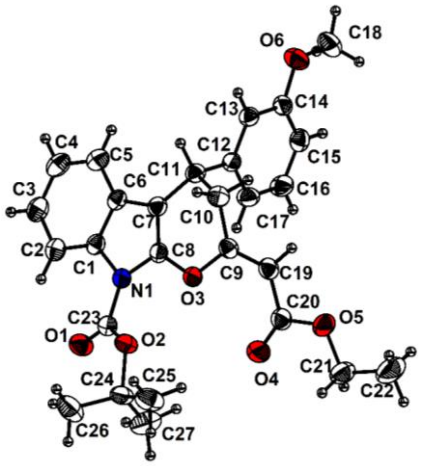

Figure S2. ORTEP view of **4an** with 30% probability of ellipsoids. ***Crystal data:*** $C_{27}H_{29}NO_6$, M = 463.51, Monoclinic, Space group *P 21/c*, a = 11.7617(4), b = 21.8252(8), c = 9.9033(3) Å, α = 90, β = 107.445(4), γ = 90°, V = 2425.26(15) Å^3, Z = 4, μ = 0.090 mm^{-1}, data/restraints/parameters: 5137/0/312, R indices (I> 2sigma(I)): R1 = 0.0546, wR2 (all data) = 0.1573. CCDC No: 2257154.

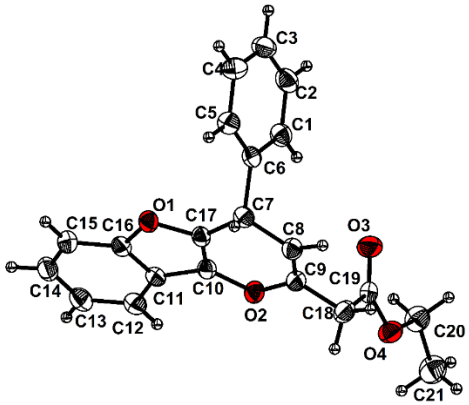

Figure S3. ORTEP view of **6aa** with 30% probability of ellipsoids. ***Crystal data:*** $C_{21}H_{18}O_4$, M = 334.35, Triclinic, Space group *P-1*, a = 8.2390(2), b = 8.5305(2), c = 12.8575(3) Å, α = 72.914(2), β = 83.275(2), γ = 75.314(2)°, V = 834.67(4) Å^3, Z = 2, μ = 0.092 mm^{-1}, data/restraints/parameters: 3575/0/227, R indices (I> 2sigma(I)): R1 = 0.0416, wR2 (all data) = 0.1170. CCDC No: 2257155.

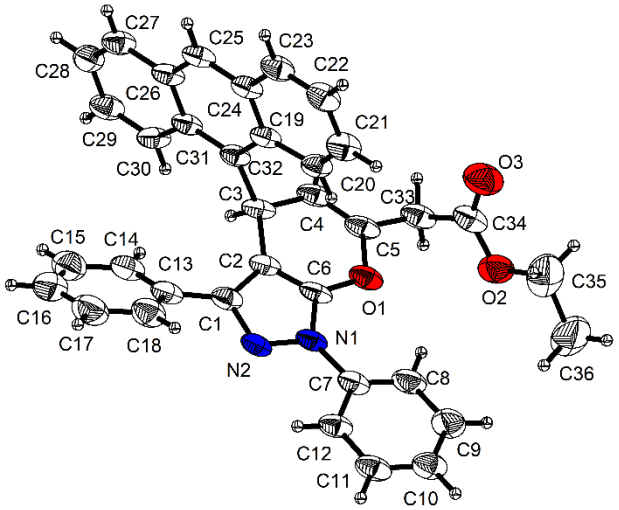

Figure S4. ORTEP view of **8al** with 30% probability of ellipsoids. ***Crystal data:*** $C_{36}H_{28}N_2O_3$, M = 536.60, Triclinic, Space group *P-1*, a = 10.5236(3), b = 11.4554(5), c = 12.9859(4) Å, α = 100.268(3), β = 113.577(3), γ = 98.024(3)^o, V = 1372.68(10) Å^3, Z = 2, μ = 0.083 mm^{-1}, data/restraints/parameters: 4864/0/371, R indices (I> 2sigma(I)): R1 = 0.1228, wR2 (all data) = 0.4444. CCDC No: 2257156. The crystal quality was poor and hence 'A' alerts' are there. However, the structure is clear.

