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$La(OTf)_3$ Catalysed One-Pot Synthesis of Pyrazole tethered Imidazo[1,2-*a*]azine Derivatives and Evaluation of their Light Emitting Properties

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Supporting Information

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General procedure for the synthesis of compounds (1a, 2a, 3a-b, 4a and 5a, 6a, 7a-b) as exemplified for ethyl 5-(4-fluorophenyl)-1-phenyl-1*H*-pyrazole-3-carboxylate and ethyl 3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (2a and 6a): To a stirred solution of β-diketoester, ethyl 2,4-dioxo-4-phenylbutanoate (**2**, 7.86 g, 33.02 mmol) in absolute EtOH (80 mL), phenylhydrazine (3.56 mL, 36.30 mmol) was added at room temperature. Thereafter, TFA (0.25 mL, 3.33 mmol) was added in catalytic amount and the reaction mixture was refluxed at 85 ^{o}C under stirring for 2 h. After the completion of reaction, as analysed by TLC, the EtOH was evaporated under reduced pressure and reaction mixture was neutralised with aqueous sodium bicarbonate and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford the desired pyrazole esters **2a** and **6a** (89%, 9.14 g). The curde product was sufficiently pure and processed as such for the next step.

General procedure for the synthesis of compounds (8a, 9a, 10a-b, 11a and 12a, 13a, 14a-b) as exemplified for (5-(4-fluorophenyl)-1-phenyl-1*H*-pyrazol-3-yl)methanol and (3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazol-5-yl)methanol (9a and 13a): To a stirred solution of pyrazole esters **2a** and **6a** (9.14 g, 29.5 mmol) in dry THF (200 mL), powdered LAH (1.68 g, 44.21 mmol) was added in small portions under nitrogen atmosphere. After complete addition of LAH at 0 ^{o}C, the reaction was stirred at room temperature till completion (30-45 min). After completion, the reaction was quenched by drop wise addition of saturated solution of NaOH at 0 ^{o}C under vigrous stirring in inert atmosphere. The reaction content was filtered through bed of celite and further washed with MeOH:DCM (05:95, v/v) to obtain a mixture of regioisomers **9a** and **13a** (91%, 7.19 g). Now, both the regioisomers of pyrazole alcohols **9a** and **13a** were separated through a silica gel column chromatography (60-120 mesh) using hexane:ethyl acetate (90:10, v/v) as an eluent. The (5-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-3-yl)methanol (**9a**) was obtained as a major product (68%, 4.92 g) while (3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl)methanol (**13a**) as a minor product (18%, 1.29 g).

General procedure for the synthesis of compounds (15a, 16a, 17a-b, 18a and 19a, 20a, 21a-b) as exemplified for 5-(4-fluorophenyl)-1-phenyl-1*H*-pyrazole-3-carbaldehyde (16a): To a stirred solution of pyrazole alcohol **9a** (4.92 g, 18.29 mmol) in dry DCM (50 mL), powdered MnO_2 (18.87 g, 219.42 mmol) was added in small portions and stirred actively at room temperature. Thereafter, the completion of the reaction, the reaction mixture was filtered through a bed of celite under suction to get a yellow filtrate. The residue over celite bed was further washed with dichloromethane. The filtrate was evaporated under reduce pressure to yield the crude solid product which was triturated with hexane to get the analytically pure product **16a** (86%, 4.21 g) as a white solid.

General procedure for the synthesis of compounds (22-23a) as exemplified for 5-(3-bromophenyl)-4-iodo-1-phenyl-1*H*-pyrazole-3-carbaldehyde (22a): To a stirred solution of

compound **17a** (1.0 g, 3.55 mmol) in dry $CHCl_3$ (10 mL), K_2CO_3 (1.47 g, 10.65 mmol) was added portionwise and stirred the reaction at room temperature for 20-30 min. Thereafter, iodine monochloride (0.23 mL, 4.35 mmol) dissolved in dry $CHCl_3$ (10 mL) was added dropwise to the reaction mixture and the stirring was continued at room temperature for 12-16 h. On completion of the reaction, as analysed by TLC, cold water was added to the reaction mixture and the product was extracted with $CHCl_3$. Finally, the organic layer was washed with the aqueous solution of sodium thiosulphate and dried over anhydrous Na_2SO_4, evaporated under reduced pressure to get the product, which was further triturated with hexane to obtain analytically pure product **22a** (91%, 1.31 g).

