Supporting Information

Ru(II)-catalyzed synthesis of indolo[2,3-*c*]isoquinoline *via* [3+3] annulation of *N,N'*-cyclic azomethine ylides and 3-diazoindolin-2-imines

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1. General Information

Commercially available reagents and solvents were used without further purification. ^{1}H NMR spectra were recorded on NMR instrument operated at 500 MHz. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). ^{13}C NMR spectra were recorded on NMR instrument operated at 125 MHz with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ 77.5 ppm). The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). HRMS was measured in ESI-MS mass spectrophotometer. Thin-layer chromatography was performed on MERCK precoated silica gel 60F-254 (0.5 mm) aluminium plates and visualized under UV light at 254 nm. Column chromatography was performed using silica gel 100-200 mesh size. All the starting materials **1a-o**[1] and **2a-f**[2], were synthesized from previously reported methods.

2. Experimental procedures

General procedure for the synthesis of azomethine ylides (1)

According to the literature reports,[1] *N,N'*-cyclic azomethine imines were prepared. Substrates **1a-o** are known compounds, and all the spectral data match with literature reports.

General procedure for the synthesis of diazoindolin-2-imines (2)

According to the literature report,[2] diazoindolin-2-imines were prepared. To an oven-dried Schlenk tube equipped with a magnetic stirring bar was added sequentially *N*-substituted indole (5 mmol), *p*-toluenesulfonyl azide (10 mmol), and DMSO (10 mL). The reaction mixture was stirred at 50 °C for 12-16 h. Then, the reaction was quenched by H_2O (200 mL) and extracted with CH_2Cl_2 (300 mL× 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using 30-40% ethyl acetate/hexane to afford the desired products **2a-f**. All the spectral data match with literature reports.

General procedure for the synthesis of indolo[2,3-*c*]isoquinolines (3a-x)

To an oven-dried reaction tube equipped with a magnetic stir bar, substituted azomethine ylides **1a-o** (50 mg, 1 equiv.), substituted diazoindolin-2-imines **2a-f (**1 equiv.) was charged, followed by addition of $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) and 2 mL DCE. The resulting reaction mixture was stirred at 65 °C for desired time (6-8 h). The solvent was directly

evaporated *via* rotavapor and the remaining crude mixture was purified by silica gel column chromatography using 5-10% ethyl acetate/hexane to afford the desired products **3a-x**.

General procedure for the synthesis 6-benzyl-6*H*-thieno[3',2':4,5]pyrido[2,3-*b*]indole 3,3-dioxide (4)

To an oven dried reaction tube, add 0.32 mmol of **3n** (1 equiv.), 0.47 mmol of *m*-chloroperbenzoic acid (1.5 equiv.) and dichloromethane (10 mL). The resulting reaction mixture was stirred at room temperature for 4 h and thus was purified by column chromatography on silica gel using 60% ethyl acetate/hexane to afford the desired product **4**.

7-Benzyl-7*H*-indolo[2,3-*c*]isoquinoline (3a): Off-white solid, yield: 95%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.17 (d, J = 0.9 Hz, 1H), 8.68 (dt, J = 8.4, 1.0 Hz, 1H), 8.52 (dt, J = 7.9, 1.0 Hz, 1H), 8.15 (dt, J = 8.2, 1.0 Hz, 1H), 7.88 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.53 (m, 1H), 7.47 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 7.40 (ddd, J = 8.2, 7.1, 1.2 Hz, 2H), 7.25–7.19 (m, 5H), 5.90 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5, 137.6, 131.0, 130.4, 129.5, 129.4, 128.9, 128.6 (2C), 127.3, 126.8 (2C), 125.0, 124.9, 123.6, 122.6, 122.4, 121.6, 120.5, 120.5, 110.4, 45.2 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{22}H_{16}N_2$: 309.1387, found: 309.1404.

7-Benzyl-2-fluoro-7*H*-indolo[2,3-*c*]isoquinoline (3b): Off-white solid, yield: 70%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.12 (d, J = 0.8 Hz, 1H), 8.42 (dt, J = 7.8, 0.9 Hz, 1H), 8.22 (dd, J = 10.3, 2.5 Hz, 1H), 8.15 (dd, J = 9.0, 5.8 Hz, 1H), 7.53 (dt, J = 8.2, 1.0 Hz, 1H), 7.48 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.42 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H), 7.29 (td, J = 8.7, 2.4 Hz, 1H), 7.26–7.20 (m, 5H), 5.88 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2 (d, J = 252.5 Hz) 150.03, 140.68, 137.95, 137.95, 137.38, 134.10, 132.30 (d, J = 10.8 Hz), 128.67, 127.41, 126.86, 125.16, 122.02, 121.96, 121.36, 120.73, 113.7 (d, J = 25.3 Hz), 110.46, 106.7 (d, J = 21. 9 Hz), 45.29 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{22}H_{15}FN_2$: 327.1293, found: 327.1288.

7-Benzyl-2-chloro-7*H*-indolo[2,3-*c*]isoquinoline (3c): Off-white solid, yield: 80%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.12 (d, J = 0.8 Hz, 1H), 8.61 (d, J = 1.9 Hz, 1H), 8.46 (dt, J = 7.9, 1.0 Hz, 1H), 8.07 (d, J = 8.7 Hz, 1H), 7.53 (dt, J = 8.1, 1.0 Hz, 1H), 7.51–7.46 (m, 2H), 7.42 (ddd, J = 8.1, 7.0, 1.3 Hz, 1H), 7.26, (m, 1H), 7.25–7.21 (m, 4H), 5.88 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.0, 148.0, 138.1, 137.3, 136.1, 133.3, 130.9, 128.7, 127.4, 126.9, 125.3, 124.5, 123.0, 122.2, 121.8, 121.2, 120.8, 110.5, 105.5, 45.3 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{22}H_{15}ClN_2$: 343.0997, found: 343.1017.

7-Benzyl-2-bromo-7*H*-indolo[2,3-*c*]isoquinoline (3d): Off-white solid, yield: 85% ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.11 (d, J = 0.8 Hz, 1H), 8.80 (d, J = 1.8 Hz, 1H), 8.46 (dt, J = 7.9, 1.0 Hz, 1H), 8.00 (d, J = 8.6 Hz, 1H), 7.62 (dd, J = 8.7, 1.8 Hz, 1H), 7.53 (dt, J = 8.1, 1.1 Hz, 1H), 7.49 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.42 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.26 (d, J = 2.5 Hz, 1H), 7.25–7.19 (m, 4H), 5.88 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.1, 148.0, 138.1, 137.3, 133.6, 130.9, 128.7, 127.4, 127.1, 126.9, 126.1, 125.3, 125.1, 123.1, 122.2, 121.2, 120.8, 110.5, 105.3, 45.3 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{22}H_{15}BrN_2$: 387.0491, found: 387.0469, *m/z* $[M+2]^+$: 389.0452.

7-Benzyl-2-methyl-7*H*-indolo[2,3-*c*]isoquinoline (3e): Off-white solid, yield: 97%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.10 (d, J = 0.8 Hz, 1H), 8.52 (dt, J = 7.7, 1.0 Hz, 1H), 8.44 (dd, J = 1.7, 0.8 Hz, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.51 (dt, J = 8.2, 0.9 Hz, 1H), 7.45 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.41 (ddd, 15.6, 8.2, 1.41 Hz, 1H), 7.37 (ddd, J = 8.3, 1.5 Hz, 1H), 7.25–7.19 (m, 5H), 5.88 (s, 2H), 2.70 (d, J = 0.9 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.1, 147.9, 141.5, 137.9, 137.6, 133.1, 129.2, 128.6 (2C), 127.3, 126.8 (2C), 125.8, 124.8, 123.3, 122.3, 121.8, 121.7, 120.3, 110.3, 105.9, 45.2, 22.7 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{23}H_{18}N_2$: 323.1543, found: 323.1536.

7-Benzyl-2-methoxy-7*H*-indolo[2,3-*c*]isoquinoline (3f): Off-white solid, yield: 95%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.03 (s, 1H), 8.42 (dt, J = 7.8, 1.0 Hz, 1H), 8.03 (d, J = 9.0 Hz, 1H), 7.89 (d, J = 2.3 Hz, 1H), 7.50 (dt, J = 8.2, 0.9 Hz, 1H), 7.45 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.40 (dd, J = 7.8, 1.2 Hz, 1H), 7.25–7.20 (m, 5H), 7.17 (dd, J = 8.9, 2.4 Hz, 1H), 5.87 (s, 2H), 4.12 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 161.9, 149.7, 148.2, 137.9, 137.6, 134.7, 131.1, 128.6 (2C), 127.3, 126.9 (2C), 124.7, 121.9, 121.7, 120.5, 120.3, 115.9, 110.3, 105.9, 101.4, 55.6, 45.2 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{23}H_{18}N_2O$: 339.1492, found: 339.1489.

7-Benzyl-*N*,*N*-dimethyl-7*H*-indolo[2,3-*c*]isoquinolin-2-amine (3g): Off-white solid, yield: 90%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.91 (s, 1H), 8.37 (dd, J = 7.1, 1.3 Hz, 1H), 7.95 (d, J = 9.1 Hz, 1H), 7.53 (d, J = 2.6 Hz, 1H), 7.46 (m, 1H), 7.40 (ddd, J = 8.1, 7.2, 1.4 Hz, 1H), 7.36 (td, J = 7.4, 1.4 Hz, 1H), 7.24–7.17 (m, 5H), 7.10 (dd, J = 9.1, 2.5 Hz, 1H), 5.85 (s, 2H), 3.27 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 149.6, 137.8, 137.7, 134.9, 133.1, 130.6, 128.6 (2C), 127.2, 126.8 (2C), 124.0, 122.2, 121.8, 120.0, 118.1, 112.6, 110.0, 104.8, 100.0, 45.1, 40.5 (2C) ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{24}H_{21}N_3$: 352.1809, found: 352.1804.

7-Benzyl-2-nitro-7*H*-indolo[2,3-*c*]isoquinoline (3h): yellow solid, yield: 70% ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.62 – 9.41 (m, 1H), 9.28 (d, J = 0.9 Hz, 1H), 8.59 (dd, J = 7.8, 1.2 Hz, 1H), 8.33–8.24 (m, 2H), 7.65–7.58 (m, 1H), 7.56 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.50 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.26 – 7.21 (m, 5H), 5.92 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.1, 150.2, 140.0, 138.6, 132.7, 130.9, 130.5 (2C), 129.3, 126.9, 124.9, 124.6, 124.3 (2C), 123.4, 122.5, 122.3, 121.2, 120.2, 109.5, 106.2, 28.0 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{22}H_{15}N_3O_2$: 354.1238, found: 354.1211.

7-Benzyl-3-bromo-7*H*-indolo[2,3-*c*]isoquinoline (3i): Off-white solid, yield: 80%,^{1}H NMR (500 MHz, $CDCl_3$): δ 9.08 (s, 1H), 8.55 (d, J = 8.8 Hz, 1H), 8.46 (d, J = 7.9 Hz, 1H), 8.30 (d, J = 2.1 Hz, 1H), 7.93 (dd, J = 8.9, 2.1 Hz, 1H), 7.54 (d, J = 8.2 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.23 (m, 5H), 5.88 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.2, 143.6, 143.5, 134.1, 131.3, 128.7 (2C), 128.4, 127.4, 126.9 (2C), 125.9, 125.4, 124.4, 122.4, 121.2, 120.7, 116.6, 116.1, 116.0, 110.5, 45.3 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{22}H_{15}BrN_2$: 387.0492, found: 387.0514, *m/z* $[M+2]^+$: 389.0496.

7-Benzyl-4-bromo-7*H*-indolo[2,3-*c*]isoquinoline (3j): Off-white solid, yield: 82%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.61 (d, J = 0.8 Hz, 1H), 8.66 (dt, J = 8.4, 0.9 Hz, 1H), 8.49 (dd, J = 8.0, 1.0 Hz, 1H), 7.78 (dt, J = 7.5, 0.9 Hz, 1H), 7.68 (ddd, J = 8.3, 7.4, 0.8 Hz, 1H), 7.57–7.53 (m, 1H), 7.50 (tt, J = 8.1, 1.0 Hz, 1H), 7.43–7.40 (m, 1H), 7.25–7.21 (m, 5H), 5.90 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.90, 148.10, 138.40, 137.33, 134.30, 131.17, 128.69 (2C), 127.81, 127.45, 126.93 (2C), 125.45, 124.41, 122.77, 122.48, 122.45, 121.16, 120.76, 110.56, 105.89, 45.30 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{22}H_{15}BrN_2$: 387.0492, found: 387.0466, *m/z* $[M+2]^+$: 389.0448.

7-Benzyl-1,2,3-trimethoxy-7*H*-indolo[2,3-*c*]isoquinoline (3k): Off-white solid, yield: 97%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.60 (m, 2H), 7.31–7.28 (m, 3H), 7.21 (ddt, J = 8.3, 5.6, 1.0 Hz, 1H), 7.13 (m, 2H), 7.01 (ddd, J = 8.1, 7.0, 0.9 Hz, 2H), 6.22 (s, 1H), 5.23 (s, 2H), 2.35 (s, 3H), 2.17 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.5, 143.5, 136.9, 136.4, 134.9, 129.4, 128.8, 127.8, 127.5, 126.7, 125.4, 124.7, 122.5, 120.1, 117.8, 109.9, 100.0, 50.1, 30.9, 21.5 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{25}H_{22}N_2O_3$: 399.1704, found: 399.1126.

7-Benzyl-7*H*-benzo[*h*]indolo[2,3-*c*]isoquinoline (3l): Off-white solid, yield: 90%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.85 (d, J = 8.3 Hz, 1H), 8.66 (d, J = 9.0 Hz, 1H), 8.58 (d, J = 7.8 Hz, 1H), 8.14 (d, J = 9.0 Hz, 1H), 7.99 (dd, J = 8.1, 1.3 Hz, 1H), 7.76 (ddd, J = 8.3, 7.0, 1.4 Hz, 1H), 7.63 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.53 (dd, J = 8.2, 1.6 Hz, 1H), 7.51 (dd, J =

6.7, 1.1 Hz, 1H), 7.42 (ddd, *J* = 8.1, 6.6, 1.6 Hz, 1H), 7.27 (d, *J* = 3.3 Hz, 4H), 7.23 (ddt, *J* = 9.4, 5.2, 2.5 Hz, 1H), 5.90 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 149.2, 144.2, 138.9, 137.5, 132.6, 132.4, 131.0, 130.4, 129.1, 128.7 (2C), 128.0, 127.4, 126.9 (2C), 126.0, 125.6, 122.8, 121.7, 121.6, 121.5, 120.4, 119.6, 110.3, 108.2, 45.2 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{26}H_{18}N_2$: 359.1543, found: 359.1539

6-Benzyl-6*H*-furo[3',2':4,5]pyrido[2,3-*b*]indole (3m): Off-white solid, yield: 82%, ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.83 (d, *J* = 0.9 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 2.1 Hz, 1H), 7.44 (m, 2H), 7.32 (m, 2H), 7.24 (m, 5H), 5.82 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 148.4, 140.7, 139.7, 138.4, 137.6, 133.5, 129.7, 128.6 (2C), 127.3, 126.9 (2C), 125.7, 121.8, 120.9, 120.4, 120.1, 110.1, 108.7, 45.4 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{20}H_{14}N_2O$: 299.1179, found: 299.1158.

6-Benzyl-6*H*-thieno[3',2':4,5]pyrido[2,3-*b*]indole (3n): Off-white solid, yield: 85%, ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 9.04 (d, *J* = 0.9 Hz, 1H), 8.29 (d, *J* = 7.9 Hz, 1H), 8.01 (dd, *J* = 5.3, 0.9 Hz, 1H), 7.94 (d, *J* = 5.4 Hz, 1H), 7.54–7.40 (m, 2H), 7.43–7.29 (m, 1H), 7.25–7.18 (m, 5H), 5.84 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 148.4, 140.7, 139.7, 138.4, 137.5, 133.5, 129.7 (2C), 128.7, 128.6, 127.3, 126.9 (2C), 125.7, 121.8, 120.9, 120.4, 120.1, 110.1, 108.7, 45.4 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{20}H_{14}N_2S$: 315.0951, found: 315.0948.

7-Benzyl-10-methyl-7*H*-indolo[2,3-*c*]isoquinoline (3p): Off-white solid, yield: 90%, ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 9.14 (d, *J* = 0.8 Hz, 1H), 8.68 (dq, *J* = 8.5, 0.9 Hz, 1H), 8.31 (dt, *J* = 1.8, 0.9 Hz, 1H), 8.14 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.87 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.53 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.29 (ddd, *J* = 8.4, 1.7, 0.7 Hz, 1H), 7.25–7.16 (m, 5H), 5.87 (s, 2H), 2.61 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 150.2, 147.8, 137.7, 136.3, 132.9, 130.9, 129.8, 129.3, 128.6 (2C), 127.3, 126.8(2C), 126.4, 124.8, 123.4, 122.6, 122.3, 121.7, 110.0, 106.0, 45.2, 21.8 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{23}H_{18}N_2$: 323.1543, found: 323.1562.

7-Benzyl-10-bromo-7*H*-indolo[2,3-*c*]isoquinoline (3q): Off-white solid, yield: 80%, ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 9.18 (d, *J* = 0.8 Hz, 1H), 8.62 (d, *J* = 1.8 Hz, 1H), 8.58 (d, *J* = 0.9 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.90 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.57 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.54 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.25–7.22 (m, 3H), 7.22–7.17 (m, 2H), 5.87 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 151.4, 137.1, 136.5, 132.6, 131.4, 129.5, 129.4, 128.7 (2C), 127.7, 127.5, 126.8 (2C), 125.2, 125.0, 124.9, 124.0, 123.1,

122.4, 113.4, 111.8, 105.5, 45.3 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{22}H_{15}BrN_2$: 387.0492, found: 387.0513, *m/z* $[M+2]^+$: 389.0495.

7-Benzyl-10-methoxy-7*H*-indolo[2,3-*c*]isoquinoline (3r): Off-white solid, yield: 92%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.61 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.14 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.97 (d, *J* = 2.4 Hz, 1H), 7.88 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.54 (ddd, *J* = 7.9, 6.9, 1.1 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 1H), 7.25–7.18 (m, 5H), 7.12 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.87 (s, 2H), 4.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.6, 150.5, 148.0, 137.7, 133.0, 132.8, 131.0, 129.4, 128.6, 127.3, 126.8, 124.7, 123.4, 123.0, 122.3, 121.8, 114.1, 111.0, 105.5, 56.2, 45.3 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{23}H_{18}N_2O$: 339.1492, found: 339.1512.

7-Benzyl-10-nitro-7*H*-indolo[2,3-*c*]isoquinoline (3s): Pale yellow solid, yield: 60%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.42 (d, *J* = 2.2 Hz, 1H), 9.25 (s, 1H), 8.87–8.46 (m, 1H), 8.37 (dd, *J* = 9.0, 2.2 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.98 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.67–7.61 (m, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.41–7.16 (m, 5H), 5.93 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.4, 141.8, 141.0, 136.4, 132.4, 132.0, 129.6, 128.9, 127.9, 126.9, 125.4, 125.4, 125.4, 125.4, 124.9, 122.5, 121.0, 120.6, 119.0, 110.1, 45.7 ppm. HRMS(ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{22}H_{15}N_3O_2$: 354.1238, found: 354.1212.

7-Benzyl-9-bromo-7*H*-indolo[2,3-*c*]isoquinoline (3u): Off-white solid, yield: 78%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.19 (s, 1H), 8.60 (d, *J* = 8.3 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.90 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.57 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.51 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.30 (m, 3H), 7.21 (m, 2H) 5.86 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7, 147.5, 138.8, 136.9, 132.6, 131.4, 129.5, 128.8 (2C), 127.6, 126.8 (2C), 125.0, 124.0, 123.7, 123.5, 122.5, 120.4, 118.7, 113.3, 106.2, 45.4 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{22}H_{15}BrN_2$: 387.0492, found: 387.0469, *m/z* $[M+2]^+$: 389.0447.

7-Methyl-7*H*-indolo[2,3-*c*]isoquinoline (3v): Off-white solid, yield: 70%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.15 (d, *J* = 0.8 Hz, 1H), 8.65 (dt, *J* = 8.5, 1.0 Hz, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 8.14 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.86 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.62 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.57 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.53 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.46–7.38 (m, 1H), 4.14 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.2, 147.8, 138.6, 132.8, 130.9, 129.4, 124.9, 124.6, 123.4, 122.5, 122.3, 121.2, 120.2, 109.5, 106.2, 28.0 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}N_2$: 233.1074, found: 233.1088.

7-Ethyl-7*H*-indolo[2,3-*c*]isoquinoline (3w): Off-white solid, yield: 50%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.15 (d, *J* = 0.7 Hz, 1H), 8.65 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.51 (dt, *J* = 7.9, 0.9 Hz, 1H), 8.14 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.96 – 7.82 (m, 1H), 7.63 (s, 1H), 7.54 (dddd, *J* = 14.8, 8.0, 6.9, 1.1 Hz, 2H), 7.41 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 4.73 (d, *J* = 7.2 Hz, 2H), 1.53 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.2, 137.5, 132.8, 130.9, 130.5, 129.3, 124.8, 124.6, 123.4, 122.5, 122.4, 121.4, 120.1, 109.6, 103.4, 36.6, 14.6 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{17}H_{14}N_2$: 247.1230, found: 247.1216.

6-Benzyl-6*H*-thieno[3',2':4,5]pyrido[2,3-*b*]indole 3,3-dioxide (4): yellow solid, yield: 95%, ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.96 (d, *J* = 0.8 Hz, 1H), 8.56 (d, *J* = 7.9 Hz, 1H), 8.52 (d, *J* = 0.9 Hz, 1H), 7.84 (d, *J* = 6.8 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.63 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.48–7.37 (m, 1H), 7.29 (d, *J* = 1.2 Hz, 2H), 7.27–7.20 (m, 1H), 5.79 (s, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 158.9, 145.8, 143.3, 142.0, 141.2, 141.1, 138.4, 134.6, 134.1, 133.9, 132.7, 132.3, 129.1, 128.6, 126.8, 115.9, 100.0, 50.0 ppm. HRMS (ESI-QToF): *m/z* $[M+H]^+$ calcd for $C_{20}H_{14}N_2O_2S$: 347.0849, found: 347.0831.

3. Mechanistic investigation

3.1 ESI-MS studies

To an oven-dried reaction tube equipped with a magnetic stir bar, substituted azomethine ylides (**1a**, 50 mg, 1 equiv.), substituted diazoindolin-2-imines (**2a**, 1 equiv.) was charged, followed by addition of $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) and 2.0 mL DCE. The resulting reaction mixture was stirred at 65 °C for desired time (6-8 h). The samples were withdrawn from the reaction tube and the mass of the crude mixture was recorded at subsequent intervals (0, 1, 2, 3, 5, 10, 20, 40, 60 and 120 mins) to predict the intermediates of the catalytic cycle.

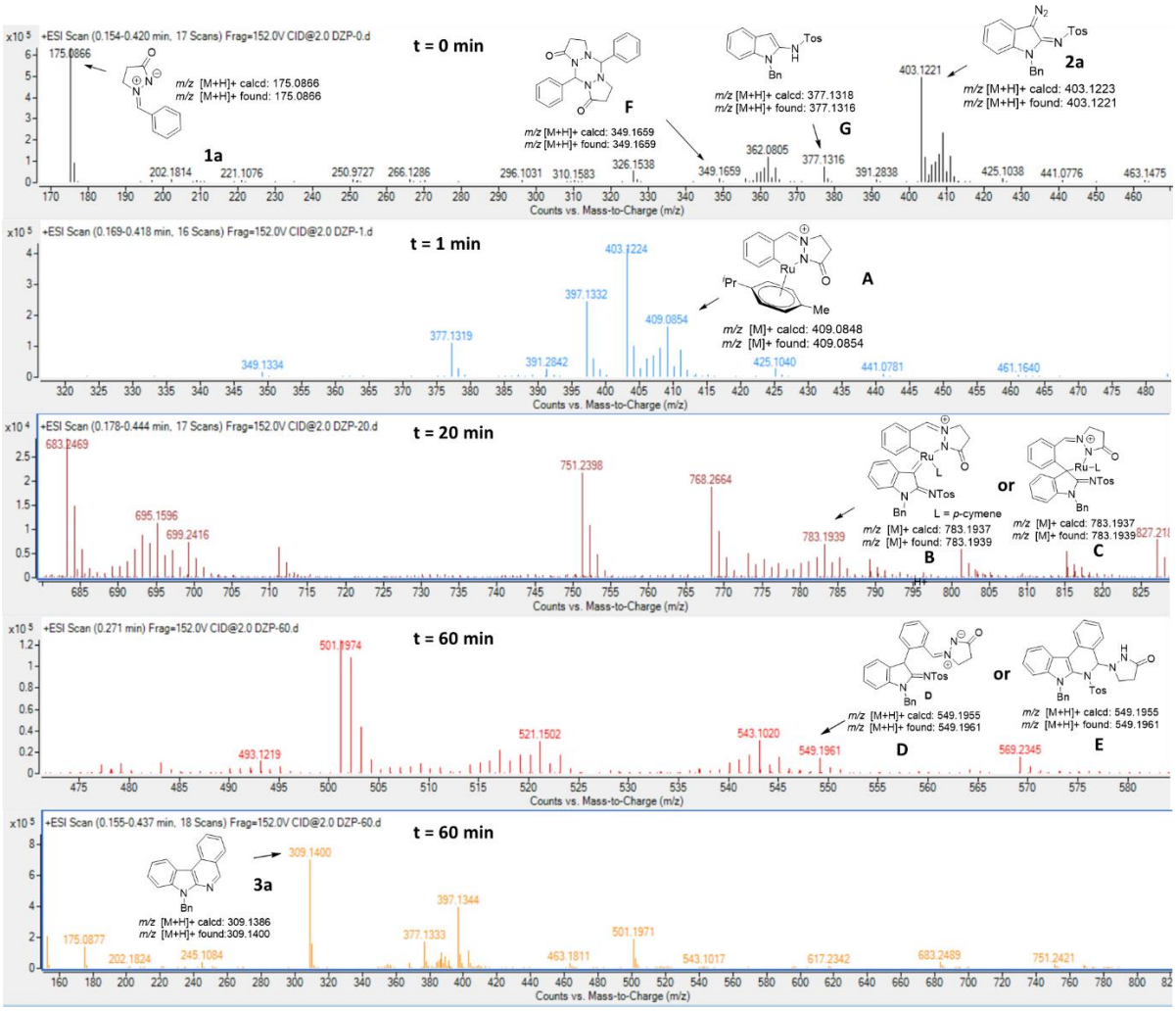

Figure S1. HRMS-(ESI-QToF) mechanistic studies of the reaction.

3.2 (H/D)-exchange experiment

To an oven-dried reaction tube equipped with a magnetic stir bar, **1a** (1 equiv.), CD_3OD (10 equiv.) $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) and 2 mL DCE. The resulting reaction mixture was stirred at room temperature for 20 min. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using methanol:dichloromethane (05:95). The result of ^1H NMR of isolated compounds revealed 60% incorporation of deuterium at both *ortho* positions.

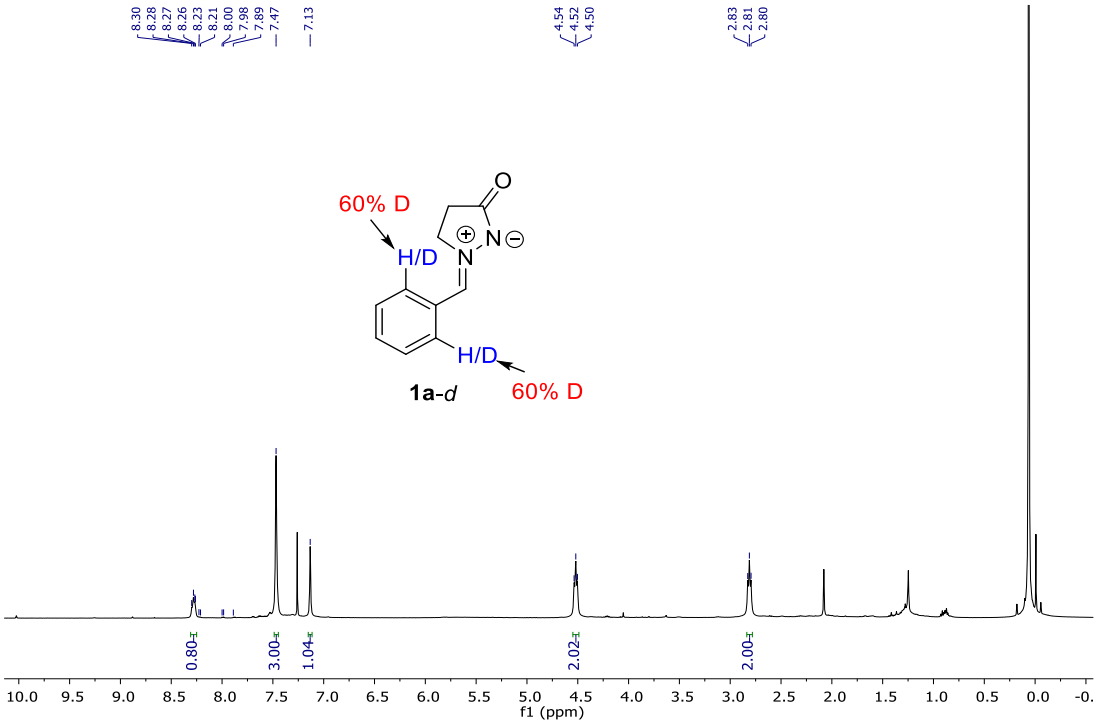

Figure S2. Deuterium exchange studies to determine the cleavage of C-H bond.

