Supporting Information

Construction of Pyrazolo[1,5-a]pyrimidines and Pyrimido[1,2-b]indazoles with Calcium Carbide as an Alkyne Source

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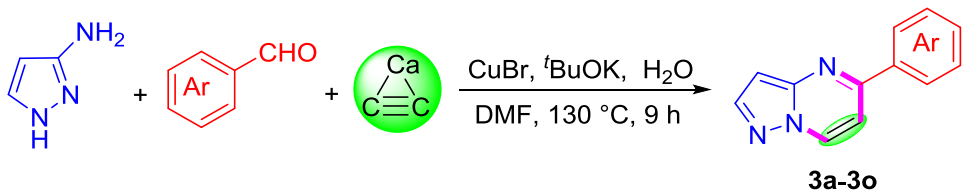
1. Experimental section

1.1 General Information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Mercury-600 MB or 400 MB instrument using $CDCl_3$ as solvent and Me_4Si as internal standard. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltronics APEX II 47e and Orbitrap Elite mass spectrometer. Melting points were observed in an electrothermal melting point apparatus (X-5, Beijing Tech Instrument Co. Ltd, China). Calcium carbide was purchased from Macklin Chemical Company (China, purity: 98%), and ground into powder (*ca.* 50−100 mesh) in a ceramic mortar prior to use. The solvents were all deoxygenated with nitrogen gas for 5 min and dehydrated with molecular sieve for over 12 h prior to use. Unless otherwise noted, the reagents were reagent grade and used without any further purification. Column chromatography was carried out on a flash chromatographic system using silica gel, and petroleum ether (60 – 90 ^{o}C) and ethyl acetate as eluent. For thin layer chromatography (TLC), silica gel plates precoated with GF-254 were used. Pyrazole-3-amine, indazole-3-amine and various (hetero)aromatic aldehydes were commercially available and purchased from Energy Chemical Company (China) and Bide Pharm Company (China).

1.2 The general procedure for the synthesis of 5-arylpyrazolo[1,5-*a*]pyrimidines (3a−3o)

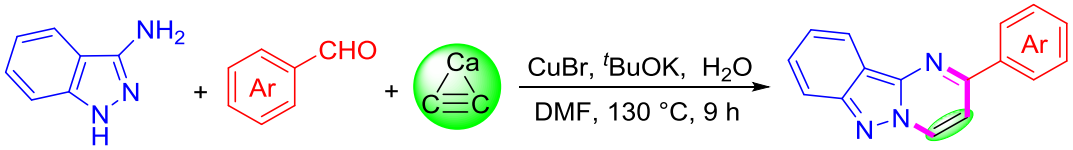


3a-3o

The mixture of pyrazole-3-amine (0.3 mmol, 24.9 mg), aromatic aldehydes (0.3 mmol), calcium carbide (0.9 mmol, 57.7 mg), cuprous bromide (0.45 mmol, 64.6 mg), potassium *tert*-butoxide (0.36 mmol, 40.4 mg), and water (1.8 mmol, 32.4 mg) in DMF (4 mL) was heated in an oil bath at 130 ℃ for 9 h. The progress of the reaction was monitored by TLC. After the reaction was complete, the mixture was filtered to remove

the solid. The liquor was extracted with ethyl acetate (3x10 mL). The extract was washed with saturated brine (3x10 mL). The obtained organic phase was dried with anhydrous sodium sulfate, concentrated under reduced pressure. The residue was subjected to column chromatography using petroleum ether, ethyl acetate, and triethylamine (v/v/v 80:10:1) as eluent to give product.

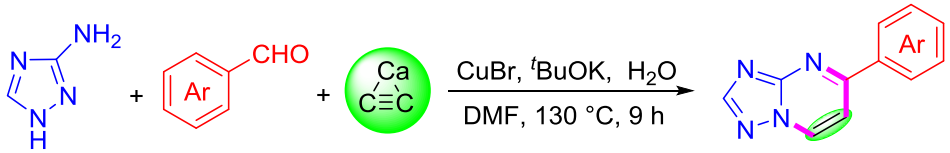
1.3 The general procedure for the synthesis of 2-arylpyrimido[1,2-*b*]indazoles (4a-4m)



4a-4m

The mixture of indazole-3-amine (0.3 mmol, 39.9 mg), aromatic aldehydes (0.3 mmol), calcium carbide (0.9 mmol, 57.7 mg), cuprous bromide (0.45 mmol, 64.6 mg), potassium *tert*-butoxide (0.36 mmol, 40.4 mg), and water (1.8 mmol, 32.4 mg) in DMF (4 mL) was heated in an oil bath at 130 ℃ for 9 h. The progress of the reaction was monitored by TLC. After the reaction was complete, the mixture was filtered to remove the solid. The liquor was extracted with ethyl acetate (3x10 mL). The extract was washed with saturated brine (3x10 mL). The obtained organic phase was dried with anhydrous sodium sulfate, concentrated under reduced pressure. The residue was subjected to column chromatography using petroleum ether, ethyl acetate, and triethylamine (v/v/v 60:10:1) as eluent to give product.

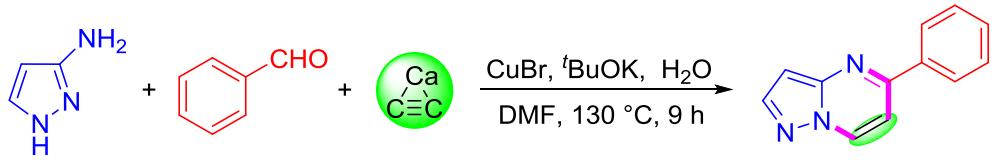
1.4 The general procedure for the synthesis of 5-aryl-[1,2,4]triazolo[1,5-*a*]pyrimidines (5a−5c)



5a-5c

The mixture of 1*H*-1,2,4-triazol-5-amine (0.3 mmol, 33.6 mg), aromatic aldehydes (0.3 mmol), calcium carbide (0.9 mmol, 57.7 mg), cuprous bromide (0.45 mmol, 64.6 mg), potassium *tert*-butoxide (0.36 mmol, 40.4 mg), and water (1.8 mmol, 32.4 mg) in DMF (4 mL) was heated in an oil bath at 130 ℃ for 9 h. The progress of the reaction was monitored by TLC. After the reaction was complete, the mixture was filtered to remove the solid. The liquor was extracted with ethyl acetate (3x10 mL). The extract was washed with saturated brine (3x10 mL). The obtained organic phase was dried with anhydrous sodium sulfate, concentrated under reduced pressure. The residue was subjected to column chromatography using petroleum ether and ethyl acetate (v/v 5:1) as eluent to give product.

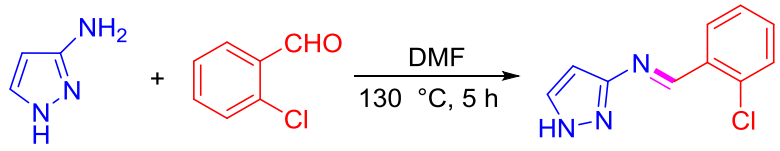
1.5 The gram scale synthesis of 3a



1a 0.74 g　　**2a** 0.95 g　　1.72 g　　**3a** 1.34 g 76%

The mixture of pyrazole-3-amine (9 mmol, 0.74 g), benzaldehyde (9 mmol, 0.95 g), calcium carbide (27 mmol, 1.72 g), cuprous bromide (13.5 mmol, 1.94 g), potassium *tert*-butoxide (10.8 mmol, 1.21 g), and water (54 mmol, 0.97 g) in DMF (50 mL) was heated in an oil bath at 130 ℃ for 9 h. The progress of the reaction was monitored by TLC. After the reaction was complete, the mixture was filtered to remove the solid. The liquor was extracted with ethyl acetate (3x50 mL). The extract was washed with saturated brine (3x50 mL). The obtained organic phase was dried with anhydrous sodium sulfate, concentrated under reduced pressure. The residue was subjected to column chromatography using petroleum ether, ethyl acetate, and triethylamine (v/v/v 80:10:1) as eluent to give product.

1.6 The synthesis of (*E*)-1-(2-chlorophenyl)-*N*-(1*H*-pyrazol-3-yl)methanimine (5)

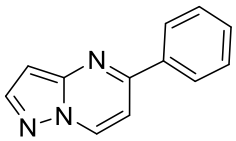


1a **5** 90%

The mixture of pyrazole-3-amine (0.5 mmol, 41.5 mg) and 2-chlorobenzaldehyde (0.5 mmol, 70.3 mg) in DMF (3 mL) was heated in an oil bath at 130 ℃ for 5 h. The progress of the reactions was monitored by TLC. After the reaction was complete, the mixture was extracted with ethyl acetate (3x10 mL). The extract was washed with saturated brine (3x10 mL). The obtained organic phase was dried with anhydrous sodium sulfate, concentrated under reduced pressure. The residue was subjected to column chromatography to give product.

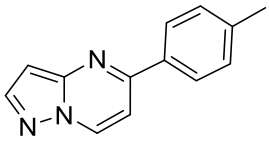
2. Analytical data for products 3a−3o, 4a−4m and 5

5-Phenylpyrazolo[1,5-*a*]pyrimidine (**3a**)[1, 2]



Yellow solid (48.0 mg, 82%). M.p. 123 – 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 7.4, 0.8 Hz, 1H), 8.13 (d, *J* = 2.3 Hz, 1H), 8.08 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.52 (s, 1H), 7.52–7.48 (m, 2H), 7.28 (s, 1H), 6.72 (dd, *J* = 2.3, 1.0 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 148.5, 145.5, 137.2, 135.1, 130.4, 128.9, 127.2, 105.4, 97.0 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{12}H_{10}N_3^+$: 196.0869; found: 196.0872.

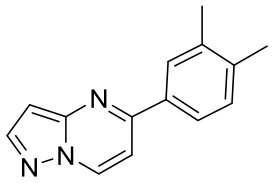
5-(*p*-Tolyl)pyrazolo[1,5-*a*]pyrimidine (**3b**)[2]



Yellow solid (43.2 mg, 69%). M.p. 123 – 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 7.4 Hz, 1H), 8.11 (d, *J* = 2.2 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz,

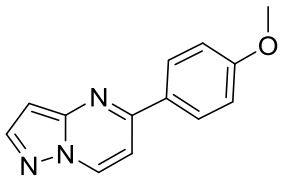
2H), 7.24 (s, 1H), 6.69 (d, *J* = 2.2 Hz, 1H), 2.43 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 148.5, 145.4, 140.8, 134.9, 134.4, 129.7, 127.1, 105.3, 96.8, 21.4 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{13}H_{12}N_3^+$: 210.1026; found: 210.1024.

5-(3,4-Dimethylphenyl)pyrazolo[1,5-*a*]pyrimidine (**3c**)



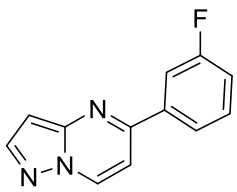
Yellow solid (47.4 mg, 71%). M.p. 124 – 126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.65 (m, 1H), 8.10 (d, *J* = 2.3 Hz, 1H), 7.90 (s, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.28 (s, 1H), 7.25 (d, *J* = 5.3 Hz, 1H), 6.70 – 6.68 (m, 1H), 2.36 (s, 3H), 2.33 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.4, 148.5, 145.4, 139.6, 137.3, 134.9, 134.7, 130.2, 128.3, 124.7, 105.4, 96.7, 19.9, 19.7 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{14}H_{14}N_3^+$: 224.1182; found: 224.1179.

5-(4-Methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine (**3d**)[2]



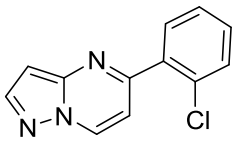
Yellow solid (43.2 mg, 64%). M.p. 175 – 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.63 (m, 1H), 8.09 (d, *J* = 2.2 Hz, 1H), 8.05 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 2H), 6.67 – 6.64 (m, 1H), 3.87 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.6, 155.8, 148.5, 145.4, 134.9, 129.6, 128.8, 114.3, 105.0, 96.5, 55.4 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{13}H_{12}N_3O^+$: 226.0975; found: 226.0974.

5-(3-Fluorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3e**)



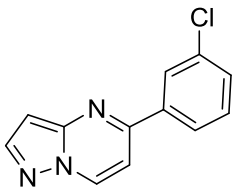
Yellow solid (46.6 mg, 73%). M.p. 120 – 121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 7.3 Hz, 1H), 8.16 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.48 (q, *J* = 7.9 Hz, 1H), 7.24 (s, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.74 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.3 (d, *J* = 247.0 Hz), 154.7 (d, *J* = 2.8 Hz), 148.4, 145.8, 139.4 (d, *J* = 7.6 Hz), 135.2, 130.4 (d, *J* = 8.1 Hz), 122.8 (d, *J* = 3.1 Hz), 117.3 (d, *J* = 21.3 Hz), 114.2 (d, *J* = 23.2 Hz), 105.2, 97.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$). δ -112.1 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{12}H_9FN_3^+$: 214.0775; found: 214.0773.

5-(2-Chlorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3f**)



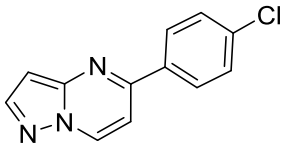
Yellow solid (46.0 mg, 67%). M.p. 129 – 131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 7.3, 0.8 Hz, 1H), 8.17 (d, *J* = 2.3 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.53 – 7.48 (m, 1H), 7.44 – 7.39 (m, 2H), 7.22 (d, *J* = 7.3 Hz, 1H), 6.76 (dd, *J* = 2.3, 0.8 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3, 148.3, 145.4, 137.4, 134.1, 132.2, 131.3, 130.7, 130.3, 127.3, 109.5, 97.4 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{12}H_9ClN_3^+$: 230.0480; found: 230.0478.

5-(3-Chlorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3g**)[3]



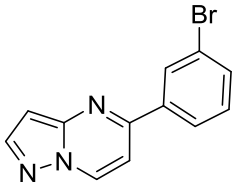
White solid (52.8 mg, 77%). M.p. 133 – 135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.70 (m, 1H), 8.15 (d, *J* = 2.2 Hz, 1H), 8.12 – 8.09 (m, 1H), 7.97 – 7.91 (m, 1H), 7.44 (d, *J* = 6.4 Hz, 2H), 7.23 (d, *J* = 7.4 Hz, 1H), 6.75 – 6.71 (m, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.6, 148.3, 145.8, 138.9, 135.3, 135.1, 130.4, 130.1, 127.4, 125.3, 105.1, 97.3 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{12}H_9ClN_3^+$: 230.0480; found: 230.0481.

5-(4-Chlorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3h**)[4]



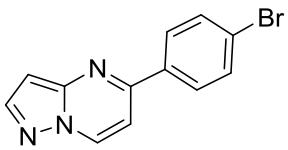
Yellow solid (53.6 mg, 78%). M.p. 172 – 174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.66 (m, 1H), 8.17 – 8.10 (m, 1H), 8.02 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 7.4 Hz, 1H), 6.74 – 6.68 (m, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.8, 148.4, 145.7, 136.7, 135.5, 135.2, 129.1, 128.5, 105.0, 97.1 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{12}H_9ClN_3^+$: 230.0480; found: 230.0477.

5-(3-Bromophenyl)pyrazolo[1,5-*a*]pyrimidine (**3i**)



White solid (62 mg, 76%). M.p. 118 – 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 7.4 Hz, 1H), 8.27 (s, 1H), 8.15 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 6.74 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 148.3, 145.8, 139.1, 135.3, 133.3, 130.4, 130.3, 125.7, 123.3, 105.1, 97.3 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{12}H_9BrN_3^+$: 273.9974; found: 273.9973.

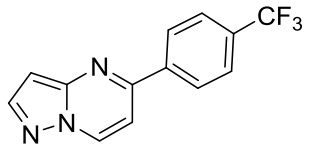
5-(4-Bromophenyl)pyrazolo[1,5-*a*]pyrimidine (**3j**)



Yellow solid (64.7 mg, 79%). M.p. 185 – 186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 7.4 Hz, 1H), 8.13 (d, *J* = 2.2 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 1.5 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$)

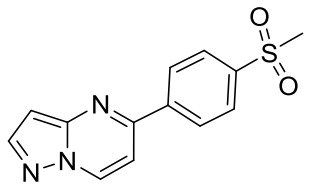
δ 154.9, 148.4, 145.7, 136.0, 135.2, 132.1, 128.7, 125.1, 104.9, 97.1 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{12}H_9BrN_3^+$: 273.9974; found: 273.9975.

5-(4-(Trifluoromethyl)phenyl)pyrazolo[1,5-*a*]pyrimidine (**3k**)[5]



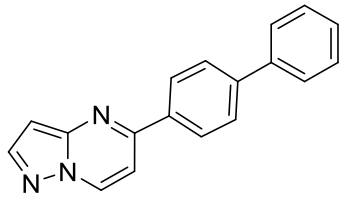
Yellow solid (59.1 mg, 75%). M.p. 115 – 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 7.4 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 2H), 8.18 (d, *J* = 2.0 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 2.3 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 148.4, 145.9, 140.4, 135.4, 132.1 (q, *J* = 32.9 Hz), 127.5, 125.9 (q, *J* = 3.9 Hz), 123.9 (q, *J* = 272.5 Hz), 105.2, 97.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$). δ -62.7 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{13}H_9F_3N_3^+$: 264.0743; found: 264.0745.

5-(4-(Methylsulfonyl)phenyl)pyrazolo[1,5-*a*]pyrimidine (**3l**)



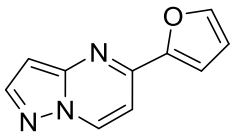
Yellow solid (59.8 mg, 73%). M.p. 199 – 201 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 7.4, 0.8 Hz, 1H), 8.28 (d, *J* = 8.7 Hz, 2H), 8.18 (d, *J* = 2.3 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 1H), 6.78 (dd, *J* = 2.3, 0.8 Hz, 1H), 3.10 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.7, 148.3, 146.1, 142.1, 141.8, 135.6, 128.1, 128.0, 105.2, 97.8, 44.5 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{13}H_{12}N_3O_2S^+$: 274.0645; found: 274.0644.

5-([1,1'-Biphenyl]-4-yl)pyrazolo[1,5-*a*]pyrimidine (**3m**)



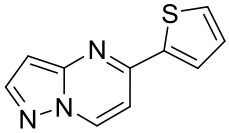
White solid (56.9 mg, 70%). M.p. 202 – 204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 7.3 Hz, 1H), 8.21 – 8.13 (m, 3H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 6.74 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7, 148.6, 145.6, 143.2, 140.1, 135.9, 135.1, 128.9, 127.9, 127.7, 127.6, 127.1, 105.3, 97.0 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{18}H_{14}N_3^+$: 272.1182; found: 272.1180.

5-(Furan-2-yl)pyrazolo[1,5-*a*]pyrimidine (**3n**)



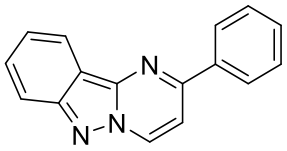
Yellow solid (40.1 mg, 72%). M.p. 117 – 119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.60 (m, 1H), 8.09 (d, *J* = 2.2 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.22 – 7.18 (m, 2H), 6.68 – 6.64 (m, 1H), 6.59 (dd, *J* = 3.4, 1.7 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.7, 148.1, 147.6, 145.5, 145.0, 135.1, 112.6, 111.8, 104.1, 96.8 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{10}H_8N_3O^+$: 186.0662; found:186.0660.

5-(Thiophen-2-yl)pyrazolo[1,5-*a*]pyrimidine (**3o**)



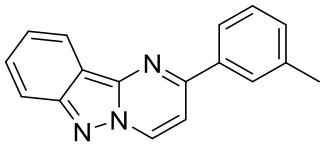
White solid (42.8 mg, 71%). M.p. 120 – 121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 7.4, 0.8 Hz, 1H), 8.09 (d, *J* = 2.3 Hz, 1H), 7.68 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.52 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.18 – 7.12 (m, 2H), 6.65 (dd, *J* = 2.3, 0.8 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.3, 148.1, 145.5, 142.9, 134.9, 130.1, 128.3, 127.5, 104.4, 96.7 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{10}H_8N_3S^+$: 202.0433; found:202.0430.

2-Phenylpyrimido[1,2-*b*]indazole (**4a**)[6-8]



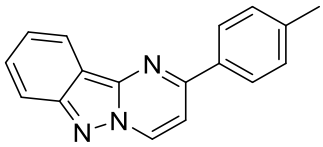
Yellow solid (61.0 mg, 83%). M.p. 169 – 171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 7.3 Hz, 1H), 8.39 (d, *J* = 8.3 Hz, 1H), 8.23 (d, *J* = 7.2 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.55 – 7.51 (m, 3H), 7.34 – 7.29 (m, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.7, 151.9, 143.7, 136.9, 133.7, 130.3, 130.0, 129.1, 127.1, 121.1, 120.8, 116.2, 113.8, 108.8 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{16}H_{12}N_3^+$: 246.1026; found: 246.1023.

2-(*m*-Tolyl)pyrimido[1,2-*b*]indazole (**4b**)[6,7]



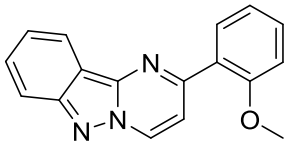
Yellow solid (56.0 mg, 72%). M.p. 155 – 157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 7.3 Hz, 1H), 8.39 (d, *J* = 8.3 Hz, 1H), 8.05 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.34 – 7.28 (m, 2H), 2.49 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.9, 151.8, 143.6, 138.8, 136.9, 133.7, 131.1, 129.9, 128.9, 127.8, 124.3, 121.1, 120.7, 116.1, 113.8, 109.0, 21.6 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{17}H_{14}N_3^+$: 260.1182; found: 260.1184. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{17}H_{14}N_3^+$: 260.1182; found: 260.1183.

2-(*p*-Tolyl)pyrimido[1,2-*b*]indazole (**4c**)[6, 7]



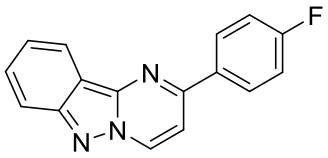
Yellow solid (57.1 mg, 69%). M.p. 183 – 185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 7.4 Hz, 1H), 8.37 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.36 – 7.27 (m, 3H), 2.44 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.8, 151.8, 143.7, 140.7, 134.1, 133.7, 129.9, 129.8, 127.0, 121.1, 120.6, 116.1, 113.7, 108.6, 21.4 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{17}H_{14}N_3^+$: 260.1182; found: 260.1180.

2-(2-Methoxyphenyl)pyrimido[1,2-*b*]indazole (**4d**)[6, 7]



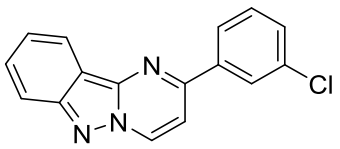
Yellow solid (57.8 mg, 70 %). M.p. 194 – 196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 7.4 Hz, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 8.15 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.92 (d, *J* = 7.4 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.48 (td, *J* = 8.4, 1.8 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.18 (td, *J* = 7.6, 1.0 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 3.94 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 152.3, 151.5, 143.7, 132.4, 131.4, 131.3, 129.7, 126.7, 121.4, 121.0, 120.5, 116.0, 113.8, 113.6, 111.6, 55.7 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{17}H_{14}N_3O^+$: 276.1131; found: 276.1127.

2-(4-Fluorophenyl)pyrimido[1,2-*b*]indazole (**4e**)[7]



Yellow solid (60.8 mg, 77%). M.p. 106 – 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 7.4 Hz, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 8.21 (dd, *J* = 9.0, 5.3 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.34 – 7.29 (m, 1H), 7.22 (d, *J* = 8.9 Hz, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2 (d, *J* = 251.4 Hz), 151.9, 151.5, 143.6, 133.8, 133.1 (d, *J* = 3.2 Hz), 130.0, 129.1 (d, *J* = 8.7 Hz), 121.0, 120.9, 116.2, 116.1 (d, *J* = 21.5 Hz), 113.7, 108.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$). δ -111.3 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{16}H_{11}FN_3^+$: 264.0932; found: 264.0929.

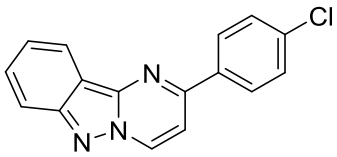
2-(3-Chlorophenyl)pyrimido[1,2-*b*]indazole (**4f**)[3, 6, 7]



Yellow solid (68.9 mg, 81 %). M.p. 142 – 144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 7.3 Hz, 1H), 8.41 – 8.33 (m, 2H), 8.09 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H),

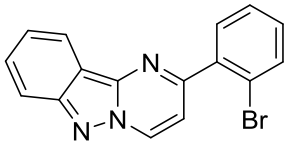
7.67 – 7.57 (m, 3H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.36 – 7.29 (m, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 150.7, 143.5, 138.8, 133.8, 133.1, 130.5, 130.2, 130.1, 125.6, 123.4, 121.1, 121.0, 116.2, 113.8, 108.5 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{16}H_{11}ClN_3^+$: 280.0636; found: 280.0637.

2-(4-Chlorophenyl)pyrimido[1,2-*b*]indazole (**4g**)[6, 7]



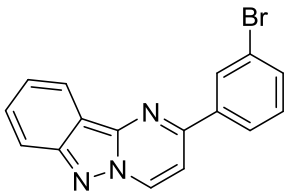
Yellow solid (67.2 mg, 82%). M.p. 151 – 153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 7.3 Hz, 1H), 8.31 (d, *J* = 8.1 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.31 − 7.27 (m, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 151.1, 143.5, 136.5, 135.2, 133.7, 130.0, 129.2, 128.3, 121.0, 116.2, 113.7, 110.0, 108.3 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{16}H_{11}ClN_3^+$: 280.0636; found: 280.0634.

2-(2-Bromophenyl)pyrimido[1,2-b]indazole (**4h**)[6]



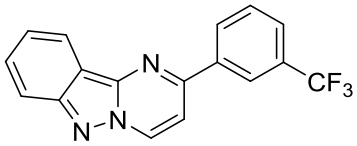
Yellow solid (70.7 mg, 73 %). M.p. 187 – 189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 7.3 Hz, 1H), 8.31 (d, *J* = 8.1 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.31 − 7.27 (m, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.5, 151.6, 143.5, 137.1, 132.7, 132.3, 131.9, 130.7, 130.4, 129.9, 127.4, 121.1, 120.9, 116.2, 113.9, 113.2 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{16}H_{11}BrN_3^+$: 324.0131; found: 324.0133.

2-(3-Bromophenyl)pyrimido[1,2-*b*]indazole (**4i**)[6]



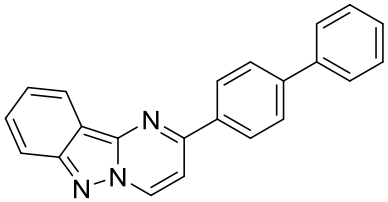
Yellow solid (76.6 mg, 79%). M.p. 162 – 164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 7.3 Hz, 1H), 8.34 (d, *J* = 8.2 Hz, 1H), 8.21 (s, 1H), 8.01 (s, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 4.4 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 150.7, 143.4, 138.6, 135.2, 133.7, 130.2, 130.1, 130.0, 127.2, 125.1, 121.1, 121.0, 116.3, 113.8, 108.4 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{16}H_{11}BrN_3^+$: 324.0131; found: 324.0130.

2-(3-Trifluoromethyl)pyrimido[1, 2-*b*]indazole (**4j**)



Yellow solid (71.4 mg, 76 %). M.p. 182 – 184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 7.3 Hz, 1H), 8.46 (s, 1H), 8.38 – 8.30 (m, 2H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.56 (m, 3H), 7.35 – 7.28 (m, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.9, 150.4, 143.4, 137.6, 133.8, 131.5 (q, *J* = 34.7 Hz), 130.1, 129.5, 126.6, 123.9 (q, *J* = 271.8 Hz), 123.8, 121.2, 121.0, 116.3, 113.8, 110.0, 108.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{17}H_{11}F_3N_3^+$: 314.0899; found: 314.0898.

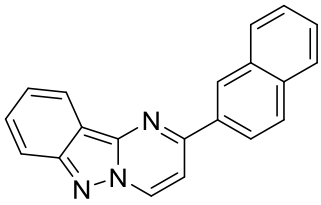
2-([1,1'-Biphenyl]-4-yl)pyrimido[1,2-*b*]indazole (**4k**)



Yellow solid (78.1 mg, 81%). M.p. 197 – 199 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 7.3 Hz, 1H), 8.40 (d, *J* = 8.3 Hz, 1H), 8.30 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 8.7 Hz,

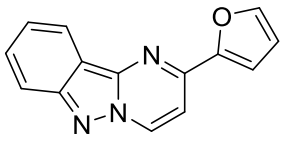
1H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.69 – 7.67 (m, 3H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.35 – 7.30 (m, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.2, 151.9, 143.7, 143.0, 140.1, 135.7, 133.7, 130.0, 128.9, 127.9, 127.7, 127.6, 127.1, 121.1, 120.8, 116.2, 113.8, 108.7 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{22}H_{16}N_3^+$: 322.1339; found:322.1336.

2-(Naphthalen-2-yl)pyrimido[1,2-*b*]indazole (**4l**)[6]



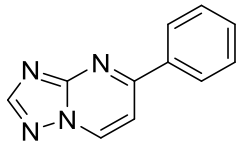
Yellow solid (62.2 mg, 76%). M.p. 147 – 149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 7.3 Hz, 1H), 8.59 (s, 1H), 8.42 – 8.37 (m, 2H), 7.98 (d, *J* = 8.7 Hz, 2H), 7.91 – 7.82 (m, 2H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.35 – 7.30 (m, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.4, 151.9, 143.7, 134.2, 134.2, 133.6, 130.0, 128.87, 128.9, 128.8, 127.8, 127.3, 127.1, 126.7, 124.1, 121.1, 120.8, 116.2, 113.9, 108.8 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{20}H_{14}N_3^+$: 296.1182; found: 296.1179.

2-(Furan-2-yl)pyrimido[1,2-*b*]indazole (**4m**)



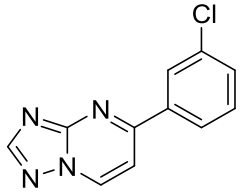
Yellow solid (55.0 mg, 78%). M.p. 166 – 168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 7.3 Hz, 1H), 8.38 – 8.33 (m, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.66 – 7.56 (m, 3H), 7.35 – 7.27 (m, 2H), 6.63 (dd, *J* = 3.5, 1.7 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.0, 151.8, 144.8, 144.5, 143.4, 133.7, 130.0, 121.2, 120.8, 116.1, 113.5, 112.8, 111.5, 107.5 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{14}H_{10}N_3O^+$: 236.0818; found: 236.0816.

5-Phenyl-[1,2,4]triazolo[1,5-*a*]pyrimidine (**5a**)[9]



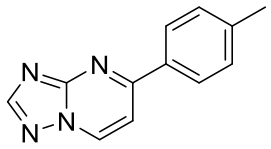
Yellow solid (43.5 mg, 74 %). M.p. 129 – 131 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 – 8.82 (m, 1H), 8.48 (d, *J* = 2.1 Hz, 1H), 8.23 – 8.15 (m, 2H), 7.60 – 7.48 (m, 4H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.9, 156.7, 155.4, 135.9, 135.7, 131.6, 129.1, 127.8, 107.6 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{11}H_9N_4^+$: 197.0822; Found:197.0823.

5-(3-Chlorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (**5b**)



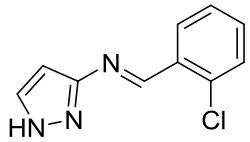
Yellow solid (53.1 mg, 77 %). M.p. 135 – 137 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 7.2 Hz, 1H), 8.52 (s, 1H), 8.22 (s, 1H), 8.06 (d, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.53 – 7.44 (m, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.4, 156.9, 155.2, 137.7, 136.0, 131.5, 130.3, 127.9, 125.8, 107.4 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{11}H_8ClN_4^+$: 231.0432; Found: 231.0430.

5-(*p*-Tolyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (**5c**)[10]



White solid (42.8 mg, 68 %). M.p. 128 – 130 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 7.2 Hz, 1H), 8.47 (s, 1H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.9, 156.6, 142.2, 135.5, 133.2, 129.8, 129.2, 127.7, 107.4, 21.5 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{12}H_{11}N_4^+$: 211.0978; Found: 211.0982.

(*E*)-1-(2-Chlorophenyl)-*N*-(1*H*-pyrazol-3-yl)methanimine (**6**)[11]



White solid (112.01 mg, 90%). M.p. (106-107 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.45 (s, 1H), 8.09 (d, *J* = 2.1 Hz, 1H), 7.94 – 7.84 (m, 3H), 7.55 – 7.50 (m, 1H), 6.81 (d, *J* = 2.1 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.7, 145.8, 142.7, 136.3, 134.1, 128.4, 125.2, 118.4, 114.7, 99.8 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{10}H_9ClN_3^+$: 206.0480; found: 206.0482.

