Electronic Supplementary Information

Simple inorganic base promoted polycyclic construction using mucohalic acid as C_3 synthon: Synthesis and AIE probe application of benzo[4,5]imidazo[1,2-a]pyridines

Kai Yang,[a,b] Zhi-Xi Chen,[b] Yong-Jun Zhou,[a] Qi Chen,[a] Shi-Wei Yu,[a] Shi-He Luo,*[a] and Zhao-Yang Wang*[a]

[a] School of Chemistry, South China Normal University, Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, Guangzhou Key Laboratory of Analytical Chemistry for Biomedicine, Guangzhou 510006, P. R. China. E-mail: wangzy@scnu.edu.cn

[b] College of pharmacy, Gannan Medical University, Ganzhou 341000, P. R. China.

E-mail: wangzy@scnu.edu.cn, pinky_r@163.com; Fax: (+86) 20-39310187; Tel.: (+86) 20-39310258

Table of Contents

General Information

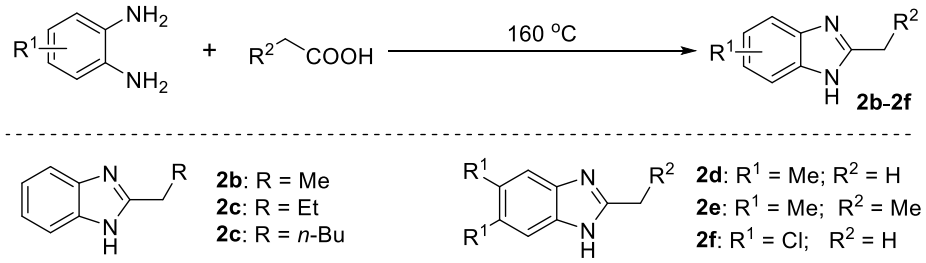
Melting point (m.p.) was performed on an X-5 digital melting point apparatus without correcting. ^{1}H, ^{13}C and ^{19}F NMR spectra were collected on a Varian AS600 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard.

High-resolution mass spectra (HRMS) were obtained with a LCMS-IT-TOF mass spectrometer. Single-crystal X-ray analysis was obtained using Bruker APEX2 Smart CCD. TLC was performed by using commercially prepared 100-400 mesh silica gel plates (GF254) and visualization was detected at 254 or 365 nm.

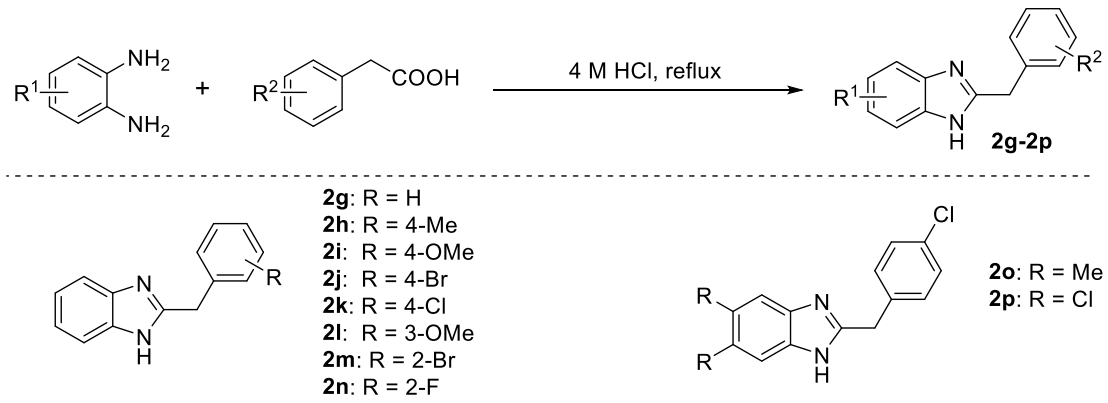
The fluorescence spectra were recorded with a Hitachi F-4600 spectrophotometer. The dynamic light scattering (DLS) experiments were performed on a Malvern Zetasizer Nano ZS90. Absolute PL quantum yields (Φ_F) were measured by Edinburgh FLS 980 fluorescence spectrometer with a calibrated integrating sphere.

All reagents and solvents were purchased from commercial sources and used without further purification. According to the literature procedure,[1, 2] 2-substituted benzimidazoles **2** (except for **2a**) were synthesized from *o*-phenylenediamines and various acids (see the following for details).

Experimental Procedure for Compounds 2b-2p

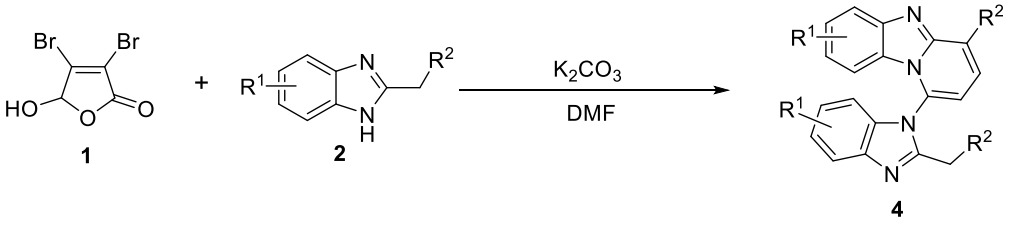


According to the reported procedure,[1] compounds **2b**-**2f** were synthesized. The appropriate aromatic diamine (2.0 mmol, 1.0 equiv.) and carboxylic acid (10 equiv.) were heated in a sealed tube at 160 ℃ for 6 h. The reaction mixture was cooled to room temperature and ammonia solution was added. The mixture was cooled in ice until the precipitate was formed. The resulting solid was recrystallised from aqueous ethanol to give the desired compounds **2b**-**2f**.

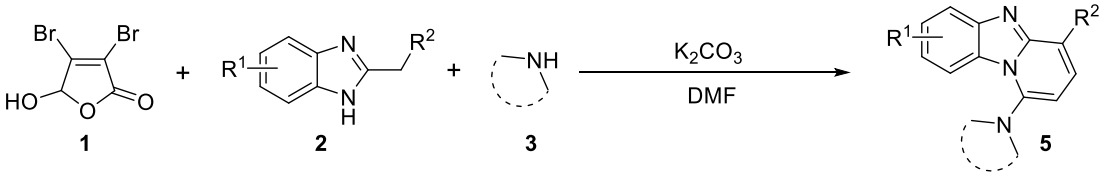


According to the reported procedure,[2] compounds **2g**-**2p** were synthesized. A mixture of appropriate aromatic diamine (2.0 mmol, 1.0 equiv) and carboxylic acid (1.5 equiv) in 4 M HCl (20.0 mL) was refluxed for 6 h. After monitoring the end of the reaction on TLC, the mixture was cooled to room temperature and neutralized by ammonia solution. And the mixture was cooled in ice until the precipitate was formed. The resulting solid was recrystallised from aqueous ethanol to give the desired compounds **2g**-**2p**.

Experimental Procedure for Compounds 4a-4o and 5a-5s



The mixture of mucobromic **1** (0.36 mmol), 2-substituted 1*H*-benzo[*d*]imidazole **2** (0.60 mmol) and K_2CO_3 (1.2 mmol) in DMF (2 mL) was stirred at room temperature 30 min, then 140 ^oC (or 120 ^oC) for 24 h. After the completion of the reaction, the reaction mixture was quenched with H_2O (15 mL) and extracted with dichloromethane (3 × 15 mL). Then, the organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product **4**.



The mixture of mucobromic **1** (0.36 mmol), 2-substituted 1*H*-benzo[*d*]imidazole **2** (0.30 mmol), heterocyclic compound **3** (0.36 mmol) and K_2CO_3 (1.2 mmol) in DMF (2 mL) was stirred at room temperature 6 h, then 140 ^oC (or 120 ^oC) for 18 h. After the completion of the reaction, the reaction mixture was quenched with H_2O (15 mL) and extracted with dichloromethane (3 × 15 mL). Then, the organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product **5**.

Characterization Data for All Products 4a-4o, 5a-5s and Intermediate 4aa

1-(2-Methyl-1*H*-benzo[*d*]imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**4a**), white solid (72 mg, 81%); m.p. 184-186 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ: 2.41 (*s*, 3H), 5.96 (*d*, *J* = 8.4 Hz, 1H), 6.94-7.03 (*m*, 3H), 7.21-7.25 (*m*, 1H), 7.38-7.47 (*m*, 2H), 7.62-7.65 (*m*, 1H), 7.92 (*d*, *J* = 8.4 Hz, 1H), 7.94-7.97 (*m*, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), δ: 13.8, 109.8, 111.3, 112.6, 119.5, 120.0, 120.1, 122.8, 123.8, 124.1, 126.2, 127.4, 128.9, 131.0, 135.4, 142.7, 144.5, 149.3, 151.3; ESI-HRMS, *m/z*: Calcd for $C_{19}H_{15}N_4$ $[M+H]^+$, 299.1291, found: 299.1294.

1-(2-Ethyl-1*H*-benzo[*d*]imidazol-1-yl)-4-methylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4b**), white solid (60 mg, 61%); m.p. 190-192 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 1.30 (*t*, *J* = 7.8 Hz, 3H), 2.57-2.71 (*m*, 2H), 2.84 (*s*, 3H), 5.90 (*d*, *J* = 8.4 Hz, 1H), 6.87 (*d*, *J* = 7.2 Hz, 1H), 6.94-6.98 (*m*, 2H), 7.18-7.21 (*m*, 1H), 7.35-7.38 (*m*, 1H), 7.40-7.43 (*m*, 2H), 7.93 (*d*, *J* = 7.8 Hz, 1H), 7.98 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 11.4, 17.8, 21.0, 109.8, 111.4, 112.6, 120.0, 120.1, 122.6, 123.6, 124.0, 125.9, 127.1, 128.0, 128.9, 129.5, 135.5, 142.7, 144.2, 149.7, 156.1; ESI-HRMS, *m/z*: Calcd for $C_{21}H_{19}N_4$ $[M+H]^+$, 327.1604, found: 327.1599.

4-Ethyl-1-(2-propyl-1*H*-benzo[*d*]imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**4c**), colorless waxy (54 mg, 51%); ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 0.90 (*t*, *J* = 7.2 Hz, 3H), 1.56 (*t*, *J* = 7.2 Hz, 3H), 1.74-1.85 (*m*, 2H), 2.56-2.65 (*m*, 2H), 3.27-3.36 (*m*, 2H), 5.91 (*d*, *J* = 8.4 Hz, 1H), 6.91 (*d*, *J* = 7.2 Hz, 1H), 6.95-6.99 (*m*, 2H), 7.19-7.22 (*m*, 1H), 7.36-7.39 (*m*, 1H), 7.41-7.44 (*m*, 2H), 7.93 (*d*, *J* = 8.4 Hz, 1H), 7.99 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 12.9, 13.9, 20.6, 24.4, 29.4, 109.8, 111.5, 112.7, 120.0, 120.1, 122.4, 123.6, 123.9, 125.0, 125.8, 127.9, 128.8, 135.1, 135.4, 142.7, 144.2, 149.3, 155.1; ESI-HRMS, *m/z*: Calcd for $C_{23}H_{23}N_4$ $[M+H]^+$, 355.1917, found: 355.1913.

4-Butyl-1-(2-pentyl-1*H*-benzo[*d*]imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**4d**), colorless waxy (57 mg, 46%); ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 0.76 (*t*, *J* = 7.2 Hz, 3H), 1.06 (*t*, *J* = 7.2 Hz, 3H), 1.15-1.20 (*m*, 2H), 1.21-1.27 (*m*, 2H), 1.55-1.63 (*m*, 2H), 1.71-1.78 (*m*, 2H), 1.94-1.99 (*m*, 2H), 2.57-2.65 (*m*, 2H), 3.22-3.31 (*m*, 2H), 5.91 (*d*, *J* = 8.4 Hz, 1H), 6.88 (*d*, *J* = 6.6 Hz, 1H), 6.94-6.98 (*m*, 2H), 7.18-7.21 (*m*, 1H), 7.35-7.39 (*m*, 1H), 7.40-7.43 (*m*, 2H), 7.93 (*d*, *J* = 7.8 Hz, 1H), 8.00 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 13.7, 14.1, 22.1, 22.7, 26.8, 27.5, 30.5, 31.0, 31.3, 109.8, 111.4, 112.7, 120.0, 120.1, 122.4, 123.6, 123.9, 125.7, 125.8, 127.9, 128.8, 133.9, 135.4, 142.7, 144.2, 149.3, 156.1; ESI-HRMS, *m/z*: Calcd for $C_{27}H_{31}N_4$ $[M+H]^+$, 411.2543, found: 411.2542.

1-(2-Benzyl-1*H*-benzo[*d*]imidazol-1-yl)-4-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4e**), white solid (96 mg, 71%); m.p. 165-167 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 4.03-4.24

(*dd*, J_1 = 13.2 Hz, J_2 = 13.2 Hz, 2H), 5.78 (*d*, *J* = 8.4 Hz, 1H), 6.72 (*d*, *J* = 7.2 Hz, 1H), 6.75 (*d*, *J* = 6.0 Hz, 2H), 6.80-6.85 (*m*, 3H), 6.87 (*d*, *J* = 8.4 Hz, 1H), 7.01 (*d*, *J* = 7.8 Hz, 1H), 7.22 (*t*, *J* = 7.2 Hz, 1H), 7.35 (*t*, *J* = 7.2 Hz, 1H), 7.39 (*t*, *J* = 7.2 Hz, 1H), 7.49-7.52 (*m*, 2H), 7.58-7.61 (*m*, 2H), 7.91 (*d*, *J* = 7.8 Hz, 1H), 7.98 (*d*, *J* = 7.8 Hz, 1H), 8.10 (*d*, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 35.2, 110.0, 111.8, 112.9, 120.3, 120.4, 122.3, 123.8, 124.4, 125.7, 126.7, 126.9, 127.5, 128.1, 128.5, 128.9, 129.1, 129.2, 129.6, 131.9, 134.3, 135.8, 136.0, 142.5, 144.5, 148.0, 153.5; ESI-HRMS, *m/z*: Calcd for $C_{31}H_{23}N_4$ $[M+H]^+$, 451.1917, found: 451.1943.

1-(2-(4-Methylbenzyl)-1*H*-benzo[*d*]imidazol-1-yl)-4-(p-tolyl)benzo[4,5]imidazo[1,2-*a*]pyridine (**4f**), white solid (104 mg, 73%); m.p. 172-173 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.03 (*s*, 3H), 2.51 (*s*, 3H), 4.08-4.19 (*dd*, J_1 = 15.6 Hz, J_2 = 15.6 Hz, 2H), 5.75 (*d*, *J* = 8.4 Hz, 1H), 6.58 (*d*, *J* = 7.8 Hz, 2H), 6.63 (*d*, *J* = 7.8 Hz, 2H), 6.79 (*d*, *J* = 7.2 Hz, 1H), 6.83-6.87 (*m*, 1H), 7.02 (*d*, *J* = 7.8 Hz, 1H), 7.22-7.25 (*m*, 1H), 7.34-7.37 (*m*, 1H), 7.39-7.42 (*m*, 1H), 7.44 (*d*, *J* = 8.4 Hz, 2H), 7.55 (*d*, *J* = 7.2 Hz, 1H), 7.92 (*d*, *J* = 7.2 Hz, 1H), 7.99 (*d*, *J* = 8.4 Hz, 1H), 8.04 (*d*, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 20.8, 21.4, 34.7, 110.0, 111.8, 113.0, 120.1, 120.3, 122.0, 123.7, 124.3, 125.5, 126.1, 127.5, 128.4, 128.7, 129.1, 129.4, 129.6, 131.2, 132.0, 133.1, 135.9, 136.5, 139.0, 142.5, 144.5, 148.0, 154.0; ESI-HRMS, *m/z*: Calcd for $C_{33}H_{27}N_4$ $[M+H]^+$, 479.2230, found: 479.2215.

1-(2-(4-Methoxybenzyl)-1*H*-benzo[*d*]imidazol-1-yl)-4-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (**4g**), white solid (101 mg, 66%); m.p. 184-186 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 3.54 (*s*, 3H), 3.92 (*s*, 3H), 4.02-4.14 (*dd*, J_1 = 15.6 Hz, J_2 = 15.6 Hz, 2H), 5.73 (*d*, *J* = 8.4 Hz, 1H), 6.30 (*d*, *J* = 8.4 Hz, 2H), 6.63 (*d*, *J* = 8.4 Hz, 2H), 6.76 (*d*, *J* = 7.2 Hz, 1H), 6.82-6.85 (*m*, 1H), 7.00 (*d*, *J* = 7.8 Hz, 1H), 7.14 (*d*, *J* = 8.4 Hz, 2H), 7.19-7.22 (*m*, 1H), 7.32-7.35 (*m*, 1H), 7.37-7.40 (*m*, 1H), 7.51 (*d*, *J* = 7.2 Hz, 1H), 7.90 (*d*, *J* = 8.4 Hz, 1H), 7.96 (*d*, *J* = 8.4 Hz, 1H), 8.11 (*d*, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 34.3, 55.1, 55.5, 110.0, 111.9, 113.0, 113.5, 114.3, 120.1, 120.3, 122.1, 123.7, 124.3, 125.5, 125.6, 126.3, 127.6, 128.4, 129.1, 129.5, 130.5, 131.6, 135.9, 142.5, 144.5, 148.1, 154.1, 158.3, 160.3; ESI-HRMS, *m/z*: Calcd for $C_{33}H_{27}N_4O_2$ $[M+H]^+$, 511.2129, found: 511.2135.

1-(2-(4-Bromobenzyl)-1*H*-benzo[*d*]imidazol-1-yl)-4-(4-bromophenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (**4h**), white solid (96 mg, 53%); m.p. 196-198 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 4.02-4.16 (*dd*, J_1 = 15.6 Hz, J_2 = 15.6 Hz, 2H), 5.75 (*d*, *J* = 8.4 Hz, 1H), 6.63 (*d*, *J* = 7.8 Hz, 2H), 6.80 (*d*, *J* = 7.2 Hz, 1H), 6.88-6.91 (*m*, 1H), 6.96 (*d*, *J* = 7.8 Hz, 2H), 7.05 (*d*, *J* = 7.8 Hz, 1H), 7.25-7.29 (*m*, 1H), 7.40-7.45 (*m*, 2H), 7.57 (*d*, *J* = 6.6 Hz, 1H), 7.76 (*d*, *J* = 8.4 Hz, 2H), 7.96 (*d*, *J* = 8.4 Hz, 1H), 7.99 (*d*, *J* = 8.4 Hz, 1H), 8.05 (*d*, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 34.5, 110.0, 111.7, 112.7, 120.5, 121.0, 122.6, 123.5, 124.0, 124.6, 126.0, 126.4, 127.4, 129.8, 130.1, 130.8, 130.9, 131.2, 132.1, 133.3, 134.6, 135.7,

142.4, 144.4, 147.5, 152.8; ESI-HRMS, *m/z*: Calcd for $C_{31}H_{21}Br_2N_4$ $[M+H]^+$, 607.0127, found: 607.0093.

1-(2-(4-Chlorobenzyl)-1*H*-benzo[*d*]imidazol-1-yl)-4-(4-chlorophenyl)benzo[4,5]imidazo [1,2-*a*]pyridine (**4i**), white solid (75 mg, 48%); m.p. 215-217 ^oC; ^1H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 4.03-4.17 (*dd*, J_1 = 15.6 Hz, J_2 = 15.6 Hz, 2H), 5.75 (*d*, *J* = 8.4 Hz, 1H), 6.69 (*d*, *J* = 8.4 Hz, 2H), 6.79-6.82 (*m*, 3H), 6.87-6.91 (*m*, 1H), 7.05 (*d*, *J* = 7.8 Hz, 1H), 7.26-7.29 (*m*, 1H), 7.39-7.44 (*m*, 2H), 7.57 (*d*, *J* = 7.2 Hz, 1H), 7.61 (*d*, *J* = 8.4 Hz, 2H), 7.95 (*d*, *J* = 8.4 Hz, 1H), 7.99 (*d*, *J* = 8.4 Hz, 1H), 8.12 (*d*, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 34.4, 110.0, 111.7, 112.7, 120.4, 120.5, 122.6, 124.0, 124.6, 126.0, 126.4, 127.4, 128.3, 129.1, 129.7, 129.8, 130.5, 130.8, 132.8, 132.9, 134.2, 135.2, 135.7, 142.4, 144.4, 147.6, 152.9; ESI-HRMS, *m/z*: Calcd for $C_{31}H_{21}Cl_2N_4$ $[M+H]^+$, 519.1138, found: 519.1158.

1-(2-(3-Methoxybenzyl)-1*H*-benzo[*d*]imidazol-1-yl)-4-(3-methoxyphenyl)benzo[4,5]imi dazo[1,2-*a*]pyridine (**4j**), white solid (103 mg, 67%); m.p. 183-185 ^oC; ^1H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 3.49 (*s*, 3H), 3.97 (*s*, 3H), 4.08-4.24 (*dd*, J_1 = 15.6 Hz, J_2 = 15.6 Hz, 2H), 5.80 (*d*, *J* = 8.4 Hz, 1H), 6.30 (*d*, *J* = 7.8 Hz, 1H), 6.33 (*s*, 1H), 6.36 (*d*, *J* = 8.4 Hz, 1H), 6.70-6.73 (*m*, 1H), 6.78 (*d*, *J* = 8.4 Hz, 1H), 6.88-6.91 (*m*, 1H), 7.04 (*d*, *J* = 7.8 Hz, 1H), 7.07-7.10 (*m*, 1H), 7.24-7.27 (*m*, 1H), 7.36-7.39 (*m*, 1H), 7.41-7.44 (*m*, 1H), 7.53 (*d*, *J* = 7.8 Hz, 1H), 7.55 (*d*, *J* = 7.2 Hz, 1H), 7.68 (*d*, *J* = 7.8 Hz, 1H), 7.71 (*s*, 1H), 7.80 (*d*, *J* = 8.4 Hz, 1H), 7.92 (*d*, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 35.3, 54.9, 55.4, 110.0, 111.7, 112.3, 112.9, 114.2, 114.5, 115.1, 120.2, 120.4, 120.8, 121.6, 122.2, 123.8, 124.4, 125.6, 126.7, 127.4, 129.1, 129.7, 129.8, 131.8, 135.6, 135.9, 137.3, 142.4, 144.5, 147.9, 153.5, 159.3, 159.8; ESI-HRMS, *m/z*: Calcd for $C_{33}H_{27}N_4O_2$ $[M+H]^+$, 511.2129, found: 511.2135.

1-(2-(2-Fluorobenzyl)-1*H*-benzo[*d*]imidazol-1-yl)-4-(2-fluorophenyl)benzo[4,5]imidazo [1,2-*a*]pyridine (**4k**), white solid (76 mg, 52%); m.p. 185-187 ^oC; ^1H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 4.20-4.29 (*dd*, J_1 = 15.6 Hz, J_2 = 15.6 Hz, 2H), 5.82 (*d*, *J* = 8.4 Hz, 1H), 6.53-6.57 (*m*, 1H), 6.60-6.63 (*m*, 1H), 6.80-6.84 (*m*, 1H), 6.85-6.92 (*m*, 3H), 7.06 (*d*, *J* = 7.8 Hz, 1H), 7.25- 7.27 (*m*, 1H), 7.31-7.34 (*m*, 1H), 7.35-7.38 (*m*, 1H), 7.40 (*d*, *J* = 7.2 Hz, 1H), 7.43 (*d*, *J* = 8.4 Hz, 1H), 7.50-7.54 (*m*, 1H), 7.61 (*d*, *J* = 6.6 Hz, 1H), 7.89 (*d*, *J* = 8.4 Hz, 1H), 7.99-8.02 (*m*, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 28.08 (*d*, *J* = 3.0 Hz), 110.03, 111.35, 112.79, 114.90 (*d*, *J* = 21.0 Hz), 116.37 (*d*, *J* = 22.5 Hz), 120.24, 120.45, 121.28 (*d*, *J* = 13.5 Hz), 122.28, 123.58 (*d*, *J* = 13.5 Hz), 123.77 (*d*, *J* = 4.5 Hz), 123.89, 124.42 (*d*, *J* = 3.0 Hz), 124.46, 125.74, 126.39, 127.56, 128.94 (*d*, *J* = 9.0 Hz), 129.10 (*d*, *J* = 4.5 Hz), 130.08, 130.68 (*d*, *J* = 3.0 Hz), 130.72, 131.96 (*d*, *J* = 3.0 Hz), 135.74, 142.45, 144.42, 147.95, 152.53, 160.11 (*d*, *J* = 247.5 Hz), 160.28 (*d*, *J* = 246.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$), *δ*, ppm: -117.2, -115.0; ESI-HRMS, *m/z*: Calcd for $C_{31}H_{21}F_2N_4$ $[M+H]^+$, 487.1729, found: 487.1779.

1-(2-(2-Bromobenzyl)-1*H*-benzo[*d*]imidazol-1-yl)-4-(2-bromophenyl)benzo[4,5]imidazo

[1,2-*a*]pyridine (**4l**), white solid (76 mg, 52%); m.p. 186-188 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 4.35-4.44 (*dd*, J_1 = 16.2 Hz, J_2 = 16.2 Hz, 2H), 5.90 (*d*, *J* = 8.4 Hz, 1H), 6.74-6.78 (*m*, 1H), 6.81 (*d*, *J* = 7.2 Hz, 1H), 6.87-6.90 (*m*, 1H), 6.91-6.94 (*m*, 1H), 7.03 (*d*, *J* = 7.8 Hz, 1H), 7.07 (*d*, *J* = 7.8 Hz, 1H), 7.13 (*d*, *J* = 7.8 Hz, 1H), 7.26-7.29 (*m*, 1H), 7.36-7.41 (*m*, 2H), 7.42-7.46 (*m*, 1H), 7.49 (*d*, *J* = 7.2 Hz, 1H), 7.53-7.56 (*m*, 1H), 7.72 (*d*, *J* = 7.8 Hz, 1H), 7.83 (*d*, *J* = 8.4 Hz, 1H), 7.99 (*d*, *J* = 8.4 Hz, 1H), 8.02 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 34.9, 110.0, 111.2, 112.9, 120.3, 120.5, 122.3, 123.4, 123.9, 124.3, 124.5, 125.8, 127.3, 127.5, 127.6, 128.7, 129.5, 130.2, 130.3, 130.9, 131.4, 131.9, 132.5, 133.6, 134.1, 135.8, 136.7, 142.5, 144.5, 148.1, 152.5; ESI-HRMS, *m/z*: Calcd for $C_{31}H_{21}Br_2N_4$ $[M+H]^+$, 607.0127, found: 607.0126.

7,8-Dimethyl-1-(2,5,6-trimethyl-1*H*-benzo[*d*]imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**4m**), white solid (61 mg, 58%); m.p. 261-263 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ: 2.07 (*s*, 3H), 2.23 (*s*, 3H), 2.33 (*s*, 3H), 2.35 (*s*, 3H), 2.40 (*s*, 3H), 5.73 (*s*, 1H), 6.73 (*s*, 1H), 6.86 (*d*, *J* = 6.6 Hz, 1H), 7.52-7.55 (*m*, 1H), 7.64 (*s*, 1H), 7.69 (*s*, 1H), 7.87 (*d*, *J* = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ: 13.7, 20.3, 20.4, 20.6, 20.8, 109.9, 110.8, 112.4, 119.0, 119.7, 119.9, 126.0, 128.0, 131.1, 132.2, 132.5, 133.2, 134.0, 135.8, 141.3, 149.0, 150.4; ESI-HRMS, *m/z*: Calcd for $C_{23}H_{23}N_4$ $[M+H]^+$, 355.1917, found: 355.1911.

1-(2-Ethyl-5,6-dimethyl-1*H*-benzo[*d*]imidazol-1-yl)-4,7,8-trimethylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4n**), white solid (59 mg, 52%); m.p. 234-236 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ: 1.27 (*t*, *J* = 7.2 Hz, 3H), 2.07 (*s*, 3H), 2.23 (*s*, 3H), 2.36 (*s*, 3H), 2.41 (*s*, 3H), 2.54-2.67 (*m*, 2H), 2.83 (*s*, 3H), 5.70 (*s*, 1H), 6.72 (*s*, 1H), 6.81 (*d*, *J* = 7.2 Hz, 1H), 7.35 (*d*, *J* = 7.2 Hz, 1H), 7.68 (*s*, 1H), 7.74 (*s*, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ: 11.5, 17.8, 20.3, 20.4, 20.6, 20.8, 20.9, 109.9, 110.9, 112.6, 119.7, 120.0, 126.3, 126.6, 128.9, 129.0, 131.9, 132.2, 133.0, 134.1, 135.4, 141.2, 143.0, 149.3, 155.2; ESI-HRMS, *m/z*: Calcd for $C_{25}H_{27}N_4$ $[M+H]^+$, 383.2230, found: 383.2249.

7,8-Dichloro-1-(5,6-dichloro-2-methyl-1*H*-benzo[*d*]imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**4o**), white solid (59 mg, 46%); m.p. 276-278 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ: 2.40 (*s*, 3H), 6.03 (*s*, 1H), 7.01 (*d*, *J* = 6.6 Hz, 1H), 7.11 (*s*, 1H), 7.67-7.71 (*m*, 1H), 7.96 (*d*, *J* = 9.0 Hz, 1H), 8.03 (*s*, 1H), 8.07 (*s*, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ: 13.9, 111.0, 112.2, 113.3, 120.2, 121.4, 121.6, 126.1, 127.0, 128.5, 128.7, 129.7, 130.0, 131.1, 134.2, 142.1, 143.8, 150.5, 153.1; ESI-HRMS, *m/z*: Calcd for $C_{19}H_{11}Cl_4N_4$ $[M+H]^+$, 434.9732, found: 434.9759.

1-(1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5a**), yellow solid (29 mg, 40%); m.p. 225-227 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 6.17 (*d*, *J* = 9.0 Hz, 1H), 6.90 (*d*, *J* = 7.2 Hz, 1H), 7.17-7.20 (*m*, 1H), 7.30 (*s*, 1H), 7.49-7.55 (*m*, 3H), 7.84-7.89 (*m*, 2H), 7.97 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 109.9, 113.0, 119.4, 120.2, 120.5, 122.5,

126.2, 127.4, 128.4, 131.2, 132.3, 137.4, 144.5, 149.1; ESI-HRMS, *m/z*: Calcd for $C_{14}H_{11}N_4$ $[M+H]^+$, 235.0978, found: 235.0976.

1-(2-Methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5b**), yellow solid (34 mg, 45%); m.p. 232-234 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 2.20 (*s*, 3H), 6.07 (*d*, *J* = 8.4 Hz, 1H), 6.88 (*d*, *J* = 7.8 Hz, 1H), 7.14 (*d*, *J* = 1.2 Hz, 1H), 7.18-7.21 (*m*, 1H), 7.32 (*d*, *J* = 1.2 Hz, 1H), 7.51-7.57 (*m*, 2H), 7.87 (*d*, *J* = 9.0 Hz, 1H), 7.97 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 12.8, 110.0, 112.7, 119.2, 120.1, 120.3, 122.7, 126.2, 127.4, 128.6, 129.7, 132.6, 144.5, 145.8, 149.0; ESI-HRMS, *m/z*: Calcd for $C_{15}H_{13}N_4$ $[M+H]^+$, 249.1135, found: 249.1131.

4-Methyl-1-(2-methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5c**), yellow solid (33 mg, 43%); m.p. 243-245 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 2.18 (*s*, 3H), 2.80 (*s*, 3H), 6.03 (*d*, *J* = 8.4 Hz, 1H), 6.80 (*d*, *J* = 7.2 Hz, 1H), 7.11 (*d*, *J* = 1.2 Hz, 1H), 7.15-7.19 (*m*, 1H), 7.30 (*d*, *J* = 1.2 Hz, 1H), 7.34 (*d*, *J* = 7.2 Hz, 1H), 7.48-7.52 (*m*, 1H), 8.00 (*d*, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 12.8, 17.7, 110.0, 112.7, 120.1, 120.5, 122.6, 125.9, 126.8, 128.0, 129.3, 129.5, 130.4, 144.2, 146.0, 149.4; ESI-HRMS, *m/z*: Calcd for $C_{16}H_{15}N_4$ $[M+H]^+$, 263.1291, found: 263.1287.

6-Butyl-1-(2-methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5d**), yellow solid (33 mg, 37%); m.p. 122-124 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 1.03 (*t*, *J* = 7.8 Hz, 3H), 1.52-1.59 (*m*, 2H), 1.89-1.94 (*m*, 2H), 2.20 (*s*, 3H), 3.13-3.26 (*m*, 2H), 6.03 (*d*, *J* = 8.4 Hz, 1H), 6.82 (*d*, *J* = 7.2 Hz, 1H), 7.12 (*d*, *J* = 1.2 Hz, 1H), 7.15-7.18 (*m*, 1H), 7.30 (*d*, *J* = 1.2 Hz, 1H), 7.33 (*d*, *J* = 7.2 Hz, 1H), 7.48-7.52 (*m*, 1H), 8.01 (*d*, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 12.8, 14.0, 22.6, 30.6, 31.0, 110.0, 112.6, 120.1, 120.5, 122.5, 125.5, 125.9, 128.0, 129.5, 130.3, 133.7, 144.2, 146.0, 149.1; ESI-HRMS, *m/z*: Calcd for $C_{19}H_{21}N_4$ $[M+H]^+$, 305.1761, found: 305.1757.

7,8-Dimethyl-1-(2-methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5e**), yellow solid (31 mg, 37%); m.p. 246-248 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 2.20 (*s*, 3H), 2.27 (*s*, 3H), 2.43 (*s*, 3H), 5.81 (*s*, 1H), 6.82 (*d*, *J* = 6.6 Hz, 1H), 7.12 (*d*, *J* = 1.2 Hz, 1H), 7.32 (*d*, *J* = 1.2 Hz, 1H), 7.46-7.49 (*m*, 1H), 7.72 (*s*, 1H), 7.82 (*d*, *J* = 9.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 12.8, 20.6, 20.8, 109.6, 112.4, 118.9, 119.7, 120.3, 125.9, 127.7, 129.5, 132.2, 135.9, 143.3, 145.8, 148.7; ESI-HRMS, *m/z*: Calcd for $C_{17}H_{17}N_4$ $[M+H]^+$, 277.1448, found: 277.1448.