3.3 KIE measurements

A mixture of **1a** (1 equiv.) and **1a-*d*$_6$** (1 equiv.), **2a** (1 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (2.5 mol%), AgSbF6 (10 mol%), and DCE (2.0 mL) were charged into an oven-dried reaction tube. The reaction mixture was stirred at 65 ºC for 20 min. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using ethyl acetate : hexane to afford the mixed products. A KIE value (kH/kD = 4) was determined on the basis of ^{1}H NMR analysis.

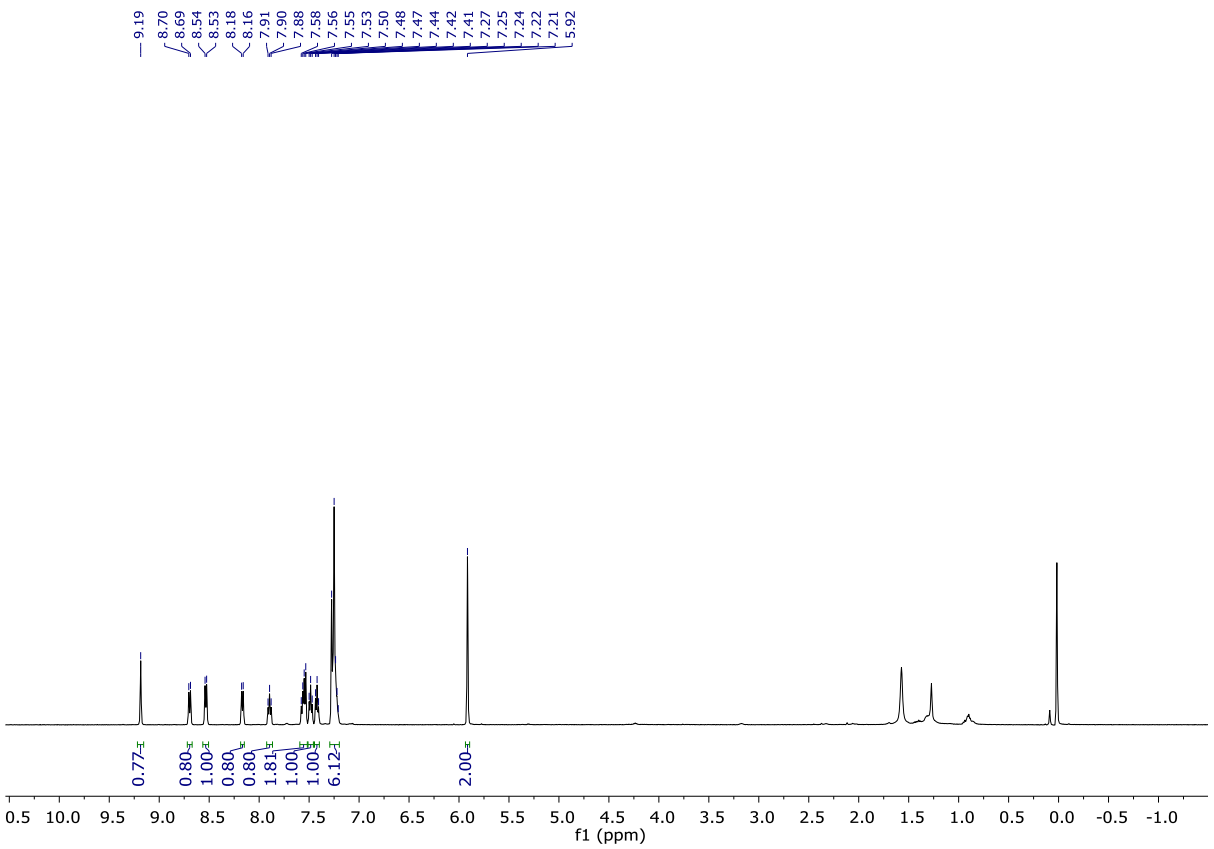

Figure S3. Kinetic isotope effect studies to identify the rate determining step of the reaction.

3.3 Competitive measurements (EWG *vs* EDG)

To an oven-dried reaction tube equipped with a magnetic stir bar, **1b** (1 equiv.), **1e** (1 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (2.5 mol%), $AgSbF_6$ (10 mol%) and 2 mL DCE. The resulting reaction mixture was stirred at room temperature for 1 h. Then, trimethoxy benzene (1 equiv.) was added as standard in the reaction mixture and filtered through column bed. The crude mixture containing a mixture of remaining starting materials and products was directly submitted for ^{1}H NMR analysis. The results of ^{1}H NMR analysis revealed that product **3b**/**3d** has been formed with a ratio of 1:1.83. It concludes that **1b** reacts 1.83 times faster than **1d**.

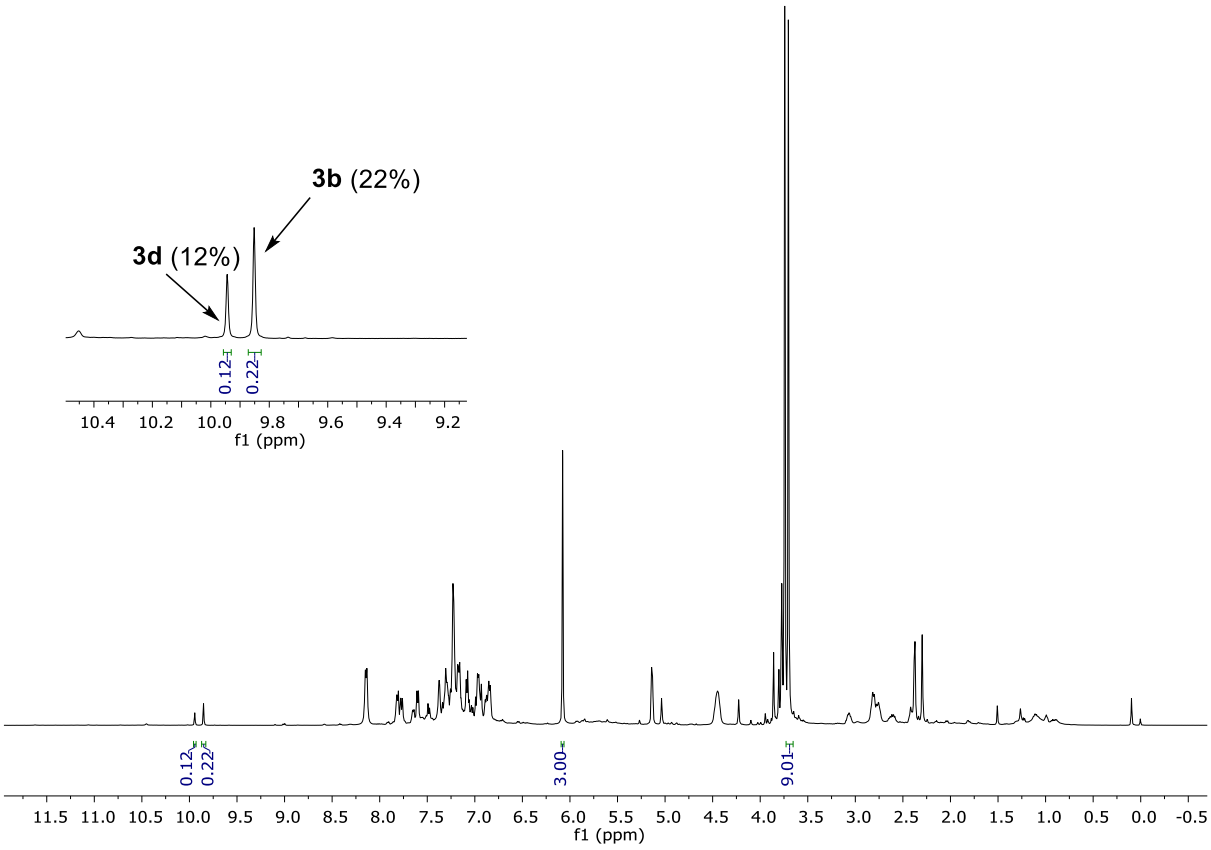

Figure S4. Competitive reactivity measurements: electron-withdrawing azomethine ylide *vs* electron-donating azomethine ylide.

References

1. (a) Cao, D. C.; Kim, H.; Kwak, J.; Joung, S. *Org. Lett*. **2022**, *24*, 1974–1978. (b) Yin, C.; Lin, L.; Zhang, D.; Feng, J.; Liu, X.; Feng, X. *J. Org. Chem*. **2015**, *80*, 9691–9699
2. Sheng, G. R.; Huang, K.; Chi, Z. H.; Ding, H. L.; Xing, Y. P.; Lu, P.; Wang, Y. G. *Org. Lett.* **2014**, *16*, 5096-5099.

Copies of ^{1}H, ^{13}C NMR and mass spectra

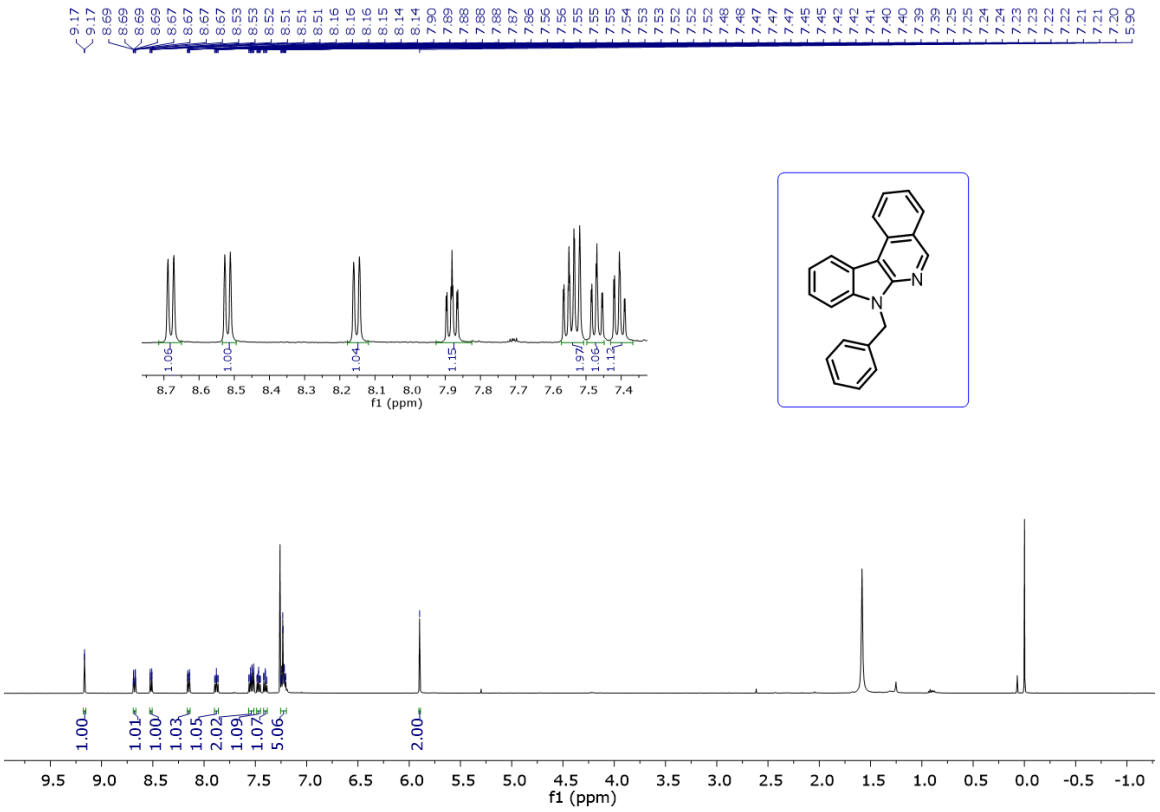

Figure S5. ^{1}H NMR of **3a** (500 MHz, $CDCl_3$)

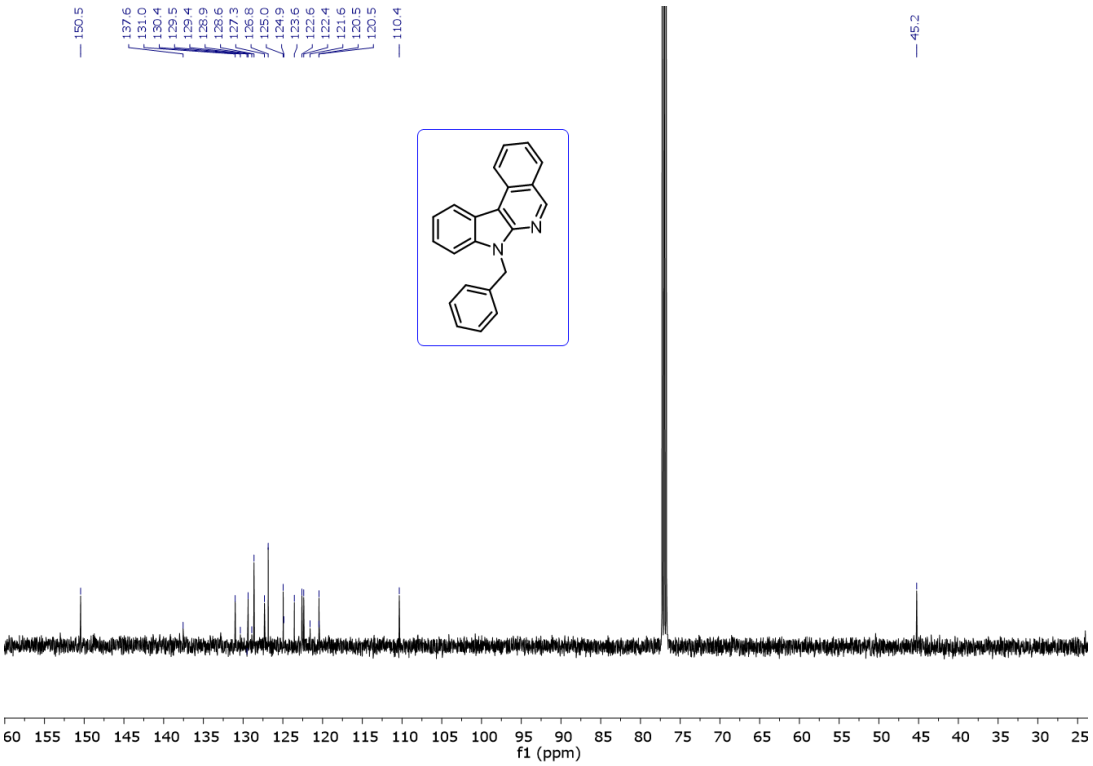

Figure S6. ^{13}C NMR of **3a** (125 MHz, $CDCl_3$)

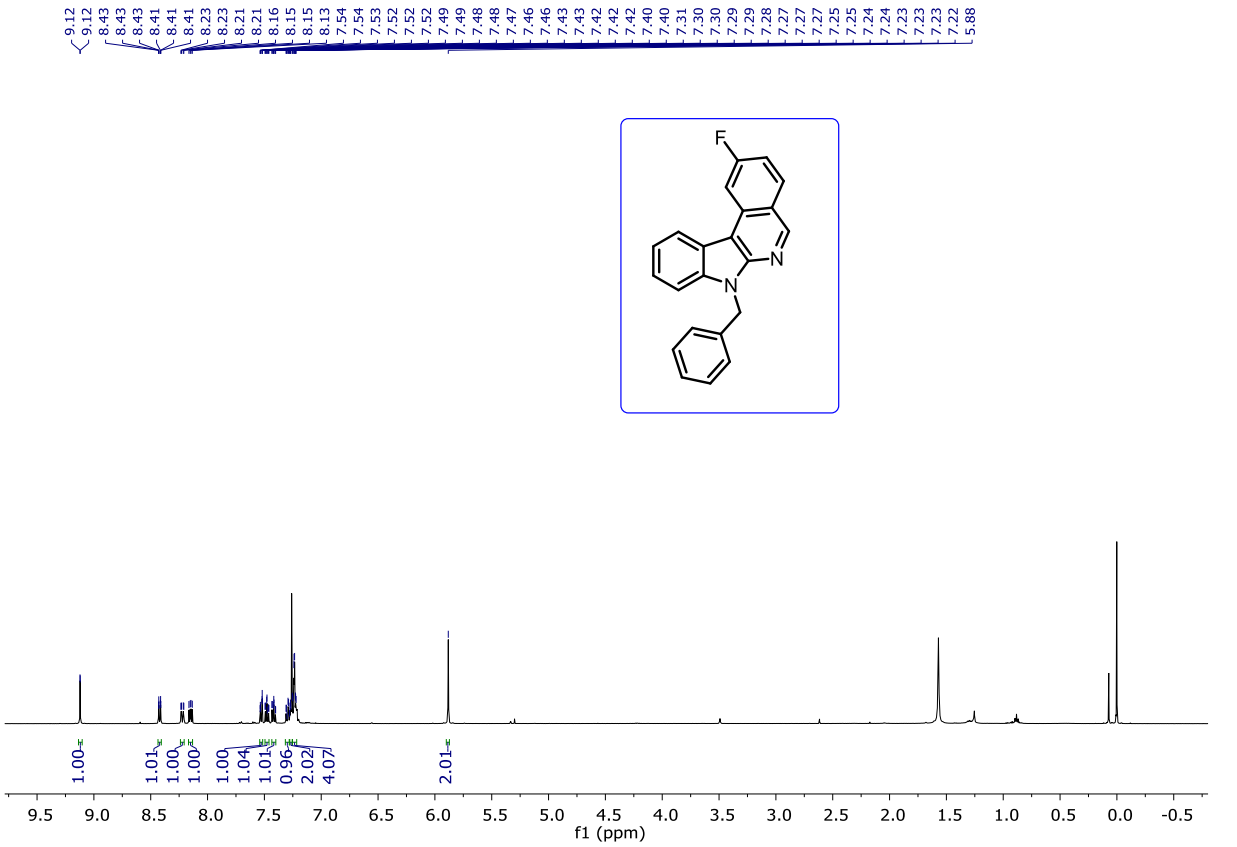

Figure S7. ^{1}H NMR of **3b** (500 MHz, $CDCl_3$)

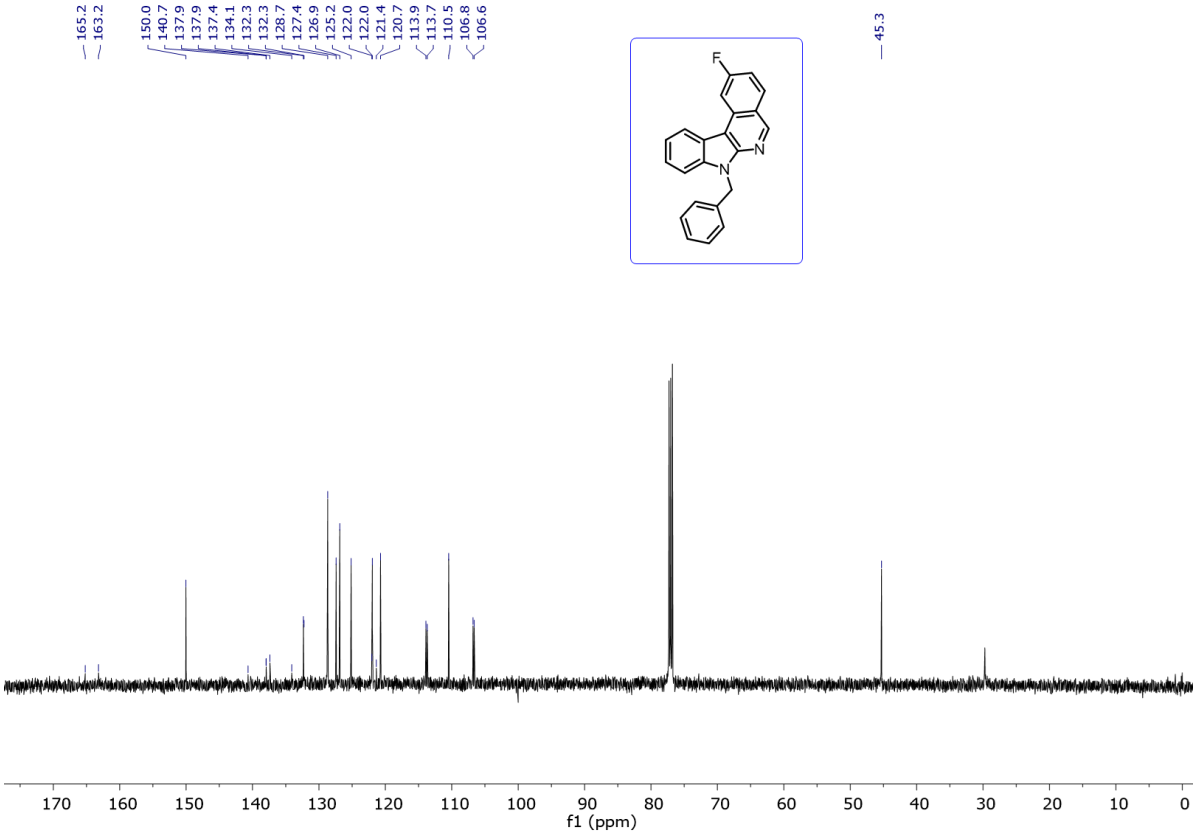

Figure S8. ^{13}C NMR of **3b** (125 MHz, $CDCl_3$)

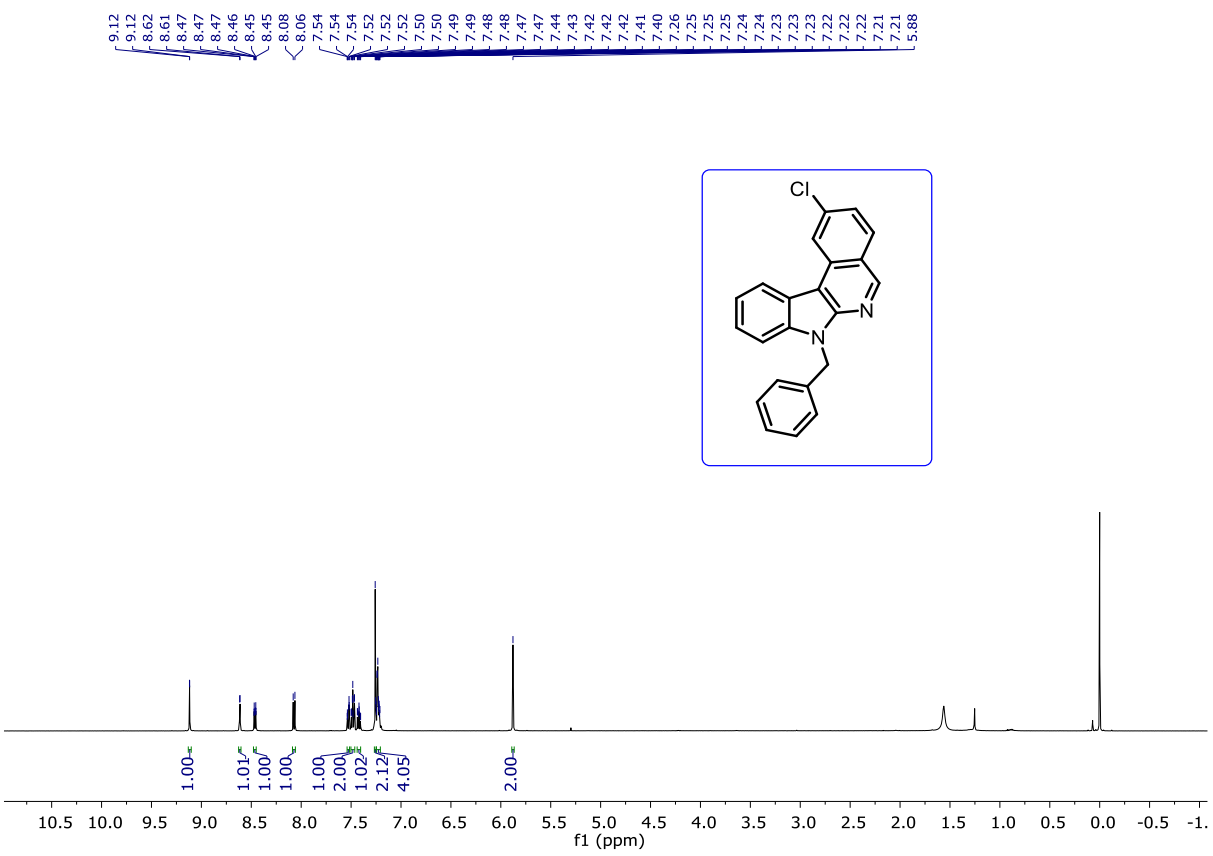

Figure S9. ^{1}H NMR of **3c** (500 MHz, $CDCl_3$)

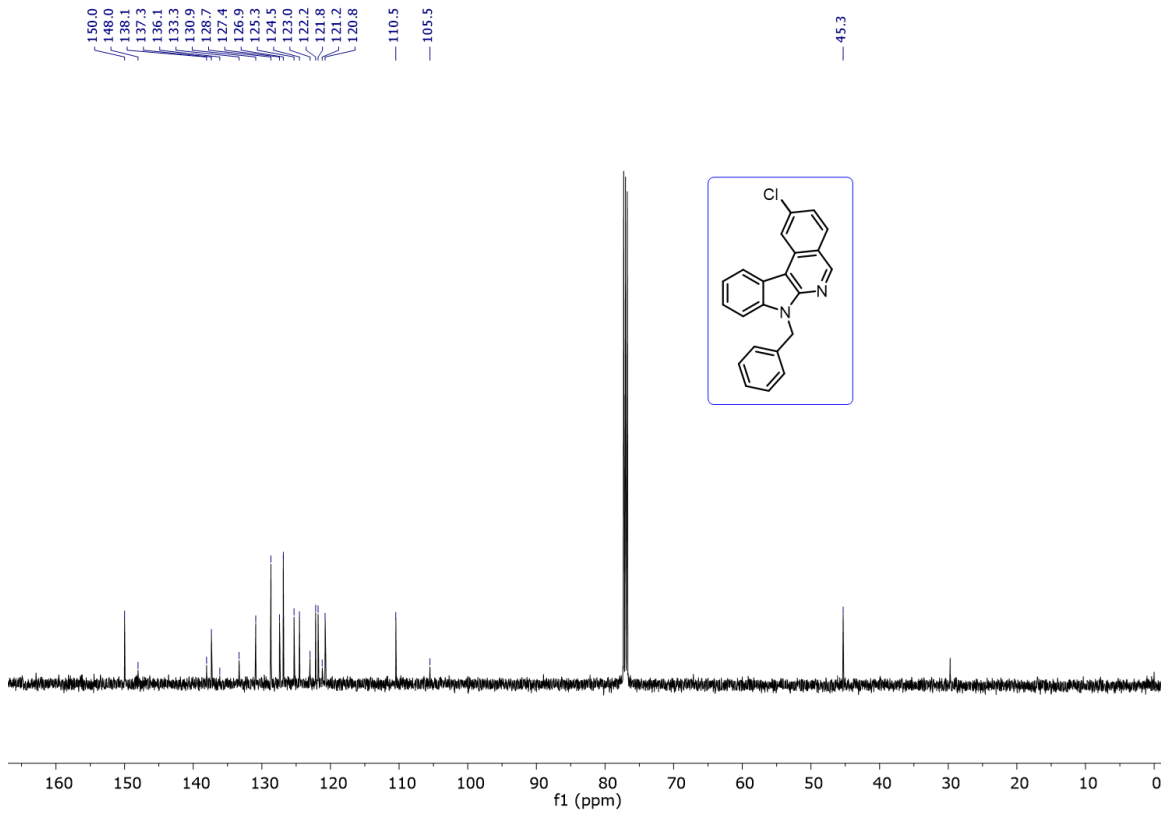

Figure S10. ^{13}C NMR of **3c** (125 MHz, $CDCl_3$)