3. References

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4. ^{1}H, ^{13}C and ^{19}F NMR spectra for products 3a−3o, 4a−4m and 5

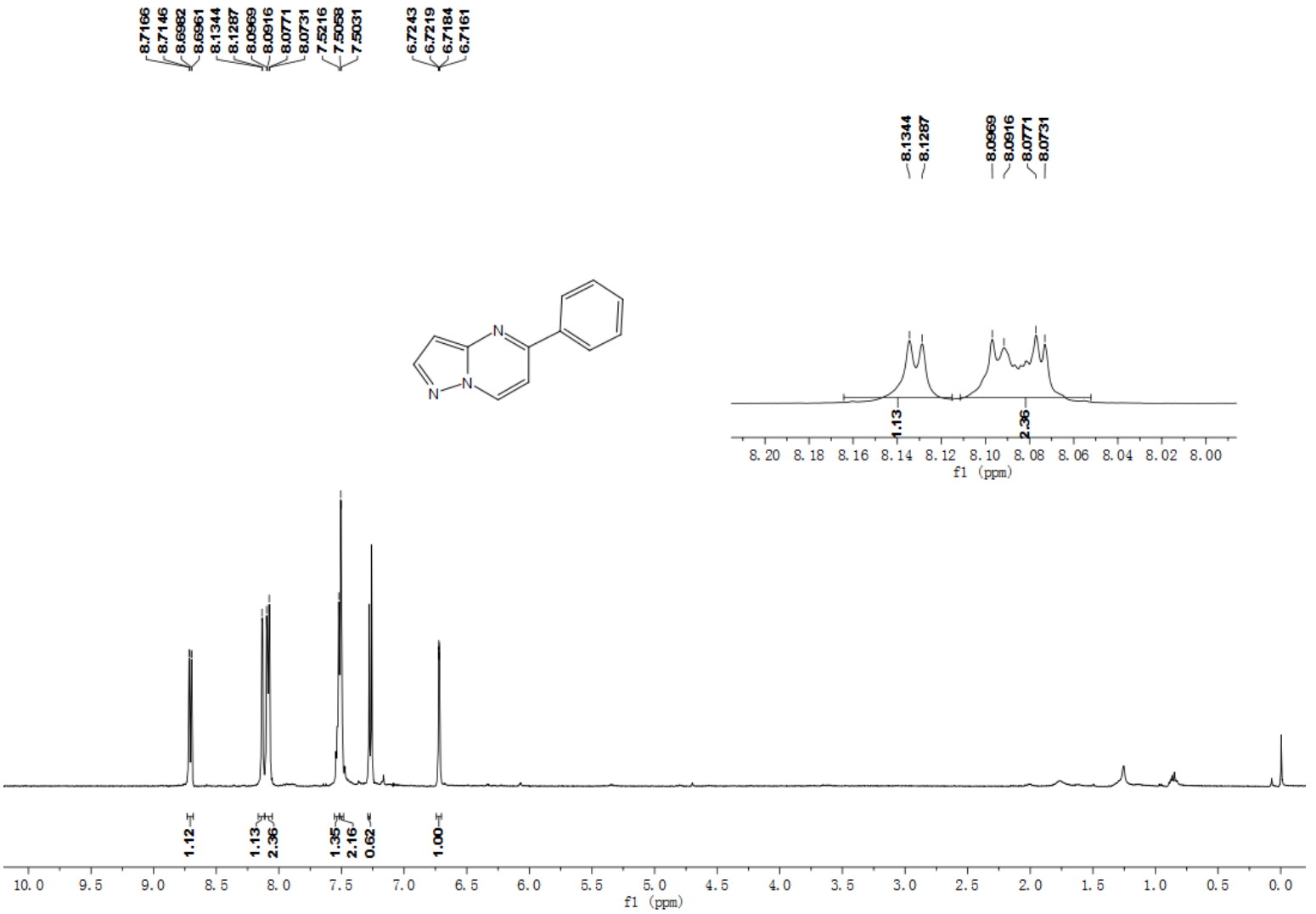

Fig S1. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-phenylpyrazolo[1,5-*a*]pyrimidine (**3a**)

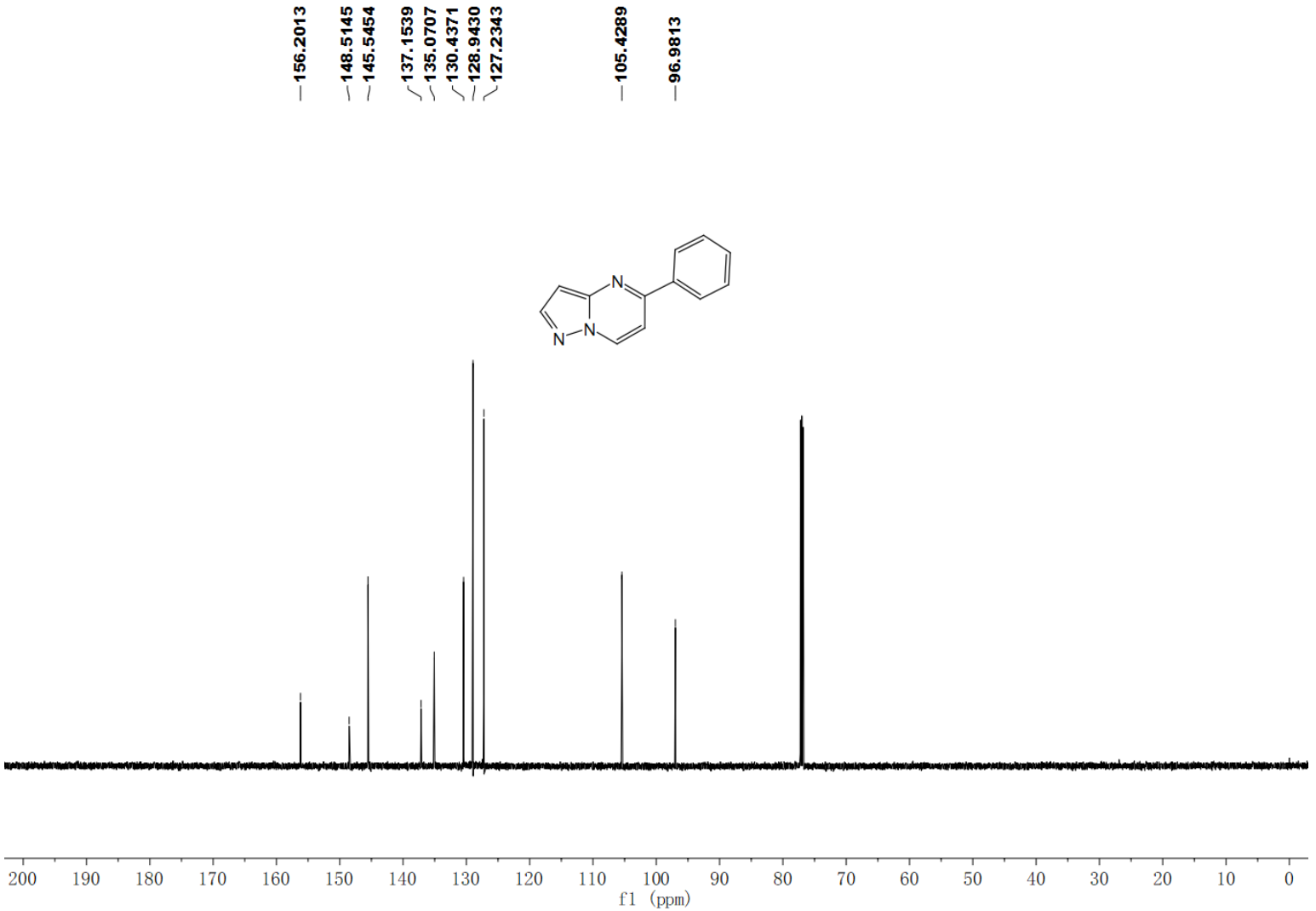

Fig S2. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-phenylpyrazolo[1,5-*a*]pyrimidine (**3a**)

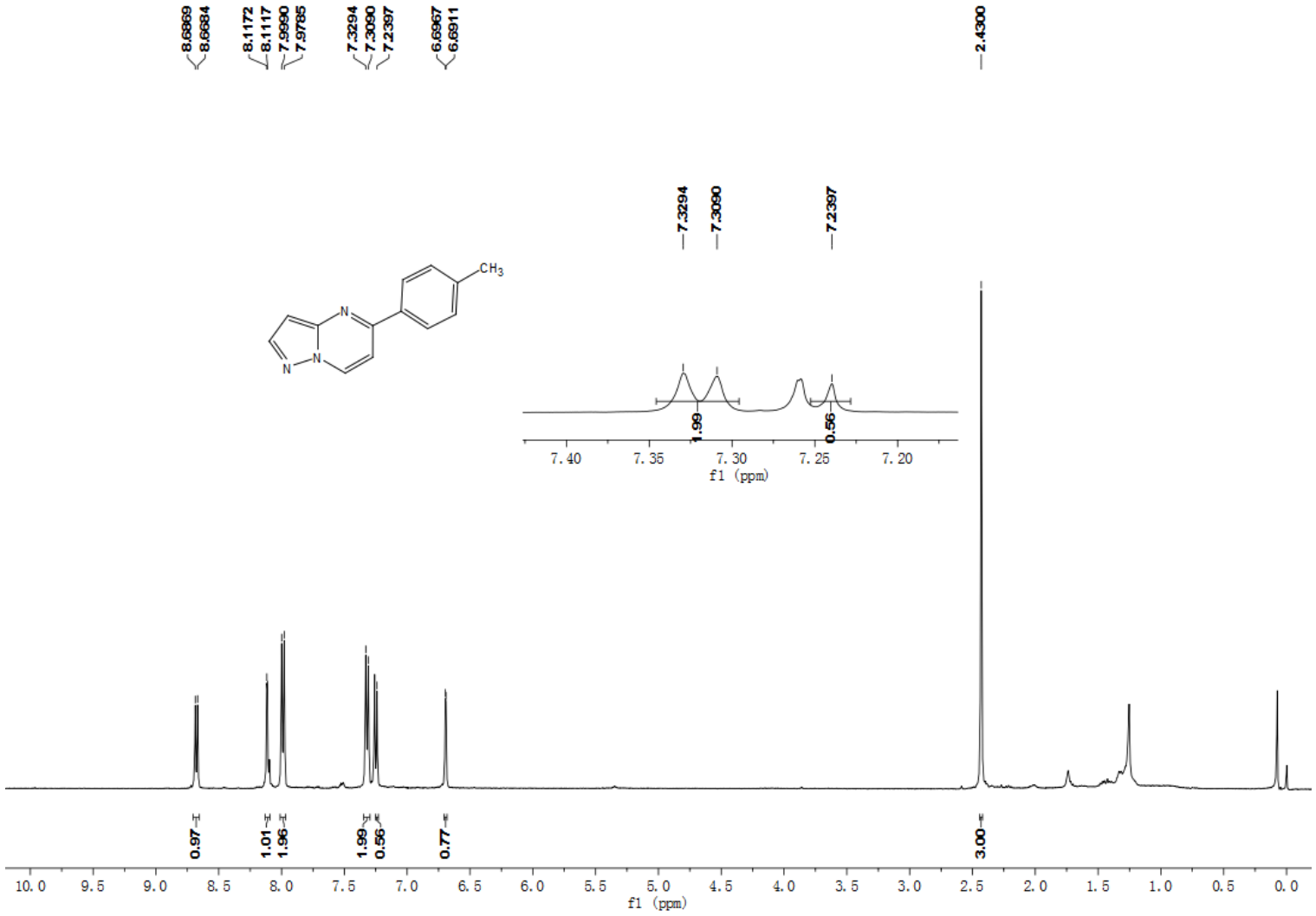

Fig S3. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(*p*-tolyl)pyrazolo[1,5-*a*]pyrimidine (**3b**)

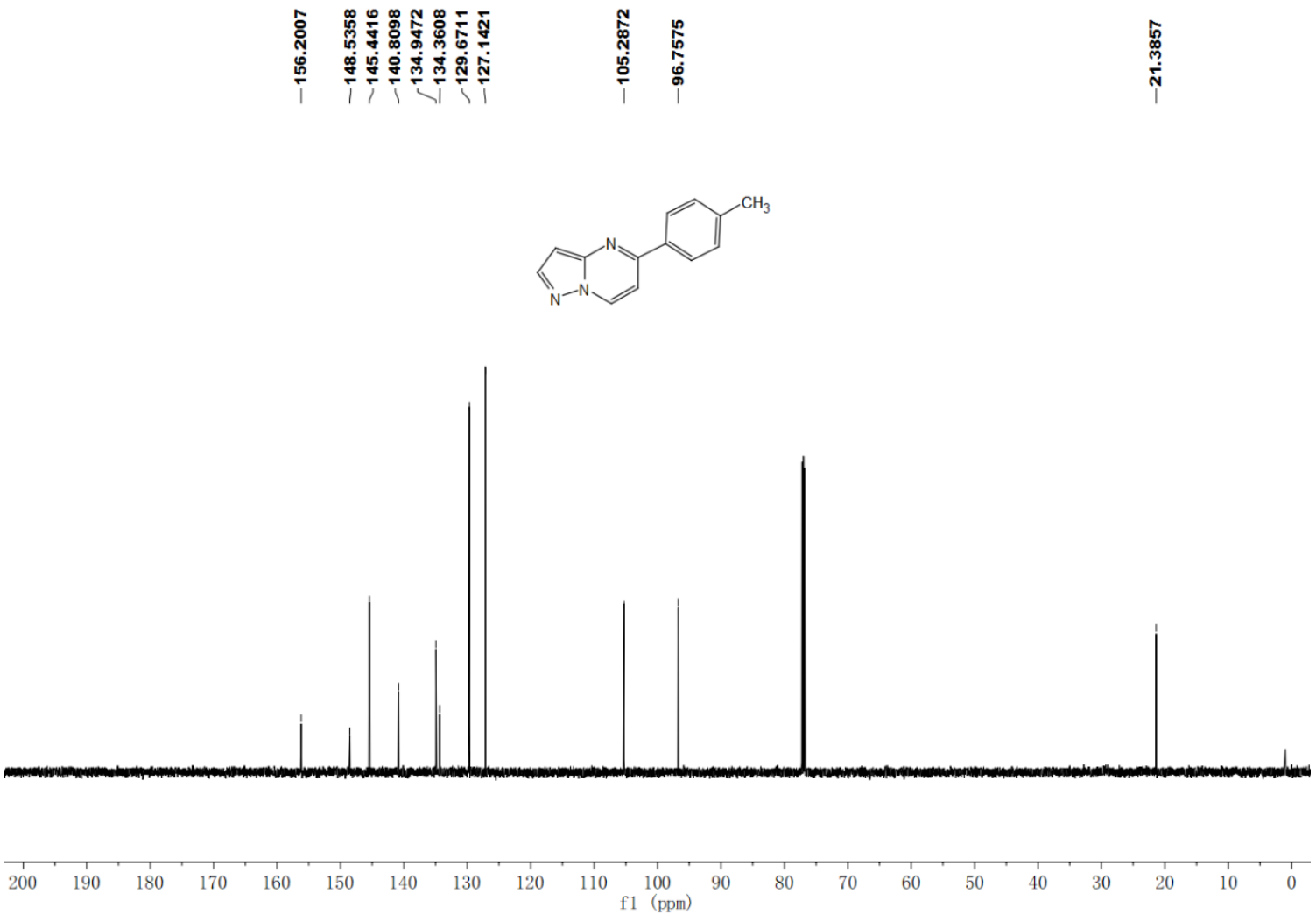

Fig S4. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(*p*-tolyl)pyrazolo[1,5-*a*]pyrimidine (**3b**)

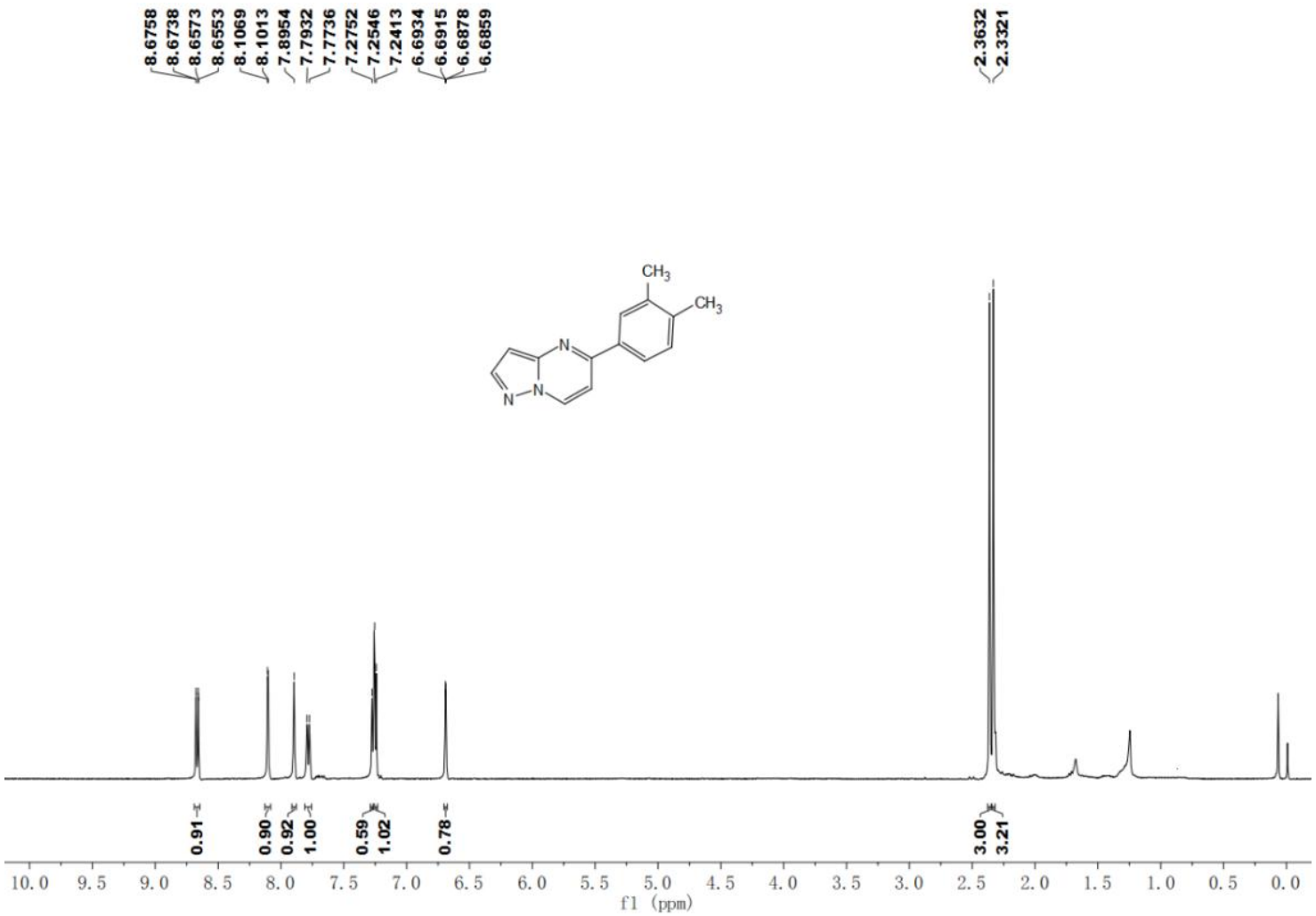

Fig S5. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(3,4-dimethylphenyl)pyrazolo[1,5-*a*]pyrimidine (**3c**)

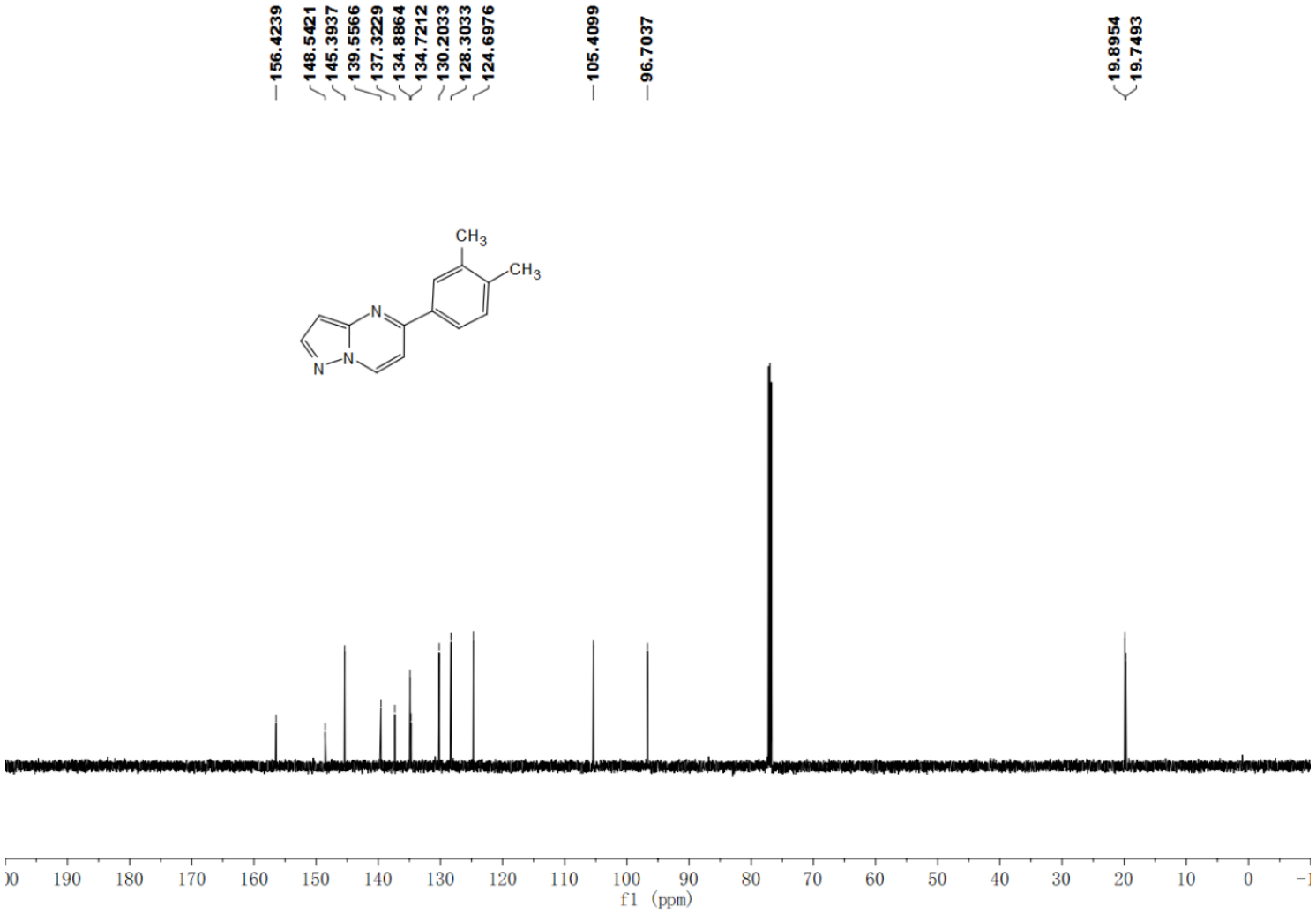

Fig S6. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(3,4-dimethylphenyl)pyrazolo[1,5-*a*]pyrimidine (**3c**)

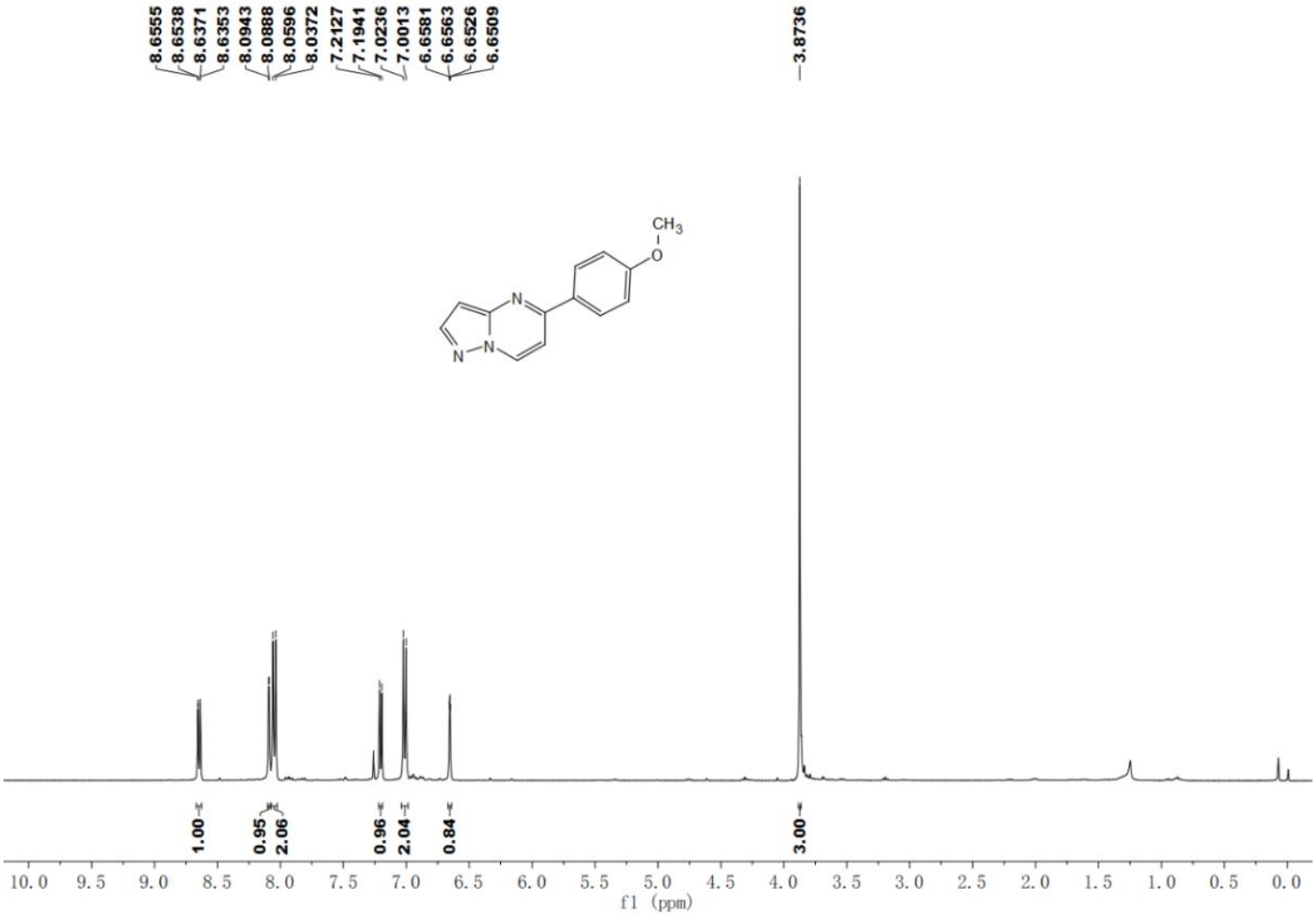

Fig S7. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(4-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine (**3d**)

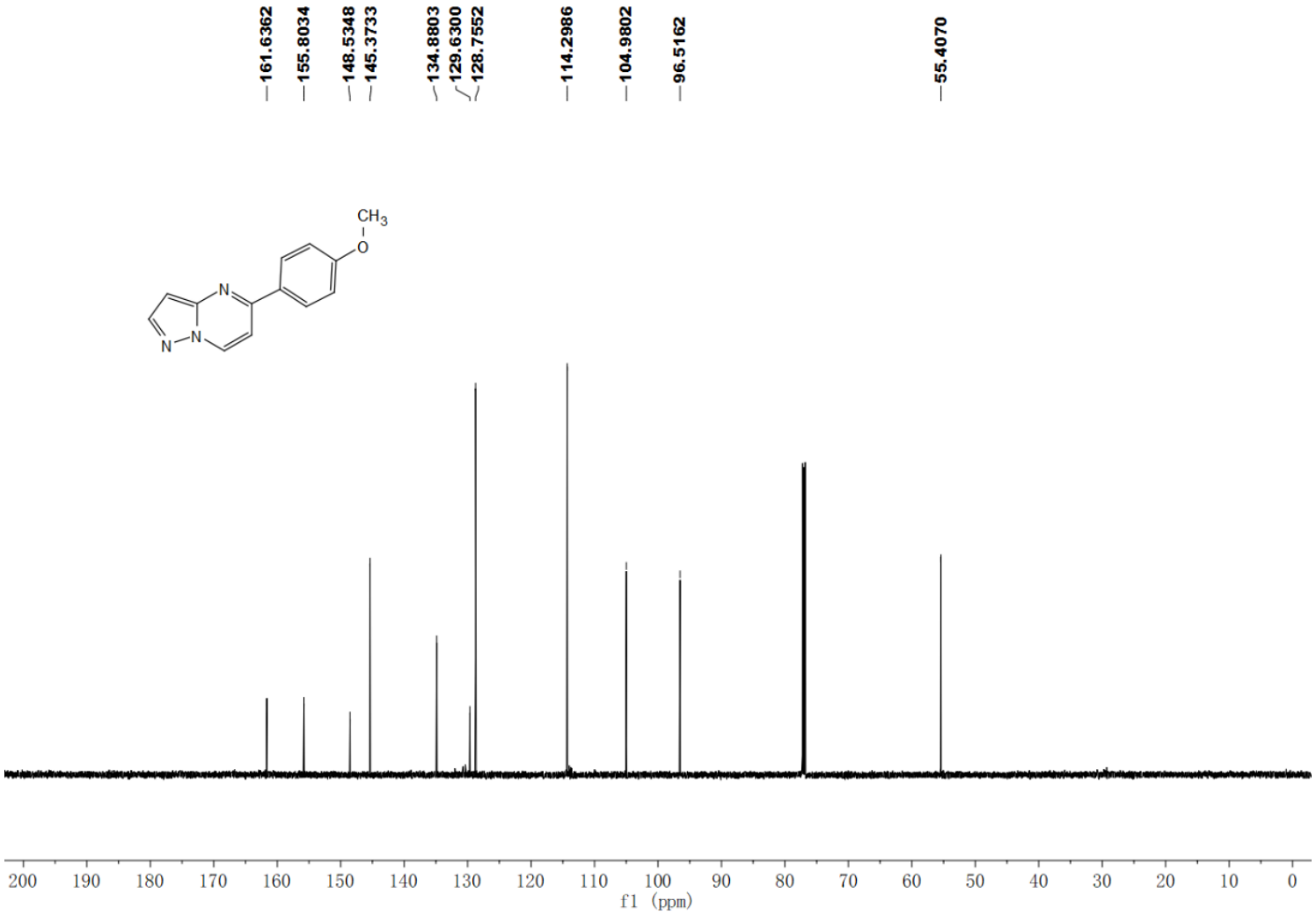

Fig S8. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(4-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine (**3d**)

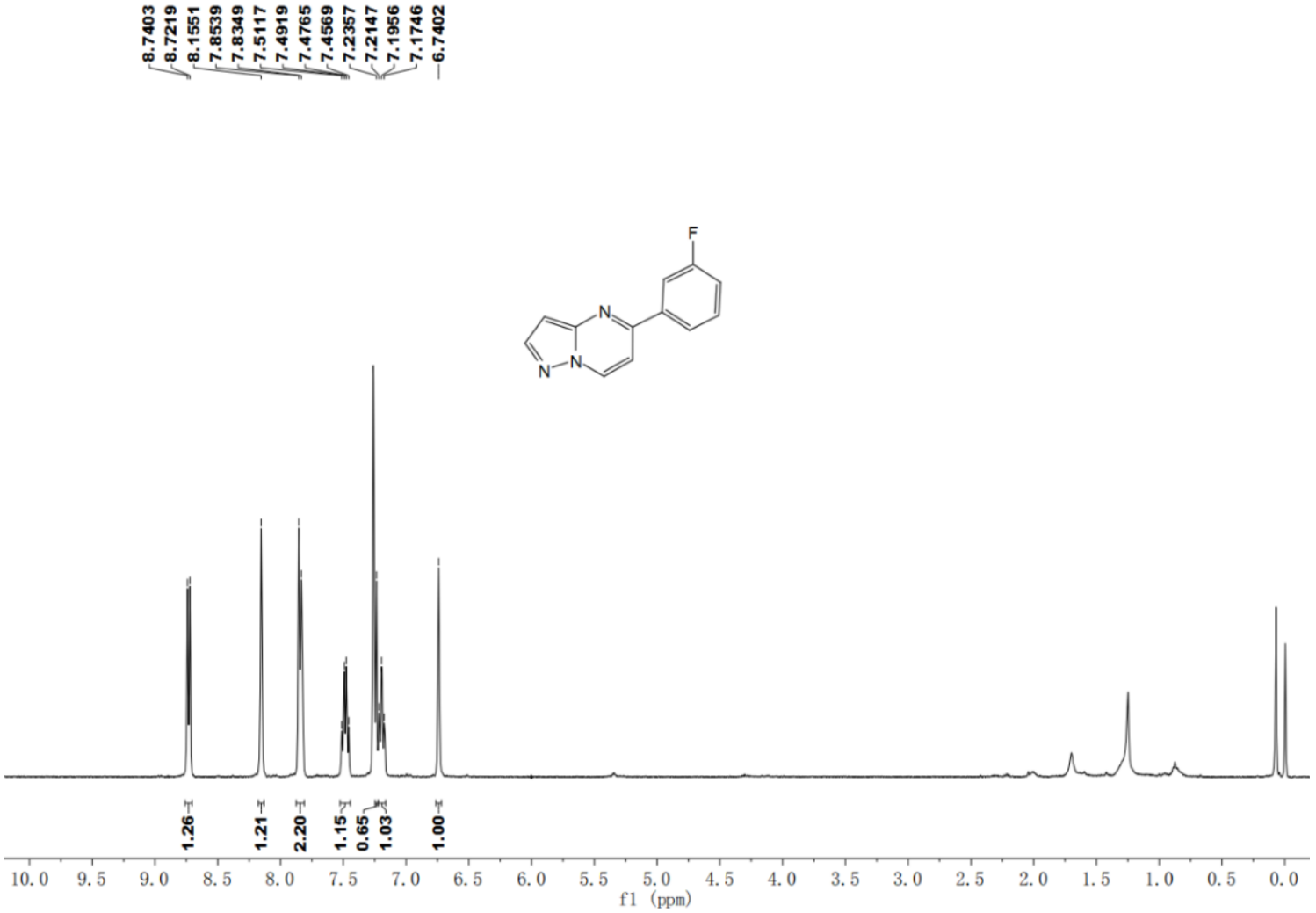

Fig S9. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(3-fluorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3e**)

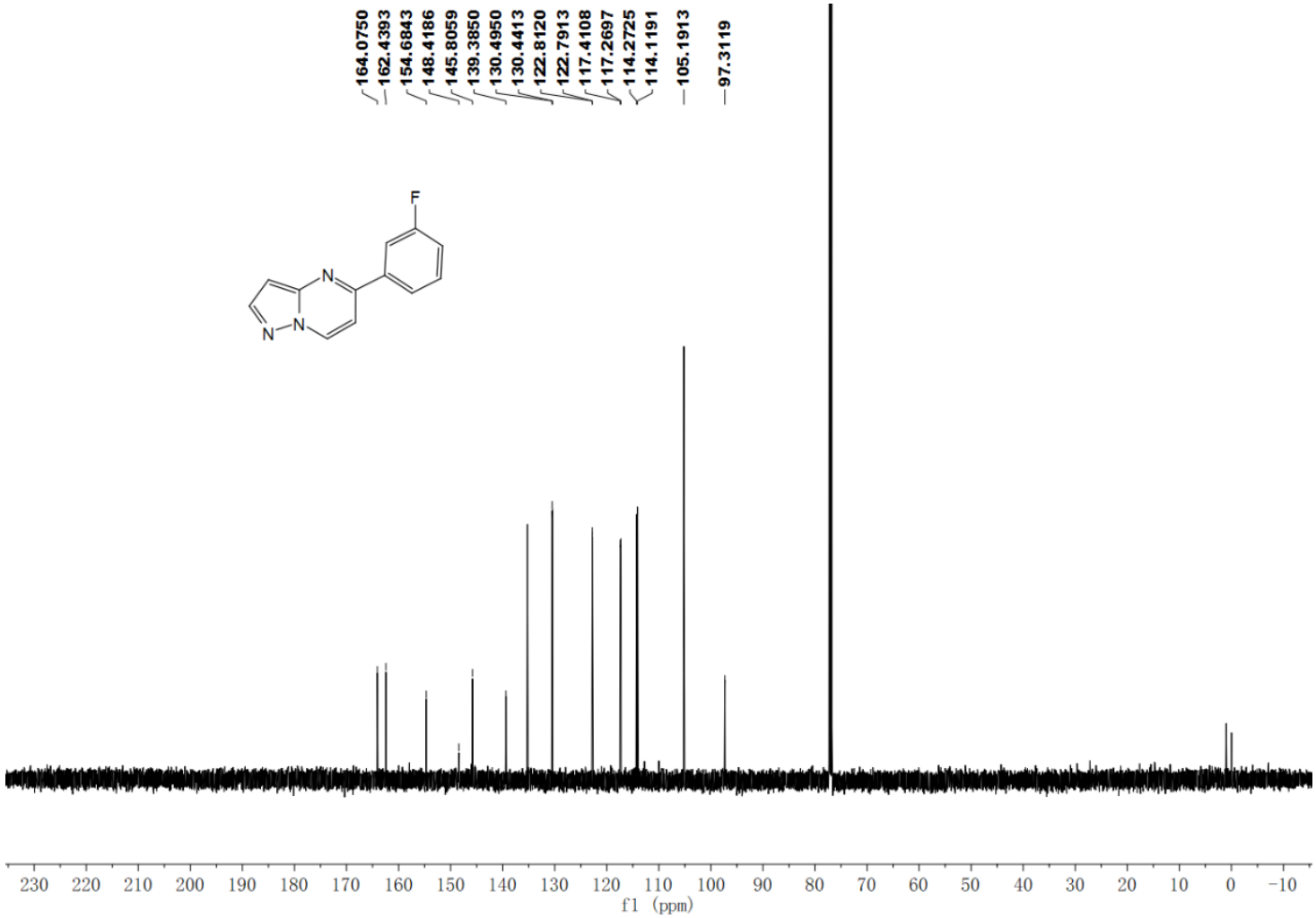

Fig S10. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(3-fluorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3e**)

Fig S11. ^{19}F NMR (376 MHz, $CDCl_3$) of 5-(3-fluorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3e**)

