Isatin as 2-Aminobenzaldehdye Surrogate: Transition Metal-free Efficient Synthesis of 2-(2'-Aminophenyl)benzothiazole Derivatives

Manpreet Singh,[a] Vaishali,[a] Avijit Kumar Paul[b] and Virender Singh[ac]*

[a]Department of Chemistry, Dr B R Ambedkar National Institute of Technology (NIT) Jalandhar, 144011, Punjab, India.

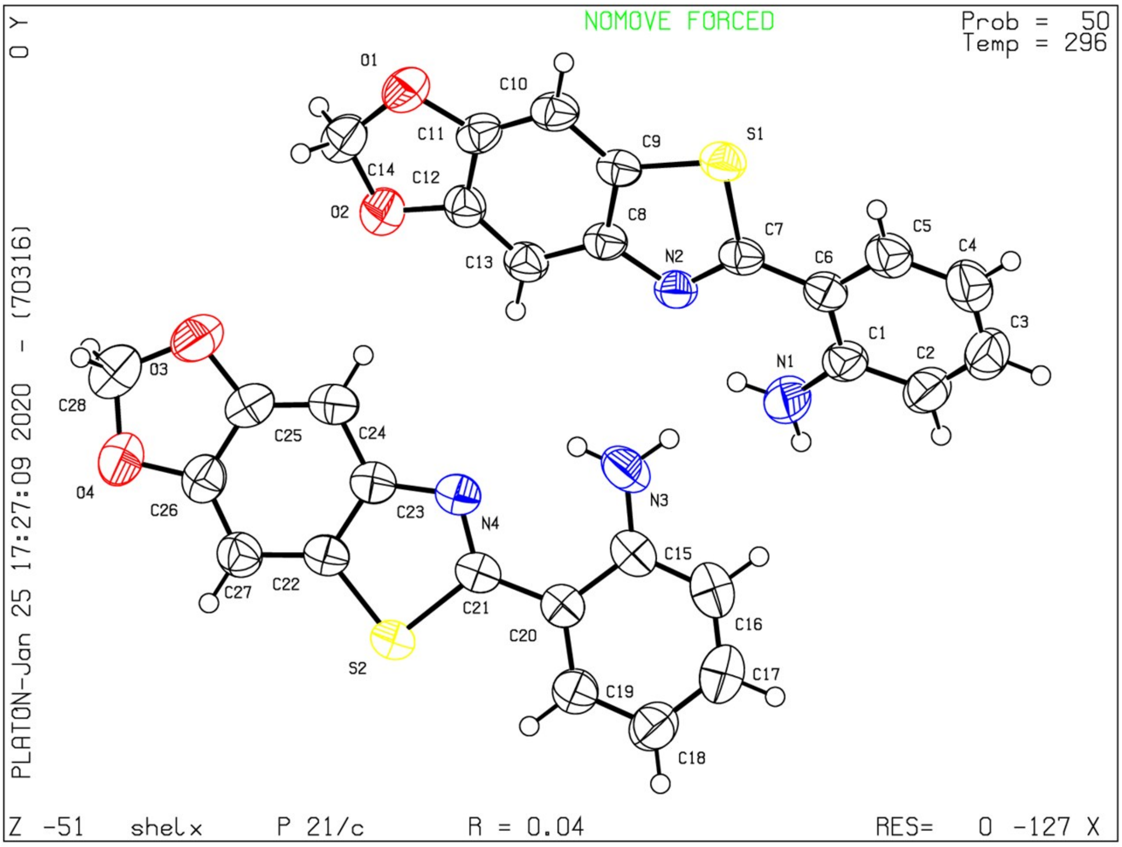
[b]Department of Chemistry, National Institute of Technology (NIT) Kurukshetra, 136119, Haryana, India

[c]Department of Chemistry, Central University of Punjab, Bathinda, 151001, Punjab, India

E mail:- singhv@nitj.ac.in, virender.singh@cup.edu.in; (+) 91-9780998060

Supporting Information

Table of Contents



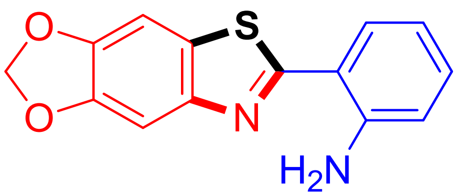


Figure S1. X-ray crystallographic analysis of 1E (CCDC 1980927)

Recrystallized from DCM/THF/MeOH (V/V/V = 1/1/1). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1980927

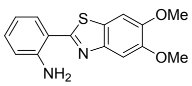
Photophysical Studies

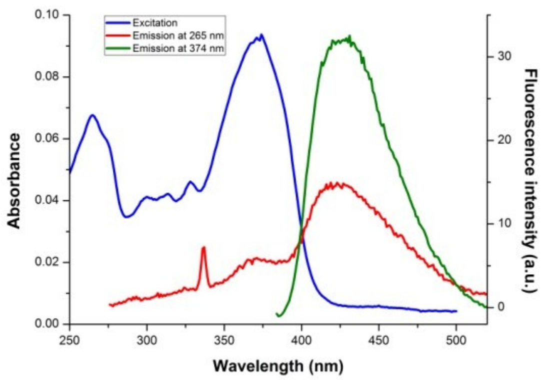
The fluorescent quantum yields (Φ) were measured relative to quinine sulfate (Φ_R = 0.546 in 0.1 M H_2SO_4 at 350 nm excitation) as a reference compound. For the measurement of UV-Vis absorption and fluorescence emission of samples, stock solutions of 1.0 mM concentration were prepared and diluted to 5.0 µM concentration using $CHCl_3$ as a solvent. These Φ_s was calculated as per this equation:

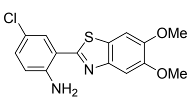
$$\Phi_S = \Phi_R \times \frac{I_S}{I_R} \times \frac{A_R}{A_S} \times \frac{{\eta_S}^2}{{\eta_R}^2}$$
$$R - \text{Reference}; S - \text{Sample}$$

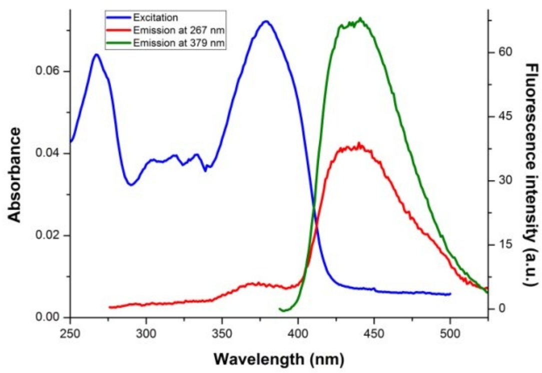
Where Φ_s is the quantum yield of sample, Φ_R is the quantum yield of quinine sulfate η is the refractive index, *I* is the integrated fluorescence intensity and *A* is the absorbance.

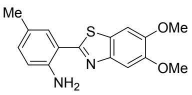
Figure S2. Photophysical properties and graphical data of 2-(2'-aminophenyl)benzothiazole derivatives

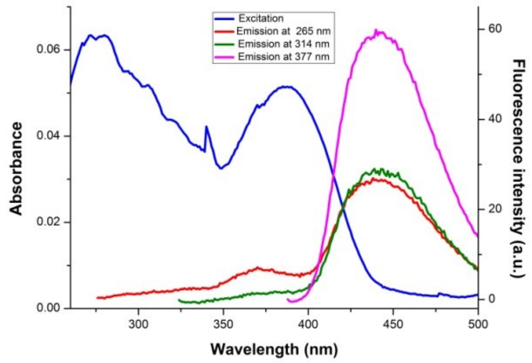
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	265	421	14.67	0.07
1A	374	425	32.06	0.04

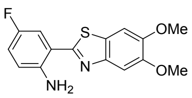


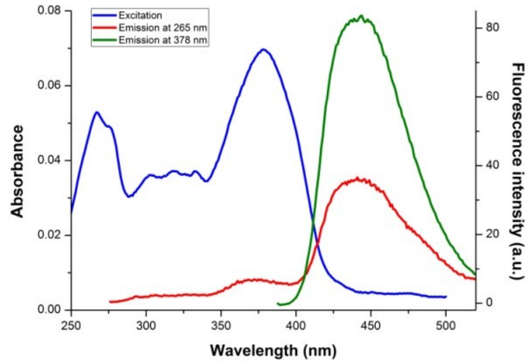
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2A	267	439	38.03	0.14
	379	441	68.09	0.15

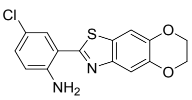


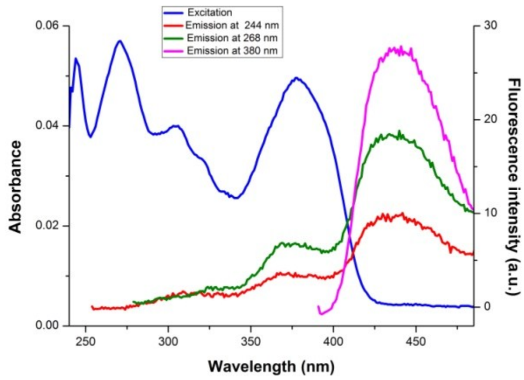
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	265	435	26.93	0.11
4A	314	445	28.32	0.09
	377	439	59.93	0.20

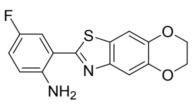


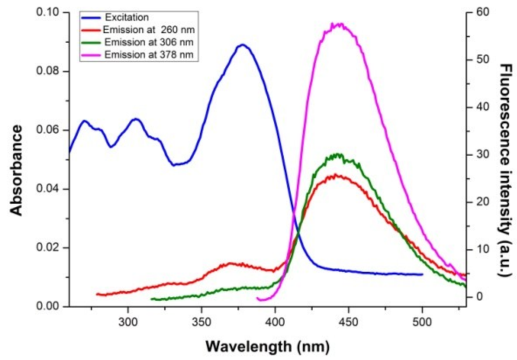
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
1D	265	437	85.66	0.18
	378	440	38.23	0.20

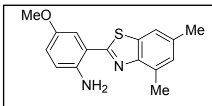


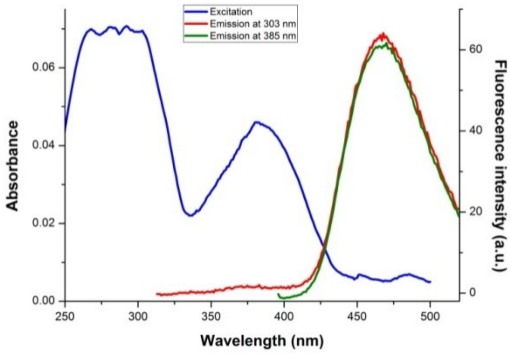
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2D	244	437	9.67	0.07
	270	439	18.86	0.11
	380	440	27.20	0.07

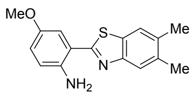


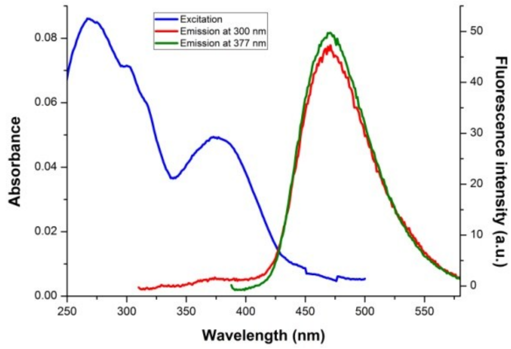
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	270	437	25.42	0.11
	306	438	31.12	0.09
3D	378	439	57.72	0.10

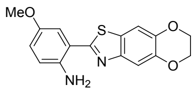


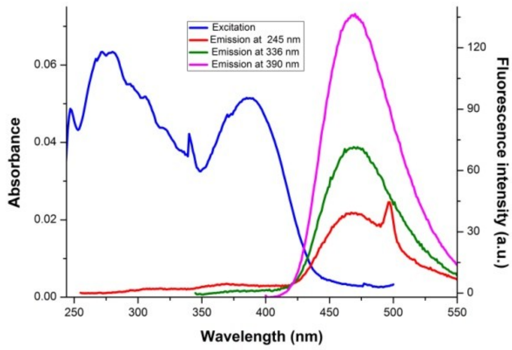
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
5B	303	468	64.13	0.17
	385	470	61.71	0.22

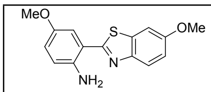


	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	300	469	46.54	0.12
5C	377	471	49.74	0.17



	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	245	467	39.56	0.19
	336	468	71.44	0.29
5D	390	470	136.59	0.44



	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	270	466	52.75	0.23
5F	322	466	86.54	0.25

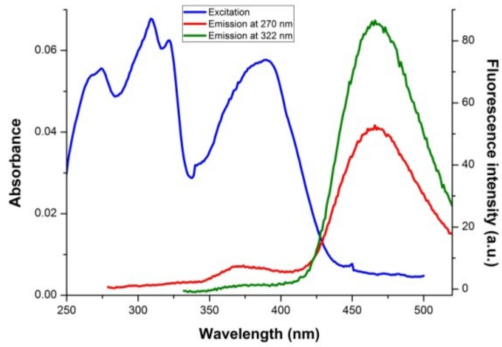
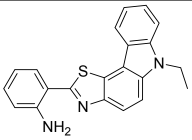
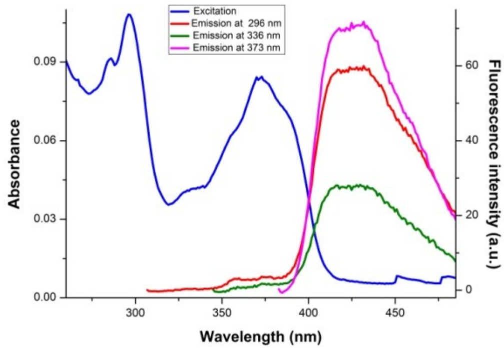
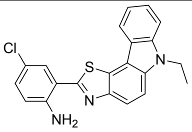
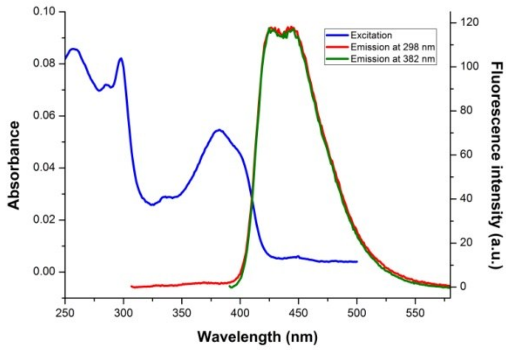


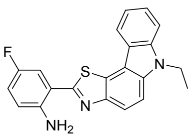
Figure S3. Photophysical properties and graphical data of 2-(6-ethyl-6*H*-thiazolo[4,5-*c*]carbazol-2-yl)aniline derivative

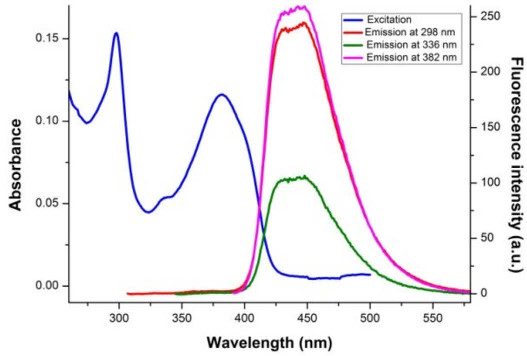
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
 1J	296	432	59.96	0.11
	336	431	28.06	0.11
	373	432	71.81	0.13

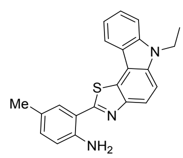


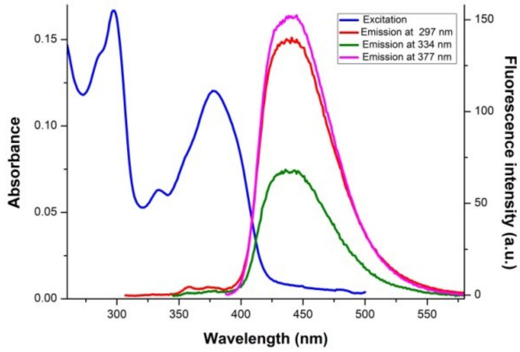
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
 2J	298	444	118.24	0.26
	382	444	117.22	0.38

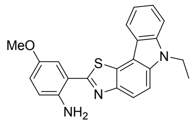


	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
 3J	298	447	244.69	0.24
	336	447	101.13	0.24
	382	447	259.17	0.36



	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
 4J	297	441	140.20	0.15
	334	437	65.23	0.18
	377	441	156.67	0.21



	UV-Vis	Fluorescence		Φ_F
 **5J**	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	267	466	411.42	0.45
	336	466	203.75	0.56
	392	466	380.52	0.60

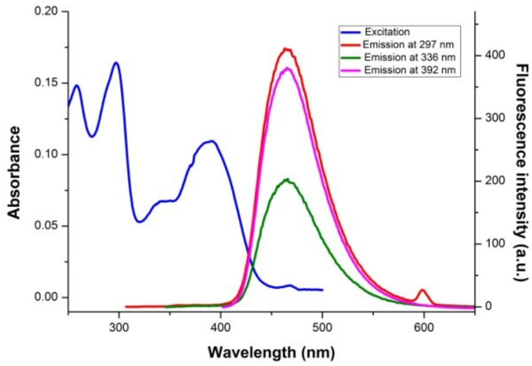
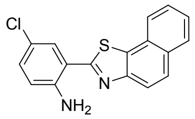
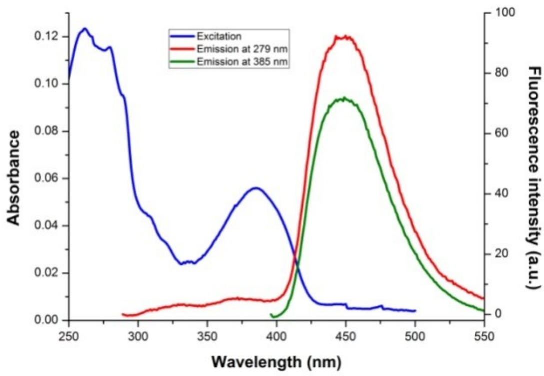
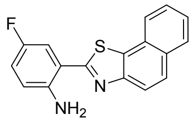
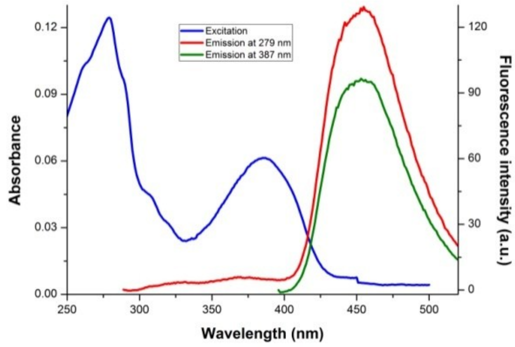


Figure S4. Photophysical properties and graphical data of 4-chloro-2-(naphtho[2,1-*d*]thiazol-2-yl)aniline derivative

	UV-Vis	Fluorescence		Φ_F
 **2K**	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	279	450	92.47	0.15
	385	449	71.99	0.20



	UV-Vis	Fluorescence		Φ_F
 **3K**	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	279	455	129.26	0.19
	387	453	96.47	0.24



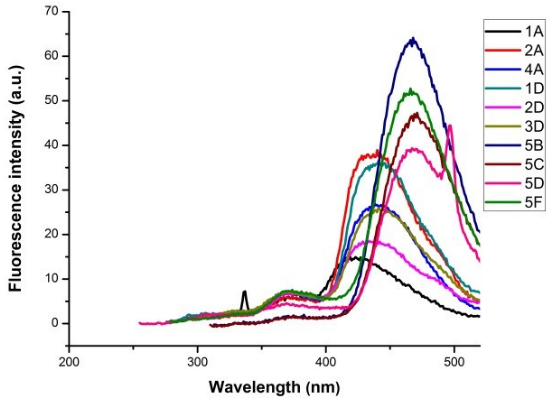


Figure S5. Fluorescence spectra of 2-(2'-aminophenyl)benzothiazoles derivatives excited (λEx) at 244–270 nm

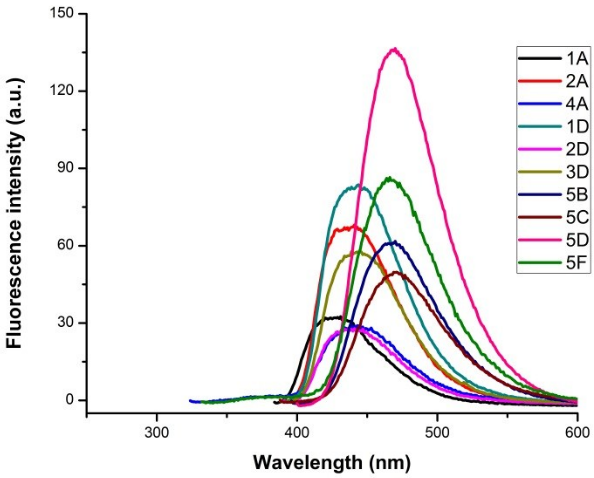


Figure S6. Fluorescence spectra of 2-(2'-aminophenyl) benzothiazoles derivatives excited (λ_{Ex}) at 314–390 nm

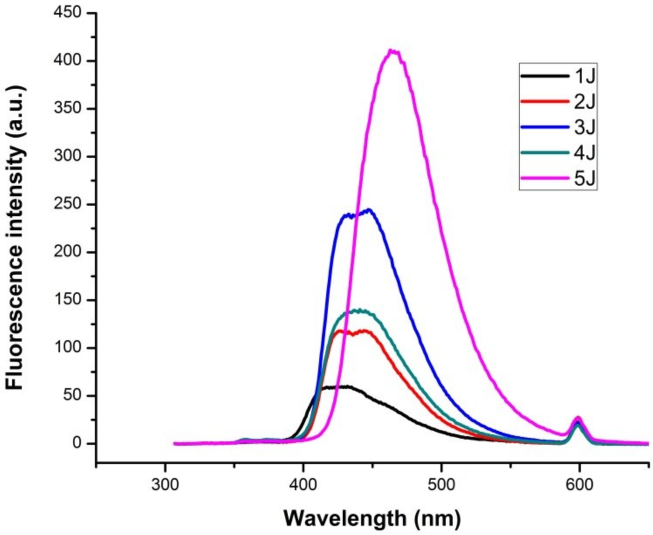


Figure S7. Fluorescence spectra of 2-(6-ethyl-6H-thiazolo[4,5-c]carbazol-2-yl) aniline derivatives excited (λ_{Ex}) at 267–298 nm

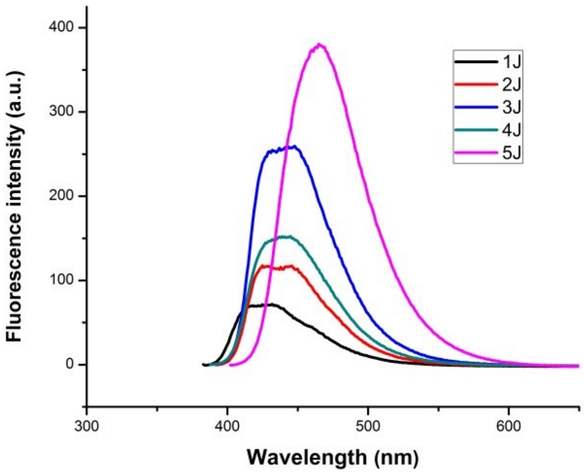


Figure S8. Fluorescence spectra of 2-(6-ethyl-6*H*-thiazolo[4,5-*c*]carbazol-2-yl) aniline derivatives excited (λ_{Ex}) at 336–392 nm

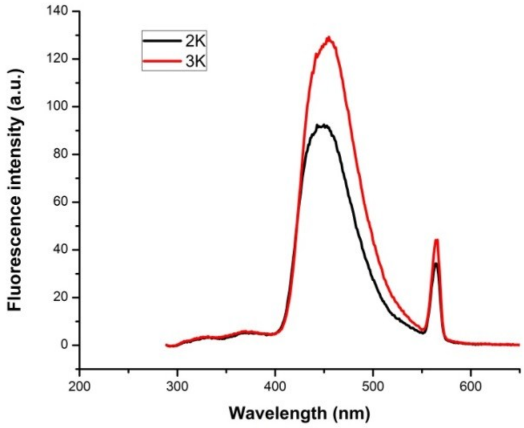


Figure S9. Fluorescence spectra of 2-(naphtho[2,1-*d*]thiazol-2-yl)anilines excited (λ_{Ex}) at 279 nm

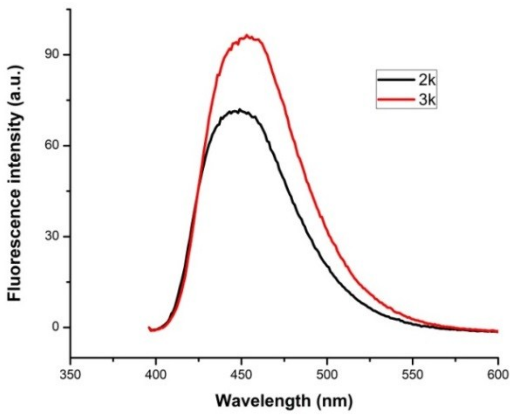


Figure S10. Fluorescence spectra of 2-(naphtho[2,1-*d*]thiazol-2-yl)anilines excited (λ_{Ex}) at 385-387 nm

Experimental data

2-(5,6-Dimethoxybenzo[*d*]thiazol-2-yl)aniline (1A). Yield: 80% (0.16 g from 0.10 g) as a yellow solid; m.p. 190-192 ^oC; R_f = 0.47 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3463 (NH), 3338 (NH), 1607 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ = 3.97 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.31 (brs, 2H, $NH_{2,}$), 6.74 (t, J = 7.6 Hz, 1H, ArH), 6.78 (d, J = 7.8 Hz, 1H, ArH), 7.18–7.21 (m, 1H, ArH), 7.30 (s, 1H, ArH), 7.47 (s, 1H, ArH), 7.66 (dd, J_1 = 7.6, J_2 = 1.1 Hz, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 56.2, 56.4, 102.3, 104.4, 115.8, 116.8, 117.0, 125.3, 129.9, 131.1, 146.3, 148.0, 148.4, 149.2, 167.7 ppm; HRMS (ESI) m/z: calcd. for $C_{15}H_{14}N_2O_2S$ [M + H^+]: 287.0854, found: 287.0836.

4-Chloro-2-(5,6-dimethoxybenzo[*d*]thiazol-2-yl)aniline (**2A**). Yield: 74% (0.13 g from 0.10 g) as a brown solid; m.p. 178-180 ^oC; R_f = 0.46 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3452 (NH), 3325 (NH), 1611 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ =3.98 (s, 6H, $(OCH_3)_2$), 6.34 (brs, 2H, NH_2), 6.72 (d, J = 8.7 Hz, 1H, ArH), 7.13 (dd, J_1 = 8.6, J_2 = 2.2 Hz, 1H, ArH), 7.30 (s, 1H, ArH), 7.46 (s, 1H, ArH), 7.60 (d, J = 2.3 Hz, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 56.3, 56.5, 102.4, 104.6, 116.8, 118.1, 121.3, 125.5, 128.9, 130.8, 144.9, 148.0, 148.8, 149.5, 166.1 ppm; HRMS (ESI) m/z: calcd. for $C_{15}H_{13}ClN_2O_2S$ [M + H^+]: 321.0465, [M + 2 + H^+]: 323.0435 found: 321.0420 (100%), 323.0399 (33%).

2-(5,6-Dimethoxybenzo[*d*]thiazol-2-yl)-4-fluoroaniline (3A). Yield: 76% (0.14 g from 0.10 g) as a yellow solid; m.p. 180-182 ^oC; R_f = 0.43 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3458 (NH), 3338 (NH), 1607 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ = 3.98 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.18 (brs, 2H, NH_2), 6.73 (dd, J_1 = 8.9, J_2 = 4.8 Hz, 1H, ArH), 6.93–6.97 (m, 1H, ArH), 7.30 (s, 1H, ArH), 7.35 (dd, J_1 = 9.7, J_2 = 2.8 Hz, 1H, ArH), 7.47 (s, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6) δ = 55.6, 55.7, 101.8, 103.8, 113.9 (d, J_{C-F} = 23.7 Hz), 114.5, 117.4 (d, J_{C-F} = 6.2 Hz), 117.7 (d, J_{C-F} = 22.5 Hz), 124.7, 142.6, 147.6 (d, J_{C-F} = 80), 147.9, 148.7, 153.6 (d, J_{C-F} = 233.7), 165.4 ppm; HRMS (ESI) m/z: calcd. for $C_{15}H_{13}FN_2O_2S$ [M + H^+]: 305.0760, found: 305.0709.

2-(5,6-Dimethoxybenzo[*d*]thiazol-2-yl)-4-methylaniline (4A). Yield: 65% (0.12 g from 0.10 g) as a yellow solid; m.p. 163-165 ^oC; R_f = 0.49 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3489 (NH), 3363 (NH), 1610 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ = 2.30 (s, 3H, CH_3), 3.97 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.13 (brs, 2H, NH_2), 6.71 (d, J = 8.2 Hz, 1H, ArH), 7.02 (dd, J_1 =

8.2, J_2 = 1.6 Hz, 1H, ArH), 7.30 (s, 1H, ArH), 7.44 (s, 1H, ArH), 7.46 (s, 1H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 20.5, 56.2, 56.5, 102.4, 104.5, 115.8, 117.1, 125.4, 126.2, 129.8, 132.2, 144.1, 148.2, 148.4, 149.2, 167.7 ppm; HRMS (ESI) m/z: calcd. for $C_{16}H_{16}N_2O_2S$ [M + H$^+$]: 301.1011, found: 301.0092.

2-(5,6-Dimethoxybenzo[*d*]thiazol-2-yl)-4-methoxyaniline (5A). Yield: 67% (0.12 g from 0.10 g) as a yellow solid; m.p. 125-128 ^{o}C; R_f = 0.30 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3324 (NH), 3200 (NH), 1604 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.82 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 5.95 (s, 2H, NH_2), 6.75 (d, J = 8.8 Hz, 1H, ArH), 6.87 (dd, J_1 = 8.8, J_2 = 2.8 Hz, 1H, ArH), 7.17 (d, J = 2.8 Hz, 1H, ArH), 7.29 (s, 1H, ArH), 7.47 (s, 1H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 56.1, 56.2, 56.4, 102.3, 104.5, 113.7, 116.2, 118.3, 118.7, 125.5, 140.7, 148.2, 148.5, 149.3, 151.3, 167.2 ppm; HRMS (ESI) m/z: calcd. for $C_{16}H_{16}N_2O_3S$ [M + H$^+$]: 317.0960, found: 317.0939.

