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Supporting Information

for

Et_3N/DMSO-supported one-pot synthesis of highly fluorescent β-carboline-linked benzothiophenones via sulfur insertion and estimation of the photophysical properties

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General information, experimental procedures, spectroscopic data, photophysical data, and copies of spectra

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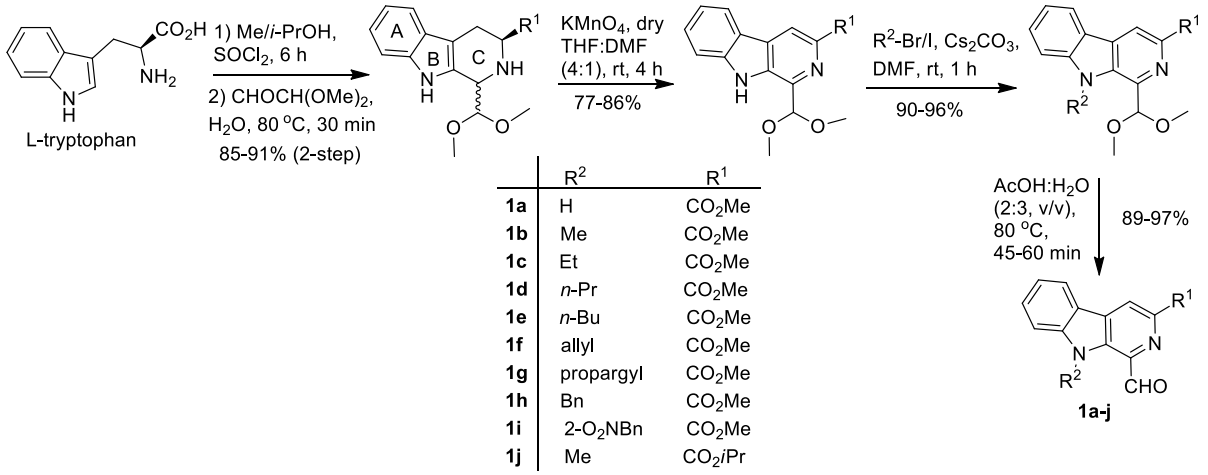
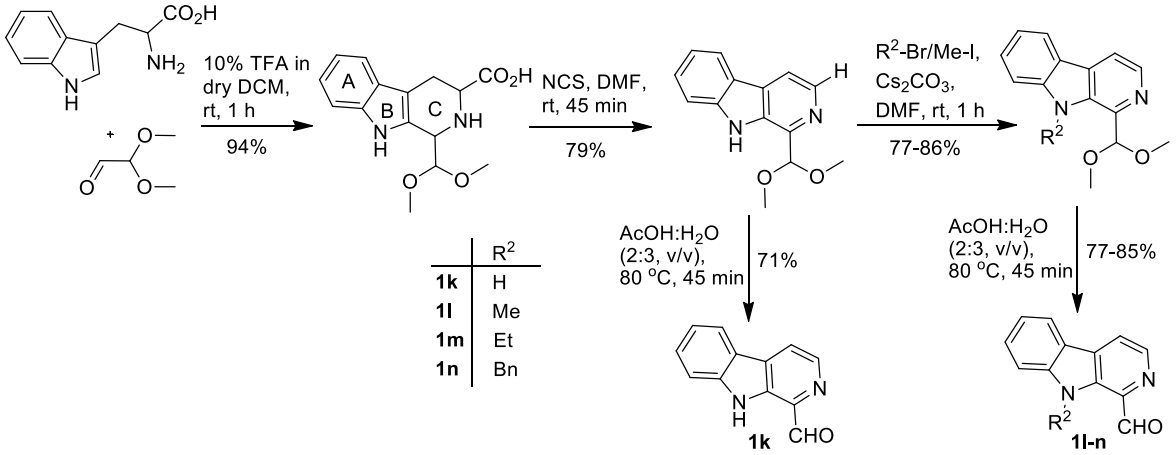
1. Synthesis of 1(3)-formyl-β-carboline derivatives



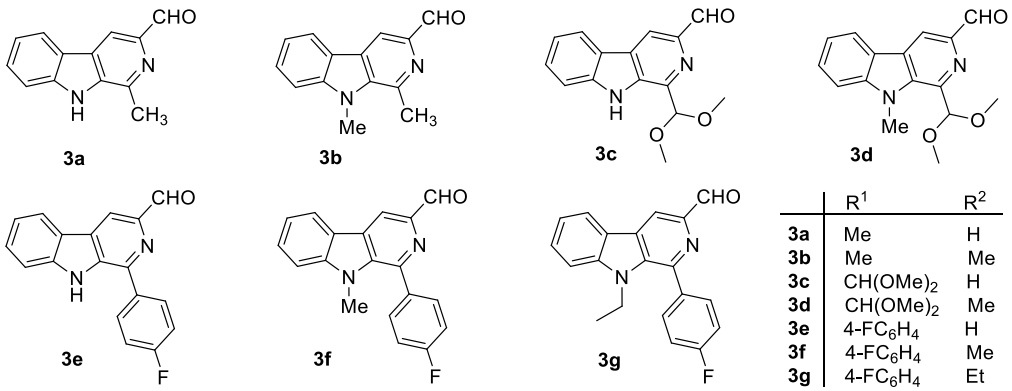
	R^2	R^1
1a	H	CO_2Me
1b	Me	CO_2Me
1c	Et	CO_2Me
1d	*n*-Pr	CO_2Me
1e	*n*-Bu	CO_2Me
1f	allyl	CO_2Me
1g	propargyl	CO_2Me
1h	Bn	CO_2Me
1i	2-O_2NBn	CO_2Me
1j	Me	CO_2iPr

Scheme S1: Synthesis of 1-formyl-9*H*-pyrido[3,4-*b*]indole derivatives [1]



	R^2
1k	H
1l	Me
1m	Et
1n	Bn

Scheme S2: Synthesis of N-alkylated Kumujian C (**1k**-**n**) [1]



	R^1	R^2
3a	Me	H
3b	Me	Me
3c	$CH(OMe)_2$	H
3d	$CH(OMe)_2$	Me
3e	4-FC_6H_4	H
3f	4-FC_6H_4	Me
3g	4-FC_6H_4	Et

Scheme S3: Synthesis of 3-formyl-9*H*-pyrido[3,4-*b*]indoles [2]

2. Experimental procedures and spectral data

General methods: Chemicals and reagents were purchased from Sigma Aldrich, Acros, Spectrochem Ltd., and Avera Synthesis, and used without further purification. Commercially available anhydrous solvents (MeOH, iPrOH, diethyl ether, DMSO, and DMF) were used as received without further distillation. Thin layer chromatography (TLC) was performed on precoated aluminium plates (E. Merck; silica gel 60 PF254, 0.25 mm). Column chromatography was performed on silica gel (SRL; 60–120 mesh). Melting points were determined in open capillary tubes on a Precision Digital melting-point apparatus (LABCO) that contained silicon oil and are uncorrected. IR spectra were recorded on an Agilent FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on an Avance III Bruker spectrometer at operating frequencies of 400 MHz, 500 MHz, 600 MHz (^{1}H), or 100 MHz, 125 MHz, or 150 MHz (^{13}C), as shown on the individual spectrum, using tetramethylsilane (TMS) as an internal standard. HRMS spectra were recorded on 6200 series TOF/6500 series QTOF B.05.01 (B5125). Elemental analysis was performed on a Carlo–Erba 108 or an Elementar Vario EL III microanalyzer. Room temperature varied between 25–40 °C. The multiplicity in the ^{1}H NMR spectra is as follows: s for singlet, d for doublet, t for triplet, q for quartet, dd for doublet of doublet, and m for multiplet.

Experimental procedure for the synthesis of β-carboline-based 2-nitrochalcone derivatives (1aA, **1bA**, **1dA, and 1hA) as exemplified for compound 1bA.** To a stirred solution of KOH (0.033 g, 0.587 mmol) in dry MeOH (4 mL), 2-nitroacetophenone (**A**, 0.080 mL, 0.587 mmol) was added at room temperature and the reaction mixture was stirred for 15 min. Thereafter, **1b** (0.15 g, 0.560 mmol) was added portionwise and the reaction mixture was allowed to stir for additional 1 h at room temperature. After completion of the reaction (as monitored by TLC), the yellow precipitate was filtered through a sintered funnel, washed twice with MeOH, and dried under vacuum to obtain 0.20 g (86%) of **1bA** as yellow solid.

(*E*)-Methyl 1-(3-(2-nitrophenyl)-3-oxoprop-1-en-1-yl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (1aA). Yield: 76% (0.24 g from 0.20 g) as a yellow solid; m.p. 203-204 ^{o}C; R_f = 0.20 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 3319 (NH), 1713 (CO_2CH_3), 1585 (CO); ^{1}H NMR and ^{13}C NMR spectra could not be recorded due to solubility problem*;* MS (ES): *m/z* (%) = 402.1 (100) $[M+1]^{+}$; $C_{22}H_{15}N_3O_5$ (401.1012):calcd. for C 65.83, H 3.77, N 10.47; found C 65.89, H 3.78, N 10.49.

(*E*)-Methyl 9-methyl-1-(3-(2-nitrophenyl)-3-oxoprop-1-en-1-yl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (1bA). Yield: 86% (0.20 g from 0.15 g) as a yellow solid; m.p. 207-208 °C; R_f = 0.30 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1717 (CO_2CH_3), 1588 (CO); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.03 (s, 3 H, NCH_3), 4.10 (s, 3 H, CO_2CH_3), 7.38 (t, *J* = 7.5 Hz, 1 H, ArH), 7.50 (d, *J* = 8.4 Hz, 1 H, ArH), 7.63 (d, *J* = 7.5 Hz, 1 H, ArH), 7.67 (d, *J* = 8.2 Hz, 2 H, ArH), 7.72 (d, *J* = 15.2 Hz, 1 H, ArH), 7.80 (t, *J* = 7.5 Hz, 1 H, ArH), 8.18 (t, *J* = 8.3 Hz, 2 H, ArH), 8.37 (d, *J* = 15.1 Hz, 1 H, ArH), 8.83 (s, 1 H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 33.6, 52.9, 110.1, 118.4, 121.2, 121.5, 122.0, 124.6, 129.0, 129.7, 130.5, 131.0, 131.5, 134.4, 136.3, 137.0, 137.6, 137.7, 139.3, 143.1, 146.8, 166.3, 191.9 ppm; MS (ES): *m*/*z* (%) = 416.1 (100) $[M+1]^+$; $C_{23}H_{17}N_3O_5$ (415.1168):calcd. for C 66.50, H 4.12, N 10.12; found C 66.61, H 4.15, N 10.18.

(*E*)-Methyl 1-(3-(2-nitrophenyl)-3-oxoprop-1-en-1-yl)-9-propyl-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (1dA). Yield: 91% (0.205 g from 0.150 g) as a yellow solid; m.p. 159-161 °C; R_f = 0.35 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1715 (CO_2CH_3), 1589 (CO); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.92 (t, *J* = 7.4 Hz, 3 H, $NCH_2CH_2CH_3$), 1.80–1.89 (m, 2 H, $NCH_2CH_2CH_3$), 4.03 (s, 3 H, CO_2CH_3), 4.38 (t, *J* = 7.5 Hz, 2 H, $NCH_2CH_2CH_3$), 7.37 (t, *J* = 7.4 Hz, 1 H, ArH), 7.49 (d, *J* = 8.3 Hz, 1 H, ArH), 7.62–7.70 (m, 3 H, ArH), 7.77–7.81 (m, 2 H, ArH), 8.17–8.20 (m, 3 H, ArH), 8.85 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 11.3, 23.3, 47.4, 52.7, 110.3, 118.4, 121.2, 121.4, 122.0, 124.6, 129.0, 129.6, 130.9, 131.0, 131.6, 134.3, 135.7, 136.8, 137.0, 137.6, 139.4, 142.6, 146.8, 166.3, 192.0 ppm; MS (ES): *m*/*z* (%) = 444.1 (100) $[M+1]^+$; $C_{25}H_{21}N_3O_5$ (443.1481):calcd. for C 67.71, H 4.77, N 9.48; found C 67.89, H 4.79, N 9.53.

(*E*)-Methyl 9-benzyl-1-(3-(2-nitrophenyl)-3-oxoprop-1-en-1-yl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (1hA). Yield: 84% (0.18 g from 0.15 g) as a yellow solid; m.p. 179-181 °C; R_f = 0.37 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1711 (CO_2CH_3), 1593 (CO); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.05 (s, 3 H, CO_2CH_3), 5.58 (s, 2 H, NCH_2), 6.83 (d, *J* = 7.1 Hz, 2 H, ArH), 7.15–7.20 (m, 3 H, ArH), 7.34–7.42 (m, 3 H, ArH), 7.54 (t, *J* = 7.6 Hz, 1 H, ArH), 7.58–7.62 (m, 2 H, ArH), 7.71 (q, *J* = 15.3 Hz, 2 H, ArH), 8.03 (d, *J* = 8.1 Hz, 1 H, ArH), 8.22 (d, *J* = 7.7 Hz, 1 H, ArH), 8.89 (s, 1 H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 49.3, 52.9, 110.3, 118.4, 121.4, 121.9, 122.1, 124.5, 125.3, 128.0, 128.6, 129.3, 130.0, 130.5, 131.7, 132.0, 134.0, 135.7, 136.1, 136.4, 137.2, 138.2, 140.4, 142.9, 146.5, 166.3, 192.5 ppm; MS (ES): *m*/*z* (%) = 492.1 (100) $[M+1]^+$; $C_{29}H_{21}N_3O_5$ (491.1481):calcd. for C 70.87, H 4.31, N 8.55; found C 70.99, H 4.31, N 8.57.

Experimental procedure for the synthesis of β-carboline-substituted benzothiophenone derivatives (2aA, **2bA**, **2dA, and 2hA) as exemplified for compound 2bA.** In a 10 mL round-bottomed flask, **1bA** (0.20 g, 0.482 mmol), sulfur powder (0.077 g, 2.41 mmol), and Et_3N (0.336 mL, 2.41 mmol) in DMSO (1 mL) were added, and the mixture stirred at 70 °C for 18 min. After completion of the reaction (TLC), the crude mixture was directly purified by column chromatography on silica gel ($CHCl_3$/MeOH 95:5, v/v) to afford 0.15 g (78%) of **2bA** as orange solid.

One-pot experimental procedure for the synthesis of 2aA–**nA**, **2bB**, **2hB**, **4aA**–**gA,** and **4eB as exemplified for compound 2bA.** In a 10 mL round-bottomed flask, to the stirred solution of KOH (0.033 g, 0.587 mmol) in dry MeOH (4 mL), 2-nitroacetophenone (0.080 mL, 0.587 mmol) was added at room temperature, and the reaction mixture was stirred for 15 min. Thereafter, **1b** (0.15 g, 0.560 mmol) was added portionwise and the reaction mixture was allowed to stirred for additional 1 h at room temperature. After completion of the reaction (TLC), excess MeOH was decanted and then evaporated under reduced pressure. Afterwards, the crude chalcone **1bA** was dissolved in DMSO (1.5 mL), followed by the sequential addition of sulfur powder (0.089 g, 2.80 mmol) and Et_3N (0.390 mL, 2.80 mmol) at room temperature. The reaction mixture was stirred at 70 °C for 18 min. After completion of the reaction (TLC), the mixture was directly purified by column chromatography on silica gel ($CHCl_3$/MeOH 95:5, v/v) to afford the analytically pure product **2bA** as orange solid in 74% yield (two step yield).

(*Z*)-Methyl 1-((3-oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2aA). Yield: 35% (0.08 g from 0.15 g) as an orange solid; m.p. 264-266 ^oC; R_f = 0.50 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 3248 (NH), 1710 (CO_2CH_3), 1659 (C=O); ^1H NMR (400 MHz, $CDCl_3$) δ = ^1H NMR (400 MHz, DMSO-d_6) δ = 4.03 (s, 3 H, CO_2CH_3), 7.36–7.41 (m, 2 H, ArH), 7.67 (d, *J* = 8.0 Hz, 1 H, ArH), 7.69–7.75 (m, 2 H, ArH), 7.78 (d, *J* = 7.9 Hz, 1 H, ArH), 7.91 (d, *J* = 7.6 Hz, 1 H, ArH), 8.46 (d, *J* = 7.9 Hz, 1 H, ArH), 8.64 (s, 1 H, ArH), 8.95 (s, 1 H, ArH), 12.89 (s, 1 H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 47.6, 121.6, 123.0, 124.7, 125.1, 126.4, 126.9, 129.8, 130.2, 131.0, 135.6, 136.3, 136.6, 137.0, 138.4, 141.5, 150.2, 166.0, 189.2 ppm; HRMS (ESI) m/z: calcd. for $C_{22}H_{14}N_2O_3S$ [M + Na^+]: 409.0623, found: 409.0673.

(*Z*)-Methyl 9-methyl-1-((3-oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2bA). Yield: 74% (0.166 g from 0.150 g) as an orange solid; m.p. 274-276 °C; R_f = 0.55 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1704 (CO_2CH_3), 1661 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.13 (s, 3 H, NCH_3), 4.31 (s, 3 H, CO_2CH_3), 7.27 (d, *J* = 6.6 Hz, 1 H, ArH), 7.38 (t, *J* = 7.2 Hz, 1 H, ArH), 7.56 (t, *J* = 6.9 Hz, 3 H, ArH), 7.67 (d, *J* = 7.6 Hz, 1 H, ArH), 7.92 (d, *J* = 7.9 Hz, 1 H, ArH), 8.18 (d, *J* = 7.7 Hz, 1 H, ArH), 8.69 (s, 1 H, ArH), 8.78 (s, 1 H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 33.6, 52.7, 110.2, 117.5, 121.4, 121.9, 124.4, 124.6, 125.5, 126.9, 129.5, 130.7, 131.0, 135.6, 136.7, 136.8, 137.1, 138.0, 142.8, 150.8, 166.3, 189.7 ppm; HRMS (ESI) m/z: calcd. for $C_{23}H_{16}N_2O_3S$ [M + Na^+]: 423.0779, found: 423.0725.

(*Z*)-Methyl 9-ethyl-1-((3-oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2cA). Yield: 75% (0.11 g from 0.10 g) as an orange solid; m.p. 210-212 °C; R_f = 0.56 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1709 (CO_2CH_3), 1672 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.68 (t, *J* = 7.2 Hz, 3 H, NCH_2CH_3), 4.14 (s, 3 H, CO_2CH_3), 4.76 (q, *J* = 7.2 Hz, 2 H, NCH_2CH_3), 7.26–7.30 (m, 1 H, ArH), 7.40 (t, *J* = 7.5 Hz, 1 H, ArH), 7.57 (dd, J_1 = 5.3 Hz, J_2 = 4.2 Hz, 2 H, ArH), 7.59 (d, *J* = 0.9 Hz, 1 H, ArH), 7.66–7.70 (m, 1 H, ArH), 7.93 (dt, J_1 = 7.7 Hz, J_2 = 1.0 Hz, 1 H, ArH), 8.21 (d, *J* = 7.8 Hz, 1 H, ArH), 8.59 (s, 1 H, ArH), 8.82 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.8, 40.9, 52.8, 110.0, 117.6, 121.4, 121.5, 122.0, 124.4, 124.6, 125.6, 126.8, 129.5, 130.7, 131.2, 135.6, 136.2, 137.1, 137.2, 142.0, 150.8, 166.3, 189.7 ppm; HRMS (ESI) m/z: calcd. for $C_{24}H_{18}N_2O_3S$ [M + Na^+]: 437.0936, found: 437.0972.

(*Z*)-Methyl 1-((3-oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-9-propyl-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2dA). Yield: 83% (0.18 g from 0.15 g) as an orange solid; m.p. 184-186 °C; R_f = 0.57 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1710 (CO_2CH_3), 1662 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.19 (t, *J* = 7.3 Hz, 3 H, $NCH_2CH_2CH_3$), 2.04–2.10 (m, 2 H, $NCH_2CH_2CH_3$), 4.13 (s, 3 H, CO_2CH_3), 4.59 (t, *J* = 7.2 Hz, 2 H, $NCH_2CH_2CH_3$), 7.25–7.29 (m, 1 H, ArH), 7.36 (t, *J* = 7.2 Hz, 1 H, ArH), 7.55 (t, *J* = 5.6 Hz, 3 H, ArH), 7.63 (d, *J* = 7.2 Hz, 1 H, ArH), 7.90 (d, *J* = 7.4 Hz, 1 H, ArH), 8.16 (d, *J* = 7.1 Hz, 1 H, ArH), 8.51 (s, 1 H, ArH), 8.76 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 11.4, 23.2, 47.4, 52.7, 110.2, 117.4, 121.3, 121.8, 124.3, 124.6, 125.4, 126.7, 129.4, 130.6, 131.1, 135.5, 136.7, 136.8, 137.1, 138.0, 142.8,

150.7, 166.2, 190.0 ppm; HRMS (ESI) m/z: calcd. for $C_{25}H_{20}N_2O_3S$ [M + H^+]: 429.1273, found: 429.1310.

(*Z*)-Methyl 9-butyl-1-((3-oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2eA). Yield: 77% (0.165 g from 0.15 g) as an orange solid; m.p. 192-194 °C; R_f = 0.60 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1711 (CO_2CH_3), 1670 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.07 (t, *J* = 7.4 Hz, 3 H, $NCH_2CH_2CH_2CH_3$), 1.59–1.68 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 2.00–2.07 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 4.15 (s, 3 H, CO_2CH_3), 4.69 (t, *J* = 7.7 Hz, 2 H, $NCH_2CH_2CH_2CH_3$), 7.26–7.30 (m, 1 H, ArH), 7.40 (t, *J* = 7.5 Hz, 1 H, ArH), 7.56–7.60 (m, 3 H, ArH), 7.66–7.77 (m, 1 H, ArH), 7.92–7.95 (m, 1 H, ArH), 8.21 (d, *J* = 7.8 Hz, 1 H, ArH), 8.60 (s, 1 H, ArH), 8.83 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0, 20.5, 31.9, 52.8, 57.6, 110.0, 110.3, 117.5, 121.4, 121.9, 124.5, 124.7, 125.6, 126.8, 129.5, 130.7, 135.6, 136.3, 137.1, 142.5, 150.8, 166.3, 184.0 ppm; HRMS (ESI) m/z: calcd. for $C_{26}H_{22}N_2O_3S$ [M + Na^+]: 465.1249, found: 465.1247.

(*Z*)-Methyl 9-allyl-1-((3-oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2fA). Yield: 70% (0.152 g from 0.15 g) as a bright yellow solid; m.p. 183-185 °C; R_f = 0.57 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1701 (CO_2CH_3), 1665 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.11 (s, 3 H, CO_2CH_3), 5.12 (d, *J* = 17.2 Hz, 1 H, =C*H*H), 5.26 (d, *J* = 1.7 Hz, 2 H, NCH_2), 5.33 (d, *J* = 10.6 Hz, 1 H, =CH*H*), 6.19–6.26 (m, 1 H, CH_2CH), 7.23–7.25 (m, 1 H, ArH), 7.38 (t, *J* = 7.4 Hz, 1 H, ArH), 7.48 (d, *J* = 8.3 Hz, 1 H, ArH), 7.54 (d, *J* = 3.2 Hz, 2 H, ArH), 7.64 (t, *J* = 7.7 Hz, 1 H, ArH), 7.87 (d, *J* = 7.6 Hz, 1 H, ArH), 8.17 (d, *J* = 7.8 Hz, 1 H, ArH), 8.46 (s, 1 H, ArH), 8.76 (s, 1 H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 48.2, 52.8, 110.2, 117.4, 118.2, 121.4, 121.6, 121.9, 124.4, 125.0, 125.5, 126.7, 129.6, 130.6, 131.1, 131.4, 135.5, 136.3, 136.7, 137.3, 137.5, 142.4, 150.7, 166.2, 189.6 ppm; HRMS (ESI) m/z: calcd. for $C_{25}H_{18}N_2O_3S$ [M + Na^+]: 449.0936, found: 449.0982.

(*Z*)-Methyl 1-((3-oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-9-(prop-2-yn-1-yl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2gA). Yield: 45% (0.13 g from 0.20 g) as a dark yellow solid; m.p. 234-236 °C; R_f = 0.60 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1704 (CO_2CH_3), 1673 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.50 (t, *J* = 2.4 Hz, 1 H, C≡CH), 4.14 (s, 3 H, CO_2CH_3), 5.39 (d, *J* = 2.4 Hz, 2 H, CH_2), 7.25–7.29 (m, 1 H, ArH), 7.42 (t, *J* = 7.5 Hz, 1 H, ArH), 7.57 (dd, J_1 = 4.6 Hz, J_2 = 1.0 Hz, 2 H, ArH), 7.60 (d, *J* = 8.3 Hz, 1 H, ArH), 7.68–7.72 (m, 1 H, ArH), 7.92 (d, *J* = 7.7 Hz, 1 H, ArH), 8.19 (d, *J* = 7.8 Hz, 1 H, ArH), 8.76 (s, 1 H, ArH), 8.78 (s, 1

H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 36.0, 52.9, 75.1, 76.8, 110.1, 117.4, 121.7, 122.0, 122.1, 124.4, 124.7, 125.5, 126.8, 129.8, 130.7, 131.6, 135.6, 136.8, 137.0, 137.3, 137.9, 141.9, 150.6, 166.1, 189.6 ppm; HRMS (ESI) m/z: calcd. for $C_{25}H_{16}N_2O_3S$ [M + Na^+]: 447.0779, found: 447.0788.

(*Z*)-Methyl 9-benzyl-1-((3-oxobenzo[b]thiophen-2(3*H*)-ylidene)methyl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2hA). Yield: 78% (0.162 g from 0.150 g) as an orange solid; m.p. 244-246 °C; R_f = 0.60 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1712 (CO_2CH_3), 1675 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.13 (s, 3 H, CO_2CH_3), 5.92 (s, 2 H, NCH_2), 7.20 (d, *J* = 7.5 Hz, 2 H, ArH), 7.22–7.25 (m, 2 H, ArH), 7.31 (d, *J* = 7.7 Hz, 2 H, ArH), 7.43 (d, *J* = 7.5 Hz, 1 H, ArH), 7.52 (t, *J* = 5.6 Hz, 2 H, ArH), 7.58 (d, *J* = 8.3 Hz, 1 H, ArH), 7.68 (t, *J* = 7.6 Hz, 1 H, ArH), 7.85 (d, *J* = 7.6 Hz, 1 H, ArH), 8.26 (d, *J* = 7.8 Hz, 1 H, ArH), 8.39 (s, 1 H, ArH), 8.84 (s, 1 H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 49.4, 52.7, 110.3, 117.4, 121.4, 121.8, 122.0, 124.3, 124.9, 125.5, 126.1, 126.7, 128.3, 129.3, 129.8, 130.6, 131.4, 135.4, 135.6, 136.7, 136.8, 137.4, 137.5, 143.1, 150.6, 166.2, 189.4 ppm; HRMS (ESI) m/z: calcd. for $C_{29}H_{20}N_2O_3S$ [M + Na^+]: 499.1092, found: 499.1119.

(*Z*)-Methyl 9-(2-nitrobenzyl)-1-((3-oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2iA). Yield: 67% (0.135 g from 0.15 g) as a dark brown solid; m.p. 238-240 °C; R_f = 0.55 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1712 (CO_2CH_3), 1675 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.11 (s, 3 H, CO_2CH_3), 6.33 (s, 2 H, NCH_2), 6.64 (d, *J* = 7.7 Hz, 1 H, ArH), 7.17–7.20 (m, 1 H, ArH), 7.36 (t, *J* = 7.7 Hz, 1 H, ArH), 7.43–7.47 (m, 2 H, ArH), 7.49 (t, *J* = 5.8 Hz, 3 H, ArH), 7.65 (t, *J* = 7.5 Hz, 1 H, ArH), 7.77 (d, *J* = 7.6 Hz, 1 H, ArH), 7.85 (s, 1 H, ArH), 8.25 (d, *J* = 7.8 Hz, 1 H, ArH), 8.47 (dd, J_1 = 8.2 Hz, J_2 = 0.9 Hz, 1 H, ArH), 8.79 (s, 1 H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 48.1, 52.9, 110.0, 117.3, 121.6, 122.1, 122.2, 123.2, 124.3, 125.5, 126.5, 126.8, 127.3, 129.3, 130.0, 130.3, 131.4, 132.3, 134.8, 135.4, 136.6, 137.1, 137.2, 138.0, 142.5, 147.1, 150.1, 166.1, 188.8 ppm; HRMS (ESI) m/z: calcd. for $C_{29}H_{19}N_3O_5S$ [M + Na^+]: 544.0943, found: 544.0899.

(*Z*)-Isopropyl 9-methyl-1-((3-oxobenzo[b]thiophen-2(3*H*)-ylidene)methyl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2jA). Yield: 64% (0.14 g from 0.15 g) as an orange solid; m.p. 180-182 °C; R_f = 0.56 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1703 (CO_2*i*-Pr), 1662 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.58 (d, *J* = 6.9 Hz, 6 H, $CO_2CH(CH_3)_2$), 4.14 (s, 1 H, $CO_2CH(CH_3)_2$), 4.32 (s, 3 H, NCH_3), 7.26–7.29 (m, 1 H, ArH), 7.39 (t, *J* = 7.5 Hz, 1 H, ArH), 7.51–7.58 (m, 3 H,

ArH), 7.68 (t, *J* = 7.7 Hz, 1 H, ArH), 7.92 (d, *J* = 7.6 Hz, 1 H, ArH), 8.20 (t, *J* = 7.6 Hz, 1 H, ArH), 8.70 (d, *J* = 3.9 Hz, 1 H, ArH), 8.79 (d, *J* = 4.7 Hz, 1 H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 22.5, 52.9, 69.5, 110.2, 117.2, 117.5, 121.4, 121.9, 124.3, 124.5, 125.5, 126.9, 129.5, 130.7, 131.1, 135.6, 136.4, 136.7, 136.8, 137.1, 142.7, 150.8, 166.2, 189.6 ppm; HRMS (ESI) m/z: calcd. for $C_{25}H_{20}N_2O_3S$ [M + Na^+]: 451.1092, found: 451.1136.

(*Z*)-2-((9-Methyl-9*H*-pyrido[3,4-*b*]indol-1-yl)methylene)benzo[*b*]thiophen-3(2*H*)-one (2lA). Yield: 77% (0.126 g from 0.100 g) as an orange solid; m.p. 248-250 °C; R_f = 0.75 (hexane/EtOAc, 70:30, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.29 (s, 3 H, NCH_3), 7.27–7.35 (m, 2 H, ArH), 7.53 (dd, J_1 = 8.2 Hz, J_2 = 1.8 Hz, 2 H, ArH), 7.56 (dd, J_1 = 6.7 Hz, J_2 = 1.2 Hz, 1 H, ArH), 7.63–7.67 (m, 1 H, ArH), 7.93–7.95 (m, 1 H, ArH), 7.97 (d, *J* = 4.9 Hz, 1 H, ArH), 8.14 (d, *J* = 7.7 Hz, 1 H, ArH), 8.68 (d, *J* = 4.9 Hz, 1 H, ArH), 8.77 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 33.6, 109.8, 115.1, 120.5, 121.0, 121.7, 124.2, 125.4, 125.9, 126.8, 129.1, 130.8, 130.9, 134.8, 135.4, 137.2, 138.6, 142.4, 150.7, 189.5 ppm; HRMS (ESI) m/z: calcd. for $C_{21}H_{14}N_2OS$ [M + H^+]: 343.0905, found: 343.0939.

(*Z*)-2-((9-Ethyl-9*H*-pyrido[3,4-*b*]indol-1-yl)methylene)benzo[*b*]thiophen-3(2*H*)-one (2mA). Yield: 74% (0.176 g from 0.15 g) as an orange solid; m.p. 256-258 °C; R_f = 0.80 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1588 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.66 (t, *J* = 7.2 Hz, 3 H, NCH_2CH_3), 4.73 (q, *J* = 7.2 Hz, 2 H, NCH_2CH_3), 7.26–7.29 (m, 1 H, ArH), 7.33 (t, *J* = 7.5 Hz, 1 H, ArH), 7.54 (dd, J_1 = 12.2 Hz, J_2 = 8.0 Hz, 3 H, ArH), 7.64 (t, *J* = 7.7 Hz, 1 H, ArH), 7.93 (d, *J* = 7.6 Hz, 1 H, ArH), 7.97 (d, *J* = 4.9 Hz, 1 H, ArH), 8.15 (d, *J* = 7.8 Hz, 1 H, ArH), 8.64 (s, 1 H, ArH), 8.67 (d, *J* = 4.9 Hz, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.6, 40.7, 109.6, 115.2, 120.5, 121.2, 121.7, 124.2, 125.4, 125.9, 126.8, 129.1, 130.9, 131.0, 135.1, 135.4, 136.2, 136.4, 138.4, 141.7, 150.7, 189.6 ppm; HRMS (ESI) m/z: calcd. for $C_{22}H_{16}N_2OS$ [M + H^+]: 357.1062, found: 357.1071.

