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

Sulfur-mediated annulation of 1,2-phenylenediamines towards benzofuro- and benzothieno-quinoxalines

Loan T. Tran,[a,b] Tuan H. Ho,[a,b] Nhu T. A. Phan,[a,b] Tung T. Nguyen,*[a,b] and Nam T. S. Phan*[a,b]

[a]Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Vietnam

[b]Vietnam National University Ho Chi Minh City, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Vietnam

*Email: tungtn@hcmut.edu.vn, ptsnam@hcmut.edu.vn

Ph: (+84 8) 38647256 ext. 5681 Fx: (+84 8) 38637504

Supporting information

1. Materials and instrumentation

All reagents and starting materials were obtained commercially and used as received without any further purification unless otherwise noted. Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). GC-MS analyses were analyzed on a Shimadzu GCMS-QP2010Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The ^{1}H NMR and ^{13}C NMR were recorded on Bruker AV 500 spectrometers. Without notice, chemical shifts were reported in ppm and referenced to the residual peak for $CDCl_3$ (δ = 7.26 ppm for ^{1}H NMR and δ = 77.2 ppm for ^{13}C NMR) or DMSO-d_6 (δ = 2.50 ppm for ^{1}H NMR and δ = 39.5 ppm for ^{13}C NMR). Splitting was reported with the following symbols: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, td =

triplet of doublets, dd = doublet of doublets, ddd = doublet of doublets of doublets, and m = multiplet. Coupling constants (*J*) were reported in hertz. HR-MS spectra were recorded by an Agilent HPLC 1200 Series coupled to Bruker micrOTOF-QII.

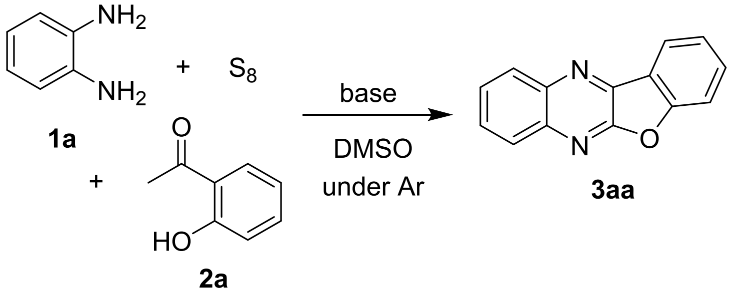
2. Studies of reaction conditions

2.1. General procedure

In a typical experiment, a vial equipped with a magnetic stir bar was charged with *o*-phenylenediamine **1a** (27.0 mg, 0.25 mmol), 2'-hydroxyacetophenone **2a**, elemental sulfur (32 mg/mmol), DABCO, and DMSO. The vial was placed on a pre-heated oil bath at 120 °C, then stirred for 30 min. Upon the completion of the reaction, ethyl acetate (2 mL) was added to dilute the reaction mixture. The GC yield of desired product was monitored by withdrawing aliquots from the resulting mixture, quenching with brine (1 mL) before extracting with ethyl acetate (3 x 1 mL), drying over anhydrous Na_2SO_4, filtering, and then analyzing the sample by GC regarding diphenyl ether (42.5 mg, 0.25 mmol) as internal standard.

2.2 Optimization studies

2.2.1. Effect of bases

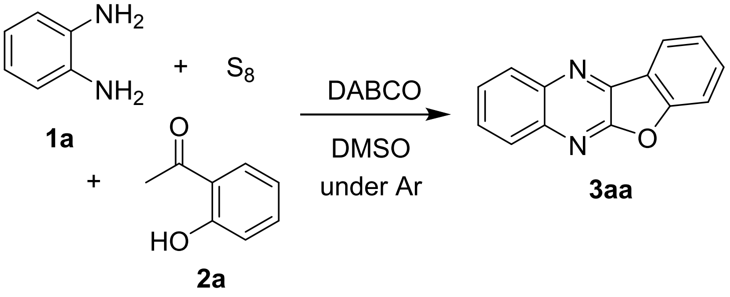


Entry	base	yield of **3aa**, %	entry	base	yield of **3aa**, %
1	NaOH	74	7	3-picoline	62
2	KOH	69	8	*N*-methyl morpholine	70

3	Na_2CO_3	71	9	*N*,*N*’-dimethylpiperazine	81
4	K_2CO_3	46	**10**	**DABCO**	**97**
5	K_3PO_4	69	11	NH_4OAc	49
6	NaOAc	56	12	no base	61

condition: **1a** (0.25 mmol), **2a** (0.5 mmol), elemental sulfur (0.5 mmol), base (0.375 mmol), DMSO (0.5 mL), 120 °C, 16 h, under argon. Yields are GC yields using diphenyl ether internal standard.

2.2.2. Effect of sulfur amount

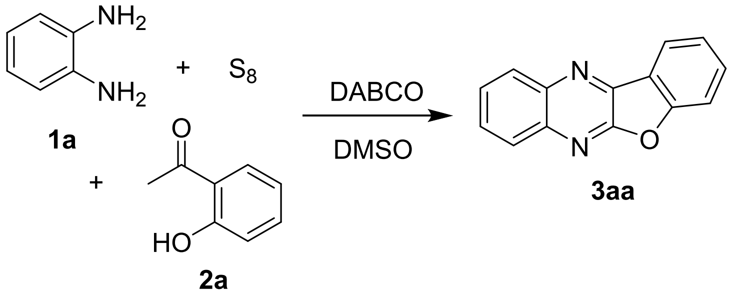


Entry	sulfur amount (equivalent)	yield of **3aa**, %
1	0	trace
2	0.25	40
3	0.5	86

4	1	92
5	1.5	95
6	2	97
7	2.5	98
8	**3**	**quantitative**
9	4	quantitative

condition: **1a** (0.25 mmol), **2a** (0.5 mmol), elemental sulfur (x equivalents), DABCO (0.375 mmol), DMSO (0.5 mL), 120 °C, 16 h, under argon. Yields are GC yields using diphenyl ether internal standard.

2.2.3. Effect of inert atmosphere

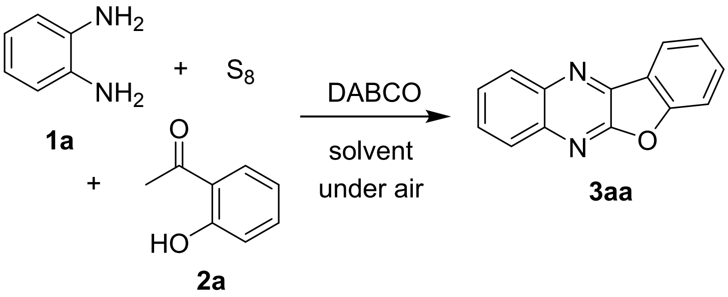


Entry		yield of **3aa**, %
1	under argon	quantitative
2	under air	quantitative

3	under oxygen	96

condition: **1a** (0.25 mmol), **2a** (0.5 mmol), elemental sulfur (3 equivalents), DABCO (0.375 mmol), DMSO (0.5 mL), 120 °C, 16 h. Yields are GC yields using diphenyl ether internal standard.

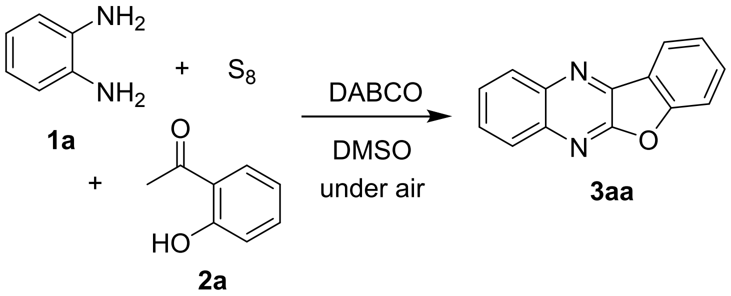
2.2.4. Effect of solvents



Entry	solvent	yield of **3aa**, %
1	*n*-butanol	12
2	1,4-dioxane	14
3	**DMSO**	**quantitative**
4	DMF	7
5	pyridine	17
6	CH_3CN	22

condition: **1a** (0.25 mmol), **2a** (0.5 mmol), elemental sulfur (3 equivalents), DABCO (0.375 mmol), solvent (0.5 mL), 120 °C, 16 h, under air. Yields are GC yields using diphenyl ether internal standard.

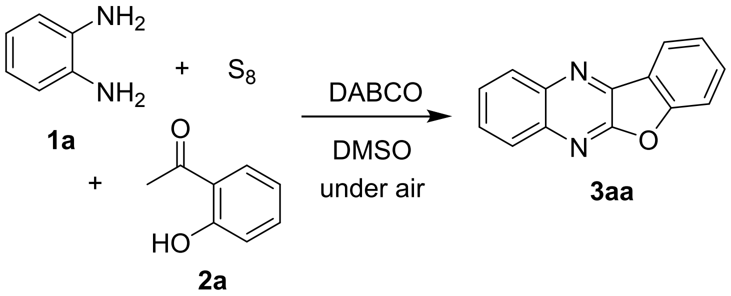
2.2.5. Effect of DMSO amount



Entry	equivalent of DMSO	yield of **3aa**, %
1	0 (solvent-free)	24
2	1	46
3	2	77
4	3	95
5	**4**	**quantitative**
6	0.1 mL	quantitative
7	0.5 mL	quantitative

condition: **1a** (0.25 mmol), **2a** (0.5 mmol), elemental sulfur (3 equivalents), DABCO (0.375 mmol), DMSO (x equivalents to y mL), 120 °C, 16 h, under air. Yields are GC yields using diphenyl ether internal standard.

2.2.7. Effect of reaction time



Entry	reaction time	yield of **3aa**, %
1	2 min	49
2	5 min	81
3	10 min	95
4	15 min	quantitative
6	30 min	quantitative
7	1h	quantitative

condition: **1a** (0.25 mmol), **2a** (0.5 mmol), elemental sulfur (3 equivalents), DABCO (0.375 mmol), DMSO (1 mmol), 120 °C, under air. Yields are GC yields using diphenyl ether internal standard.

3. Copies of NMR spectra

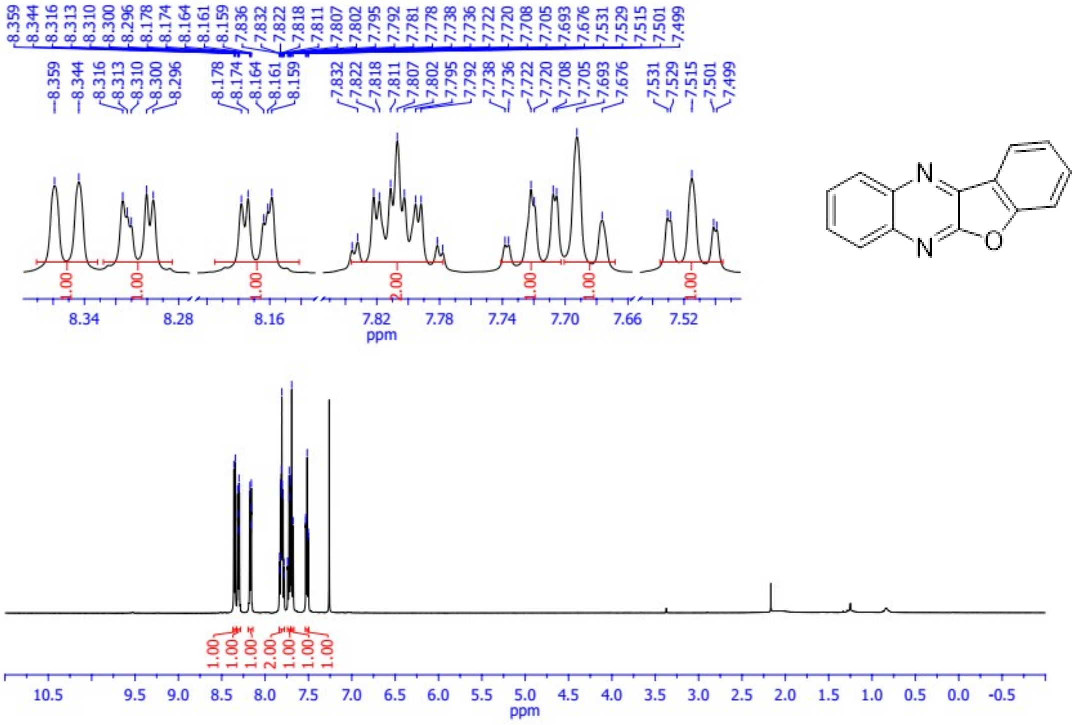


Fig. S1. ^{1}H NMR spectrum of **3aa**.

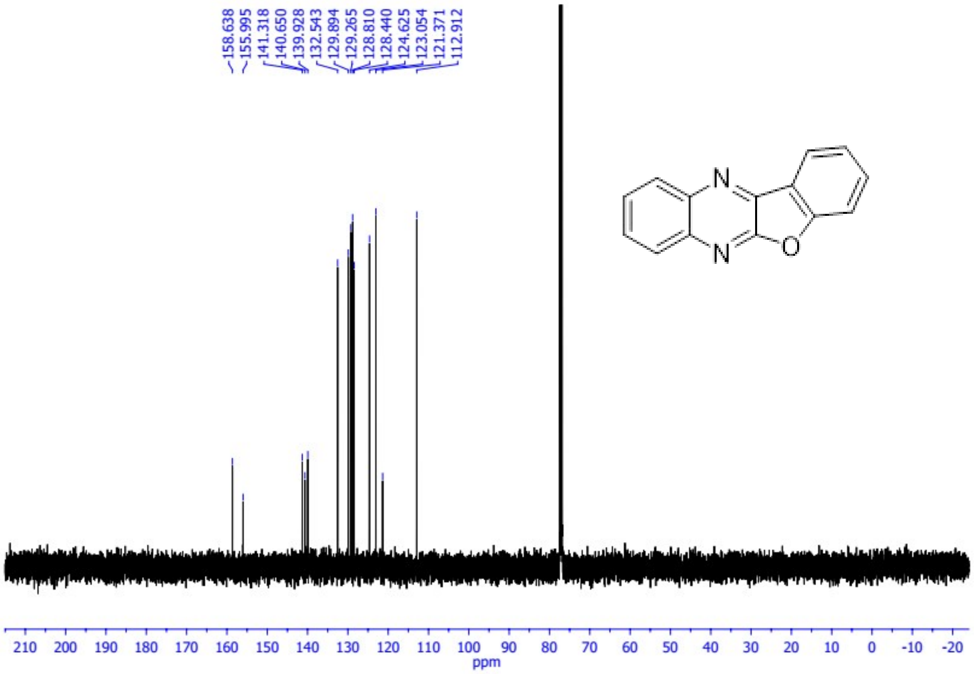


Fig. S2. ^{13}C NMR spectrum of **3aa**.

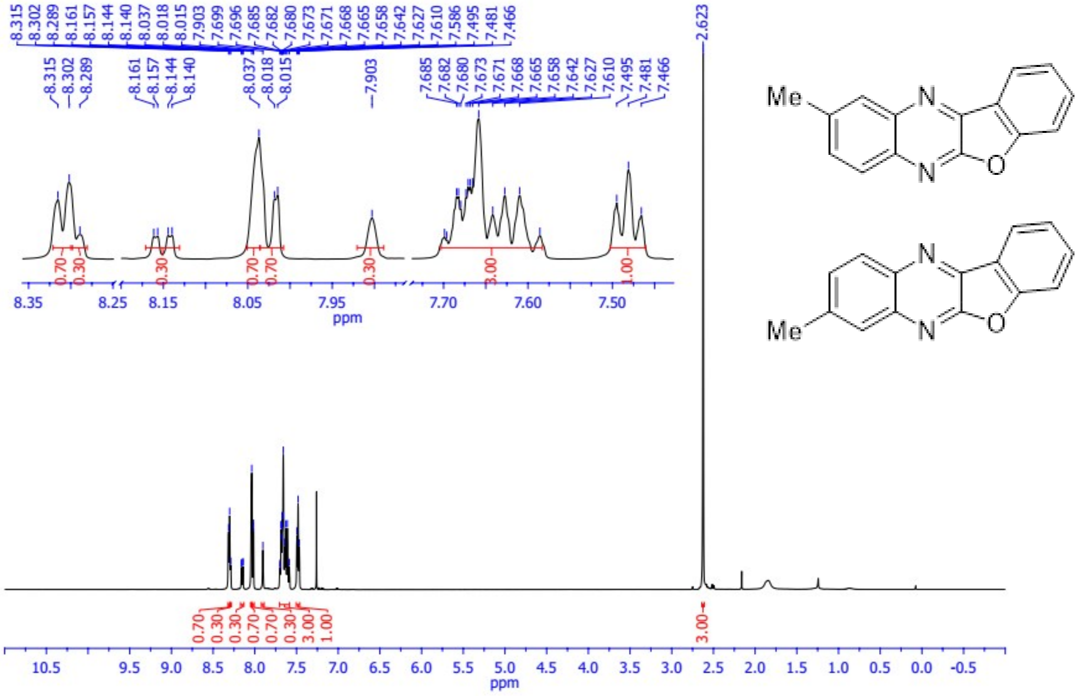


Fig. S3. ^{1}H NMR spectrum of **3ba + 3b'a.**

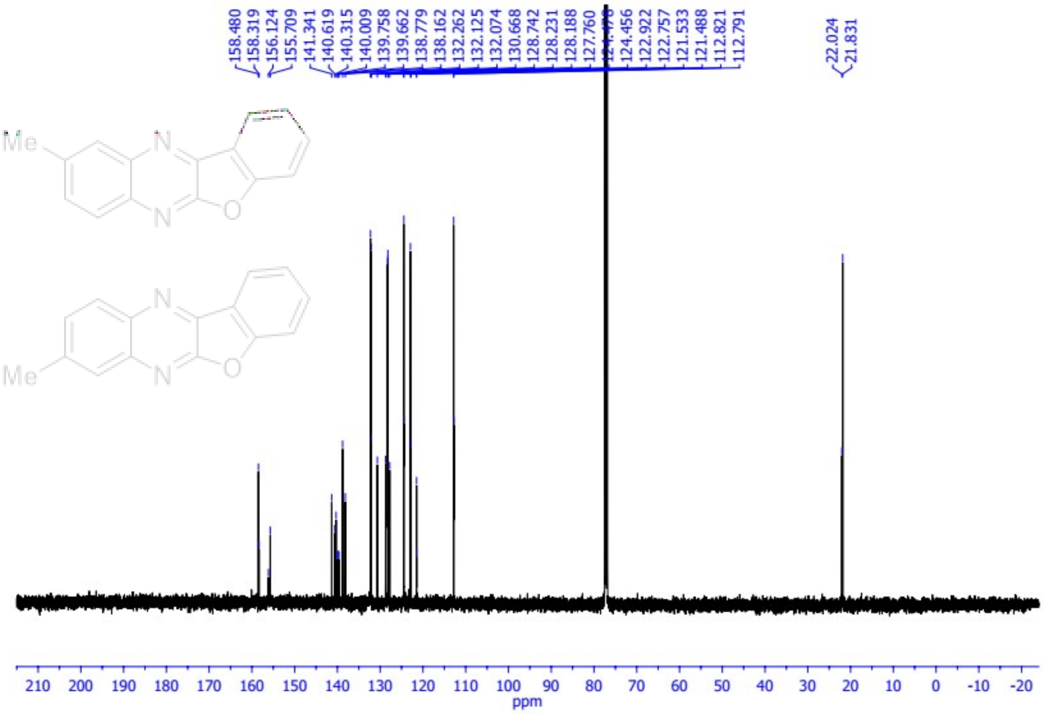


Fig. S4. ^{13}C NMR spectrum of **3ba**+ **3b'a**.