5-Bromo-2-(5,6-dimethoxybenzo[*d*]thiazol-2-yl)aniline (6A). Yield: 52% (0.084 g from 0.100 g); m.p. 194-196 ^{o}C; R_f = 0.56 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3442 (NH), 3299 (NH), 1622 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.97 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.42 (brs, 2H, NH_2), 6.83 (d, J = 7.6 Hz, 1H, ArH), 6.94 (s, 1H, ArH), 7.29–7.31 (m, 1H, ArH), 7.45 (d, J = 3.2 Hz, 1H, ArH), 7.48 (d, J = 8.4 Hz, 1H, ArH) ppm; The ^{13}C-NMR spectrum of **6A** could not be recorded due to solubility problem in $CDCl_3$ as well as DMSO-d_6; HRMS (ESI) m/z: calcd. for $C_{15}H_{13}BrN_2O_2S$ [M + H$^+$]: 364.9959, [M + 2 + H$^+$]: 366.9939 found: 364.9946 (100%), 366.9923 (97%).

2-Bromo-6-(5,6-dimethoxybenzo[*d*]thiazol-2-yl)aniline (7A). Yield: 62% (0.10 g from 0.10 g) as a yellow solid; m.p. 181-182 ^{o}C; R_f = 0.51 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3480 (NH), 3376 (NH), 1611 (CONH); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.98 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 6.61 (t, J = 7.9 Hz, 1H, ArH), 6.96 (s, 2H, NH_2), 7.29 (s, 1H, ArH), 7.47 (s, 1H, ArH), 7.49 (dd, J_1 = 7.8, J_2 = 1.3 Hz, 1H, ArH), 7.63 (dd, J_1 = 7.9, J_2 = 1.3 Hz, 1H, ArH) ppm; ^{13}C NMR (125 MHz, DMSO-d$_6$) δ = 55.8, 56.0, 103.2, 104.4, 109.8, 115.6, 116.9, 124.7, 129.1, 134.3, 143.6, 146.9, 148.4, 149.3, 165.8 ppm; HRMS (ESI) m/z: calcd. for $C_{15}H_{13}BrN_2O_2S$ [M + H$^+$]: 364.9959, [M + 2 + H$^+$]: 366.9939, found: 364.9951 (100%), 366.9931 (97%).

2-(5,6-Dimethoxybenzo[*d*]thiazol-2-yl)-6-fluoroaniline (8A). Yield: 54% (0.10 g from 0.10 g) as a brown solid; m.p. 203-205 ^{o}C; R_f = 0.56 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$

= 3490 (NH), 3320 (NH), 1622 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.98 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 6.38 (s, 2H, NH_2), 6.63–6.67 (m, 1H, ArH), 7.02–7.06 (m, 1H, ArH), 7.30 (s, 1H, ArH), 7.44 (d, J = 8.0 Hz, 1H, ArH), 7.48 (s, 1H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 56.2, 56.4, 102.3, 104.5, 115.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.8, 117.5, 117.6, 124.8, 124.9, 125.4, 135.6 (d, $J_{C\text{-}F}$ = 14.3 Hz), 148.3 (d, $J_{C\text{-}F}$ = 79.9 Hz), 149.0 (d, $J_{C\text{-}F}$ = 91.2 Hz), 151.9 (d, $J_{C\text{-}F}$ = 237.3 Hz), 166.5 ppm; HRMS (ESI) m/z: calcd. for $C_{15}H_{13}FN_2O_2S$ [M + H$^+$]: 305.0760, found: 305.0733.

2-(6,7-Dihydro-[1,4]dioxino[2',3':4,5]benzo[1,2-*d*]thiazol-2-yl)aniline (1D). Yield: 64% (0.12 g from 0.10 g) as a yellow solid; m.p. 148-150 °C; R_f = 0.59 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3444 (NH), 3386 (NH), 1681 (CONH); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.32 (s, 4H, $(OCH_2)_2$), 6.32 (brs, 2H, NH_2), 6.71–6.74 (m, 1H, ArH), 6.76–6.78 (m, 1H, ArH), 7.18–7.21 (m, 1H, ArH), 7.30 (s, 1H, ArH), 7.45 (s, 1H, ArH), 7.63 (dd, J_1 = 7.9, J_2 = 1.3 Hz, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 64.4, 64.5, 108.3, 109.9, 115.7, 116.8, 117.0, 126.4, 130.1, 131.3, 142.8, 143.3, 146.5, 148.7, 168.2 ppm; HRMS (ESI) m/z: calcd. for $C_{15}H_{12}N_2O_2S$ [M + H$^+$]: 285.0698, found: 285.0663.

2-([1,3]Dioxolo[4',5':4,5]benzo[1,2-*d*]thiazol-6-yl)aniline (1E). Yield: 78% (0.14 g from 0.10 g) as a yellow solid; m.p. 130-132 °C; R_f = 0.76 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3489 (NH), 3392 (NH), 1681 (CONH); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.06 (s, 2H, OCH_2), 6.27 (s, 2H, NH_2), 6.73 (t, J = 7.5 Hz, 1H, ArH), 6.77 (d, J = 8.1 Hz, 1H, ArH), 7.17–7.21 (m, 1H, ArH), 7.24 (s, 1H, ArH), 7.38 (s, 1H, ArH), 7.62–7.63 (m, 1H, ArH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ = 100.6, 101.8, 113.7, 115.7, 116.5, 125.4, 129.2, 131.1, 146.3, 146.9, 147.5, 148.0, 167.2 ppm; HRMS (ESI) m/z: calcd. for $C_{14}H_{10}N_2O_2S$ [M + H$^+$]: 271.0541, found: 271.0509.

4-Chloro-2-(6,7-dihydro-[1,4]dioxino[2',3':4,5]benzo[1,2-*d*]thiazol-2-yl)aniline (2D). Yield: 68% (0.12 g from 0.10 g) as a yellow solid; m.p. 181-183 °C; R_f = 0.51 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3450 (NH), 3288 (NH), 1612 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.33 (s, 4H, $(OCH_2)_2$), 6.33 (brs, 2H, NH_2), 6.71 (d, J = 8.7 Hz, 1H, ArH), 7.13 (dd, J_1 = 8.7, J_2 = 2.3 Hz, 1H, ArH), 7.32 (s, 1H, ArH), 7.45 (s, 1H, ArH), 7.59 (d, J = 2.3 Hz, 1H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$+DMSO-d_6) δ = 62.2, 62.4, 106.7, 107.6, 112.9, 116.4, 116.9, 123.6, 126.2, 129.0, 141.2, 141.7, 144.4, 146.2, 164.1 ppm; HRMS (ESI) m/z: calcd. for

$C_{15}H_{11}ClN_2O_2S$ [M + H$^+$]: 319.0308, [M + 2 + H$^+$]: 321.0279, found: 319.0269 (100%), 321.0245 (33%).

2-(6,7-Dihydro-[1,4]dioxino[2',3':4,5]benzo[1,2-*d*]thiazol-2-yl)-4-fluoroaniline (3D). Yield: 60% (0.11 g from 0.10 g) as a yellow solid; m.p. 188-190 ^{o}C; R_f = 0.53 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3355 (NH), 3271 (NH), 1602 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.33 (s, 4H, $(OCH_2)_2$), 6.15 (brs, 2H, NH_2), 6.72 (dd, J_1 = 8.9, J_2 = 4.7 Hz, 1H, ArH), 6.93–6.97 (m, 1H, ArH), 7.31–7.34 (m, 2H, ArH), 7.46 (s, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6) δ = 63.1, 63.2, 107.9 (d, $J_{C\text{-}F}$ = 140 Hz), 113.1, 113.2, 113.5, 116.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 117.5 (d, $J_{C\text{-}F}$ = 23 Hz), 124.8, 141.9, 142.4, 142.6, 147.3, 152.7 (d, $J_{C\text{-}F}$ = 231 Hz), 165.3 ppm; HRMS (ESI) m/z: calcd. for $C_{15}H_{11}FN_2O_2S$ [M + H$^+$]: 303.0604, found: 303.0600.

2-(4,6-Dimethylbenzo[*d*]thiazol-2-yl)-4-methoxyaniline (5B). Yield: 81% (0.13 g from 0.10 g) as a yellow solid; m.p. 128-130 ^{o}C; R_f = 0.71 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3374 (NH), 3275 (NH), 1503 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.45 (s, 3H, CH_3), 2.69 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 6.09 (brs, 2H, NH_2), 6.77 (d, J = 8.8 Hz, 1H, ArH), 6.89 (dd, J_1 = 8.8, J_2 = 2.6 Hz, 1H, ArH), 7.09 (s, 1H, ArH), 7.19 (d, J = 2.6 Hz, 1H, ArH), 7.50 (s, 1H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 18.6, 21.7, 56.1, 113.7, 116.1, 118.4, 118.5, 119.1, 128.4, 131.8, 133.4, 135.1, 141.0, 151.3, 166.7 ppm; HRMS (ESI) m/z: calcd. for $C_{16}H_{16}N_2OS$ [M + H$^+$]: 285.1062, found: 285.1032.

2-(5,6-Dimethylbenzo[*d*]thiazol-2-yl)-4-methoxyaniline (5C). Yield: 85% (0.14 g from 0.10 g) as a brown solid; m.p. 130-132 ^{o}C; R_f = 0.65 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3413 (NH), 3300 (NH), 1661 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.39 (s, 6H, $(CH_3)_2$), 3.82 (s, 3H, OCH_3), 6.04 (brs, 2H, NH_2), 6.75 (d, J = 8.8 Hz, 1H, ArH), 6.87–6.89 (m, 1H, ArH), 7.19 (d, J = 2.7 Hz, 1H, ArH), 7.62 (s, 1H, ArH), 7.76 (s, 1H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 20.3, 56.11, 113.7, 116.0, 118.3, 119.2, 119.7, 121.3, 122.9, 130.7, 134.5, 135.3, 141.1, 151.2, 152.7, 167.8 ppm; HRMS (ESI) m/z: calcd. for $C_{16}H_{16}N_2OS$ [M + H$^+$]: 285.1062, found: 285.1035.

2-(6,7-Dihydro-[1,4]dioxino[2',3':4,5]benzo[1,2-*d*]thiazol-2-yl)-4-methoxyaniline (5D). Yield: 76% (0.13 g from 0.10 g) as a yellow solid; m.p. 125-128 ^{o}C; R_f = 0.54 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3445 (NH), 3366 (NH), 1610 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.81 (s, 3H, OCH_3), 4.32 (s, 4H, $(OCH_2)_2$), 5.97 (brs, 2H, NH_2), 6.74 (d, J= 8.8 Hz, 1H, ArH), 6.87 (dd, J_1 = 8.8, J_2 = 2.7 Hz, 1H, ArH), 7.15 (d, J = 2.7 Hz, 1H, ArH), 7.31 (s, 1H, ArH), 7.46 (s, 1H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 56.1, 64.4, 64.5, 108.3, 110.0, 113.7, 116.0, 118.3, 119.1, 126.5, 140.9, 142.9, 143.4, 148.9, 151.3, 167.7 ppm; HRMS (ESI) m/z: calcd. for $C_{16}H_{14}N_2O_3S$ [M + H$^+$]: 315.0803, found: 315.0783.

2-([1,3]Dioxolo[4',5':4,5]benzo[1,2-*d*]thiazol-6-yl)-4-methoxyaniline (5E). Yield: 75% (0.13 g from 0.10 g) as a yellow solid; m.p. 155-157 ^{o}C; R_f = 0.67 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3476 (NH), 3325 (NH), 1599 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.83 (s, 3H, OCH_3), 5.94 (s, 2H, NH_2), 6.08 (s, 2H, OCH_2), 6.77 (d, J = 8.9 Hz, 1H, ArH), 6.89 (dd, J_1 = 8.8, J_2 = 2.7 Hz, 1H, ArH), 7.16 (d, J = 2.7 Hz, 1H, ArH), 7.28 (s, 1H, ArH), 7.41 (s, 1H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 56.1, 100.1, 101.8, 102.4, 113.4, 116.0, 118.4, 118.8, 126.6, 140.7, 146.7, 147.8, 148.8, 151.3, 167.3 ppm; HRMS (ESI) m/z: calcd. for $C_{15}H_{12}N_2O_3S$ [M + H$^+$]: 301.0647, found: 301.0602.

4-Methoxy-2-(6-methoxybenzo[*d*]thiazol-2-yl)aniline (5F). Yield: 77% (0.125 g from 0.100 g) as a yellow solid; m.p. 120-122 ^{o}C; R_f = 0.64 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3438 (NH), 3288 (NH), 1598 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.82 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 5.97 (s, 2H, NH_2), 6.76 (d, J = 8.8 Hz, 1H, ArH), 6.88 (dd, J_1 = 8.8, J_2 = 2.8 Hz, 1H, ArH), 7.06 (dd, J_1 = 8.9, J_2 = 2.5 Hz, 1H, ArH), 7.17 (d, J = 2.7 Hz, 1H, ArH), 7.34 (d, J = 2.4 Hz, 1H, ArH), 7.86 (d, J = 8.9 Hz, 1H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$+DMSO-d_6) δ = 55.16, 55.31, 103.3, 112.7, 114.4, 114.6, 117.6, 118.4, 122.3, 133.9, 140.6, 147.5, 150.1, 156.9, 166.6 ppm; HRMS (ESI) m/z: calcd. for $C_{15}H_{14}N_2O_2S$ [M + H$^+$]: 287.0854, found: 287.0821.

2-Bromo-6-(5,6-dimethylbenzo[*d*]thiazol-2-yl)aniline (7C). Yield: 56% (0.083 g from 0.100 g) as a yellow solid; m.p. 140-142 ^{o}C; R_f = 0.62 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3480 (NH), 3330 (NH), 1604 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.39 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 6.60–6.64 (m, 1H, ArH), 7.04 (s, 2H, NH_2), 7.51 (dd, J_1 = 7.3, J_2 = 4.0 Hz, 1H, ArH), 7.63 (s, 1H, ArH), 7.67 (d, J = 8.0 Hz, 1H, ArH), 7.77 (s, 1H, ArH) ppm; The ^{13}C-NMR spectrum of **7C** could not be recorded due to solubility problem in $CDCl_3$ as well as DMSO-d_6; HRMS (ESI) m/z: calcd. for $C_{15}H_{13}BrN_2O_2S$ [M + H$^+$]: 333.0061, [M + 2 + H$^+$]: 335.0041, found: 333.0029 (100%), 335.0022 (97.3%).

2-(6-Ethyl-6*H*-thiazolo[4,5-*c*]carbazol-2-yl)aniline (1J). Yield: 60% (0.116 g from 0.100 g) as a brown solid; m.p. 140-142 ^{o}C; R_f = 0.59 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3464 (NH), 3320 (NH), 1590 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.49 (t, J = 7.2 Hz, 3H, CH_2CH_3), 4.48 (q, J = 7.2 Hz, 2H, CH_2CH_3), 6.43 (brs, 2H, NH_2), 6.79–6.83 (m, 2H, ArH), 7.21–7.25 (m, 1H, ArH), 7.36–7.39 (m, 1H, ArH), 7.51–7.53 (m, 2H, ArH), 7.54–7.56 (m, 1H, ArH), 7.85 (dd, J_1 = 7.8, J_2 = 1.2 Hz, 1H, ArH), 8.09 (d, J = 8.8 Hz, 1H, ArH), 8.17 (d, J = 7.7 Hz, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.2, 38.1, 107.9, 109.0, 115.4, 116.1, 116.8, 117.1, 119.6, 120.2, 121.4, 122.0, 125.6, 126.3, 130.1, 131.0, 137.6, 139.9, 146.5, 148.4, 165.7 ppm; HRMS (ESI) m/z: calcd. for $C_{21}H_{17}N_3S$ [M + H$^+$]: 344.1221, found: 344.1174.

4-Chloro-2-(6-ethyl-6*H*-thiazolo[4,5-*c*]carbazol-2-yl)aniline (2J). Yield: 80% (0.167 g from 0.100 g) as a brown solid; m.p. 170-172 ^{o}C; R_f = 0.54 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3471 (NH), 3287 (NH), 1594 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.50 (t, J = 7.1 Hz, 3H, CH_2CH_3), 4.48 (q, J = 7.0 Hz, 2H, CH_2CH_3), 6.40 (brs, 1H, NH_2), 6.76 (d, J = 8.6 Hz, 1H, ArH), 7.15–7.17 (m, 1H, ArH), 7.39 (t, J = 7.1 Hz, 1H, ArH), 7.51–7.56 (m, 3H, ArH), 7.79–7.80 (m, 1H, ArH), 8.09 (d, J = 8.7 Hz, 1H, ArH), 8.16 (d, J = 7.8 Hz, 1H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.2, 38.2, 108.2, 109.1, 115.4, 117.0, 118.1, 119.8, 120.3, 121.4, 121.9, 125.8, 126.3, 129.1, 130.7, 137.7, 139.9, 145.0, 148.2, 164.1 ppm; HRMS (ESI) m/z: calcd. for $C_{21}H_{16}ClN_3S$ [M + H$^+$]: 378.0832, [M + 2 + H$^+$]: 380.0802, found: 378.0809 (100%), 380.0801 (33%).

2-(6-Ethyl-6*H*-thiazolo[4,5-*c*]carbazol-2-yl)-4-fluoroaniline (3J).Yield: 72% (0.157 g from 0.100 g) as a brown solid; m.p. 200-202 ^{o}C; R_f = 0.60 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3496 (NH), 3310 (NH), 1599 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.50 (t, J = 7.1 Hz, 3H, CH_2CH_3), 4.48 (q, J = 7.2 Hz, 2H, CH_2CH_3), 6.24 (brs, 2H, NH_2), 6.77 (dd, J_1 = 8.7, J_2 = 4.7 Hz, 1H, ArH), 6.96–7.00 (m, 1H, ArH), 7.39 (t, J = 7.1 Hz, 1H, ArH), 7.53 (t, J = 6.3 Hz, 2H, ArH), 7.55–7.56 (m, 2H, ArH), 8.10 (d, J = 8.6 Hz, 1H, ArH), 8.16 (d, J = 7.7 Hz, 1H, ArH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ = 13.9, 37.5, 109.1, 109.9, 113.4 (d, $J_{C\text{-}F}$ = 7.5 Hz), 114.0, 114.1, 114.2, 117.8, 118.6 (d, $J_{C\text{-}F}$ = 22.5 Hz), 119.8 (d, $J_{C\text{-}F}$ = 43.7 Hz), 120.5, 120.7, 124.9, 125.8, 137.2, 139.4, 144.0, 147.6, 153.2 (d, $J_{C\text{-}F}$ = 230 Hz), 163.5 ppm; HRMS (ESI) m/z: calcd. for $C_{21}H_{16}FN_3S$ [M + H$^+$]: 362.1127, found: 362.1122.

2-(6-Ethyl-6*H*-thiazolo[4,5-*c*]carbazol-2-yl)-4-methylaniline (4J). Yield: 68% (0.151 g from 0.100 g) as a yellow solid; m.p. 140-142 ^oC; R_f = 0.61 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3499 (NH), 3306 (NH), 1612 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ = 1.50 (t, J = 7.2 Hz, 3H, CH_2CH_3), 2.36 (s, 3H, CH_3), 4.48 (q, J = 7.2 Hz, 2H, CH_2CH_3), 6.24 (s, 2H, NH_2), 6.76 (d, J = 8.2 Hz, 1H, ArH), 7.05–7.06 (m, 1H, ArH), 7.36–7.39 (m, 1H, ArH), 7.51–7.53 (m, 2H, ArH), 7.56 (d, J = 6.8 Hz, 1H, ArH), 7.66 (s, 1H, ArH), 8.09 (d, J = 8.7 Hz, 1H, ArH), 8.19 (d, J = 7.7 Hz, 1H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.2, 20.6, 38.1, 107.8, 109.0, 115.4, 116.0, 117.0, 119.6, 120.2, 121.4, 122.0, 125.6, 126.3, 130.1, 132.0, 137.5, 139.9, 144.2, 148.5, 165.7 ppm; HRMS (ESI) m/z: calcd. for $C_{22}H_{19}N_3S$ [M + H^+]: 358.1378, found: 358.1366.

2-(6-Ethyl-6*H*-thiazolo[4,5-*c*]carbazol-2-yl)-4-methoxyaniline (5J). Yield: 78% (0.164 g from 0.100 g) as a yellow solid; m.p. 145-146 ^oC; R_f = 0.54 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3396 (NH), 3290 (NH), 1594 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ = 1.50 (t, J = 7.2 Hz, 3H, CH_2CH_3), 3.89 (s, 3H, OCH_3), 4.49 (q, J = 7.2 Hz, 2H, CH_2CH_3), 6.08 (brs, 2H, NH_2), 6.80 (d, J = 8.8 Hz, 1H, ArH), 6.90 (dd, J_1 = 8.8, J_2 = 2.8 Hz, 1H, ArH), 7.36 (dd, J_1 = 4.6, J_2 = 2.0 Hz, 1H, ArH), 7.38–7.40 (m, 1H, ArH), 7.51–7.54 (m, 2H, ArH), 7.56 (dd, J_1 = 6.2, J_2 = 1.6 Hz, 1H, ArH), 8.10 (d, J = 8.7 Hz, 1H, ArH), 8.18 (d, J = 7.7 Hz, 1H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.2, 38.1, 56.2, 107.9, 109.0, 113.4, 115.3, 116.3, 118.4, 118.9, 119.6, 120.2, 121.3, 121.9, 125.6, 126.3, 137.5, 139.8, 140.9, 148.4, 151.4, 165.2 ppm; HRMS (ESI) m/z: calcd. for $C_{22}H_{19}N_3OS$ [M + H^+]: 374.1327, found: 374.1321.

4-Chloro-2-(naphtho[2,1-*d*]thiazol-2-yl)aniline (2K). Yield: 85% (0.146 g from 0.100 g) as a yellow solid; m.p. 175-177 ^oC; R_f = 0.71 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3438 (NH), 3293 (NH), 1613 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ = 6.43 (brs, 2H, NH_2), 6.75 (d, J = 8.7 Hz, 1H, ArH), 7.17 (dd, J_1 = 8.7, J_2 = 2.3 Hz, 1H, ArH), 7.54–7.57 (m, 1H, ArH), 7.60–7.63 (m, 1H, ArH), 7.76 (d, J = 2.3 Hz, 1H, ArH), 7.87 (d, J = 8.8 Hz, 1H, ArH), 7.96 (d, J = 8.1 Hz, 1H, ArH), 8.02 (t, J = 8.3 Hz, 2H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6) δ = 112.9, 116.8, 117.4, 119.4, 123.5, 124.5, 125.7, 125.8, 126.6, 127.4, 127.9, 129.1, 129.4, 144.7, 149.7, 165.0 ppm; HRMS (ESI) m/z: calcd. for $C_{17}H_{11}ClN_2S$ [M + H^+]: 311.0410, [M + 2 + H^+]: 311.0386, found: 313.0380 (100%), 313.0369 (33%).

4-Fluoro-2-(naphtho[2,1-*d*]thiazol-2-yl)aniline (3K). Yield: 74% (0.132 g from 0.100 g) as a yellow solid; m.p. 144-145 °C; R_f = 0.64 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3382 (NH), 3284 (NH), 1606 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.25 (brs, 2H, NH_2), 6.77 (dd, J_1 = 8.9, J_2 = 4.8 Hz, 1H, ArH), 6.97–7.01 (m, 1H, ArH), 7.50 (dd, J_1 = 9.6, J_2 = 2.8 Hz, 1H, ArH), 7.56 (t, J = 7.7 Hz, 1H, ArH), 7.60–7.64 (m, 1H, ArH), 7.87 (d, J = 8.8 Hz, 1H, ArH), 7.97 (d, J = 8.0 Hz, 1H, ArH), 8.03 (dd, J_1 = 8.3, J_2 = 5.3 Hz, 2H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 115.3 (d, $J_{C\text{-}F}$ = 23 Hz), 118.1 (d, $J_{C\text{-}F}$ = 8.0 Hz), 118.9 (d, $J_{C\text{-}F}$ = 23 Hz), 121.4, 125.8 (d, $J_{C\text{-}F}$ = 70 Hz), 127.4 (d, $J_{C\text{-}F}$ = 25 Hz), 127.9, 129.1, 130.5, 131.1, 143.1, 151.8, 155.9, 167.2 ppm; HRMS (ESI) m/z: calcd. for $C_{17}H_{11}FN_2S$ [M + H$^+$]: 295.0705, found: 295.0665.

***N*-(4-Fluoro-2-(naphtho[1,2-*d*]thiazol-2-yl)phenyl)acetamide (8)**. Yield: 78% (0.089 g from 0.100 g) as a light yellow solid; m.p. 175-177 °C; R_f = 0.47 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3395 (NH), 1691 (CONH), 1601 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.35 (s, 3H, CH_3), 7.17–7.21 (m, 1H, ArH), 7.60–7.63 (m, 2H, ArH), 7.66 (t, J = 7.5 Hz, 1H, ArH), 7.93 (d, J = 8.8 Hz, 1H, ArH), 8.00 (d, J = 8.0 Hz, 1H, ArH), 8.03 (d, J = 8.7 Hz, 1H, ArH), 8.06 (d, J = 8.0 Hz, 1H, ArH), 8.81 (dd, J_1 = 9.2, J_2 = 5.3 Hz, 1H, ArH), 12.32 (s, 1H, NH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 25.6, 115.4 (d, $J_{C\text{-}F}$ = 23.7 Hz), 118.6 (d, $J_{C\text{-}F}$ = 21.2 Hz), 121.0, 122.8, 122.9, 125.4, 126.8, 127.7, 128.2, 129.2, 131.0, 131.4, 134.4, 140.0, 151.0, 158.9, 166.4, 169.2 ppm; HRMS (ESI) m/z: calcd. for $C_{19}H_{13}FN_2OS$ [M + H$^+$]: 337.0811, found: 337.0801.

***N*-(2-([1,3]Dioxolo[4',5':4,5]benzo[1,2-*d*]thiazol-6-yl)phenyl)benzamide (9)**. Yield: 88% (0.122 g from 0.100 g) as a yellow solid; m.p. 198-200 °C; R_f = 0.59 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3416 (NH), 1705 (CONH), 1595 (C=N); ^{1}H NMR (500 MHz, DMSO-d$_6$) δ = 6.00 (s, 2H, OCH_2), 7.06–7.09 (m, 1H, ArH), 7.19 (s, 1H, ArH), 7.24 (s, 1H, ArH), 7.37–7.40 (m, 1H, ArH), 7.47–7.53 (m, 3H, ArH), 7.72 (dd, J_1 = 7.7, J_2 = 1.2 Hz, 1H, ArH), 8.07 (dd, J_1 = 7.7, J_2 = 1.7 Hz, 2H, ArH), 8.88–8.90 (m, 1H, ArH), 13.14 (s, 1H, NH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 100.3, 101.9, 102.2, 119.8, 120.5, 120.9, 123.4, 126.8, 127.9, 128.9, 128.8, 129.3, 130.3, 131.7, 132.0, 138.0, 147.9, 148.4 ppm; HRMS (ESI) m/z: calcd. for $C_{21}H_{14}N_2O_3S$ [M + H$^+$]: 375.0803, found: 375.0788.

***N*-(2-([1,3]Dioxolo[4',5':4,5]benzo[1,2-*d*]thiazol-6-yl)phenyl)-4-methylbenzene sulfonamide (10)**. Yield: 65% (0.102 g from 0.100 g) as a yellow solid; m.p. 172-174 °C; R_f = 0.54 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3462 (NH), 1602 (C=N); ^{1}H NMR (500

MHz, $CDCl_3$) δ = 2.28 (s, 3H, CH_3), 6.11 (s, 2H, OCH_2), 7.06 (d, J = 8.1 Hz, 2H, ArH), 7.08–7.10 (m, 1H, ArH), 7.23 (s, 1H, ArH), 7.31–7.35 (m, 2H, ArH), 7.51 (s, 1H, ArH), 7.61–7.63 (m, 2H, ArH), 7.73 (d, J = 8.1 Hz, 1H, ArH), 12.09 (s, 1H, NH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.6, 100.0, 102.2, 102.6, 120.5, 120.7, 123.8, 126.8, 127.2, 129.3, 129.5, 131.2, 136.5, 136.6, 143.6, 147.7, 148.5, 166.0 ppm; HRMS (ESI) m/z: calcd. for $C_{21}H_{16}N_2O_4S_2$ [M + H^+]: 425.0630, found: 425.0608.

***N*-(2-([1,3]Dioxolo[4',5':4,5]benzo[1,2-*d*]thiazol-6-yl)phenyl)-2-bromoacetamide (11).** Yield: 90% (0.130 g from 0.100 g) as an off white solid; m.p. 205-207 °C; R_f = 0.69 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3389 (NH), 1691 (CONH), 1599 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ = 4.13 (s, 2H, CH_2Br), 6.10 (s, 2H, OCH_2), 7.19 (dd, J_1 = 11.8, J_2 = 4.4 Hz, 1H, ArH), 7.27 (s, 1H, ArH), 7.44–7.47 (m, 1H, ArH), 7.48 (s, 1H, ArH), 7.79 (dd, J_1 = 8.1, J_2 = 1.3 Hz, 1H, ArH), 8.73 (d, J = 7.9 Hz, 1H, ArH), 12.96 (s, 1H, NH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 30.1, 100.2, 102.2, 102.4, 120.4, 121.1, 124.2, 127.1, 129.3, 131.4, 136.8, 147.6, 148.0, 148.4, 165.4, 166.3 ppm; HRMS (ESI) m/z: calcd. for $C_{16}H_{11}BrN_2O_3S$ [M + H^+]: 390.9752, found: 390.9718.

(*Z*)-5-Chloro-3-((3,4-dimethoxyphenyl)imino)indolin-2-one (12). Yield: 89% as an Orange solid; m.p. 205-207 °C; R_f = 0.69 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm)$^{-1}$ = 3425 (NH), 1681 (CONH), 1606 (C=N); ^1H NMR (500 MHz, $CDCl_3$) δ = 3.88 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 6.71 (dd, J_1 = 8.3, J_2 = 2.1 Hz, 1H, ArH), 6.75 (d, J = 2.1 Hz, 1H, ArH), 6.88 (d, J = 8.3 Hz, 1H, ArH), 6.94 (d, J = 8.3 Hz, 1H, ArH), 7.17 (d, J = 1.9 Hz, 1H, ArH), 7.31 (dd, J_1 = 8.3, J_2 = 2.1 Hz, 1H, ArH), 8.95 (s, 1H, NH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 56.2, 56.3, 104.2, 110.9, 111.5, 113.1, 117.2, 125.6, 128.0, 133.9, 142.1, 144.2, 148.0, 149.8, 152.5, 165.5 ppm; HRMS (ESI) m/z: calcd. for $C_{16}H_{13}ClN_2O_3$ [M + H^+]: 317.0693, found: 317.0658.