^{1}H/ ^{13}C/ ^{19}F spectra

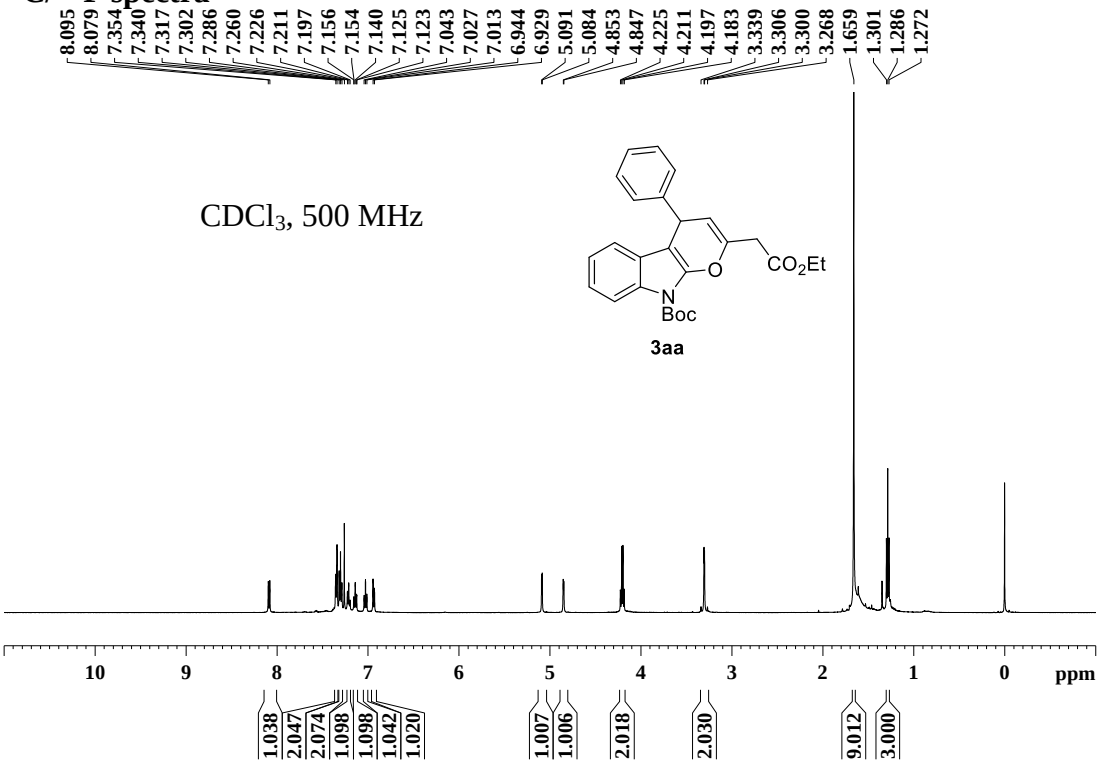

Figure S5: ^{1}H NMR spectrum of compound **3aa**

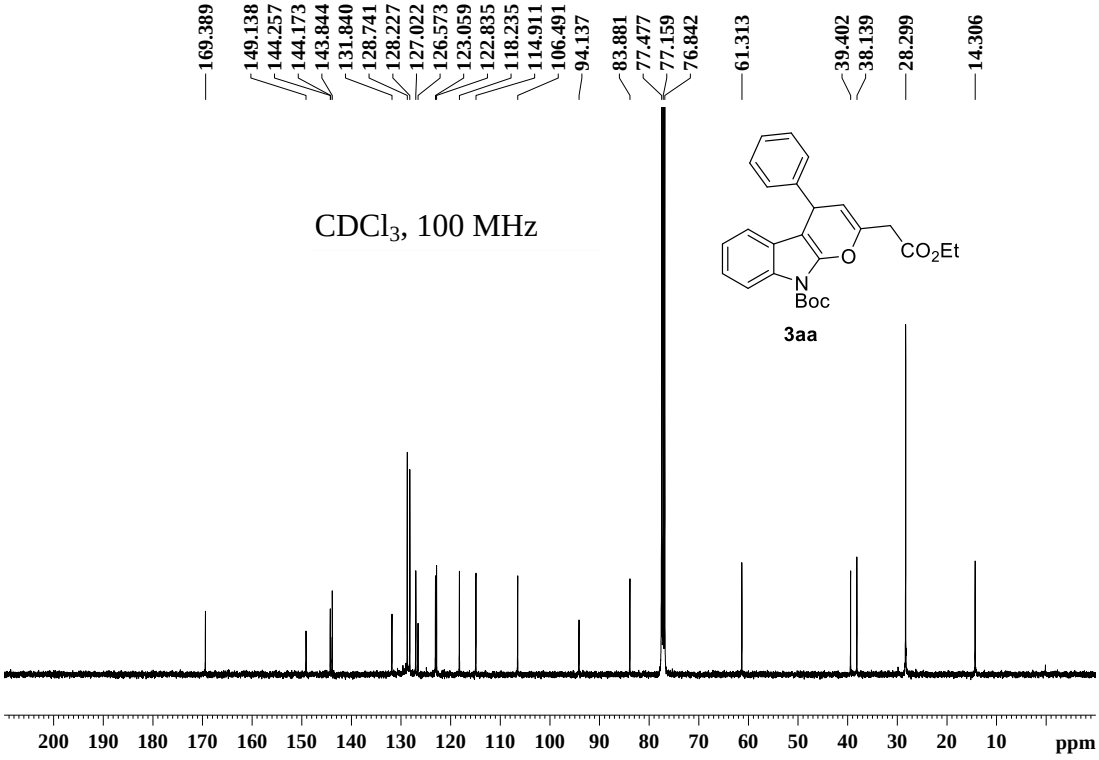

Figure S6: ^{13}C NMR spectrum of compound **3aa**

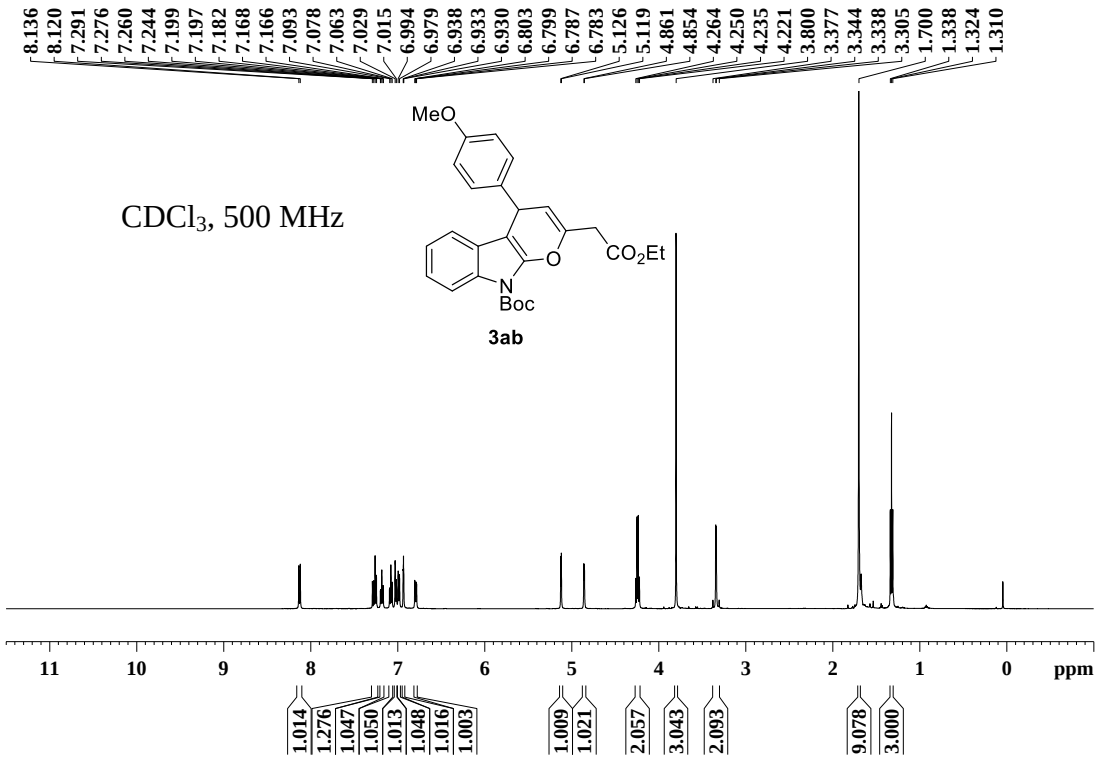

Figure S7: ^{1}H NMR spectrum of compound **3ab**

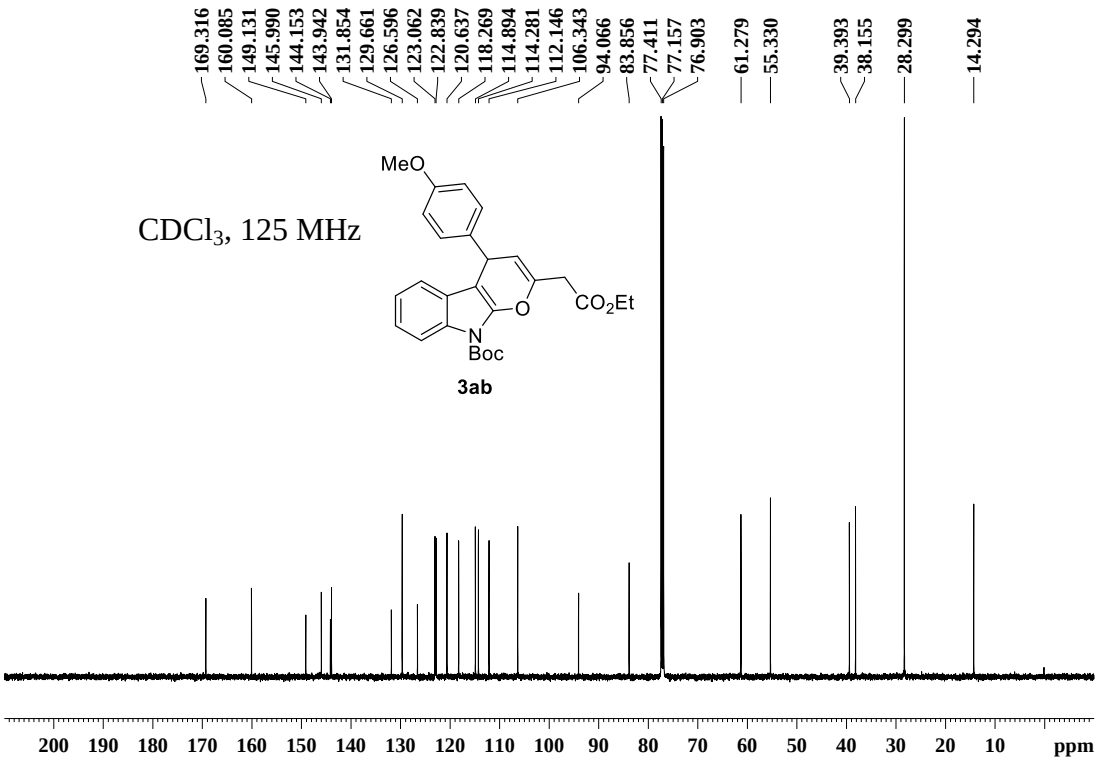

Figure S8: ^{13}C NMR spectrum of compound **3ab**

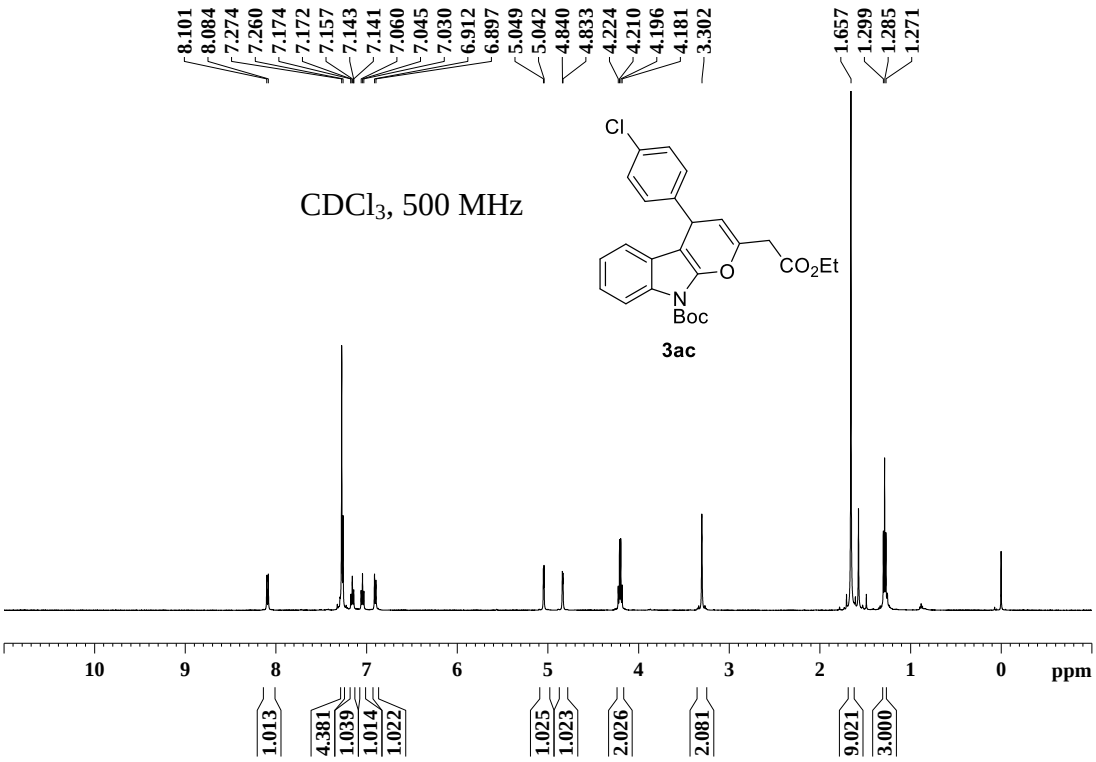

Figure S9: ^{1}H NMR spectrum of compound **3ac**

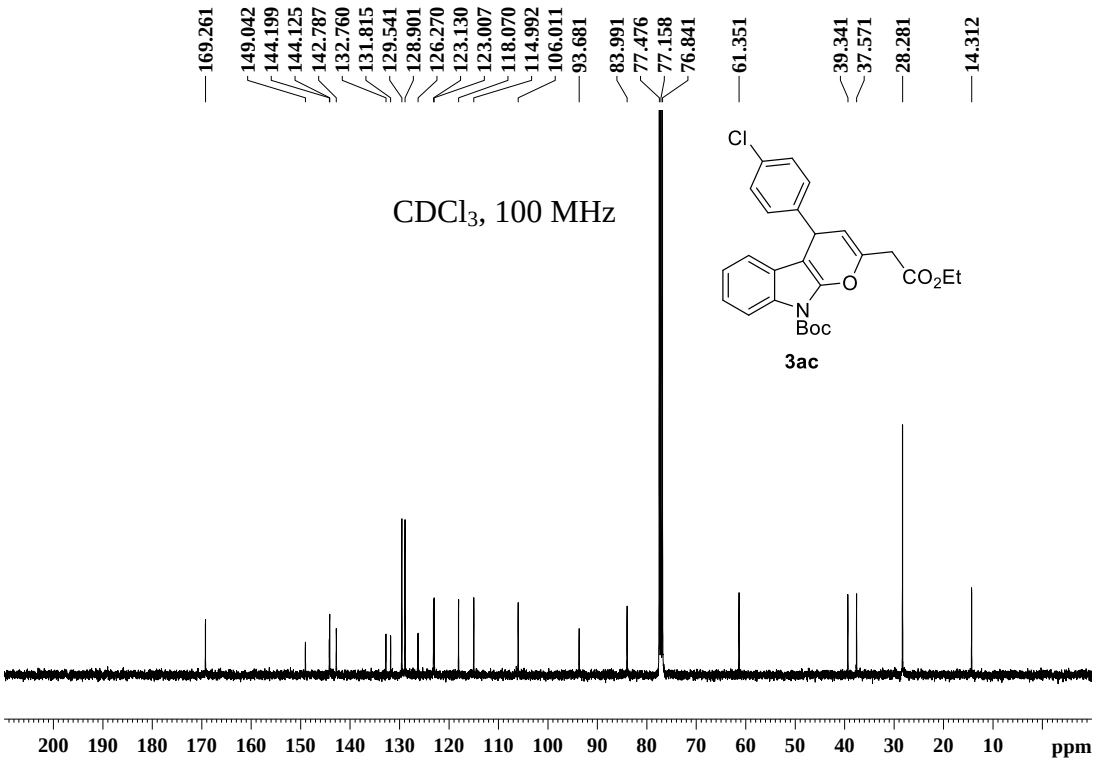

Figure S10: ^{13}C NMR spectrum of compound **3ac**

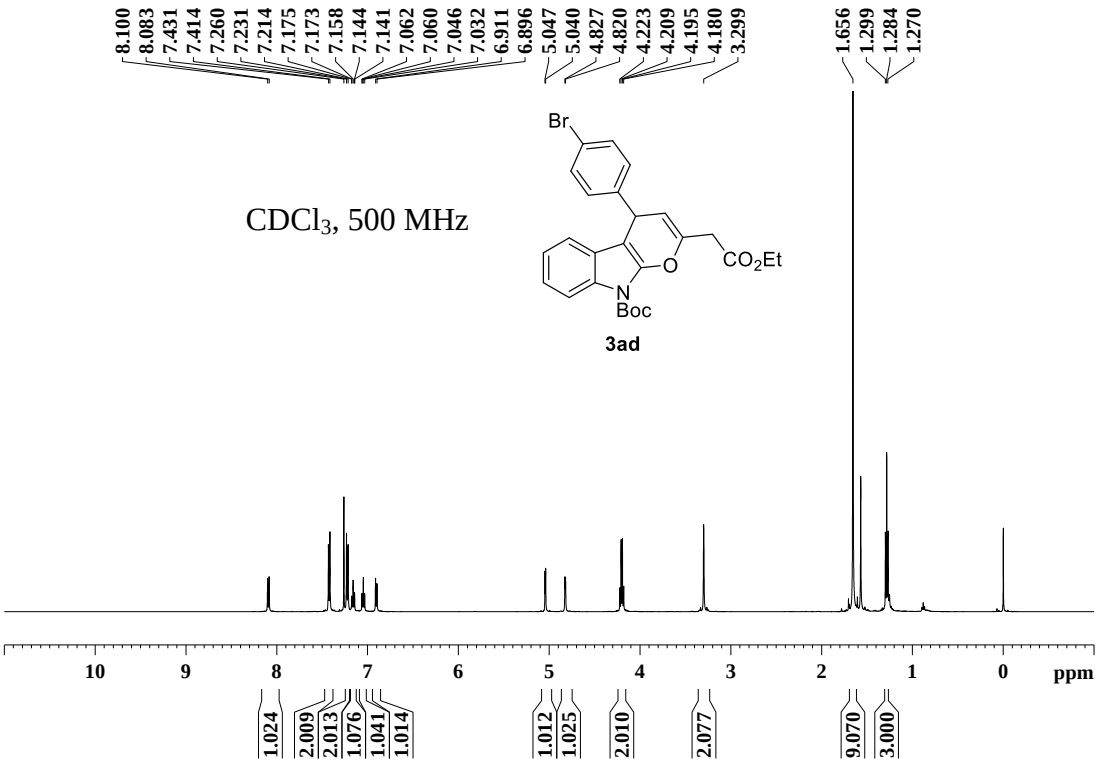

Figure S11: ^{1}H NMR spectrum of compound **3ad**

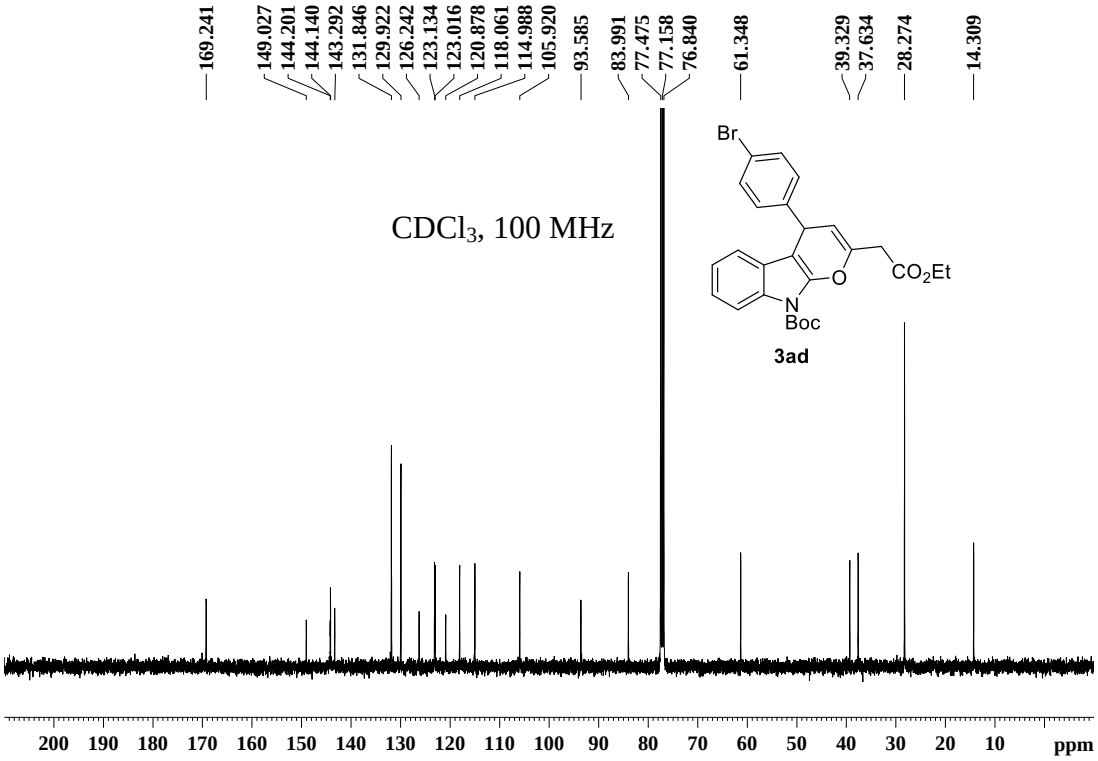

Figure S12: ^{13}C NMR spectrum of compound **3ad**

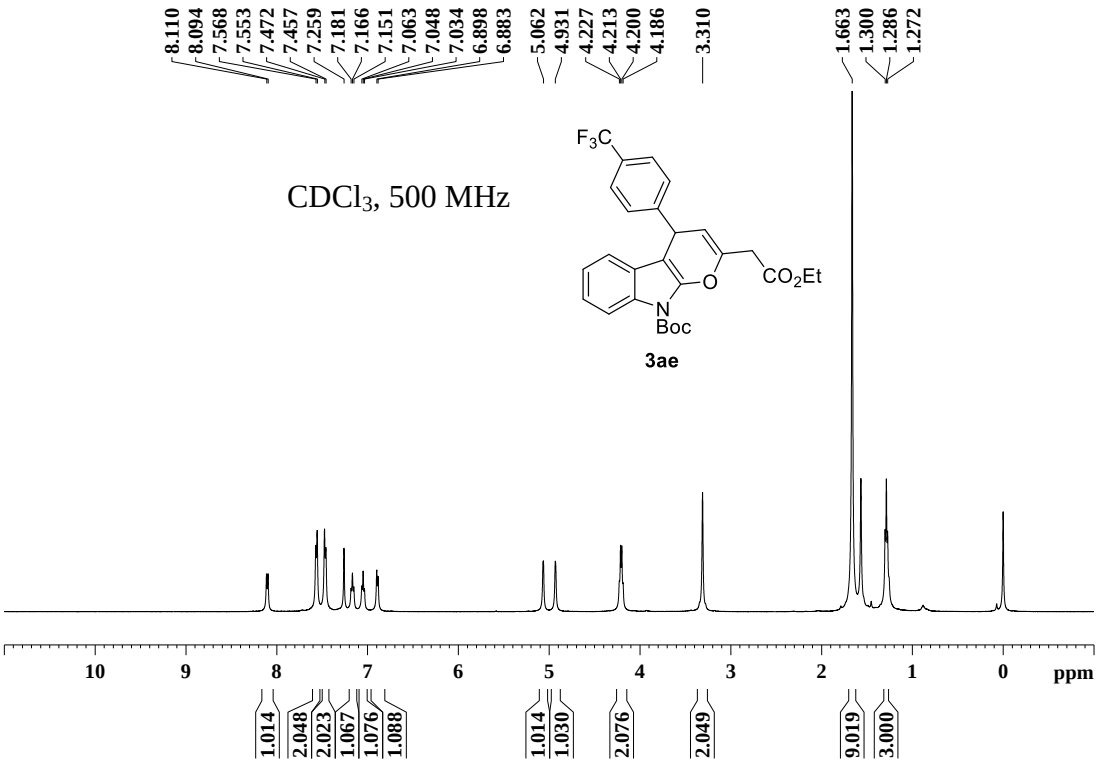

Figure S13: ^{1}H NMR spectrum of compound **3ae**

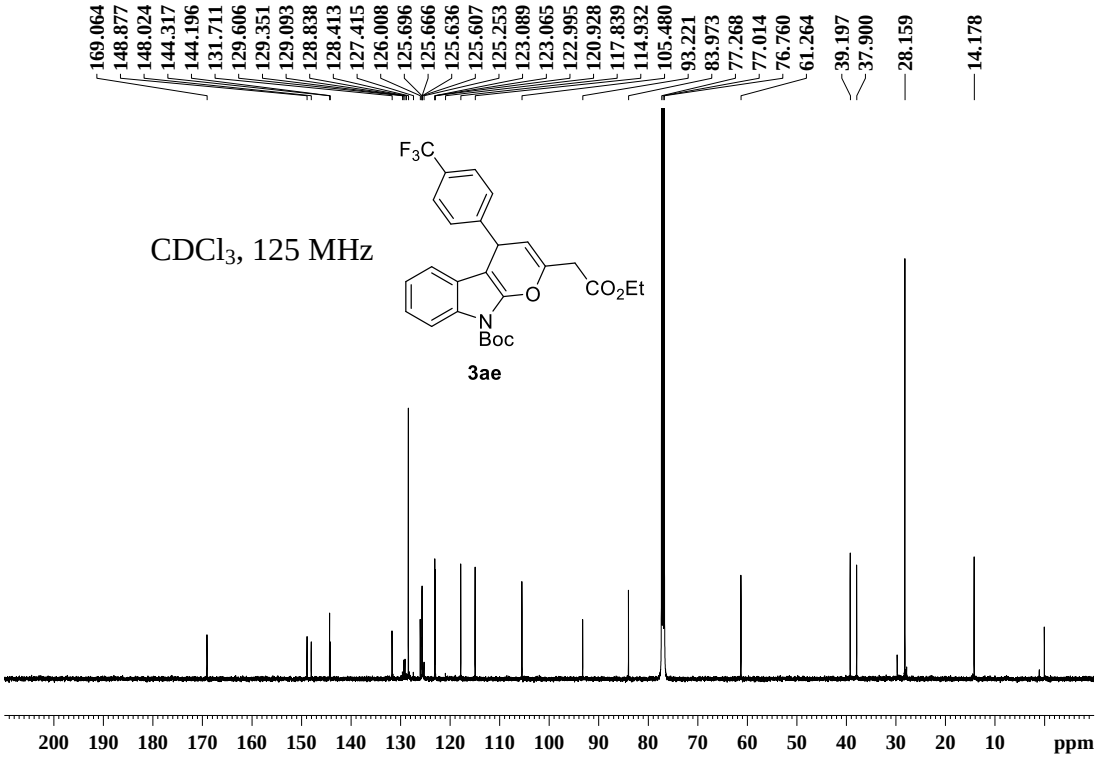

Figure S14: ^{13}C NMR spectrum of compound **3ae**

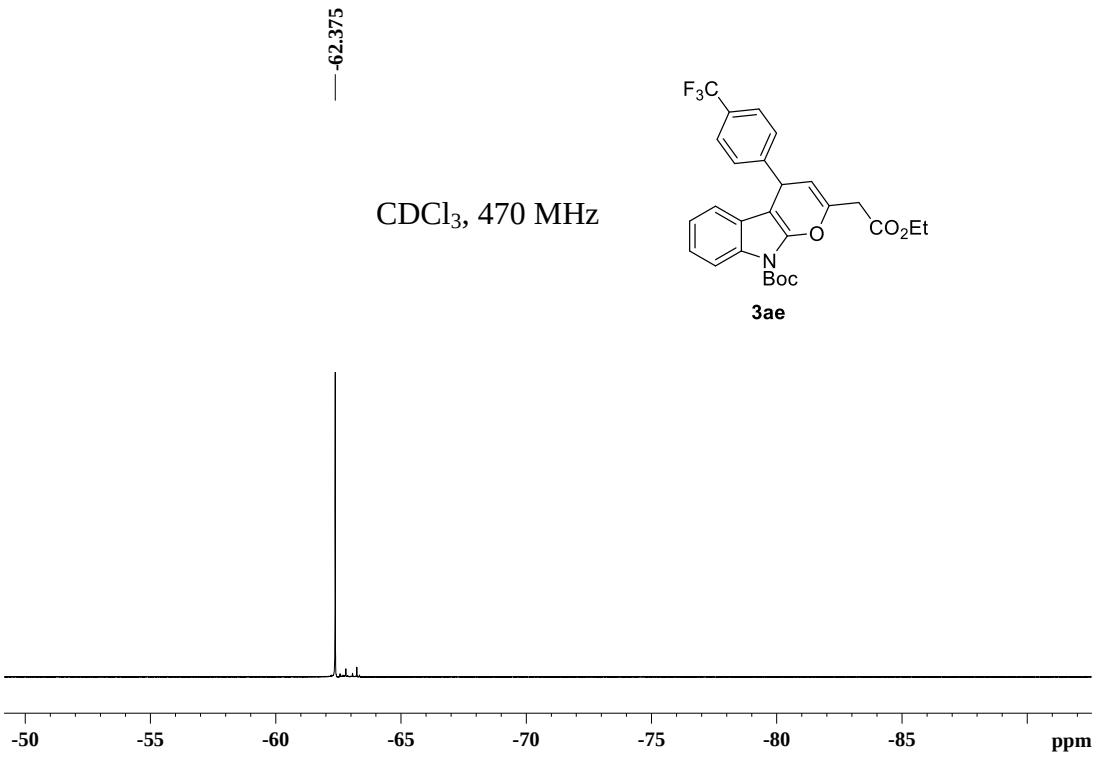

Figure S15: ^{19}F NMR spectrum of compound **3ae**

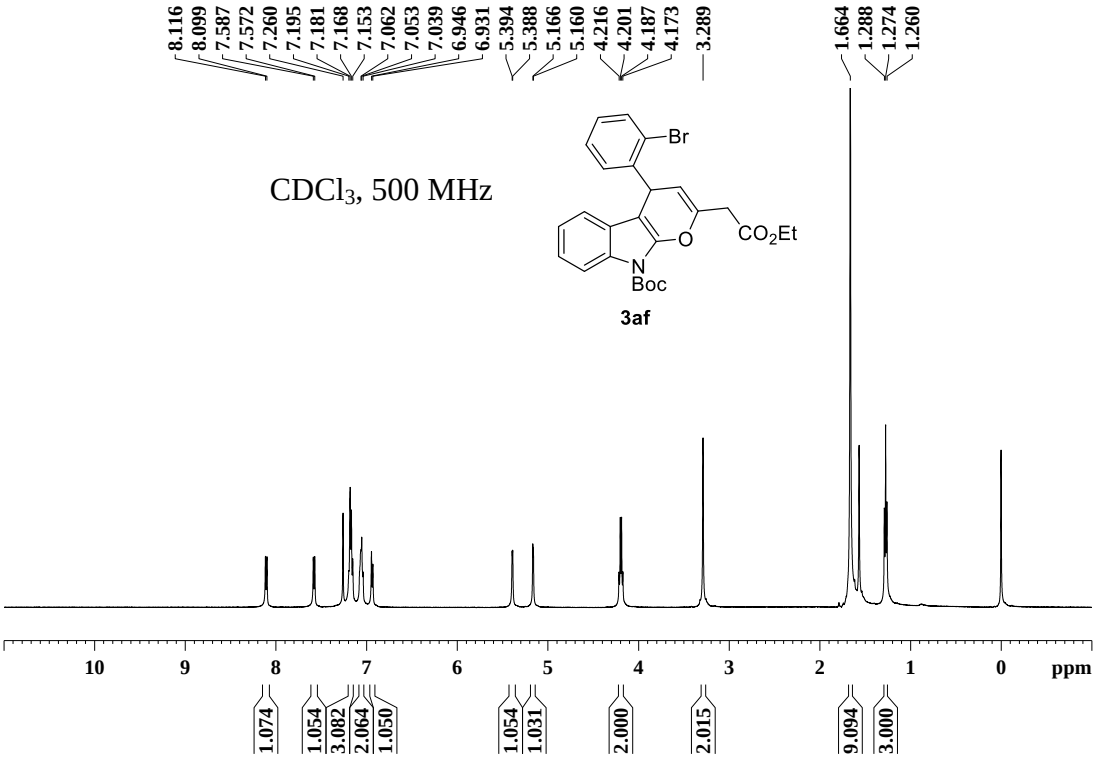

Figure S16: ^{1}H NMR spectrum of compound **3af**

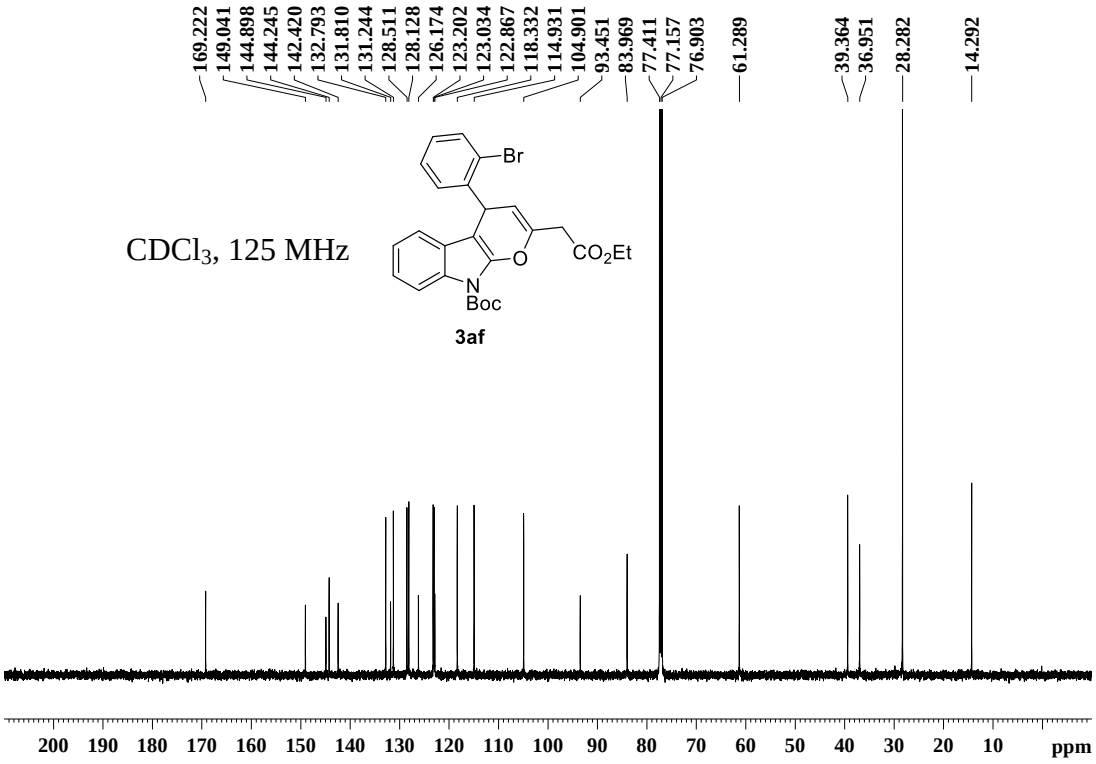

Figure S17: ^{13}C NMR spectrum of compound **3af**

