Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Bifunctional acidic ionic liquids-catalyzed decarboxylative cascade synthesis of quinoxalines in water under ambient conditions

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Supporting Information

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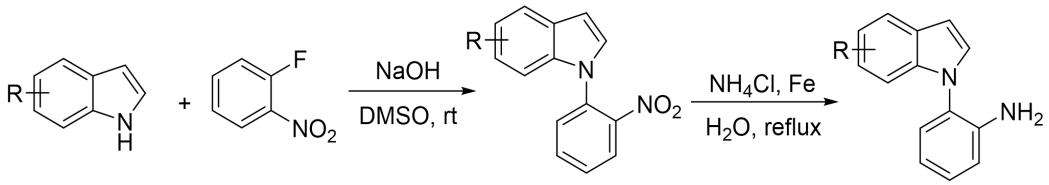
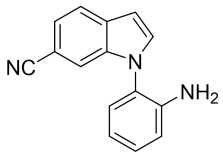
1. General Information

All purchased reagents were used without further purification unless otherwise noted. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F254); visualization of the developed chromatogram was performed by fluorescence. ^{1}H nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on a Bruker Ascend 400 spectrometer, chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for $CDCl_3$.Infrared spectra (IR) data were recorded on a TENSOR 27 FT-IR spectrometer and recorded in wave numbers (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. **1a**–**1p** were prepared according to literature methods.[1] **2b**–**2j** and **2m**–**2p** were prepared according to literature methods.[2]

2. Preparation of Substrates

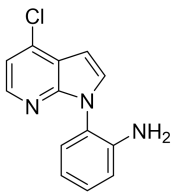


To a stirred solution of indole (1.0 mmol) and 2-nitro-benzene (1.0 mmol) in DMSO (1.0 mL), NaOH (1.0 mmol) was added portion wise and is stirred vigorously at room temperature for 1.5 h. After completion of the reaction, the mixture was diluted by H_2O, and extracted by EtOAc. The combined organic layer was washed with brine and dried by anhydrous $MgSO_4$. The solution was evaporated and the residue was added NH_4Cl (0.5 eq) and Fe (8 eq) in H_2O (5.0 mL), and then refluxed for 4 h. Subsequently, the reaction was quenched by H_2O and extracted by EtOAc. The organic layer was dried by anhydrous $MgSO_4$. Finally, the solution was evaporated and the mixture was purified by column chromatography on silica gel to afford the product.



1-(2-Aminophenyl)-1*H*-indole-6-carbonitrile (1f)

Pale yellow solid (179.0 mg, 63% yield). petroleum ether (PE)/ethyl acetate (EA) = 10:1, R_f = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.2 Hz, 1H), 7.53 (s, 1H), 7.49 – 7.41 (m, 2H), 7.34 (q, J = 8.7 Hz, 1H), 7.20 (d, J = 7.8 Hz, 1H), 6.93 (dd, J = 19.3, 7.8 Hz, 2H), 6.81 (d, J = 3.1 Hz, 1H), 3.61 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 135.3, 132.4, 131.7, 130.0, 128.5, 123.4, 123.1, 121.8, 120.5, 118.8, 116.6, 115.9, 104.8, 104.0 ppm. IR (KBr): 3463, 3371, 2208, 1618, 1498, 1454, 1330, 1218, 921, 864, 810, 752. HRMS (ESI) m/z calculated for $C_{15}H_{12}N_3$ $[M+H]^+$ 234.1026, found 234.1020.



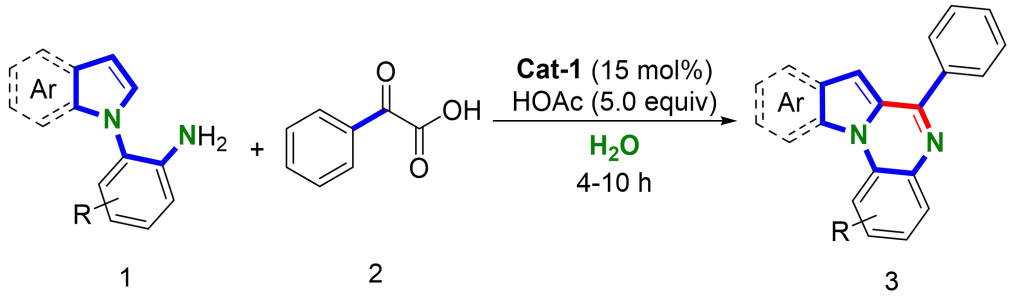
2-(4-Chloro-1H-pyrrolo[2,3-*b*]pyridin-1-yl)aniline (1k)

Pale yellow solid (161.0 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H),

7.43 (s, 1H), 7.31 (s, 2H), 6.89 (d, J = 9.2 Hz, 4H), 3.86 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 144.1, 142.8, 136.6, 130.1, 129.5, 128.4, 124.4, 120.3, 119.1, 117.4, 116.6, 100.2 ppm. IR (KBr): 3442, 3352, 3110, 1616, 1504, 1404, 1263, 1081, 1022, 897, 804, 733 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{11}ClN_3$ $[M+H]^+$ 244.0636, found 244.0630.

3. Reaction Results

General Procedure for the synthesis of quinoxalines (**GP**): A pressure tube was charged with **Cat-1** (15 mol%), 2-(1H-indol-1-yl)anilines **1** (1 mmol), 2-oxoacetic acids **2** (1.2 mmol), HOAc (5 eq) and H_2O (3.0 mL). The reaction mixture was stirred at room tempture for 6–12h under air condition. After cooling to room temperature, the target product **3** was obtained by filtration and washing with H_2O or ^{i}PrOH.



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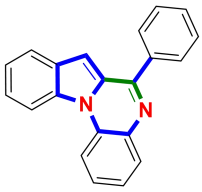
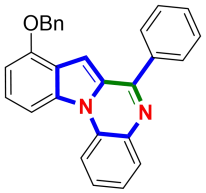


3aa

6-Phenylindolo[1,2-*a*]quinoxaline (3aa)

Yellow solid (90%, 26.5 mg). According to the **GP**, the product **3aa** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (t, J = 9.1 Hz, 2H), 8.14 (dd, J = 8.0, 1.6 Hz, 1H), 8.12 – 8.03 (m, 2H), 7.98 (d, J = 8.0 Hz, 1H), 7.72 – 7.57 (m, 5H), 7.50 (td, J = 7.3, 3.6 Hz, 2H), 7.30 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 138.3, 136.3, 133.1, 130.6, 130.2, 130.0, 129.2, 129.2, 128.7, 128.7, 128.4, 124.4, 124.2, 122.8, 122.7, 114.7, 114.6, 102.5 ppm.

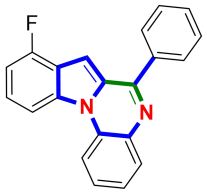


3ba

8-(Benzyloxy)-6-phenylindolo[1,2-*a*]quinoxaline (3ba)

Yellow solid (96%, 38.4 mg). According to the **GP**, the product **3ba** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 1H),

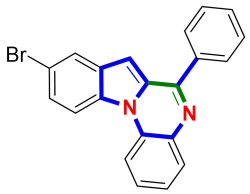
8.31 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 7.3 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.68 (q, *J* = 6.8 Hz, 5H), 7.55 (dd, *J* = 20.8, 7.9 Hz, 4H), 7.44 (dt, *J* = 11.2, 6.6 Hz, 3H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.29 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 156.4, 153.6, 138.2, 136.8, 136.5, 134.3, 130.3, 130.1, 129.9, 128.7, 128.6, 128.6, 128.1, 128.0, 127.5, 126.5, 125.4, 124.3, 121.2, 114.7, 107.7, 102.9, 100.0, 70.2 ppm.



3ca

8-Fluoro-6-phenylindolo[1,2-*a*]quinoxaline (3ca)

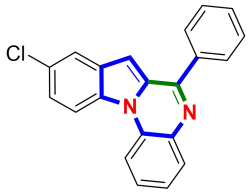
Yellow solid (90%, 28.1 mg). According to the **GP**, the product **3ca** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.58 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 8.24 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.14 – 8.04 (m, 2H), 7.74 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.67 (p, *J* = 3.5, 3.1 Hz, 3H), 7.63 – 7.55 (m, 2H), 7.50 (s, 1H), 7.20 (dd, *J* = 9.5, 7.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 163.9 (d, *J* = 249.0 Hz), 135.8, 135.0, 134.0, 133.2, 130.7, 130.6, 130.3, 130.1, 129.2, 128.8, 128.6, 124.7, 124.4, 122.8, 115.8 (d, *J* = 21.5 Hz), 114.7 (d, *J* = 8.6 Hz), 113.7, 102.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) *δ* –78.32 ppm.



3da

9-Bromo-6-phenylindolo[1,2-*a*]quinoxaline (3da)

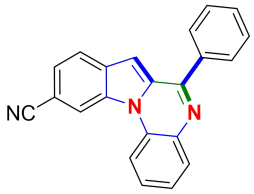
Yellow solid (92%, 34.2 mg), mp 260–261°C. According to the **GP**, the product **3da** is obtained by washing filtration and with water. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.41 (d, *J* = 8.3 Hz, 1H), 8.29 – 8.20 (m, 2H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.06 – 7.99 (m, 2H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.62 (dd, *J* = 7.0, 3.6 Hz, 4H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.15 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 156.0, 137.9, 136.3, 132.5, 132.0, 131.5, 131.5, 130.8, 130.2, 129.8, 129.5, 128.8, 128.6, 128.6, 124.6, 116.3, 114.6, 101.3, 86.8 ppm. IR (KBr): 3701, 3110, 3055, 1720, 1539, 1444, 1379, 1326, 1207, 1124, 1062, 1018, 748, 688 cm^{-1}. HRMS (ESI) m/z: calculated for $C_{21}H_{14}BrN_2$ $[M+H]^+$ 373.0335, found 373.0329.



3ea

9-Chloro-6-phenylindolo[1,2-*a*]quinoxaline (3ea)

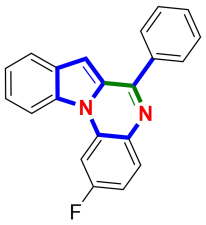
Yellow solid (91%, 29.9 mg), mp 230–231°C. According to the **GP**, the product **3ea** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, J = 12.4, 8.8 Hz, 2H), 8.17 (dd, J = 8.0, 1.8 Hz, 1H), 8.10 – 8.02 (m, 2H), 7.94 (d, J = 2.3 Hz, 1H), 7.71 (dd, J = 7.3, 1.7 Hz, 1H), 7.64 (dd, J = 4.9, 2.1 Hz, 3H), 7.60 – 7.50 (m, 2H), 7.24 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 147.3, 137.9, 136.3, 135.2, 131.3, 130.8, 130.2, 130.1, 129.8, 128.7, 128.6, 128.4, 124.6, 121.8, 119.9, 115.6, 114.5, 101.7 ppm. IR (KBr): 3058, 2916, 2858, 1604, 1531, 1446, 1384, 1211, 1076, 1070, 908, 854, 738, 684 cm^{-1}. HRMS (ESI) m/z: calculated for $C_{21}H_{14}ClN_2$ $[M+H]^+$ 329.0840, found 329.0836.



3fa

6-Phenylindolo[1,2-a]quinoxaline-10-carbonitrile (3fa)

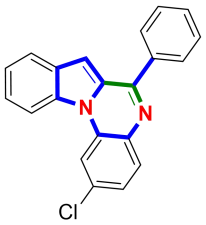
Yellow solid (89%, 28.4 mg). PE/EA = 30:1, R_f = 0.26, mp 279–280°C. According to the **GP**, The product **3fa** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.50 (d, J = 8.4 Hz, 1H), 8.23 – 8.16 (m, 1H), 8.09 – 8.01 (m, 3H), 7.77 (t, J = 7.8 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.66 – 7.56 (m, 4H), 7.35 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 137.6, 137.1, 136.4, 131.7, 131.6, 131.2, 130.4, 129.9, 129.3, 128.8, 128.6, 125.4, 124.8, 123.6, 120.1, 119.7, 114.6, 106.5, 102.5. IR (KBr): 3699, 3124, 3044, 2918, 2217, 1729, 1515, 1442, 1373, 1303, 1215, 821, 744, 694 cm^{-1}. HRMS (ESI) m/z: calculated for $C_{22}H_{13}N_3$ $[M+H]^+$ 320.1182, found 320.1178.



3ga

2-Fluoro-6-phenylindolo[1,2-*a*]quinoxaline (3ga)

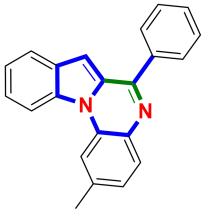
Yellow solid (93%, 29.0 mg). According to the **GP**, the product **3ga** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.7 Hz, 1H), 8.25 (d, J = 10.3 Hz, 1H), 8.08 (dd, J = 23.6, 7.3 Hz, 3H), 7.98 (d, J = 8.1 Hz, 1H), 7.65 – 7.59 (m, 4H), 7.51 (t, J = 7.5 Hz, 1H), 7.30 (s, 1H), 7.21 (t, J = 8.4 Hz, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, J = 246.2 Hz), 155.3, 138.0, 132.9 (d, J = 8.1 Hz), 132.0 (d, J = 9.9 Hz), 130.8, 130.1, 129.4, 128.7, 128.7, 128.6, 124.9, 123.1, 122.9, 114.2, 111.5 (d, J = 22.6 Hz), 102.9, 102.1, 101.8 ppm.^{19}F NMR (376 MHz, $CDCl_3$) δ –106.73 ppm.



3ha

2-Chloro-6-phenylindolo[1,2-*a*]quinoxaline (3ha)

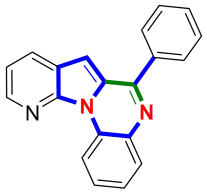
Yellow solid (95%, 31.2 mg). According to the **GP**, the product **3ha** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 2.1 Hz, 1H), 8.39 (d, J = 8.6 Hz, 1H), 8.05 (dd, J = 6.5, 3.0 Hz, 2H), 8.01 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.66 – 7.56 (m, 4H), 7.52 – 7.39 (m, 2H), 7.28 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 137.8, 134.7, 133.7, 132.9, 131.3, 130.6, 130.3, 129.3, 128.7, 128.7, 128.6, 124.9, 124.4, 123.1, 122.9, 114.7, 114.3, 103.3 ppm.



3ia

2-Methyl-6-phenylindolo[1,2-*a*]quinoxaline (3ia)

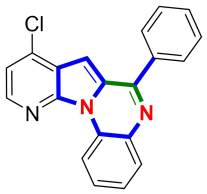
Yellow solid (94%, 29.0 mg). According to the **GP**, the product **3ia** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.8 Hz, 1H), 8.40 (s, 1H), 8.23 (d, J = 8.2 Hz, 1H), 8.09 (d, J = 7.1 Hz, 2H), 8.03 (d, J = 8.1 Hz, 1H), 7.73 (q, J = 7.0, 6.6 Hz, 4H), 7.56 (s, 2H), 7.40 (d, J = 8.2 Hz, 1H), 2.72 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 140.7, 134.1, 133.6, 131.9, 129.7, 129.6, 129.2, 127.8, 127.2, 126.6, 126.4, 125.1, 123.6, 123.4, 121.9, 115.3, 114.9, 107.8, 22.4 ppm.



3ja

6-Phenylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoxaline (3ja)

Yellow solid (87%, 25.7 mg). According to the **GP**, the product **3ja** is obtained by filtration and washing with water and ^{i}PrOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (d, J = 8.3 Hz, 1H), 8.76 (dd, J = 4.5, 1.6 Hz, 1H), 8.25 (dd, J = 8.1, 1.7 Hz, 1H), 8.09 (ddd, J = 10.1, 6.8, 1.7 Hz, 3H), 7.77 – 7.66 (m, 1H), 7.63 (dd, J = 5.1, 1.9 Hz, 3H), 7.52 (t, J = 7.6 Hz, 1H), 7.43 (dd, J = 8.0, 4.5 Hz, 1H), 7.17 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 145.5, 144.9, 137.9, 135.6, 130.5 130.2, 129.7, 128.9, 128.8, 128.6, 128.1, 127.5, 124.8, 121.2, 118.6, 117.6, 99.2 ppm.

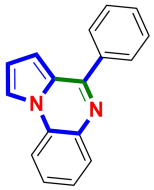


3ka

8-Chloro-6-phenylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoxaline (3ka)

Yellow solid (55%, 18.1 mg). mp 190–191 °C. According to the **GP**, the crude product was purified by flash column chromatography, PE/EA = 30:1, R_f = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (dd, J = 8.4, 1.3 Hz, 1H), 8.64 (d, J = 5.0 Hz, 1H), 8.10 (ddq, J = 10.7, 5.6, 3.6, 2.6 Hz, 3H), 7.77 – 7.68 (m, 1H), 7.66 (tt, J = 6.2, 3.2 Hz, 3H), 7.60 – 7.51 (m, 1H), 7.48 (d, J = 5.0 Hz, 1H), 7.27 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 145.8, 144.8, 137.7, 137.6, 135.8, 131.5, 130.3, 129.9, 129.2, 128.6, 128.3, 127.7, 125.3, 120.7, 118.5, 117.6, 97.4 ppm. IR (KBr): 3683, 3149, 3053, 2923, 1913,

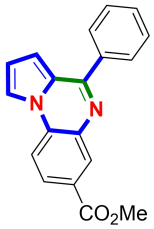
1720, 1581, 1537, 1460, 1407, 1342, 1128, 817, 752, 702 cm^{-1}. HRMS (ESI) m/z: calculated for $C_{20}H_{12}N_3$ $[M+H]^+$ 330.0793, found 330.0789.



3la

4-Phenylpyrrolo[1,2-a]quinoxaline (3la)

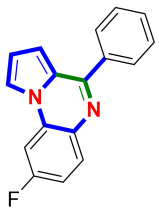
Gray white solid (90%, 22.0 mg). According to the **GP**, the product **3la** is obtained by filtration and washing with water. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.9, 1.6 Hz, 1H), 8.05 (dd, J = 7.5, 2.2 Hz, 3H), 7.92 (d, J = 8.1 Hz, 1H), 7.66 – 7.53 (m, 4H), 7.50 (td, J = 7.6, 1.5 Hz, 1H), 7.04 (d, J = 4.0 Hz, 1H), 6.94 (t, J = 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 138.5, 136.3, 130.3, 129.8, 128.6, 128.6, 127.5, 127.2, 125.4, 125.3, 114.6, 114.0, 113.6, 108.7.



3ma

Methyl 4-phenylpyrrolo[1,2-a]quinoxaline-7-carboxylate (3ma)

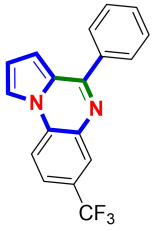
Gray white solid (85%, 25.7 mg), mp 184–185 °C. According to the **GP**, the product **3ma** is obtained by filtration and washing with water. ^1H NMR (600 MHz, $CDCl_3$) δ 8.73 (d, J = 2.0 Hz, 1H), 8.17 (dd, J = 8.5, 1.9 Hz, 1H), 8.03 – 7.97 (m, 3H), 7.89 (d, J = 8.6 Hz, 1H), 7.55 (dd, J = 5.2, 1.9 Hz, 3H), 7.04 (dd, J = 4.0, 1.3 Hz, 1H), 6.94 (dd, J = 4.0, 2.7 Hz, 1H), 3.97 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 155.2, 135.8, 132.2, 130.2, 130.1, 129.9, 128.8, 128.6, 128.3, 127.1, 125.5, 115.3, 114.9, 113.7, 109.6, 52.3 ppm. IR (KBr): 3095, 2929, 1710, 1602, 1483, 1417, 1369, 1292, 1193, 1097, 756, 721, 686 cm^{-1}. HRMS (ESI) m/z: calculated for $C_{18}H_{12}N_2O_2$ $[M+H]^+$ 303.1128, found 333.1124.



3na

8-Fluoro-4-phenylpyrrolo[1,2-a]quinoxaline (3na)

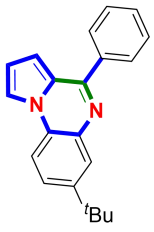
Gray white solid (88%, 23.1 mg).According to the **GP**, the product **3na** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.00 (m, 3H), 7.92 (s, 1H), 7.63 – 7.56 (m, 4H), 7.23 (t, J = 8.6 Hz, 1H), 7.05 (d, J = 4.2 Hz, 1H), 6.97 (t, J = 3.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, J = 246.6 Hz), 153.6, 138.2, 132.9, 132.0 (d, J = 9.6 Hz), 129.9, 128.6, 128.6, 127.8 (d, J = 11.5 Hz), 125.1, 114.8, 114.5, 113.2 (d, J = 22.9 Hz), 108.9, 100.5 (d, J = 26.8 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ –110.86 ppm.



3oa

4-Phenyl-7-(trifluoromethyl)pyrrolo[1,2-a]quinoxaline (3oa)

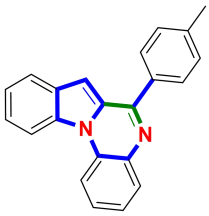
Gray white solid (84%, 26.2 mg). According to the **GP**, the product **3oa** is obtained by filtration and washing with water and ^{i}PrOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.11 – 7.98 (m, 4H), 7.79 (d, J = 8.5 Hz, 1H), 7.66 – 7.56 (m, 3H), 7.12 (d, J = 4.1 Hz, 1H), 7.04 – 6.98 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 137.9, 136.0, 130.2, 129.2, 128.7, 128.6, 127.7–127.8 (m), 127.2, 125.5, 123.8 (d, J = 3.4 Hz), 122.6, 115.3, 114.9, 114.3, 109.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ –203.27 ppm.



3pa

7-(*tert*-Butyl)-4-phenylpyrrolo[1,2-*a*]quinoxaline (3pa)

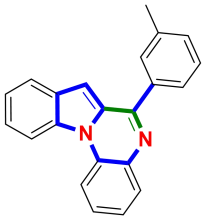
Gray white solid (80%, 24.0 mg), mp 166–167 °C. According to the **GP**, the product **3pa** is obtained by filtration and washing with water and ^{i}PrOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.04 (d, J = 6.7 Hz, 2H), 8.00 (s, 1H), 7.84 (dd, J = 8.7, 2.6 Hz, 1H), 7.65 – 7.55 (m, 4H), 7.01 (d, J = 4.1 Hz, 1H), 6.91 (d, J = 3.5 Hz, 1H), 1.47 (d, J = 2.7 Hz, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 148.6, 138.7, 136.8, 129.7, 129.0, 128.6, 126.7, 125.4, 125.2, 124.9, 114.4, 113.8, 113.3, 108.5, 34.8, 31.5 ppm. IR (KBr): 2960, 2869, 1583, 1483, 1446, 1415, 1365, 1271, 808, 713, 698 cm^{-1}. HRMS (ESI) m/z: calculated for $C_{21}H_{21}N_2$ $[M+H]^+$ 301.1699, found 301.1696.



3ab

6-(3-Methoxyphenyl)indolo[1,2-*a*]quinoxaline (3ab)

Yellow solid (90%, 27.8 mg). According to the **GP**, the product **3ab** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dd, J = 15.3, 8.6 Hz, 2H), 8.30 (d, J = 8.1 Hz, 1H), 8.01 (t, J = 8.1 Hz, 3H), 7.78 – 7.65 (m, 2H), 7.57 (d, J = 6.0 Hz, 1H), 7.53 (d, J = 4.5 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 2.55 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 140.2, 136.4, 135.5, 133.1, 130.9, 130.5, 129.3, 129.3, 128.9, 128.6, 128.2, 124.3, 124.2, 122.8, 122.6, 114.7, 114.6, 102.5, 21.5 ppm.

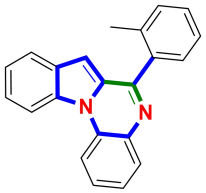


3ac

6-(2-Tolyl)indolo[1,2-*a*]quinoxaline (3ac)

Yellow solid (88%, 27.1 mg), mp 138–139 °C, According to the **GP**, the product **3ac** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.43 (m, 2H), 8.21 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 11.0 Hz, 2H), 7.76 – 7.60 (m, 2H), 7.59 – 7.41 (m, 4H), 7.39 (s, 1H), 2.57 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 138.9, 136.1, 133.9, 133.6, 131.8, 129.9, 129.4, 129.3, 129.1, 128.9, 128.7, 128.5, 127.3, 126.0, 125.5, 124.7, 123.1, 114.8, 114.6,

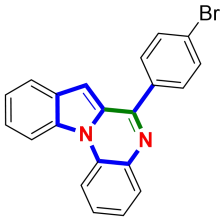
105.2, 21.5 ppm. IR (KBr): 3683, 3049, 1714, 1600, 1527, 1448, 1377, 1244, 1022, 794, 732, 626 cm^{-1}. HRMS (ESI) m/z: calculated for $C_{22}H_{17}N_2$ $[M+H]^+$ 309.1386, found 309.1382.



3ad

6-(*o*-Tolyl)indolo[1,2-*a*]quinoxaline (3ad)

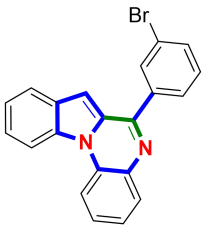
Yellow solid (80%, 24.7 mg). According to the **GP**, the product **3ad** is obtained by filtration and washing with water and ^{i}PrOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, J = 17.2, 8.5 Hz, 2H), 8.16 (d, J = 6.4 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 7.8 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.50 (dh, J = 20.8, 7.4 Hz, 5H), 6.90 (s, 1H), 2.43 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 137.3, 136.5, 136.1, 133.1, 130.9, 130.6, 130.4, 129.9, 129.3, 129.2, 128.8, 128.5, 125.8, 124.4, 124.2, 122.9, 122.7, 114.8, 114.7, 102.5, 19.7 ppm.



3ae

6-(4-Bromophenyl)indolo[1,2-*a*]quinoxaline (3ae)

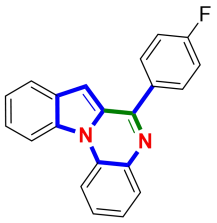
Yellow solid (88%, 32.8 mg). According to the **GP**, the product **3ae** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (t, J = 9.4 Hz, 2H), 8.11 (dd, J = 7.9, 1.5 Hz, 1H), 7.98 (t, J = 8.3 Hz, 3H), 7.76 (d, J = 8.1 Hz, 2H), 7.73 – 7.58 (m, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 137.2, 136.7, 136.2, 134.8, 133.2, 131.9, 130.6, 130.3, 129.2, 128.8, 128.7, 124.6, 124.5, 124.4, 122.9, 114.8, 114.9, 102.3 ppm.



3af

6-(3-Bromophenyl)indolo[1,2-*a*]quinoxaline (3af)

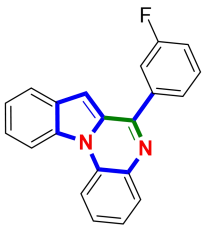
Yellow solid (80%, 29.9 mg). According to the **GP**, the product **3af** is obtained by filtration and washing with water and ^{i}PrOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, J = 11.3, 8.5 Hz, 2H), 8.22 (d, J = 2.0 Hz, 1H), 8.12 (dd, J = 7.9, 1.6 Hz, 1H), 8.00 (t, J = 8.1 Hz, 2H), 7.75 (dd, J = 8.1, 2.1 Hz, 1H), 7.72 – 7.57 (m, 2H), 7.50 (td, J = 8.0, 2.0 Hz, 3H), 7.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 140.1, 136.0, 133.1, 133.1, 131.6, 130.6, 130.2, 129.8, 129.2, 128.8, 128.7, 127.3, 126.5, 124.7, 124.4, 122.9, 122.9, 114.7, 114.6, 102.4 ppm.



3ag

6-(4-Fluorophenyl)indolo[1,2-*a*]quinoxaline (3ag)

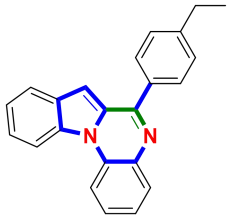
Yellow solid (82%, 27.8 mg). According to the **GP**, the product **3ag** is obtained by filtration and washing with water and ^{i}PrOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, J = 12.2, 8.5 Hz, 2H), 8.18 (d, J = 8.0 Hz, 1H), 8.10 (dd, J = 8.5, 5.4 Hz, 2H), 8.00 (d, J = 8.1 Hz, 1H), 7.67 (dt, J = 19.7, 7.6 Hz, 2H), 7.52 (td, J = 7.6, 2.8 Hz, 2H), 7.39 – 7.30 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9 (d, J = 248.9 Hz), 155.0, 135.8, 134.0, 133.2, 130.7, 130.6, 130.3, 130.1, 129.2, 128.8, 128.6, 124.7, 124.4, 122.8, 115.8 (d, J = 21.5 Hz), 114.7 (d, J = 8.6 Hz), 113.7, 102.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ –76.11 ppm.



3ah

6-(3-Fluorophenyl)indolo[1,2-*a*]quinoxaline (3ah)

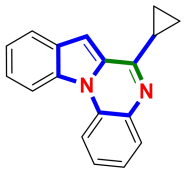
Yellow solid (84%, 26.2 mg). According to the **GP**, the product **3ah** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, J = 11.2, 8.5 Hz, 2H), 8.12 (dd, J = 7.9, 1.6 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.80 (dt, J = 9.6, 2.1 Hz, 1H), 7.73 – 7.64 (m, 1H), 7.66 – 7.55 (m, 2H), 7.50 (ddd, J = 8.7, 7.3, 2.1 Hz, 2H), 7.37 – 7.28 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, J = 245.1 Hz), 154.8, 140.3 (d, J = 7.5 Hz), 136.1, 133.1, 130.6, 130.3 (d, J = 8.2 Hz), 130.2, 129.2, 128.7, 128.7, 124.6, 124.4, 124.4, 124.3, 122.9 (d, J = 4.0 Hz), 116.9 (d, J = 21.1 Hz), 115.8 (d, J = 22.6 Hz), 114.7, 114.6, 102.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ –112.24 ppm.



3ai

6-(4-Ethylphenyl)indolo[1,2-*a*]quinoxaline (3ai)

Yellow solid (90%, 29.0 mg). PE/EA = 30:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (t, J = 8.6 Hz, 2H), 8.13 (d, J = 7.9 Hz, 1H), 7.99 (dd, J = 17.1, 7.9 Hz, 3H), 7.62 (dt, J = 20.3, 7.9 Hz, 2H), 7.53 – 7.43 (m, 4H), 7.32 (s, 1H), 2.84 (q, J = 7.6 Hz, 2H), 1.39 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 146.5, 136.4, 135.8, 133.1, 130.5, 130.2, 129.2, 129.2, 128.7, 128.2, 128.2, 124.3, 124.2, 122.8, 122.6, 114.6, 114.6, 102.5, 28.9, 15.6 ppm.