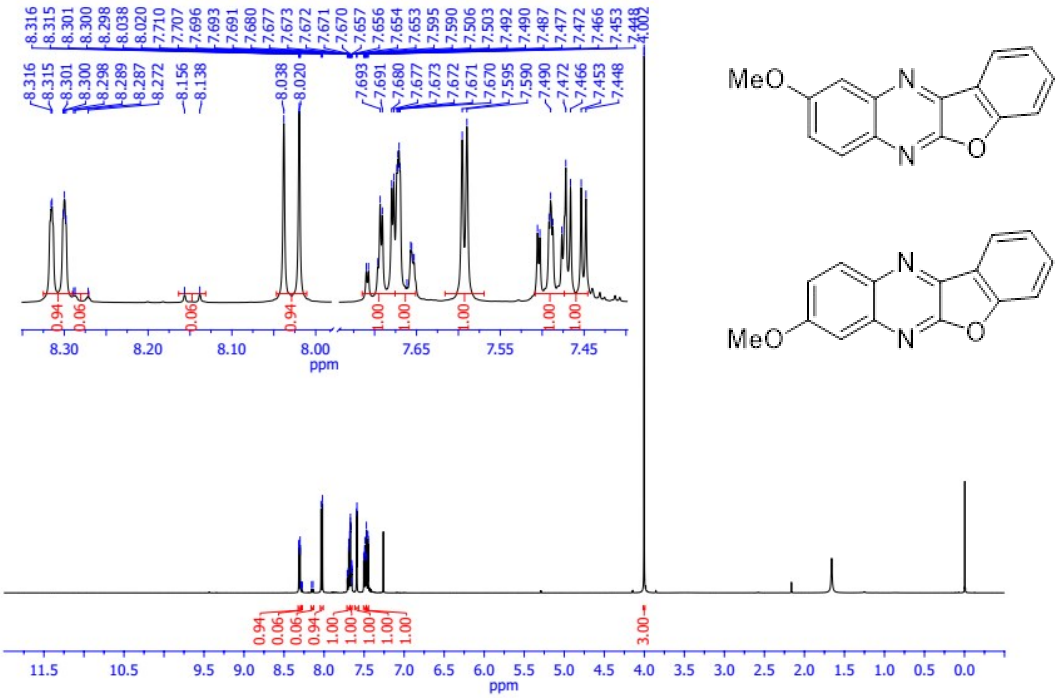


Fig. S5. ^{1}H NMR spectrum of **3ca** + **3c'a.**

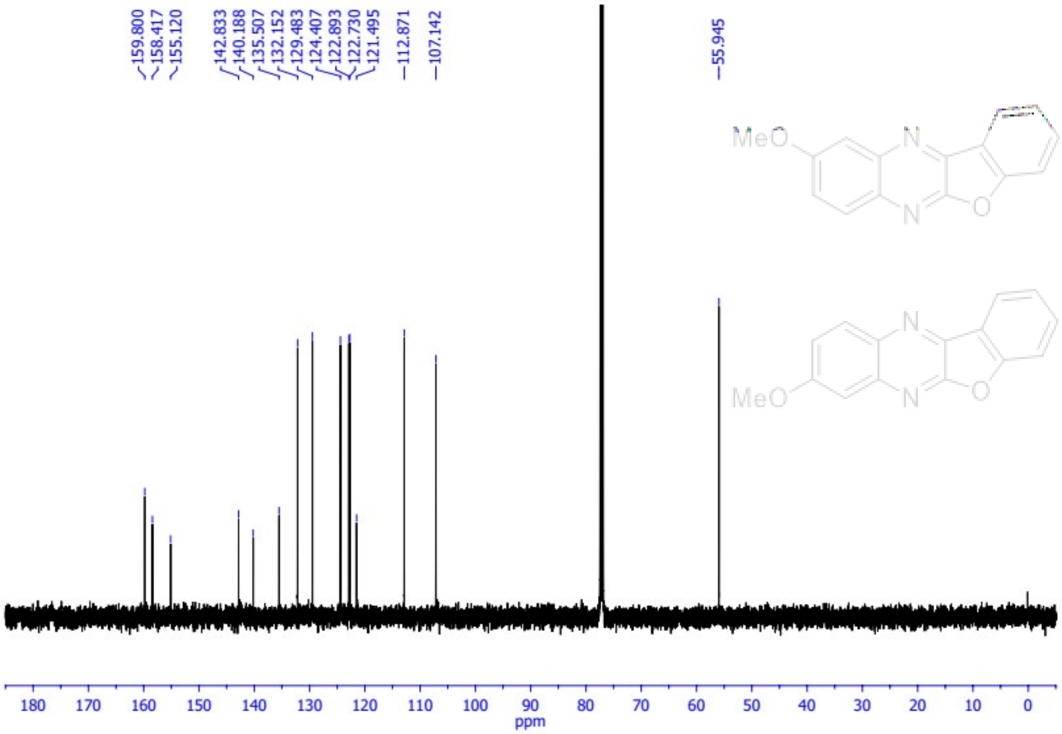


Fig. S6. ^{13}C NMR spectrum of **3ca + 3c'a**.

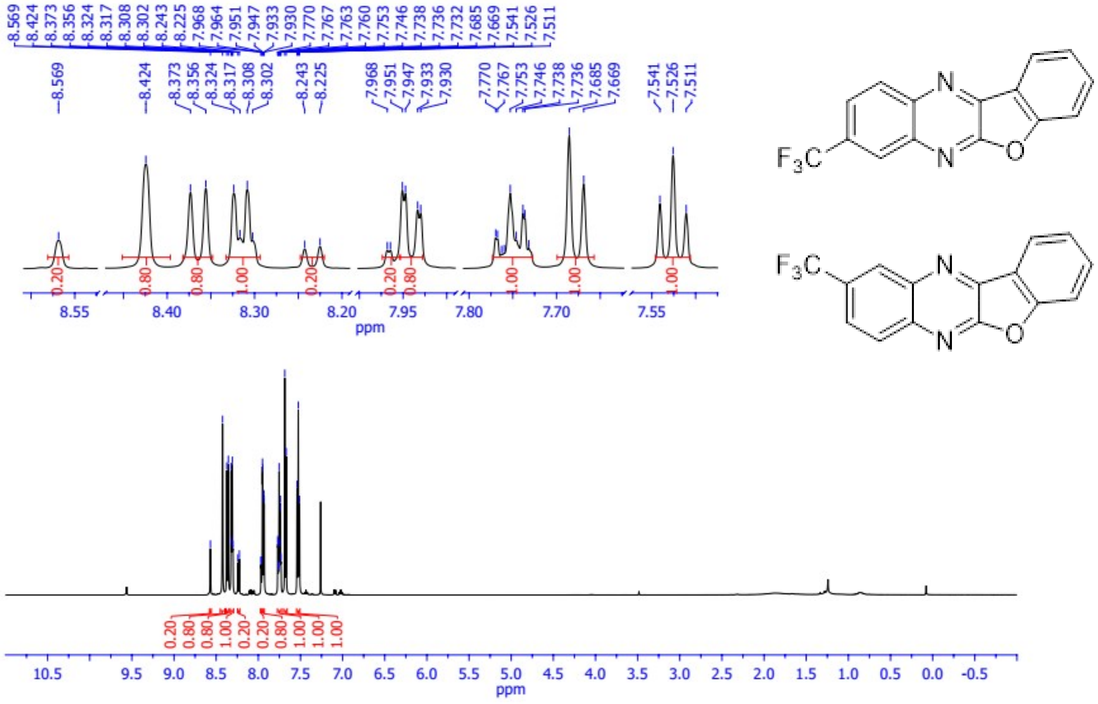


Fig. S7. ^{1}H NMR spectrum of **3da** + **3d'a.**

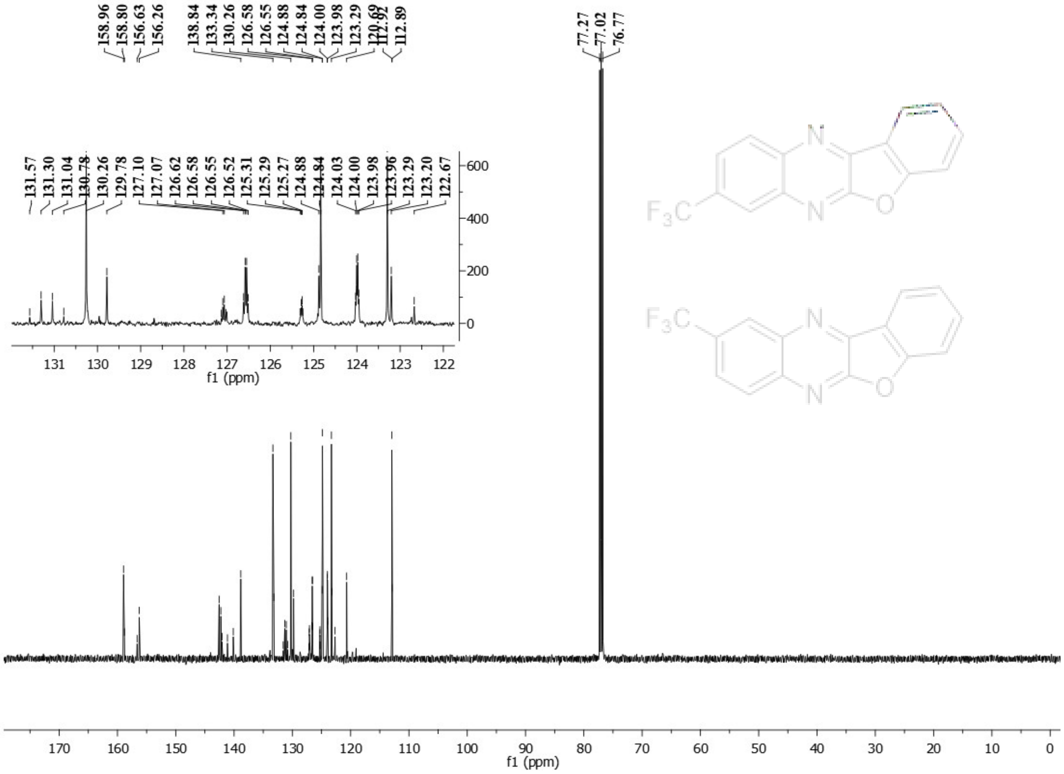


Fig. S8. ^{13}C NMR spectrum of **3da** + **3d’a**.

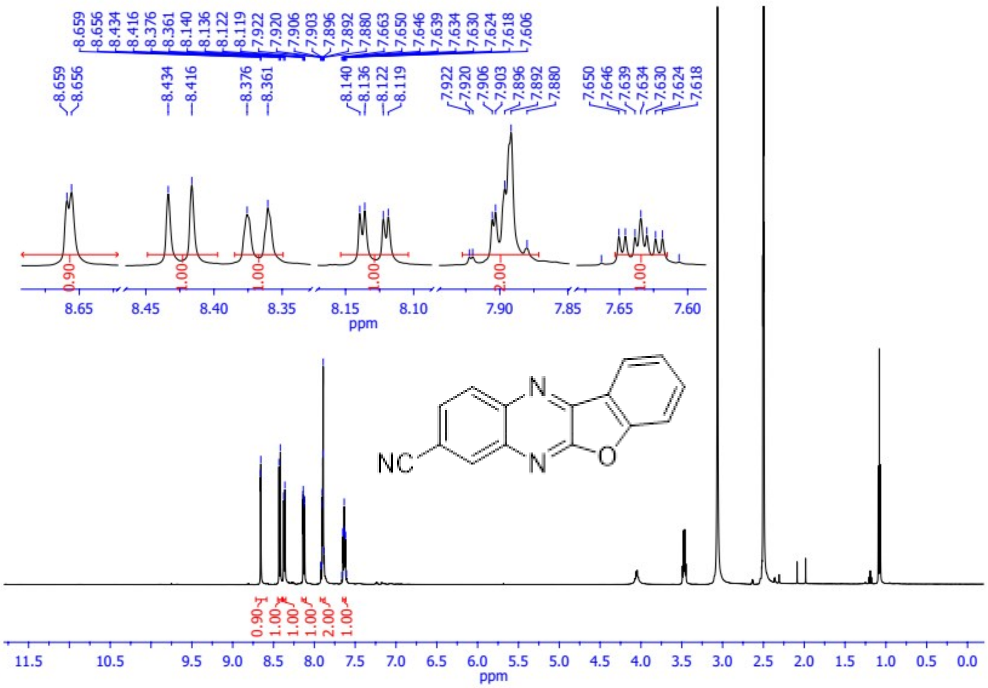


Fig. S9. ^{1}H NMR spectrum of **3ea.**

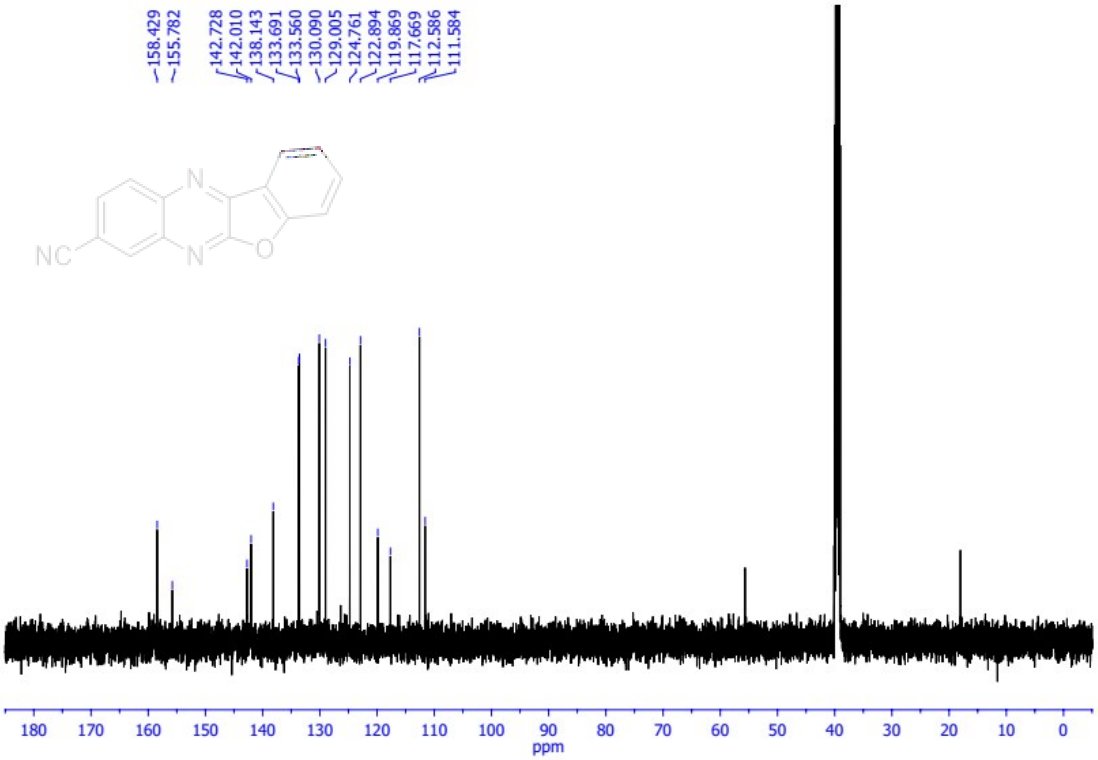


Fig. S10. ^{13}C NMR spectrum of **3ea**.

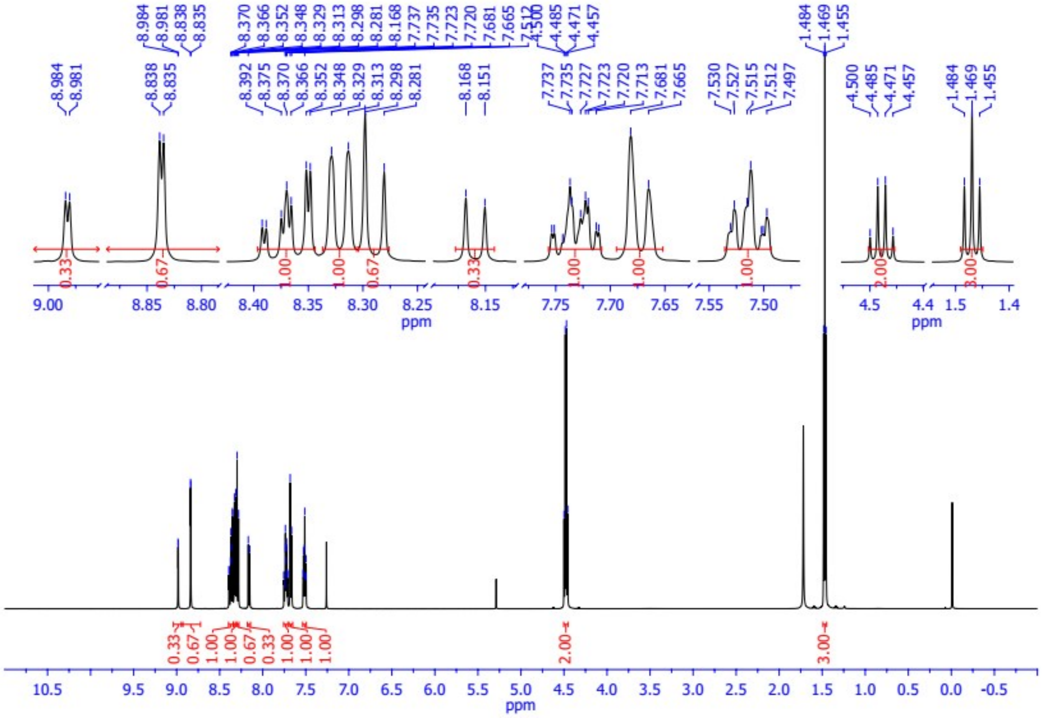


Fig. S11. ^{1}H NMR spectrum of **3fa** + **3f'a.**

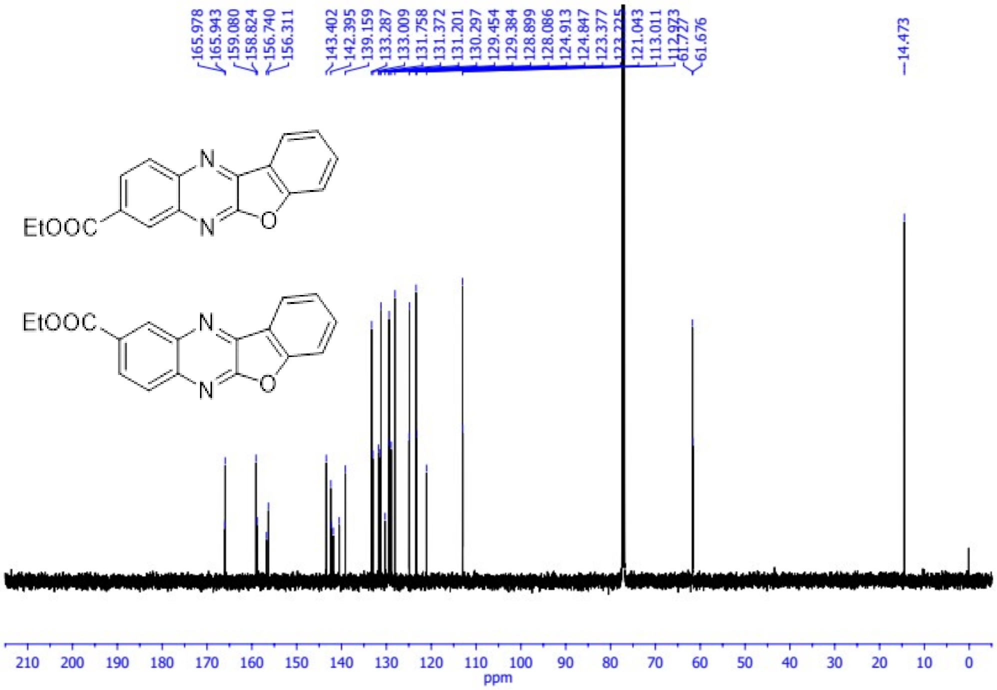


Fig. S12. ^{13}C NMR spectrum of **3fa** + **3f'a**.

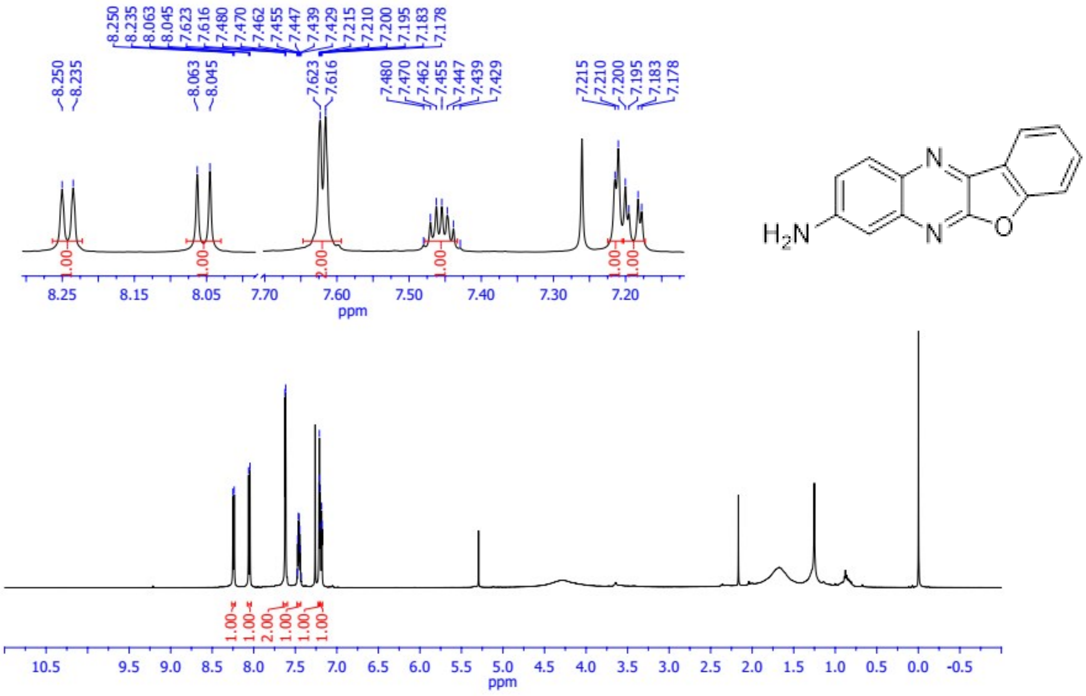


Fig. S13. ^{1}H NMR spectrum of **3ga.**

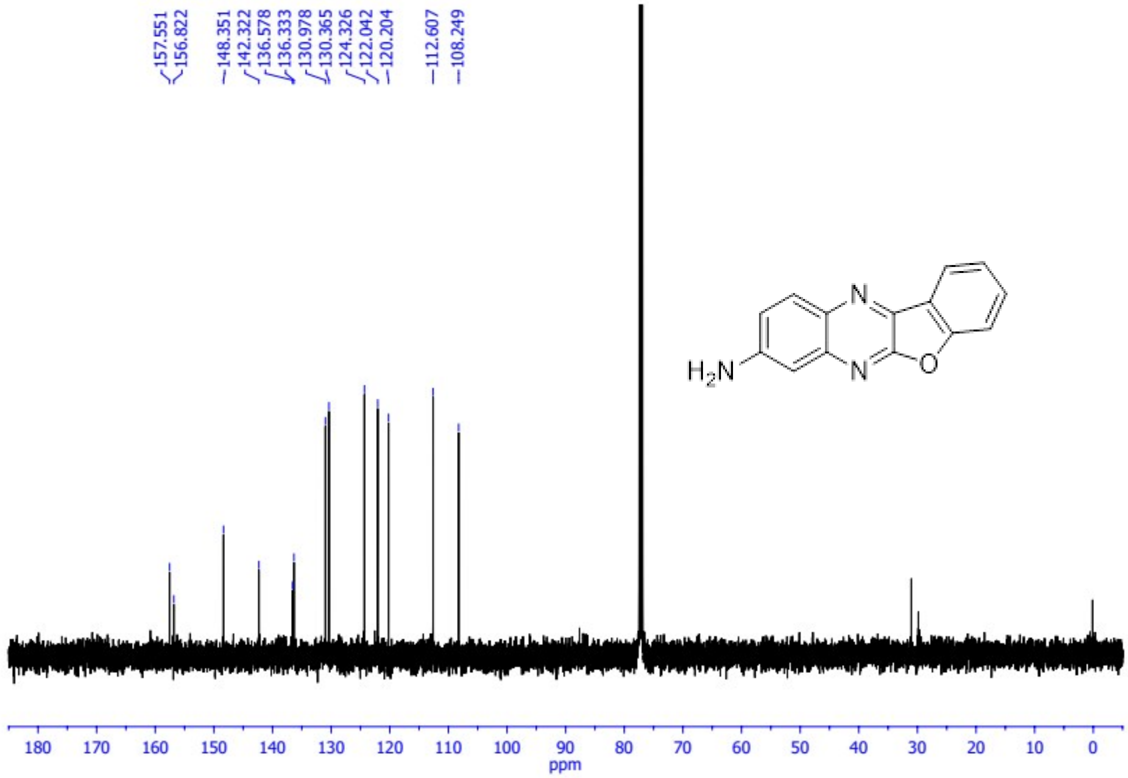


Fig. S14. ^{13}C NMR spectrum of **3ga**.

