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

AcOH-Mediated Metal Free Approach towards Synthesis of Bis β-Carbolines and Imidazopyridoindole Derivatives and Assessment of their Photophysical Properties

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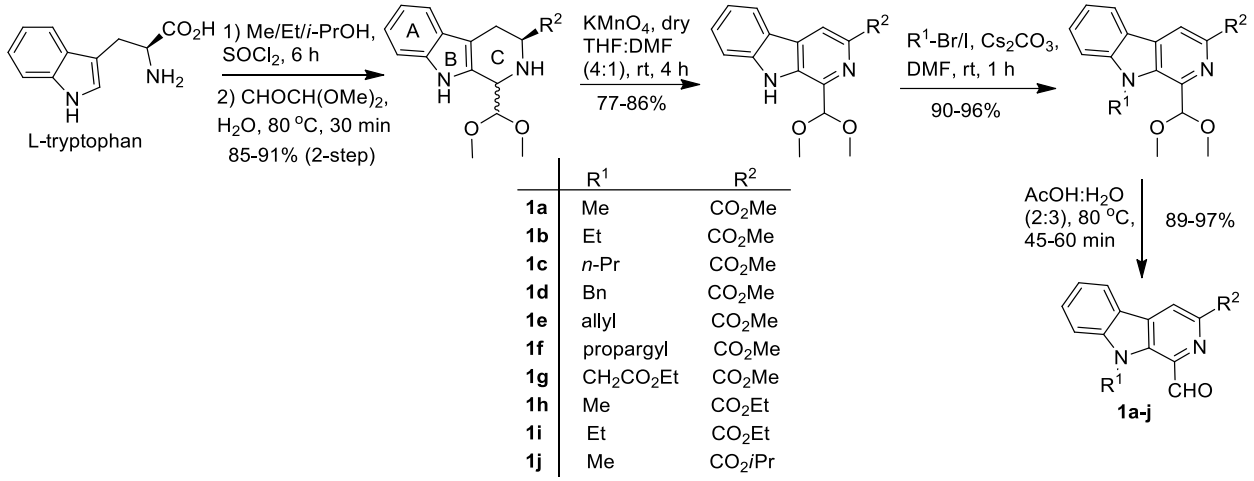
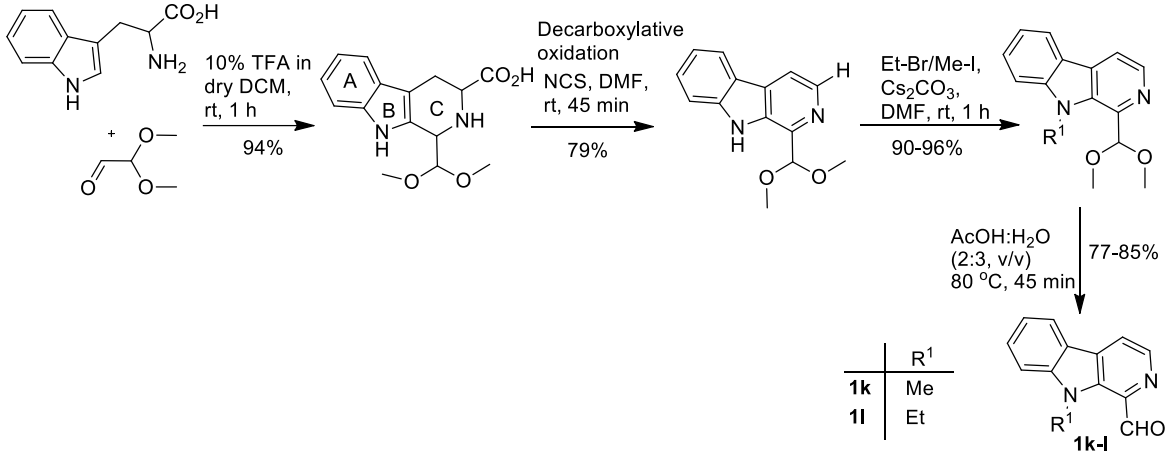


	R^1	R^2
1a	Me	CO_2Me
1b	Et	CO_2Me
1c	*n*-Pr	CO_2Me
1d	Bn	CO_2Me
1e	allyl	CO_2Me
1f	propargyl	CO_2Me
1g	CH_2CO_2Et	CO_2Me
1h	Me	CO_2Et
1i	Et	CO_2Et
1j	Me	CO_2iPr

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

Synthesis of N-alkylated Kumujian C (1k-l)



	R^1
1k	Me
1l	Et

Scheme 1. Synthesis of 1-formyl-9*H*-pyrido[3,4-*b*]indole derivatives[2]

Experimental Section

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, toluene, ACN, diethylether, and DMF) were used as received without further distillation. Thin layer chromatography (TLC) was performed on precoated aluminum 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-ended 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. ^1H and ^{13}C NMR spectra were recorded on an Avance III Bruker spectrometer at operating frequencies of 400 MHz, 500MHz, 600MHz (^1H) or 100 MHz, 125 MHz, 150 MHz (^{13}C), as shown

in the individual spectrum, by 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.

Procedure for the synthesis of methyl 1-(4,5-diphenyl-1*H*-imidazol-2-yl)-9-methyl-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (3a). To a stirred suspension of **2** (0.078 g, 0.37 mmol) and ammonium acetate (0.143 g, 1.86 mmol) in 3 mL of acetic acid; **1a** (0.10 g, 0.37 mmol) was added and the reaction content was heated to 100 °C for 1 h. After completion of reaction as examined by TLC, the reaction content was poured into ice cold water, yellow precipitates were formed which were filtered through sintered funnel and dried under vacuum. The crude product was purified through silica gel (60-120 mesh size) column chromatography using hexane : EtOAc (80:20, v/v) to obtain the pure product (**3a**) as pale yellow solid (0.024 g, 14%; R_f = 0.70 (hexane/EtOAc, 60:40, v/v).

Methyl 1-(4,5-diphenyl-1*H*-imidazol-2-yl)-9-methyl-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (3a). Yield: 14% (0.024 g from 0.10 g) as a pale yellow solid; m.p. 246-248 °C; R_f = 0.70 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 3407 (NH), 1705 (CO_2CH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.03 (s, 3 H, NCH_3), 4.59 (s, 3 H, CO_2CH_3), 7.30–7.42 (m, 7 H, ArH), 7.61 (d, *J* = 8.1 Hz, 3 H, ArH), 7.68–7.73 (m, 3 H, ArH), 8.21 (d, *J* = 7.8 Hz, 1 H, ArH), 8.82 (s, 1 H, ArH), 11.51 (s, 1 H, NH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 34.6, 52.4, 110.8, 117.1, 121.0, 121.3, 121.5, 126.9, 127.7, 128.0, 128.2, 128.4, 128.5, 128.8, 129.3, 130.9, 131.5, 133.6, 135.2, 135.6, 136.1, 138.1, 143.8, 144.1, 166.2 ppm; MS (ES): *m/z* (%) = 459.1 (100) $[M+1]^+$; $C_{29}H_{22}N_4O_2$ (458.1743): calcd. for C 75.97, H 4.84, N 12.22; found for C 76.09, H 4.85, N 12.18.

Procedure for the synthesis of methyl 1-cyano-9-methyl-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (5a). To a stirred solution of **1a** (0.05, 0.186 mmol), ammonium acetate (0.036 g, 0.466 mmol) and $NaHCO_3$ (0.024, 0.28 mmol) in 1 mL of DMF; Iodine (0.009 g, 0.037 mmol) was added and the reaction content was stirred at room temperature for 1 h. After completion of reaction as examined by TLC, the reaction content was poured into ice cold water, extracted with EtOAc (3 x 10 mL) and the combined organic layer was washed with 5% aq. $Na_2S_2O_3$ (15 mL). The organic layer was dried over anhydrous Na_2SO_4 and excess of solvent was evaporated under reduced pressure. The crude product was purified through silica gel (60-120 mesh size) column chromatography using hexane : EtOAc (80:20, v/v) to obtain the pure product (**5a**) as light brown solid (0.022 g, 45%; R_f = 0.60 (hexane/EtOAc, 70:30, v/v).

Methyl 1-cyano-9-methyl-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (5a). Yield: 45% (0.022 g from 0.050 g) as a light brown solid; m.p. 194-196 °C; R_f = 0.60 (hexane/EtOAc, 70:30, v/v); IR (neat):

ν_{max} (cm^{-1}) = 2235 (CN), 1706 (CO_2CH_3); ^1H NMR (400 MHz, $CDCl_3$) δ = 4.09 (s, 3 H, NCH_3), 4.34 (s, 3 H, CO_2CH_3), 7.30 (t, *J* = 7.6 Hz, 1 H, ArH), 7.59 (d, *J* = 8.4 Hz, 1 H, ArH), 7.77 (t, *J* = 7.8 Hz, 1 H, ArH), 8.24 (d, *J* = 7.9 Hz, 1 H, ArH), 9.02 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.0, 53.3, 110.4, 114.1, 116.6, 120.3, 120.6, 122.2, 122.3, 130.7, 131.8, 138.5, 138.8, 143.1, 166.3 ppm; MS (ES): *m/z* (%) = 266.1 (100) $[M+1]^+$; $C_{15}H_{11}N_3O_2$ (265.0851): calcd. for C 67.92, H 4.18, N 15.84; found for C 68.05, H 4.15, N 15.89.

General Procedure for the preparation of compounds 4a-j as exemplified for methyl 3-(3-(methoxycarbonyl)-9-methyl-9*H*-pyrido[3,4-*b*]indol-1-yl)-11-methyl-11-imidazo[1',5':1,2] pyrido[3,4-*b*]indole-5 carboxylate (4a). To a stirred suspension of **1a** (0.40 g, 1.49 mmol) in 8 mL of acetic acid; ammonium acetate (0.144 g, 1.86 mmol) was added and the reaction content was stirred at room temperature for 2 h. It was observed that suspension of **1a** in AcOH turned into a clear solution with the progress of reaction. After completion of reaction as examined by TLC, the reaction content was poured into ice cold water, yellow precipitates were formed which were filtered through sintered funnel and dried under vacuum. The crude product was washed with 10 mL of methanol and finally triturated and washed twice with 10 mL of anhydrous diethyl ether to obtain analytically pure product (**4a**) as the yellow solid (0.35 g, 91%; R_f = 0.30 (hexane/EtOAc, 60:40, v/v). A clean reaction was obtained at room temperature in all cases (**4a-4j)** and no column chromatographic purification was required (except **4f**).

Methyl 3-(3-(methoxycarbonyl)-9-methyl-9*H*-pyrido[3,4-*b*]indol-1-yl)-11-methyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (4a). Yield: 91% (0.35 g from 0.20 g) as a yellow solid; m.p. 220-222 °C; R_f = 0.30 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 1724 (CO_2CH_3); ^1H NMR (400 MHz, $CDCl_3$) δ = 3.32 (s, 3 H, CO_2CH_3), 3.99 (s, 3 H, NCH_3), 4.01 (s, 3 H, CO_2CH_3), 4.24 (s, 3 H, NCH_3), 7.35 (t, *J* = 7.5 Hz, 1 H, ArH), 7.40 (t, *J* = 7.4 Hz, 1 H, ArH), 7.48 (t, *J* = 7.6 Hz, 1 H, ArH), 7.54–7.57 (m, 2 H, ArH), 7.67 (t, *J* = 8.0 Hz, 1 H, ArH), 7.95 (d, *J* = 7.8 Hz, 1 H, ArH), 8.04 (s, 1 H, ArH), 8.18 (s, 1 H, ArH), 8.25 (d, *J* = 7.8 Hz, 1 H, ArH), 8.91 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 32.1, 33.4, 51.9, 52.7, 109.8, 110.3, 110.5, 115.7, 117.6, 119.7, 119.8, 120.1, 120.9, 121.4, 121.6, 121.8, 123.5, 124.8, 124.9, 129.2, 131.6, 132.0, 135.9, 136.0, 136.3, 138.5, 140.0, 143.6, 163.5, 166.6 ppm; HRMS (ESI) m/z: calcd. for $C_{30}H_{23}N_5O_4$ $[M + H^+]$: 518.1828, found: 518.1825.

Methyl 11-ethyl-3-(9-ethyl-3-(methoxycarbonyl)-9*H*-pyrido[3,4-*b*]indol-1-yl)-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (4b). Yield: 85% (0.33 g from 0.20 g) as a yellow solid; m.p. >250 °C; R_f = 0.32 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 1711 (CO_2CH_3); ^1H NMR (400 MHz, $CDCl_3$) δ = 1.23 (t, *J* = 7.2 Hz, 3 H, NCH_2CH_3), 1.61 (t, *J* = 7.2 Hz, 3 H, NCH_2CH_3), 3.28 (s, 3 H, CO_2CH_3), 4.00 (s, 3 H, CO_2CH_3), 4.50 (q, *J* = 7.2 Hz, 1 H, $NCHHCH_3$), 4.71 (q, *J* = 7.2 Hz, 2 H, NCH_2CH_3), 5.23 (q, *J* = 7.2 Hz, 1 H, $NCHHCH_3$), 7.34–7.42 (m, 2 H, ArH), 7.49 (t, *J* = 7.5 Hz, 1 H, ArH), 7.56–7.62 (m, 2 H, ArH), 7.68 (d, *J* = 4.6 Hz, 1 H, ArH), 8.00 (d, *J* = 7.8 Hz, 1 H, ArH), 8.10 (d, *J* = 6.4 Hz, 2 H, ArH), 8.27 (d, *J* = 7.7 Hz, 1 H, ArH), 8.91 (s, 1 H, ArH) ppm; ^{13}C

NMR (150 MHz, $CDCl_3$) δ = 14.8, 15.0, 40.3, 41.2, 53.0, 53.1, 110.1, 114.1, 117.0, 117.7, 120.5, 121.2, 121.9, 122.1, 122.9, 123.0, 125.6, 126.5, 127.8, 129.8, 130.0, 131.3, 132.1, 134.2, 134.4, 134.8, 137.0, 139.5, 142.0, 143.7, 161.7, 165.2 ppm; HRMS (ESI) m/z: calcd. for $C_{32}H_{27}N_5O_4$ [M + H^+]: 546.2141, found: 546.2137.

Methyl 3-(3-(methoxycarbonyl)-9-propyl-9*H*-pyrido[3,4-*b*]indol-1-yl)-11-propyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (4c). Yield: 88% (0.34 g from 0.20 g) as a yellow solid; m.p. 202-204 °C; R_f = 0.38 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 1712 (CO_2CH_3); ^1H NMR (400 MHz, $CDCl_3$) δ = 0.65 (t, *J* = 7.4 Hz, 3 H, $NCH_2CH_2CH_3$), 1.08 (t, *J* = 7.4 Hz, 3 H, $NCH_2CH_2CH_3$), 1.56–1.61 (m, 1 H, NCH_2CHHCH_3), 1.71–1.75 (m, 1 H, NCH_2CHHCH_3), 2.01–2.07 (m, 2 H, $NCH_2CH_2CH_3$), 3.24 (s, 3 H, CO_2CH_3), 4.00 (s, 3 H, CO_2CH_3), 4.29–4.36 (m, 1 H, $NCHHCH_2CH_3$), 4.57 (q, *J* = 6.8 Hz, 2 H, $NCH_2CH_2CH_3$), 5.18–5.25 (m, 1 H, $NCHHCH_2CH_3$), 7.32 (d, *J* = 7.4 Hz, 1 H, ArH), 7.39 (d, *J* = 7.5 Hz, 1 H, ArH), 7.45 (d, *J* = 7.8 Hz, 1 H, ArH), 7.54–7.60 (m, 2 H, ArH), 7.66 (t, *J* = 7.5 Hz, 1 H, ArH), 7.96 (d, *J* = 7.7 Hz, 1 H, ArH), 8.04 (s, 1 H, ArH), 8.06 (s, 1 H, ArH), 8.25 (d, *J* = 7.8 Hz, 1 H, ArH), 8.91 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 11.5, 11.6, 22.4, 23.4, 46.8, 46.9, 51.8, 52.7, 110.0, 110.5, 110.8, 115.6, 117.6, 119.5, 119.7, 120.4, 120.8, 121.3, 121.6, 121.7, 123.5, 124.7, 124.8, 129.1, 131.2, 131.9, 135.6, 136.2, 138.3, 139.6, 143.0, 163.5, 166.5 ppm; HRMS (ESI) m/z: calcd. for $C_{34}H_{31}N_5O_4$ [M + H^+]: 574.2454, found: 574.2451.

Methyl 11-benzyl-3-(9-benzyl-3-(methoxycarbonyl)-9*H*-pyrido[3,4-*b*]indol-1-yl)-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (4d). Yield: 72% (0.28 g from 0.20 g) as a yellow solid; m.p. 163-165 °C; R_f = 0.50 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 1710 (CO_2CH_3); ^1H NMR (400 MHz, $CDCl_3$) δ = 3.03 (s, 3 H, CO_2CH_3), 4.00 (s, 3 H, CO_2CH_3), 5.43–5.67 (m, 2 H, CH_2Ph), 5.88 (d, *J* = 5.1 Hz, 2 H, CH_2Ph), 6.69–6.71 (m, 1 H, ArH), 6.76 (d, *J* = 7.4 Hz, 2 H, ArH), 6.92 (dd, J_1 = 13.0 Hz, J_2 = 5.3 Hz, 3 H, ArH), 7.15 (d, *J* = 7.6 Hz, 2 H, ArH), 7.31 (d, *J* = 7.4 Hz, 2 H, ArH), 7.39 (d, *J* = 9.7 Hz, 2 H, ArH), 7.43–7.47 (m, 1 H, ArH), 7.50–7.56 (m, 3 H, ArH), 7.63 (d, *J* = 7.6 Hz, 1 H, ArH), 7.85 (s, 1 H, ArH), 8.02 (d, *J* = 7.4 Hz, 1 H, ArH), 8.28 (d, *J* = 7.9 Hz, 1 H, ArH), 8.92 (s, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 48.7, 48.9, 51.5, 52.7, 110.1, 110.9, 111.3, 115.7, 117.4, 119.8, 120.9, 121.2, 121.7, 121.8, 123.6, 124.6, 125.2, 126.1, 126.7, 127.2, 128.0, 128.2, 128.6, 129.3, 129.4, 131.5, 132.1, 135.2, 136.1, 137.5, 139.9, 143.3, 163.0, 166.4 ppm; HRMS (ESI) m/z: calcd. for $C_{42}H_{31}N_5O_4$ [M + H^+]: 670.2454, found: 670.2464.

Methyl 11-allyl-3-(9-allyl-3-(methoxycarbonyl)-9*H*-pyrido[3,4-*b*]indol-1-yl)-11*H*-imidazo [1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (4e). Yield: 75% (0.29 g from 0.20 g) as an orange red solid; m.p. 207-209 °C; R_f = 0.40 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 1709 (CO_2CH_3); ^1H NMR (400 MHz, $CDCl_3$) δ = 3.28 (s, 3 H, CO_2CH_3), 4.01 (s, 3 H, CO_2CH_3), 4.83–4.94 (m, 3 H, NCH_2 and =C*H*H), 4.99 (d, *J* = 17.4 Hz, 1 H, =CH*H*), 5.28 (d, *J* = 9.8 Hz, 3 H, NCH_2 and =C*H*H), 5.83–5.90 (m, 2 H, =CH*H* and CH_2CH), 6.14–6.20 (m, 1 H, CH_2CH), 7.37–7.42 (m, 2 H, ArH), 7.45–7.50 (m, 2 H, ArH), 7.59 (d, *J* = 8.3 Hz, 1 H, ArH), 7.66 (t, *J* = 7.6 Hz, 1 H, ArH), 8.00 (d,

J = 7.8 Hz, 1 H, ArH), 8.03 (s, 1 H, ArH), 8.09 (s, 1 H, ArH), 8.27 (d, *J* = 7.9 Hz, 1 H, ArH), 8.92 (s, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 47.3, 48.0, 51.8, 52.7, 110.0, 110.7, 111.2, 115.6, 117.0, 117.5, 117.7, 119.7, 119.9, 120.7, 121.1, 121.6, 121.7, 121.9, 123.6, 124.5, 125.0, 129.2, 131.4, 131.6, 132.0, 133.2, 135.2, 136.0, 139.6, 142.9, 163.4, 166.5 ppm; HRMS (ESI) m/z: calcd. for $C_{34}H_{27}N_5O_4$ [M + H^+]: 570.2063, found: 570.2088.

Methyl 3-(3-(methoxycarbonyl)-9-(prop-2-yn-1-yl)-9*H*-pyrido[3,4-*b*]indol-1-yl)-11-(prop-2-yn-1-yl)-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (4f). Yield: 57% (0.22 g from 0.20 g) as an orange red solid; m.p. 188-190 °C; R_f = 0.40 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 1714 (CO_2CH_3);^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.05 (d, *J* = 2.6 Hz, 1 H, C≡CH), 2.42 (t, *J* = 2.3 Hz, 1 H, C≡CH), 3.24 (s, 3 H, CO_2CH_3), 4.02 (s, 3 H, CO_2CH_3), 5.30–5.37 (m, 3 H, NC*H*H and NCH_2), 6.10 (d, *J* = 15.5 Hz, 1 H, NCH*H*), 7.39 (t, *J* = 7.5 Hz, 1 H, ArH), 7.43–7.46 (m, 1 H, ArH), 7.52 (t, *J* = 7.4 Hz, 1 H, ArH), 7.62 (d, *J* = 8.2 Hz, 1 H, ArH), 7.71 (t, *J* = 2.6 Hz, 2 H, ArH), 7.99 (d, *J* = 8.3 Hz, 1 H, ArH), 8.08 (s, 1 H, ArH), 8.27 (t, *J* = 3.9 Hz, 2 H, ArH), 8.90 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = spectra could not be recorded due to solubility problem in $CDCl_3$ & DMSO-d_6; MS (ES): *m/z* (%) = 566.0 (100) $[M+1]^+$; $C_{34}H_{23}N_5O_4$ (565.1750): calcd. for C 72.20, H 4.10, N 12.38; found for C 72.29, H 4.12, N 12.42. HRMS (ESI) m/z: calcd. for $C_{34}H_{23}N_5O_4$ [M + H^+]: 566.1828, found: 566.1827.

Methyl 11-(2-ethoxy-2-oxoethyl)-3-(9-(2-ethoxy-2-oxoethyl)-3-(methoxycarbonyl)-9*H*-pyrido[3,4-*b*]indol-1-yl)-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (4g). Yield: 82% (0.32 g from 0.20 g) as an orange red solid; m.p. 237-239 °C; R_f = 0.35 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 1726 ($CO_2CH_2CH_3$), 1713 (CO_2CH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.25 (t, *J* = 7.1 Hz, 6 H, 2 x $CO_2CH_2CH_3$), 3.23 (s, 3 H, CO_2CH_3), 4.02 (s, 3 H, CO_2CH_3), 4.05 (s, 1 H, NC*H*H), 4.08 (s, 2 H, NCH_2), 4.13 (s, 1 H, NCH*H*), 5.21–5.40 (m, 4 H, 2 x $CO_2CH_2CH_3$), 7.38 (t, *J* = 6.4 Hz, 1 H, ArH), 7.44–7.49 (m, 3 H, ArH), 7.67 (t, *J* = 7.4 Hz, 2 H, ArH), 7.99 (s, 1 H, ArH), 7.92 (s, 1 H, ArH), 8.27 (d, *J* = 7.7 Hz, 2 H, ArH), 8.91 (s, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 14.1, 14.3, 46.9, 47.6, 51.7, 52.8, 61.5, 62.4, 109.6, 110.4, 111.5, 115.6, 117.5, 119.1, 119.9, 121.6, 121.9, 122.0, 123.6, 124.8, 125.4, 129.6, 131.4, 132.4, 135.2, 136.6, 138.2, 139.8, 143.4, 163.2, 166.2, 167.7, 168.5 ppm; HRMS (ESI) m/z: calcd. for $C_{36}H_{31}N_5O_8$ [M + H^+]: 662.2251, found: 662.2243.

Ethyl 3-(3-(ethoxycarbonyl)-9-methyl-9*H*-pyrido[3,4-*b*]indol-1-yl)-11-methyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (4h). Yield: 90% (0.35 g from 0.20 g) as a yellow solid; m.p. >250 °C; R_f = 0.35 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 1711 ($CO_2CH_2CH_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.96 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 1.46 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 3.77 (q, *J* = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 4.00 (s, 3 H, NCH_3), 4.22 (s, 3 H, NCH_3), 4.38–4.56 (m, 2 H, $CO_2CH_2CH_3$), 7.35 (t, *J* = 7.3 Hz, 1 H, ArH), 7.39 (t, *J* = 7.6 Hz, 1 H, ArH), 7.48 (t, *J* = 7.7 Hz, 1 H, ArH), 7.55 (d, J_1 = 8.3 Hz, J_2 = 2.8 Hz, 2 H, ArH), 7.66 (d, *J* = 7.3 Hz, 1 H, ArH), 7.97 (d, *J* = 7.8 Hz, 1 H, ArH), 8.02 (s, 1 H, ArH), 8.17 (s, 1 H, ArH), 8.25 (d, *J* = 7.8 Hz, 1 H, ArH), 8.88

(s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.9, 14.6, 32.0, 33.3, 61.3, 61.5, 109.8, 110.3, 110.5, 115.6, 117.4, 119.7, 120.5, 120.8, 121.3, 121.6, 121.7, 123.5, 124.8, 124.9, 129.1, 131.5, 131.9, 135.9, 136.2, 136.5, 138.7, 139.9, 143.6, 163.1, 165.9 ppm; HRMS (ESI) m/z: calcd. for $C_{32}H_{27}N_5O_4$ [M + H^+]: 546.2141, found: 546.2110.

Ethyl 3-(3-(ethoxycarbonyl)-9-ethyl-9*H*-pyrido[3,4-*b*]indol-1-yl)-11-ethyl-11*H*-imidazo [1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (4i). Yield: 80% (0.31 g from 0.20 g) as a yellow solid; m.p. 200-202 °C; R_f = 0.40 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 1712 ($CO_2CH_2CH_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.98 (t, *J* = 7.0 Hz, 3 H, NCH_2CH_3), 1.26 (t, *J* = 7.1 Hz, 3 H, NCH_2CH_3), 1.46 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 1.63 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 3.66 (q, *J* = 7.1 Hz, 1 H, $NCHHCH_3$), 3.84 (q, *J* = 7.1 Hz, 1 H, $NCHHCH_3$), 4.39 (q, *J* = 7.0 Hz, 1 H, $NCHHCH_3$), 4.51 (q, *J* = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 4.71 (q, *J* = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 5.23 (q, *J* = 7.1 Hz, 1 H, $NCHHCH_3$), 7.34–7.41 (m, 2 H, ArH), 7.48 (t, *J* = 7.3 Hz, 1 H, ArH), 7.56–7.61 (m, 2 H, ArH), 7.67 (t, *J* = 7.6 Hz, 1 H, ArH), 8.02 (d, *J* = 7.8 Hz, 1 H, ArH), 8.08 (s, 1 H, ArH), 8.11 (s, 1 H, ArH), 8.27 (d, *J* = 7.8 Hz, 1 H, ArH), 8.89 (s, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 14.0, 14.2, 14.6, 15.1, 40.1, 40.2, 61.2, 61.5, 109.7, 110.6, 115.5, 117.4, 119.4, 119.8, 120.7, 120.8, 121.3, 121.8, 122.0, 123.7, 124.5, 124.8, 129.0, 130.8, 132.0, 134.9, 136.1, 136.2, 138.8, 139.0, 142.6, 163.0, 165.9 ppm; HRMS (ESI) m/z: calcd. for $C_{34}H_{31}N_5O_4$ [M + H^+]: 574.2454, found: 574.2502.

Isopropyl 3-(3-(isopropoxycarbonyl)-9-methyl-9*H*-pyrido[3,4-*b*]indol-1-yl)-11-methyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (4j). Yield: 85% (0.33 g from 0.20 g) as a yellow solid; m.p. >250 °C; R_f = 0.45 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 1710 (CO_2i-Pr); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.98 (d, *J* = 5.6 Hz, 3 H, $CO_2CH(CH_3)_2$), 1.08 (d, *J* = 5.6 Hz, 3 H, $CO_2CH(CH_3)_2$), 1.41 (d, *J* = 6.2 Hz, 3 H, $CO_2CH(CH_3)_2$), 1.43 (d, *J* = 6.2 Hz, 3 H, $CO_2CH(CH_3)_2$), 4.00 (s, 3 H, NCH_3), 4.26 (s, 3 H, NCH_3), 4.58–4.65 (m, 1 H, CO_2CH), 5.27–5.33 (m, 1 H, CO_2CH), 7.33–7.38 (m, 2 H, ArH), 7.48 (t, *J* = 7.6 Hz, 1 H, ArH), 7.56 (d, *J* = 8.3 Hz, 2 H, ArH), 7.67 (t, *J* = 7.5 Hz, 1 H, ArH), 8.01 (d, *J* = 6.2 Hz, 2 H, ArH), 8.18 (s, 1 H, ArH), 8.26 (d, *J* = 7.8 Hz, 1 H, ArH), 8.83 (s, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 21.4, 21.6, 22.2, 32.0, 33.1, 68.8, 69.1, 109.9, 110.2, 110.5, 115.6, 117.4, 119.5, 119.7, 120.7, 121.3, 121.7, 121.8, 123.5, 124.7, 129.0, 131.4, 131.8, 135.9, 136.5, 136.7, 139.0, 139.9, 143.6, 162.5, 165.2 ppm; HRMS (ESI) m/z: calcd. for $C_{34}H_{31}N_5O_4$ [M + H^+]: 574.2454, found: 574.2452.

11-methyl-3-(9-methyl-9*H*-pyrido[3,4-*b*]indol-1-yl)-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole (4k). Yield: 91% (0.052 g from 0.030 g) as a yellow solid; m.p. 202-204 °C; R_f = 0.35 (hexane/EtOAc, 70:30, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.66 (s, 3 H, NCH_3), 4.23 (s, 3 H, NCH_3), 7.27–7.37 (m, 3 H, ArH), 7.43–7.52 (m, 3 H, ArH), 7.63 (t, *J* = 7.5 Hz, 1 H, ArH), 7.95 (d, *J* = 7.7 Hz, 1 H, ArH), 8.04 (s, 1 H, ArH), 8.08 (d, *J* = 4.4 Hz, 1 H, ArH), 8.19 (d, *J* = 7.6 Hz, 1 H, ArH), 8.40 (d, *J* = 7.1 Hz, 1 H, ArH), 8.62 (d, *J* = 4.2 Hz, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.8, 32.7, 107.9, 109.4, 110.1, 110.7, 115.0, 116.2, 117.5, 119.5, 120.1, 120.4, 121.1, 121.6,

123.1, 124.1, 128.9, 129.7, 131.4, 133.6, 136.2, 136.5, 138.4, 139.3, 143.2 ppm; HRMS (ESI) m/z: calcd. for $C_{26}H_{19}N_5$ [M + H^+]: 402.1719, found: 402.1733.

11-ethyl-3-(9-ethyl-9*H*-pyrido[3,4-*b*]indol-1-yl)-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole (4l). Yield: 90% (0.103 g from 0.06 g) as a yellow solid; m.p. 166-168 °C; R_f = 0.40 (hexane/EtOAc, 70:30, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.95 (t, *J* = 7.1 Hz, 3 H, NCH_2CH_3), 1.62 (t, *J* = 7.2 Hz, 3 H, NCH_2CH_3), 4.38 (q, *J* = 7.1 Hz, 2 H, NCH_2CH_3), 4.69 (q, *J* = 7.2 Hz, 2 H, NCH_2CH_3), 7.29 (d, *J* = 6.7 Hz, 3 H, ArH), 7.45 (d, *J* = 6.5 Hz, 1 H, ArH), 7.52 (dd, J_1 = 18.9 Hz, J_2 = 7.6 Hz, 2 H, ArH), 7.62 (d, *J* = 8.1 Hz, 1 H, ArH), 7.97 (d, *J* = 7.9 Hz, 2 H, ArH), 8.12 (s, 1 H, ArH), 8.21–8.26 (m, 2 H, ArH), 8.64 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.8, 15.3, 39.6, 40.0, 107.9, 109.3, 110.2, 110.9, 115.2, 116.0, 117.2, 119.6, 120.1, 120.4, 121.4, 121.7, 123.4, 123.6, 124.1, 128.7, 128.8, 131.7, 133.4, 135.2, 136.7, 138.4, 142.1 ppm; HRMS (ESI) m/z: calcd. for $C_{28}H_{23}N_5$ [M + H^+]: 430.3032, found: 430.3009.

General procedure for the synthesis of compounds 1aA-aC, 1fB, 1aE-aH, 1bE, 1dE, 1fE, 1fI, DD, DE, DG, JJ, 2aK and 2DK as exemplified for methyl 11-methyl-3-propyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (1aG): To a stirred solution of *n*-butyraldehyde (**G)** (0.13 mL, 1.49 mmol) and ammonium acetate (0.144 g, 1.86 mmol) in acetic acid, methyl 1-formyl-9-methyl-9*H*-pyrido[3,4-*b*]indole-3-carboxylate **1a** (0.20 g, 0.746 mmol) was added at room temperature and the reaction was continued for 2 h. After the completion of reaction as monitored by TLC, the excess of acetic acid was evaporated under reduced pressure. The crude product was purified through silica gel (60-120 mesh) column chromatography by using hexane: ethyl acetate (80:20, v/v) as an eluent to obtain **1aG** as the yellow solid (0.17 g, 71%; R_f = 0.35 (hexane/EtOAc, 70:30, v/v).

Methyl 11-methyl-3-phenyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (1aA).[Ref. 2] Yield: 49% (0.13 g from 0.20 g) as a pale yellow solid; m.p. 147-149 °C (Reported m. p. 148-149 °C); R_f = 0.35 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm^{-1}) = 1712 (CO_2CH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.25 (s, 3 H, NCH_3), 4.22 (s, 3 H, CO_2CH_3), 7.34 (t, *J* = 7.6 Hz, 1 H, ArH), 7.41 (d, *J* = 7.4 Hz, 1 H, ArH), 7.47–7.53 (m, 4 H, ArH), 7.67 (d, *J* = 7.2 Hz, 2 H, ArH), 7.93 (s, 1 H, ArH), 7.96 (s, 1 H, ArH), 8.09 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.8, 51.6, 109.2, 109.6, 116.8, 119.3, 119.4, 119.9, 121.4, 123.3, 124.3, 124.6, 126.1, 128.6, 128.8, 132.3, 133.3, 139.7, 142.8, 163.4 ppm; HRMS (ESI) m/z: calcd. for $C_{22}H_{17}N_3O_2$ [M + H^+]: 356.1321, found: 356.1178.

Methyl 3-(2-hydroxyphenyl)-11-methyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (1aB). Yield: 61% (0.17 g from 0.20 g) as a yellow solid; m.p. >250 °C; R_f = 0.30 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm^{-1}) = 3028 (OH), 1710 (CO_2CH_3); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 3.40 (s, 3 H, CO_2CH_3), 4.18 (s, 3 H, NCH_3), 6.91 (t, *J* = 7.4 Hz, 1 H, ArH), 7.17 (d, *J* = 8.1 Hz, 1 H, ArH), 7.26–7.29 (m, 1 H, ArH), 7.35 (t, *J* = 7.0 Hz, 1 H, ArH), 7.37 (d, *J* = 7.7 Hz, 1 H, ArH), 7.47 (t, *J* = 7.6 Hz, 1 H, ArH), 7.50 (d, *J* = 8.2 Hz, 1 H, ArH), 7.93 (d, *J* = 7.7 Hz, 1 H, ArH),

8.04 (s, 1 H, ArH), 8.05 (s, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 32.1, 52.2, 109.8, 109.9, 117.2, 117.7, 118.0, 118.5, 119.1, 119.6, 120.1, 121.8, 123.5, 123.8, 124.0, 125.0, 130.2, 132.5, 139.9, 154.9, 163.4 ppm; HRMS (ESI) m/z: calcd. for $C_{22}H_{17}N_3O_3$ [M + H^+]: 372.1348, found: 372.1308.

Methyl 3-(4-fluorophenyl)-11-methyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (1aC).[Ref. 2] Yield: 50% (0.14 g from 0.20 g) as a pale yellow solid; m.p. 112-114 °C (Reported m.p. 111-112 °C); R_f = 0.40 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm^{-1}) = 1711 (CO_2CH_3); The similar ^{1}H and ^{13}C-NMR spectrum was obtained as reported in Ref 17. MS (ES): *m*/*z* (%) = 374.2 (100) $[M+1]^+$; $C_{22}H_{16}FN_3O_2$ (373.1227).

Methyl 3-(2-hydroxyphenyl)-11-(prop-2-yn-1-yl)-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (1fB). Yield: 67% (0.18 g from 0.20 g) as a yellow solid; m.p. 186-188 °C; R_f = 0.35 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm^{-1}) = 3271 (OH), 1711 (CO_2CH_3); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.43 (s, 1 H, C≡CH), 3.40 (s, 3 H, CO_2CH_3), 5.30 (s, 2 H, NCH_2), 6.92 (t, *J* = 7.4 Hz, 1 H, ArH), 7.17 (d, *J* = 8.2 Hz, 1 H, ArH), 7.28 (d, *J* = 5.2 Hz, 1 H, ArH), 7.39 (d, *J* = 7.4 Hz, 2 H, ArH), 7.50 (t, *J* = 7.5 Hz, 1 H, ArH), 7.58 (d, *J* = 8.3 Hz, 1 H, ArH), 7.96 (d, *J* = 7.6 Hz, 1 H, ArH), 8.05 (s, 1 H, ArH), 8.15 (s, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 34.8, 52.2, 74.6, 76.7, 109.8, 110.6, 117.1, 117.6, 117.7, 119.1, 119.8, 120.9, 122.3, 123.4, 123.7, 123.8, 125.4, 130.2, 131.6, 139.0, 141.3, 154.9, 163.3 ppm; HRMS (ESI) m/z: calcd. for $C_{24}H_{17}N_3O_3$ [M + H^+]: 396.1348, found: 396.1344.

Methyl 11-methyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (1aE). [Ref.2] Yield: 48% (0.10 g from 0.20 g) as a light yellow solid; m.p. 178-180 °C (Reported m.p. 177-178 °C); R_f = 0.20 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm^{-1}) = 1708 (CO_2CH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.03 (s, 3 H, NCH_3), 4.11 (s, 3 H, CO_2CH_3), 7.35 (t, *J* = 7.8 Hz, 1 H, ArH), 7.46–7.49 (m, 2 H, ArH), 7.94 (d, *J* = 7.4 Hz, 2 H, ArH), 8.29 (s, 1 H, ArH), 9.57 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.5, 52.4, 108.7, 109.6, 115.8, 116.8, 118.2, 119.2, 121.4, 123.0, 124.7, 131.6, 132.6, 139.5, 162.6 ppm; HRMS (ESI) m/z: calcd. for $C_{16}H_{13}N_3O_2$ [M + H^+]: 280.1008, found: 280.0950.

Methyl 3,11-dimethyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (1aF).[Ref. 2] Yield: 53% (0.115 g from 0.20 g) as a light brown solid; m.p. 169-171 °C, (Reported m.p. 168–169 °C); R_f = 0.25 (hexane/ EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm^{-1}) = 2927, 2835, 2120, 1912, 1706, 1470, 1353; The similar ^{1}H and ^{13}C-NMR spectrum was obtained as reported in Ref 17. MS (ES): m/z (%) = 294.1 (100) $[M+1]^+$; $C_{17}H_{15}N_3O_2$ (293.1164).

Methyl 11-methyl-3-propyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (1aG). Yield: 71% (0.17 g from 0.20 g) as a yellow solid; m.p. 95-96 °C; R_f = 0.35 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm^{-1}) = 1711 (CO_2CH_3); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.96 (s, 3 H,

$CH_2CH_2CH_3$), 1.83 (d, *J* = 6.1 Hz, 2 H, $CH_2CH_2CH_3$), 2.97 (s, 2 H, $CH_2CH_2CH_3$), 4.03 (s, 6 H, NCH_3 and CO_2CH_3), 7.28 (s, 1 H, ArH), 7.41 (s, 2 H, ArH), 7.84 (d, *J* = 6.4 Hz, 1 H, ArH), 7.89 (s, 1 H, ArH), 7.92 (s, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 14.1, 20.2, 31.8, 32.6, 52.7, 108.3, 109.6, 117.2, 118.3, 118.4, 119.2, 121.3, 123.4, 124.4, 132.9, 139.6, 144.5, 163.3 ppm; HRMS (ESI) m/z: calcd. for $C_{19}H_{19}N_3O_2$ [M + H^+]: 322.1556, found: 322.1557.

Methyl 3-isopropyl-11-methyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (1aH).[Ref 2] Yield: 54% (0.13 g from 0.20 g) as a pale yellow solid; m.p. 124-126 °C; R_f = 0.50 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm^{-1}) = 1703 (CO_2CH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.38 (d, *J* = 6.7 Hz, 6 H, $CH(CH_3)_2$), 3.40–3.50 (m, 1 H, $CH(CH_3)_2$), 4.03 (s, 3 H, NCH_3), 4.15 (s, 3 H, CO_2CH_3), 7.31 (t, *J* = 7.4 Hz, 1 H, ArH), 7.42 (t, *J* = 7.4 Hz, 1 H, ArH), 7.48 (d, *J* = 8.2 Hz, 1 H, ArH), 7.90 (d, *J* = 7.8 Hz, 1 H, ArH), 7.97 (s, 1 H, ArH), 7.98 (s, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 21.2, 28.6, 31.9, 52.8, 108.2, 109.6, 117.3, 118.7, 119.2, 121.4, 123.4, 123.6, 124.4, 133.0, 139.7, 149.7, 163.8 ppm; MS (ES): *m/z* (%) = 322.1 (100) $[M+1]^+$; $C_{19}H_{19}N_3O_2$(321.1477): calcd. for C 71.01, H 5.96, N 13.08; found for C 71.11, H 5.99, N 13.13.

Methyl 11-ethyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (1bE). Yield: 53% (0.11 g from 0.20 g) as a yellow solid; m.p. 189-191 °C; R_f = 0.25 (hexane/EtOAc, 50:50, v/v); IR (neat): ν_{max} (cm^{-1}) = 1698 (CO_2CH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.53 (d, *J* = 7.2 Hz, 3 H, NCH_2CH_3), 4.02 (s, 3 H, CO_2CH_3), 4.50 (q, *J* = 7.2 Hz, 2 H, NCH_2CH_3), 7.33 (t, *J* = 6.8 Hz, 1 H, ArH), 7.43–7.49 (m, 2 H, ArH), 7.85 (s, 1 H, ArH), 7.92 (t, *J* = 9.2 Hz, 1 H, ArH), 8.27 (s, 1 H, ArH), 9.55 (s, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.8, 40.1, 52.5, 109.2, 109.7, 116.2, 117.0, 119.0, 119.5, 121.6, 122.1, 123.6, 124.8, 132.2, 138.9, 163.1 ppm; HRMS (ESI) m/z: calcd. for $C_{17}H_{15}N_3O_2$ [M + H^+]: 294.1243, found: 294.1251.

Methyl 11-benzyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (**1dE**). [Ref.2] Yield: 48% (0.10 g from 0.20 g) as a light brown solid; m.p. 154-156 ° C (Reported m.p. 156–157 °C); R_f = 0.25 (hexane/EtOAc, 50:50, v/v); IR (neat): ν_{max} (cm^{-1}) = 2926, 2840, 2121, 1708, 1504, 1434, 1359, 1231, 1134, 912, 793, 742, 650; The similar ^{1}H and ^{13}C-NMR spectrum was obtained as reported in Ref 17. MS (ES): m/z (%) = 356.1 (100) $[M+1]^+$; $C_{22}H_{17}N_3O_2$ (355.1321).