(*Z*)-2-((9-Benzyl-9*H*-pyrido[3,4-*b*]indol-1-yl)methylene)benzo[*b*]thiophen-3(2*H*)-one (2nA). Yield: 60% (0.132 g from 0.15 g) as an orange solid; m.p. 228-231 °C; R_f = 0.85 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1672 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.85 (s, 2 H, CH_2Ph), 7.20–7.24 (m, 3 H, ArH), 7.27 (d, *J* = 8.7 Hz, 1 H, ArH), 7.33 (d, *J* = 7.5 Hz, 2 H, ArH), 7.37 (d, *J* = 7.4 Hz, 1 H, ArH), 7.46 (d, *J* = 7.7 Hz, 1 H, ArH), 7.51 (t, *J* = 8.0 Hz, 2 H, ArH), 7.62 (t, *J* = 7.6 Hz, 1 H, ArH), 7.85 (d, *J* = 7.6 Hz, 1 H, ArH), 7.98 (d, *J* = 5.5 Hz, 1 H, ArH), 8.18 (d, *J* = 7.8 Hz, 1 H, ArH), 8.40 (s, 1 H, ArH), 8.66 (d, *J* = 5.0 Hz, 1 H, ArH) ppm; ^{13}C NMR (125

MHz, $CDCl_3$) δ = 49.3, 109.9, 115.1, 120.9, 121.1, 121.8, 124.1, 125.3, 126.1, 126.3, 126.6, 128.1, 129.2, 129.4, 130.8, 131.1, 134.8, 135.2, 136.1, 136.5, 136.9, 138.8, 142.7, 150.5, 189.3 ppm; HRMS (ESI) m/z: calcd. for $C_{27}H_{18}N_2OS$ [M + Na^+]: 441.1038, found: 441.1066.

(*Z*)-Methyl 1-((5-chloro-3-oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-9-methyl-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2bB). Yield: 65% (0.157 g from 0.15 g) as an orange solid; m.p. >250 °C; R_f = 0.75 (hexane/EtOAc, 80:20, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.13 (s, 3 H, CO_2CH_3), 4.32 (s, 3 H, NCH_3), 7.23 (d, *J* = 8.2 Hz, 1 H, ArH), 7.39 (t, *J* = 7.4 Hz, 1 H, ArH), 7.56 (d, *J* = 8.1 Hz, 2 H, ArH), 7.67–7.71 (m, 1 H, ArH), 7.83 (d, *J* = 8.1 Hz, 1 H, ArH), 8.18 (d, *J* = 7.7 Hz, 1 H, ArH), 8.69 (s, 1 H, ArH), 8.80 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 33.6, 52.9, 110.2, 117.7, 121.5, 121.9, 124.3, 125.2, 126.2, 127.6, 129.6, 131.2, 137.1, 142.1, 142.8, 152.5, 159.2, 162.7, 166.2, 188.2 ppm; HRMS (ESI) m/z: calcd. for $C_{23}H_{15}ClN_2O_3S$ [M + H^+]: 435.0570, found: 435.0570.

(*Z*)-methyl 9-benzyl-1-((5-chloro-3-oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (2hB). Yield: 68% (0.100 g from 0.100 g) as an orange solid; m.p. 232-234 °C; R_f = 0.85 (hexane/EtOAc, 80:20, v/v); IR (neat): ν_{max} = 1662 (C=O); ^{1}H NMR and ^{13}C NMR spectra could not be recorded due to solubility problem; HRMS (ESI) m/z: calcd. for $C_{29}H_{19}ClN_2O_3S$ [M + H^+]: 511.0883, found: 511.0869.

(*Z*)-2-((1-Methyl-9*H*-pyrido[3,4-*b*]indol-3-yl)methylene)benzo[*b*]thiophen-3(2*H*)-one (4aA). Yield: 51% (0.125 g from 0.150 g) as a brown solid; m.p. 223-225 °C; R_f = 0.50 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} = 3283 (NH), 1658 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6) δ = 2.90 (s, 3 H, $ArCH_3$), 7.31 (dd, J_1 = 15.7 Hz, J_2 = 7.8 Hz, 2 H, ArH), 7.58 (t, *J* = 7.5 Hz, 1 H, ArH), 7.63–7.67 (m, 2 H, ArH), 7.74 (d, *J* = 7.8 Hz, 1 H, ArH), 7.82 (d, *J* = 7.6 Hz, 1 H, ArH), 8.05 (s, 1 H, ArH), 8.21 (d, *J* = 7.8 Hz, 1 H, ArH), 8.50 (s, 1 H, ArH), 12.03 (s, 1 H, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 20.4, 112.4, 119.3, 120.2, 121.1, 121.8, 124.3, 125.3, 125.9, 127.5, 128.4, 129.7, 130.3, 134.3, 135.3, 140.7, 142.6, 188.2 ppm; HRMS (ESI) m/z: calcd. for $C_{21}H_{14}N_2OS$ [M - H^+]: 341.0749, found: 341.0766.

(*Z*)-2-((1,9-Dimethyl-9*H*-pyrido[3,4-*b*]indol-3-yl)methylene)benzo[*b*]thiophen-3(2*H*)-one (4bA). Yield: 78% (0.124 g from 0.10 g) as a brown solid; m.p. 218-221 °C; R_f = 0.60 (hexane/EtOAc, 60:40, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.25 (s, 3 H, $ArCH_3$), 4.22 (s, 3 H, NCH_3), 7.26 (d, *J* = 3.8 Hz, 1 H, ArH), 7.37 (t, *J* = 7.5 Hz, 1 H, ArH), 7.50 (d, *J* = 8.4 Hz, 1 H,

ArH), 7.57 (d, *J* = 3.5 Hz, 2 H, ArH), 7.65 (t, *J* = 7.5 Hz, 1 H, ArH), 7.95 (d, *J* = 7.6 Hz, 1 H, ArH), 8.10 (s, 1 H, ArH), 8.15 (s, 1 H, ArH), 8.17 (d, *J* = 7.8 Hz, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 23.9, 32.5, 109.9, 118.5, 120.6, 121.7, 124.0, 125.0, 126.7, 128.6, 129.3, 131.3, 131.8, 134.9, 135.4, 141.6, 142.2, 142.4, 150.4, 189.6 ppm; HRMS (ESI) m/z: calcd. for $C_{22}H_{16}N_2OS$ [M + H^+]: 357.1061, found: 357.1066.

(*Z*)-2-((1-(Dimethoxymethyl)-9*H*-pyrido[3,4-*b*]indol-3-yl)methylene)benzo[*b*]thiophen-3(2*H*)-one (4cA). Yield: 57% (0.085 g from 0.100 g) as a brown solid; m.p. 188-190 ^{o}C; R_f = 0.70 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 3404 (NH), 1662 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.62 (s, 6 H, $CH(OCH_3)_2$), 5.83 (s, 1 H, CH), 7.22–7.25 (m, 1 H, ArH), 7.31 (td, J_1 = 6.4 Hz, J_2 = 3.1 Hz, 1 H, ArH), 7.52–7.54 (m, 2 H, ArH), 7.56 (d, *J* = 6.2 Hz, 2 H, ArH), 7.91 (d, *J* = 7.7 Hz, 1 H, ArH), 8.10 (s, 1 H, ArH), 8.14 (d, *J* = 7.9 Hz, 1 H, ArH), 8.21 (s, 1 H, ArH), 9.41 (s, 1 H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 55.0, 106.8, 112.1, 120.0, 120.7, 121.2, 121.8, 124.0, 125.1, 126.7, 129.1, 130.7, 131.1, 131.6, 131.9, 132.9, 135.0, 140.6, 141.8, 150.2, 189.7 ppm; HRMS (ESI) m/z: calcd. for $C_{23}H_{18}N_2O_3S$ [M + Na^+]: 425.0936, found: 425.0922.

(*Z*)-2-((1-(Dimethoxymethyl)-9-methyl-9*H*-pyrido[3,4-*b*]indol-3-yl)methylene)benzo[*b*] thiophen-3(2*H*)-one (4dA). Yield: 68% (0.10 g from 0.10 g) as a brown solid; m.p. 182-184 ^{o}C; R_f = 0.75 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} = 1665 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.64 (s, 6 H, $CH(OCH_3)_2$), 4.23 (s, 3 H, NCH_3), 5.84 (s, 1 H, CH), 7.22–7.26 (m, 1 H, ArH), 7.34 (t, *J* = 7.4 Hz, 1 H, ArH), 7.51 (d, *J* = 8.3 Hz, 1 H, ArH), 7.55 (d, *J* = 3.2 Hz, 2 H, ArH), 7.63 (t, *J* = 7.6 Hz, 1 H, ArH), 7.93 (d, *J* = 7.6 Hz, 1 H, ArH), 8.11 (s, 1 H, ArH), 8.15 (d, *J* = 7.7 Hz, 1 H, ArH), 8.26 (s, 1 H, ArH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 33.7, 56.1, 110.3, 110.4, 120.1, 120.6, 121.2, 121.3, 124.0, 125.1, 126.7, 128.9, 131.2, 131.4, 131.6, 134.0, 134.9, 140.1, 141.3, 143.0, 150.2, 189.5 ppm; HRMS (ESI) m/z: calcd. for $C_{24}H_{20}N_2O_3S$ [M + Na^+]: 439.1092, found: 439.1129.

(*Z*)-2-((1-(4-Fluorophenyl)-9*H*-pyrido[3,4-*b*]indol-3-yl)methylene)benzo[*b*]thiophen-3(2*H*)-one (4eA). Yield: 69% (0.10 g from 0.10 g) as a brown solid; R_f = 0.60 (hexane/EtOAc, 80:20, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (dd, J_1 = 7.5 Hz, J_2 = 3.8 Hz, 1 H, ArH), 7.30 (d, *J* = 8.3 Hz, 2 H, ArH), 7.48 (d, *J* = 3.3 Hz, 3 H, ArH), 7.58 (d, *J* = 7.5 Hz, 2 H, ArH), 7.80 (d, *J* = 7.6 Hz, 1 H, ArH), 8.04 (s, 1 H, ArH), 8.08 (d, *J* = 8.2 Hz, 1 H, ArH), 8.17 (d, *J* = 10.3 Hz, 1 H, ArH), 8.20–8.26 (m, 2 H, ArH), 11.23 (s, 1 H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 112.5, 115.7, 115.9, 119.2, 120.6, 121.5, 124.0, 124.9, 126.4, 128.6, 130.5, 130.7, 130.8, 131.9, 133.1,

134.3, 134.8, 141.4, 149.9, 189.4 ppm; HRMS (ESI) m/z: calcd. for $C_{26}H_{15}FN_2OS$ [M + H^+]: 423.0967, found: 423.0956.

(*Z*)-2-((1-(4-Fluorophenyl)-9-methyl-9*H*-pyrido[3,4-*b*]indol-3-yl)methylene)benzo[*b*]thiophen-3(2*H*)-one (4fA). Yield: 79% (0.113 g from 0.10 g) as an brown solid; R_f = 0.65 (hexane/EtOAc, 80:30, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.58 (s, 3 H, NCH_3), 7.21–7.24 (m, 1 H, ArH), 7.33 (d, *J* = 8.7 Hz, 2 H, ArH), 7.39 (s, 1 H, ArH), 7.50 (dd, J_1 = 7.1 Hz, J_2 = 3.0 Hz, 3 H, ArH), 7.64–7.67 (m, 1 H, ArH), 7.84 (dd, J_1 = 8.7 Hz, J_2 = 5.4 Hz, 2 H, ArH), 7.90 (d, *J* = 7.6 Hz, 1 H, ArH), 8.14 (s, 1 H, ArH), 8.21 (d, *J* = 7.8 Hz, 1 H, ArH), 8.25 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 33.7, 110.4, 115.4 (d, *J* = 21.0 Hz), 118.8, 121.0, 121.5, 121.8, 124.1, 125.1,126.7, 129.2, 131.0 (d, *J* = 6.0 Hz), 131.4, 131.8 (d, \ *J* = 8 Hz), 131.9, 132.0, 135.0, 142.2, 143.2, 143.5, 150.2, 163.5 (d, *J* = 251.2 Hz), 189.7 ppm; HRMS (ESI) m/z: calcd. for $C_{27}H_{17}FN_2OS$ [M + H^+]: 437.1124, found: 437.1109.

(*Z*)-2-((9-Ethyl-1-(4-fluorophenyl)-9*H*-pyrido[3,4-*b*]indol-3-yl)methylene)benzo[*b*]thiophen-3(2*H*)-one (4gA). Yield: 73% (0.103 g from 0.10 g) as a brown solid; R_f = 0.70 (hexane/EtOAc, 80:20, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.02 (t, *J* = 7.1 Hz, 3 H, NCH_2CH_3), 4.13 (q, *J* = 7.1 Hz, 2 H, NCH_2CH_3), 7.21–7.25 (m, 1 H, ArH), 7.29–7.34 (m, 2 H, ArH), 7.37 (d, *J* = 7.1 Hz, 1 H, ArH), 7.47–7.53 (m, 3 H, ArH), 7.62–7.66 (m, 1 H, ArH), 7.79–7.83 (m, 2 H, ArH), 7.92 (d, *J* = 7.2 Hz, 1 H, ArH), 8.16 (s, 1 H, ArH), 8.23 (d, *J* = 7.7 Hz, 1 H, ArH), 8.28 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.1, 39.7, 110.7, 115.5 (d, *J* = 21.0 Hz), 118.8, 120.9, 121.9, 124.1, 125.1, 126.7, 129.0, 131.1, 131.3 (d, *J* = 5.0 Hz), 131.8 (d, *J* = 44.0 Hz), 133.7, 134.8, 135.6, 142.3 (d, *J* = 31.0 Hz), 143.2, 150.3, 163.5 (d, *J* = 246.0 Hz), 189.7 ppm; HRMS (ESI) m/z: calcd. for $C_{28}H_{19}FN_2OS$ [M + H^+]: 451.1280, found: 451.1280.

(*Z*)-5-Chloro-2-((1-(4-fluorophenyl)-9*H*-pyrido[3,4-*b*]indol-3-yl)methylene)benzo[*b*]thiophen-3(2*H*)-one (4eB). Yield: 48% (0.076 g from 0.10 g) as an orange solid; m.p. 233-235 ^{o}C; R_f = 0.70 (hexane/EtOAc, 80:20, v/v); IR (neat): ν_{max} = 3383 (NH), 1669 (C=O); ^{1}H NMR and ^{13}C NMR spectra could not be recorded due to solubility problem; HRMS (ESI) m/z: calcd. for $C_{26}H_{14}ClFN_2OS$ [M + H^+]: 457.0578, found: 457.0565.

One-pot experimental procedure for the synthesis of 6C. In a 10 mL round-bottomed flask, to the stirred suspension of Cs_2CO_3 (0.182 g, 0.560 mmol) in dry THF (4 mL), **5** (0.100 g,

0.373 mmol) was added and the mixture stirred for 10 min. Thereafter, 2-nitrobenzaldehyde (**C**, 0.062 g, 0.410 mmol) was added and the reaction mixture was stirred for additional 2 h at room temperature. After completion of the reaction (TLC), THF was evaporated under reduced pressure. In a reaction vial, the crude chalcone **5C** was dissolved in DMSO (1 mL) followed by the sequential addition of sulfur powder (0.060 g, 1.86 mmol) and Et_3N (0.260 mL, 1.86 mmol) at room temperature. The reaction mixture was stirred at 70 °C for 1 h. After completion of the reaction, the mixture was directly purified by column chromatography on silica gel (hexane/EtOAc 60:40, v/v) to afford 0.056 g (39%) of **6C** as light-brown solid (two step yield).

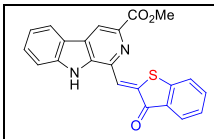
Methyl 1-(benzo[*b*]thiophene-2-carbonyl)-9-benzyl-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (6C). Yield: 39% (0.052 g from 0.10 g) as a yellow solid; m.p. 228-231 ^oC; R_f = 0.85 (hexane/EtOAc, 80:20, v/v); IR (neat): ν_{max} = 1658 (C=O); ^1H NMR (400 MHz, $CDCl_3$) δ = 4.04 (s, 3 H, CO_2CH_3), 5.75 (s, 2 H, NCH_2), 6.72–6.76 (m, 3 H, ArH), 6.81 (t, *J* = 7.2 Hz, 2 H, ArH), 7.34 (t, *J* = 7.8 Hz, 1 H, ArH), 7.43–7.48 (m, 2 H, ArH), 7.62 (d, *J* = 8.4 Hz, 1 H), 7.68–7.74 (m, 2 H, ArH), 7.75 (s, 1 H, ArH), 7.86 (dd, J_1 = 8.2 Hz, J_2 = 0.7 Hz, 1 H, ArH), 8.32 (d, *J* = 7.8 Hz, 1 H, ArH), 9.09 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 48.6, 53.0, 110.8, 119.5, 121.3, 121.8, 121.9, 122.8, 124.7, 126.4, 126.7, 127.5, 127.6, 128.4, 130.0, 132.6, 135.2, 135.4, 135.7, 136.1, 139.1, 139.4, 142.4, 143.6, 143.7, 166.2, 186.5 ppm; HRMS (ESI) m/z: calcd. for $C_{29}H_{20}N_2O_3S$ [M + H^+]: 477.1273, found: 477.1290.

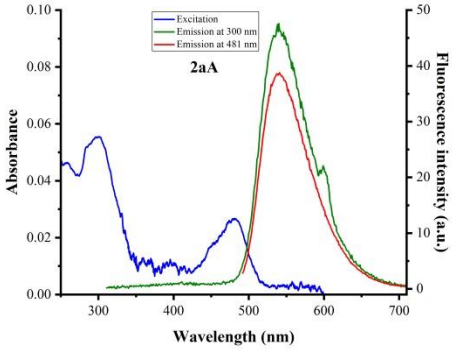
3. References:

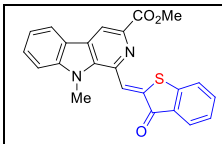
[1] Singh, D.; Kumar, V.; Devi, N.; Malakar, C. C.; Shankar, R.; Singh, V. *Adv. Synth. Catal.*, **2017**, *359*, 1213–1226.

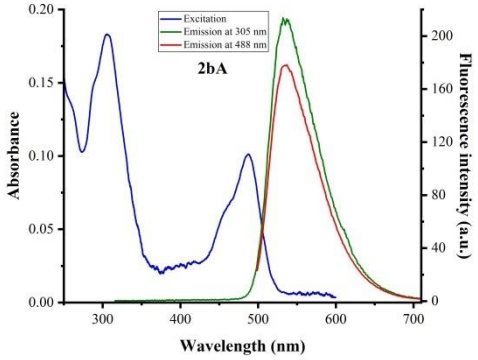
[2] Devi, N.; Singh, D.; Kaur, G.; Mor, S.; Putta, V. P. R. K.; Polina, S.; Malakar, C. C.; Singh, V. *New J. Chem.*, **2017**, *41*, 1082–1093.

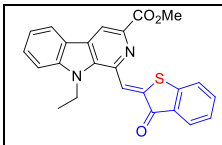
4. Photophysical properties and graphical data

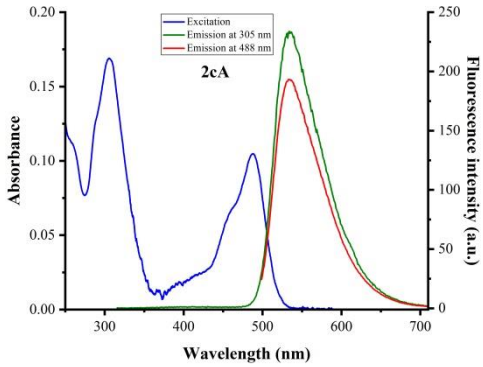
	UV-Vis	Fluorescence		
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	Φ_F
 **2aA**	300.50	539.95	47.61	0.186
	481.00	540.88	38.78	0.295

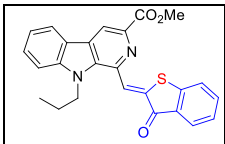


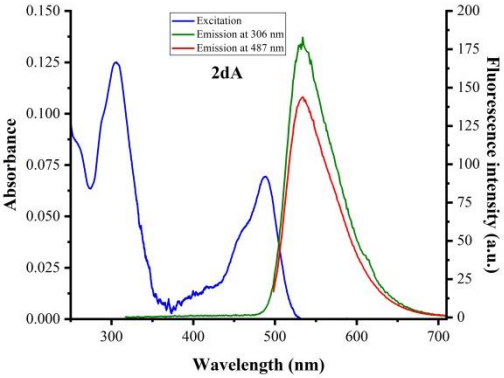
	UV-Vis	Fluorescence		
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	Φ_F
 2**bA**	305.20	531.94	213.81	0.229
	487.78	536.86	178.31	0.342



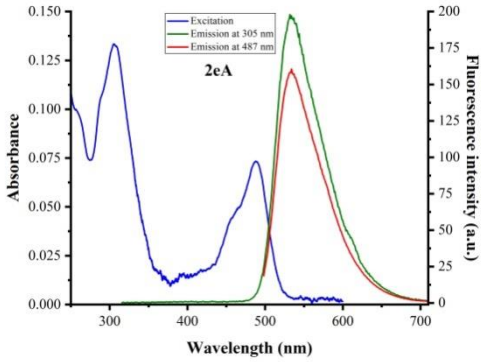
	UV-Vis	Fluorescence		
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	Φ_F
 **2cA**	305.40	533.89	233.89	0.265
	488.18	532.83	193.36	0.347



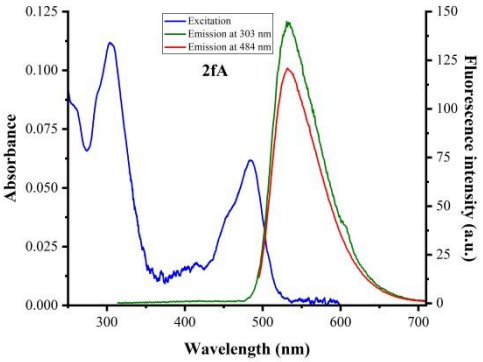
	UV-Vis	Fluorescence		
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	Φ_F
 **2dA**	306.13	534.02	182.87	0.274
	487.50	534.02	143.78	0.383



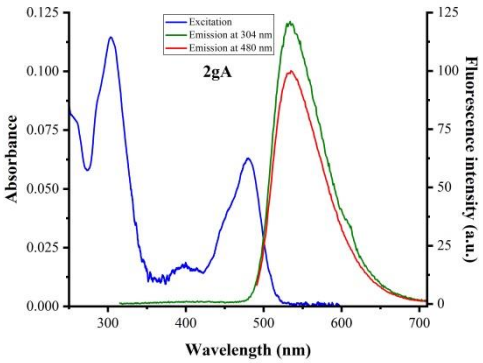
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2eA	304.93	531.94	197.94	0.279
	487.49	534.02	160.50	0.400



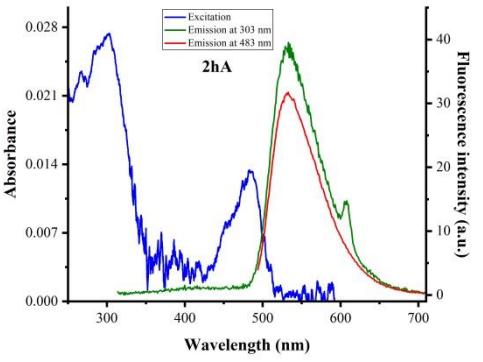
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2fA	303.41	530.89	144.88	0.256
	483.69	531.94	121.01	0.374



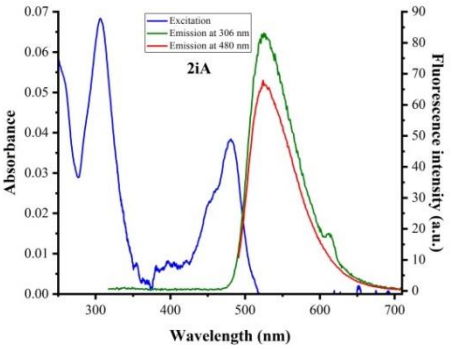
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2gA	303.61	534.02	121.25	0.221
	480.49	535.07	100.11	0.328



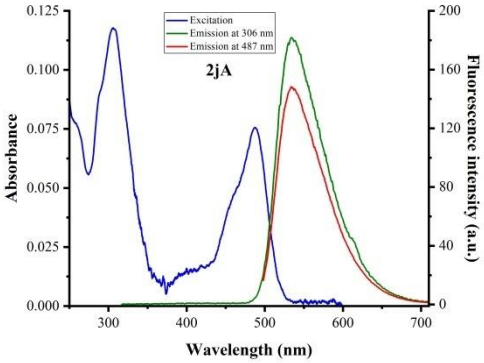
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2hA	303.21	532.98	39.57	0.302
	482.90	532.83	31.74	0.473



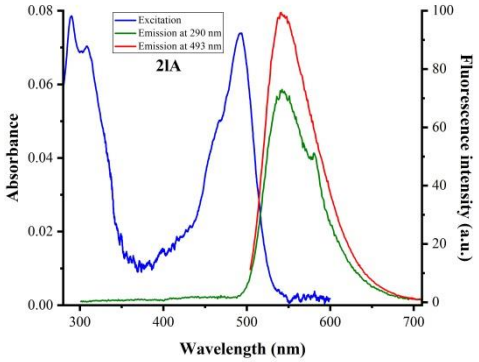
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2iA	306.21 480.08	525.07 524.91	83.13 67.85	0.243 0.337



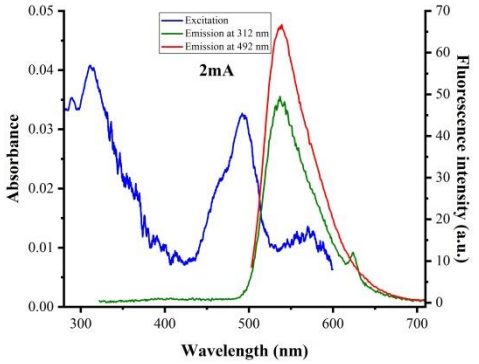
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2jA	305.89 487.51	534.02 534.98	181.82 148.43	0.304 0.378



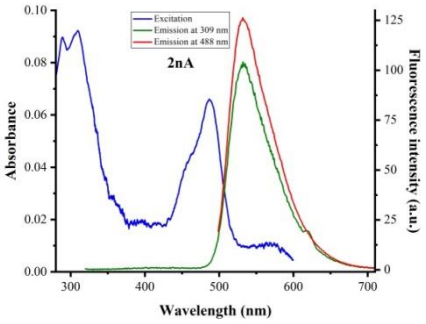
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2lA	289.98 492.53	542.05 541.08	72.89 99.43	0.189 0.253



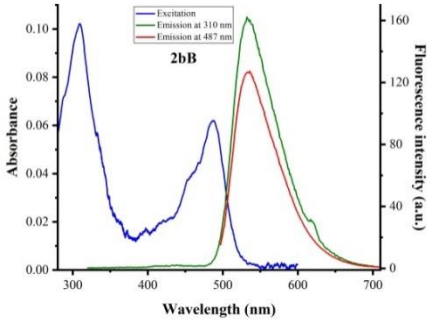
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2mA	311.59 491.81	537.01 538.95	49.49 66.73	0.223 0.366



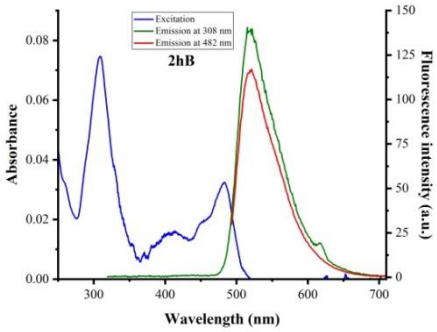
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2nA	309.56	531.94	104.13	0.213
	487.74	531.79	126.29	0.349



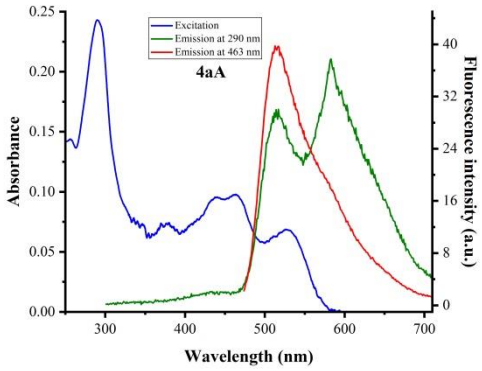
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2bB	309.67	531.94	162.21	0.301
	486.62	535.97	127.26	0.378



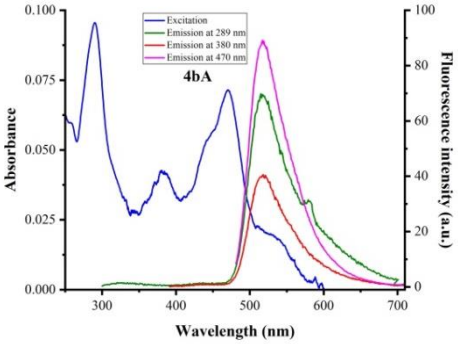
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2hB	308.54	515.78	140.57	0.330
	482.71	521.54	116.95	0.258



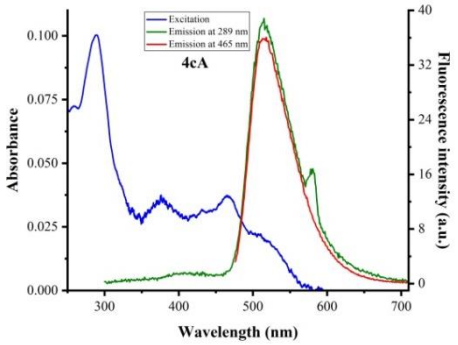
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
4aA	289.82	522.94	37.76	0.052
	463.50	512.83	39.76	0.095



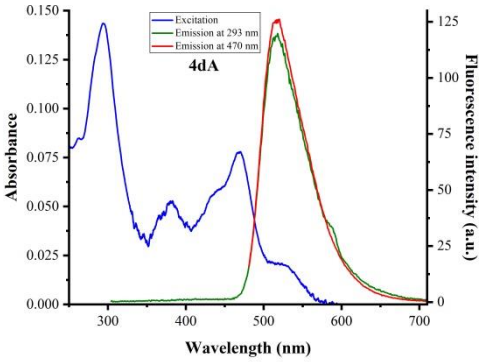
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
4bA	289.62	514.64	69.79	0.167
	380.09	518.04	40.58	0.179
	470.77	517.02	89.14	0.219



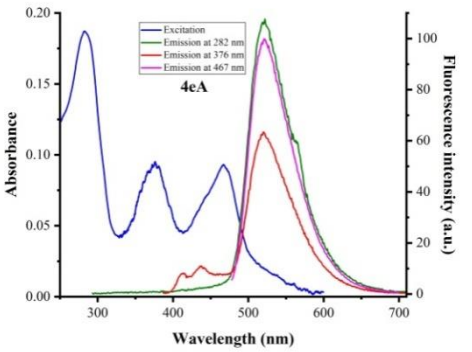
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
4cA	289.17	514.91	38.82	0.079
	465.41	518.05	36.06	0.179



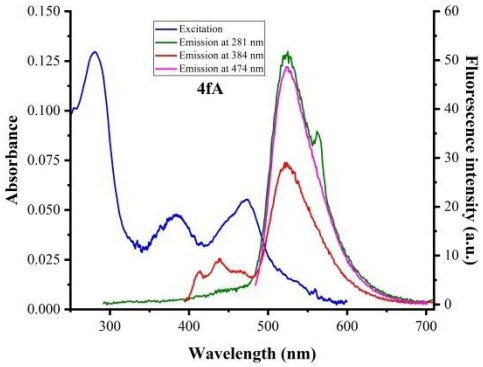
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
4dA	293.41	518.05	119.83	0.160
	470.59	520.01	126.18	0.291



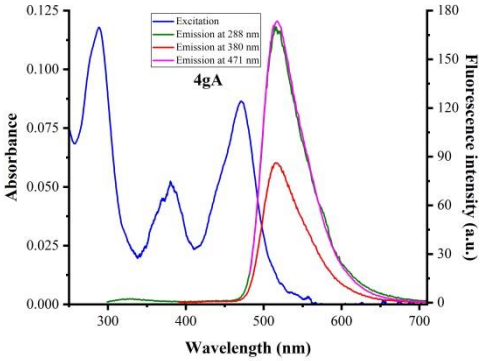
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
4eA	282.56	521.94	107.64	0.111
	376.41	519.85	63.43	0.141
	466.89	521.04	99.98	0.196



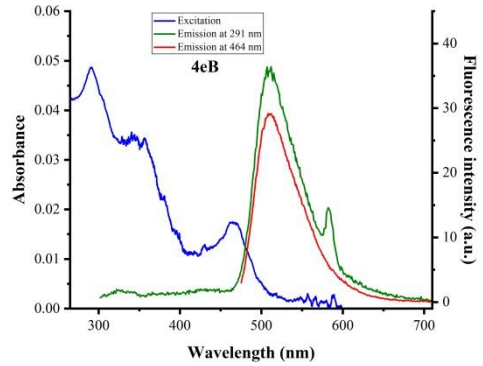
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
4fA	280.74	524.92	51.79	0.080
	383.74	520.89	29.12	0.141
	473.79	522.98	48.80	0.158



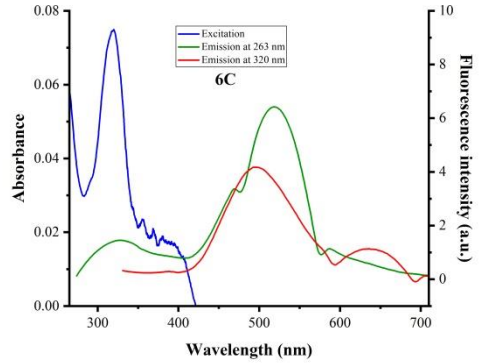
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
4gA	288.53	514.02	170.41	0.252
	380.11	517.01	86.20	0.284
	471.56	517.90	173.56	0.257



	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
4eB	291.19	511.94	36.39	0.150
	464.27	508.04	29.47	0.225



	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
6C	263.14	525.96	13.60	0.034
	320.64	490.41	4.48	0.016



5. ^{1}H NMR and ^{13}C NMR spectra

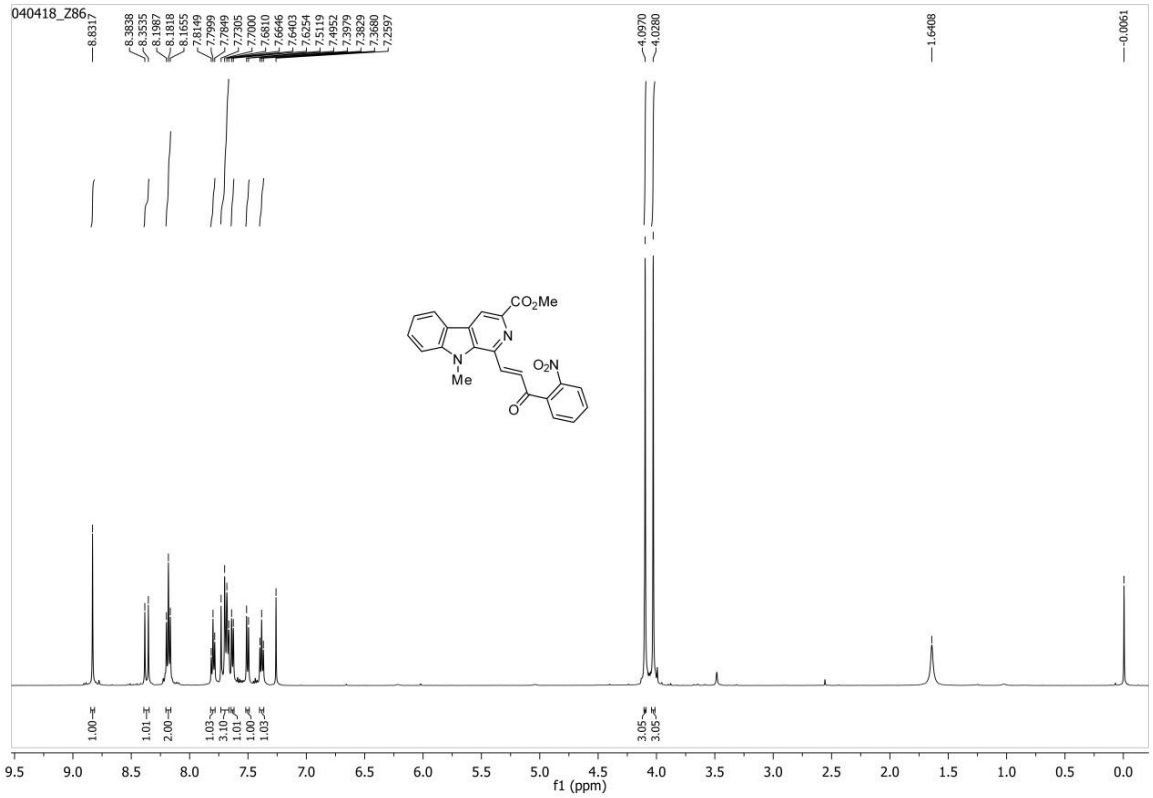


Figure S1. ^{1}H NMR spectrumof **1bA**.

