A Facile Tandem Decyanation/Cyanation Reaction of α-Iminonitriles toward Cyano-Substituted Amides

Zhengwang Chen,*[,†,‡] Pei Liang,[†] Botao Liu,[†] Haiqing Luo,[†] Jing Zheng,[†] Xiaowei Wen,[†] Tanggao Liu,[†] Min Ye*[,†]

[†] Key Laboratory of Organo-pharmaceutical Chemistry of Jiangxi province, Gannan Normal University, Ganzhou, 341000, China. Fax: +86 797-8793670; Tel: +86 797-8793670; E-mail: chenzwang@126.com; yemin811@gnnu.cn
[‡] Key Laboratory of Functional Molecular Engineering of Guangdong Province, South China University of Technology, Guangzhou, 510640, China.

Supporting Information

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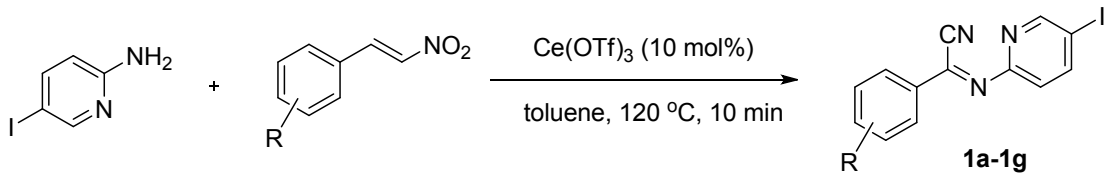
A. General method

^{1}H and ^{13}C NMR spectra were obtained on a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, chloroform is solvent with TMS as the internal standard unless otherwise noted. Mass spectra were recorded on a GC-MS spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Elemental analyses were performed with a Vario EL elemental analyzer. Silica gel (300-400 mesh) was used for flash column chromatograph, eluting (unless otherwise stated) with ethyl acetate/petroleum ether (PE) (60-90 ^{o}C) mixture.

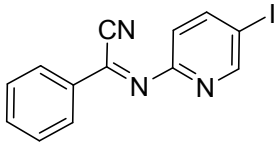
B. General procedure for iodo-substituted α-iminonitriles

Iodo-substituted α-iminonitriles 1 used were prepared by the following procedures A and B.

Procedure A (1a-1g):[1]

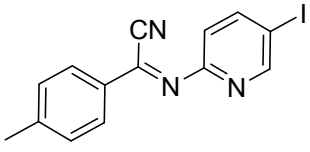


A mixture of 5-iodo-2-aminopyridine (0.3 mmol), nitroalkene (0.3 mmol) and $Ce(OTf)_3$ (10 mol%) in toluene (1.5 mL) was placed in a test tube (10 mL) equipped with a magnetic stirring bar. The mixture was stirred at 120 °C for 10 minutes. After the reaction was finished, water (5 mL) was added and the solution was extracted with ethyl acetate (3×5 mL), the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.



(Z)-*N*-(5-iodopyridin-2-yl)benzimidoyl cyanide (1a)

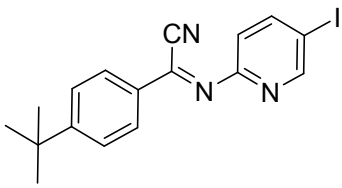
Yellow solid; mp: 100-102 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, J = 1.7 Hz, 1H), 8.21 (dd, J = 5.3, 3.4 Hz, 2H), 8.13 (dd, J = 8.3, 2.2 Hz, 1H), 7.63 (ddd, J = 6.6, 3.8, 1.2 Hz, 1H), 7.54 (dd, J = 10.4, 4.7 Hz, 2H), 7.10 – 7.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 154.8, 146.4, 141.1, 133.5, 133.4, 129.0, 128.7, 120.4, 111.2, 91.6. MS (EI) m/z: 332, 307, 204, 154, 127, 103, 77, 64, 51, 28. HRMS (ESI): calcd. for $C_{13}H_9IN_3$ $[M+H]^+$ 333.9836; found 333.9843.



(Z)-*N*-(5-iodopyridin-2-yl)-4-methylbenzimidoyl cyanide (1b)

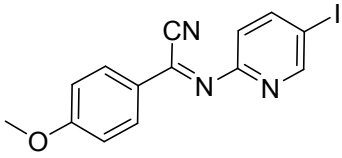
Yellow solid; mp: 133-135 ^{o}C; ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 8.76 (d, J = 1.5 Hz, 1H), 8.08 (d, J = 8.3 Hz, 3H), 7.31 (d, J = 8.1 Hz, 2H), 7.04 (d, J = 8.3 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 154.7, 146.3, 144.6, 141.0, 136.2, 130.9, 129.7, 128.7, 120.2, 111.3, 91.2, 21.6. MS (EI) m/z: 304, 224, 209, 181, 112, 77, 63, 39. HRMS (ESI): calcd. for $C_{14}H_{11}IN_3$ $[M+H]^+$ 347.9992; found 348.0000.



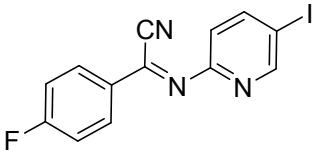
(Z)-4-(*tert*-butyl)-*N*-(5-iodopyridin-2-yl)benzimidoyl cyanide (1c)

Yellow solid; mp: 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 1.8 Hz, 1H), 8.13 (d, J = 8.6 Hz, 2H), 8.09 (dd, J = 8.4, 2.0 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.06 (d, J = 8.3 Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 157.7, 154.8, 146.3, 141.1, 130.9, 128.7, 126.0, 111.3, 91.2, 35.2, 31.0. MS (EI) m/z: 292, 213, 119, 105, 78, 51. HRMS (ESI): calcd. for $C_{17}H_{17}IN_3$ $[M+H]^+$ 390.0462; found 390.0464.



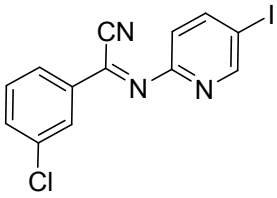
(Z)-N-(5-iodopyridin-2-yl)-4-methoxybenzimidoyl cyanide (1d)

Yellow solid; mp: 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (s, 1H), 8.14 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.4 Hz, 1H), 7.00 (t, J = 8.8 Hz, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 158.2, 154.7, 146.2, 140.3, 130.8, 126.3, 120.2, 114.4, 111.3, 90.8, 55.5. HRMS (ESI): calcd. for $C_{14}H_{11}IN_3O$ $[M+H]^+$ 363.9941; found 363.9945.



(Z)-4-fluoro-N-(5-iodopyridin-2-yl)benzimidoyl cyanide (1e)

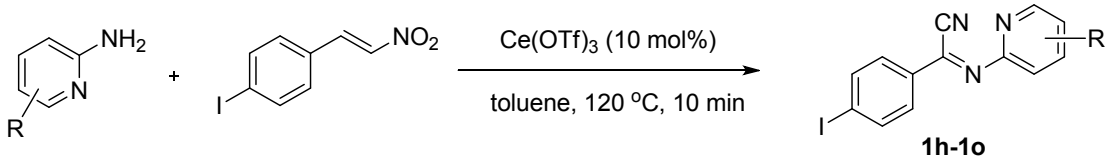
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 2.0 Hz, 1H), 8.25-8.20 (m, 2H), 8.13-8.10 (m, 1H), 7.24-7.19 (m, 2H), 7.07 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8 (d, J = 253.0 Hz), 157.6, 154.9, 146.5, 139.7, 131.2 (d, J = 9.0 Hz), 129.8 (d, J = 3.0 Hz), 120.6, 116.4 (d, J = 22.0 Hz), 111.2, 91.8. MS (EI) m/z: 351, 325, 299, 224, 204, 172, 145, 103, 77, 50, 26. HRMS (ESI): calcd. for $C_{13}H_8FIN_3$ $[M+H]^+$ 351.9741; found 351.9744.



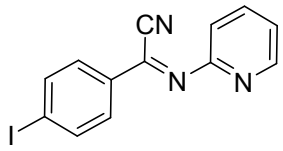
(Z)-3-chloro-*N*-(5-iodopyridin-2-yl)benzimidoyl cyanide (1f)

Yellow solid; mp: 109-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (s, 1H), 8.21 (d, J = 1.6 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 154.9, 146.6, 139.5, 135.4, 135.2, 133.4, 130.3, 128.3, 127.2, 121.1, 111.1, 92.3. HRMS (ESI): calcd. for $C_{13}H_8ClIN_3$ $[M+H]^+$ 367.9446; found 367.9450.

Procedure A (1h-1o):[1]

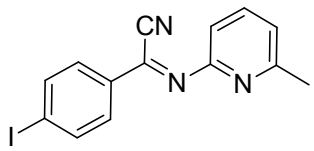


A mixture of 2-aminopyridine (0.3 mmol), (*E*)-1-iodo-4-(2-nitrovinyl)benzene (0.3 mmol) and $Ce(OTf)_3$ (10 mol%) in toluene (1.5 mL) was placed in a test tube (10 mL) equipped with a magnetic stirring bar. The mixture was stirred at 120 °C for 10 minutes. After the reaction was finished, water (5 mL) was added and the solution was extracted with ethyl acetate (3×5 mL), the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.



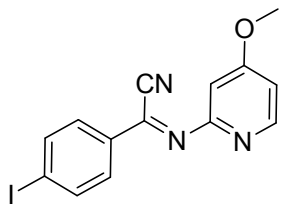
(Z)-4-iodo-*N*-(pyridin-2-yl)benzimidoyl cyanide (1h)

Yellow solid; mp: 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (dd, J = 4.8, 1.2 Hz, 1H), 7.95-7.88 (m, 4H), 7.86-7.82 (m, 1H), 7.31-7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 148.9, 140.0, 138.4, 138.3, 133.2, 129.8, 123.2, 118.8, 111.3, 101.1. MS (EI) m/z: 332, 206, 154, 104, 78, 51. HRMS (ESI): calcd. for $C_{13}H_9IN_3$ $[M+H]^+$ 333.9836; found 333.9839.



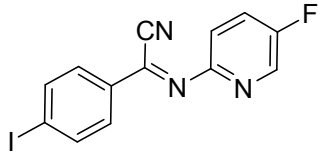
(Z)-4-iodo-*N*-(6-methylpyridin-2-yl)benzimidoyl cyanide (1i)

Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93-7.86 (m, 4H), 7.71 (t, J = 8.0 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 158.1, 139.8, 138.4, 138.2, 133.2, 129.8, 122.7, 115.3, 111.2, 110.9, 23.8. MS (EI) m/z: 347, 320, 220, 168, 118, 91, 65, 39. HRMS (ESI): calcd. for $C_{14}H_{11}IN_3$ $[M+H]^+$ 347.9992; found 347.9997.



(Z)-4-iodo-*N*-(4-methoxypyridin-2-yl)benzimidoyl cyanide (1j)

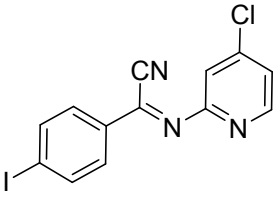
Yellow solid; mp: 99-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, J = 5.6 Hz, 1H), 7.92-7.87 (m, 4H), 6.81 (dd, J = 5.6, 2.4 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 160.4, 149.7, 140.2, 138.2, 133.1, 129.8, 111.2, 109.9, 103.8, 101.1, 55.5. HRMS (ESI): calcd. for $C_{14}H_{11}IN_3$ $[M+H]^+$ 363.9941; found 363.9945



(Z)-*N*-(5-fluoropyridin-2-yl)-4-iodobenzimidoyl cyanide (1k)

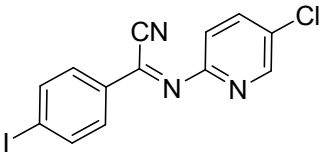
Yellow solid; mp: 102-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 2.8 Hz, 1H), 7.93-7.88 (m, 4H),

7.58-7.53 (m, 1H), 7.35-7.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0 (d, J = 256 Hz), 154.4, 139.6, 138.3, 136.8 (d, J = 26 Hz), 133.2, 129.8, 125.2 (d, J = 20 Hz), 121.0 (d, J = 5 Hz), 111.4, 101.2. MS (EI) m/z: 350, 224, 197, 172, 114, 96, 76, 50. HRMS (ESI): calcd. for $C_{13}H_8FIN_3$ $[M+H]^+$ 351.9741; found 351.9748.



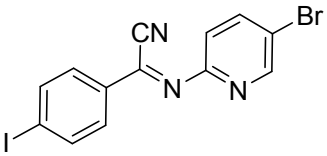
(Z)-*N*-(4-chloropyridin-2-yl)-4-iodobenzimidoyl cyanide (1l)

Yellow solid; mp: 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (dd, J = 3.6, 2.4 Hz, 1H), 7.93-7.89 (m, 4H), 7.31-7.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 149.6, 145.7, 141.2, 138.4, 132.9, 130.0, 123.4, 119.0, 111.0, 101.7. MS (EI) m/z: 367, 337, 240, 188, 109, 103, 76, 50. HRMS (ESI): calcd. for $C_{13}H_8ClIN_3$ $[M+H]^+$ 367.9446; found 367.9448



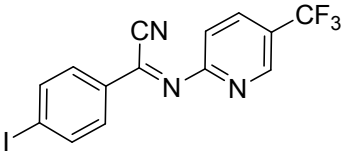
(Z)-*N*-(5-chloropyridin-2-yl)-4-iodobenzimidoyl cyanide (1m)

Yellow solid; mp: 139-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (d, J = 2.4 Hz, 1H), 7.93-7.88 (m, 4H), 7.80 (dd, J = 8.4, 2.4 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 147.6, 140.2, 138.3, 138.0, 133.0, 131.5, 129.9, 120.2, 111.2, 101.5. MS (EI) m/z: 367, 366, 332, 240, 188, 153, 112, 103, 76, 50. HRMS (ESI): calcd. for $C_{13}H_8ClIN_3$ $[M+H]^+$ 367.9446; found 367.9450.



(Z)-*N*-(5-bromopyridin-2-yl)-4-iodobenzimidoyl cyanide (1n)

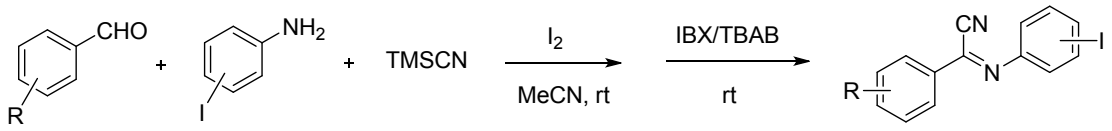
Yellow solid; mp: 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, J = 2.4 Hz, 1H), 7.95 (dd, J = 8.4, 2.4 Hz, 1H), 7.93-7.88 (m, 4H), 7.20 (dd, J = 8.4, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 149.9, 140.9, 138.7, 138.4, 133.0, 130.3, 129.9, 120.5, 111.2, 101.5. MS (EI) m/z: 410, 332, 284, 234, 204, 153, 114, 103, 76, 50. HRMS (ESI): calcd. for $C_{13}H_8BrIN_3$ $[M+H]^+$ 411.8941; found 411.8943.



(Z)-4-iodo-*N*-(5-(trifluoromethyl)pyridin-2-yl)benzimidoyl cyanide (1o)

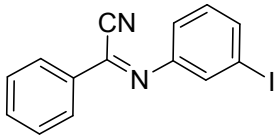
Yellow solid; mp: 129-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (d, J = 2.0 Hz, 1H), 8.09 (dd, J = 8.4, 2.0 Hz, 1H), 7.97-7.91 (m, 4H), 7.37 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 146.3 (q, J = 4 Hz), 141.9, 138.6, 138.5, 135.7 (q, J = 4 Hz), 132.6, 130.0, 124.6 (q, J = 271 Hz), 118.0, 110.7, 102.2. MS (EI) m/z: 400, 382, 274, 222, 146, 126, 75, 50. HRMS (ESI): calcd. for $C_{14}H_8F_3IN_3$ $[M+H]^+$ 401.9710; found 401.9717.

Procedure B (1p-1w):[2]



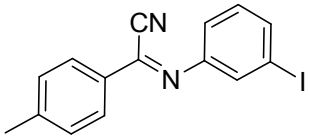
1p-1w

A mixture of aldehyde (0.3 mmol), amine (0.3 mmol), I_2 (0.03 mmol), TMSCN (0.33 mmol in acetonitrile (1.5 mL) was placed in a test tube (10 mL) equipped with a magnetic stirring bar. The mixture was stirred at room temperature for one hour. Then the IBX (0.33mmol) and tetrabutylammonium bromide (0.33 mmol) were added, and the mixture was stirred at room temperature for 8 h. After the reaction was finished, water (5 mL) was added and the solution was extracted with ethyl acetate (3×5 mL), the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.



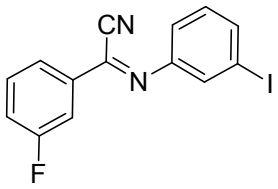
(Z)-*N*-(3-iodophenyl)benzimidoyl cyanide (1p)

Yellow solid; mp: 74-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (dd, J = 5.3, 3.4 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.58 – 7.51 (m, 3H), 7.20 (t, J = 7.8 Hz, 1H), 7.17 – 7.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 140.7, 135.8, 133.2, 133.0, 130.6, 129.1, 129.0, 128.2, 119.1, 110.3, 94.2. HRMS (ESI): calcd. for $C_{14}H_{10}IN_2$ $[M+H]^+$ 332.9883; found 332.9883.



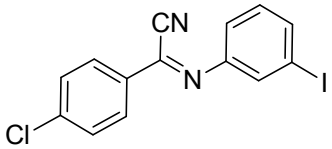
(Z)-*N*-(3-iodophenyl)-4-methylbenzimidoyl cyanide (1q)

Yellow solid; mp: 101-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.4 Hz, 2H), 7.64-7.61 (m, 1H), 7.50 (t, J = 2.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 7.13-7.10 (m, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4, 144.3, 140.8, 135.7, 130.8, 130.6, 129.8, 129.2, 128.3, 119.2, 110.5, 94.2, 21.6. HRMS (ESI): calcd. for $C_{15}H_{12}IN_2$ $[M+H]^+$ 347.0040; found 347.0042.



(Z)-3-fluoro-*N*-(3-iodophenyl)benzimidoyl cyanide (1r)

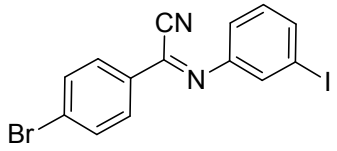
Yellow solid; mp: 60-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.89 (m, 1H), 7.85-7.82 (m, 1H), 7.66-7.64 (m, 1H), 7.54-7.49 (m, 2H), 7.33-7.28 (m, 1H), 7.22-7.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7 (d, J = 247 Hz), 149.5, 139.2 (d, J = 4 Hz), 136.2, 135.1 (d, J = 8 Hz), 130.6 (d, J = 8 Hz), 130.6, 129.2, 124.4 (d, J = 3 Hz), 120.2 (d, J = 21 Hz), 119.1, 114.5 (d, J = 24 Hz), 110.1, 94.2. HRMS (ESI): calcd. for $C_{14}H_9FIN_2$ $[M+H]^+$ 350.9789; found 350.9795.



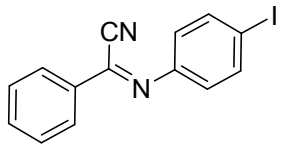
(Z)-4-chloro-*N*-(3-iodophenyl)benzimidoyl cyanide (1s)

Yellow solid; mp: 99-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 – 8.05 (m, 2H), 7.67 – 7.64 (m, 1H), 7.54 – 7.50 (m, 3H), 7.20 (t, J = 7.8 Hz, 1H), 7.14 (ddd, J = 8.0, 1.8, 1.1 Hz, 1H). ^{13}C

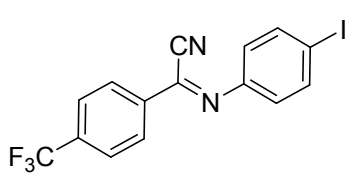
NMR (100 MHz, $CDCl_3$): δ = 149.9, 139.7, 139.5, 136.2, 131.7, 130.7, 129.5, 129.4, 129.3, 119.2, 110.2, 94.3. HRMS (ESI): calcd. for $C_{14}H_9ClIN_2$ $[M+H]^+$ 366.9493; found 366.9499.



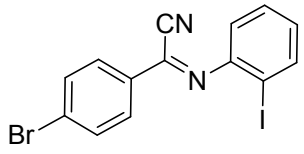
(Z)-4-bromo-*N*-(3-iodophenyl)benzimidoyl cyanide (1t)
Yellow solid; mp: 119-121 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 – 7.97 (m, 2H), 7.70 – 7.64 (m, 3H), 7.53 (t, J = 1.7 Hz, 1H), 7.20 (t, J = 7.8 Hz, 1H), 7.15 (ddd, J = 8.0, 1.8, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8, 139.6, 136.2, 132.4, 132.1, 130.7, 129.6, 129.3, 128.4, 119.2, 110.1, 94.3. HRMS (ESI): calcd. for $C_{14}H_9BrIN_2$ $[M+H]^+$ 410.8988; found 410.8986.



(Z)-*N*-(4-iodophenyl)benzimidoyl cyanide (1u)
Yellow solid; mp: 142-144 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 7.5 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5, 140.2, 138.3, 133.3, 133.1, 129.0, 128.2, 122.2, 110.6, 92.0. HRMS (ESI): calcd. for $C_{14}H_{10}IN_2$ $[M+H]^+$ 332.9883; found 332.9883.



(Z)-*N*-(4-iodophenyl)-4-(trifluoromethyl)benzimidoyl cyanide (1v)
Yellow solid; mp: 94-96 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, J = 8.2 Hz, 2H), 7.85 – 7.76 (m, 4H), 7.04 – 6.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 138.4, 138.4, 136.3, 134.4 (q, J = 32 Hz), 128.5, 126.0 (q, J = 4 Hz), 123.4 (q, J = 270 Hz), 122.0, 110.3, 93.1. HRMS (ESI): calcd. for $C_{15}H_9F_3IN_2$ $[M+H]^+$ 400.9757; found 400.9759.



(Z)-4-bromo-N-(2-iodophenyl)benzimidoyl cyanide (1w)
Yellow solid; mp: 118-120 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10-8.06 (m, 2H), 7.96 (dd, J = 8.0, 1.2 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.48-7.44 (m, 1H), 7.12 (dd, J = 8.0, 1.2 Hz, 1H), 7.06-7.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 139.5, 139.3, 132.5, 132.0, 129.8, 129.2, 128.6, 128.5, 118.6, 110.0, 92.2. HRMS (ESI): calcd. for $C_{14}H_9BrIN_2$ $[M+H]^+$ 410.8988; found 410.8992.

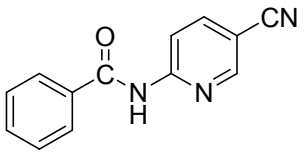
C. General procedure for the synthesis of cyano-substituted pyridyl amides

A mixture of α-iminonitriles (0.2 mmol), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (3 equiv), THF (0.5 mL) and H_2O (0.5 mL) in argon atmosphere was placed in a test tube (10 mL) equipped with a magnetic stirring bar. The mixture was stirred at 70 °C for 12 h. After the reaction was finished, water (5 mL) was added and the solution was extracted with ethyl acetate (3×5 mL), the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.

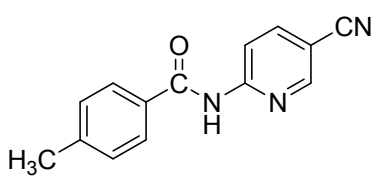
D. General procedure for the synthesis of cyano-substituted phenyl amides

A mixture of α-iminonitriles (0.2 mmol), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (3 equiv), CH_3CN (1 mL) and H_2O (1 equiv) in argon atmosphere was placed in a test tube (10 mL) equipped with a magnetic stirring bar. The mixture was stirred at 70 °C for 12 h. After the reaction was finished, water (5 mL) was added and the solution was extracted with ethyl acetate (3×5 mL), the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.

E. Analytical data for target compounds

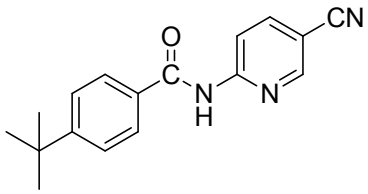


***N*-(5-Cyanopyridin-2-yl)benzamide (3a)[3]**
yellow solid (41 mg, 92%); mp: 187-189 °C; R_f = 0.43 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99 (s, 1H), 8.53 – 8.51 (m, 1H), 8.46 (d, J = 2.0 Hz, 1H), 7.98 – 7.95 (m, 1H), 7.92 – 7.89 (m, 2H), 7.63 – 7.58 (m, 1H), 7.53 – 7.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 154.0, 151.5, 141.6, 133.3, 132.8, 128.9, 127.3, 116.6, 113.7, 105.0. MS (EI) m/z: 223, 194, 105, 77, 51, 28.



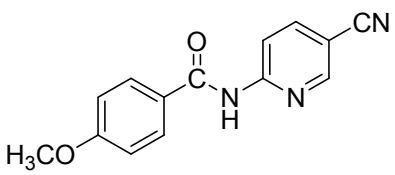
***N*-(5-Cyanopyridin-2-yl)-4-methylbenzamide (3b)**
white solid (41 mg, 88%); mp: 151-153 °C; R_f = 0.45 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (s, 1H), 8.54 – 8.51 (m, 2H), 7.99 – 7.96 (m, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.32 (d,

J = 8.0 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 154.1, 151.6, 143.7, 141.5, 130.4, 129.6, 127.3, 116.7, 113.6, 104.9, 21.5. MS (EI) m/z: 237, 119, 91, 65, 39. Anal. Calcd for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71; Found: C, 70.56; H, 4.73; N, 17.82. HRMS (ESI): calcd. for $C_{14}H_{12}N_3O$ $[M+H]^+$ 238.0975; found 238.0982.



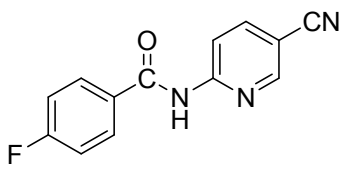
4-(*tert*-Butyl)-*N*-(5-cyanopyridin-2-yl)benzamide (3c)

white solid (47 mg, 85%); mp: 174-176 °C; R_f = 0.60 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (s, 1H), 8.55 – 8.49 (m, 2H), 7.97 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 156.8, 154.1, 151.6, 141.5, 130.4, 127.2, 125.9, 116.7, 113.6, 104.9, 35.1, 31.0. MS (EI) m/z: 279, 250, 161, 146, 118, 91, 77. Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.10; H, 6.13; N, 15.04; Found: C, 72.84; H, 6.23; N, 15.23. HRMS (ESI): calcd. for $C_{17}H_{18}N_3O$ $[M+H]^+$ 280.1444; found 280.1449.



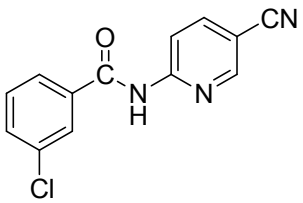
***N*-(5-Cyanopyridin-2-yl)-4-methoxybenzamide (3d)**

yellow solid (38 mg, 76%); mp: 144-146 °C; R_f = 0.27 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 8.56-8.55 (m, 1H), 8.53-8.50 (m, 1H), 7.99 – 7.96 (m, 1H), 7.91 – 7.87 (m, 2H), 7.01 – 6.99 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 163.3, 154.2, 151.6, 141.5, 129.3, 125.3, 116.7, 114.2, 113.6, 104.8, 55.5. MS (EI) m/z: 253, 135, 107, 92, 77. Anal. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59; Found: C, 66.07; H, 4.45; N, 16.47. HRMS (ESI): calcd. for $C_{14}H_{12}N_3O_2$ $[M+H]^+$ 254.0924; found 254.0933.



***N*-(5-Cyanopyridin-2-yl)-4-fluorobenzamide (3e)**

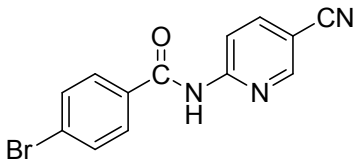
white solid (36 mg, 75%); mp: 162-164 °C; R_f = 0.45 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 8.59 (s, 1H), 8.51 (d, J = 8.8 Hz, 1H), 8.02 – 7.99 (m, 1H), 7.97 – 7.93 (m, 2H), 7.24 – 7.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5 (d, J = 253.0 Hz), 164.6, 153.8, 151.6, 141.7, 129.9 (d, J = 4.0 Hz), 129.4 (d, J = 3.0 Hz), 116.6, 116.2 (d, J = 22.0 Hz), 113.7, 105.3. MS (EI) m/z: 241, 212, 123, 95, 75, 50. Anal. Calcd for $C_{13}H_8FN_3O$: C, 64.73; H, 3.34; N, 17.42; Found: C, 64.46; H, 3.42; N, 17.53. HRMS (ESI): calcd. for $C_{13}H_9FN_3O$ $[M+H]^+$ 242.0724; found 242.0733.



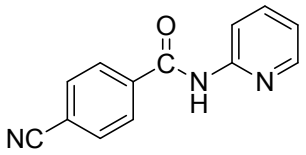
3-Chloro-*N*-(5-cyanopyridin-2-yl)benzamide (3f)

white solid (41 mg, 80%); mp: 131-133 °C; R_f = 0.45 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (s, 1H), 8.52 – 8.48 (m, 2H), 8.00 – 7.97 (m, 1H), 7.90 – 7.89 (m, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.58

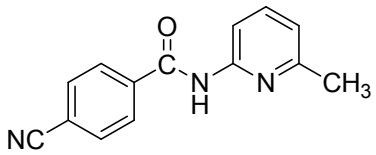
– 7.55 (m, 1H), 7.47 – 7.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5, 153.7, 151.5, 141.7, 135.2, 135.0, 132.8, 130.2, 127.7, 125.2, 116.5, 113.8, 105.4. MS (EI) m/z: 257, 228, 139, 111, 75, 50. Anal. Calcd for $C_{13}H_8ClN_3O$: C, 60.60; H, 3.13; N, 16.31; Found: C, 60.28; H, 3.22; N, 16.43. HRMS (ESI): calcd. for $C_{13}H_9ClN_3O$ $[M+H]^+$ 258.0429; found 258.0435.



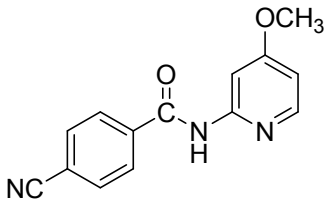
4-Bromo-*N*-(5-cyanopyridin-2-yl)benzamide (3g)
white solid (47 mg, 78%); mp: 180-182 °C; R_f = 0.46 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (s, 1H), 8.58 (d, J = 1.2 Hz, 1H), 8.50 (d, J = 8.4 Hz, 1H), 8.01 – 7.98 (m, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 153.8, 151.6, 141.7, 132.3, 132.1, 128.8, 127.9, 116.5, 113.7, 105.4. MS (EI) m/z: 301, 274, 183, 157, 104, 76, 50. Anal. Calcd for $C_{13}H_8BrN_3O$: C, 51.68; H, 2.67; N, 13.91; Found: C, 51.40; H, 2.61; N, 14.07. HRMS (ESI): calcd. for $C_{13}H_9BrN_3O$ $[M+H]^+$ 301.9924; found 301.9927.



