

SUPPORTING INFORMATION

Room-Temperature Palladium-Catalysed Suzuki-Miyaura Coupling of Arylboric Acid with Aryl Chlorides†

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1. General Methods

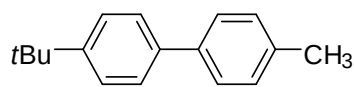
All reactions were conducted under an inert atmosphere of high pure argon. Anhydrous dioxane and benzene (PhH) were purchased from Sigma-Aldrich and used without further purification. Dimethoxyethane (DME), tetrahydrofuran (THF) were dried by Na refluxing with benzophenone as indicator. ^1H and ^{13}C NMR spectra were obtained on a Varian Unity INOVA 400/54 spectrometer in CDCl_3 , CD_3OD or $\text{DMSO}-d_6$ with TMS as the internal standard. Mass spectra were obtained on a VG Auto spec 3000 or on a Finnigan MAT90 instrument. Silica gel H (Qingdao Sea Chemical Factory, Qingdao, China) was used for column chromatography. Spots on TLC (silica gel G) were detected by ultraviolet light. Commercially available reagents and solvents were purchased from Sigma-Aldrich, Aladdin, ChengDu Kelong Chemical Co.,Ltd., Duodian-Chemical and were directly used without further purification.

2. Procedure and characterization of Pd-catalyzed Suzuki reaction

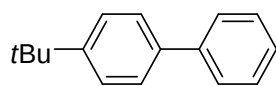
General procedure for the Pd-catalyzed Suzuki cross-coupling of aryl chlorides with arylboronic acids:

An oven-dried 10 mL reaction vial was sealed with plug after been equipped with a stir bar and charged with aryl chloride (0.2 mmol), arylboronic acid (0.24 mmol, 1.2 equiv) and K_2CO_3 (55mg, 0.4mmol, 2equiv) under an inert atmosphere of high pure argon. A stock solution of $\text{Pd}(\text{OAc})_2$ (6.28 mg, 0.028 mmol) and NiXantphos (23.19 mg, 0.042 mmol) in 7 mL of dry THF was prepared through 1h stirring under 45°C . For each reaction, a solution of $\text{Pd}(\text{OAc})_2$ (0.896 mg, 0.004 mmol) and NiXantphos (3.312 mg, 0.006 mmol) in 1 mL of dry THF was taken up by syringe and added to the reaction vial, followed by the addition of 0.2 mL H_2O . The reaction mixture was then stirred for 6h at room temperature. The

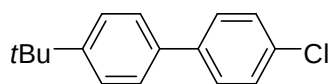
crude material was purified by chromatography on silica gel to give the desired products.



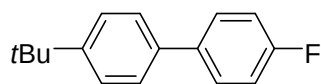
4-*tert*-butyl-4'-methylbiphenyl (3a): This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 1-chloro-4-methylbenzene (**2a**, 25.2 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with petroleum ether) to give the product (42.5 mg, 95% yield) as a white solid. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.¹



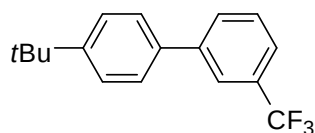
4-*tert*-butylbiphenyl (3b): This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and chlorobenzene (**2b**, 22.5 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with petroleum ether) to give the product (39.5 mg, 94% yield) as a white solid. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.¹



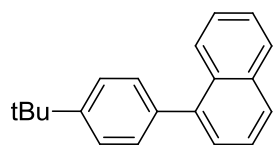
4-*tert*-butyl-4'-chlorobiphenyl (3c): This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 1,4-dichlorobenzene (**2c**, 29.4 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with petroleum ether) to give the product (46.9 mg, 96% yield) as a white solid. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.²



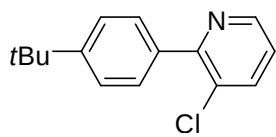
4-tert-butyl-4'-fluorobiphenyl (3d): This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 1-chloro-4-fluorobenzene (**2d**, 26.11 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with petroleum ether) to give the product (44.7 mg, 98% yield) as a white solid. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.³



4'-tert-butyl-3-(trifluoromethyl)biphenyl (3e): This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 1-chloro-3-(trifluoromethyl)benzene (**2e**, 36.11 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with petroleum ether) to give the product (51.7 mg, 93% yield) as colorless liquid. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.⁴

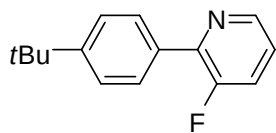


1-(4-(tert-butyl)phenyl)naphthalene (3f): This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 1-chloronaphthalene (**2f**, 32.5 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:5) to give the product (46.5 mg, 90% yield) as a colorless crystal. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.⁵



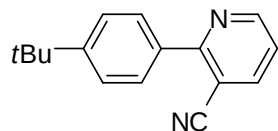
2-(4-(tert-butyl)phenyl)-3-chloropyridine (3g):

This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 2,3-dichloropyridine (**2g**, 29.6 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:20) to give the product (44.6 mg, 91% yield) as colourless liquid. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ_{H} 8.57 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.78 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.20 (dd, $J_1 = 8.4$ Hz, $J_2 = 4.8$ Hz, 1H), 1.36 (s, 9H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ_{C} 156.5, 151.8, 147.5, 138.0, 135.3, 130.0, 129.0, 125.0, 122.8, 34.7, 31.3 ppm. HRMS calculated for $\text{C}_{15}\text{H}_{17}\text{ClN}$, 246.10440, found 246.10440, $[\text{M}+\text{H}]^+$ and $\text{C}_{15}\text{H}_{16}\text{ClNNa}$, 268.08635, found 268.08628, $[\text{M}+\text{Na}]^+$.

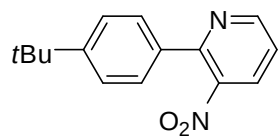


2-(4-(tert-butyl)phenyl)-3-fluoropyridine (3h):

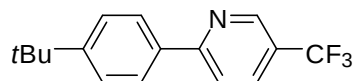
This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-3-fluoropyridine (**2h**, 26.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:15) to give the product (44.9 mg, 98% yield) as colourless liquid. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ_{H} 8.55 (d, $J = 4.8$, 1H), 7.97 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.54-7.48 (m, 1H), 7.29 (dd, $J_1 = 8.4$ Hz, $J_2 = 4.8$ Hz, 1H), 1.41 (s, 9H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ_{C} 157.5 (d, $J = 258.5$ Hz), 152.3, 146.3 (d, $J = 10.5$ Hz), 145.3 (d, $J = 5.5$ Hz), 132.5 (d, $J = 10.5$ Hz), 128.4 (d, $J = 5.5$ Hz), 125.4, 124.0 (d, $J = 50.5$ Hz), 123.1 (d, $J = 3.9$ Hz), 34.7, 31.2 ppm. HRMS calculated for $\text{C}_{15}\text{H}_{16}\text{FNa}$, 252.11590, found 252.11590, $[\text{M}+\text{Na}]^+$.



2-(4-(tert-butyl)phenyl)nicotinonitrile (3i): This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 2-Chloro-3-cyano pyridine (**2i**, 27.7 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:5) to give the product (45.81 mg, 97% yield) as a white solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ_{H} 8.86 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.6$ Hz, 1H), 8.05 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.35 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.8$ Hz, 1H), 1.36 (s, 9H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ_{C} 160.9, 153.5, 152.6, 141.9, 134.3, 128.6, 125.7, 121.2, 117.9, 107.1, 34.8, 31.2 ppm. HRMS calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{Na}$, 259.12057, found 259.12052, $[\text{M}+\text{Na}]^+$.

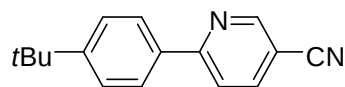


2-(4-(tert-butyl)phenyl)-3-nitropyridine (3j): This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 2-Chloro-3-nitropyridine (**2j**, 31.7 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:5) to give the product (50.19 mg, 98% yield) as a light yellow solid. $^1\text{H-NMR}$ (400MHz, CDCl_3): δ_{H} 8.83 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.6$ Hz, 1H), 8.11 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.40 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.8$ Hz, 1H), 1.34 (s, 9H).. $^{13}\text{C-NMR}$ (100MHz, CDCl_3): δ_{C} 160.9, 153.4, 152.6, 141.9, 134.3, 128.6, 125.7, 121.2, 117.9, 107.1, 34.8, 31.2 ppm. HRMS calculated for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{Na}$, 279.11040, found 279.11042, $[\text{M}+\text{Na}]^+$.



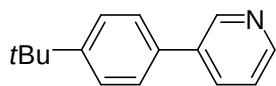
2-(4-(tert-butyl)phenyl)-5-(trifluoromethyl)pyridine

(3k): This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:40) to give the product (55.23 mg, 99% yield) as a light yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ_H 8.93 (br.s, 1H), 7.98 (d, *J* = 8.8 Hz), 7.96 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 1.37 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃): δ_C 160.6 (d, *J* = 1.3 Hz), 153.4, 146.5 (q, *J* = 4.0 Hz), 135.1, 133.8 (q, *J* = 3.5 Hz), 127.0, 125.9, 124.6 (q, *J* = 280.5 Hz), 119.7, 34.8, 31.2 ppm. HRMS calculated for C₁₆H₁₆F₃NNa, 302.11271, found 302.11264, [M+Na]⁺.

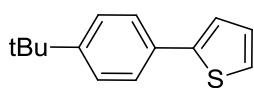


6-(4-(tert-butyl)phenyl)nicotinonitrile (3l):

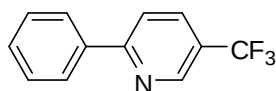
This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 2-Chloro-5-cyanopyridine (**2l**, 27.71 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:15) to give the product (46.75 mg, 95% yield) as a white solid. ¹H-NMR (400 MHz, CDCl₃): δ_H 8.84 (dd, *J*₁ = 4.8 Hz, *J*₂ = 1.2 Hz, 1H), 7.95-7.92 (m, 3H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.41 (dd, *J*₁ = 4.8 Hz, *J*₂ = 1.2 Hz, 1H), 1.36 (s, 9H). ¹³C-NMR (100MHz, CDCl₃): δ_C 158.6, 153.6, 150.6, 134.5, 126.7, 126.7, 126.1, 122.8, 121.8, 121.0, 116.9, 34.8, 31.2 ppm. HRMS calculated for C₁₆H₁₆N₂Na, 259.12059, found 259.12057, [M+Na]⁺.



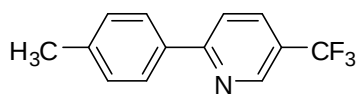
3-(4-(tert-butyl)phenyl)pyridine (3m): This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 3-Chloropyridine (**2m**, 19 μ L, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with petroleum ether) to give the product (27.46 mg, 65% yield) as a light yellow solid. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.⁶



2-(4-(tert-butyl)phenyl)thiophene (3n): This reaction was performed following General Procedure with 4-*tert*-butylphenylboronic acid (**1a**, 42.7 mg, 0.24 mmol, 1.2 equiv) and 2-chlorothiophene (**2n**, 23.7mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:5) to give the product (39.4 mg, 92% yield) as a white crystal. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.⁷

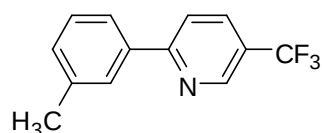


2-phenyl-5-(trifluoromethyl)pyridine (4a): This reaction was performed following General Procedure with phenylboronic acid (**1b**, 29.2 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:40) to give the product (42.8 mg, 96% yield) as a white solid. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.⁸

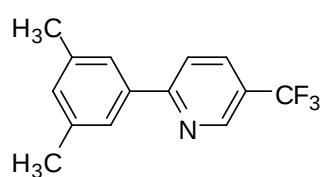


2-(p-tolyl)-5-(trifluoromethyl)pyridine (4b): This reaction was performed following General Procedure with p-tolylboronic acid (**1c**,

32.4 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:40) to give the product (44.1 mg, 93% yield) as a white solid. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.⁹

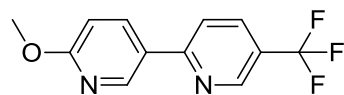


2-(m-tolyl)-5-(trifluoromethyl)pyridine (4c): This reaction was performed following General Procedure with m-tolylboronic acid (**1d**, 32.6 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:20) to give the product (44.5 mg, 94% yield) as a yellow crystal. ^1H -NMR (400 MHz, CDCl_3): δ_{H} 8.93 (s, 1H), 7.97 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H), 7.86-7.79 (m, 3H), 7.40 (t, $J = 8.4$ Hz, 1H), 7.30 (d, $J = 8.4$ Hz, 1H), 2.45 (s, 3H). ^{13}C -NMR (100MHz, CDCl_3): δ_{C} 160.8, 146.5 (q, $J = 4.6$ Hz), 138.7, 137.9, 133.9 (q, $J = 3.5$ Hz) 130.8, 128.8, 127.9, 125.13, 124.6 (q, $J = 280.5$ Hz), 124.3, 120.1, 21.5 ppm.



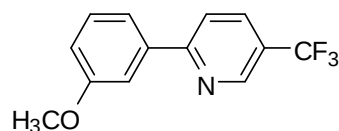
2-(3,5-dimethylphenyl)-5-(trifluoromethyl)pyridine (4d): This reaction was performed following General Procedure with 3,5-dimethylphenylboronic Acid (**1e**, 35.9 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:10) to give the product (46.7 mg, 93% yield) as yellow liquid. ^1H -NMR (400 MHz, CDCl_3): δ_{H} 8.92 (br. s, 1H), 7.96 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H), 7.82 (d, $J = 8.4$ Hz, 1H), 7.63 (s, 2H), 7.12 (s, 1H), 2.41 (s, 6H). ^{13}C -NMR

(100MHz, CDCl₃): δ_C 161.0, 146.5 (q, J = 4.6 Hz), 138.6, 137.9, 133.8 (q, J = 3.5 Hz), 131.7, 125.1, 124.8 (q, J = 280.5 Hz), 120.1, 21.43 ppm.



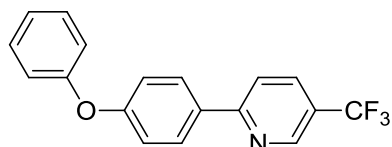
6'-methoxy-5-(trifluoromethyl)-2,3'-bipyridine (4e):

This reaction was performed following General Procedure with 4-methoxyphenylboronic acid (**1f**, 36.47 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:5) to give the product (41.51 mg, 82% yield) as a white crystal. The ¹H and ¹³C{¹H} NMR data for this compound match the literature data.¹⁰



2-(3-methoxyphenyl)-5-(trifluoromethyl)pyridine (4f):

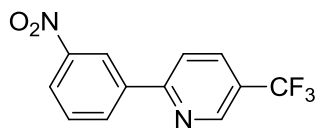
This reaction was performed following General Procedure with 3-methoxyphenylboronic acid (**1g**, 36.47 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:10) to give the product (40.51 mg, 80% yield) as a brown yellow crystal. The ¹H and ¹³C{¹H} NMR data for this compound match the literature data.¹¹



2-(4-phenoxyphenyl)-5-(trifluoromethyl)pyridine (4g):

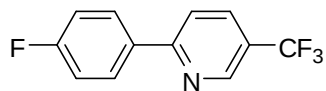
This reaction was performed following General Procedure with (4-phenoxyphenyl)boronic acid (**1h**, 51.4 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude

material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:5) to give the product (56.7 mg, 90% yield) as a white crystal. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.¹²



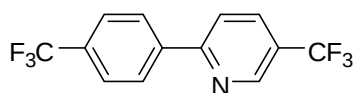
2-(3-nitrophenyl)-5-(trifluoromethyl)pyridine (4h): This

reaction was performed following General Procedure with (3-nitrophenyl)boronic acid (**1l**, 40 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:5) to give the product (50.4 mg, 94% yield) as a white crystal. ^1H -NMR (400 MHz, CDCl_3): δ_{H} 8.98 (s, 1H), 8.90 (t, $J = 2.0$ Hz, 1H), 8.41 (d, $J = 8.0$ Hz, 1H), 8.32 (d, $J = 8.0$ Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.69 (t, $J = 8.0$ Hz, 1H); ^{13}C -NMR (100MHz, CDCl_3): δ_{C} 157.8, 148.8, 146.9 (q, $J = 4.6$ Hz), 139.5, 134.4 (q, $J = 3.5$ Hz), 132.9, 130.0, 126.0 (q, $J = 28.5$ Hz), 125.6 (q, $J = 280.5$ Hz), 124.5, 122.1, 120.1 ppm. HRMS calculated for $\text{C}_{12}\text{H}_7\text{F}_3\text{N}_2\text{O}_2\text{Na}$, 291.03518, found 291.03528, $[\text{M}+\text{Na}]^+$.



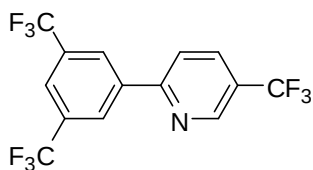
2-(4-fluorophenyl)-5-(trifluoromethyl)pyridine (4i): This

reaction was performed following General Procedure with p-Fluorophenylboronic acid (**1j**, 33.58 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:30) to give the product (44.8 mg, 93% yield) as a white crystal. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.¹³



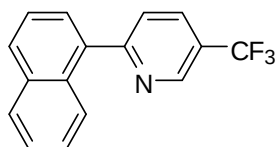
5-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)pyridine (4j):

This reaction was performed following General Procedure with Trifluoromethylphenyl (**1k**, 45.58 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:30) to give the product (51.8 mg, 89% yield) as a white solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ_{H} 8.98 (br. s, 1H), 8.15 (d, $J = 8.4$ Hz, 2H), 8.04 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz, 1H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 8.4$ Hz, 2H). $^{13}\text{C-NMR}$ (100MHz, CDCl_3): δ_{C} 159.0, 146.8 (q, $J = 4.6$ Hz), 141.1, 134.2 (q, $J = 3.5$ Hz), 131.8 (q, $J = 324.9$ Hz), 127.6, 125.9 (q, $J = 28.5$ Hz), 125.5 (q, $J = 280.5$ Hz), 122.6, 122.1, 120.3 ppm.

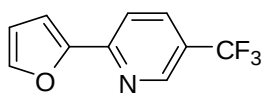


2-(3,5-bis(trifluoromethyl)phenyl)-5-(trifluoromethyl)pyridine (4k):

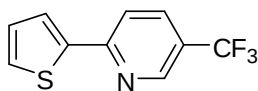
This reaction was performed following General Procedure with 3,5-Bis(trifluoromethyl)phenylboronic acid (**1l**, 61.9 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:30) to give the product (63.2 mg, 88% yield) as a light yellow solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ_{H} 9.00 (br. s, 1H), 8.52 (s, 2H), 8.09 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H), 7.98 (s, 1H), 7.95 (d, $J = 8.4$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ_{C} 157.2, 147.0 (q, $J = 4.0$ Hz), 139.7, 134.6 (q, $J = 3.4$ Hz), 132.4 (q, $J = 334.0$ Hz), 127.3 (q, $J = 30.0$ Hz), 126.3 (q, $J = 332.2$ Hz), 124.6 (d, $J = 161.7$ Hz), 123.5 (q, $J = 35.7$ Hz), 121.9 (d, $J = 166.0$ Hz), 120.2 ppm.



2-(naphthalen-1-yl)-5-(trifluoromethyl)pyridine (4l): This reaction was performed following General Procedure with Naphthalene-1-boronic acid (**1m**, 41.2 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:10) to give the product (52.4 mg, 96% yield) as a brown yellow crystal. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.¹⁴

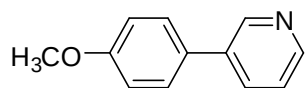


2-(furan-2-yl)-5-(trifluoromethyl)pyridine (4m): This reaction was performed following General Procedure with 2-Furanboronic acid (**1n**, 26.8 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:10) to give the product (29.84 mg, 70% yield) as brown yellow liquid. ^1H -NMR (400 MHz, CDCl_3): δ_{H} 8.82 (br. s, 1H), 7.93 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.58 (br. s, 1H), 7.19 (d, $J = 3.6$ Hz, 1H), 6.57 (dd, $J_1 = 3.6$ Hz, $J_2 = 2.0$ Hz, 1H). ^{13}C -NMR (100 MHz, CDCl_3): δ_{C} 152.4, 152.1, 146.5 (q, $J = 4.0$ Hz), 144.5, 133.9 (q, $J = 3.4$ Hz), 124.4 (q, $J = 280.8$ Hz), 122.2, 117.8, 112.5, 111.0 ppm. HRMS calculated for $\text{C}_{10}\text{H}_7\text{F}_3\text{NO}$, 214.04742, found 214.04789, $[\text{M}+\text{H}]^+$.