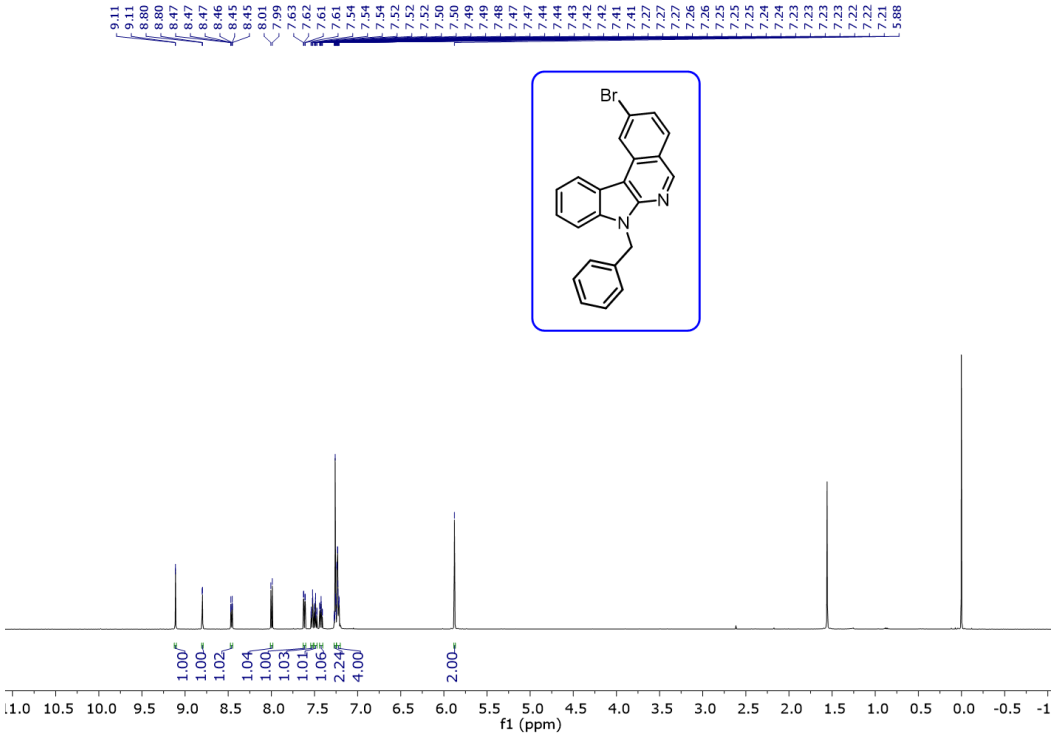

Figure S11. ^{1}H NMR of **3d** (500 MHz, $CDCl_3$)

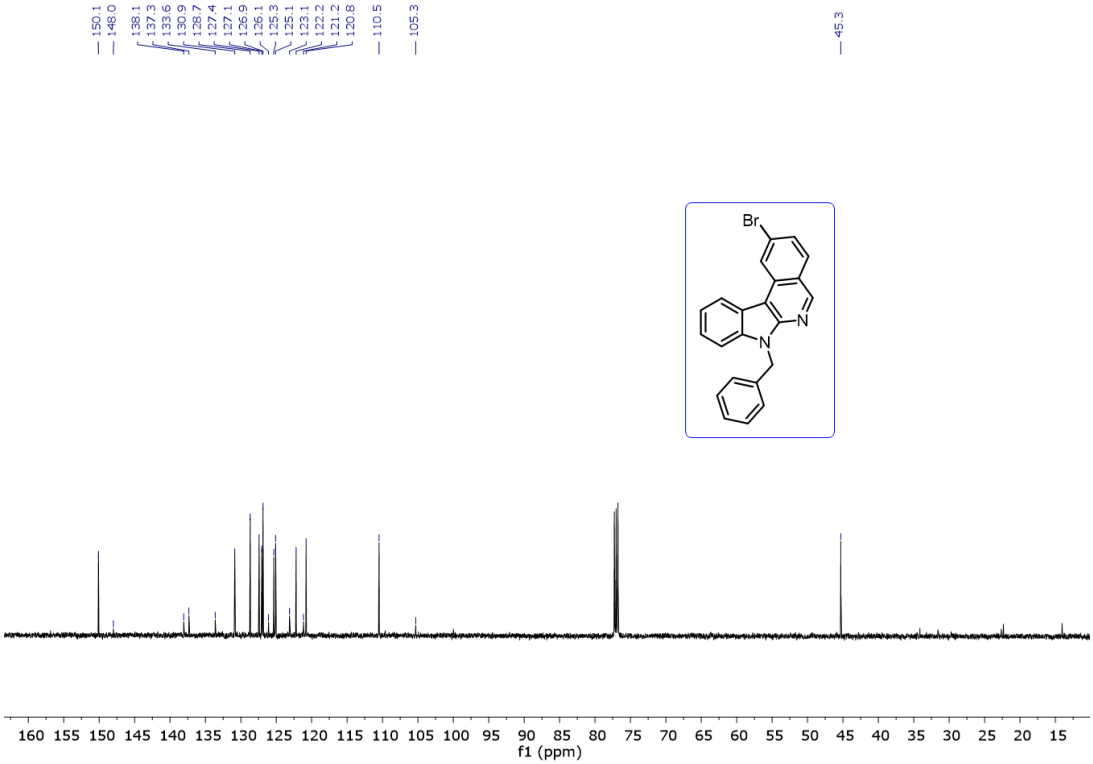

Figure S12. ^{13}C NMR of **3d** (125 MHz, $CDCl_3$)

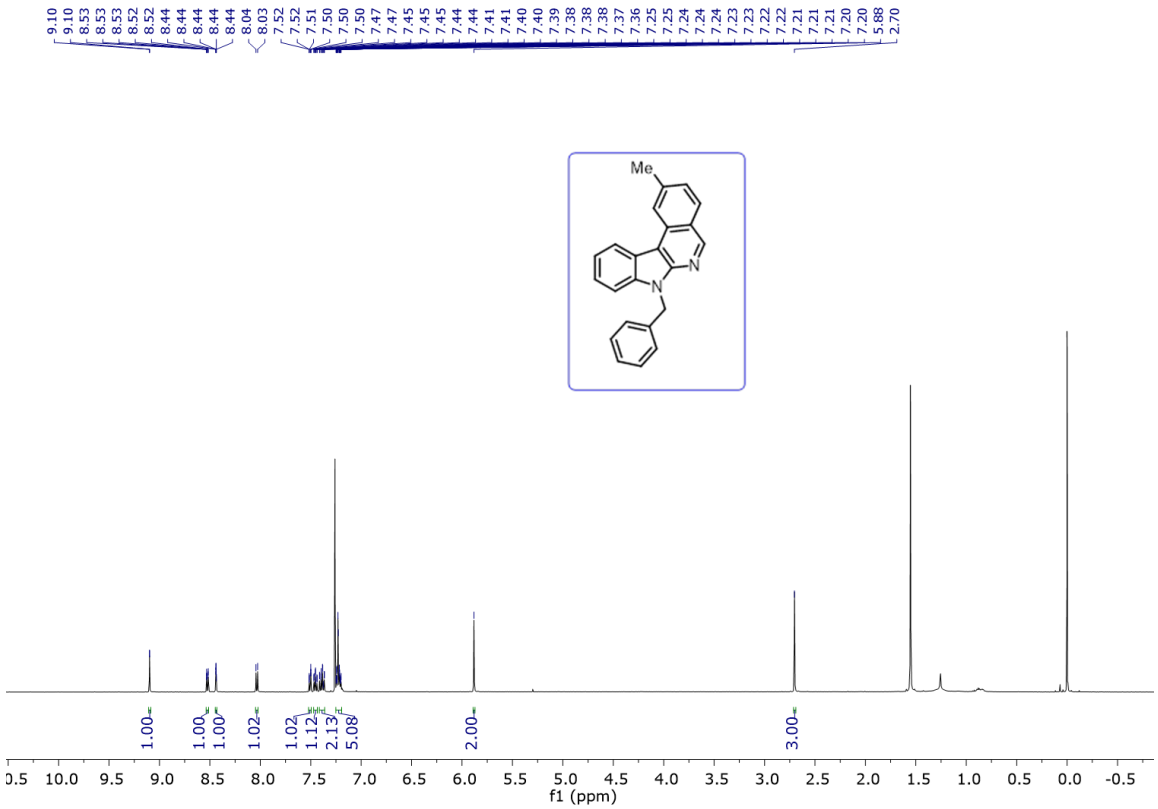

Figure S13. ^{1}H NMR of **3e** (500 MHz, $CDCl_3$)

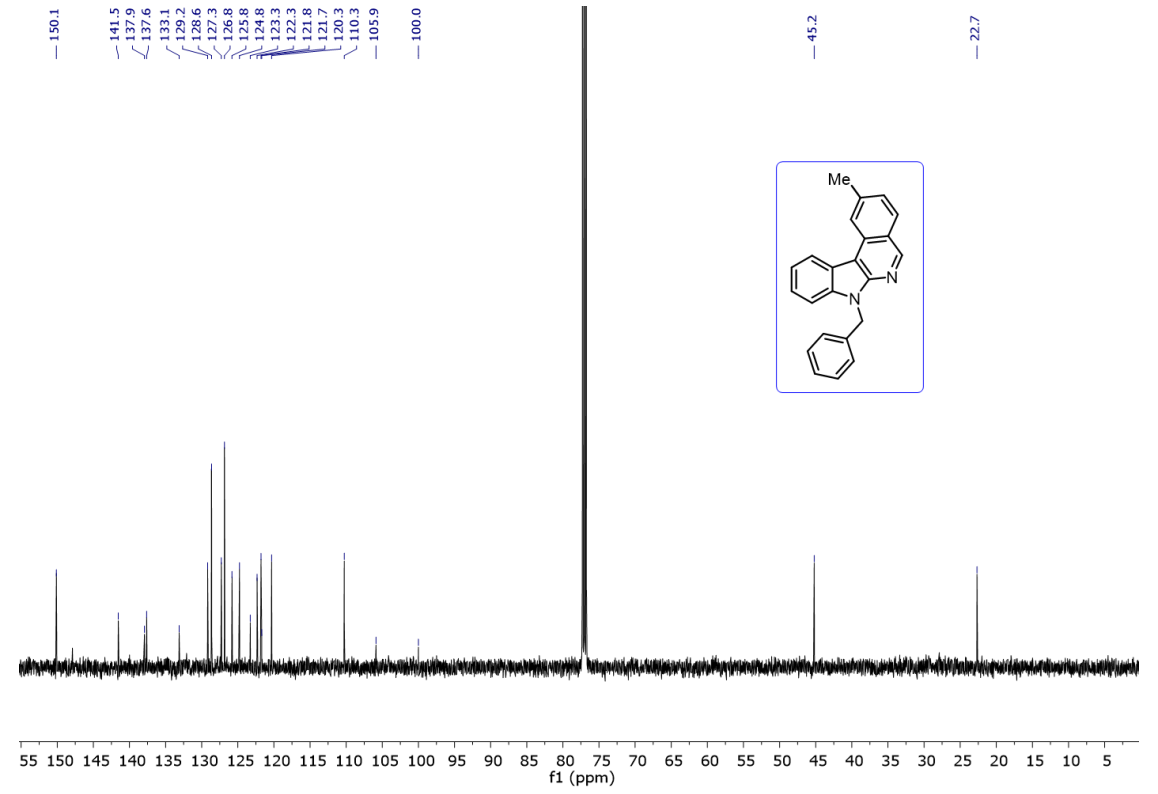

Figure S14. ^{13}C NMR of **3e** (125 MHz, $CDCl_3$)

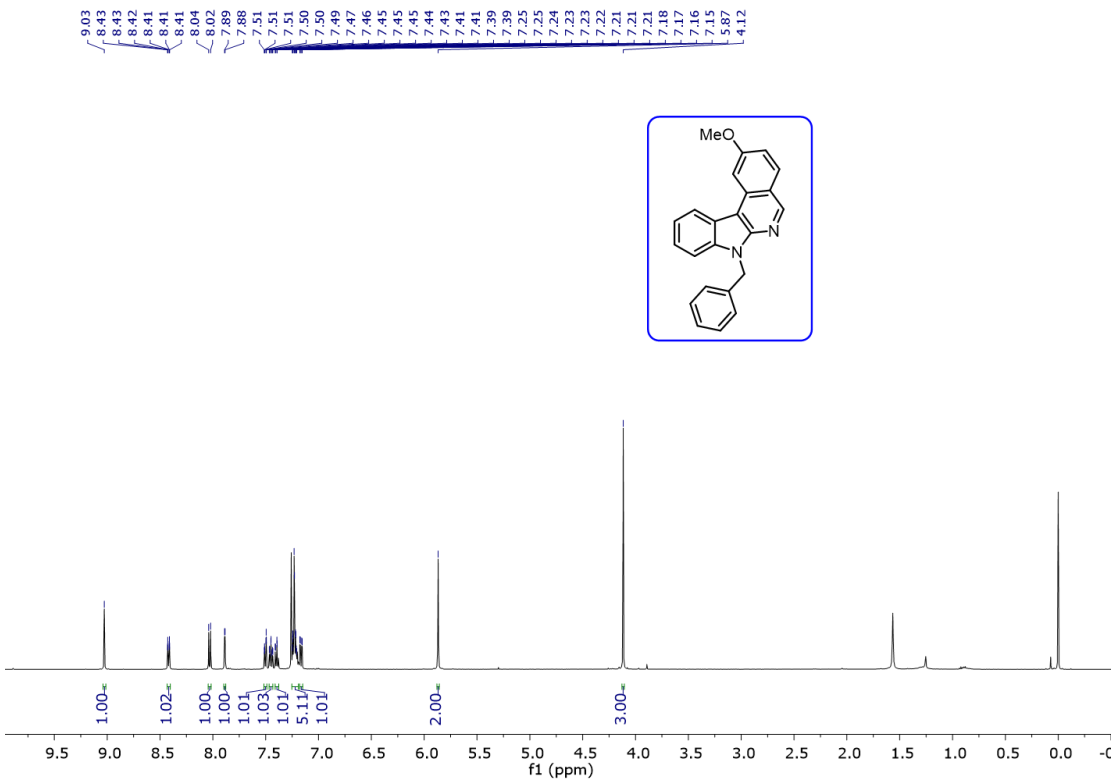

Figure S15. ^{1}H NMR of **3f** (500 MHz, $CDCl_3$)

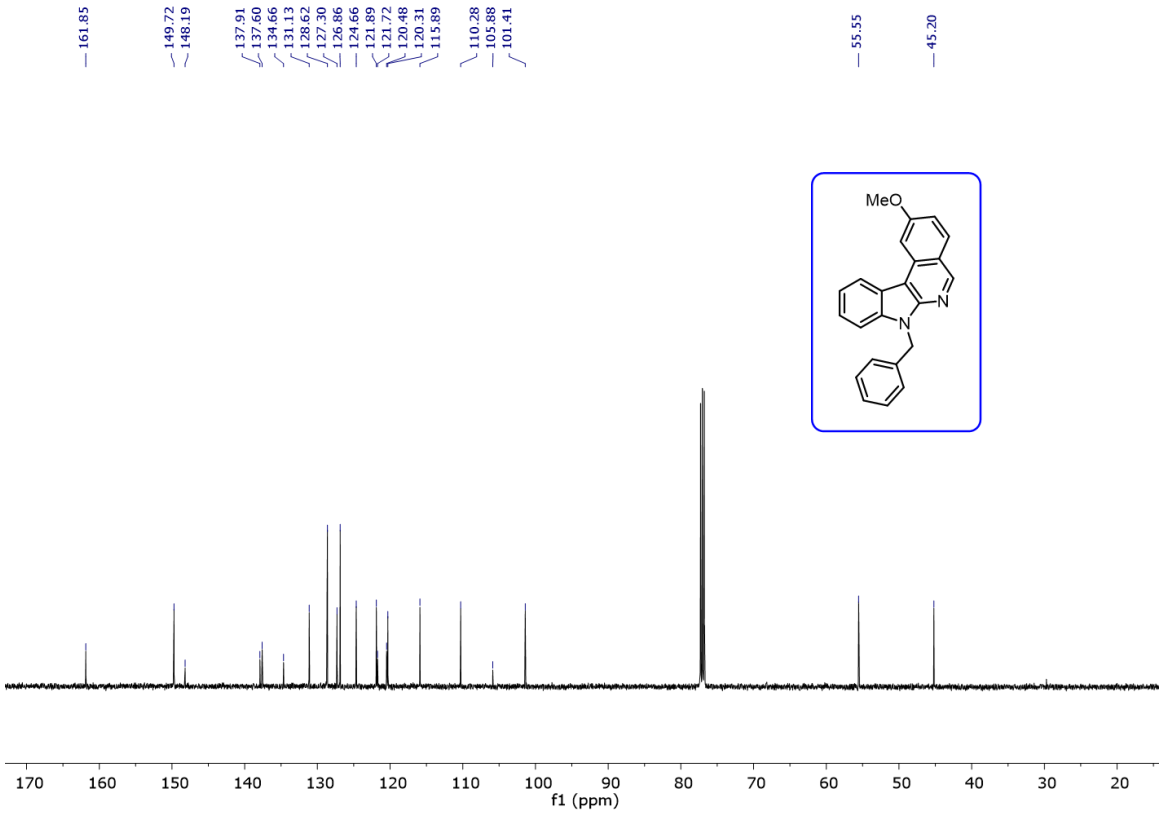

Figure S16. ^{13}C NMR of **3f** (125 MHz, $CDCl_3$)

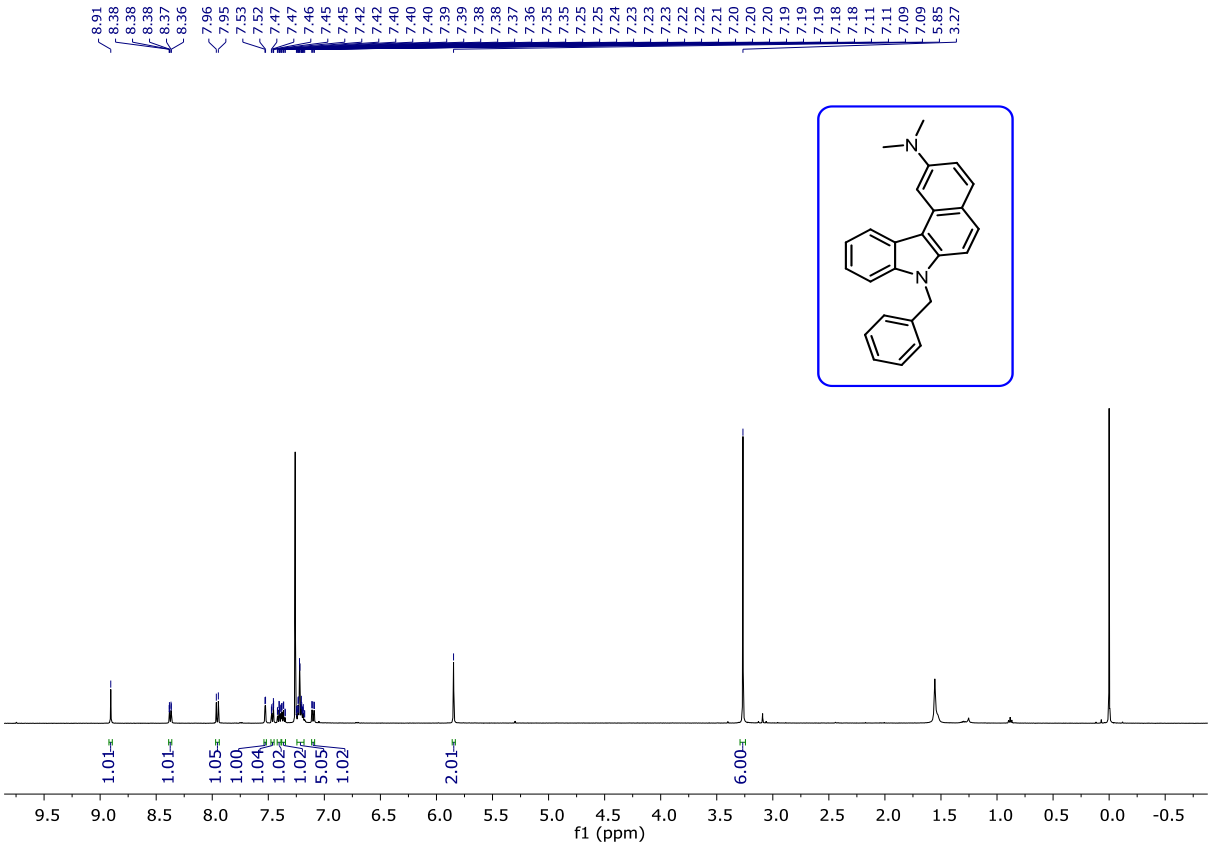

Figure S17. ^{1}H NMR of **3g** (500 MHz, $CDCl_3$)

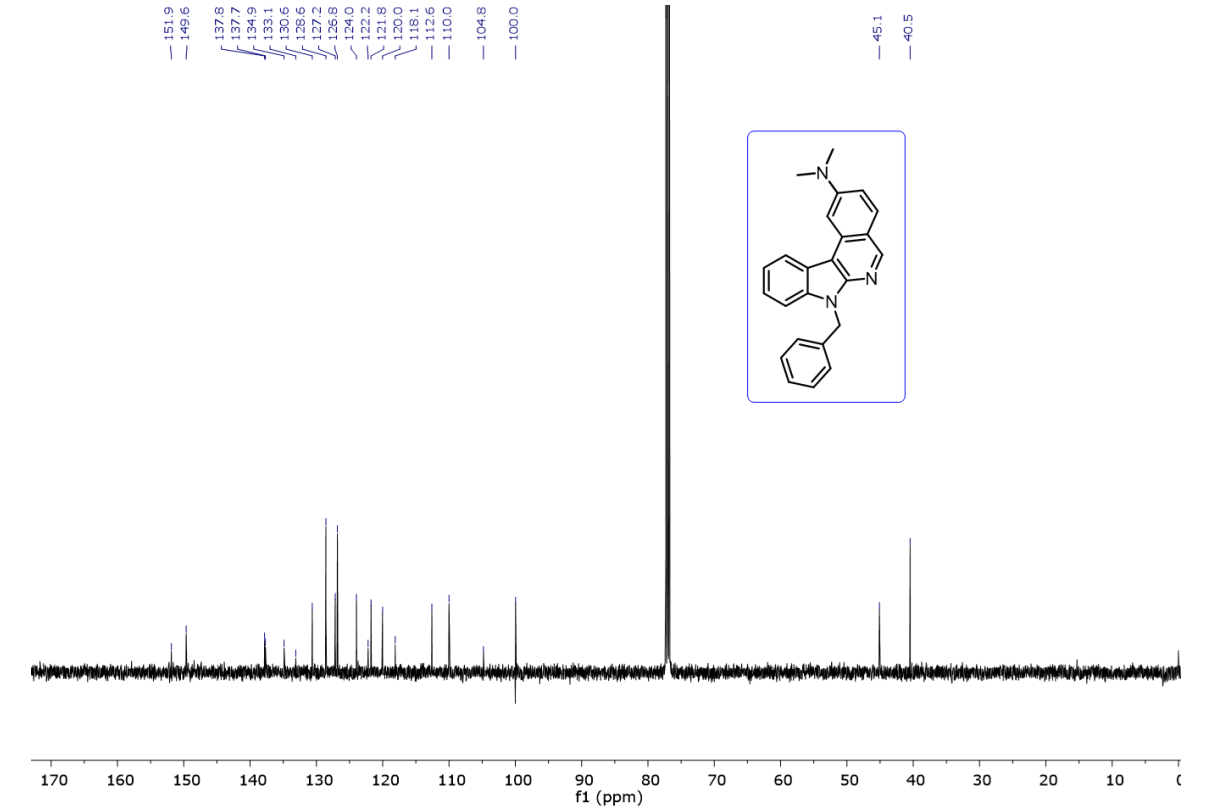

Figure S18. ^{13}C NMR of **3g** (125 MHz, $CDCl_3$)

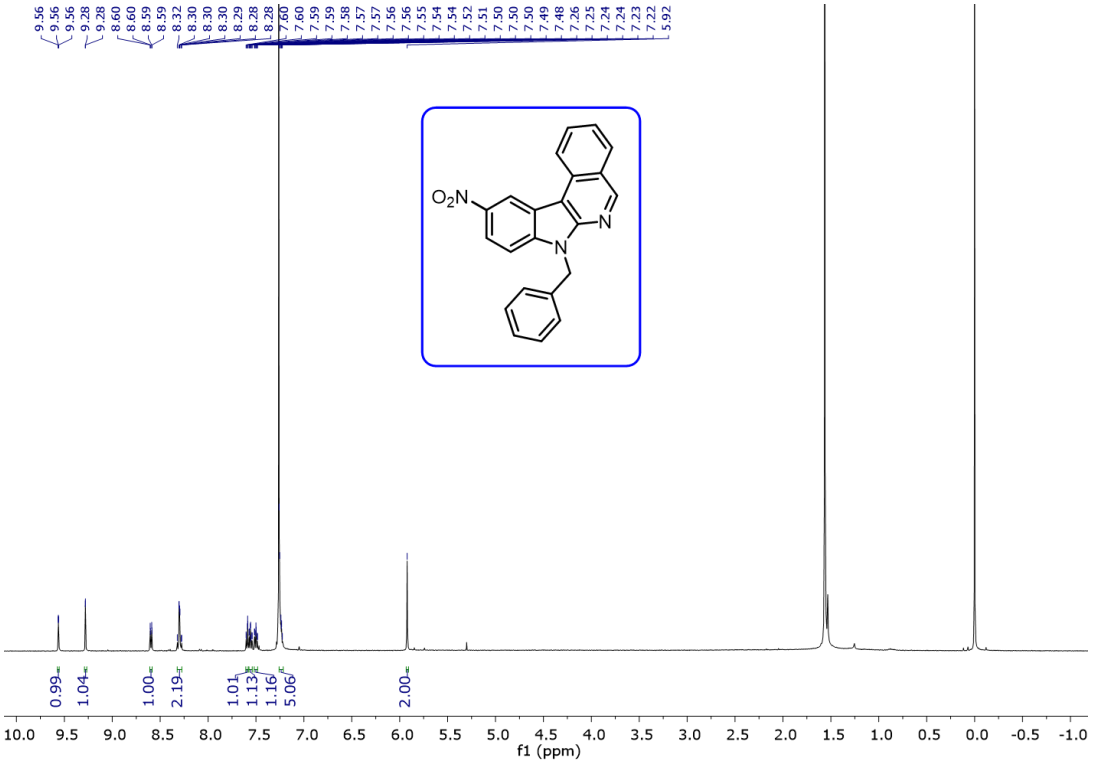

Figure S19. ^{1}H NMR of **3h** (500 MHz, $CDCl_3$) (5-nitro)

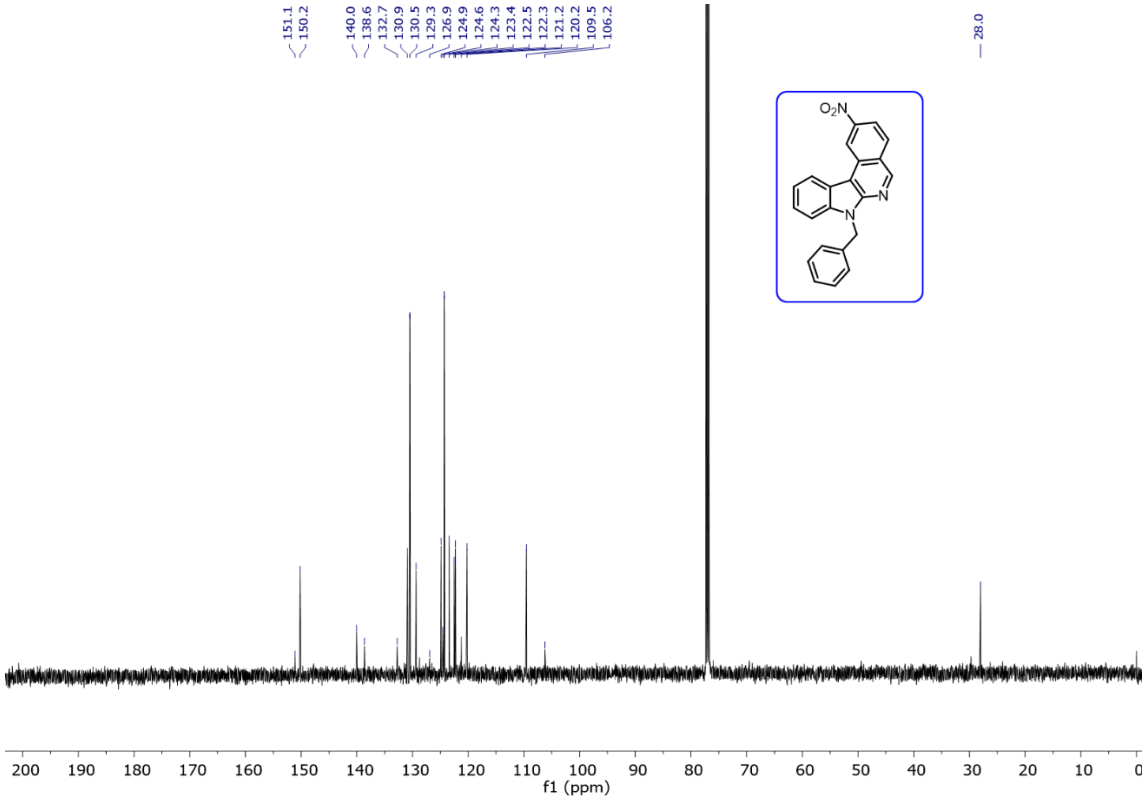

Figure S20. ^{13}C NMR of **3h** (125 MHz, $CDCl_3$)