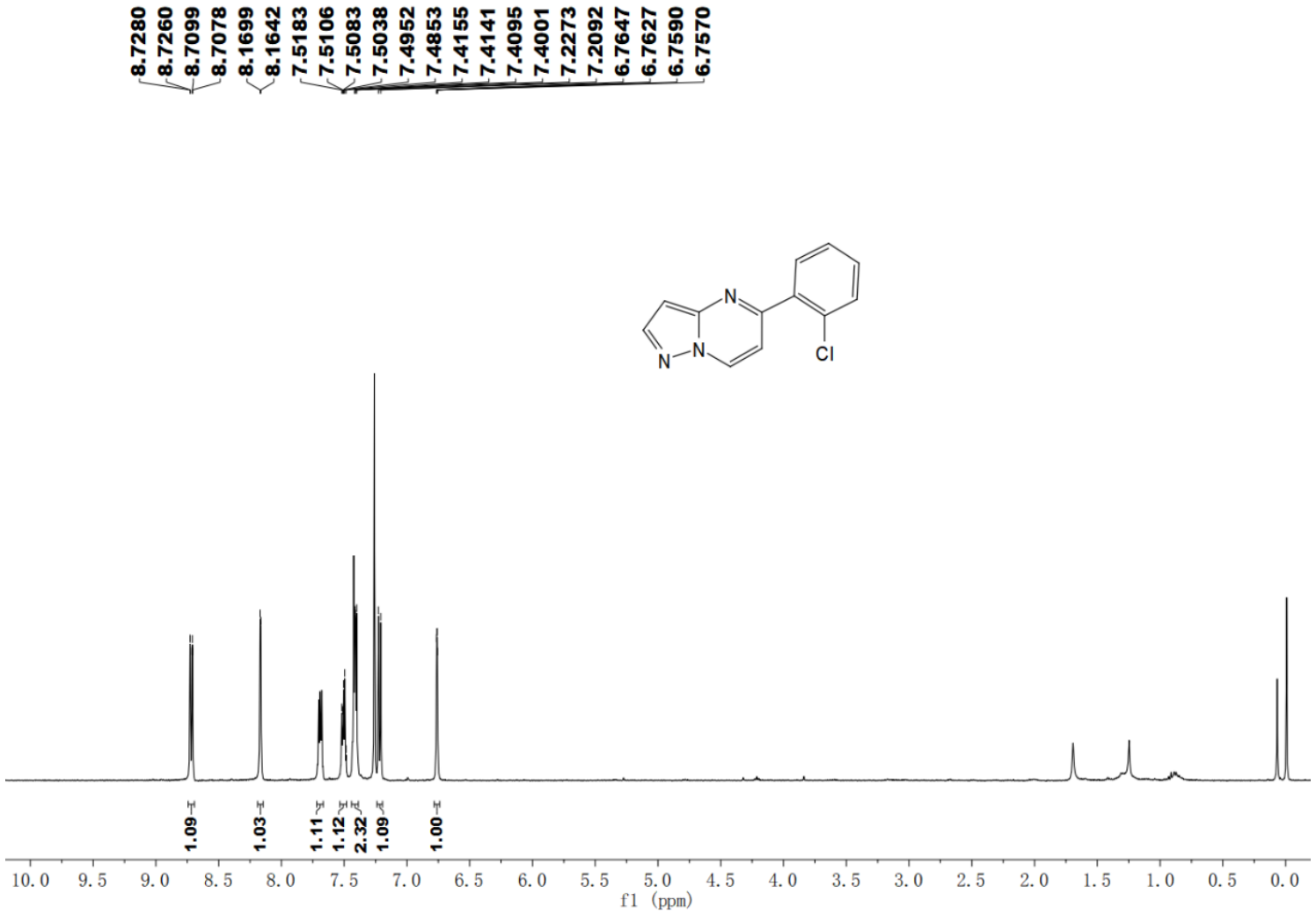

Fig S12. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(2-chlorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3f**)

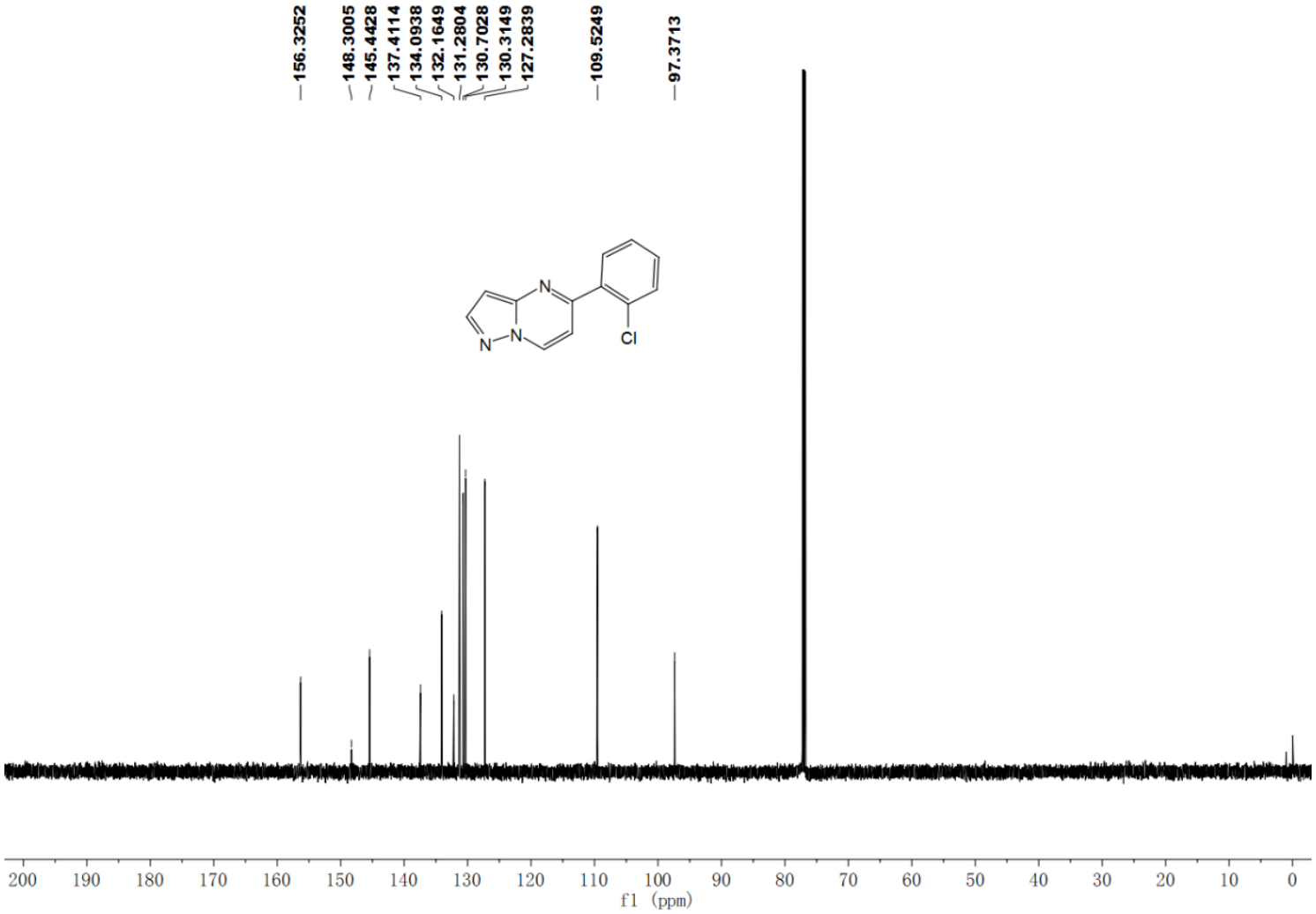

Fig S13. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(2-chlorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3f**)

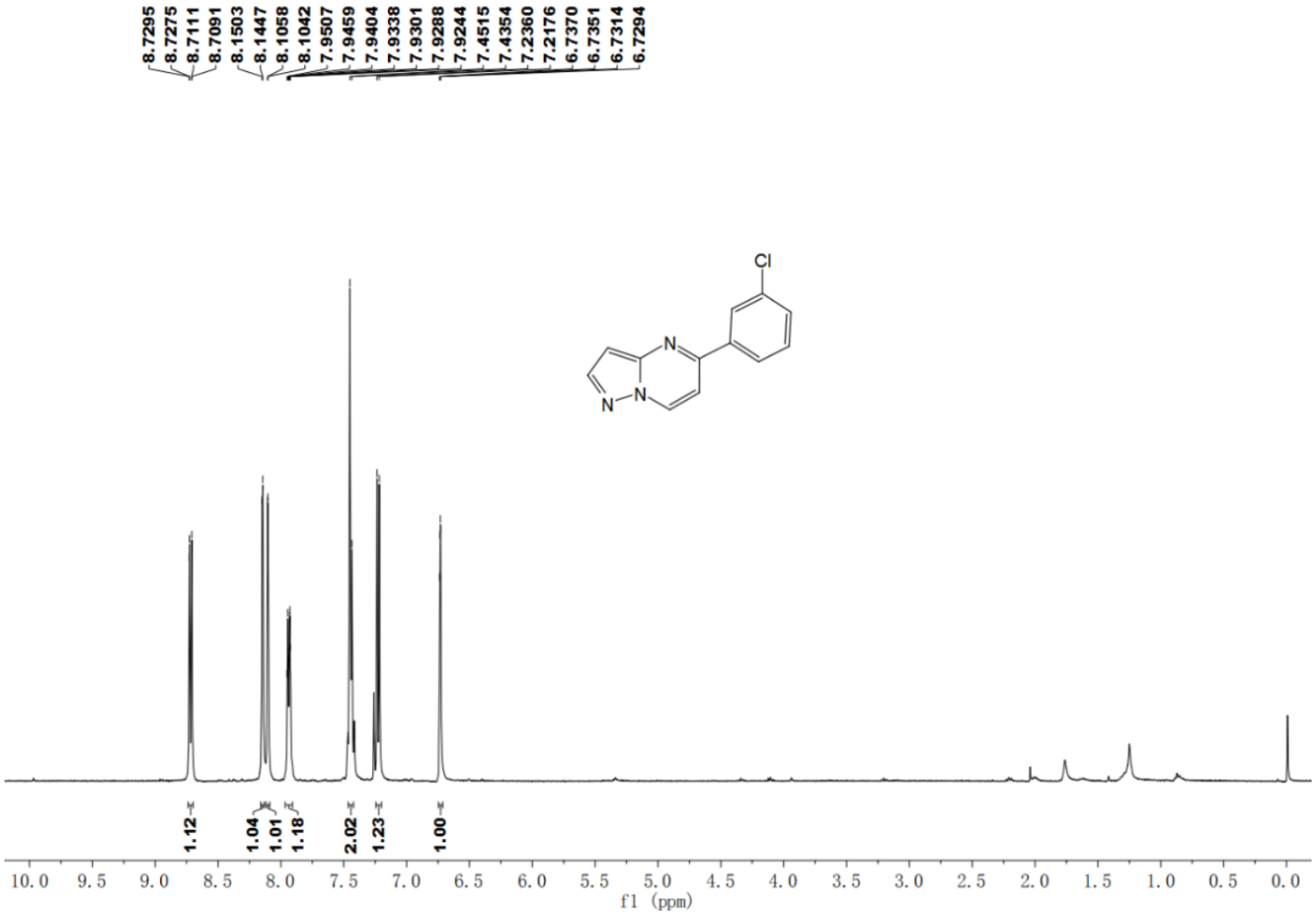

Fig S14. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(3-chlorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3g**)

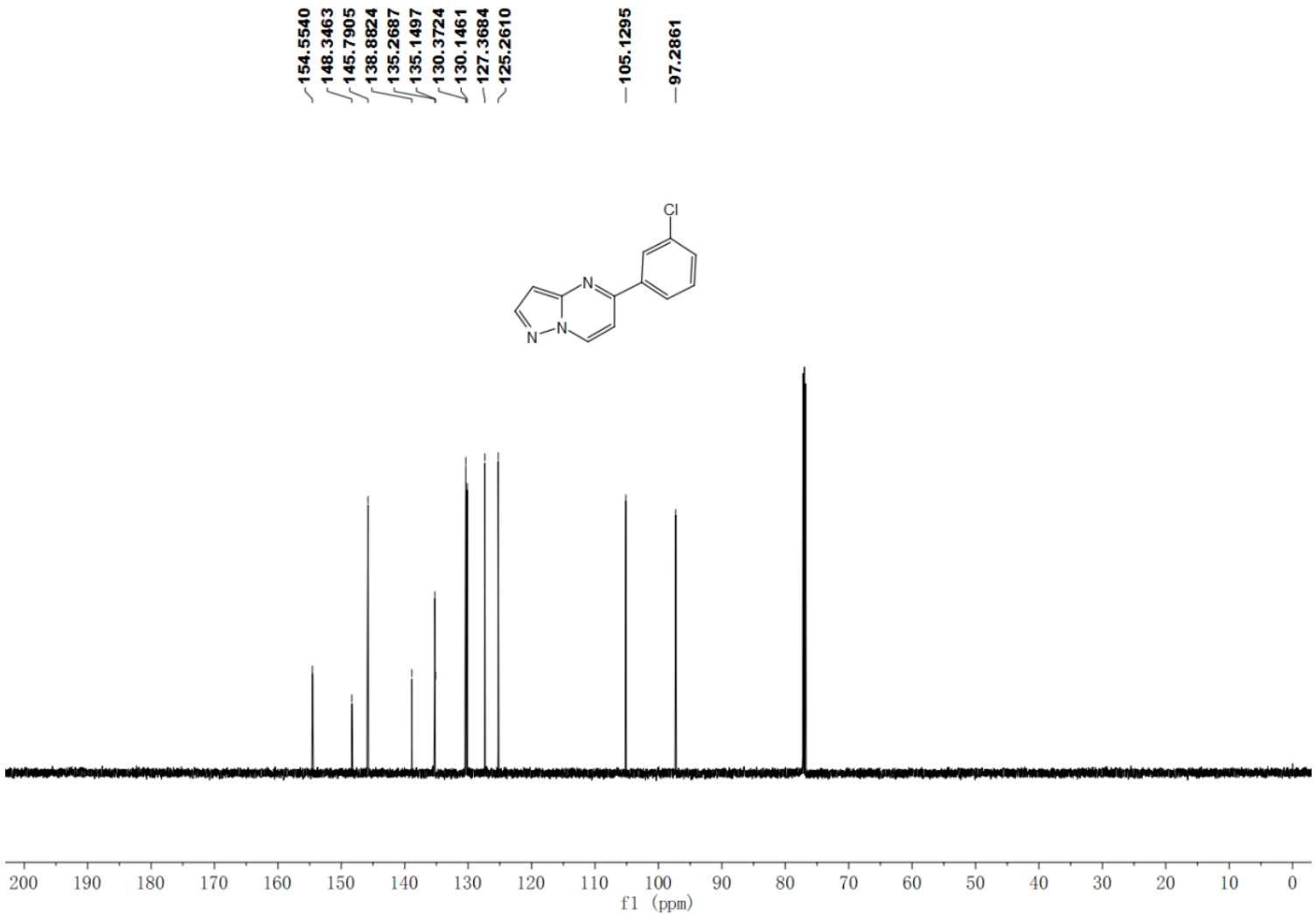

Fig S15. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(3-chlorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3g**)

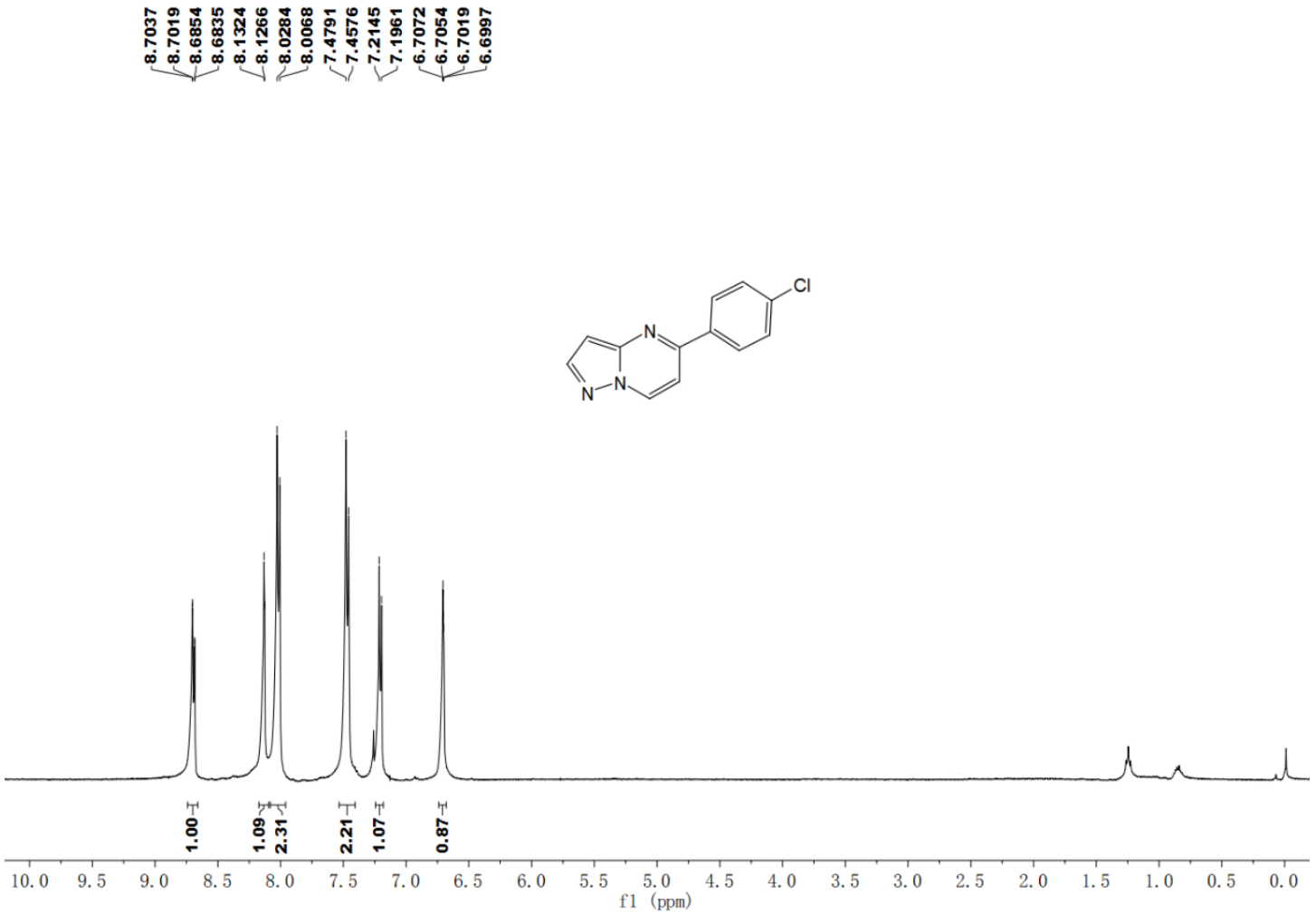

Fig S16. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(4-chlorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3h**)

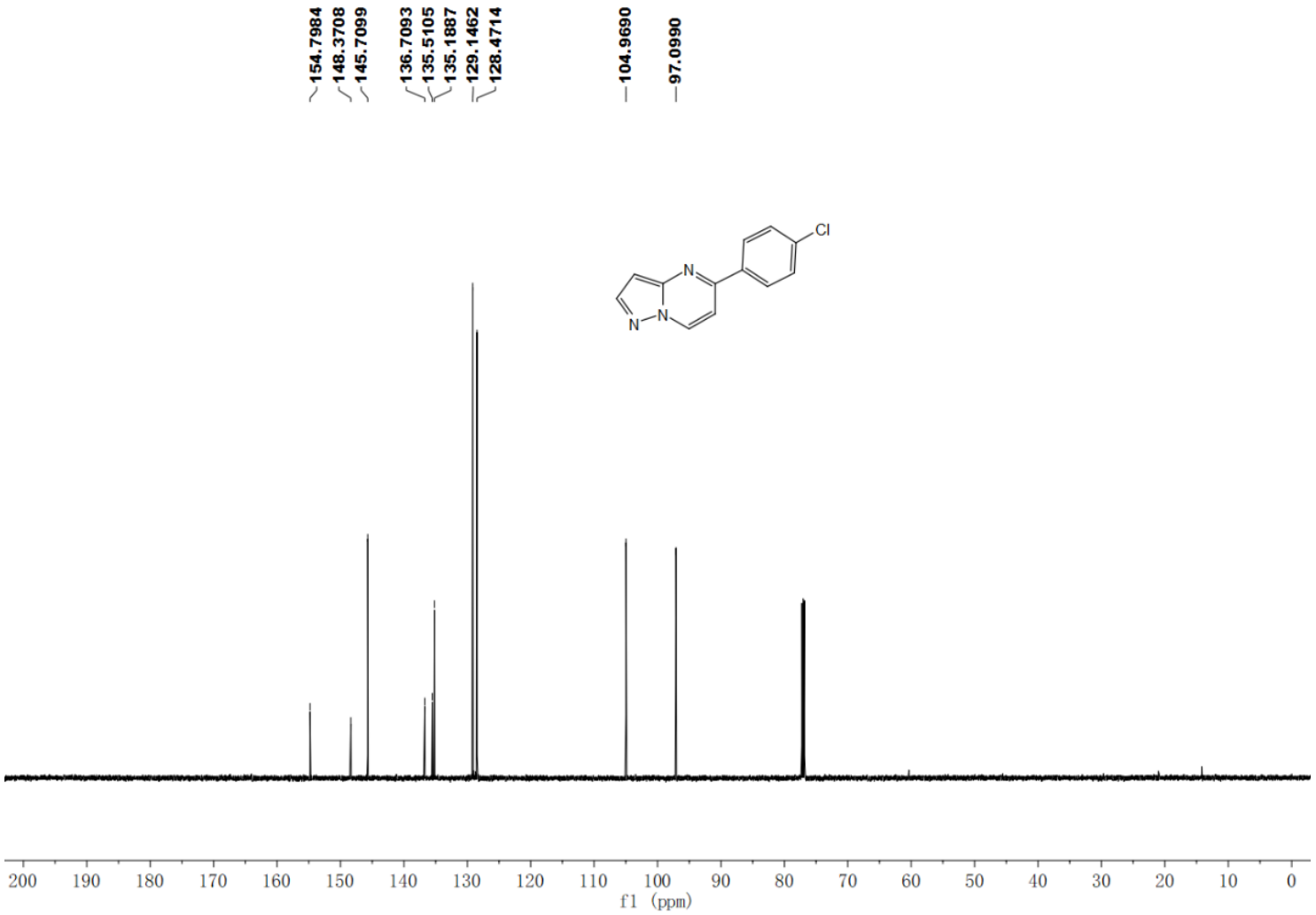

Fig S17. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(4-chlorophenyl)pyrazolo[1,5-*a*]pyrimidine (**3h**)

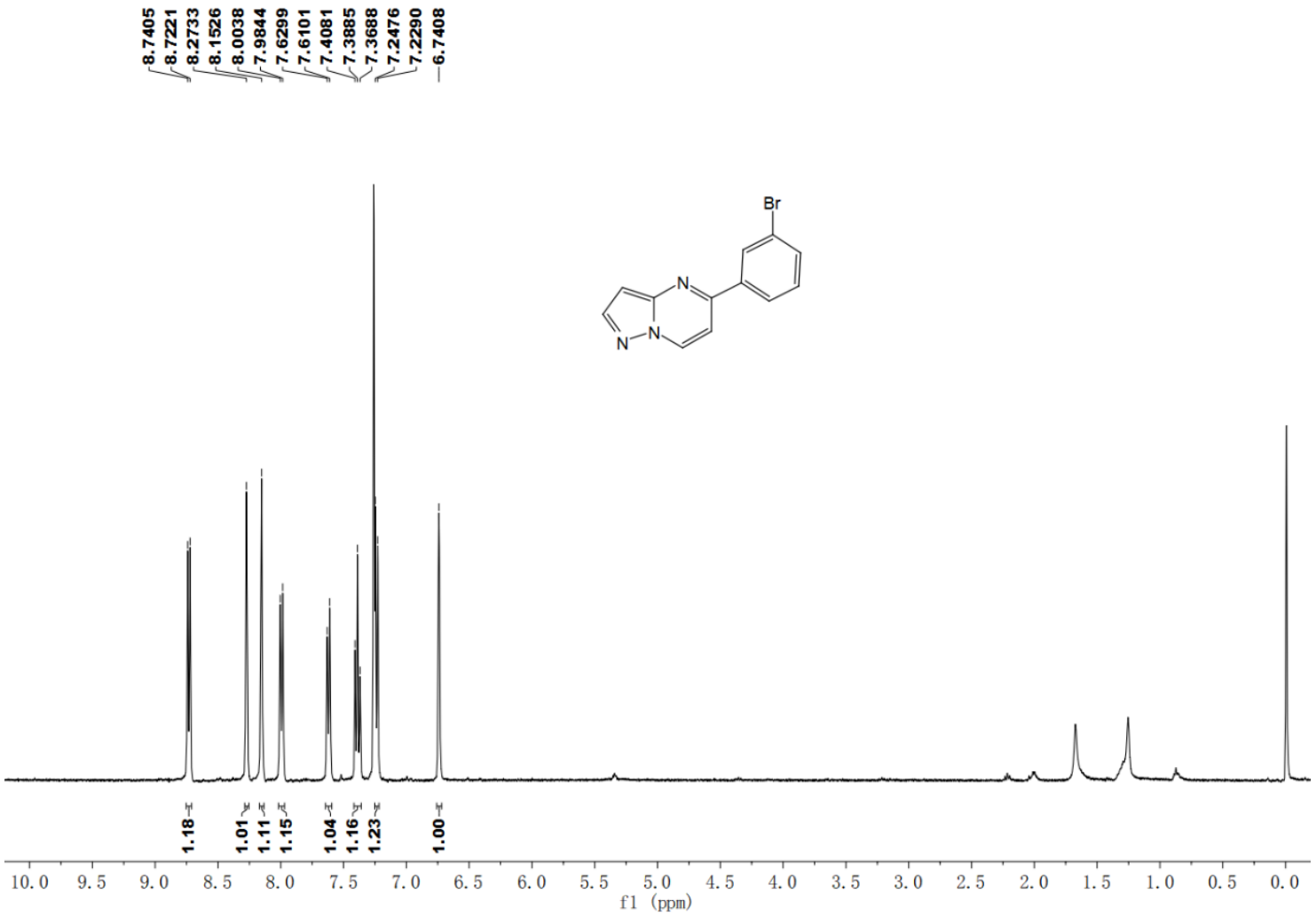

Fig S18. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(3-bromophenyl)pyrazolo[1,5-*a*]pyrimidine (**3i**)

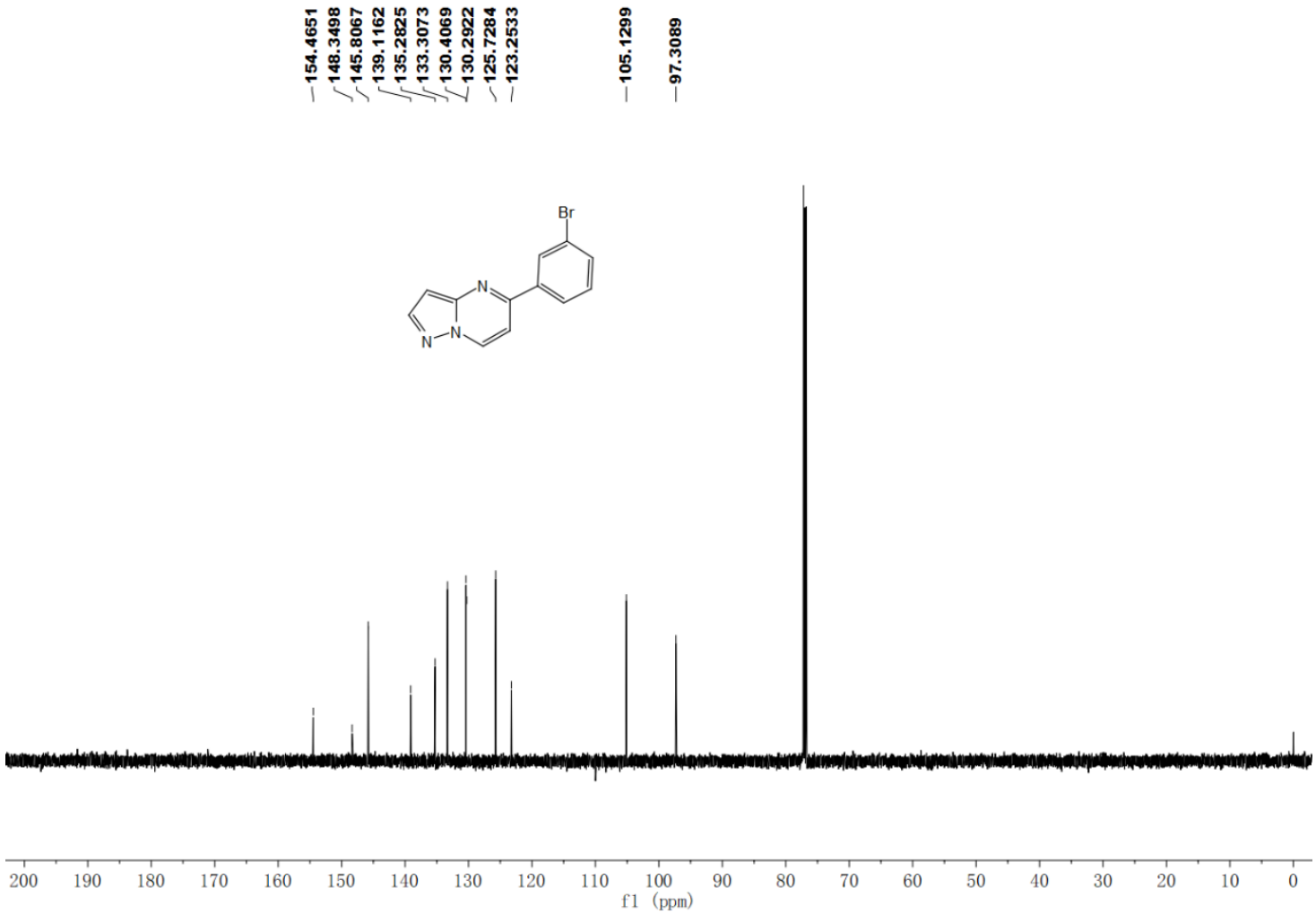

Fig S19. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(3-bromophenyl)pyrazolo[1,5-*a*]pyrimidine (**3i**)

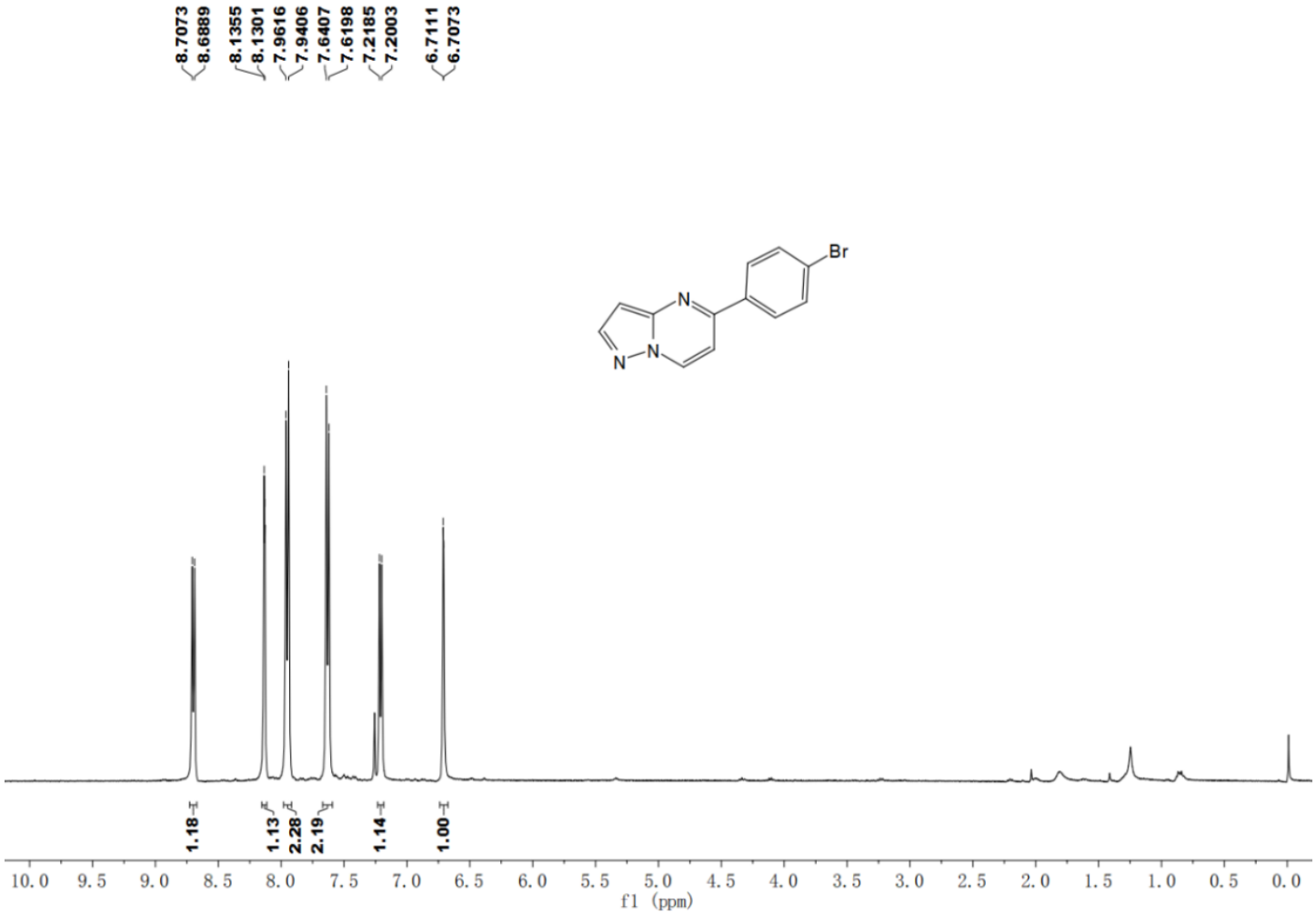

Fig S20. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(4-bromophenyl)pyrazolo[1,5-*a*]pyrimidine (**3j**)

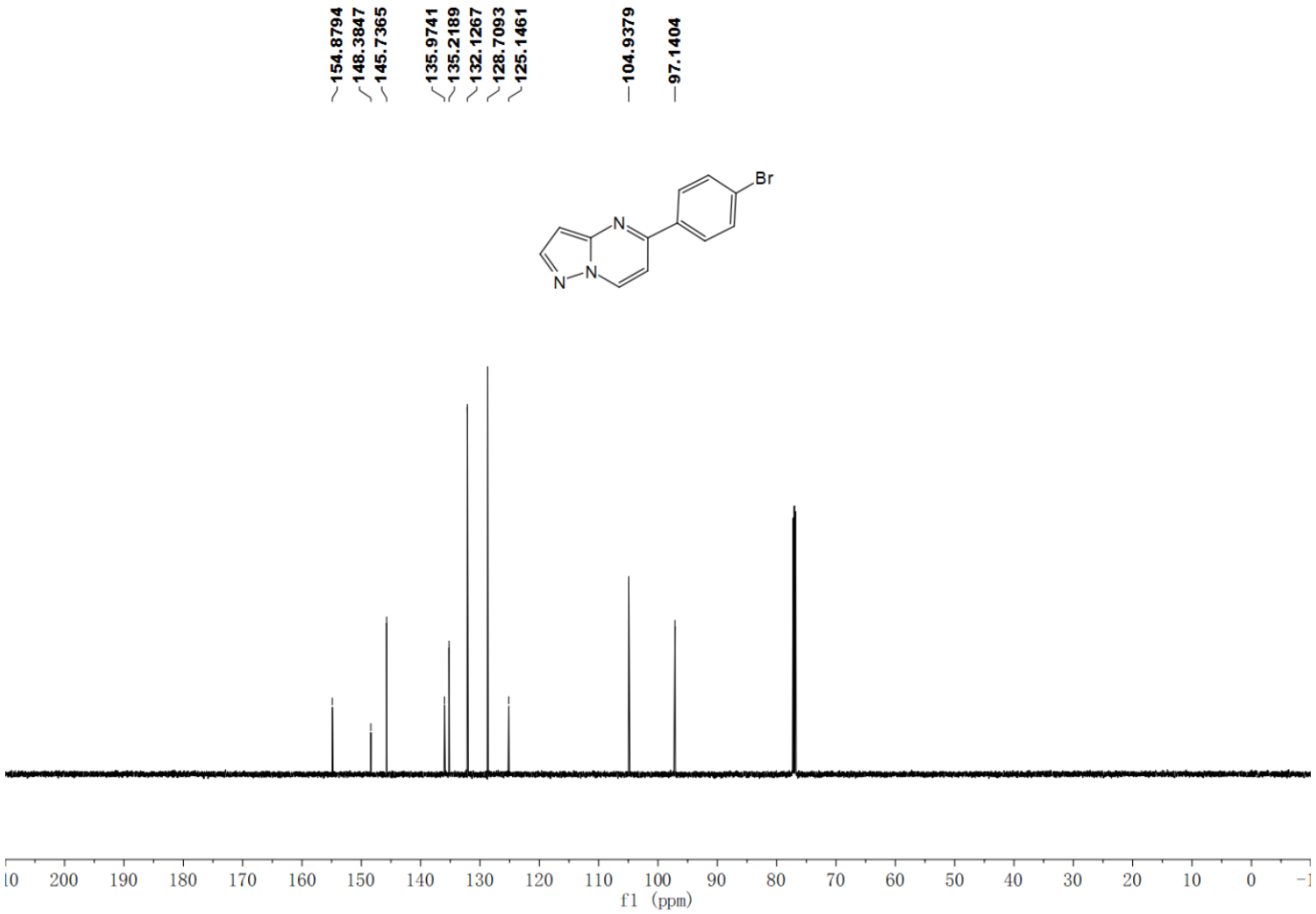

Fig S21. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(4-bromophenyl)pyrazolo[1,5-*a*]pyrimidine (**3j**)