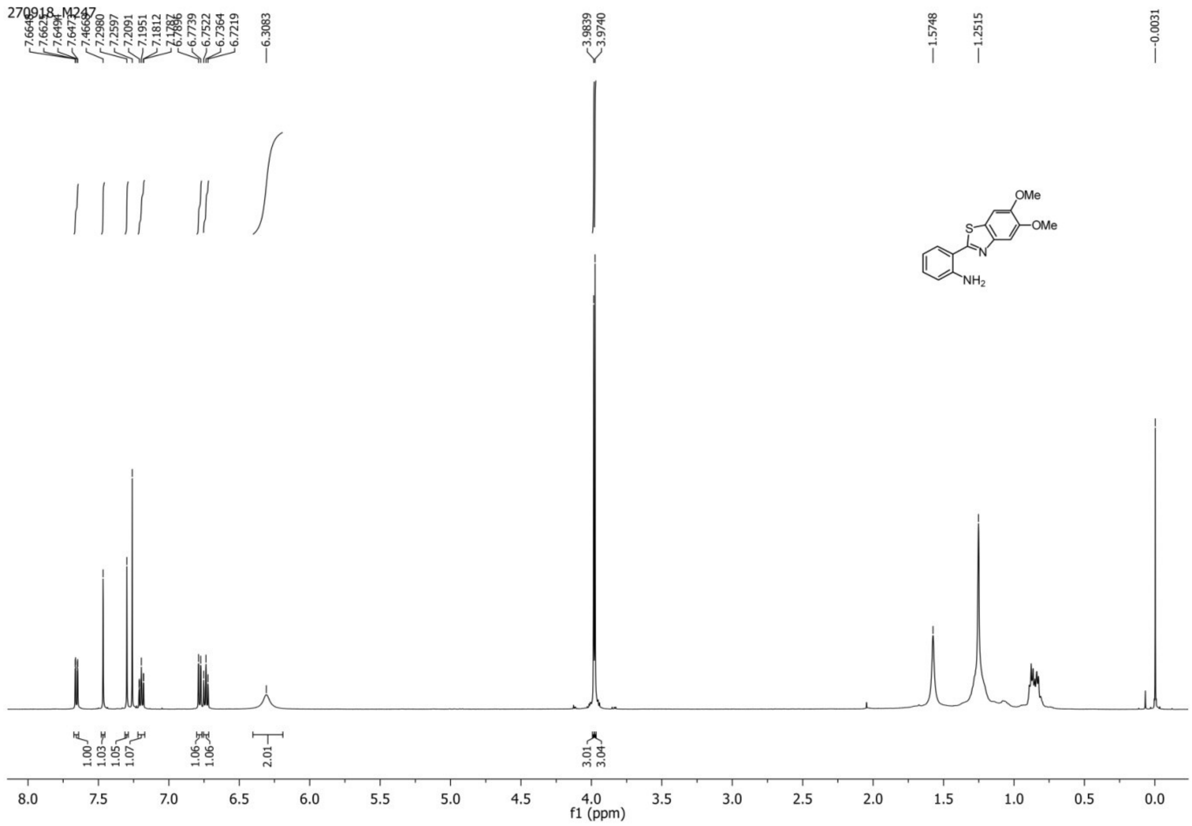


Figure S11. ^{1}H-NMR spectrum of **1A** in $CDCl_3$.

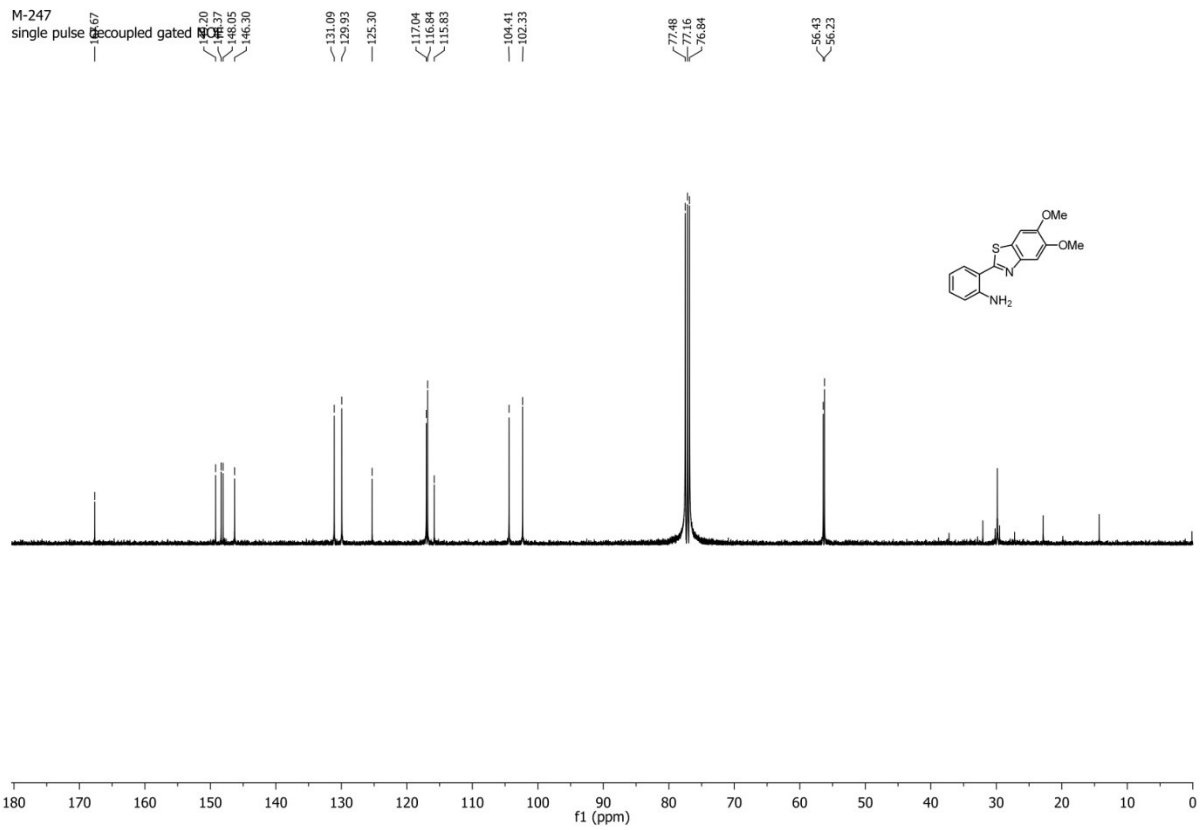


Figure S12. ^{13}C-NMR spectrum of **1A** in $CDCl_3$.

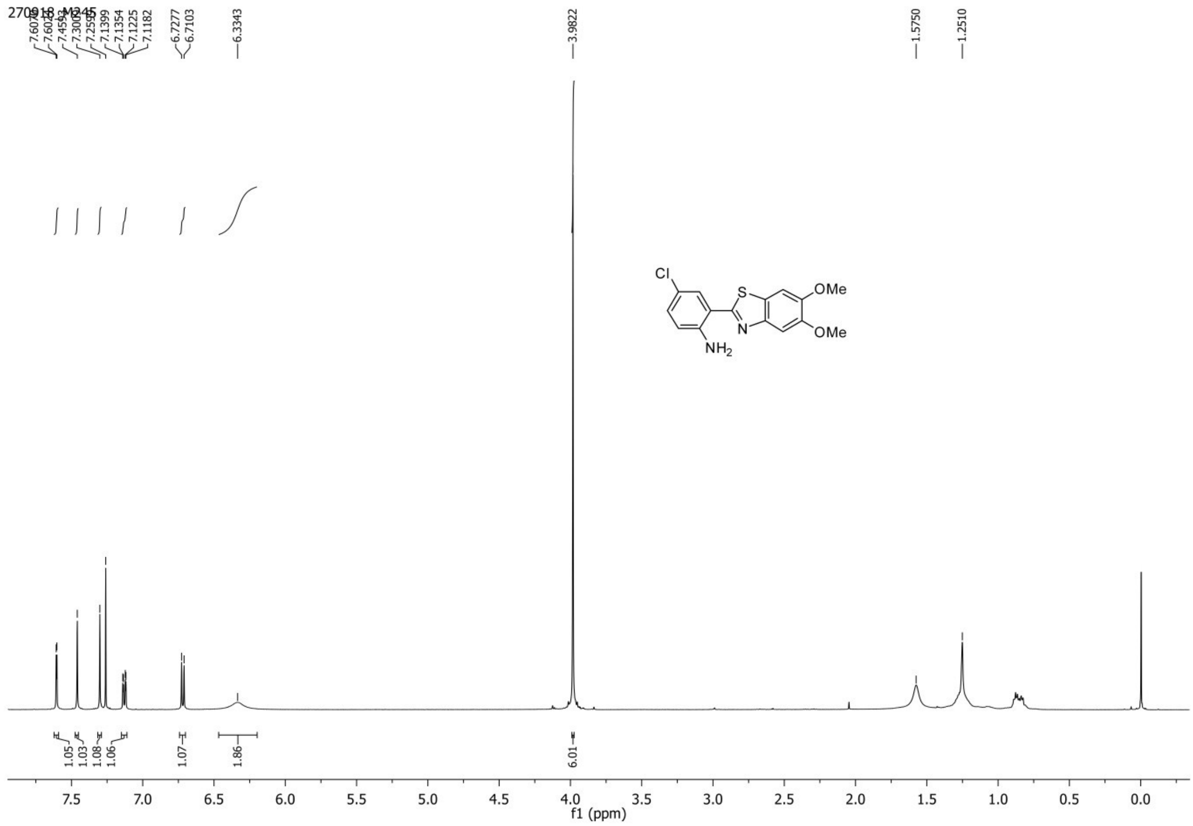


Figure S13. ^{1}H-NMR spectrum of **2A** in $CDCl_3$.

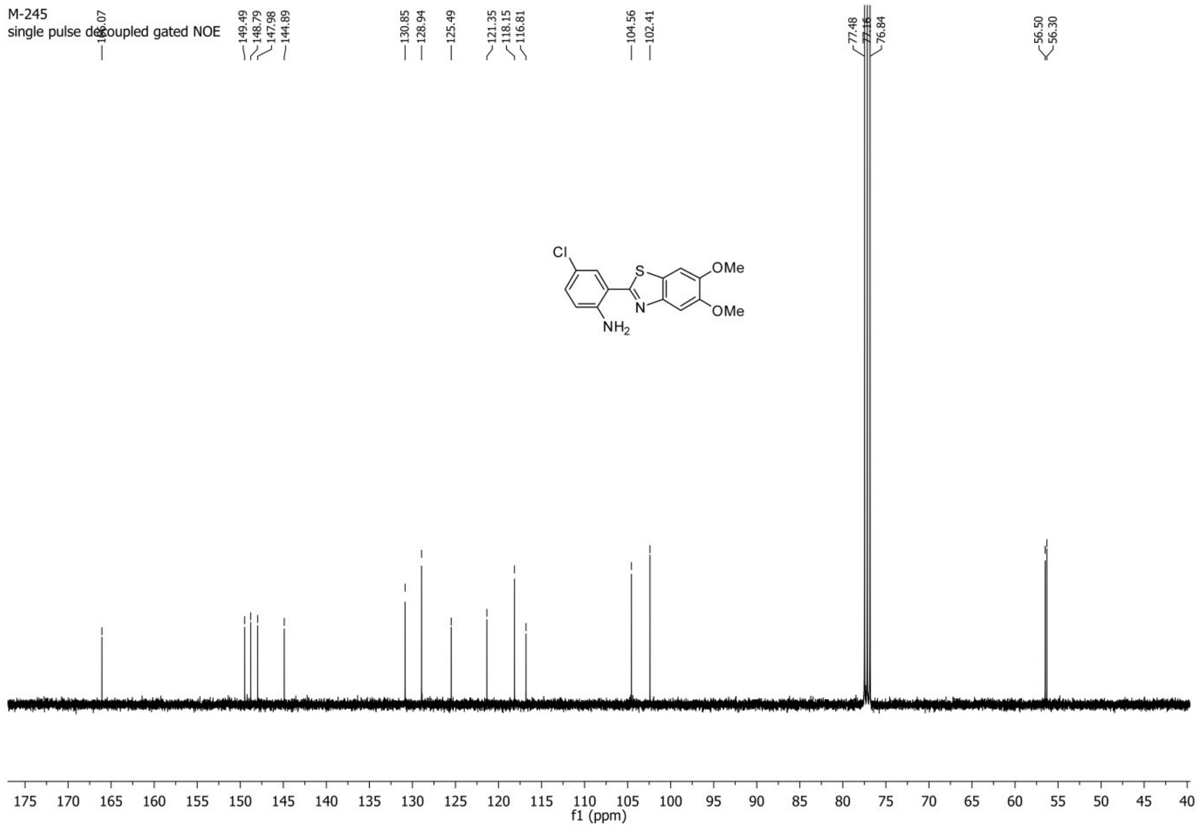


Figure S14. ^{13}C-NMR spectrum of **2A** in $CDCl_3$.

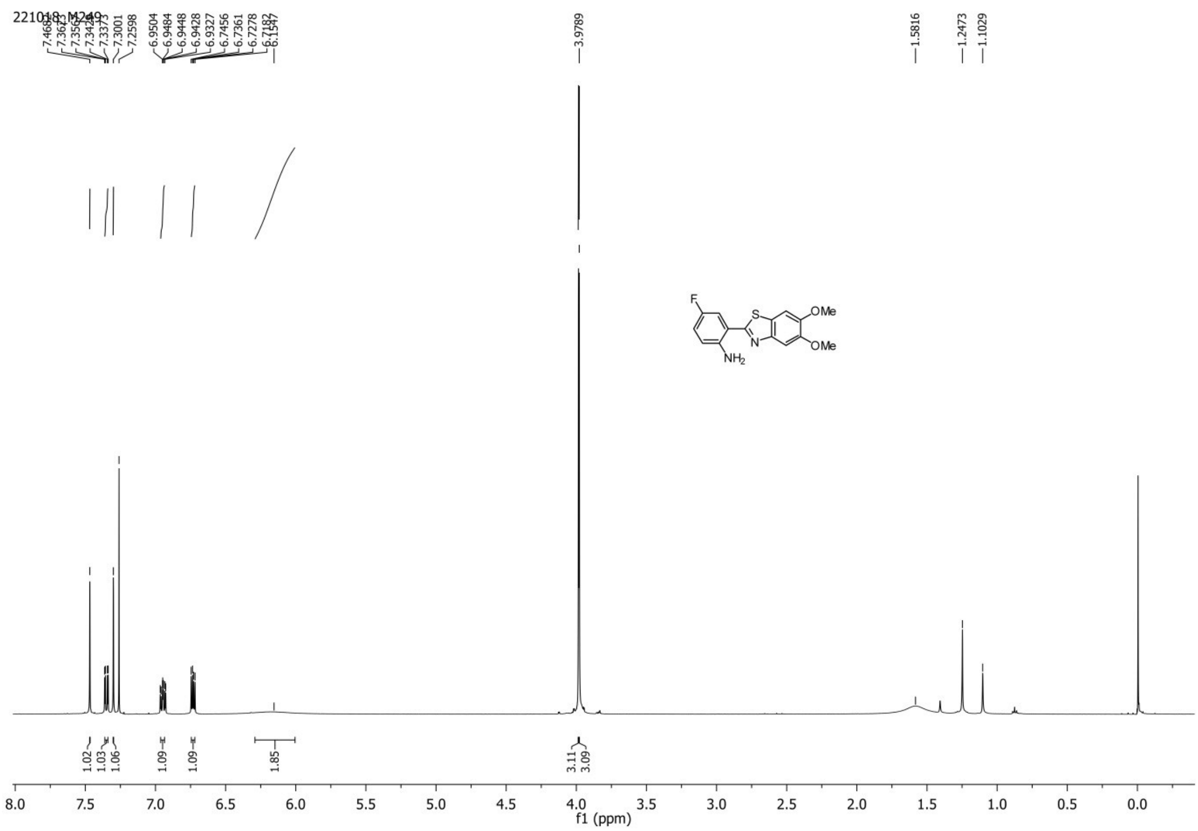


Figure S15. ^{1}H-NMR spectrum of **3A** in $CDCl_3$.

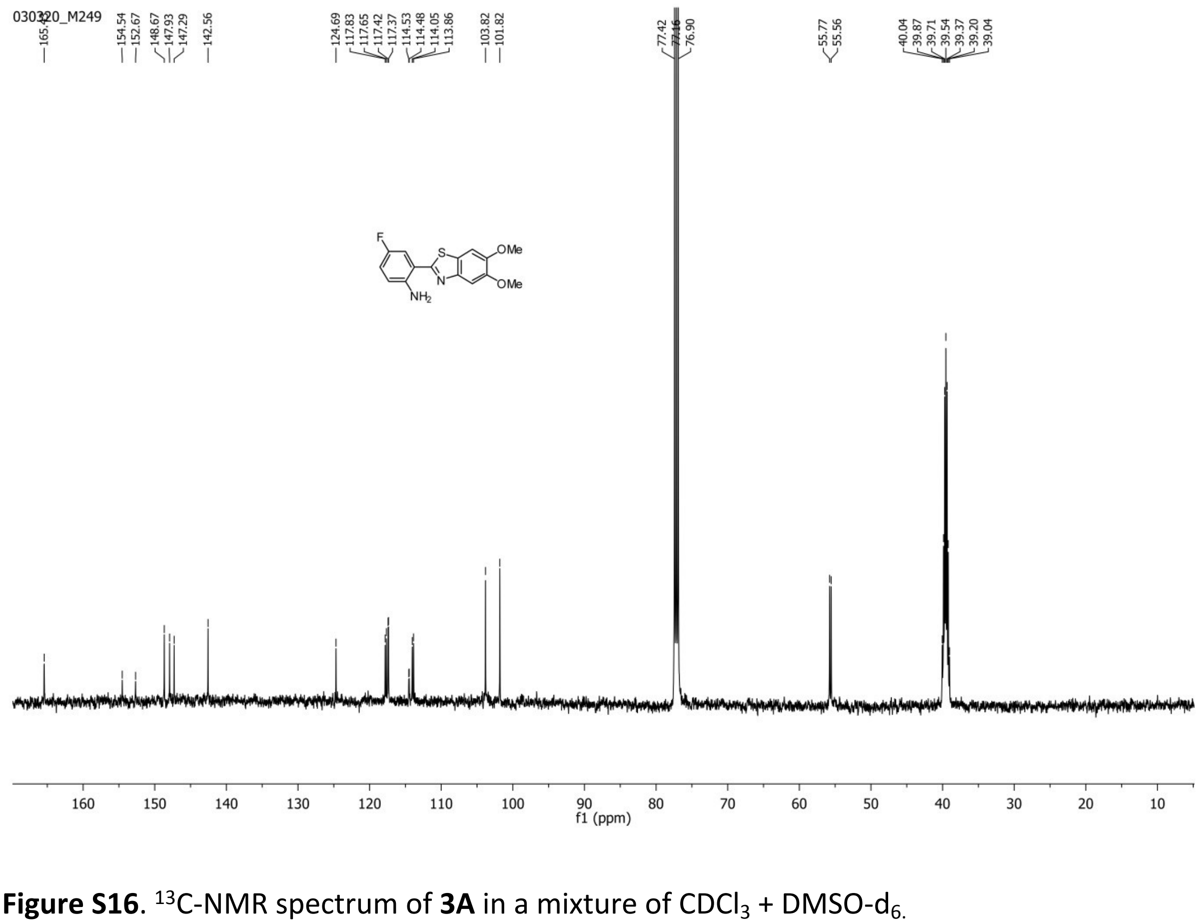


Figure S16. ^{13}C-NMR spectrum of **3A** in a mixture of $CDCl_3$ + DMSO-d_6.

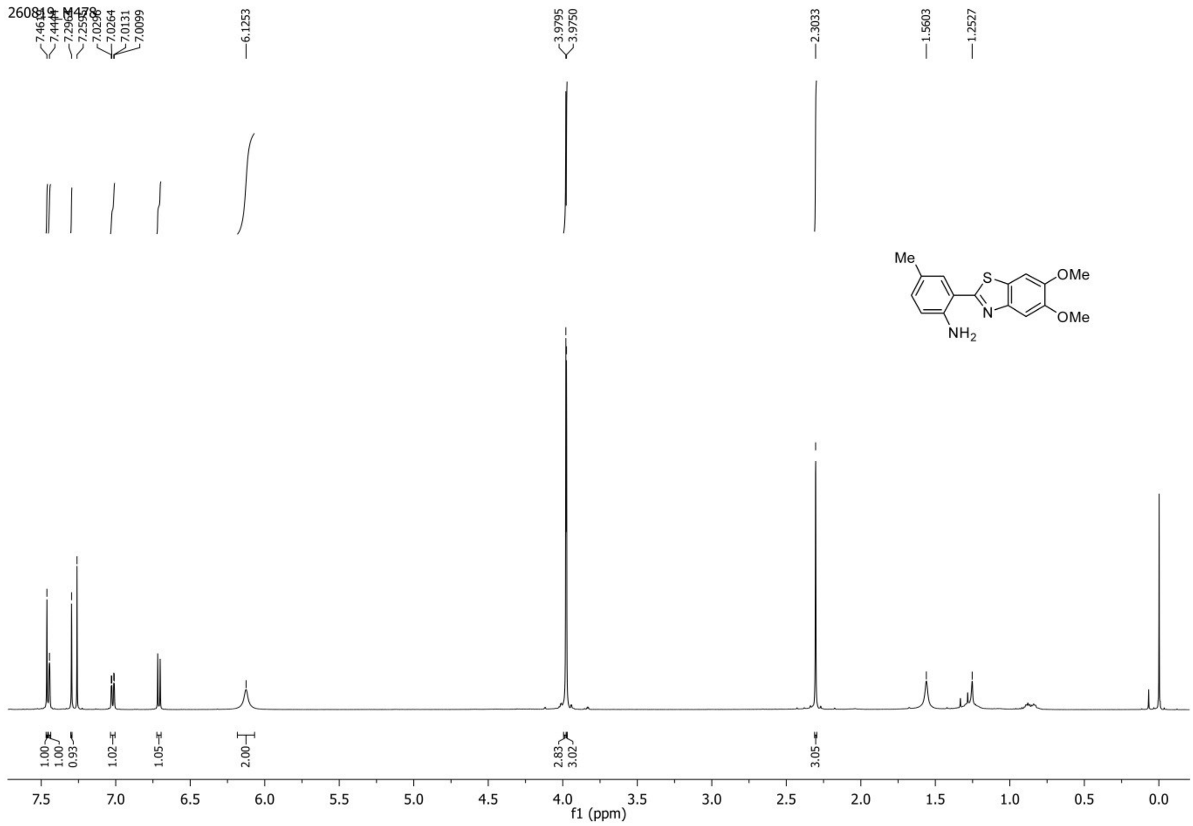


Figure S17. ^{1}H-NMR spectrum of **4A** in $CDCl_3$.

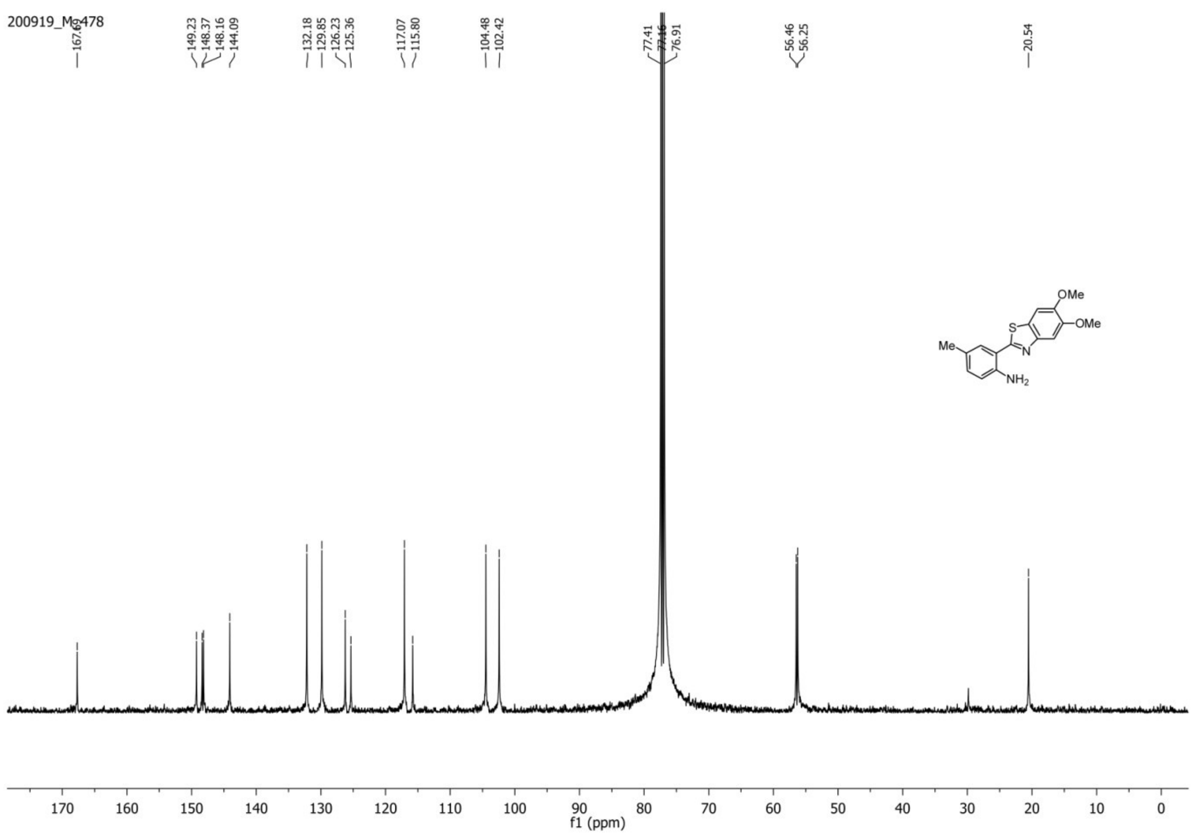


Figure S18. ^{13}C-NMR spectrum of **4A** in $CDCl_3$.

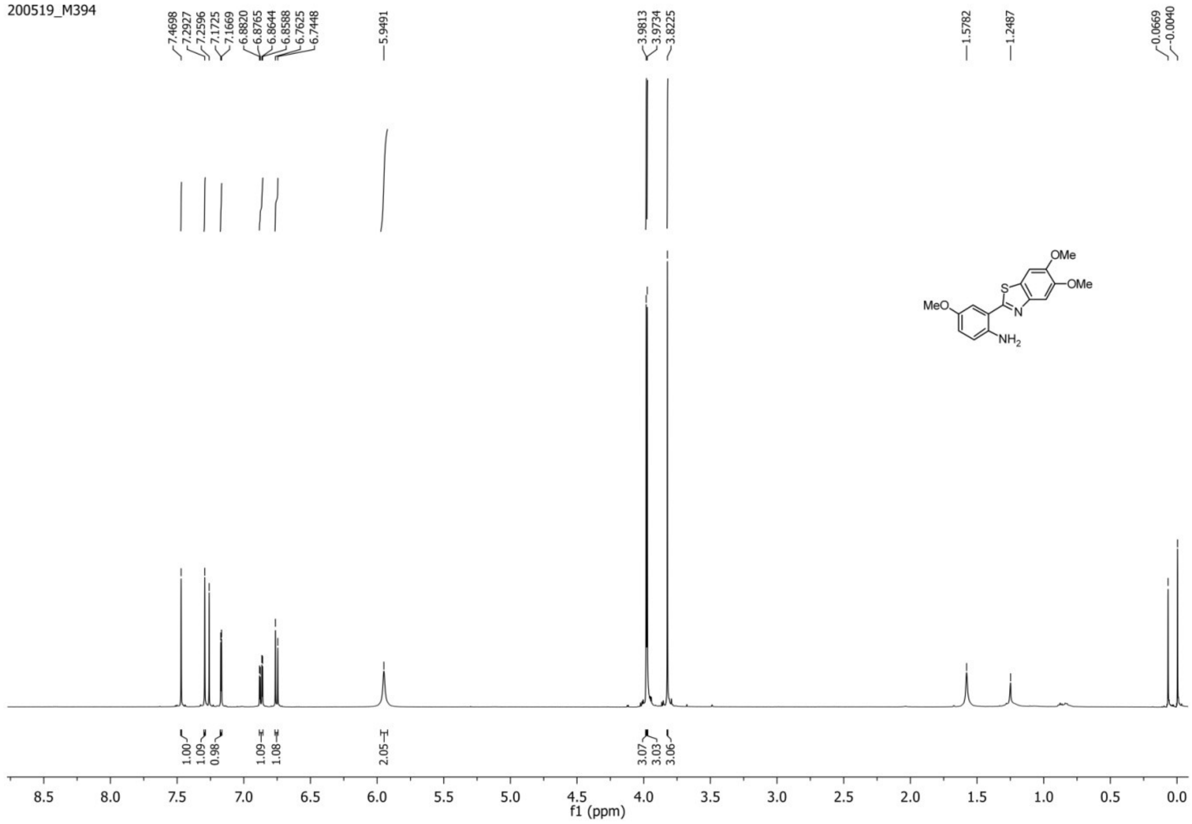


Figure S19. ^{1}H-NMR spectrum of **5A** in $CDCl_3$.

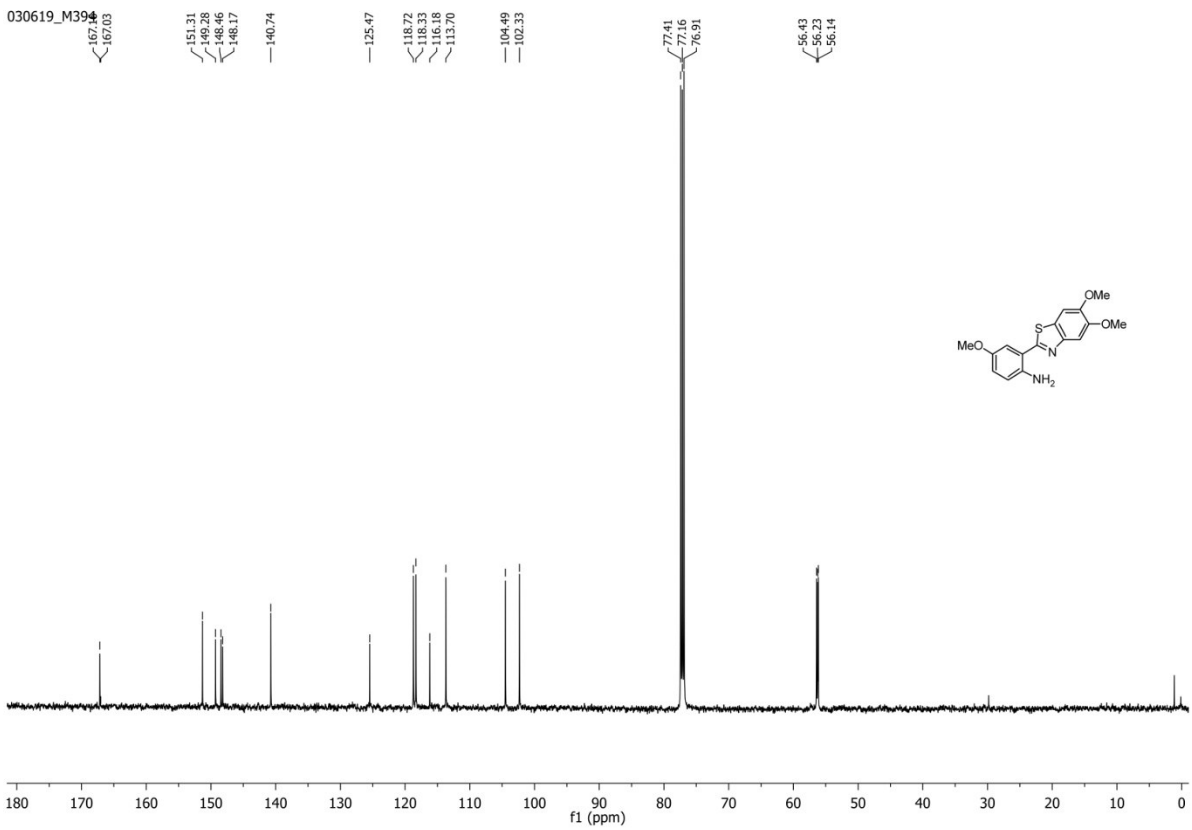


Figure S20. ^{13}C-NMR spectrum of **5A** in $CDCl_3$.