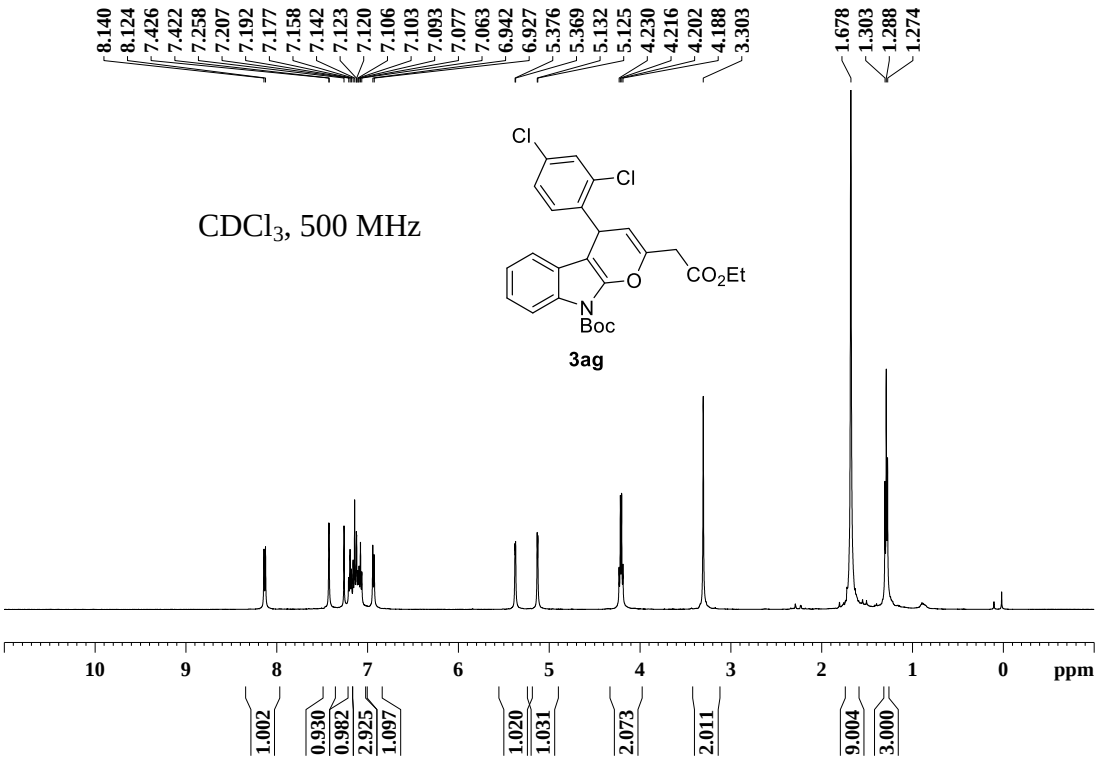

Figure S18: ^{1}H NMR spectrum of compound **3ag**

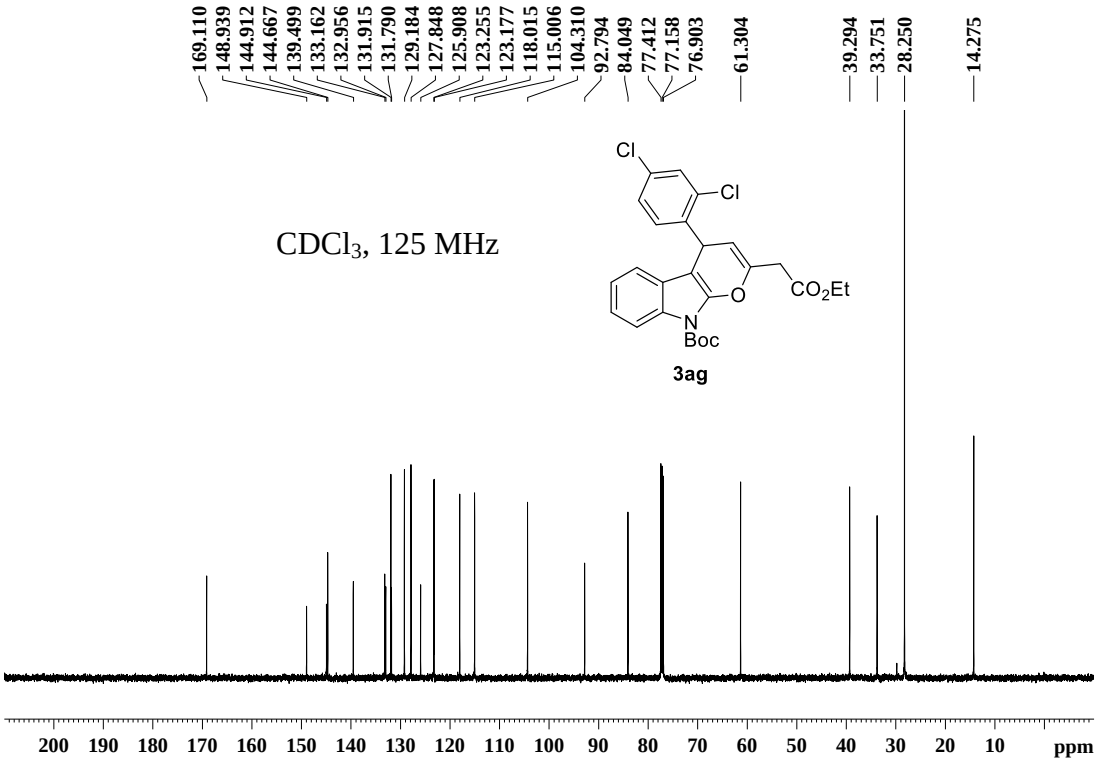

Figure S19: ^{13}C NMR spectrum of compound **3ag**

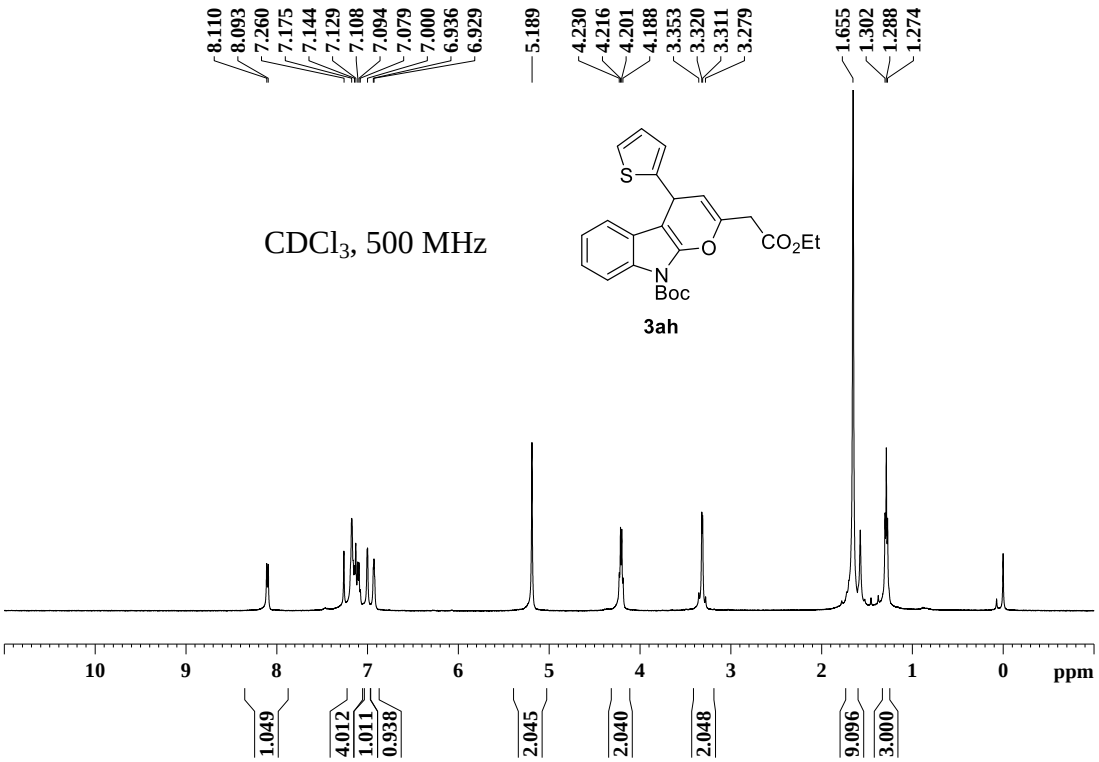

Figure S20: ^{1}H NMR spectrum of compound **3ah**

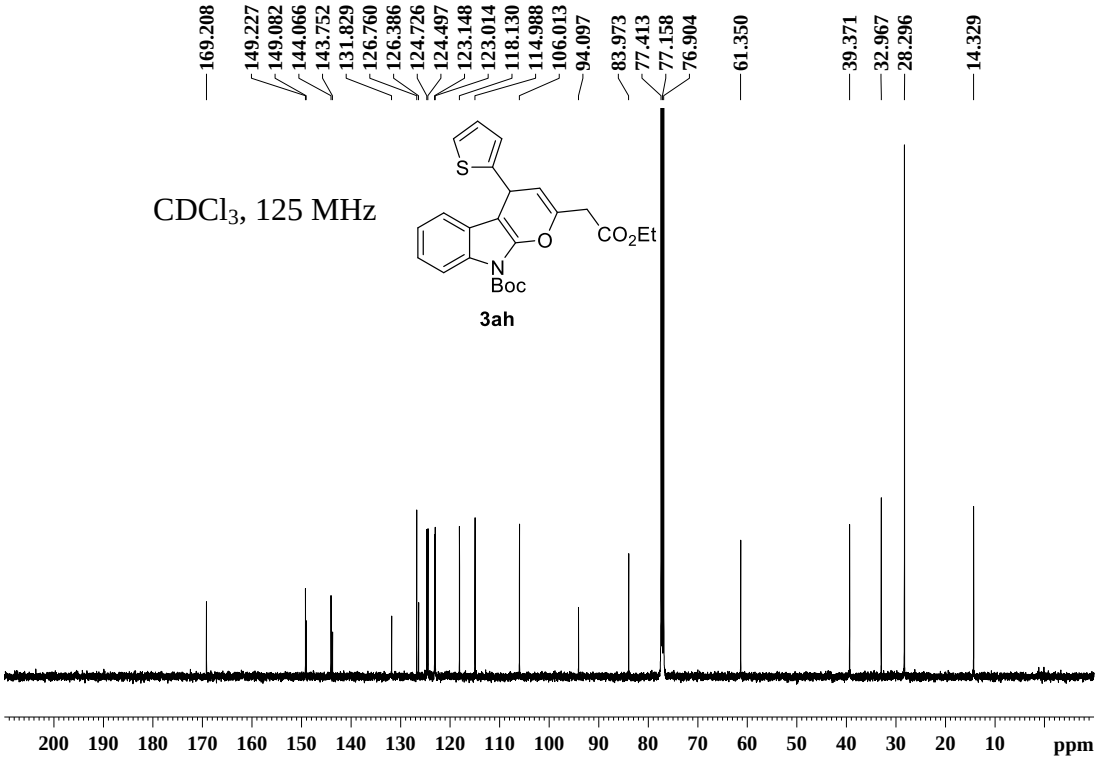

Figure S21: ^{13}C NMR spectrum of compound **3ah**

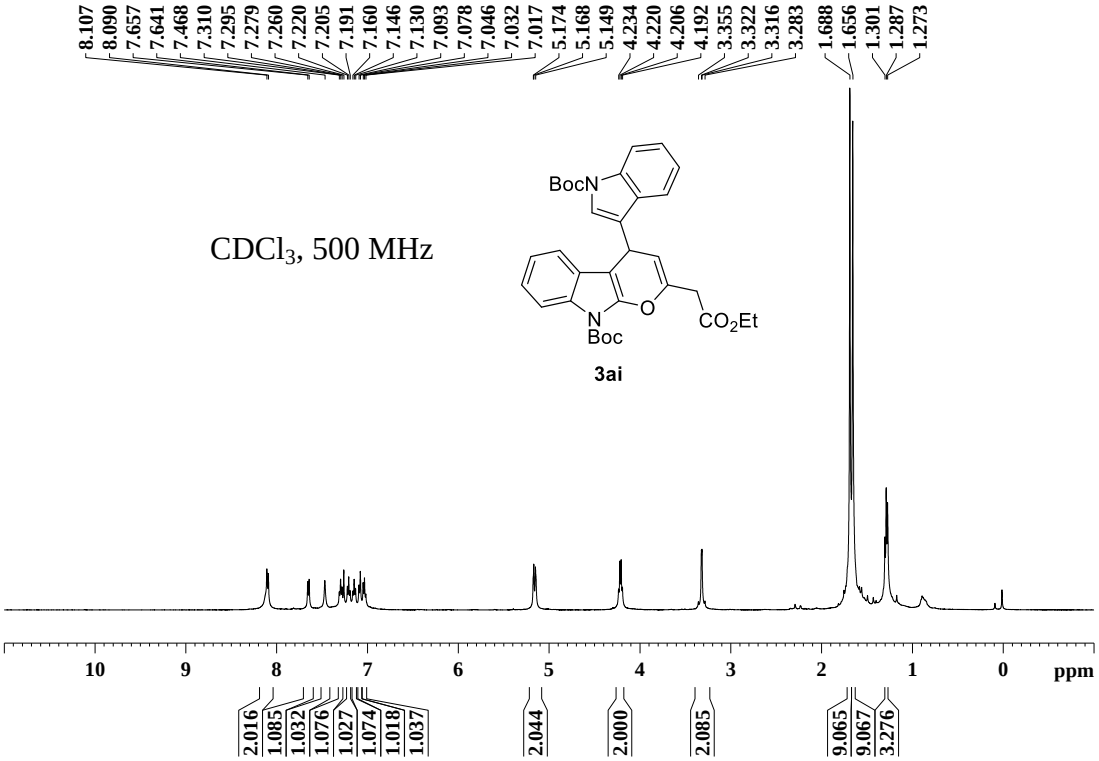

Figure S22: ^{1}H NMR spectrum of compound **3ai**

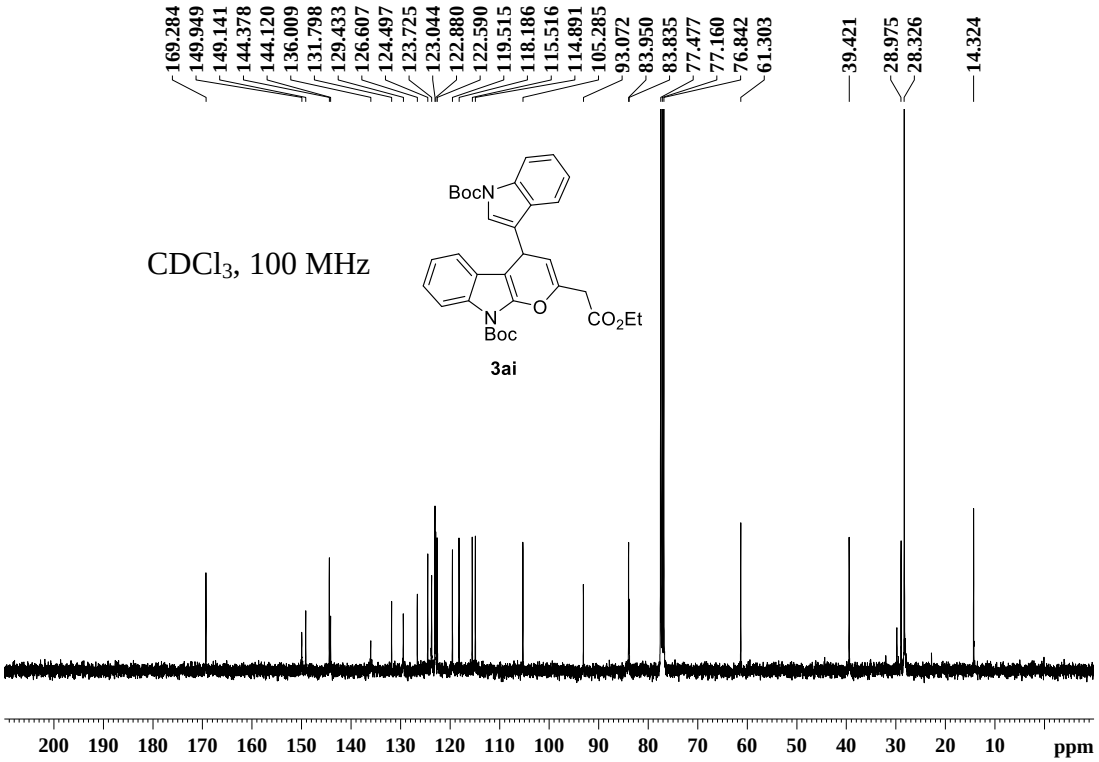

Figure S23: ^{13}C NMR spectrum of compound **3ai**

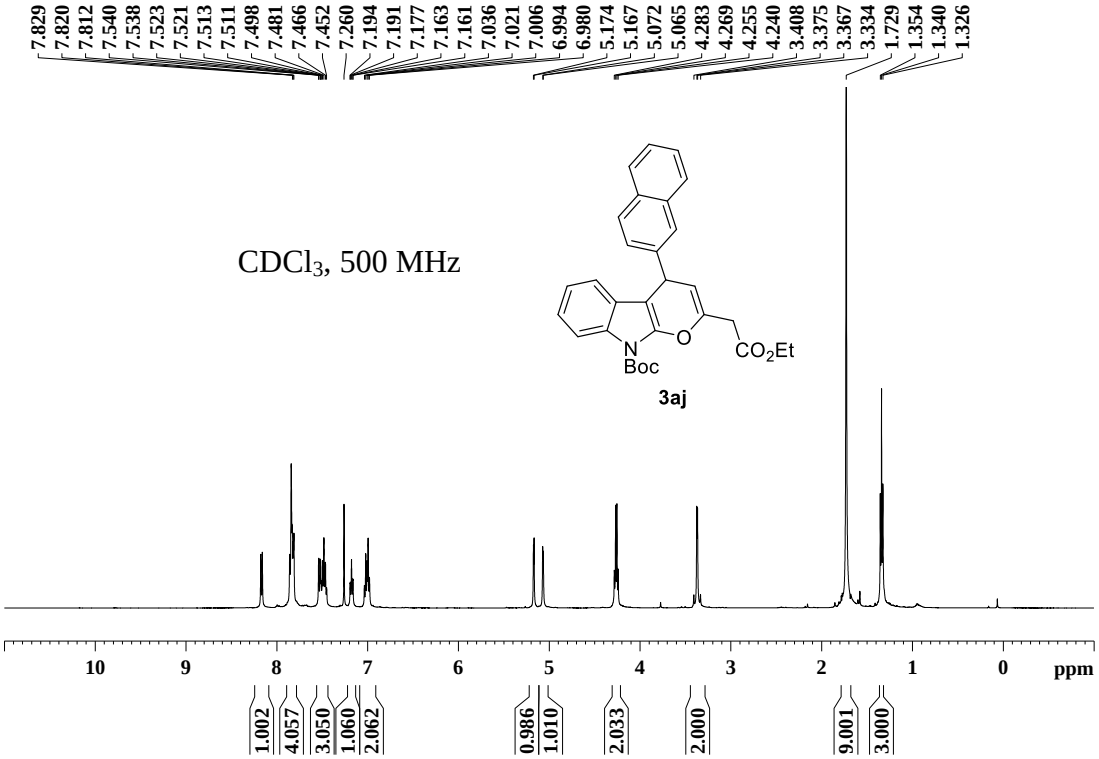

Figure S24: ^{1}H NMR spectrum of compound **3aj**

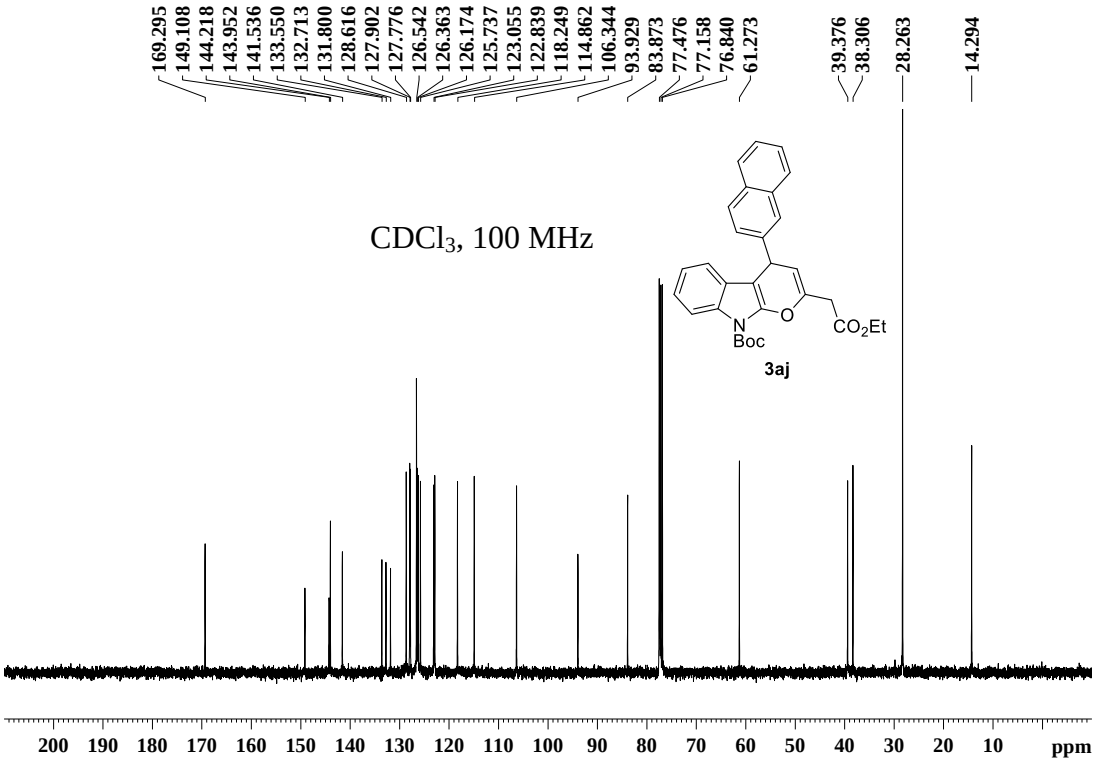

Figure S25: ^{13}C NMR spectrum of compound **3aj**

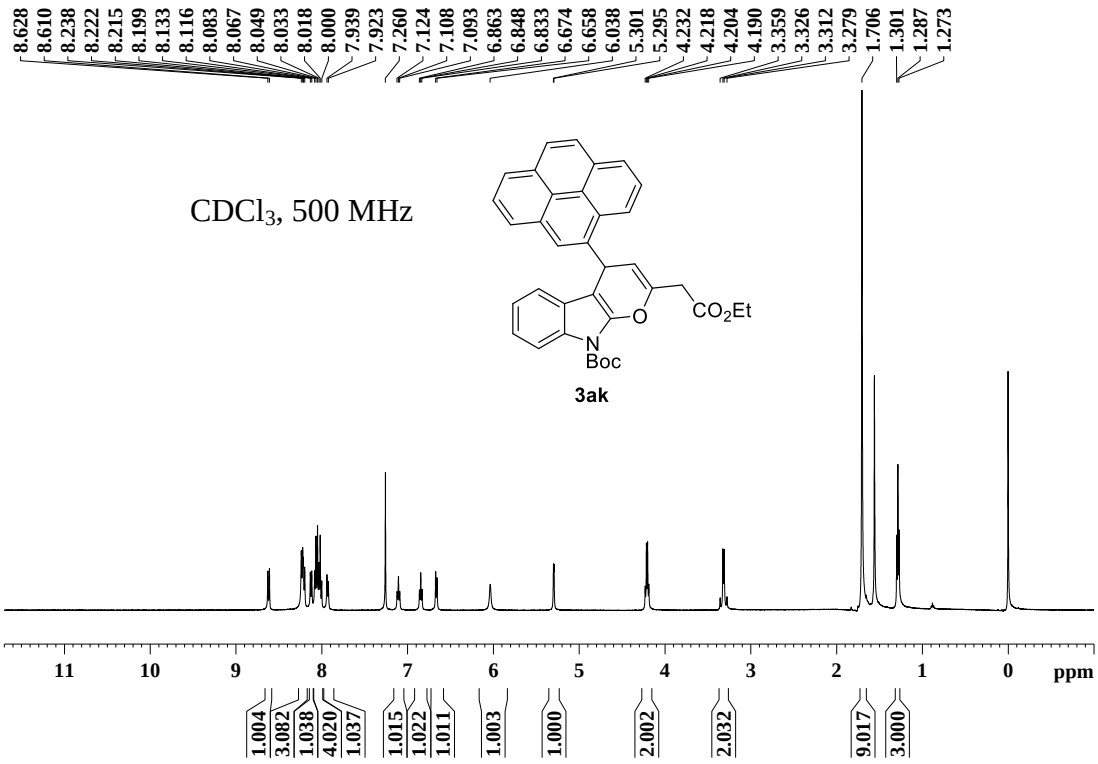

Figure S26: ^{1}H NMR spectrum of compound **3ak**

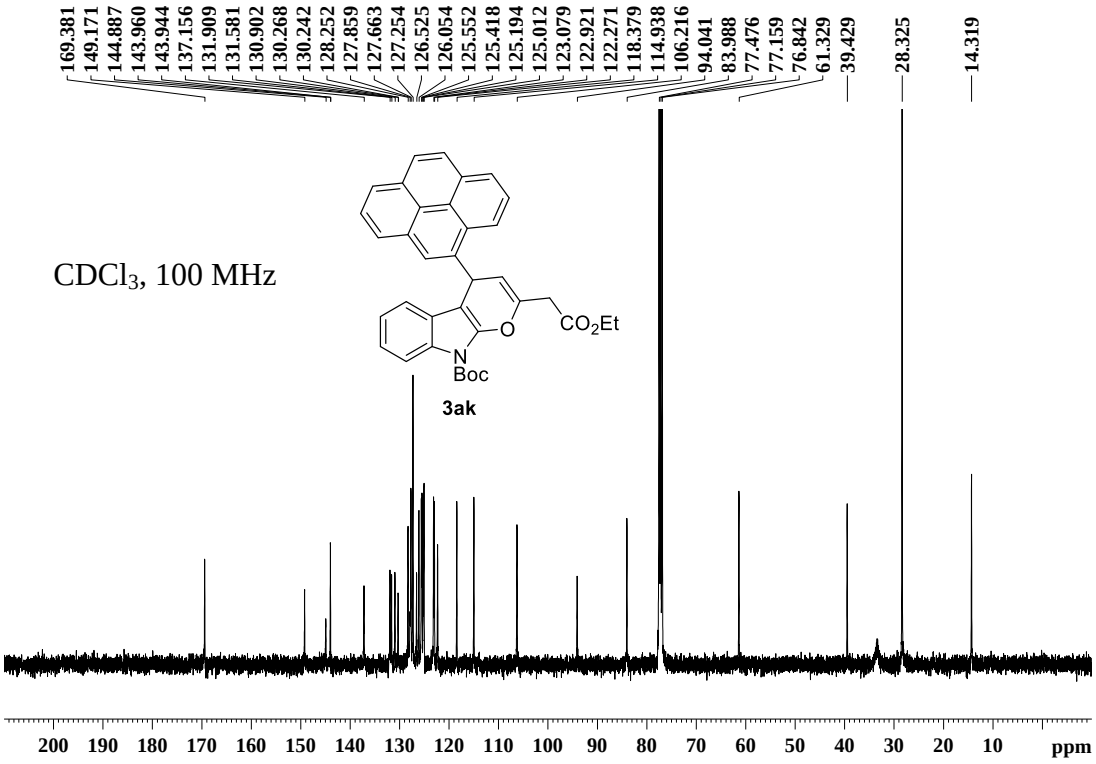

Figure S27: ^{13}C NMR spectrum of compound **3ak**

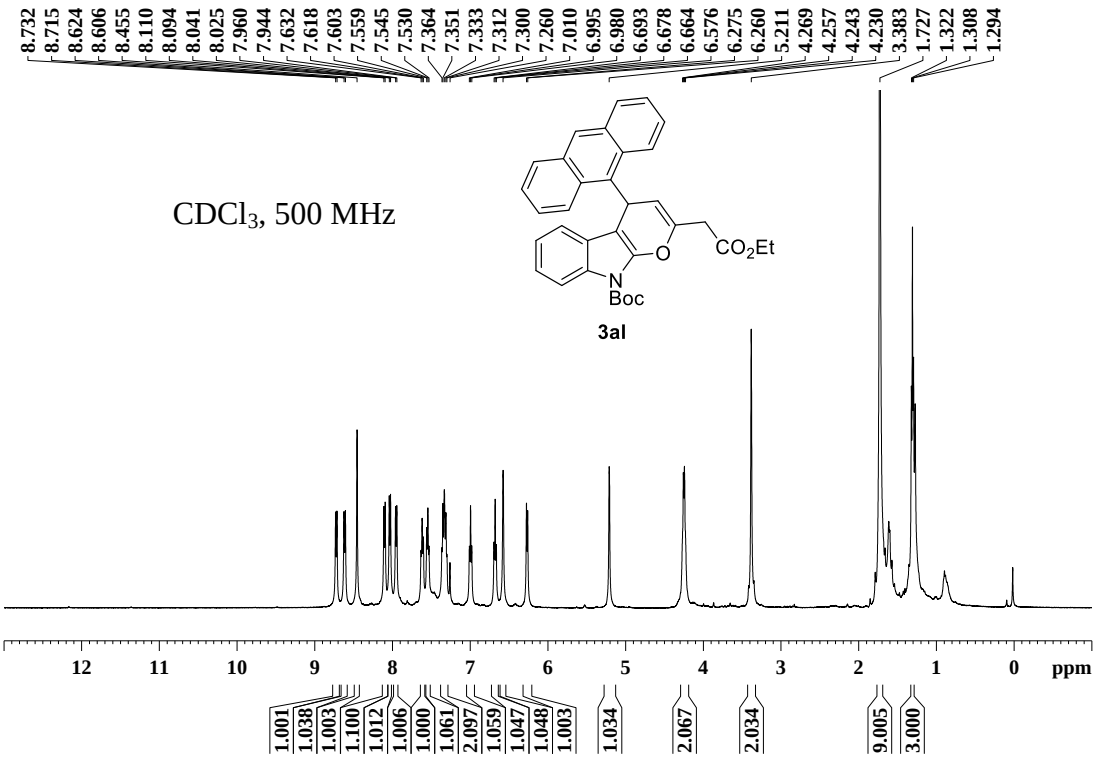

Figure S28: ^{1}H NMR spectrum of compound **3al**

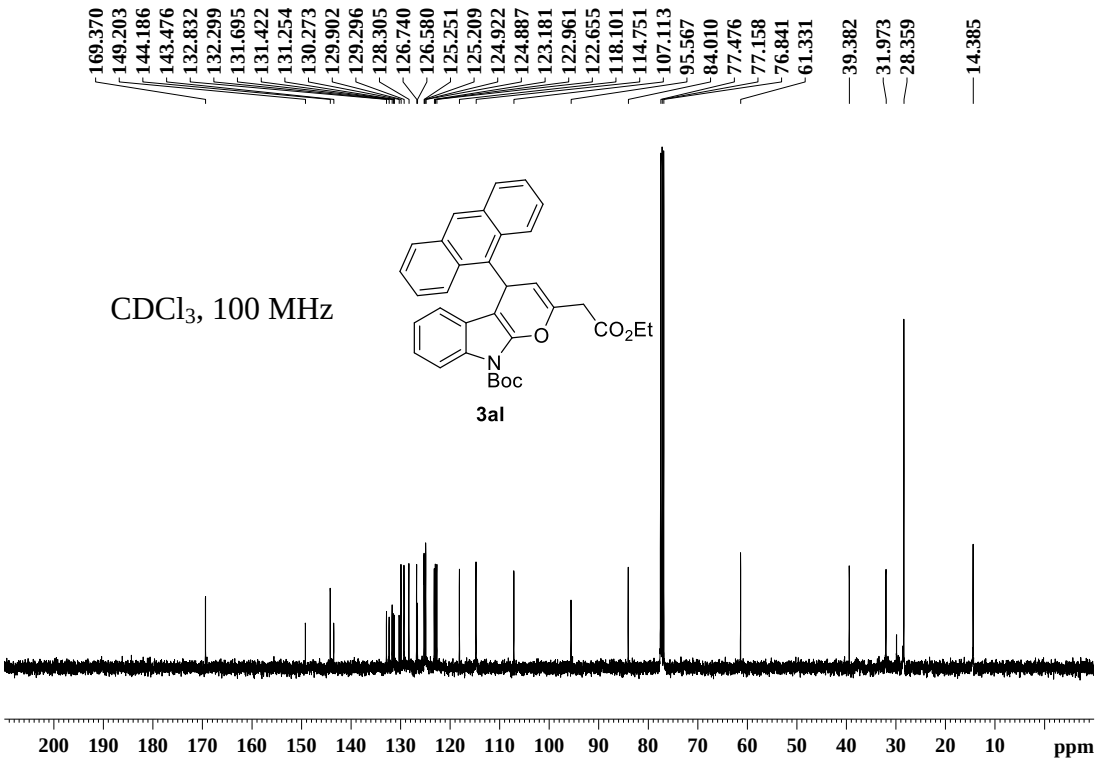

Figure S29: ^{13}C NMR spectrum of compound **3al**

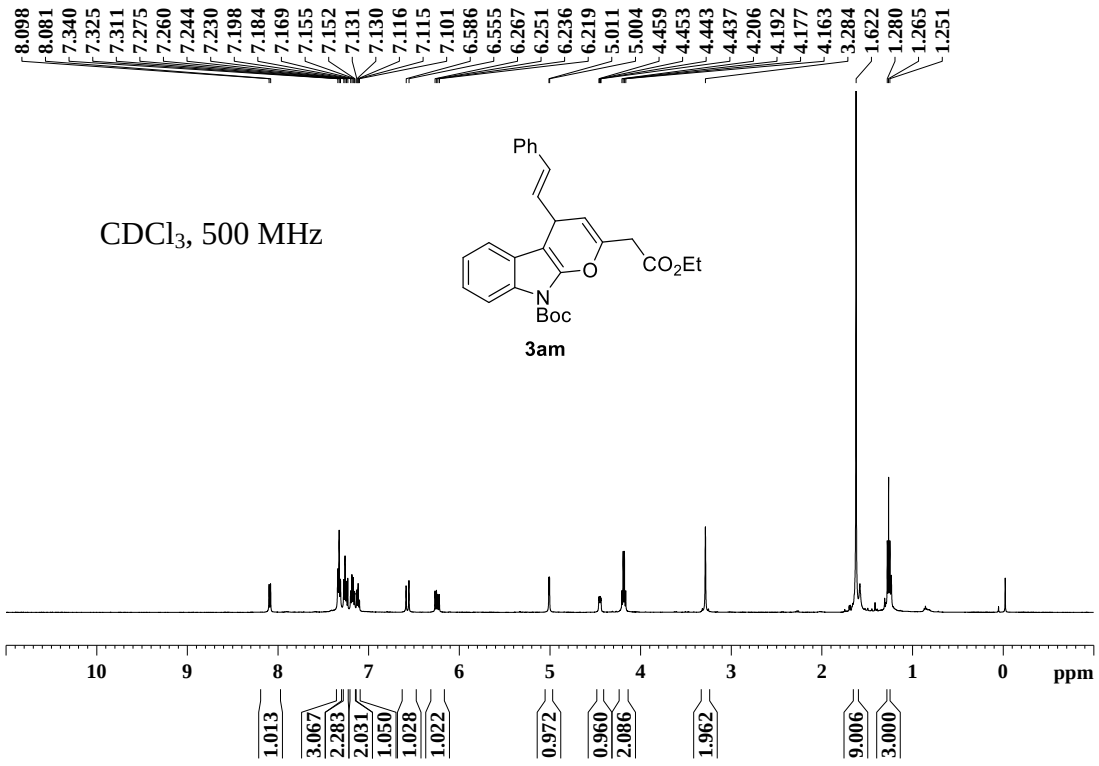

Figure S30: ^{1}H NMR spectrum of compound **3am**

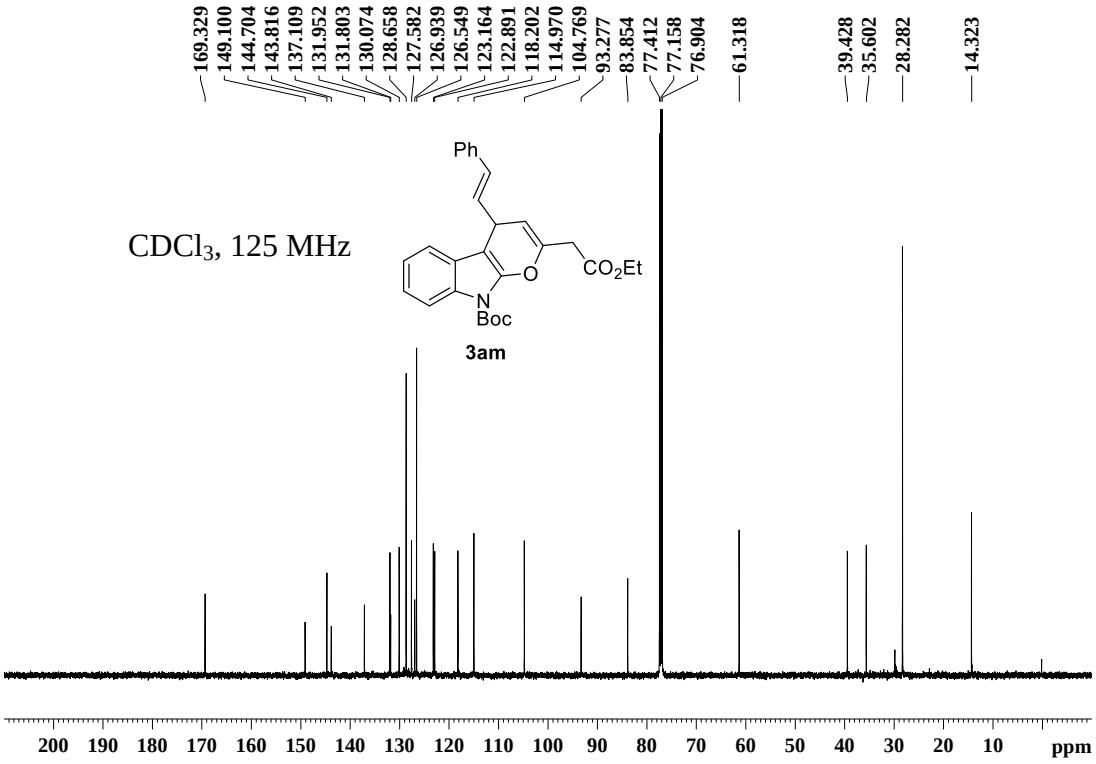