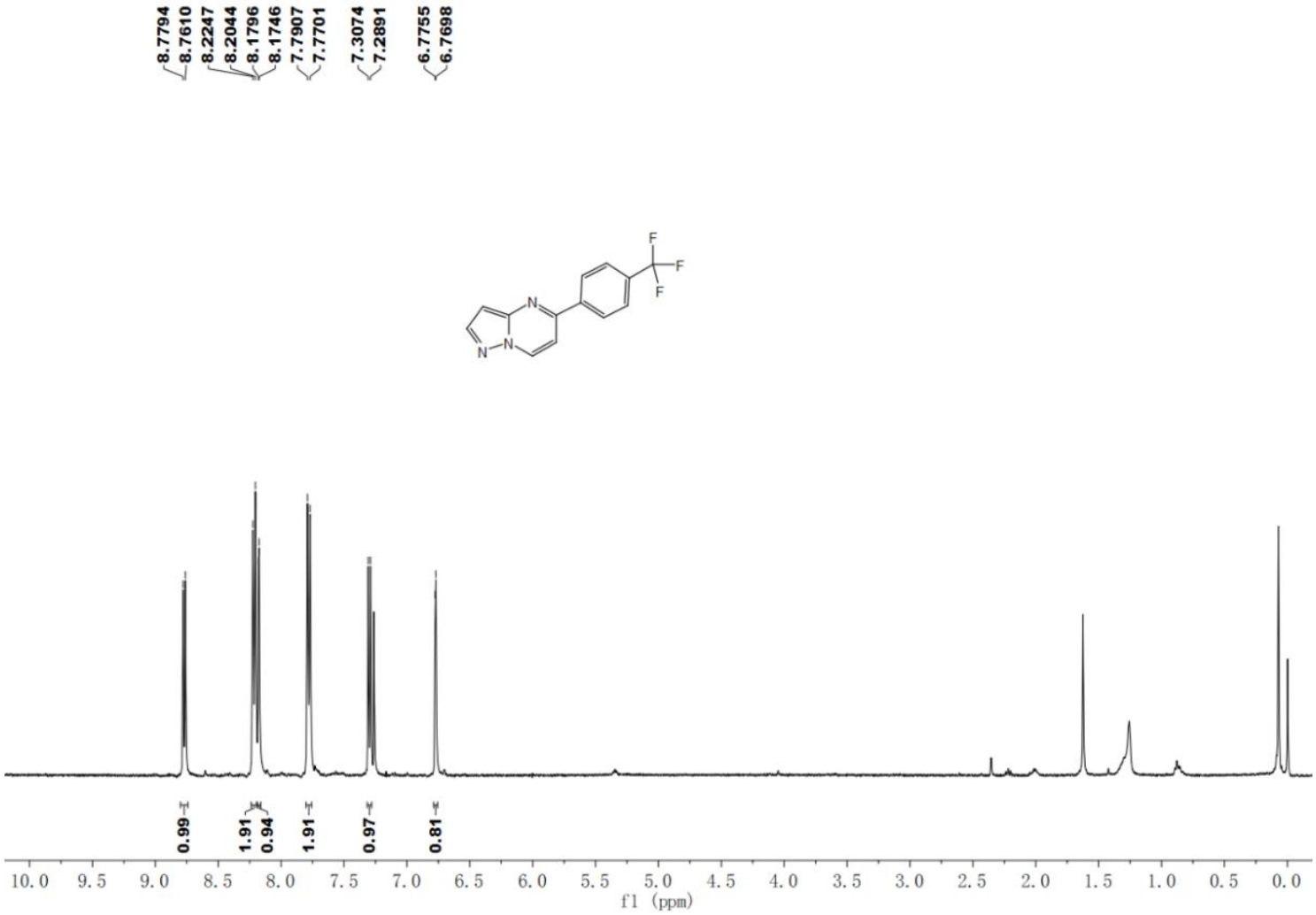

Fig S22. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(4-(trifluoromethyl)phenyl)pyrazolo[1,5-*a*]pyrimidine (**3k**)

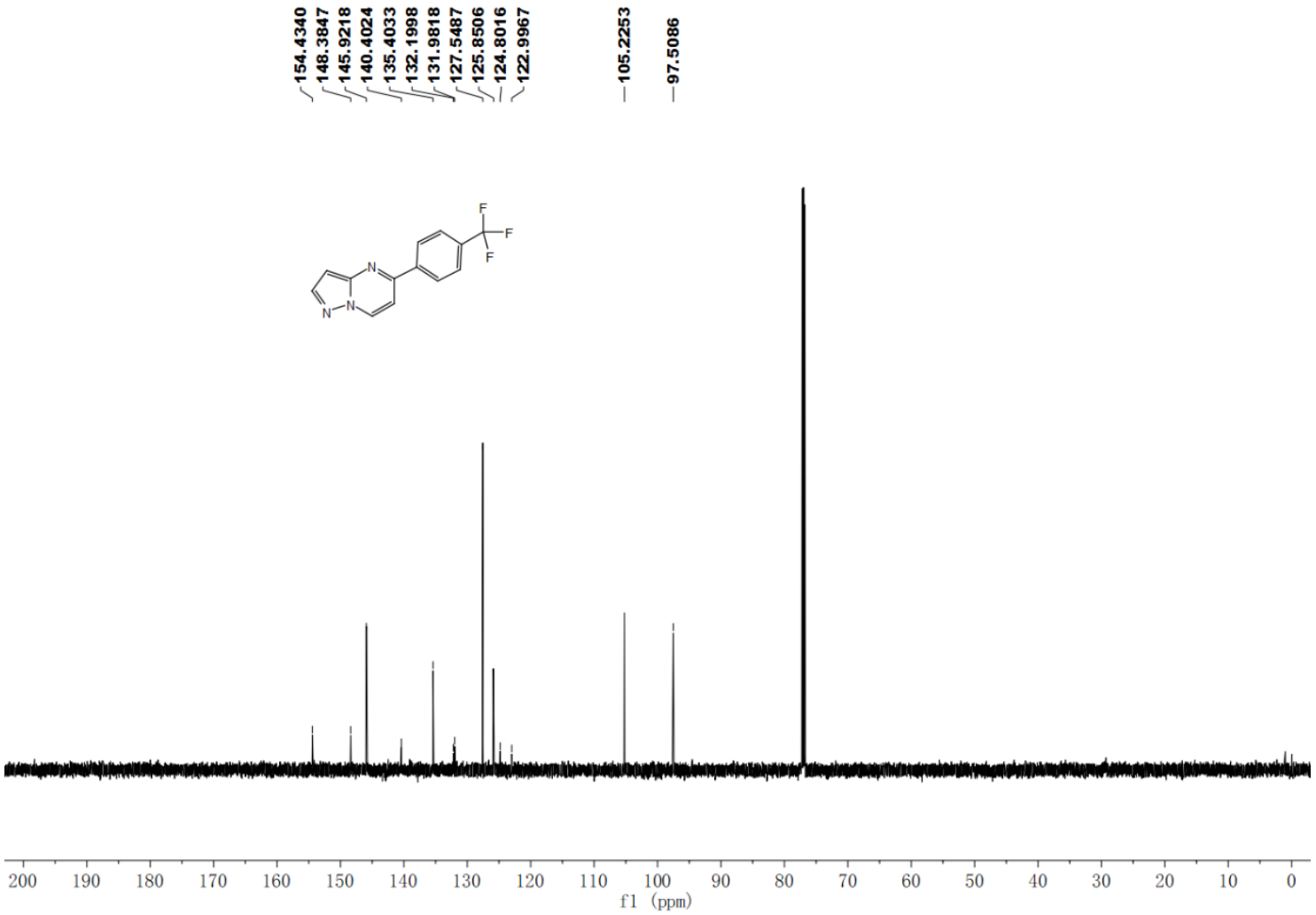

Fig S23. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(4-(trifluoromethyl)phenyl)pyrazolo[1,5-*a*]pyrimidine (**3k**)

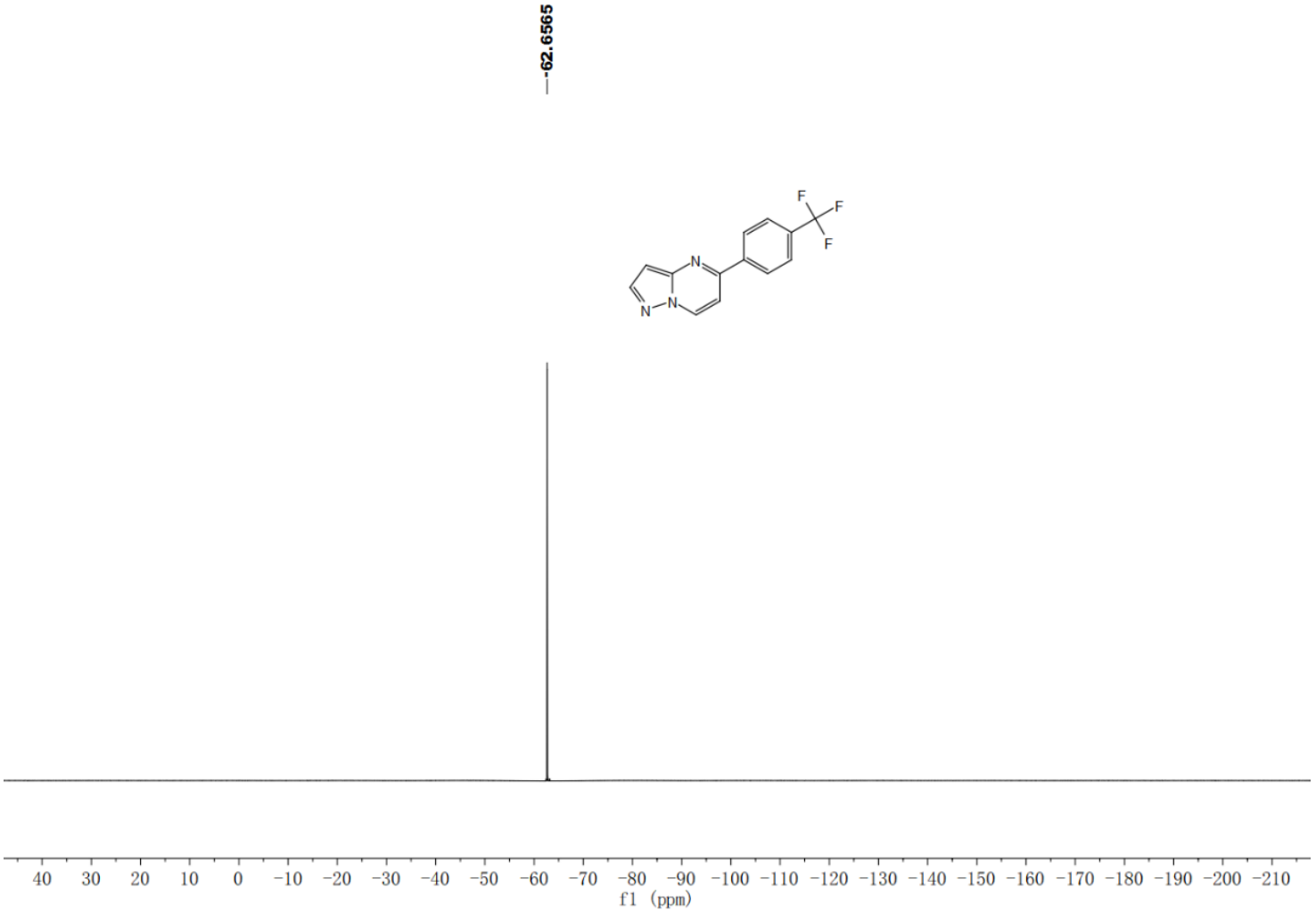

Fig S24. ^{19}F NMR (376 MHz, $CDCl_3$) of 5-(4-(trifluoromethyl)phenyl)pyrazolo[1,5-*a*]pyrimidine (**3k**)

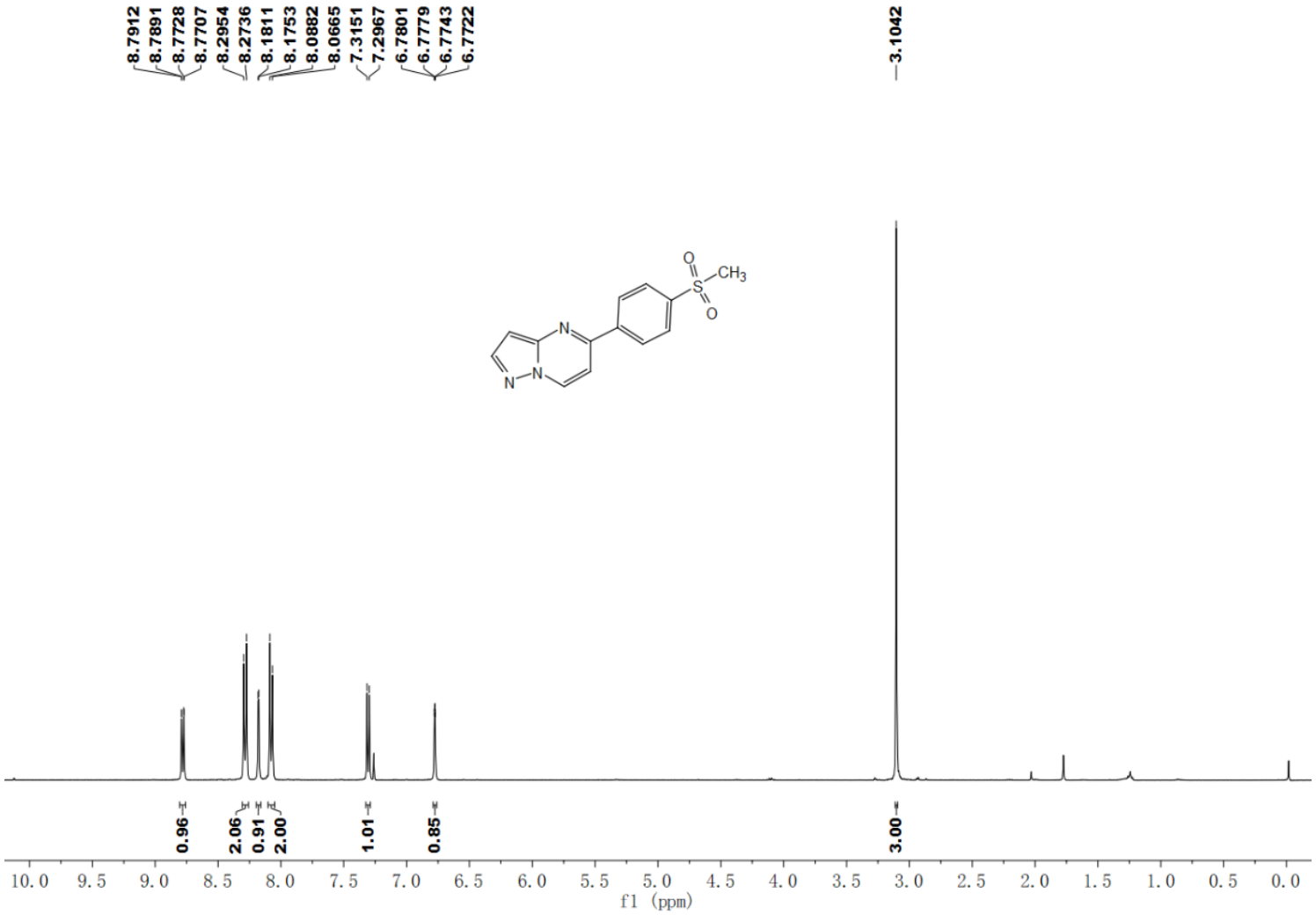

Fig S25. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(4-(methylsulfonyl)phenyl)pyrazolo[1,5-*a*]pyrimidine (**3l**)

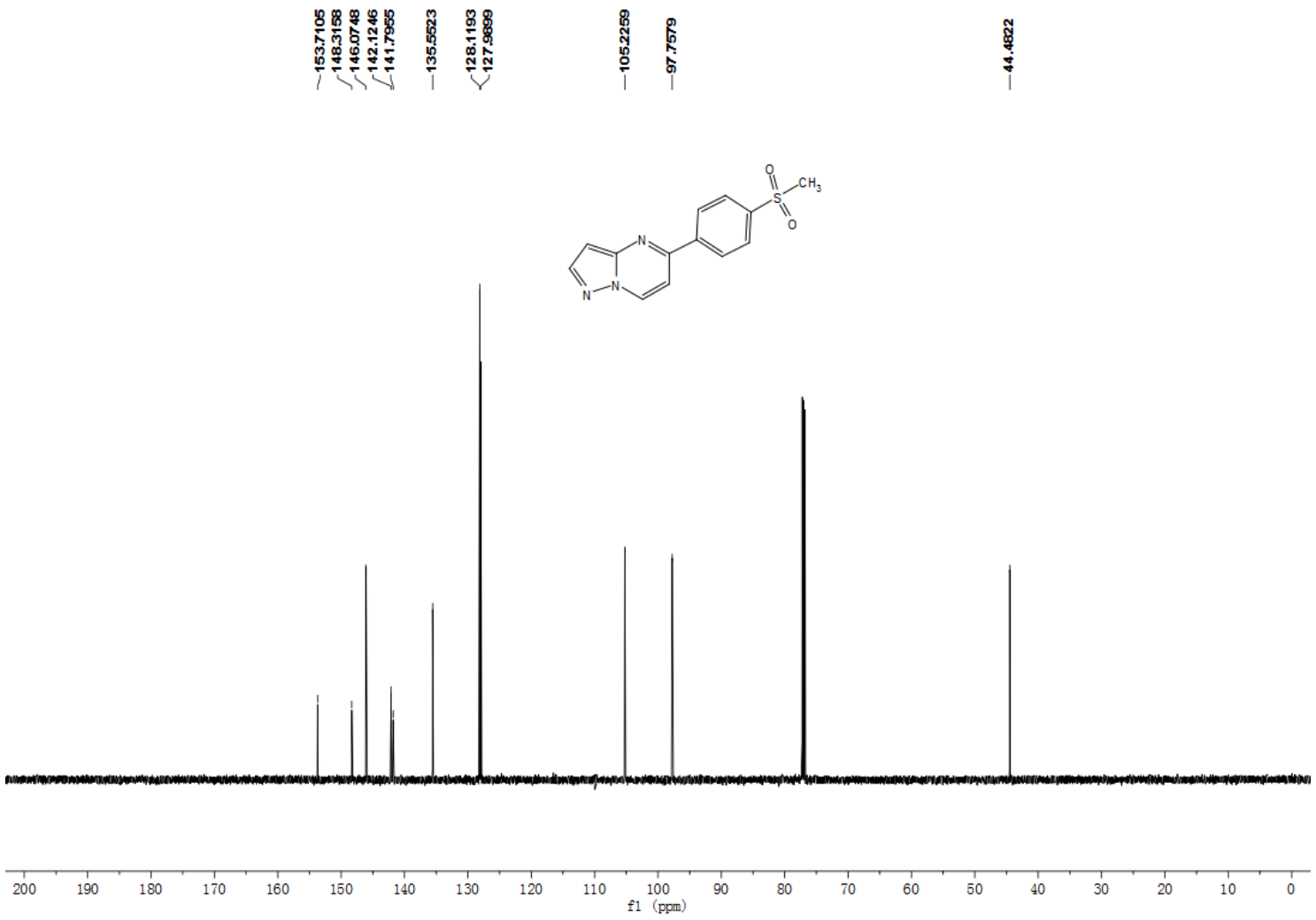

Fig S26. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(4-(methylsulfonyl)phenyl)pyrazolo[1,5-*a*]pyrimidine (**3l**)

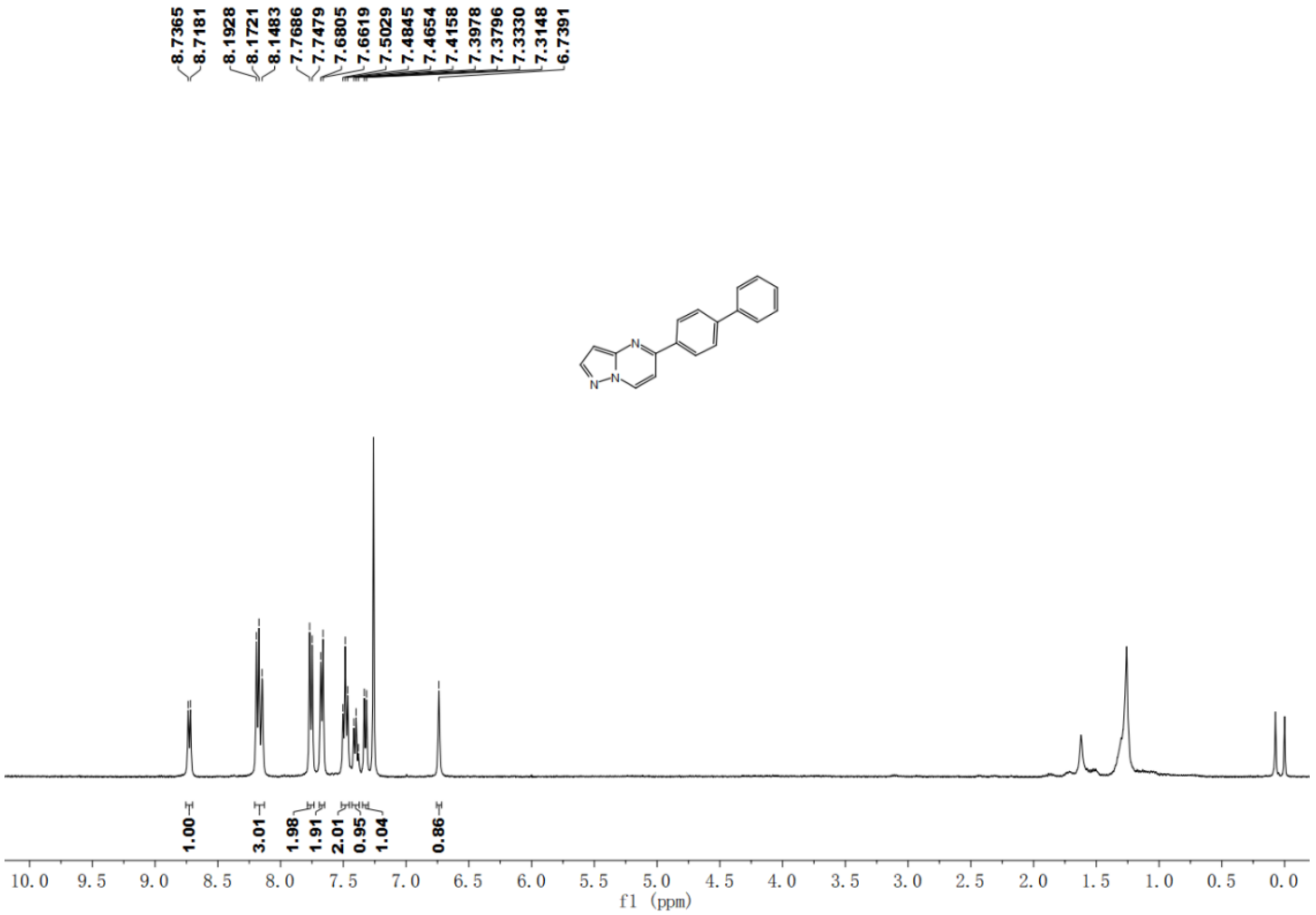

Fig S27. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-([1,1'-biphenyl]-4-yl)pyrazolo[1,5-*a*]pyrimidine (**3m**)

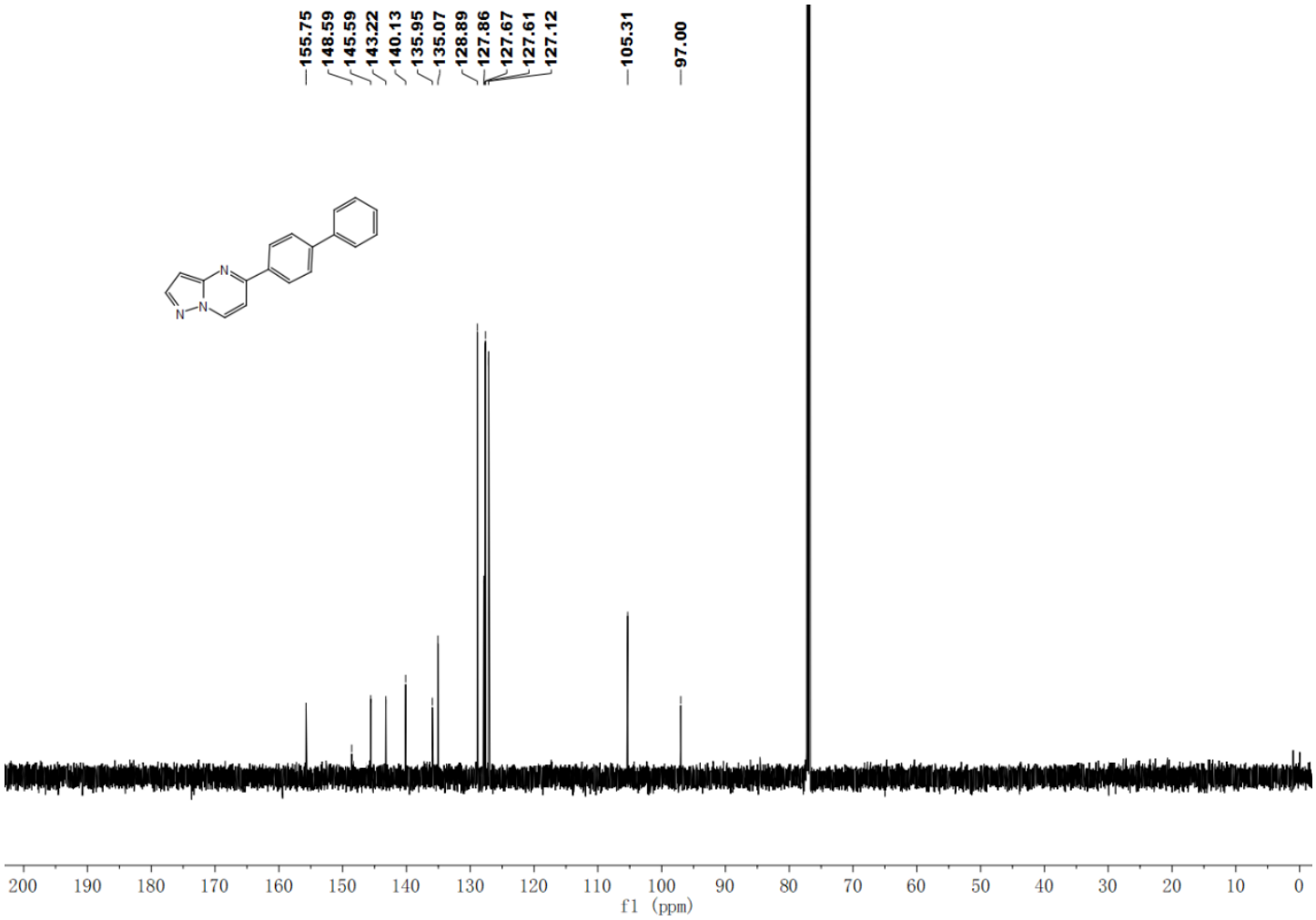

Fig S28. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-([1,1'-biphenyl]-4-yl)pyrazolo[1,5-*a*]pyrimidine (**3m**)

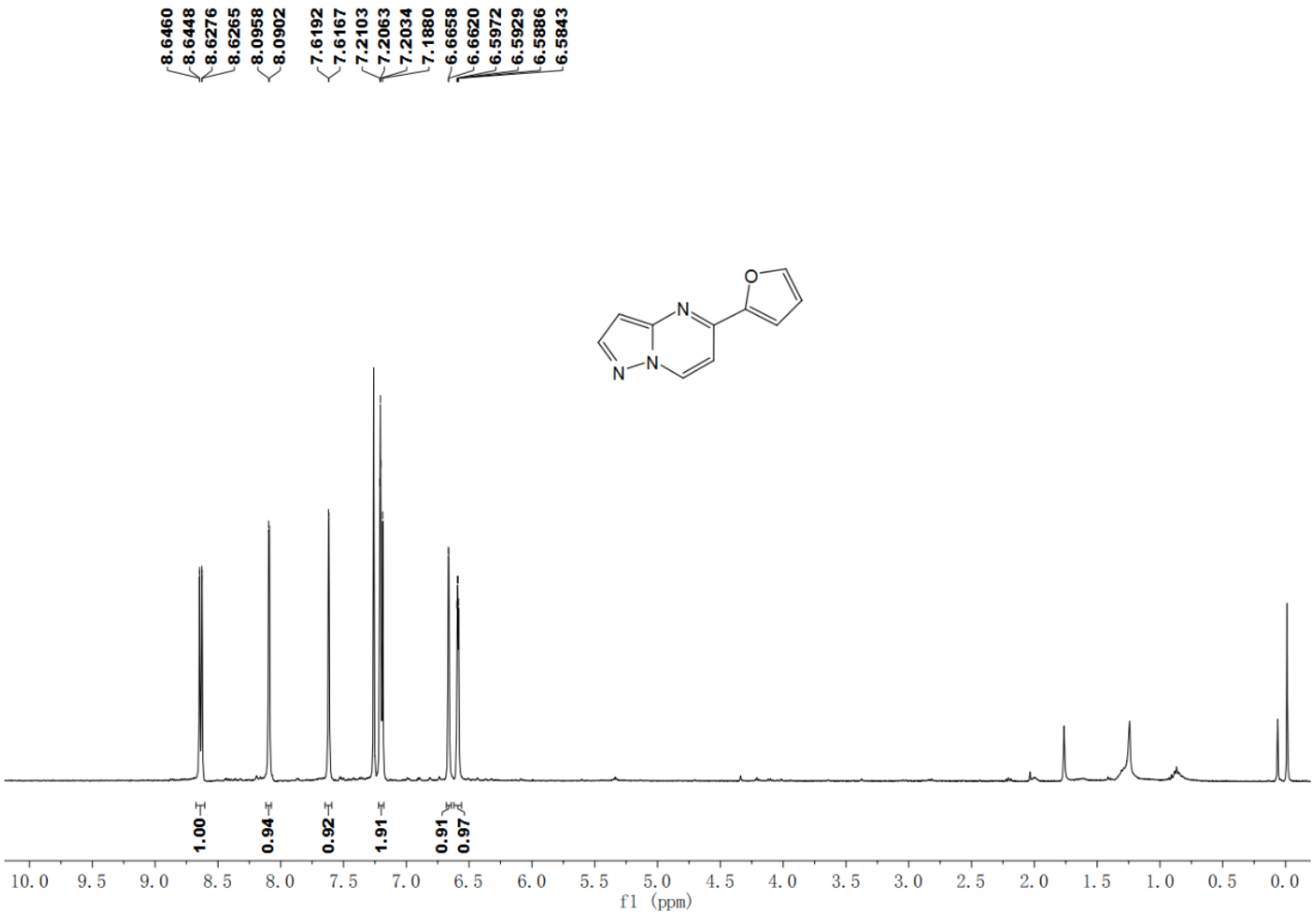

Fig S29. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(furan-2-yl)pyrazolo[1,5-*a*]pyrimidine (**3n**)

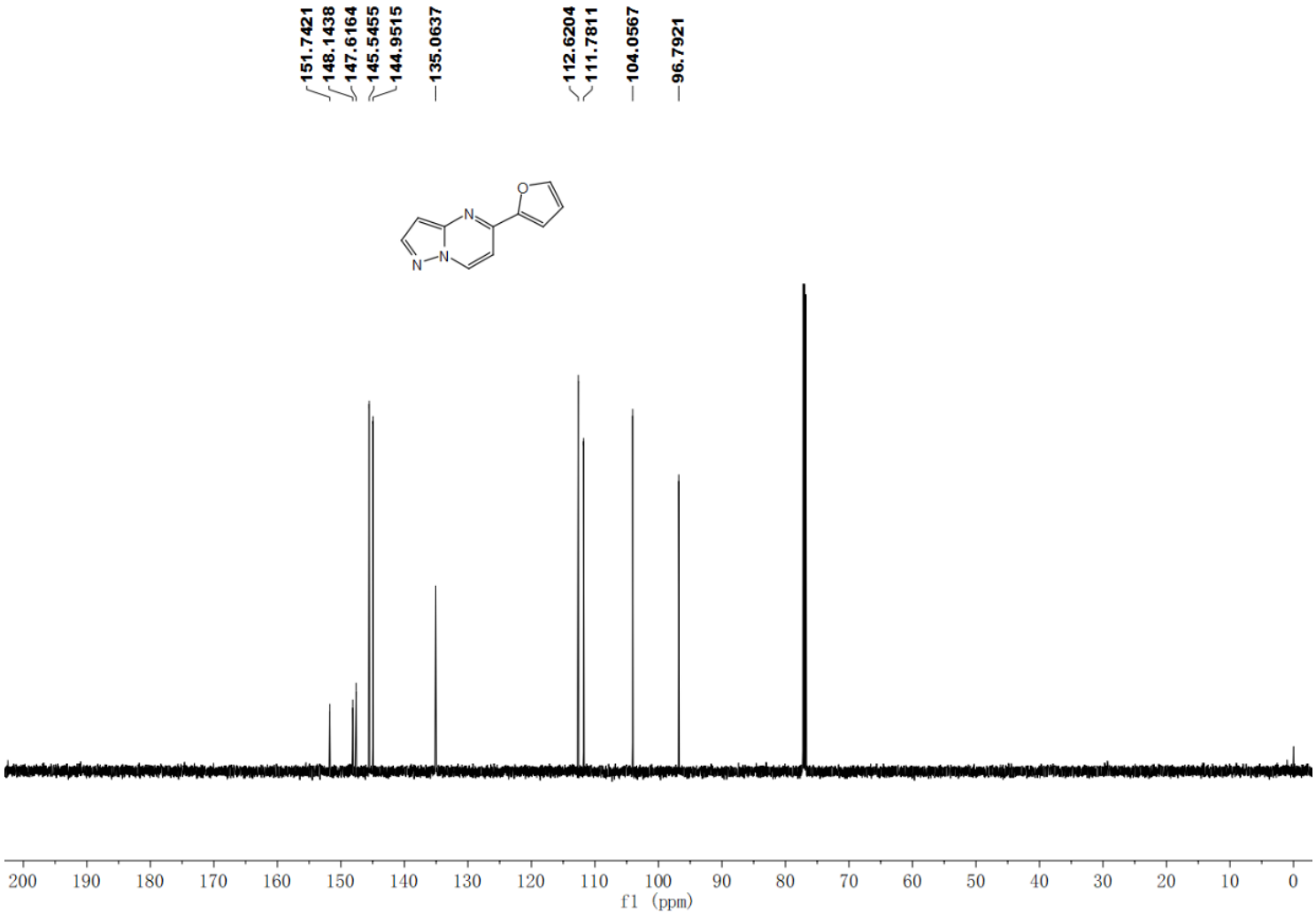

Fig S30. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(furan-2-yl)pyrazolo[1,5-*a*]pyrimidine (**3n**)