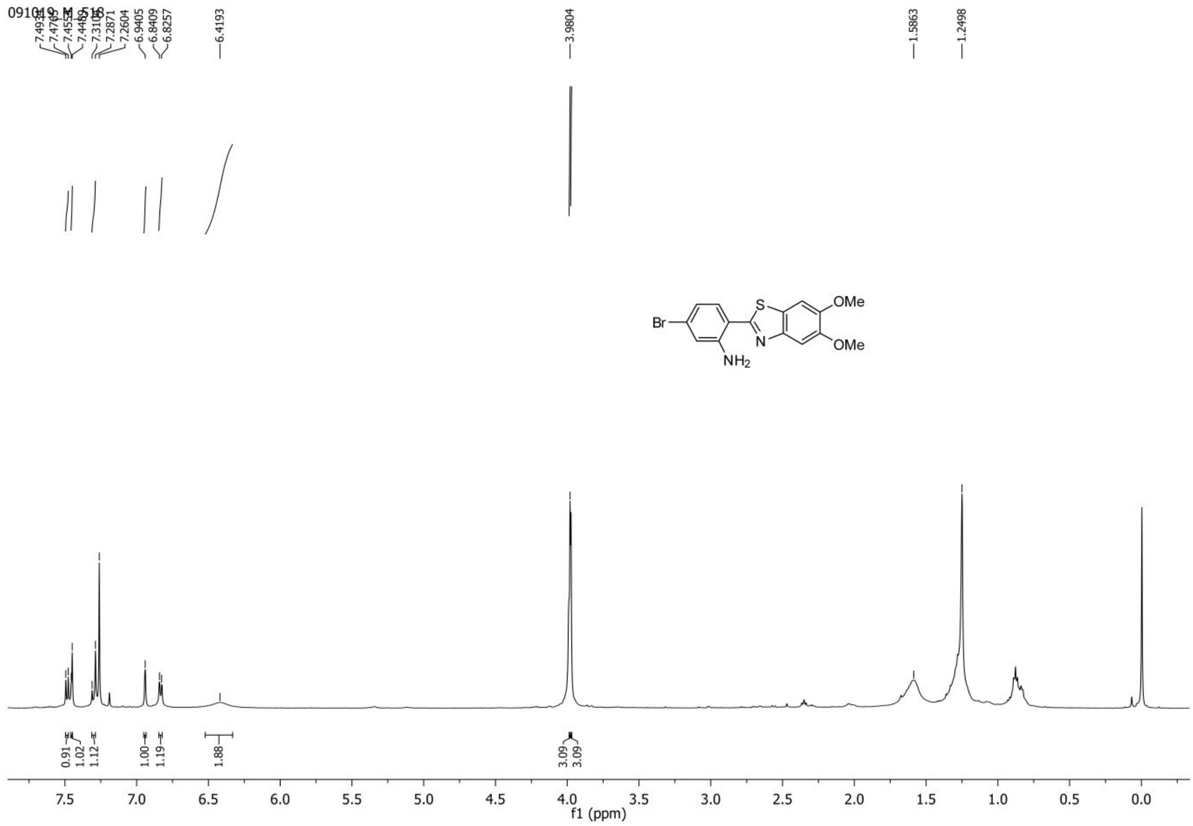


Figure S21. ^{1}H-NMR spectrum of **6A** in $CDCl_3$.

It is mentioned that the ^{13}C-NMR spectrum of **6A** could not be recorded due to solubility problem in $CDCl_3$ as well as DMSO-d_6.

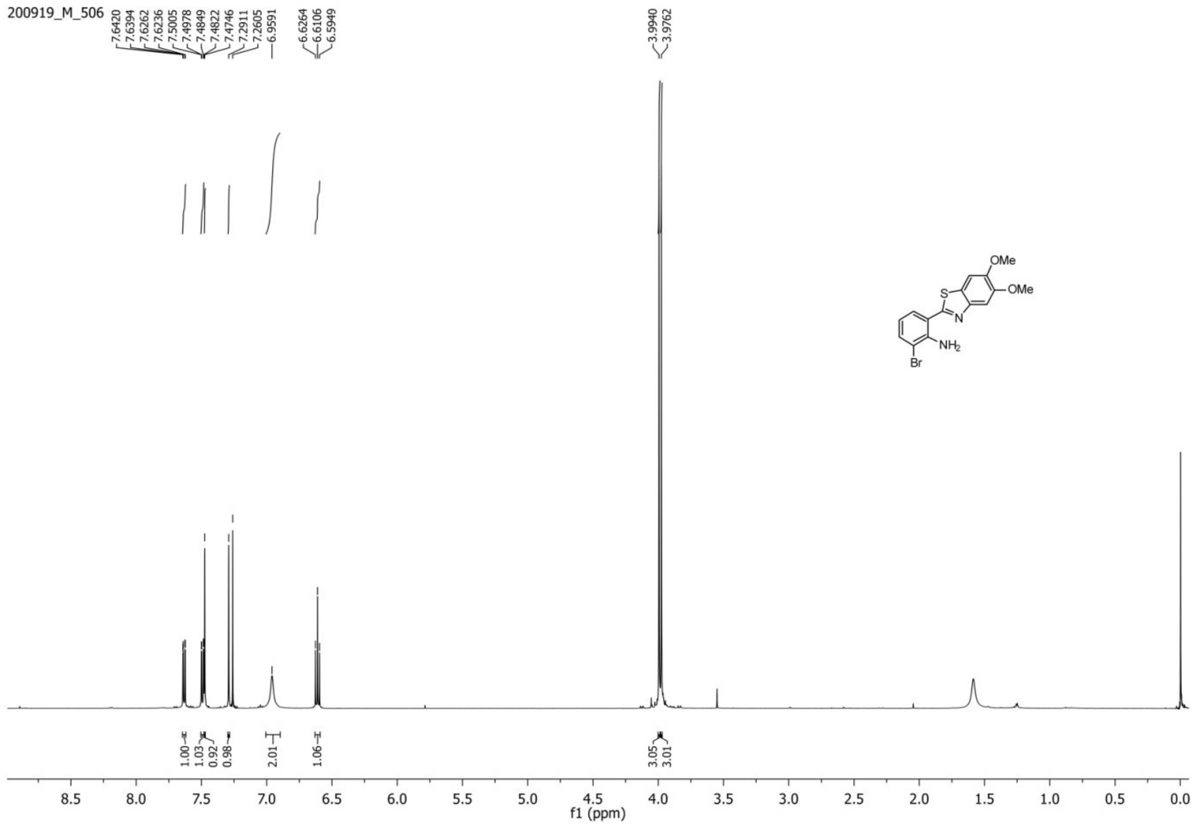


Figure S22. ^{1}H-NMR spectrum of **7A** in $CDCl_3$.

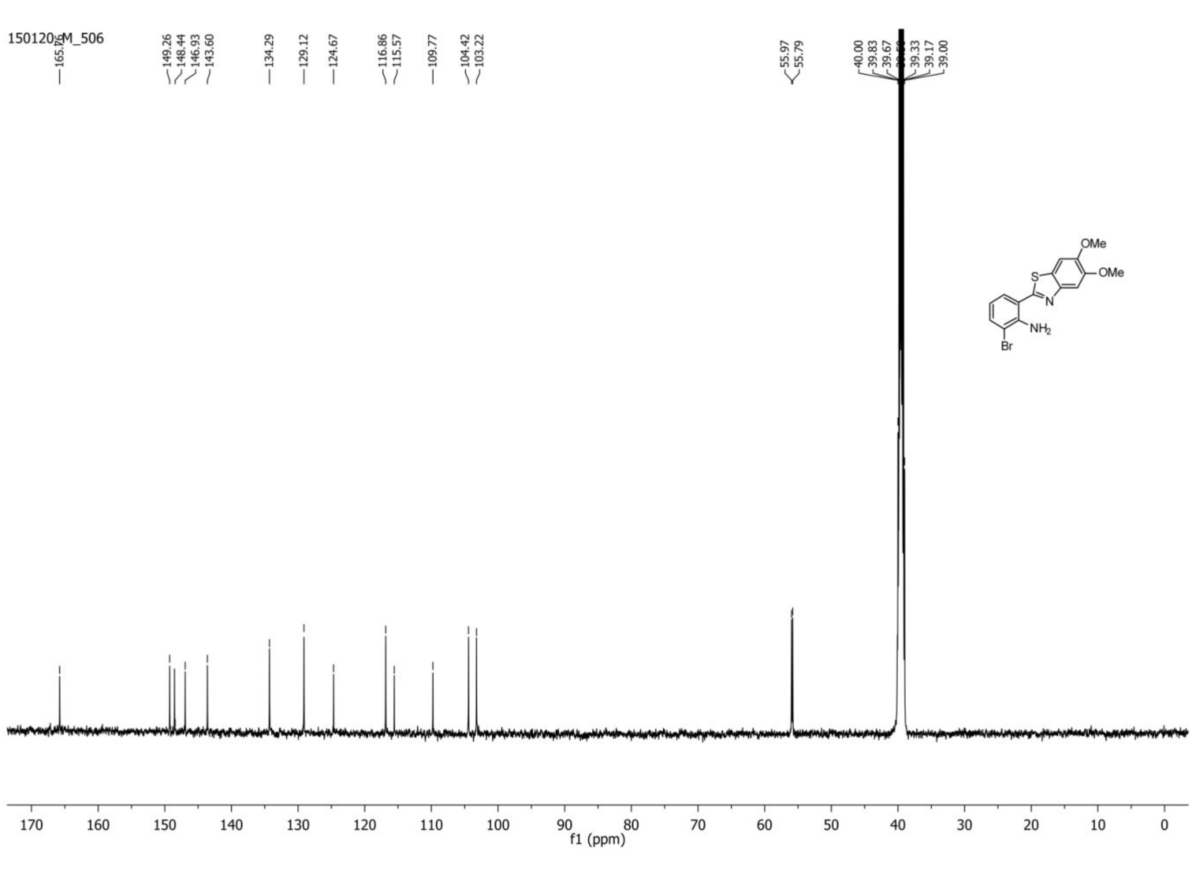


Figure S23. ^{13}C-NMR spectrum of **7A** in DMSO-d_6.

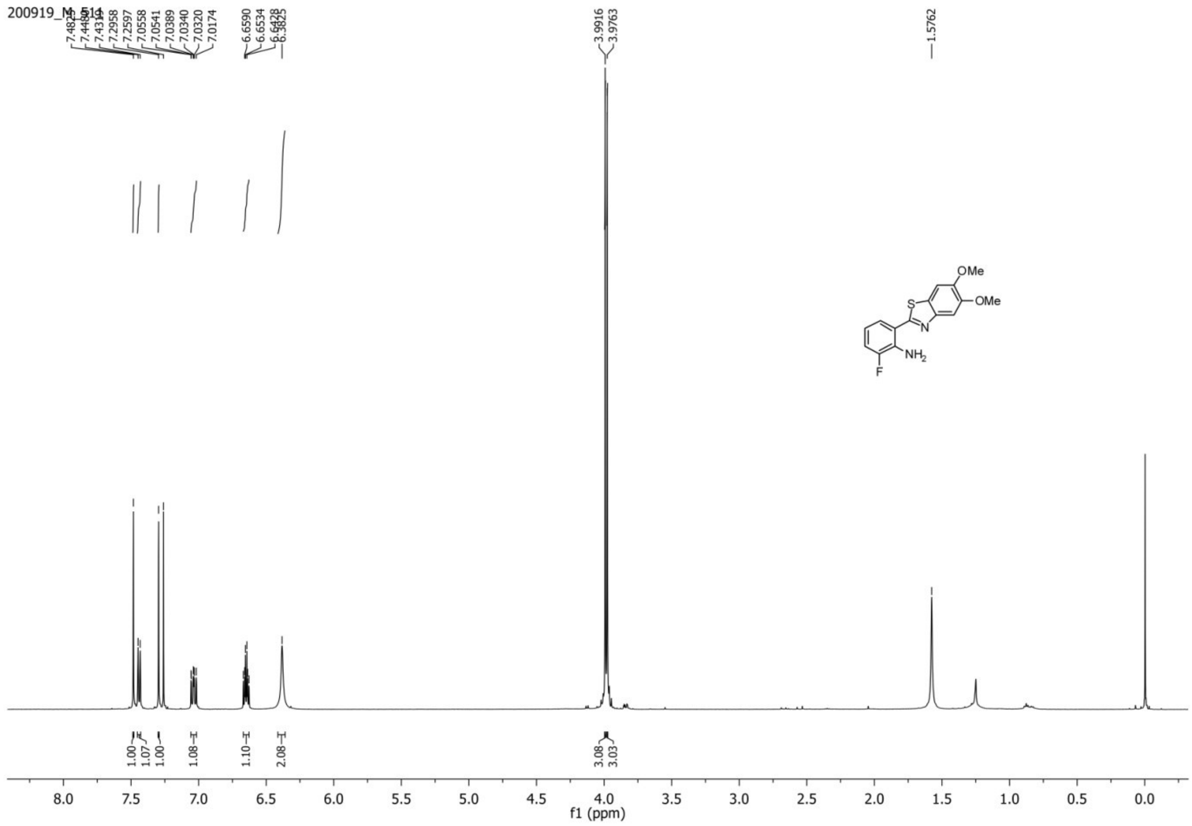


Figure S24. ^{1}H-NMR spectrum of **8A** in $CDCl_3$.

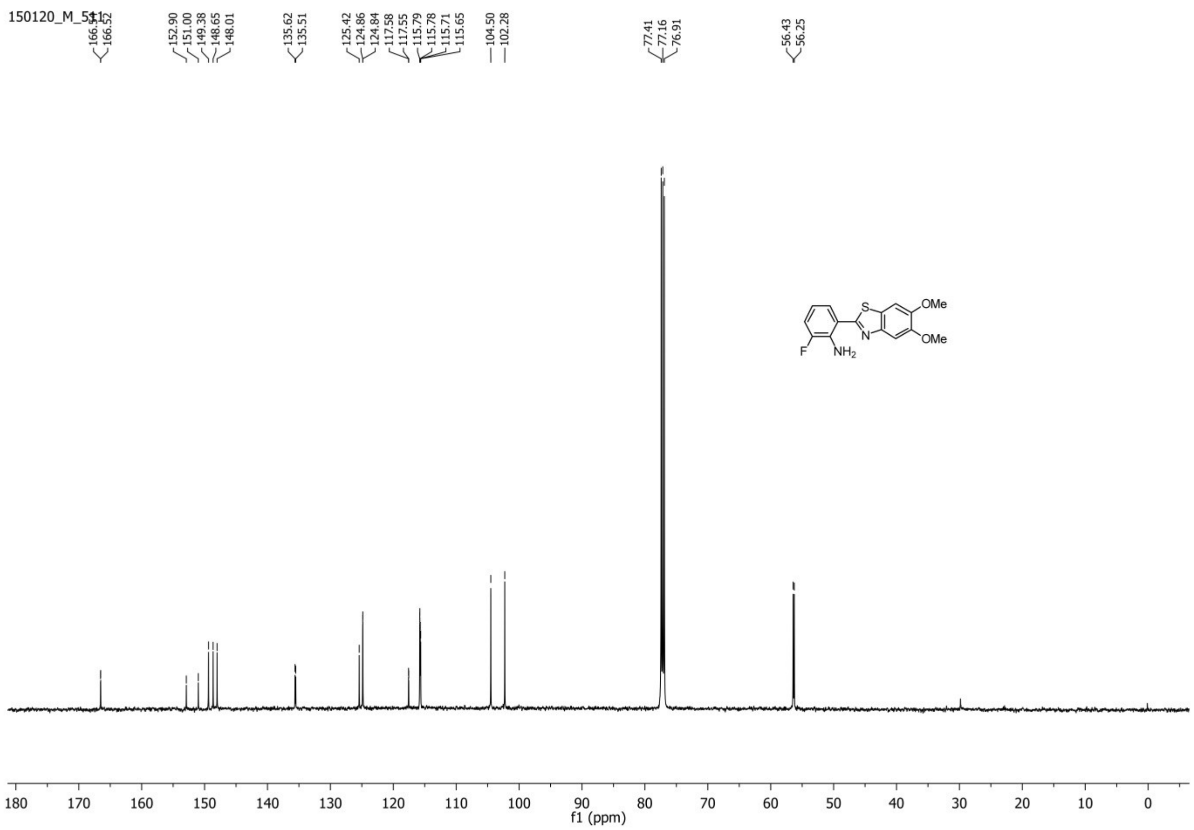


Figure S25. ^{13}C-NMR spectrum of **8A** in $CDCl_3$.

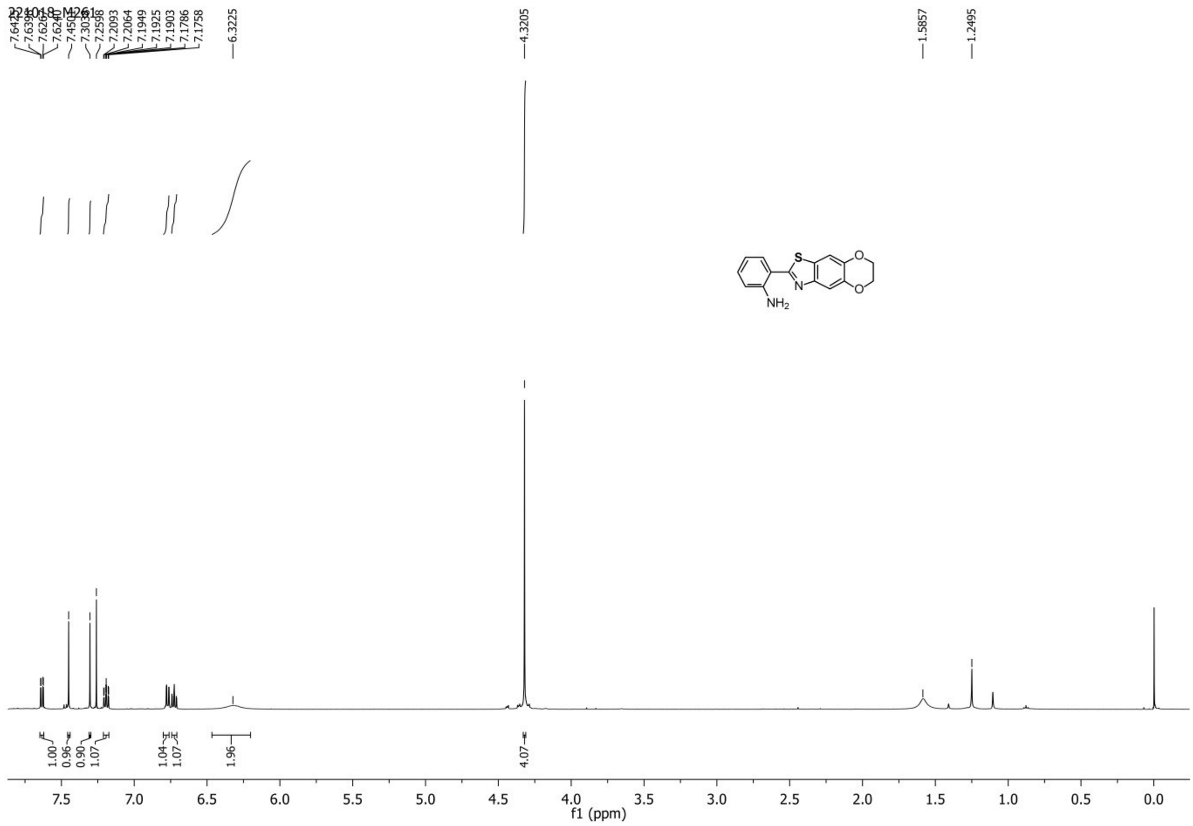


Figure S26. ^{1}H-NMR spectrum of **1D** in $CDCl_3$.

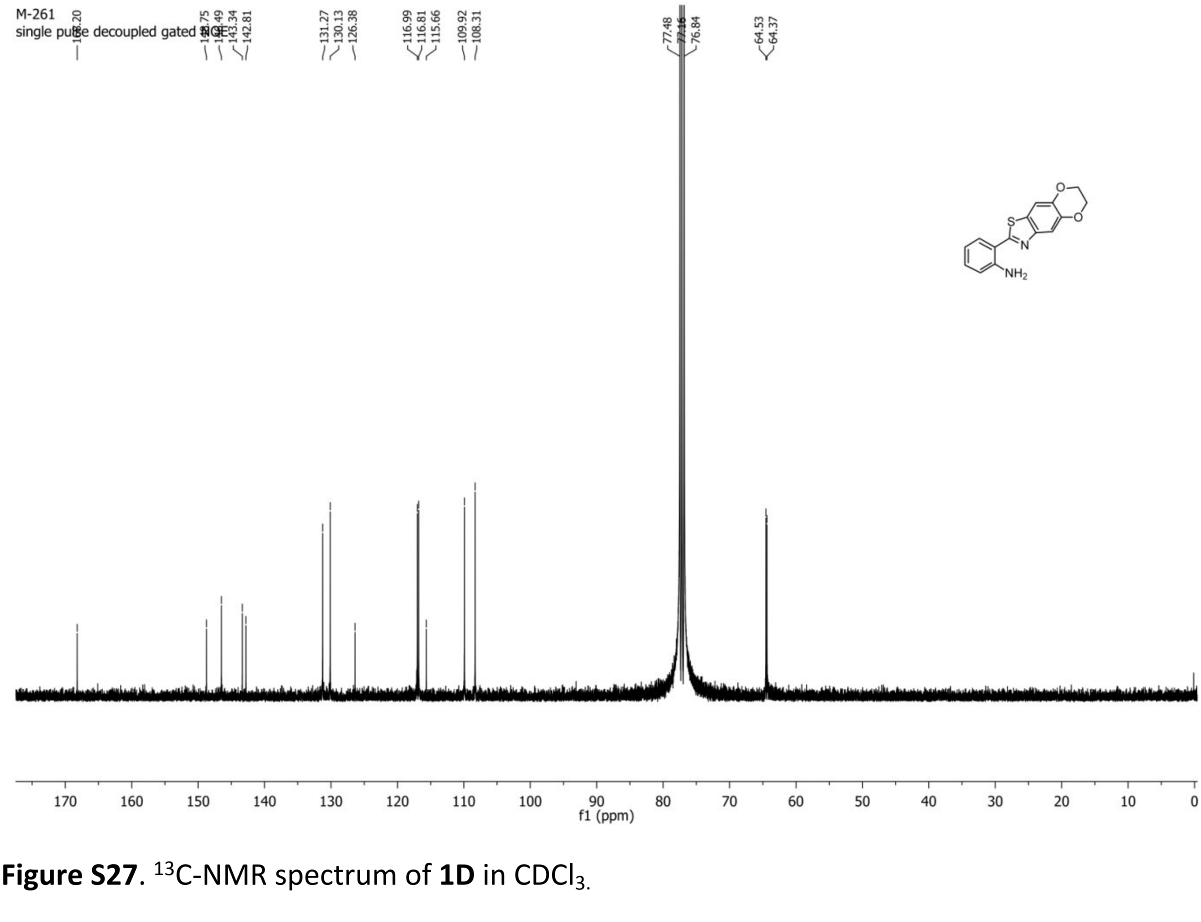


Figure S27. ^{13}C-NMR spectrum of **1D** in $CDCl_3$.

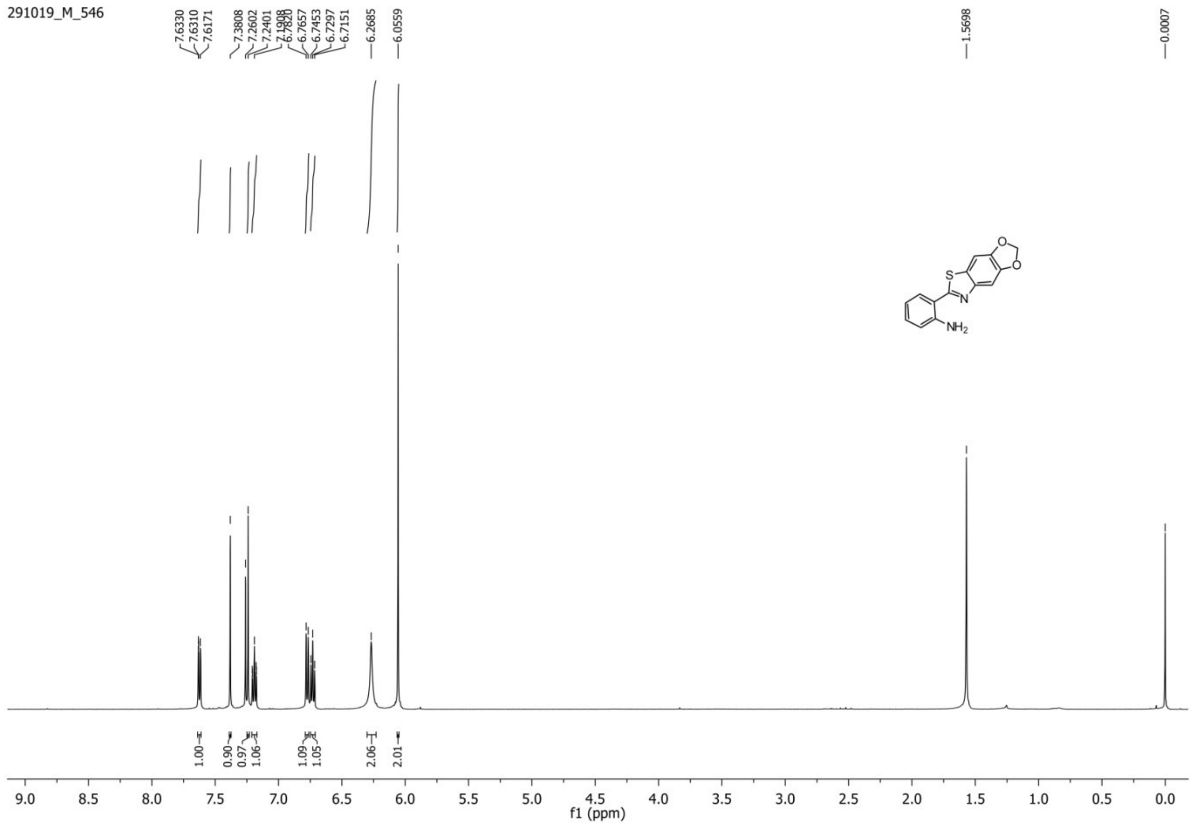


Figure S28. ^{1}H-NMR spectrum of **1E** in $CDCl_3$.

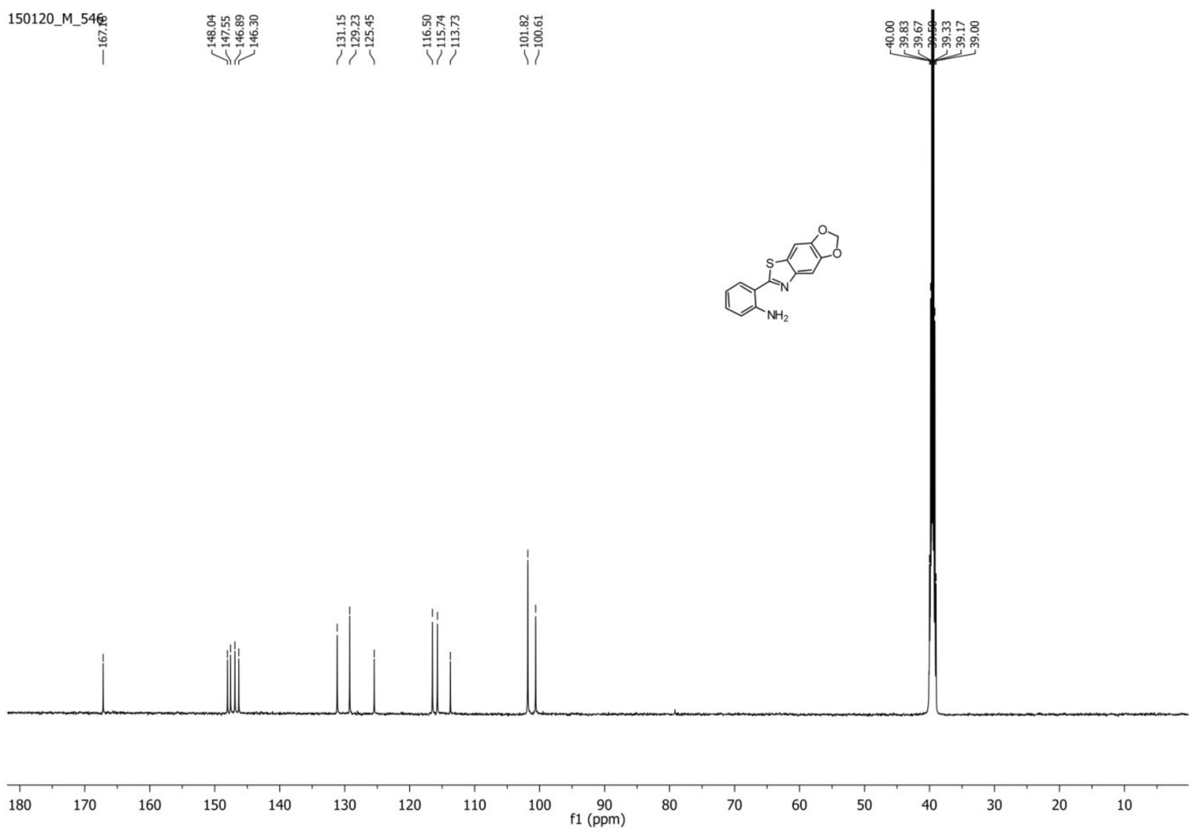


Figure S29. ^{13}C-NMR spectrum of **1E** in DMSO-d_6.

