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Supplementary Information

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1. Experimental Procedures

General Methods. All reagents and solvents were commercially available and used without further purification. All reactions were monitored by thin-layer chromatography (TLC). Purification of all products was carried out by flash chromatography using 200-300 mesh silica gel. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ascend instrument at 400 MHz, 100 MHz respectively. Chemical shifts were reported in (δ=0.00 ppm) referenced to an internal TMS standard for ^{1}H NMR, $CDCl_3$ (δ=77.0) for ^{13}C NMR. The following abbreviations were used to explain multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, hept=heptap-let, m=multiplet, and br=broad. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight). GC-MS spectra were recorded on a Shimazu-GC-MS 2010QP-Ultra.

Preparation of starting materials. A 50 mL Schlenk tube was charged with 2-aminobenzothiazole derivatives (6.5 mmol) and 10 mL of THF, and then isoamyl nitrite (14.3 mmol) was added slowly into the solution. The resultant mixture was refluxed for 30 minutes, and poured into ice-water, and the resultant aqueous mixture was extracted with ethyl acetate (3×30 mL). The organic layers extracts were combined and washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuum and purified by column chromatography, giving the desired benzothiazoles in similar yields with the reported procedure.

General procedures for the synthesis of formylated benzothiazole. A sealable reaction tube equipped with a magnetic stirrer bar was charged with benzothiazole (20.3 mg, 0.15 mmol), 1,3-dioxolane (1 mL), *tert*-butyl hydroperoxide (TBHP, 5.0-6.0 M in decane, 68.1 uL, 0.375 mmol), Upon completion, the reaction mixture was concentrated on a rotary evaporator and transferred to a 20 mL scintillation vial in 5 mL acetone followed by addition of 5 mL aqueous 6 M HCl. The mixture is stirred for 8 h to hydrolyze the acetal to the desired aldehyde. The solution was then diluted with 25 mL saturated sodium bicarbonate and extracted with 3 × 25 mL ethyl acetate. The organic layers extracts were dried with anhydrous sodium sulfate, concentrated, and purified by automated column chromatography on silica gel (eluted with PE/EA 50:1 to 30:1) to provide the desired product 3.

General procedures for the synthesis of formylated isoquinoline. A sealable reaction tube equipped with a magnetic stirrer bar was charged with isoquinoline (19.4 mg, 0.15 mmol), 1,3-dioxolane (1 mL), DCE (1 mL), *tert*-butyl hydroperoxide (TBHP, 5.0-6.0 M in decane, 68.1 uL, 0.375 mmol). Upon completion, the reaction mixture is concentrated on a rotary evaporator and transferred to a 5 mL dram vial. The resulting solution was cooled to 0°C in an ice bath, then BCl_3 (1.0 M in CH_2Cl_2, 1 mL) was added dropwise. The reaction was then warmed to room temperature, stirred for 10 min, and then quenched with H_2O (1 mL) and stirred for 30 min at this temperature. The solution was basified with 1 M LiOH, and the aqueous layer was extracted with CH_2Cl_2 (1 mL × 3). The combined organic fractions were collected and concentrated in vacuo. The crude residue was purified by flash chromatography on silica gel to afford analytically pure product.

2. Characterization Data

*2-(1,3-Dioxolan-2-yl)benzothiazole (**2a**).* Colorless oil. Yield: 26.1 mg (84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.50–7.38 (m, 2H), 6.24 (s, 1H), 4.22–4.05 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 153.3, 135.0, 126.2, 125.7, 123.8, 121.9, 100.5, 65.7 ppm. HRMS (ESI-TOF) calcd for $C_{10}H_9NO_2S$. $[M+H]^+$ 208.0427, found 208.0429.

*2-(1,3-dioxolan-4-yl)benzo[d]thiazole(**2a'**).* Colorless oil. Yield: 2.2 mg (7%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.13 (d, J = 7.9 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.58 – 7.42 (m, 2H), 5.54 (dd, J = 7.0, 4.4 Hz, 1H), 5.22 (s, 1H), 5.05 (s, 1H), 4.35 (dd, J = 8.4, 7.2 Hz, 1H), 4.15 (dd, J = 8.5, 4.4 Hz, 1H). HRMS (ESI-TOF) calcd for $C_{10}H_9NO_2S$. $[M+H]^+$ 208.0427, found 208.0427.

*Benzothiazole-2-carbaldehyde (**3a**)*. White solid. mp 65–66 ℃. Yield: 20.0 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.28–8.23 (m, 1H), 8.04–7.99 (m, 1H), 7.65–7.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.5, 165.4, 153.6, 136.4, 128.4, 127.4, 125.8, 122.7 ppm. HRMS (ESI-TOF) calcd for C_8H_5NaNOS. $[M+Na]^+$ 185.9990, found 185.9989.

*6-Methylbenzothiazole-2-carbaldehyde (**3b**)*. Yellow solid. mp 66–67 ℃. Yield: 18.9 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.78 (s, 1H), 7.46–7.39 (m, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.5, 164.4, 151.8, 139.3, 136.7, 129.3, 125.3, 122.1, 21.9 ppm. HRMS (ESI-TOF) calcd for C_9H_8NOS. $[M+H]^+$ 178.0327, found 178.0321.

*6-Methoxybenzothiazole-2-carbaldehyde (**3c**)*. Yellow solid. mp 81–82 ℃. Yield: 15.6 mg (54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.10 (d, J = 9.1 Hz, 1H), 7.39 (d, J = 2.3 Hz, 1H), 7.23–7.19 (m, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 163.0, 160.4, 148.3, 138.7, 126.5, 118.3, 103.7, 55.9 ppm. HRMS (ESI-TOF) calcd for $C_9H_8NO_2S$. $[M+H]^+$ 194.0276, found 194.0275.

*6-(tert-butyl)Benzothiazole-2-carbaldehyde (**3d**)*. Pale yellow oil. Yield: 26.9 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.16 (d, J = 8.8 Hz, 1H), 7.98 (s, 1H), 7.71–7.65 (m, 1H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.5, 164.8, 152.5, 151.7, 136.7, 126.0, 125.1, 118.4, 35.5, 31.4 ppm. HRMS (ESI-TOF) calcd for $C_{12}H_{14}NOS$. $[M+H]^+$ 220.0796, found 220.0791.

*6-Fluorobenzothiazole-2-carbaldehyde (**3e**)*. Yellow solid. mp 61–62 ℃. Yield: 14.1 mg (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.26–8.17 (m, 1H), 7.70–7.65 (m, 1H), 7.41–7.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 165.3 (d, J = 3.7 Hz), 162.4 (d, J = 251.7 Hz), 150.3, 137.8 (d, J = 11.6 Hz), 127.2 (d, J = 9.9 Hz), 116.8 (d, J = 25.5 Hz), 108.6 (d, J = 26.8 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.80 ppm. HRMS (ESI-TOF) calcd for C_8H_5FNOS. $[M+H]^+$ 182.0076, found 182.0070.

*6-Chlorobenzothiazole-2-carbaldehyde (**3f**)*. Yellow solid. mp 98–99 ℃. Yield: 18.3 mg (62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.15 (d, J = 8.8 Hz, 1H), 7.98 (d, J = 1.8 Hz, 1H), 7.60–7.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 165.7, 152.1, 137.5, 134.8, 128.5, 126.6, 122.2 ppm. HRMS (ESI-TOF) calcd for $C_8H_5NaClNOS$. $[M+Na]^+$ 219.9600, found 219.9605.

*6-Bromobenzothiazole-2-carbaldehyde (**3g**)*. Yellow solid. mp 111–112 ℃. Yield: 23.1 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.15 (d, J = 1.6 Hz, 1H), 8.08 (d, J = 8.8 Hz, 1H), 7.76–7.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 165.7, 152.4, 137.9, 131.2, 126.8, 125.2, 122.7 ppm. HRMS (ESI-TOF) calcd for C_8H_5BrNOS. $[M+H]^+$ 241.9275, found 241.9275.

*6-(Trifluoromethoxy)benzothiazole-2-carbaldehyde (**3h**)*. Yellow solid. mp 89–90 ℃. Yield: 21.5 mg (58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.27 (d, J = 9.0 Hz, 1H), 7.87 (s, 1H), 7.49 (d, J = 8.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 166.4, 151.9, 148.8, 137.4, 127.0, 121.4, 120.2 (q, J = 257.0 Hz), 114.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.87 ppm. HRMS (ESI-TOF) calcd for $C_9H_5F_3NO_2S$. $[M+H]^+$ 247.9993, found 247.9993.

*Ethyl 2-formylbenzothiazole-6-carboxylate (**3i**)*. Yellow solid. mp 119–120 °C. Yield: 21.2 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.73 (s, 1H), 8.27 (s, 2H), 4.50–4.42 (q, J = 7.1 Hz, 2H), 1.48–1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 168.0, 165.5, 156.0, 136.1, 130.3, 128.2, 125.5, 124.8, 61.7, 14.3 ppm. HRMS (ESI-TOF) calcd for $C_{11}H_{10}BrNO_3S$. $[M+H]^+$ 236.0381, found 236.0376.

*6-(Trifluoromethyl)benzothiazole-2carbaldehyde (**3j**)*. Colorless oil. Yield: 14.9 mg (43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.40–8.31 (m, 2H), 7.88–7.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 167.9, 155.3, 136.3, 130.3 (q, J = 33.0 Hz), 126.3, 124.2 (q, J = 3.0 Hz), 123.7 (q, J = 271 Hz), 120.5 (q, J = 4.3 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.97 ppm. HRMS (ESI-TOF) calcd for $C_9H_5F_3NOS$. $[M+H]^+$ 232.0044, found 232.0045.

*4-Methylbenzothiazole-2-carbaldehyde (**3m**)*. White solid. mp 63–64 ℃. Yield: 19.4 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.49–7.43 (m, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 164.2, 153.2, 136.5, 136.2, 128.5, 127.6, 120.0, 18.3 ppm. HRMS (ESI-TOF) calcd for C_9H_7NaNOS. $[M+Na]^+$ 200.0146, found 200.0141.

*5-Bromobenzothiazole-2-carbaldehyde (**3n**)*. White solid. mp 146–147 °C Yield: 22.7 mg (63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.40 (d, *J* = 1.7 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.68 (m, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ 185.1, 166.7, 154.6, 135.1, 131.6 128.5 123.7, 121.1 ppm. HRMS (ESI-TOF) calcd for C_8H_5BrNOS. $[M+H]^+$ 241.9275, found 241.9270.

*4-Chlorobenzothiazole-2-carbaldehyde (**3o**)*. White solid. mp 115–116 °C .Yield: 18.9 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 165.9, 150.7, 137.8, 130.9, 128.9, 127.6, 121.2 ppm. HRMS (ESI-TOF) calcd for C_8H_5ClNOS. $[M+H]^+$ 197.9780, found 197.9783.

*5,6-Dimethylbenzothiazole-2-carbaldehyde (**3p**)*. White solid. mp 98–99 ℃. Yield: 21.2 mg (74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 7.97 (s, 1H), 7.73 (s, 1H), 2.43 (d, *J* = 2.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.5, 164.3, 152.5, 139.0, 137.2, 134.2, 125.5, 122.2, 20.6, 20.3 ppm. HRMS (ESI-TOF) calcd for $C_{10}H_9NaNOS$. $[M+Na]^+$ 214.0303, found 214 .0297.

*4,6-Dichlorobenzothiazole-2-carbaldehyde (**3q**)*. White solid. mp 125–126 ℃ Yield: 14.5 mg (42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.91 (d, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.8, 166.1, 149.5, 138.4, 134.8, 131.4, 128.4, 120.8 ppm. HRMS (ESI-TOF) calcd for $C_8H_3NaCl_2NOS$. $[M+Na]^+$ 253.9210, found 253.9205.

*Ethyl 2-formyl-4-methylthiazole-5-carboxylate (**3r**)*. Pale yellow oil. Yield: 22.7 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 4.44–4.34 (q, *J* = 7.1 Hz, 2H), 2.82 (s, 3H), 1.43–1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.2, 165.6, 161.6, 161.5, 128.4, 62.0, 17.4, 14.2 ppm. HRMS (ESI-TOF) calcd for $C_8H_{10}NO_3S$. $[M+H]^+$ 200.0381, found 200.0384.

*2-(1,3-Dioxolan-2-yl)-1-methyl-1H-benzoimidazole (**3s**)*. Colorless oil. Yield: 12.2 mg (40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.40–7.23 (m, 3H), 6.14 (s, 1H), 4.30–4.07 (m, 4H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 141.9, 136.5, 123.4, 122.3, 120.5, 109.4, 99.0, 65.5, 30.3 ppm. HRMS (ESI-TOF) calcd for $C_{11}H_{12}N_2O_2$. $[M+H]^+$ 205.0977, found 205.0976.

*1-(benzo[d]thiazol-2-yl)ethan-1-one (**3t**)*. White solid. Yield: 16.7 mg (63%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 – 8.20 (m, 2H), 7.66 (pd, *J* = 7.2, 1.4 Hz, 2H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.37, 166.91, 153.46, 137.05, 128.40, 127.79, 125.52, 123.59, 26.44 ppm. HRMS (ESI-TOF) calcd for C_9H_7NOS. $[M+H]^+$ 178.0321, found 178.0315.

*1-(5-methylbenzo[d]thiazol-2-yl)ethan-1-one (**3u**)*. White solid. Yield: 16.6 mg (55%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (d, *J* = 9.1 Hz, 1H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.25 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.89 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.26, 159.85, 147.92, 139.23, 126.30, 118.20, 105.09, 56.35, 26.26 ppm. HRMS (ESI-TOF) calcd for $C_{10}H_9NOS$. $[M+H]^+$ 192.0478, found 192.0454.

*1-(6-bromobenzo[d]thiazol-2-yl)ethan-1-one (**3v**)*. White solid. Yield: 21.8 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.5 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.64 (dd, *J* = 8.6, 1.8 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.94, 154.65, 136.15, 130.89, 128.15, 123.53, 120.61, 26.15 ppm. HRMS (ESI-TOF) calcd for C_9H_6BrNOS. $[M+H]^+$ 255.9426, found 255.9421.

*Isoquinoline-1-carbaldehyde (**6a**)*. Yellow solid. mp 81–82 ℃. Yield: 15.1 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 9.36–9.27 (m, 1H), 8.75 (d, *J* = 5.5 Hz, 1H), 7.95–7.87 (m, 2H), 7.80–7.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 149.9, 142.5, 136.9, 130.8, 130.0, 126.9, 126.3, 125.7, 125.5 ppm. HRMS (ESI-TOF) calcd for $C_{10}H_8NO$. $[M+H]^+$ 158.0606, found 158.0608.

*6-Methylisoquinoline-1-carbaldehyde (**6b**)*.[12] Yellow solid. mp 74–75 ℃. Yield: 15.1 mg (59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (s, 1H), 9.20 (d, *J* = 8.8 Hz, 1H), 8.70 (d, *J* = 5.5 Hz, 1H), 7.79 (d, *J* = 5.5 Hz, 1H), 7.67 (s, 1H), 7.62–7.54 (m, 1H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 149.6, 142.5, 141.3, 137.3, 132.4, 125.8, 125.4, 125.0, 124.8, 22.0 ppm.

*6-Methoxyisoquinoline-1-carbaldehyde (**6c**)*. Red solid. mp 79–80 ℃. Yield: 17.9 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1H), 9.21 (d, *J* = 9.4 Hz, 1H), 8.66 (d, *J* = 5.5 Hz, 1H), 7.76 (d, *J* = 5.5 Hz, 1H), 7.41–7.32 (m, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 161.0, 149.3, 143.0, 139.0, 127.5, 124.5, 123.1, 122.2, 104.3, 55.5 ppm.

HRMS (ESI-TOF) calcd for $C_{11}H_{10}NO_2$. $[M+H]^+$ 188.0712, found 188.0700.

*6-Fluoroisoquinoline-1-carbaldehyde (**6d**)*.[14] White solid. mp 79–80 ℃. Yield: 13.7 mg (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 9.43–9.36 (m, 1H), 8.76 (d, *J* = 5.6 Hz, 1H), 7.85 (d, *J* = 5.6 Hz, 1H), 7.56–7.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 163.2 (d, *J* = 254.9 Hz), 149.7, 143.4, 138.7 (d, *J* = 10.3 Hz), 129.2 (d, *J* = 9.3 Hz), 124.9 (d, *J* = 5.4 Hz), 123.5, 120.5 (d, *J* = 25.0 Hz), 110.2 (d, *J* = 20.8 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.55 ppm.

*6-Chloroisoquinoline-1-carbaldehyde (**6e**)*. Yellow solid. mp 92–93 ℃. Yield: 20.1 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1H), 9.27 (d, *J* = 9.2 Hz, 1H), 8.76 (d, *J* = 5.6 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.79 (d, *J* = 5.5 Hz, 1H), 7.70–7.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 149.9, 143.5, 137.7, 137.3, 131.0, 127.6, 125.7, 124.4, 124.3 ppm. HRMS (ESI-TOF) calcd for $C_{10}H_7ClNO$. $[M+H]^+$ 192.0216, found 192.0211.

*6-Bromoisoquinoline-1-carbaldehyde (**6f**)*[14]. Red solid. mp 116–117 ℃. Yield: 23.3 mg (66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 9.20 (d, *J* = 9.2 Hz, 1H), 8.78 (d, *J* = 5.5 Hz, 1H), 8.09 (d, *J* = 1.8 Hz, 1H), 7.86–7.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 150.0, 143.5, 138.0, 133.5, 129.1, 127.5, 125.9, 124.6, 124.2 ppm.

*7-Bromoisoquinoline-1-carbaldehyde (**6g**)*[13]. Yellow solid. mp 113–114 ℃. Yield: 16.6 mg (47%). ^{1}H NMR (400 MHz, CDCl3) δ 10.33 (s, 1H), 9.52 (s, 1H), 8.78 (d, *J* = 5.5 Hz, 1H), 7.90–7.73 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 148.7, 142.9, 135.3, 134.5, 128.4, 128.1, 126.9, 125.2, 124.7 ppm.

*5-Methoxyisoquinoline-1-carbaldehyde (**6h**)*. Yellow solid. mp 112–113 ℃. Yield: 17.4 mg (62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.86 (d, *J* = 8.7 Hz, 1H), 8.75 (d, *J* = 5.6 Hz, 1H), 8.31 (d, *J* = 5.6 Hz, 1H), 7.69–7.60 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 4.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 154.5, 149.2, 142.1, 130.4, 129.9, 127.1, 120.1, 117.3, 107.9, 55.7 ppm. HRMS (ESI-TOF) calcd for $C_{11}H_{10}NO_2$. $[M+H]^+$ 188.0712, found 188.0706.

*4-Methoxyisoquinoline-1-carbaldehyde (**6i**)*. Yellow solid. mp 90–91 ℃. Yield: 16.8 mg (60%).^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 9.37–9.31 (m, 1H), 8.30 (s, 1H), 8.29–8.21 (m, 1H), 7.79–7.70 (m, 2H), 4.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 153.8, 143.6, 130.3, 129.8, 128.1, 127.4, 125.3, 123.2, 121.3, 56.5 ppm. HRMS (ESI-TOF) calcd for $C_{11}H_{10}NO_2$. $[M+H]^+$ 188.0712, found 188.0718.

*5-chloroisoquinoline-1-carbaldehyde (**6k**)*[12]. Yellow solid，mp: 135–136 ℃. Yield: 19.8 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 9.27 (d, *J* = 8.6 Hz, 1H), 8.85 (d, *J* = 5.7 Hz, 1H), 8.31 (d, *J* = 5.7 Hz, 1H), 7.86–7.81 (m, 1H), 7.70–7.63 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 148.9, 144.5, 135.6, 132.0, 130.9, 127.2, 126.3, 126.1, 125.4 ppm.

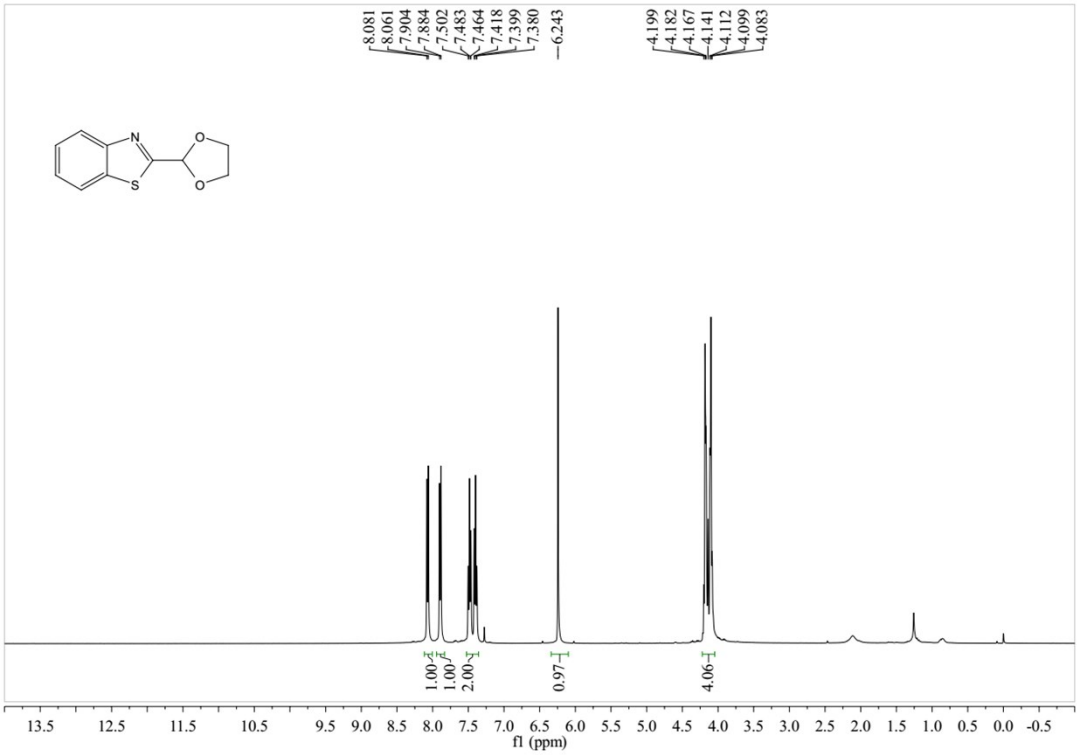
*4-bromoisoquinoline-1-carbaldehyde (**6l**)*[14]. Yellow solid，mp: 112–113 ℃. Yield: 19.7 mg (56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 9.33 (d, *J* = 8.3 Hz, 1H), 8.92 (s, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.87-7.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 148.9, 144.5, 135.6, 132.0, 130.9, 127.2, 126.3, 126.1, 125.4 ppm.

*4-Methylquinoline-2-carbaldehyde (**6m**)*[14]. Yellow solid. mp 72–73 ℃. Yield: 13.9 mg (54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.87 (s, 1H), 7.82 (d, *J* = 1.4 Hz,

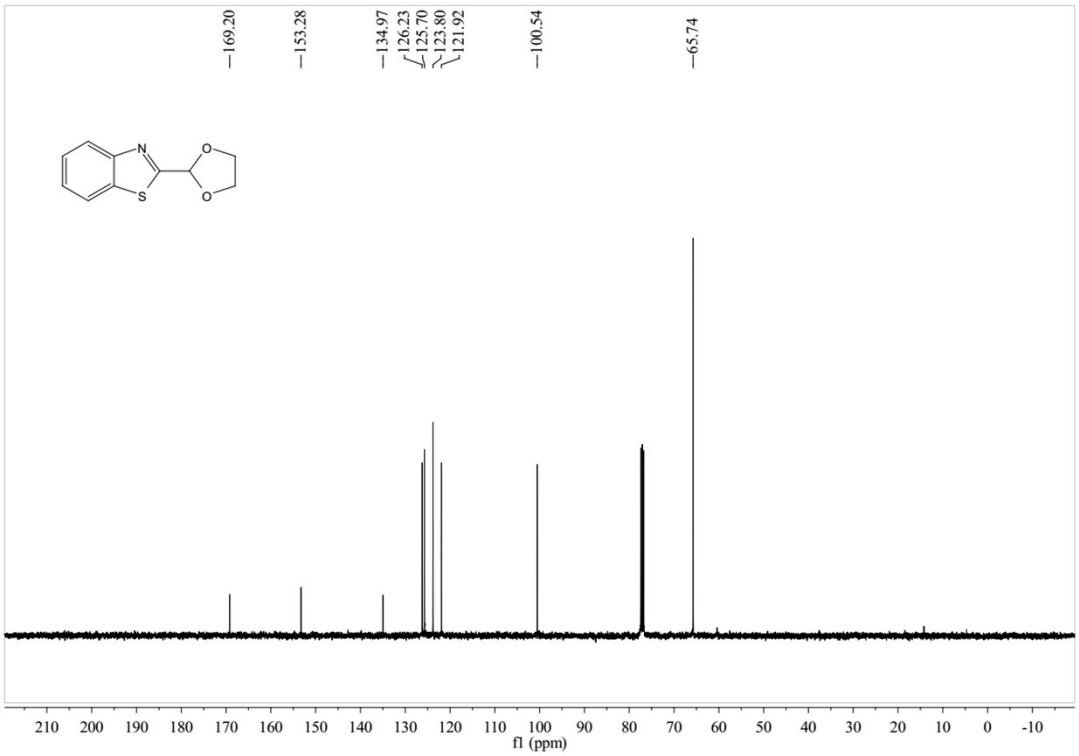
1H), 7.75–7.67 (m, 1H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 152.2, 147.7, 146.1, 131.0, 130.1, 129.0, 124.0, 117.9, 18.9 ppm.

