

Supporting Information

Regioselective synthesis of 3,4-diarylpyrimido[1,2-*b*]indazole derivatives enabled by iron-catalyzed ring-opening of styrene oxides

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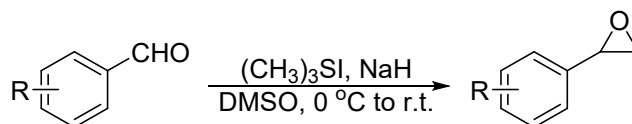
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1. General

All substrates 3-aminoindazoles (**1**), aldehydes (**2**) and styrene oxide (**3a**) reagents were commercially available and used without further purification. All 3-aminoindazoles (**1**) and aldehydes (**2**) and styrene oxide (**3**) are known compounds. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). ¹H spectra were recorded in CDCl₃ on 400 MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ¹³C spectra were recorded in CDCl₃ on 100 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS analysis of compounds was performed with a time-of-flight mass spectrometer (microTOF-Q, Bruker Daltonik, Germany) equipped with an electrospray ionization source. The X-ray crystal-structure determinations of **4l** were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected. All reactions were heated by a metal sand bath (WATTCAS, LAB-500, <https://www.wattcas.com>).

2. Typical procedures for the synthesis of substrates (3b-3i)



Trimethylsulfonium iodide (20.0 mmol) and sodium hydride (60% in oil, 20.0 mmol) were dissolved in DMSO (15 mL) at 0 °C under an argon atmosphere. After stirring for 20 minutes, the corresponding aldehyde (12.0 mmol) dissolved in DMSO (20 mL) was added dropwise. The reaction was then stirred at room temperature overnight. The mixture was poured into cold water (60 mL), and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water (30 mL × 2), and dried over Na₂SO₄. The crude epoxide was purified using flash chromatography.

3. General procedure for the synthesis of compounds 4 (4a as an example)

3-Aminoindazole **1a** (133.15 mg, 1.0 mmol), benzaldehyde **2a** (106.12 mg, 1.0 mmol), styrene oxide **3a** (120.15 mg, 1.0 mmol), FeCl₃ (40.55 mg, 0.25 mmol), 1,4-dioxane (2 mL) were charged into a pressure tube (35 mL) and were stirred at 110 °C for 14 h. After disappearance of the reactant (monitored by TLC), added 50 mL water to the mixture, then

extracted with EtOAc 3 times (3×50 mL). The extract was dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the product **4a** as a yellow solid (273.2 mg, 85% yield).

4. General procedure for the synthesis of compounds **5** (**5a** as an example)

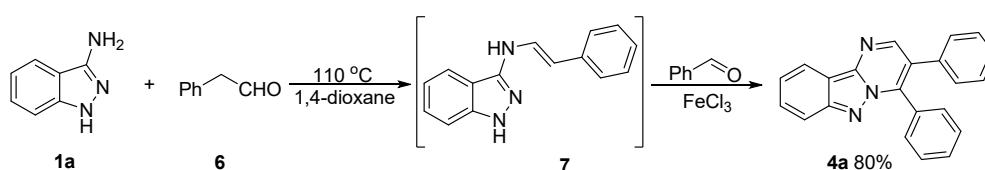
3-Aminoindazole **1a** (66.57 mg, 0.5 mmol), styrene oxide **3a** (120.15 mg, 1.0 mmol), CuBr (7.2 mg, 0.05 mmol), TfOH (7.5 mg, 0.05 mmol), DMSO (2 mL) were charged into a pressure tube (35 mL) and were stirred at 130 °C for 16 h. After disappearance of the reactant (monitored by TLC), added 50 mL water to the mixture, then extracted with EtOAc 3 times (3×50 mL). The extract was dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 8:1) to afford the product **5a** as a yellow solid (199.2 mg, 57% yield).

5. Experimental details

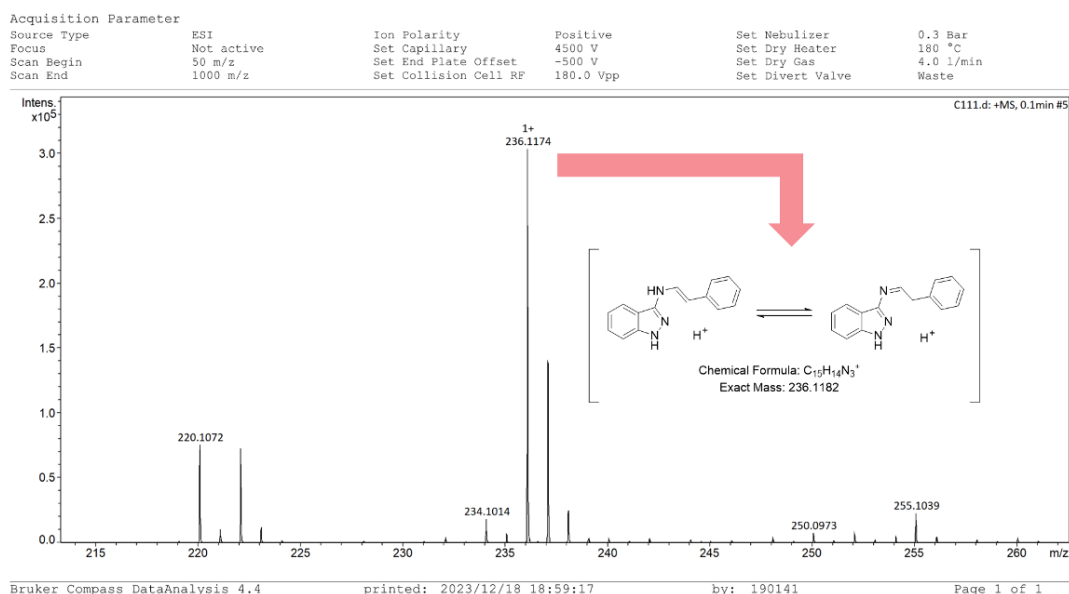
(1) The methodology applicable for scale-up synthesis (**4a** as an example)

3-Aminoindazole **1a** (666 mg, 5.0 mmol), benzaldehyde **2a** (531 mg, 5.0 mmol), styrene oxide **3a** (600 mg, 5.0 mmol), FeCl_3 (203 mg, 1.25 mmol), 1,4-dioxane (10 mL) were charged into a pressure tube (150 mL) and were stirred at 110 °C. After disappearance of the reactant (monitored by TLC), and added 250 mL water to the mixture, then extracted with EtOAc 3 times (3×250 mL). The extract was dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the product **4a** as a yellow solid (1.28 g, 80% yield).

(2) Control experiment: (Scheme 5b)

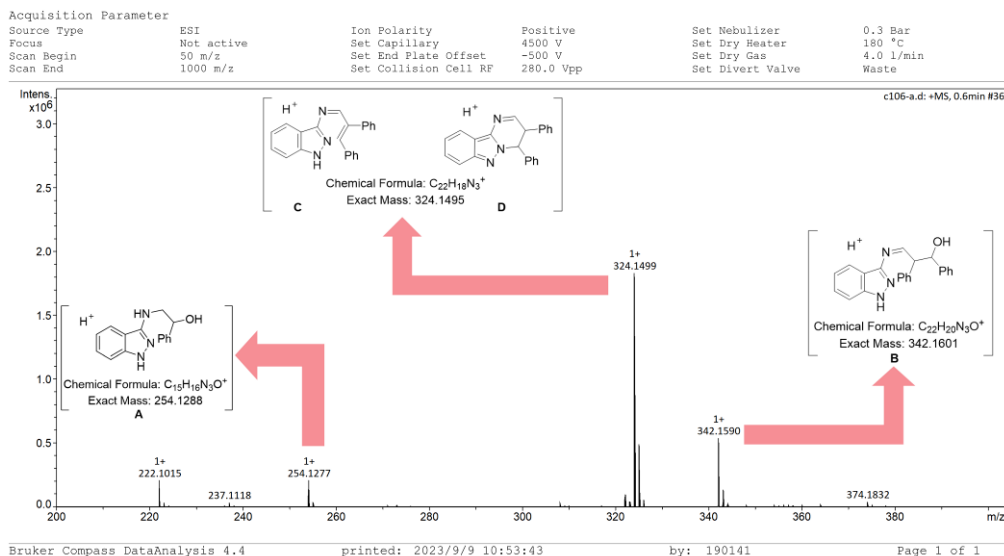


3-Aminoindazoles **1a** (133.15 mg, 1.0 mmol), phenylacetaldehyde **6** (120.15 mg, 1.0 mmol) and 1,4-dioxane (2 mL) were charged into a pressure tube (35 mL) and were stirred at 110 °C for 4h. Delightfully, 236.1174 was detected by HRMS. It is speculated that 236.1174 may belong to enamine intermediate **7** or imine intermediate with identical m/z values. HRMS (ESI): m/z [M + H]⁺ calcd for C₁₅H₁₄N₃: 236.1182; found: 236.1174. Then, benzaldehyde **2a** (106.12 mg, 1.0 mmol) and FeCl₃ (40.55 mg, 0.25 mmol) were added without further purification, afterward, the mixture was stirred at 110 °C for 10 h. Added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was dried over anhydrous Na₂SO₄ and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the product **4a** as a yellow solid (257.1 mg, 80% yield).

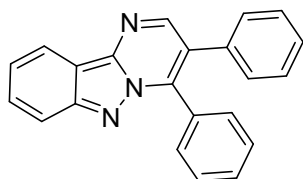


(3) Analysis of the reaction solution by HRMS

3-Aminoindazole **1a** (133.15 mg, 1.0 mmol), benzaldehyde **2a** (106.12 mg, 1.0 mmol), styrene oxide **3a** (120.15 mg, 1.0 mmol), FeCl₃ (40.55 mg, 0.25 mmol), 1,4-dioxane (2 mL) were charged into a tube (35 mL) and were stirred at 110 °C for 14 h under an Ar atmosphere. Delightfully, 254.1277, 324.1499 and 342.1590 were detected in situ during analysis of the reaction solution by HRMS. It is speculated that 254.1277 may belong to intermediate **A** {HRMS (ESI): m/z [M + H]⁺ calcd for C₁₅H₁₆N₃O: 254.1288; found: 254.1277.}, 342.1590 may belong to intermediate **B** {HRMS (ESI): m/z [M + H]⁺ calcd for C₂₂H₂₀N₃O: 342.1601; found: 342.1590.}. Another 324.1499 may belong to intermediate **C** or **D** {HRMS (ESI): m/z [M + H]⁺ calcd for C₂₂H₁₈N₃: 324.1495; found: 324.1499.}, and the structures of the intermediates **C** and **D** could not be discerned from one another.

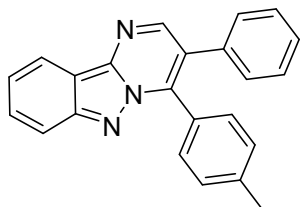


6. Characterization data for compounds



3,4-diphenylpyrimido[1,2-*b*]indazole (4a):

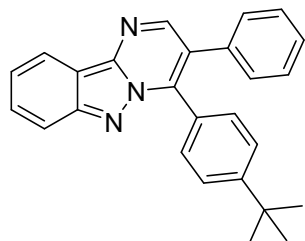
Yield 85% (273.2 mg; petroleum ether/EtOAc = 20:1); light yellow solid; mp 227–229 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.75 (s, 1H), 8.37 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 8.8$ Hz, 1H), 7.63–7.58 (m, 1H), 7.57–7.53 (m, 2H), 7.46–7.40 (m, 3H), 7.34–7.28 (m, 4H), 7.24–7.20 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 151.3, 147.2, 143.7, 142.9, 135.0, 130.7, 130.2, 130.1, 130.0, 129.6, 128.5(2), 128.5(0), 127.8, 125.3, 121.0, 120.5, 116.7, 113.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{22}H_{16}N_3$: 322.1339; found: 322.1336.



3-phenyl-4-(*p*-tolyl)pyrimido[1,2-*b*]indazole (4b):

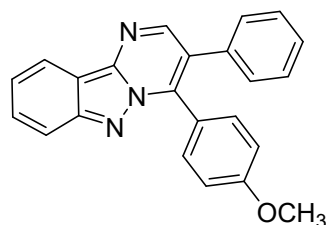
Yield 84% (281.8 mg; petroleum ether/EtOAc = 30:1); light yellow solid; mp 204–206 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.64 (s, 1H), 8.27 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.53–7.47 (m, 1H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.25–7.20 (m, 4H), 7.16–7.12 (m, 4H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 151.2, 147.2, 143.7, 143.1, 140.3, 135.2,

130.6, 130.2, 129.5, 129.2, 128.5, 127.7, 126.9, 125.1, 120.9, 120.5, 116.7, 113.6, 21.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{23}H_{18}N_3$: 336.1495; found: 336.1499.



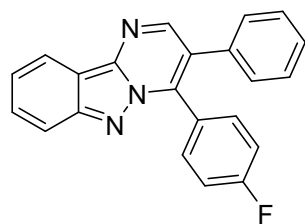
4-(4-(tert-butyl)phenyl)-3-phenylpyrimido[1,2-*b*]indazole (4c):

Yield 81% (305.8 mg; petroleum ether/EtOAc = 30:1); light yellow solid; mp 241–243 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.73 (s, 1H), 8.36 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.62–7.57 (m, 1H), 7.52–7.48 (m, 2H), 7.44–7.41 (m, 2H), 7.34–7.28 (m, 4H), 7.22–7.18 (m, 2H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.2, 151.2, 147.3, 143.7, 143.1, 135.2, 130.5, 130.2, 129.5, 128.4, 127.7, 126.8, 125.4, 125.2, 120.9, 120.6, 116.7, 113.6, 34.9, 31.1; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{24}N_3$: 378.1965; found: 378.1970.



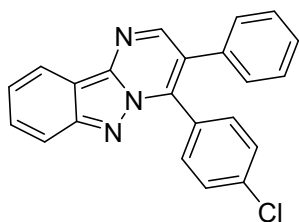
4-(4-methoxyphenyl)-3-phenylpyrimido[1,2-*b*]indazole (4d):

Yield 78% (274.1 mg; petroleum ether/EtOAc = 20:1); light yellow solid; mp 270–272 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.65 (s, 1H), 8.29 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.56–7.50 (m, 1H), 7.48–7.43 (m, 2H), 7.28–7.22 (m, 4H), 7.19–7.15 (m, 2H), 6.89–6.84 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.8, 151.2, 147.3, 143.8, 142.9, 135.4, 132.5, 130.2, 129.5, 128.6, 127.8, 125.1, 121.9, 120.9, 120.6, 116.7, 114.0, 113.7, 55.3; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{23}H_{18}N_3O$: 352.1444; found: 352.1449.



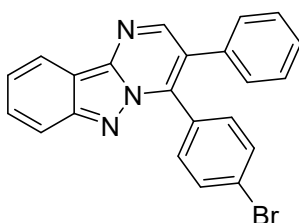
4-(4-fluorophenyl)-3-phenylpyrimido[1,2-*b*]indazole (4e):

Yield 83% (281.7 mg; petroleum ether/EtOAc = 30:1); light yellow solid; mp 231–233 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.65 (s, 1H), 8.28 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.55–7.45 (m, 3H), 7.30–7.20 (m, 4H), 7.15–7.10 (m, 2H), 7.04 (t, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 164.6, 162.1, 151.2, 147.2, 143.7, 141.8, 134.8, 133.1, 133.0, 130.2, 129.7, 128.7, 128.0, 125.9(3), 125.8(9), 125.3, 121.1, 120.6, 116.6, 116.0, 115.7, 113.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{22}H_{15}FN_3$: 340.1245; found: 340.1258.



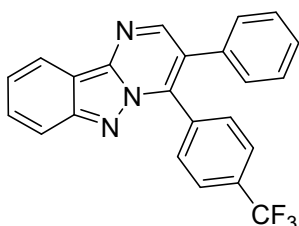
4-(4-chlorophenyl)-3-phenylpyrimido[1,2-*b*]indazole (4f):

Yield 83% (295.3 mg; petroleum ether/EtOAc = 30:1); light yellow solid; mp 234–236 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.72 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.65–7.56 (m, 1H), 7.55–7.37 (m, 4H), 7.35–7.15 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.2, 147.1, 143.7, 141.5, 136.2, 134.6, 132.2, 130.1, 129.7, 128.9, 128.7, 128.4, 128.0, 125.2, 121.1, 120.6, 116.6, 113.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅ClN₃: 356.0949; found: 356.0958.



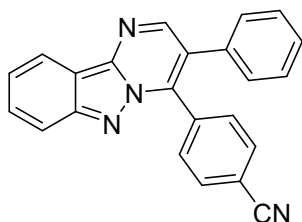
4-(4-bromophenyl)-3-phenylpyrimido[1,2-*b*]indazole (4g):

Yield 82% (328.2 mg; petroleum ether/EtOAc = 30:1); light yellow solid; mp 238–240 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.73 (s, 1H), 8.36 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.58–7.64 (m, 1H), 7.59–7.54 (m, 2H), 7.47–7.42 (m, 2H), 7.36–7.32 (m, 4H), 7.23–7.20 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.2, 147.2, 143.7, 141.5, 134.6, 132.4, 131.8, 130.1, 129.8, 128.8(3), 128.7(5), 128.1, 125.2, 124.7, 121.2, 120.6, 116.6, 113.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅BrN₃: 400.0444; found: 400.0446.



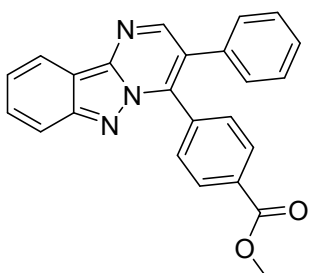
3-phenyl-4-(4-(trifluoromethyl)phenyl)pyrimido[1,2-*b*]indazole (4h):

Yield 61% (237.5 mg; petroleum ether/EtOAc = 30:1); light yellow solid; mp 229–231 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.76 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.70 (s, 4H), 7.65–7.60 (m, 1H), 7.38–7.32 (m, 4H), 7.23–7.18 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.3, 147.1, 143.7, 141.0, 134.3, 133.7, 132.3, 132.0, 131.7, 131.4, 130.2, 129.9, 128.8, 128.3, 127.7, 125.6, 125.5(4), 125.5(0), 125.4(7), 125.0, 122.3, 121.4, 120.6, 119.6, 116.6, 113.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₅F₃N₃: 390.1213; found: 390.1219.



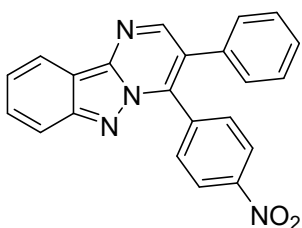
4-(3-phenylpyrimido[1,2-*b*]indazol-4-yl)benzonitrile (4i):

Yield 73% (252.9 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 231–233 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.76 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.74–7.68 (m, 4H), 7.66–7.61 (m, 1H), 7.39–7.33 (m, 4H), 7.22–7.18 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.3, 147.0, 143.7, 140.3, 134.7, 134.0, 132.2, 131.7, 130.1, 130.0, 128.9, 128.4, 125.4, 121.5, 120.6, 118.2, 116.6, 113.7(4), 113.7(2); HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₅N₄: 347.1291; found: 347.1289.



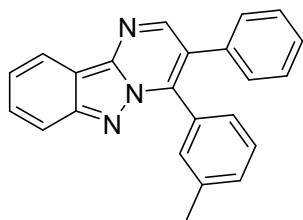
methyl 4-(3-phenylpyrimido[1,2-*b*]indazol-4-yl)benzoate (4j):

Yield 74% (280.8 mg; petroleum ether/EtOAc = 20:1); light yellow solid; mp 228–230 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.76 (s, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.66–7.59 (m, 3H), 7.37–7.34 (m, 1H), 7.33–7.30 (m, 3H), 7.22–7.19 (m, 2H), 3.94 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 166.4, 151.3, 147.1, 143.7, 141.6, 134.5, 134.4, 131.3, 130.9, 130.1, 129.8, 129.7, 128.7, 128.2, 125.4, 121.3, 120.6, 116.6, 113.7, 52.3; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₄H₁₈N₃O₂: 380.1394; found: 380.1397.



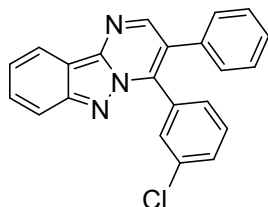
4-(4-nitrophenyl)-3-phenylpyrimido[1,2-*b*]indazole (4k):

Yield 52% (190.5 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 240–242 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.78 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.32–8.26 (m, 2H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.80–7.75 (m, 2H), 7.67–7.61 (m, 1H), 7.40–7.33 (m, 4H), 7.24–7.19 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.3, 148.4, 147.0, 143.7, 140.0, 136.5, 134.0, 132.2, 130.1(3), 130.0(7), 129.0, 128.5, 125.6, 123.7, 121.6, 120.6, 116.6, 113.8; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅N₄O₂: 367.1190; found: 367.1189.



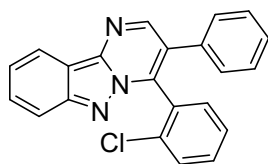
3-phenyl-4-(*m*-tolyl)pyrimido[1,2-*b*]indazole (4l):

Yield 78% (261.6 mg; petroleum ether/EtOAc = 30:1); light yellow solid; mp 165–167 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.74 (s, 1H), 8.37 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.63–7.57 (m, 1H), 7.37 (s, 1H), 7.35–7.28 (m, 6H), 7.27–7.24 (m, 1H), 7.24–7.20 (m, 2H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.3, 147.2, 143.7, 143.1, 138.2, 135.0, 131.1, 130.9, 130.1, 129.9, 129.5(3), 128.4(5), 128.4, 127.7(8), 127.7(5), 125.3, 120.9, 120.5, 116.7, 113.6, 21.5; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₈N₃: 336.1495; found: 336.1494.



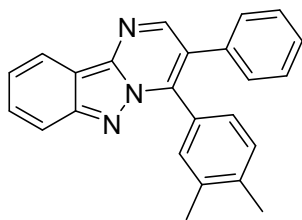
4-(3-chlorophenyl)-3-phenylpyrimido[1,2-*b*]indazole (4m):

Yield 76% (270.4 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 190–193 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.74 (s, 1H), 8.37 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.65–7.58 (m, 2H), 7.45–7.41 (m, 1H), 7.41–7.36 (m, 2H), 7.36–7.32 (m, 4H), 7.25–7.20 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.3, 147.1, 143.7, 141.1, 134.4(8), 134.4(5), 131.7, 130.8, 130.3, 130.1, 129.8(3), 129.7(8), 129.0, 128.7, 128.2, 125.4, 121.3, 120.6, 116.7, 113.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅ClN₃: 356.0949; found: 356.0948.



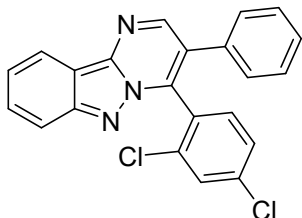
4-(2-chlorophenyl)-3-phenylpyrimido[1,2-*b*]indazole (4n):

Yield 73% (259.8 mg; petroleum ether/EtOAc = 12:1); yellow solid; mp 176–178 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.78 (s, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.64–7.58 (m, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.47–7.41 (m, 1H), 7.37–7.34 (m, 1H), 7.33–7.26 (m, 7H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.4, 146.4, 143.3, 140.6, 134.4, 134.3, 131.5, 131.4, 130.2, 130.0, 129.6(2), 129.5(8), 128.5, 128.2, 127.2, 126.2, 121.2, 120.5, 116.9, 113.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅ClN₃: 356.0949; found: 356.0957.