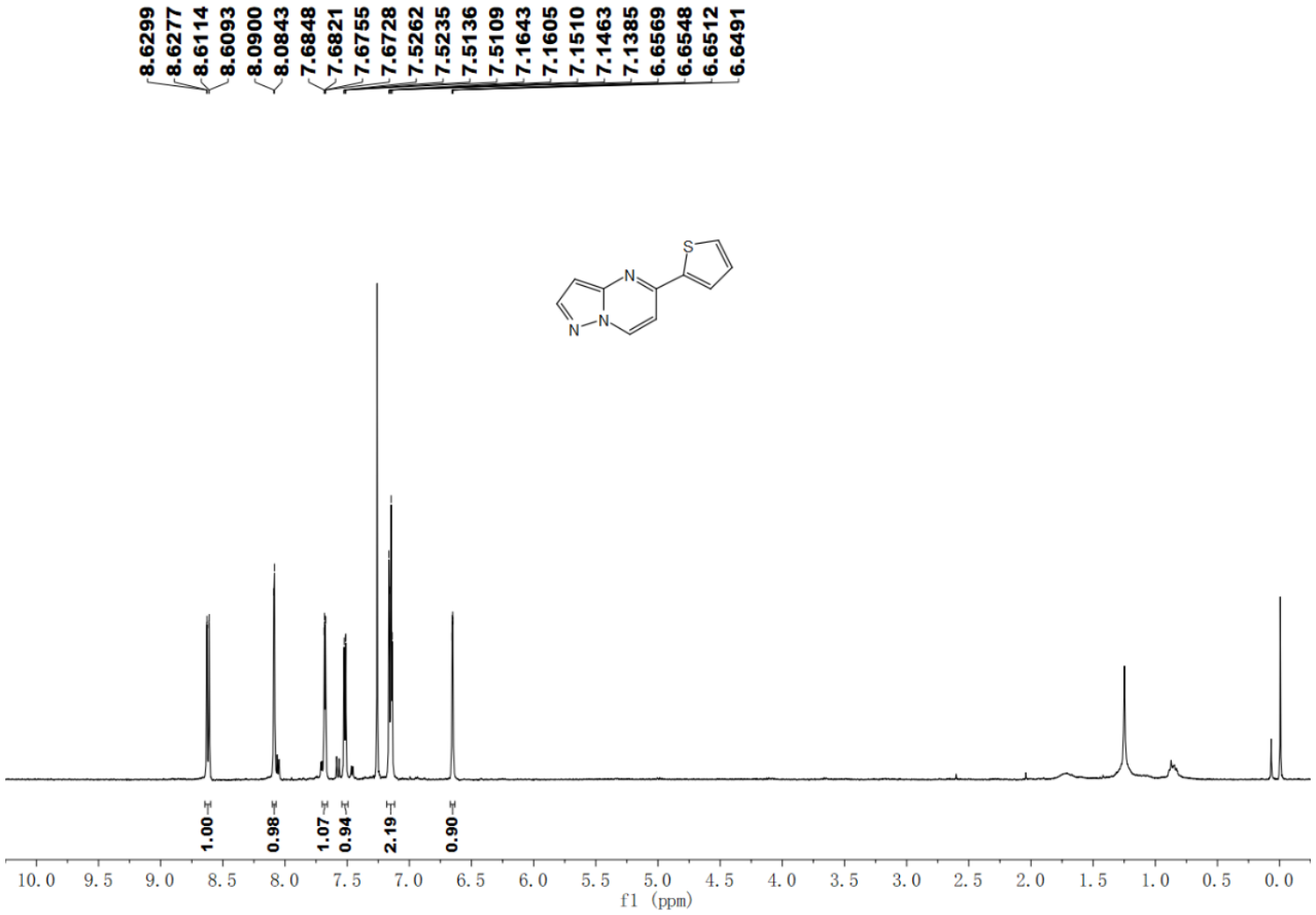

Fig S31. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(thiophen-2-yl)pyrazolo[1,5-*a*]pyrimidine (**3o**)

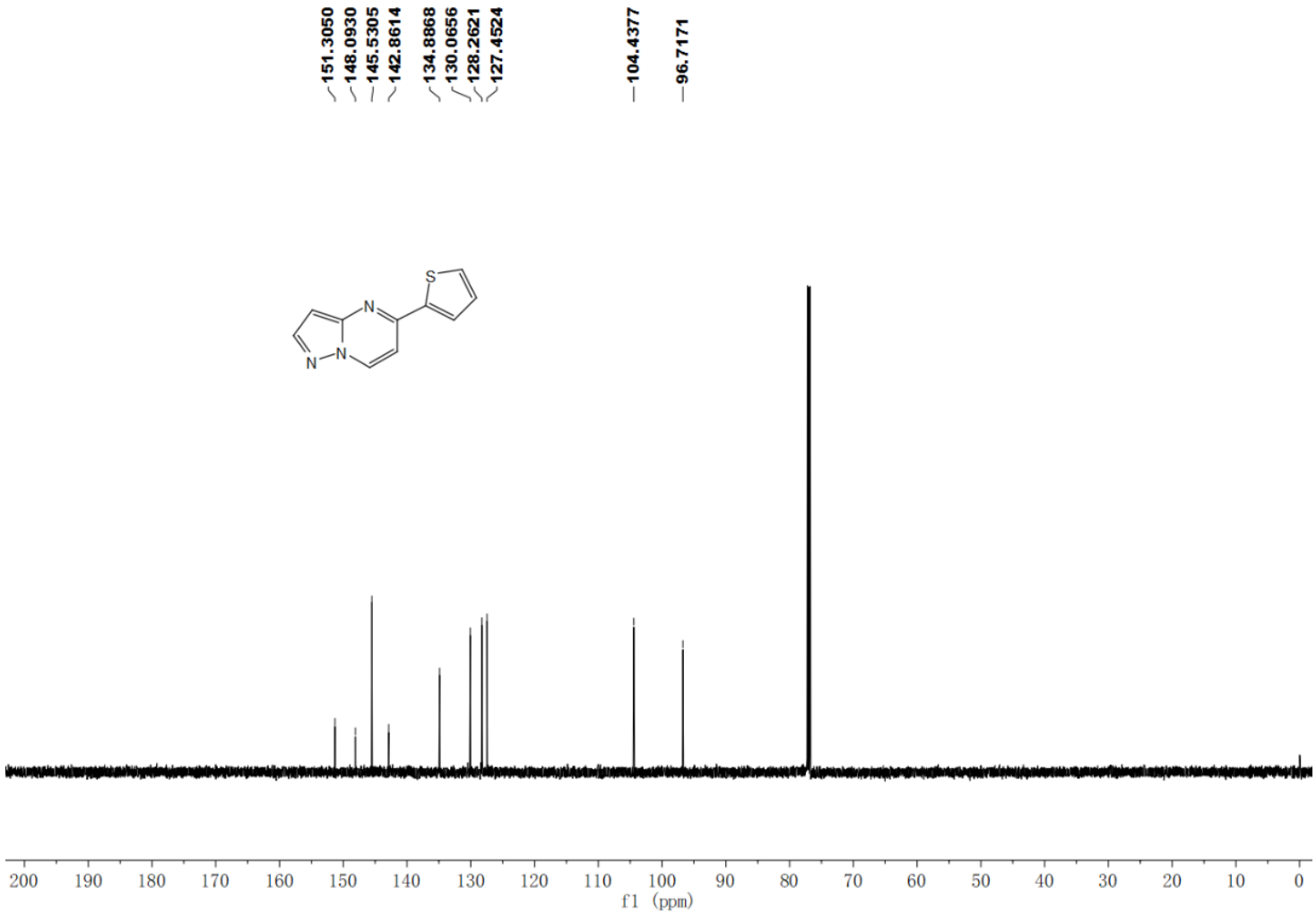

Fig S32. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(thiophen-2-yl)pyrazolo[1,5-*a*]pyrimidine (**3o**)

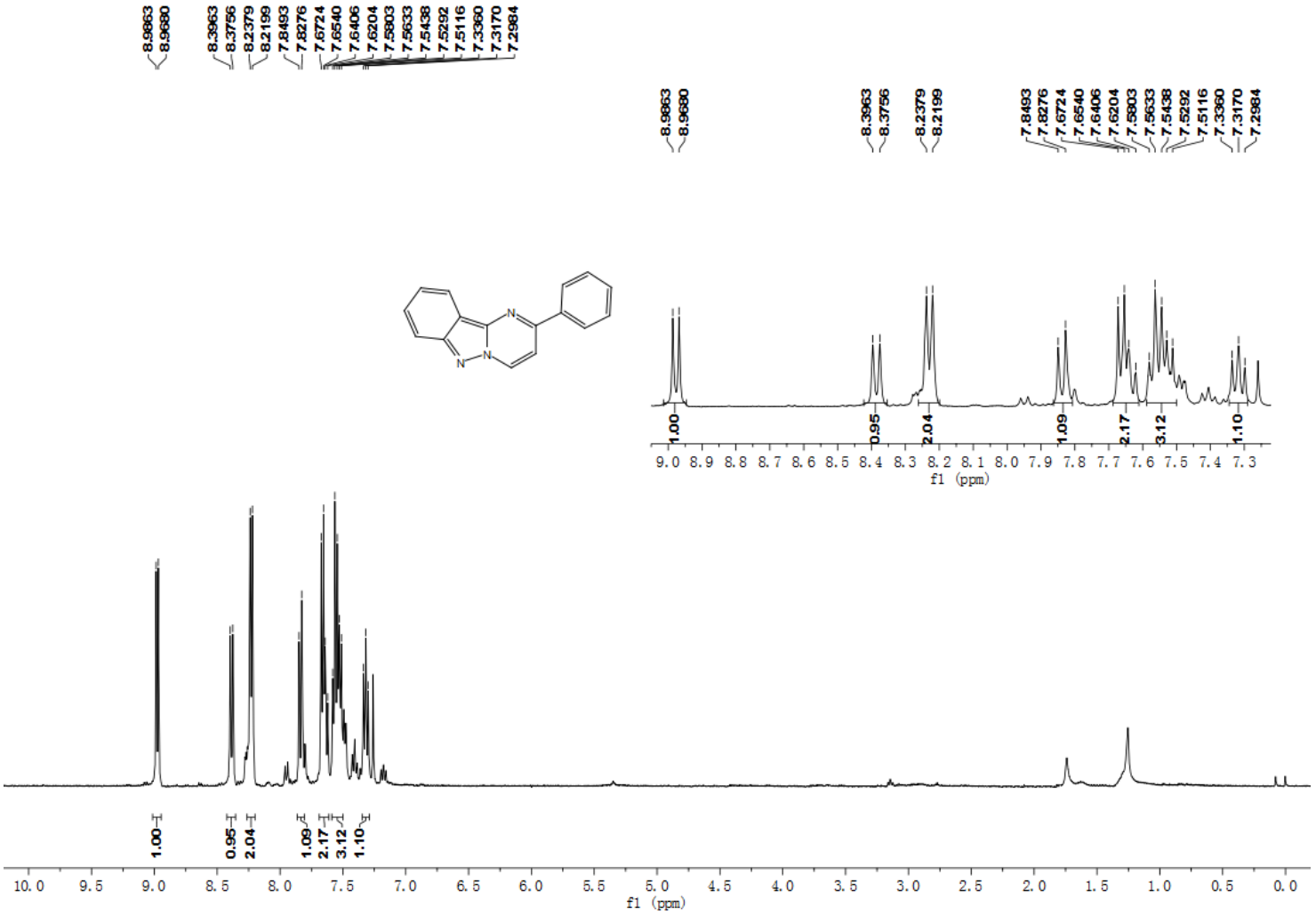

Fig S33. ^{1}H NMR ($CDCl_3$, 400 MHz) of 2-phenylpyrimido[1,2-*b*]indazole (**4a**)

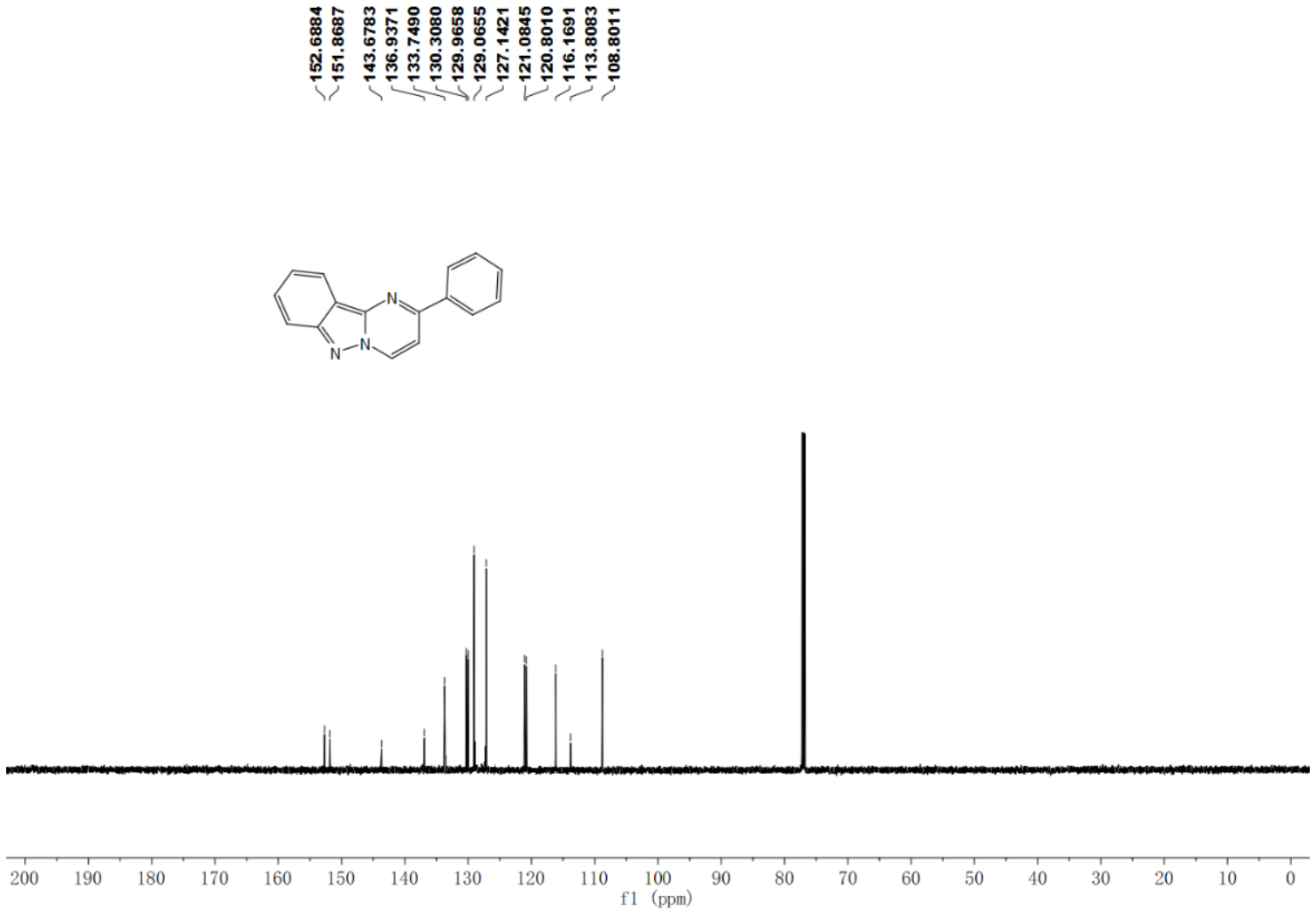

Fig S34. ^{13}C NMR ($CDCl_3$, 151 MHz) of 2-phenylpyrimido[1,2-*b*]indazole (**4a**)

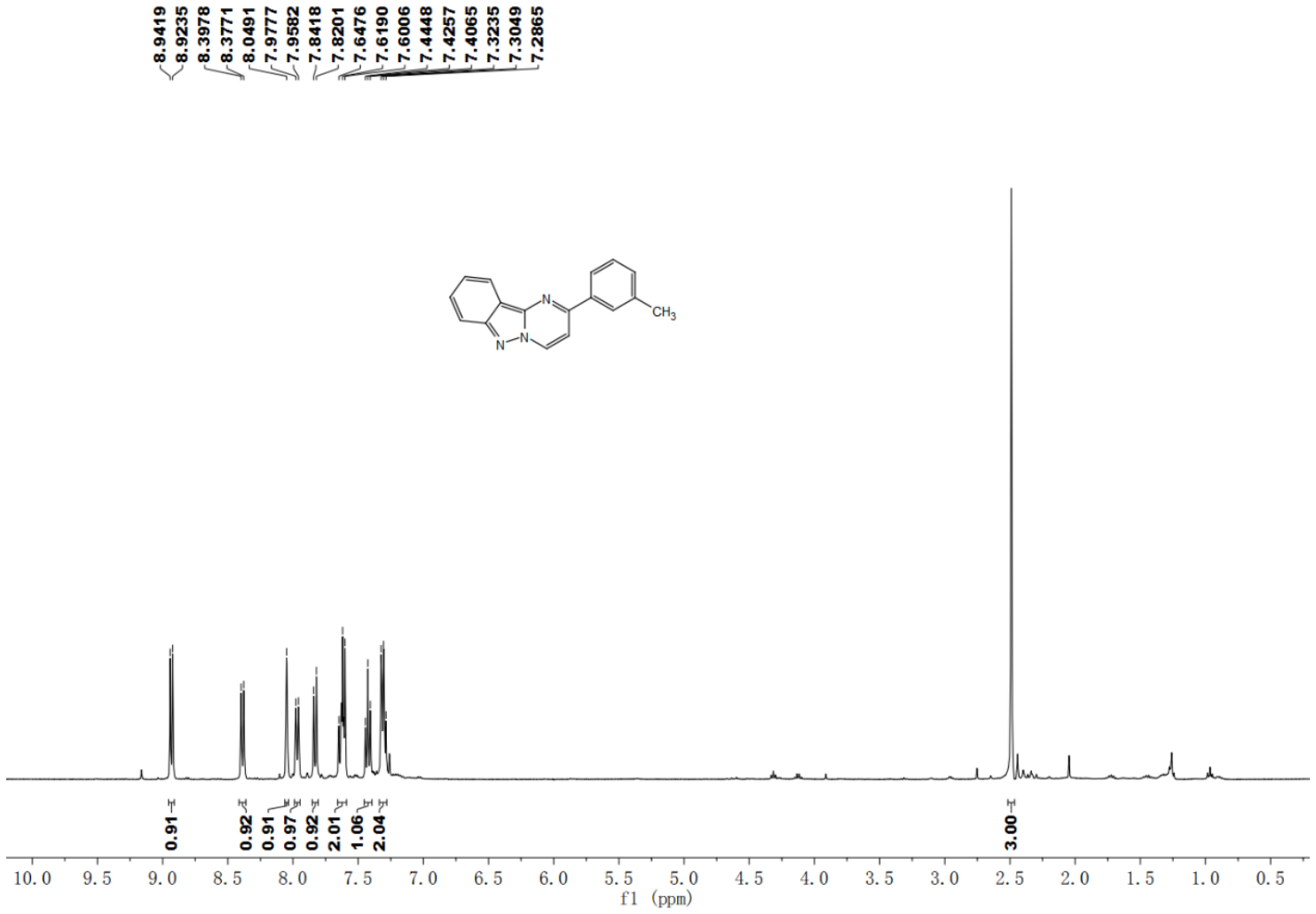

Fig S35. ^{1}H NMR ($CDCl_3$, 400 MHz) of 2-(*m*-tolyl)pyrimido[1,2-*b*]indazole (**4b**)

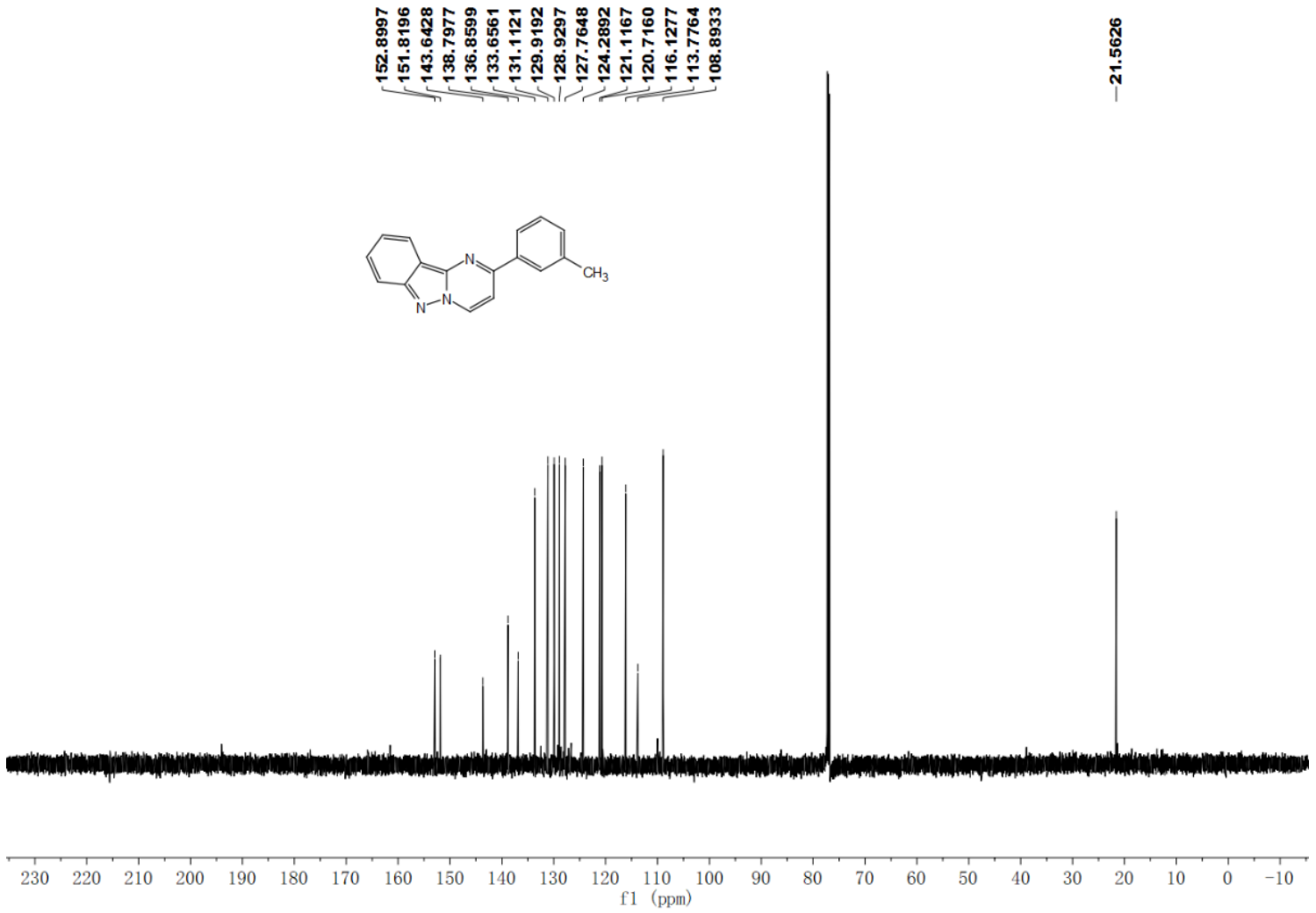

Fig S36. ^{13}C NMR ($CDCl_3$, 151 MHz) of 2-(*m*-tolyl)pyrimido[1,2-*b*]indazole (**4b**)

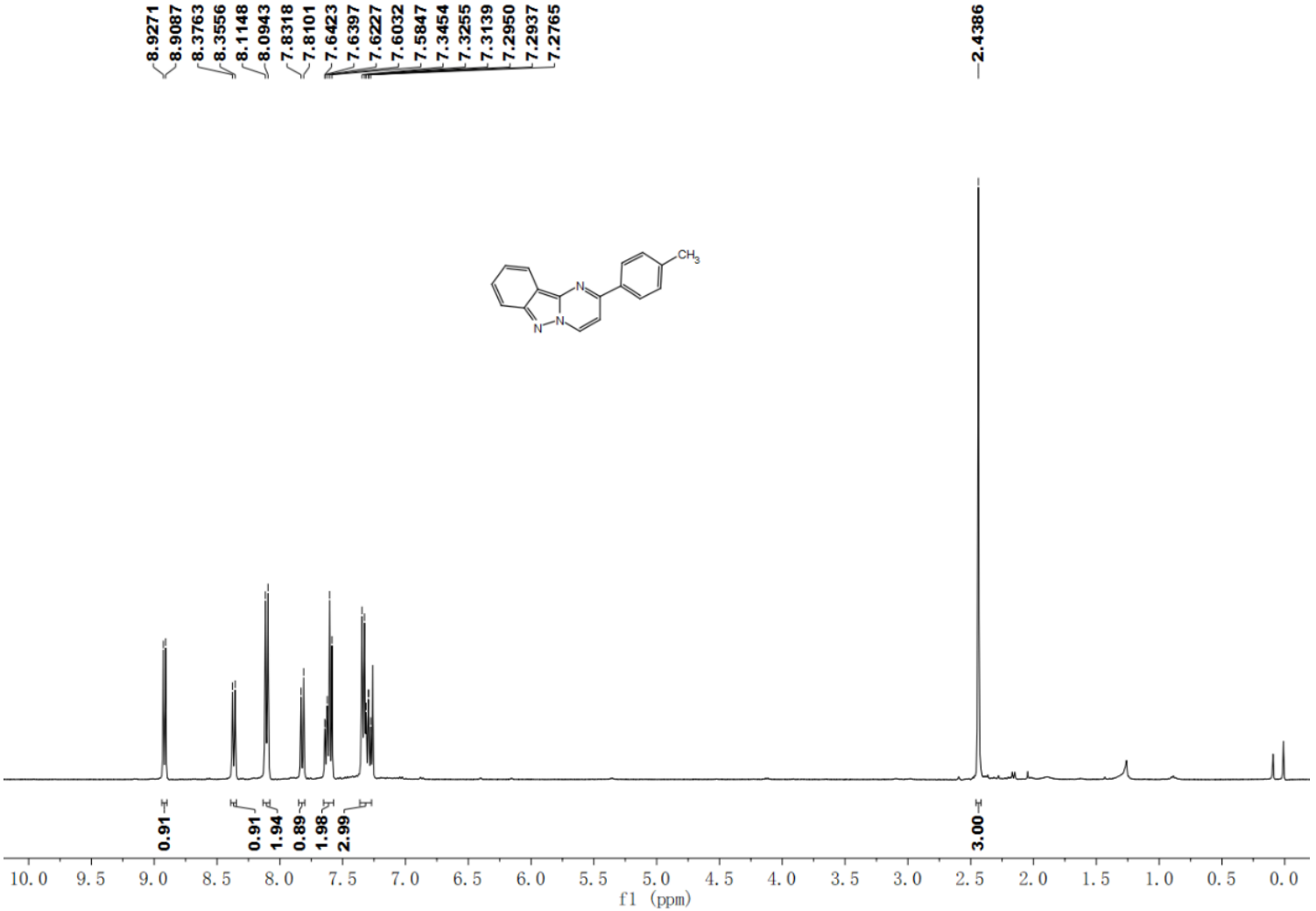

Fig S37. ^{1}H NMR ($CDCl_3$, 400 MHz) of 2-(*p*-tolyl)pyrimido[1,2-*b*]indazole (**4c**)

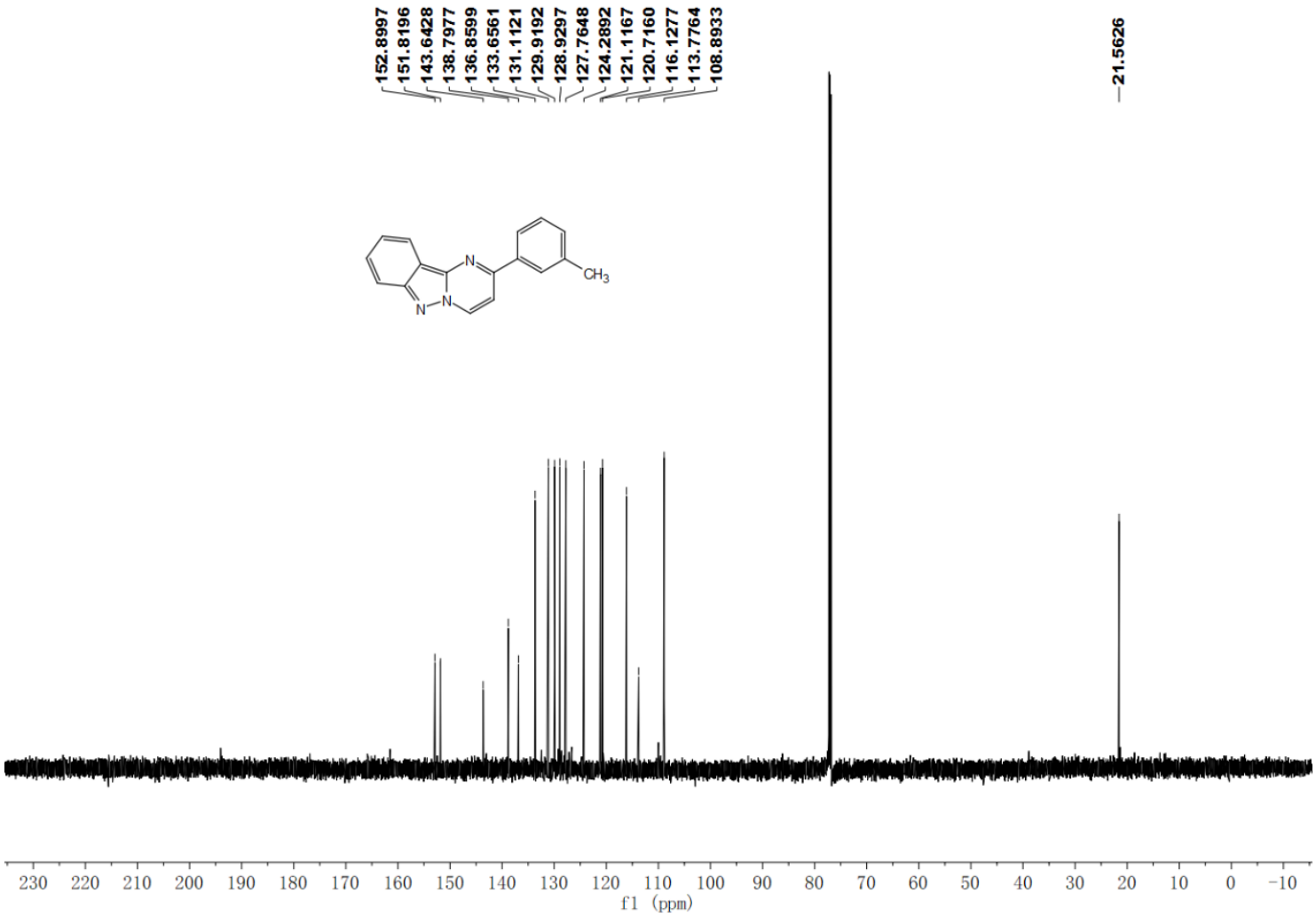

Fig S38. ^{13}C NMR ($CDCl_3$, 151 MHz) of 2-(*p*-tolyl)pyrimido[1,2-*b*]indazole (**4c**)

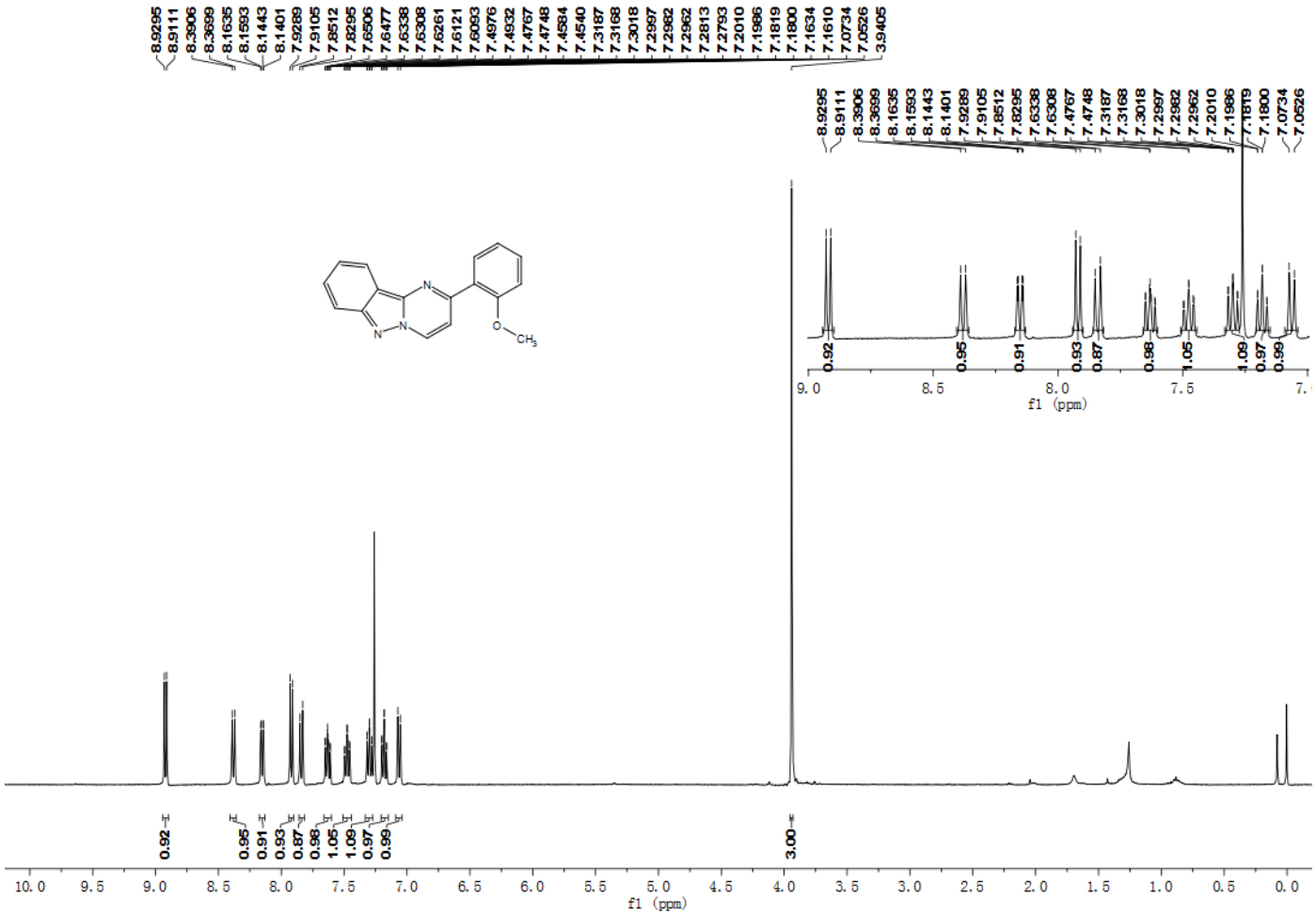

Fig S39. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-(4-Methoxy)pyrimido[1,2-*b*]indazole (**4d**)

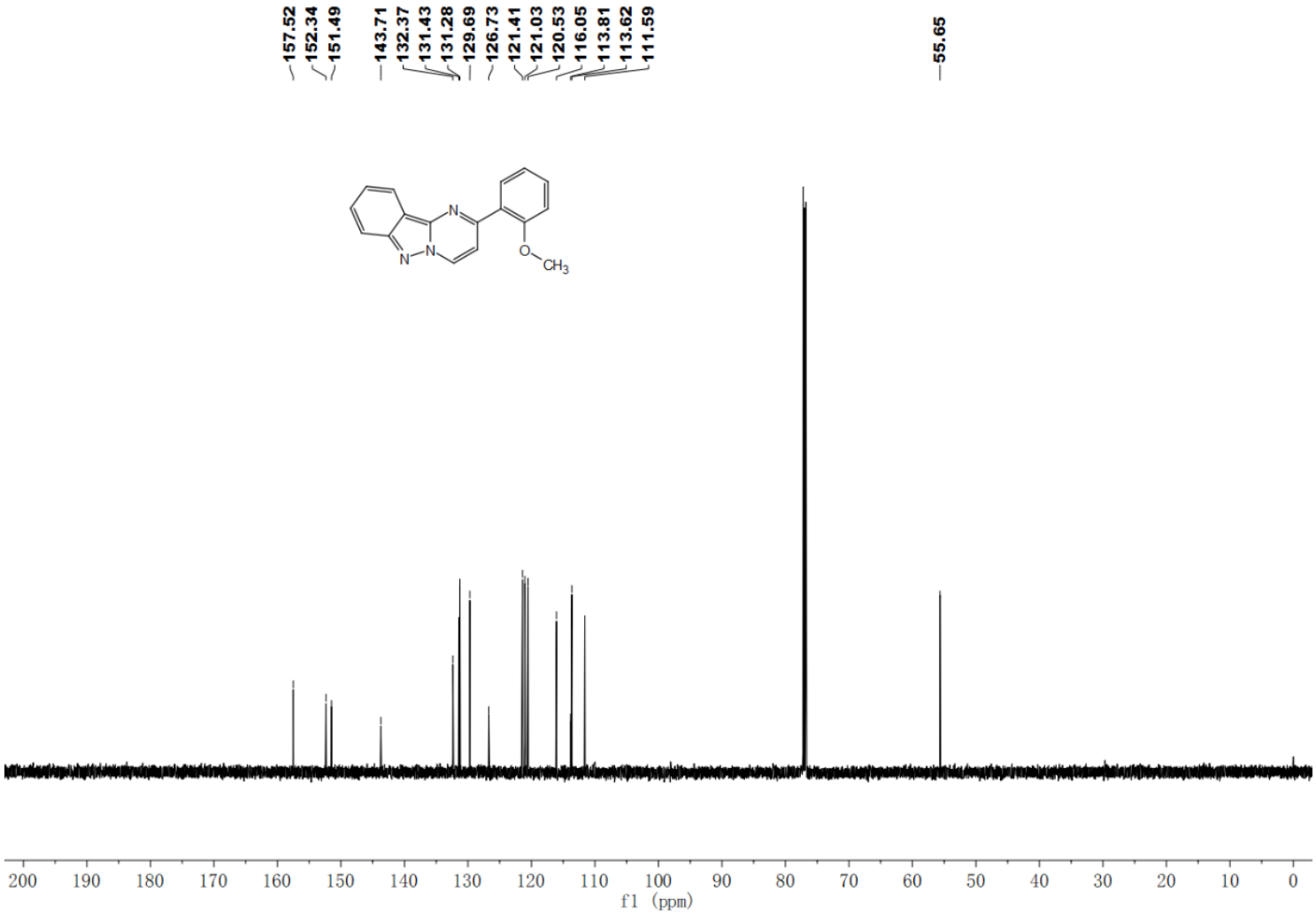

Fig S40. ^{13}C NMR (151 MHz, $CDCl_3$) of 2-(4-Methoxy)pyrimido[1,2-*b*]indazole **(4d)**