3. Spectra of ^{1}H NMR and ^{13}C NMR

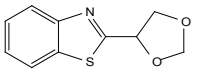
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 2a

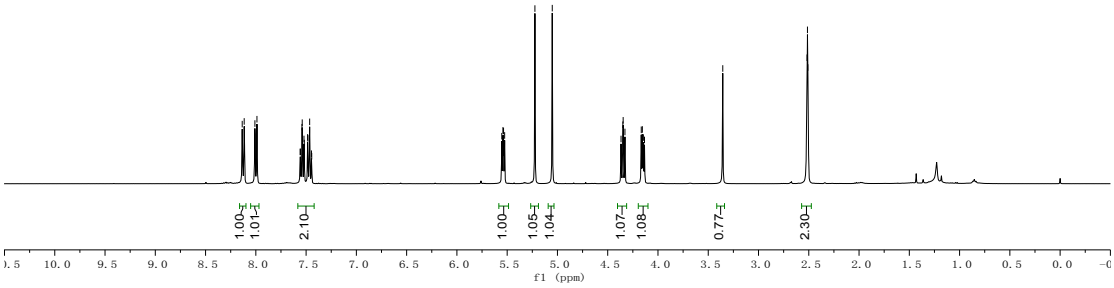


^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 2

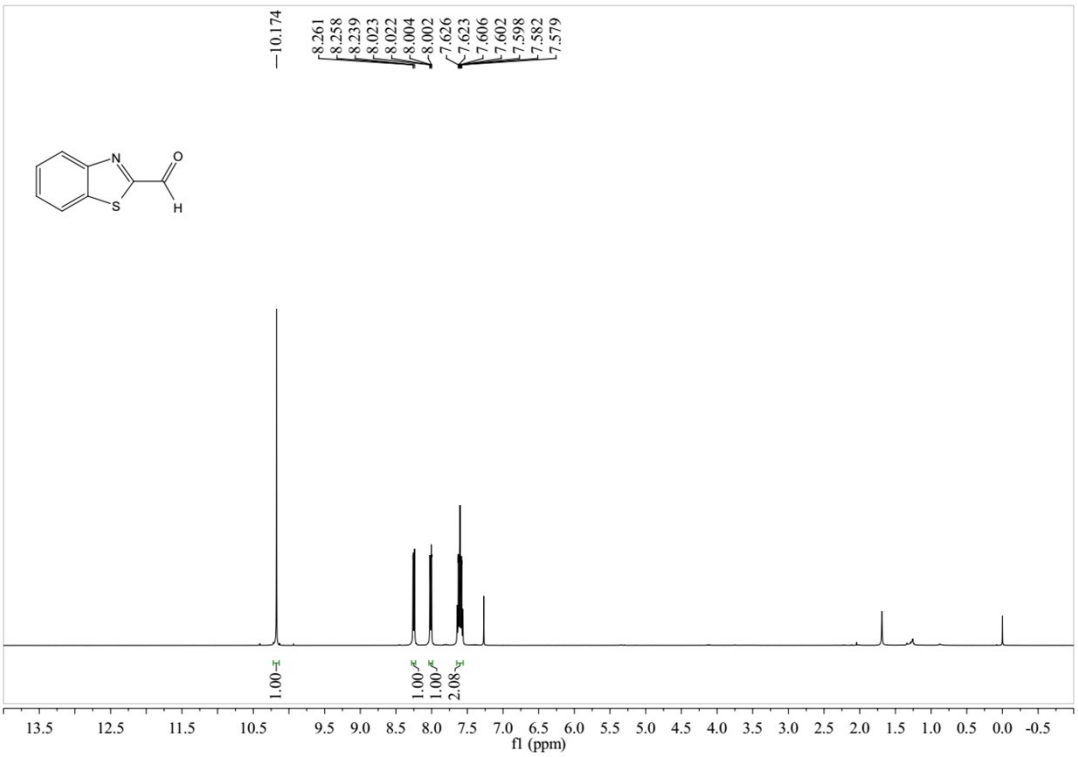


^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 2a'

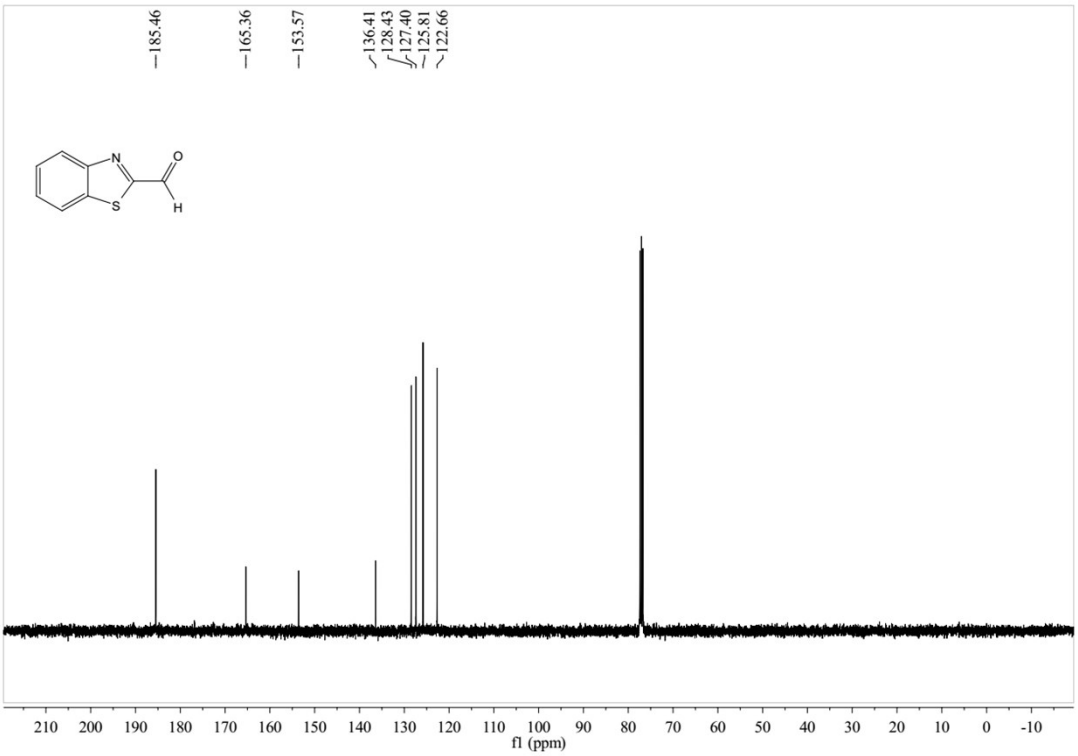




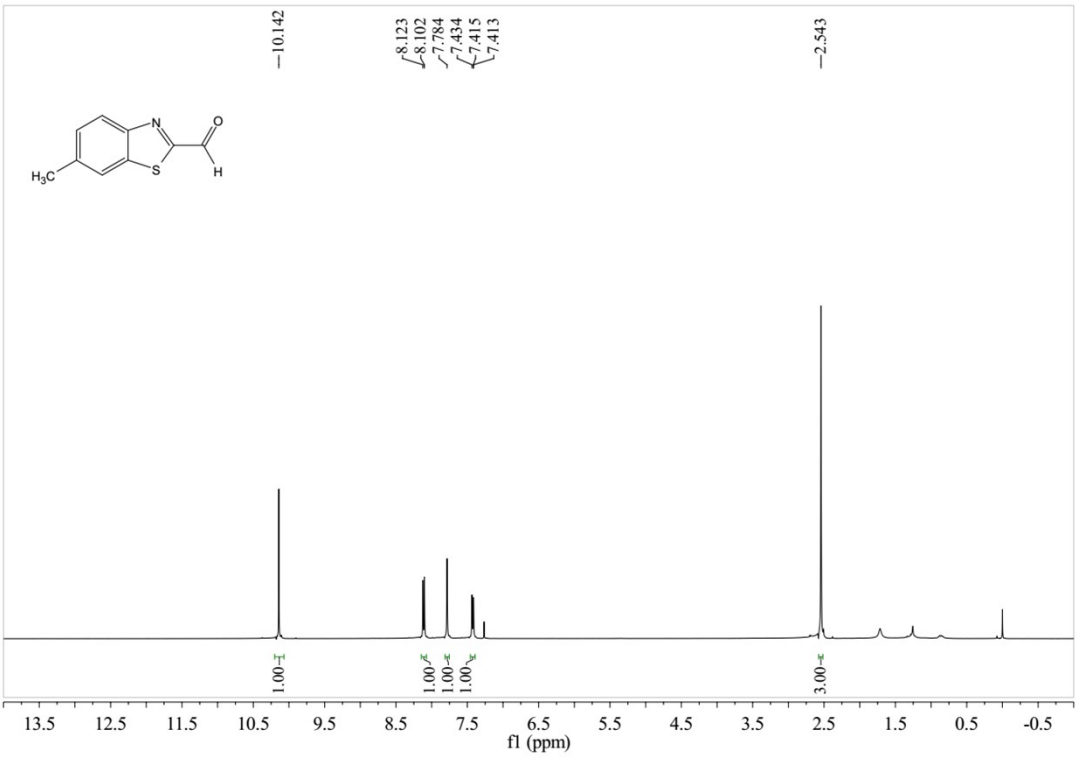
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3a



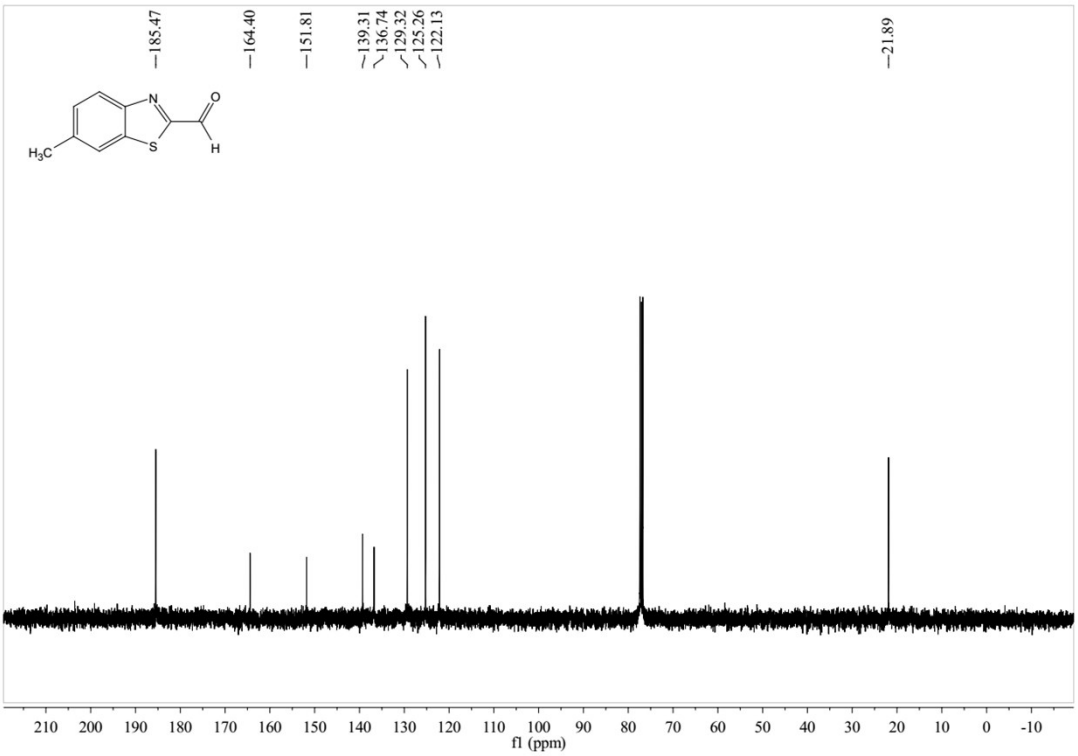
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3a



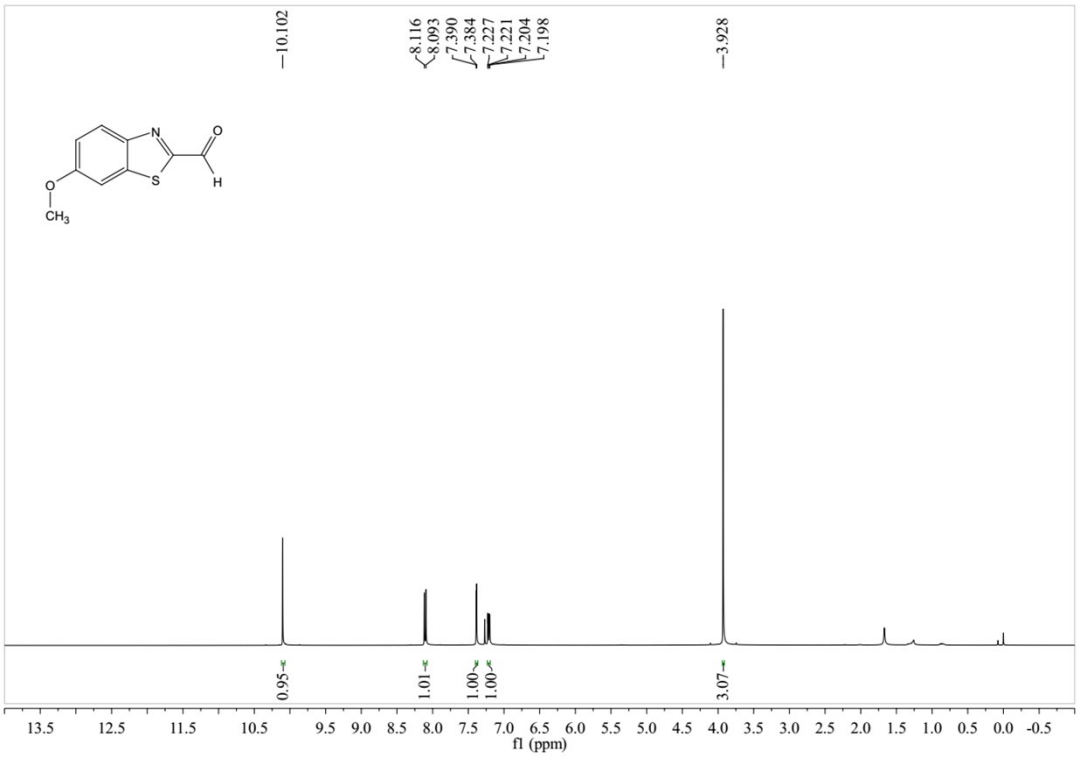
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3b



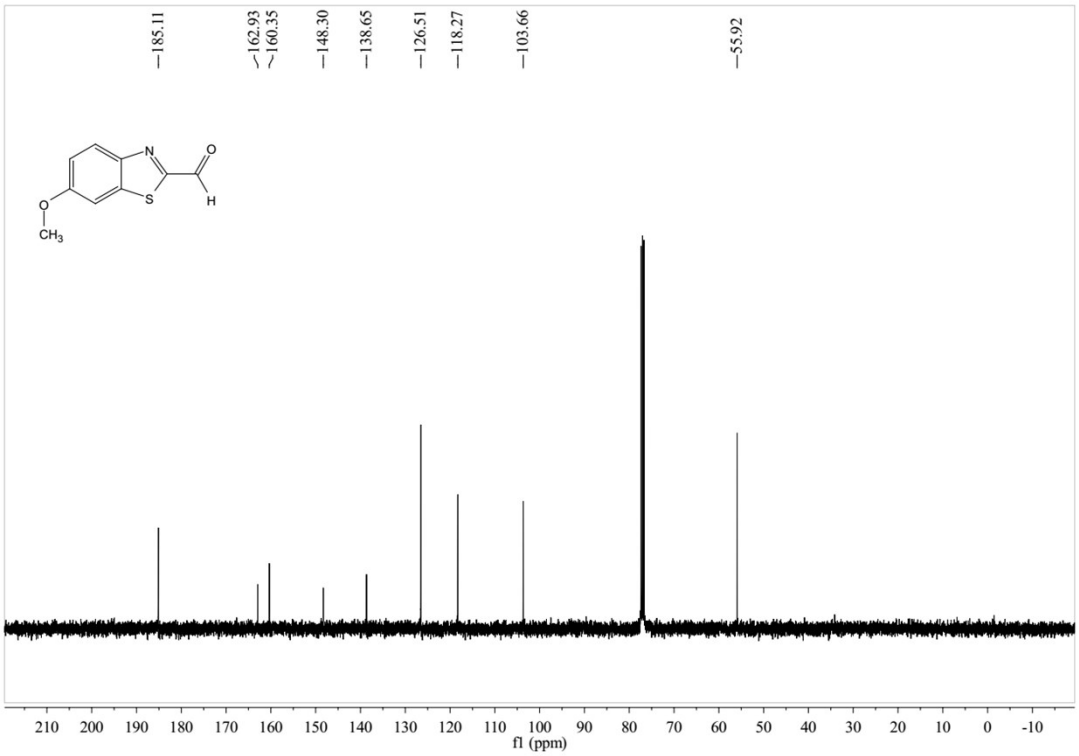
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3b



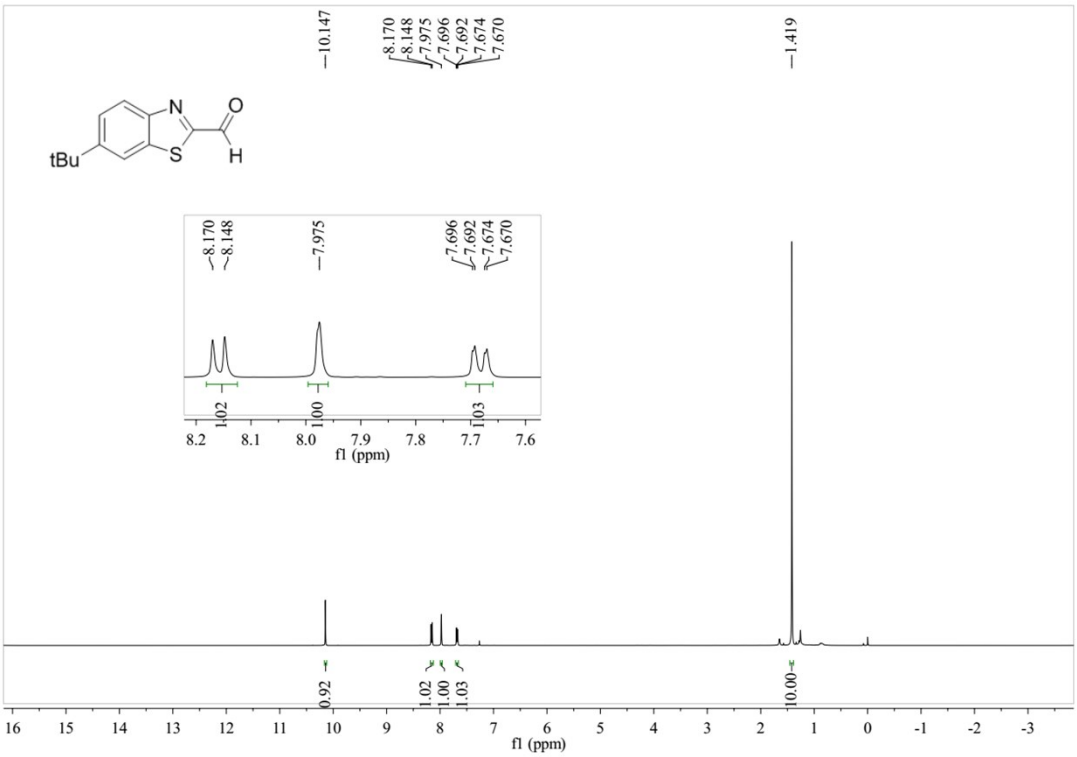
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3c



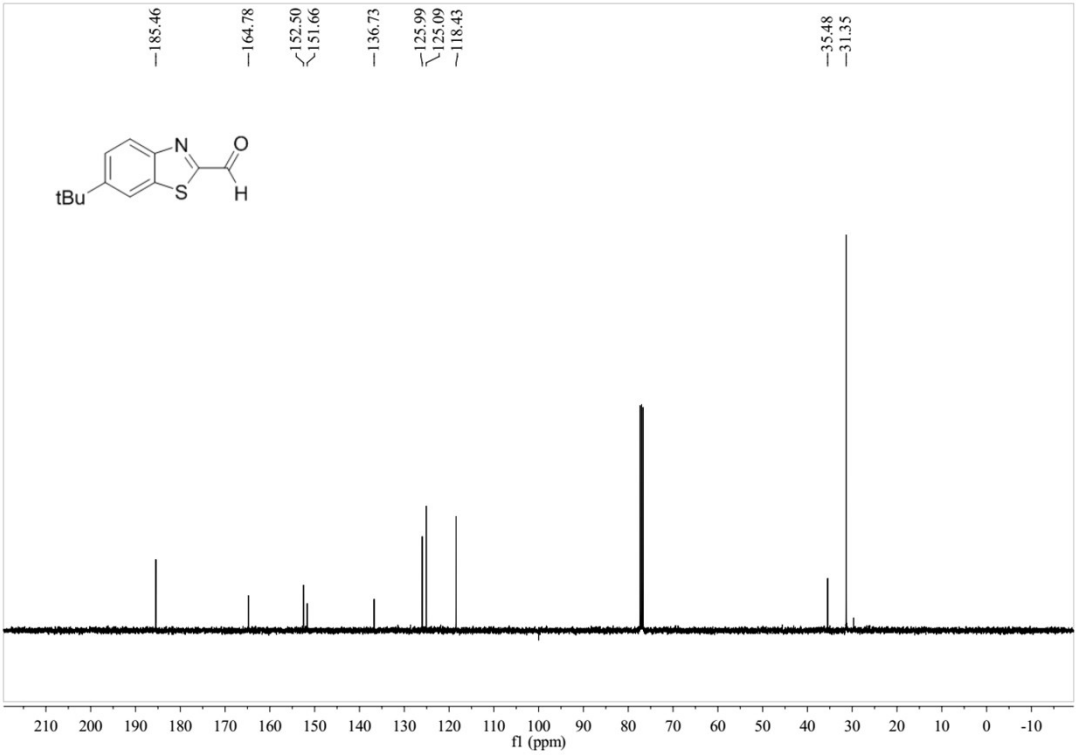
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3c



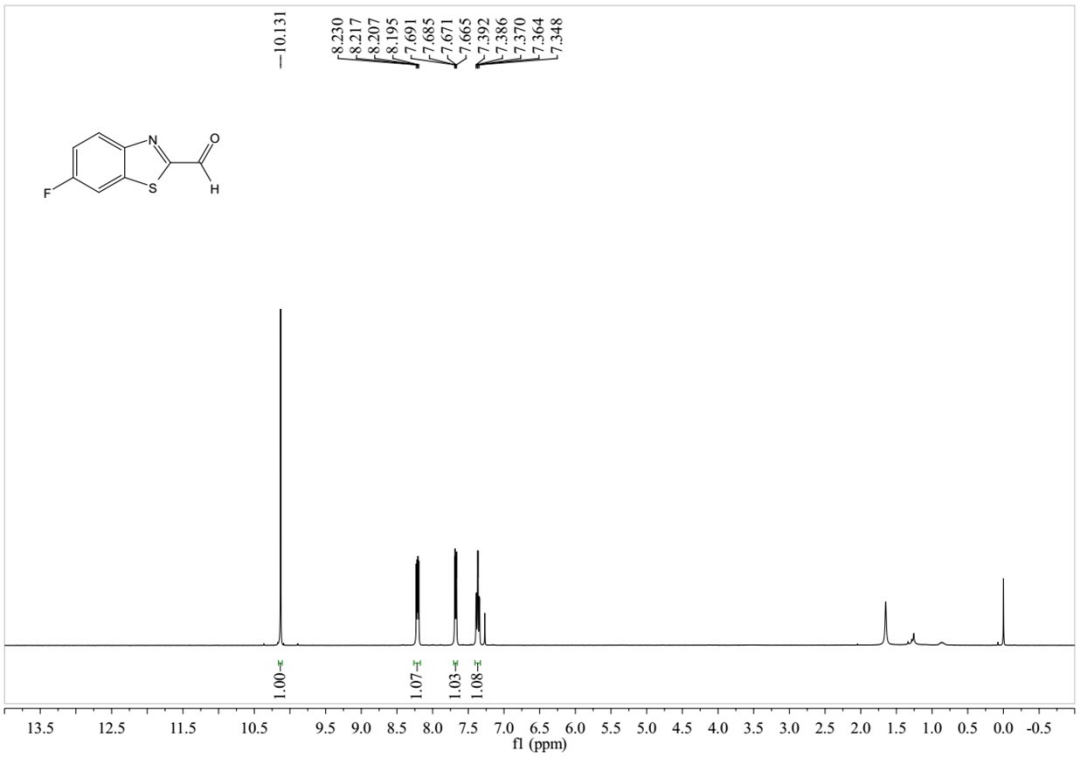
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3d