7,8-Dichloro-1-(2-methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5f**), yellow solid (30 mg, 32%); m.p. 252-254 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 2.22 (*s*, 3H), 6.11 (*s*, 1H), 6.94 (*d*, *J* = 6.6 Hz, 1H), 7.13 (*d*, *J* = 1.2 Hz, 1H), 7.36 (*d*, *J* = 1.2 Hz, 1H), 7.59-7.62 (*m*, 1H), 7.85 (*d*, *J* = 9.6 Hz, 1H), 8.05 (*s*, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 12.8, 110.8, 114.0, 119.3, 119.9, 121.0, 126.3, 126.7, 129.8, 130.2, 130.8, 132.4, 143.7,

145.5, 150.3; ESI-HRMS, *m/z*: Calcd for $C_{15}H_{11}ClN_4$ $[M+H]^+$, 317.0355, found: 317.0382.

1-(1*H*-imidazol-1-yl)-4-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5g**), yellow solid (54 mg, 53%); m.p. 151-153 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 3.91 (*s*, 3H), 6.12 (*d*, *J* = 8.4 Hz, 1H), 6.94 (*d*, *J* = 7.2 Hz, 1H), 7.10 (*d*, *J* = 8.4 Hz, 2H), 7.14-7.18 (*m*, 1H), 7.31 (*d*, *J* = 1.2 Hz, 1H), 7.47-7.51 (*m*, 2H), 7.53 (*d*, *J* = 7.2 Hz, 1H), 7.87 (*s*, 1H), 8.00 (*d*, *J* = 8.4 Hz, 1H), 8.05 (*d*, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 55.5, 110.2, 112.9, 114.3, 120.5, 120.7, 122.4, 125.6, 125.9, 127.8, 128.2, 130.3, 130.4, 131.0, 131.7, 137.6, 144.6, 148.1, 160.3; ESI-HRMS, *m/z*: Calcd for $C_{21}H_{17}N_4O$ $[M+H]^+$, 341.1397, found: 341.1397.

4-(4-Methoxyphenyl)-1-(2-methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5h**), yellow solid (63 mg, 60%); m.p. 73-75 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 2.24 (*s*, 3H), 3.91 (*s*, 3H), 6.05 (*d*, *J* = 8.4 Hz, 1H), 6.94 (*d*, *J* = 7.2 Hz, 1H), 7.11 (*d*, *J* = 9.0 Hz, 2H), 7.16 (*d*, *J* = 1.2 Hz, 1H), 7.17-7.20 (*m*, 1H), 7.32 (*d*, *J* = 1.2 Hz, 1H), 7.49-7.52 (*m*, 1H), 7.56 (*d*, *J* = 7.2 Hz, 1H), 8.01 (*d*, *J* = 8.4 Hz, 1H), 8.06 (*d*, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 12.9, 55.5, 110.3, 112.6, 114.3, 120.4, 120.5, 122.7, 125.8, 126.0, 127.8, 128.2, 129.6, 130.4, 130.7, 131.6, 144.6, 146.0, 148.1, 160.3; ESI-HRMS, *m/z*: Calcd for $C_{22}H_{19}N_4O$ $[M+H]^+$, 355.1553, found: 335.1549.

1-(2-Ethyl-1*H*-imidazol-1-yl)-4-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5i**), yellow solid (46 mg, 42%); m.p. 82-84 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 1.21 (*t*, *J* = 7.2 Hz, 3H), 2.42-2.57 (*m*, 2H), 3.89 (*s*, 3H), 6.02 (*d*, *J* = 9.0 Hz, 1H), 6.92 (*d*, *J* = 7.2 Hz, 1H), 7.09 (*d*, *J* = 9.0 Hz, 2H), 7.13 (*d*, *J* = 1.2 Hz, 1H), 7.15-7.18 (*m*, 1H), 7.34 (*d*, *J* = 1.2 Hz, 1H), 7.47-7.50 (*m*, 1H), 7.54 (*d*, *J* = 7.2 Hz, 1H), 8.01 (*d*, *J* = 7.8 Hz, 1H), 8.06 (*d*, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 11.8, 20.2, 55.4, 110.5, 112.8, 114.3, 120.3, 120.4, 122.6, 125.8, 125.9, 127.8, 128.2, 129.6, 130.4, 130.6, 131.4, 144.5, 148.1, 150.7, 160.3; ESI-HRMS, *m/z*: Calcd for $C_{23}H_{21}N_4O$ $[M+H]^+$, 369.1710, found: 369.1690.

1-(2-Methyl-1*H*-imidazol-1-yl)-4-(*p*-tolyl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5j**), yellow solid (57 mg, 57%); m.p. 78-80 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 2.25 (*s*, 3H), 2.47 (*s*, 3H), 6.05 (*d*, *J* = 8.4 Hz, 1H), 6.94 (*d*, *J* = 7.2 Hz, 1H), 7.16 (*d*, *J* = 1.2 Hz, 1H), 7.17-7.20 (*m*, 1H), 7.32 (*d*, *J* = 1.2 Hz, 1H), 7.39 (*d*, *J* = 8.4 Hz, 2H), 7.48-7.52 (*m*, 1H), 7.58 (*d*, *J* = 7.2 Hz, 1H), 7.98 (*d*, *J* = 8.4 Hz, 2H), 8.02 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 12.9, 21.4, 110.2, 112.6, 120.4, 120.5, 122.7, 125.9, 126.3, 127.8, 129.0, 129.5, 129.6, 131.0, 132.0, 132.9, 139.0, 144.6, 146.0, 148.1; ESI-HRMS, *m/z*: Calcd for $C_{22}H_{19}N_4$ $[M+H]^+$, 339.1604, found: 339.1598.

4-(4-Chlorophenyl)-1-(2-methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5k**), yellow solid (54 mg, 51%); m.p. 69-71 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 2.26 (*s*, 3H), 6.05 (*d*, *J* = 8.4 Hz, 1H), 6.97 (*d*, *J* = 7.2 Hz, 1H), 7.17 (*d*, *J* = 1.2 Hz, 1H), 7.20-7.23 (*m*,

1H), 7.34 (*d*, *J* = 1.2 Hz, 1H), 7.51-7.54 (*m*, 1H), 7.57 (*d*, *J* = 8.4 Hz, 2H), 7.61 (*d*, *J* = 7.2 Hz, 1H), 8.02 (*d*, *J* = 8.4 Hz, 1H), 8.06 (*d*, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 12.9, 110.1, 112.7, 120.4, 120.5, 123.0, 126.2, 126.7, 127.8, 129.0, 129.7, 130.5, 130.7, 131.6, 134.2, 135.1, 144.6, 145.9, 147.7; ESI-HRMS, *m/z*: Calcd for $C_{22}H_{19}N_4$ $[M+H]^+$, 359.1058, found: 359.1048.

4-(3-Methoxyphenyl)-1-(2-methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5l**), yellow solid (43 mg, 49%); m.p. 49-51 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.26 (*s*, 3H), 3.93 (*s*, 3H), 6.06 (*d*, *J* = 8.4 Hz, 1H), 6.96 (*d*, *J* = 7.2 Hz, 1H), 7.04-7.06 (*m*, 1H), 7.17 (*d*, *J* = 1.2 Hz, 1H), 7.18-7.21 (*m*, 1H), 7.34 (*d*, *J* = 1.2 Hz, 1H), 7.48-7.53 (*m*, 2H), 7.62 (*d*, *J* = 7.2 Hz, 1H), 7.64 (*d*, *J* = 7.8 Hz, 1H), 7.67-7.68 (*m*, 1H), 8.02 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 12.9, 55.4, 110.2, 112.6, 114.6, 115.0, 120.4, 120.6, 121.6, 122.8, 126.0, 126.9, 127.8, 129.7, 129.8, 131.3, 131.8, 137.1, 144.6, 146.0, 147.9, 159.8; ESI-HRMS, *m/z*: Calcd for $C_{22}H_{19}N_4O$ $[M+H]^+$, 355.1553, found: 335.1558.

4-(2-Bromophenyl)-1-(2-methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5m**), yellow solid (67 mg, 56%); m.p. 75-77 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.28 (*s*, 3H), 6.09 (*d*, *J* = 8.4 Hz, 1H), 6.97 (*d*, *J* = 7.2 Hz, 1H), 7.19-7.22 (*m*, 2H), 7.35 (*d*, *J* = 1.2 Hz, 1H), 7.36-7.40 (*m*, 1H), 7.48-7.51 (*m*, 2H), 7.53 (*d*, *J* = 7.2 Hz, 1H), 7.66 (*d*, *J* = 7.2 Hz, 1H), 7.79 (*d*, *J* = 7.8 Hz, 1H), 7.99 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 12.9, 109.6, 112.7, 120.4, 120.6, 122.9, 123.4, 126.2, 127.6, 127.8, 129.4, 129.8, 130.3, 131.4, 131.8, 132.0, 133.5, 136.7, 144.6, 145.9, 147.9; ESI-HRMS, *m/z*: Calcd for $C_{21}H_{16}BrN_4$ $[M+H]^+$, 403.0553, found: 403.0551.

4-(2-Fluorophenyl)-1-(2-methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5n**), yellow solid (63 mg, 61%); m.p. 60-62 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.26 (*s*, 3H), 6.06 (*d*, *J* = 8.4 Hz, 1H), 6.95 (*d*, *J* = 7.2 Hz, 1H), 7.16 (*d*, *J* = 1.2 Hz, 1H), 7.18-7.20 (*m*, 1H), 7.27-7.29 (*m*, 1H), 7.32 (*d*, *J* = 1.2 Hz, 1H), 7.34-7.37 (*m*, 1H), 7.45-7.50 (*m*, 2H), 7.62 (*d*, *J* = 7.2 Hz, 1H), 7.94-7.99 (*m*, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 12.93, 109.86, 112.66, 116.33 (*d*, *J* = 22.5 Hz), 120.39, 120.52, 122.86, 123.40 (*d*, *J* = 13.5 Hz), 124.41 (*d*, *J* = 4.5 Hz), 126.14, 126.24, 127.81, 129.21 (*d*, *J* = 3.0 Hz), 129.73, 130.72 (*d*, *J* = 7.5 Hz), 131.88, 131.94 (*d*, *J* = 3.0 Hz), 144.53, 145.93, 147.90, 160.0 (*d*, *J* = 247.5 Hz); ^{19}F NMR (564 MHz, $CDCl_3$), *δ*, ppm: 115.1; ESI-HRMS, *m/z*: Calcd for $C_{21}H_{16}FN_4$ $[M+H]^+$, 343.1354, found: 343.1351.

4-(4-Chlorophenyl)-7,8-dimethyl-1-(2-methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5o**), yellow solid (55 mg, 48%); m.p. 221-223 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.23 (*s*, 3H), 2.27 (*s*, 3H), 2.41 (*s*, 3H), 5.80 (*s*, 1H), 6.89 (*d*, *J* = 7.2 Hz, 1H), 7.15 (*d*, *J* = 1.2 Hz, 1H), 7.33 (*d*, *J* = 1.2 Hz, 1H), 7.51-7.54 (*m*, 3H), 7.76 (*s*, 1H), 8.04 (*d*, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 12.9, 20.7, 20.9, 109.7, 112.3, 120.1, 120.4, 125.9,

126.2, 128.9, 129.5, 130.2, 130.4, 131.3, 132.5, 134.4, 134.9, 135.8, 143.4, 145.9, 147.2; ESI-HRMS, *m/z*: Calcd for $C_{23}H_{20}ClN_4$ $[M+H]^+$, 387.1371, found: 387.1370.

7,8-Dichloro-4-(4-chlorophenyl)-1-(2-methyl-1*H*-imidazol-1-yl)benzo[4,5]imidazo[1,2-a]pyridine (**5p**), yellow solid (57 mg, 44%); m.p. 182-184 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 2.24 (*s*, 3H), 6.09 (*s*, 1H), 7.00 (*d*, *J* = 7.2 Hz, 1H), 7.14 (*d*, *J* = 1.8 Hz, 1H), 7.36 (*d*, *J* = 1.8 Hz, 1H), 7.54 (*d*, *J* = 9.0 Hz, 2H), 7.63 (*d*, *J* = 7.2 Hz, 1H), 8.00 (*d*, *J* = 9.0 Hz, 2H), 8.07 (*s*, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 12.9, 111.0, 114.0, 120.0, 121.4, 126.6, 126.9, 127.6, 129.1, 130.1, 130.4, 130.7, 130.9, 131.3, 133.5, 135.5, 143.6, 145.6, 149.0; ESI-HRMS, *m/z*: Calcd for $C_{21}H_{14}Cl_3N_4$ $[M+H]^+$, 427.0279, found: 427.0279.

4-(4-Methoxyphenyl)-1-(1*H*-pyrazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5q**), yellow solid (53 mg, 52%); m.p. 126-128 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 3.92 (*s*, 3H), 6.03 (*d*, *J* = 8.4 Hz, 1H), 6.73-6.75 (*m*, 1H), 6.99 (*d*, *J* = 7.2 Hz, 1H), 7.12 (*d*, *J* = 9.0 Hz, 2H), 7.12-7.16 (*m*, 1H), 7.45-7.49 (*m*, 1H), 7.55 (*d*, *J* = 7.8 Hz, 1H), 7.86 (*d*, *J* = 1.8 Hz, 1H), 8.00 (*d*, *J* = 8.4 Hz, 1H), 8.03 (*d*, *J* = 1.8 Hz, 1H), 8.06 (*d*, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 55.5, 108.3, 110.2, 113.4, 114.2, 120.3, 121.9, 125.6, 125.7, 127.8, 128.4, 130.5, 131.7, 132.2, 133.3, 142.5, 144.4, 148.1, 160.2; ESI-HRMS, *m/z*: Calcd for $C_{21}H_{17}N_4O$ $[M+H]^+$, 341.1397, found: 341.1392.

4-(4-Methoxyphenyl)-1-(1*H*-1,2,4-triazol-1-yl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5r**), yellow solid (56 mg, 55%); m.p. 195-197 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 3.93 (*s*, 3H), 6.09 (*d*, *J* = 8.4 Hz, 1H), 7.02 (*d*, *J* = 7.2 Hz, 1H), 7.12 (*d*, *J* = 9.0 Hz, 2H), 7.17-7.20 (*m*, 1H), 7.49-7.53 (*m*, 1H), 7.56 (*d*, *J* = 7.2 Hz, 1H), 8.03 (*d*, *J* = 8.4 Hz, 1H), 8.08 (*d*, *J* = 9.0 Hz, 2H), 8.47 (*s*, 1H), 8.59 (*s*, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 55.5, 110.9, 112.7, 114.3, 120.7, 122.5, 125.1, 126.0, 127.7, 128.0, 129.5, 130.5, 133.0, 144.6, 145.5, 147.9, 153.8, 160.2; ESI-HRMS, *m/z*: Calcd for $C_{20}H_{16}N_5O$ $[M+H]^+$, 342.1349, found: 342.1349.

1-(1*H*-benzo[*d*]imidazol-1-yl)-4-(4-methoxyphenyl)benzo[4,5]imidazo[1,2-*a*]pyridine (**5s**), yellow solid (49 mg, 42%); m.p. 207-209 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 3.93 (*s*, 3H), 6.02 (*d*, *J* = 8.4 Hz, 1H), 6.96-6.99 (*m*, 1H), 7.03 (*d*, *J* = 7.8 Hz, 1H), 7.14 (*d*, *J* = 8.4 Hz, 2H), 7.17 (*d*, *J* = 8.4 Hz, 1H), 7.32-7.35 (*m*, 1H), 7.41-7.44 (*m*, 1H), 7.45-7.48 (*m*, 1H), 7.61 (*d*, *J* = 7.2 Hz, 1H), 8.01 (*d*, *J* = 8.4 Hz, 1H), 8.06 (*d*, *J* = 8.4 Hz, 1H), 8.11 (*d*, *J* = 8.4 Hz, 2H), 8.21 (*s*, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 55.5, 110.6, 111.2, 113.0, 114.3, 120.5, 121.2, 122.4, 124.1, 125.1, 125.7, 125.8, 127.8, 128.2, 129.1, 130.5, 131.9, 134.2, 142.1, 143.1, 144.7, 148.4, 160.4; ESI-HRMS, *m/z*: Calcd for $C_{25}H_{19}N_4O$ $[M+H]^+$, 391.1553, found: 391.1550.

3,3-Bis(2-methyl-1*H*-benzo[*d*]imidazol-1-yl)acrylaldehyde (**4aa**), colorless waxy; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 2.22 (*s*, 3H), 2.33 (*s*, 3H), 6.41 (*d*, *J* = 7.2 Hz, 1H), 7.09 (*d*, *J* = 7.2 Hz, 1H), 7.24-7.31 (*m*, 3H), 7.34-7.39 (*m*, 2H), 7,75 (*d*, *J* = 8.4 Hz, 1H), 7,80 (*d*, *J* =

7.8 Hz, 1H), 9.58 (*d*, *J* = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 14.6, 15.1, 109.8, 110.4, 117.7, 120.4, 120.5, 124.7, 124.9, 125.0, 125.1, 133.9, 135.7, 140.9, 142.5, 142.8, 150.9, 151.2, 188.4; ESI-HRMS, *m/z*: Calcd for $C_{19}H_{17}N_4O$ $[M+H]^+$, 317.1397, found: 317.1394.

Data of Single-crystal X-ray Analysis

Table S1. Crystal data and structure refinement for **4a**.

Compound	**4a**
Empirical formula	$C_{19}H_{14}N_4$
Formula weight	298.34
Temperature (K)	293.15
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions (Å, °)	a = 7.8364(10), b = 16.955(3), c =11.2061(19) α = 90, β = 94.406(13), γ = 90
Volume (Å^3)	1484.5(4)
Z	4
Density (calculated) (Mg/m^3)	1.335
Absorption coefficient (mm^{-1})	0.082
F(000)	624
Theta range for data collection	3.507 to 24.999 deg
Index ranges	-9<=h<=9, -13<=k<=20, -12<=l<=13
Reflections collected	6190
Independent reflections	2613 [R(int) = 0.0627]
Completeness to theta = 24.999 °	0.997
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.916
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2613 / 0 / 209
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R_1 = 0.0647, wR_2 = 0.0865
R indices (all data)	R_1 = 0.1349, wR_2 = 0.1115
Extinction coefficient	n/a
Largest diff. peak and hole	0.170 and -0.189 e.Å^{-3}

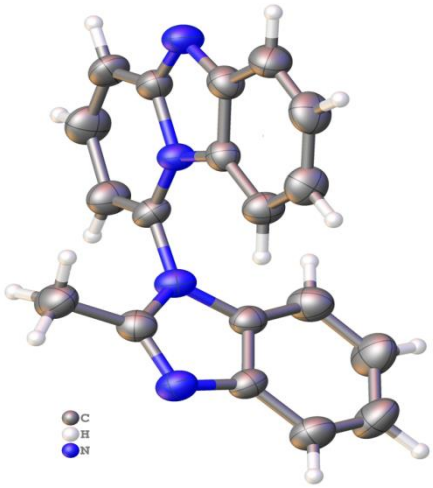


Fig. S1. The molecular structure of **4a**.

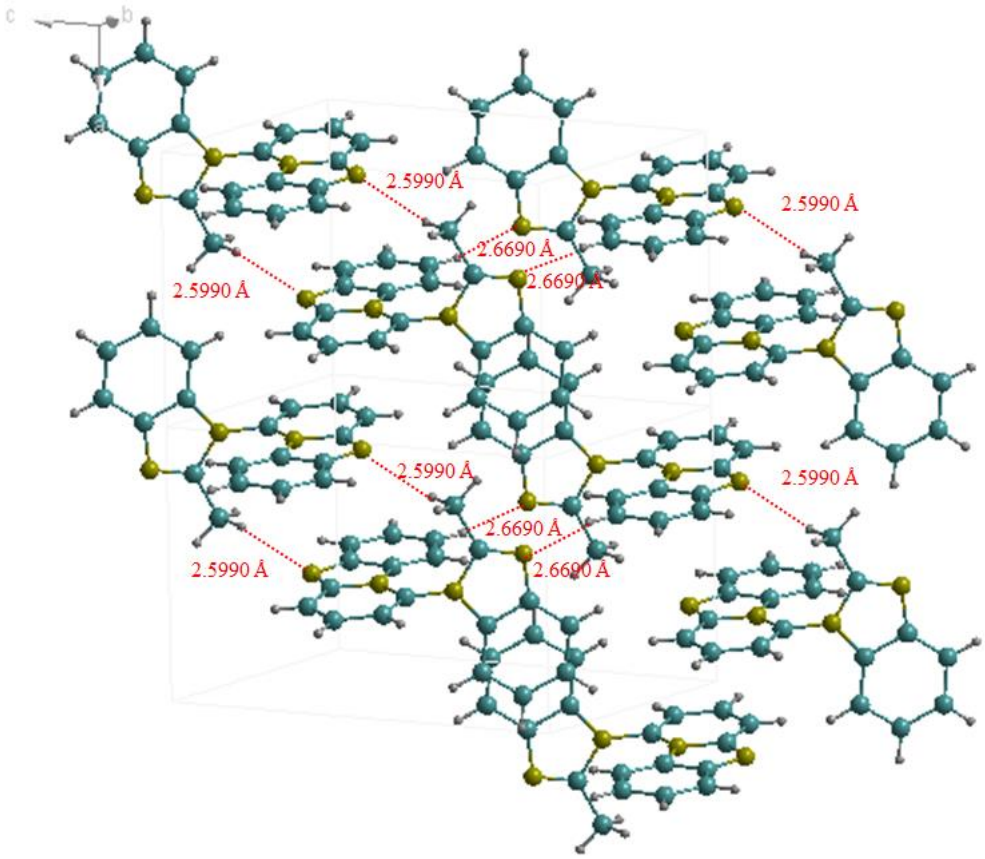


Fig. S2. Top view of packing structure of **4a** crystal.

Table S2. Crystal data and structure refinement for **4i**.

Compound	**4i**
Empirical formula	$C_{31}H_{20}Cl_2N_4$
Formula weight	519.41
Temperature (K)	290
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P -1
Unit cell dimensions (Å, °)	a = 9.1302(6), b = 11.9492(9), c =11.8521(7) α = 78.067(5), β = 75.145(5), γ = 67.721(6)
Volume ($Å^3$)	1244.66(15)
Z	2
Density (calculated) (Mg/m^3)	1.386
Absorption coefficient (mm^{-1})	0.290
F(000)	536.00
Theta range for data collection	7.092 to 58.65°
Index ranges	-12<=h<=11, -12<=k<=16, -17<=I<=15
Reflections collected	10948
Independent reflections	5742 [R(int) = 0.0265, R(sigma) = 0.0481]
Completeness to theta = 29.325	840
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.615
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5742 / 0 / 334
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R_1 = 0.0577, wR_2 = 0.1163
R indices (all data)	R_1 = 0.0920, wR_2 = 0.1327
Extinction coefficient	n/a
Largest diff. peak and hole	0.43 and -0.38 e.$Å^{-3}$

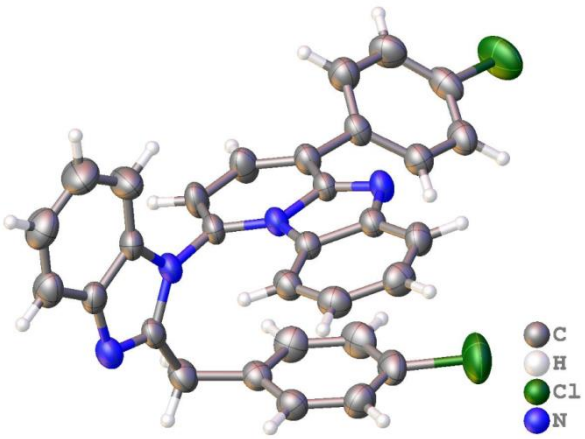


Fig. S3. The molecular structure of **4i**.

Table S3. Crystal data and structure refinement for **5g**.

Compound	**5g**
Empirical formula	$C_{21}H_{16}N_4O$
Formula weight	340.38
Temperature (K)	150
Wavelength (Å)	1.54184
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	a = 14.9018(14), b = 25.7373(3), c = 8.7556(8) α = 90, β = 93.9084(9), γ = 90
Volume ($Å^3$)	3350.27(5)
Z	8
Density (calculated) (Mg/m^3)	1.350
Absorption coefficient (mm^{-1})	0.691
F(000)	1424.0
Theta range for data collection (°)	5.944 to 148.332
Index ranges	-18<=h<=17, -31<=k<=331, -7<=I<=10
Reflections collected	23917
Independent reflections	6731 [R(int) = 0.0255, R(sigma) = 0.0220]
Completeness to theta = 74.166	989
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.764
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6731 / 0 / 472
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R_1 = 0.0385, wR_2 = 0.0998
R indices (all data)	R_1 = 0.0434, wR_2 = 0.1036
Extinction coefficient	n/a
Largest diff. peak and hole ($e.Å^{-3}$)	0.43 and -0.27

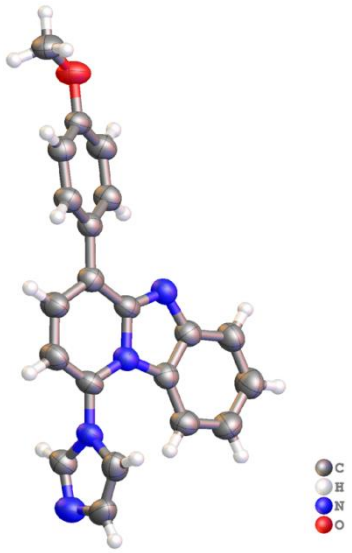


Fig. S4. The molecular structure of **5g**.

NMR Spectra for All Compounds 4a-4o, 5q-5s and Intermediate 4aa

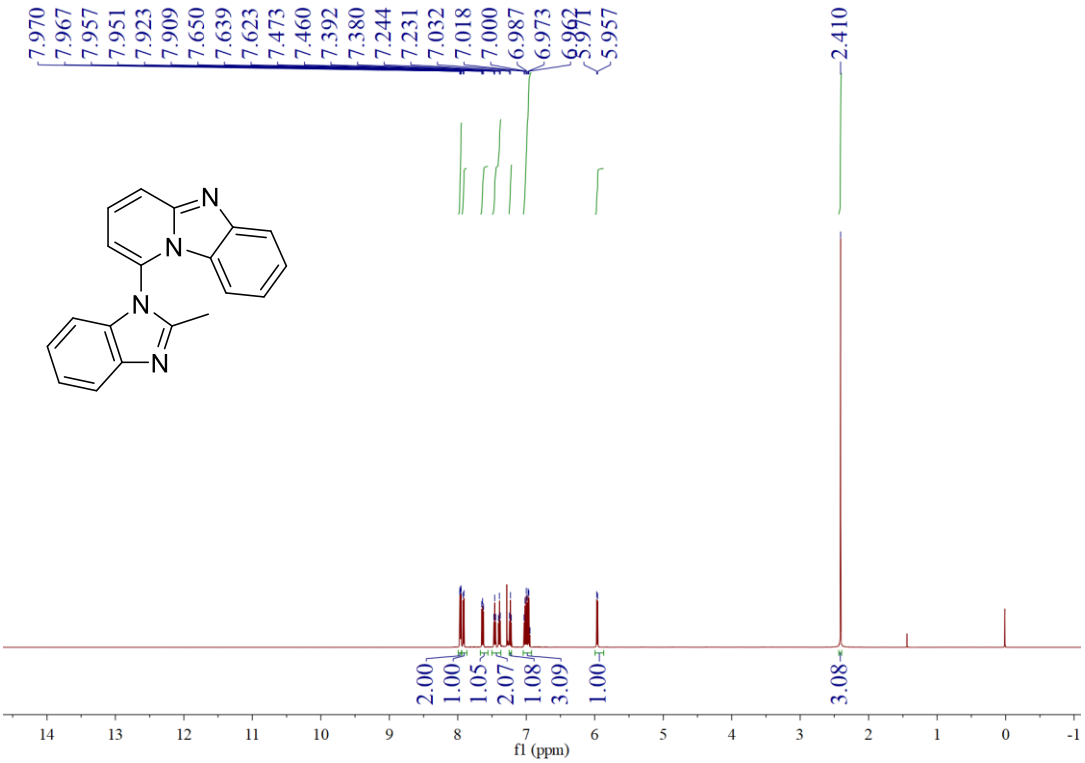


Fig. S5. ^{1}H NMR spectrum of compound **4a**.

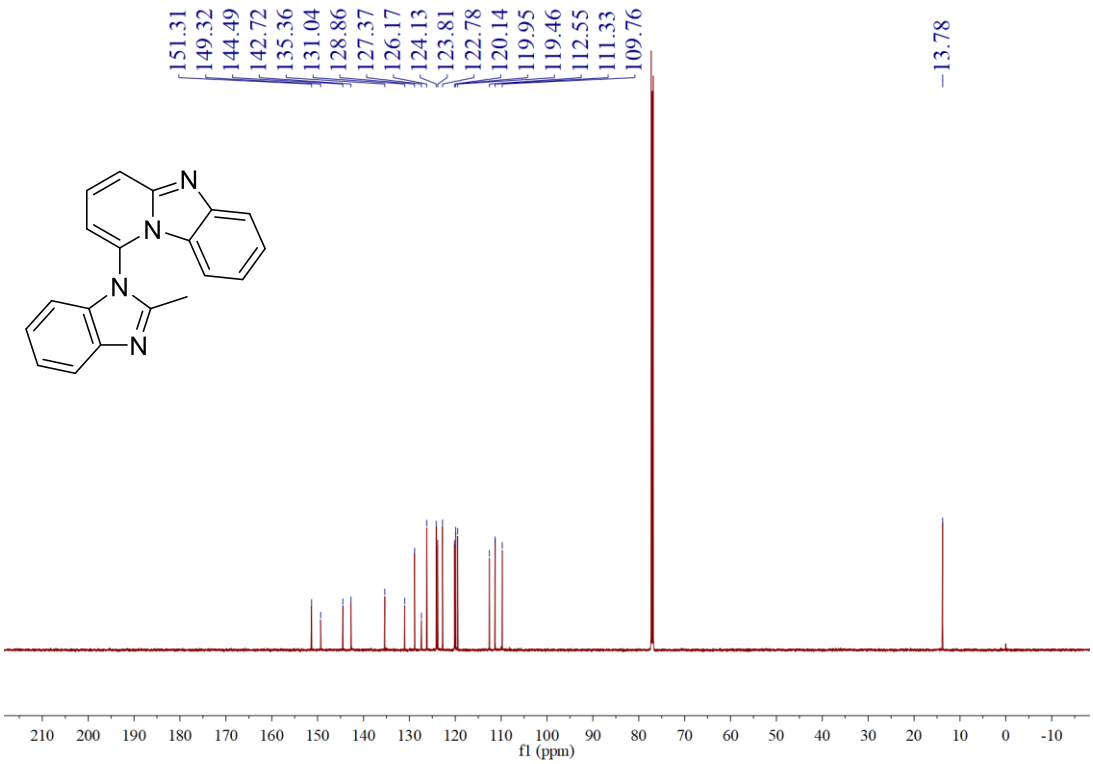


Fig. S6. ^{13}C NMR spectrum of compound **4a**.

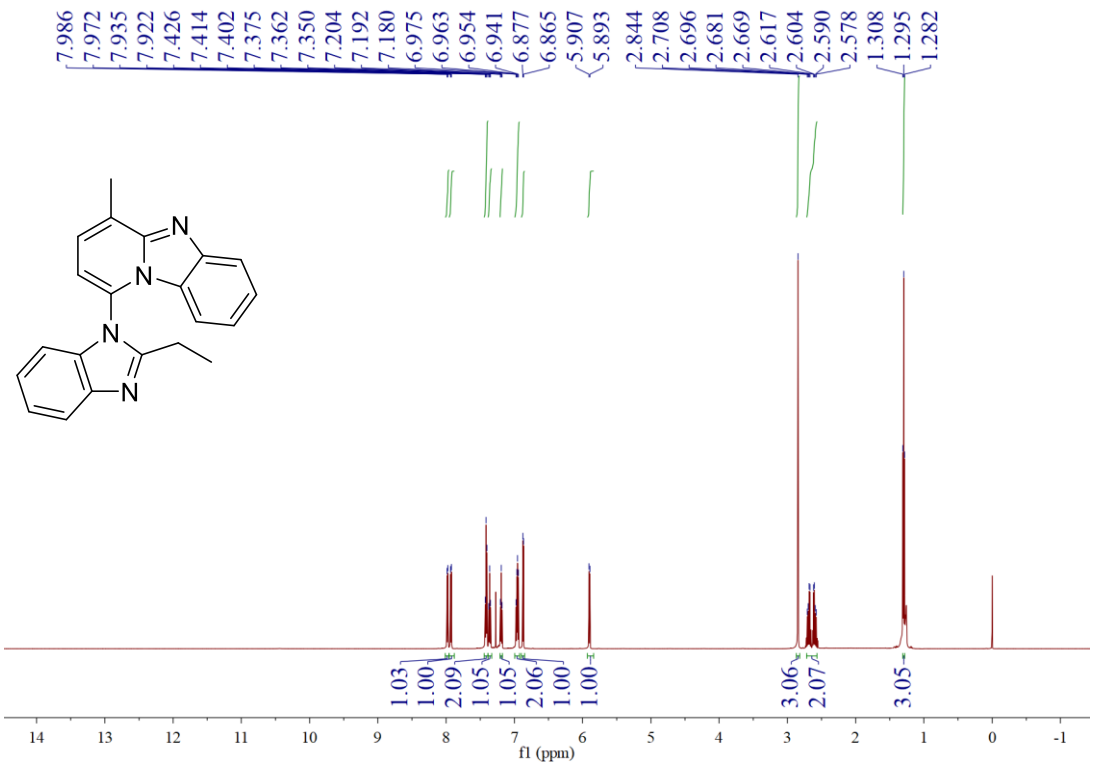


Fig. S7. ^{1}H NMR spectrum of compound **4b**.