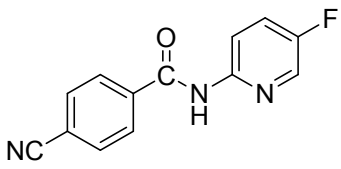
4-Cyano-*N*-(pyridin-2-yl)benzamide (4a)[4]
white solid (37 mg, 83%); mp: 151-153 °C; R_f = 0.20 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.09 (s, 1H), 8.36 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 4.0 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.80 – 7.75 (m, 3H), 7.11 – 7.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 151.0, 147.7, 138.7, 138.1, 132.6, 127.9, 120.4, 117.7, 115.7, 114.4. MS (EI) m/z: 231, 206, 179, 104, 78, 51.



4-Cyano-*N*-(6-methylpyridin-2-yl)benzamide (4b)[5]
white solid (38 mg, 80%); mp: 132-134 °C; R_f = 0.28 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.68-7.64 (m, 1H), 6.95 (d, J = 7.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8, 157.0, 150.2, 138.9, 138.2, 132.5, 127.8, 119.9, 117.7, 115.6, 111.1, 23.8. MS (EI) m/z: 237, 208, 130, 102, 75, 39.

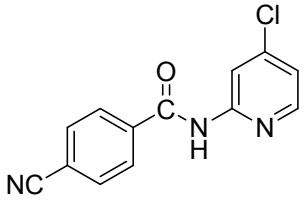


4-Cyano-*N*-(4-methoxypyridin-2-yl)benzamide (4c)
white solid (36 mg, 72%); mp: 206-208 °C; R_f = 0.14 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.22 (s, 1H), 8.02 (d, J = 8.4 Hz, 4H), 7.78 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 3.2 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 164.3, 152.8, 148.0, 138.1, 132.5, 128.0, 117.8, 115.7, 108.1, 99.4, 55.5. MS (EI) m/z: 253, 224, 130, 102, 75, 51. Anal. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59; Found: C, 66.12; H, 4.46; N, 16.71. HRMS (ESI): calcd. for $C_{14}H_{12}N_3O_2$ $[M+H]^+$ 254.0924; found 254.0932.



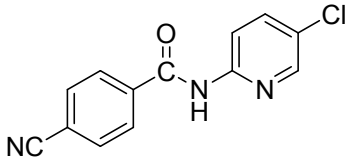
4-Cyano-*N*-(5-fluoropyridin-2-yl)benzamide (4d)

white solid (37 mg, 78%); mp: 192-194 °C; R_f = 0.38 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (s, 1H), 8.39-8.36 (m, 1H), 8.13 (d, J = 4.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.54 – 7.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5, 156.7 (d, J = 251.0 Hz), 147.1, 137.8, 135.6 (d, J = 26.0 Hz), 132.6, 127.8, 125.4 (d, J = 19.0 Hz), 117.7, 115.9, 115.1 (d, J = 4.0 Hz). MS (EI) m/z: 241, 212, 130, 102, 75, 51. Anal. Calcd for $C_{13}H_8FN_3O$: C, 64.73; H, 3.34; N, 17.42; Found: C, 64.49; H, 3.42; N, 17.53. HRMS (ESI): calcd. for $C_{13}H_9FN_3O$ $[M+H]^+$ 242.0724; found 242.0731.



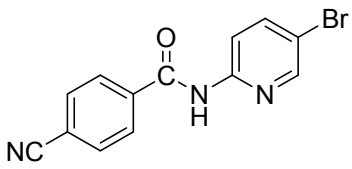
***N*-(4-Chloropyridin-2-yl)-4-cyanobenzamide (4e)**

white solid (38 mg, 75%); mp: 185-187 °C; R_f = 0.28 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (s, 1H), 8.46 (d, J = 1.6 Hz, 1H), 8.18 (d, J = 5.2 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.14 – 7.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8, 151.8, 148.4, 146.4, 137.6, 132.7, 127.9, 120.9, 117.6, 116.1, 114.5. MS (EI) m/z: 257, 228, 130, 102, 75, 51. Anal. Calcd for $C_{13}H_8ClN_3O$: C, 60.60; H, 3.13; N, 16.31; Found: C, 60.21; H, 3.25; N, 16.43. HRMS (ESI): calcd. for $C_{13}H_9ClN_3O$ $[M+H]^+$ 258.0429; found 258.0438.



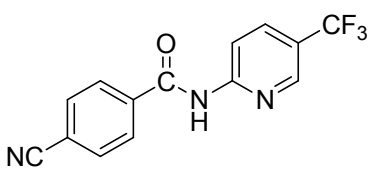
***N*-(5-Chloropyridin-2-yl)-4-cyanobenzamide (4f)**

white solid (41 mg, 80%); mp: 220-222 °C; R_f = 0.44 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (s, 1H), 8.35 (d, J = 8.8 Hz, 1H), 8.22 (s, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.75 – 7.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7, 149.2, 146.7, 138.2, 137.7, 132.7, 127.8, 127.6, 117.6, 116.0, 114.9. MS (EI) m/z: 257, 228, 130, 102, 75, 51. Anal. Calcd for $C_{13}H_8ClN_3O$: C, 60.60; H, 3.13; N, 16.31; Found: C, 60.34; H, 3.21; N, 16.39. HRMS (ESI): calcd. for $C_{13}H_9ClN_3O$ $[M+H]^+$ 258.0429; found 258.0434.



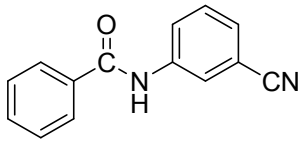
***N*-(5-Bromopyridin-2-yl)-4-cyanobenzamide (4g)**

white solid (46 mg, 77%); mp: 221-223 °C; R_f = 0.46 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 1H), 8.34 (d, J = 2.4 Hz, 1H), 8.30 (d, J = 8.8 Hz, 1H), 8.02 – 8.00 (m, 2H), 7.89 – 7.87 (m, 1H), 7.82 – 7.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7, 149.6, 148.9, 141.0, 137.7, 132.7, 127.8, 117.6, 116.0, 115.5, 115.4. MS (EI) m/z: 303, 272, 207, 130, 75, 51. Anal. Calcd for $C_{13}H_8BrN_3O$: C, 51.68; H, 2.67; N, 13.91; Found: C, 51.37; H, 2.75; N, 13.86. HRMS (ESI): calcd. for $C_{13}H_9BrN_3O$ $[M+H]^+$ 301.9924; found 301.9931.



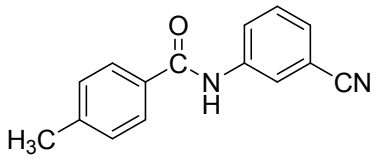
4-Cyano-*N*-(5-(trifluoromethyl)pyridin-2-yl)benzamide (4h)

white solid (47 mg, 81%); mp: 213-215 °C; R_f = 0.48 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94 (s, 1H), 8.51 (d, J = 9.2 Hz, 2H), 8.04 (d, J = 8.4 Hz, 2H), 8.02 – 7.99 (m, 1H), 7.82 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 153.5, 145.4 (q, J = 4.0 Hz), 137.4, 136.0 (q, J = 4.0 Hz), 132.7, 127.9, 123.3 (q, J = 270.0 Hz), 117.5, 116.3, 113.6. MS (EI) m/z: 291, 262, 130, 102, 75, 51. Anal. Calcd for $C_{14}H_8F_3N_3O$: C, 57.74; H, 2.77; N, 14.43; Found: C, 57.52; H, 2.64; N, 14.59. HRMS (ESI): calcd. for $C_{14}H_9F_3N_3O$ $[M+H]^+$ 292.0692; found 292.0699.



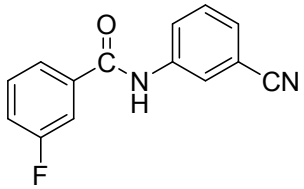
***N*-(3-Cyanophenyl)benzamide (5a)[6]**

white solid (33 mg, 75%); mp: 138-139 °C; R_f = 0.32 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (s, 1H), 8.05 (s, 1H), 7.86 (d, J = 8.0 Hz, 3H), 7.58 – 7.54 (m, 1H), 7.49 – 7.39 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 138.8, 134.0, 132.3, 129.9, 128.8, 127.8, 127.1, 124.4, 123.3, 118.4, 113.0. MS (EI) m/z: 222, 105, 77, 51.



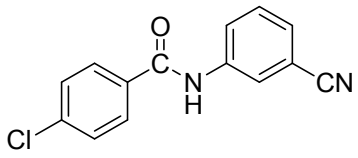
***N*-(3-Cyanophenyl)-4-methylbenzamide (5b)**

white solid (32 mg, 69%); mp: 152-154 °C; R_f = 0.34 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 1H), 8.04 – 8.03 (m, 1H), 7.87 – 7.84 (m, 1H), 7.76 – 7.74 (m, 2H), 7.46 – 7.42 (m, 1H), 7.40 – 7.38 (m, 1H), 7.27 (d, J = 8.4 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 143.0, 138.9, 131.2, 129.9, 129.6, 127.7, 127.0, 124.1, 123.2, 118.4, 113.1, 21.5. MS (EI) m/z: 236, 119, 91, 65, 39. Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86; Found: C, 76.03; H, 5.22; N, 11.99. HRMS (ESI): calcd. for $C_{15}H_{13}N_2O$ $[M+H]^+$ 237.1022; found 237.1025.



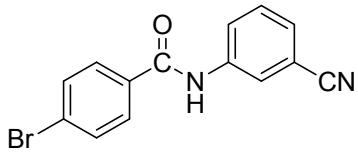
***N*-(3-Cyanophenyl)-3-fluorobenzamide (5c)**

white solid (35 mg, 73%); mp: 138-140 °C; R_f = 0.32 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, DMSO): δ = 10.61 (s, 1H), 8.24 (s, 1H), 8.03 (s, 1H), 7.82 – 7.76 (m, 2H), 7.63 – 7.57 (m, 3H), 7.49 – 7.45 (m, 1H). ^{13}C NMR (100 MHz, DMSO): δ = 165.0 (d, J = 3.0 Hz), 162.3 (d, J = 243.0 Hz), 140.1, 137.0 (d, J = 7.0 Hz), 131.1 (d, J = 8.0 Hz), 130.6, 127.8, 125.3, 124.4 (d, J = 3.0 Hz), 123.5, 119.4, 119.1 (d, J = 10.0 Hz), 115.0 (d, J = 23.0 Hz), 111.9. MS (EI) m/z: 240, 123, 95, 75, 39. Anal. Calcd for $C_{14}H_9FN_2O$: C, 69.99; H, 3.78; N, 11.66; Found: C, 69.72; H, 3.90; N, 11.75. HRMS (ESI): calcd. for $C_{14}H_{10}FN_2O$ $[M+H]^+$ 241.0772; found 241.0776.



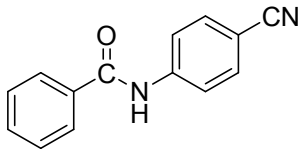
4-Chloro-*N*-(3-cyanophenyl)benzamide (5d)

yellow solid (34 mg, 66%); mp: 130-132 °C; R_f = 0.34 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, DMSO): δ = 10.62 (s, 1H), 8.24 (d, J = 0.8 Hz, 1H), 8.04 – 8.01 (m, 1H), 8.00 – 7.97 (m, 2H), 7.65 – 7.61 (m, 2H), 7.58 – 7.57 (m, 2H). ^{13}C NMR (100 MHz, DMSO): δ = 165.3, 140.2, 137.3, 133.4, 130.6, 130.1, 129.0, 127.7, 125.3, 123.5, 119.1, 111.9. MS (EI) m/z: 256, 139, 111, 75, 50. Anal. Calcd for $C_{14}H_9ClN_2O$: C, 65.51; H, 3.53; N, 10.91; Found: C, 65.26; H, 3.65; N, 11.07. HRMS (ESI): calcd. for $C_{14}H_{10}ClN_2O$ $[M+H]^+$ 257.0476; found 257.0479.



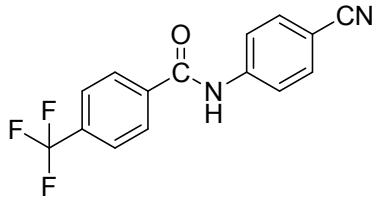
4-Bromo-*N*-(3-cyanophenyl)benzamide (5e)[7]

white solid (39 mg, 65%); mp: 177-179 °C; R_f = 0.34 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, DMSO): δ = 10.61 (s, 1H), 8.23 (s, 1H), 8.04 – 8.02 (m, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.58 – 7.57 (m, 2H). ^{13}C NMR (100 MHz, DMSO): δ = 165.4, 140.2, 133.8, 131.9, 130.6, 130.3, 127.7, 126.2, 125.3, 123.5, 119.1, 111.9. MS (EI) m/z: 302, 183, 155, 104, 76, 50.



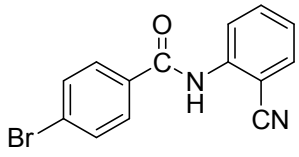
***N*-(4-Cyanophenyl)benzamide (5f)[8]**

yellow solid (37 mg, 84%); mp: 154-156 °C; R_f = 0.28 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.51 – 7.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 142.0, 134.1, 133.3, 132.4, 128.9, 127.1, 119.9, 118.7, 107.3. MS (EI) m/z: 222, 105, 77, 51.



***N*-(4-Cyanophenyl)-4-(trifluoromethyl)benzamide (5g)**

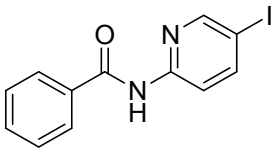
white solid (48 mg, 83%); mp: 150-152 °C; R_f = 0.36 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (s, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 142.0, 137.3, 133.9 (q, J = 33.0 Hz), 133.2, 127.7, 125.7 (q, J = 4.0 Hz), 123.3 (q, J = 270.0 Hz), 120.3, 118.8, 107.3. MS (EI) m/z: 290, 173, 145, 95, 75, 50. Anal. Calcd for $C_{15}H_9F_3N_2O$: C, 62.07; H, 3.13; N, 9.65; Found: C, 61.81; H, 3.24; N, 9.74. HRMS (ESI): calcd. for $C_{15}H_{10}F_3N_2O$ $[M+H]^+$ 291.0740; found 291.0743.



4-Bromo-*N*-(2-cyanophenyl)benzamide (5h)[9]

white solid (46 mg, 77%); mp: 178-180 °C; R_f = 0.36 (ethyl acetate / petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, J = 8.4 Hz, 1H), 8.34 (s, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.67 – 7.62 (m, 4H), 7.25 – 7.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 140.3, 134.3, 132.5, 132.3, 132.1, 128.7, 127.6, 124.4, 121.2, 116.3, 102.3. MS

(EI) m/z: 302, 267, 183, 155, 104, 76, 50.



***N*-(5-iodopyridin-2-yl)benzamide (6a)[10]**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (s, 1H), 8.44-8.43 (m, 1H), 8.26-8.23 (m, 1H), 8.02-7.99 (m, 1H), 7.92-7.89 (m, 2H), 7.60-7.56 (m, 1H), 7.52-7.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 153.8, 150.7, 146.3, 133.9, 132.4, 128.9, 127.2, 115.9, 85.8. MS (EI) m/z: 324, 295, 105, 77, 51, 38.

F. Reference

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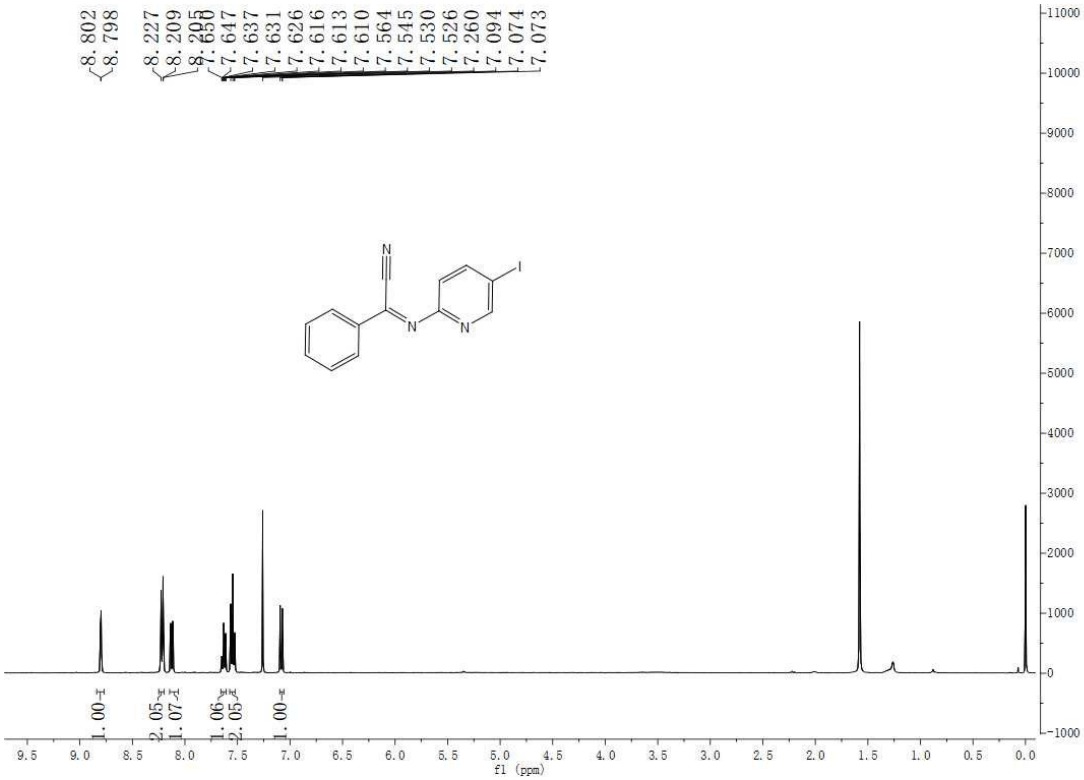
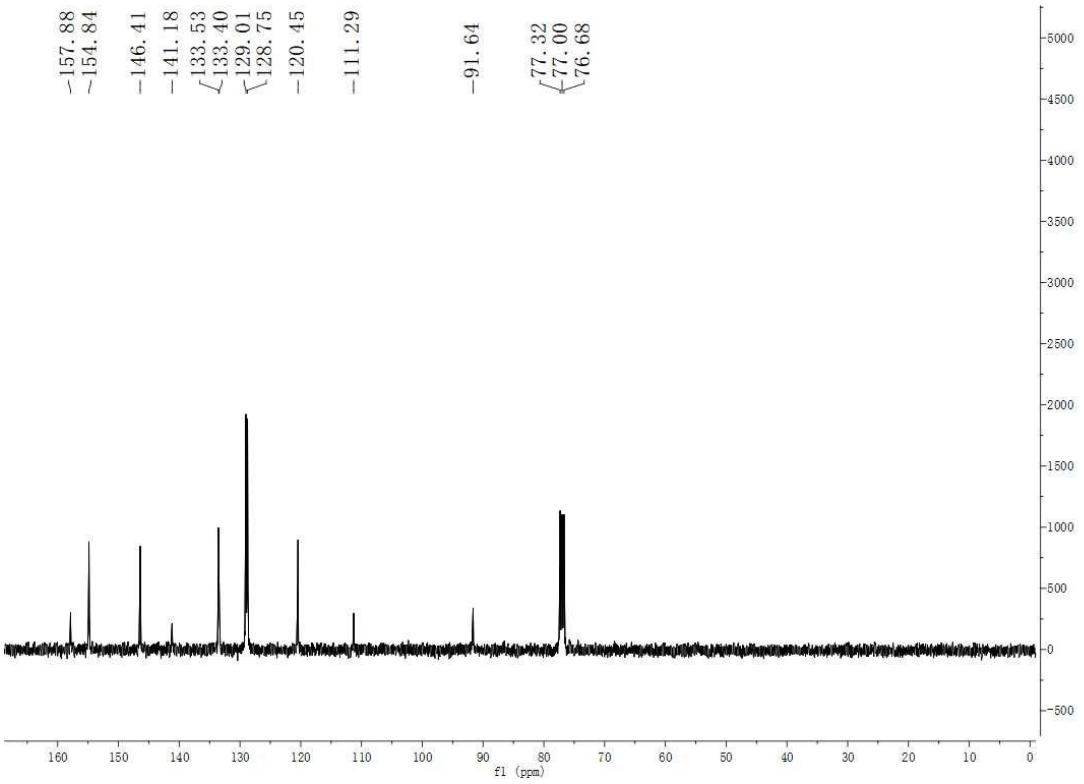
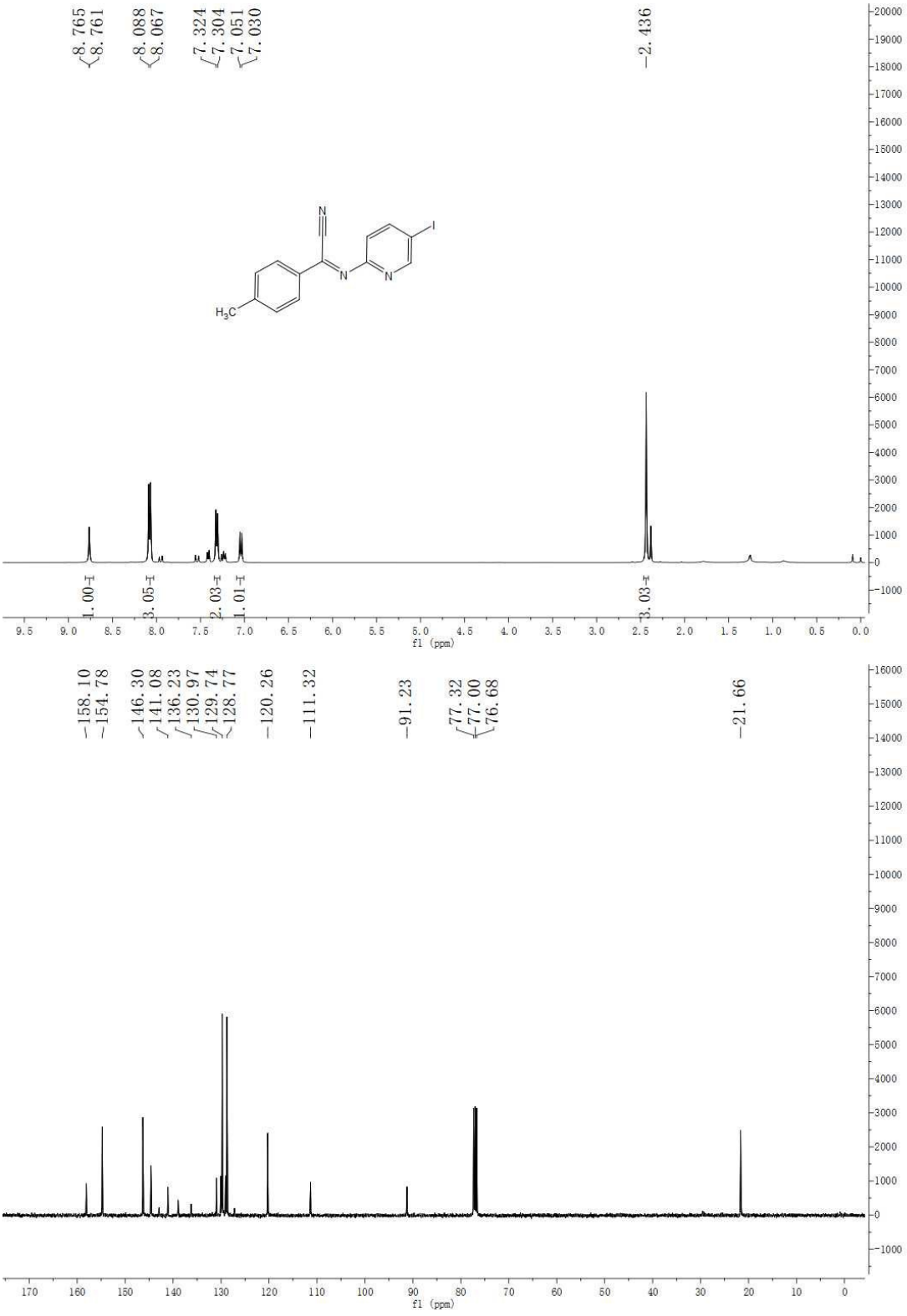
G. NMR and GC-MS spectra

^{1}H NMR and ^{13}C NMR of (Z)-*N*-(5-iodopyridin-2-yl)benzimidoyl cyanide (1a)

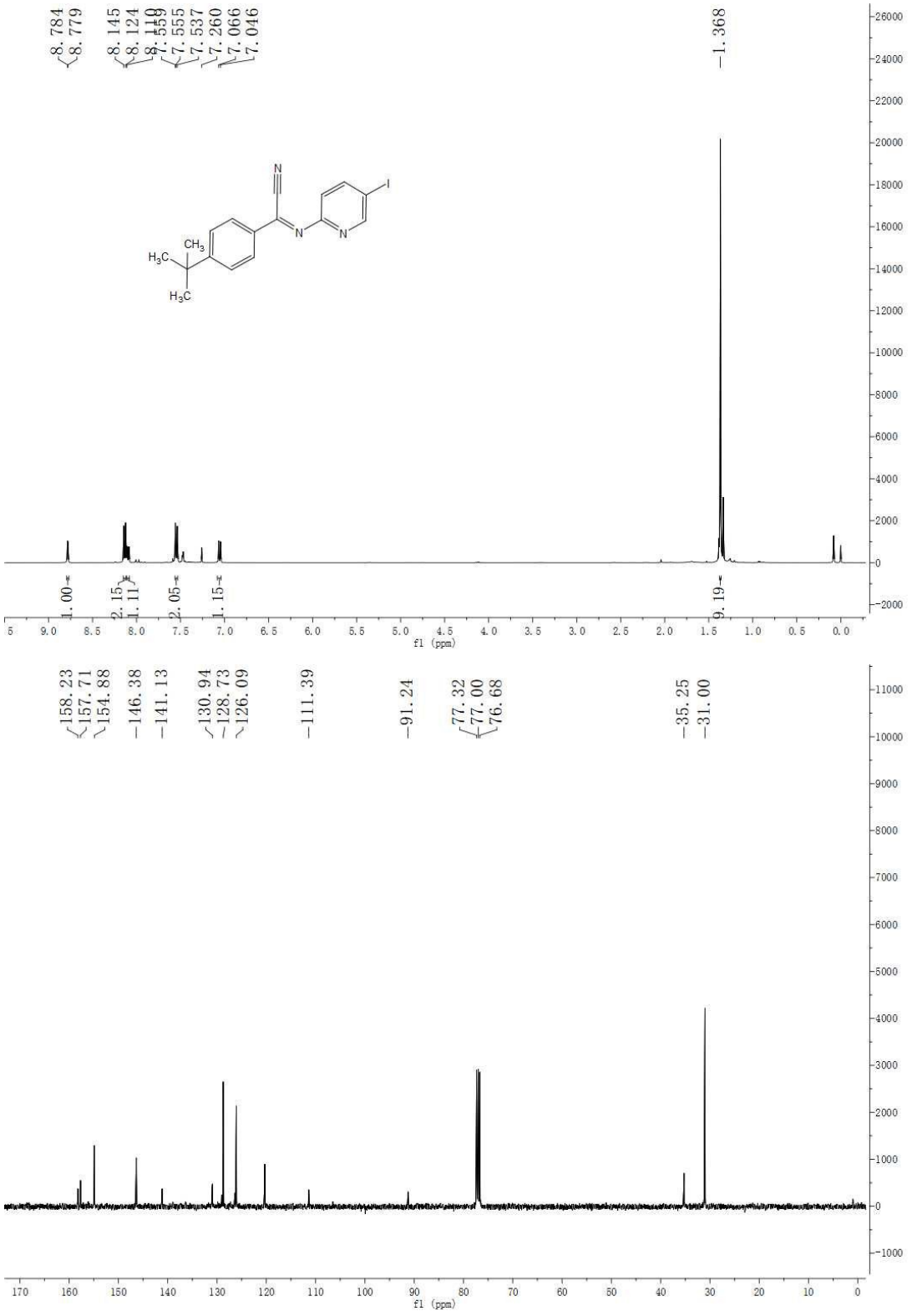




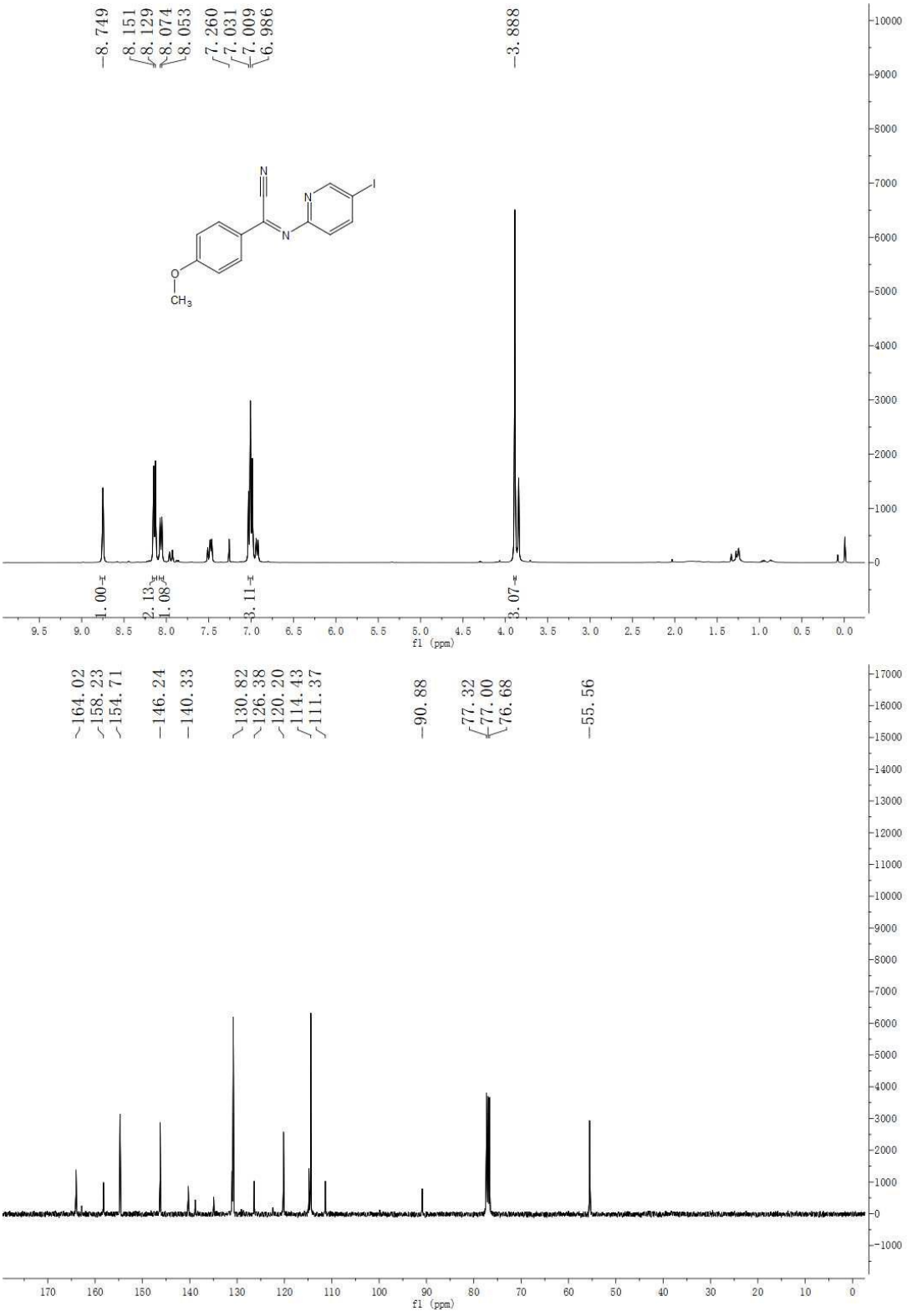
^{1}H NMR and ^{13}C NMR of (Z)-*N*-(5-iodopyridin-2-yl)-4-methylbenzimidoyl cyanide (1b)