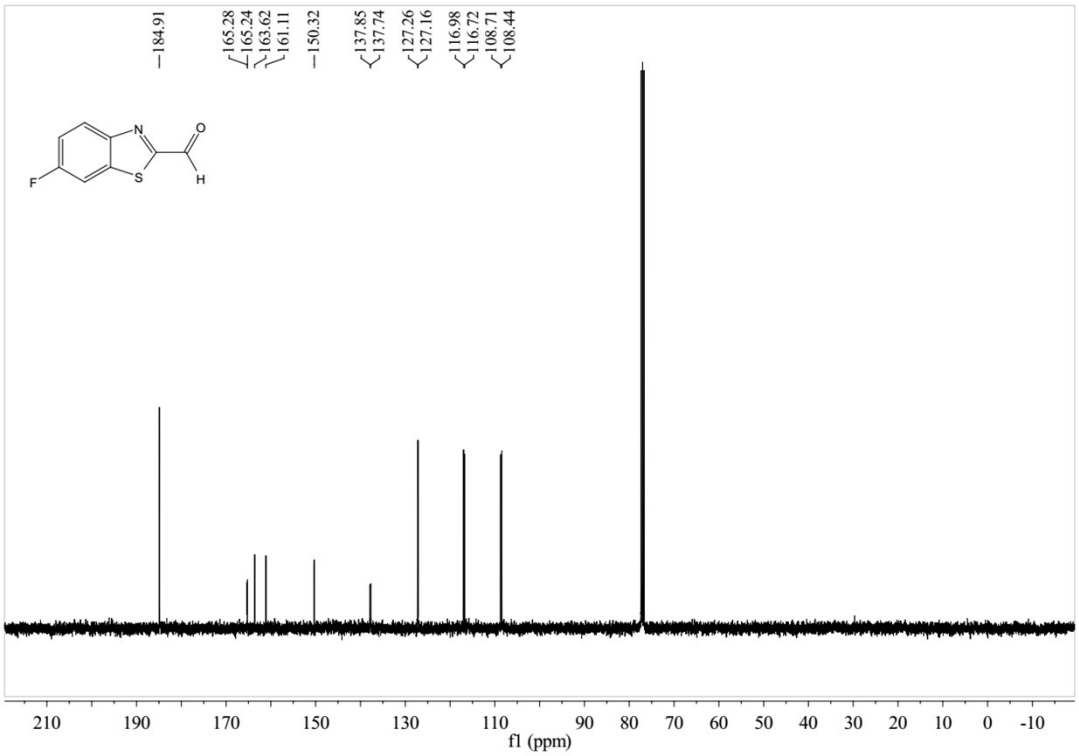
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3d



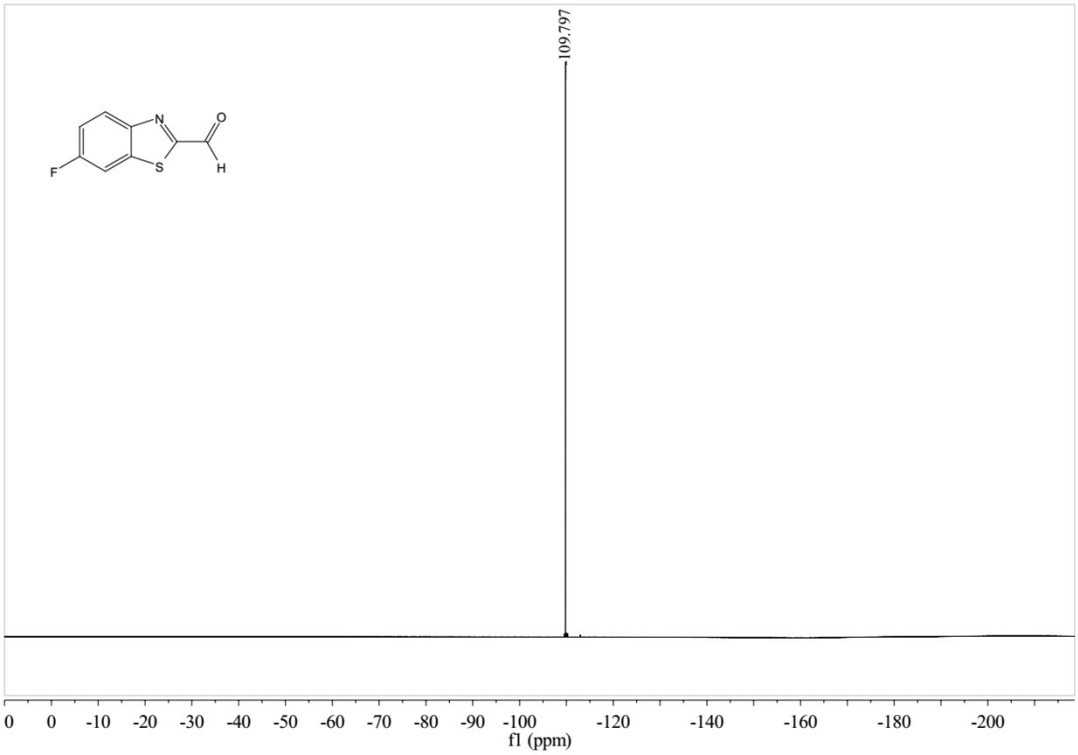
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3e



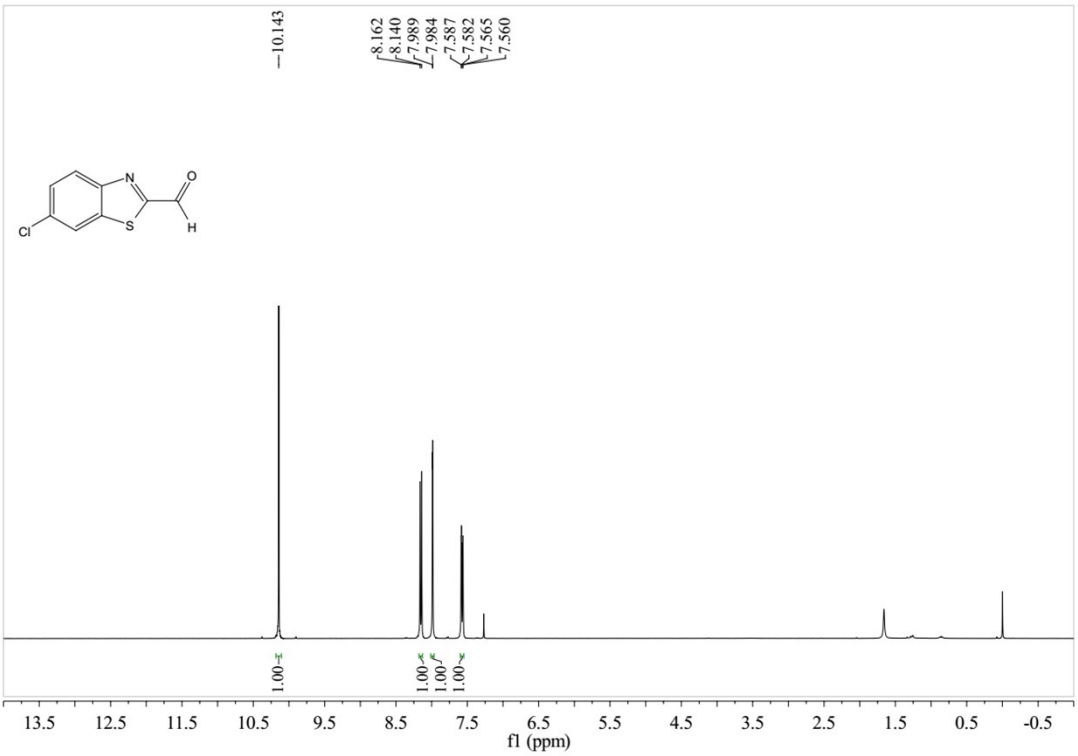
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3e



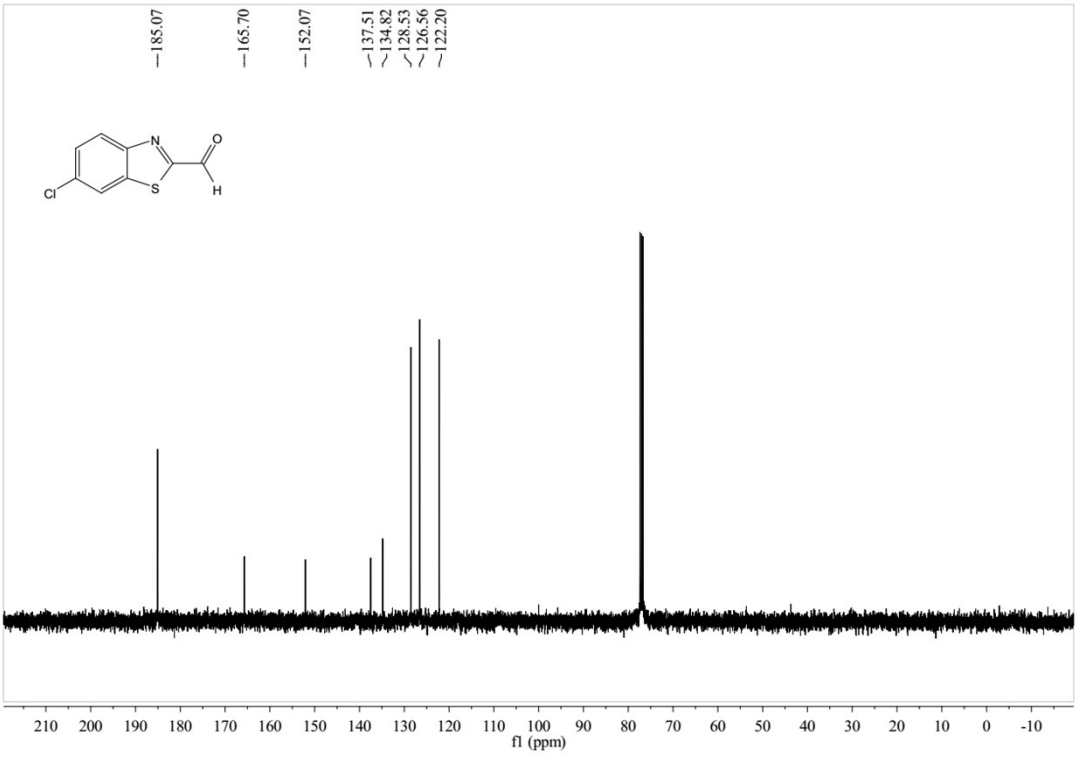
^{19}F NMR (396 MHz, $CDCl_3$) Spectra of 3e



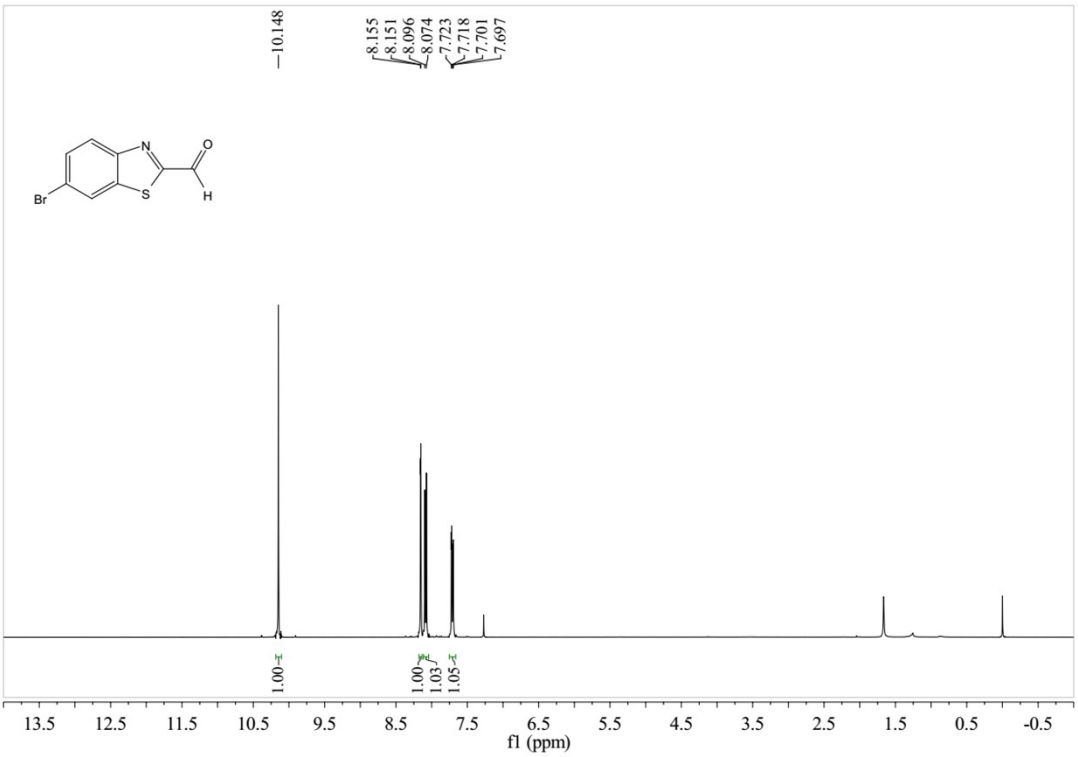
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3f



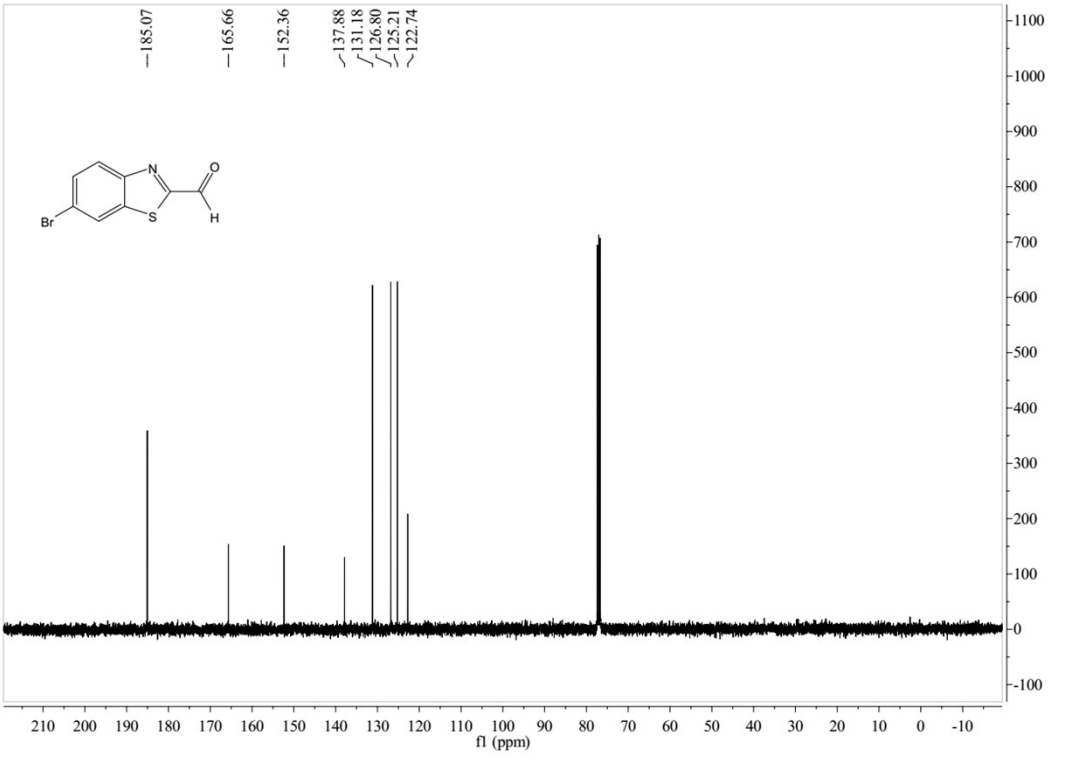
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3f



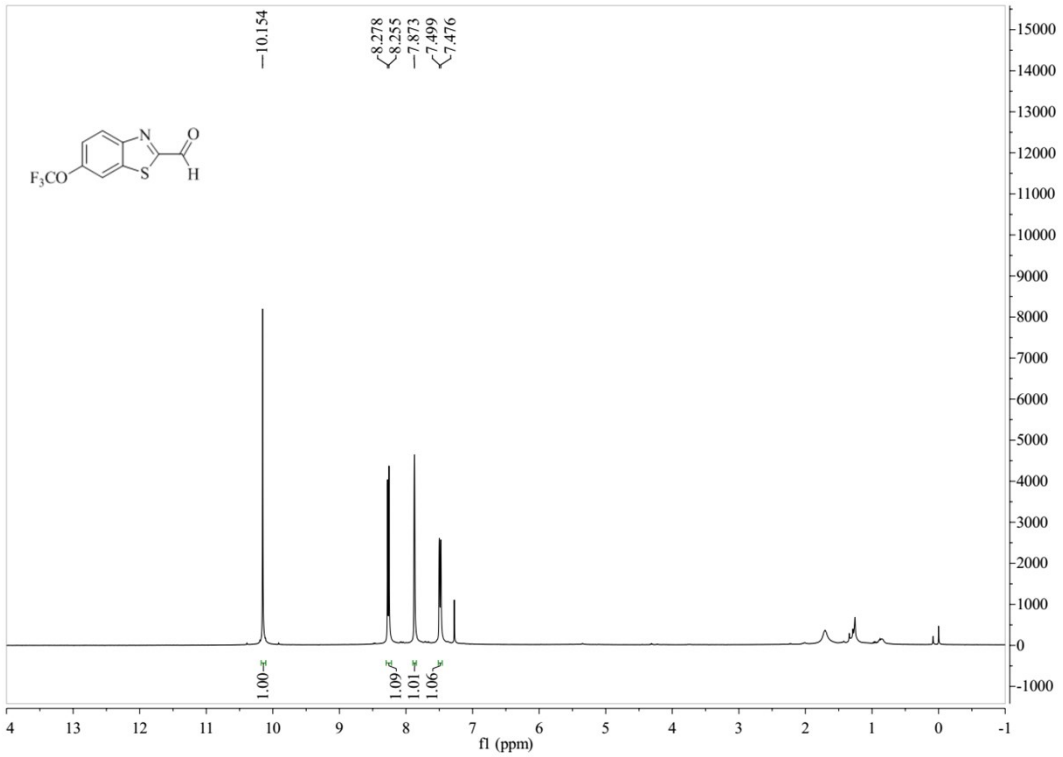
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3g



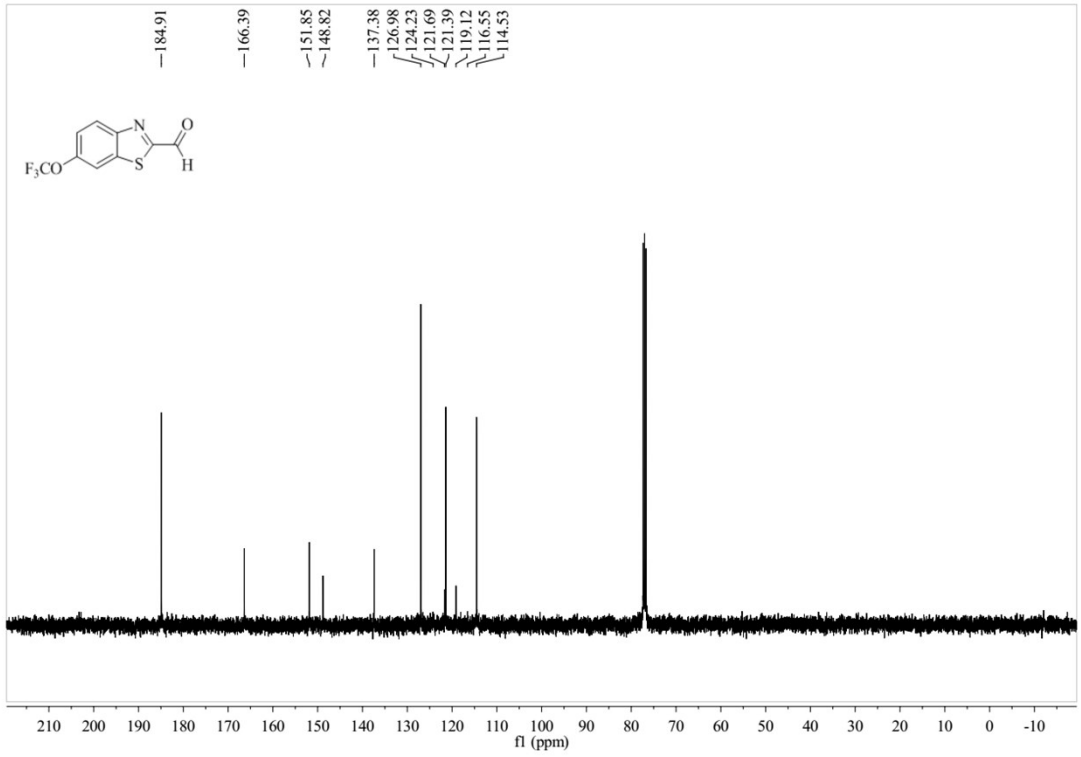
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3g



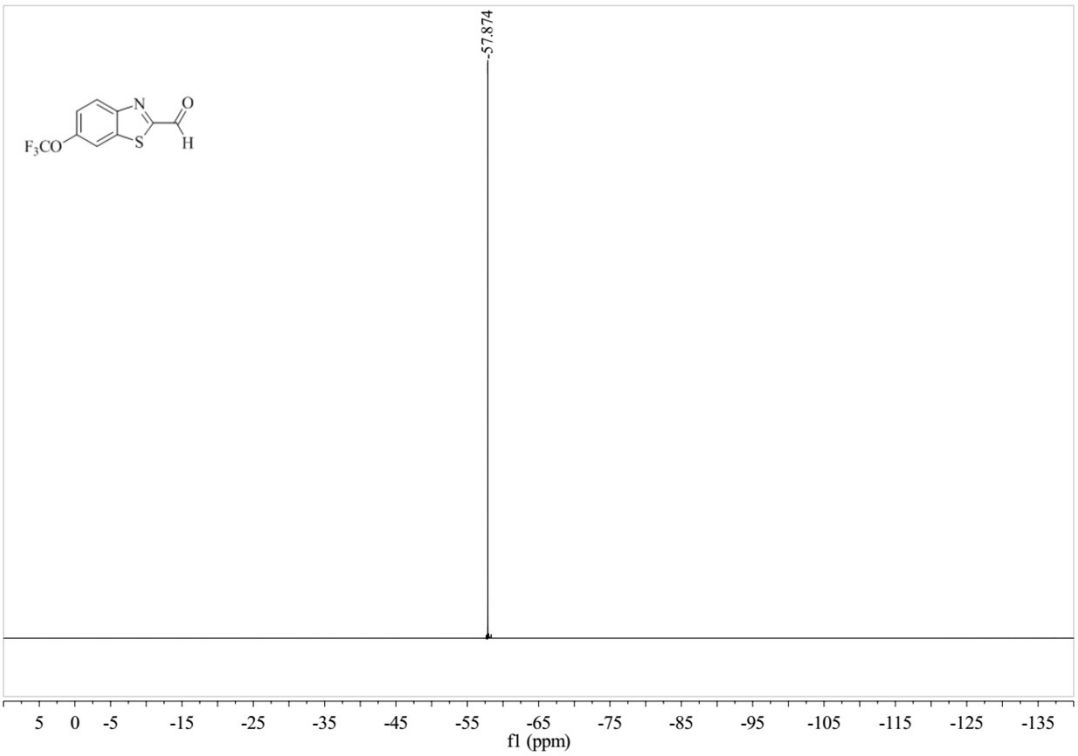
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3h



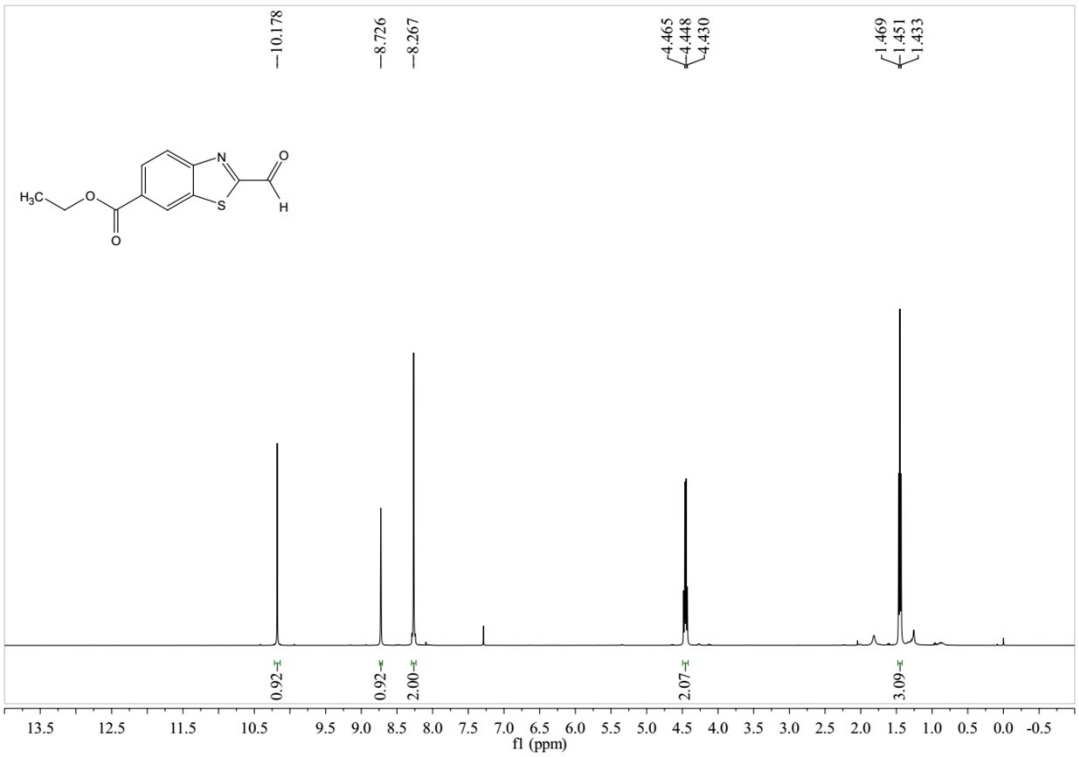
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3h



