Supporting information

Selective and efficient synthesis of *trans*-arylvinylboronates and *trans*-hetarylvinylboronates using palladium catalyzed cross-coupling

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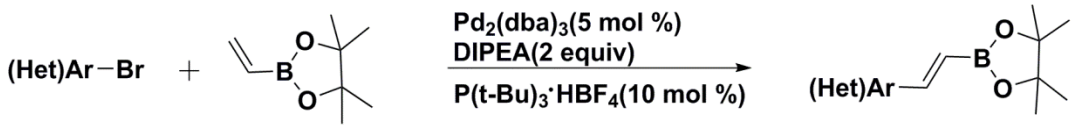
1. General Information

All reactions were carried out with magnetic stirring and in dried glassware. Standard syringe techniques were applied for transfer of dry solvents. All solvents before used were dried and distilled under standard methods. All materials were from commercial suppliers and used without purification. We used DMSO-d_6 as the solvent of all products for the ^{1}H and ^{13}C NMR assays, which spectra were recorded on a Bruker AVANCEIII 400 spectrometer. Chemical shifts (δ) were reported in ppm relative to Me_4Si (internal standard) and coupling constants (*J*) were reported in Hz. Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 101 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Thin layer chromatography (TLC) and Column chromatography were used Qingdao Haiyang Silica gel F-254 plates and Qingdao Haiyang Silica gel 60 (300-400 mesh). HPLC analysis was performed on an UltiMate 3000 HPLC system (Dionex, USA). High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Experimental Section

2.1 General procedure for the Heck coupling of pinacol vinylboronate with (het)arylbromides

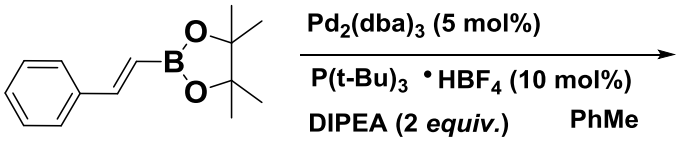


A mixture of vinylboronate pinacol ester (2.2 mmol, 1.1 equiv.), the corresponding aryl and hetaryl bromides (2.0 mmol, 1.0 equiv.), DIPEA (4.0 mmol, 2.0 equiv.), $Pd_2(dba)_3$ (0.1 mmol, 5 mol %) and $P(t\text{-}Bu)_3 \cdot HBF_4$ (0.2 mmol,

10 mol %) in dry toluene (8.0 mL) was stirred at 95 ℃ for 3 h under N_2 atmosphere. Then the reaction mixture was evaporated under vacuum. H_2O (5 mL) was added to the residual mixture. The mixture was extracted with ethyl acetate (10 mL x 3), and the combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under vacuum. The residue was purified by silica gel chromatography using EtOAc/*n*-hexene as eluent to afford the products.

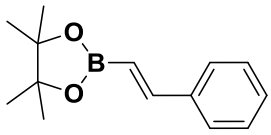
2.2 Protodeborylation of 5C

Heck reaction product **5C** was re-treated to the optimized reaction condition to determine whether protodeborylation of **5C** was occurred.



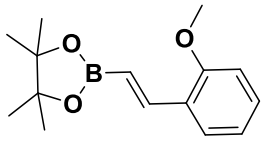
A mixture of 5C (0.5 mmol, 115 mg) , DIPEA (1 mmol, 2.0 *equiv.*), $Pd_2(dba)_3$ (0.025 mmol, 5 mol %) and P(t-Bu)$_3$ ⋅HBF$_4$ (0.05 mmol, 10 mol %) in dry toluene (5.0 mL) was stirred at 95 ℃ for 1.5h and 3 h under N_2 atmosphere. Then HPLC assay the amount of **5D** (protodeborylation).

2.3 ^{1}H and ^{13}C NMR spectra of synthesized trans-(het)arylvinylboronates



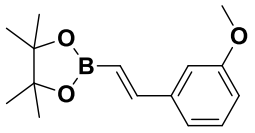
(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (7A)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 – 7.54 (m, 2H), 7.41 – 7.30 (m, 4H), 6.16 (d, *J* = 18.4 Hz, 1H), 1.24 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.68, 137.34, 129.61, 129.16, 127.49, 83.49, 25.10; HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{20}BO_2$ $[M+H]^+$: 231.1557, found: 231.1537.



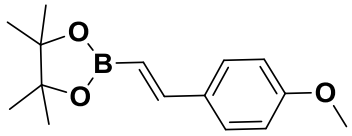
(E)-2-(2-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7B)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.72 – 7.62 (m, 2H), 7.36 (ddd, *J* = 8.6, 7.3, 1.7 Hz, 1H), 7.09 – 7.03 (m, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.13 (d, *J* = 18.6 Hz, 1H), 3.87 (s, 3H), 1.28 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.25, 143.79, 130.97, 126.83, 125.76, 121.02, 111.91, 83.39, 55.88, 25.09; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{22}BO_3$ $[M+H]^+$: 261.1663, found: 261.1426.



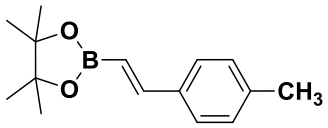
(E)-2-(3-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7C)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 – 7.28 (m, 2H), 7.21 – 7.15 (m, 2H), 6.97 – 6.91 (m, 1H), 6.19 (d, *J* = 18.4 Hz, 1H), 3.81 (s, 3H), 1.28 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.01, 149.60, 138.83, 130.13, 119.91, 115.43, 112.53, 83.48, 55.52, 25.09; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{22}BO_3$ $[M+H]^+$: 261.1663, found: 261.1657.



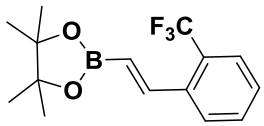
(E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7D)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.58 – 7.47 (m, 2H), 7.26 (d, *J* = 18.4 Hz, 1H), 6.99 – 6.84 (m, 2H), 5.97 (d, *J* = 18.4 Hz, 1H), 3.77 (s, 3H), 1.24 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.57, 149.36, 130.15, 129.00, 114.55, 83.30, 55.63, 25.09; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{22}BO_3$ $[M+H]^+$: 261.1663, found: 261.1537.



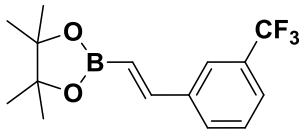
(E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (7E)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 – 7.42 (m, 2H), 7.26 (d, *J* = 18.4 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.06 (d, *J* = 18.5 Hz, 1H), 2.31 (s, 3H), 1.24 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.65, 139.26, 134.68, 129.76, 127.47, 83.42, 25.10, 21.37; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{21}BO_2Na$ $[M+Na]^+$: 267.1533, found: 267.1531.



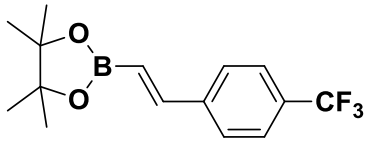
(E)-4,4,5,5-tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (7F)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.78 – 7.67 (m, 2H), 7.64 – 7.51 (m, 2H), 6.28 (d, *J* = 18.0 Hz, 1H), 1.26 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.35(d, *J* = 1.5 Hz) , 136.95(d, *J* = 2.2 Hz), 133.33, 129.60, 128.06, 126.18(d, *J* = 6.0 Hz), 123.37 (q, *J* = 272 Hz), 83.54, 25.07; ^{19}F NMR (376 MHz, DMSO-d_6) δ -54.96; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{18}BF_3O_2Na$ $[M+Na]^+$: 321.1250, found:321.1242.



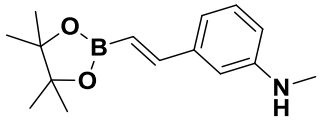
(E)-4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (7G)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 (dd, *J* = 4.5, 2.3 Hz, 2H), 7.70 – 7.54 (m, 2H), 7.40 (d, *J* = 18.5 Hz, 1H), 6.30 (d, *J* = 18.5 Hz, 1H), 1.24 (d, *J* = 3.0 Hz, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.76, 138.42, 130.73(q, *J* = 32 Hz), 130.29, 130.12(d, *J*=3.0 Hz) 129.97, 125.75(q, *J*=271 Hz), 124.03(q, *J*=11 Hz), 83.56 , 24.98; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -58.19; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{18}BF_3O_2Na$ $[M+Na]^+$: 321.1250, found: 321.1233.



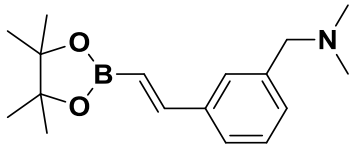
(E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (7H)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 18.5 Hz, 1H), 6.33 (d, J = 18.5 Hz, 1H), 1.26 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.82, 141.21, 129.44(q, J = 32 Hz), 128.11, 125.98(q, J=4.0Hz), 124.06 (q, J = 270 Hz) 83.71 , 25.06; ^{19}F NMR (376 MHz, DMSO-d_6) δ -58.17; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{19}BF_3O_2$ $[M+H]^+$: 299.1431, found:299.1256 .



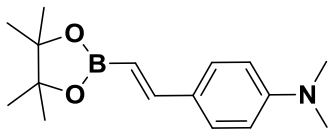
(E)-N-methyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (7I)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.21 (d, J = 18.4 Hz, 1H), 7.08 (t, J = 7.8 Hz, 1H), 6.78 – 6.72 (m, 1H), 6.69 (t, J = 2.0 Hz, 1H), 6.53 (dd, J = 8.1, 2.3 Hz, 1H), 6.03 (d, J = 18.4 Hz, 1H), 5.65 (s, 1H), 2.69 (d, J = 1.6 Hz, 3H), 1.24 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.83, 150.59, 137.92, 129.55, 115.20, 113.54, 110.05, 83.36, 30.14, 25.09; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{23}BNO_2$ $[M+H]^+$: 260.1823, found:260.1531.



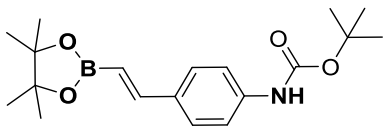
(E)-N,N-dimethyl-1-(3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)methanamine (7J)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82 (d, J = 1.8 Hz, 1H), 7.66 (dt, J = 7.3, 1.7 Hz, 1H), 7.54 – 7.42 (m, 2H), 7.31 (d, J = 18.4 Hz, 1H), 6.22 (d, J = 18.4 Hz, 1H), 4.33 (s, 2H), 2.73 (s, 6H), 1.25 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.84, 137.86, 132.02, 131.36, 129.84, 129.73, 128.78, 83.61, 59.85, 42.19, 25.09; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{27}BNO_2$ $[M+H]^+$: 288.2136, found: 288.2137.



(E)-N,N-dimethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (7K)

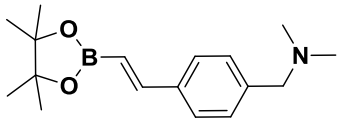
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 18.3 Hz, 1H), 6.68 (d, J = 8.9 Hz, 2H), 5.80 (d, J = 18.3 Hz, 1H), 2.94 (s, 6H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.38, 150.16, 128.74, 125.30, 112.29, 83.08, 81.81, 24.95; HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{25}BNO_2$ $[M+H]^+$: 274.1979, found: 274.1972.



Tert-butyl (E)-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)carbamate (7L)

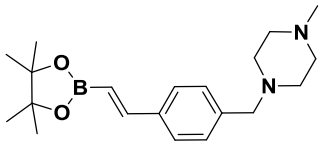
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 (s, 1H), 7.47 (s, 4H), 7.22 (d, J = 18.4 Hz, 1H), 5.98 (d, J = 18.4

Hz, 1H), 1.48 (s, 9H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.06, 149.43, 140.96, 131.26, 128.12, 118.37, 83.32, 79.70, 28.55, 24.94; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{28}BNO_4Na$ $[M+Na]^+$: 368.2009, found: 368.2011.



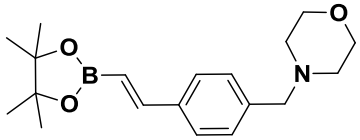
(E)-N,N-dimethyl-1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)methanamine (7M)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.33 (d, *J* = 18.5 Hz, 1H), 6.23 (d, *J* = 18.5 Hz, 1H), 4.32 (s, 2H), 2.72 (s, 6H), 1.25 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.73, 138.38, 131.89, 131.52, 127.85, 83.61, 59.58, 42.13, 25.11; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{27}BNO_2$ $[M+H]^+$: 288.2136, found:288.2411.



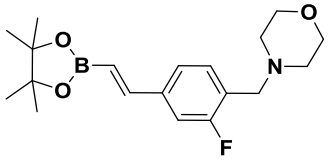
(E)-1-methyl-4-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzyl)piperazine (7N)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (d, *J* = 7.3 Hz, 2H), 7.39 – 7.20 (m, 3H), 6.21 – 6.00 (m, 1H), 3.66 – 3.50 (m, 4H), 3.45 (s, 2H), 2.34 (s, 4H), 1.39 – 1.13 (m, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.34, 138.85, 136.49, 129.75, 127.50, 126.56, 83.50, 60.99, 53.10, 49.63, 42.62, 25.11; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{32}BN_2O_2$ $[M+H]^+$: 343.2558, found: 343.2562.



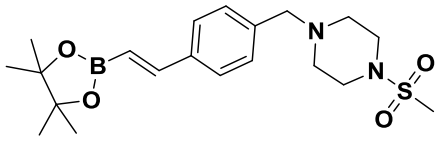
(E)-4-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzyl)morpholine (7O)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (d, *J* = 7.3 Hz, 2H), 7.39 – 7.20 (m, 3H), 6.21 – 6.00 (m, 1H), 3.66 – 3.50 (m, 4H), 3.45 (s, 2H), 2.34 (s, 4H), 1.39 – 1.13 (m, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.48, 139.51, 136.20, 129.65, 127.38, 83.46, 66.65, 62.55, 53.63, 25.09; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{29}BNO_3$ $[M+H]^+$: 330.2241, found: 330.2074.



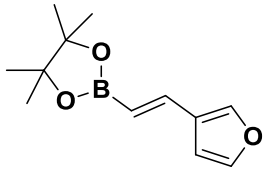
(E)-4-(2-fluoro-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzyl)morpholine (7P)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48 – 7.33 (m, 3H), 7.28 (d, *J* = 18.4 Hz, 1H), 6.19 (d, *J* = 18.4 Hz, 1H), 3.56 (t, *J* = 4.6 Hz, 4H), 3.50 (s, 2H), 2.37 (t, *J* = 4.5 Hz, 4H), 1.25 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.70, 160.26, 148.14, 138.78, 132.19, 125.50, 123.39, 113.71, 83.59, 66.62, 54.35, 25.09; ^{19}F NMR (376 MHz, DMSO-d_6) δ -114.71; HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{28}BFNO_3$ $[M+H]^+$: 348.2147, found: 348.2148.



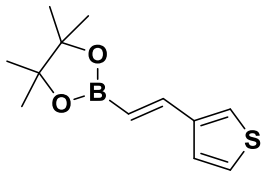
(E)-1-(methylsulfonyl)-4-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzyl)piperazine (7Q)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.58 (d, J = 7.8 Hz, 2H), 7.39 – 7.29 (m, 3H), 6.16 (d, J = 18.4 Hz, 1H), 3.57 (s, 2H), 3.15 (t, J = 4.8 Hz, 4H), 2.91 (s, 3H), 2.50 (t, J = 4.8 Hz, 4H), 1.29 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.44, 139.54, 136.30, 129.58, 127.44, 83.48, 61.61, 52.23, 45.92, 34.04, 25.10; HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{32}BN_2O_4S$ $[M+H]^+$: 407.2177, found: 407.2177.



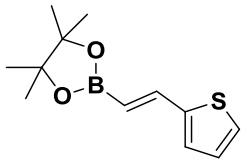
(E)-2-(2-(furan-3-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9B)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (d, J = 1.5 Hz, 1H), 7.69 (d, J = 1.8 Hz, 1H), 7.24 (d, J = 18.3 Hz, 1H), 6.85 (d, J = 2.0 Hz, 1H), 5.83 (d, J = 18.3 Hz, 1H), 1.26 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.84, 143.63, 140.00, 125.93, 107.96, 83.30, 25.06; HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{17}BNO_3Na$ $[M+Na]^+$: 243.1169, found: 243.1472.



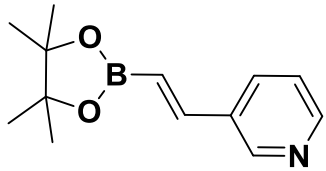
(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (9C)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.76 (dd, J = 2.9, 1.2 Hz, 1H), 7.58 (dd, J = 5.1, 2.9 Hz, 1H), 7.48 (dd, J = 5.1, 1.3 Hz, 1H), 7.35 (d, J = 18.4 Hz, 1H), 5.97 (d, J = 18.4 Hz, 1H), 1.28 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.70, 141.30, 127.51, 126.51, 125.67, 83.38, 25.09; HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{17}BO_2SNa$ $[M+Na]^+$: 259.0940, found: 259.1458.



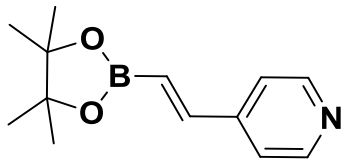
(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (9D)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 (dd, J = 5.1, 1.0 Hz, 1H), 7.47 (d, J = 18.1 Hz, 1H), 7.34 (dd, J = 3.7, 1.1 Hz, 1H), 7.12 (dd, J = 5.1, 3.6 Hz, 1H), 5.79 (d, J = 18.1 Hz, 1H), 1.28 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.40, 142.36, 129.40, 128.59, 127.95, 83.54, 25.07; HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{17}BO_2SNa$ $[M+Na]^+$: 259.0940, found: 259.1086.



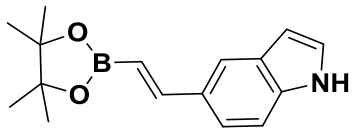
(E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (9F)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.77 (d, J = 2.1 Hz, 1H), 8.53 (dd, J = 4.8, 1.6 Hz, 1H), 8.05 (dd, J = 8.0, 2.2 Hz, 1H), 7.46 – 7.28 (m, 2H), 6.32 (d, J = 18.5 Hz, 1H), 1.26 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.32, 149.36, 146.24, 133.83, 132.84, 124.23, 83.64, 25.08; HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_{19}BNO_2$ $[M+H]^+$: 232.1510, found: 232.1667.



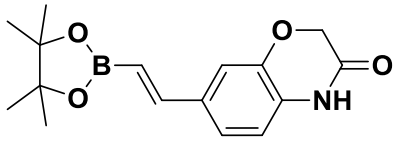
(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (9G)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.62 – 8.51 (m, 2H), 7.59 – 7.50 (m, 2H), 7.28 (d, *J* = 18.5 Hz, 1H), 6.44 (d, *J* = 18.5 Hz, 1H), 1.25 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.61, 147.02, 144.23, 121.69, 83.84, 25.08; HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_{19}BNO_2$ $[M+H]^+$: 232.1510, found: 232.1547.



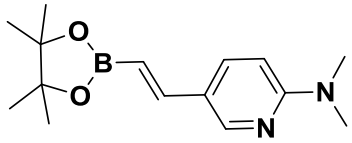
(E)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1H-indole (9H)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.23 (s, 1H), 7.58 – 7.47 (m, 2H), 7.45 – 7.36 (m, 2H), 7.29 (dd, *J* = 8.3, 1.5 Hz, 1H), 6.44 (d, *J* = 2.5 Hz, 1H), 6.04 (d, *J* = 18.3 Hz, 1H), 1.25 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.49, 136.46, 130.67, 129.19, 127.50, 120.61, 118.24, 111.54, 101.82, 83.27, 25.13 . HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{20}BNO_2Na$ $[M+Na]^+$: 292.1485, found: 292.1488.



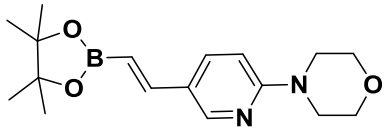
(E)-6-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2H-benzo[b][1,4]oxazin-3(4H)-one (9I)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.77 (s, 1H), 7.19 (d, *J* = 18.4 Hz, 1H), 7.14 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 5.90 (d, *J* = 18.4 Hz, 1H), 4.60 (s, 2H), 1.24 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.04, 148.89, 144.63, 131.87, 127.92, 123.06, 116.79, 114.04, 83.46, 67.20, 25.09; HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{20}BNO_4Na$ $[M+Na]^+$: 324.1383, found: 324.1383.



(E)-N,N-dimethyl-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridin-2-amine (9J)

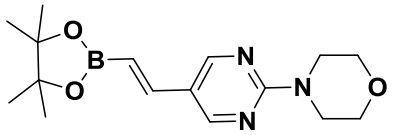
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (d, *J* = 2.4 Hz, 1H), 7.78 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.19 (d, *J* = 18.4 Hz, 1H), 6.64 (d, *J* = 9.0 Hz, 1H), 5.86 (d, *J* = 18.4 Hz, 1H), 3.05 (s, 6H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.48, 148.96, 147.22, 134.75, 121.27, 111.82, 106.25, 83.19, 38.05, 25.10; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{24}BN_2O_2$ $[M+H]^+$: 275.1932, found: 275.1926.