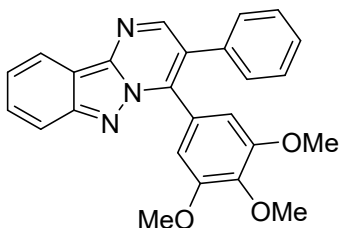
4-(3,4-dimethylphenyl)-3-phenylpyrimido[1,2-*b*]indazole (4o):

Yield 71% (248.1 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 176–178 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.72 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.62–7.57 (m, 1H), 7.35 (s, 1H), 7.34–7.29 (m, 4H), 7.25–7.21 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 1H), 2.29 (s, 3H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.2, 147.3, 143.7, 143.3, 139.0, 136.8, 135.3, 131.5, 130.2, 129.8, 129.5, 128.5, 128.2, 127.7, 127.3, 125.1, 120.8, 120.6, 116.8, 113.6, 19.9, 19.8; HRMS (ESI): *m/z* [*M* + *H*]⁺ calcd for C₂₄H₂₀N₃: 350.1652; found: 350.1648.



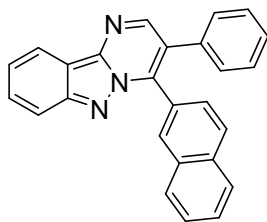
4-(2,4-dichlorophenyl)-3-phenylpyrimido[1,2-*b*]indazole (4p):

Yield 87% (339.5 mg; petroleum ether/EtOAc = 20:1); light yellow solid; mp 194–196 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.75 (s, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.62–7.56 (m, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.36–7.31 (m, 4H), 7.30–7.22 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.3, 146.3, 143.2, 139.3, 136.8, 135.3, 134.0, 132.3, 130.0, 129.7, 129.5, 128.7, 128.6, 128.3, 127.7, 126.3, 121.3, 120.5, 116.7, 113.7; HRMS (ESI): *m/z* [*M* + *H*]⁺ calcd for C₂₂H₁₄Cl₂N₃: 390.0559; found: 390.0560.



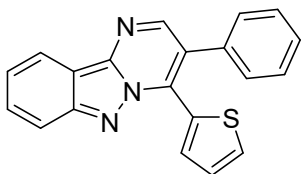
3-phenyl-4-(3,4,5-trimethoxyphenyl)pyrimido[1,2-*b*]indazole (4q):

Yield 43% (176.9 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 195–197 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.74 (s, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.66–7.61 (m, 1H), 7.37–7.32 (m, 4H), 7.26–7.22 (m, 2H), 6.83 (s, 2H), 3.91 (s, 3H), 3.66 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 153.1, 151.3, 147.2, 143.9, 142.6, 139.3, 135.4, 129.9, 129.7, 128.7, 127.9, 125.3, 124.5, 121.0, 120.6, 116.7, 113.6, 108.5, 60.9, 56.0; HRMS (ESI): *m/z* [*M* + *H*]⁺ calcd for C₂₅H₂₂N₃O₃: 412.1656; found: 412.1648.



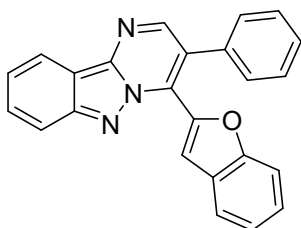
4-(naphthalen-2-yl)-3-phenylpyrimido[1,2-*b*]indazole (4r):

Yield 75% (278.6 mg; petroleum ether/EtOAc = 20:1); yellow solid; mp 248–250 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.79 (s, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 8.07 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.65–7.58 (m, 2H), 7.57–7.52 (m, 1H), 7.51–7.45 (m, 1H), 7.36–7.31 (m, 1H), 7.26 (s, 5H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.3, 147.3, 143.8, 142.8, 135.0, 133.8, 132.8, 131.2, 130.2, 129.6, 128.7, 128.6, 128.2, 127.9, 127.8, 127.4(4), 127.3(6), 127.2, 126.4, 125.5, 121.0, 120.6, 116.7, 113.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₆H₁₈N₃: 372.1495; found: 372.1500.



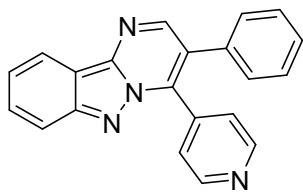
3-phenyl-4-(thiophen-2-yl)pyrimido[1,2-*b*]indazole (4s):

Yield 76% (248.8 mg; petroleum ether/EtOAc = 30:1); light yellow solid; mp 195–197 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.62 (s, 1H), 8.37 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.68–7.61 (m, 2H), 7.50 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.46–7.42 (m, 3H), 7.40–7.32 (m, 3H), 7.03 (dd, *J* = 5.2, 4.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 150.9, 146.8, 144.0, 136.9, 136.1, 134.5, 131.2, 130.0, 129.8, 129.7, 129.0, 128.4, 126.4, 124.7, 121.2, 120.7, 116.6, 113.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₀H₁₄N₃S: 328.0903; found: 328.0896.



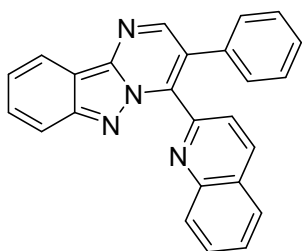
4-(benzofuran-2-yl)-3-phenylpyrimido[1,2-*b*]indazole (4t):

Yield 82% (296.4 mg; petroleum ether/EtOAc = 50:1); yellow solid; mp 216–218 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.64 (s, 1H), 8.59 (d, *J* = 1.2 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.74–7.70 (m, 1H), 7.67–7.62 (m, 1H), 7.46–7.40 (m, 3H), 7.40–7.37 (m, 2H), 7.37–7.32 (m, 1H), 7.29–7.21 (m, 2H), 7.10–7.06 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.6, 151.2, 146.9, 145.0, 143.9, 136.2, 131.8, 129.9, 129.7, 128.2, 128.1, 127.7, 126.7, 124.9, 123.4, 122.5, 121.4, 120.7, 116.7, 116.6, 113.6, 111.3; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₄H₁₆N₃O: 362.1288; found: 362.1294.



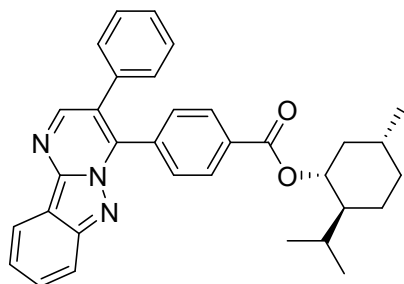
3-phenyl-4-(pyridin-4-yl)pyrimido[1,2-*b*]indazole (4u):

Yield 67% (216.0 mg; petroleum ether/EtOAc = 5:1); yellow solid; mp 197–199 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.00 (s, 1H), 8.59 (dd, *J* = 4.4, 1.6 Hz, 2H), 8.41–8.38 (m, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.72–7.67 (m, 1H), 7.45–7.39 (m, 5H), 7.39–7.36 (m, 1H), 7.31–7.28 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 152.2, 150.5, 149.8, 145.4, 142.6, 135.0, 133.4, 130.3, 129.7, 129.1, 128.8, 125.9, 124.1, 121.6, 120.9, 116.4, 113.9; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₁H₁₅N₄: 323.1291; found: 323.1288.



3-phenyl-4-(quinolin-2-yl)pyrimido[1,2-*b*]indazole (4v):

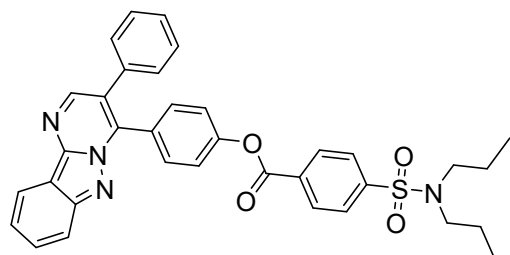
Yield 84% (312.8 mg; petroleum ether/EtOAc = 5:1); yellow solid; mp 238–240 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.07 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.84 (t, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.70–7.63 (m, 2H), 7.56–7.51 (m, 1H), 7.38–7.32 (m, 2H), 7.32–7.29 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 155.7, 152.1, 151.9, 147.5, 142.4, 136.2, 136.0, 133.5, 130.0, 129.8, 129.7, 129.6, 128.5, 127.8, 127.4, 127.3(2), 127.2(6), 126.7, 121.8, 121.3, 121.2, 116.3, 114.0; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₅H₁₇N₄: 373.1448; found: 373.1448.



(1*R*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-(3-phenylpyrimido[1,2-*b*]indazol-4-yl)benzoate (4w):

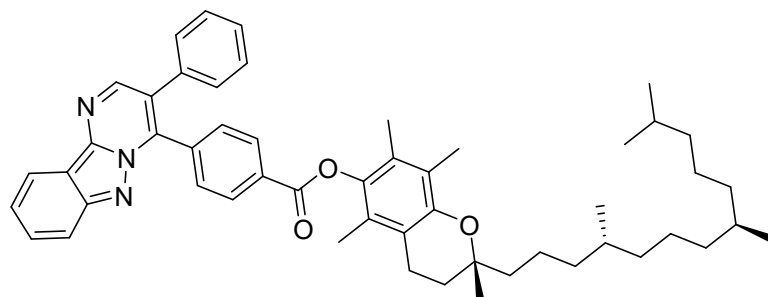
Yield 76% (382.8 mg; petroleum ether/EtOAc = 20:1); yellow solid; mp 239–244 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.75 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.13–8.09 (m, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.66–7.58 (m, 3H), 7.36–7.31 (m, 4H), 7.24–7.20 (m, 2H), 4.95 (td, *J* = 10.8, 4.4 Hz, 1H), 2.17–2.10 (m, 1H), 2.03–1.93 (m, 1H), 1.77–1.70 (m, 2H), 1.61–1.51 (m, 2H), 1.16–1.05 (m, 2H), 0.97–0.91 (m, 7H), 0.81 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 165.3, 151.2, 147.1, 143.7, 141.6, 134.5, 134.3, 132.1, 130.8, 130.1, 129.7(3), 129.6(5), 128.7, 128.1, 125.3, 121.2, 120.5, 116.6, 113.7, 75.2, 47.2, 40.9, 34.2.

31.4, 26.3, 23.4, 22.0, 20.8, 16.3; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{33}H_{34}N_3O_2$: 504.2646; found: 504.2644.



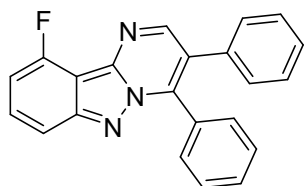
4-(3-phenylpyrimido[1,2-*b*]indazol-4-yl)phenyl 4-(*N,N*-dipropylsulfamoyl)benzoate (4x):

Yield 75% (453.5 mg; petroleum ether/EtOAc = 5:1); yellow solid; mp 186–188 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.76 (s, 1H), 8.37 (d, $J = 8.4$ Hz, 1H), 8.34–8.29 (m, 2H), 7.99–7.93 (m, 2H), 7.84 (d, $J = 8.8$ Hz, 1H), 7.70–7.65 (m, 2H), 7.65–7.60 (m, 1H), 7.39–7.31 (m, 6H), 7.28–7.24 (m, 2H), 3.17–3.10 (m, 4H), 1.63–1.52 (m, 4H), 0.89 (t, $J = 7.6$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 163.2, 151.6, 151.2, 147.2, 145.0, 143.7, 141.7, 134.7, 132.5, 132.4, 130.8, 130.2, 129.7, 128.7, 128.1, 127.8, 127.2, 125.4, 121.7, 121.1, 120.6, 116.6, 113.7, 49.9, 21.9, 11.1; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{35}H_{33}N_4O_4S$: 605.2217; found: 605.2211.



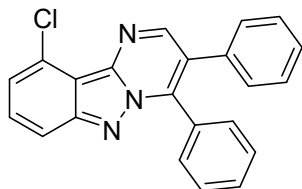
(*R*)-2,5,7,8-tetramethyl-2-((4*S*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(3-phenylpyrimido[1,2-*b*]indazol-4-yl)benzoate (4y):

Yield 77% (599.1 mg; petroleum ether/EtOAc = 12:1); yellow solid; mp 88–90 °C; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.75 (s, 1H), 8.37 (d, $J = 8.0$ Hz, 1H), 8.29 (d, $J = 8.4$ Hz, 2H), 7.84 (d, $J = 8.8$ Hz, 1H), 7.74–7.70 (m, 2H), 7.63–7.57 (m, 1H), 7.36–7.30 (m, 4H), 7.26–7.22 (m, 2H), 2.62 (t, $J = 6.4$ Hz, 2H), 2.13 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 1.85–1.75 (m, 2H), 1.61–1.50 (m, 3H), 1.46–1.35 (m, 4H), 1.32–1.21 (m, 10H), 1.18–1.00 (m, 7H), 0.89–0.84 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 164.4, 151.2, 149.5, 147.1, 143.7, 141.3, 140.4, 134.9, 134.4, 131.1, 130.8, 130.2, 130.1, 129.8, 128.8, 128.2, 126.7, 125.4, 125.0, 123.1, 121.2, 120.5, 117.4, 116.6, 113.7, 75.0, 40.3, 39.6, 39.3, 37.4, 37.2, 32.7, 31.1, 30.9, 27.9, 24.7, 24.4, 24.1, 23.6, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 13.1, 12.2, 11.8; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{52}H_{64}N_3O_3$: 778.4942; found: 778.4911.



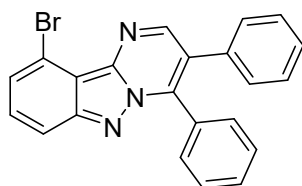
10-fluoro-3,4-diphenylpyrimido[1,2-*b*]indazole (4z):

Yield 77% (261.3 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 229–231 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.84 (s, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.56–7.52 (m, 2H), 7.53–7.48 (m, 1H), 7.48–7.40 (m, 3H), 7.34–7.29 (m, 3H), 7.25–7.19 (m, 2H), 6.94 (dd, *J* = 10.4, 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.3, 155.7, 152.9(4), 152.8(9), 148.4, 143.1, 142.1, 142.0, 134.6, 130.7, 130.3, 130.1, 129.9, 129.8, 129.7, 128.6, 128.5, 128.0, 125.6, 112.7, 112.6, 104.8, 104.7, 104.2, 104.1; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅FN₃: 340.1245; found: 340.1243.



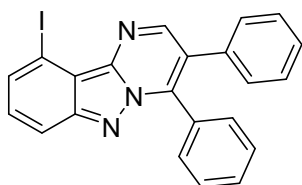
10-chloro-3,4-diphenylpyrimido[1,2-*b*]indazole (4aa):

Yield 80% (284.7 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 222–224 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.88 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.55–7.51 (m, 2H), 7.49–7.45 (m, 1H), 7.45–7.40 (m, 3H), 7.32–7.27 (m, 4H), 7.23–7.19 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.9, 148.1, 143.0(0), 142.9(8), 134.6, 130.6, 130.2, 130.1, 129.7, 129.5, 128.6, 128.5, 128.0, 127.2, 125.6, 121.2, 115.3, 111.3; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅ClN₃: 356.0949; found: 356.0953.



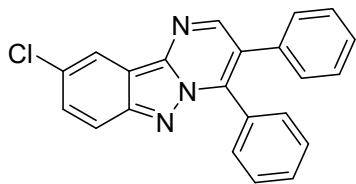
10-bromo-3,4-diphenylpyrimido[1,2-*b*]indazole (4ab):

Yield 79% (316.2 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 225–227 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.90 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.54–7.47 (m, 3H), 7.46–7.39 (m, 4H), 7.32–7.28 (m, 3H), 7.22–7.18 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.8, 147.8, 143.3, 143.0, 134.6, 130.6, 130.2, 130.1, 129.8, 129.7, 128.6, 128.5, 128.0, 125.7, 124.7, 115.9, 114.4, 112.6; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅BrN₃: 400.0444; found: 400.0449.



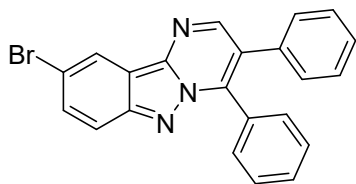
10-iodo-3,4-diphenylpyrimido[1,2-*b*]indazole (4ac):

Yield 84% (375.7 mg; petroleum ether/EtOAc = 20:1); yellow solid; mp 230–232 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.93 (s, 1H), 7.81 (d, *J* = 3.2 Hz, 1H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.53–7.49 (m, 2H), 7.46–7.39 (m, 3H), 7.32–7.28 (m, 3H), 7.26–7.23 (m, 1H), 7.22–7.18 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.5, 147.1, 143.7, 142.9, 134.6, 131.8, 130.6, 130.1, 130.0, 129.7, 128.5(3), 128.4(7), 127.9, 125.8, 116.6, 114.9, 84.4; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅IN₃: 448.0305; found: 448.0301.



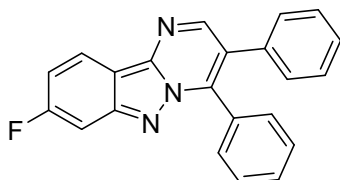
9-chloro-3,4-diphenylpyrimido[1,2-*b*]indazole (4ad):

Yield 61% (217.1 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 255–257 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.75 (s, 1H), 8.34–8.31 (m, 1H), 7.78–7.74 (m, 1H), 7.55–7.50 (m, 3H), 7.47–7.41 (m, 3H), 7.33–7.29 (m, 3H), 7.24–7.19 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 149.5, 147.8, 143.1(4), 143.0(9), 134.7, 130.7(0), 130.6(6), 130.3, 130.2, 129.7, 128.6(0), 128.5(6), 128.0, 126.4, 125.7, 119.6, 118.2, 114.2; HRMS (ESI): m/z [M + H]⁺ calcd for C₂₂H₁₅ClN₃: 356.0949; found: 356.0956.



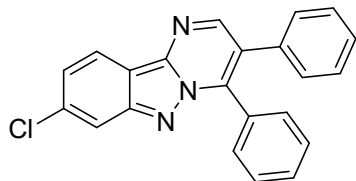
9-bromo-3,4-diphenylpyrimido[1,2-*b*]indazole (4ae):

Yield 78% (312.2 mg; petroleum ether/EtOAc = 20:1); yellow solid; mp 272–274 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.76 (s, 1H), 8.52–8.50 (m, 1H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.64 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.56–7.51 (m, 2H), 7.48–7.41 (m, 3H), 7.34–7.29 (m, 3H), 7.24–7.20 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 149.6, 147.9, 143.2, 142.9, 134.7, 133.0, 130.7, 130.3, 130.2, 129.7, 128.6(1), 128.5(6), 128.0, 125.8, 122.9, 118.5, 115.0, 113.9; HRMS (ESI): m/z [M + H]⁺ calcd for C₂₂H₁₅BrN₃: 400.0444; found: 400.0436.



8-fluoro-3,4-diphenylpyrimido[1,2-*b*]indazole (4af):

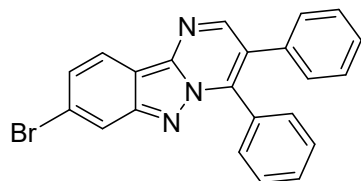
Yield 74% (251.1 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 220–222 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.75 (s, 1H), 8.32 (dd, *J* = 9.2, 5.6 Hz, 1H), 7.56–7.51 (m, 2H), 7.47–7.37 (m, 4H), 7.34–7.28 (m, 3H), 7.24–7.17 (m, 2H), 7.13–7.05 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 165.2, 162.7, 151.9, 151.7, 148.0, 143.7, 143.1, 134.7, 130.7, 130.2(3), 130.1(5), 129.8, 128.6, 128.5, 127.9, 125.2, 122.6, 122.5, 112.1, 111.9, 110.7, 100.6, 100.4; HRMS (ESI): m/z [M + H]⁺ calcd for C₂₂H₁₅FN₃: 340.1245; found: 340.1252.



8-chloro-3,4-diphenylpyrimido[1,2-*b*]indazole (4ag):

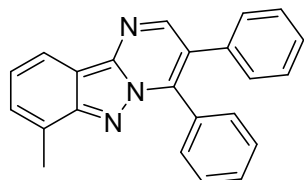
Yield 80% (284.7 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 216–218 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.76 (s, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 1.6 Hz,

1H), 7.55–7.51 (m, 2H), 7.47–7.40 (m, 3H), 7.33–7.29 (m, 3H), 7.26–7.23 (m, 1H), 7.23–7.19 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.4, 148.1, 143.7, 143.2, 135.5, 134.7, 130.7, 130.3, 130.1, 129.7, 128.6, 128.5, 128.0, 125.6, 122.3, 121.8, 115.8, 112.1; HRMS (ESI): m/z [M + H]⁺ calcd for C₂₂H₁₅ClN₃: 356.0949; found: 356.0959.



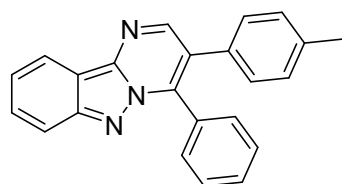
8-bromo-3,4-diphenylpyrimido[1,2-*b*]indazole (4ah):

Yield 74% (296.2 mg; petroleum ether/EtOAc = 30:1); yellow solid; mp 222–224 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.76 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.00–7.98 (m, 1H), 7.55–7.51 (m, 2H), 7.47–7.40 (m, 3H), 7.39 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.33–7.29 (m, 3H), 7.23–7.19 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.8, 148.1, 143.7, 143.2, 134.7, 130.7, 130.3, 130.1, 129.7, 128.6, 128.5, 128.0, 125.7, 124.6, 123.9, 121.9, 119.1, 112.3; HRMS (ESI): m/z [M + H]⁺ calcd for C₂₂H₁₅BrN₃: 400.0444; found: 400.0448.



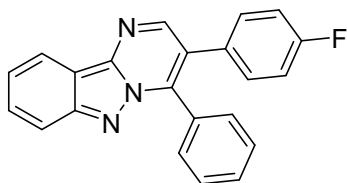
7-methyl-3,4-diphenylpyrimido[1,2-*b*]indazole (4ai):

Yield 62% (208.0 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 178–180 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.71 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.63–7.58 (m, 2H), 7.45–7.35 (m, 4H), 7.33–7.28 (m, 3H), 7.26–7.21 (m, 3H), 2.64 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.3, 147.0, 143.9, 142.8, 135.3, 131.1, 130.2, 130.0, 129.9, 128.7, 128.5, 128.2, 127.8, 126.7, 124.9, 121.2, 117.9, 113.2, 16.8; HRMS (ESI): m/z [M + H]⁺ calcd for C₂₃H₁₈N₃: 336.1495; found: 336.1492.



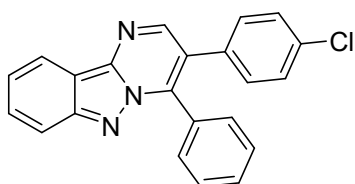
4-phenyl-3-(*p*-tolyl)pyrimido[1,2-*b*]indazole (4aj):

Yield 81% (271.7 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 202–204 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.73 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.62–7.58 (m, 1H), 7.57–7.53 (m, 2H), 7.47–7.42 (m, 3H), 7.34–7.29 (m, 1H), 7.10 (s, 4H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.2, 147.4, 143.6, 142.7, 137.7, 131.9, 130.7, 130.2, 130.0(2), 130.0(0), 129.5, 129.3, 128.5, 125.3, 120.9, 120.5, 116.7, 113.6, 21.2; HRMS (ESI): m/z [M + H]⁺ calcd for C₂₃H₁₈N₃: 336.1495; found: 336.1498.