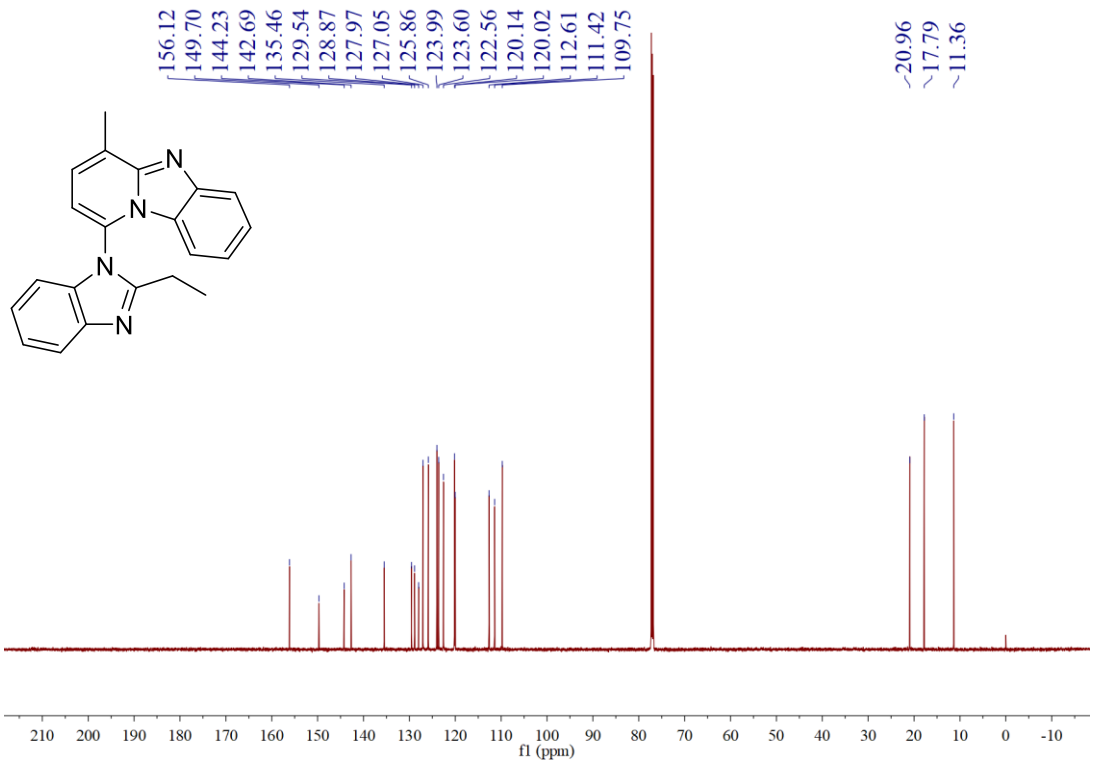


Fig. S8. ^{13}C NMR spectrum of compound **4b**.

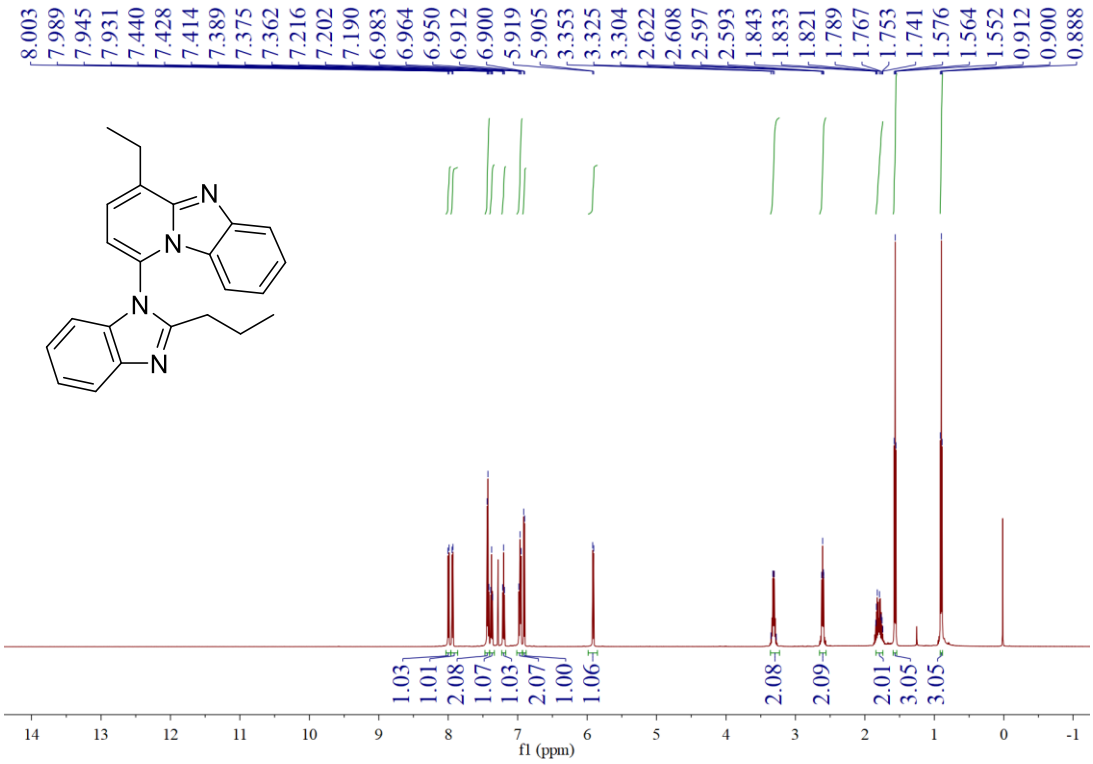


Fig. S9. ^{1}H NMR spectrum of compound **4c**.

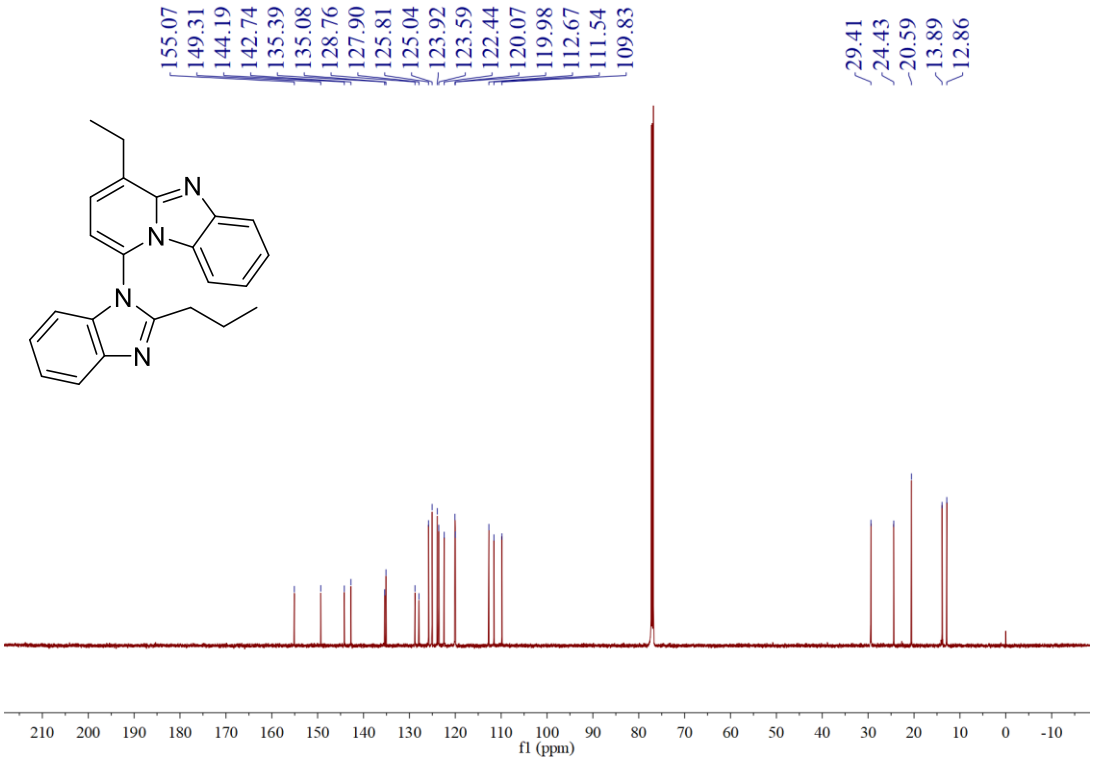


Fig. S10. ^{13}C NMR spectrum of compound **4c**.

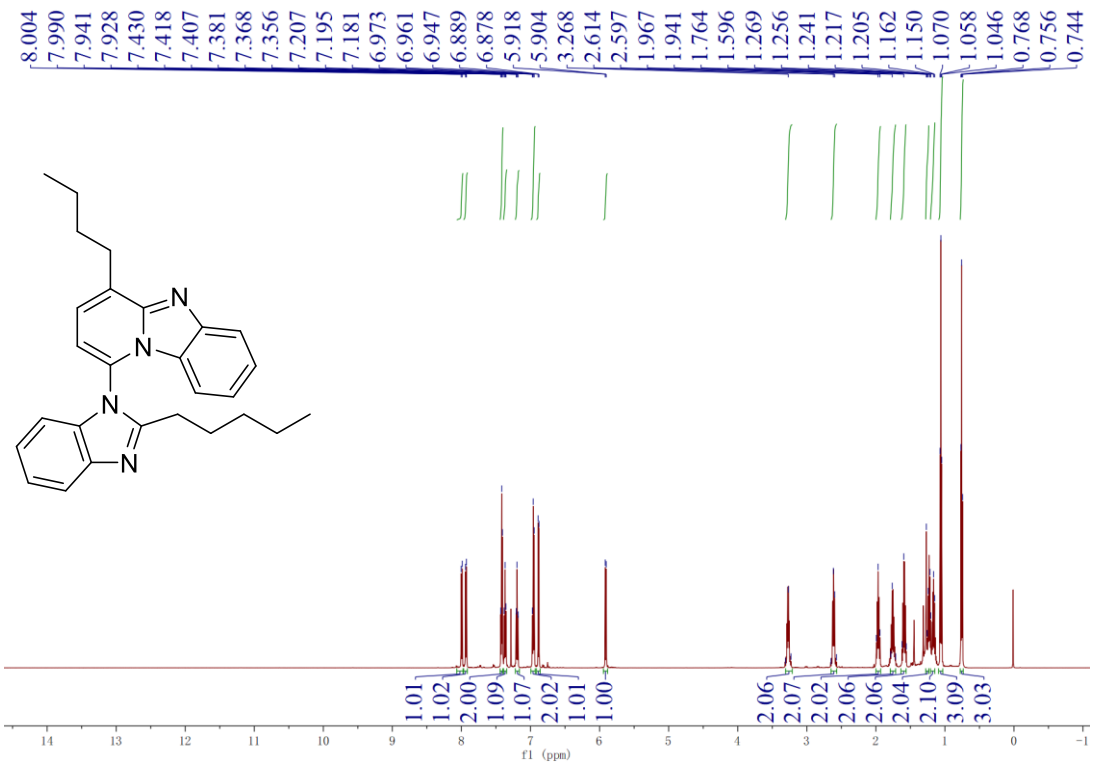


Fig. S11. ^{1}H NMR spectrum of compound **4d**.

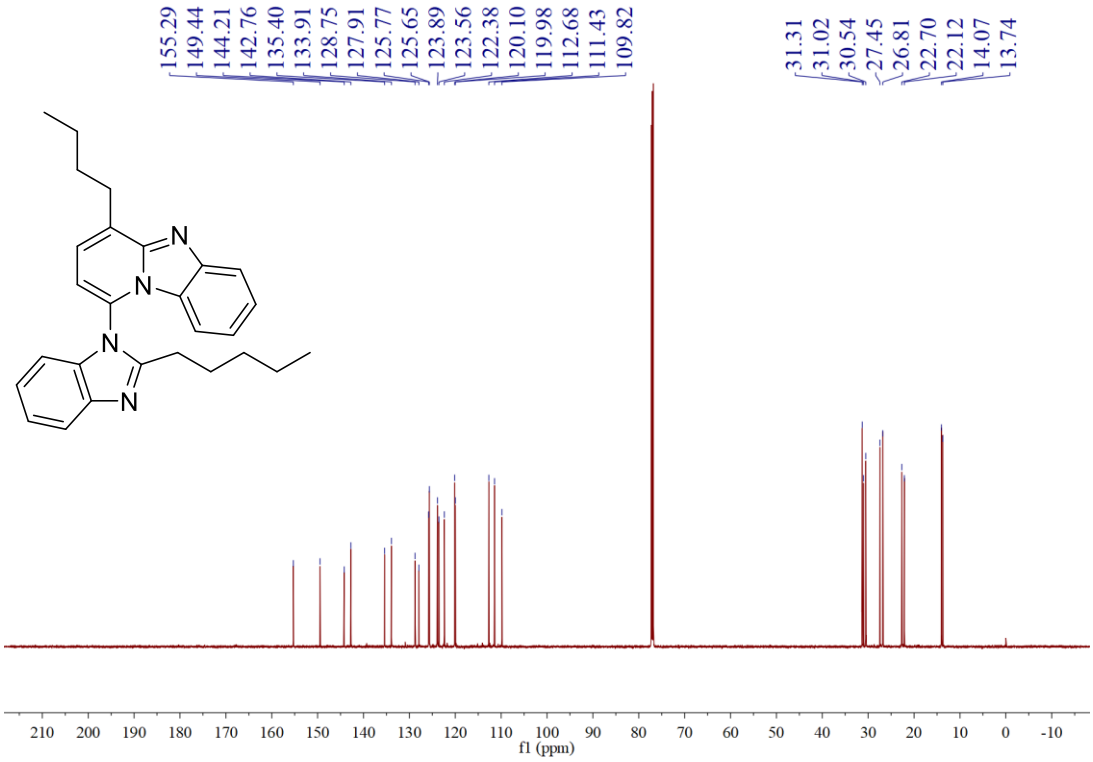


Fig. S12. ^{13}C NMR spectrum of compound **4d**.

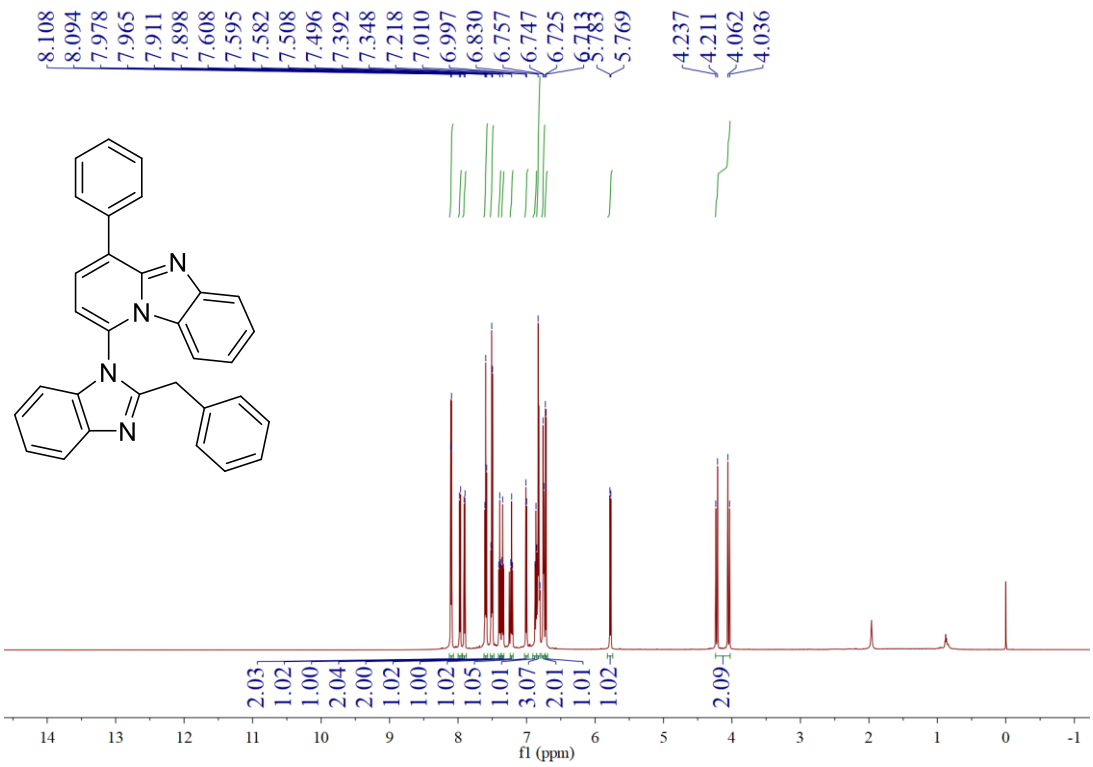


Fig. S13. ^{1}H NMR spectrum of compound **4e**.

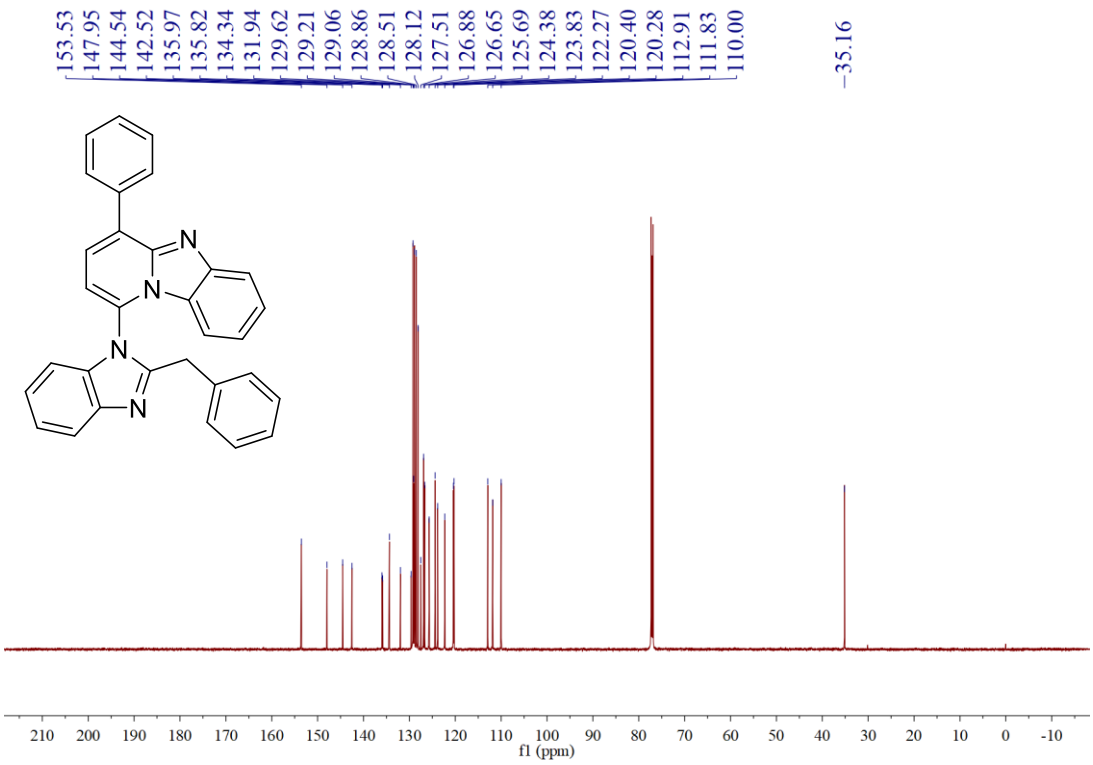


Fig. S14. ^{13}C NMR spectrum of compound **4e**.

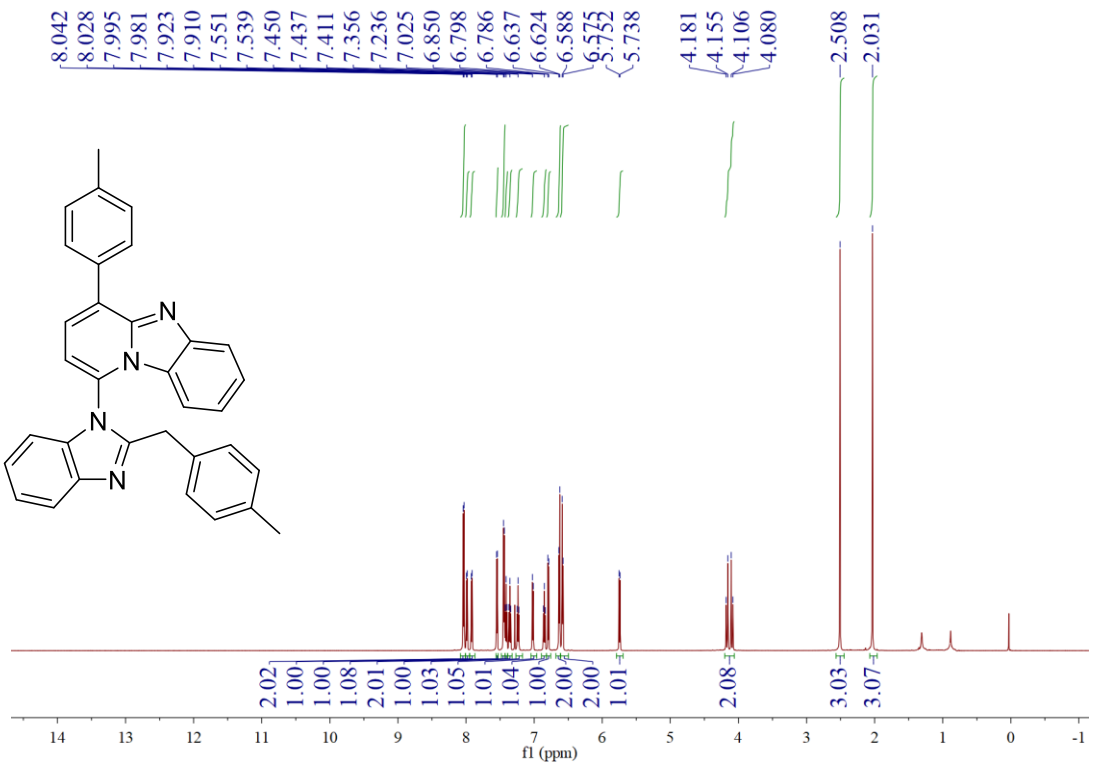


Fig. S15. ^{1}H NMR spectrum of compound **4f**.

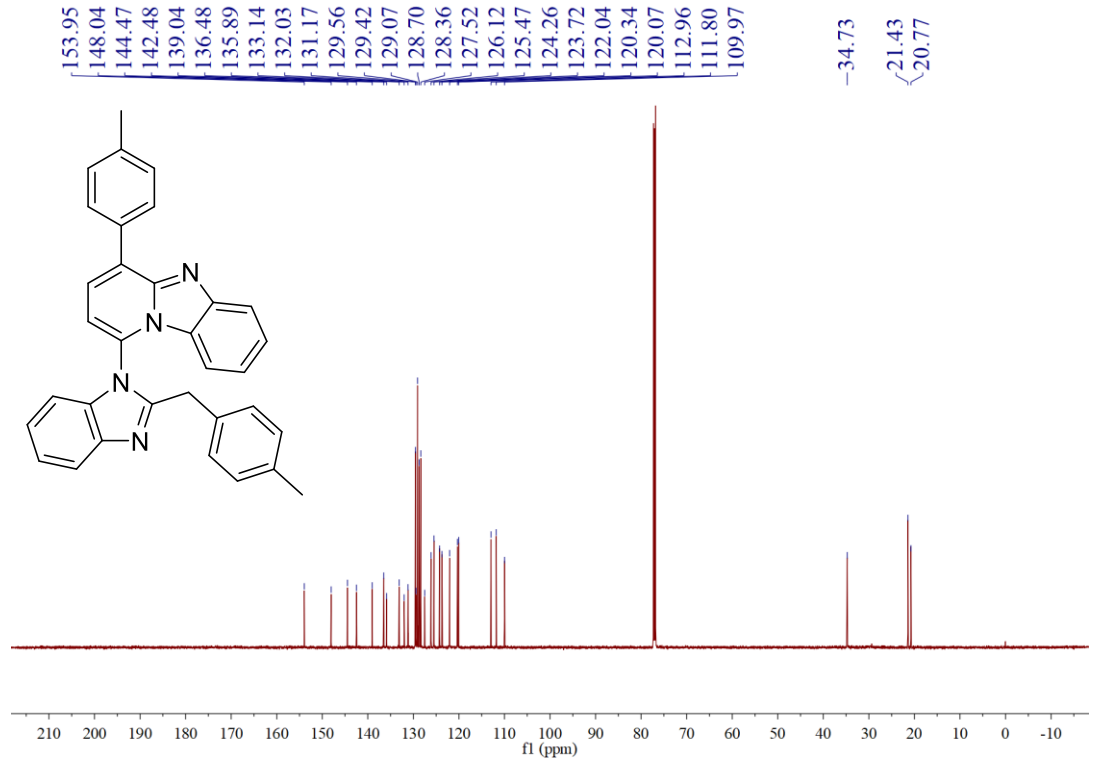


Fig. S16. ^{13}C NMR spectrum of compound **4f**.

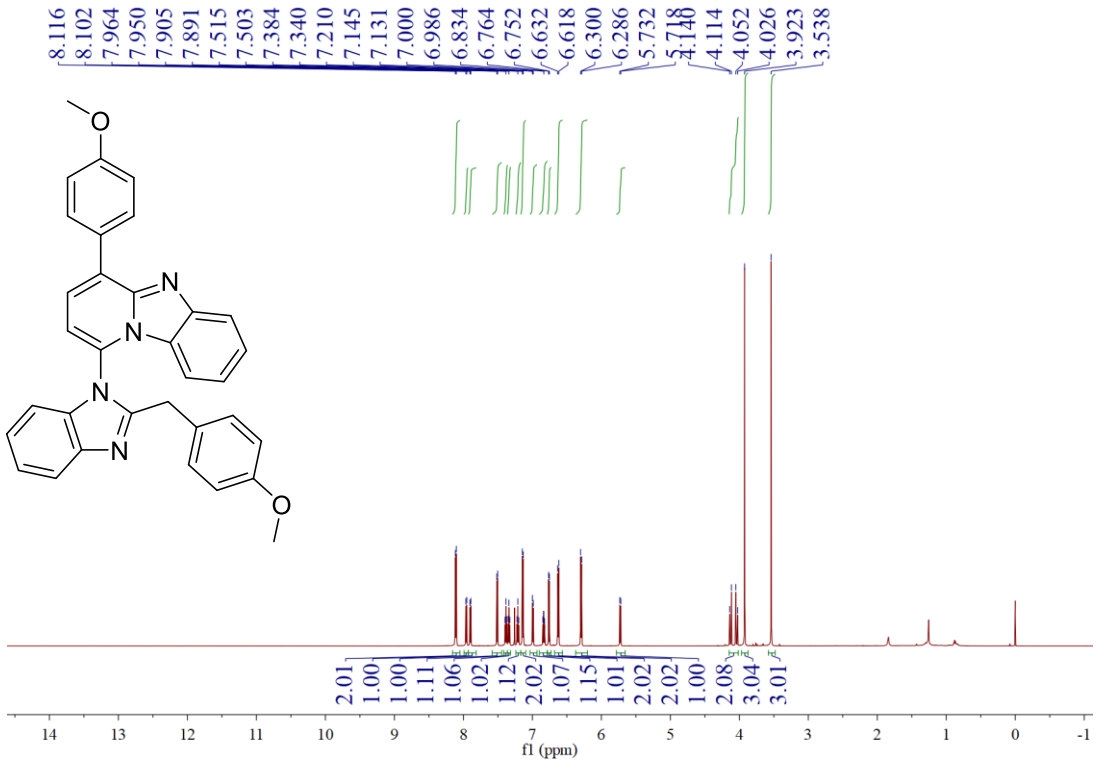


Fig. S17. ^{1}H NMR spectrum of compound **4g**.

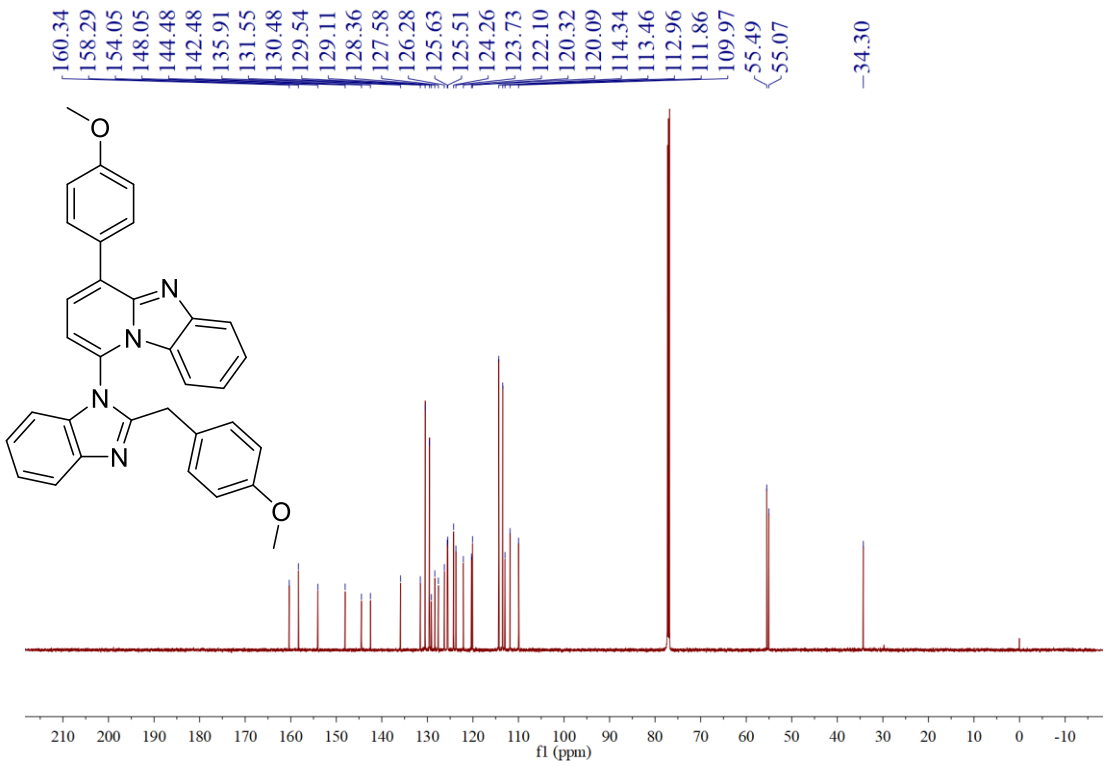


Fig. S18. ^{13}C NMR spectrum of compound **4g**.

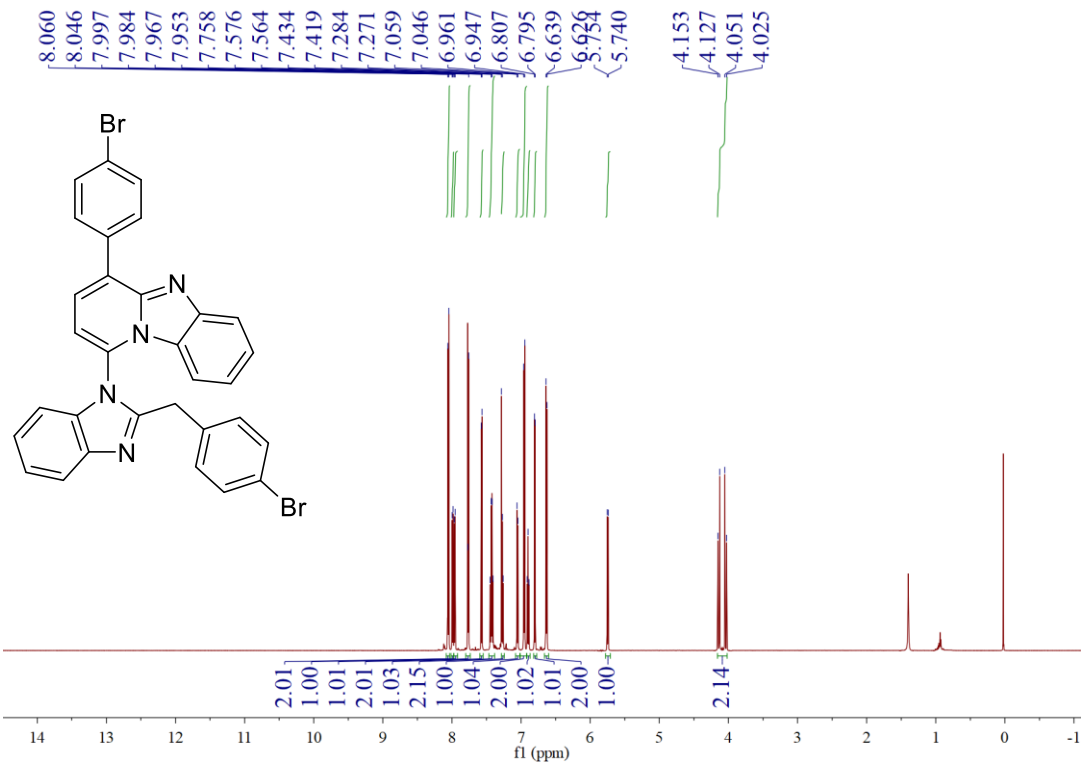


Fig. S19. ^{1}H NMR spectrum of compound **4h**.

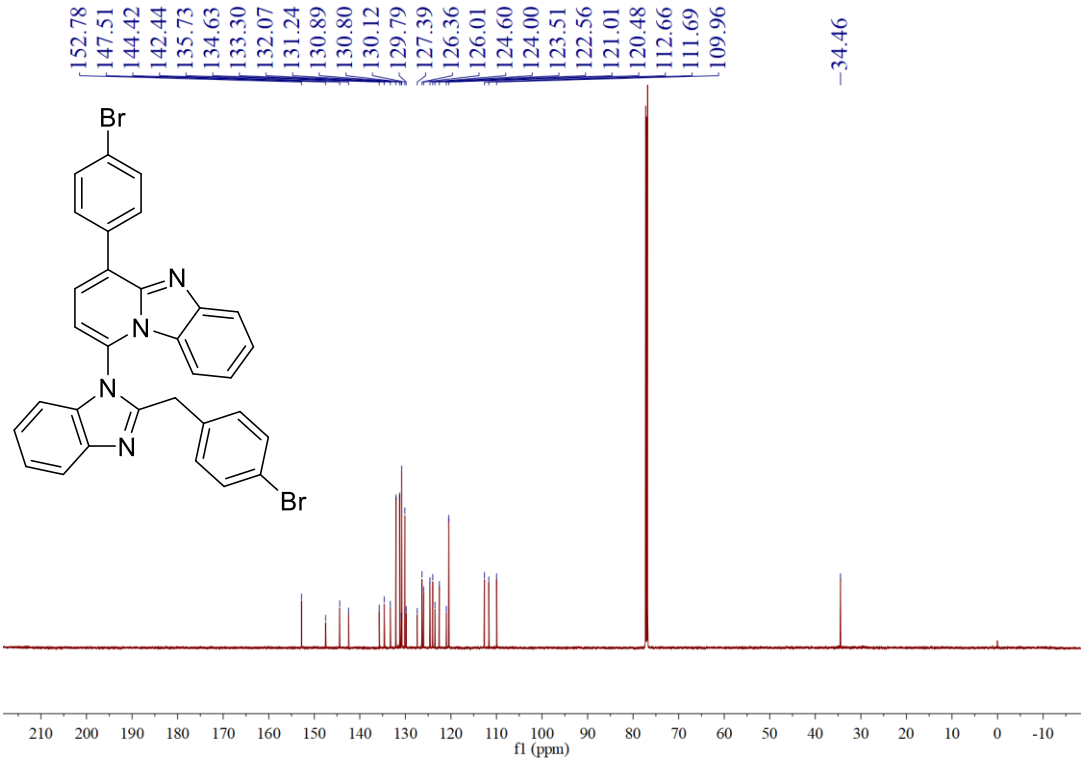


Fig. S20. ^{13}C NMR spectrum of compound **4h**.