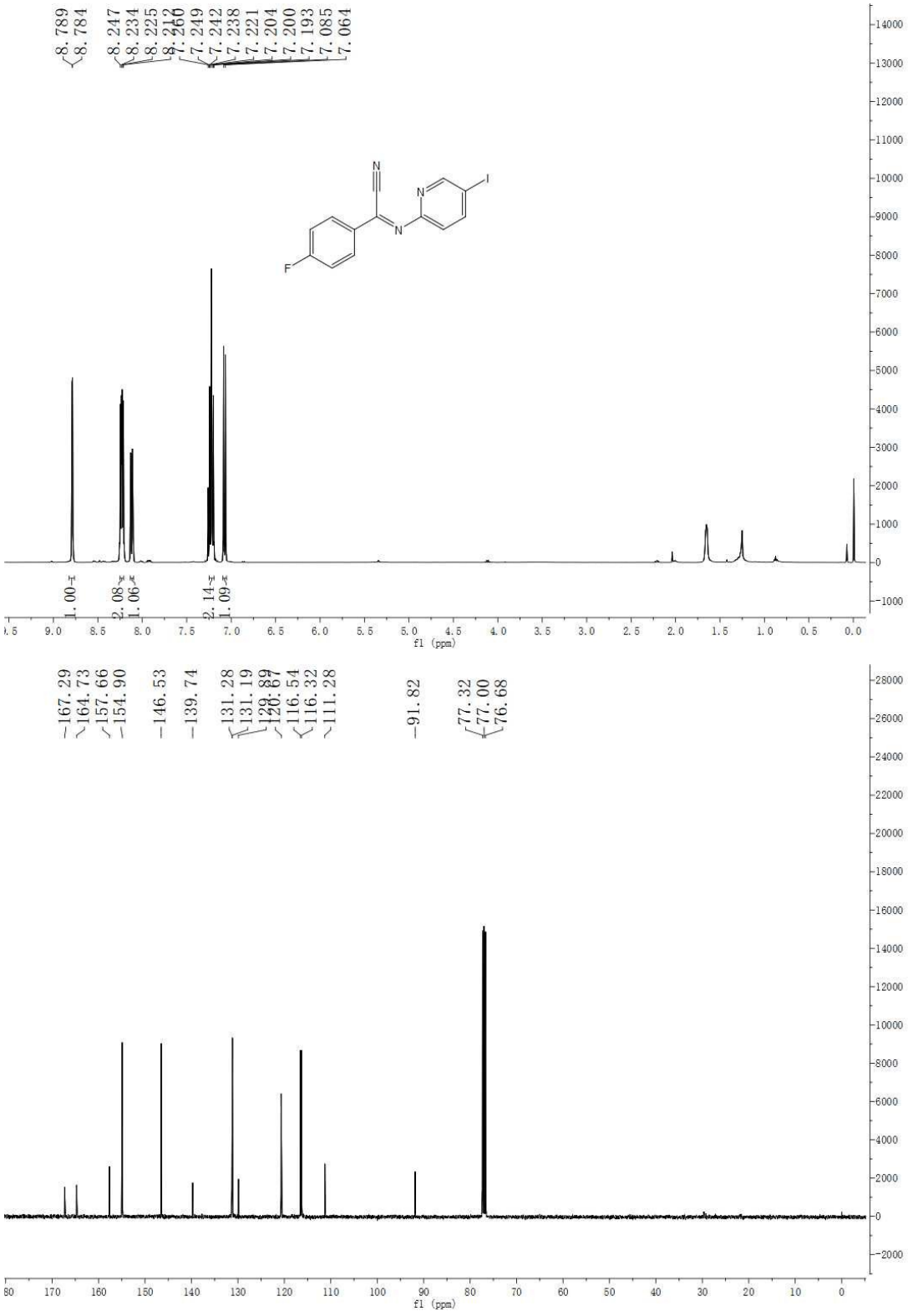
^{1}H NMR and ^{13}C NMR of (Z)-4-(*tert*-butyl)-*N*-(5-iodopyridin-2-yl)benzimidoyl cyanide (1c)



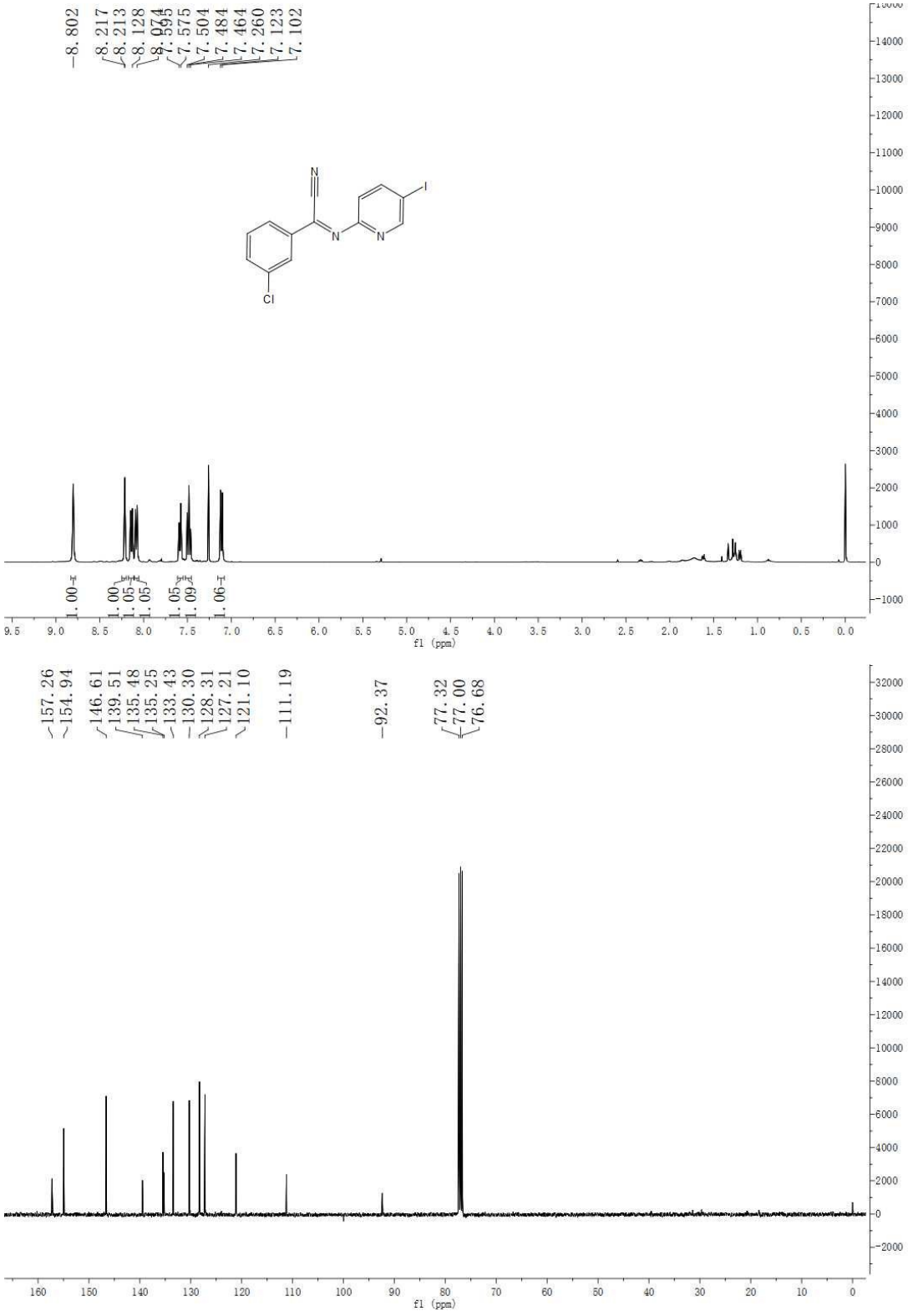
^{1}H NMR and ^{13}C NMR of (Z)-N-(5-iodopyridin-2-yl)-4-methoxybenzimidoyl cyanide (1d)



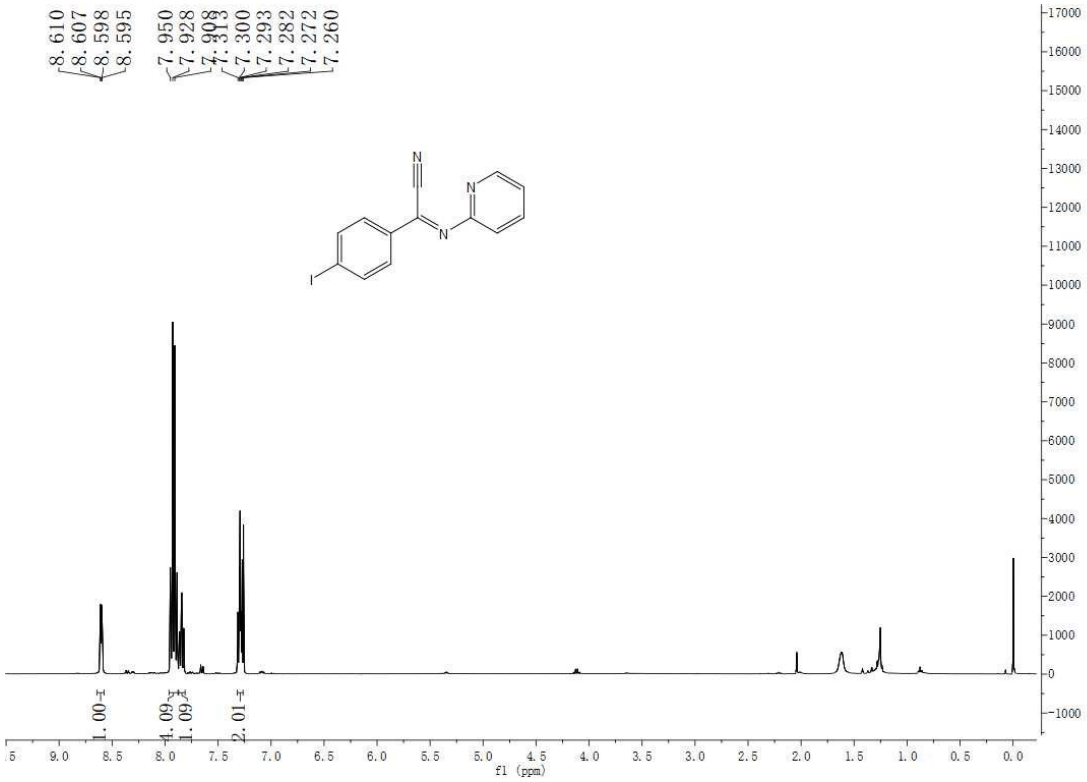
^{1}H NMR and ^{13}C NMR of (Z)-4-fluoro-N-(5-iodopyridin-2-yl)benzimidoyl cyanide (1e)

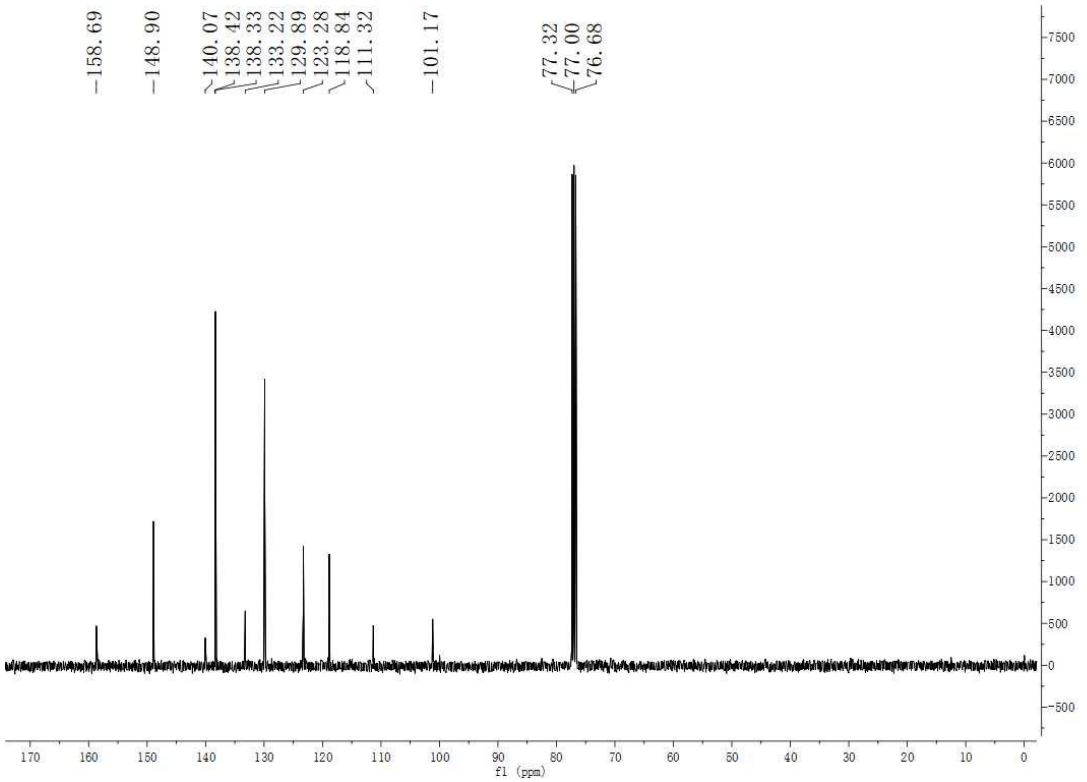


^{1}H NMR and ^{13}C NMR of (Z)-3-chloro-*N*-(5-iodopyridin-2-yl)benzimidoyl cyanide (1f)

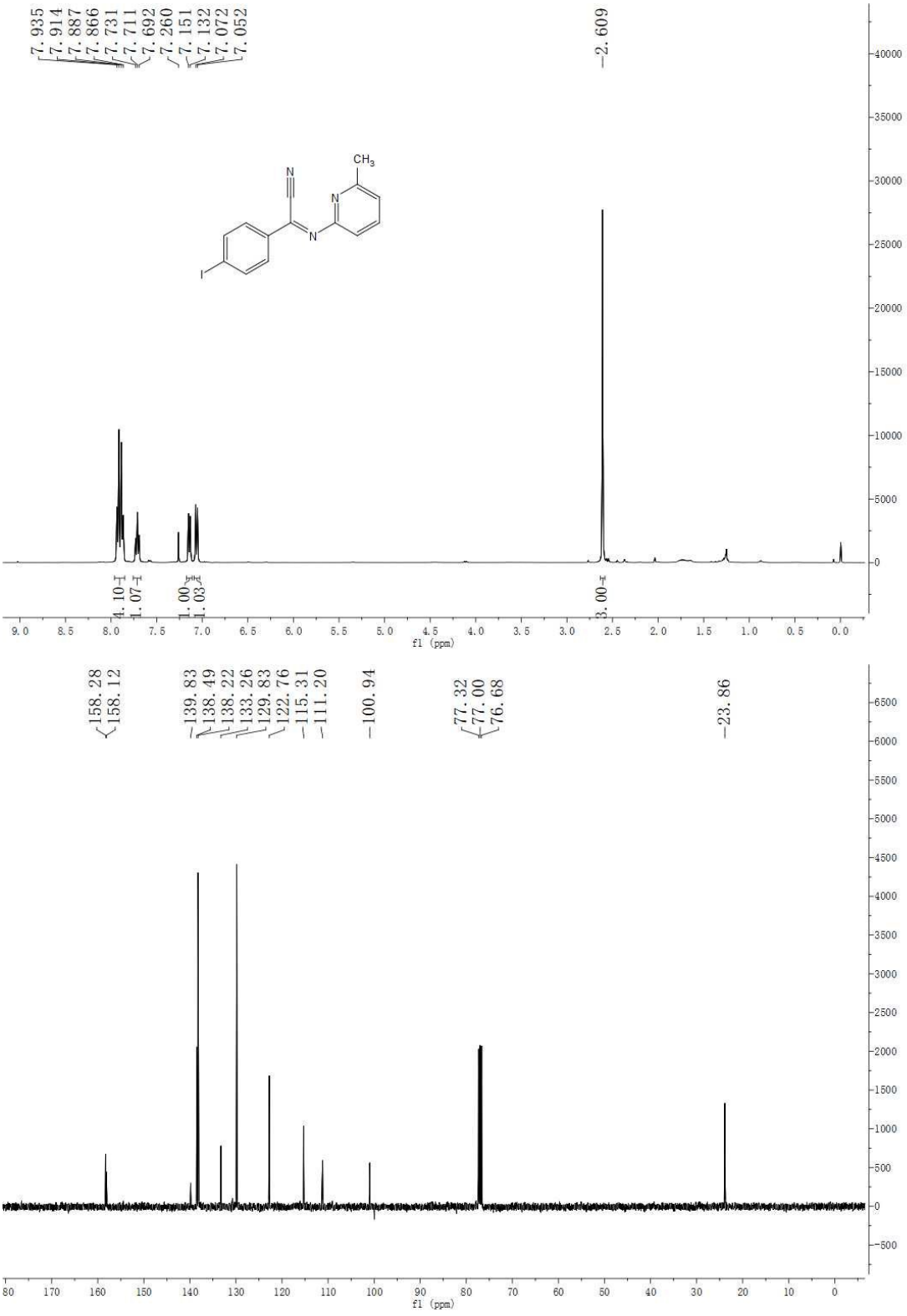


^{1}H NMR and ^{13}C NMR of (Z)-4-iodo-*N*-(pyridin-2-yl)benzimidoyl cyanide (1h)

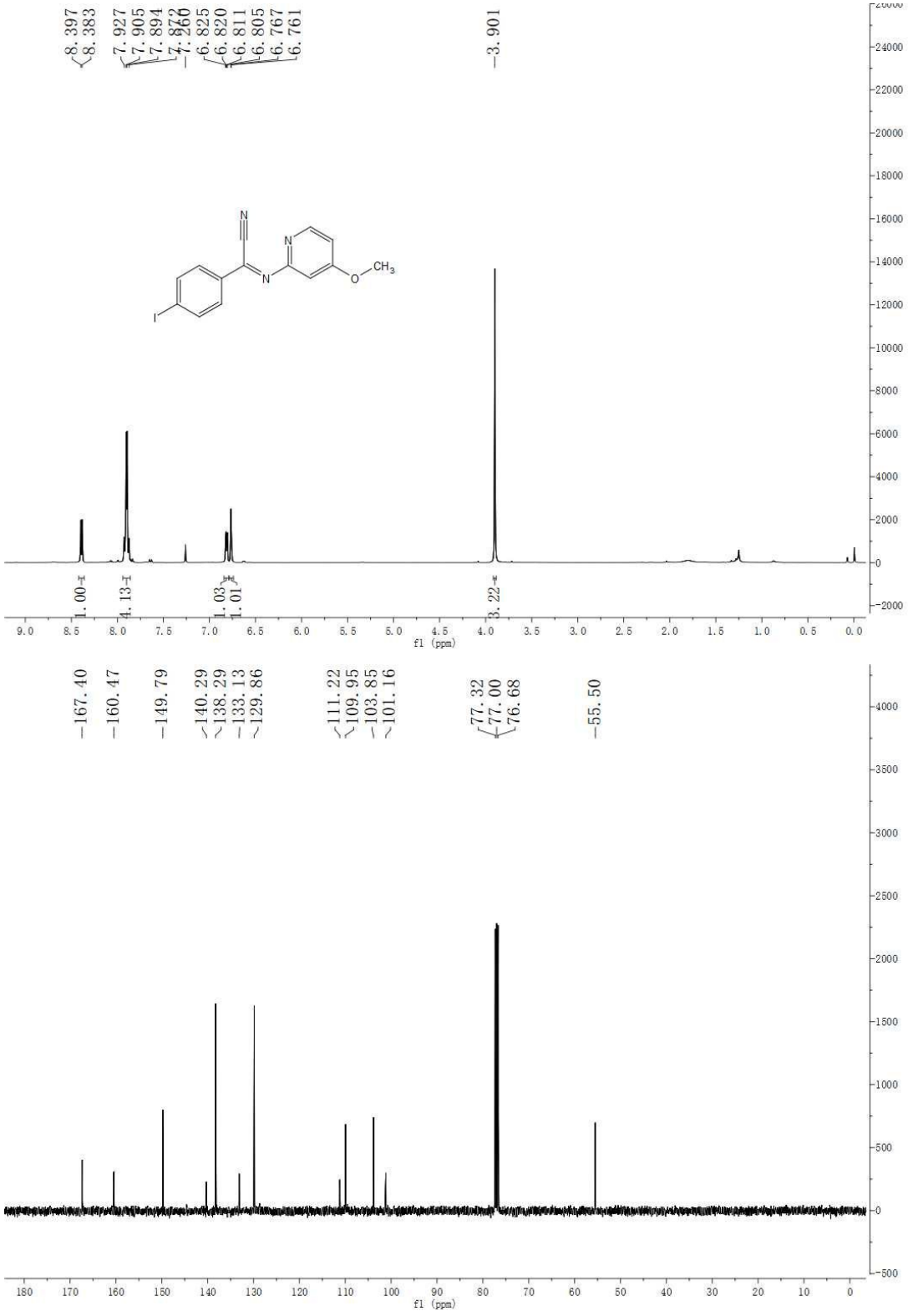




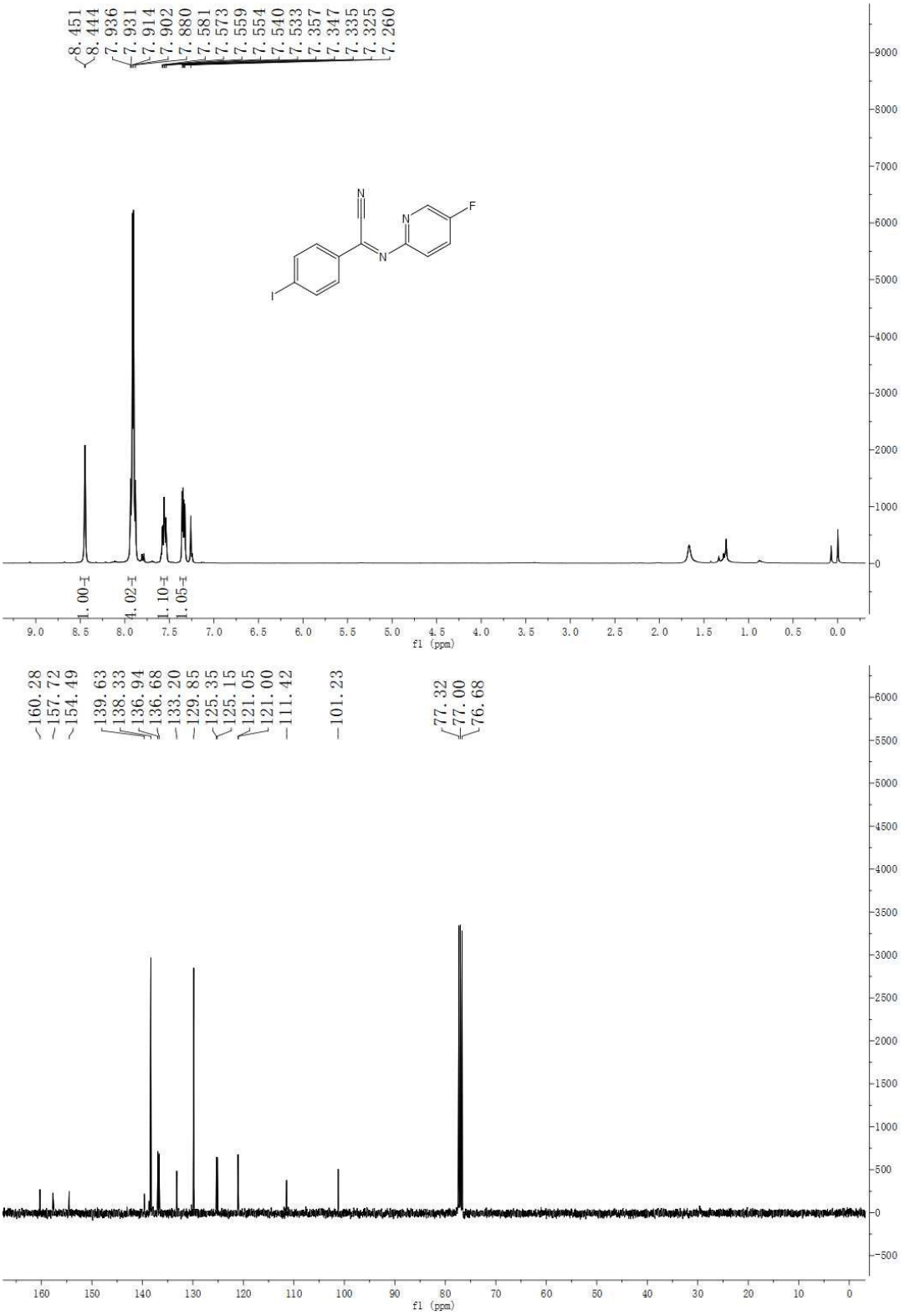
^{1}H NMR and ^{13}C NMR of (Z)-4-iodo-*N*-(6-methylpyridin-2-yl)benzimidoyl cyanide (1i)



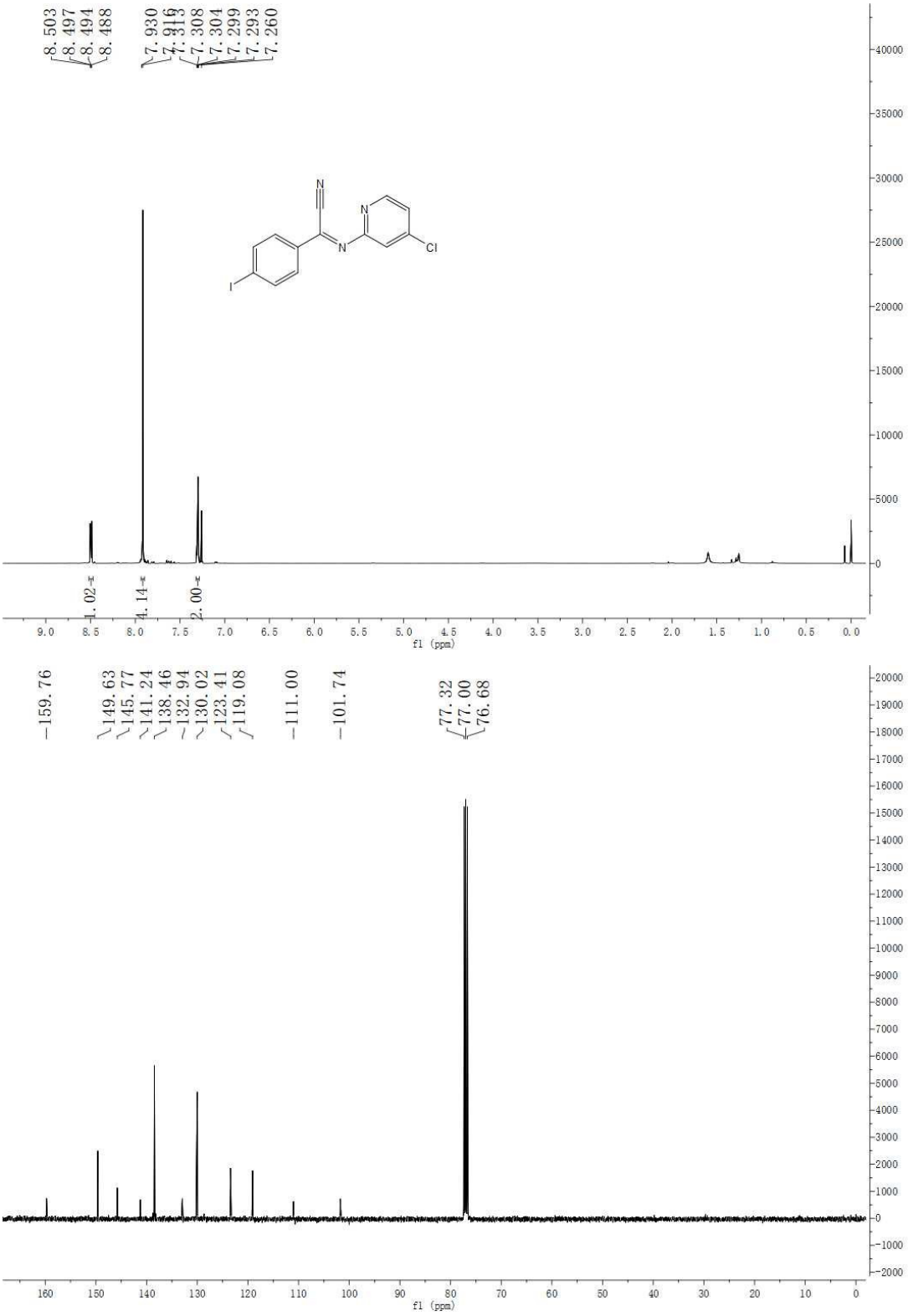
^{1}H NMR and ^{13}C NMR of (Z)-4-iodo-*N*-(4-methoxypyridin-2-yl)benzimidoyl cyanide (1j)



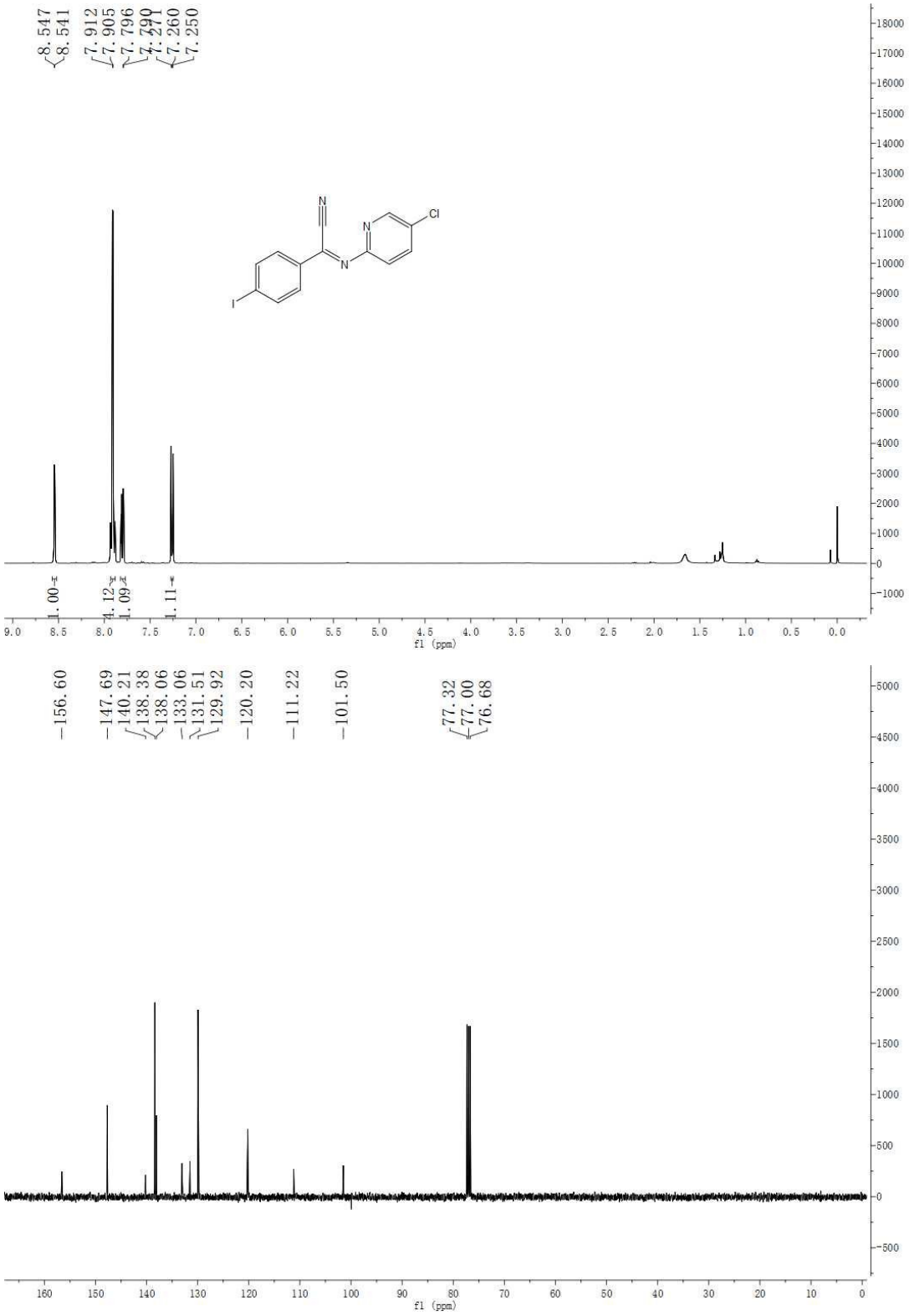
^{1}H NMR and ^{13}C NMR of (Z)-*N*-(5-fluoropyridin-2-yl)-4-iodobenzimidoyl cyanide (1k)