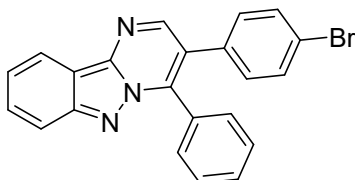
3-(4-fluorophenyl)-4-phenylpyrimido[1,2-*b*]indazole (4ak):

Yield 82% (278.3 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 212–214 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.70 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.63–7.57 (m, 1H), 7.55–7.51 (m, 2H), 7.48–7.41 (m, 3H), 7.35–7.30 (m, 1H), 7.20–7.15 (m, 2H), 7.03–6.96 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.6, 161.1, 151.3, 146.9, 143.7, 142.9, 131.9, 131.8, 130.9(4), 130.9(0), 130.6, 130.2, 129.8, 129.7, 128.6, 124.3, 121.1, 120.5, 116.7, 115.8, 115.6, 113.6; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅FN₃: 340.1245; found: 340.1246.



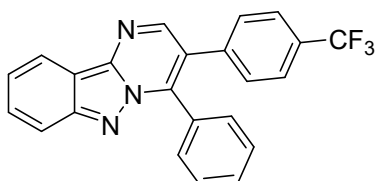
3-(4-chlorophenyl)-4-phenylpyrimido[1,2-*b*]indazole (4al):

Yield 74% (263.3 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 226–228 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.69 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.63–7.58 (m, 1H), 7.56–7.50 (m, 2H), 7.49–7.43 (m, 3H), 7.36–7.31 (m, 1H), 7.30–7.26 (m, 2H), 7.16–7.12 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.4, 146.7, 143.7, 142.9, 134.2, 133.5, 131.4, 130.6, 130.3, 129.7(x2), 128.8, 128.7, 124.1, 121.2, 120.6, 116.7, 113.6; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅ClN₃: 356.0949; found: 356.0952.



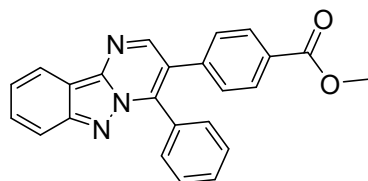
3-(4-bromophenyl)-4-phenylpyrimido[1,2-*b*]indazole (4am):

Yield 76% (304.2 mg; petroleum ether/EtOAc = 12:1); yellow solid; mp 241–243 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.70 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.64–7.58 (m, 1H), 7.56–7.52 (m, 2H), 7.50–7.42 (m, 5H), 7.36–7.31 (m, 1H), 7.11–7.06 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.4, 146.6, 143.8, 142.8, 134.0, 131.8, 131.7, 130.6, 130.3, 129.8, 129.7, 128.7, 124.1, 122.4, 121.2, 120.6, 116.8, 113.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅BrN₃: 400.0444; found: 400.0450.



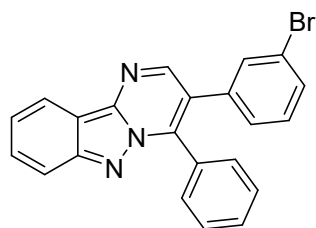
4-phenyl-3-(4-(trifluoromethyl)phenyl)pyrimido[1,2-*b*]indazole (4an):

Yield 41% (159.7 mg; petroleum ether/EtOAc = 20:1); yellow solid; mp 175–177 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.43 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 2H), 8.25–8.20 (m, 2H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.77 (s, 1H), 7.69–7.61 (m, 4H), 7.38–7.33 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.7, 150.5, 145.5, 144.9, 140.5(8), 140.5(7), 131.9, 131.5, 131.2, 130.1, 129.5, 128.9, 127.4, 126.0(3), 125.9(9), 125.9(5), 125.9, 125.4, 122.7, 121.2, 116.7, 114.0, 108.5; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₅F₃N₃: 390.1213; found: 390.1215.



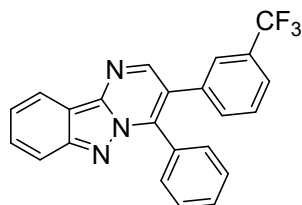
methyl 4-(4-phenylpyrimido[1,2-*b*]indazol-3-yl)benzoate (4ao):

Yield 75% (284.6 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 218–220 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.74 (s, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.00–7.95 (m, 2H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.65–7.59 (m, 1H), 7.56–7.51 (m, 2H), 7.48–7.41 (m, 3H), 7.37–7.32 (m, 1H), 7.32–7.28 (m, 2H), 3.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 166.5, 151.5, 146.5, 143.9, 143.1, 139.8, 130.7, 130.4, 130.2, 129.8, 129.7, 129.6, 129.5, 128.7, 124.2, 121.3, 120.6, 116.8, 113.7, 52.3; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₄H₁₈N₃O₂: 380.1394; found: 380.1401.



3-(3-bromophenyl)-4-phenylpyrimido[1,2-*b*]indazole (4ap):

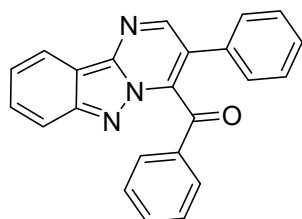
Yield 77% (308.2 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 163–167 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.71 (s, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.64–7.59 (m, 1H), 7.57–7.52 (m, 2H), 7.50–7.40 (m, 5H), 7.36–7.32 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.12–7.08 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.5, 146.6, 143.8, 143.1, 137.1, 133.0, 131.0, 130.6, 130.4, 130.0, 129.8, 129.6, 128.9, 128.7, 123.8, 122.5, 121.2, 120.6, 116.8, 113.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₅BrN₃: 400.0444; found: 400.0441.



4-phenyl-3-(3-(trifluoromethyl)phenyl)pyrimido[1,2-*b*]indazole (4aq):

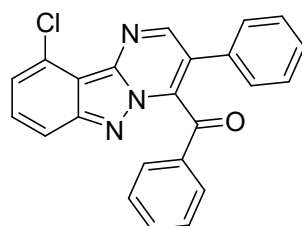
Yield 57% (221.9 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 197–199 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.75 (s, 1H), 8.41–8.36 (m, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.66–7.61 (m, 1H), 7.59–7.55 (m, 1H), 7.54–7.50 (m, 2H), 7.50–7.41 (m, 6H), 7.38–7.33 (m,

1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 151.5, 146.4, 143.9, 143.3, 135.9, 133.4(1), 133.4(0), 131.2, 130.9, 130.6, 130.5, 129.9, 129.5, 129.1, 128.8, 127.1, 127.0(3), 126.9(9), 126.9(5), 125.0, 124.7(0), 124.6(6), 124.6(2), 124.5(8), 123.8, 122.3, 121.3, 120.7, 116.8, 113.7; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{15}\text{F}_3\text{N}_3$: 390.1213; found: 390.1212.



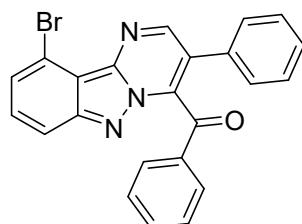
phenyl(3-phenylpyrimido[1,2-*b*]indazol-4-yl)methanone (5a):

Yield 57% (199.2 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 204–206 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.08 (s, 1H), 8.33 (d, $J = 8.0$ Hz, 1H), 7.99–7.94 (m, 2H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.73–7.68 (m, 1H), 7.65–7.59 (m, 1H), 7.47 (t, $J = 8.0$ Hz, 2H), 7.43–7.35 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 192.6, 152.2, 150.5, 141.2, 135.7, 134.0, 133.8, 133.0, 130.6, 130.3, 129.0, 128.8, 128.6, 126.4, 121.9, 121.0, 116.5, 114.0; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{16}\text{N}_3\text{O}$: 350.1288; found: 350.1304.



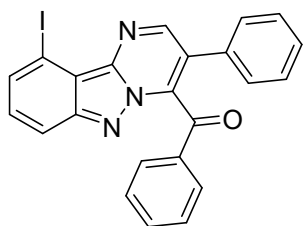
(10-chloro-3-phenylpyrimido[1,2-*b*]indazol-4-yl)(phenyl)methanone (5b):

Yield 52% (199.6 mg; petroleum ether/EtOAc = 10:1); yellow solid; mp 184–186 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.07 (s, 1H), 8.10–8.06 (m, 2H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.65–7.61 (m, 1H), 7.61–7.57 (m, 1H), 7.49 (t, $J = 8.0$ Hz, 2H), 7.41 (s, 5H), 7.36 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 191.9, 152.9, 150.9, 140.4, 135.5, 133.9, 133.8, 133.2, 130.7, 130.4, 129.1, 129.0, 128.9, 128.5, 127.9, 127.1, 122.2, 115.1, 112.1; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{15}\text{ClN}_3\text{O}$: 384.0898; found: 384.0901.



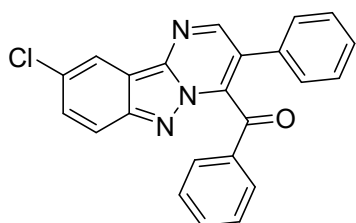
(10-bromo-3-phenylpyrimido[1,2-*b*]indazol-4-yl)(phenyl)methanone (5c):

Yield 52% (222.7 mg; petroleum ether/EtOAc = 12:1); yellow solid; mp 185–187 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.07 (s, 1H), 8.15–8.10 (m, 2H), 7.90–7.86 (m, 1H), 7.67–7.61 (m, 1H), 7.59–7.55 (m, 1H), 7.56–7.53 (m, 1H), 7.53–7.48 (m, 2H), 7.42 (s, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 191.7, 152.8, 150.4, 140.7, 135.5, 133.8(9), 133.8(7), 133.3, 130.8, 130.6, 129.1, 129.0, 128.8, 128.5, 127.3, 125.7, 115.7, 114.9, 113.4; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{15}\text{BrN}_3\text{O}$: 428.0393; found: 428.0390.



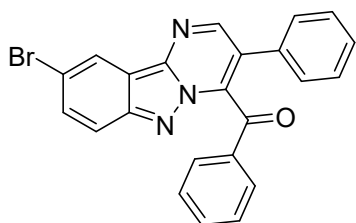
(10-iodo-3-phenylpyrimido[1,2-*b*]indazol-4-yl)(phenyl)methanone (5d):

Yield 51% (242.4 mg; petroleum ether/EtOAc = 10:1); yellow solid; mp 182–184 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.07 (s, 1H), 8.21–8.16 (m, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.44–7.36 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 191.7, 152.5, 149.4, 141.0, 135.5, 134.0, 133.8, 133.3, 132.8, 131.0(0), 130.9(5), 129.0, 128.9, 128.8, 128.5, 127.5, 116.5, 115.9, 84.7; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₅IN₃O: 476.0254; found: 476.0260.



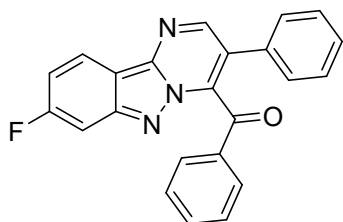
(9-chloro-3-phenylpyrimido[1,2-*b*]indazol-4-yl)(phenyl)methanone (5e):

Yield 56% (214.9 mg; petroleum ether/EtOAc = 12:1); yellow solid; mp 230–232 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.05 (s, 1H), 8.28 (d, *J* = 2.0 Hz, 1H), 7.97–7.93 (m, 2H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.64–7.59 (m, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.40 (s, 5H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 192.4, 151.2, 150.4, 140.5, 135.6, 134.1, 133.6, 133.3, 131.4, 130.6, 129.1, 129.0(3), 128.9(6), 128.7, 127.5, 127.0, 120.0, 118.1, 114.6; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₅ClN₃O: 384.0898; found: 384.0903.



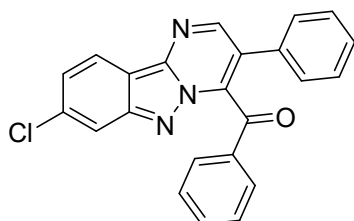
(9-bromo-3-phenylpyrimido[1,2-*b*]indazol-4-yl)(phenyl)methanone (5f):

Yield 54% (231.3 mg; petroleum ether/EtOAc = 8:1); yellow solid; mp 231–233 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.05 (s, 1H), 8.50–8.46 (m, 1H), 7.98–7.93 (m, 2H), 7.81 (d, *J* = 9.2 Hz, 1H), 7.76–7.72 (m, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.40 (s, 5H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 192.3, 151.3, 150.5, 140.3, 135.5, 134.1, 133.7, 133.6, 133.3, 130.5, 129.1, 129.0, 128.9, 128.7, 127.0, 123.3, 118.2, 115.2, 115.0; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₅BrN₃O: 428.0393; found: 428.0384.



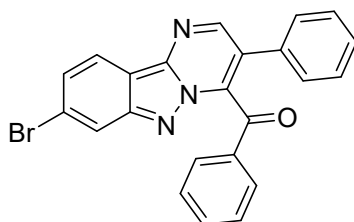
(8-fluoro-3-phenylpyrimido[1,2-*b*]indazol-4-yl)(phenyl)methanone (5g):

Yield 51% (187.4 mg; petroleum ether/EtOAc = 12:1); yellow solid; mp 216–218 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.06 (s, 1H), 8.29 (dd, *J* = 9.2, 5.2 Hz, 1H), 7.96–7.91 (m, 2H), 7.65–7.59 (m, 1H), 7.51–7.44 (m, 3H), 7.41–7.37 (m, 5H), 7.14 (td, *J* = 9.2, 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 192.6, 165.5, 163.1, 152.9, 152.8, 151.5, 141.3, 135.5, 134.1, 133.5, 133.2, 130.5, 129.1, 129.0, 128.9, 128.6, 126.2, 123.1, 123.0, 113.0, 112.7, 110.9, 100.6, 100.4; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₅FN₃O: 368.1194; found: 368.1204.



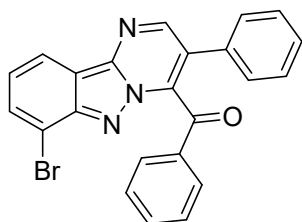
(8-chloro-3-phenylpyrimido[1,2-*b*]indazol-4-yl)(phenyl)methanone (5h):

Yield 55% (211.1 mg; petroleum ether/EtOAc = 15:1); yellow solid; mp 231–233 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.07 (s, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 7.96–7.88 (m, 3H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39 (s, 5H), 7.34–7.29 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 192.5, 152.4, 151.6, 141.2, 136.4, 135.5, 134.1, 133.5, 133.3, 130.5, 129.1, 129.0, 128.9, 128.6, 126.7, 123.2, 122.2, 115.7, 112.4; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₅ClN₃O: 384.0898; found: 384.0901.



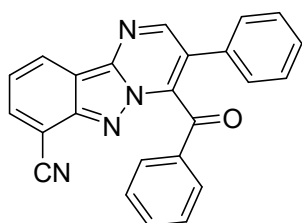
(8-bromo-3-phenylpyrimido[1,2-*b*]indazol-4-yl)(phenyl)methanone (5i):

Yield 55% (235.6 mg; petroleum ether/EtOAc = 12:1); yellow solid; mp 231–233 °C; ¹H NMR (400 MHz, CDCl₃): 9.07 (s, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 8.11–8.08 (m, 1H), 7.96–7.91 (m, 2H), 7.65–7.60 (m, 1H), 7.50–7.43 (m, 3H), 7.40 (s, 5H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 192.5, 152.8, 151.6, 146.0, 141.3, 135.5, 134.1, 133.3, 130.5, 129.7, 129.1, 128.6, 127.3, 126.8, 125.6, 124.7, 122.3, 119.0, 112.6; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₅BrN₃O: 428.0393; found: 428.0378.



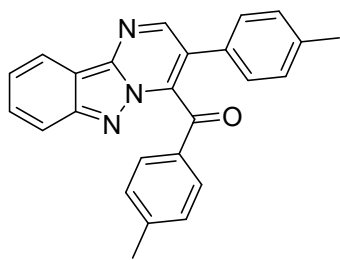
(7-bromo-3-phenylpyrimido[1,2-*b*]indazol-4-yl)(phenyl)methanone (5j):

Yield 52% (222.7 mg; petroleum ether/EtOAc = 12:1); brown solid; mp 78–80 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.21 (s, 1H), 8.31–8.27 (m, 1H), 7.95–7.90 (m, 3H), 7.65–7.60 (m, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.40 (s, 5H), 7.25–7.22 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 192.4, 151.9, 150.4, 141.8, 135.4, 134.2, 133.7, 133.4, 133.0, 130.5, 129.2, 129.0(2), 128.9(7), 128.7, 127.1, 122.6, 120.4, 115.1, 109.9; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₅BrN₃O: 428.0393; found: 428.0386.



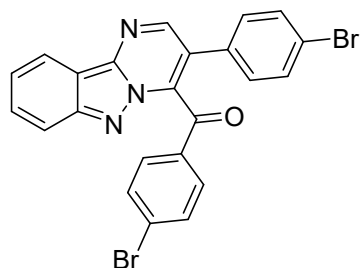
4-benzoyl-3-phenylpyrimido[1,2-*b*]indazole-7-carbonitrile (5k):

Yield 55% (205.9 mg; petroleum ether/EtOAc = 5:1); yellow solid; mp 174–176 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.23 (s, 1H), 8.59–8.55 (m, 1H), 8.10–8.07 (m, 1H), 7.95–7.89 (m, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.45–7.38 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 192.2, 152.9, 150.8, 141.7, 136.4, 135.2, 134.3, 133.9, 133.0, 130.4, 129.3(x2), 129.0, 128.7, 127.8, 126.6, 121.0, 116.5, 114.5, 99.8; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₄H₁₅N₄O: 375.1240; found: 375.1237.



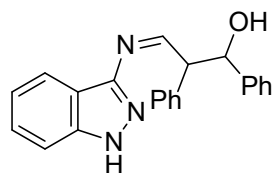
***p*-tolyl(3-(*p*-tolyl)pyrimido[1,2-*b*]indazol-4-yl)methanone (5l):**

Yield 52% (196.3 mg; petroleum ether/EtOAc = 10:1); yellow solid; mp 278–280 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.05 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.72–7.66 (m, 1H), 7.38–7.34 (m, 1H), 7.32–7.26 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 192.4, 152.1, 151.1, 145.1, 141.1, 138.8, 133.2, 132.9, 130.9, 130.8, 130.2, 129.8, 129.4, 128.9, 126.4, 121.8, 121.0, 116.4, 113.9, 21.9, 21.2; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₅H₂₀N₃O: 378.1601; found: 378.1607.



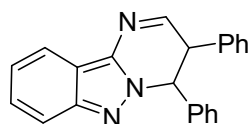
(4-bromophenyl)(3-(4-bromophenyl)pyrimido[1,2-*b*]indazol-4-yl)methanone (5m):

Yield 51% (258.7 mg; petroleum ether/EtOAc = 12:1); yellow solid; mp 210–212 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.04 (s, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.89–7.85 (m, 2H), 7.68–7.64 (m, 2H), 7.58–7.54 (m, 2H), 7.43–7.38 (m, 1H), 7.28–7.25 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 191.2, 152.4, 149.0, 144.6, 141.0, 134.4, 133.0, 132.8, 132.3, 132.1, 130.5, 129.7, 128.8, 125.5, 123.5, 122.4, 121.0, 116.7, 114.1; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₄Br₂N₃O: 505.9498; found: 505.9489.



(*Z*)-3-((1H-indazol-3-yl)imino)-1,2-diphenylpropan-1-ol (B):

Yield 23% (78.5 mg; petroleum ether/EtOAc = 8:1); yellow solid; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.99 (s, 1H), 7.93–7.83 (m, 3H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.52–7.43 (m, 3H), 7.38–7.30 (m, 3H), 7.30–7.25 (m, 2H), 7.25–7.21 (m, 1H), 7.19–7.14 (m, 1H), 6.41 (dd, *J* = 8.0, 3.6 Hz, 1H), 4.75–4.63 (m, 1H), 4.26–4.36 (m, 1H), 3.85 (t, *J* = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 158.4, 148.0, 140.7, 138.1, 136.2, 131.8, 128.9, 128.7, 128.5, 127.8, 127.0, 126.4, 123.0, 120.0, 118.3, 111.8, 65.1, 63.5; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₂₀N₃O: 342.1601; found: 342.1606.



3,4-diphenyl-3,4-dihydropyrimido[1,2-*b*]indazole (D):

Yield 57% (184.3 mg; petroleum ether/EtOAc = 5:1); yellow solid; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.23 (d, *J* = 4.8 Hz, 1H), 7.49 (dd, *J* = 9.6, 8.8 Hz, 2H), 7.42–7.37 (m, 2H), 7.25–7.23 (m, 1H), 7.23–7.20 (m, 2H), 7.20–7.17 (m, 2H), 7.16–7.12 (m, 2H), 6.89–6.83 (m, 1H), 6.82–6.77 (m, 2H), 5.29 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 148.4, 140.5, 136.5, 128.6(3), 128.6(1), 128.2, 127.5, 126.9, 126.6, 125.2, 120.6, 118.9, 118.5, 116.9, 110.7, 107.0, 63.2, 53.4; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₈N₃: 324.1495; found: 324.1493.