Figure S31: ^{13}C NMR spectrum of compound **3am**

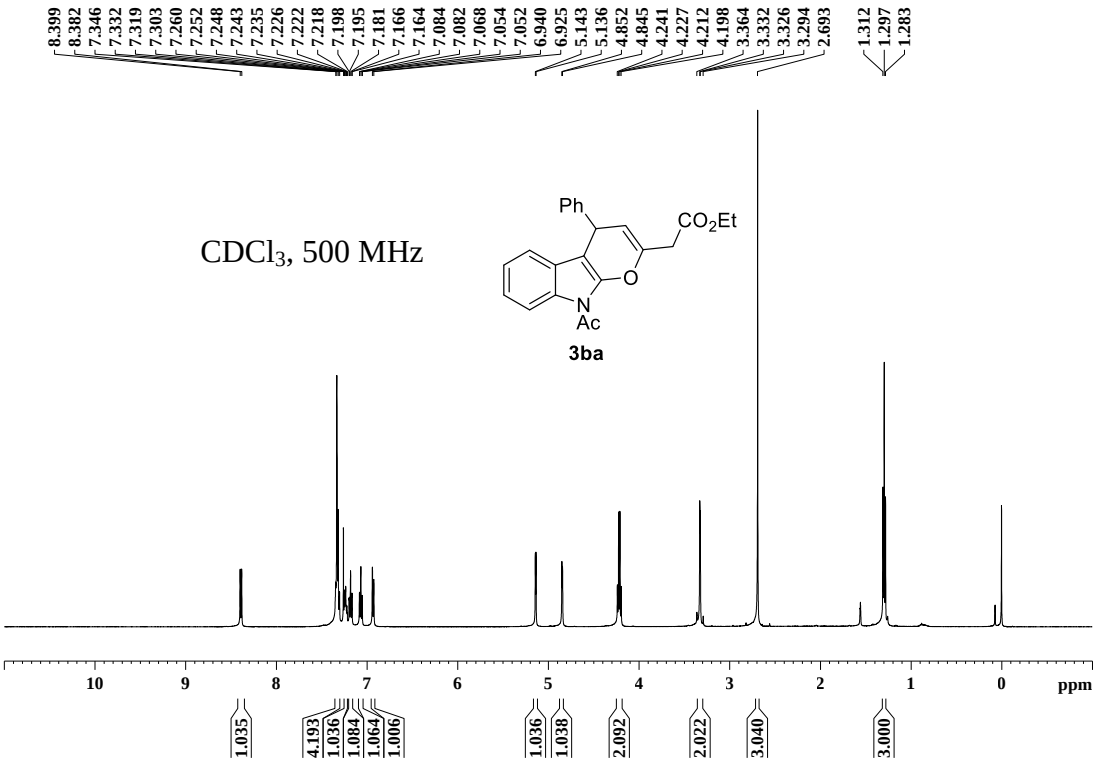

Figure S32: ^{1}H NMR spectrum of compound **3ba**

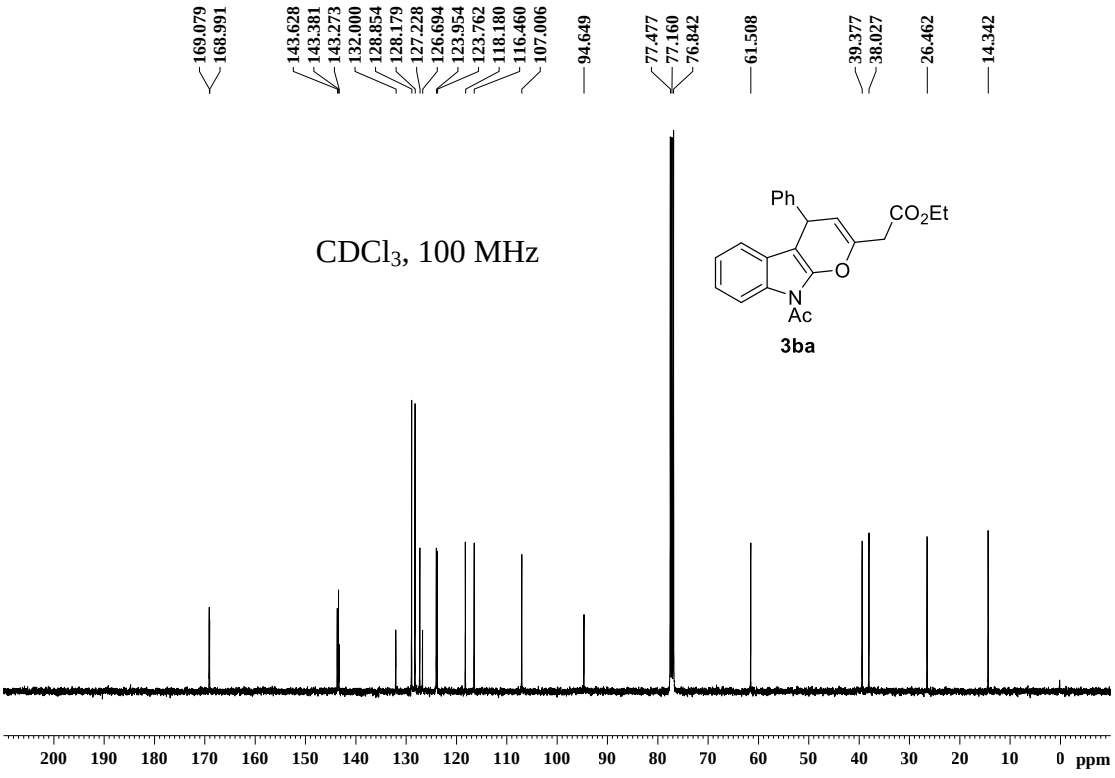

Figure S33: ^{13}C NMR spectrum of compound **3ba**

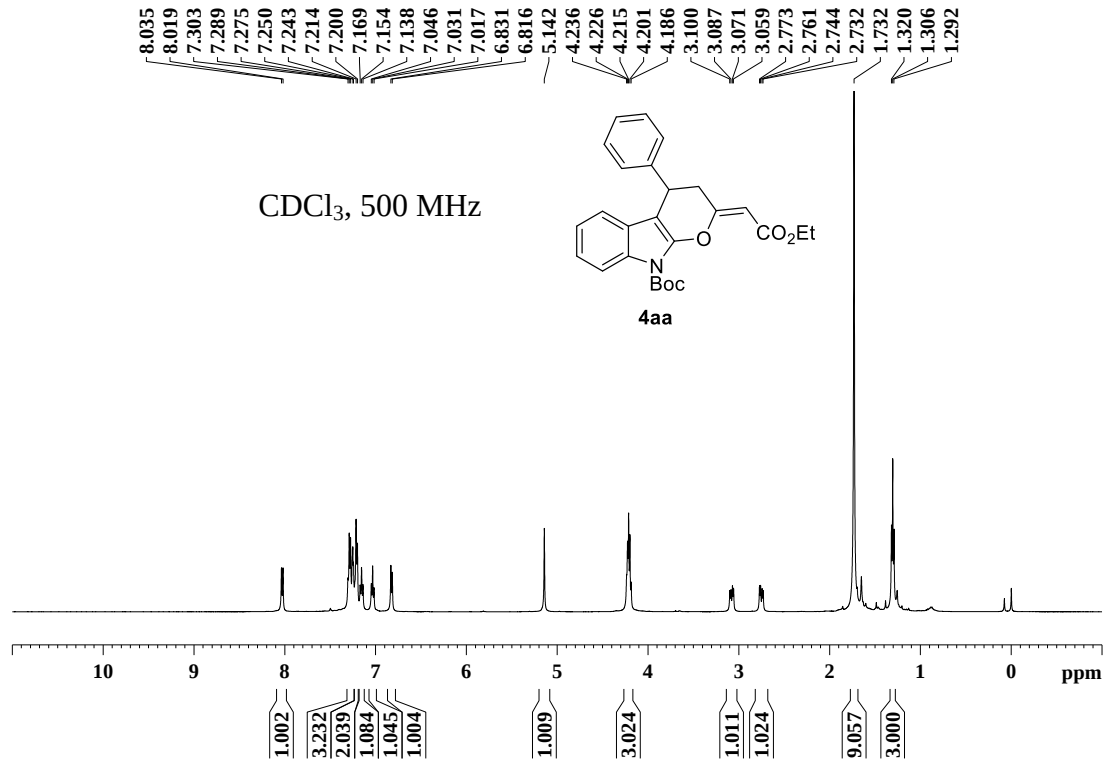

Figure S34: ^{1}H NMR spectrum of compound **4aa**

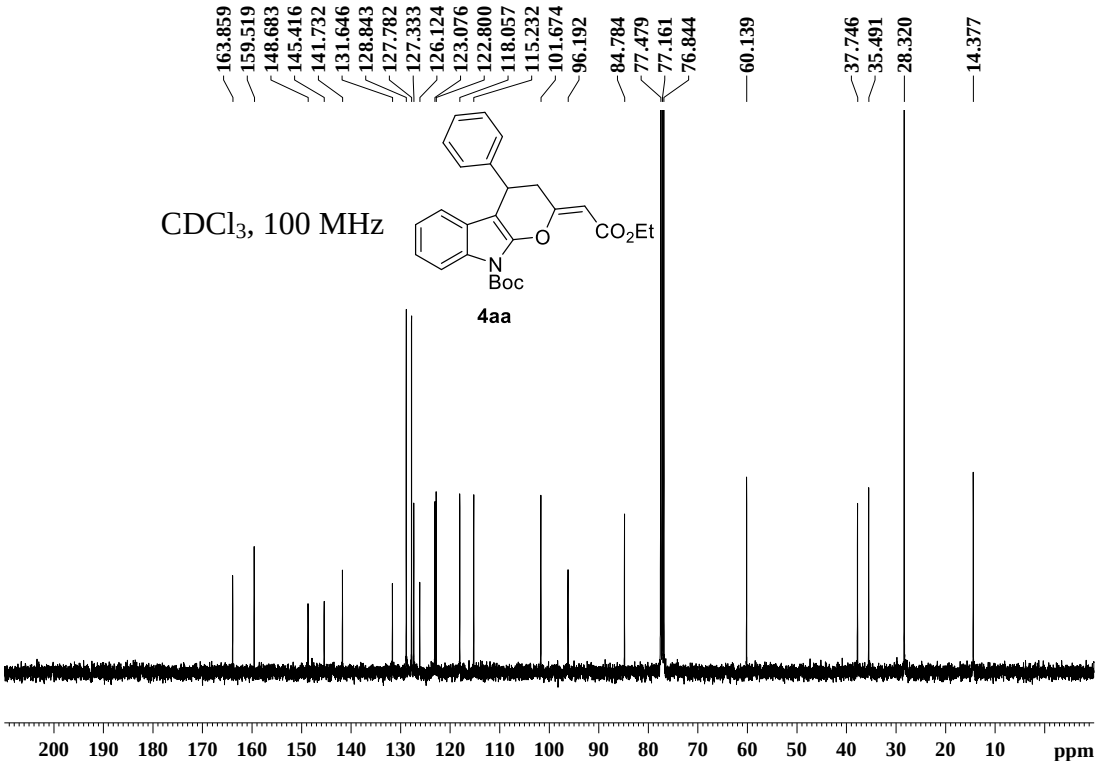

Figure S35: ^{13}C NMR spectrum of compound **4aa**

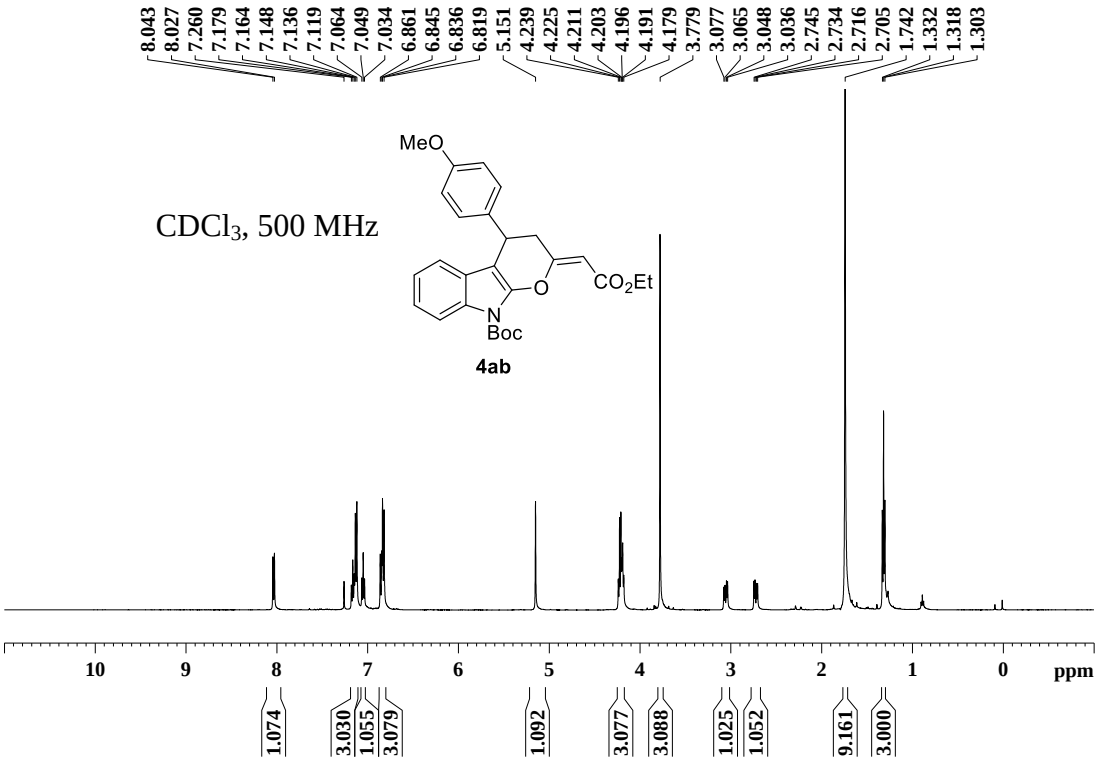

Figure S36: ^{1}H NMR spectrum of compound **4ab**

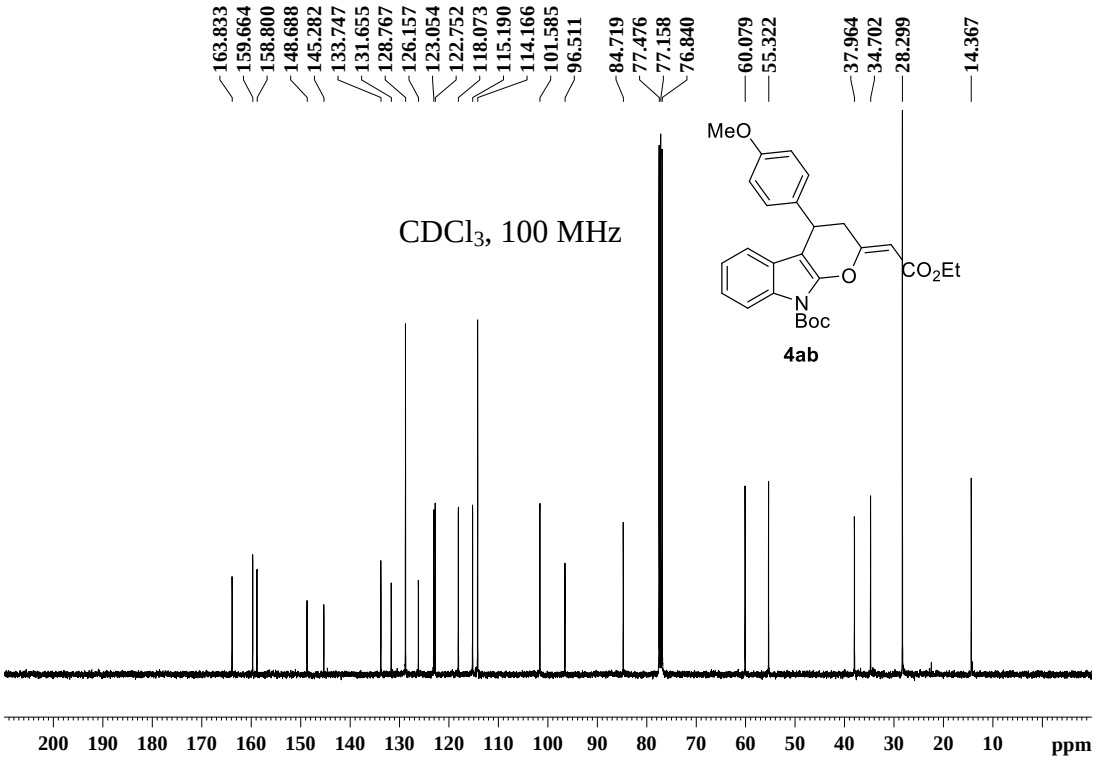

Figure S37: ^{13}C NMR spectrum of compound **4ab**

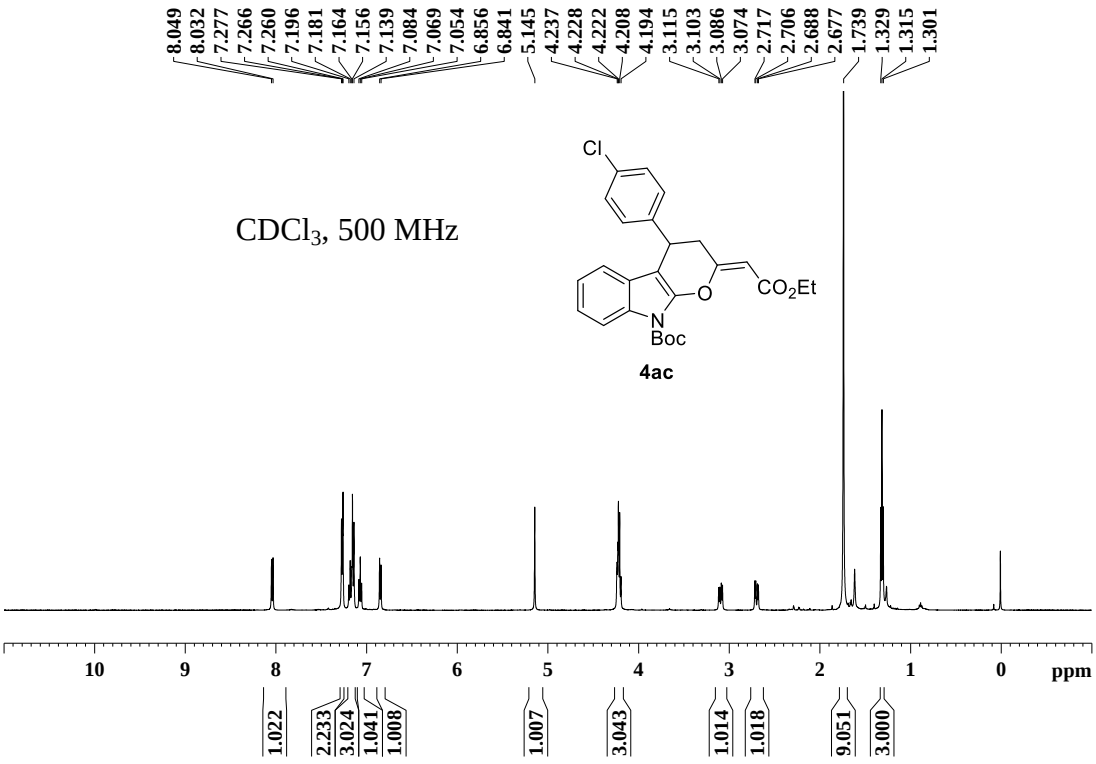

Figure S38: ^{1}H NMR spectrum of compound **4ac**

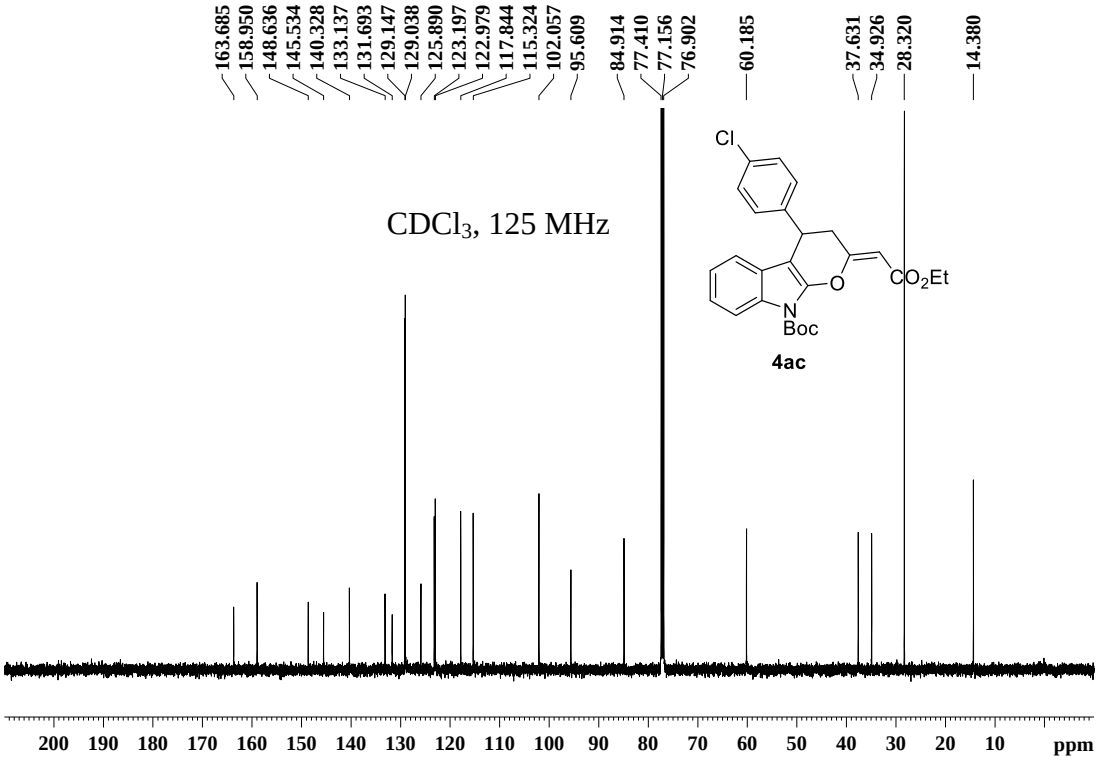

Figure S39: ^{13}C NMR spectrum of compound **4ac**

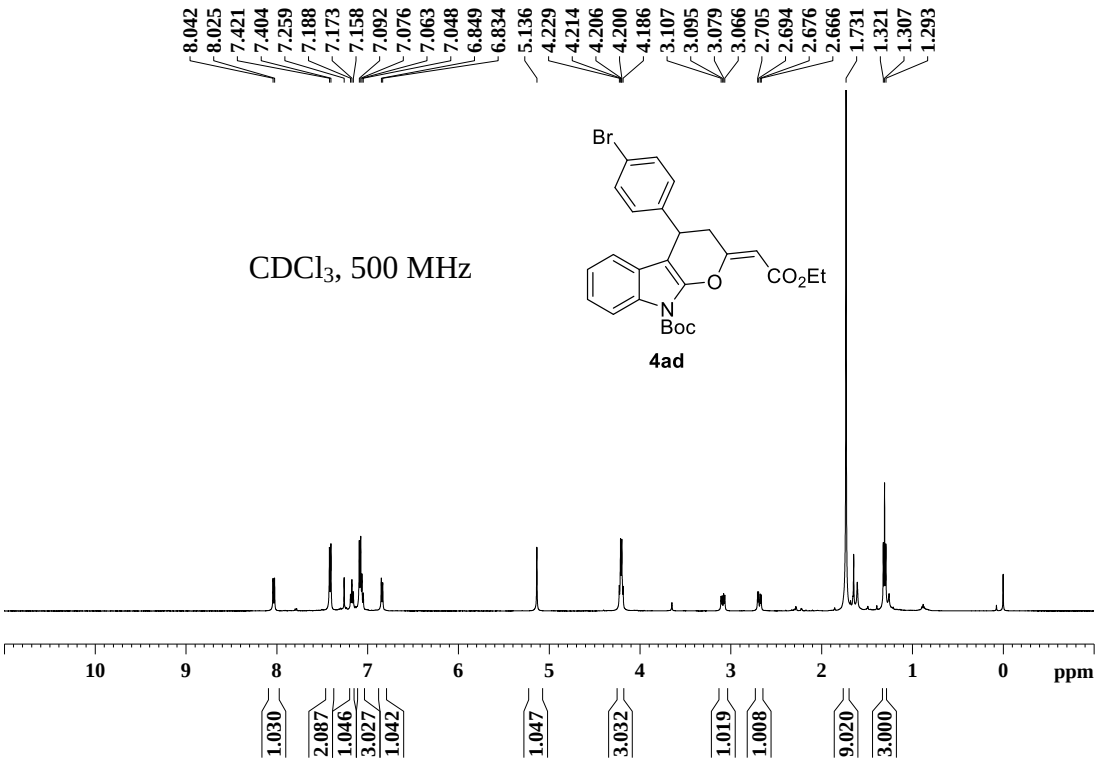

Figure S40: ^{1}H NMR spectrum of compound **4ad**

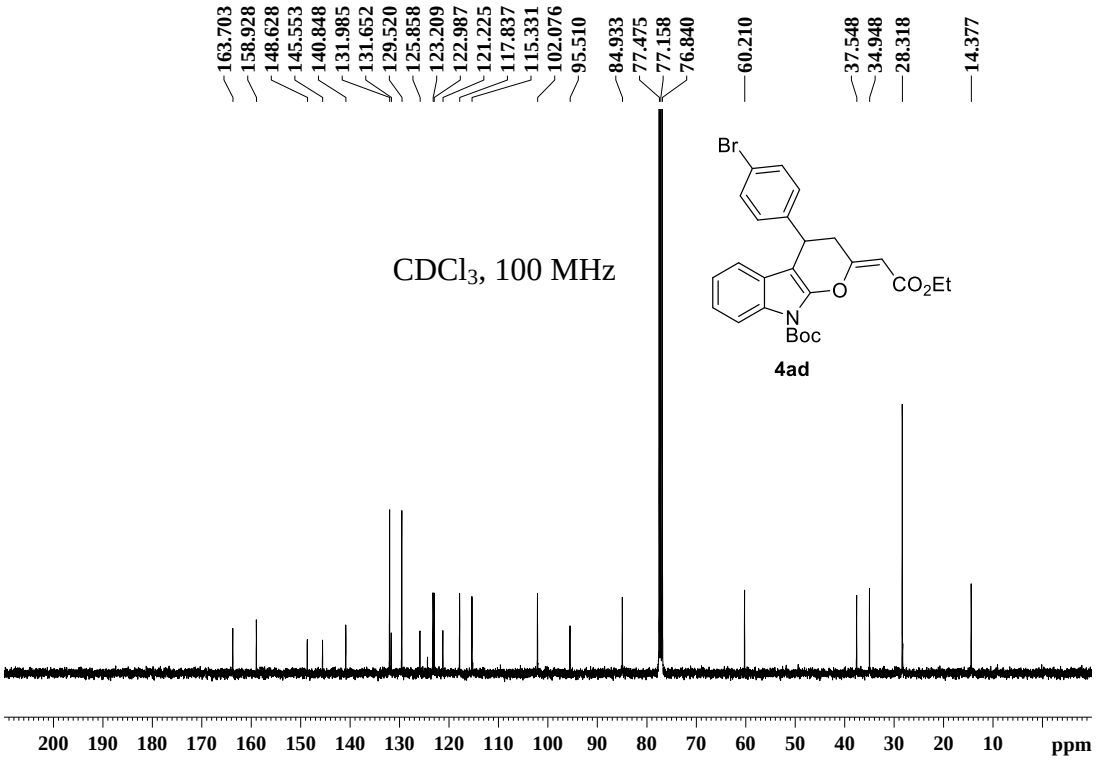

Figure S41: ^{13}C NMR spectrum of compound **4ad**

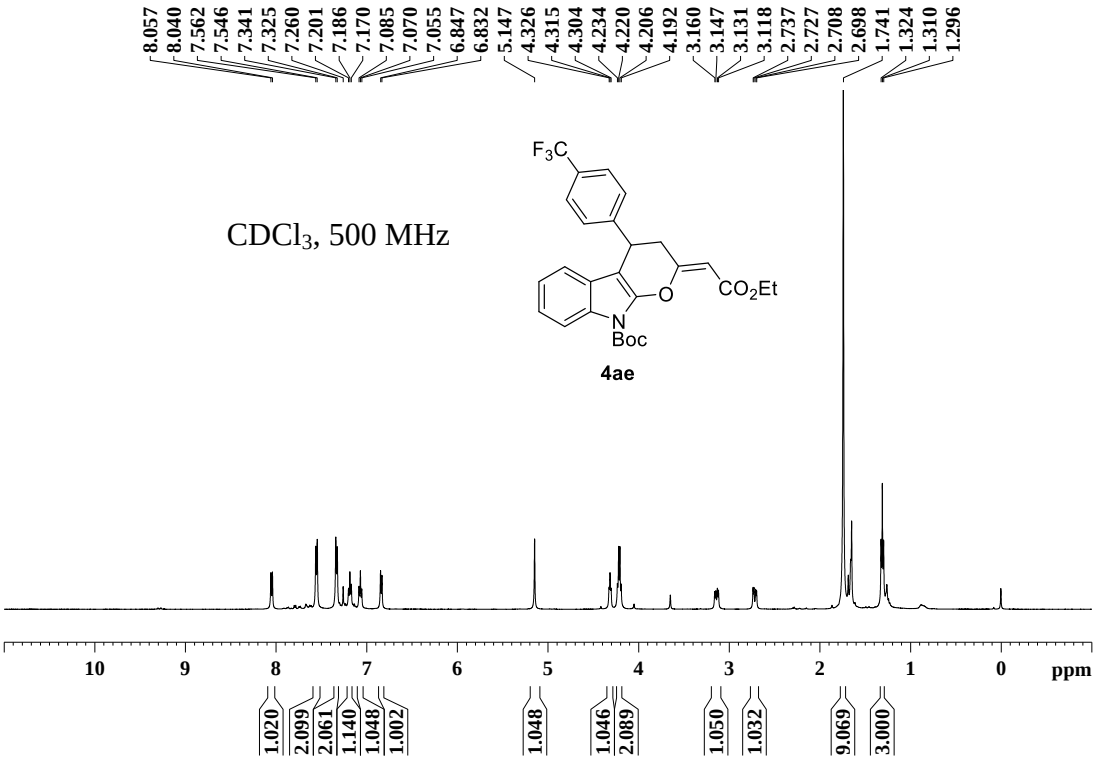

Figure S42: ^{1}H NMR spectrum of compound **4ae**

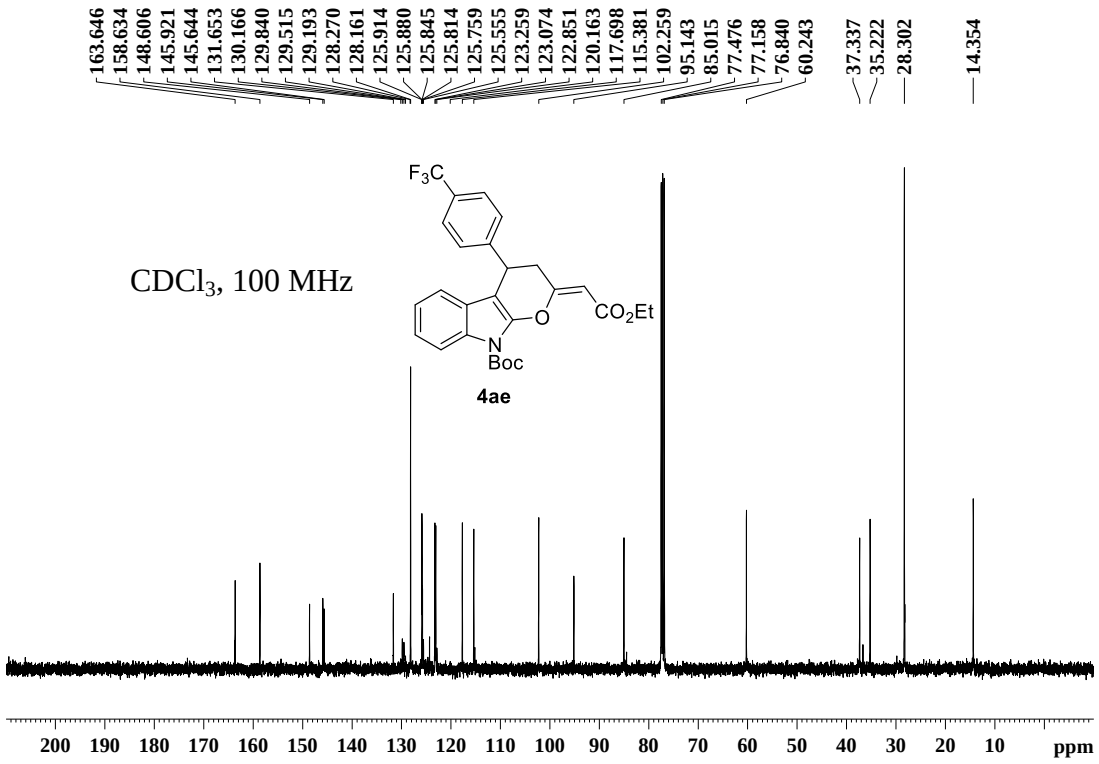

Figure S43: ^{13}C NMR spectrum of compound **4ae**

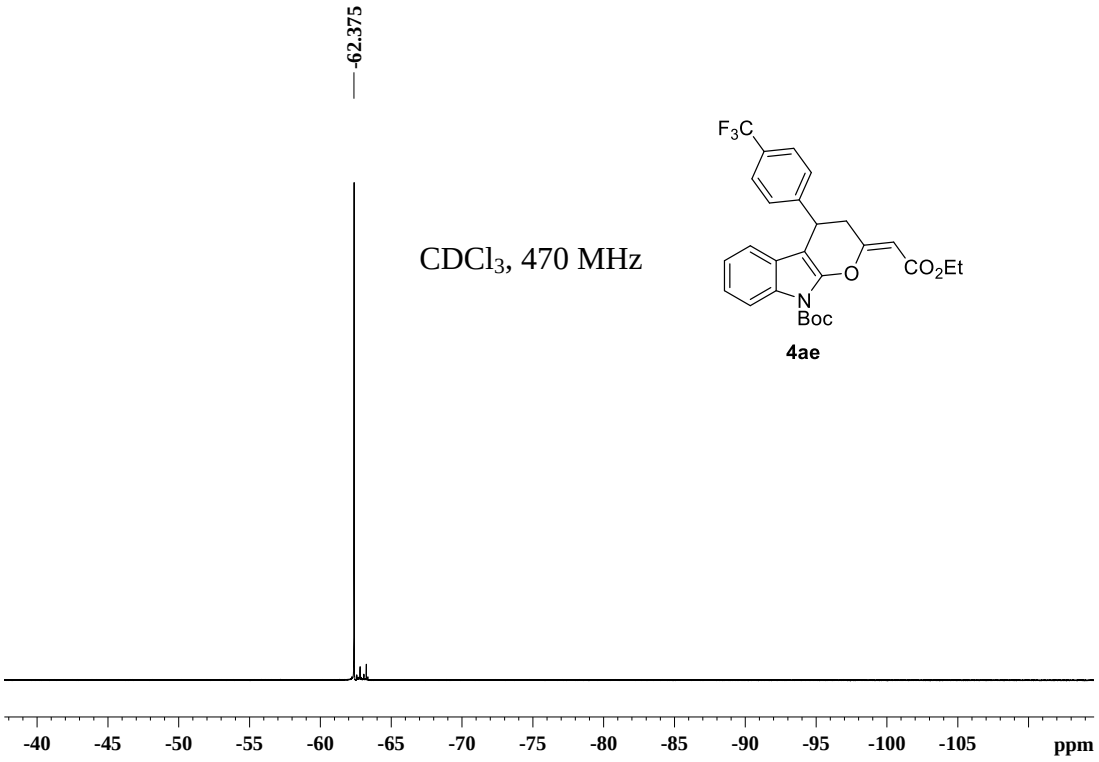

Figure S44: ^{19}F NMR spectrum of compound **4ae**