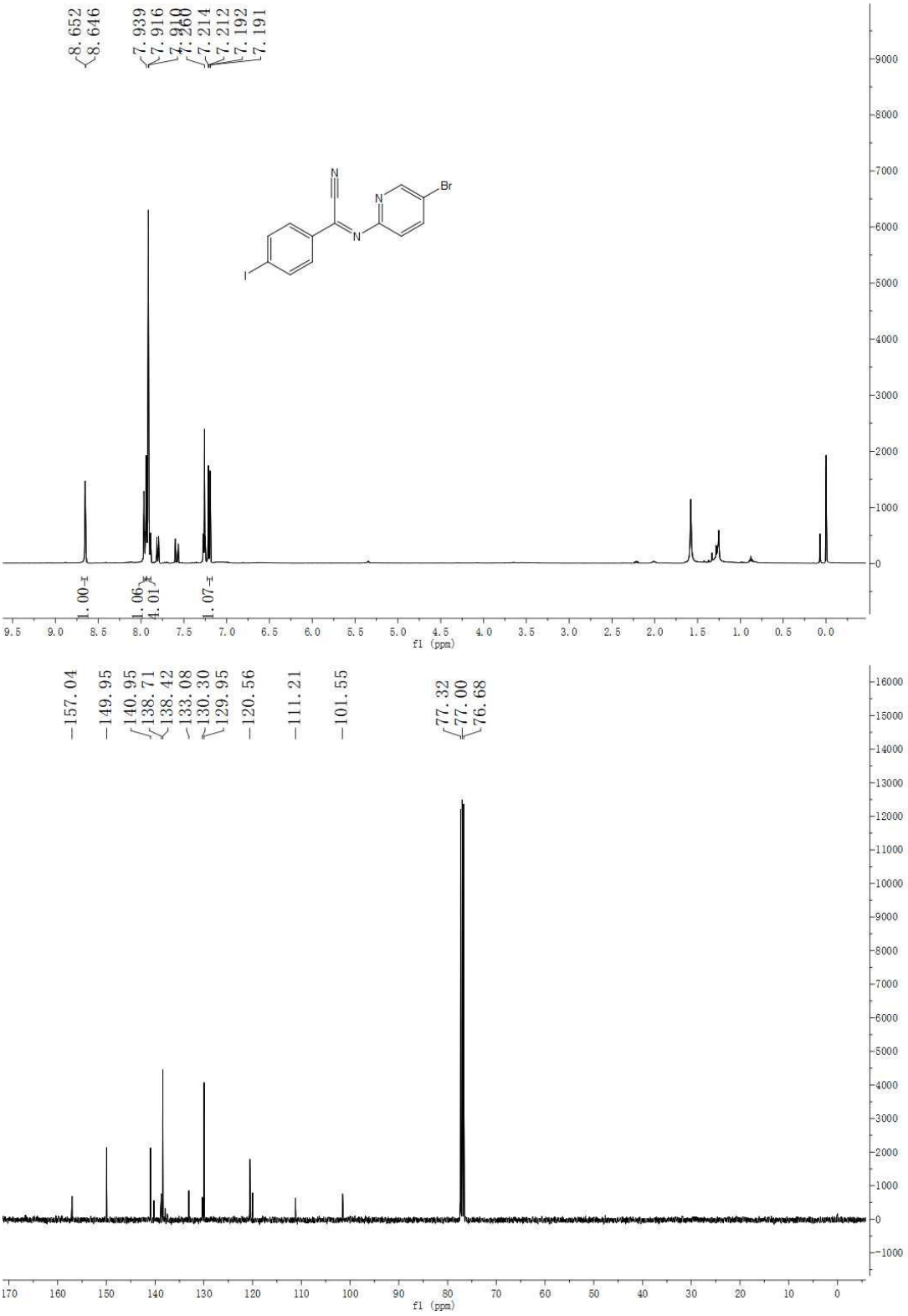
^{1}H NMR and ^{13}C NMR of (Z)-*N*-(4-chloropyridin-2-yl)-4-iodobenzimidoyl cyanide (1l)



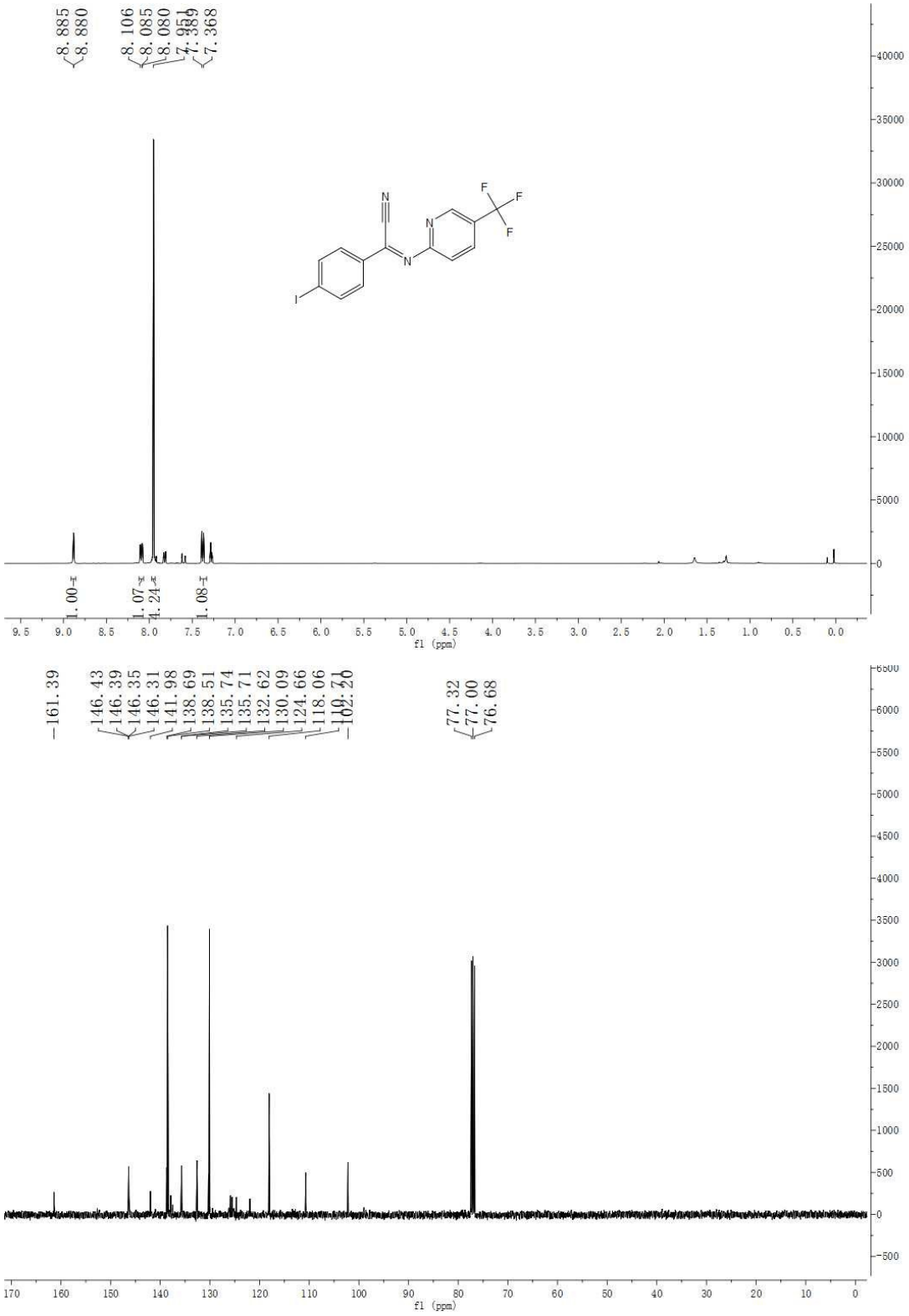
^{1}H NMR and ^{13}C NMR of (Z)-*N*-(5-chloropyridin-2-yl)-4-iodobenzimidoyl cyanide (1m)



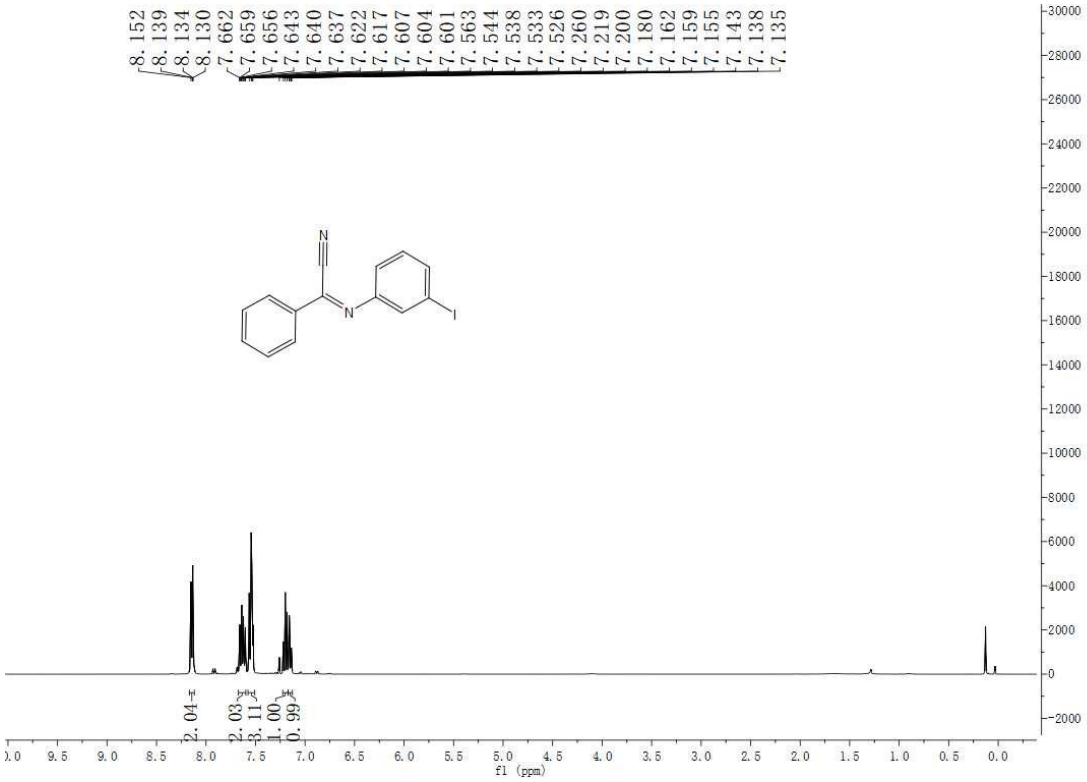
^{1}H NMR and ^{13}C NMR of (Z)-*N*-(5-bromopyridin-2-yl)-4-iodobenzimidoyl cyanide (1n)

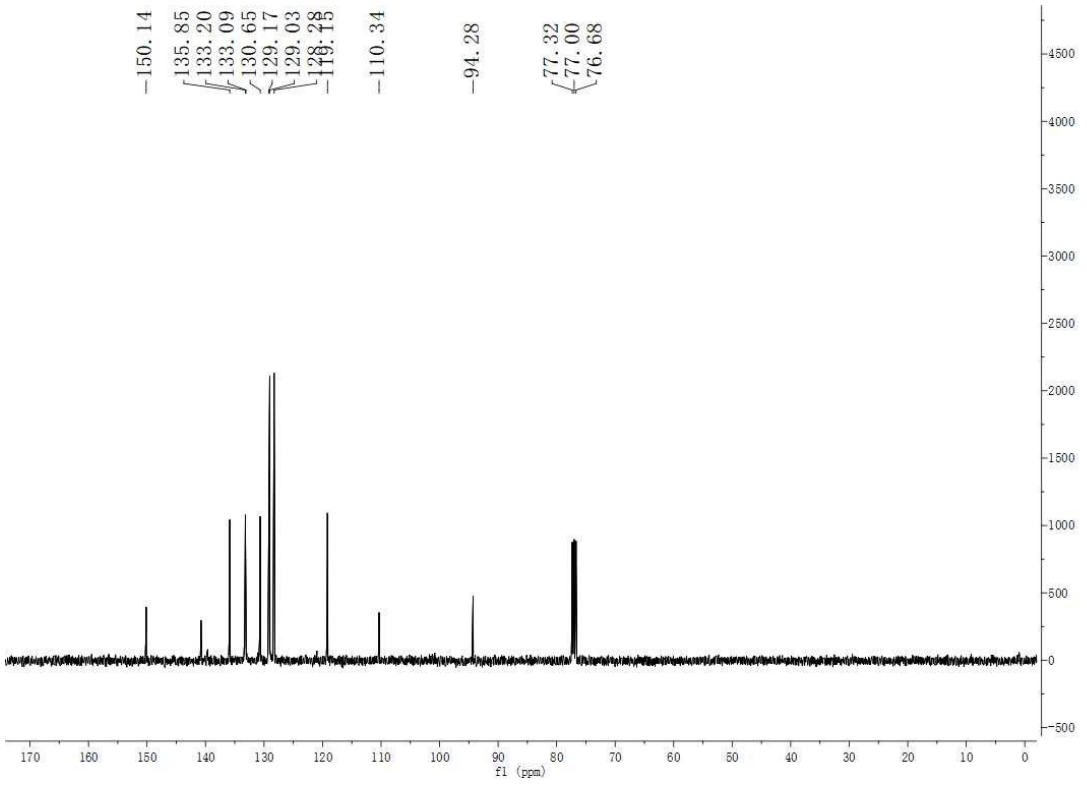


^{1}H NMR and ^{13}C NMR of (Z)-4-iodo-*N*-(5-(trifluoromethyl)pyridin-2-yl)benzimidoyl cyanide (1o)

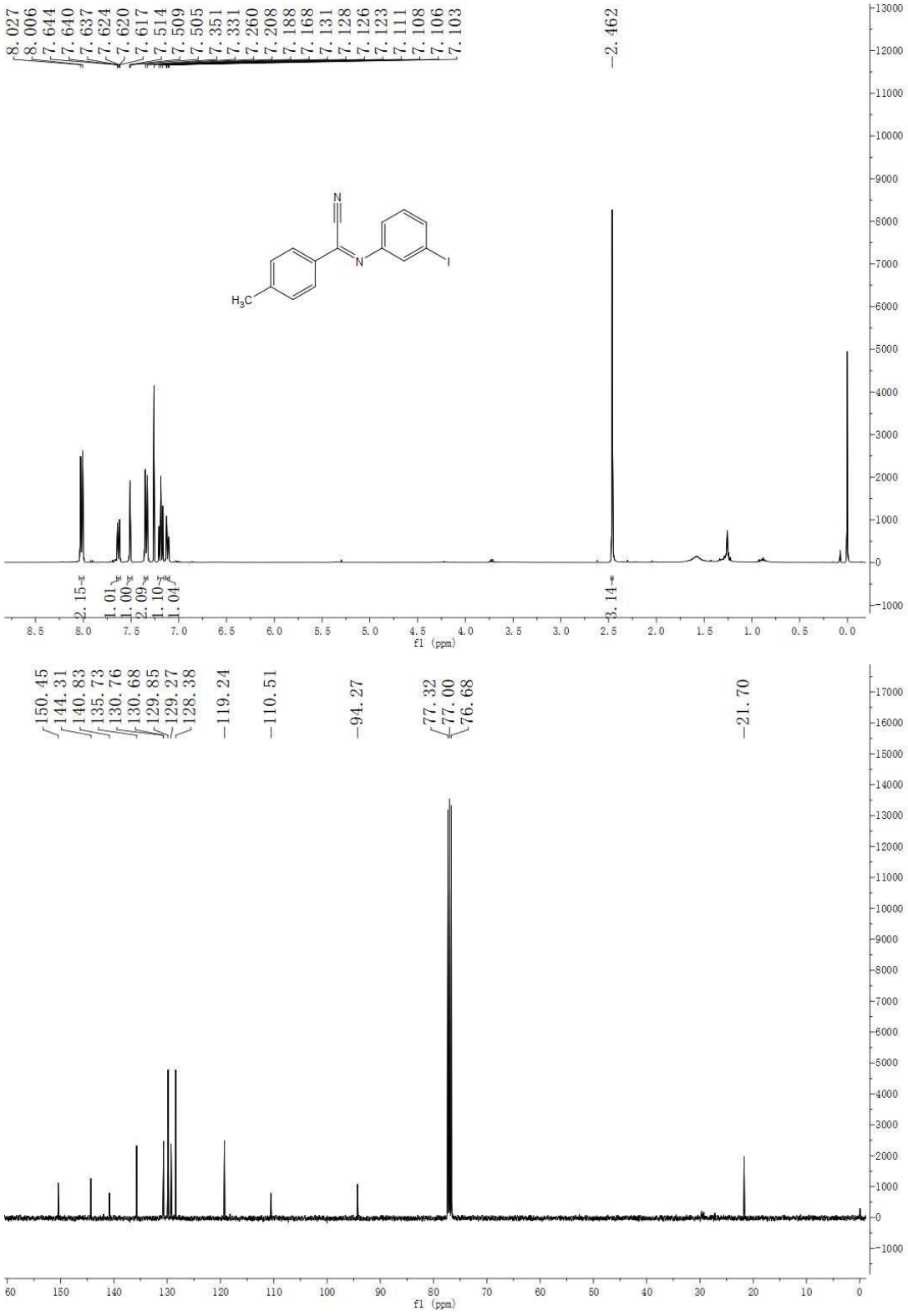


^{1}H NMR and ^{13}C NMR of (Z)-*N*-(3-iodophenyl)benzimidoyl cyanide (1p)

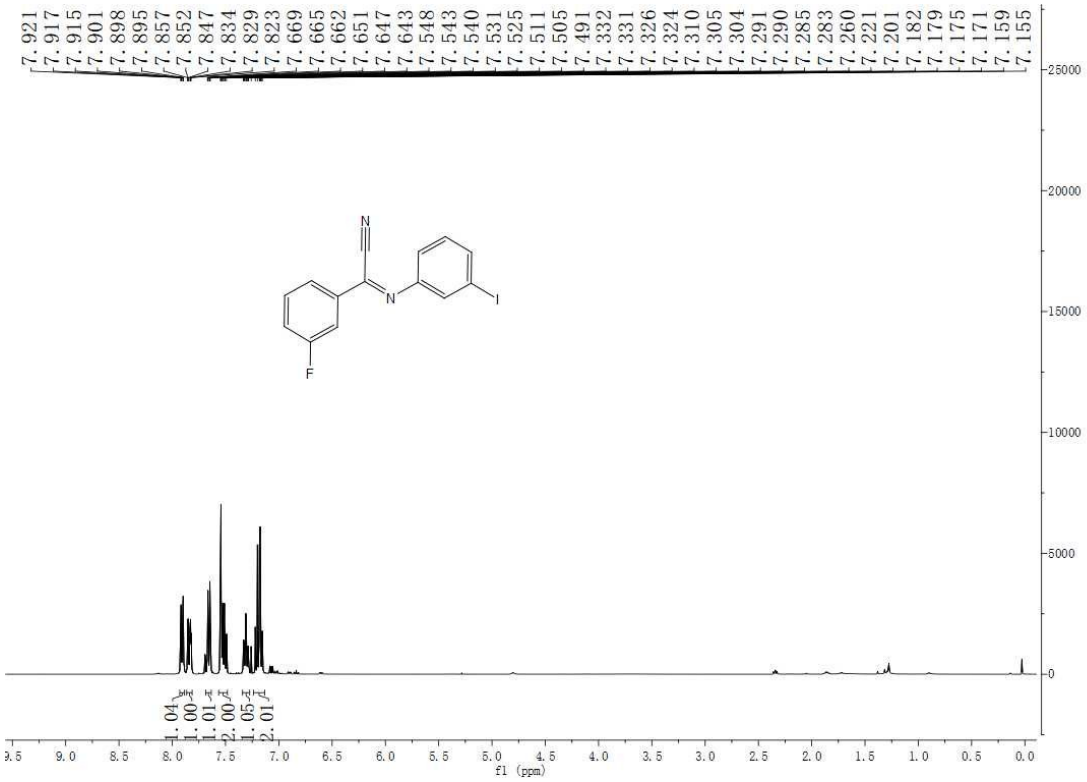


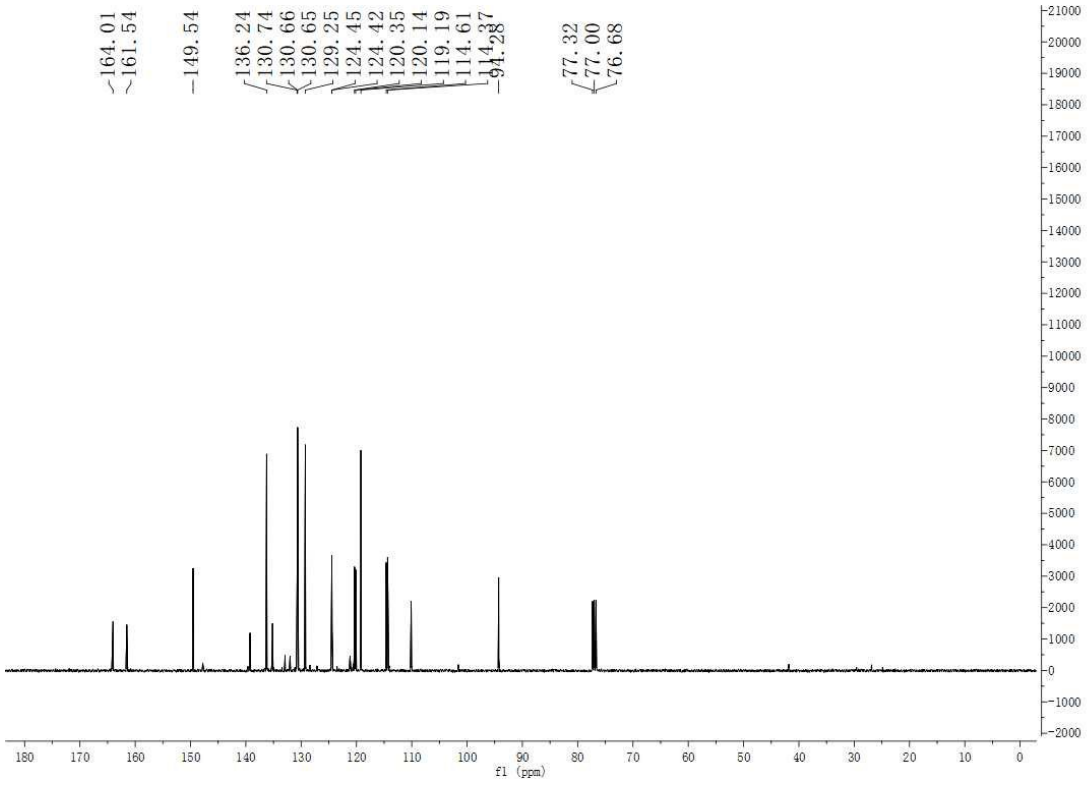


^{1}H NMR and ^{13}C NMR of (Z)-*N*-(3-iodophenyl)-4-methylbenzimidoyl cyanide (1q)

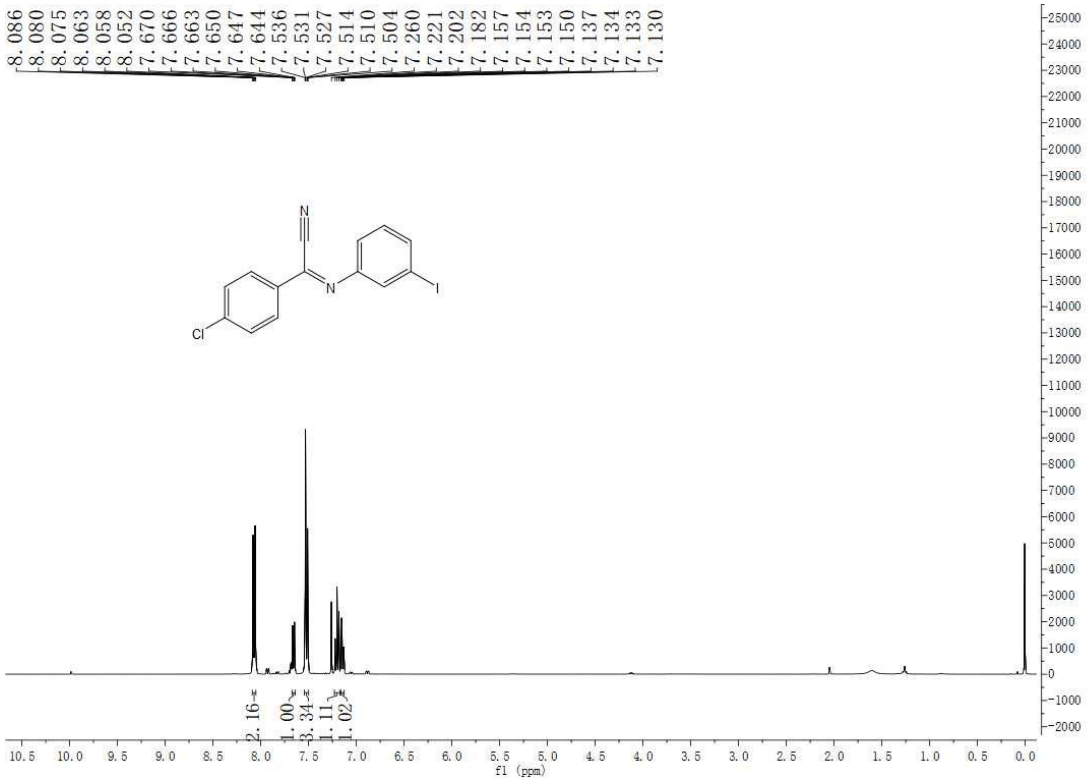


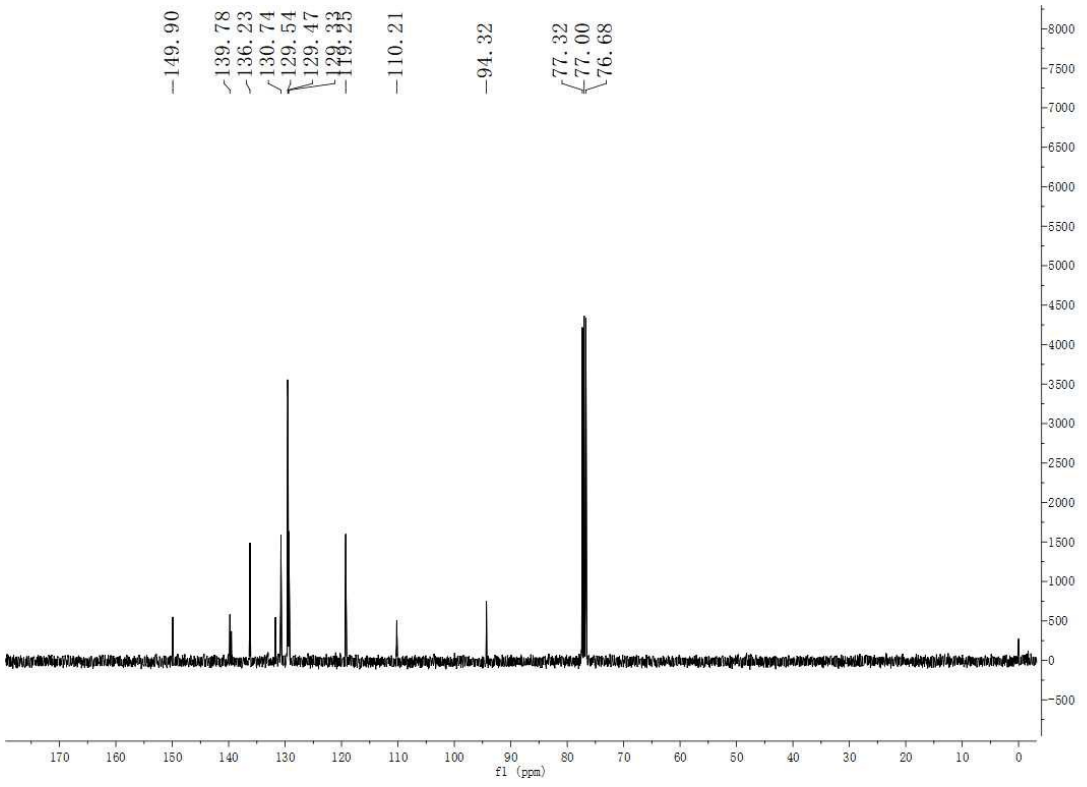
^{1}H NMR and ^{13}C NMR of (Z)-3-fluoro-*N*-(3-iodophenyl)benzimidoyl cyanide (1r)