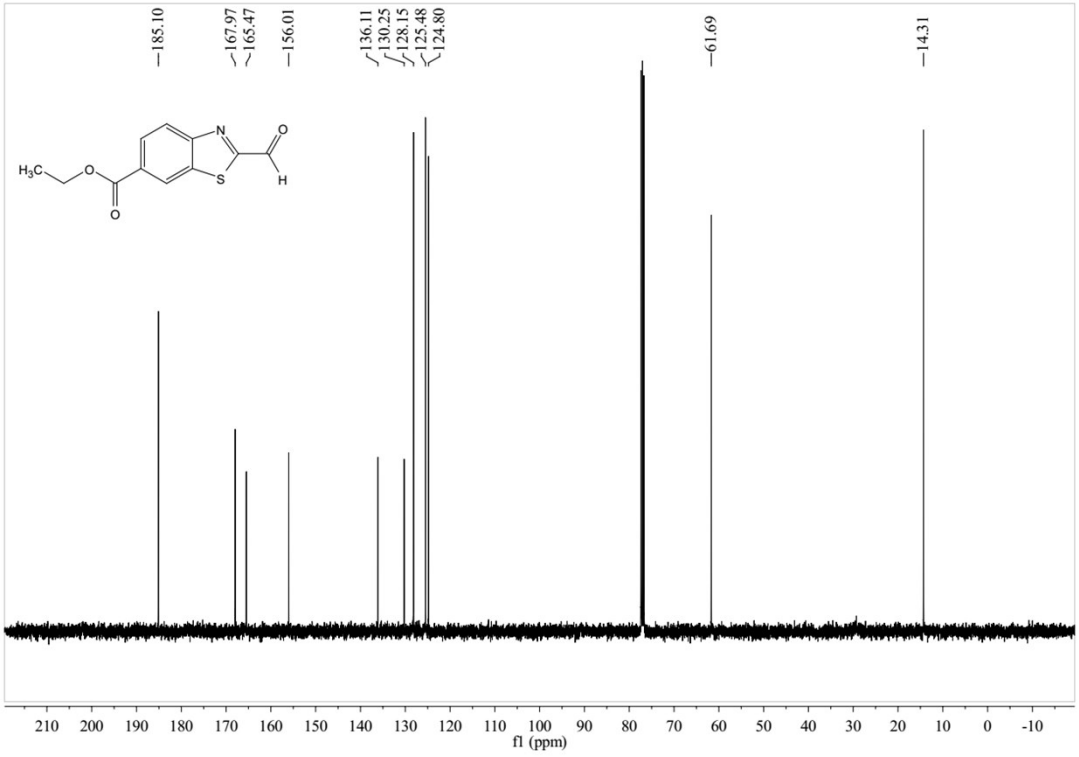
^{19}F NMR (396 MHz, $CDCl_3$) Spectra of 3h



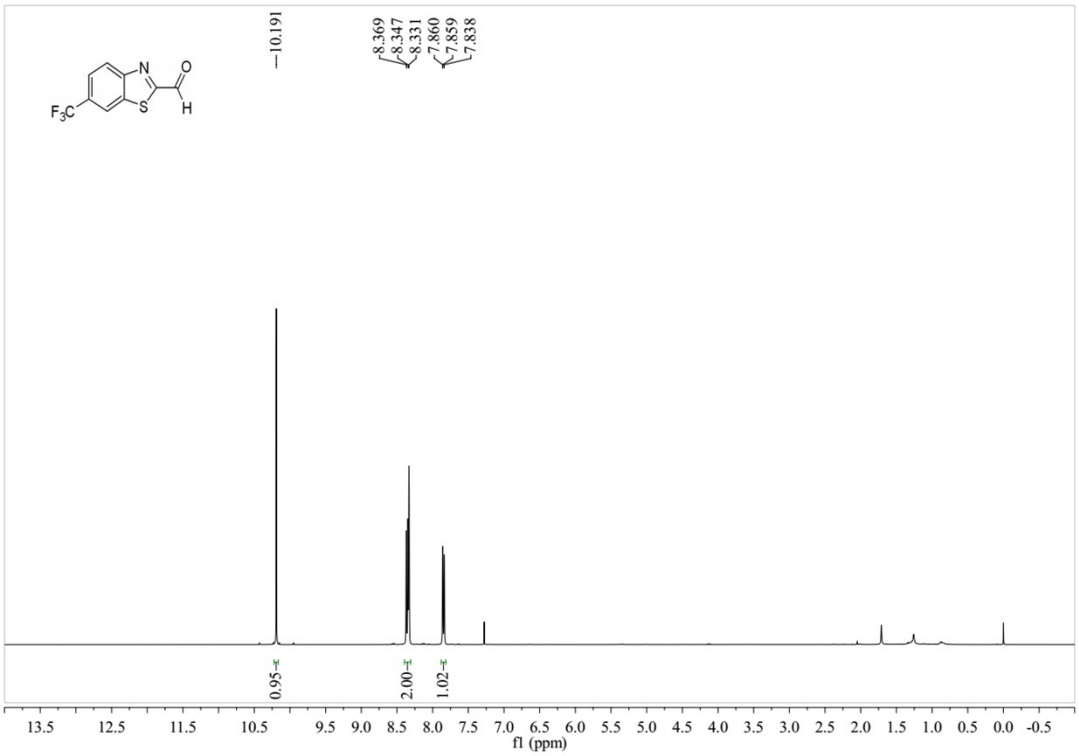
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3i



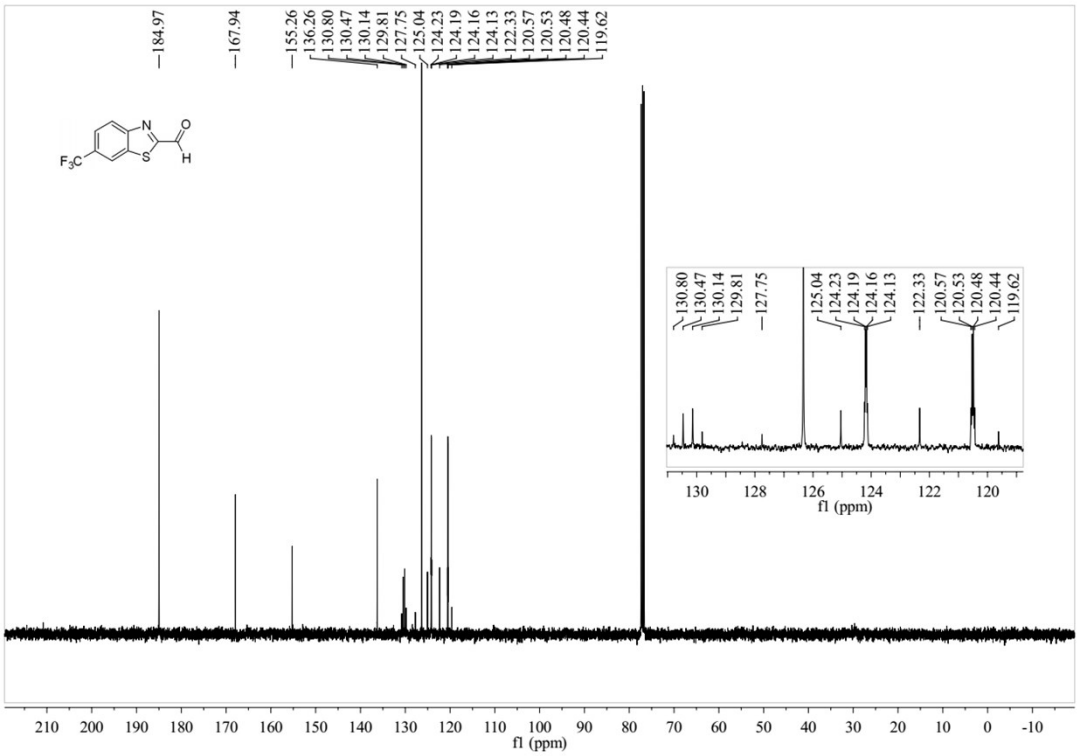
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3i



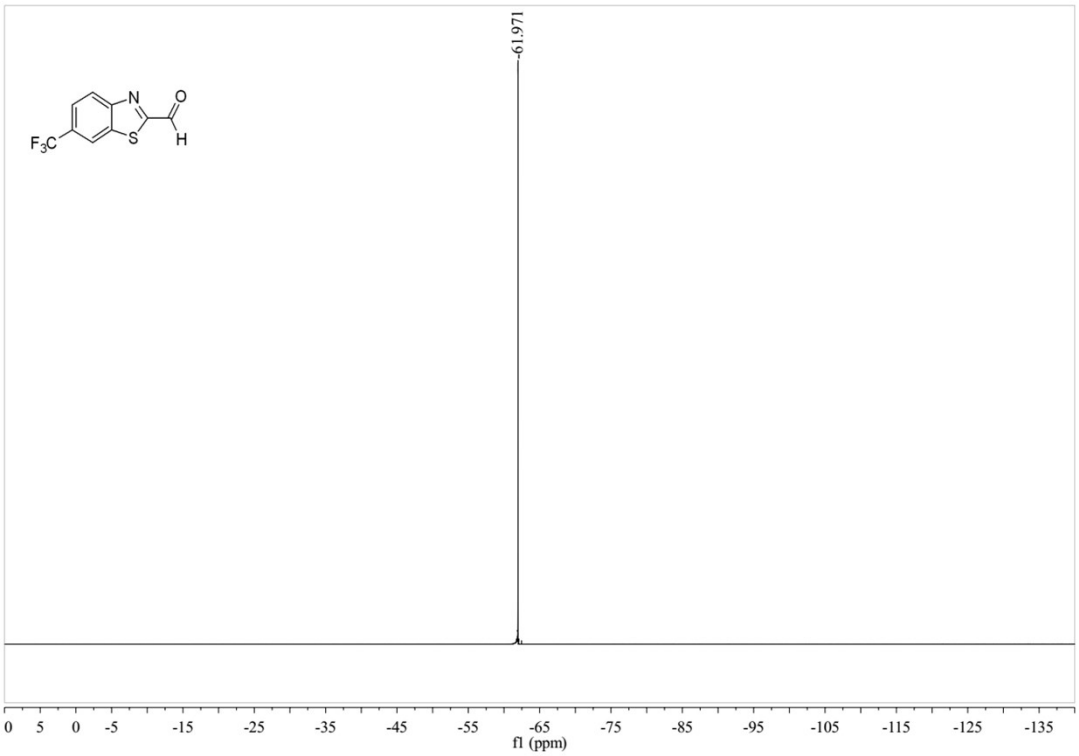
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3j



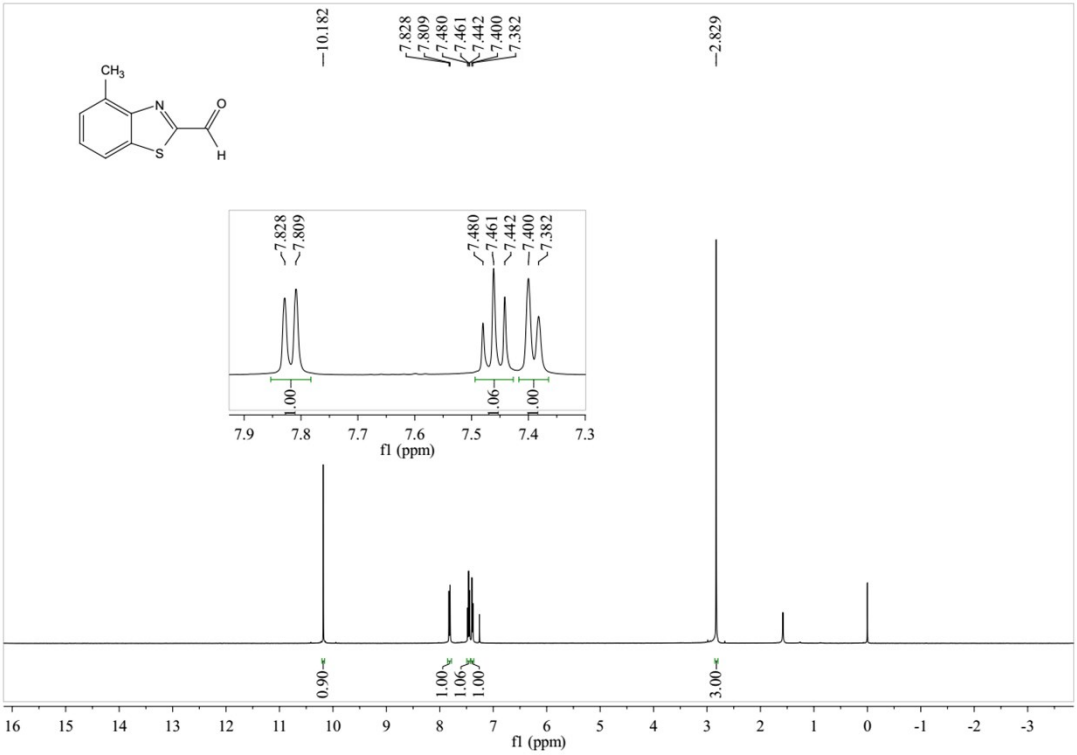
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3j



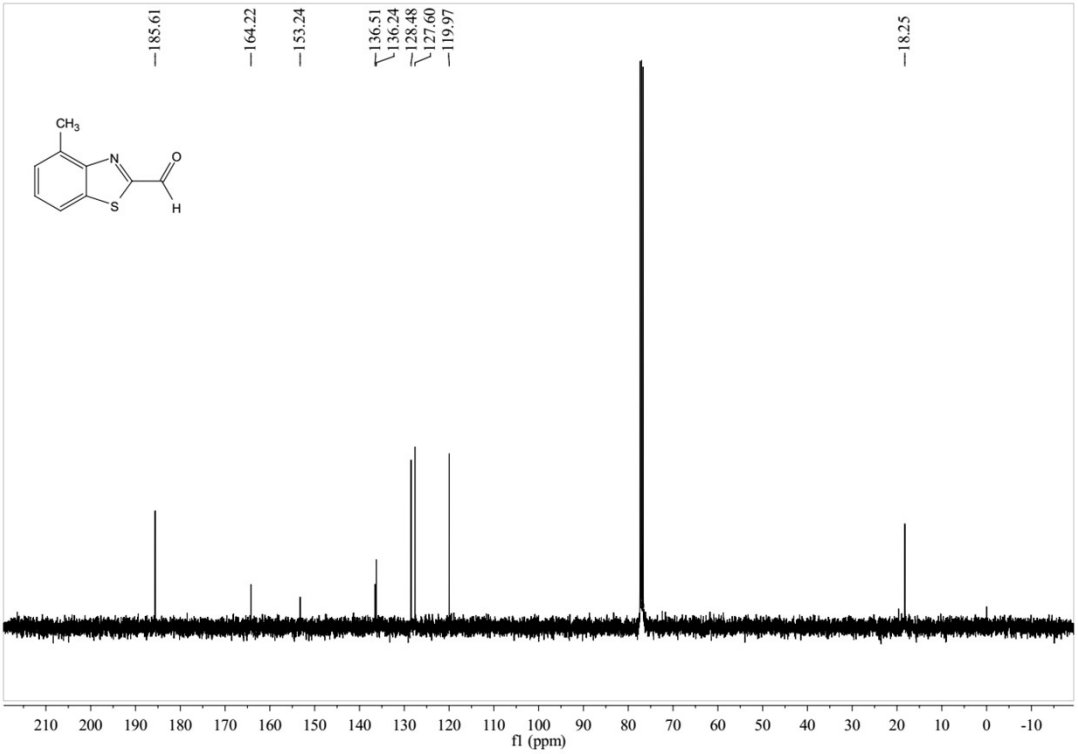
^{19}F NMR (396 MHz, $CDCl_3$) Spectra of 3j



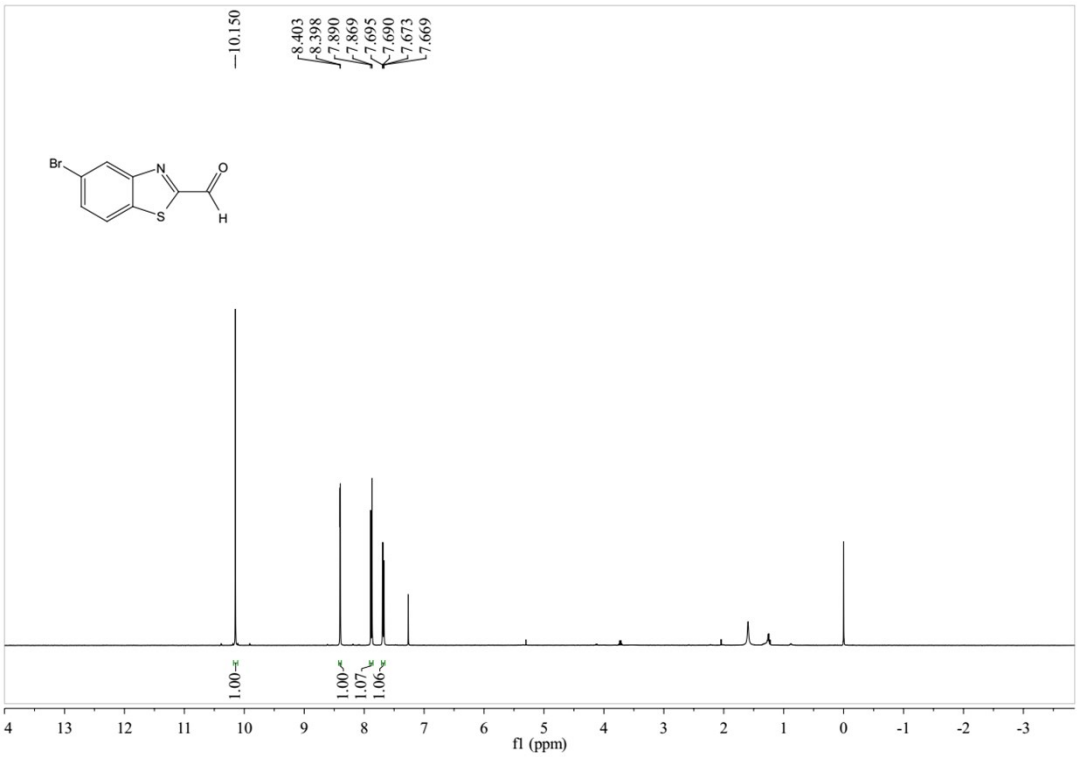
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3m



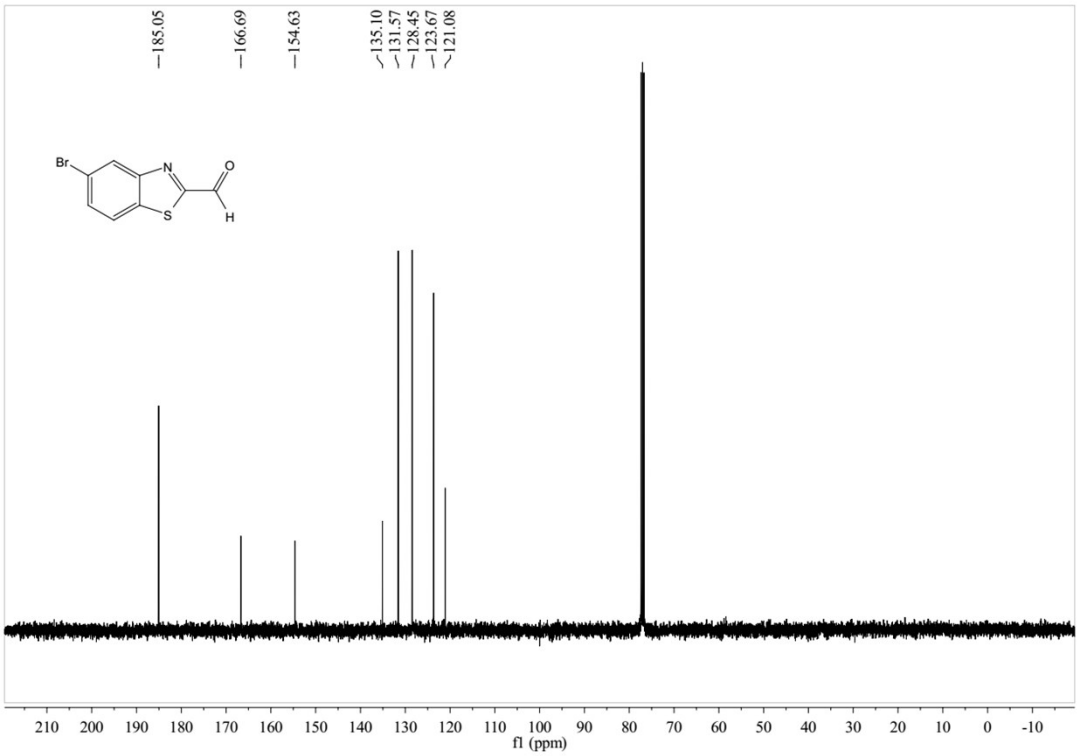
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3m



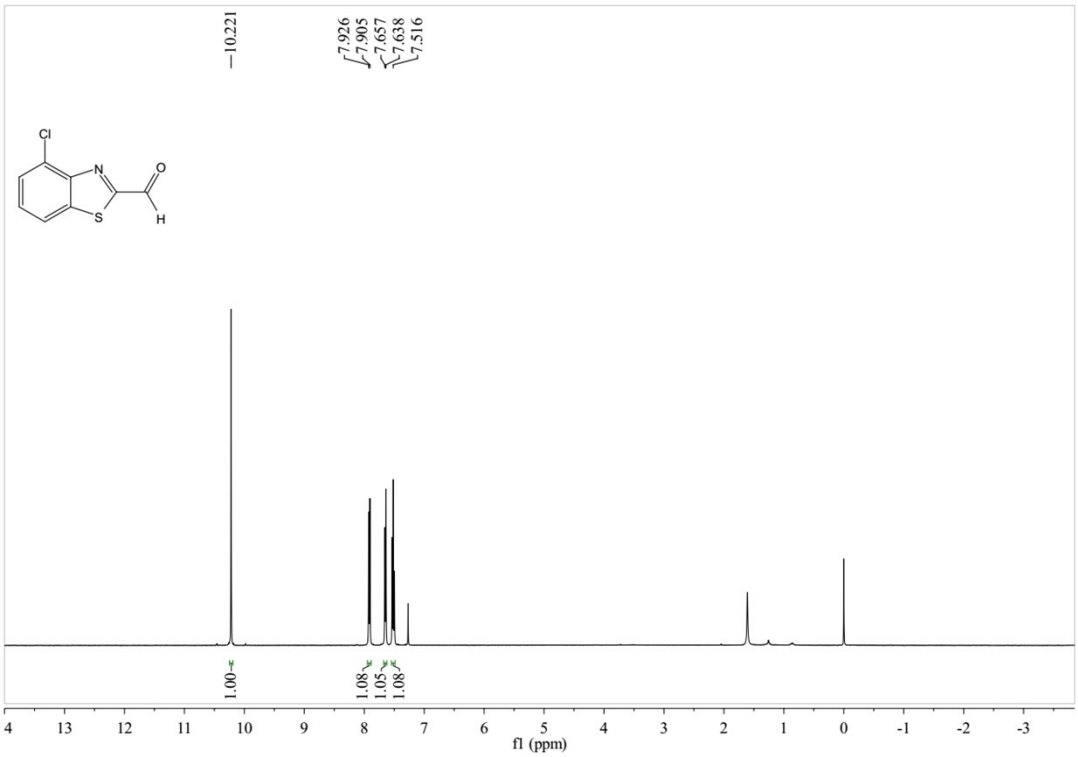
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3n



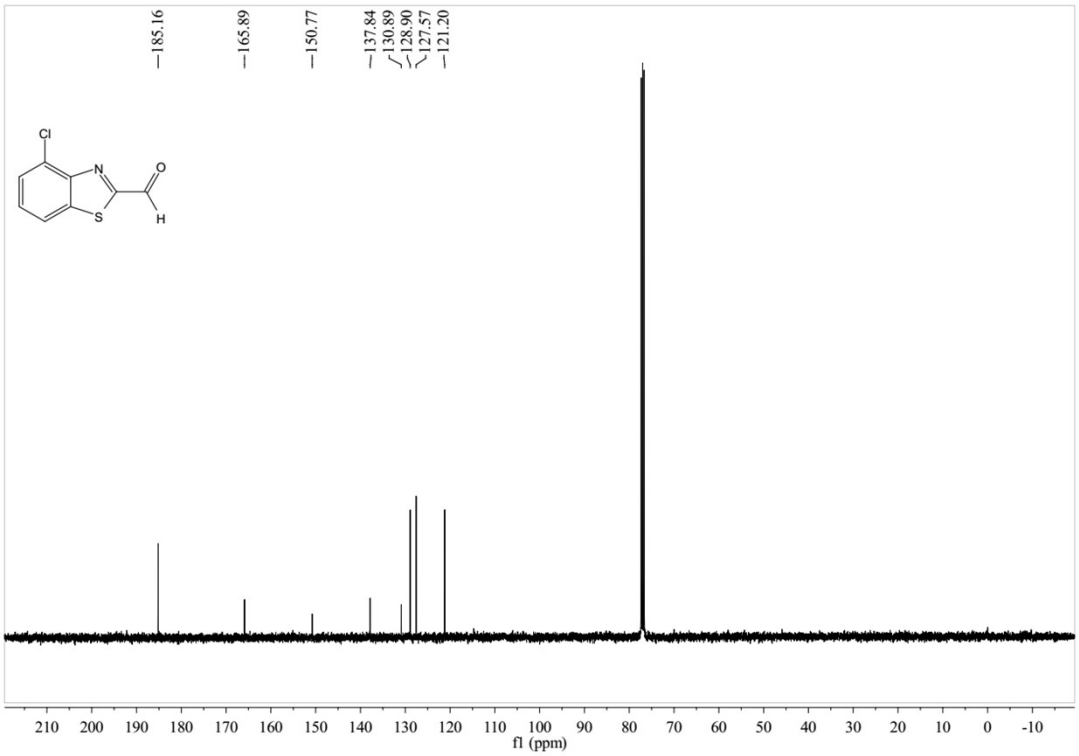
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3n