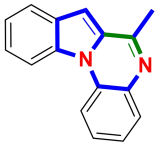


3aj

6-Cyclopropylindolo[1,2-a]quinoxaline (3aj)

Yellow solid (50%,13.0 mg). According to the **GP**, the crude product was purified by flash column chromatography, PE/EA = 30:1, R_f = 0.28. mp 154–155°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 8.5 Hz, 2H), 8.03 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.38 (s, 1H), 2.57 (tt, J = 8.3, 4.7 Hz, 1H), 1.45 (dt, J = 6.6, 3.4 Hz, 2H), 1.19 (dd, J = 8.0, 3.1 Hz,

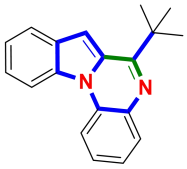
2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 136.1, 132.9, 130.4, 130.1, 129.6, 129.2, 127.1, 124.0, 123.9, 122.6, 122.5, 114.6, 114.6, 99.3, 14.3, 9.2 ppm. IR (KBr): 3685, 3095, 2947, 2929, 1712, 1527, 1409, 1265, 1205, 1076, 1029, 806 cm^{-1}. HRMS (ESI) m/z: calculated for $C_{18}H_{15}N_2$ $[M+H]^+$ 259.1230, found 259.1227.



3ak

6-Methylindolo[1,2-*a*]quinoxaline (3ak)

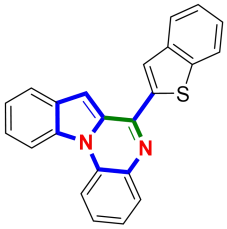
Yellow solid (90%, 20.9 mg). According to the **GP**, the product **3ak** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (t, J = 8.6 Hz, 2H), 8.00 (dd, J = 7.9, 2.1 Hz, 2H), 7.67 – 7.55 (m, 2H), 7.48 (q, J = 7.8 Hz, 2H), 7.21 (s, 1H), 2.86 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 135.8, 132.97, 130.3, 129.8, 129.6, 129.1, 127.8, 124.3, 124.1, 122.7, 122.6, 114.6, 114.6, 100.1, 22.4 ppm.



3al

6-(*tert*-Butyl)indolo[1,2-a]quinoxaline (3al)

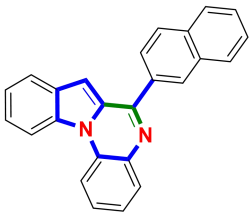
Pale yellow solid (68%, 18.7 mg),mp 126–127°C. According to the **GP**, the crude product **3al** was purified by flash column chromatography. PE/EA = 40:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (tt, J = 7.8, 3.0 Hz, 2H), 8.06 (d, J = 10.6, 6.7, 2.4 Hz, 2H), 7.71 – 7.56 (m, 2H), 7.56 – 7.42 (m, 3H), 1.75 (d, J = 3.6 Hz, 9H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 135.5, 131.9, 130.4, 130.0, 128.8, 127.9, 127.4, 123.9 123.8, 122.5, 122.5, 114.6, 114.4, 102.0, 39.7, 29.5 ppm. IR (KBr): 3679, 3132, 3053, 2958, 1722, 1448, 1357, 1058, 800, 742 cm^{-1}. HRMS (ESI) m/z calculated for $C_{19}H_{19}N_2$ $[M+H]^+$ 275.1543, found 275.1538.



3am

6-(Benzo[*b*]thiophen-2-yl)indolo[1,2-*a*]quinoxaline (3am)

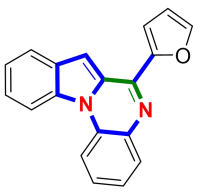
Yellow solid (92%, 32.2 mg). According to the **GP**, the product **3am** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, J = 8.5, 5.9 Hz, 2H), 8.28 (s, 1H), 8.09 (dd, J = 8.0, 1.6 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.97 (ddd, J = 9.1, 5.9, 3.4 Hz, 2H), 7.68 – 7.54 (m, 3H), 7.52 – 7.43 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 142.4, 140.7, 140.1, 135.7, 132.9, 130.5, 130.0, 129.3, 128.7, 127.7, 125.8, 125.4, 124.7, 124.6, 124.5, 124.3, 122.9, 122.8, 122.4, 121.1, 114.6, 101.5 ppm.



3an

6-(Naphthalen-1-yl)indolo[1,2-*a*]quinoxaline (3an)

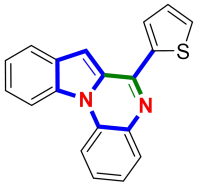
Yellow solid (88%, 30.3 mg). According to the **GP**, the product **3an** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 – 8.52 (m, 3H), 8.23 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 8.12 – 8.03 (m, 2H), 7.99 (dd, J = 8.3, 4.6 Hz, 2H), 7.70 (t, J = 7.8 Hz, 1H), 7.69 – 7.58 (m, 3H), 7.52 (q, J = 7.4 Hz, 2H), 7.43 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 136.1, 135.8, 134.9, 134.4, 133.4, 133.1, 130.1, 129.7, 129.4, 128.9, 128.9, 128.8, 128.6, 127.9, 127.4, 126.7, 125.8, 125.2, 124.6, 123.1, 123.0, 114.8, 114.7, 104.3 ppm.



3ao

7-(Furan-2-yl)indolo[1,2-*a*]quinoxaline (3ao)

Yellow solid (90%, 25.6 mg). According to the **GP**, the product **3ao** is obtained by filtration and washing with water. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 – 8.47 (m, 2H), 8.05 (dd, J = 7.9, 1.5 Hz, 1H), 8.01 (dd, J = 8.0, 1.2 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.58 (dddd, J = 18.2, 8.5, 7.1, 1.4 Hz, 2H), 7.48 (d, J = 3.4 Hz, 1H), 7.49 – 7.41 (m, 2H), 6.68 (dd, J = 3.5, 1.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 144.9, 144.7, 135.8, 132.8, 130.3, 130.1, 129.5, 128.3, 126.9, 124.4, 124.2, 122.9, 122.8, 114.7, 114.6, 113.3, 112.1, 102.1 ppm.



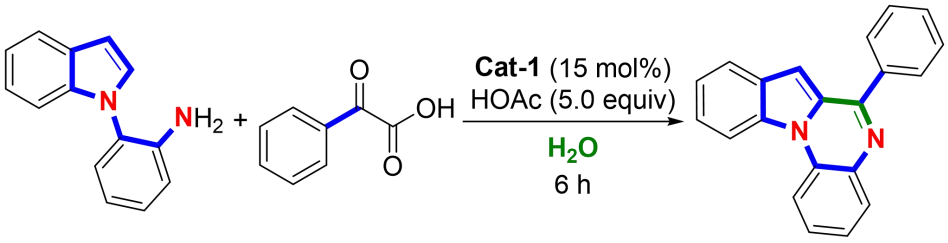
3ap

6-(Thiophen-2-yl)indolo[1,2-*a*]quinoxaline (3ap)

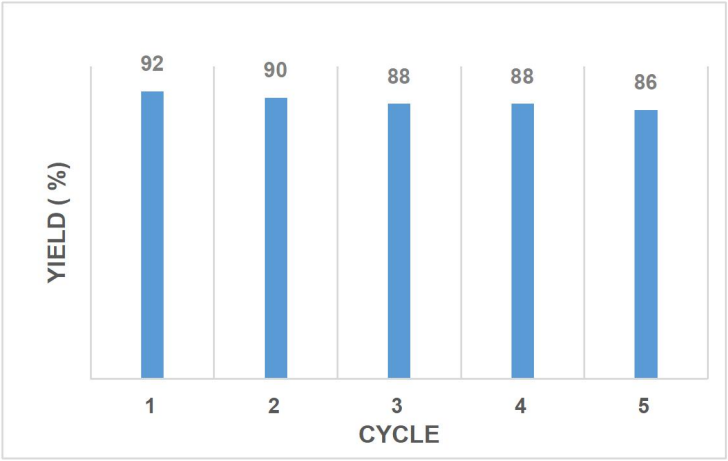
Yellow solid (92%, 27.6 mg), mp 146–147°C. According to the **GP**, the product **3ap** is obtained by filtration and washing with water. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (t, J = 7.5 Hz, 2H), 8.10 – 8.03 (m, 2H), 7.99 (d, J = 8.0 Hz, 1H), 7.60 (td, J = 13.4, 12.7, 6.3 Hz, 4H), 7.47 (q, J = 6.9 Hz, 2H), 7.30 (q, J = 3.7, 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 142.0, 135.8, 132.9, 132.2, 130.9, 130.2, 129.9, 129.3, 128.9, 128.6, 128.3, 127.9, 127.8, 124.5, 124.2, 122.8, 114.6, 101.7 ppm. IR (KBr): 3051, 2916, 1600, 1515, 1429, 1365, 1203, 1116, 1051, 842, 744, 713 cm^{-1}. HRMS (ESI) m/z calculated for $C_{19}H_{13}N_2S$ $[M+H]^+$ 301.0794, found 301.0785.

4. Catalyst Recovery

The feasibility of recycling the catalyst system was studied under the optimized reaction condition according to **GP**. To a pressure tube was charged with **Cat-1** (15 mol%), 2-(1*H*-indol-1-yl)anilines **1a** (1 mmol), phenylglyoxylic acid **2a** (1.2 mmol), HOAc (5 eq) and H_2O (3.0 mL). The reaction mixture was stirred at room temperature for 6 h under Air. After completion of the reaction, the target product was obtained by filtration and washed by ^{i}PrOH. The remains were further subjected to the subsequent reactions. The following reactions can conduct smoothly and need to add nothing but new substrates, affording the pure product **3aa** (27 mg, 92%), (26 mg, 90%), (26 mg, 88%), (26 mg, 88%), and (25 mg, 86%) in five cycles, respectively.

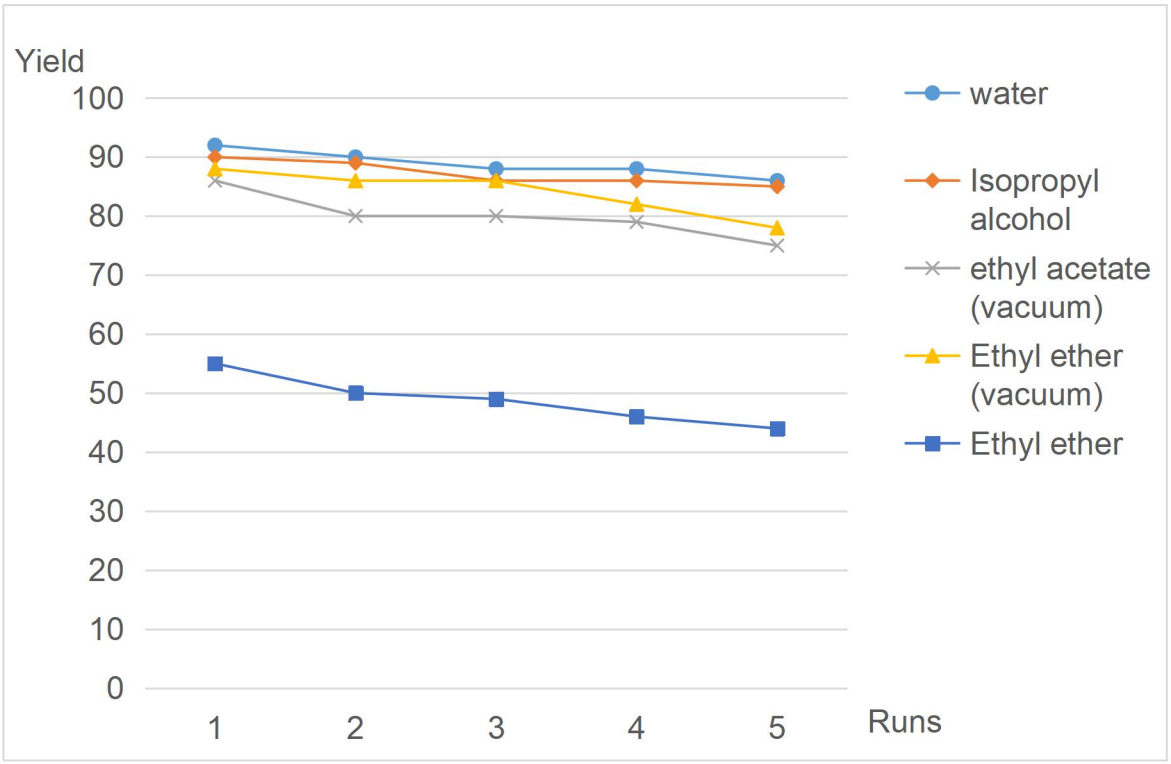


1a **2a** **3aa**

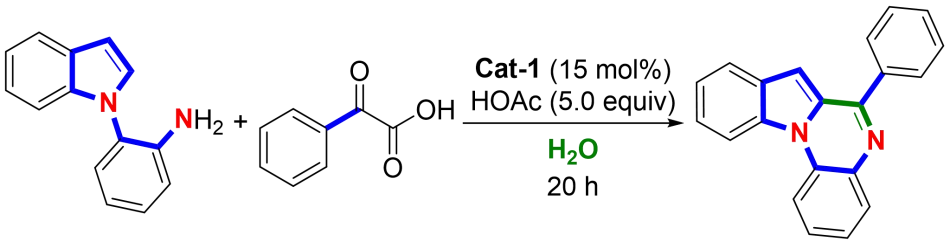


The product was separated ether by filtration or by extraction owing to the different solubility of the product and catalyst by using different solvent. In this respect, the impact of reaction solvents and extraction solvents on recycling were tested. On one hand, the reaction solvents were tested. After completion of the reaction, the product was facile separated by filtration with the filtrate reused directly when H_2O or *i*PrOH was used as solvent. A comparable results were obtained when H_2O or *i*PrOH was used as solvent. On the other hand, the extraction solvents (ethyl ether and ethyl acetate) were tested when H_2O was used as reaction solvent, the product was simply separated by extraction and the remains reused in subsequent reactions. The results showed ethyl ether is the better solvent.

The purity of the ILs was also investigated by using ethyl ether as extraction solvent. After the extraction, the control experiments were set for the remains used directly and subjected to vacuum to remove the rest of solvents. The data showed the remains subjected to vacuum gave the better yields on recycling. It means the higher purity of the ILs, the better results were obtained on recycling.



5. Large-Scale Transformation and Synthetic Utility

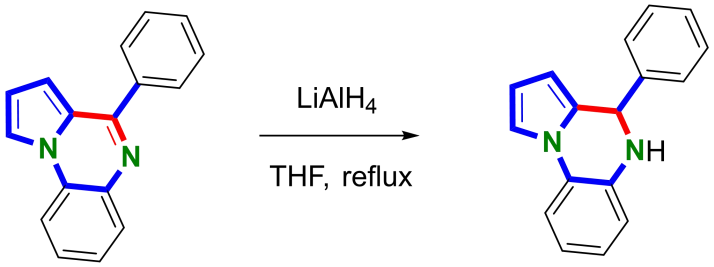


1a
3 mmol

2a
1.2 equiv

3aa
yield: 81%

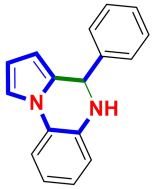
A pressure tube was charged with **Cat-1** (15 mol%), 2-(1*H*-indol-1-yl)aniline **1a** (3 mmol), phenylglyoxylic acid **2a** (3.6 mmol), HOAc (5 eq) and H_2O (3.0 mL). The reaction mixture was stirred at room tempture for 20 h under air. After completion of the reaction, the target product **3aa** was obtained by solid filtration and washing with H_2O.



3la

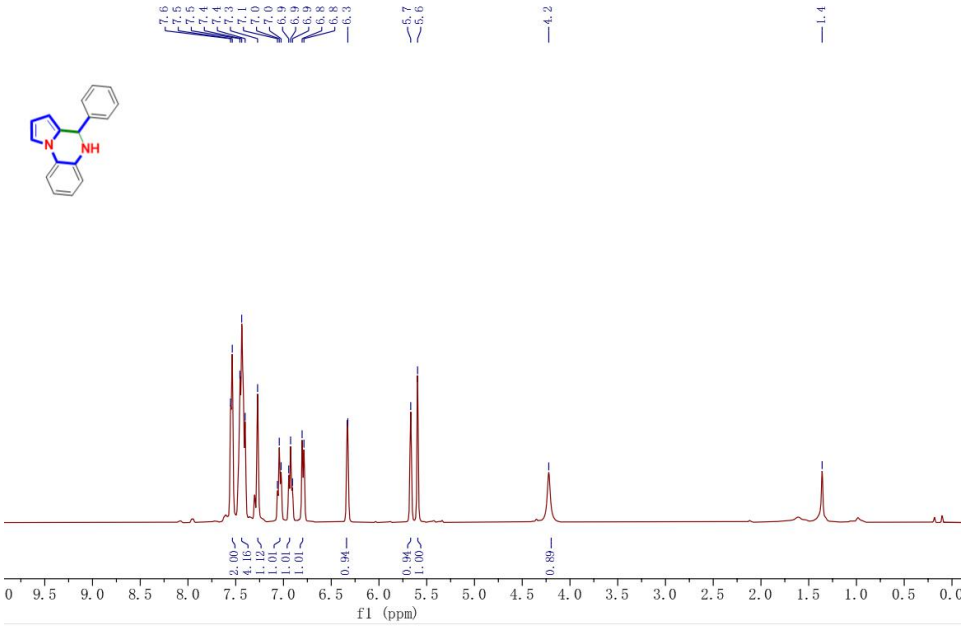
3la'

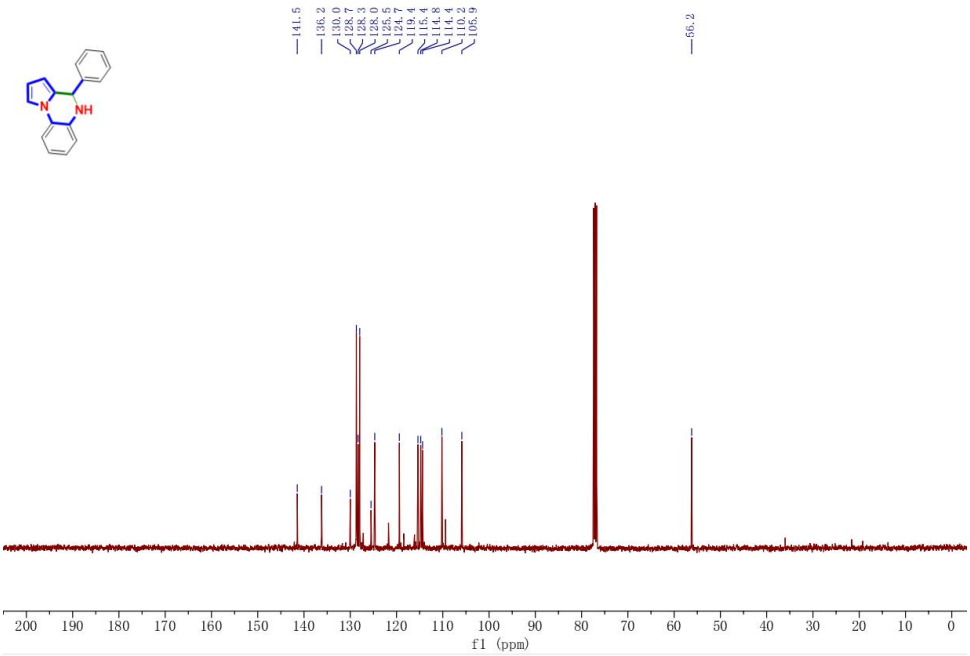
To a stirred solution of 4-phenylpyrrolo[1,2-a]quinoxaline **3la** (0.1 mmol) in anhydrous THF (1 mL), $LiAlH_4$ (0.4 mmol) was added portion wise. The reaction was refluxed with stirring for 17 h under Ar condition. After cooling to room temperature, the reaction was quenched with ethyl acetate and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to afford the product **3la'** in 50% yield.

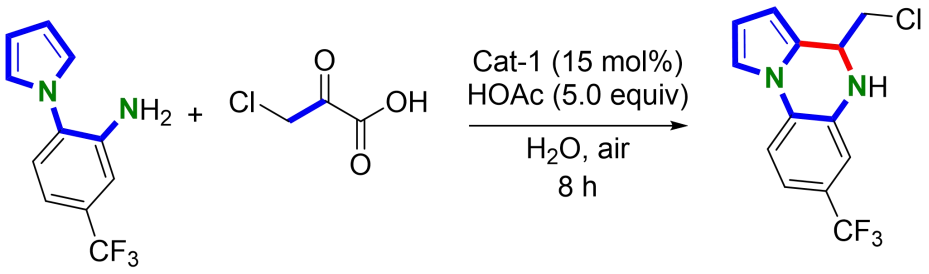


(*R*)-4-Phenyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline 3la'

Pale white solid (50%, 12.0 mg). According to the **GP**, the crude product was purified by flash column chromatography. PE/EA = 30:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.48 – 7.37 (m, 4H), 7.28 – 7.23 (m, 1H), 7.03 (td, J = 7.6, 1.3 Hz, 1H), 6.92 (td, J = 7.0, 6.3, 1.9 Hz, 1H), 6.80 (dd, J = 8.0, 1.3 Hz, 1H), 6.31 (t, J = 3.2 Hz, 1H), 5.65 (d, J = 3.4 Hz, 1H), 5.60 (s, 1H), 4.23 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 136.2, 129.9, 128.7, 128.3, 127.9, 125.5, 124.7, 119.4, 115.4, 114.8, 114.4, 110.2, 105.9, 56.2 ppm.





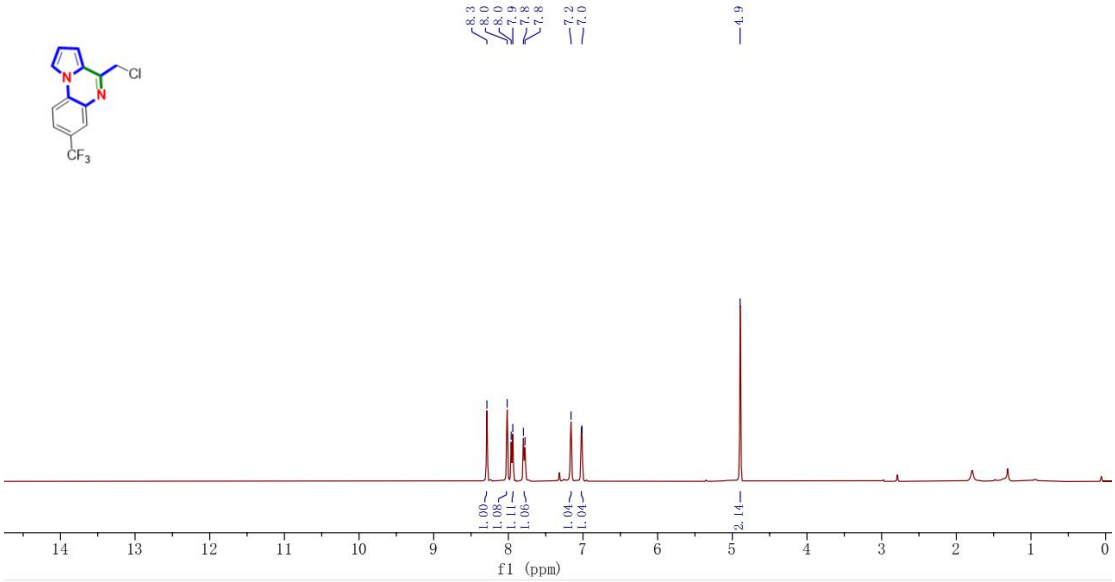


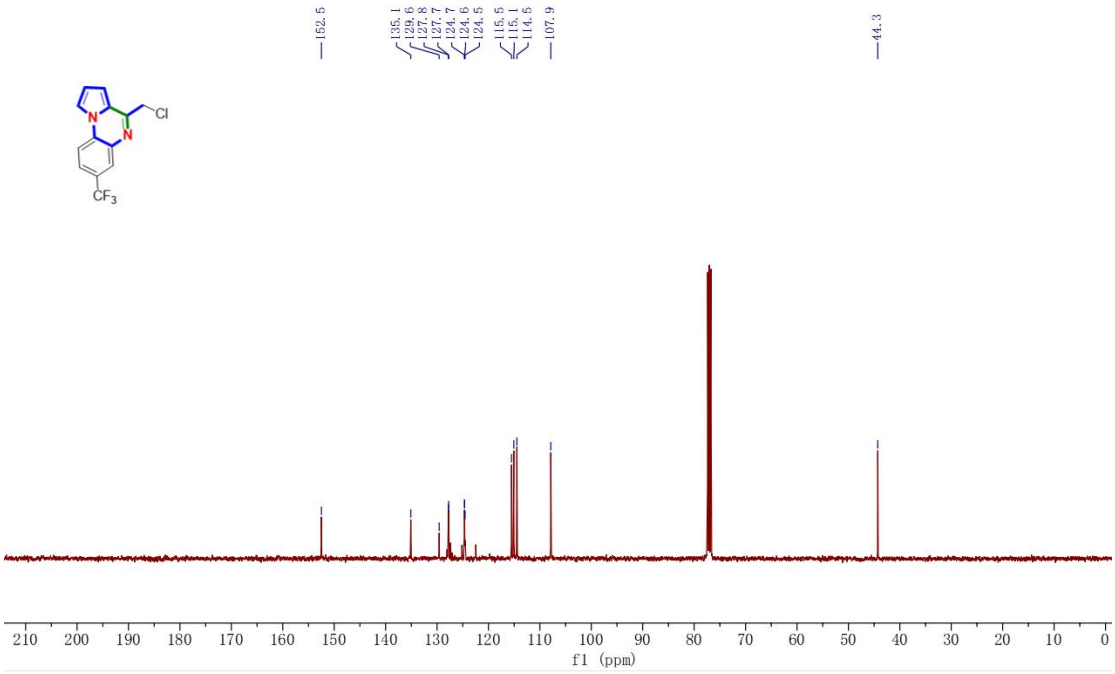
1o **2q** **3oq**

A pressure tube was charged with **Cat-1** (15 mol%), 2-(1H-pyrrol-1-yl)aniline **1o** (0.1 mmol), 2-chloroacetaldehyde (0.12 mmol), HOAc (5 eq) and H_2O (1 mL). The reaction mixture was stirred at room tempture for 8 h under Air. The product was then extracted with ethyl acetate (10 mL × 3 times). The organic layers were combined, washed with water (10 mL × 3 times) and brine solution (10 mL). Finally, the organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure to dryness. The residue was purified by silica gel chromatography to afford the product **3oq** in 80% yield.

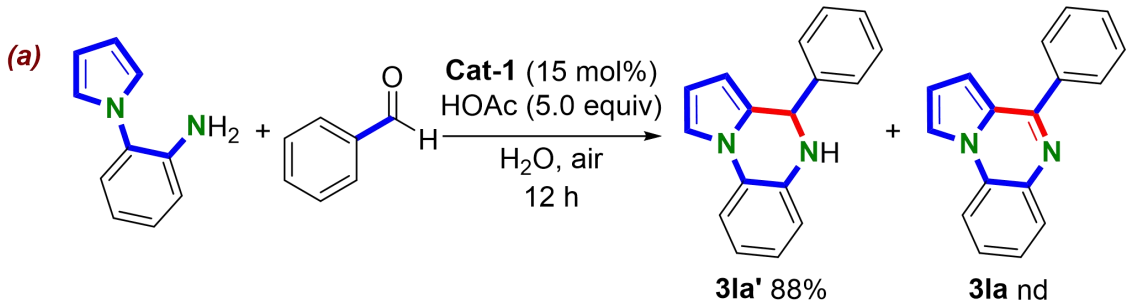
3-(Chloromethyl)-7-(trifluoromethyl)pyrrolo[1,2-*a*]quinoxaline (3oq)

Pale white solid (80%, 23.2 mg). PE/EA = 30:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.02 (s, 1H), 7.95 (d, J = 8.7 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.16 (s, 1H), 7.01 (s, 1H), 4.90 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 135.1, 129.6, 127.8, 127.7, 124.7, 124.6, 124.5, 115.5, 115.1, 114.5, 107.9, 44.3 ppm.

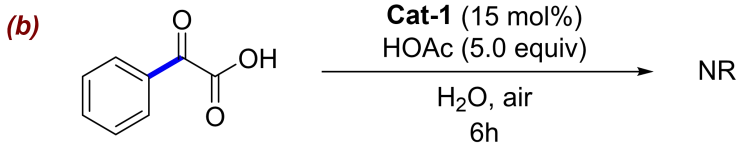

8.3
8.0
8.0
7.9
7.8
7.8
7.2
7.0
4.9
Cl
N
N
CF3
1.00
1.08
1.11
1.06
1.04
1.04
2.14
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


152.5
135.1
129.6
127.8
127.7
124.7
124.6
124.5
115.5
115.1
114.5
107.9
44.3
Cl
N
N
CF3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

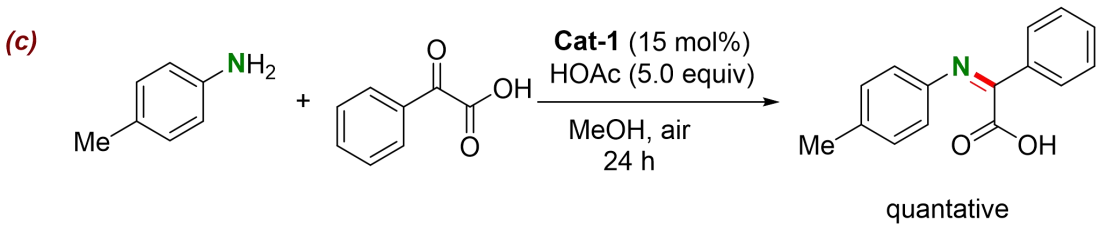
6. Mechanistic Studies



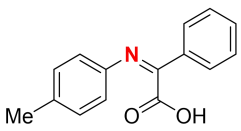
According to the **GP**, 2-(1*H*-pyrrol-1-yl)aniline (0.1 mmol) and benzaldehyde (0.12 mmol) was employed under standard reaction conditions. However, the dihydroquinoxaline **3la'** was obtained in 88% yield rather than quinoxaline **3la**.



Phenylglyoxylic acid (0.1 mmol) was subjected to the reaction, no conversion was observed under standard conditions.