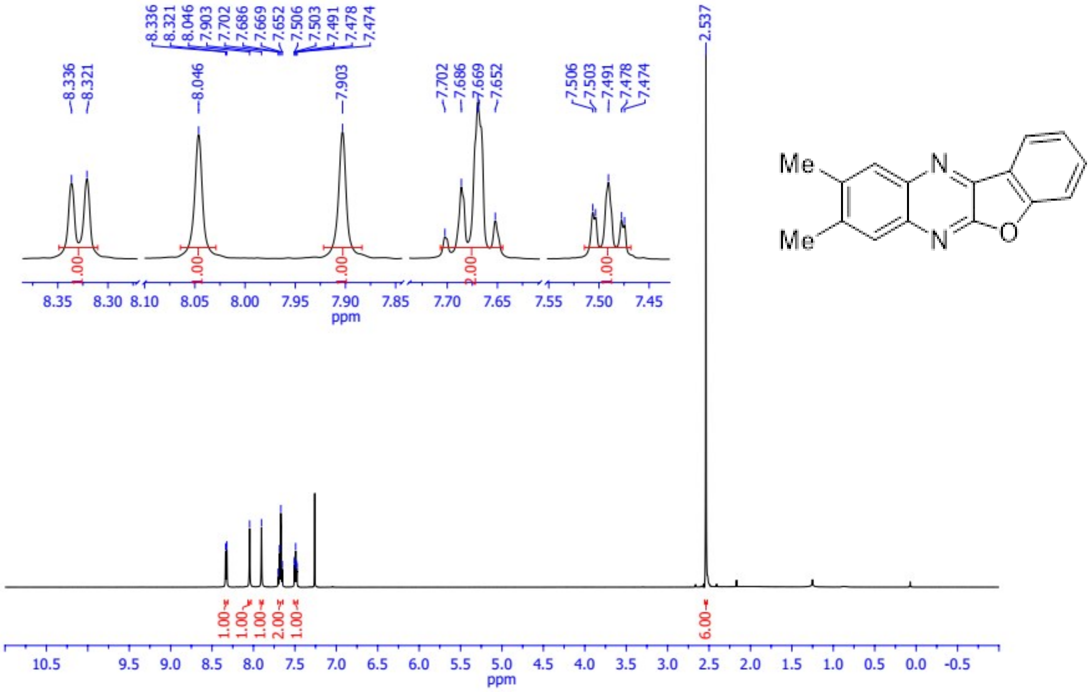


Fig. S15. ^{1}H NMR spectrum of **3ha.**

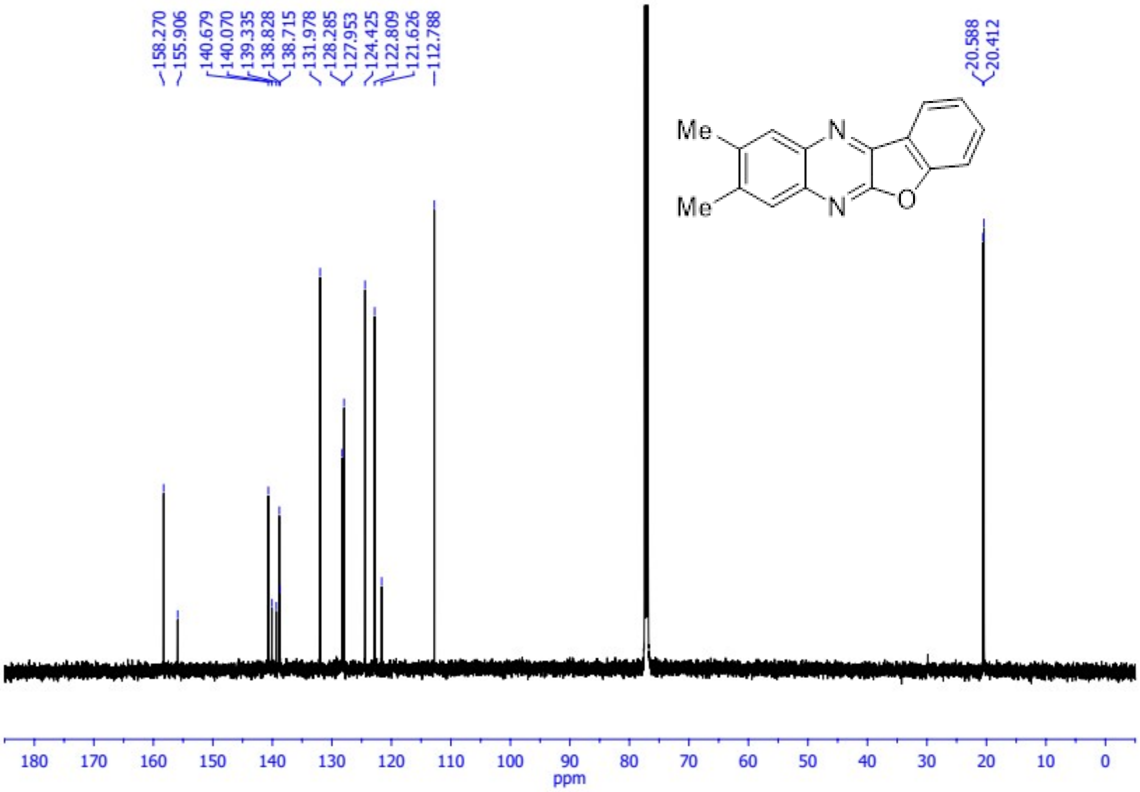


Fig. S16. ^{13}C NMR spectrum of **3ha**.

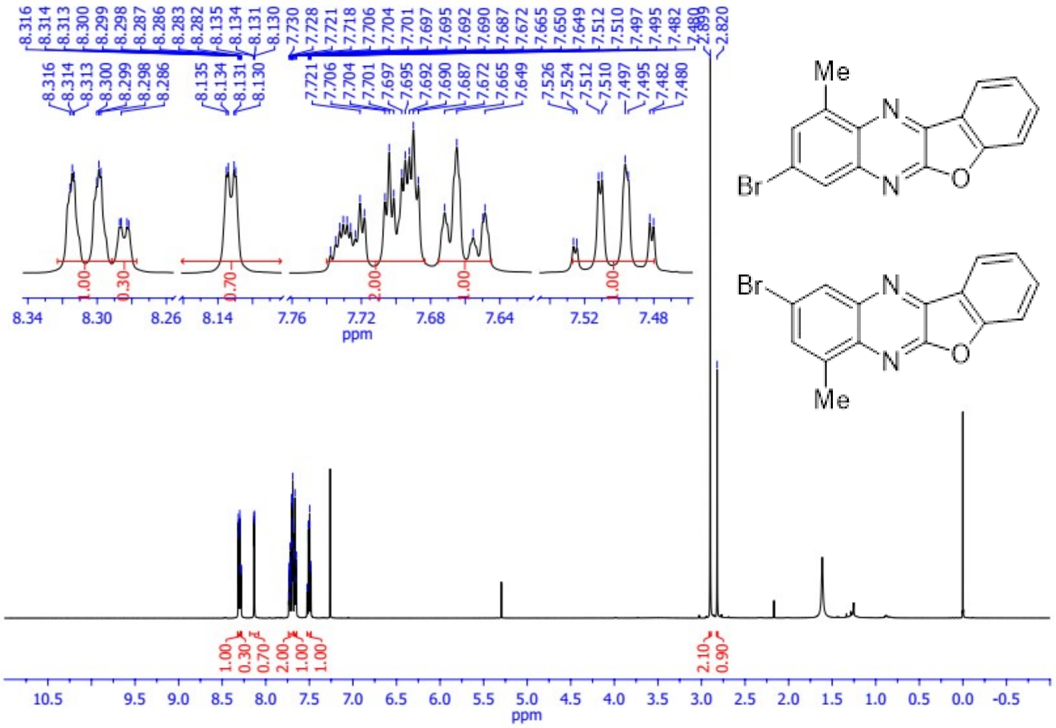


Fig. S17. ^{1}H NMR spectrum of **3ia** + **3i'a.**

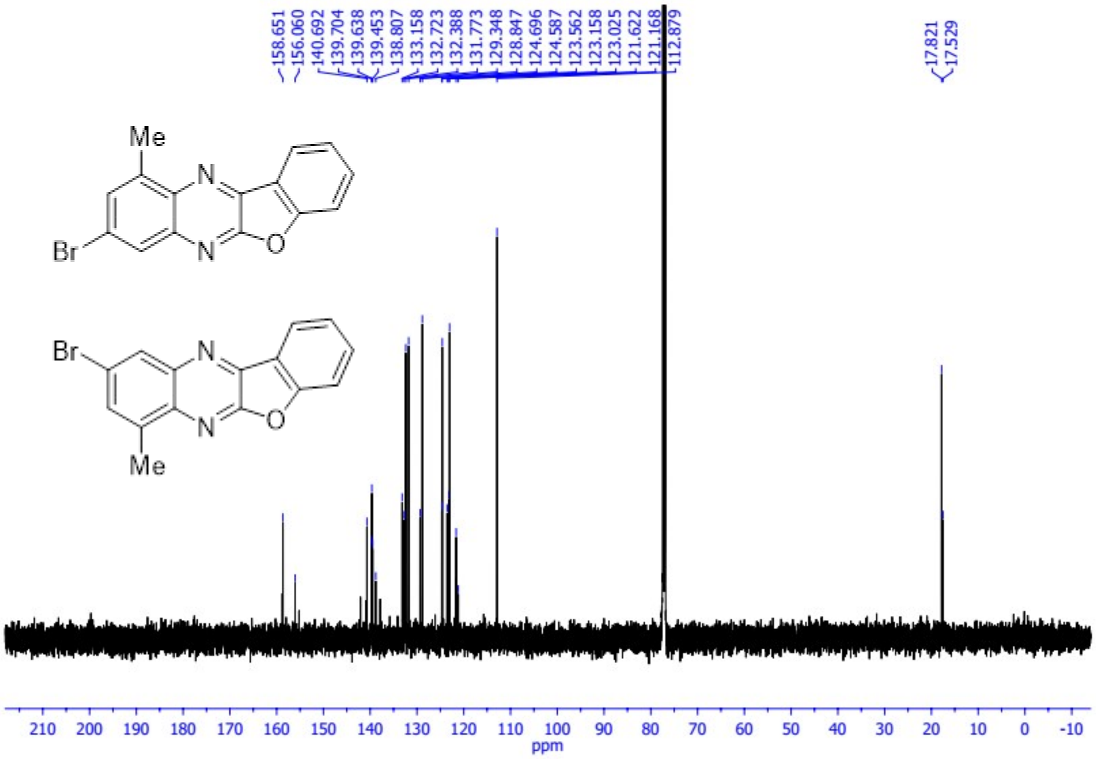


Fig. S18. ^{13}C NMR spectrum of **3ia + 3i'a**.

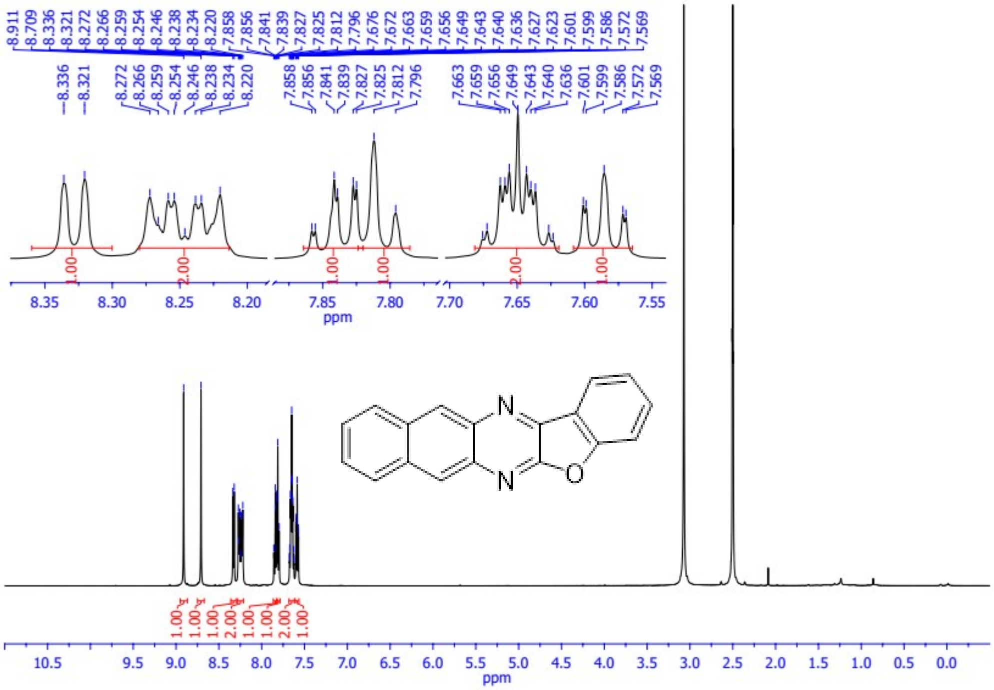


Fig. S19. ^{1}H NMR spectrum of **3ja.**

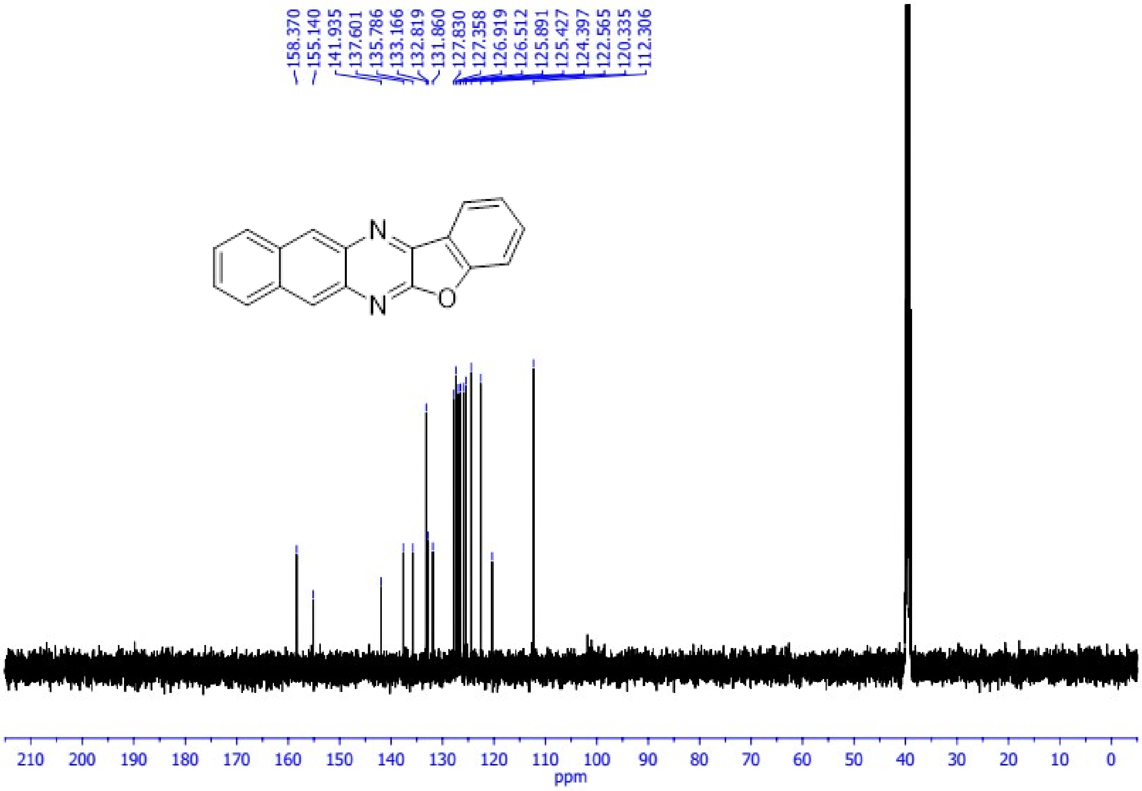


Fig. S20. ^{13}C NMR spectrum of **3ja**.

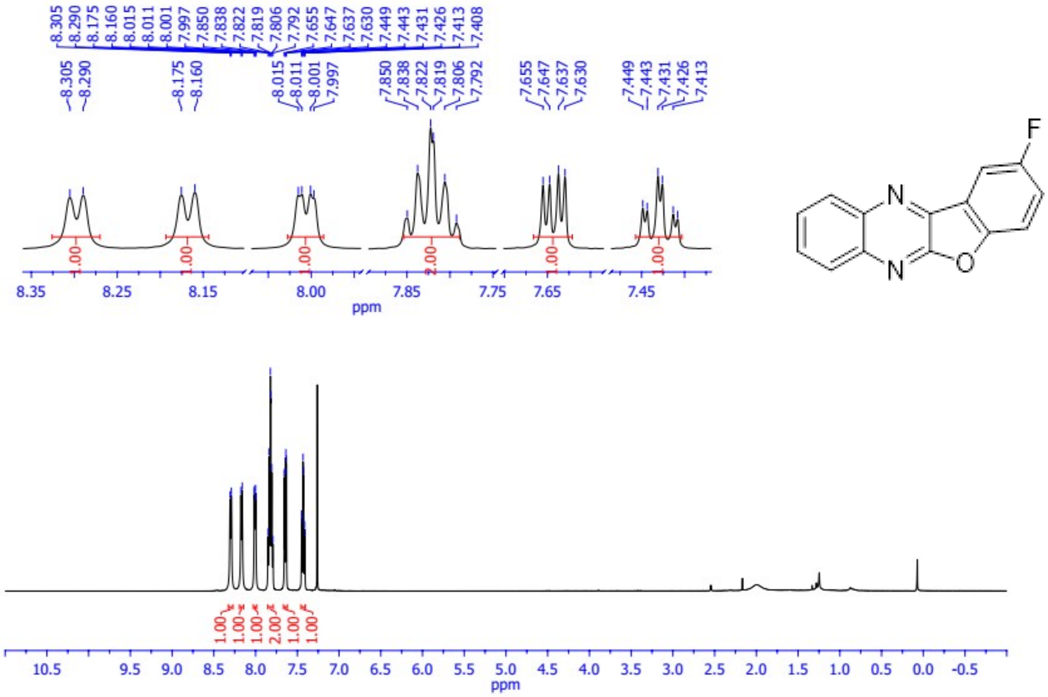


Fig. S21. ^{1}H NMR spectrum of **3ab.**

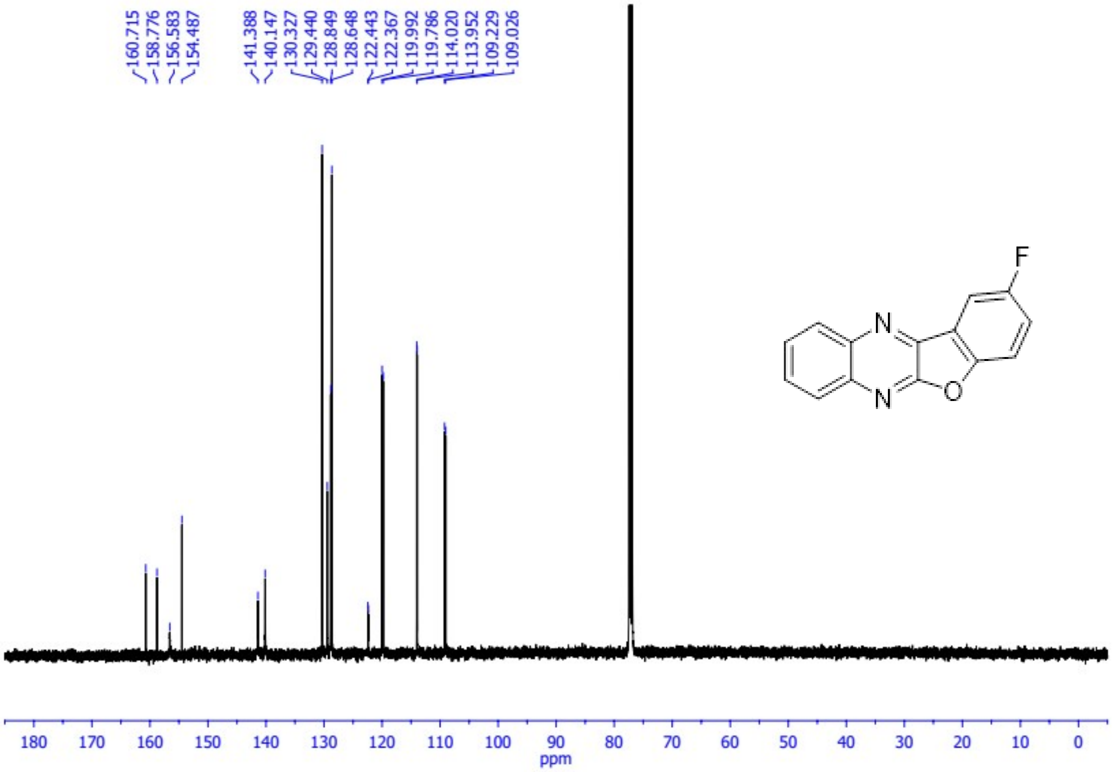


Fig. S22. ^{13}C NMR spectrum of **3ab**.