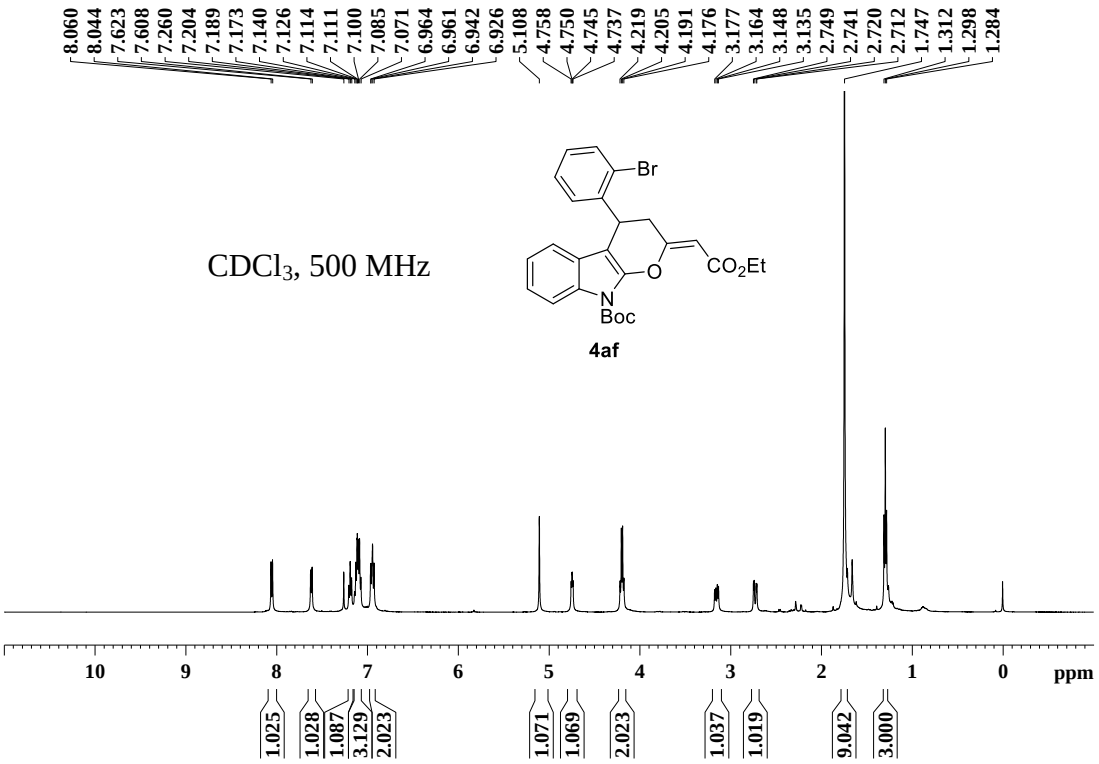

Figure S45: ^{1}H NMR spectrum of compound **4af**

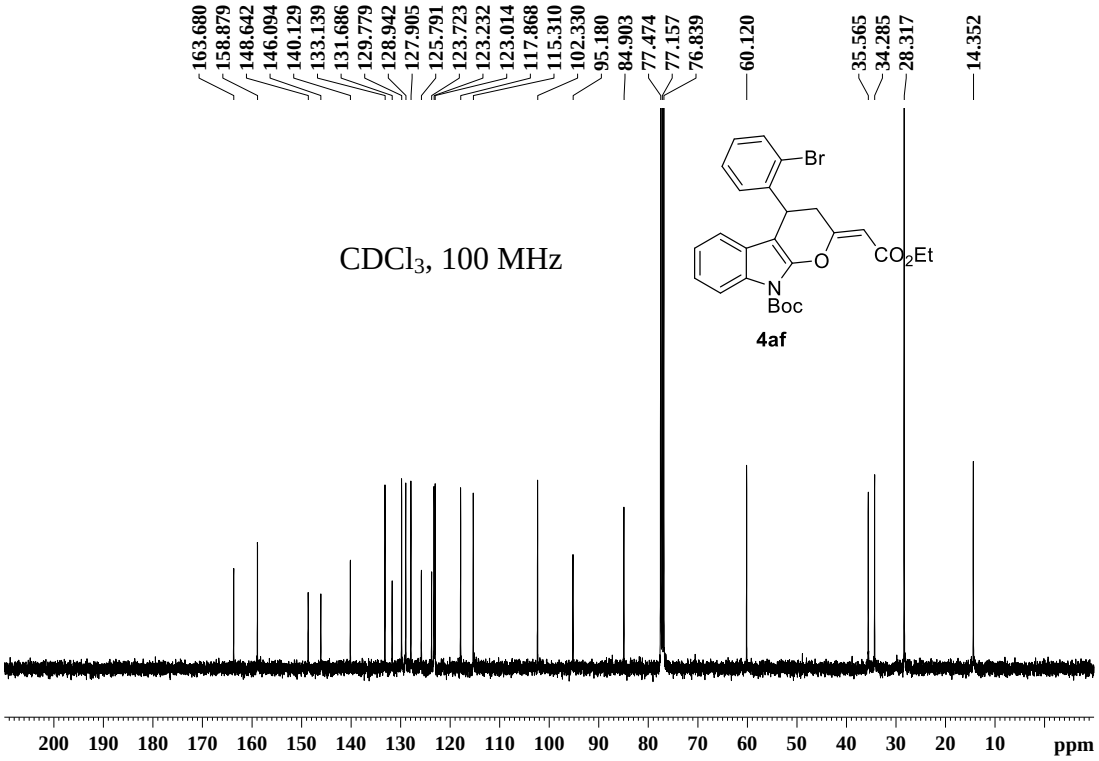

Figure S46: ^{13}C NMR spectrum of compound **4af**

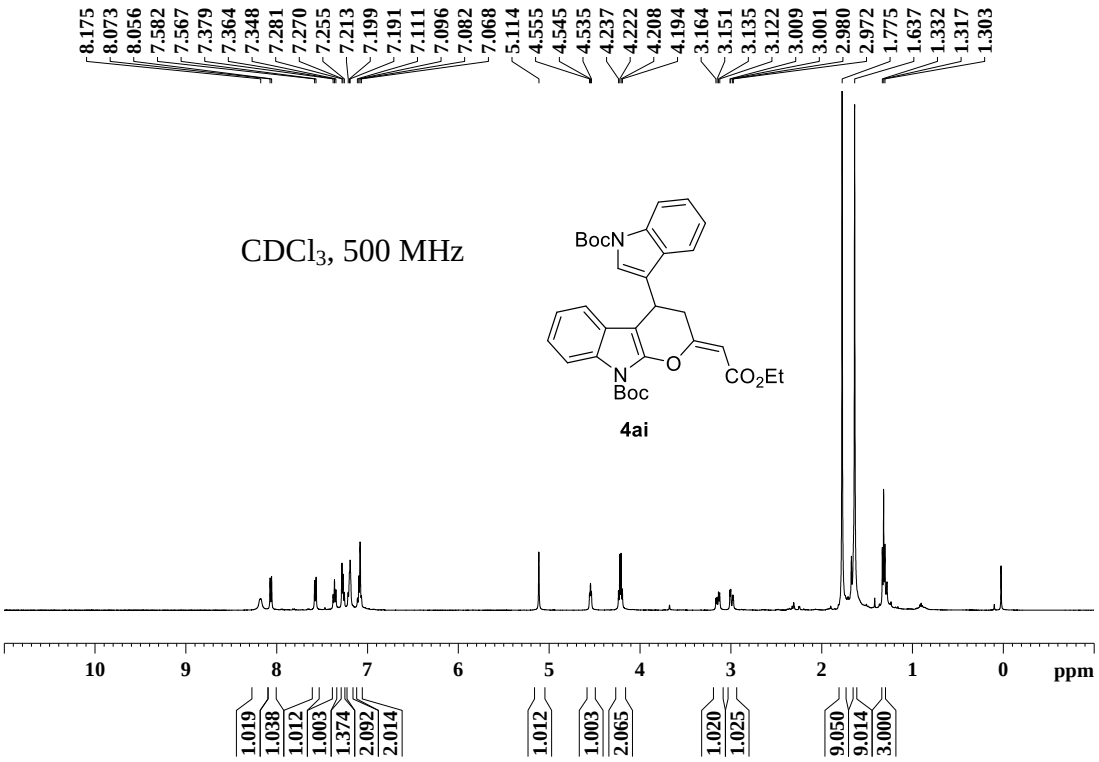

Figure S47: ^{1}H NMR spectrum of compound **4ai**

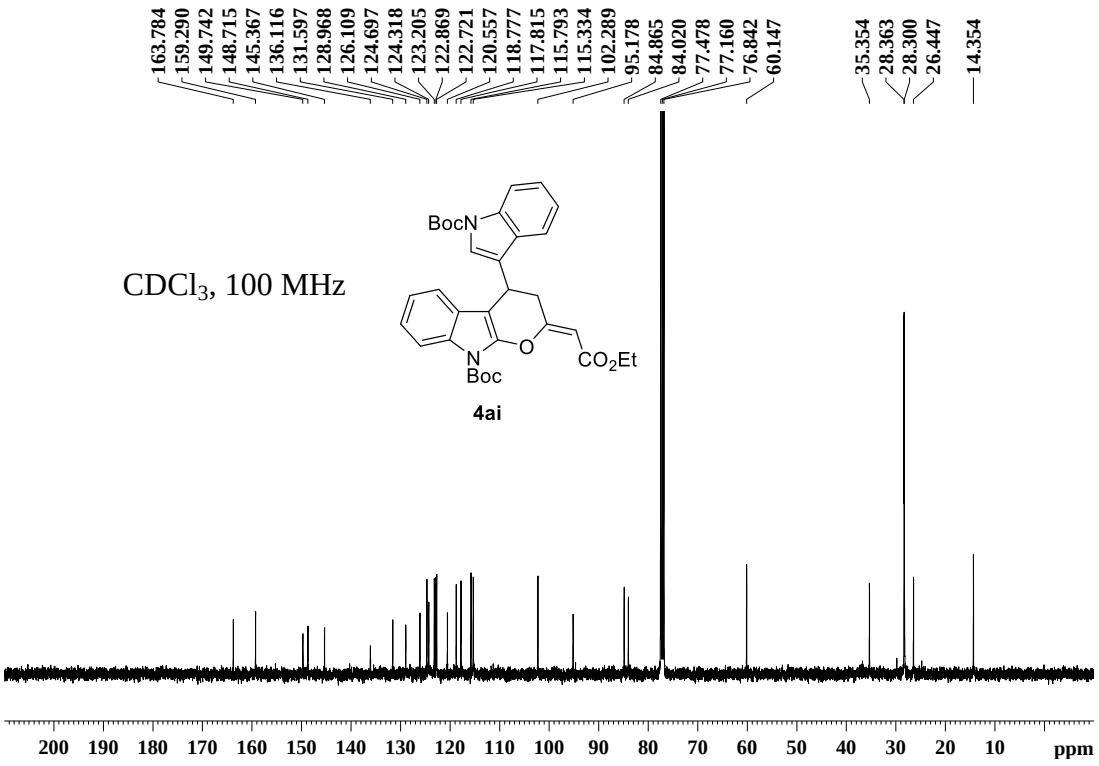

Figure S48: ^{13}C NMR spectrum of compound **4ai**

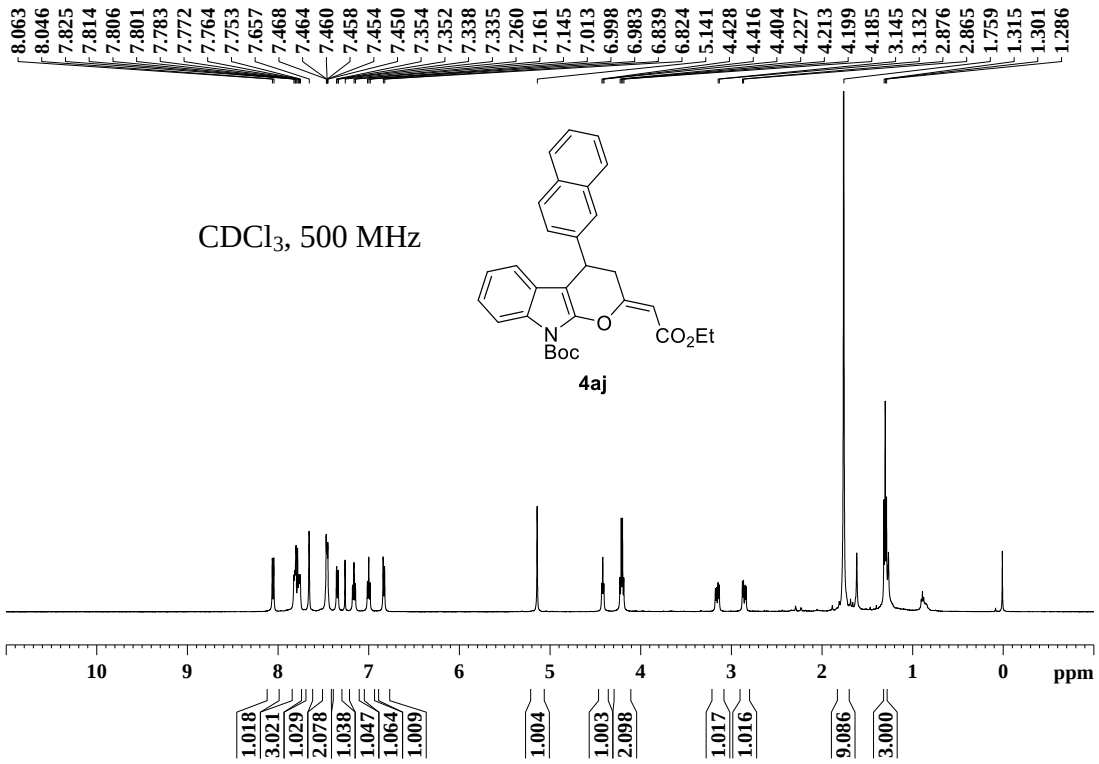

Figure S49: ^{1}H NMR spectrum of compound **4aj**

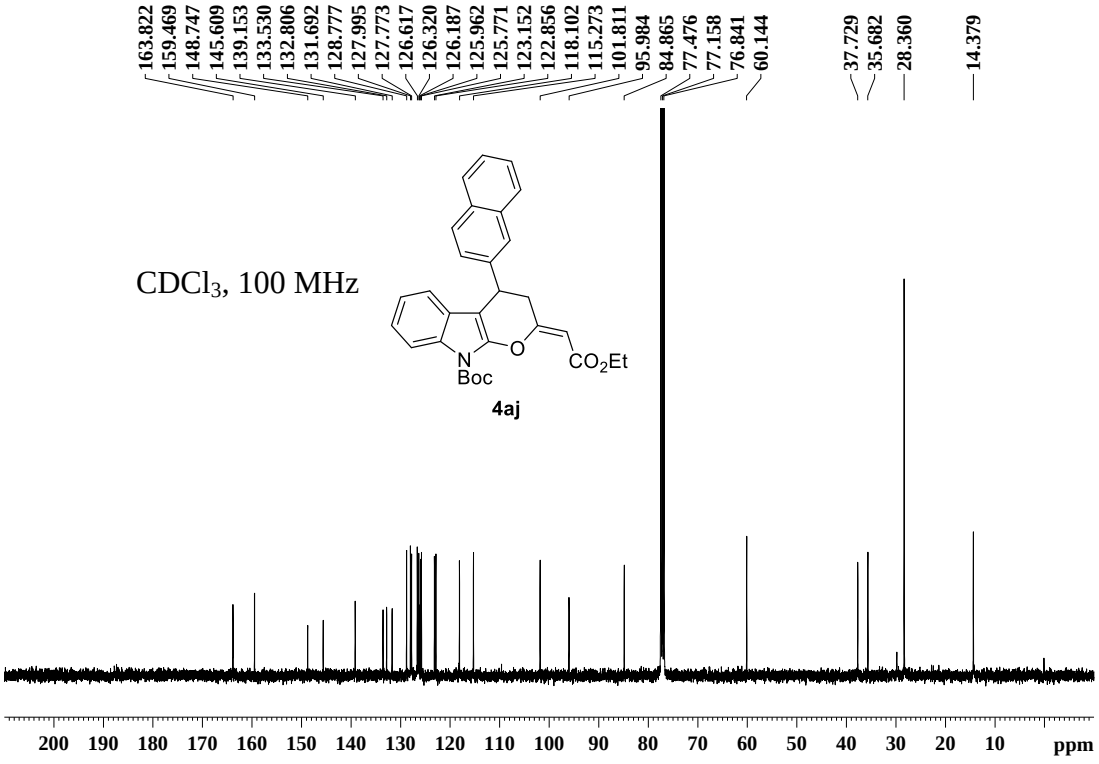

Figure S50: ^{13}C NMR spectrum of compound **4aj**

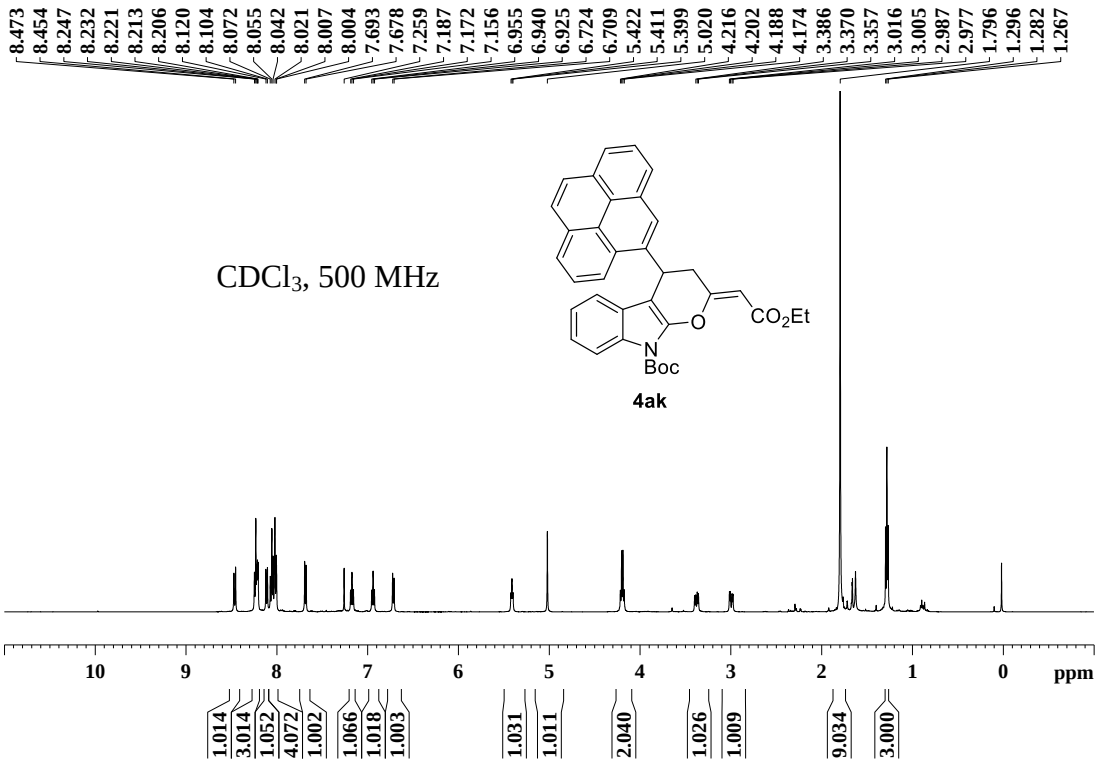

Figure S51: ^{1}H NMR spectrum of compound **4ak**

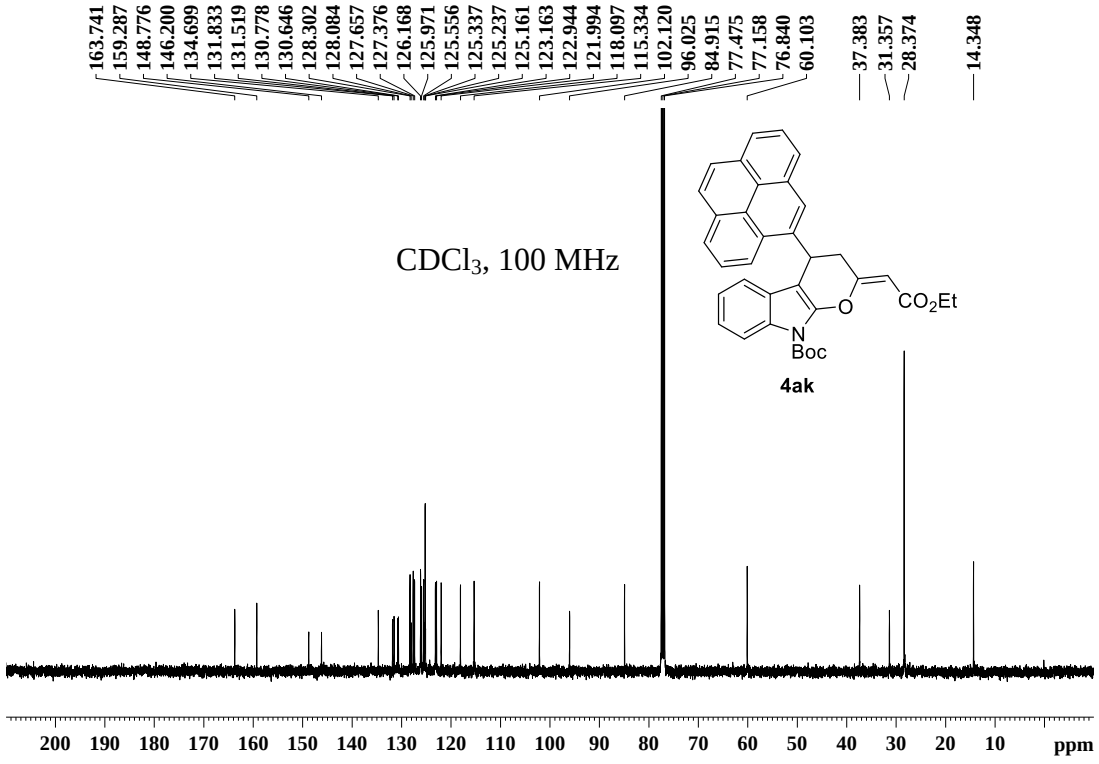

Figure S52: ^{13}C NMR spectrum of compound **4ak**

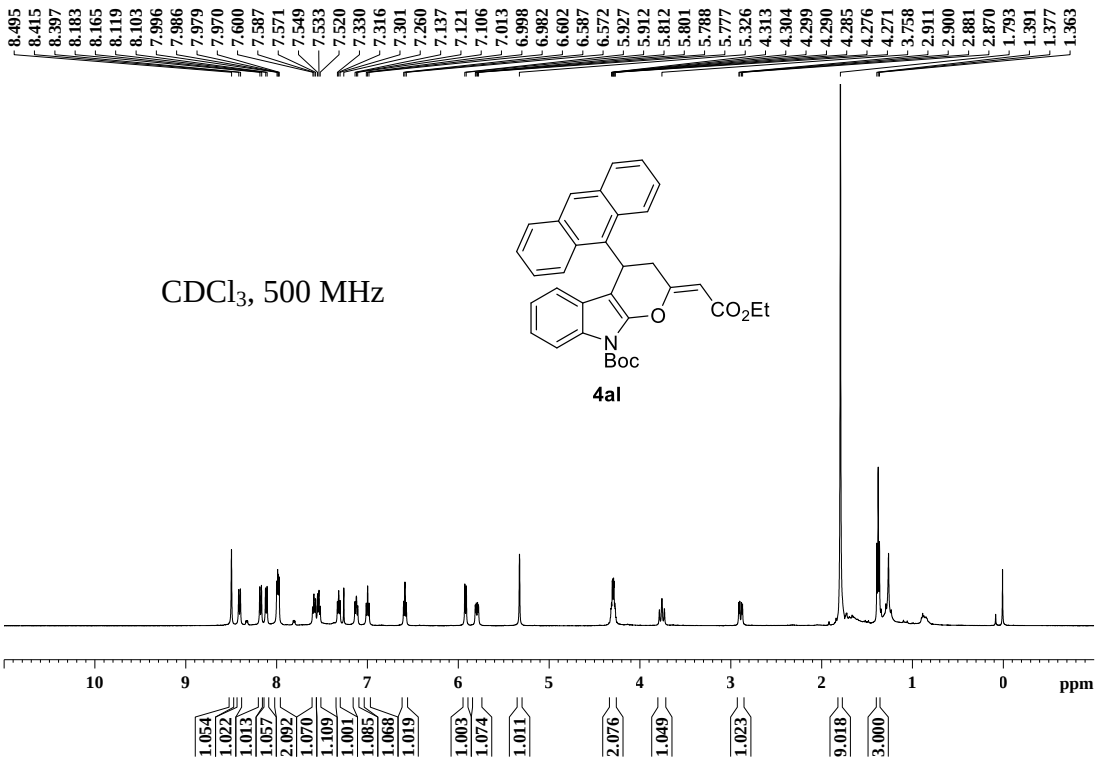

Figure S53: ^{1}H NMR spectrum of compound **4al**

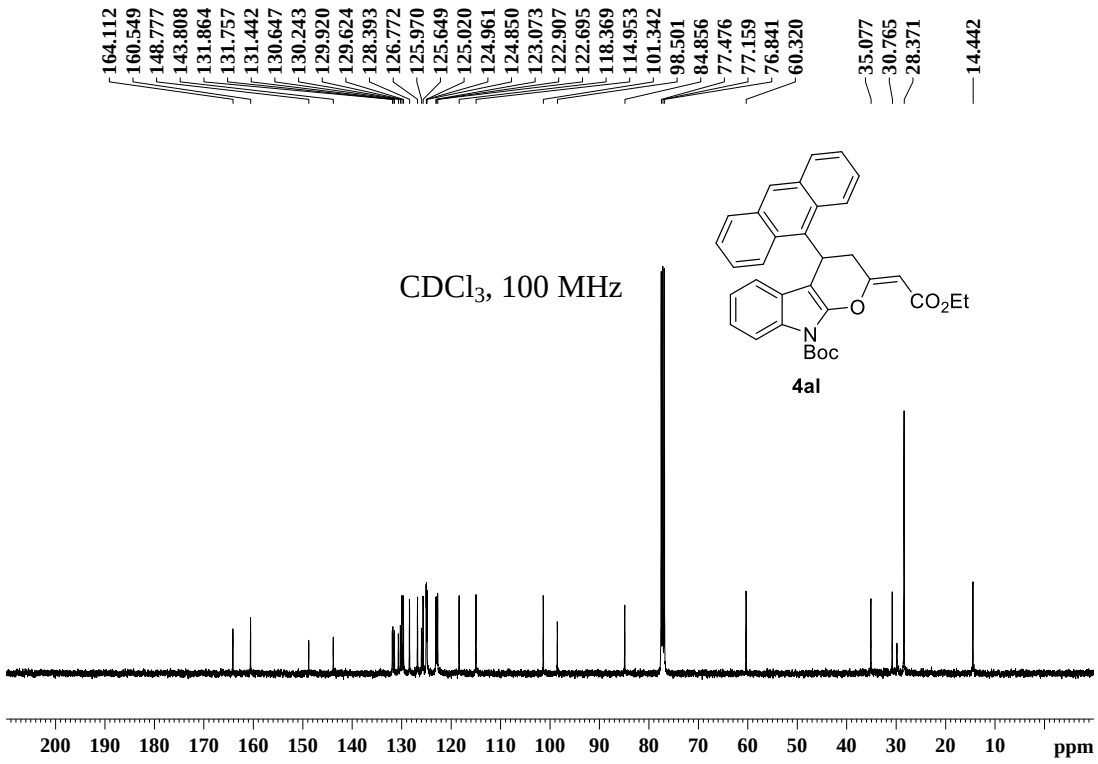

Figure S54: ^{13}C NMR spectrum of compound **4al**

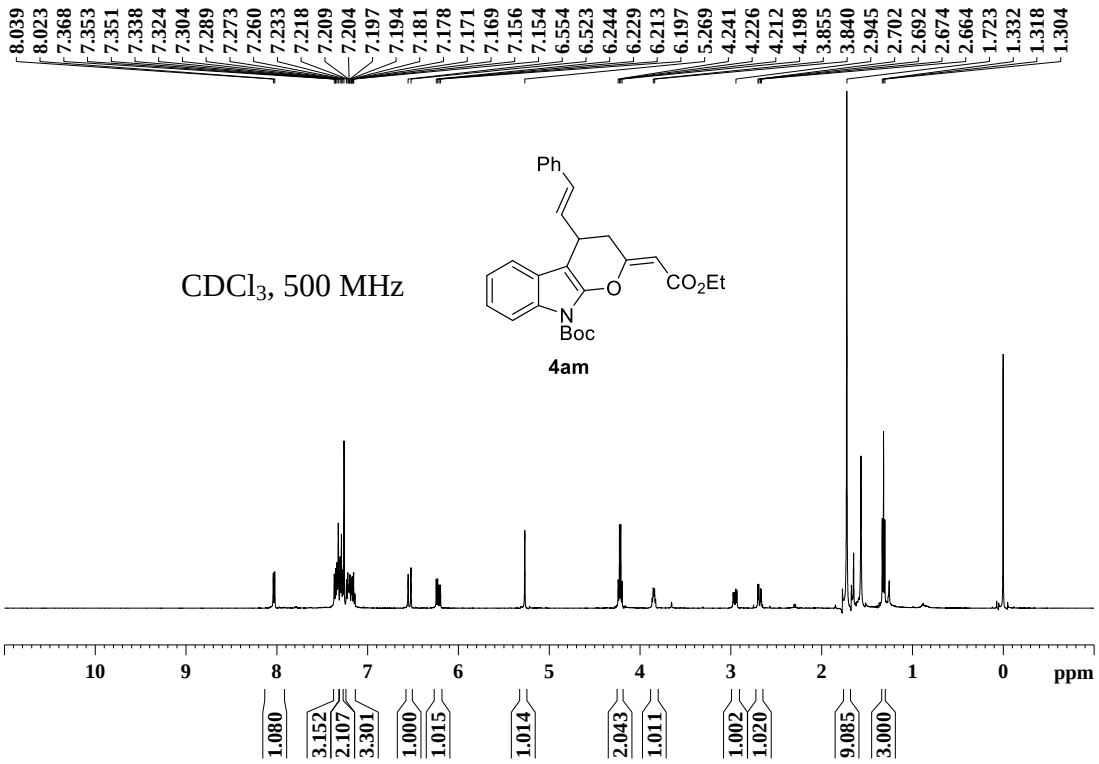

Figure S55: ^{1}H NMR spectrum of compound **4am**

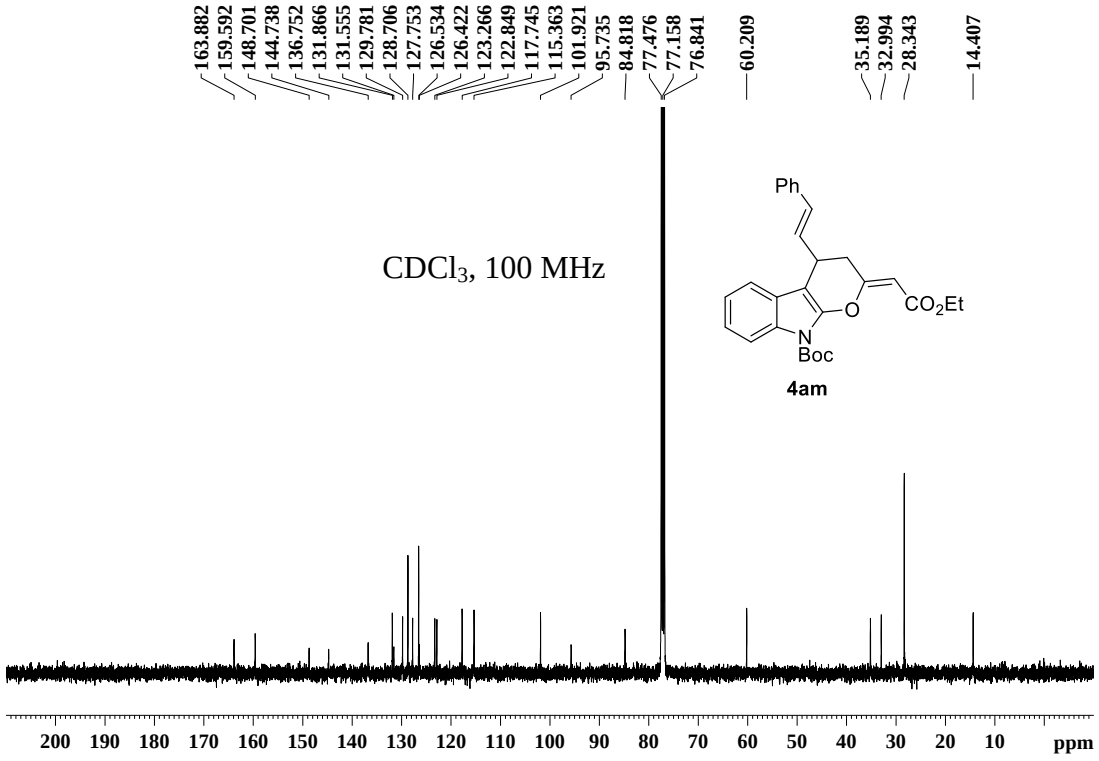

Figure S56: ^{13}C NMR spectrum of compound **4am**

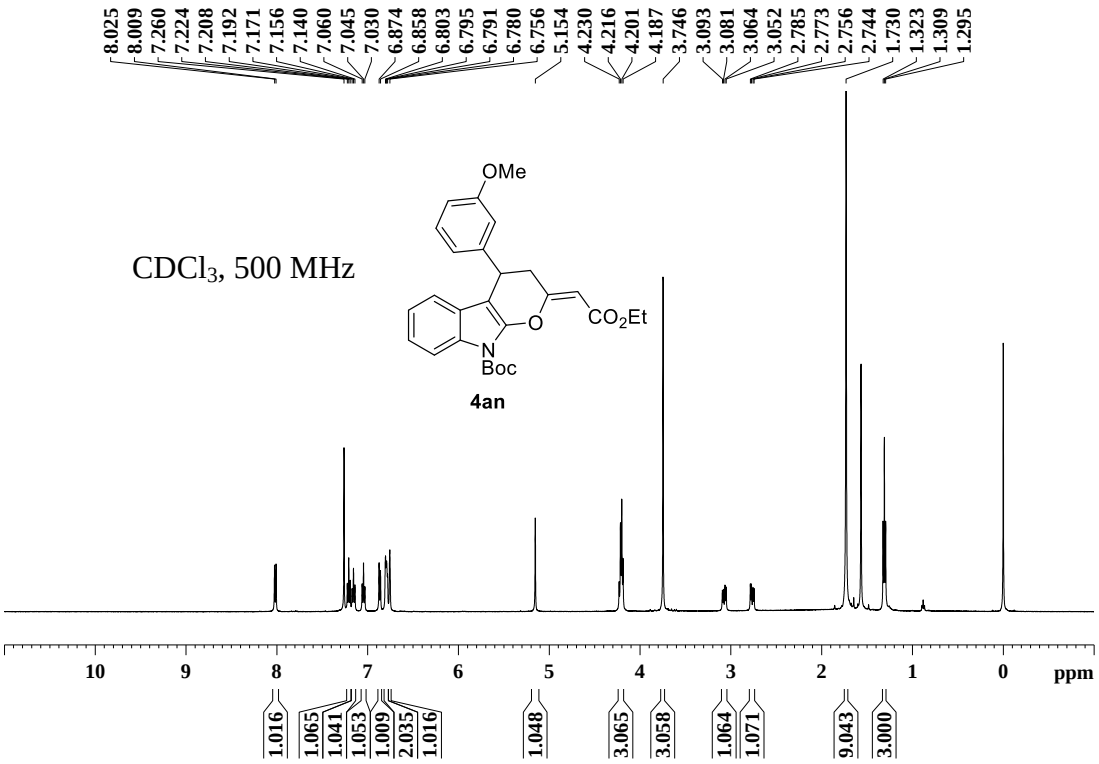

Figure S57: ^{1}H NMR spectrum of compound **4an**

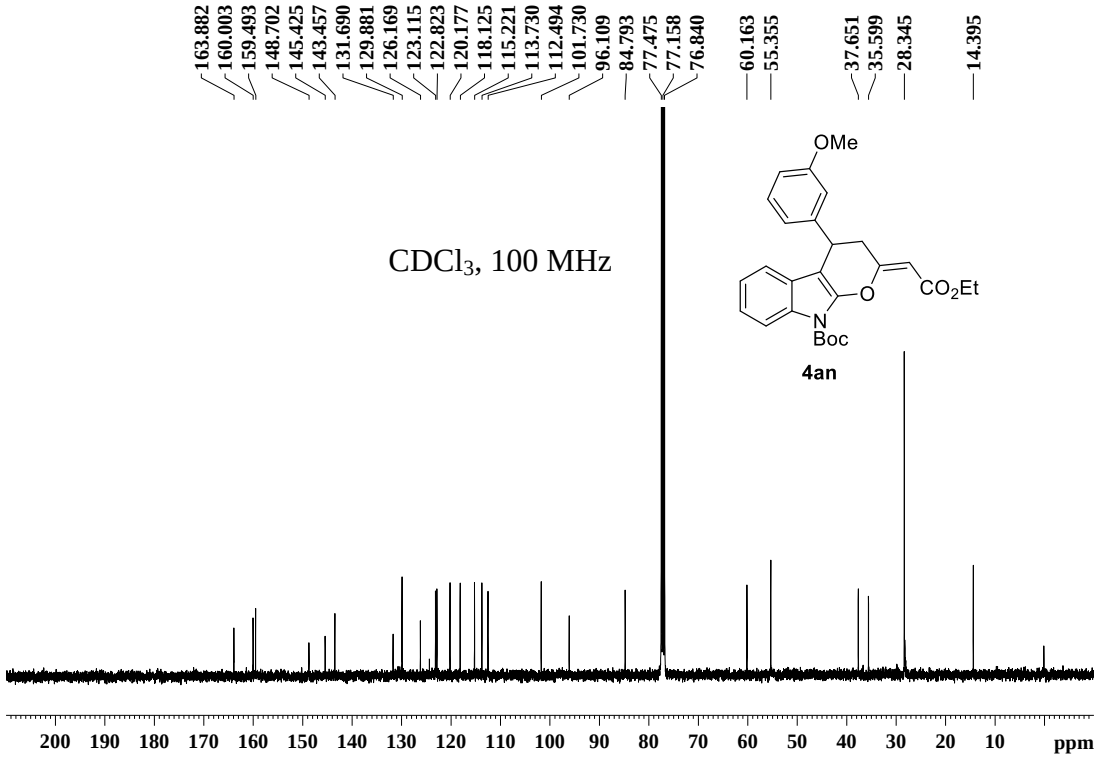