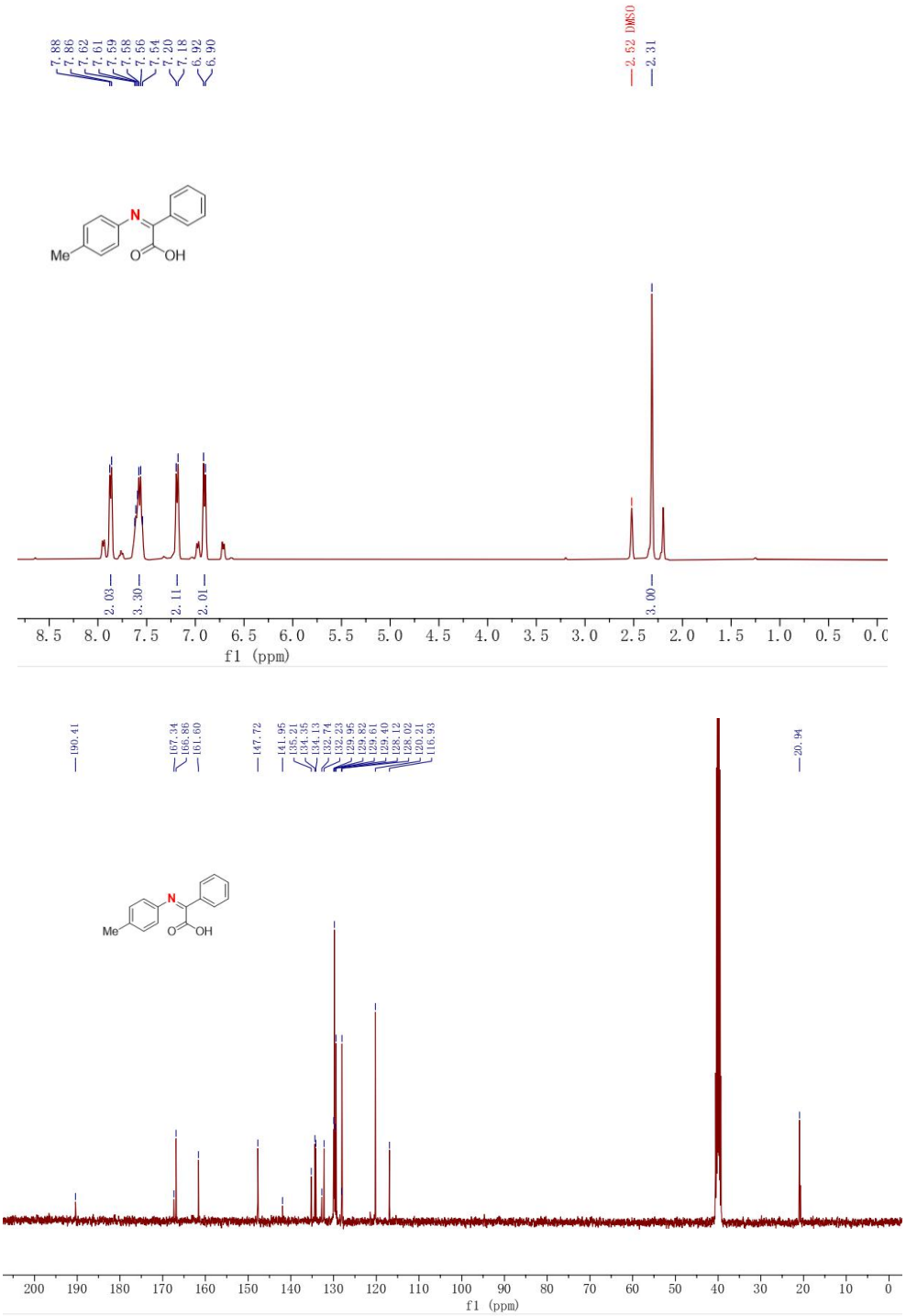


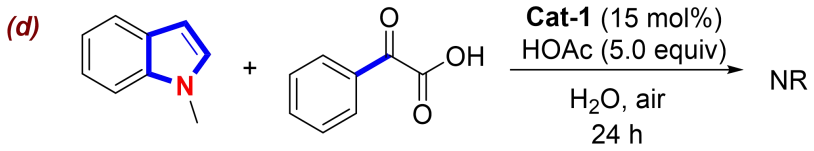
A pressure tube was charged with **Cat-1** (15 mol%), *p*-toluidine (0.1 mmol), phenylglyoxylic acid (0.12 mmol), HOAc (5 eq) and MeOH (1 mL). The reaction mixture was stirred at room temperature for 24 h under Air. After completion of the reaction, a large amount of solid was precipitated, filtered and washed with methanol to obtain imine acid in quantitative yield.



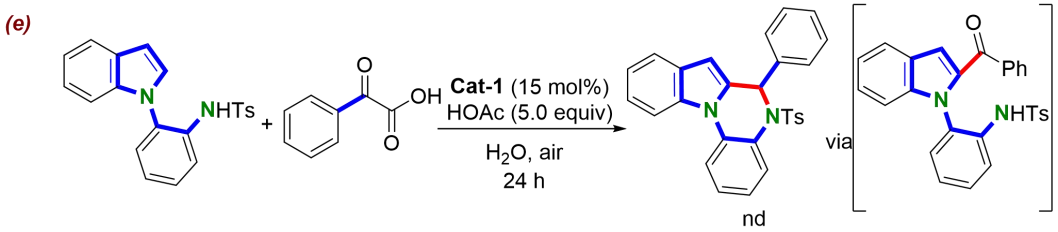
(*Z*)-2-Phenyl-2-(*p*-tolylimino)acetic acid

White solid (100%, 24 mg). According to the **GP**, the product **3aa** is obtained by filtration and washing with CH_2Cl_2. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (d, J = 7.3 Hz, 2H), 7.59 (dt, J = 15.0, 7.2 Hz, 3H), 7.20 (d, J = 7.8 Hz, 2H), 6.92 (d, J = 7.7 Hz, 2H), 2.33 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ 166.9, 161.6, 147.7, 134.4, 132.2, 129.8, 129.4, 128.0, 120.2, 116.9, 20.9 ppm.

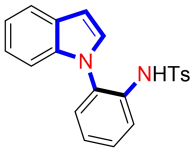




According to the **GP**, 1-methyl-1*H*-indole (0.1 mmol) and phenylglyoxylic acid (0.12 mmol) was employed under standard reaction conditions, no conversion was observed under standard conditions.

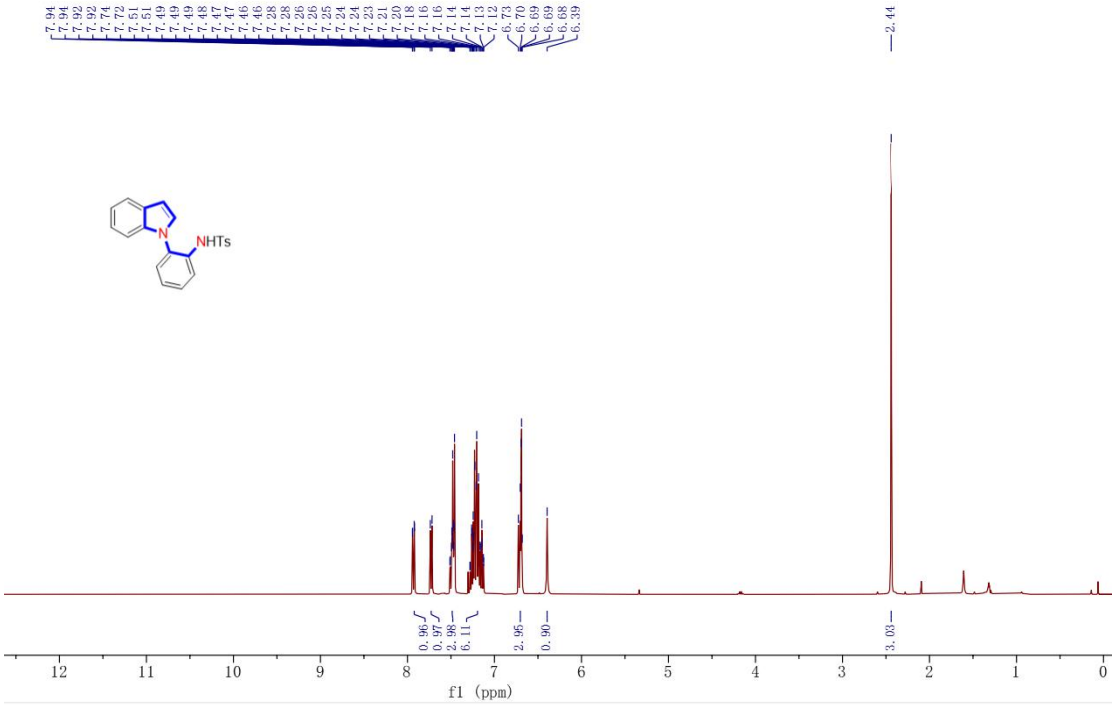


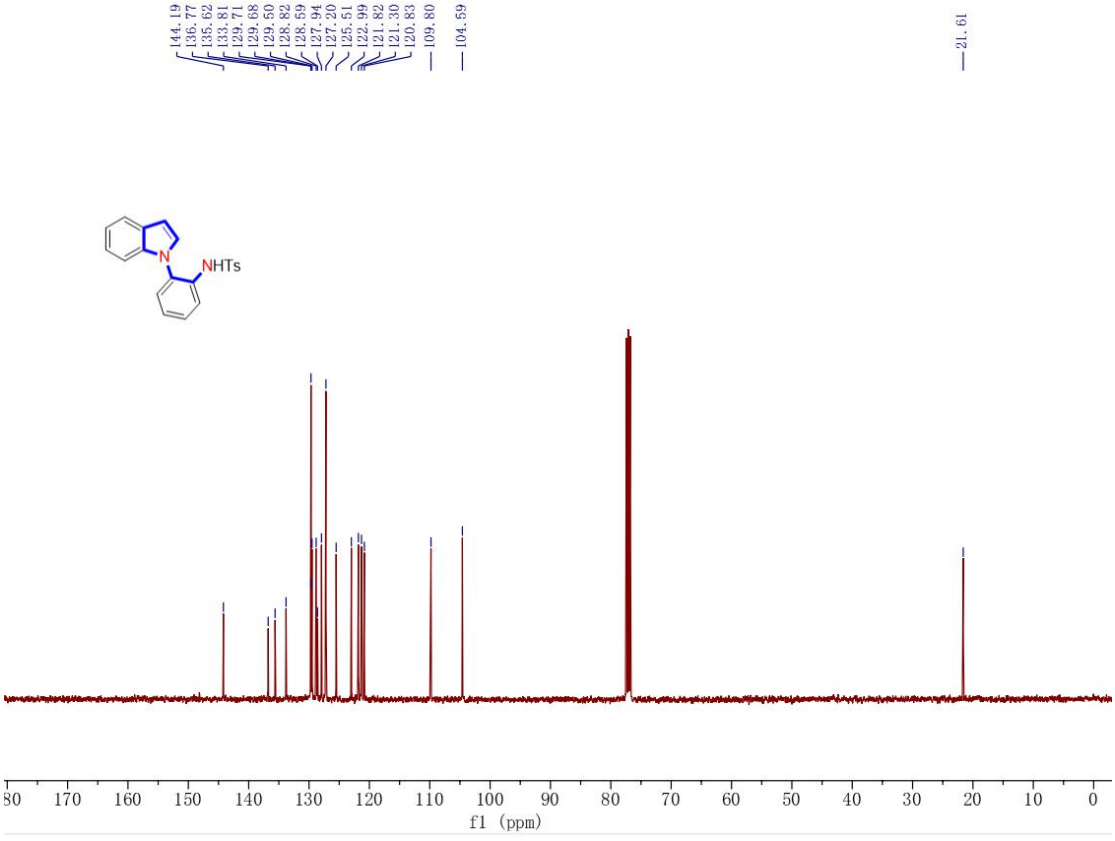
According to the **GP**, *N*-(2-(1*H*-indol-1-yl)phenyl)-4-methylbenzenesulfonamide (0.12 mmol) was employed under standard reaction conditions. However, no desired cyclic product was observed, which exclude the reaction underwent acetylated process.



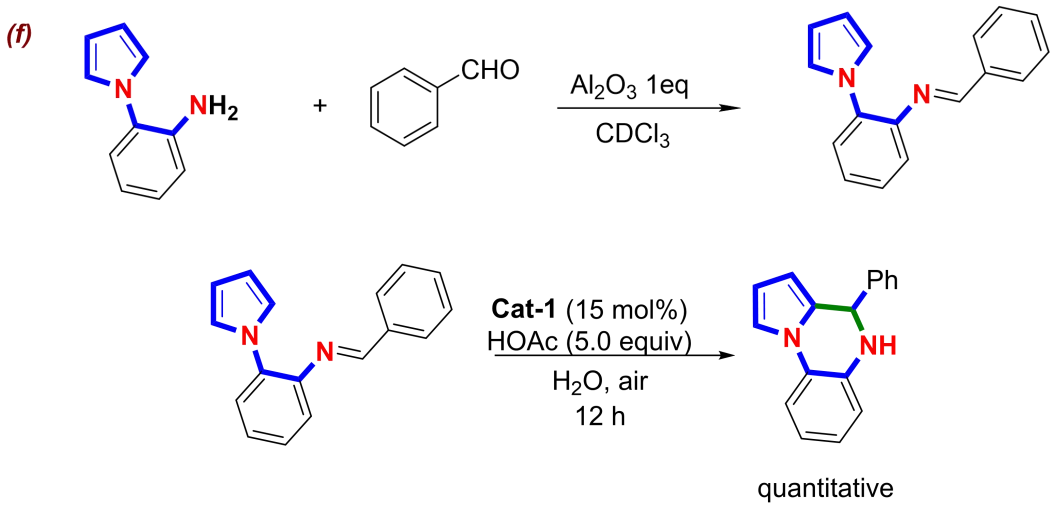
***N*-(2-(1*H*-indol-1-yl)phenyl)-4-methylbenzenesulfonamide**

Pale white solid (70 % 25 mg). According to the **GP**, the crude product was purified by flash column chromatography. PE/EA = 40:1, R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.3, 1.3 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.33 – 7.17 (m, 5H), 7.14 (td, J = 7.6, 7.0, 1.2 Hz, 1H), 6.75 – 6.66 (m, 3H), 6.39 (s, 1H), 2.44 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.19, 136.77, 135.62, 133.81, 129.71, 129.68, 129.50, 128.82, 128.59, 127.94, 127.20, 125.51, 122.99, 121.82, 121.30, 120.83, 109.80, 104.59, 21.61 ppm.


7.94
7.94
7.92
7.92
7.74
7.72
7.51
7.51
7.49
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.28
7.28
7.26
7.26
7.25
7.24
7.24
7.23
7.21
7.20
7.18
7.16
7.14
7.14
7.13
7.12
6.73
6.70
6.69
6.69
6.68
6.68
6.39
2.44
NHTs
0.96
0.97
2.98
6.11
2.95
0.90
3.03
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

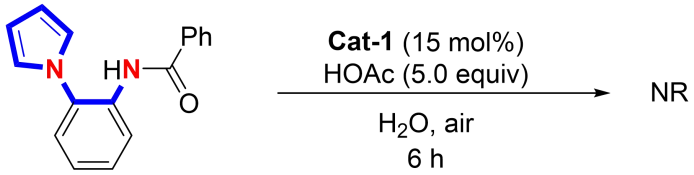

144.19
136.77
135.62
133.81
129.71
129.68
129.50
128.82
128.59
127.94
127.20
125.51
122.99
121.82
121.30
120.83
109.80
104.59
21.61
NHTs
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(f)

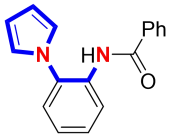


A pressure tube was charged with 2-(1*H*-pyrrol-1-yl)aniline (0.1 mmol), benzaldehyde (0.12 mmol), Al_2O_3 (1 eq) and $CDCl_3$ (0.3 mL). The reaction mixture was stirred at room temperature for 18 h under Ar condition. The product formation was detected by ^{1}H NMR, the reaction mixture was then evaporated. Afterwards, **Cat-1** (15 mol%), HOAc (5 eq) and H_2O (1 mL) were added to the reaction mixture and stirred for 12 h in the air, dihydroquinoxaline was generated in quantitative yield.

(g)



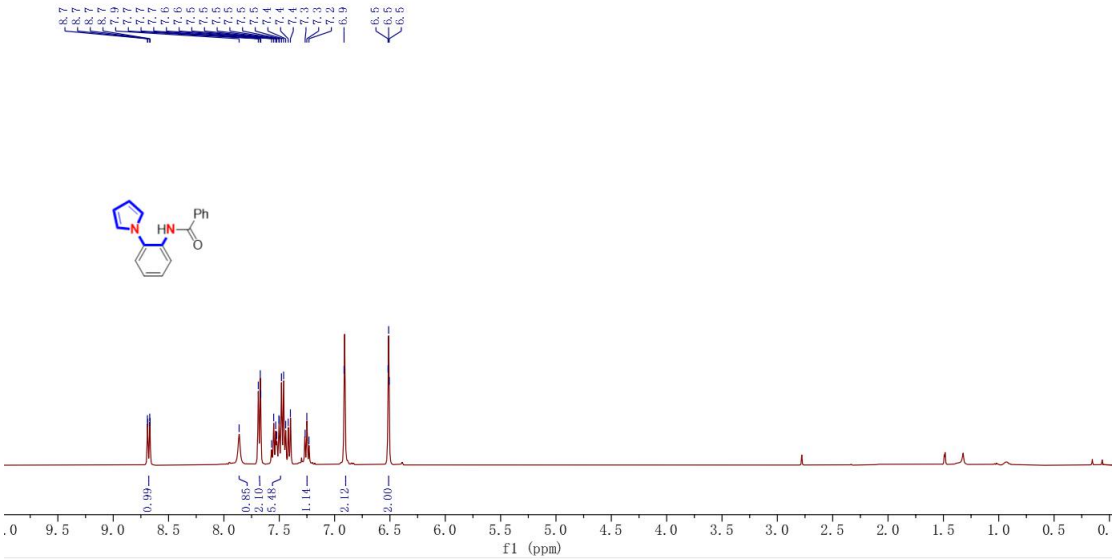
N-(2-(2,3-Dihydro-1*H*-pyrrol-1-yl)phenyl)benzamide **B** was subjected to the reaction under standard conditions, however, no reaction occurred.

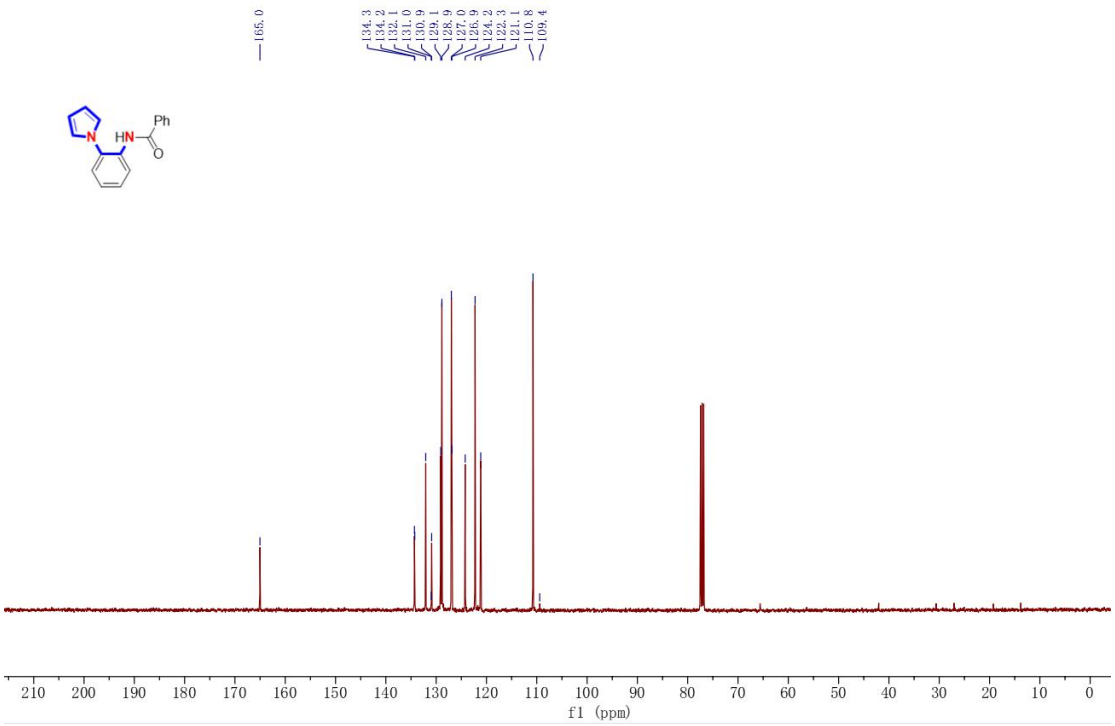


***N*-(2-(1H-pyrrol-1-yl)phenyl)benzamide**

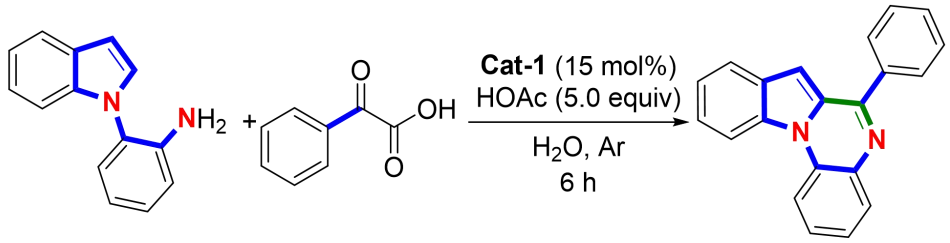
Pale white solid (70 %, 25 mg). According to the **GP**, the crude product was purified by flash column chromatography. PE/EA = 40:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.86 (s, 1H), 7.71 – 7.64 (m, 2H), 7.54 (q, *J* = 6.3, 5.3 Hz, 1H), 7.47 (q, *J* = 8.4, 7.6 Hz, 3H), 7.41 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.25 (td, *J* = 7.7, 1.5 Hz, 1H), 6.91 (t, *J* = 2.1 Hz, 2H), 6.51 (t, *J* = 2.1 Hz, 2H) ppm. ^{13}C NMR (101 MHz,

$CDCl_3$) δ 165.0, 134.3, 134.3, 132.1, 130.9, 130.9, 129.1, 128.9, 126.9, 126.8, 124.2, 122.3, 121.1, 110.75, 109.4 ppm.





(g)



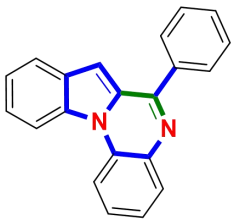
A pressure tube was charged with **Cat-1** (15 mol%), 2-(1*H*-pyrrol-1-yl)aniline **1a** (0.1 mmol), phenylglyoxylic acid **2a** (0.12 mmol), HOAc (5 eq) and H_2O (1 mL)， The reaction mixture was stirred at room tempture for 12 h under Ar, affording **1aa** in 90 % yield.

7. Comparison of Representative Reported Methods with This Work

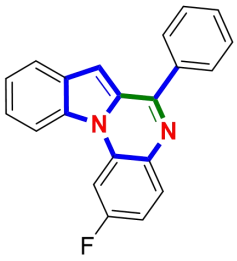
Green metrics of the target compounds 3aa, 3ga, 3ha, 3ah.

Quantitative green metrics of the products **3aa**, **3ga**, **3ha**, **3ah**, including atom economy (AE), E-factor, carbon efficiency (CE), reaction mass efficiency (RME), mass intensity (MI), and mass productivity (MP), were calculated in the present protocol and representative references.

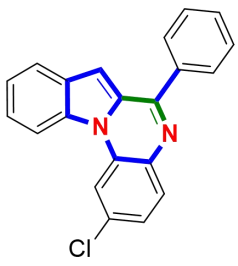
Entry	Year	Group	Solvent	Catalyst/Reagen	Temp (°C)	Time (h)	Yield (%)	Purification	E-factor
1	2015	Nath[3]	EtOH	p-DBSA(10 %), $KMnO_4$(1eq)	25	0.5	40–75	Chromatography	6.9–17.6
2	2016	Ma[4]	DMSO	TsOH·H_2O(0.25eq)	120	12	96–34	Chromatography	13.2–48.9
3	2017	Ma[5]	DCE/H_2O	$(NH4)_2S_2O_8$ (0.9eq)	80	10	33–95	Chromatography	37.9–172.4
4	2017	Jiang[6]	-	O_2	160	12	53–93	Chromatography	46.1–64.9
5	2020	Ma[7]	DMSO	KI(0.5eq)	120	8	40–88	Chromatography	21.0–57.7
6	2020	Huang[8]	*t*AmOH	$[Ru(p\text{-}cymene)Cl_2]_2$ (2.5mol%), $AgNTf_2$ (20 mol%)	100	12	44–92	Chromatography	32.7–57.3
7	2020	Jung[9]	DCE	TBHP(4eq)	80	12	38–84	Chromatography	72.0–166.2
8	2021	Ma[2]	^{i}PrOH	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ (5 mol%)	120	15	15–93	Chromatography	18.4–121.5
9	2021	Ji[10]	toluene/1, 4-dioxane	$Pd(dba)_2$(10 mol%), $AgSbF_6$ (25 mol%)	130	24	38–85	Chromatography	42.1–75.5



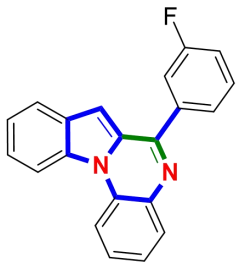
3aa



3ga



3ha



3ah

This work

	3aa	**3ga**	**3ha**	**3ah**
AE	82	83	84	83
E-factor	1.71	1.54	1.41	1.83
CE	80	83	85	75
RME	68	73	74	64
MI	2.71	2.54	2.41	2.83
MP	36	39	41	35

Ma[2] Group

	3aa	**3ga**	**3ha**	**3ah**
AE	68	69	70	60
E-factor	16.7	16.1	14.6	15.98
CE	51	50	52	60
RME	48	48	52	52
MI	17.7	17.1	15.6	16.98
MP	6	6	6	6

Ji[1] Group

	3aa	**3ga**	**3ha**	**3ah**
AE	82	83	84	83
E-factor	40.31	46.7	40.7	39.15
CE	60	49	53	57
RME	51.4	54	59	47
MI	41.31	47.7	41.7	40.15
MP	2	2	2	2

8. References

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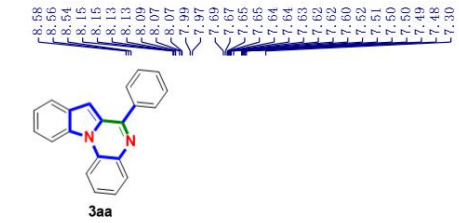
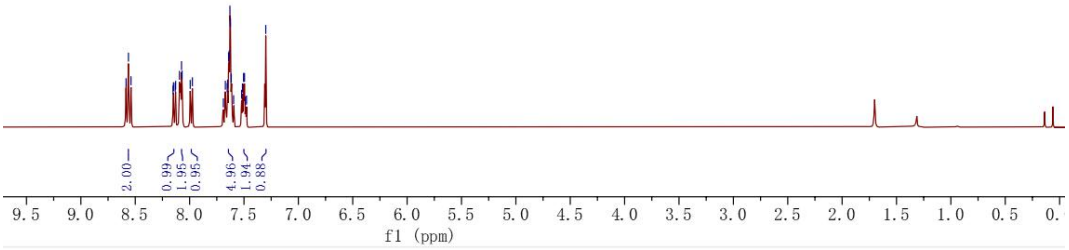
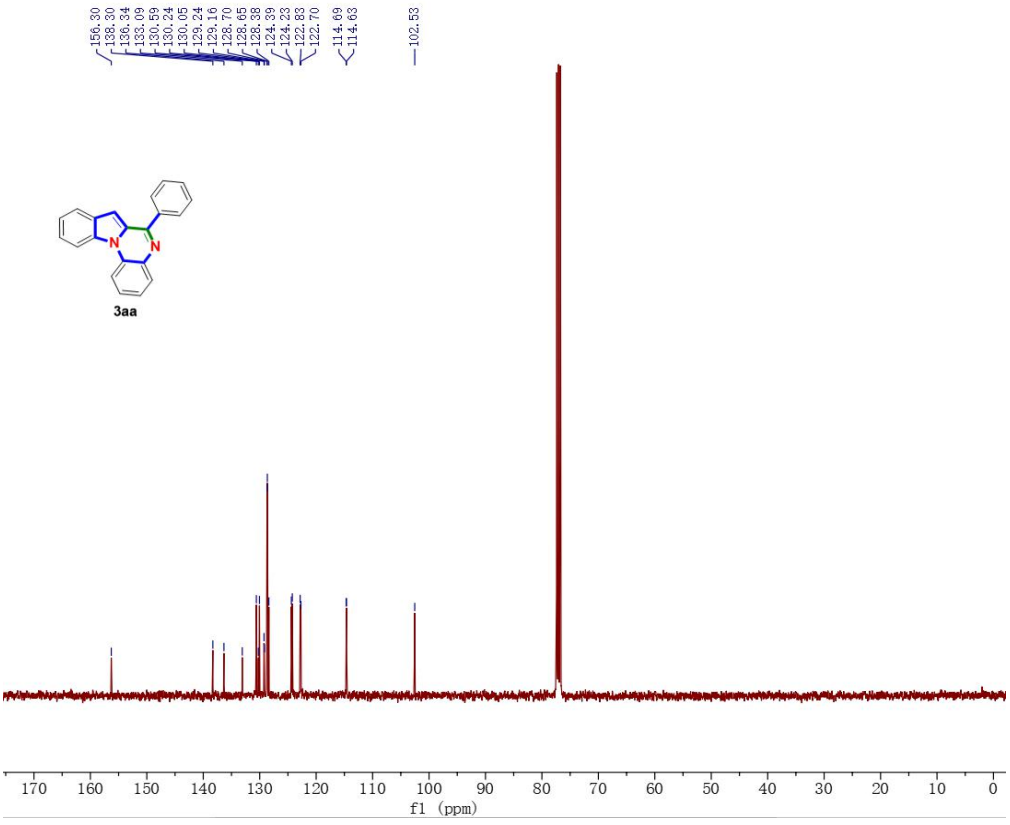
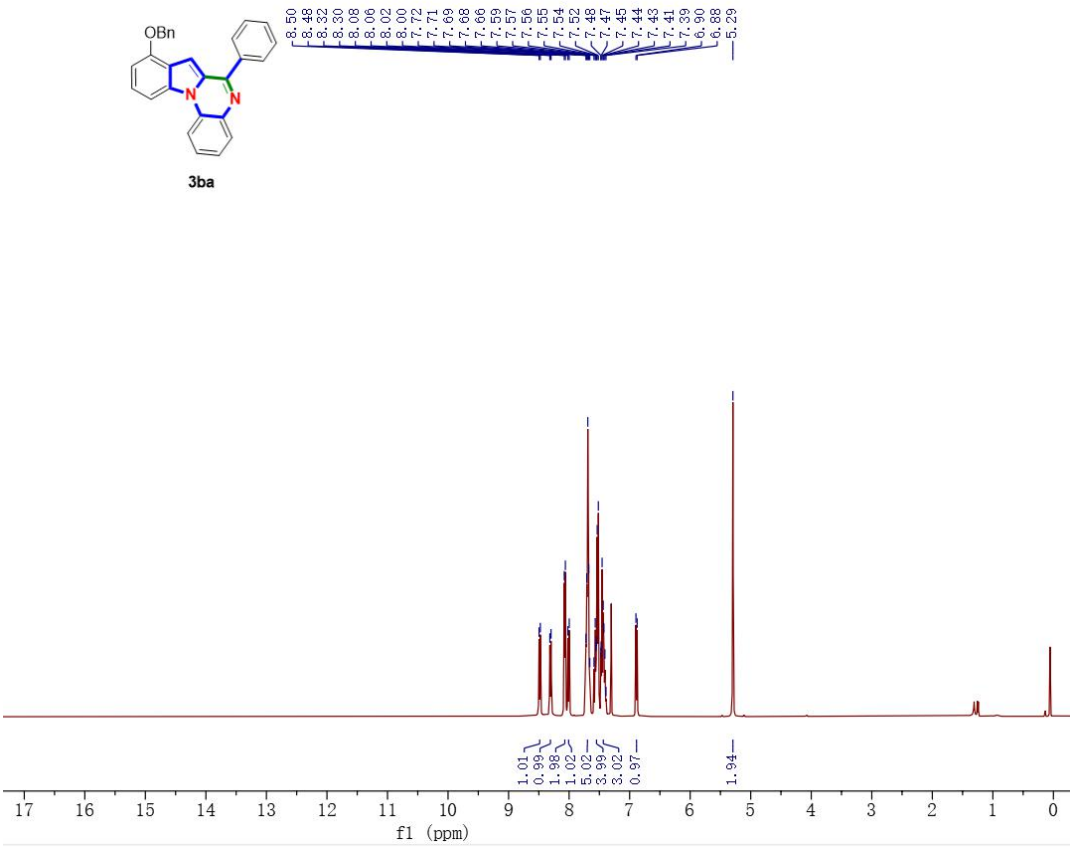
(10) G.-B. Jiang, G. Yang, X.-Q. Liu, S.-C. Wang and F.-H. Ji, Palladium-Catalyzed Sequential Acylation/Annulation of Indoles with Acyl Chlorides Using Primary Amine as the Directing Group, *New J. Chem.*, 2021, **45**, 104.