Methyl 11-(prop-2-yn-1-yl)-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (1fE). Yield: 43% (0.09 g from 0.20 g) as a yellow solid; m.p. 249-251 °C; R_f = 0.25 (hexane/EtOAc, 50:50, v/v); IR (neat): ν_{max} (cm^{-1}) = 1698 (CO_2CH_3); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.41 (s, 1 H, C≡CH), 4.06 (s, 3 H, CO_2CH_3), 5.30 (s, 2 H, NCH_2), 7.39 (t, *J* = 7.2 Hz, 1 H, ArH), 7.50 (t, *J* = 7.5 Hz, 1 H, ArH), 7.59 (d, *J* = 8.5 Hz, 1 H, ArH), 7.99 (d, *J* = 7.7 Hz, 1 H, ArH), 8.08 (s, 1 H, ArH), 8.40 (s, 1 H, ArH), 9.66 (s, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 34.8, 52.6, 74.4, 109.7, 109.8, 116.8, 117.2, 119.7, 119.8, 125.2, 132.6, 139.0, 163.1 ppm; HRMS (ESI) m/z: calcd. for $C_{18}H_{13}N_3O_2$ [M + H^+]: 304.1086, found: 304.1082.

3-Ethyl 5-methyl 11-(prop-2-yn-1-yl)-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-3,5-dicarboxylate (1fl). Yield: 35% (0.09 g from 0.20 g) as a yellow solid; m.p. 198-200 °C; R_f = 0.35 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm^{-1}) = 1714 (CO_2CH_3 and $CO_2CH_2CH_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 1.48 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 2.40 (s, 1 H, C≡CH), 3.97 (s, 3 H, CO_2CH_3), 4.50 (q, *J* = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 5.29 (s, 2 H, NCH_2), 7.38 (t, *J* = 7.3 Hz, 1 H, ArH), 7.52 (t, *J* = 7.6 Hz, 1 H, ArH), 7.58 (d, *J* = 8.2 Hz, 1 H, ArH), 7.97 (d, *J* = 7.8 Hz, 1 H, ArH), 8.09 (d, *J* = 8.1 Hz, 2 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.5, 34.8, 52.6, 62.0, 74.7, 76.6, 109.9, 112.5, 115.9, 120.1, 120.8, 121.3, 122.2, 123.2, 125.3, 126.0, 130.4, 133.6, 139.1, 160.3, 163.9 ppm; HRMS (ESI) m/z: calcd. for $C_{21}H_{17}N_3O_4$ [M + H^+]: 376.1297, found: 376.1265.

3-(Pyridin-2-yl)imidazo[1,5-*a*]pyridine (DD). [Ref. 3] Yield: 73% (0.20 g from 0.15 g) as a pale yellow solid; m.p. 105-106 °C (Reported m.p. 105-107 °C); R_f = 0.20 (hexane/EtOAc, 90:10, v/v); IR (neat): ν_{max} (cm^{-1}) = 2927, 2858, 2119, 1585, 1492, 1249; ^1H NMR (600 MHz, $CDCl_3$) δ = 6.71 (t, *J* = 6.7 Hz, 1 H, ArH), 6.84 (t, *J* = 7.1 Hz, 1 H, ArH), 7.17 (t, *J* = 5.8 Hz, 1 H, ArH), 7.52 (d, *J* = 9.0 Hz, 1 H, ArH), 7.59 (s, 1 H, ArH), 7.76 (t, *J* = 7.7 Hz, 1 H, ArH), 8.34 (d, *J* = 8.0 Hz, 1 H, ArH), 8.62 (d, *J* = 2.2 Hz, 1 H, ArH), 9.95 (d, *J* = 7.1 Hz, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 113.6, 118.1, 120.2, 121.1, 121.6, 121.8, 126.1, 133.0, 135.5, 136.6, 148.2, 151.2 ppm; HRMS (ESI) m/z: calcd. for $C_{12}H_9N_3$ [M + H^+]: 196.0875, found: 196.0877.

Imidazo[1,5-*a*]pyridine (DE). Yield: 77% (0.34 g from 0.40 g) as a brown oil; R_f = 0.25 (hexane/EtOAc, 50:50, v/v); IR (neat): ν_{max} (cm^{-1}) = 3124, 2496, 1708, 1366, 1250, 1111; ^1H NMR (600 MHz, $CDCl_3$) δ = 6.55 (t, *J* = 6.6 Hz, 1 H, ArH), 6.69 (t, *J* = 7.9 Hz, 1 H, ArH), 7.39–7.42 (m, 2 H, ArH), 7.90 (d, *J* = 7.0 Hz, 1 H, ArH), 8.17 (s, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 113.2, 118.5, 119.0, 119.5, 122.3, 127.5, 130.3 ppm; HRMS (ESI) m/z: calcd. for $C_7H_6N_2$ [M + H^+]: 119.0609, found: 119.0600.

3-Propylimidazo[1,5-*a*]pyridine (DG). [Ref. 3] Yield: 57% (0.17 g from 0.20 g) as a brown oil; R_f = 0.30 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm^{-1}) = 2966, 2877, 1709, 1364, 1254, 1045; ^1H NMR (600 MHz, $CDCl_3$) δ = 1.00 (t, *J* = 7.2 Hz, 3 H, $CH_2CH_2CH_3$), 1.81–1.87 (m, 2 H, $CH_2CH_2CH_3$), 2.94 (t, *J* = 7.3 Hz, 2 H, $CH_2CH_2CH_3$), 6.51 (t, *J* = 6.5 Hz, 1 H, ArH), 6.60–6.65 (m, 1 H, ArH), 7.35 (s, 1 H, ArH), 7.37 (d, *J* = 9.2 Hz, 1 H, ArH), 7.69 (d, *J* = 7.0 Hz, 1 H, ArH) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 14.0, 20.5, 28.3, 112.5, 117.9, 118.8, 120.6, 130.2, 138.8 ppm; MS (ES): *m/z* (%) = 161.0 (100) $[M+1]^+$; $C_{10}H_{12}N_2$ (160.1000): calcd. for C 74.97, H 7.55, N 17.48; found for C 75.04, H 7.58, N 17.53.

7-Chloro-3-(4-chloropyridin-2-yl)imidazo[1,5-*a*]pyridine (JJ). Yield: 54% (0.10 g from 0.10 g) as a pale yellow solid; m.p. 121-123 °C; R_f = 0.60 (hexane/EtOAc, 90:10, v/v); IR (neat): ν_{max} (cm^{-1}) = 2927, 2113, 1576, 1488, 1357, 1254; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.69 (dd, J_1 = 7.7 Hz, J_2 = 2.0 Hz, 1 H, ArH), 7.20 (dd, J_1 = 5.4 Hz, J_2 = 1.9 Hz, 1 H, ArH), 7.52 (s, 2 H, ArH), 8.35 (d, *J* = 1.9 Hz, 1 H, ArH), 8.49 (d, *J* = 5.4 Hz, 1 H, ArH), 9.87 (d, *J* = 7.7 Hz, 1 H, ArH) ppm;^{13}C NMR (100 MHz,

$CDCl_3$) δ = 115.5, 116.6, 121.2, 121.7, 122.2, 126.9, 133.2, 134.7, 144.7, 149.3, 151.9 ppm; HRMS (ESI) m/z: calcd. for $C_{12}H_7Cl_2N_3$ [M + H^+]: 264.0095, found: 264.0087.

6-bromo-3-(5-bromopyridin-2-yl)imidazo[1,5-*a*]pyridine (KK). Yield: 37% (0.035 g from 0.05 g) as a light brown solid; m.p. 190-192 °C; R_f = 0.57 (hexane/EtOAc, 90:10, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.93 (d, *J* = 9.4 Hz, 1 H, ArH), 7.43 (d, *J* = 9.4 Hz, 1 H, ArH), 7.59 (s, 1 H, ArH), 7.88 (dd, J_1 = 8.6 Hz, J_2 = 2.0 Hz, 1 H, ArH), 8.20 (d, *J* = 8.6 Hz, 1 H, ArH), 8.68 (d, *J* = 1.3 Hz, 1 H, ArH), 10.03 (s, 1 H, ArH) ppm;^{13}C NMR (100 MHz, $CDCl_3$) δ = 109.7, 118.6, 118.9, 122.5, 123.1, 124.1, 125.9, 131.4, 134.8, 139.5, 148.9, 149.3 ppm; HRMS (ESI) m/z: calcd. for $C_{12}H_7Br_2N_3$ [M + H^+]: 351.9085, found: 351.9109.

5-bromo-3-(6-bromopyridin-2-yl)imidazo[1,5-*a*]pyridine (LL). Yield: 32% (0.030 g from 0.05 g) as a pale yellow solid; m.p. 162-164 °C; R_f = 0.50 (hexane/EtOAc, 90:10, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.64–6.72 (m, 1 H, ArH), 6.94 (d, *J* = 6.7 Hz, 1 H, ArH), 7.53 (t, *J* = 7.2 Hz, 2 H, ArH), 7.66 (t, *J* = 7.3 Hz, 2 H, ArH), 7.77 (d, *J* = 7.3 Hz, 1 H, ArH) ppm;^{13}C NMR (100 MHz, $CDCl_3$) δ = 112.3, 117.8, 120.4, 120.5, 121.7, 124.5, 127.6, 138.4, 140.1, 151.9 ppm; HRMS (ESI) m/z: calcd. for $C_{12}H_7Br_2N_3$ [M + H^+]: 351.9085, found: 351.9098.

Methyl 3-formyl-11-methyl-11*H*-imidazo[1',5':1,2]pyrido[3,4-*b*]indole-5-carboxylate (2aK). Yield: 74% (0.17 g from 0.20 g) as a light brown solid; m.p. 193-194 °C; R_f = 0.25 (hexane/EtOAc, 50:50, v/v); IR (neat): ν_{max} (cm^{-1}) = 1720 (CO_2CH_3), 1690 (CHO); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 3.87 (s, 3 H, NCH_3), 3.98 (s, 3 H, CO_2CH_3), 7.30 (t, *J* = 6.9 Hz, 1 H, ArH), 7.36 (d, *J* = 7.9 Hz, 1 H, ArH), 7.42 (t, *J* = 6.9 Hz, 1 H, ArH), 7.81 (d, *J* = 8.3 Hz, 2 H, ArH), 8.03 (s, 1 H, ArH), 9.47 (s, 1 H, CHO) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 31.6, 52.5, 108.9, 109.7, 116.0, 116.9, 118.5, 119.3, 121.6, 123.2, 124.8, 132.8, 139.7, 162.8, 175.3 ppm; MS (ES): *m/z* (%) = 308.1 (100) $[M+1]^+$; $C_{17}H_{13}N_3O_3$ (307.0957): calcd. for C 66.44, H 4.26, N 13.67; found for C 66.53, H 4.28, N 13.70.

Imidazo[1,5-*a*]pyridine-3-carbaldehyde (2DK). Yield: 82% (0.45 g from 0.40 g) as a grey solid; m.p. 60-62 °C; R_f = 0.30 (hexane/EtOAc, 80:20, v/v); IR (neat): ν_{max} (cm^{-1}) = 1651 (CHO); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.05 (t, *J* = 6.5 Hz, 1 H, ArH), 7.23-7.27 (m, 1 H, ArH), 7.72 (d, *J* = 8.9 Hz, 1 H, ArH), 7.75 (s, 1 H, ArH), 9.52 (d, *J* = 6.7 Hz, 1 H, ArH), 9.98 (s, 1 H, CHO) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 116.8, 118.1, 125.3, 125.5, 125.9, 135.1, 135.8, 179.8 ppm; MS (ES): *m/z* (%) = 147.1 (100) $[M+1]^+$; $C_8H_6N_2O$ (146.0480): calcd. for C 65.75, H 4.14, N 19.17; found for C 65.83, H 4.17, N 19.22.

General procedure for the synthesis of compound 6-7 as exemplified for 3-(pyridin-2-yl)imidazo[1,5-*a*]pyridine-1-carbaldehyde (7): To a stirred solution of anhydrous DMF (3 mL) at 0 °C, $POCl_3$ (0.19 mL, 2.04 mmol) was added drop-wise and the reaction mixture was stirred for 10 min to prepare the Vilsmeier reagent. Thereafter, **DD** (0.20 g, 1.02 mmol) dissolved in DMF (2 mL) was added and the reaction mixture was stirred at room temperature for 10 min and then heated at 80 °C for 2 h. After completion of reaction as monitored by TLC, the reaction

content was poured into ice cold water and extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield the crude solid product which was purified through column chromatography by using hexane/EtOAc (9:1, v/v) as an eluent to afford **7** as a light brown solid (0.15 g, 65%; R*f* = 0.20 (hexane/EtOAc, 80:20, v/v).

Methyl 1-formyl-3-(3-(methoxycarbonyl)-9-methyl-9*H*-pyrido[3,4-*b*]indol-1-yl)-11-methyl-11*H*-imidazo[1',5':1,2] pyrido[3,4-*b*]indole-5-carboxylate (6). Yield: 76% (0.08 g from 0.10 g) as a yellow solid; m.p. >250 °C; R_f = 0.40 (hexane/EtOAc, 60:40, v/v); IR (neat): ν_{max} (cm^{-1}) = 1710 (CO_2CH_3), 1677 (CHO); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.33 (s, 3 H, CO_2CH_3), 4.01 (s, 3 H, NCH_3), 4.06 (s, 3 H, NCH_3), 4.30 (s, 3 H, CO_2CH_3), 7.42 (t, *J* = 7.7 Hz, 2 H, ArH), 7.60–7.64 (m, 4 H, ArH), 7.69 (d, *J* = 7 8 Hz, 1 H, ArH), 8.07 (d, *J* = 7.9 Hz, 1 H, ArH), 8.27 (s, 1 H, ArH), 8.95 (s, 1 H, ArH), 10.34 (s, 1 H, CHO) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 33.4, 35.8, 52.3, 52.8, 110.5, 111.3, 116.4, 117.2, 118.1, 120.3, 120.4, 121.2, 121.5, 121.8, 122.2, 122.7, 126.0, 127.1, 129.5, 131.9, 132.0, 132.3, 135.1, 135.9, 139.8, 142.7, 143.6, 163.0, 166.2, 185.3 ppm; HRMS (ESI) m/z: calcd. for $C_{31}H_{23}N_5O_5$ [M + H^+]: 546.1777, found: 546.1782.

3-(Pyridin-2-yl)imidazo[1,5-*a*]pyridine-1-carbaldehyde (7). Yield: 65% (0.15 g from 0.20 g) as a light brown solid; m.p. 141-143 °C; R_f = 0.20 (hexane/EtOAc, 80:20, v/v); IR (neat): ν_{max} (cm^{-1}) = 3118, 2811, 2782, 2119, 1851, 1664, 1493, 1158; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02 (t, *J* = 6.9 Hz, 1 H, ArH), 7.29–7.38 (m, 2 H, ArH), 7.85 (t, *J* = 7.8 Hz, 1 H, ArH), 8.35–8.43 (m, 2 H, ArH), 8.66 (d, *J* = 4.7 Hz, 1 H, ArH), 10.15 (d, *J* = 7.1 Hz, 1 H, ArH), 10.17 (s, 1 H, CHO) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 116.0, 119.2, 122.7, 123.1, 127.4, 127.6, 130.6, 135.7, 137.1, 148.4, 150.2, 186.1 ppm; HRMS (ESI) m/z: calcd. for $C_{13}H_9N_3O$ [M + H^+]: 224.0824, found: 224.0820.

General procedure for the synthesis of 1-(imidazo[1,5-*a*]pyridin-3-yl)but-3-en-1-ol (8). To a stirred solution of allyl bromide (0.15 mL, 1.70 mmol) in 4 mL of THF:H_2O (1:1 v/v,), Indium powder (0.086 g, 0.75 mmol) and imidazo[1,5-*a*]pyridine-3-carbaldehyde **2DK** (0.10 g, 0.68 mmol) was added at room temperature and stirred the content for 20 min. After the completion of reaction as monitored by TLC, the reaction mixture was poured into water and extracted with ethyl acetate (2 x 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield the crude product which was purified through column chromatography by using silica gel (60-120 mesh size) and hexane: ethyl acetate (7:3, v/v) as an eluent to afford **8** as a brown oil (0.085 g, 66%; R_f = 0.20 (hexane/EtOAc, 70:30, v/v).

1-(Imidazo[1,5-*a*]pyridin-3-yl)but-3-en-1-ol (8). Yield: 66% (0.085 g from 0.100 g) as a brown oil; R_f = 0.20 (hexane/EtOAc, 70:30, v/v); IR (neat): ν_{max} (cm^{-1}) = 3082, 2916, 2854, 1714, 1641, 1436, 1328, 1039; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.89 (t, *J* = 6.9 Hz, 2 H, CH_2), 5.13 (dd, J_1 = 7.8 Hz, J_2 = 5.1 Hz, 2 H, C*H*OH and CHO*H*), 5.16–5.22 (m, 2 H, =CH*H*), 5.88–5.93 (m, 1 H, C*H*CH_2), 6.56 (t, *J* = 6.6 Hz, 1 H, ArH), 6.71 (dd, J_1 = 9.1 Hz, J_2 = 6.4 Hz, 1 H, ArH), 7.31 (s, 1 H, ArH), 7.40 (d, *J* = 9.1 Hz, 1 H, ArH), 8.15 (d, *J* = 7.1 Hz, 1 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 39.6,

67.0, 112.5, 118.1, 118.5, 118.6, 118.9, 122.3, 131.3, 134.0, 139.2 ppm; MS (ES): *m*/*z* (%) = 189.2 (100) $[M+1]^+$; $C_{11}H_{12}N_2O$ (188.0950): calcd. for C 70.19, H 6.43, N 14.88; found for C 70.30, H 6.47, N 14.94.

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2. D. Singh, V. Kumar, N. Devi, C. C. Malakar, R. Shankar and V. Singh, *Adv. Synth. Catal.,* 2017, **359**, 1213.
3. M. Li, Y. Xie, Y. Ye, Y. Zou, H. Jiang and W. Zeng, *Org. Lett.,* 2014, **16**, 6232.

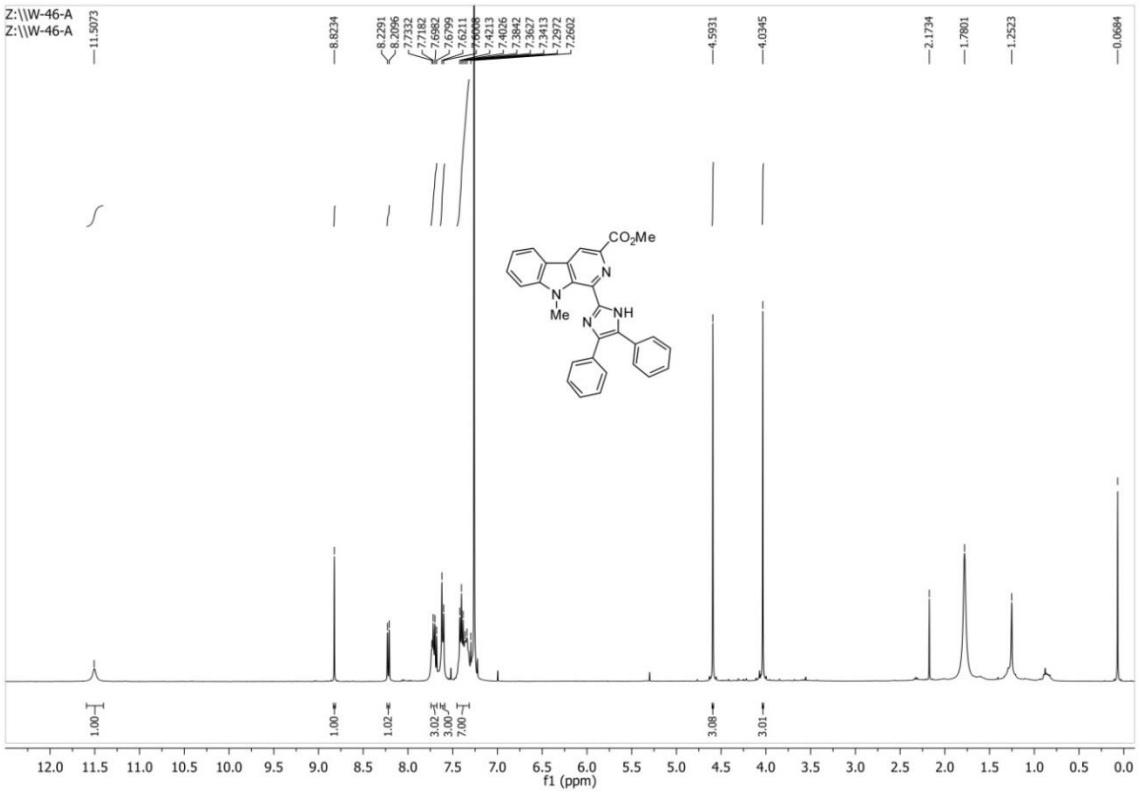


Figure S1. ^{1}H-NMR spectrum of **3a**.

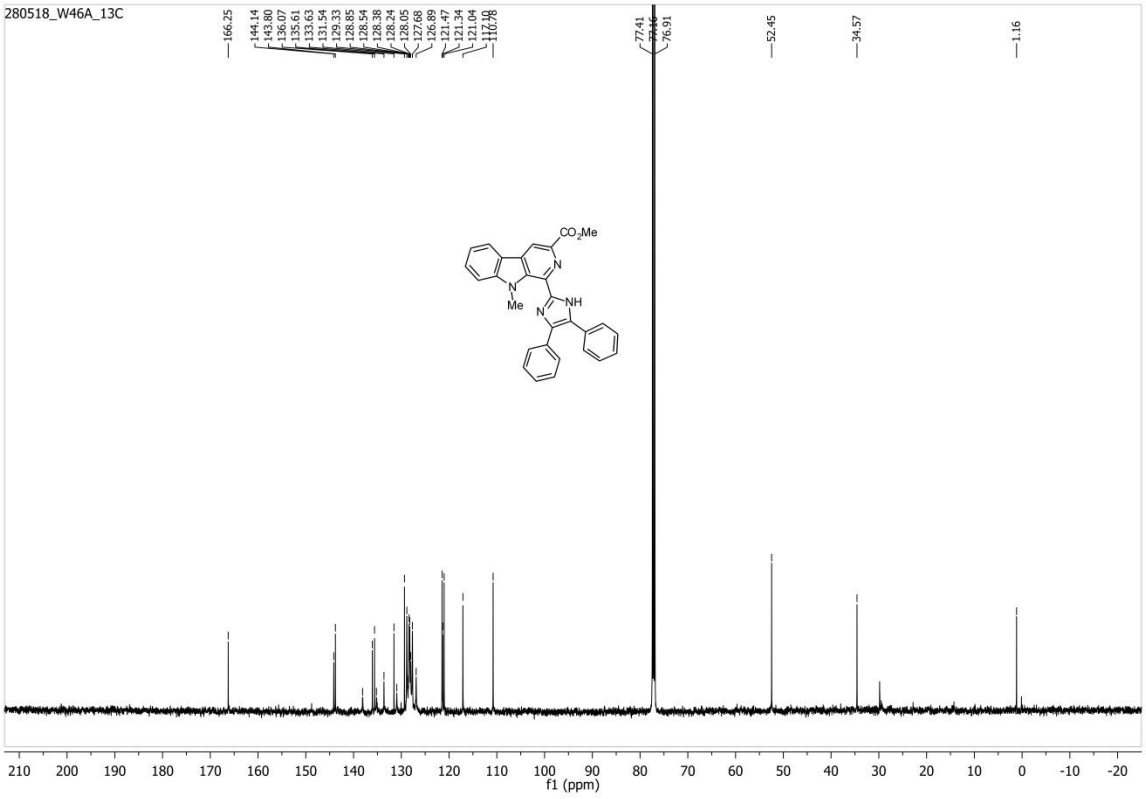


Figure S2. ^{13}C-NMR spectrum of **3a**.

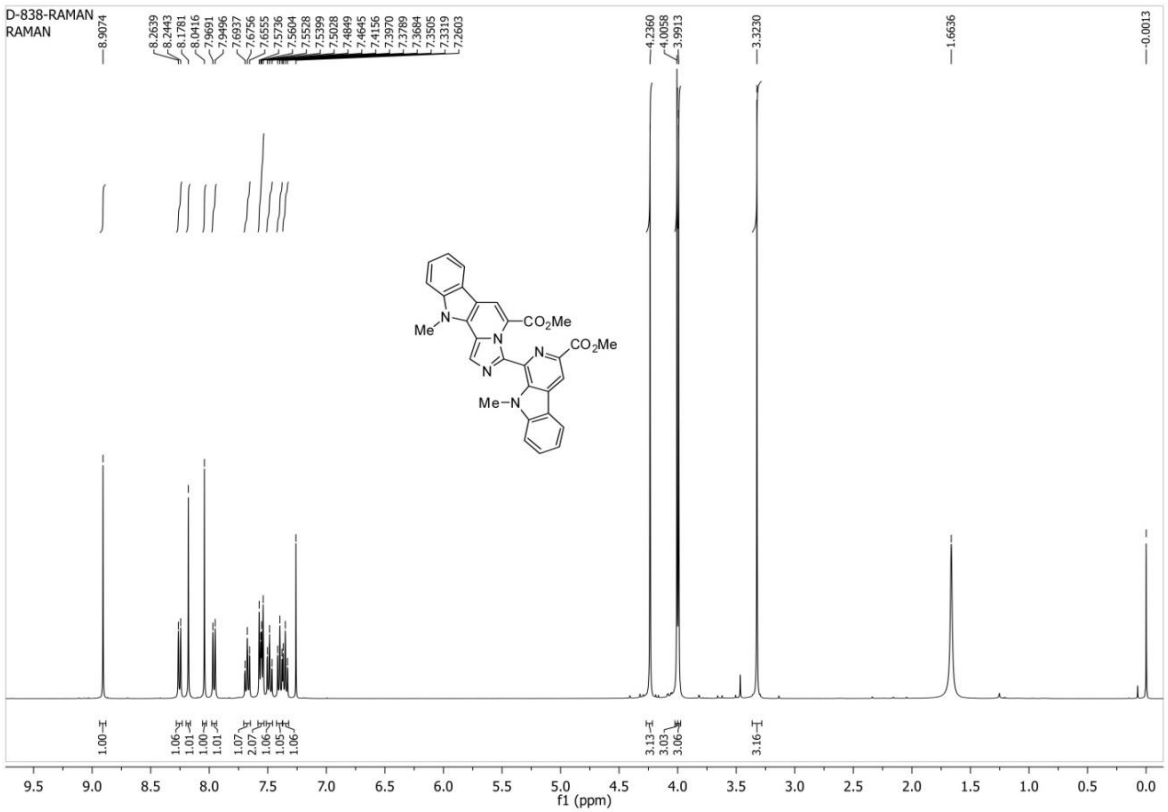


Figure S3. ^{1}H-NMR spectrum of **4a**.

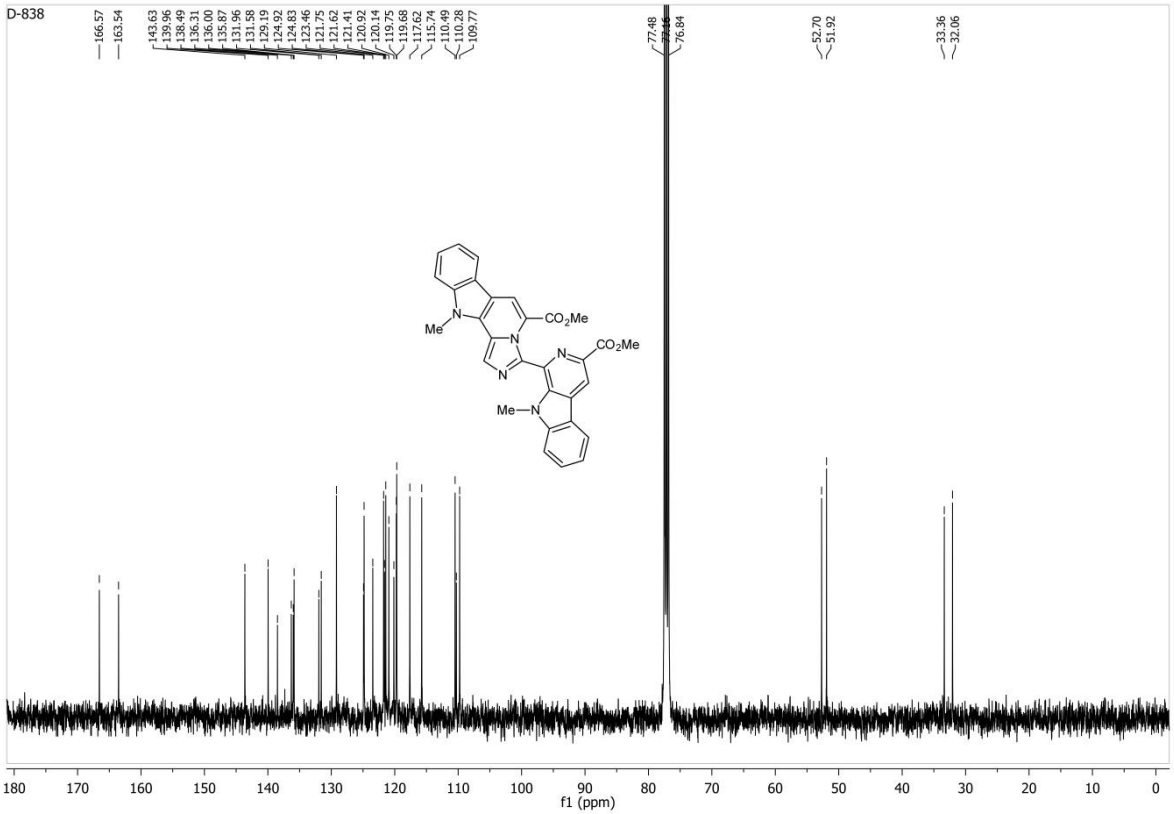
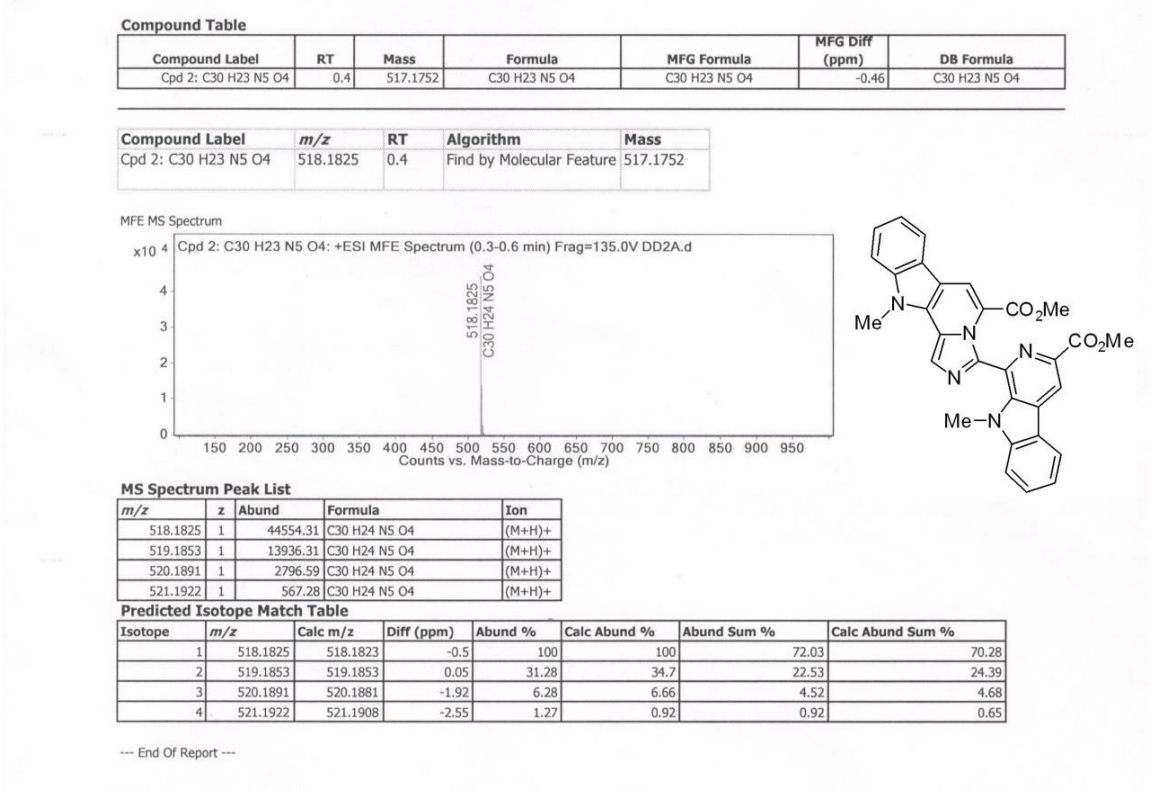


Figure S4. ^{13}C-NMR spectrum of **4a**.



Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 2: C30 H23 N5 O4	0.4	517.1752	C30 H23 N5 O4	C30 H23 N5 O4	-0.46	C30 H23 N5 O4

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C30 H23 N5 O4	518.1825	0.4	Find by Molecular Feature	517.1752

MFE MS Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
518.1825	1	44554.31	C30 H24 N5 O4	(M+H)+
519.1853	1	13936.31	C30 H24 N5 O4	(M+H)+
520.1891	1	2796.59	C30 H24 N5 O4	(M+H)+
521.1922	1	567.28	C30 H24 N5 O4	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	518.1825	518.1823	-0.5	100	100	72.03	70.28
2	519.1853	519.1853	0.05	31.28	34.7	22.53	24.39
3	520.1891	520.1881	-1.92	6.28	6.66	4.52	4.68
4	521.1922	521.1908	-2.55	1.27	0.92	0.92	0.65

--- End Of Report ---

Figure S5. HRMS spectrum of **4a**.

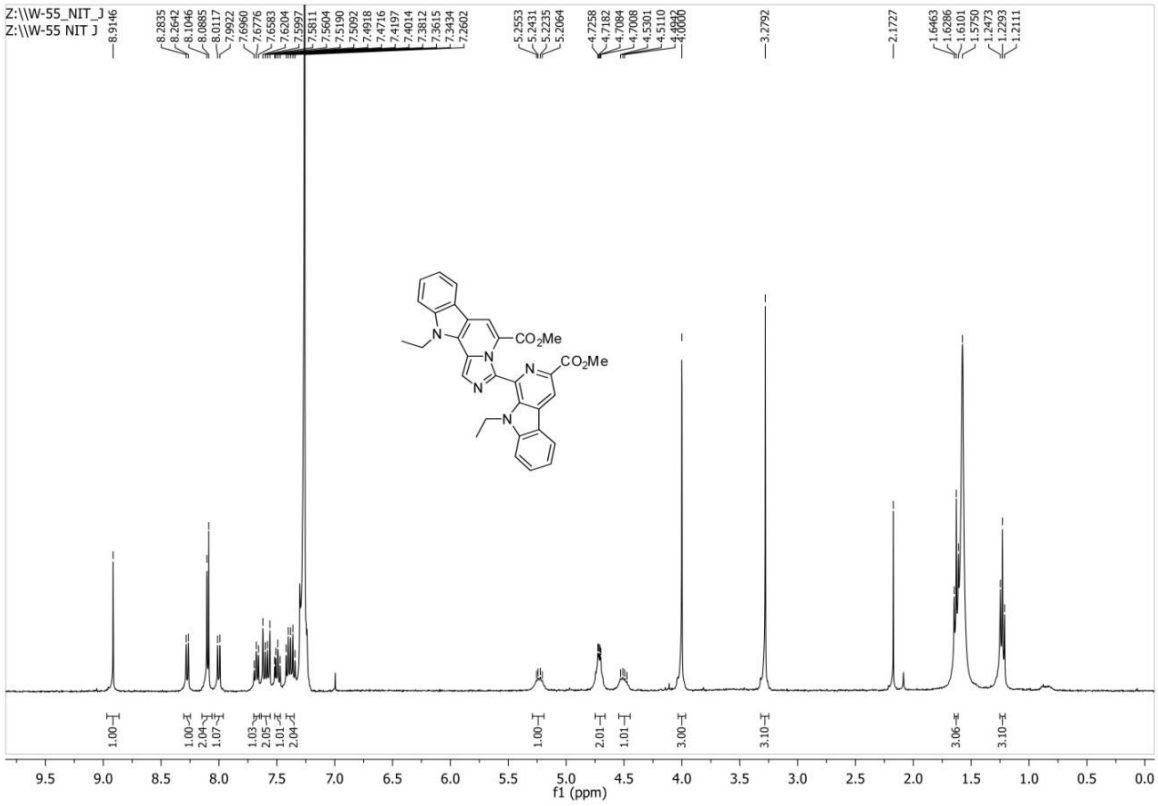


Figure S6. ^{1}H-NMR spectrum of **4b**.

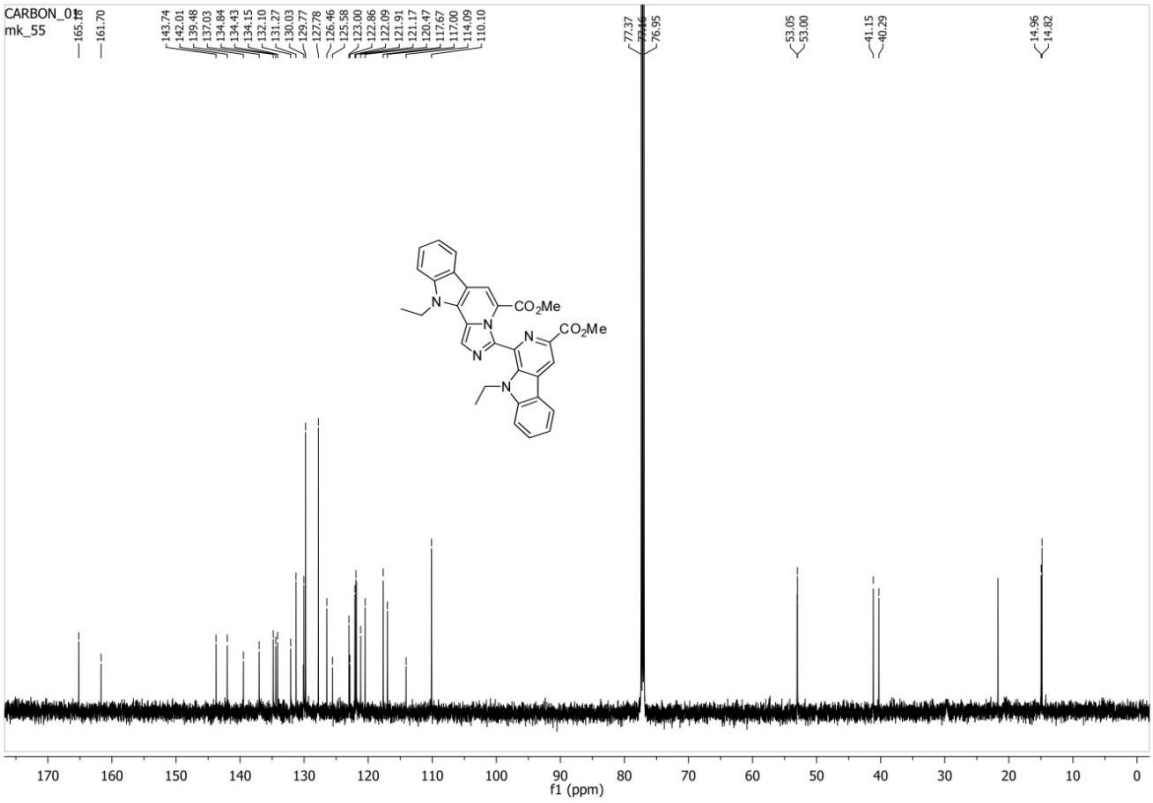


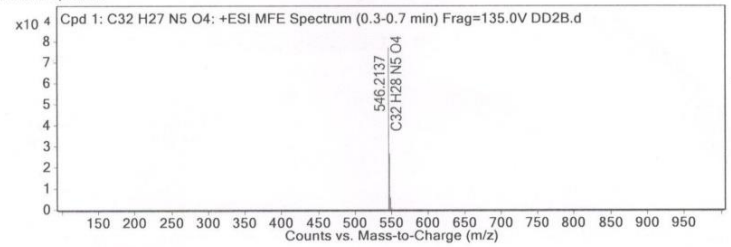
Figure S7. ^{13}C-NMR spectrum of **4b**.

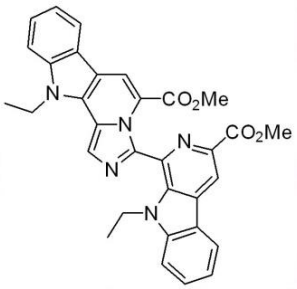
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C32 H27 N5 O4	0.4	545.2065	C32 H27 N5 O4	C32 H27 N5 O4	-0.29	C32 H27 N5 O4

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C32 H27 N5 O4	546.2137	0.4	Find by Molecular Feature	545.2065

MFE MS Spectrum





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
546.2137	1	77106.27	C32 H28 N5 O4	(M+H)+
547.2168	1	26494.14	C32 H28 N5 O4	(M+H)+
548.2196	1	5462.13	C32 H28 N5 O4	(M+H)+
549.2249	1	864.2	C32 H28 N5 O4	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	546.2137	546.2136	-0.26	100	100	70.14	68.76
2	547.2168	547.2167	-0.24	34.36	36.91	24.1	25.38
3	548.2196	548.2195	-0.18	7.08	7.44	4.97	5.12
4	549.2249	549.2222	-4.86	1.12	1.07	0.79	0.74

--- End Of Report ---

Figure S8. HRMS spectrum of **4b**.

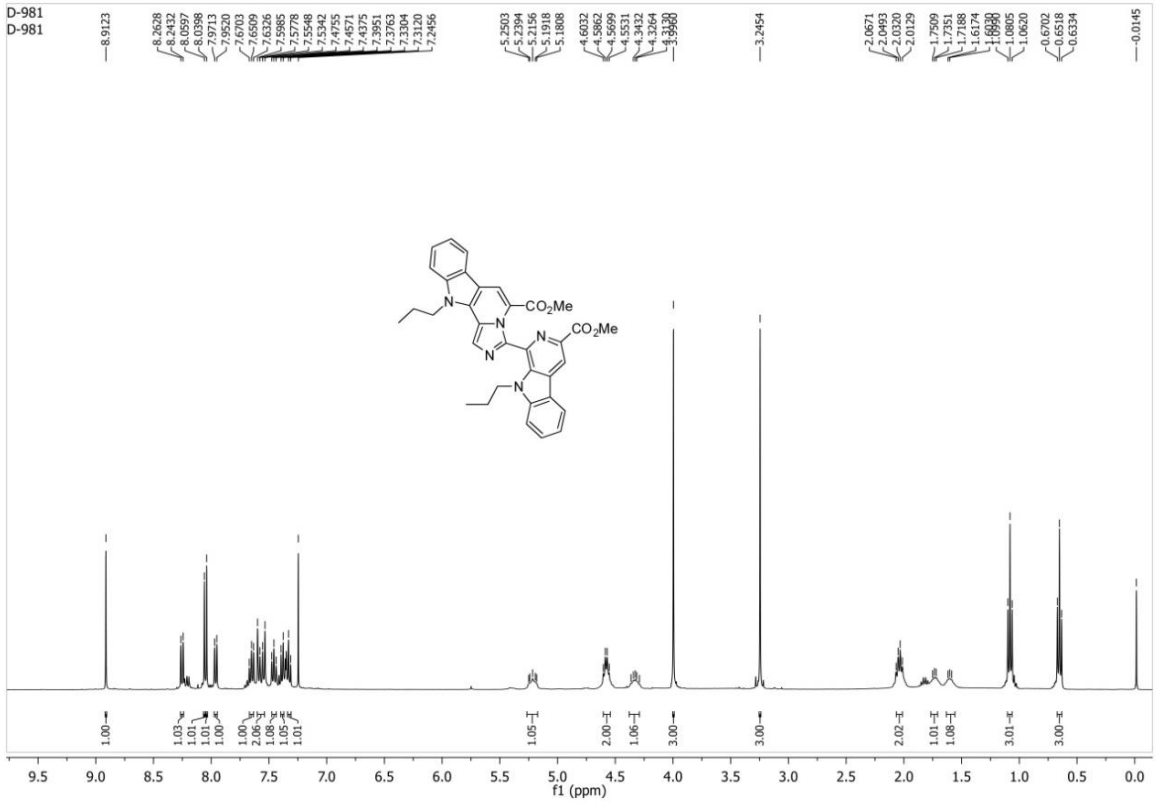


Figure S9. ^{1}H-NMR spectrum of **4c**.