Figure S58: ^{13}C NMR spectrum of compound **4an**

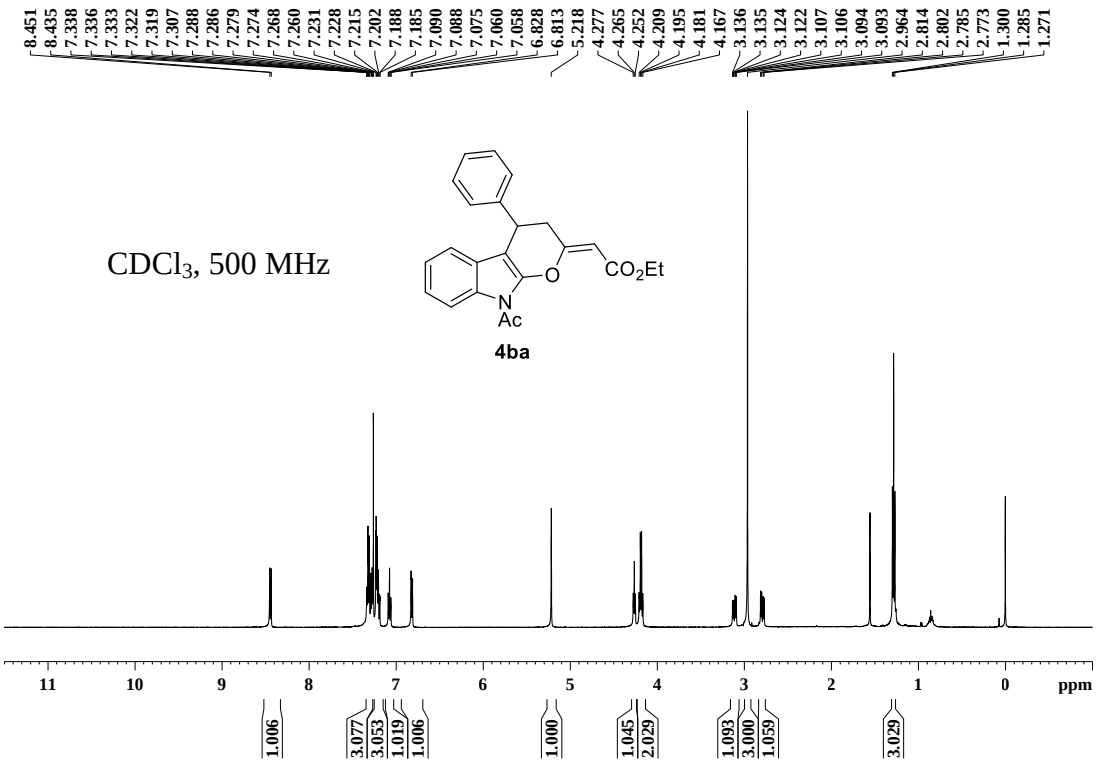

Figure S59: ^{1}H NMR spectrum of compound **4ba**

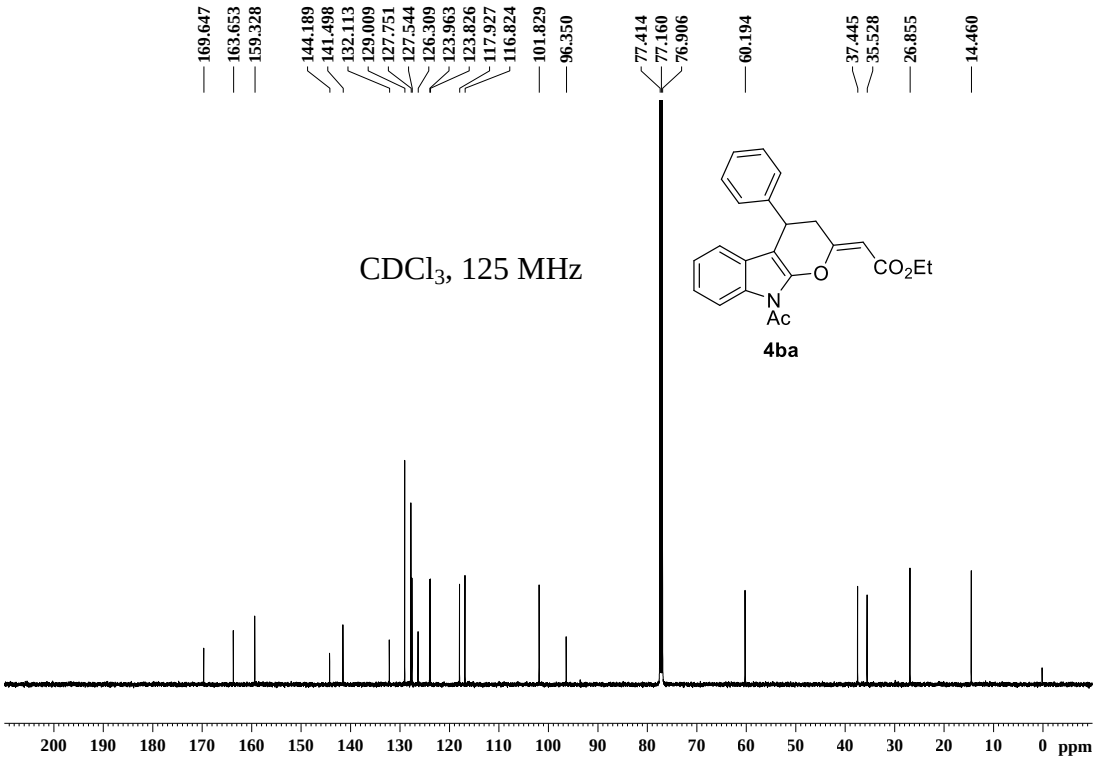

Figure S60: ^{13}C NMR spectrum of compound **4ba**

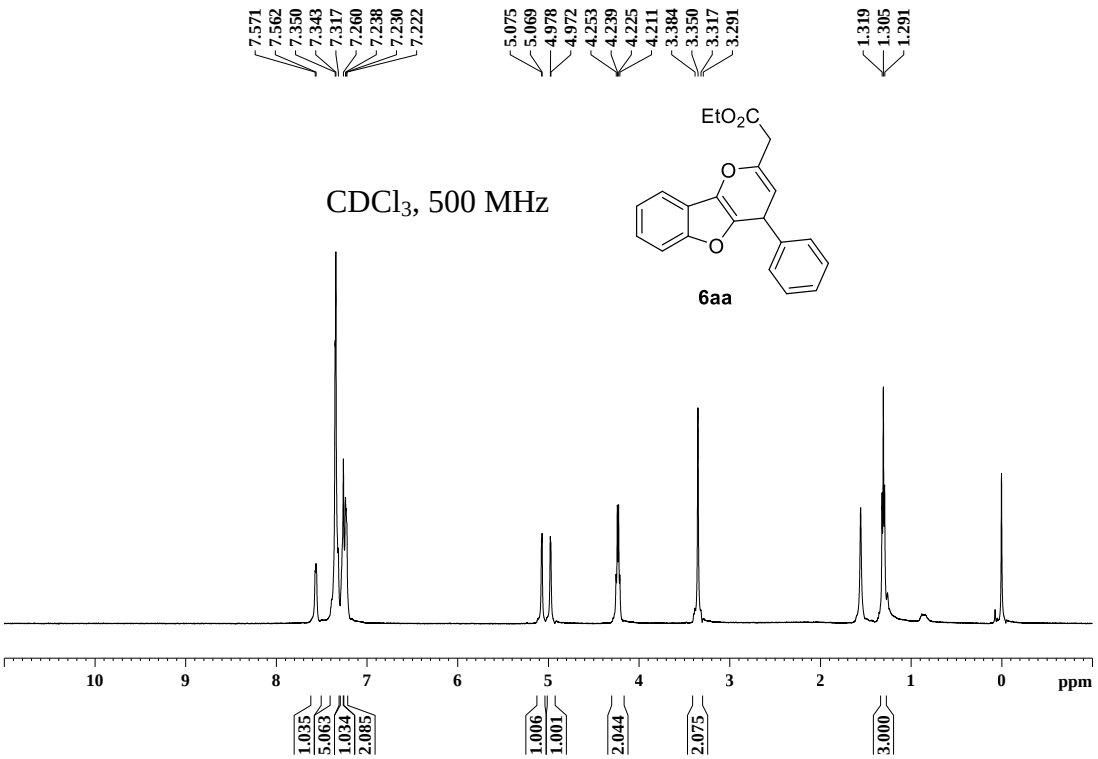

Figure S61: ^{1}H NMR spectrum of compound **6aa**

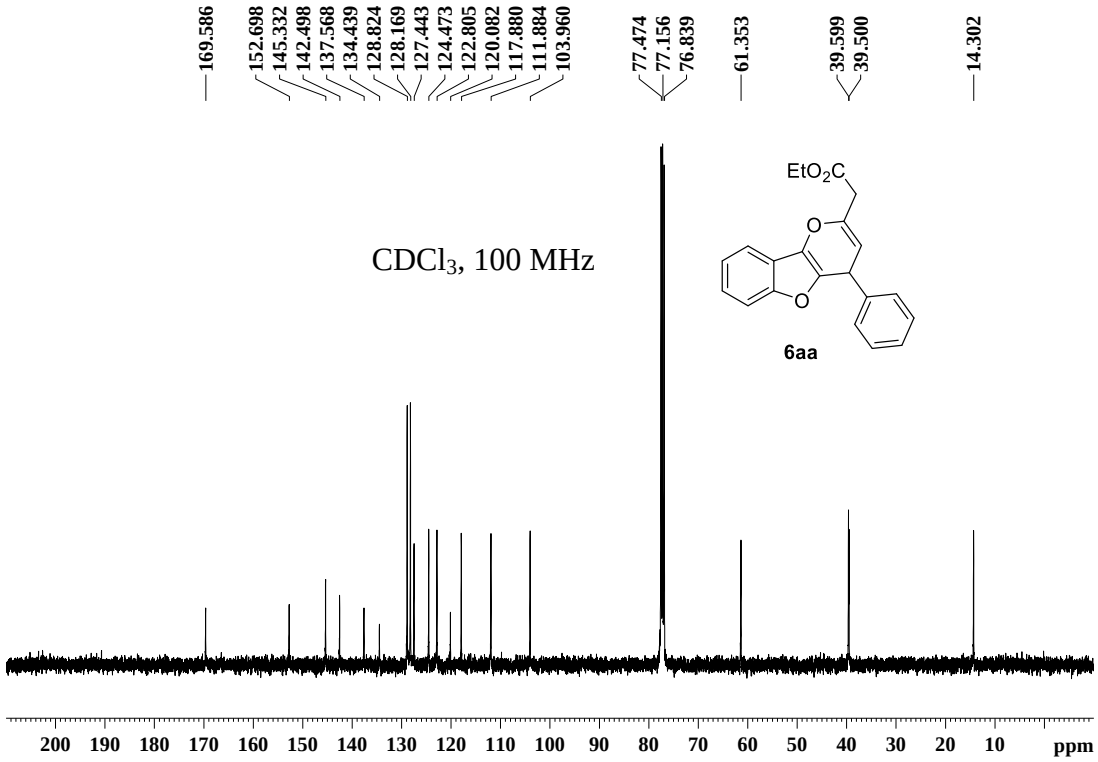

Figure S62: ^{13}C NMR spectrum of compound **6aa**

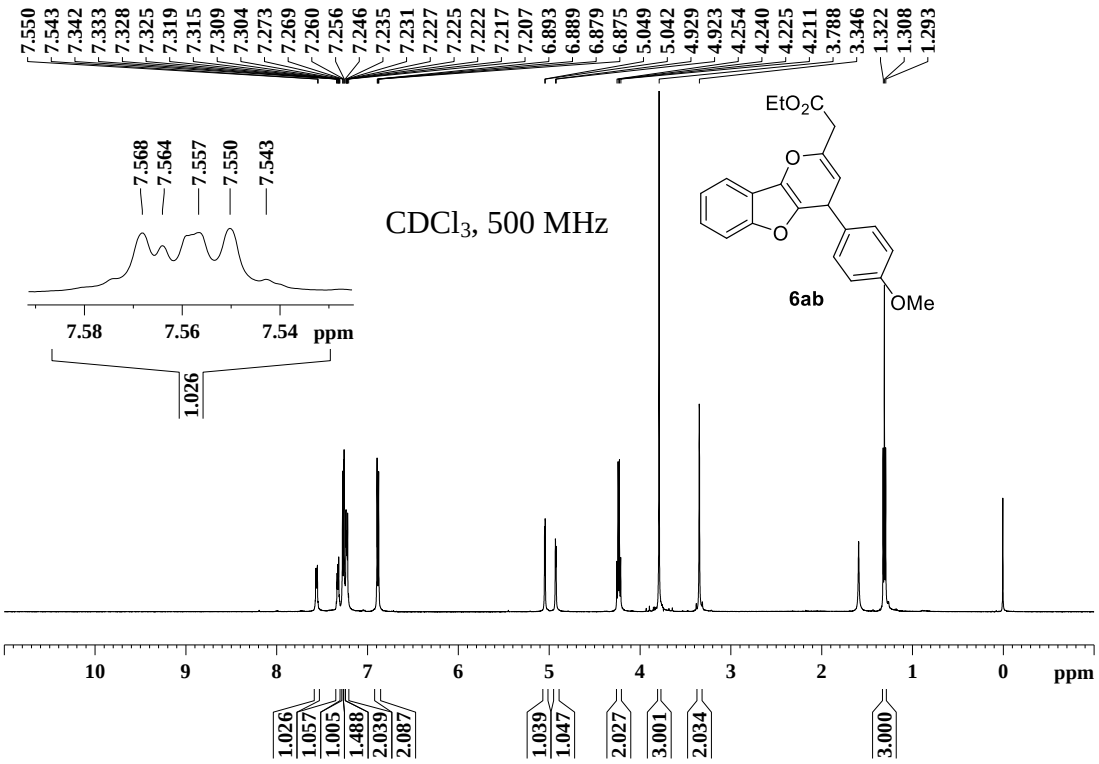

Figure S63: ^{1}H NMR spectrum of compound **6ab**

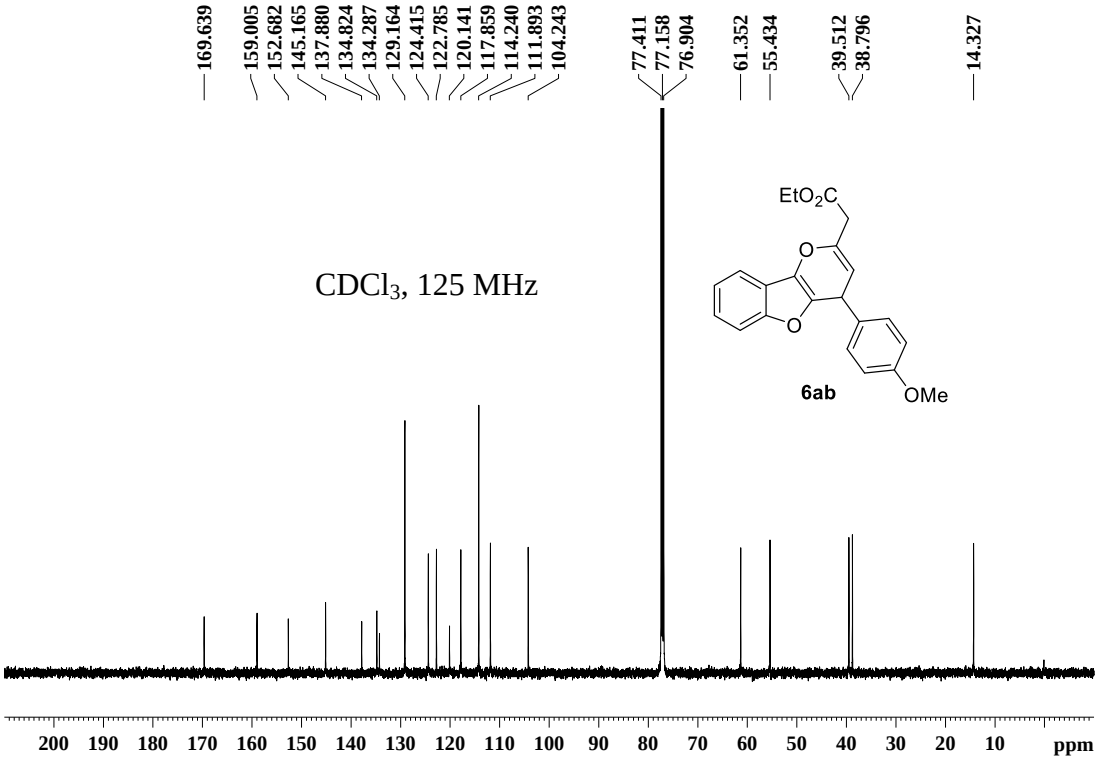

Figure S64: ^{13}C NMR spectrum of compound **6ab**

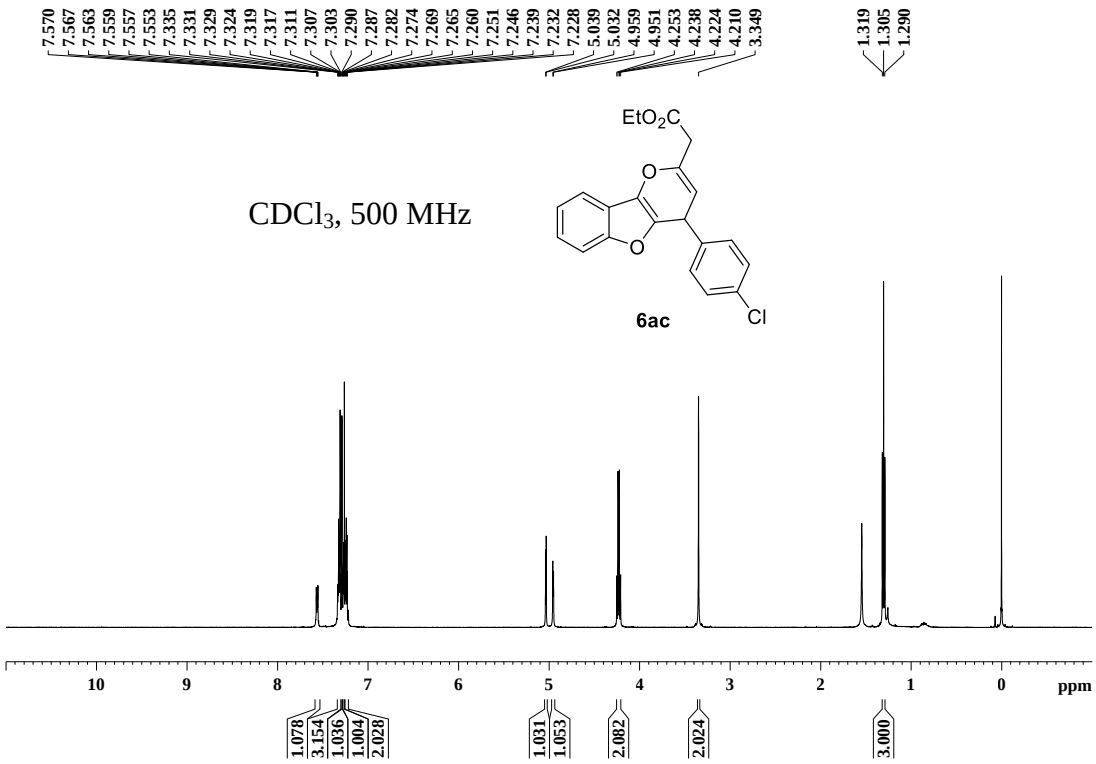

Figure S65: ^{1}H NMR spectrum of compound **6ac**

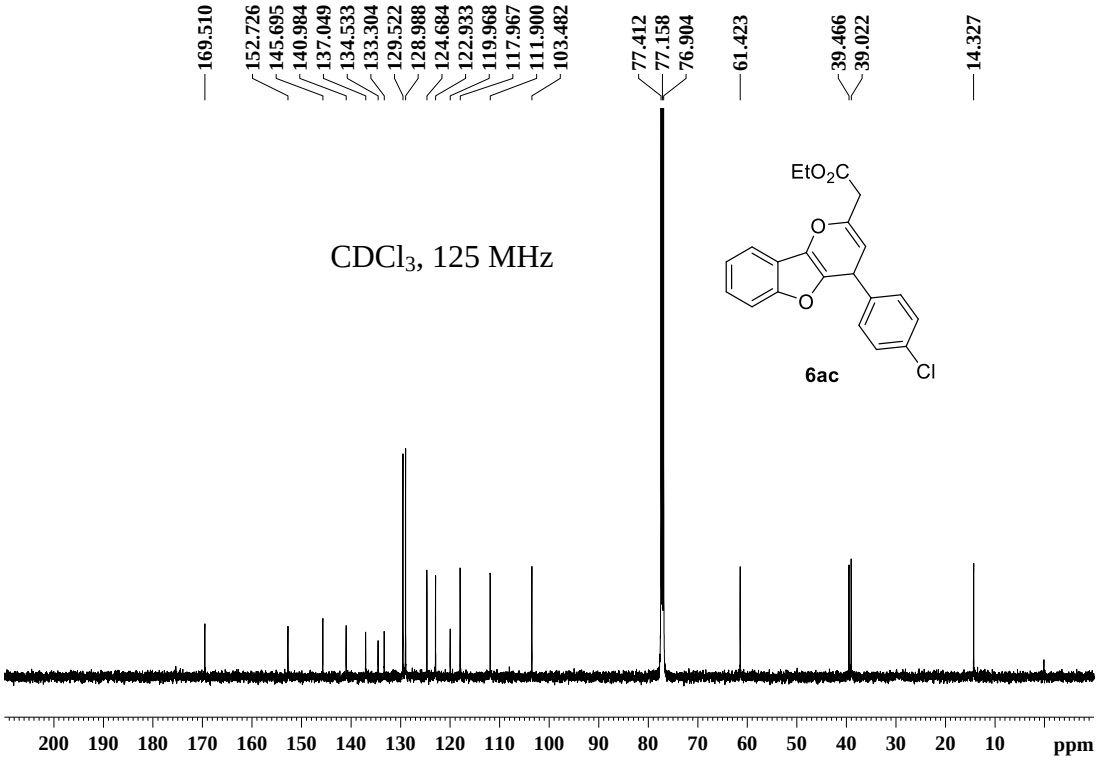

Figure S66: ^{13}C NMR spectrum of compound **6ac**

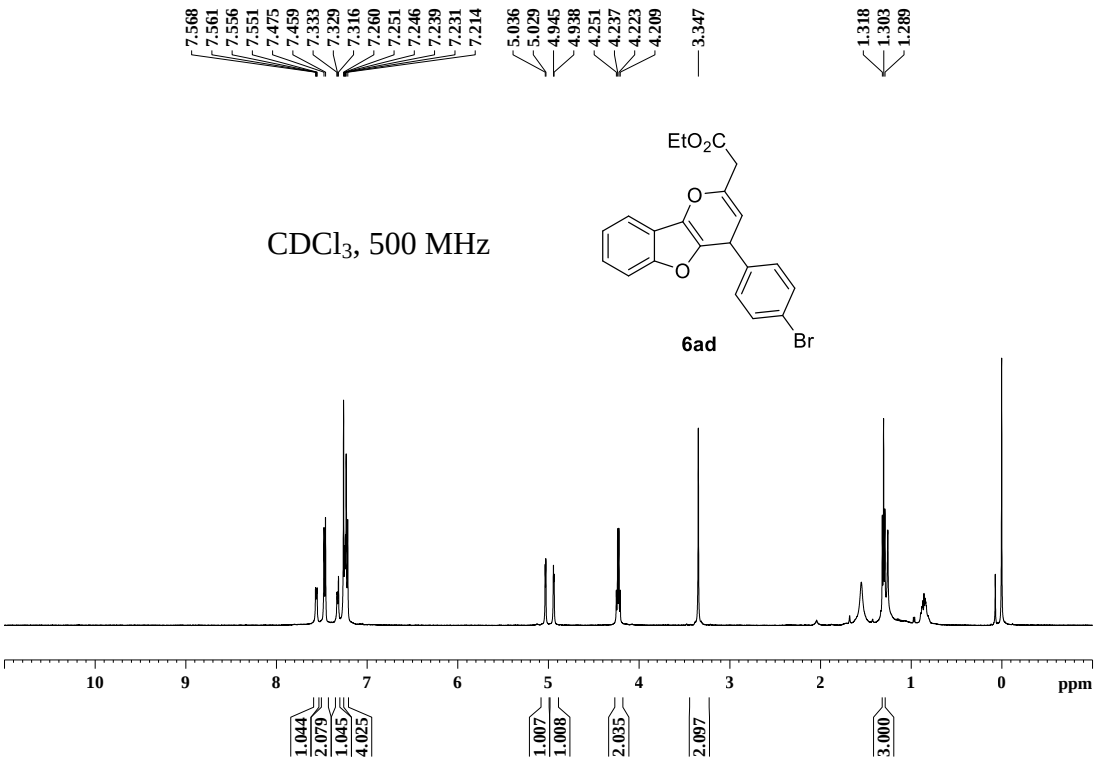

Figure S67: ^{1}H NMR spectrum of compound **6ad**

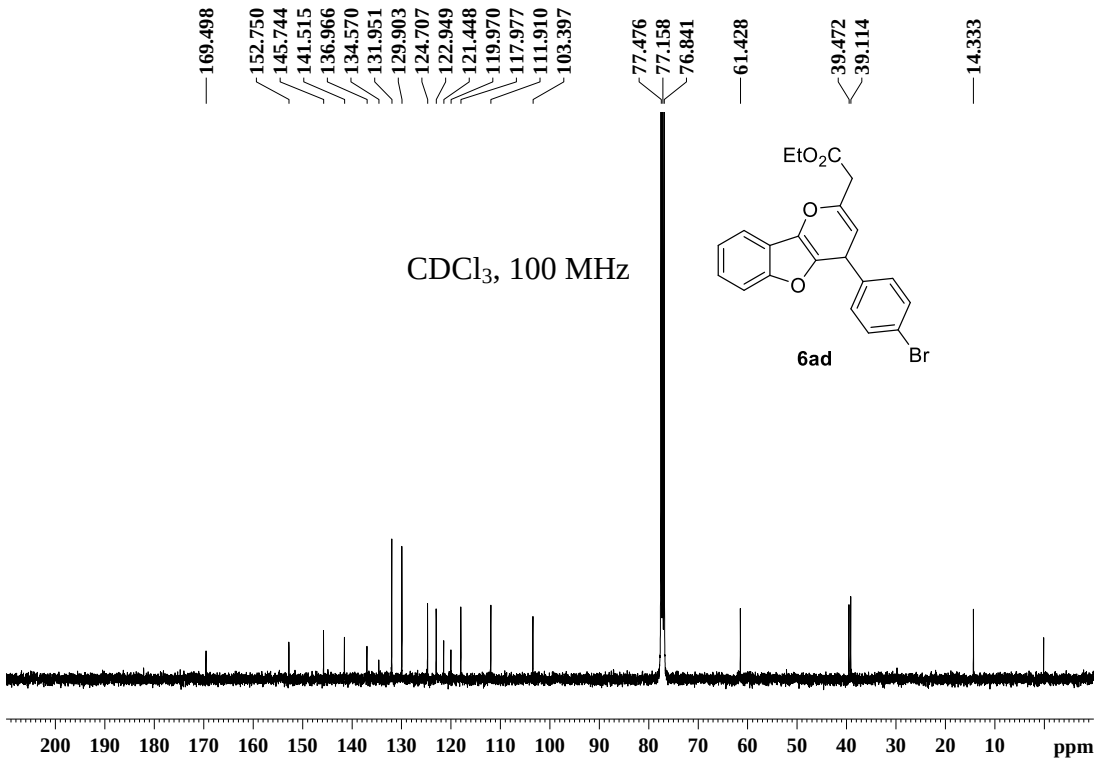

Figure S68: ^{13}C NMR spectrum of compound **6ad**

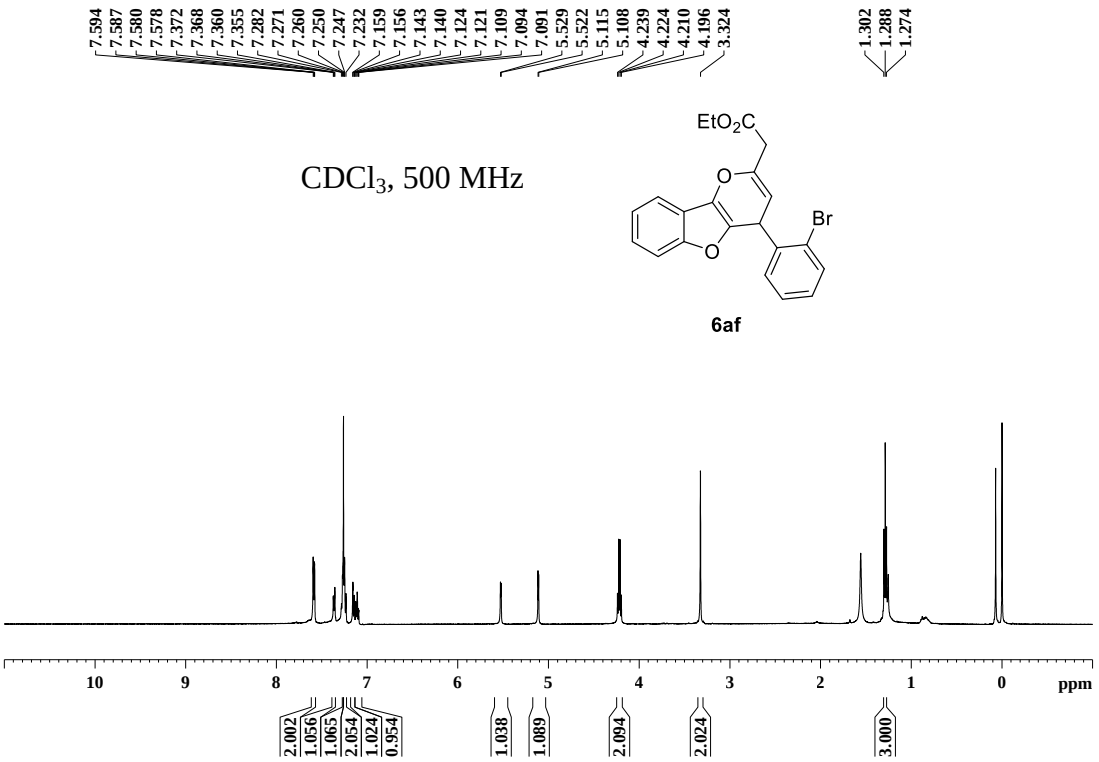

Figure S69: ^{1}H NMR spectrum of compound **6af**

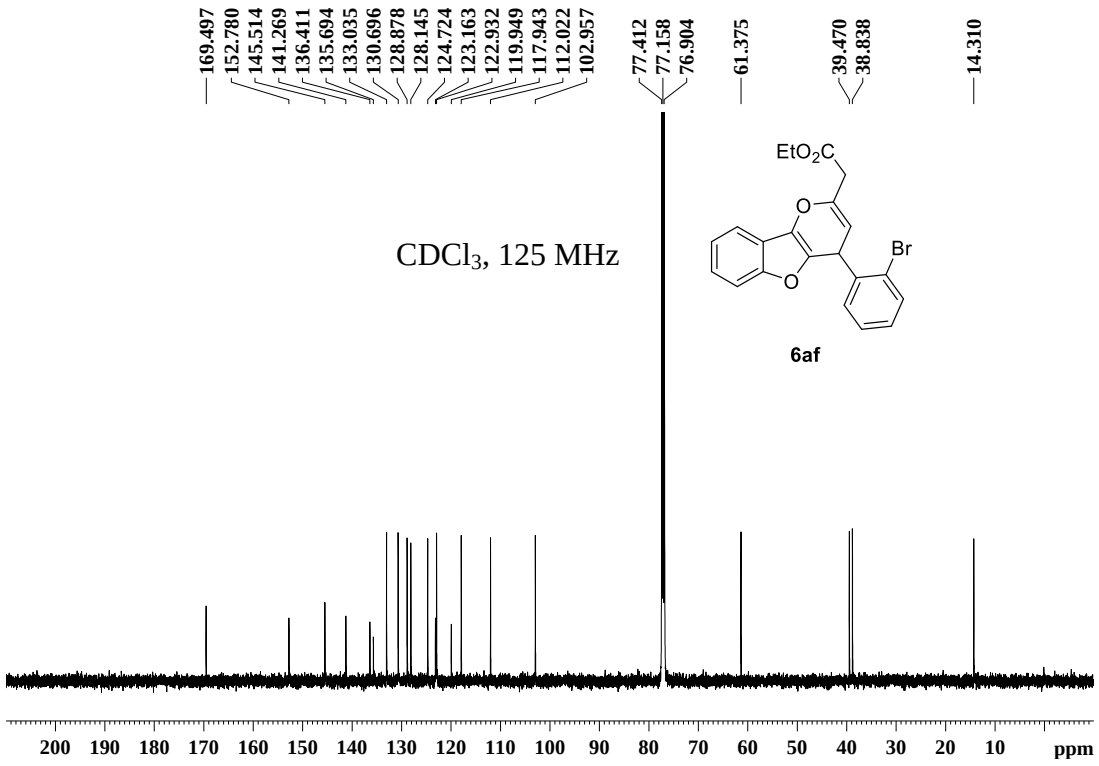

Figure S70: ^{13}C NMR spectrum of compound **6af**

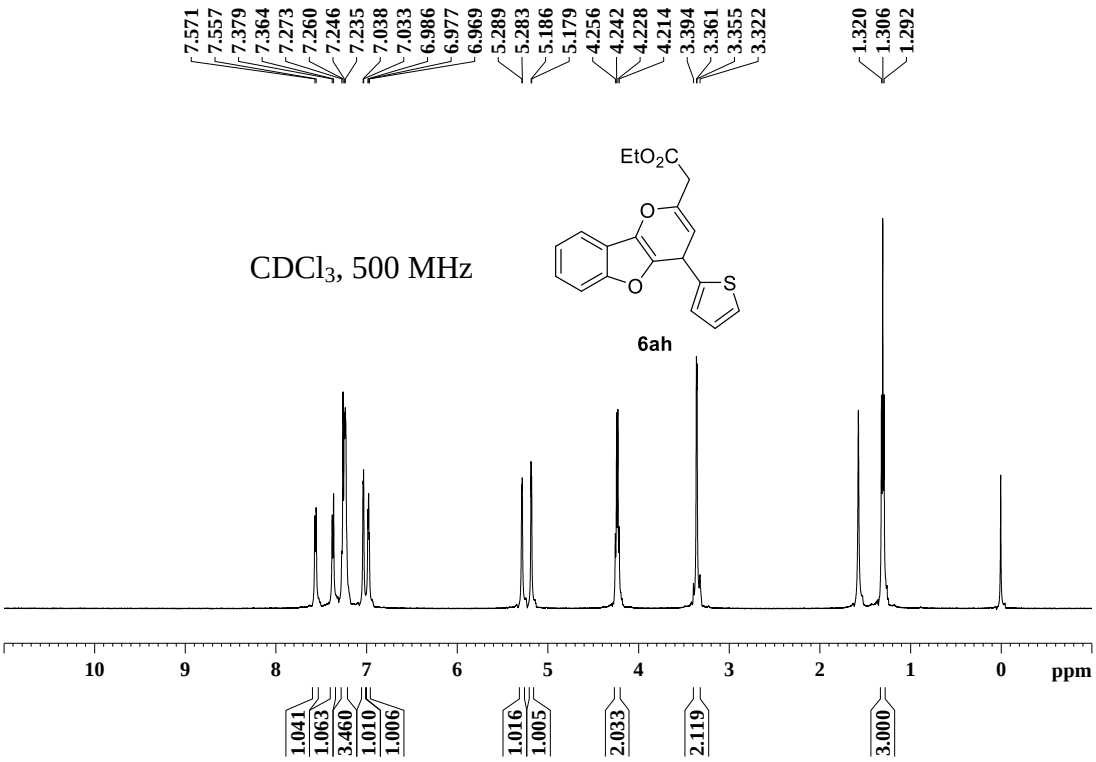

Figure S71: ^{1}H NMR spectrum of compound **6ah**