(E)-4-(5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridin-2-yl)morpholine (9K)

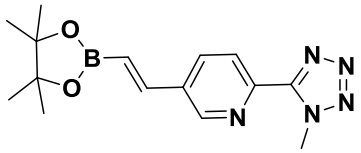
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (d, *J* = 2.3 Hz, 1H), 7.83 (dd, J = 9.0, 2.5 Hz, 1H), 7.21 (d, *J* = 18.4 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 5.93 (d, *J* = 18.4 Hz, 1H), 3.69 (t, *J* = 4.9 Hz, 4H), 3.57 – 3.45

(m, 4H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.50, 148.65, 146.80, 135.19, 123.03, 107.25, 83.28, 66.37, 45.29, 25.10; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{26}BN_2O_3$ $[M+H]^+$: 317.2037, found: 317.2035.



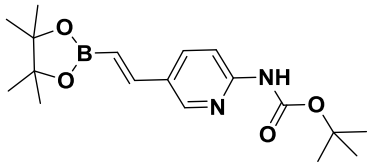
(E)-4-(5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyrimidin-2-yl)morpholine (9L)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.69 (s, 2H), 7.21 (d, *J* = 18.6 Hz, 1H), 6.10 (d, *J* = 18.6 Hz, 1H), 3.80 (dd, *J* = 5.7, 3.8 Hz, 4H), 3.71 (dd, *J* = 5.7, 3.9 Hz, 4H), 1.29 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.29, 157.25, 144.04, 120.25, 83.40, 66.38, 44.39, 25.10; HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{25}BN_3O_3$ $[M+H]^+$: 318.1990, found: 318.1992.



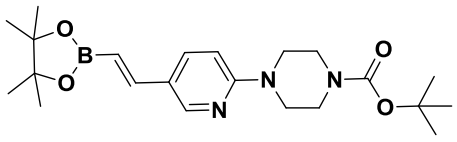
(E)-2-(1-methyl-1H-tetrazol-5-yl)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (9M)

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.04 (d, *J* = 2.1 Hz, 1H), 8.36 (dd, *J* = 8.3, 2.2 Hz, 1H), 8.30 – 8.25 (m, 1H), 7.48 (d, *J* = 18.5 Hz, 1H), 6.51 (d, *J* = 18.5 Hz, 1H), 4.47 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.18, 149.41, 145.03, 144.56, 135.52, 134.41, 124.46, 83.84, 37.17, 25.10; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{21}BN_5O_2$ $[M+H]^+$: 314.1789, found: 314.1902.



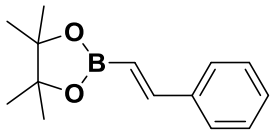
Tert-butyl (E)-(5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridin-2-yl)carbamate (9N)

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.91 (s, 1H), 8.40 (d, *J* = 2.3 Hz, 1H), 8.01 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.26 (d, *J* = 18.4 Hz, 1H), 6.12 (d, *J* = 18.5 Hz, 1H), 1.48 (s, 9H), 1.24 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.28, 153.06, 148.22, 146.10, 135.68, 127.79, 112.39, 83.50, 80.26, 28.47, 25.10; HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{27}BN_2O_4Na$ $[M+Na]^+$: 369.1962, found: 369.1964.

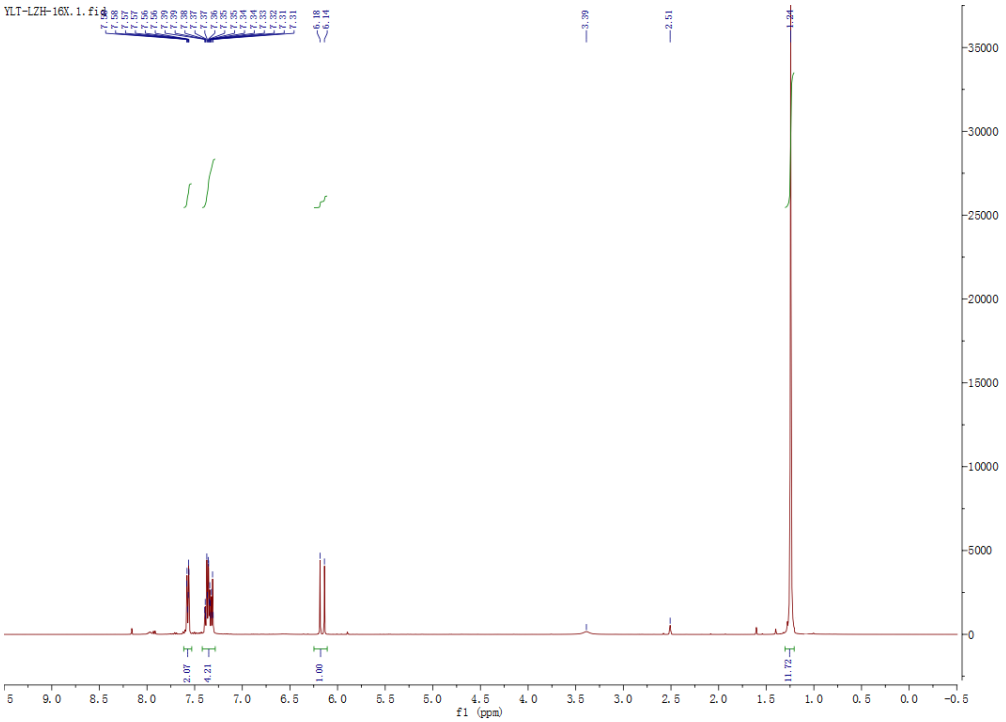


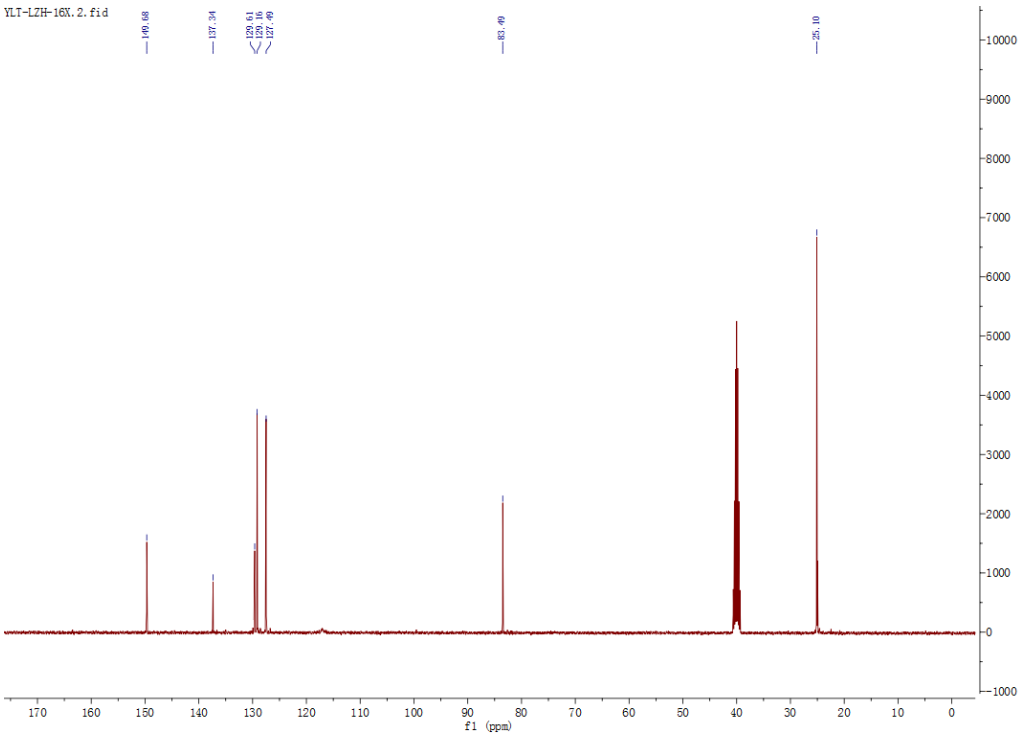
Tert-butyl(E)-4-(5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridin-2-yl)piperazine-1-carboxylate (9O)

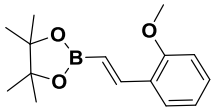
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.25 (d, *J* = 2.3 Hz, 1H), 7.83 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.20 (d, *J* = 18.4 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 5.93 (d, *J* = 18.4 Hz, 1H), 3.60 – 3.51 (m, 4H), 3.41 (dd, *J* = 6.6, 3.8 Hz, 4H), 1.43 (s, 9H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.10, 154.37, 148.69, 146.79, 135.25, 122.85, 107.41, 83.28, 79.51, 40.46, 28.53, 25.11; HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{35}BN_3O_4$ $[M+H]^+$: 416.2721, found: 416.2709.



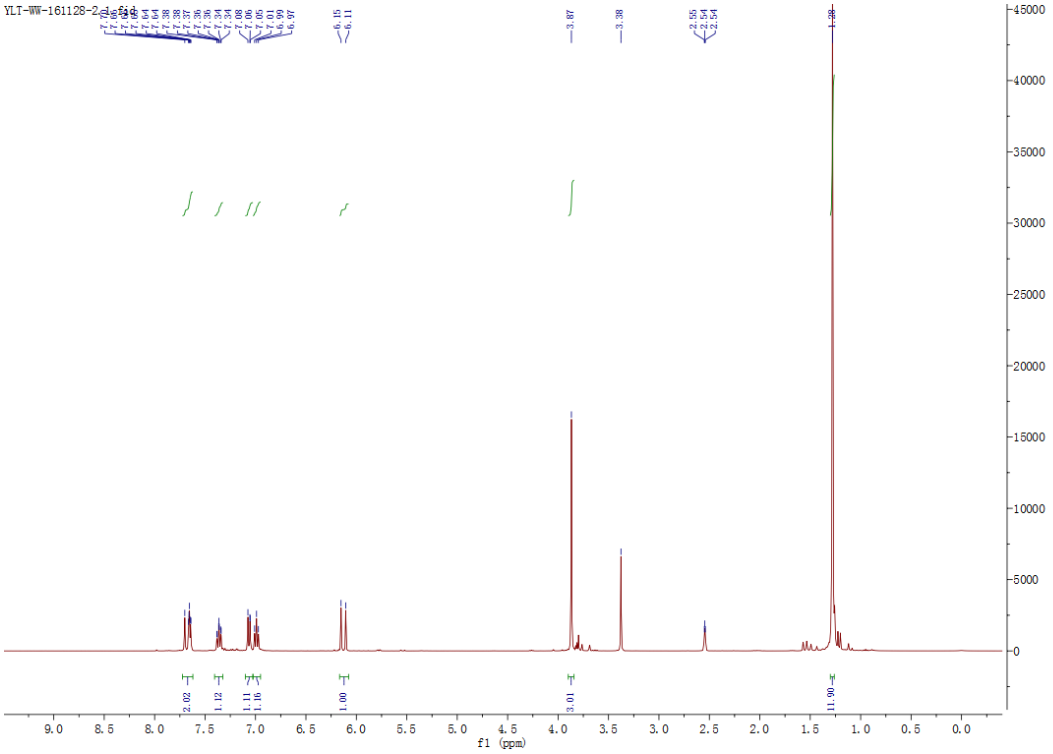
(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (7A)

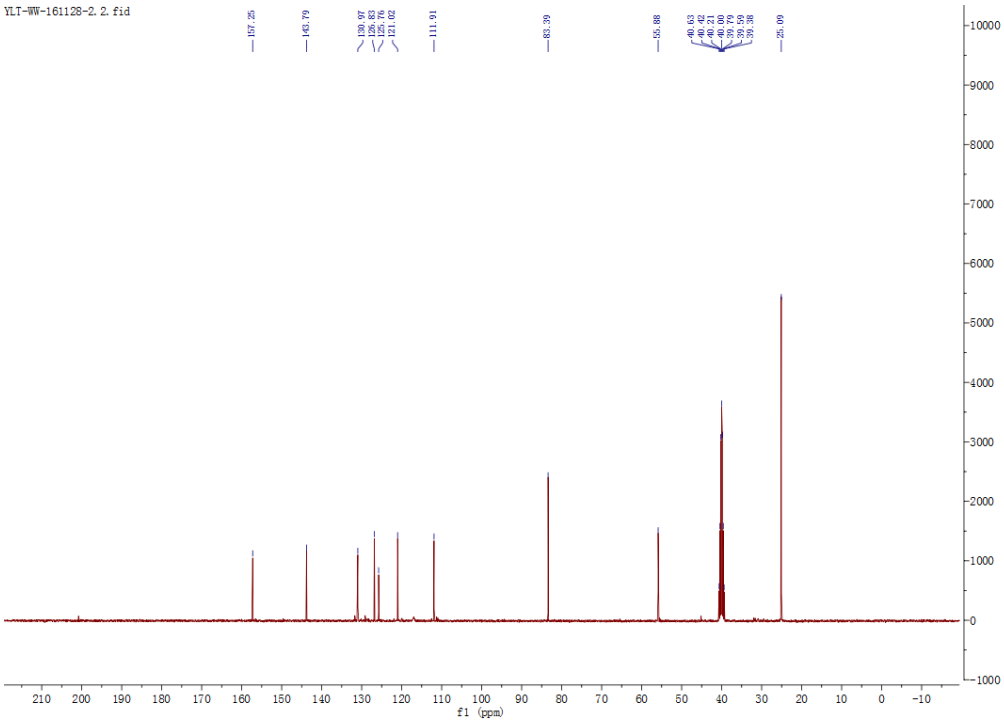


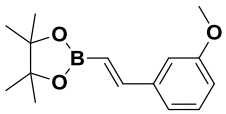




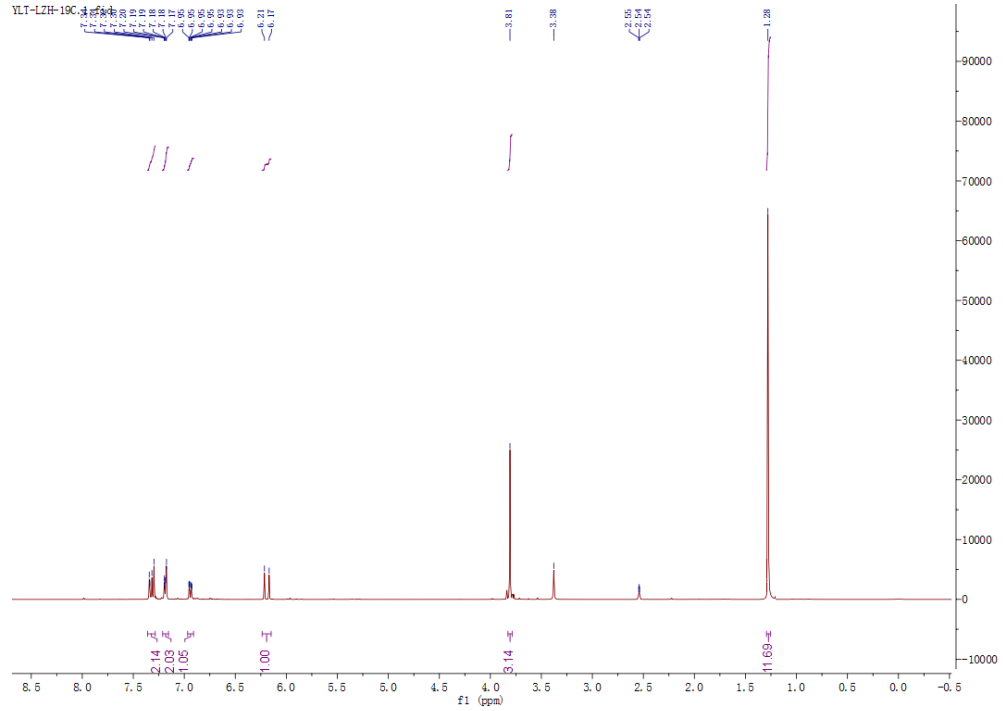
(E)-2-(2-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7B)

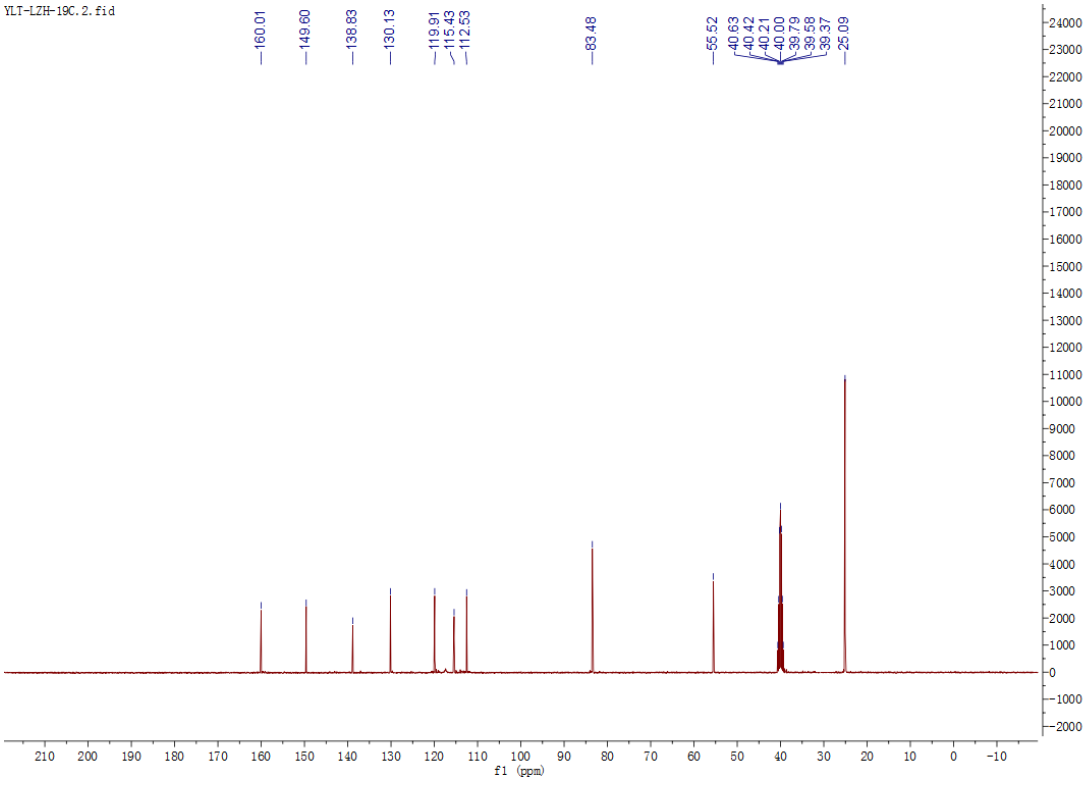


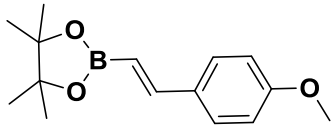




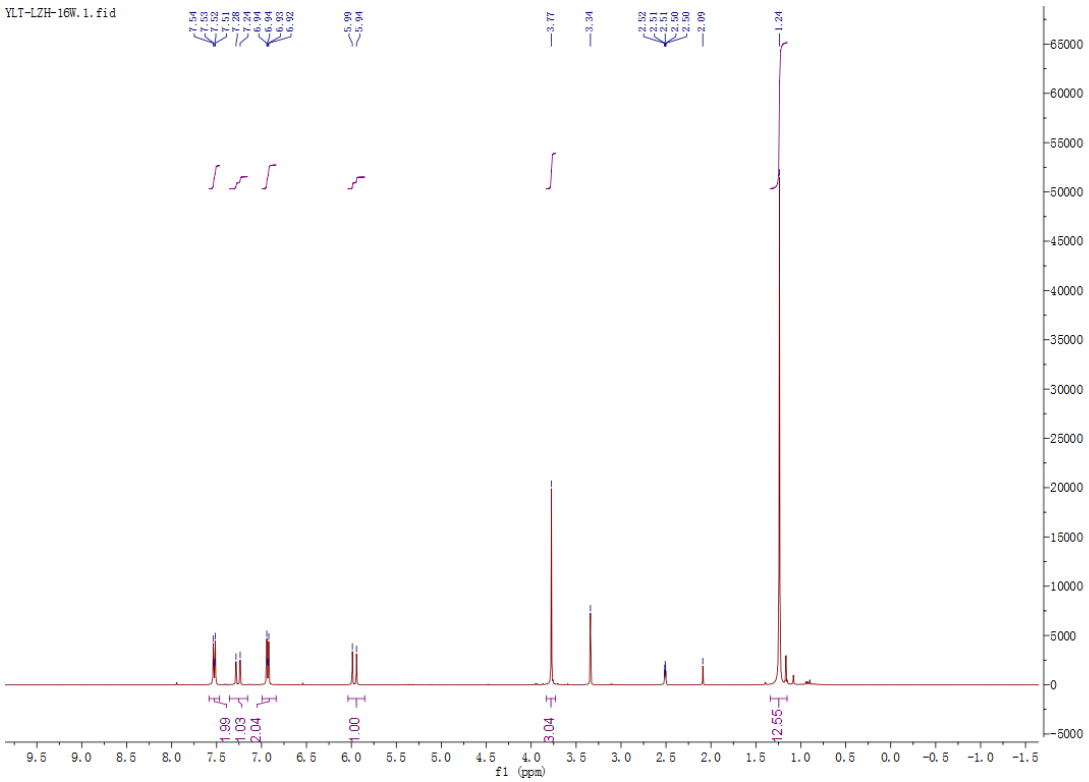
(E)-2-(3-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7C)