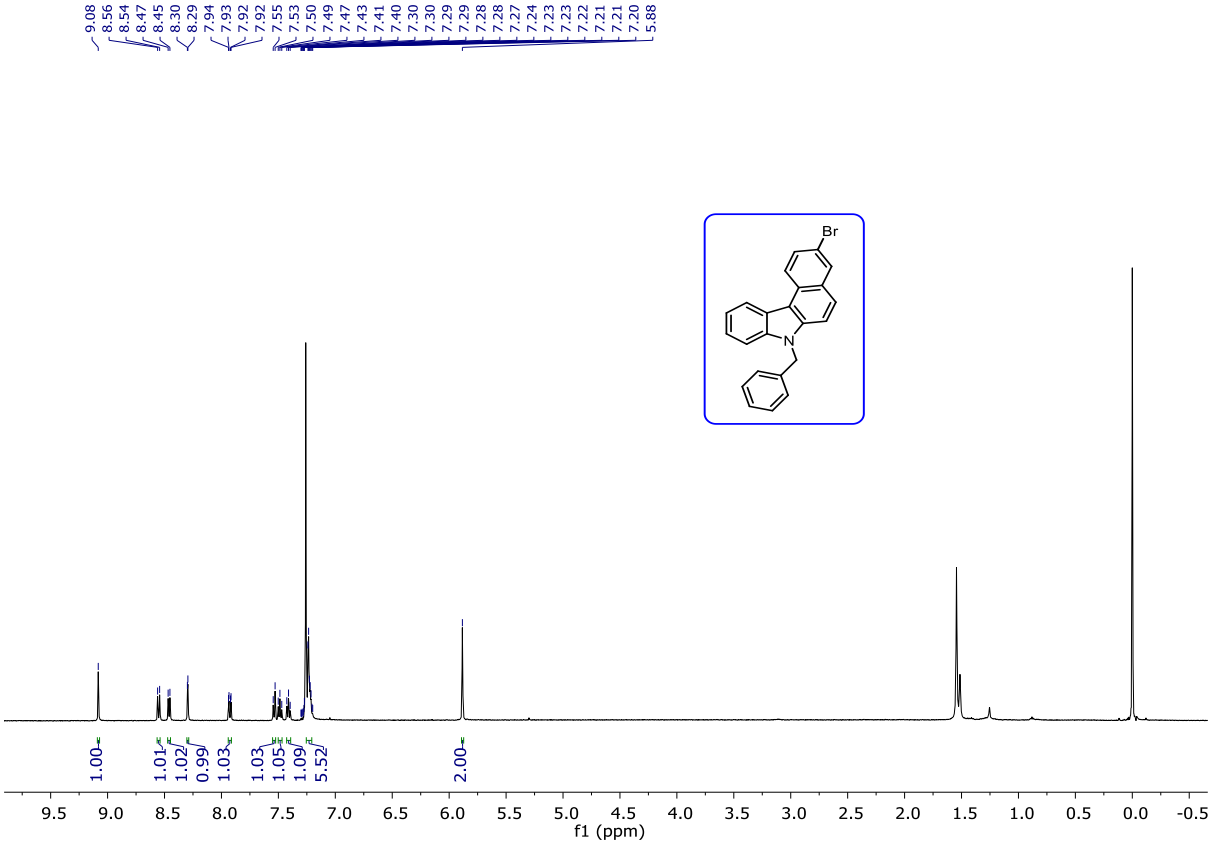

Figure S21. ^{1}H NMR of **3i** (500 MHz, $CDCl_3$)

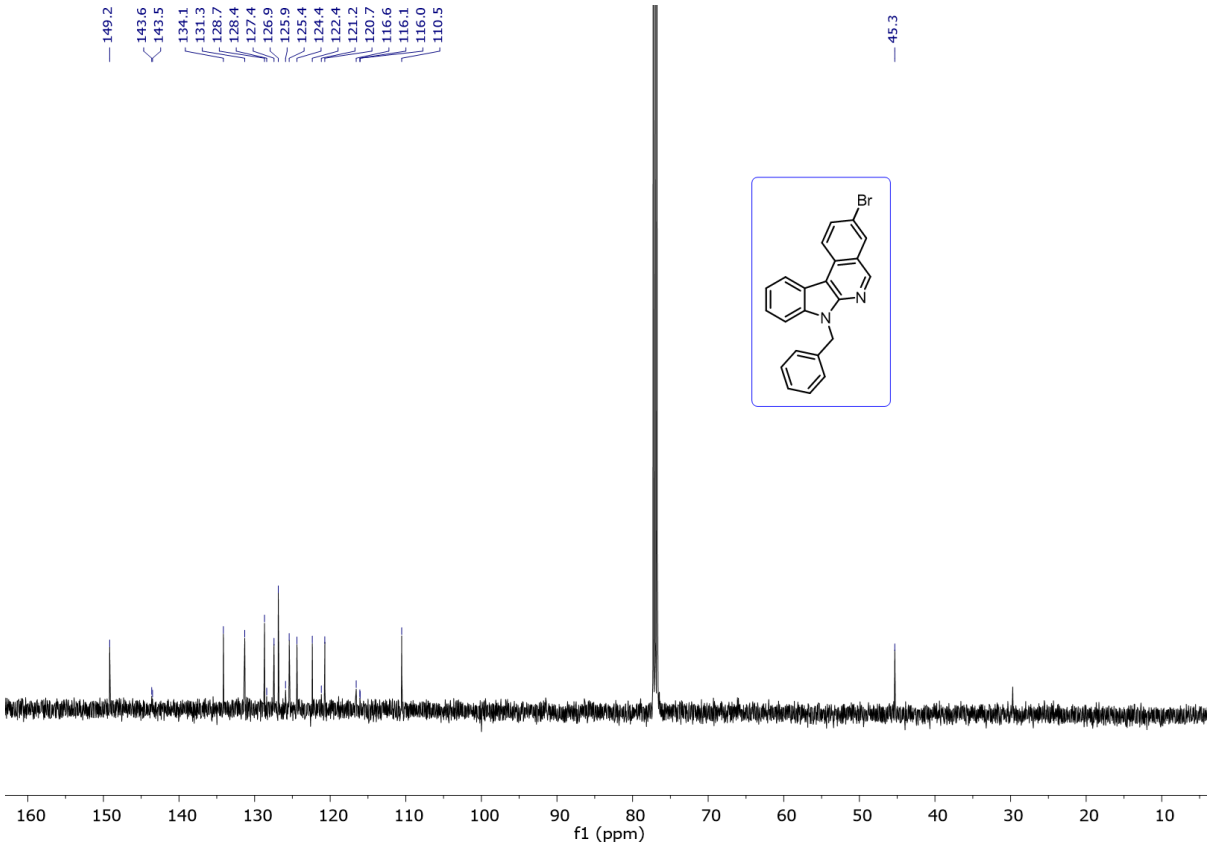

Figure S22. ^{13}C NMR of **3i** (125 MHz, $CDCl_3$)

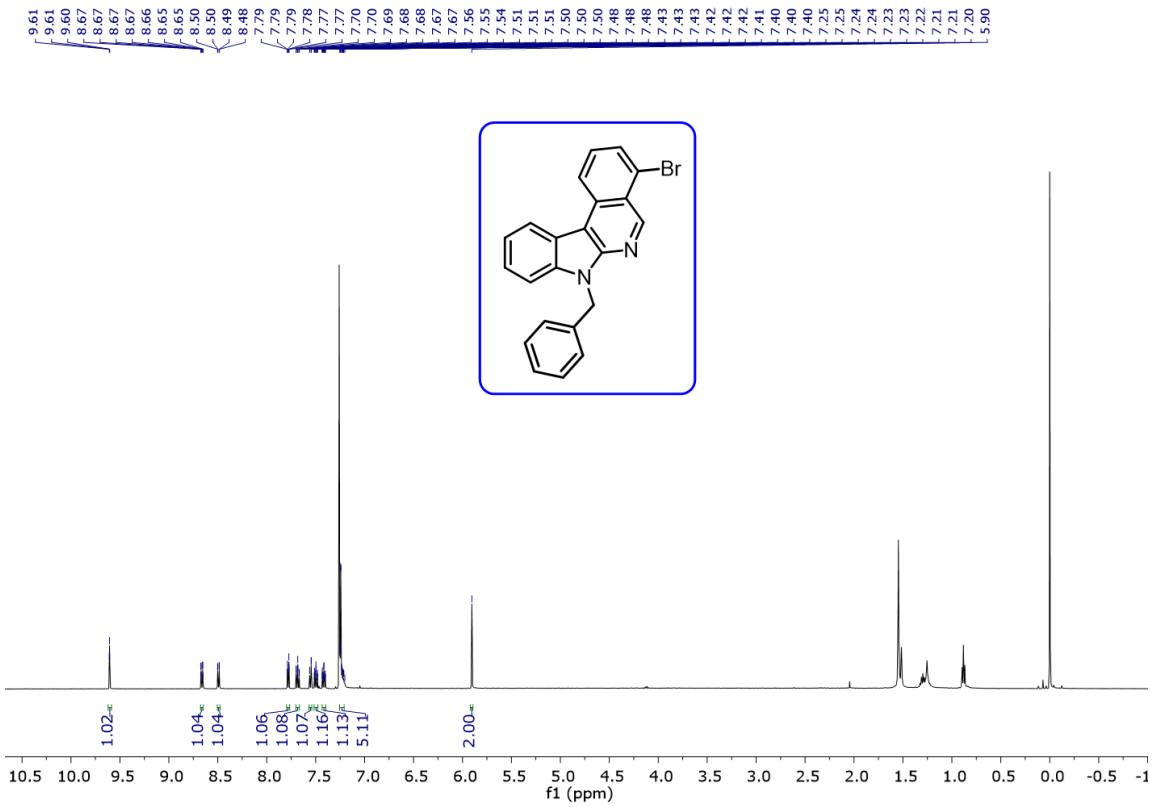

Figure S23. ^{1}H NMR of **3j** (500 MHz, $CDCl_3$)

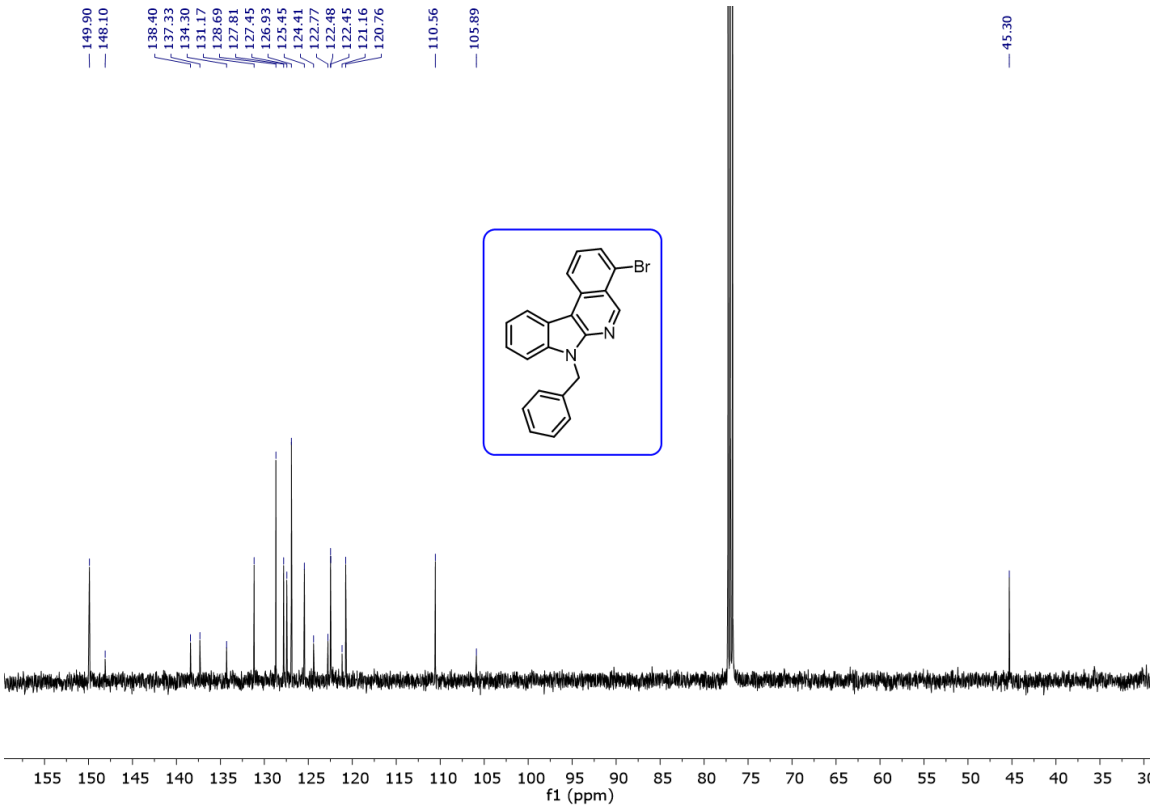

Figure S24. ^{13}C NMR of **3j** (125 MHz, $CDCl_3$)

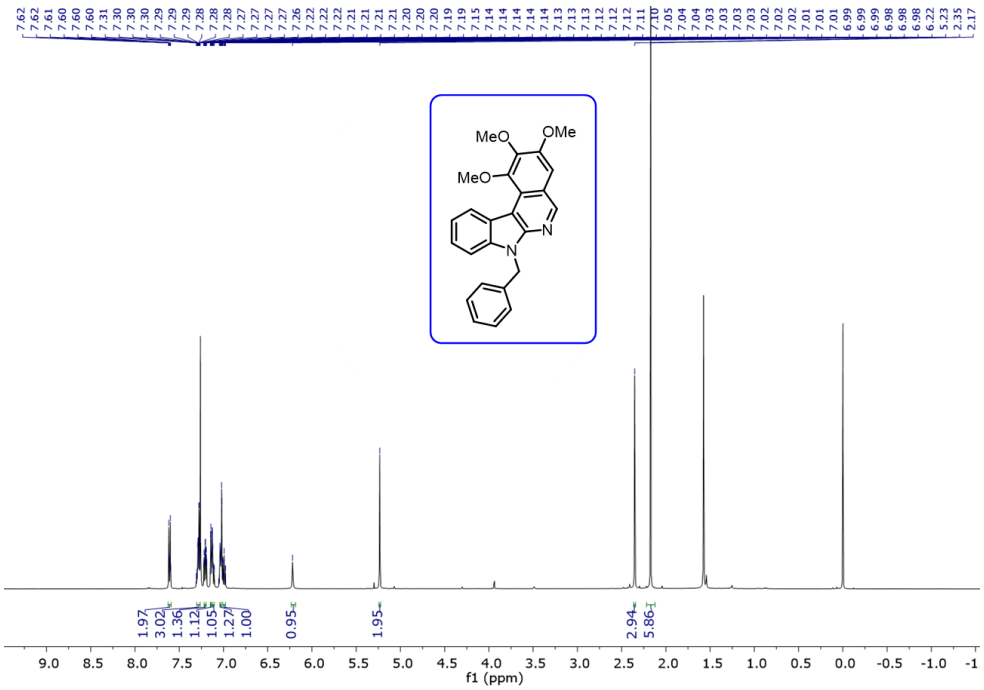

Figure S25. ^{1}H NMR of **3k** (500 MHz, $CDCl_3$)

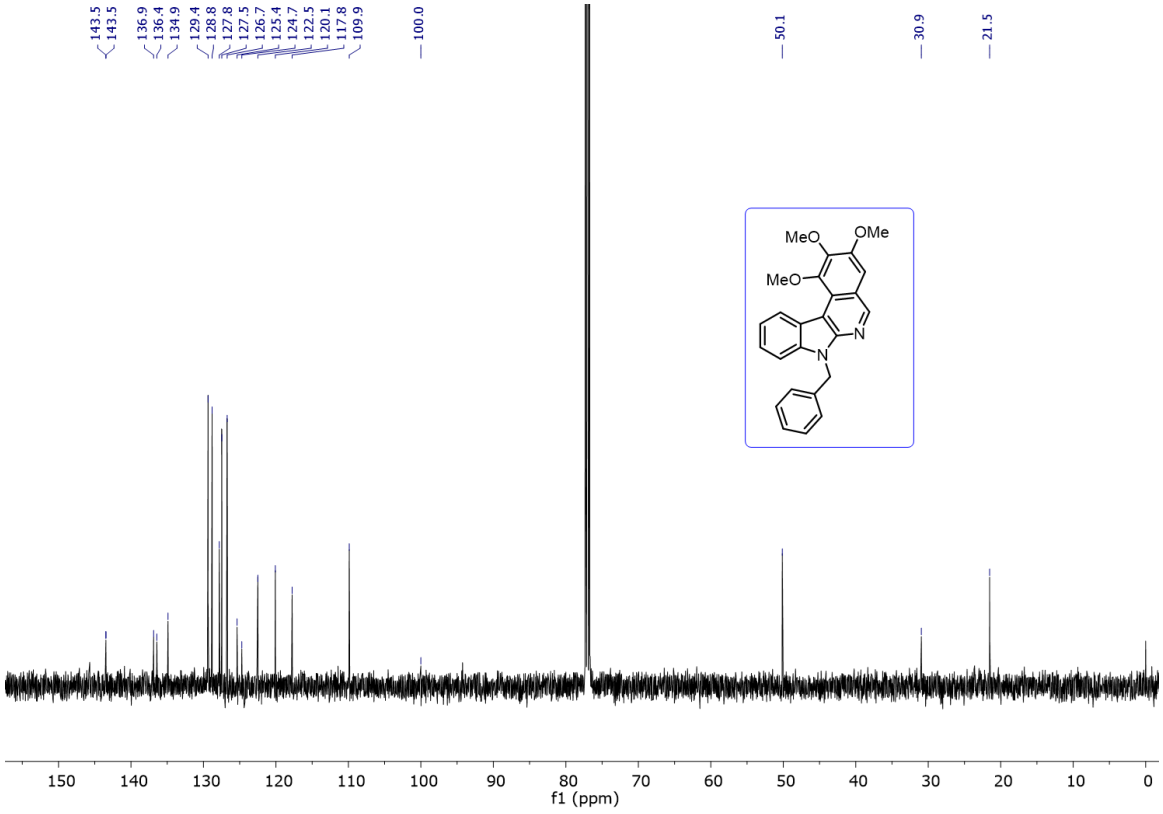

Figure S26. ^{13}C NMR of **3k** (125 MHz, $CDCl_3$)

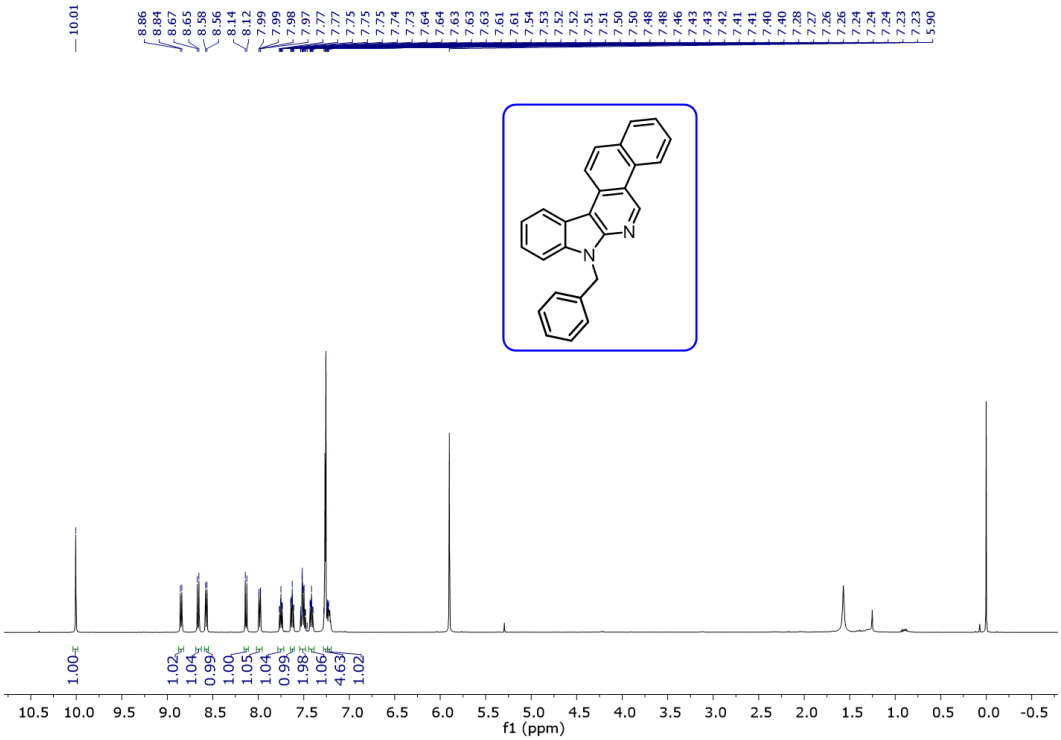

Figure S27. ^{1}H NMR of **3l** (500 MHz, $CDCl_3$)-

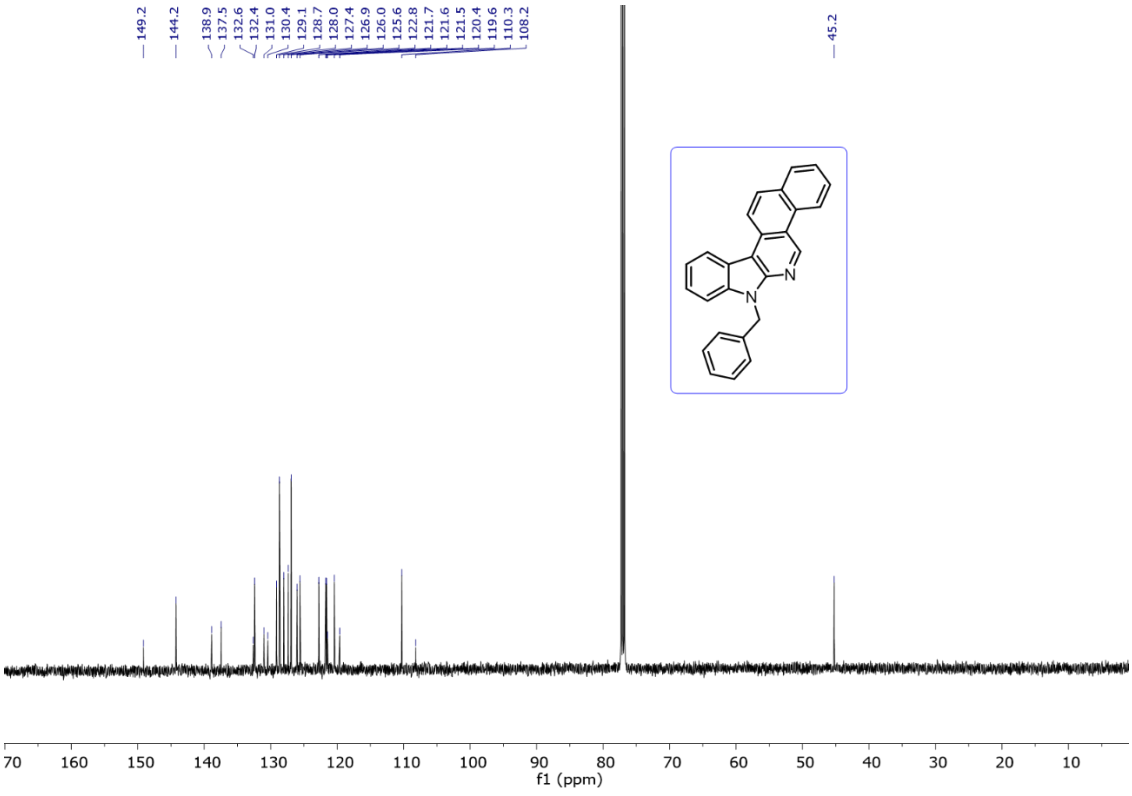

Figure S28. ^{13}C NMR of **3l** (125 MHz, $CDCl_3$)

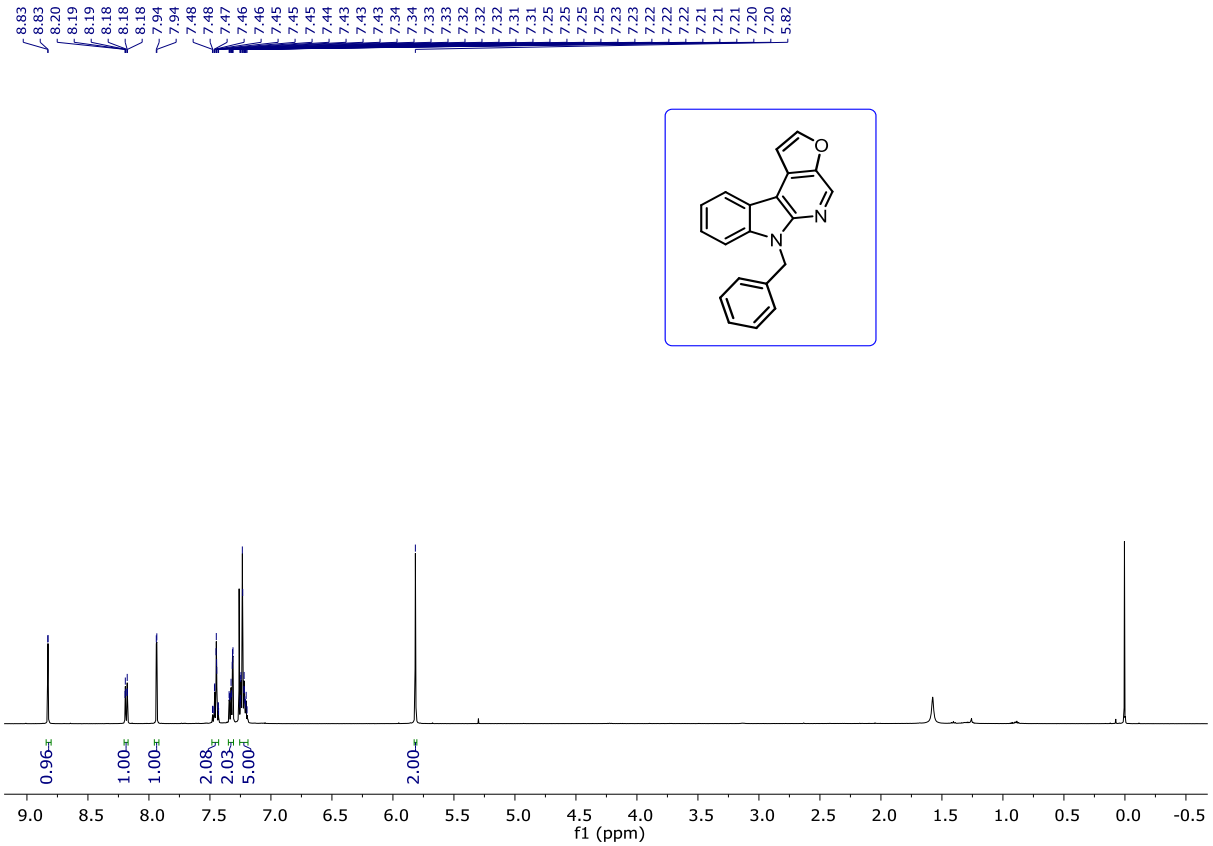

Figure S29. ^{1}H NMR of **3m** (500 MHz, $CDCl_3$)