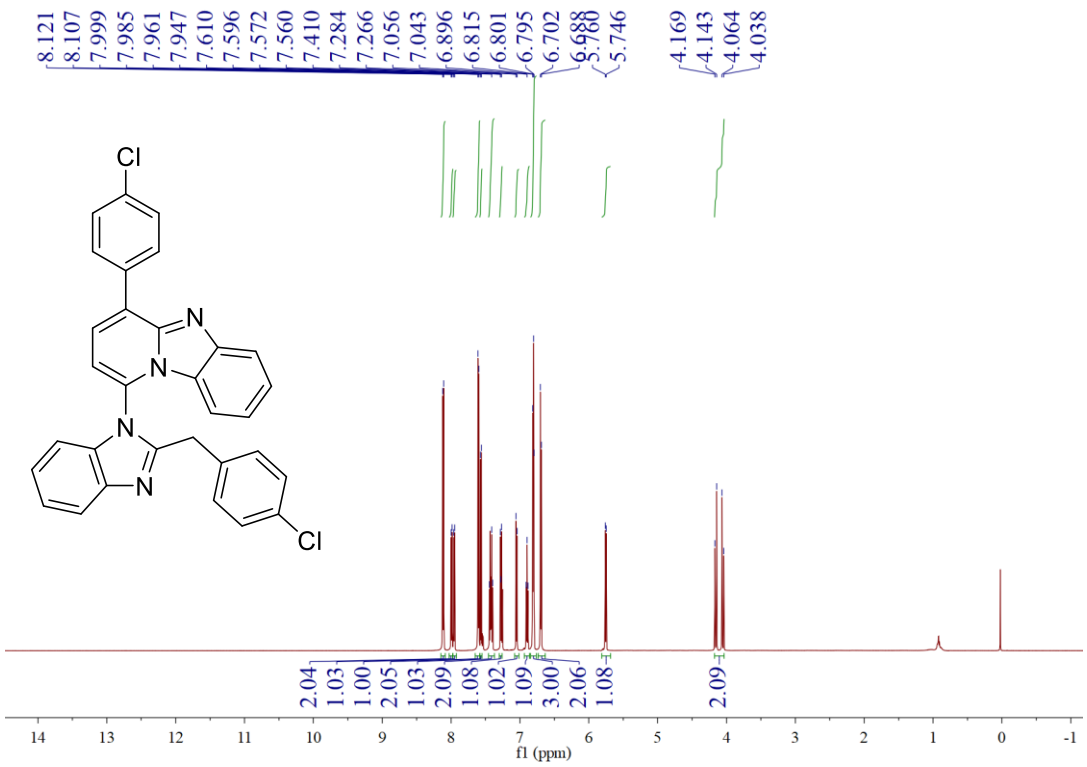


Fig. S21. ^{1}H NMR spectrum of compound **4i**.

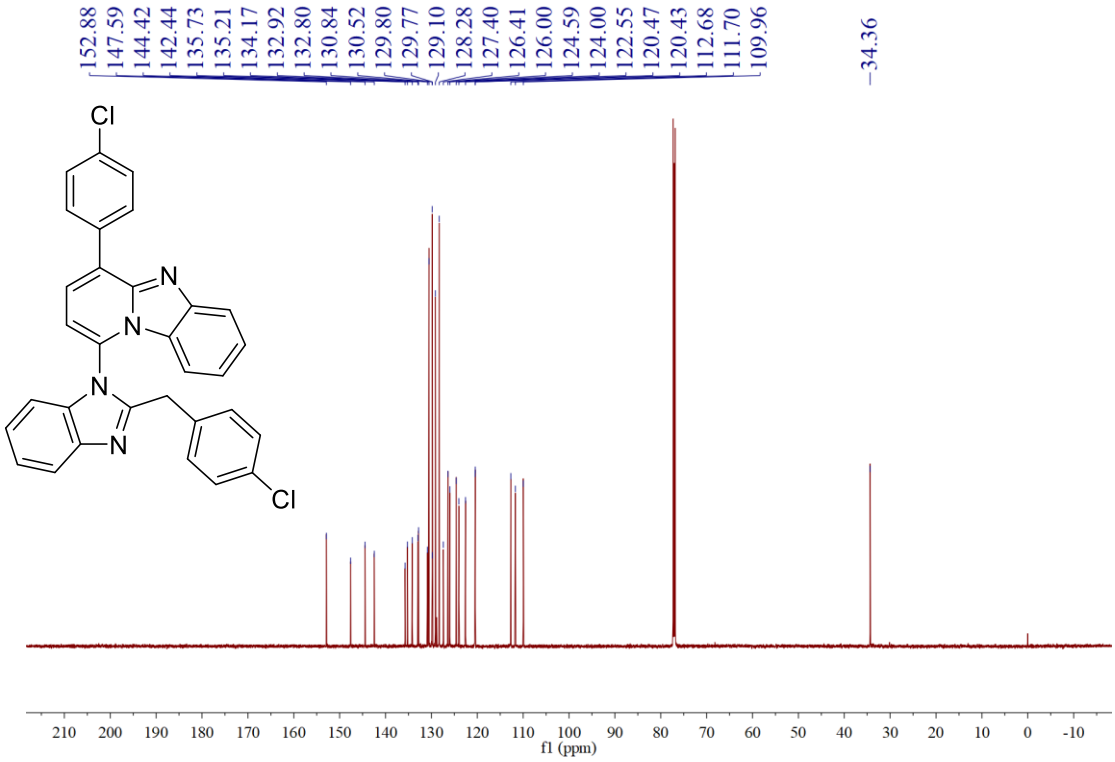


Fig. S22. ^{13}C NMR spectrum of compound **4i**.

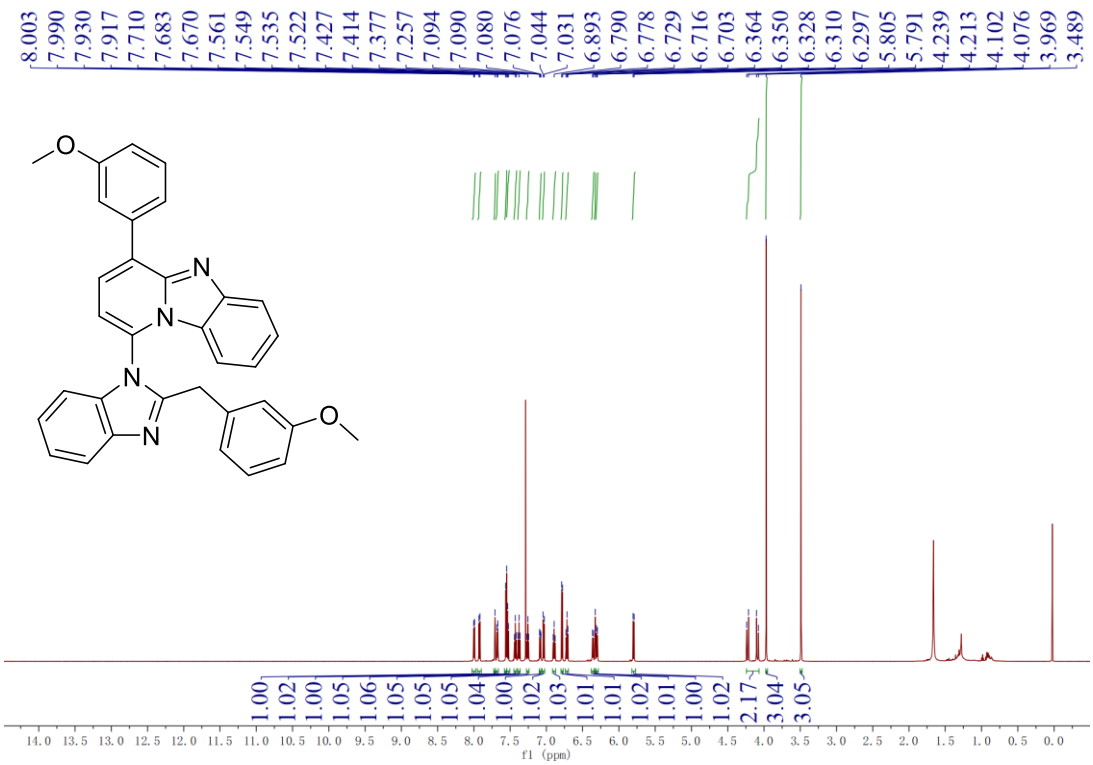


Fig. S23. ^{1}H NMR spectrum of compound **4j**.

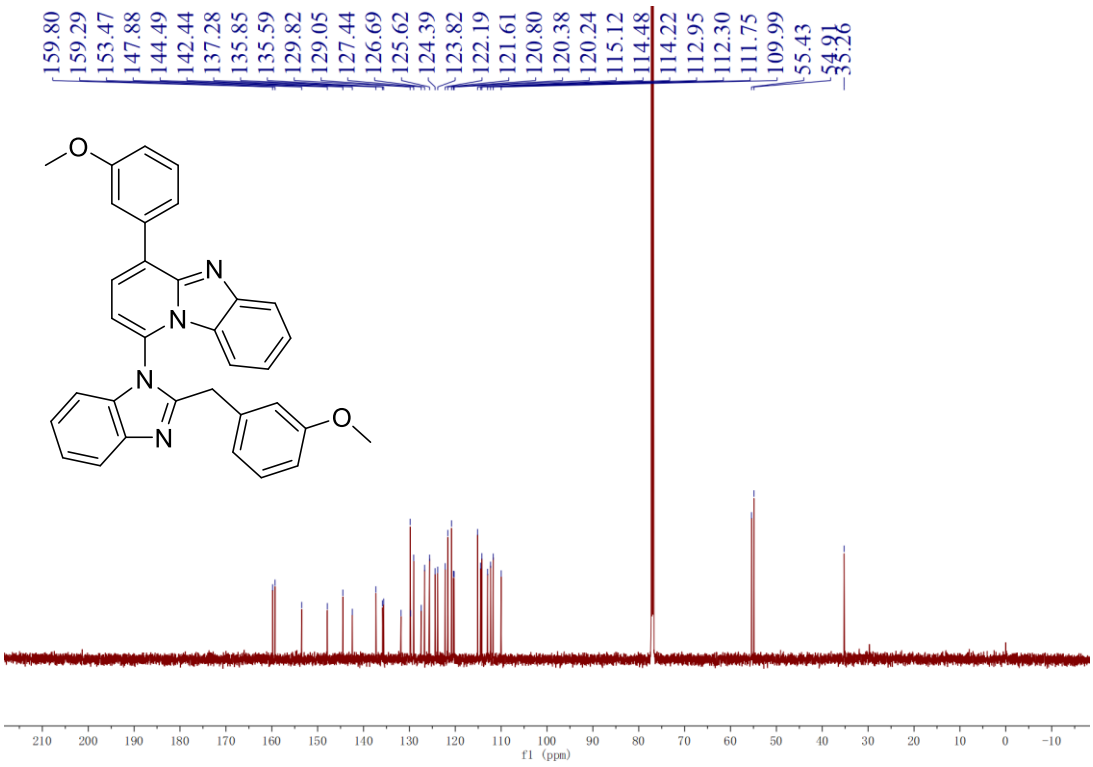


Fig. S24. ^{13}C NMR spectrum of compound **4j**.

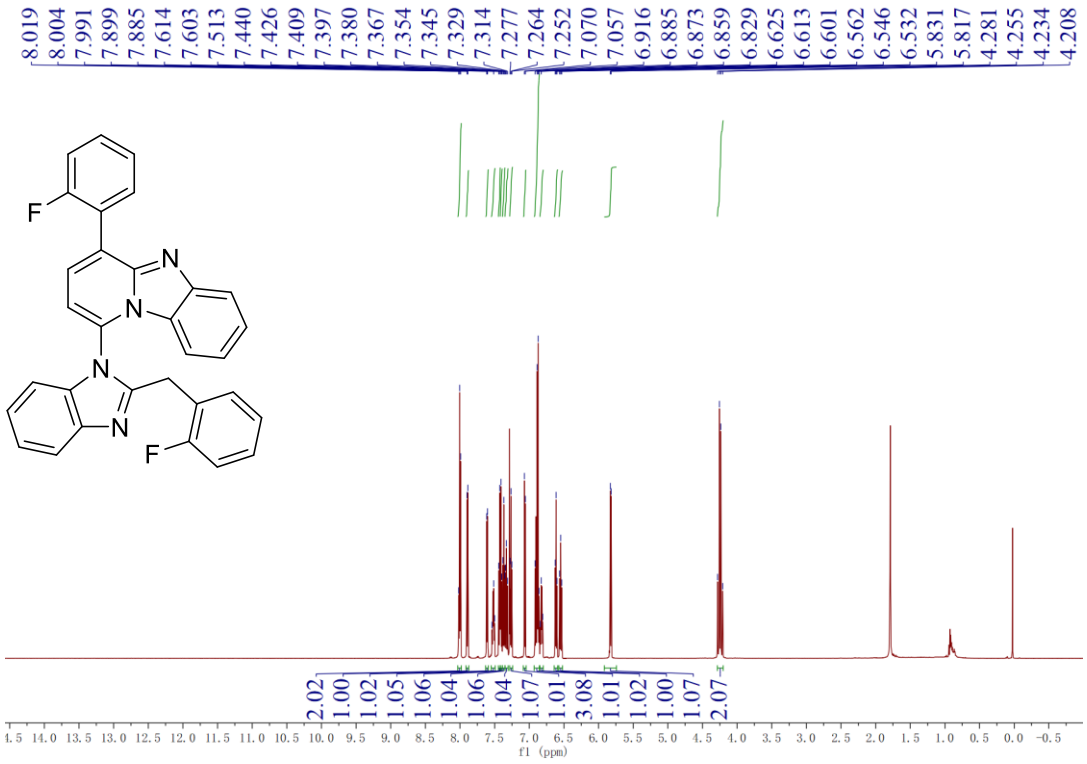


Fig. S25. ^{1}H NMR spectrum of compound **4k**.

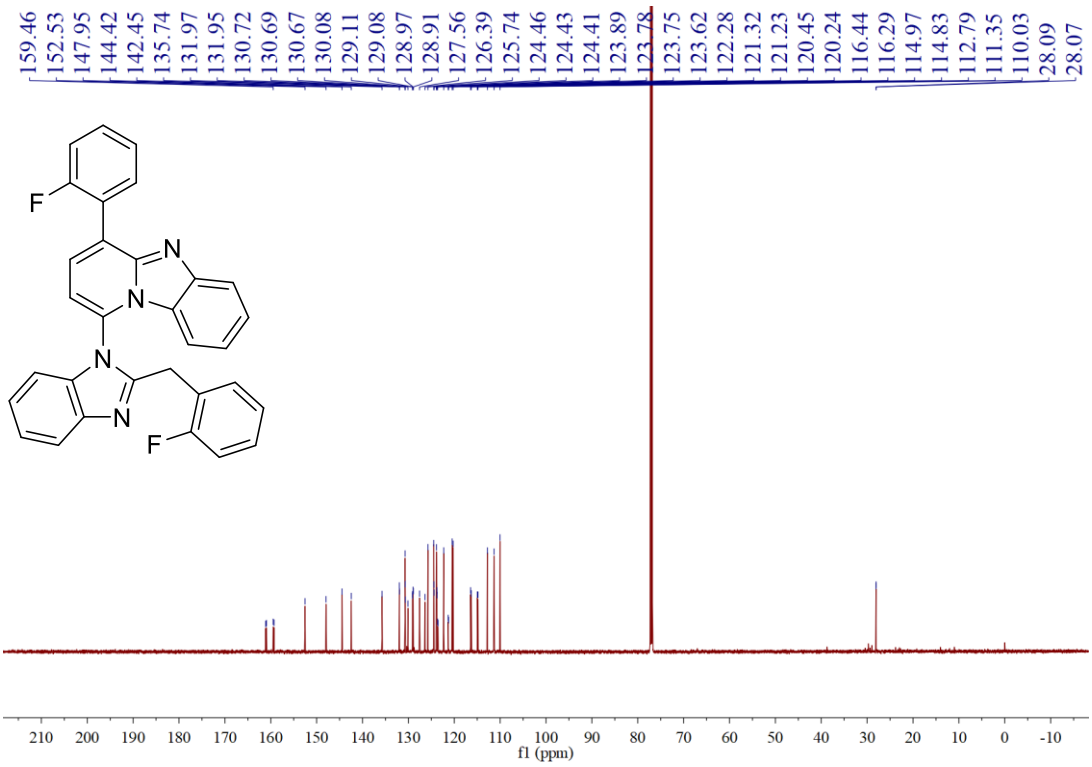


Fig. S26. ^{13}C NMR spectrum of compound **4k**.

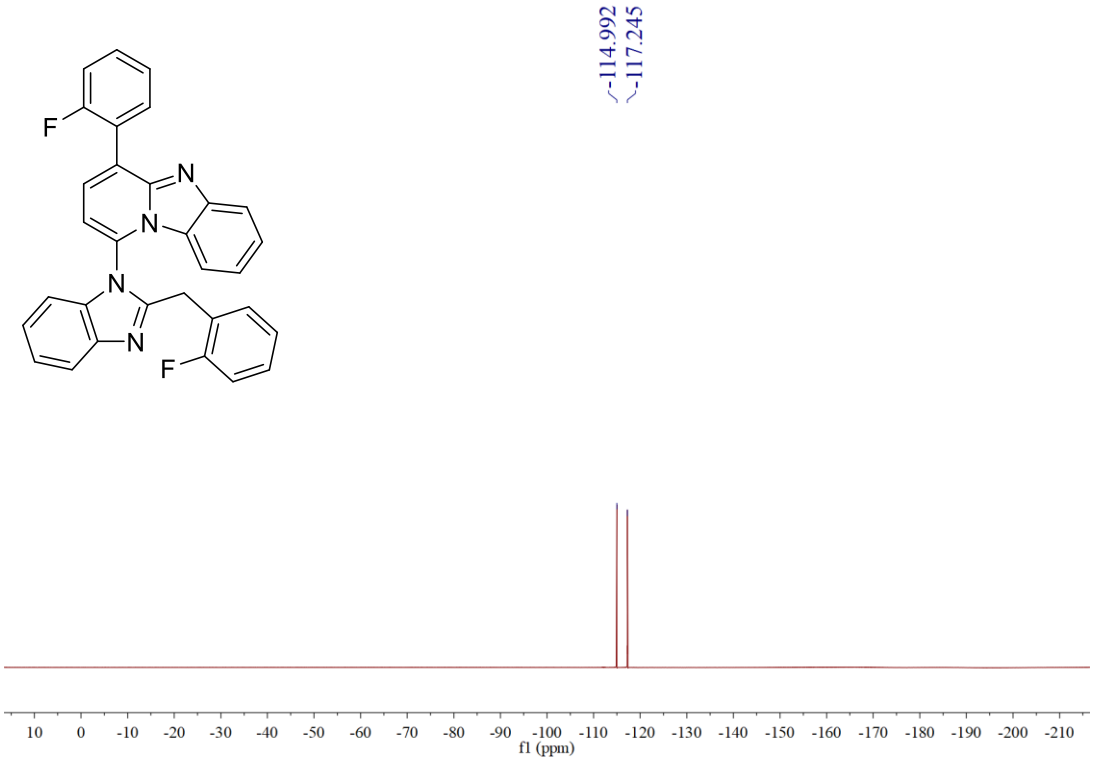


Fig. S27. ^{19}F NMR spectrum of compound **4k**.

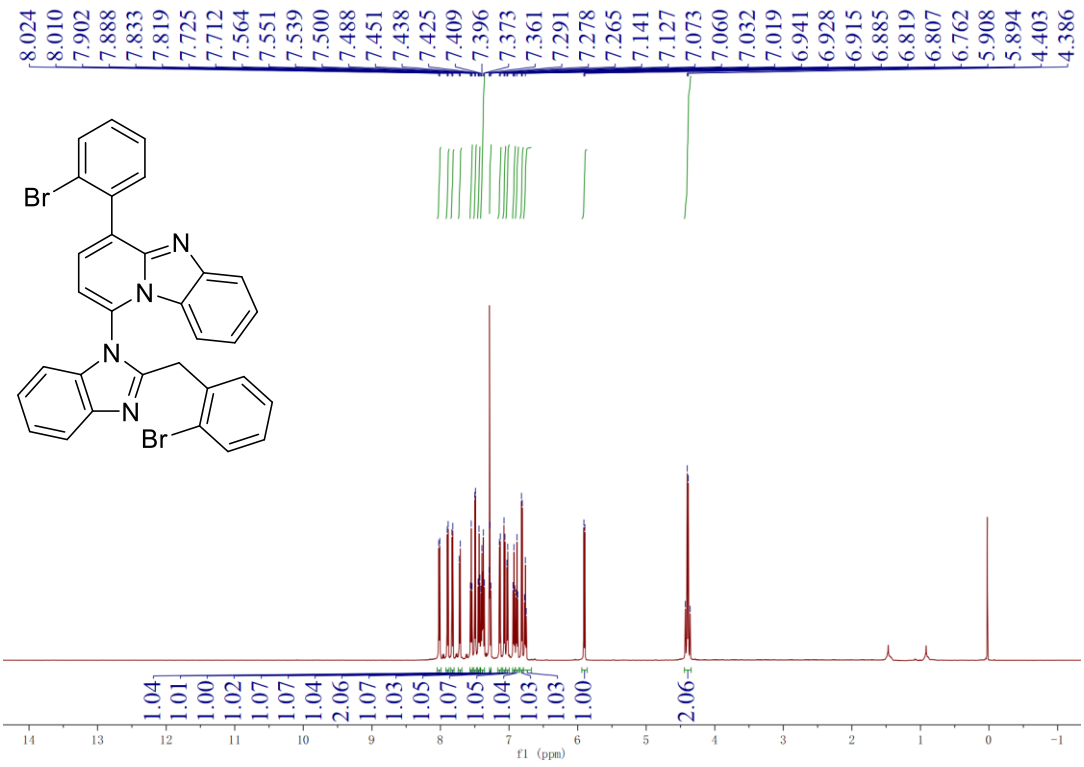


Fig. S28. ^{1}H NMR spectrum of compound **4l**.

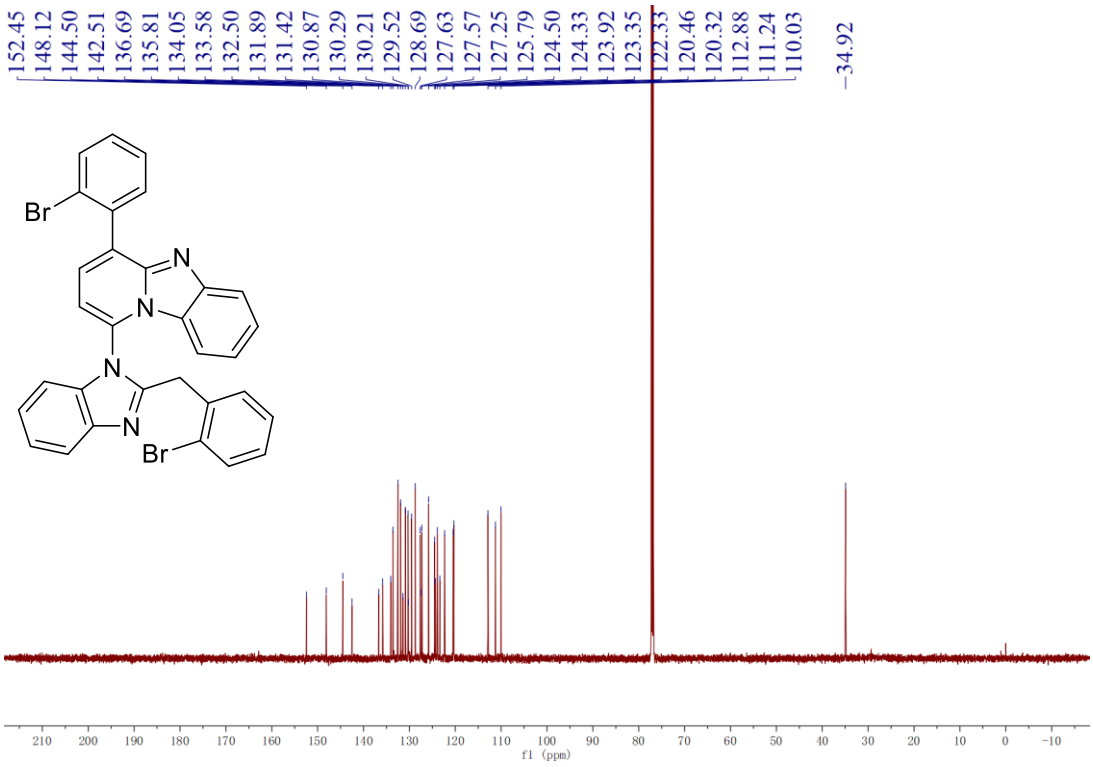


Fig. S29. ^{13}C NMR spectrum of compound **4l**.

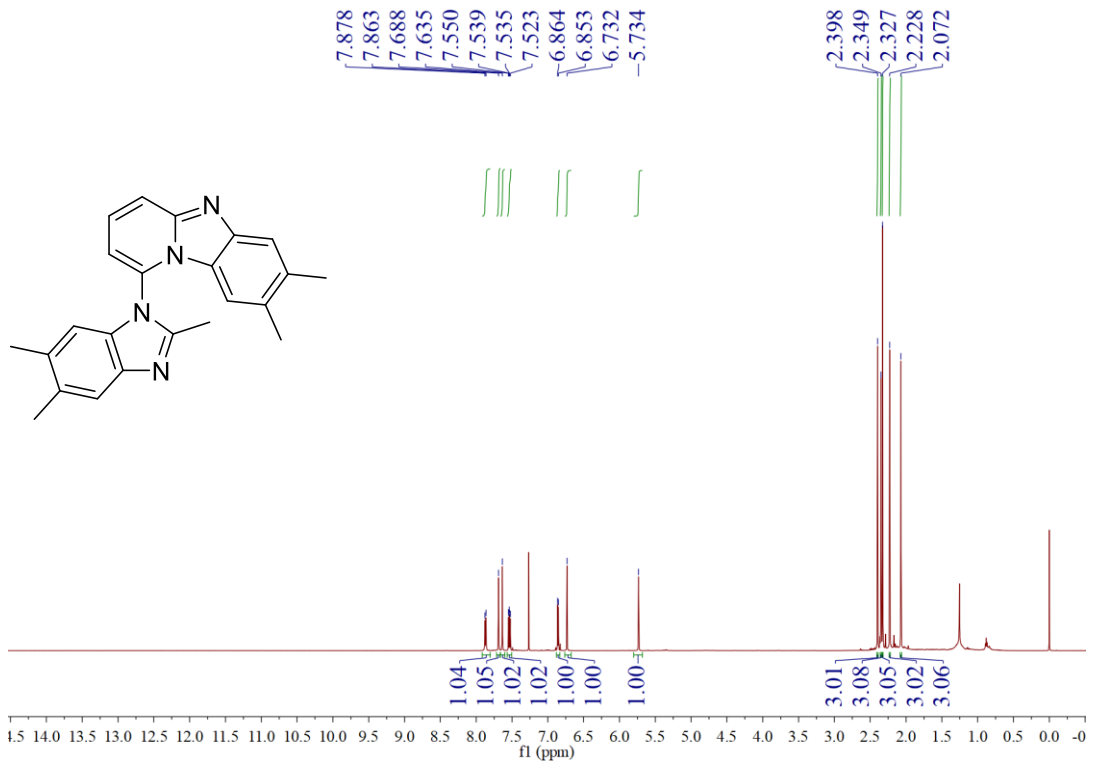


Fig. S30. ^{1}H NMR spectrum of compound **4m**.

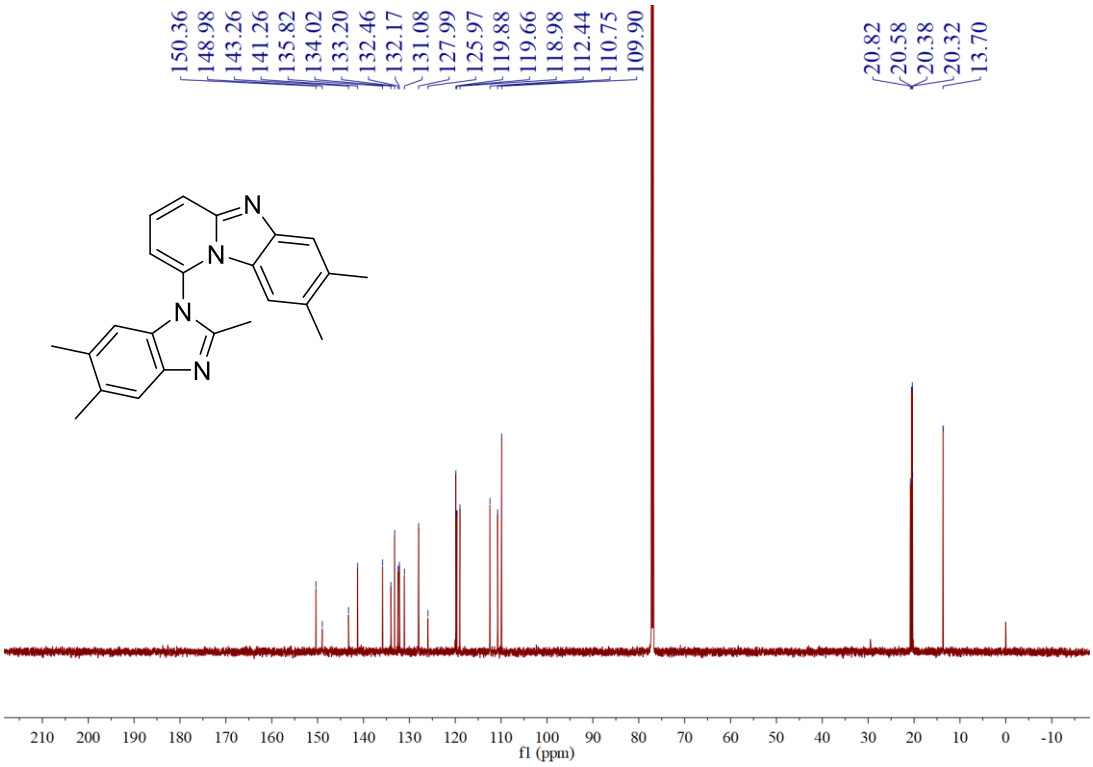


Fig. S31. ^{13}C NMR spectrum of compound **4m**.

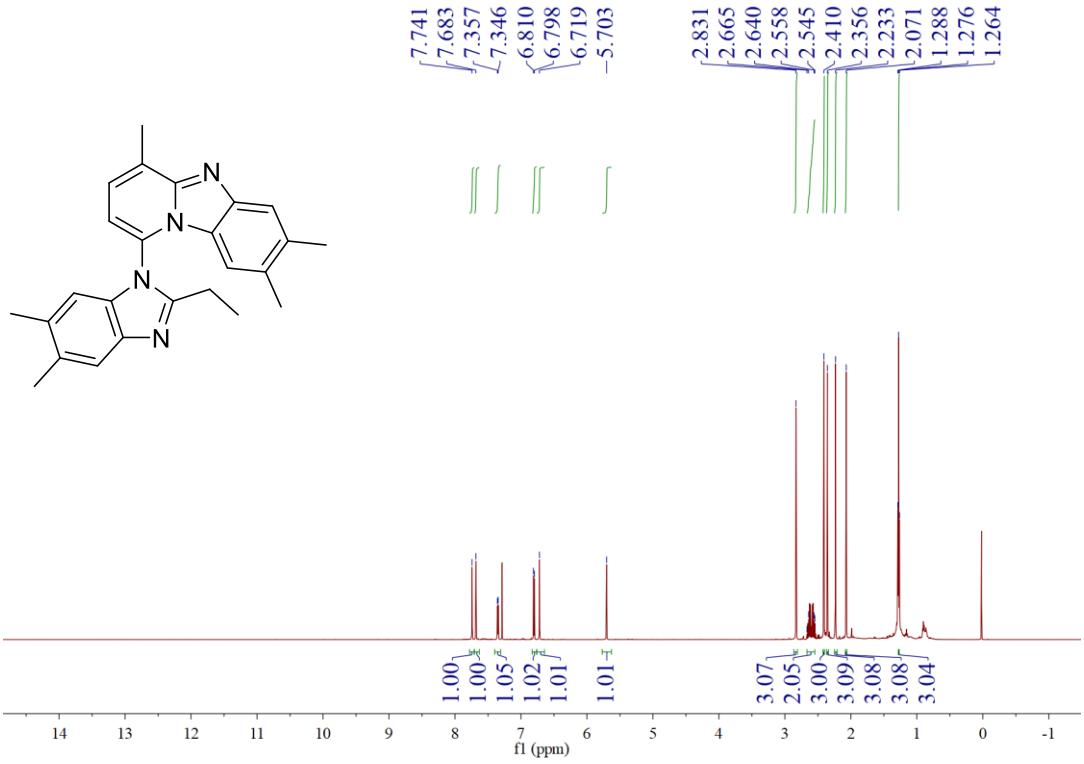


Fig. S32. ^{1}H NMR spectrum of compound **4n**.