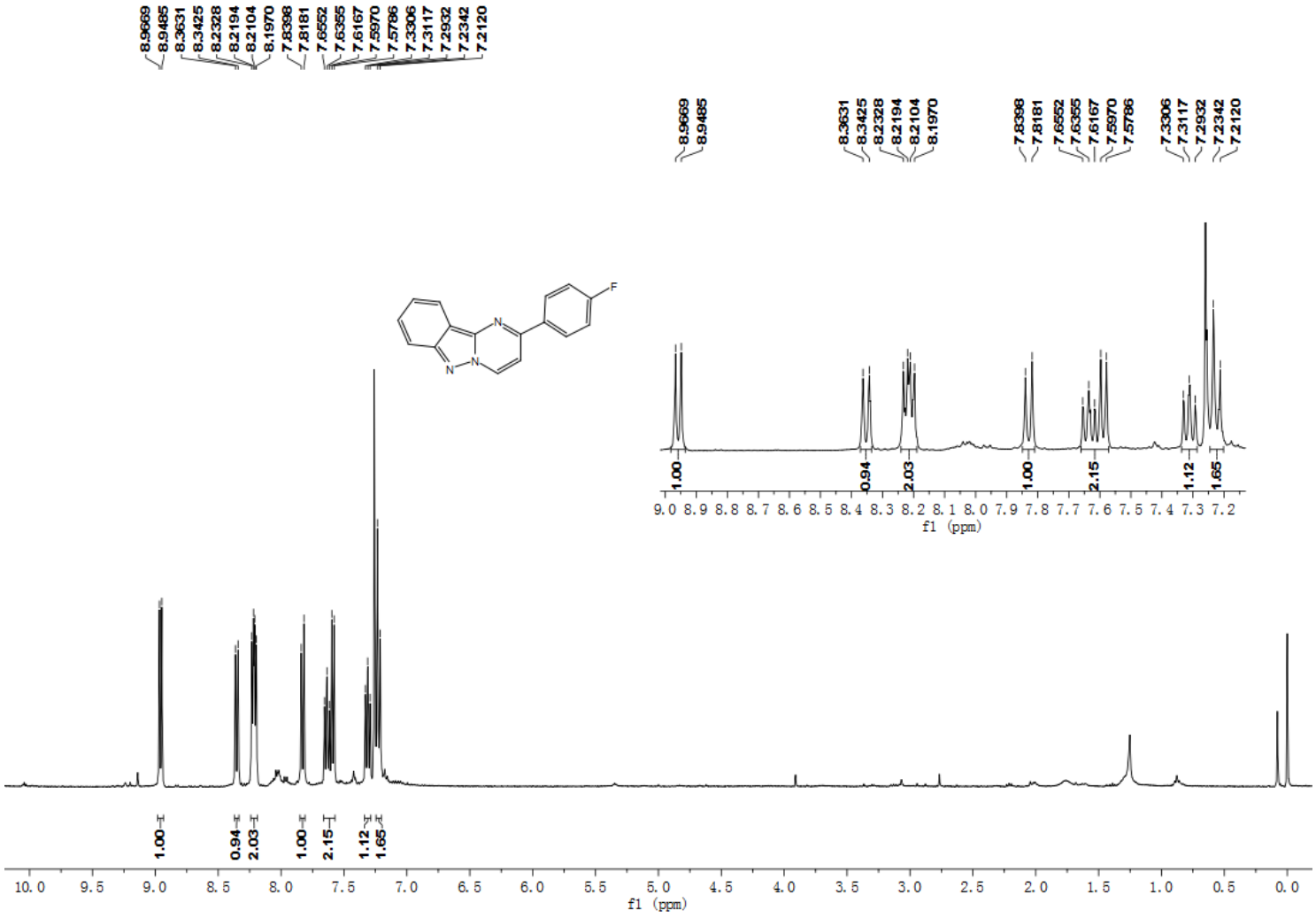

Fig S41. ^{1}H NMR ($CDCl_3$, 400 MHz) of 2-(4-fluorophenyl)pyrimido[1,2-*b*]indazole (**4e**)

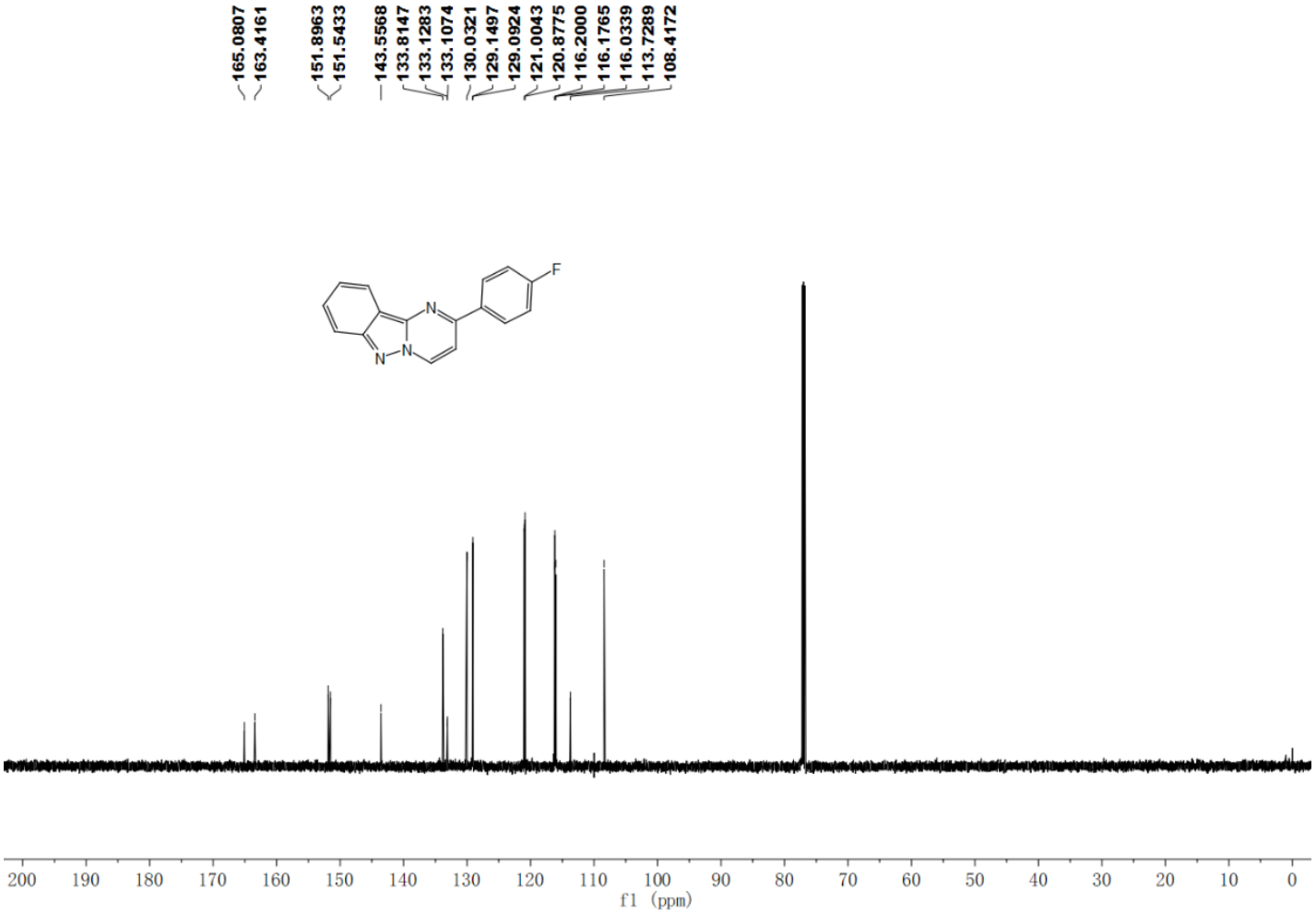

Fig S42. ^{13}C NMR ($CDCl_3$, 151 MHz) of 2-(4-fluorophenyl)pyrimido[1,2-*b*]indazole (**4e**)

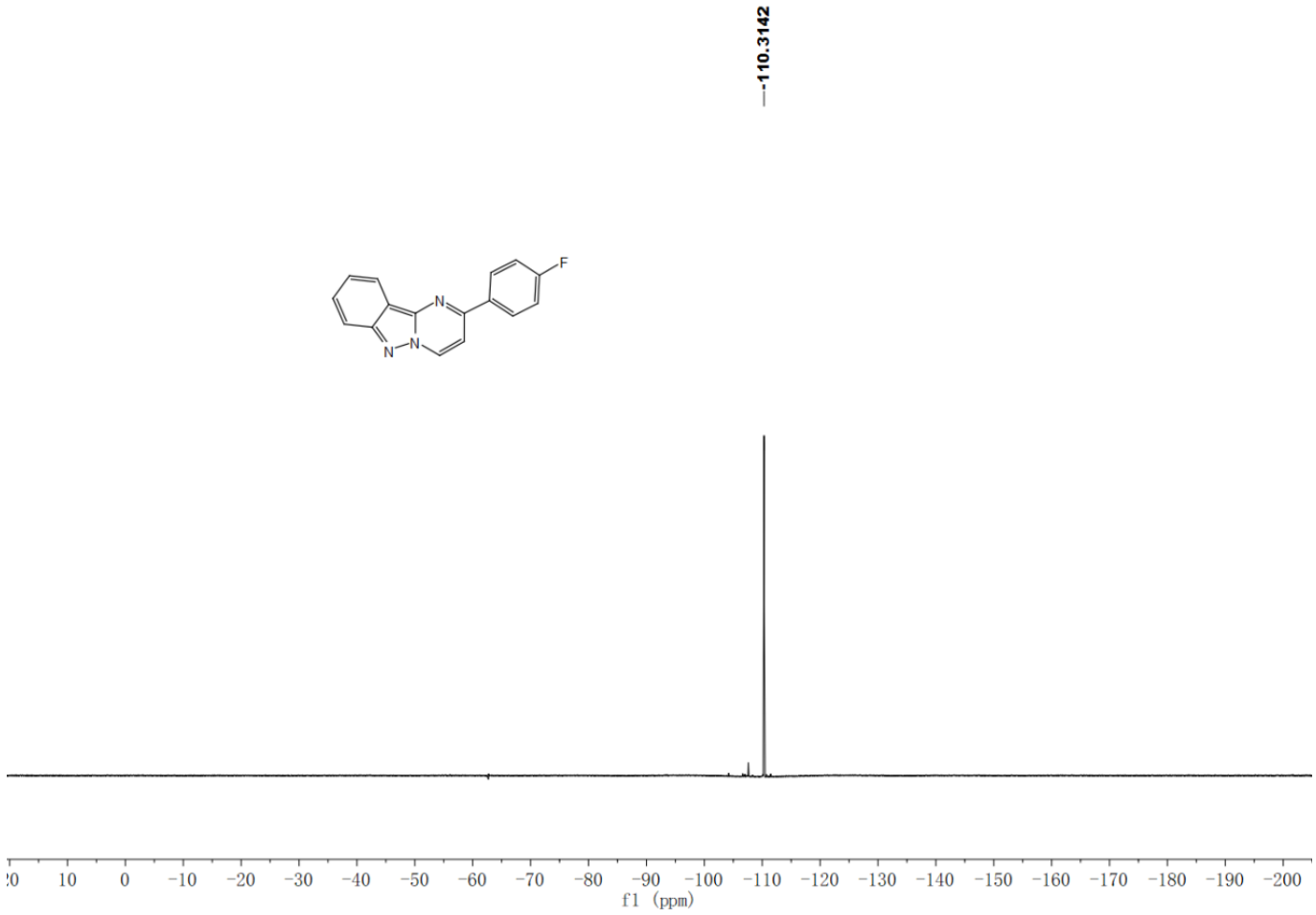

Fig S43. ^{19}F NMR (376 MHz, $CDCl_3$) of 2-(4-fluorophenyl)pyrimido[1,2-*b*]indazole (**4e**)

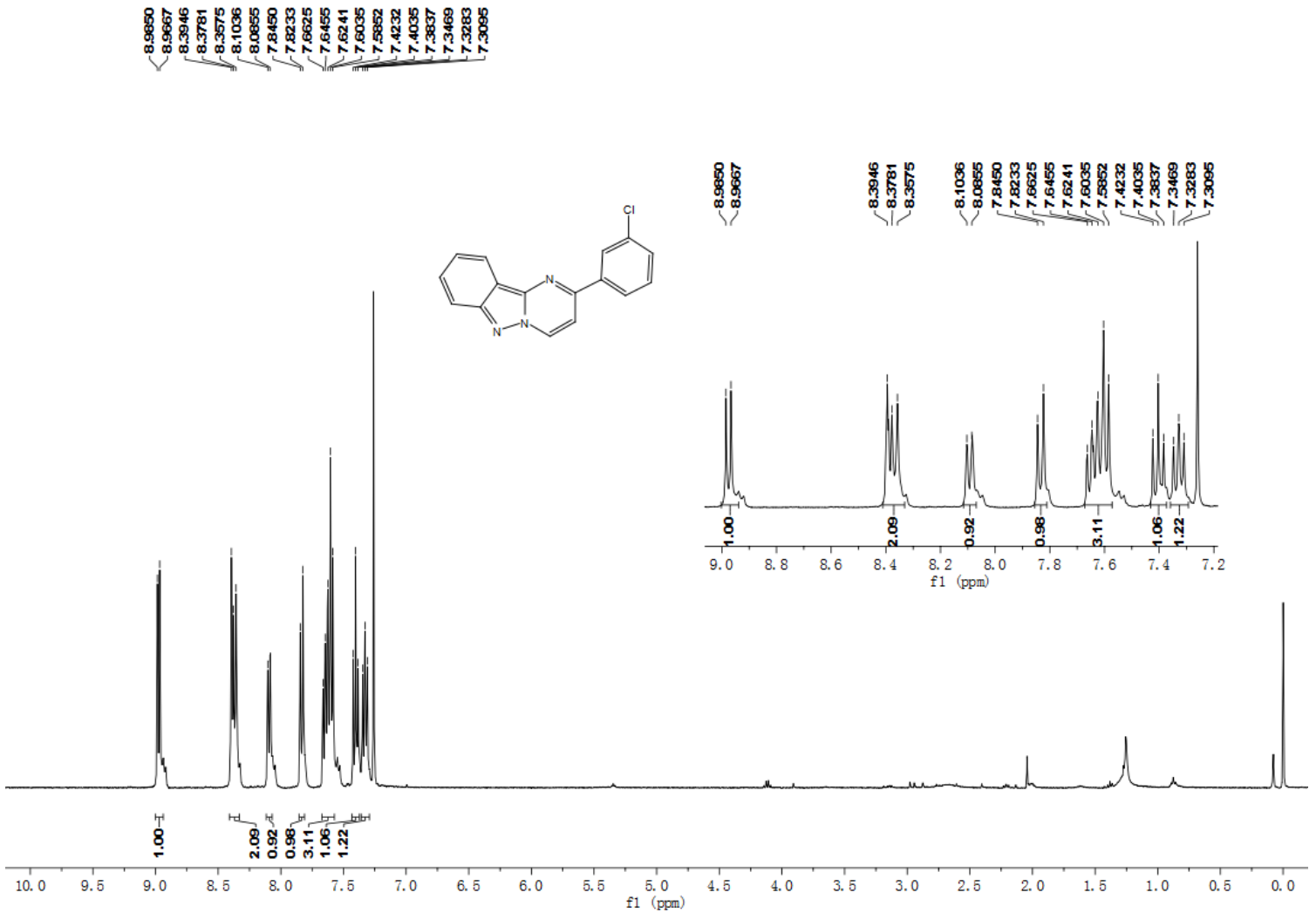

Fig S44. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-(3-chlorophenyl)pyrimido[1,2-*b*]indazole **(4f)**

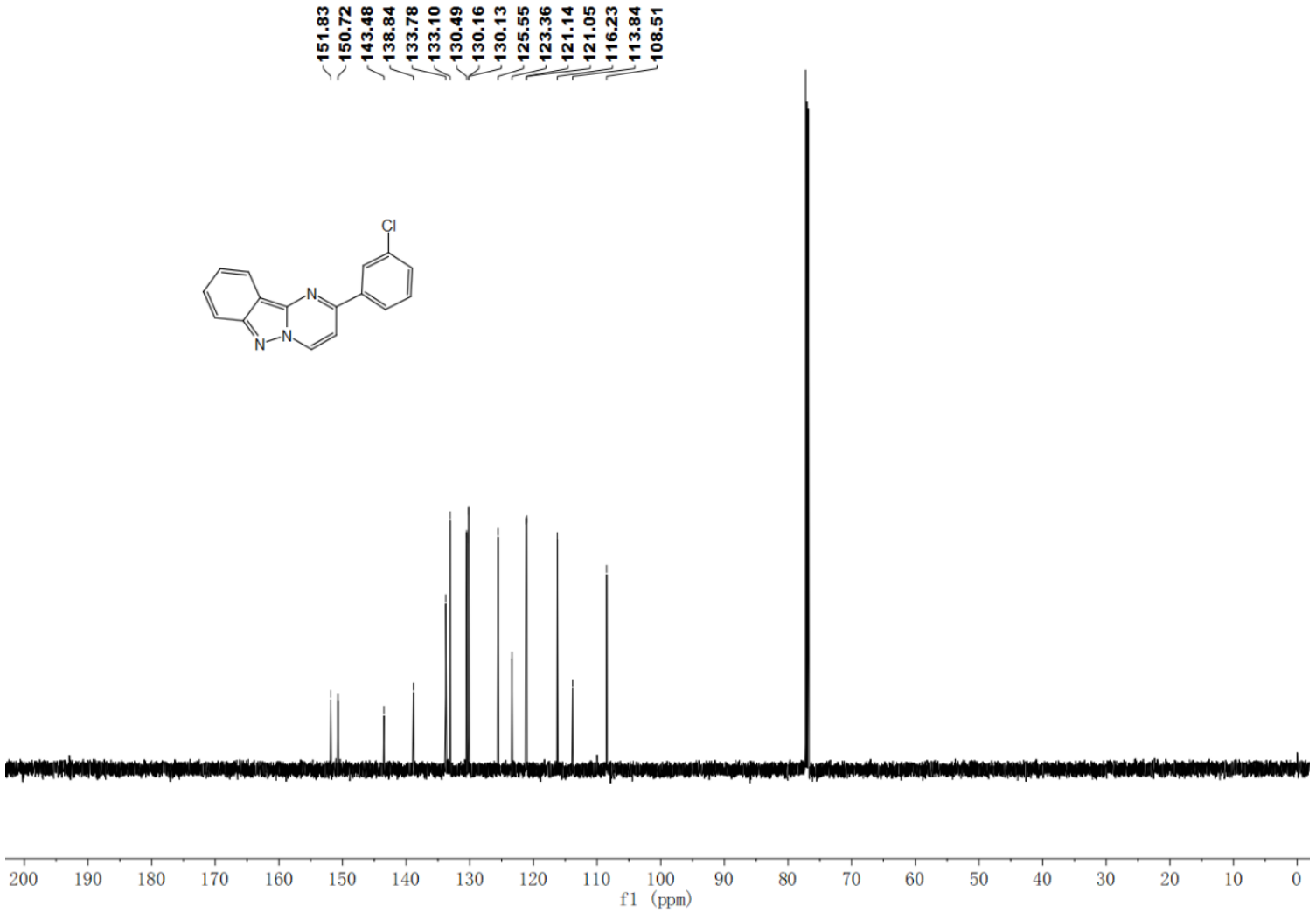

Fig S45. ^{13}C NMR (151 MHz, $CDCl_3$) of 2-(3-chlorophenyl)pyrimido[1,2-*b*]indazole **(4f)**

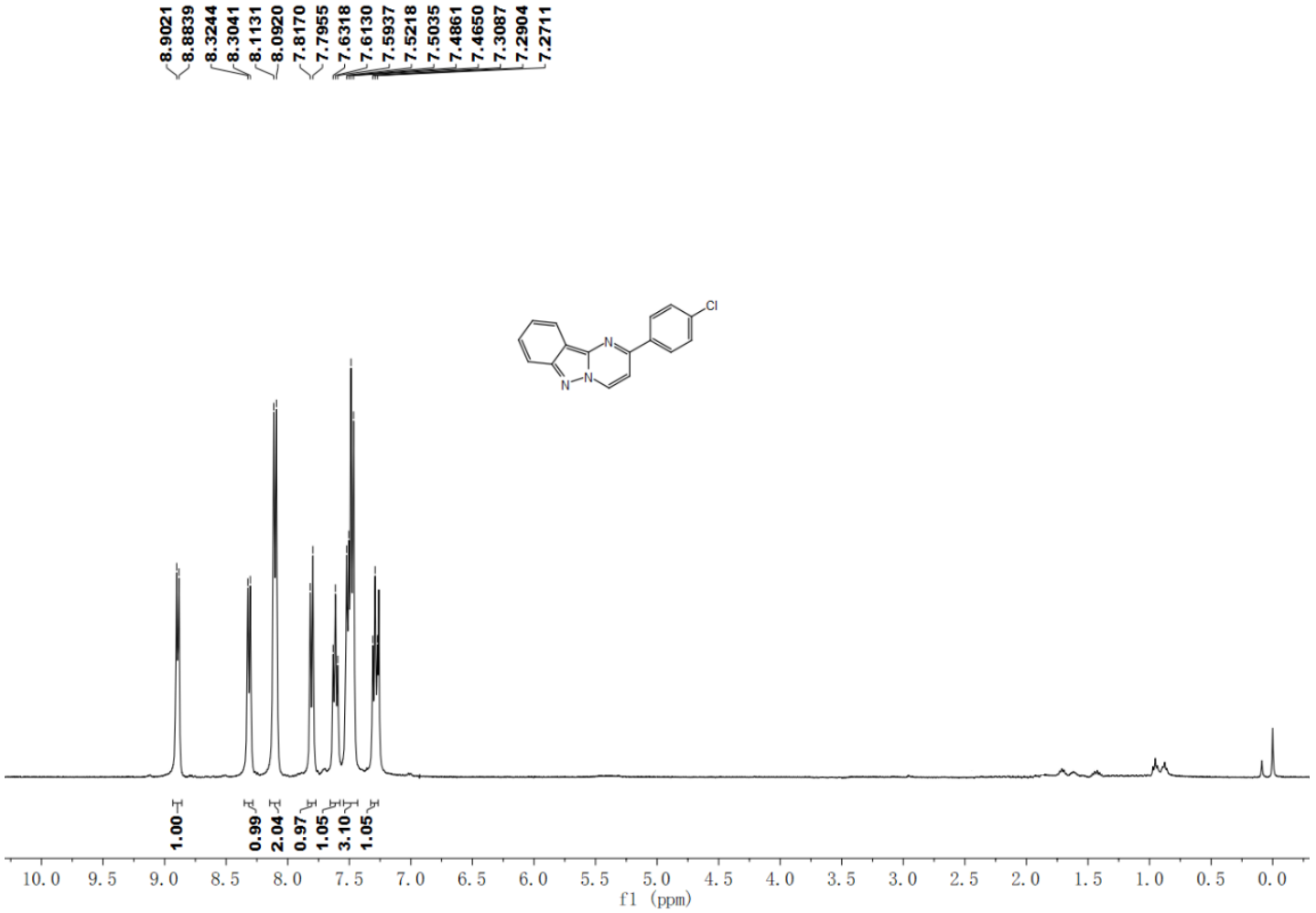

Fig S46. ^{1}H NMR ($CDCl_3$, 400 MHz) of 2-(4-chlorophenyl)pyrimido[1,2-*b*]indazole (**4g**)

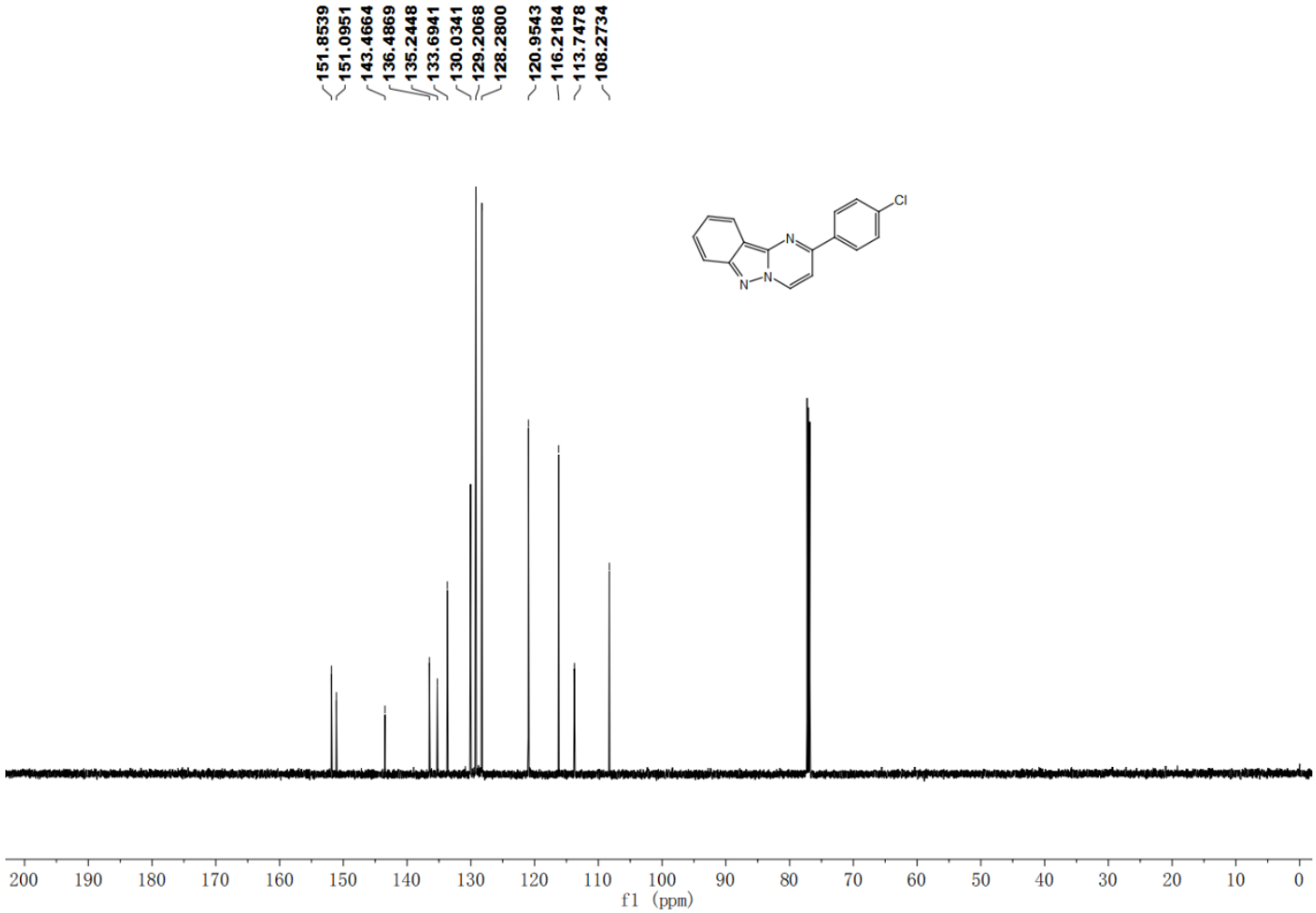

Fig S47. ^{13}C NMR ($CDCl_3$, 151 MHz) of 2-(4-chlorophenyl)pyrimido[1,2-*b*]indazole (**4g**)

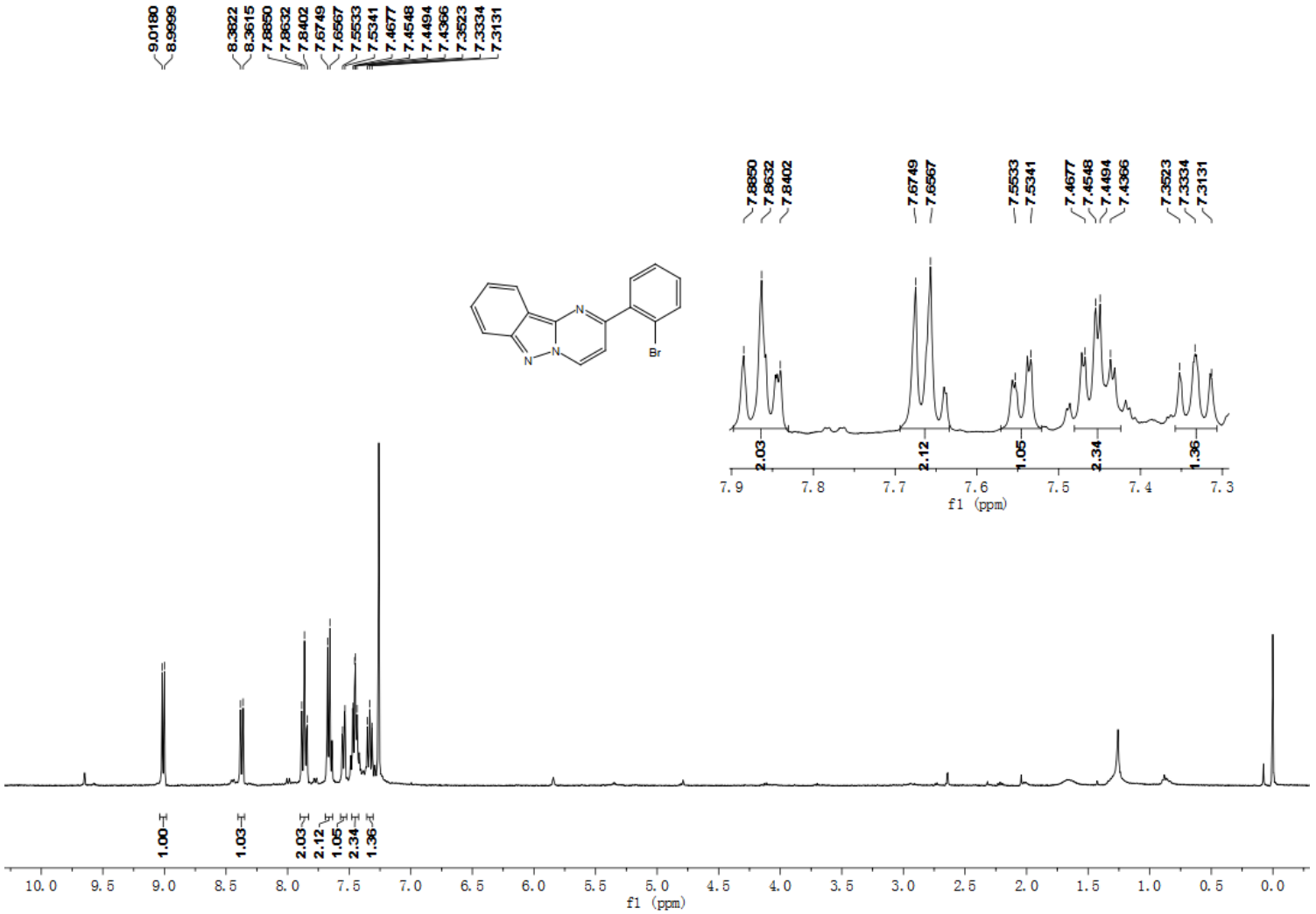

Fig S48. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-bromophenyl)pyrimido[1,2-*b*]indazole **(4h)**

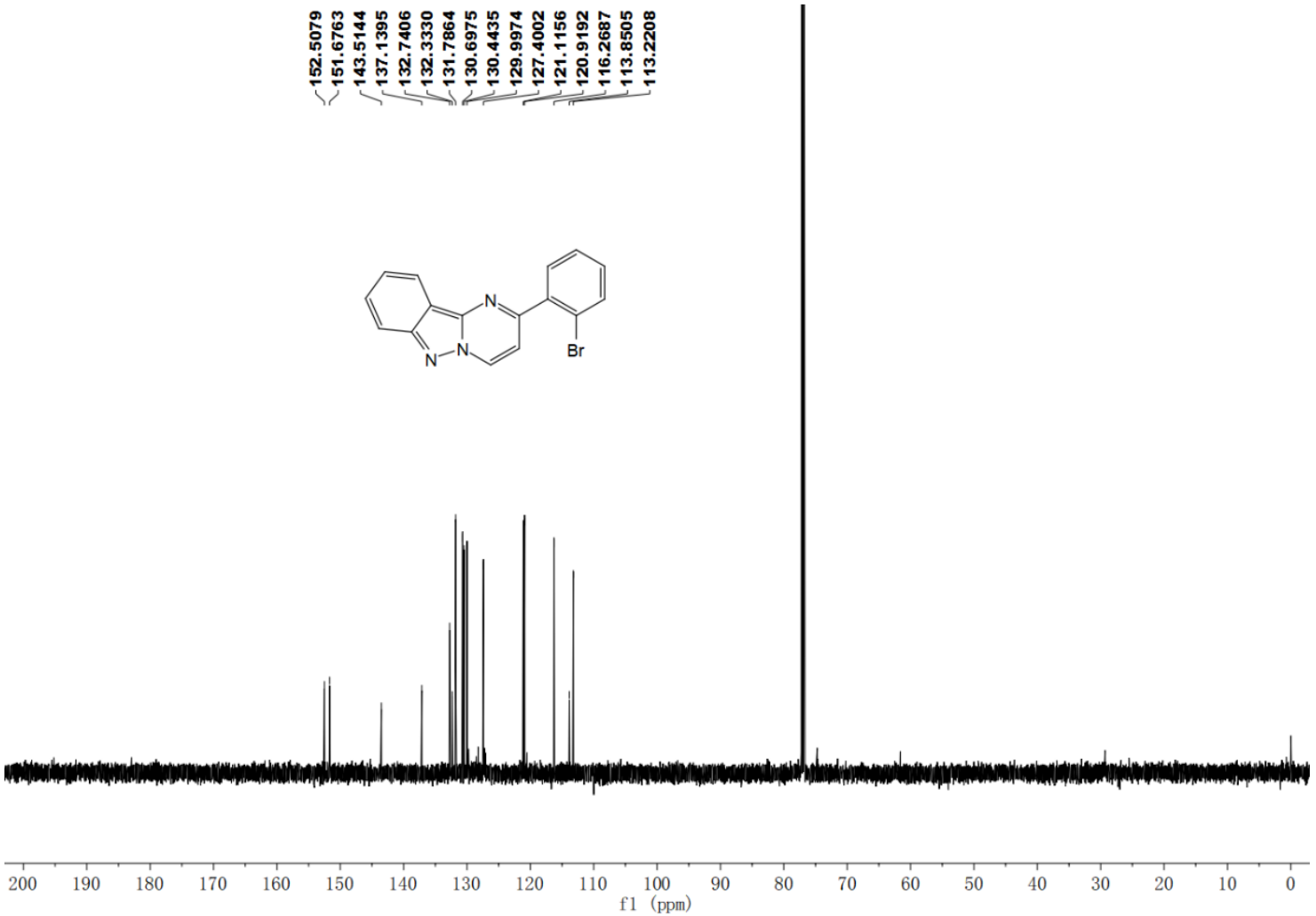

Fig S49. ^{13}C NMR (151 MHz, $CDCl_3$) of 2-(2-bromophenyl)pyrimido[1,2-*b*]indazole (**4h**)