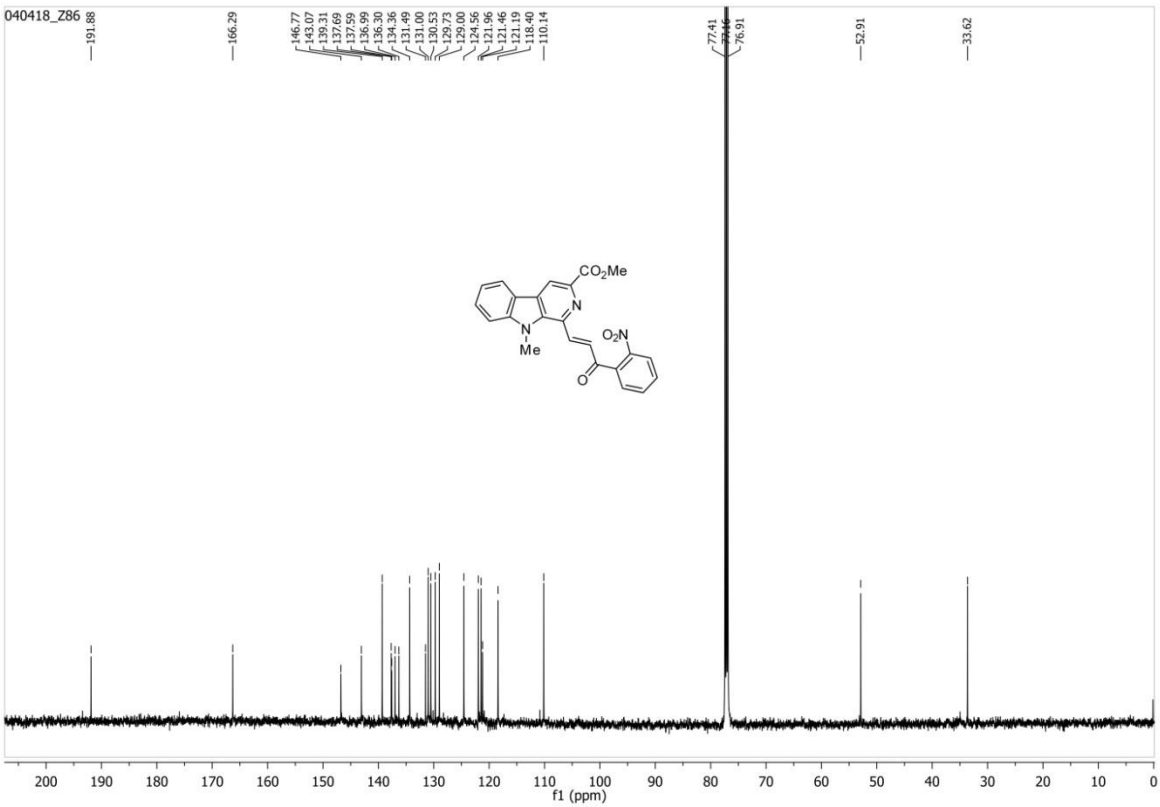


Figure S2. ^{13}C NMR spectrumof **1bA**.

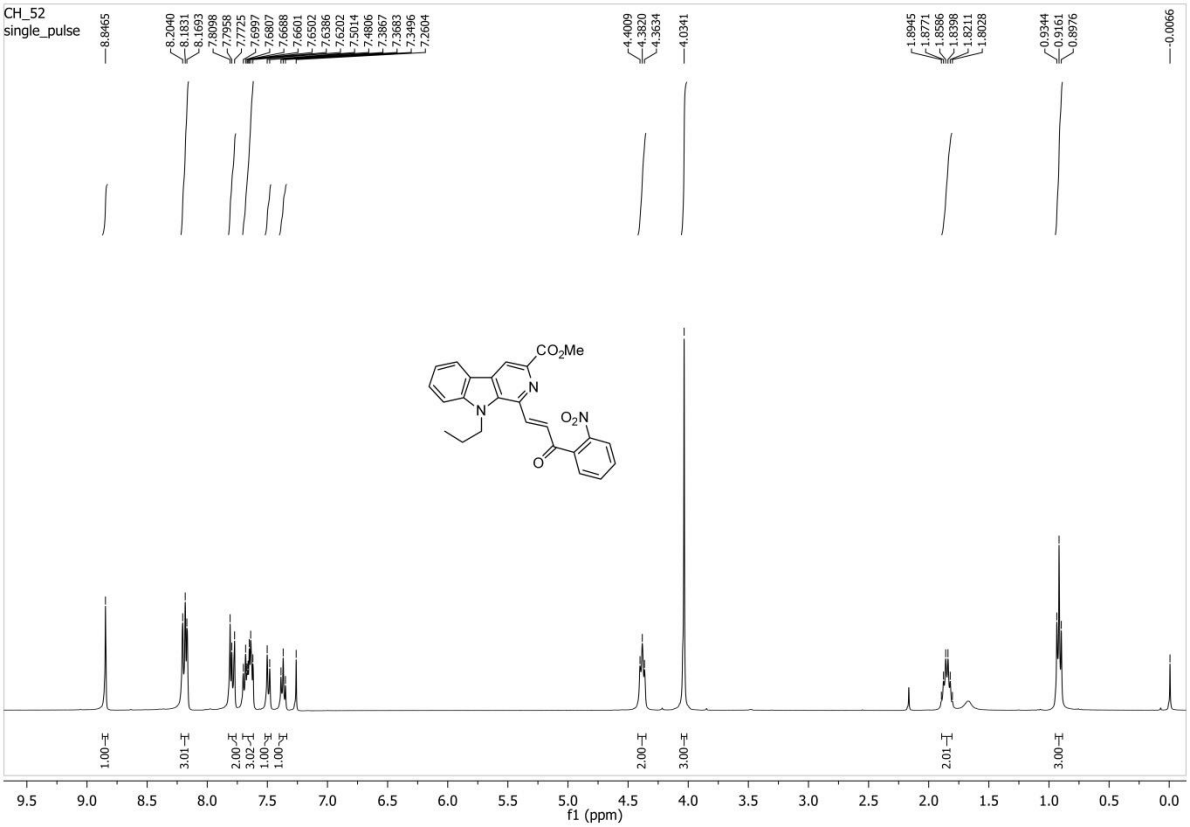


Figure S3. ^{1}H NMR spectrumof **1dA**.

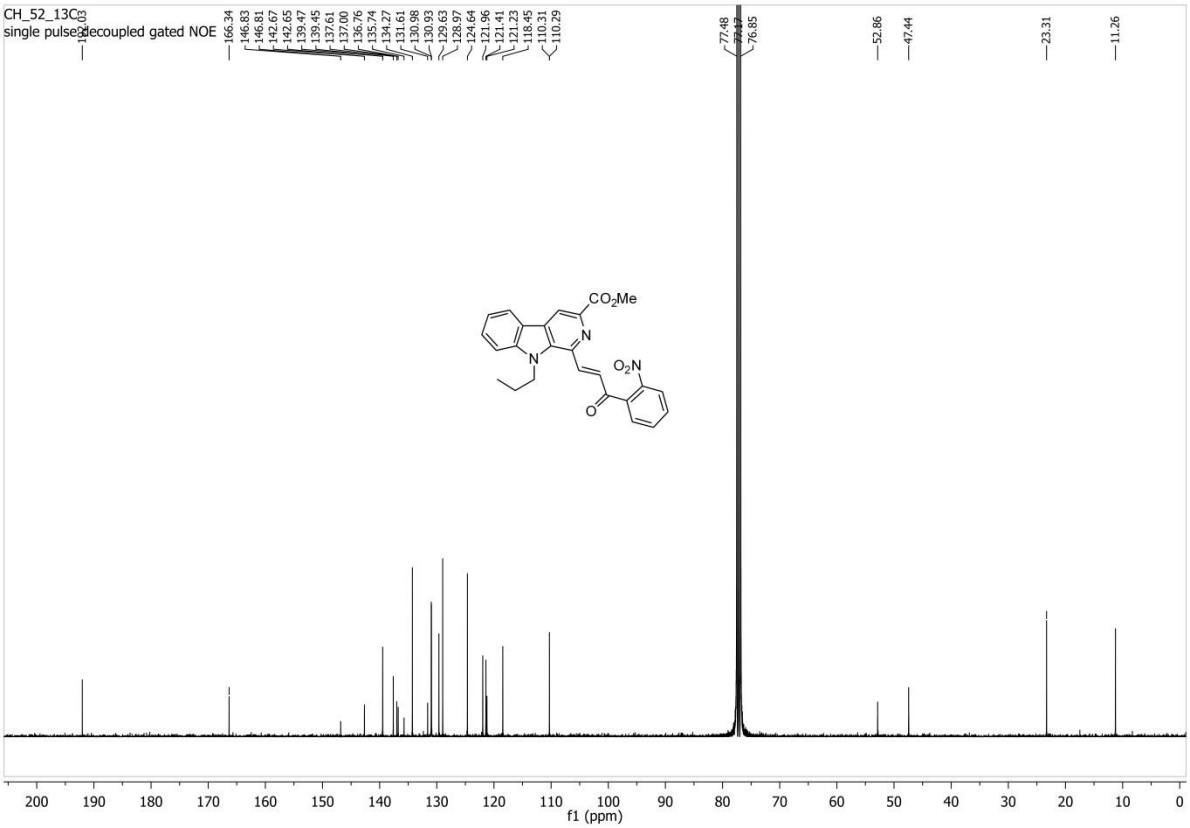


Figure S4. ^{13}C NMR spectrumof **1dA**.

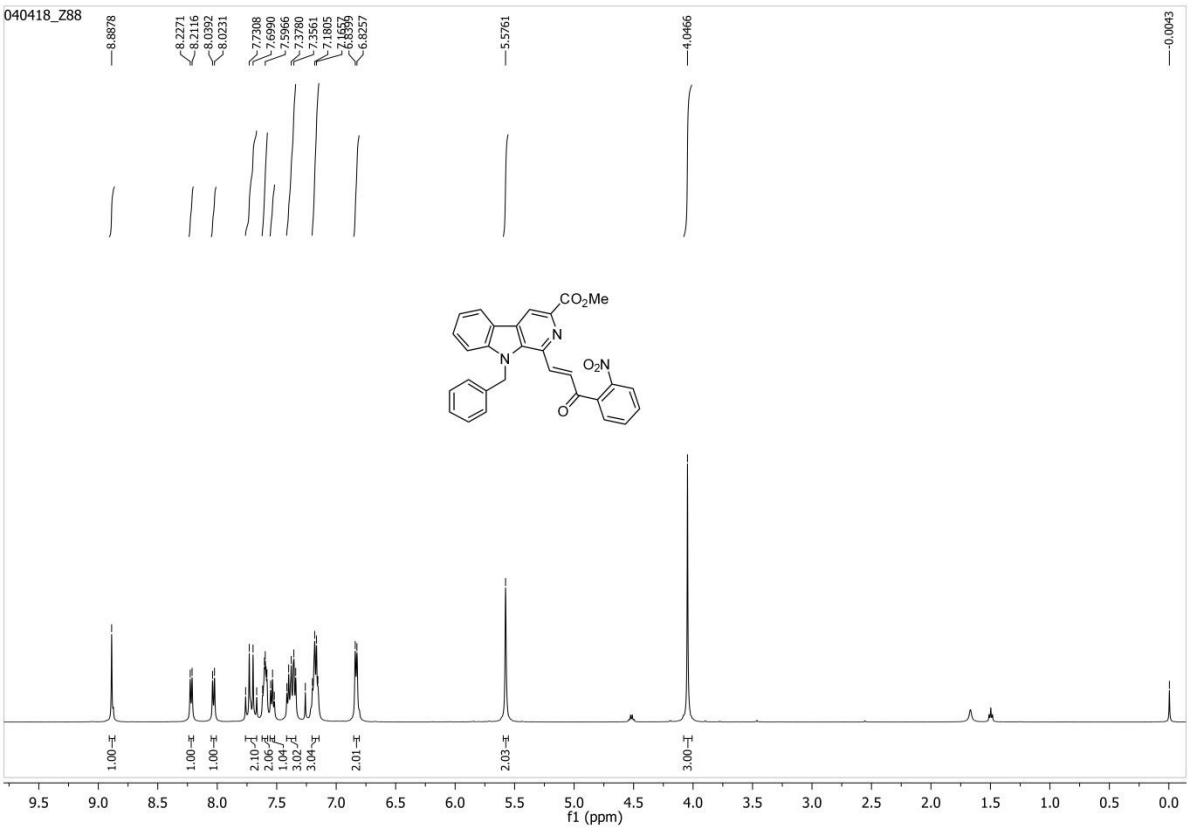


Figure S5. ^{1}H NMR spectrumof **1hA**.

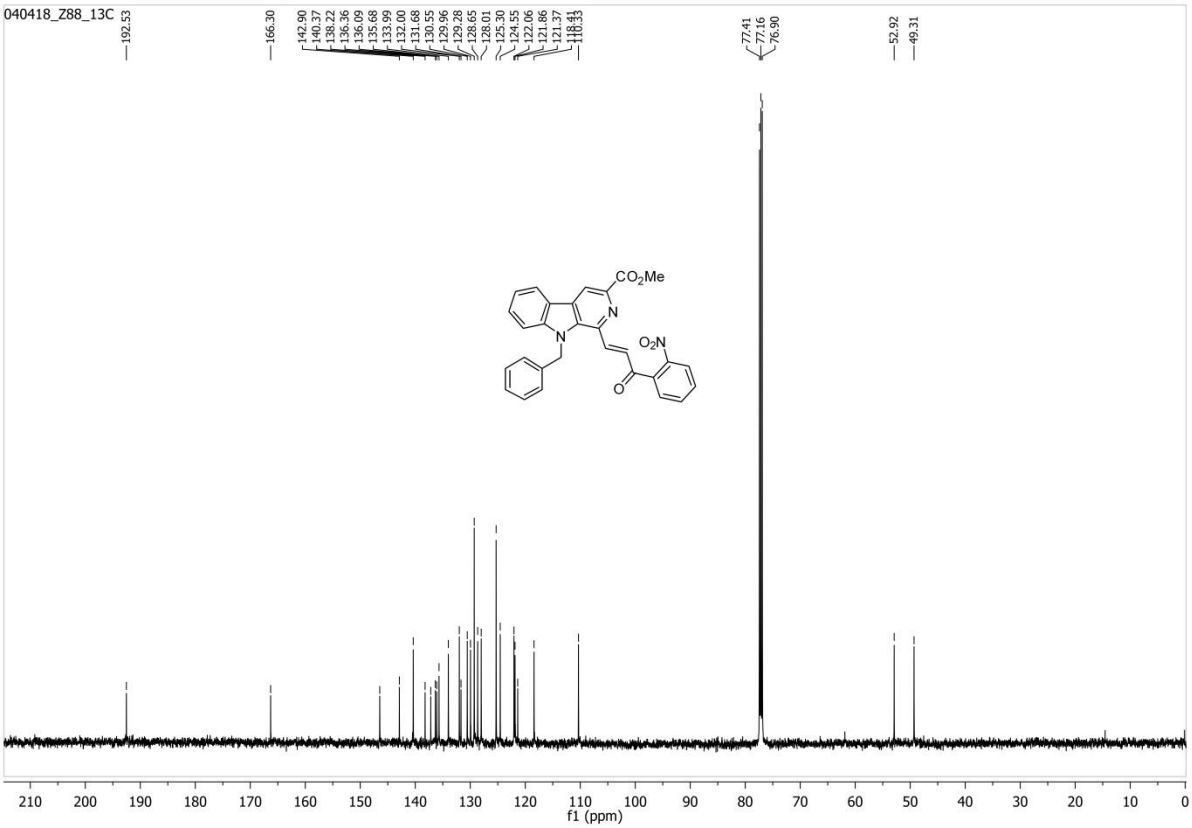


Figure S6. ^{13}C NMR spectrumof **1hA**.

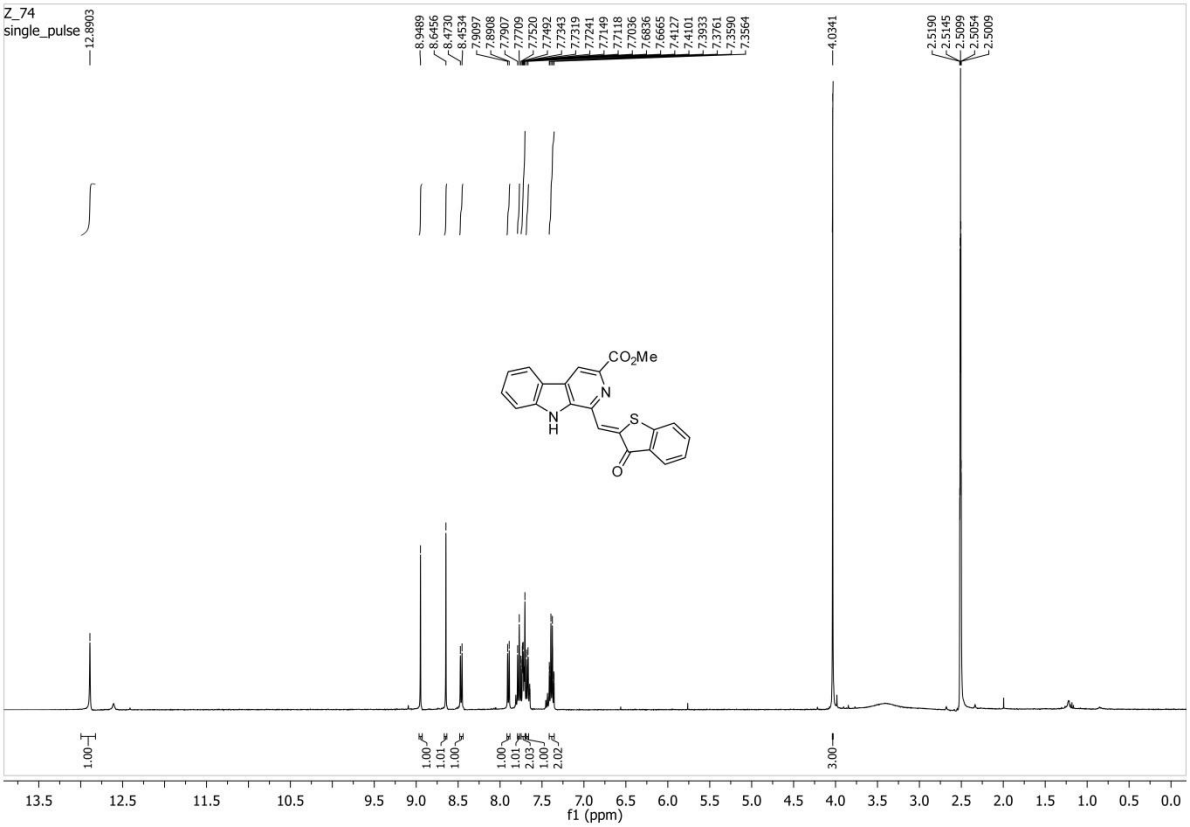


Figure S7. ^{1}H NMR spectrumof **2aA**.

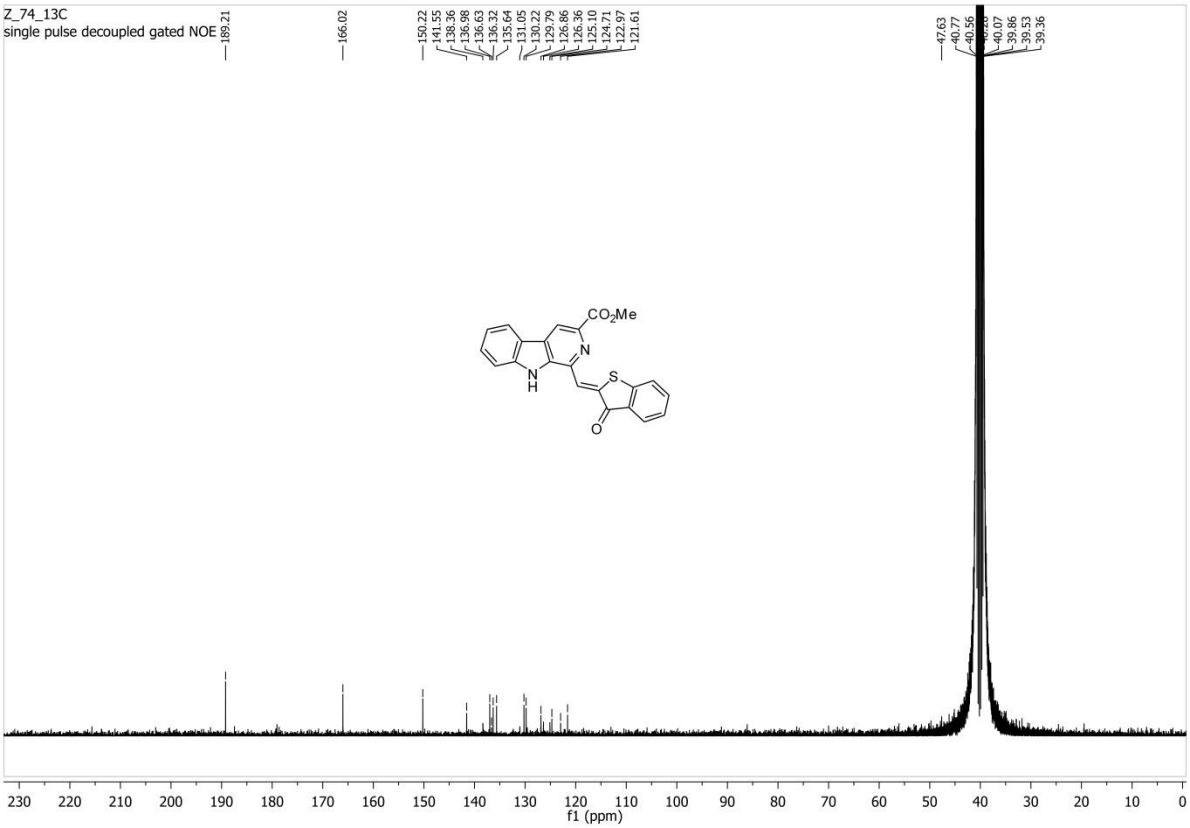


Figure S8. ^{13}C NMR spectrumof **2aA**.

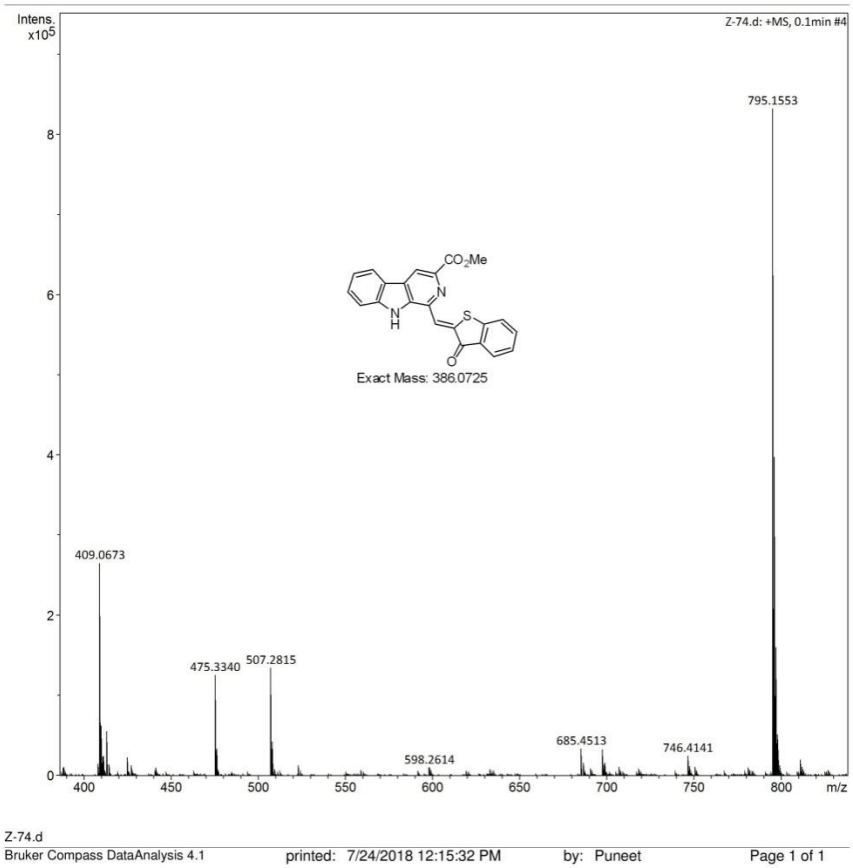


Figure S9. HRMS spectrum of **2aA**.

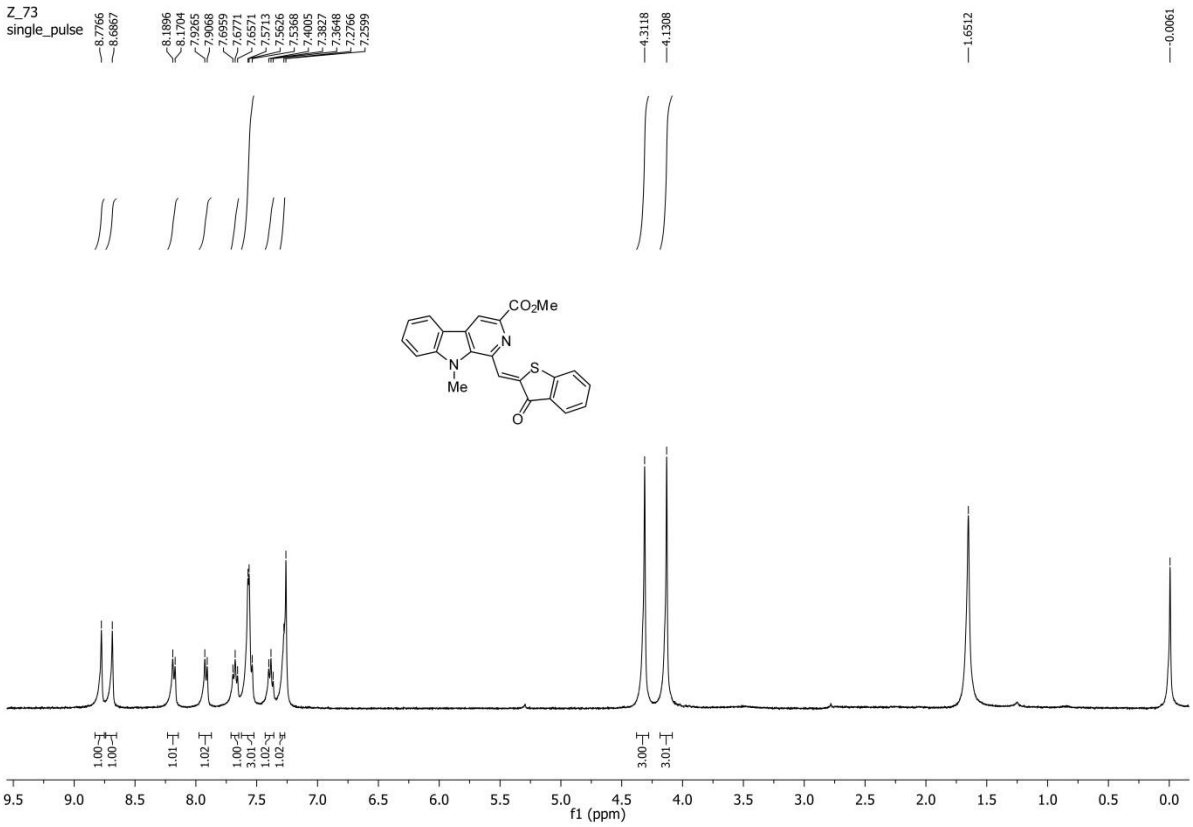


Figure S10. ^{1}H NMR spectrumof **2bA**.

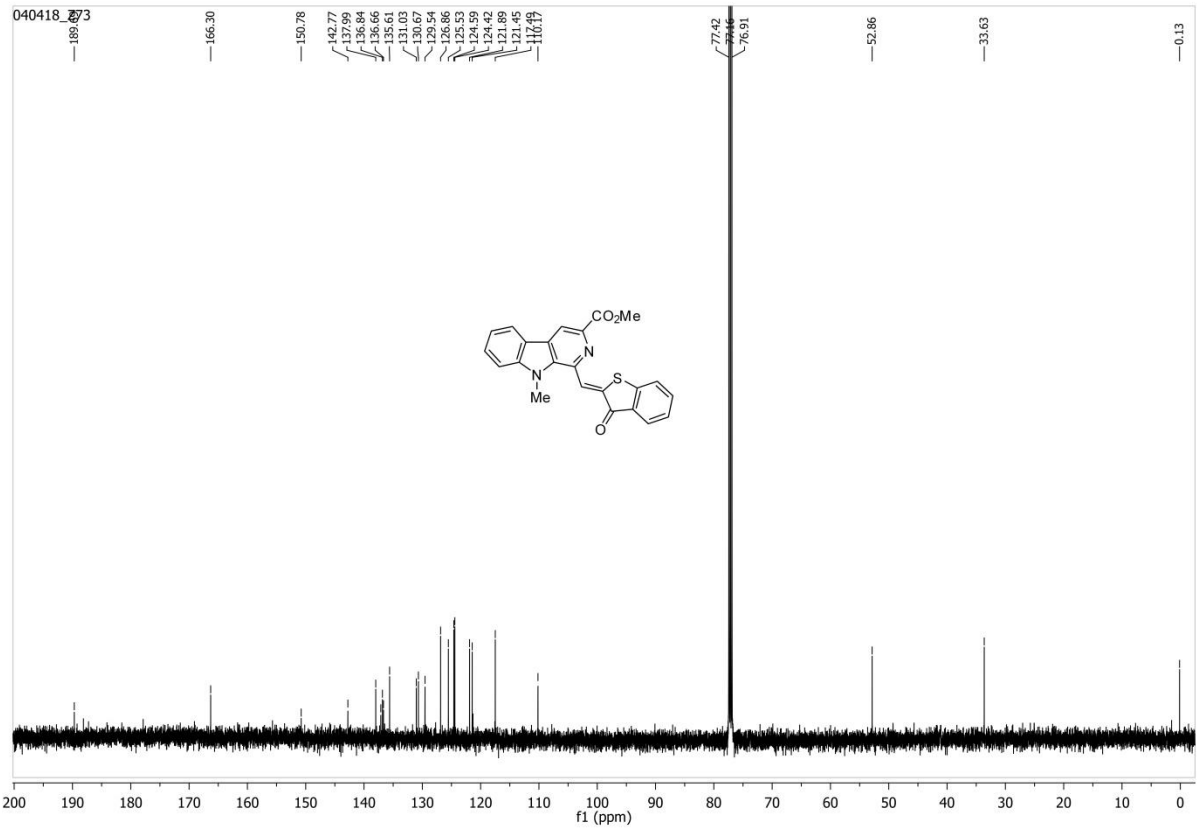


Figure S11. ^{13}C NMR spectrumof **2bA**.