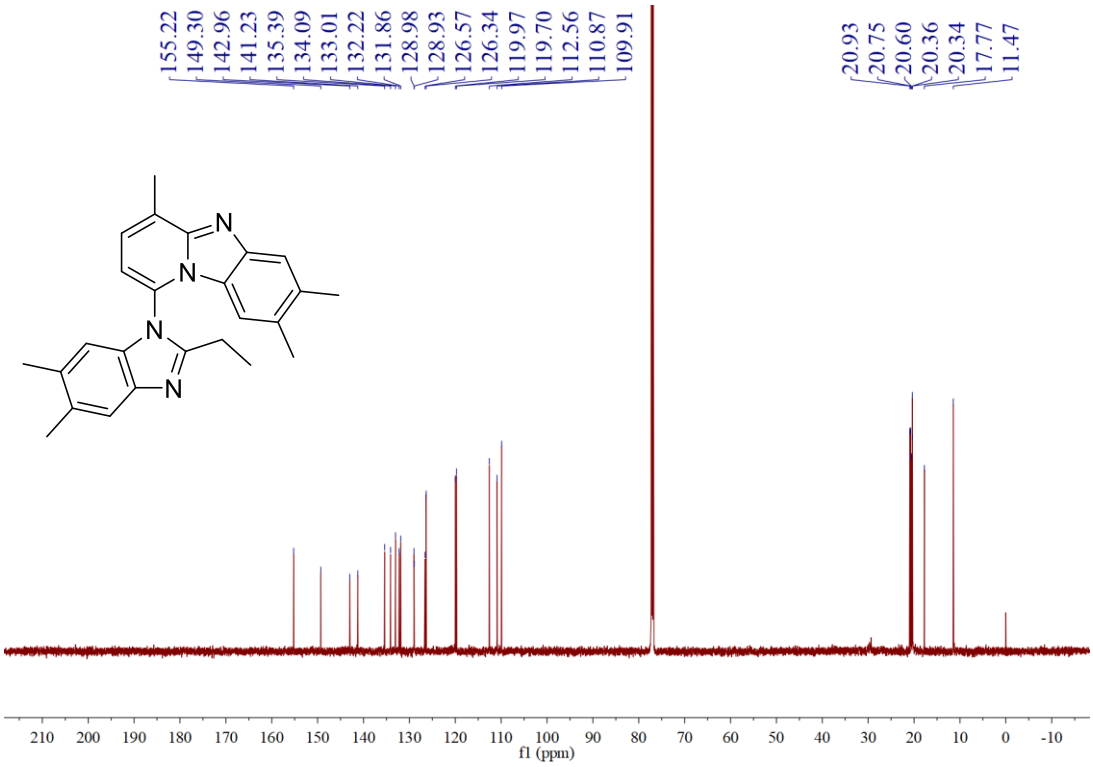


Fig. S33. ^{13}C NMR spectrum of compound **4n**.

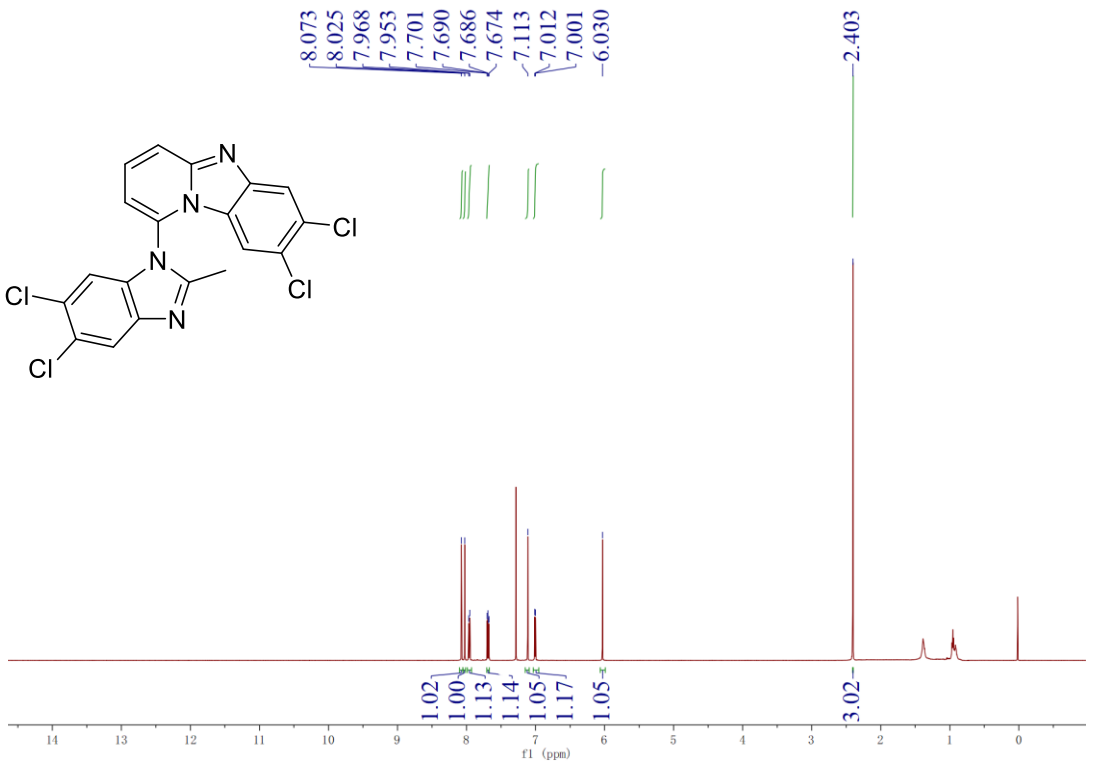


Fig. S34. ^{1}H NMR spectrum of compound **4o**.

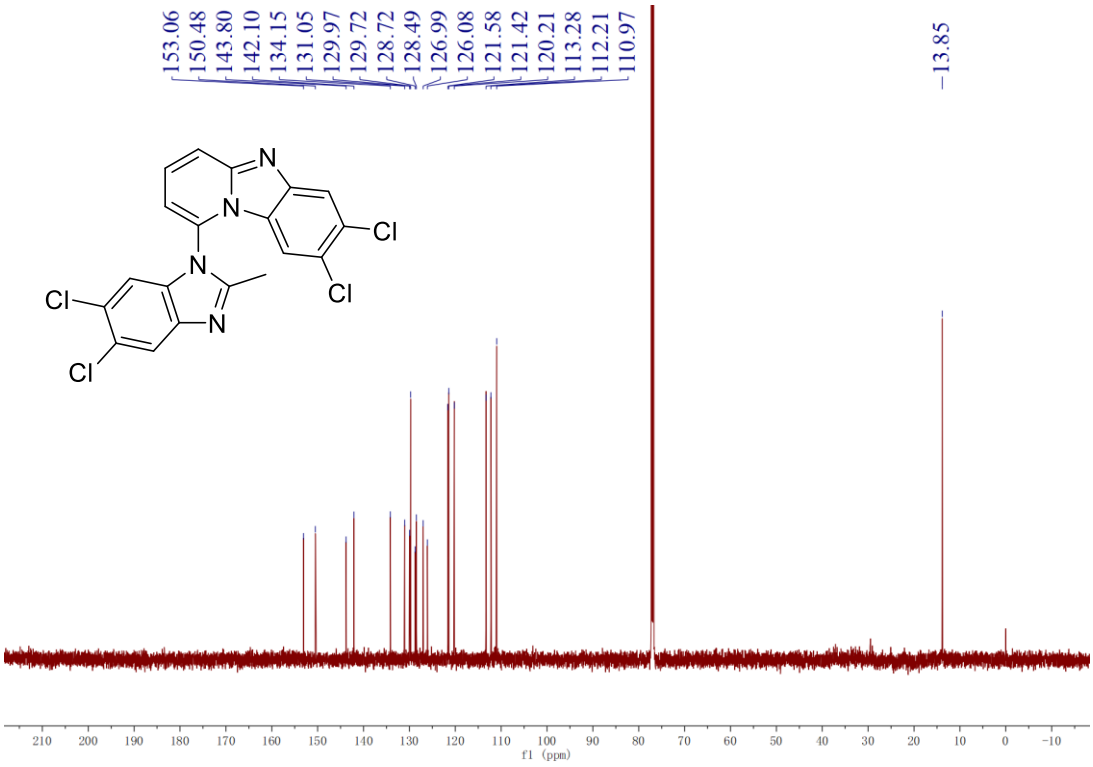


Fig. S35. ^{13}C NMR spectrum of compound **4o**.

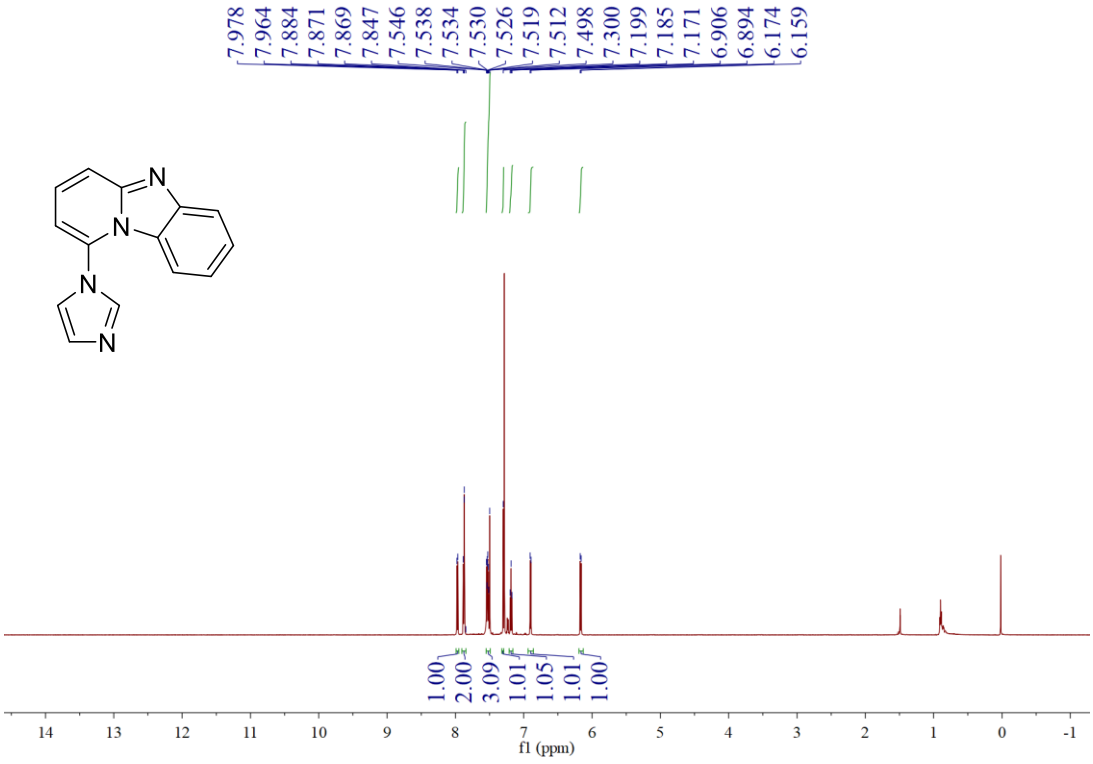


Fig. S36. ^{1}H NMR spectrum of compound **5a**.

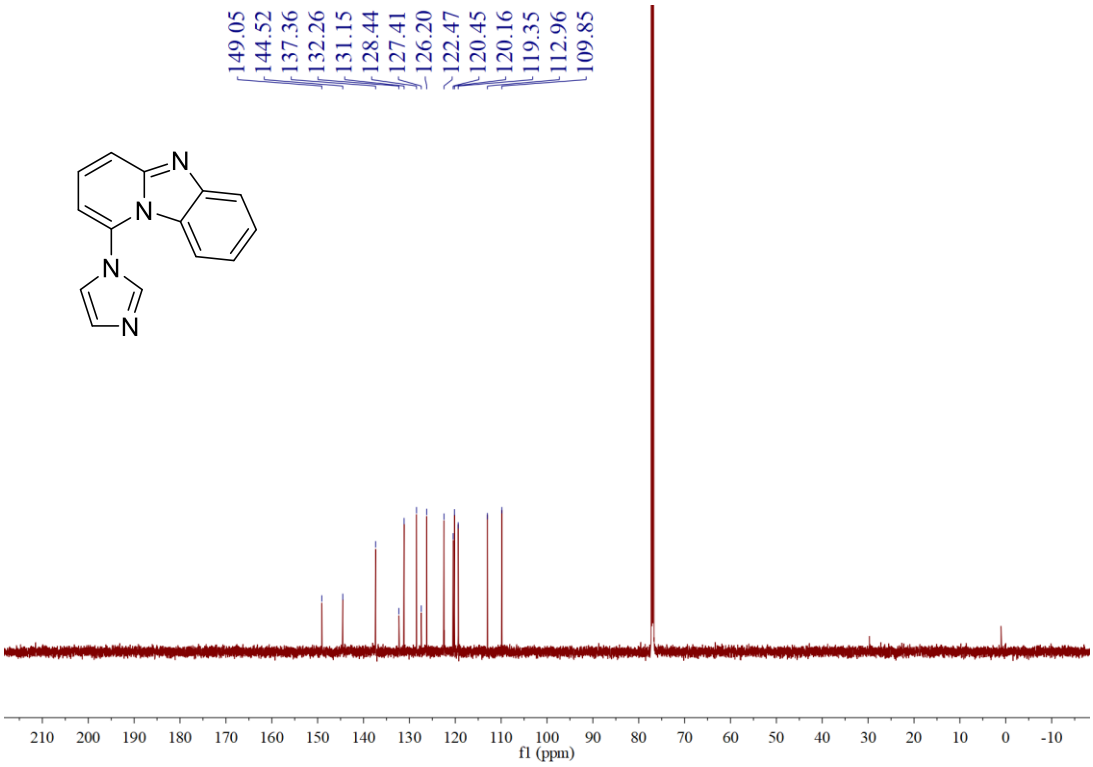


Fig. S37. ^{13}C NMR spectrum of compound **5a**.

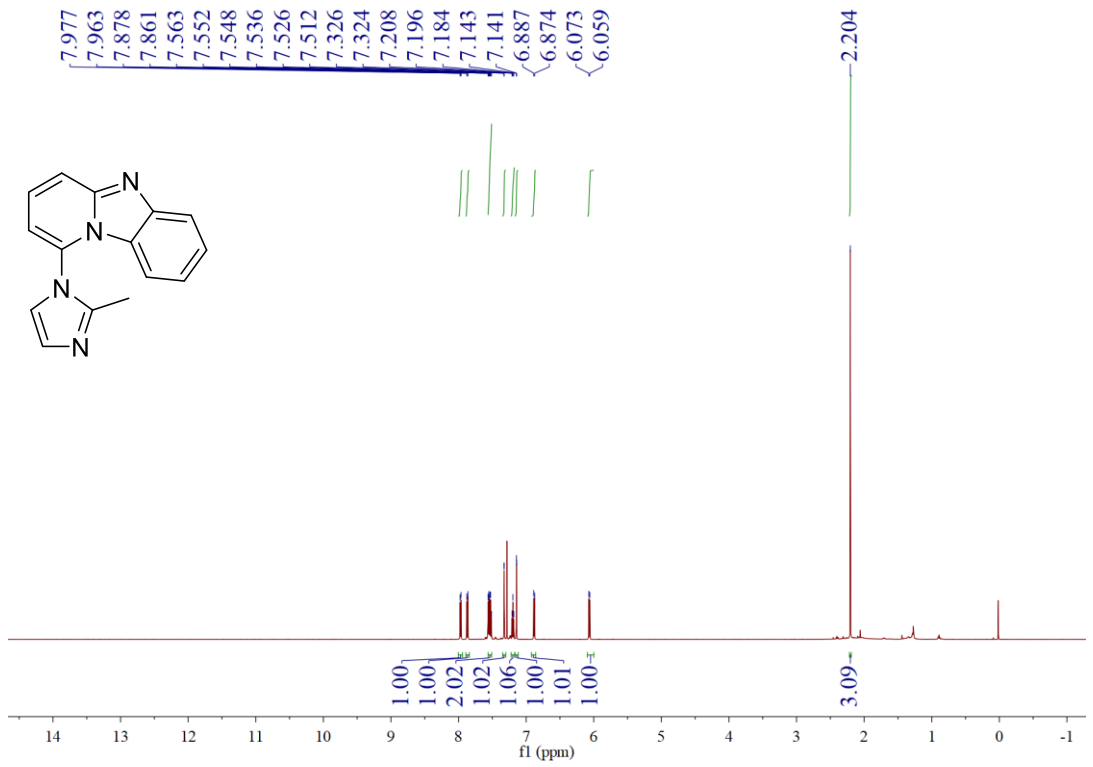


Fig. S38. ^{1}H NMR spectrum of compound **5b**.

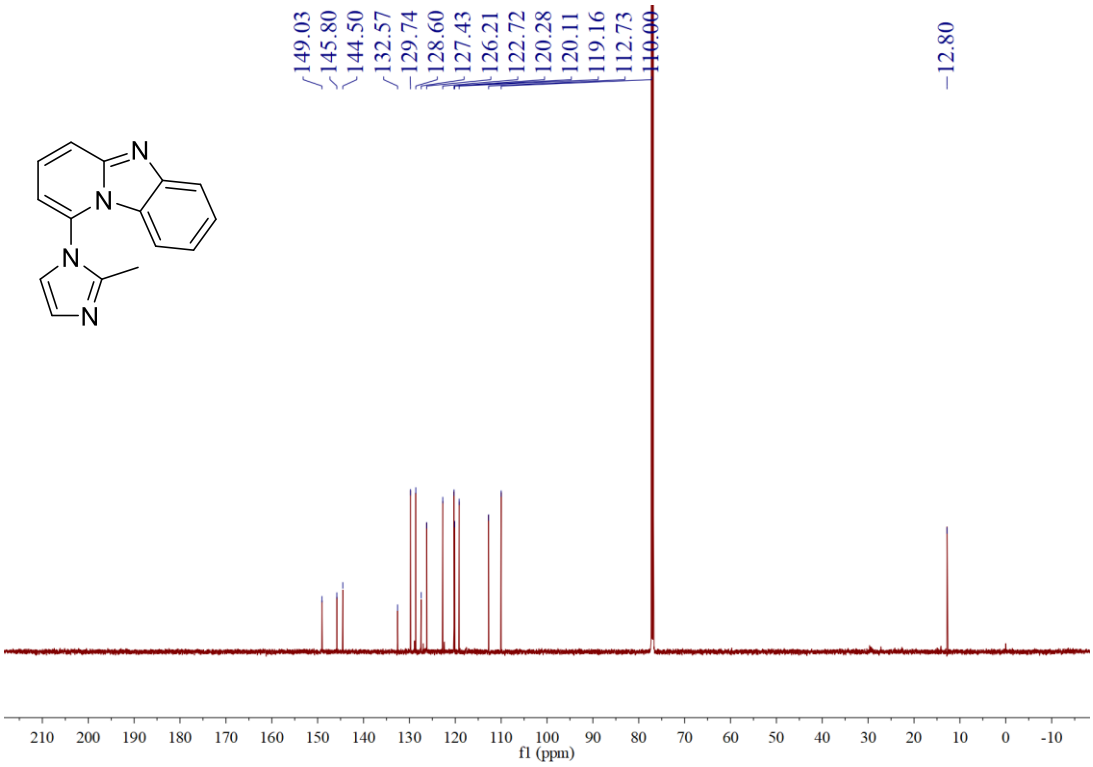


Fig. S39. ^{13}C NMR spectrum of compound **5b**.

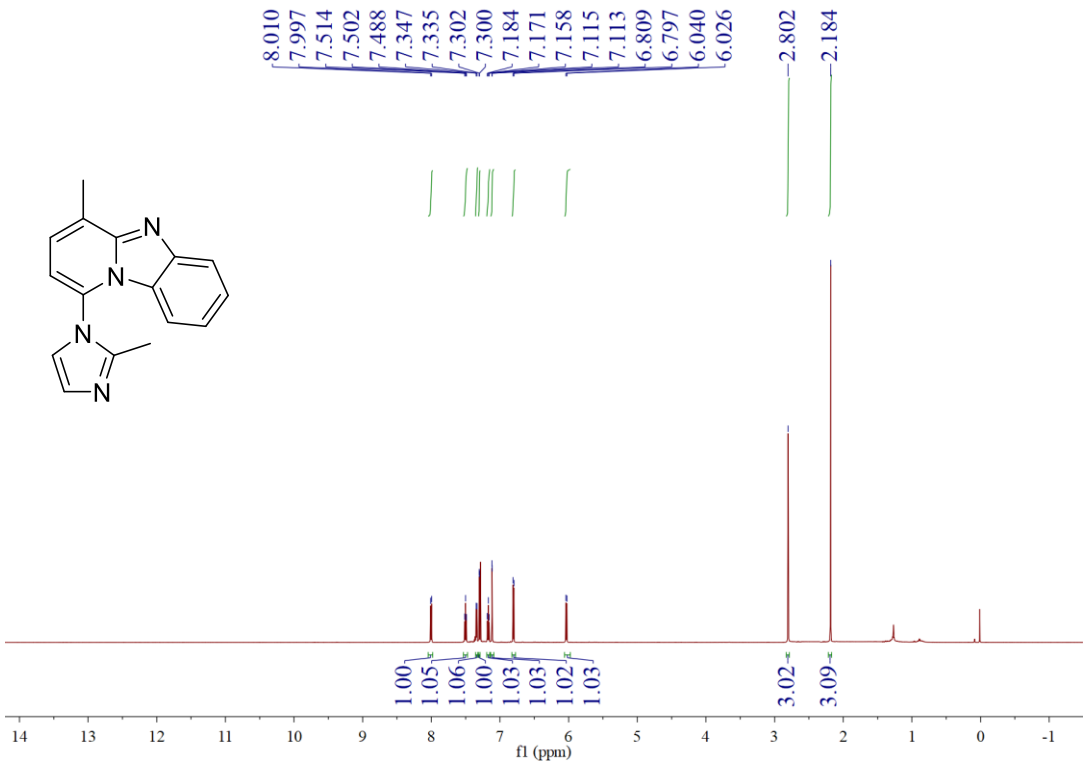


Fig. S40. ^{1}H NMR spectrum of compound **5c**.

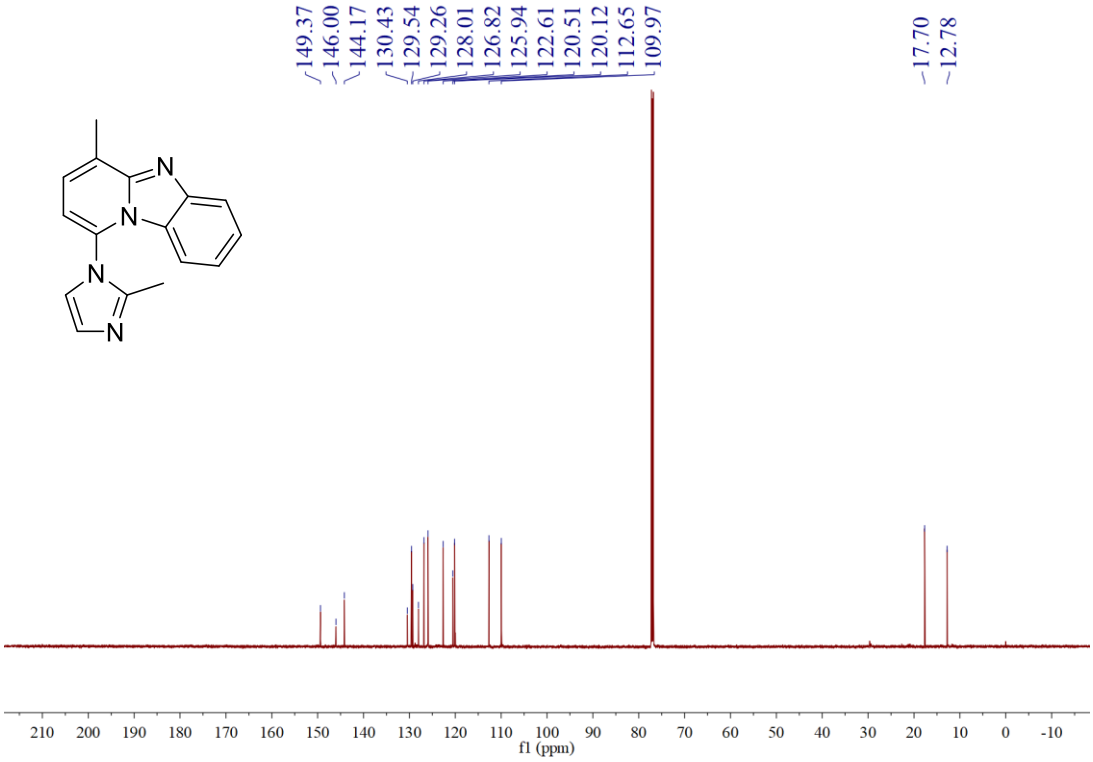


Fig. S41. ^{13}C NMR spectrum of compound **5c**.

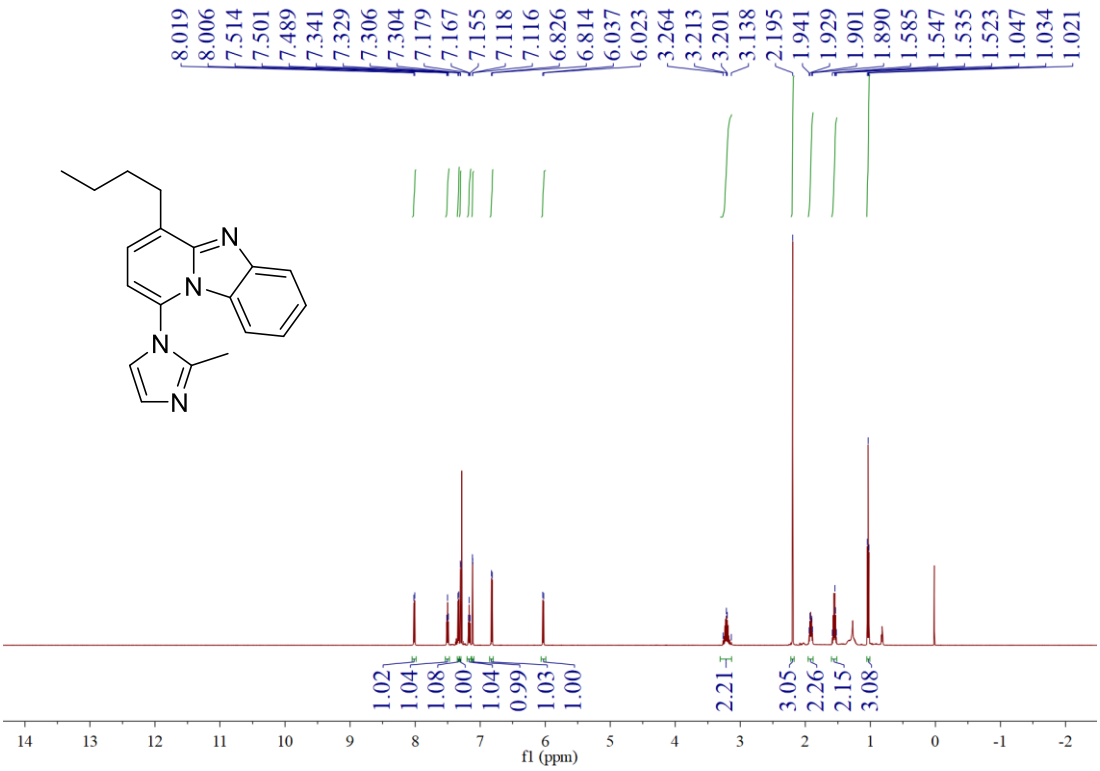


Fig. S42. ^{1}H NMR spectrum of compound **5d**.

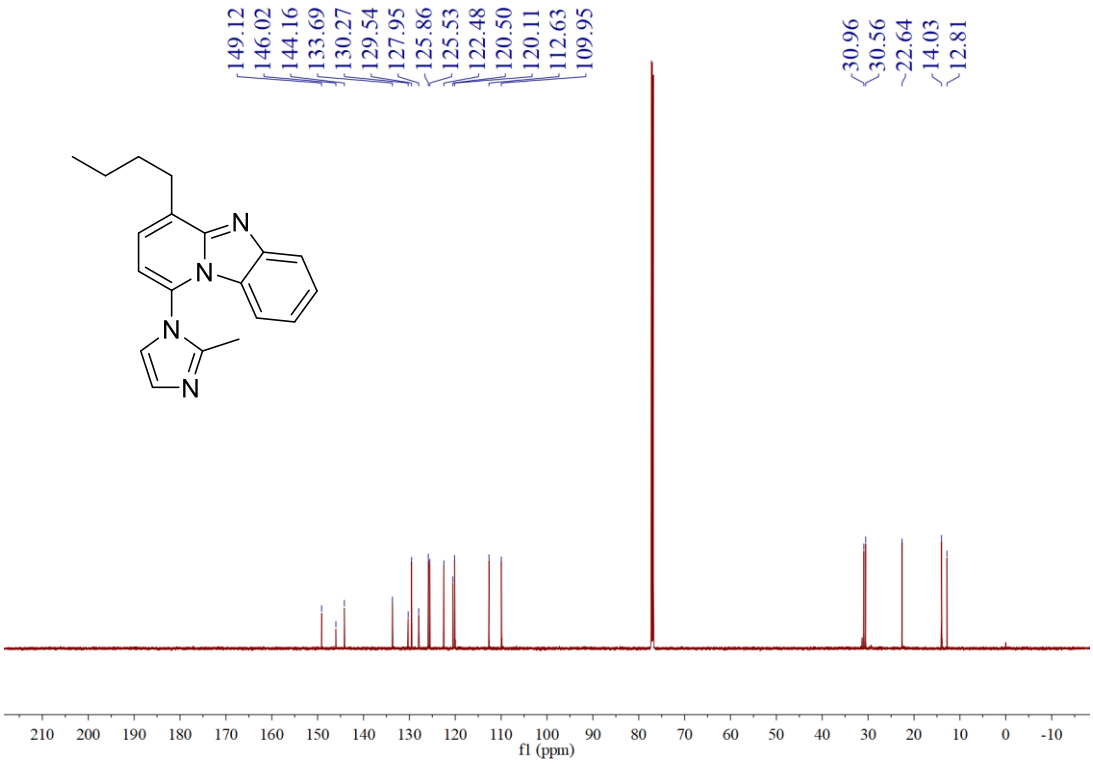


Fig. S43. ^{13}C NMR spectrum of compound **5d**.

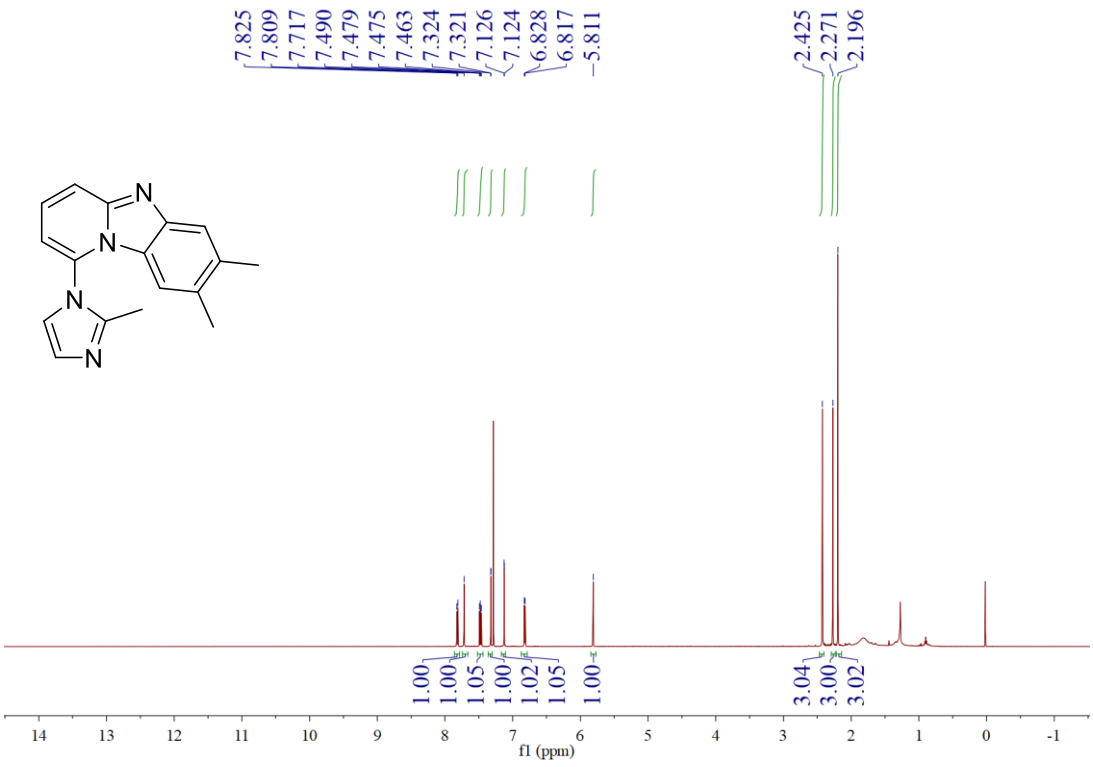


Fig. S44. ^{1}H NMR spectrum of compound **5e**.

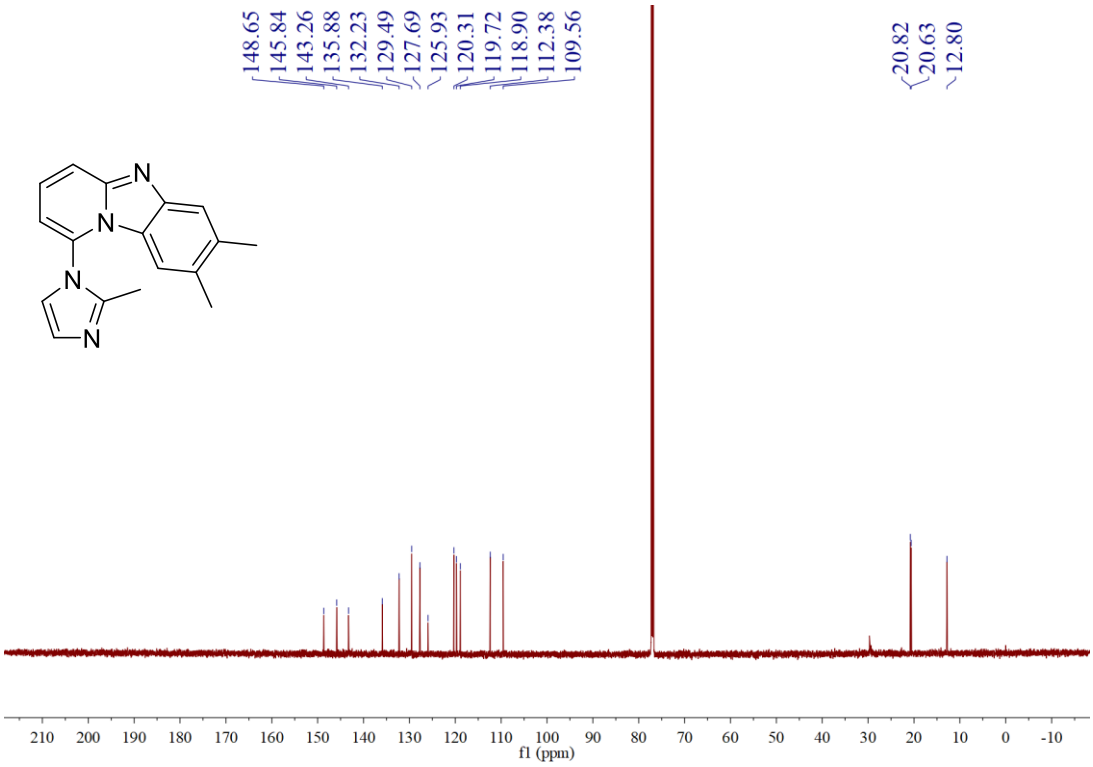


Fig. S45. ^{13}C NMR spectrum of compound **5e**.