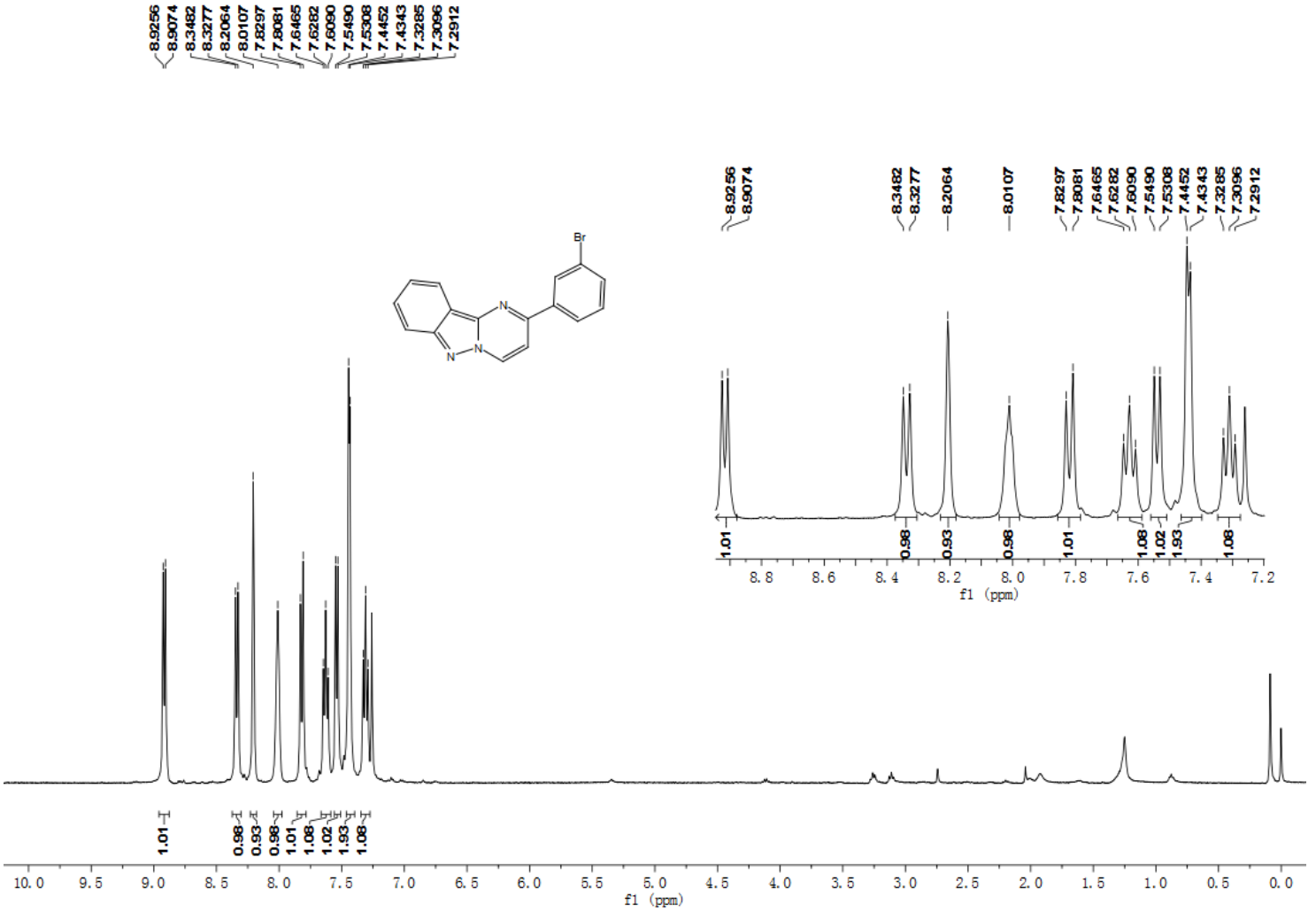

Fig S50. ^{1}H NMR ($CDCl_3$, 400 MHz) of 2-(3-bromophenyl)pyrimido[1,2-*b*]indazole (**4i**)

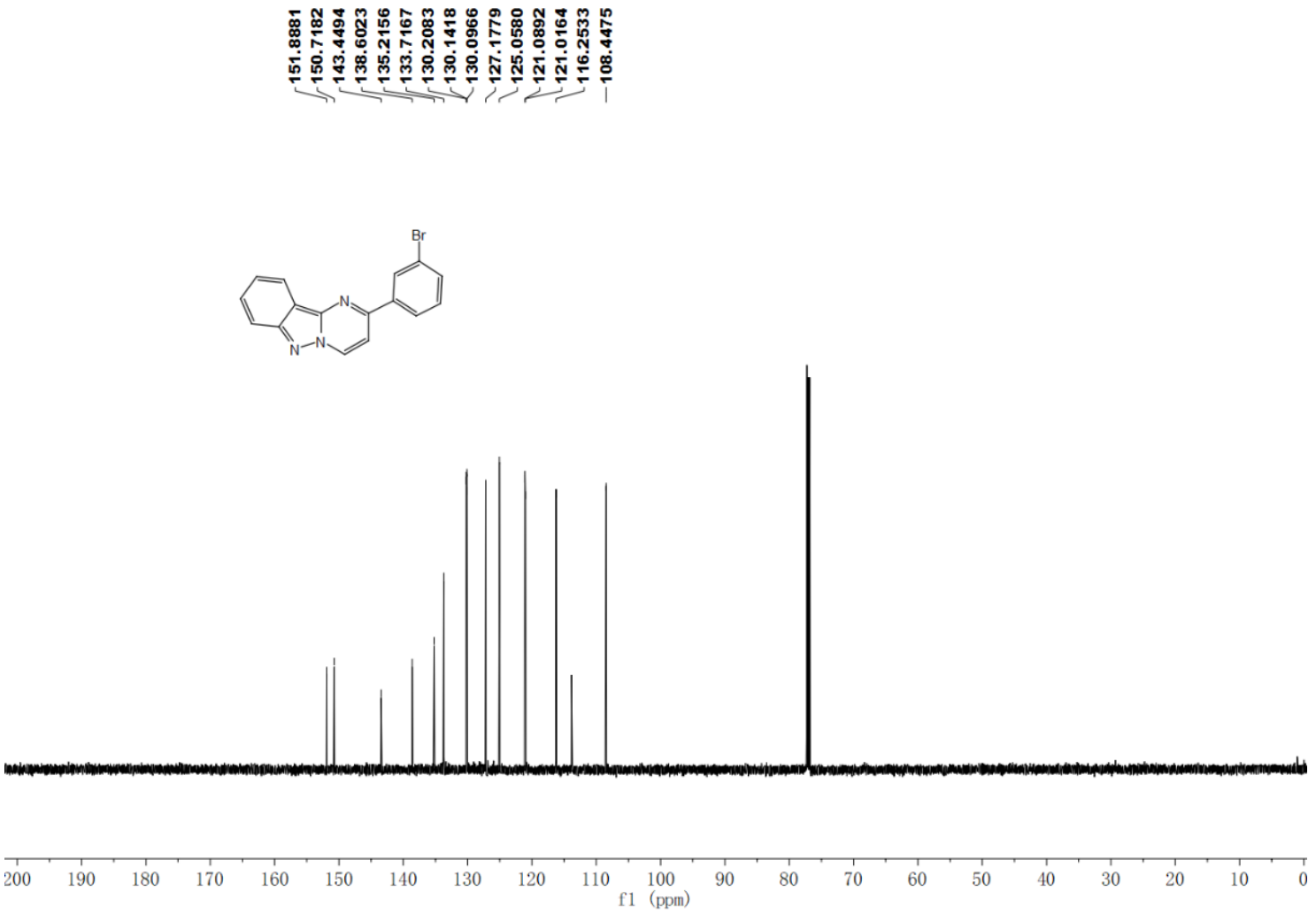

Fig S51. ^{13}C NMR ($CDCl_3$, 151 MHz) of 2-(3-bromophenyl)pyrimido[1,2-*b*]indazole (**4i**)

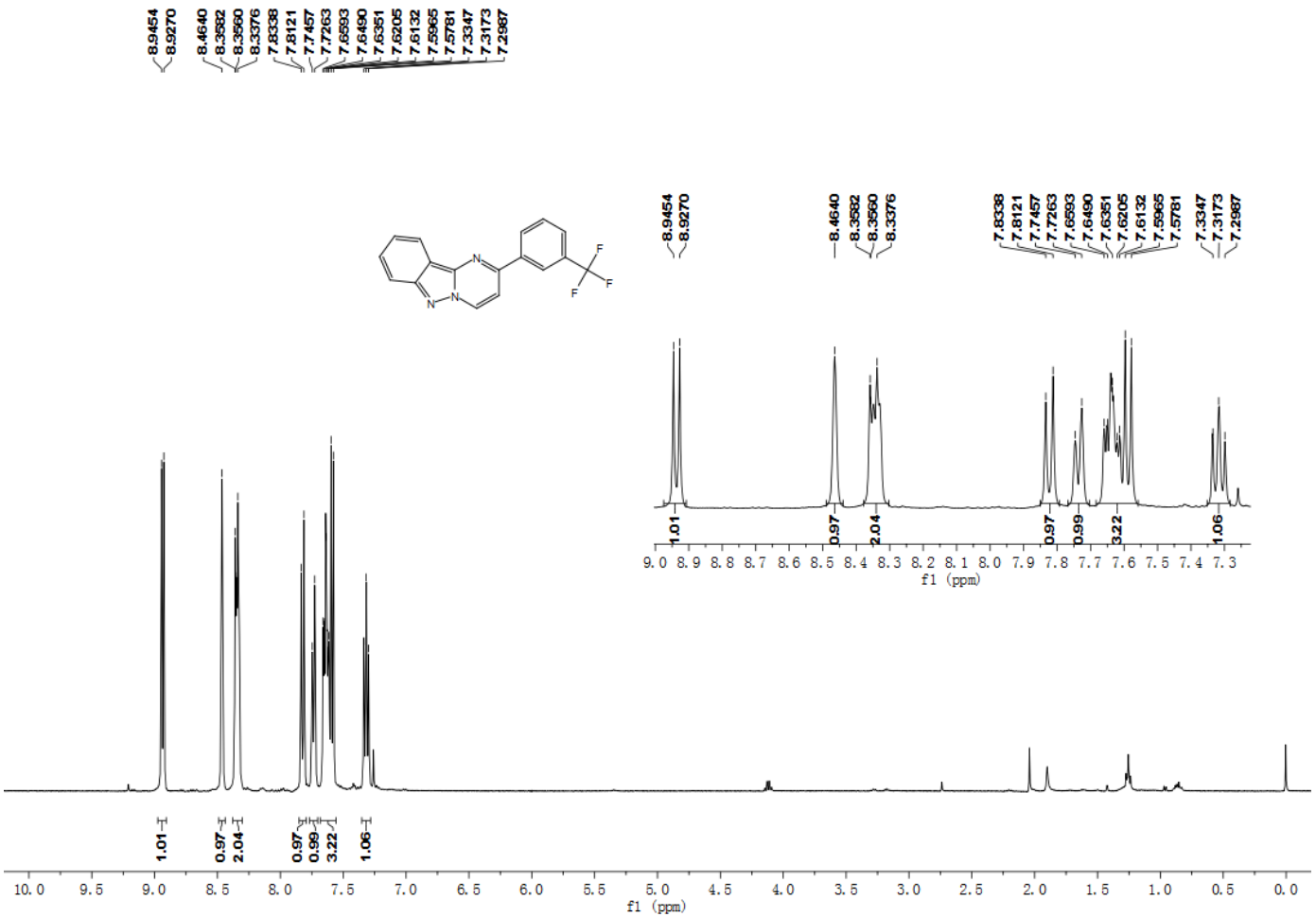

Fig S52. ^{1}H NMR (400 MHz, $CDCl_3$) of 2-(3-trifluoromethyl)pyrimido[1,2-*b*]indazole (**4j**)

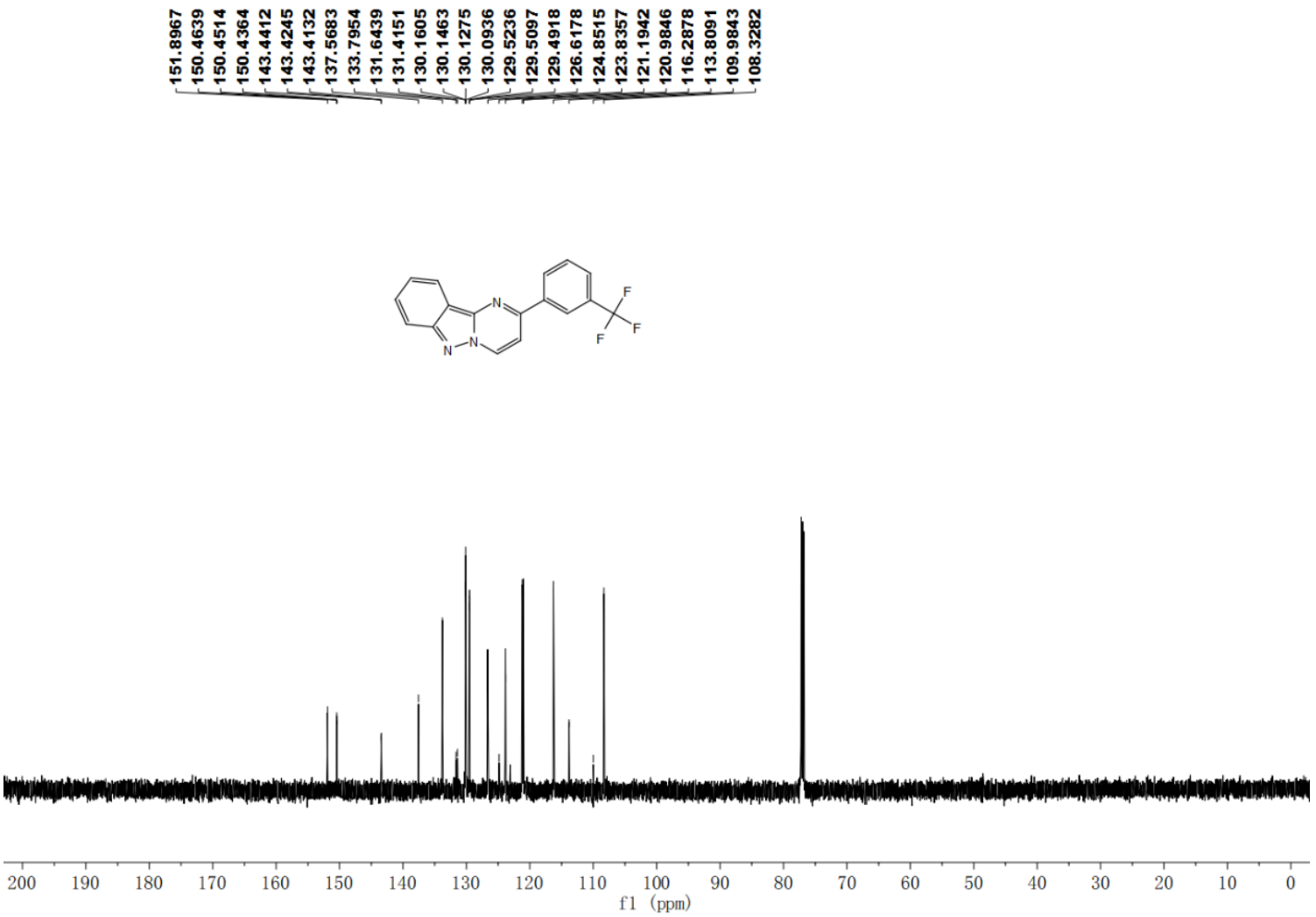

Fig S53. ^{13}C NMR (151 MHz, $CDCl_3$) of 2-(3-trifluoromethyl)pyrimido[1,2-*b*]indazole (**4j**)

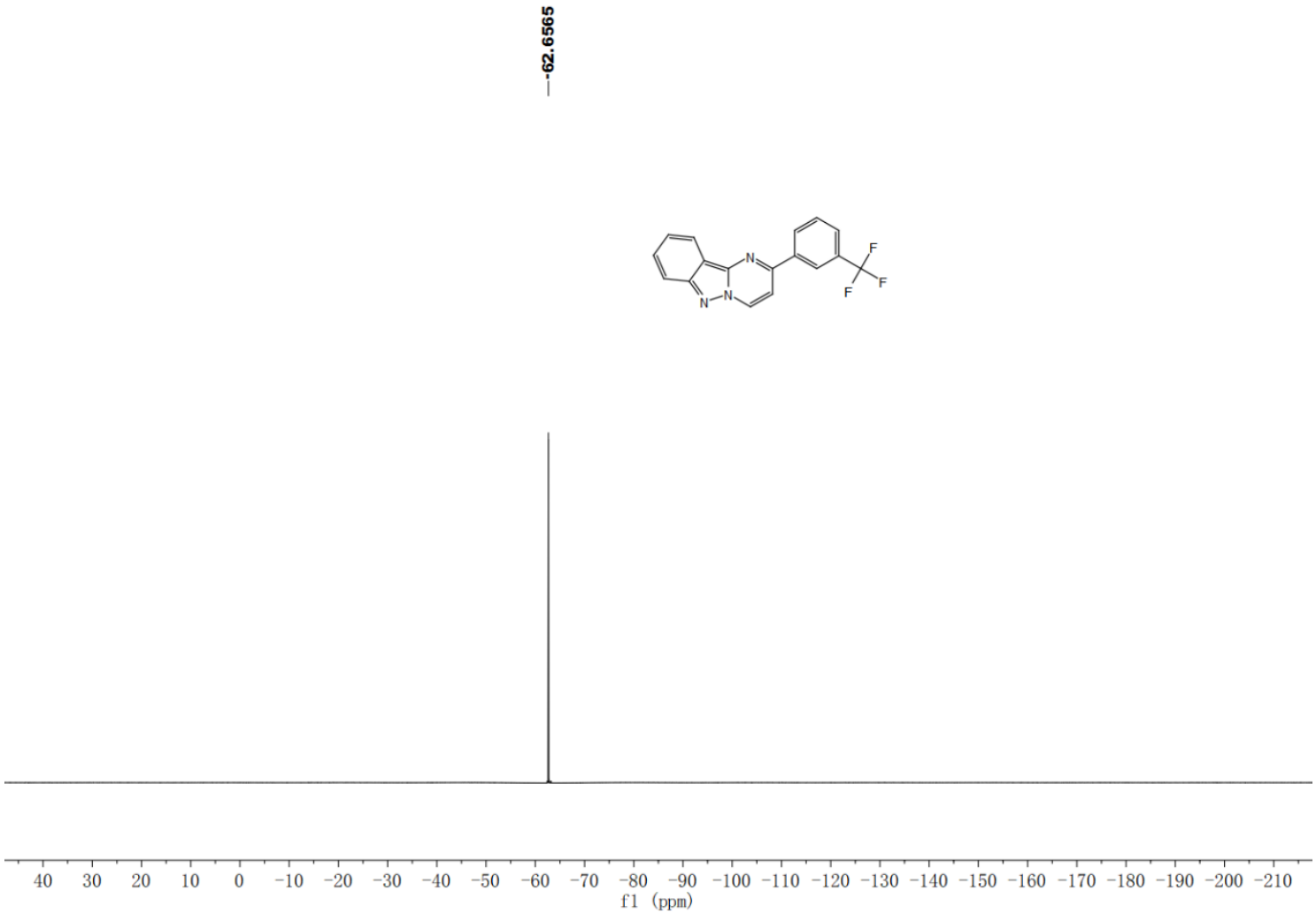

Fig S54. ^{19}F NMR (376 MHz, $CDCl_3$) of 2-(3-trifluoromethyl)pyrimido[1,2-*b*]indazole (**4j**)

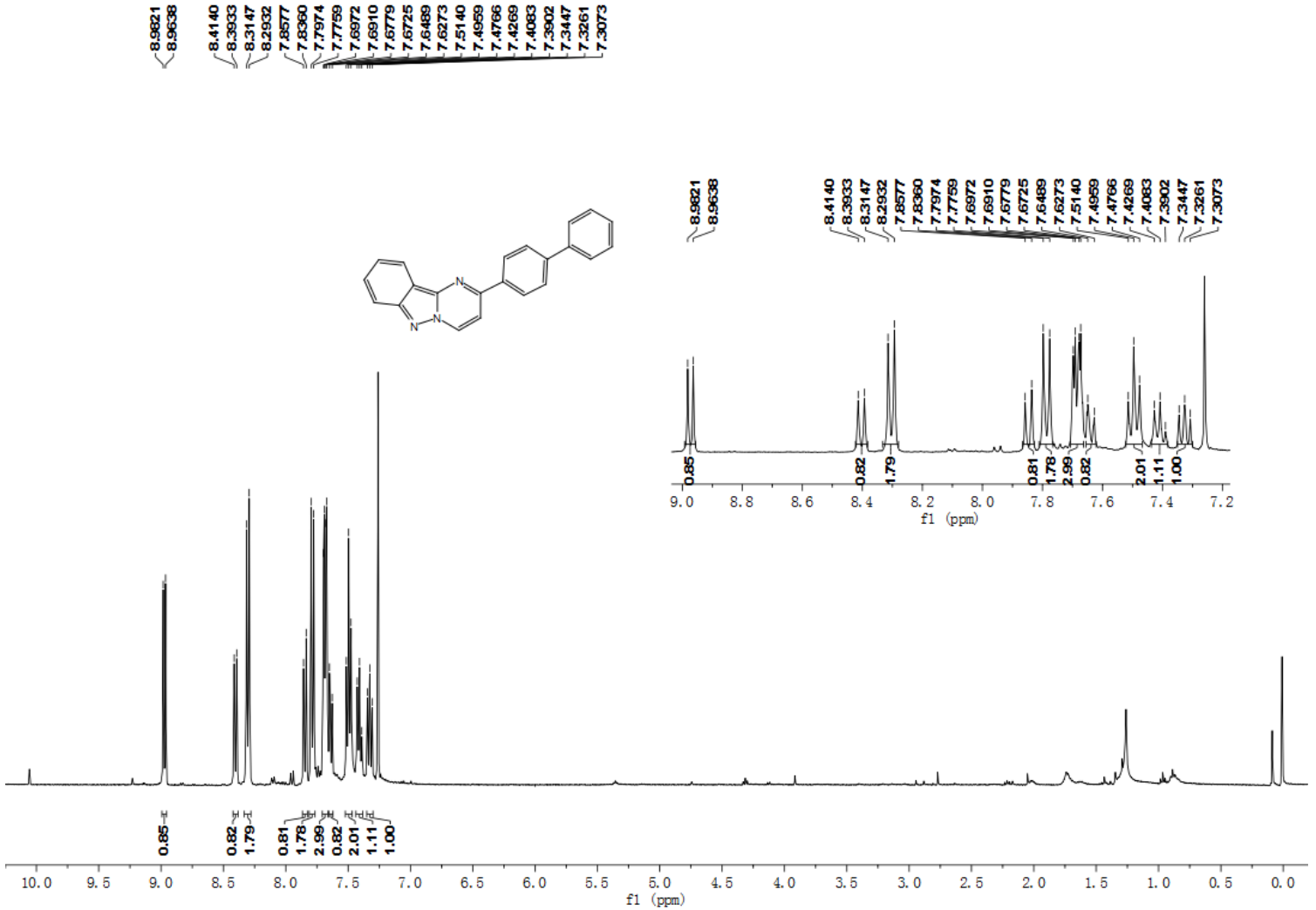

Fig S55. ^{1}H NMR ($CDCl_3$, 400 MHz) of 2-([1,1'-biphenyl]-4-yl)pyrimido[1,2-*b*]indazole (**4k**)

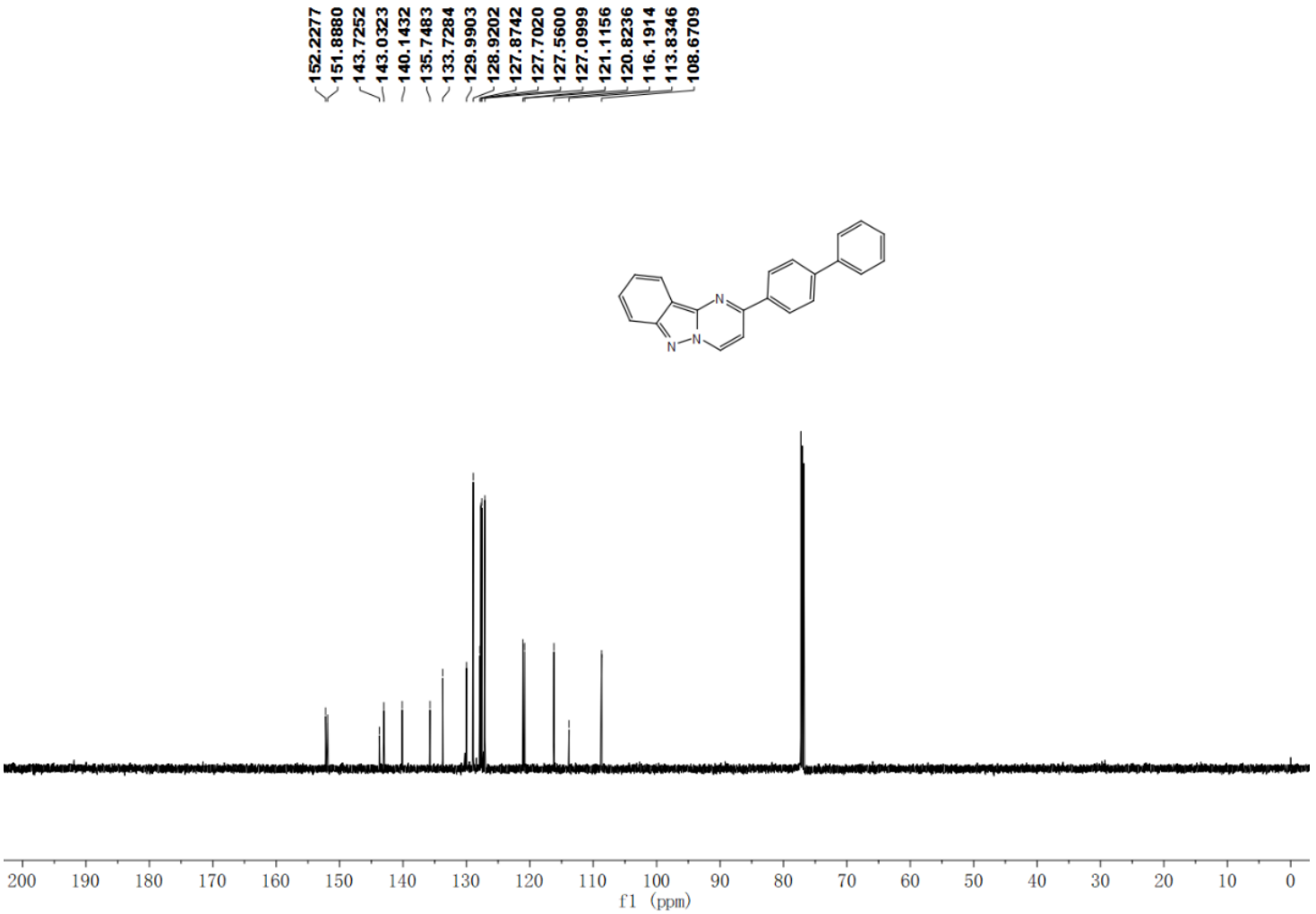

Fig S56. ^{13}C NMR ($CDCl_3$, 151 MHz) of 2-([1,1'-biphenyl]-4-yl)pyrimido[1,2-*b*]indazole (**4k**)

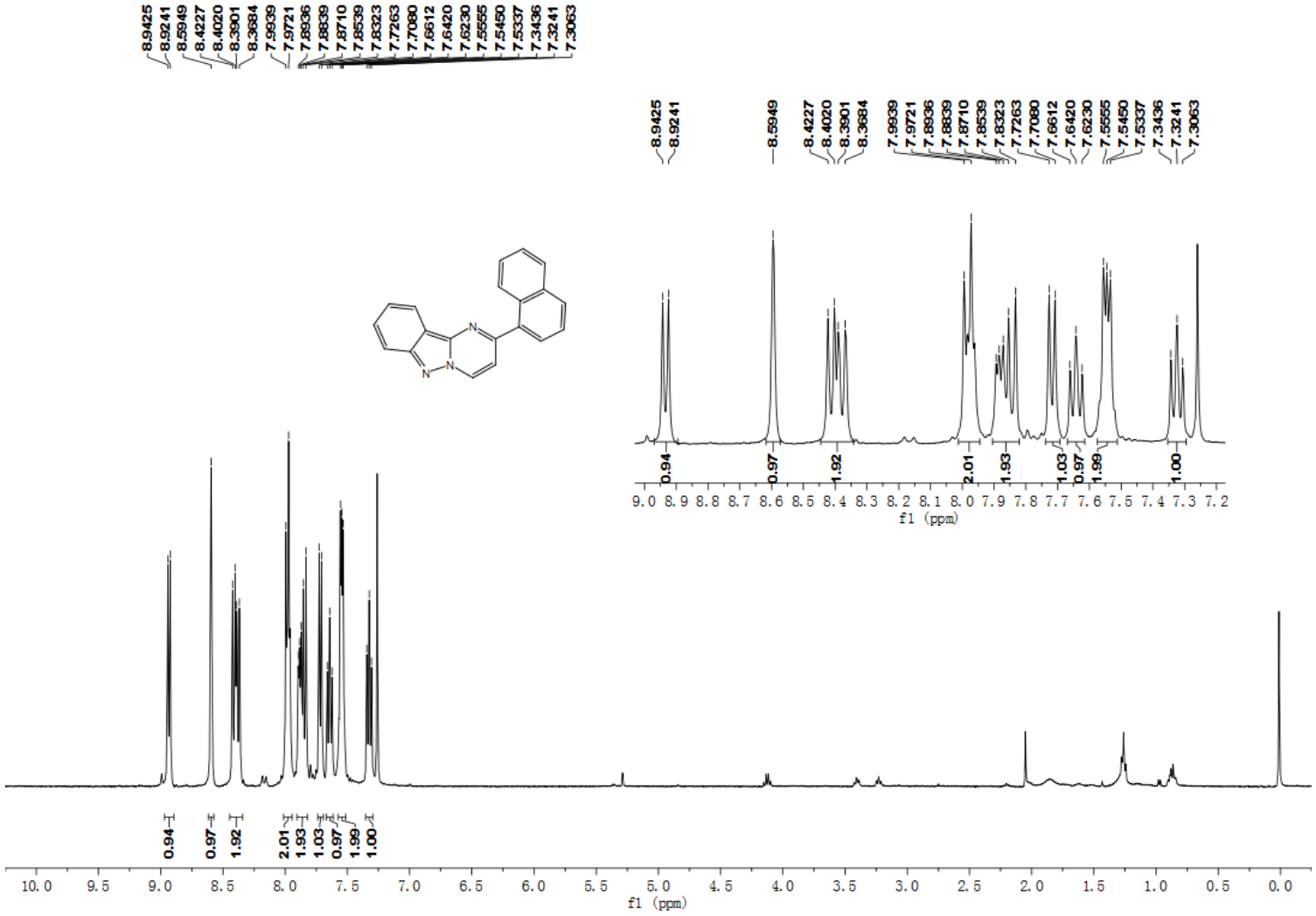

Fig S57. ^{1}H NMR ($CDCl_3$, 400 MHz) of 2-(naphthalen-2-yl)pyrimido[1,2-*b*]indazole (**4l**)

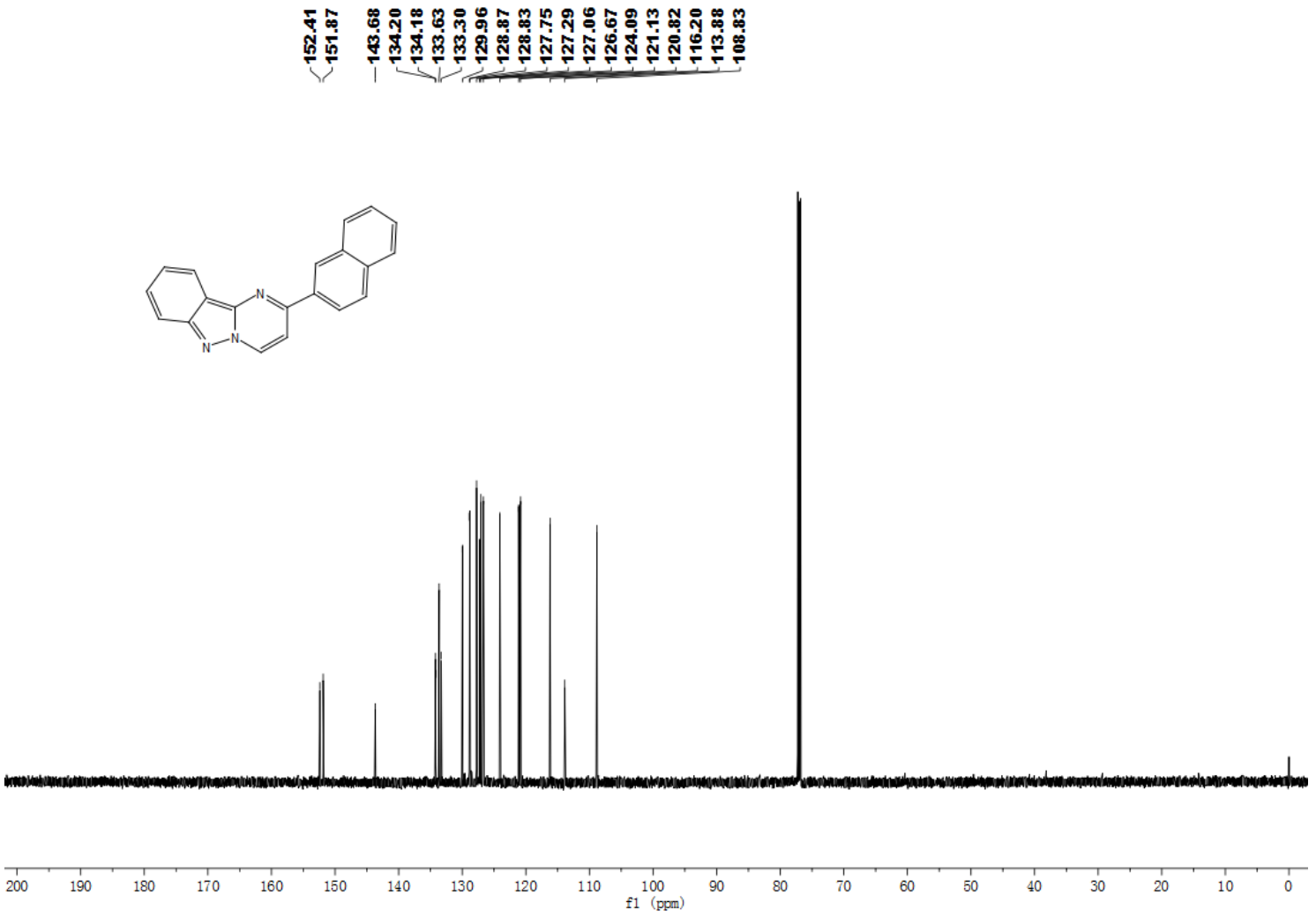

Fig S58. ^{13}C NMR ($CDCl_3$, 151 MHz) of 2-(naphthalen-2-yl)pyrimido[1,2-*b*]indazole (**4l**)

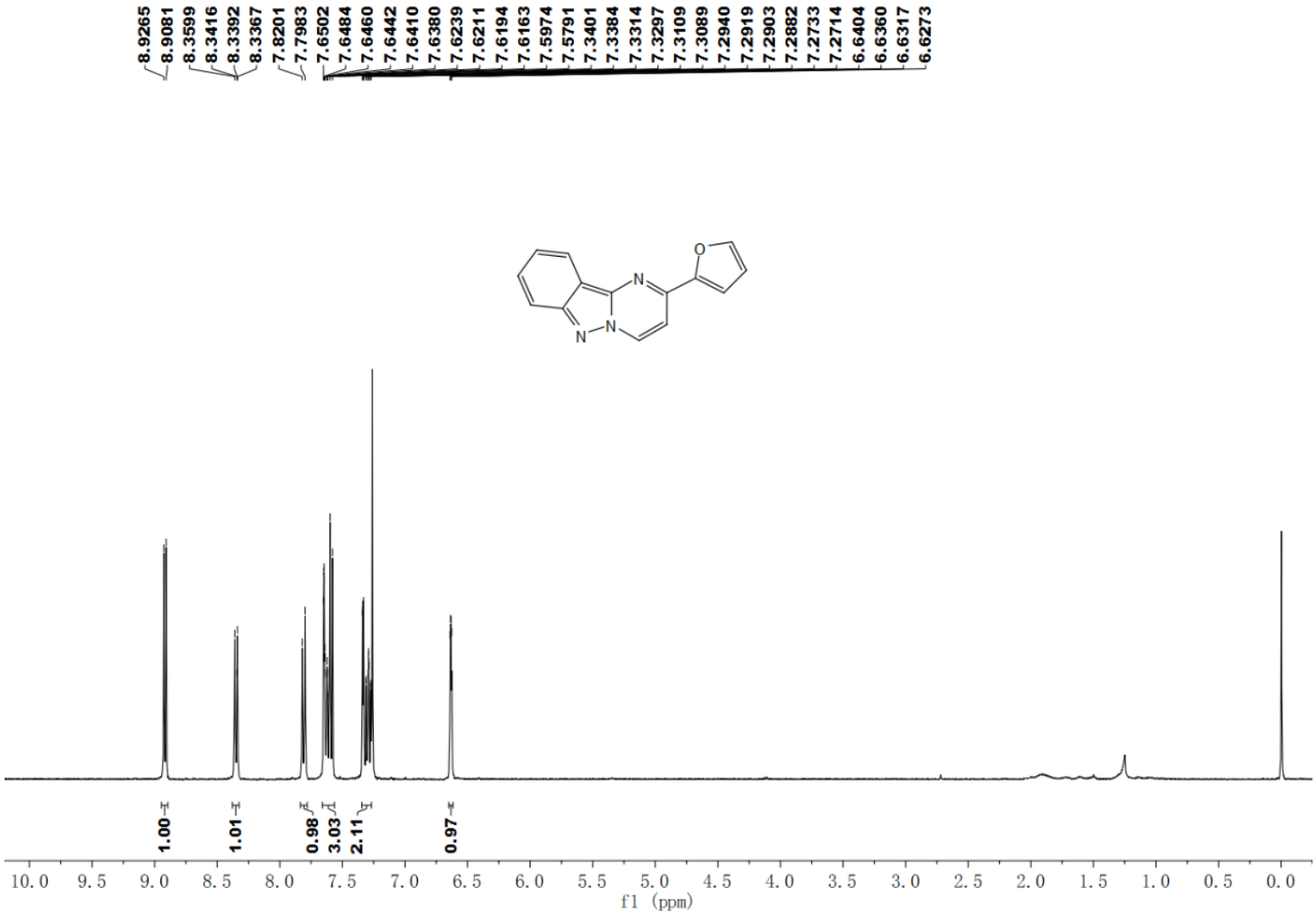

Fig S59. ^{1}H NMR ($CDCl_3$, 400 MHz) of 2-(furan-2-yl)pyrimido[1,2-*b*]indazole (**4m**)