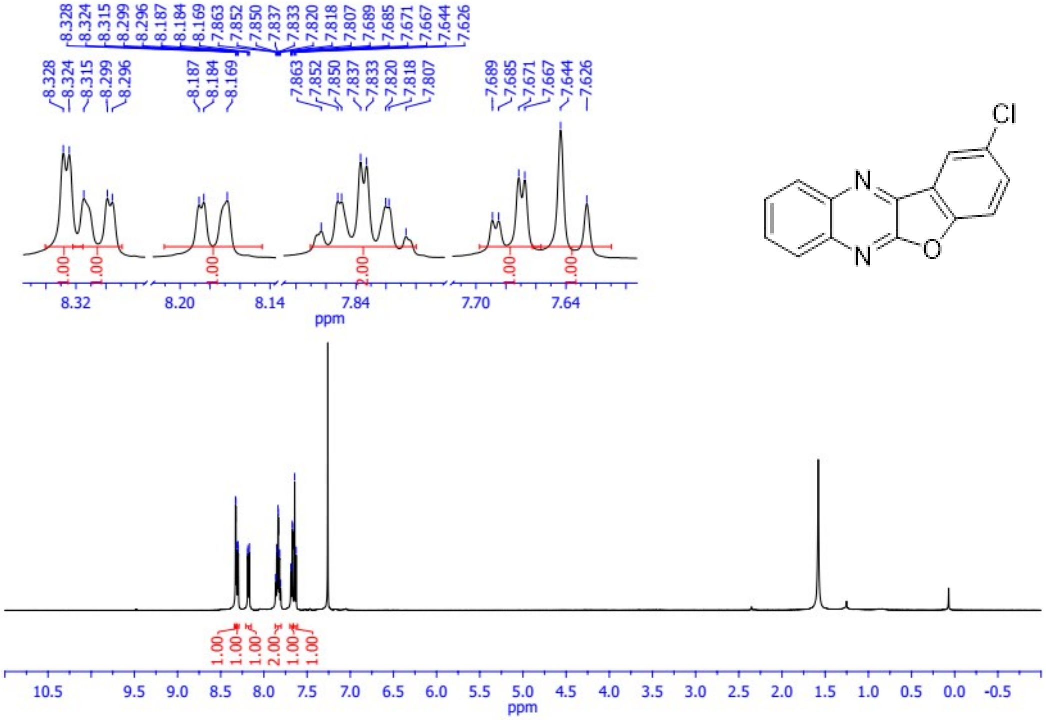


Fig. S23. ^{1}H NMR spectrum of **3ac.**

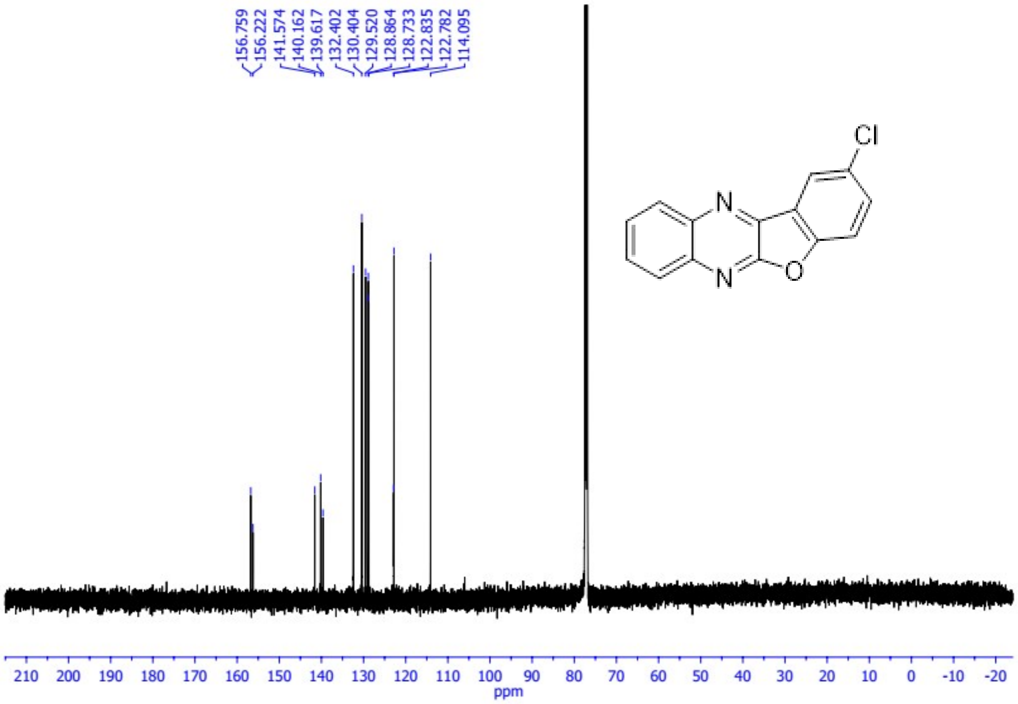


Fig. S24. ^{13}C NMR spectrum of **3ac**.

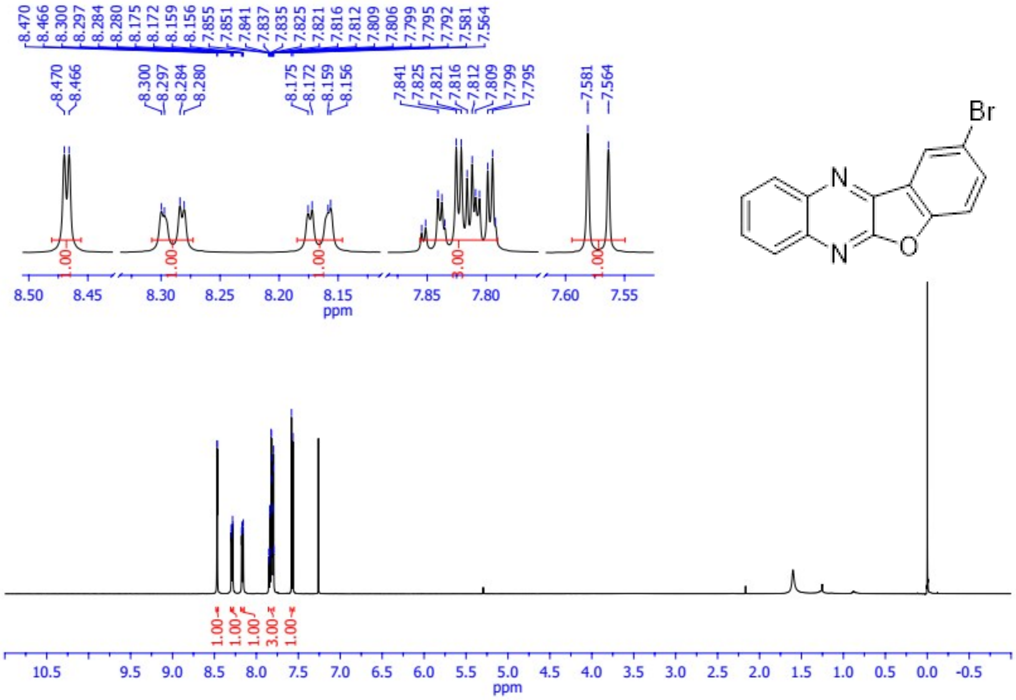


Fig. S25. ^{1}H NMR spectrum of **3ad.**

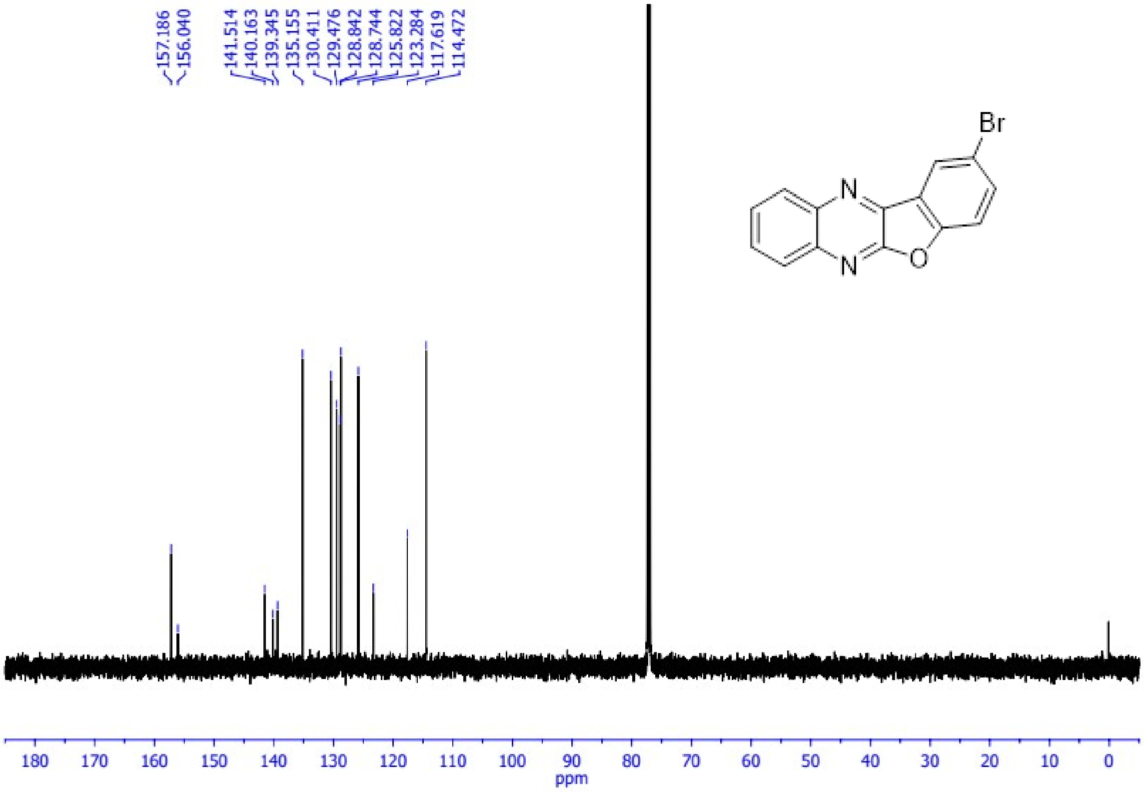


Fig. S26. ^{13}C NMR spectrum of **3ad**.

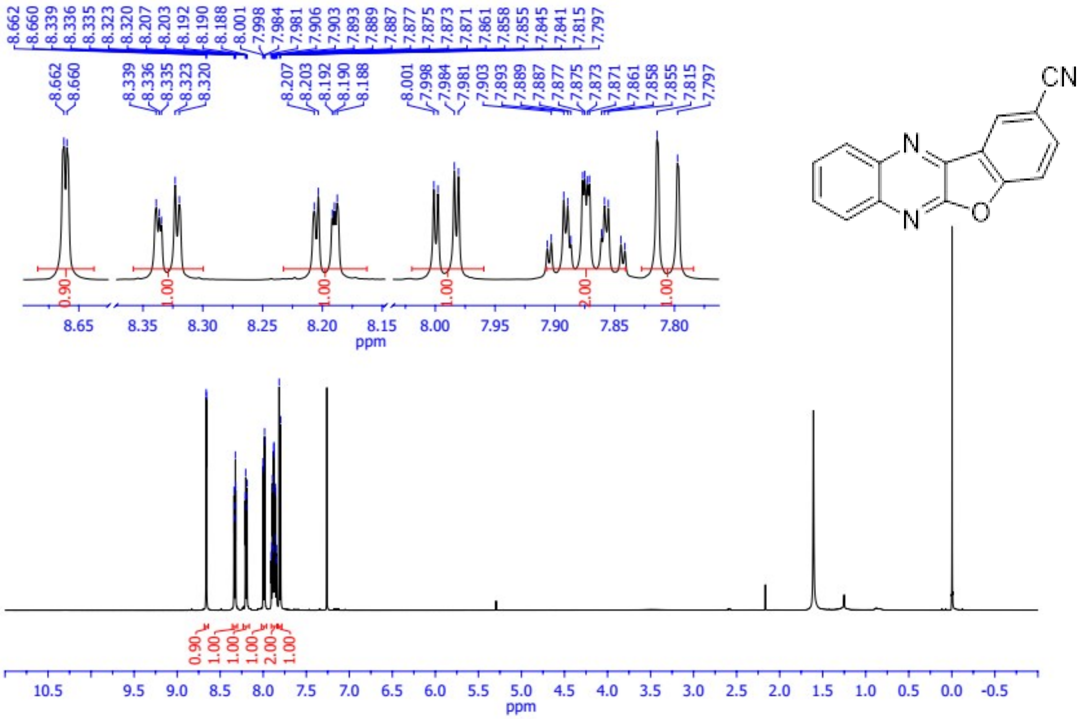


Fig. S27. ^{1}H NMR spectrum of **3ae.**

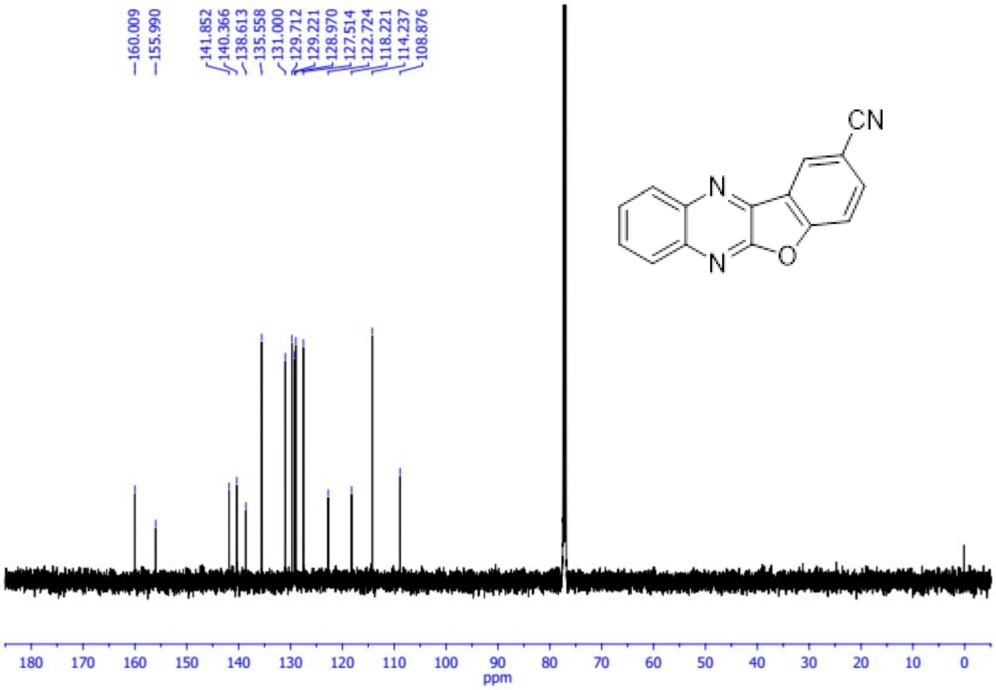


Fig. S28. ^{13}C NMR spectrum of **3ae**.

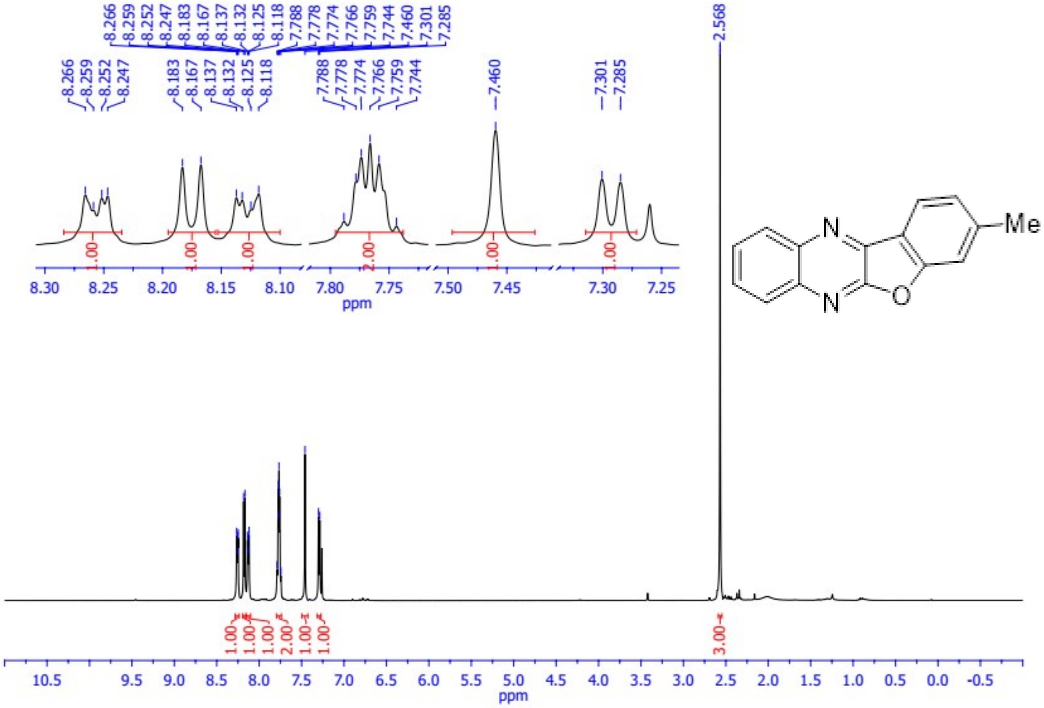


Fig. S29. ^{1}H NMR spectrum of **3af.**

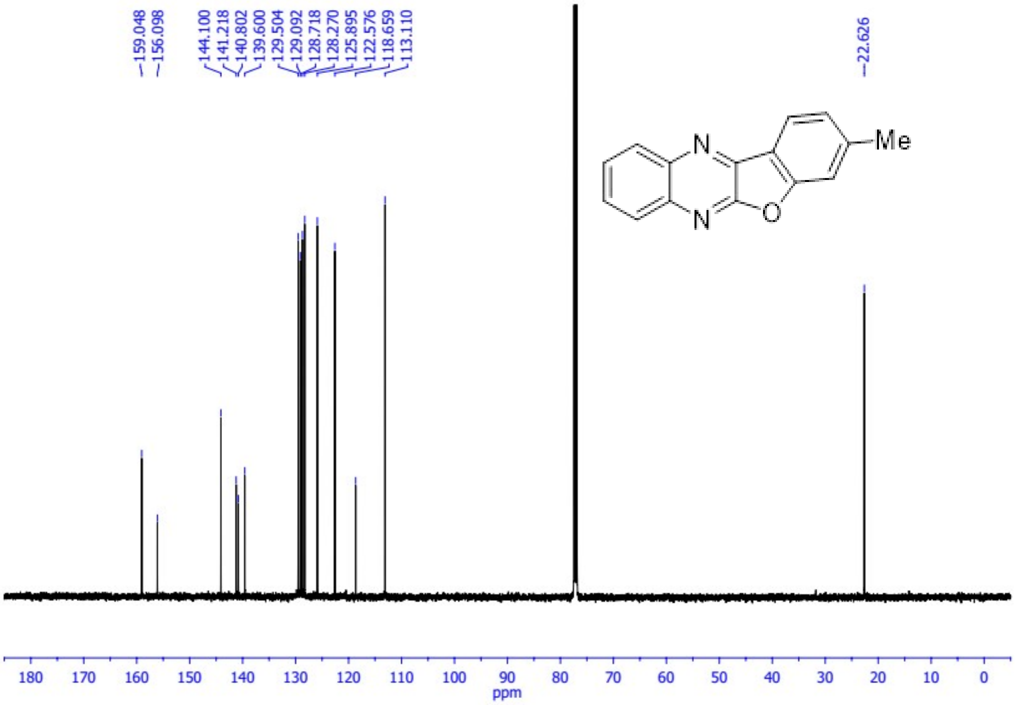


Fig. S30. ^{13}C NMR spectrum of **3af**.