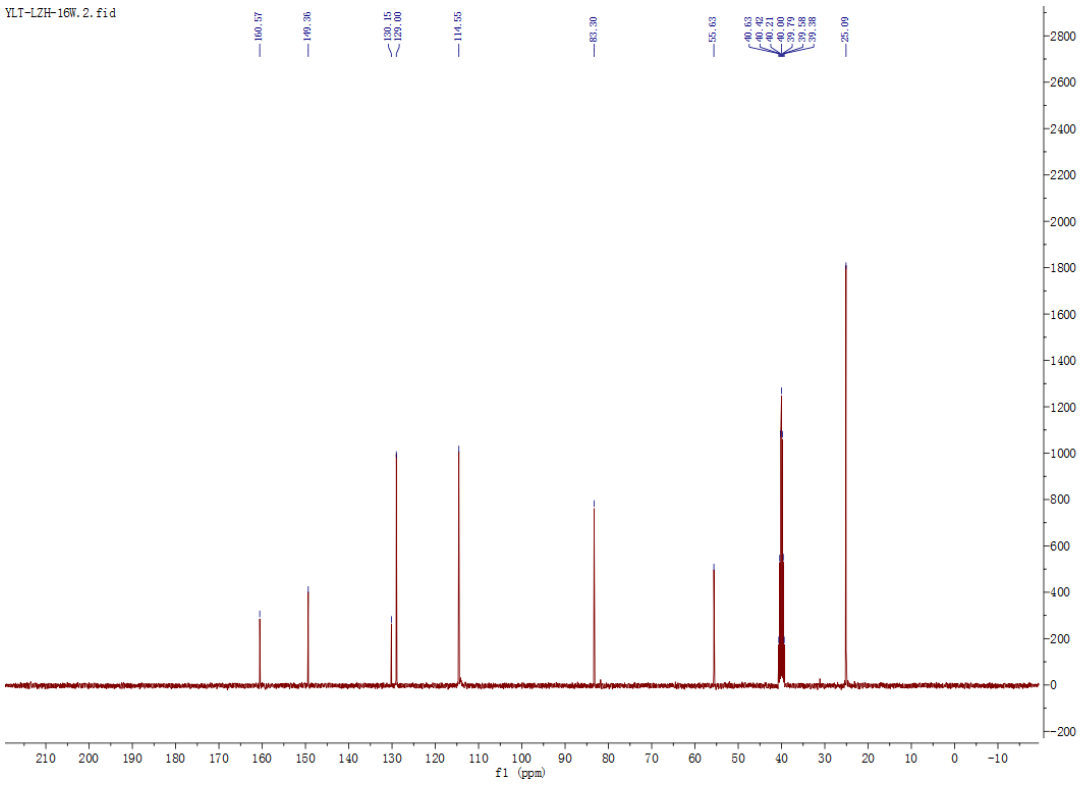


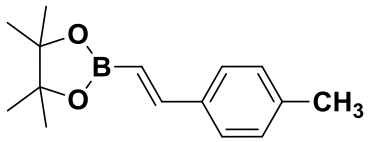




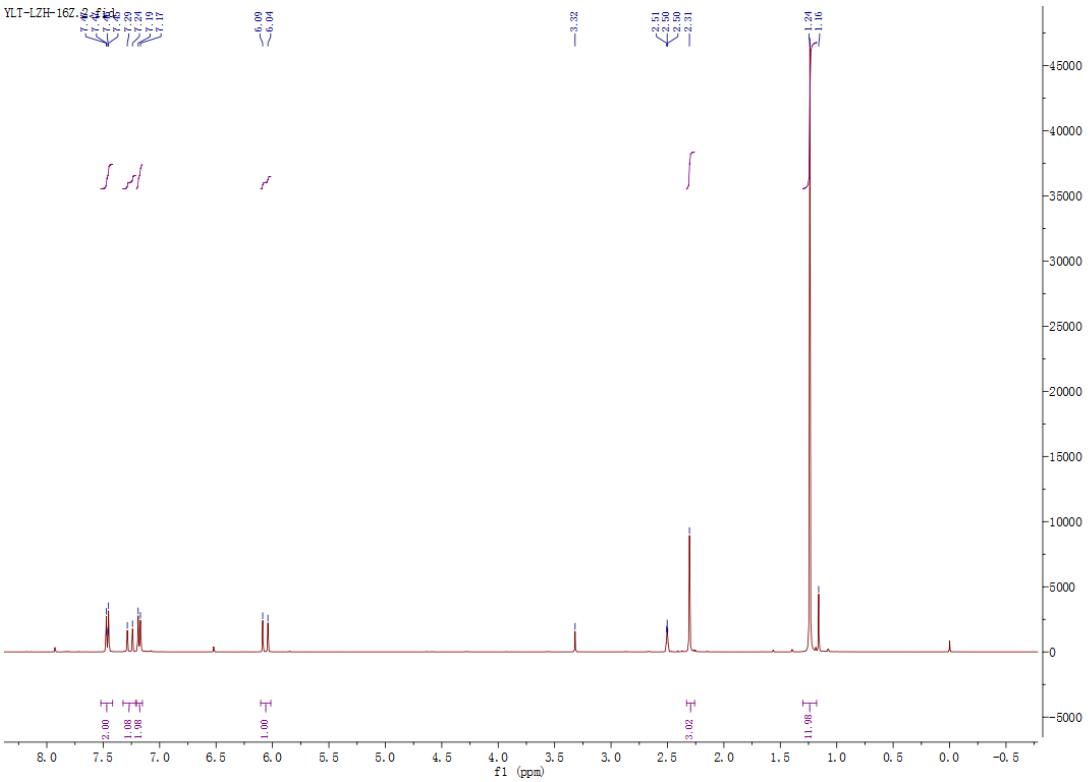
(E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7D)

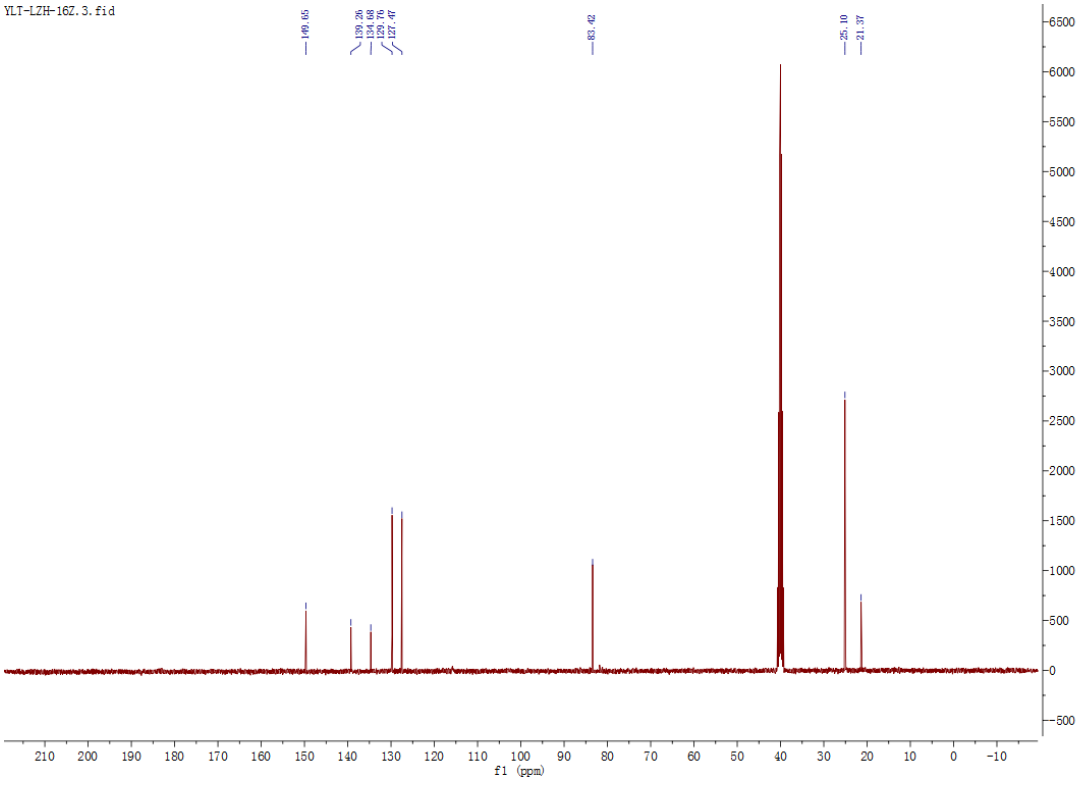


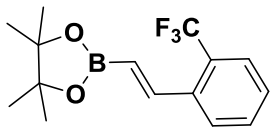




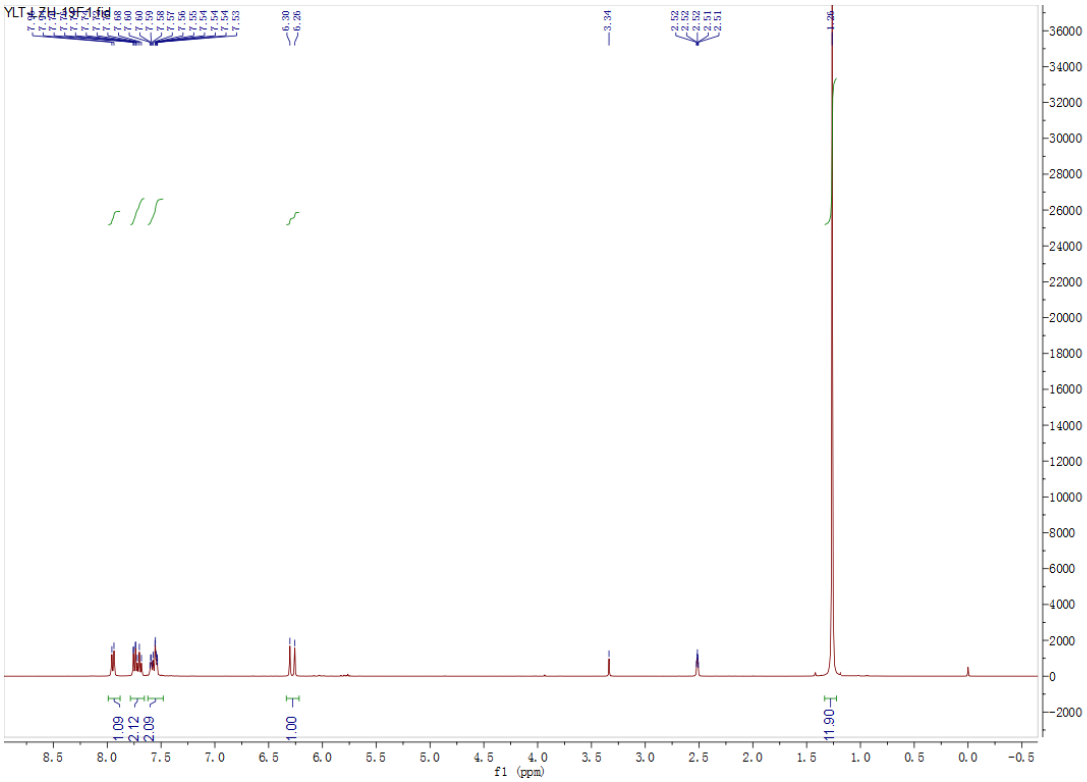
(E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (7E)







(E)-4,4,5,5-tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (7F)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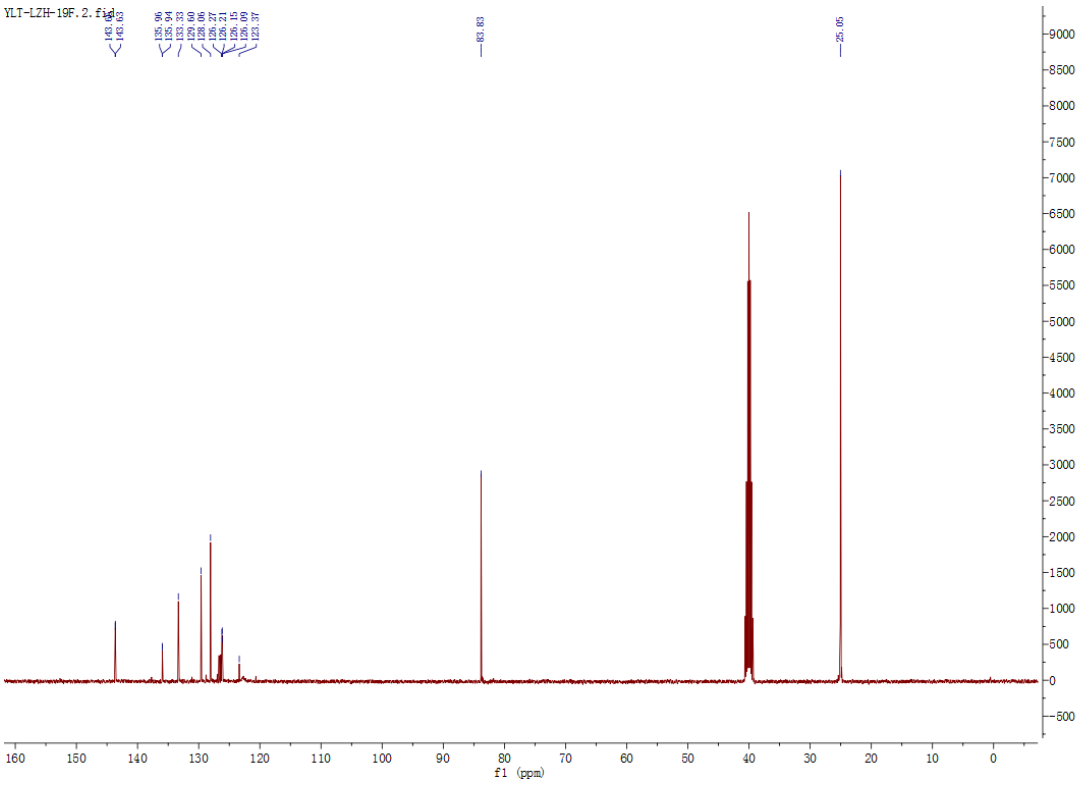
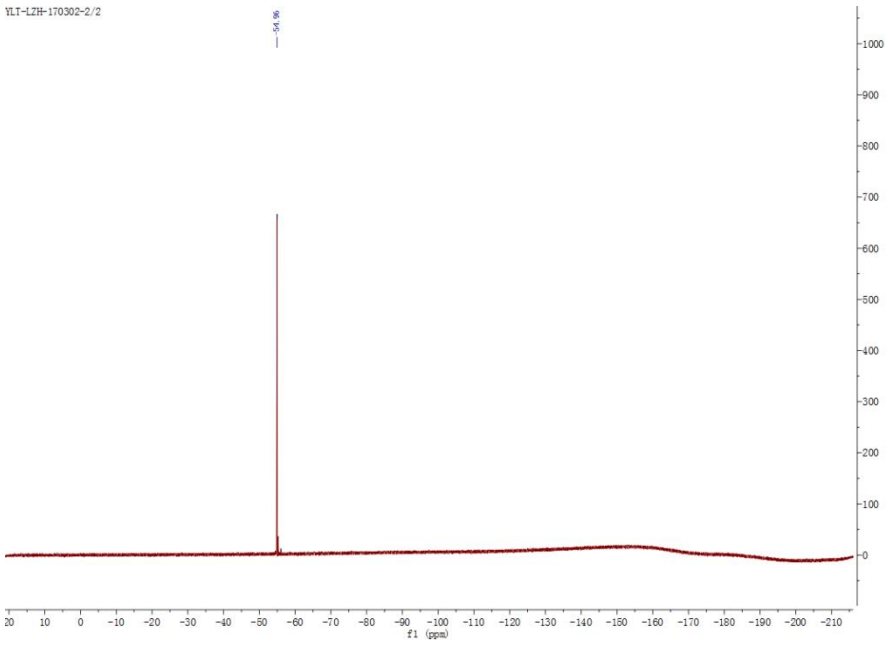
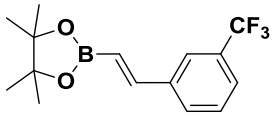
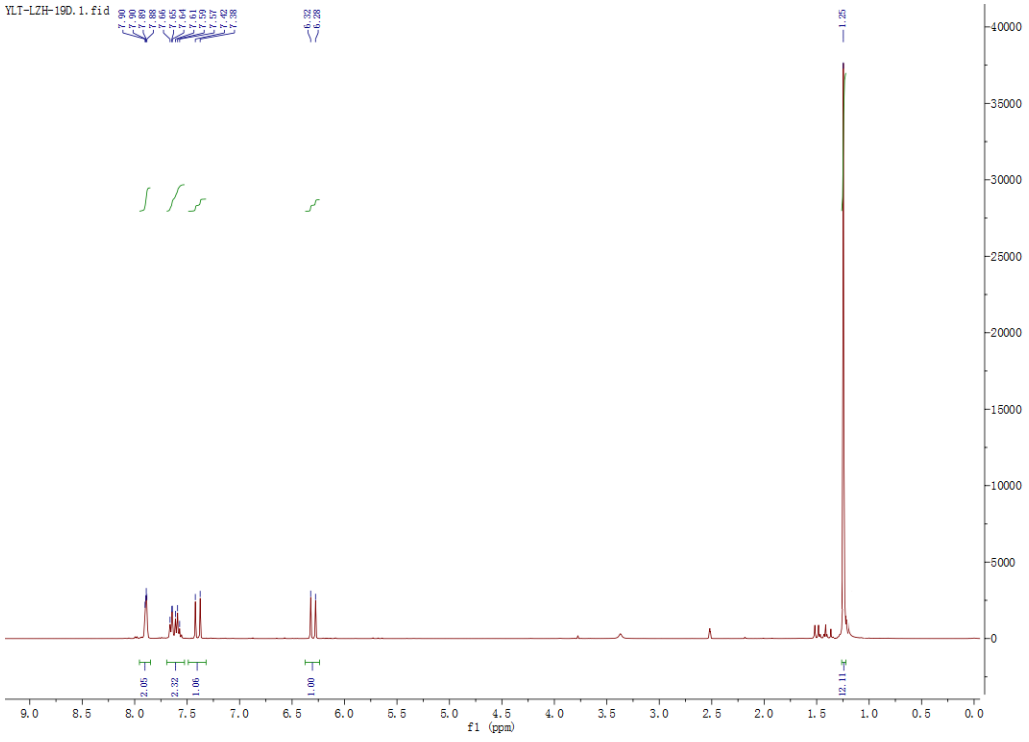
11.90
f1 (ppm)

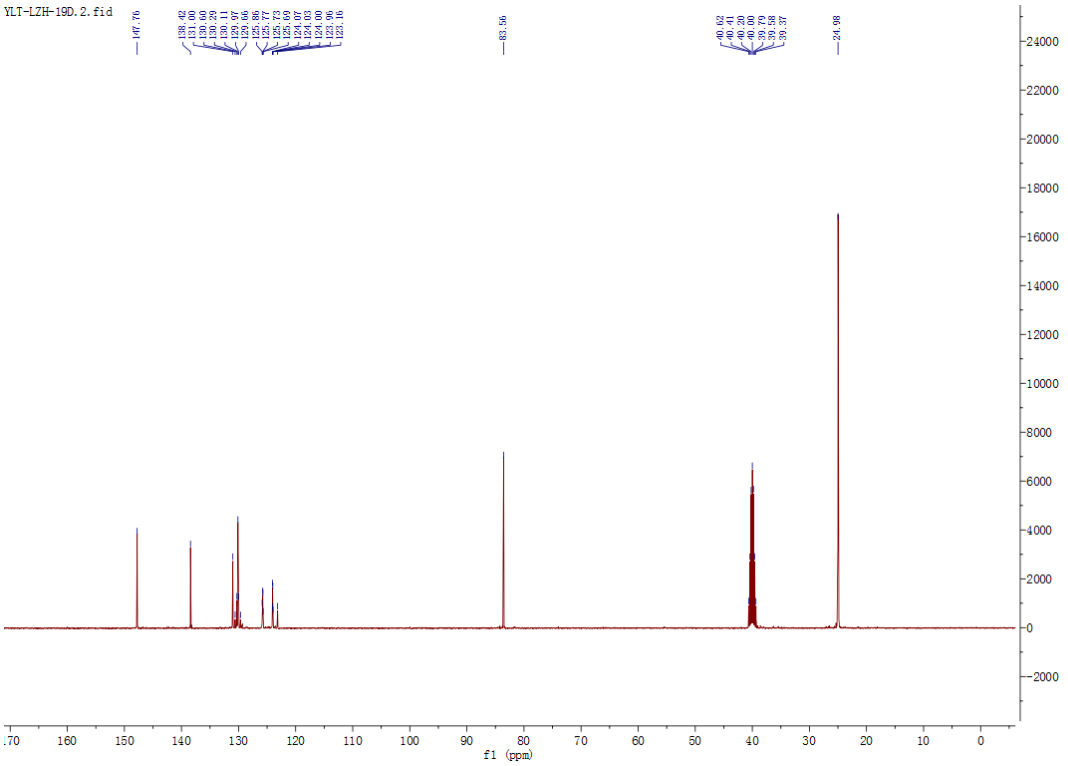

YLT-LZH-19F.2.fid
143.63
135.96
135.94
133.33
129.60
128.06
126.27
126.21
126.15
126.09
123.37
83.83
25.05
f1 (ppm)