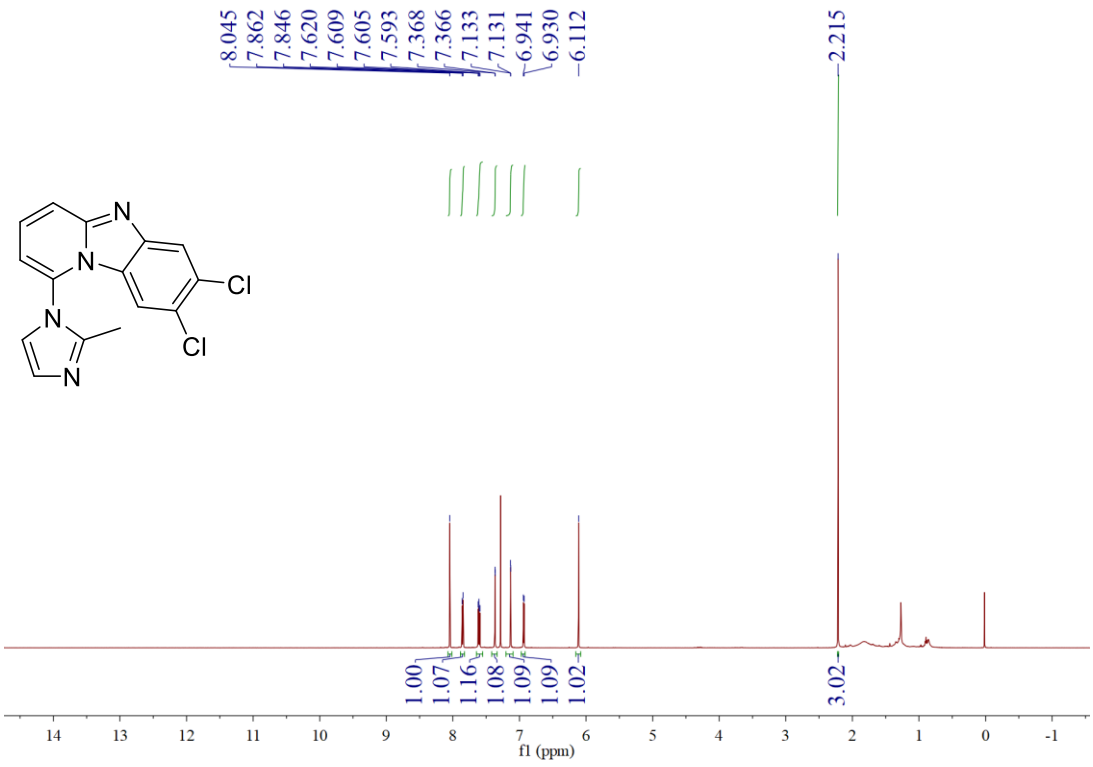


Fig. S46. ^{1}H NMR spectrum of compound **5f**.

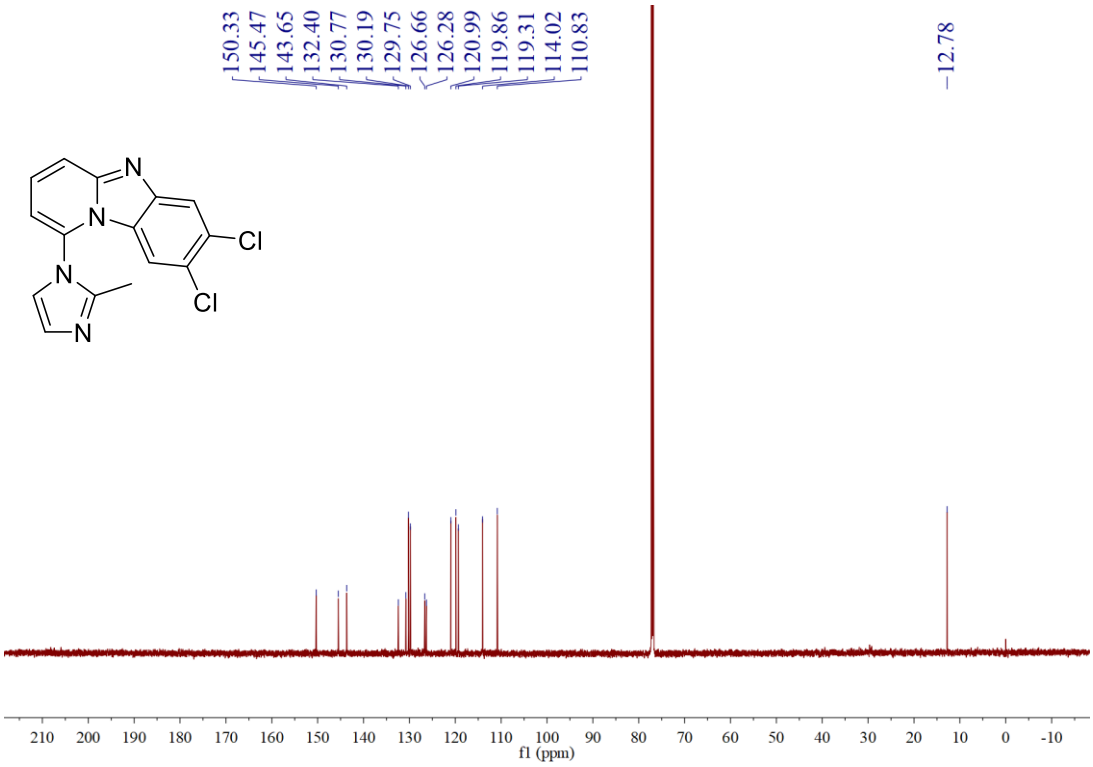


Fig. S47. ^{13}C NMR spectrum of compound **5f**.

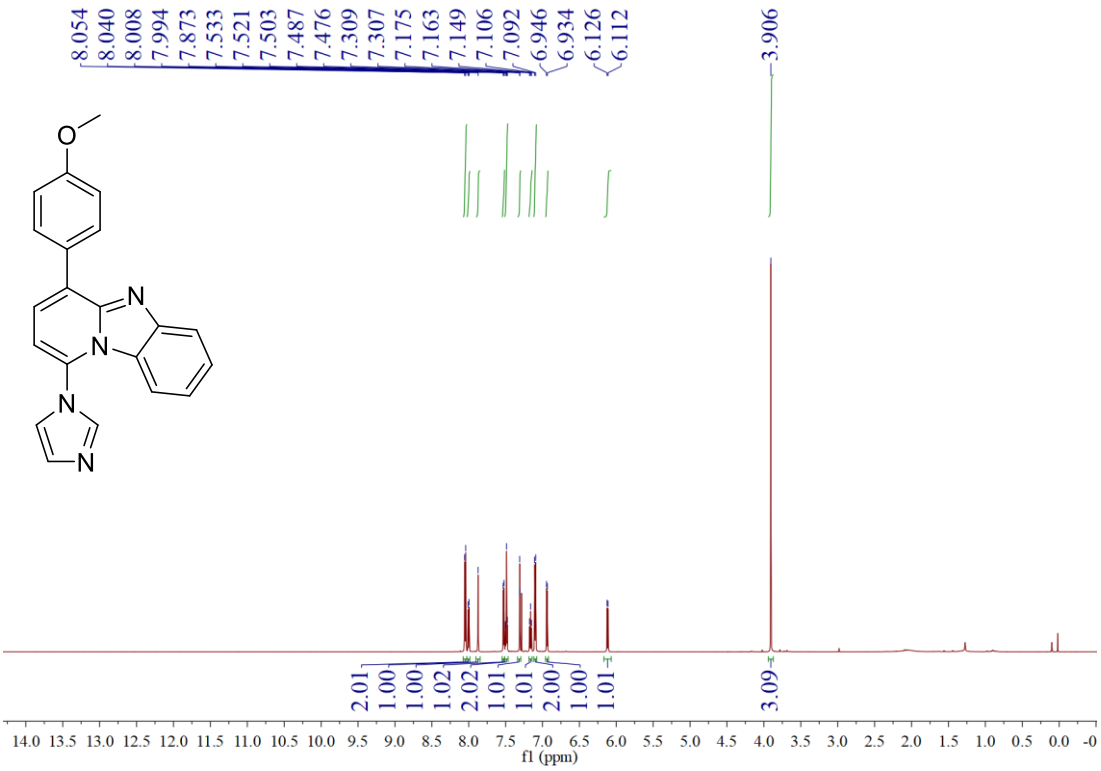


Fig. S48. ^{1}H NMR spectrum of compound **5g**.

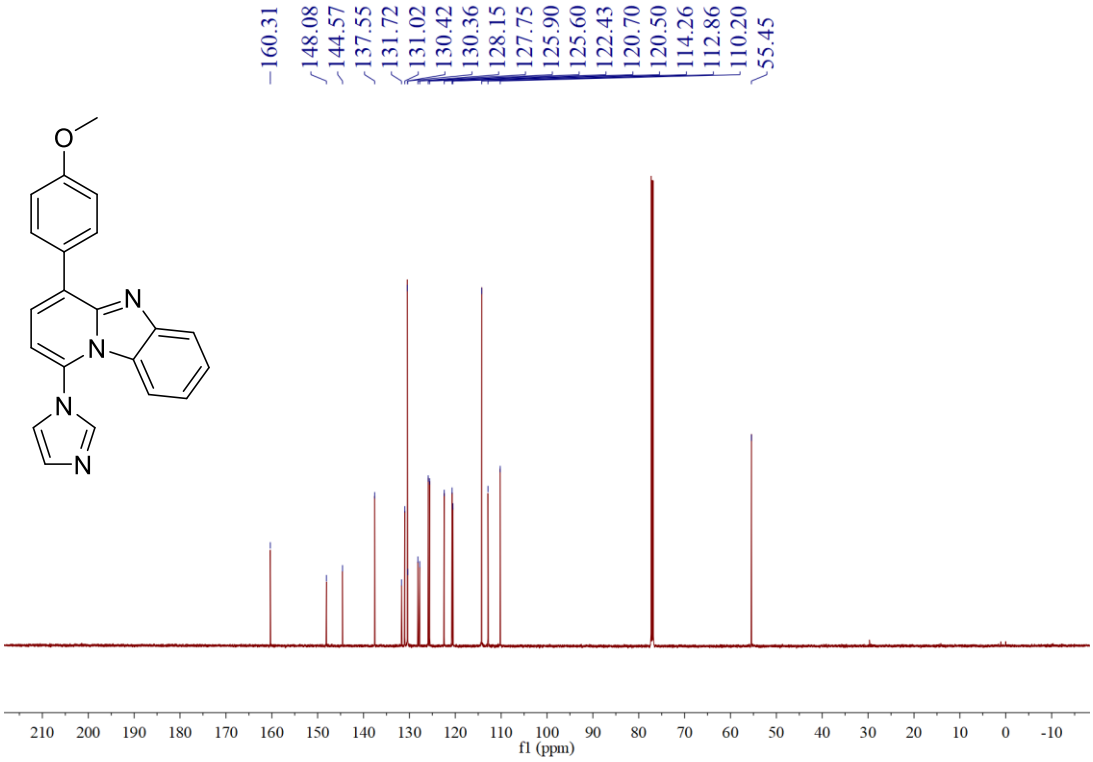


Fig. S49. ^{13}C NMR spectrum of compound **5g**.

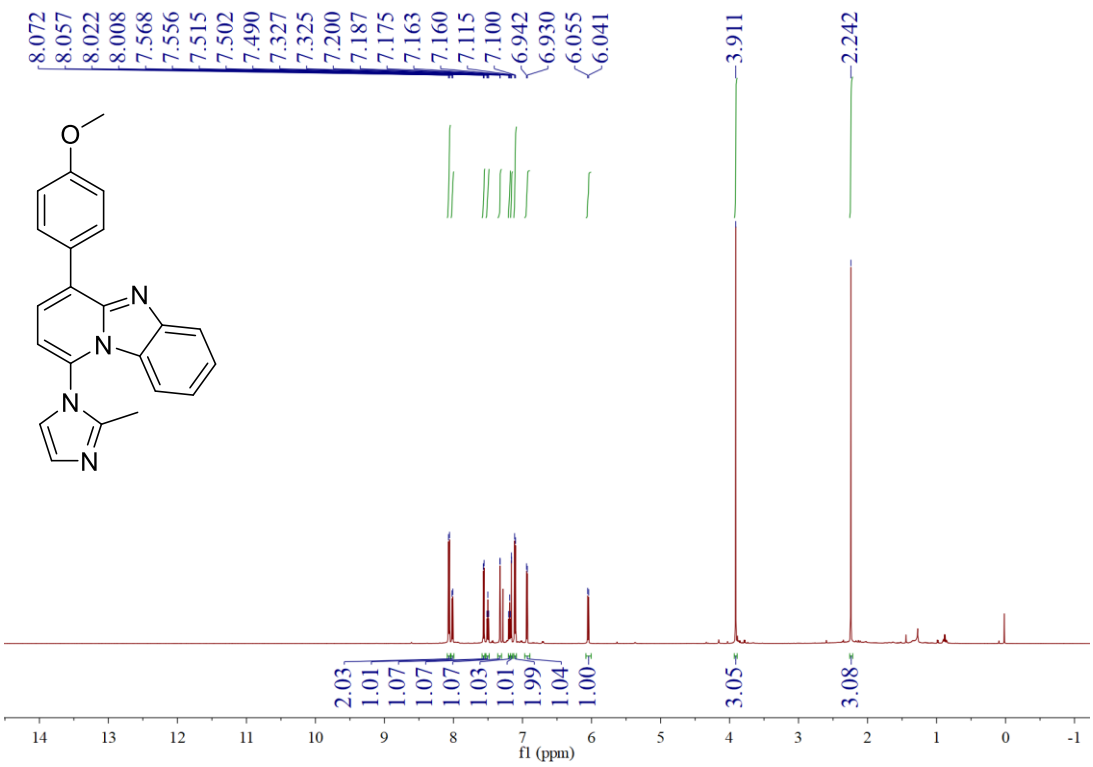


Fig. S50. ^{1}H NMR spectrum of compound **5h**.

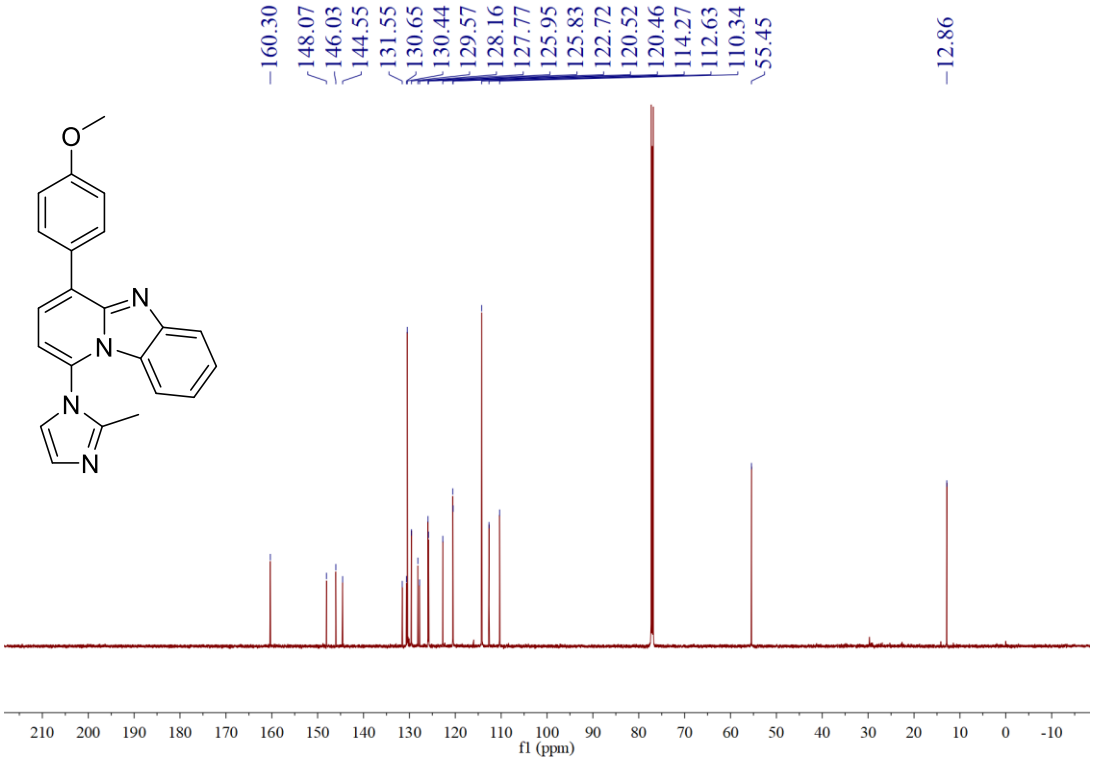


Fig. S51. ^{13}C NMR spectrum of compound **5h**.

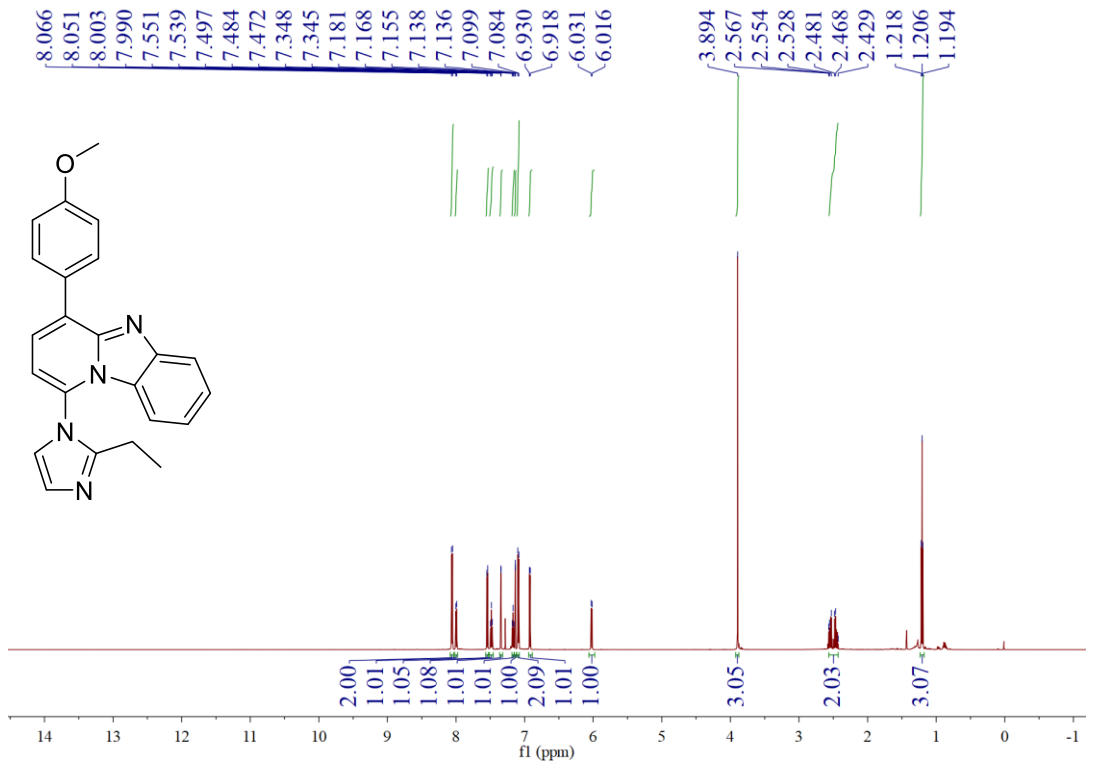


Fig. S52. ^{1}H NMR spectrum of compound **5i**.

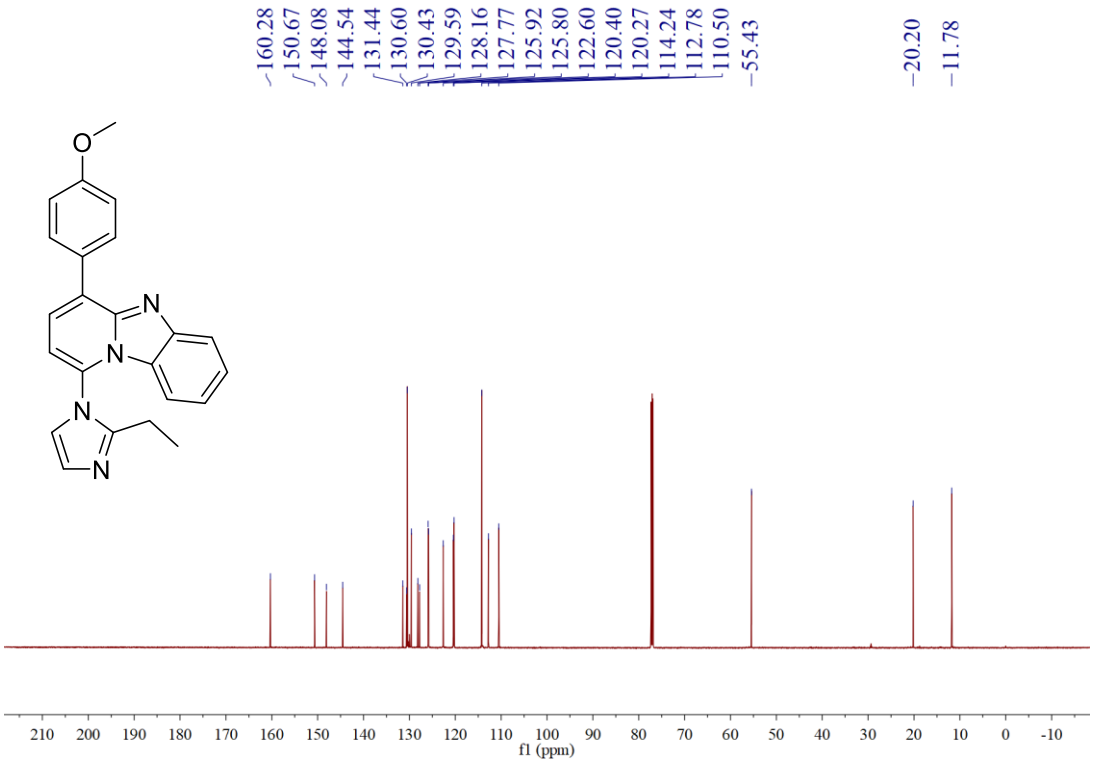


Fig. S53. ^{13}C NMR spectrum of compound **5i**.

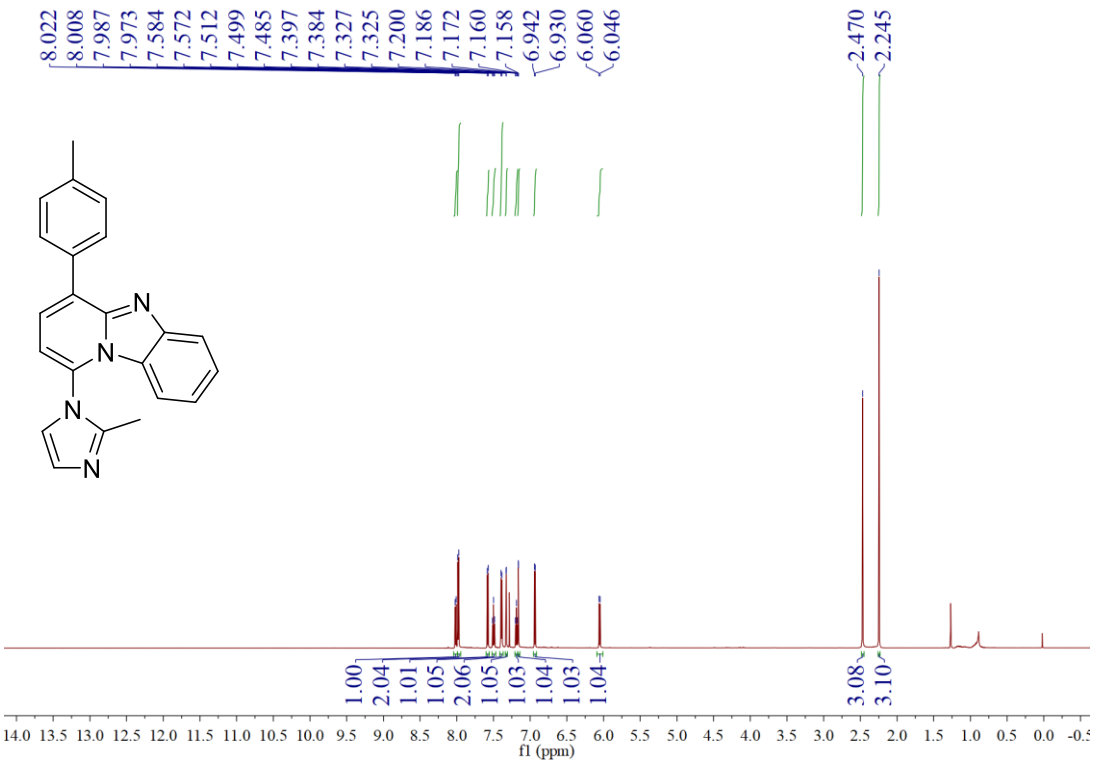


Fig. S54. ^{1}H NMR spectrum of compound **5j**.

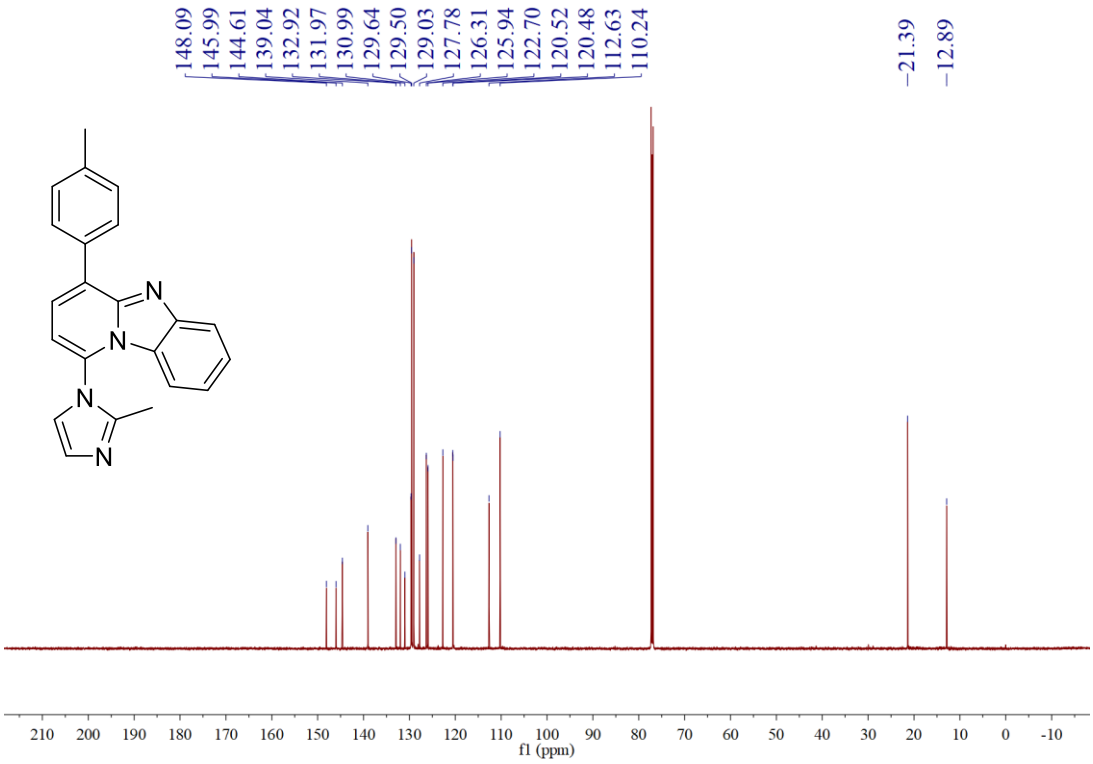


Fig. S55. ^{13}C NMR spectrum of compound **5j**.

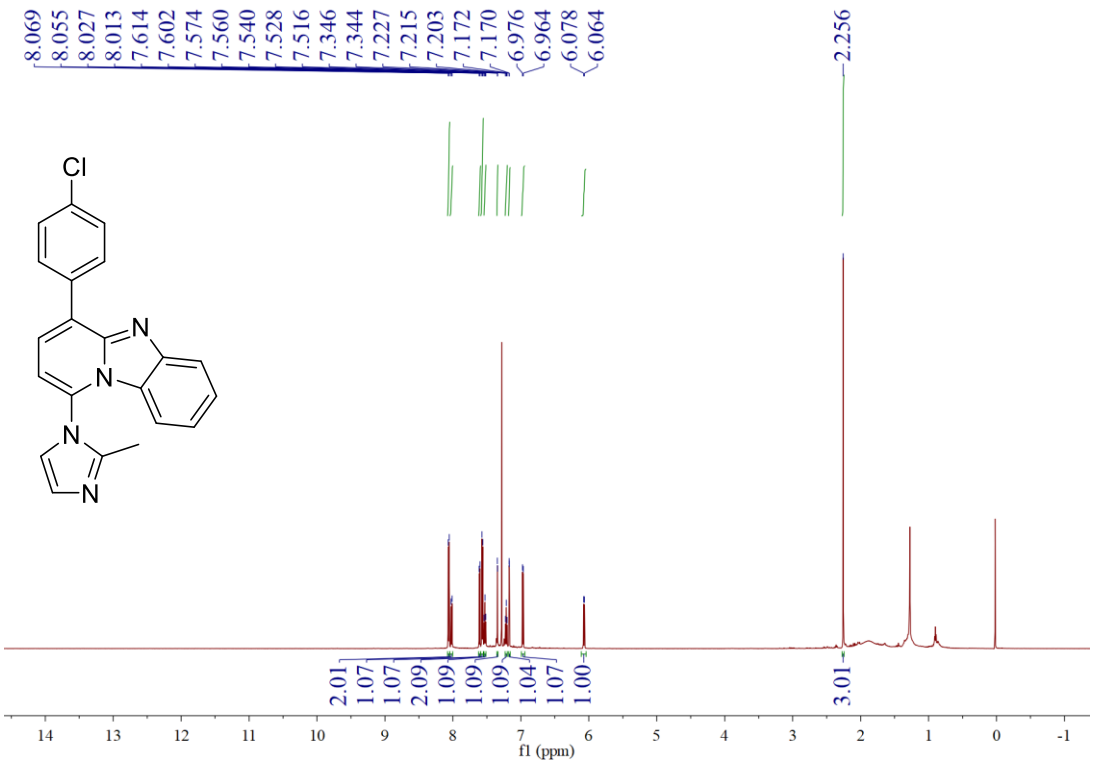


Fig. S56. ^{1}H NMR spectrum of compound **5k**.

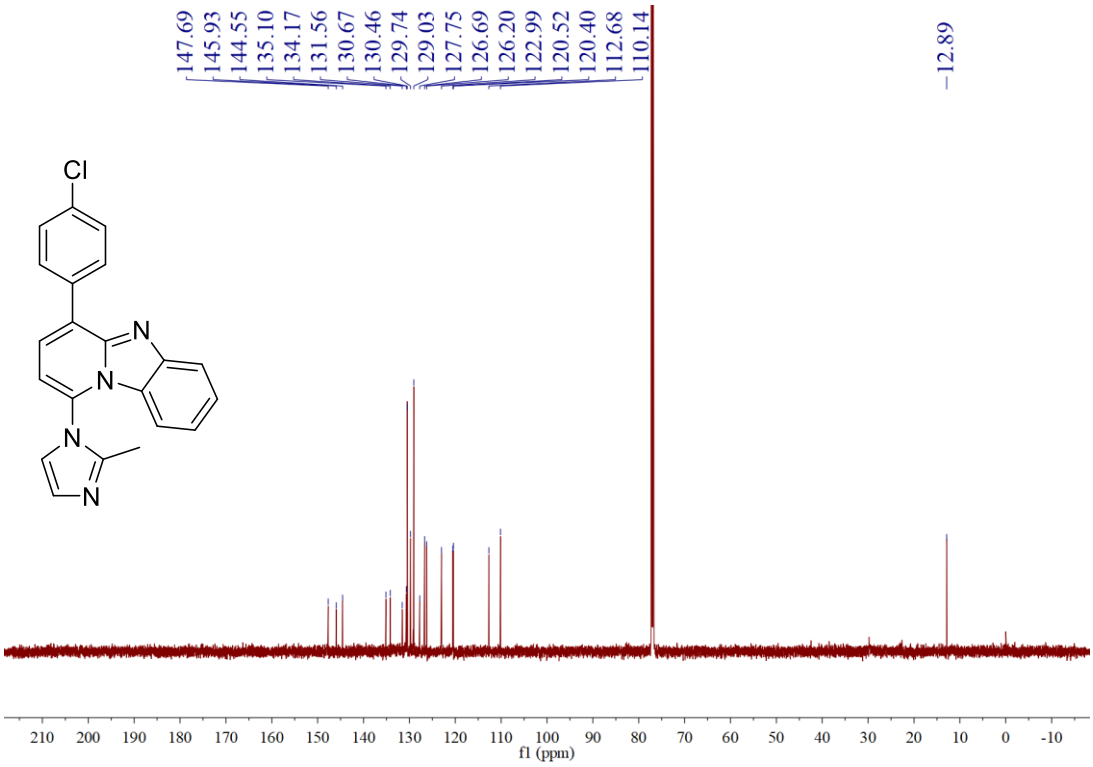


Fig. S57. ^{13}C NMR spectrum of compound **5k**.