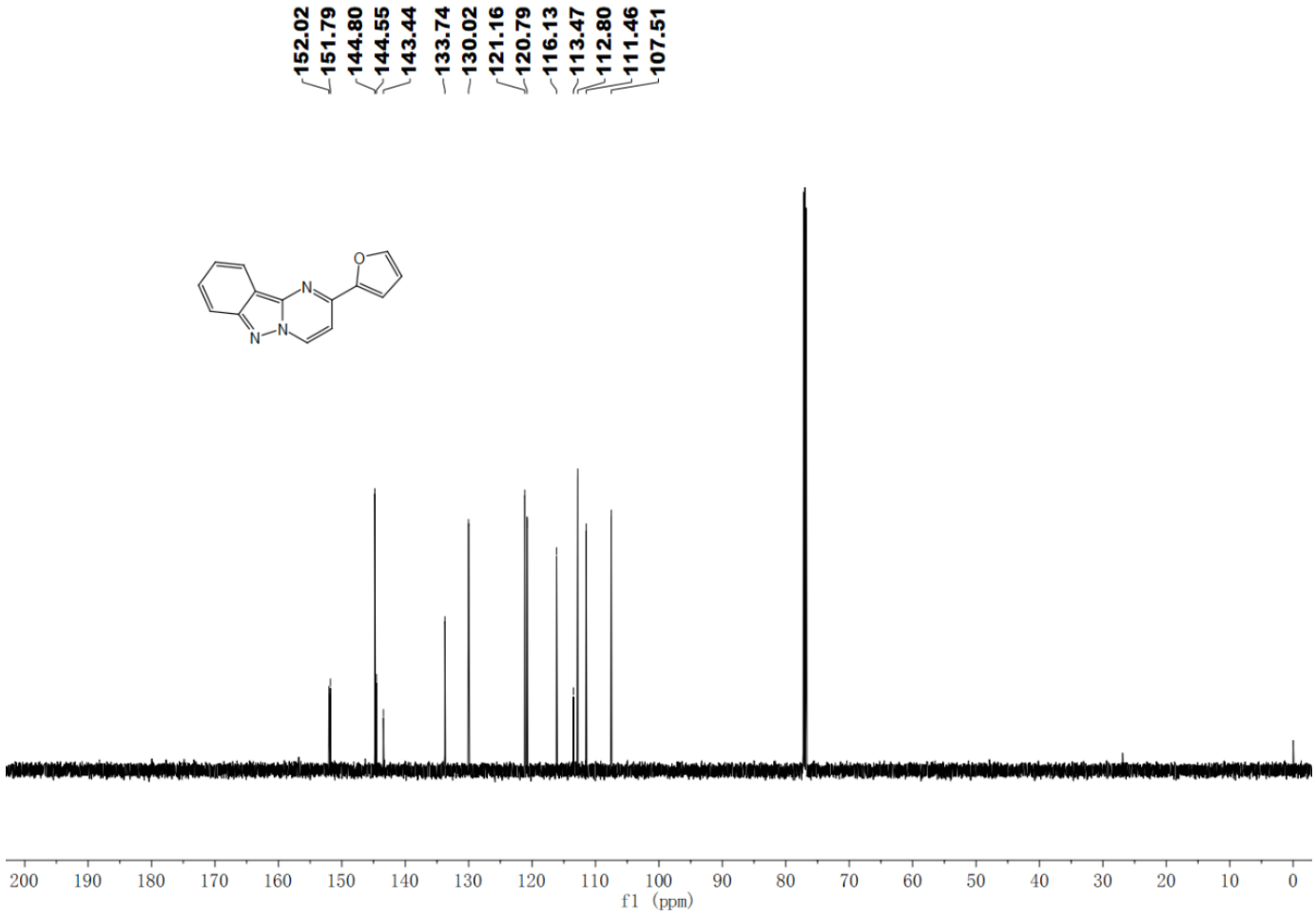

Fig S60. ^{13}C NMR ($CDCl_3$, 151 MHz) of 2-(furan-2-yl)pyrimido[1,2-*b*]indazole (**4m**)

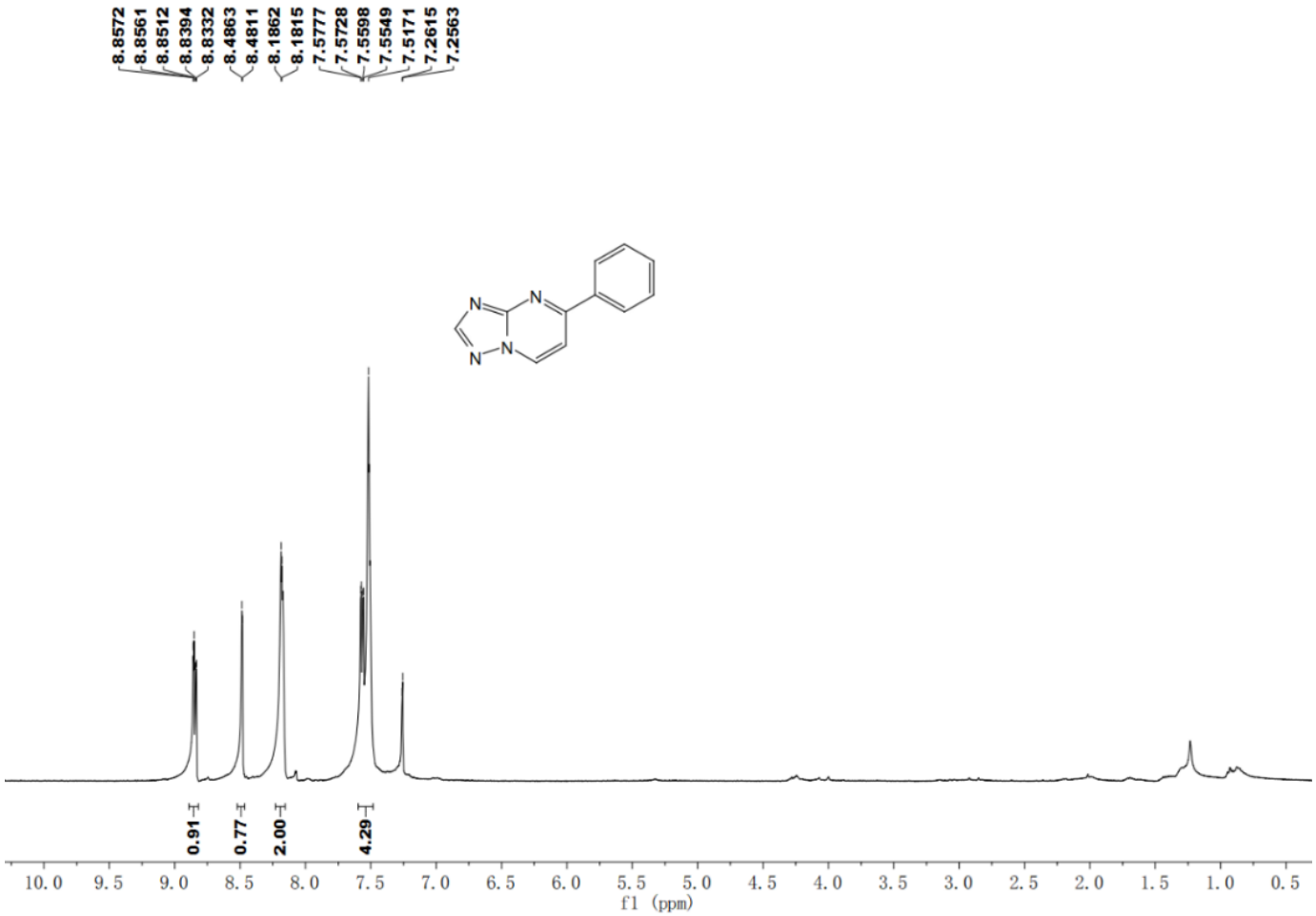

Fig 61. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-phenyl-[1,2,4]triazolo[1,5-*a*]pyrimidine (**5a**)

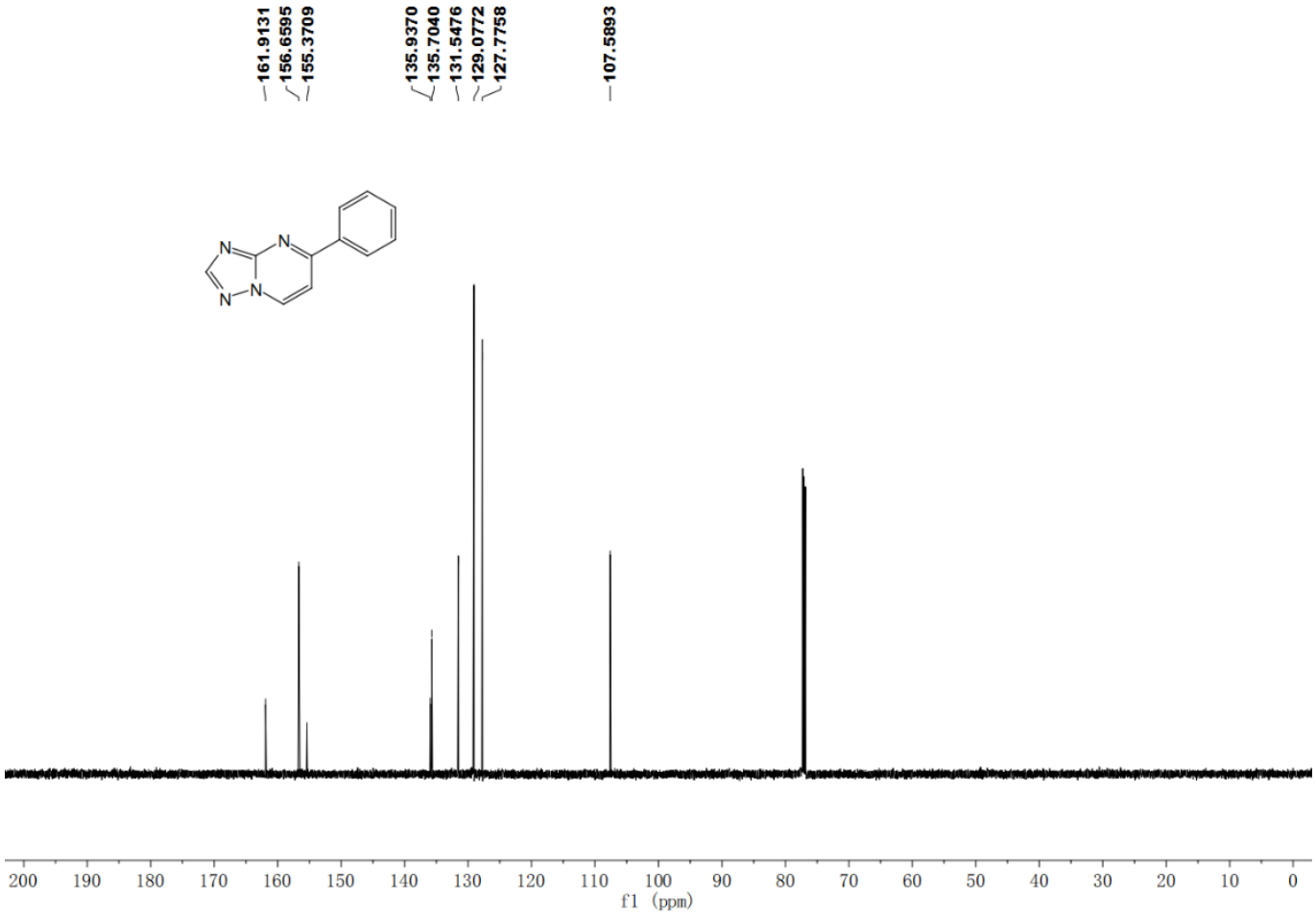

Fig 62. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-phenyl-[1,2,4]triazolo[1,5-*a*]pyrimidine (**5a**)

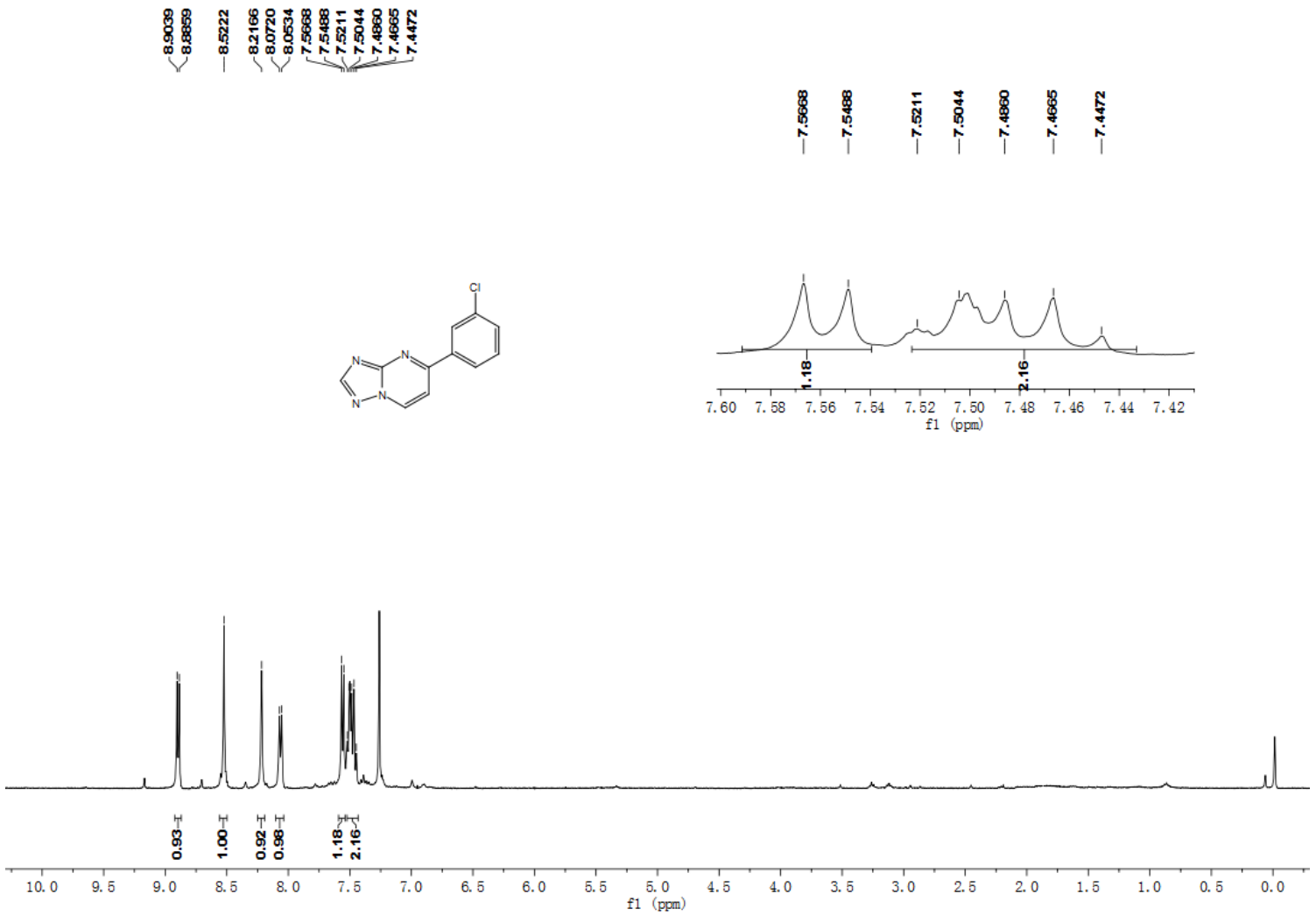

Fig 63. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(3-chlorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (**5b**)

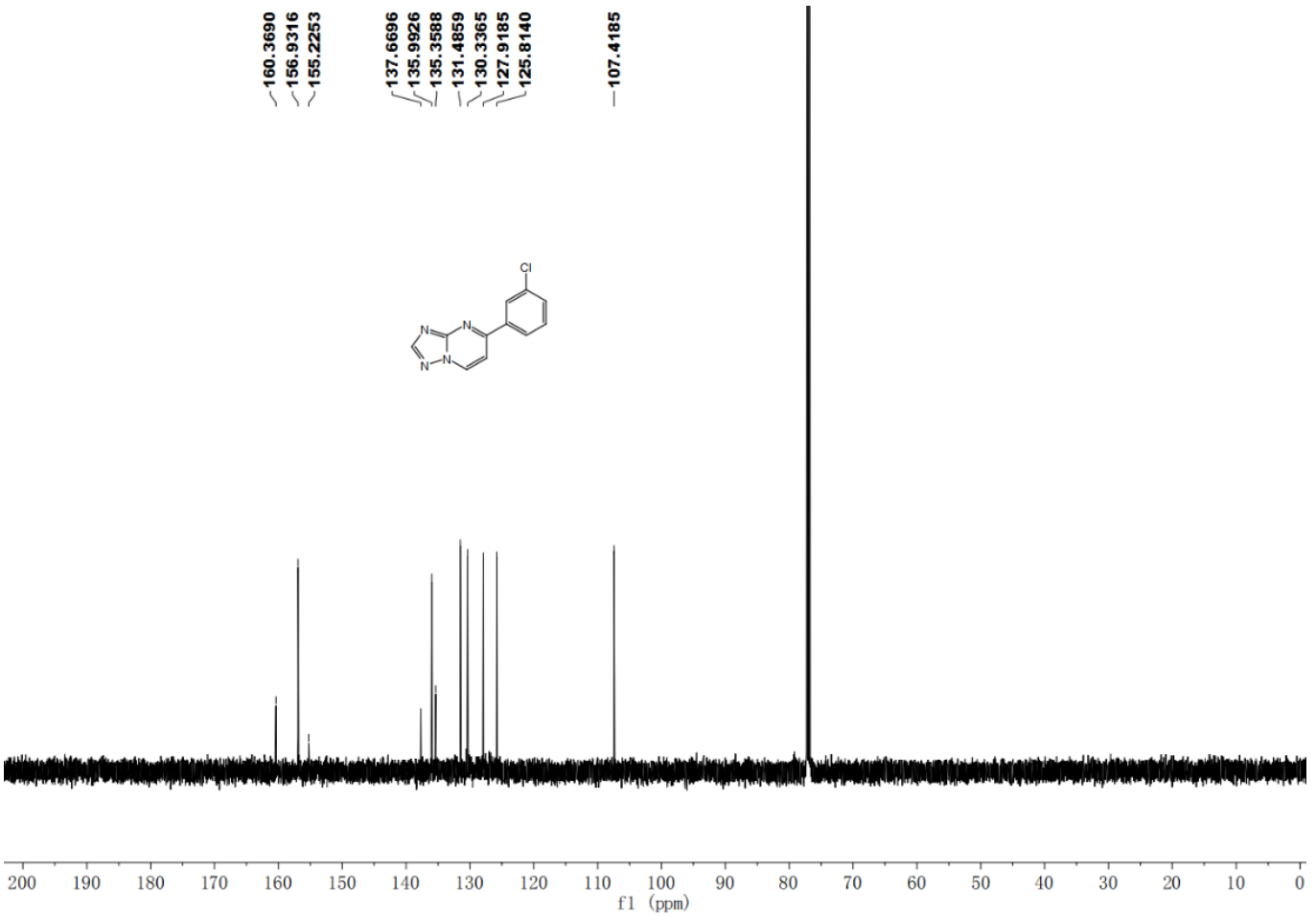

Fig 64. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(3-chlorophenyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (**5b**)

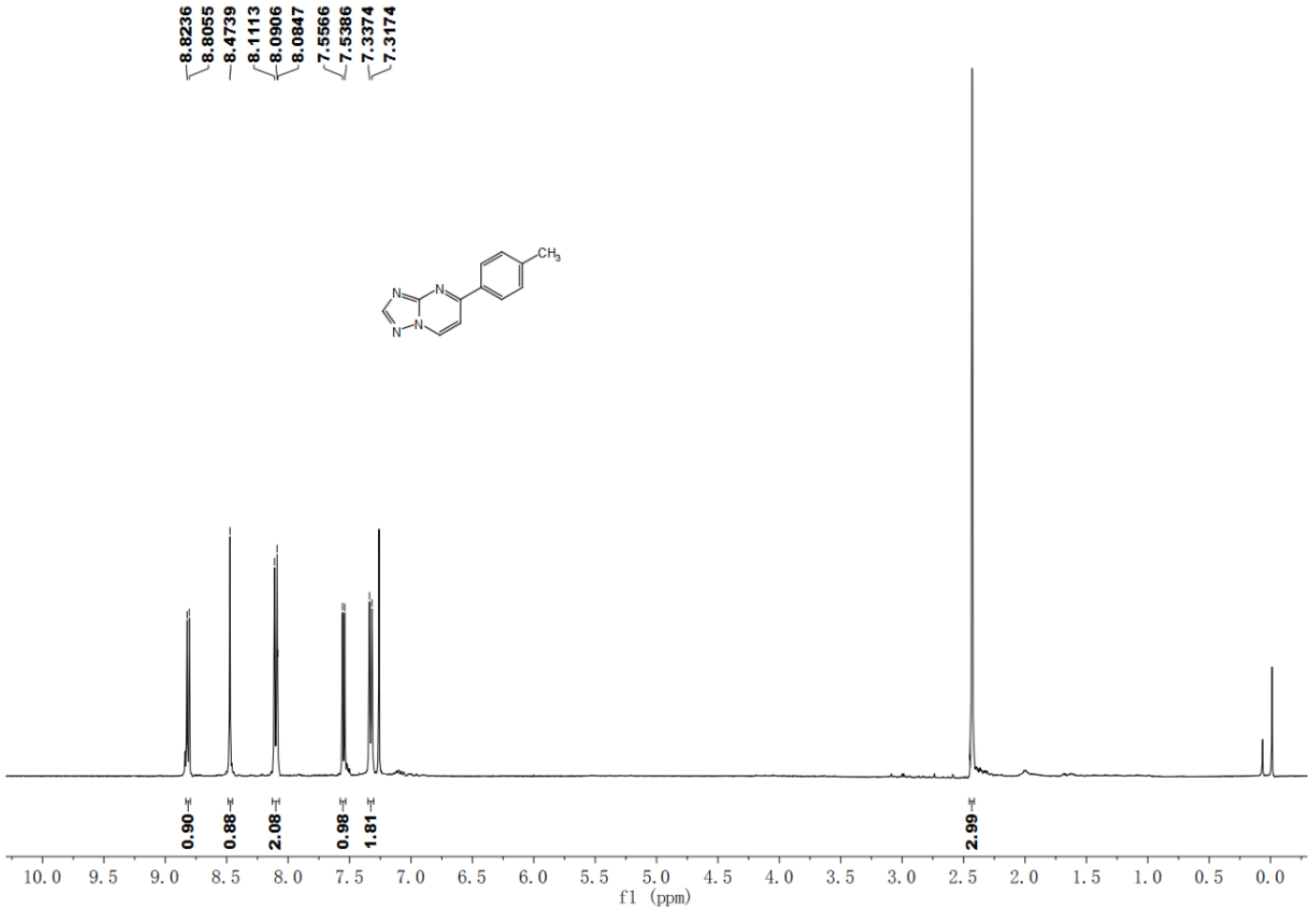

Fig 65. ^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(*p*-tolyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (**5c**)

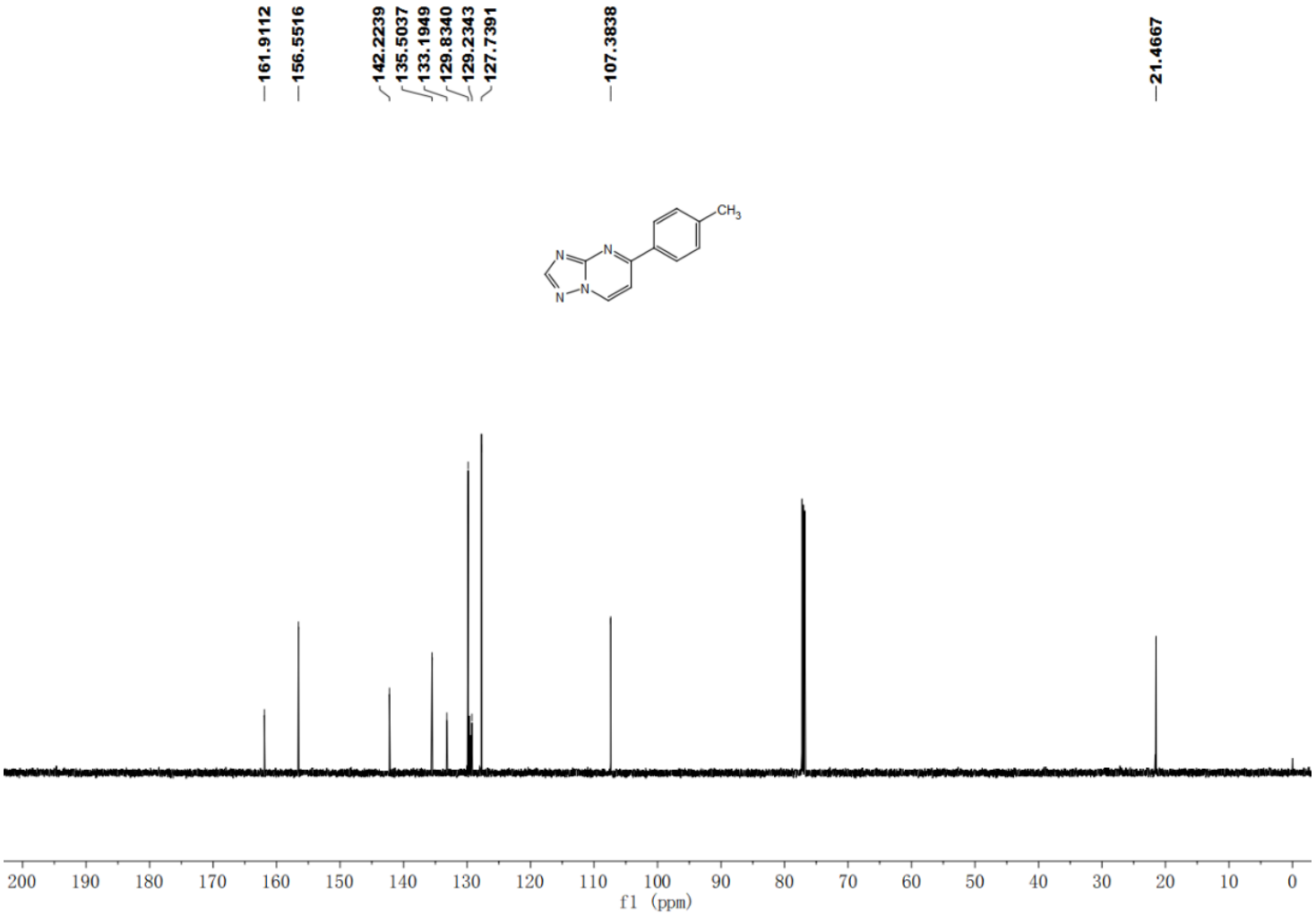

Fig 66. ^{13}C NMR ($CDCl_3$, 151 MHz) of 5-(*p*-tolyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine (**5c**)

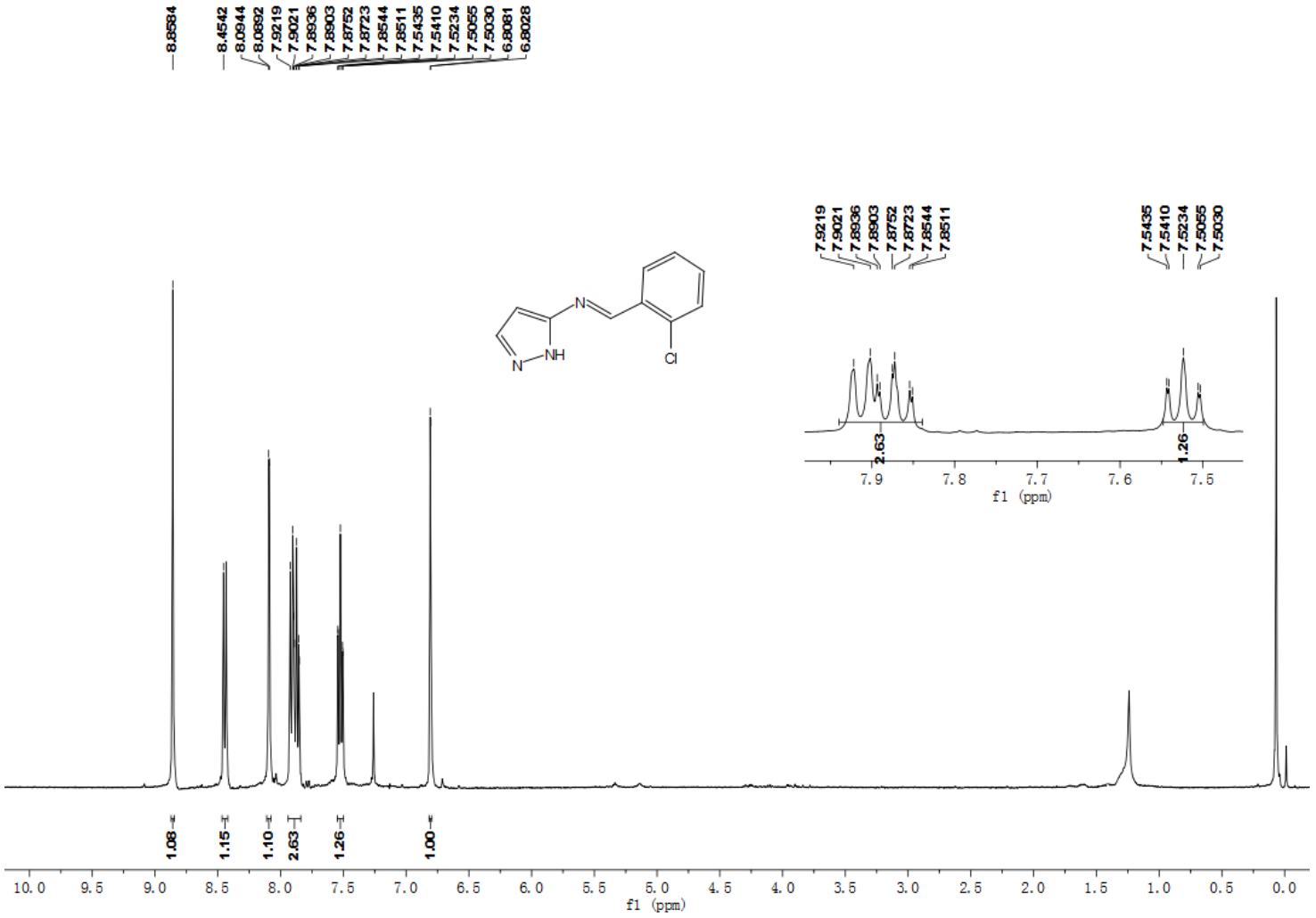

Fig S67. ^{1}H NMR ($CDCl_3$, 400 MHz) of (*E*)-1-(2-chlorophenyl)-*N*-(1*H*-pyrazol-3-yl)methanimine (**6**)

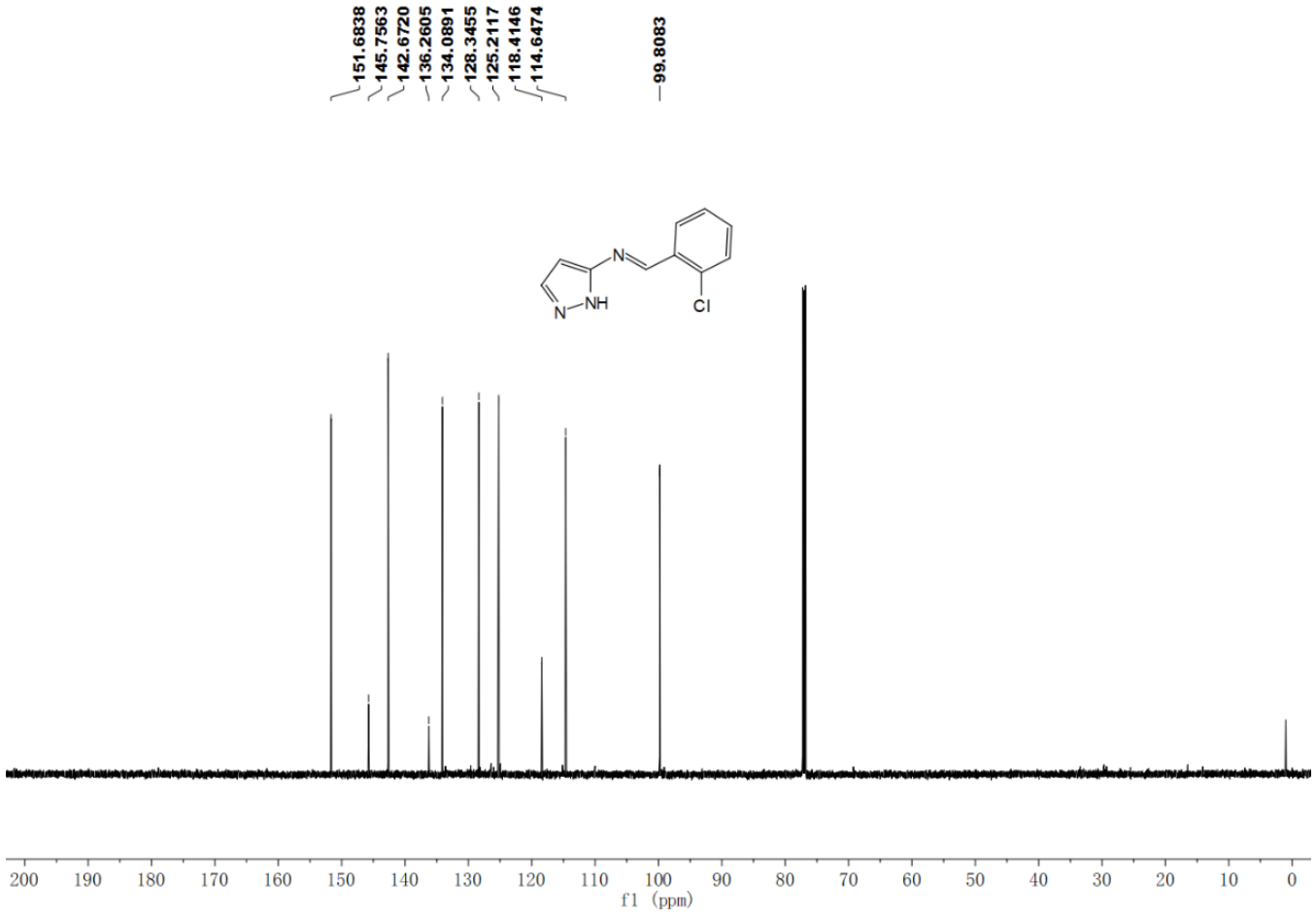

Fig S68. ^{13}C NMR ($CDCl_3$, 151 MHz) of (*E*)-1-(2-chlorophenyl)-*N*-(1*H*-pyrazol-3-yl)methanimine (**6**)