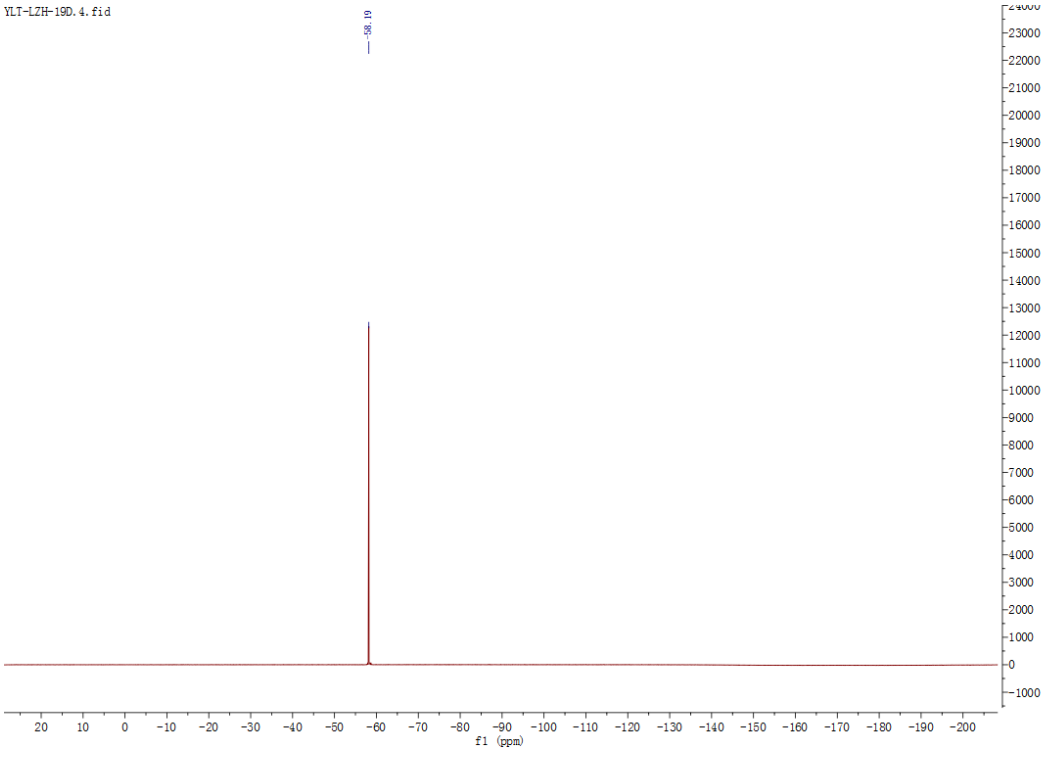


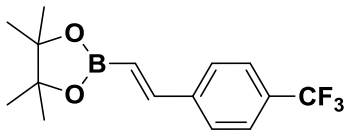


(E)-4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (7G)

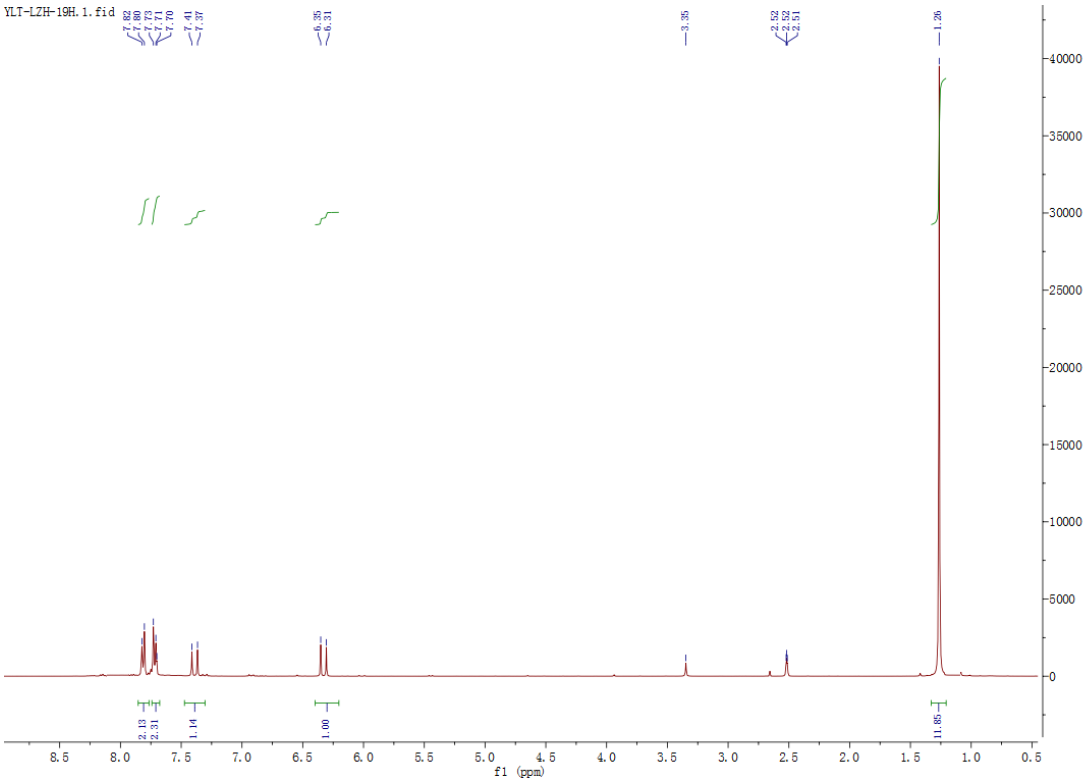








(E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (7H)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7.80
7.73
7.71
7.70
7.41
7.37
6.35
6.31
3.35
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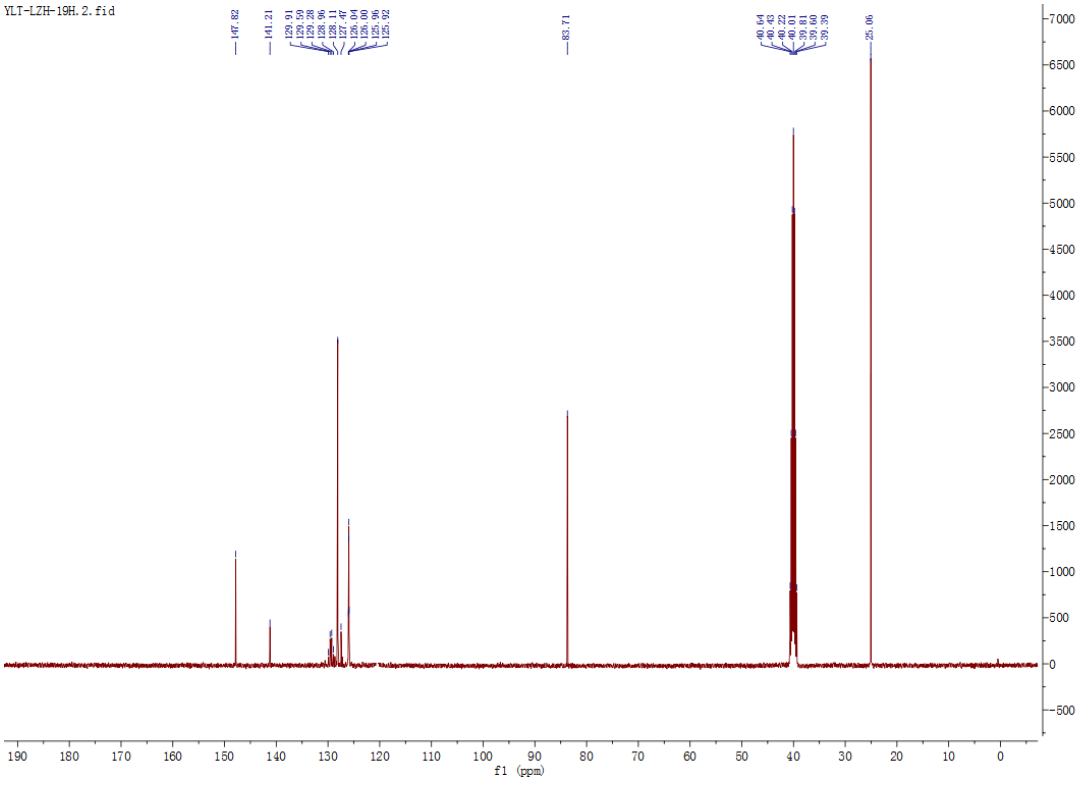
2.52
2.51
1.26
2.13
2.31
1.14
1.00
11.85
f1 (ppm)


YLT-LZH-19H.2.fid
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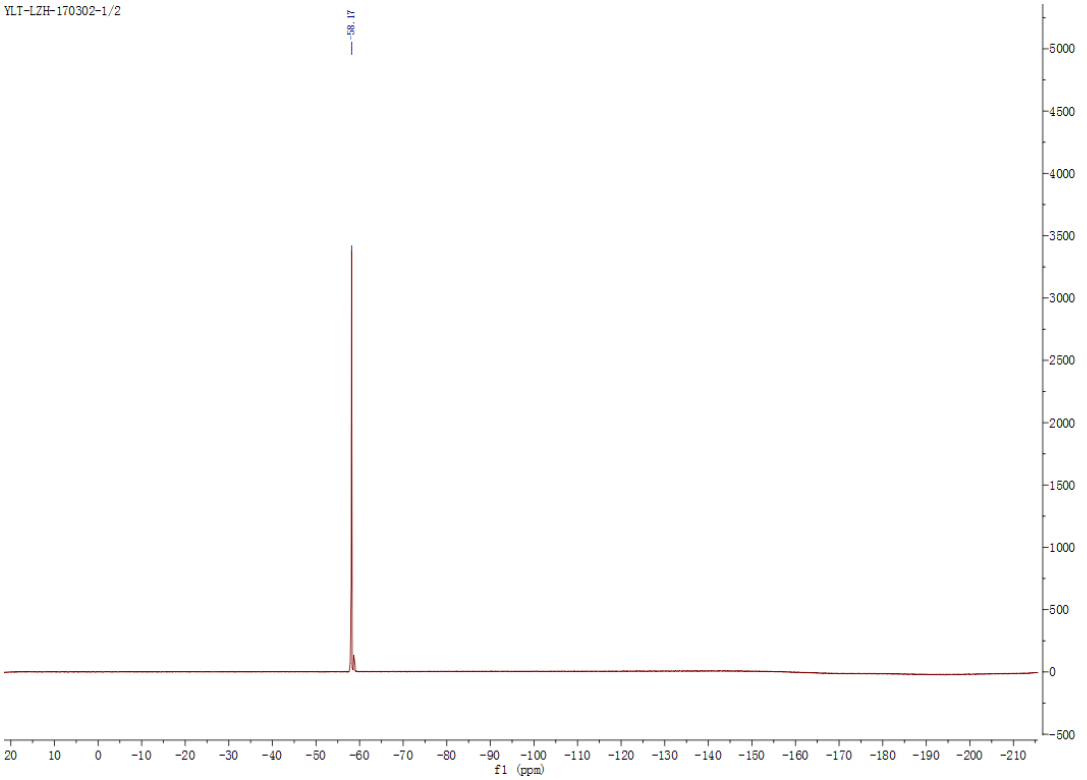
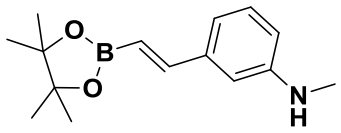
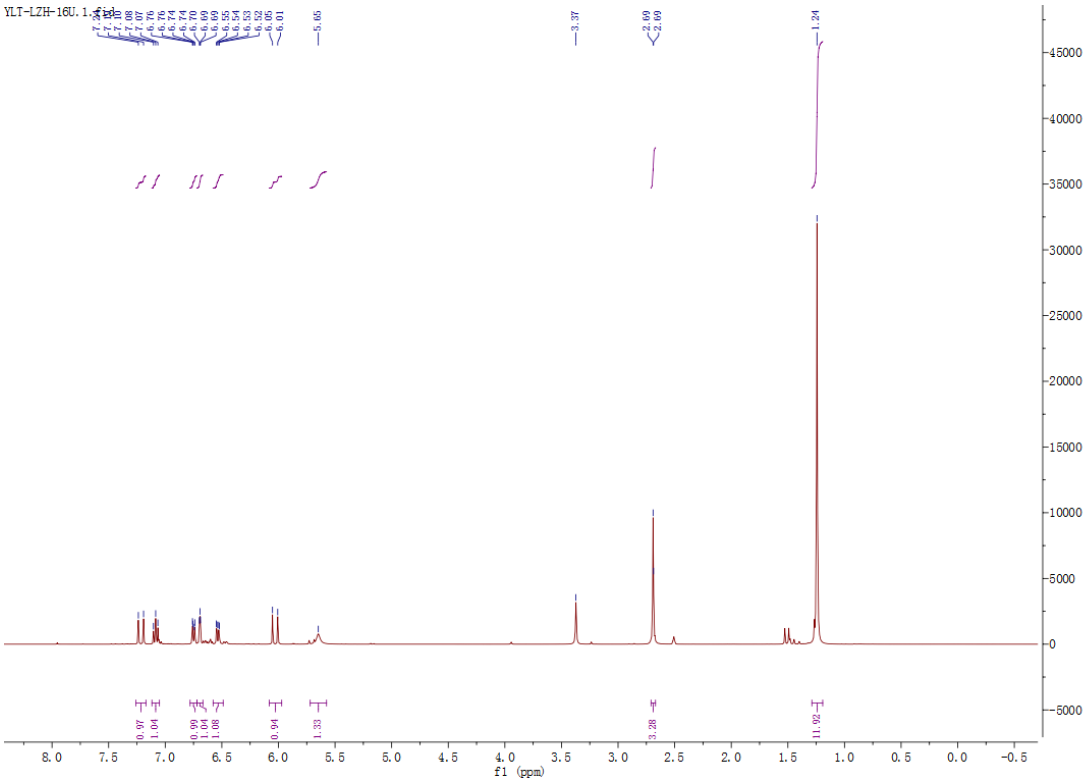
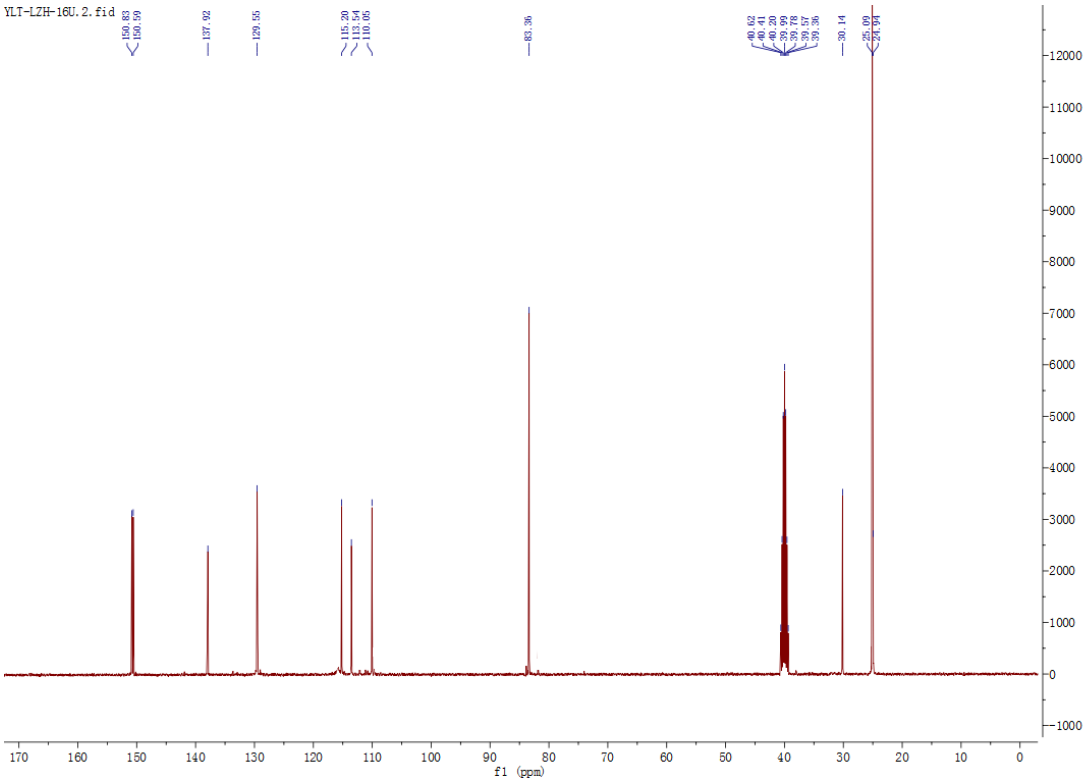
141.21
129.91
129.59
129.38
128.96
128.11
127.47
126.04
125.80
125.96
125.92
83.71
40.64
40.43
40.22
40.01
39.81
39.60
39.39
25.86
f1 (ppm)

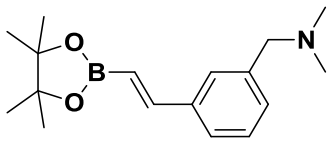




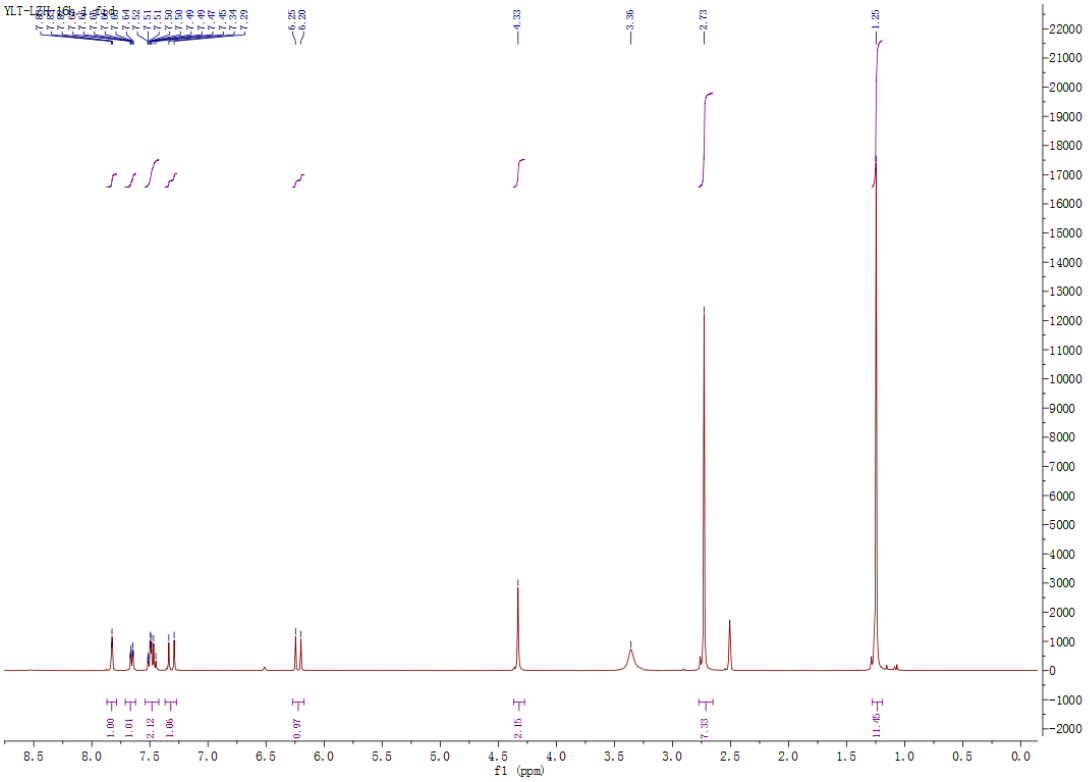
(E)-N-methyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (7I)