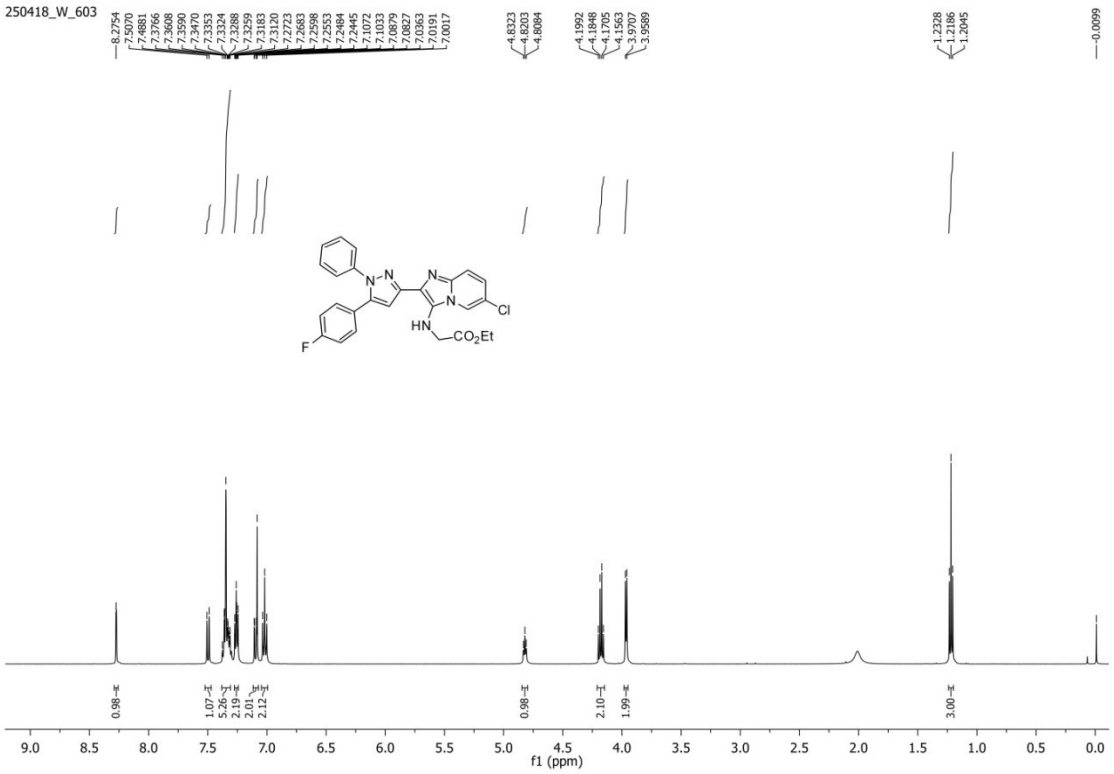


Figure S1. ^{1}H-NMR spectrum of **16aGY.**

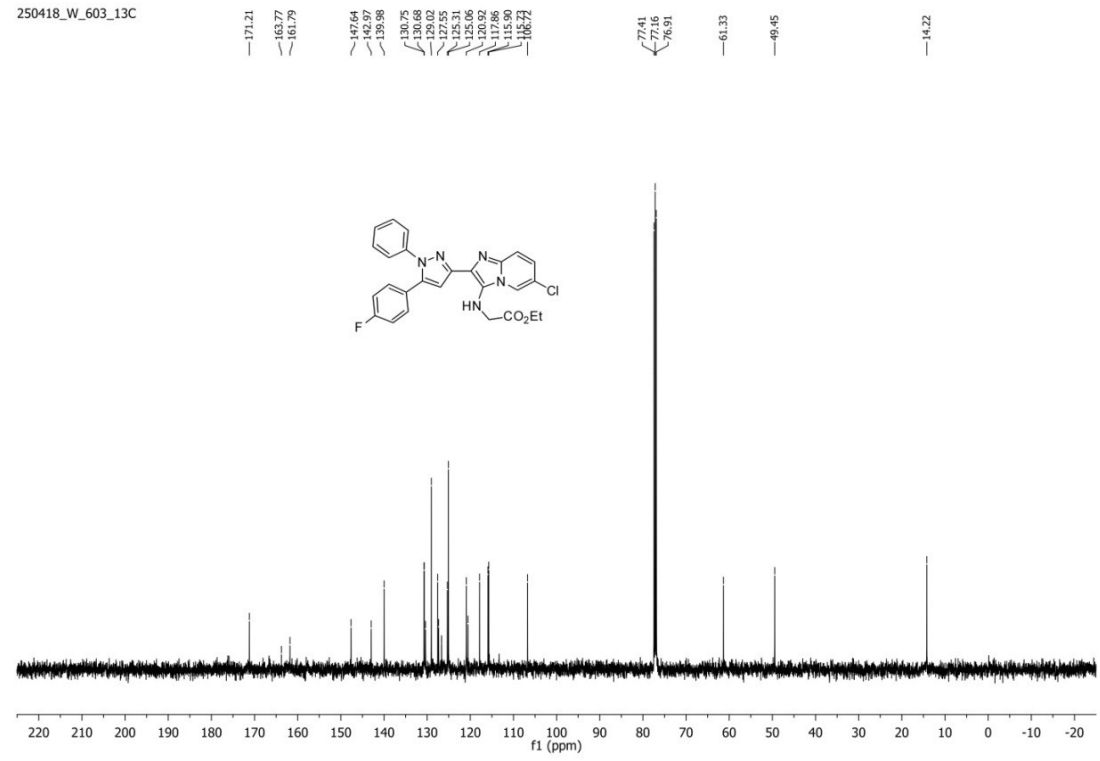


Figure S2. ^{13}C-NMR spectrum of **16aGY.**

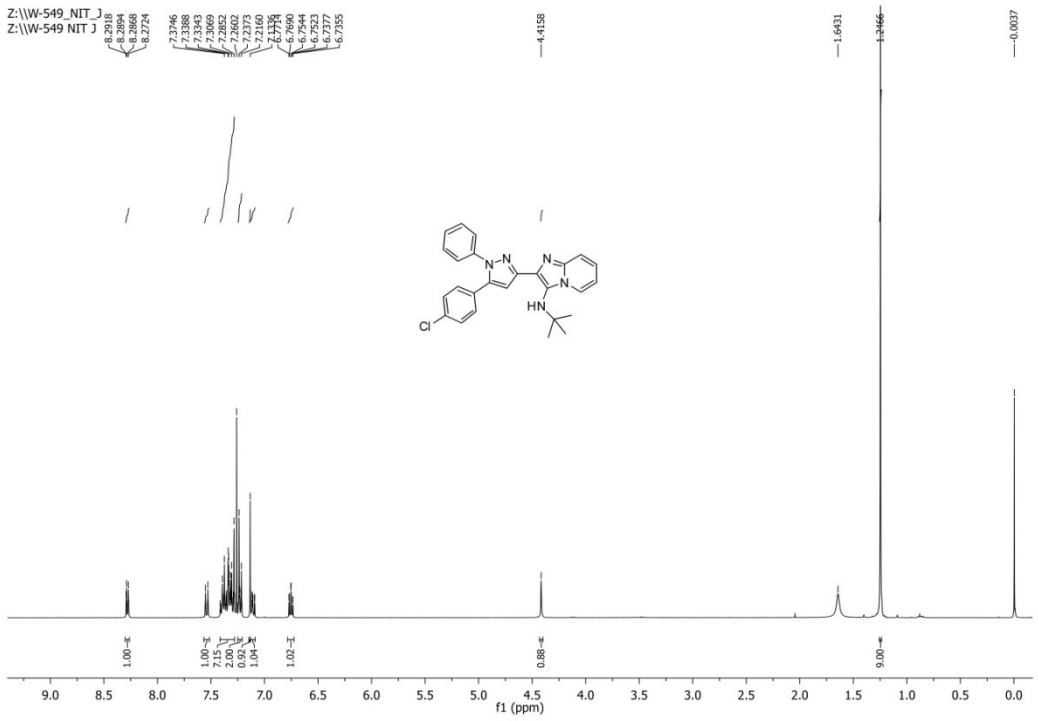


Figure S3. ^{1}H-NMR spectrum of **17aAX.**

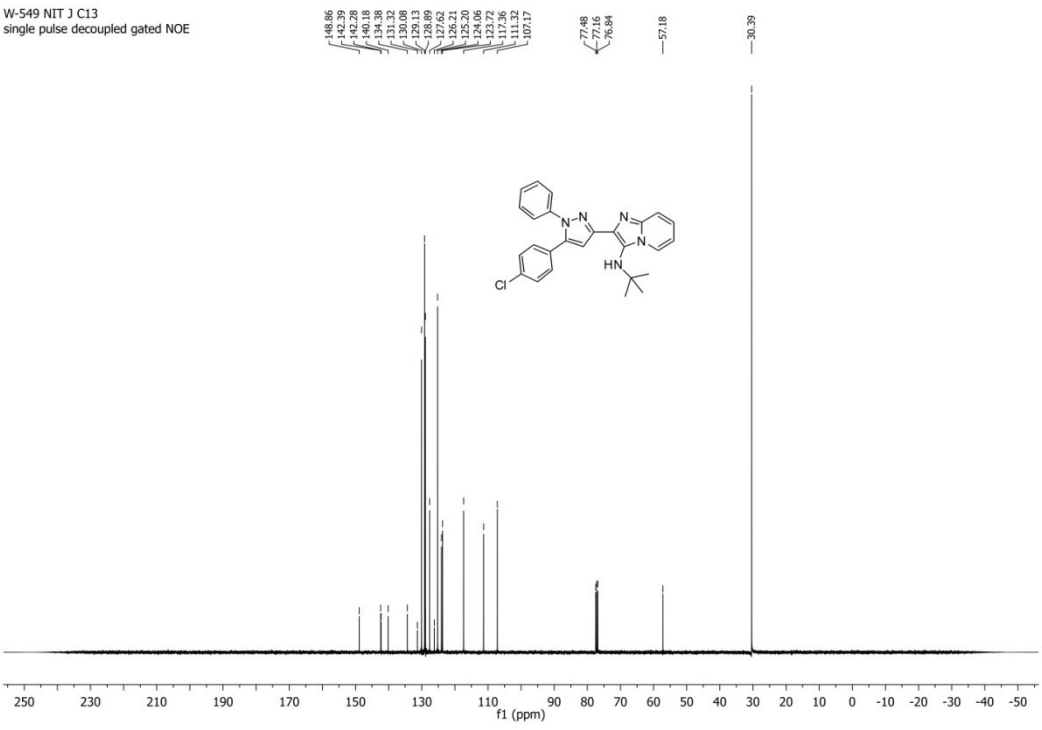


Figure S4. ^{13}C-NMR spectrum of **17aAX.**

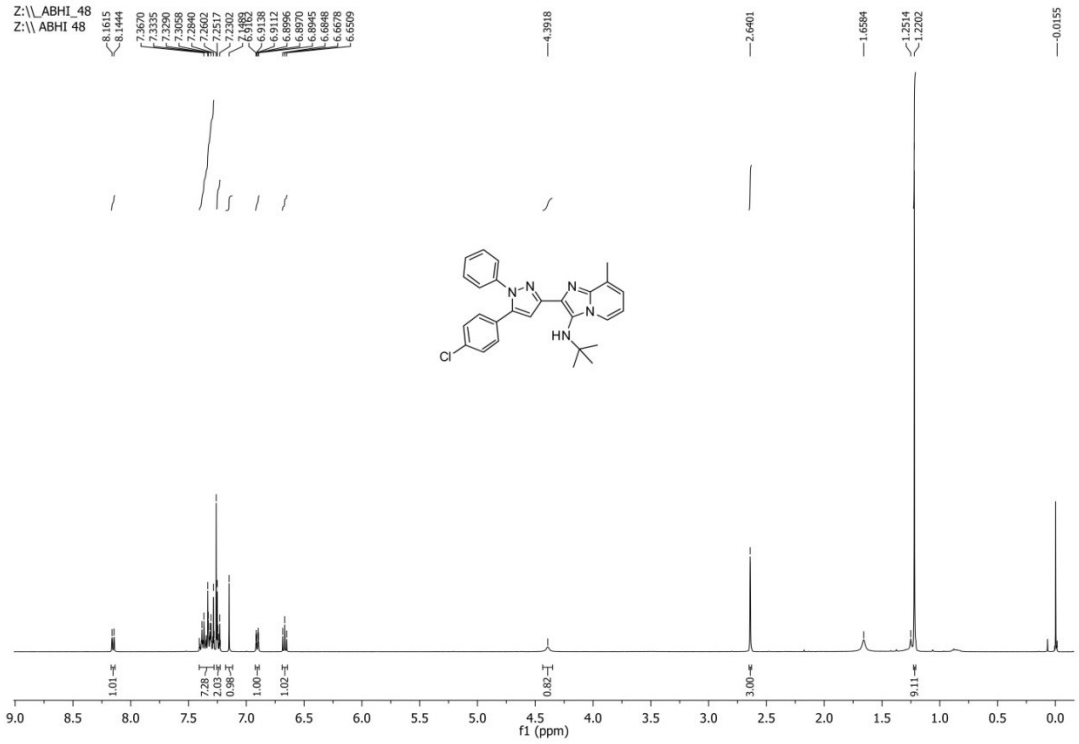


Figure S5. ^{1}H-NMR spectrum of **17aBX.**

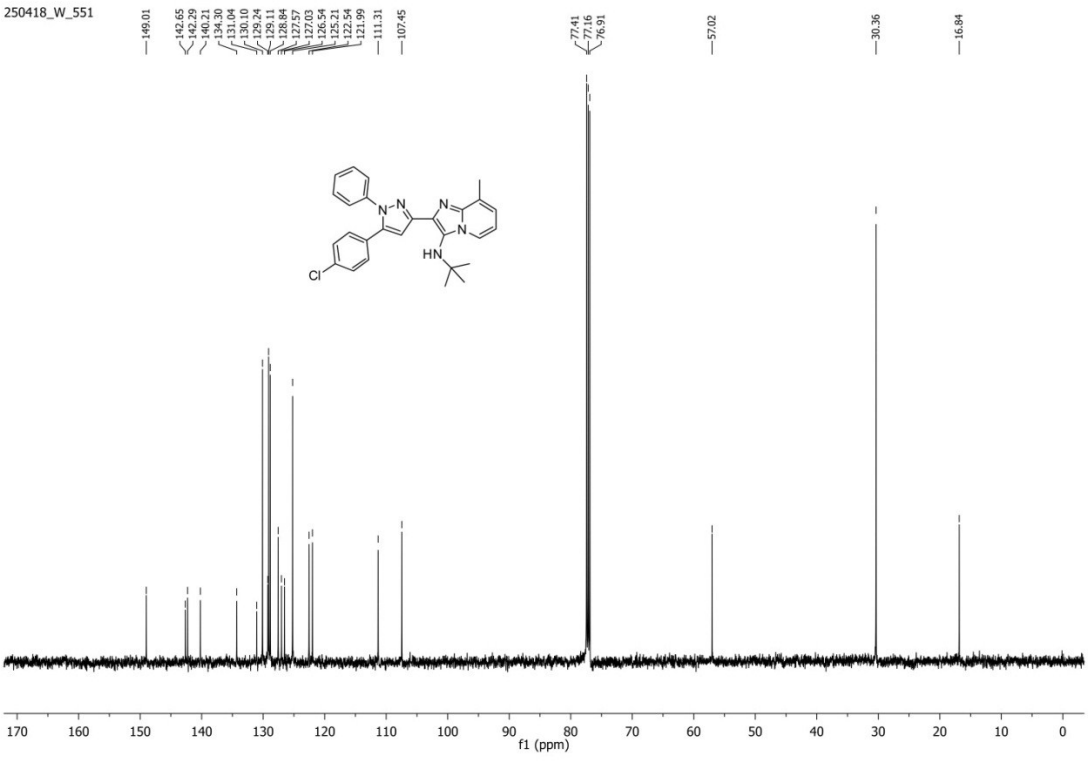


Figure S6. ^{13}C-NMR spectrum of **17aBX.**

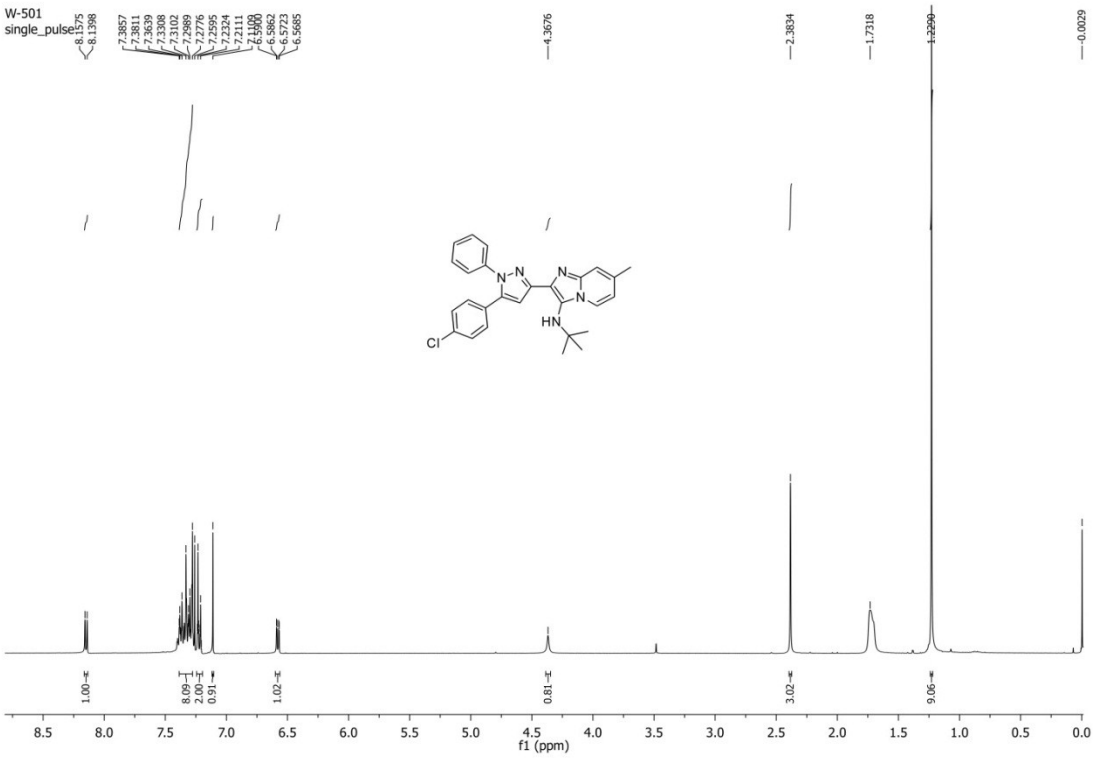


Figure S7. ^{1}H-NMR spectrum of **17aCX.**

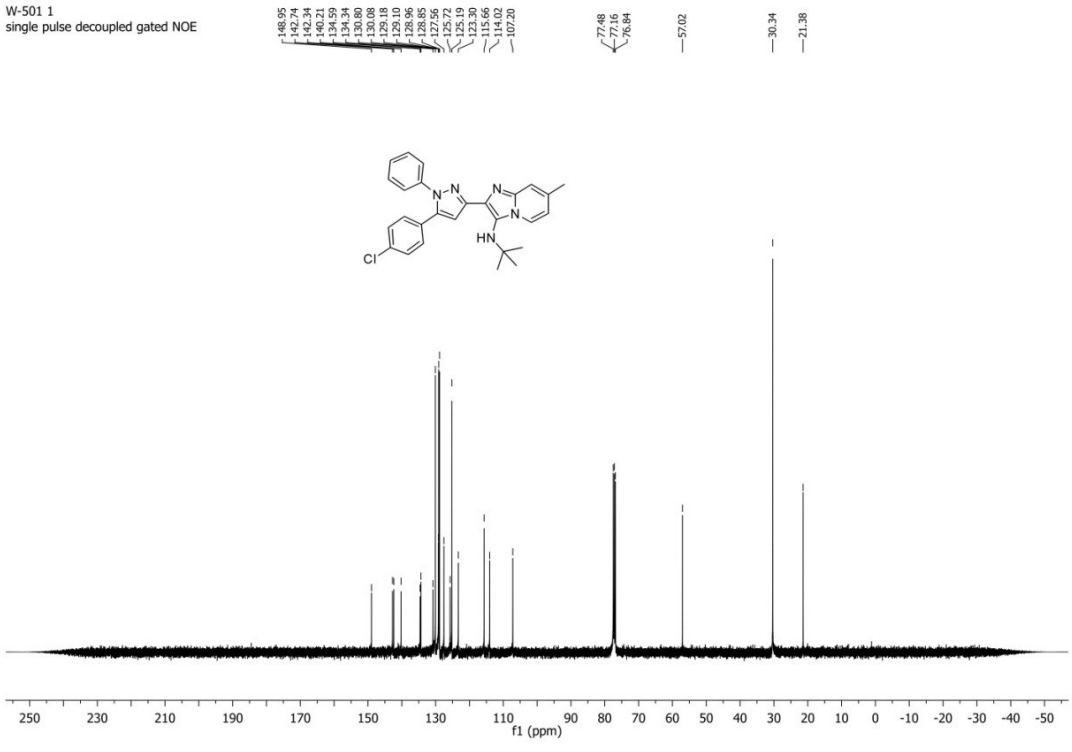


Figure S8. ^{13}C-NMR spectrum of **17aCX.**

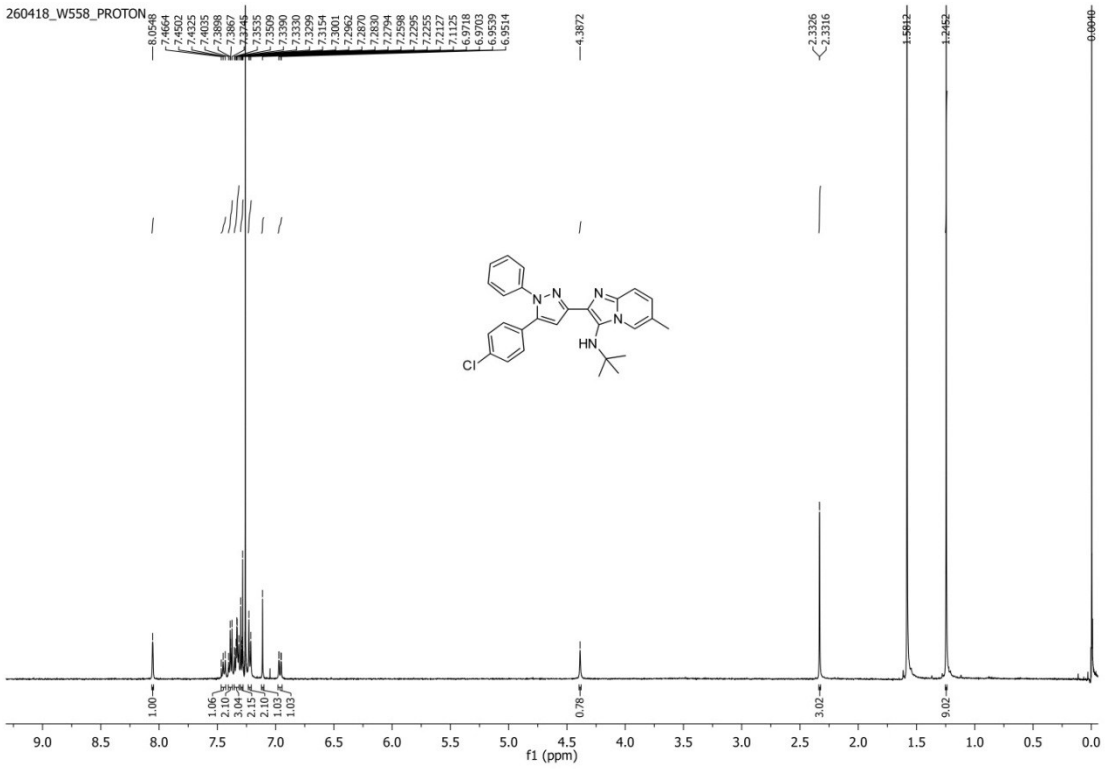


Figure S9. ^{1}H-NMR spectrum of **17aDX.**

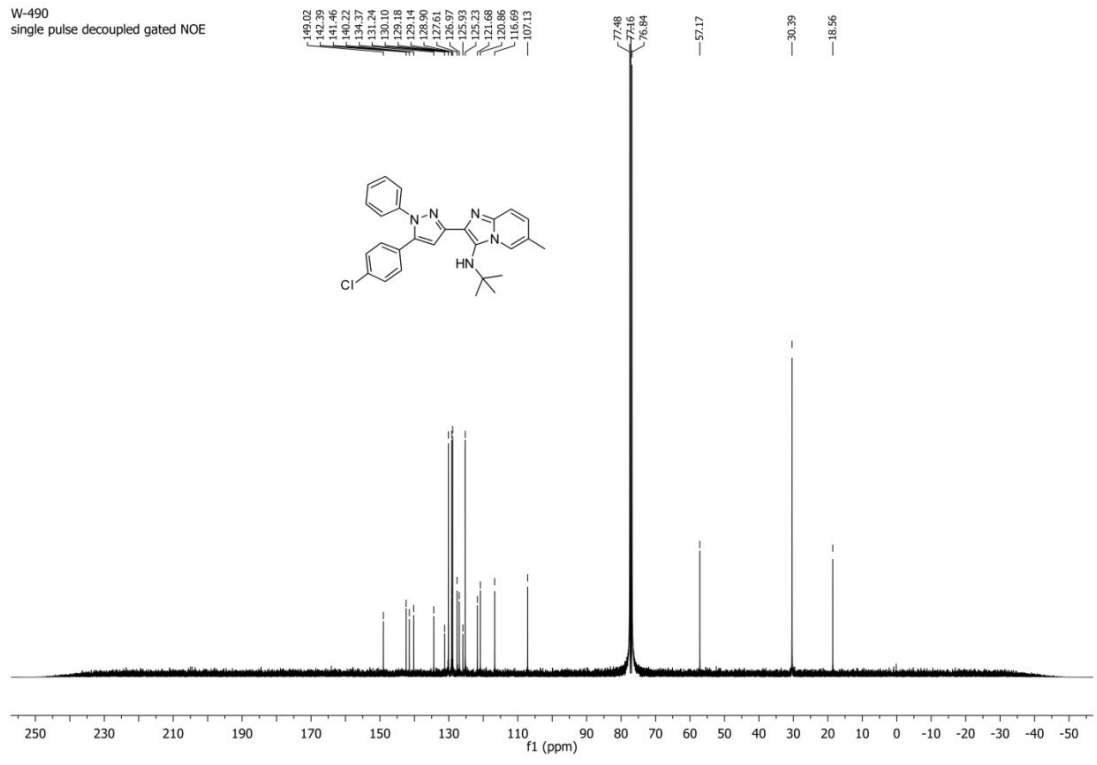


Figure S10. ^{13}C-NMR spectrum of **17aDX.**

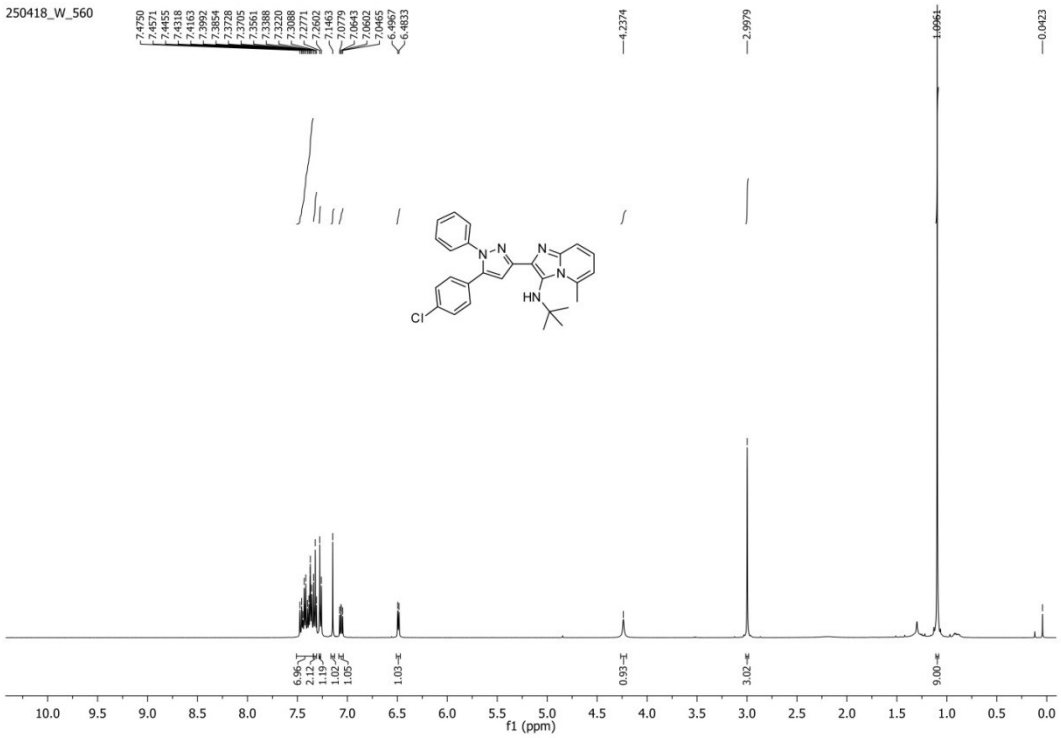


Figure S11. ^{1}H-NMR spectrum of **17aEX.**

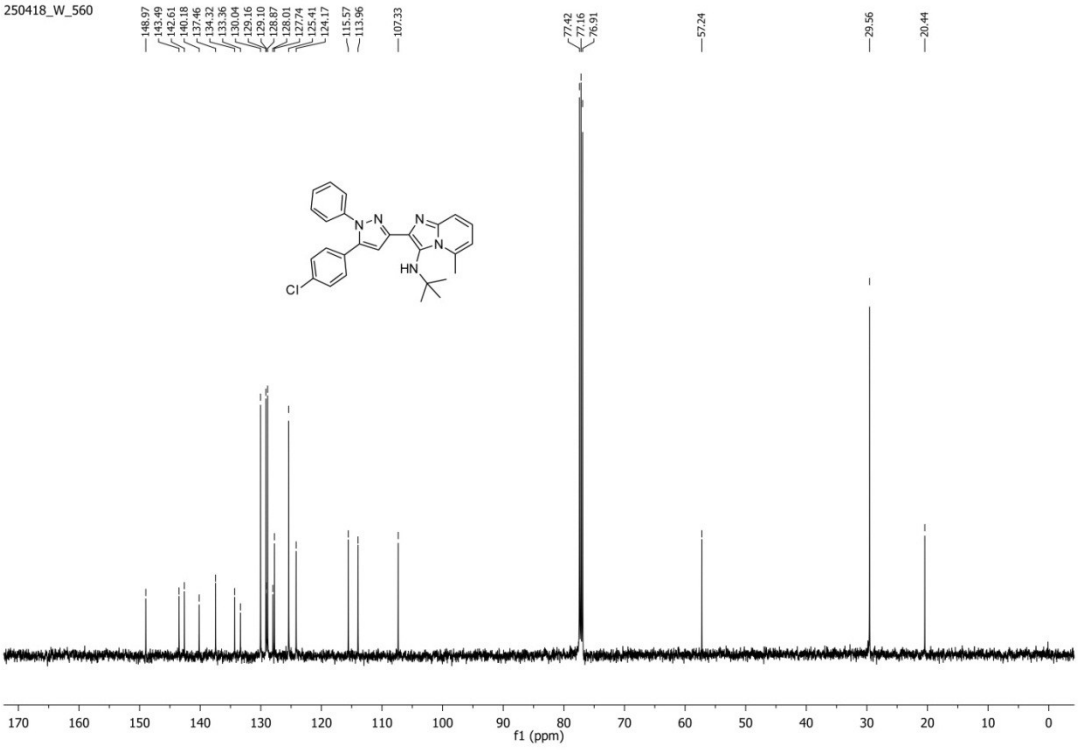


Figure S12. ^{13}C-NMR spectrum of **17aEX.**

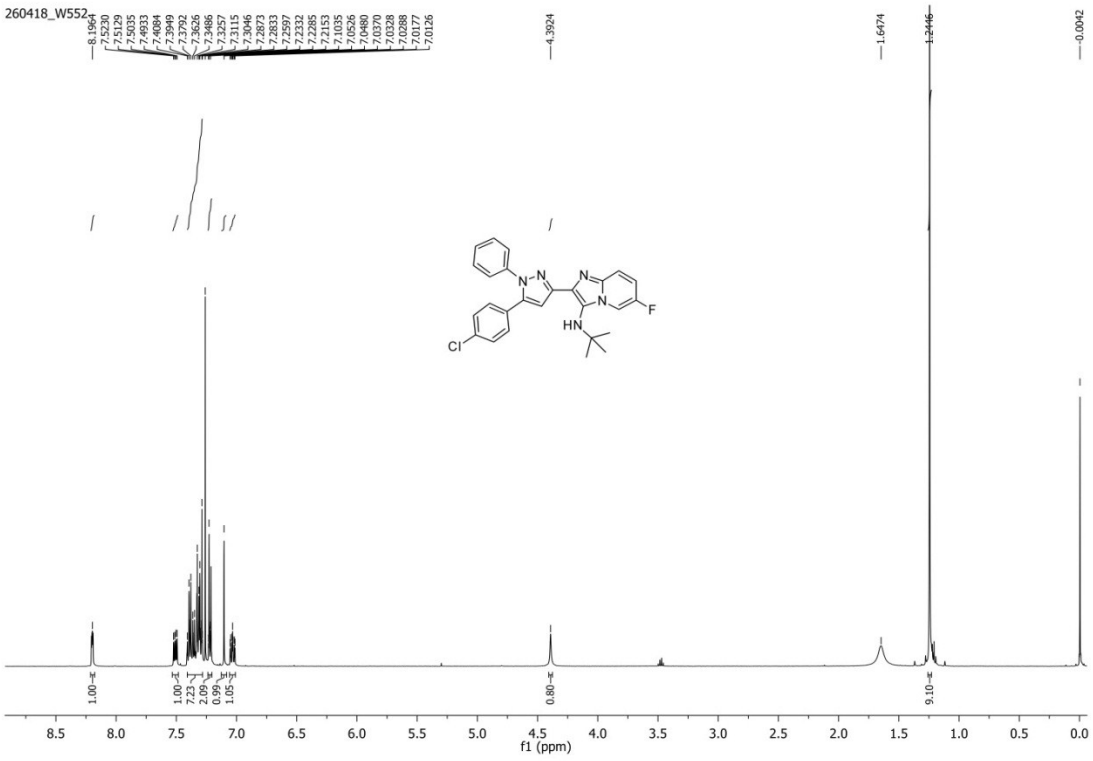


Figure S13. ^{1}H-NMR spectrum of **17aFX.**

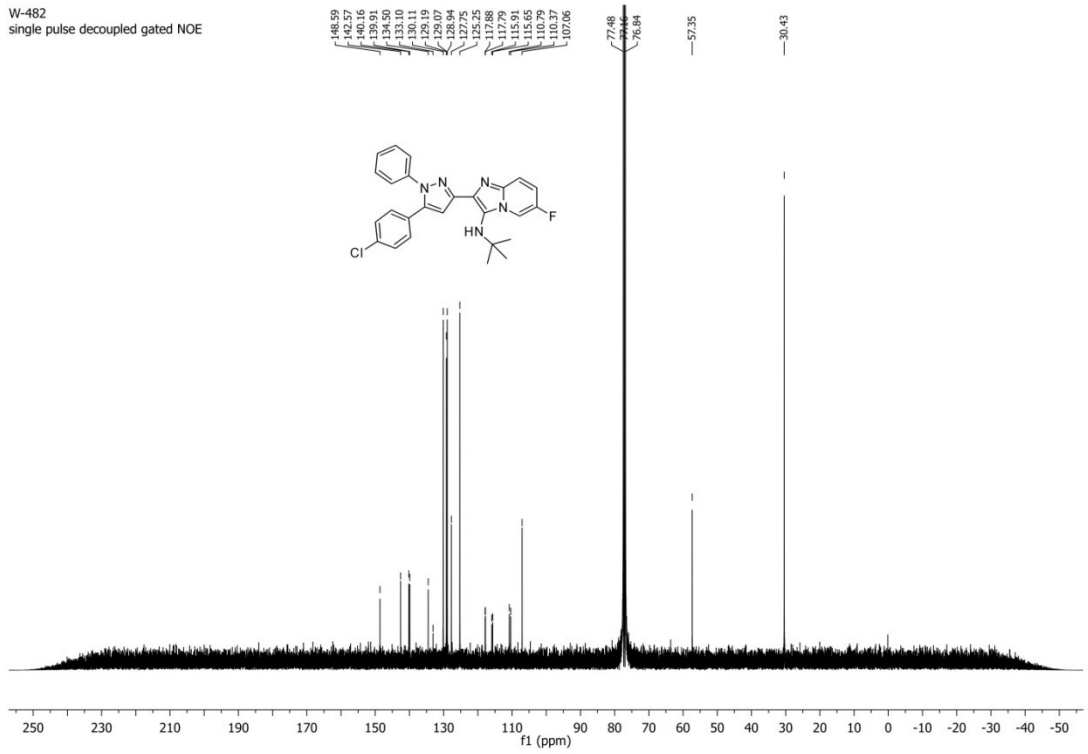


Figure S14. ^{13}C-NMR spectrum of **17aFX.**

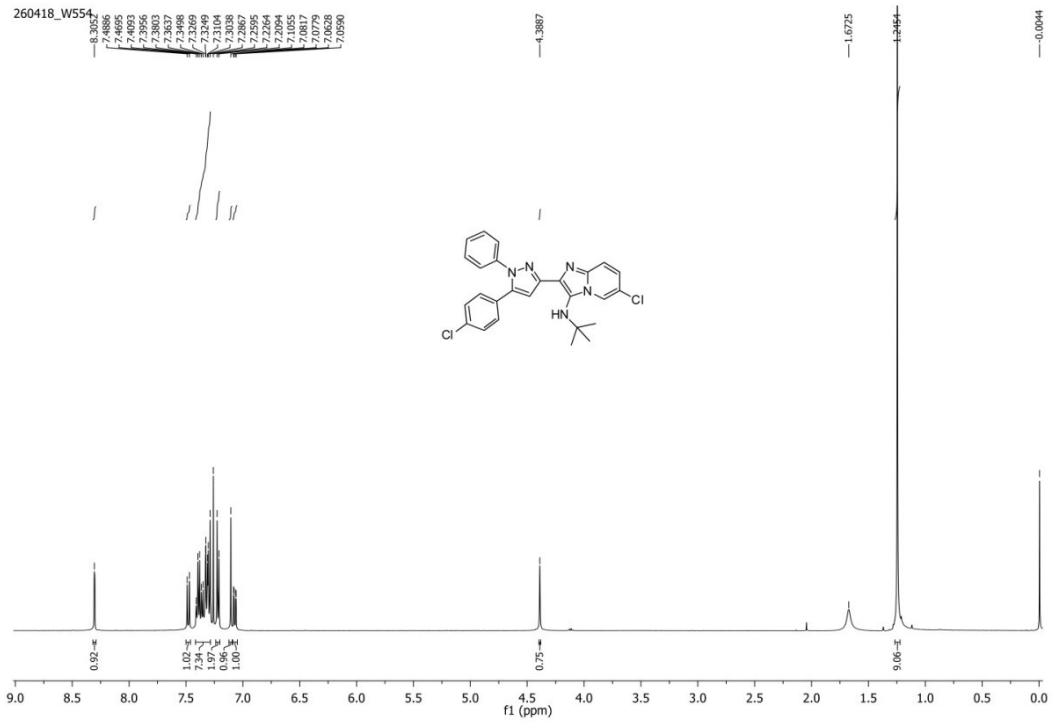


Figure S15. ^{1}H-NMR spectrum of **17aGX.**

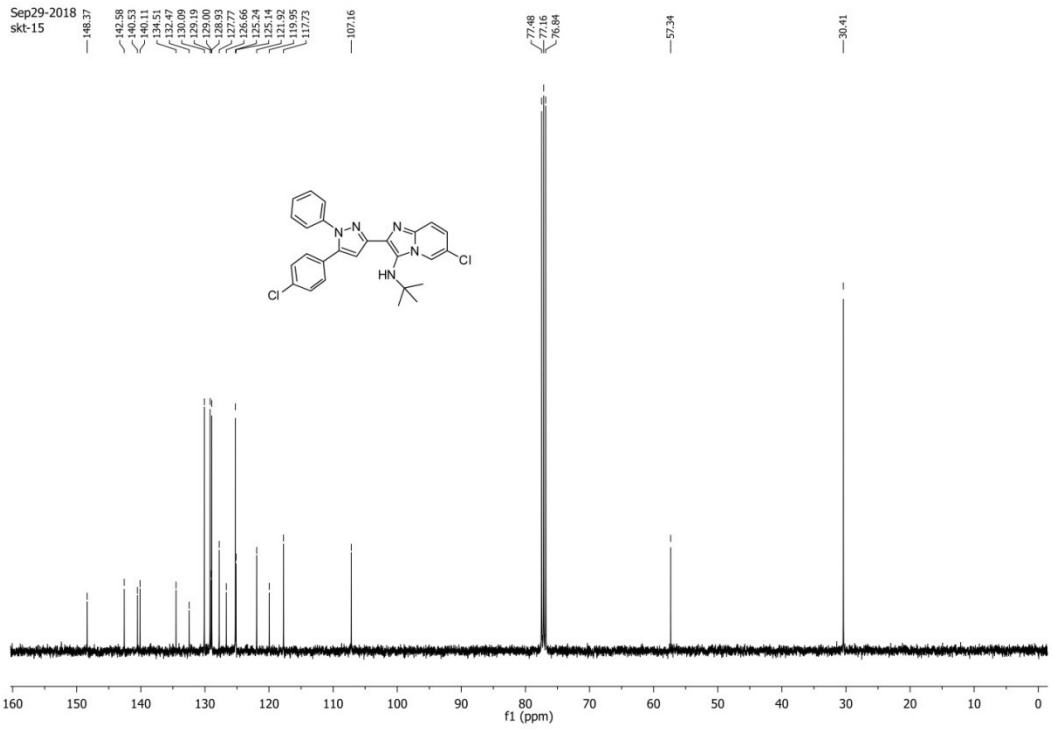