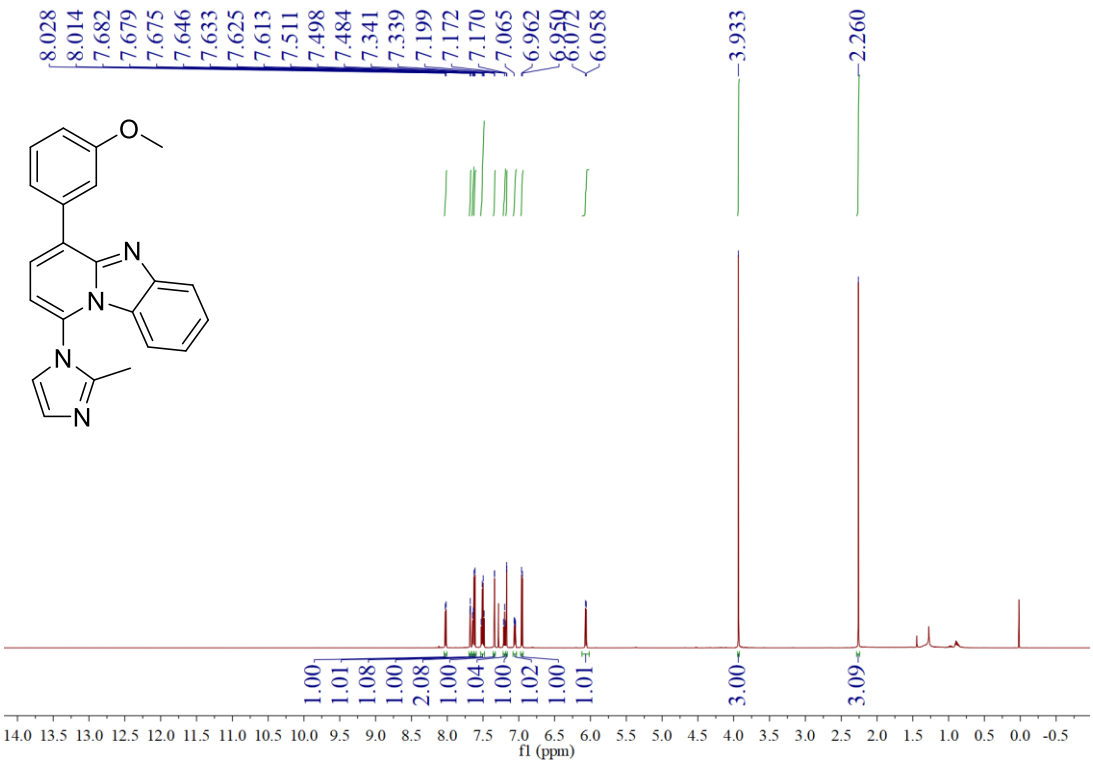


Fig. S58. ^{1}H NMR spectrum of compound **5l**.

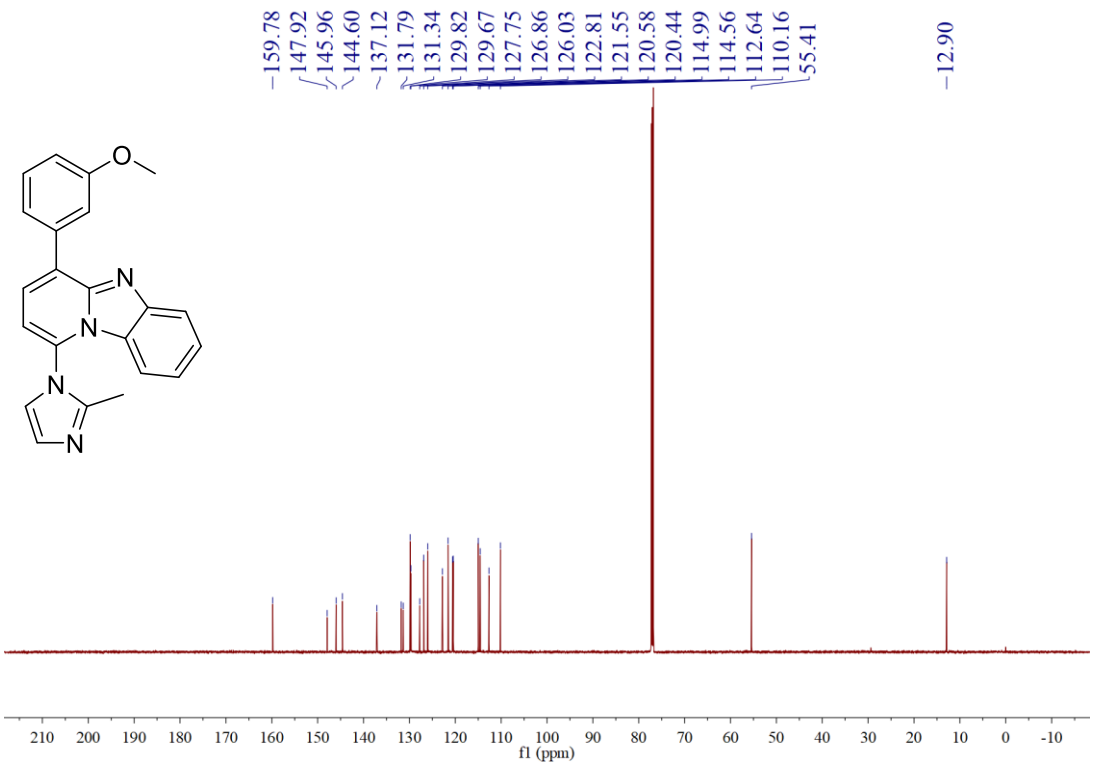


Fig. S59. ^{13}C NMR spectrum of compound **5l**.

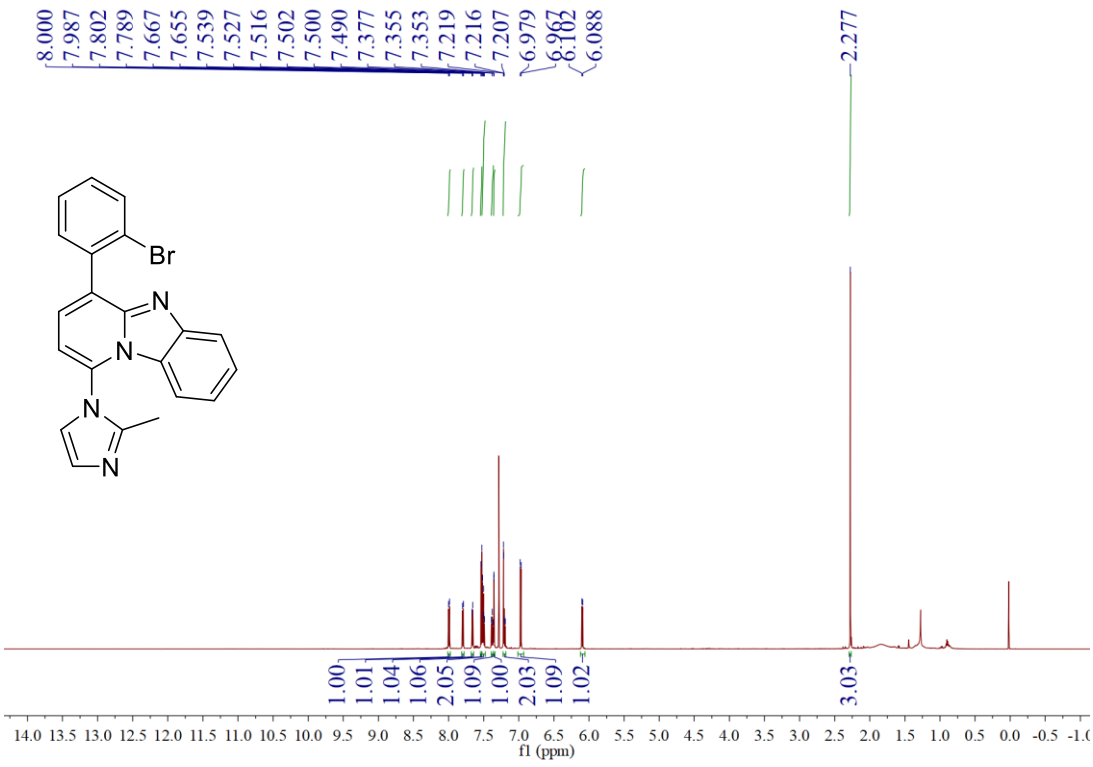


Fig. S60. ^{1}H NMR spectrum of compound **5m**.

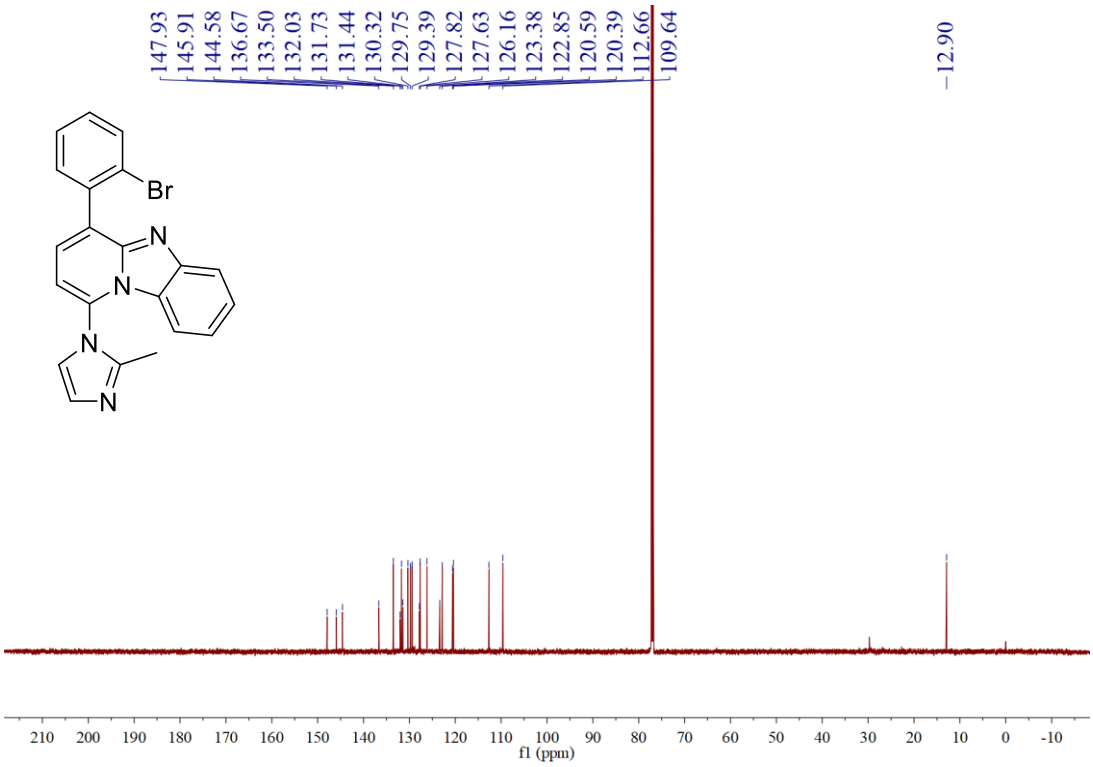


Fig. S61. ^{13}C NMR spectrum of compound **5m.**

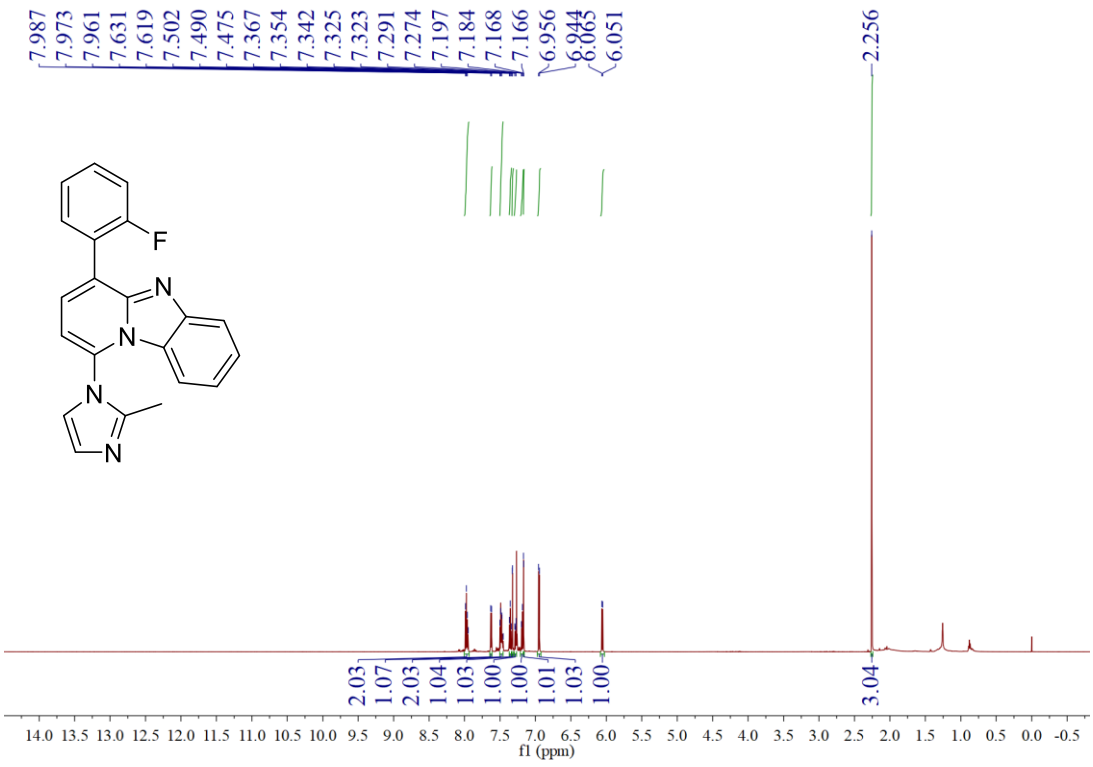


Fig. S62. ^{1}H NMR spectrum of compound **5n**.

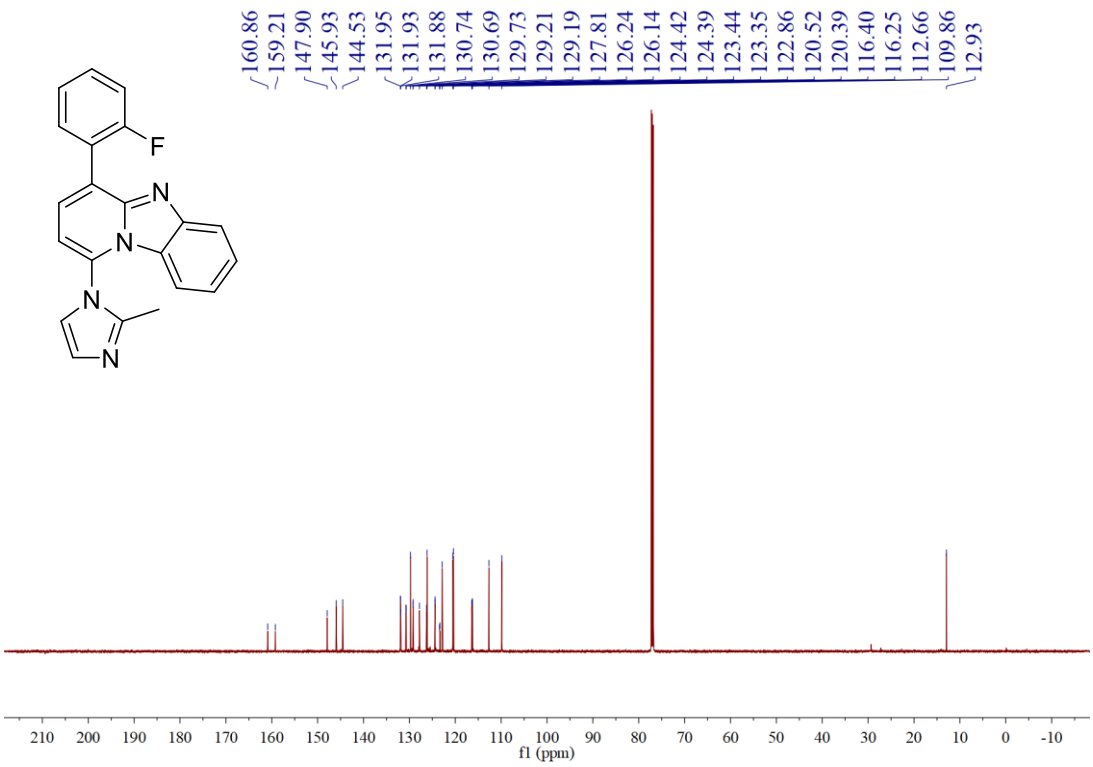


Fig. S63. ^{13}C NMR spectrum of compound **5n**.

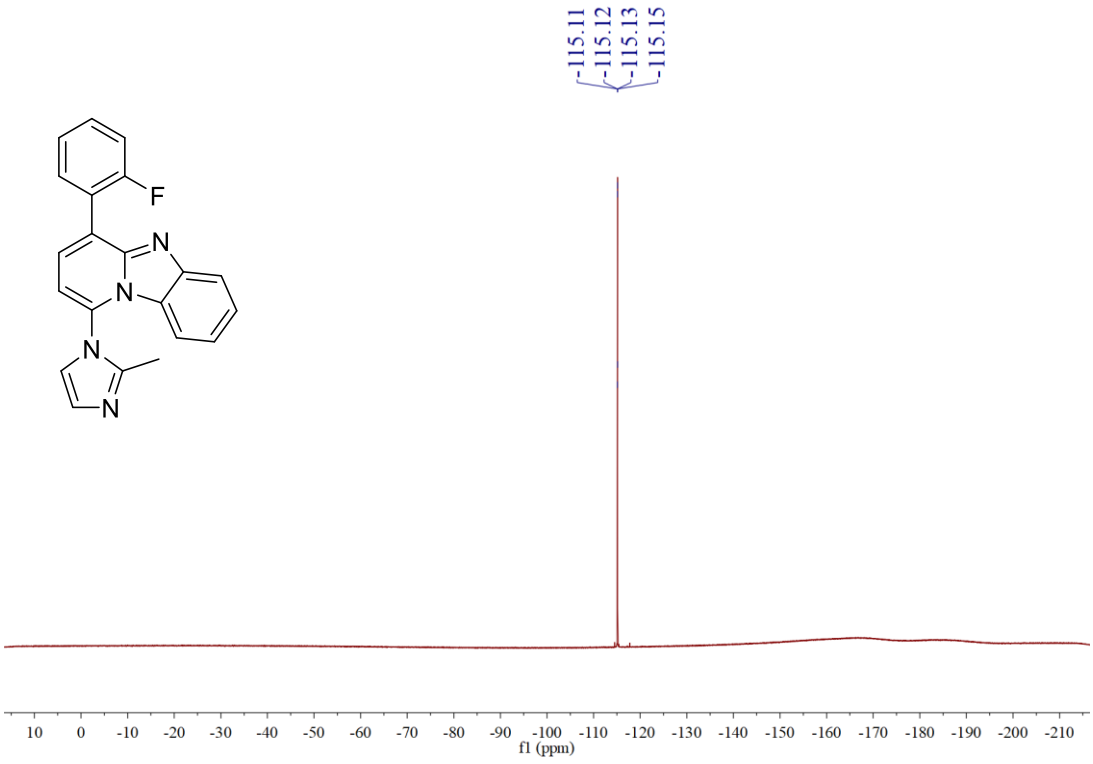


Fig. S64. ^{19}F NMR spectrum of compound **5n**.

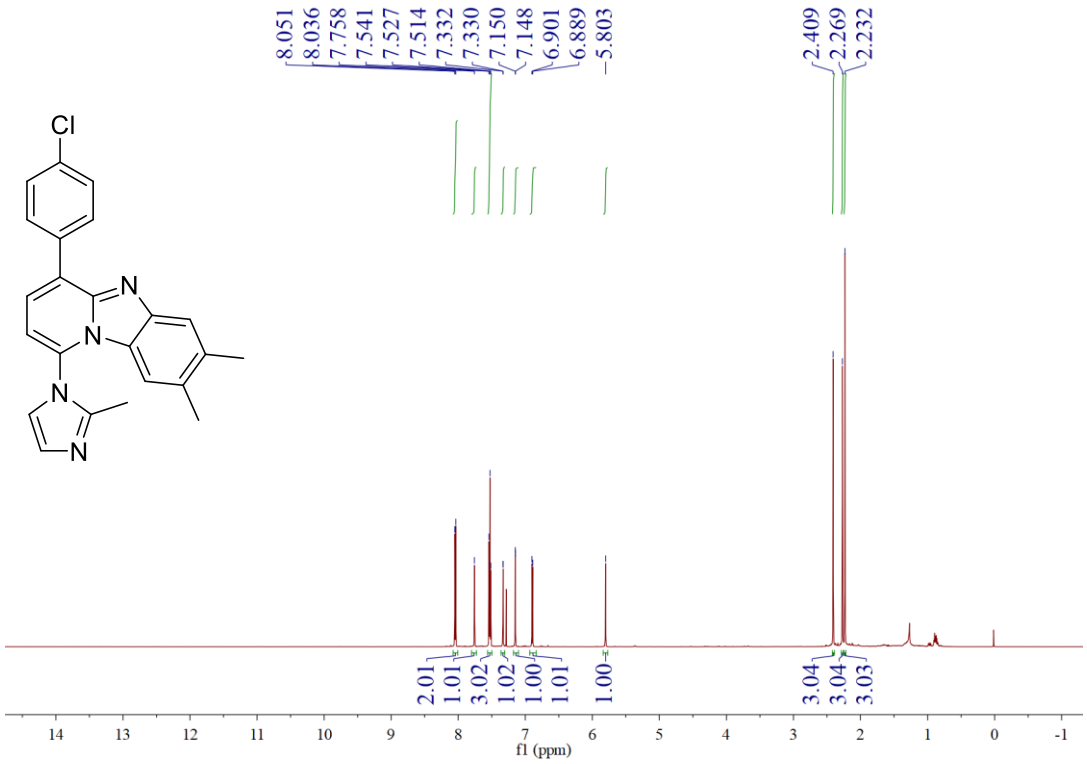


Fig. S65. ^{1}H NMR spectrum of compound **5o**.

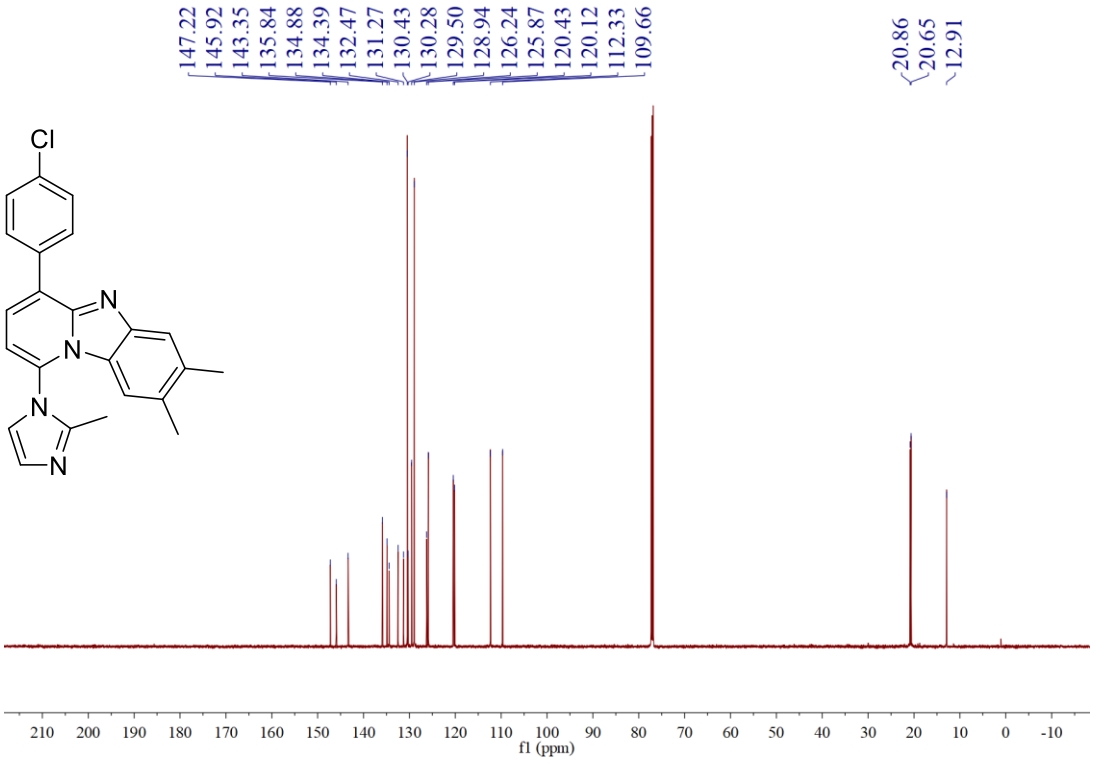


Fig. S66. ^{13}C NMR spectrum of compound **5o**.

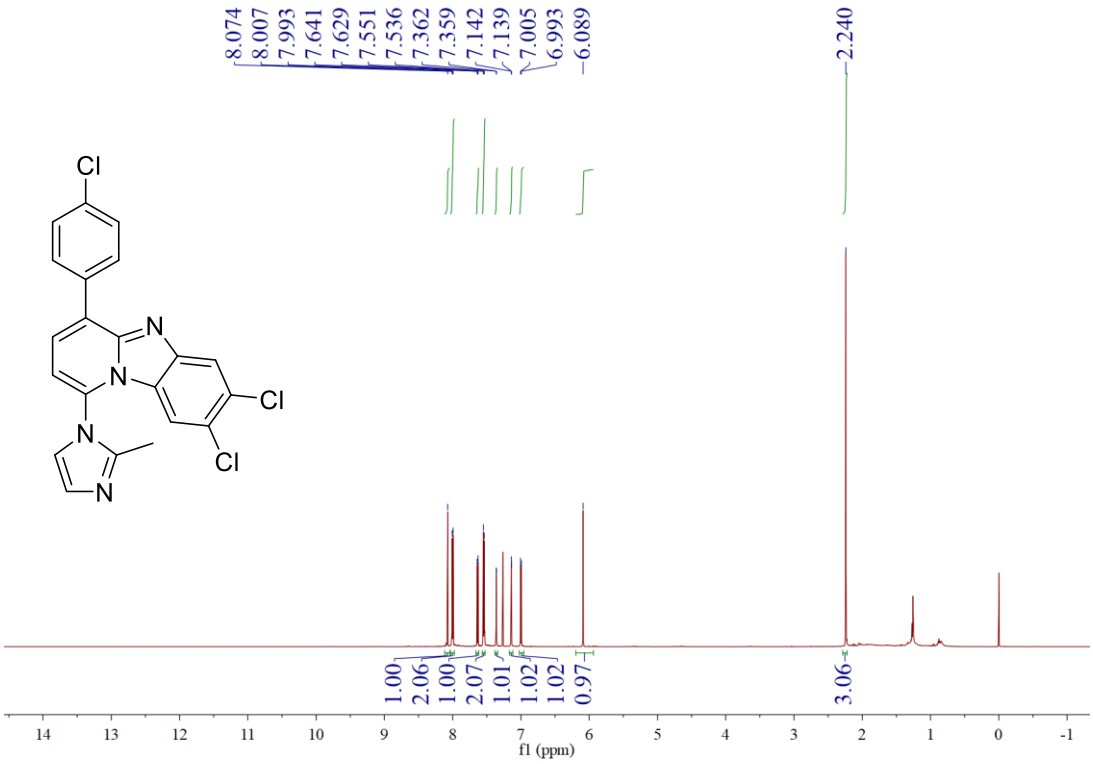


Fig. S67. ^{1}H NMR spectrum of compound **5p**.

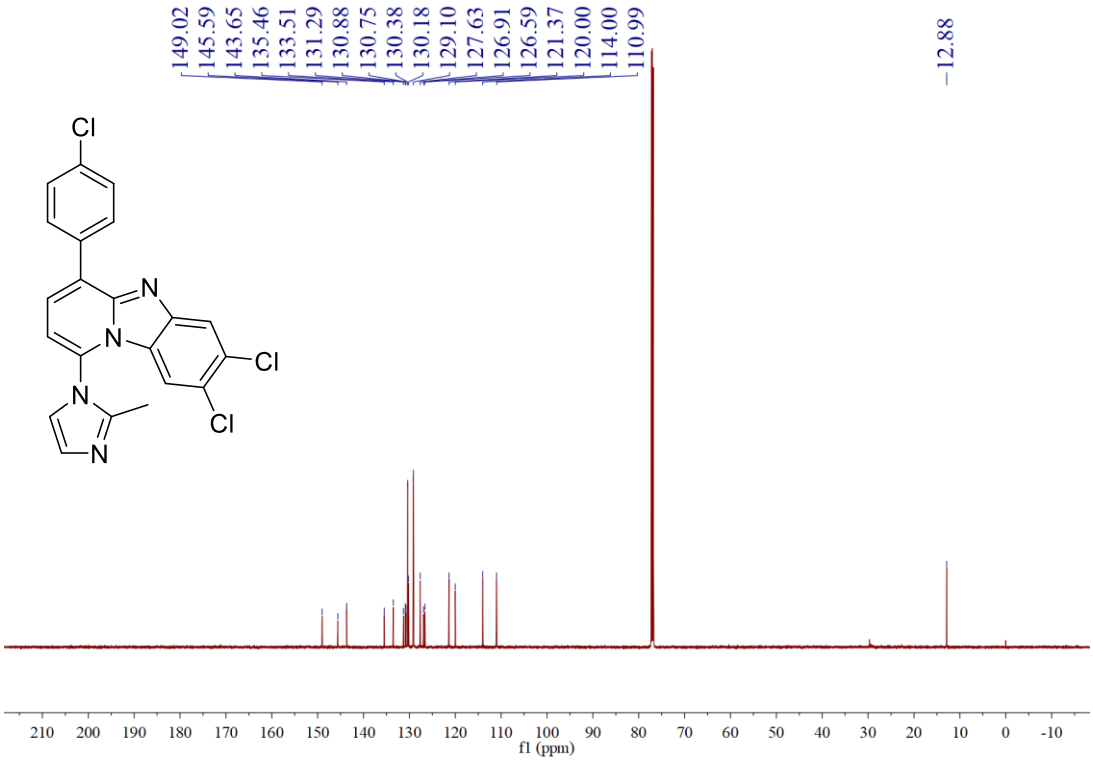


Fig. S68. ^{13}C NMR spectrum of compound **5p**.

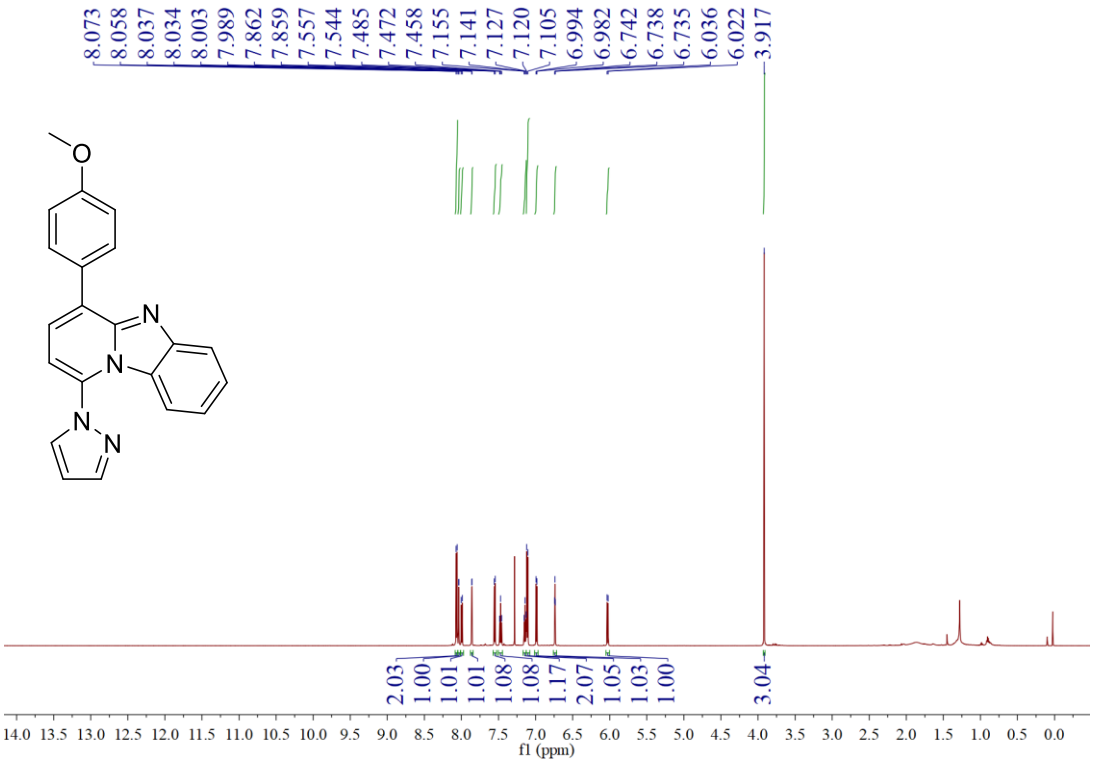


Fig. S69. ^{1}H NMR spectrum of compound **5q**.