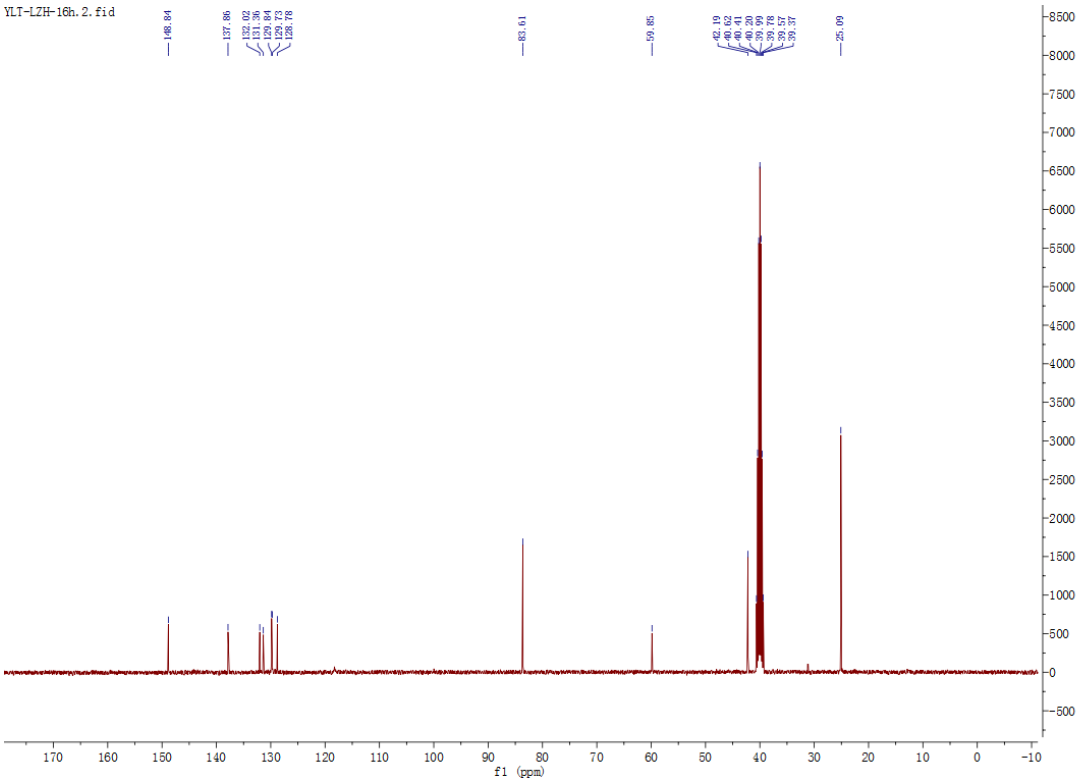


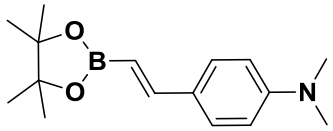




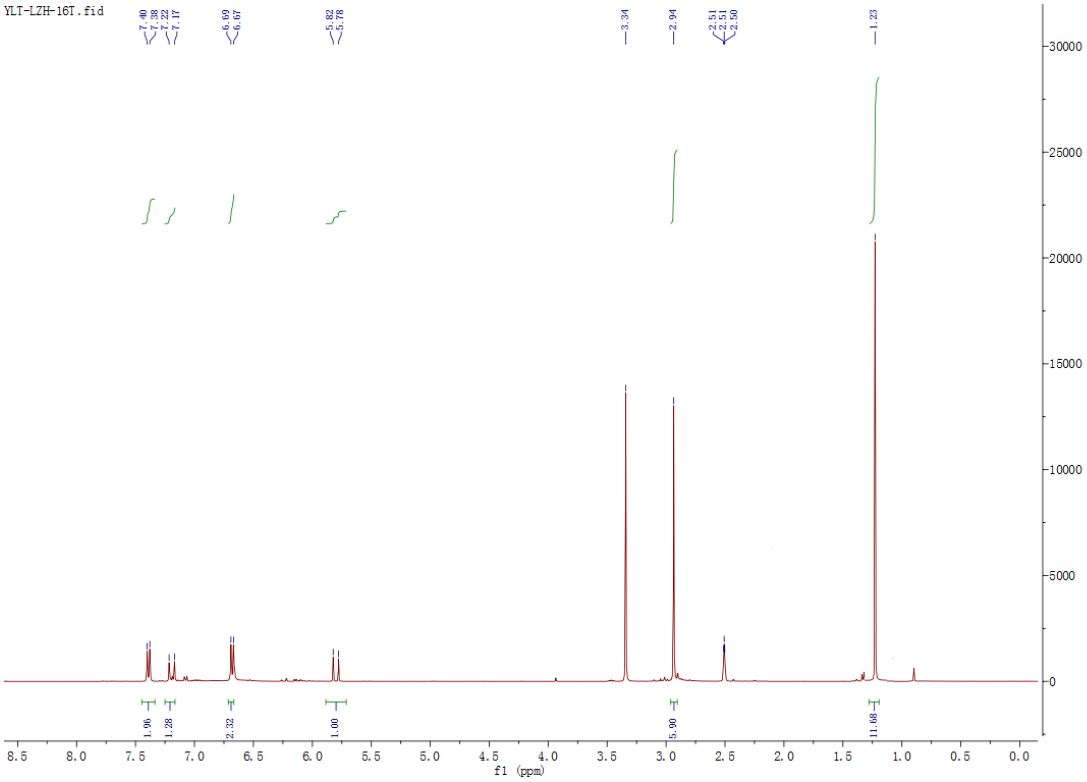
(E)-N,N-dimethyl-1-(3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)methanamine (7J)

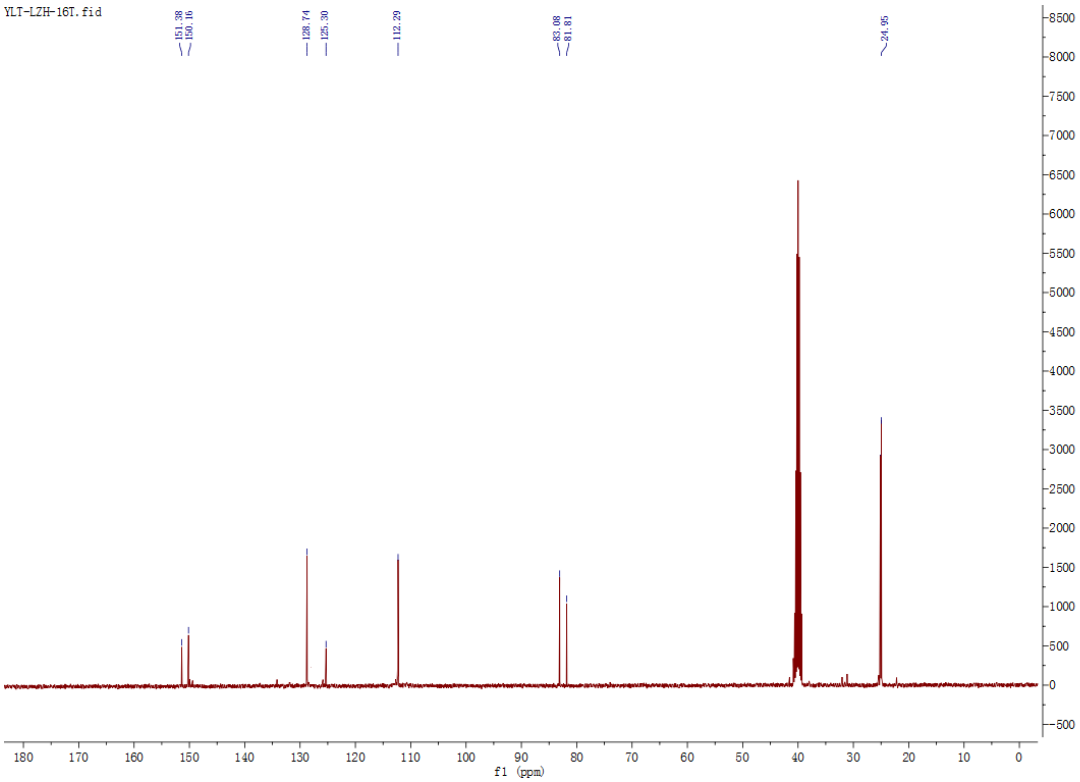


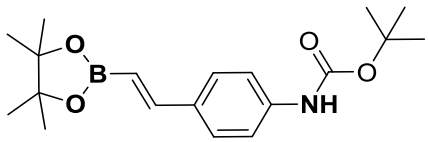




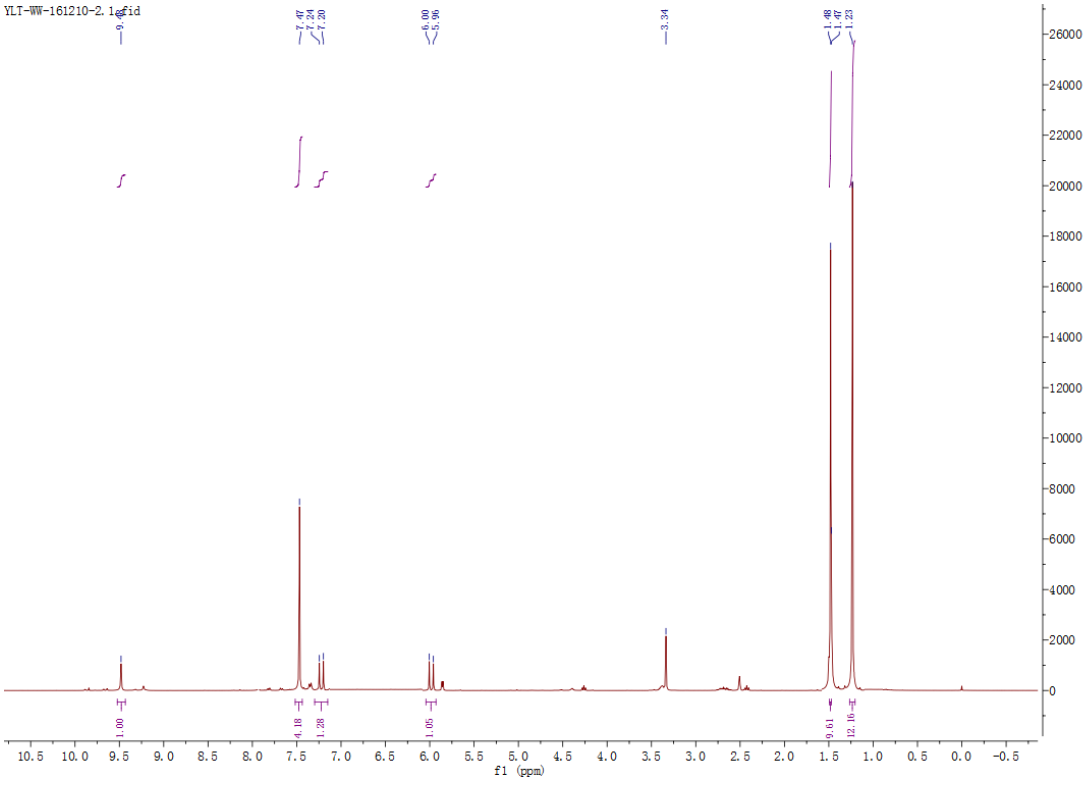
(E)-N,N-dimethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (7K)

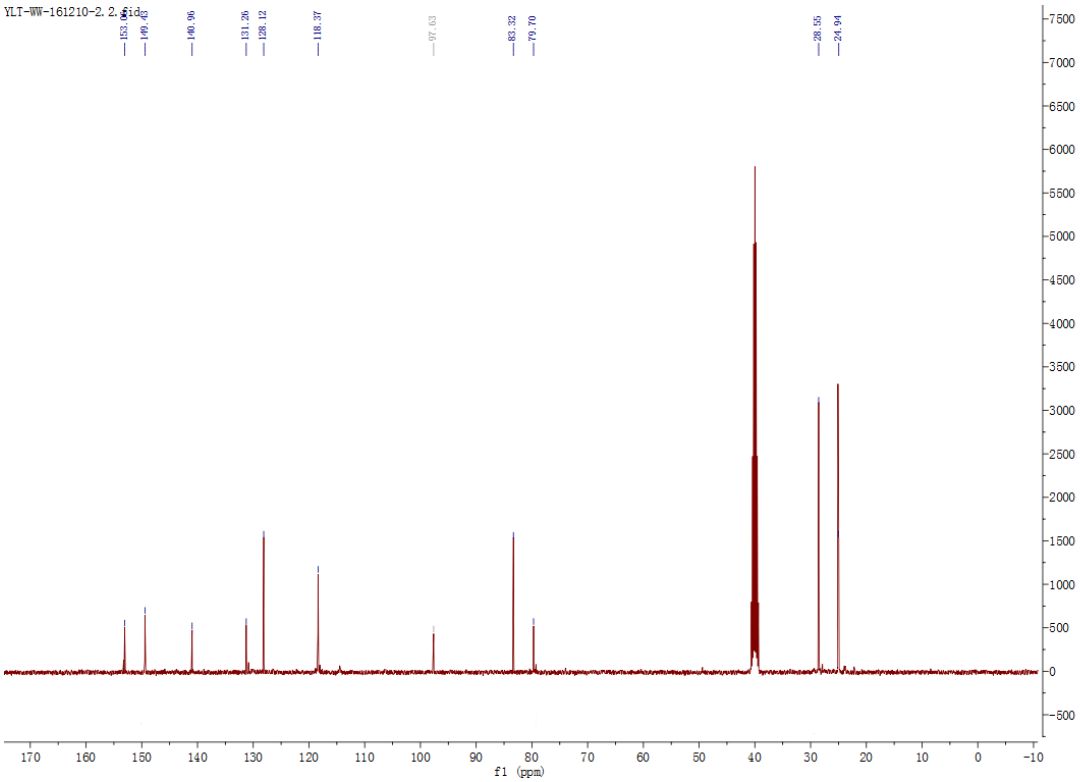


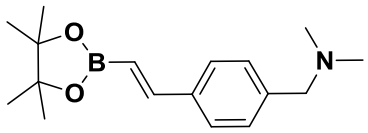




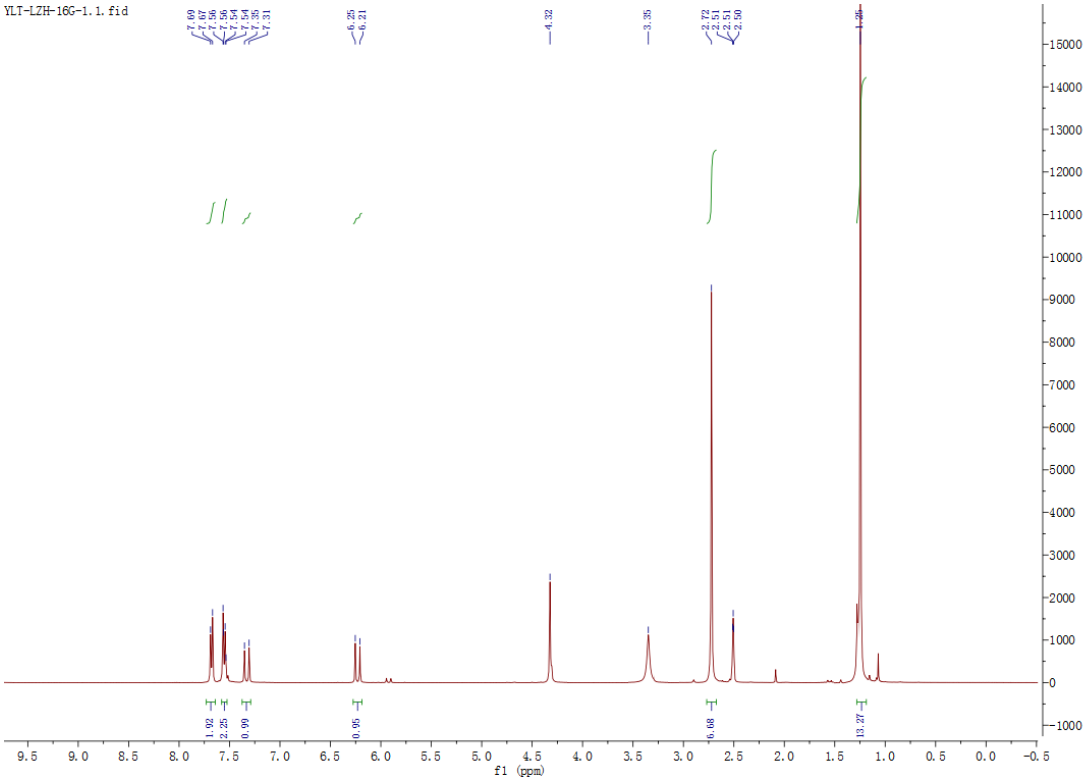
Tert-butyl-(E)-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)carbamate (7L)

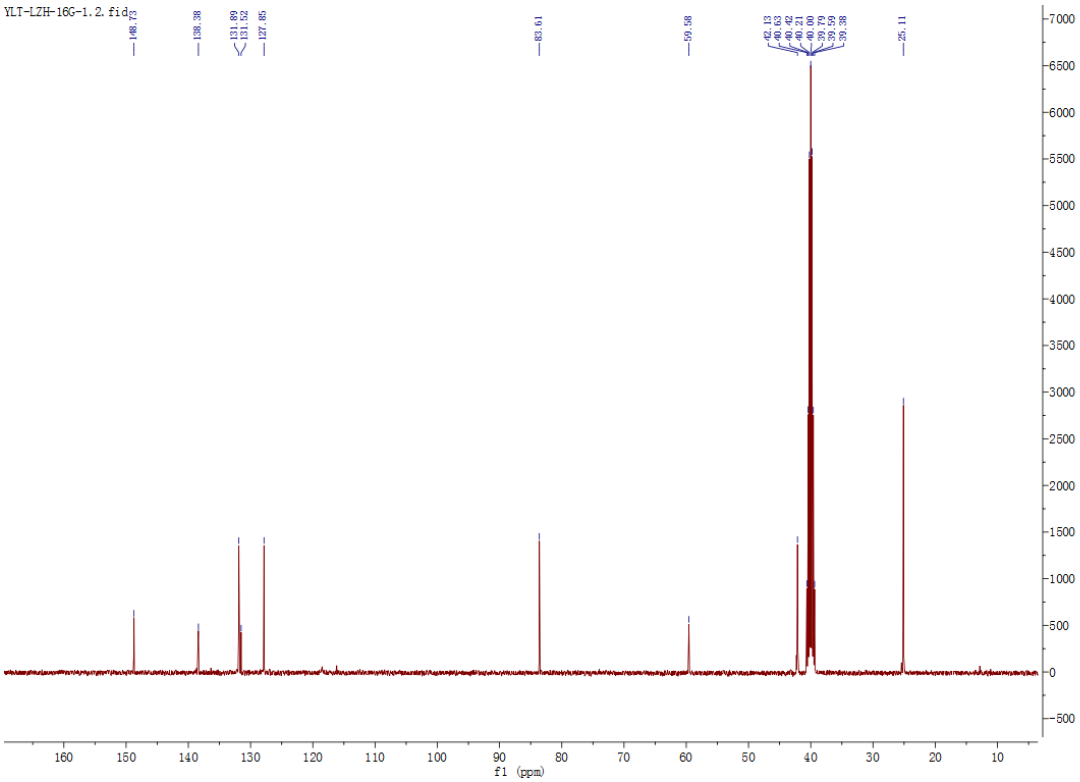


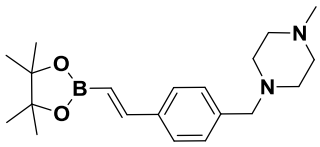




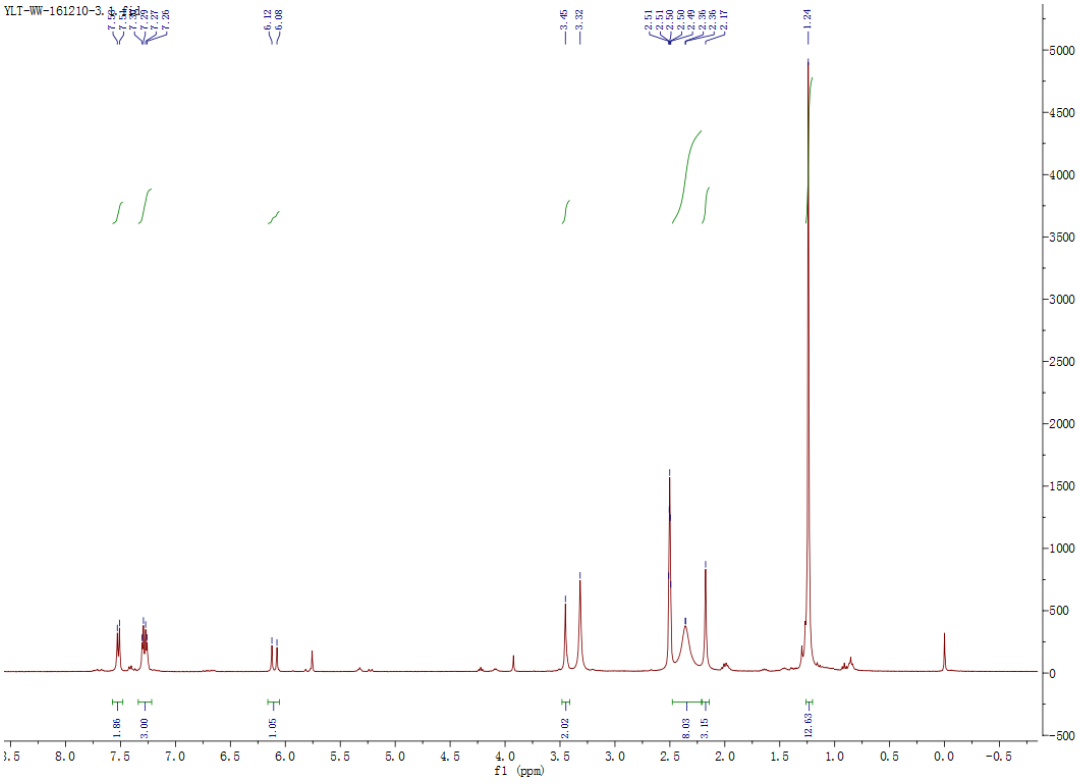
(E)-N,N-dimethyl-1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)methanemine (7M)