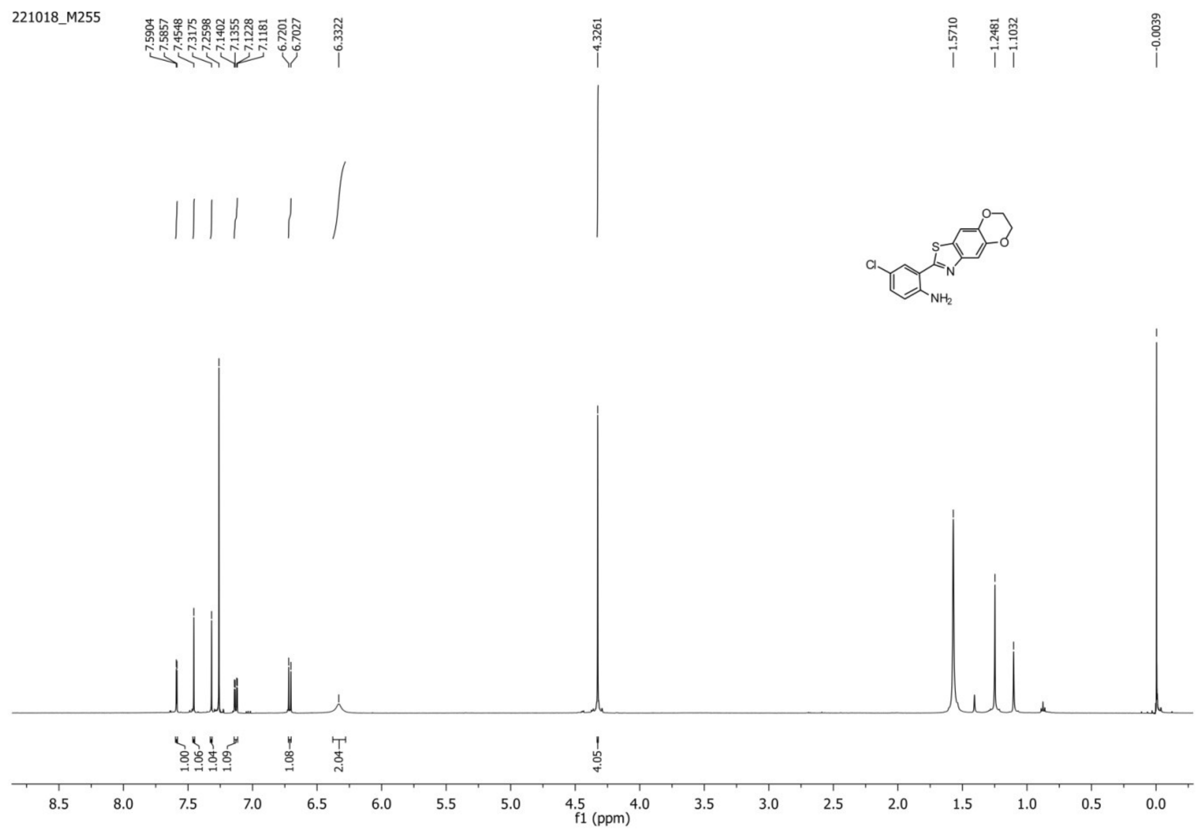


Figure S30. ^{1}H-NMR spectrum of **2D** in $CDCl_3$.

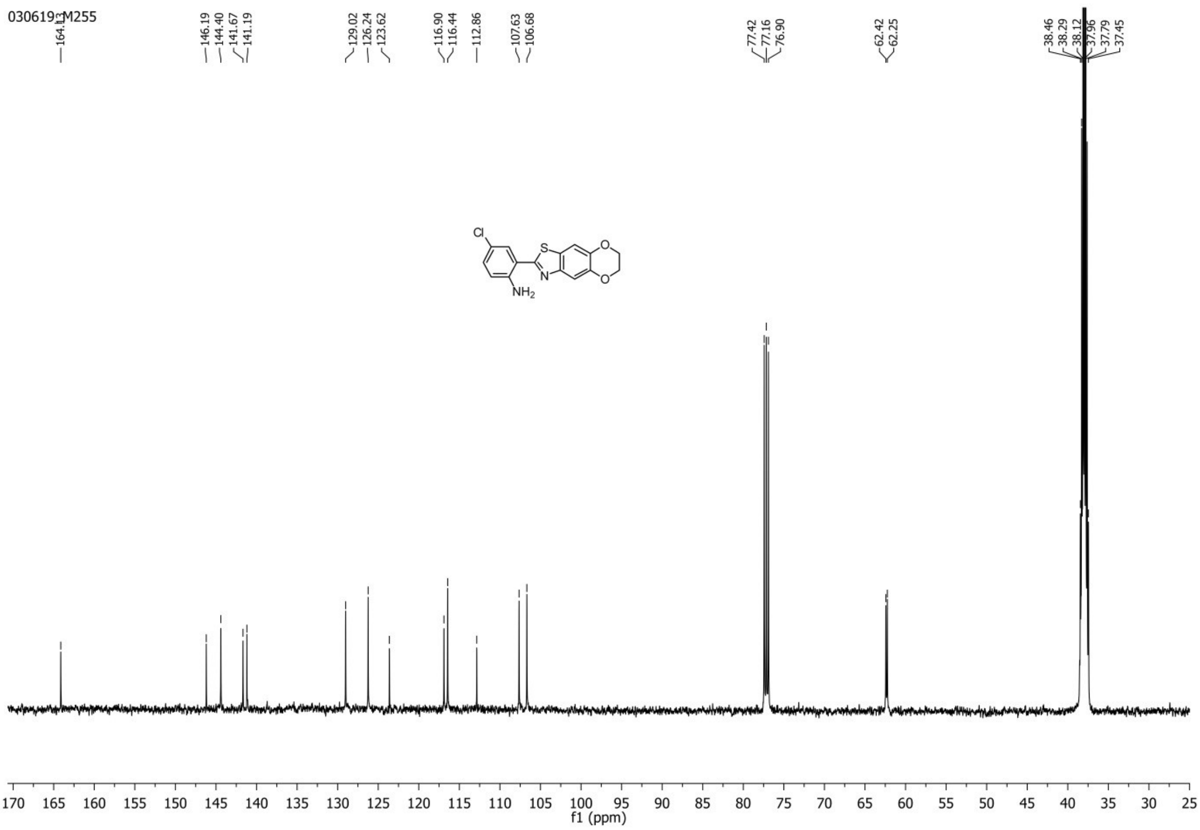


Figure S31. ^{13}C-NMR spectrum of **2D** in $CDCl_3$ + DMSO-d_6.

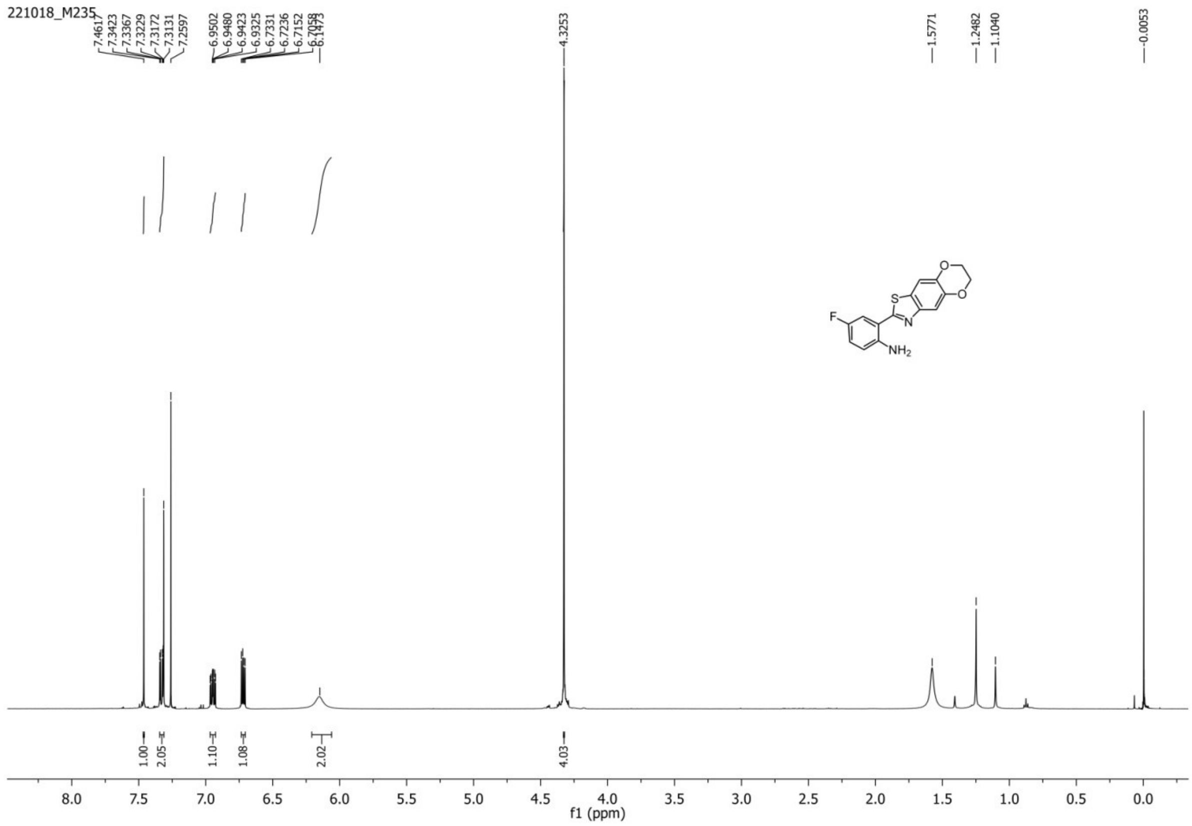


Figure S32. ^{1}H-NMR spectrum of **3D** in $CDCl_3$.

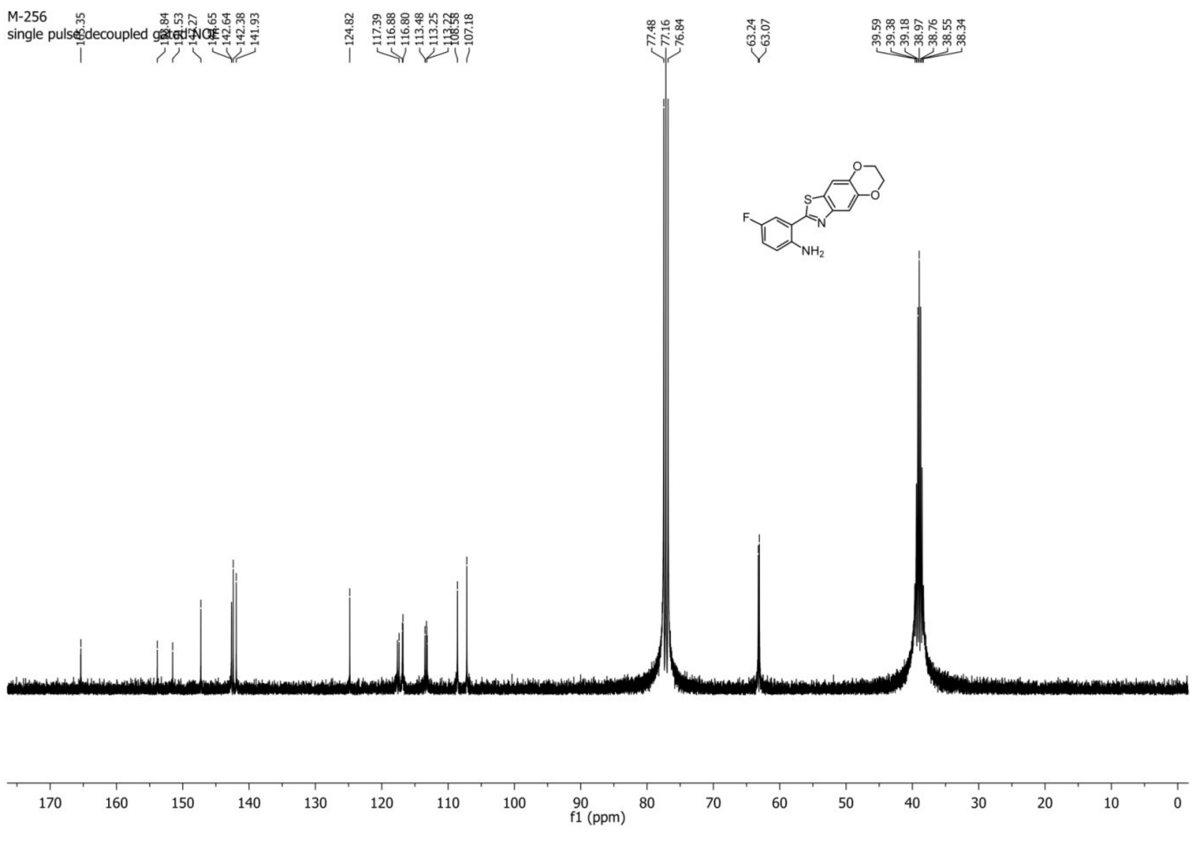


Figure S33. ^{13}C-NMR spectrum of **3D** in $CDCl_3$ + DMSO-d_6.

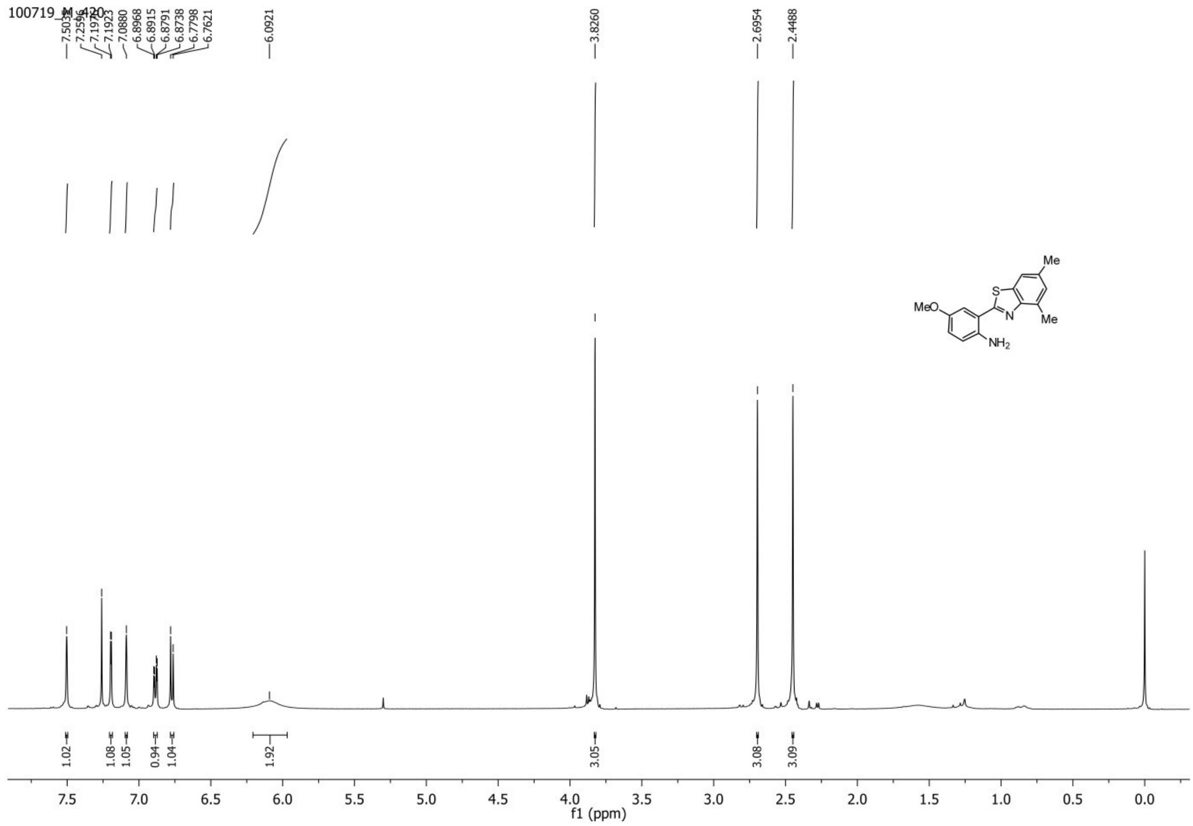


Figure S34. ^{1}H-NMR spectrum of **5B** in $CDCl_3$.

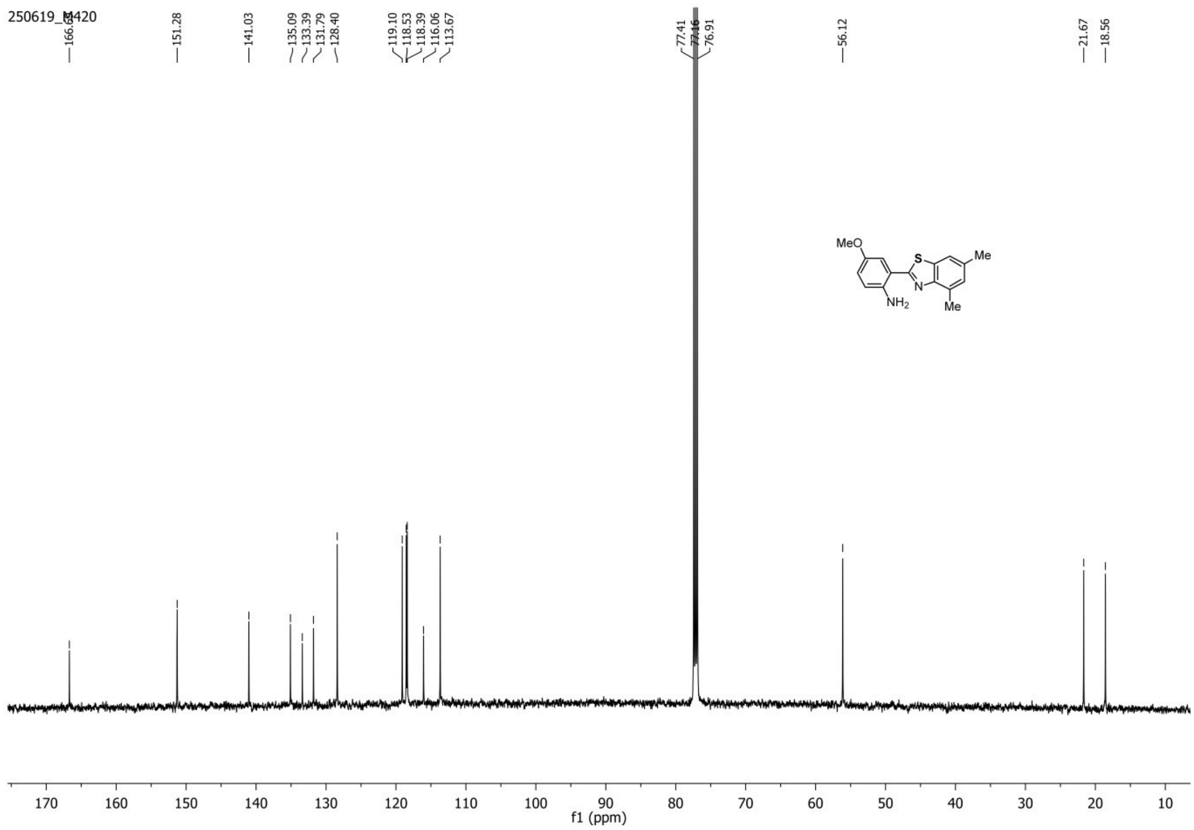


Figure S35. ^{13}C-NMR spectrum of **5B** in $CDCl_3$

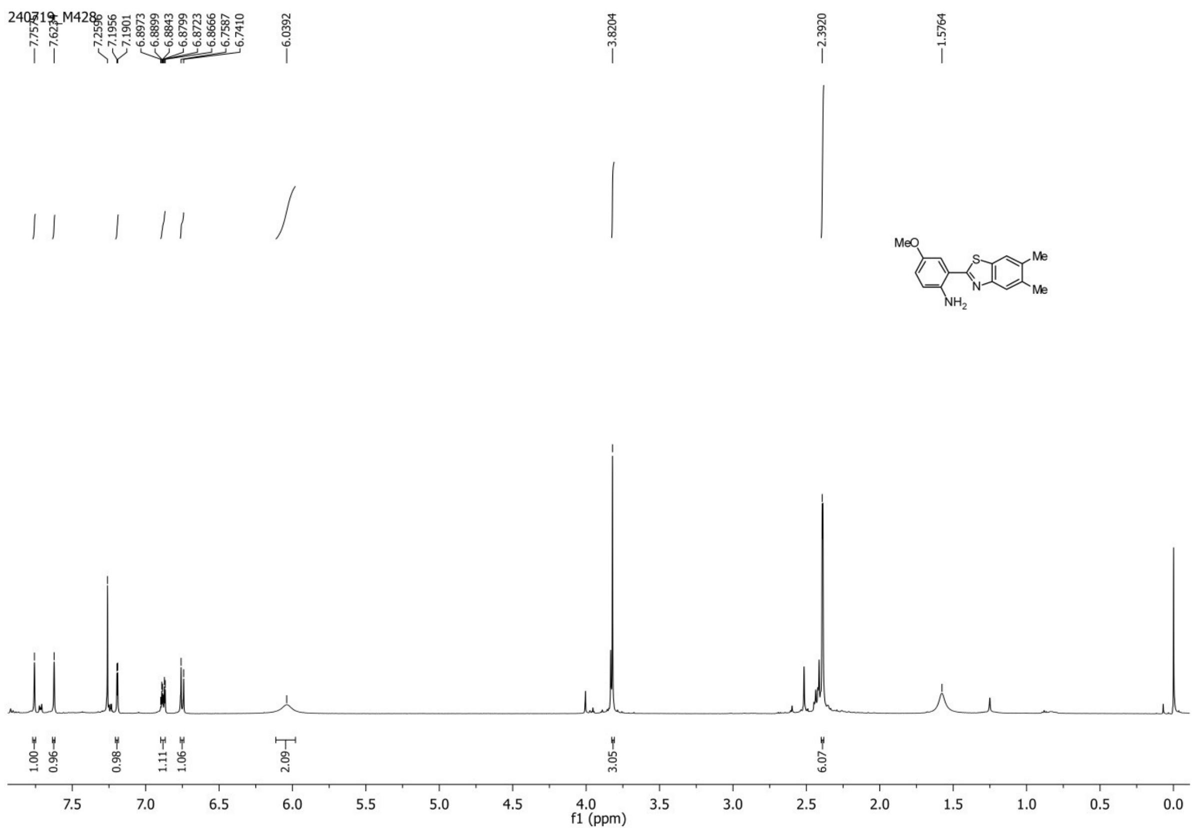


Figure S36. ^{1}H-NMR spectrum of **5C** in $CDCl_3$

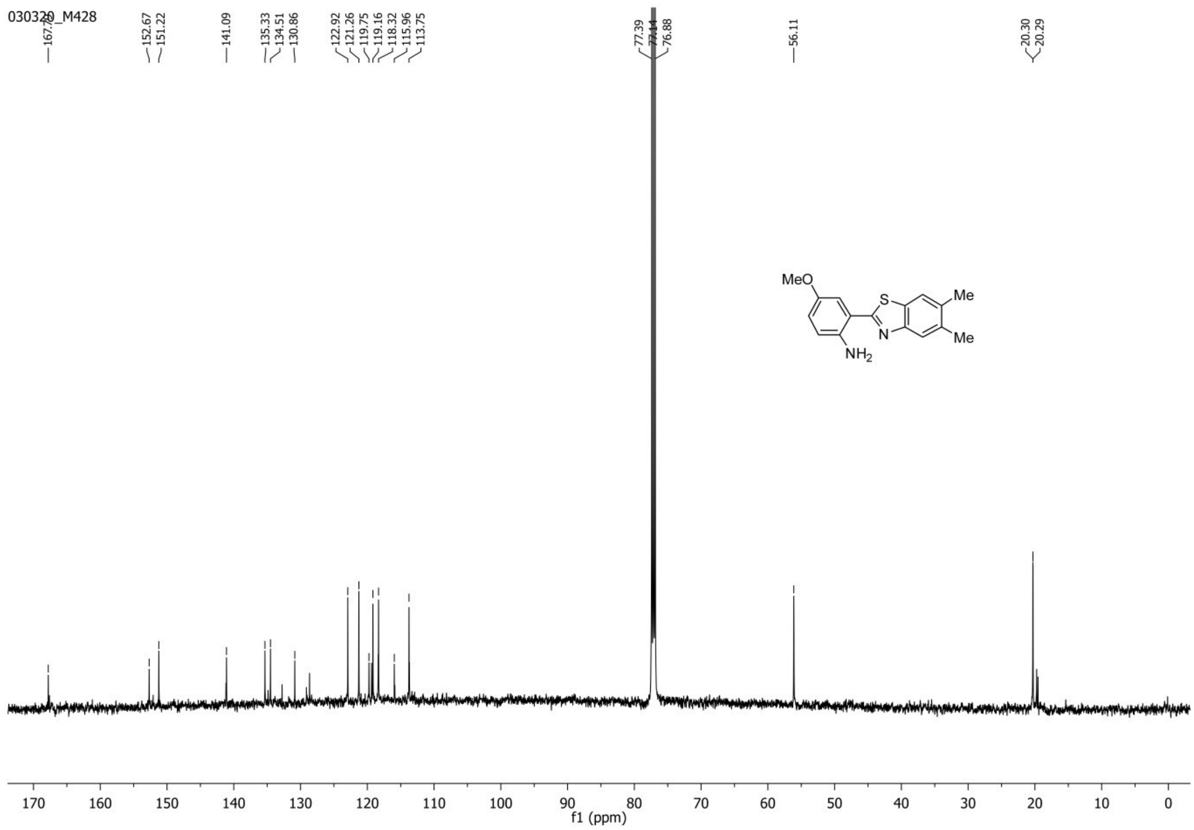


Figure S37. ^{13}C-NMR spectrum of **5C** in $CDCl_3$

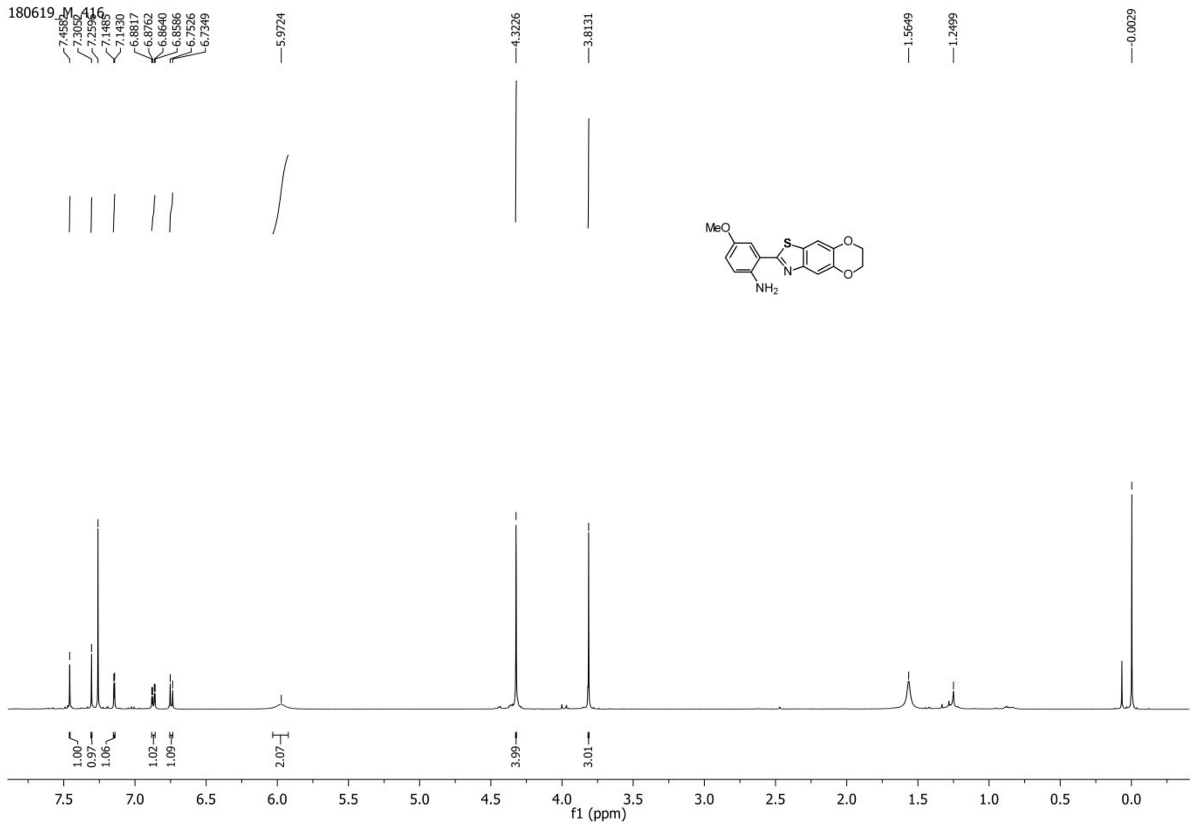


Figure S38. ^{1}H-NMR spectrum of **5D** in $CDCl_3$

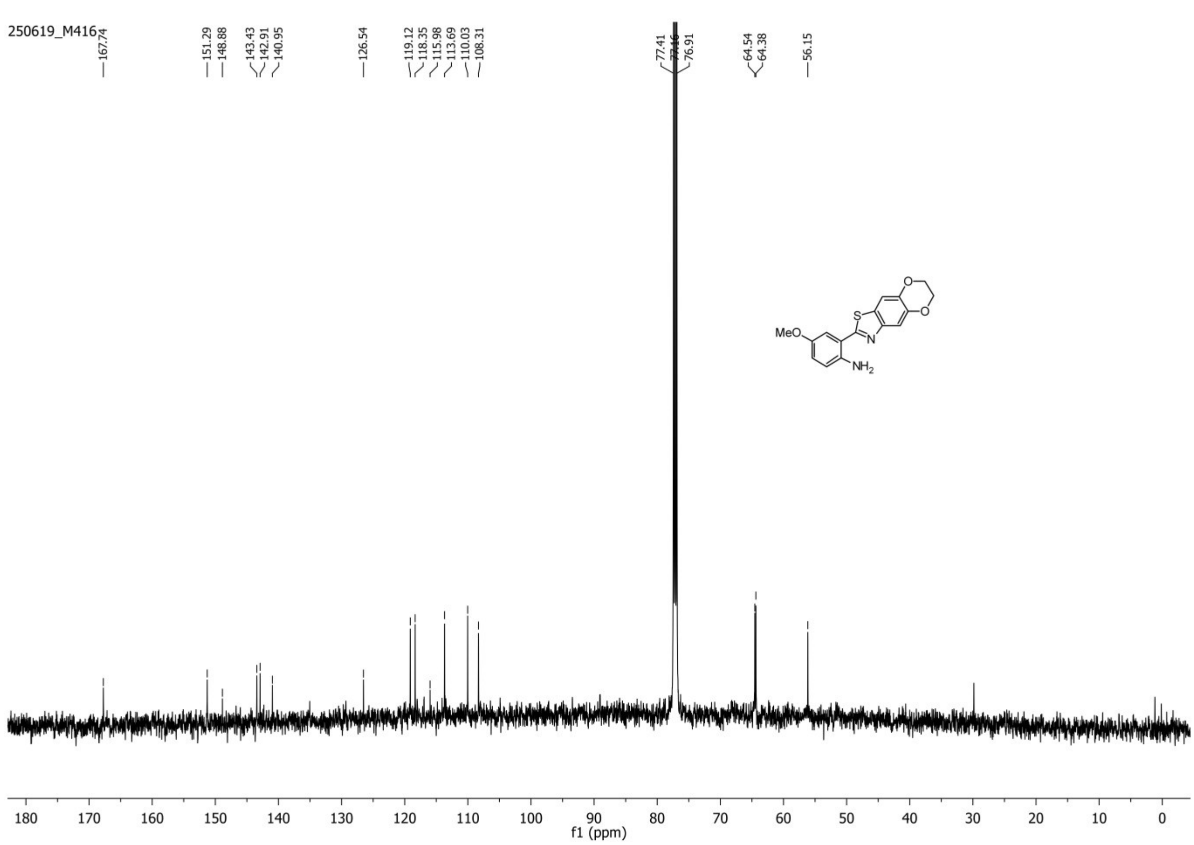


Figure S39. ^{13}C-NMR spectrum of **5D** in $CDCl_3$

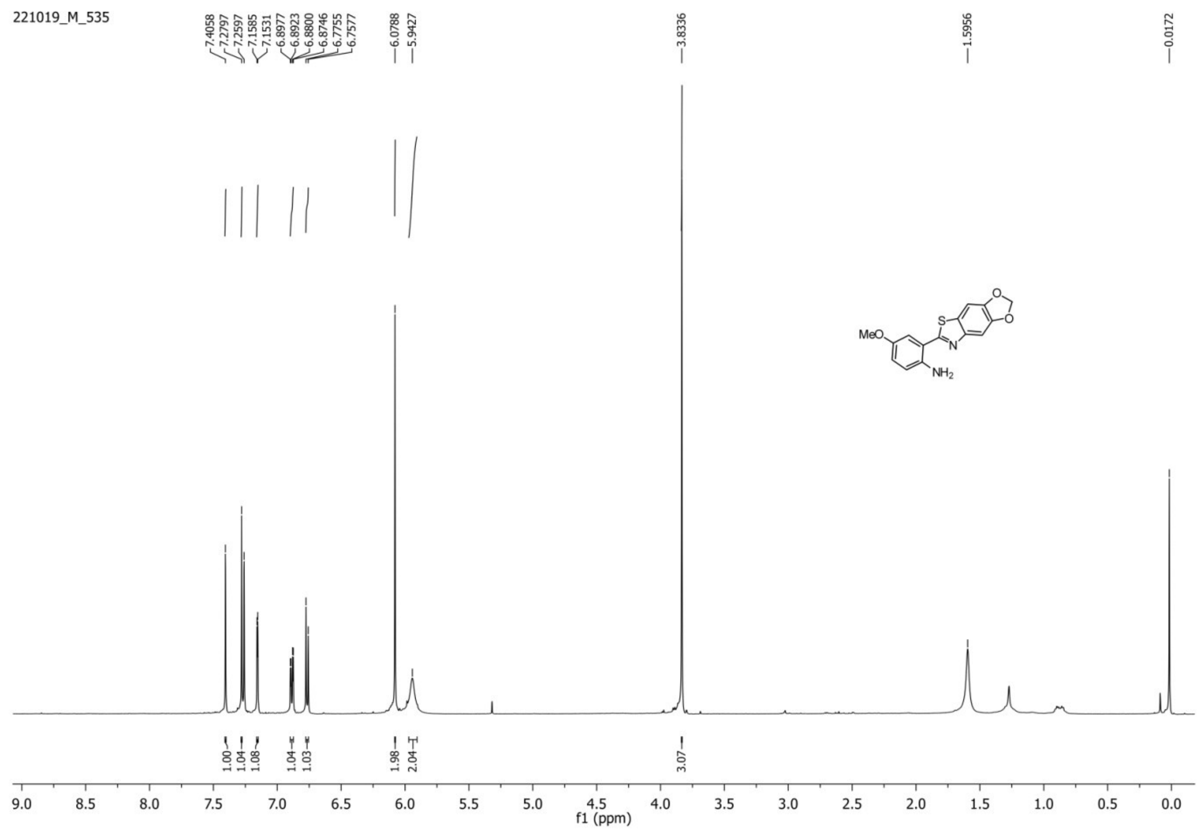


Figure S40. ^{1}H-NMR spectrum of **5E** in $CDCl_3$.