2-(thiophen-2-yl)-5-(trifluoromethyl)pyridine (4n): This reaction was performed following General Procedure with 2-thiophenylboronic acid (**1o**, 30.7 mg, 0.24 mmol, 1.2 equiv) and 2-chloro-5-(trifluoromethyl) pyridine (**2k**, 36.3 mg, 0.2 mmol, 1.0 equiv). The crude material was purified by chromatography

on silica gel (eluted with EtOAc:petroleum ether = 1:20) to give the product (43.5 mg, 95% yield) as a white solid. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for this compound match the literature data.¹⁵



3-(4-methoxyphenyl)pyridine (5a): This reaction was performed following General Procedure with 4-Methoxyphenylboronic acid (**1f**, 1.6 g, 10.56 mmol, 1.2 equiv) and 3-Chloropyridine (**2m**, 0.82 mL, 8.8 mmol, 1.0 equiv). The crude material was purified by chromatography on silica gel (eluted with EtOAc:petroleum ether = 1:4) to give the product (0.97 g, 60% yield) as a brown solid. ^1H -NMR (400 MHz, CDCl_3): δ_{H} 8.81 (dd, $J_1 = 2.4$ Hz, $J_2 = 0.8$ Hz, 1H), 8.54 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.2$ Hz, 1H), 7.84 (dq, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.54 (d, $J = 8.8$ Hz, 2H), 7.33 (ddd, $J_1 = 8.0$ Hz, $J_2 = 4.8$ Hz, $J_3 = 0.8$ Hz, 1H), 7.01 (d, $J = 8.8$ Hz, 2H), 3.86 (s, 3H). ^{13}C -NMR (100 MHz, CDCl_3): δ_{C} 159.7, 147.9, 147.8, 136.2, 133.9, 130.2, 128.2, 123.5, 114.5, 55.4 ppm. HRMS calculated for $\text{C}_{10}\text{H}_{12}\text{NO}$, 186.09134, found 186.09131, $[\text{M}+\text{H}]^+$.

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4-*tert*-butyl-4'-methylbiphenyl (3a)

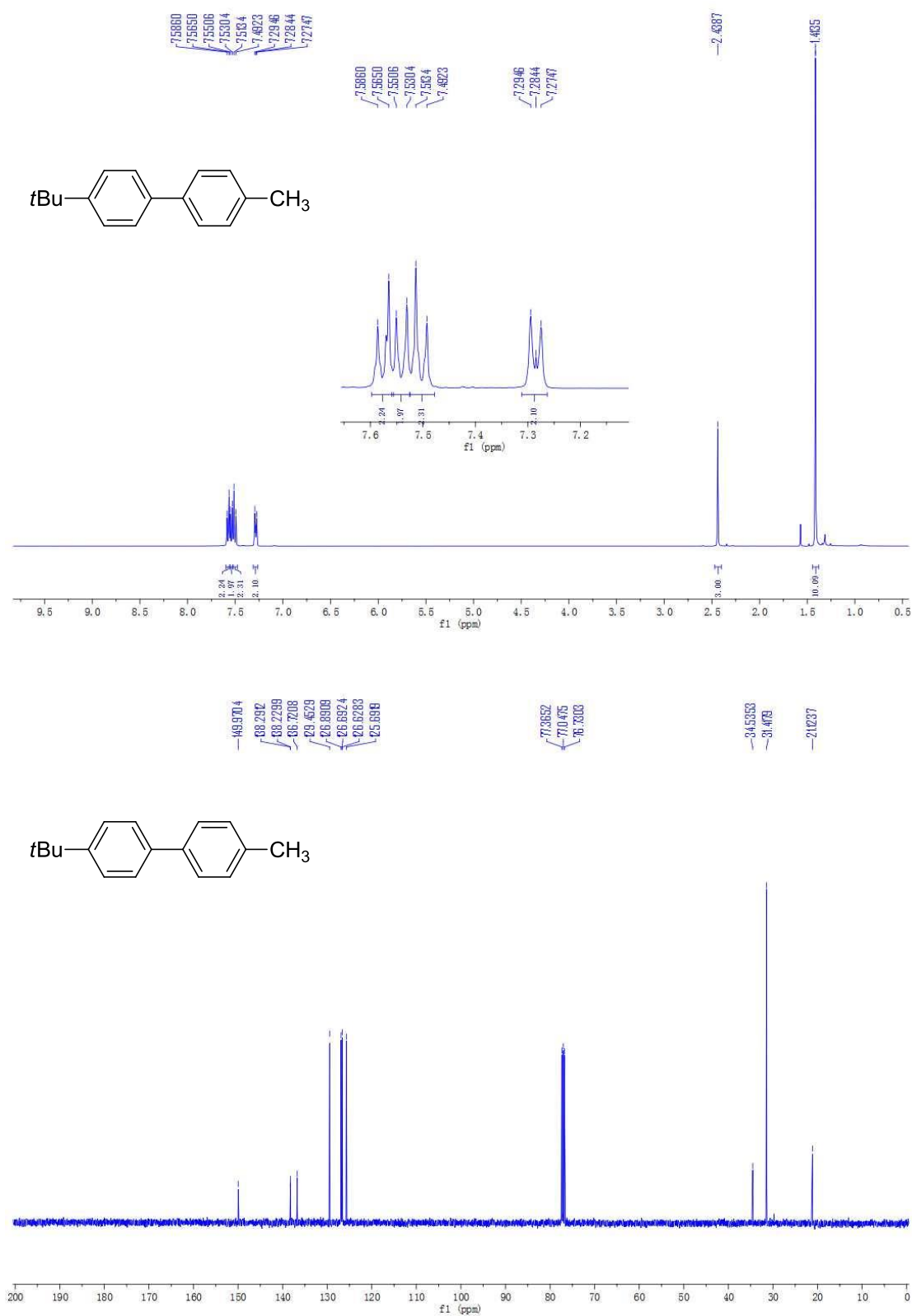


Fig. S1 ¹H and ¹³C NMR spectra of 4-*tert*-butyl-4'-methylbiphenyl (**3a**)

4-*tert*-butylbiphenyl (3b)

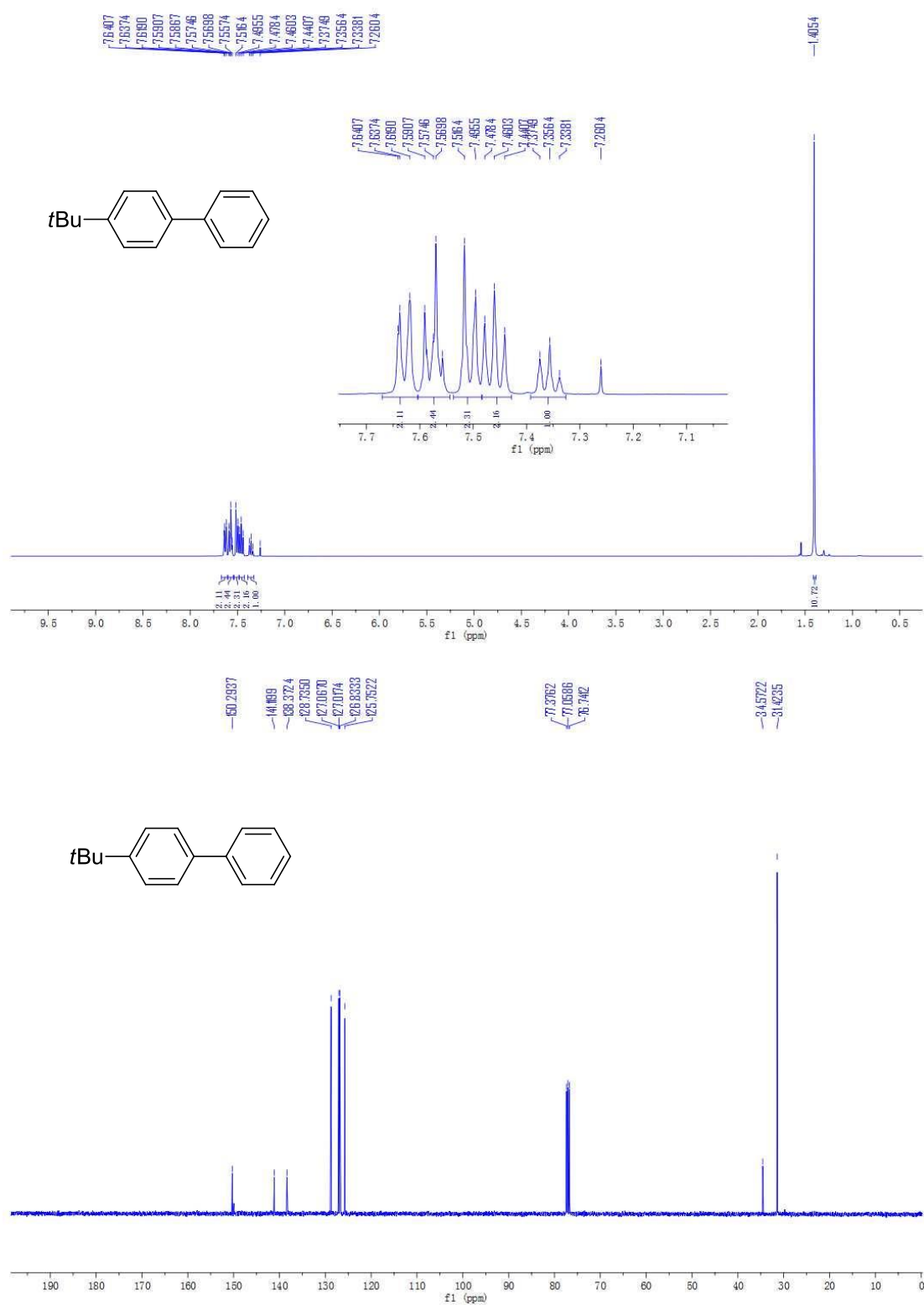


Fig. S2 ¹H and ¹³C NMR spectra of 4-*tert*-butylbiphenyl (3b)

4-*tert*-butyl-4'-chlorobiphenyl (3c)

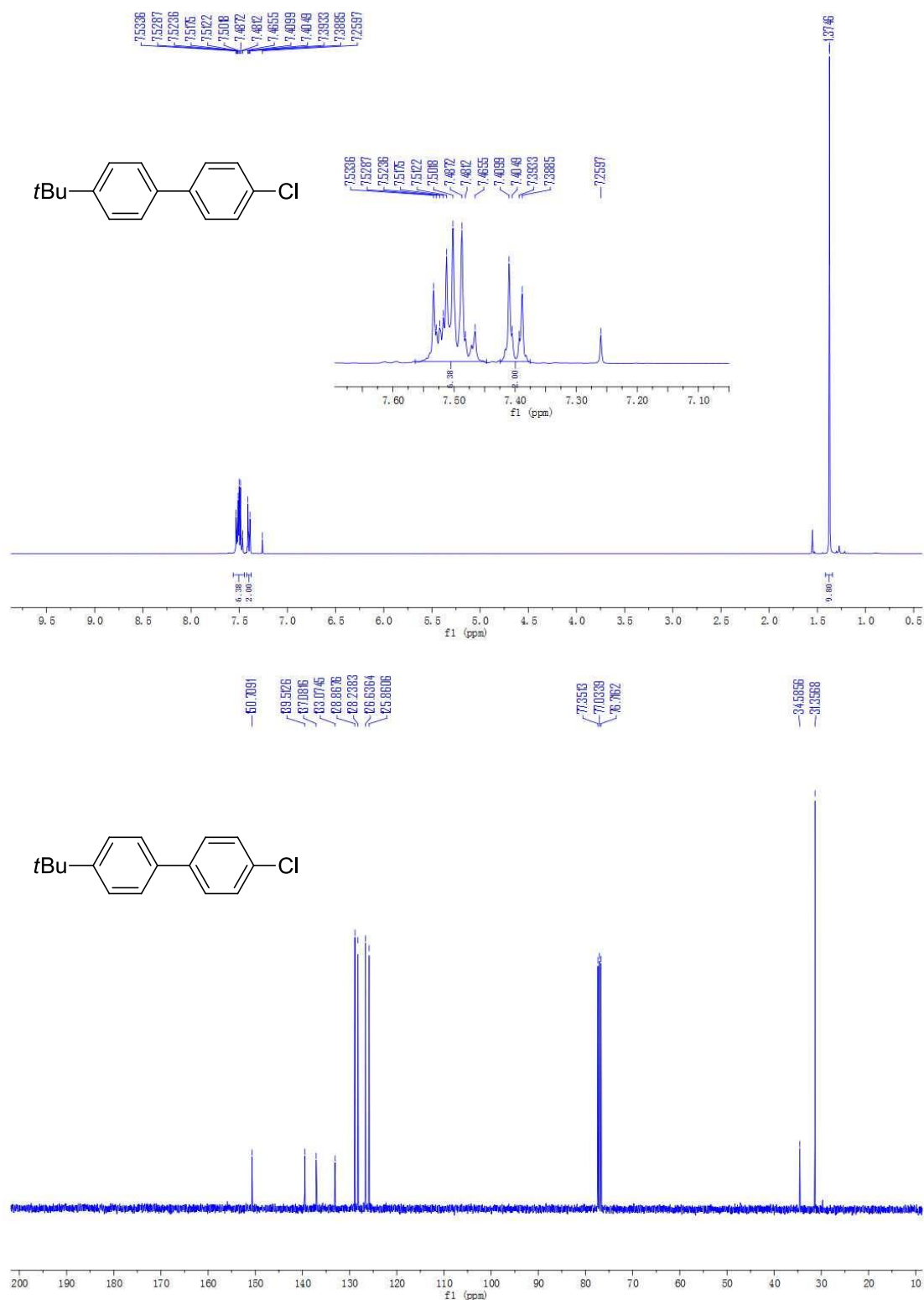


Fig. S3 ¹H and ¹³C NMR spectra of 4-*tert*-butyl-4'-chlorobiphenyl (3c)

4-*tert*-butyl-4'-fluorobiphenyl (3d)

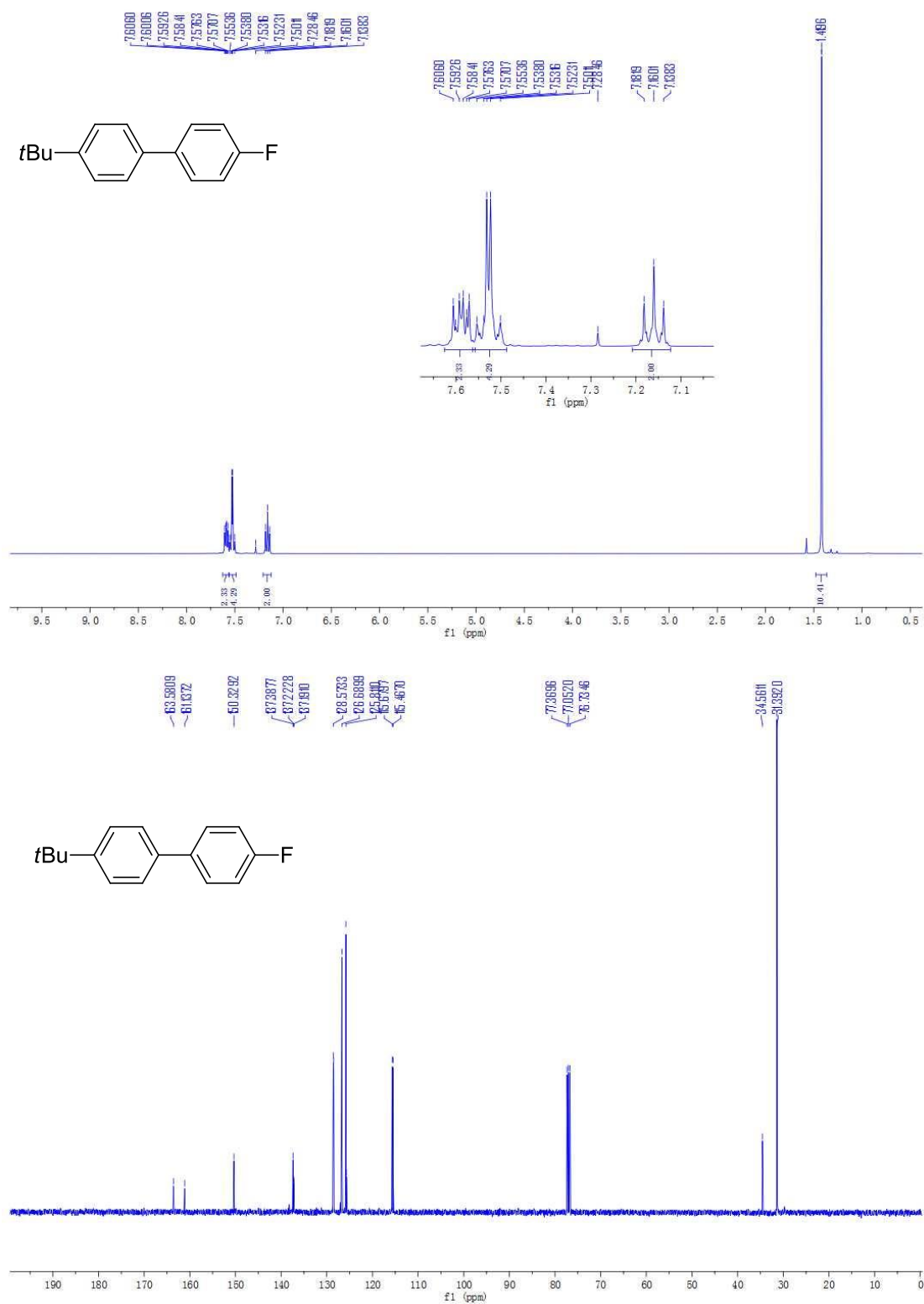


Fig. S4 ¹H and ¹³C NMR spectra of 4-*tert*-butyl-4'-fluorobiphenyl (3d)

4'-*tert*-butyl-3-(trifluoromethyl)biphenyl (**3e**)