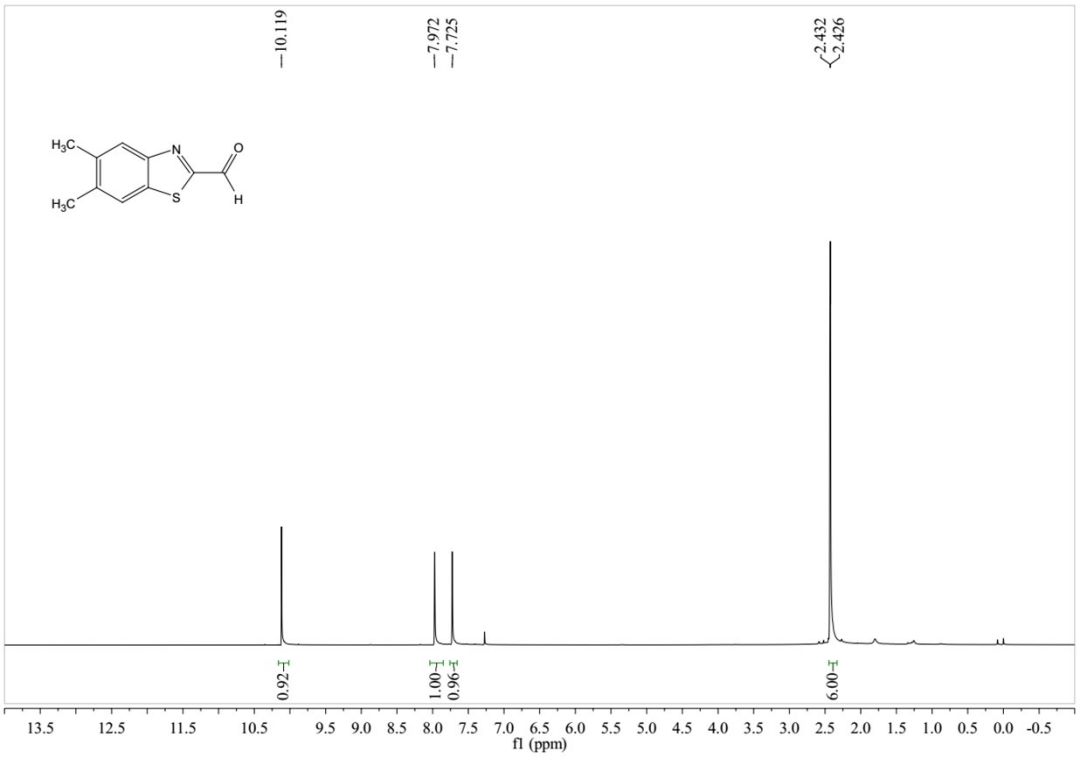
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3o



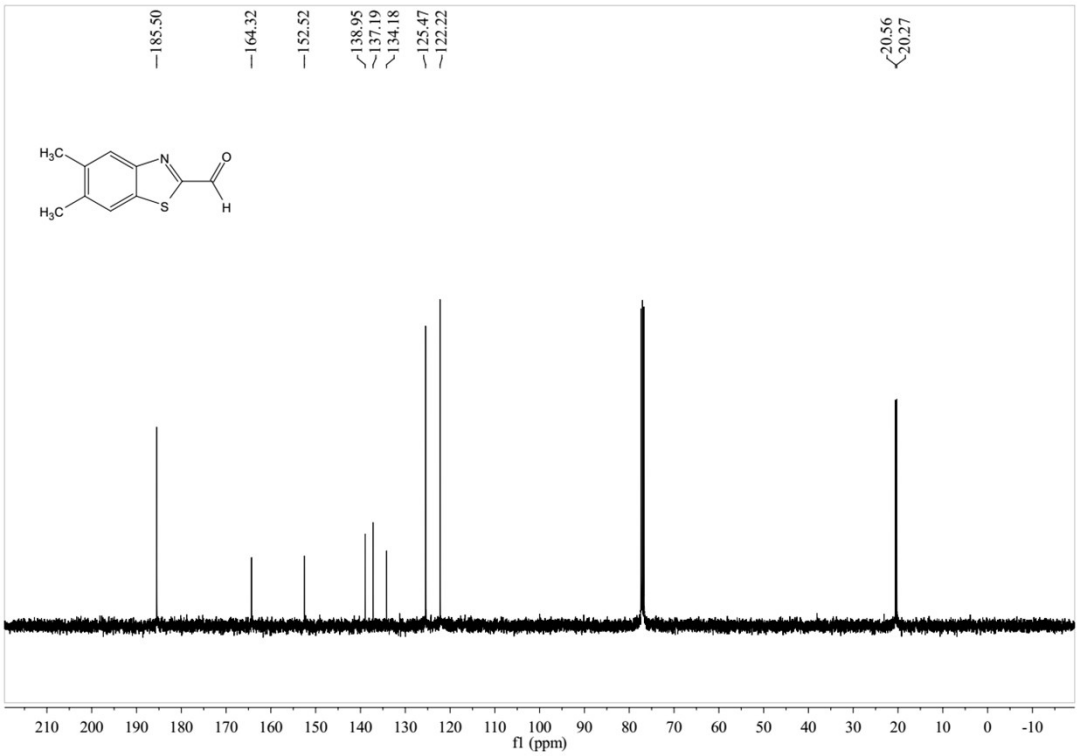
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3o



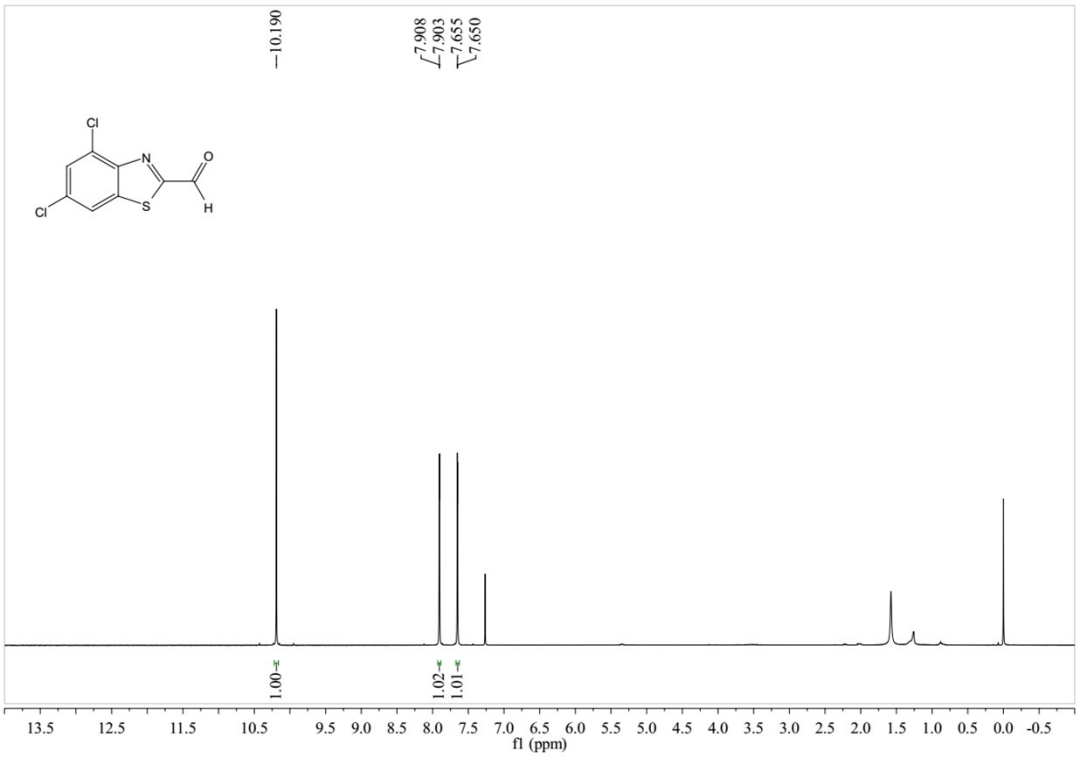
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3p



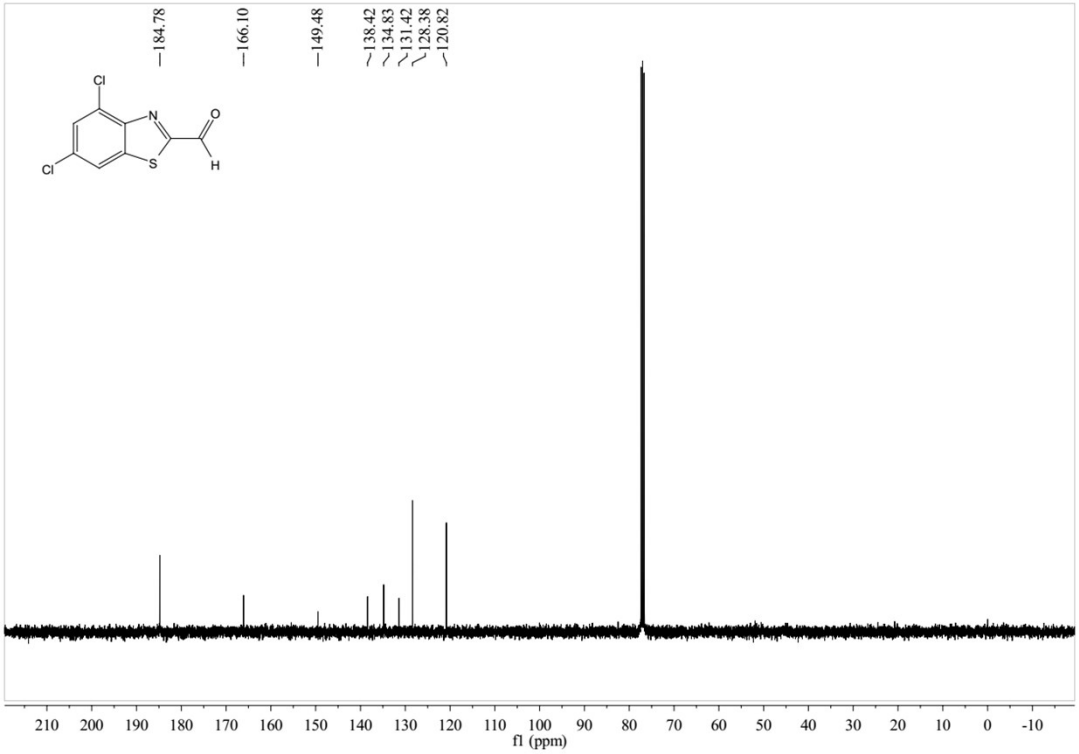
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3p



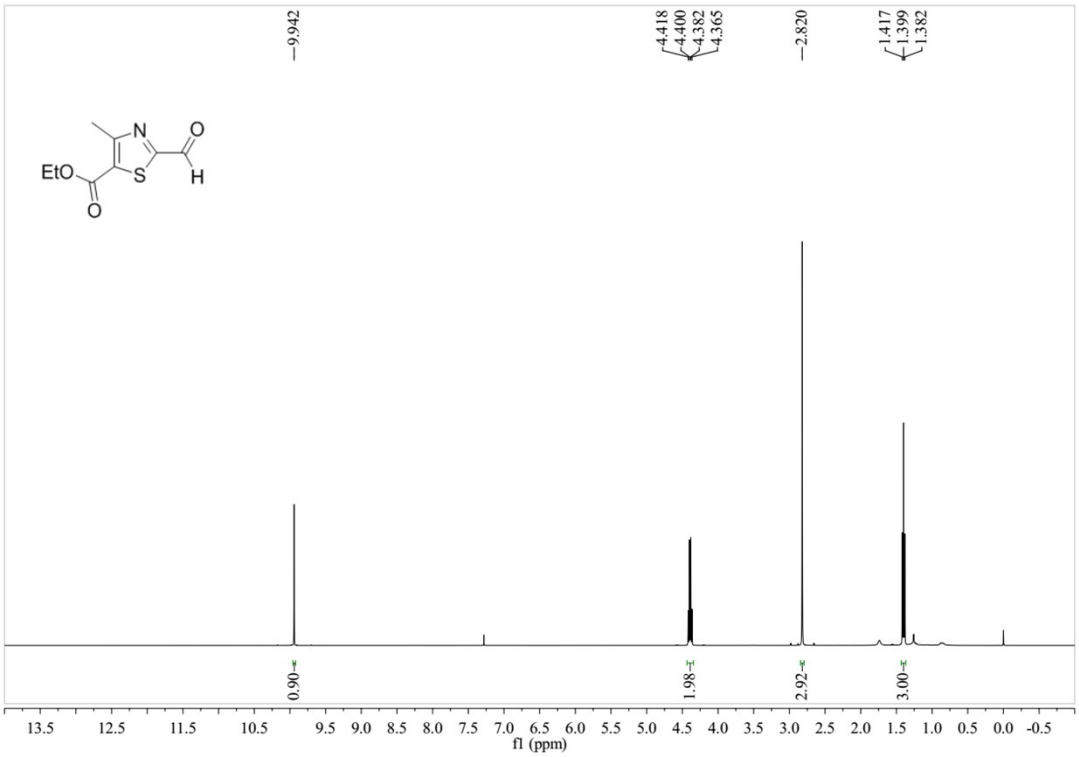
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3q



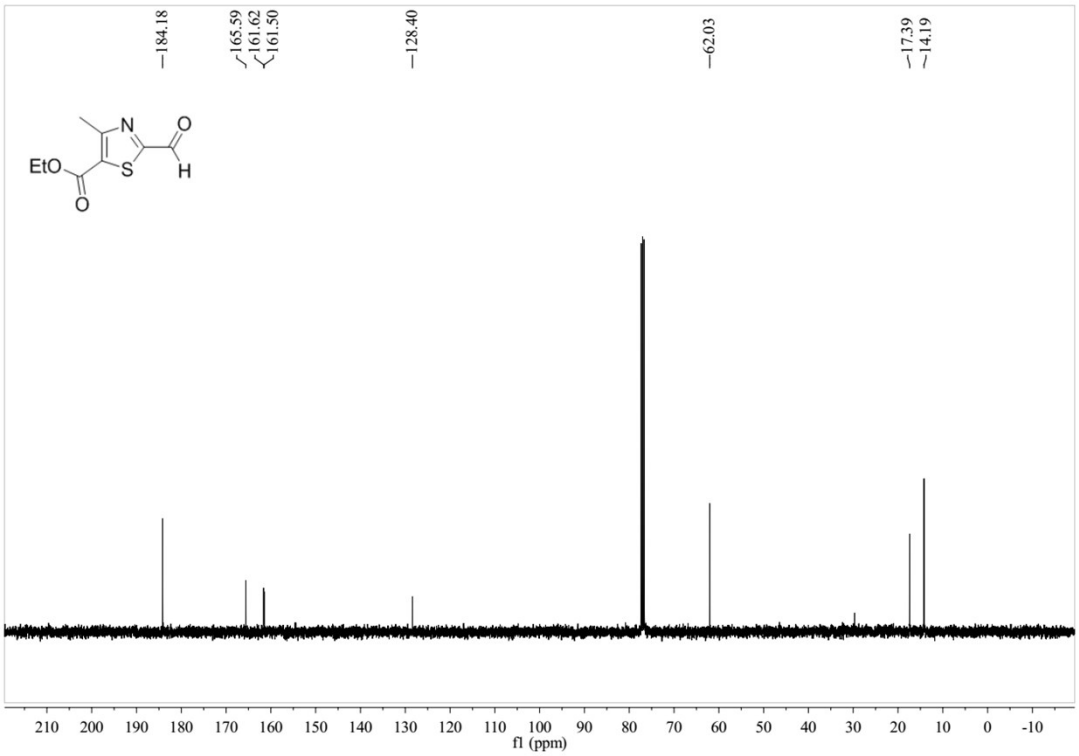
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3q



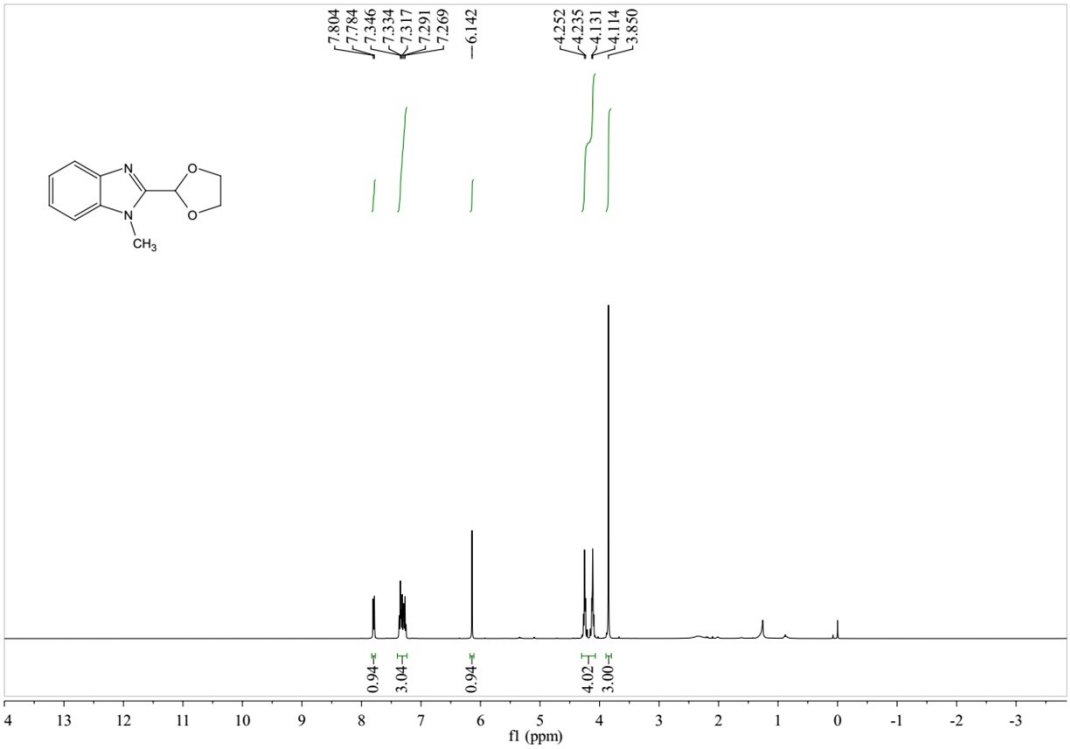
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3r



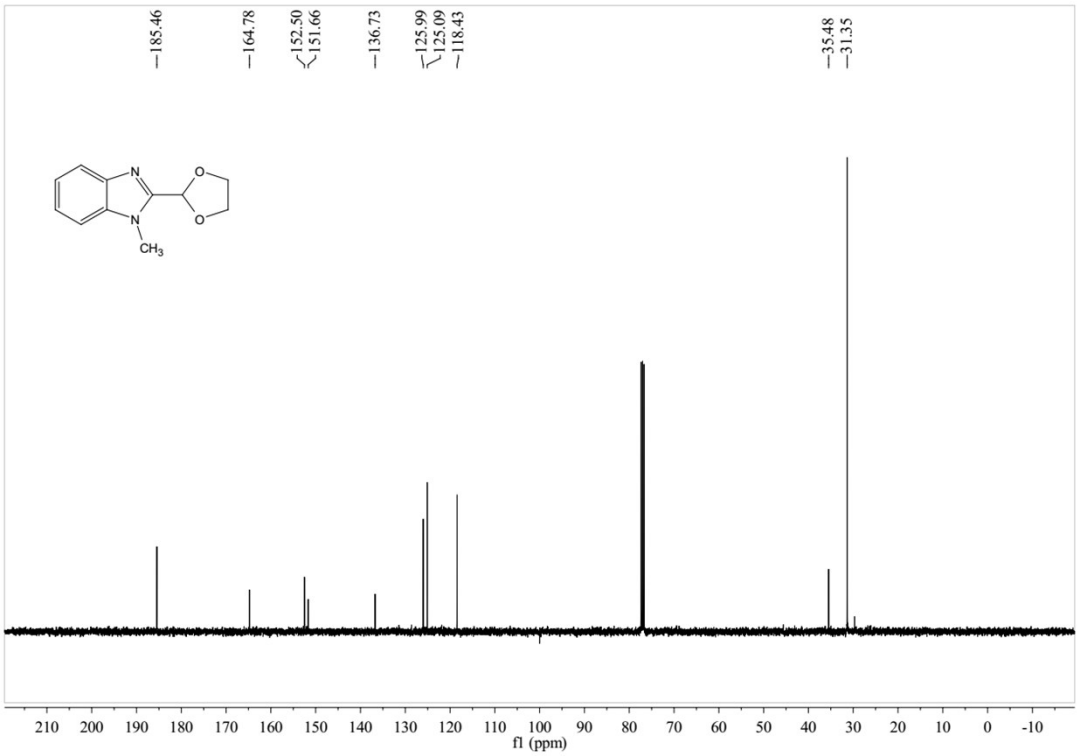
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3r



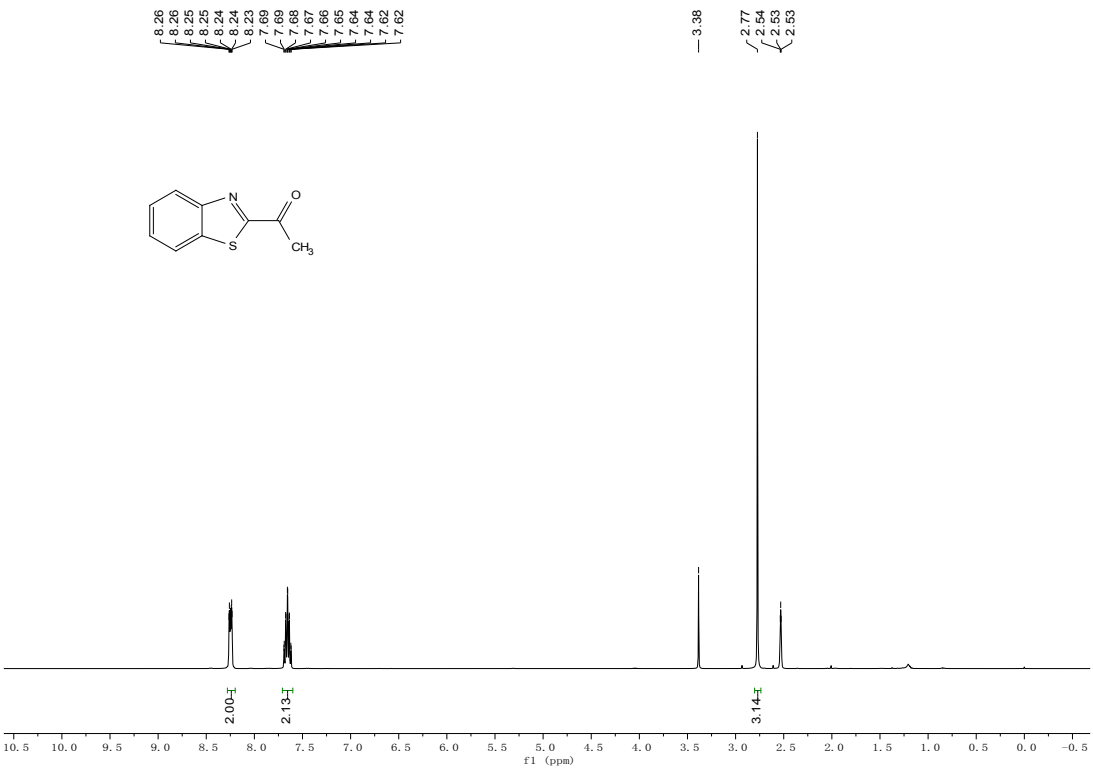
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3s