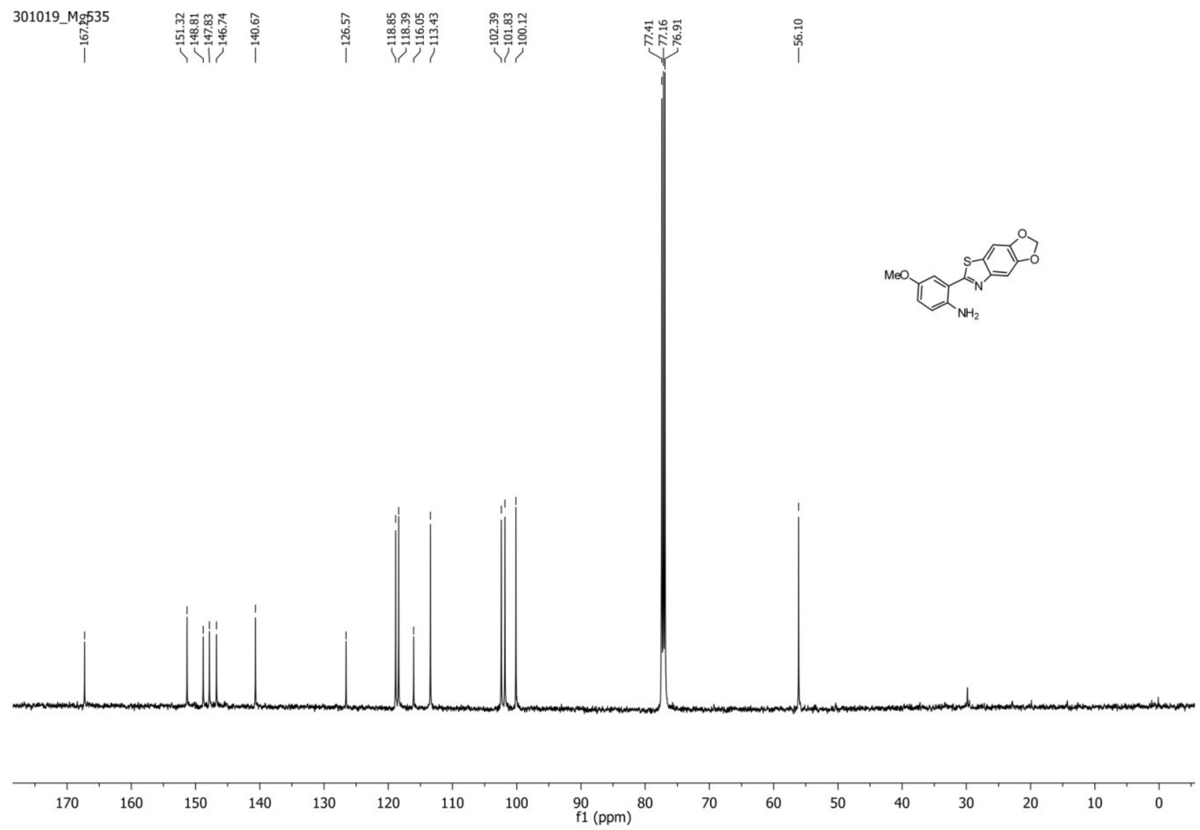


Figure S41. ^{1}H-NMR spectrum of **5E** in $CDCl_3$.

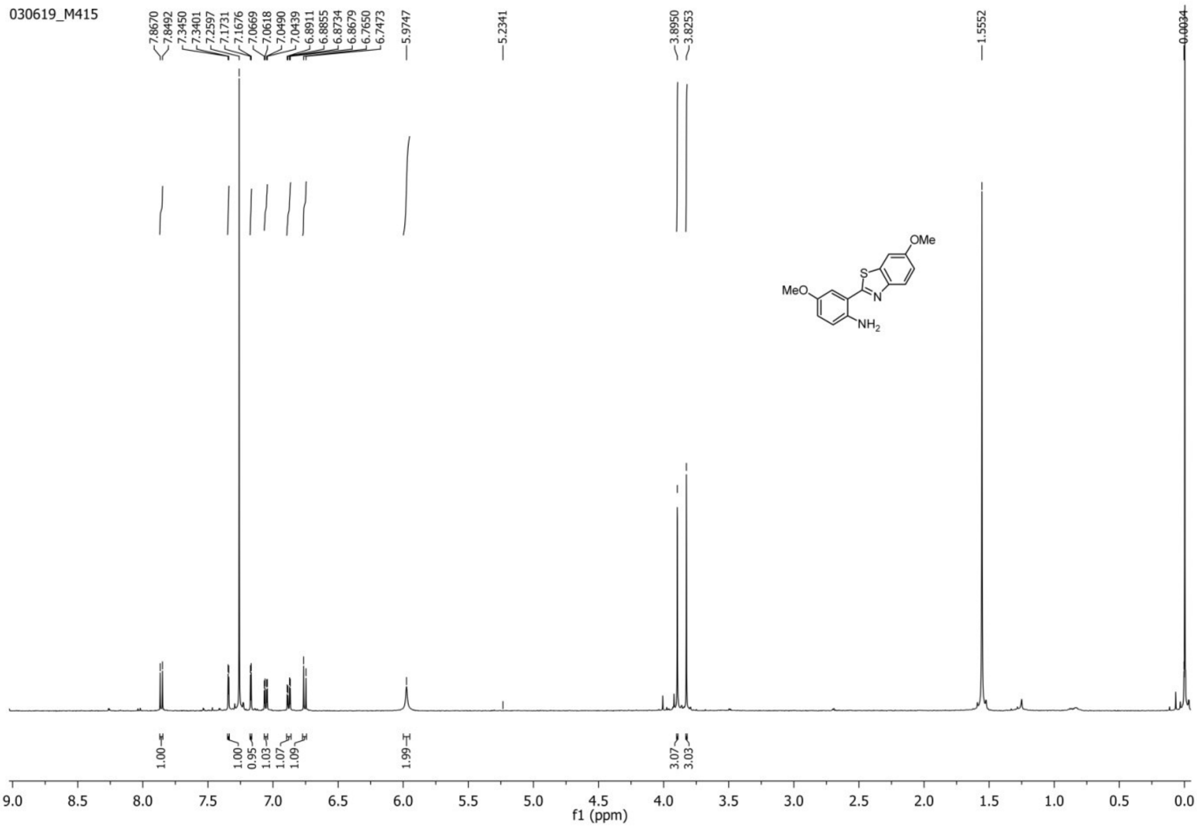


Figure S42. ^{1}H-NMR spectrum of **5F** in $CDCl_3$.

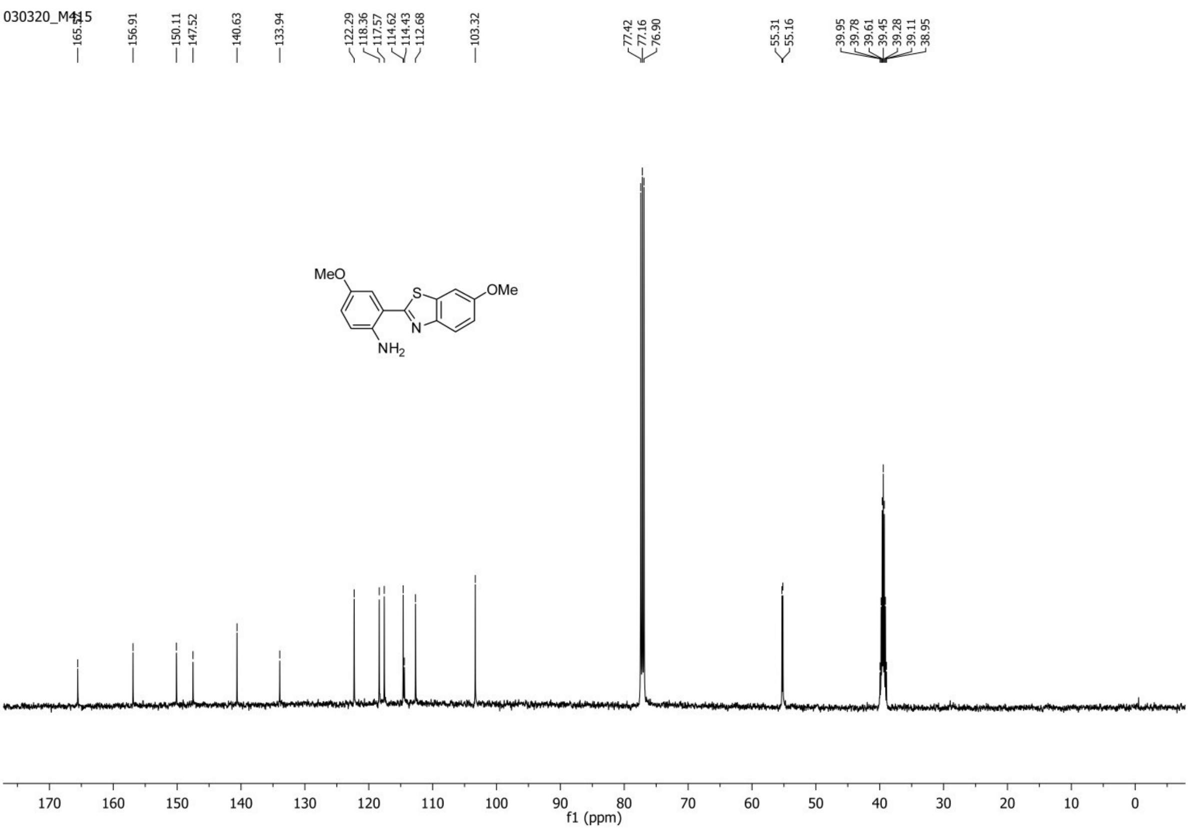


Figure S43. ^{13}C-NMR spectrum of **5F** in a mixture of $CDCl_3$ + DMSO-d_6.

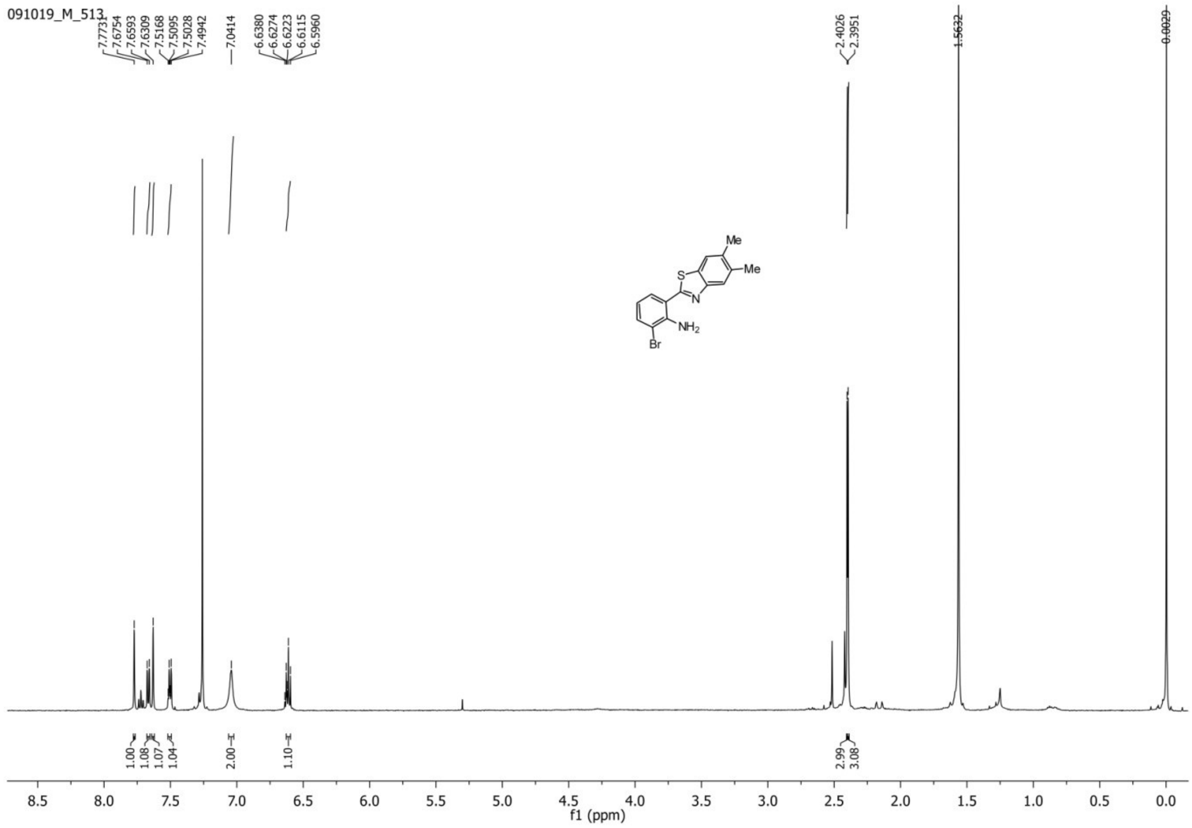


Figure S44. ^{1}H-NMR spectrum of **7C** in $CDCl_3$.

It is mentioned that the ^{13}C-NMR spectrum of **7C** could not be recorded due to solubility problem in $CDCl_3$ as well as DMSO-d_6.

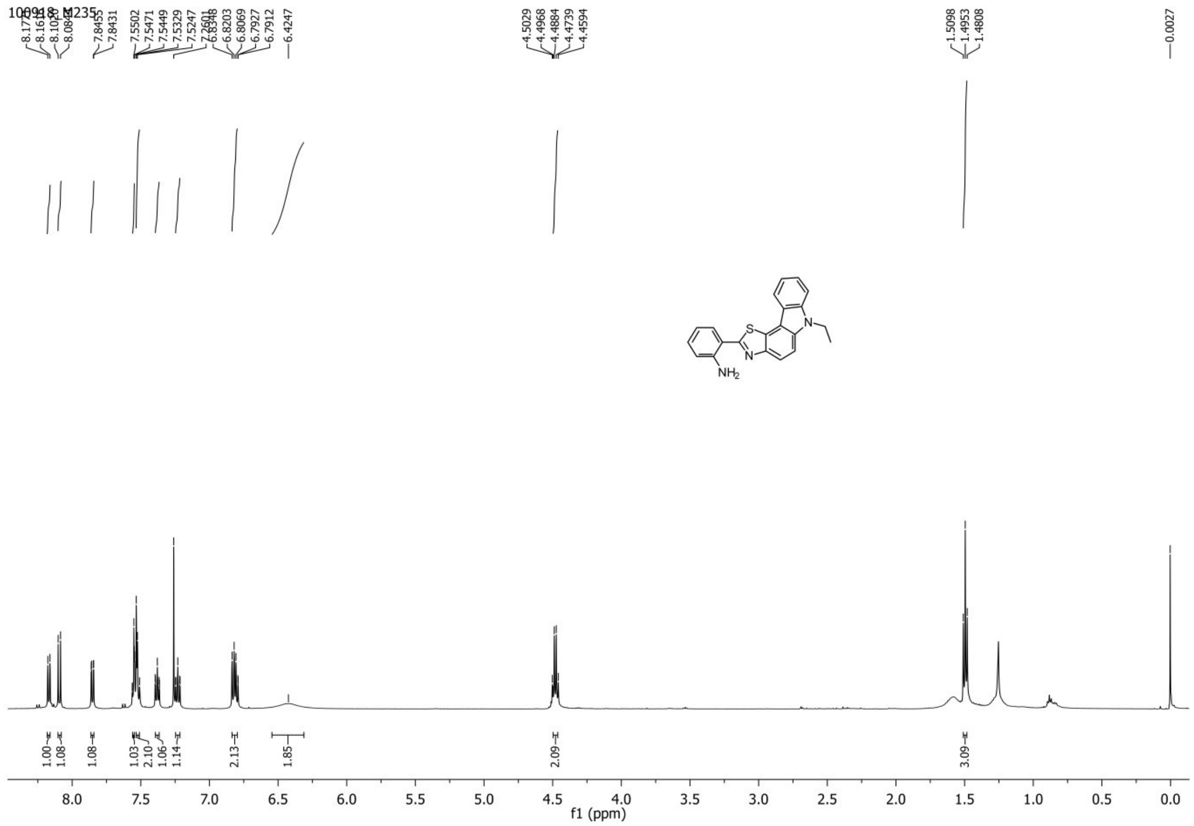


Figure S45. ^{1}H-NMR spectrum of **1J** in $CDCl_3$.

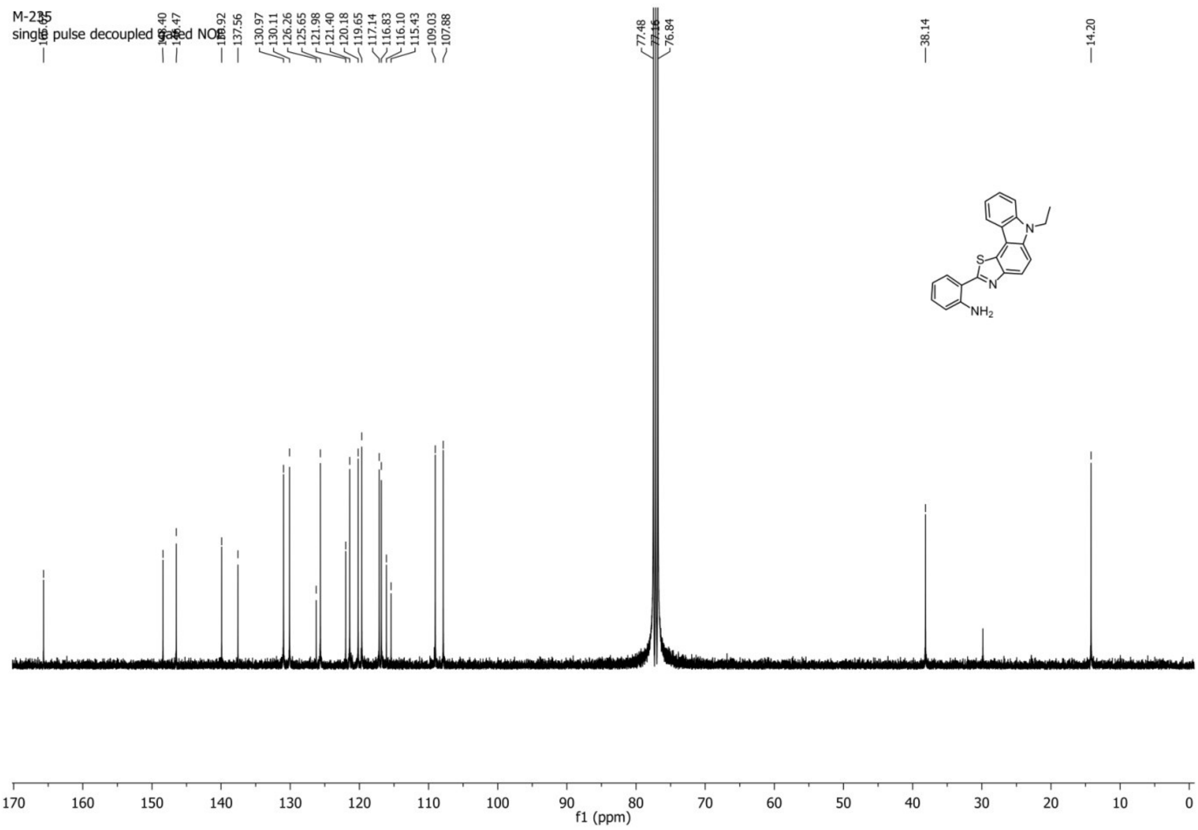


Figure S46. ^{13}C-NMR spectrum of **1J** in $CDCl_3$.

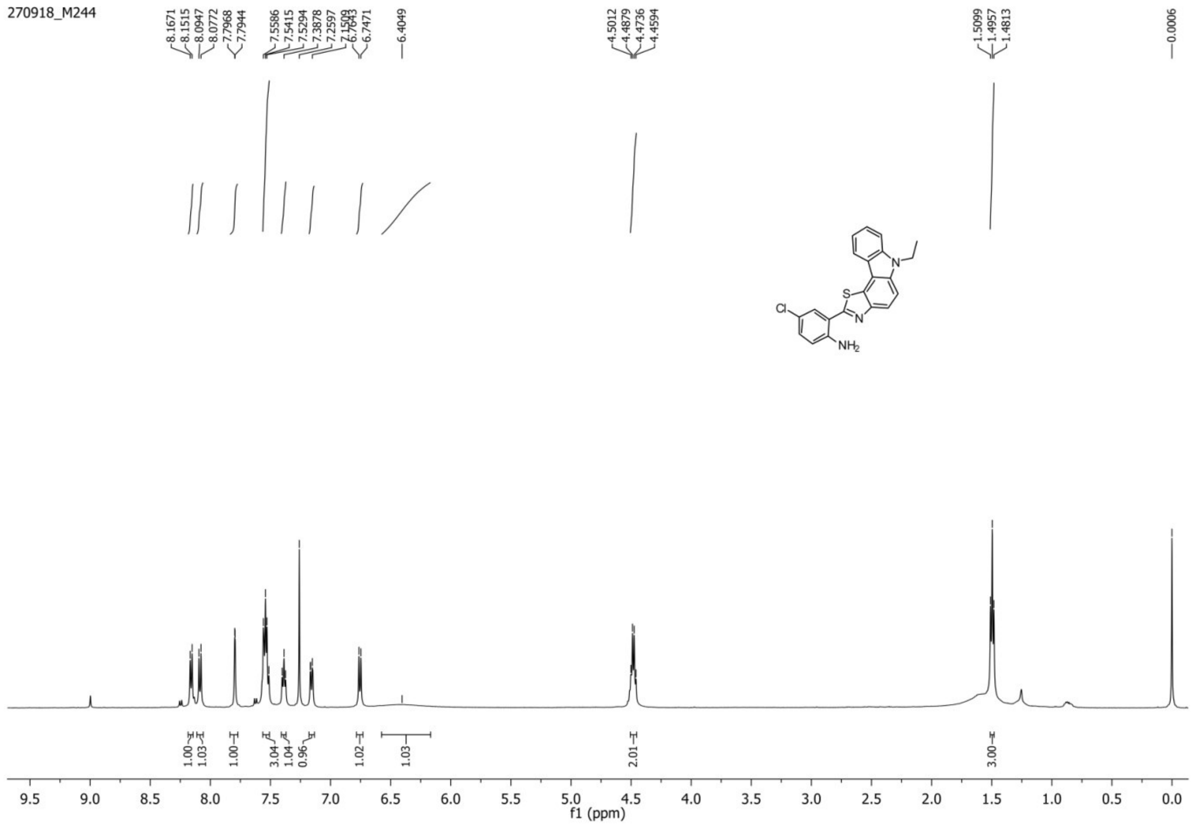


Figure S47. ^{1}H-NMR spectrum of **2J** in $CDCl_3$.

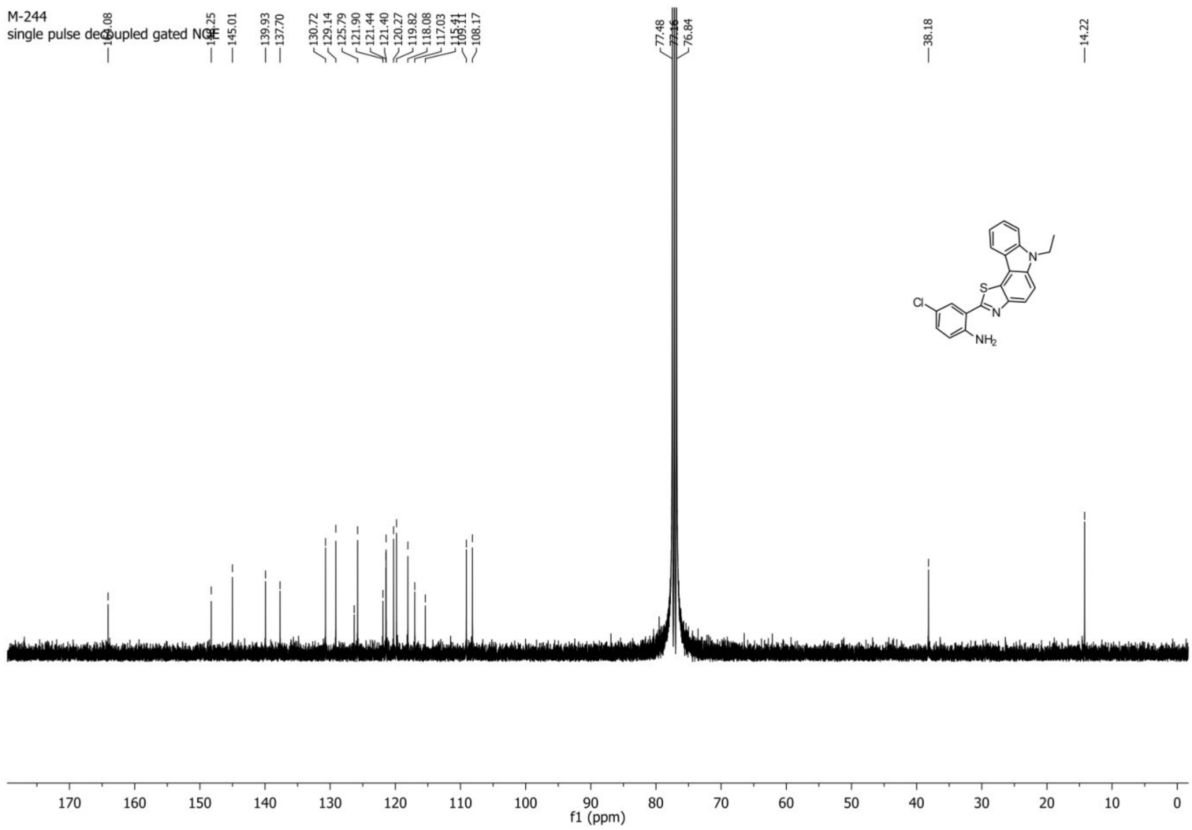


Figure S48. ^{13}C-NMR spectrum of **2J** in in $CDCl_3$.

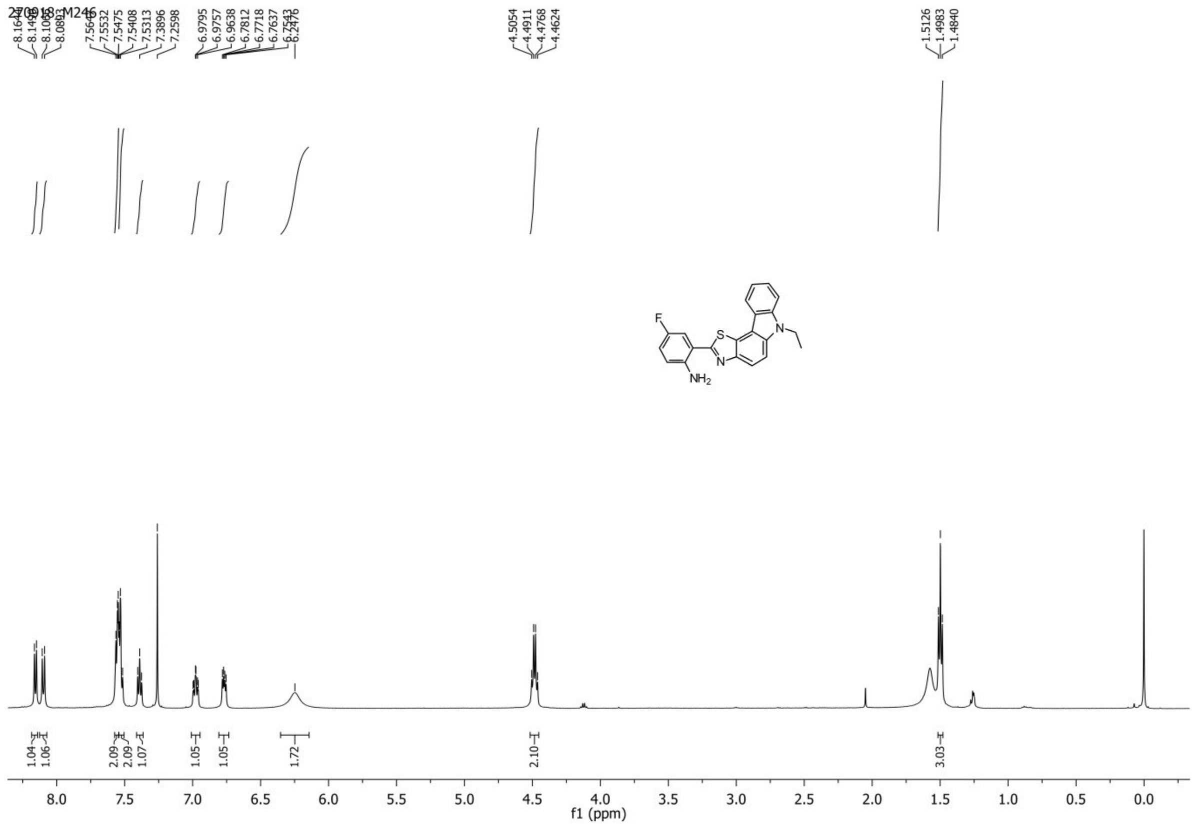


Figure S49. ^{1}H-NMR spectrum of **3J** in $CDCl_3$.