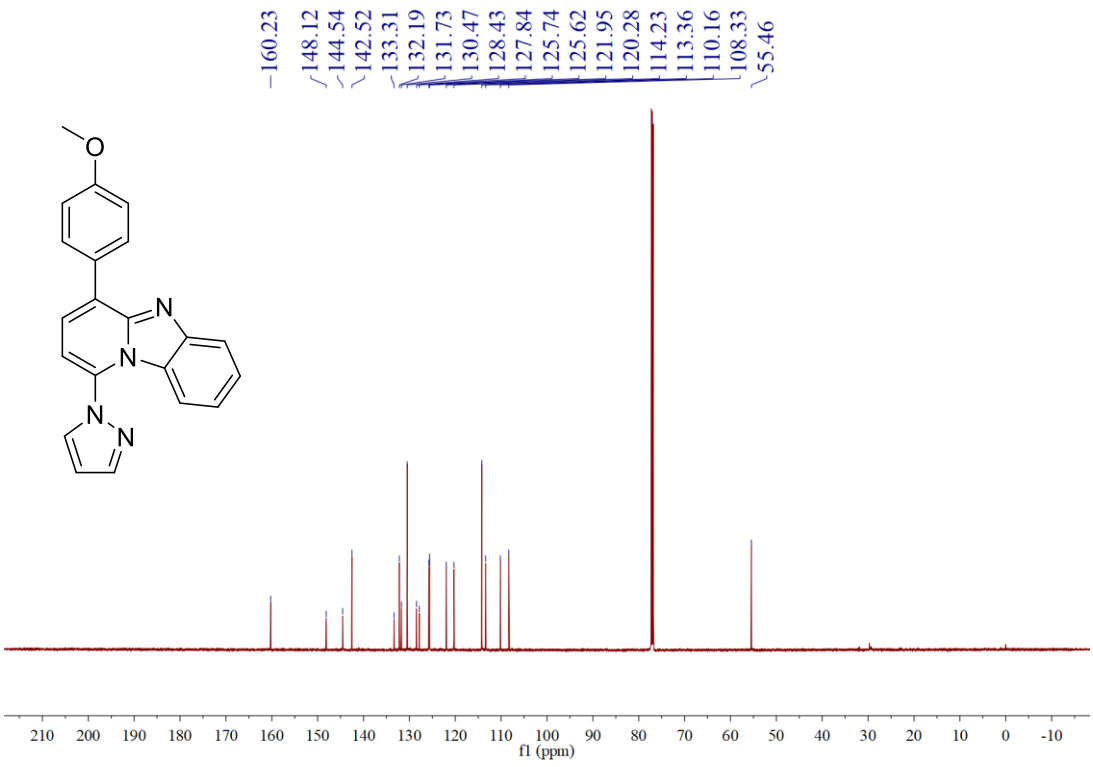


Fig. S70. ^{13}C NMR spectrum of compound **5q**.

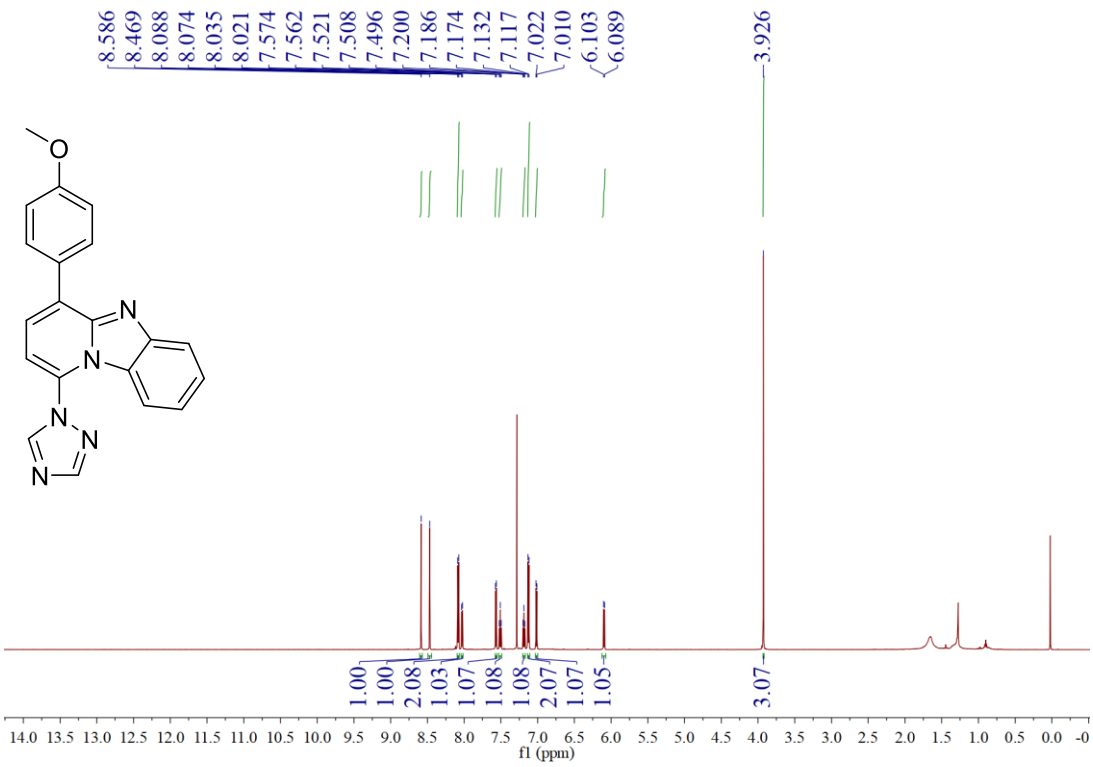


Fig. S71. ^{1}H NMR spectrum of compound **5r**.

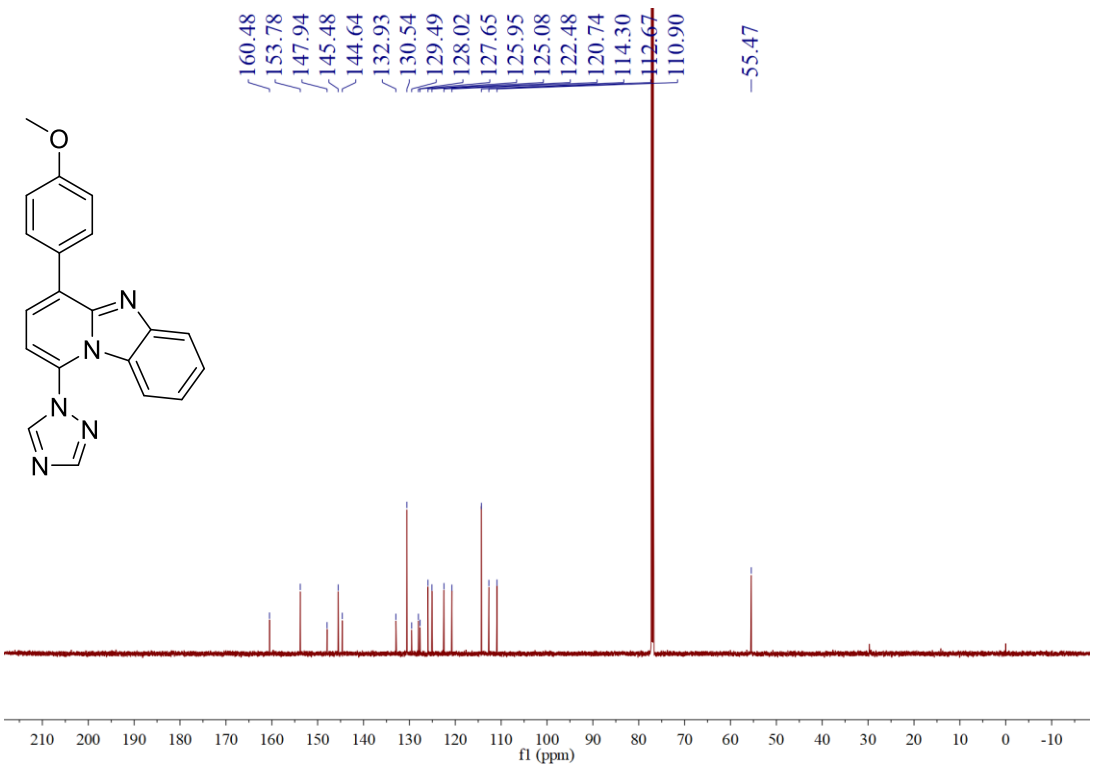


Fig. S72. ^{13}C NMR spectrum of compound **5r**.

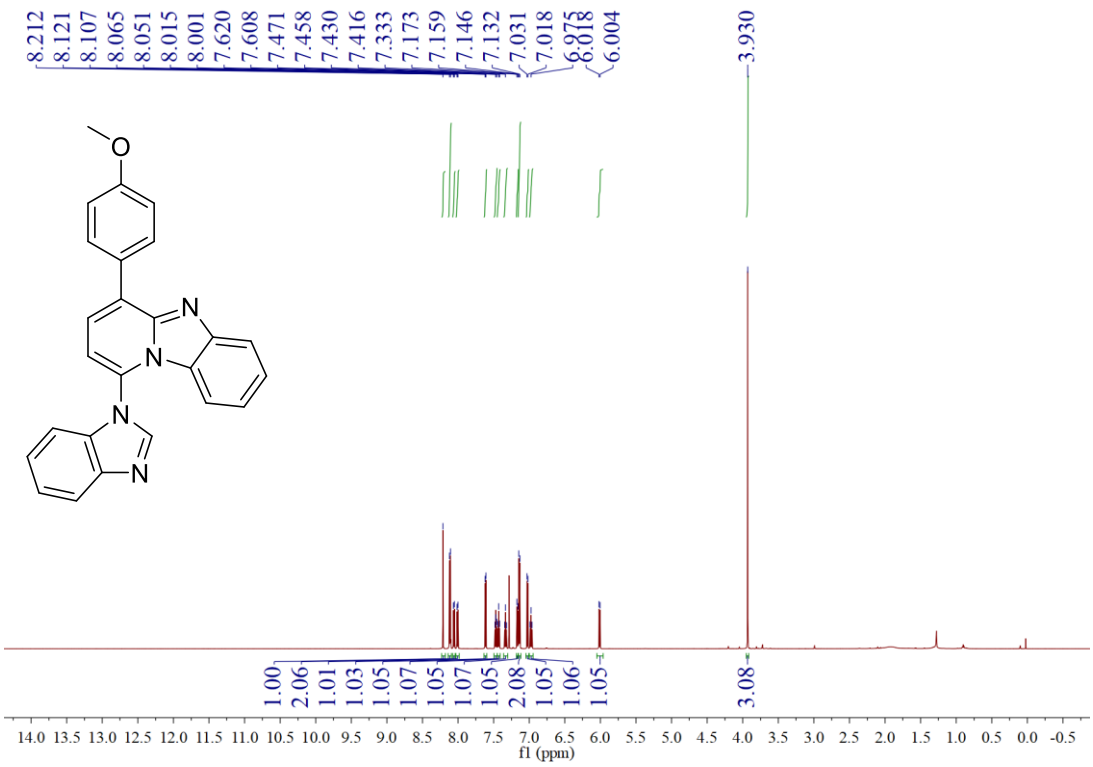


Fig. S73. ^{1}H NMR spectrum of compound **5s**.

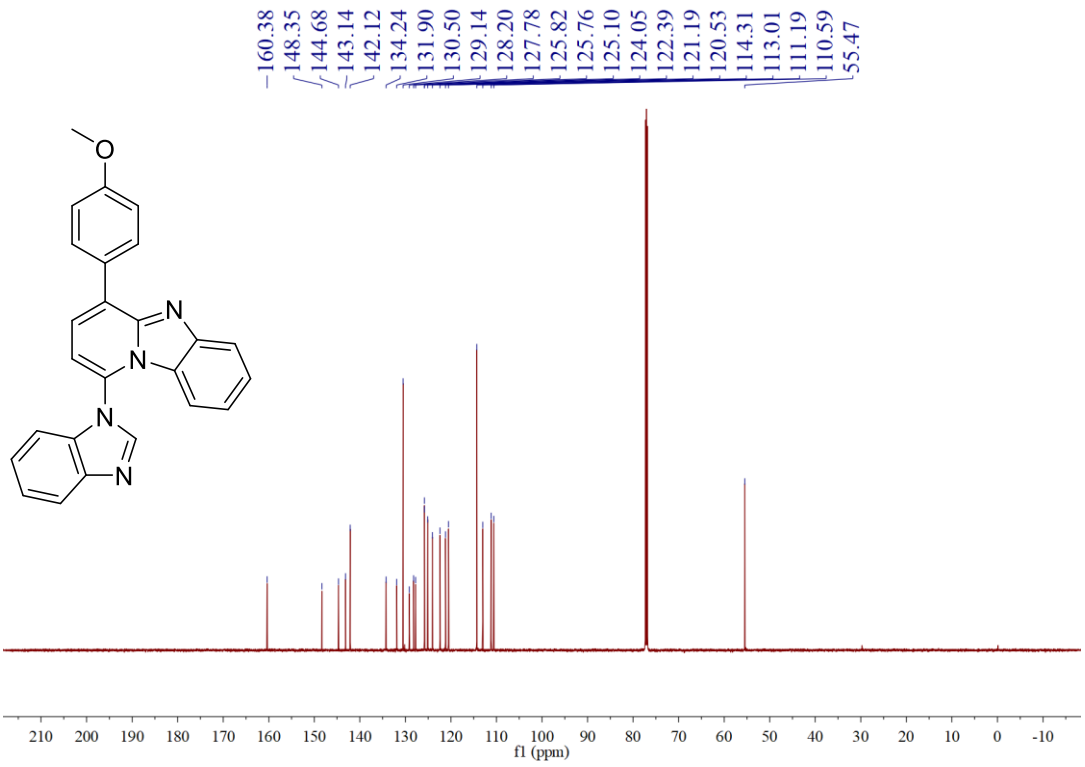


Fig. S74. ^{13}C NMR spectrum of compound **5s**.

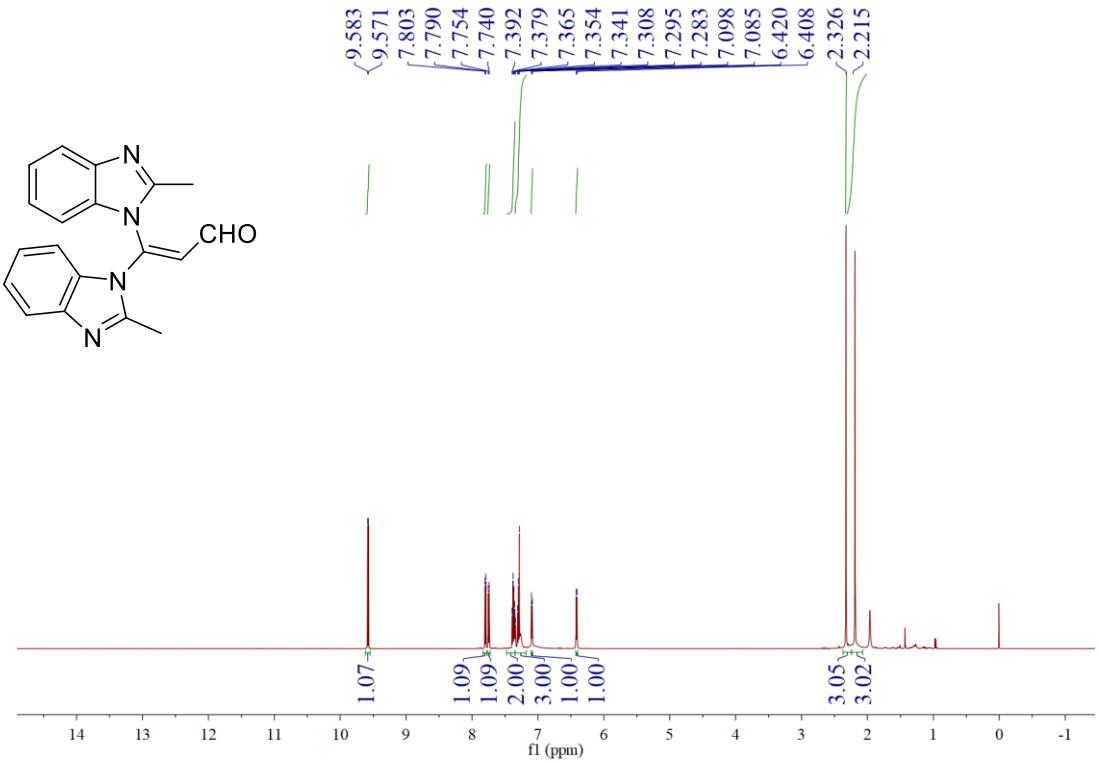


Fig. S75. ^{1}H NMR spectrum of compound **4aa**.

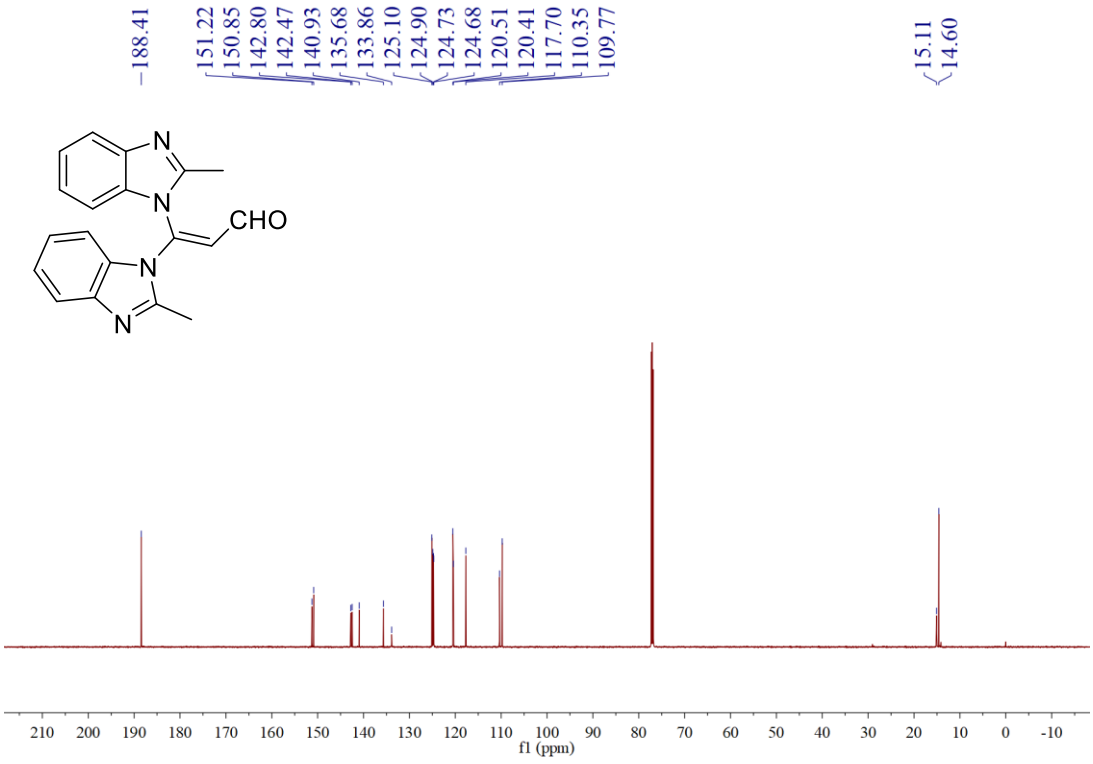


Fig. S76. ^{13}C NMR spectrum of compound **4aa**.

Emission Spectra of Compound 4a in Different Solvents

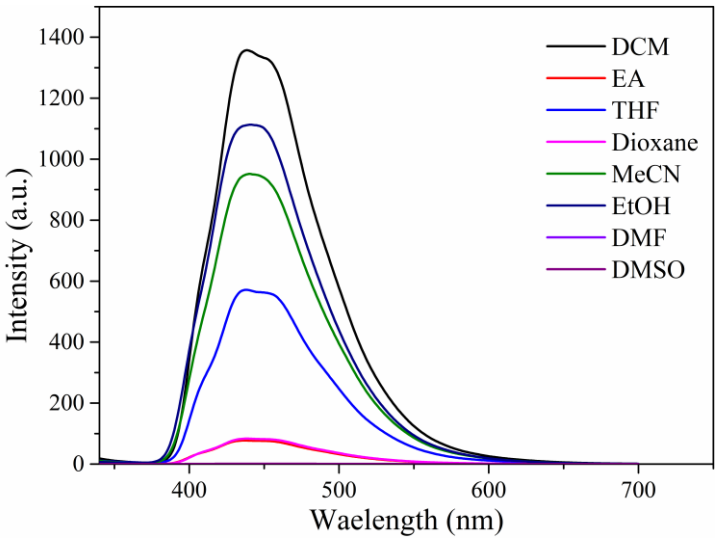


Fig. S77. Emission spectra of compound **4a** in different polar solvents (c = 10 μM, λ_{ex} = 249 nm).

Table S4. Absolute quantum yields (Φ_F) of **4a** in different THF/H_2O mixture (c = 10 μM).

No.	f_w (vol%)	Φ_F [%][a]
1	0	47.50
2	10	58.68
3	20	68.07
4	30	75.60
5	40	79.22
6	50	84.21
7	60	86.92
8	70	89.31
9	80	91.42
10	90	89.27
11	95	88.19

[a] Absolute quantum yields (Φ_F) of **4a** in different THF/H_2O mixture with increasing f_w to 95% (c = 10 μM).

Fluorescence Responses of 4a to NAEs

1. Fluorescence titration

Global concern regarding the environmental and public security impact of nitroaromatic explosives (NAEs) has increased greatly in recent years.[3] Compared with other NAEs, picric acid (PA) is of relatively high burst energy, toxicity and solubility in water. PA can enter the body through the respiratory tract or skin contact and cause diseases such as dermatitis, bronchitis, etc. More seriously, it can result in the chronic poisoning of liver, kidney, and other tissues, and even death.[3] Therefore, the development of reliable sensing materials for rapid and sensitive detection of PA in aqueous solution has received special attention.[4-6] Being an electron deficient species, PA is expected to quench the emission *via* the photoinduced electron transfer (PET) mechanism and non-radiative electron decay processes.[7]

Caution! Aromatic explosives, e.g., PA and 2,4-dinitrophenol (DNP), used in the present study are highly explosive and should be used only in small quantities.

Thus, based on the previous researches of fluorescent probes in our laboratory[7-12] and the fact that compound **4a** shows the best fluorescence intensity at a f_w of 80% (water/THF), we used **4a** as an example to study the photoluminescence spectra of **4a** upon adding the PA solution into the THF/H_2O solvent (f_w = 80%). With the addition of the PA solution (0-10 equiv.) into the **4a** solution, the fluorescence intensity of compound **4a** at 442 nm is significantly decreased. Particularly, when the PA concentration is 100 μM, the fluorescence quenching efficiency can reach 94.9% (see **Fig. 3** in the main text).

2. Limit of detection (LOD)

Limit of detection (LOD) is usually used as the standard for judging probe sensitivity. First, the standard deviation (δ) of the blank measurements (n = 10) is calculated, and δ = 1.6758. Then, a calibration curve is plotted between the luminescence intensity of **4a** in 442 nm and the concentration of PA, the slope of the calibration curve K = -43.7 (**Fig. S78**).

According to the literature,[9] LOD is determined by using the equation:

$$\mathrm{LOD} = 3\delta/\mathrm{K}$$

The corresponding LOD can be calculated to be 1.15×10^{-7} M (26.3 ppb). This value of LOD possesses certain advantages among the reported PA probes.[4,8,13-19]

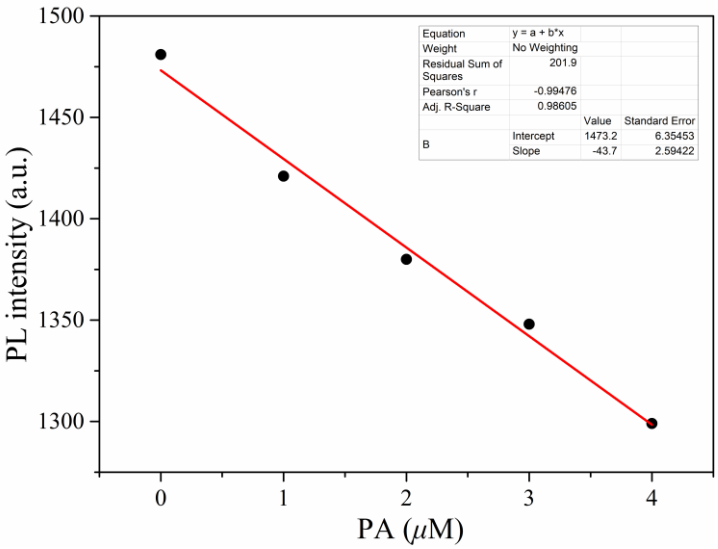


Fig. S78. The fluorescence intensity of **4a** at 442 nm as a function of picric acid concentration.

3. Stern-Volmer quenching constant (K*sv*)

To further evaluate the quenching efficiency, the fluorometric titration data of **4a** are transformed to the Stern-Volmer plot as shown in **Fig. S79**.

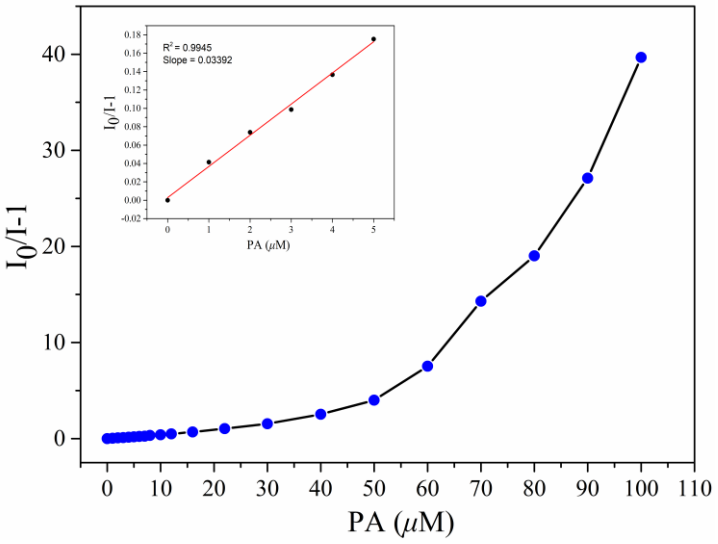


Fig. S79. Stern-Volmer plot in response to PA.

According to the literature,[10] Stern-Volmer quenching constant (K*sv*) can be calculated *via* the Stern-Volmer equation:

$$I_0 / I\text{-}1 = Ksv\,[Q]$$

Where I_0 and I are the fluorescence intensities observed in the absence and presence of PA, respectively; [Q] is the quencher concentration. Thus, the quenching constant K*sv* is calculated to be 3.39 × 10^4 M^{-1}, and this value is higher than those of some reported PA probes.[4,8,13-16,20,21]

4. DFT studies for quenching mechanism

The quenching mechanism of **4a** towards PA may be confirmed *via* theoretical calculations. Therefore, the DFT studies were carried out by using the B3LYP/6-31G basis set. The HOMO-LUMO energy levels and their DE values for **4a** and PA are summarized in **Fig. S80**.

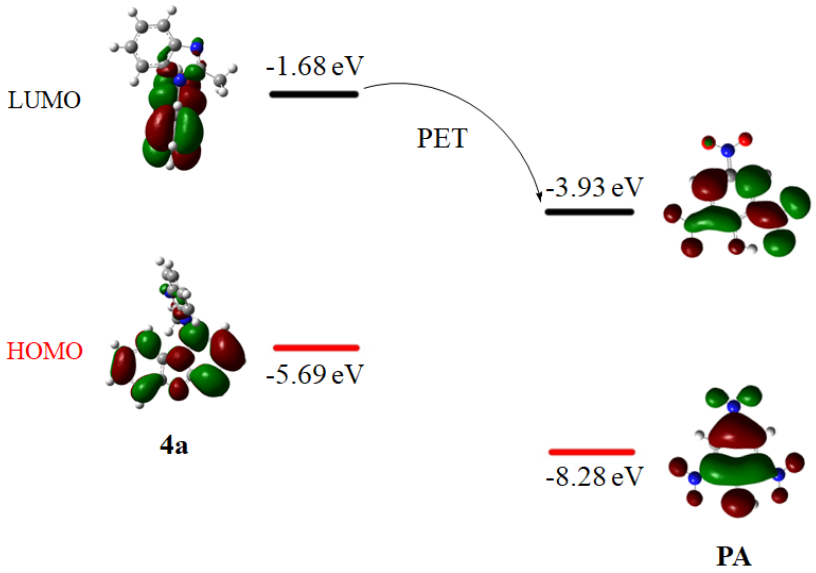


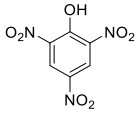
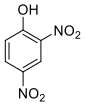
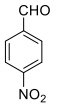
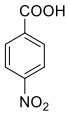
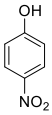
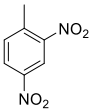
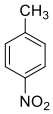
Fig. S80. HOMOs–LUMOs of **4a** and PA calculated by the DFT methods.

The HOMO and LUMO energy levels of **4a** are -5.69 eV and -1.68 eV, while those of PA are -8.28 eV and -3.93 eV, respectively. The LUMO energy of electron-deficient PA is higher than the HOMO energy of **4a** but lower than the LUMO energy of **4a**, so the electron transfer from the LUMO of **4a** to the LUMO of PA is feasible. This result clearly reveals that the PET can occur from **4a** to PA.

5. Fluorometric detection experiments of other NAEs

We further explored the fluorometric detection experiments of other NAEs to study the selectivity of **4a** (see **Table S5**). When 10 equivalents of other NAEs (or analogues) are added dropwise to the THF/H_2O (f_w = 80%) solution of **4a**, the fluorescence intensity is quenched to different degrees.

Table S5. Sensing performance of **4a** towards NAEs (or analogues).

NAEs	Structure	Quenching efficiency[a]	NAEs	Structure	Quenching efficiency[a]
PA (picric acid)		94.9%	**2-HBAc** (2-hydroxybenzoic acid)		83.3%
2,4-DNP (2,4-dinitrophenol)		69.0%	**2-NA** (2-nitroaniline)		66.6%
4-NBA (4-nitrobenzaldehyde)		62.9%	**4-NBAc** (4-nitrobenzoic acid)		61.4%
4-NP (4-nitrophenol)		23.9%	**4-DNT** (1-methyl-2,4-dinitrobenzene)		21.5%
NM (Nitromethane)	CH_3NO_2	8.8%	**NB** (nitrobenzene)		7.6%
PhOH (phenol)		5.5%	**4-NT** (4-nitrotoluene)		2.7%

[a] The quenching efficiency were calculated after adding 10 equiv. NACs into **4a** solution.

In a word, **4a** can be used as a fluorescent AIE probe to detect PA by "turn-off" response in aqueous system and has the advantages of low detection limit and large quenching constant. At the same time, **4a** also has a moderate response to some other NAEs.

References

[1] D. Obermayer, D. Znidar, G. Glotz, A. Stadler, D. Dallinger and C. O. Kappe, *J. Org. Chem*., 2016, **81**, 11788.

[2] H. Qin, Y.-Y. Miao, J. Xu, Q.-R. Bi, W. Qu, W.-Y. Liu, F. Feng and H.-P. Sun, *Org. Chem. Front*., 2019, **6**, 205.

[3] Y.-F. Zhao, L.-B. Xu, F.-L. Kong and L. Yu, *Chem. Eng. J*. 2021, **416**, 129090.

[4] C. Pherkkhuntod, V. Ervithayasuporn, S. Chanmungkalakul, C. Wang, X. G. Liu, D. J. Harding and S. Kiatkamjornwong, *Sens. Actuators, B*, 2021, **330**, 129287.

[5] W.-M. Wan, D. Tian, Y.-N. Jing, X.-Y. Zhang, W. Wu, H. Ren and H.-L. Bao, *Angew. Chem., Int. Ed*., 2018, **57**, 15510.

[6] J. M. Delente, D. Umadevi, S. Shanmugaraju, O. Kotova, G. W. Watson and T. Gunnlaugsson, *Chem. Commun.*, 2020, **56**, 2562.

[7] S.-H. Chen, K. Jiang, J.-Y. Lin, K. Yang, X.-Y. Cao, X.-Y. Luo and Z.-Y. Wang, *J. Mater. Chem. C*, 2020, **8**, 8257.

[8] B.-W. Wang, K. Jiang, J.-X. Li, S.-H. Luo, Z.-Y. Wang and H.-F. Jiang, *Angew. Chem. Int. Ed*., 2020, **59**, 2338.

[9] Y.-C. Wu, J.-P. Huo, L. Cao, S. Ding, L.-Y. Wang, D.-R. Cao and Z.-Y. Wang, *Sens. Actuators, B*, 2016, **237**, 865.

[10] K. Jiang, S.-H. Luo, C.-M. Pang, B.-W. Wang, H.-Q. Wu and Z.-Y. Wang, *Dyes Pigm.*, 2019, **162**, 367.

[11] K. Jiang, S.-H. Chen, S.-H. Luo, C.-M. Pang, X.-Y. Wu and Z.-Y. Wang, *Dyes Pigm.*, 2019, **167**, 164.

[12] C.-M. Pang, X.-Y. Cao, Y. Xiao, S.-H. Luo, Q. Chen, Y.-J. Zhou and Wang, Z.-Y. *iScience*, 2021, **24**, 103126.

[13] X. Lu, G.-C. Zhang, D.-D. Li. X.-H. Tian, W. Ma, S.-L. Li, Q. Zhang, H.-P. Zhou, J.-Y. Wu and Y.-P. Tian, *Dyes Pigm*., 2019, **170**, 107641.

[14] S.-L. Yi, Z. Lu, Z.-H. Xie and L.-X. Hou, *Talanta*, 2020, **208**, 120372.

[15] J. M. Mohan, K. Amreen, M. B. Kulkarni, A. Javed, S. K. Dubey, S. Goel, *Colloids Surf. B Biointerfaces*, 2021, **208**, 112056.

[16] Y.-T. Fan, T. Tao, H.-J. Wang, Z.-Y. Liu, W. Huang and H. Cao, *Dyes Pigm*., 2021, **191**, 109355.

[17] J.-F. Zhang, J.-J. Wu, G.-D. Tang, J.-Y. Feng, F.-M. Luo, B. Xu and C. Zhang, *Sens. Actuators, B*, 2018, **272**, 166.

[18] Y.-P, Zhuang, J.-Y. Yao, Z.-Y. Zhuang, C.-J. Ni, H.-M. Yao, D.-L. Su, J. Zhou and Z.-J. Zhao, *Dyes Pigm*., 2020, **174**, 108041.

[19] J.-X. Li, X.-R. Zhuang, N.-X. Zhang, L.-Y. Zhao, Q.-F. Yang and X. Zhang, *Inorg. Chim. Acta*, 2019, **497**, 119096.

[20] X.-D. Yu, J.-B. Guo, P. Peng, F.-J. Shen, Y.-J. Li, L.-J. Geng and T. Wang, *Appl. Surf. Sci*., 2019, **487**, 473.

[21] W.-Y. Dong, Q.-H. Ma, Z.-H. Ma, Q. Duan, X.-L. Lü, N.-N. Qiu, T. Fei and Z.-M. Su, *Dyes Pigm*., 2020, **172**, 107799.