7. Crystallographic data and molecular structure of 4I

The crystal of **4I** for X-ray diffraction study has been obtained through the dissolving of compound in CHCl₃, followed by slow evaporation of the solvent at room temperature. The crystal was kept at 296(2)K during data collection. CCDC 2374105 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

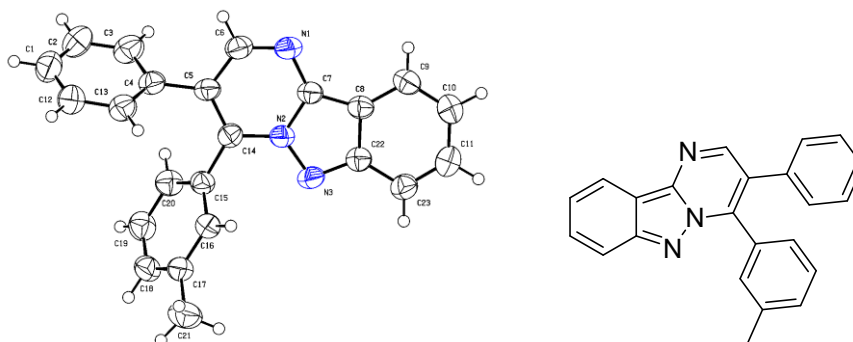
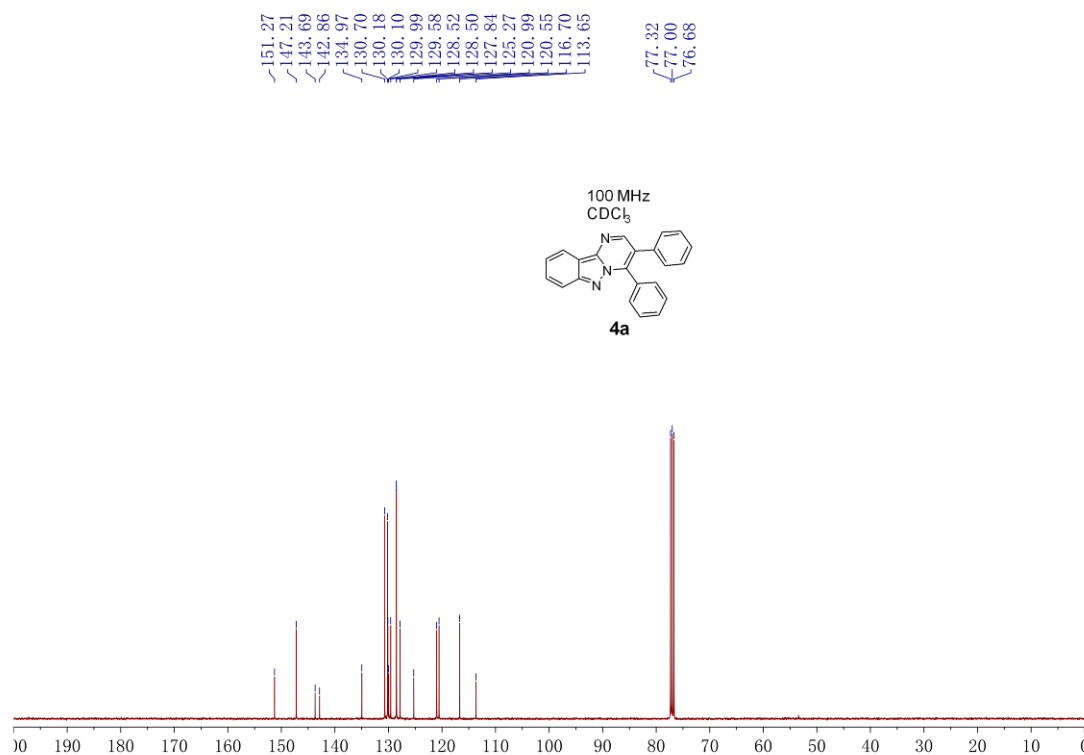
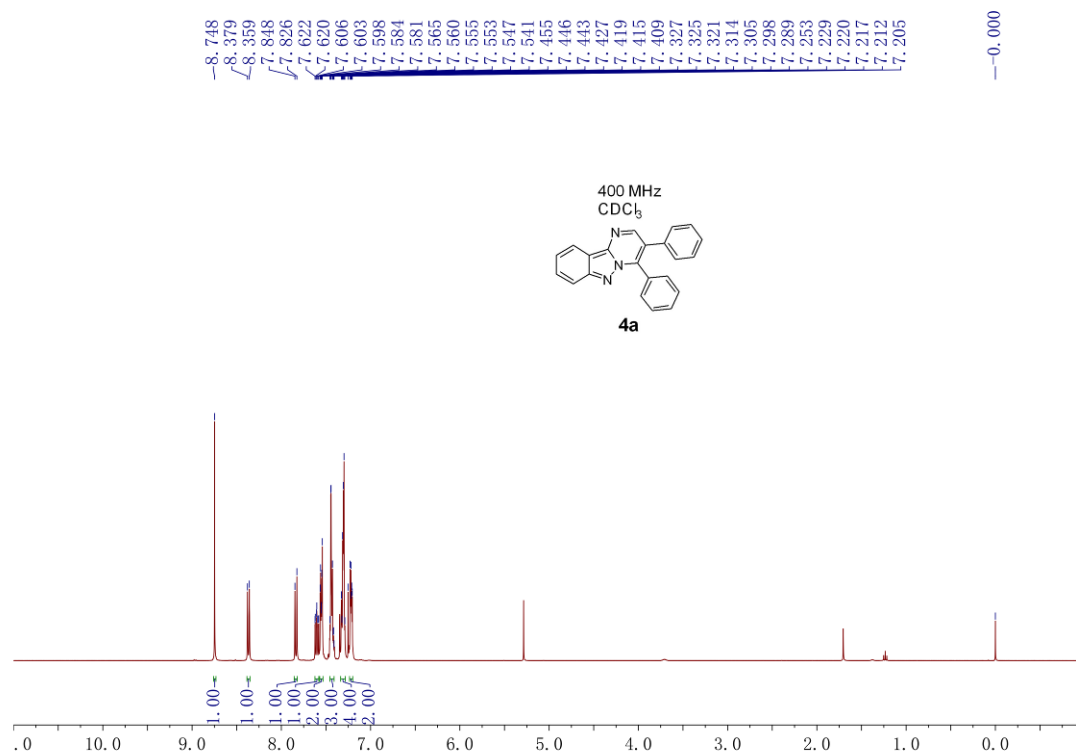
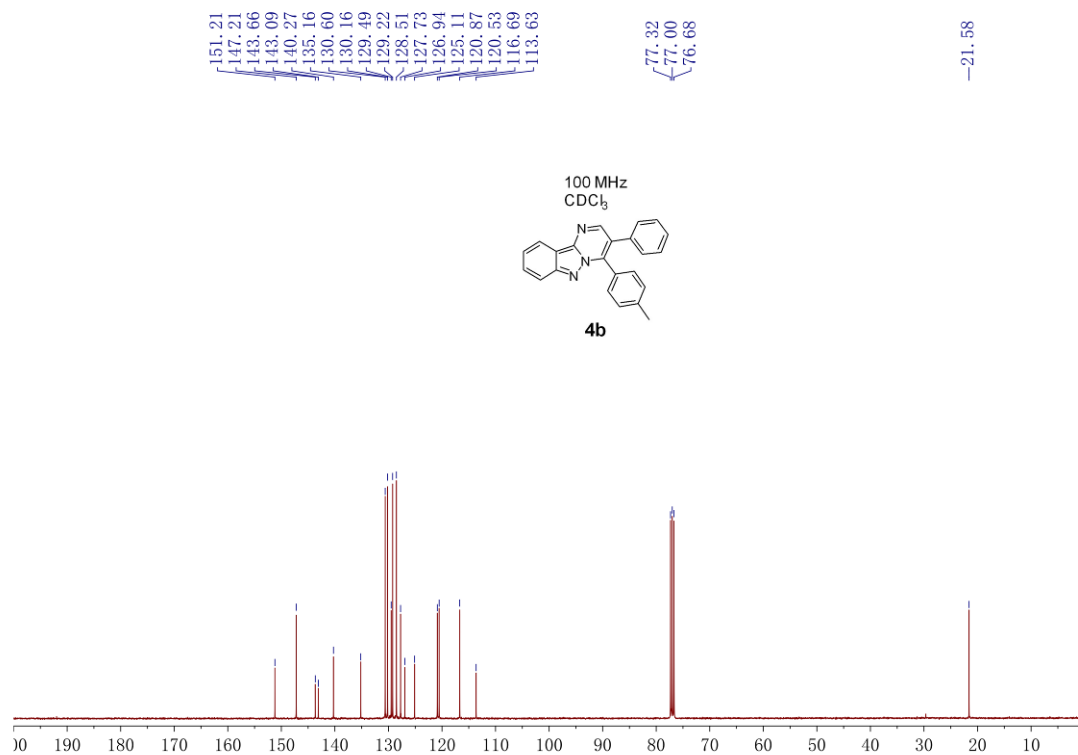
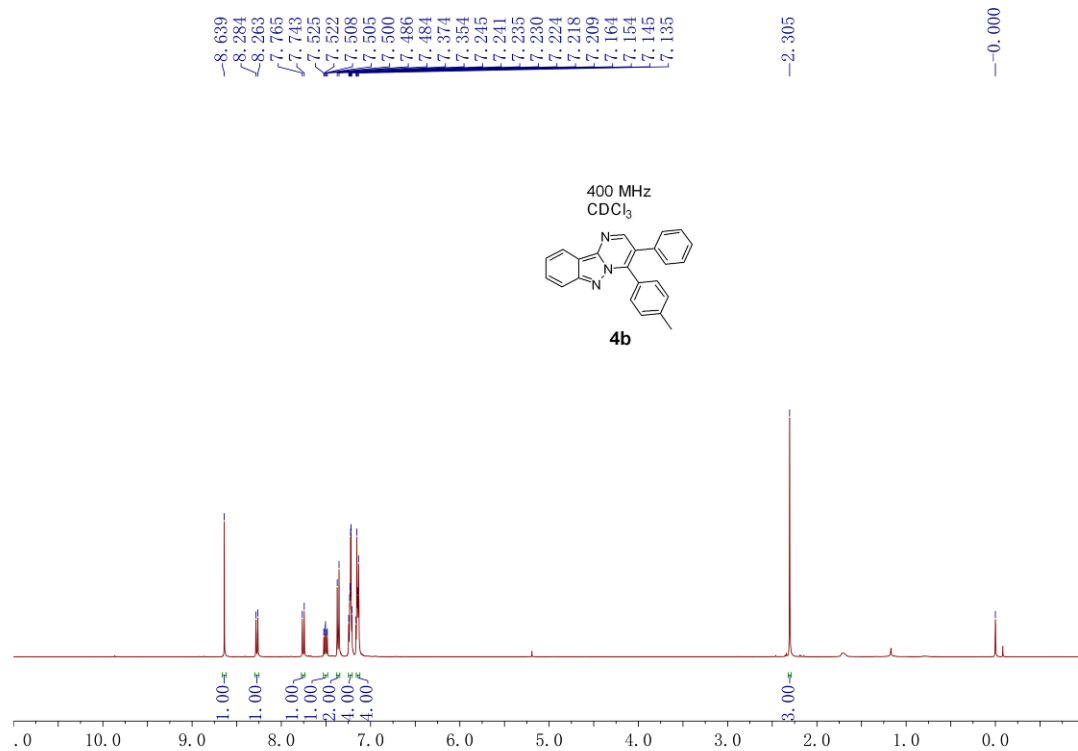


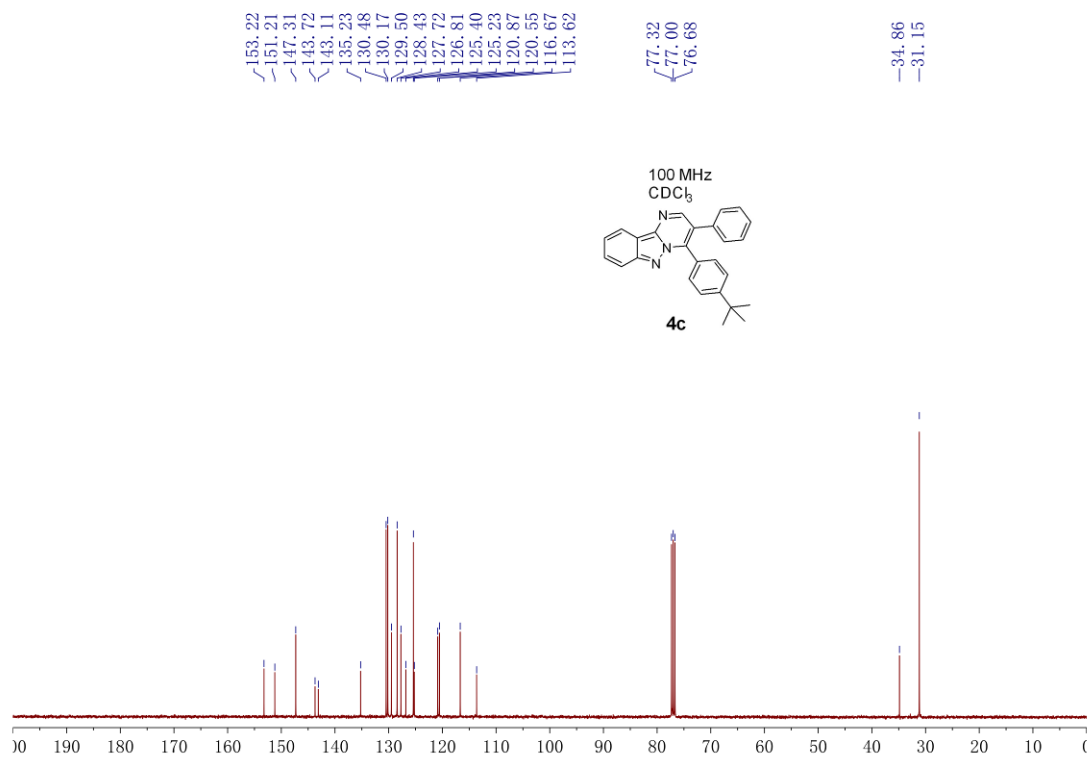
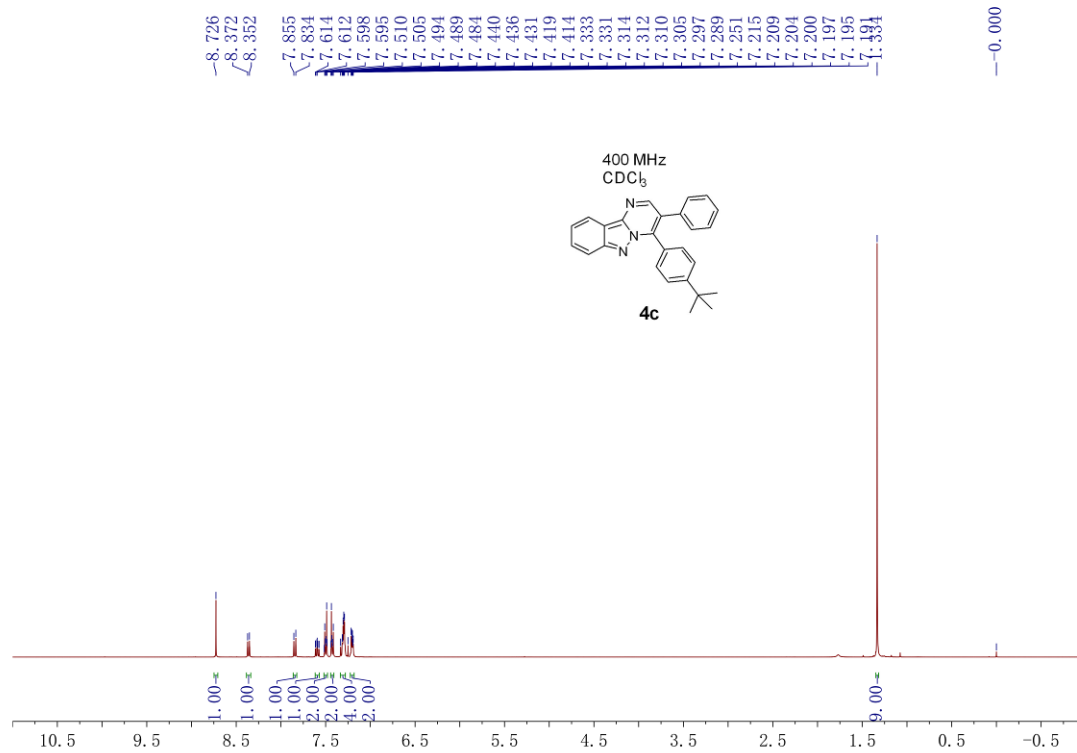
Figure S1. X-ray crystal structure of **4I**; the ellipsoids depicted at the 50% probability level.

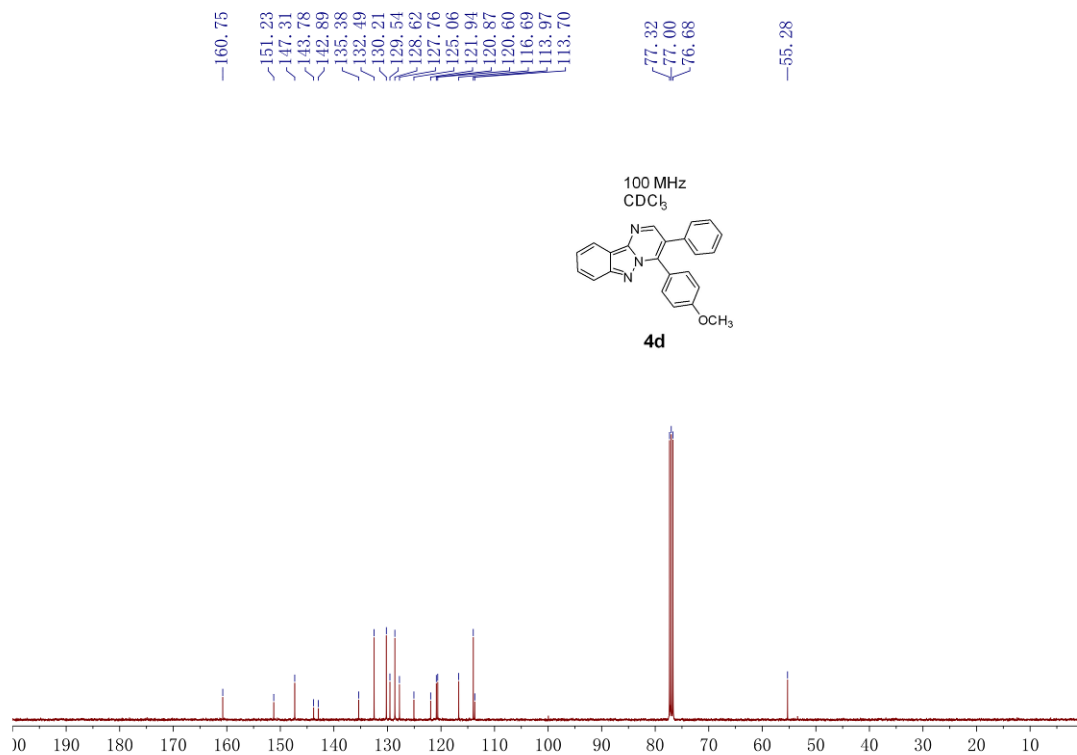
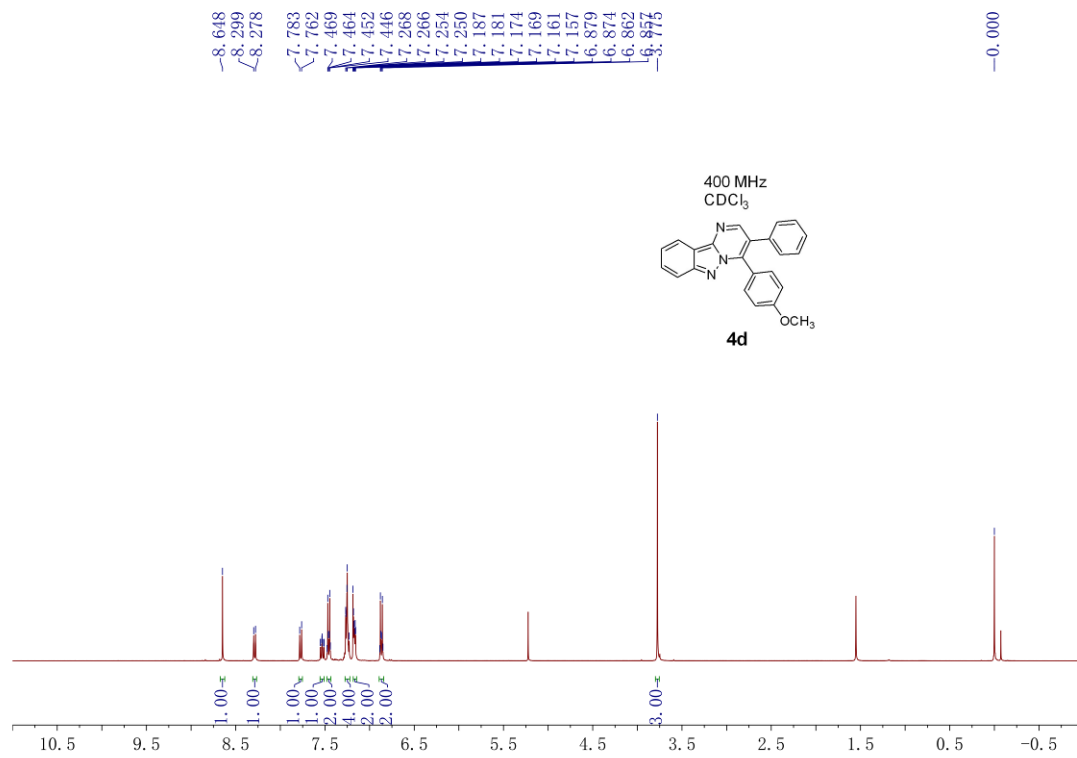
Empirical formula	C ₂₃ H ₁₇ N ₃		Absorption coefficient	0.078 mm ⁻¹
Formula weight	335.39		F(000)	352.0
Temperature	296(2) K		Crystal size	0.19 × 0.16 × 0.15 mm ³
Crystal system	triclinic		Theta range for data collection	4.198 to 55.29°
Space group	P-1		Reflections collected	5080
Unit cell dimensions	a = 9.185(8) Å	α = 80.364(9)°	Independent reflections	3817 [R _{int} = 0.0341, R _{sigma} = 0.0815]
	b = 10.136(8) Å	β = 67.002(9)°	Data / restraints / parameters	3817/0/236
	c = 10.439(9) Å	γ = 73.546(10)°	Goodness-of-fit on F ²	0.940
Volume	856.2(12) Å ³		Final R indices [I > 2σ(I)]	R ₁ = 0.0626, wR ₂ = 0.1555
Z	2		R indices (all data)	R ₁ = 0.1262, wR ₂ = 0.1989
Density (calculated)	1.301 g/cm ³		Largest diff. peak and hole	0.23 / -0.18 e.Å ⁻³

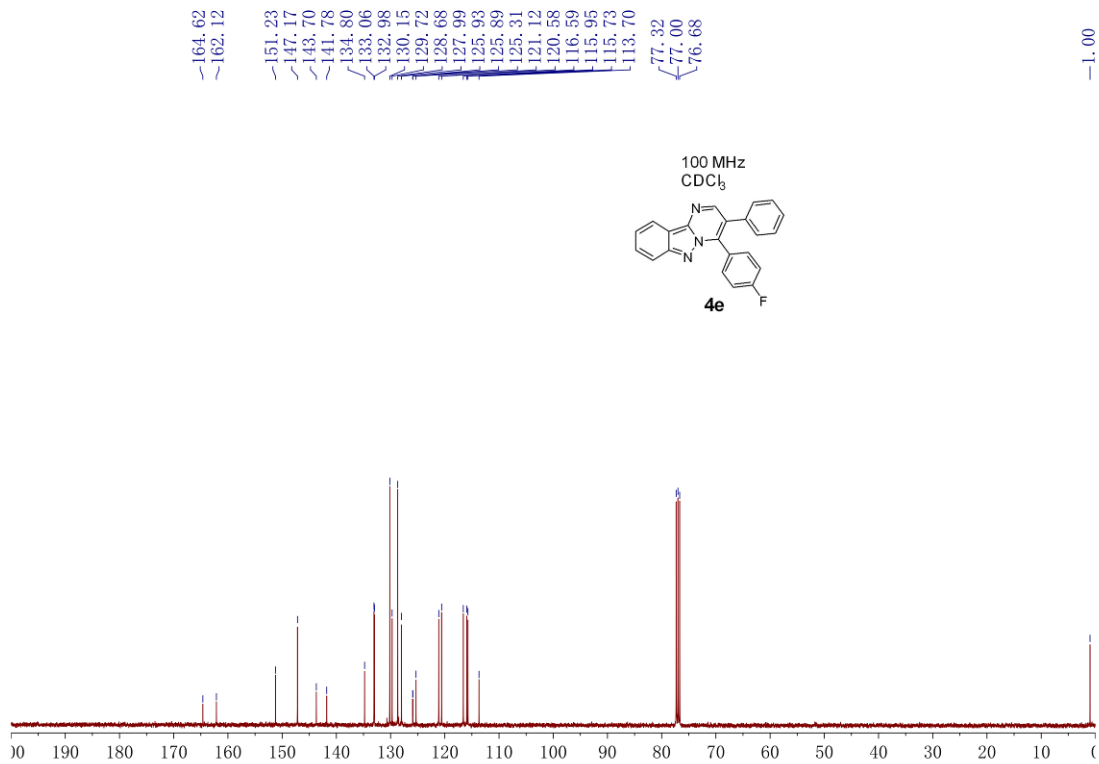
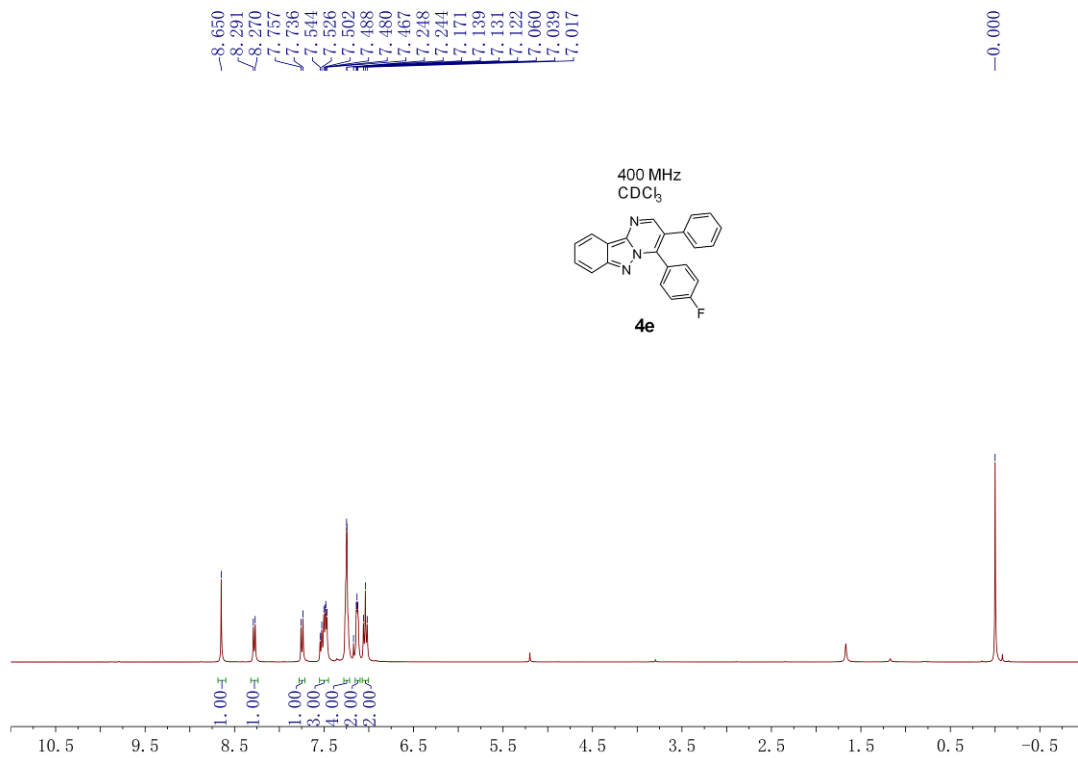
8. NMR spectra