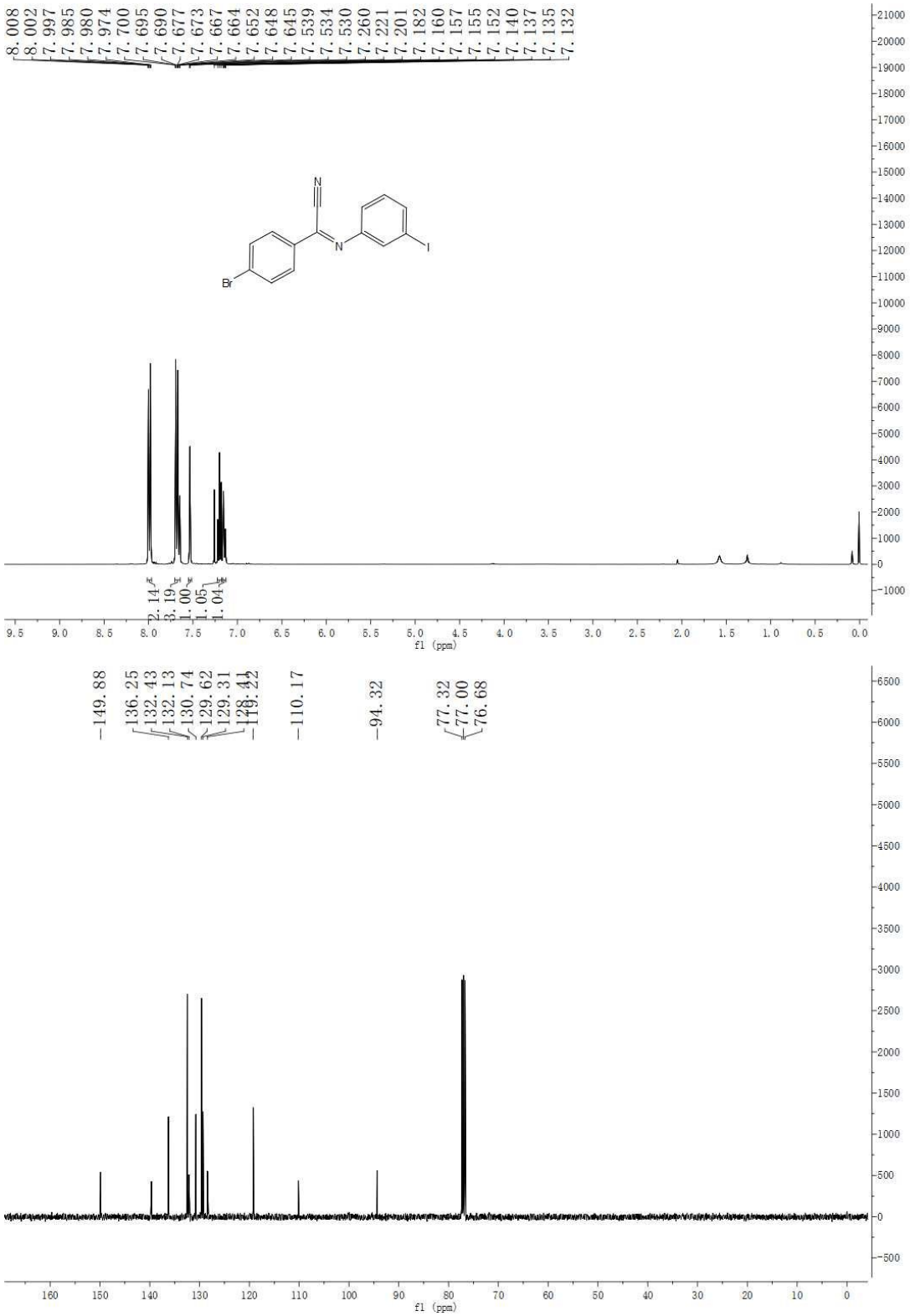


^{1}H NMR and ^{13}C NMR of (Z)-4-chloro-*N*-(3-iodophenyl)benzimidoyl cyanide (1s)

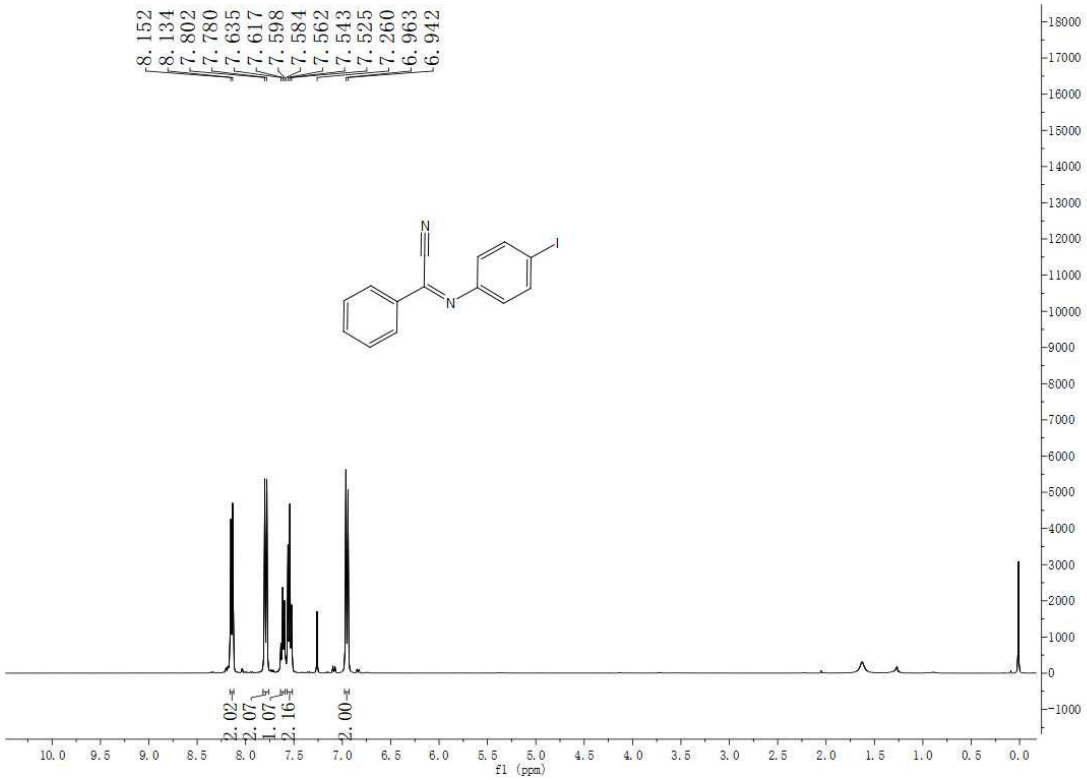


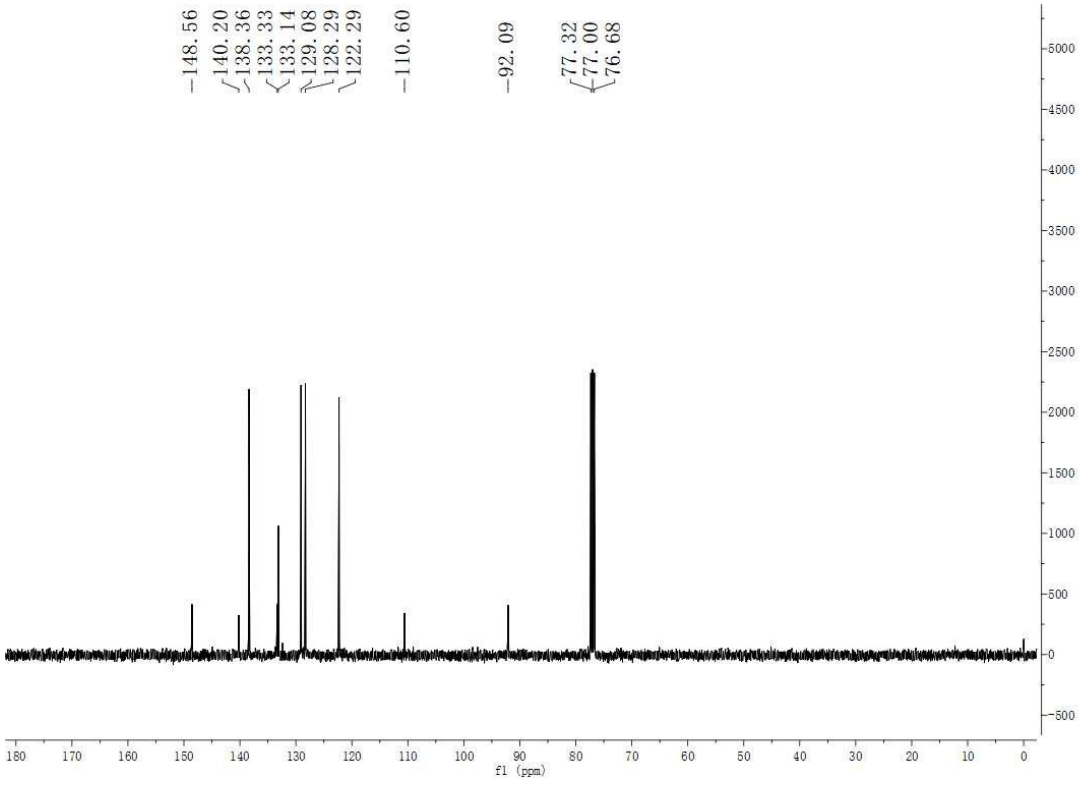


^{1}H NMR and ^{13}C NMR of (Z)-4-bromo-*N*-(3-iodophenyl)benzimidoyl cyanide (1t)



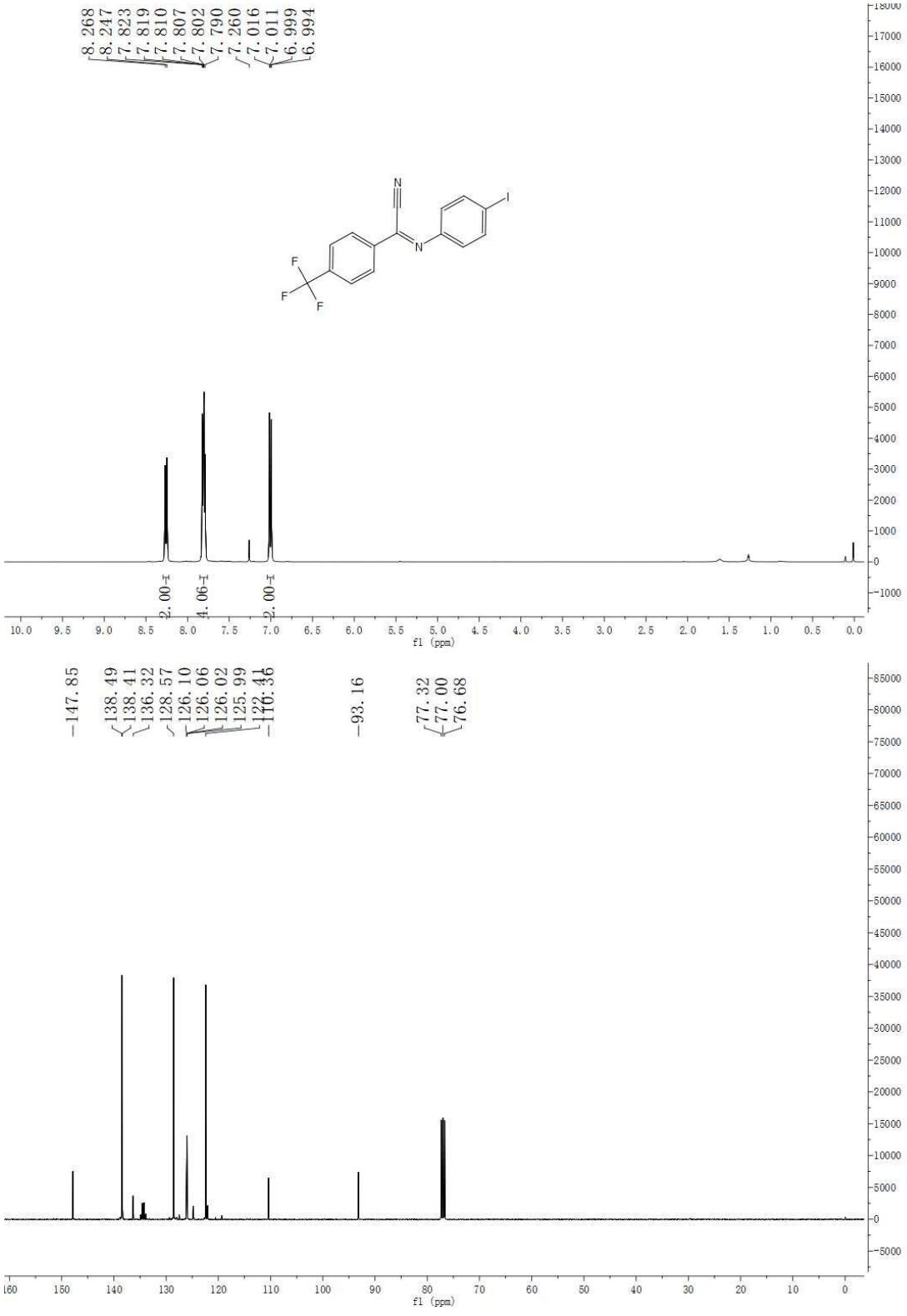
^{1}H NMR and ^{13}C NMR of (Z)-*N*-(4-iodophenyl)benzimidoyl cyanide (1u)





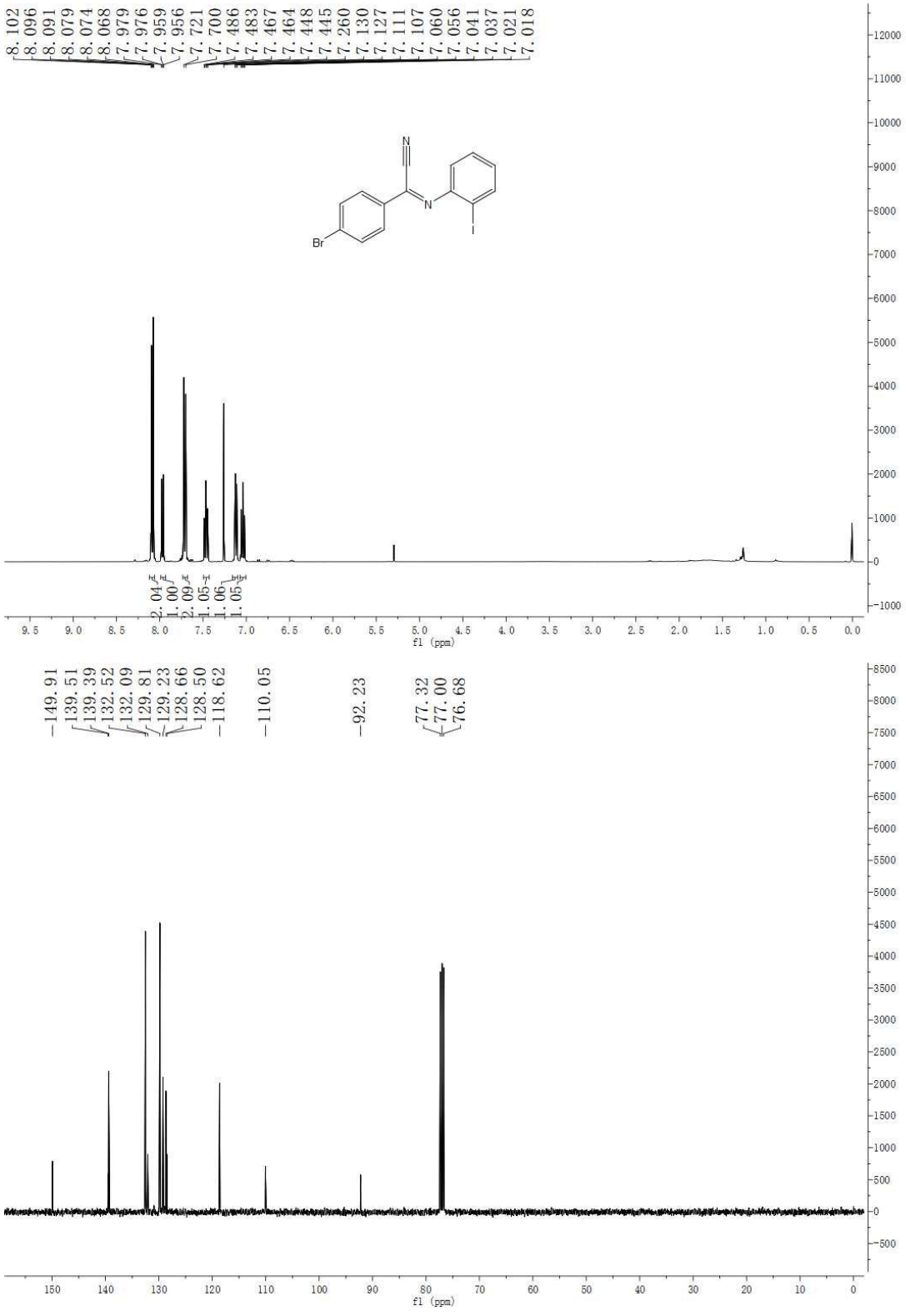
^{1}H NMR and ^{13}C NMR of (Z)-*N*-(4-iodophenyl)-4-(trifluoromethyl)benzimidoyl

cyanide (1v)

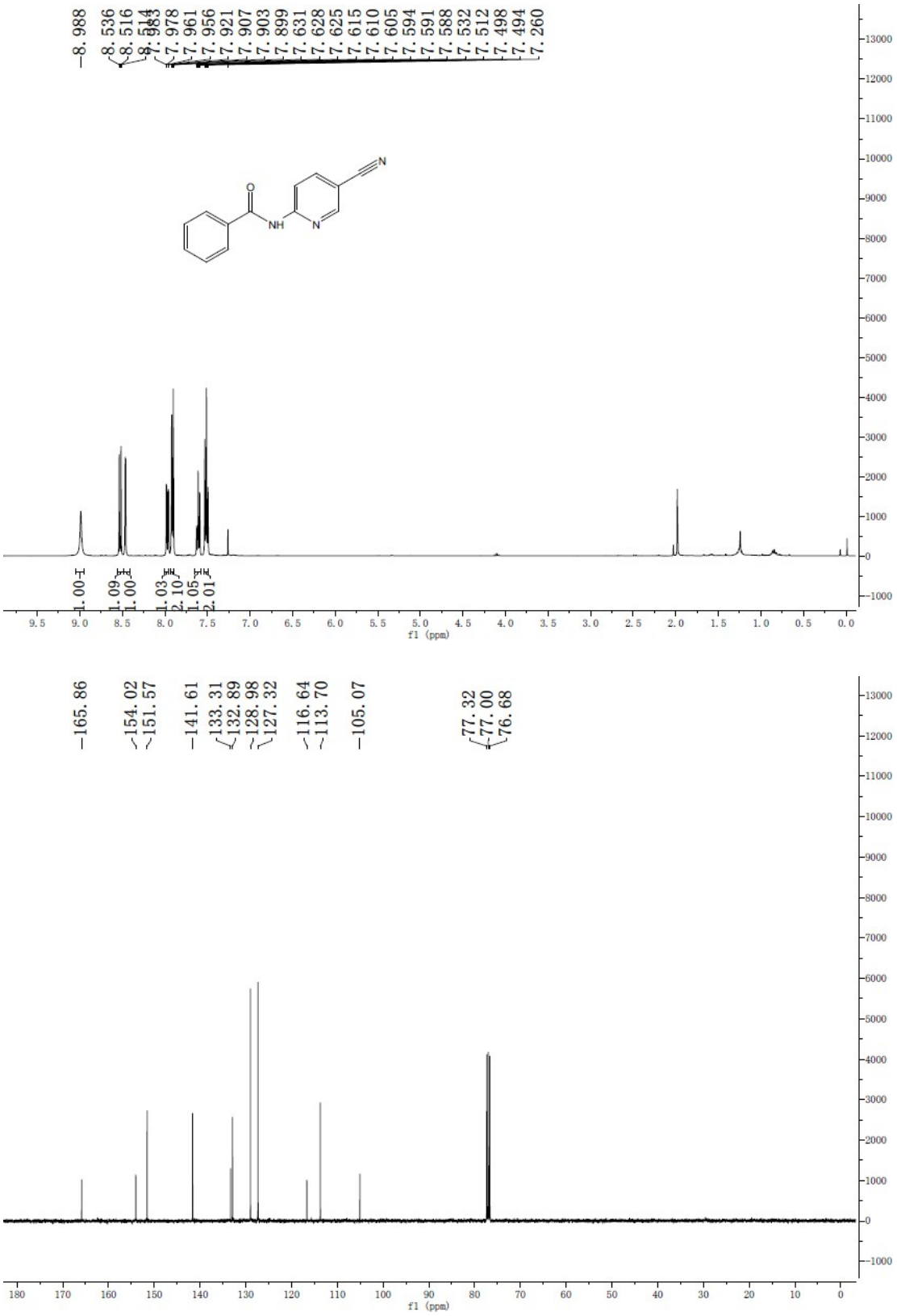


^{1}H NMR and ^{13}C NMR of (Z)-4-bromo-N-(2-iodophenyl)benzimidoyl cyanide

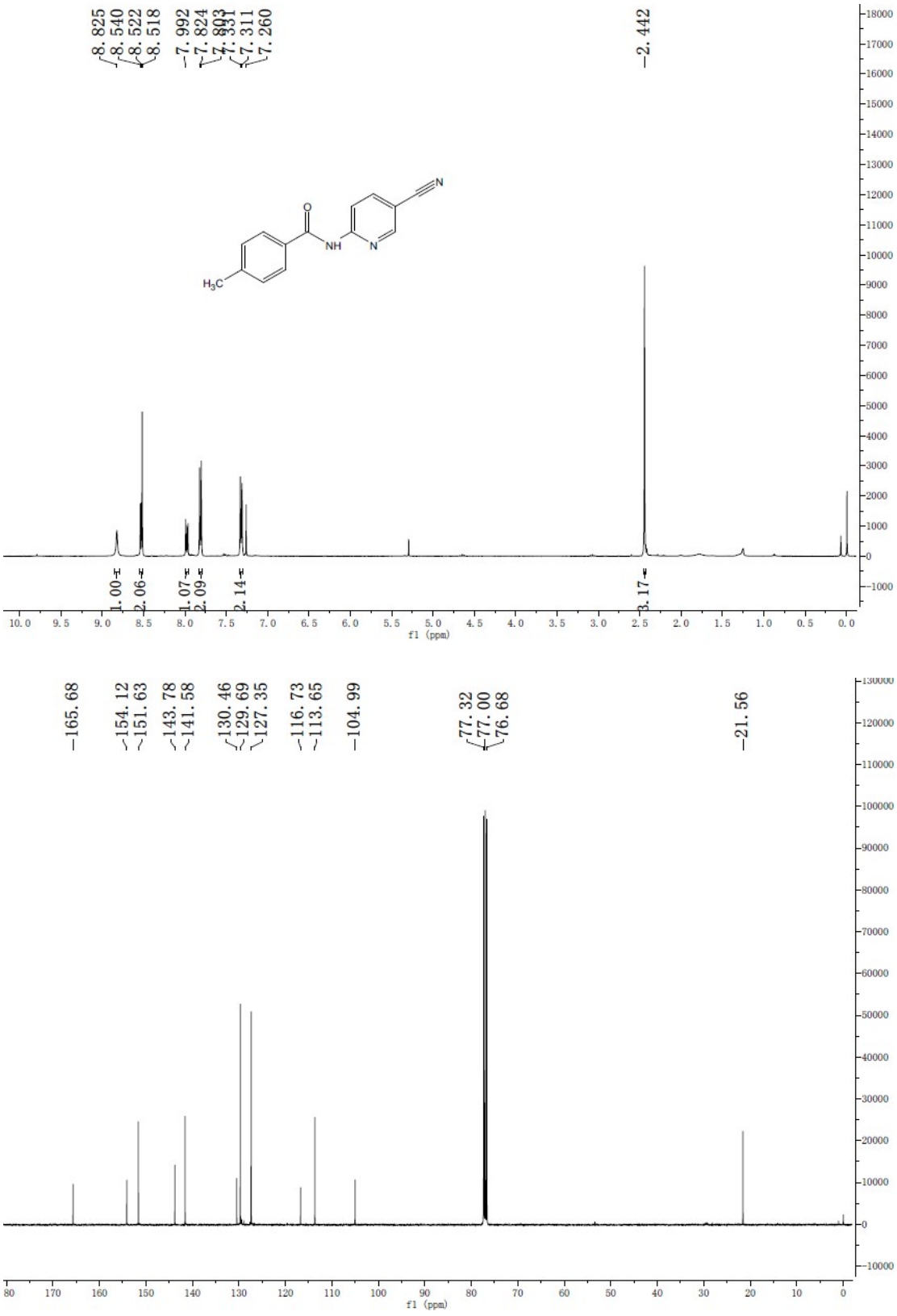
(1w)



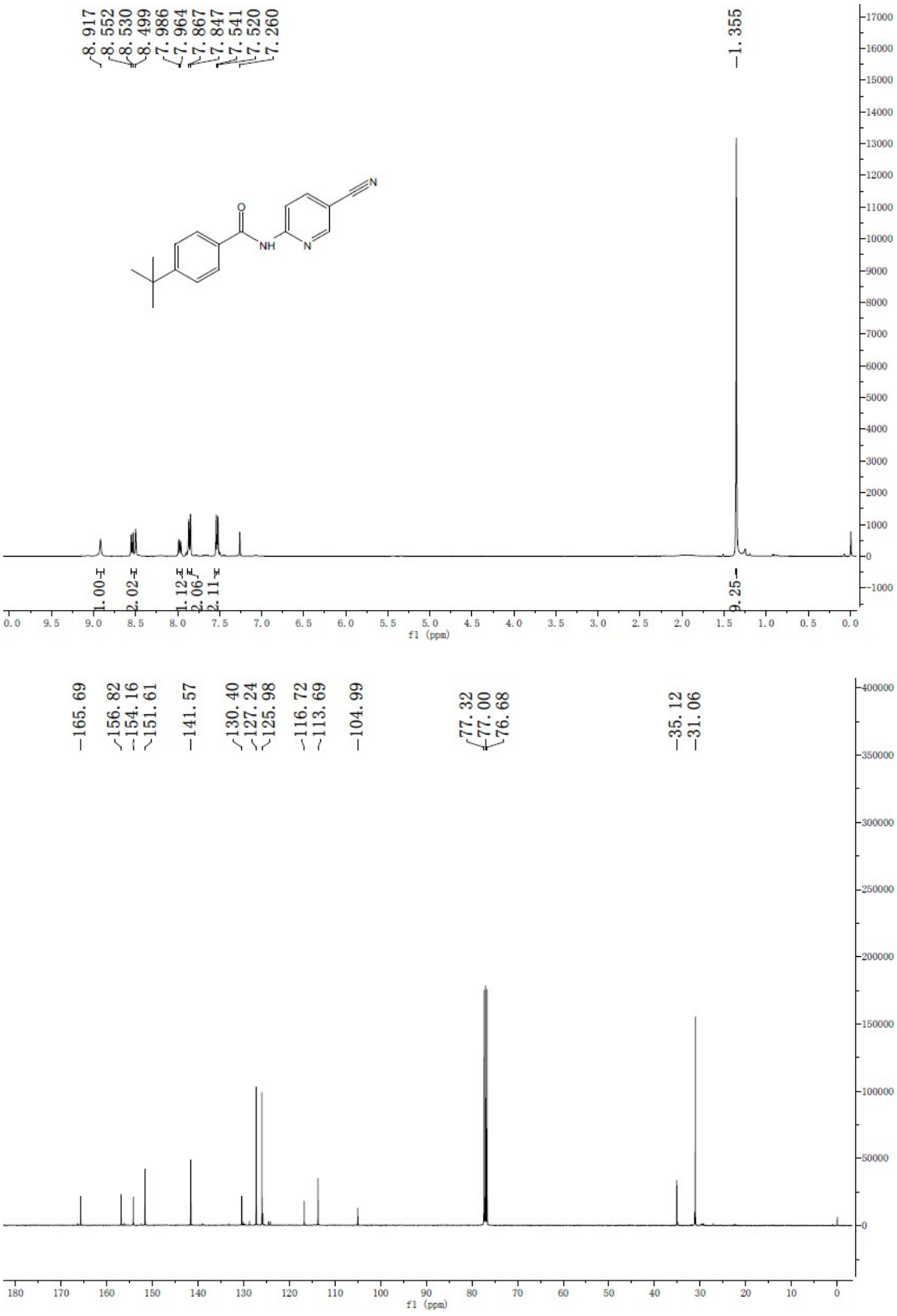
^{1}H NMR and ^{13}C NMR of N-(5-cyanopyridin-2-yl)benzamide (3a)



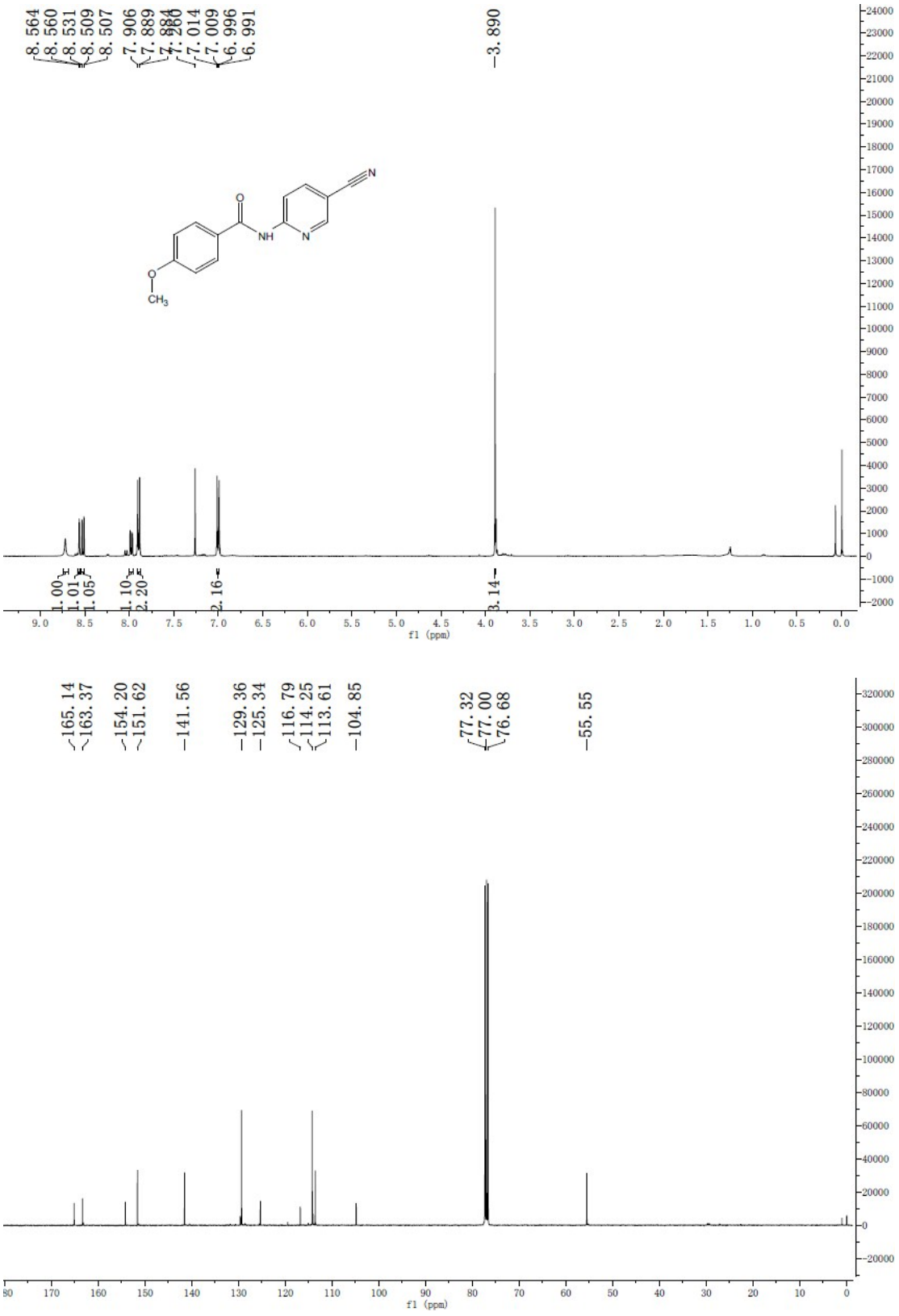
^{1}H NMR and ^{13}C NMR of N-(5-cyanopyridin-2-yl)-4-methylbenzamide (3b)