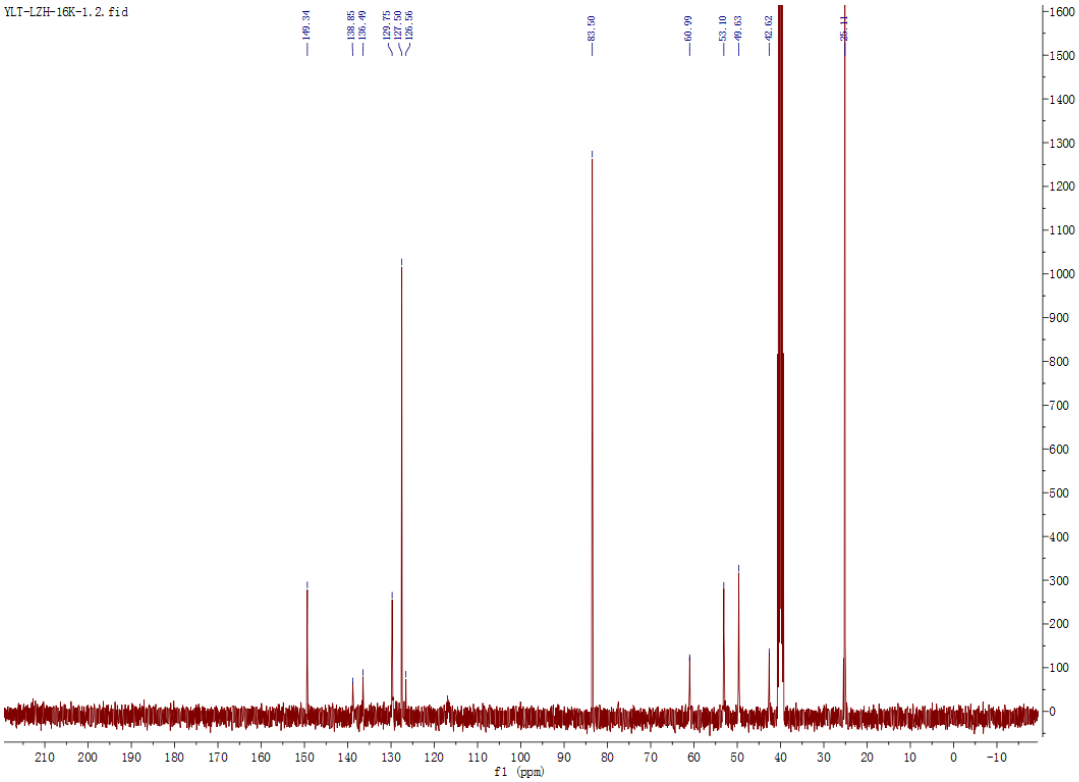


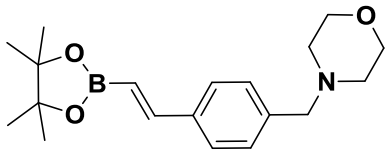




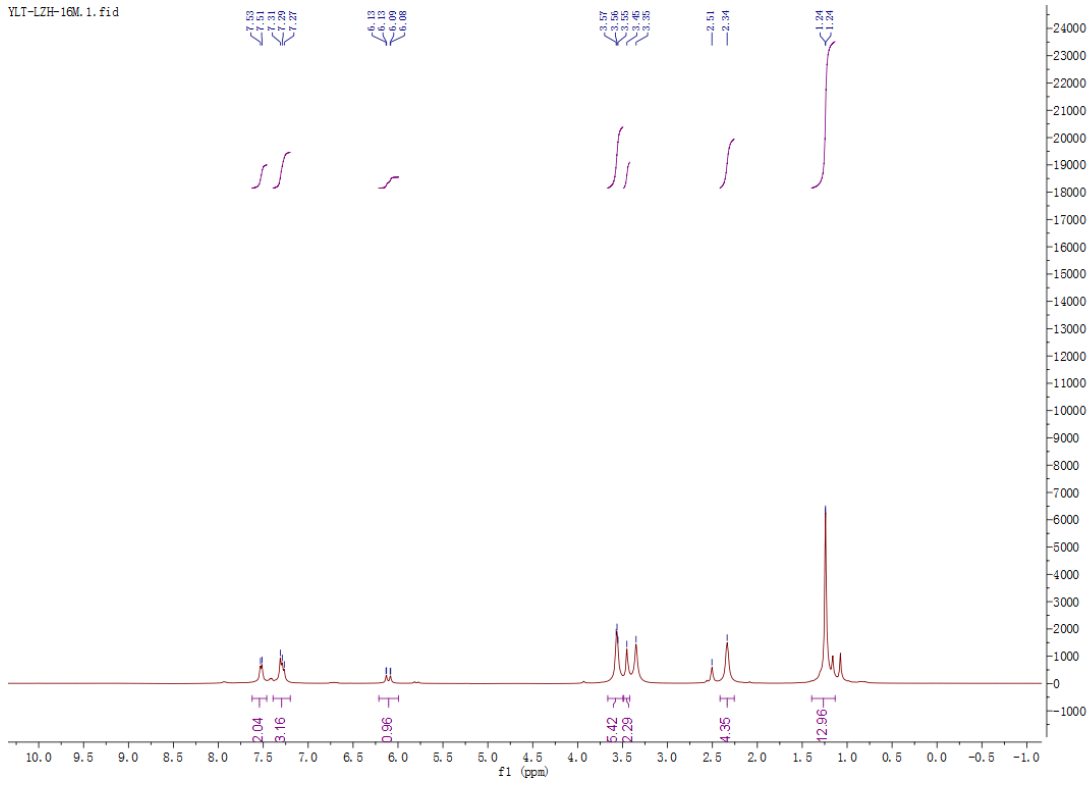
(E)-1-methyl-4-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzyl)piperazine (7N)

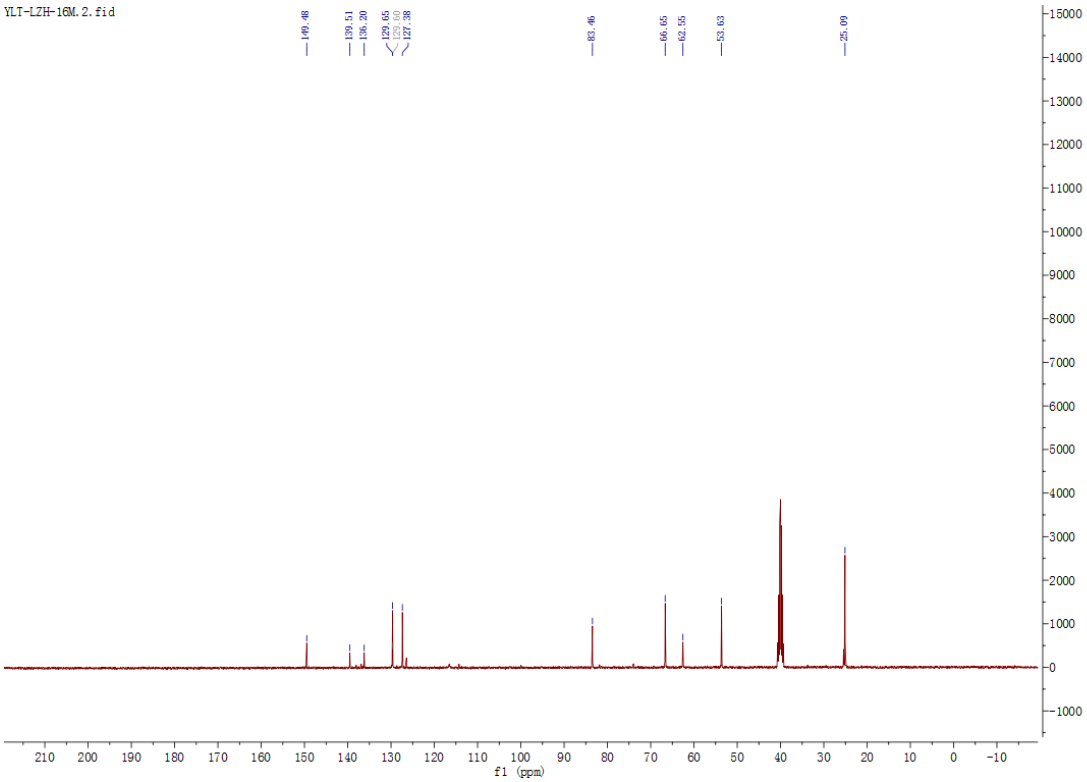


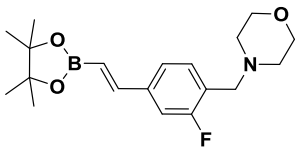




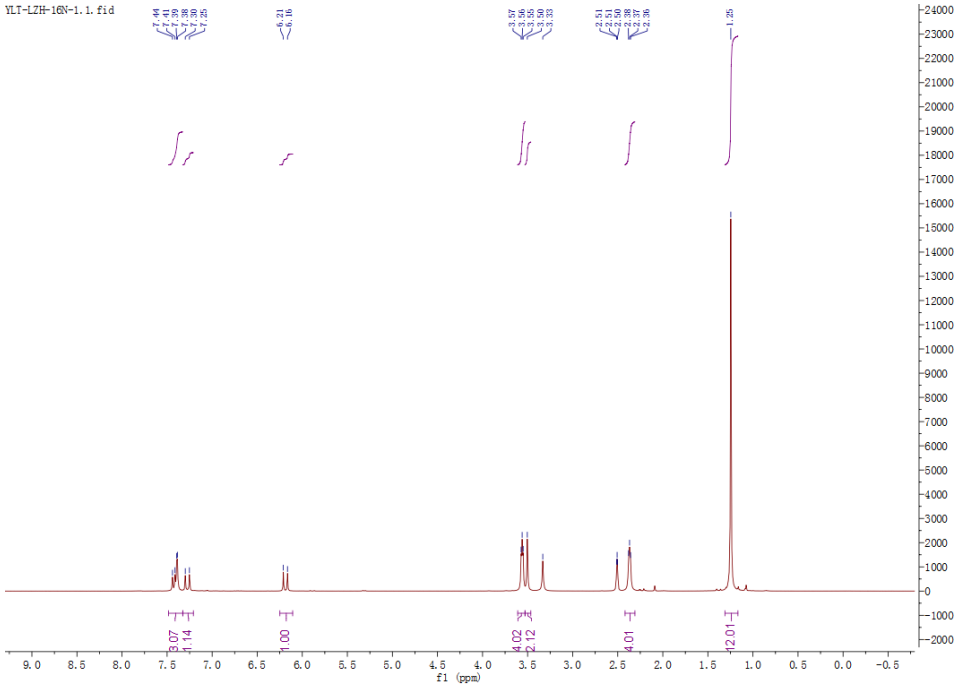
(E)-4-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzyl)morpholine (7O)

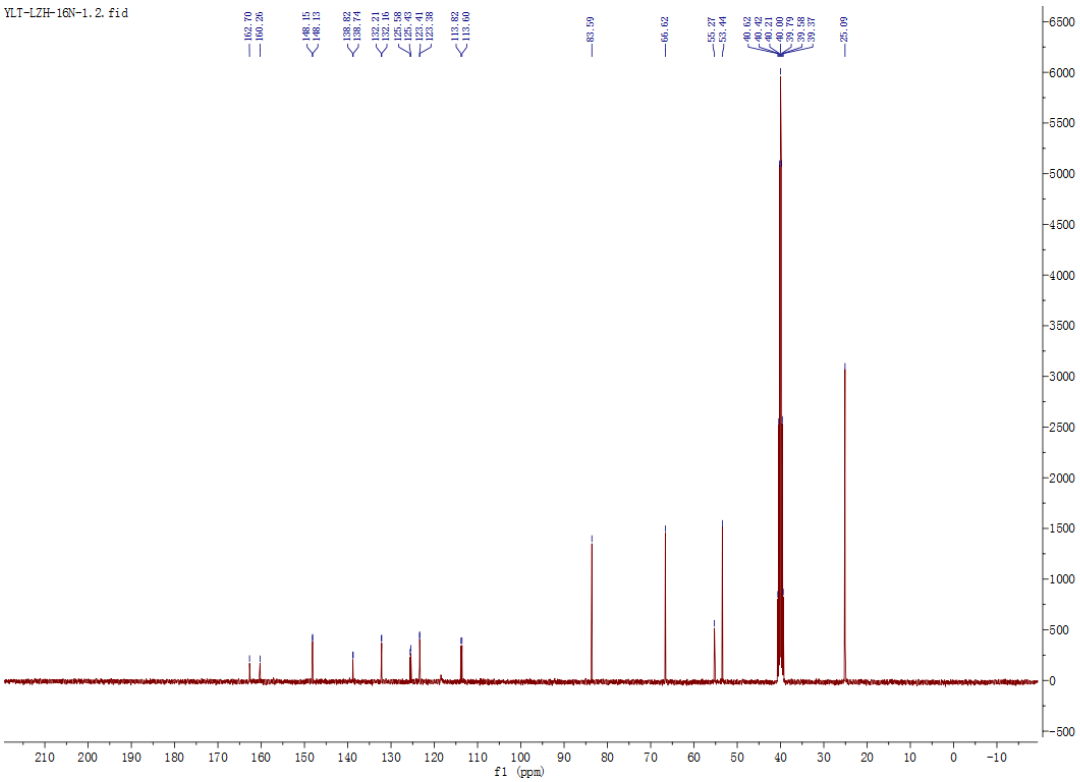


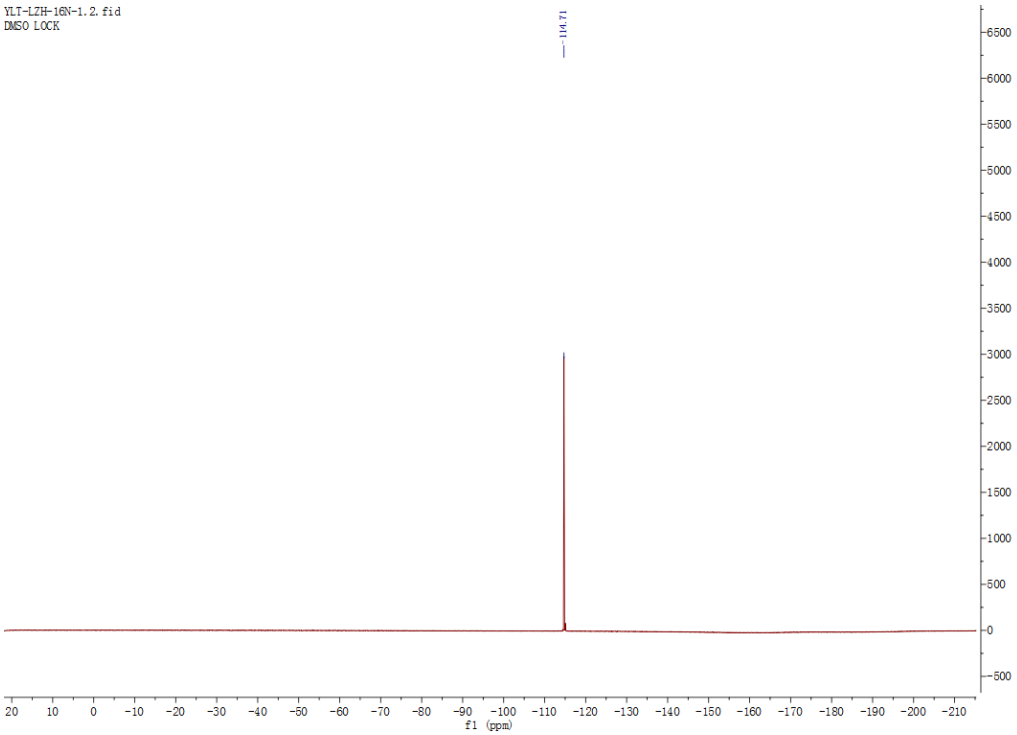


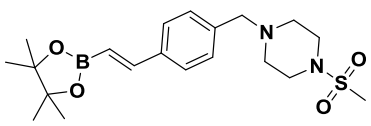


(E)-4-(2-fluoro-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzyl)morpholine (7P)

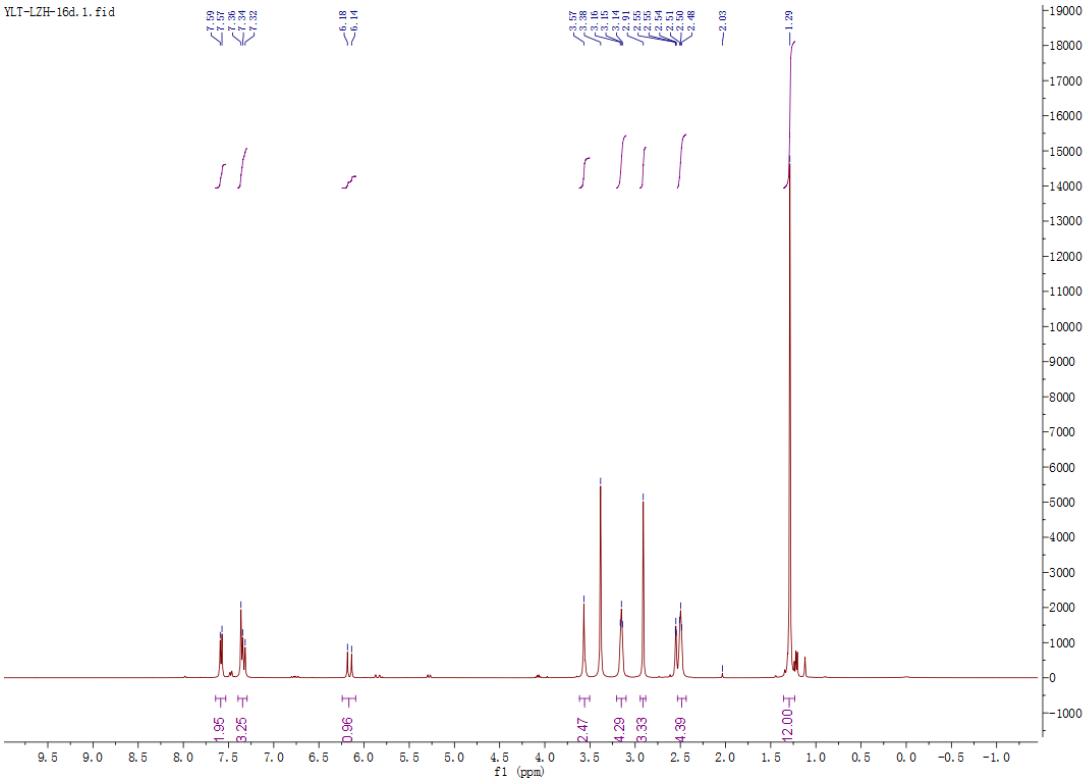


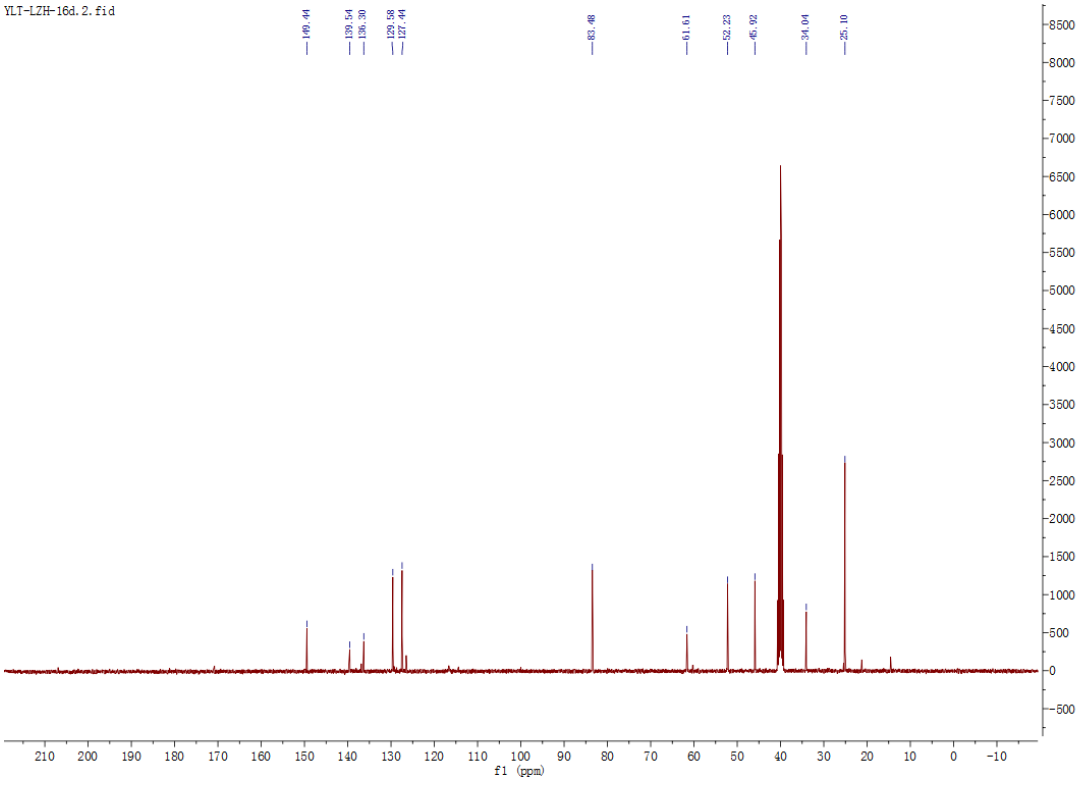


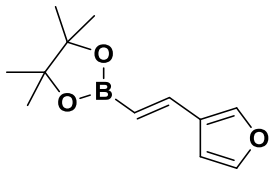




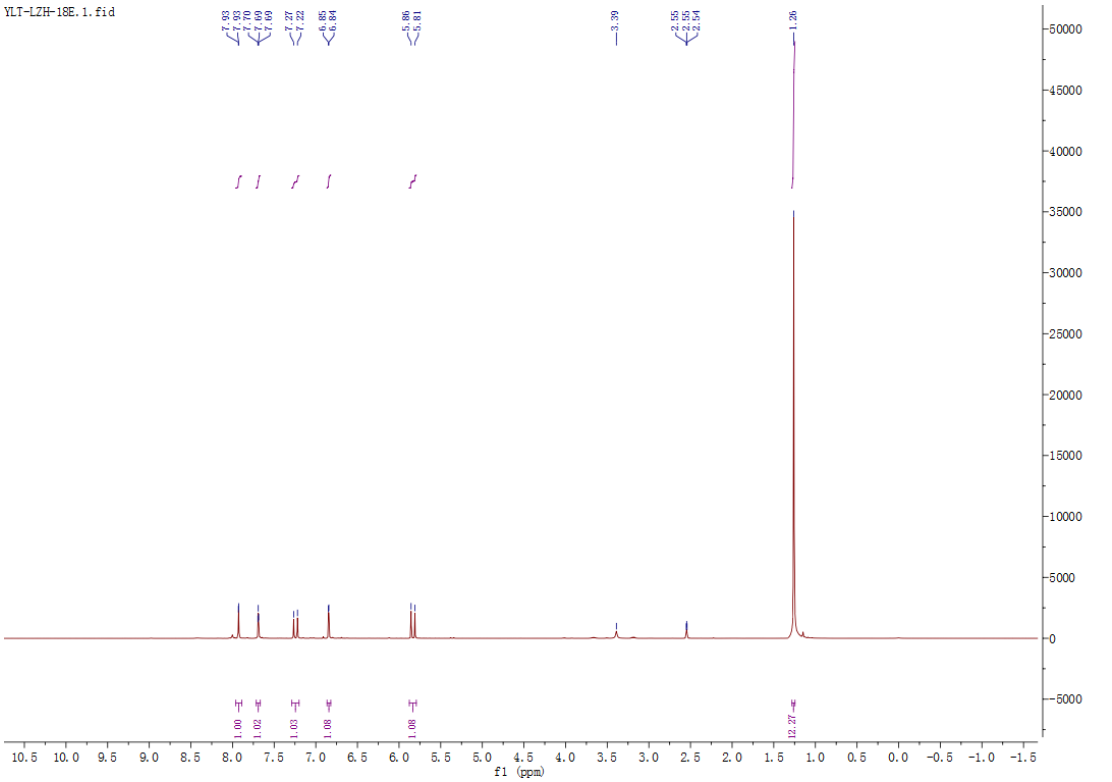
(E)-1-(methylsulfonyl)-4-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzyl)piperazine (7Q)