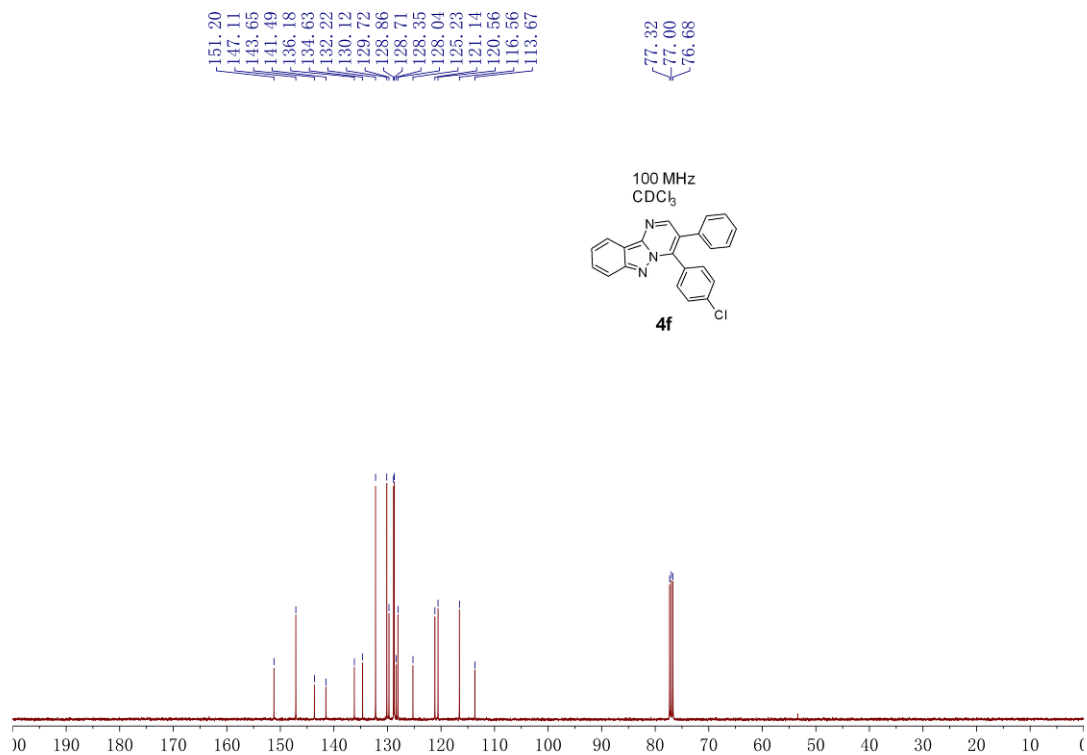
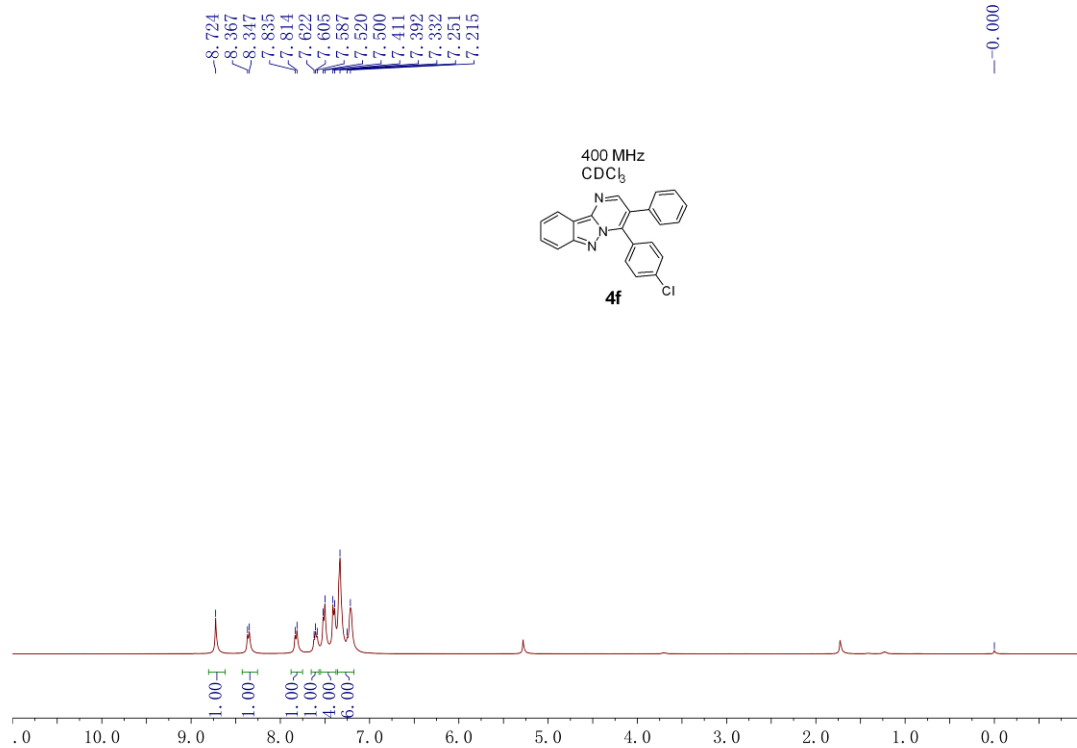


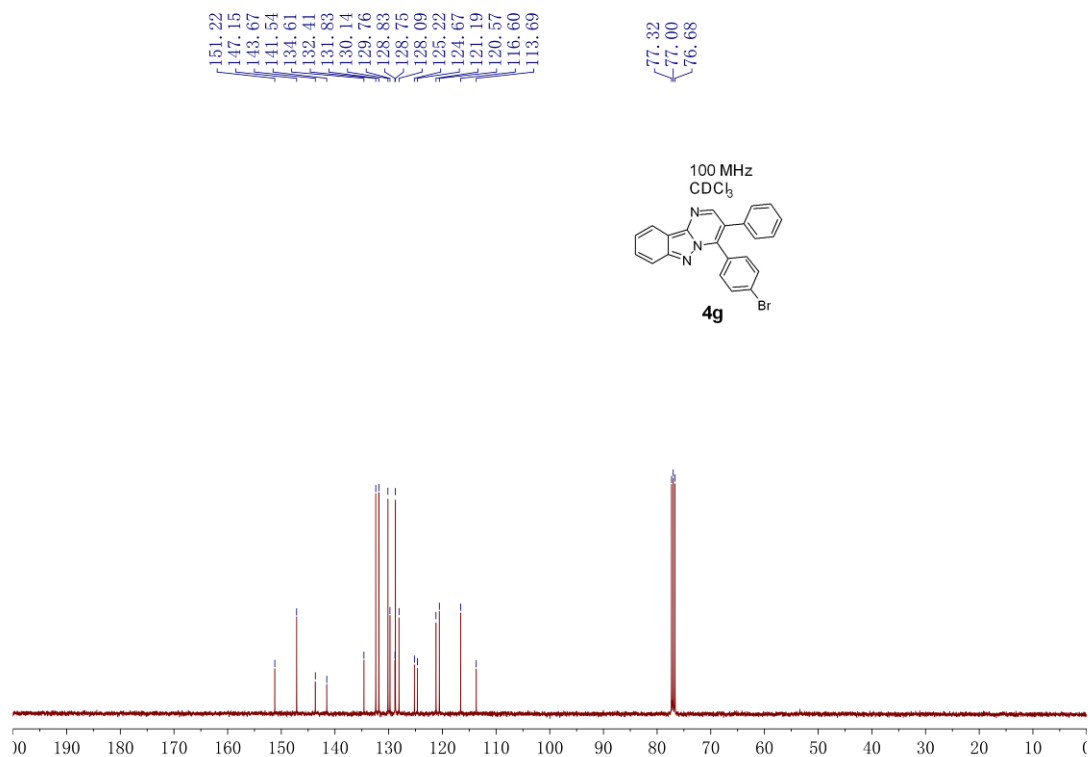
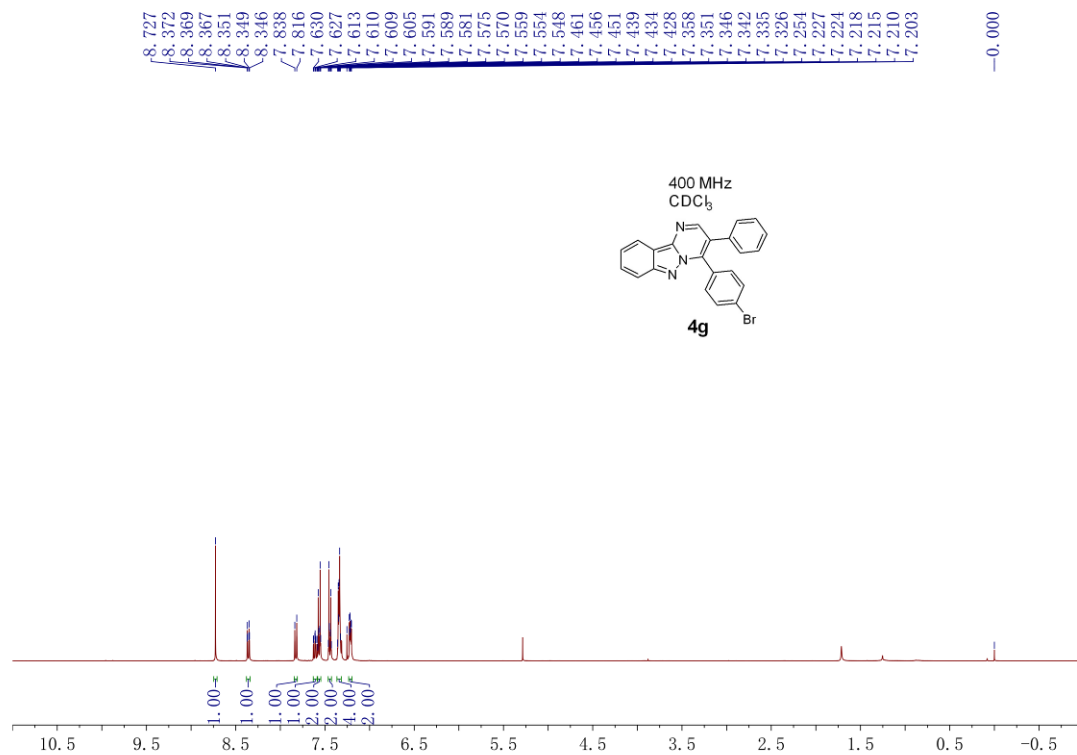


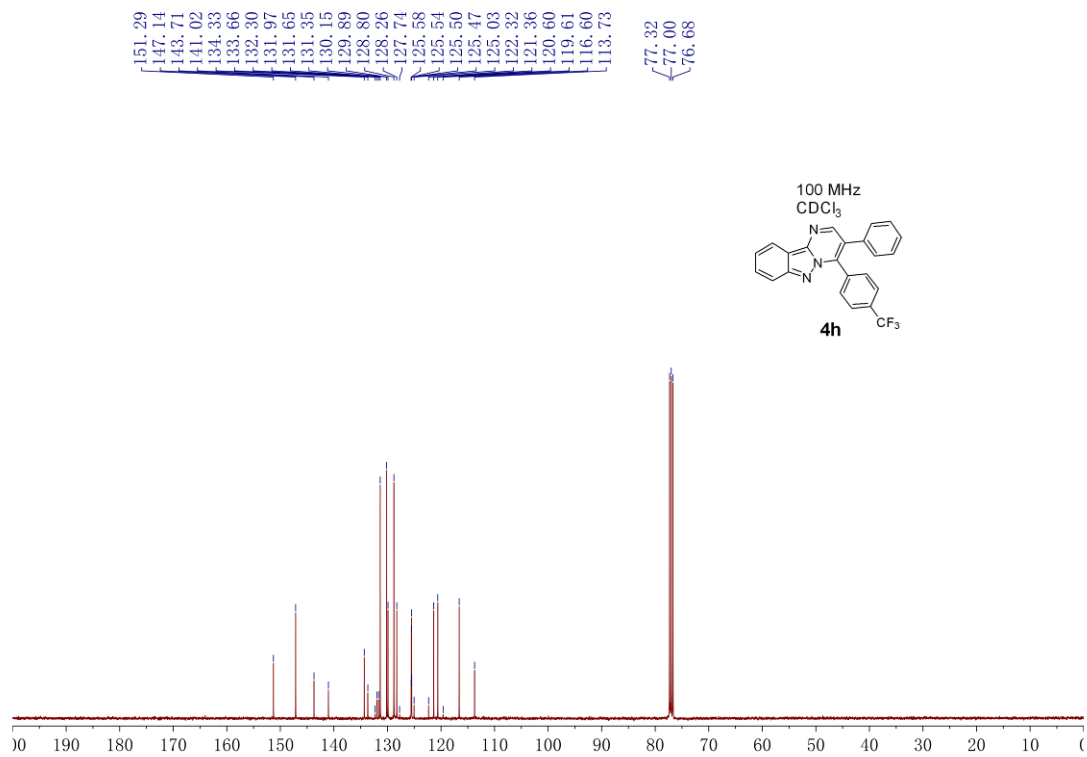
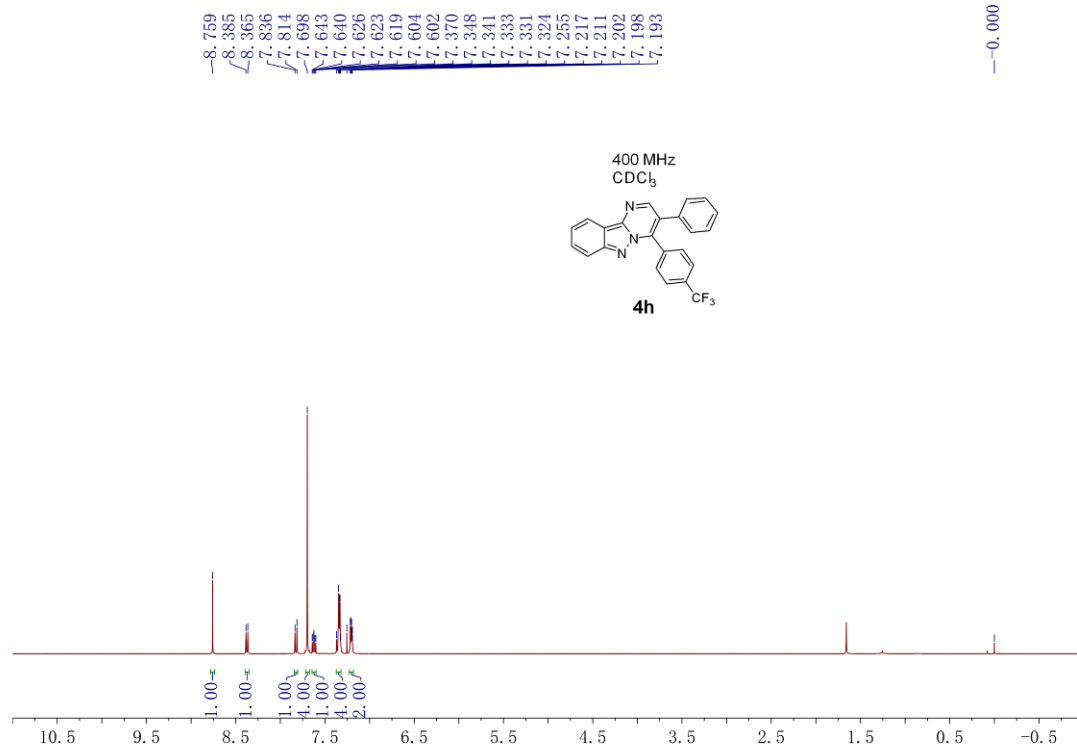


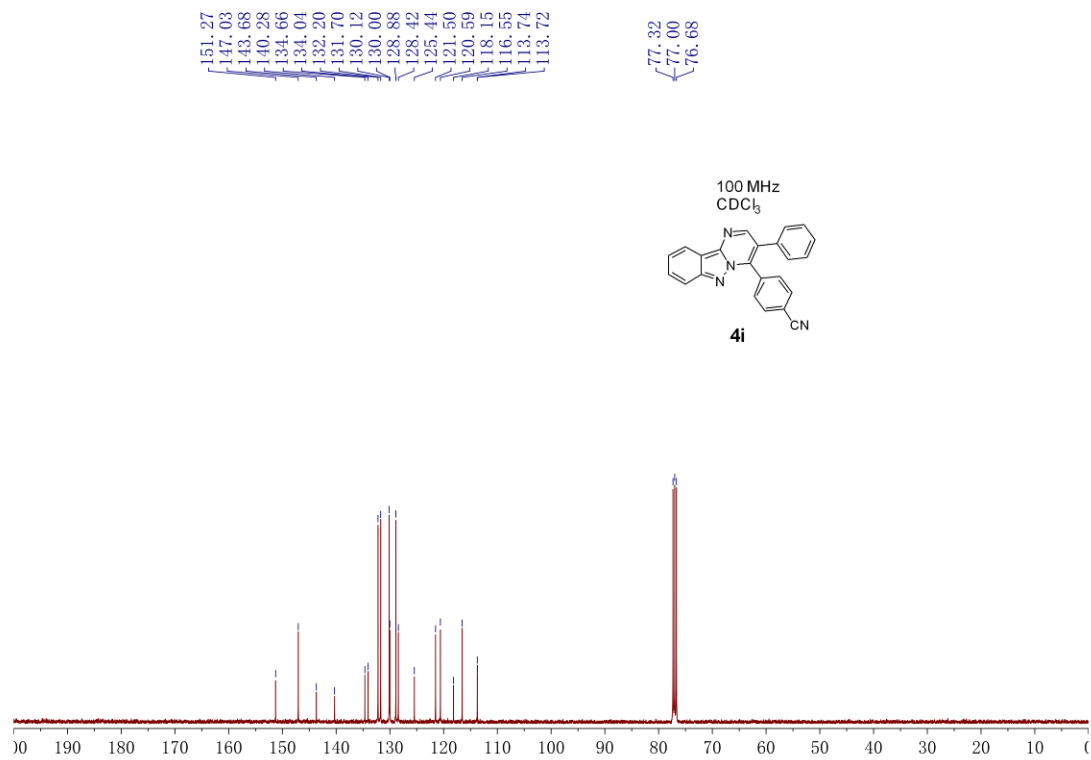
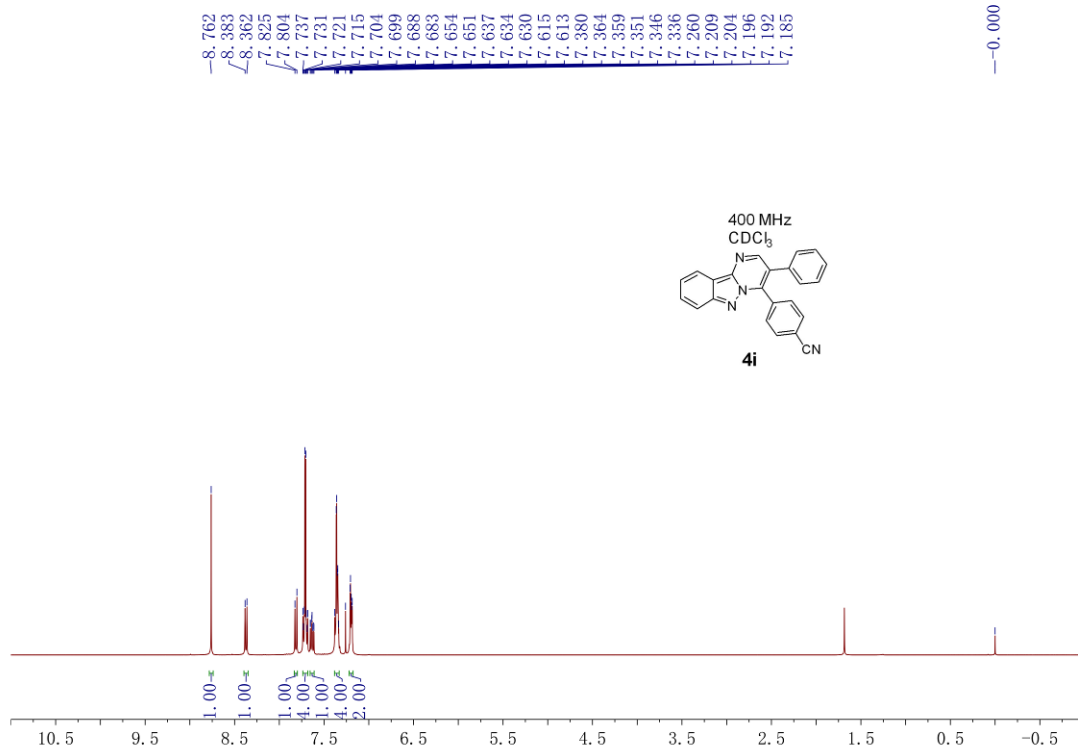