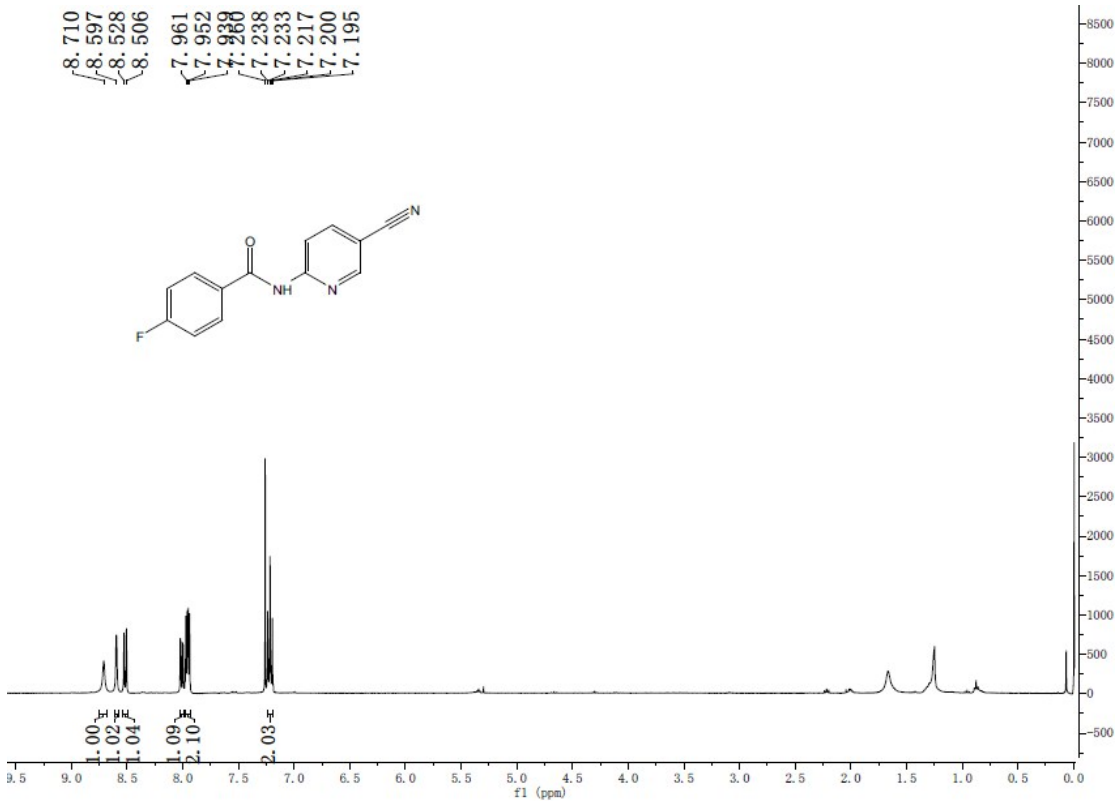
^{1}H NMR and ^{13}C NMR of 4-(tert-butyl)-N-(5-cyanopyridin-2-yl)benzamide (3c)

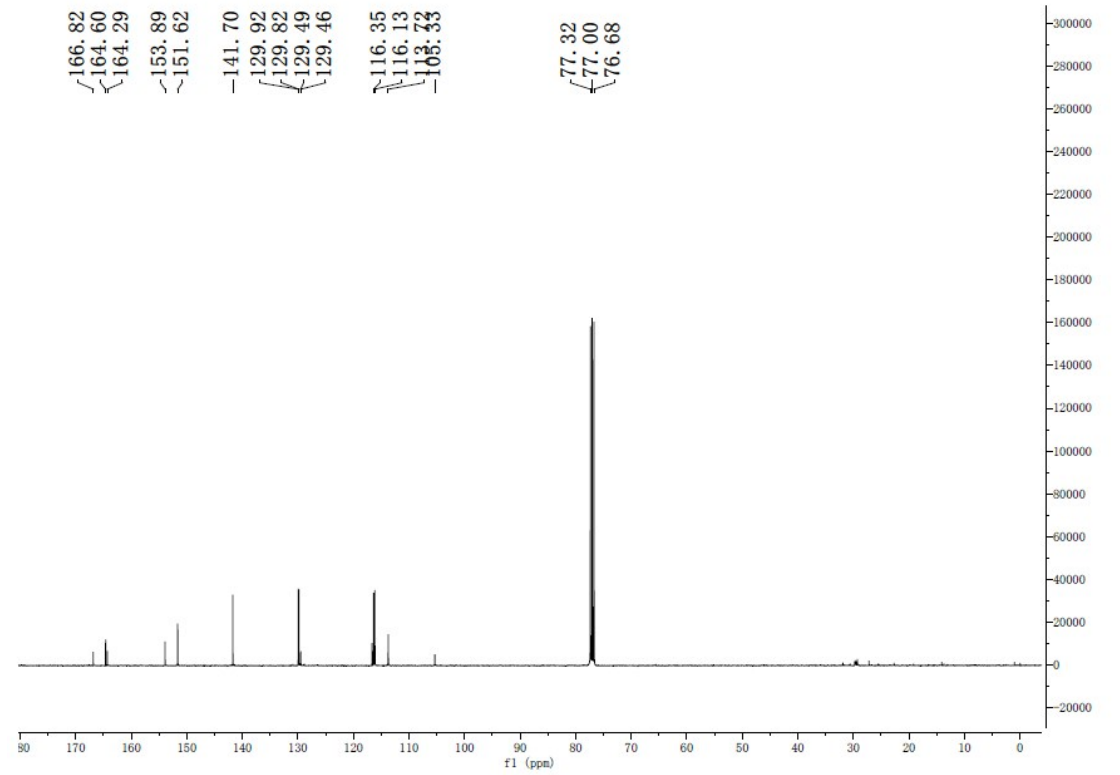


^{1}H NMR and ^{13}C NMR of N-(5-cyanopyridin-2-yl)-4-methoxybenzamide (3d)

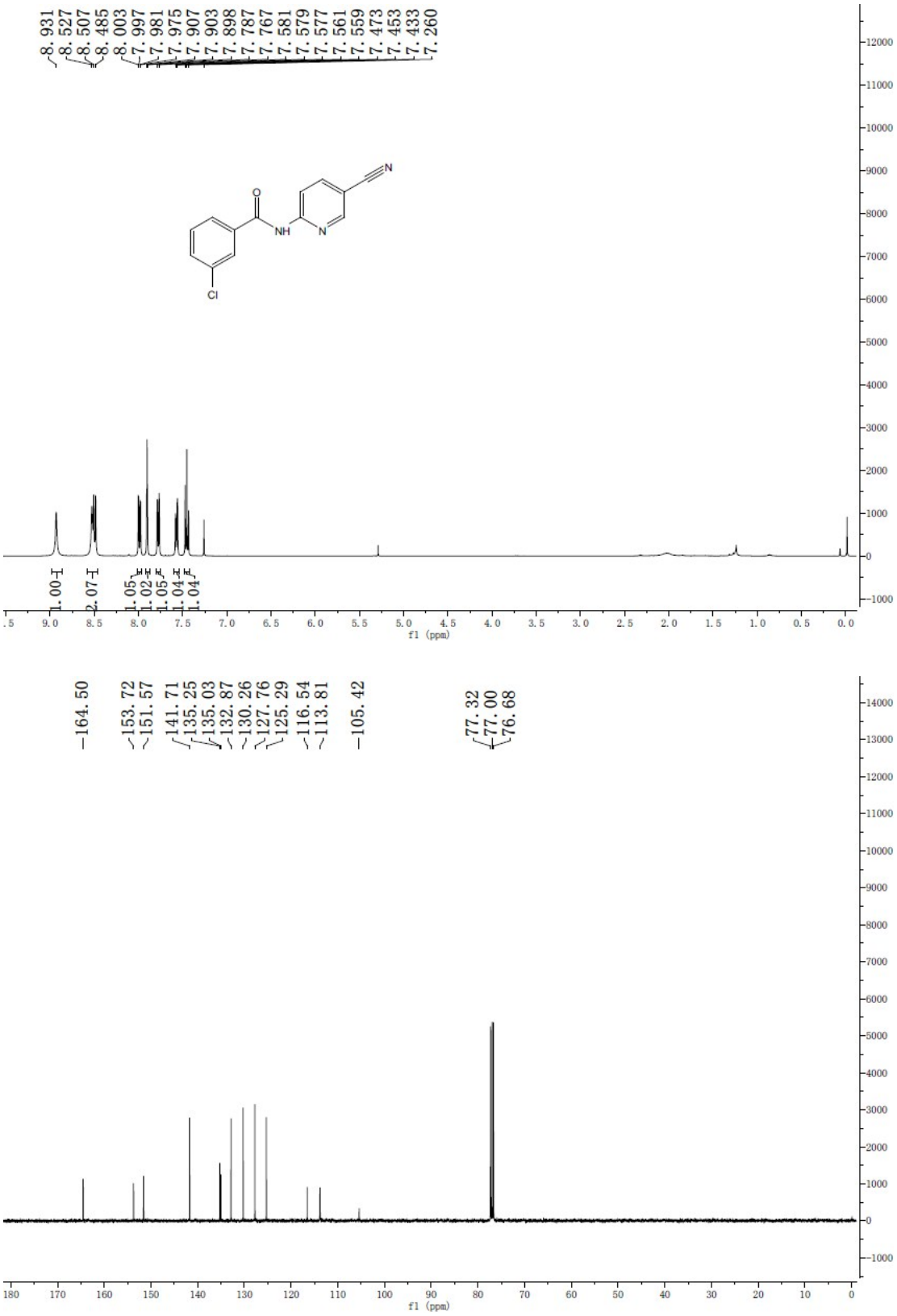


^{1}H NMR and ^{13}C NMR of N-(5-cyanopyridin-2-yl)-4-fluorobenzamide (3e)

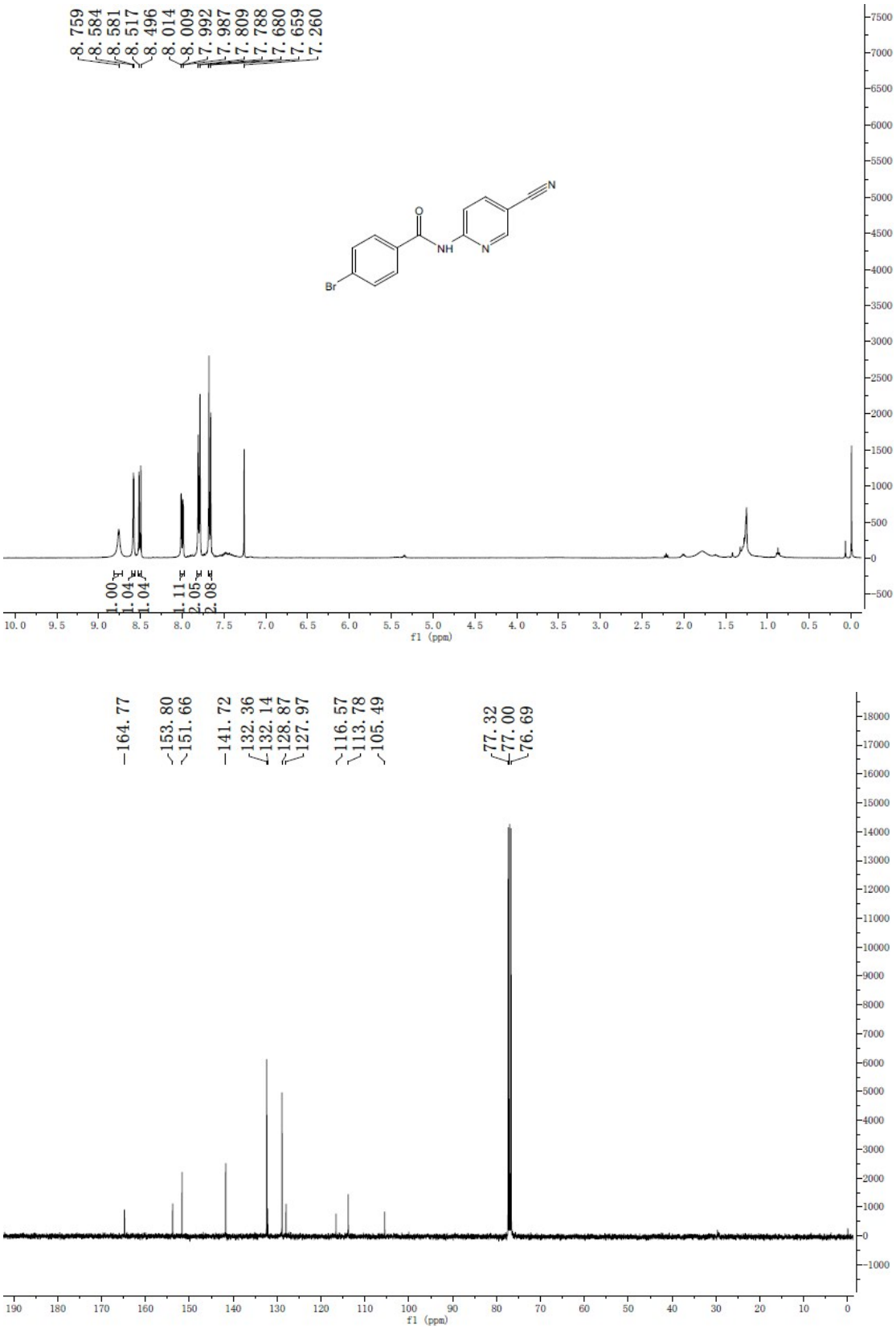




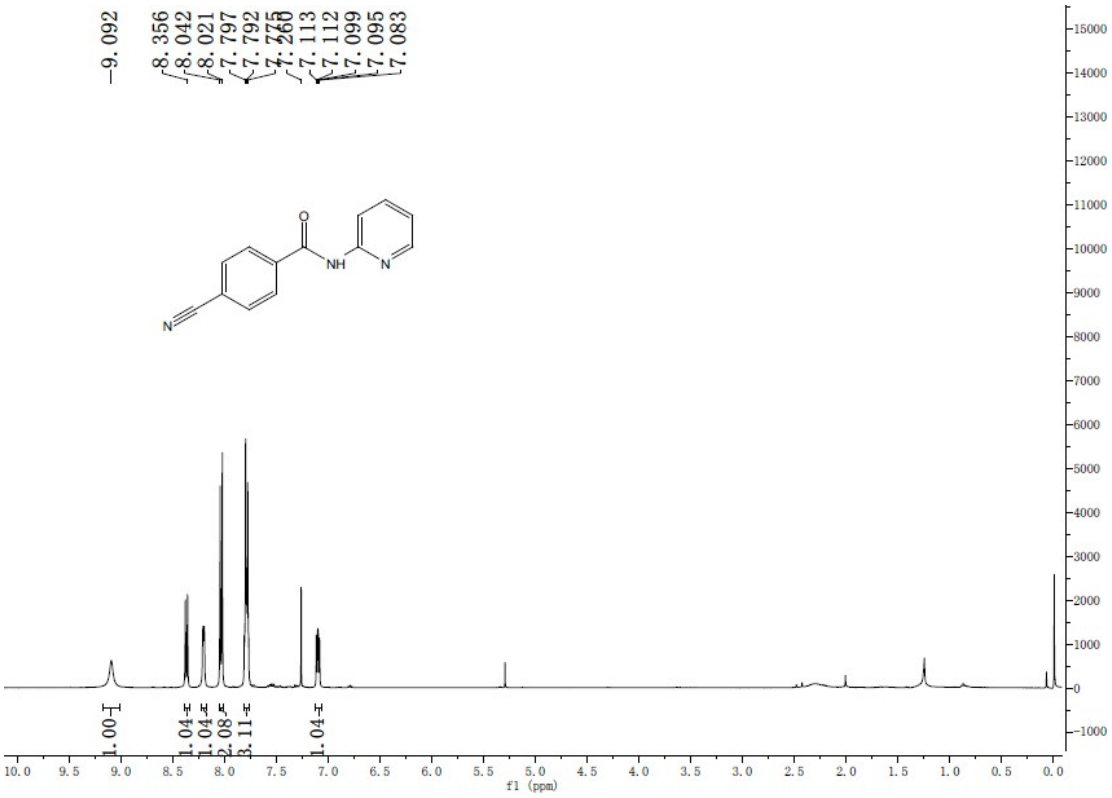
^{1}H NMR and ^{13}C NMR of 3-chloro-N-(5-cyanopyridin-2-yl)benzamide (3f)

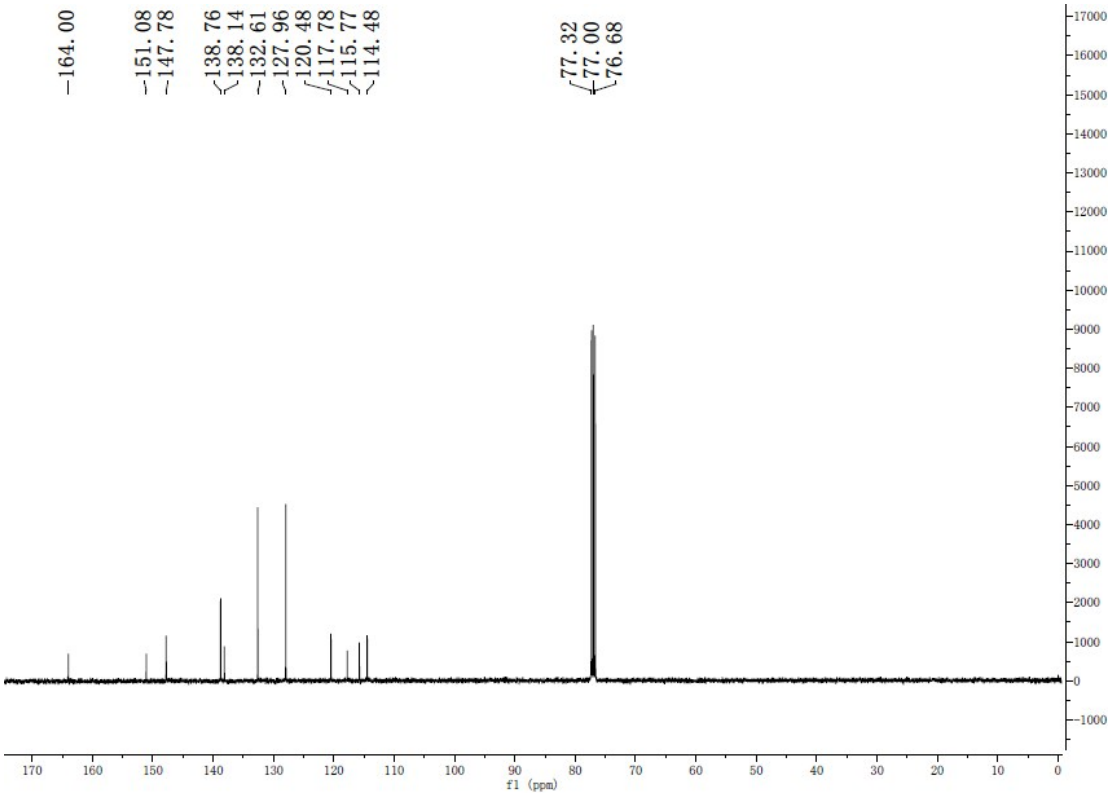


^{1}H NMR and ^{13}C NMR of 4-bromo-N-(5-cyanopyridin-2-yl)benzamide (3g)

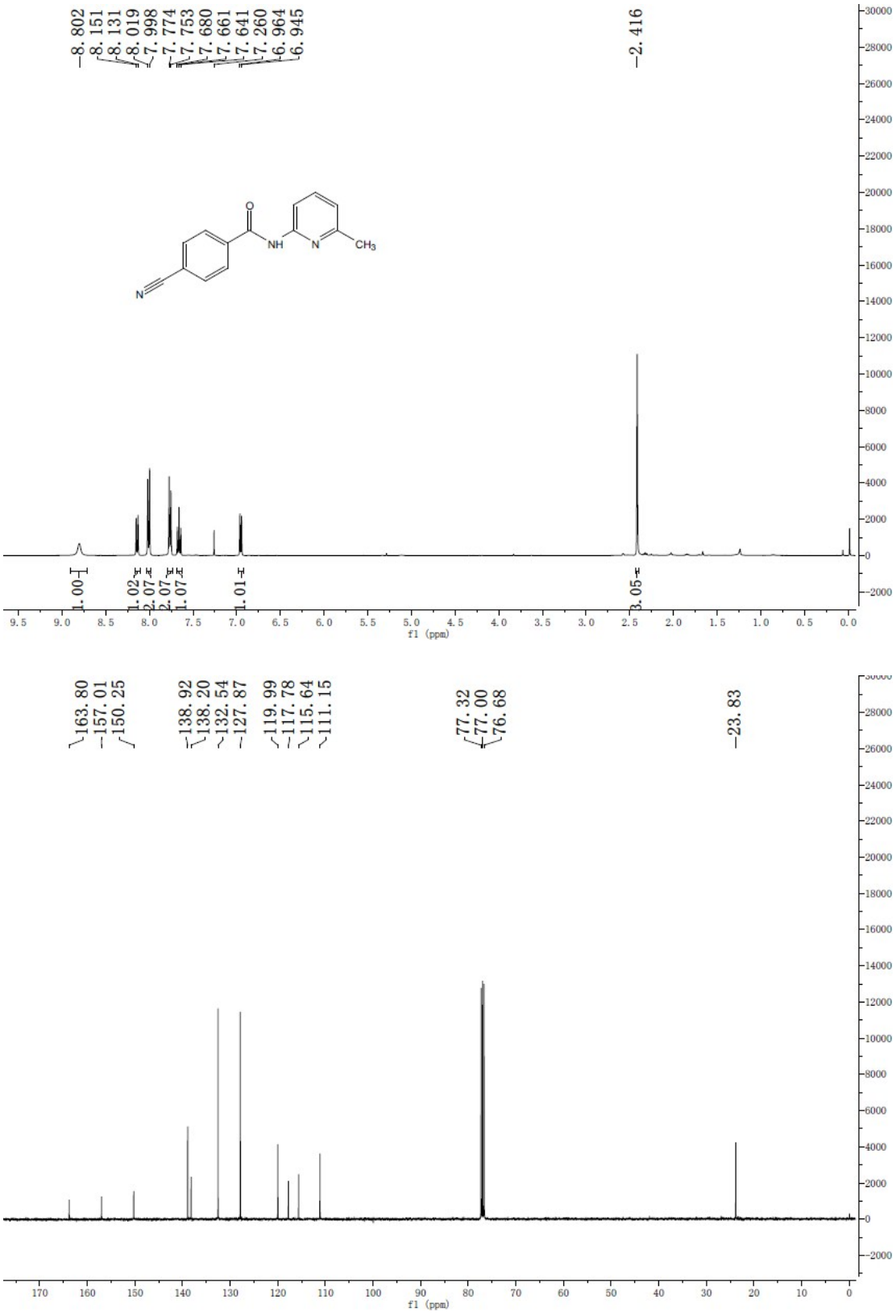


^{1}H NMR and ^{13}C NMR of 4-cyano-N-(pyridin-2-yl)benzamide (4a)

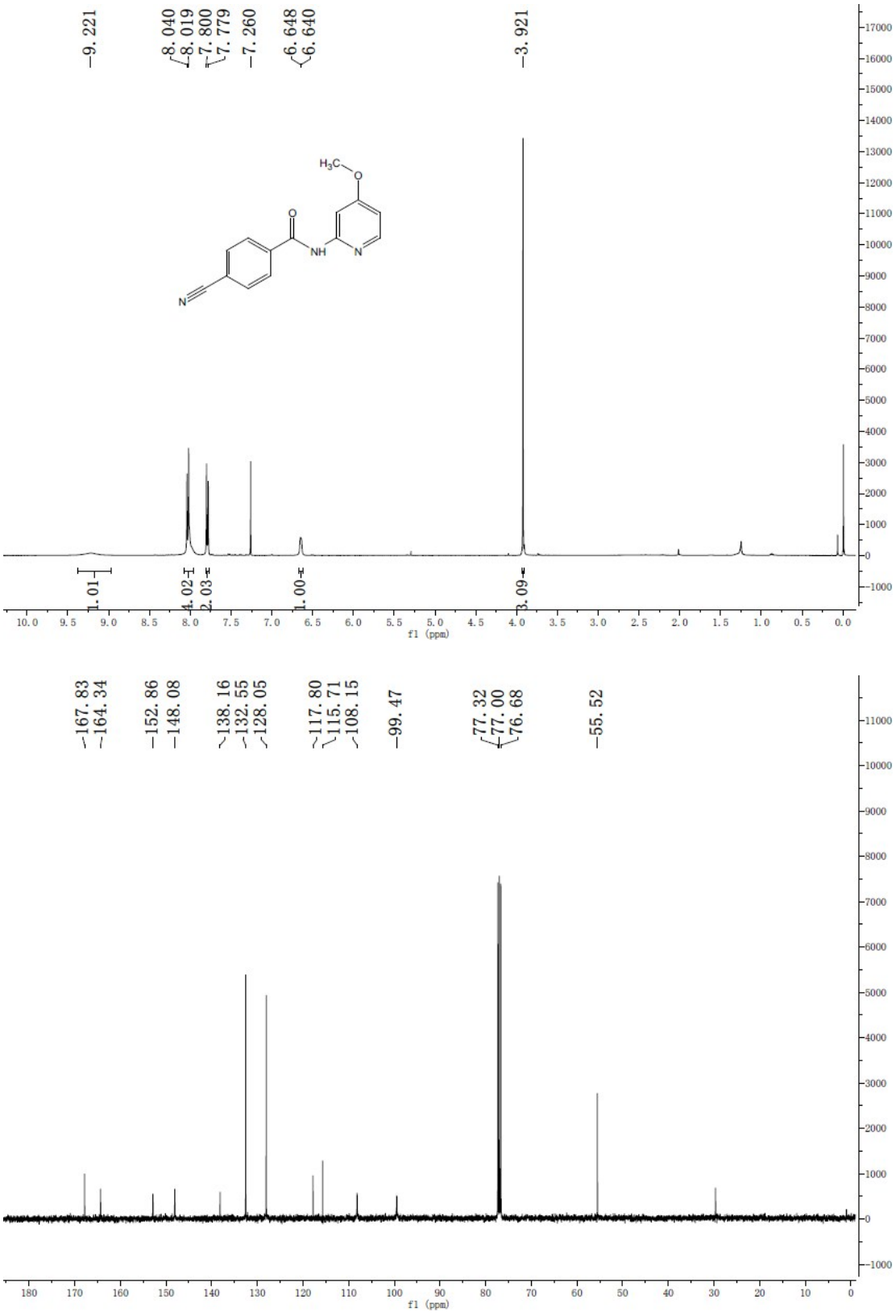




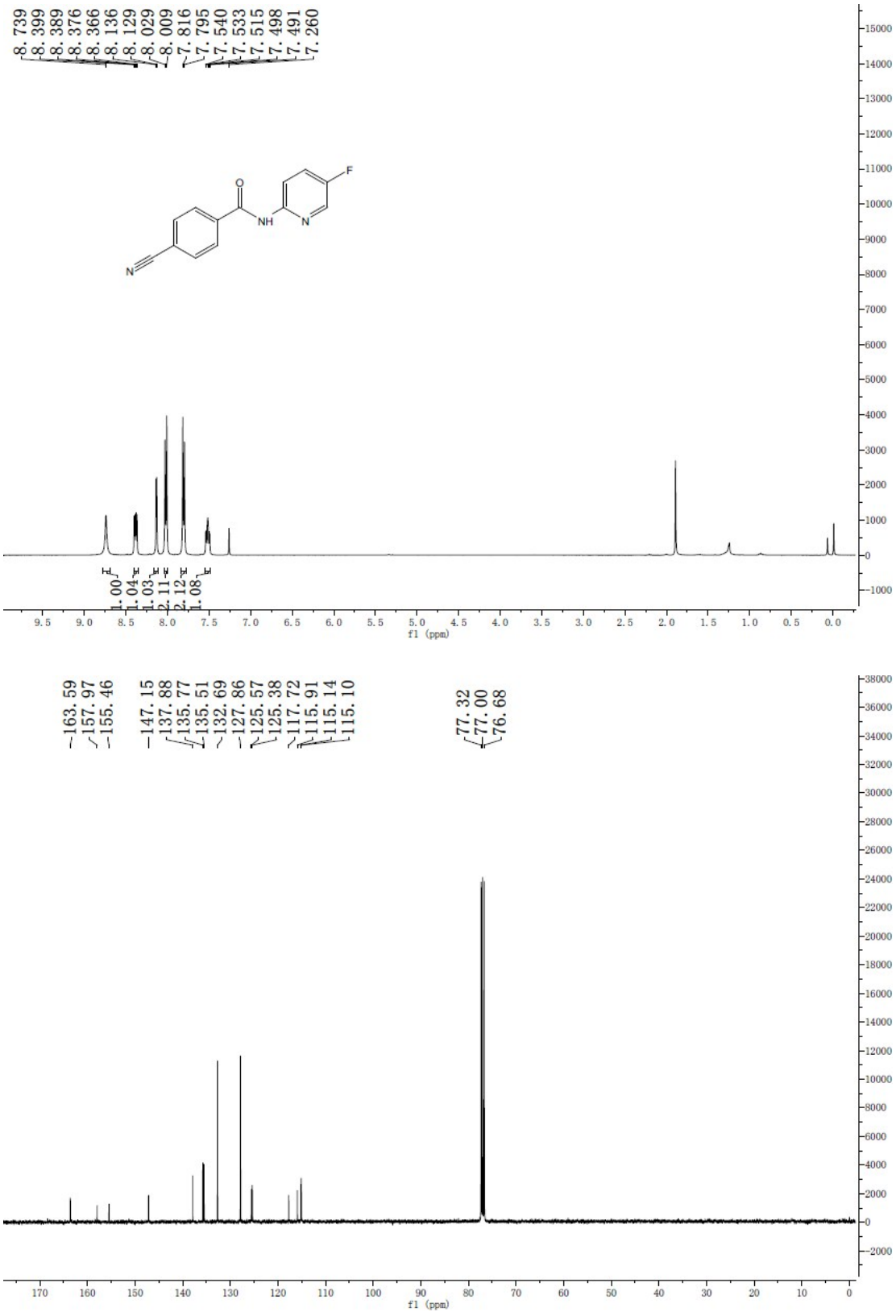
^{1}H NMR and ^{13}C NMR of 4-cyano-N-(6-methylpyridin-2-yl)benzamide (4b)