Figure S16. ^{13}C-NMR spectrum of **17aGX.**

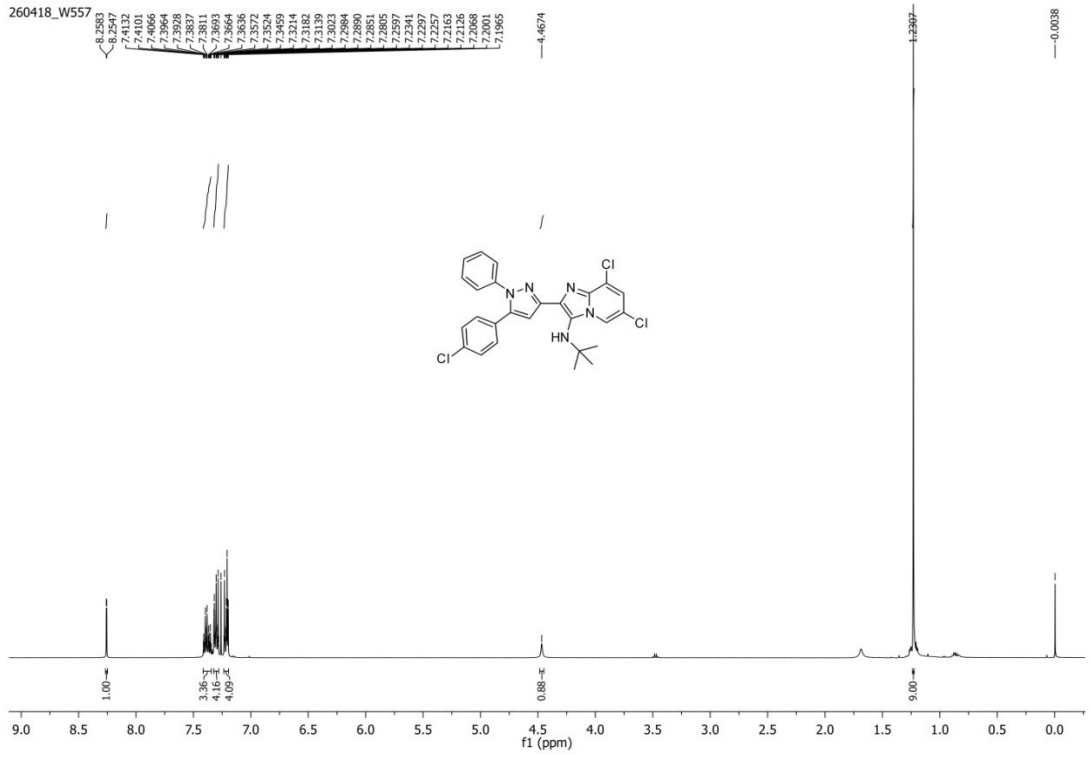


Figure S17. ^{1}H-NMR spectrum of **17aHX.**

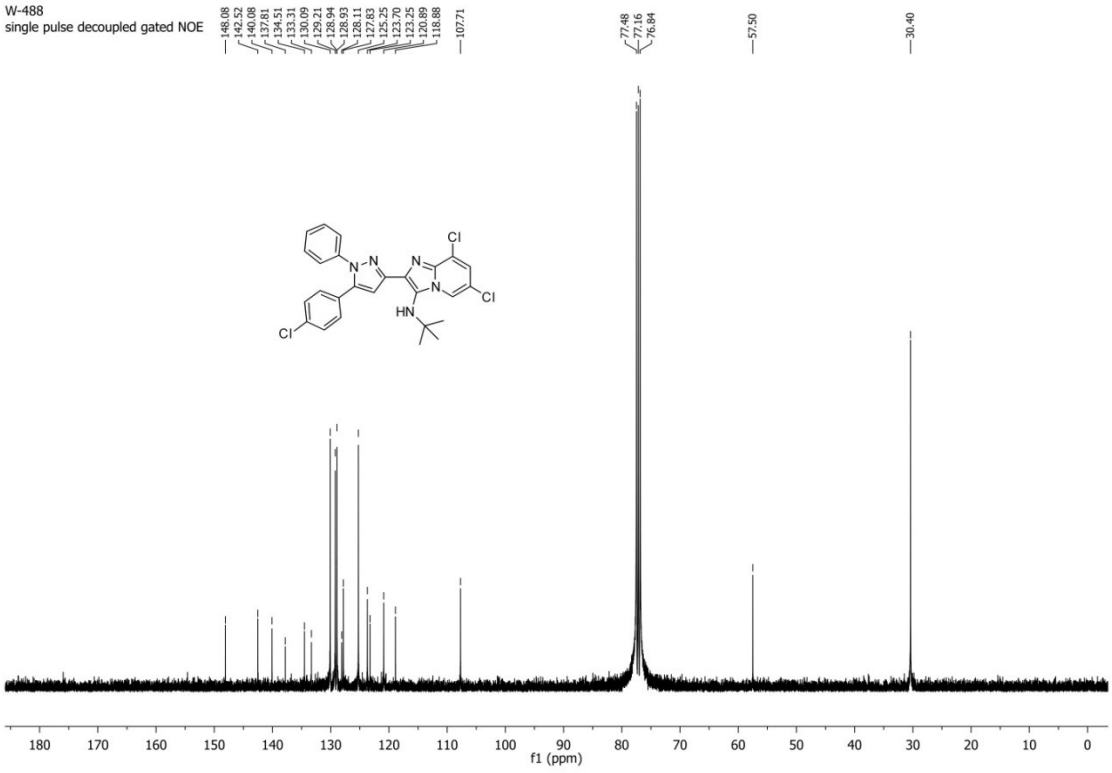


Figure S18. ^{13}C-NMR spectrum of **17aHX.**

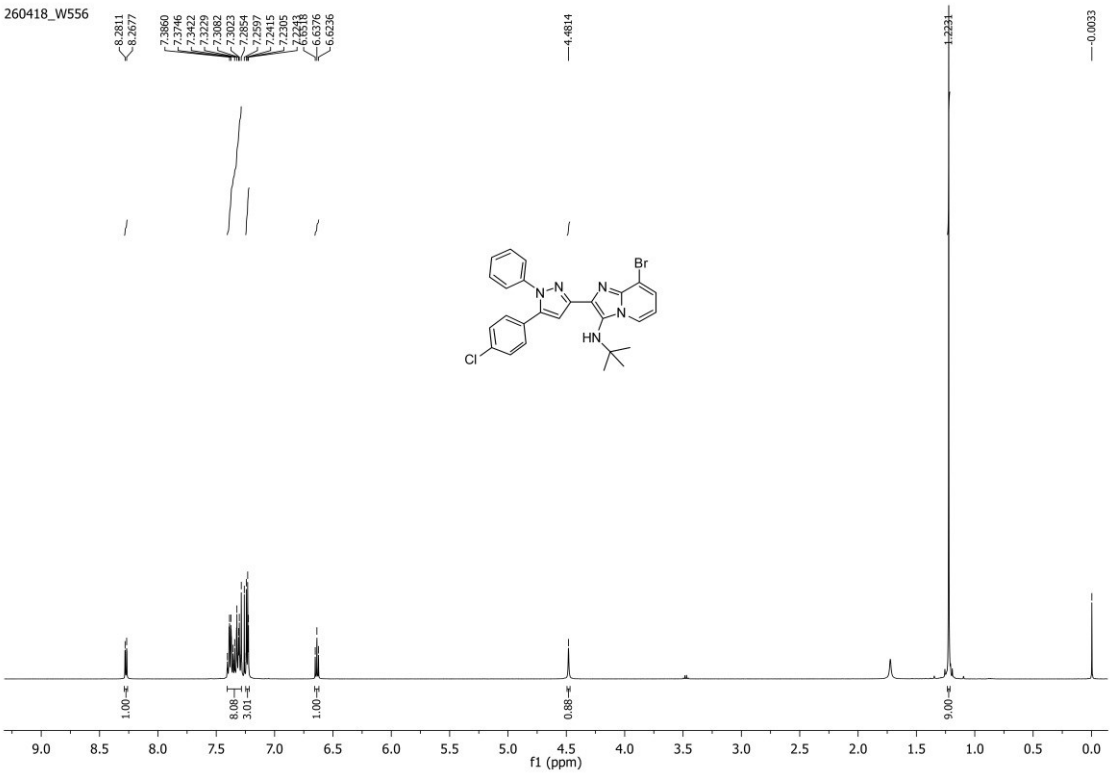


Figure S19. ^{1}H-NMR spectrum of **17aIX.**

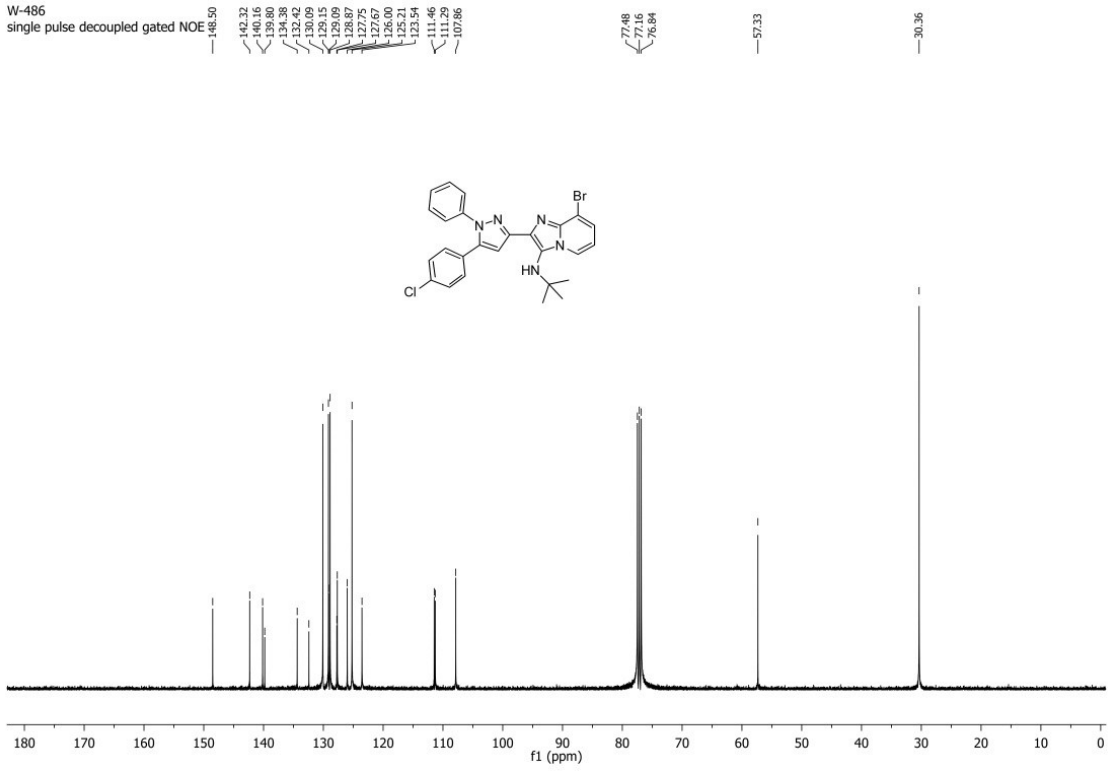


Figure S20. ^{13}C-NMR spectrum of **17aIX.**

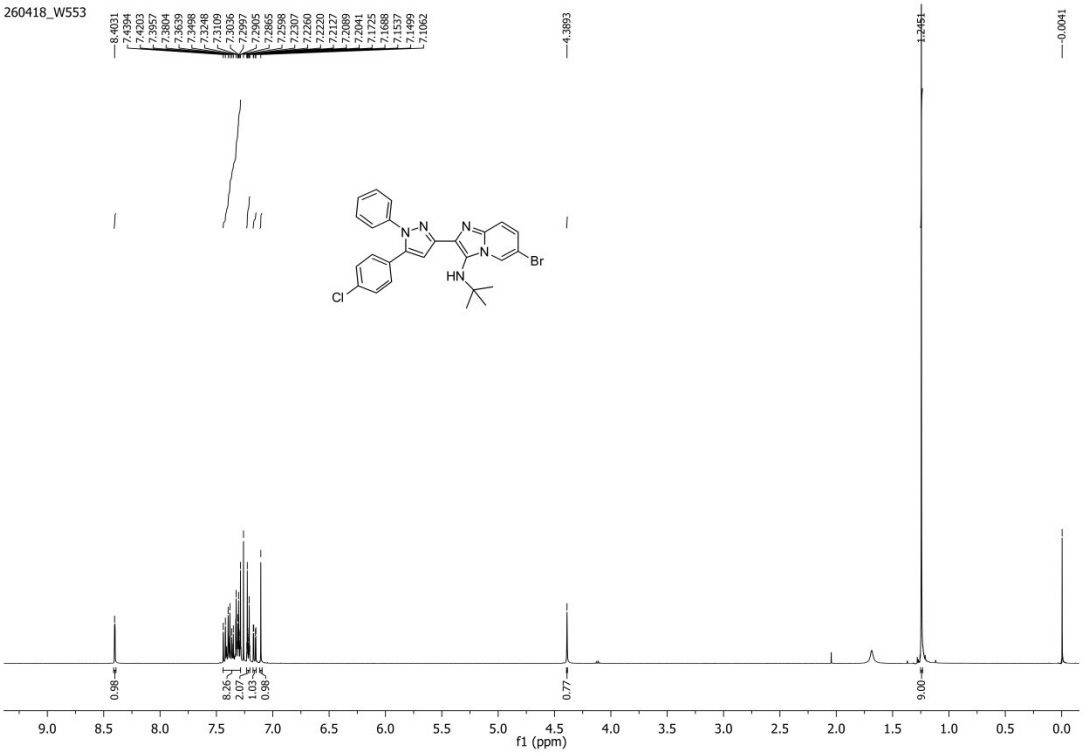


Figure S21. ^{1}H-NMR spectrum of **17aJX.**

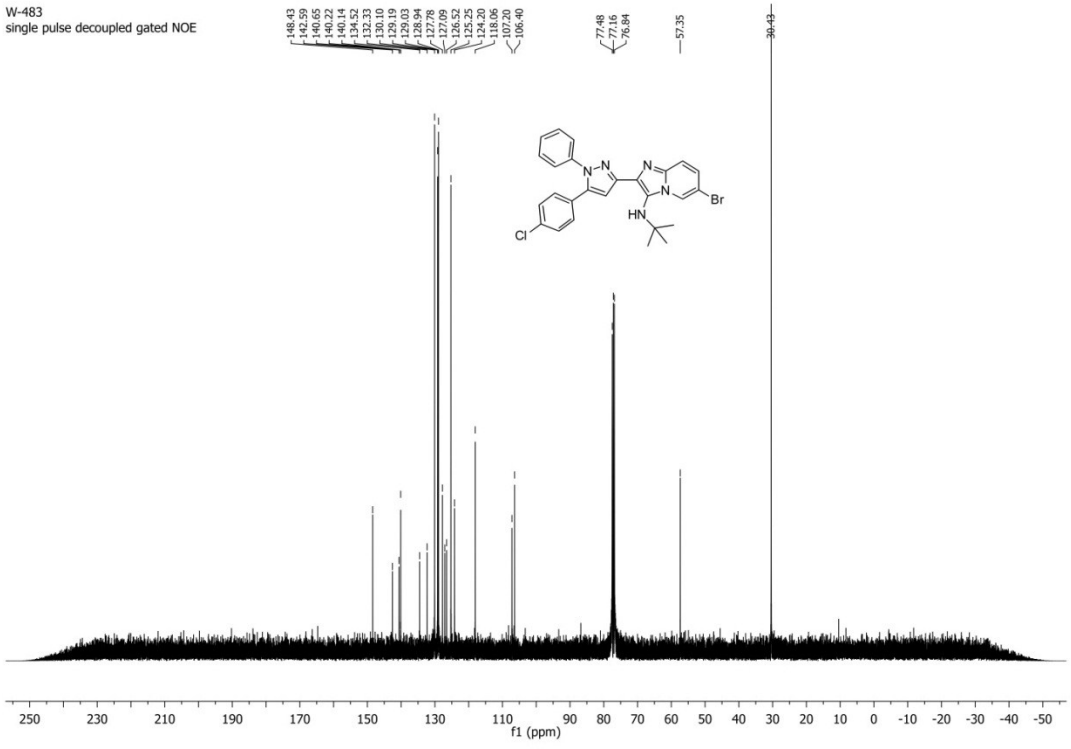


Figure S22. ^{13}C-NMR spectrum of **17aJX.**

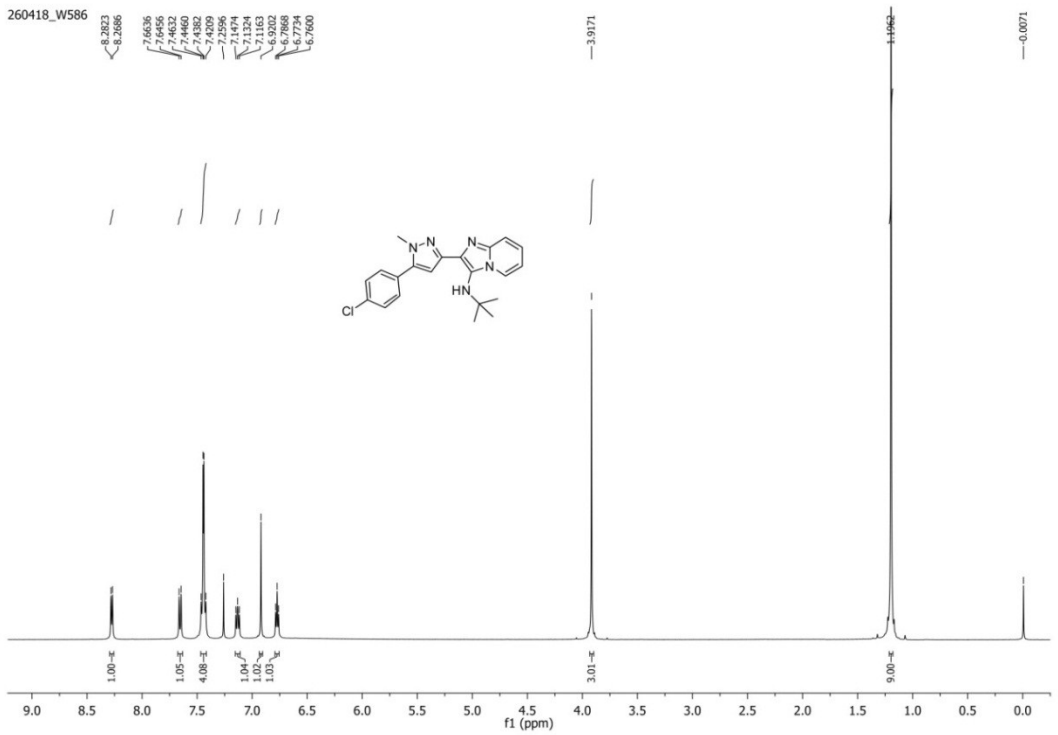


Figure S23. ^{1}H-NMR spectrum of **17bAX.**

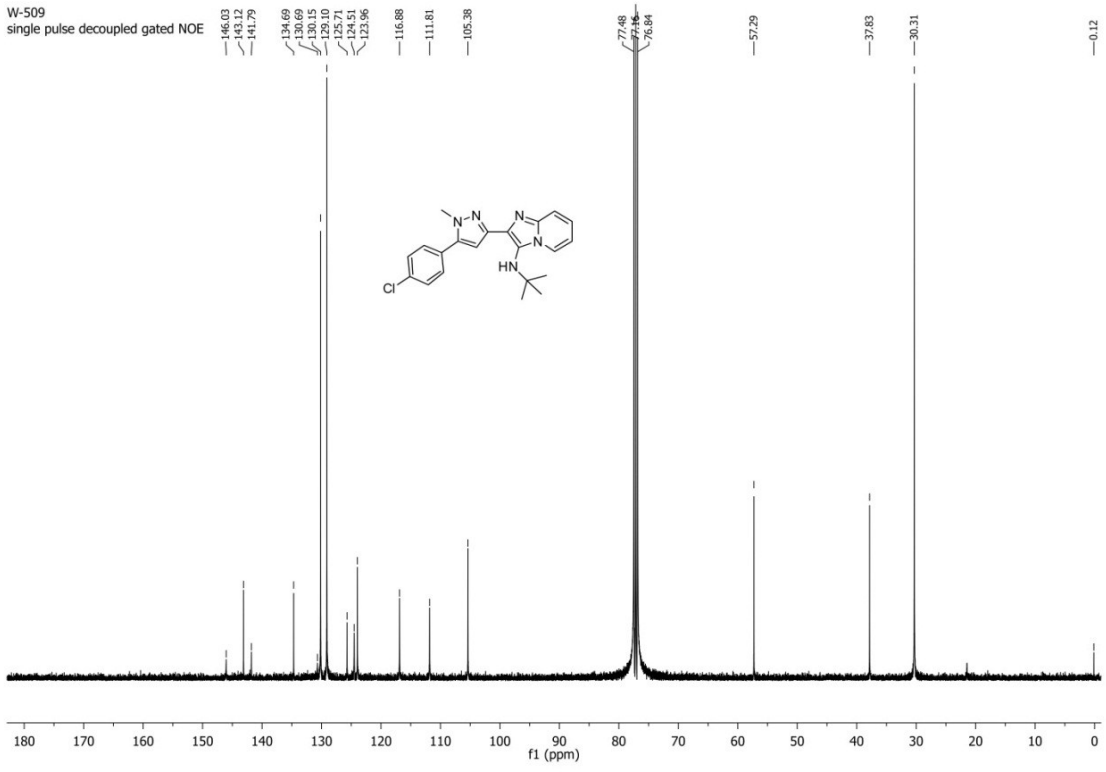


Figure S24. ^{13}C-NMR spectrum of **17bAX.**

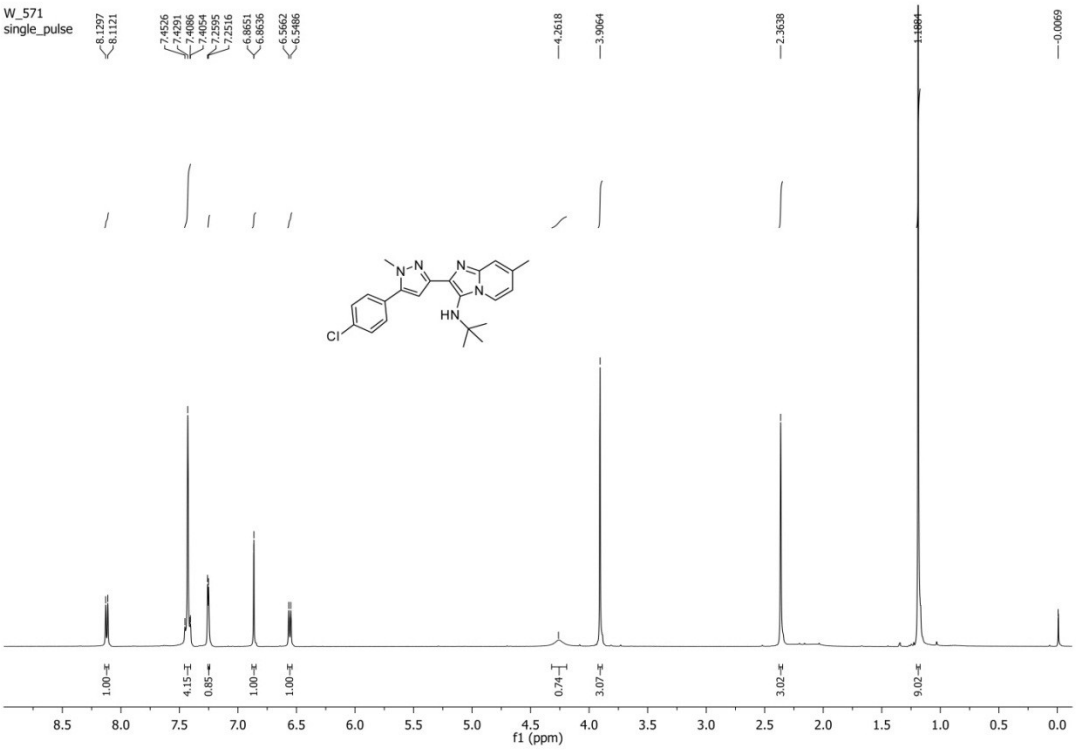


Figure S25. ^{1}H-NMR spectrum of **17bCX.**

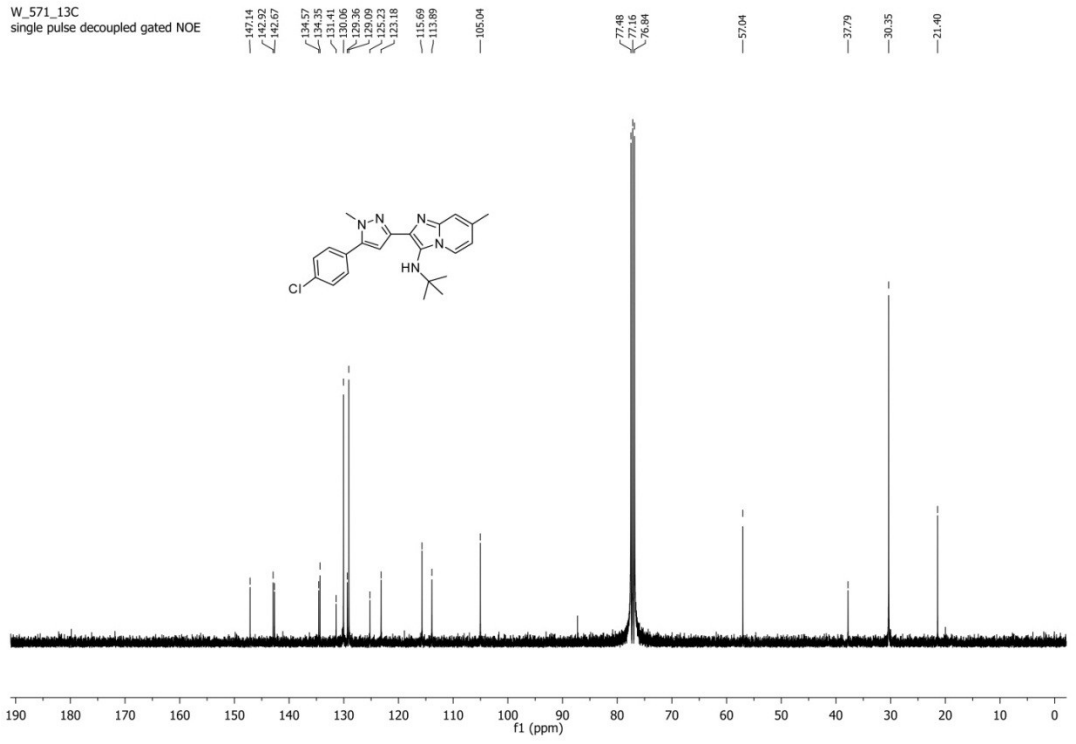


Figure S26. ^{13}C-NMR spectrum of **17bCX.**

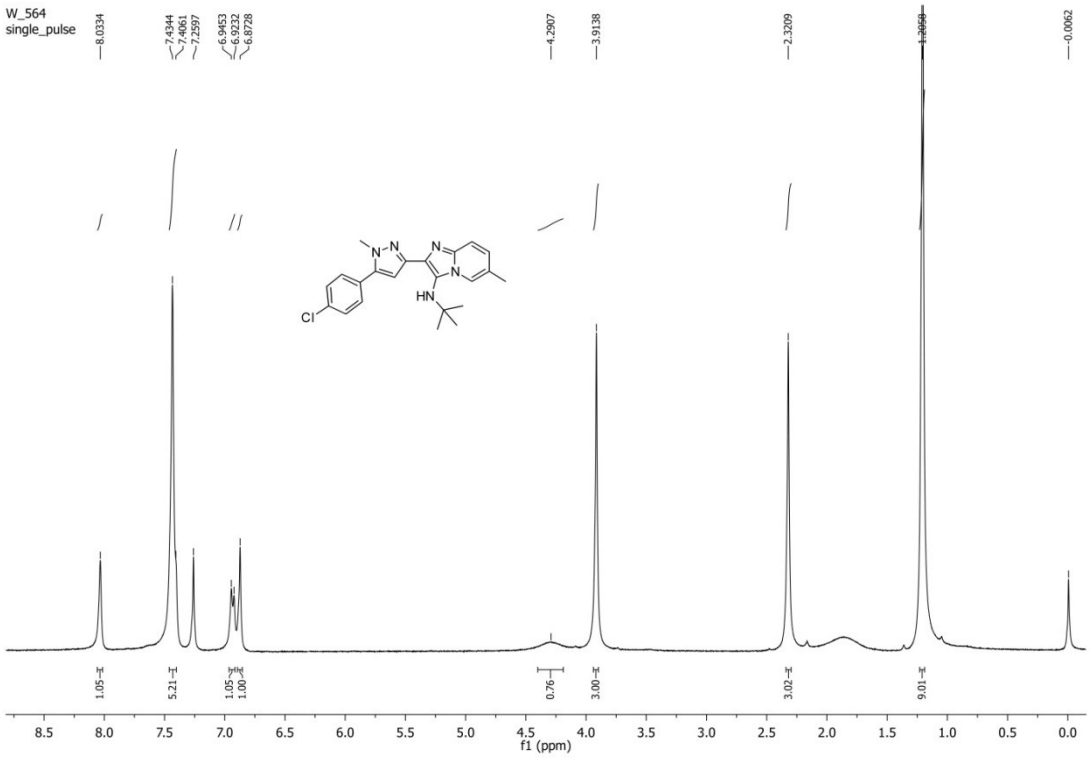


Figure S27. ^{1}H-NMR spectrum of **17bDX.**

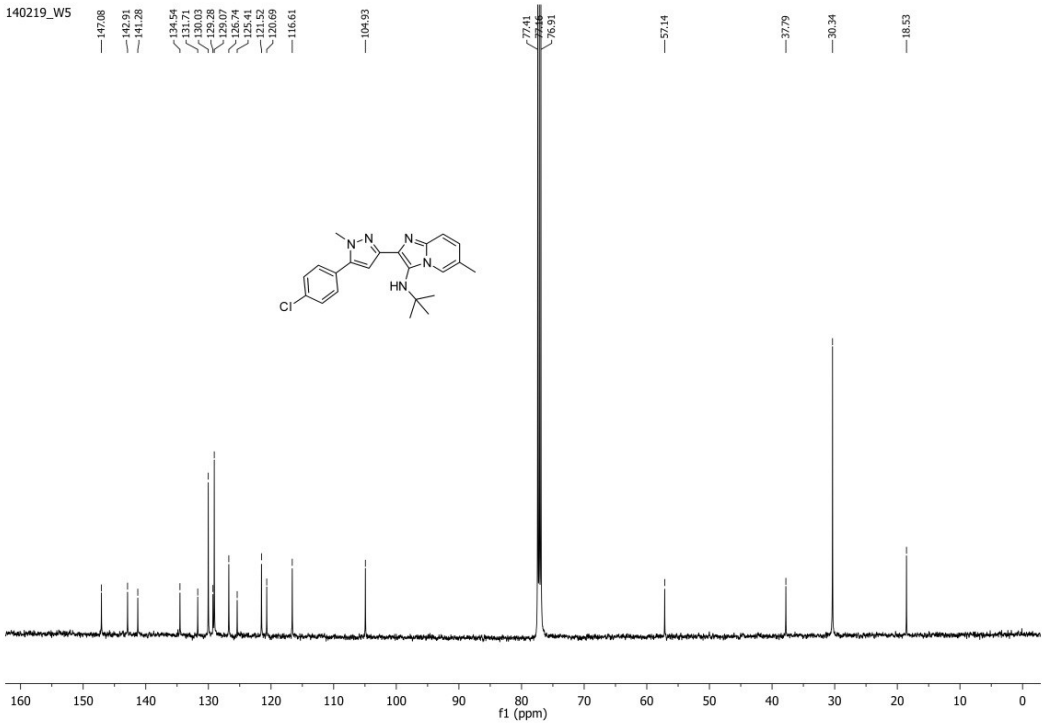


Figure S28. ^{13}C-NMR spectrum of **17bDX.**

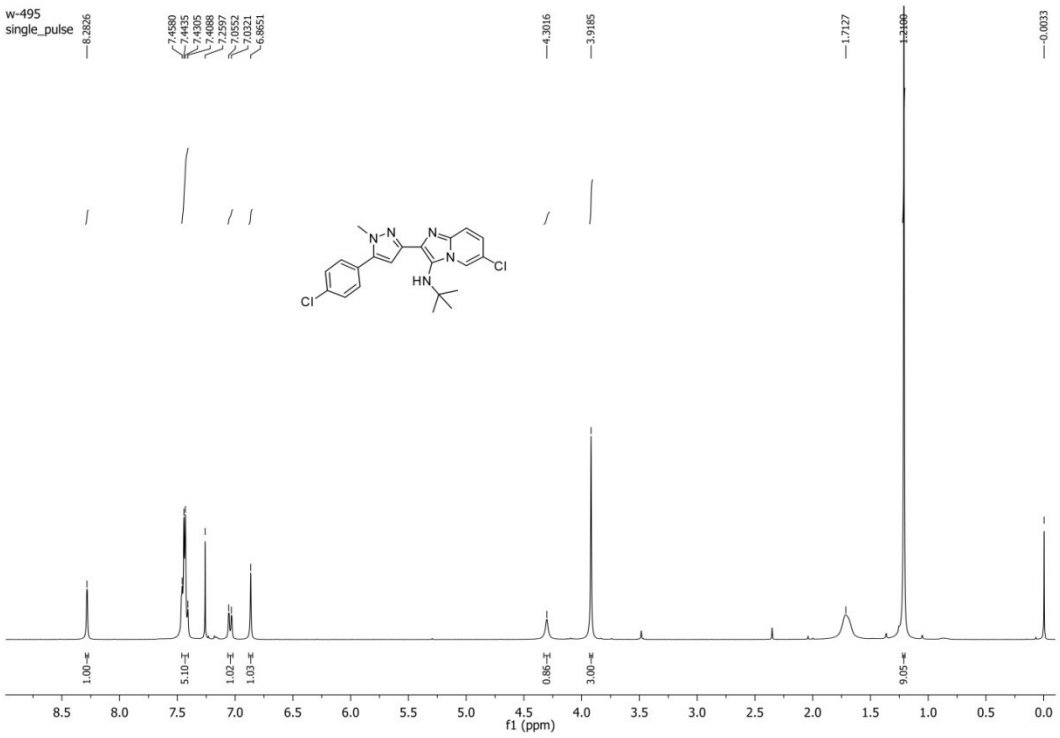


Figure S29. ^{1}H-NMR spectrum of **17bGX.**

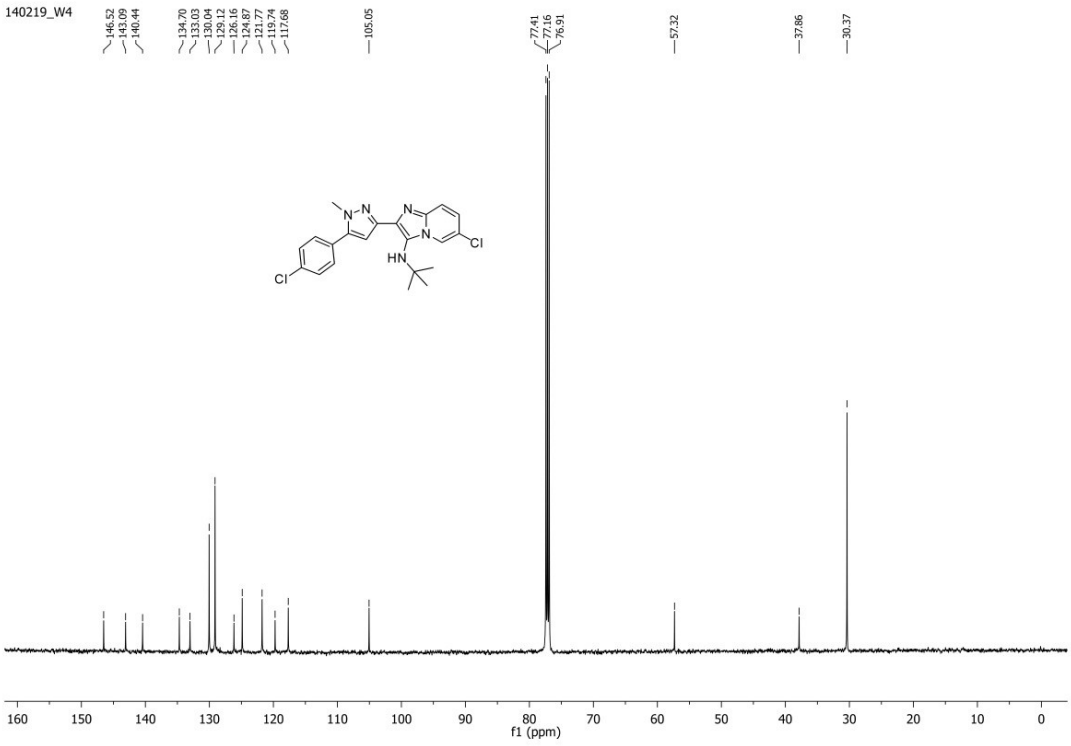


Figure S30. ^{13}C-NMR spectrum of **17bGX.**

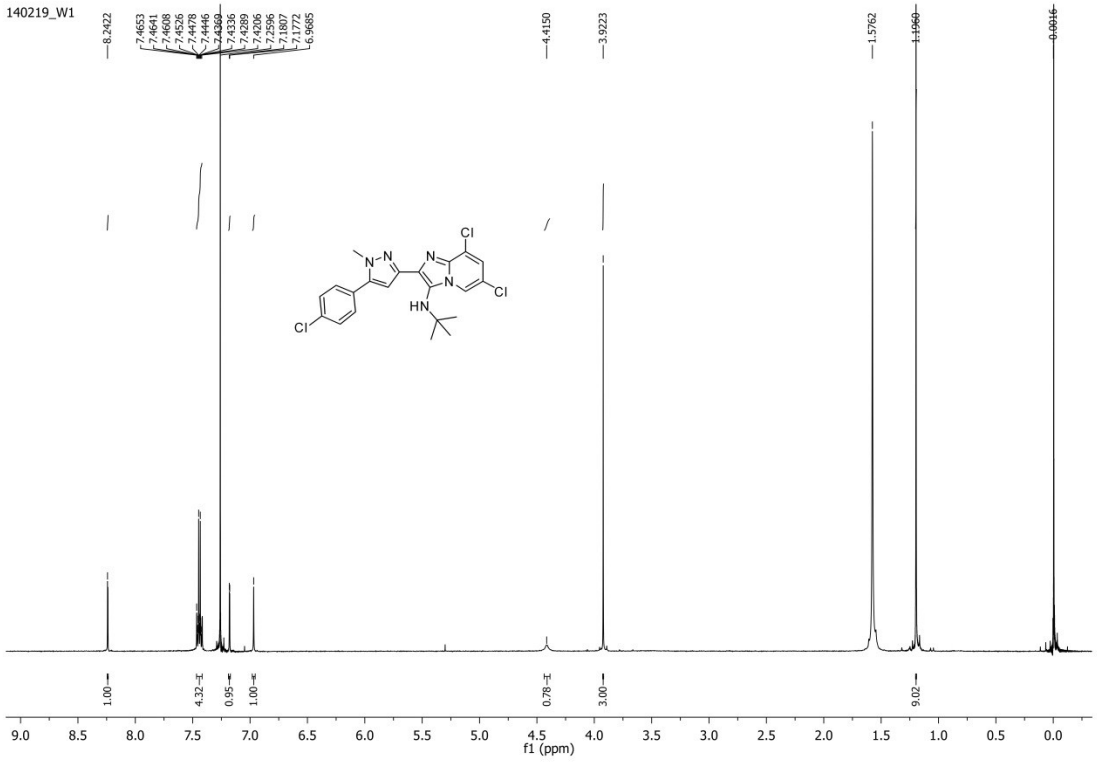


Figure S31. ^{1}H-NMR spectrum of **17bHX.**

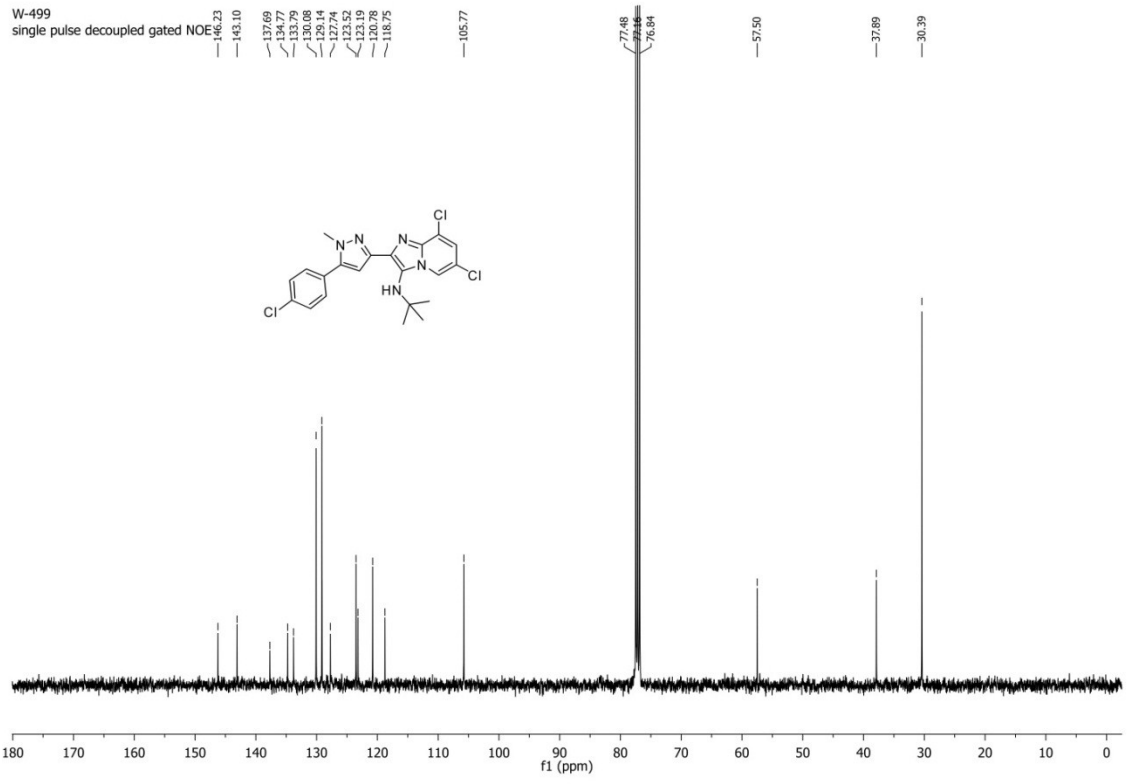