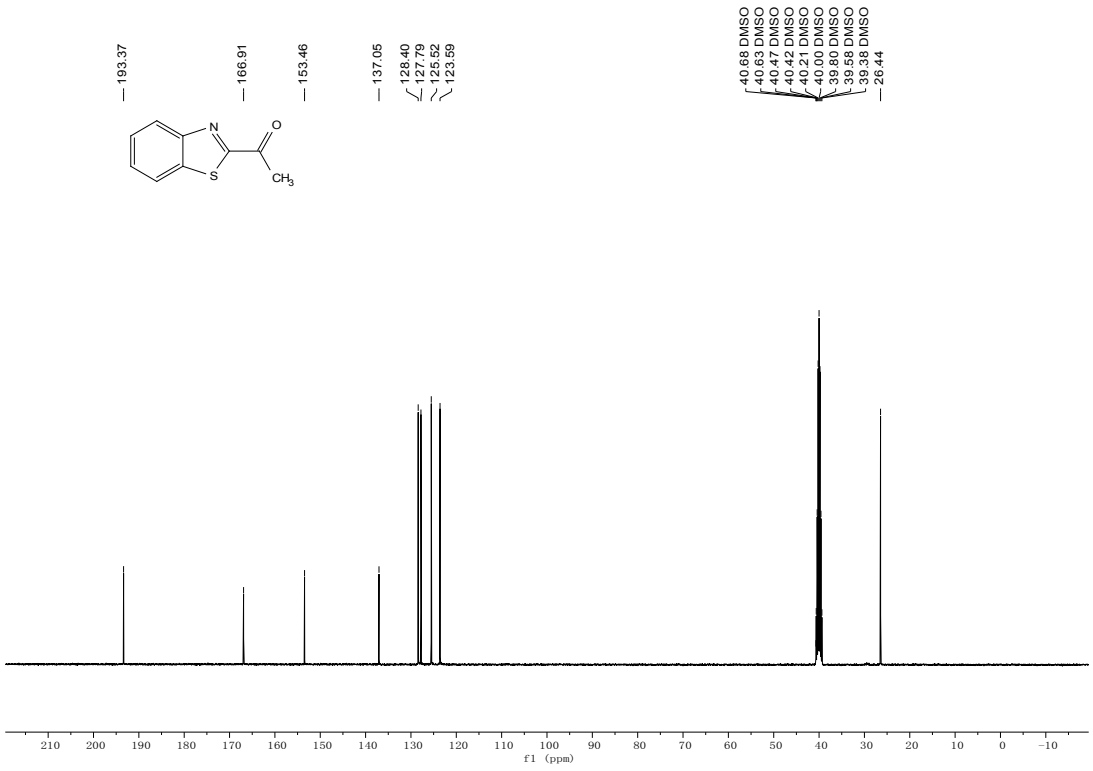
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3s



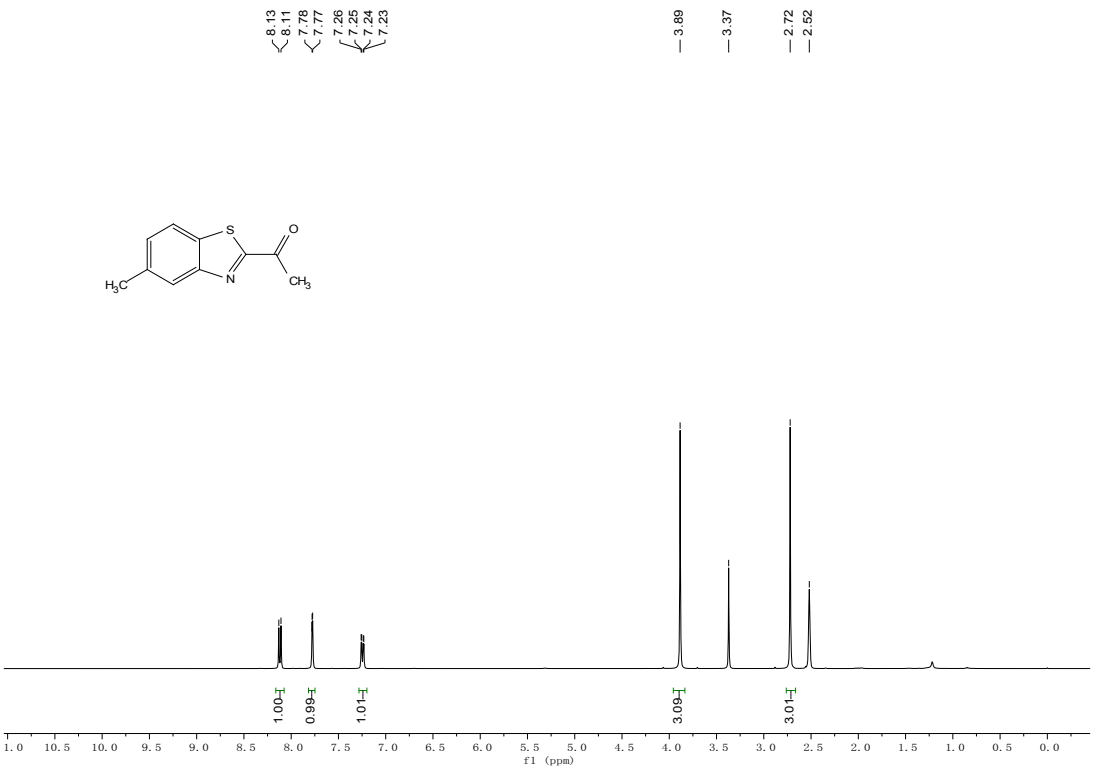
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3t



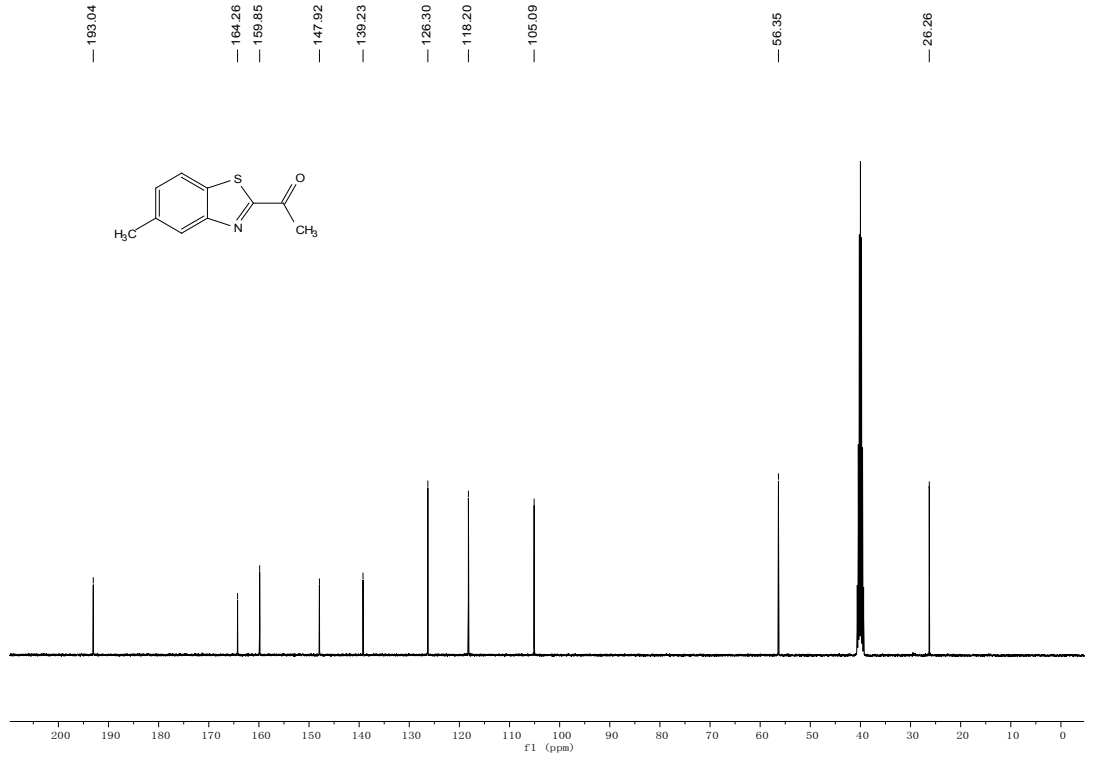
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3t



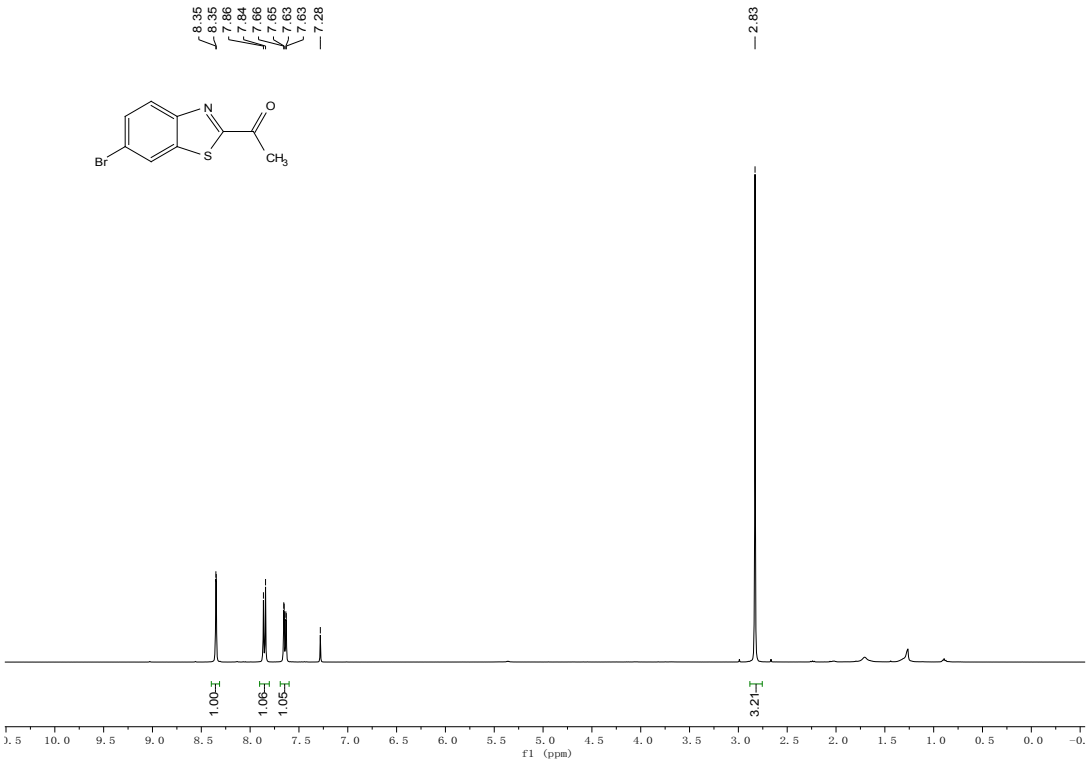
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3u



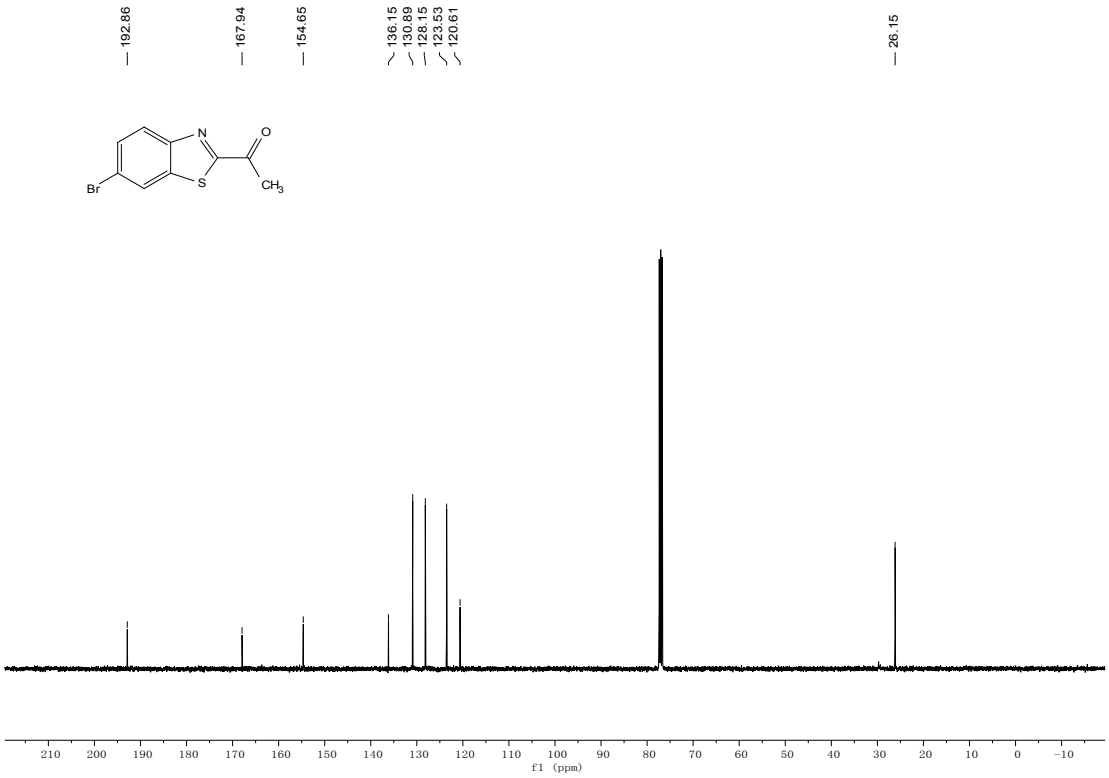
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3u



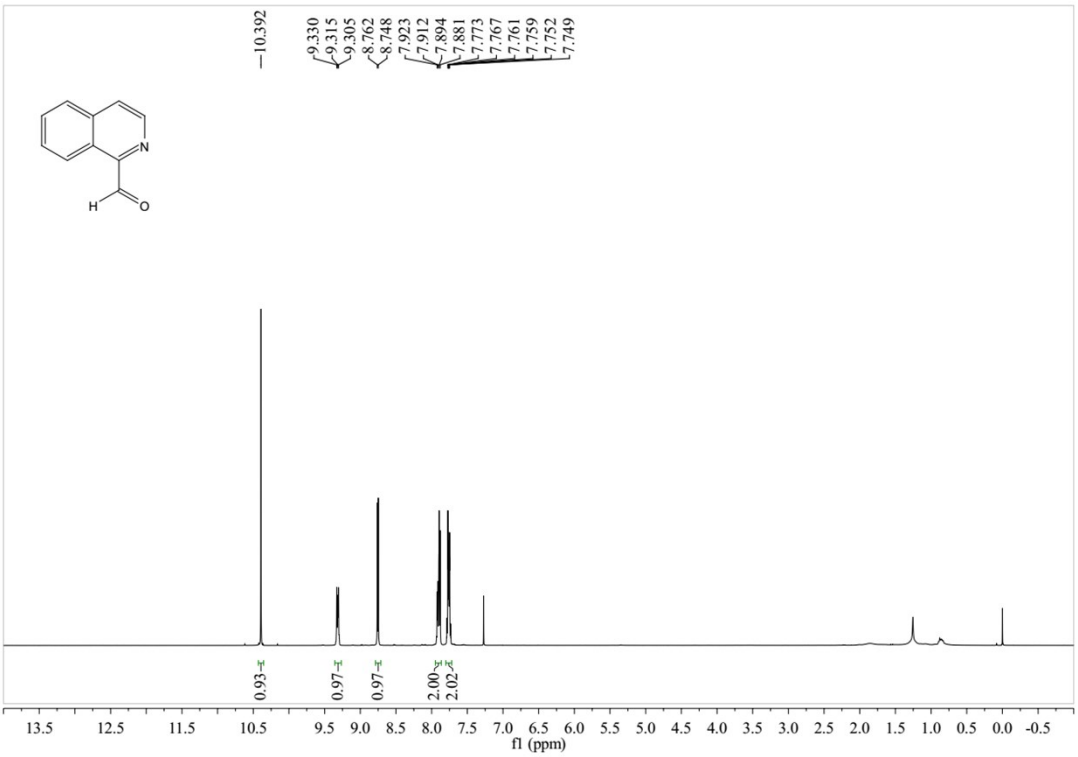
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 3v



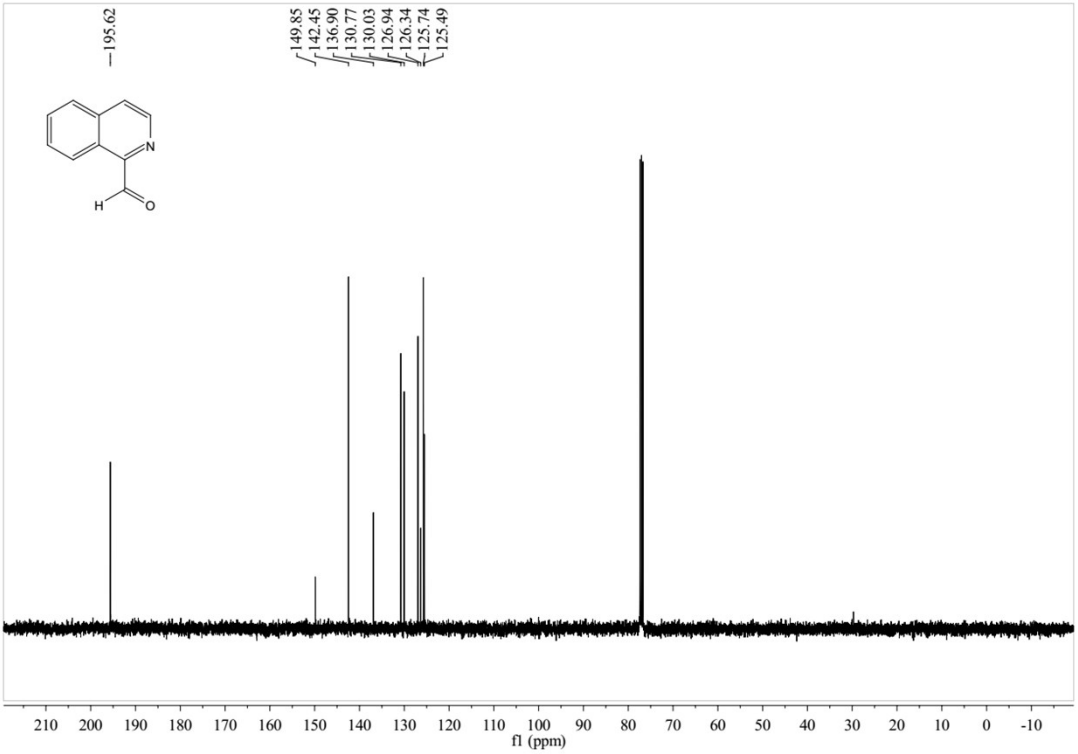
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 3v



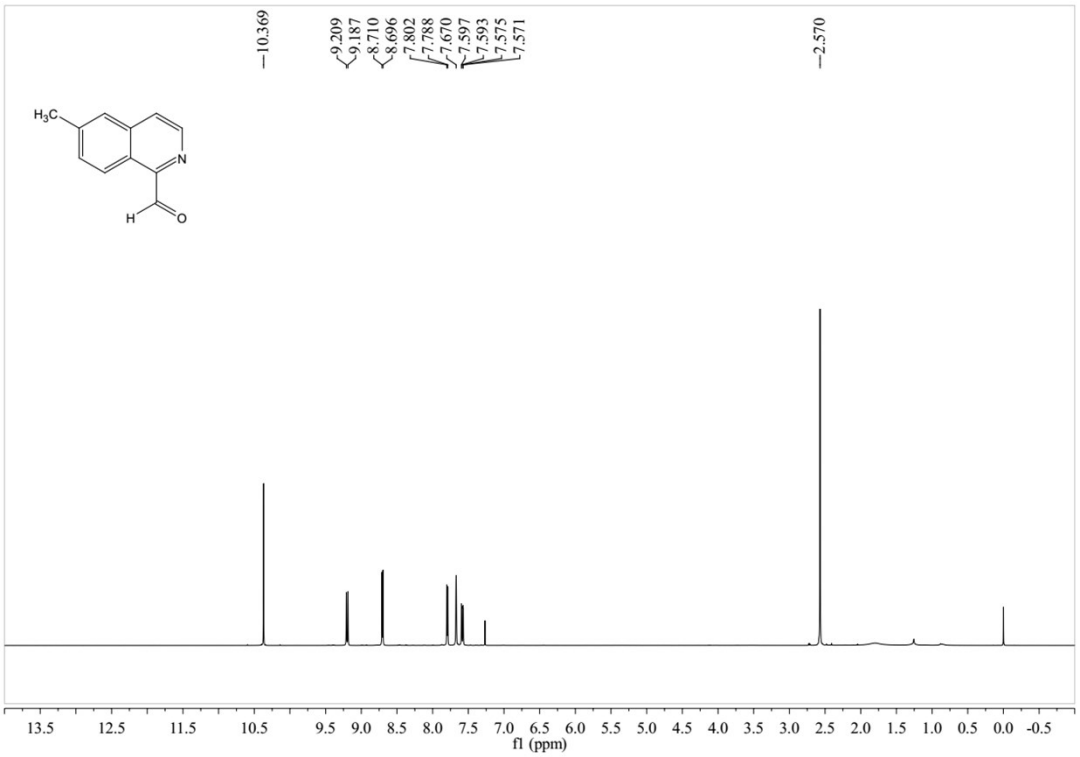
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6a



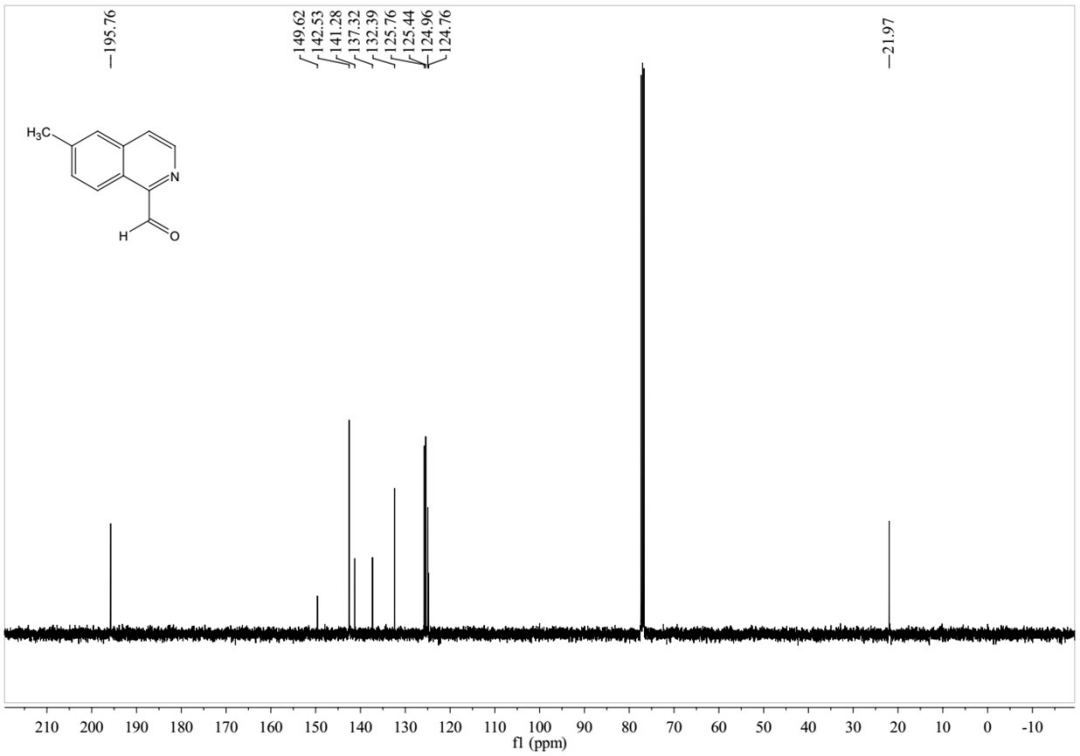
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6a



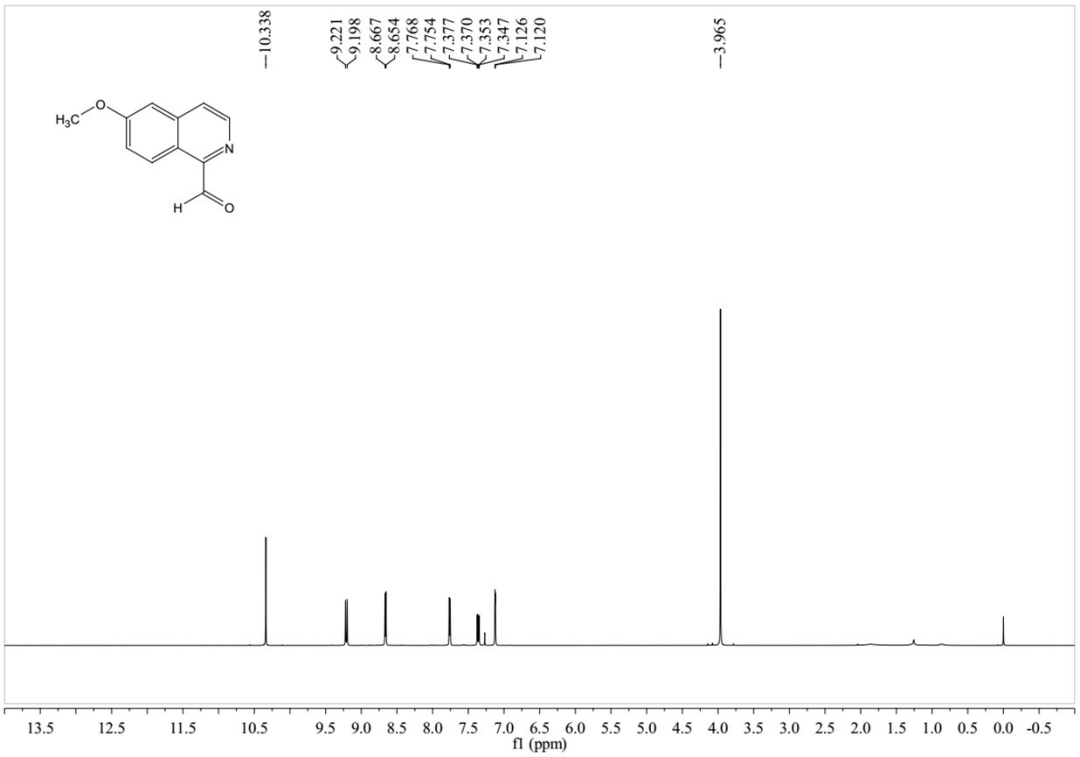
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6b