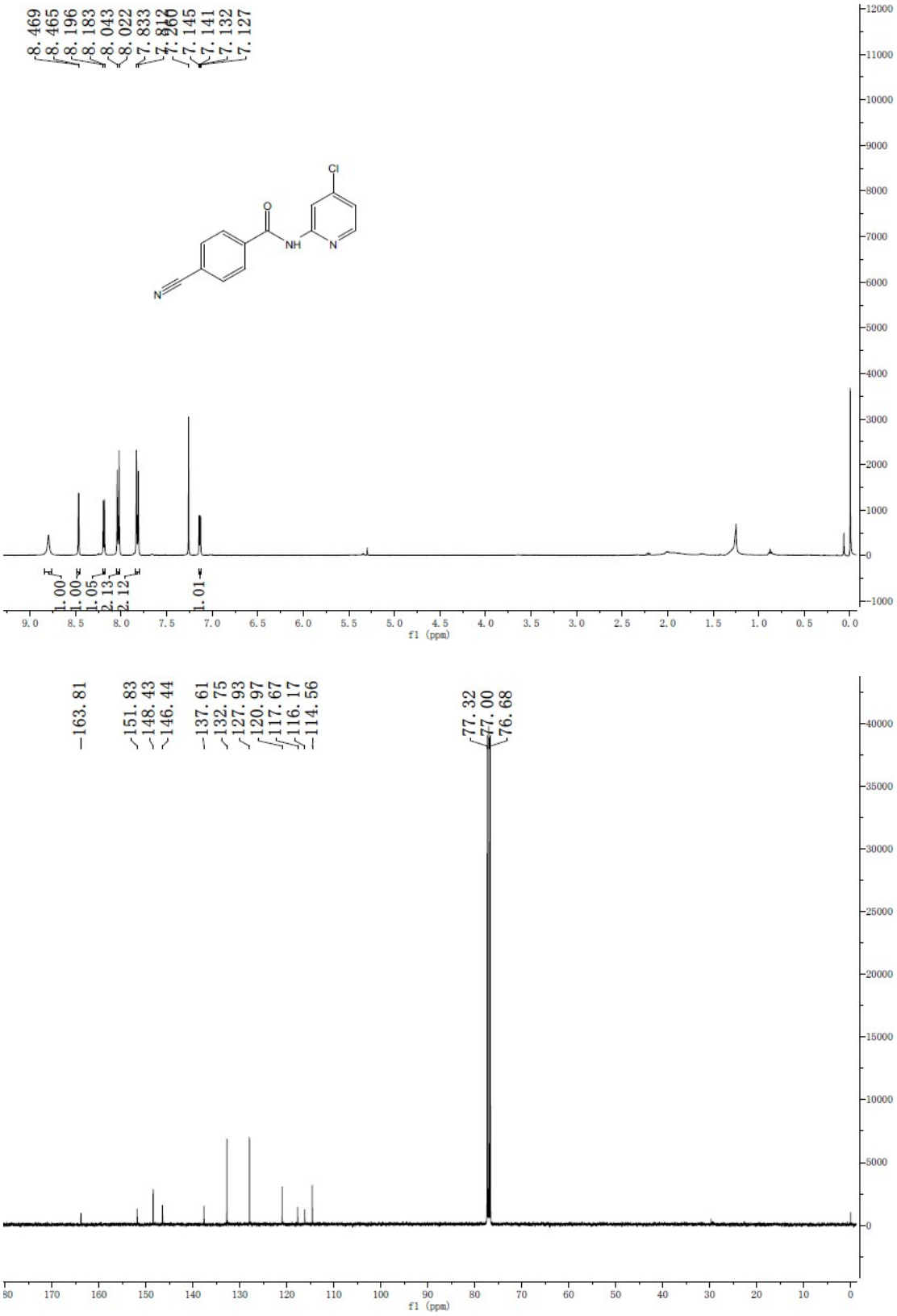
^{1}H NMR and ^{13}C NMR of 4-cyano-N-(4-methoxypyridin-2-yl)benzamide (4c)



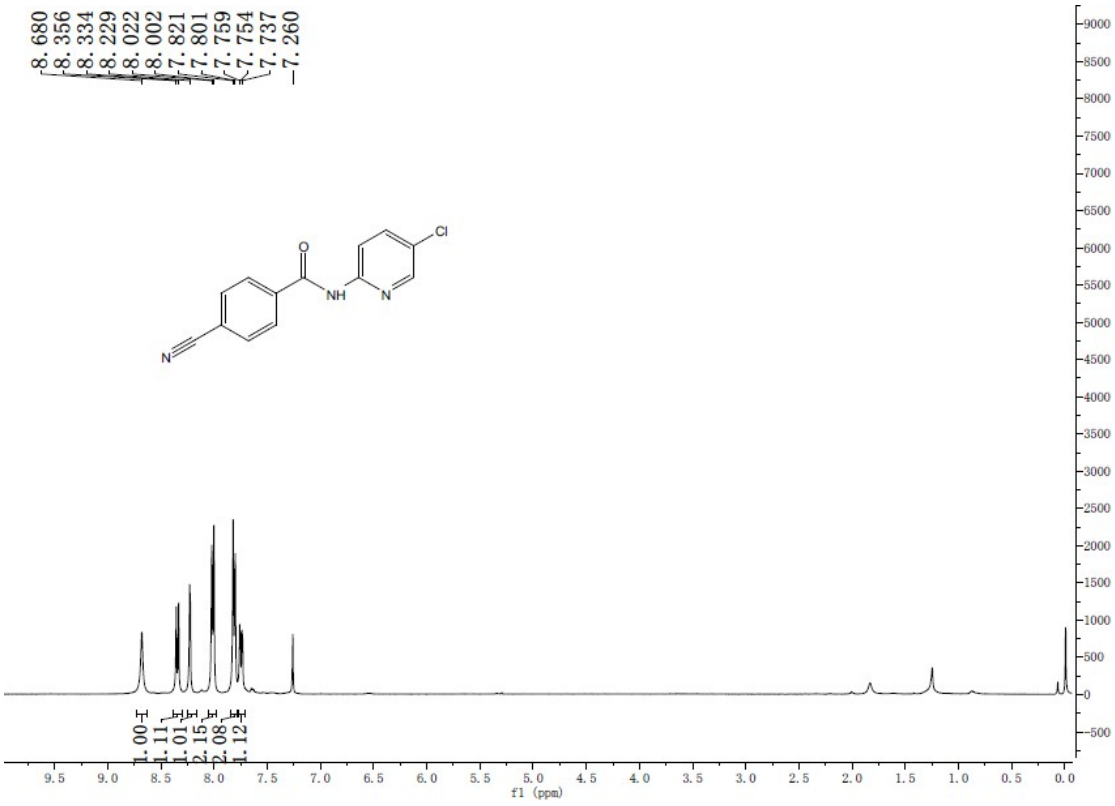
^{1}H NMR and ^{13}C NMR of 4-cyano-N-(5-fluoropyridin-2-yl)benzamide (4d)

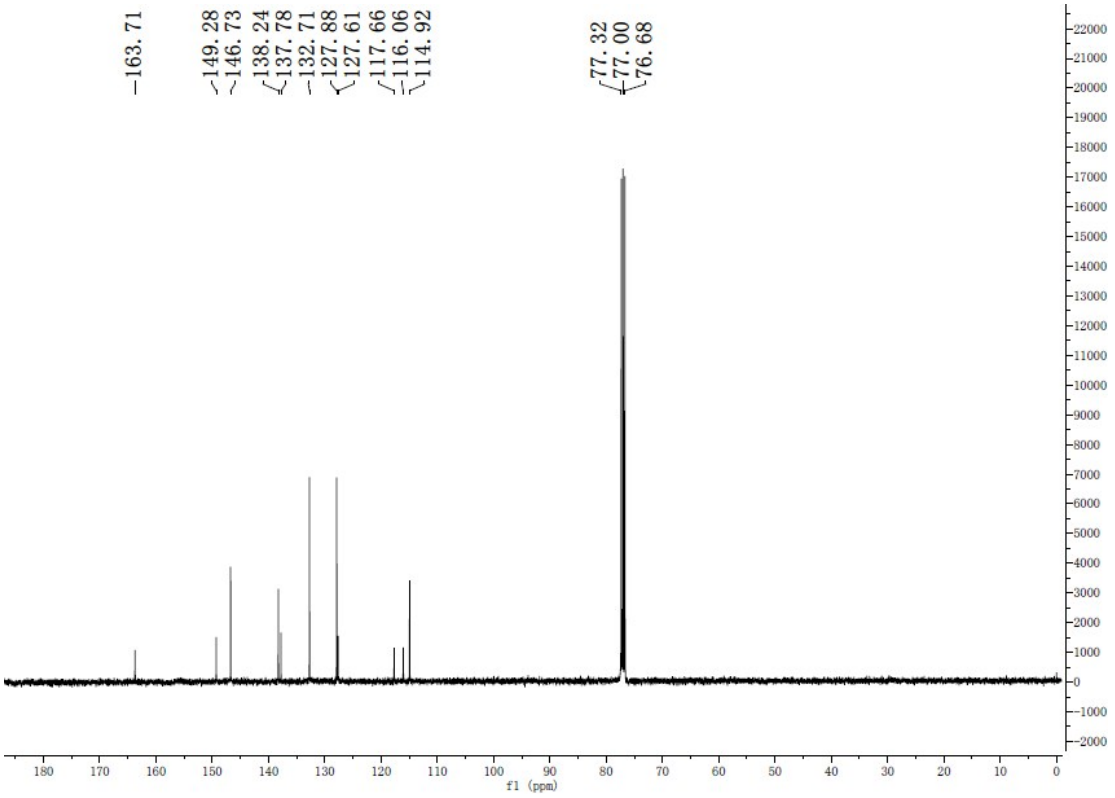


^{1}H NMR and ^{13}C NMR of N-(4-chloropyridin-2-yl)-4-cyanobenzamide (4e)

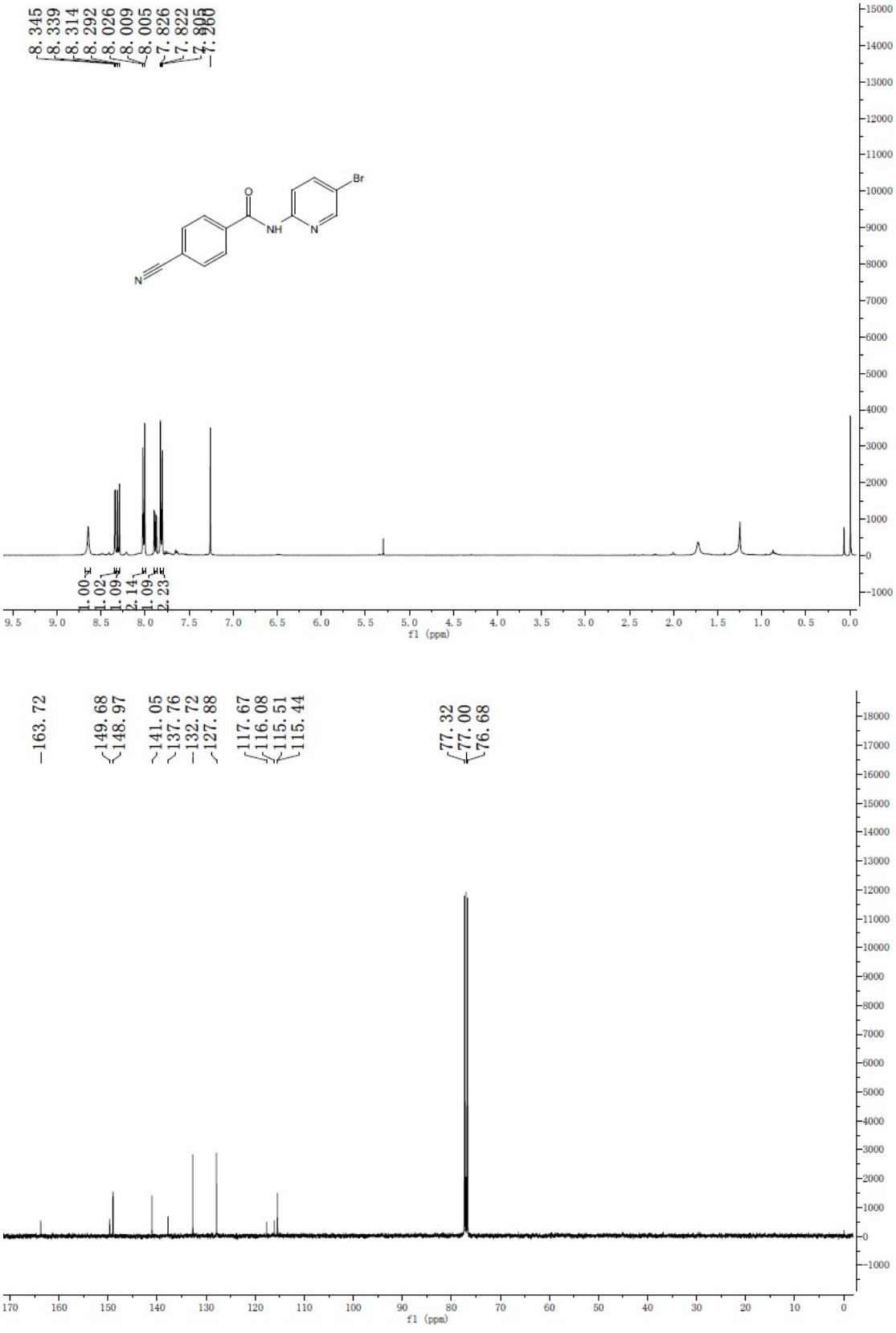


^{1}H NMR and ^{13}C NMR of N-(5-chloropyridin-2-yl)-4-cyanobenzamide (4f)



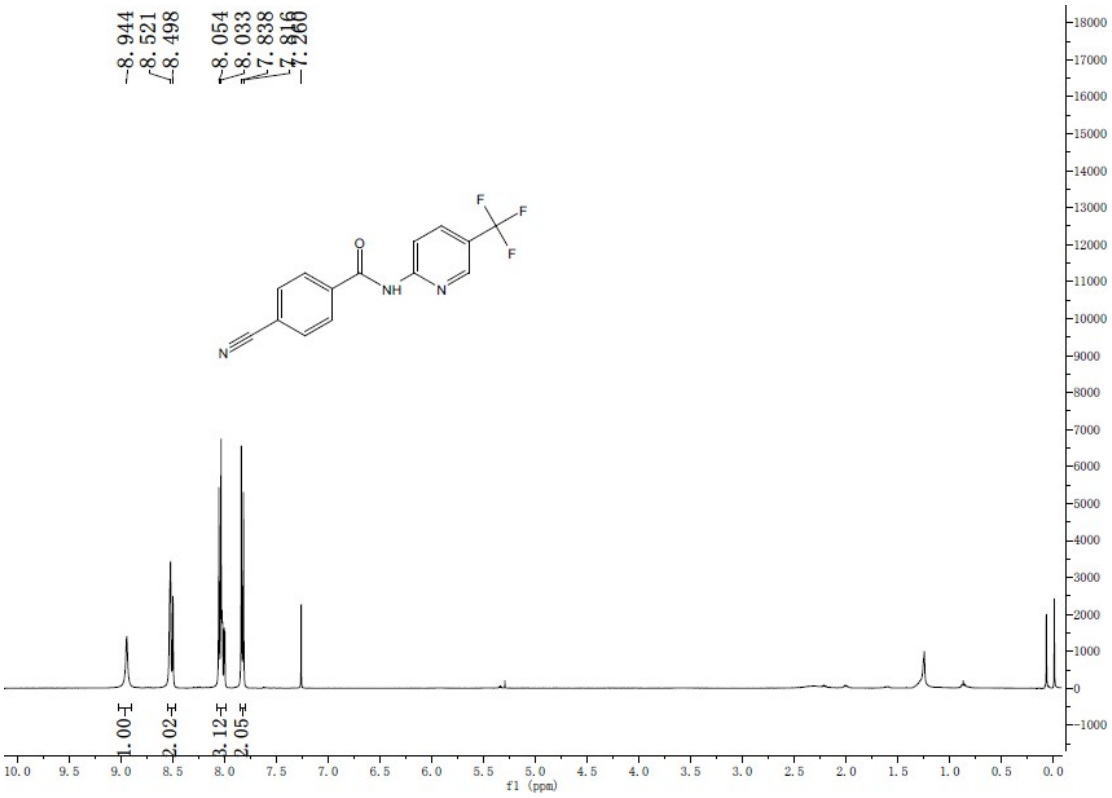


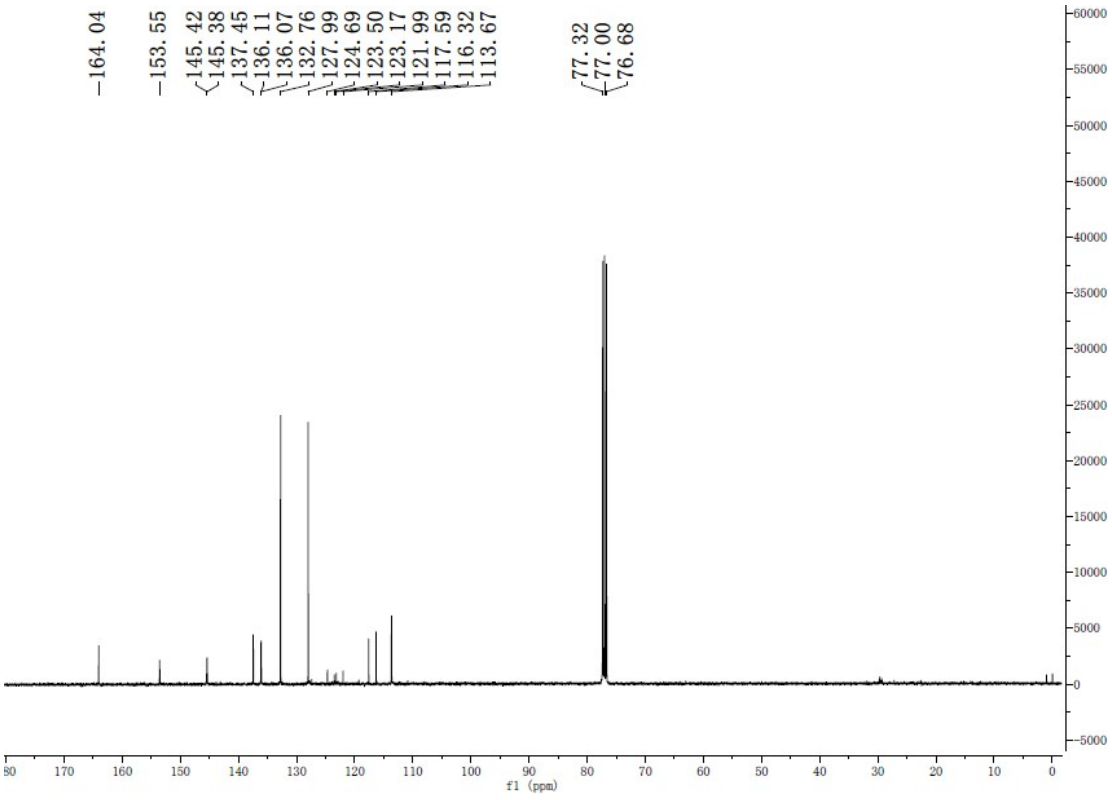
^{1}H NMR and ^{13}C NMR of N-(5-bromopyridin-2-yl)-4-cyanobenzamide (4g)



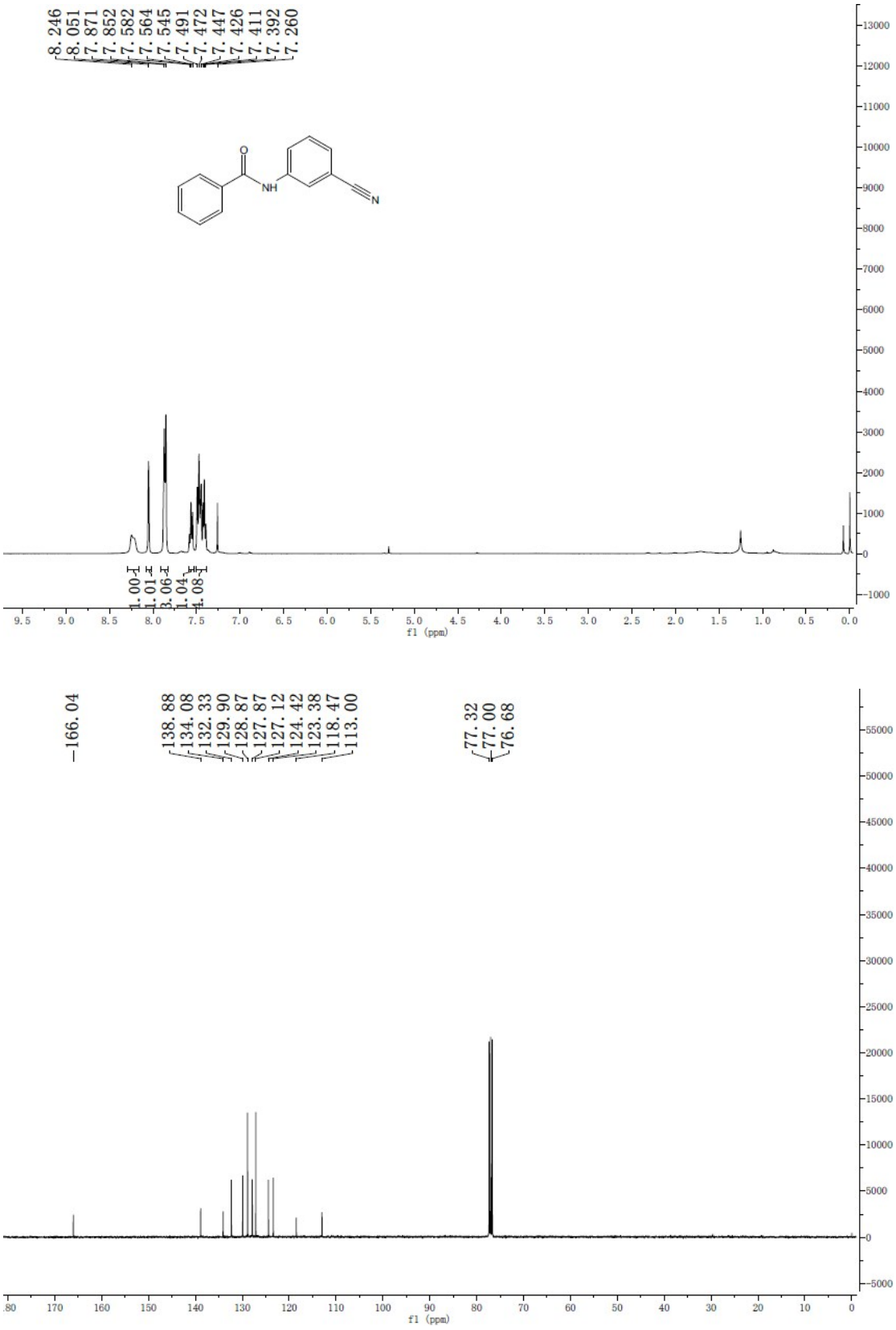
^{1}H NMR and ^{13}C NMR of 4-cyano-N-(5-(trifluoromethyl)pyridin-2-yl)benzamide

(4h)

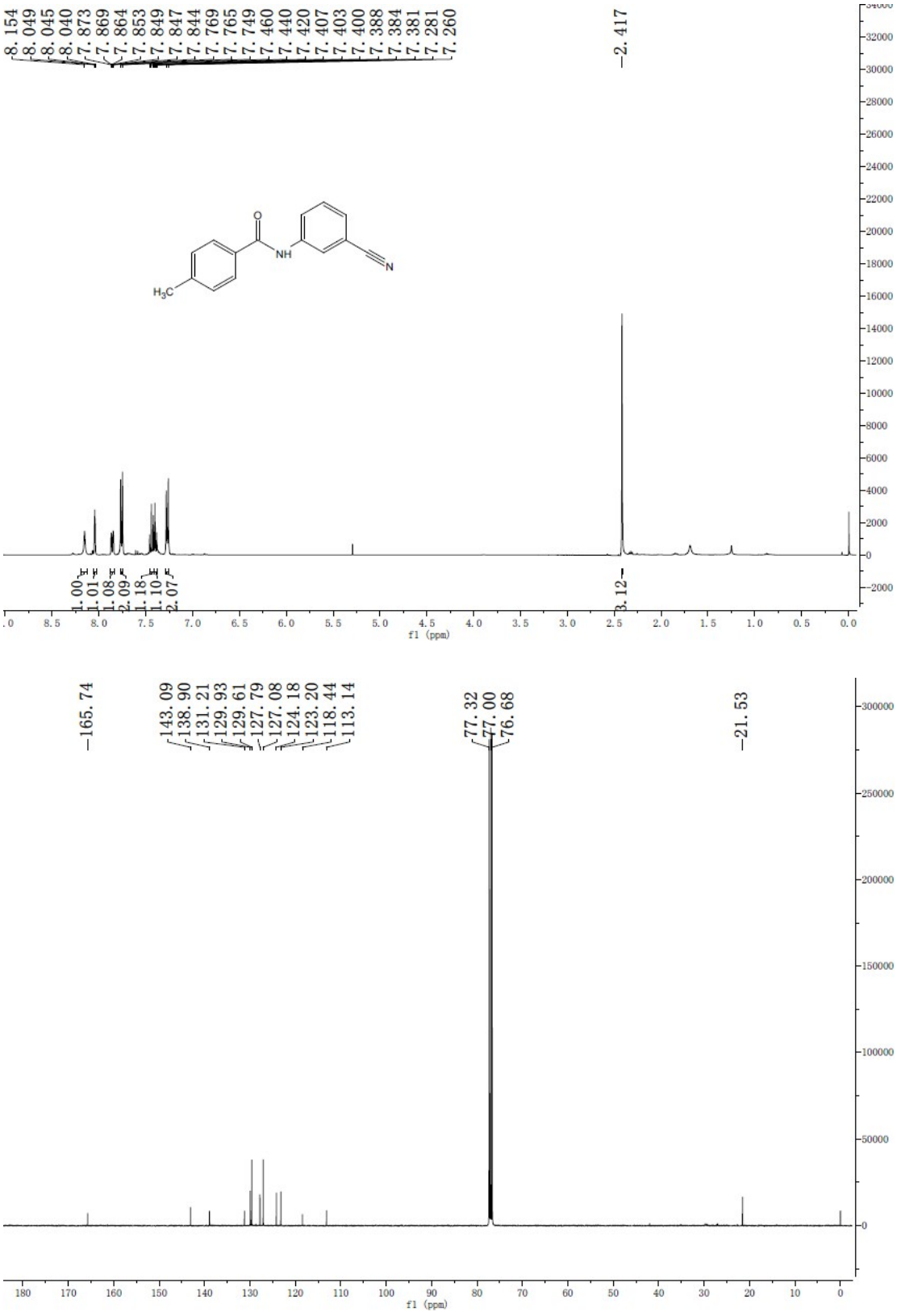




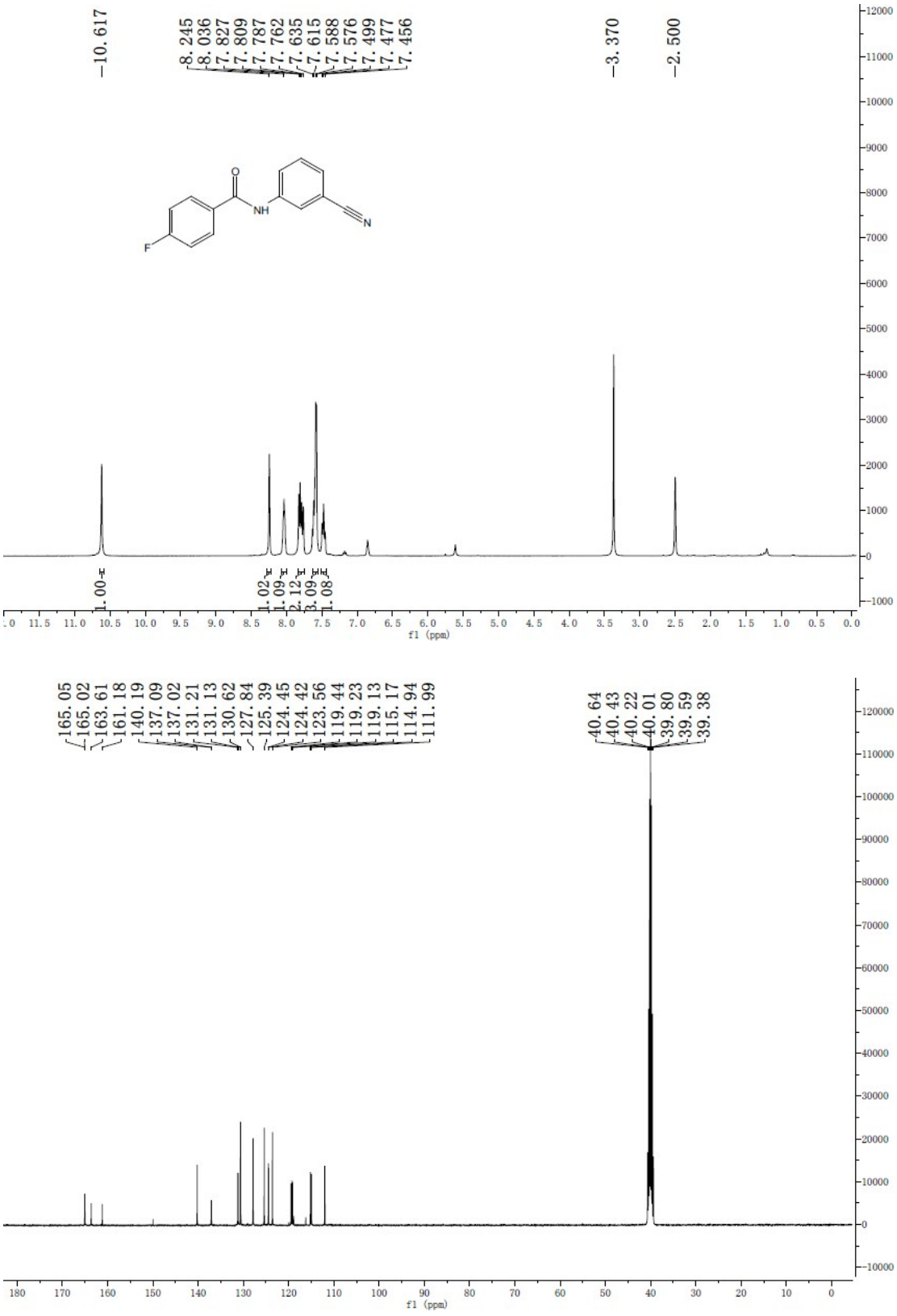
^{1}H NMR and ^{13}C NMR of N-(3-cyanophenyl)benzamide (5a)