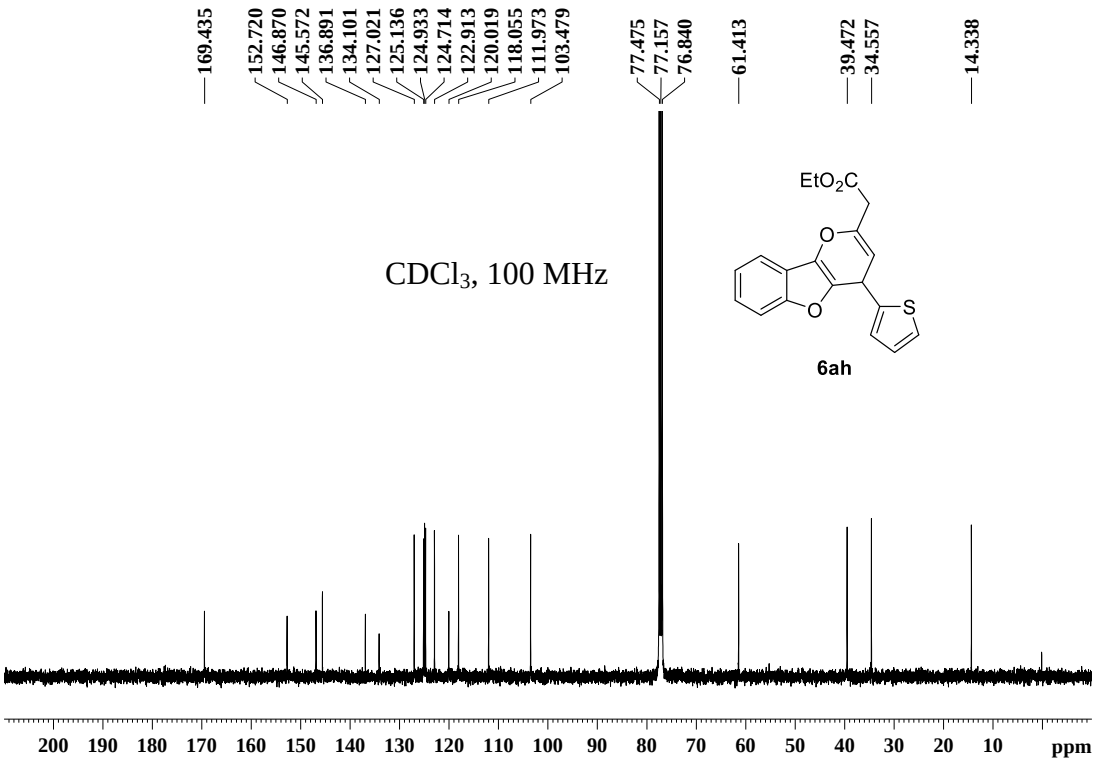

Figure S72: ^{13}C NMR spectrum of compound **6ah**

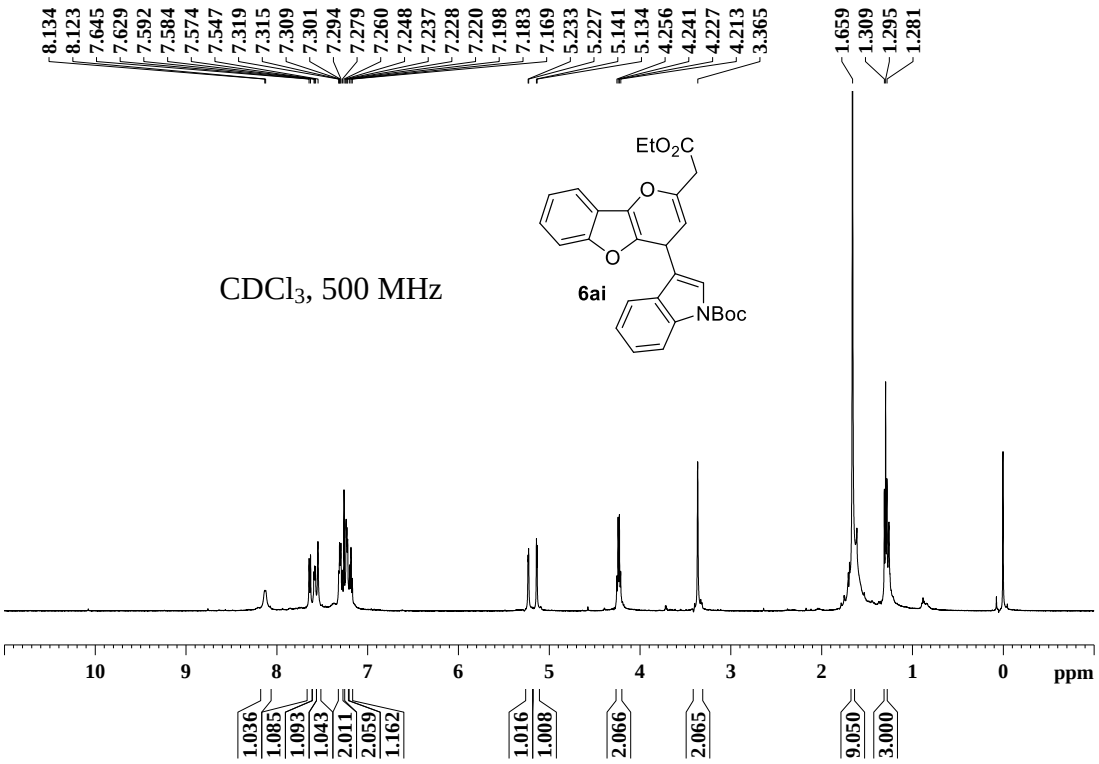

Figure S73: ^{1}H NMR spectrum of compound **6ai**

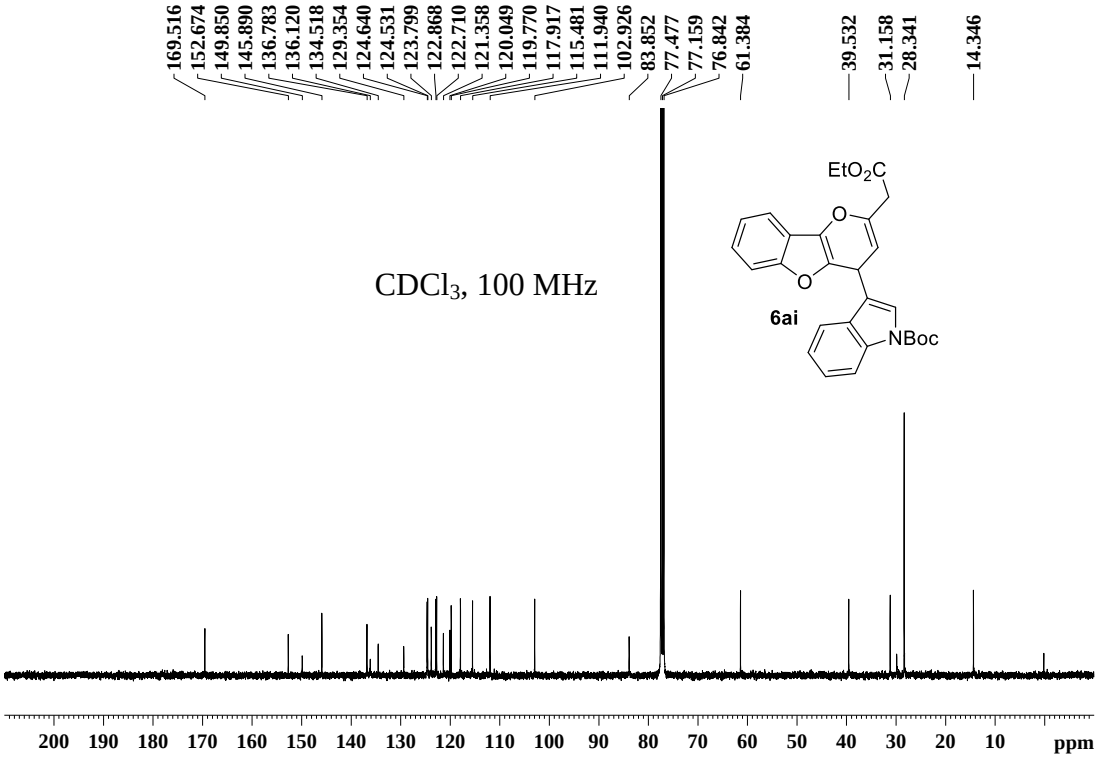

Figure S74: ^{13}C NMR spectrum of compound **6ai**

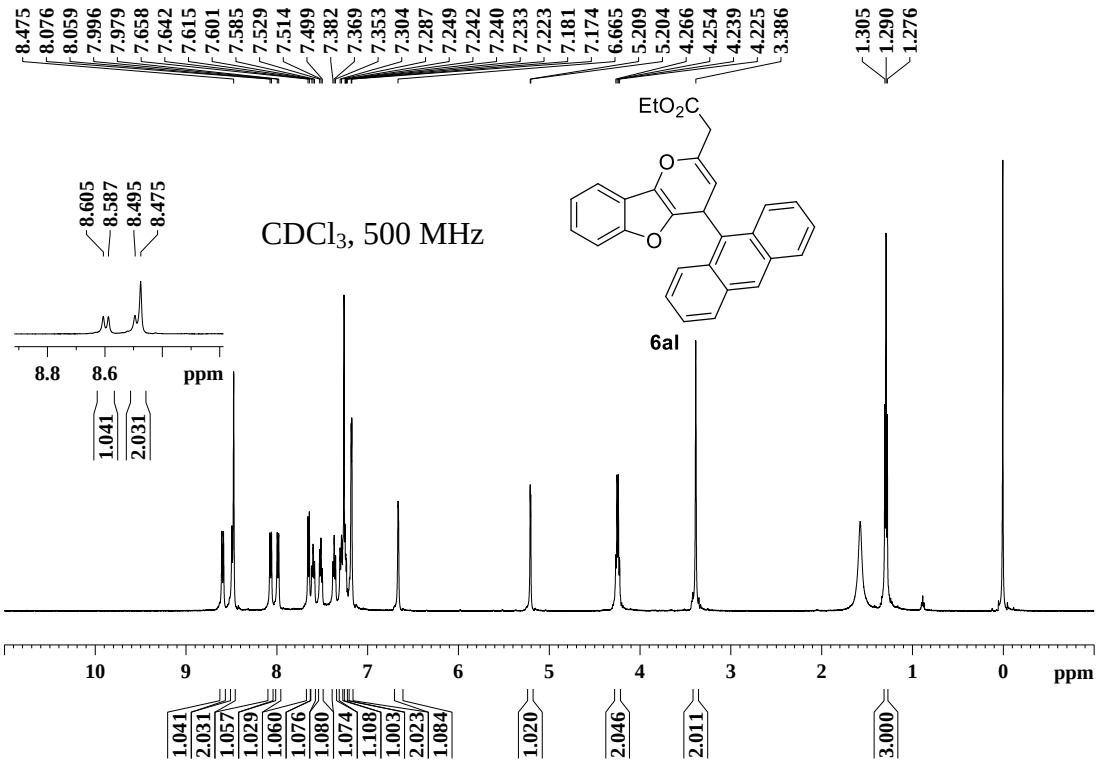

Figure S75: ^{1}H NMR spectrum of compound **6al**

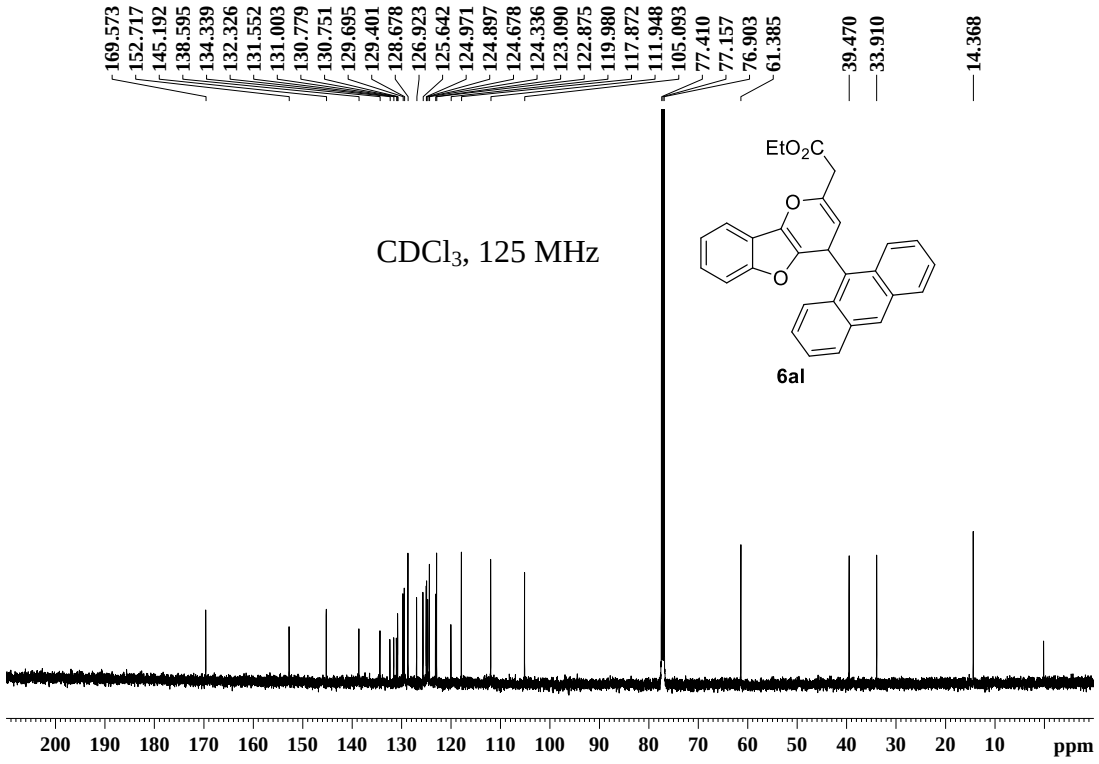

Figure S76: ^{13}C NMR spectrum of compound **6al**

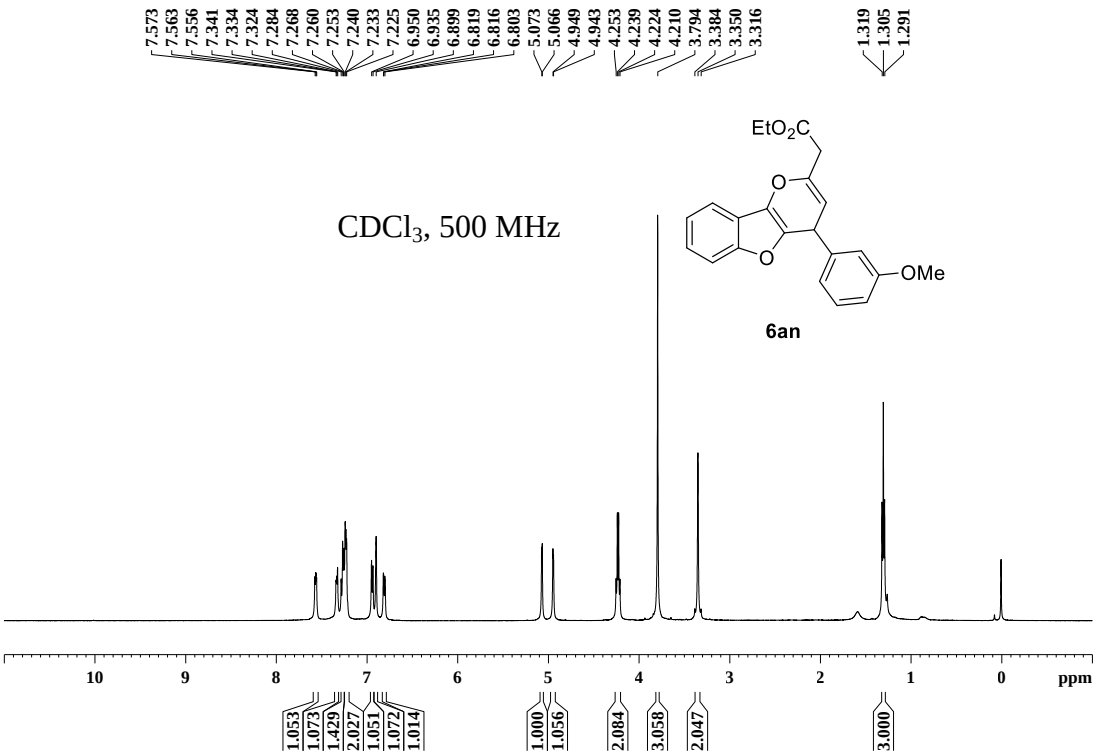

Figure S77: ^{1}H NMR spectrum of compound **6an**

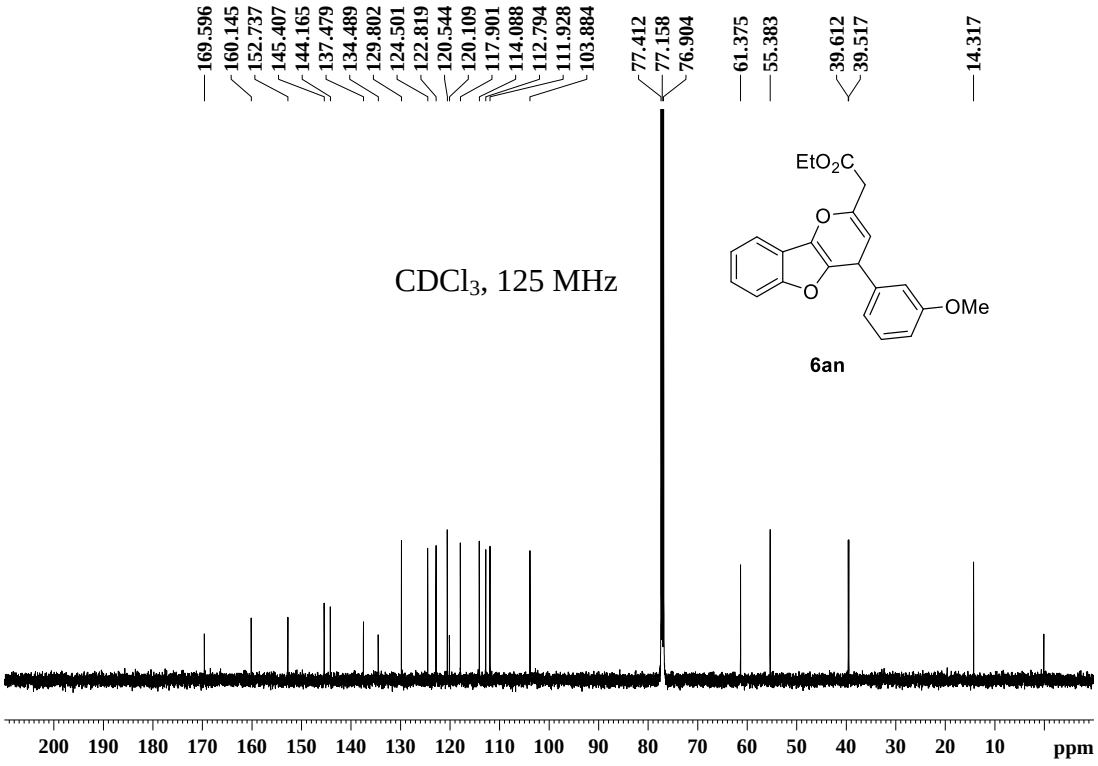

Figure S78: ^{13}C NMR spectrum of compound **6an**

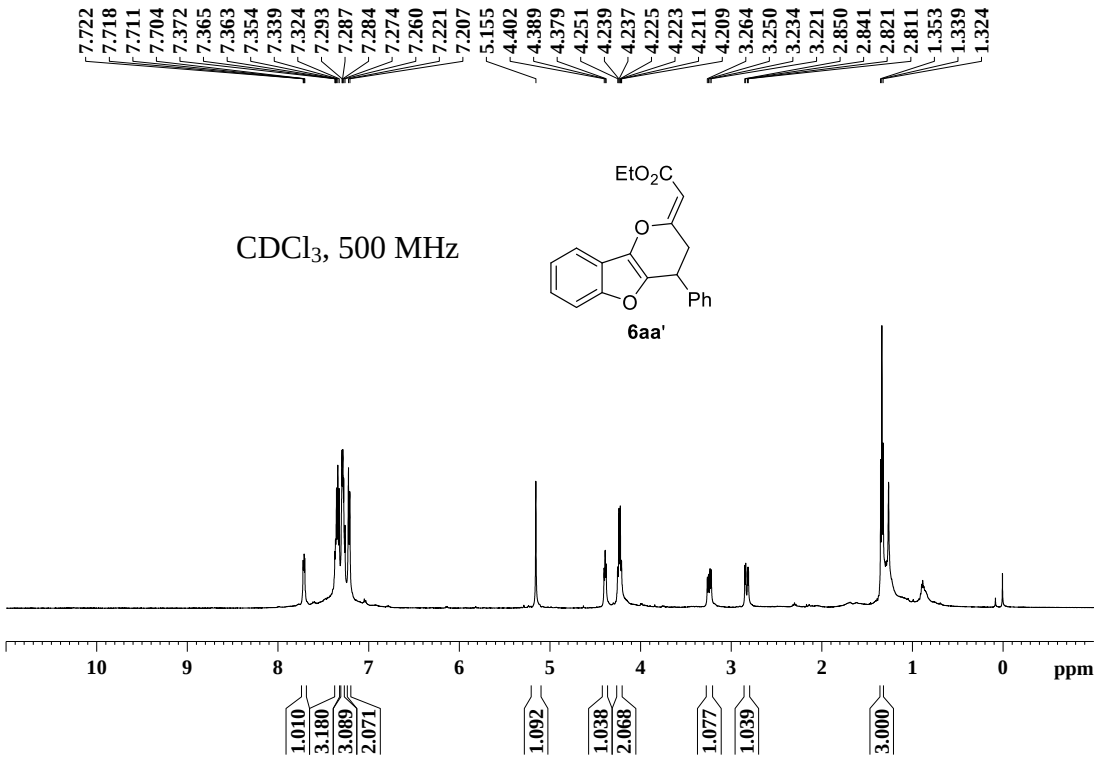

Figure S79: ^{1}H NMR spectrum of compound **6aa'**

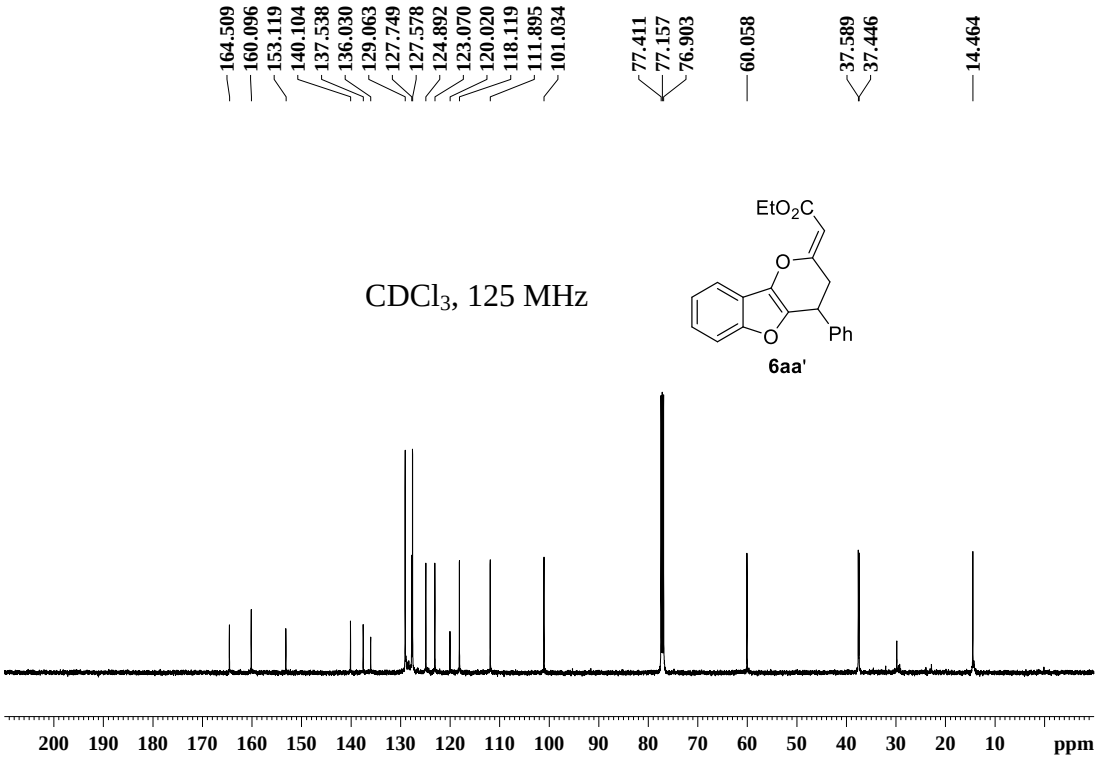

Figure S80: ^{13}C NMR spectrum of compound **6aa'**

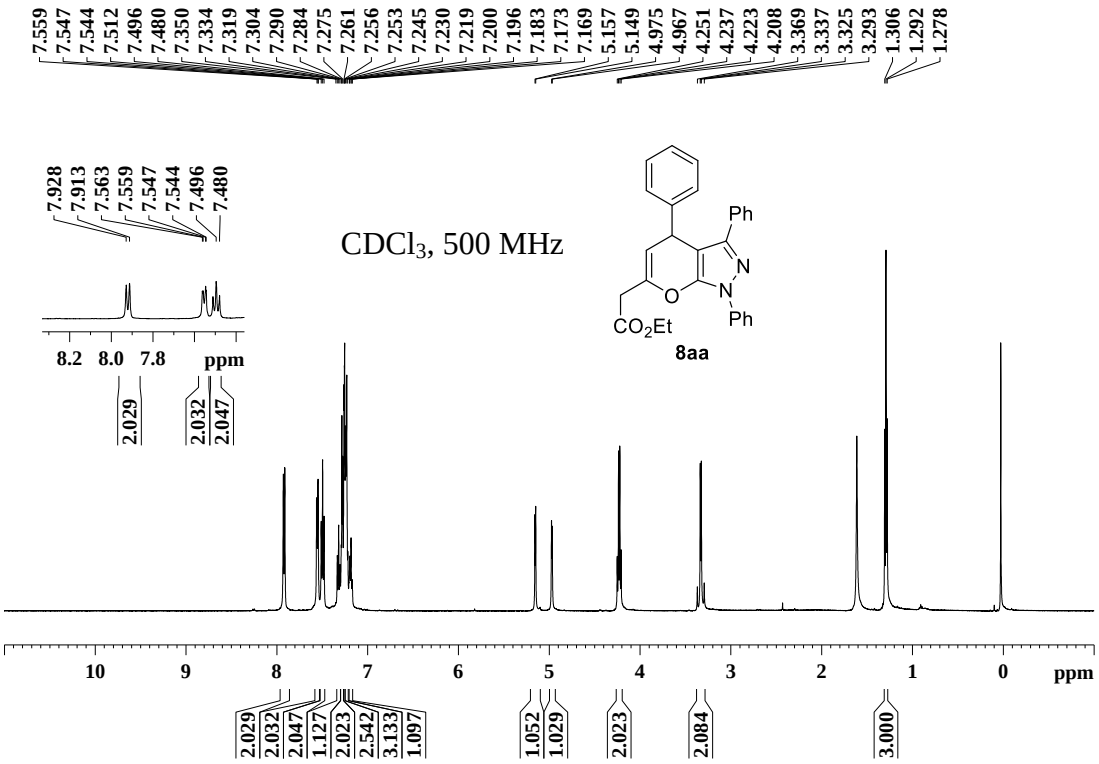

Figure S81: ^{1}H NMR spectrum of compound **8aa**

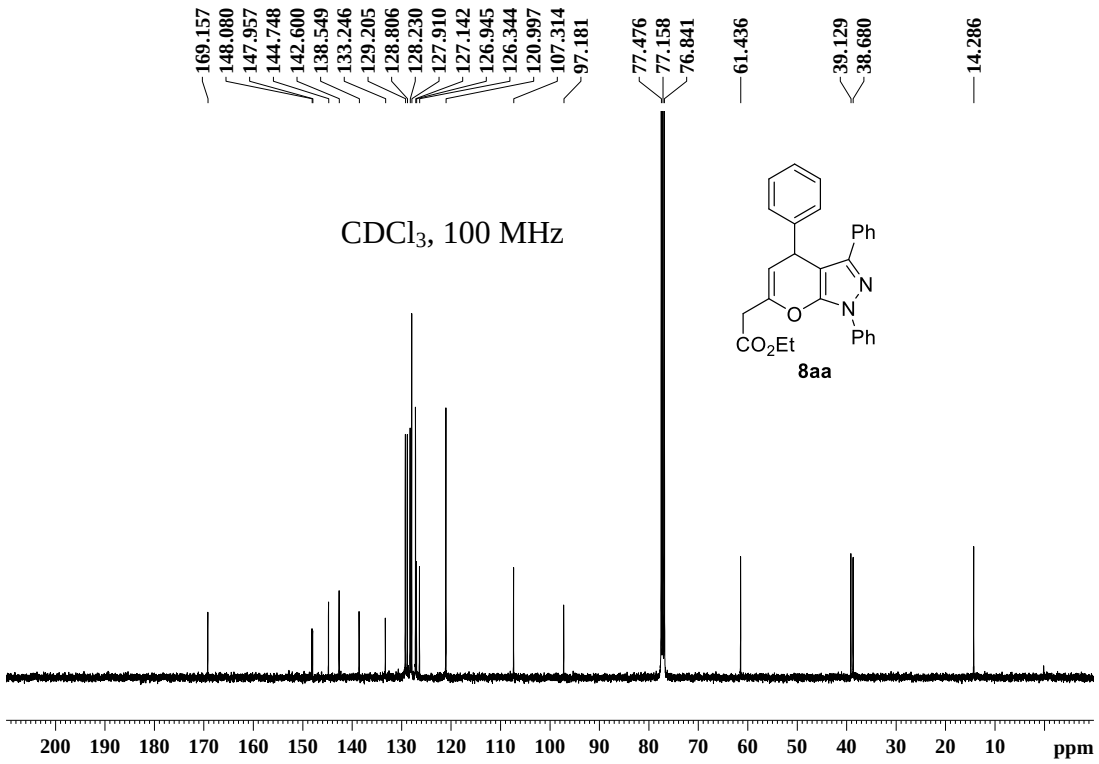

Figure S82: ^{13}C NMR spectrum of compound **8aa**

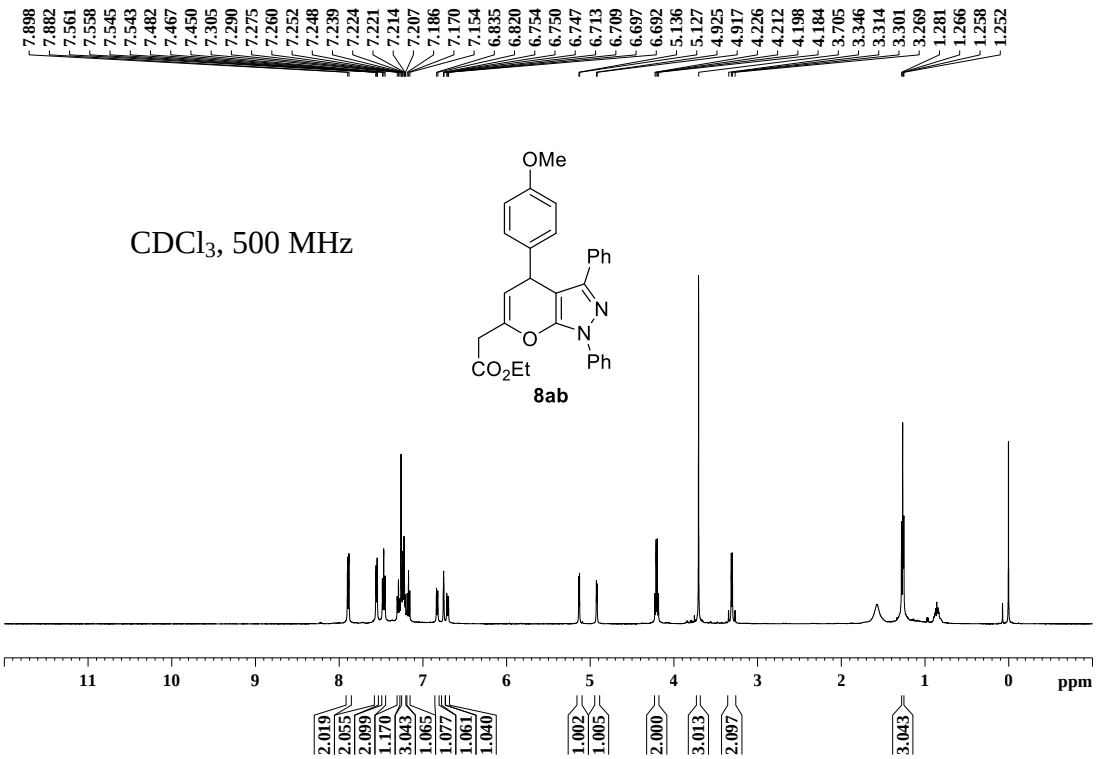

Figure S83: ^{1}H NMR spectrum of compound **8ab**

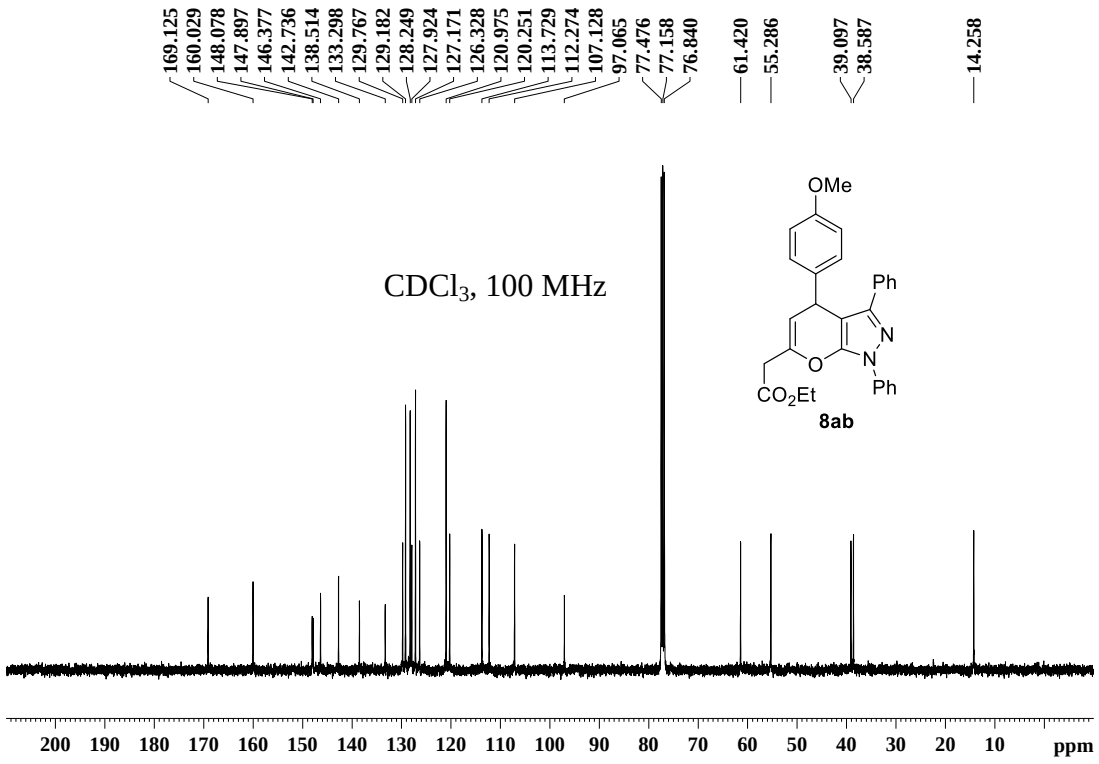

Figure S84: ^{13}C NMR spectrum of compound **8ab**

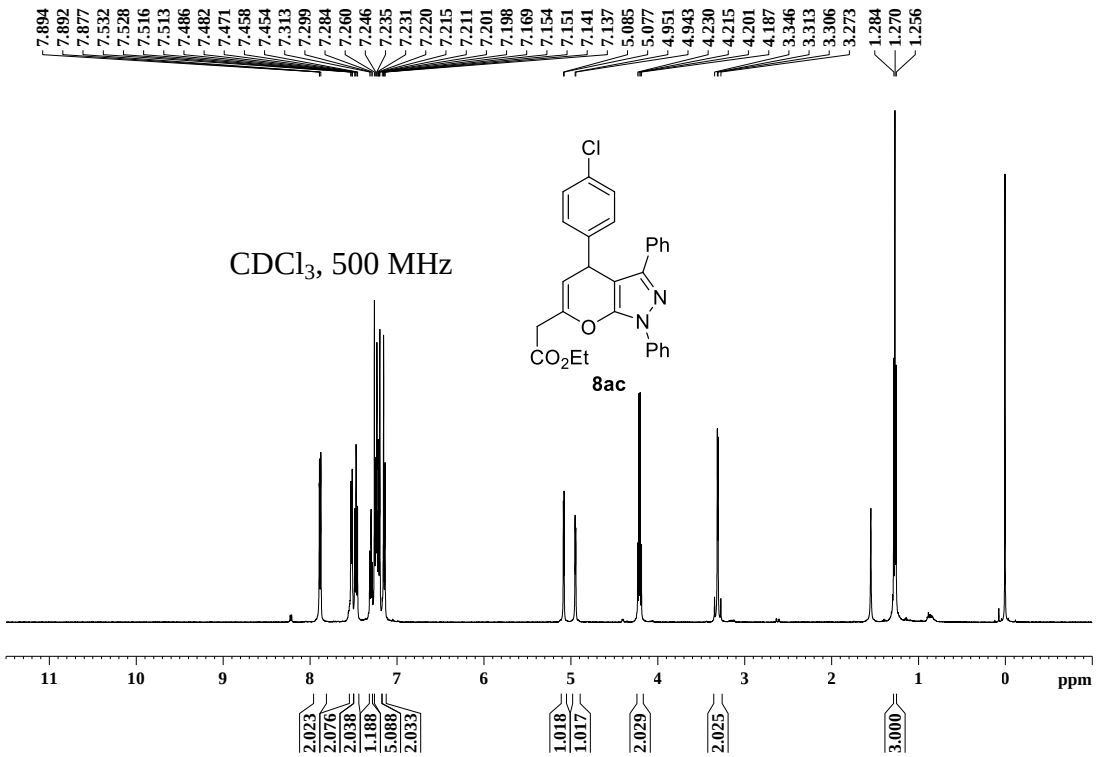