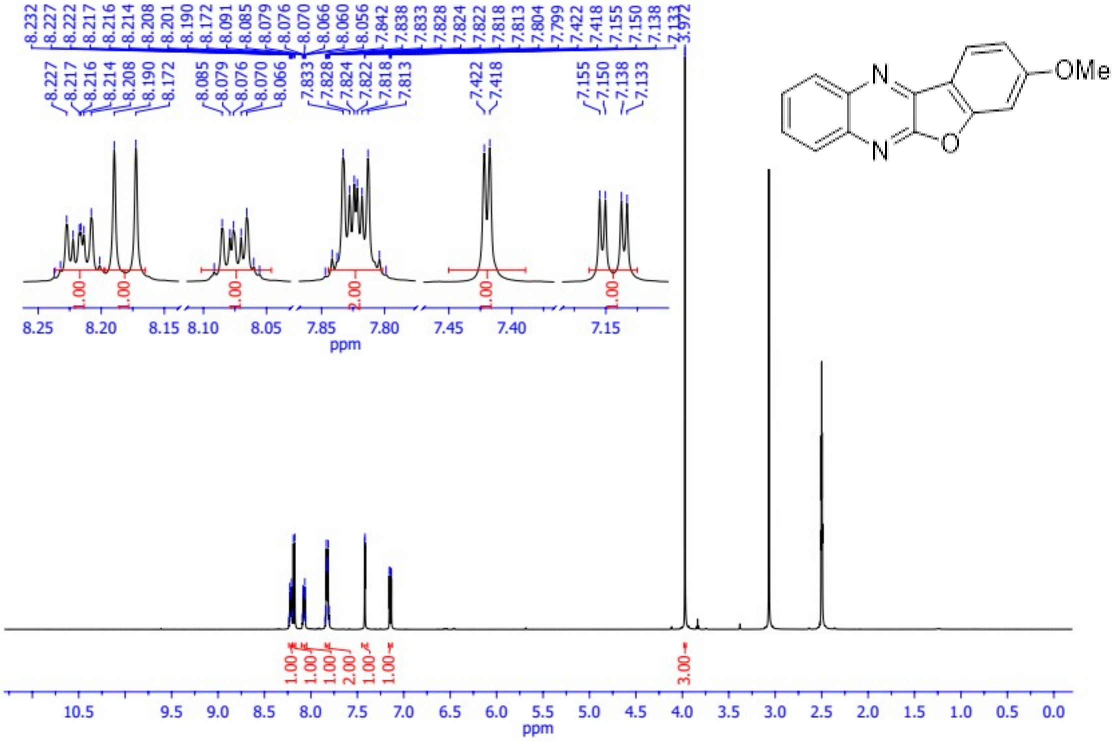


Fig. S31. ^{1}H NMR spectrum of **3ag.**

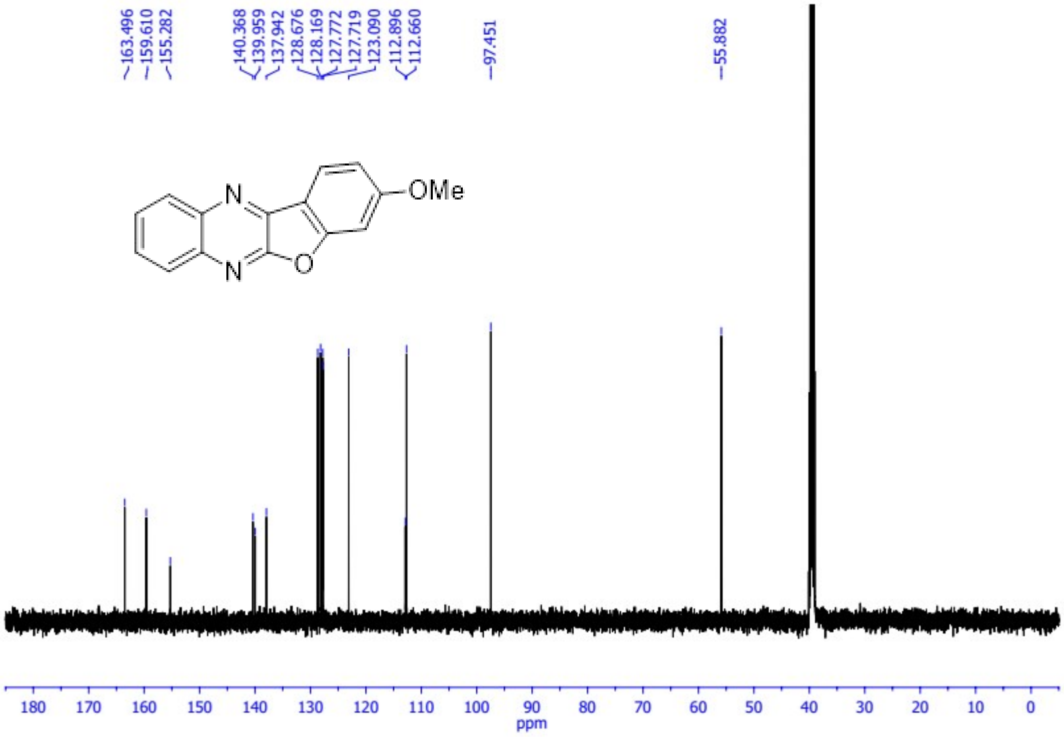


Fig. S32. ^{13}C NMR spectrum of **3ag**.

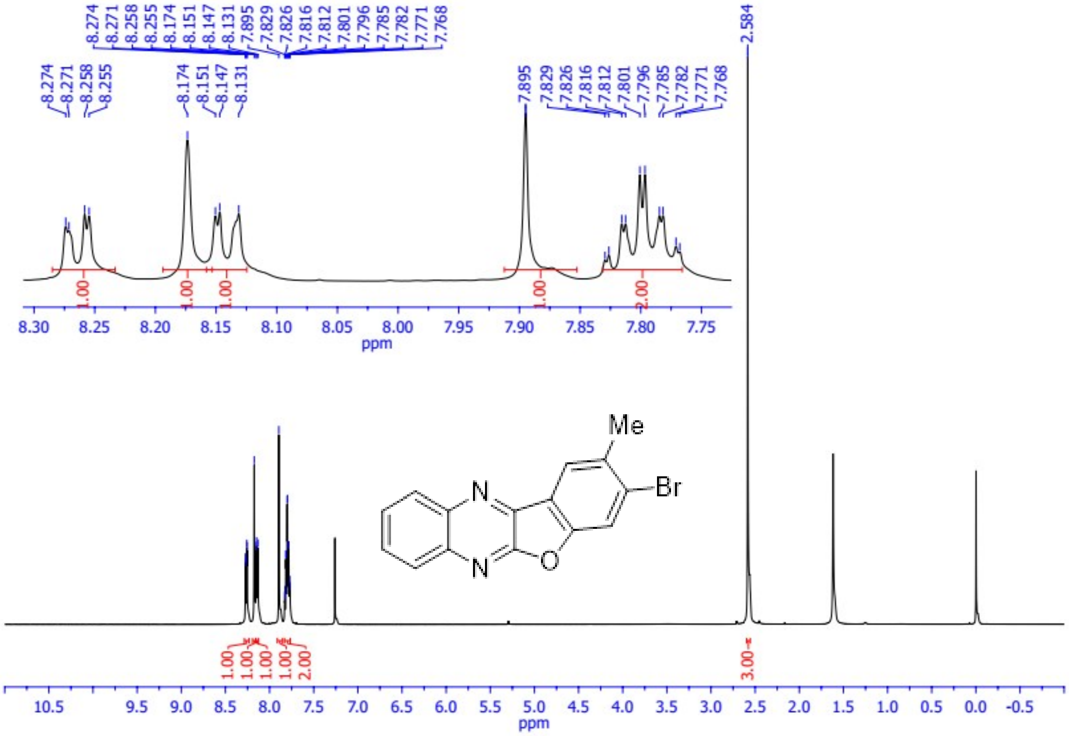


Fig. S33. ^{1}H NMR spectrum of **3ah.**

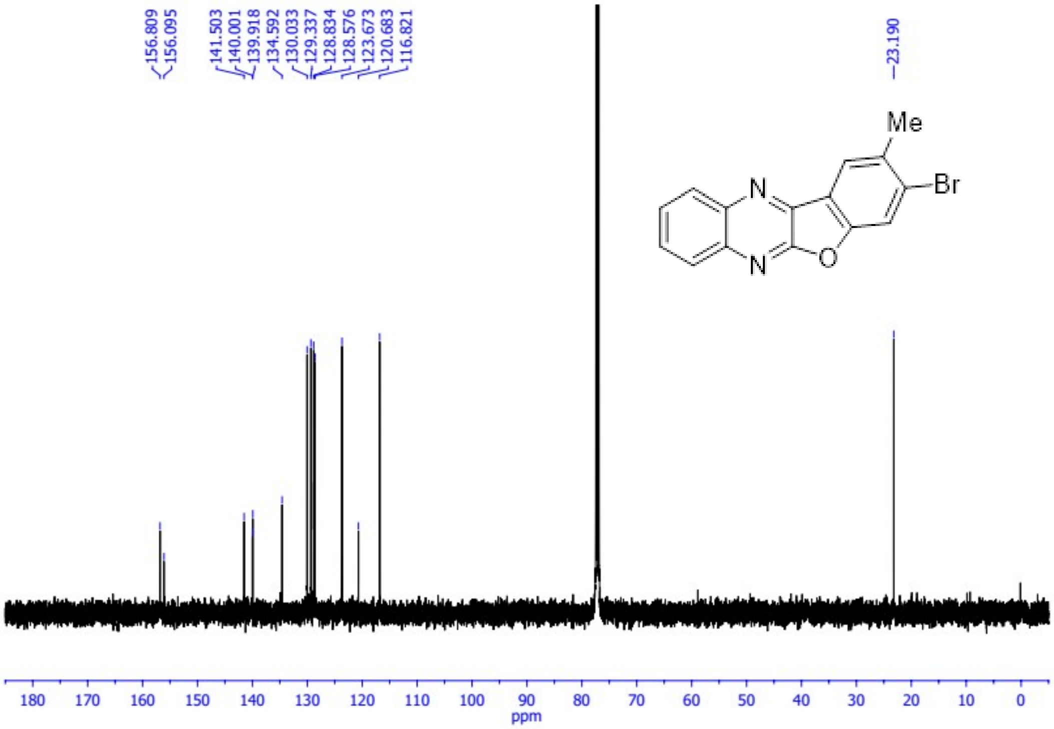


Fig. S34. ^{13}C NMR spectrum of **3ah**.

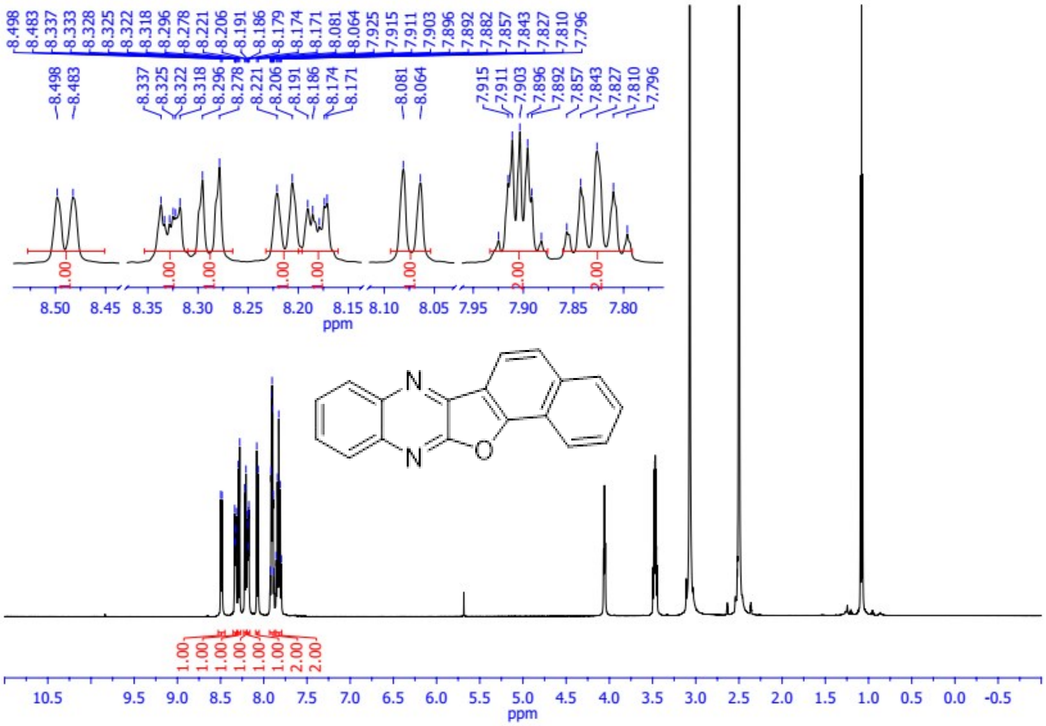


Fig. S35. ^{1}H NMR spectrum of **3ai.**

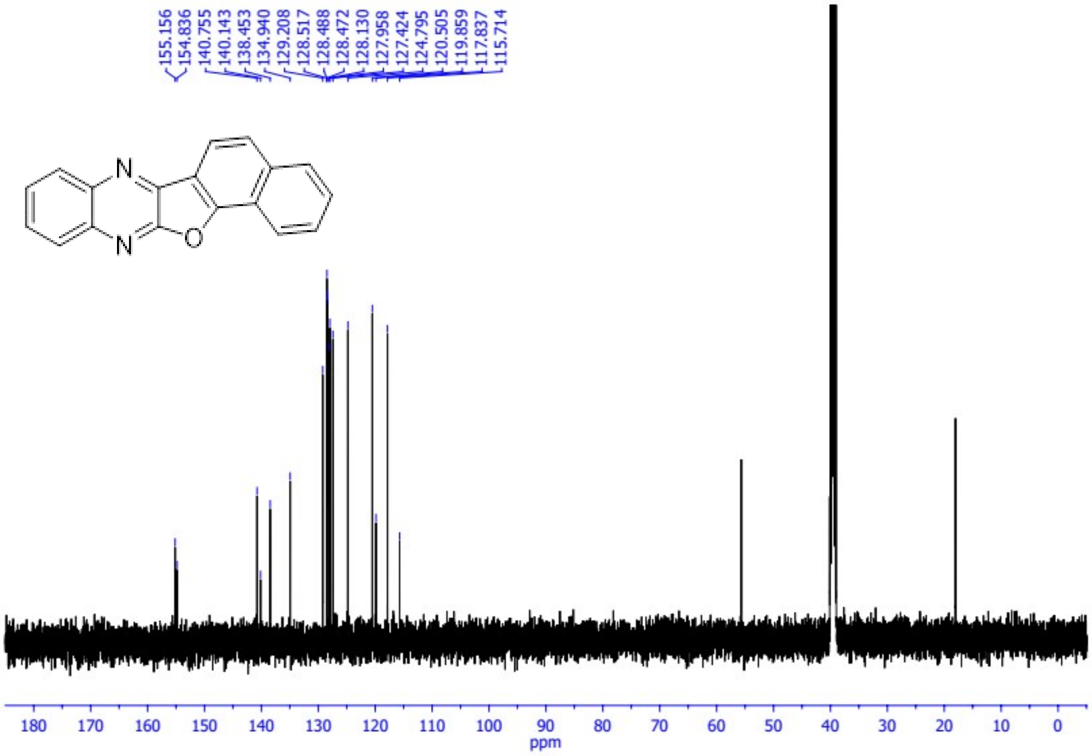


Fig. S36. ^{13}C NMR spectrum of **3ai**.

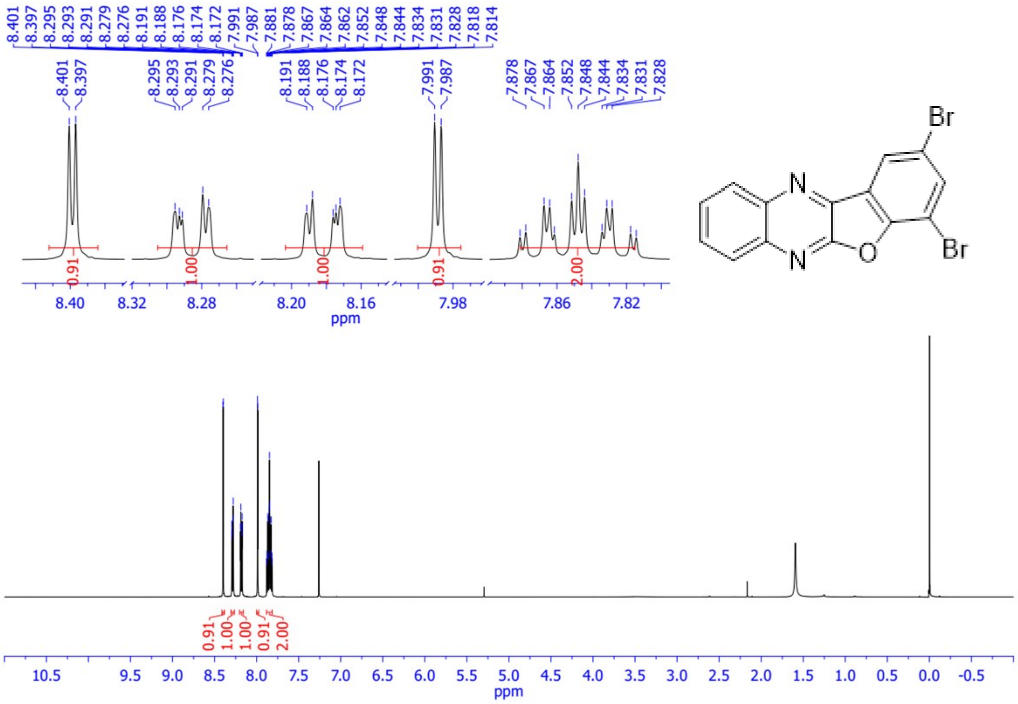


Fig. S37. ^{1}H NMR spectrum of **3aj.**

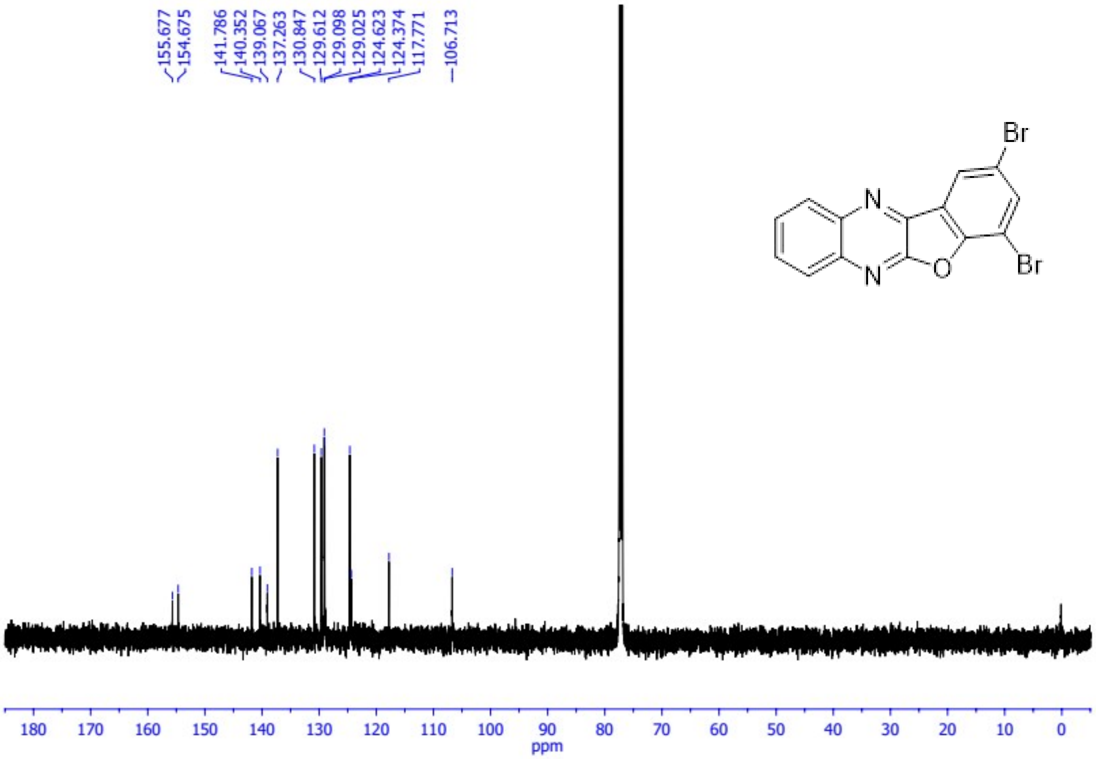


Fig. S38. ^{13}C NMR spectrum of **3aj**.