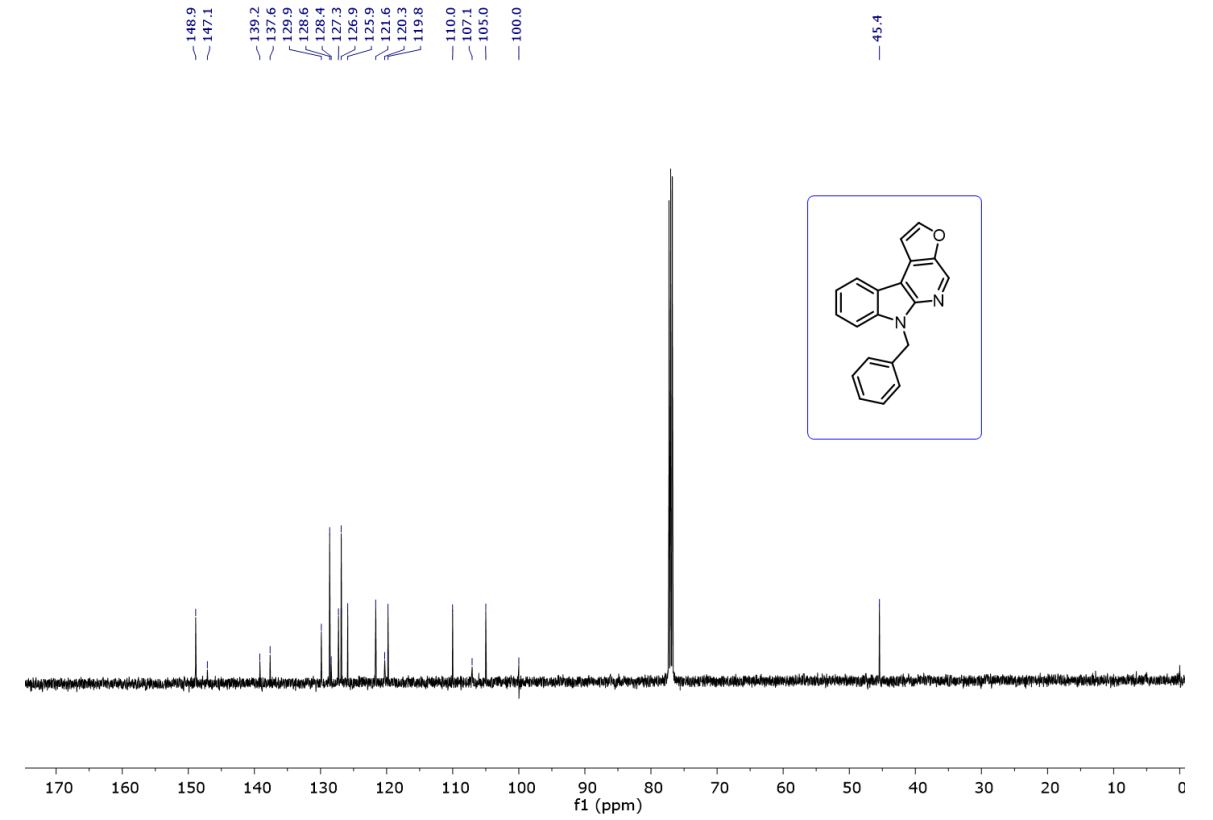

Figure S30. ^{13}C NMR of **3m** (125 MHz, $CDCl_3$)

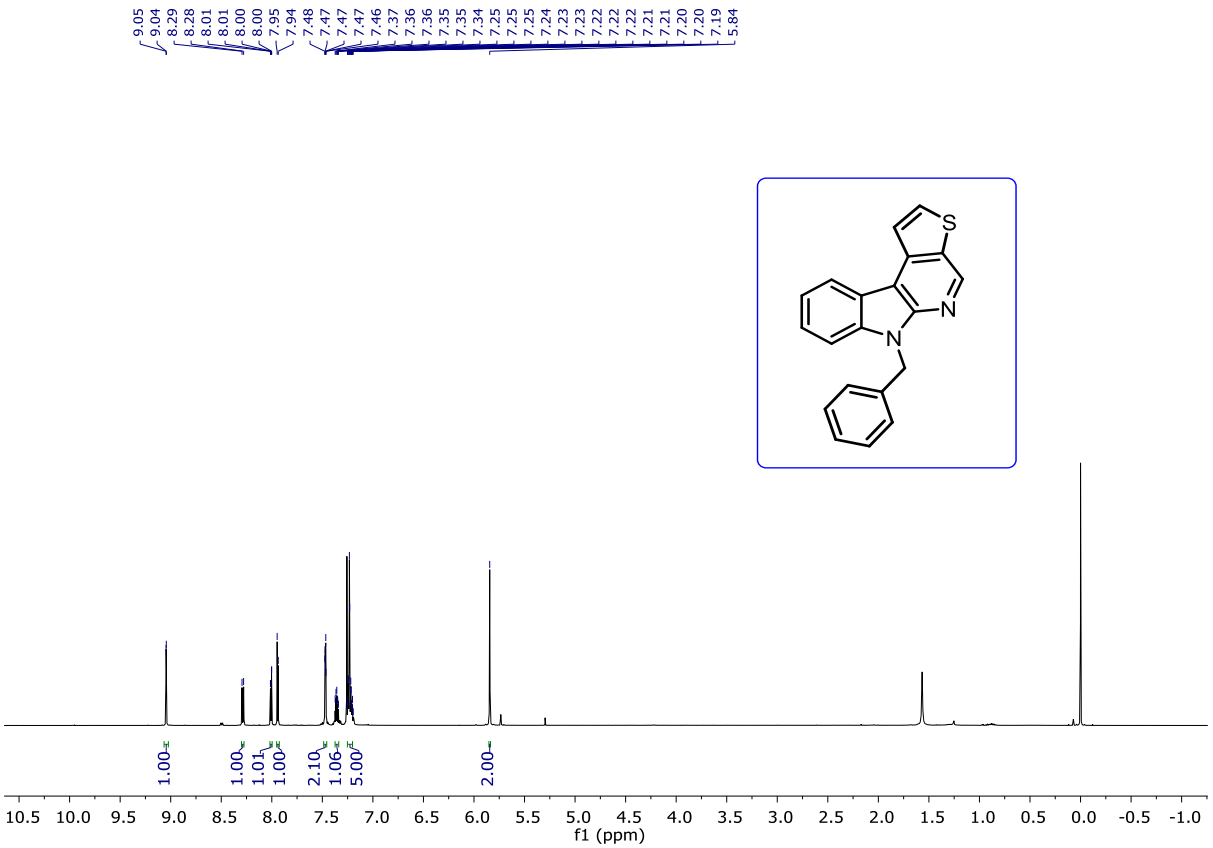

Figure S31. ^{1}H NMR of **3n** (500 MHz, $CDCl_3$)

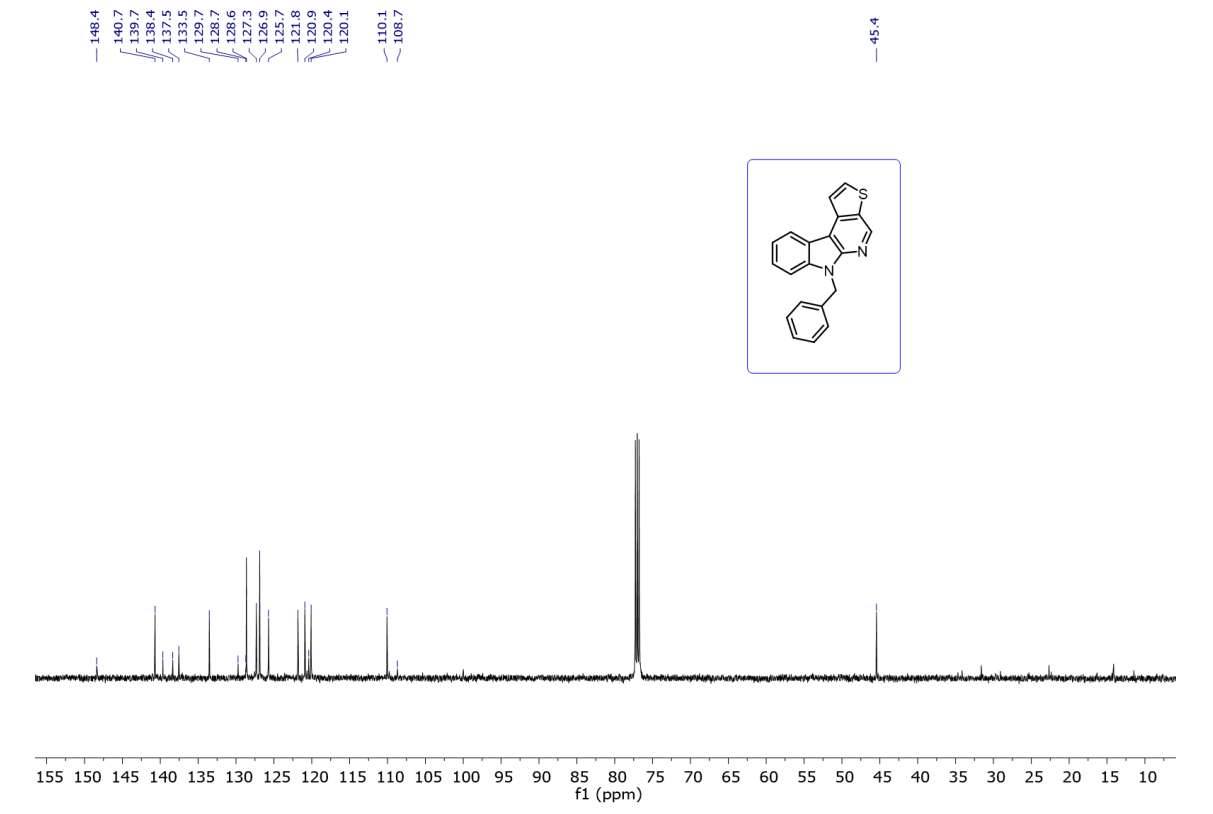

Figure S32. ^{13}C NMR of **3n** (125 MHz, $CDCl_3$)

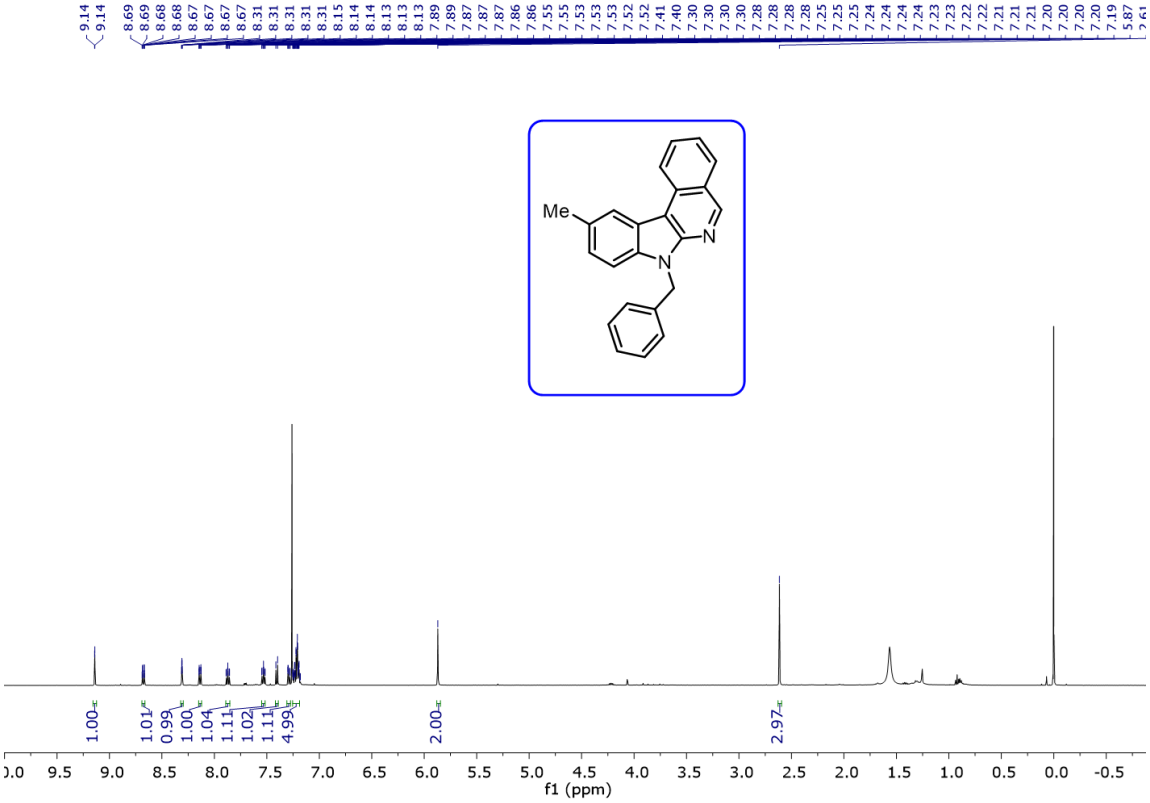

Figure S33. ^{1}H NMR of **3p** (500 MHz, $CDCl_3$)

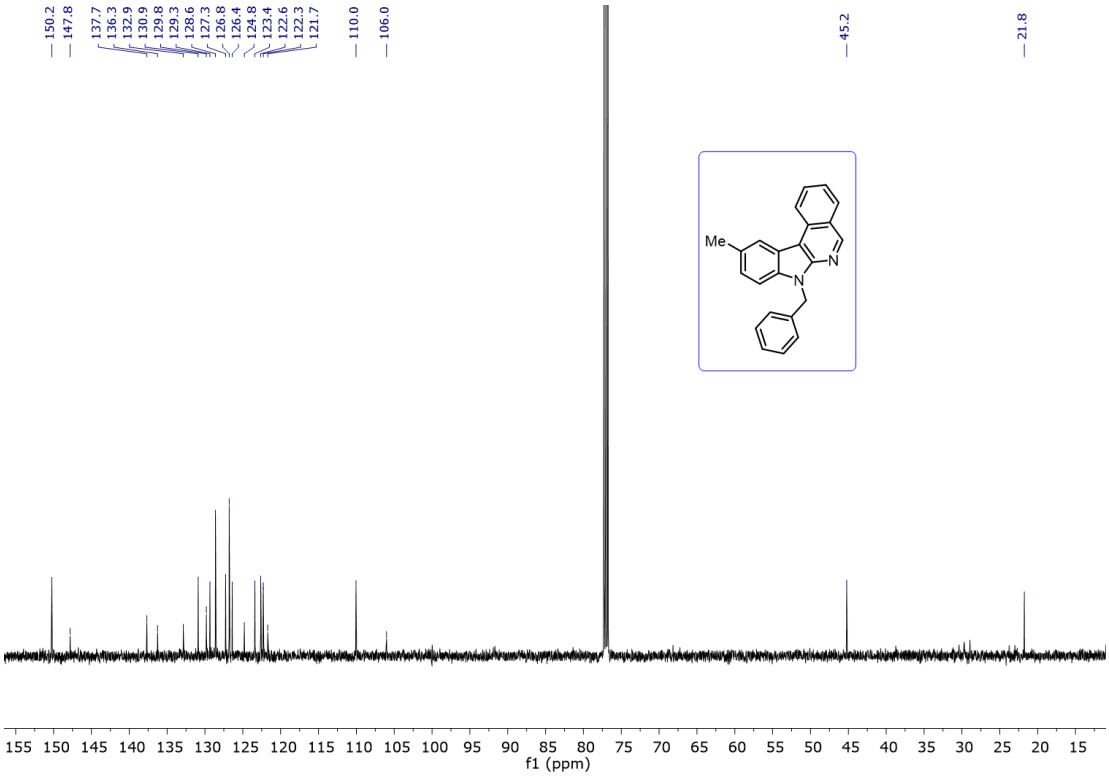

Figure S34. ^{13}C NMR of **3p** (125 MHz, $CDCl_3$)

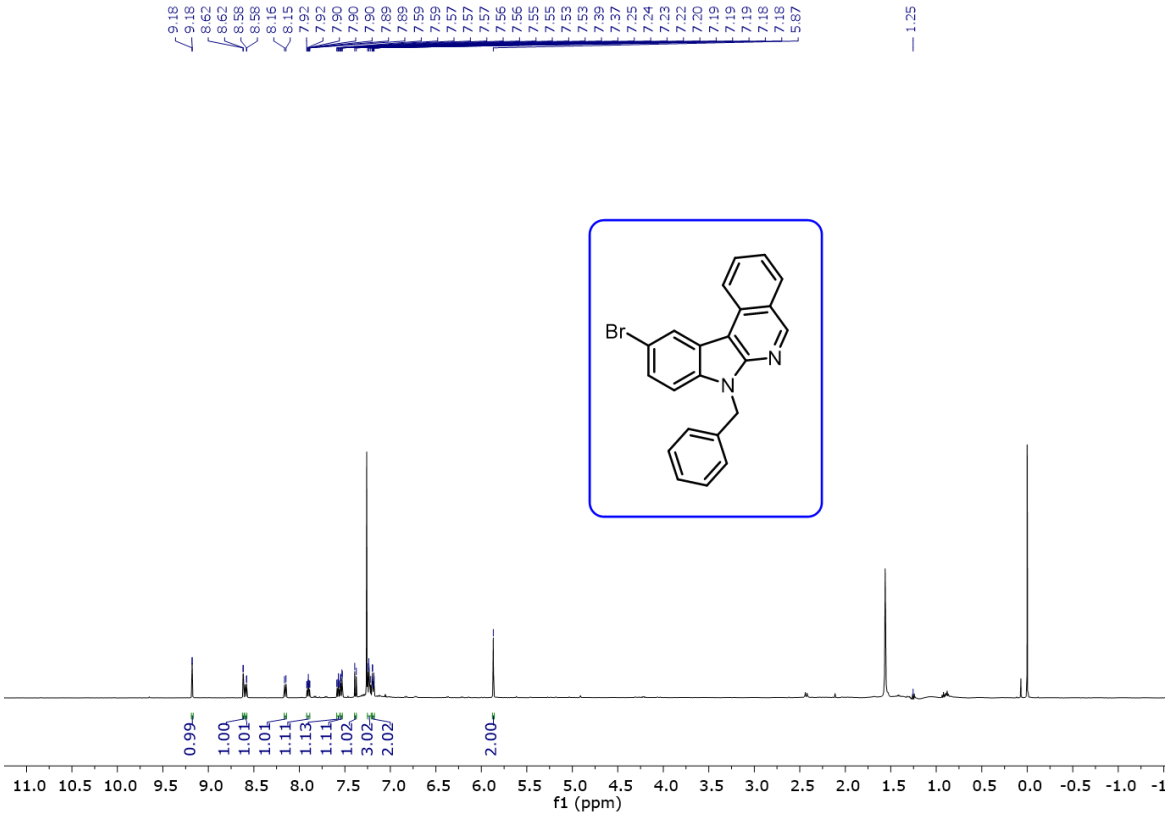

Figure S35. ^{1}H NMR of **3q** (500 MHz, $CDCl_3$)

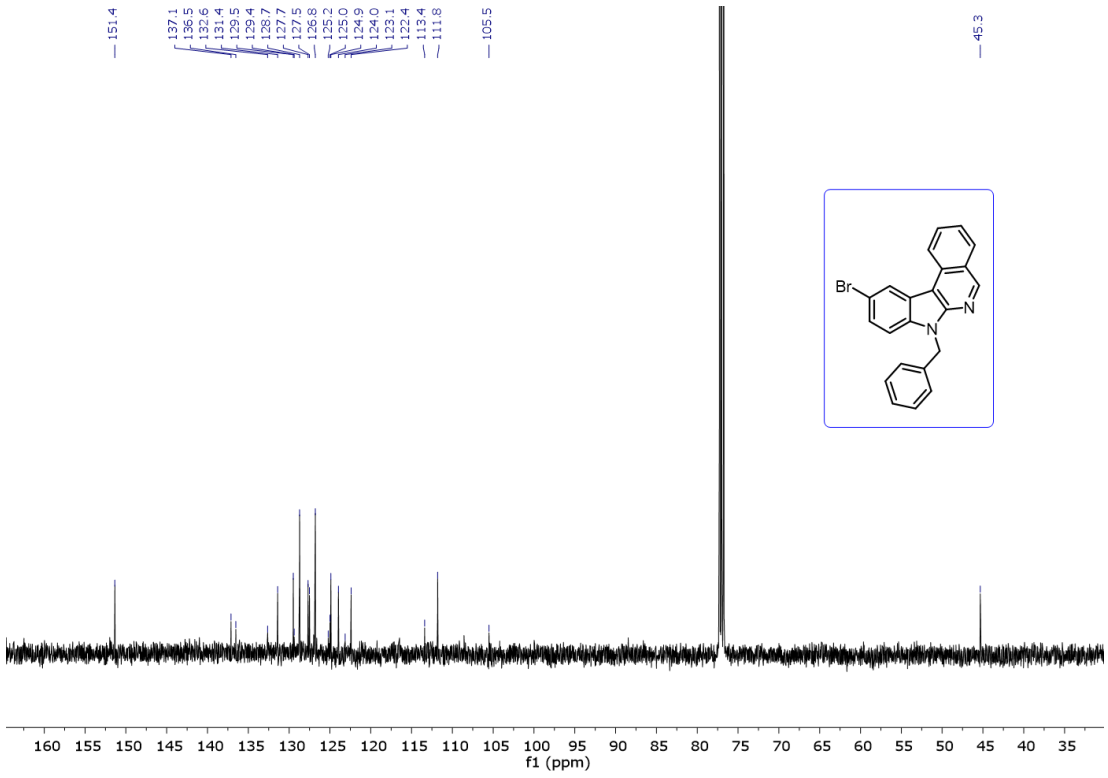

Figure S36. ^{13}C NMR of **3q** (125 MHz, $CDCl_3$)

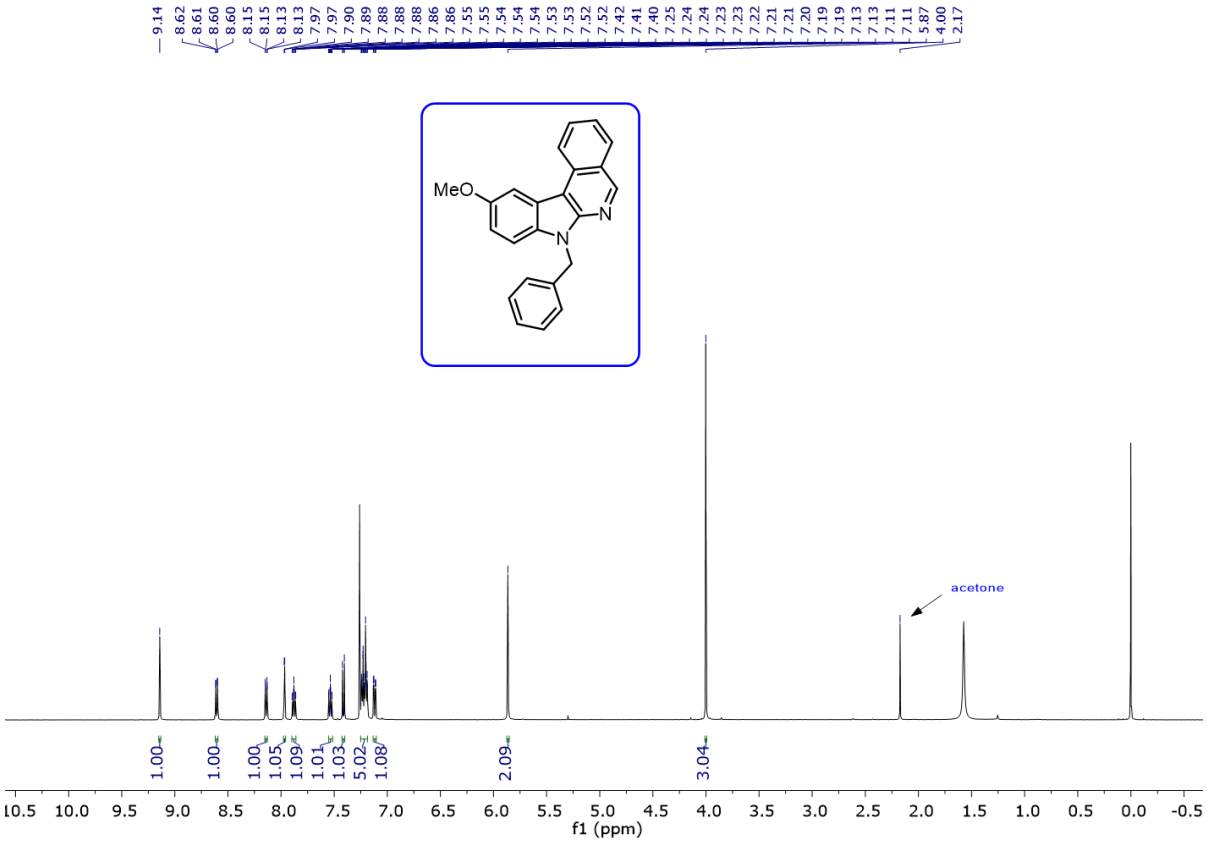

Figure S37. ^{1}H NMR of **3r** (500 MHz, $CDCl_3$)

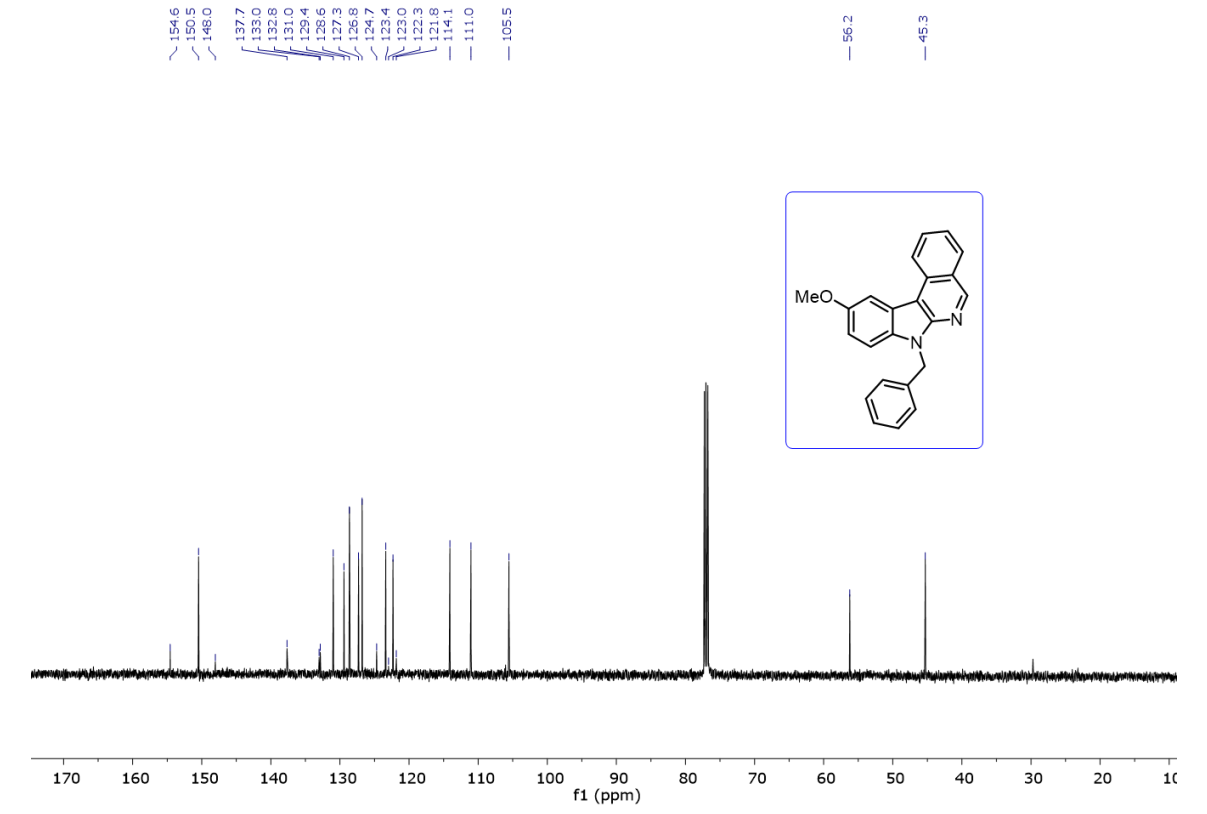

Figure S38. ^{13}C NMR of **3r** (125 MHz, $CDCl_3$)