9. NMR Spectra





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8.00
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7.69
7.68
7.66
7.59
7.57
7.56
7.55
7.54
7.52
7.48
7.47
7.45
7.44
7.43
7.41
7.39
6.90
6.88
5.29
1.01
0.99
1.98
1.02
5.02
3.99
3.02
0.97
1.94
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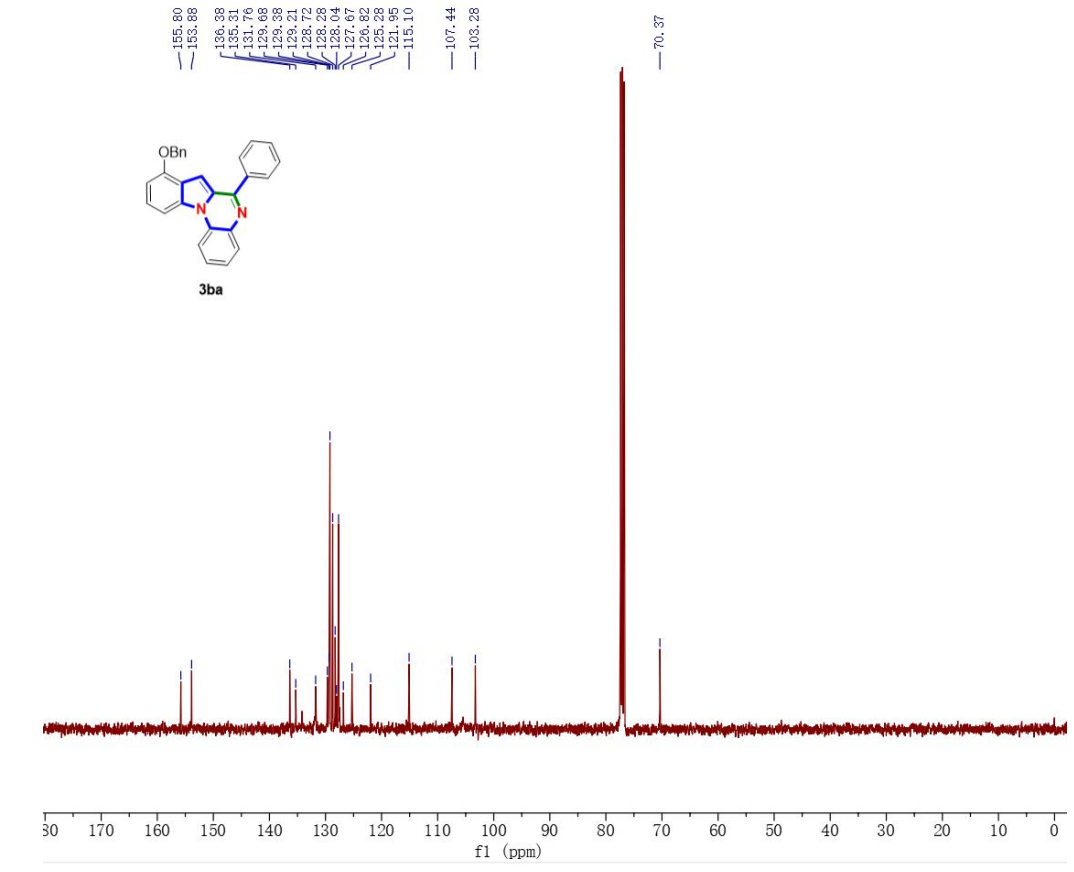
f1 (ppm)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126.82
125.28
121.95
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107.44
103.28
70.37
OBn
N
N
3ba
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.59
8.57
8.35
8.33
8.25
8.24
8.23
8.22
8.09
8.08
8.08
7.75
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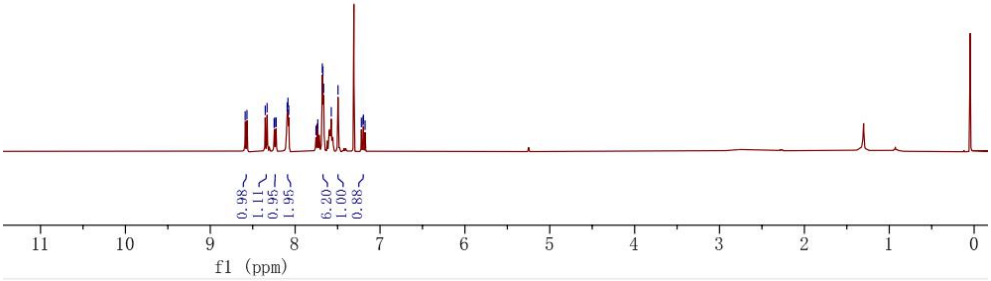
7.20
7.18


F
N
N

3ca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8
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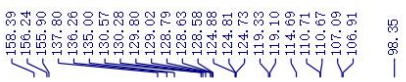
6
5
4
3
2
1
0
f1 (ppm)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128.58
124.88
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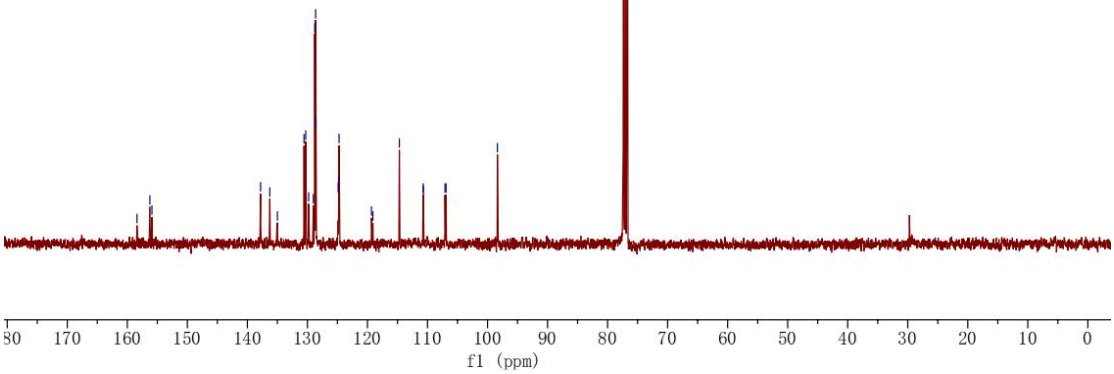
106.91
98.35


F
N
N

3ca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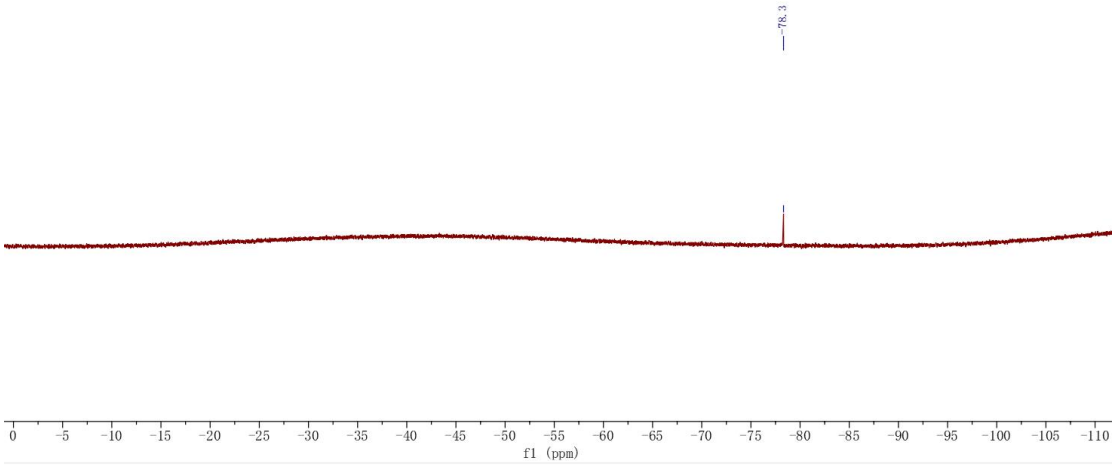
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8.27
8.25
8.22
8.12
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8.03
8.02
8.02
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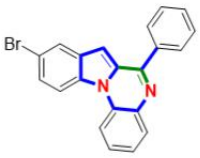
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N

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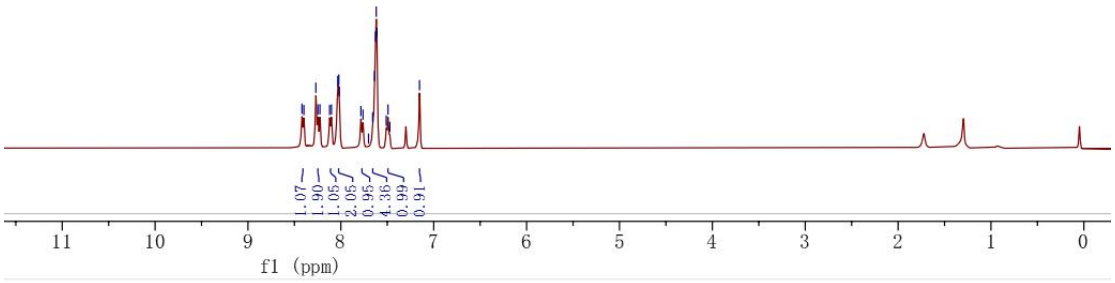
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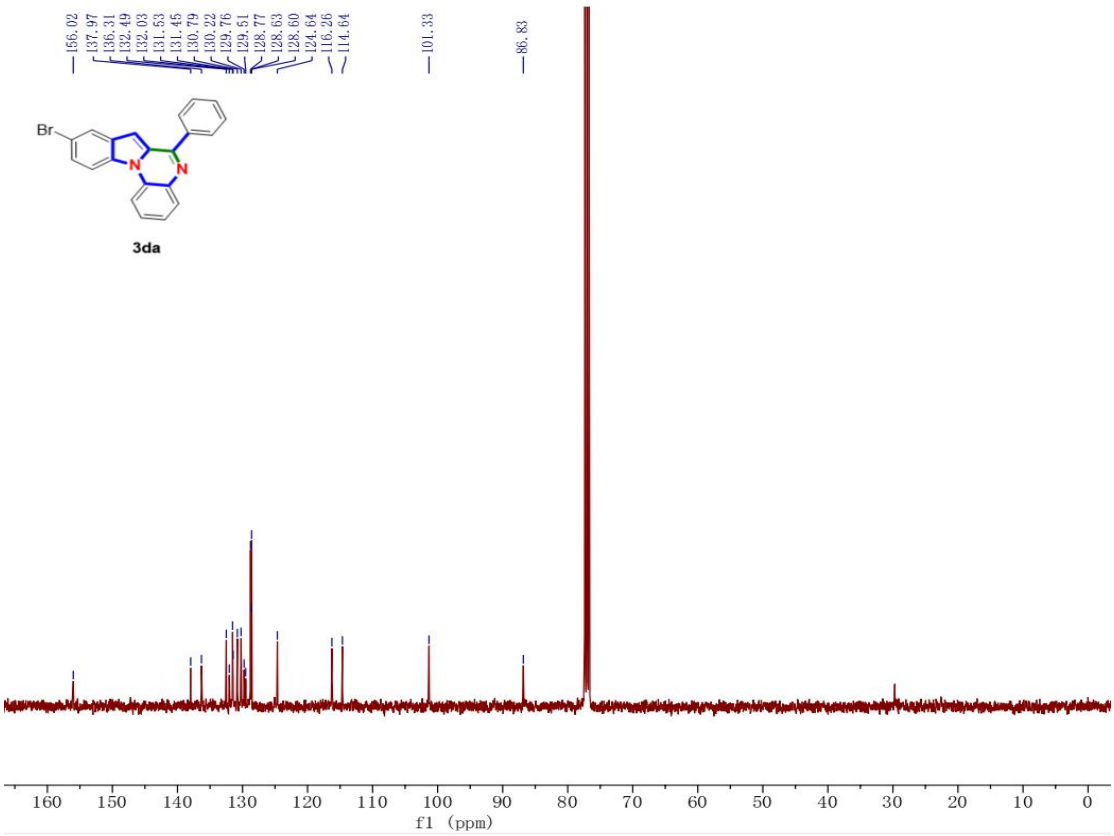
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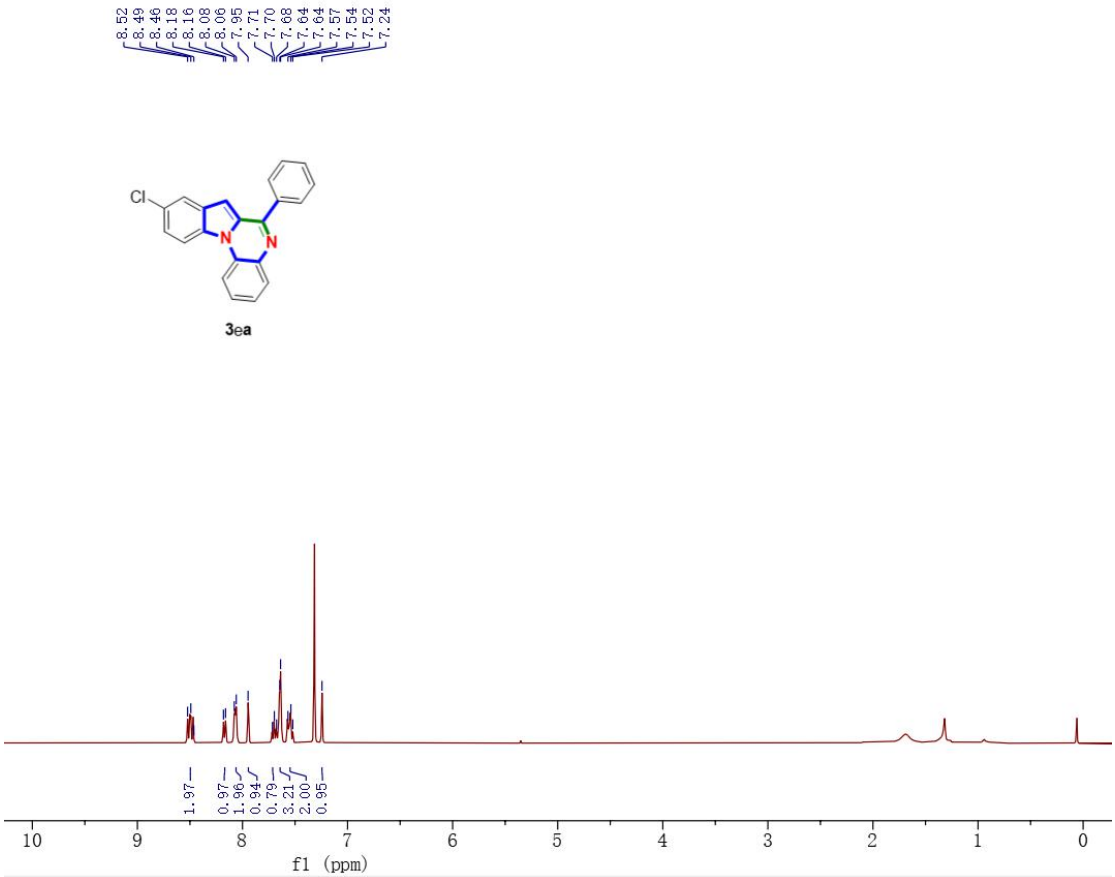
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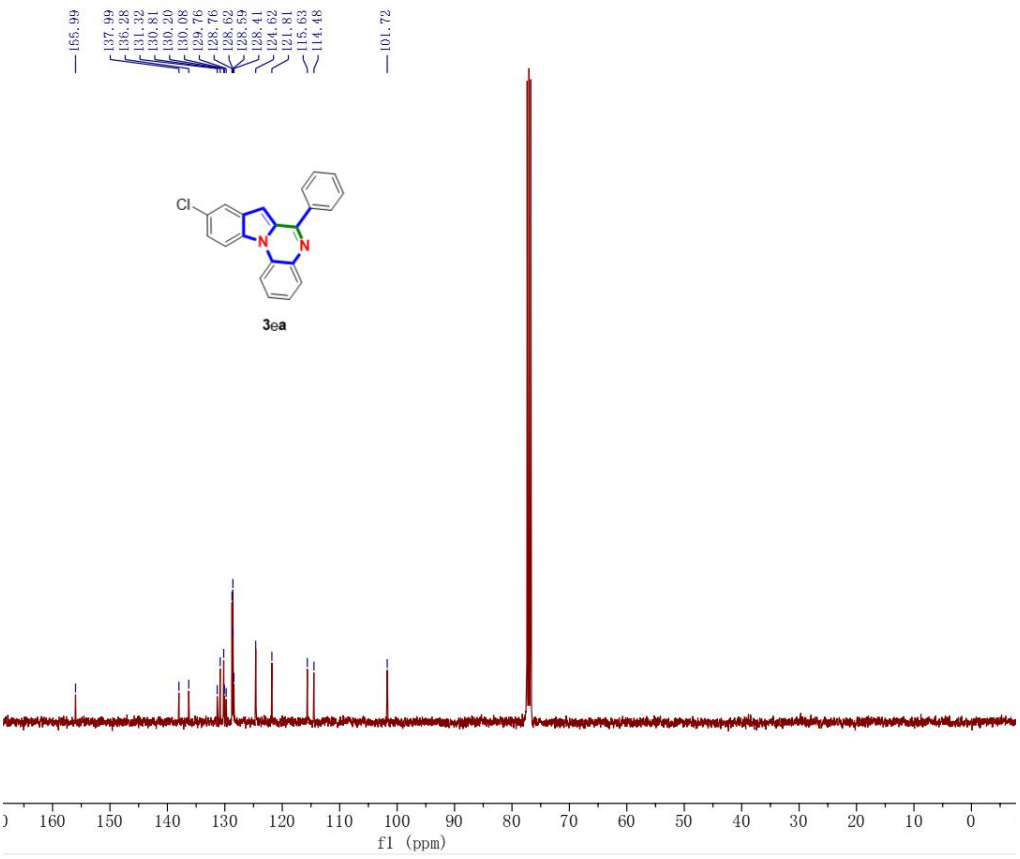
3ea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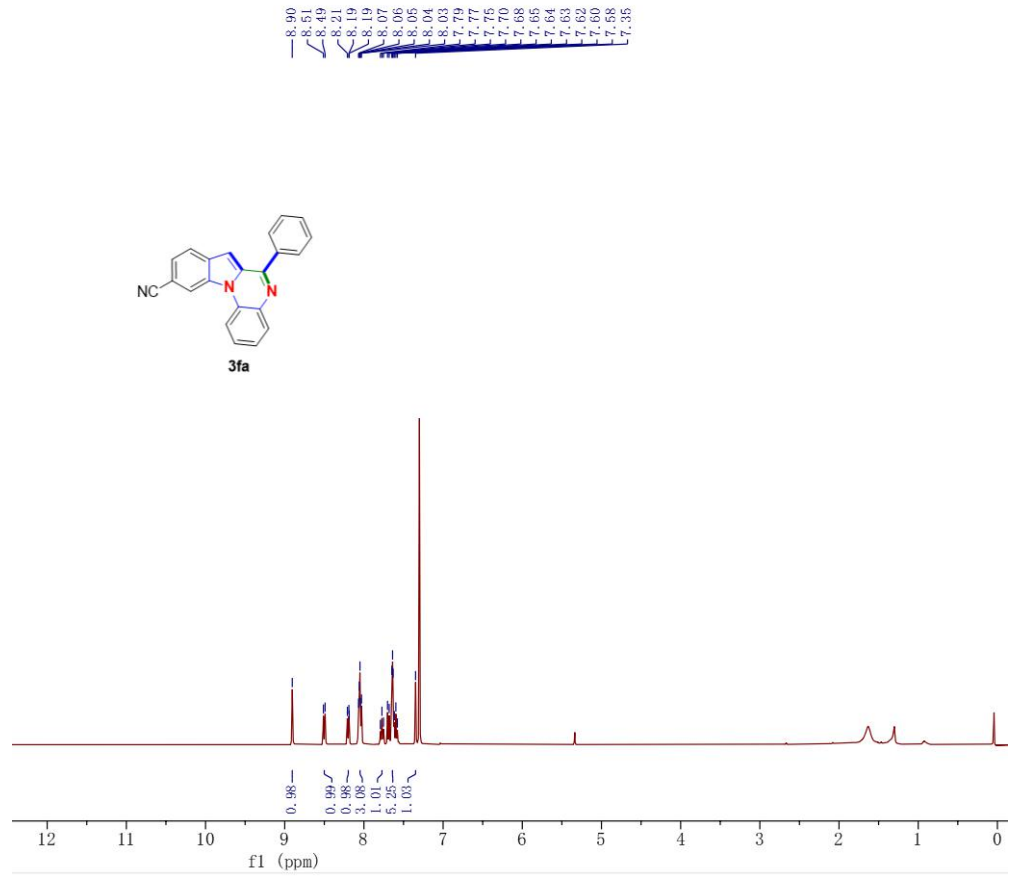
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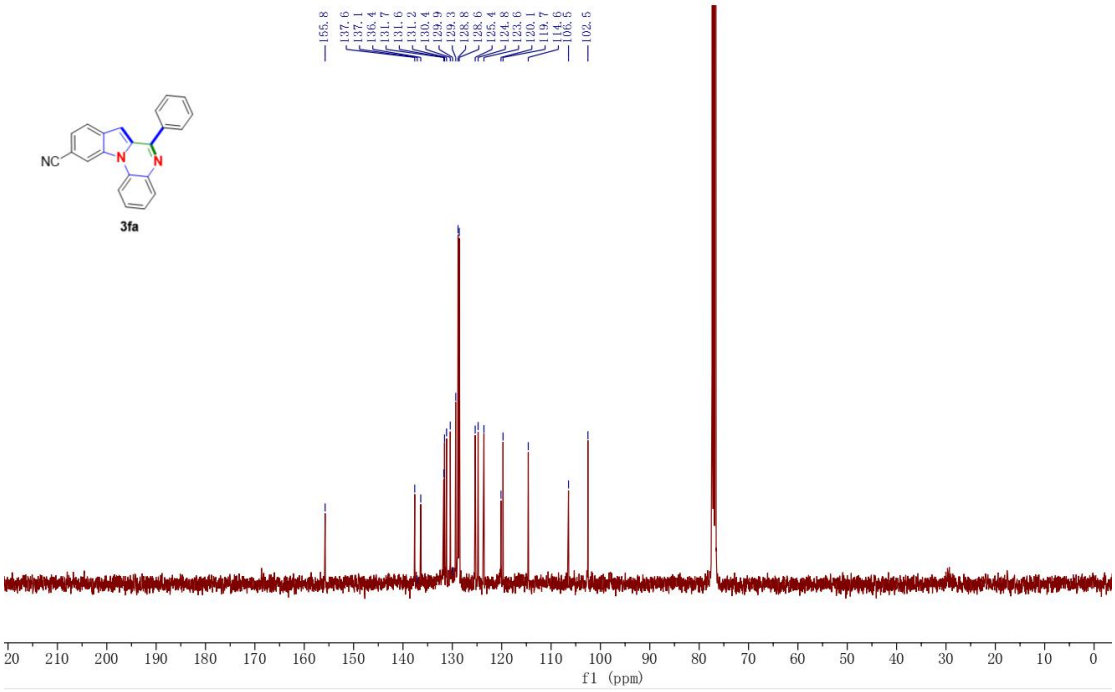
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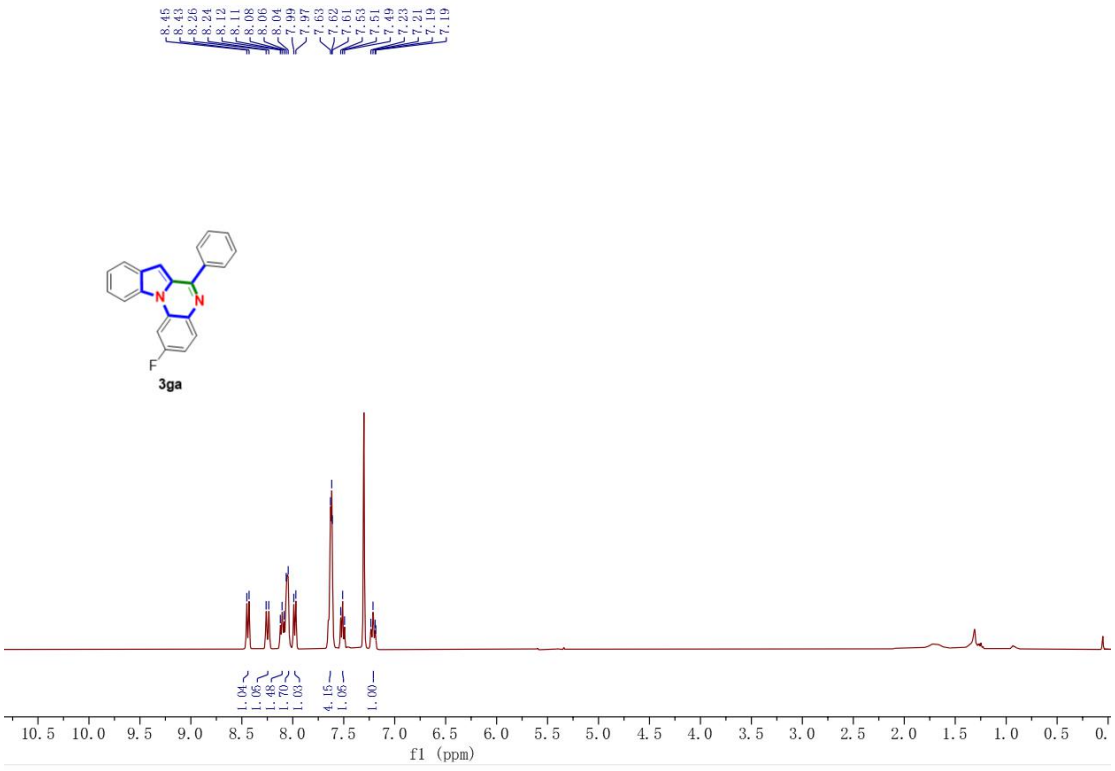
f1 (ppm)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F
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1.05
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1.70
1.03
4.15
1.05
1.00
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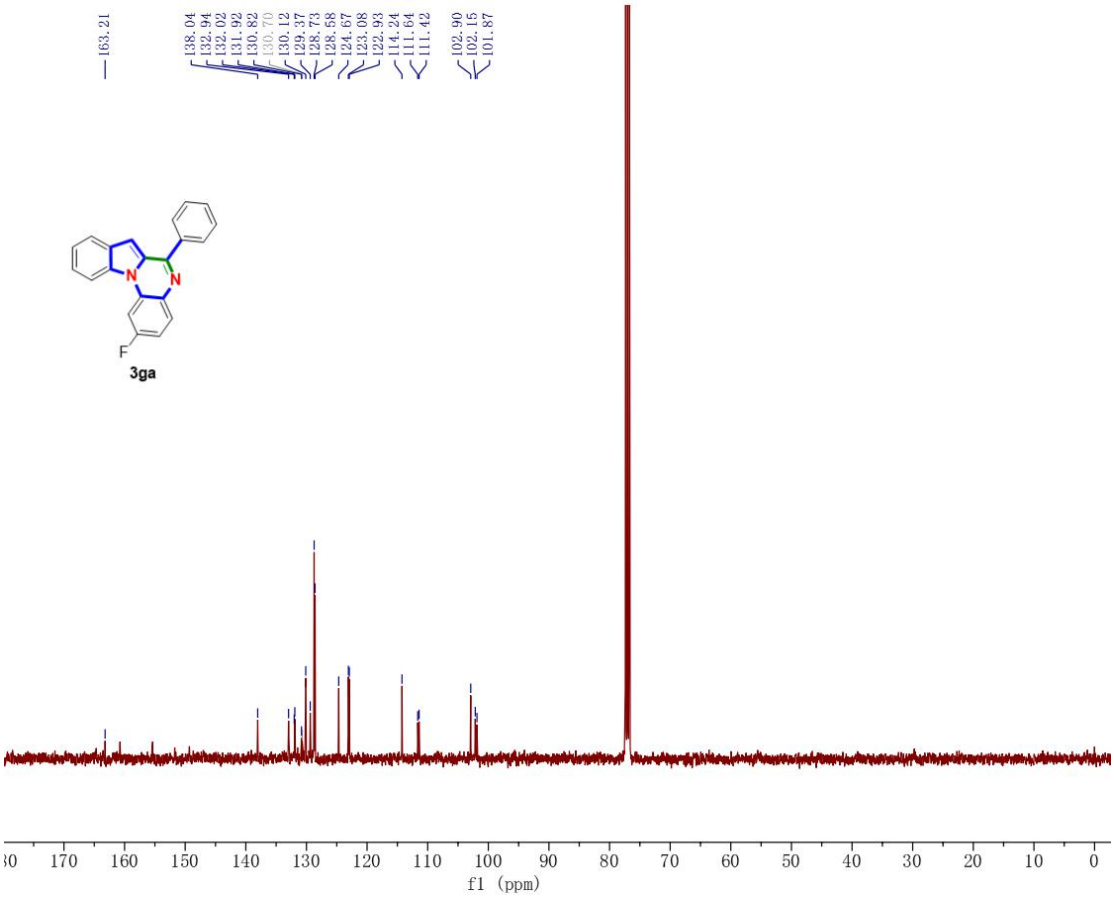
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132.94
132.02
131.92
130.82
130.70
130.12
129.37
128.73
128.58
124.67
123.08
122.93
114.24
111.64
111.42
102.90
102.15
101.87
F
3ga
170
160
150
140
130
120
110
100
90
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70
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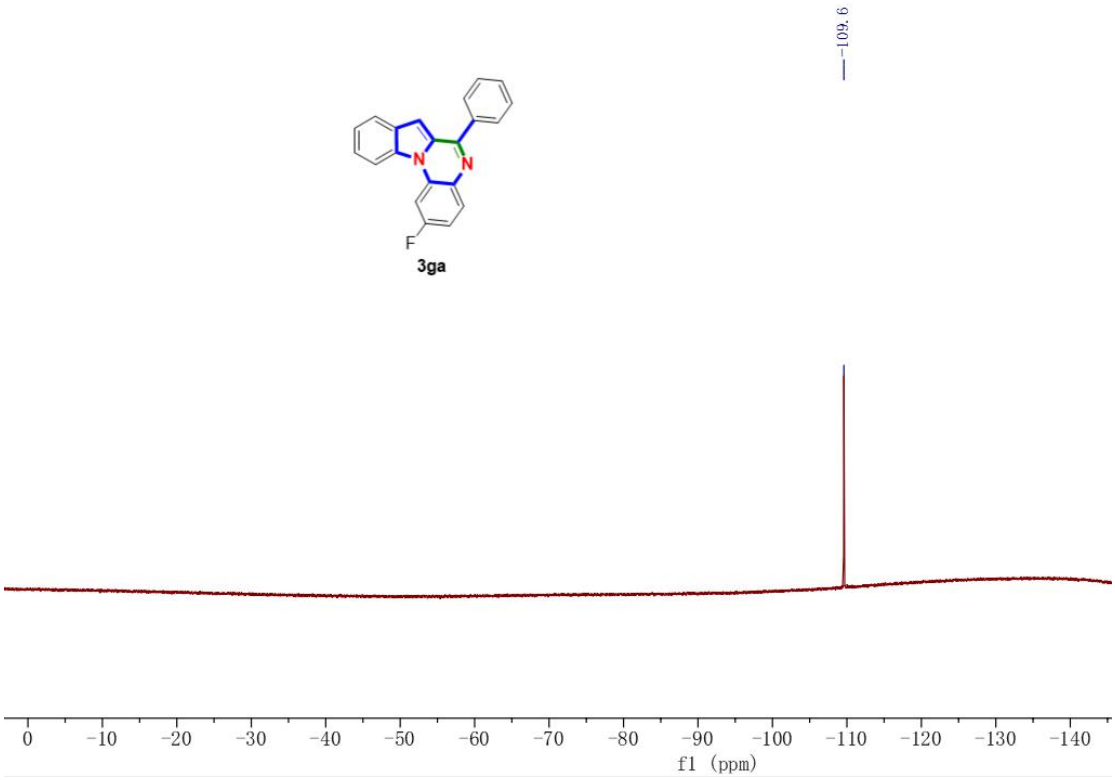
50
40
30
20
10
0
f1 (ppm)