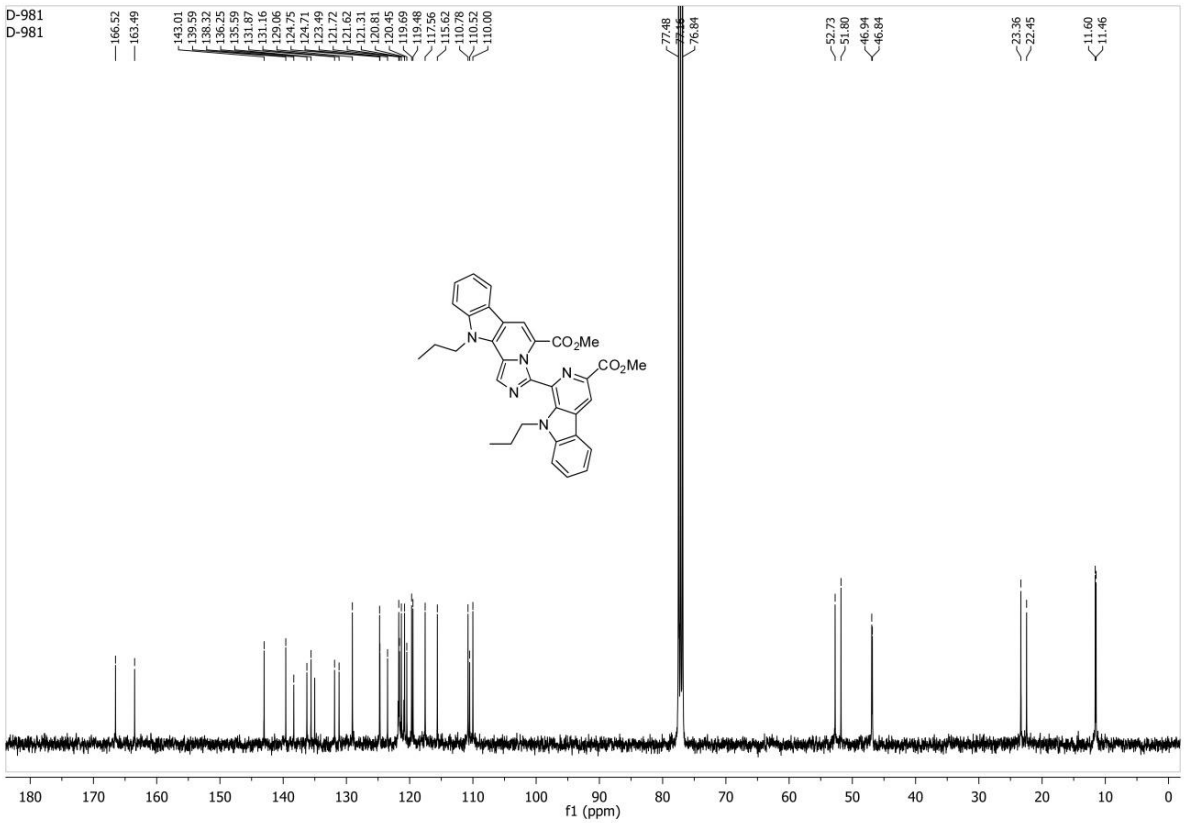
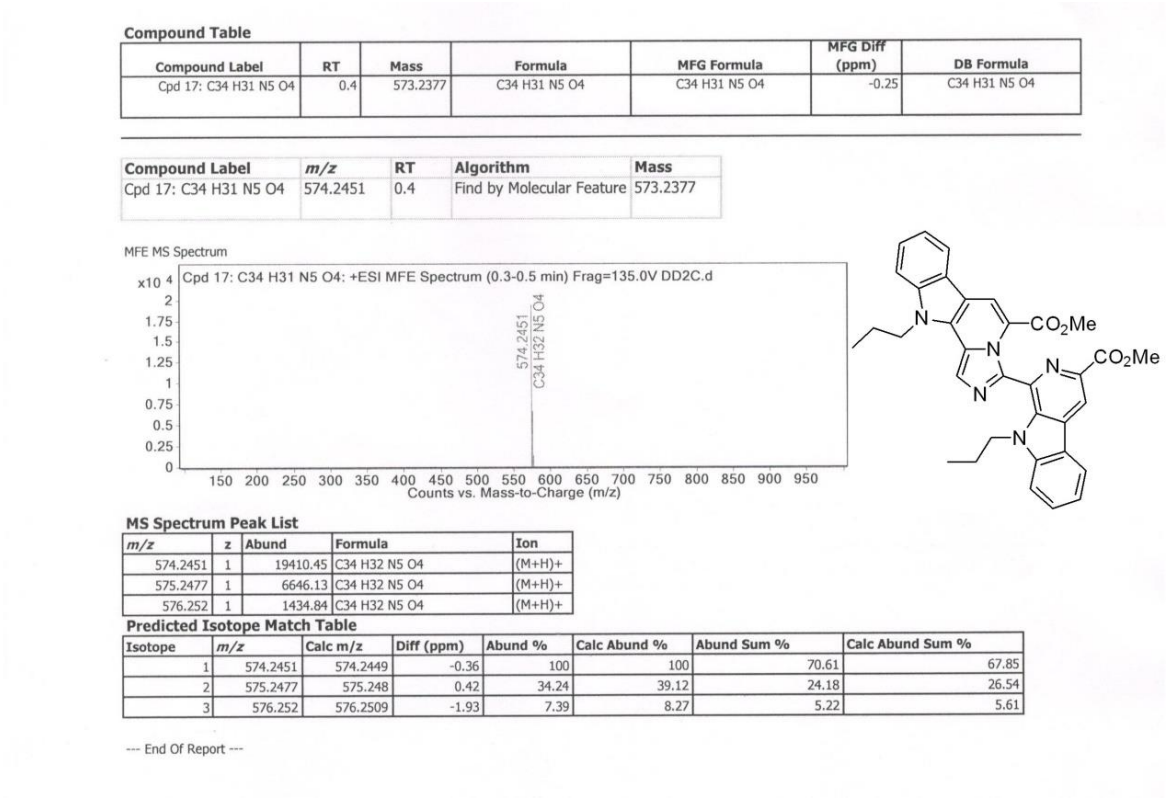


Figure S10. ^{13}C-NMR spectrum of **4c**.



Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 17: C34 H31 N5 O4	0.4	573.2377	C34 H31 N5 O4	C34 H31 N5 O4	-0.25	C34 H31 N5 O4

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 17: C34 H31 N5 O4	574.2451	0.4	Find by Molecular Feature	573.2377

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
574.2451	1	19410.45	C34 H32 N5 O4	(M+H)+
575.2477	1	6646.13	C34 H32 N5 O4	(M+H)+
576.252	1	1434.84	C34 H32 N5 O4	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	574.2451	574.2449	-0.36	100	100	70.61	67.85
2	575.2477	575.248	0.42	34.24	39.12	24.18	26.54
3	576.252	576.2509	-1.93	7.39	8.27	5.22	5.61

--- End Of Report ---

Figure S11. HRMS spectrum of **4c**.

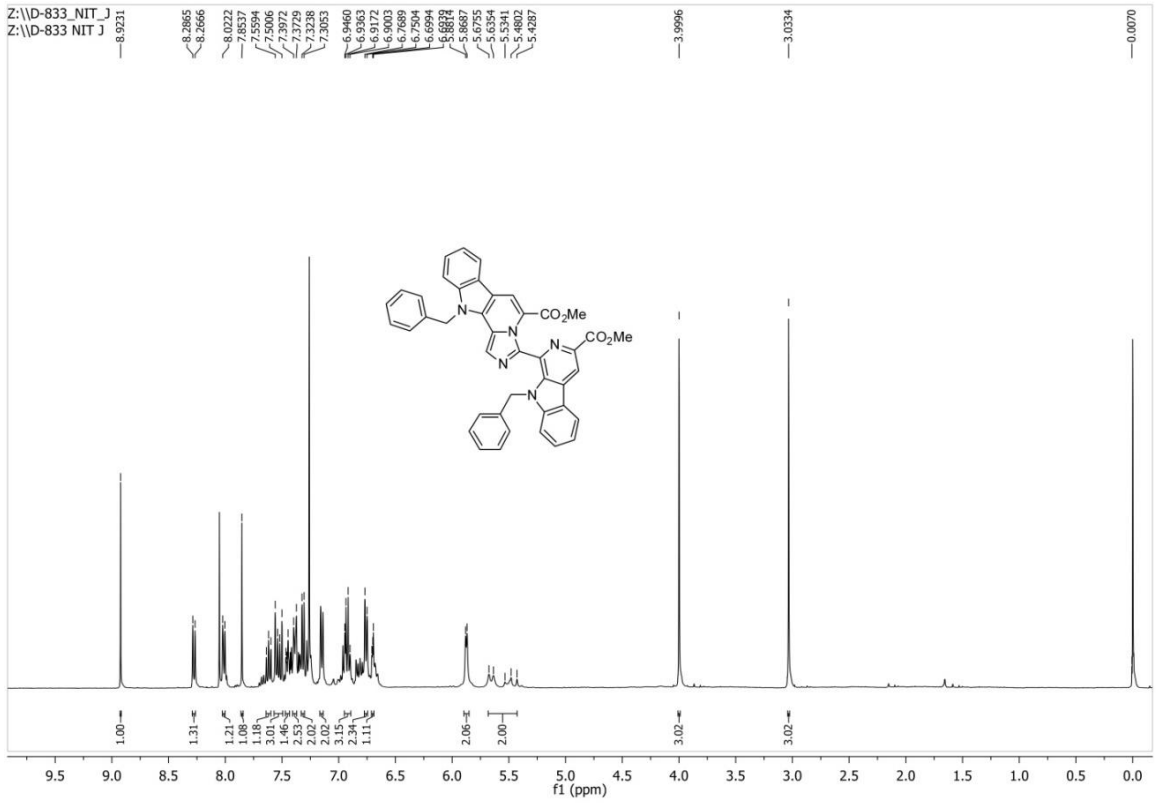


Figure S12. ^{1}H-NMR spectrum of **4d**.

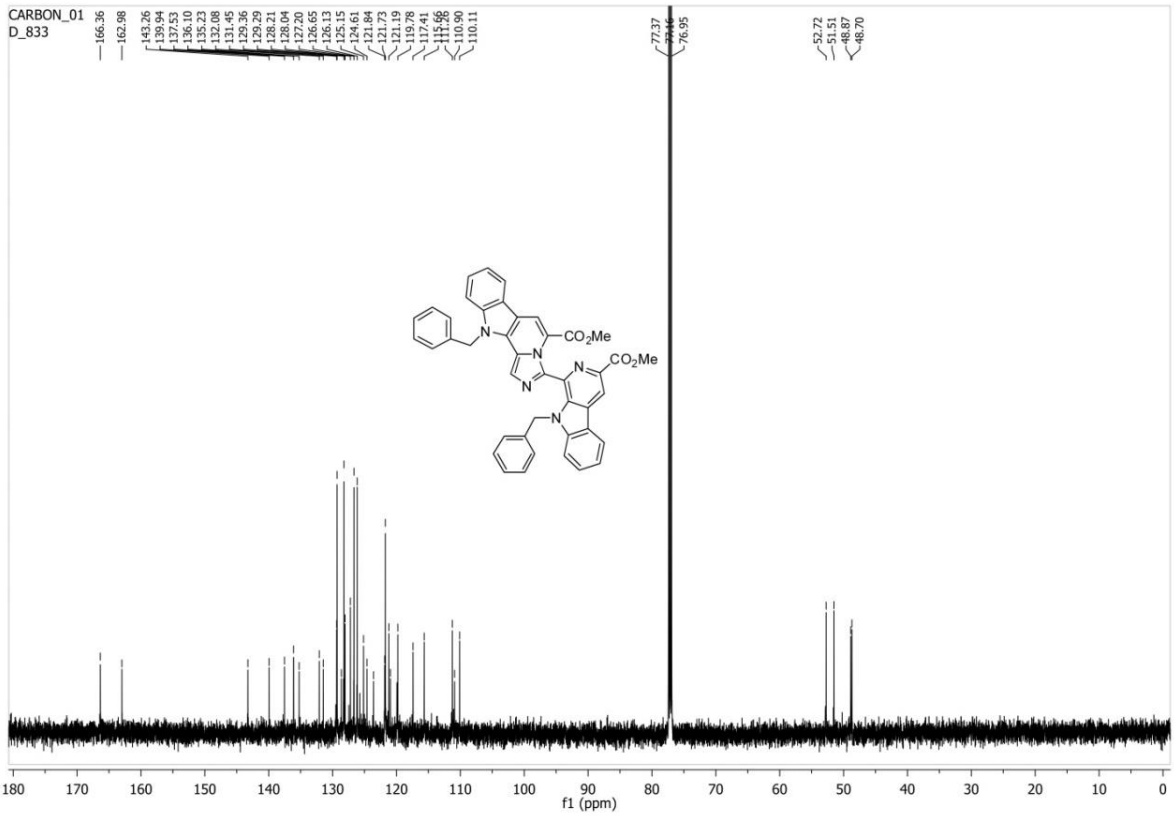


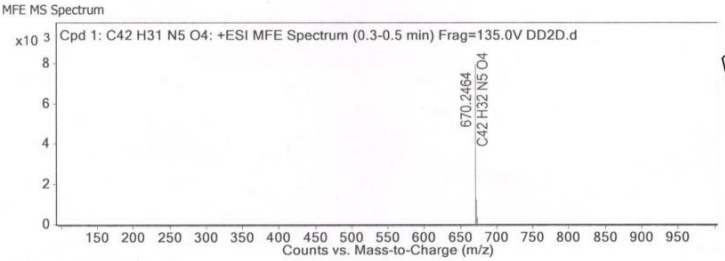
Figure S13. ^{13}C-NMR spectrum of **4d**.

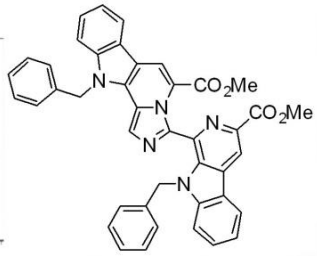
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C42 H31 N5 O4	0.4	669.2389	C42 H31 N5 O4	C42 H31 N5 O4	-1.91	C42 H31 N5 O4

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C42 H31 N5 O4	670.2464	0.4	Find by Molecular Feature	669.2389

MFE MS Spectrum





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
670.2464	1	7985.72	C42 H32 N5 O4	(M+H)+
671.2486	1	3716.2	C42 H32 N5 O4	(M+H)+
672.2542	1	1220.19	C42 H32 N5 O4	(M+H)+
673.2486	1	309.06	C42 H32 N5 O4	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	670.2464	670.2449	-2.33	100	100	60.36	61.79
2	671.2486	671.248	-0.86	46.54	47.77	28.09	29.52
3	672.2542	672.251	-4.76	15.28	11.98	9.22	7.4
4	673.2486	673.2539	7.88	3.87	2.09	2.34	1.29

--- End Of Report ---

Figure S14. HRMS spectrum of **4d**.

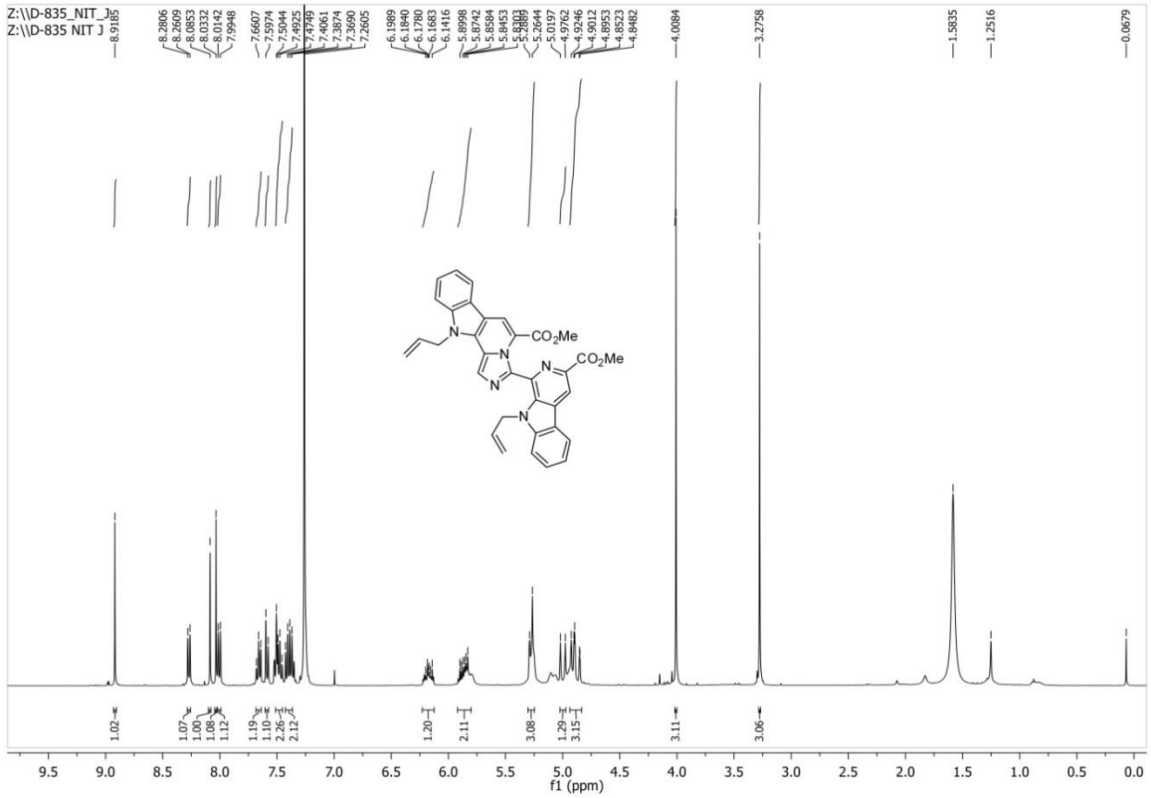


Figure S15. ^{1}H-NMR spectrum of **4e**.

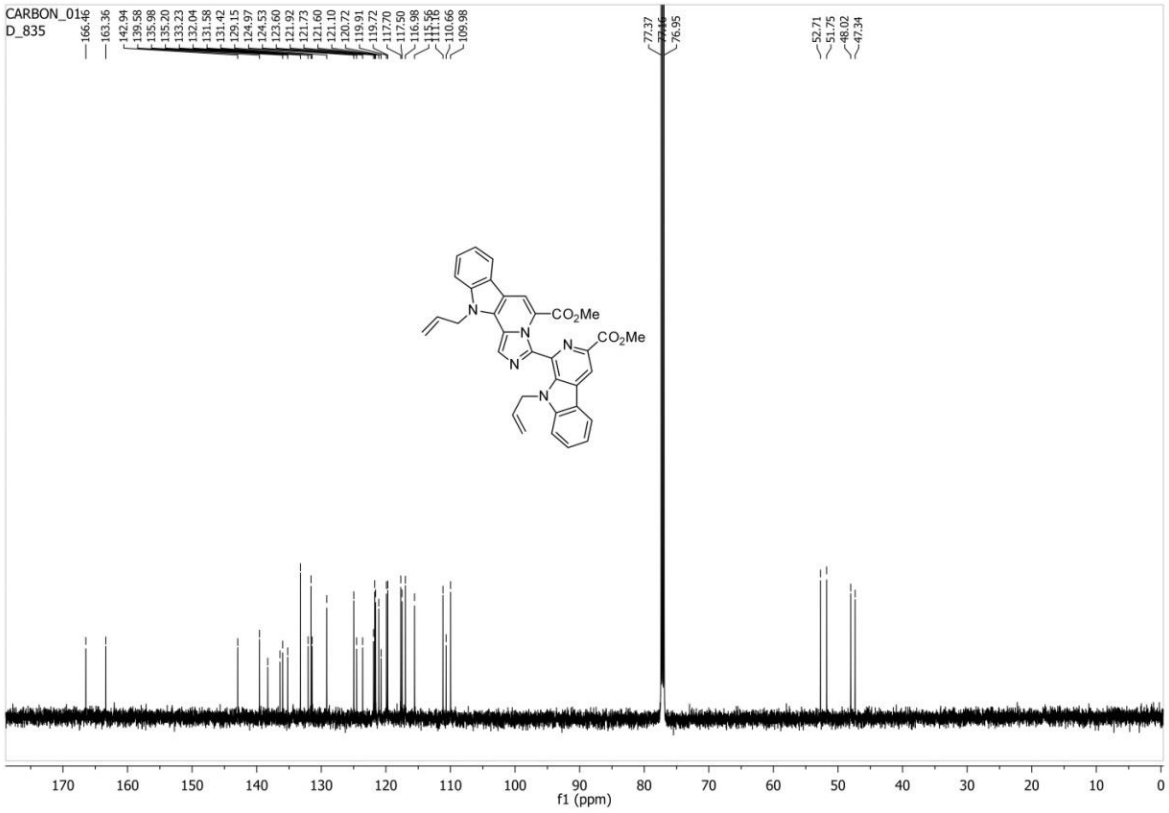


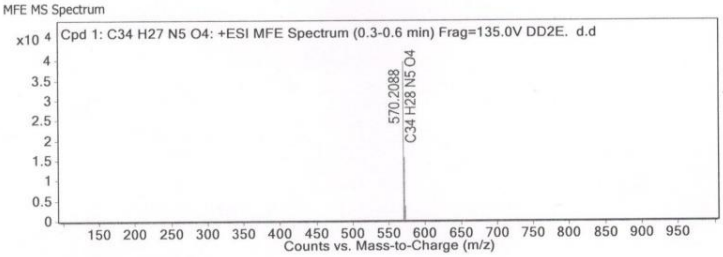
Figure S16. ^{13}C-NMR spectrum of **4e**.

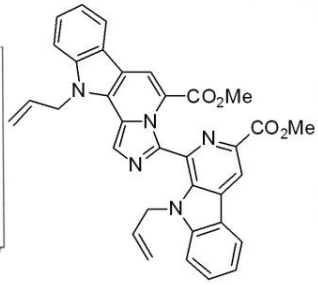
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C34 H27 N5 O4	0.4	569.2015	C34 H27 N5 O4	C34 H27 N5 O4	8.5	C34 H27 N5 O4

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C34 H27 N5 O4	570.2088	0.4	Find by Molecular Feature	569.2015

MFE MS Spectrum





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
570.2088	1	39675.48	C34 H28 N5 O4	(M+H)+
571.2121	1	15684.42	C34 H28 N5 O4	(M+H)+
572.2137	1	3580.66	C34 H28 N5 O4	(M+H)+
573.2166	1	656.53	C34 H28 N5 O4	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	570.2088	570.2136	8.45	100	100	66.57	67.31
2	571.2121	571.2167	8.08	39.53	39.07	26.32	26.3
3	572.2137	572.2196	10.32	9.02	8.25	6.01	5.56
4	573.2166	573.2223	9.97	1.65	1.24	1.1	0.83

--- End Of Report ---

Figure S17. HRMS spectrum of **4e**.

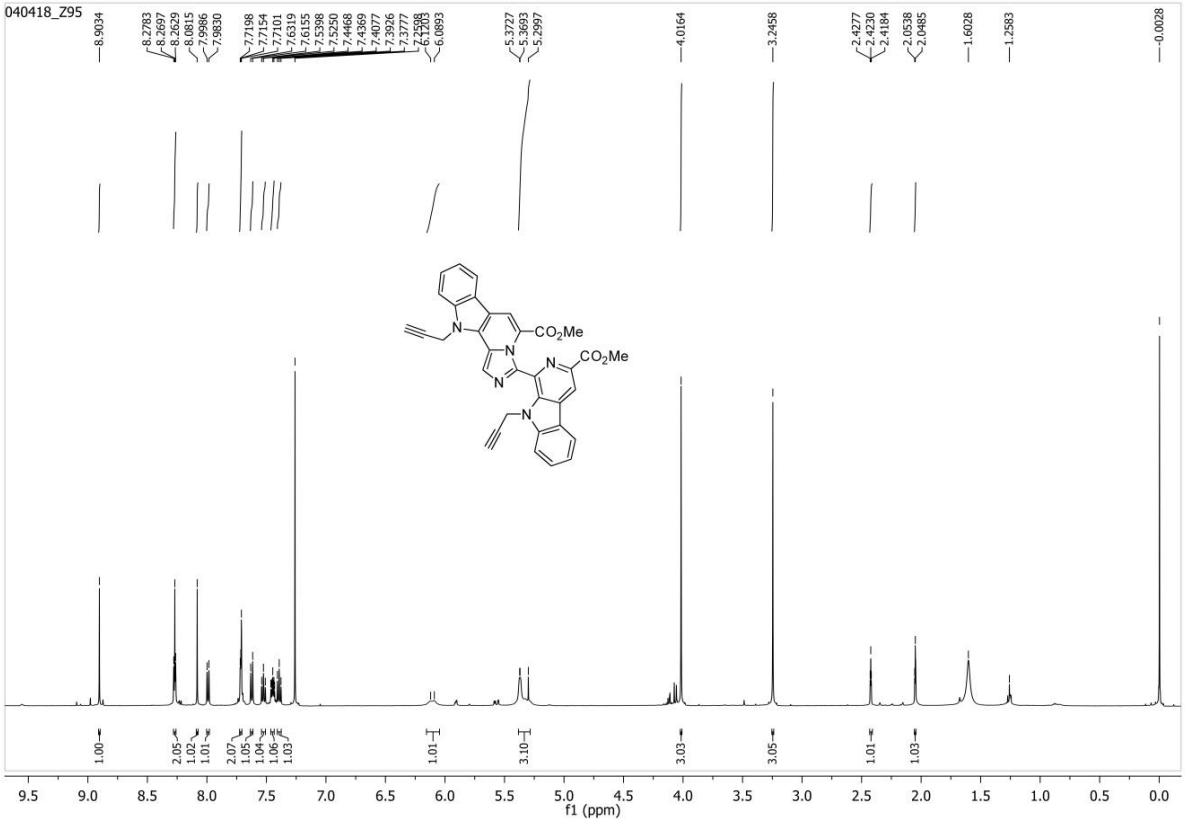


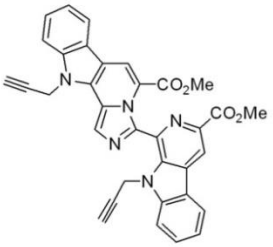
Figure S18. ^{1}H-NMR spectrum of **4f**.

Sample Group		Info.
Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.01 (B5125)	

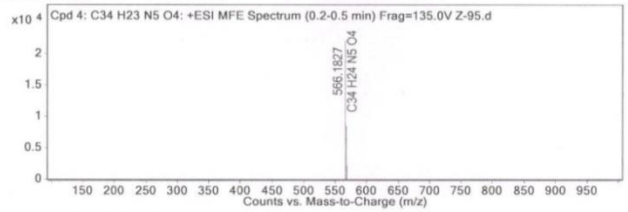
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 4: C34 H23 N5 O4	0.3	565.1755	C34 H23 N5 O4	C34 H23 N5 O4	-0.82	C34 H23 N5 O4

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 4: C34 H23 N5 O4	566.1827	0.3	Find by Molecular Feature	565.1755



MFE MS Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
566.1827	1	22167.82	C34 H24 N5 O4	(M+H)+
567.1858	1	8543.93	C34 H24 N5 O4	(M+H)+
568.1888	1	2116.33	C34 H24 N5 O4	(M+H)+
569.1927	1	397.69	C34 H24 N5 O4	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	566.1827	566.1823	-0.74	100	100	66.72	67.34
2	567.1858	567.1854	-0.83	38.54	39.03	25.71	26.28
3	568.1888	568.1882	-1.06	9.55	8.24	6.37	5.55
4	569.1927	569.191	-2.91	1.79	1.23	1.2	0.83

--- End Of Report ---

Figure S19. HRMS spectrum of **4f**.

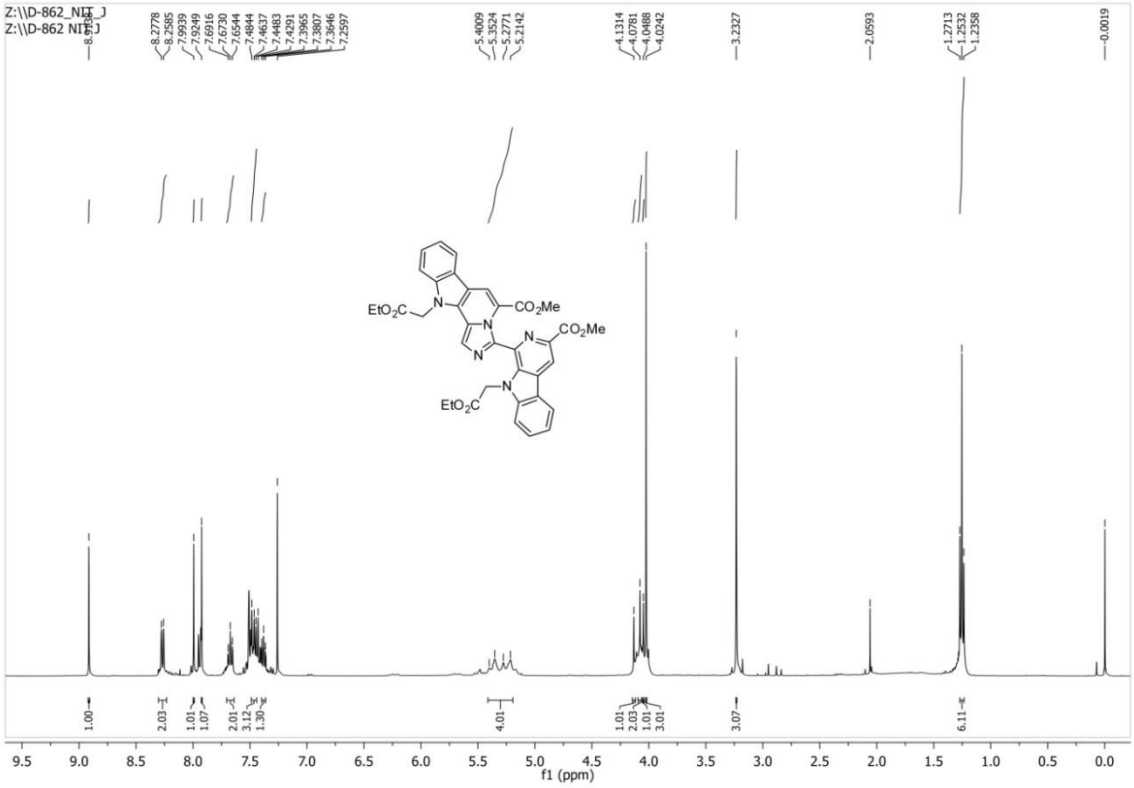


Figure S20. ^{1}H-NMR spectrum of **4g**.

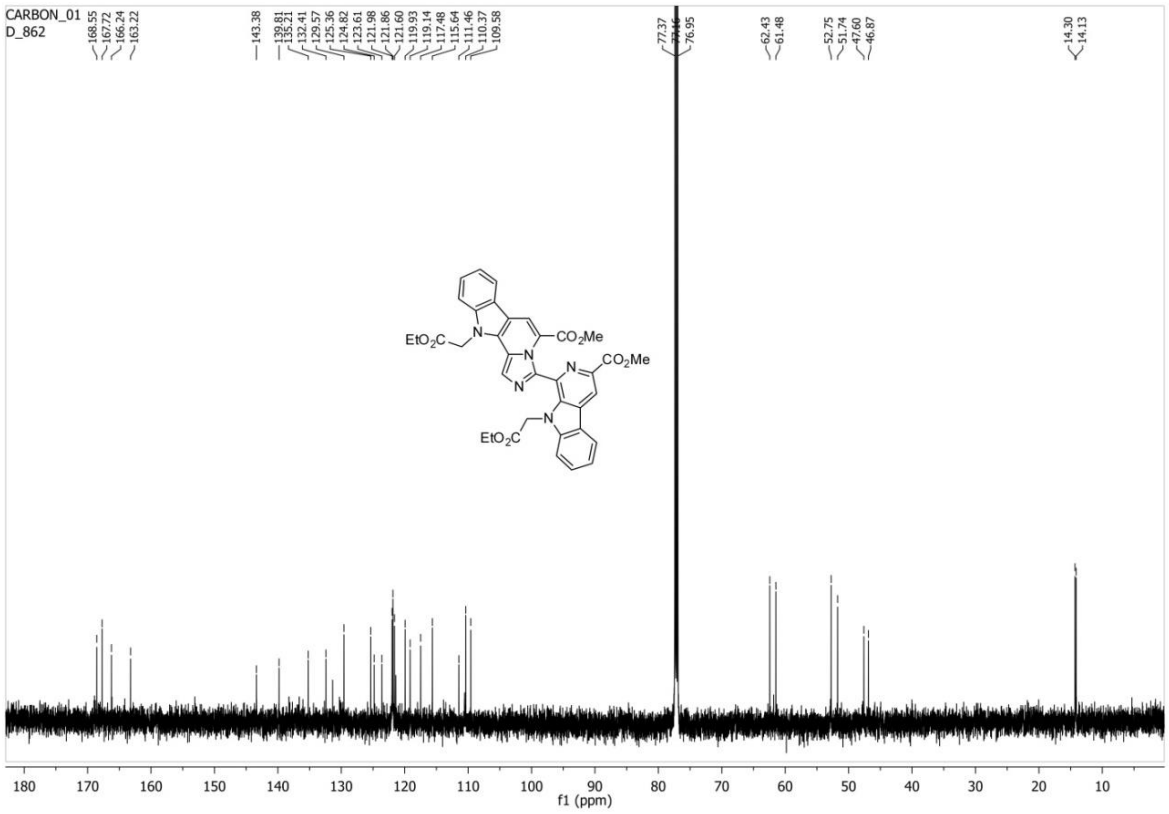


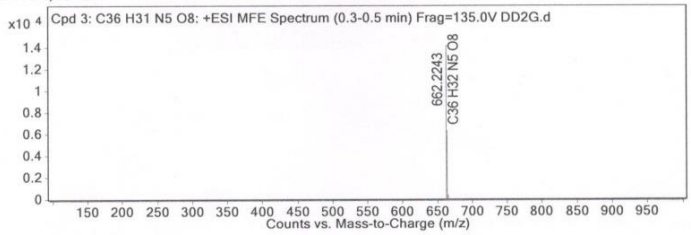
Figure S21. ^{13}C-NMR spectrum of **4g**.

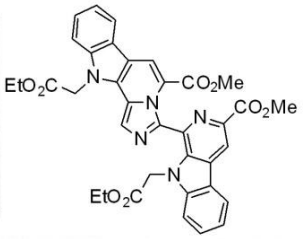
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 3: C36 H31 N5 O8	0.4	661.2172	C36 H31 N5 O8	C36 H31 N5 O8	0.06	C36 H31 N5 O8

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: C36 H31 N5 O8	662.2243	0.4	Find by Molecular Feature	661.2172

MFE MS Spectrum





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
662.2243	1	14199.84	C36 H32 N5 O8	(M+H)+
663.2275	1	6318.96	C36 H32 N5 O8	(M+H)+
664.2314	1	1476.41	C36 H32 N5 O8	(M+H)+
665.2374	1	405.01	C36 H32 N5 O8	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	662.2243	662.2245	0.36	100	100	63.39	65.26
2	663.2275	663.2276	0.16	44.5	41.44	28.21	27.04
3	664.2314	664.2304	-1.44	10.4	10.01	6.59	6.54
4	665.2374	665.2331	-6.52	2.85	1.78	1.81	1.16

--- End Of Report ---

Figure S22. HRMS spectrum of **4g**.

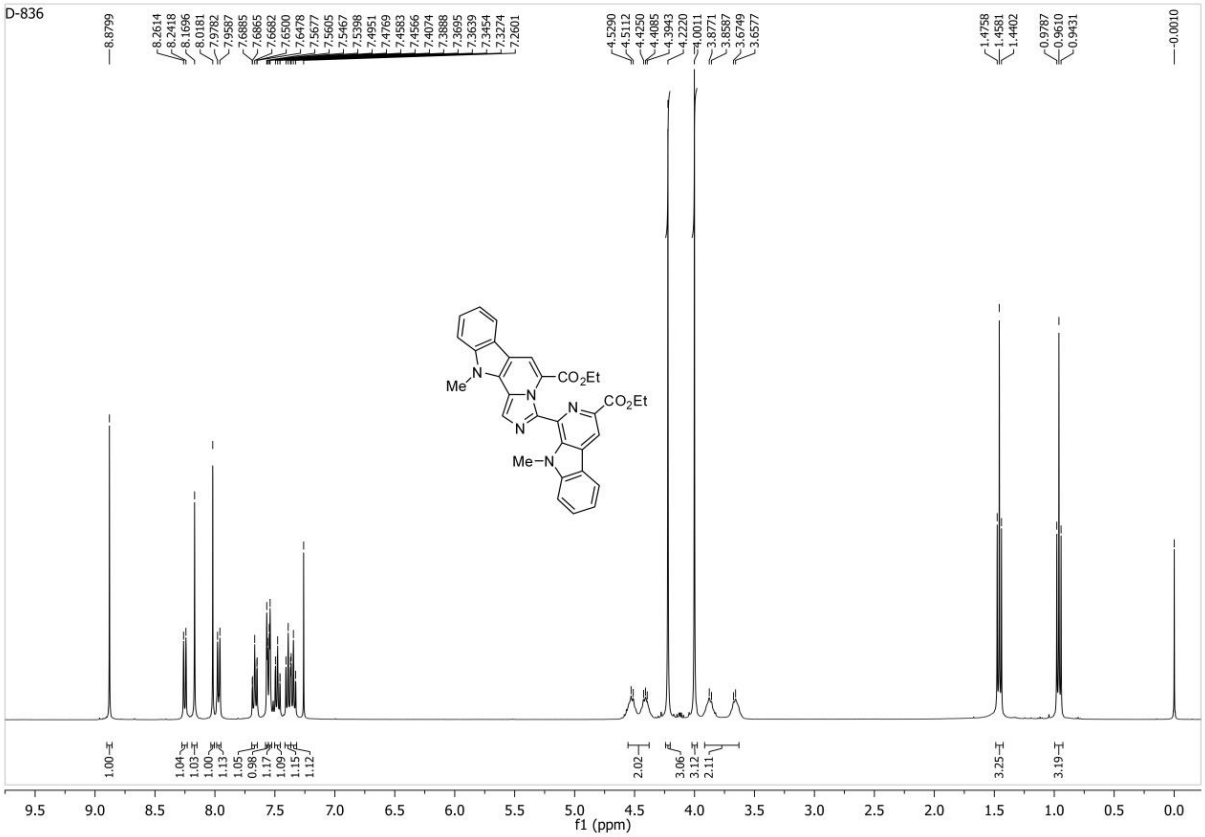


Figure S23. ^{1}H-NMR spectrum of **4h**.

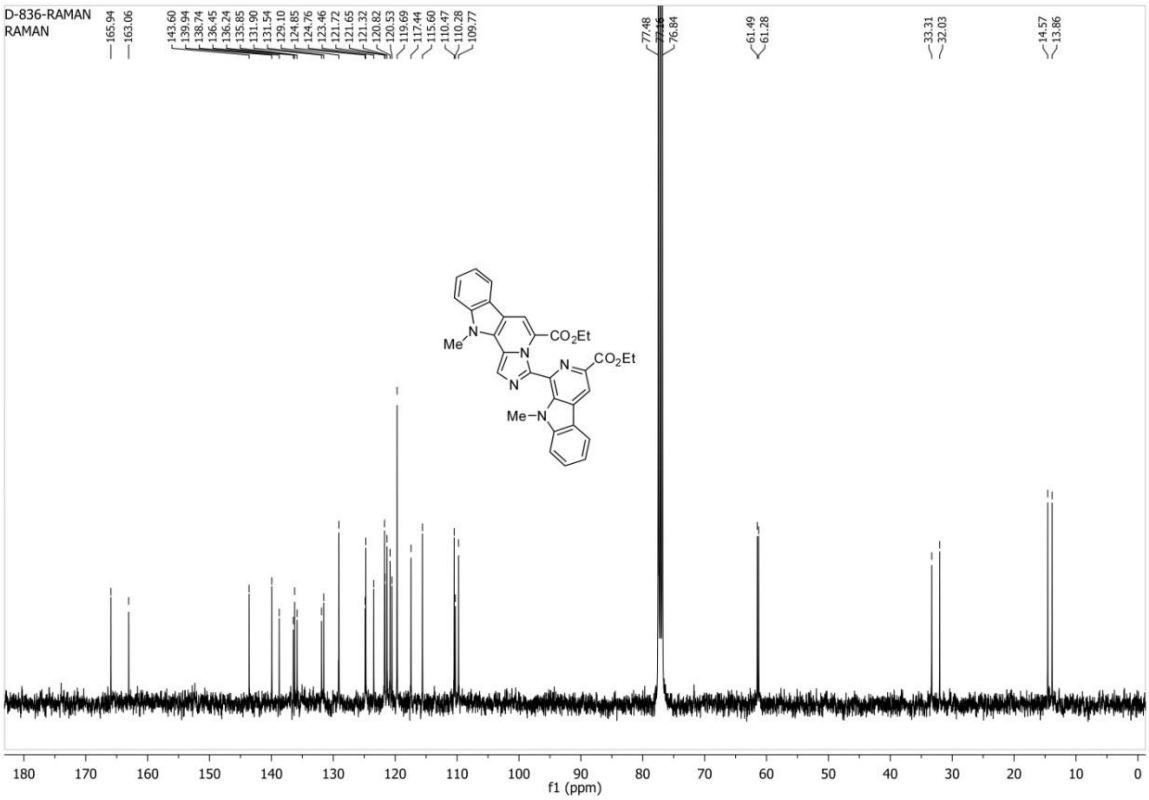


Figure S24. ^{13}C-NMR spectrum of **4h**.

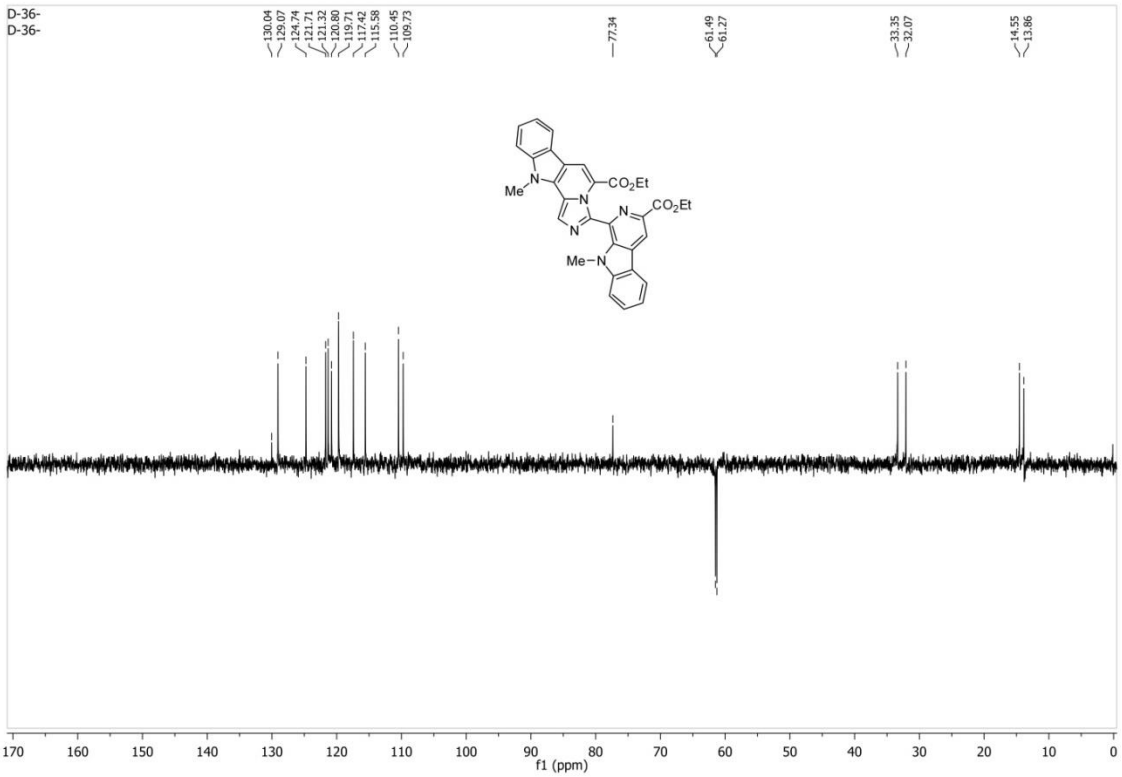


Figure S25. DEPT-135 NMR spectrum of **4h**.