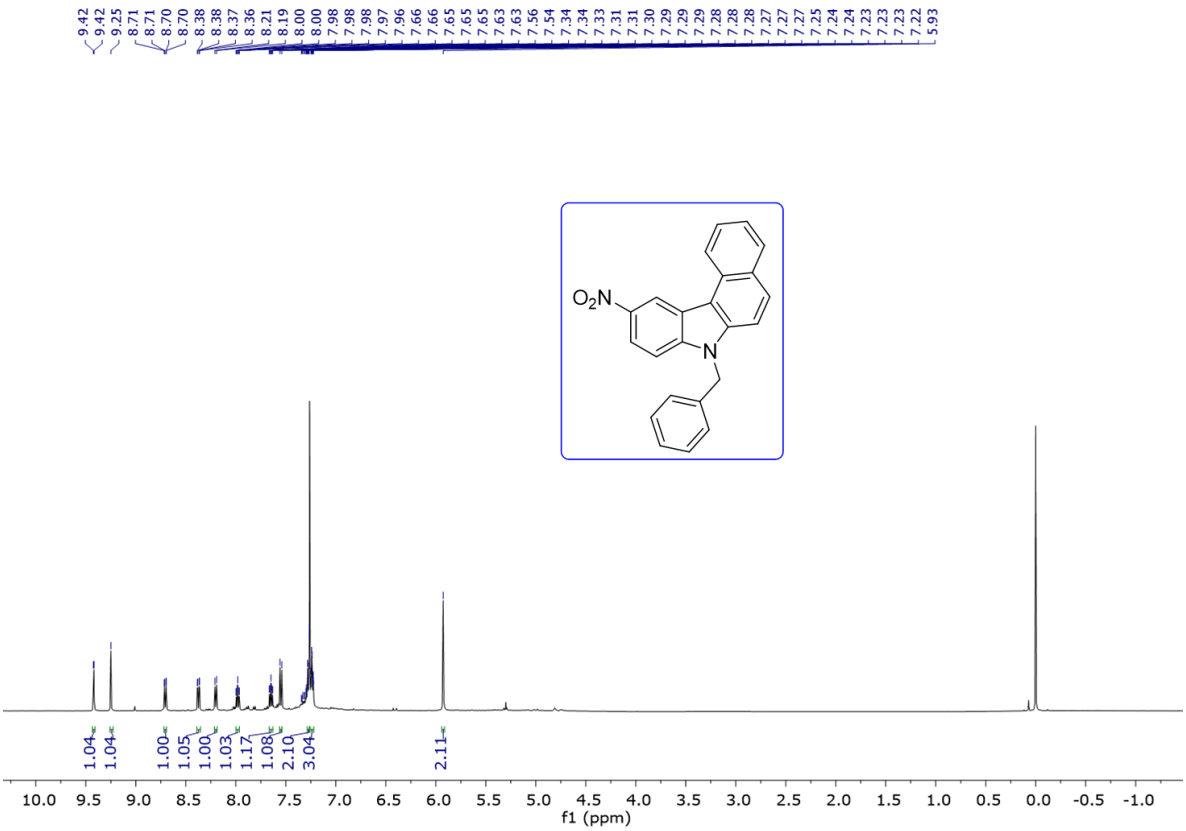

Figure S39. ^{1}H NMR of **3s** (500 MHz, $CDCl_3$)

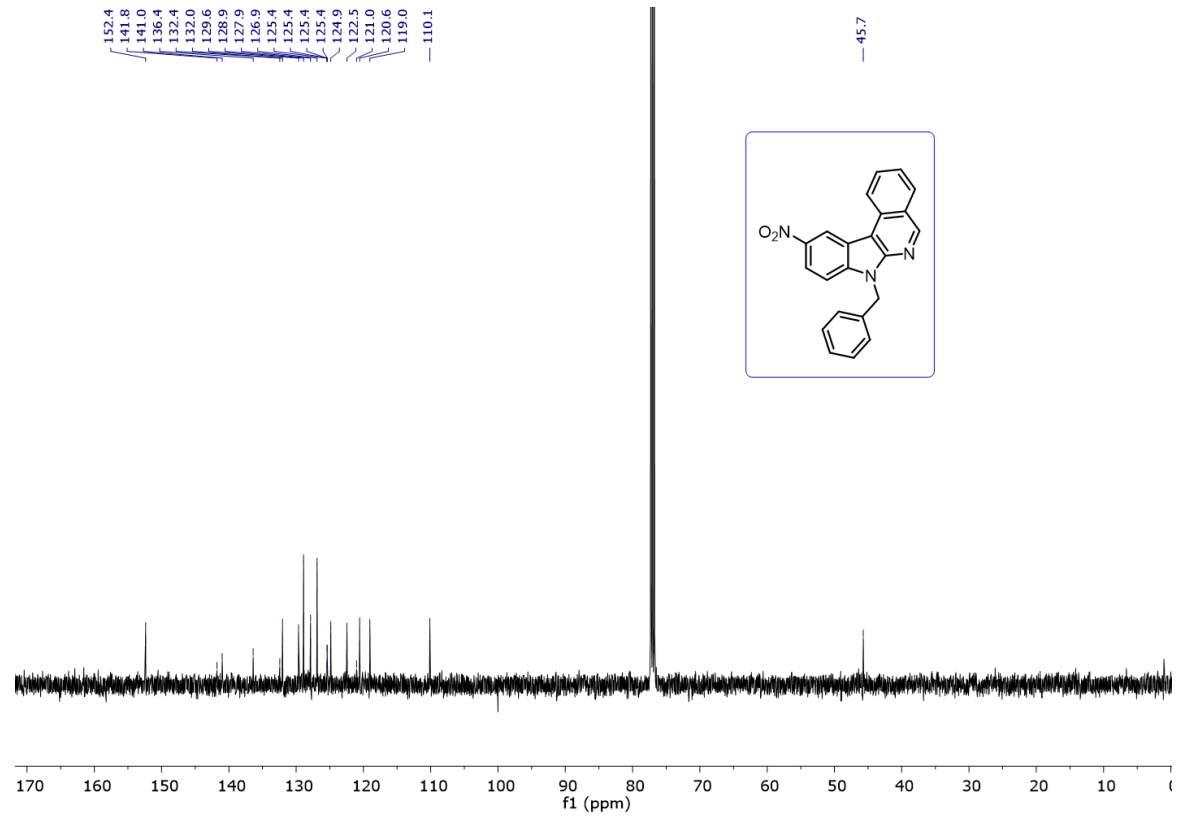

Figure S40. ^{13}C NMR of **3s** (125 MHz, $CDCl_3$)

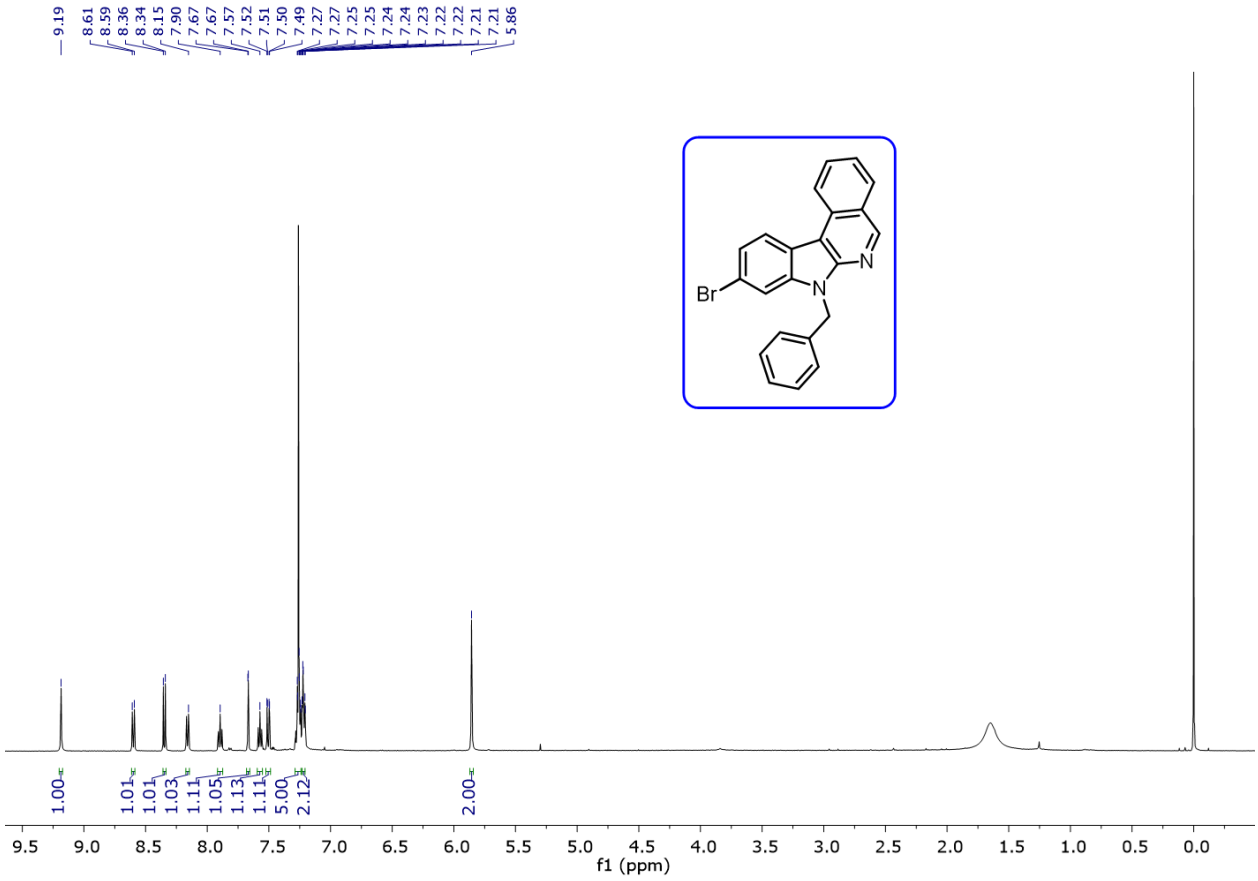

Figure S41. ^{1}H NMR of **3u** (500 MHz, $CDCl_3$)

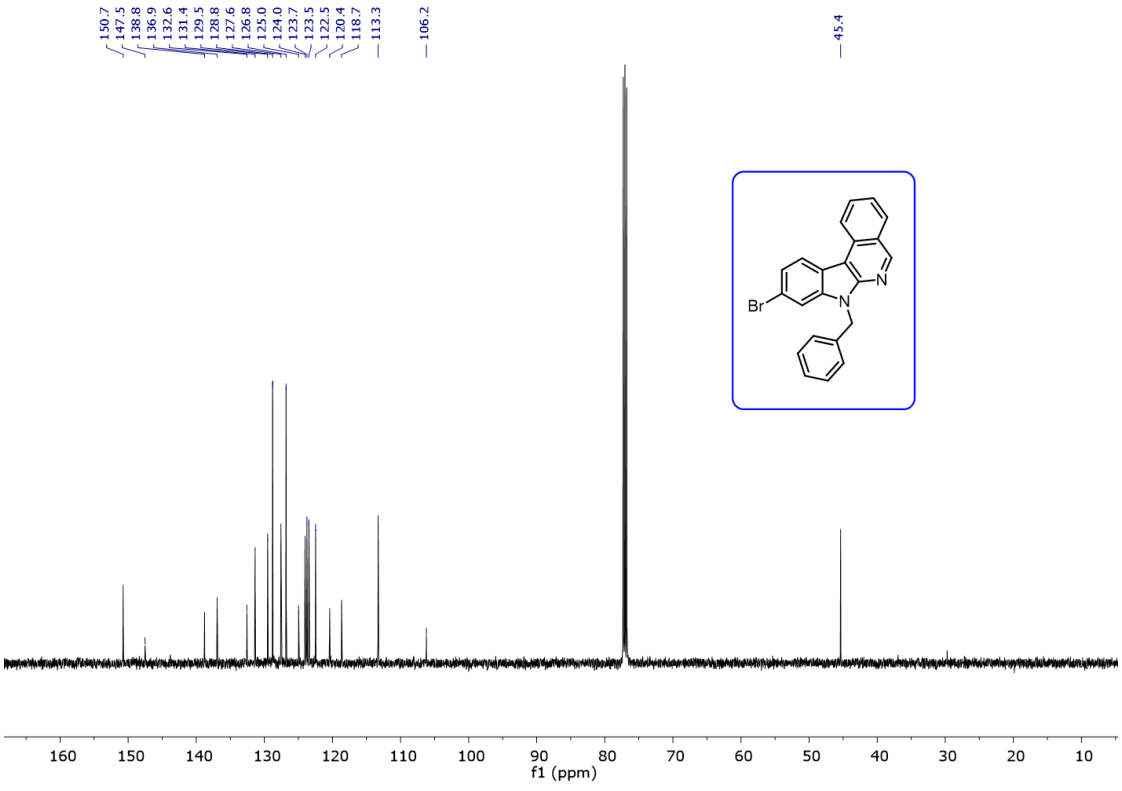

Figure S42. ^{13}C NMR of **3u** (125 MHz, $CDCl_3$)

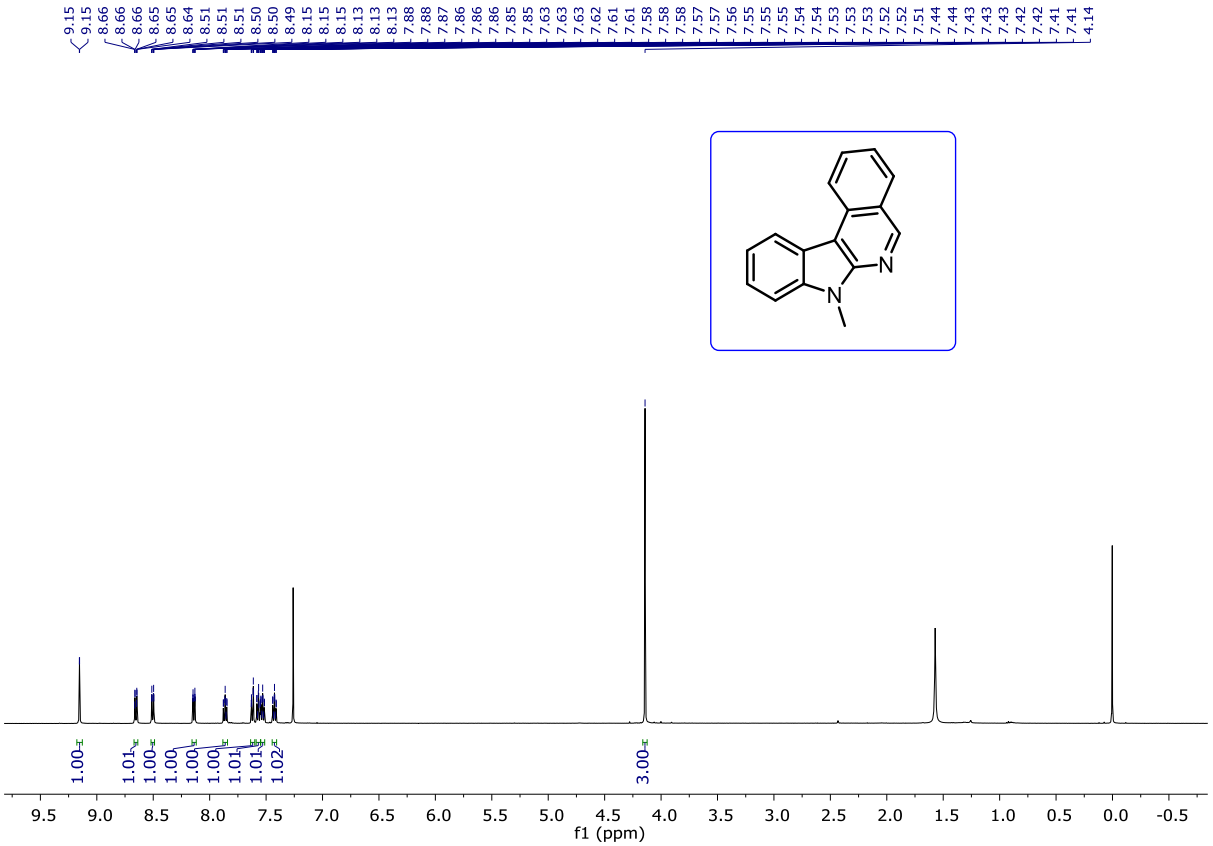

Figure S43. ^{1}H NMR of **3v** (500 MHz, $CDCl_3$)

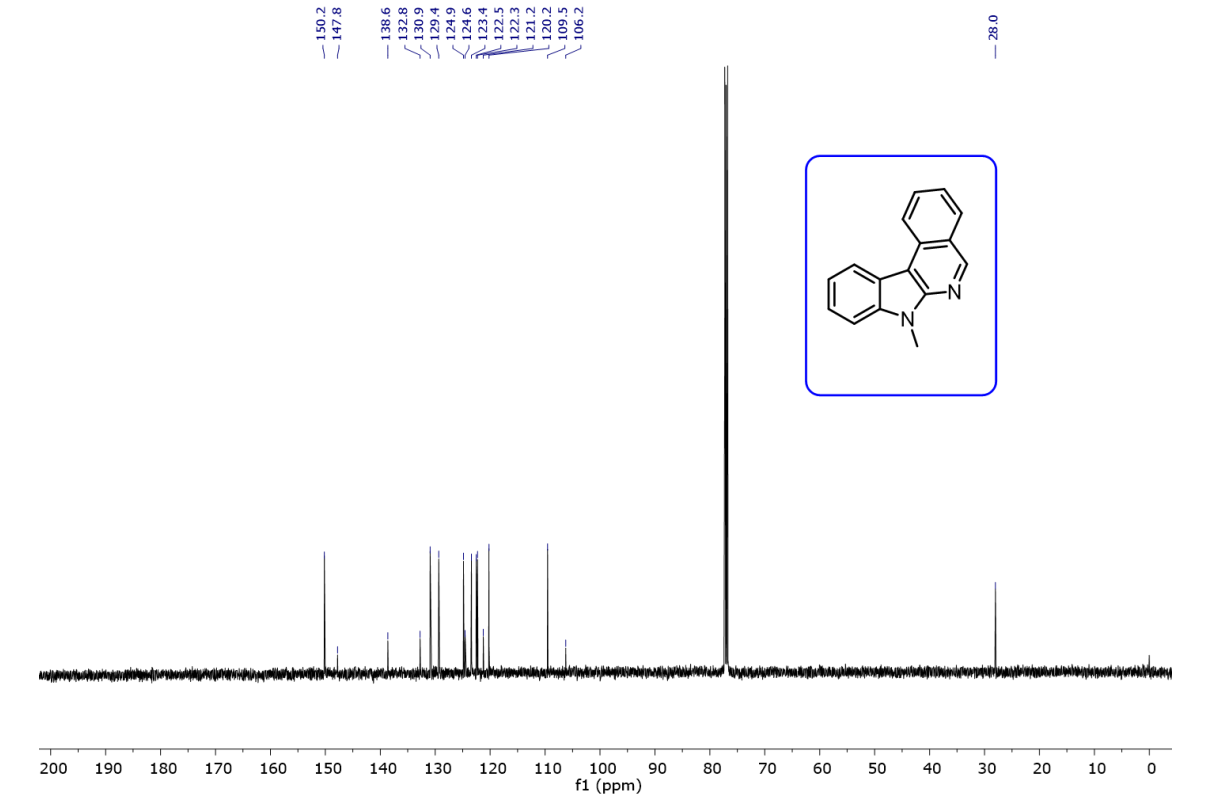

Figure S44. ^{13}C NMR of **3v** (125 MHz, $CDCl_3$)

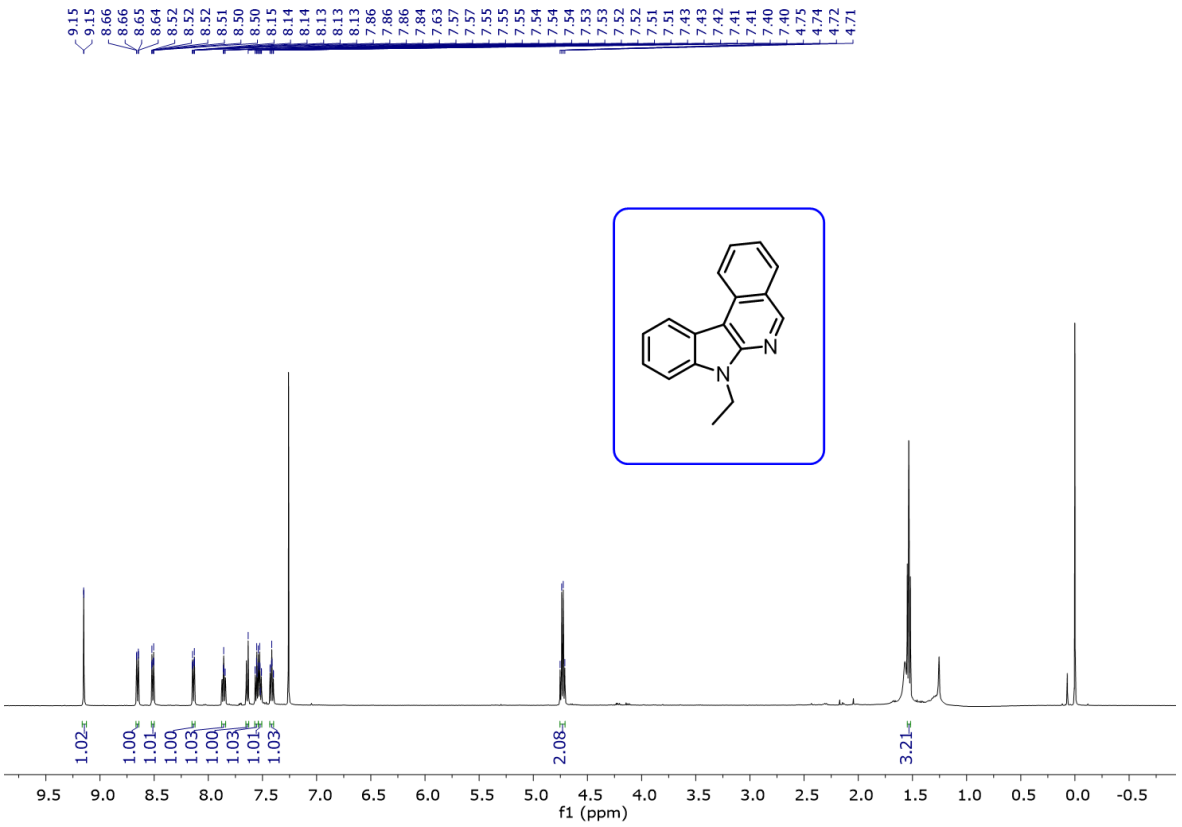

Figure S45. ^{1}H NMR of **3w** (500 MHz, $CDCl_3$)

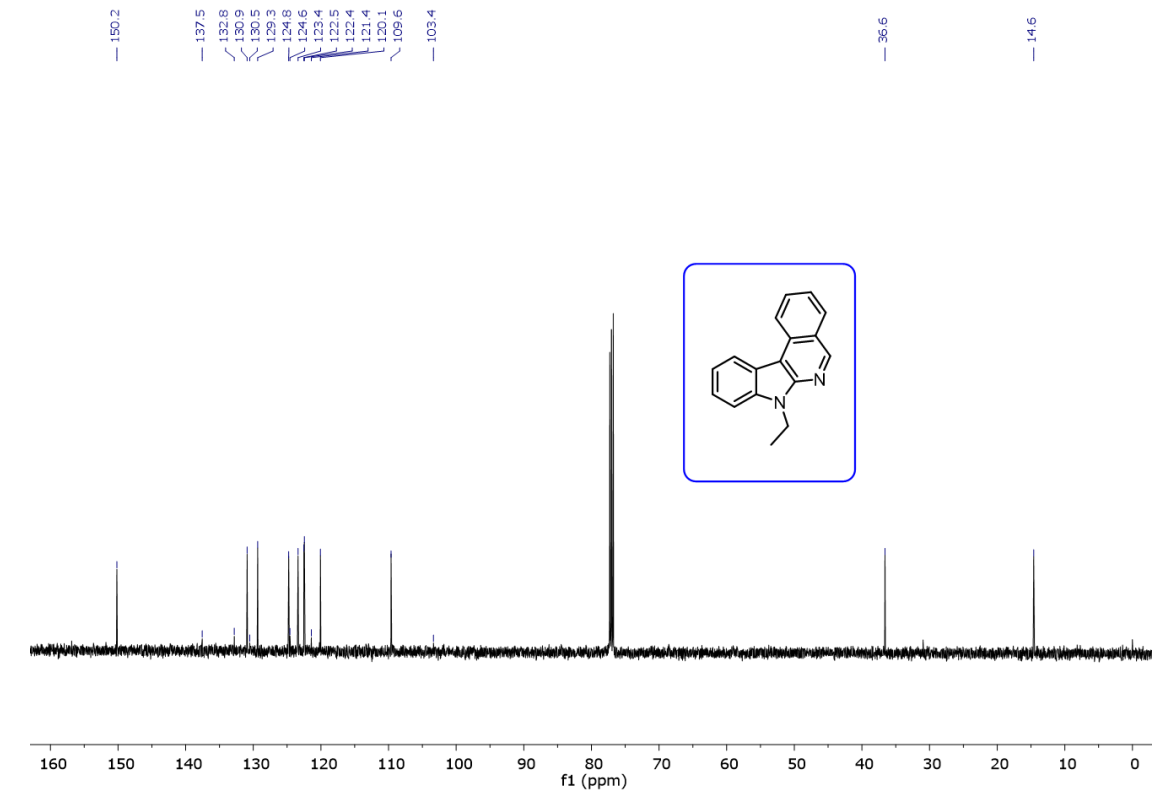

Figure S46. ^{13}C NMR of **3w** (125 MHz, $CDCl_3$)

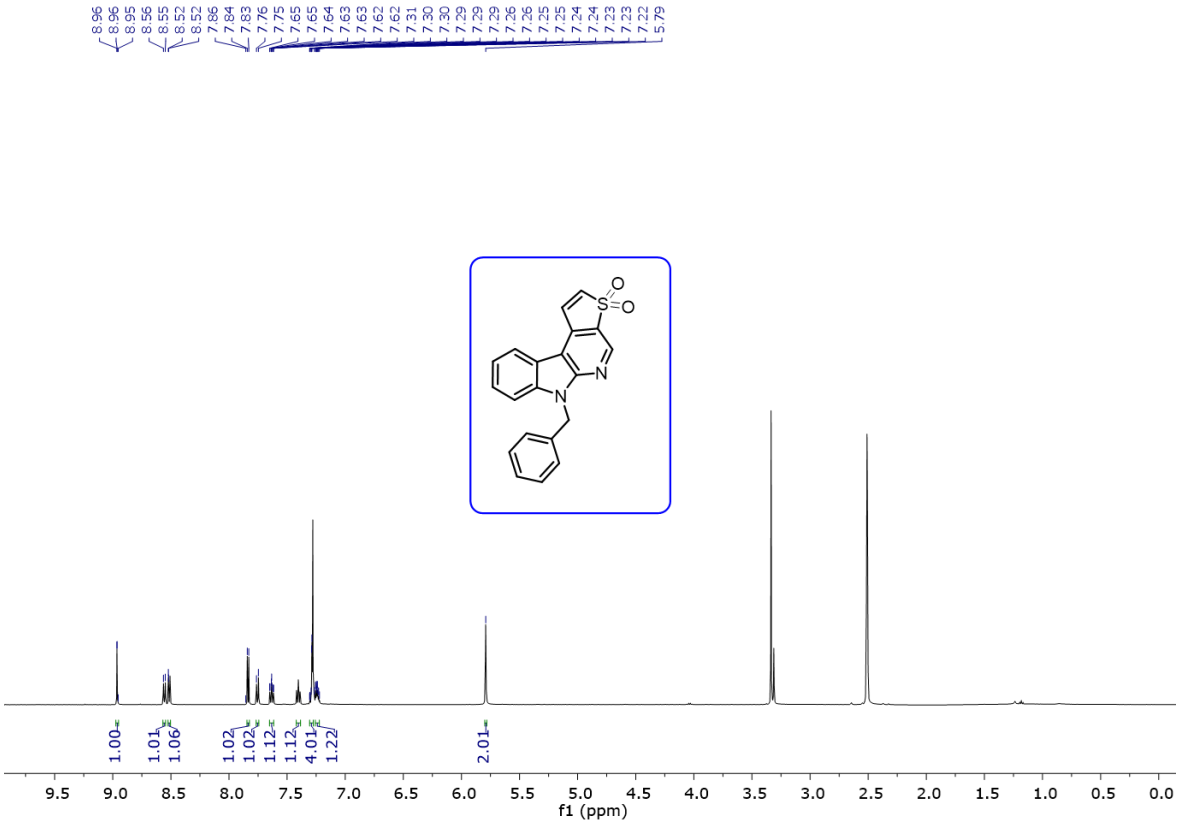

Figure S47. ^{1}H NMR of **4** (500 MHz, $CDCl_3$)