-109.6
F
3ga
0
-10
-20
-30
-40
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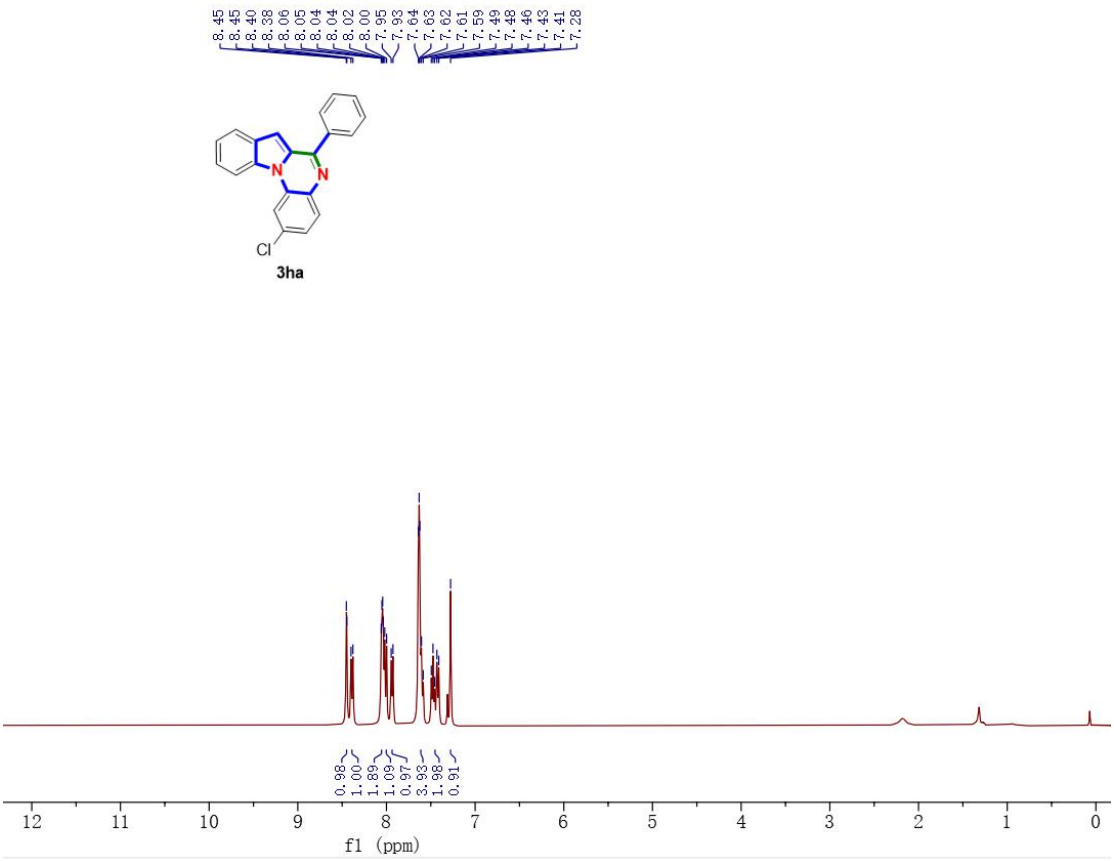
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)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8.45
8.40
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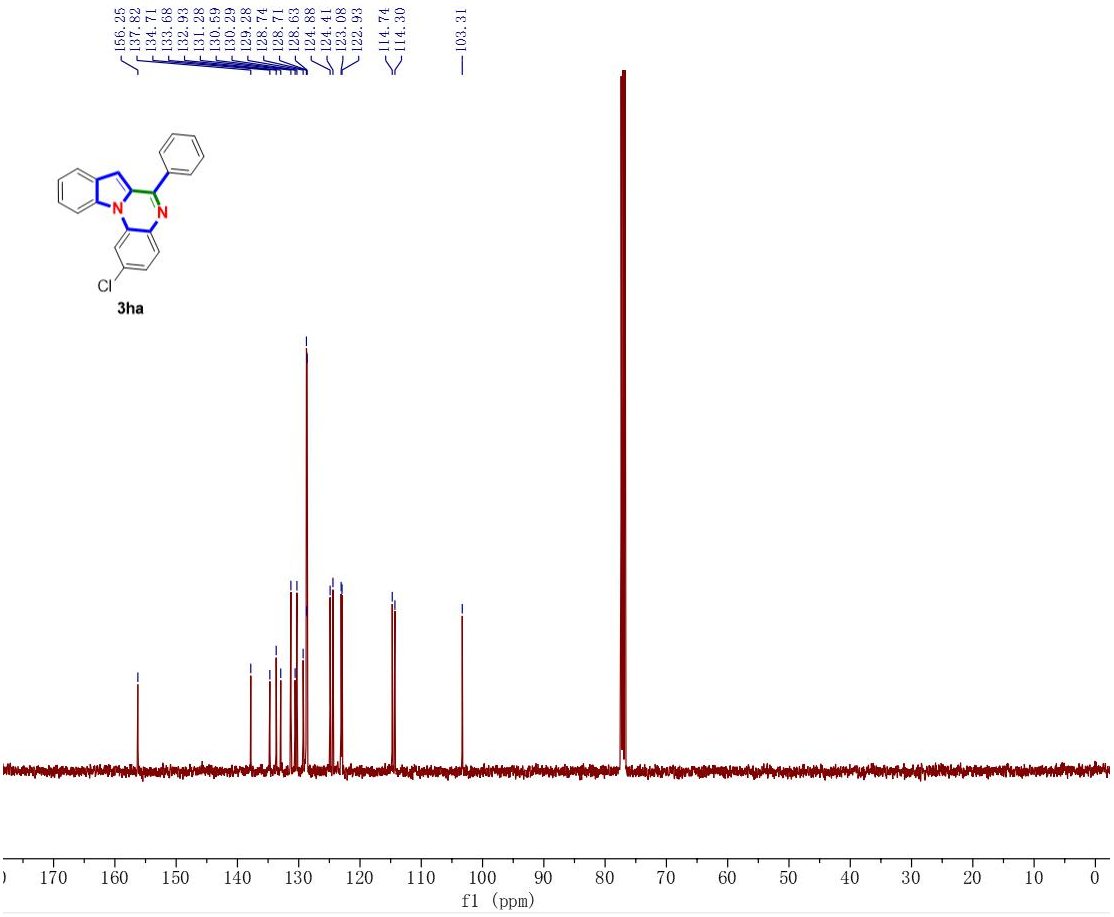
8.05
8.04
8.04
8.02
8.00
7.95
7.93
7.64
7.63
7.62
7.61
7.59
7.49
7.48
7.46
7.43
7.41
7.28
N
N
Cl
3ha
0.98
1.00
1.89
1.09
0.97
3.93
1.98
0.91
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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137.82
134.71
133.68
132.93
131.28
130.59
130.29
129.28
128.74
128.71
128.63
124.88
124.41
123.08
122.93
114.74
114.30
103.31
N
N
Cl
3ha
170
160
150
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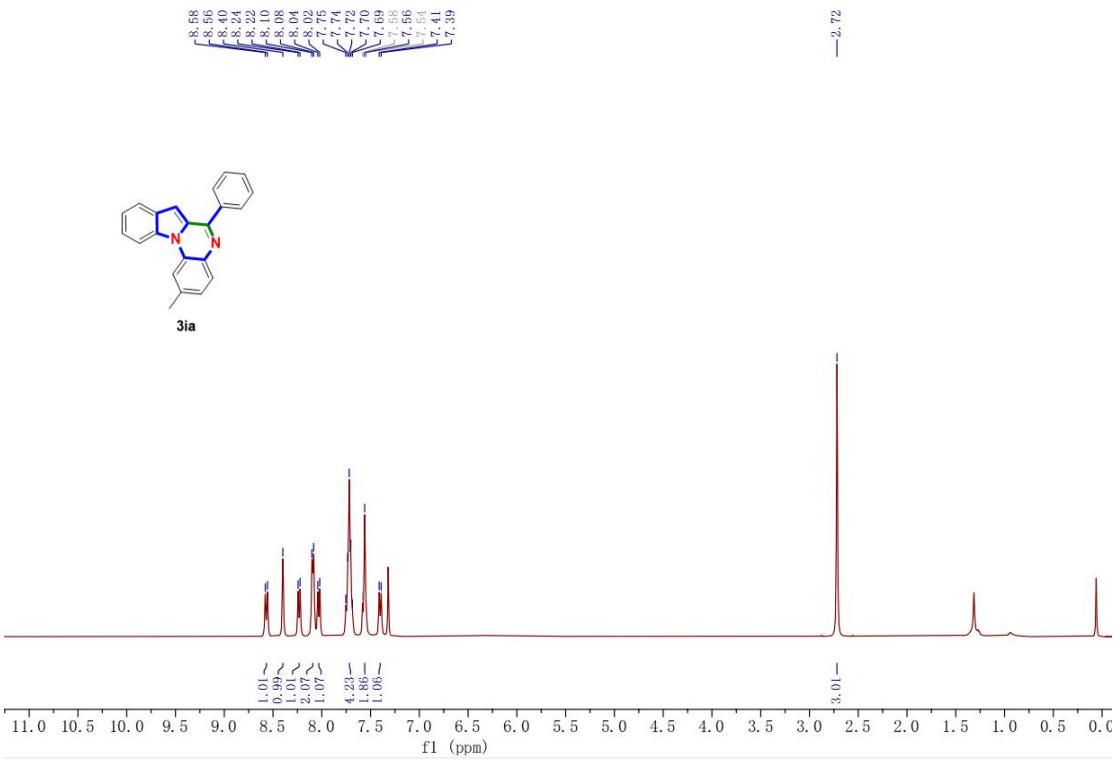
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

\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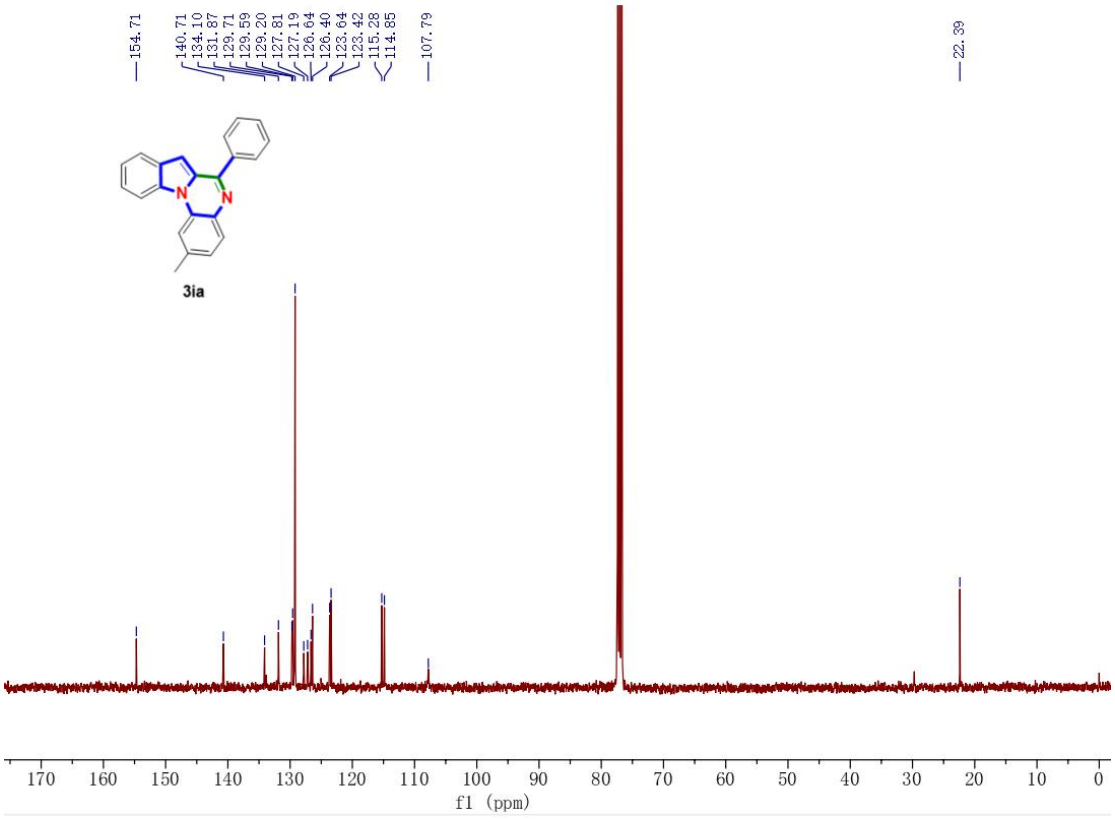
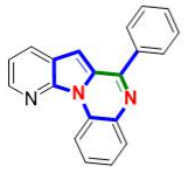
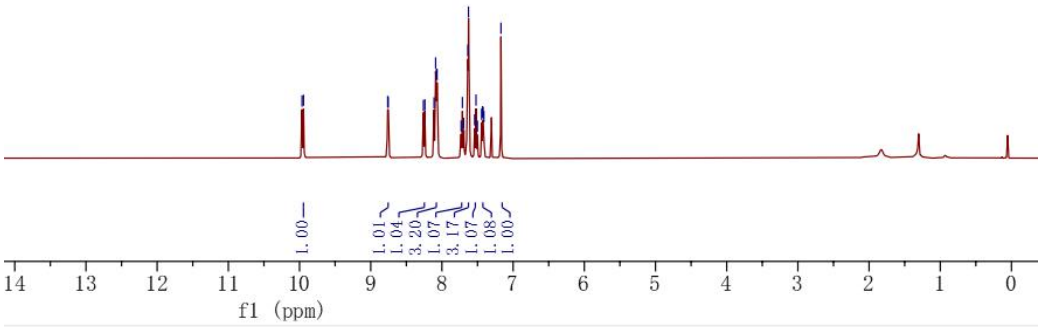
8.56
8.40
8.24
8.22
8.10
8.08
8.04
8.02
7.75
7.74
7.72
7.70
7.69
7.68
7.66
7.61
7.41
7.39
2.72
3ia
1.01
0.99
1.01
2.07
1.07
4.23
1.86
1.06
3.01
f1 (ppm)

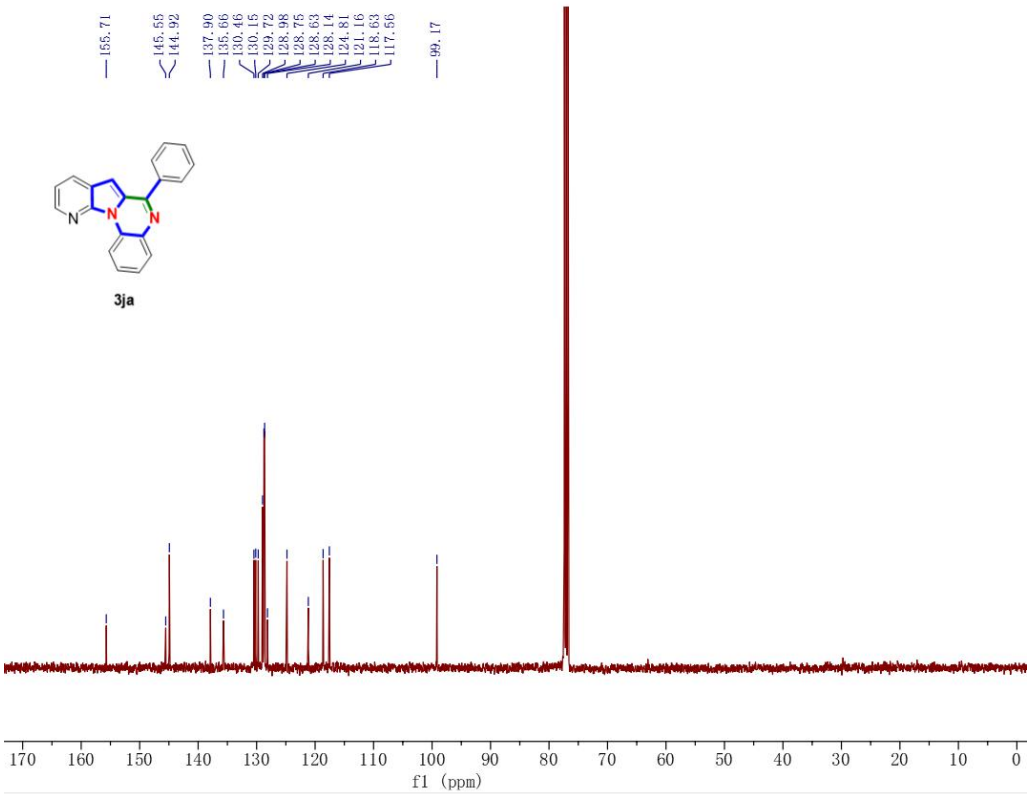

154.71
140.71
134.10
131.87
129.71
129.59
129.20
127.81
127.19
126.64
126.40
123.64
123.42
115.28
114.85
107.79
22.39
3ia
f1 (ppm)


9.96
9.94
8.76
8.75
8.26
8.24
8.11
8.09
8.08
8.07
7.73
7.71
7.69
7.64
7.63
7.54
7.52
7.50
7.44
7.43
7.42
7.41
7.17

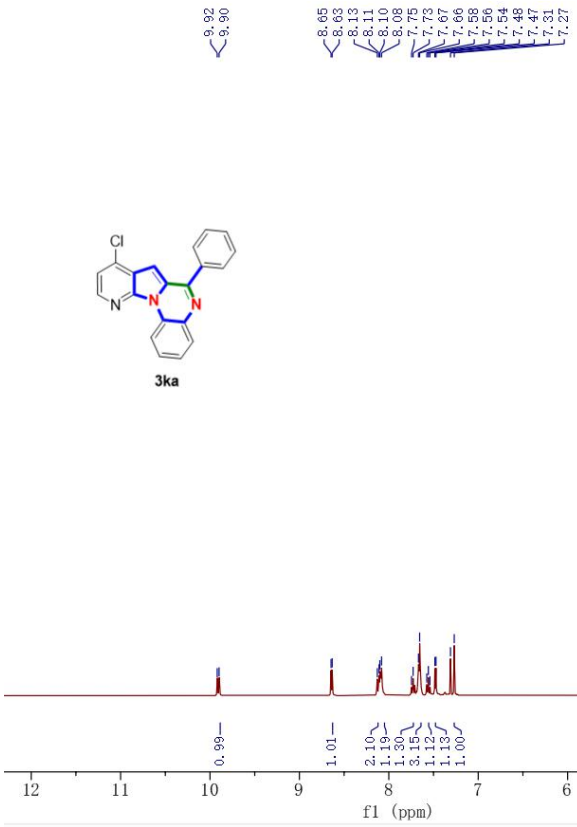


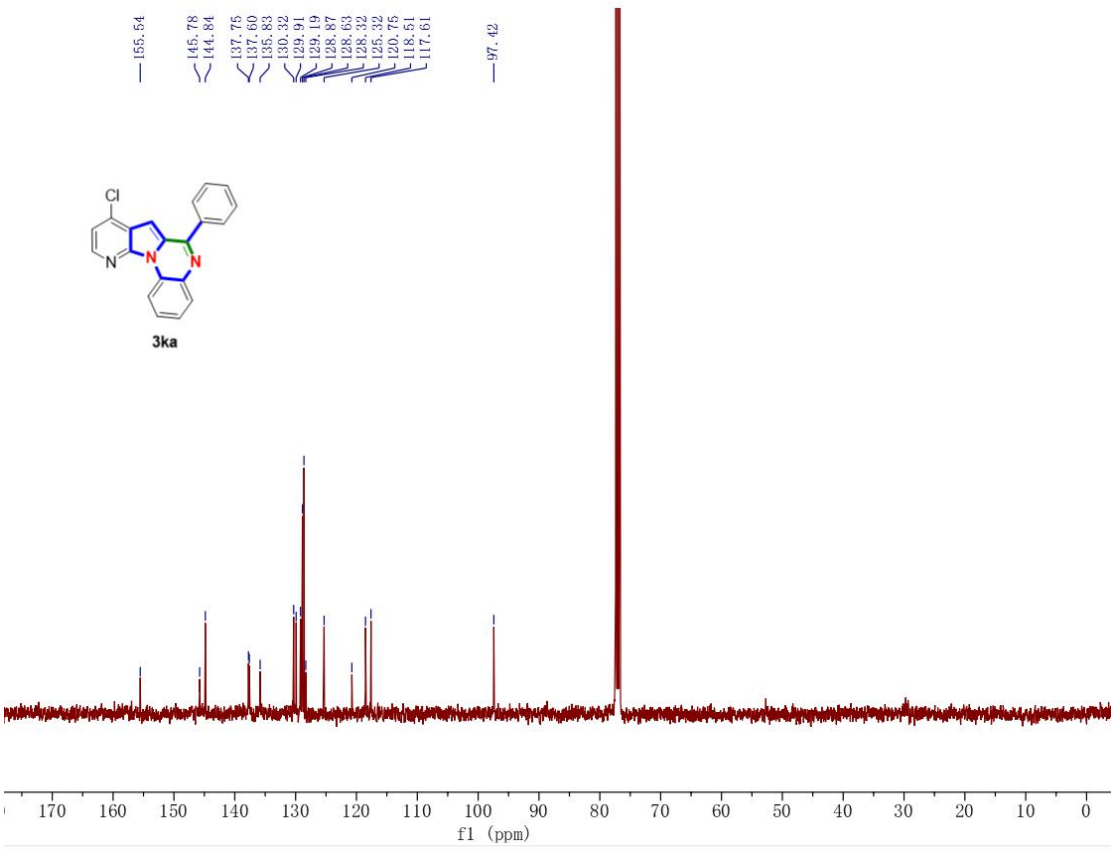
3ja

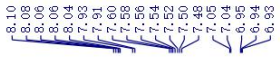

1.00
1.01
1.04
3.20
1.07
3.17
1.07
1.08
1.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

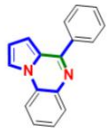

155.71
145.55
144.92
137.90
135.66
130.46
130.15
129.72
128.98
128.75
128.63
128.14
124.81
121.16
118.63
117.56
99.17
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ja

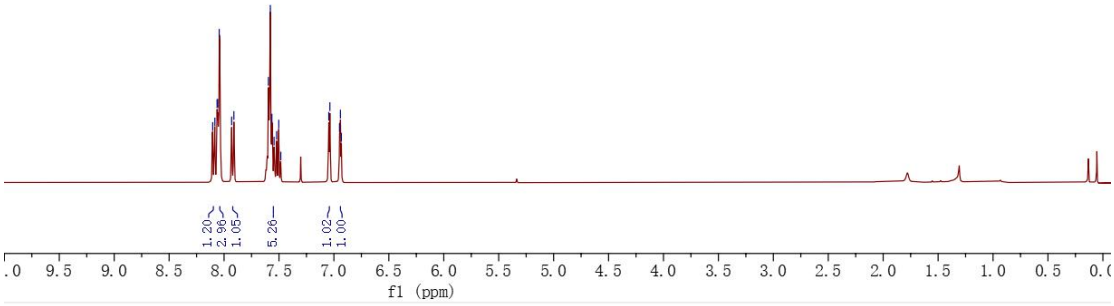

9.92
9.90
8.65
8.63
8.13
8.11
8.10
8.08
7.75
7.73
7.67
7.66
7.58
7.56
7.54
7.48
7.47
7.31
7.27
Cl
N
N
N
3ka
0.99
1.01
2.10
1.19
1.30
3.15
1.12
1.13
1.00
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

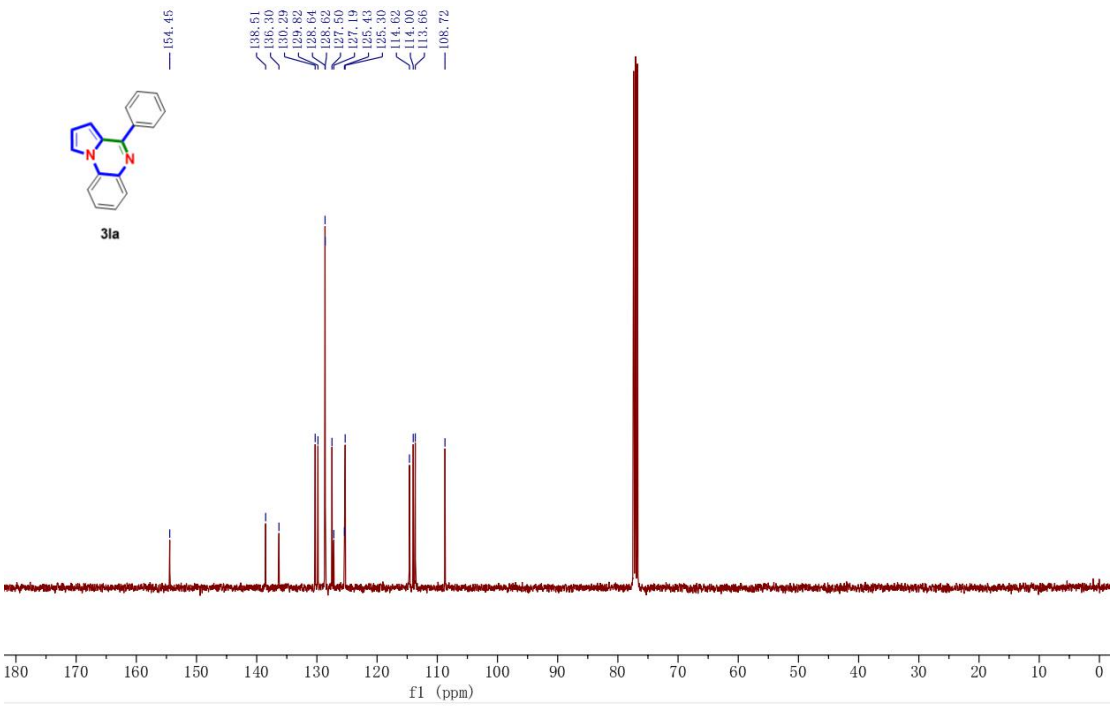

155.54
145.78
144.84
137.75
137.60
135.83
130.32
129.91
129.19
128.87
128.63
128.32
125.32
120.75
118.51
117.61
97.42
Cl
N
N
N
3ka
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.10
8.08
8.06
8.06
8.04
7.93
7.91
7.60
7.58
7.56
7.54
7.52
7.50
7.48
7.05
7.04
6.95
6.94
6.93