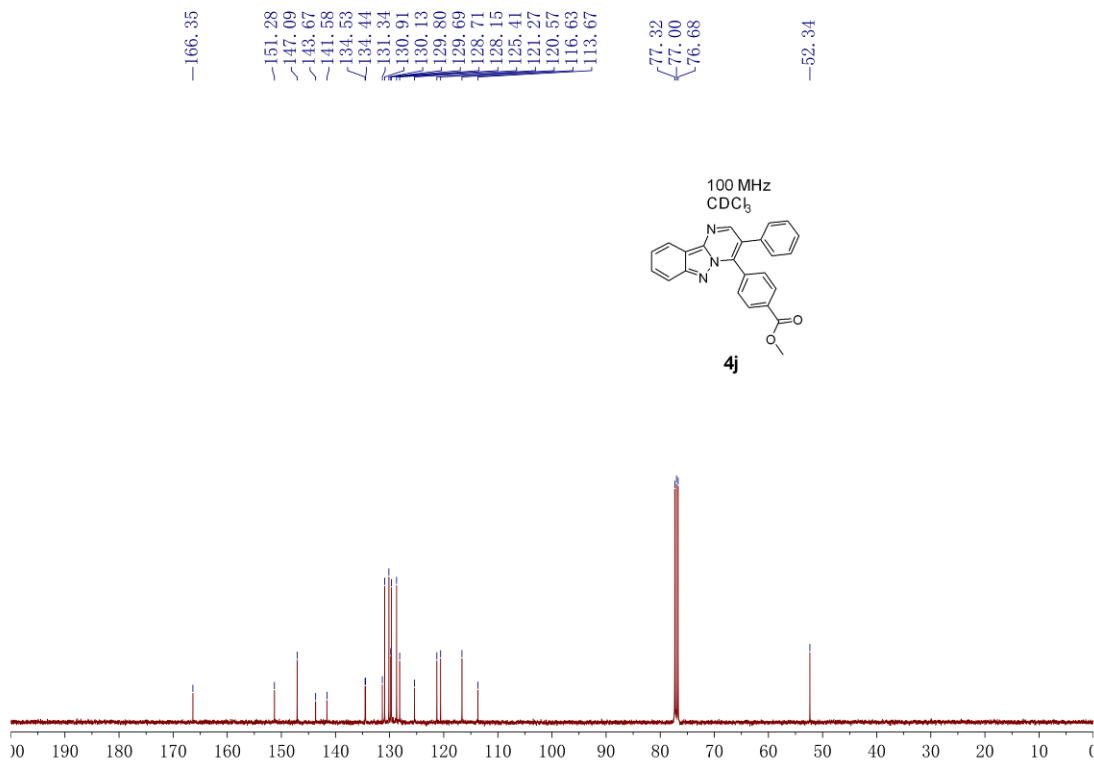
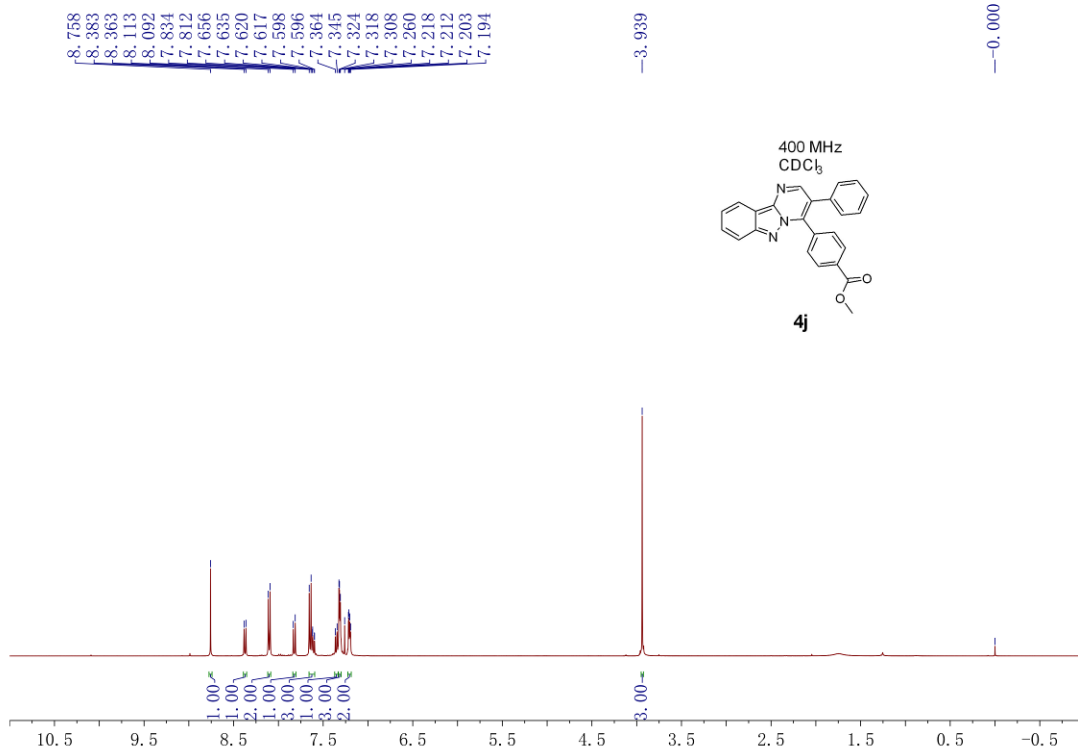


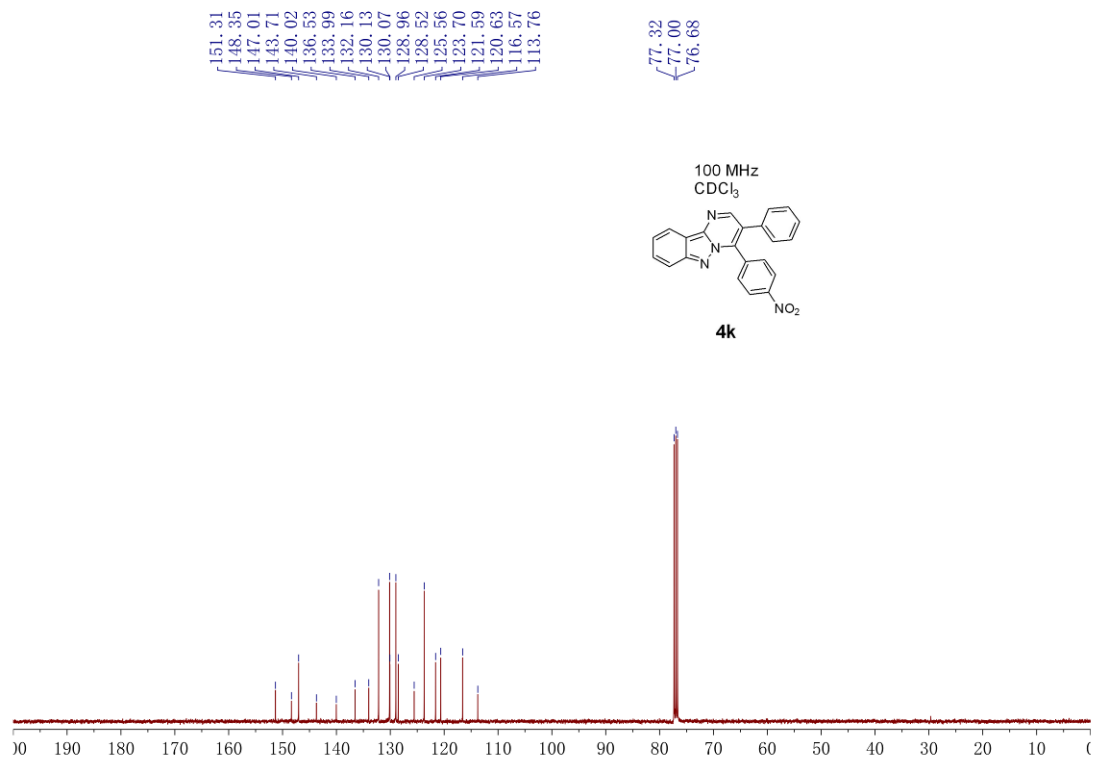
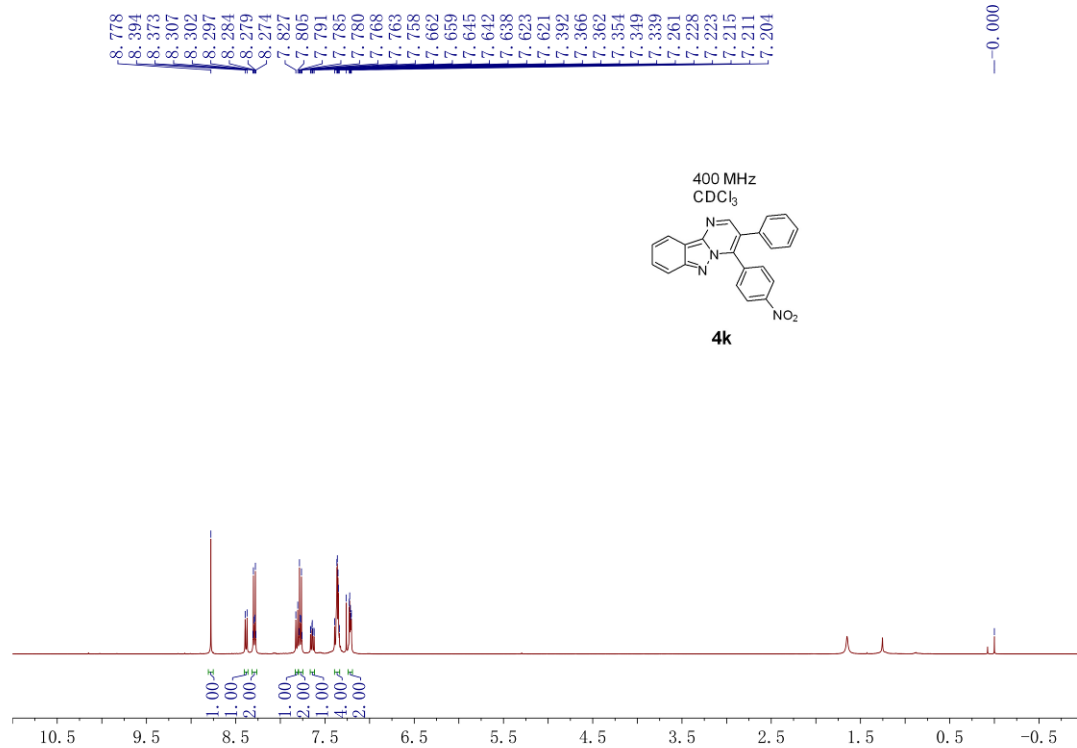


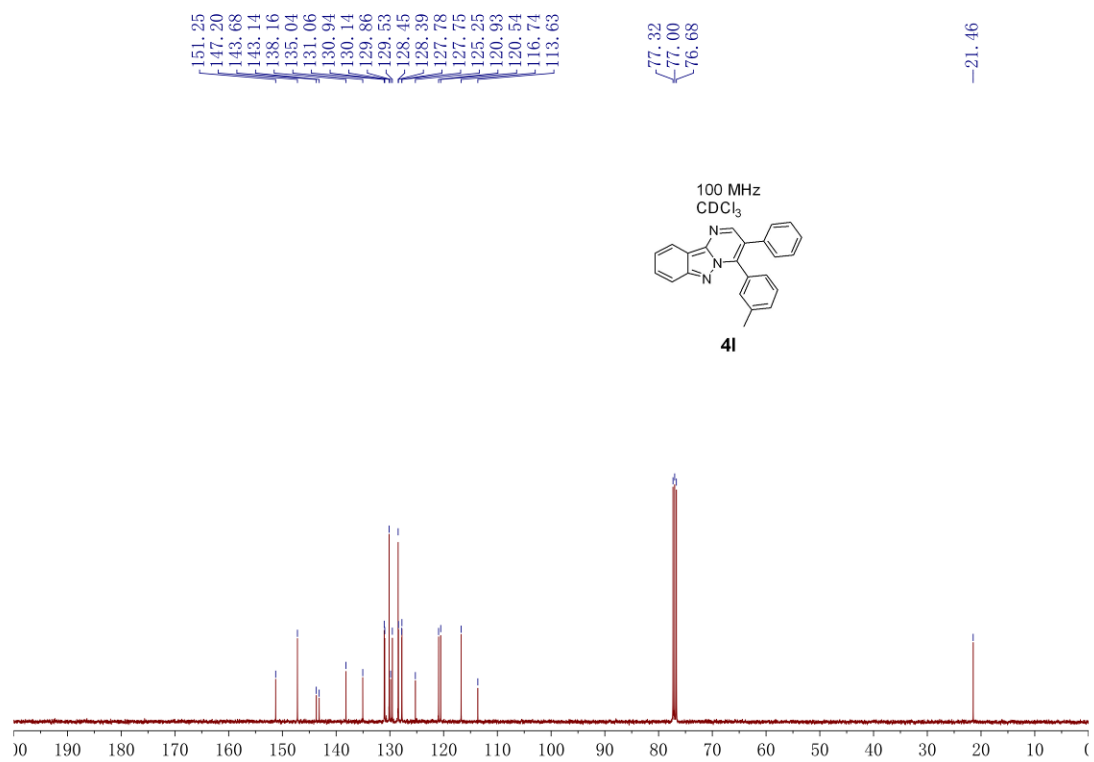
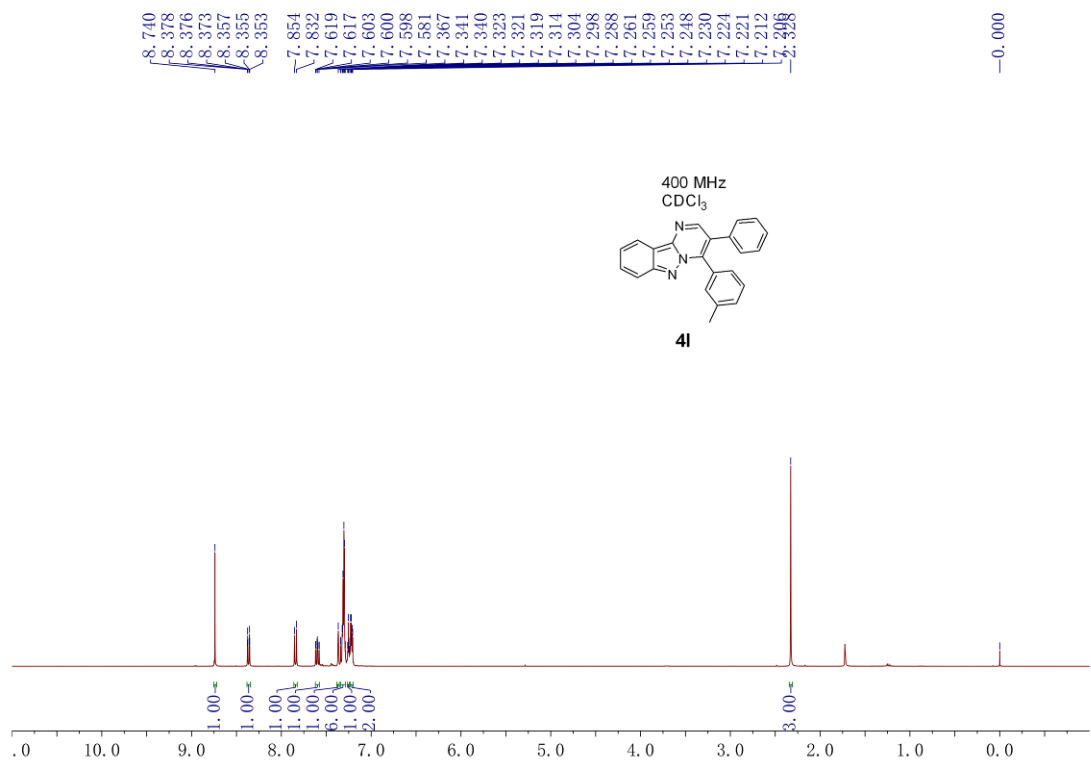


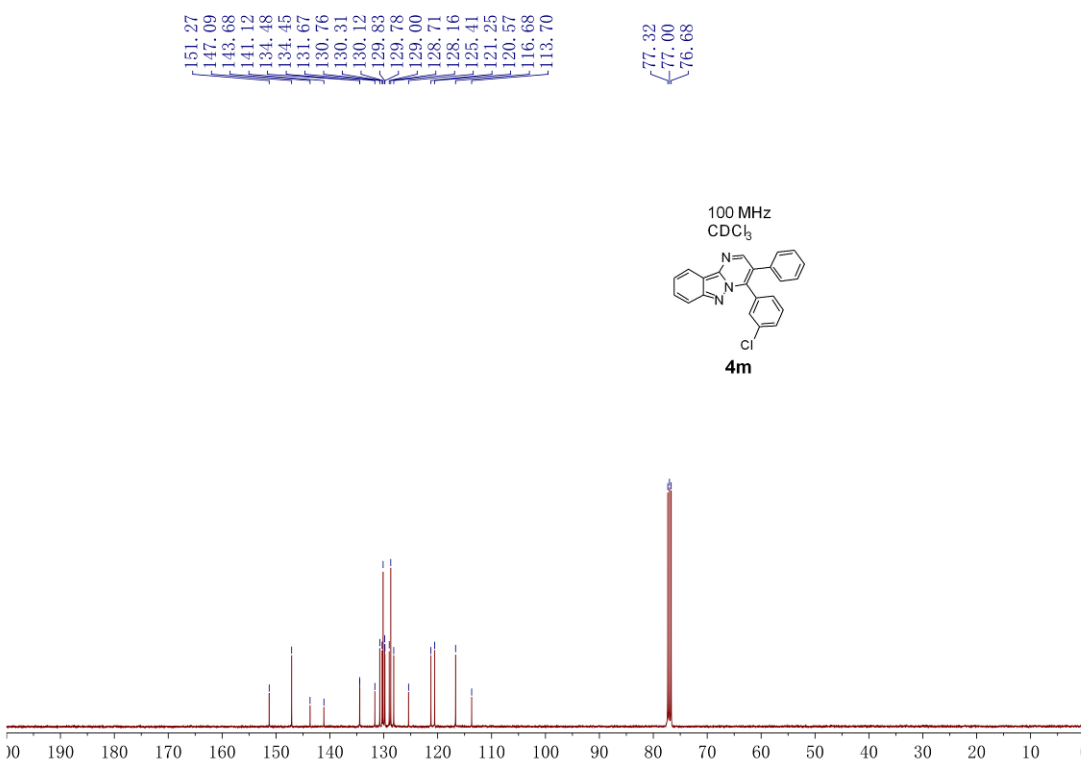
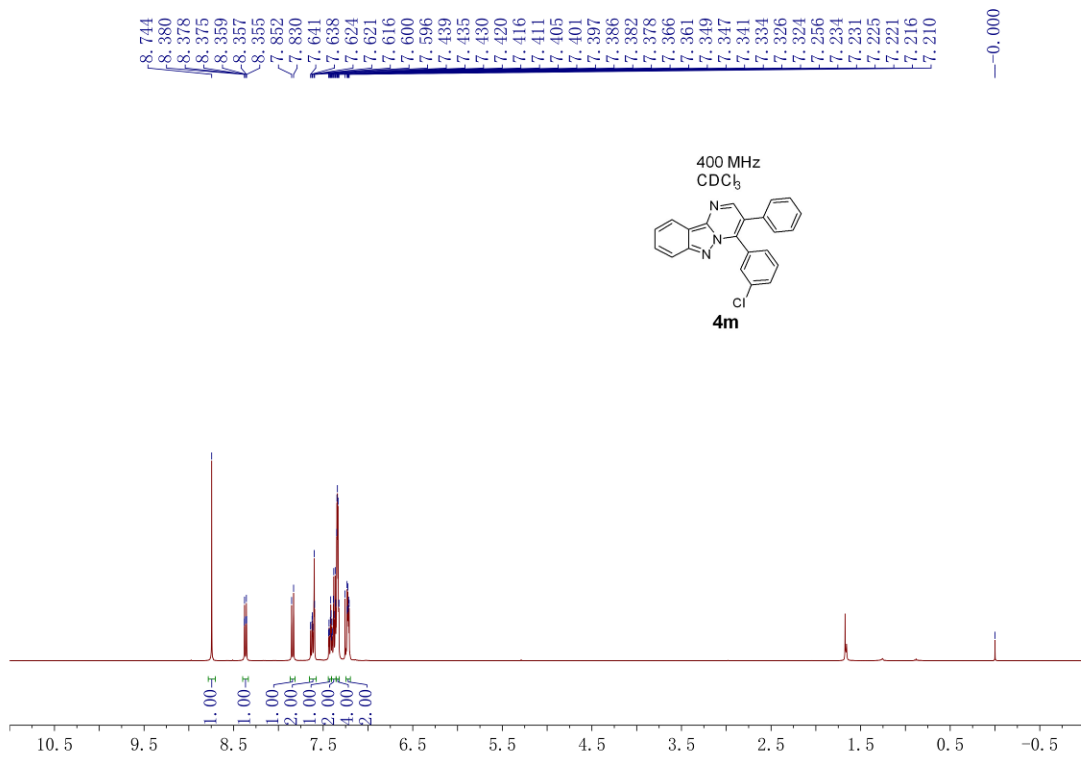