Figure S32. ^{13}C-NMR spectrum of **17bHX.**

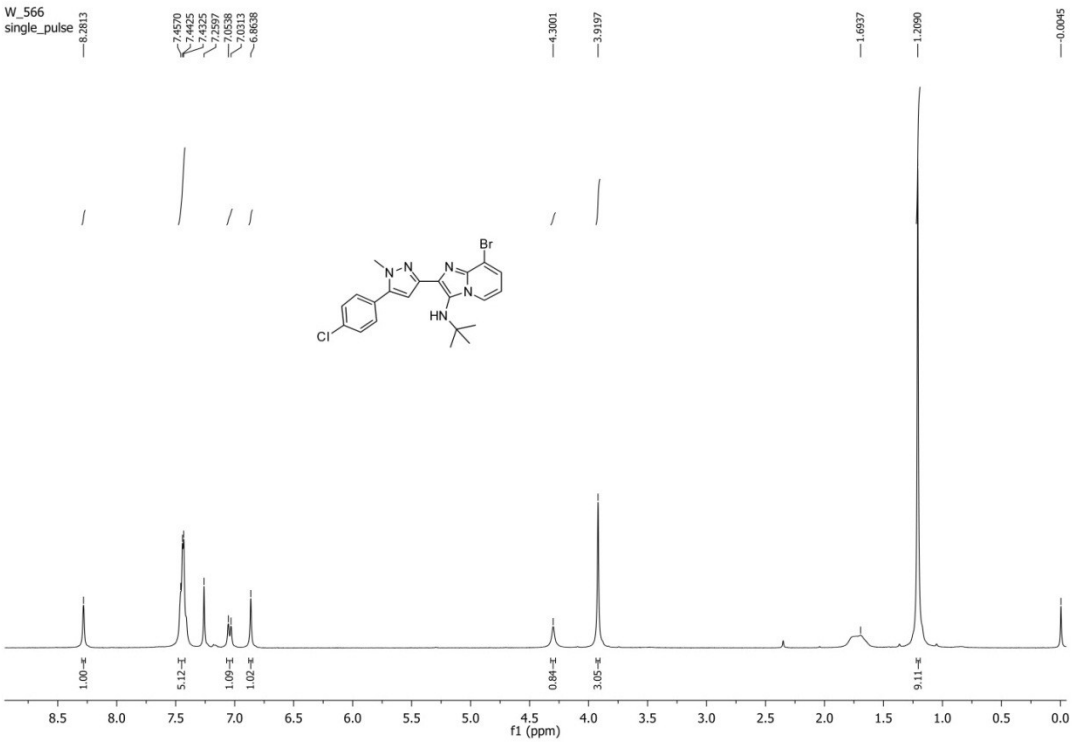


Figure S33. ^{1}H-NMR spectrum of **17bIX.**

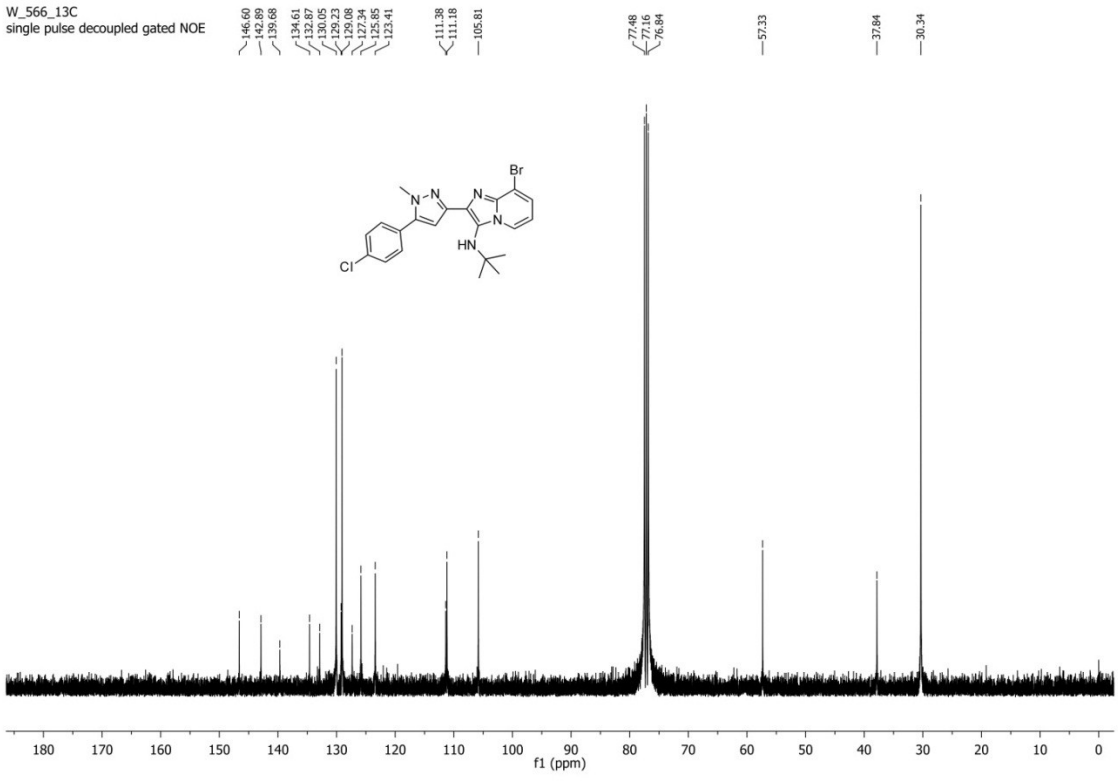


Figure S34. ^{13}C-NMR spectrum of **17bIX.**

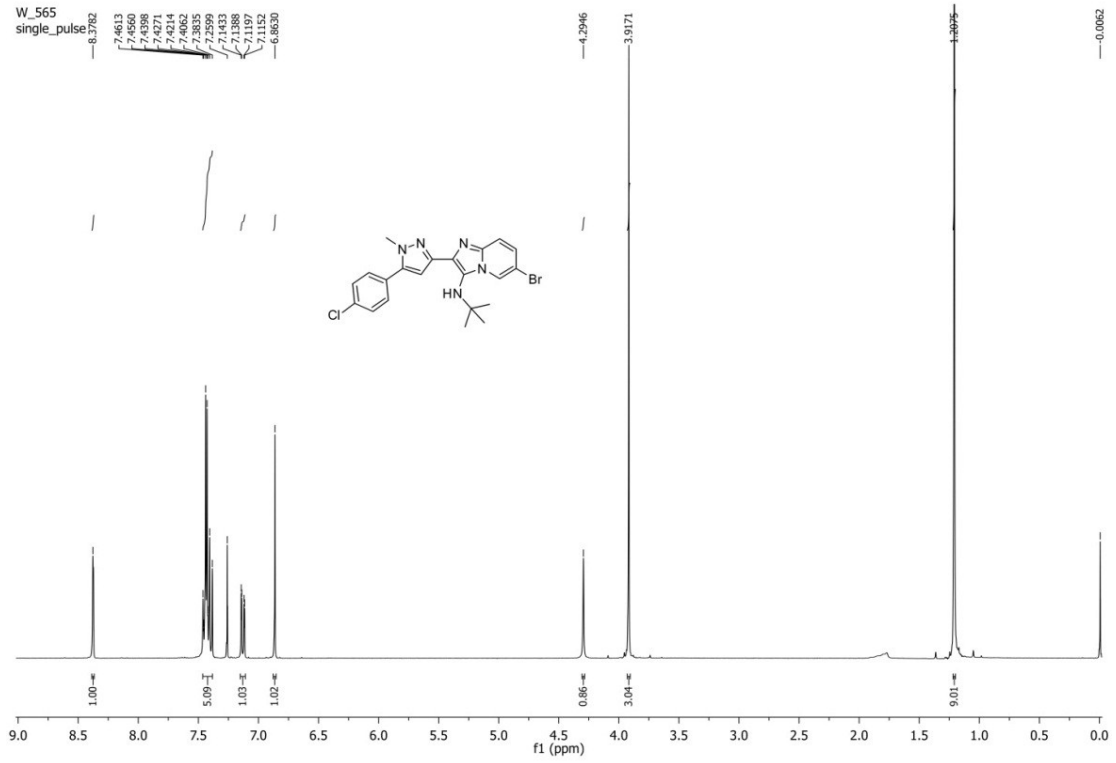


Figure S35. ^{1}H-NMR spectrum of **17bJX.**

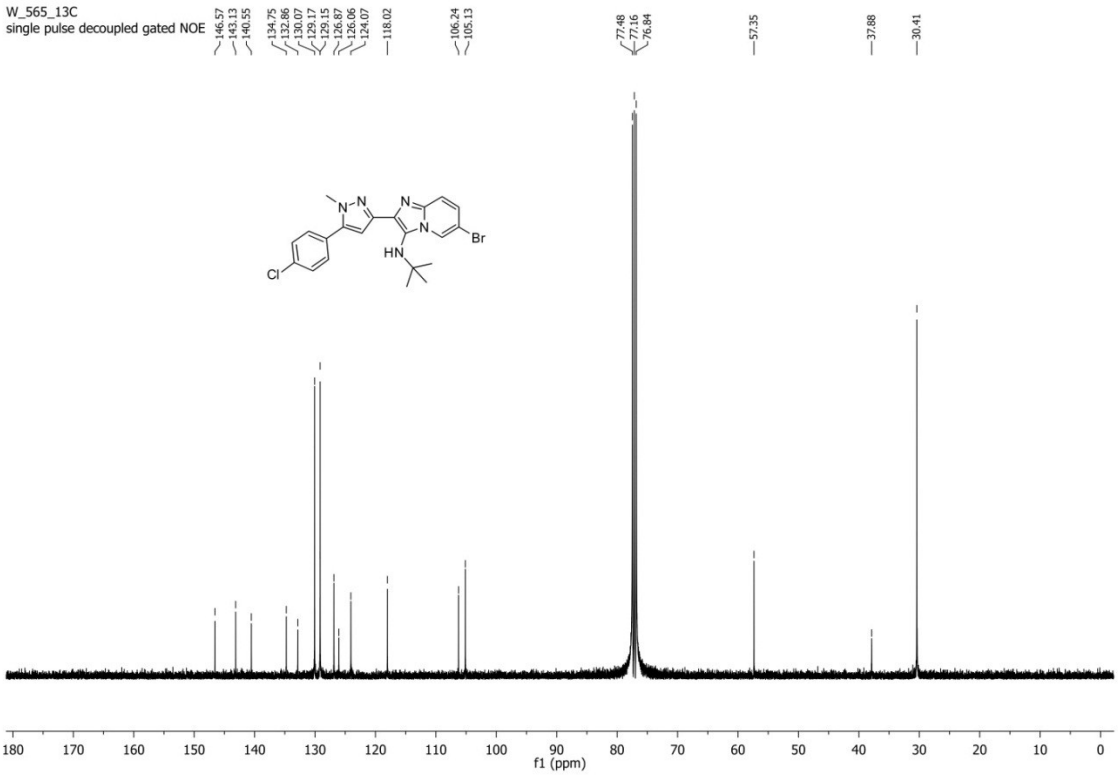


Figure S36. ^{13}C-NMR spectrum of **17bJX.**

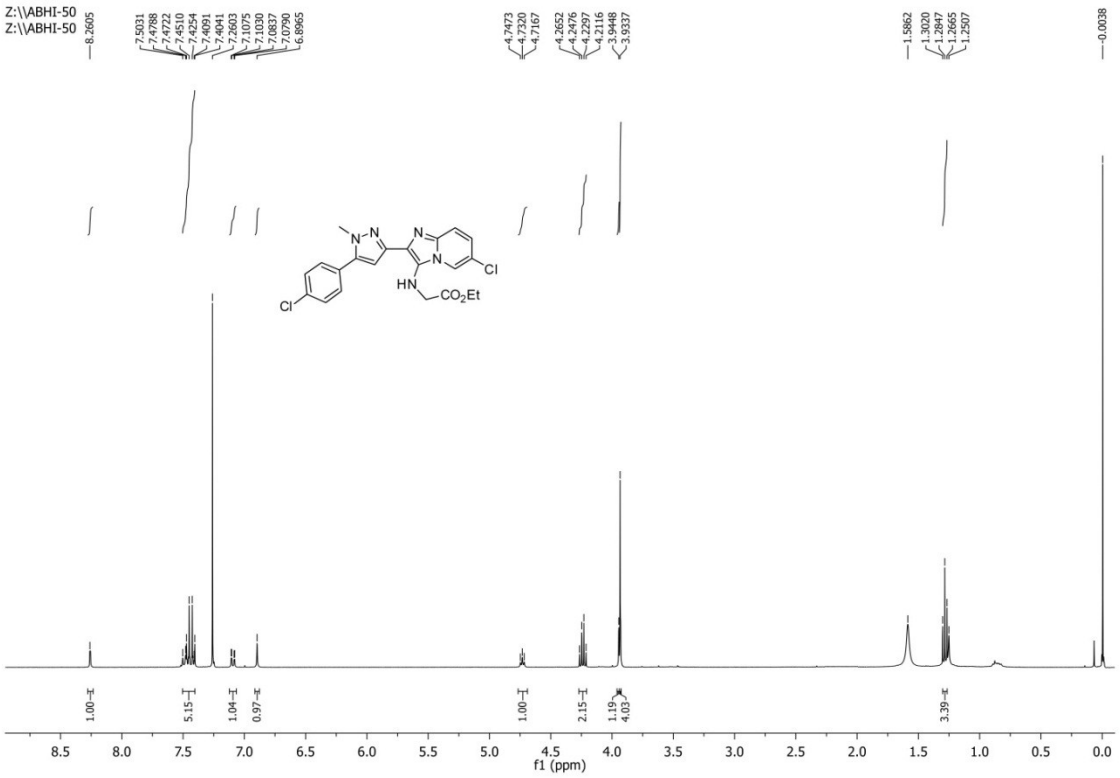


Figure S37. ^{1}H-NMR spectrum of **17bGY.**

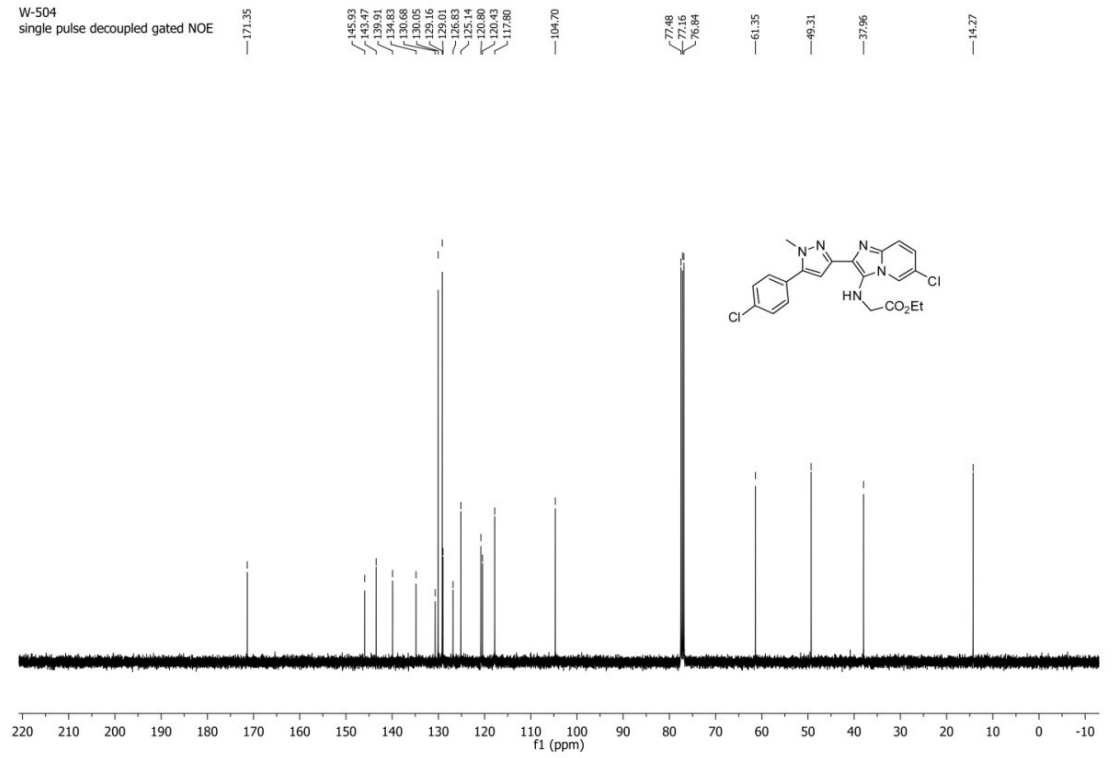


Figure S38. ^{13}C-NMR spectrum of **17bGY.**

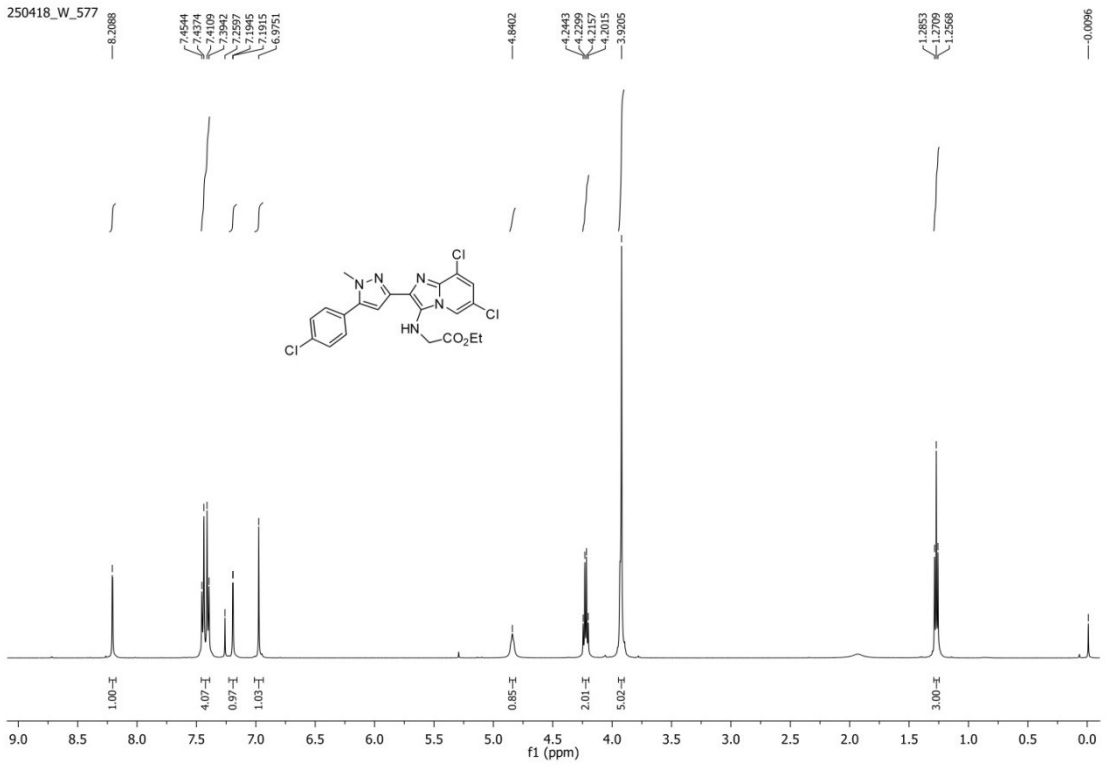


Figure S39. ^{1}H-NMR spectrum of **17bHY.**

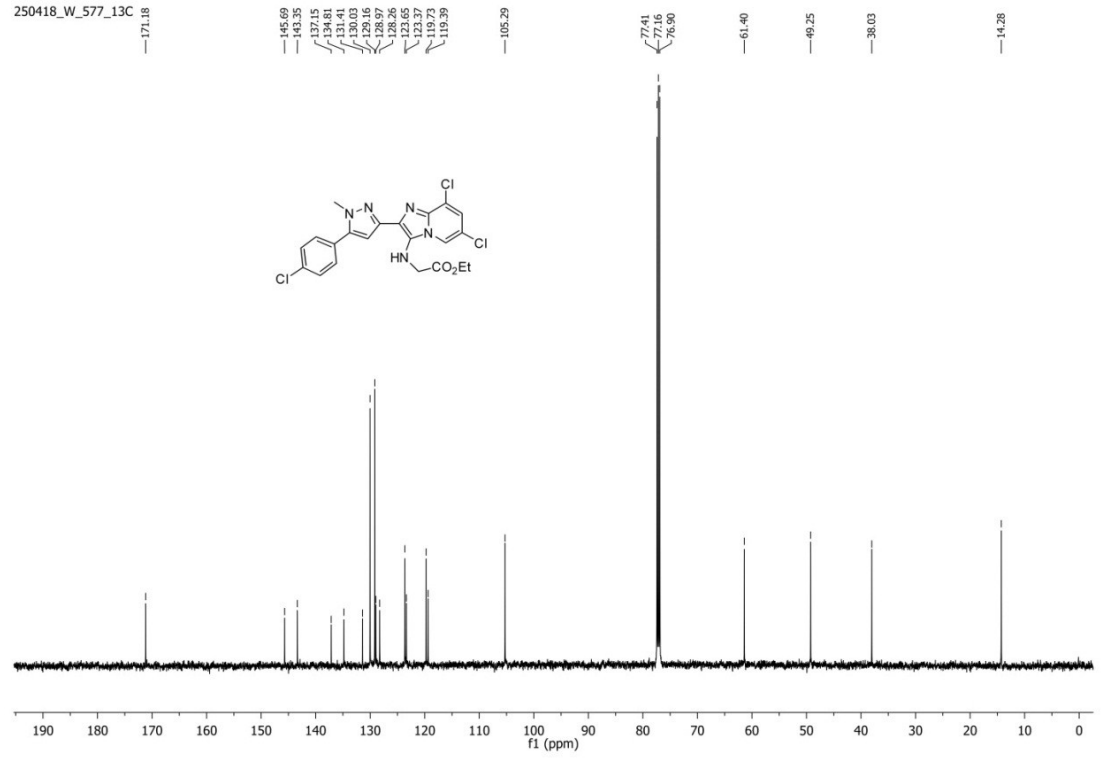


Figure S40. ^{13}C-NMR spectrum of **17bHY.**

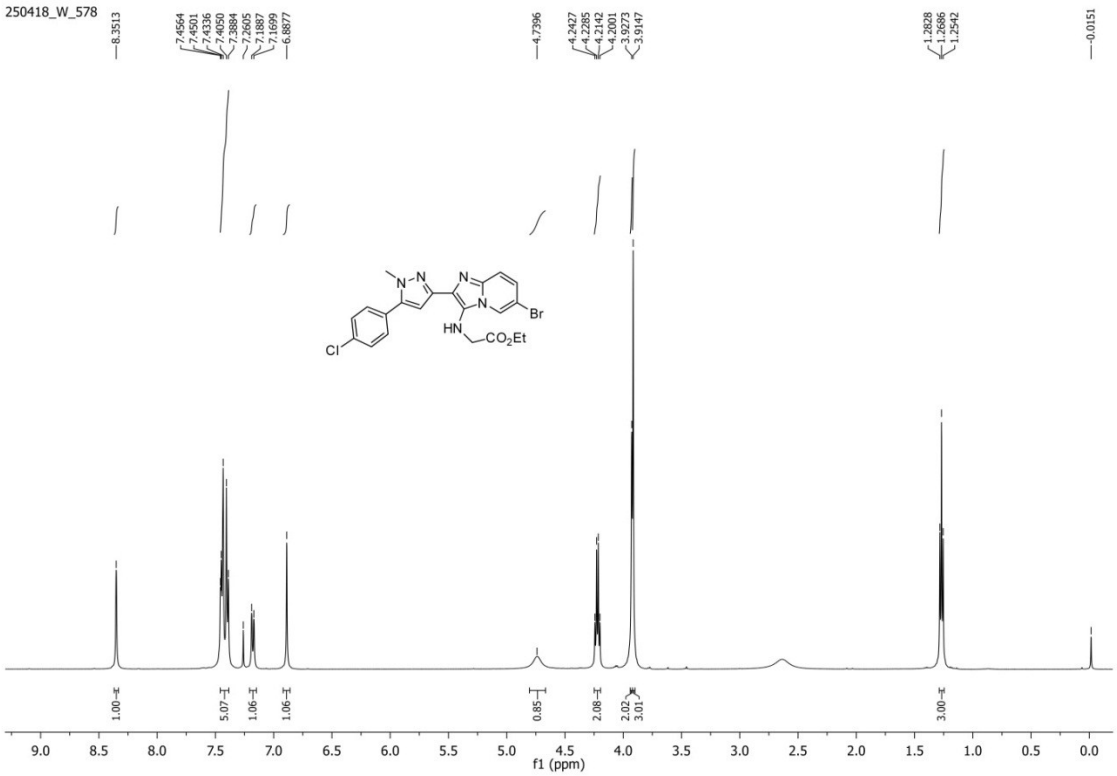


Figure S41. ^{1}H-NMR spectrum of **17bJY.**

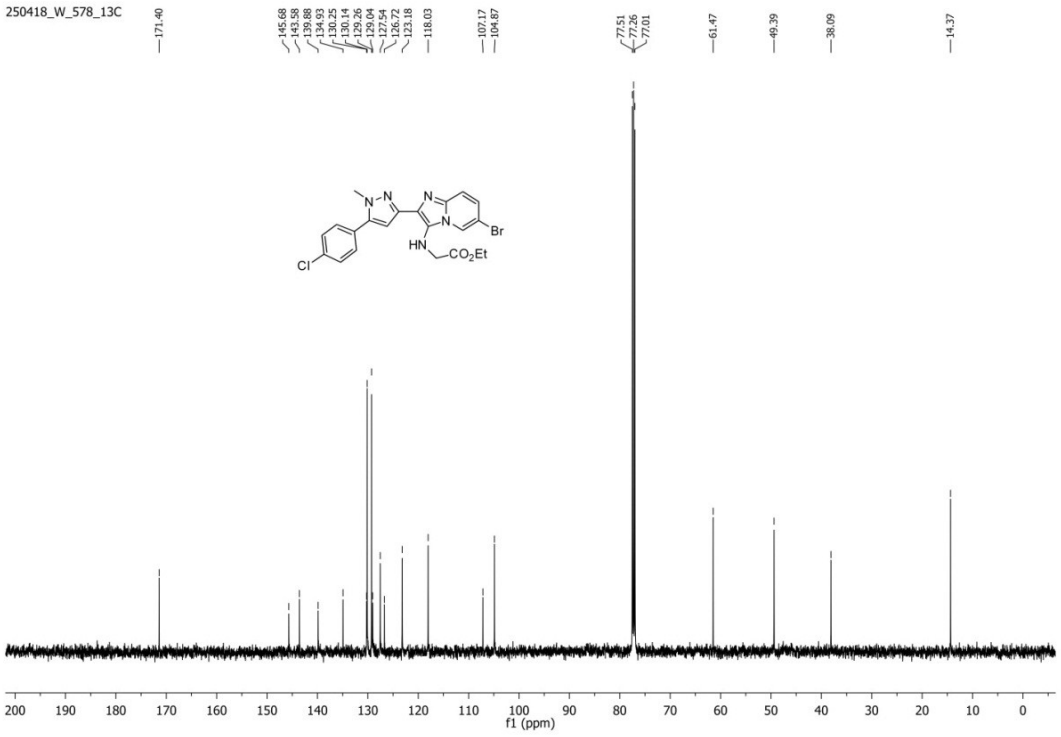


Figure S42. ^{13}C-NMR spectrum of **17bJY.**

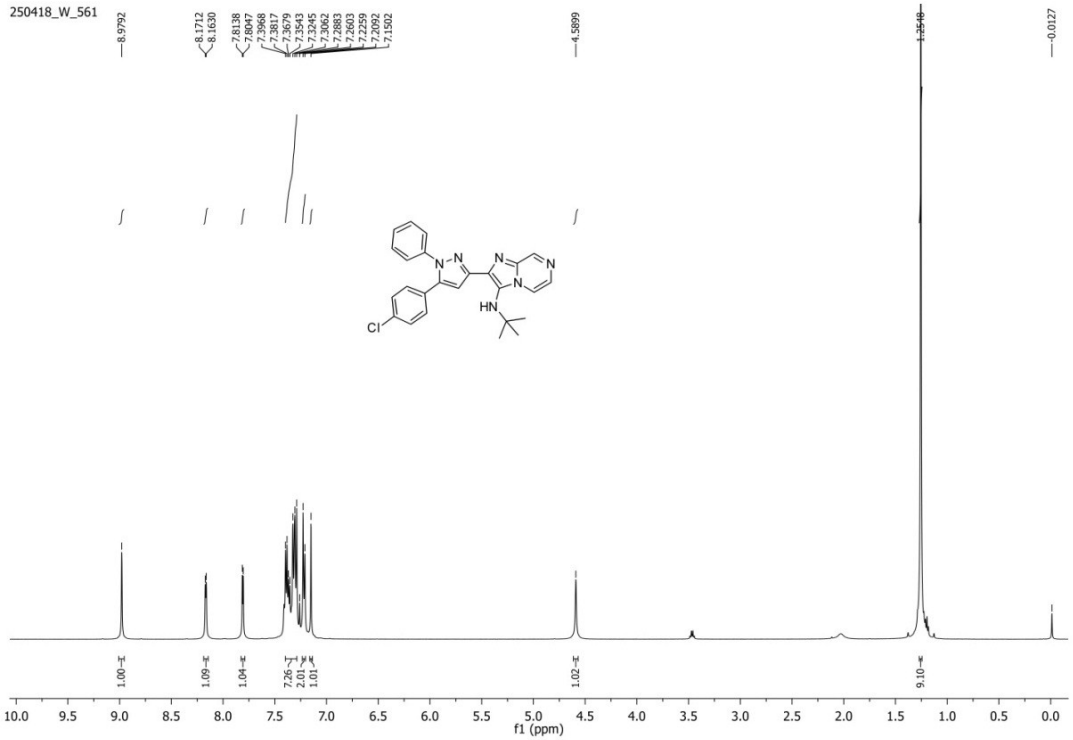


Figure S43. ^{1}H-NMR spectrum of **17aKX.**

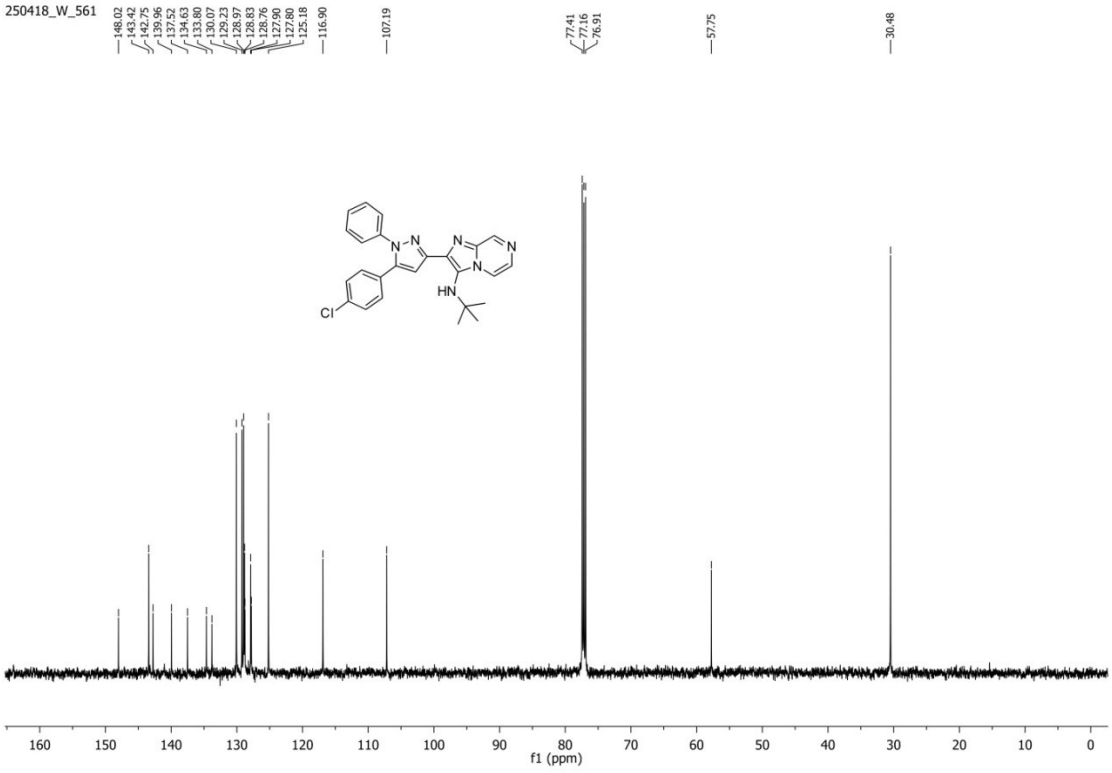


Figure S44. ^{13}C-NMR spectrum of **17aKX.**

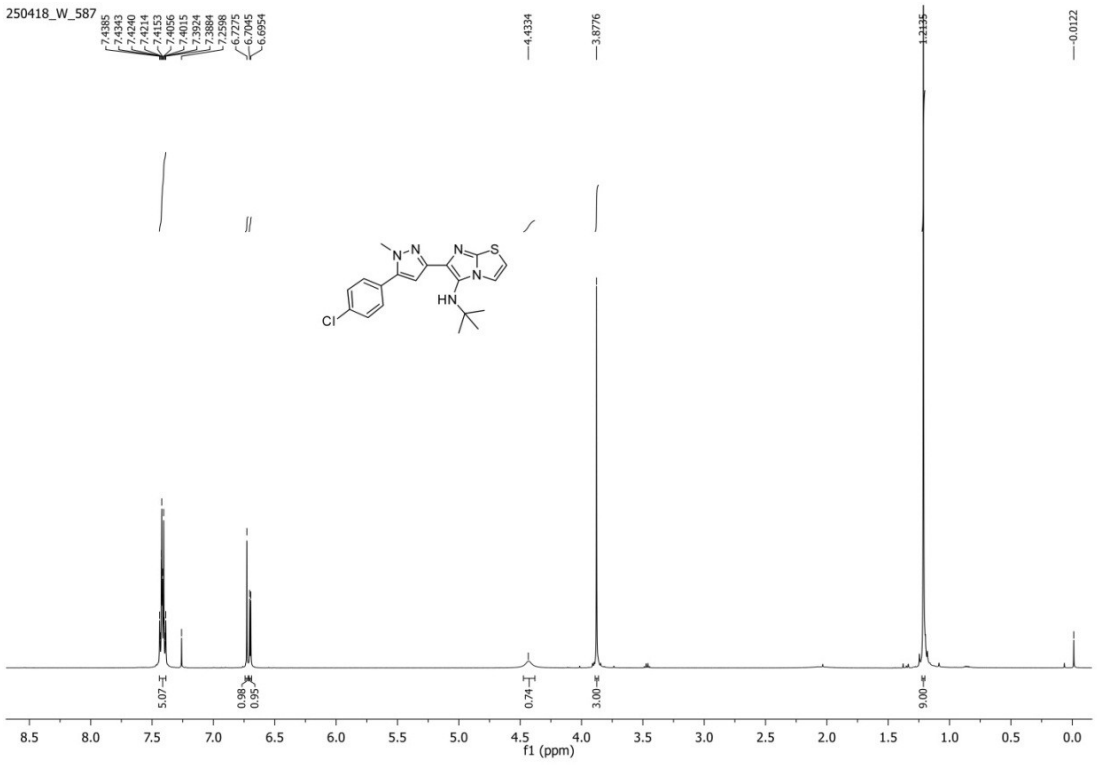


Figure S45. ^{1}H-NMR spectrum of **17bLX.**

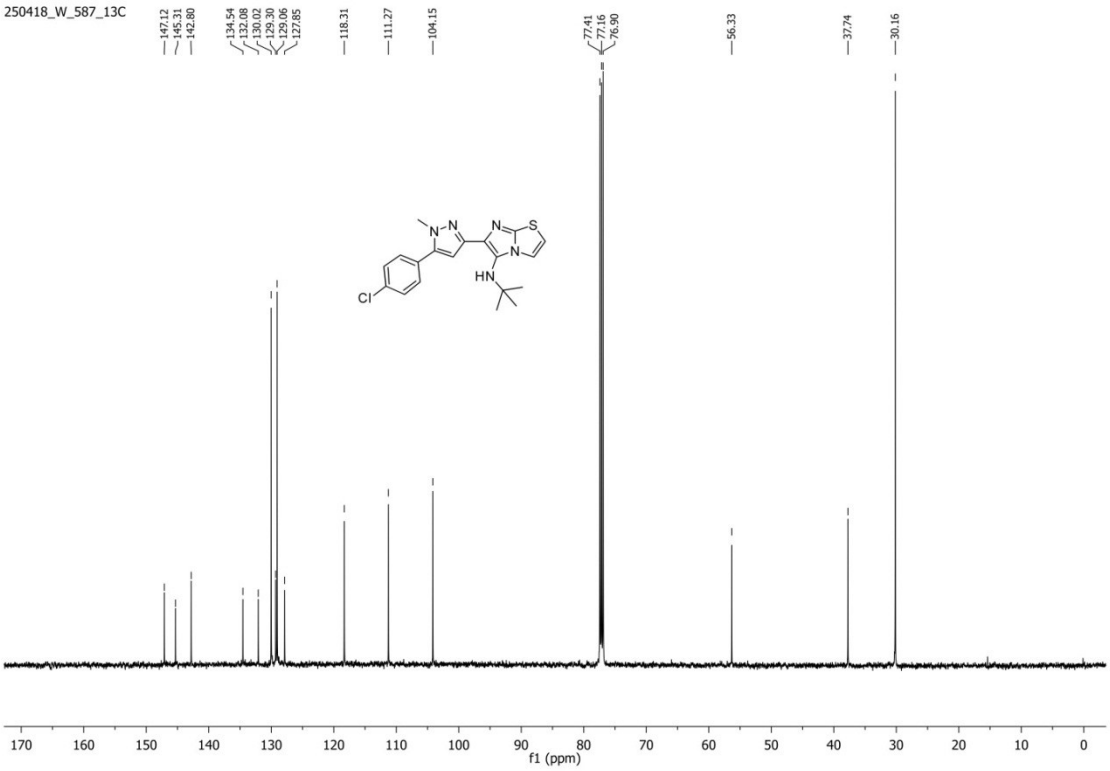


Figure S46. ^{13}C-NMR spectrum of **17bLX.**

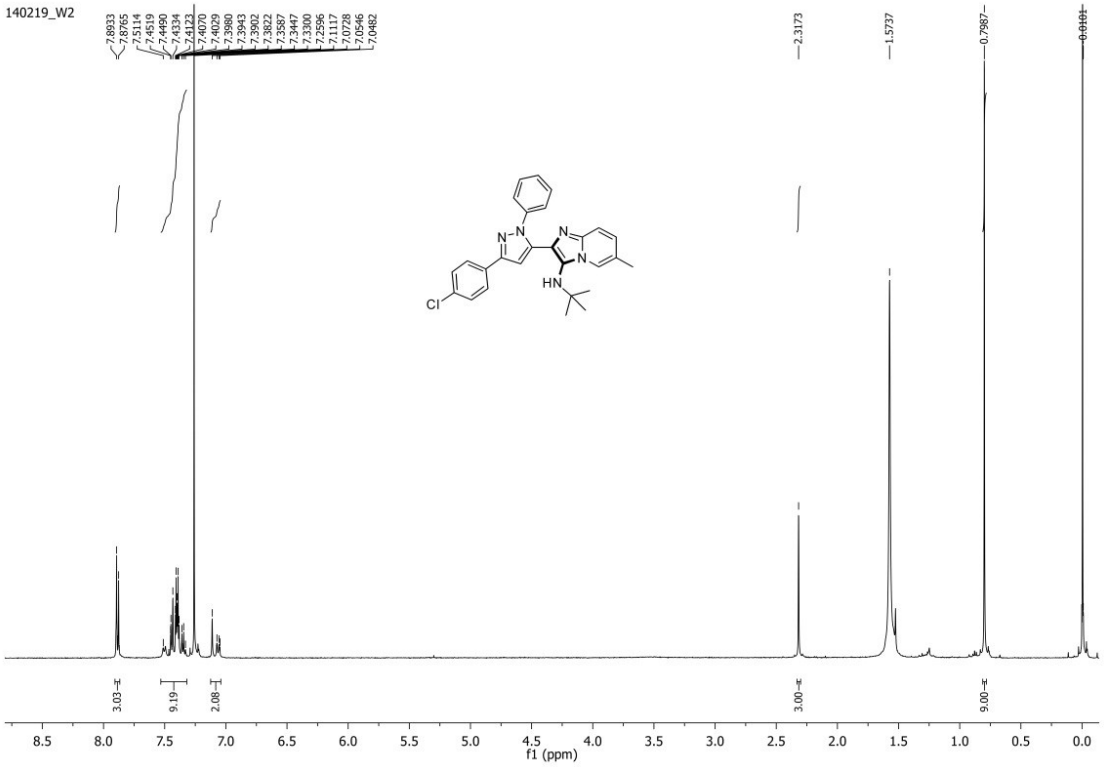


Figure S47. ^{1}H-NMR spectrum of **21aDX.**