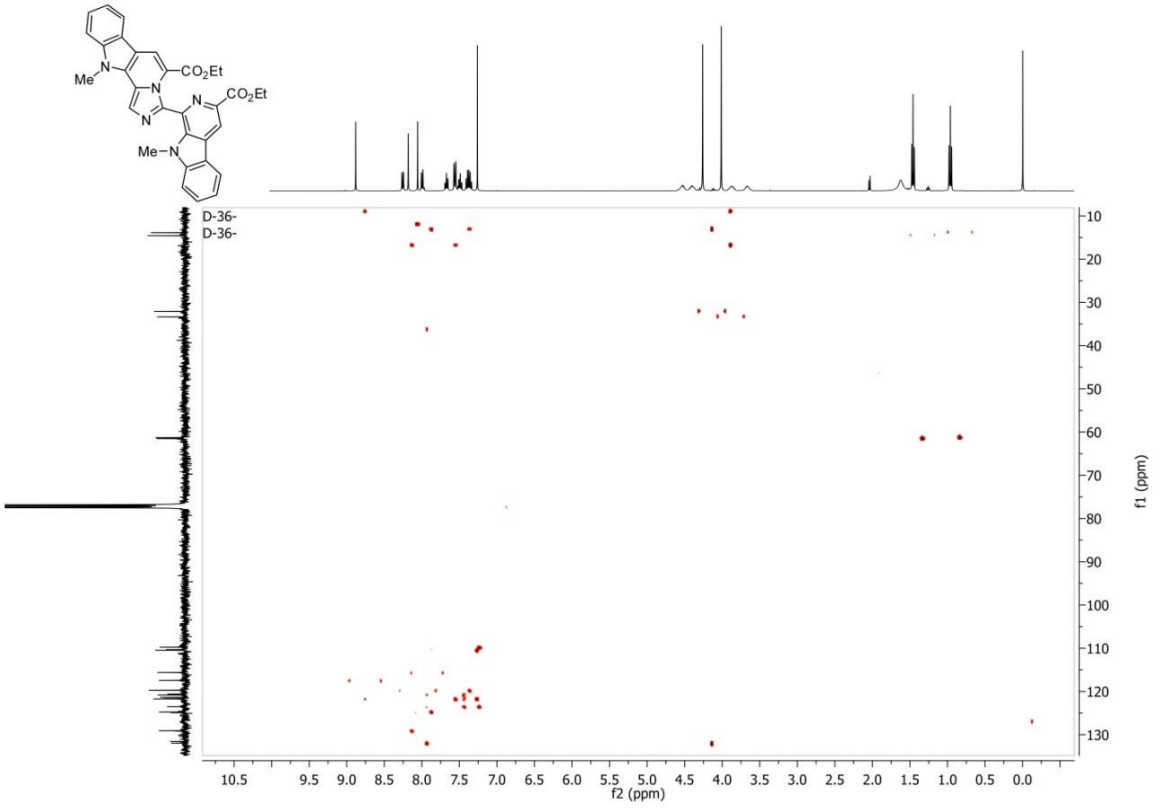


Figure S26. HMBC NMR spectrum of **4h**.

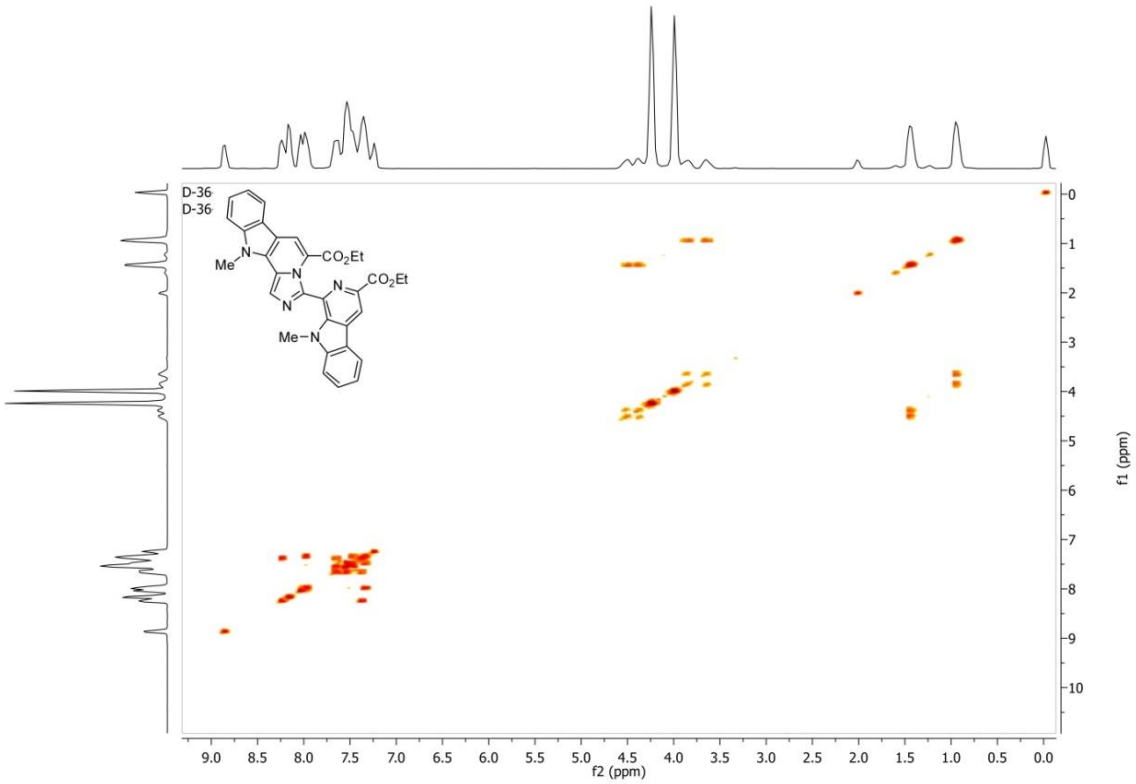


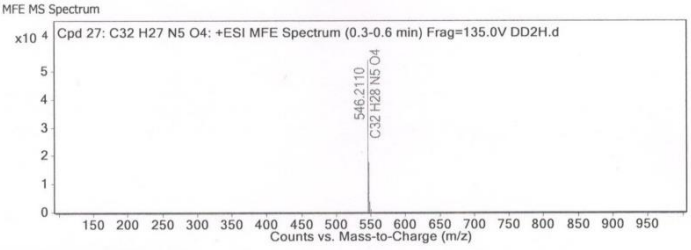
Figure S27. COSY NMR spectrum of **4h**.

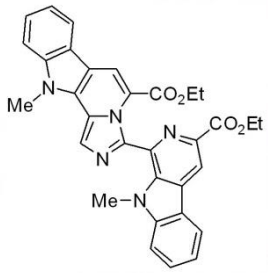
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 27: C32 H27 N5 O4	0.4	545.2039	C32 H27 N5 O4	C32 H27 N5 O4	4.47	C32 H27 N5 O4

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 27: C32 H27 N5 O4	546.211	0.4	Find by Molecular Feature	545.2039

MFE MS Spectrum





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
546.211	1	54050.86	C32 H28 N5 O4	(M+H)+
547.2142	1	17570.94	C32 H28 N5 O4	(M+H)+
548.2184	1	3813.23	C32 H28 N5 O4	(M+H)+
549.222	1	825.8	C32 H28 N5 O4	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	546.211	546.2136	4.71	100	100	70.88	68.76
2	547.2142	547.2167	4.4	32.51	36.91	23.04	25.38
3	548.2184	548.2195	1.97	7.05	7.44	5	5.12
4	549.222	549.2222	0.42	1.53	1.07	1.08	0.74

--- End Of Report ---

Figure S28. HRMS spectrum of **4h**.

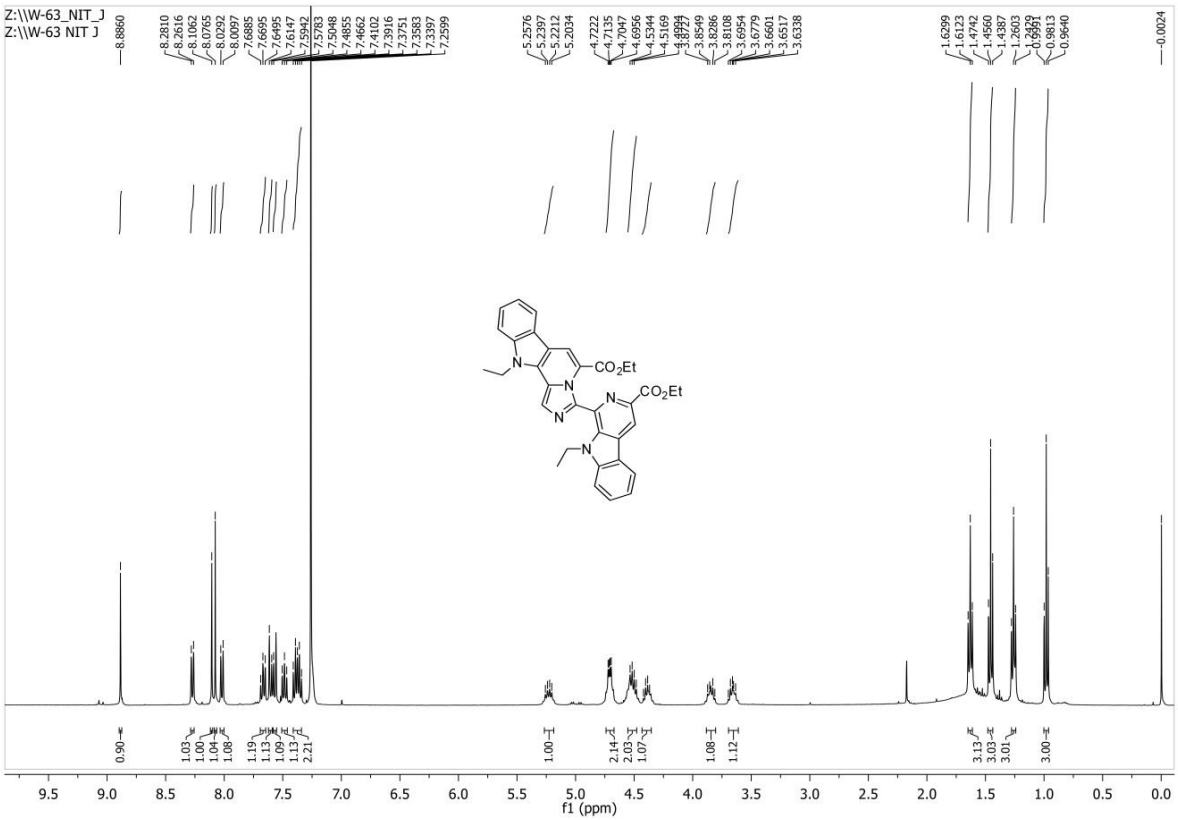


Figure S29. ^{1}H-NMR spectrum of **4i**.

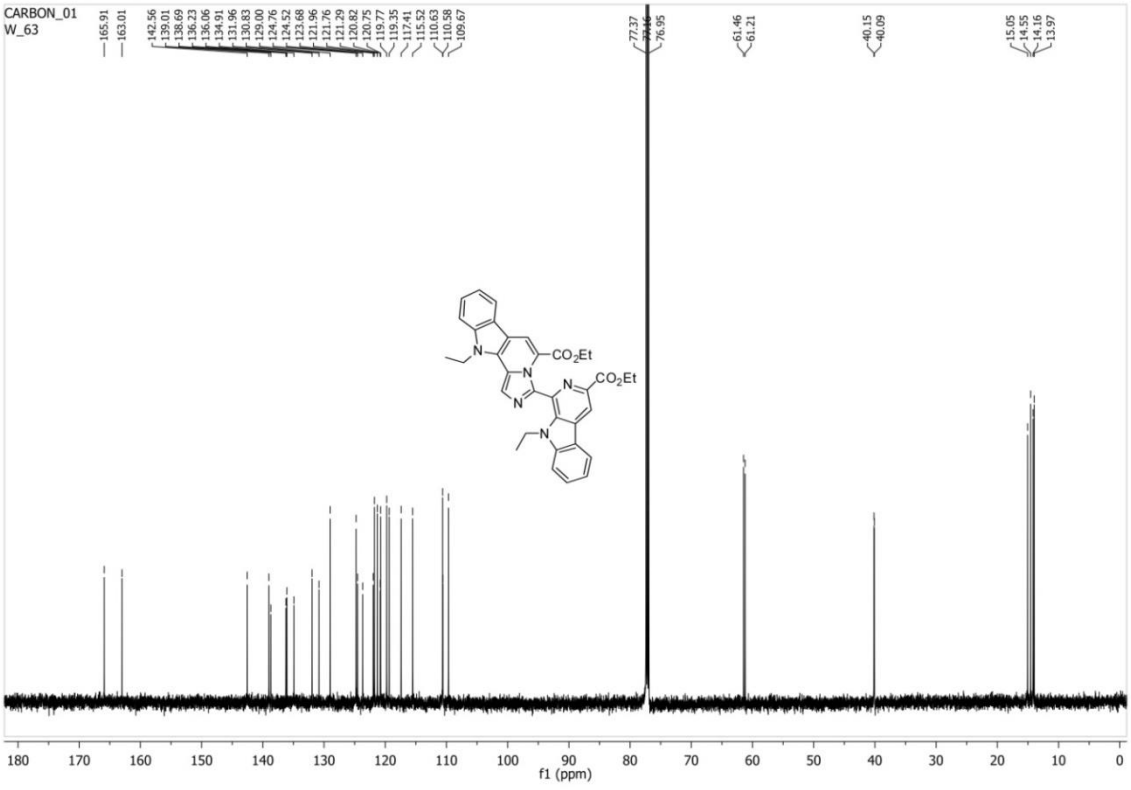


Figure S30. ^{13}C-NMR spectrum of **4i**.

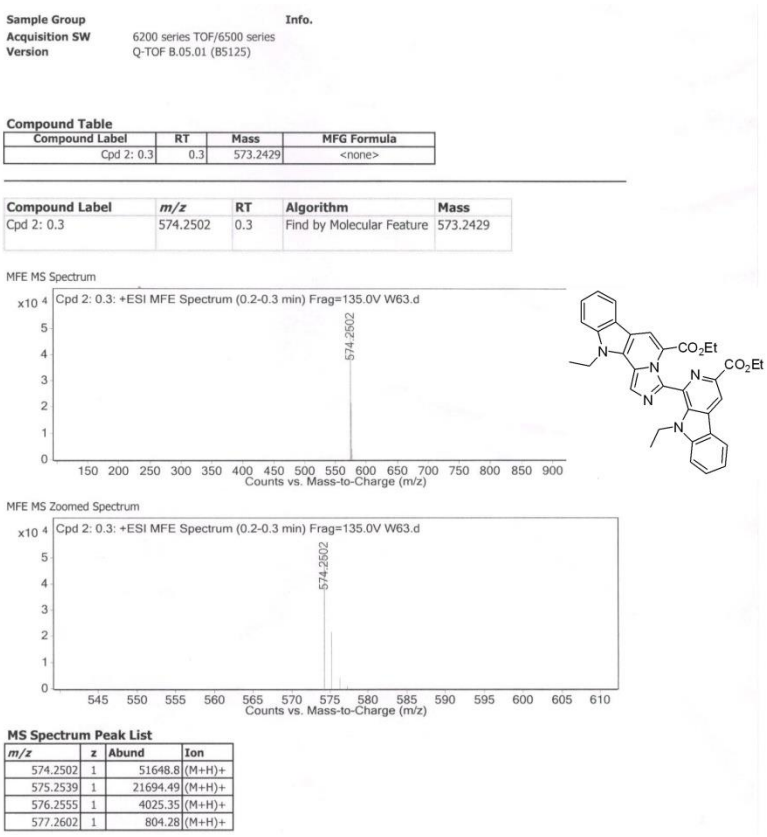


Figure S31. HRMS spectrum of **4i**.

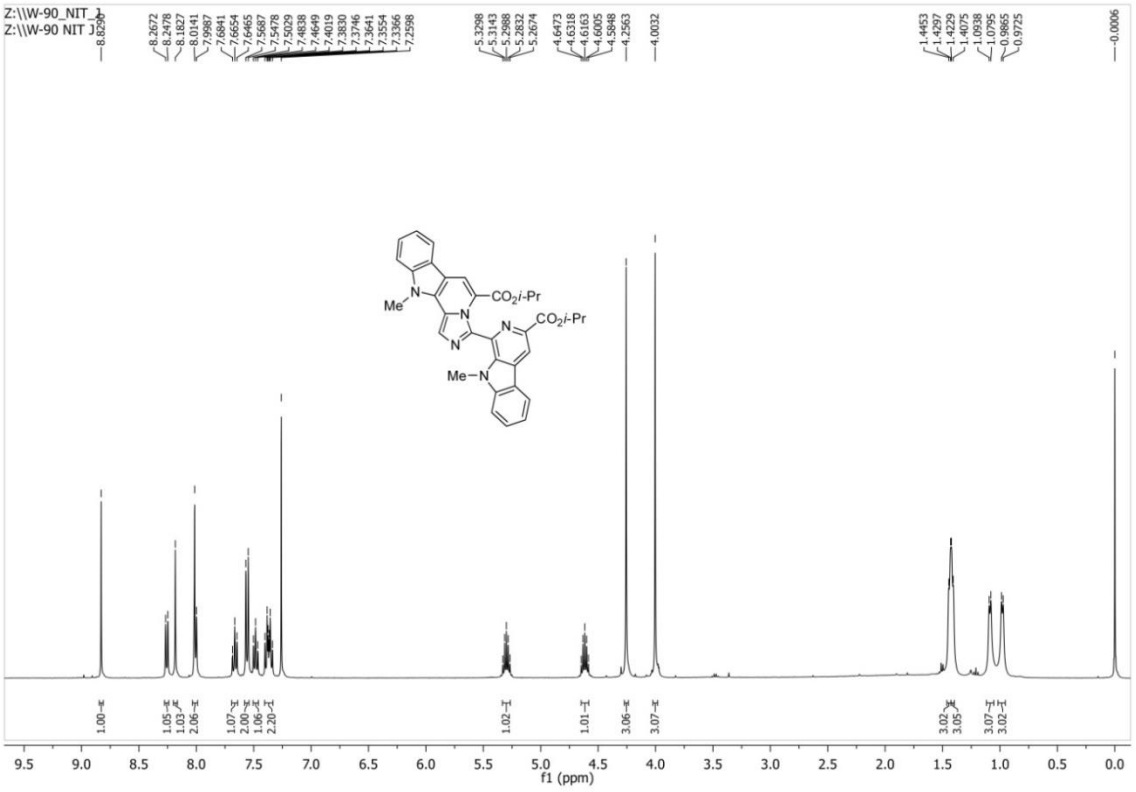


Figure S32. ^{1}H-NMR spectrum of **4j**.

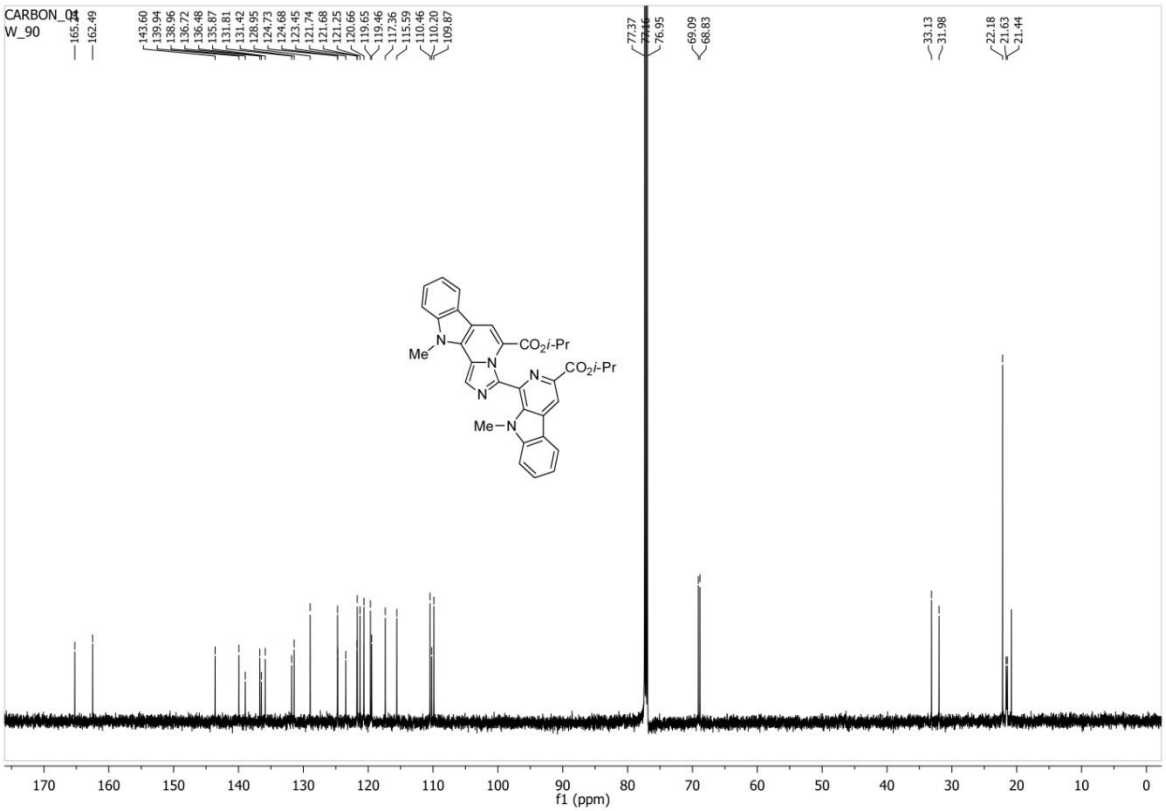
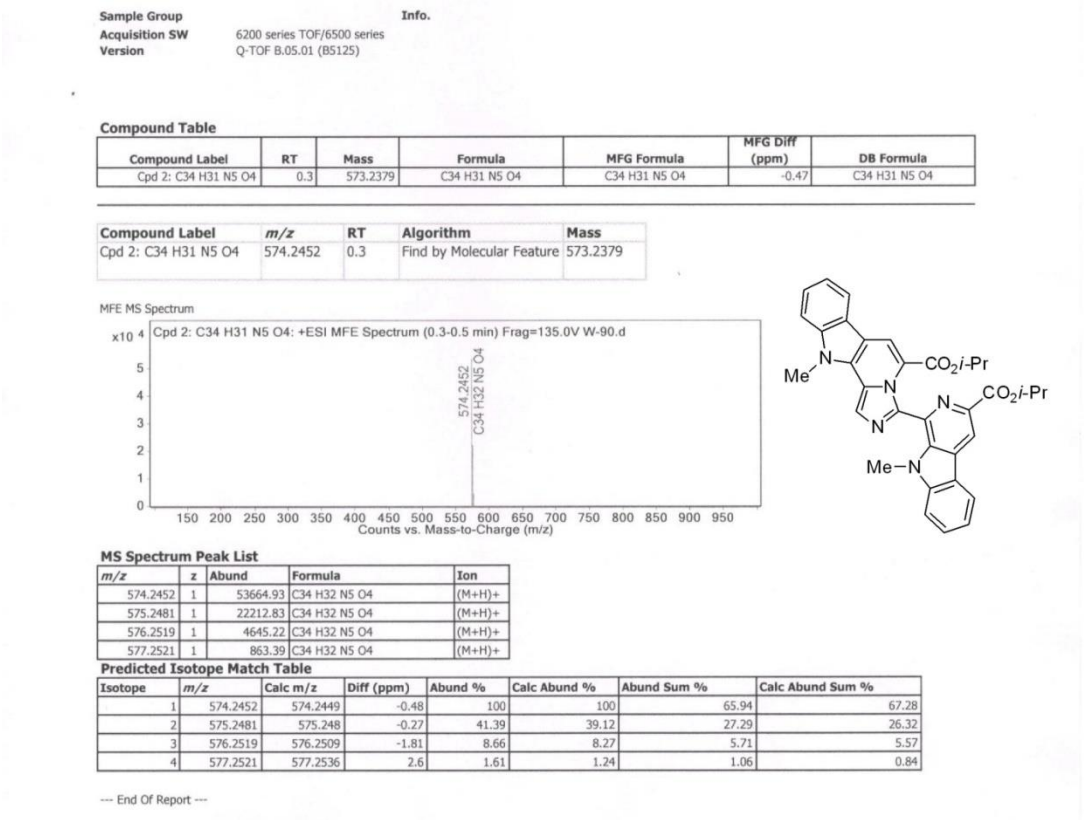


Figure S33. ^{13}C-NMR spectrum of **4j**.



Sample Group		Info.
Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.01 (B5125)	

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 2: C34 H31 N5 O4	0.3	573.2379	C34 H31 N5 O4	C34 H31 N5 O4	-0.47	C34 H31 N5 O4

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C34 H31 N5 O4	574.2452	0.3	Find by Molecular Feature	573.2379

MFE MS Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
574.2452	1	53664.93	C34 H32 N5 O4	(M+H)+
575.2481	1	22212.83	C34 H32 N5 O4	(M+H)+
576.2519	1	4645.22	C34 H32 N5 O4	(M+H)+
577.2521	1	863.39	C34 H32 N5 O4	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	574.2452	574.2449	-0.48	100	100	65.94	67.28
2	575.2481	575.248	-0.27	41.39	39.12	27.29	26.32
3	576.2519	576.2509	-1.81	8.66	8.27	5.71	5.57
4	577.2521	577.2536	2.6	1.61	1.24	1.06	0.84

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Figure S34. HRMS spectrum of **4j**.

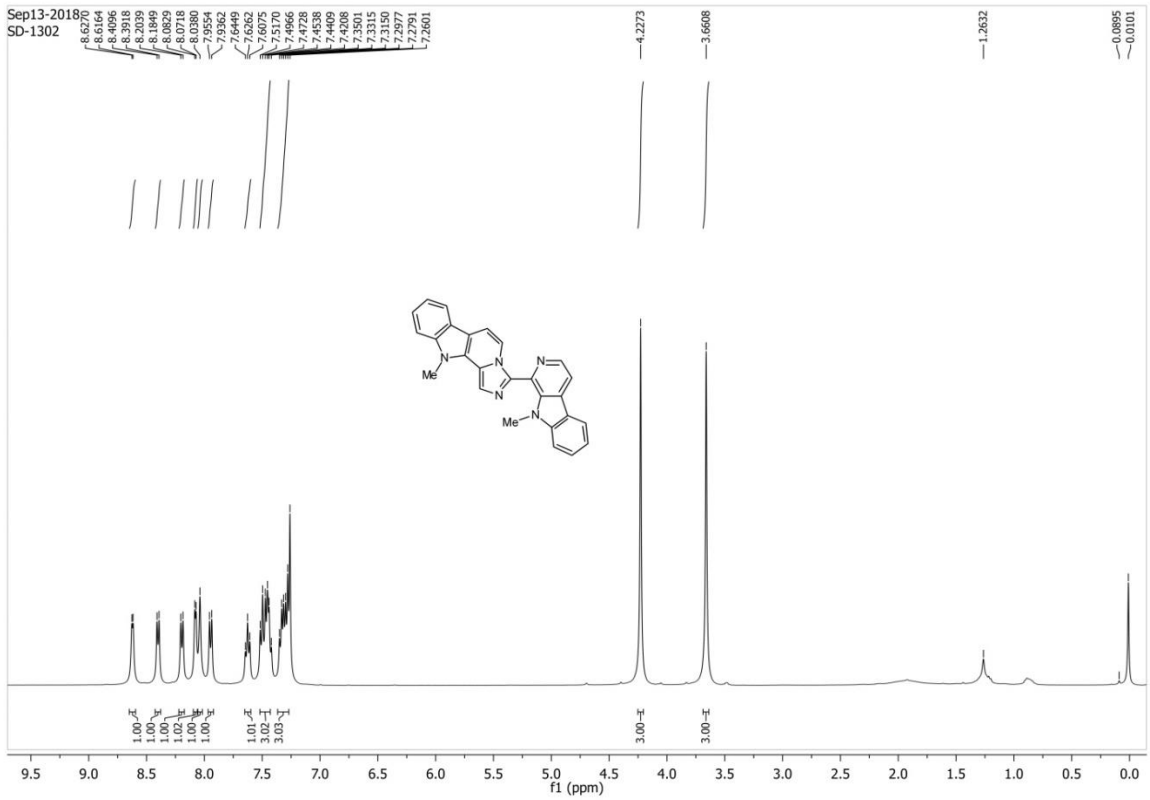


Figure S35. ^{1}H-NMR spectrum of **4k**.

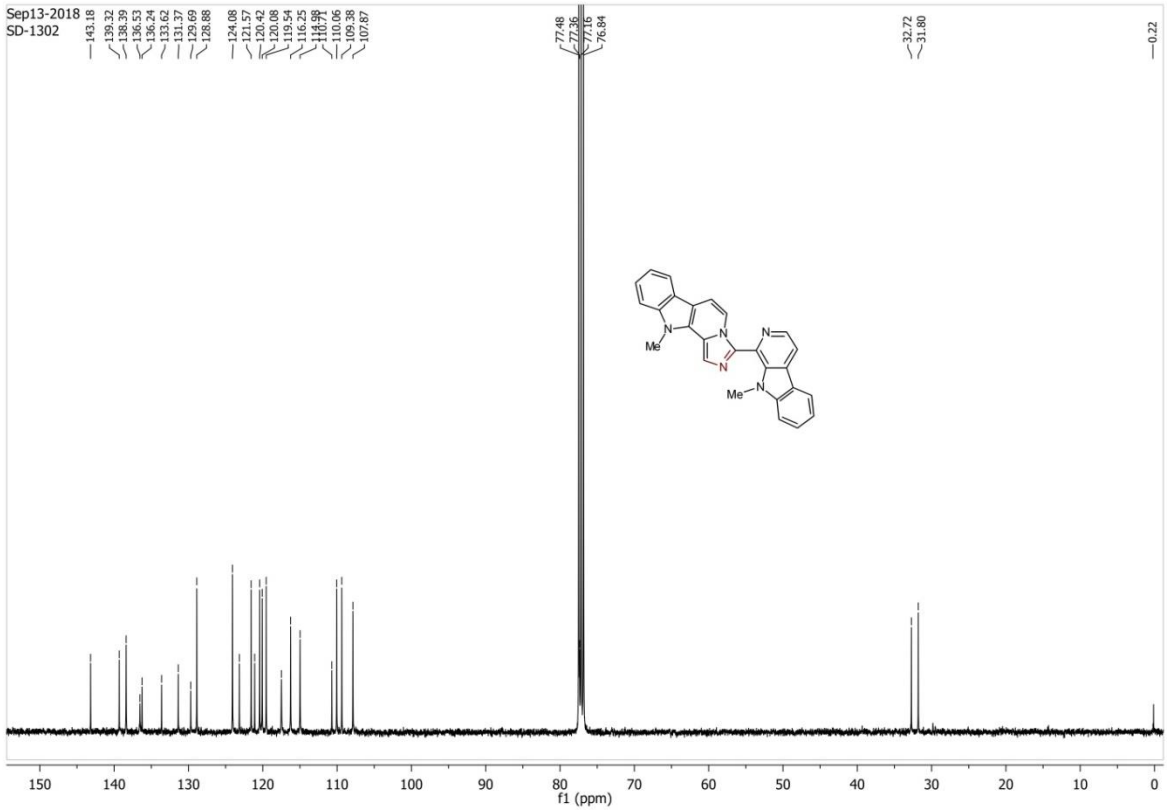


Figure S36. ^{13}C-NMR spectrum of **4k**.

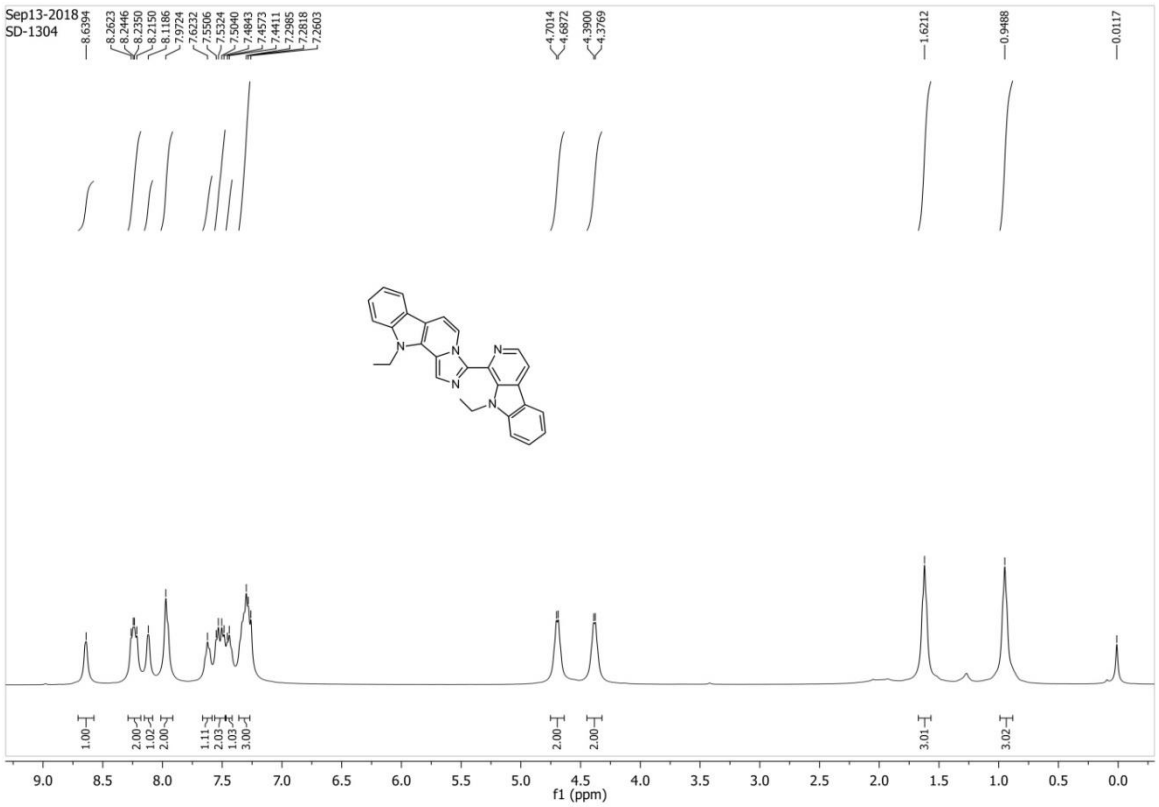


Figure S37. ^{1}H-NMR spectrum of **4l**.

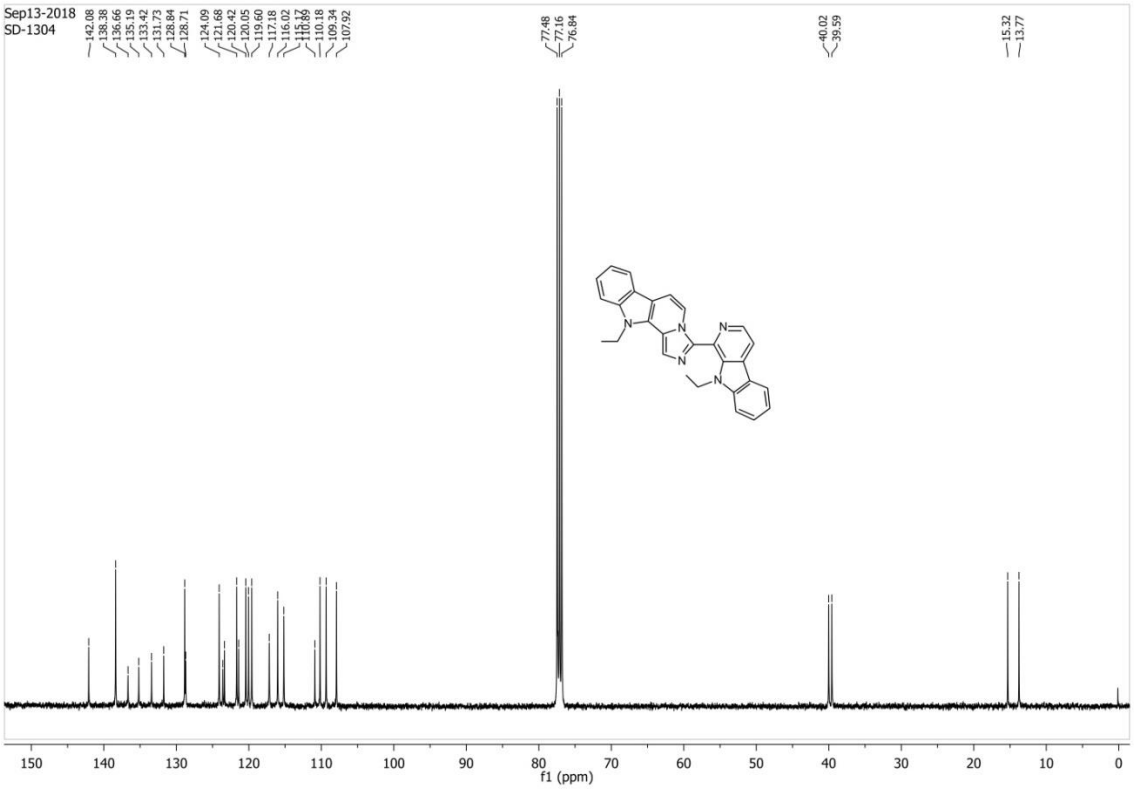


Figure S38. ^{1}H-NMR spectrum of **4l**.

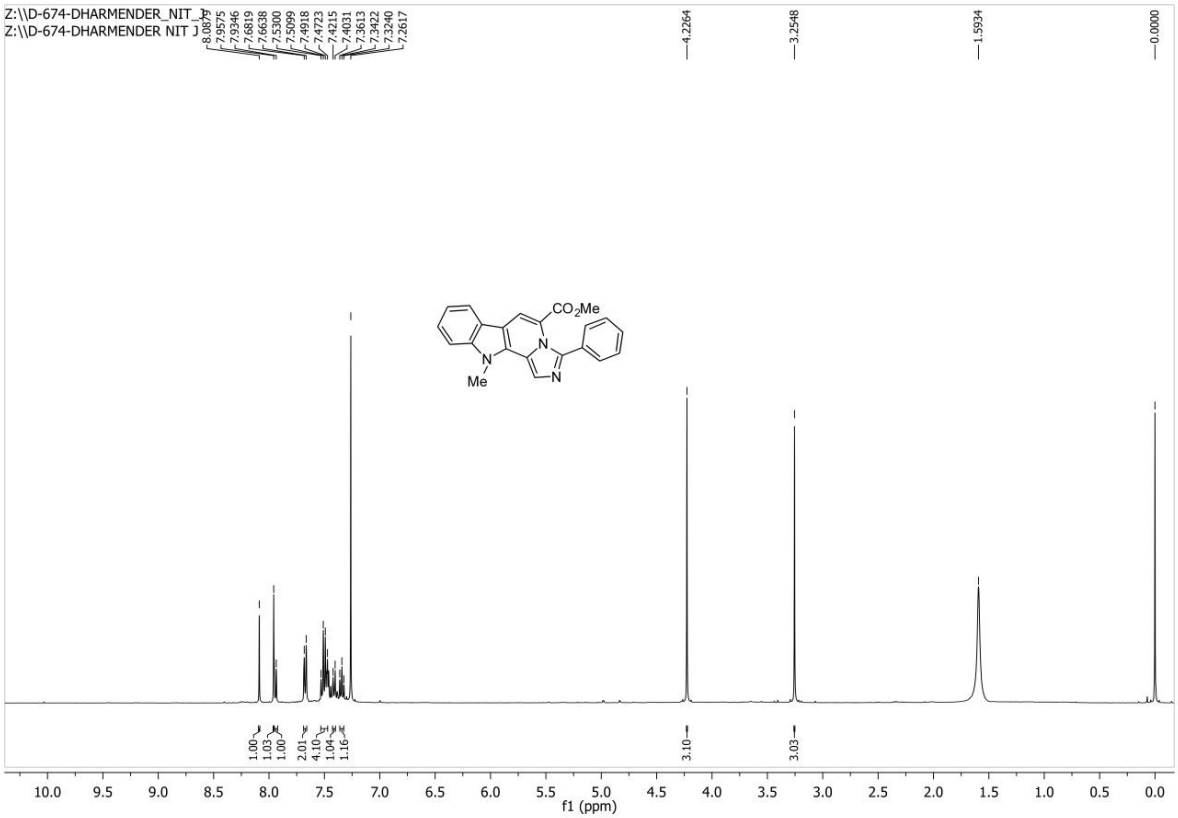


Figure S39. ^{1}H-NMR spectrum of **1aA**.