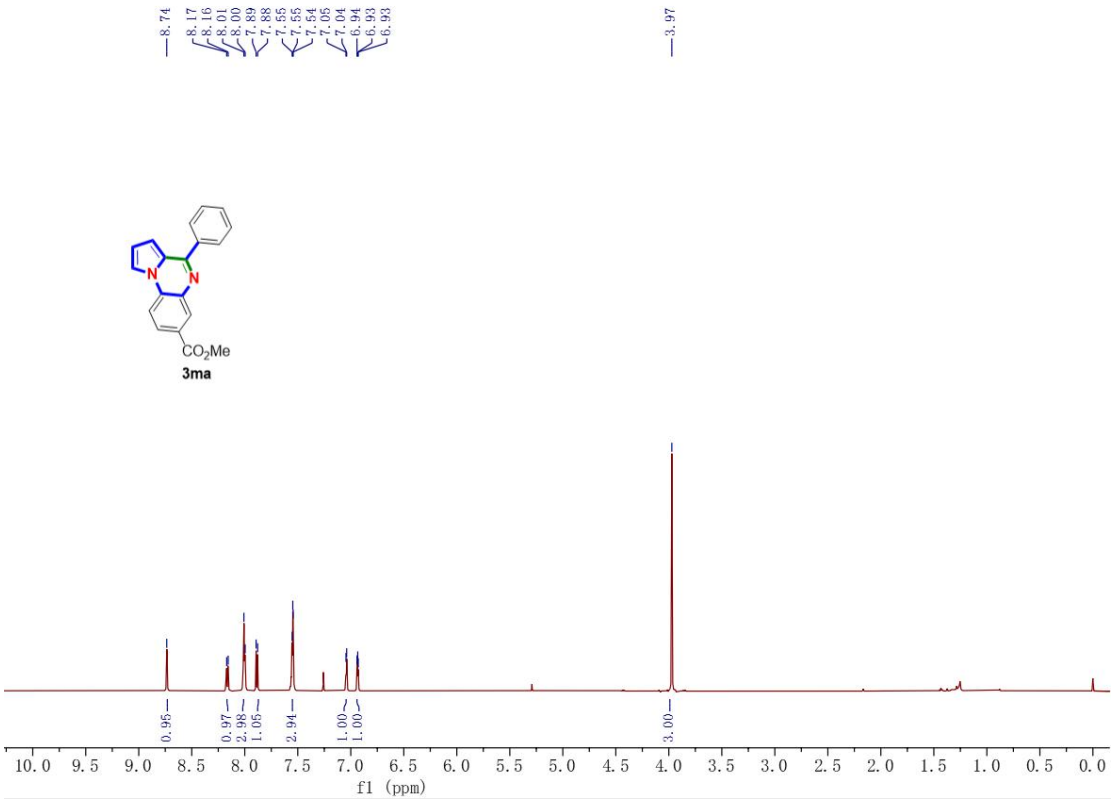


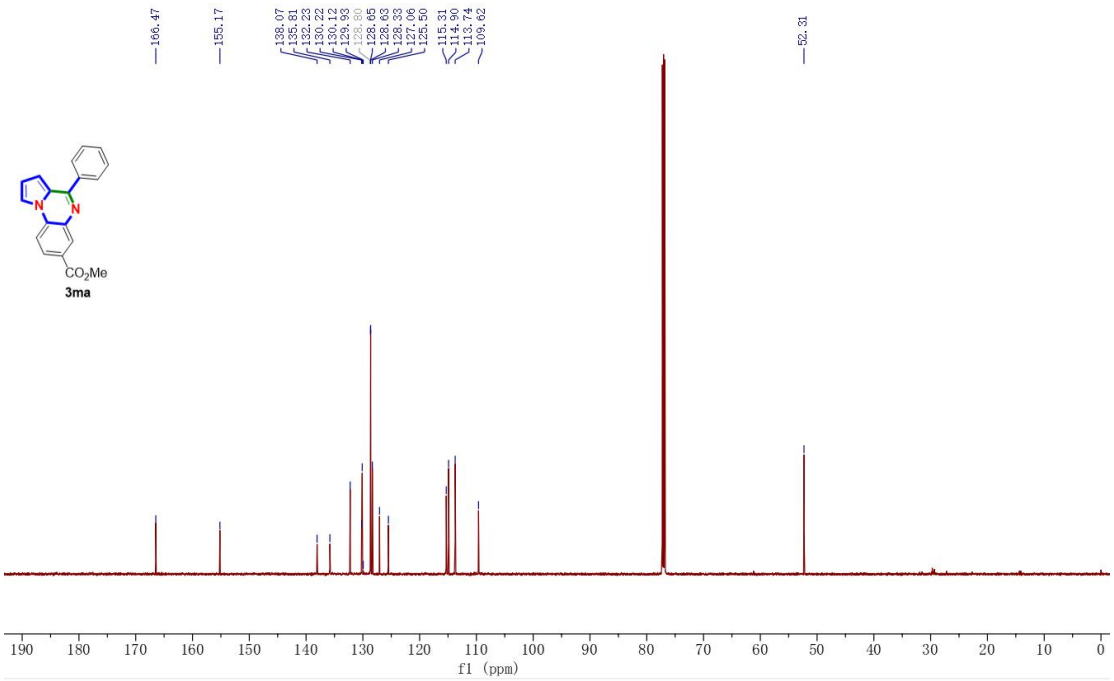
3la


1.20
2.98
1.05
5.26
1.02
1.00
f1 (ppm)


154.45
138.51
136.30
130.29
129.82
128.64
128.62
127.50
127.19
125.43
125.30
114.62
114.00
113.66
108.72
f1 (ppm)

3la


8.74
8.17
8.16
8.01
8.00
7.89
7.88
7.55
7.54
7.05
7.04
6.94
6.93
6.93
3.97
CO2Me
3ma
0.95
0.97
2.98
1.05
2.94
1.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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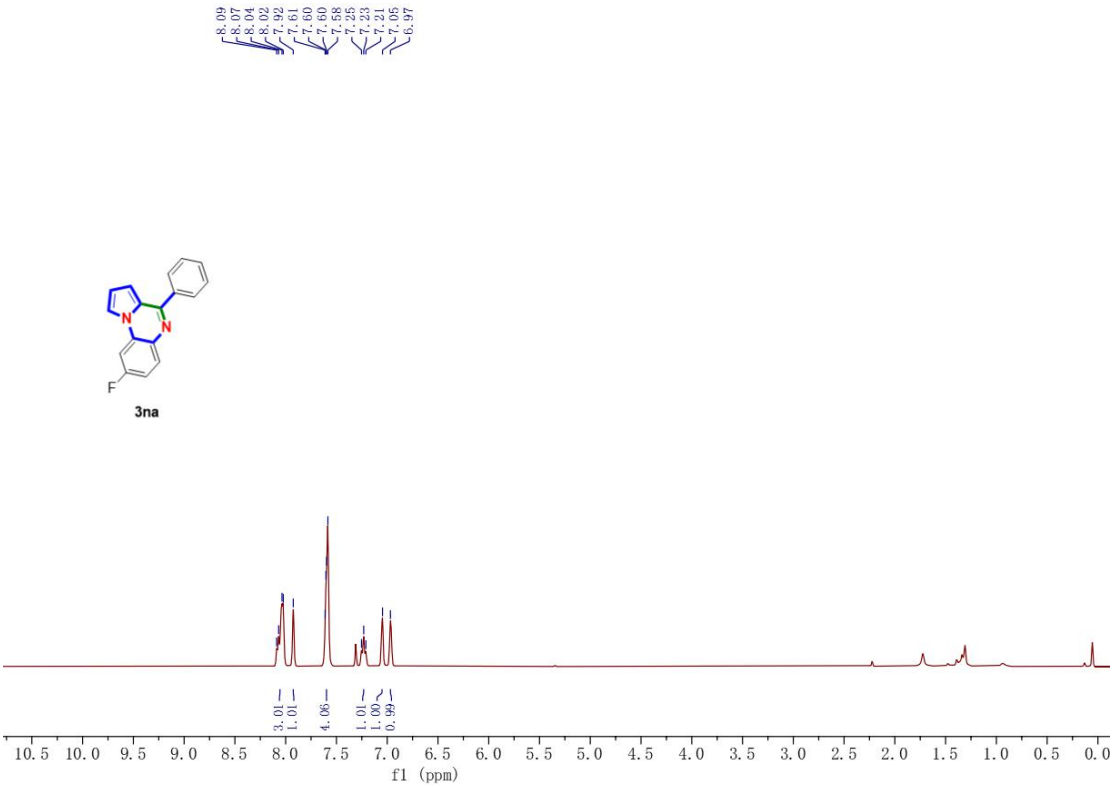
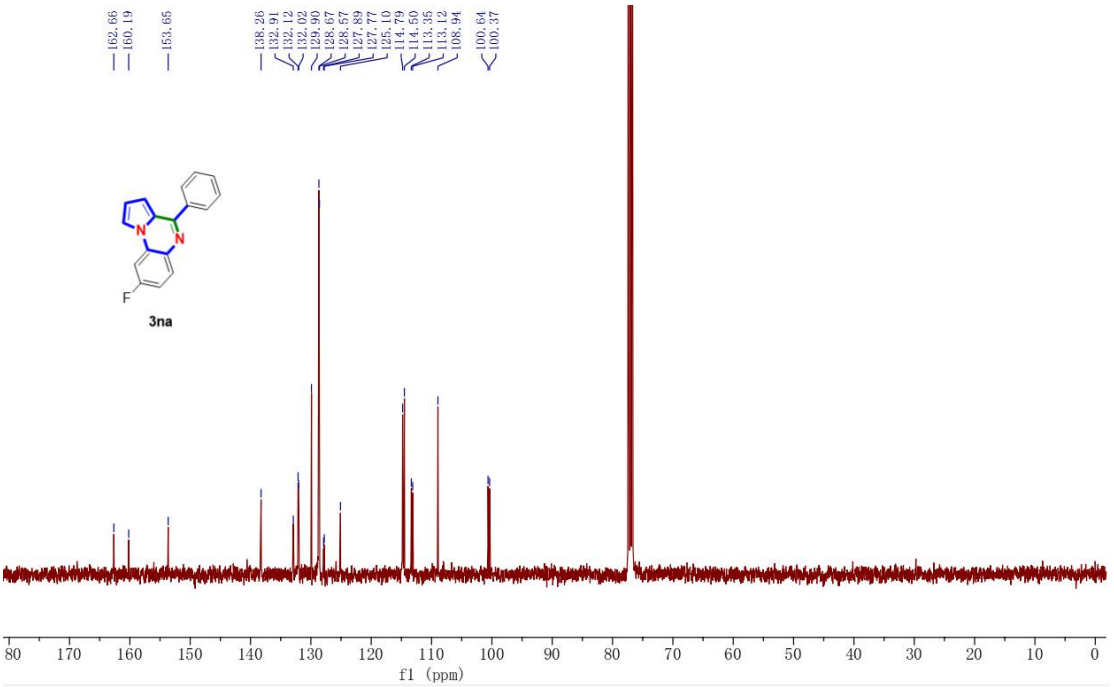
138.07
135.81
132.23
130.22
130.12
129.93
128.80
128.65
128.63
128.33
127.06
125.50
115.31
114.90
113.74
109.62
52.31
CO2Me
3ma
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

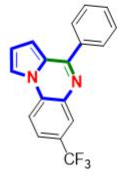

8.09
8.07
8.04
8.02
7.92
7.61
7.60
7.60
7.58
7.25
7.23
7.21
7.05
6.97
3na
3.01
1.01
4.06
1.01
1.00
0.99
f1 (ppm)


162.66
160.19
153.65
138.26
132.91
132.12
132.02
129.90
128.67
128.57
127.89
127.77
125.10
114.79
114.50
113.35
113.12
108.94
100.64
100.37
3na
f1 (ppm)

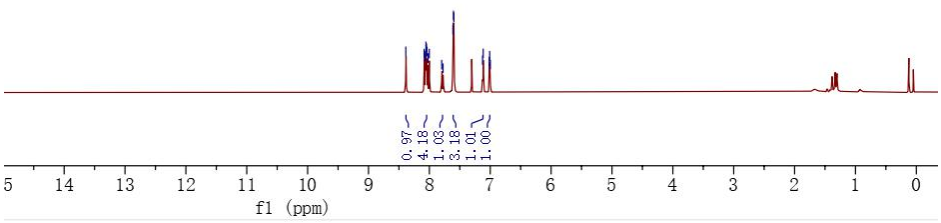
3na

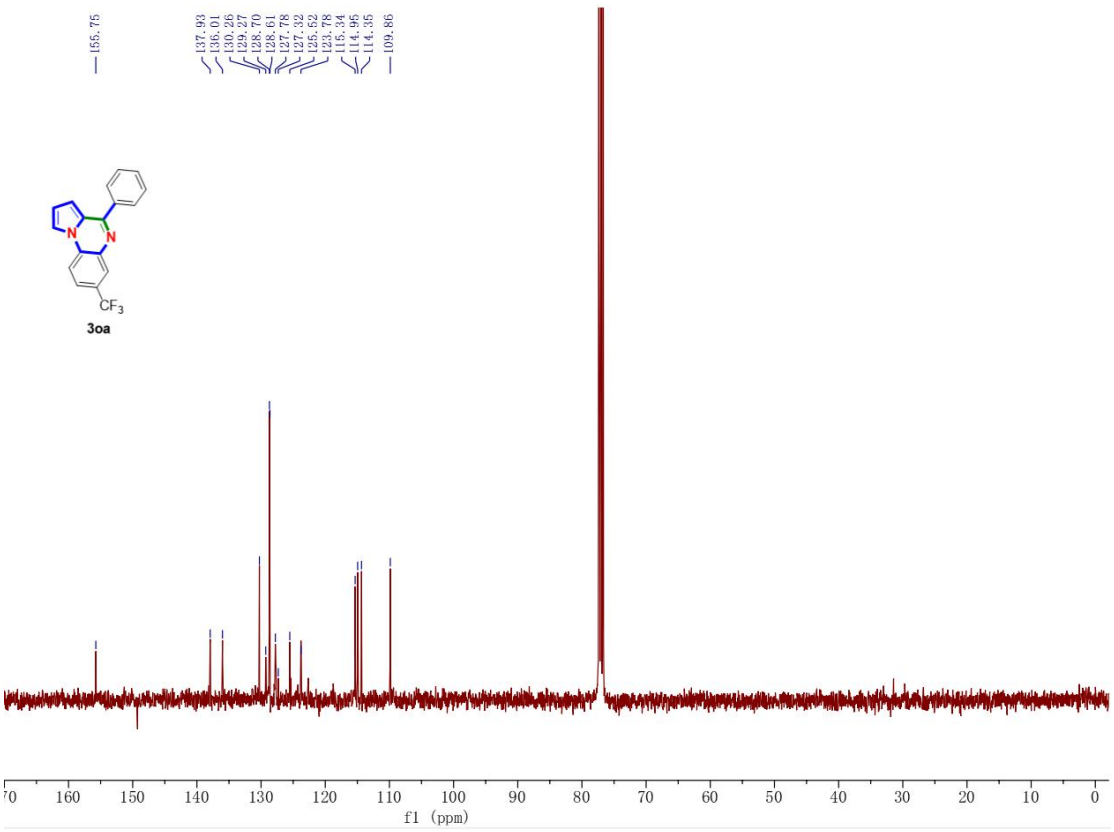
-110.8
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


8.39
8.09
8.08
8.06
8.06
8.05
8.04
8.02
8.00
7.80
7.78
7.61
7.60
7.60
7.13
7.12
7.02
7.01
7.00



3oa


0.97
4.18
1.03
3.18
1.01
1.00
5
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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137.93
136.01
130.26
129.27
128.70
128.61
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127.32
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123.78
115.34
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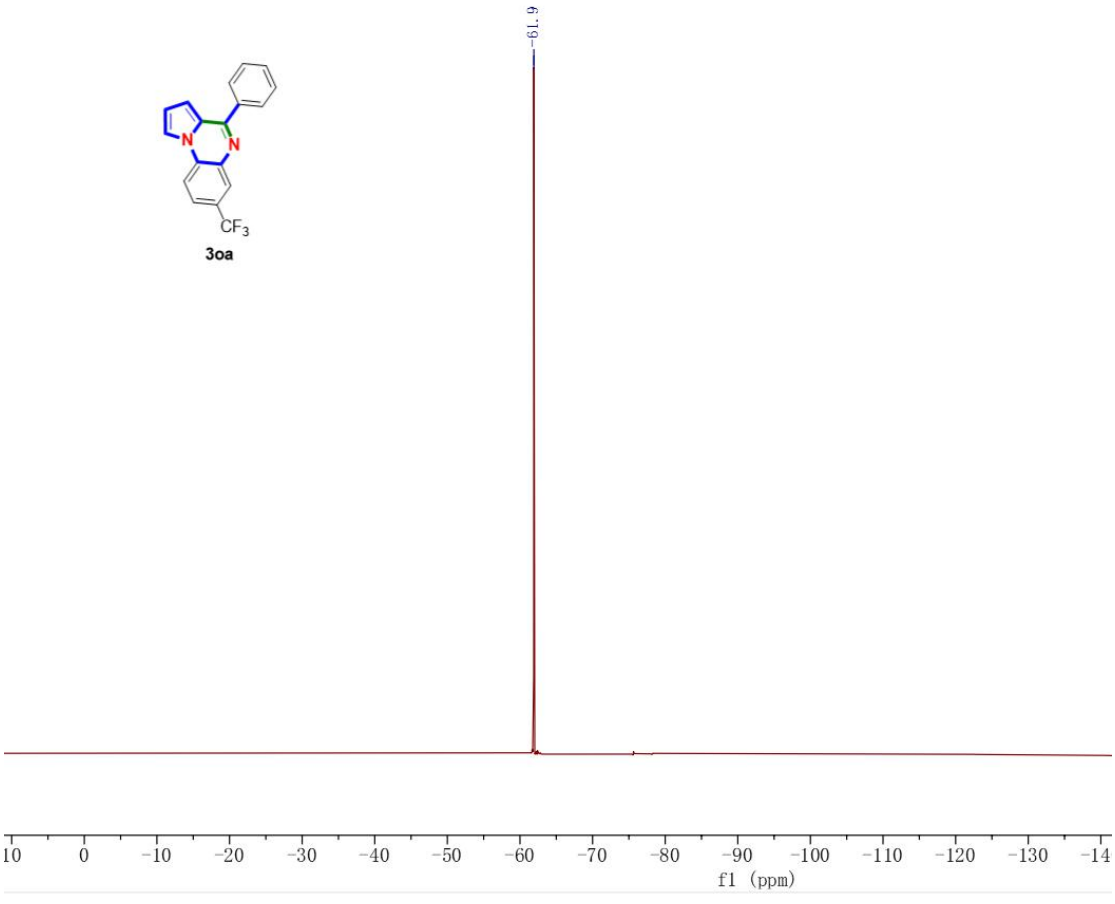
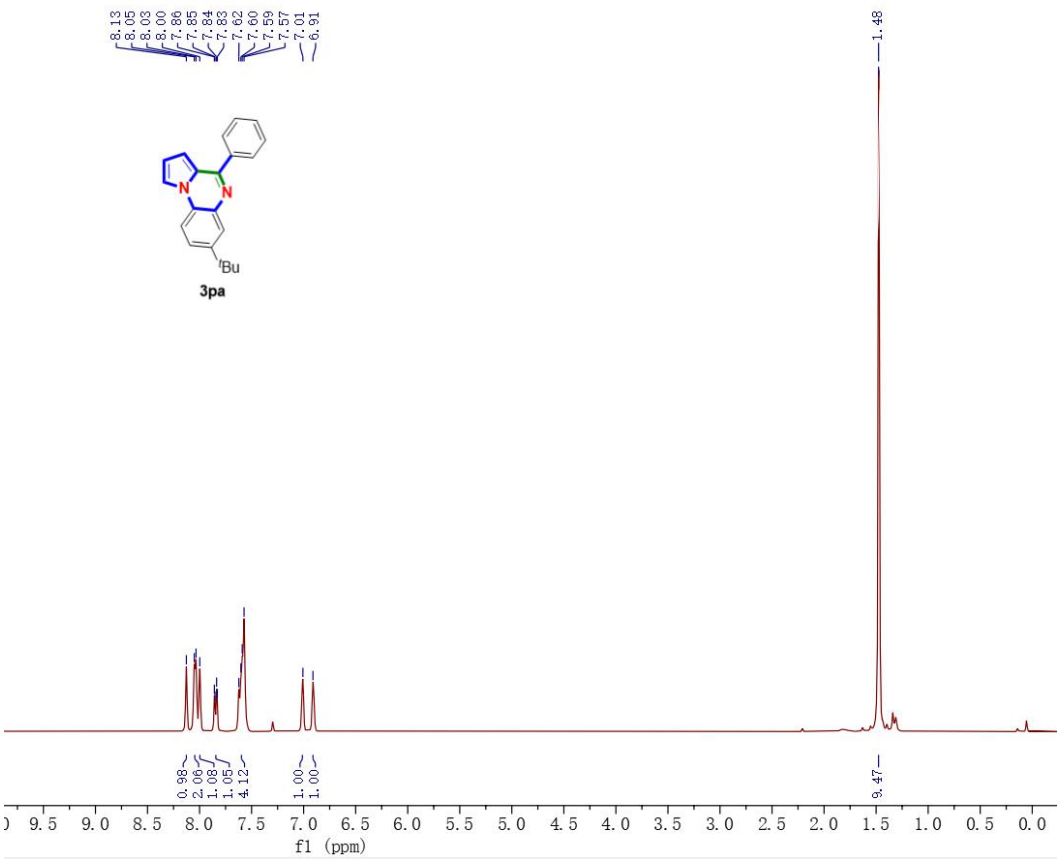
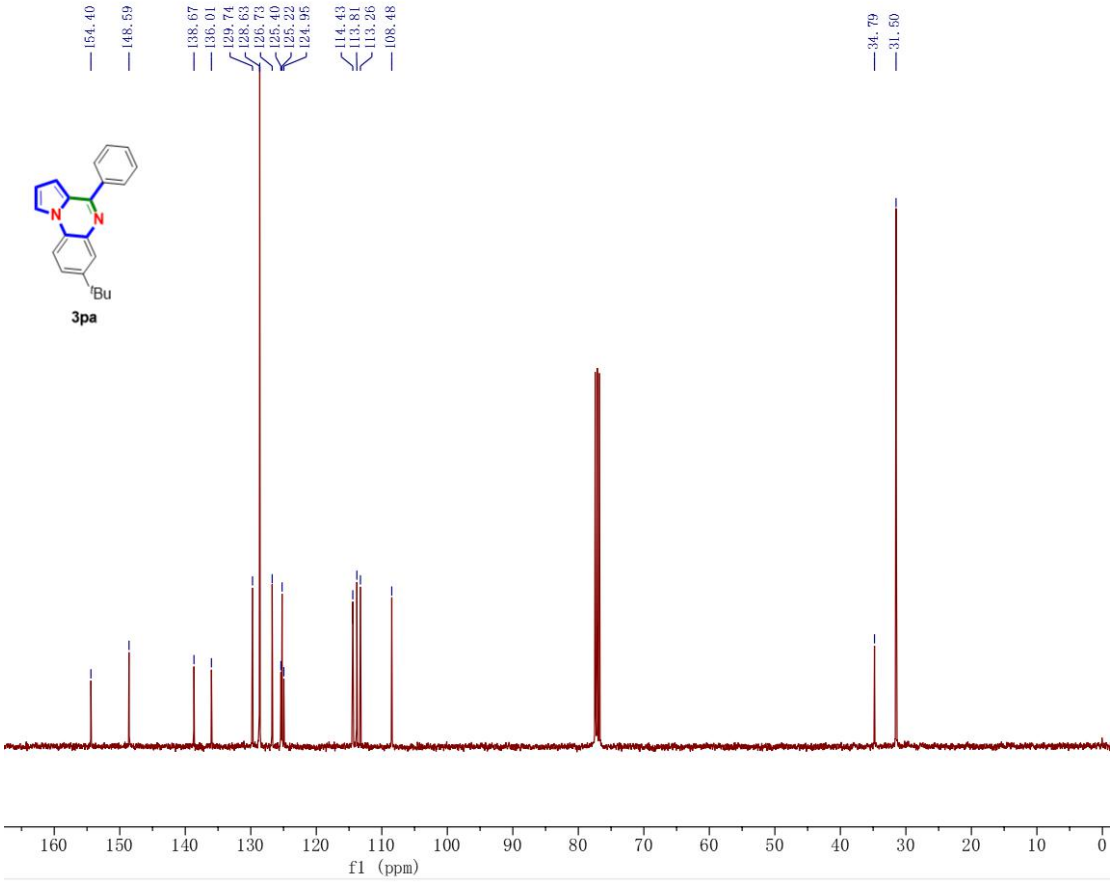
109.86
N
N
CF3
3oa
f1 (ppm)


-61.9
N
N
CF3
3oa
f1 (ppm)


8.13
8.05
8.03
8.00
7.86
7.85
7.84
7.83
7.62
7.60
7.59
7.57
7.01
6.91
1.48
tBu
3pa
0.98
2.06
1.08
1.05
4.12
1.00
1.00
9.47
f1 (ppm)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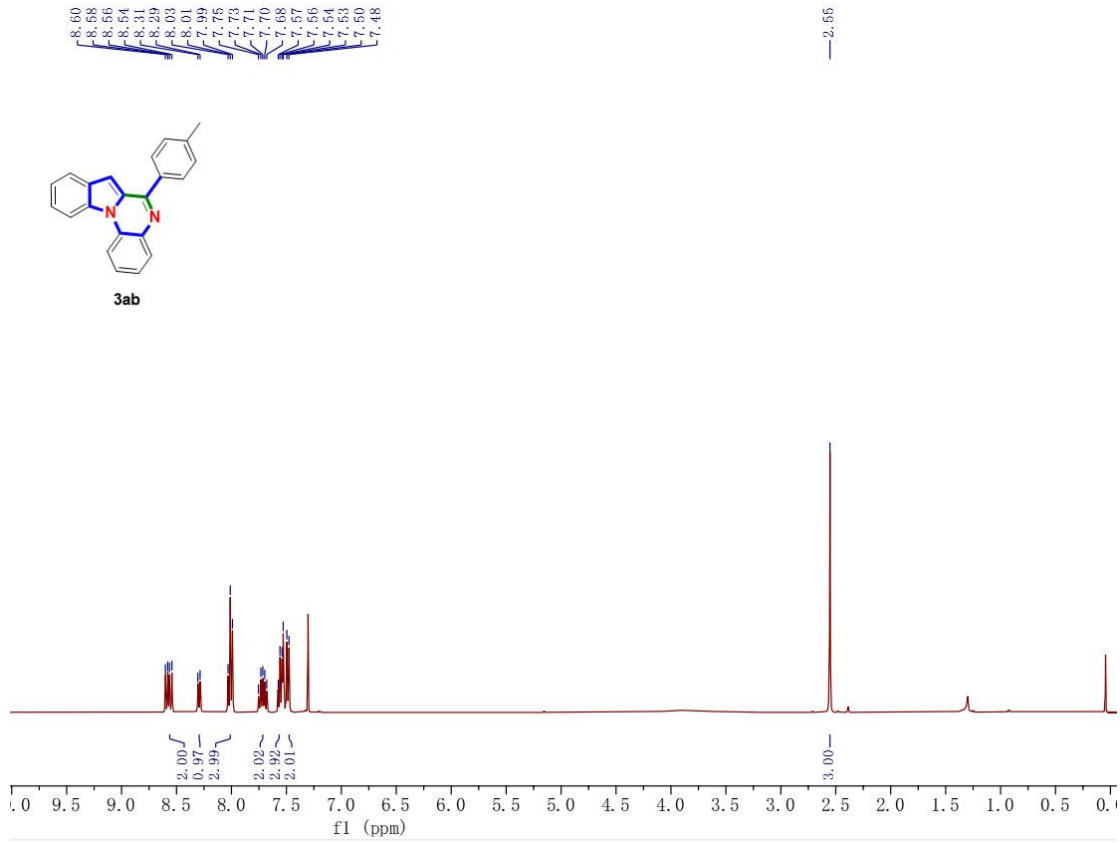
129.74
128.63
126.73
125.40
125.22
124.95
114.43
113.81
113.26
108.48
34.79
31.50
tBu
3pa
f1 (ppm)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8.58
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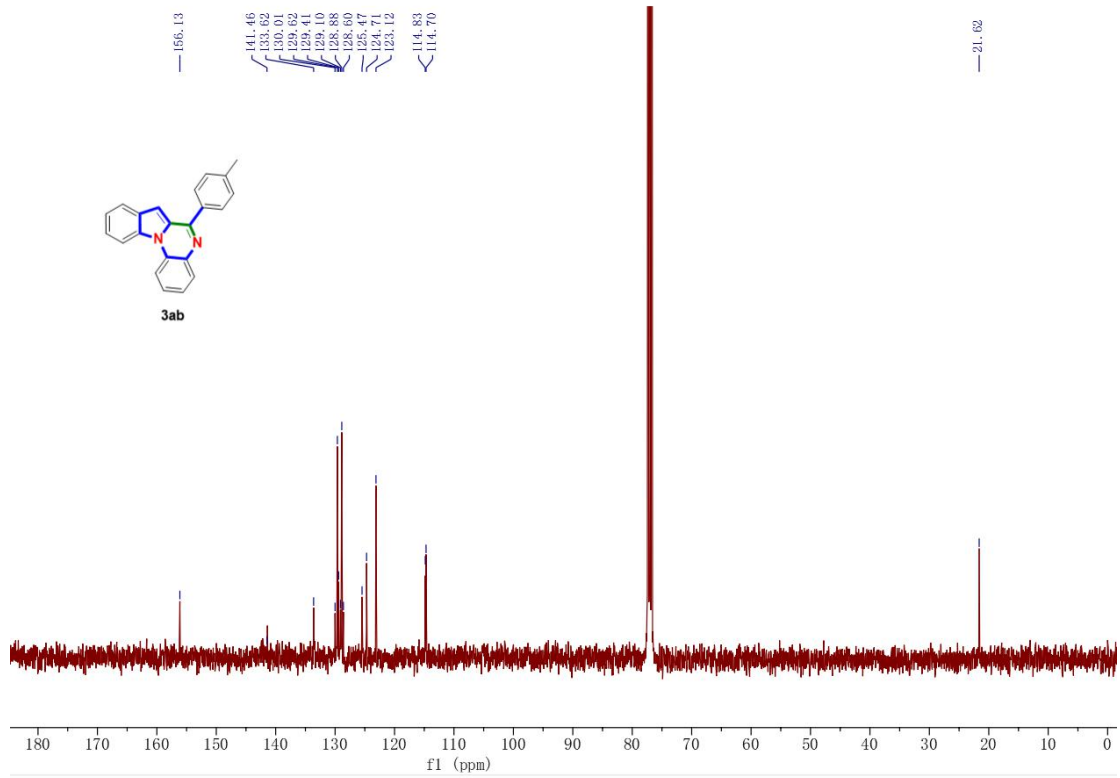
8.31
8.29
8.03
8.01
7.99
7.75
7.73
7.71
7.70
7.68
7.57
7.56
7.54
7.53
7.50
7.48
2.55
3ab
2.00
0.97
2.99
2.02
2.92
2.01
3.00
f1 (ppm)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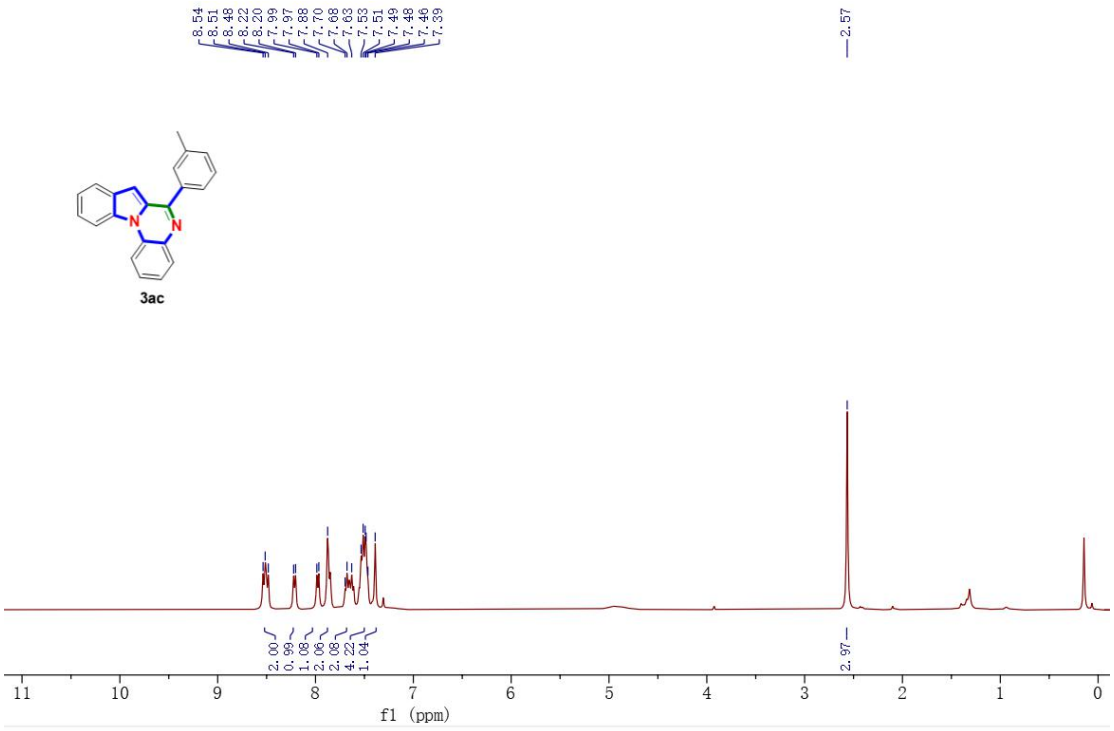
141.46
133.62
130.01
129.62
129.41
129.10
128.88
128.60
125.47
124.71
123.12
114.83
114.70
21.62
3ab
f1 (ppm)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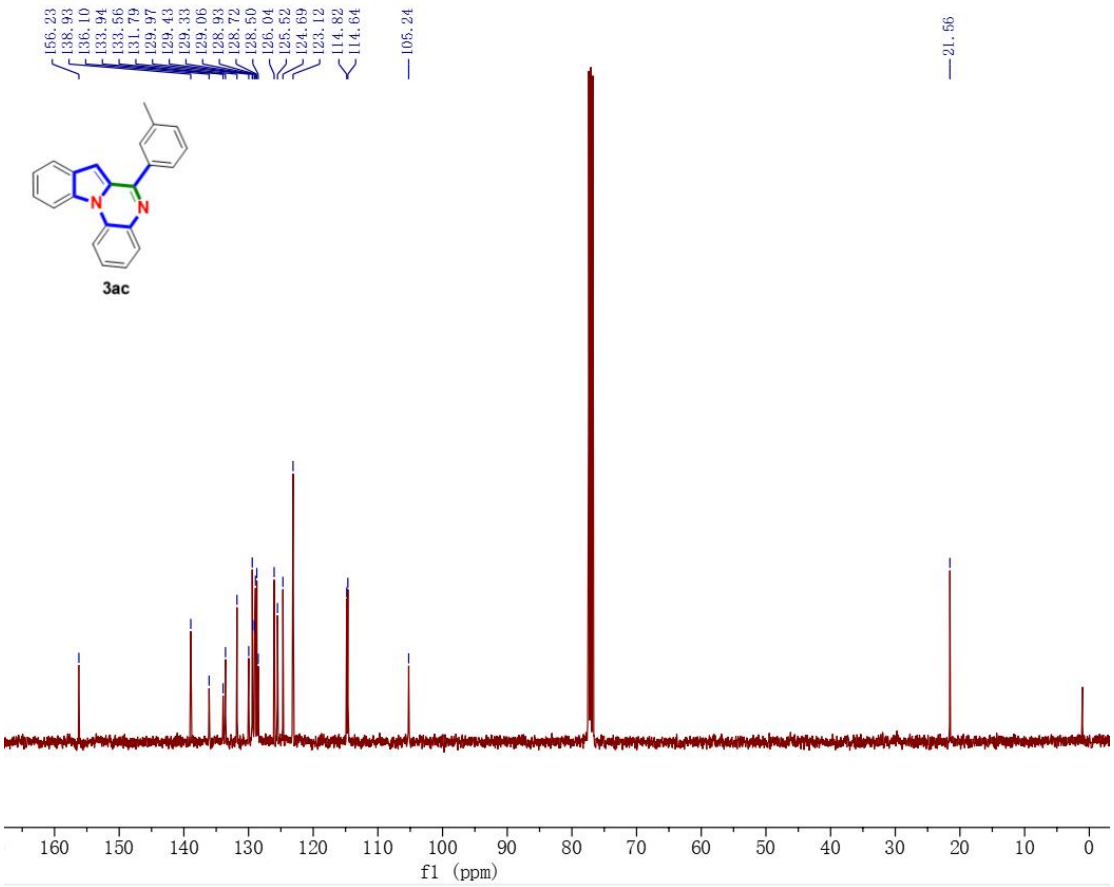
7.97
7.88
7.70
7.68
7.63
7.53
7.51
7.49
7.48
7.46
7.39
2.57
3ac
2.00
0.99
1.08
2.06
2.08
4.22
1.04
2.97
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