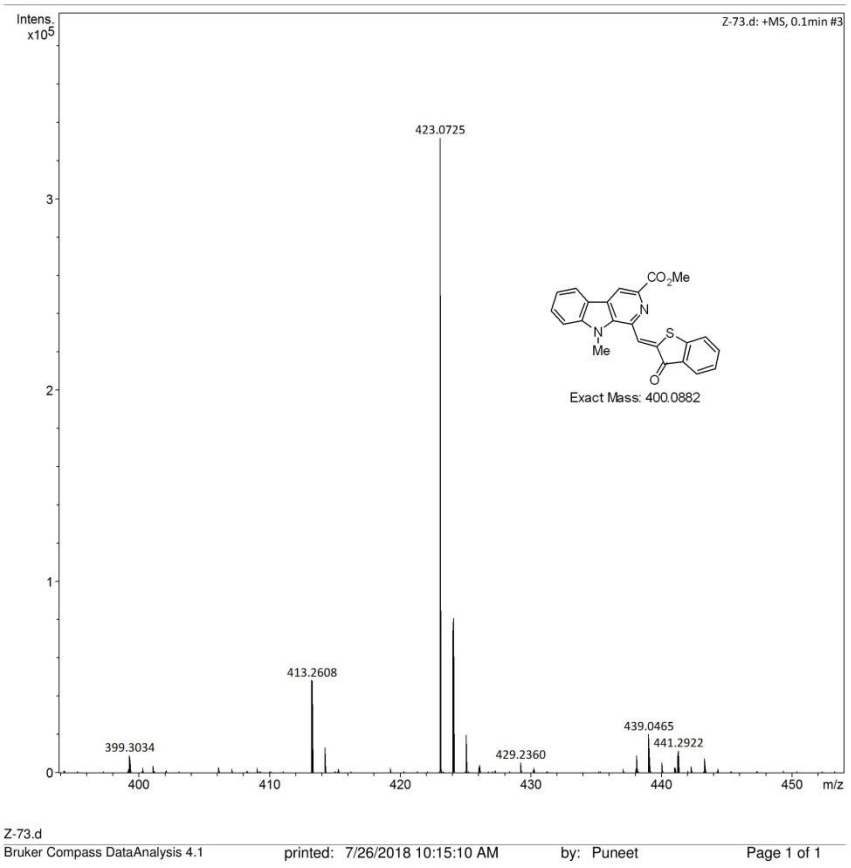


Figure S12. HRMS spectrum of **2bA**.

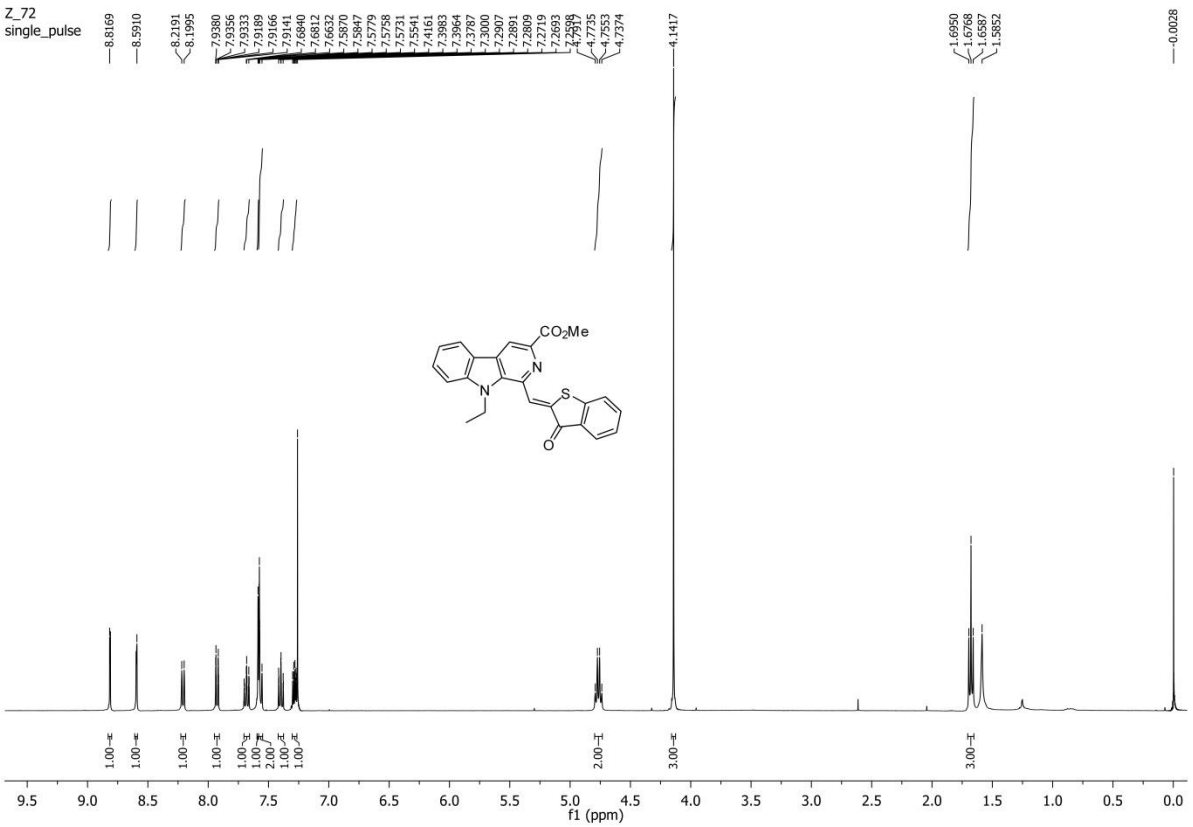


Figure S13. ^{1}H NMR spectrumof **2cA**.

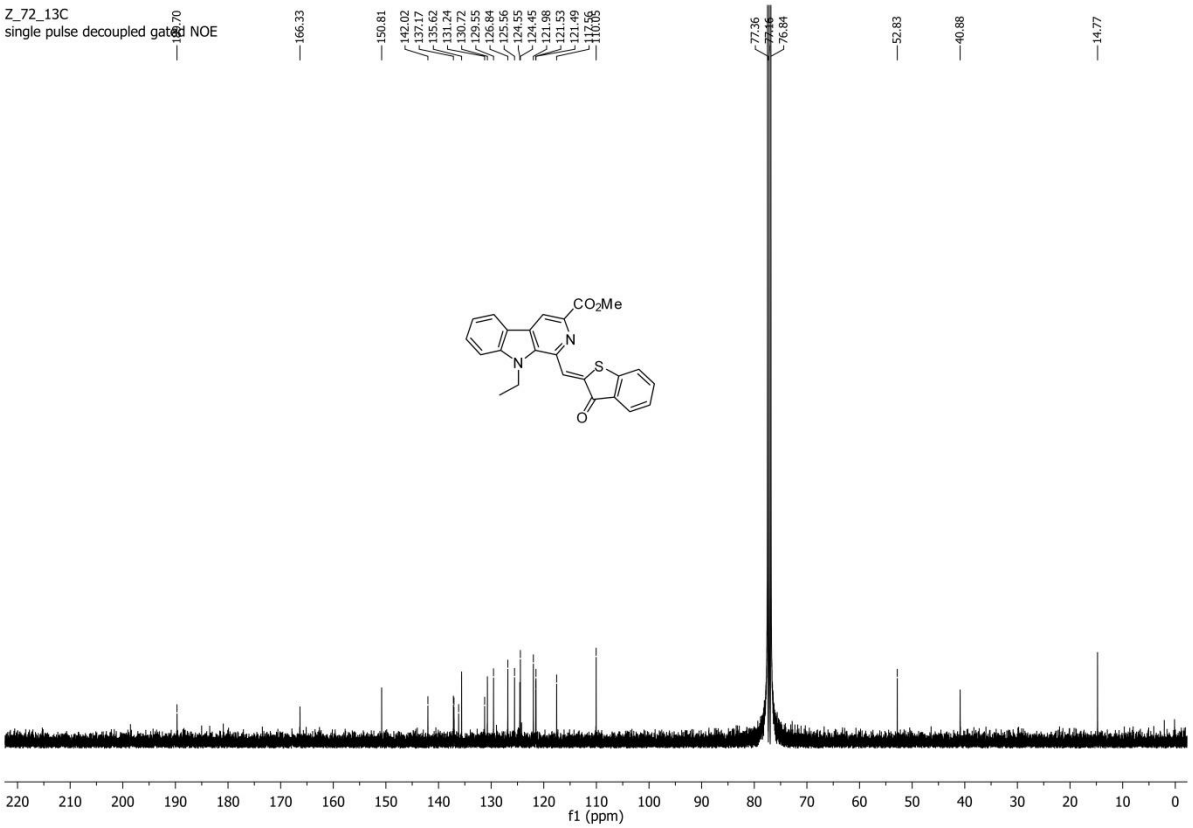


Figure S14. ^{13}C NMR spectrumof **2cA**.

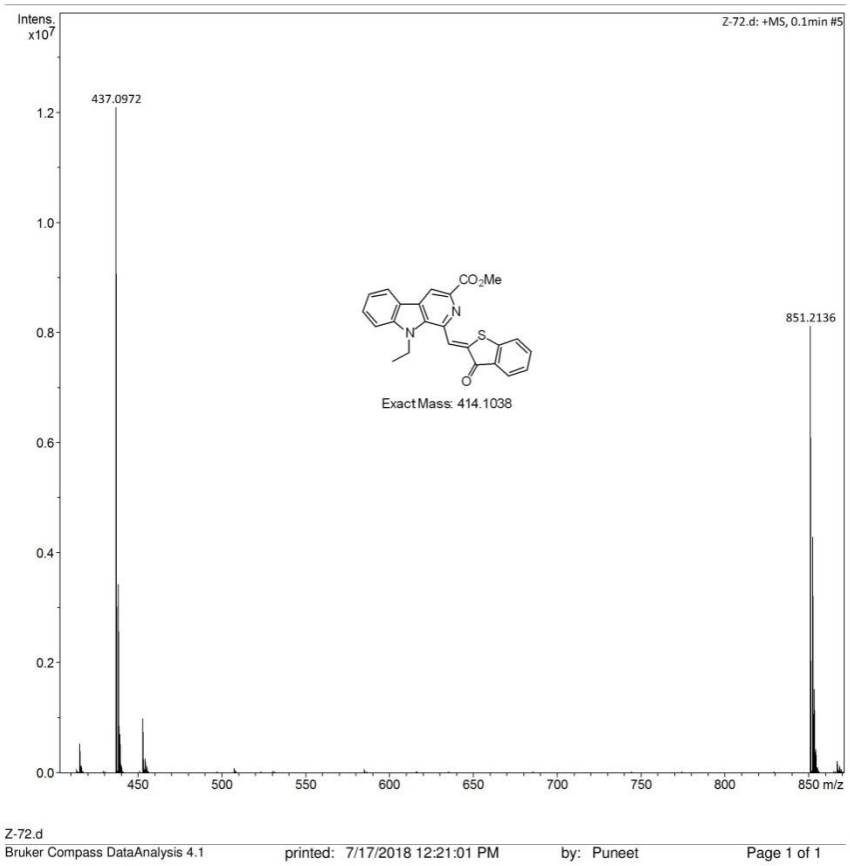


Figure S15. HRMS spectrum of **2cA**.

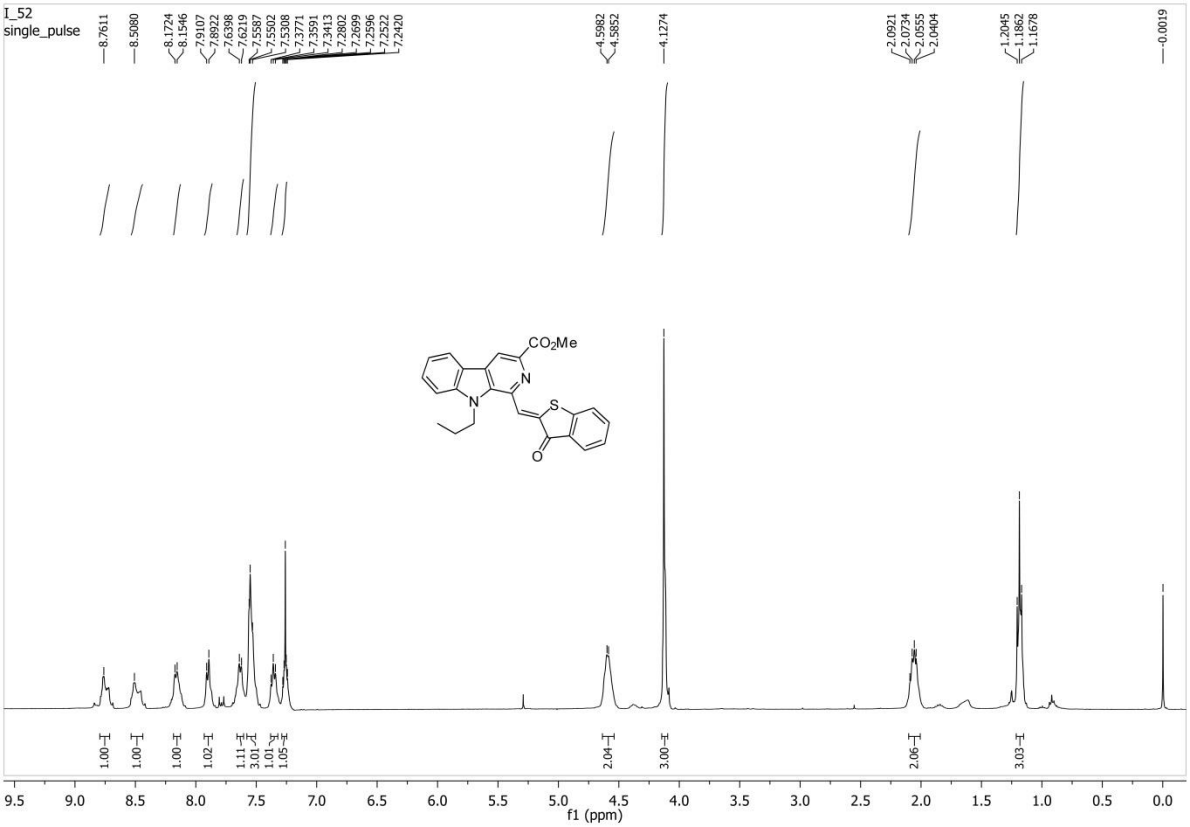


Figure S16. ^{1}H NMR spectrumof **2dA**.

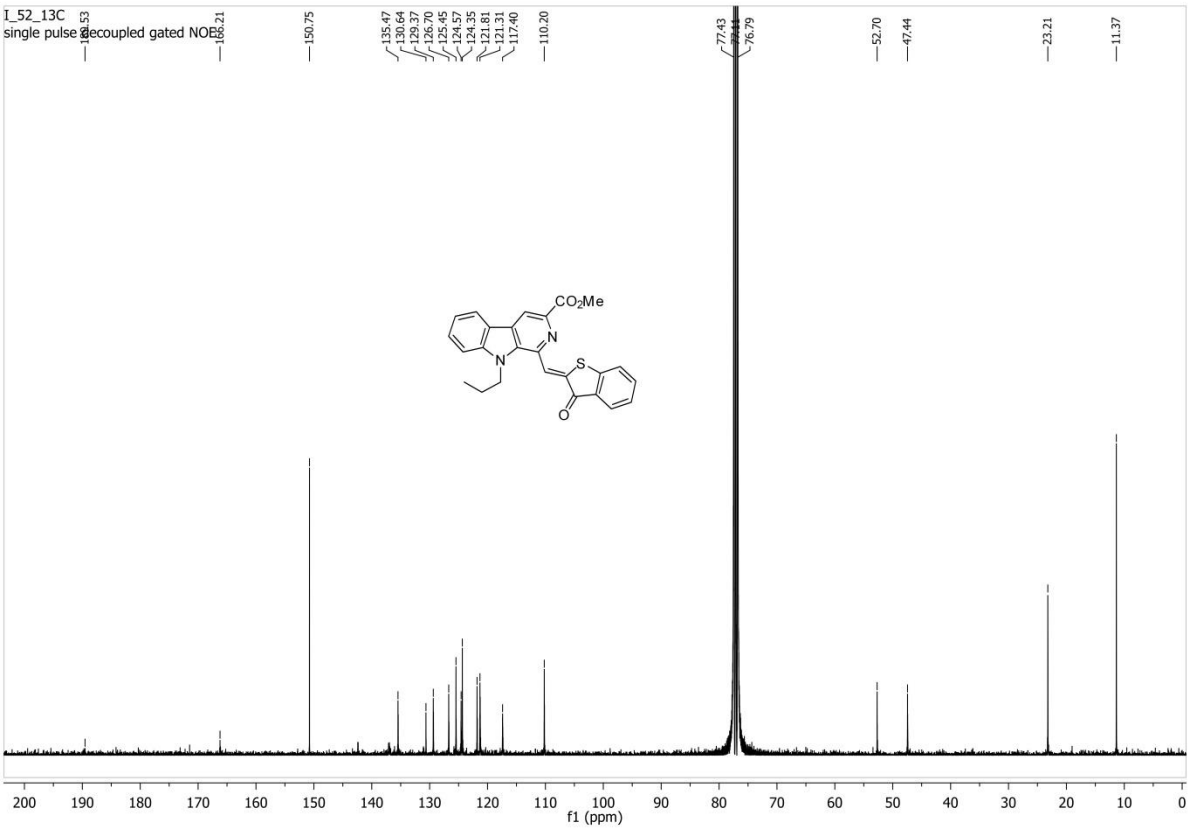


Figure S17. ^{13}C NMR spectrumof **2dA**.

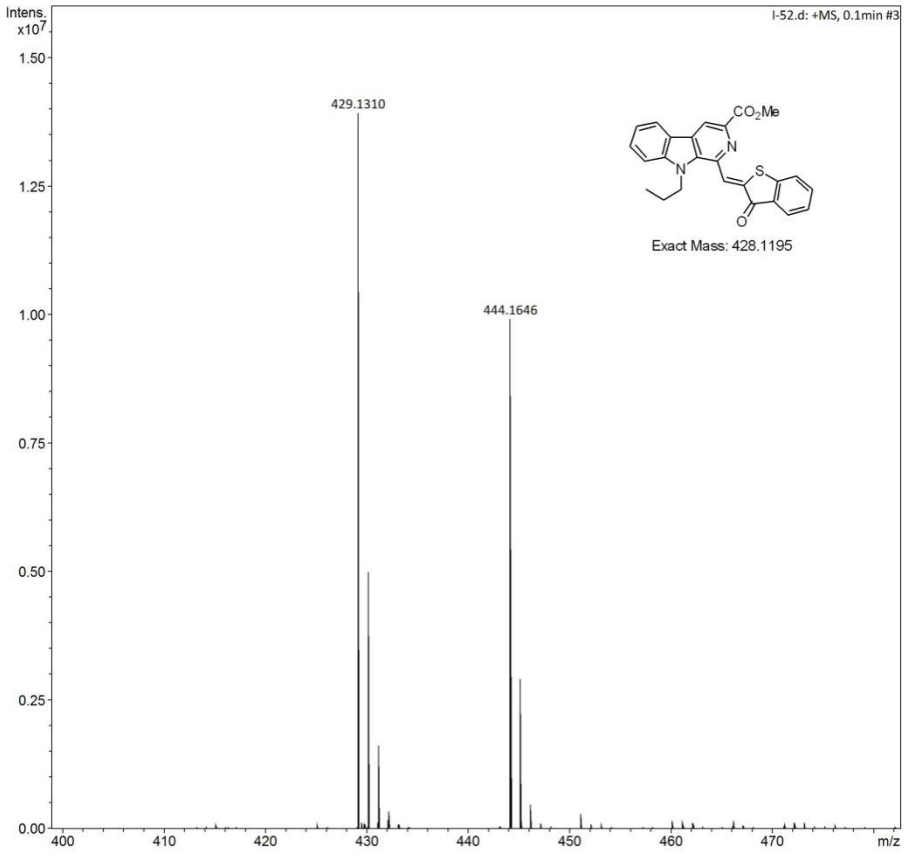


Figure S18. HRMS spectrum of **2dA**.

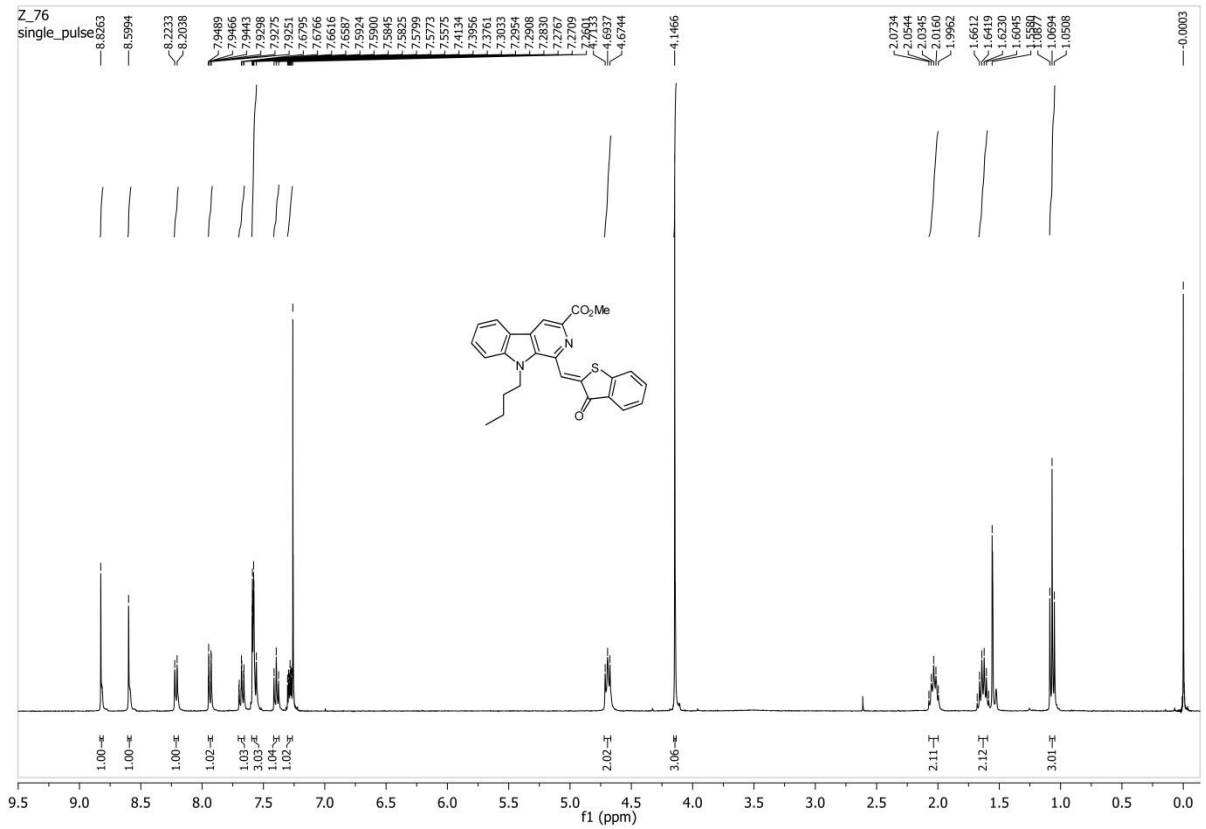


Figure S19. ^{1}H NMR spectrumof **2eA**.

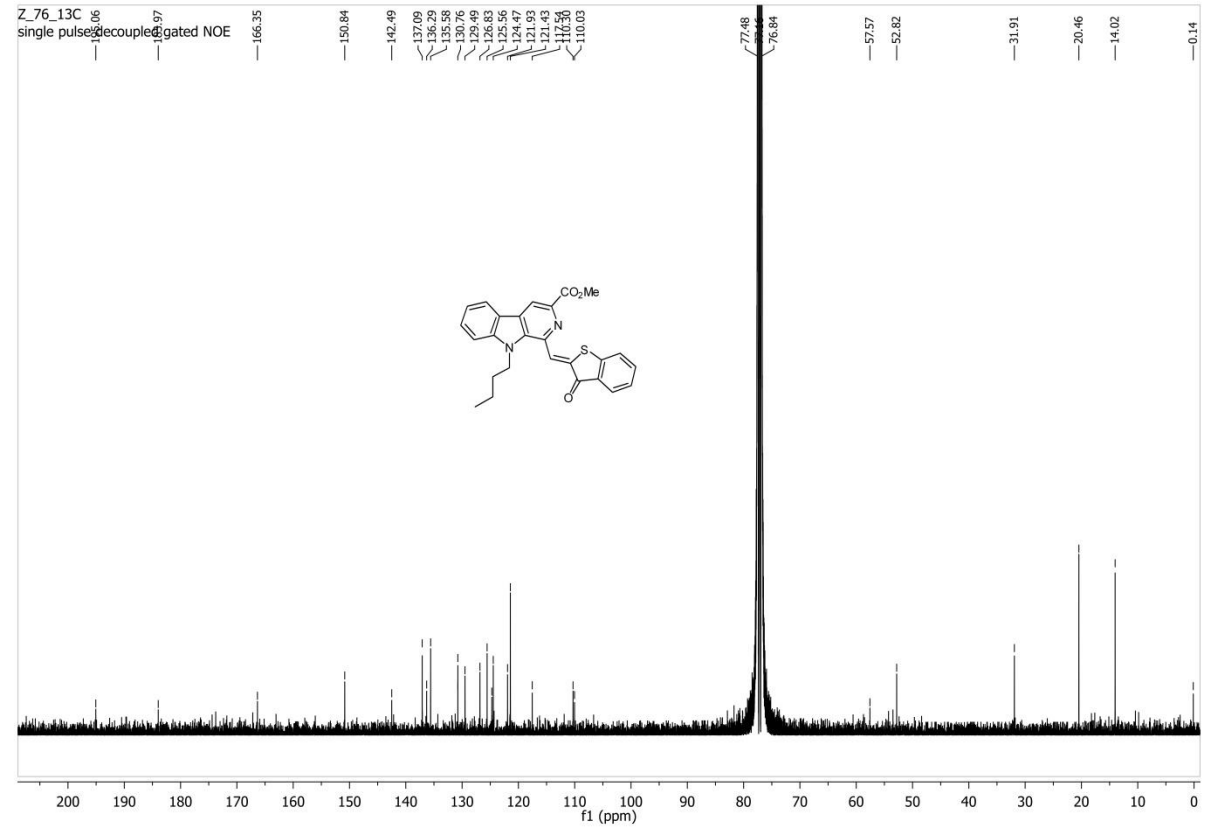


Figure S20. ^{13}C NMR spectrumof **2eA**.

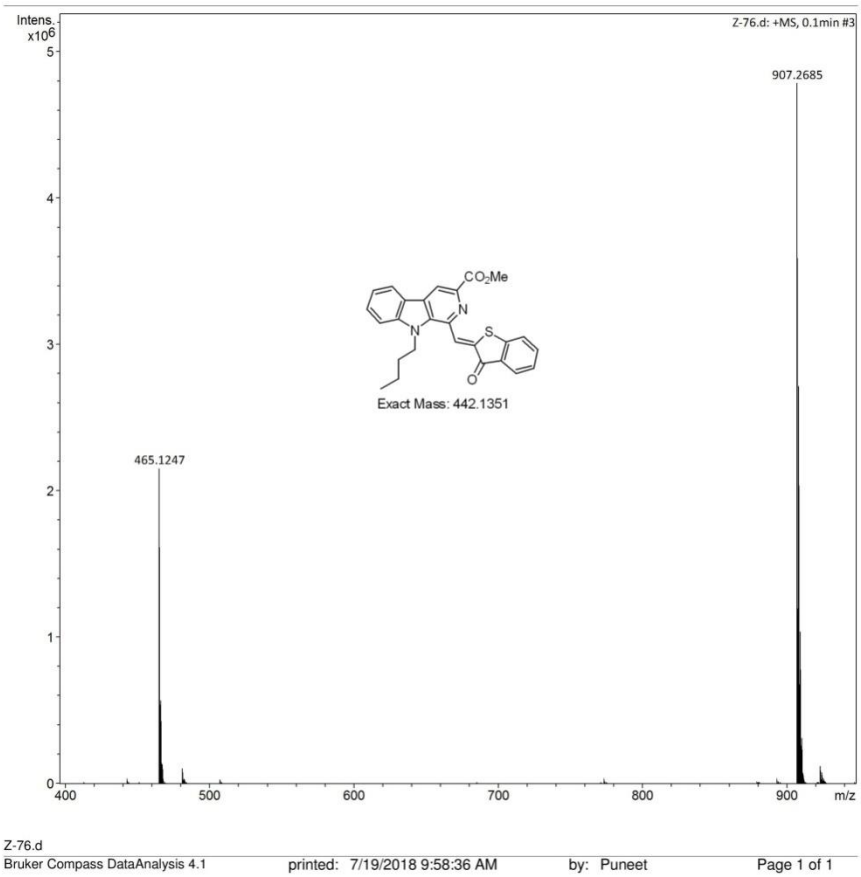


Figure S21. HRMS spectrum of **2eA**.

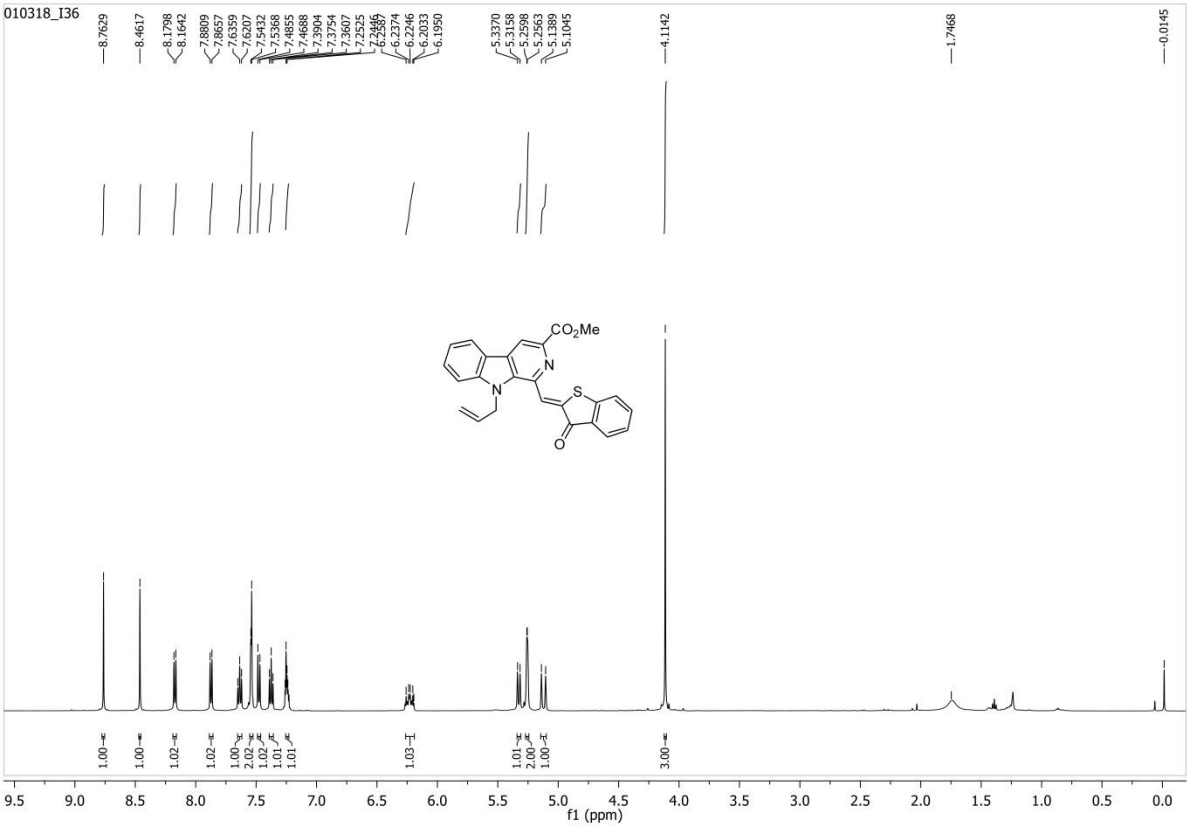


Figure S22. ^{1}H NMR spectrumof **2fA**.