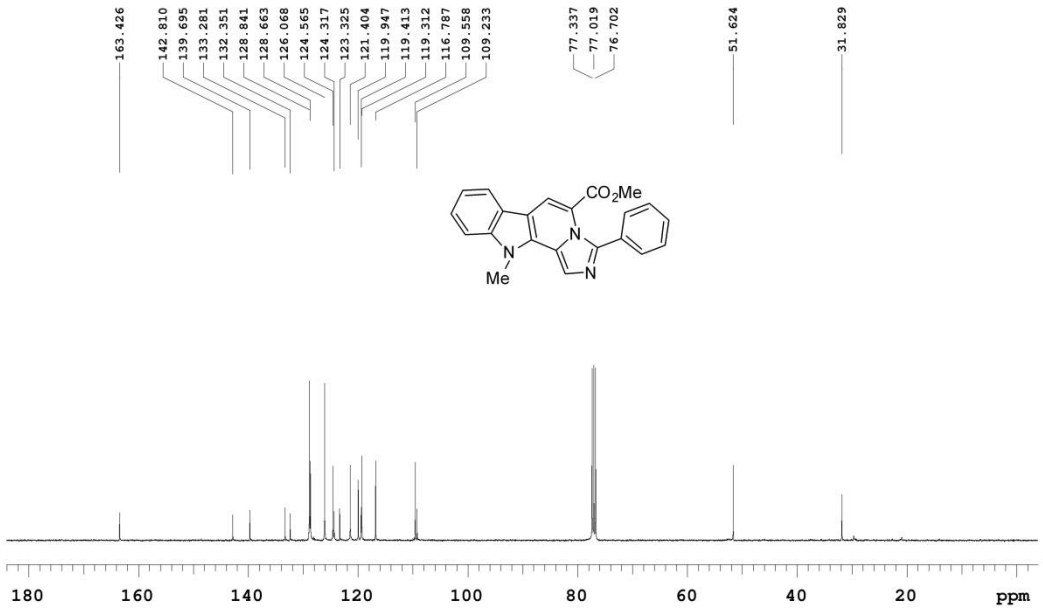
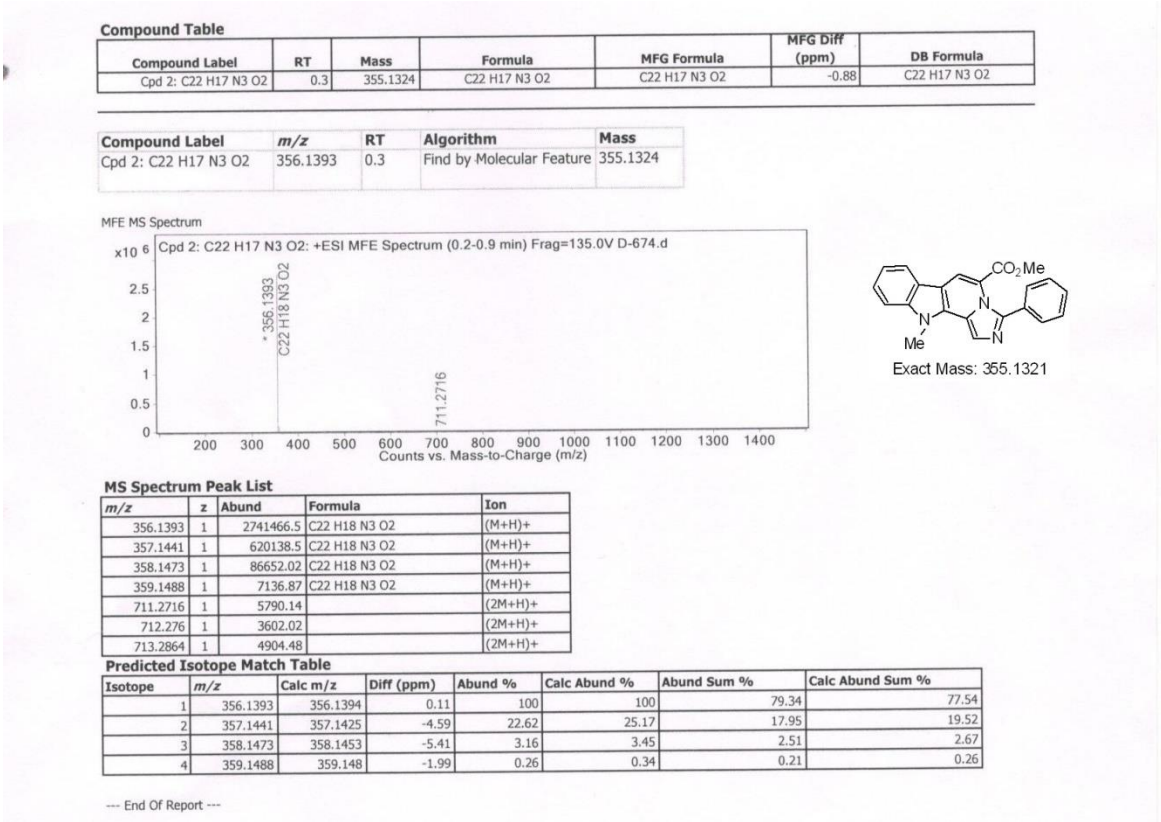


Figure S40. ^{13}C-NMR spectrum of **1aA**.



Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 2: C22 H17 N3 O2	0.3	355.1324	C22 H17 N3 O2	C22 H17 N3 O2	-0.88	C22 H17 N3 O2

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C22 H17 N3 O2	356.1393	0.3	Find by Molecular Feature	355.1324

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
356.1393	1	2741466.5	C22 H18 N3 O2	(M+H)+
357.1441	1	620138.5	C22 H18 N3 O2	(M+H)+
358.1473	1	86652.02	C22 H18 N3 O2	(M+H)+
359.1488	1	7136.87	C22 H18 N3 O2	(M+H)+
711.2716	1	5790.14		(2M+H)+
712.276	1	3602.02		(2M+H)+
713.2864	1	4904.48		(2M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	356.1393	356.1394	0.11	100	100	79.34	77.54
2	357.1441	357.1425	-4.59	22.62	25.17	17.95	19.52
3	358.1473	358.1453	-5.41	3.16	3.45	2.51	2.67
4	359.1488	359.148	-1.99	0.26	0.34	0.21	0.26

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Figure S41. HRMS spectrum of **1aA**.

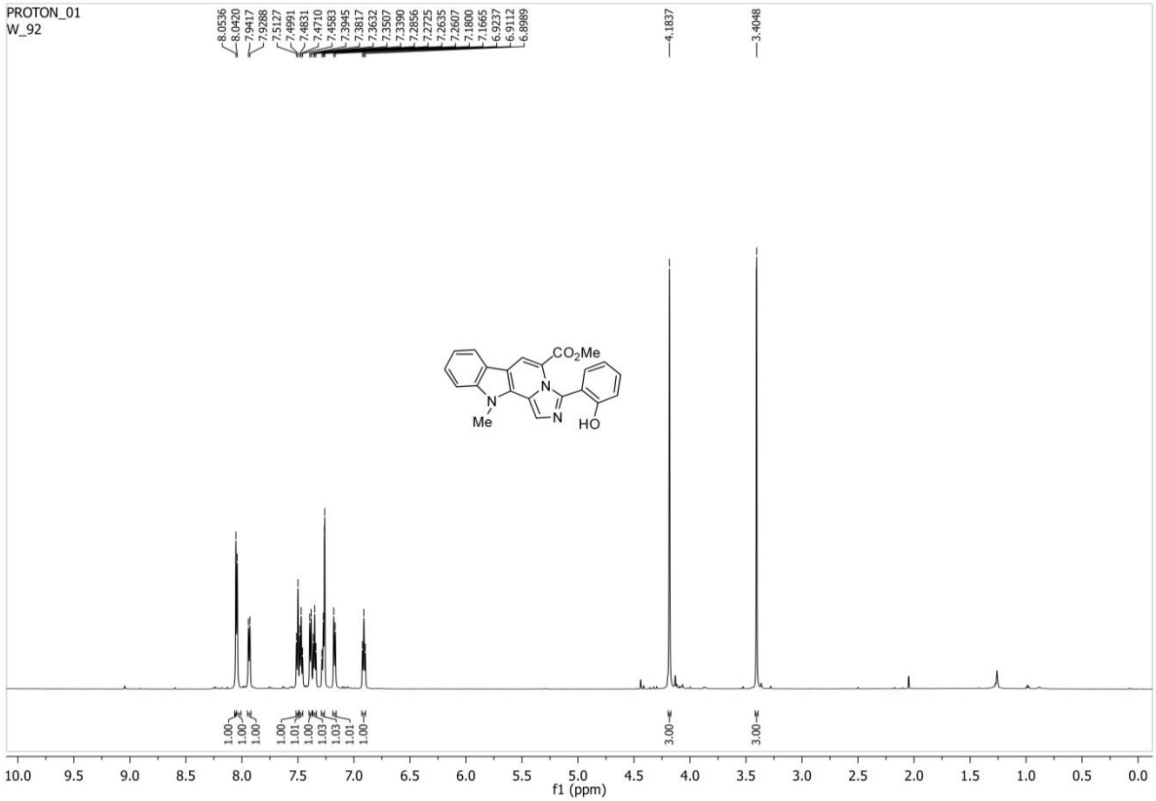


Figure S42. ^{1}H-NMR spectrum of **1aB**.

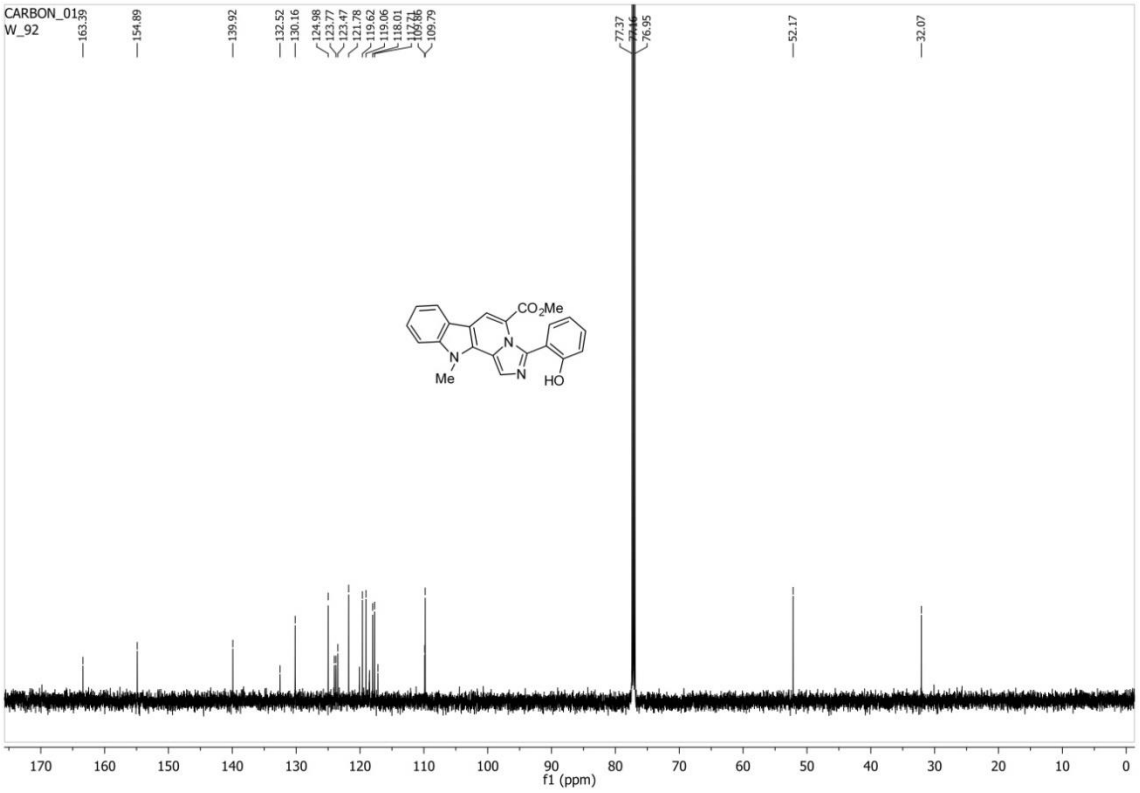


Figure S43. ^{13}C-NMR spectrum of **1aB**.

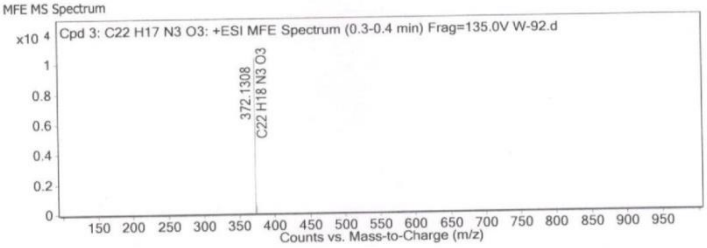
Sample Group **Info.**
Acquisition SW 6200 series TOF/6500 series
Version Q-TOF B.05.01 (B5125)

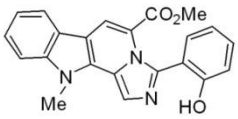
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 3: C22 H17 N3 O3	0.3	371.123	C22 H17 N3 O3	C22 H17 N3 O3	10.87	C22 H17 N3 O3

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: C22 H17 N3 O3	372.1308	0.3	Find by Molecular Feature	371.123

MFE MS Spectrum





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
372.1308	1	10339.76	C22 H18 N3 O3	(M+H)+
373.1318	1	3329.37	C22 H18 N3 O3	(M+H)+
374.1342	1	550.39	C22 H18 N3 O3	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	372.1308	372.1343	9.21	100	100	72.72	77.59
2	373.1318	373.1374	15.01	32.2	25.21	23.41	19.56
3	374.1342	374.1401	15.86	5.32	3.66	3.87	2.84

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Figure S44. HRMS spectrum of **1aB**.

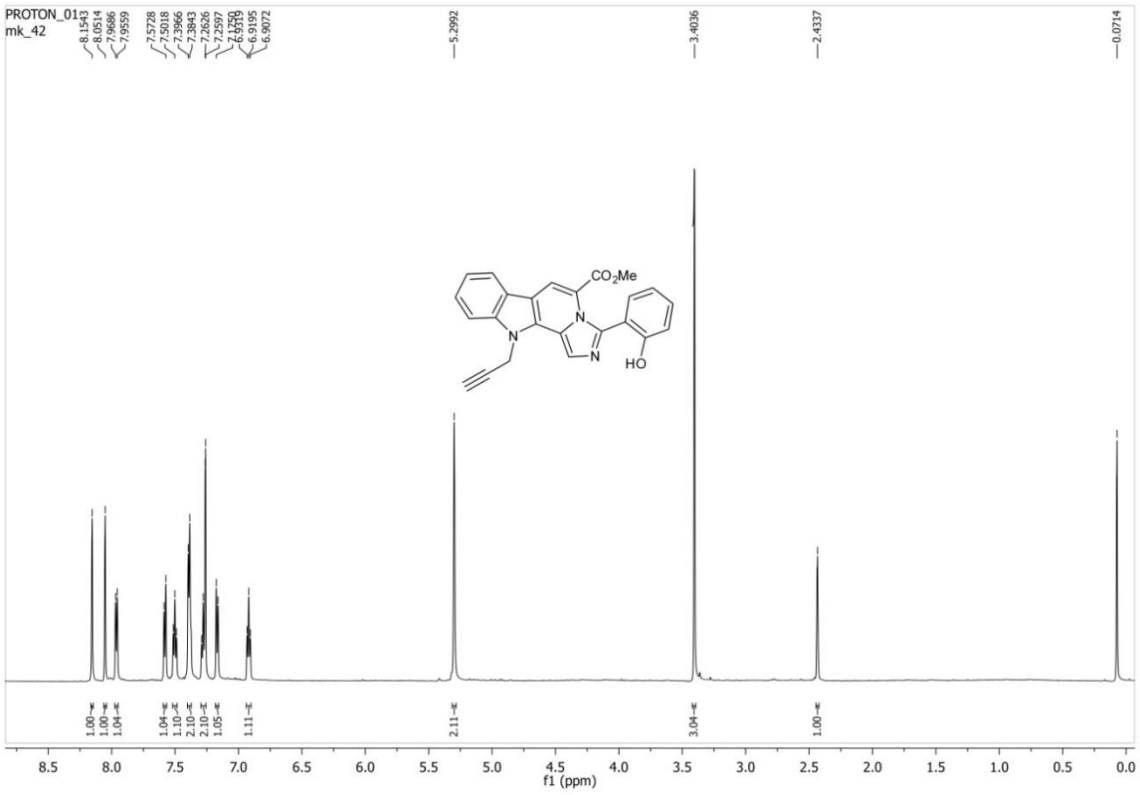


Figure S45. ^{1}H-NMR spectrum of **1fB**.

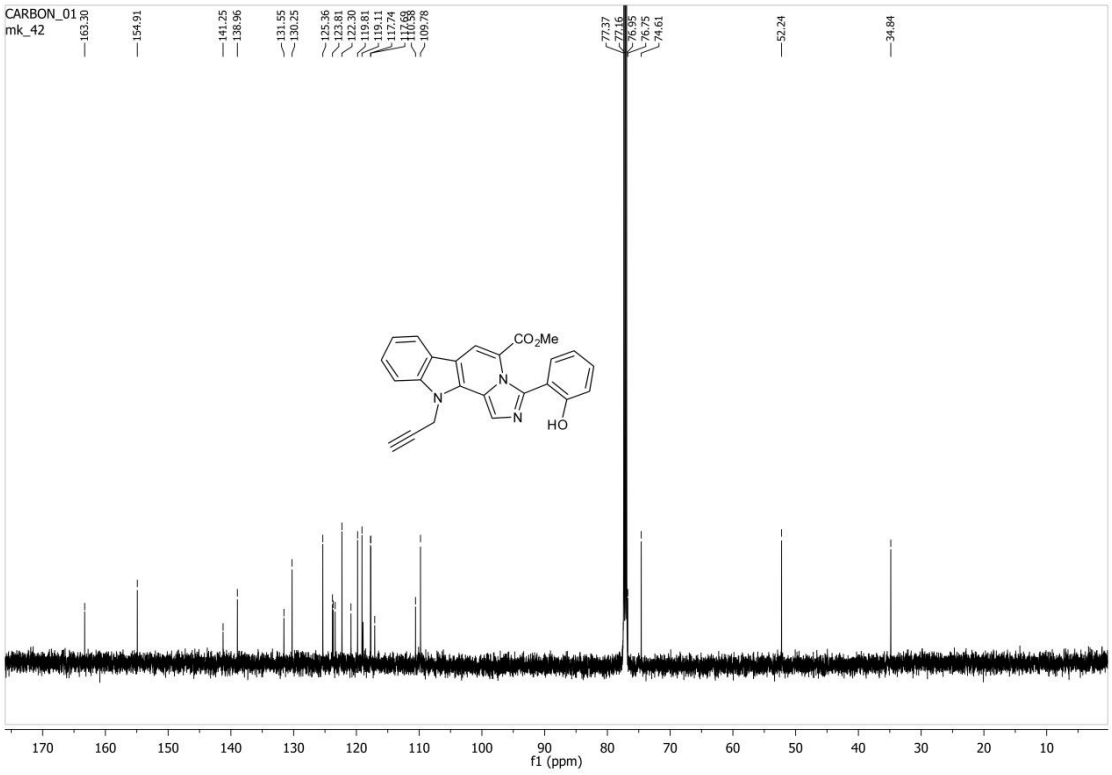


Figure S46. ^{13}C-NMR spectrum of **1fB**.

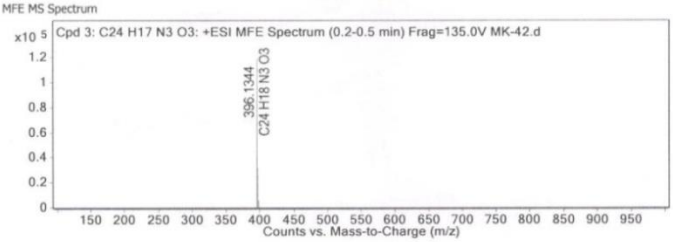
Sample Group		Info.
Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.01 (B5125)	

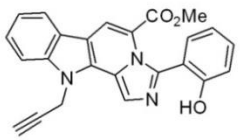
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 3: C24 H17 N3 O3	0.3	395.1272	C24 H17 N3 O3	C24 H17 N3 O3	-0.44	C24 H17 N3 O3

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: C24 H17 N3 O3	396.1344	0.3	Find by Molecular Feature	395.1272

MFE MS Spectrum





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
396.1344	1	118794.03	C24 H18 N3 O3	(M+H)+
397.1375	1	31650.04	C24 H18 N3 O3	(M+H)+
398.1408	1	5216.89	C24 H18 N3 O3	(M+H)+
399.1426	1	782.46	C24 H18 N3 O3	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	396.1344	396.1343	-0.46	100	100	75.93	75.72
2	397.1375	397.1374	-0.22	26.64	27.38	20.23	20.73
3	398.1408	398.1402	-1.54	4.39	4.22	3.33	3.2
4	399.1426	399.1429	0.71	0.66	0.47	0.5	0.36

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Figure S47. HRMS spectrum of **1fB**.

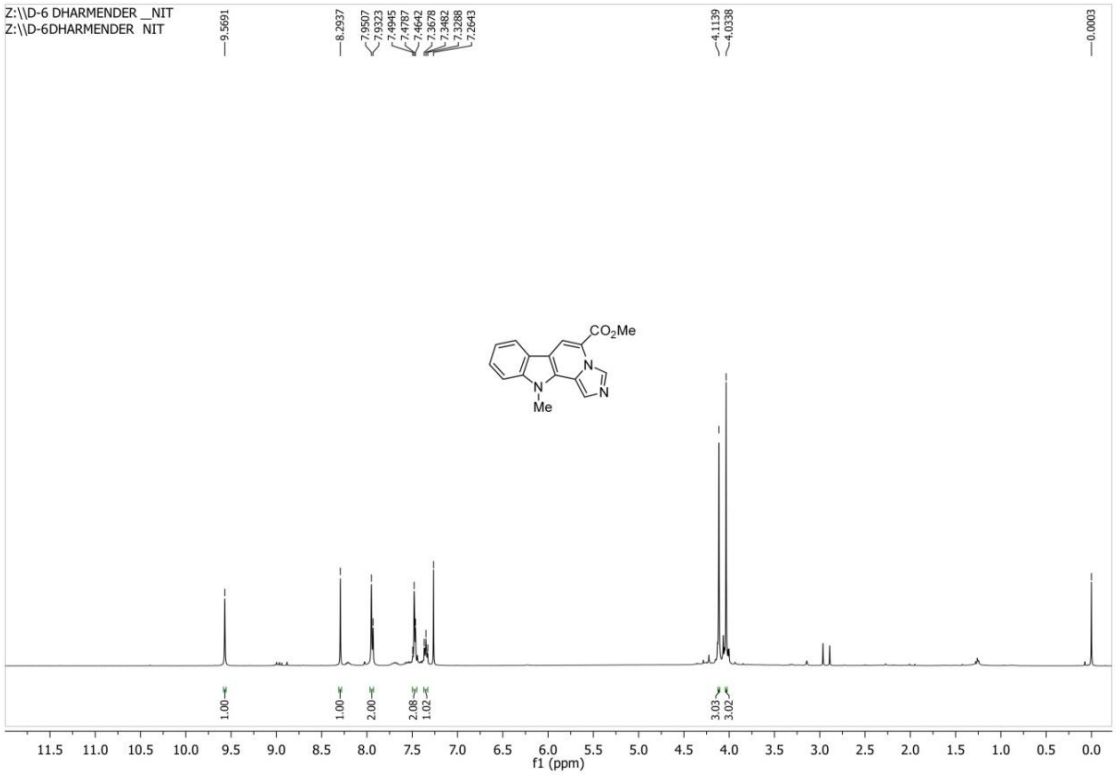


Figure S48. ^{1}H-NMR spectrum of **1aE**.

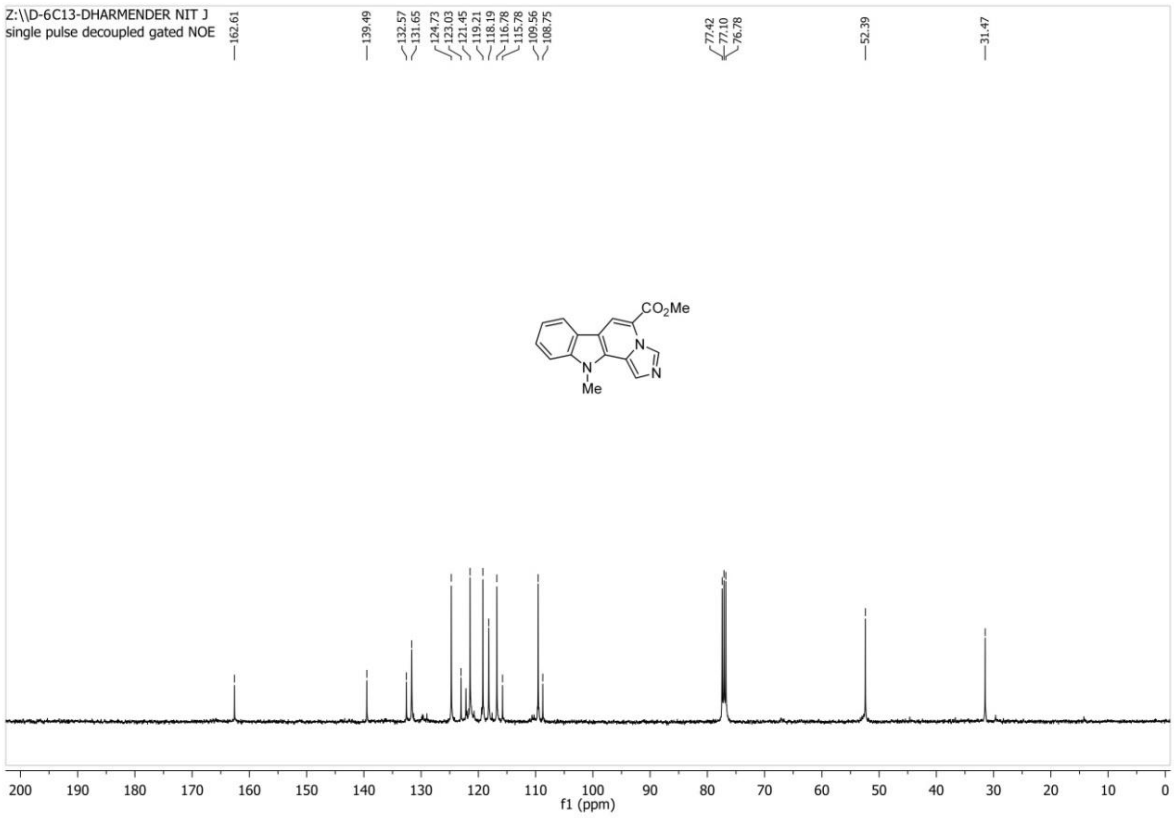


Figure S49. ^{13}C-NMR spectrum of **1aE**.

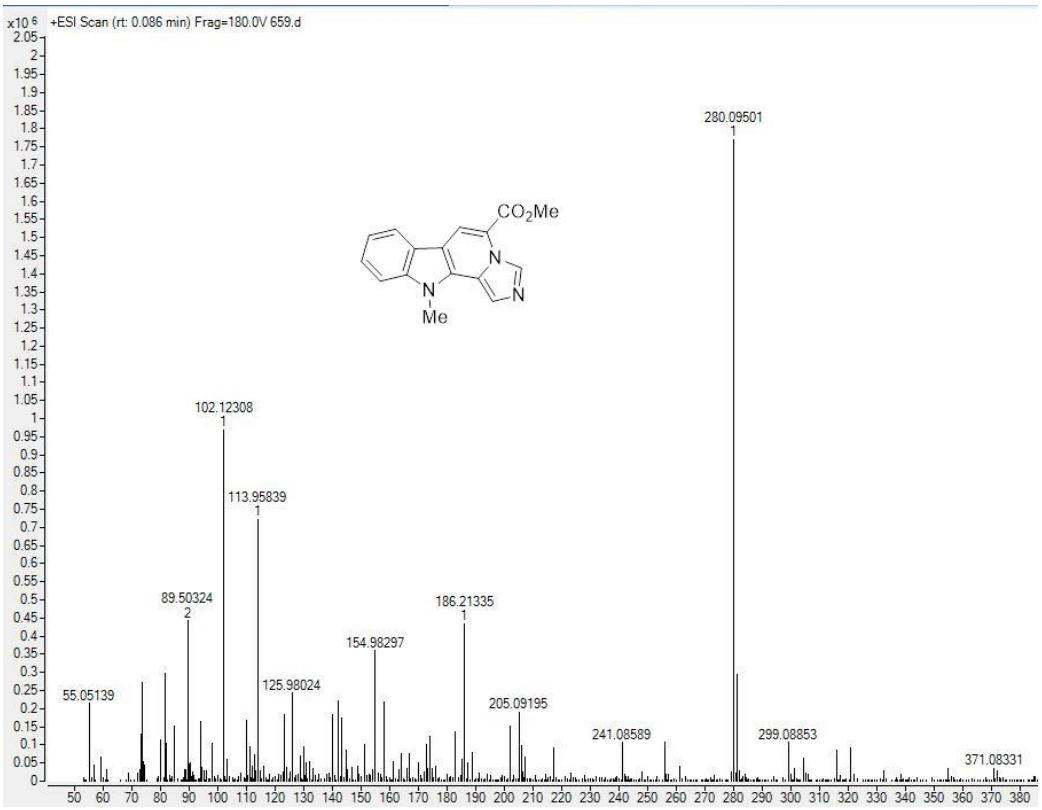


Figure S50. HRMS spectrum of **1aE**.

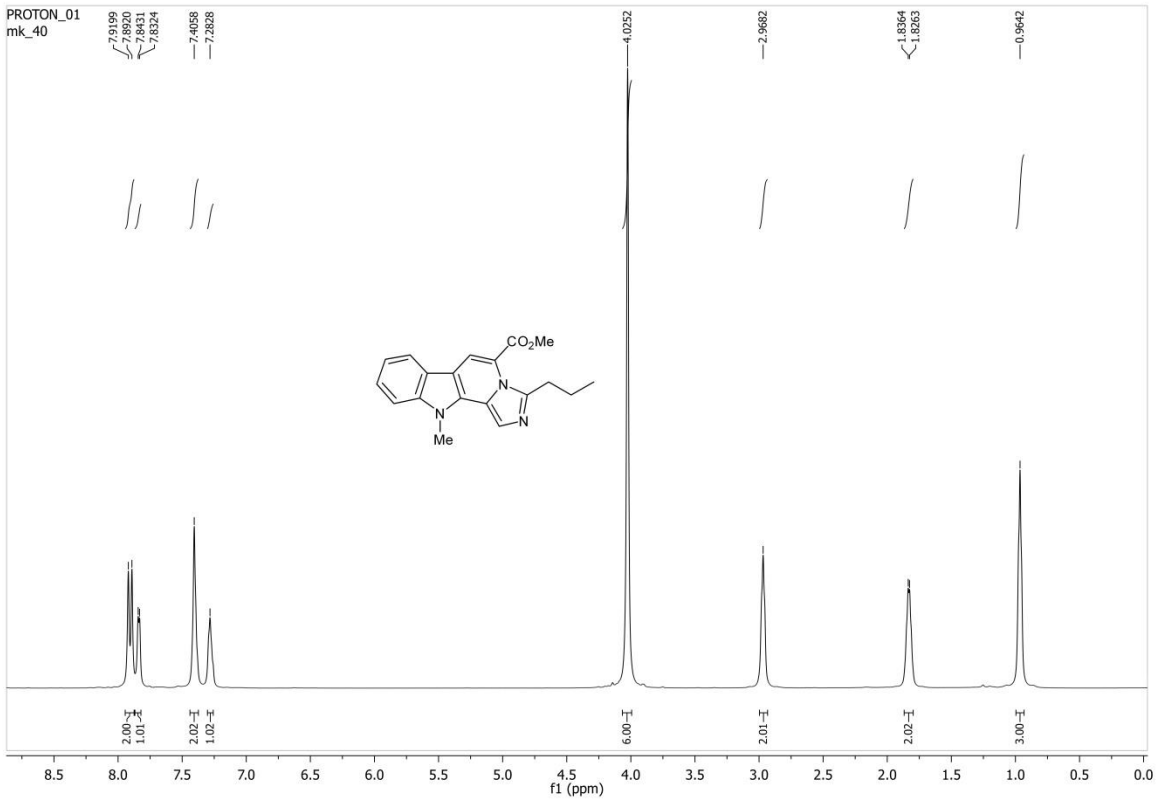


Figure S51. ^{1}H-NMR spectrum of **1aG**.

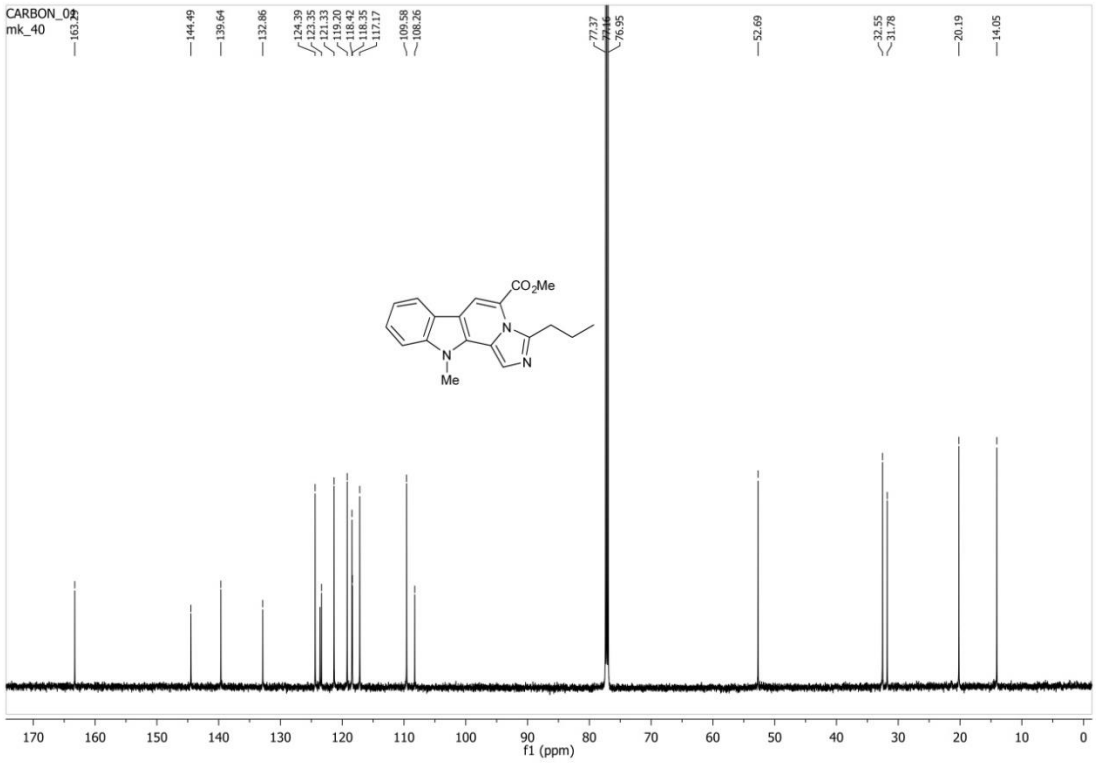


Figure S52. ^{13}C-NMR spectrum of **1aG**.

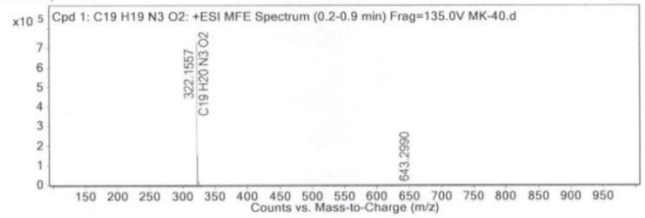
Sample Group		Info.
Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.01 (B5125)	

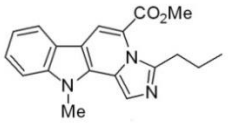
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C19 H19 N3 O2	0.3	321.1484	C19 H19 N3 O2	C19 H19 N3 O2	-2.12	C19 H19 N3 O2

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C19 H19 N3 O2	322.1557	0.3	Find by Molecular Feature	321.1484

MFE MS Spectrum





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
322.1557	1	729553.94	C19 H20 N3 O2	(M+H)+
323.1588	1	152525.94	C19 H20 N3 O2	(M+H)+
324.1616	1	19209.52	C19 H20 N3 O2	(M+H)+
325.1639	1	1956.26	C19 H20 N3 O2	(M+H)+
326.1603	1	352.25	C19 H20 N3 O2	(M+H)+
643.299	1	209.45		(2M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	322.1557	322.155	-2.12	100	100	80.74	80.05
2	323.1588	323.1581	-2.1	20.91	21.95	16.88	17.57
3	324.1616	324.1608	-2.19	2.63	2.71	2.13	2.17
4	325.1639	325.1635	-1.26	0.27	0.24	0.22	0.19
5	326.1603	326.1661	17.7	0.05	0.02	0.04	0.01

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Figure S53. HRMS spectrum of **1aG**.

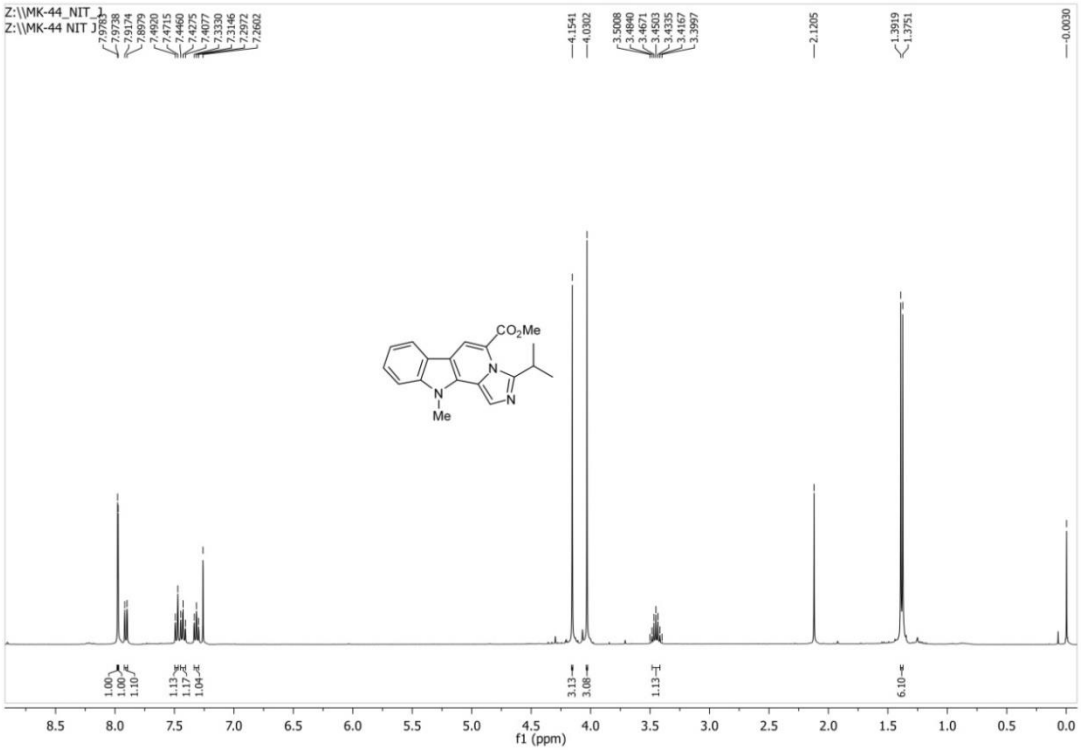


Figure S54. ^{1}H-NMR spectrum of **1aH**.

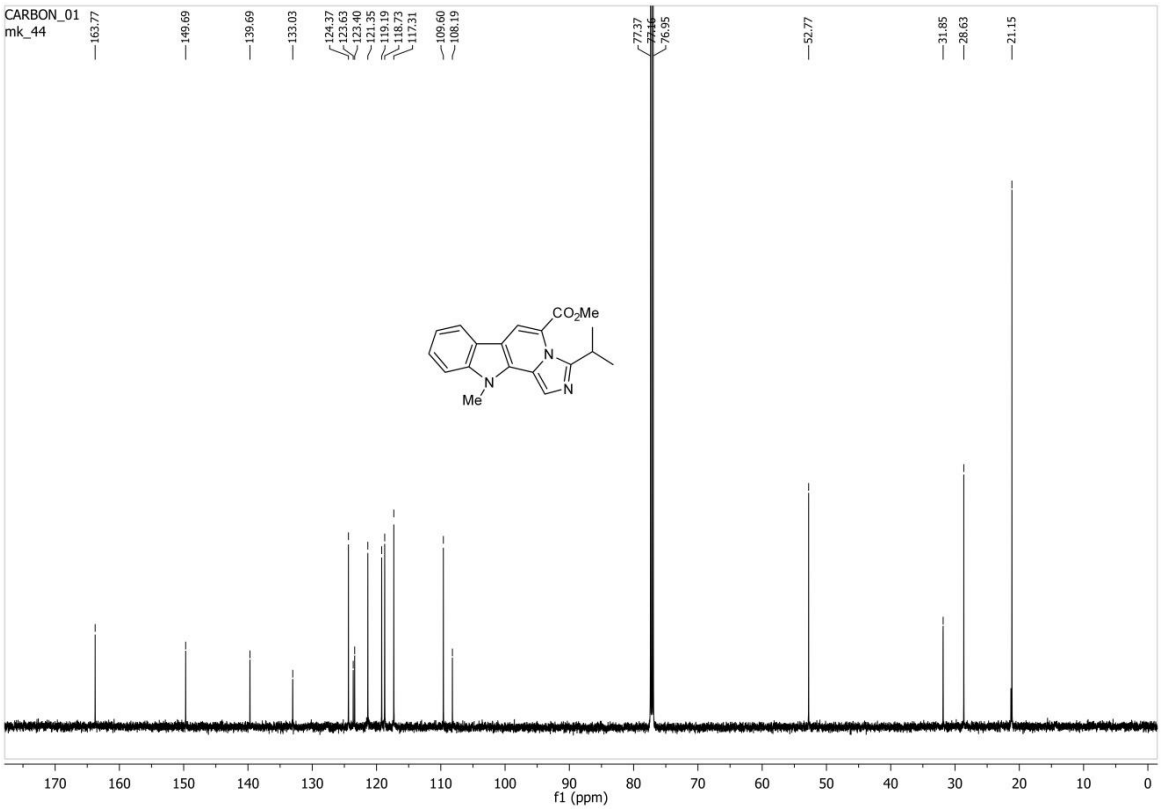


Figure S55. ^{13}C-NMR spectrum of **1aH**.

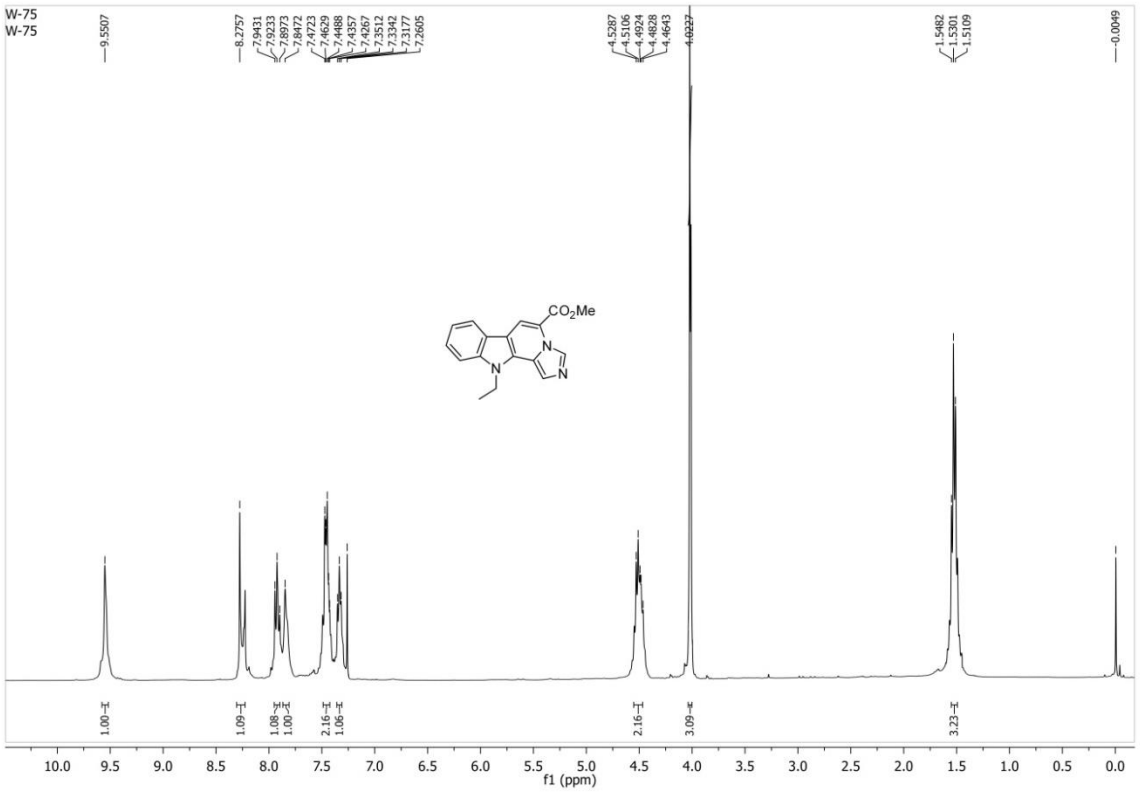


Figure S56. ^{1}H-NMR spectrum of **1bE**.