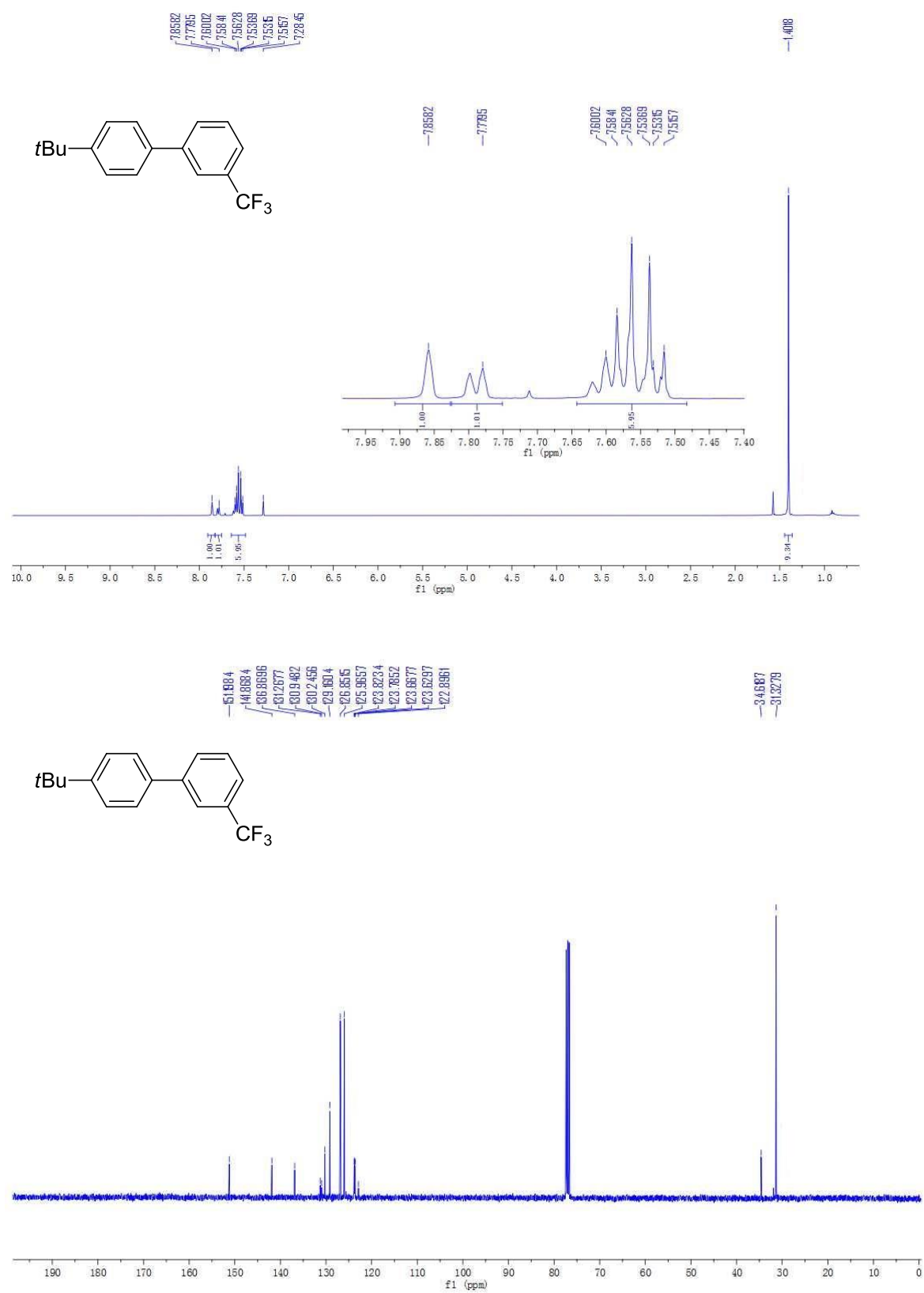


Fig. S5 ¹H and ¹³C NMR spectra of 4'-*tert*-butyl-3-(trifluoromethyl)biphenyl (**3e**)

1-(4-(*tert*-butyl)phenyl)naphthalene (3f)

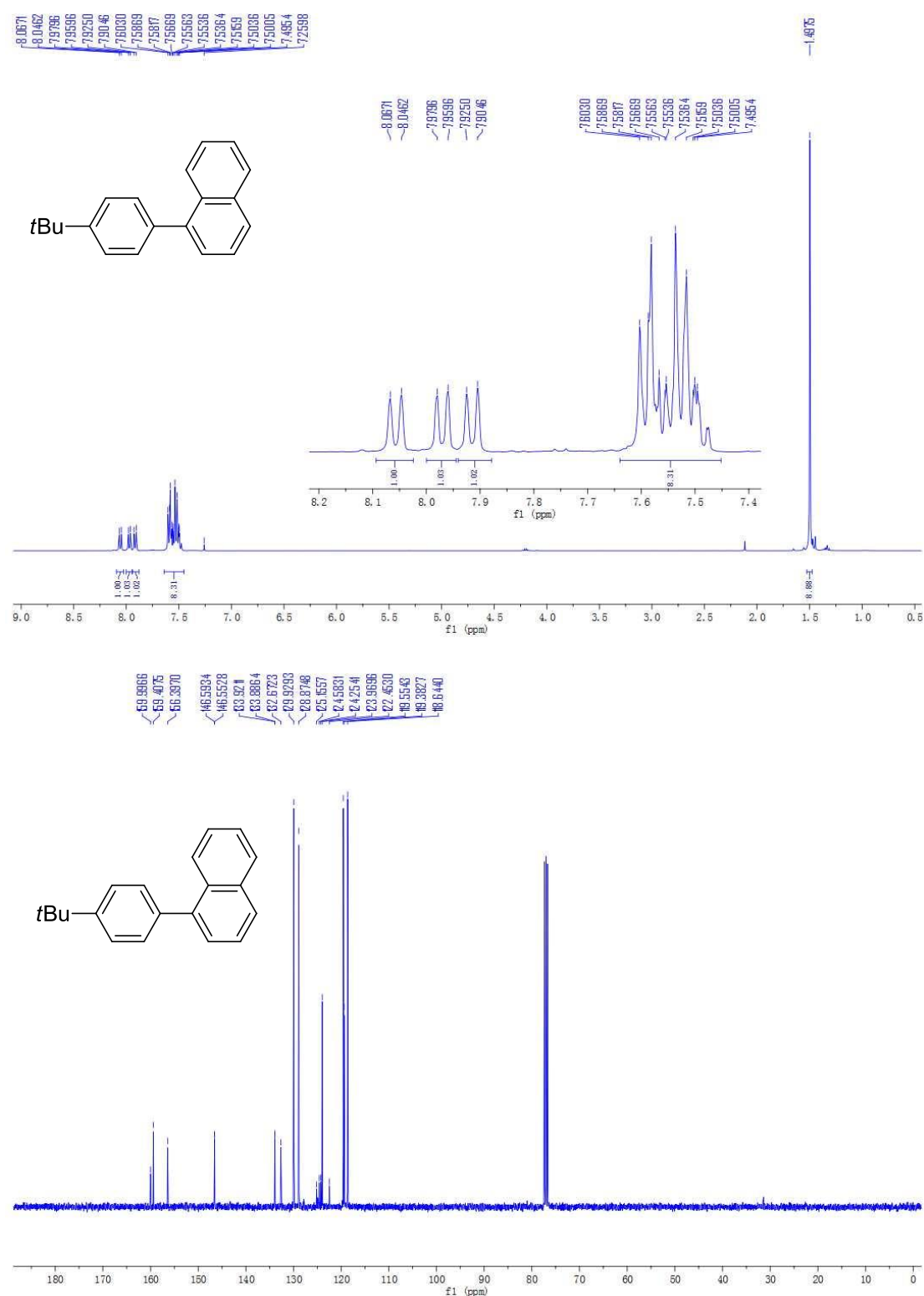


Fig. S6 ¹H and ¹³C NMR spectra of 1-(4-(*tert*-butyl)phenyl)naphthalene (3f)

2-(4-*tert*-butylphenyl)-3-chloropyridine (3g)

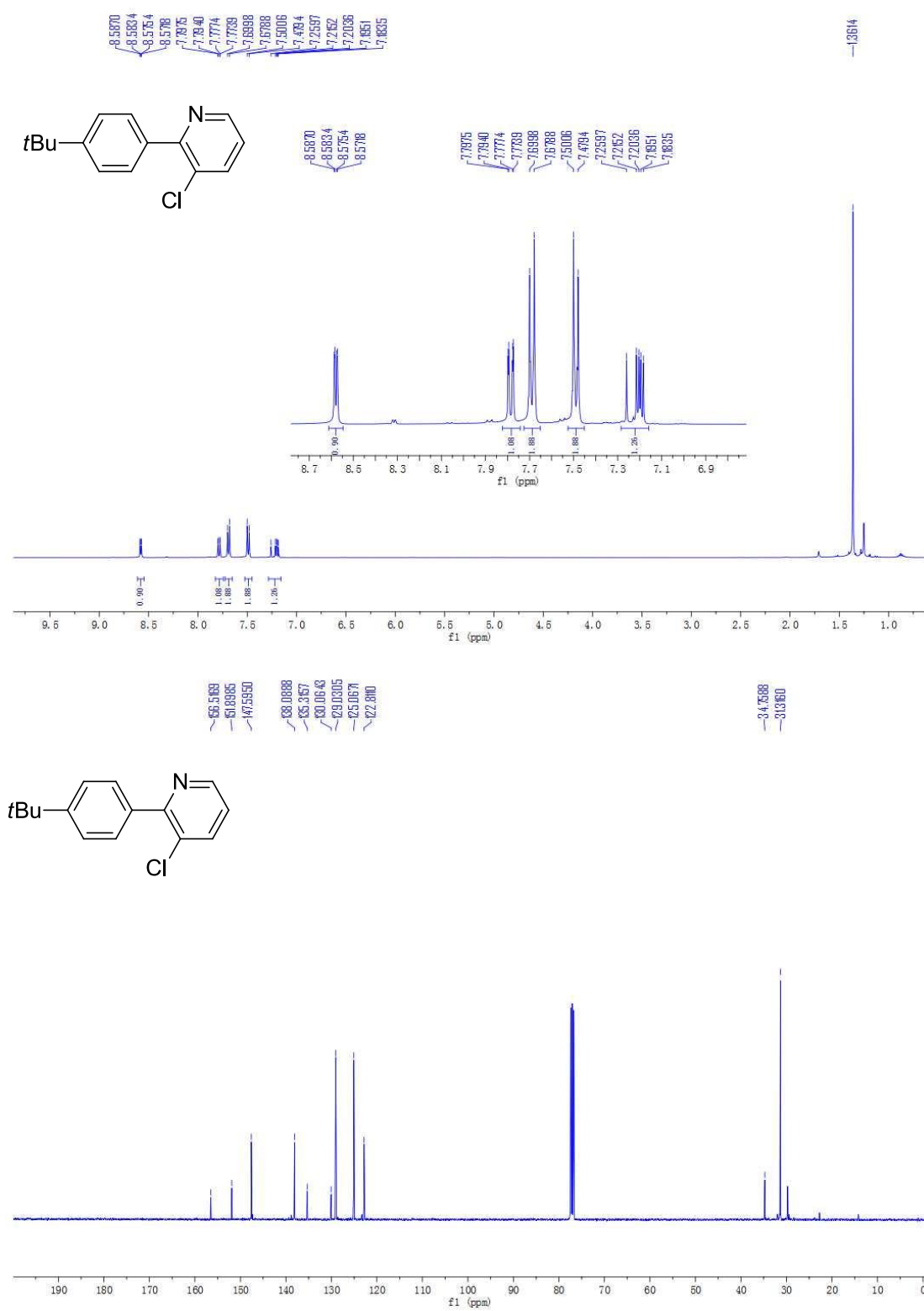


Fig. S7 ¹H and ¹³C NMR spectra of 2-(4-*tert*-butylphenyl)-3-chloropyridine (**3g**)

2-(4-*tert*-butylphenyl)-3-fluoropyridine (3h)

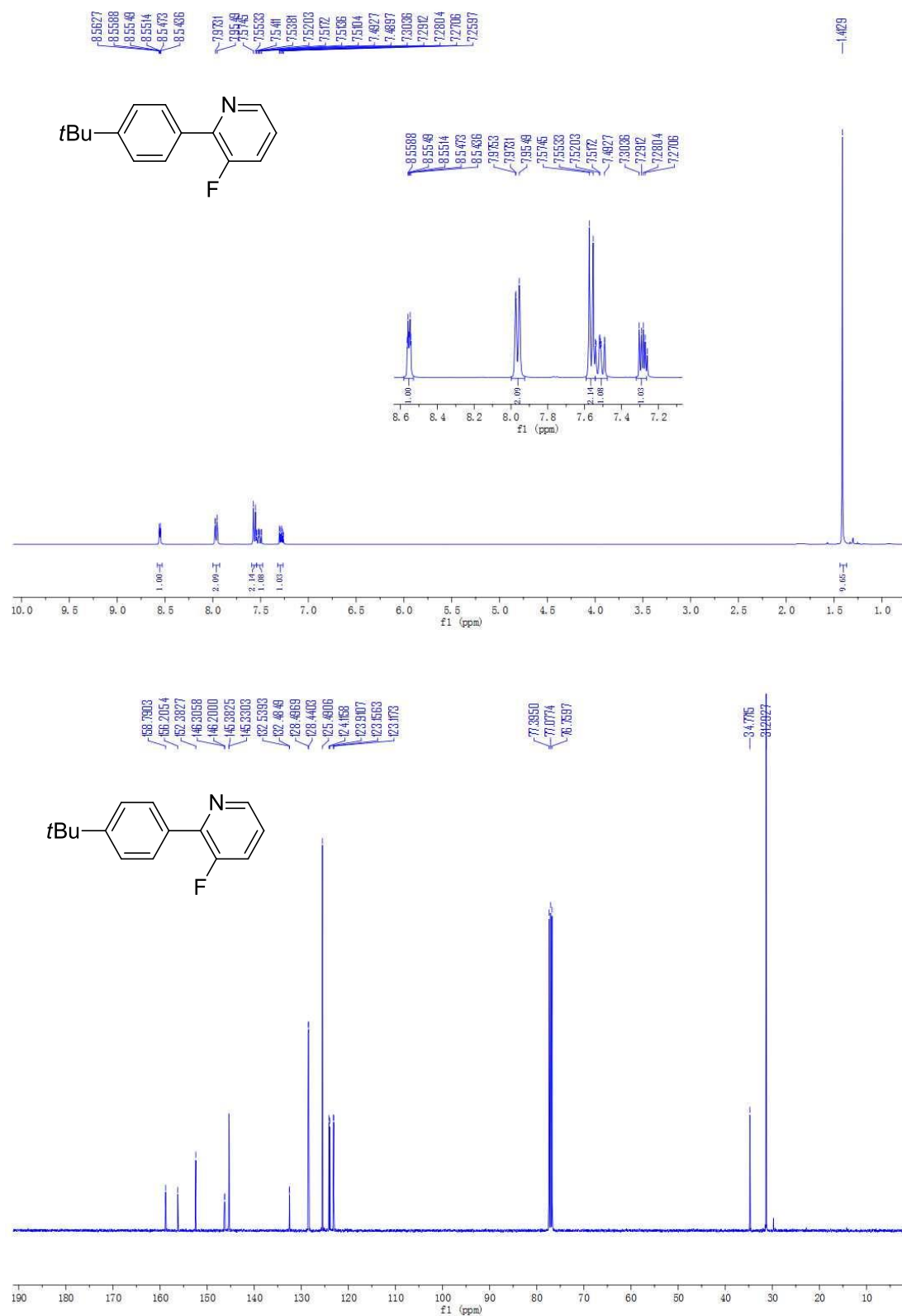


Fig. S8 ¹H and ¹³C NMR spectra of 2-(4-*tert*-butylphenyl)-3-fluoropyridine (3h)

2-(4-*tert*-butylphenyl)nicotinonitrile (**3i**)

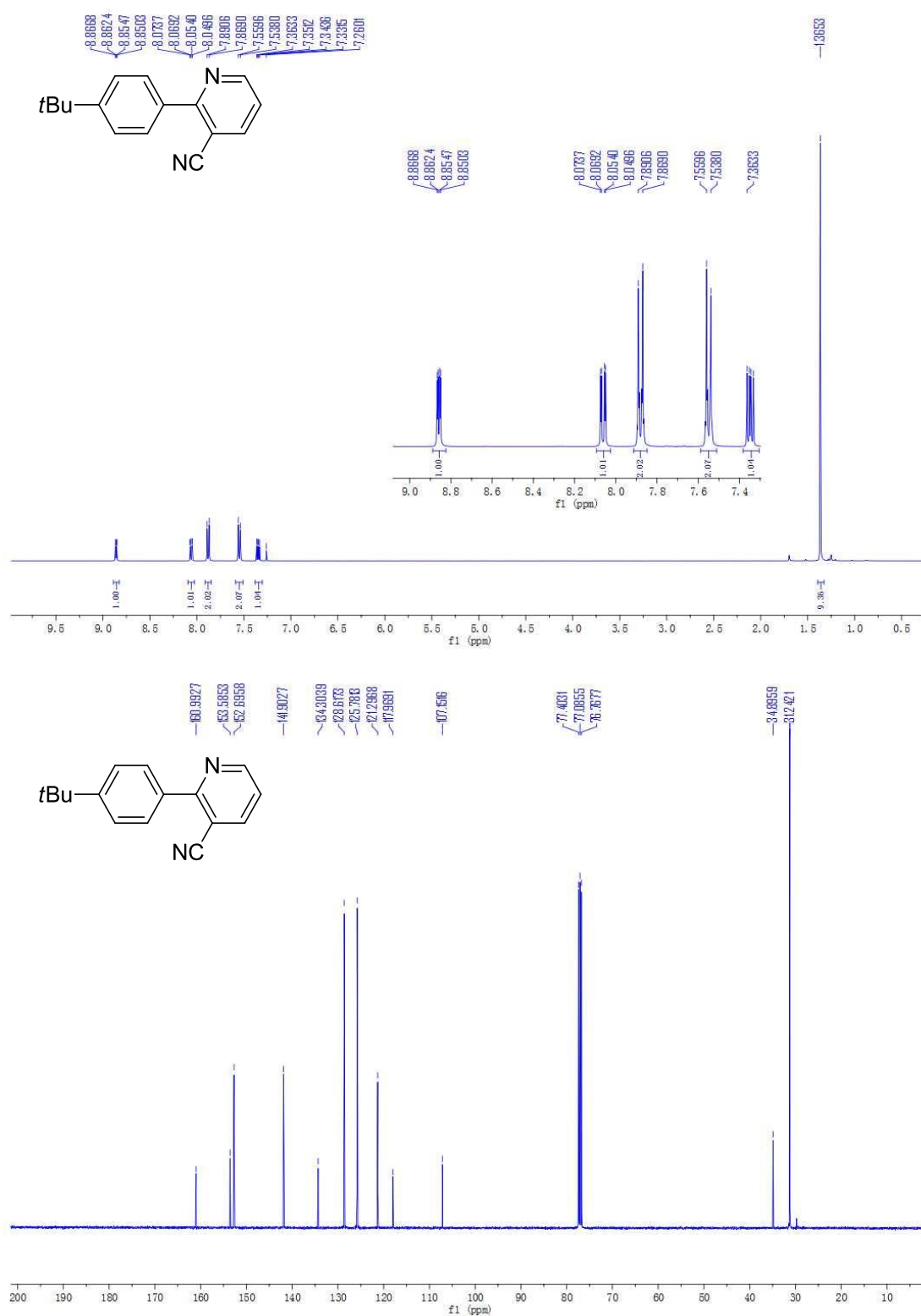


Fig. S9 ¹H and ¹³C NMR spectra of 2-(4-*tert*-butylphenyl)nicotinonitrile (**3i**)

2-(4-*tert*-butylphenyl)-3-nitropyridine (3j)