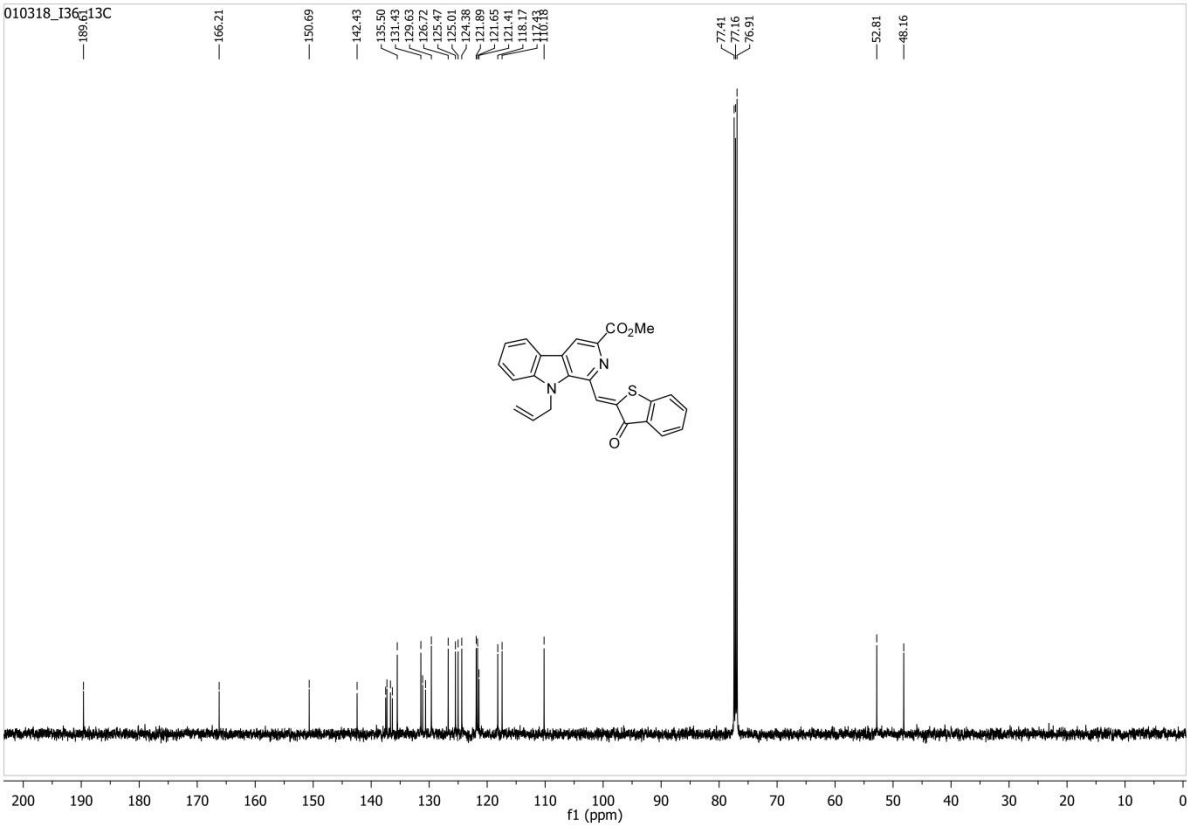


Figure S23. ^{13}C NMR spectrumof **2fA**.

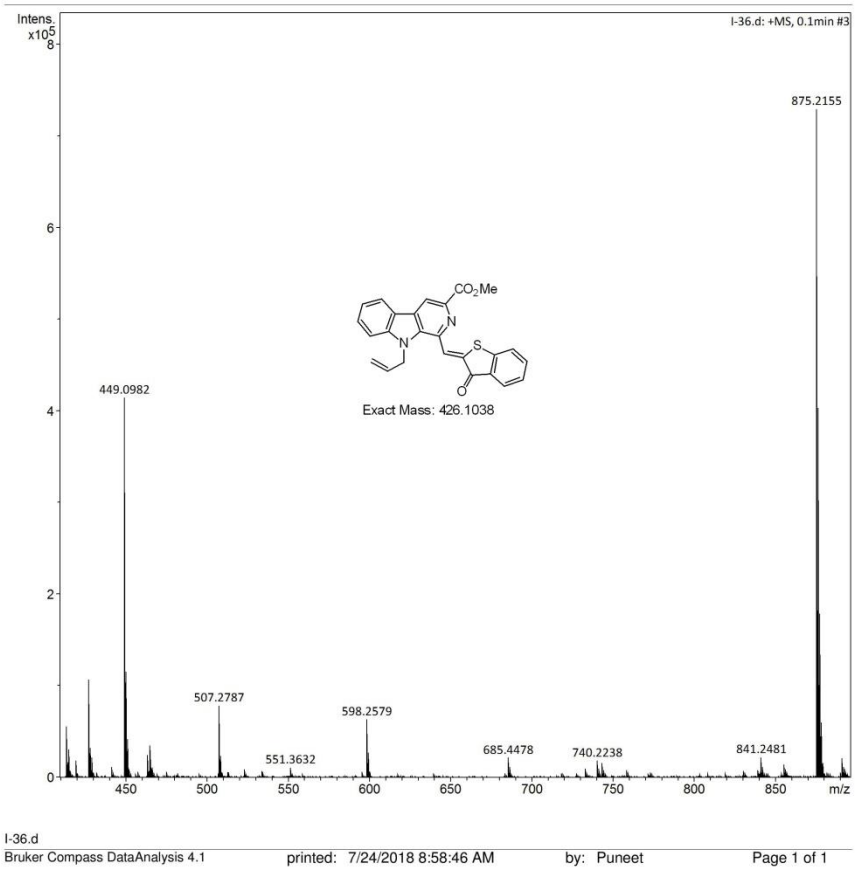


Figure S24. HRMS spectrum of **2fA**.

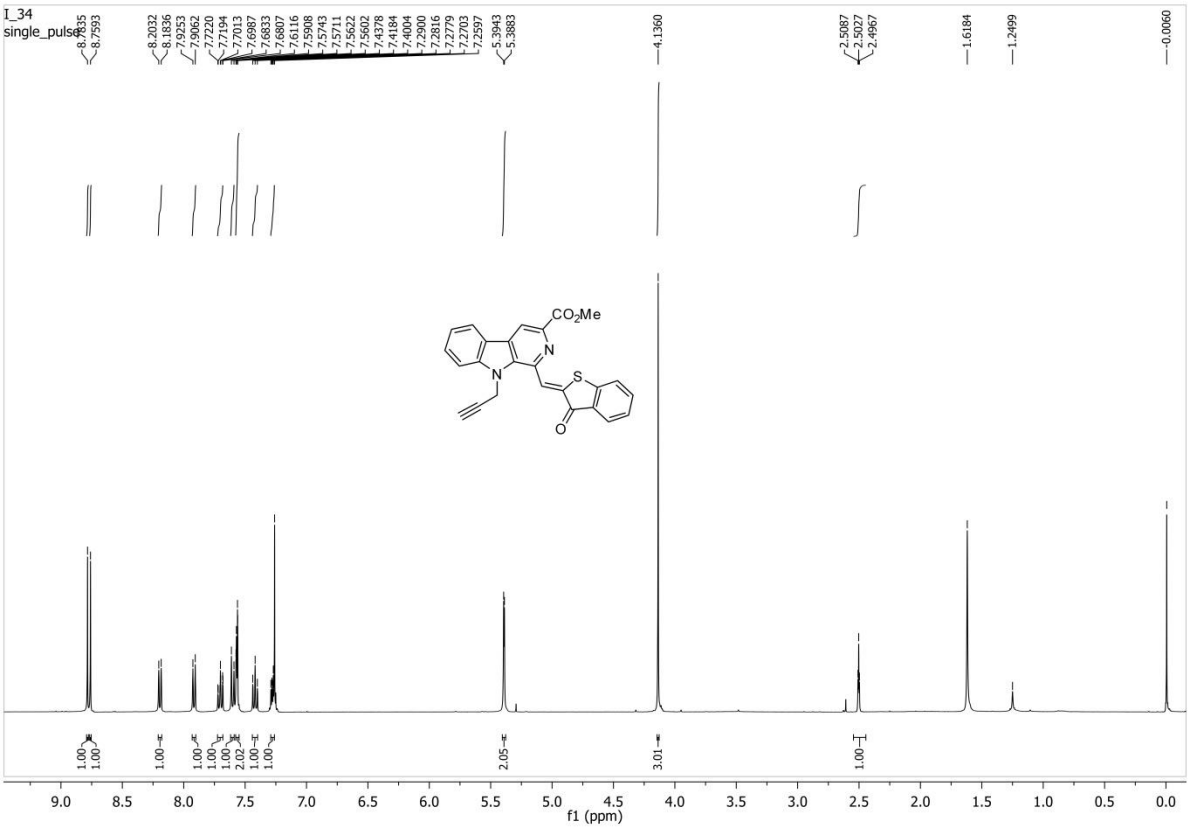


Figure S25. ^{1}H NMR spectrumof **2gA**.

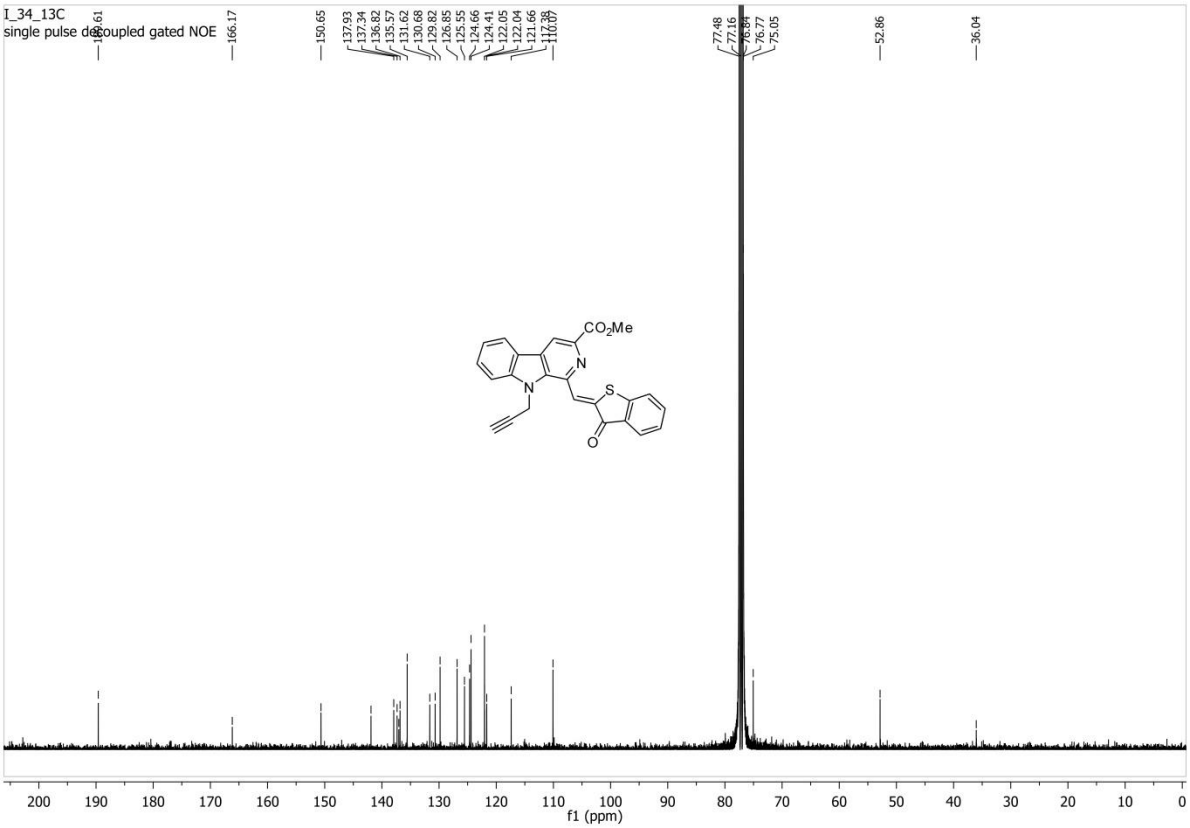


Figure S26. ^{13}C NMR spectrumof **2gA**.

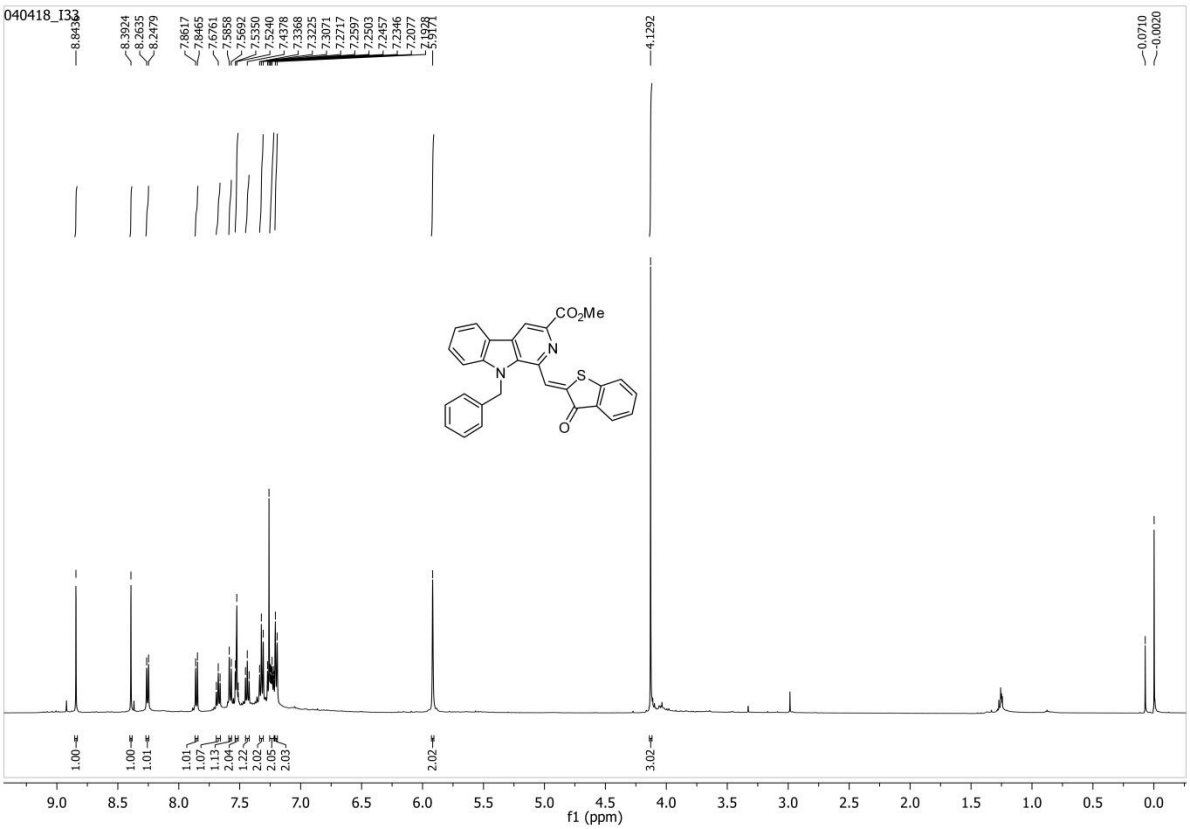


Figure S27. ^{1}H NMR spectrumof **2hA**.

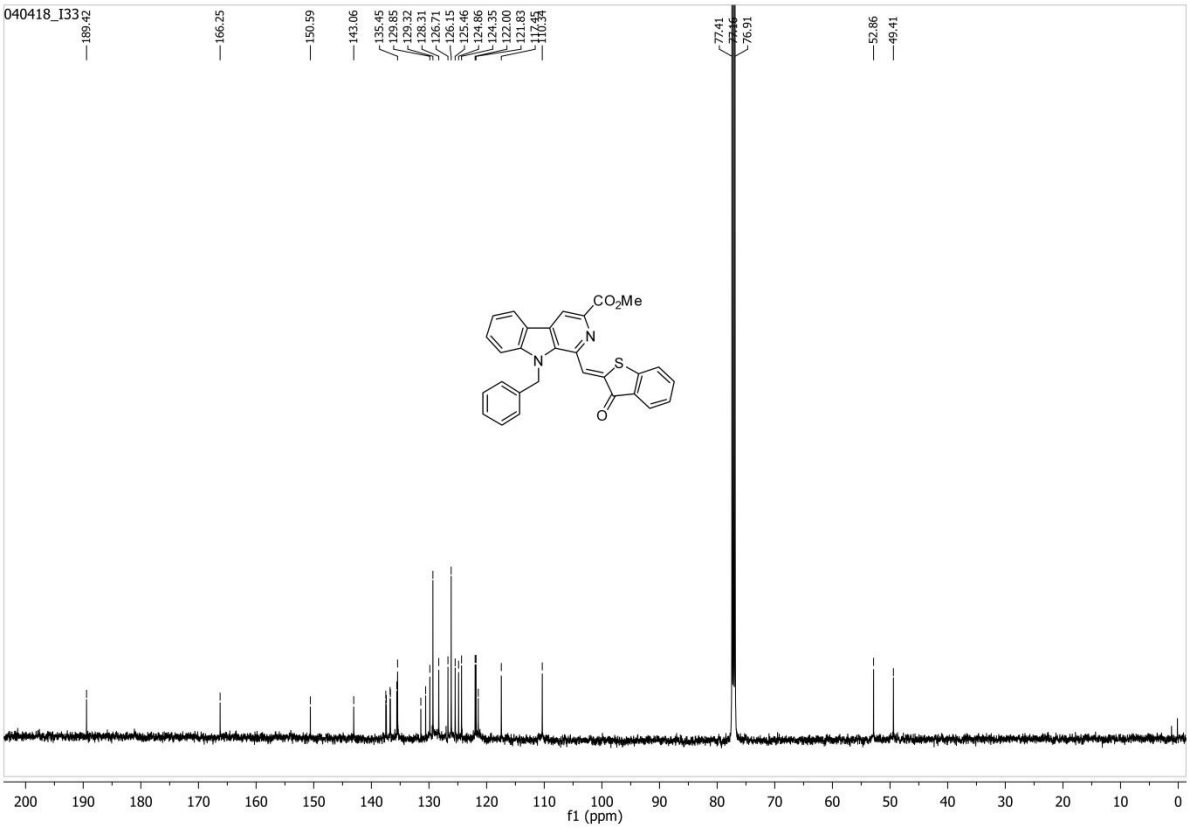


Figure S28. ^{13}C NMR spectrumof **2hA**.

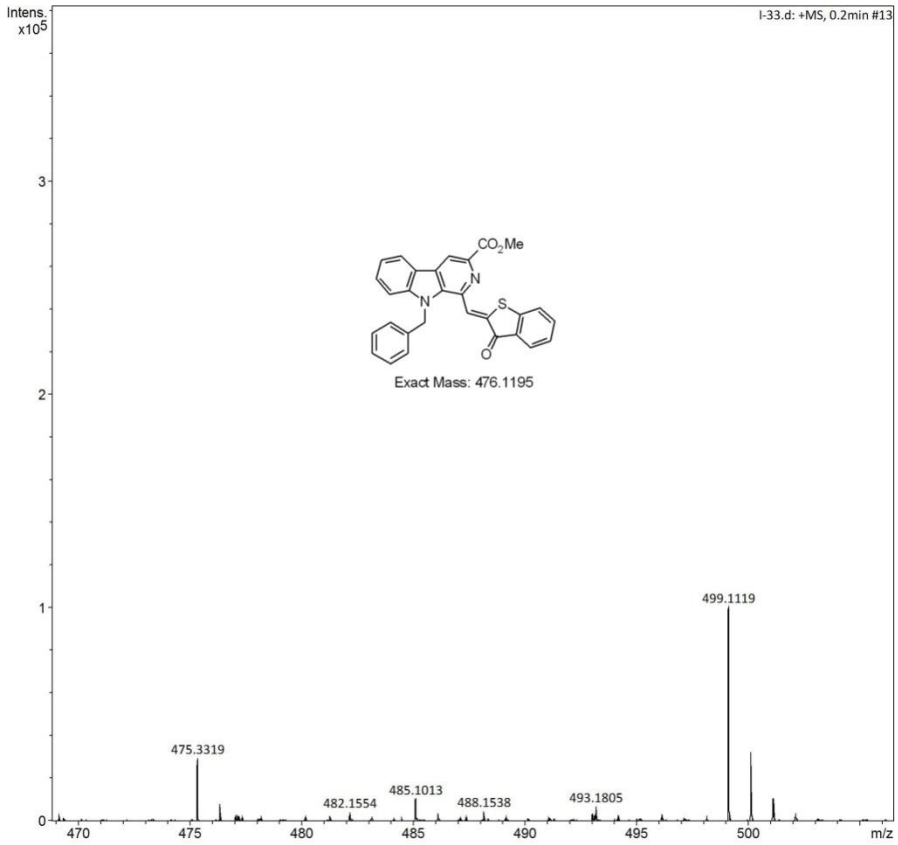


Figure S29. HRMS spectrum of **2hA**.

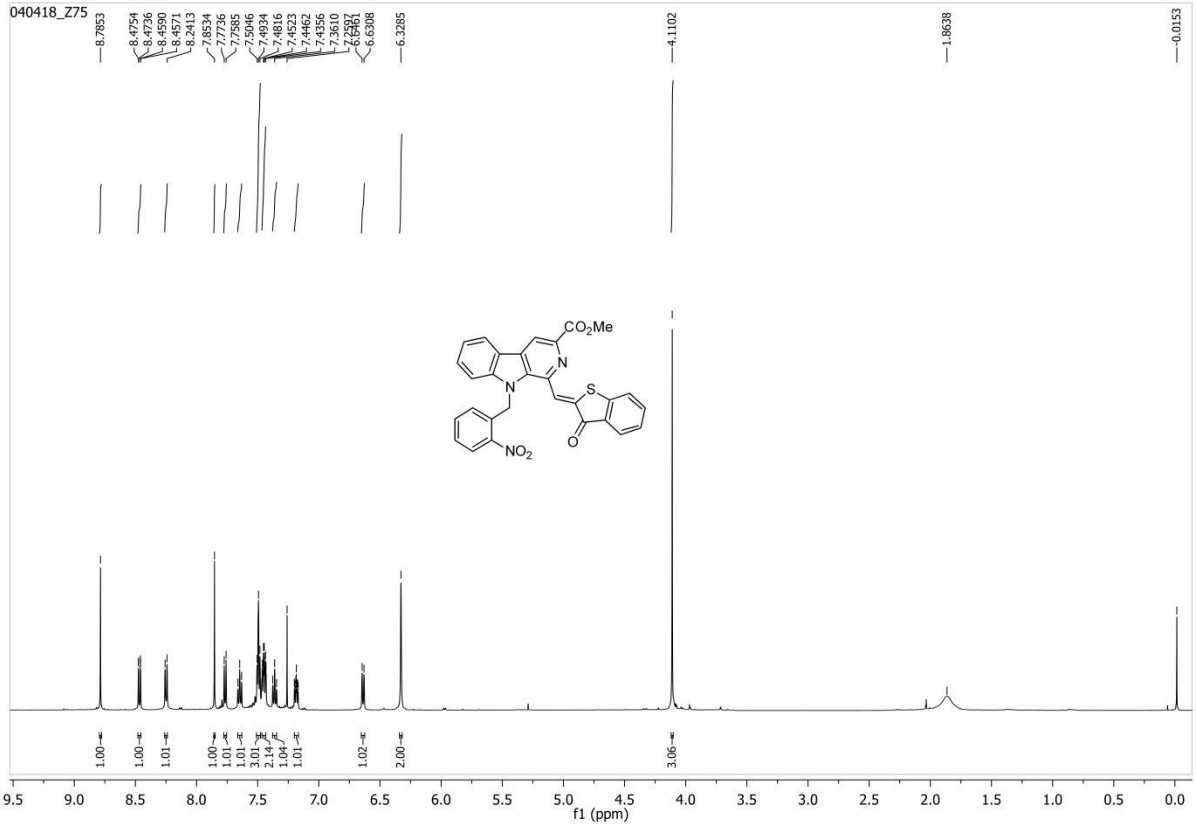


Figure S30. ^{1}H NMR spectrumof **2iA**.

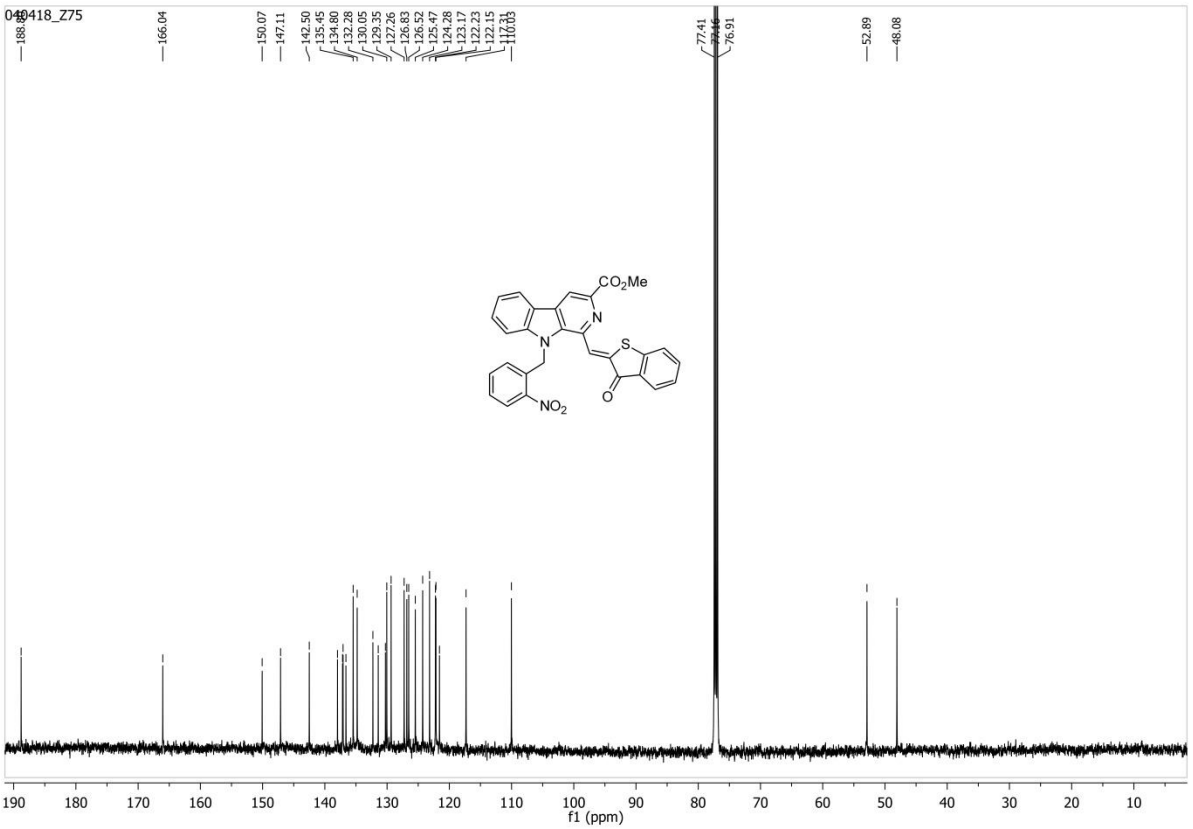


Figure S31. ^{13}C NMR spectrumof **2iA**.

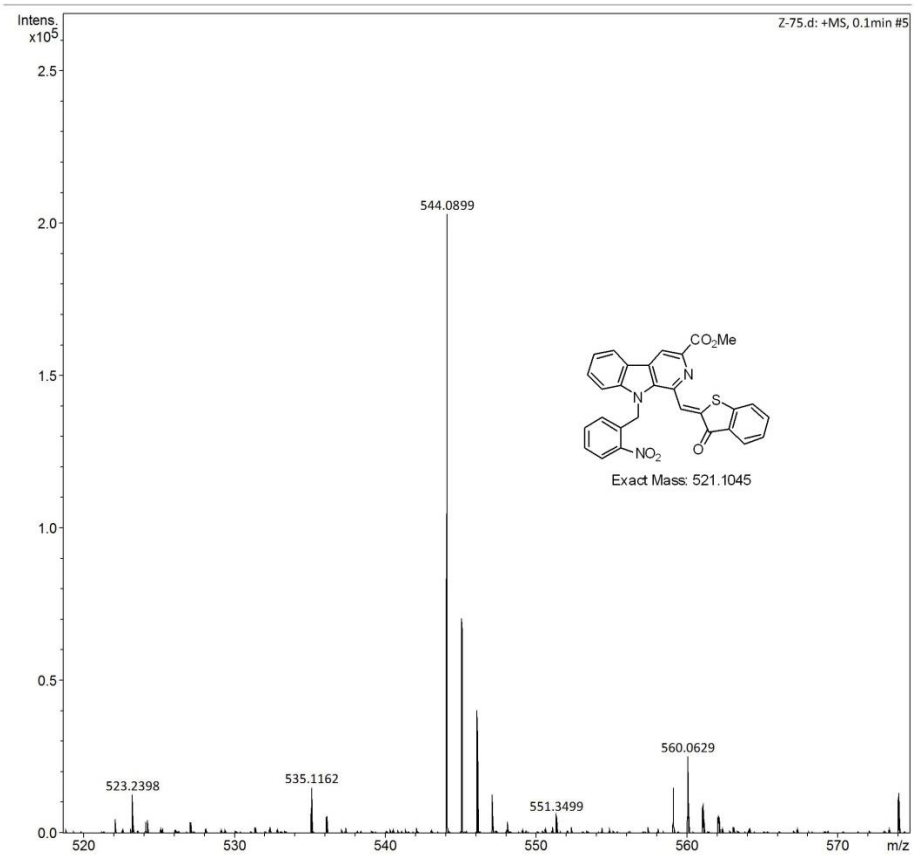


Figure S32. HRMS spectrum of **2iA**.

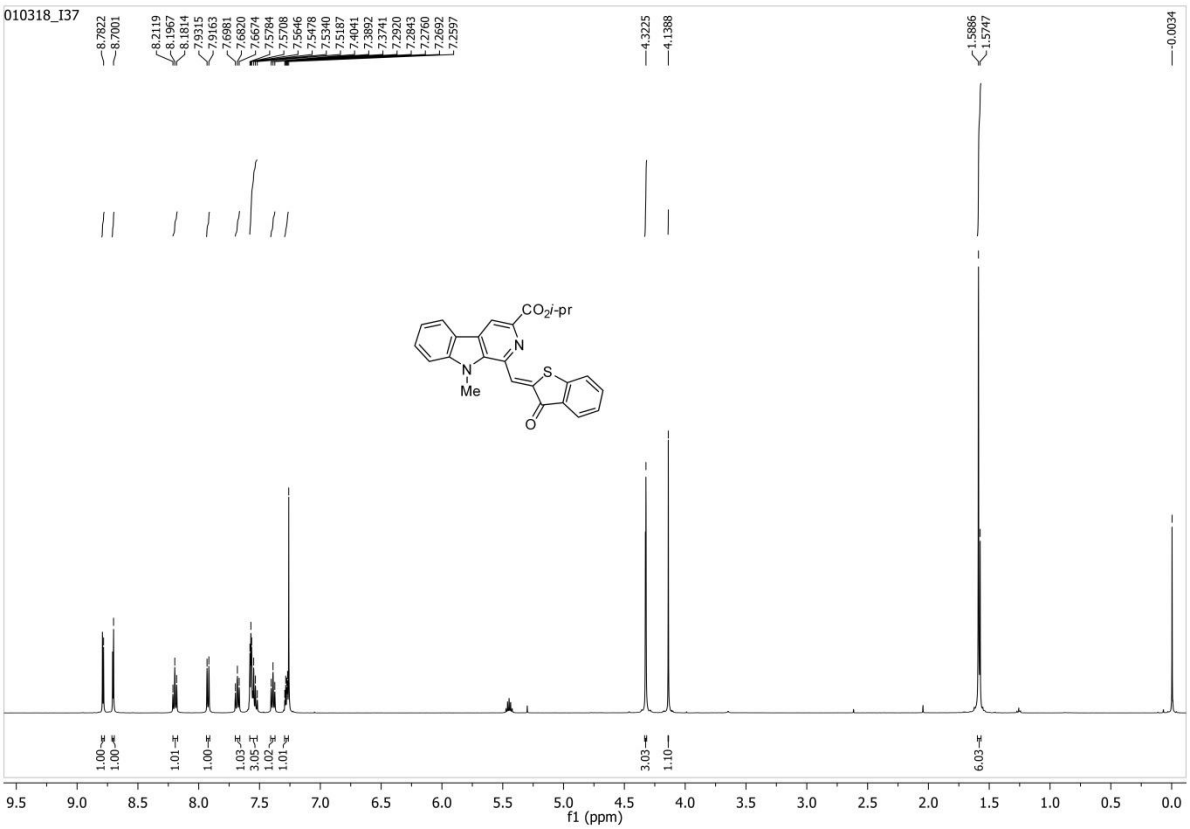


Figure S33. ^{1}H NMR spectrumof **2jA**.

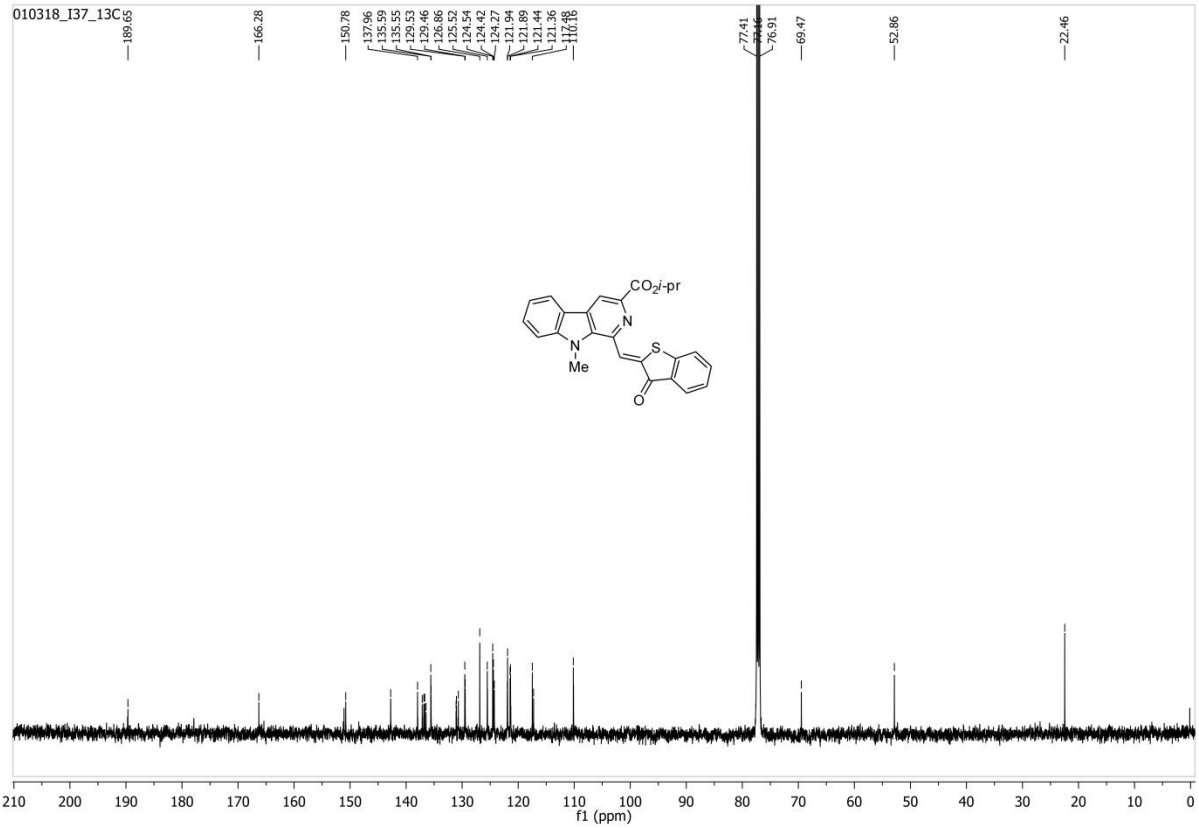


Figure S34. ^{13}C NMR spectrumof **2jA**.