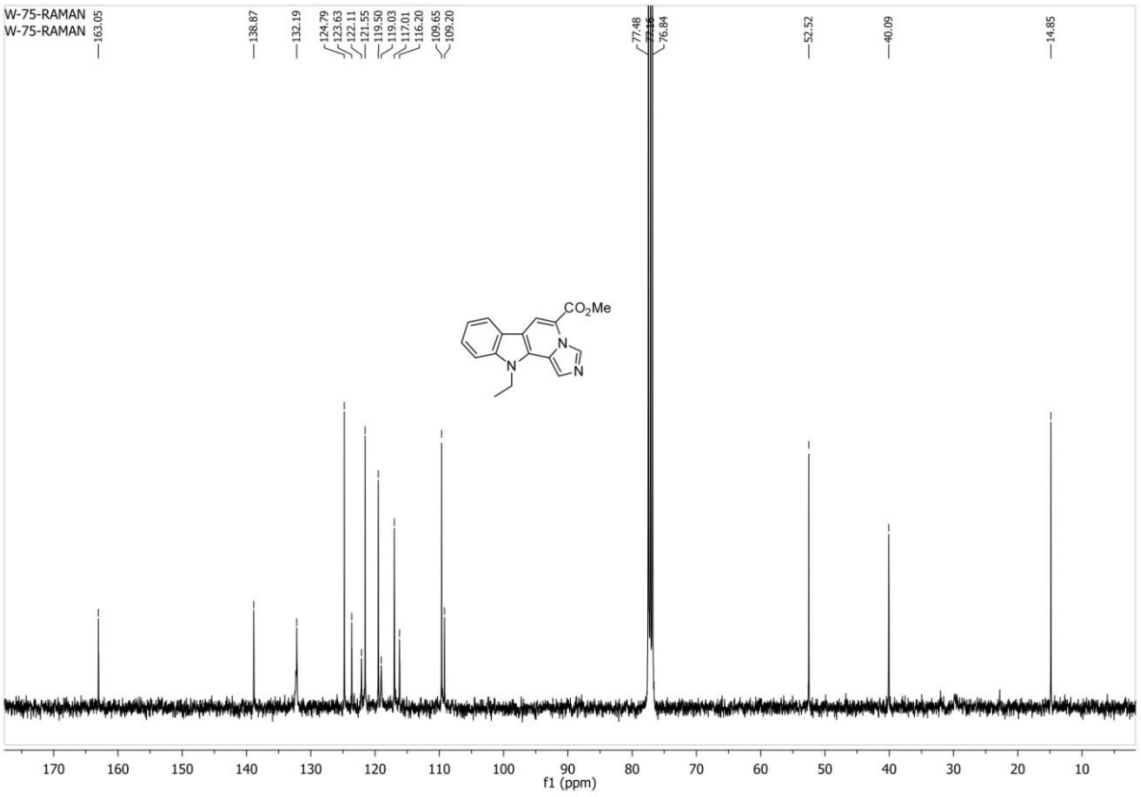


Figure S57. ^{13}C-NMR spectrum of **1bE**.

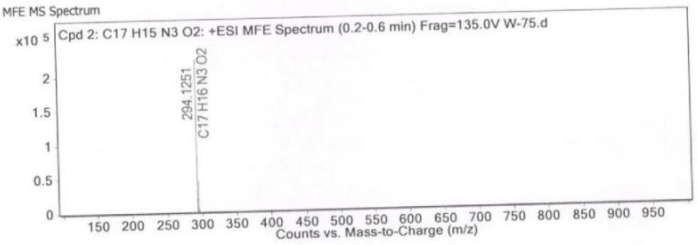
Sample Group Info.
Acquisition SW 6200 series TOF/6500 series
Version Q-TOF B.05.01 (B5125)

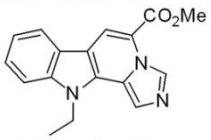
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 2: C17 H15 N3 O2	0.3	293.1178	C17 H15 N3 O2	C17 H15 N3 O2	-4.66	C17 H15 N3 O2

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C17 H15 N3 O2	294.1251	0.3	Find by Molecular Feature	293.1178

MFE MS Spectrum





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
294.1251	1	224258.95	C17 H16 N3 O2	(M+H)+
295.1281	1	45296.34	C17 H16 N3 O2	(M+H)+
296.1314	1	5033.19	C17 H16 N3 O2	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	294.1251	294.1237	-4.62	100	100	81.67	81.97
2	295.1281	295.1267	-4.52	20.2	19.74	16.5	16.18
3	296.1314	296.1294	-6.58	2.24	2.26	1.83	1.85

--- End Of Report ---

Figure S58. HRMS spectrum of **1bE**.

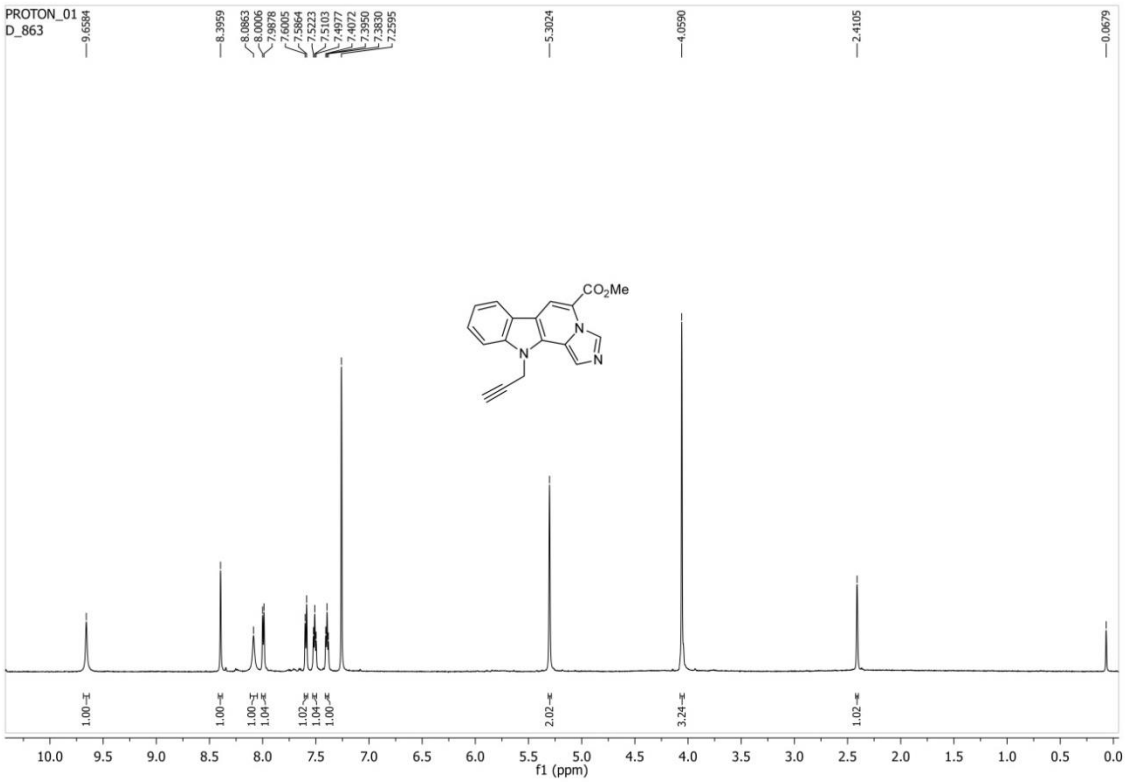


Figure S59. ^{1}H-NMR spectrum of **1fE**.

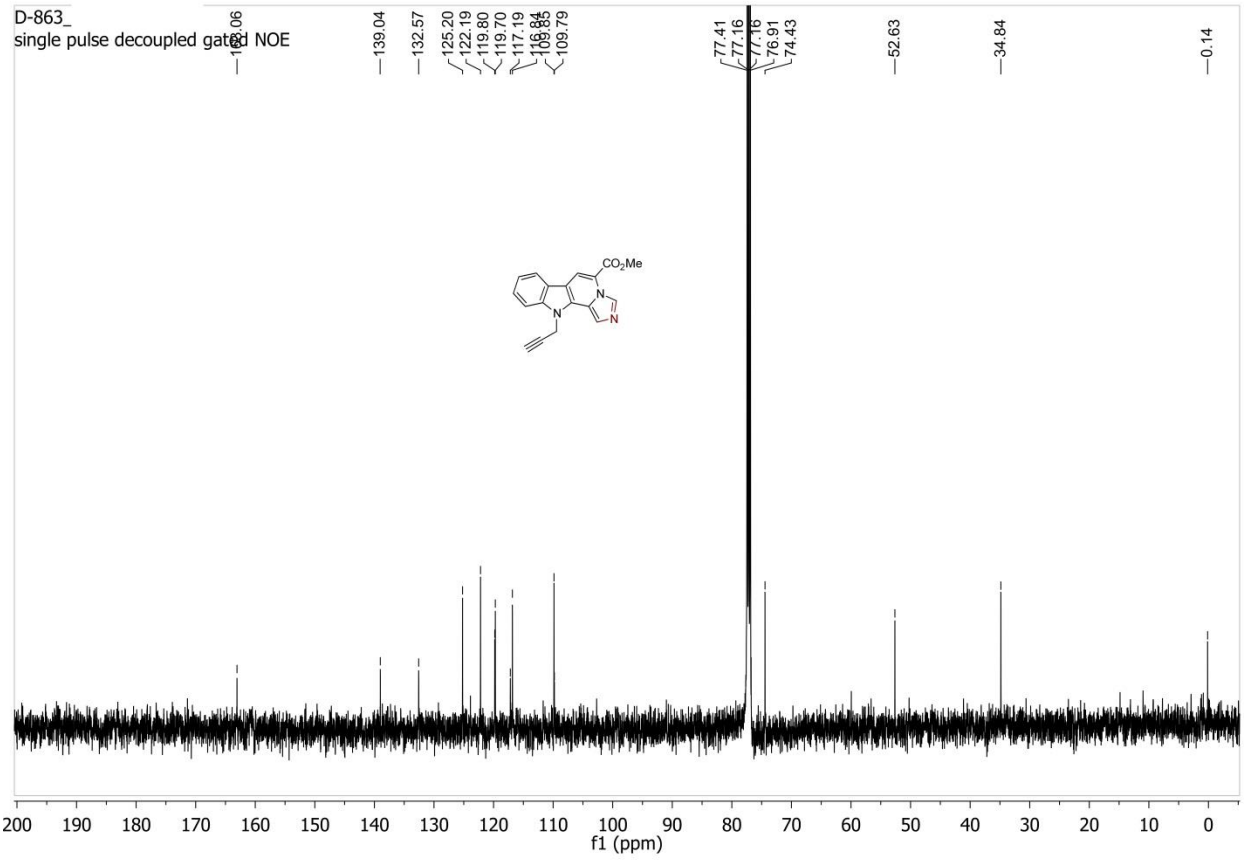
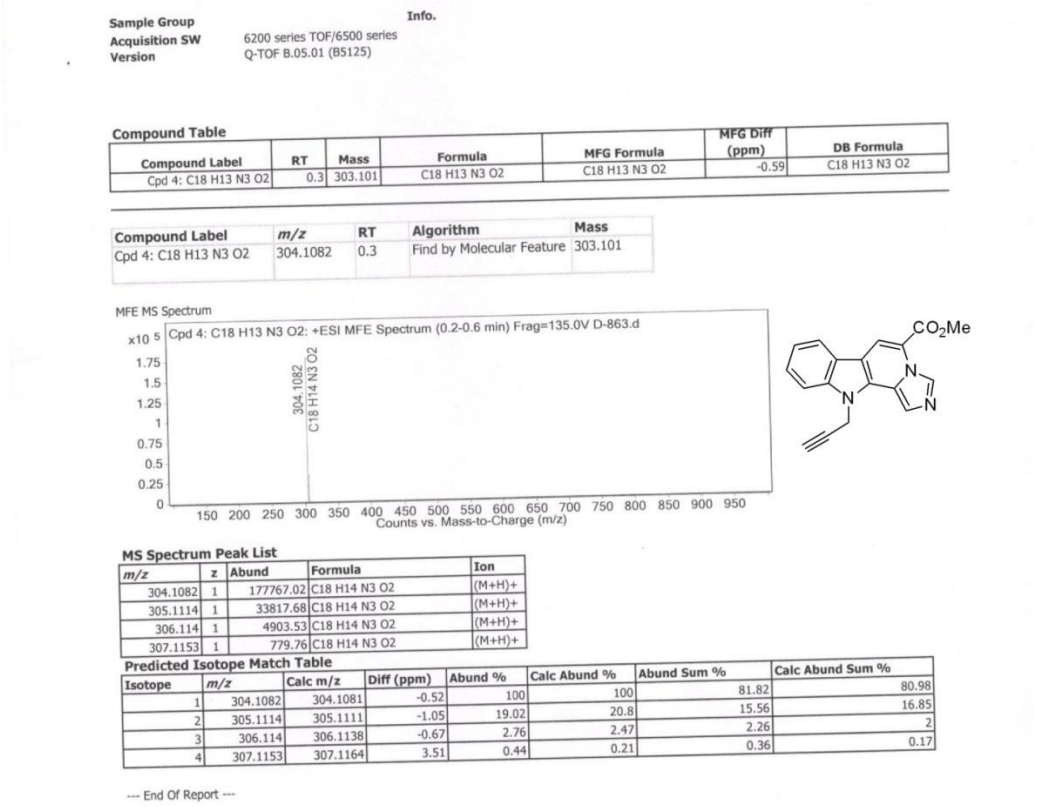


Figure S60. ^{13}C-NMR spectrum of **1fE**.



Info.

Sample Group	
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 4: C18 H13 N3 O2	0.3	303.101	C18 H13 N3 O2	C18 H13 N3 O2	-0.59	C18 H13 N3 O2

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 4: C18 H13 N3 O2	304.1082	0.3	Find by Molecular Feature	303.101

MFE MS Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
304.1082	1	177767.02	C18 H14 N3 O2	(M+H)+
305.1114	1	33817.68	C18 H14 N3 O2	(M+H)+
306.114	1	4903.53	C18 H14 N3 O2	(M+H)+
307.1153	1	779.76	C18 H14 N3 O2	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	304.1082	304.1081	-0.52	100	100	81.82	80.98
2	305.1114	305.1111	-1.05	19.02	20.8	15.56	16.85
3	306.114	306.1138	-0.67	2.76	2.47	2.26	2
4	307.1153	307.1164	3.51	0.44	0.21	0.36	0.17

--- End Of Report ---

Figure S61. HRMS spectrum of **1fE**.

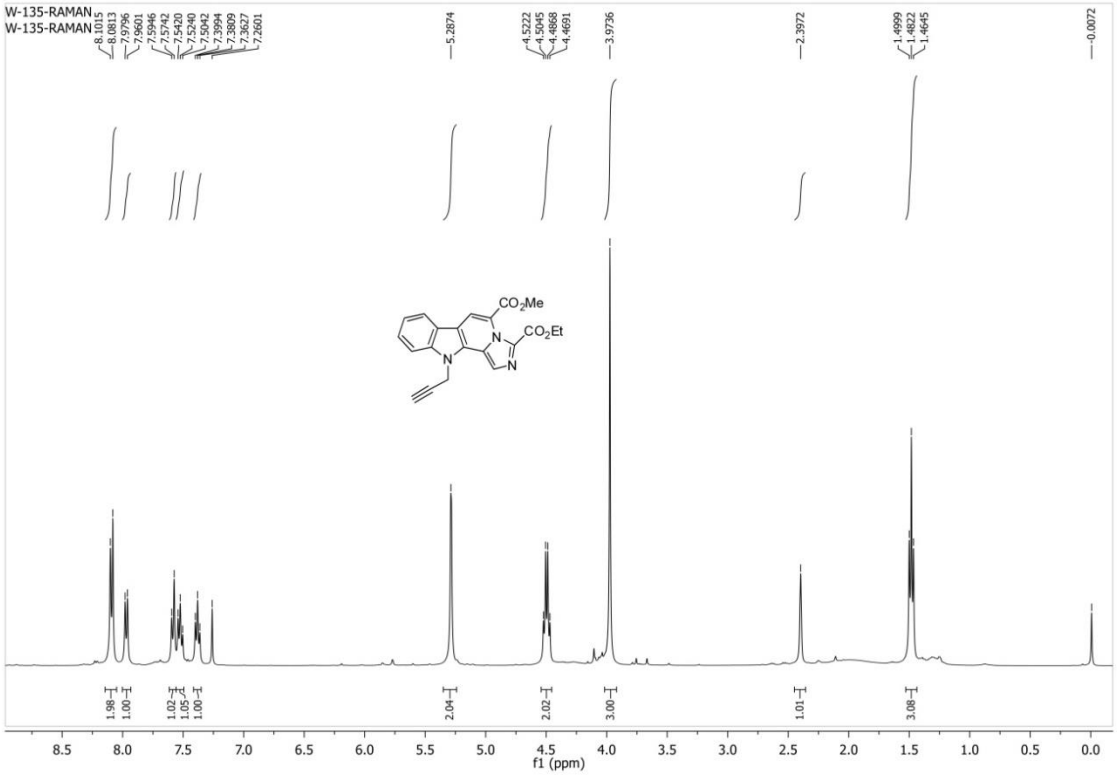


Figure S62. ^{1}H-NMR spectrum of **1fI**.

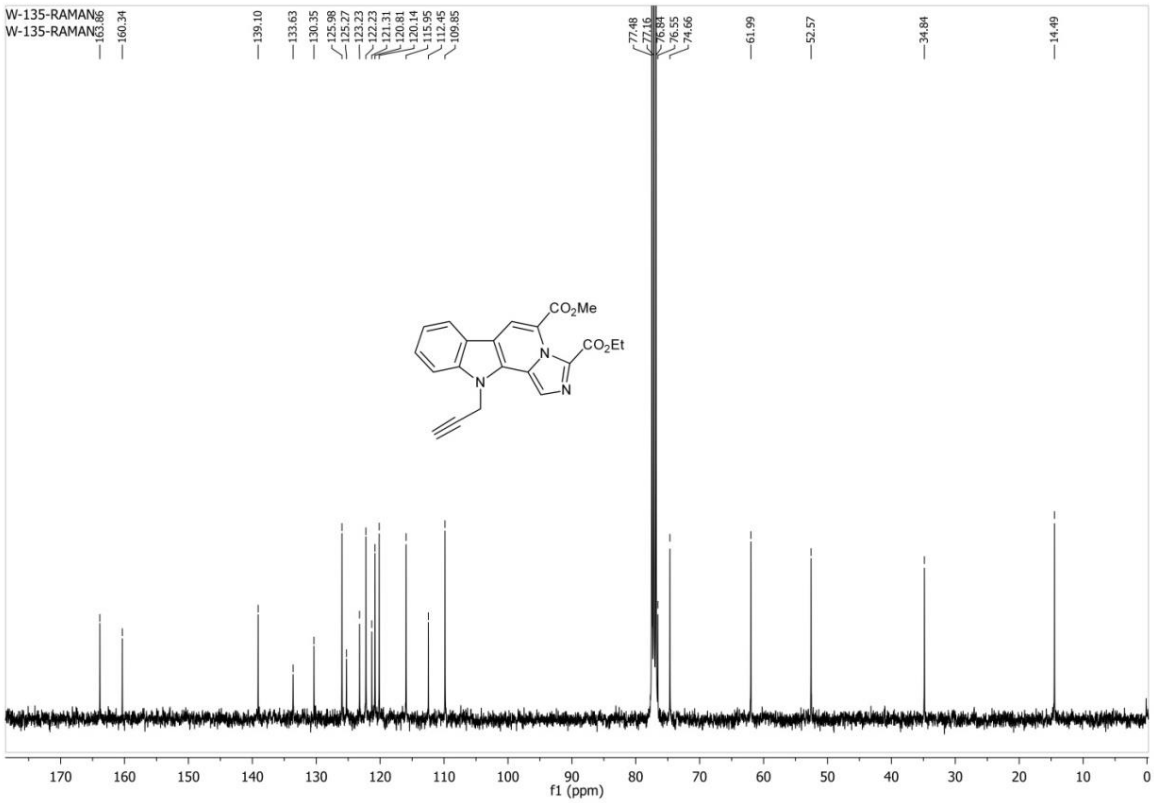
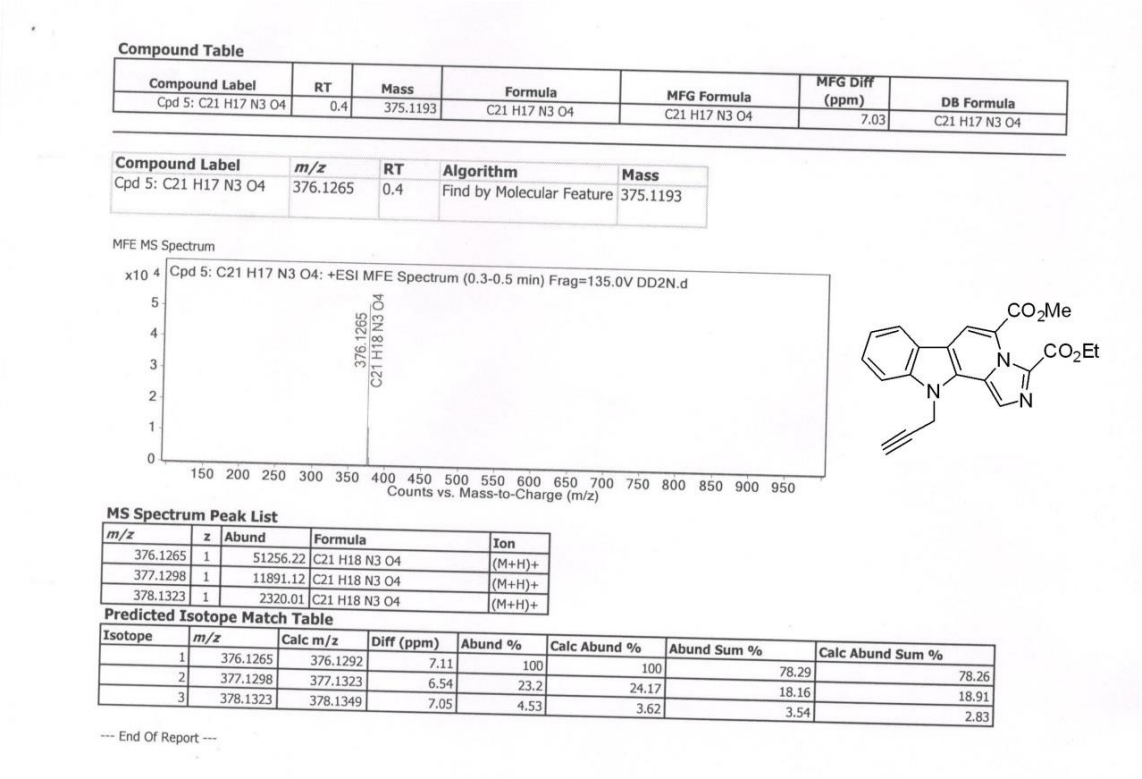


Figure S63. ^{13}C-NMR spectrum of **1fl**.



Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 5: C21 H17 N3 O4	0.4	375.1193	C21 H17 N3 O4	C21 H17 N3 O4	7.03	C21 H17 N3 O4

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 5: C21 H17 N3 O4	376.1265	0.4	Find by Molecular Feature	375.1193

MFE MS Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
376.1265	1	51256.22	C21 H18 N3 O4	(M+H)+
377.1298	1	11891.12	C21 H18 N3 O4	(M+H)+
378.1323	1	2320.01	C21 H18 N3 O4	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	376.1265	376.1292	7.11	100	100	78.29	78.26
2	377.1298	377.1323	6.54	23.2	24.17	18.16	18.91
3	378.1323	378.1349	7.05	4.53	3.62	3.54	2.83

--- End Of Report ---

Figure S64. HRMS spectrum of **1fl**.

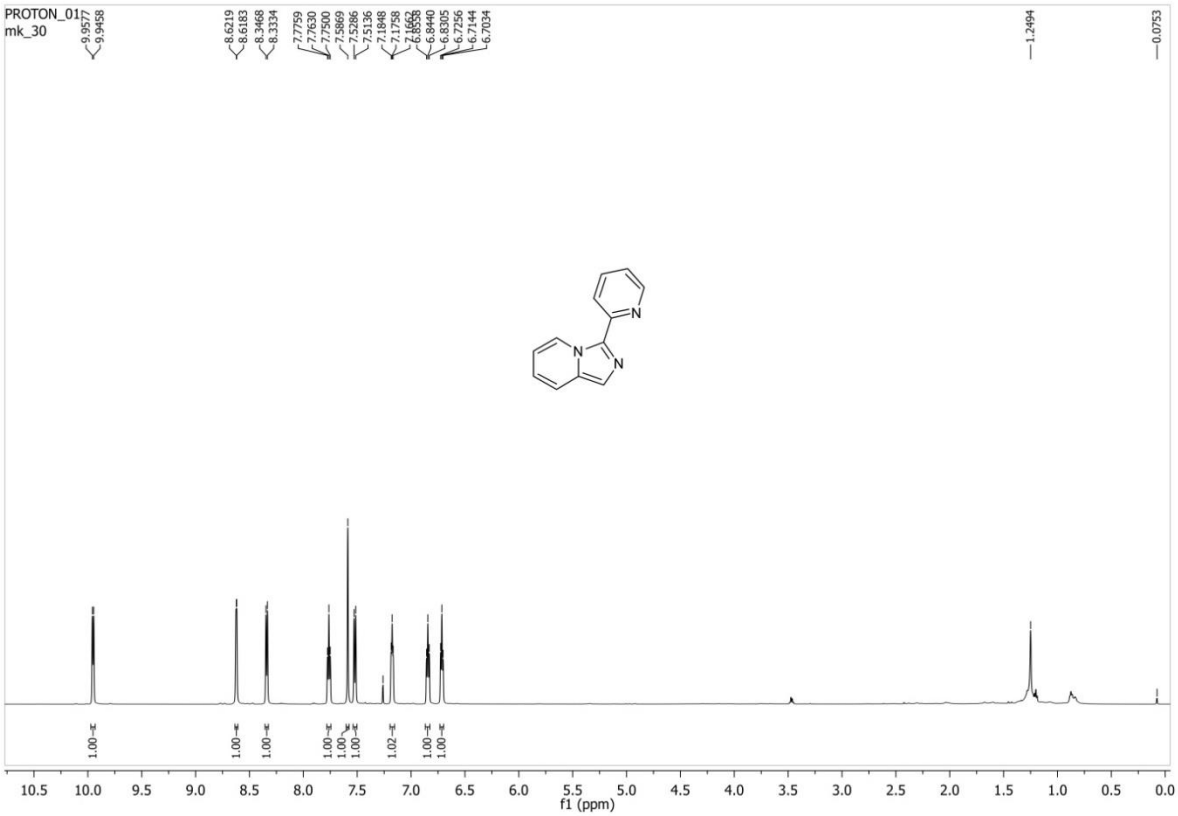


Figure S65. ^{1}H-NMR spectrum of **DD**.

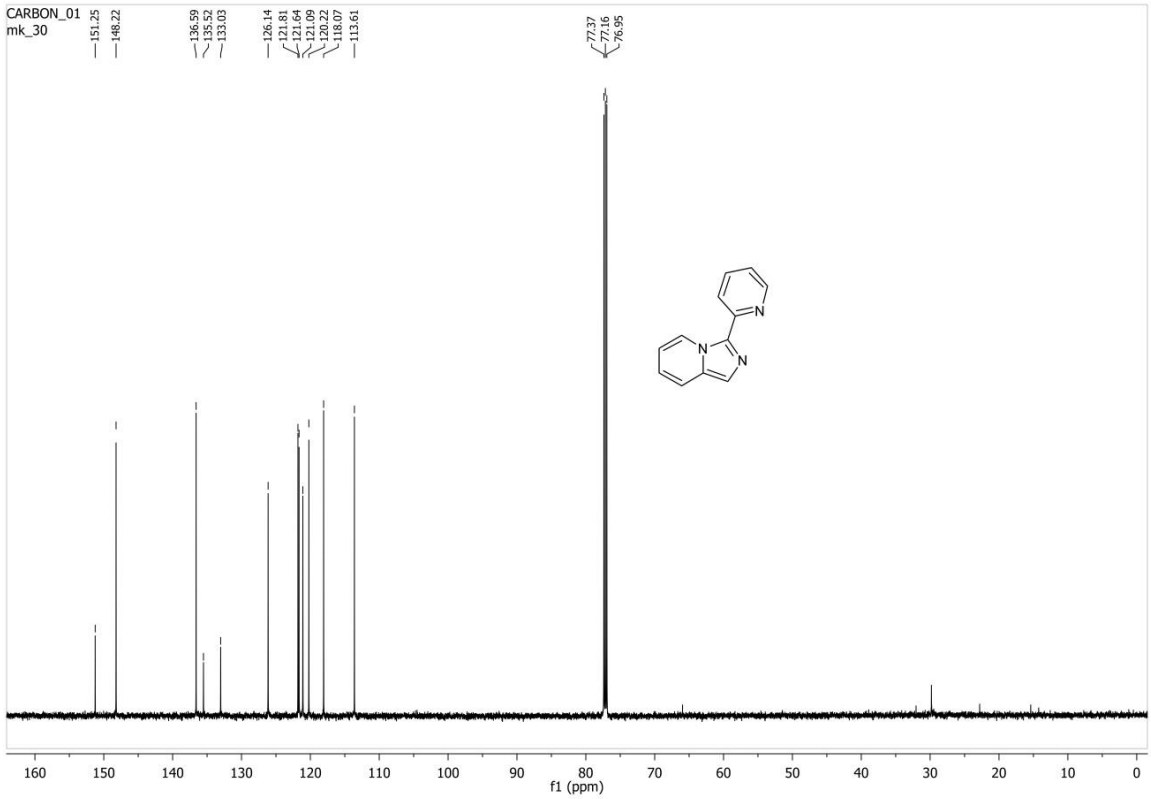


Figure S66. ^{13}C-NMR spectrum of **DD**.

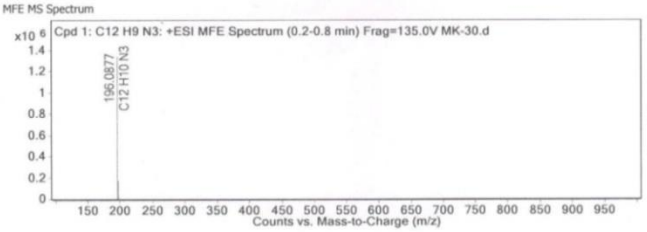
Sample Group		Info.
Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.01 (B5125)	

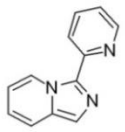
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C12 H9 N3	0.3	195.0805	C12 H9 N3	C12 H9 N3	-4.42	C12 H9 N3

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C12 H9 N3	196.0877	0.3	Find by Molecular Feature	195.0805

MFE MS Spectrum





MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
196.0877	1	1335569.38	C12 H10 N3	(M+H)+
197.0912	1	176377.19	C12 H10 N3	(M+H)+
198.0943	1	11943.33	C12 H10 N3	(M+H)+
199.096	1	858.95	C12 H10 N3	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	196.0877	196.0869	-4	100	100	87.59	86.83
2	197.0912	197.0898	-7.1	13.21	14.19	11.57	12.32
3	198.0943	198.0927	-8.17	0.89	0.93	0.78	0.81
4	199.096	199.0955	-2.84	0.06	0.04	0.06	0.03

--- End Of Report ---

Figure S67. HRMS spectrum of **DD**.

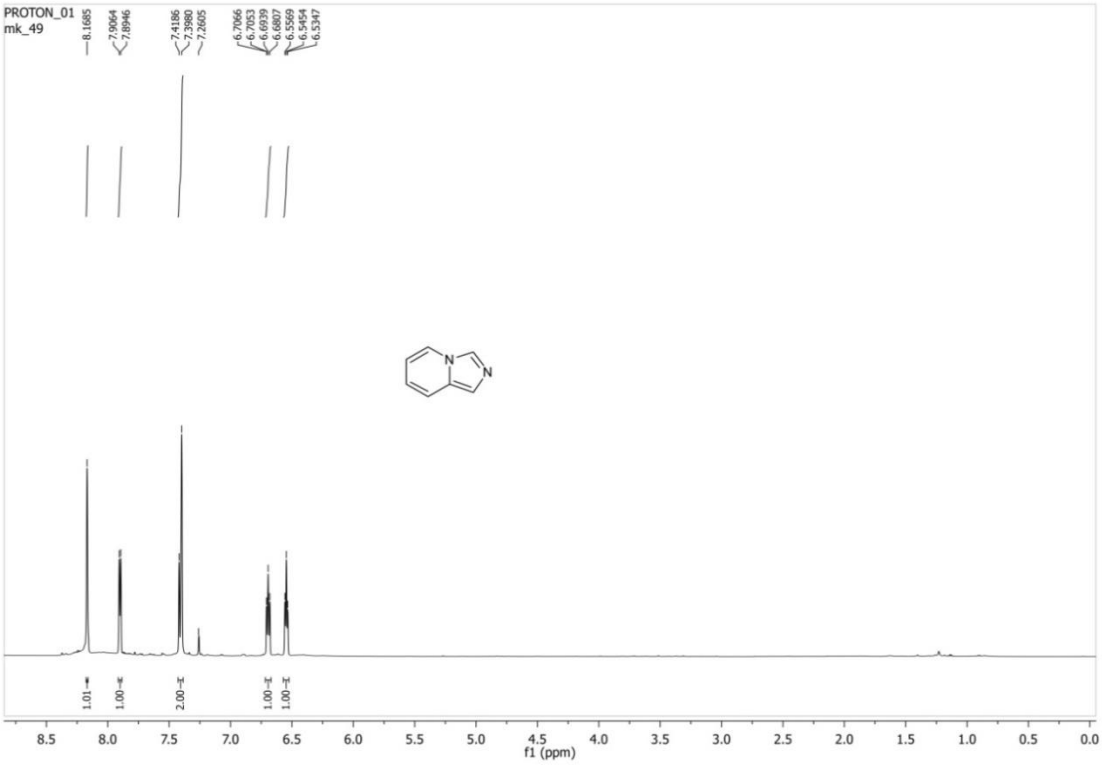


Figure S68. ^{1}H-NMR spectrum of **DE**.

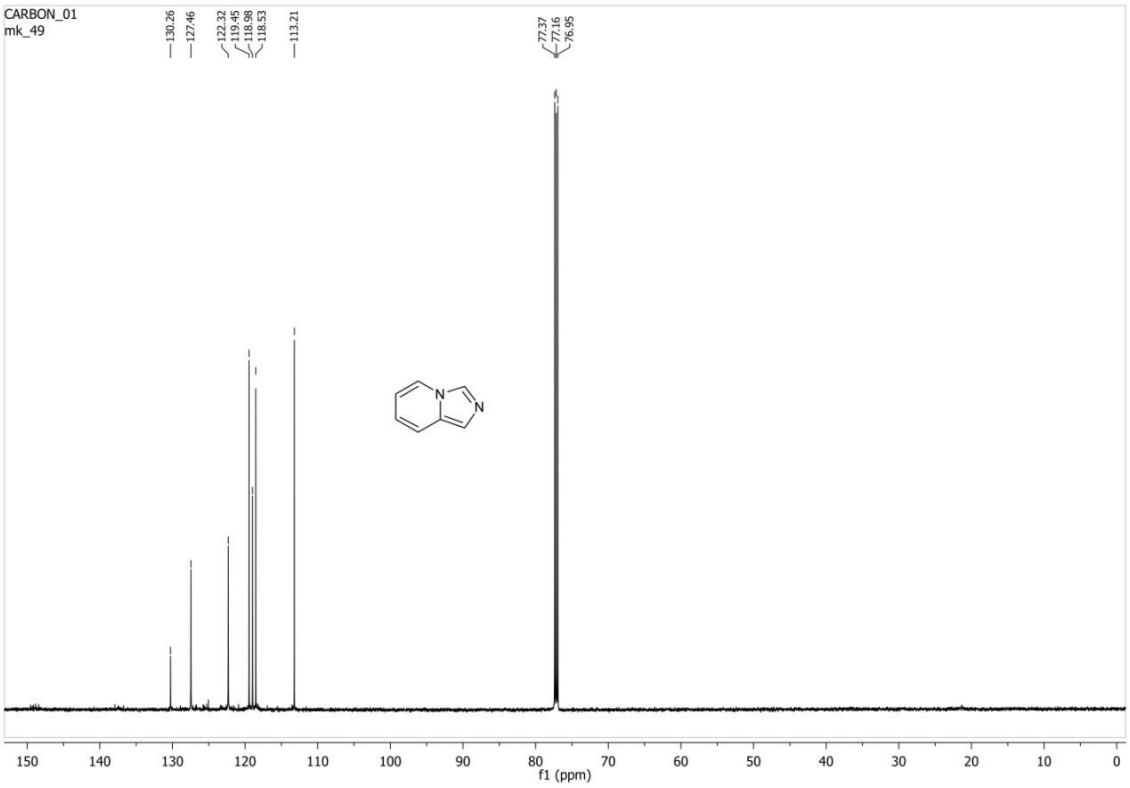
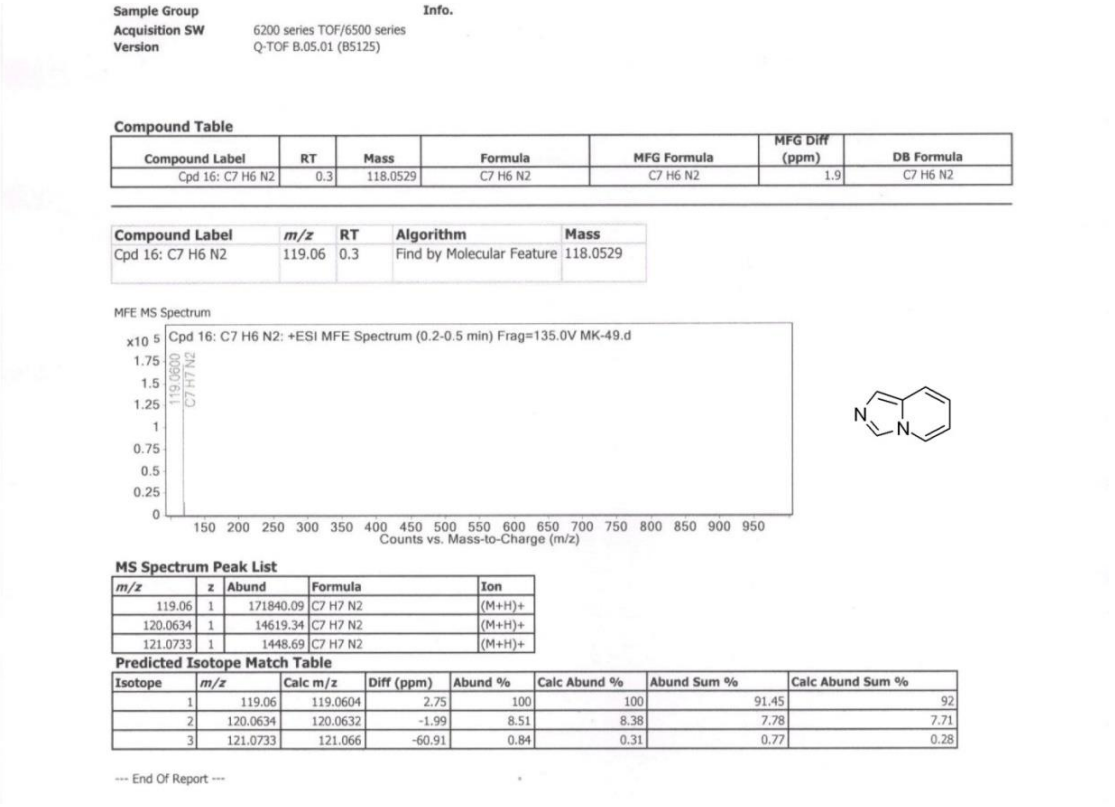


Figure S69. ^{13}C-NMR spectrum of **DE**.



Sample Group **Info.**
Acquisition SW 6200 series TOF/6500 series
Version Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 16: C7 H6 N2	0.3	118.0529	C7 H6 N2	C7 H6 N2	1.9	C7 H6 N2

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 16: C7 H6 N2	119.06	0.3	Find by Molecular Feature	118.0529

MFE MS Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
119.06	1	171840.09	C7 H7 N2	(M+H)+
120.0634	1	14619.34	C7 H7 N2	(M+H)+
121.0733	1	1448.69	C7 H7 N2	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	119.06	119.0604	2.75	100	100	91.45	92
2	120.0634	120.0632	-1.99	8.51	8.38	7.78	7.71
3	121.0733	121.066	-60.91	0.84	0.31	0.77	0.28

--- End Of Report ---

Figure S70. HRMS spectrum of **DE.**

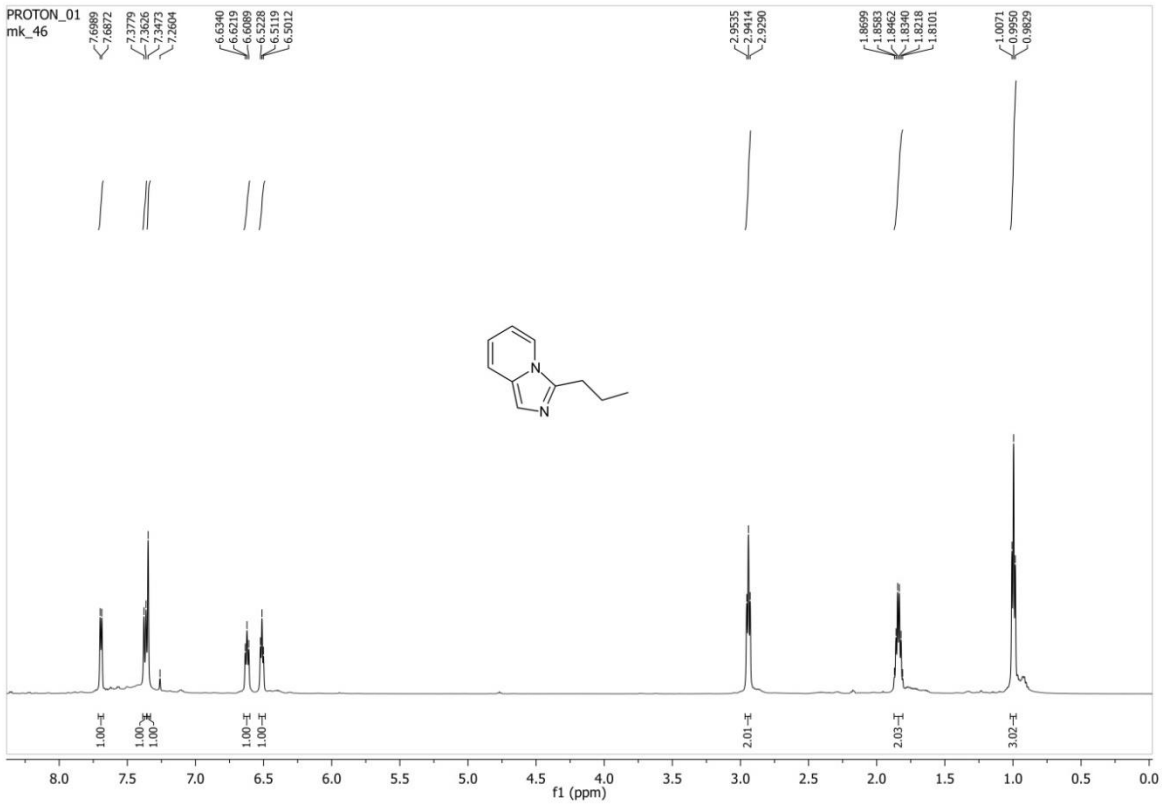


Figure S71. ^{1}H-NMR spectrum of **DG**.