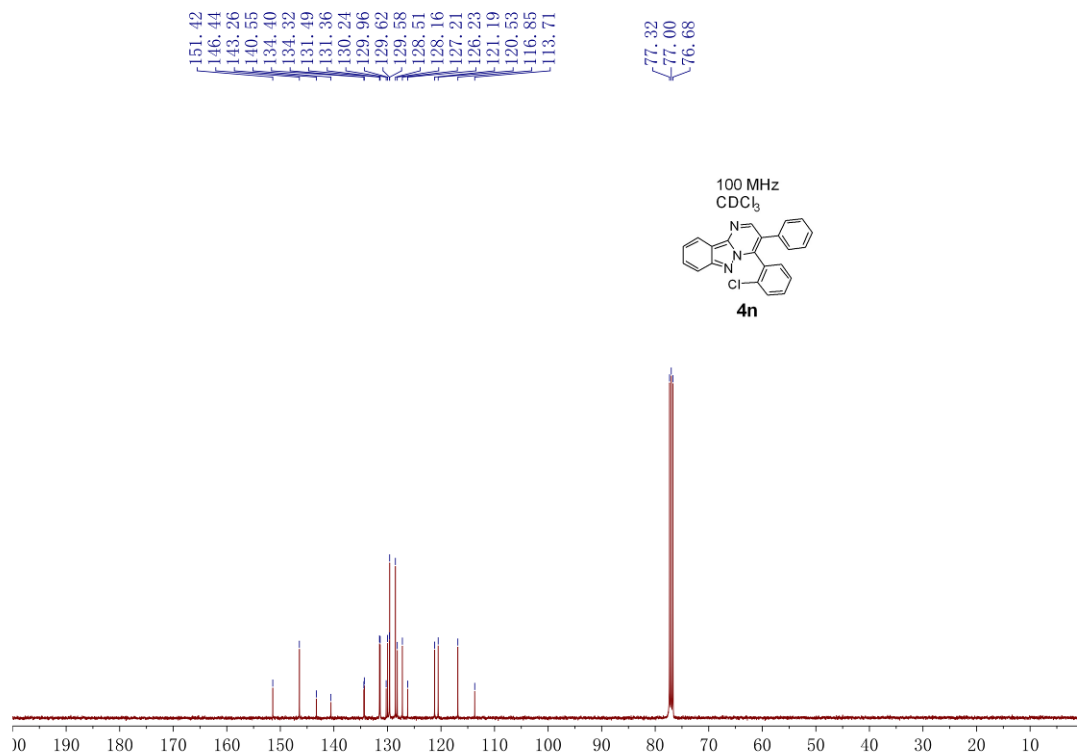
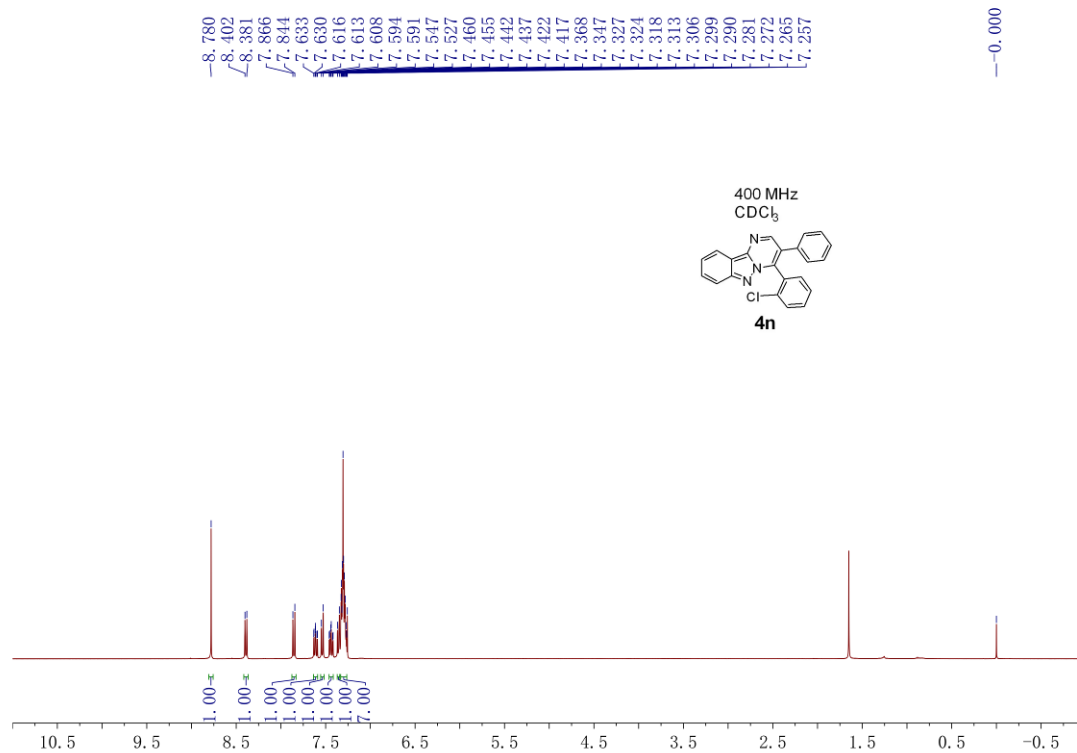


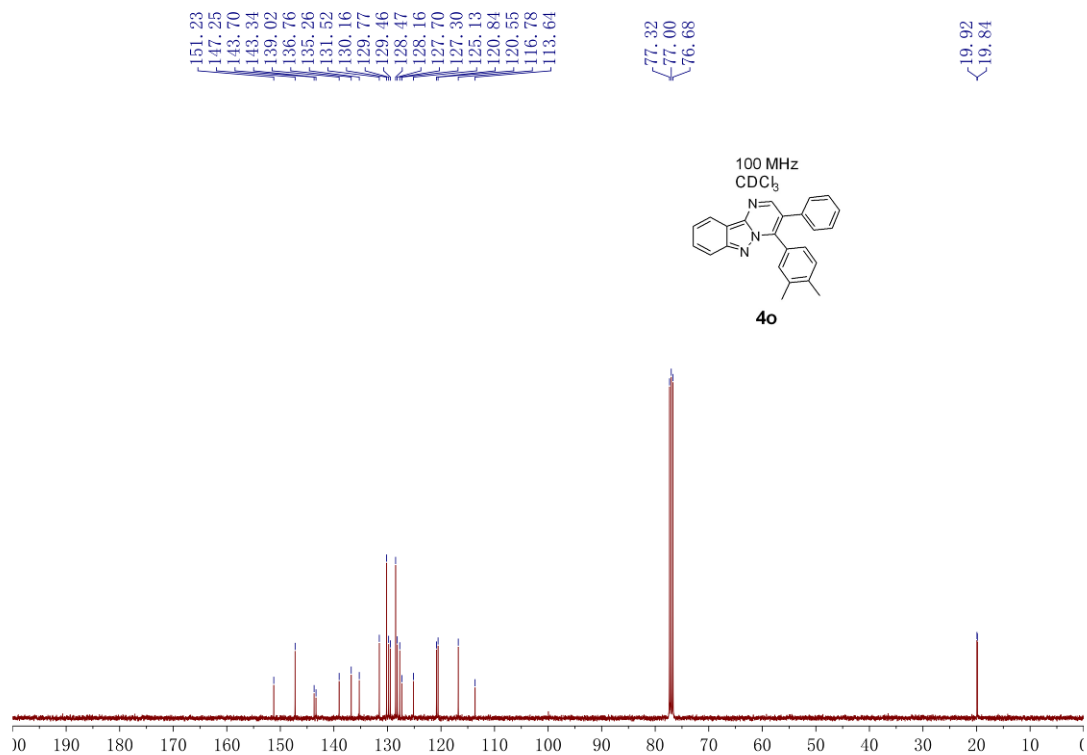
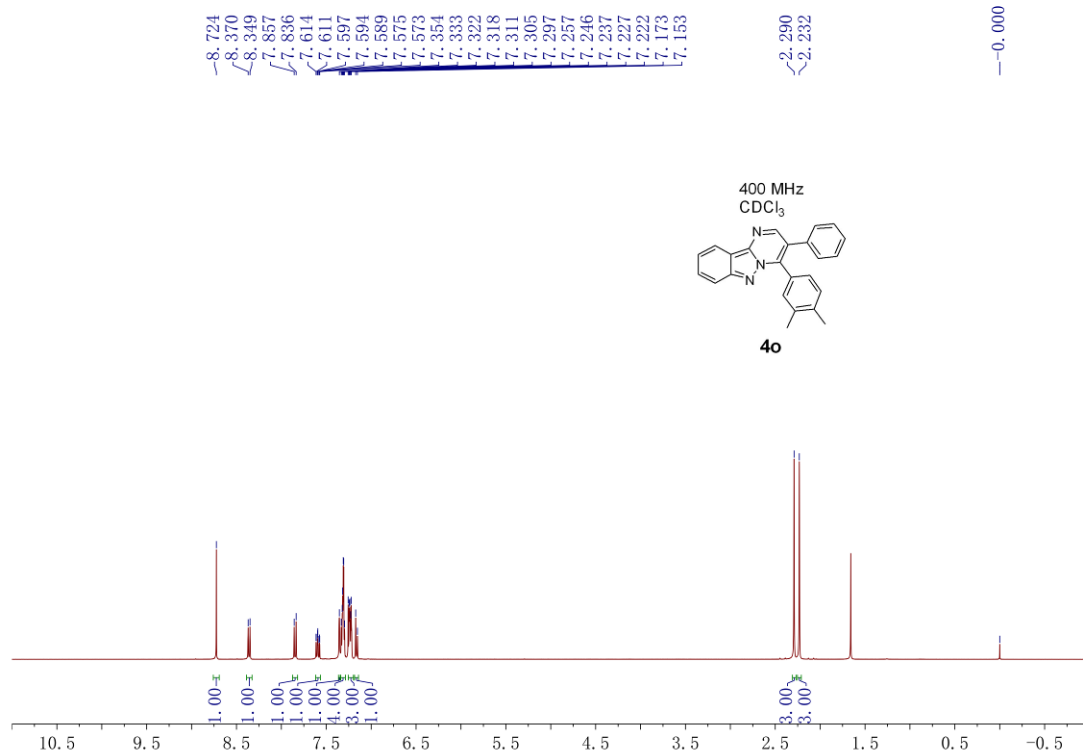


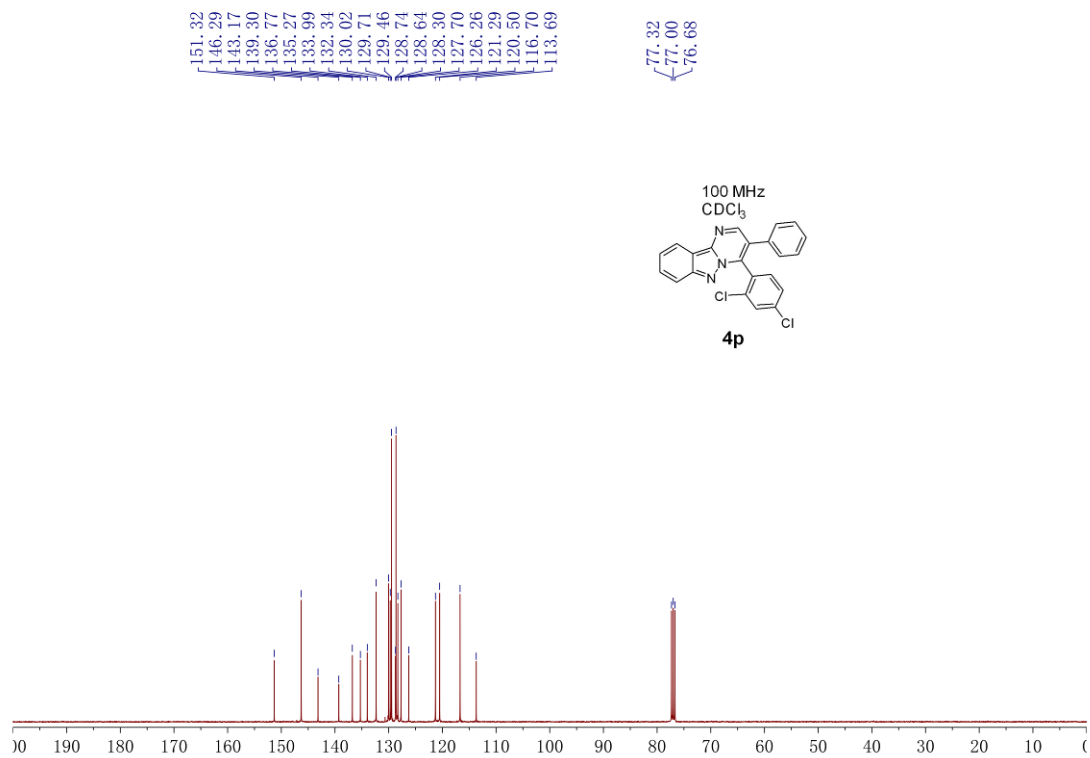
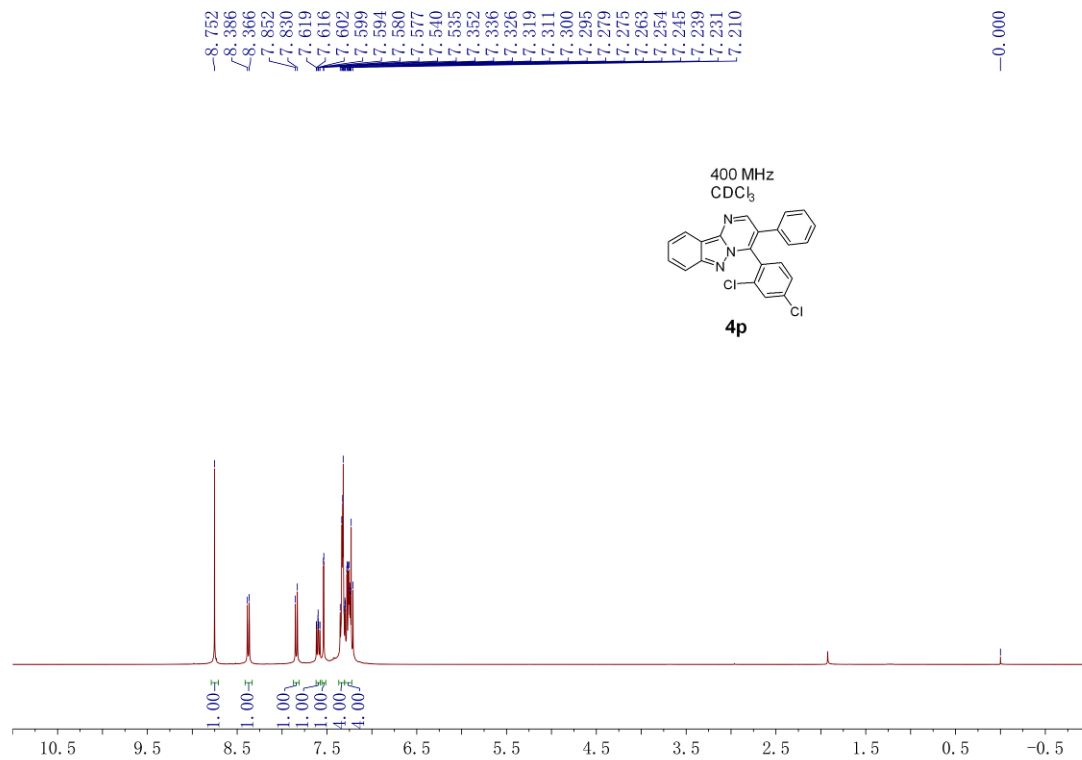


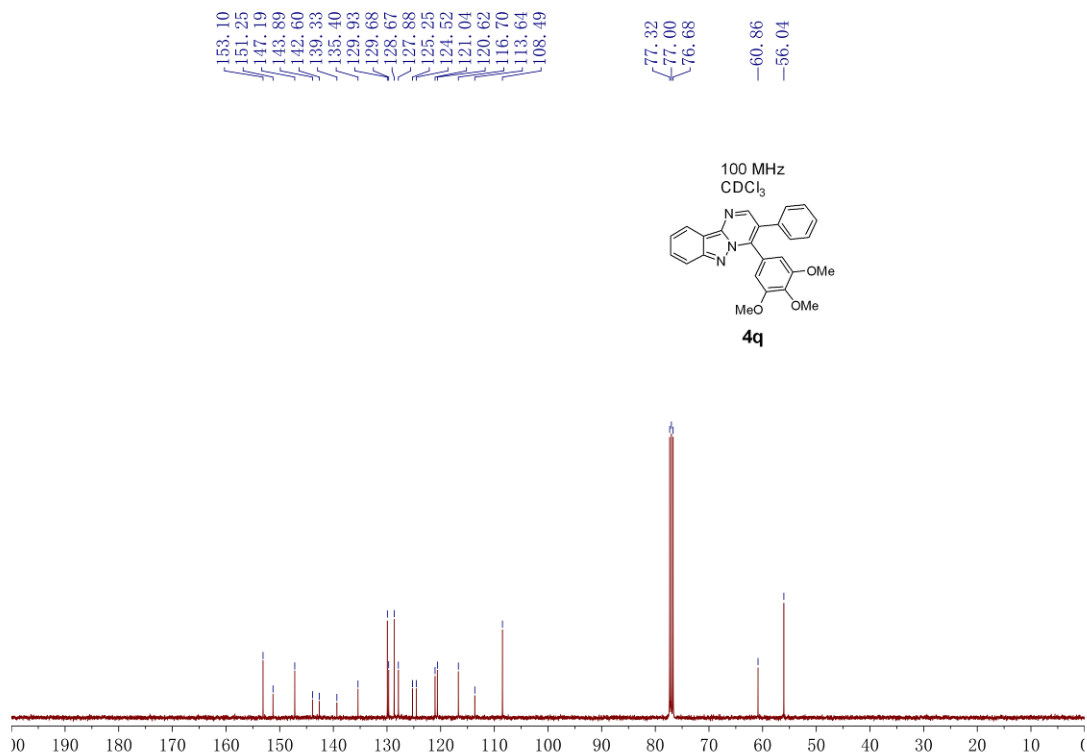
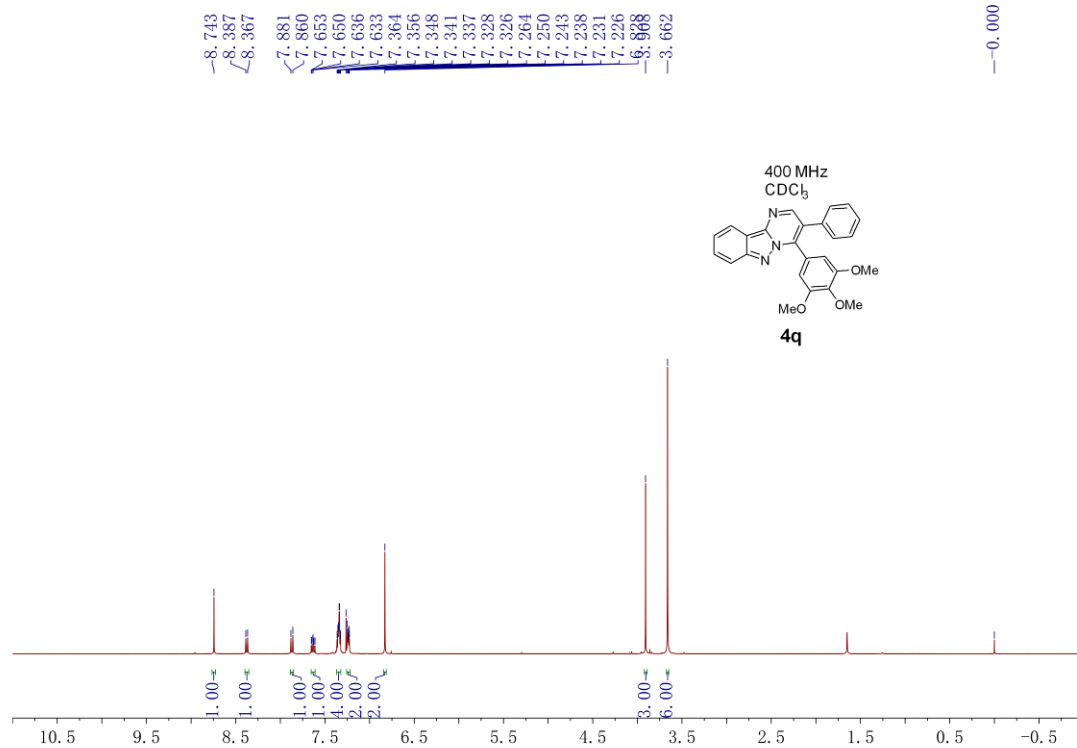


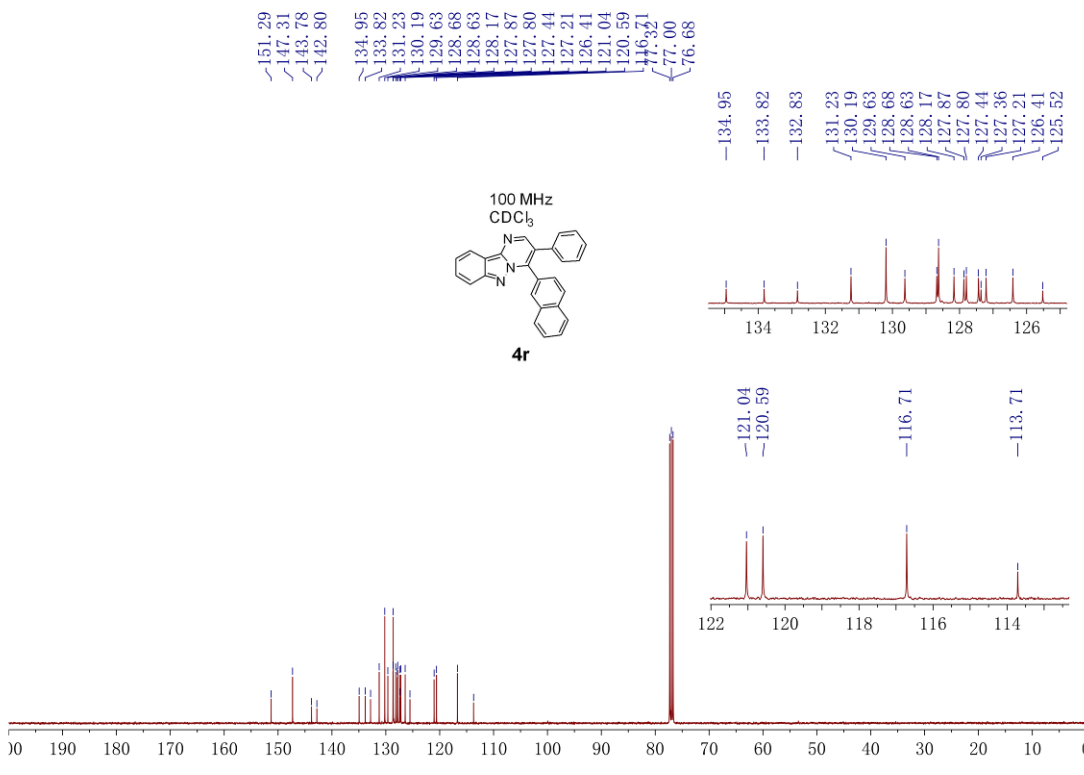
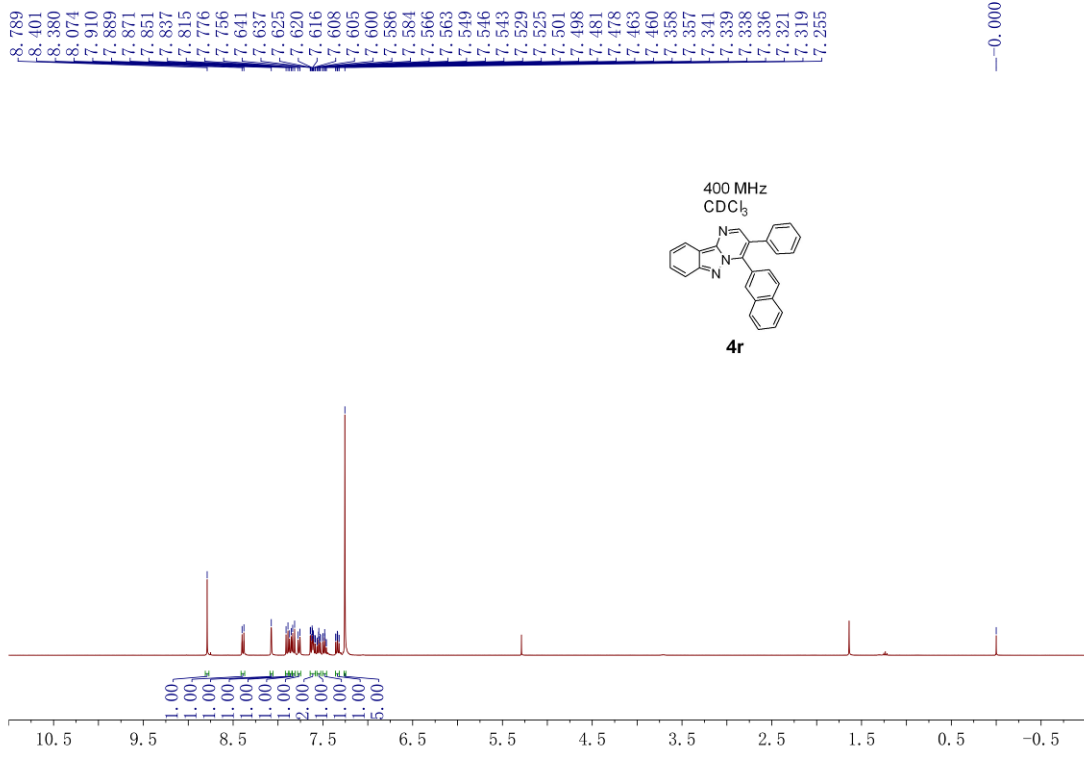