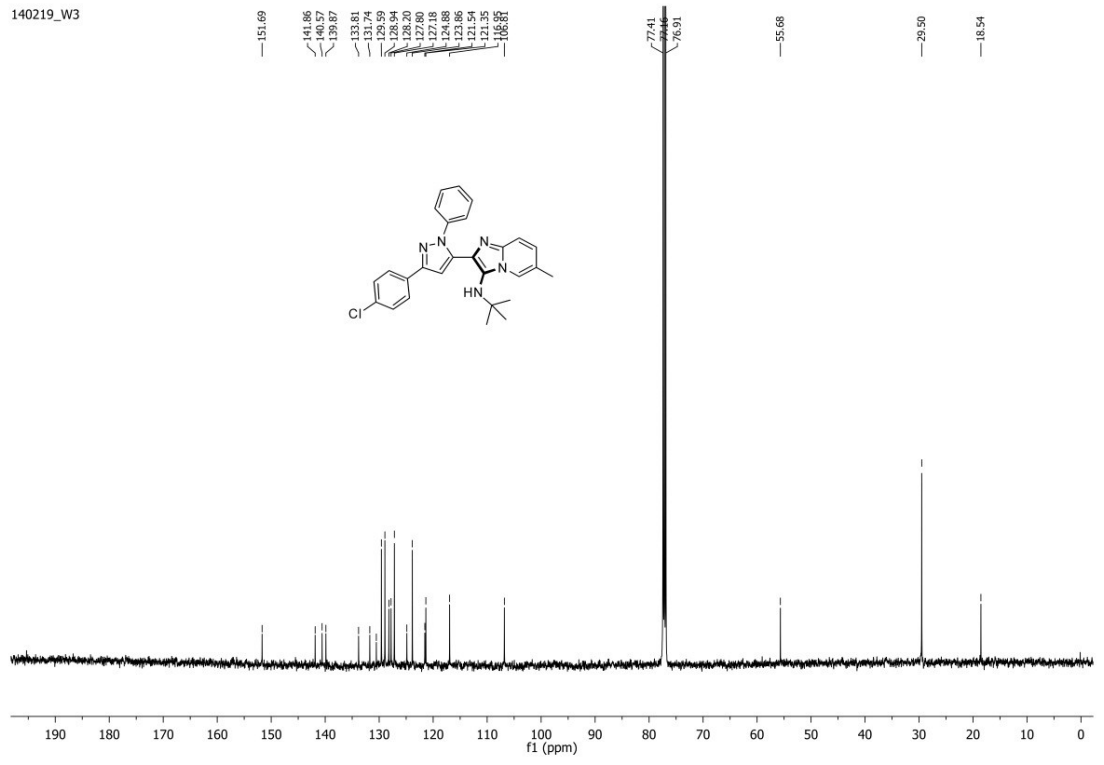


Figure S48. ^{13}C-NMR spectrum of **21aDX.**

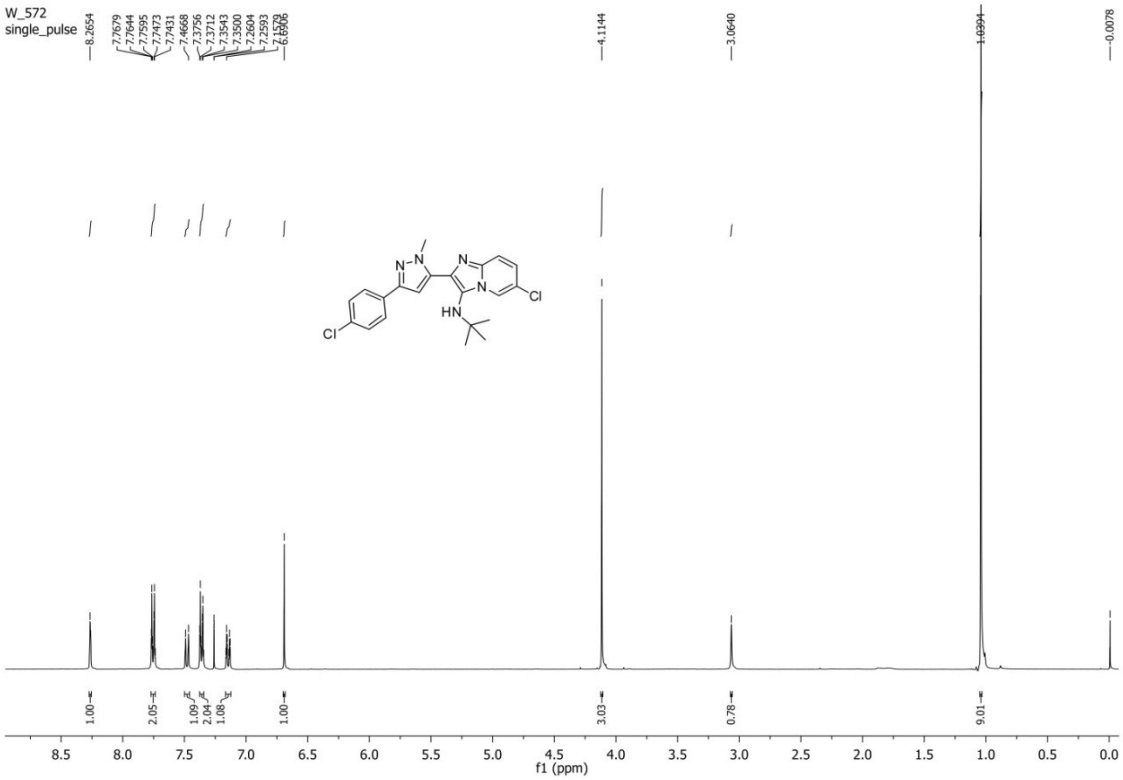


Figure S49. ^{1}H-NMR spectrum of **21bGX.**

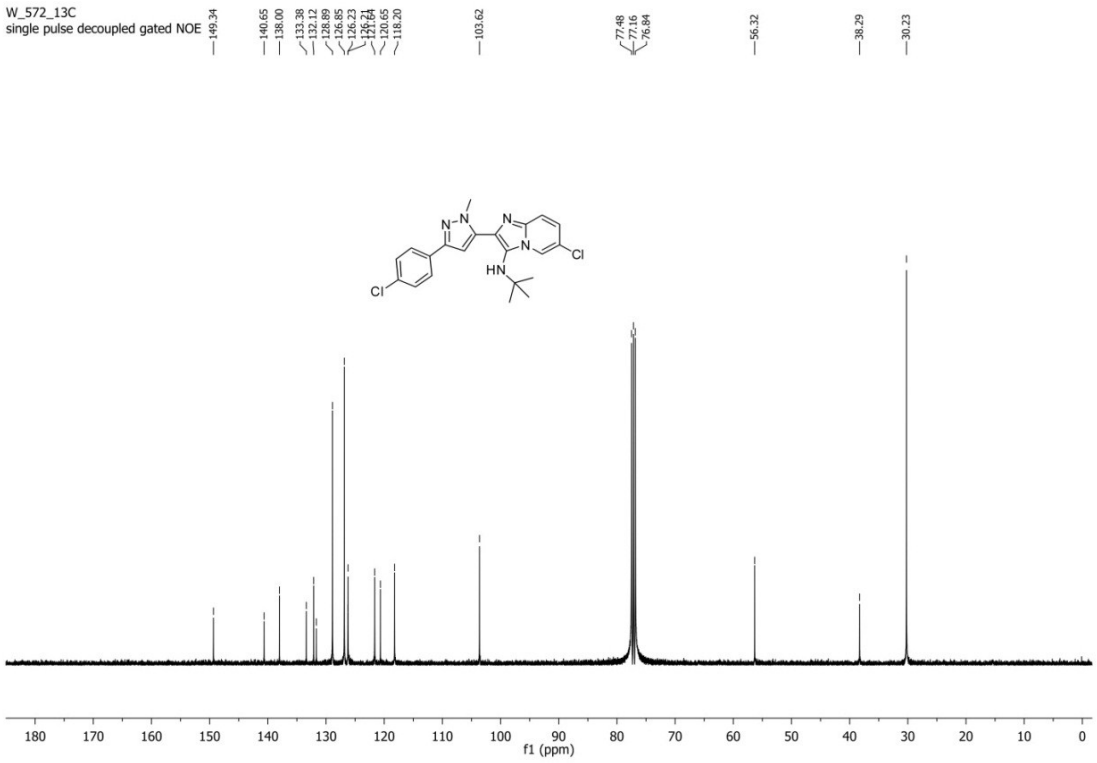


Figure S50. ^{13}C-NMR spectrum of **21bGX.**

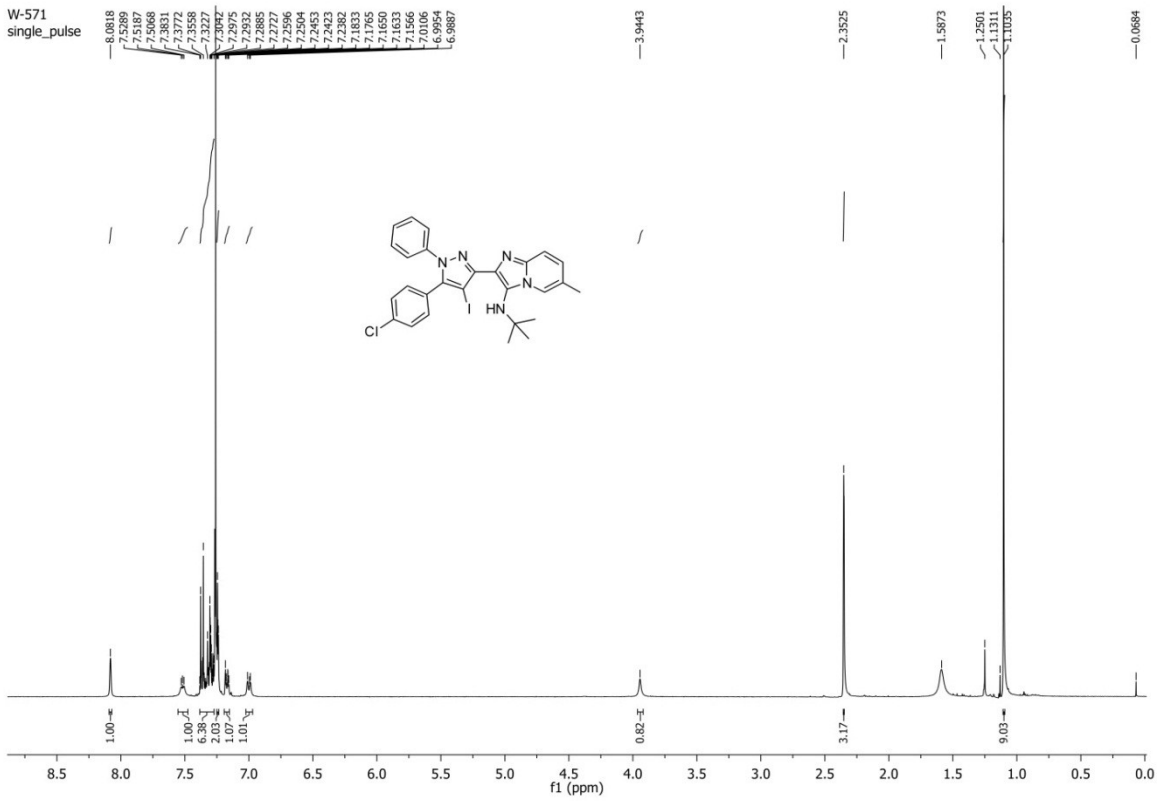


Figure S51. ^{1}H-NMR spectrum of **22aDX.**

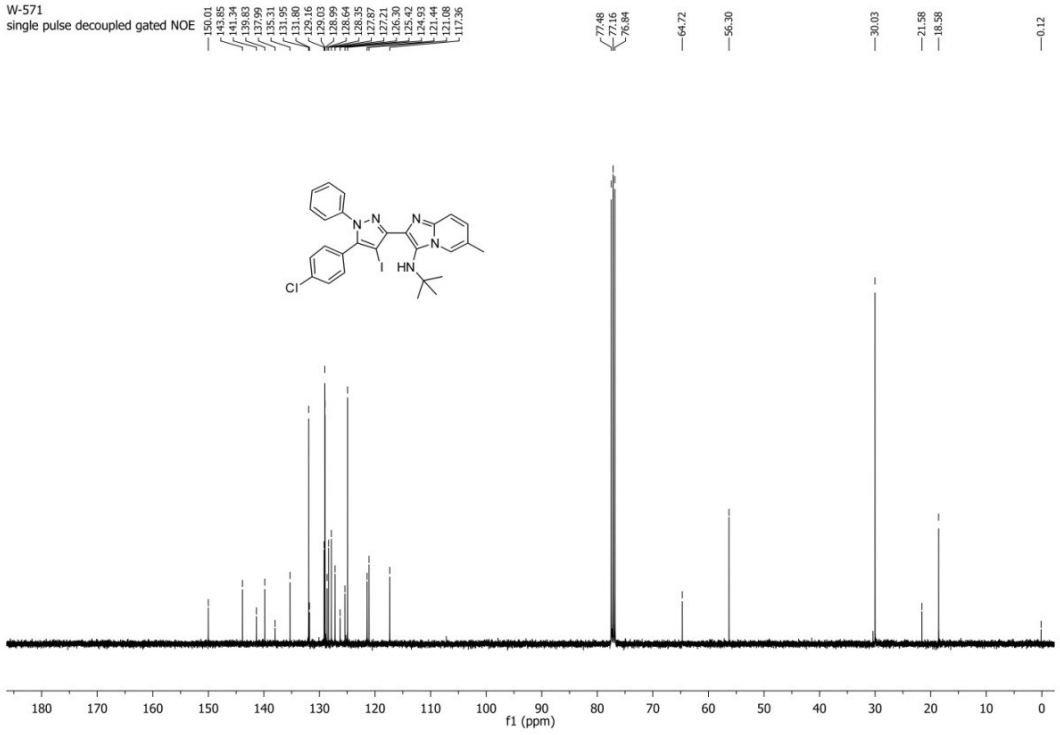


Figure S52. ^{13}C-NMR spectrum of **22aDX.**

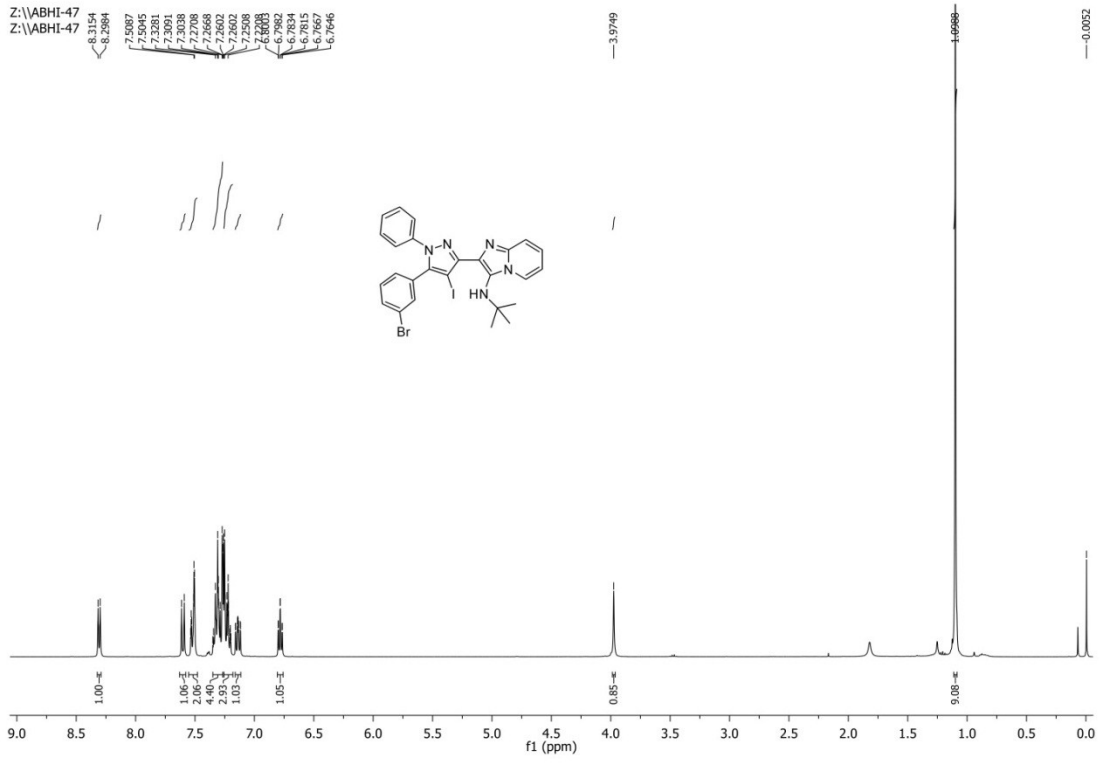


Figure S53. ^{1}H-NMR spectrum of **23aAX.**

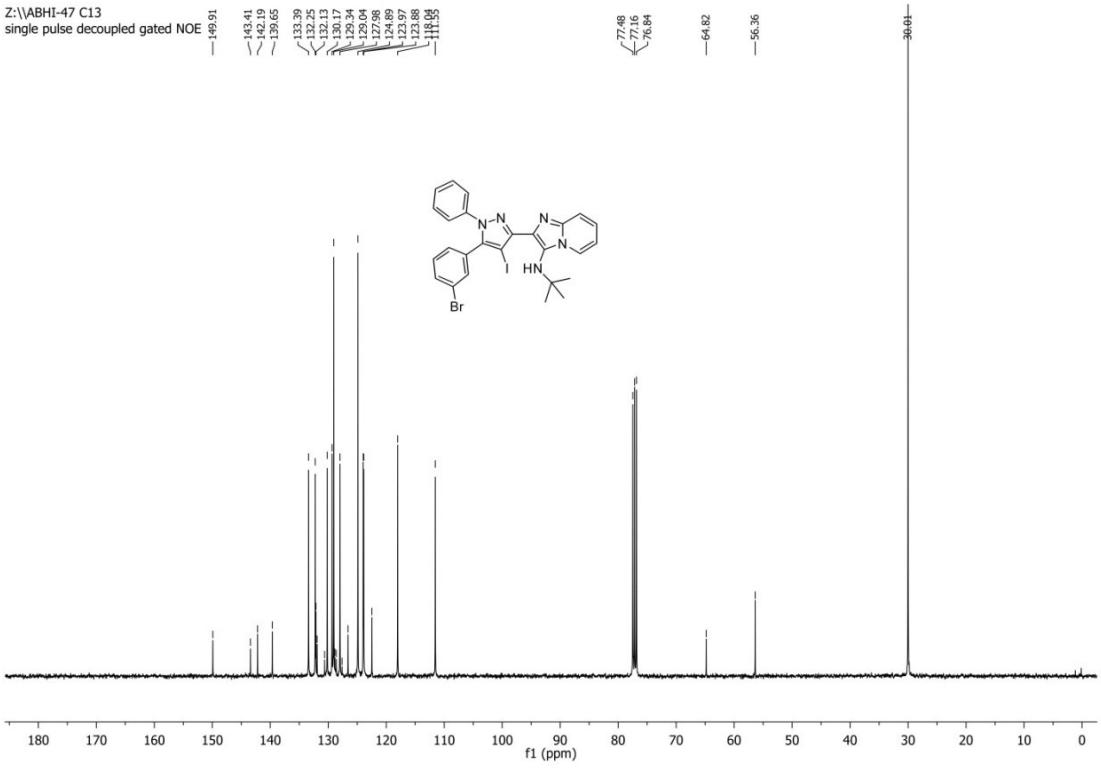


Figure S54. ^{13}C-NMR spectrum of **23aAX.**

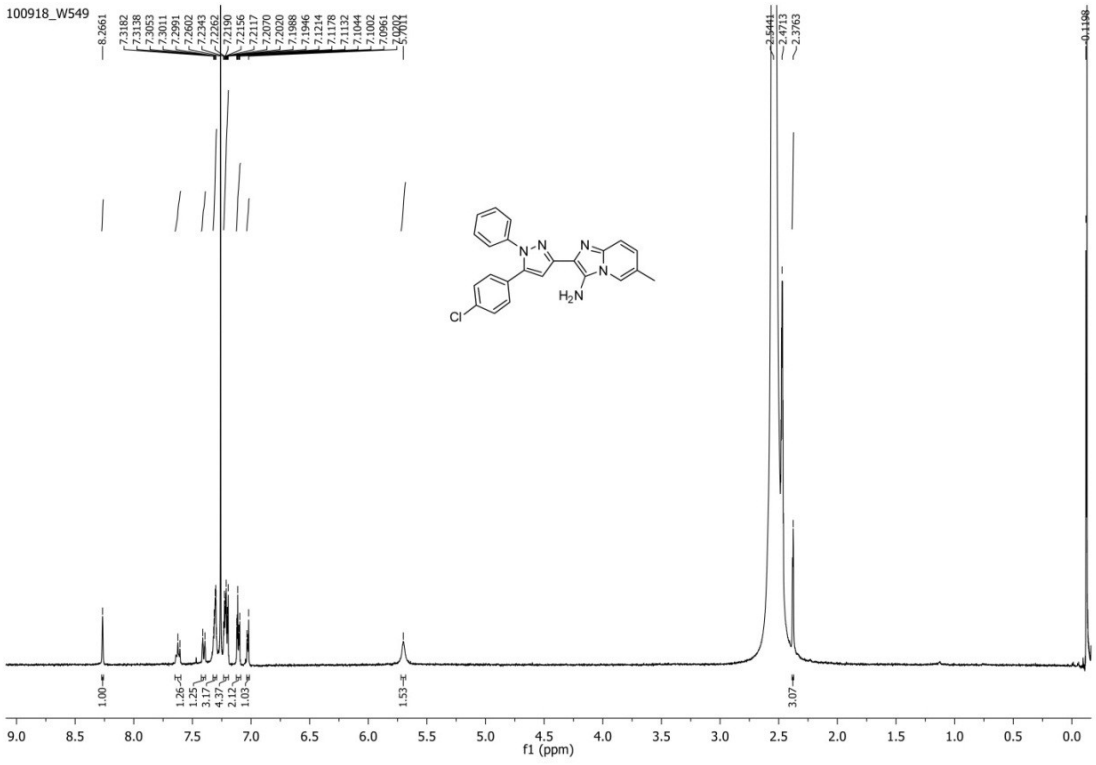


Figure S55. ^{1}H-NMR spectrum of **24aDX.**

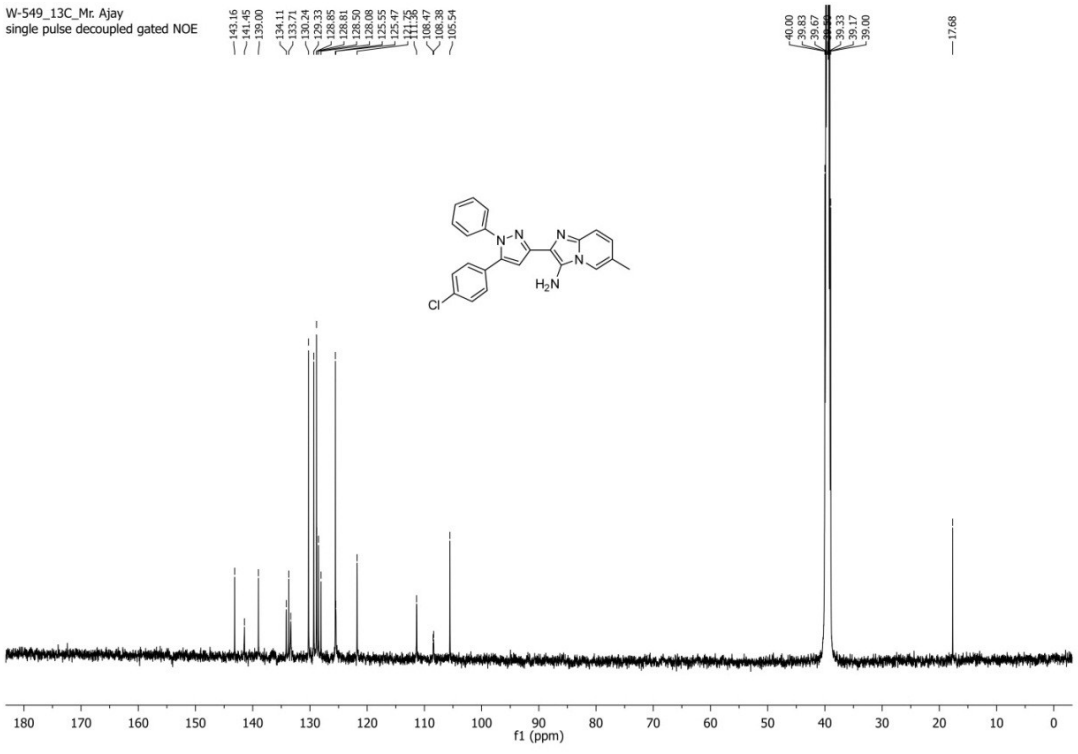


Figure S56. ^{13}C-NMR spectrum of **24aDX.**

Photophysical studies of synthesized compounds:

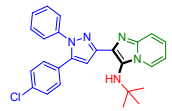
The fluorescent quantum yield (Φ) was measured relative to quinine sulfate (Φ = 0.546) (0.1 M H_2SO_4 at 350 nm excitation) as a reference compound. For the measurement of UV-Vis absorption and fluorescence emission of samples, stock solution (1.0 mM) was prepared in $CHCl_3$ and diluted to final concentration (2.0 µM) using $CHCl_3$. These quantum yields (QY) were calculated by using the equation as follows:

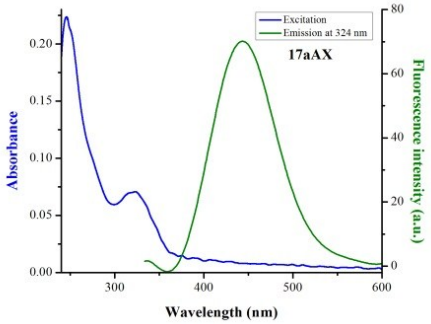