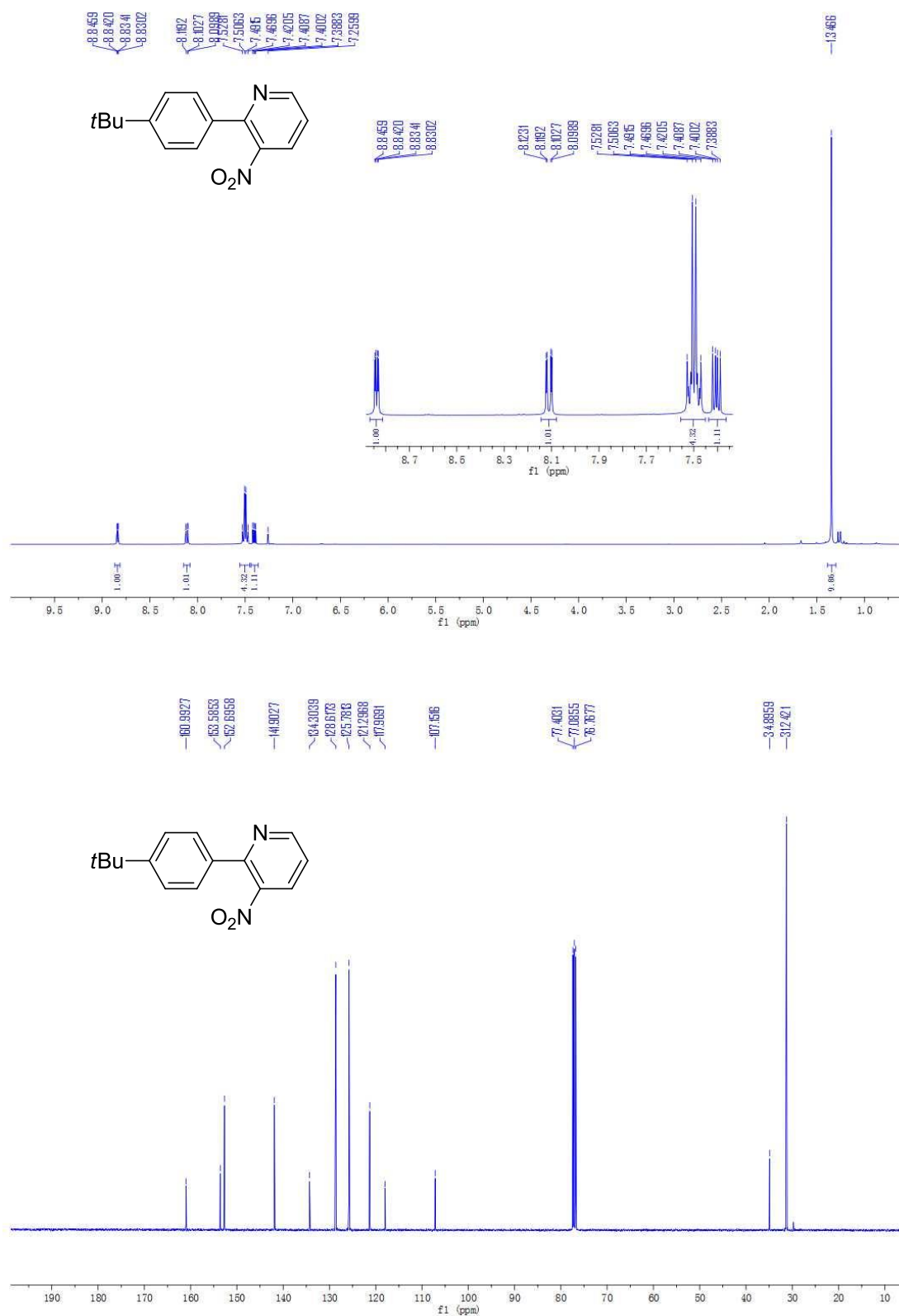


Fig. S10 ¹H and ¹³C NMR spectra of 2-(4-*tert*-butylphenyl)-3-nitropyridine (3j)

2-(4-*tert*-butylphenyl)-5-(trifluoromethyl)pyridine (3k)

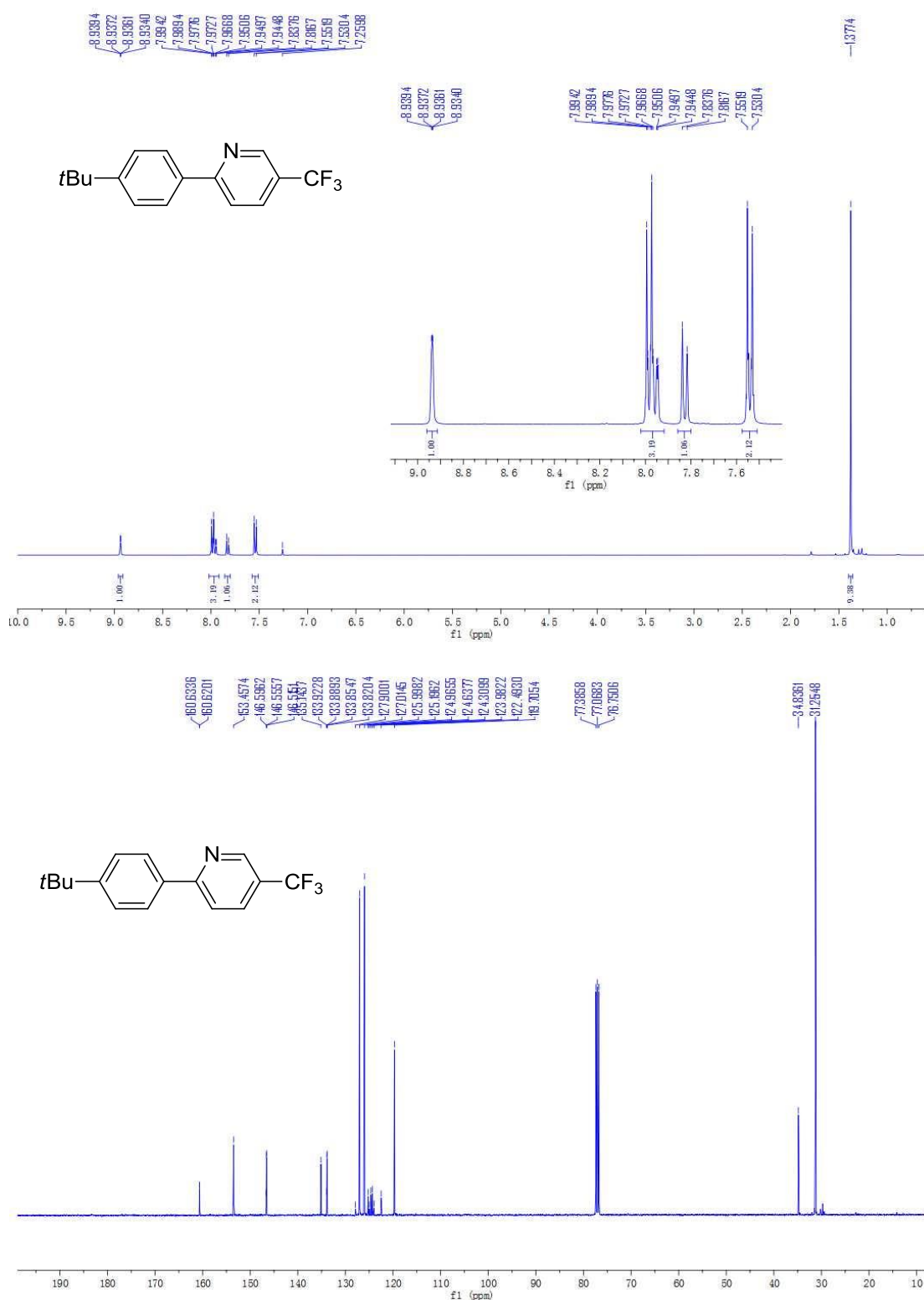


Fig. S11 ¹H and ¹³C NMR spectra of 2-(4-*tert*-butylphenyl)-5-(trifluoromethyl)pyridine (**3k**)

6-(4-*tert*-butylphenyl)nicotinonitrile (3l)

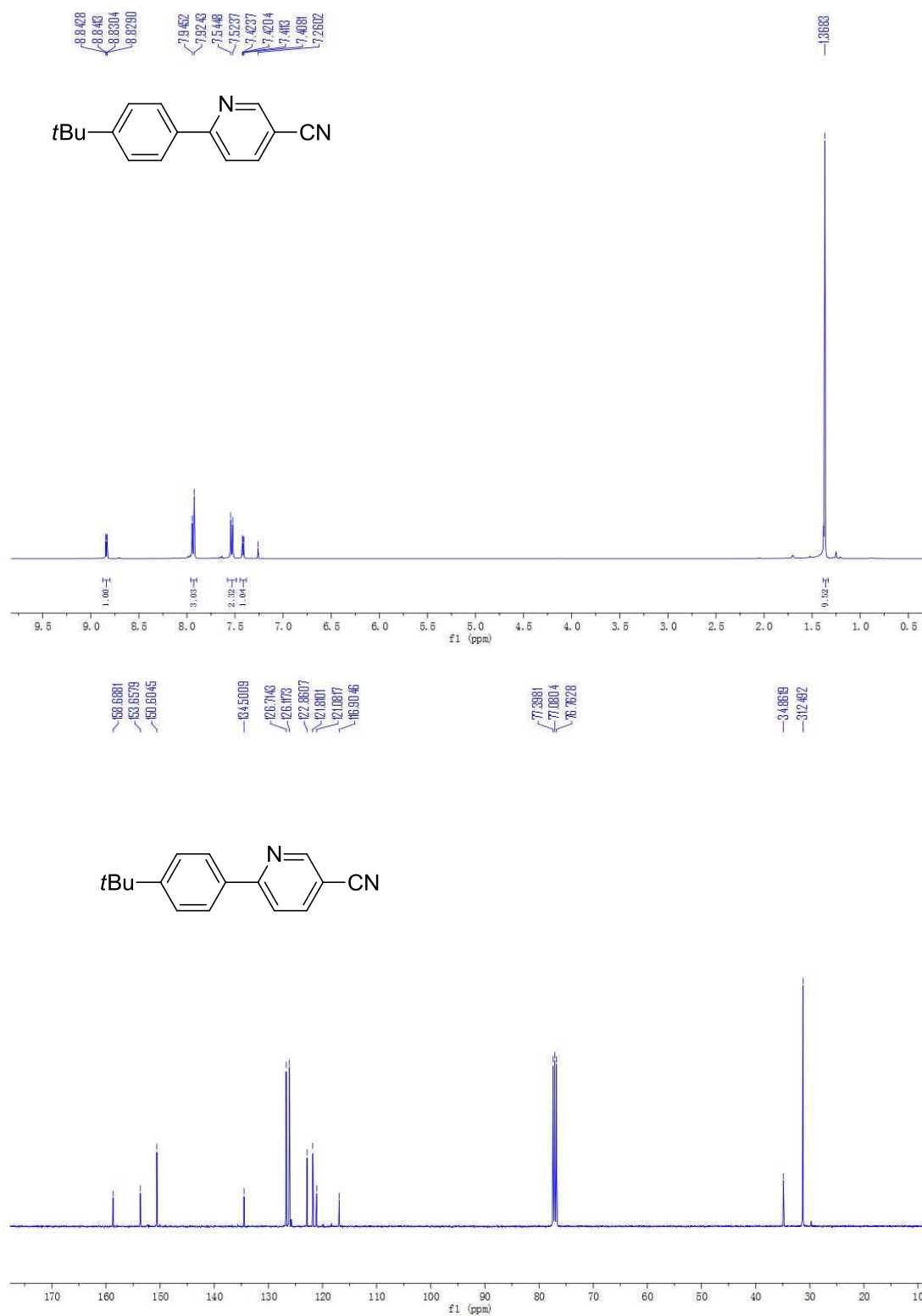
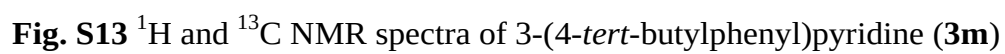


Fig. S12 ¹H and ¹³C NMR spectra of 6-(4-*tert*-butylphenyl)nicotinonitrile (**3l**)

Chemical structure of 4-tert-butylpyridine is shown above the spectrum. The spectrum displays peaks corresponding to the structure, with chemical shifts (ppm) labeled above the peaks: 8.762, 8.501, 8.494, 7.8099, 7.8056, 7.8043, 7.8002, 7.7902, 7.7858, 7.7845, 7.7802, 7.4764, 7.4544, 7.4454, 7.4234, 7.2932, 7.283, 7.2747, 7.2686, 7.2626, 7.2566, 7.1845, and 29337. Integration values are shown below the peaks: 1.00, 1.01, 1.02, 4.14, 1.06, and 9.19.



2-(4-(*tert*-butyl)phenyl)thiophene (3n)

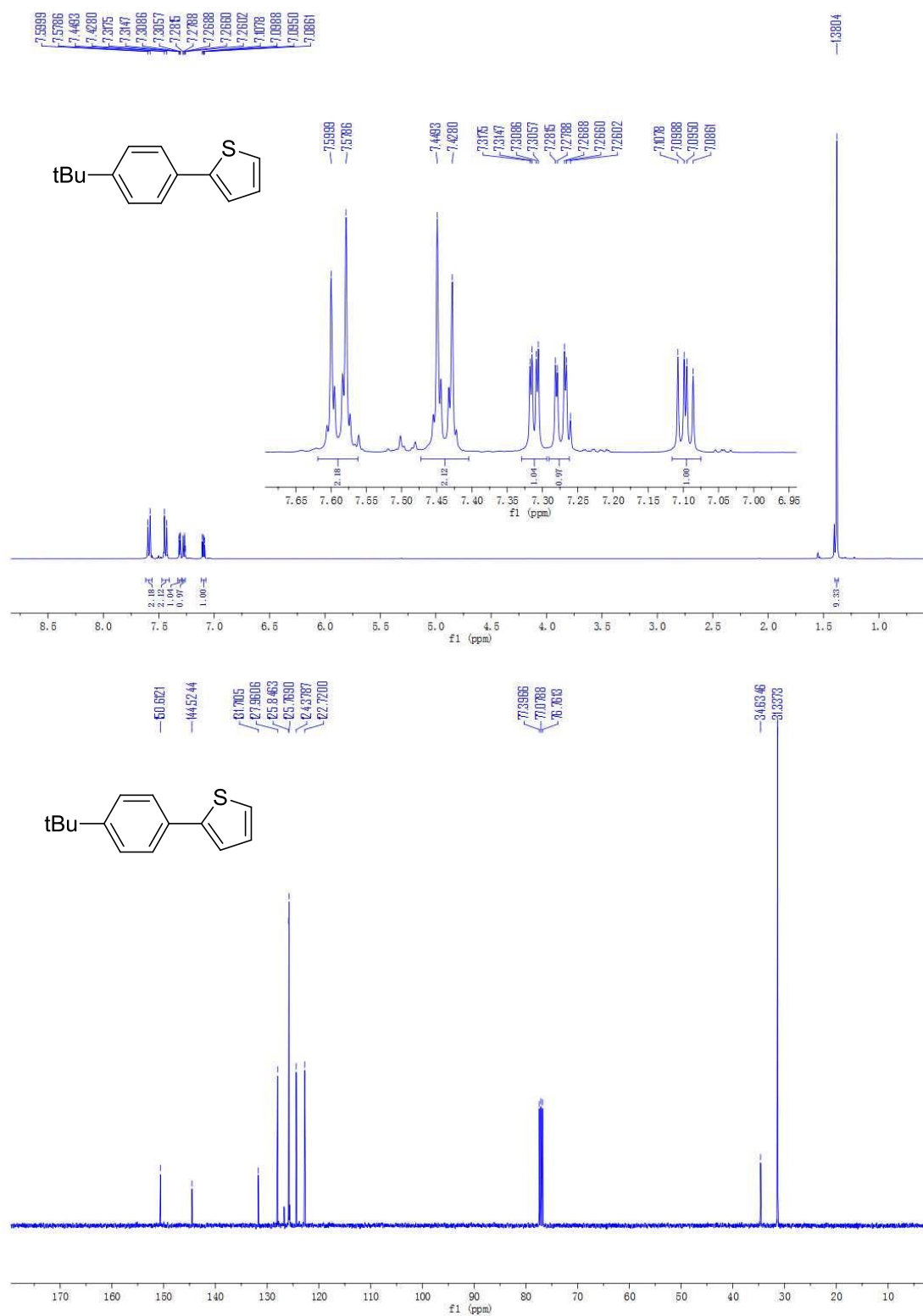


Fig. S14 ¹H and ¹³C NMR spectra of 2-(4-(*tert*-butyl)phenyl)thiophene (3n)

¹H NMR Spectrum (Top):

Chemical structure: Cc1ccc(cc1)-c2cc(C(F)(F)F)cn2

Peak list (ppm): 9.00, 8.9786, 8.9776, 8.07816, 8.07716, 8.07616, 8.07516, 8.07416, 8.07316, 8.07216, 8.07116, 8.07016, 8.06916, 8.06816, 8.06716, 8.06616, 8.06516, 8.06416, 8.06316, 8.06216, 8.06116, 8.06016, 8.05916, 8.05816, 8.05716, 8.05616, 8.05516, 8.05416, 8.05316, 8.05216, 8.05116, 8.05016, 8.04916, 8.04816, 8.04716, 8.04616, 8.04516, 8.04416, 8.04316, 8.04216, 8.04116, 8.04016, 8.03916, 8.03816, 8.03716, 8.03616, 8.03516, 8.03416, 8.03316, 8.03216, 8.03116, 8.03016, 8.02916, 8.02816, 8.02716, 8.02616, 8.02516, 8.02416, 8.02316, 8.02216, 8.02116, 8.02016, 8.01916, 8.01816, 8.01716, 8.01616, 8.01516, 8.01416, 8.01316, 8.01216, 8.01116, 8.01016, 8.00916, 8.00816, 8.00716, 8.00616, 8.00516, 8.00416, 8.00316, 8.00216, 8.00116, 8.00016, 7.99916, 7.99816, 7.99716, 7.99616, 7.99516, 7.99416, 7.99316, 7.99216, 7.99116, 7.99016, 7.98916, 7.98816, 7.98716, 7.98616, 7.98516, 7.98416, 7.98316, 7.98216, 7.98116, 7.98016, 7.97916, 7.97816, 7.97716, 7.97616, 7.97516, 7.97416, 7.97316, 7.97216, 7.97116, 7.97016, 7.96916, 7.96816, 7.96716, 7.96616, 7.96516, 7.96416, 7.96316, 7.96216, 7.96116, 7.96016, 7.95916, 7.95816, 7.95716, 7.95616, 7.95516, 7.95416, 7.95316, 7.95216, 7.95116, 7.95016, 7.94916, 7.94816, 7.94716, 7.94616, 7.94516, 7.94416, 7.94316, 7.94216, 7.94116, 7.94016, 7.93916, 7.93816, 7.93716, 7.93616, 7.93516, 7.93416, 7.93316, 7.93216, 7.93116, 7.93016, 7.92916, 7.92816, 7.92716, 7.92616, 7.92516, 7.92416, 7.92316, 7.92216, 7.92116, 7.92016, 7.91916, 7.91816, 7.91716, 7.91616, 7.91516, 7.91416, 7.91316, 7.91216, 7.91116, 7.91016, 7.90916, 7.90816, 7.90716, 7.90616, 7.90516, 7.90416, 7.90316, 7.90216, 7.90116, 7.90016, 7.89916, 7.89816, 7.89716, 7.89616, 7.89516, 7.89416, 7.89316, 7.89216, 7.89116, 7.89016, 7.88916, 7.88816, 7.88716, 7.88616, 7.88516, 7.88416, 7.88316, 7.88216, 7.88116, 7.88016, 7.87916, 7.87816, 7.87716, 7.87616, 7.87516, 7.87416, 7.87316, 7.87216, 7.87116, 7.87016, 7.86916, 7.86816, 7.86716, 7.86616, 7.86516, 7.86416, 7.86316, 7.86216, 7.86116, 7.86016, 7.85916, 7.85816, 7.85716, 7.85616, 7.85516, 7.85416, 7.85316, 7.85216, 7.85116, 7.85016, 7.84916, 7.84816, 7.84716, 7.84616, 7.84516, 7.84416, 7.84316, 7.84216, 7.84116, 7.84016, 7.83916, 7.83816, 7.83716, 7.83616, 7.83516, 7.83416, 7.83316, 7.83216, 7.83116, 7.83016, 7.82916, 7.82816, 7.82716, 7.82616, 7.82516, 7.82416, 7.82316, 7.82216, 7.82116, 7.82016, 7.81916, 7.81816, 7.81716, 7.81616, 7.81516, 7.81416, 7.81316, 7.81216, 7.81116, 7.81016, 7.80916, 7.80816, 7.80716, 7.80616, 7.80516, 7.80416, 7.80316, 7.80216, 7.80116, 7.80016, 7.79916, 7.79816, 7.79716, 7.79616, 7.79516, 7.79416, 7.79316, 7.79216, 7.79116, 7.79016, 7.78916, 7.78816, 7.78716, 7.78616, 7.78516, 7.78416, 7.78316, 7.78216, 7.78116, 7.78016, 7.77916, 7.77816, 7.77716, 7.77616, 7.77516, 7.77416, 7.77316, 7.77216, 7.77116, 7.77016, 7.76916, 7.76816, 7.76716, 7.76616, 7.76516, 7.76416, 7.76316, 7.76216, 7.76116, 7.76016, 7.75916, 7.75816, 7.75716, 7.75616, 7.75516, 7.75416, 7.75316, 7.75216, 7.75116, 7.75016, 7.74916, 7.74816, 7.74716, 7.74616, 7.74516, 7.74416, 7.74316, 7.74216, 7.74116, 7.74016, 7.73916, 7.73816, 7.73716, 7.73616, 7.73516, 7.73416, 7.73316, 7.73216, 7.73116, 7.73016, 7.72916, 7.72816, 7.72716, 7.72616, 7.72516, 7.72416, 7.72316, 7.72216, 7.72116, 7.72016, 7.71916, 7.71816, 7.71716, 7.71616, 7.71516, 7.71416, 7.71316, 7.71216, 7.71116, 7.71016, 7.70916, 7.70816, 7.70716, 7.70616, 7.70516, 7.70416, 7.70316, 7.70216, 7.70116, 7.70016, 7.69916, 7.69816, 7.69716, 7.69616, 7.69516, 7.69416, 7.69316, 7.69216, 7.69116, 7.69016, 7.68916, 7.68816, 7.68716, 7.68616, 7.68516, 7.68416, 7.68316, 7.68216, 7.68116, 7.68016, 7.67916, 7.67816, 7.67716, 7.67616, 7.67516, 7.67416, 7.67316, 7.67216, 7.67116, 7.67016, 7.66916, 7.66816, 7.66716, 7.66