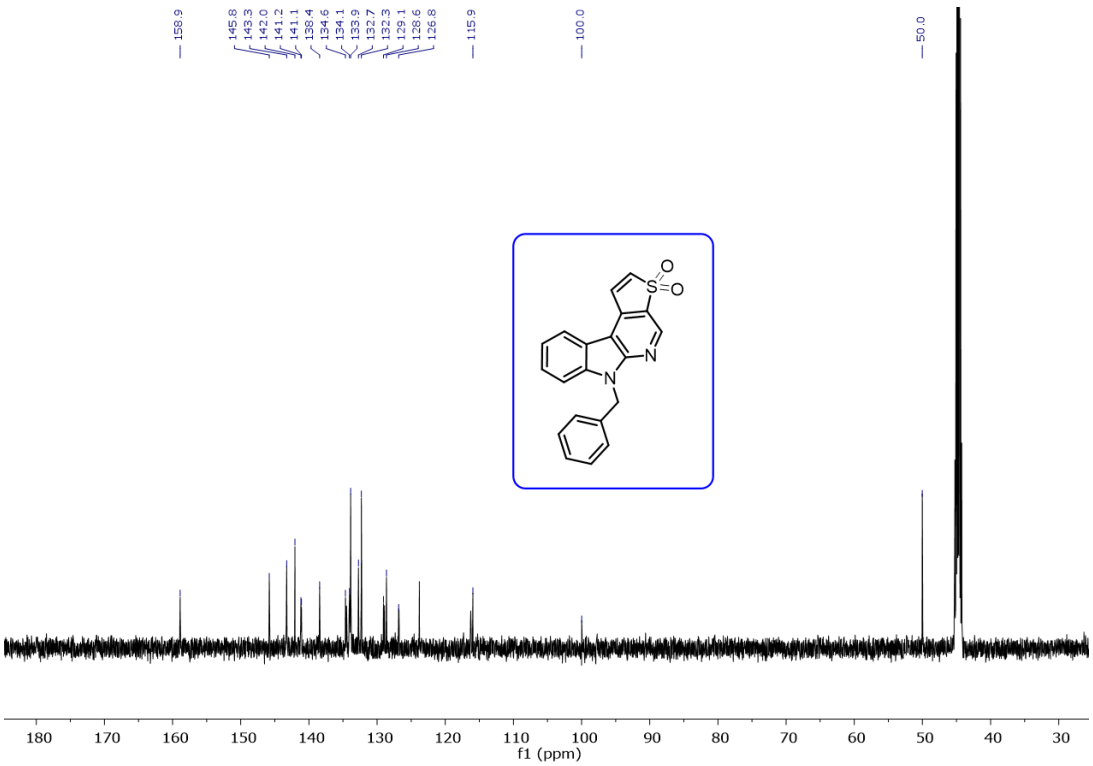

Figure S48. ^{13}C NMR of **4** (125 MHz, DMSO-d_6)

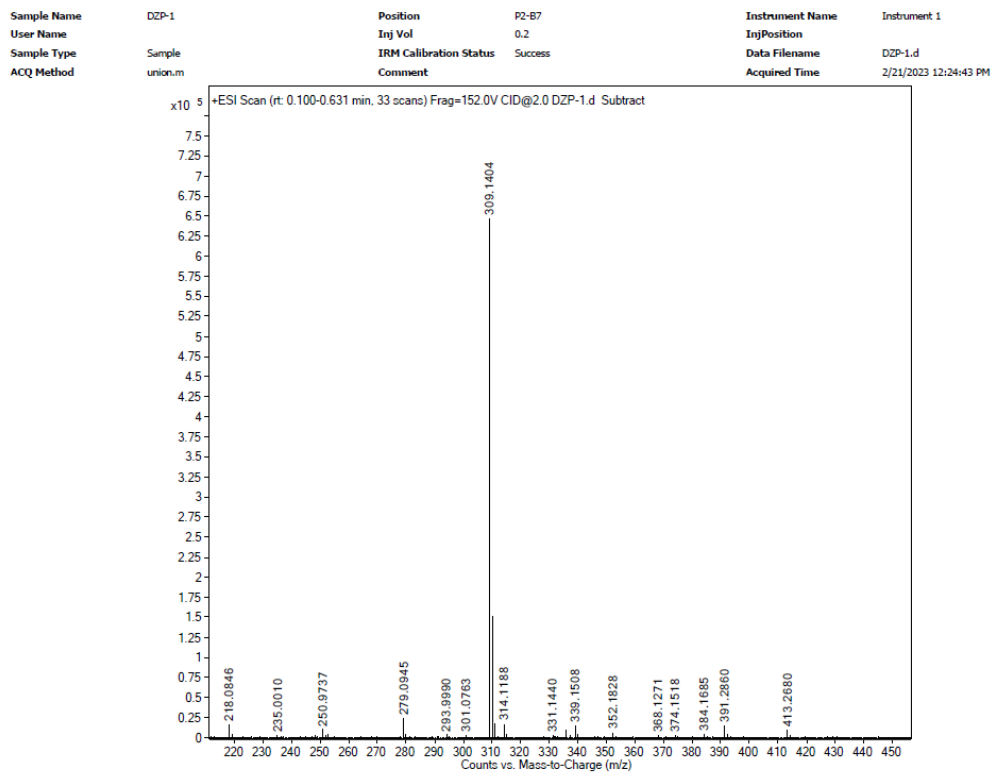

Figure S49. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3a**

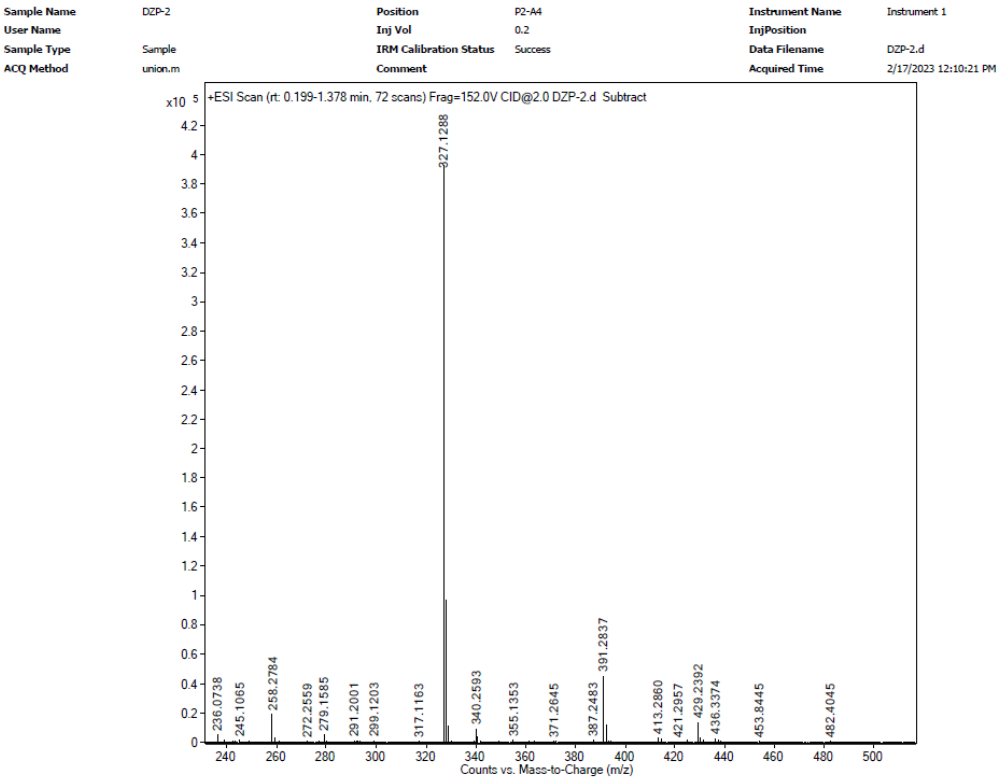

Figure S50. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for found for **3b**