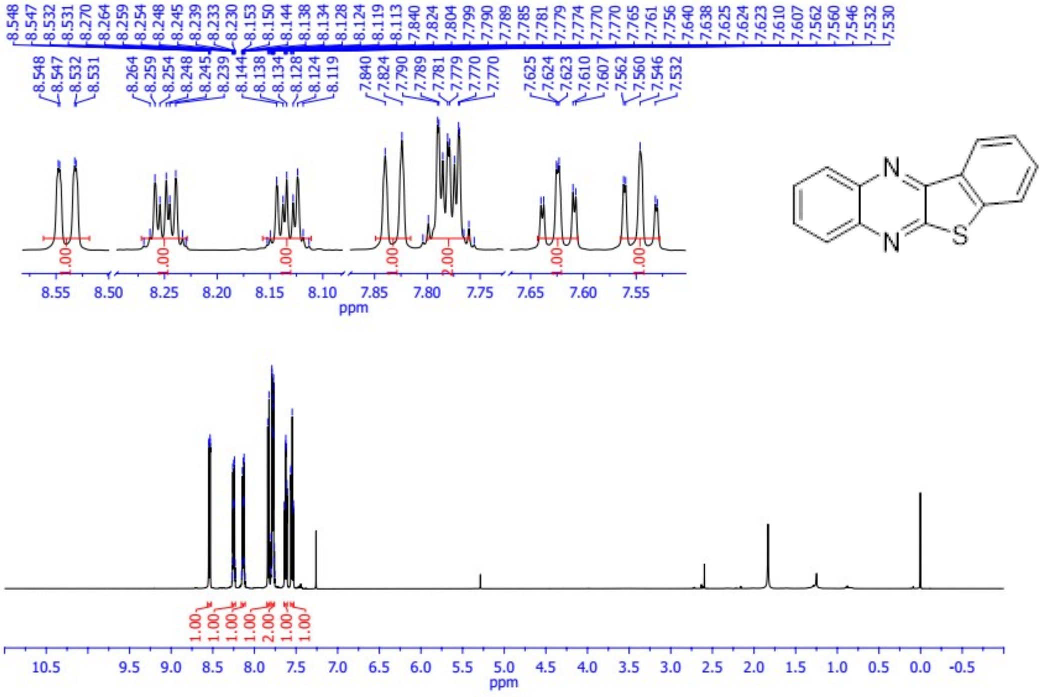


Fig. S39. ^{1}H NMR spectrum of **5aa.**

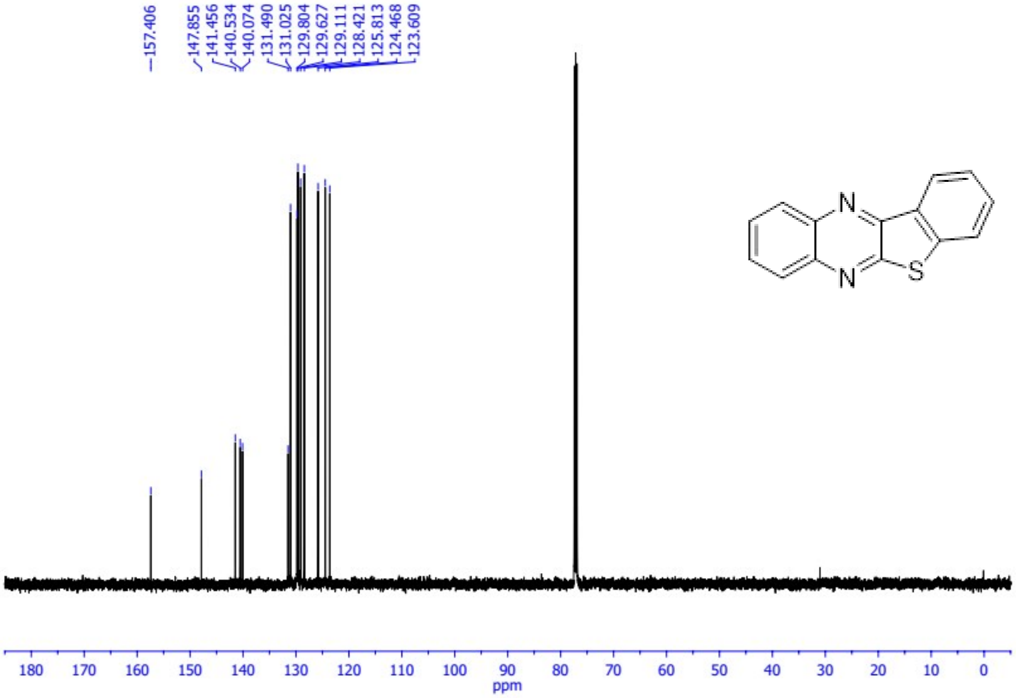


Fig. S40. ^{13}C NMR spectrum of **5aa**.

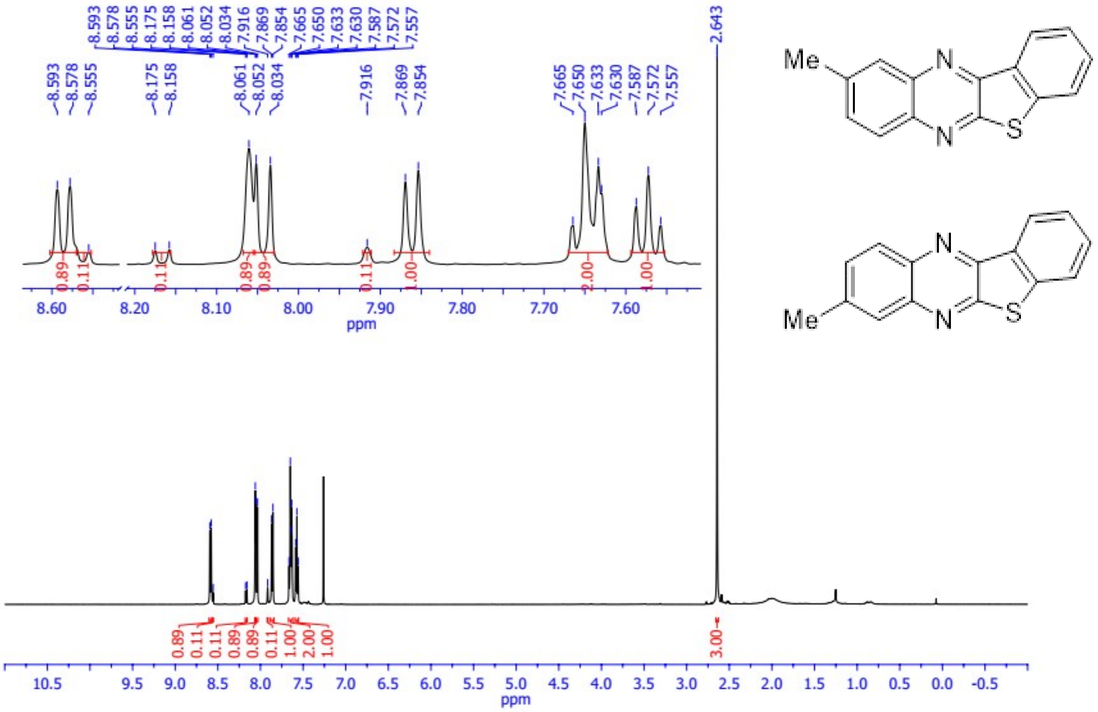


Fig. S41. ^{1}H NMR spectrum of **5ba** + **5b'a.**

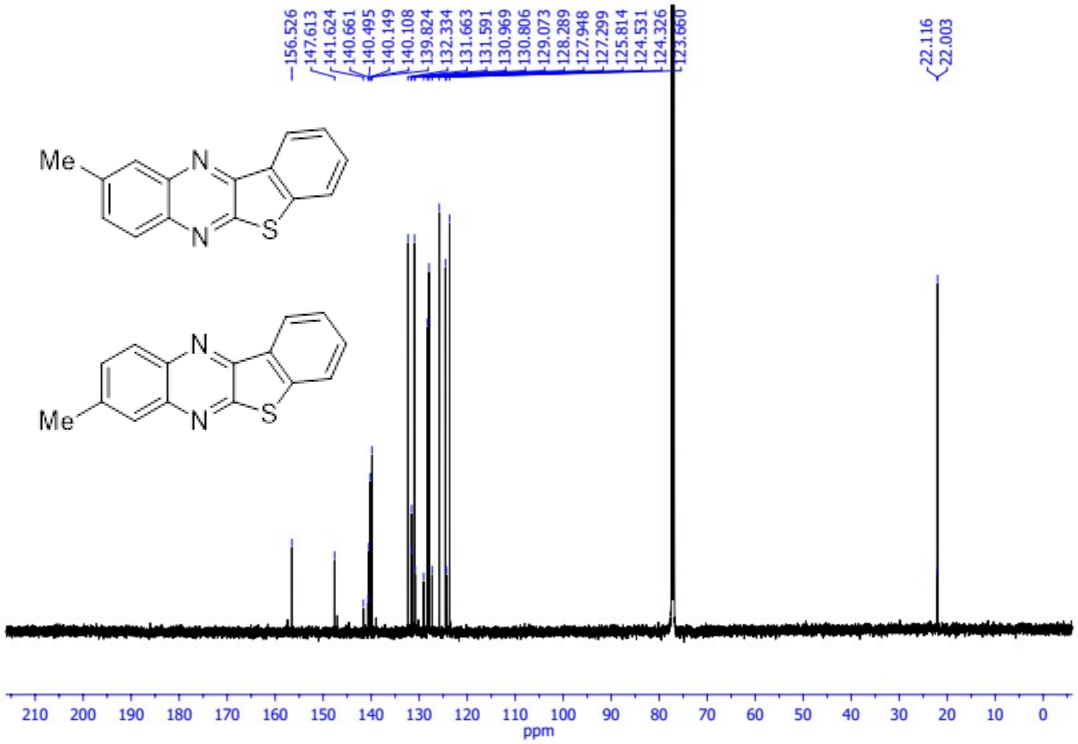


Fig. S42. ^{13}C NMR spectrum of **5ba + 5b'a**.

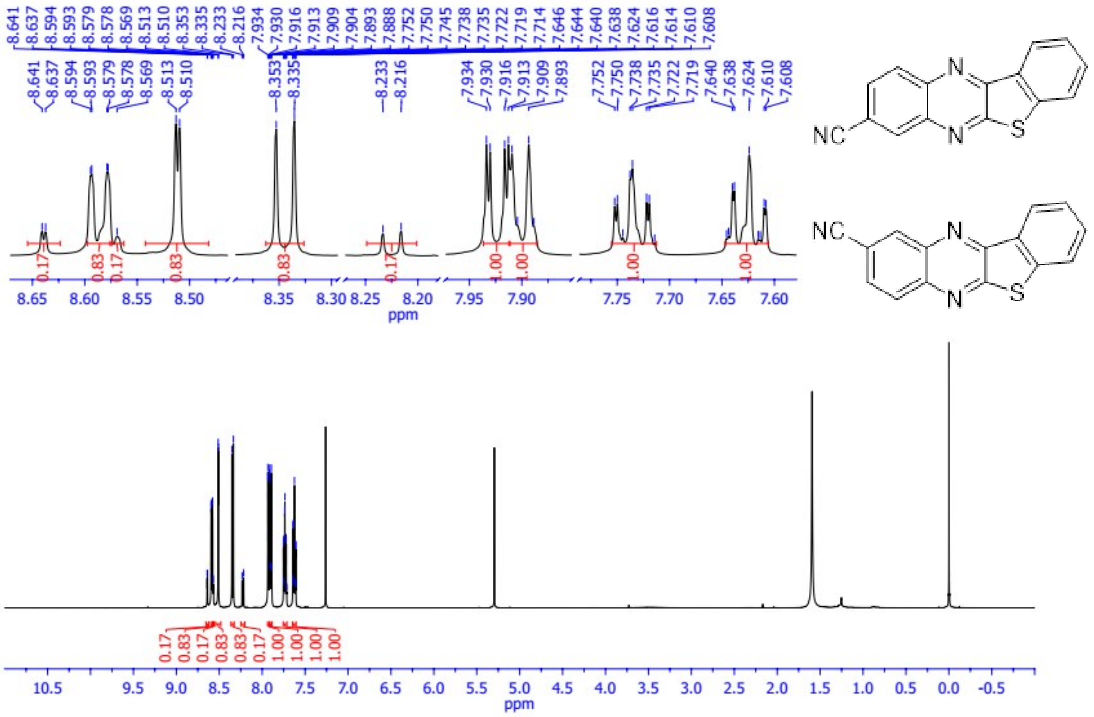


Fig. S43. ^{1}H NMR spectrum of **3ea** + **3e'a.**

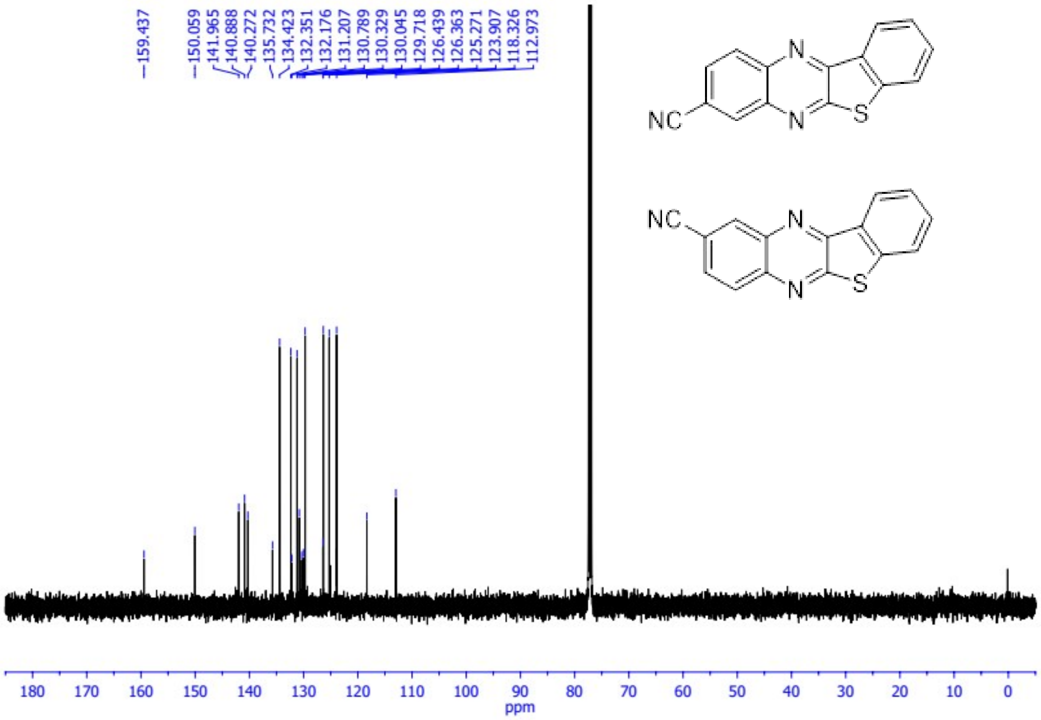


Fig. S44. ^{13}C NMR spectrum of **3ea** + **3e'a**.

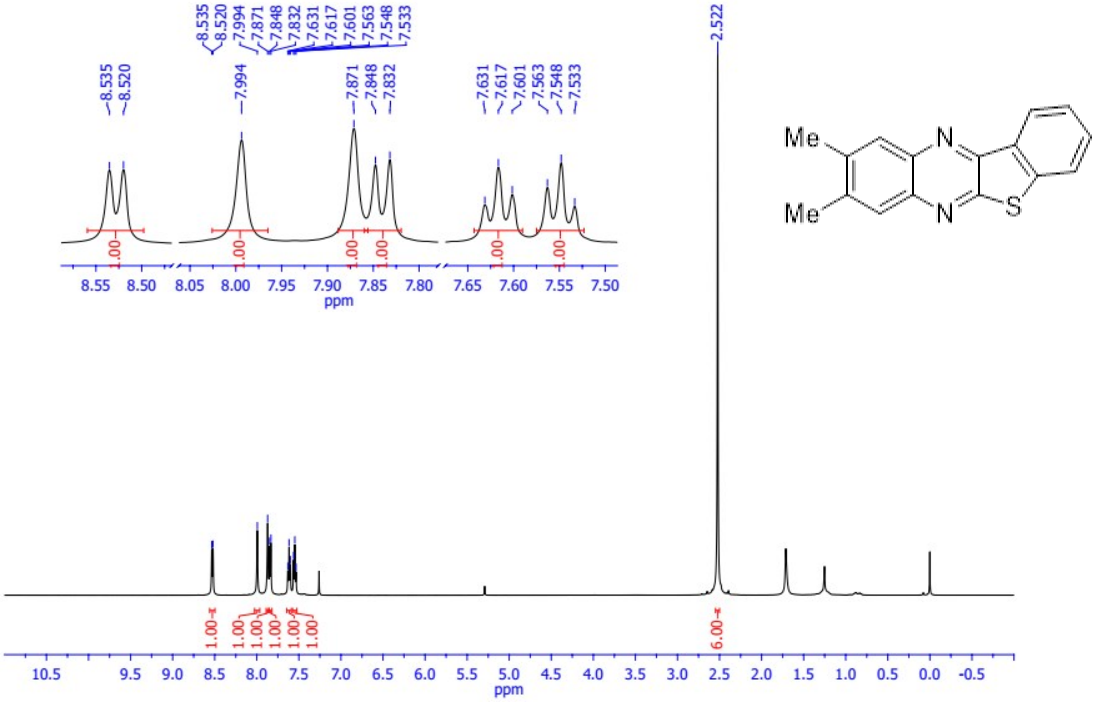


Fig. S45. ^{1}H NMR spectrum of **5ha.**

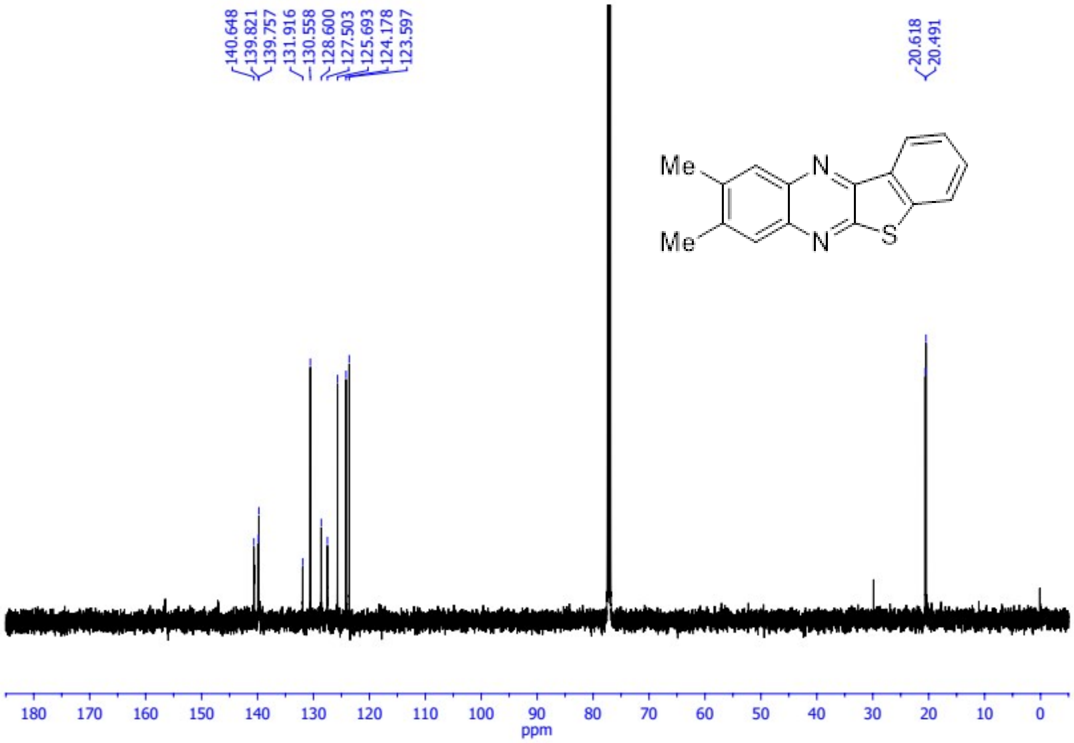


Fig. S46. ^{13}C NMR spectrum of **5ha**.