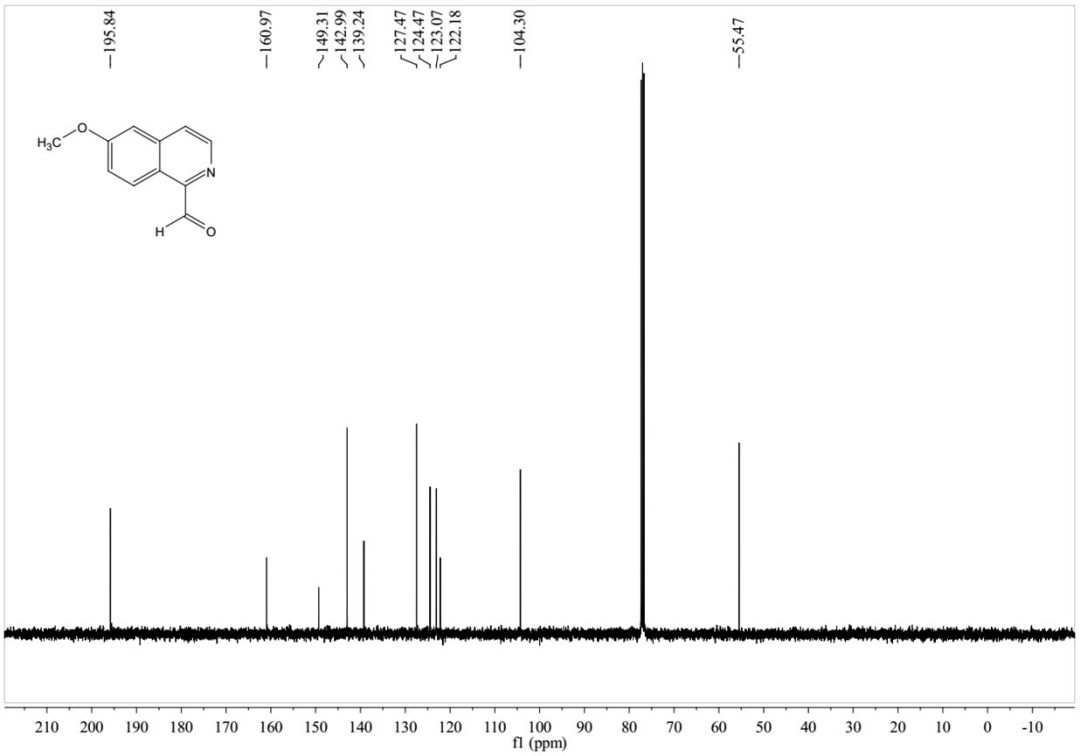
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6b



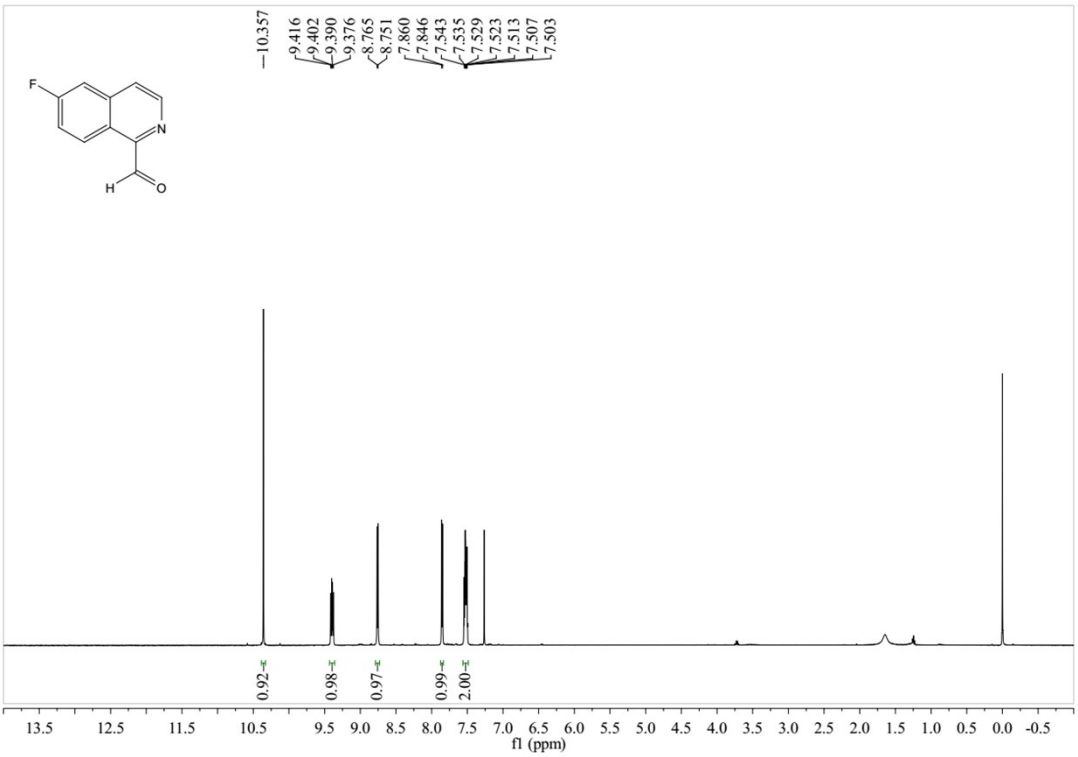
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6c



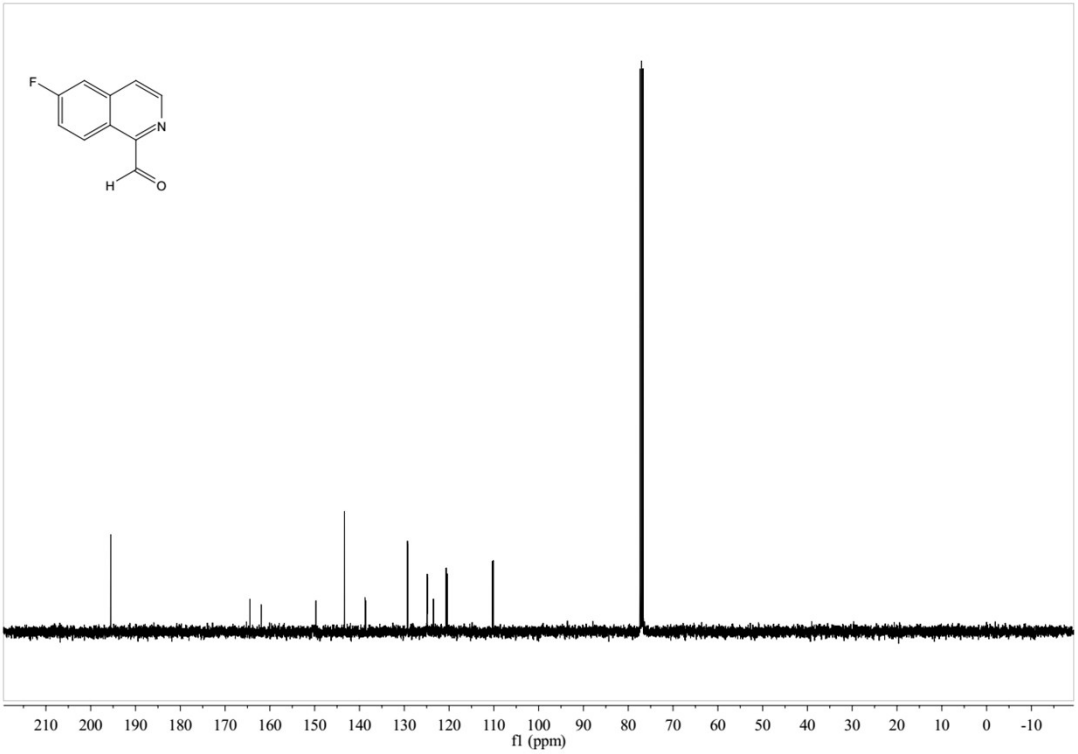
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6c



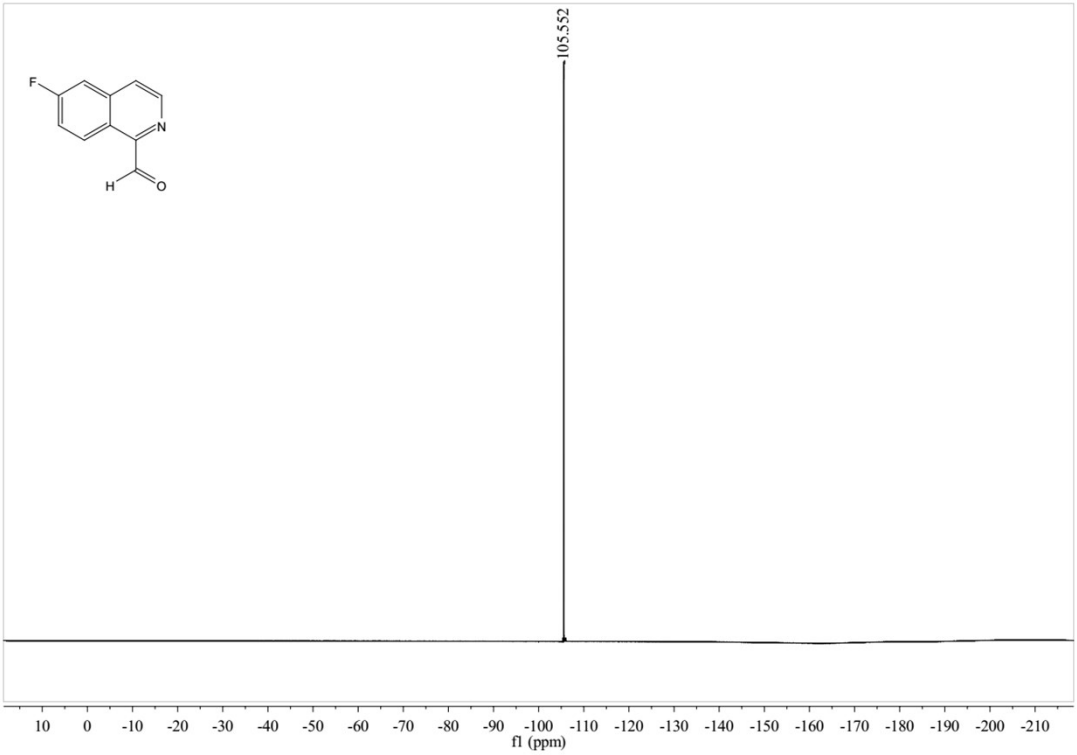
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6d



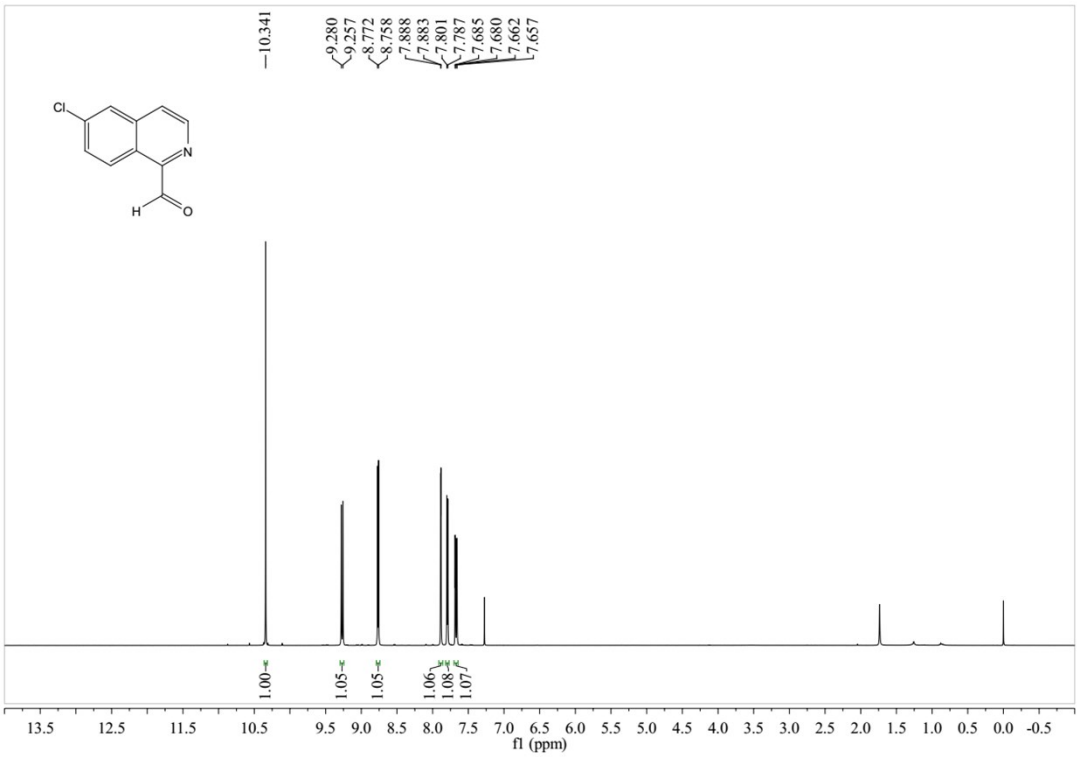
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6d



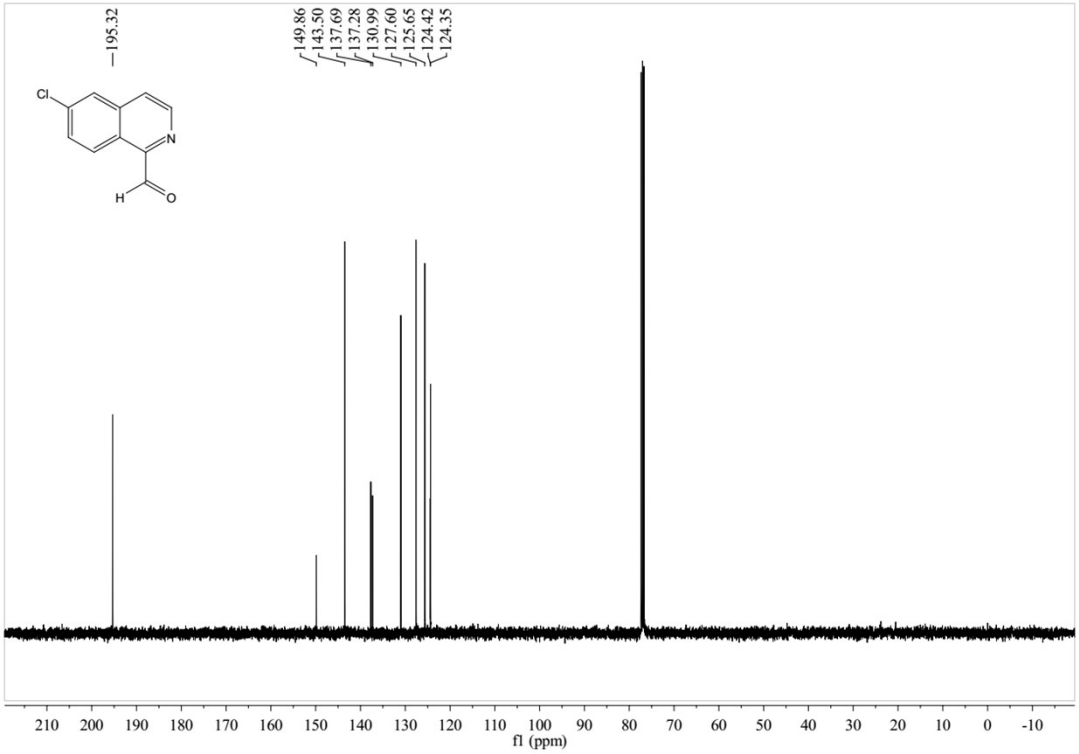
^{19}F NMR (396 MHz, $CDCl_3$) Spectra of 6d



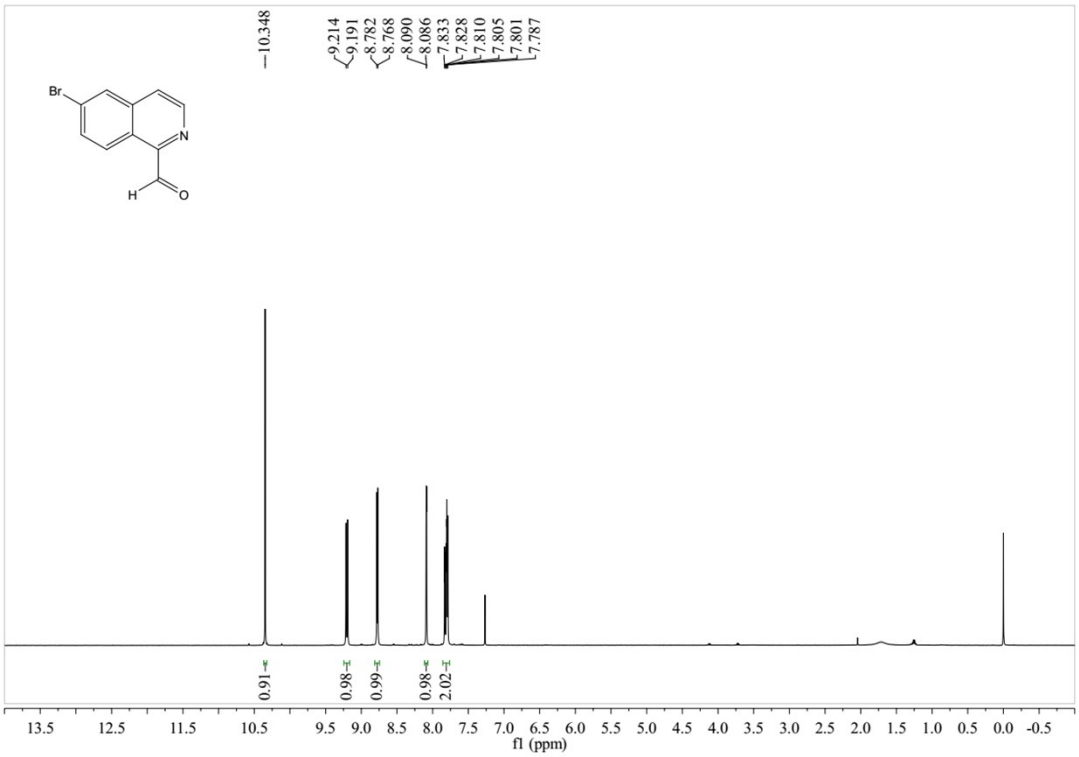
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6e



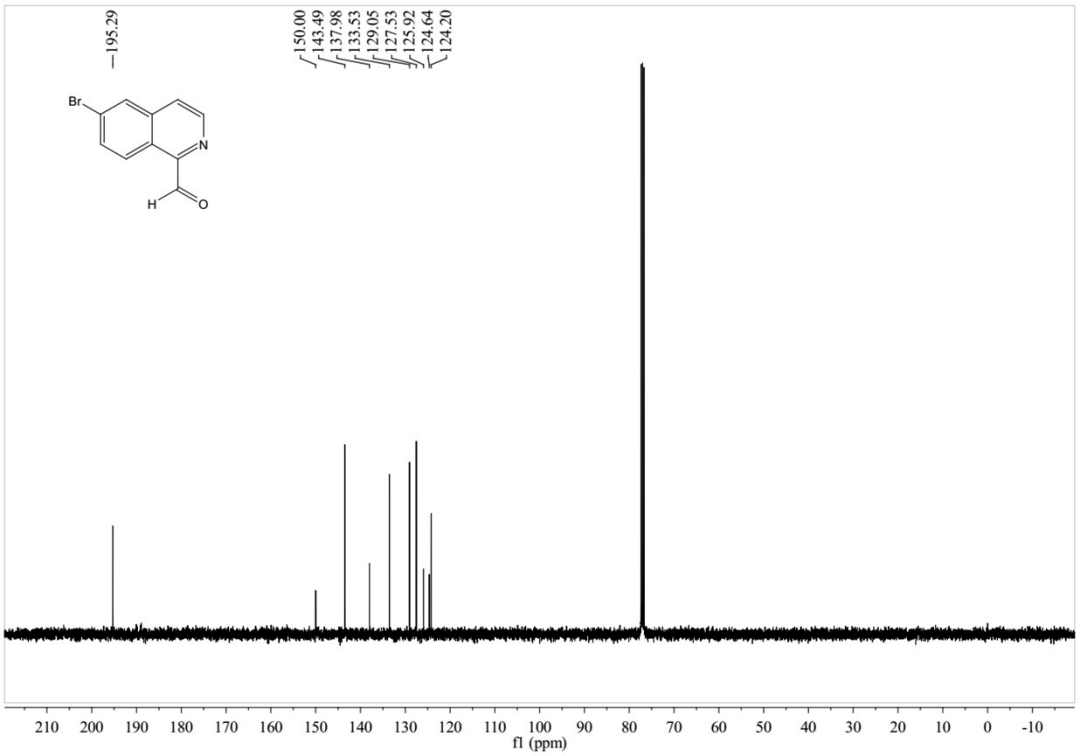
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6e



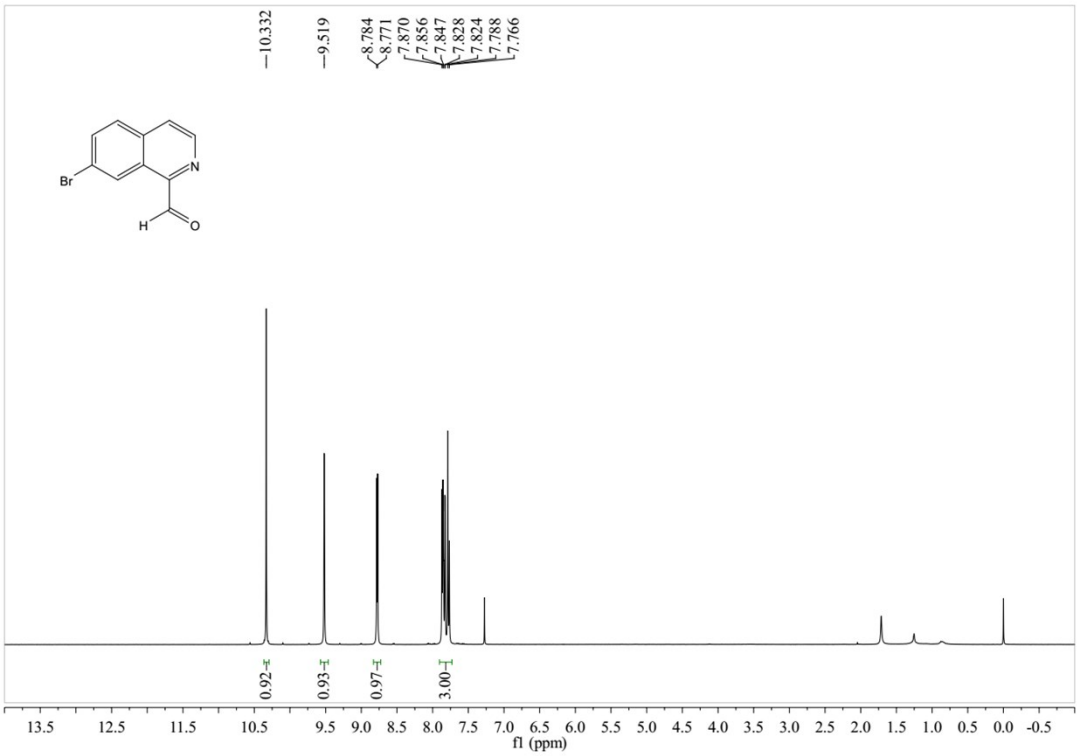
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6f