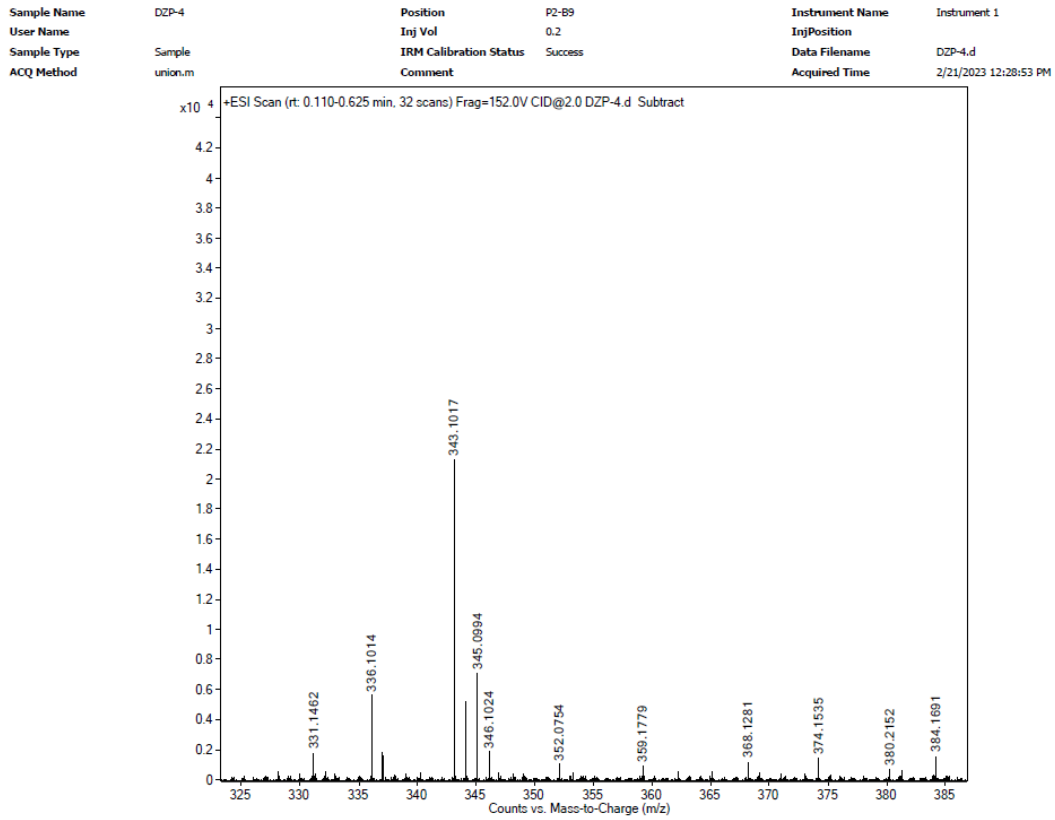

Figure S51. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3c**

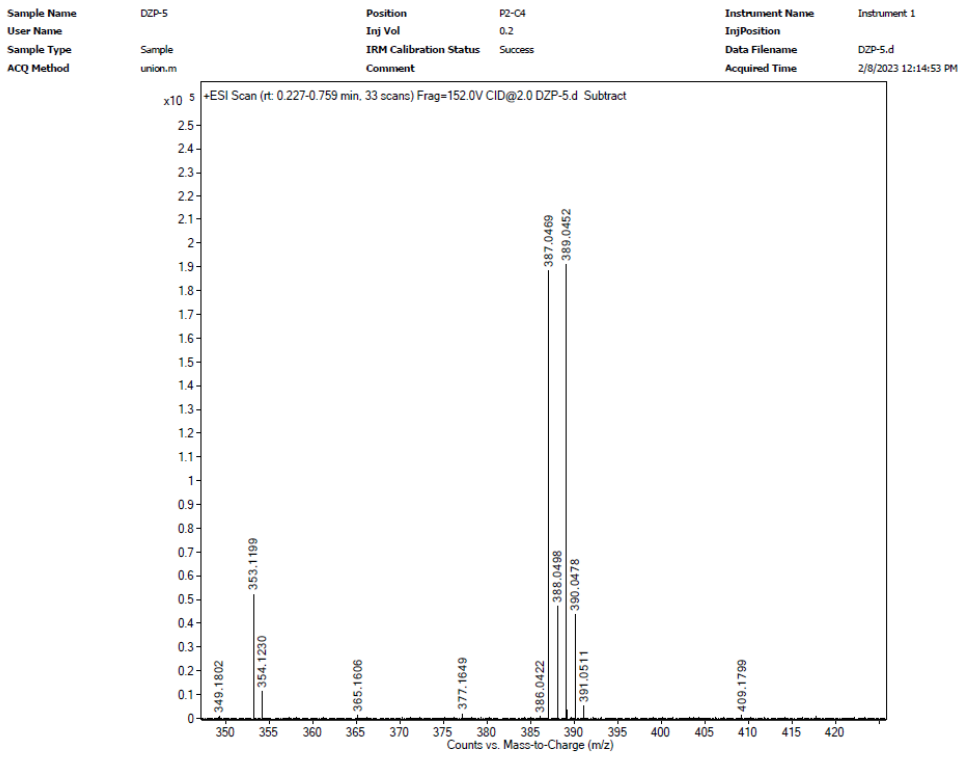

Figure S52. HRMS (ESI-QToF) of **3d**

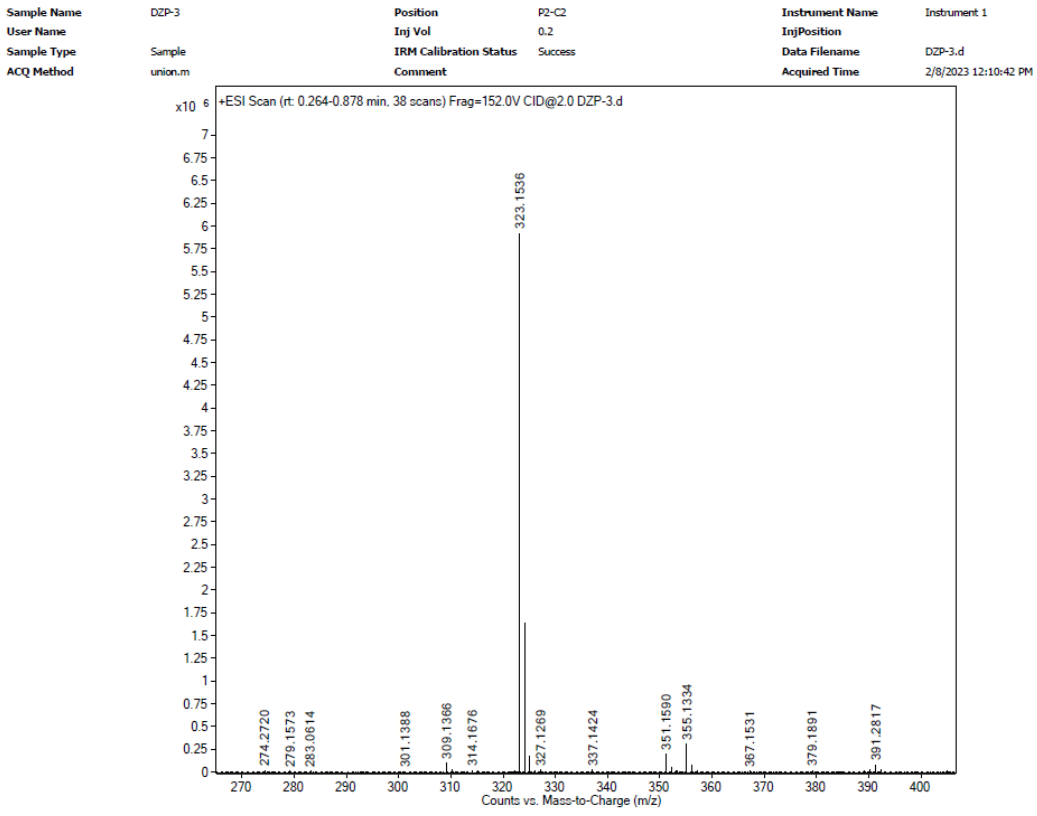

Figure S53. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3e**

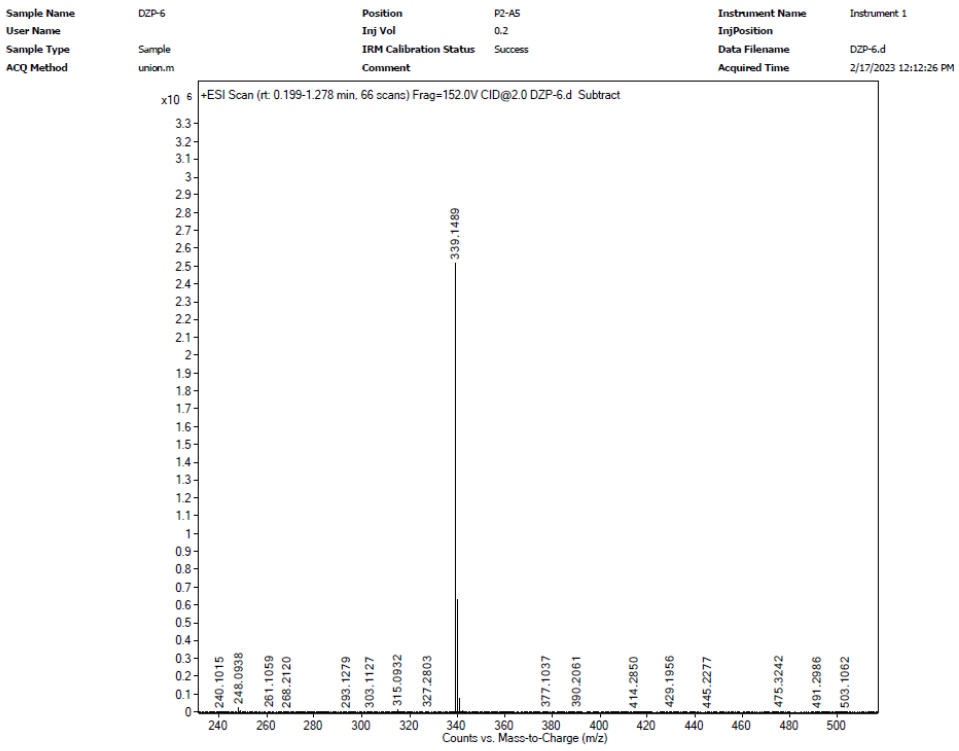

Figure S54. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3f**

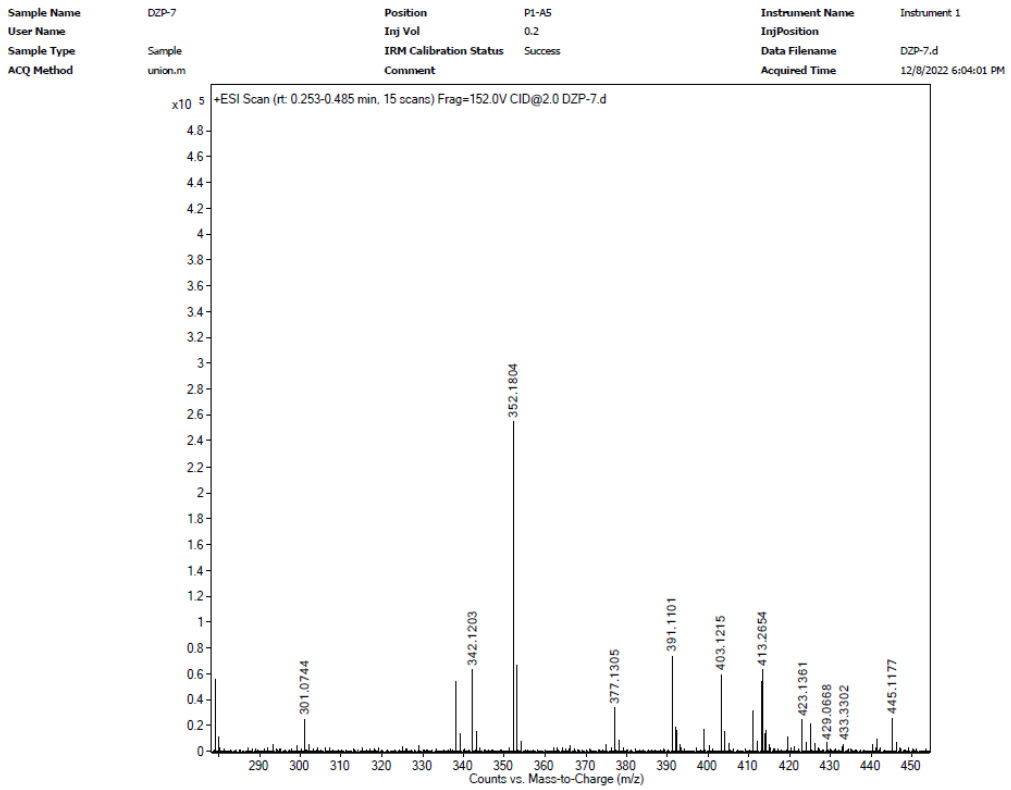

Figure S55. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3g**

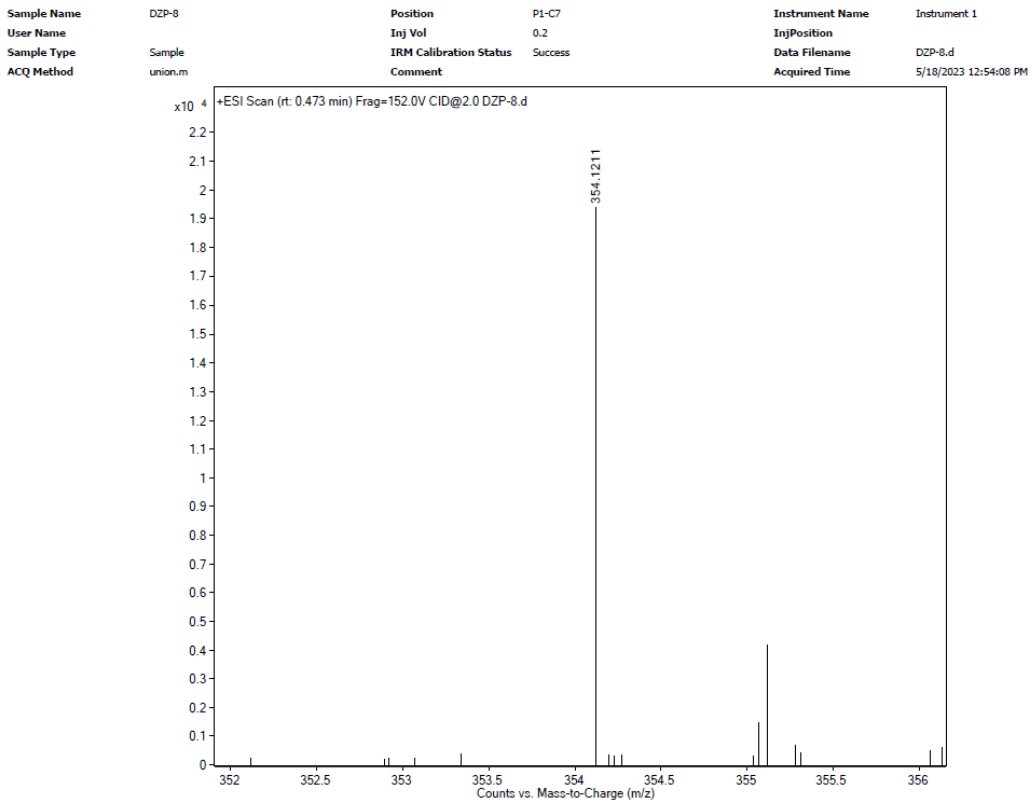

Figure S56. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3h**

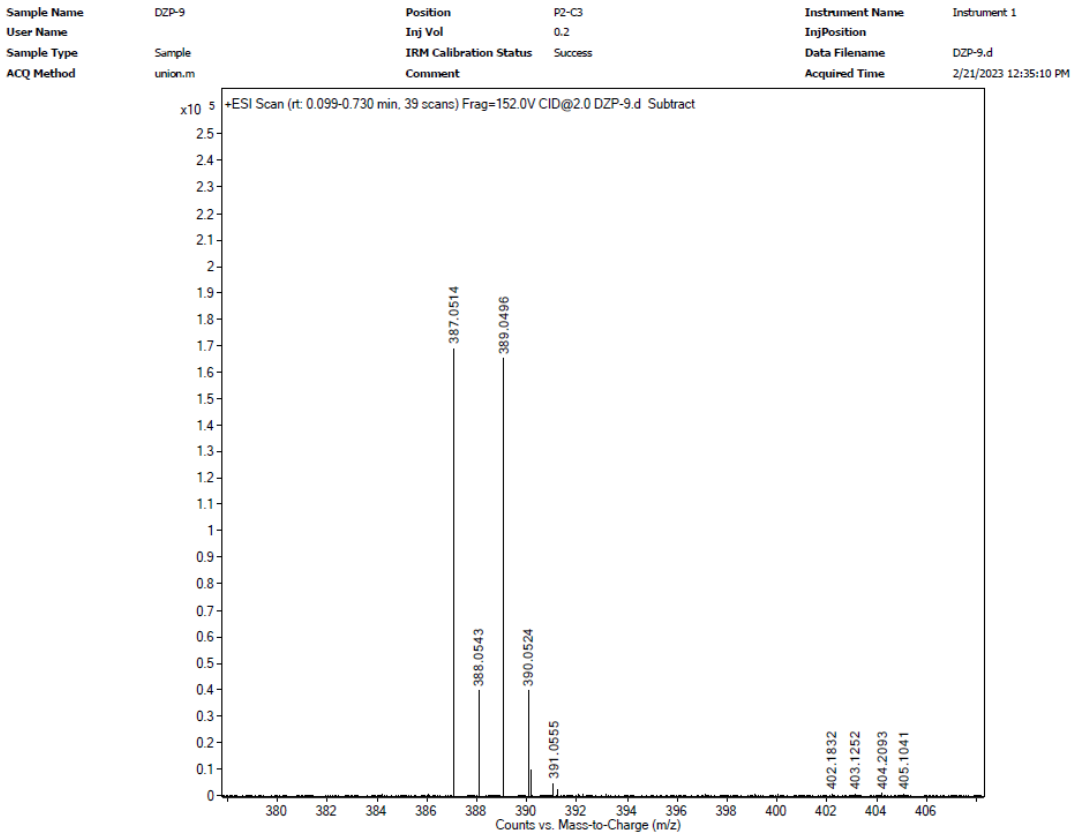

Figure S57. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3i**

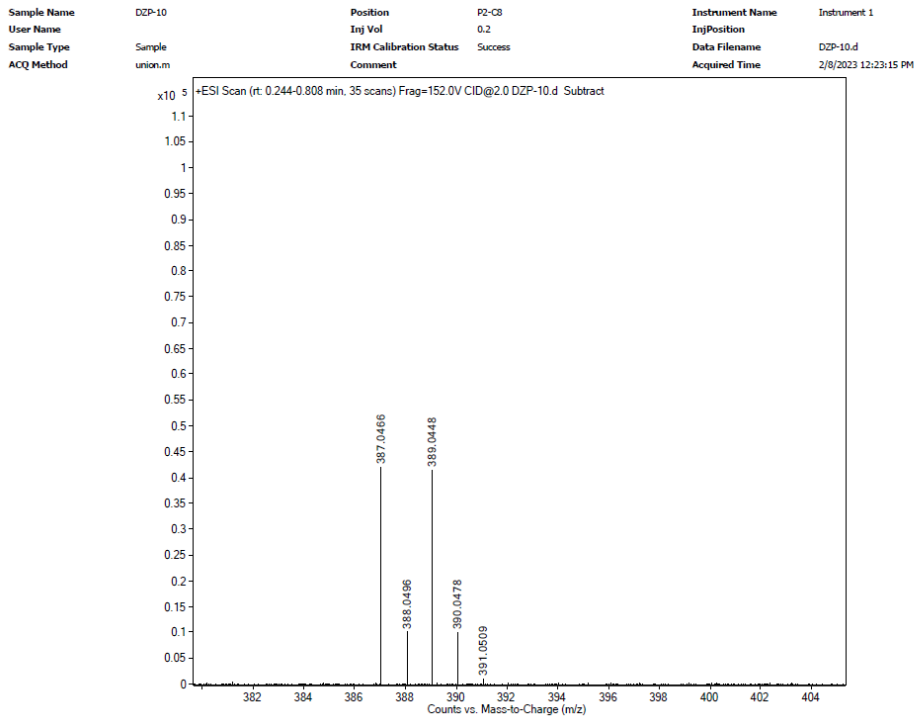

Figure S58. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3j**

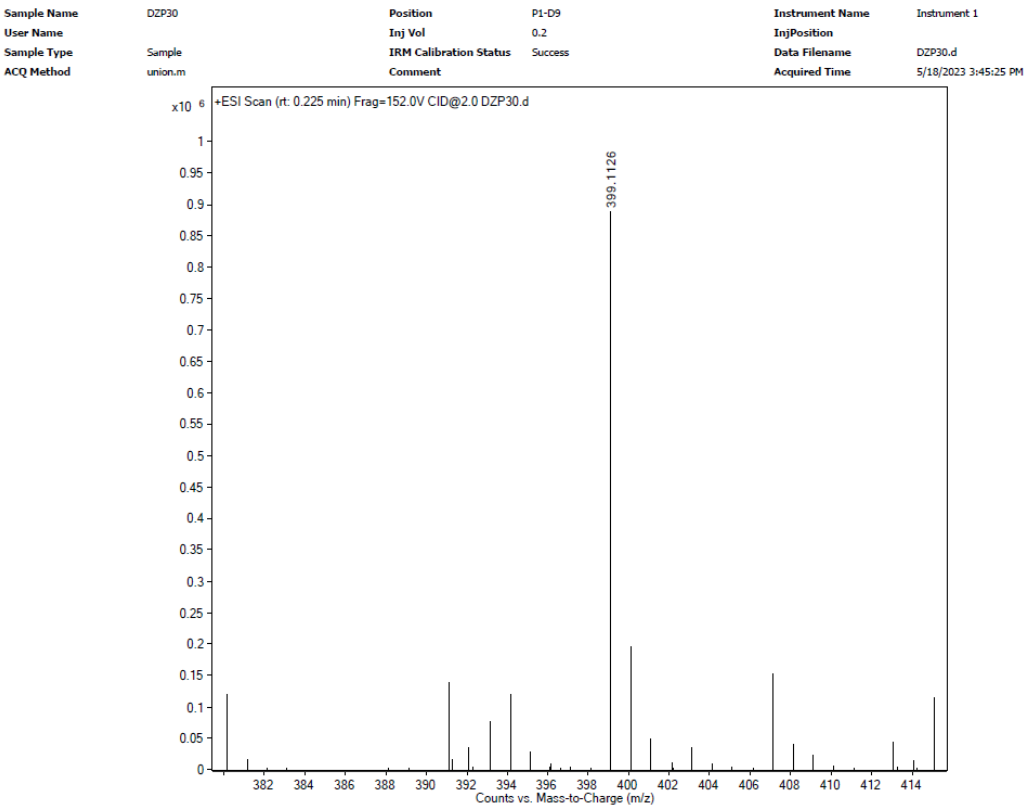

Figure S59. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3k**

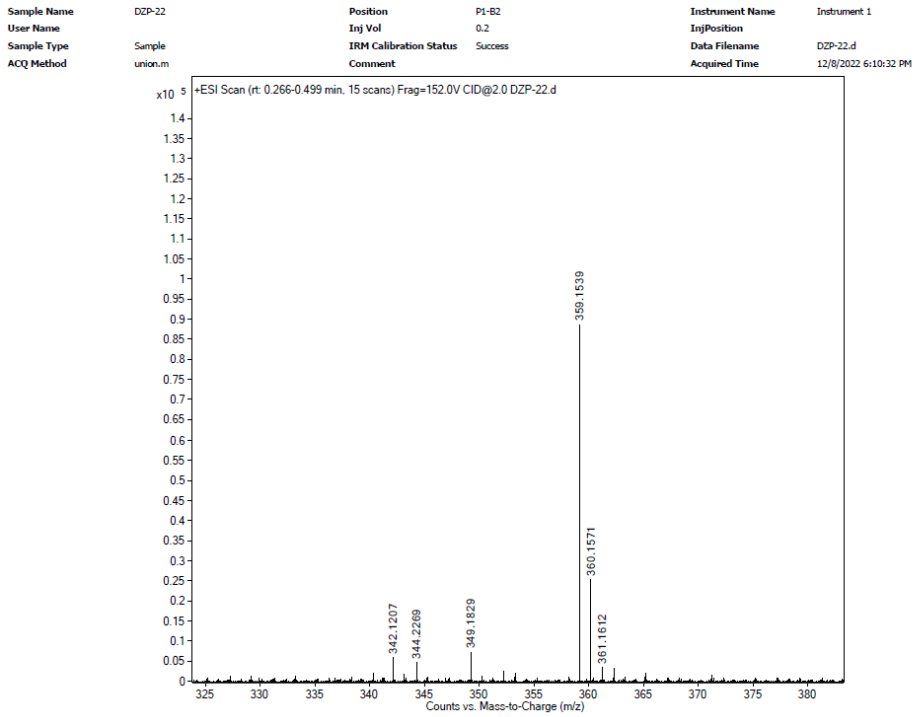

Figure S60. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3l**

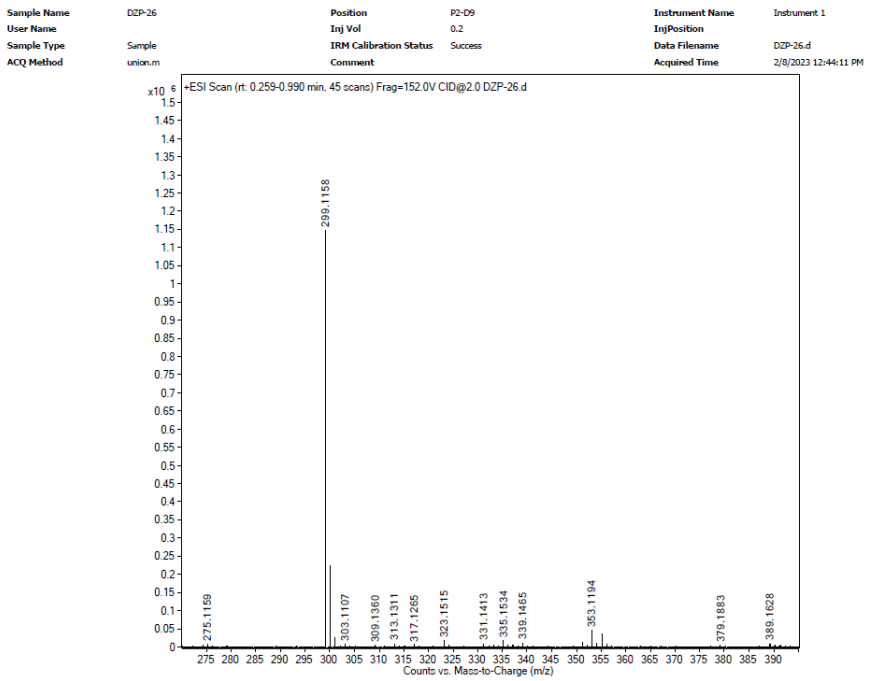

Figure S61. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3m**

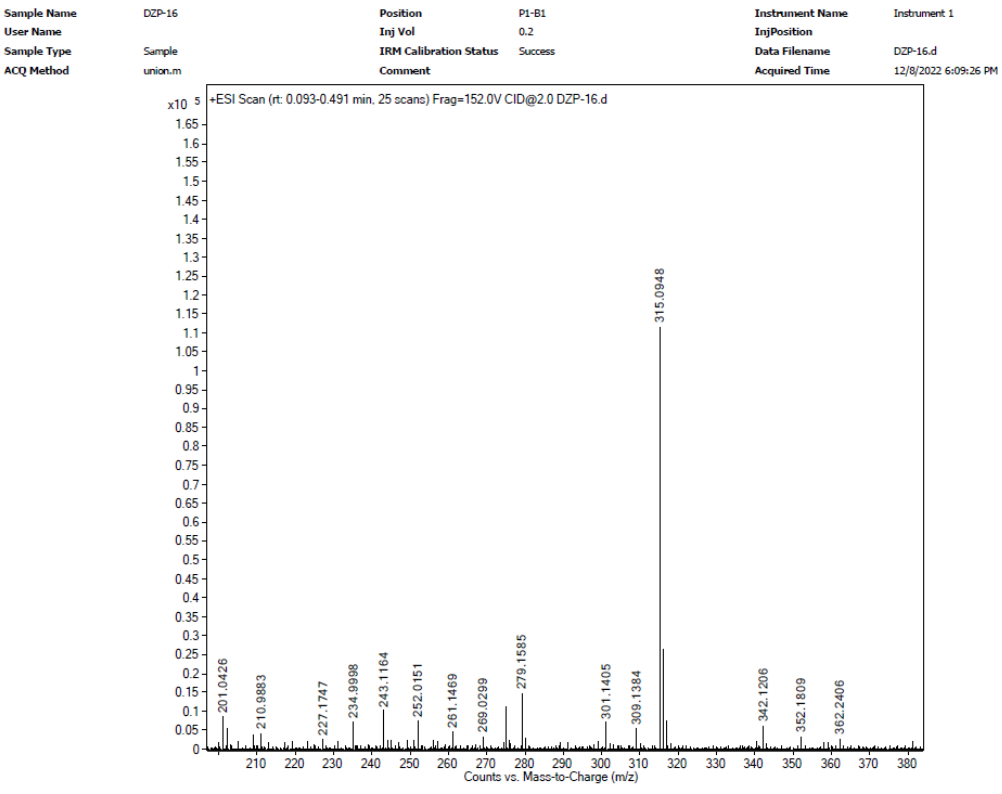

Figure S62. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3n**

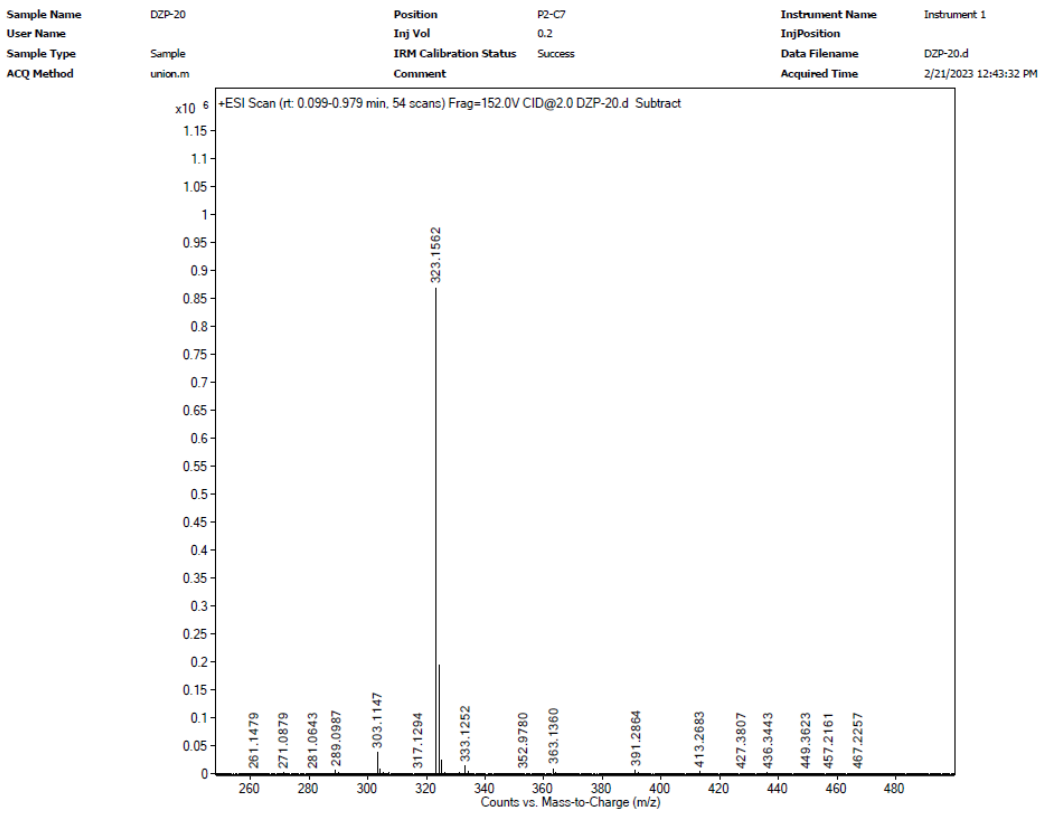

Figure S63. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3p**

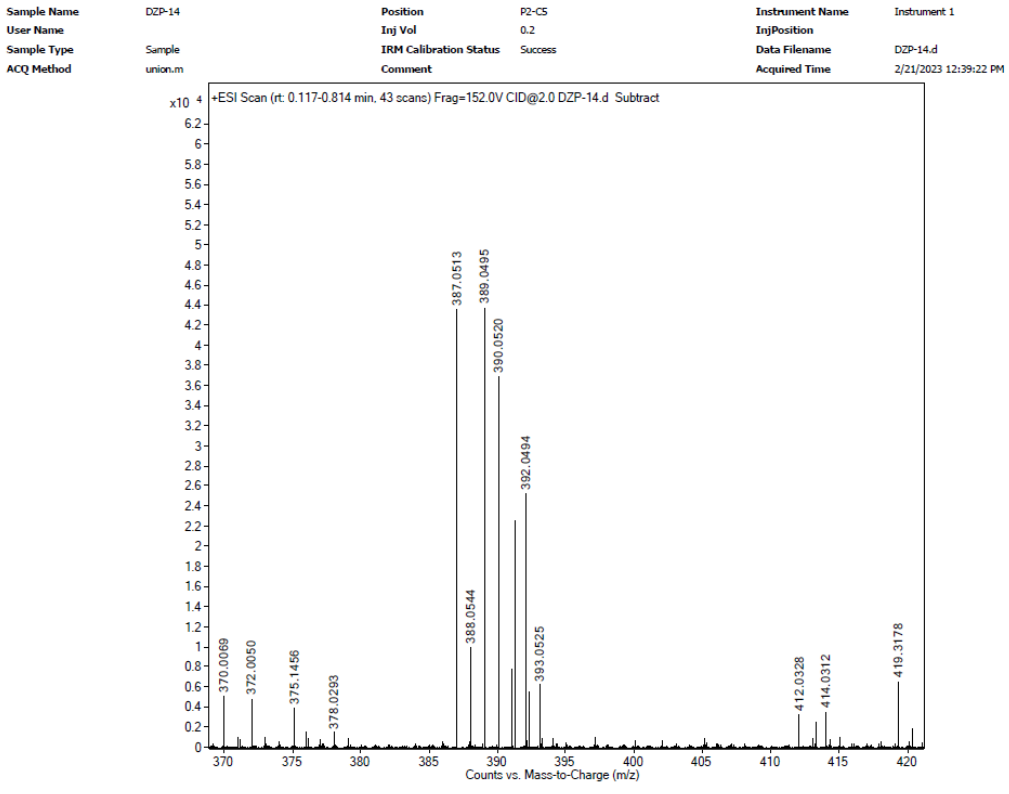

Figure S64. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3q**

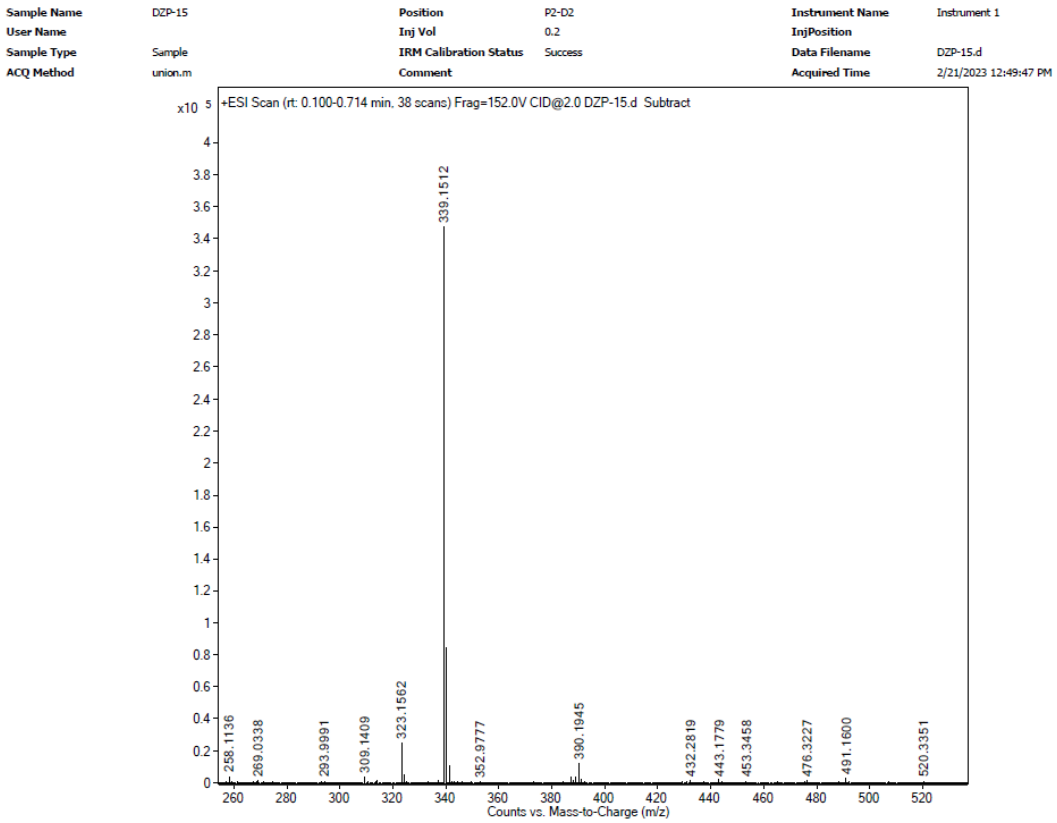

Figure S65. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3r**

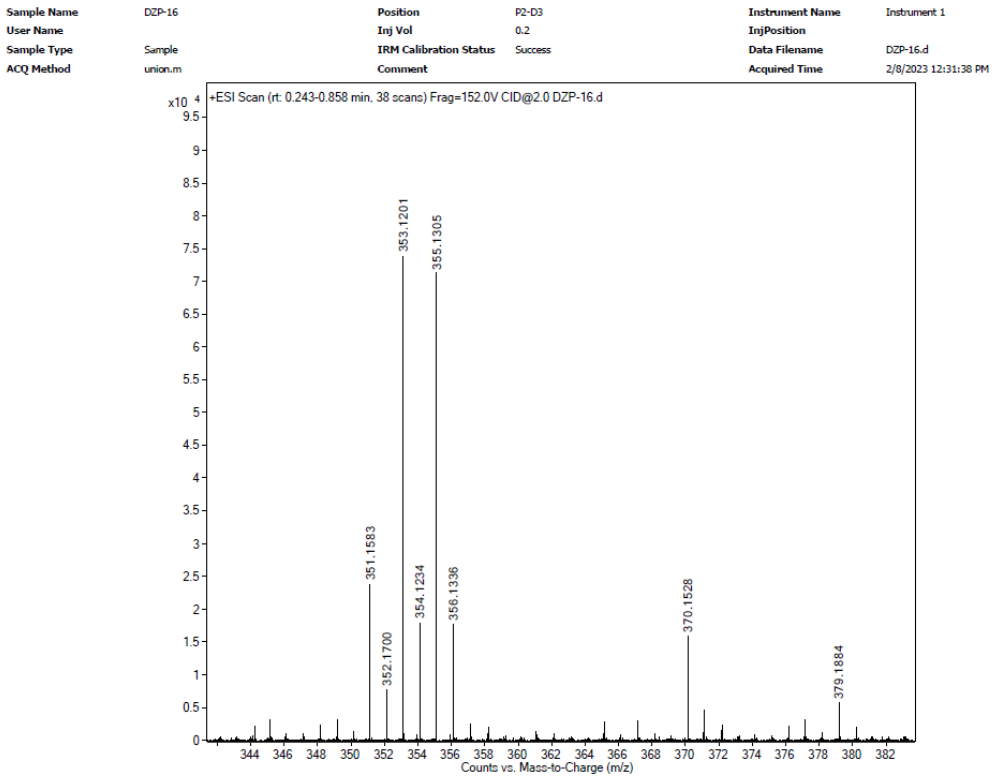

Figure S66. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3s**

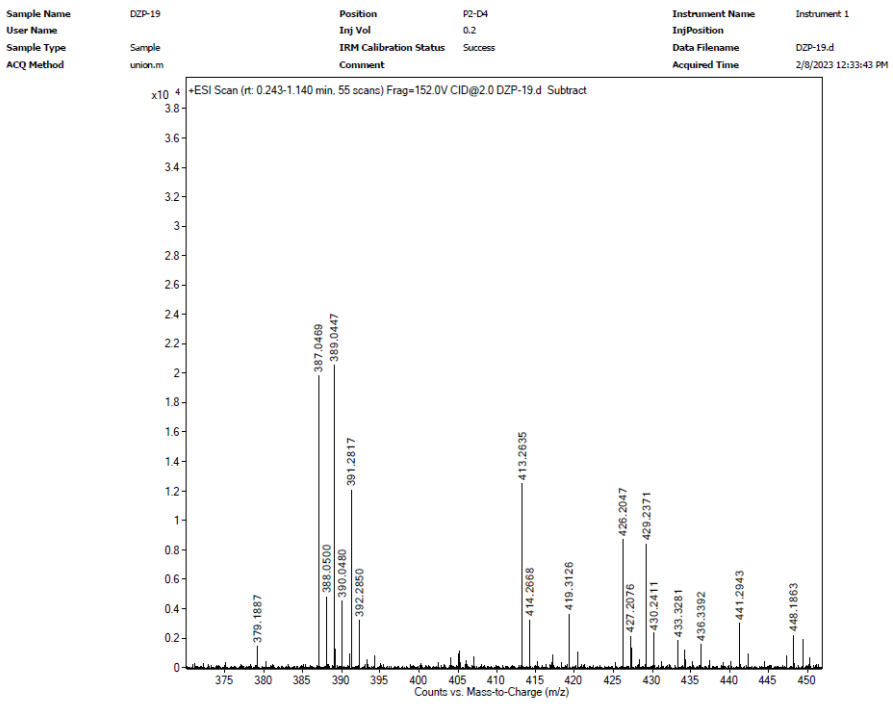

Figure S67. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3u**

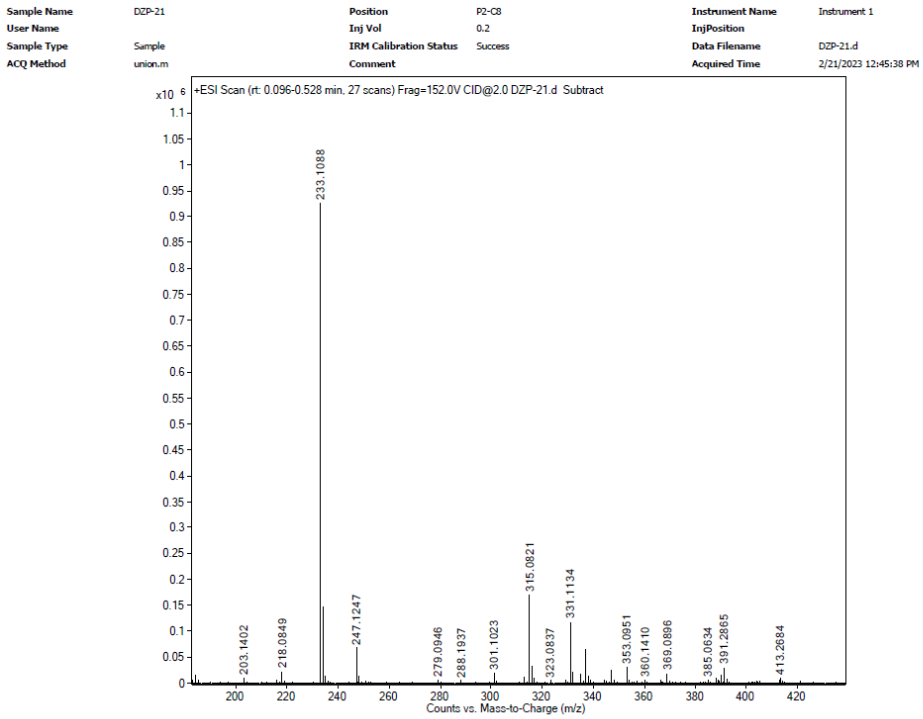

Figure S68. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3v**

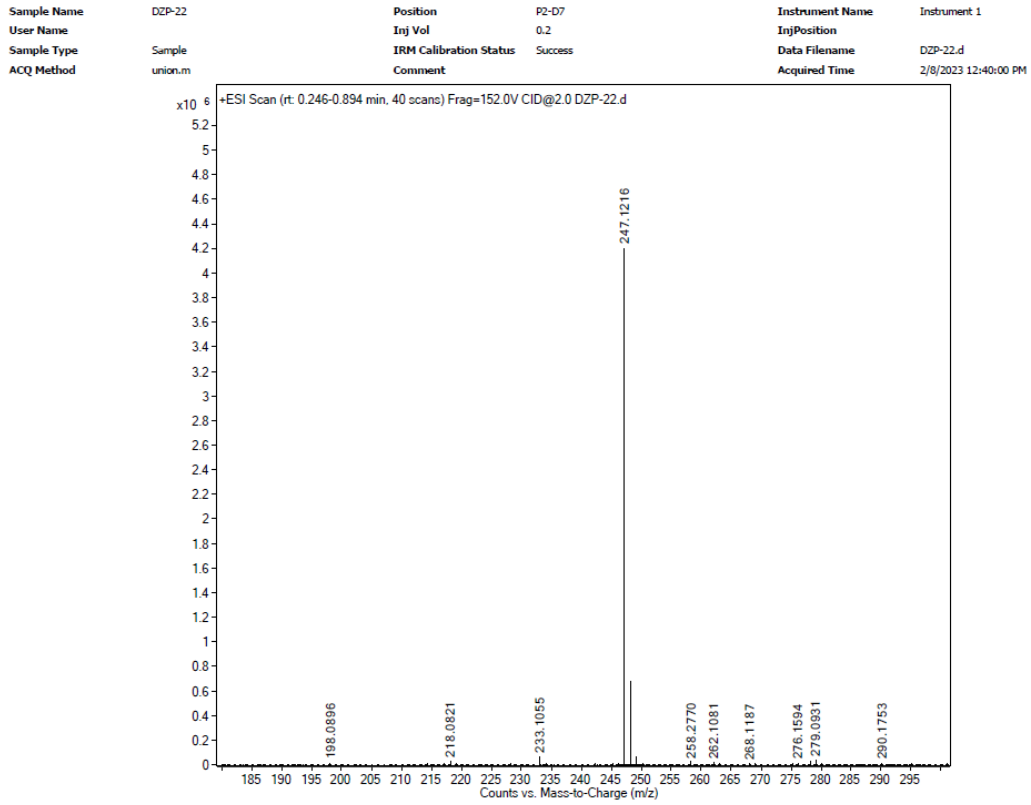

Figure S69. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **3w**

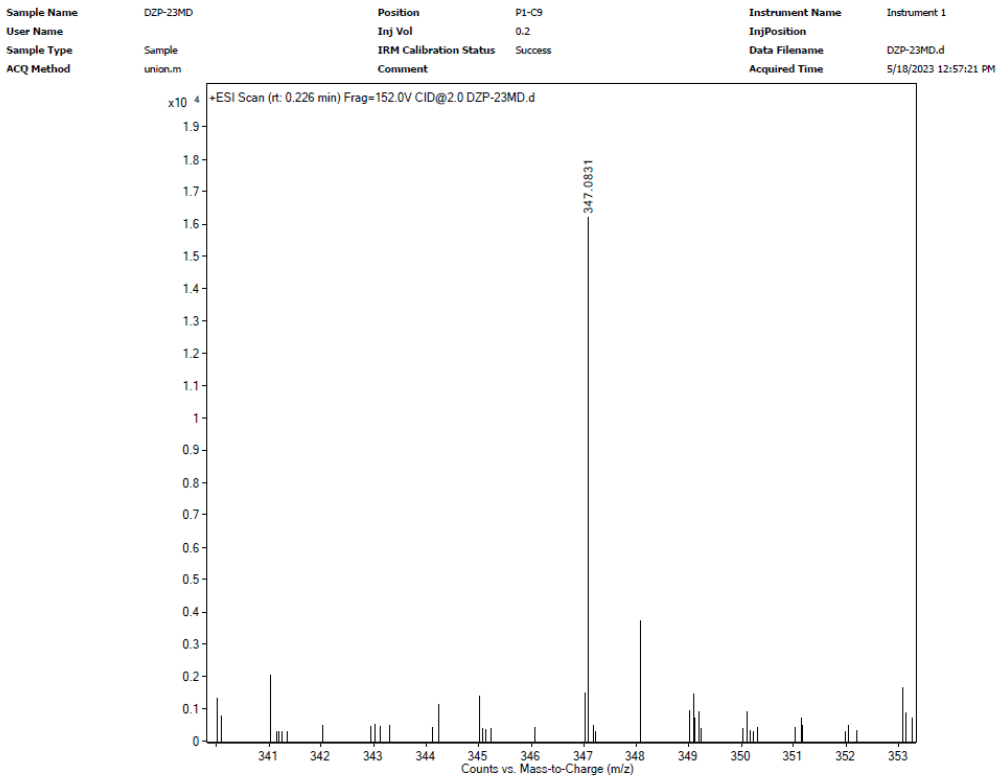

Figure S70. HRMS (ESI-QToF) *m/z* $[M+H]^+$ found for **4**.