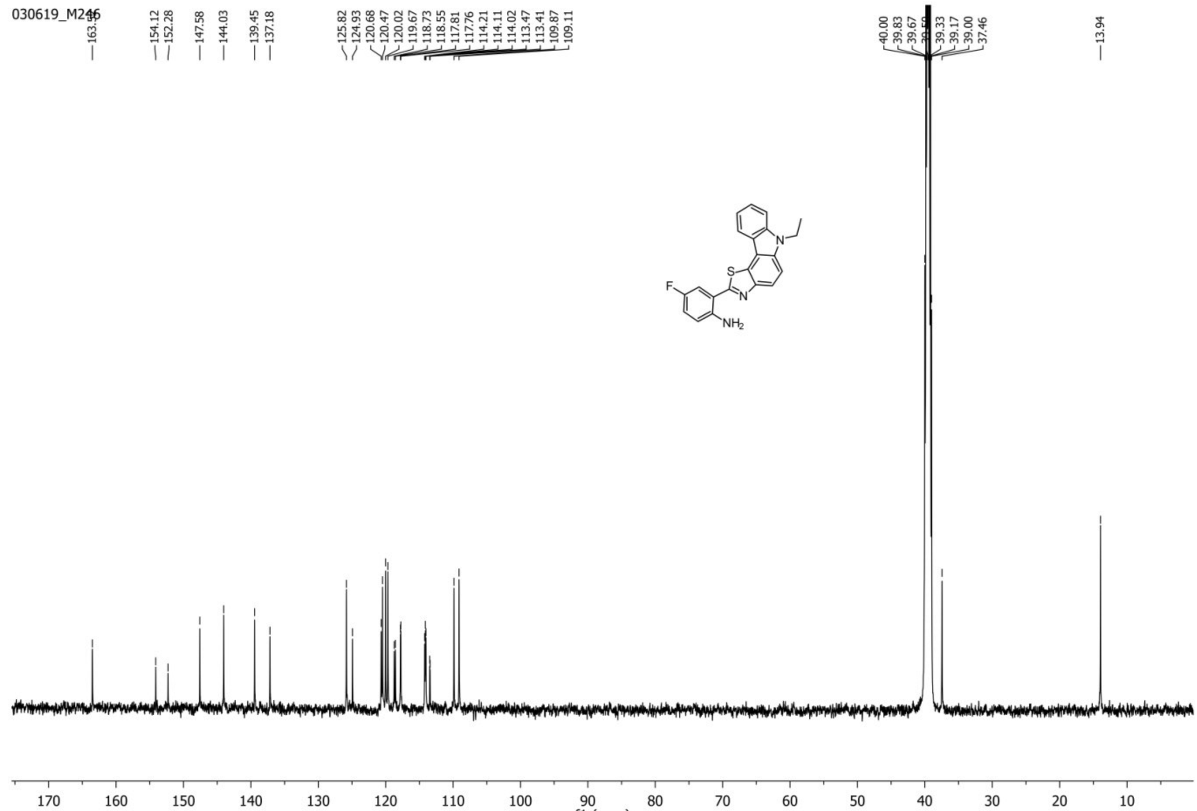


Figure S50. ^{13}C-NMR spectrum of **3J** in DMSO-d_6.

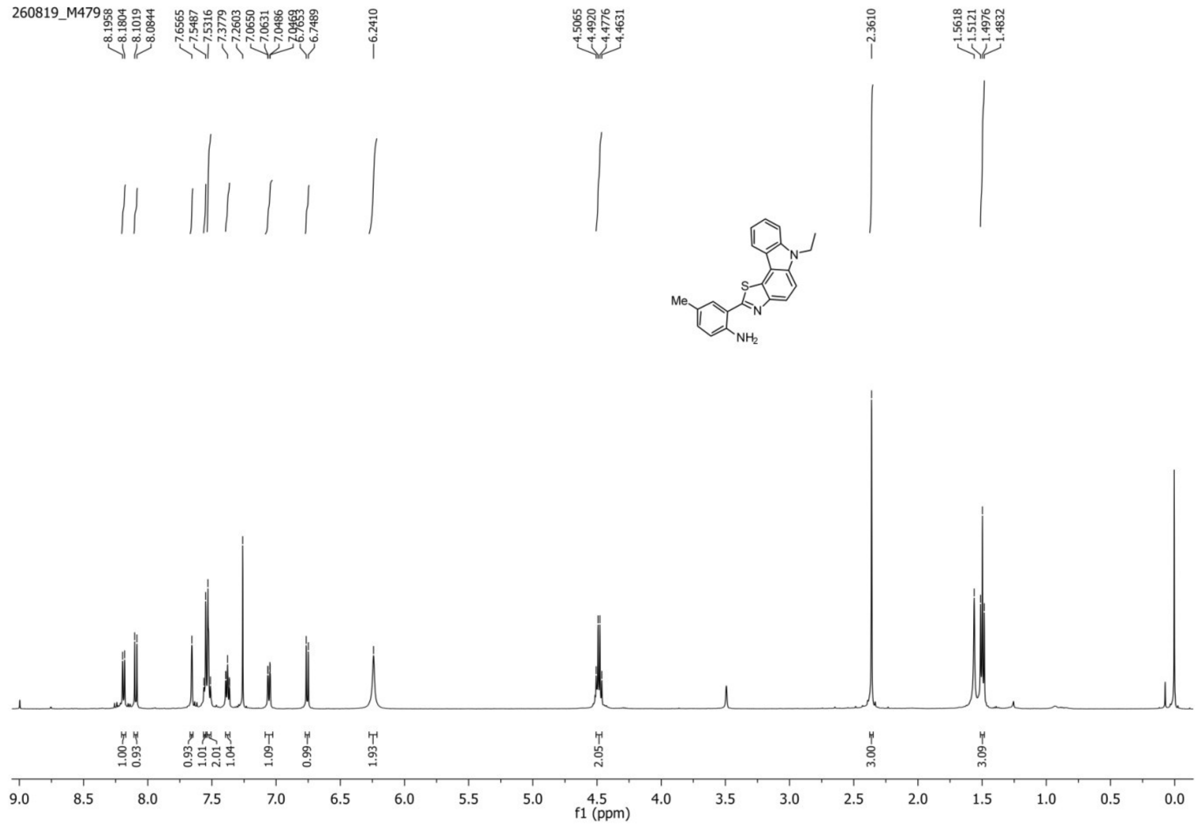


Figure S51. ^{1}H-NMR spectrum of **4J** in $CDCl_3$.

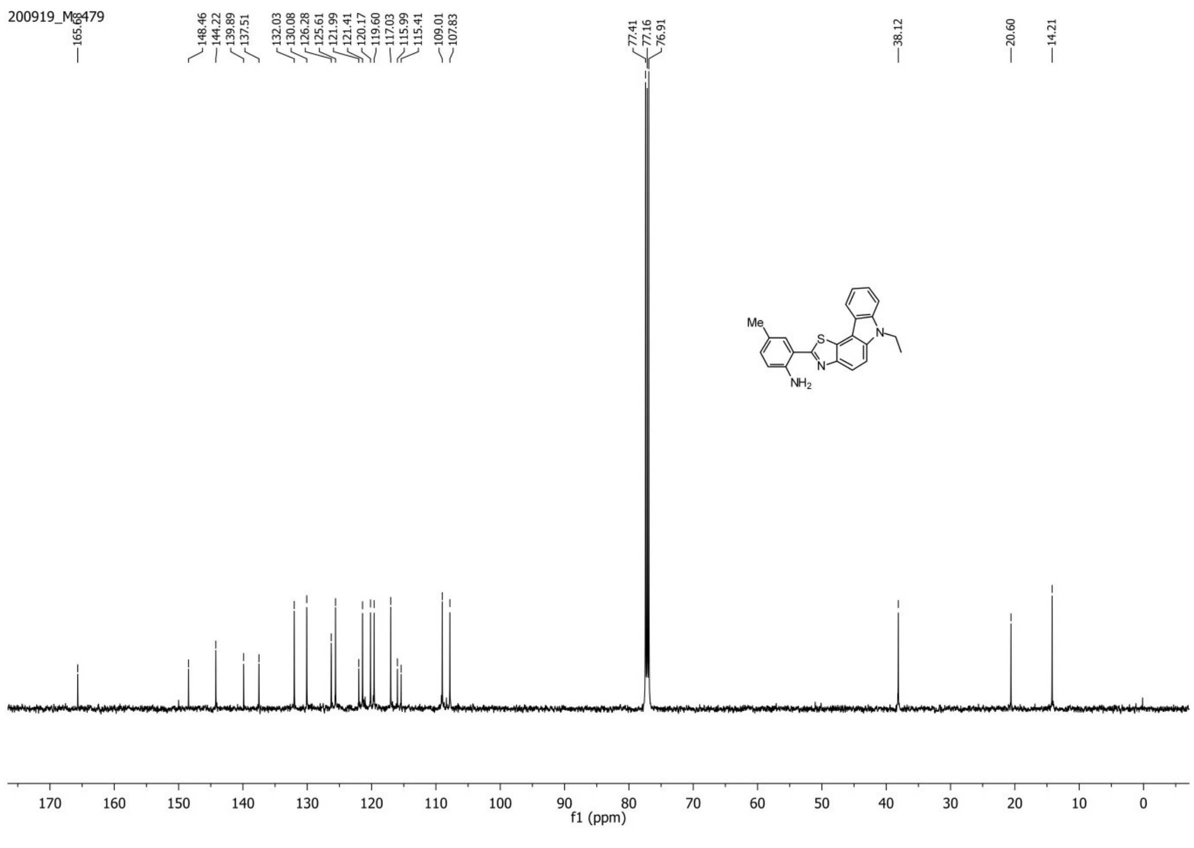


Figure S52. ^{13}C-NMR spectrum of **4J** in $CDCl_3$.

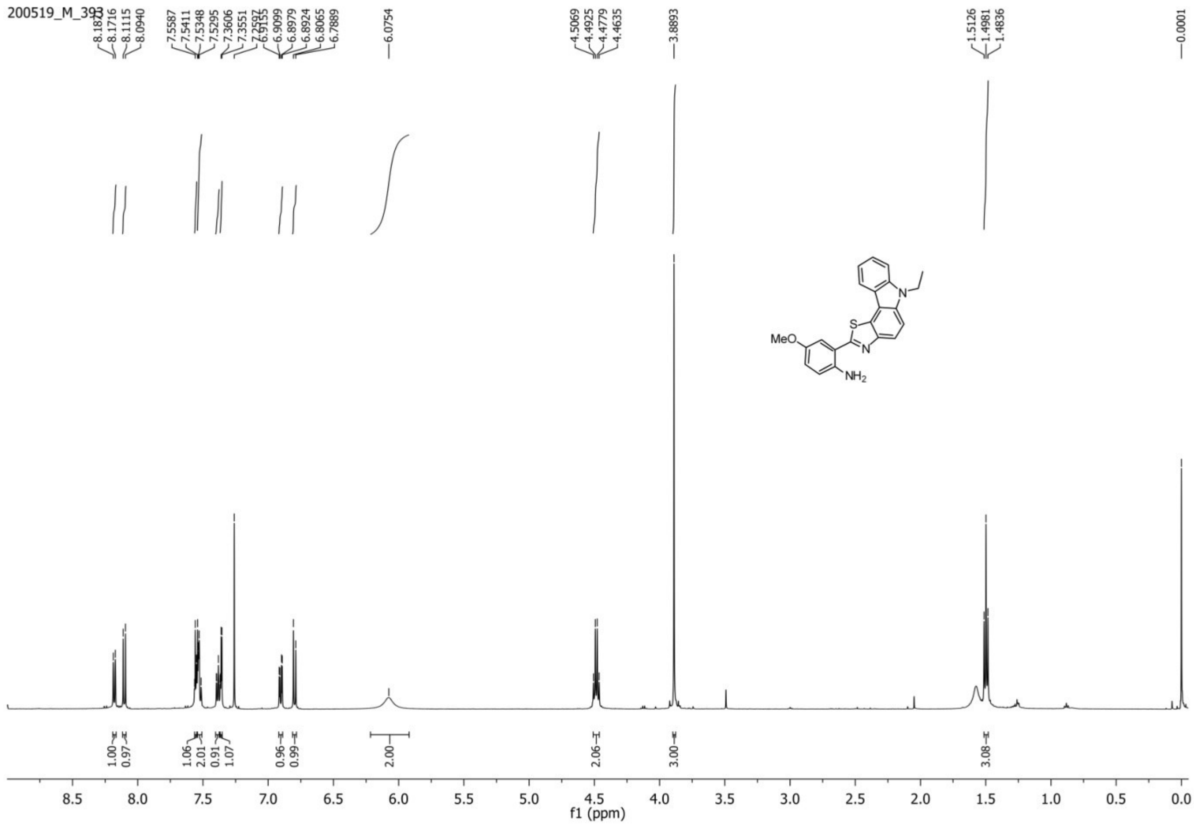


Figure S53. ^{1}H-NMR spectrum of **5J** in $CDCl_3$.

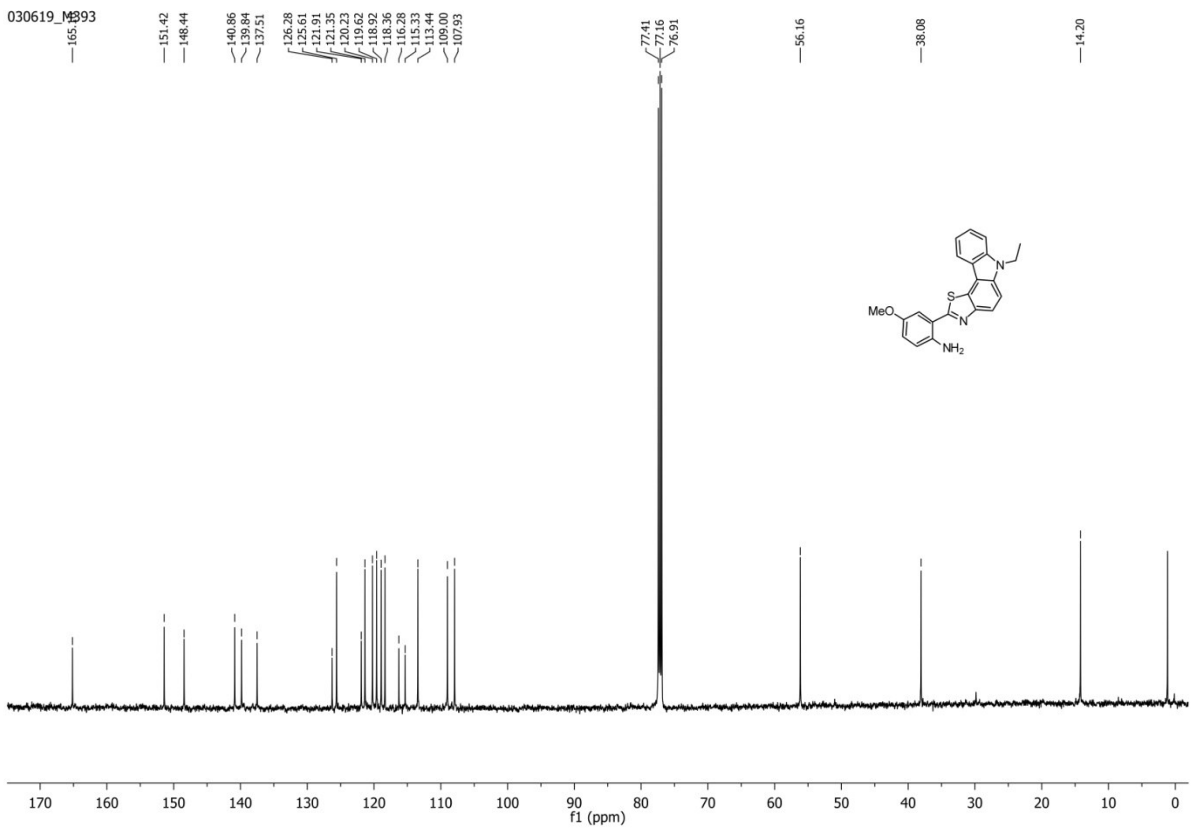


Figure S54. ^{13}C-NMR spectrum of **5J** in $CDCl_3$.

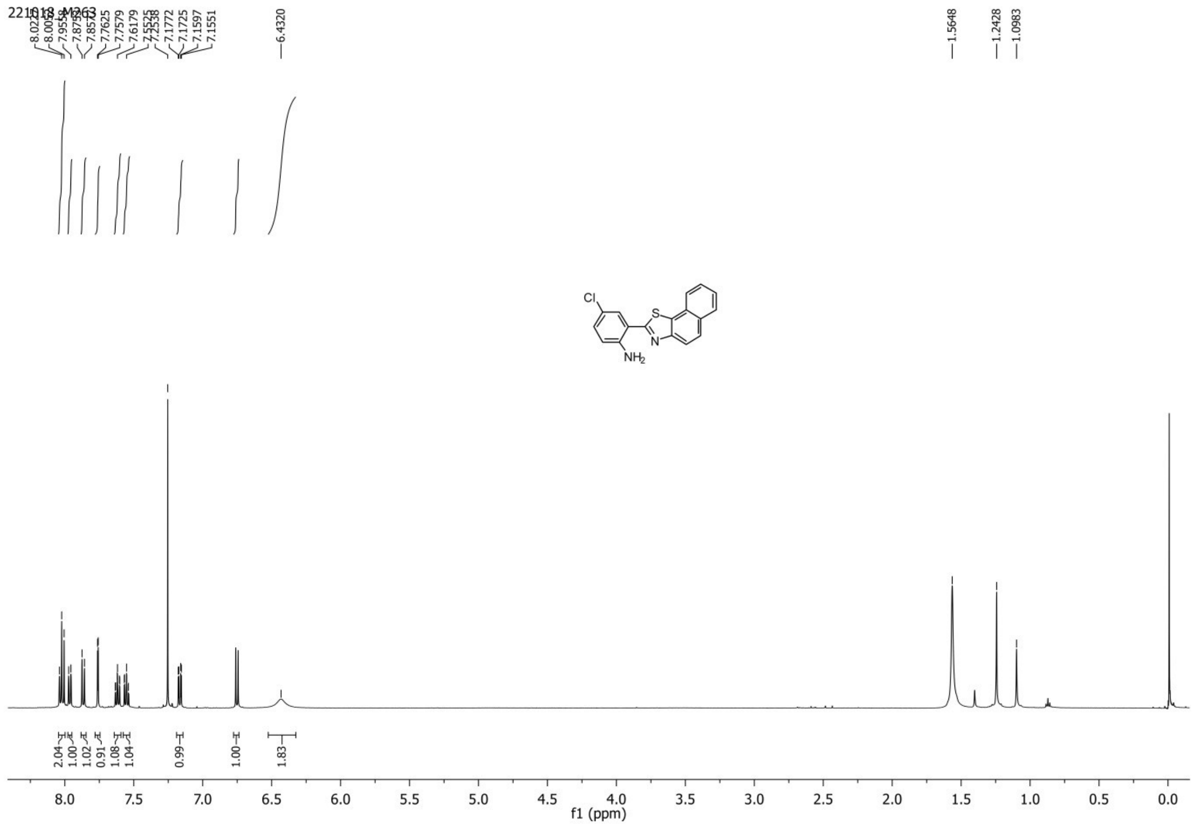


Figure S55. ^{1}H-NMR spectrum of **2K** in $CDCl_3$.

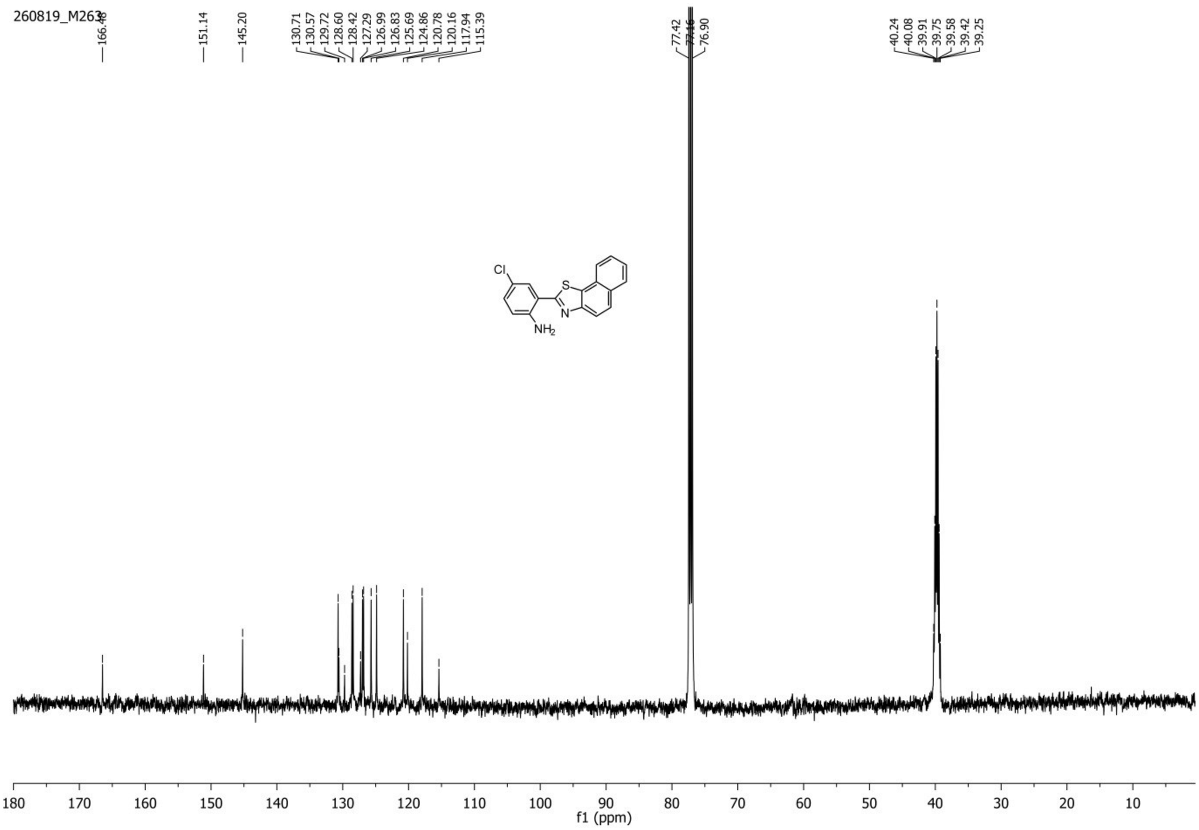


Figure S56. ^{13}C-NMR spectrum of **2K** in a mixture of $CDCl_3$ + DMSO-d_6**.**

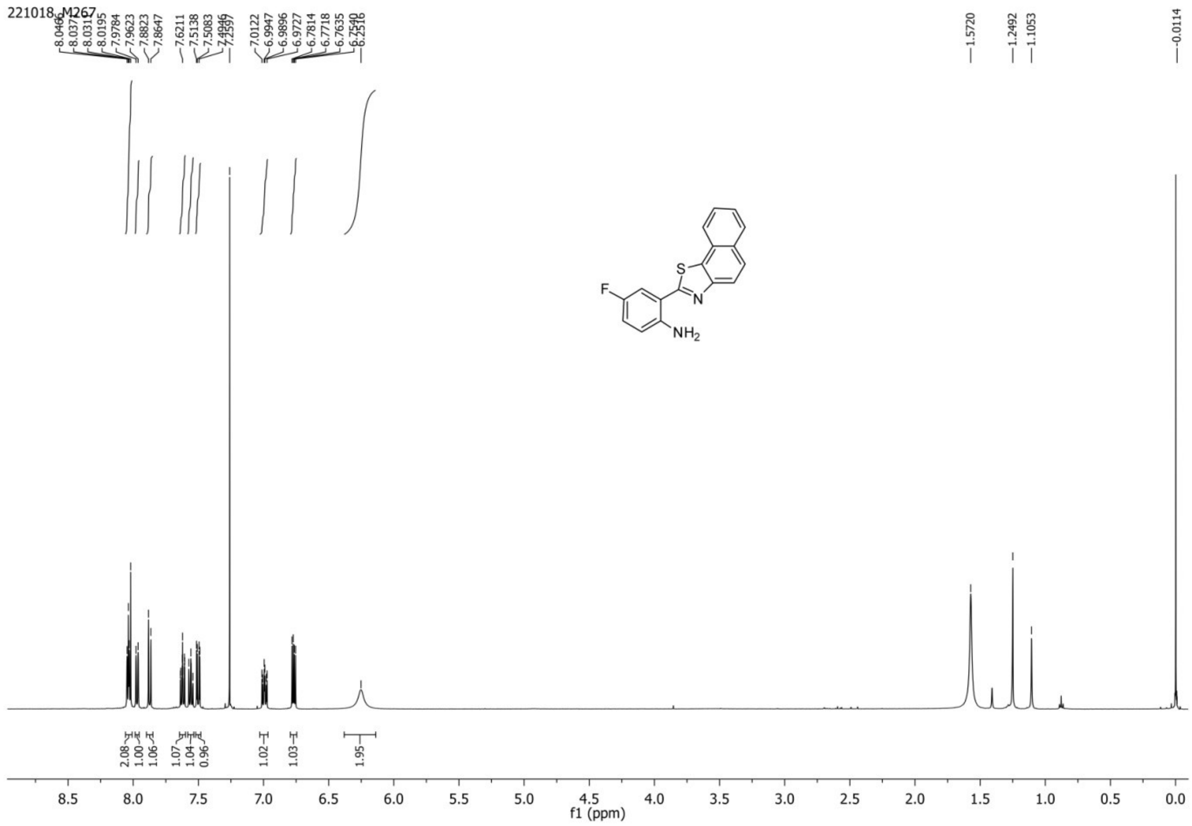


Figure S57. ^{1}H-NMR spectrum of **3K** in $CDCl_3$.

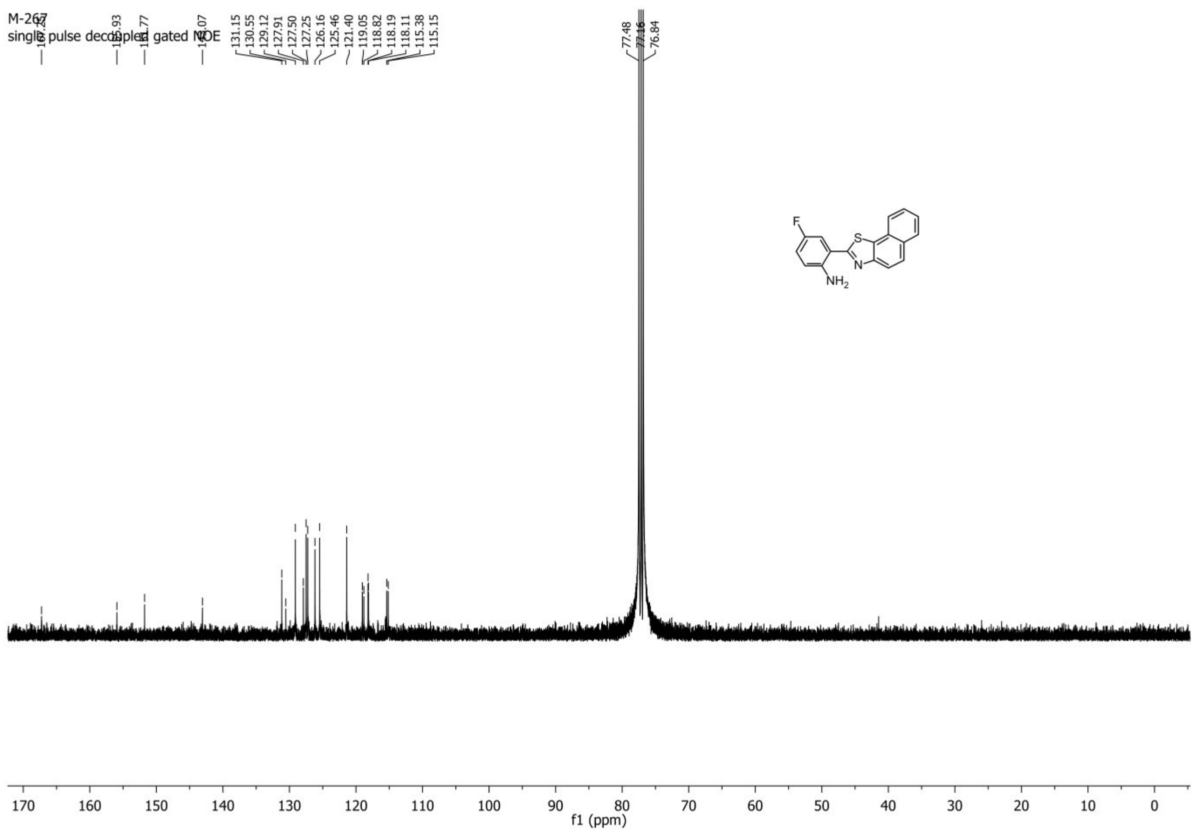


Figure S58. ^{13}C-NMR spectrum of **3K** in $CDCl_3$.