30

2-p-tolyl-5-(trifluoromethyl)pyridine (4b)

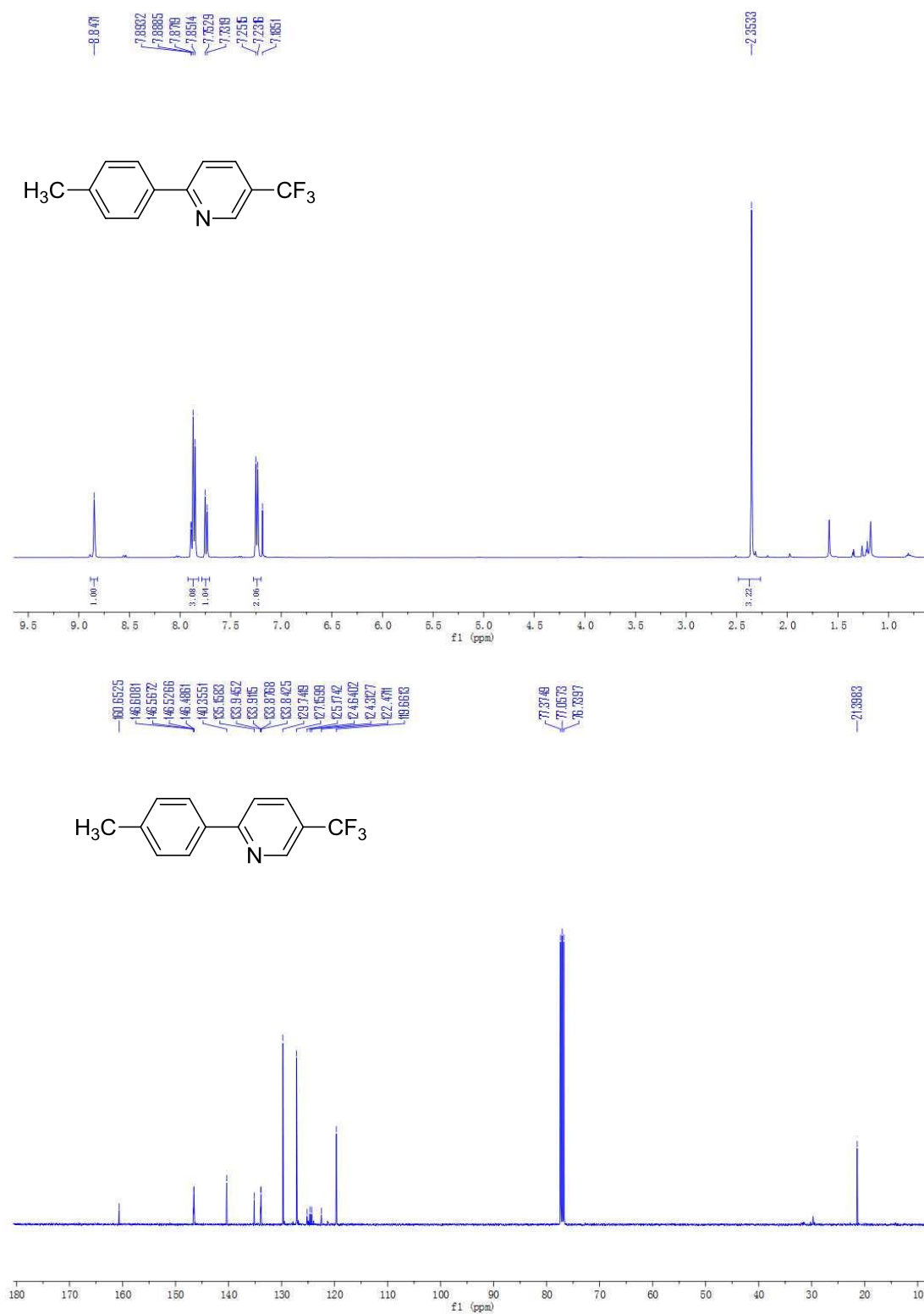


Fig. S16 ¹H and ¹³C NMR spectra of 2-p-tolyl-5-(trifluoromethyl)pyridine (**4b**)

2-m-tolyl-5-(trifluoromethyl)pyridine (4c)

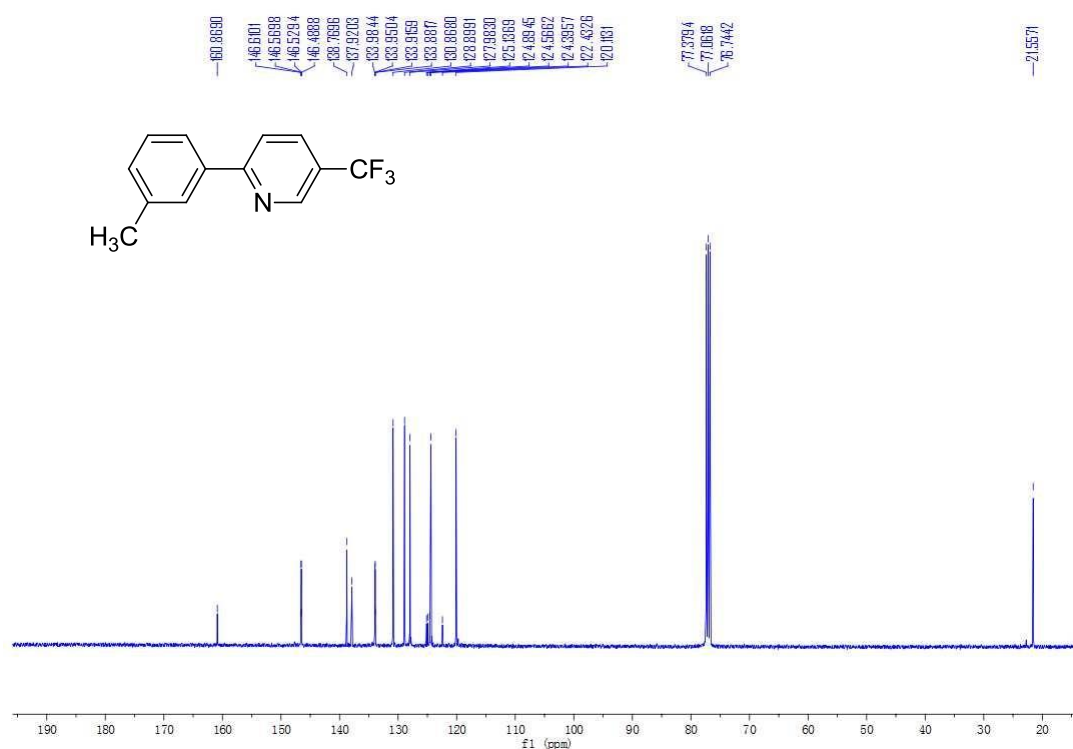
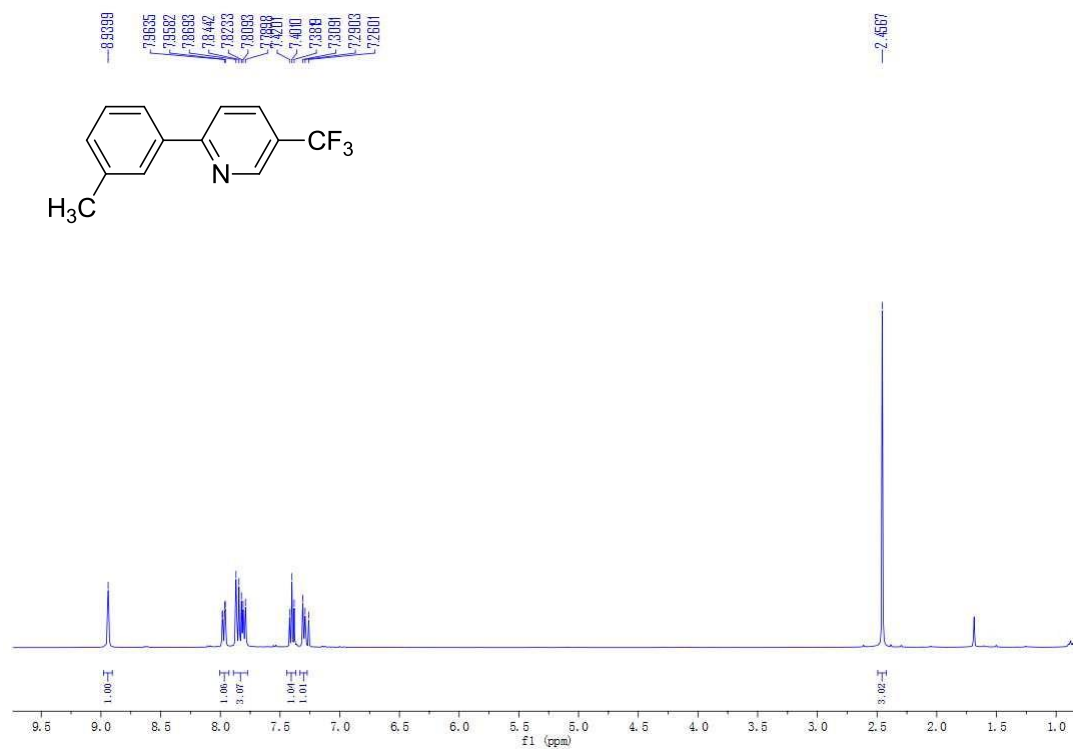


Fig. S17 ¹H and ¹³C NMR spectra of 2-m-tolyl-5-(trifluoromethyl)pyridine (4c)

2-(3,5-dimethylphenyl)-5-(trifluoromethyl)pyridine (4d)

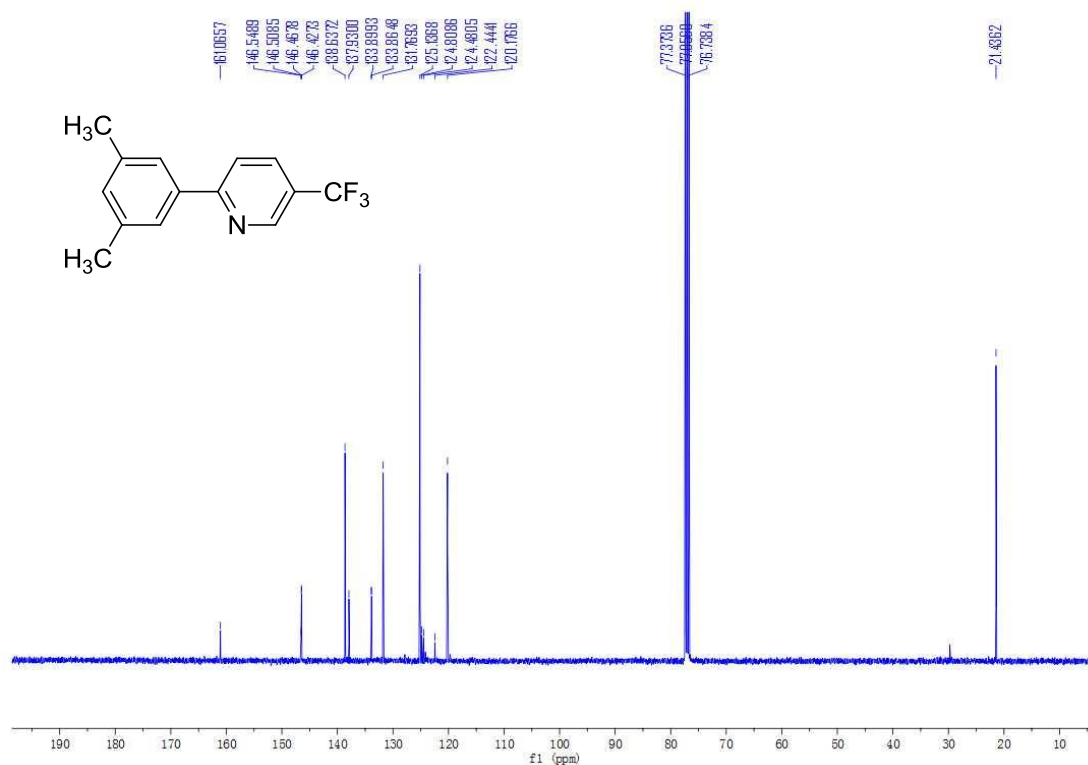
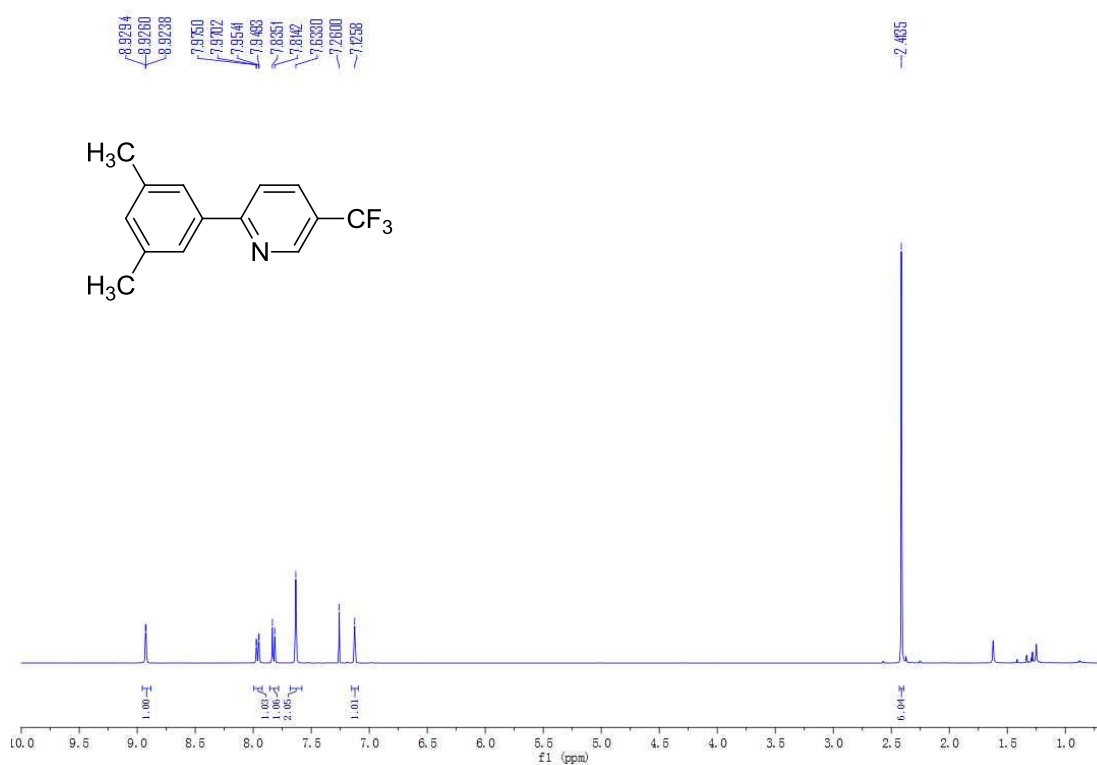


Fig.18 ¹H and ¹³C NMR spectra of 2-(3,5-dimethylphenyl)-5-(trifluoromethyl)pyridine(4d)

6'-methoxy-5-(trifluoromethyl)-2,3'-bipyridine (4e)

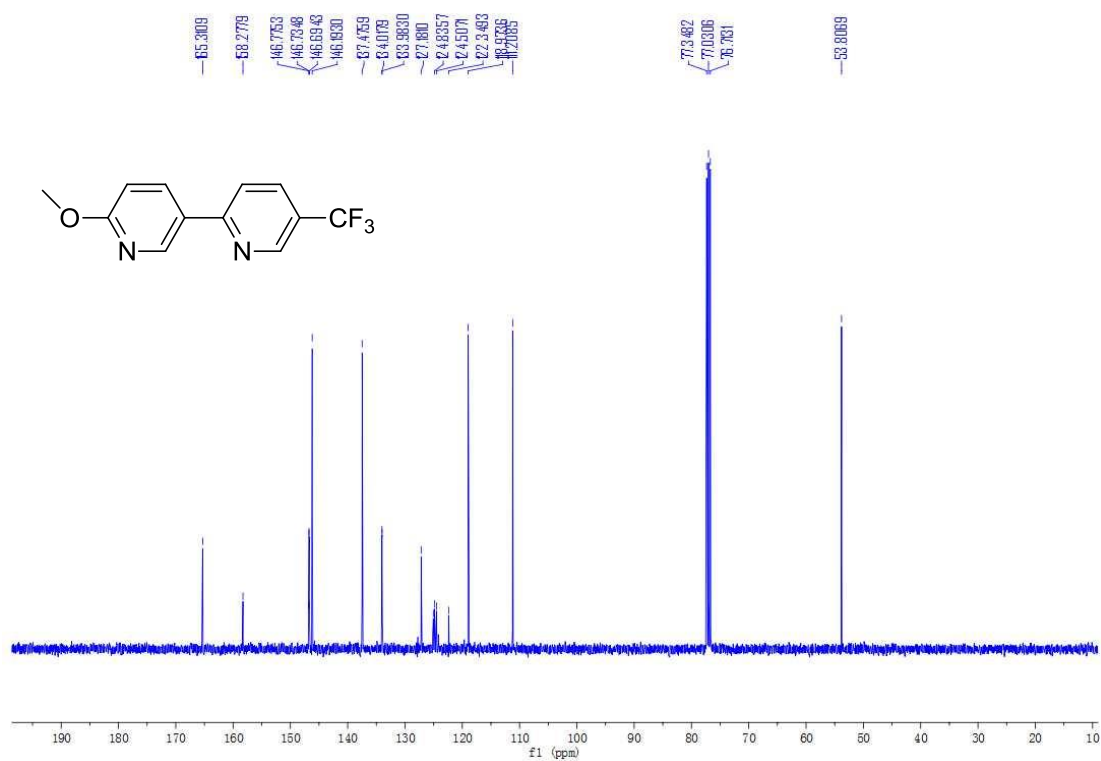
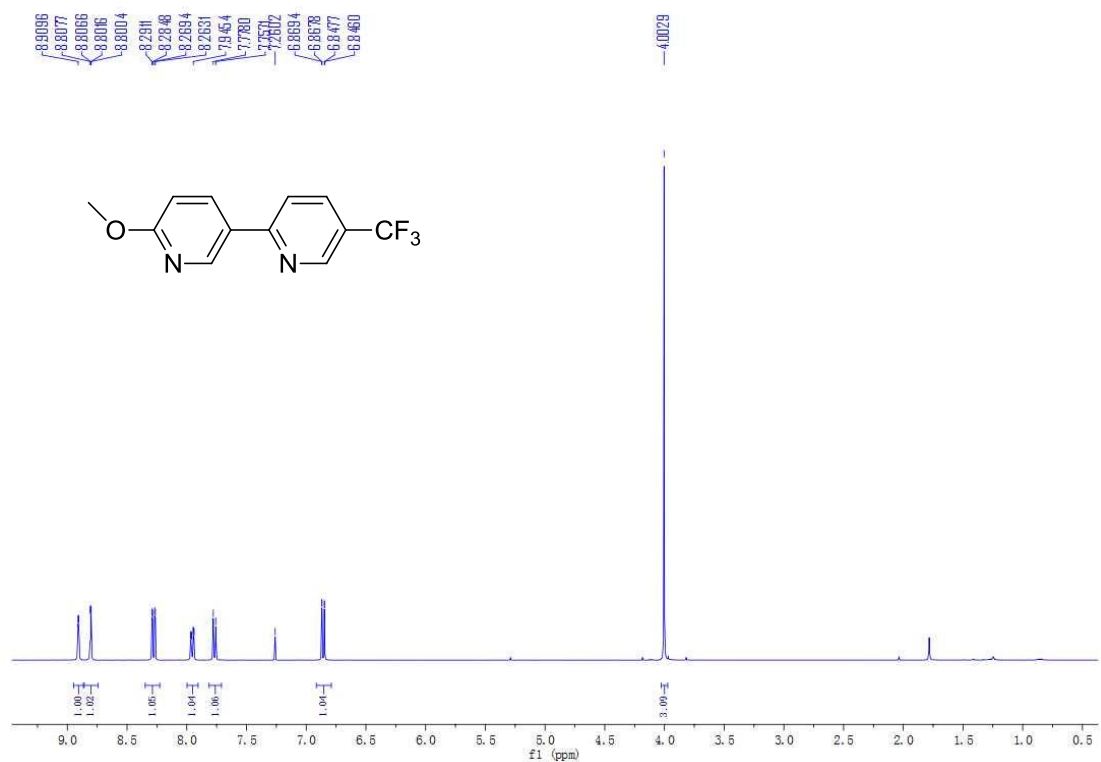