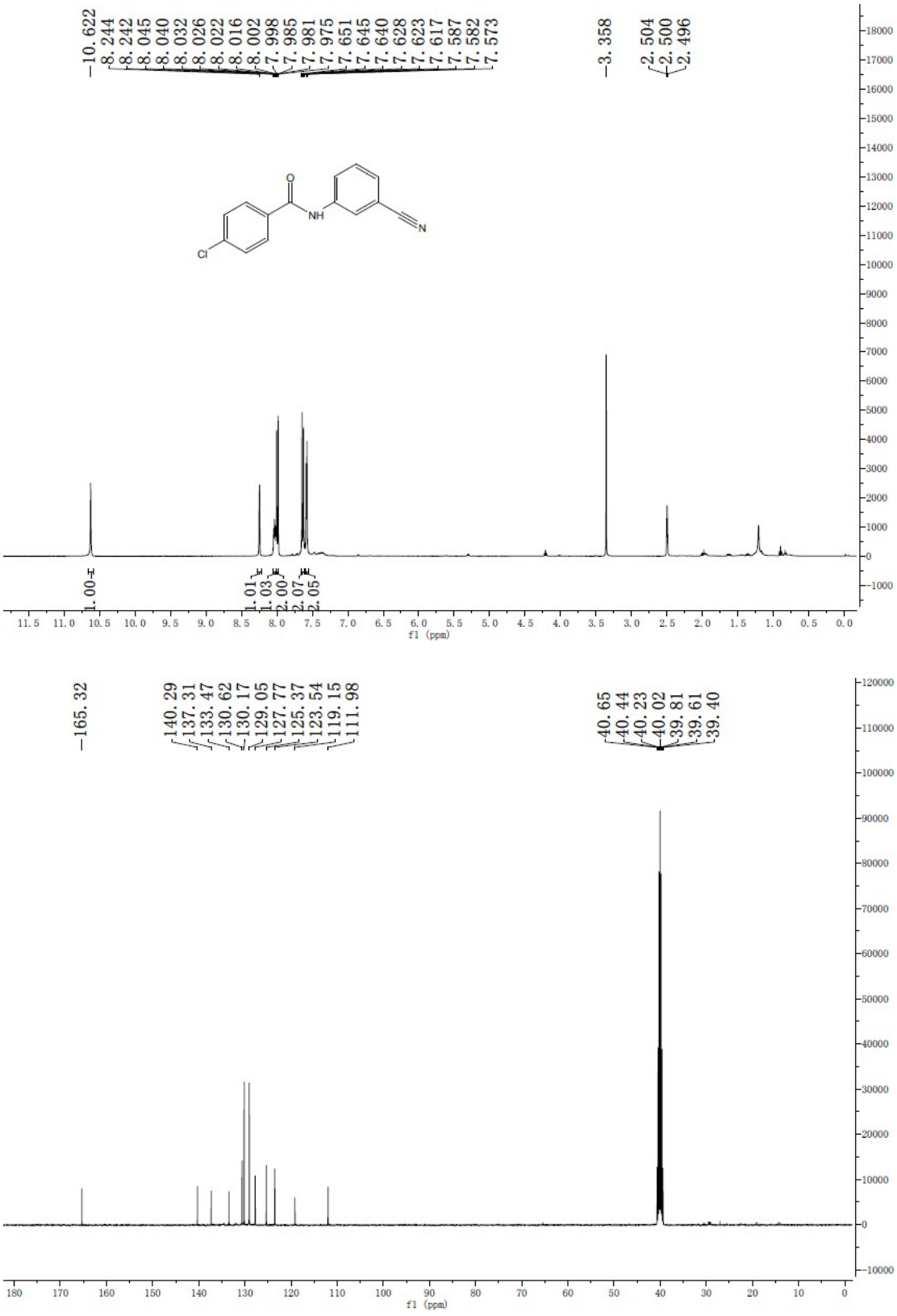
^{1}H NMR and ^{13}C NMR of N-(3-cyanophenyl)-4-methylbenzamide (5b)



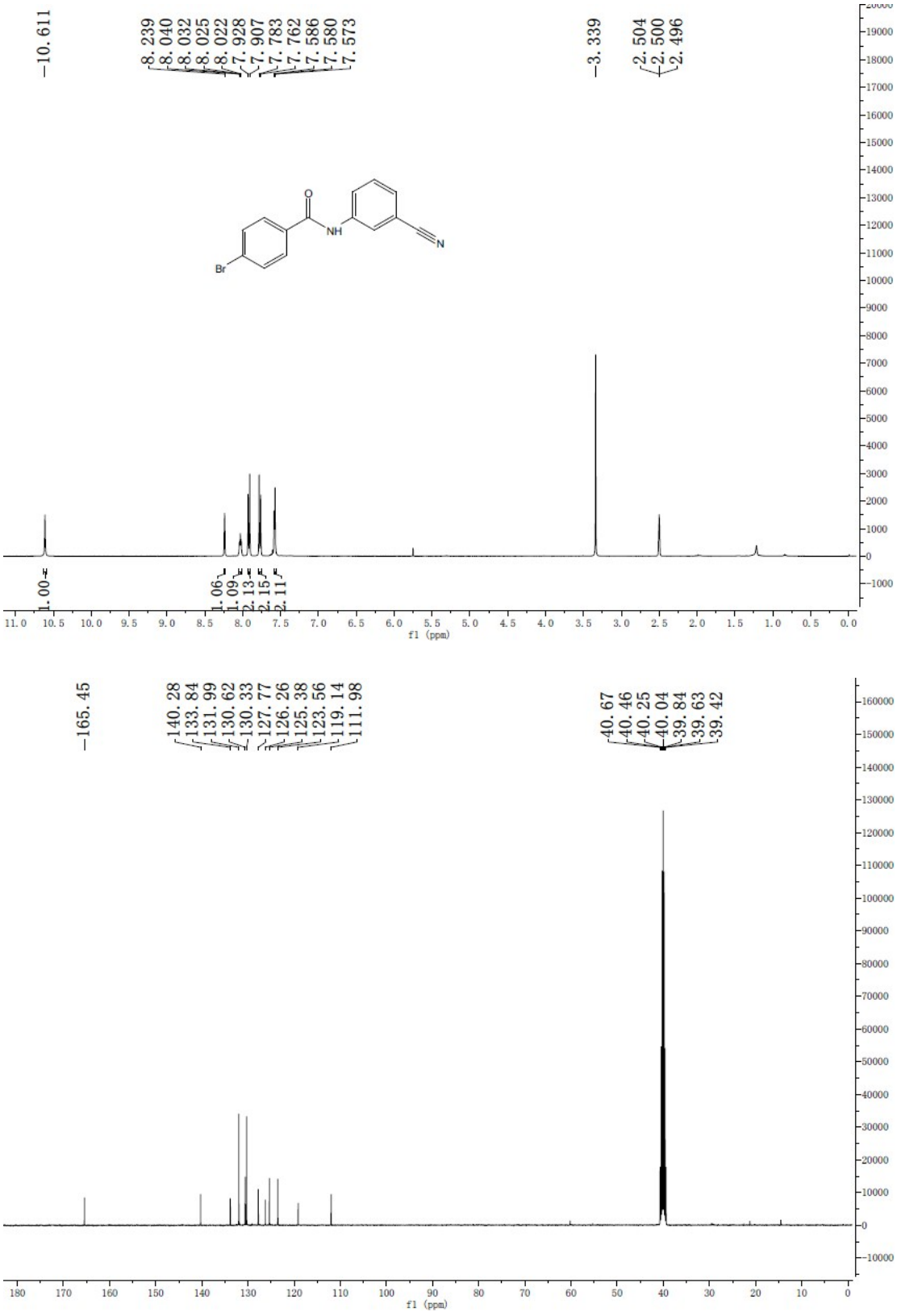
^{1}H NMR and ^{13}C NMR of N-(3-cyanophenyl)-3-fluorobenzamide (5c)



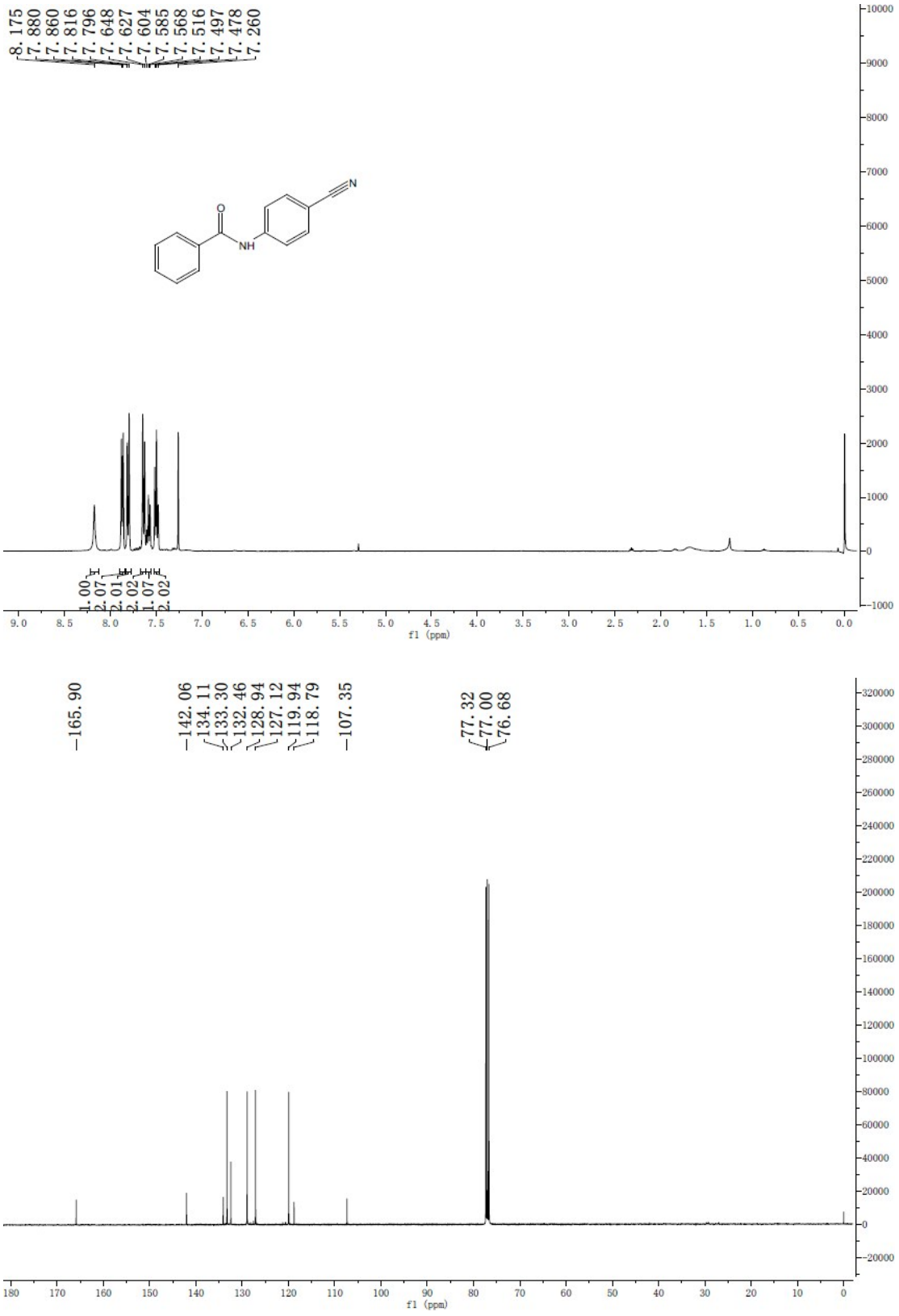
^{1}H NMR and ^{13}C NMR of 4-chloro-N-(3-cyanophenyl)benzamide (5d)



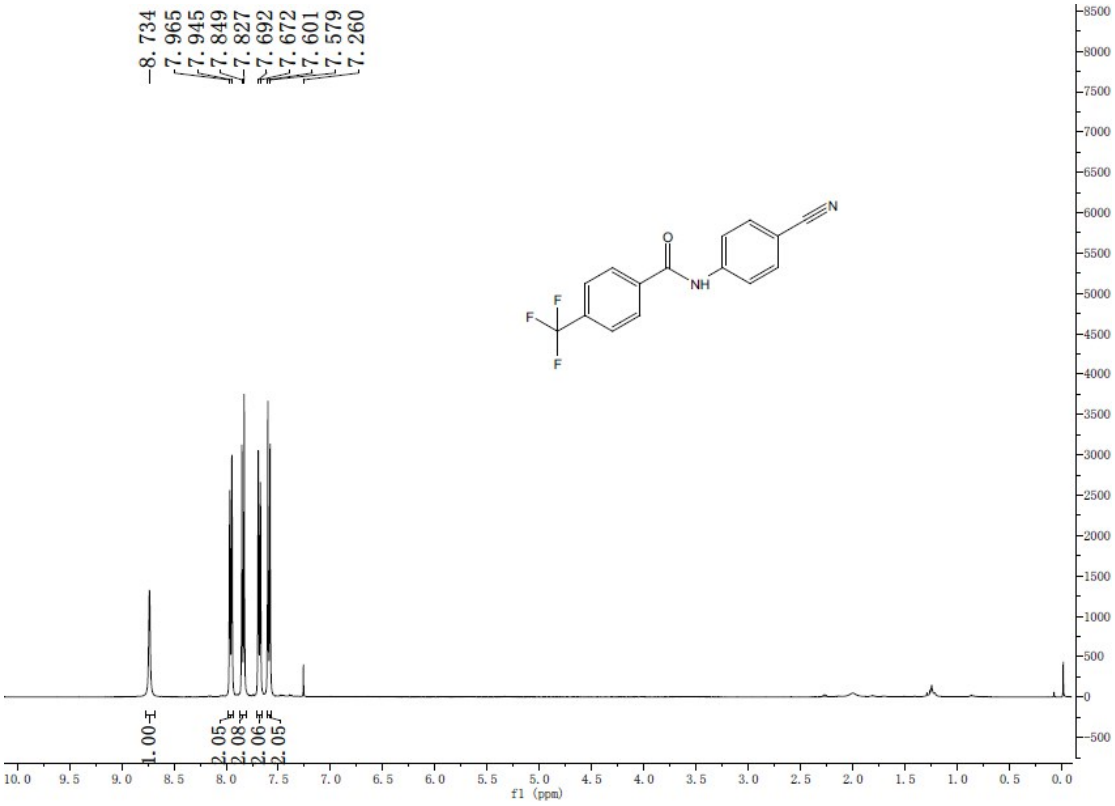
^{1}H NMR and ^{13}C NMR of 4-bromo-N-(3-cyanophenyl)benzamide (5e)

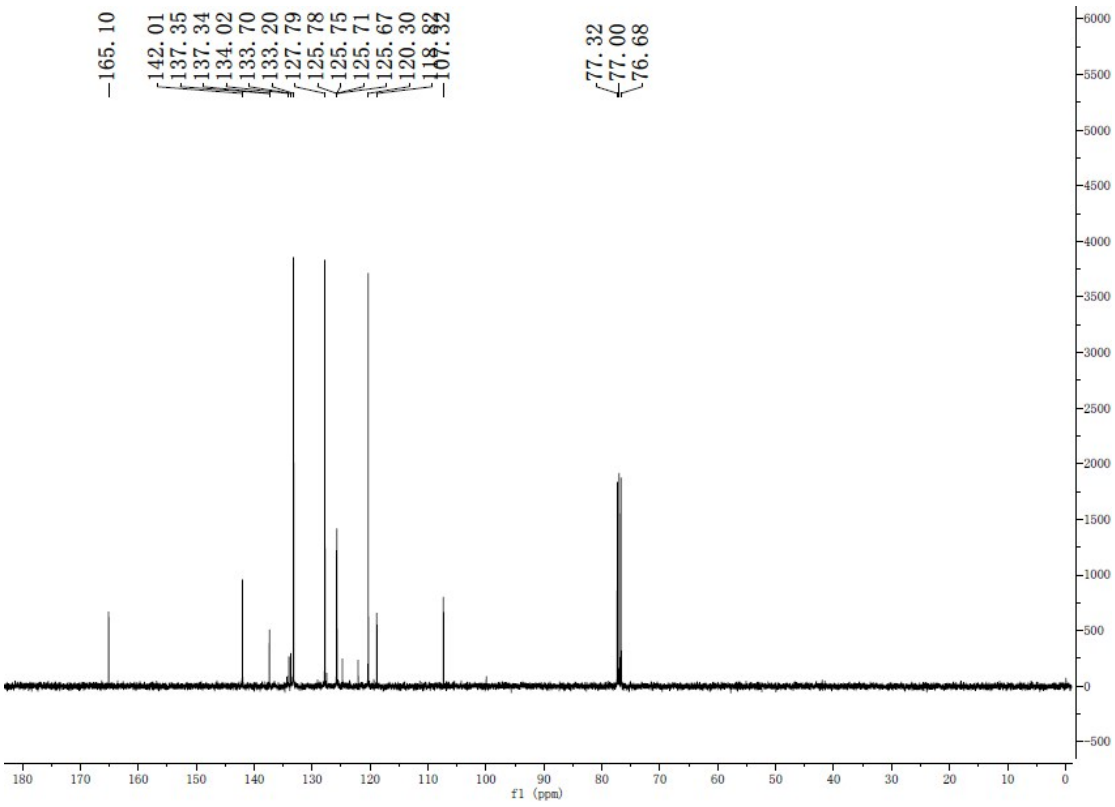


^{1}H NMR and ^{13}C NMR of N-(4-cyanophenyl)benzamide (5f)

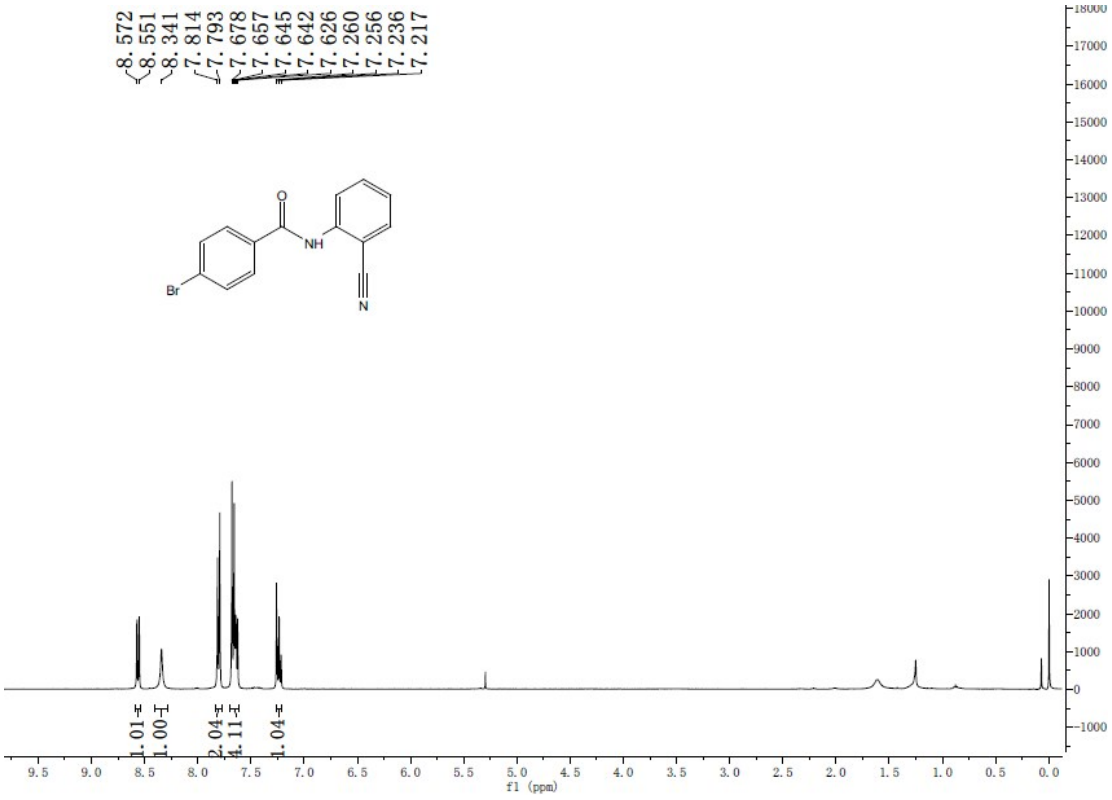


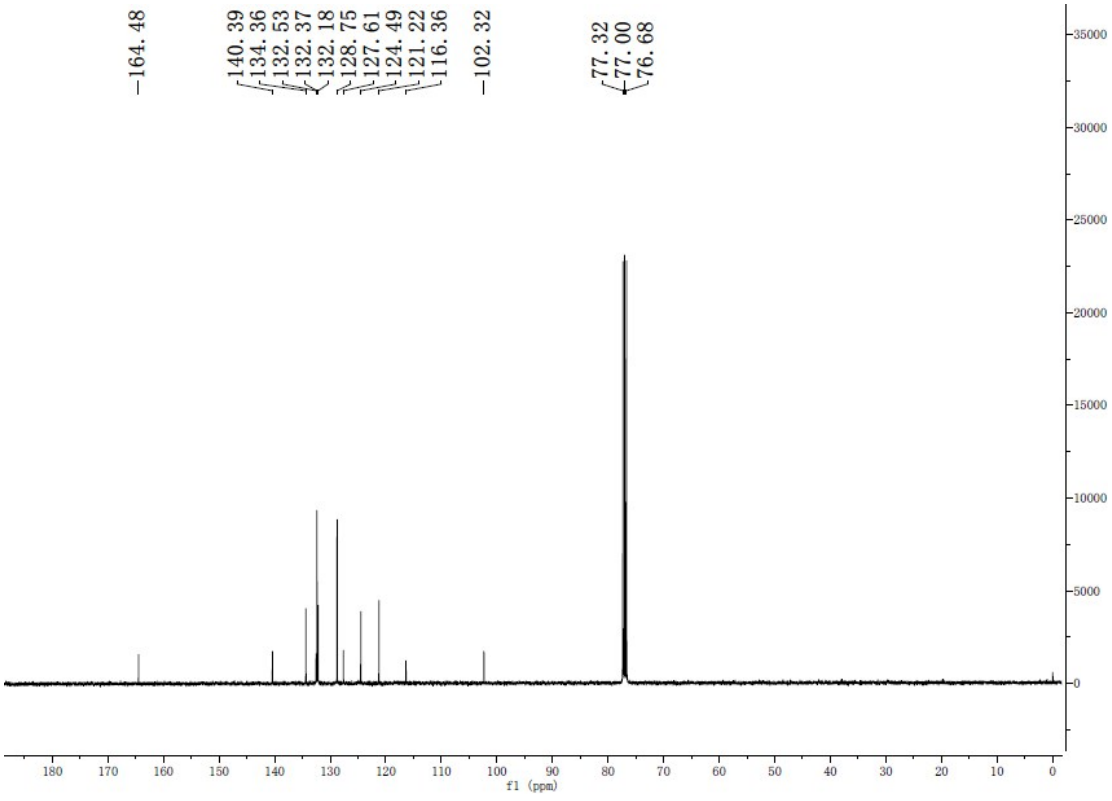
^{1}H NMR and ^{13}C NMR of N-(4-cyanophenyl)-4-(trifluoromethyl)benzamide (5g)



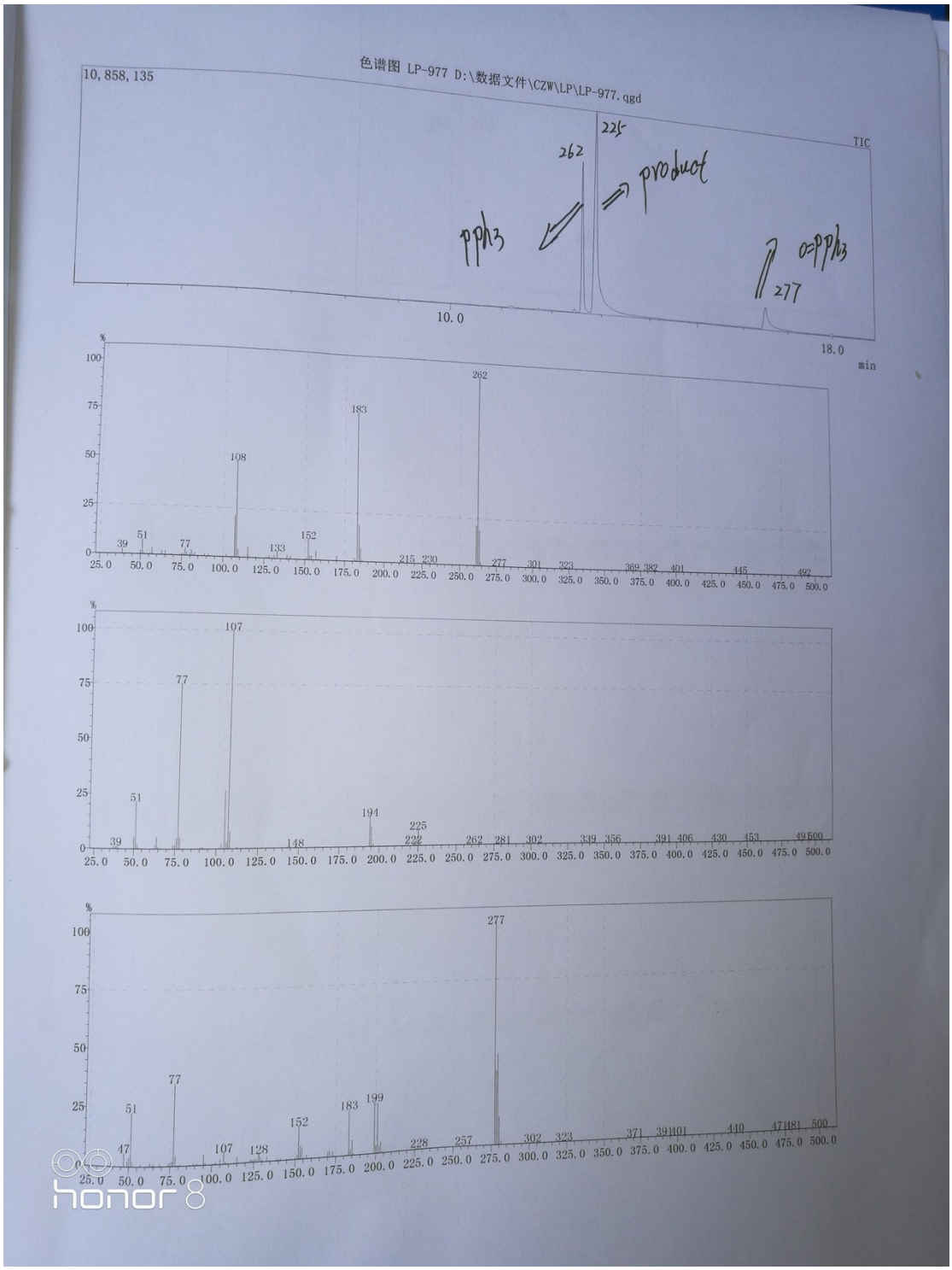


^{1}H NMR and ^{13}C NMR of 4-bromo-N-(2-cyanophenyl)benzamide (5h)

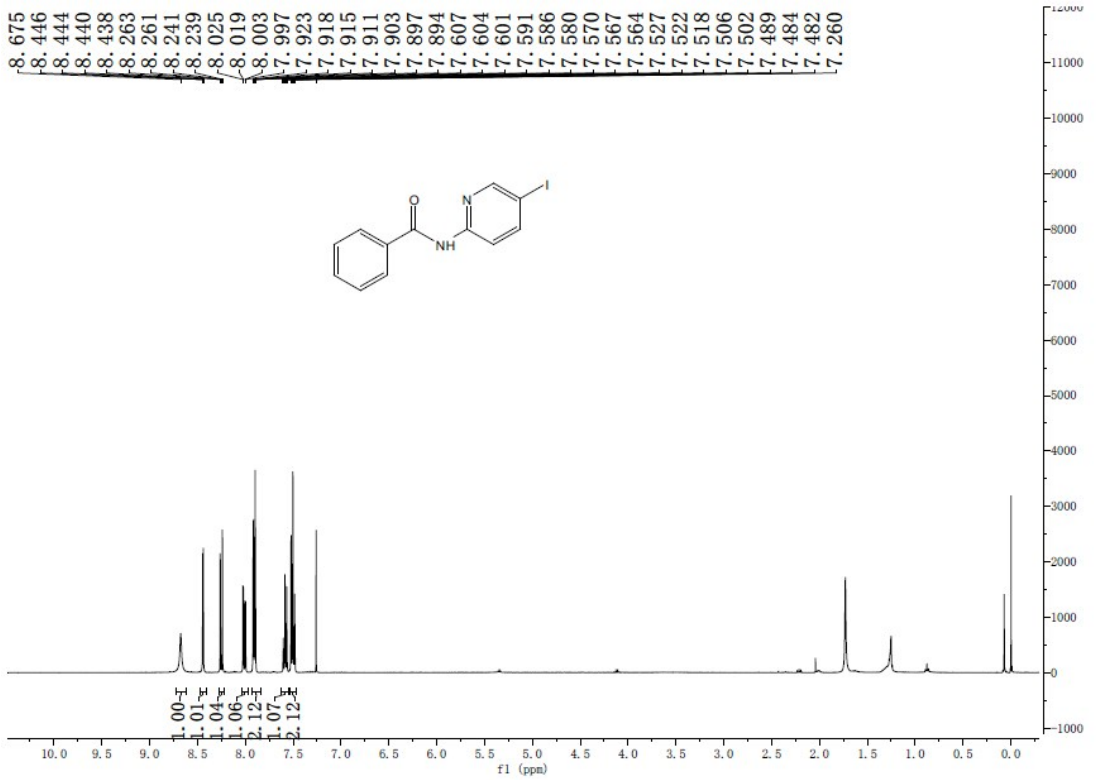




GC-MS spectra of 3a-O^{18}



^{1}H NMR and ^{13}C NMR of *N*-(5-iodopyridin-2-yl)benzamide (6a)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7.570
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7.527
7.522
7.518
7.506
7.502
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7.484
7.482
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N
I
NH
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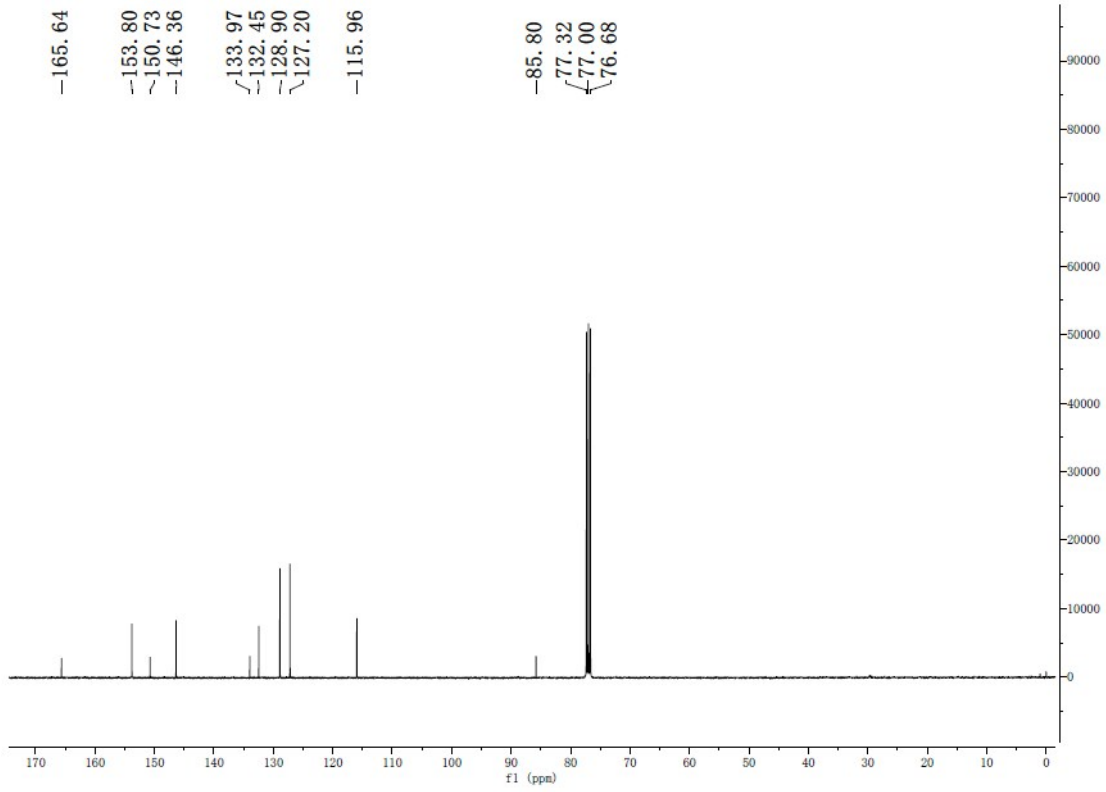
1.01
1.04
1.06
2.12
1.07
2.12
f1 (ppm)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115.96
85.80
77.32
77.00
76.68
f1 (ppm)