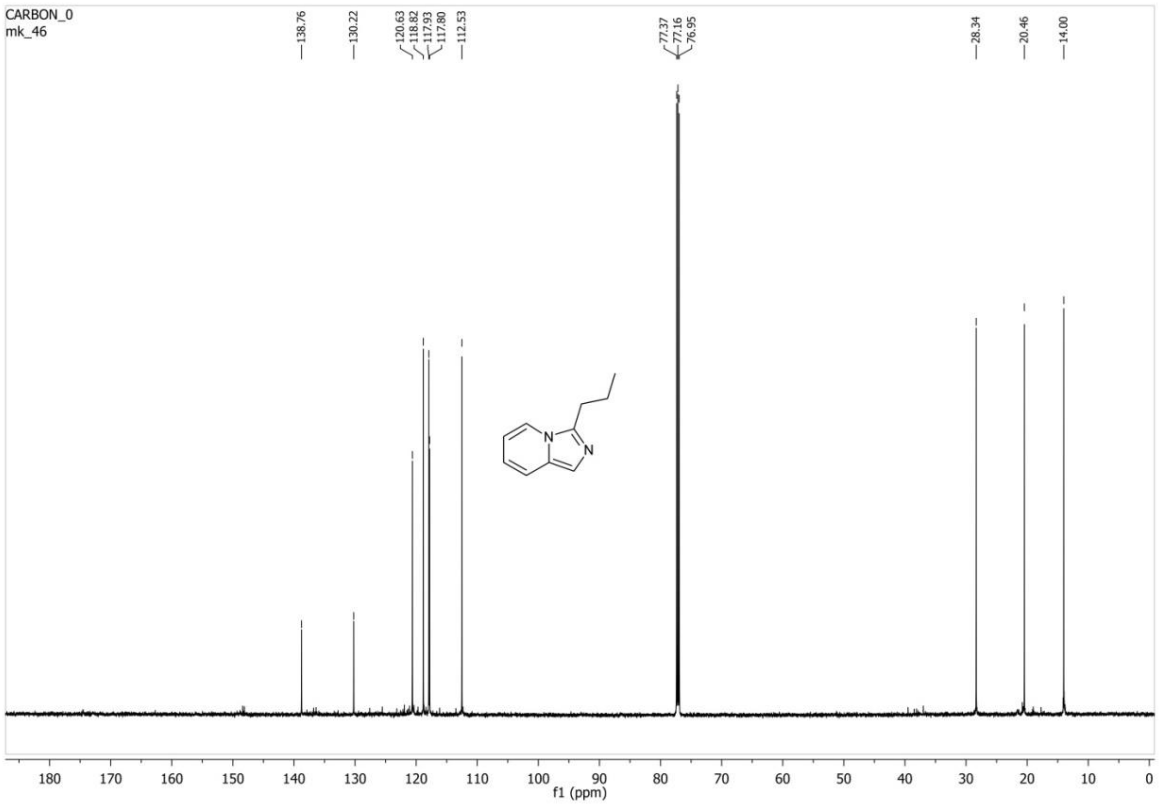


Figure S72. ^{13}C-NMR spectrum of **DG**.

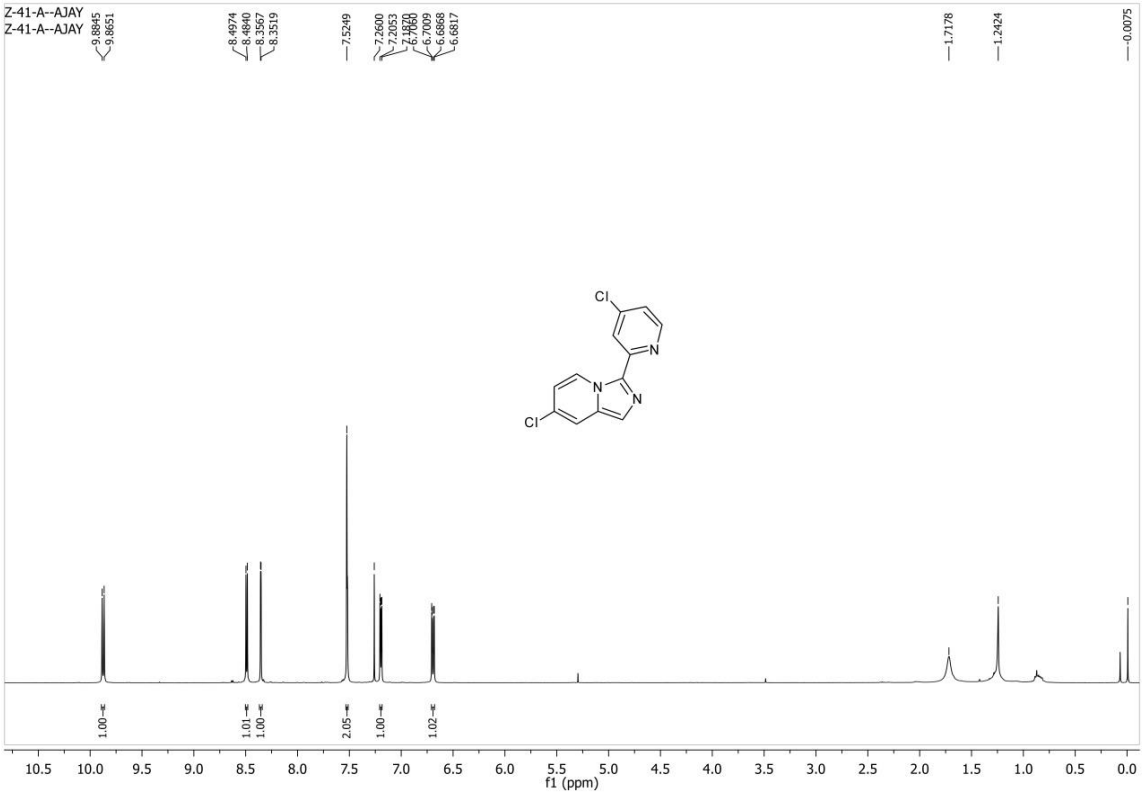


Figure S73. ^{1}H-NMR spectrum of **JJ**.

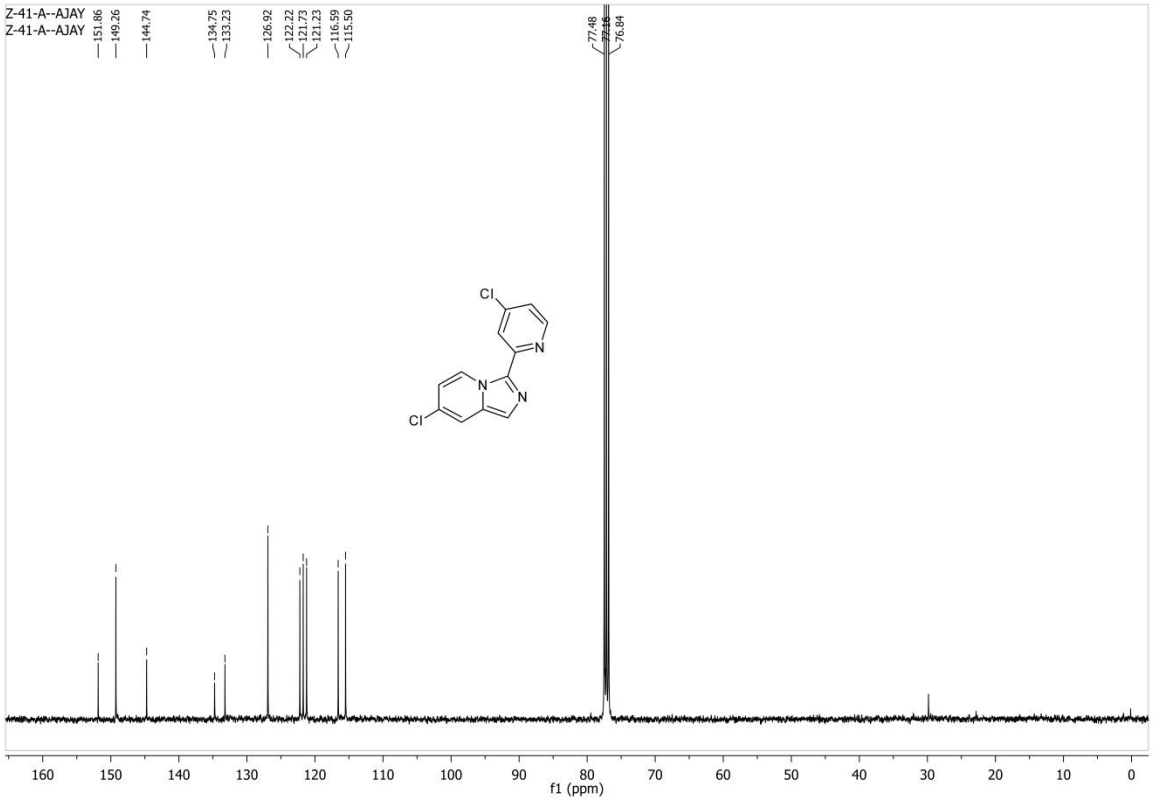
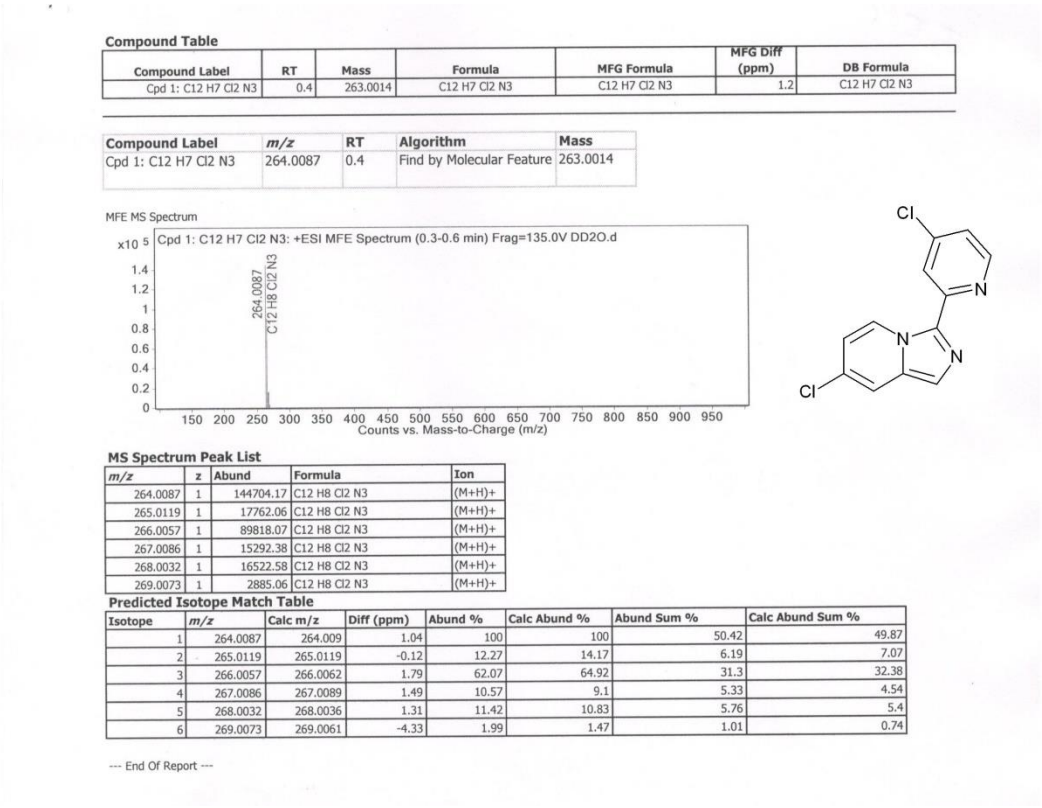


Figure S74. ^{13}C-NMR spectrum of **JJ**.



Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C12 H7 Cl2 N3	0.4	263.0014	C12 H7 Cl2 N3	C12 H7 Cl2 N3	1.2	C12 H7 Cl2 N3

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C12 H7 Cl2 N3	264.0087	0.4	Find by Molecular Feature	263.0014

MFE MS Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
264.0087	1	144704.17	C12 H8 Cl2 N3	(M+H)+
265.0119	1	17762.06	C12 H8 Cl2 N3	(M+H)+
266.0057	1	89818.07	C12 H8 Cl2 N3	(M+H)+
267.0086	1	15292.38	C12 H8 Cl2 N3	(M+H)+
268.0032	1	16522.58	C12 H8 Cl2 N3	(M+H)+
269.0073	1	2885.06	C12 H8 Cl2 N3	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	264.0087	264.009	1.04	100	100	50.42	49.87
2	265.0119	265.0119	-0.12	12.27	14.17	6.19	7.07
3	266.0057	266.0062	1.79	62.07	64.92	31.3	32.38
4	267.0086	267.0089	1.49	10.57	9.1	5.33	4.54
5	268.0032	268.0036	1.31	11.42	10.83	5.76	5.4
6	269.0073	269.0061	-4.33	1.99	1.47	1.01	0.74

--- End Of Report ---

Figure S75. HRMS spectrum of **JJ**.

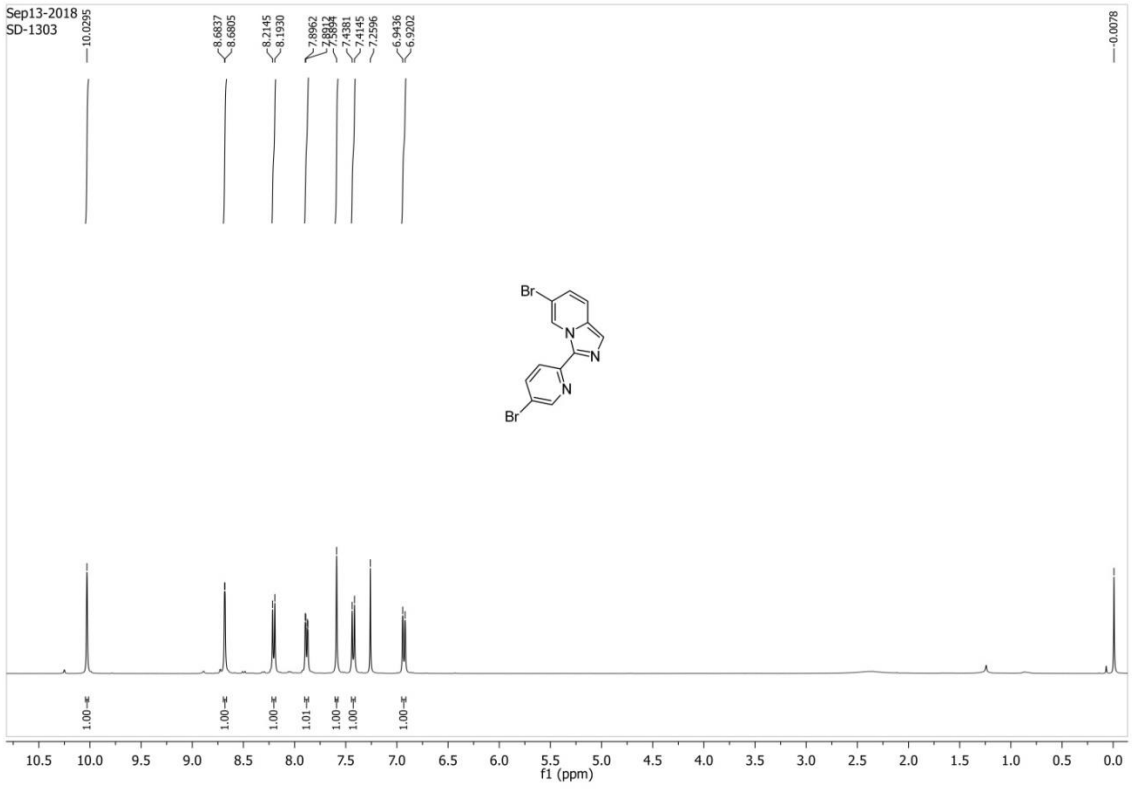


Figure S76. ^{1}H-NMR spectrum of **KK**.

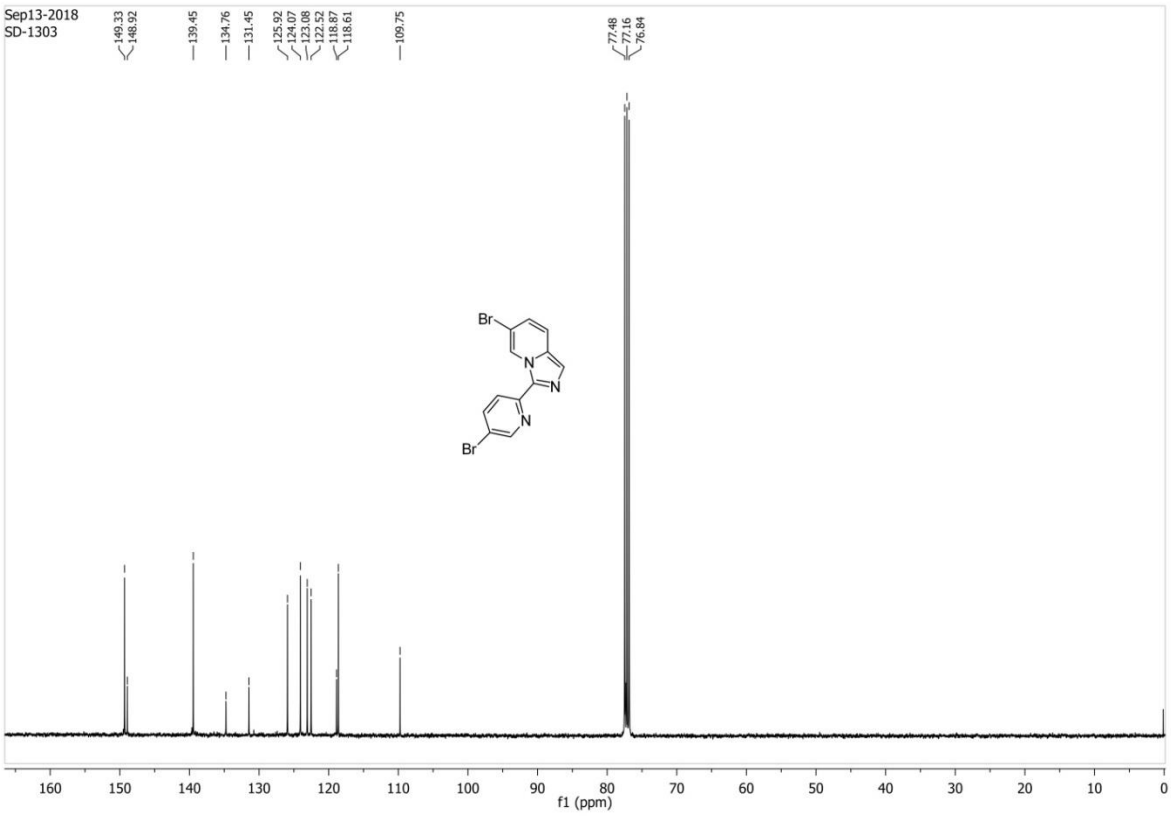


Figure S77. ^{13}C-NMR spectrum of **KK**.

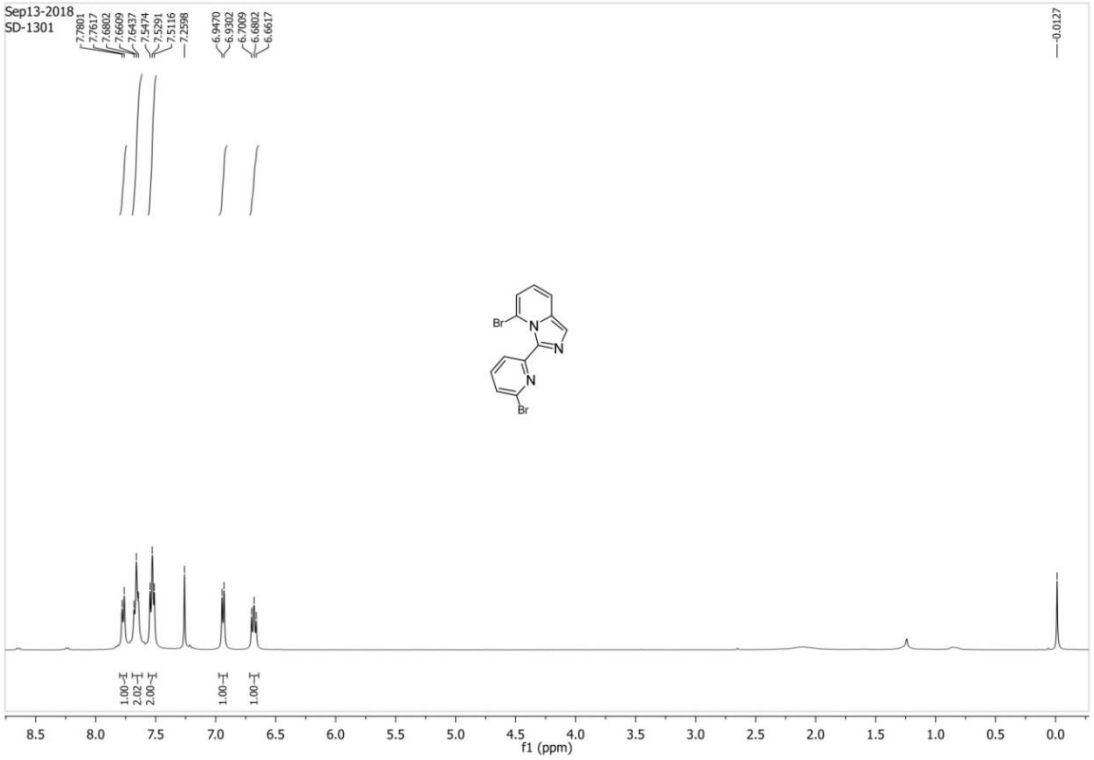


Figure S78. ^{1}H-NMR spectrum of **LL**.

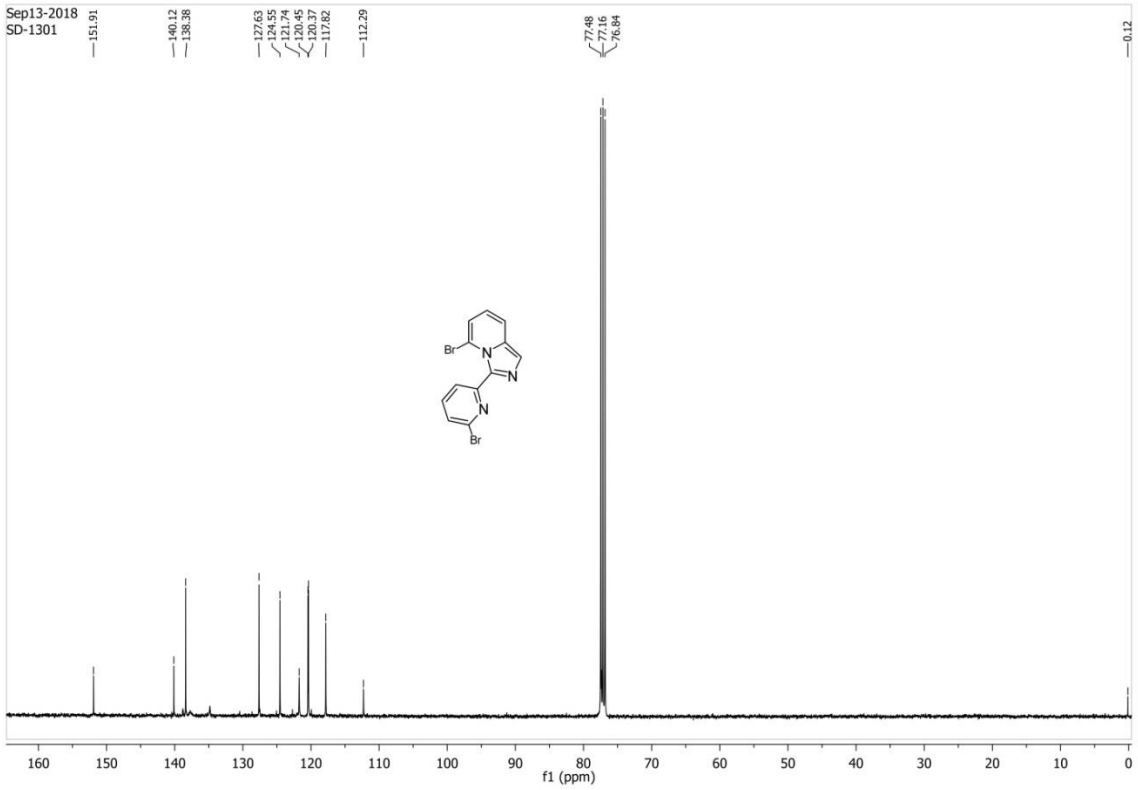


Figure S79. ^{13}C-NMR spectrum of **LL**.

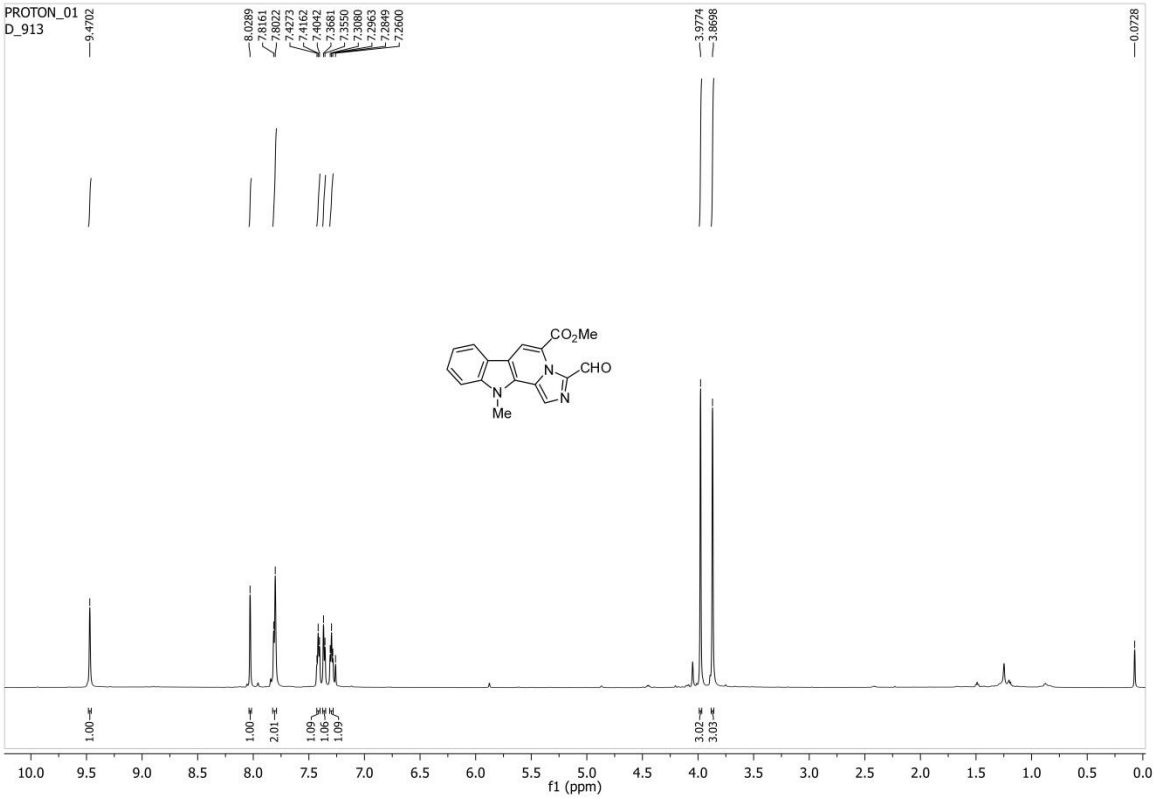


Figure S80. ^{1}H-NMR spectrum of **2aK**.

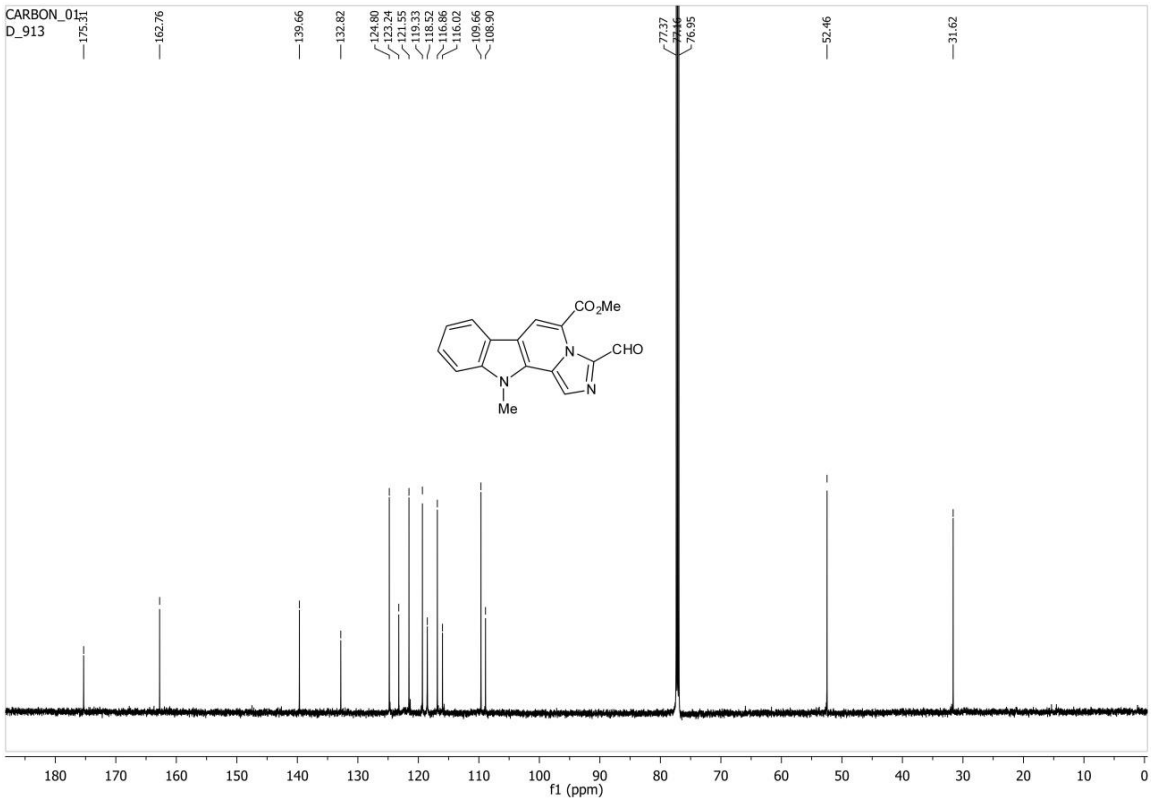


Figure S81. ^{13}C-NMR spectrum of **2aK**.

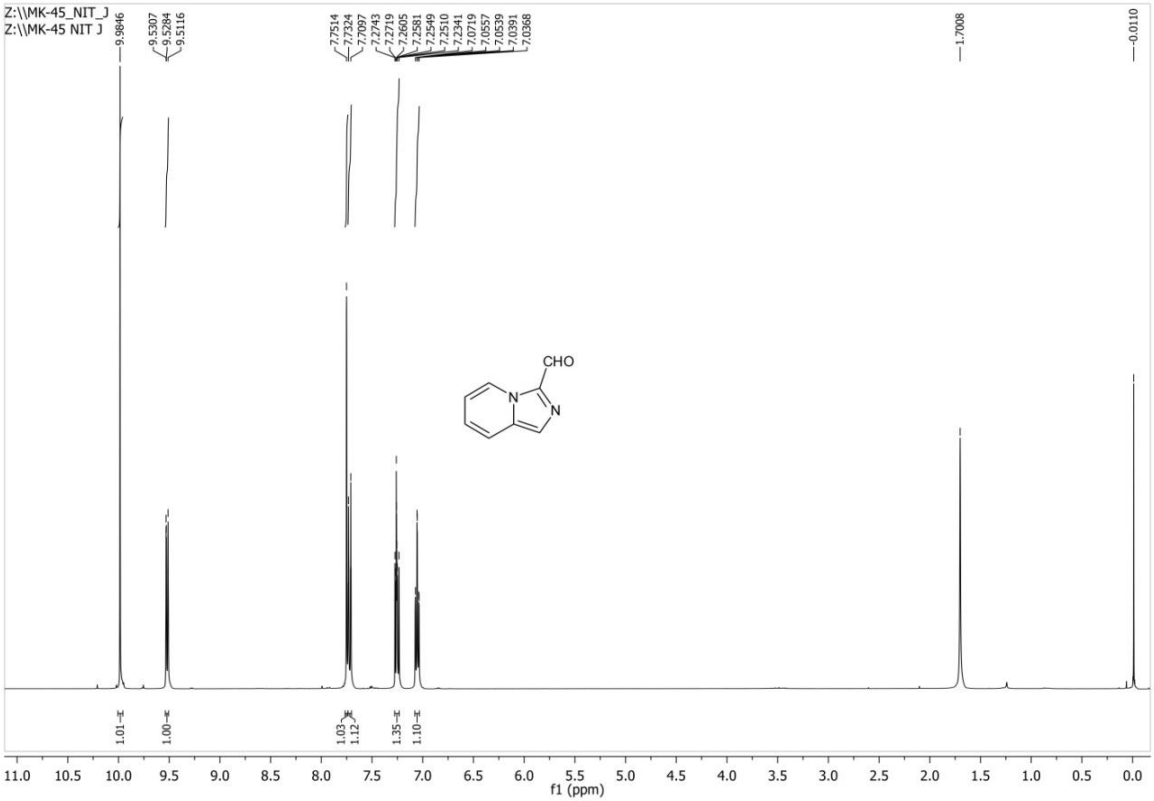


Figure S82. ^{1}H-NMR spectrum of **2DK**.

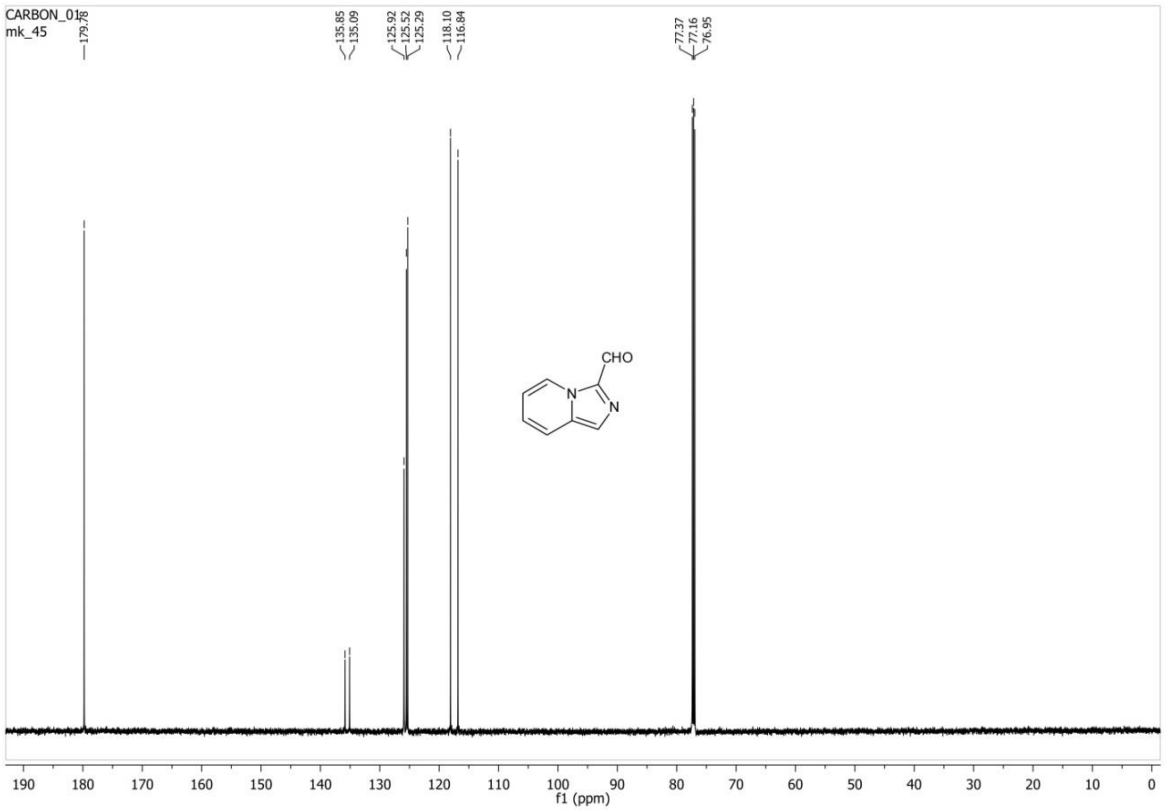


Figure S83. ^{13}C-NMR spectrum of **2DK**.

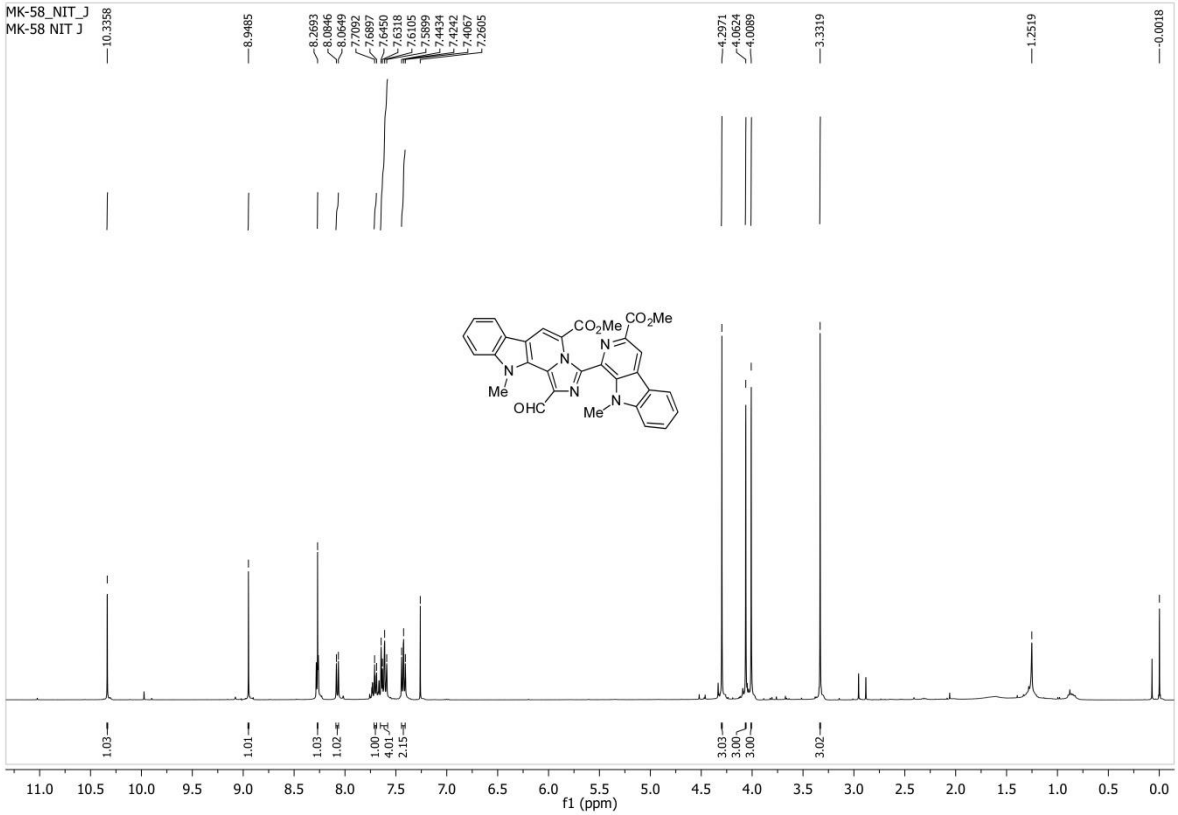


Figure S84. ^{1}H-NMR spectrum of **6**.

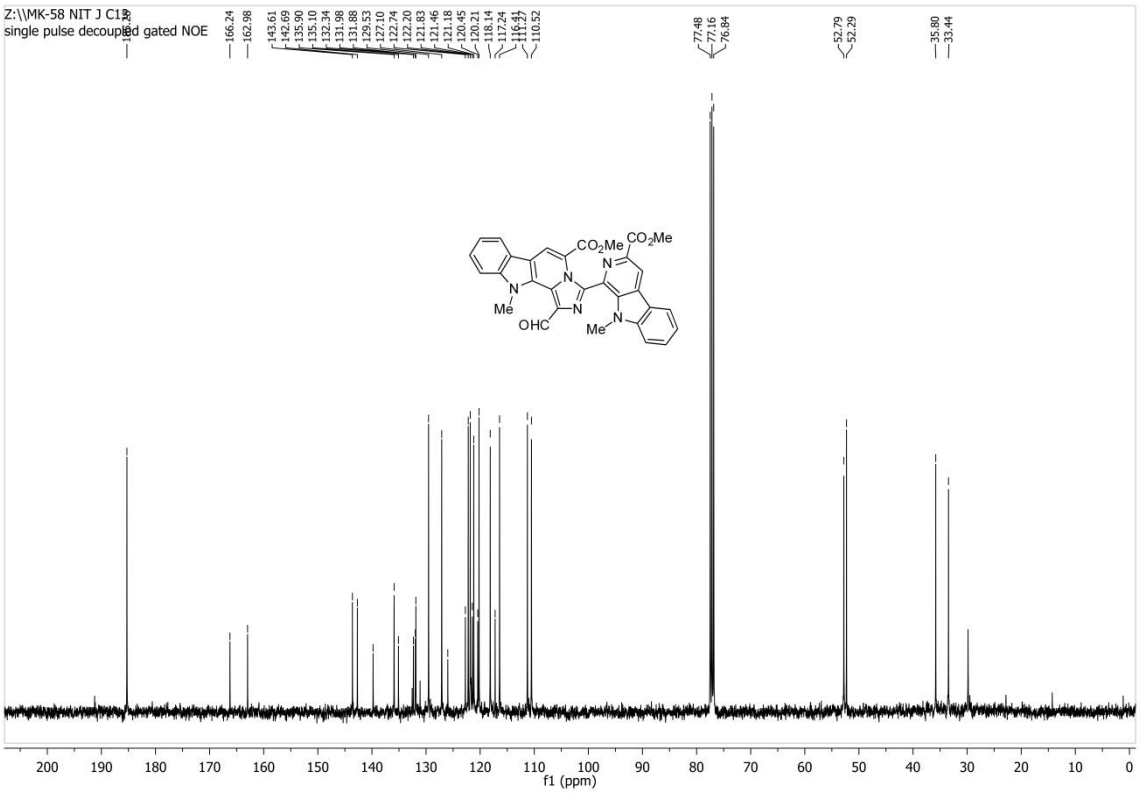
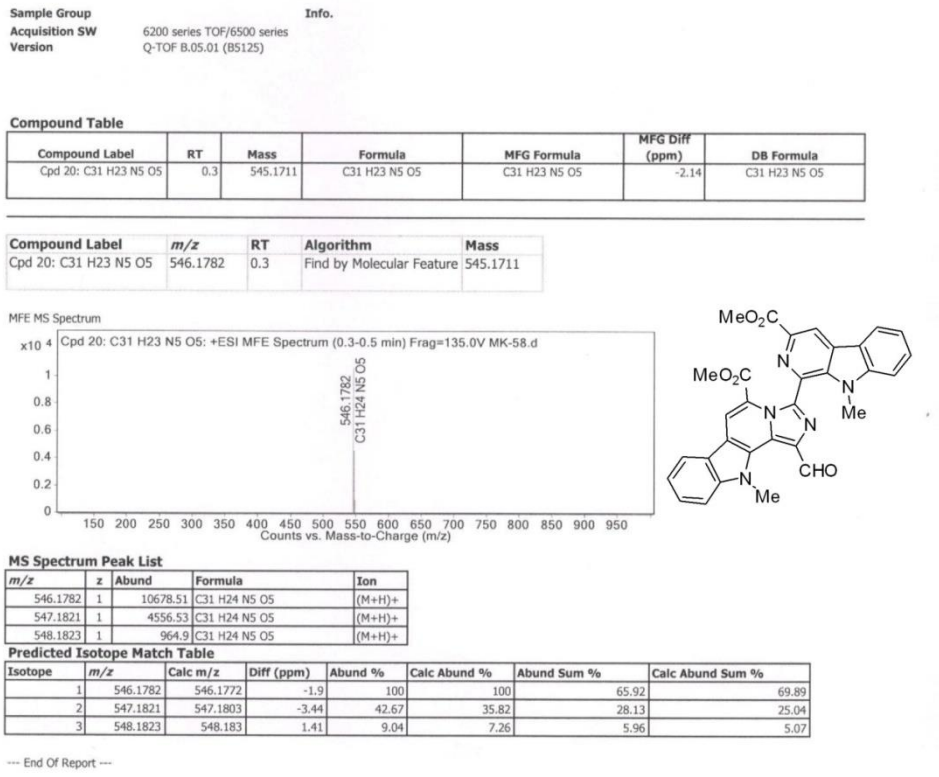


Figure S85. ^{13}C-NMR spectrum of **6**.