Fig.19 ¹H and ¹³C NMR spectra of 6'-methoxy-5-(trifluoromethyl)-2,3'-bipyridine (4e)

2-(3-methoxyphenyl)-5-(trifluoromethyl)pyridine (4f)

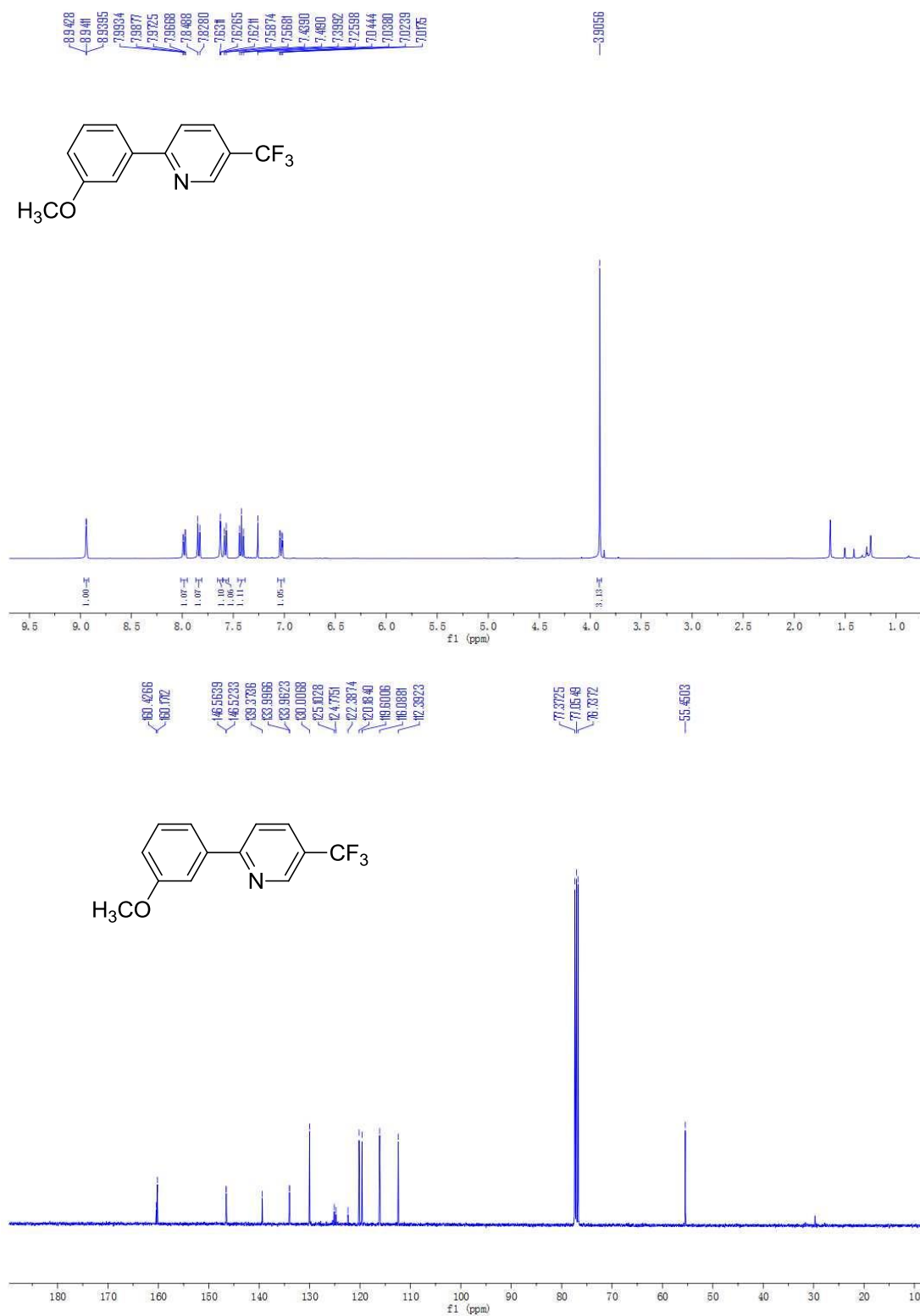


Fig. S20 ¹H and ¹³C NMR spectra of 2-(3-methoxyphenyl)-5-(trifluoromethyl)pyridine (**4f**)

2-(4-phenoxyphenyl)-5-(trifluoromethyl)pyridine (4g)

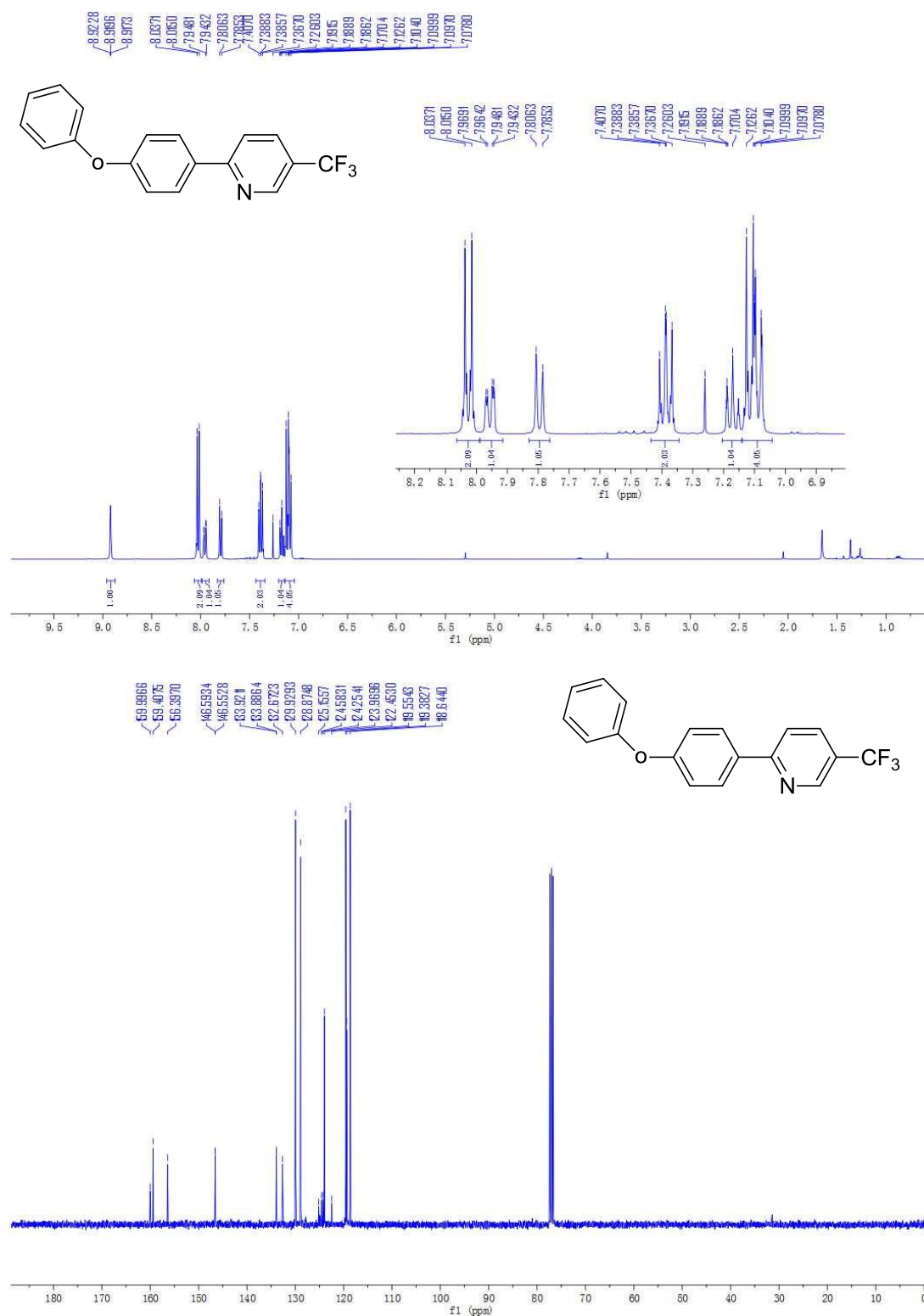


Fig. S21 ¹H and ¹³C NMR spectra of 2-(4-phenoxyphenyl)-5-(trifluoromethyl)pyridine (**4g**)

2-(3-nitrophenyl)-5-(trifluoromethyl)pyridine (4h)

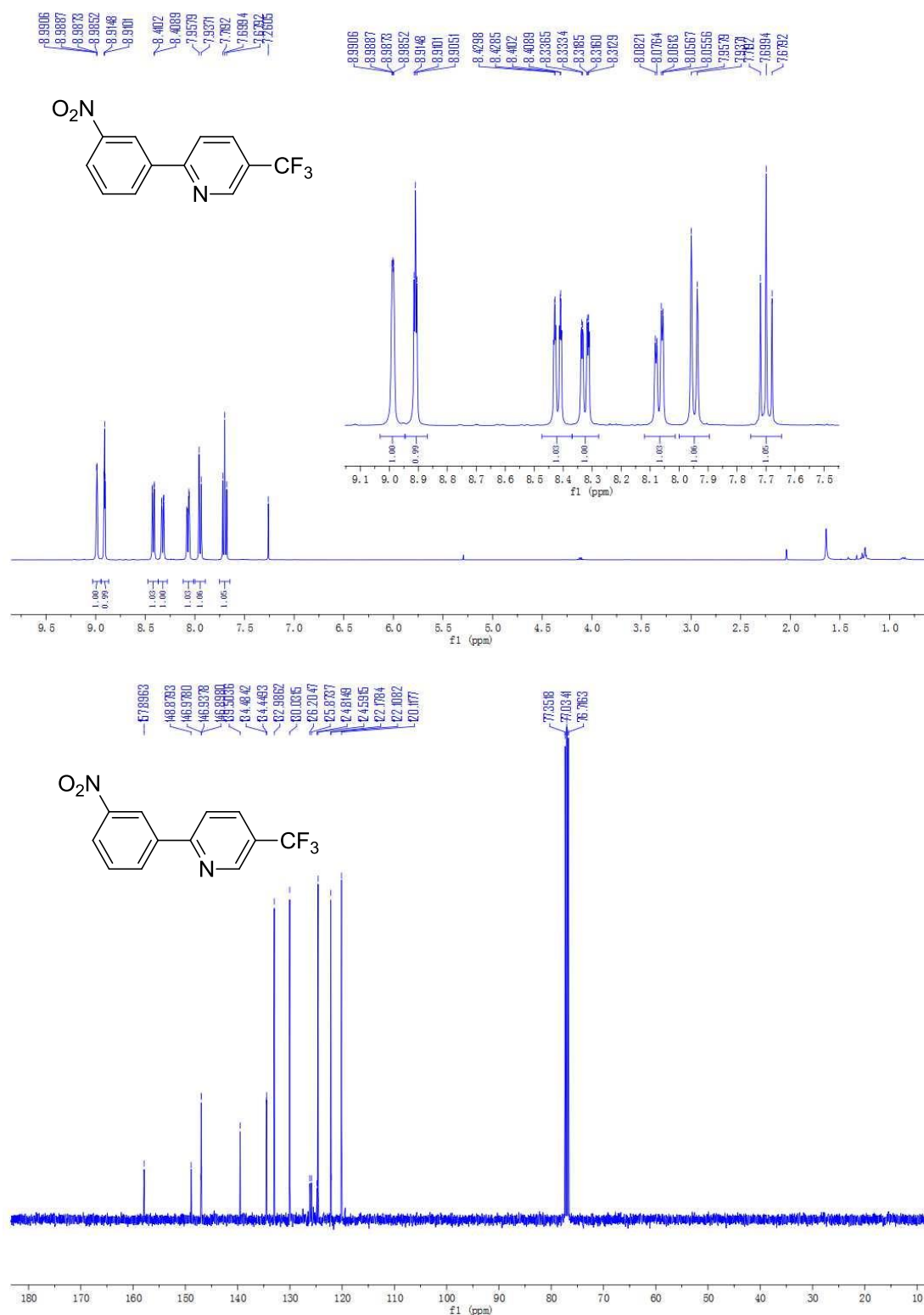


Fig. S22 ¹H and ¹³C NMR spectra of 2-(3-nitrophenyl)-5-(trifluoromethyl)pyridine (**4h**)

2-(4-fluorophenyl)-5-(trifluoromethyl)pyridine (4i)

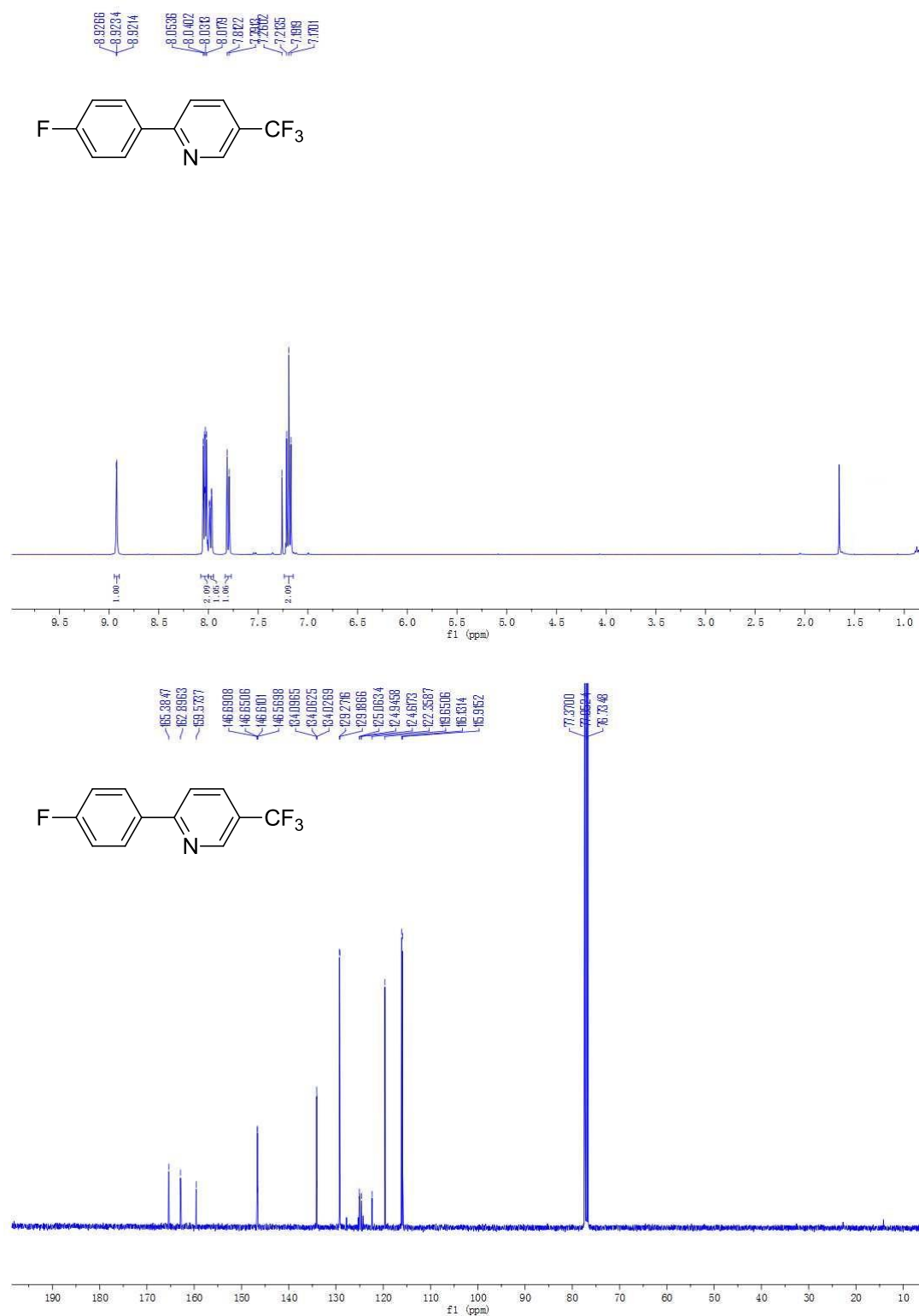


Fig. S23 ¹H and ¹³C NMR spectra of 2-(4-fluorophenyl)-5-(trifluoromethyl)pyridine (**4i**)

5-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)pyridine (4j)