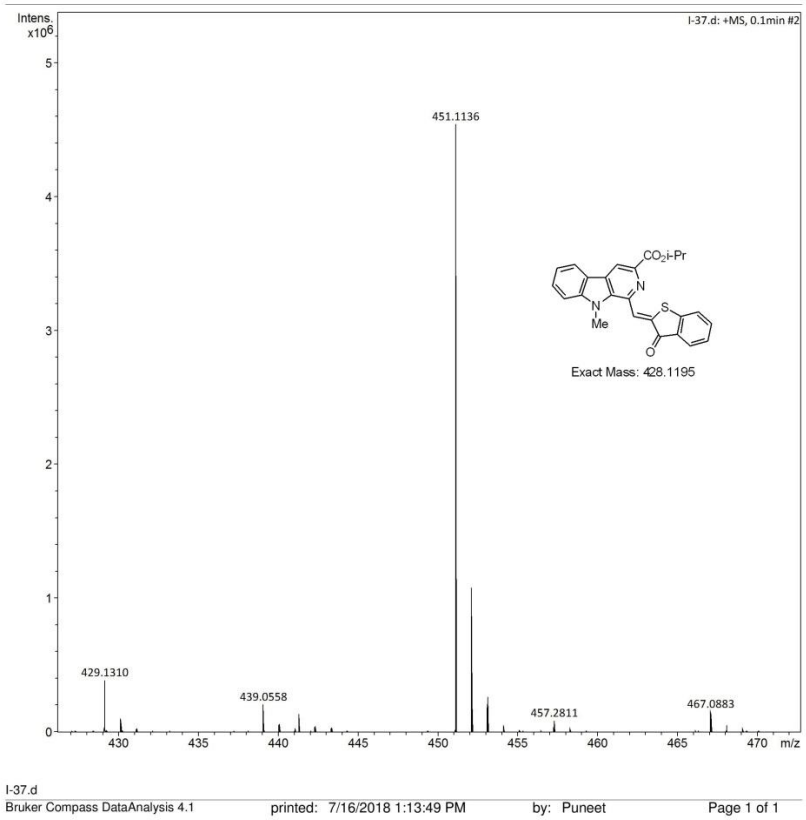


Figure S35. HRMS spectrum of **2jA**.

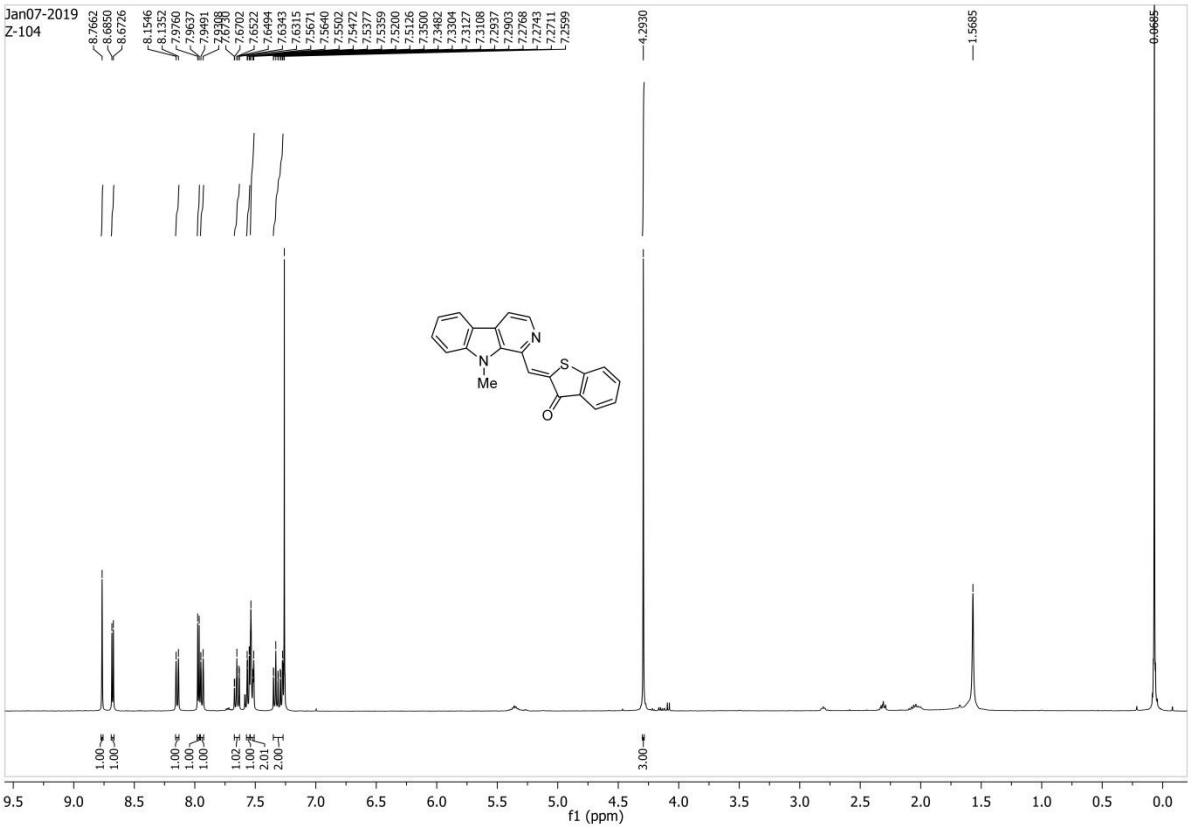


Figure S36. ^{1}H NMR spectrumof **2lA**.

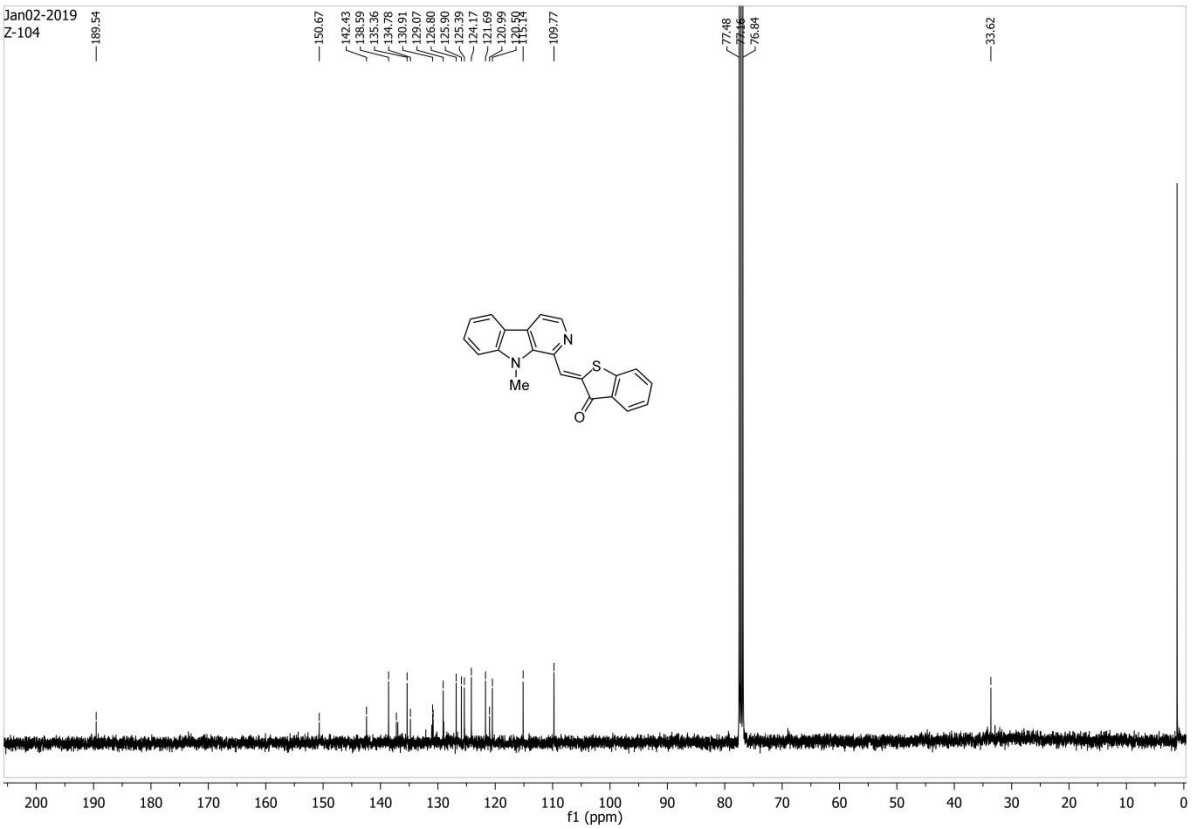


Figure S37. ^{13}C NMR spectrumof **2lA**.

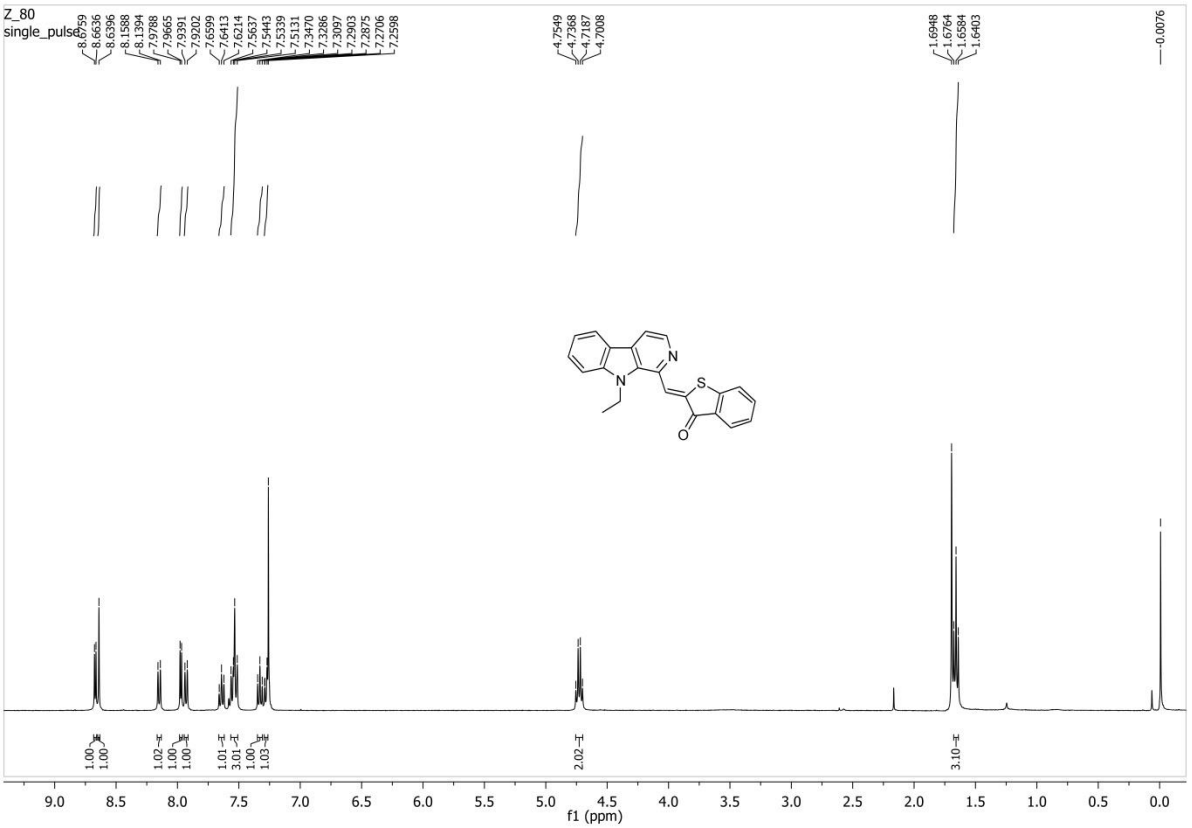


Figure S38. ^{1}H NMR spectrumof **2mA**.

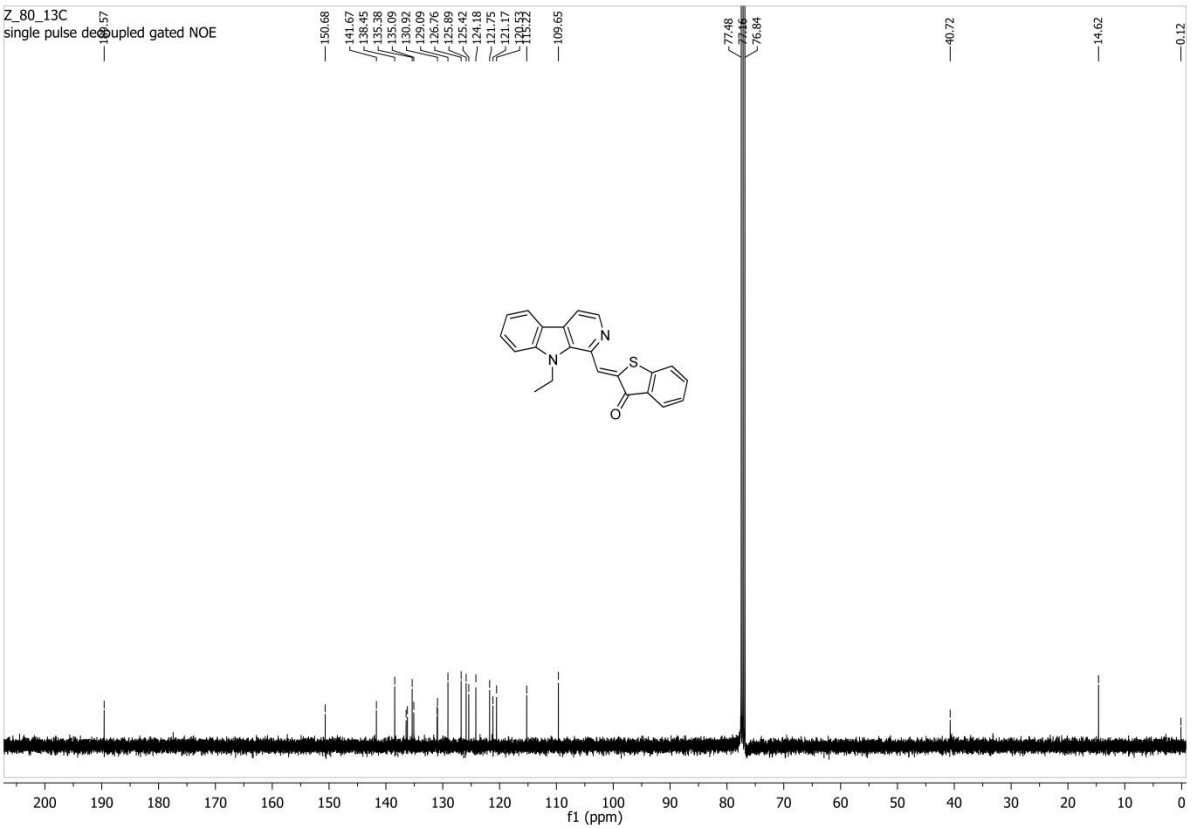


Figure S39. ^{13}C NMR spectrumof **2mA**.

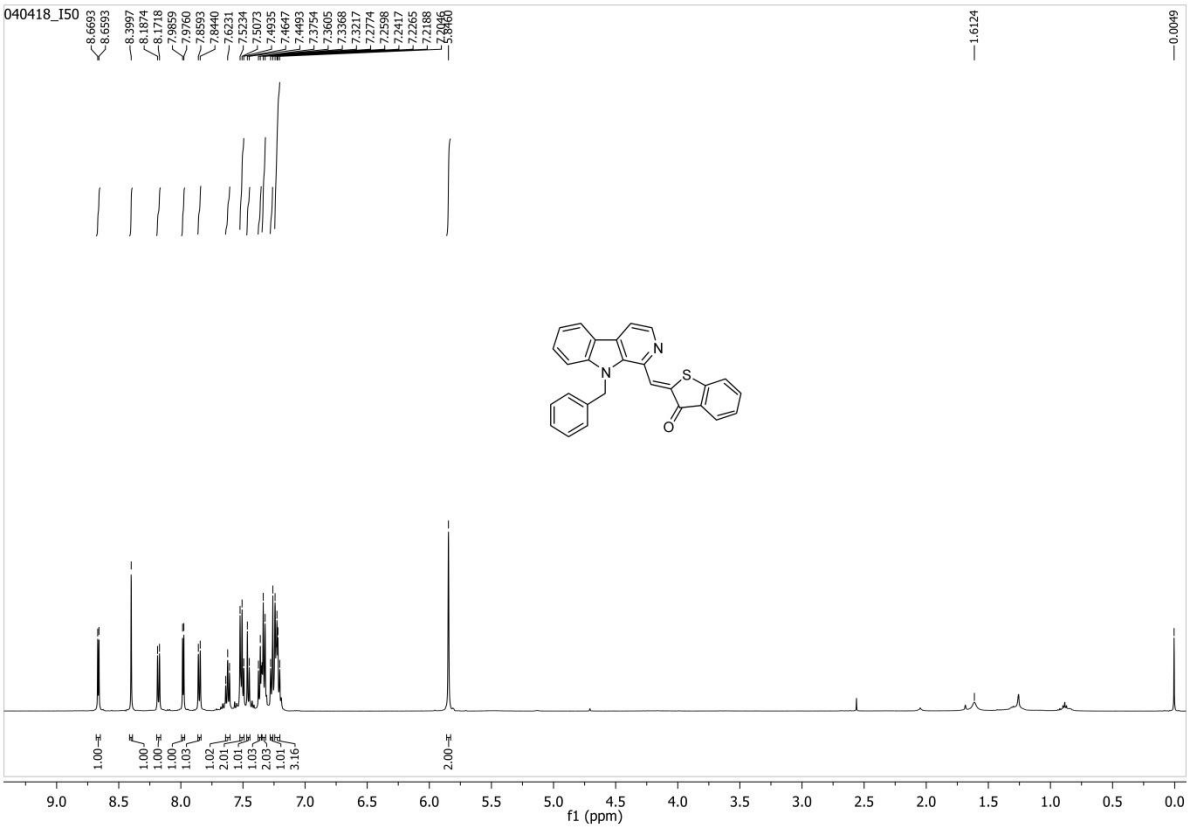


Figure S40. ^{1}H NMR spectrumof **2nA**.

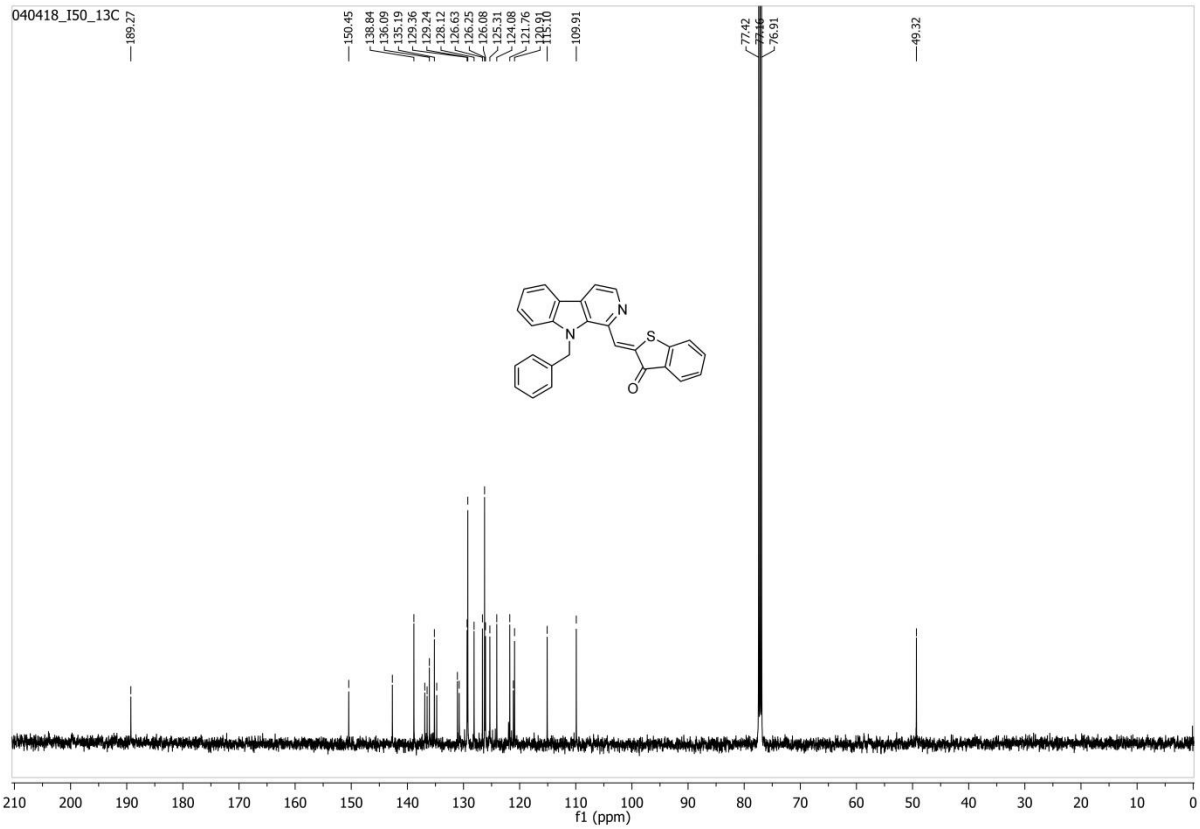


Figure S41. ^{13}C NMR spectrumof **2nA**.

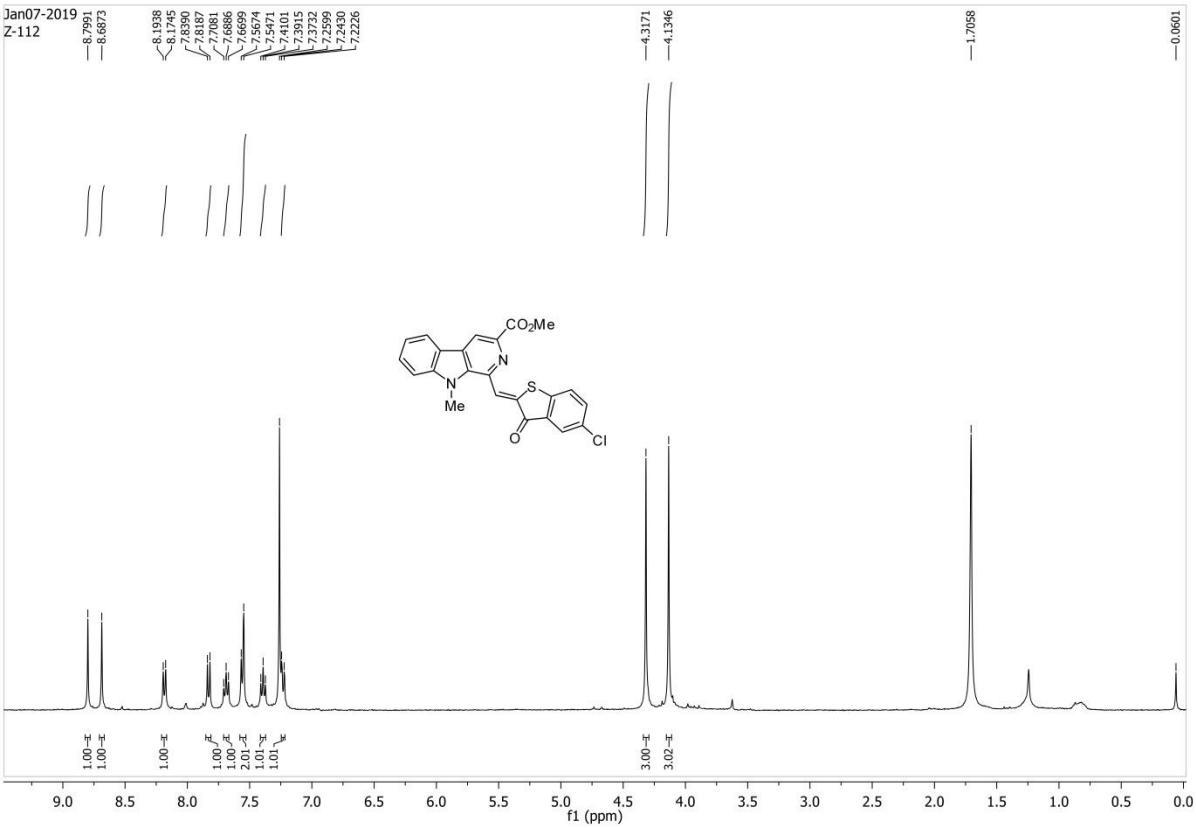


Figure S42. ^{1}H NMR spectrumof **2bB**.

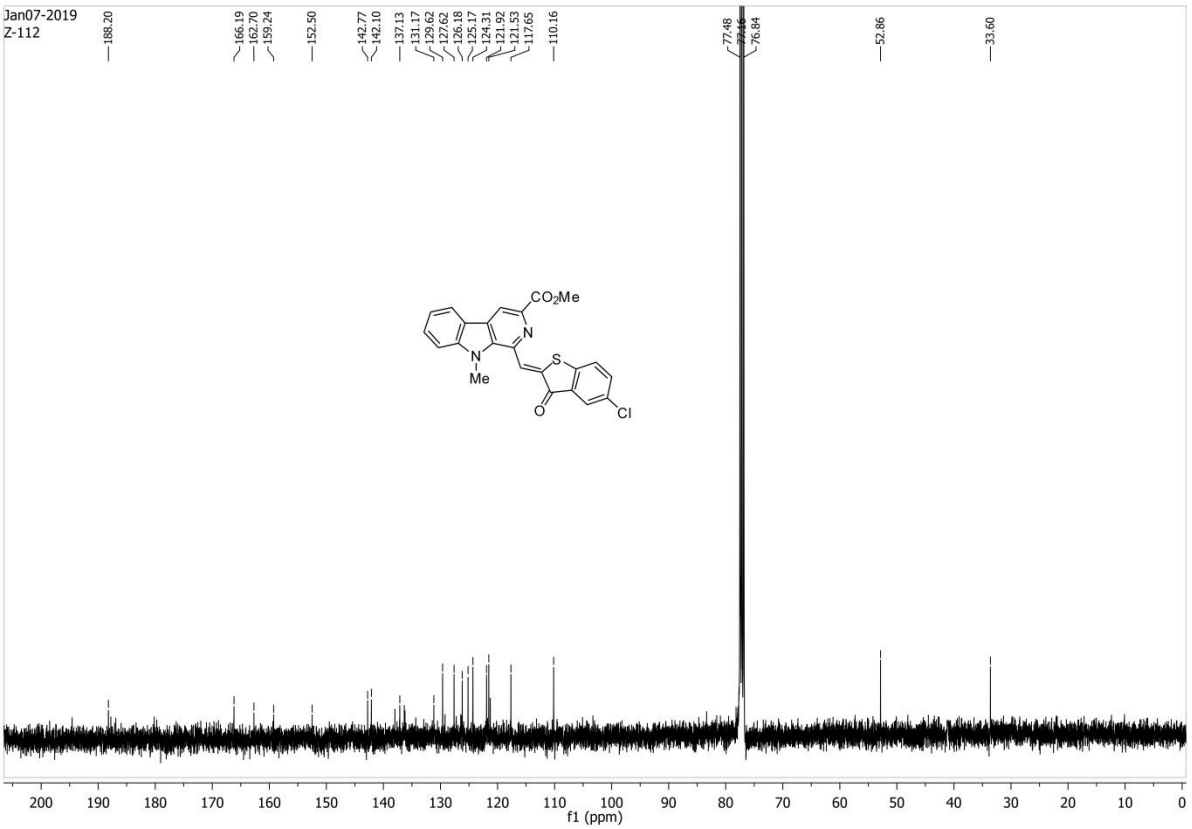
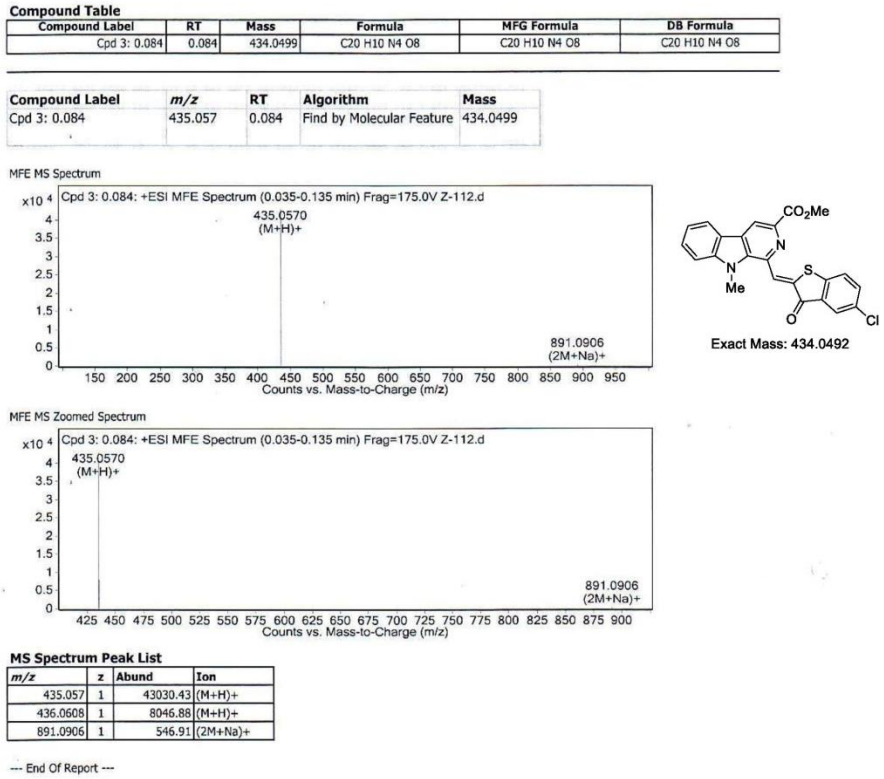


Figure S43. ^{13}C NMR spectrumof **2bB**.



Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	DB Formula
Cpd 3: 0.084	0.084	434.0499	C20 H10 N4 O8	C20 H10 N4 O8	C20 H10 N4 O8

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: 0.084	435.057	0.084	Find by Molecular Feature	434.0499

MFE MS Spectrum

Exact Mass: 434.0492

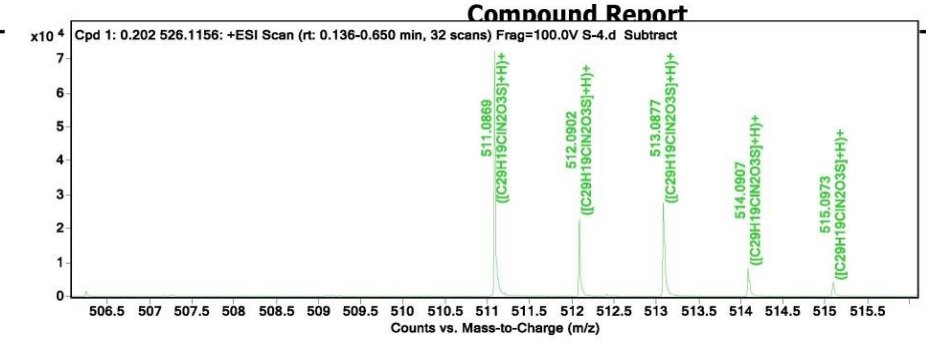
MFE MS Zoomed Spectrum

MS Spectrum Peak List

m/z	z	Abund	Ion
435.057	1	43030.43	(M+H)+
436.0608	1	8046.88	(M+H)+
891.0906	1	546.91	(2M+Na)+

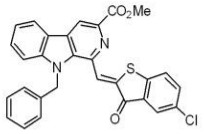
--- End Of Report ---

Figure S44. HRMS spectrum of **2bB**.



MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
511.0869	511.0878	1.62	1	72567.85	C29H19ClN2O3S	(M+H)+
512.0902	512.0909	1.38	1	23229.96	C29H19ClN2O3S	(M+H)+
513.0877	513.086	-3.39	1	27617.25	C29H19ClN2O3S	(M+H)+
514.0907	514.0883	-4.64	1	8417.9	C29H19ClN2O3S	(M+H)+
515.0973	515.087	-20.03	1	4172.86	C29H19ClN2O3S	(M+H)+
516.101	516.0876	-26.08	1	1345.47	C29H19ClN2O3S	(M+H)+
517.1011	517.089	-23.48	1	334.21	C29H19ClN2O3S	(M+H)+



Exact Mass: 510.0805

Instrument Info : Agilent Technologies 6545 Q-TOF LC/MS

Note: Please acknowledge the work done by HRMS Facility at BITS Pilani, Pilani Campus funded by DST-FIST in your publication.