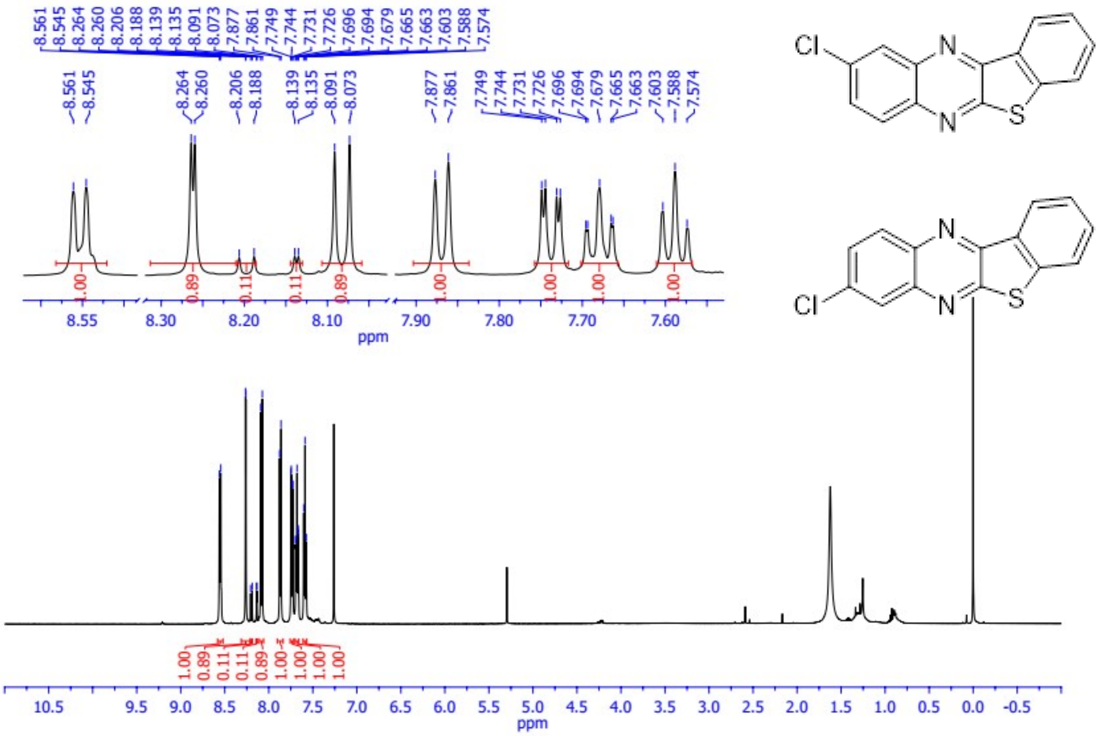


Fig. S47. ^{1}H NMR spectrum of **5la** + **5l'a.**

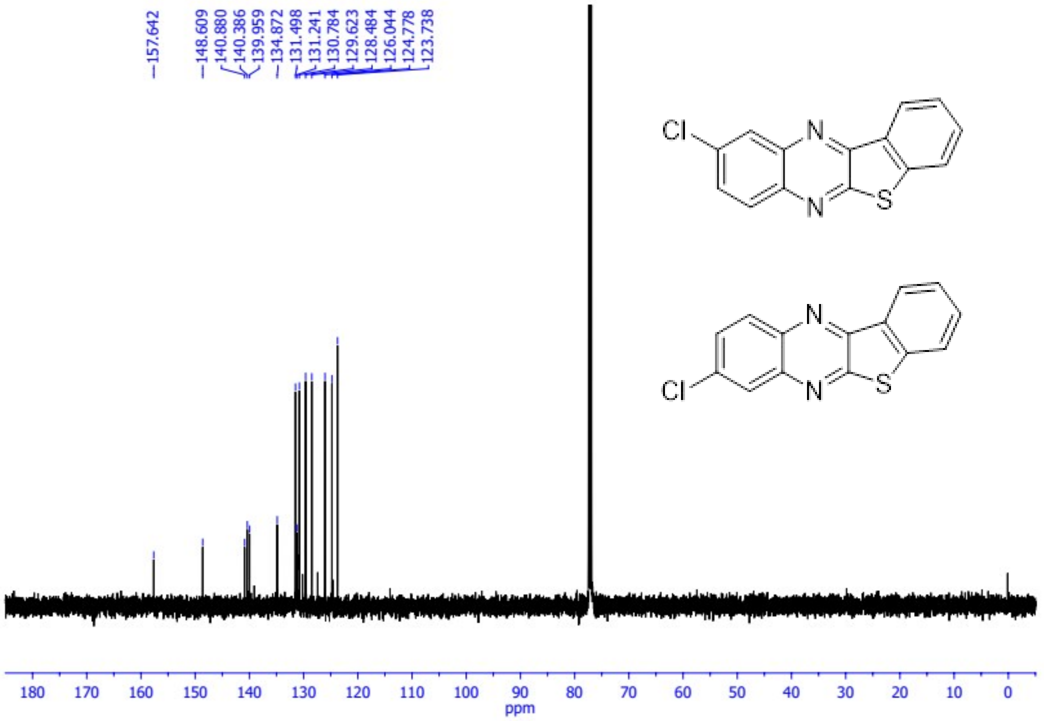


Fig. S48. ^{13}C NMR spectrum of **5la** + **5l'a**.

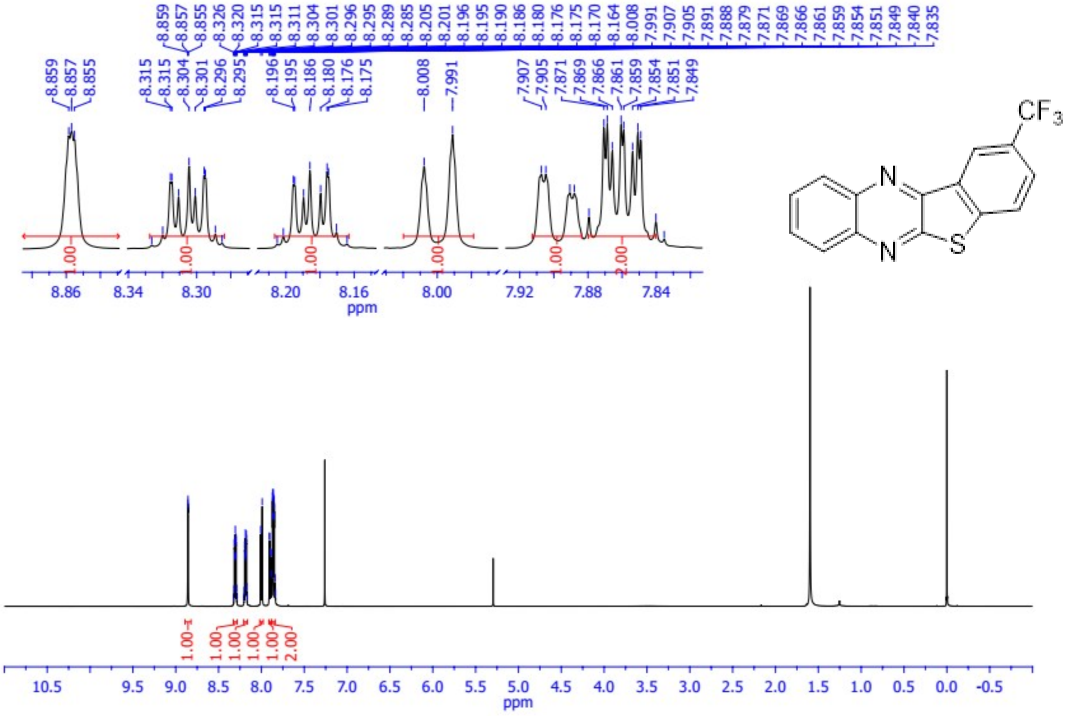


Fig. S49. ^{1}H NMR spectrum of **5ab.**

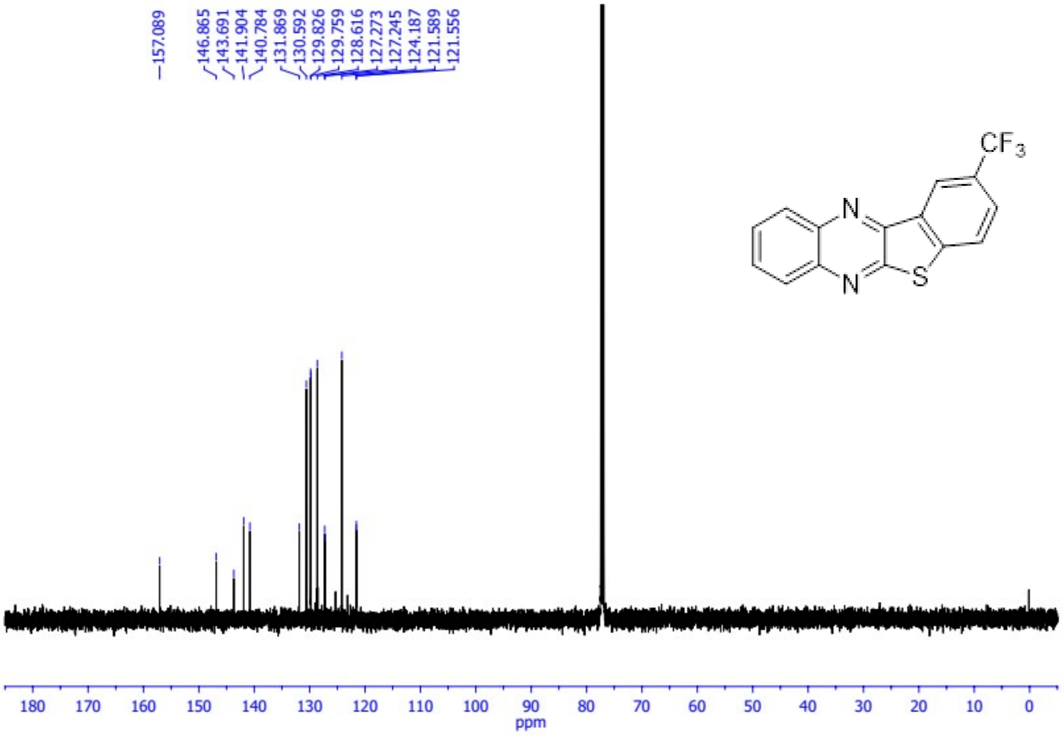


Fig. S50. ^{13}C NMR spectrum of **5ab**.

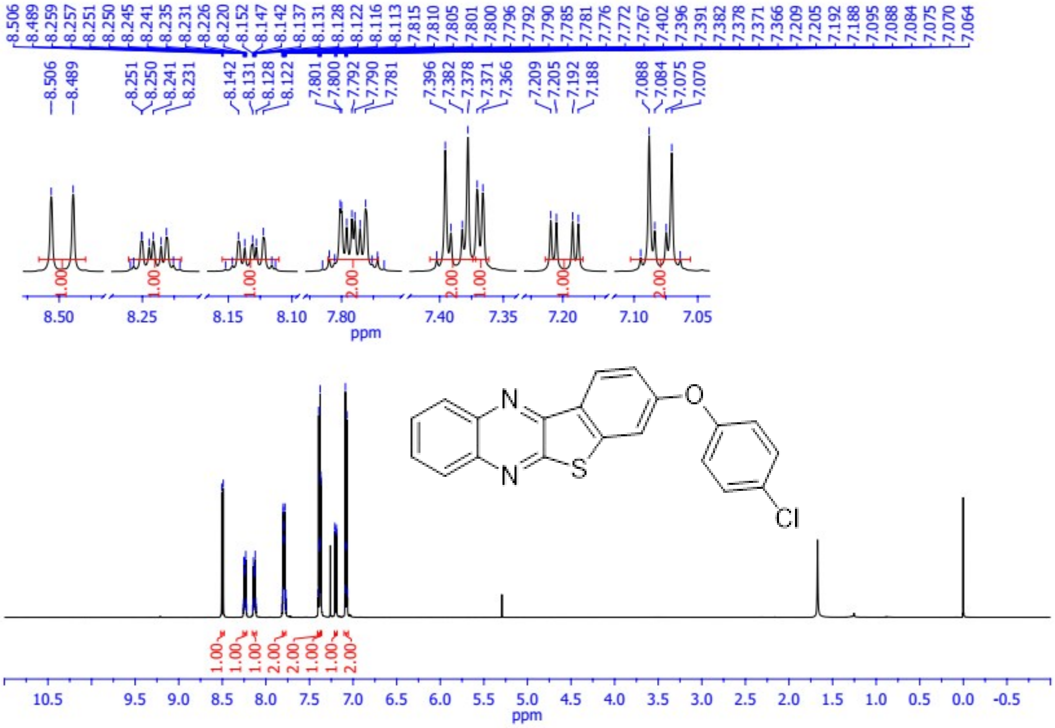


Fig. S51. ^{1}H NMR spectrum of **5ac.**

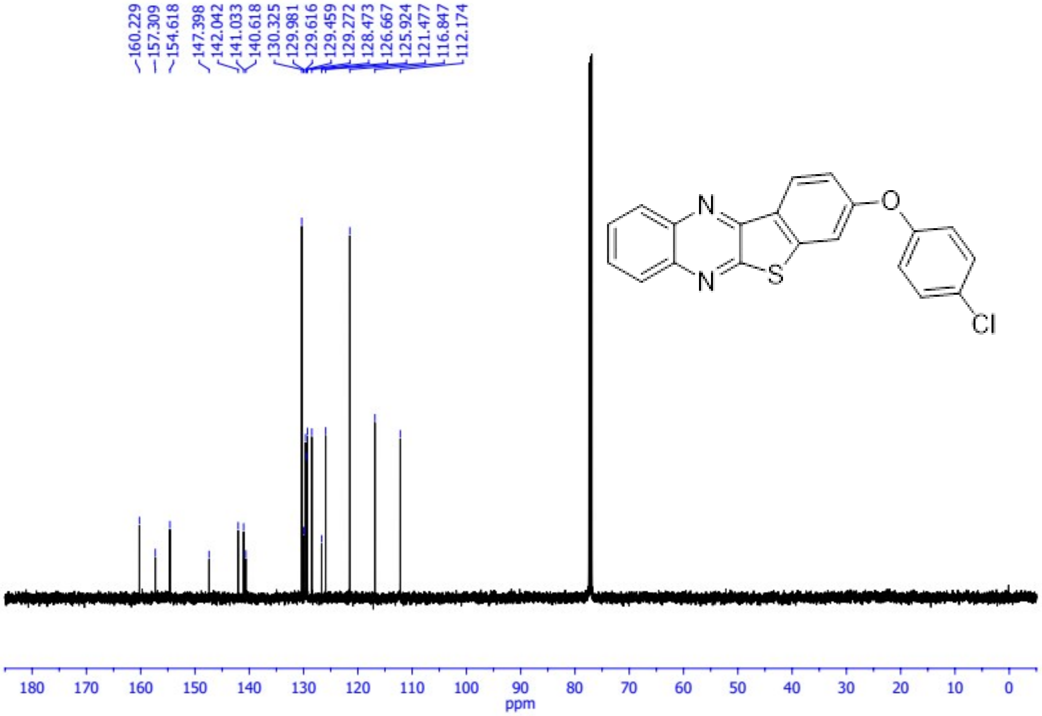


Fig. S52. ^{13}C NMR spectrum of **5ac**.

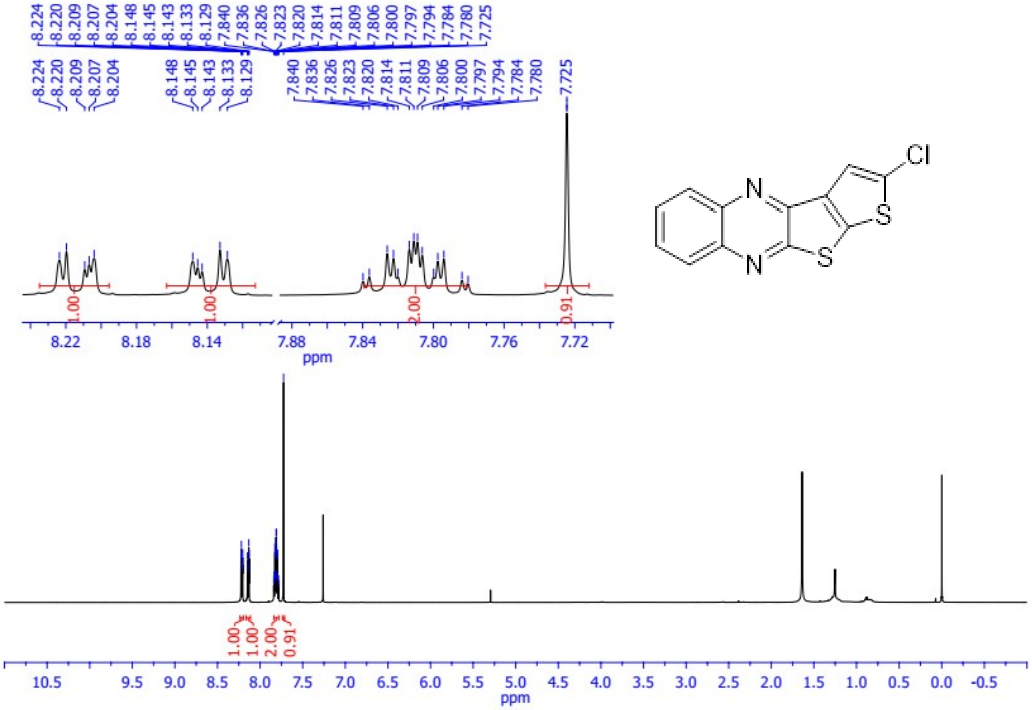


Fig. S53. ^1H NMR spectrum of **5ad.**

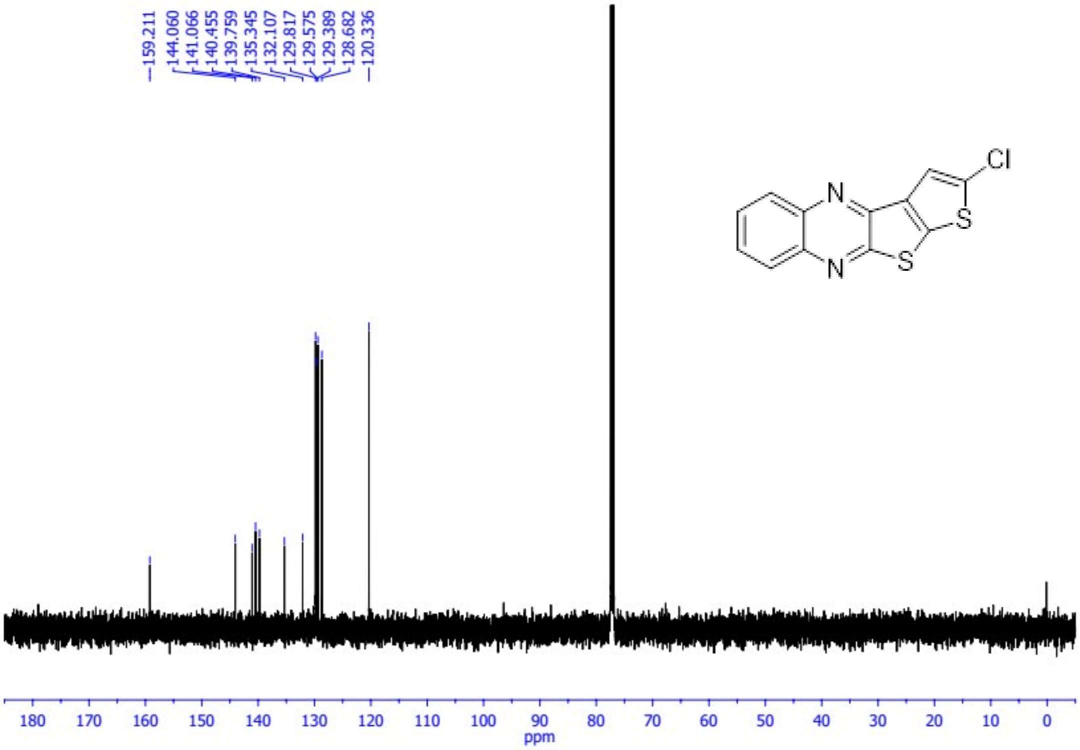


Fig. S54. ^{13}C NMR spectrum of **5ad.**

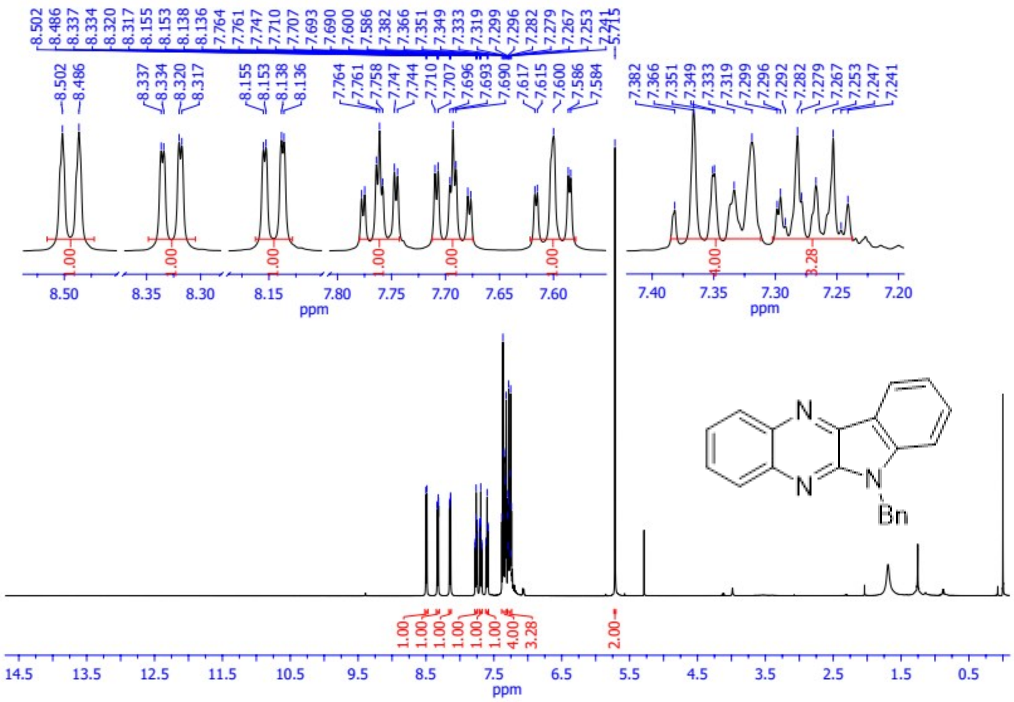


Fig. S55. ^{1}H NMR spectrum of **7aa.**

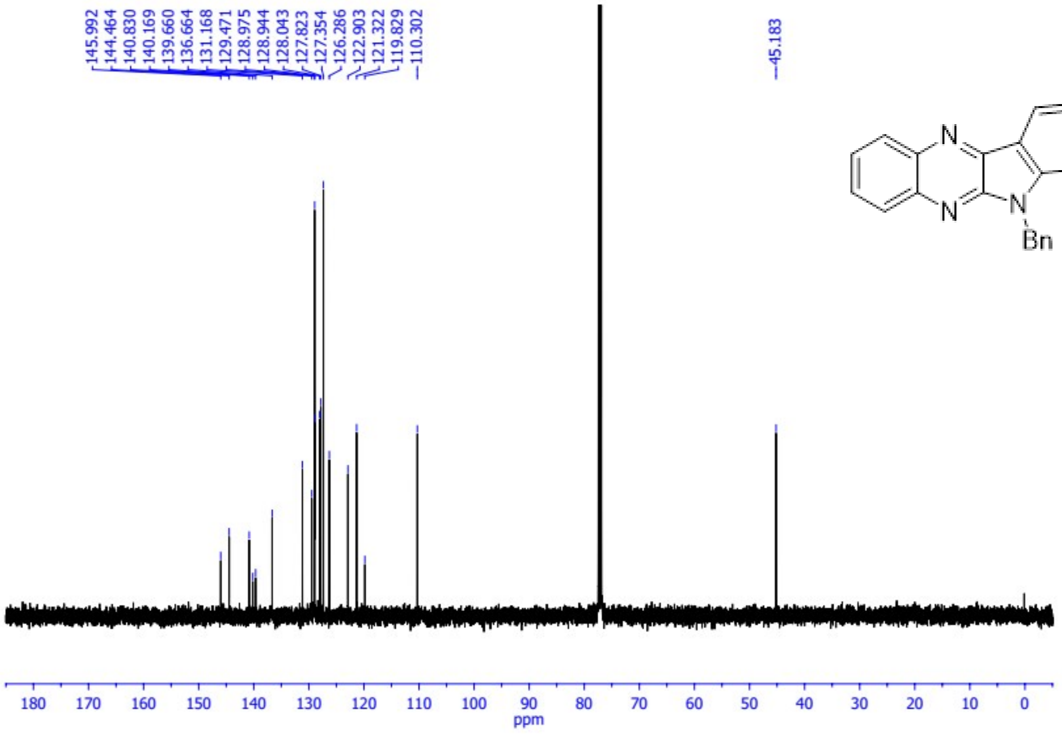


Fig. S56. ^{13}C NMR spectrum of **7aa**.