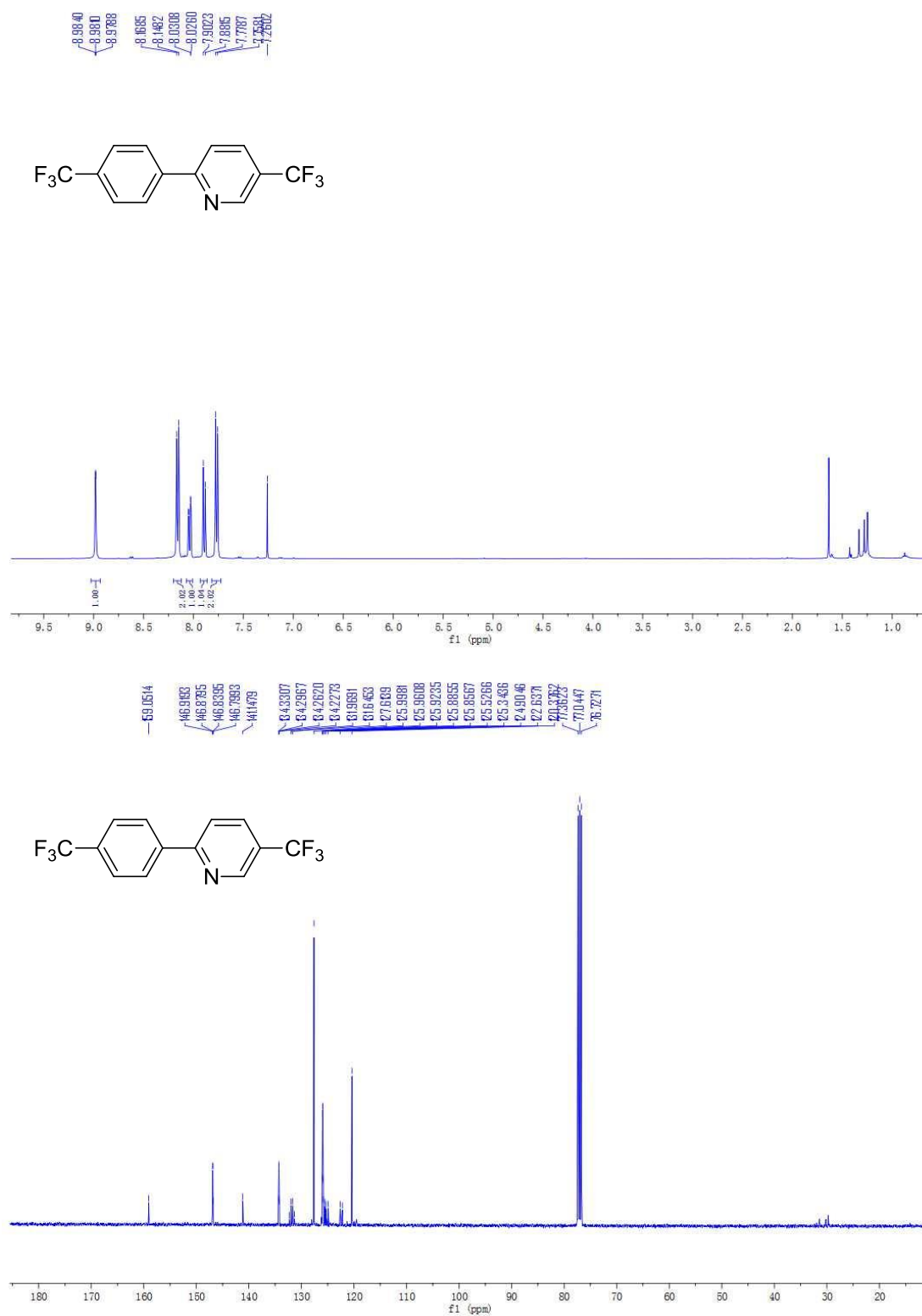


Fig. S24 ¹H and ¹³C NMR spectra of 5-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)pyridine (**4j**)

2-(3,5-bis(trifluoromethyl)phenyl)-5-(trifluoromethyl)pyridine (4k)

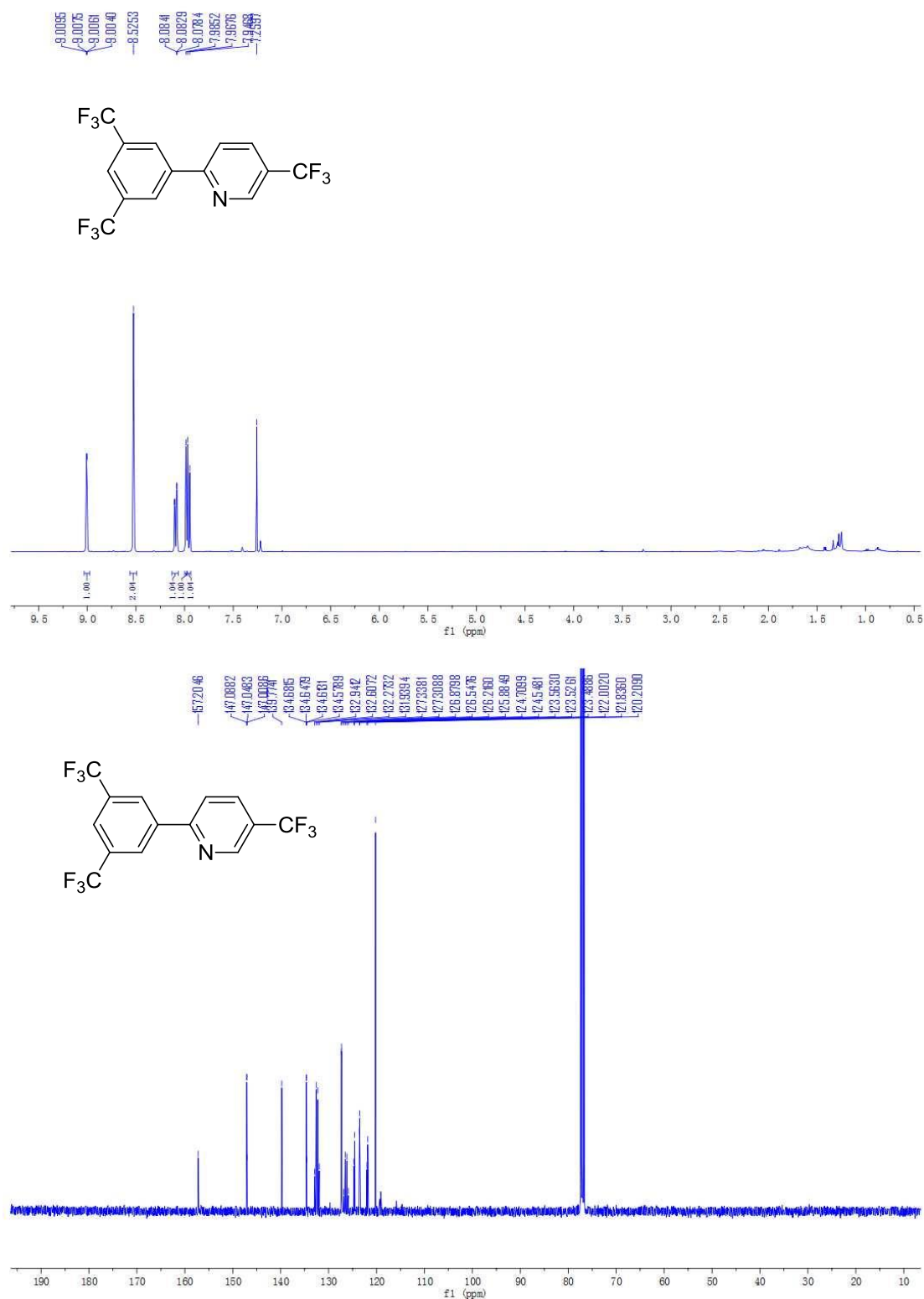


Fig. S25 ¹H and ¹³C NMR spectra of 2-(3,5-bis(trifluoromethyl)phenyl)-5-(trifluoromethyl)pyridine (**4k**)

2-(naphthalen-1-yl)-5-(trifluoromethyl)pyridine (4l)

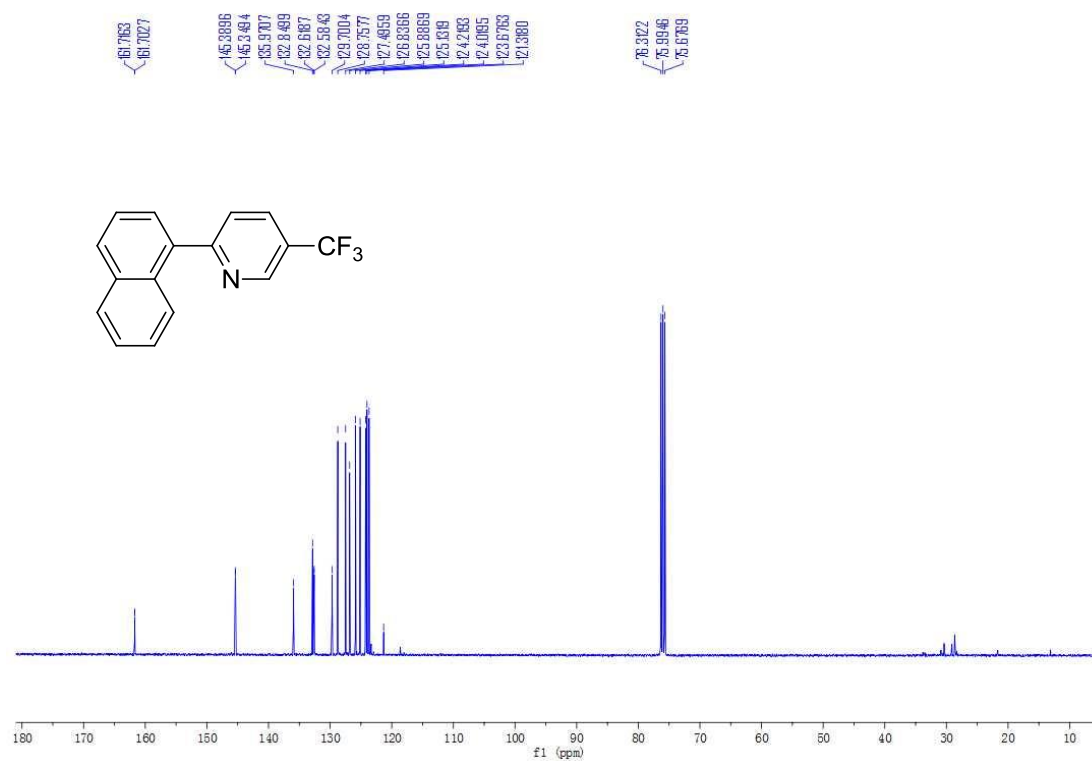
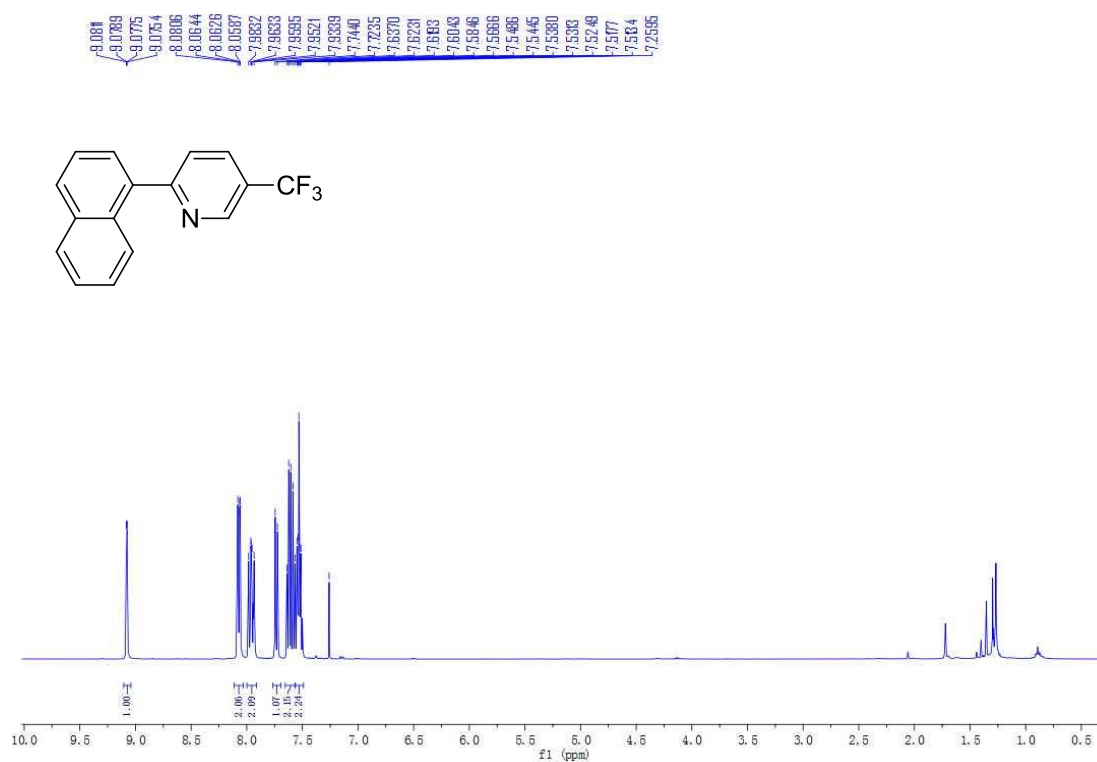


Fig. S26 ¹H and ¹³C NMR spectra of 2-(naphthalen-1-yl)-5-(trifluoromethyl)pyridine (4l)

2-(furan-2-yl)-5-(trifluoromethyl)pyridine (4m)

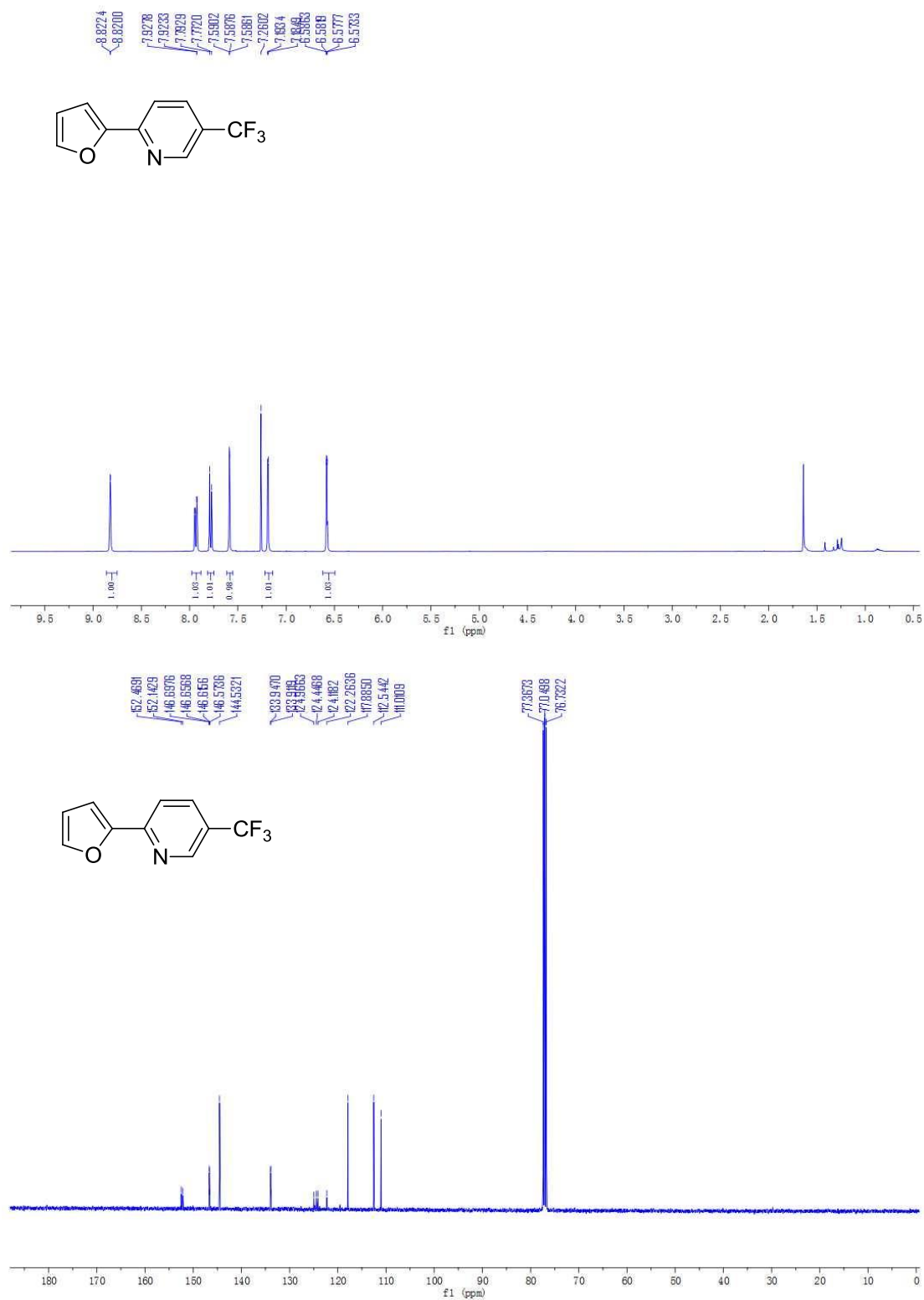


Fig.27 ¹H and ¹³C NMR spectra of 2-(furan-2-yl)-5-(trifluoromethyl)pyridine(**4m**)

2-(thiophen-2-yl)-5-(trifluoromethyl)pyridine (4n)

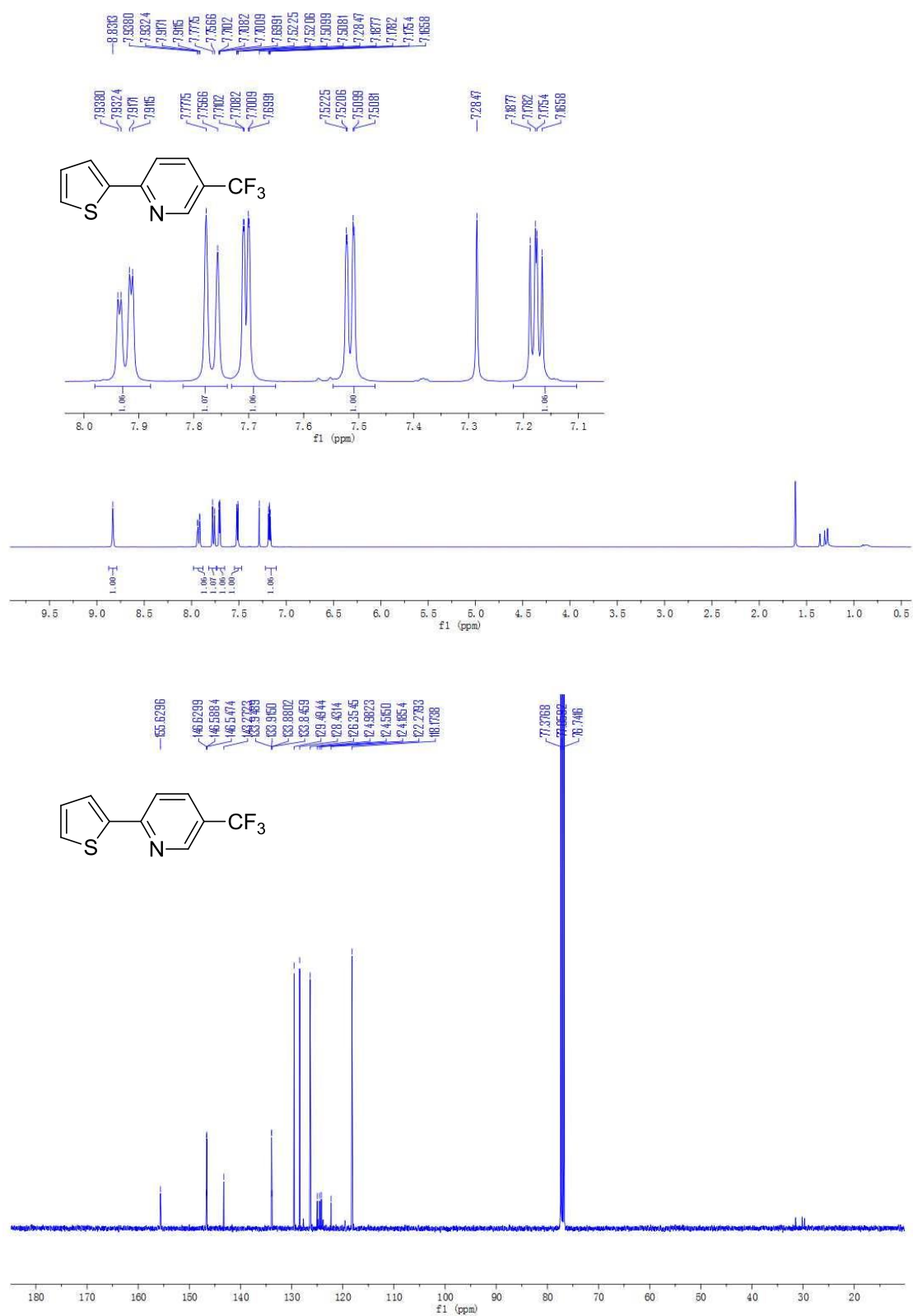


Fig. S28 ¹H and ¹³C NMR spectra of
2-(thiophen-2-yl)-5-(trifluoromethyl)pyridine (**4n**)

3-(4-methoxyphenyl)pyridine (5a)