---End Of Report---

Figure S45. HRMS spectrum of **2hB**.

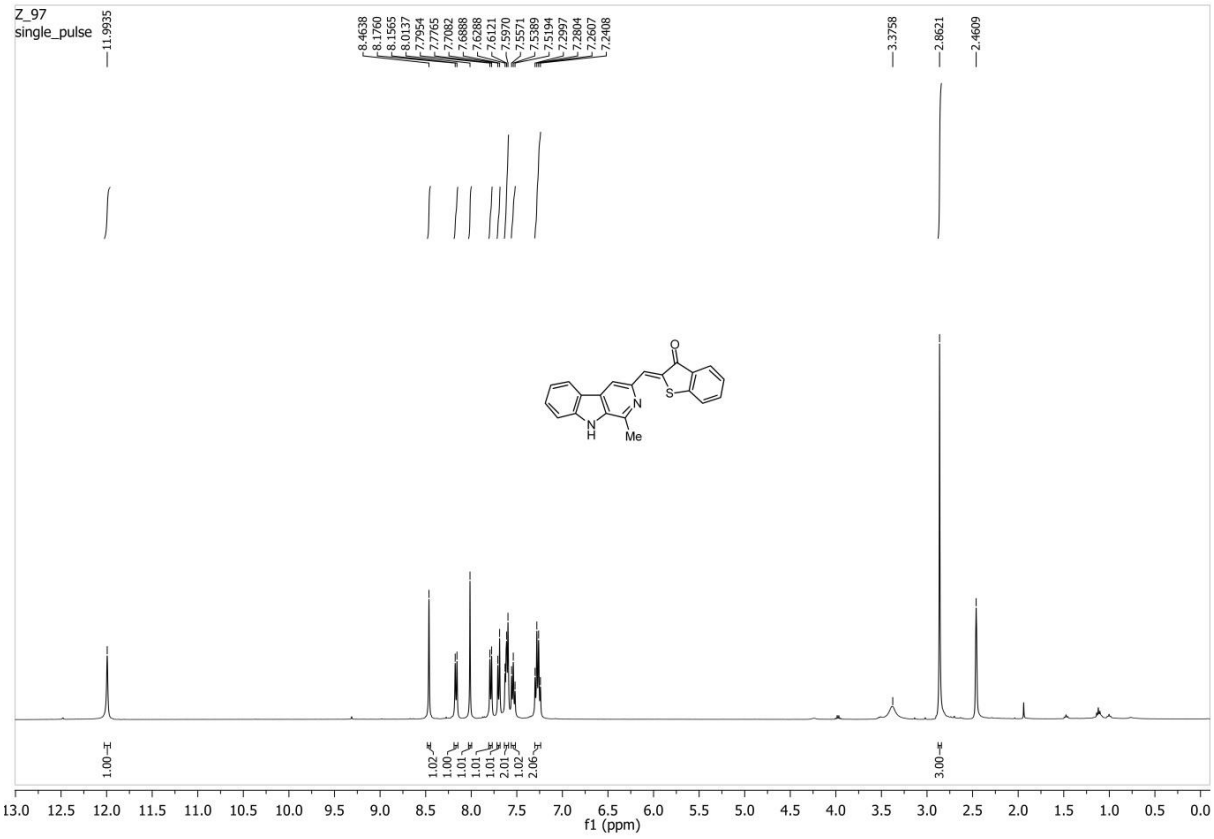


Figure S46. ^{1}H NMR spectrumof **4aA**.

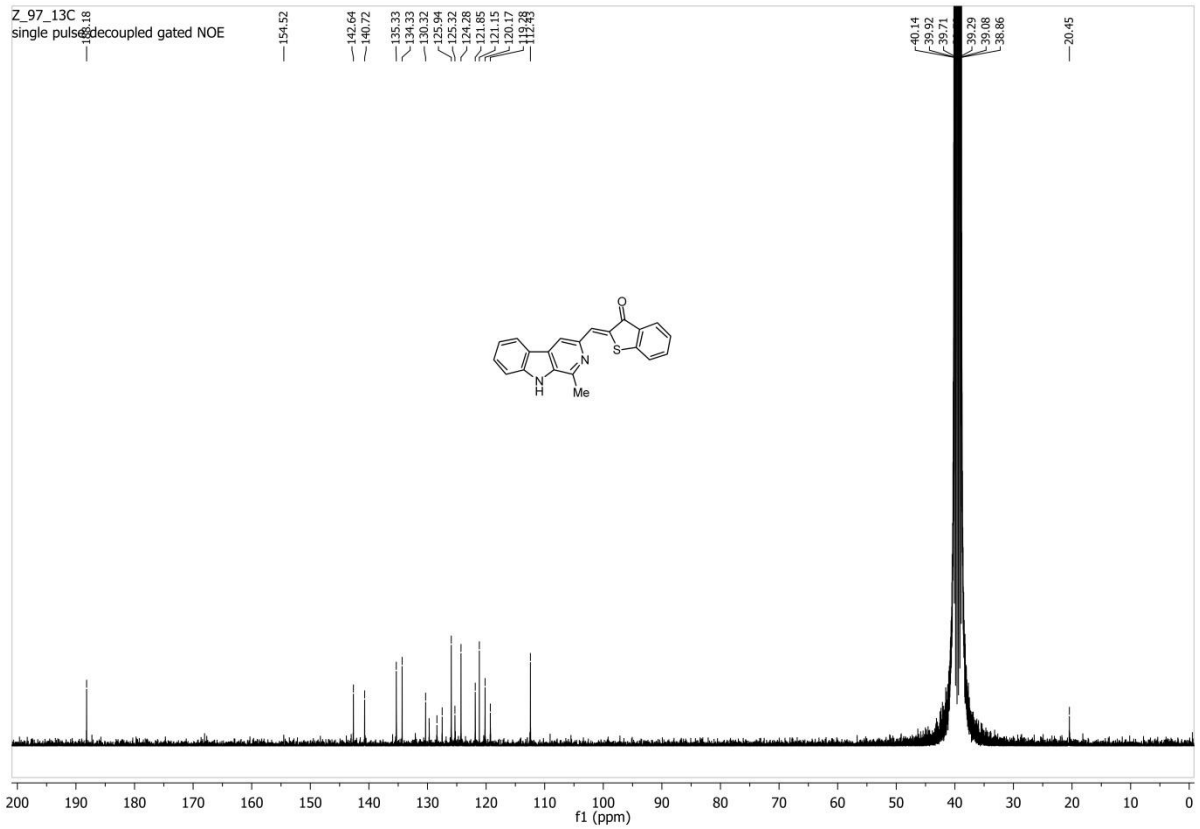


Figure S47. ^{13}C NMR spectrumof **4aA**.

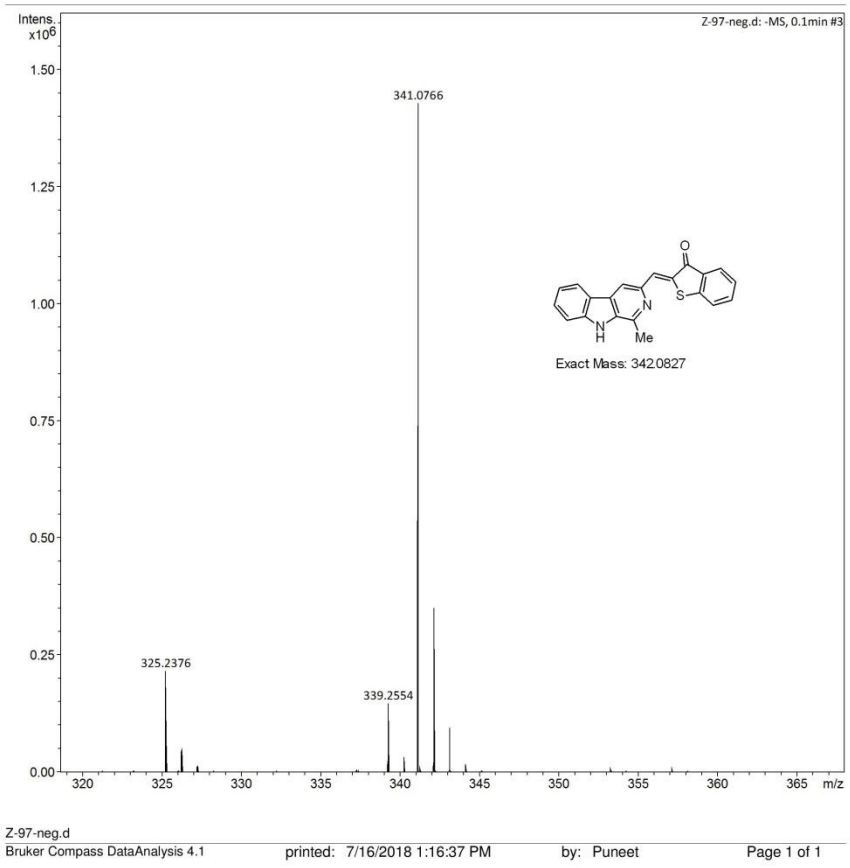


Figure S48. HRMS spectrum of **4aA**.

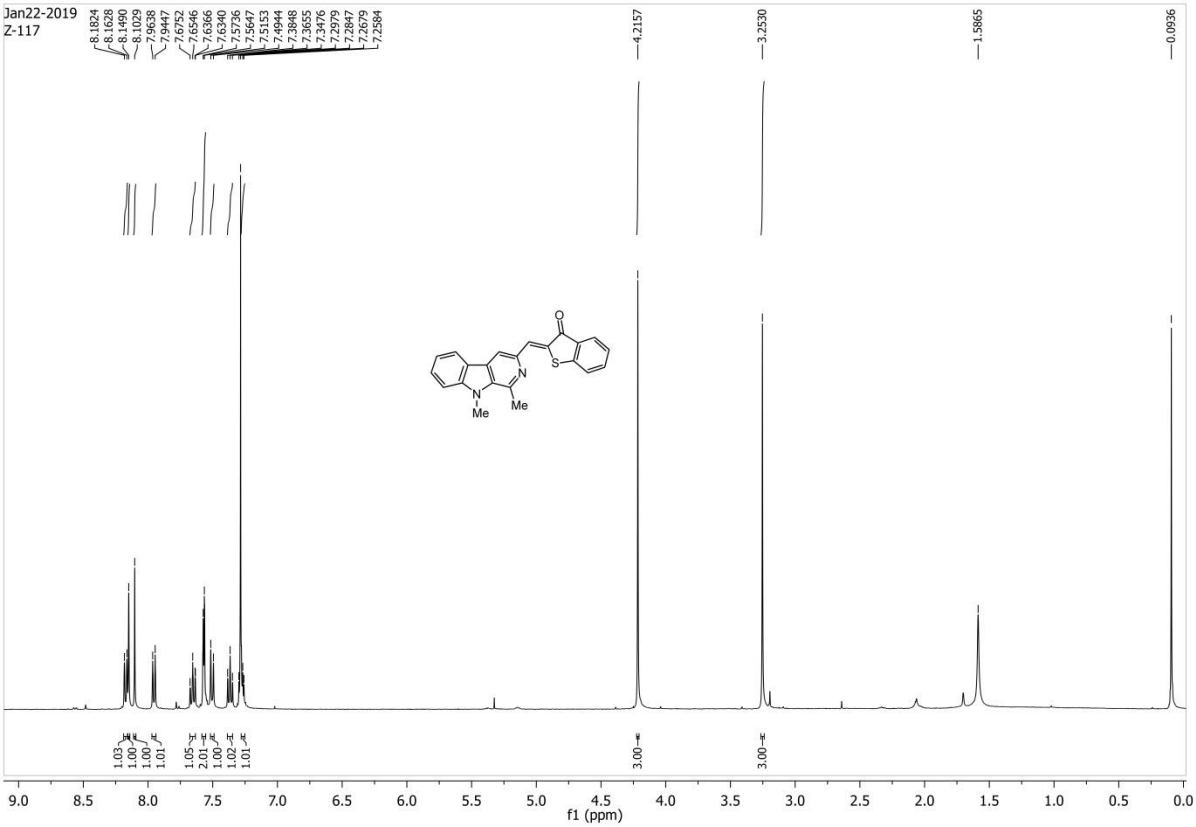


Figure S49. ^{1}H NMR spectrumof **4bA**.

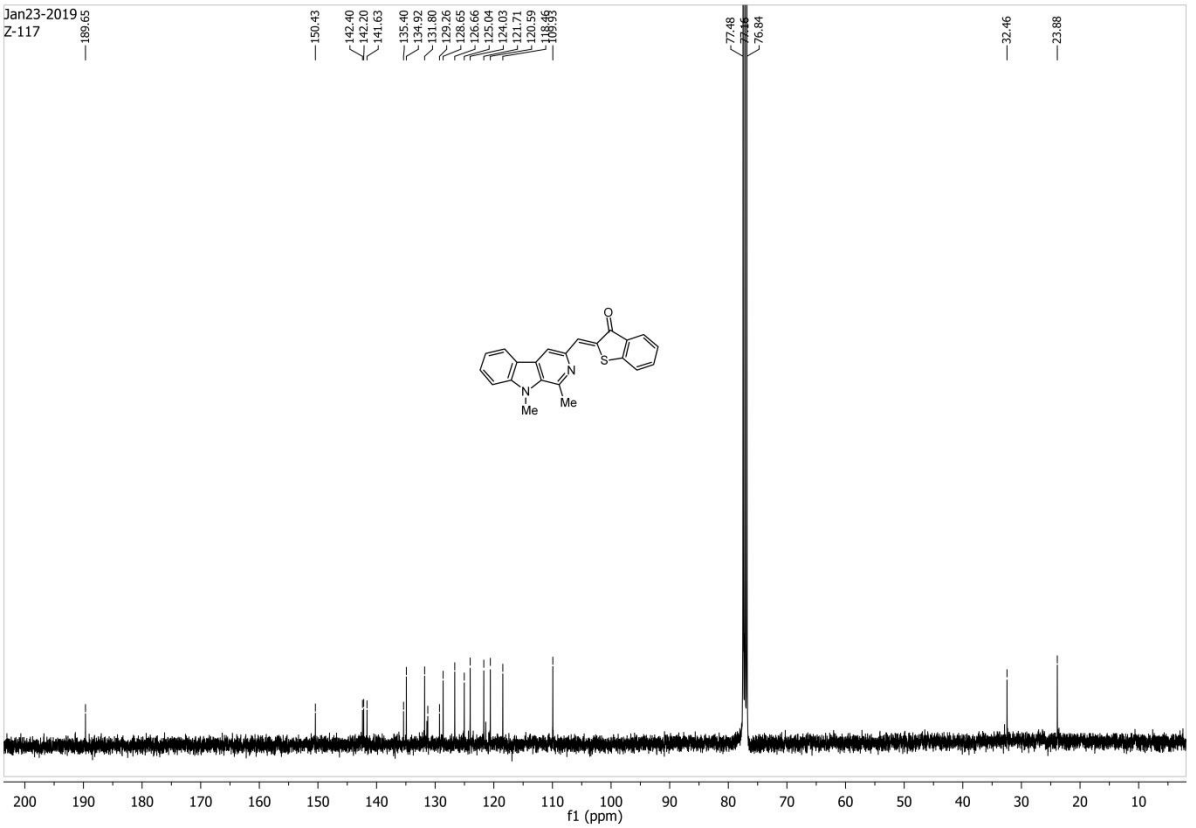


Figure S50. ^{13}C NMR spectrumof **4bA**.

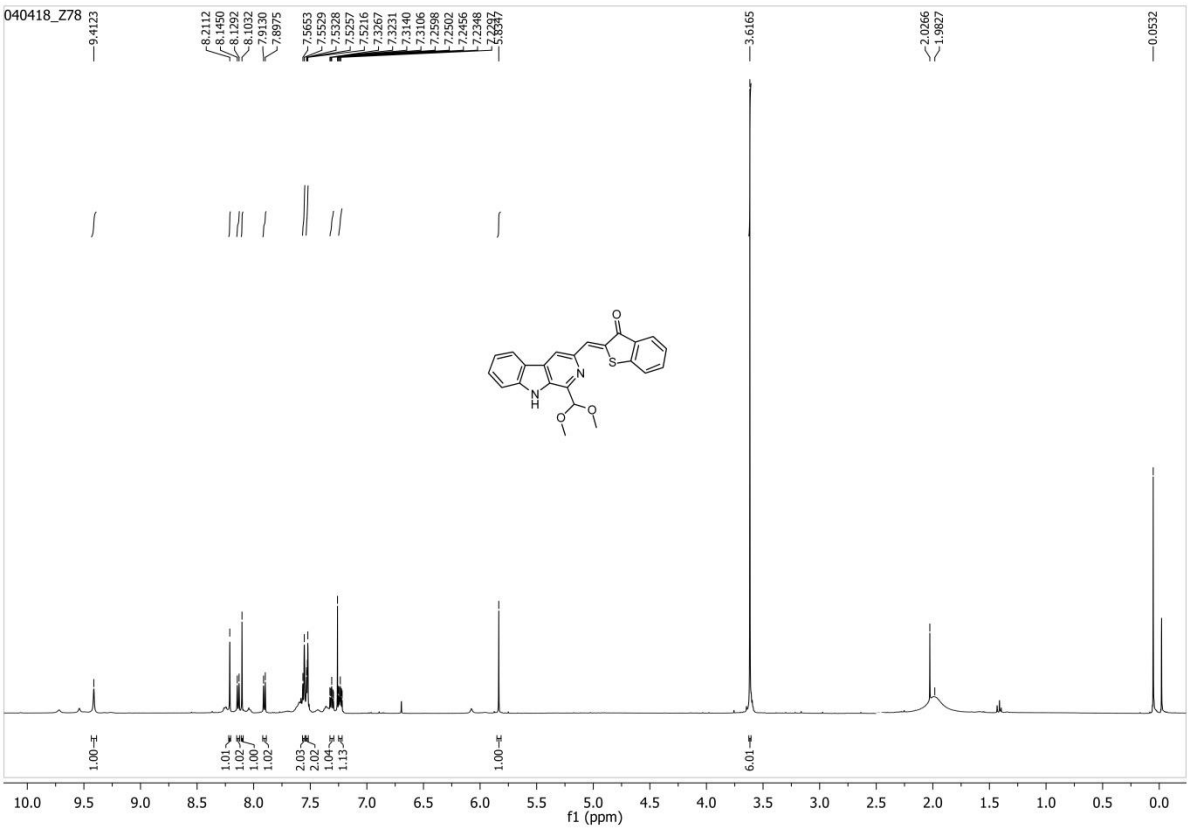


Figure S52. ^{1}H NMR spectrumof **4cA**.

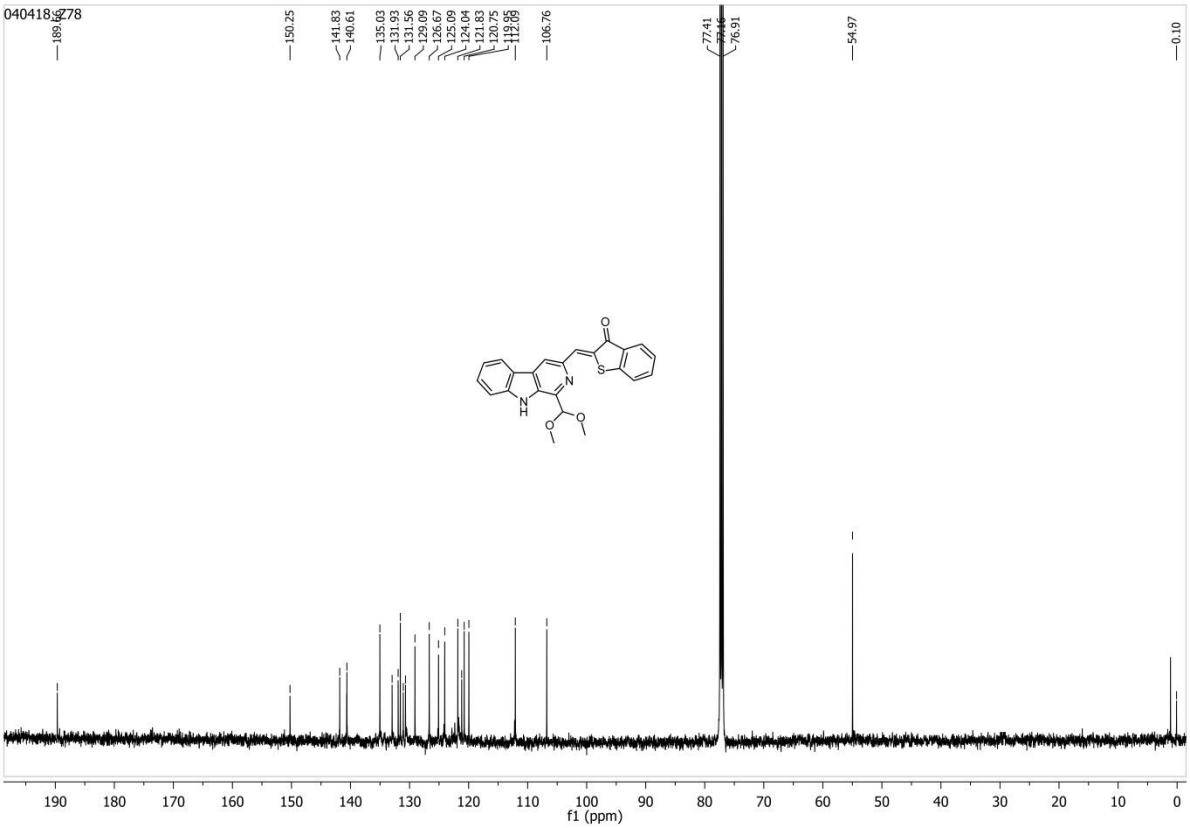


Figure S52. ^{13}C NMR spectrumof **4cA**.

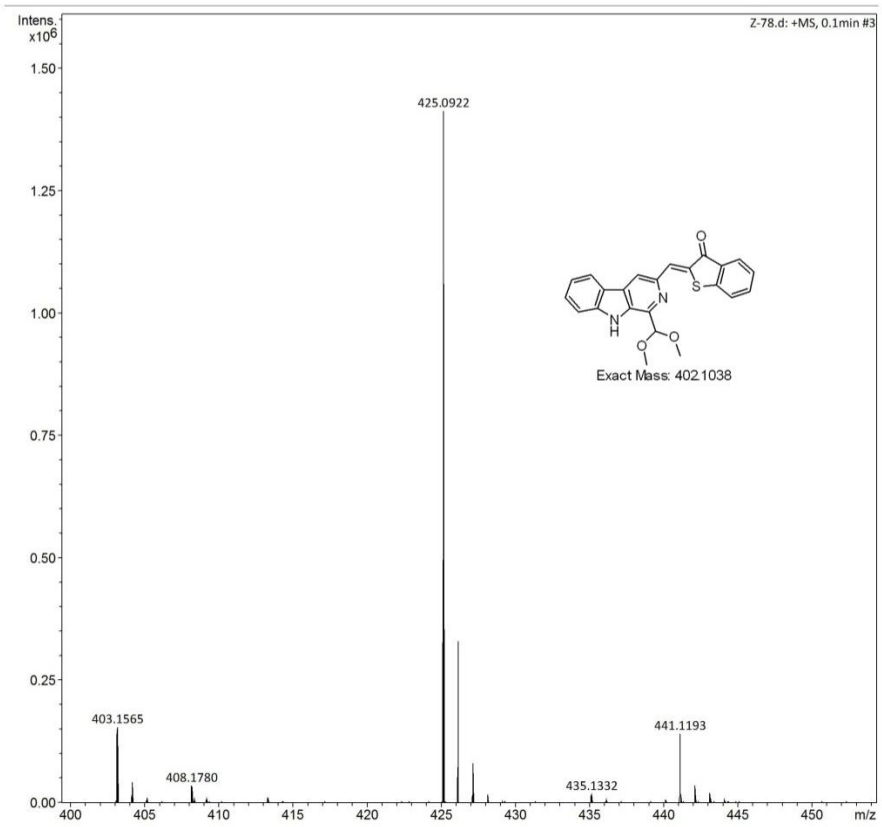


Figure S53. HRMS spectrum of **4cA**.

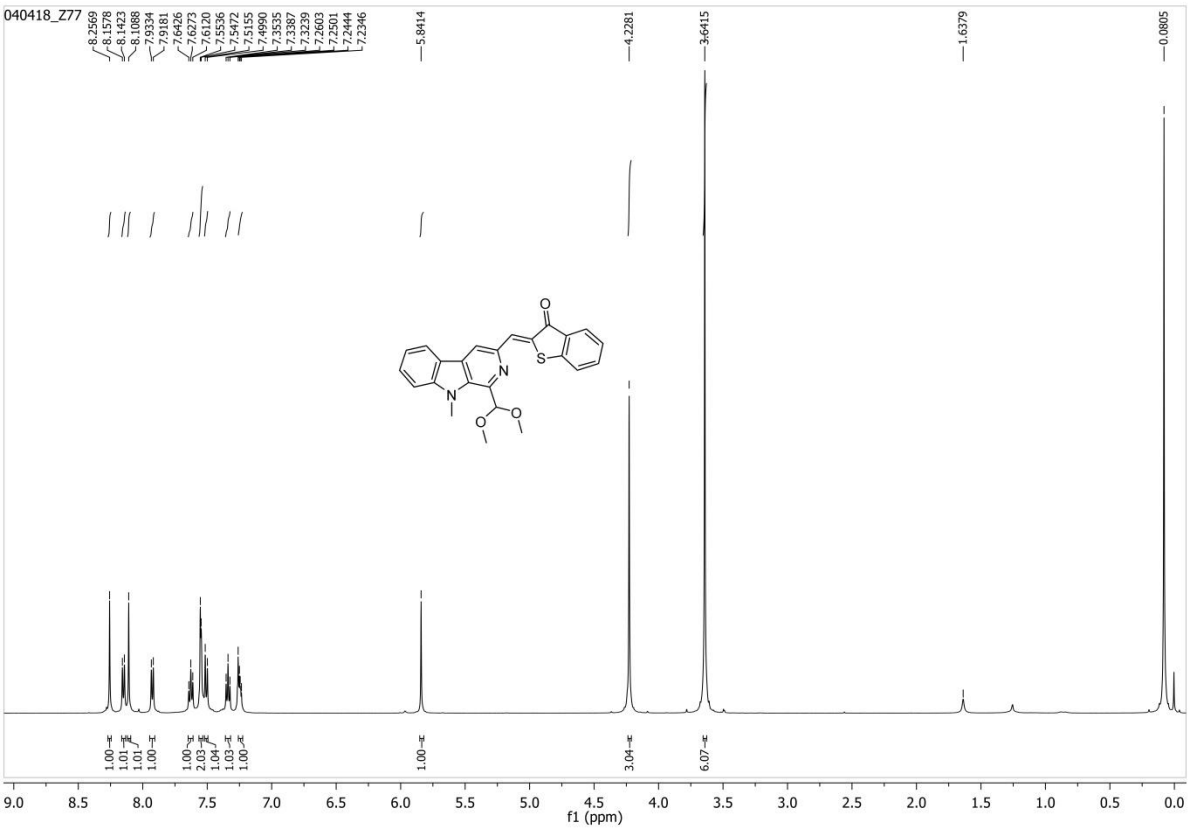


Figure S54. ^{1}H NMR spectrumof **4dA**.

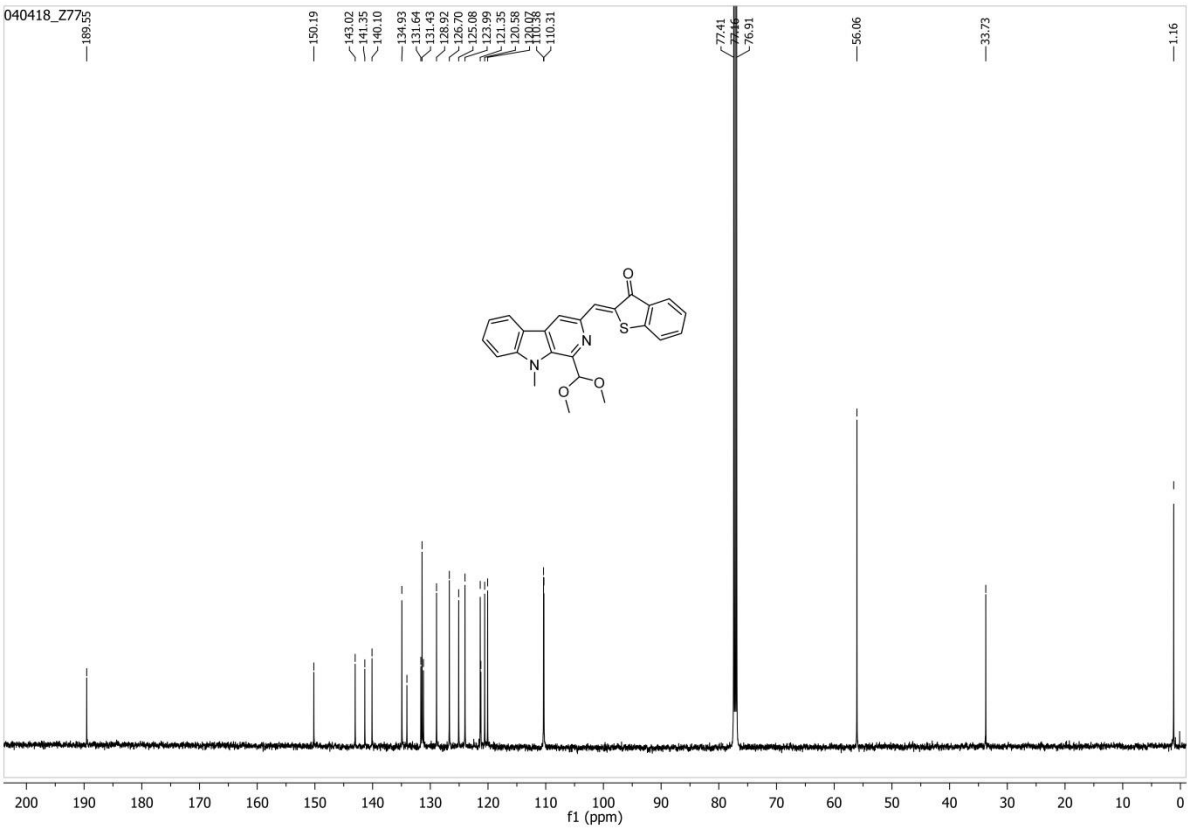


Figure S55. ^{13}C NMR spectrumof **4dA**.

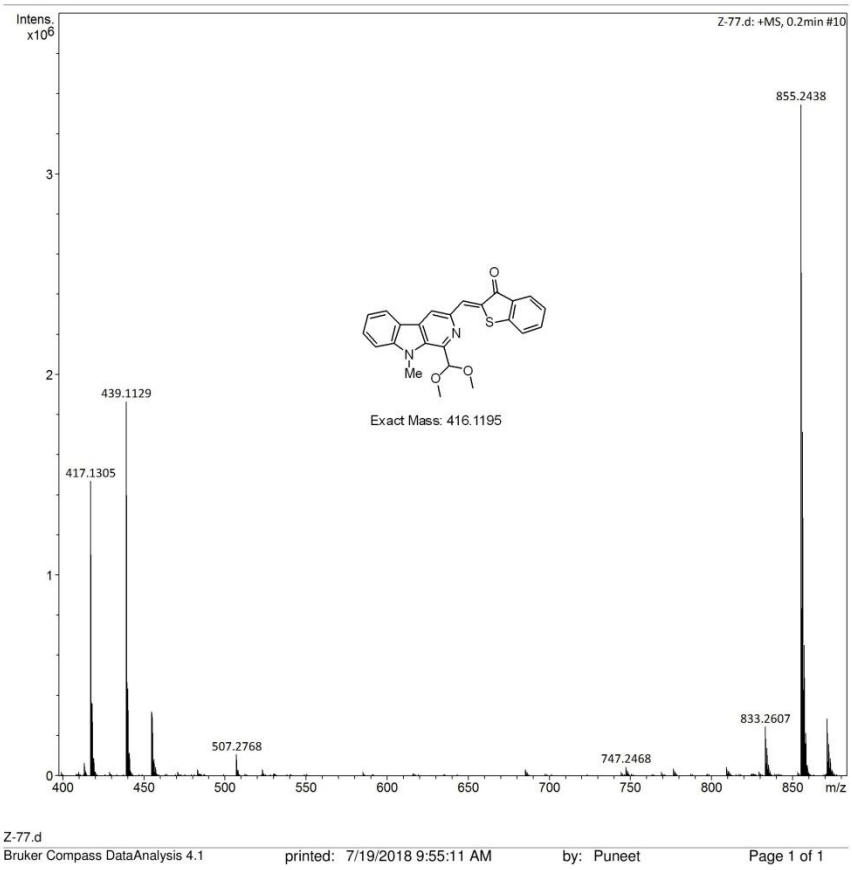


Figure S56. HRMS spectrum of **4dA**.