156.23
138.93
136.10
133.94
133.56
131.79
129.97
129.43
129.33
129.06
128.93
128.72
128.50
126.04
125.52
124.69
123.12
114.82
114.64
105.24
21.56
3ac
160
150
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130
120
110
100
90
80
70
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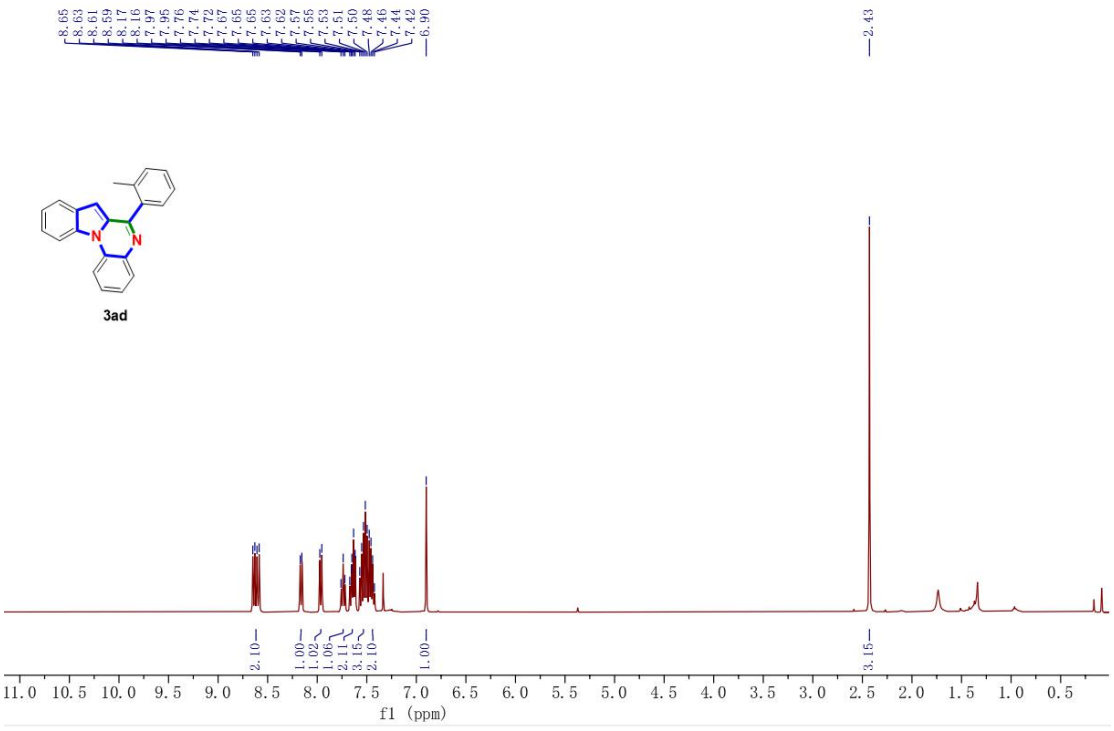
50
40
30
20
10
0
f1 (ppm)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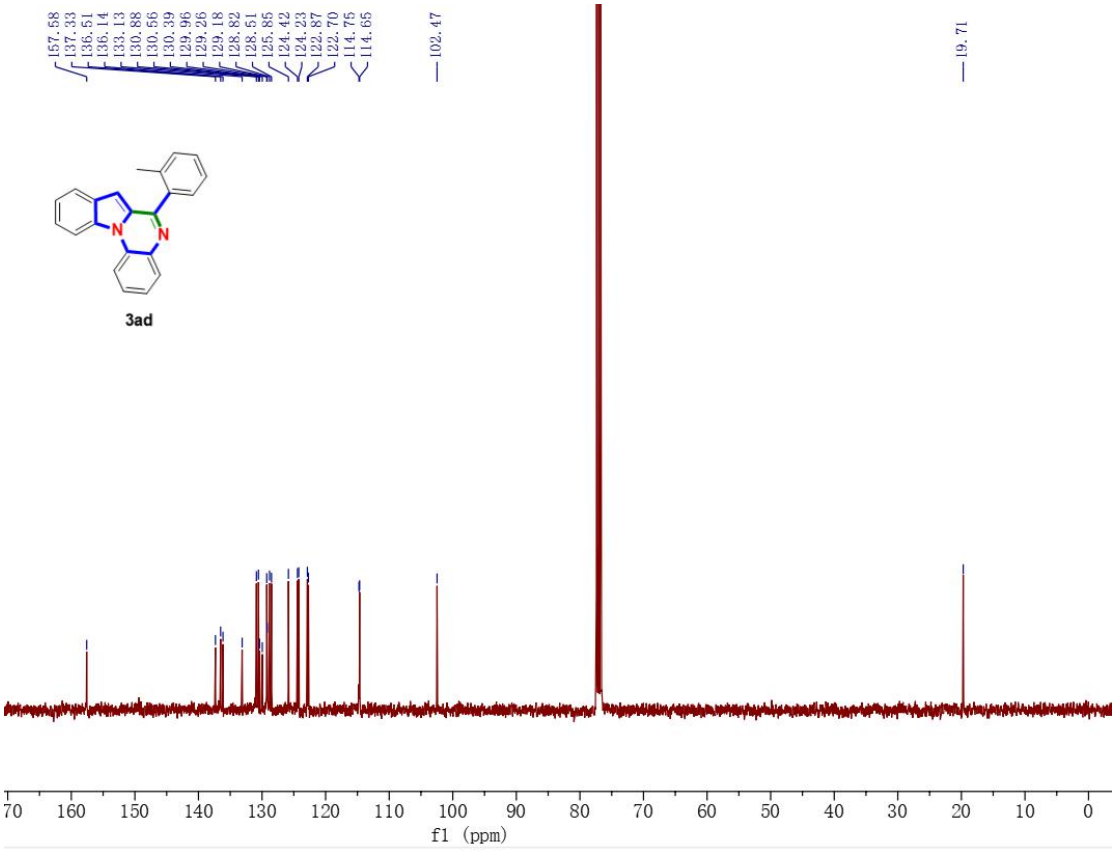
8.63
8.61
8.59
8.17
8.16
7.97
7.95
7.76
7.74
7.72
7.67
7.65
7.63
7.62
7.57
7.55
7.53
7.51
7.50
7.48
7.46
7.44
7.42
6.90
2.43
3ad
2.10
1.00
1.02
1.06
2.11
3.15
2.10
1.00
3.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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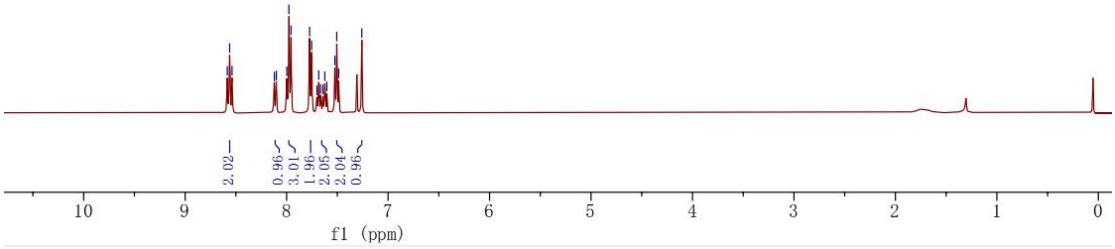
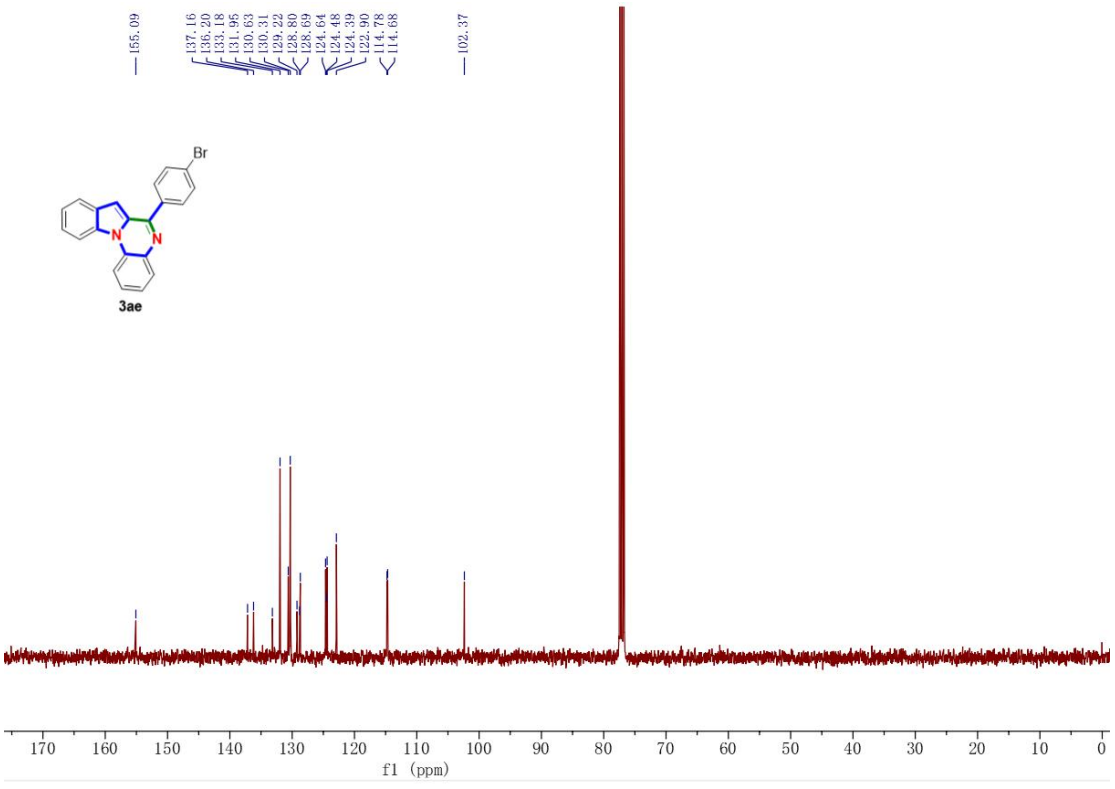
136.14
133.13
130.88
130.56
130.39
129.96
129.26
129.18
128.82
128.51
125.85
124.42
124.23
122.87
122.70
114.75
114.65
102.47
19.71
3ad
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.58
8.56
8.54
8.12
8.10
8.00
7.98
7.96
7.77
7.75
7.70
7.68
7.67
7.64
7.62
7.60
7.52
7.51
7.49
7.26


Br
N
N

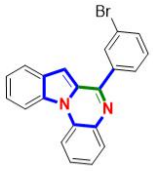
3ae


2.02
0.96
3.01
1.96
2.05
2.04
0.96
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

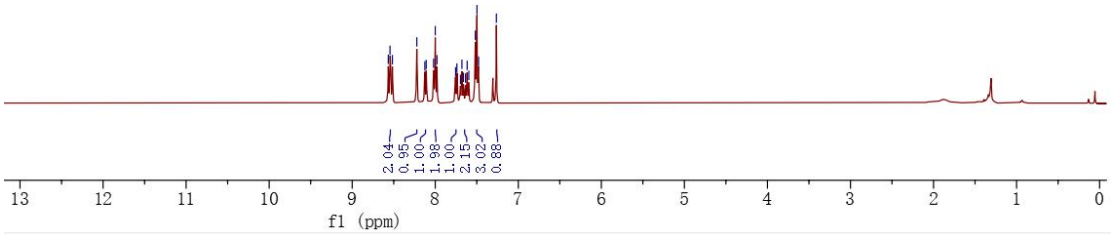

155.09
137.16
136.20
133.18
131.95
130.63
130.31
129.22
128.80
128.69
124.64
124.48
124.39
122.90
114.78
114.68
102.37
Br
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

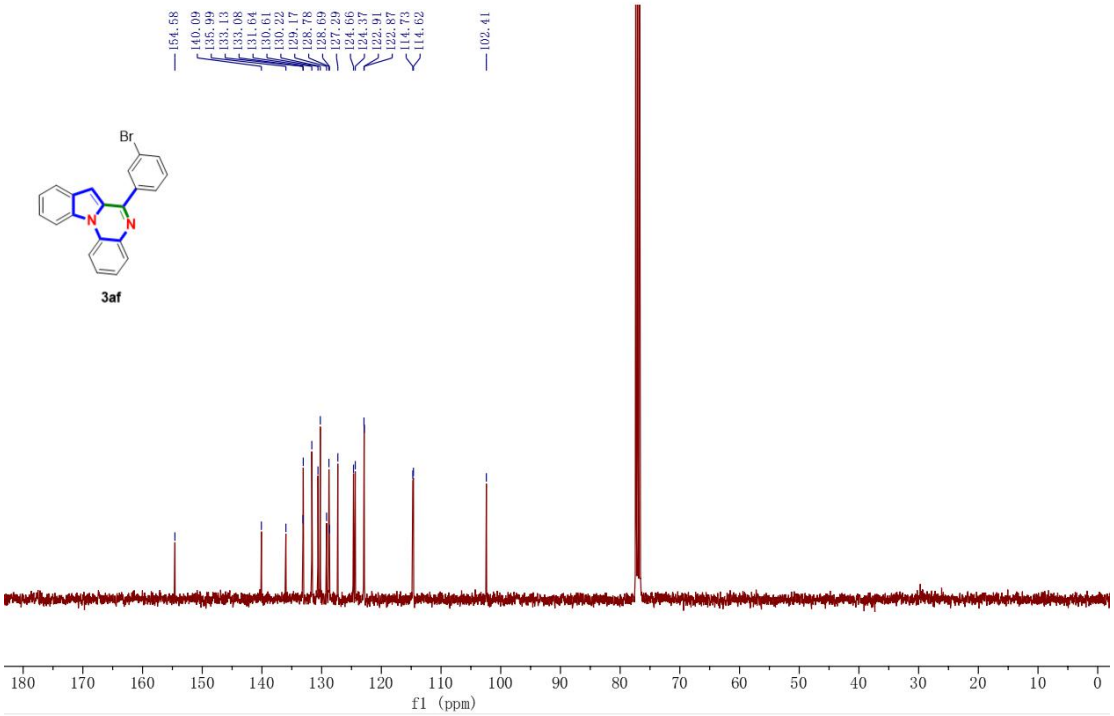
3ae


8.57
8.54
8.52
8.22
8.13
8.11
8.02
8.00
7.98
7.75
7.74
7.70
7.68
7.66
7.63
7.62
7.60
7.52
7.50
7.48
7.26


Br
N
N

3af

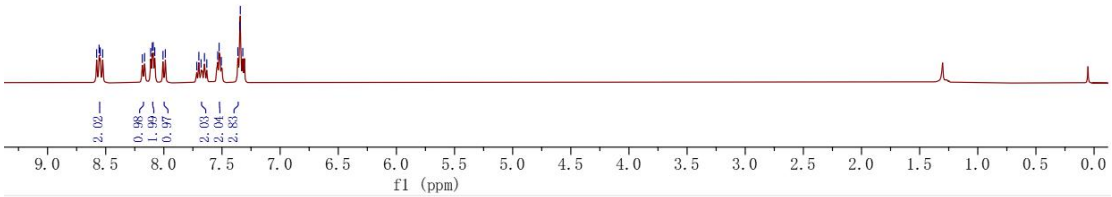

2.04
0.95
1.00
1.98
1.00
2.15
3.02
0.88
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


154.58
140.09
135.99
133.13
133.08
131.64
130.61
130.22
129.17
128.78
128.69
127.29
124.66
124.37
122.91
122.87
114.73
114.62
102.41
Br
N
N
3af
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

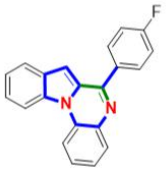

8.58
8.56
8.55
8.53
8.19
8.17
8.11
8.10
8.09
8.08
8.01
7.99
7.72
7.70
7.68
7.65
7.63
7.54
7.52
7.51
7.36
7.35
7.34
7.32


F
N
N

3ag


2.02
0.98
1.99
0.97
2.03
2.04
2.83
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.25
162.76
155.06
135.80
134.05
133.19
130.75
130.66
130.29
130.14
129.20
128.84
128.59
124.71
124.38
122.87
115.91
115.69
114.73
114.65
102.78


F
N
N

3ag

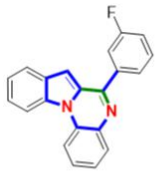
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
N
N

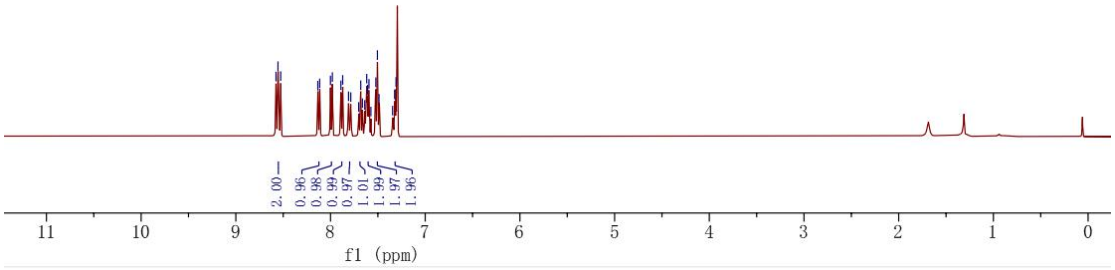
3ag

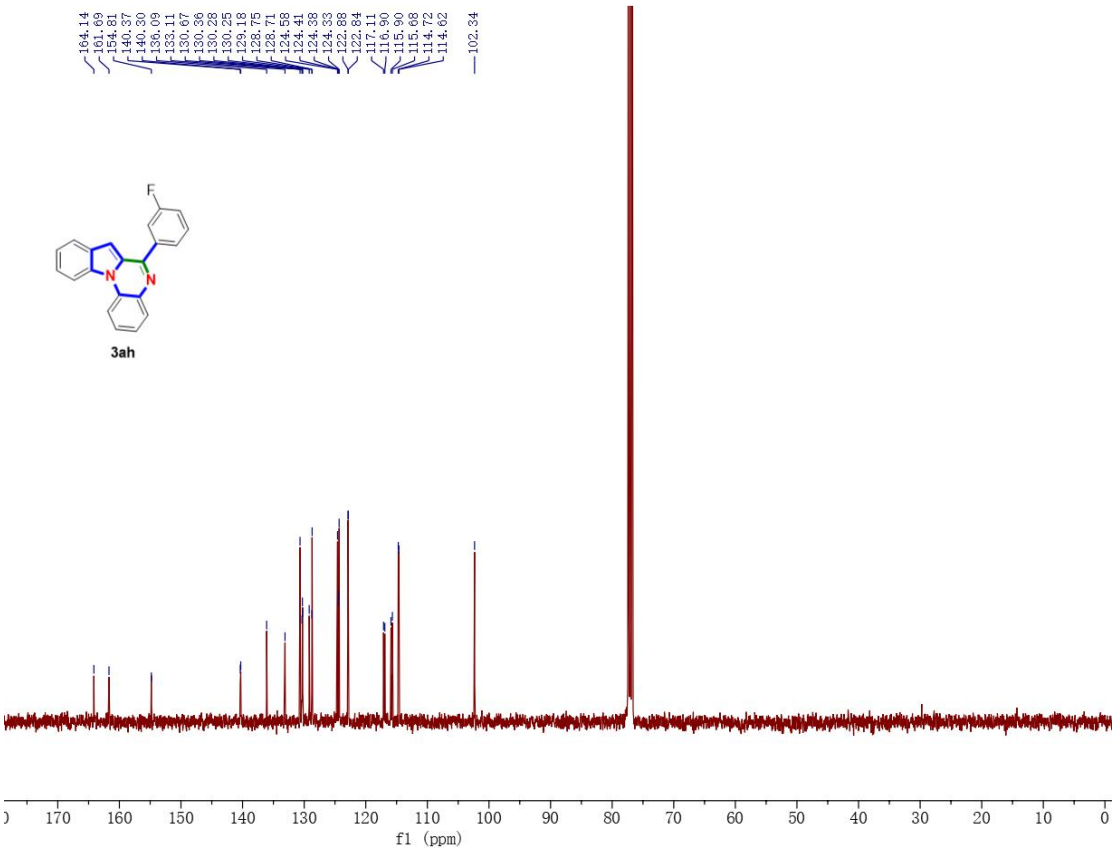
-76.1
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
f1 (ppm)

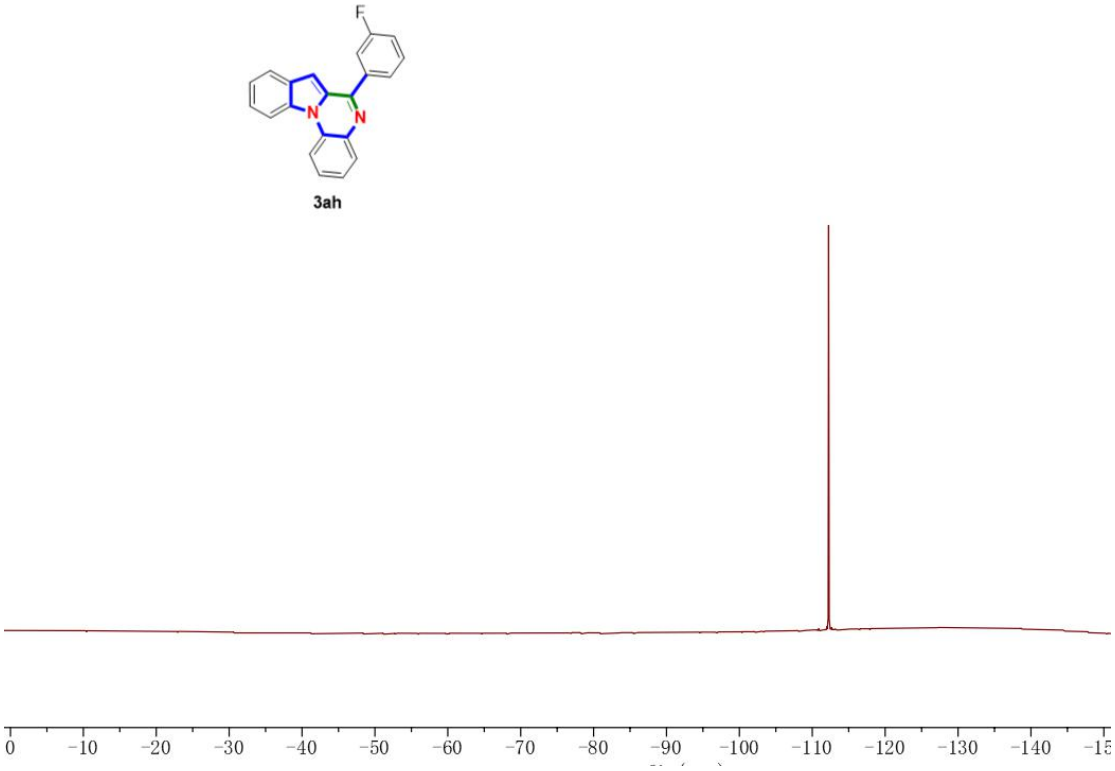

8.58
8.55
8.53
8.13
8.11
8.00
7.98
7.89
7.87
7.81
7.79
7.70
7.68
7.66
7.64
7.62
7.61
7.59
7.57
7.52
7.50
7.49
7.34
7.32
7.31

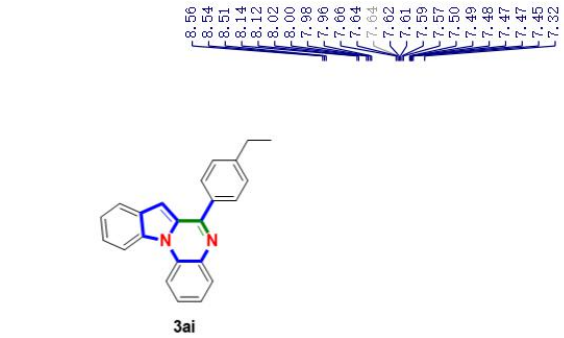

F
N
N

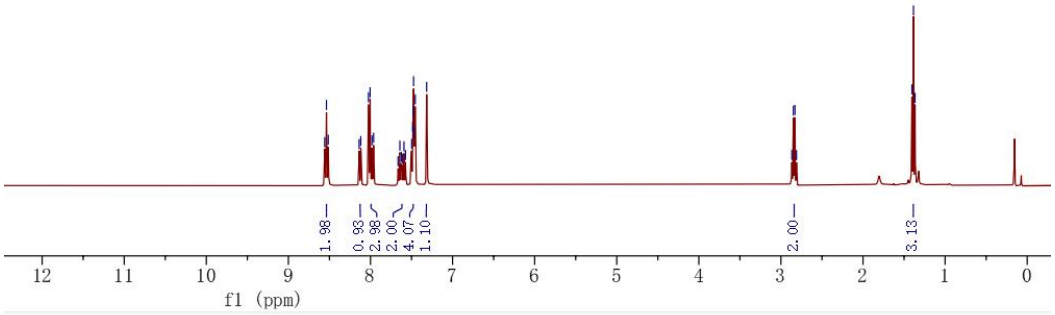
3ah

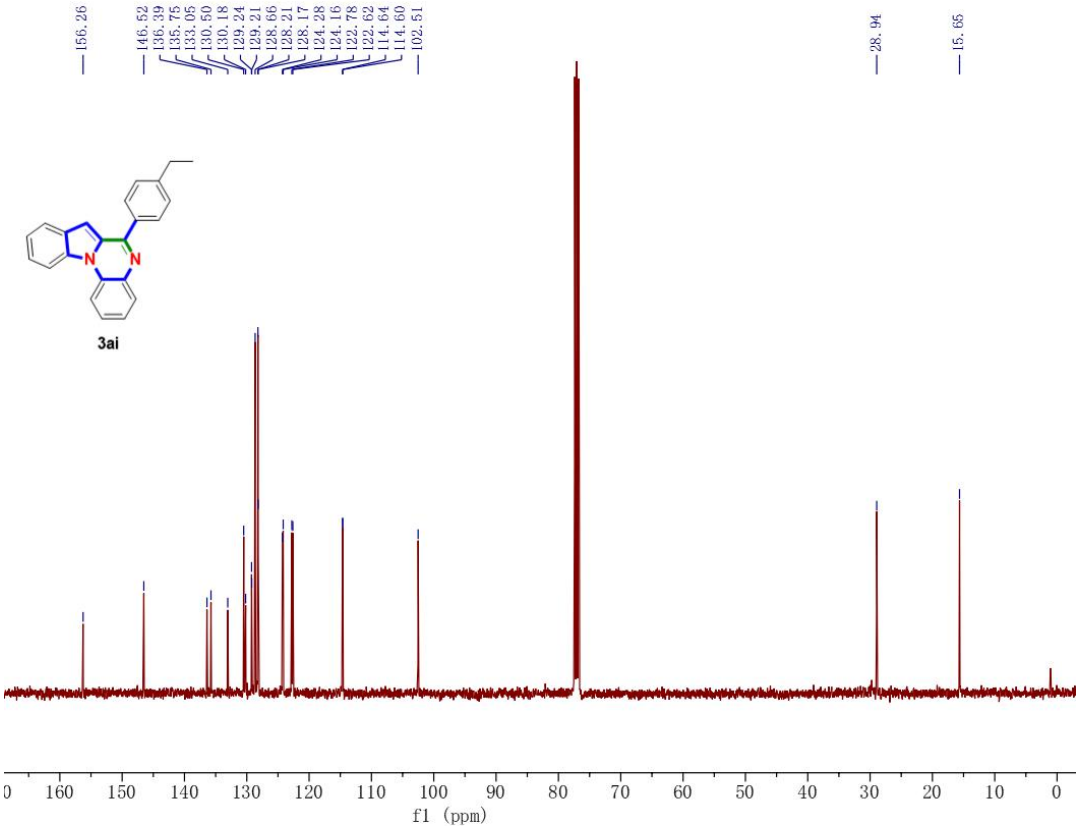

2.00
0.96
0.98
0.99
0.97
1.01
1.00
1.97
1.96
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