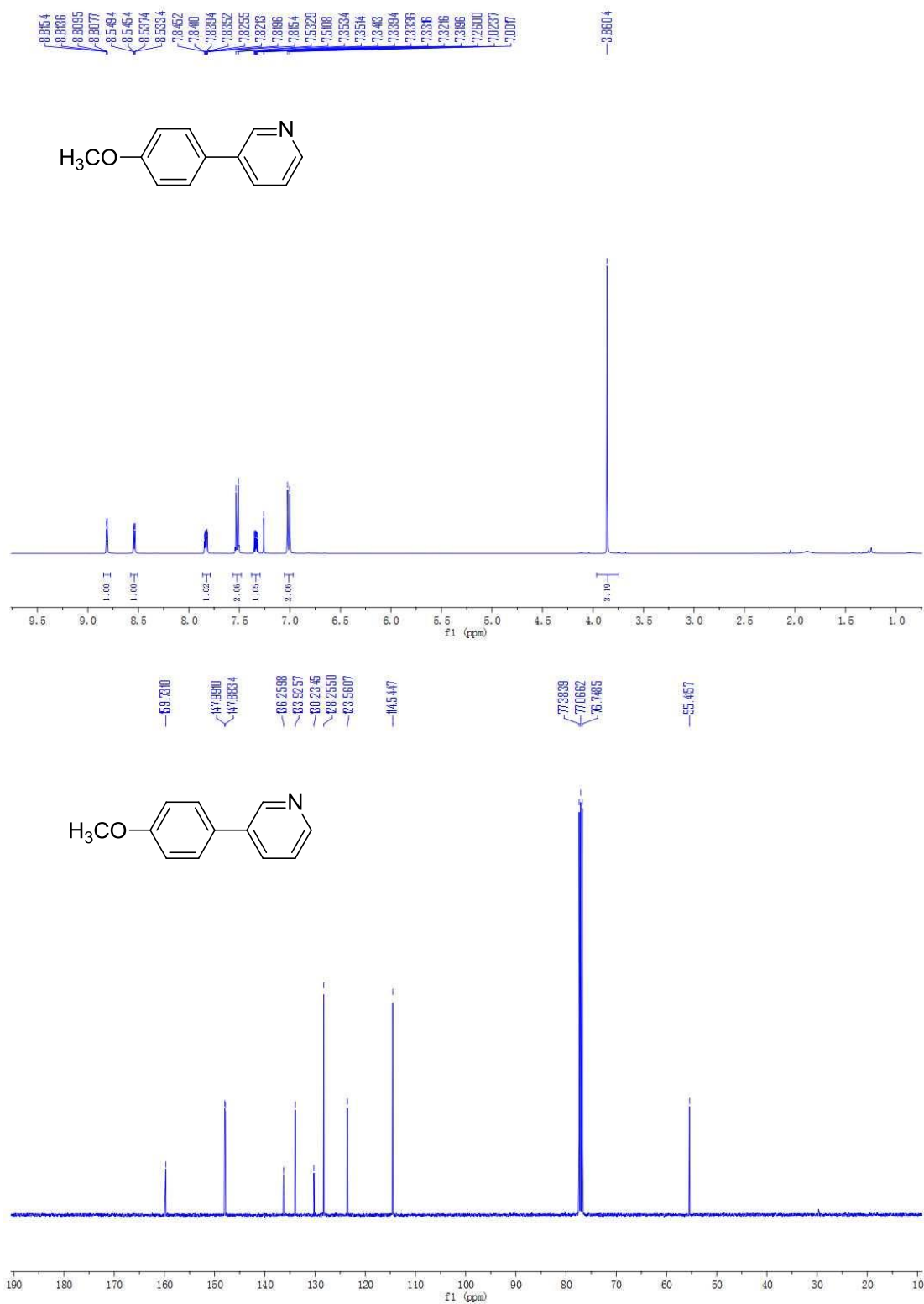


Fig. S29 ¹H and ¹³C NMR spectra of 3-(4-methoxyphenyl)pyridine (5a)

Mass Spectrum SmartFormula Report

Analysis Info

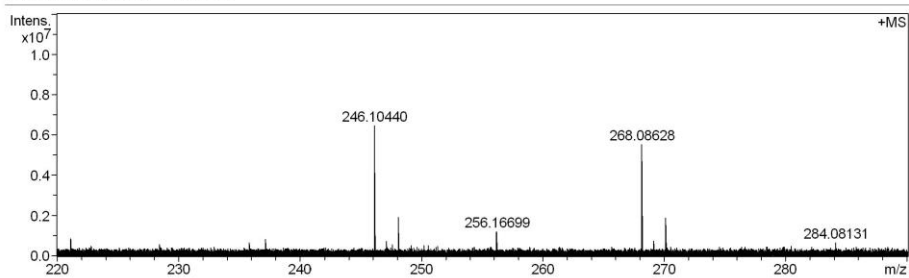
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 Method NaFA-original-pos
 Sample Name WSQ-3G
 Comment

Acquisition Date 11/30/2015 12:11:52 PM

Operator
 Instrument solarix

Acquisition Parameter

Polarity	Positive	n/a	n/a	No. of Laser Shots	200
n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
Broadband Low Mass	86.0 m/z	n/a	n/a	n/a	n/a
Broadband High Mass	1500.0 m/z	n/a	n/a	n/a	n/a
Acquisition Mode	Single MS	n/a	n/a	Calibration Date	Mon Nov 30 11:06:33
Pulse Program	basic	n/a	n/a	Data Acquisition Size	2048576
Source Accumulation	0.050 sec	n/a	n/a	Apodization	Sine-Bell Multiplication
Ion Accumulation Time	0.300 sec	n/a	n/a		
Flight Time to Acq. Cell	0.001 sec				



Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSig ma	rdb	e ⁻ Conf	N-R ule
246.10440	1	C 15 H 17 Cl N	100.00	246.10440	0.00	0.19	33.6	7.5	even	ok
268.08628	1	C 15 H 16 Cl N Na	100.00	268.08635	0.25	0.37	27.8	7.5	even	ok

Fig. S30 HRMS spectra of **3g**

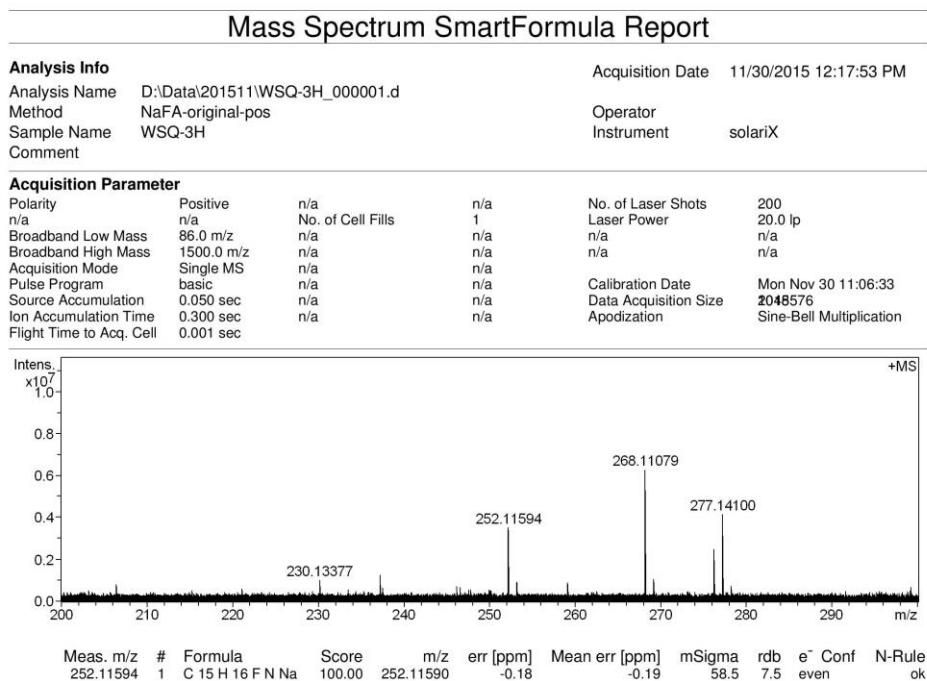


Fig. S31 HRMS spectra of **3h**

Mass Spectrum SmartFormula Report

Analysis Info		Acquisition Date	11/30/2015 1:25:44 PM
Analysis Name	D:\Data\201511\WSQ-3I_000001.d	Operator	
Method	NaFA-original-pos	Instrument	solarix
Sample Name	WSQ-3I		
Comment			

Acquisition Parameter					
Polarity	Positive	n/a	n/a	No. of Laser Shots	200
n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
Broadband Low Mass	86.0 m/z	n/a	n/a	n/a	n/a
Broadband High Mass	1500.0 m/z	n/a	n/a	n/a	n/a
Acquisition Mode	Single MS	n/a	n/a		
Pulse Program	basic	n/a	n/a	Calibration Date	Mon Nov 30 11:06:33
Source Accumulation	0.050 sec	n/a	n/a	Data Acquisition Size	2048576
Ion Accumulation Time	0.300 sec	n/a	n/a	Apodization	Sine-Bell Multiplication
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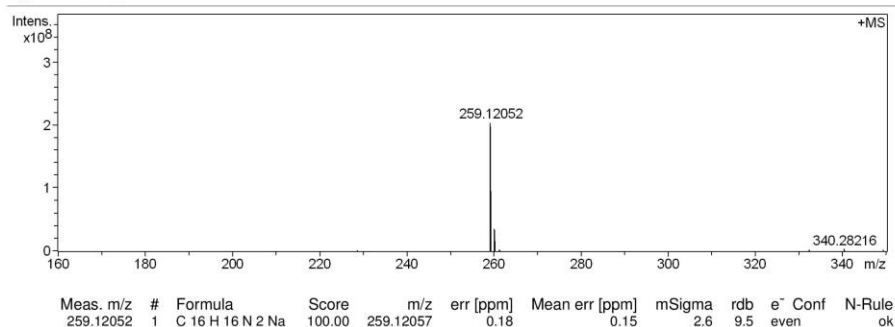


Fig. S32 HRMS spectra of **3i**

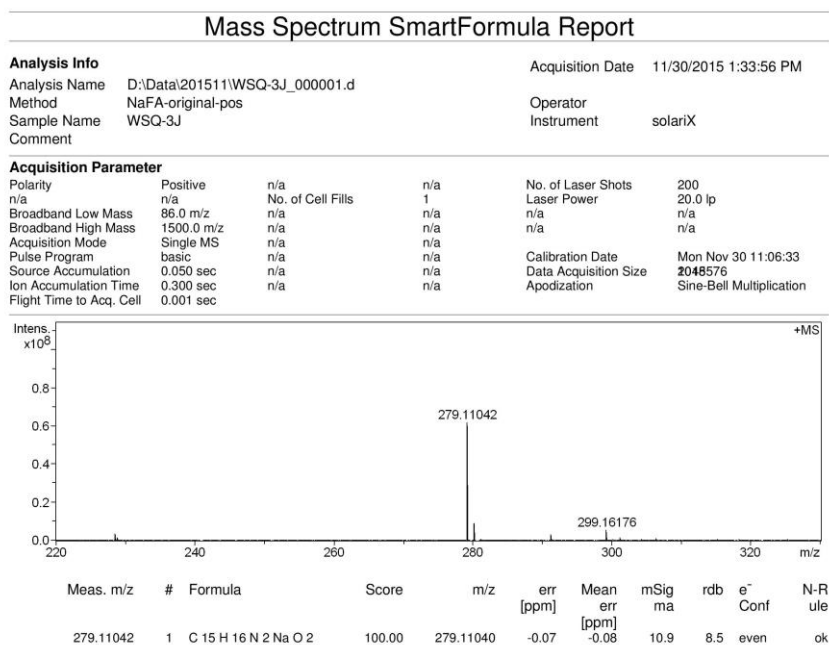


Fig. S33 HRMS spectra of **3j**

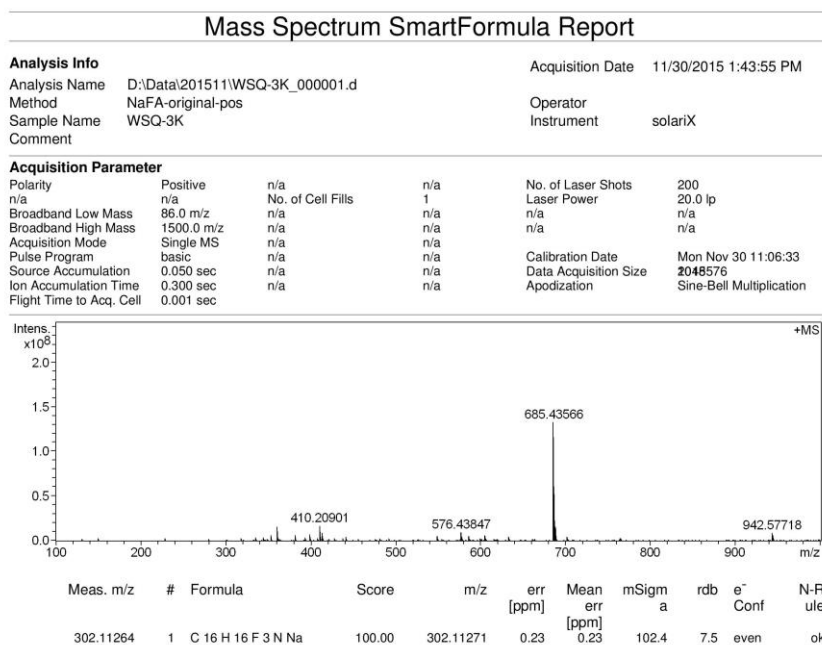
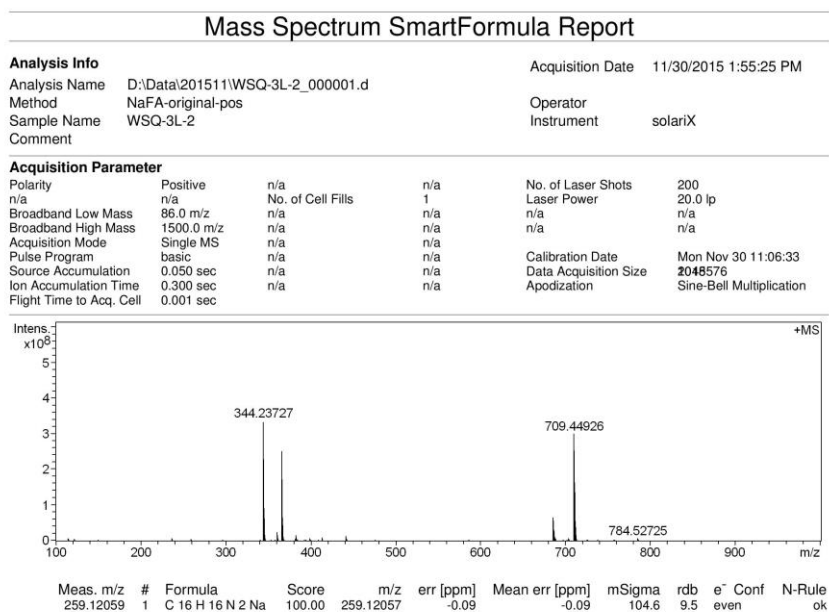


Fig. S34 HRMS spectra of **3k**

**Fig. S35** HRMS spectra of **3l**

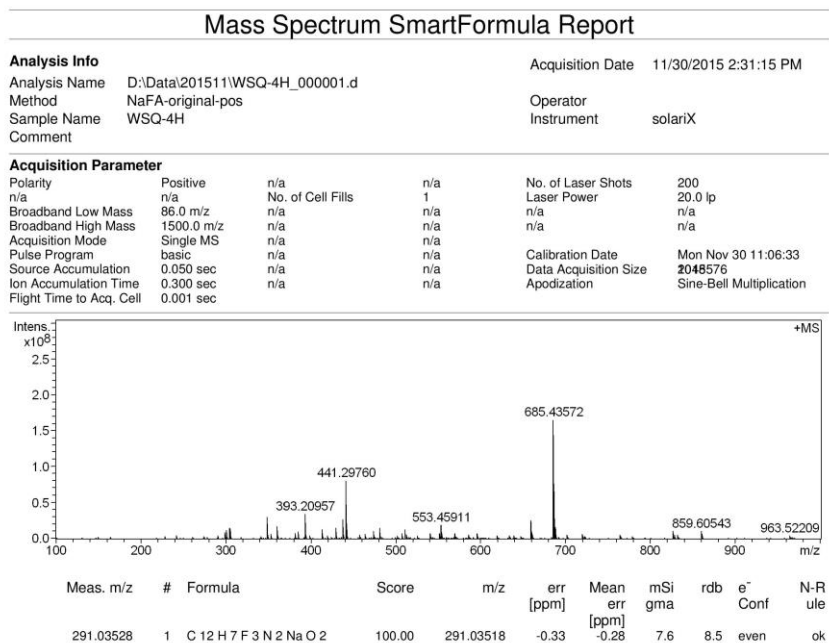


Fig. S36 HRMS spectra of **4h**

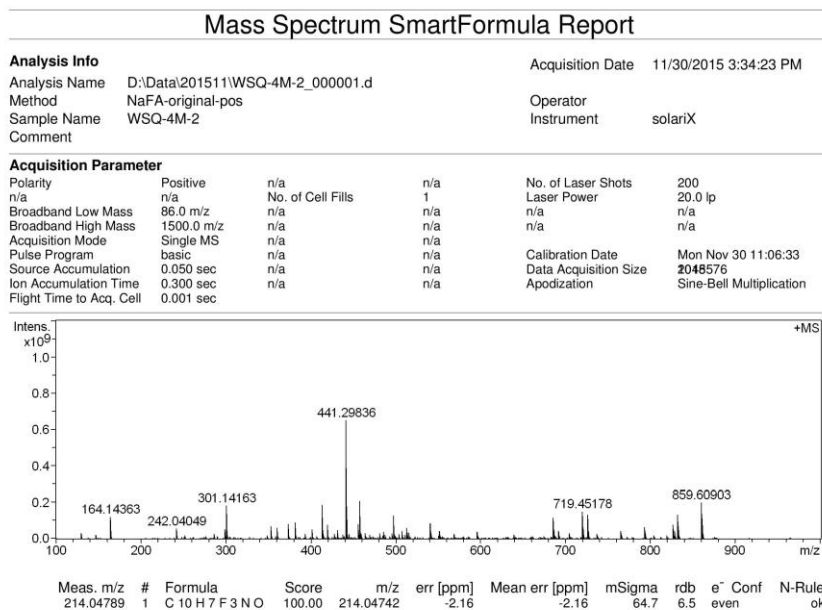


Fig. S37 HRMS spectra of **4m**

Mass Spectrum SmartFormula Report

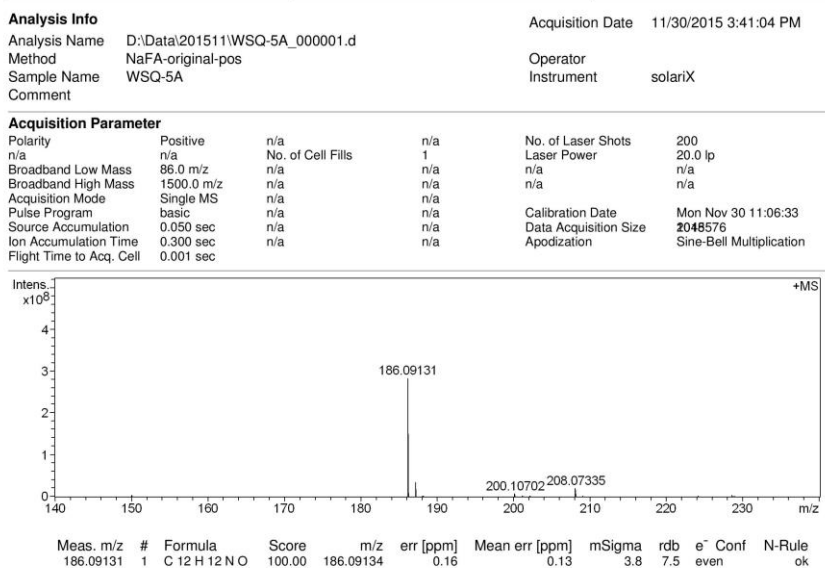


Fig. S38 HRMS spectra of 5a