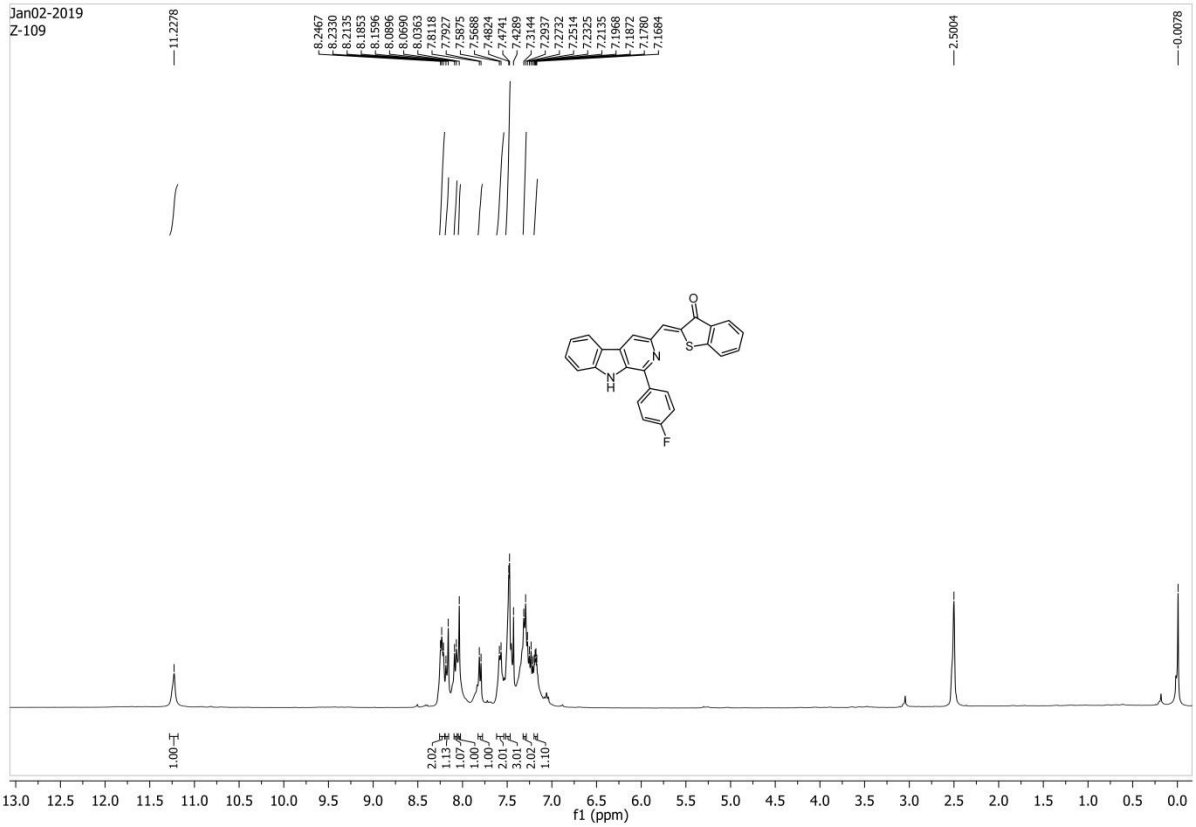


Figure S57. ^{1}H NMR spectrumof **4eA**.

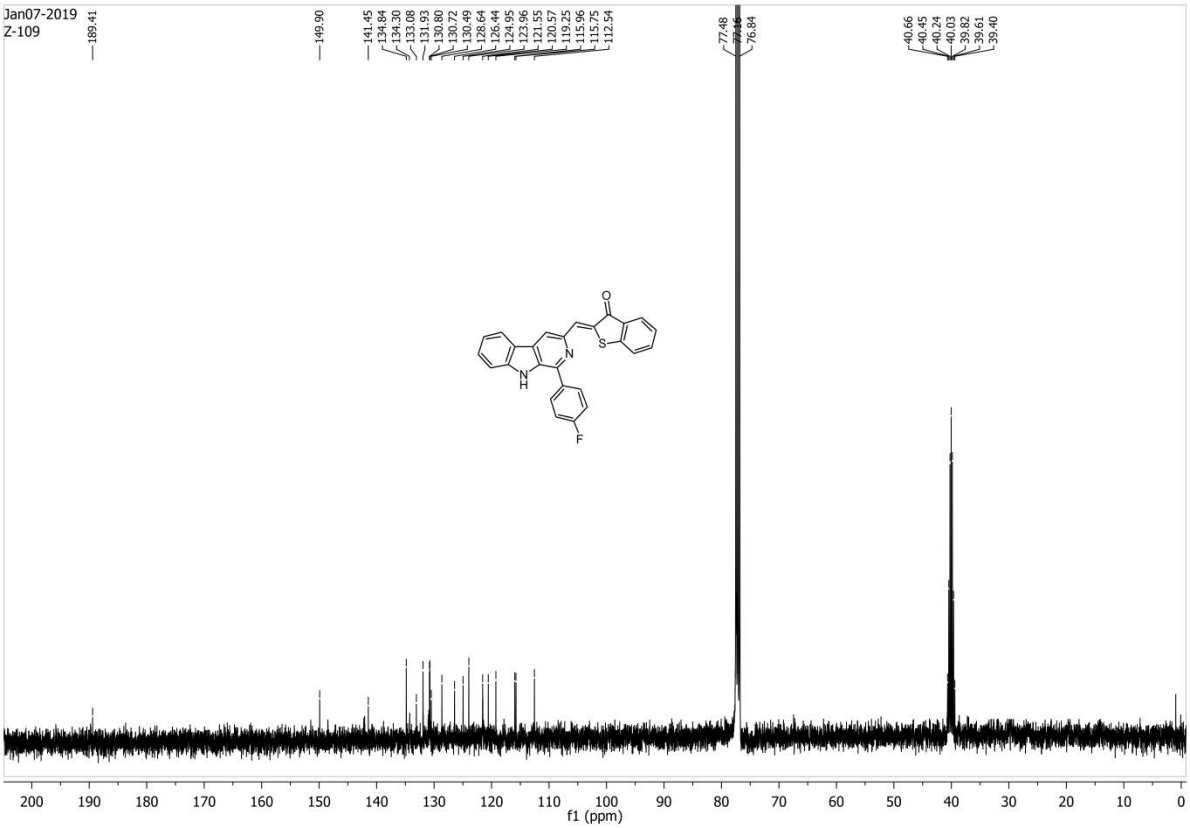


Figure S58. ^{13}C NMR spectrumof **4eA**.

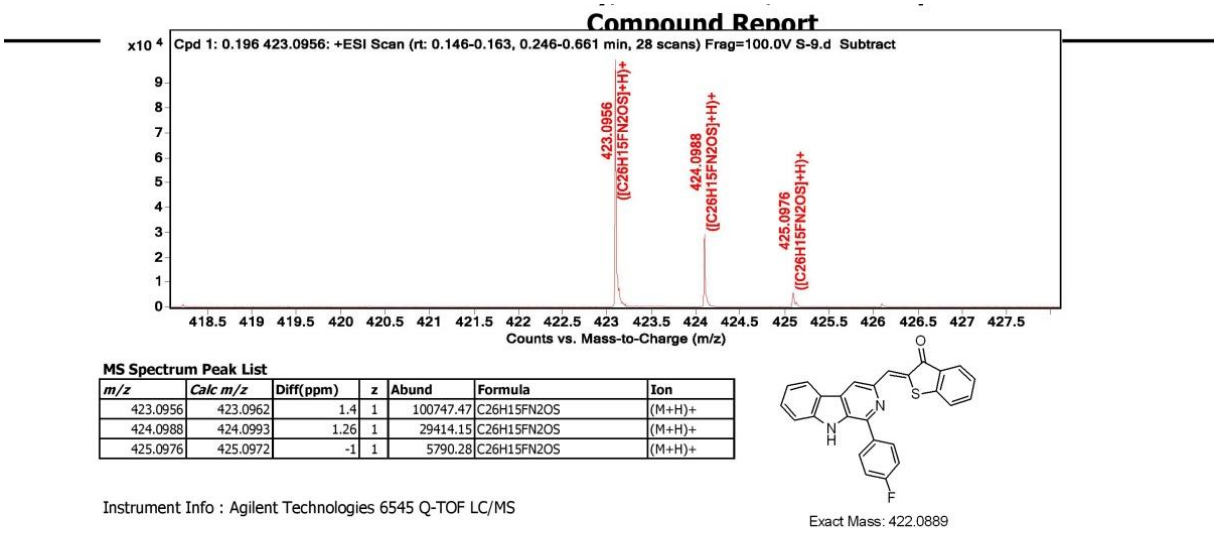


Figure S59. HRMS spectrum of **4eA**.

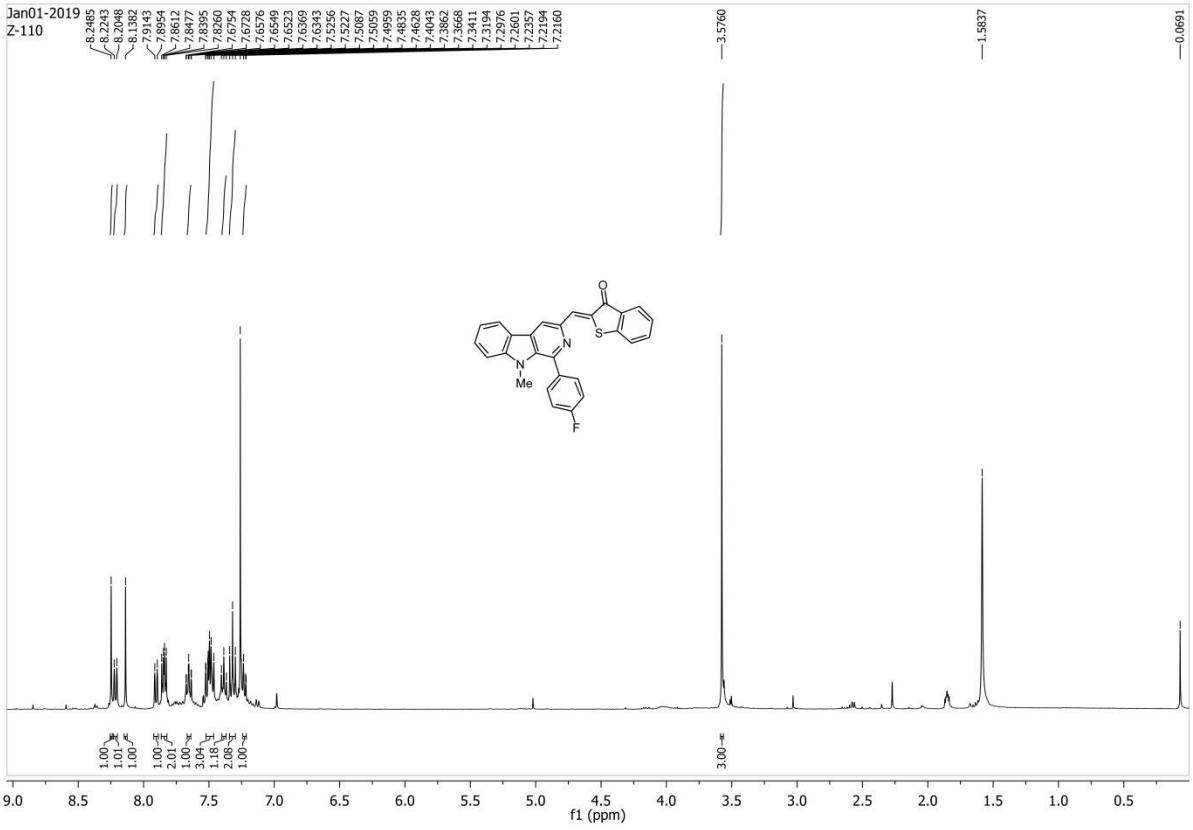


Figure S60. ^{1}H NMR spectrumof **4fA**.

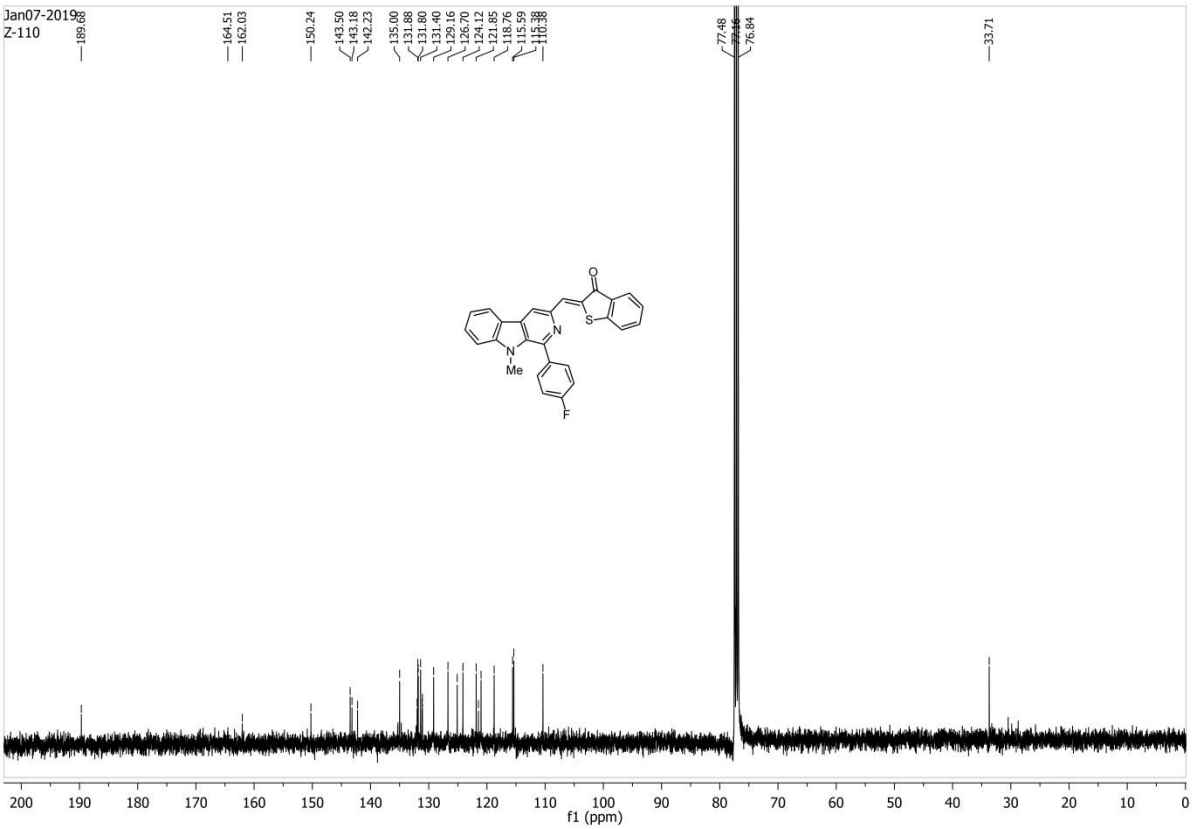


Figure S61. ^{13}C NMR spectrumof **4fA**.

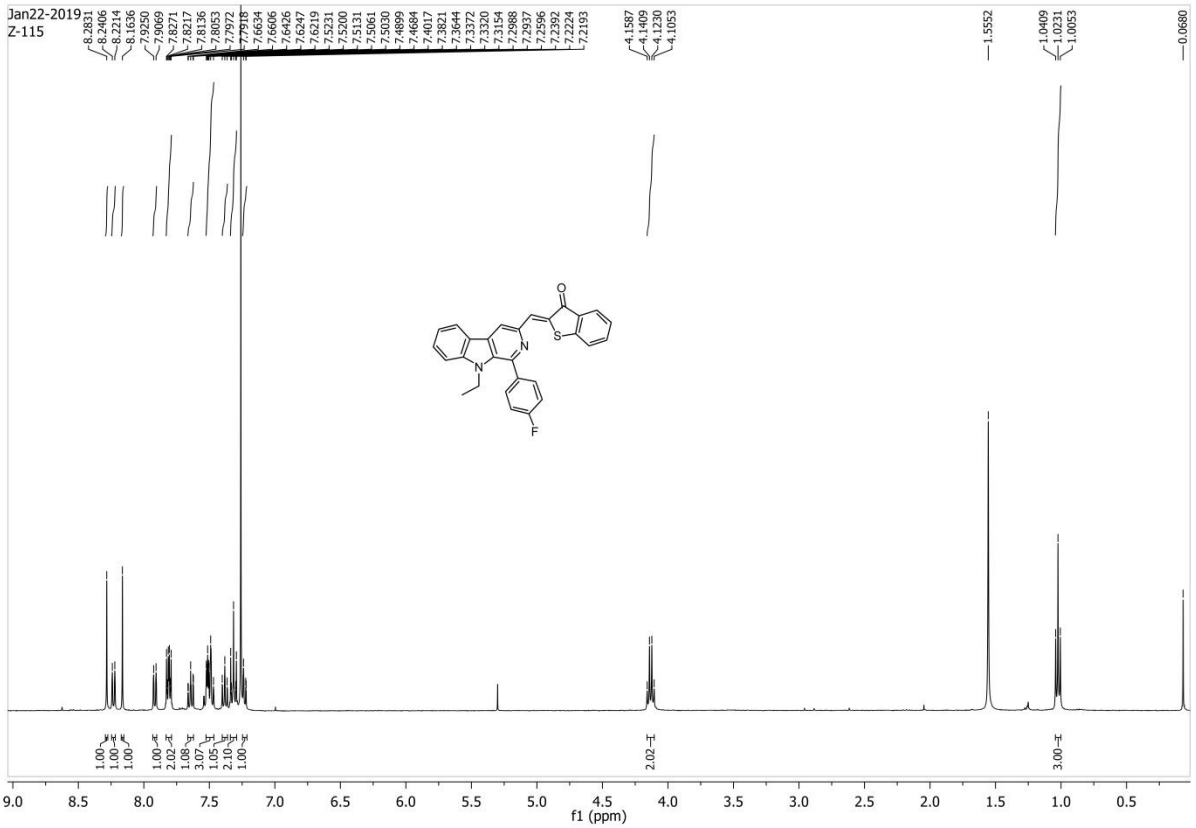


Figure S62. ^{1}H NMR spectrumof **4gA**.

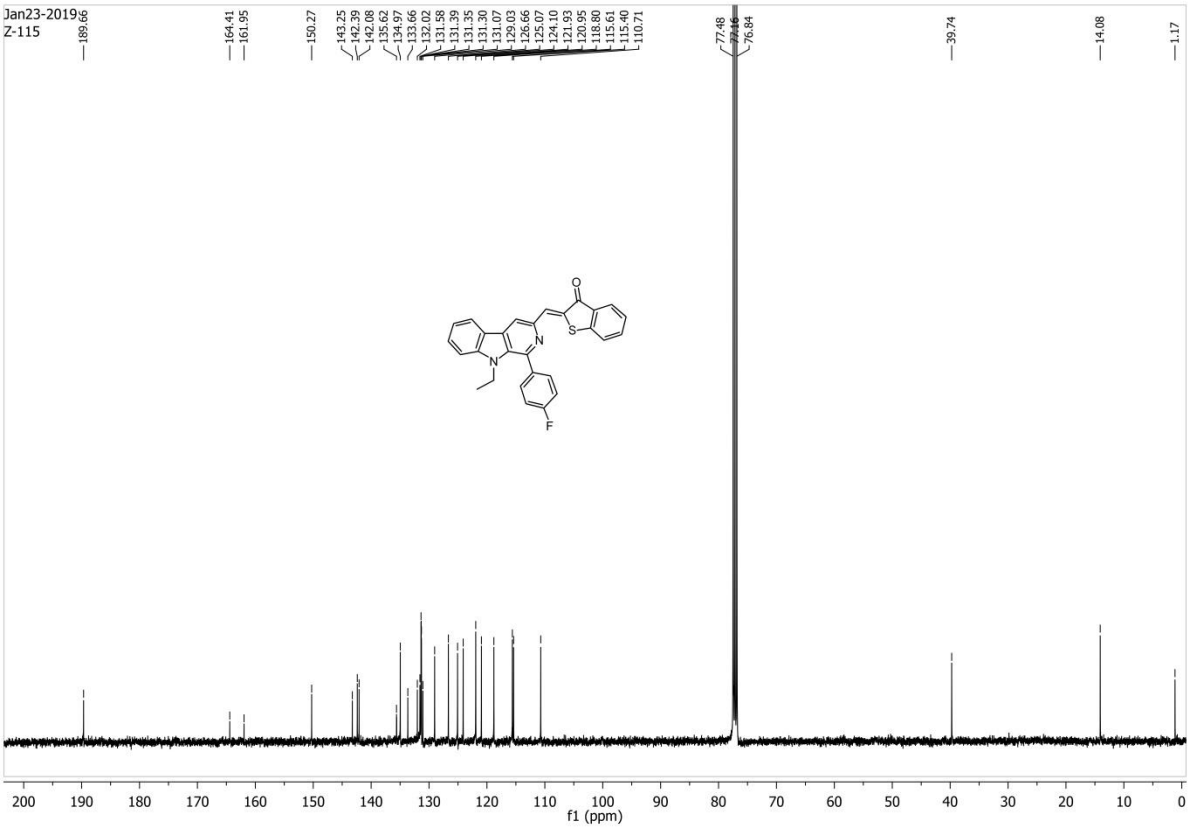
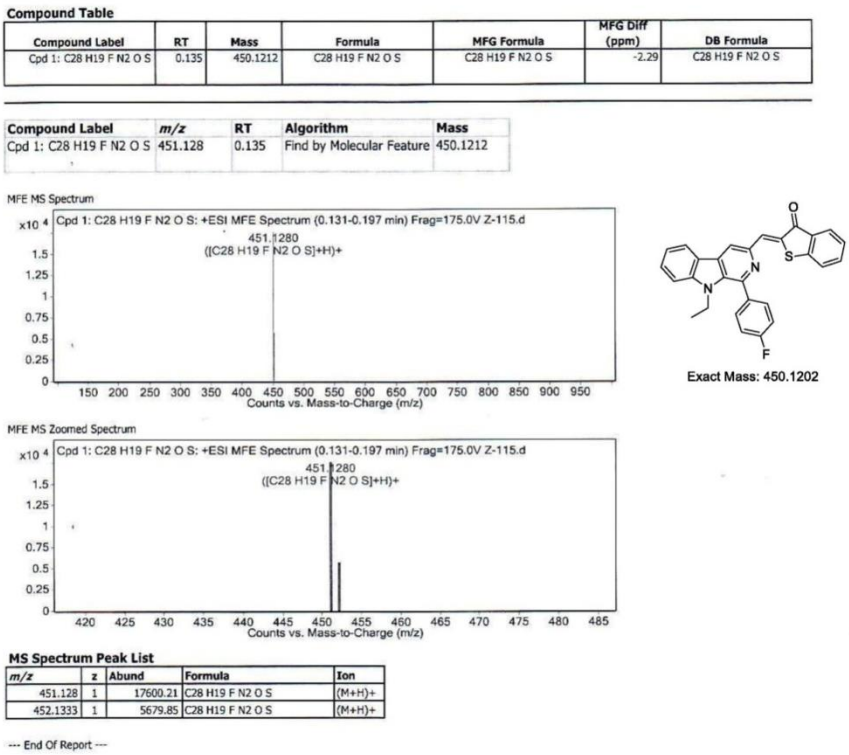


Figure S63. ^{13}C NMR spectrumof **4gA**.



Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C28 H19 F N2 O S	0.135	450.1212	C28 H19 F N2 O S	C28 H19 F N2 O S	-2.29	C28 H19 F N2 O S

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C28 H19 F N2 O S	451.128	0.135	Find by Molecular Feature	450.1212

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
451.128	1	17600.21	C28 H19 F N2 O S	(M+H)+
452.1333	1	5679.85	C28 H19 F N2 O S	(M+H)+

--- End Of Report ---

Figure S64. HRMS spectrum of **4gA**.

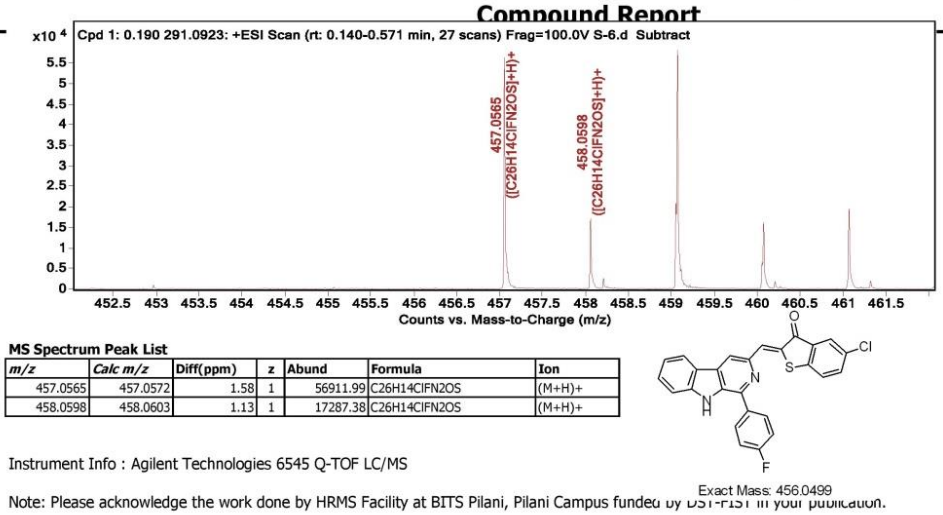


Figure S65. HRMS spectrum of **4eB**.

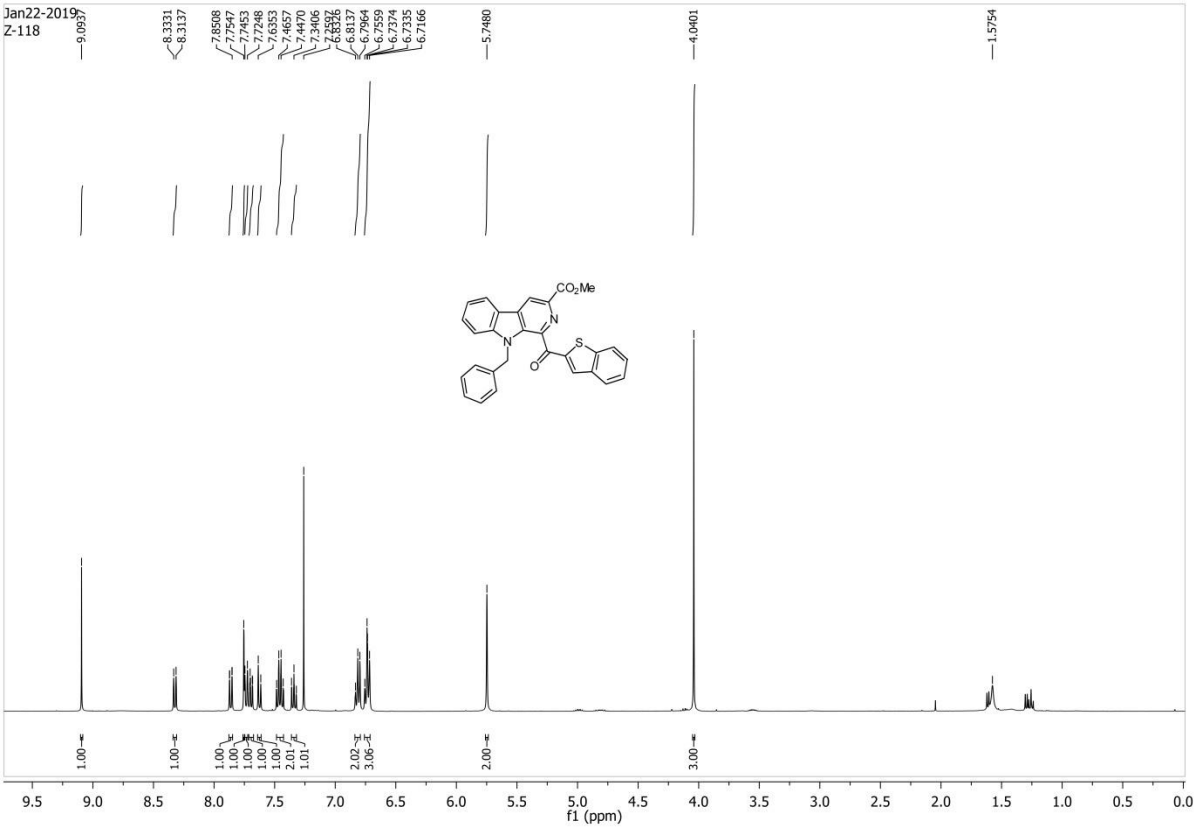


Figure S66. ^{1}H NMR spectrumof **6C**.

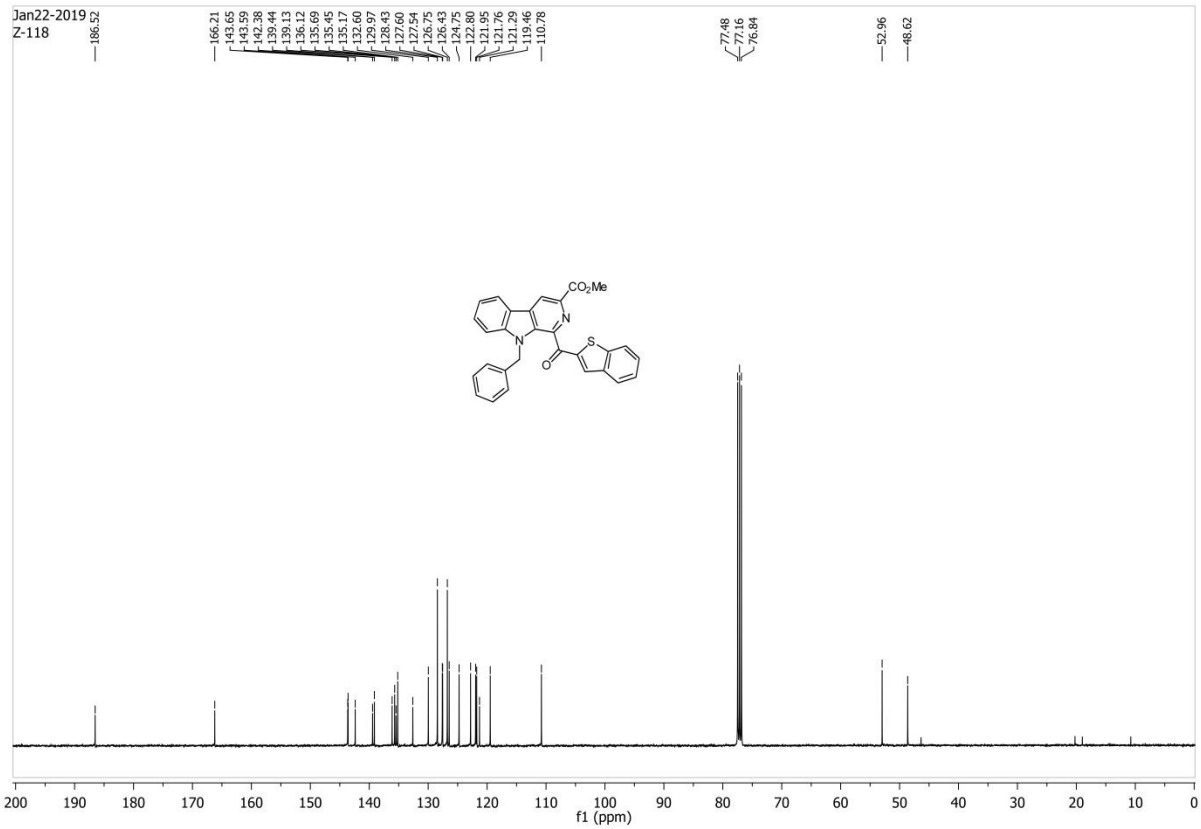


Figure S67. ^{13}C NMR spectrumof **6C**.

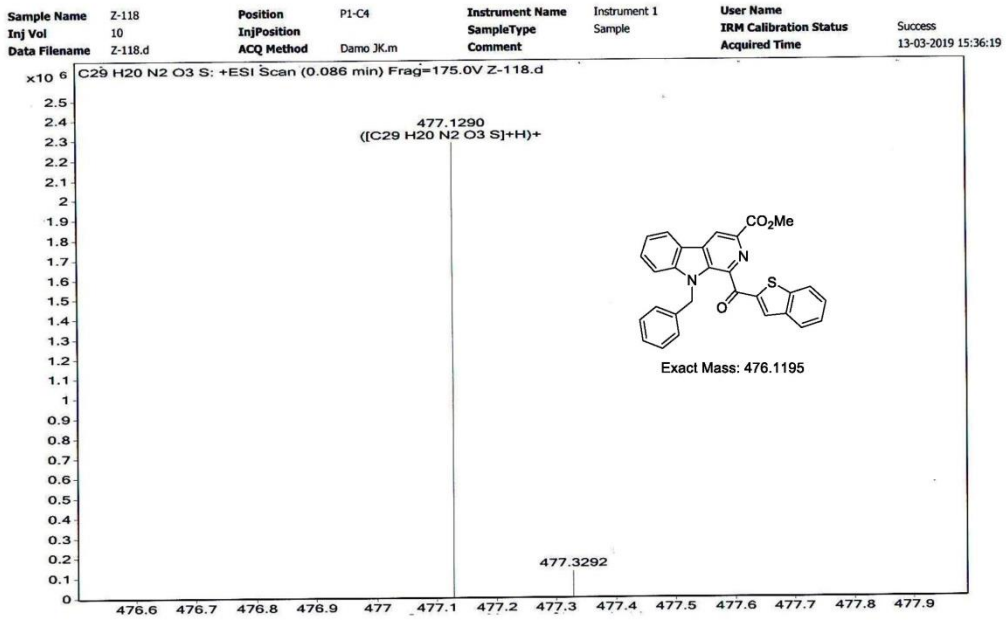


Figure S68. HRMS spectrum of **6C**.