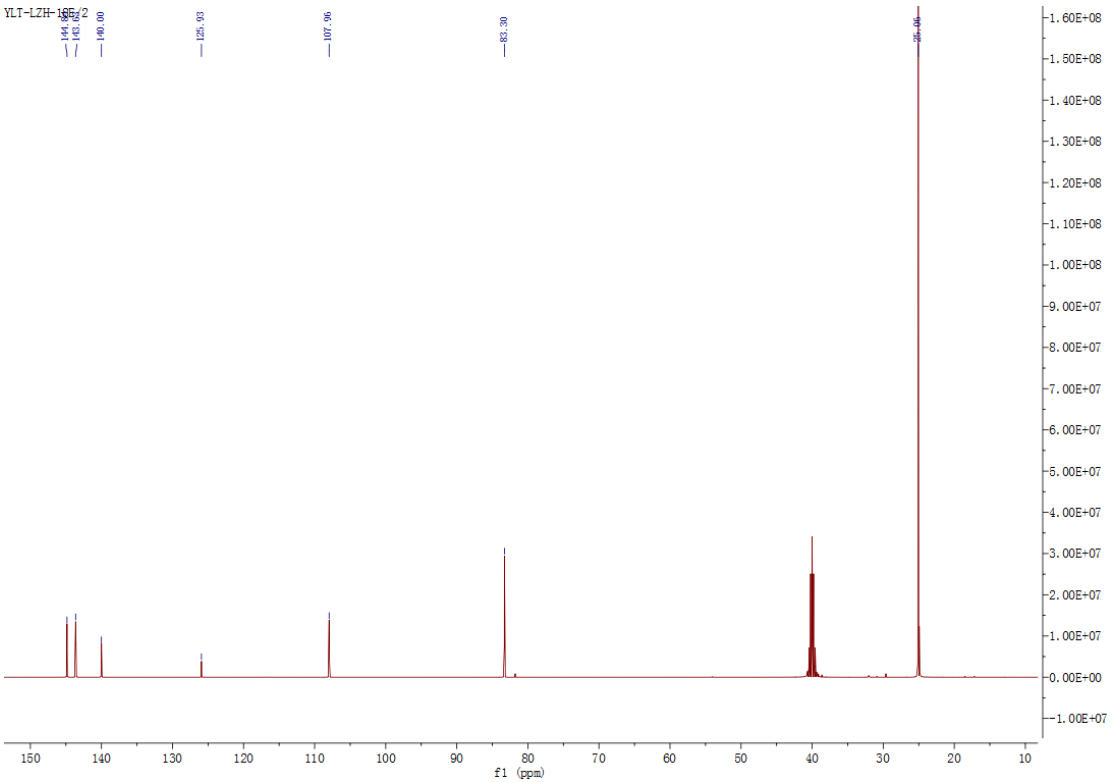


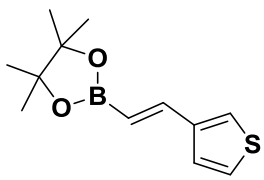




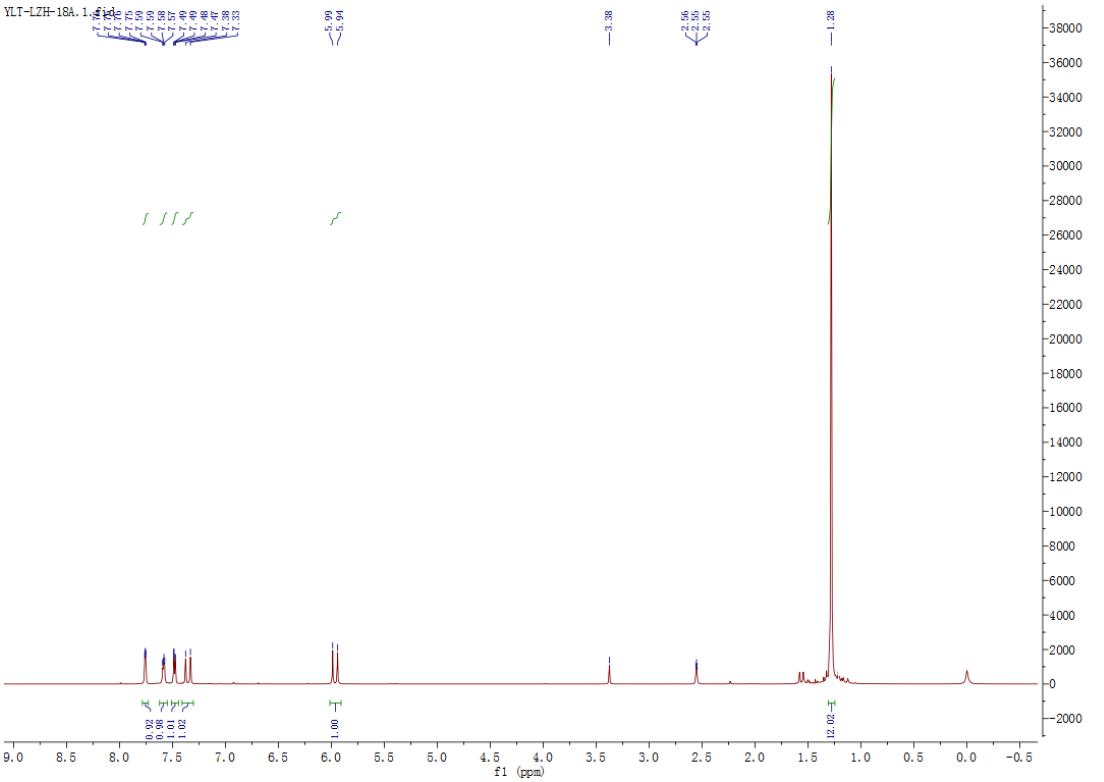
(E)-2-(2-(furan-3-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9B)

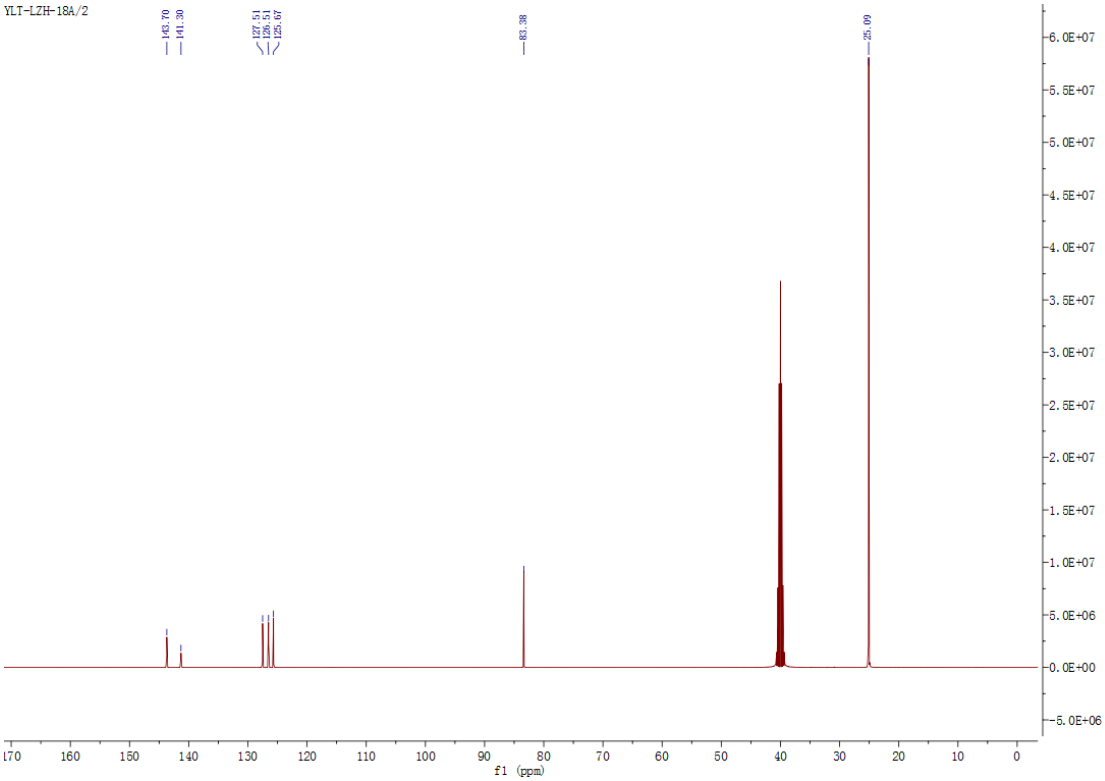


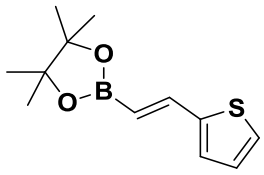




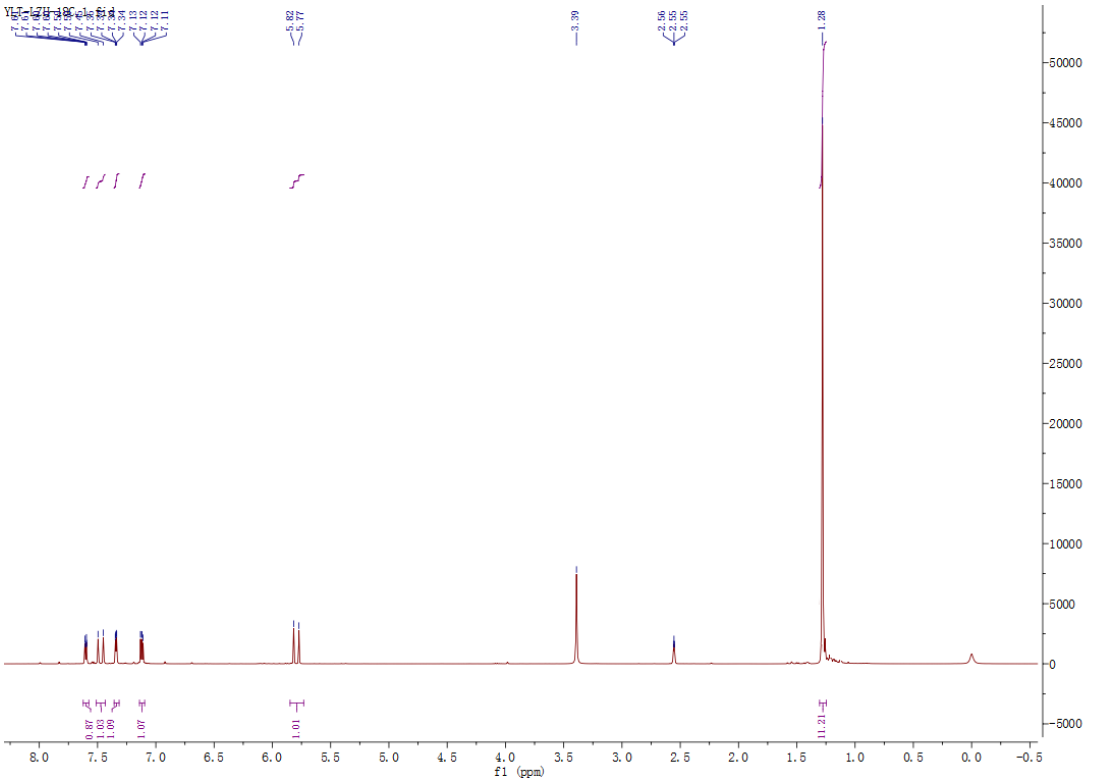
(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (9C)

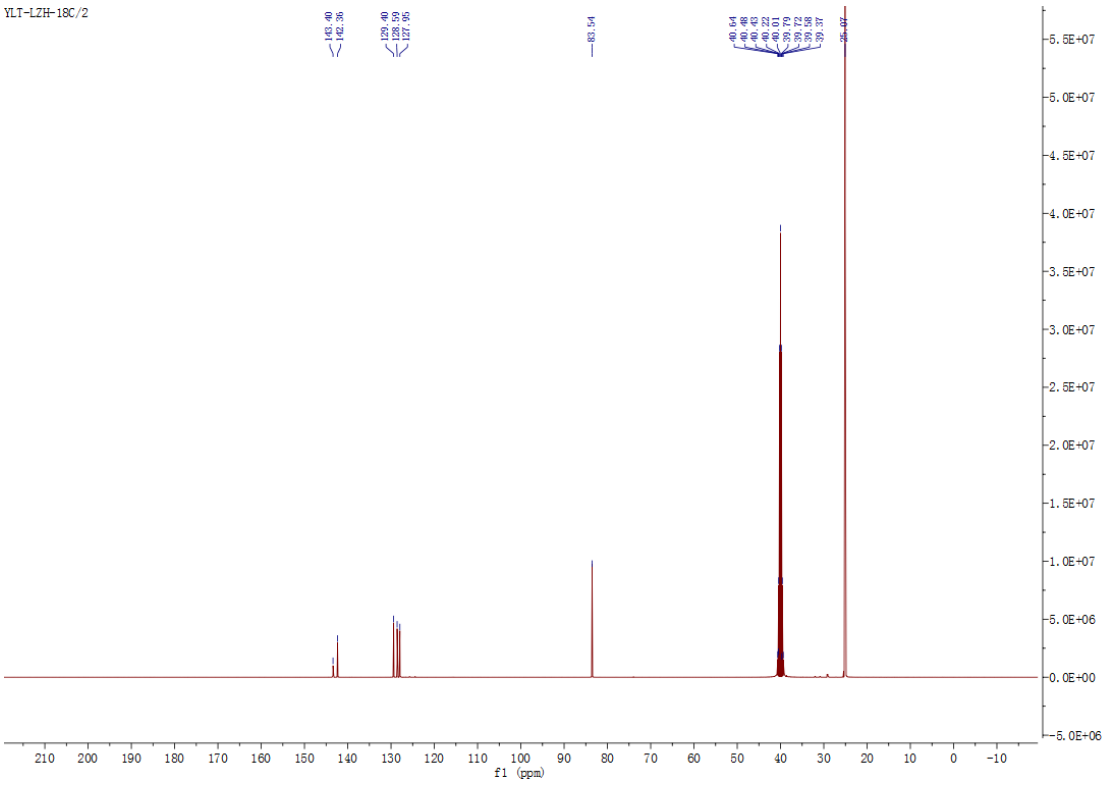


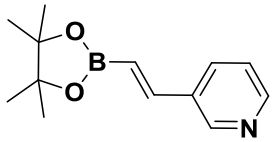




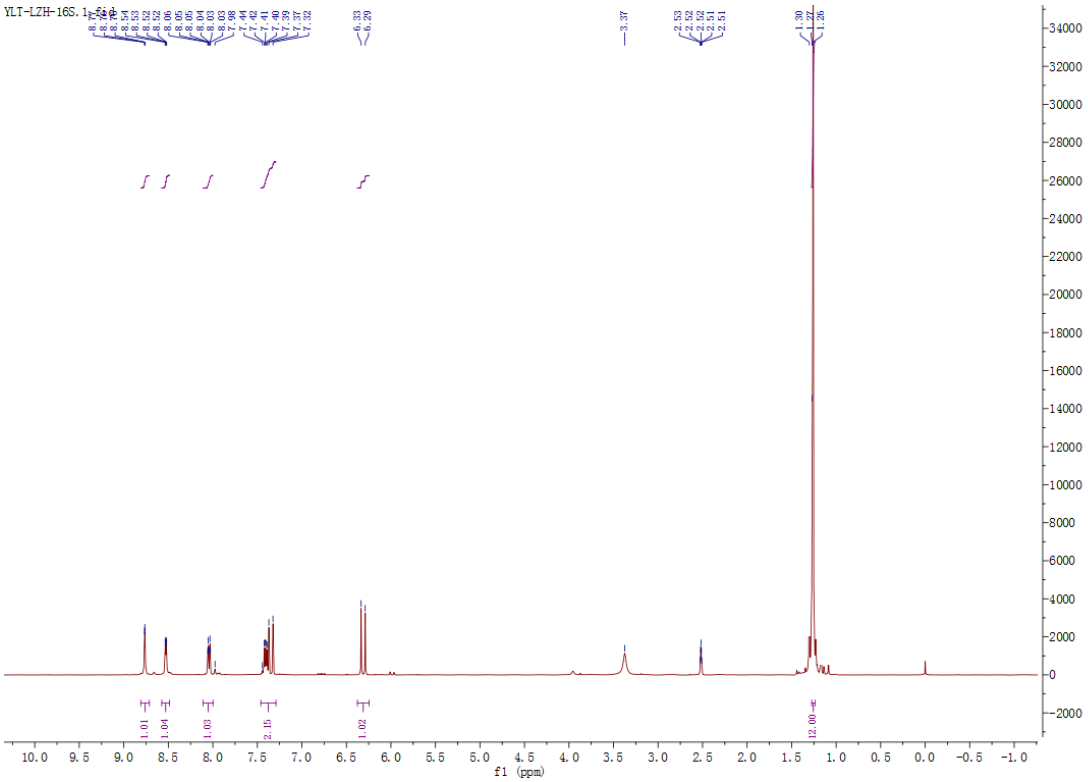
(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (9D)