$$\Phi_S = \Phi_R \times \frac{I_S}{I_R} \times \frac{A_R}{A_S} \times \frac{\eta_S^{\,2}}{\eta_R^{\,2}}$$

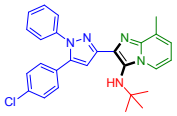
$$R - \text{Reference}; S - \text{Sample}$$

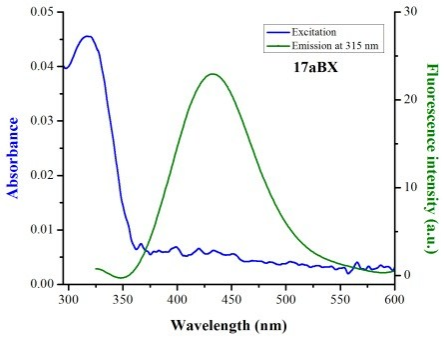
where ϕ is the quantum yields, η is the refractive index of the solvent, I is the integrated fluorescence intensity and A is the absorbance.

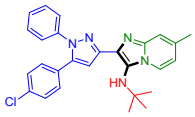
Figure S57. Photophysical properties and graphical data of pyrazole tethered imidazo[1,2-*a*]pyridine derivatives derived from 2-aminopyridines containing electron donating substituents:

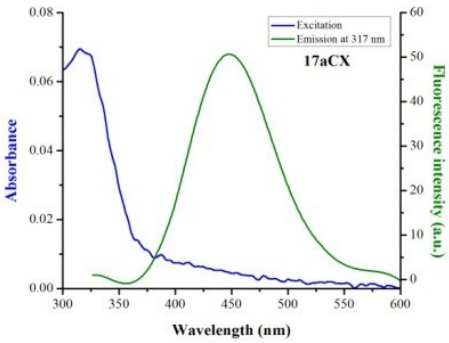
17aAX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	324.30	443.21	74.81	0.43

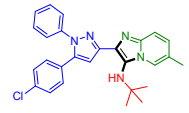


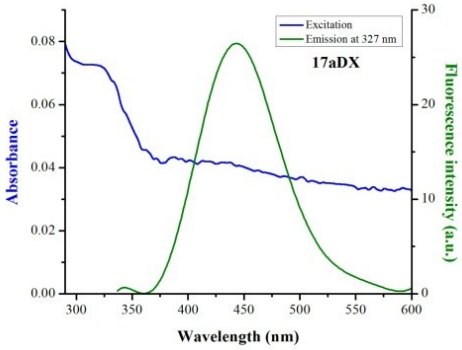
17aBX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	315.21	431.69	24.14	0.23

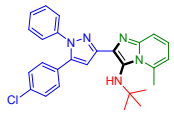


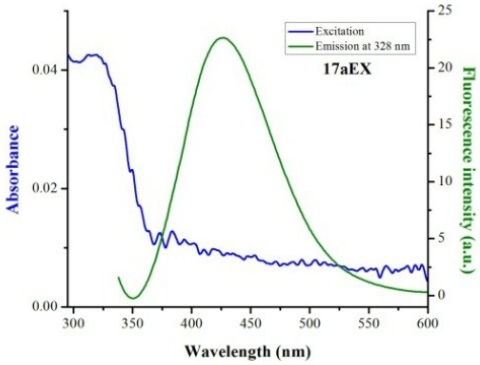
17aCX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	317.12	440.17	58.31	0.33

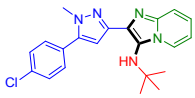


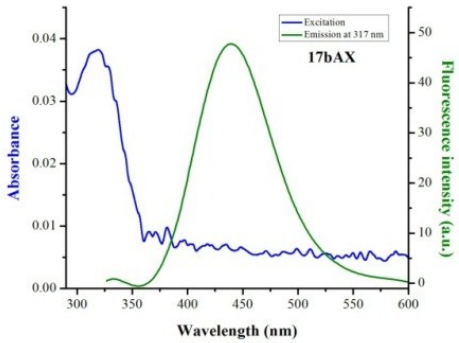
17aDX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	327.45	445.20	27.57	0.16

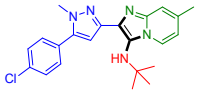


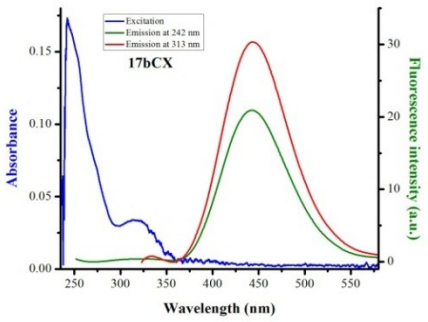
17aEX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	328.02	430.06	22.59	0.25