164.14
161.69
154.81
140.37
140.30
136.09
133.11
130.67
130.36
130.28
130.25
129.18
128.75
128.71
124.58
124.41
124.38
124.33
122.88
122.84
117.11
116.90
115.90
115.68
114.72
114.62
102.34
F
N
N
3ah
f1 (ppm)

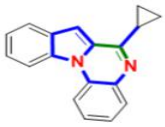

F
N
N
3ah


8.56
8.54
8.51
8.14
8.12
8.02
8.00
7.98
7.96
7.66
7.64
7.64
7.62
7.61
7.59
7.57
7.50
7.49
7.48
7.47
7.47
7.45
7.32
2.87
2.85
2.83
2.81
1.40
1.39
1.37
3ai

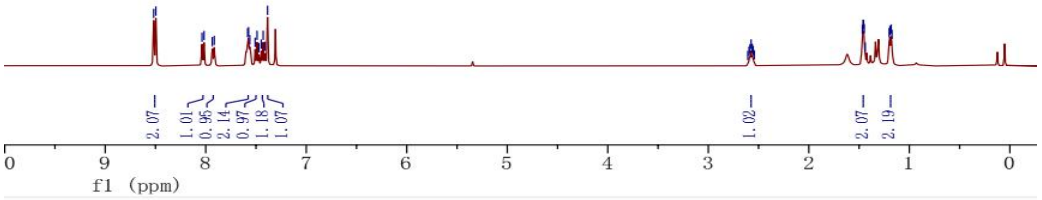

1.98
0.93
2.98
2.00
4.07
1.10
2.00
3.13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


156.26
146.52
136.39
135.75
133.05
130.50
130.18
129.24
129.21
128.66
128.21
128.17
124.28
124.16
122.78
122.62
114.64
114.60
102.51
28.94
15.65
3ai
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

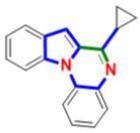

8.52
8.50
8.04
8.02
7.94
7.92
7.58
7.57
7.56
7.51
7.49
7.47
7.45
7.43
7.41
7.38
2.61
2.59
2.59
2.57
2.56
2.55
2.54
1.47
1.46
1.46
1.45
1.44
1.20
1.19
1.18
1.17



3aj

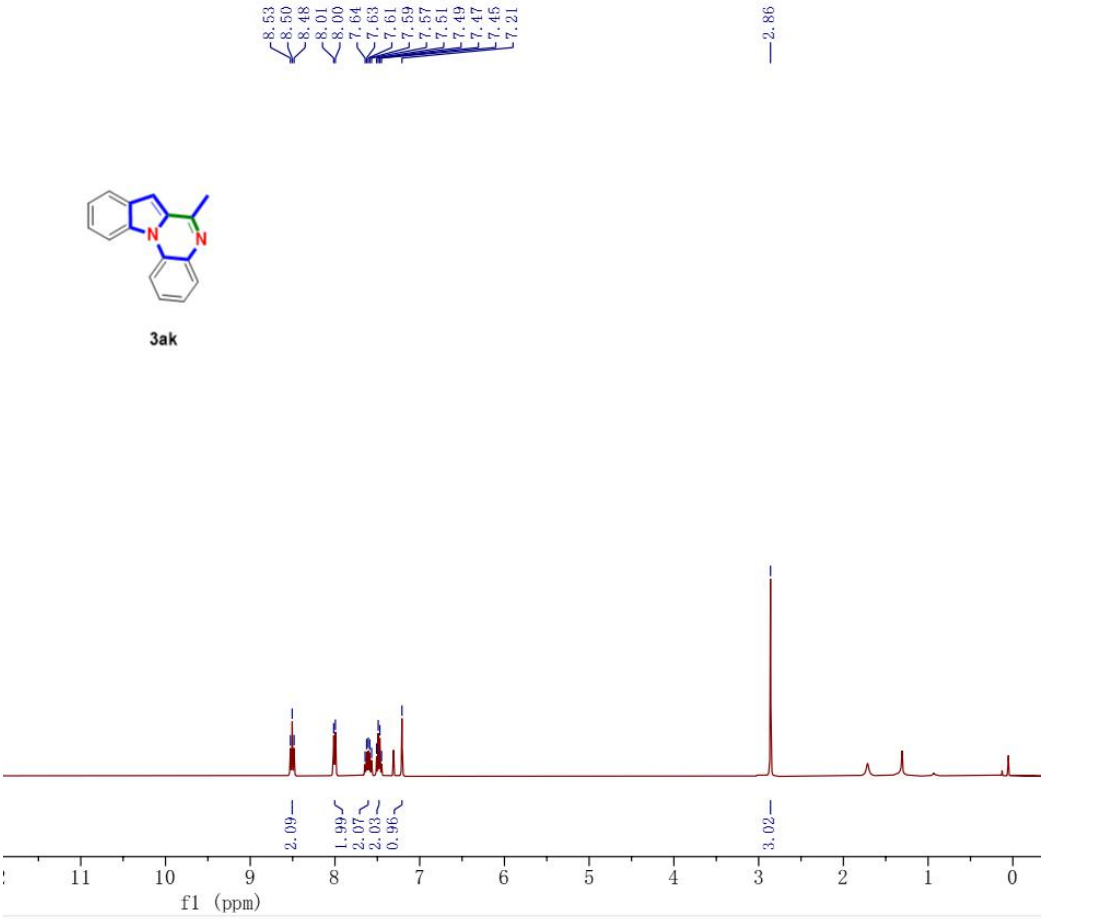

2.07
1.01
0.96
2.14
0.97
1.18
1.07
1.02
2.07
2.19
0
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

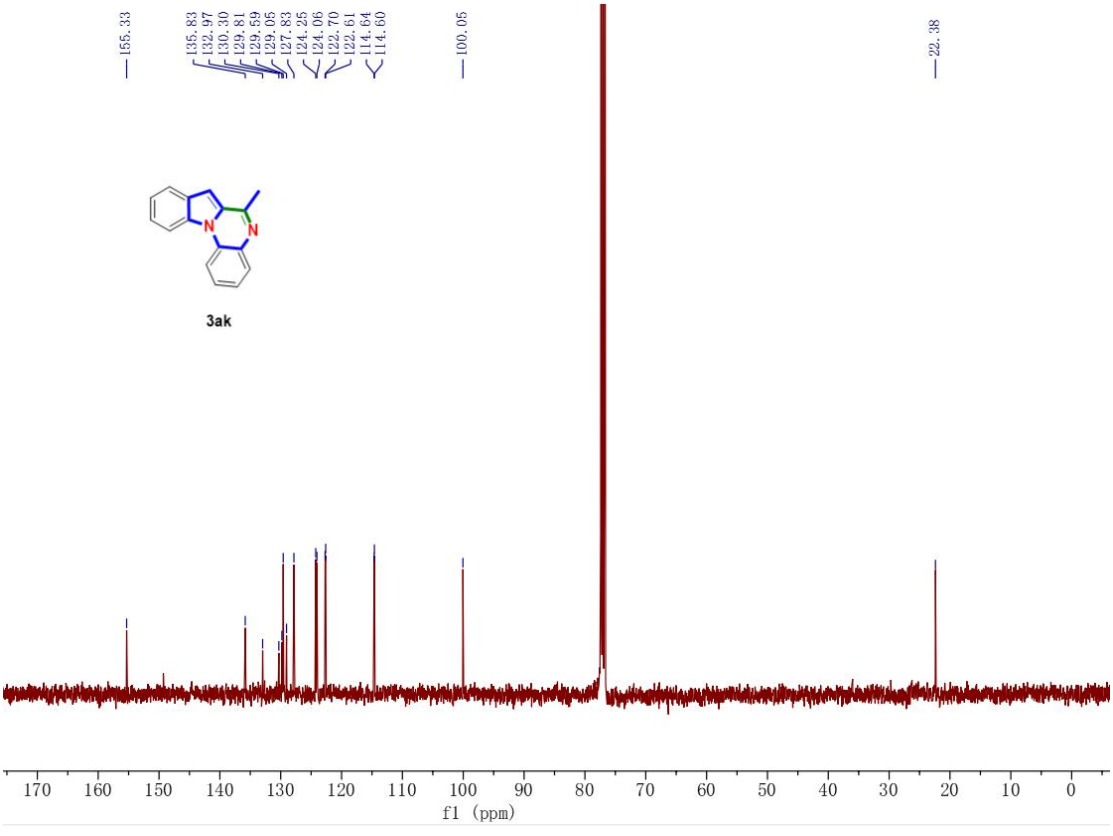

159.08
136.06
132.98
130.38
130.05
129.60
129.18
127.13
124.00
123.91
122.65
122.47
114.64
114.55
99.32
14.29
9.18

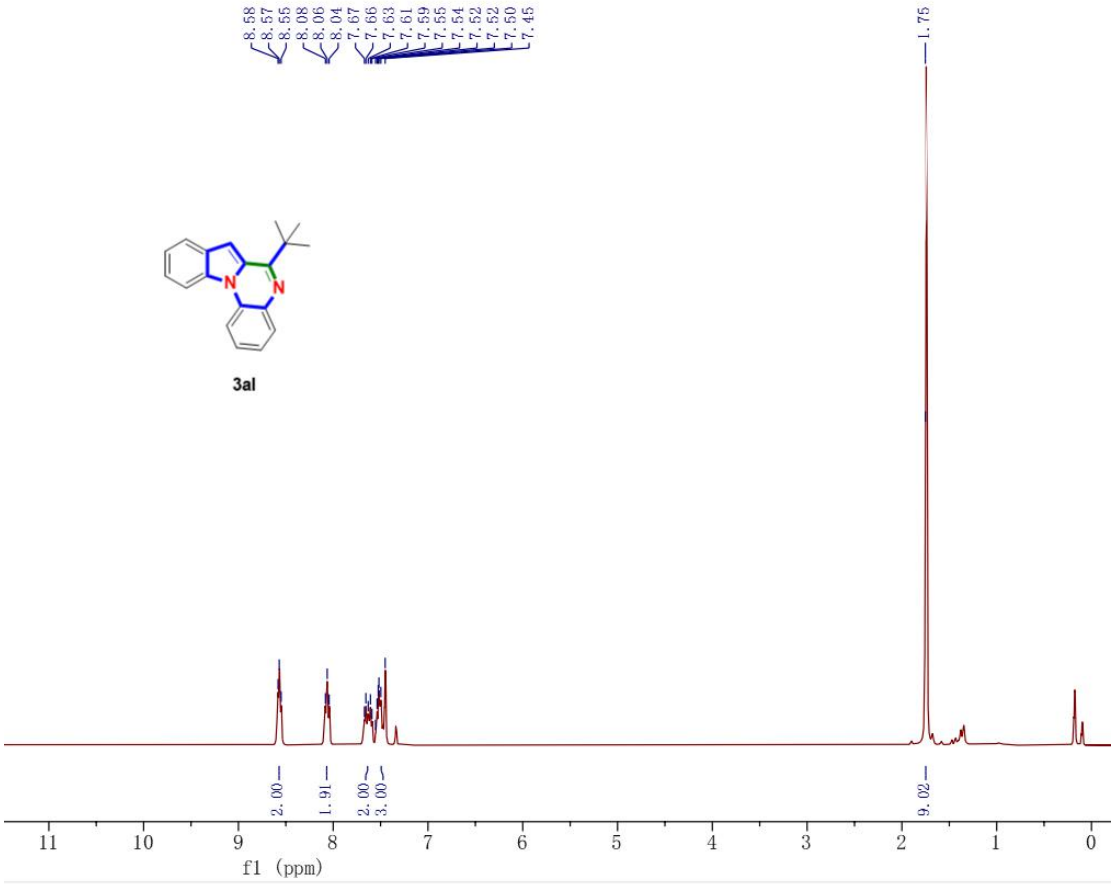


3aj

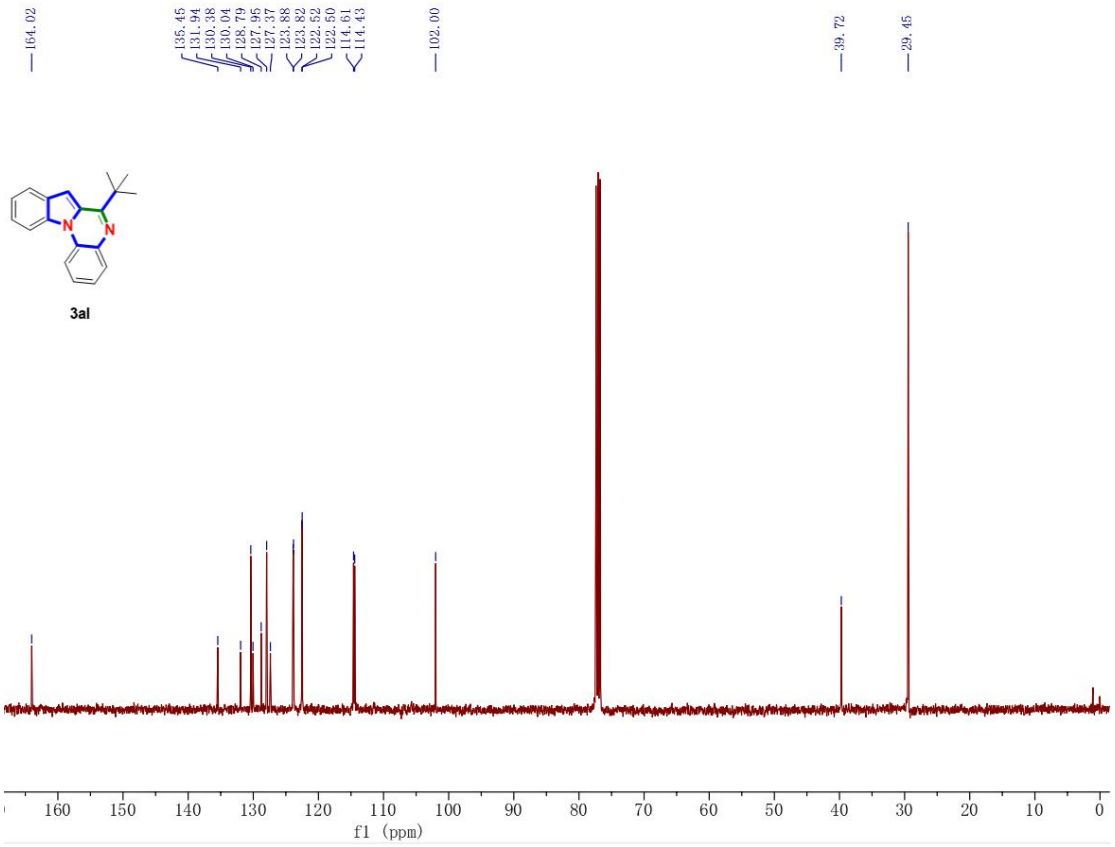
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.53
8.50
8.48
8.01
8.00
7.64
7.63
7.61
7.59
7.57
7.51
7.49
7.47
7.45
7.21
2.86
3ak
2.09
1.99
2.07
2.03
0.96
3.02
f1 (ppm)

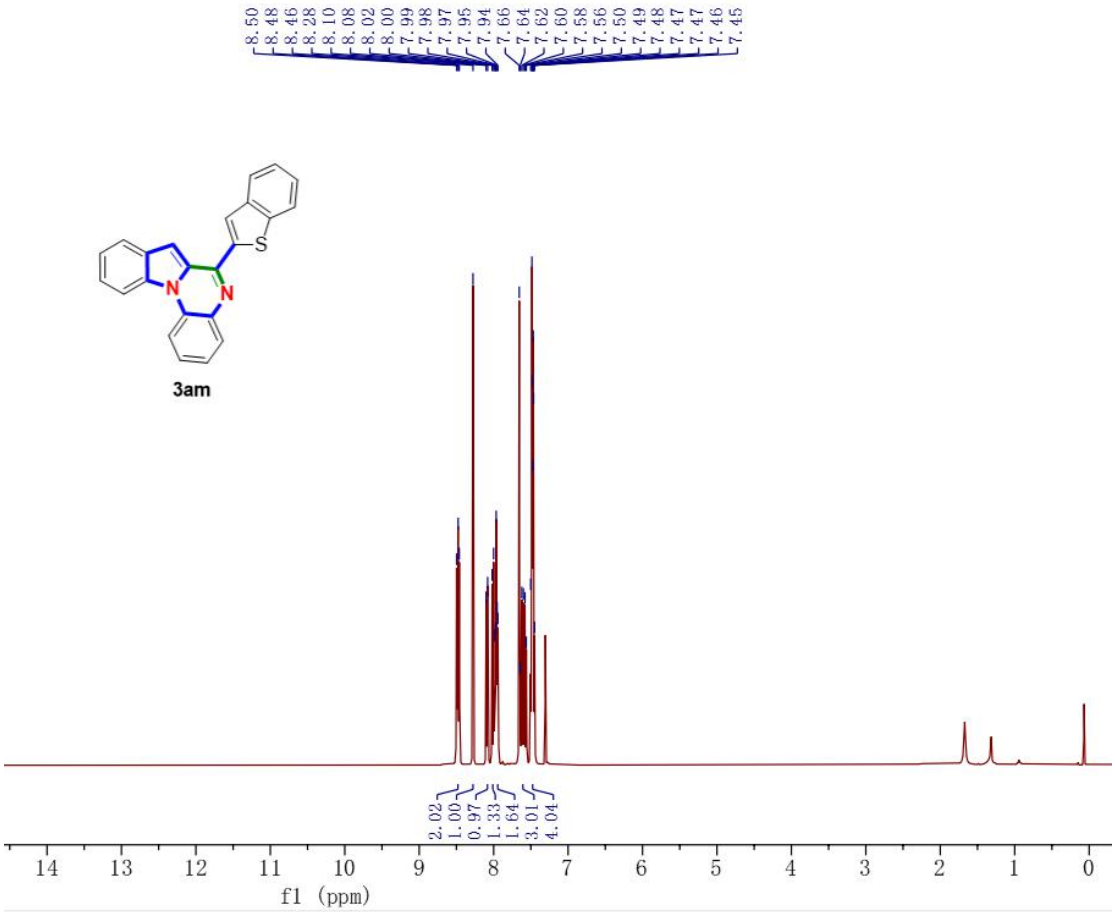

155.33
135.83
132.97
130.30
129.81
129.59
129.05
127.83
124.25
124.06
122.70
122.61
114.64
114.60
100.05
22.38
3ak
f1 (ppm)

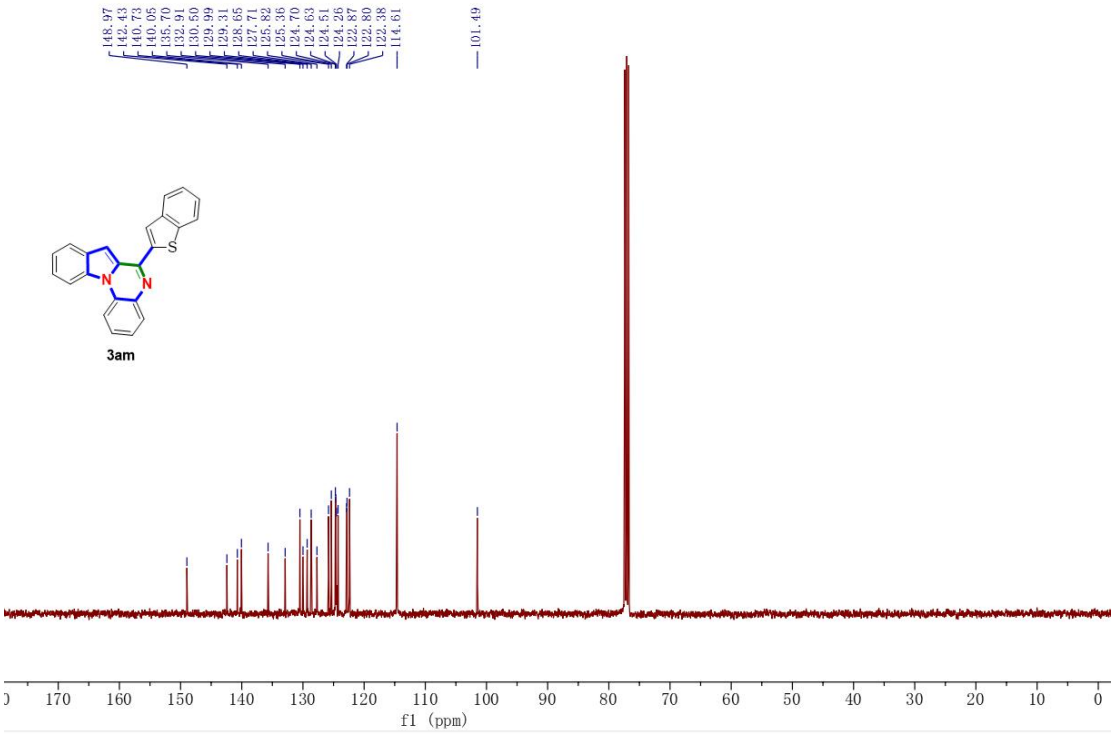

8.58
8.57
8.55
8.08
8.06
8.04
7.67
7.66
7.63
7.61
7.59
7.55
7.54
7.52
7.52
7.50
7.45
1.75
2.00
1.91
2.00
3.00
9.02
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

3al


164.02
135.45
131.94
130.38
130.04
128.79
127.95
127.37
123.88
123.82
122.52
122.50
114.61
114.43
102.00
39.72
29.45
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3al


8.50
8.48
8.46
8.28
8.10
8.08
8.02
8.00
7.99
7.98
7.97
7.95
7.94
7.66
7.64
7.62
7.60
7.58
7.56
7.50
7.49
7.48
7.47
7.47
7.46
7.45
3am
2.02
1.00
0.97
1.33
1.64
3.01
4.04
f1 (ppm)


148.97
142.43
140.73
140.05
135.70
132.91
130.50
129.99
129.31
128.65
127.71
125.82
125.36
124.70
124.63
124.51
124.25
122.87
122.80
122.38
114.61
101.49
3am
f1 (ppm)


8.60
8.59
8.57
8.56
8.54
8.24
8.22
8.17
8.15
8.10
8.07
8.05
8.05
8.01
8.00
7.99
7.98
7.72
7.70
7.68
7.67
7.65
7.63
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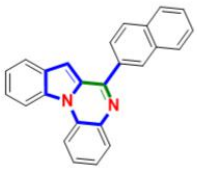
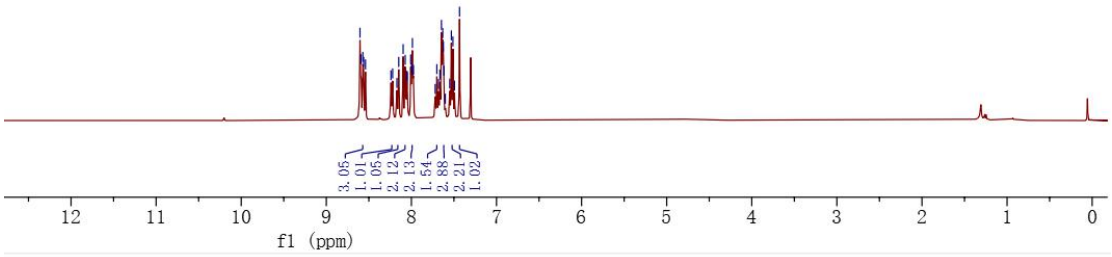
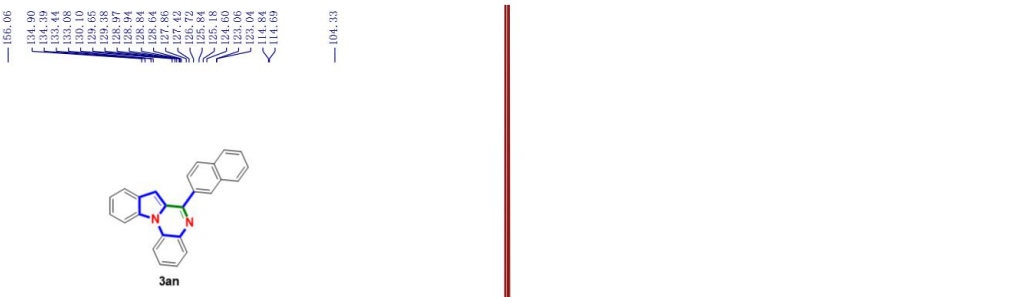
7.60
7.55
7.53
7.51
7.49
7.43

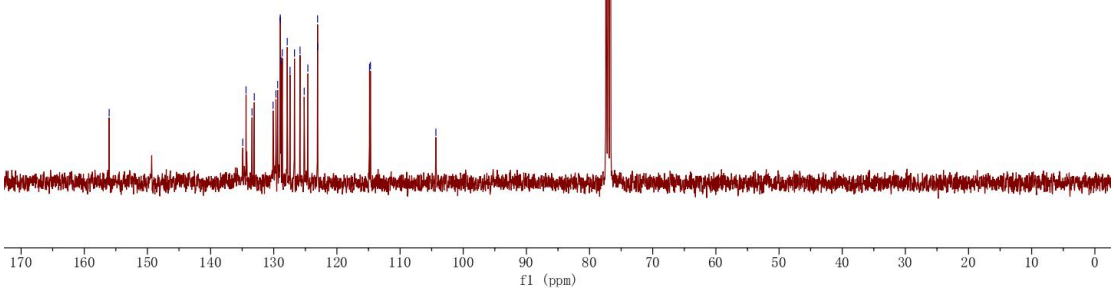


3an

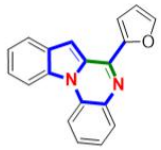

3.05
1.01
1.05
2.12
2.13
1.54
2.88
2.21
1.02
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


156.06
134.90
134.39
133.44
133.08
130.10
129.65
129.38
128.97
128.94
128.84
128.64
127.86
127.42
126.72
125.84
125.18
124.60
123.06
123.04
114.84
114.69
104.33

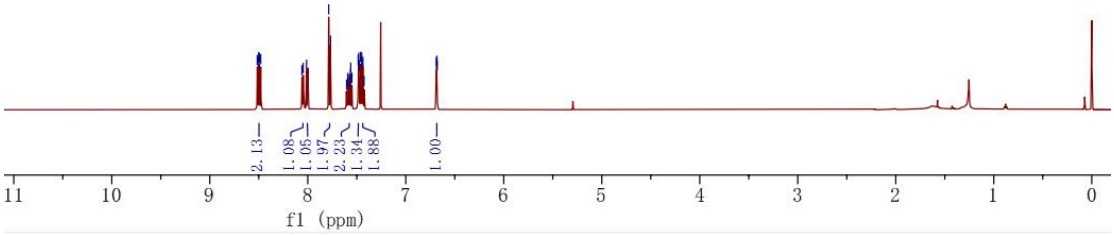
3an


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

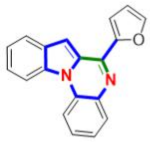

8.52
8.50
8.50
8.49
8.48
8.06
8.05
8.01
7.79
7.77
7.60
7.59
7.58
7.57
7.56
7.56
7.55
7.49
7.48
7.47
7.46
7.45
7.44
7.43
6.69
6.68
6.68
6.68


O
N
N

3ao


2.13
1.08
1.05
1.97
2.23
1.34
1.88
1.00
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

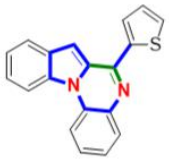

152.41
144.98
144.68
135.81
132.80
130.29
130.11
129.51
128.26
126.86
124.41
124.24
122.94
122.76
114.65
114.61
113.33
112.12
102.08


O
N
N

3ao

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.50
8.48
8.46
8.08
8.08
8.07
8.06
8.00
7.98
7.64
7.62
7.61
7.59
7.55
7.49
7.47
7.46
7.44
7.30



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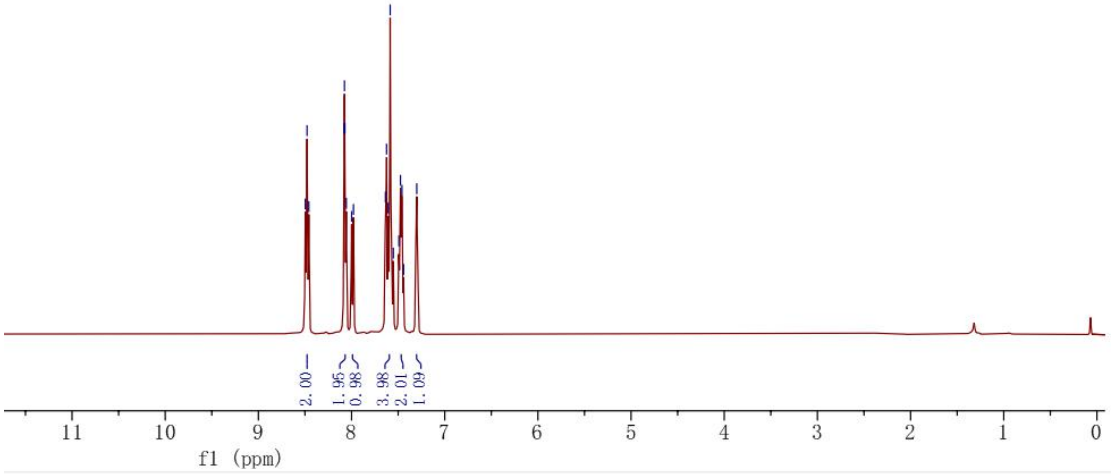
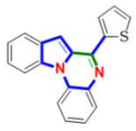

2.00
1.95
0.98
3.98
2.01
1.09
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


148.95
142.01
135.77
132.98
130.24
129.94
129.28
128.97
128.64
128.25
127.85
127.82
124.46
124.22
122.79
114.60
101.68



3ap

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)