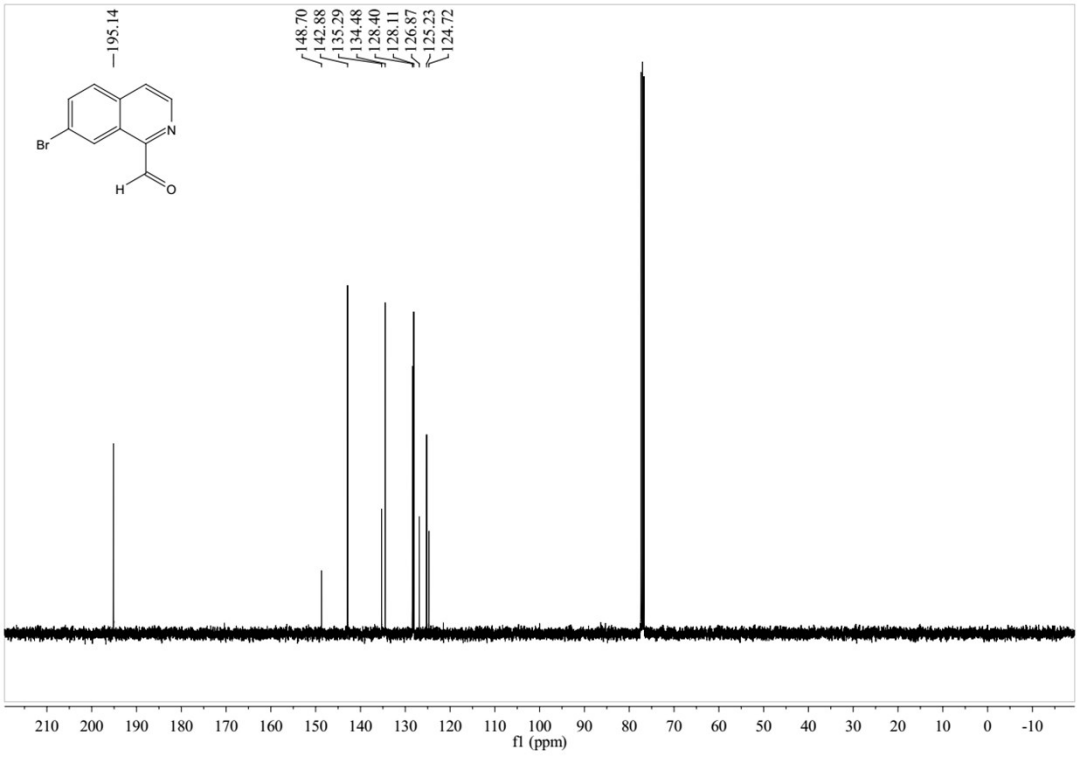
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6f



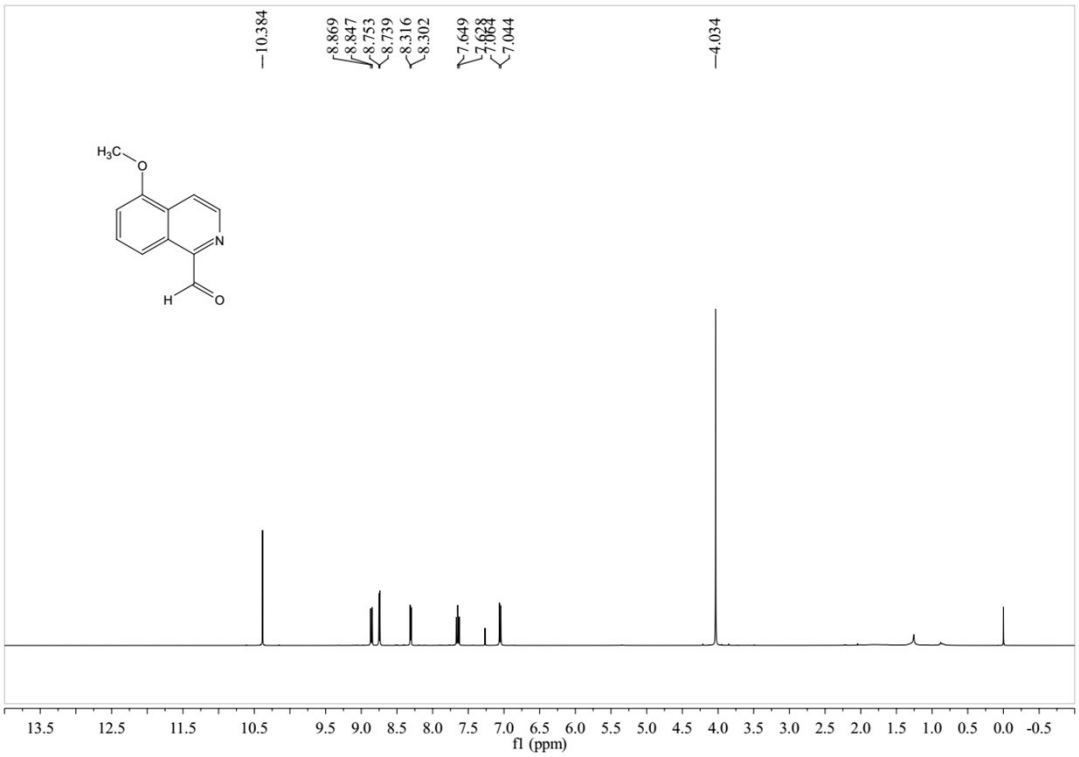
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6g



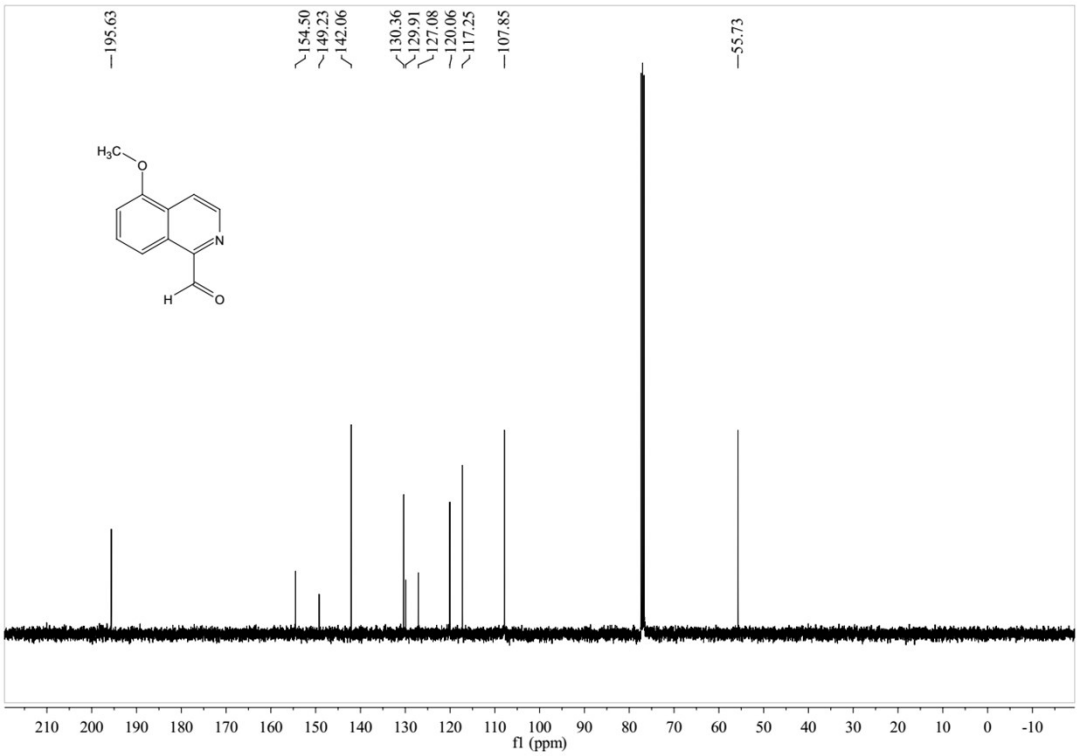
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6g



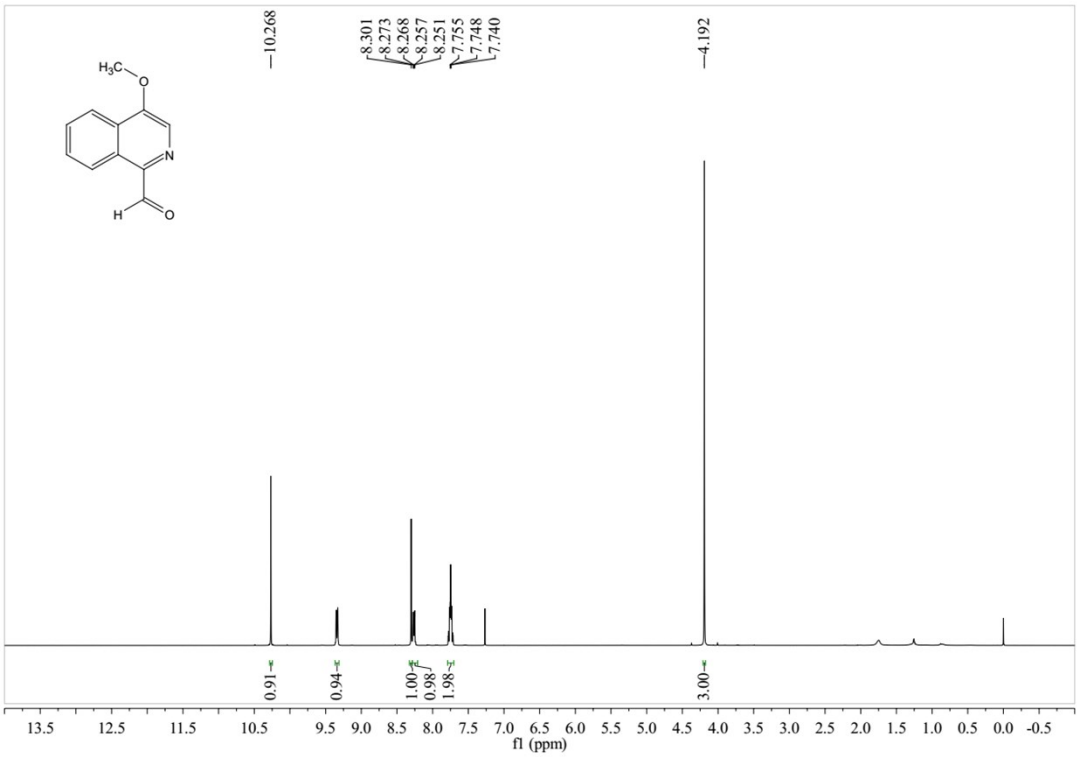
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6h



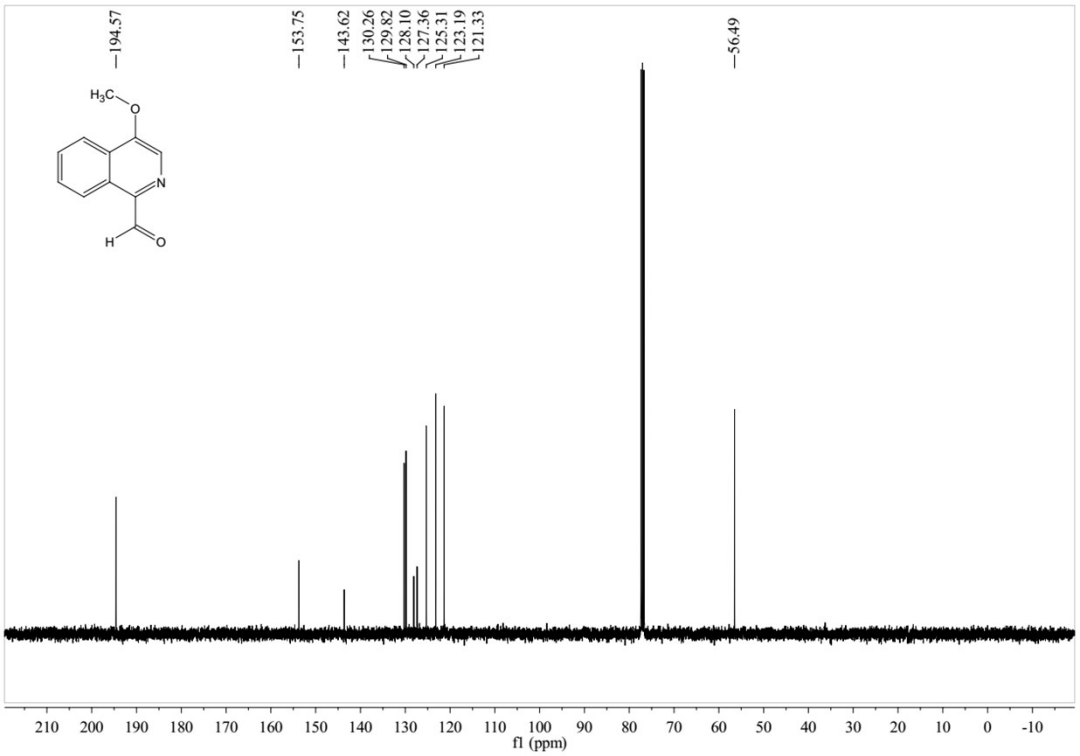
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6h



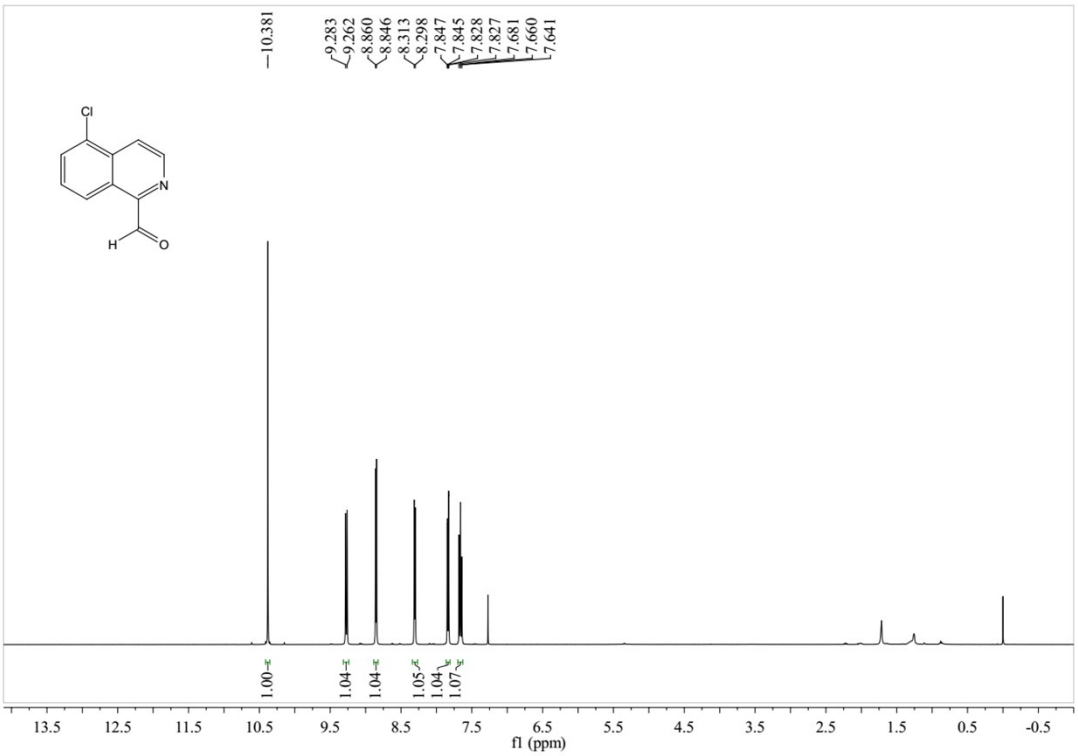
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6i



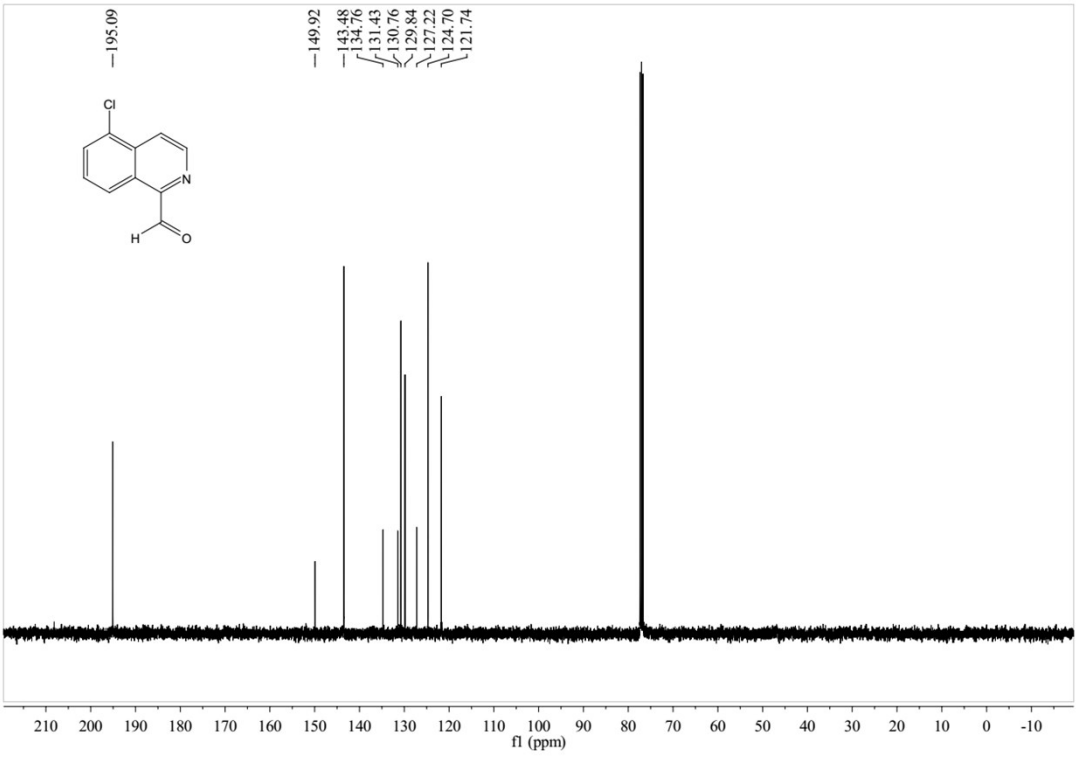
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6i



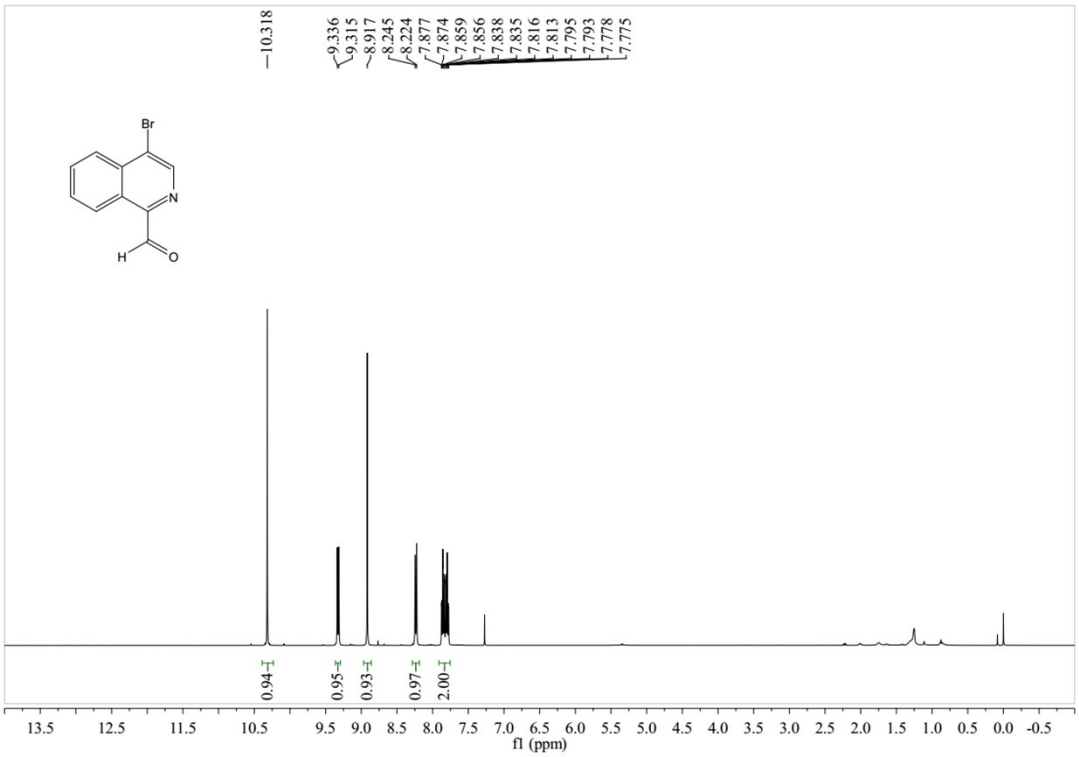
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6k



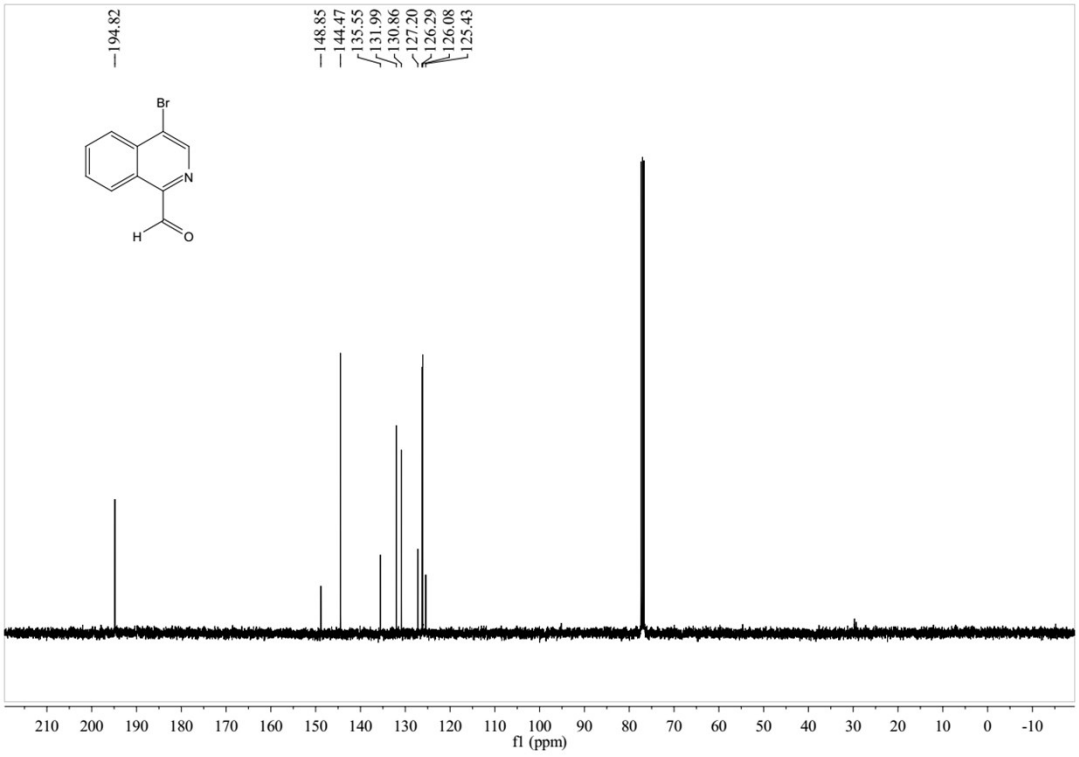
^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6k



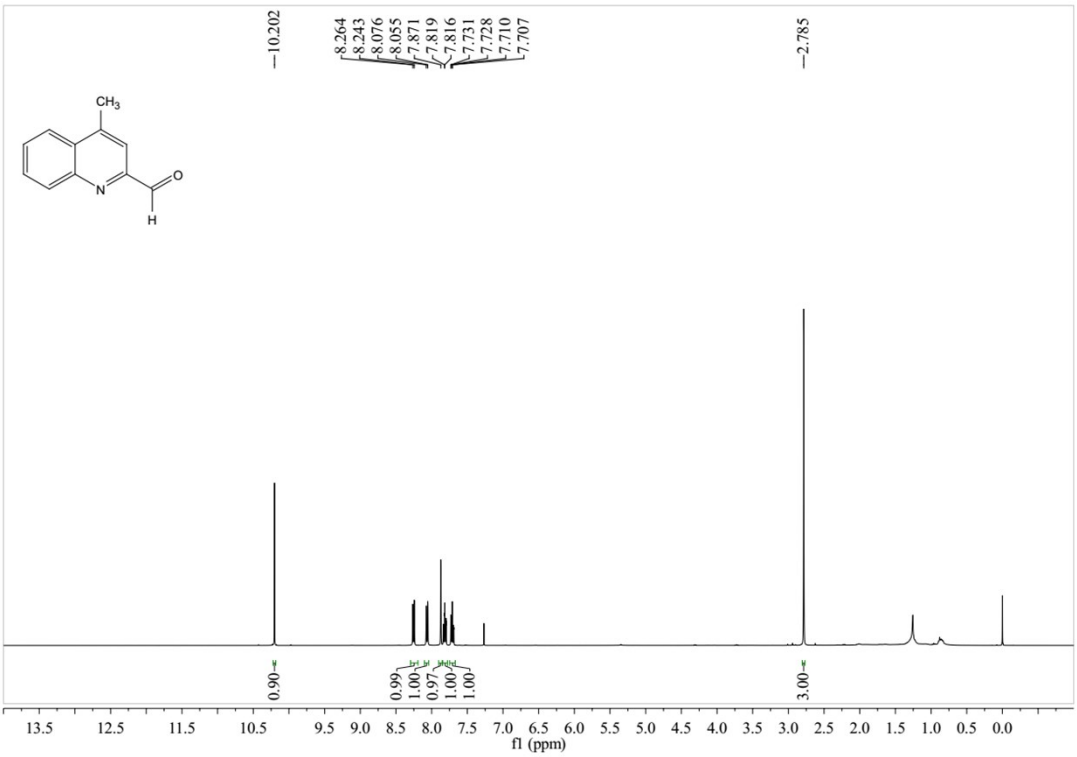
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6l



^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6l



^{1}H NMR (400 MHz, $CDCl_3$) Spectra of 6m



^{13}C NMR (100 MHz, $CDCl_3$) Spectra of 6m