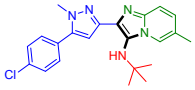


17bAX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	317.30	435.32	48.27	0.52



17bCX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	242.22	435.93	21.11	0.05
	313.72	442.64	30.42	0.40



17bDX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	329.16	435.68	35.31	0.23

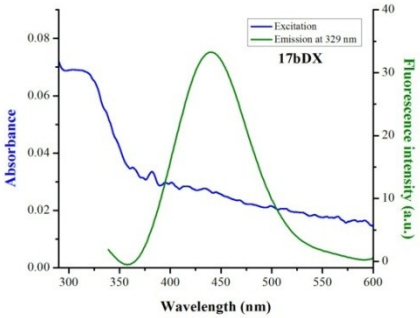
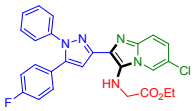
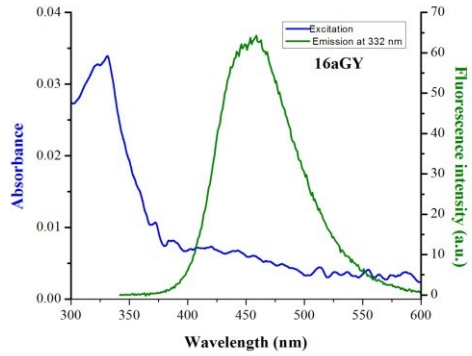
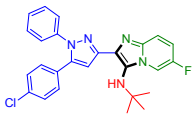
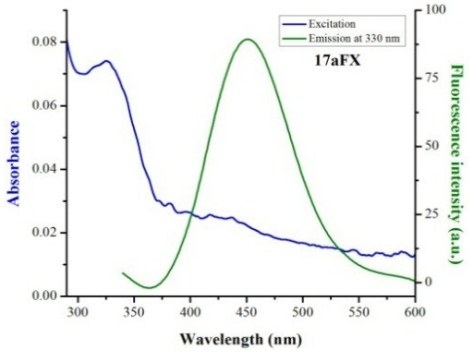


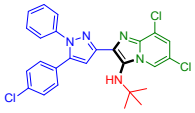
Figure S58: Photophysical properties and graphical data of pyrazolyl imidazo[1,2-*a*]pyridine derivatives derived from 2-aminopyridines containing halogens (F, Cl and Br) as the electron withdrawing substituents:

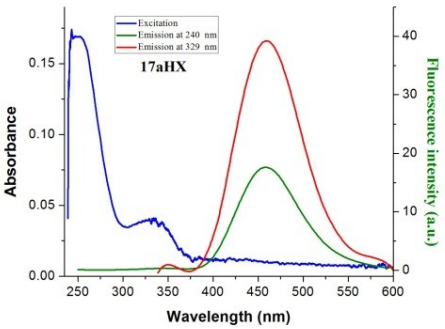
16aGY	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	332	460.4	6.14	0.75

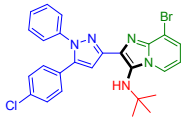


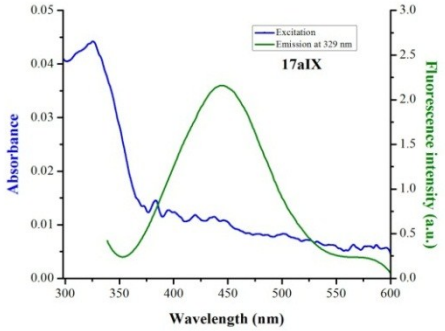
17aFX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	330.30	456.06	92.27	0.53

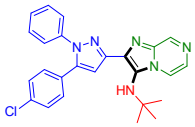


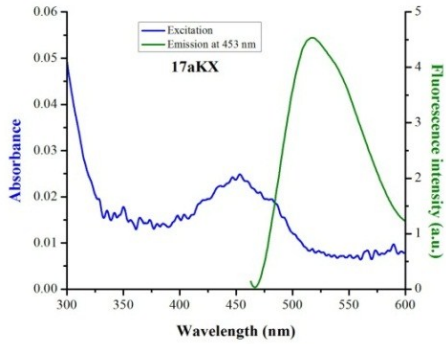
17aHX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	240.63	460.10	17.59	0.05
	329.18	457.84	41.61	0.43

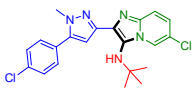


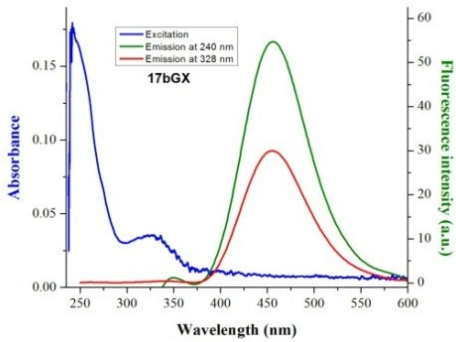
17aIX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	329.73	443.70	2.66	0.03