Figure S85: ^{1}H NMR spectrum of compound **8ac**

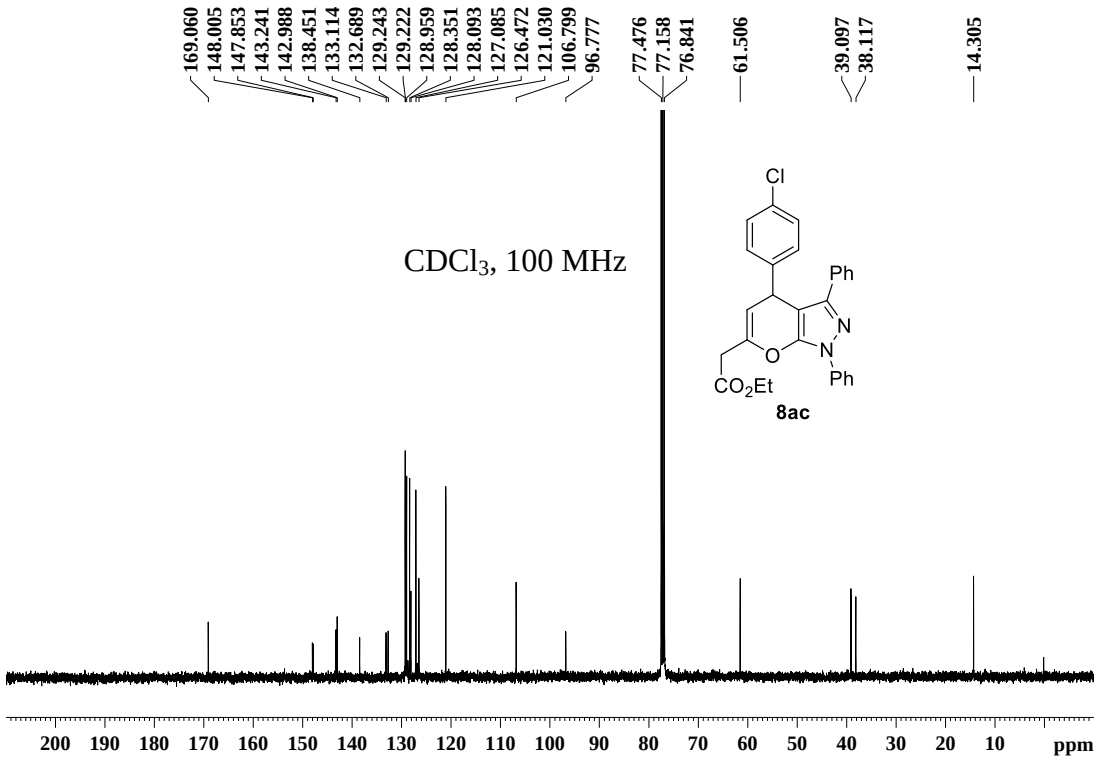

Figure S86: ^{13}C NMR spectrum of compound **8ac**

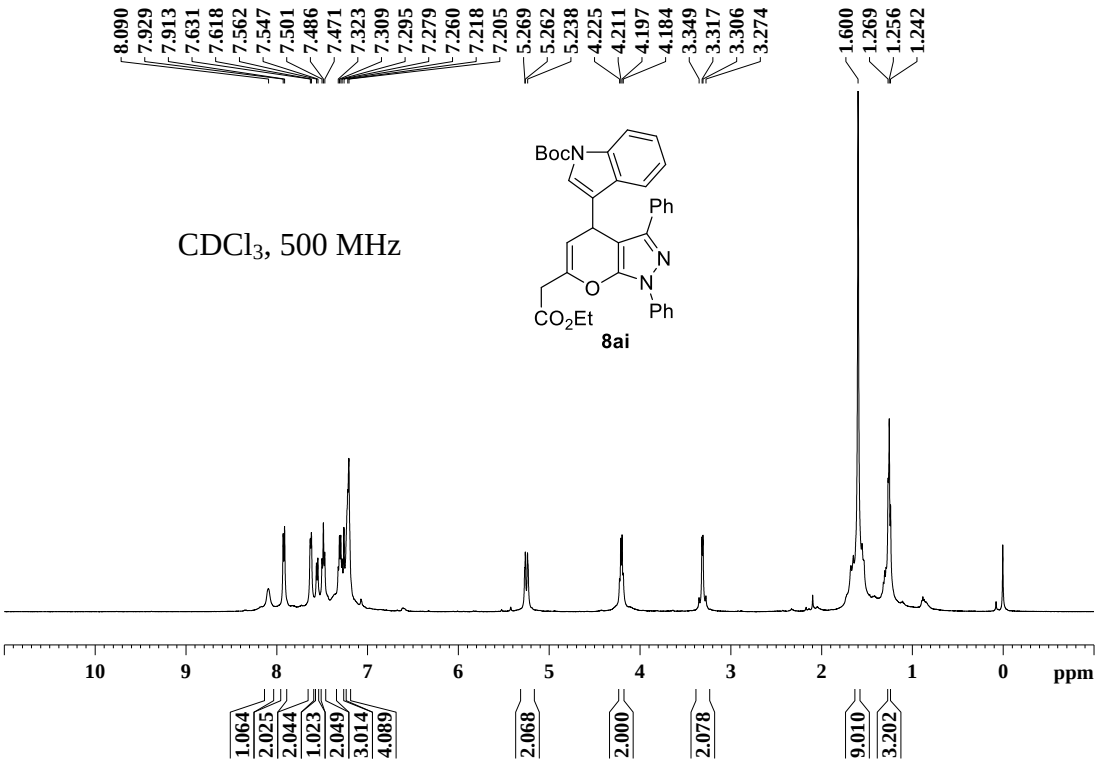

Figure S87: ^{1}H NMR spectrum of compound **8ai**

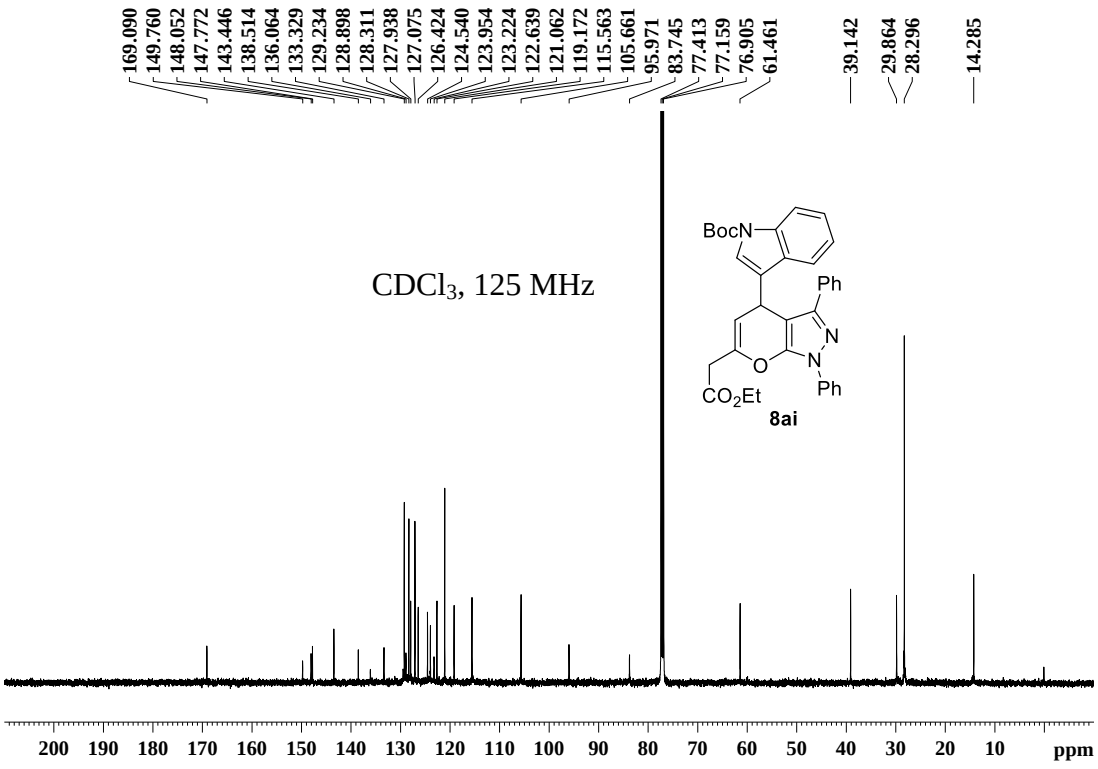

Figure S88: ^{13}C NMR spectrum of compound **8ai**

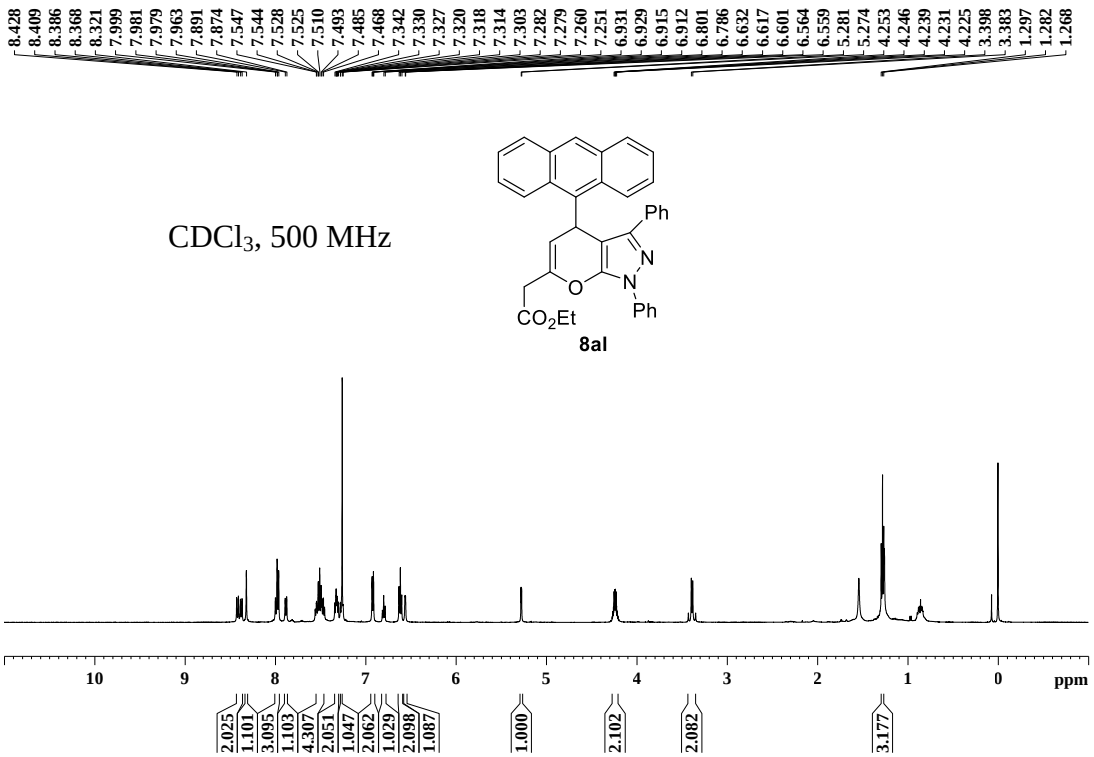

Figure S89: ^{1}H NMR spectrum of compound **8al**

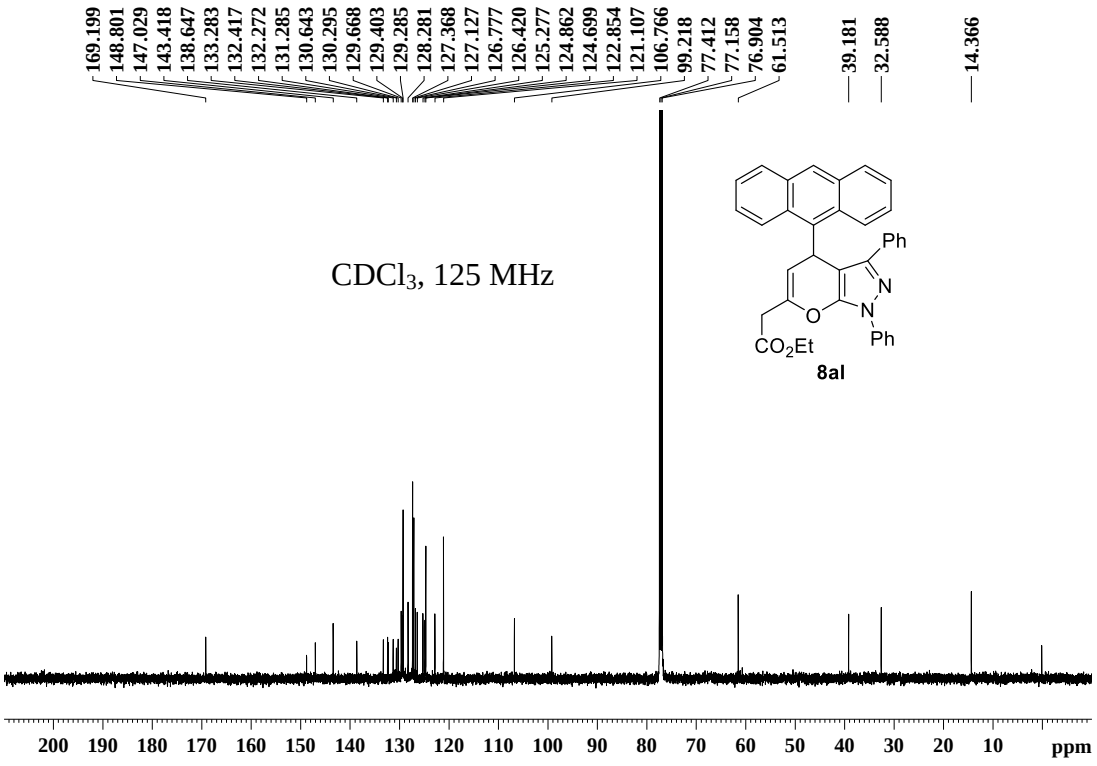

Figure S90: ^{13}C NMR spectrum of compound **8al**

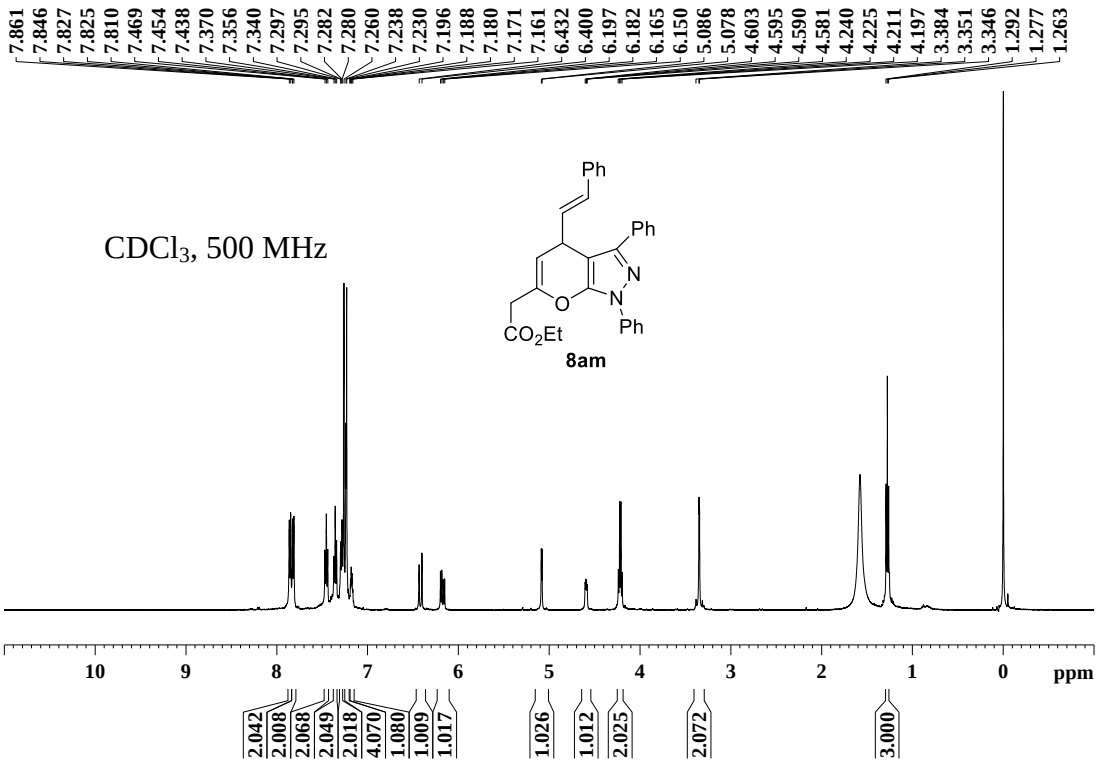

Figure S91: ^{1}H NMR spectrum of compound **8am**

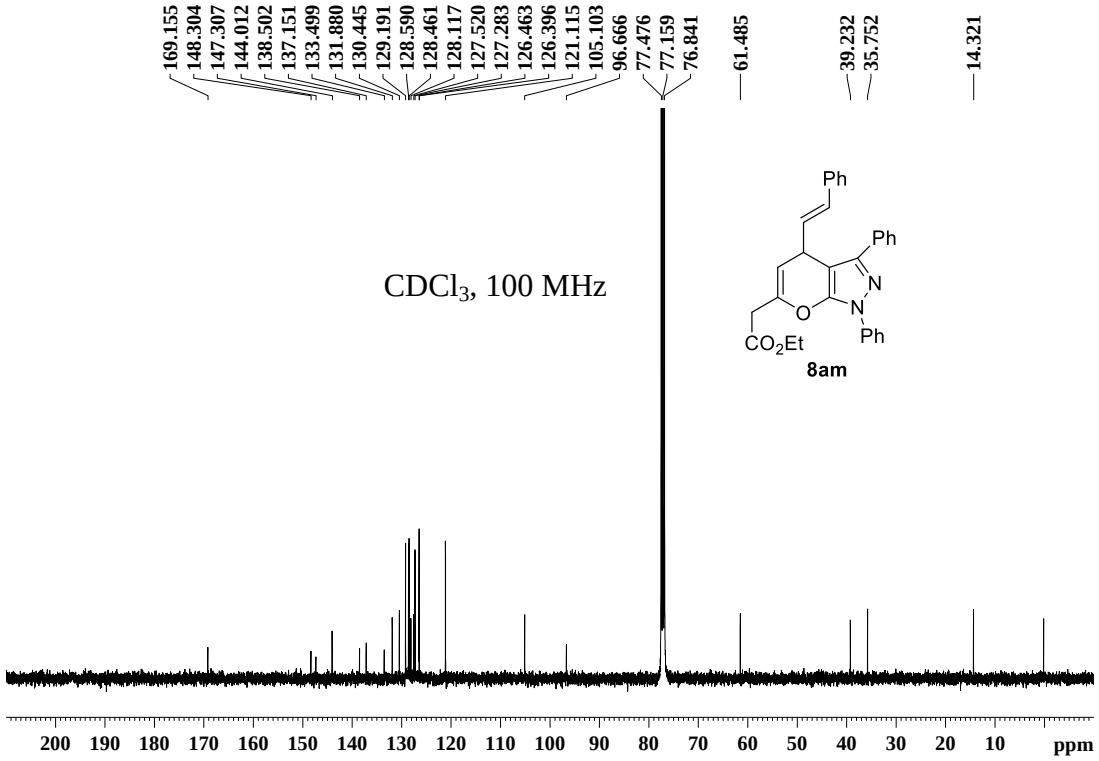

Figure S92: ^{13}C NMR spectrum of compound **8am**

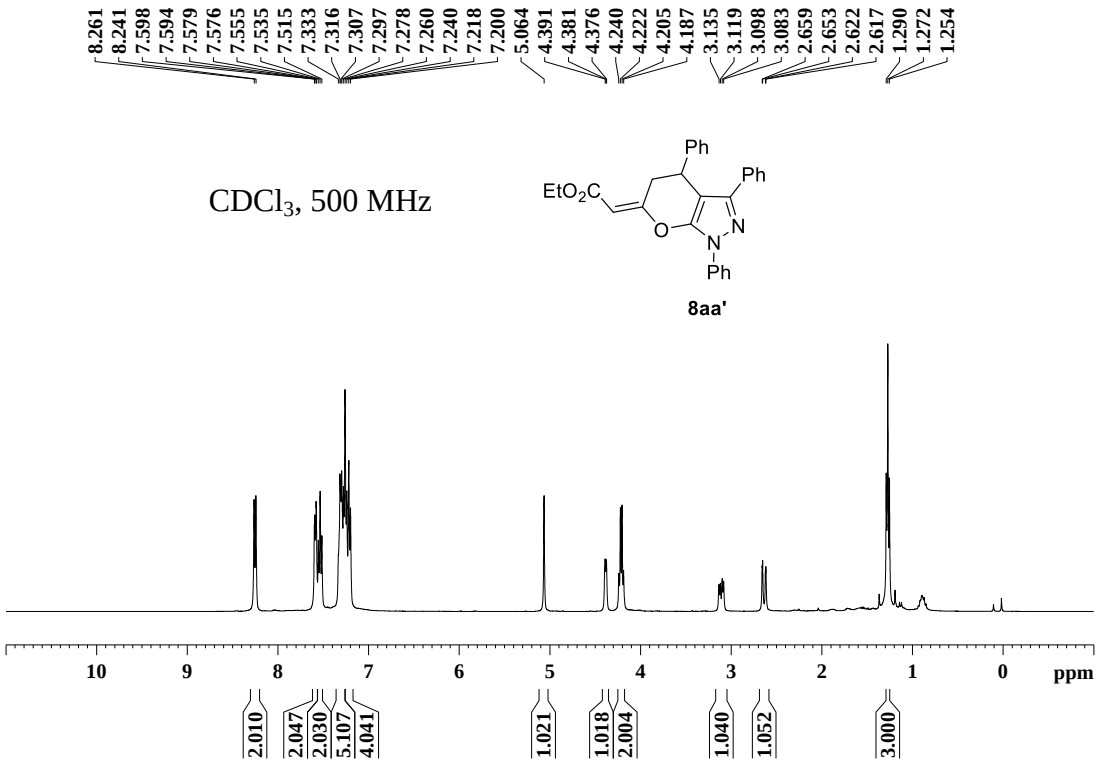

Figure S93: ^{1}H NMR spectrum of compound **8aa'**

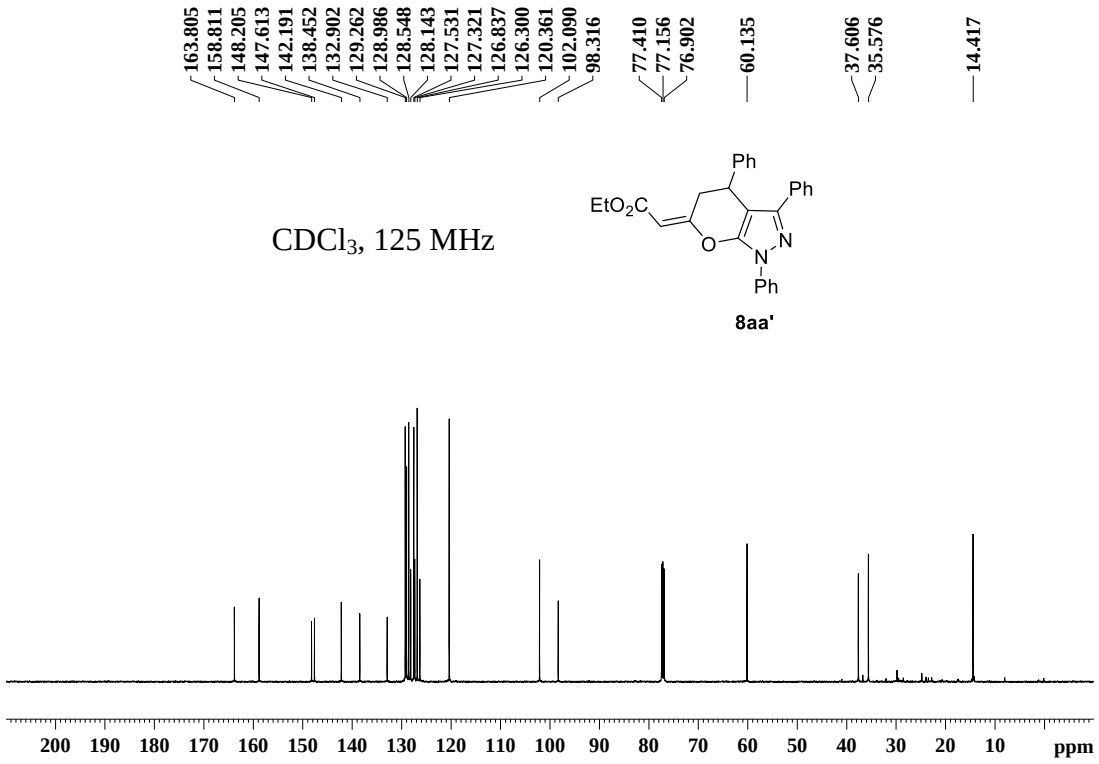

Figure S94: ^{13}C NMR spectrum of compound **8aa'**

(3) Reference:

1. (a) Sheldrick, G. M. SADABS, Siemens Area Detector Absorption Correction, University of Gottingen, Germany, 1996; (b) Sheldrick, G. M. SHELX97- 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 Xray System, WI, USA, 1999, version 5.10; (d) Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339; (e) Sheldrick, G.M. *Acta Cryst.* **2015**, *A71*, 3; *C71*, 3.