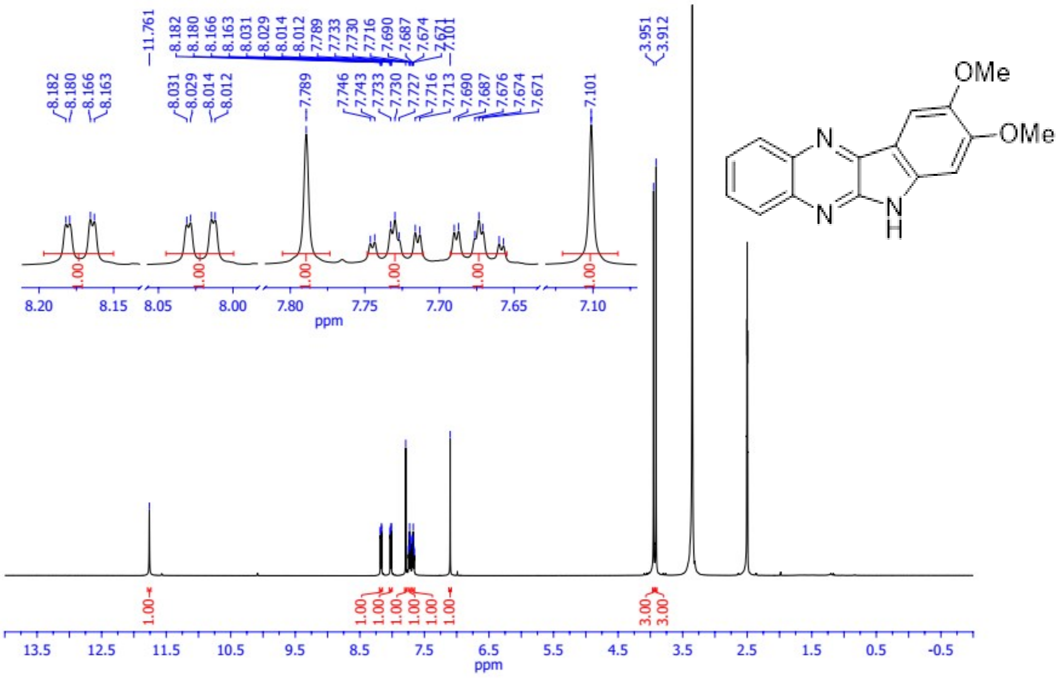


Fig. S57. ^{1}H NMR spectrum of **7ab.**

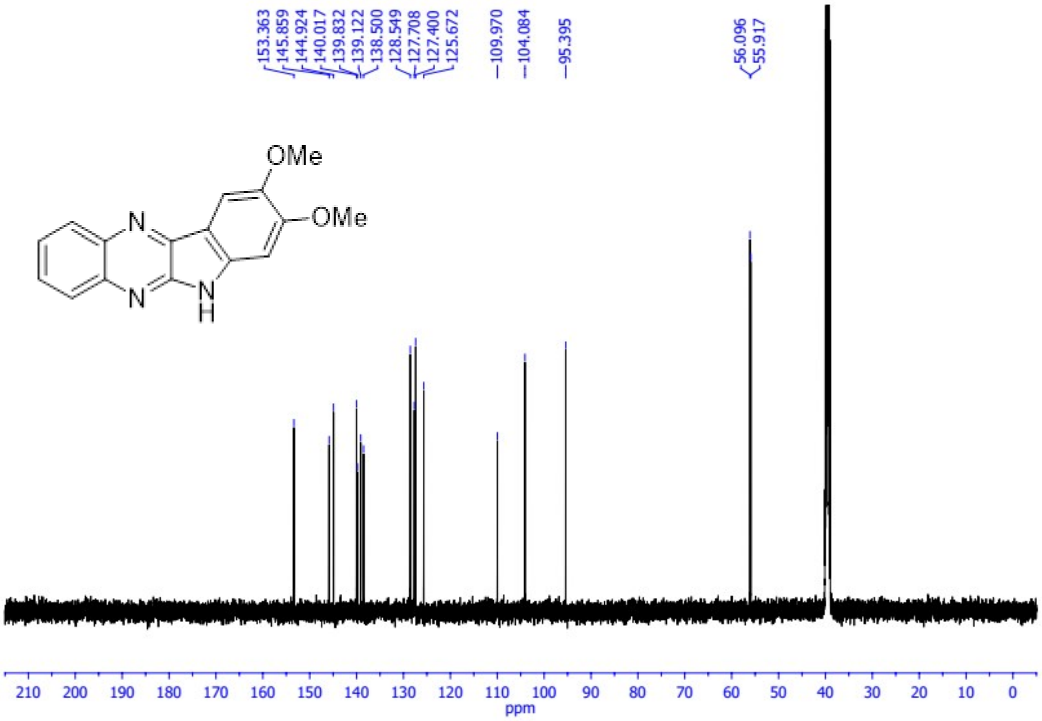


Fig. S58. ^{13}C NMR spectrum of **7ab**.

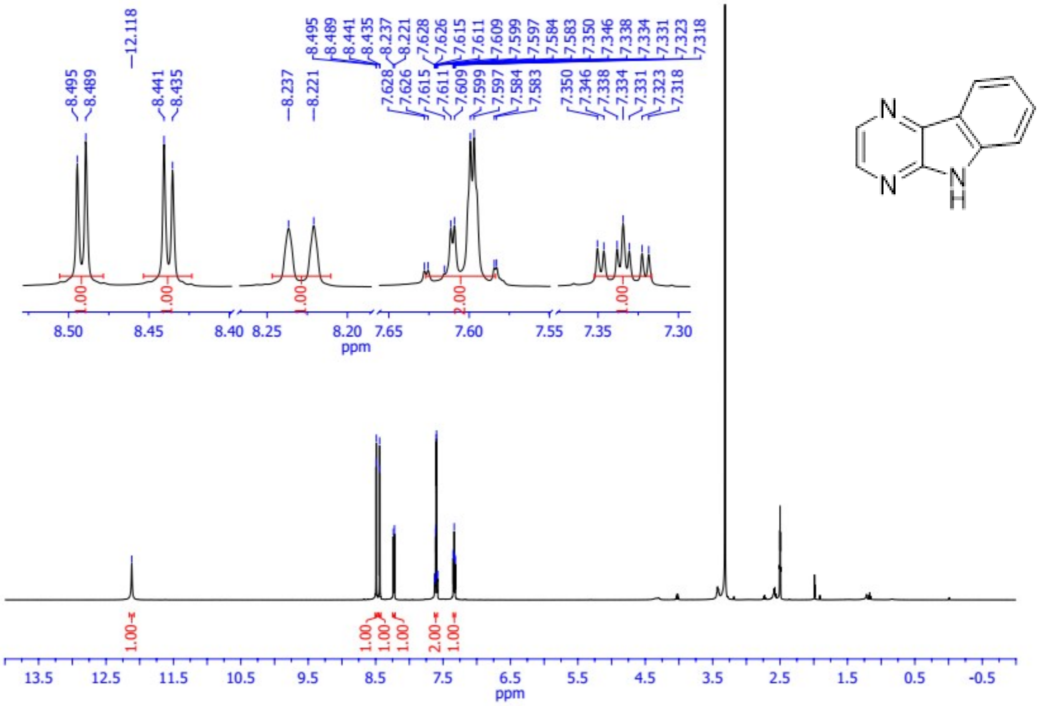


Fig. S59. ^{1}H NMR spectrum of **8.**

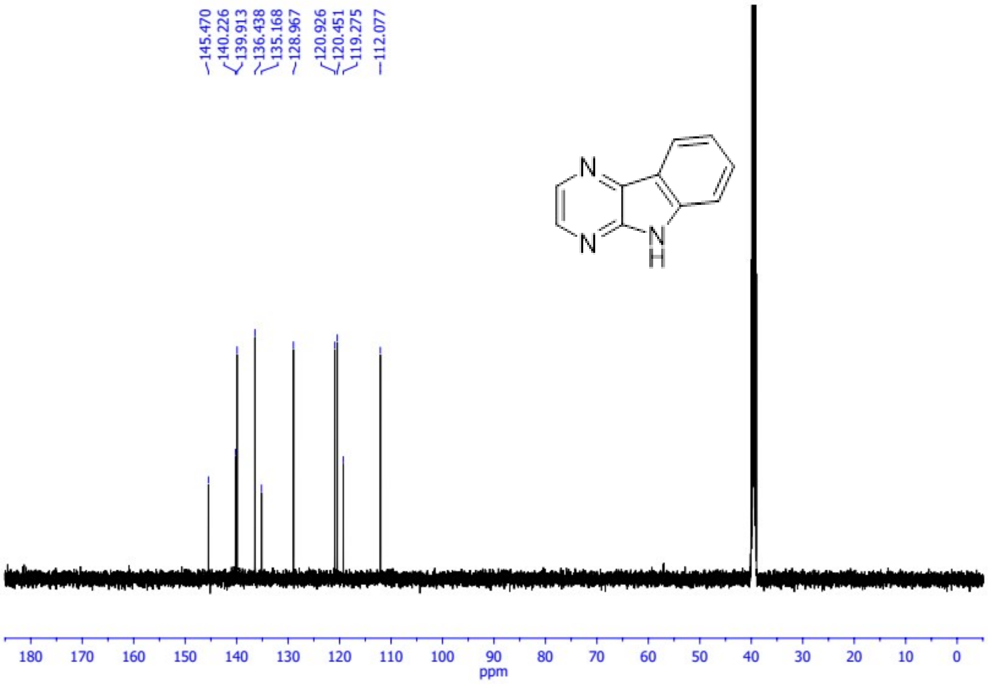


Fig. S60. ^{13}C NMR spectrum of **8**.

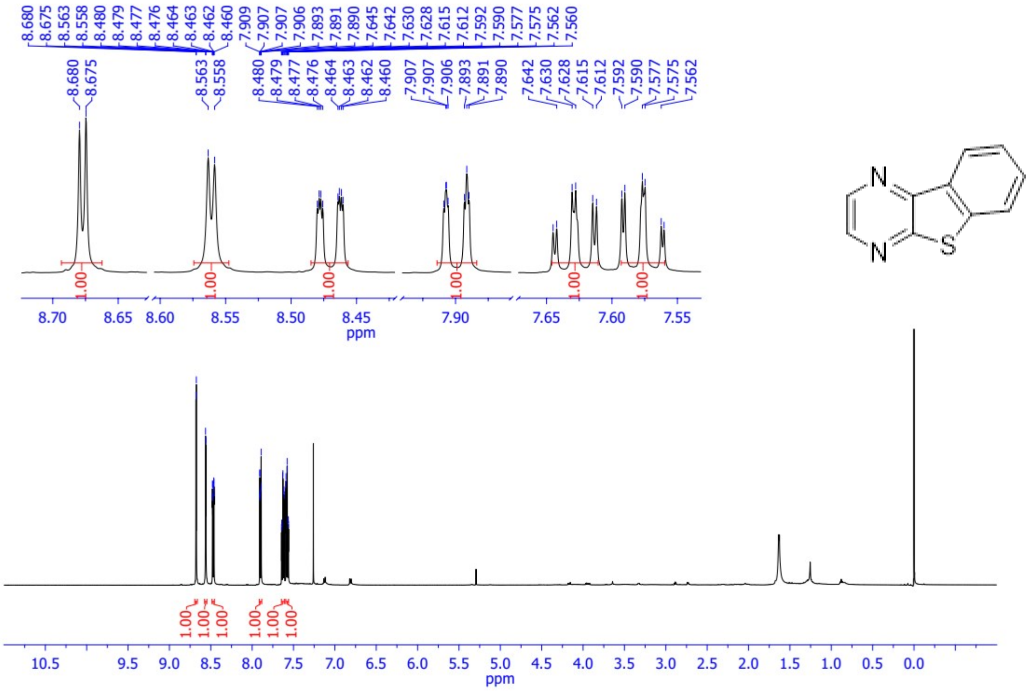


Fig. S61. ^{1}H NMR spectrum of **9.**

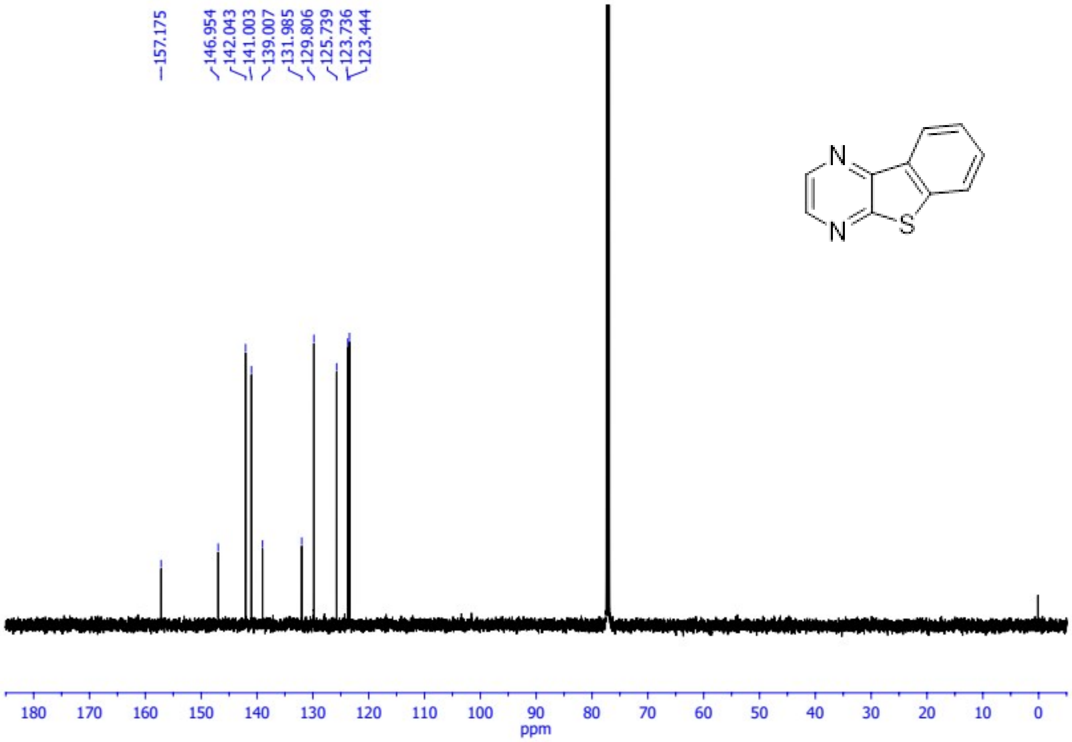
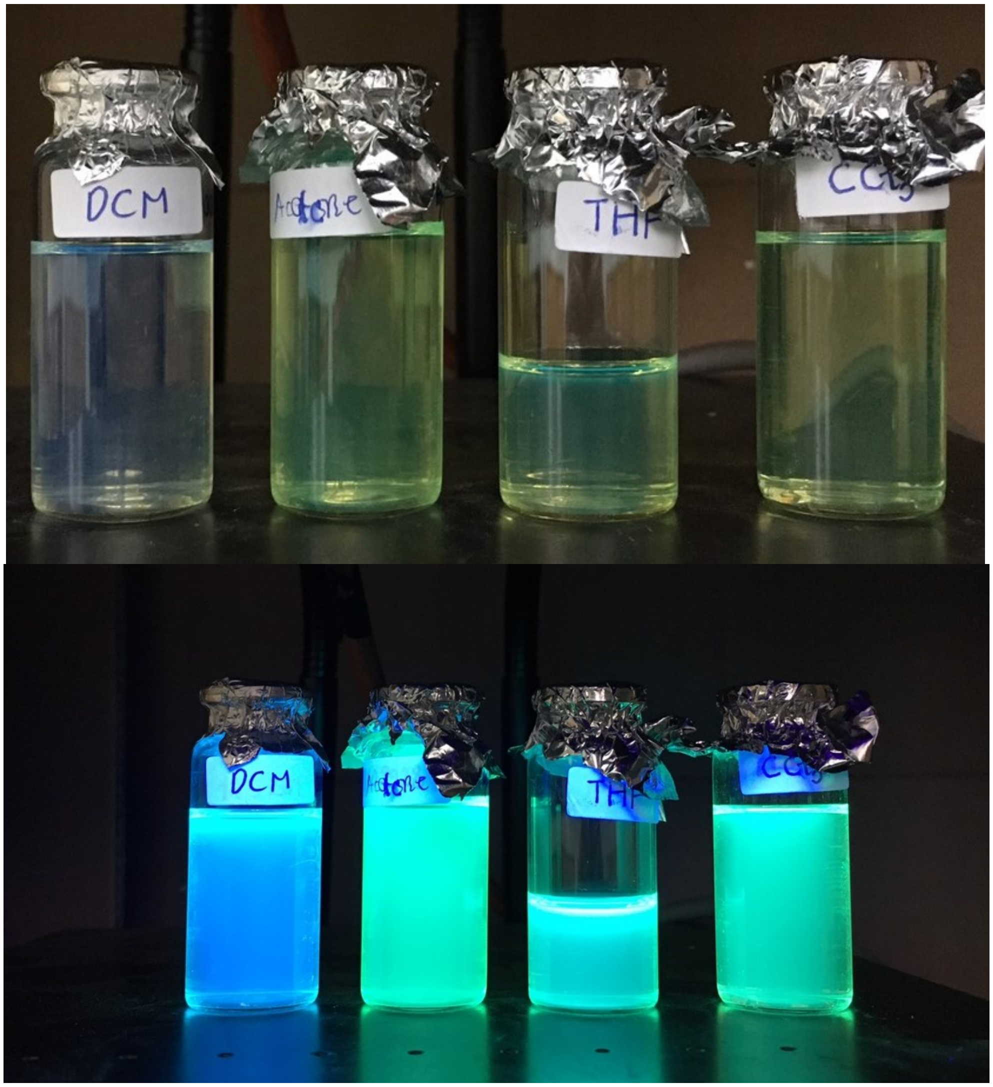


Fig. S62. ^{13}C NMR spectrum of **9.**

4. Study of photophysical properties



Solutions (concentration 4.5 * 10^{-5} M) of compound **3ga** in different solvents: (from left to right) CH_2Cl_2, acetone, THF, and $CHCl_3$. Top: without irradiation, bottom: irradiation with λ = 365 nm.

5. Limitation of reaction scope

The following compounds gave the products in less than 10% yields.