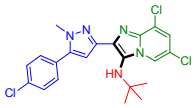


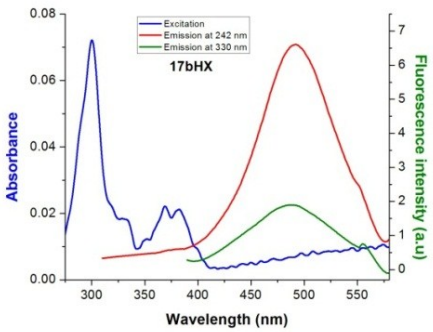
17aKX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	453.33	521.37	4.32	0.07

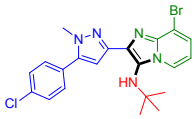


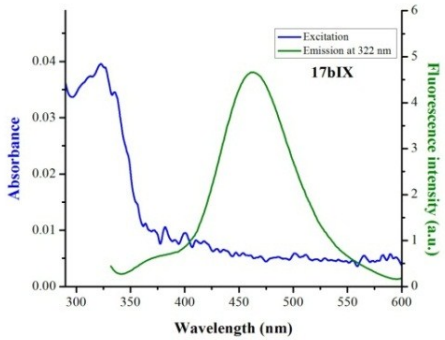
17bGX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	240.11	448.31	30.42	0.08
	328.86	455.38	55.35	0.65

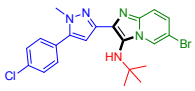


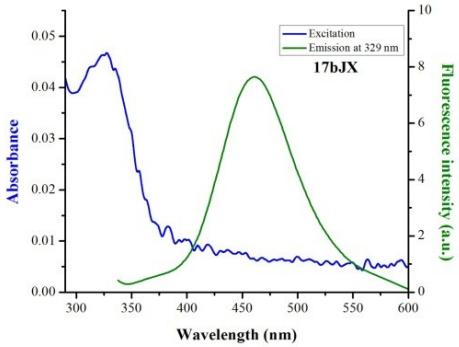
17bHX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	242.9	454.87	33.92	0.11
	330	458.38	51.67	0.83

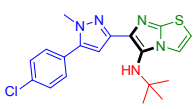


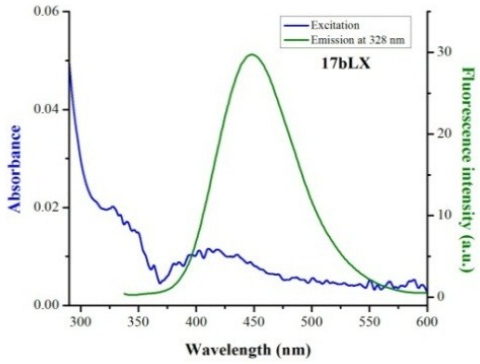
17bIX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	322.53	452.85	4.93	0.05

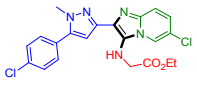


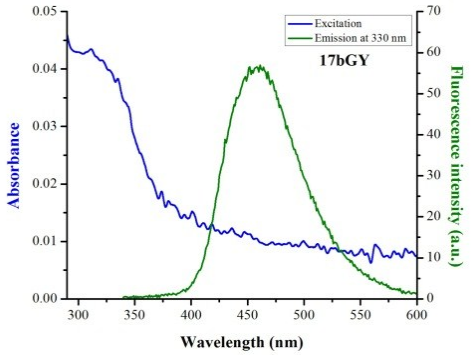
17bJX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	328.92	459.21	7.54	0.07

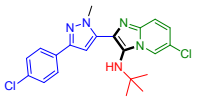


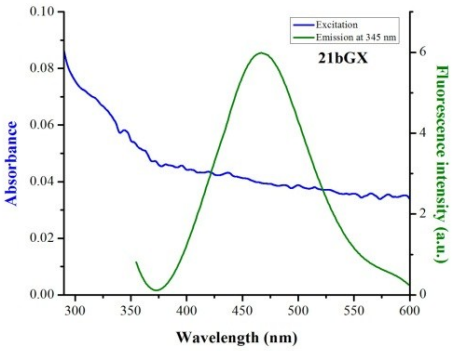
17bLX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	328.02	456.91	29.51	0.78

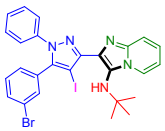


17bGY	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	330.08	459.15	56.33	0.58



21bGX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	345.06	465.84	6.71	0.05



23aAX	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	320	460.4	6.64	0.14