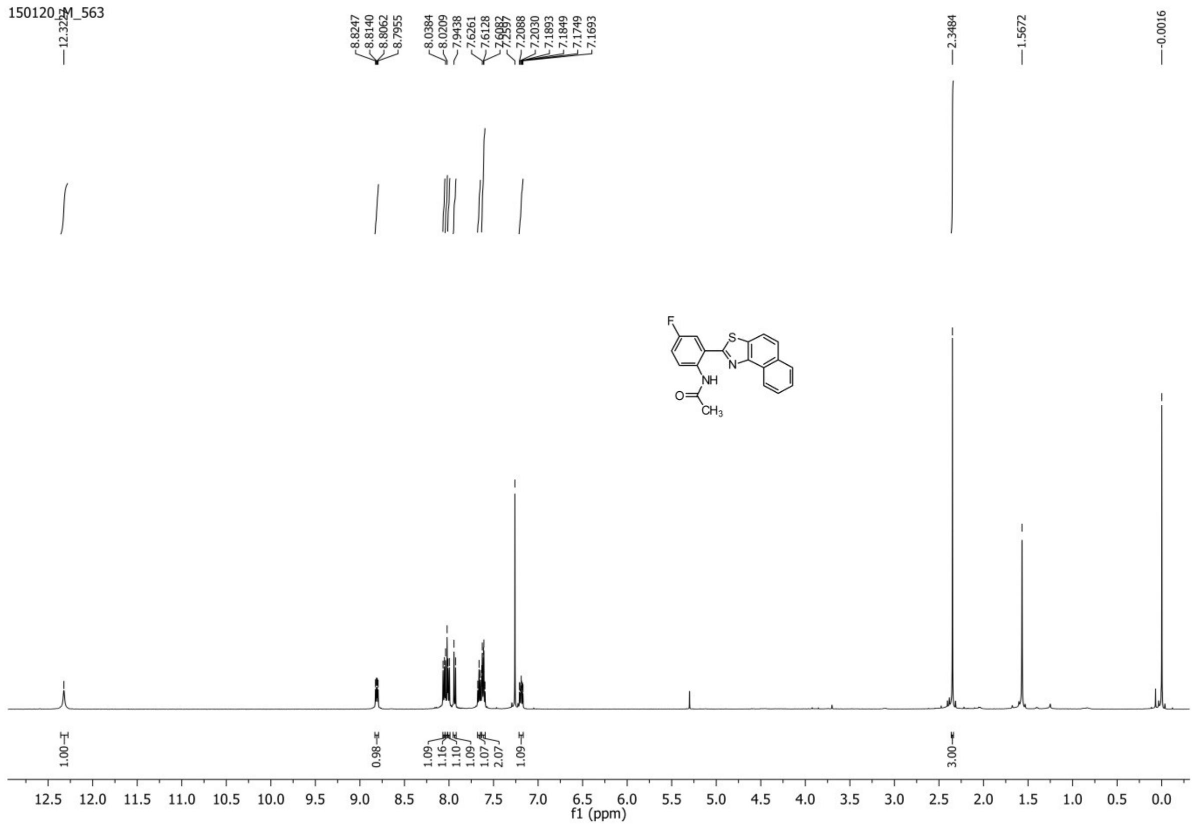


Figure S59. ^{1}H-NMR spectrum of **8** in $CDCl_3$.

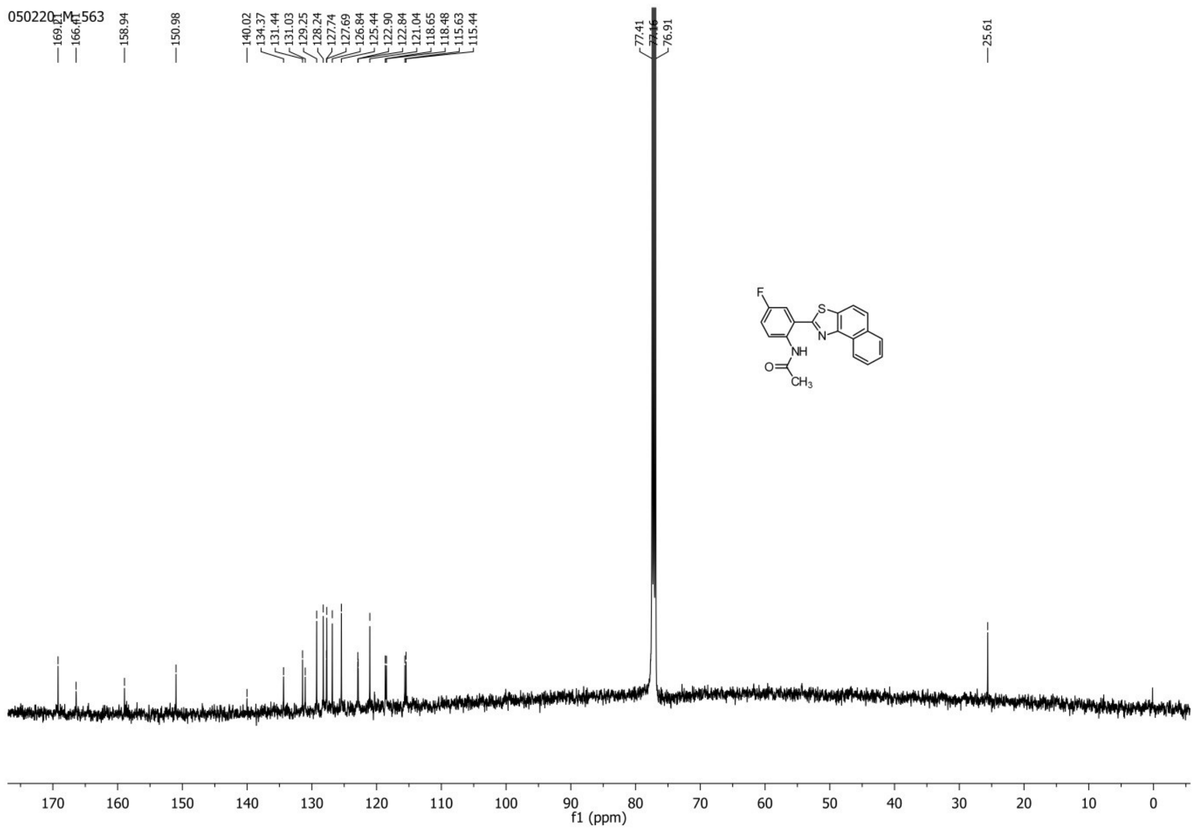


Figure S60. ^{13}C-NMR spectrum of **8** in $CDCl_3$.

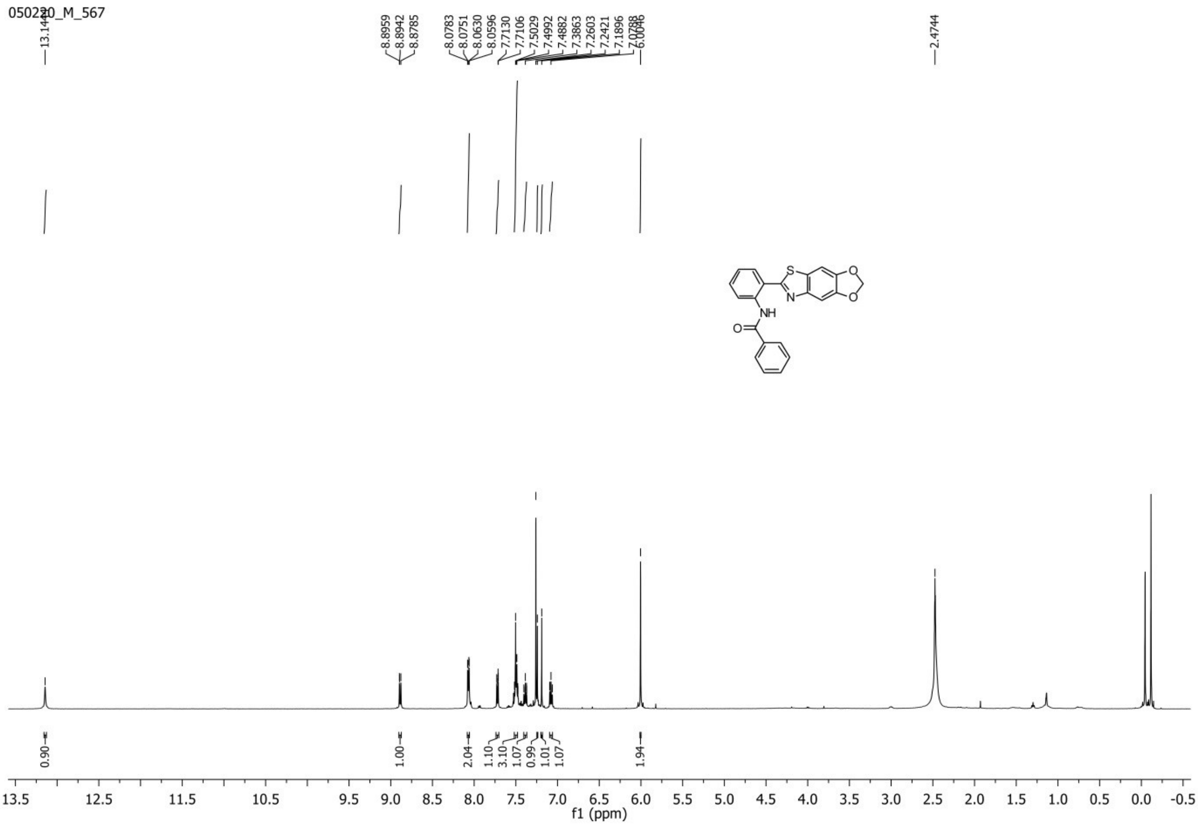


Figure S61. ^{1}H-NMR spectrum of **9** in $CDCl_3$.

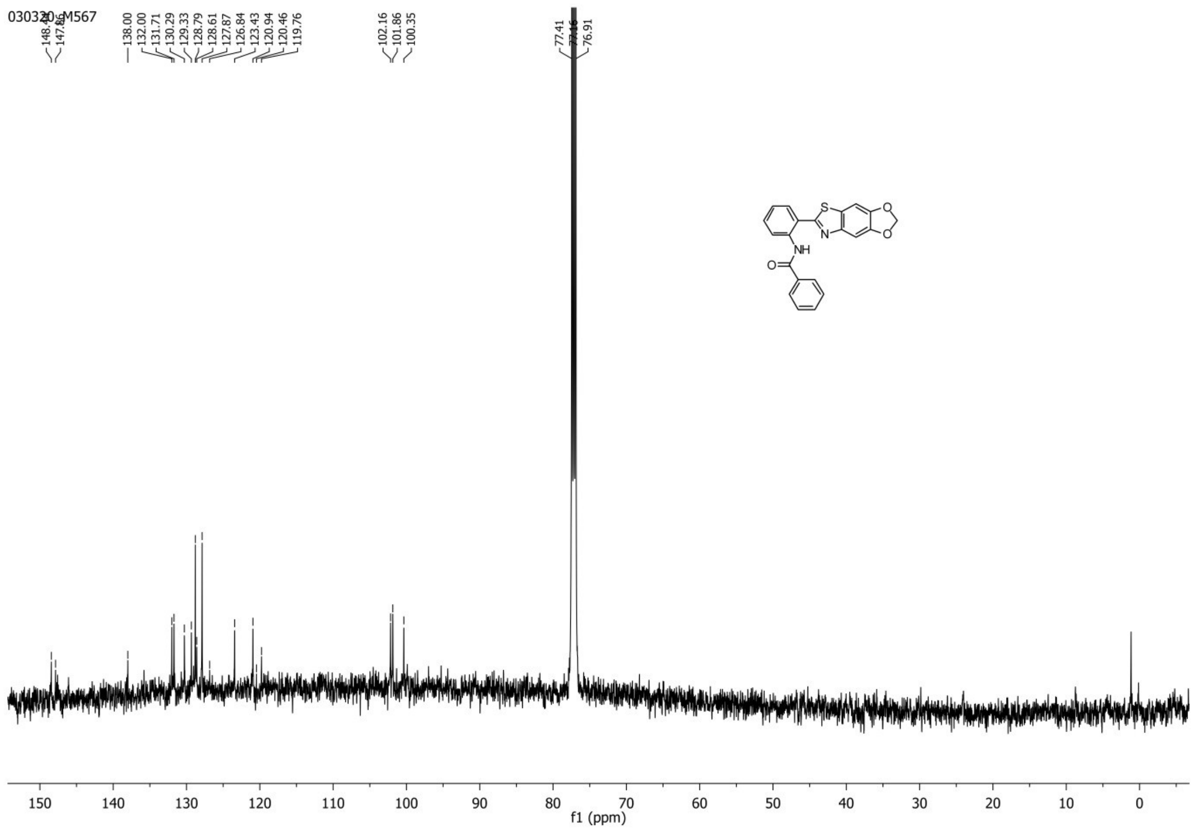


Figure S62. ^{13}C-NMR spectrum of **9** in $CDCl_3$.

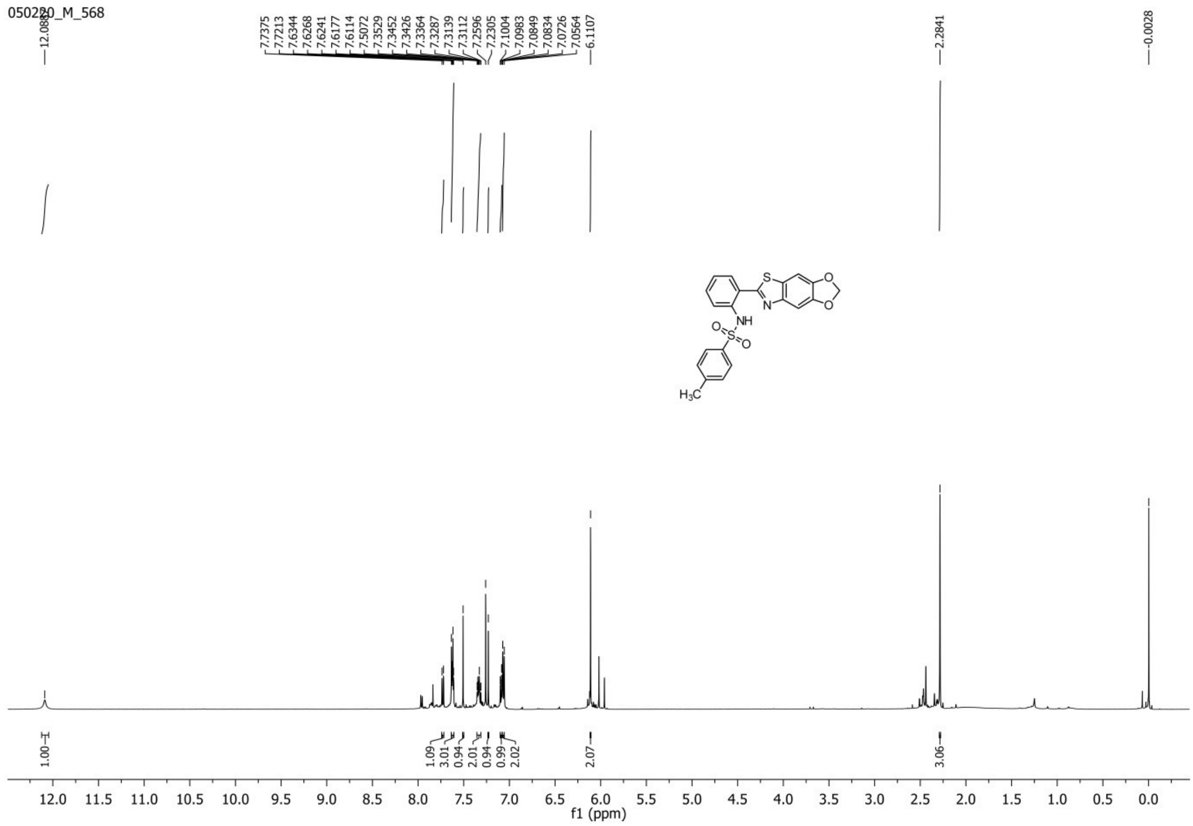


Figure S63. ^{1}H-NMR spectrum of **10** in $CDCl_3$.

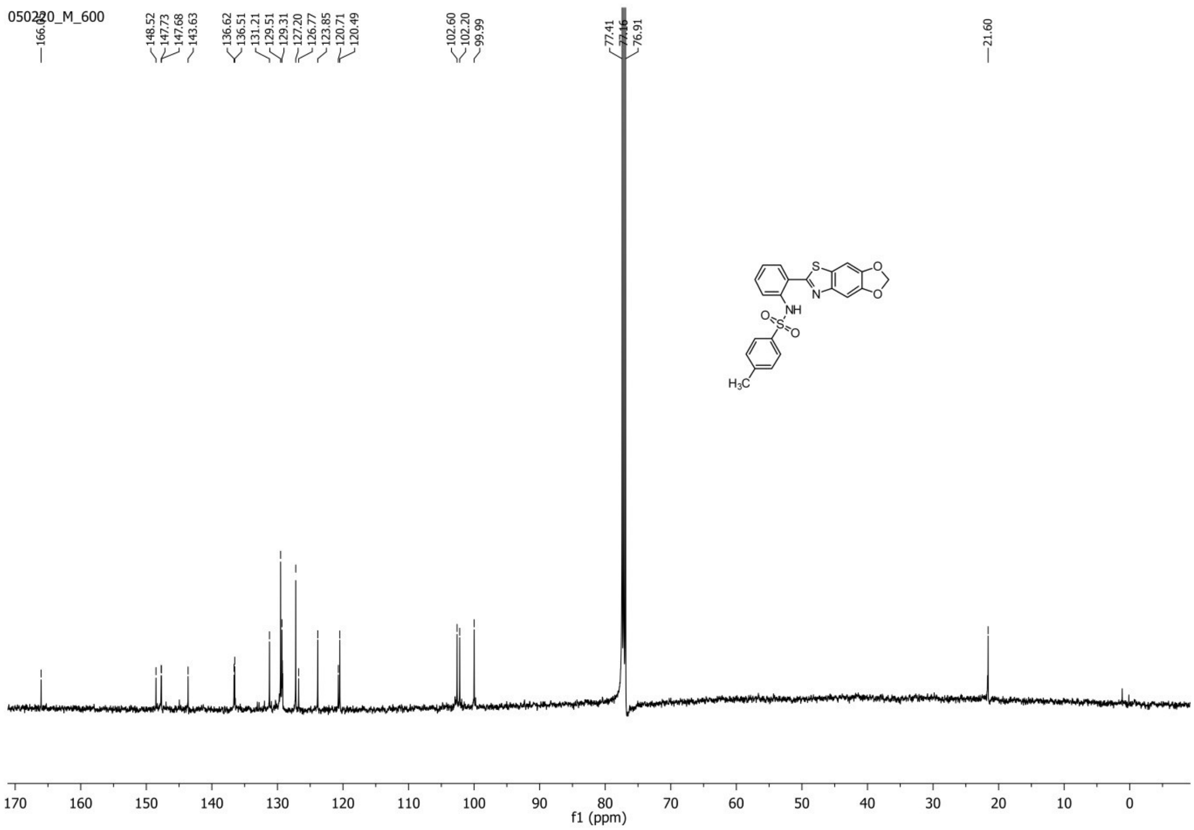


Figure S64. ^{13}C-NMR spectrum of **10** in $CDCl_3$.

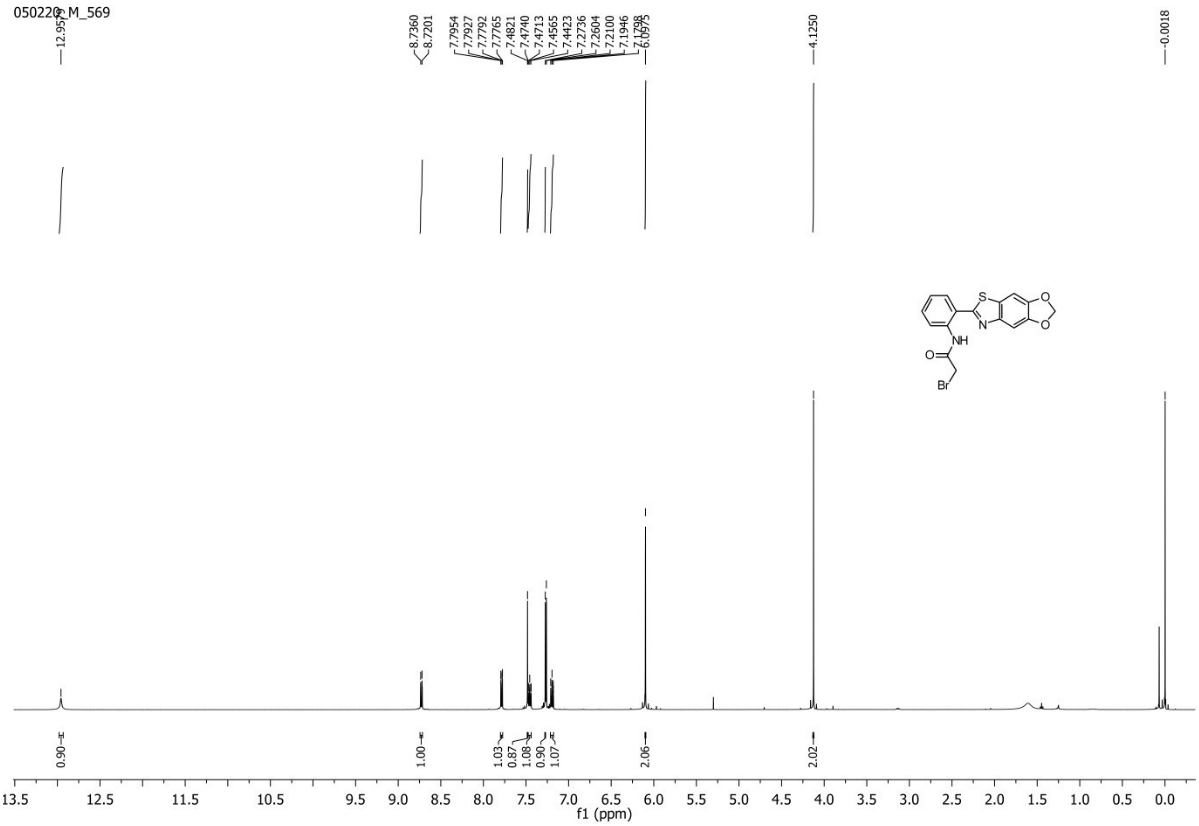


Figure S65. ^{1}H-NMR spectrum of **11** in $CDCl_3$.

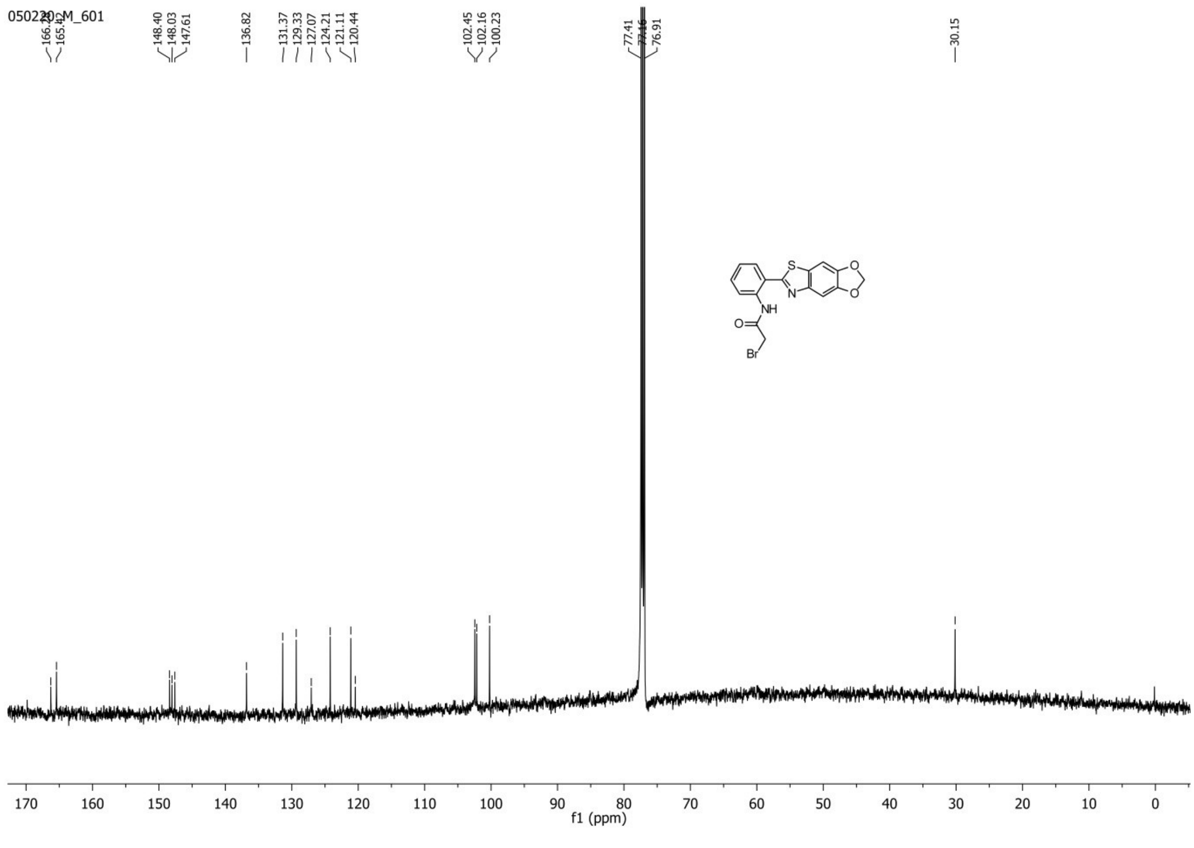


Figure S66. ^{13}C-NMR spectrum of **11** in $CDCl_3$.

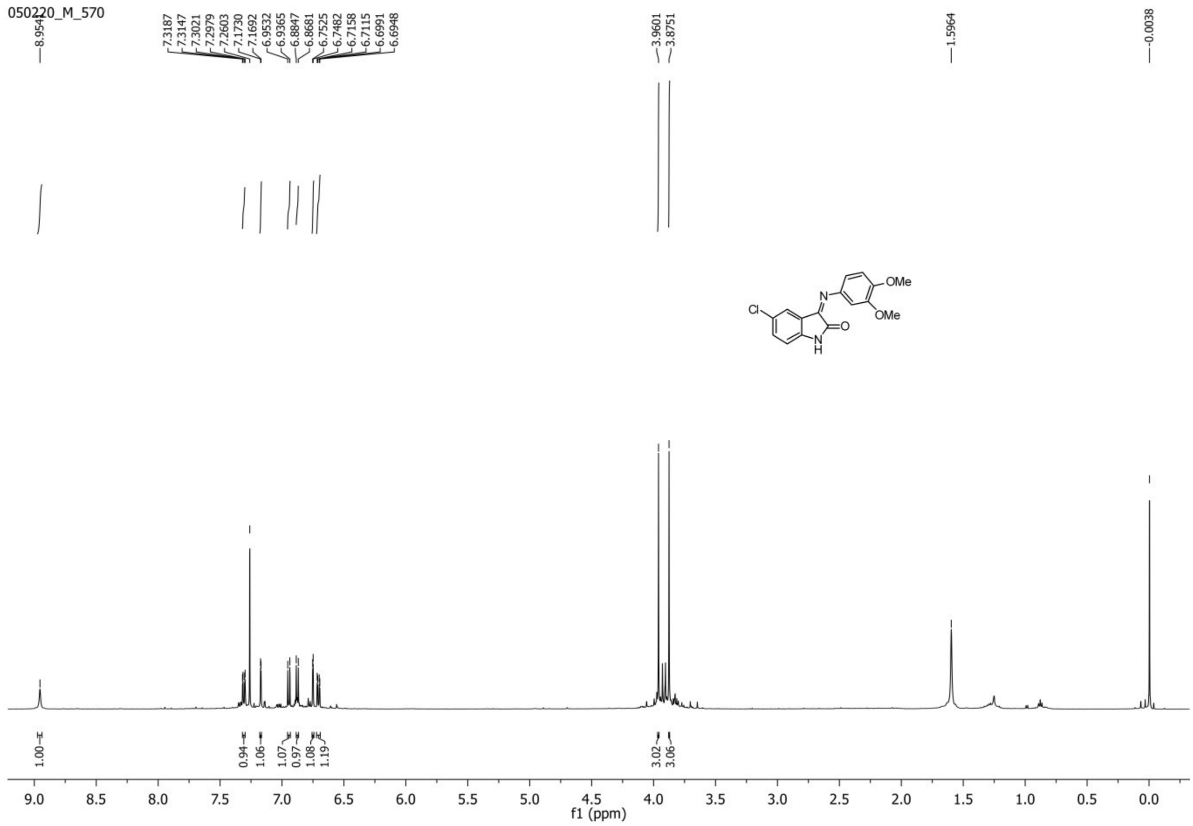


Figure S67. ^{1}H-NMR spectrum of **12** in $CDCl_3$.

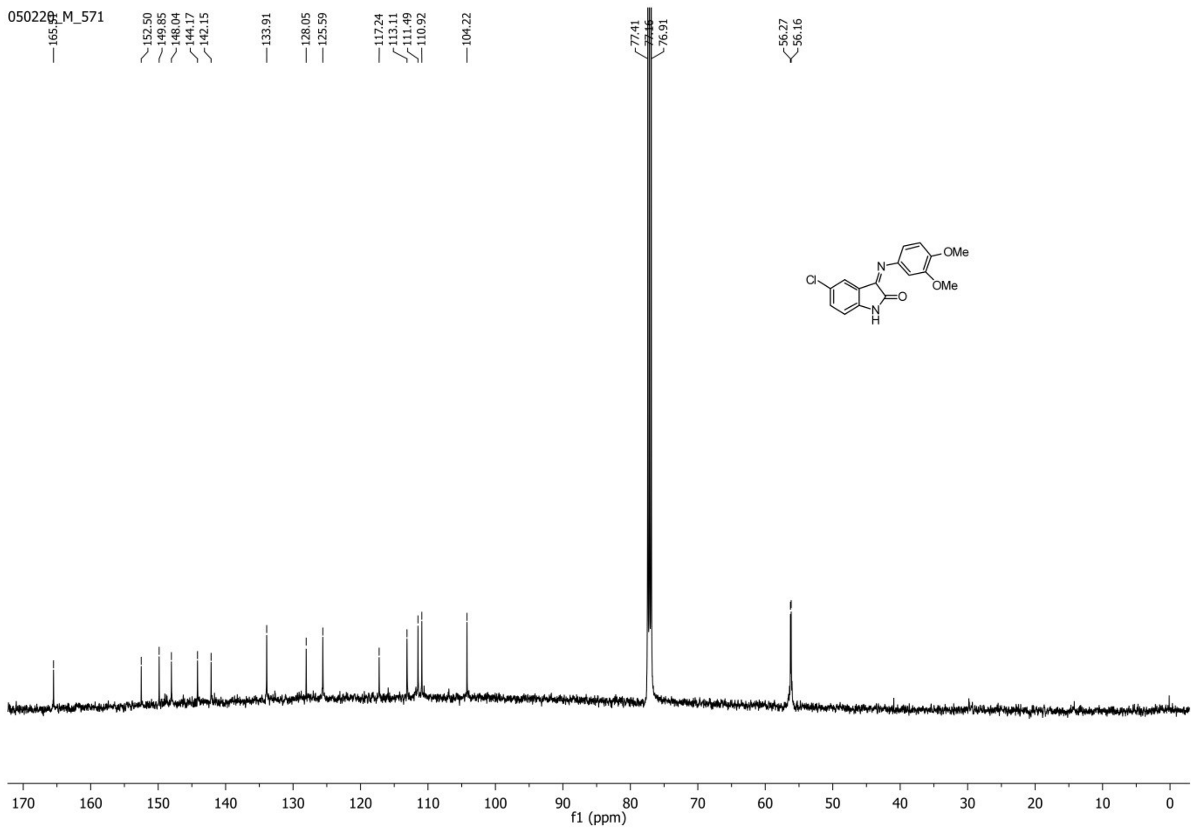


Figure S68. ^{13}C-NMR spectrum of **12** in $CDCl_3$.