Sample Group	**Info.**
Acquisition SW	6200 series TOF/6500 series
Version	Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 20: C31 H23 N5 O5	0.3	545.1711	C31 H23 N5 O5	C31 H23 N5 O5	-2.14	C31 H23 N5 O5

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 20: C31 H23 N5 O5	546.1782	0.3	Find by Molecular Feature	545.1711

MFE MS Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
546.1782	1	10678.51	C31 H24 N5 O5	(M+H)+
547.1821	1	4556.53	C31 H24 N5 O5	(M+H)+
548.1823	1	964.9	C31 H24 N5 O5	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	546.1782	546.1772	-1.9	100	100	65.92	69.89
2	547.1821	547.1803	-3.44	42.67	35.82	28.13	25.04
3	548.1823	548.183	1.41	9.04	7.26	5.96	5.07

--- End Of Report ---

Figure S86. HRMS spectrum of **6**.

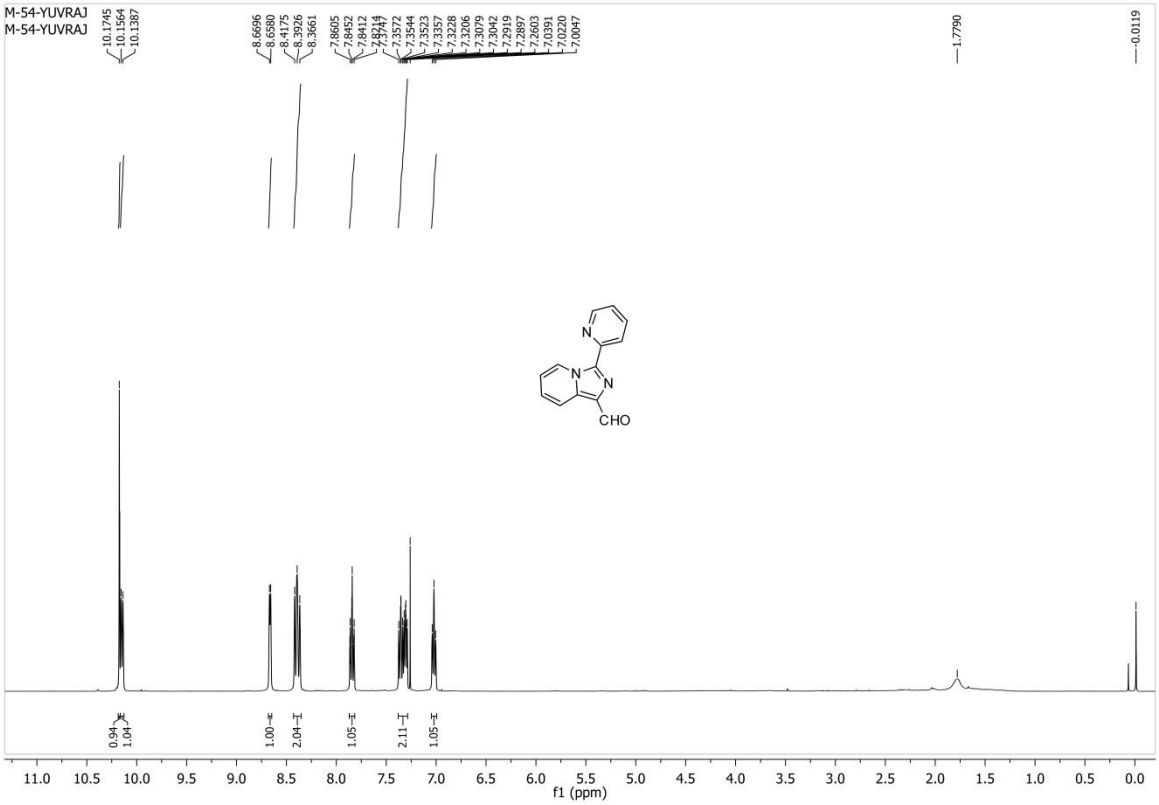


Figure S87. ^{1}H-NMR spectrum of **7**.

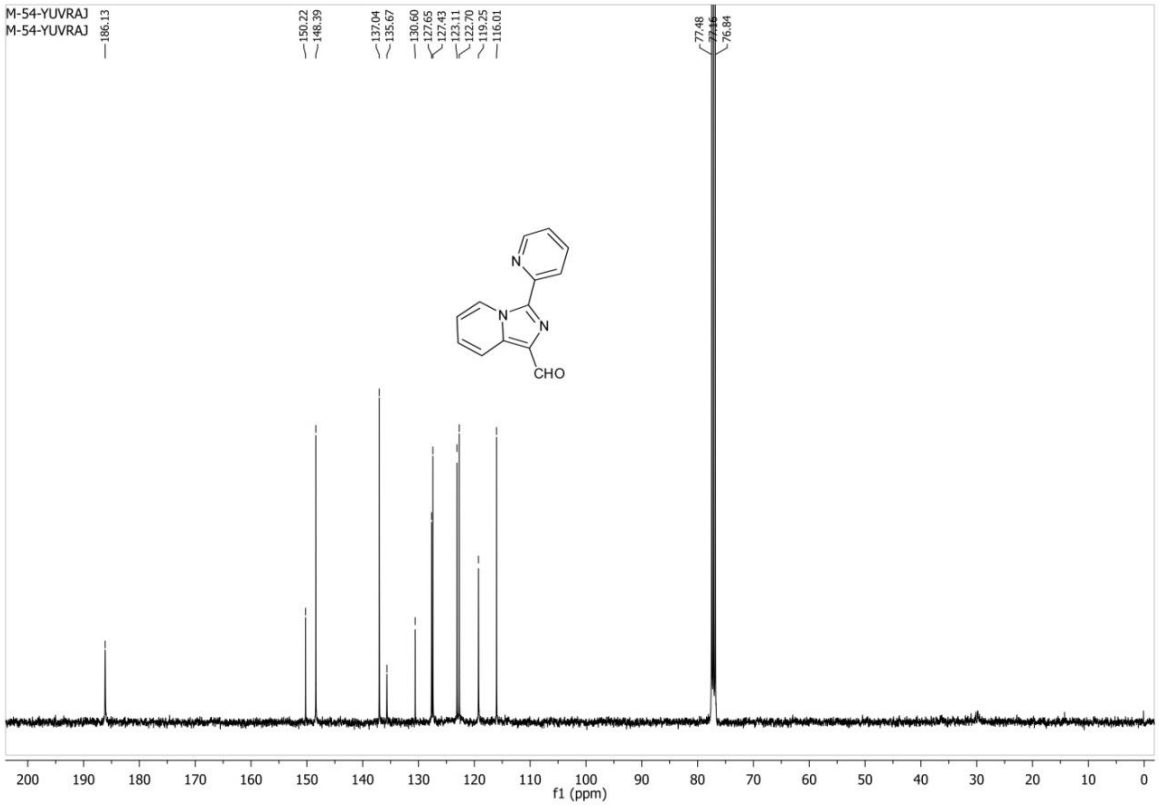
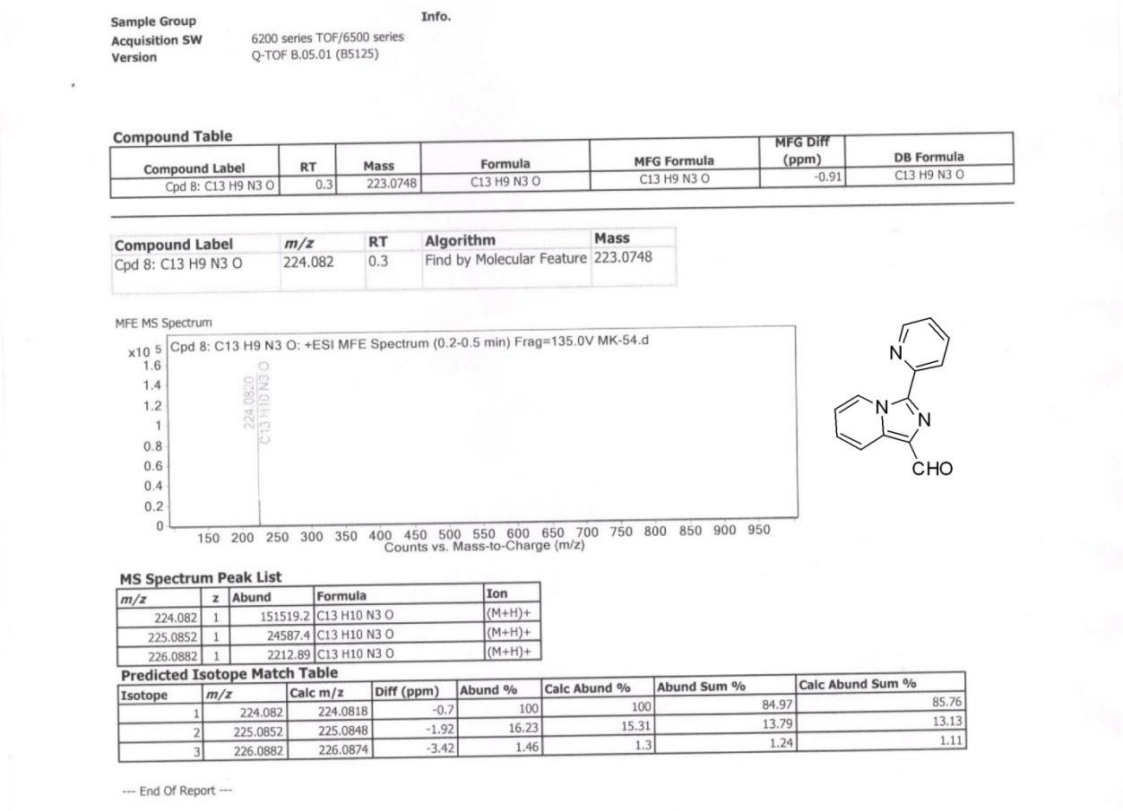


Figure S88. ^{13}C-NMR spectrum of **7**.



Info.

Sample Group	
Acquisition SW	6200 series TOF/6500 series
Version	Q-TOF B.05.01 (B5125)

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 8: C13 H9 N3 O	0.3	223.0748	C13 H9 N3 O	C13 H9 N3 O	-0.91	C13 H9 N3 O

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 8: C13 H9 N3 O	224.082	0.3	Find by Molecular Feature	223.0748

MFE MS Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
224.082	1	151519.2	C13 H10 N3 O	(M+H)+
225.0852	1	24587.4	C13 H10 N3 O	(M+H)+
226.0882	1	2212.89	C13 H10 N3 O	(M+H)+

Predicted Isotope Match Table

Isotope	*m/z*	Calc m/z	Diff (ppm)	Abund %	Calc Abund %	Abund Sum %	Calc Abund Sum %
1	224.082	224.0818	-0.7	100	100	84.97	85.76
2	225.0852	225.0848	-1.92	16.23	15.31	13.79	13.13
3	226.0882	226.0874	-3.42	1.46	1.3	1.24	1.11

--- End Of Report ---

Figure S89. HRMS spectrum of **7**.

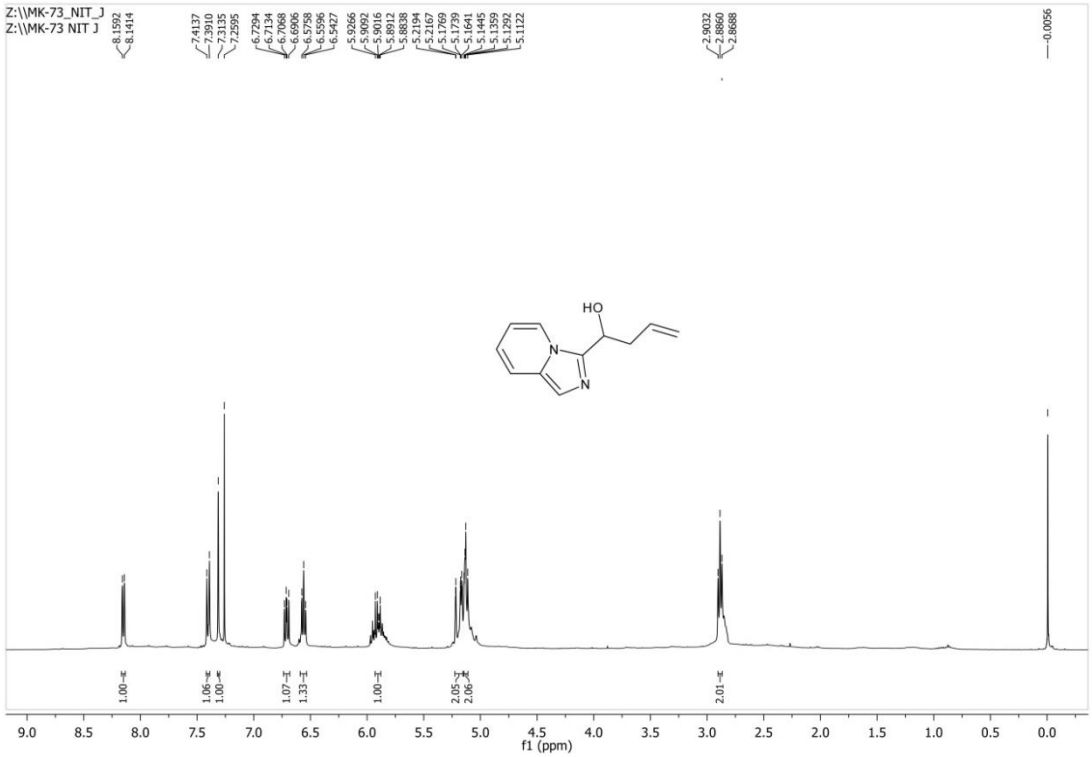


Figure S90. ^{1}H-NMR spectrum of **8**.

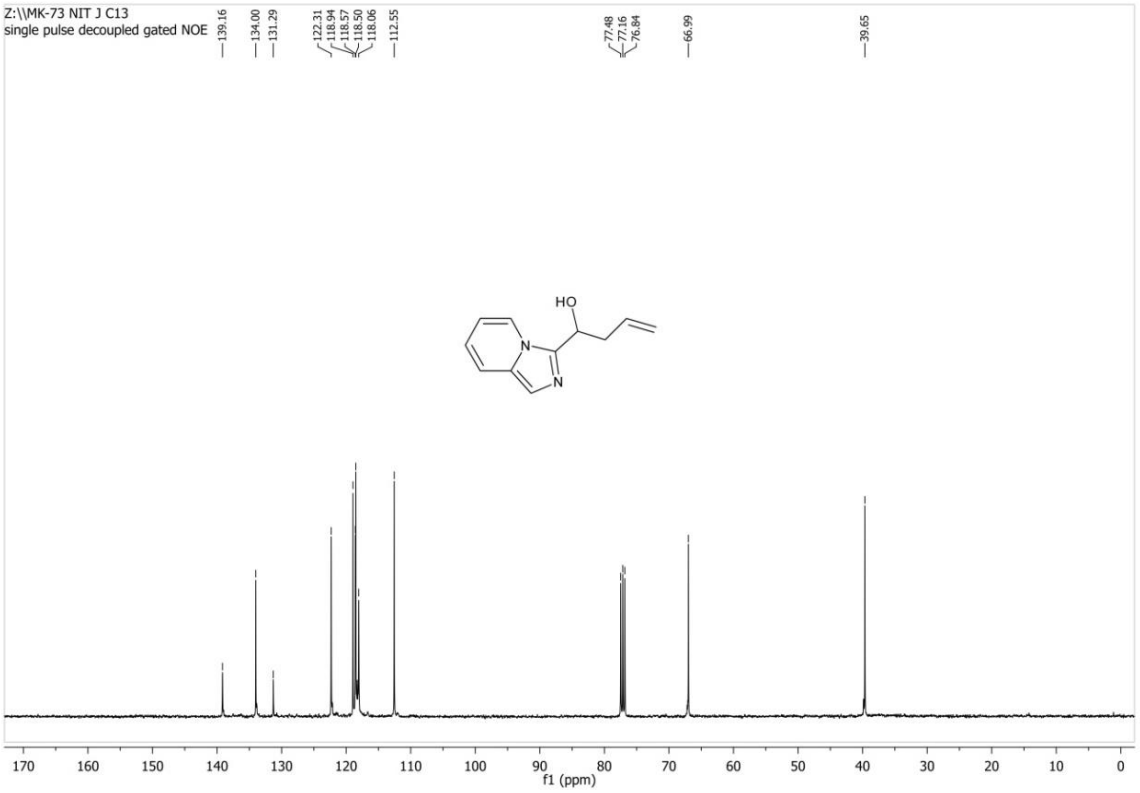


Figure S91. ^{13}C-NMR spectrum of **8**.

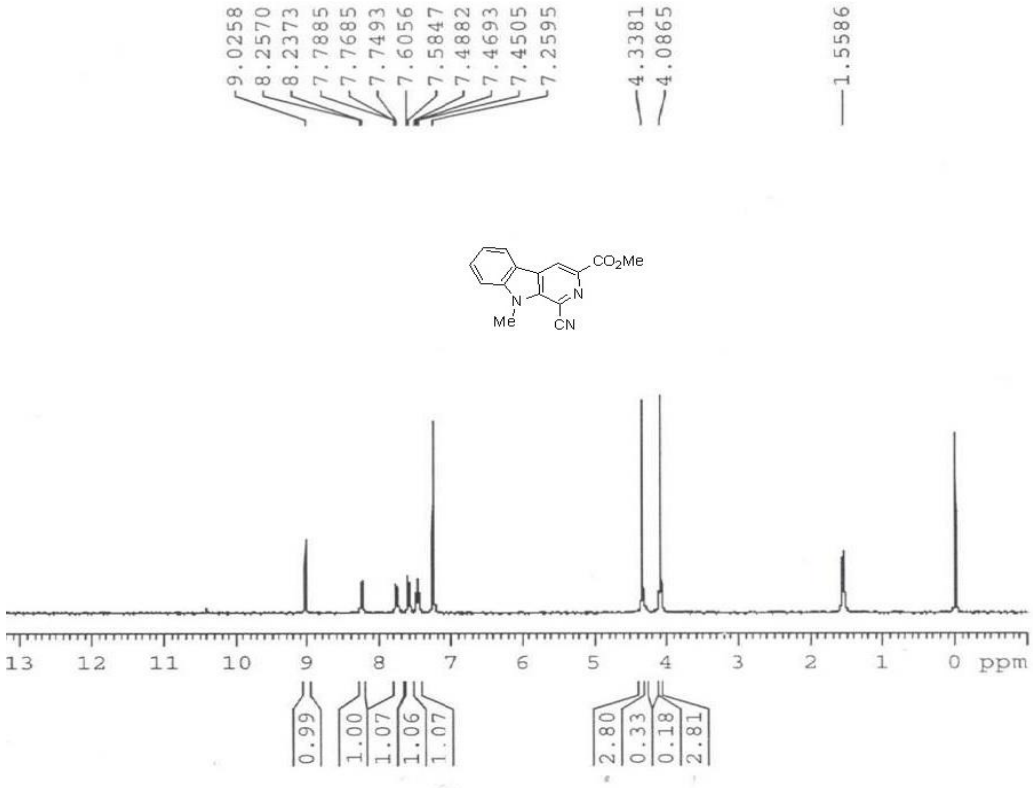


Figure S92. ^{1}H-NMR spectrum of **5a**.

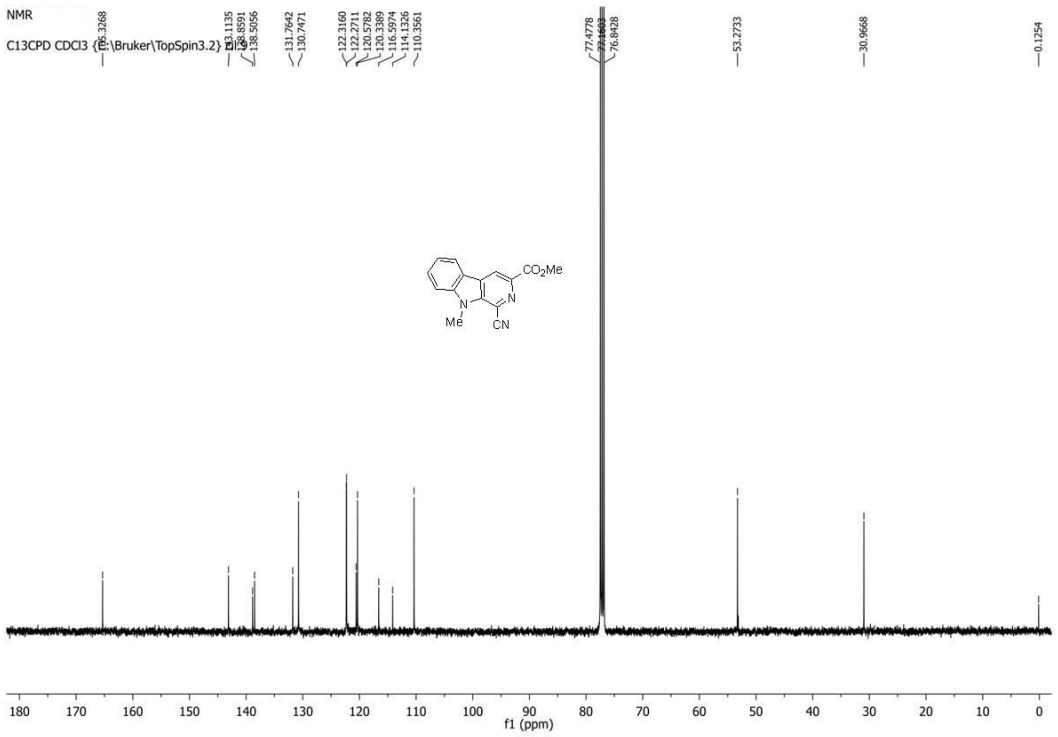


Figure S93. ^{13}C-NMR spectrum of **5a**.

Photophysical studies of synthesised compounds

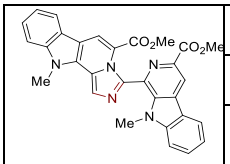
The fluorescent quantum yield (Φ) was measured relative to quinine sulfate (Φ_R = 0.546) (0.1 M H_2SO_4 at 350 nm excitation) as a reference compound. For the measurement of UV-Vis absorption and fluorescence emission of samples, stock solution (1.0 mM) was prepared and diluted to final concentration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

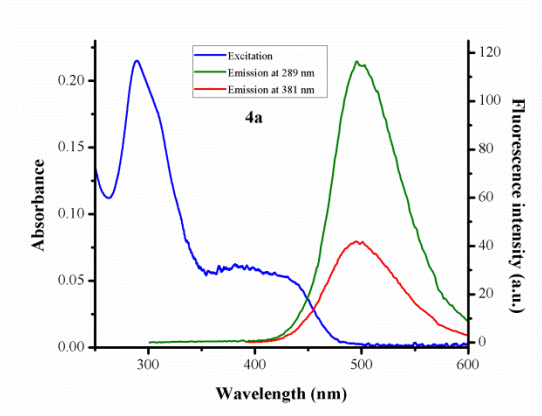
$$\Phi_S = \Phi_R \times \frac{I_S}{I_R} \times \frac{A_R}{A_S} \times \frac{{\eta_S}^2}{{\eta_R}^2}$$

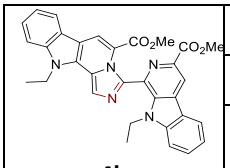
R – Reference; *S* - Sample

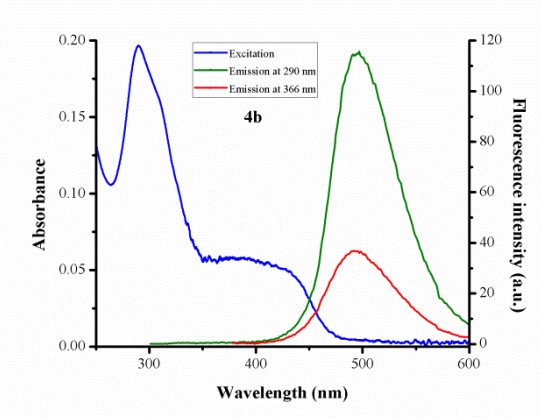
where Φ_R was the quantum yields of quinine sulfate, η was the refractive index of the solvent, *I* was the integrated fluorescence intensity and *A* was the absorbance. The concentration of samples should be sufficiently diluted not to occur concentration quenching.

Figure S94. Photophysical properties and graphical data of β-carboline dimers (**4a-l** and **6**).

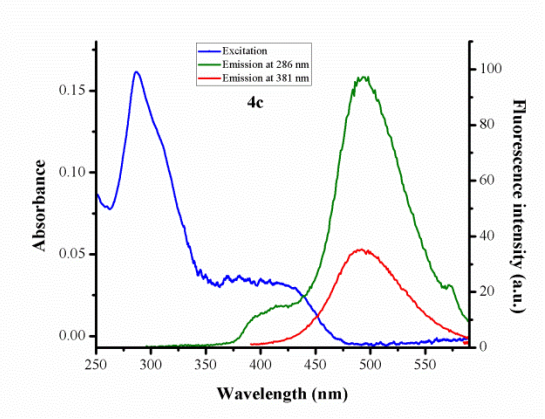
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	288.89	495.90	116.46	0.107
4a	381.37	494.43	40.82	0.136



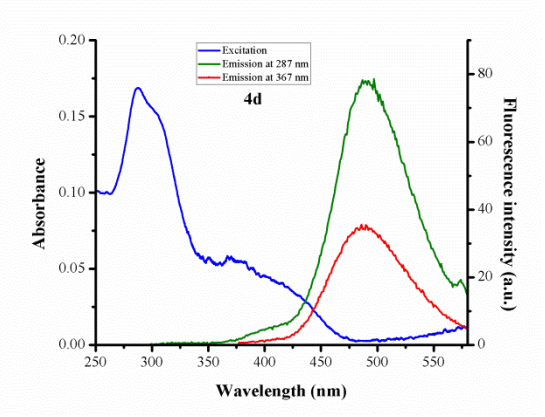
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	289.63	496.96	115.75	0.112
4b	366.18	497.02	36.28	0.127



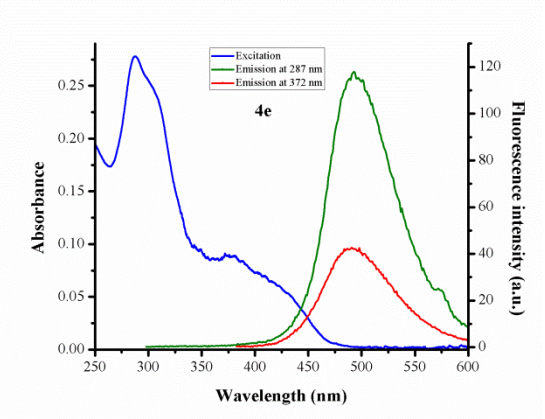
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	286.53	498.03	97.36	0.131
4c	380.58	492.27	35.17	0.152



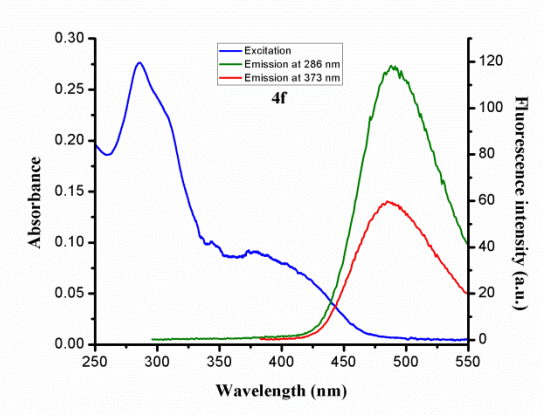
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	287.08	496.96	78.59	0.102
4d	366.70	489.94	35.15	0.130



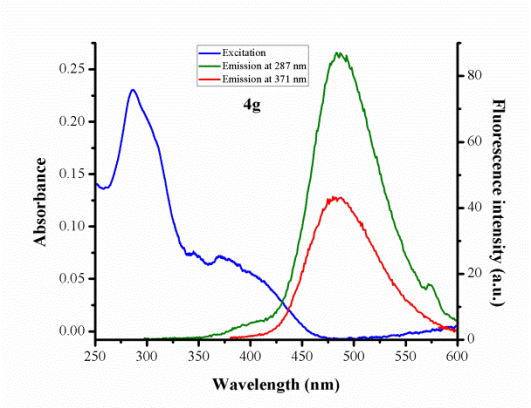
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	287.29	492.87	118.02	0.084
4e	371.83	491.33	42.21	0.096



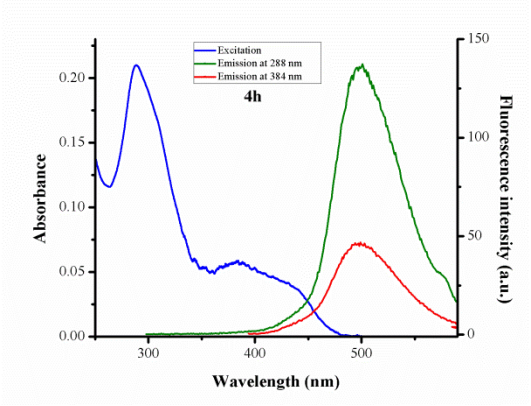
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	285.59	488.05	118.38	0.088
4f	373.32	484.92	59.81	0.132



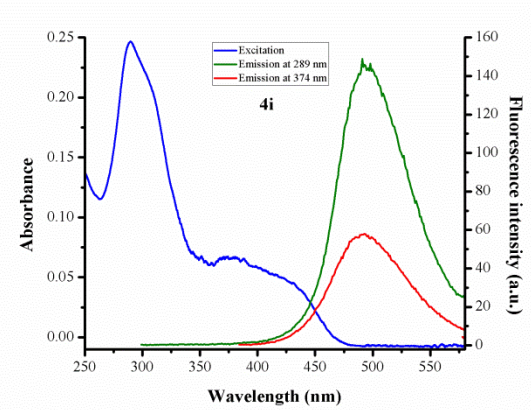
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	286.66	482.98	87.09	0.081
4g	370.69	479.75	43.41	0.127



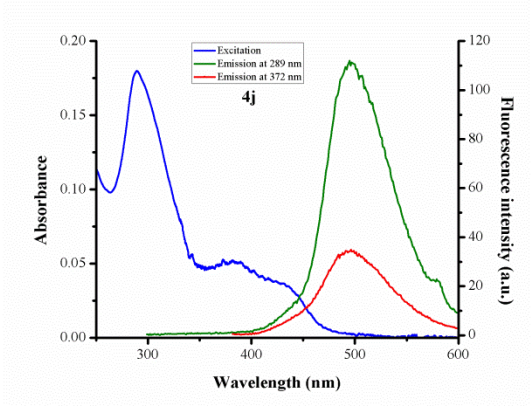
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	288.23	501.04	137.35	0.128
4h	384.10	499.26	46.24	0.158

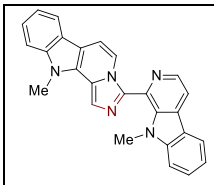


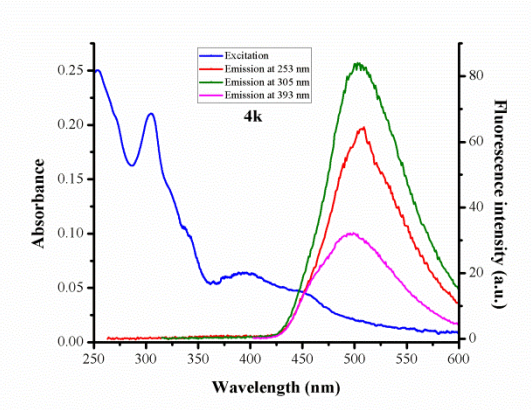
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	289.39	490.90	148.94	0.117
4i	374.21	493.03	57.97	0.177

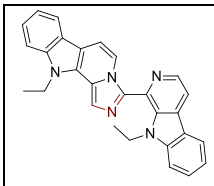


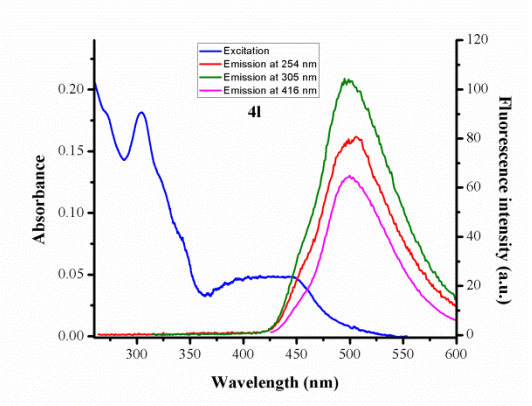
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
	289.29	494.84	111.95	0.124
4j	372.37	495.95	34.75	0.137

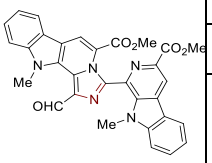


	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
 **4k**	253.30	508.95	64.55	0.055
	305.06	502.98	84.08	0.090
	393.14	499.33	32.18	0.115



	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
 **4l**	253.90	505.82	80.80	0.080
	304.63	494.84	104.31	0.126
	415.67	499.74	64.85	0.256



	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
 **6**	282.14	465.09	89.80	0.096
	327.08	463.93	90.41	0.111
	371.82	463.99	67.47	0.120

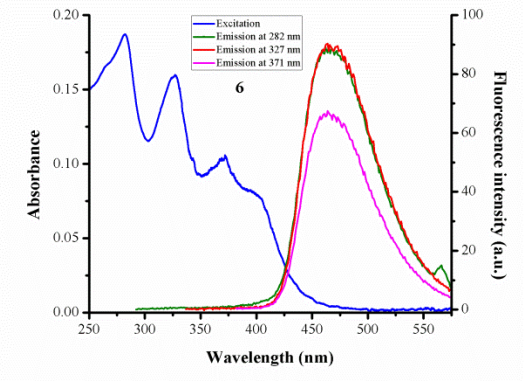
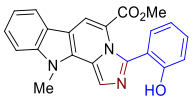
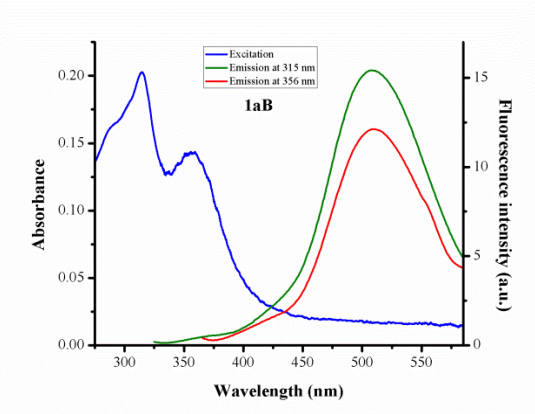
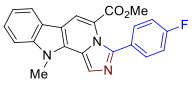
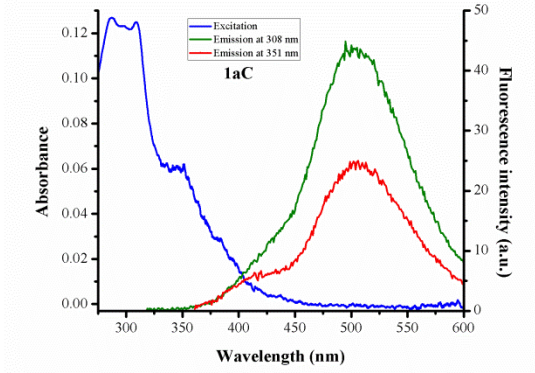


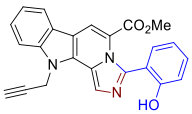
Figure S95. Photophysical properties and graphical data of imidazo[3,4-*b*]pyridine derivatives.

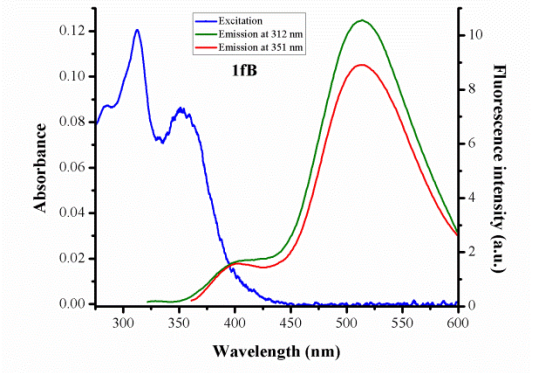
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
 **1aB**	314.81	510.61	15.73	0.020
	355.62	516.06	12.47	0.021

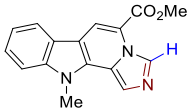


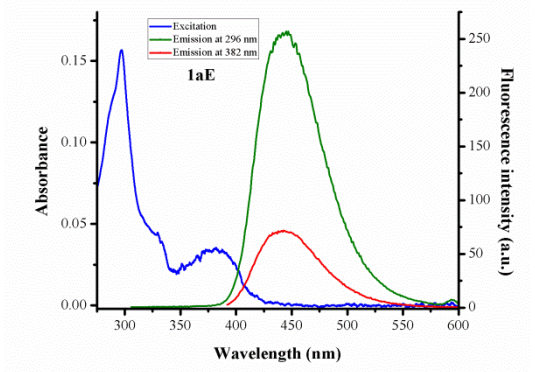
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
 **1aC**	308.51	495.54	44.03	0.096
	351.59	505.86	24.69	0.108



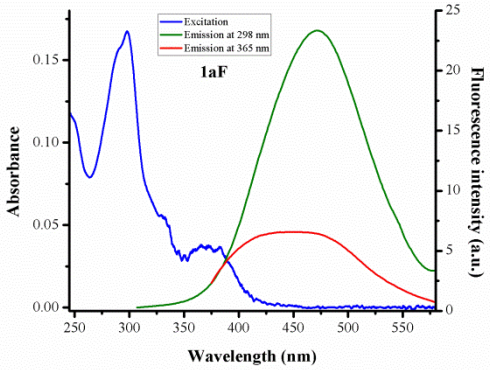
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
 **1fB**	312.51	514.11	10.93	0.024
	351.00	516.01	09.08	0.028



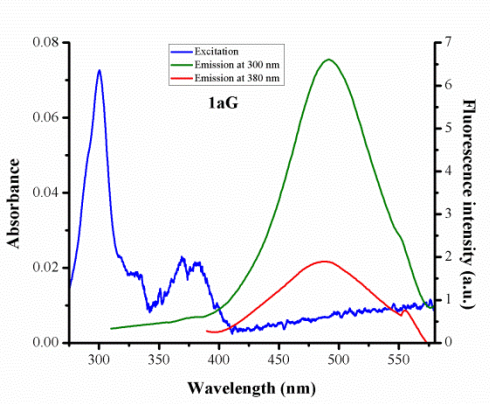
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
 **1aE**	296.89	445.08	251.15	0.295
	382.08	443.03	71.75	0.365



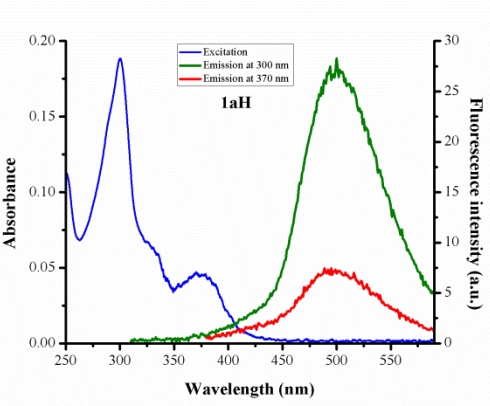
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
1aF	297.90	476.02	23.58	0.040
	365.51	470.80	6.86	0.059



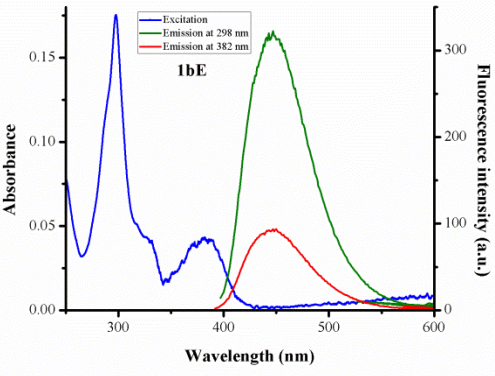
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
1aG	300.34	499.37	6.82	0.024
	379.89	489.61	1.91	0.021



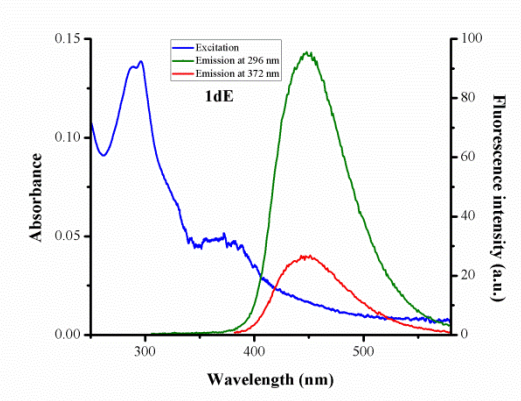
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
1aH	300.29	499.79	27.77	0.034
	370.37	494.99	07.40	0.039



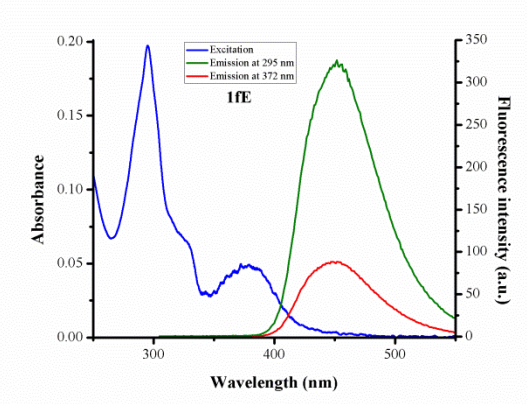
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
1bE	297.61	446.96	319.92	0.335
	382.06	449.49	93.63	0.398



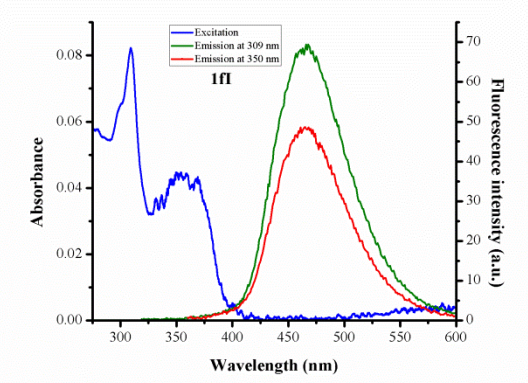
	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
1dE	295.81	448.06	95.62	0.140
	372.37	450.94	26.68	0.106



	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
1fE	295.12	451.96	326.41	0.311
	372.36	448.03	88.25	0.331



	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
1fI	309.03	465.90	69.43	0.171
	349.60	465.41	48.52	0.217



	UV-Vis	Fluorescence		Φ_F
	λ_{Ex} (nm)	λ_{Em} (nm)	Intensity	
2aK	297.06	446.81	268.66	0.327
	382.28	443.93	77.77	0.384