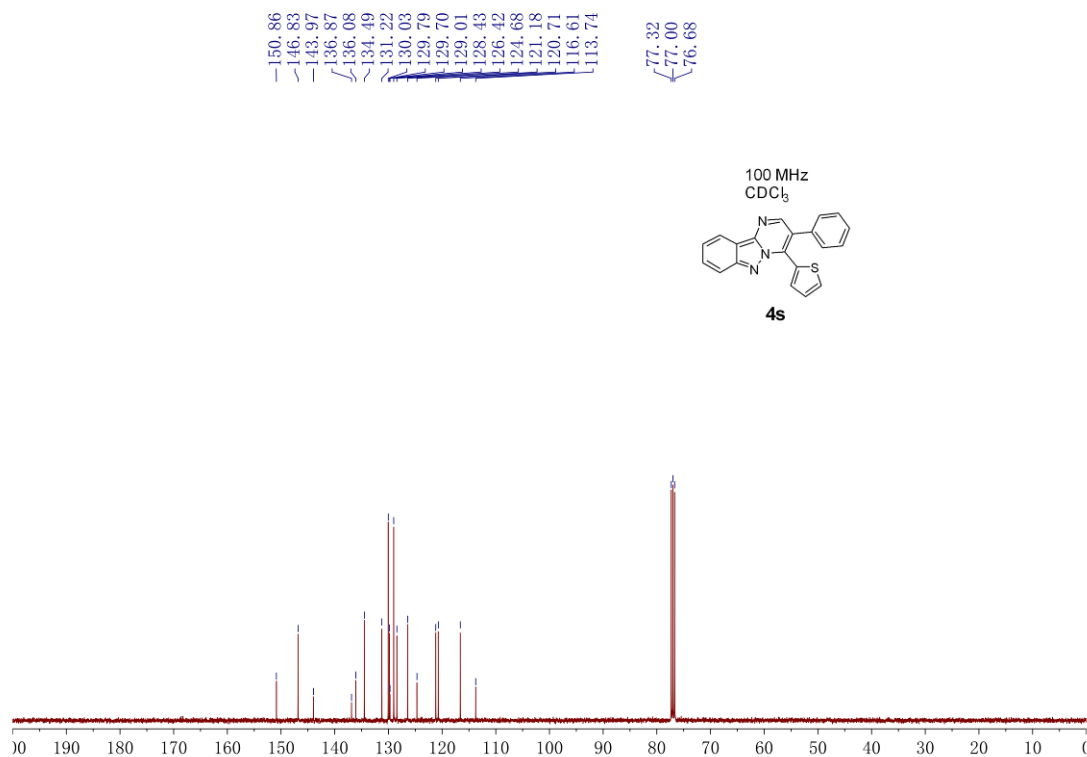
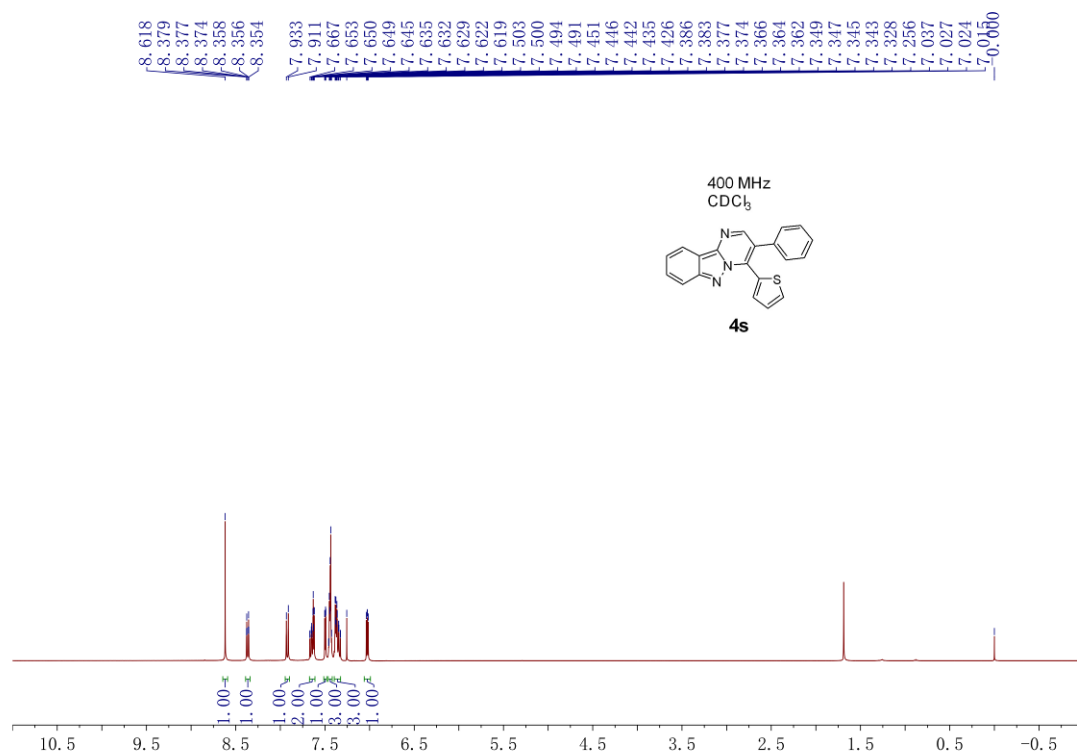


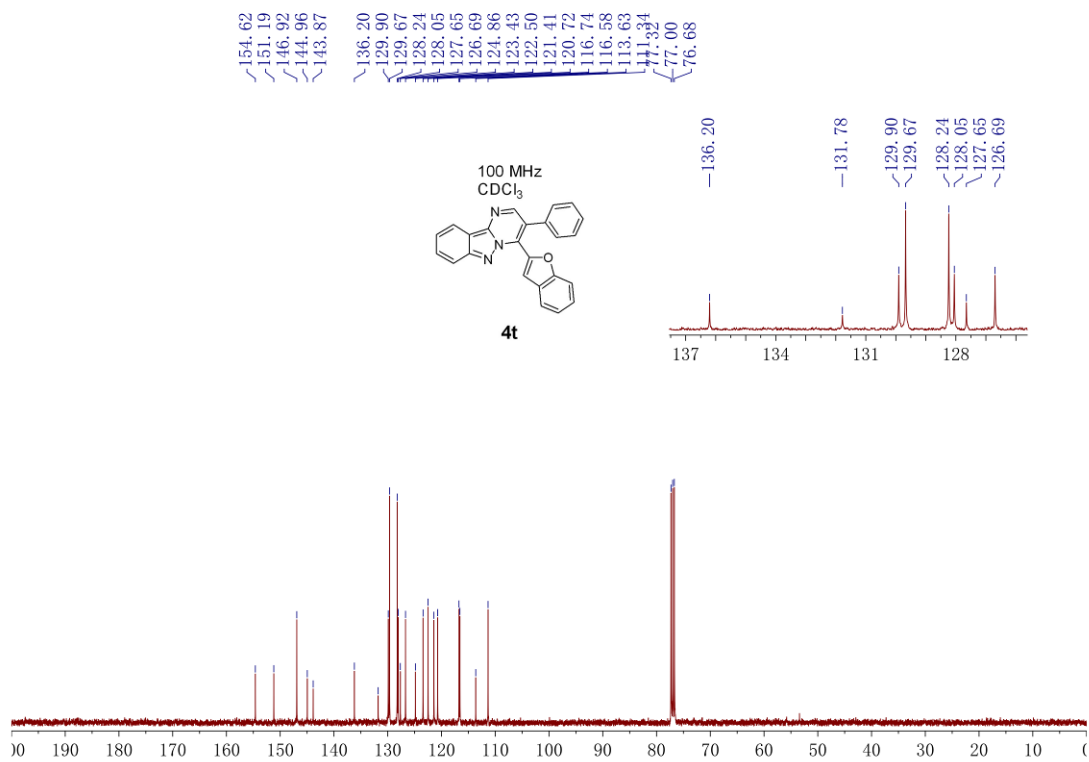
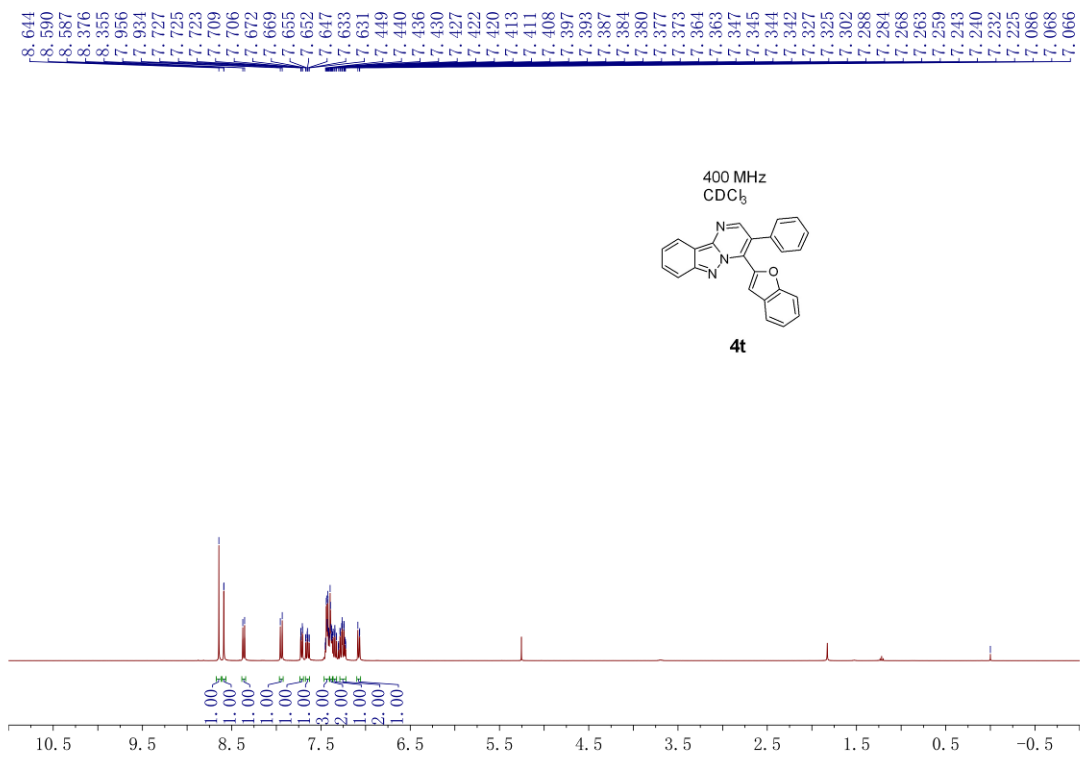


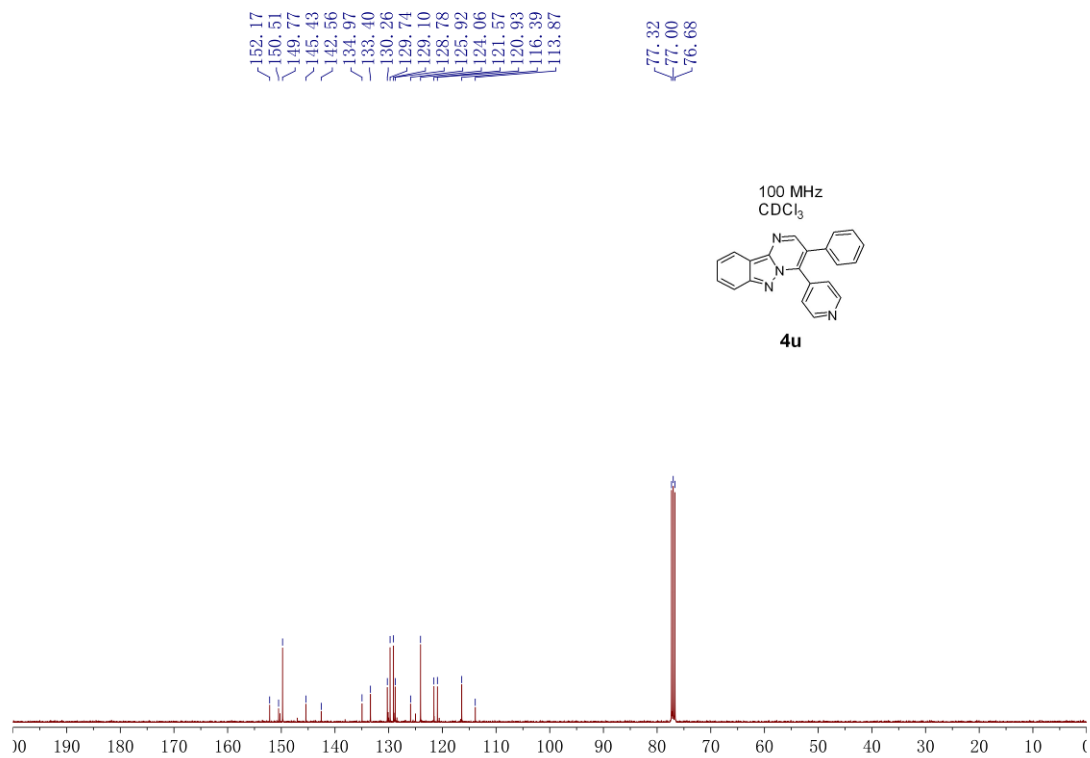
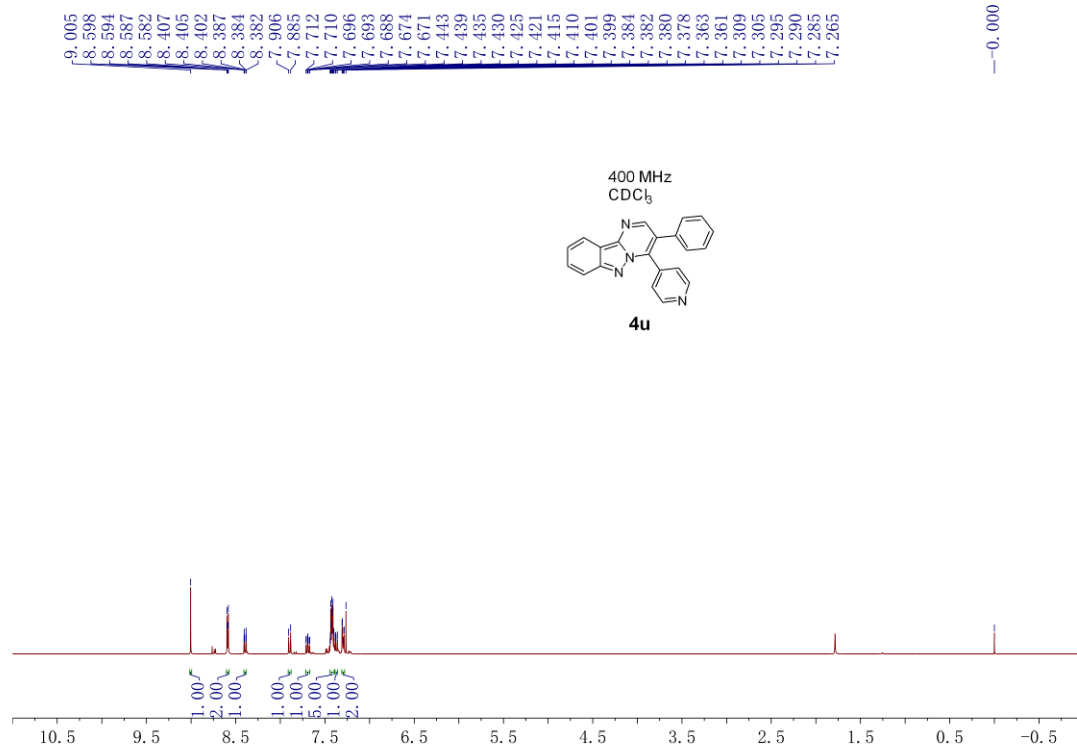


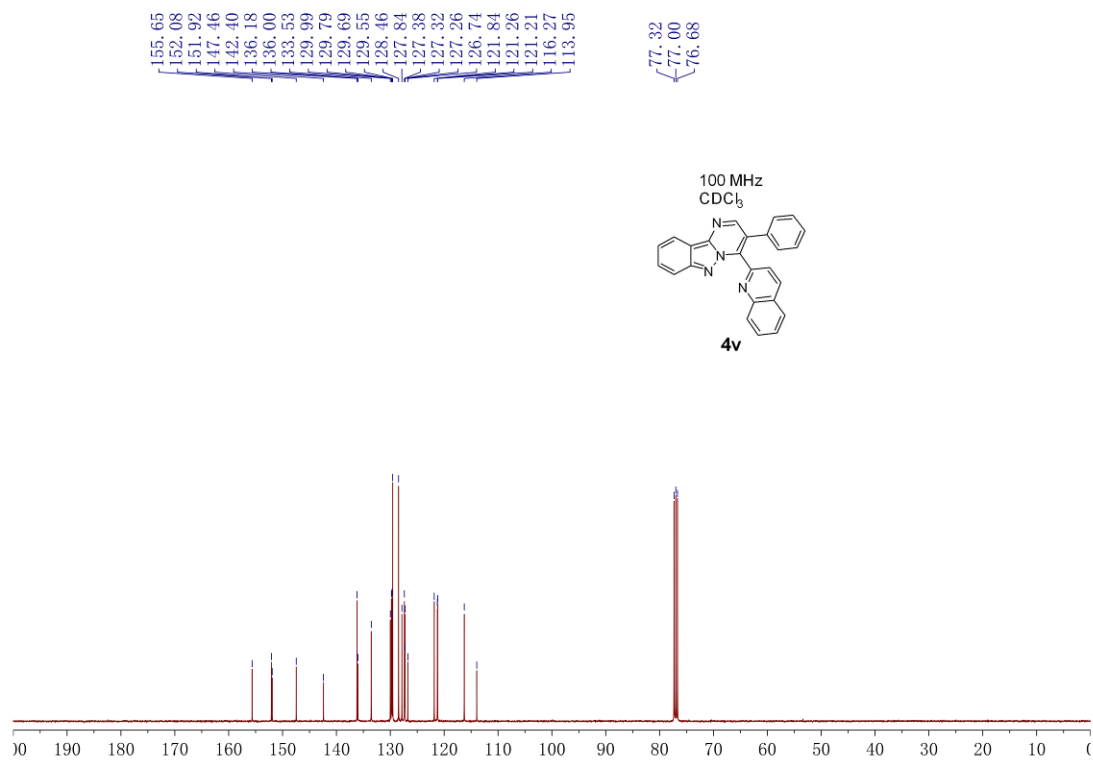
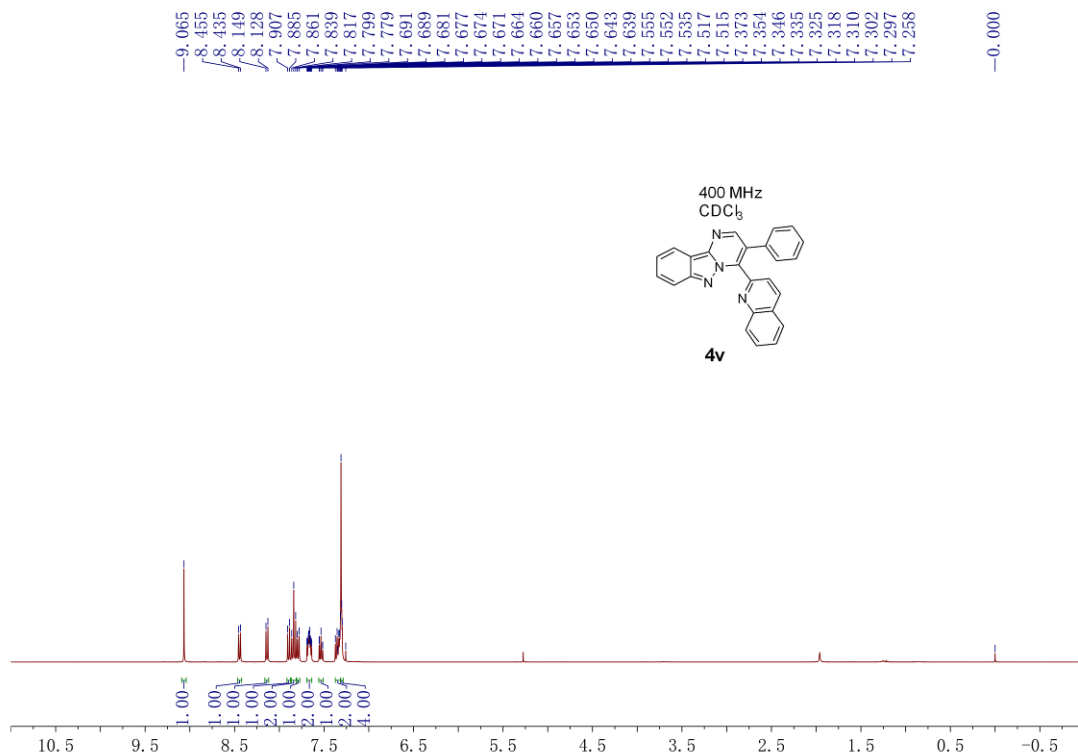






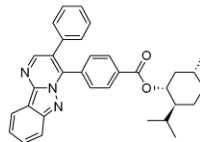




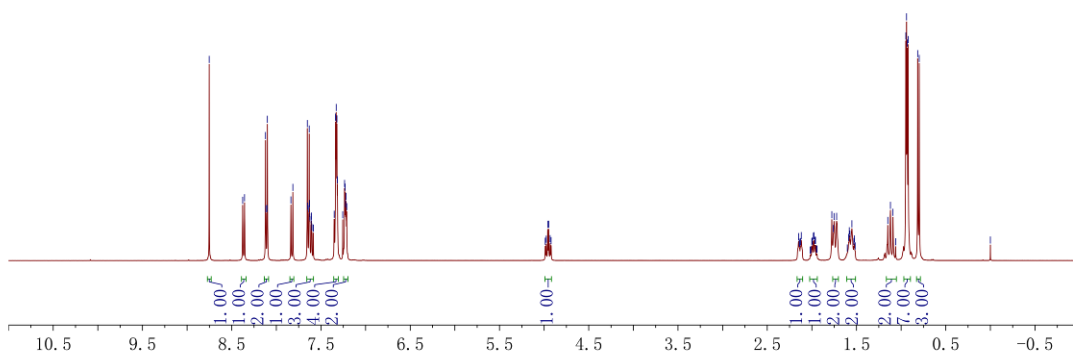


8.752
8.377
8.356
8.121
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8.104
8.100
7.837
7.815
7.653
7.649
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7.632
7.627
7.625
7.610
7.607
7.603
7.588
7.586
7.352
7.337
7.329
7.321
7.316
7.256
7.236
7.229
7.225
7.220
7.212
4.976
4.960
4.949
4.933
2.148
2.119
1.983
1.977
1.776
1.759
1.752
1.723
1.588
1.581
1.573
1.551
1.523
1.149
1.120
1.092
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0.939
0.931
0.921
0.814
0.797

400 MHz
CDCl₃



4w



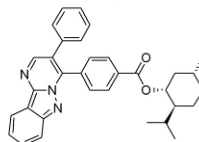
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151.24
147.11
143.65
141.64
134.46
134.27
132.06
130.80
130.13
129.73
129.65
128.73
128.10
125.32
121.20
120.54
116.64
113.66

77.32
77.00
76.68
75.18

47.19
40.87
34.21
31.39
26.32
23.41
22.01
20.78
16.34

100 MHz
CDCl₃



4w