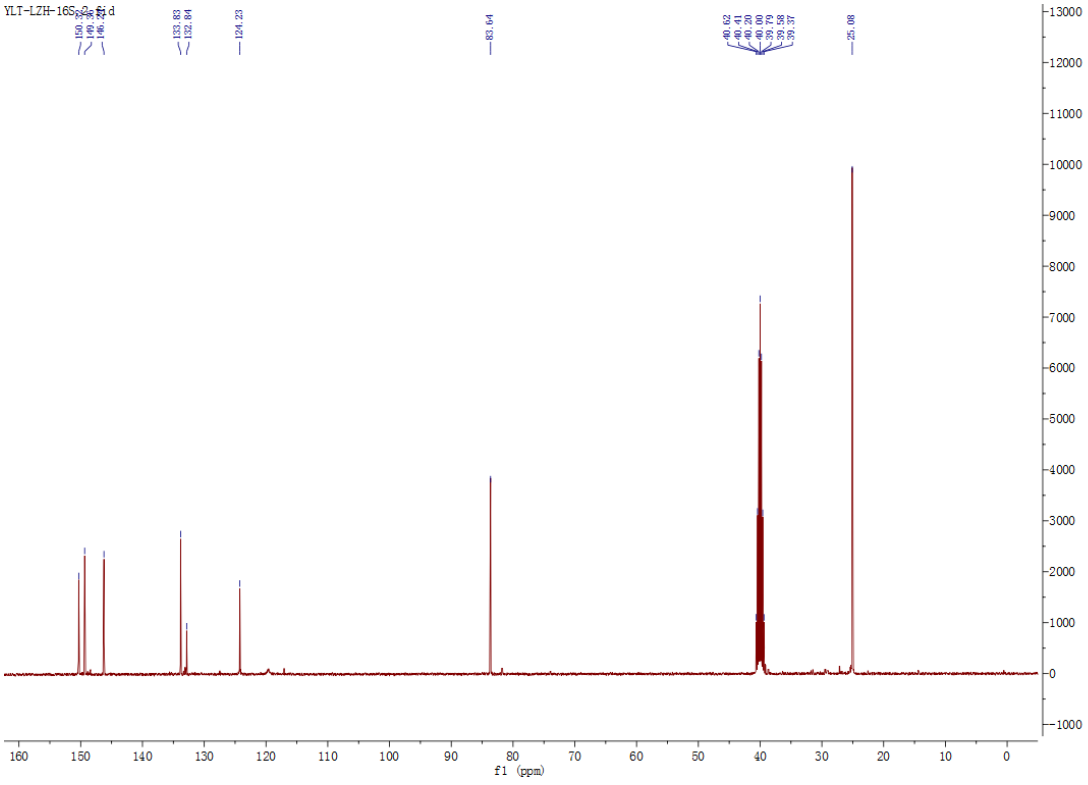


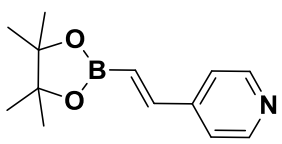




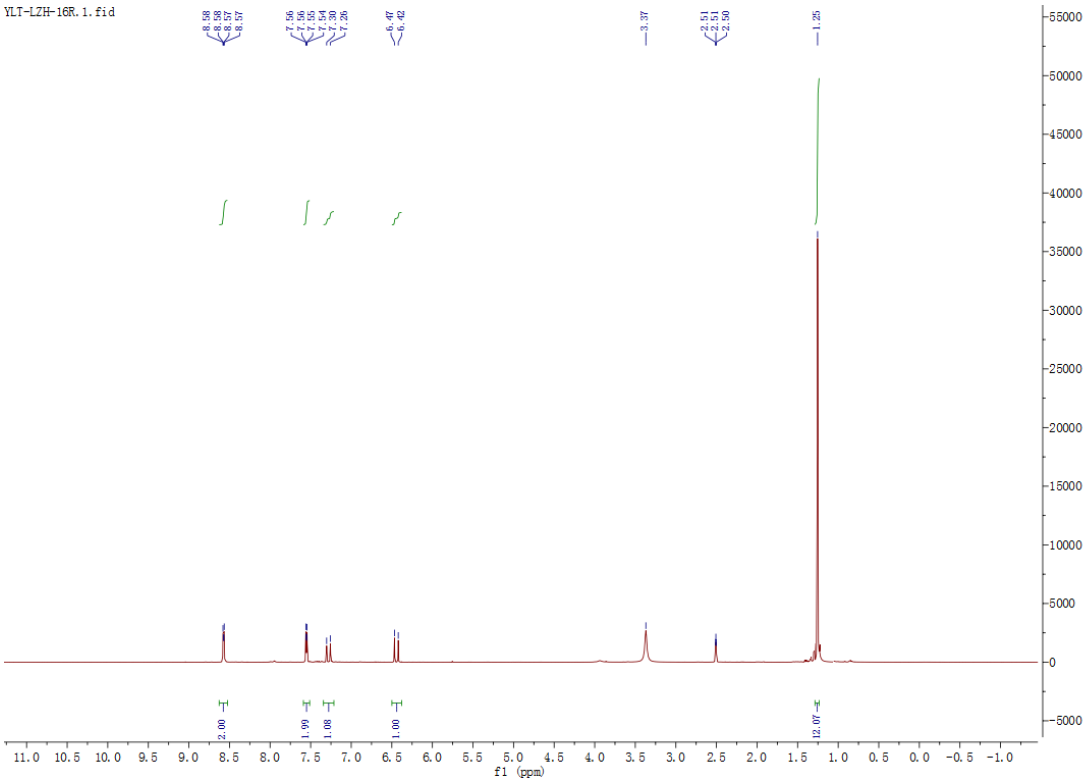
(E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (9F)

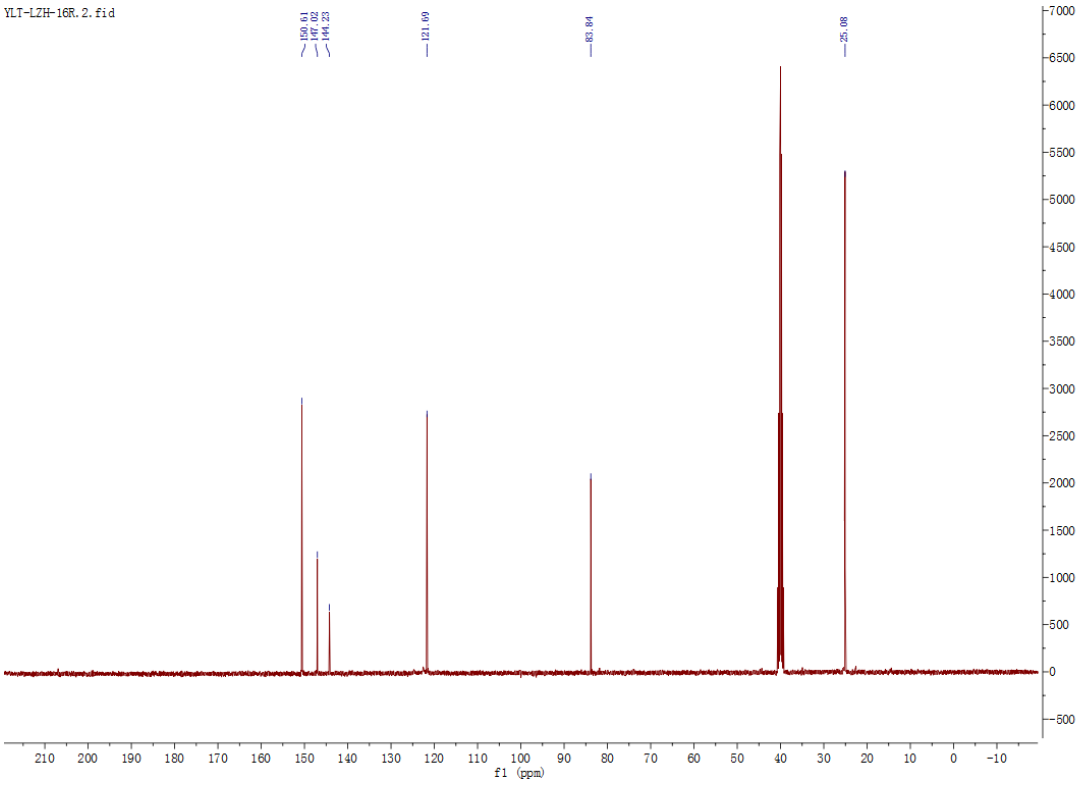


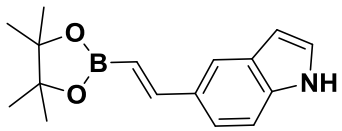




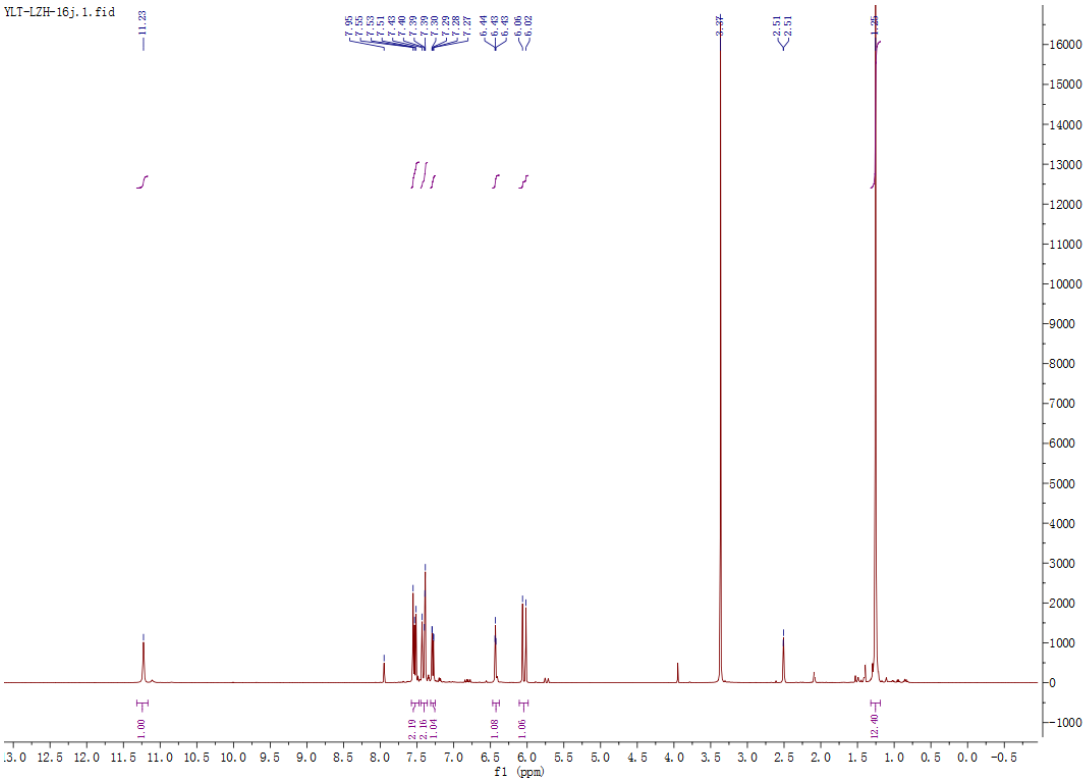
(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (9G)

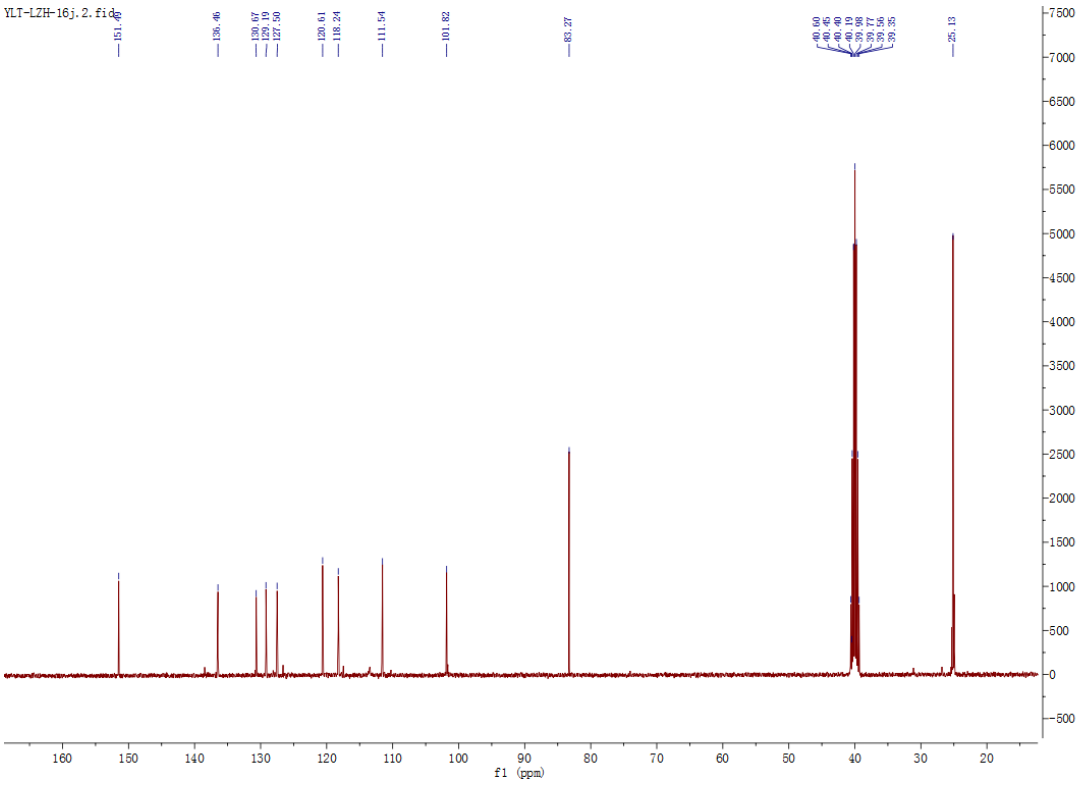


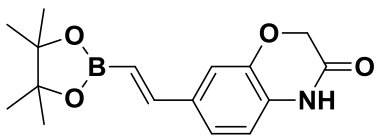




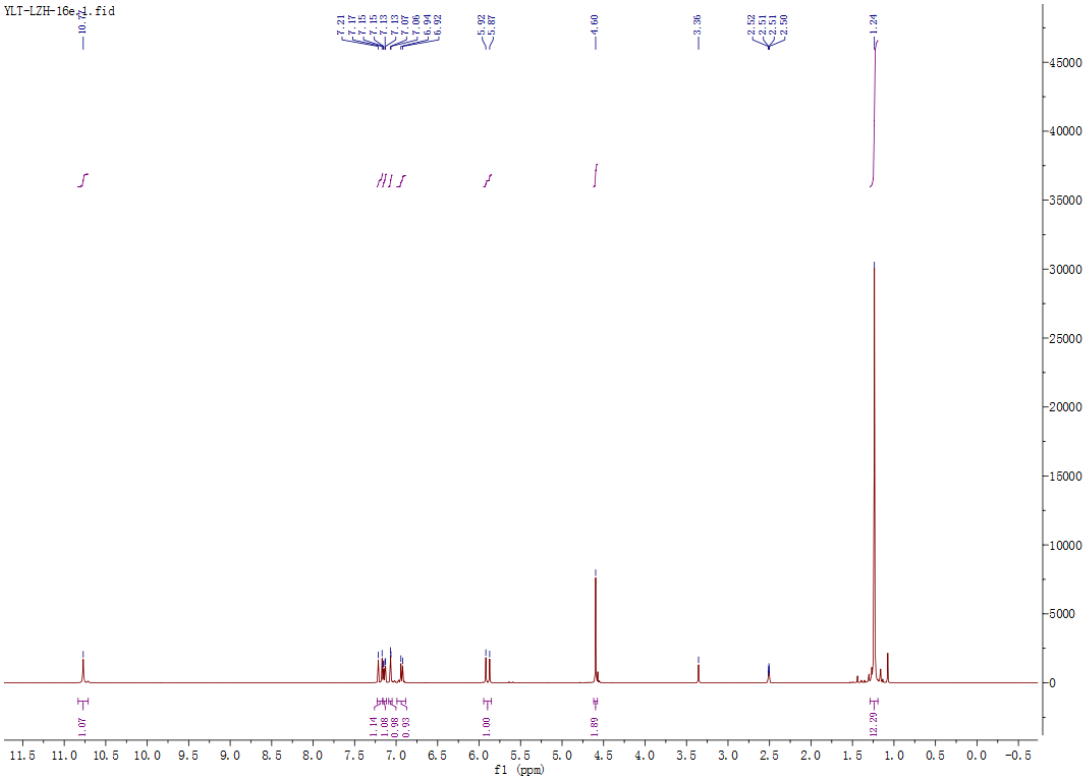
(E)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1H-indole (9H)

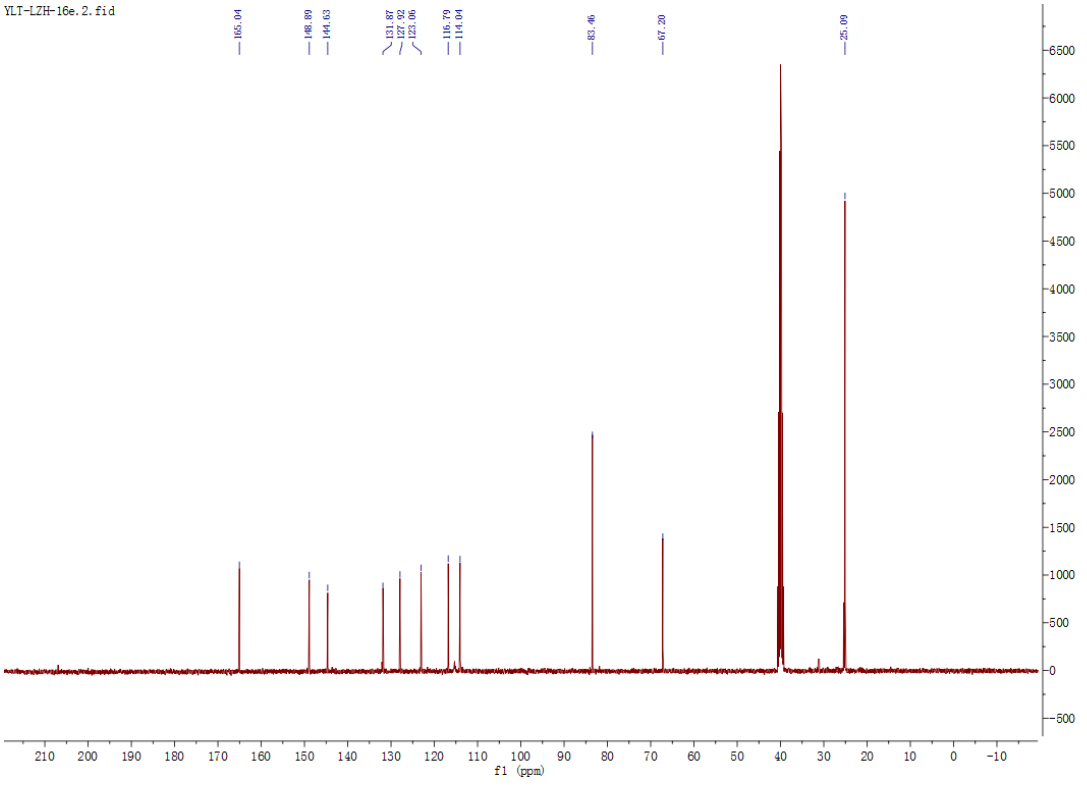


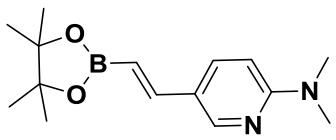




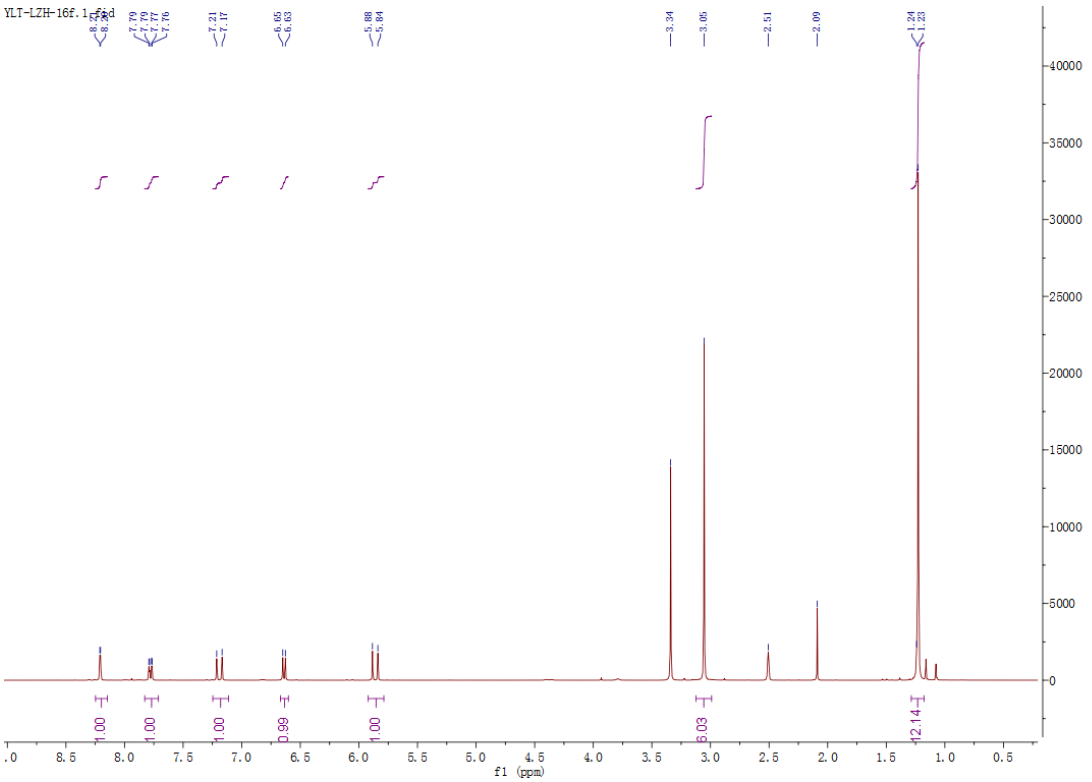
(E)-6-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2H-benzo[b][1,4]oxazin-3(4H)-one (9I)

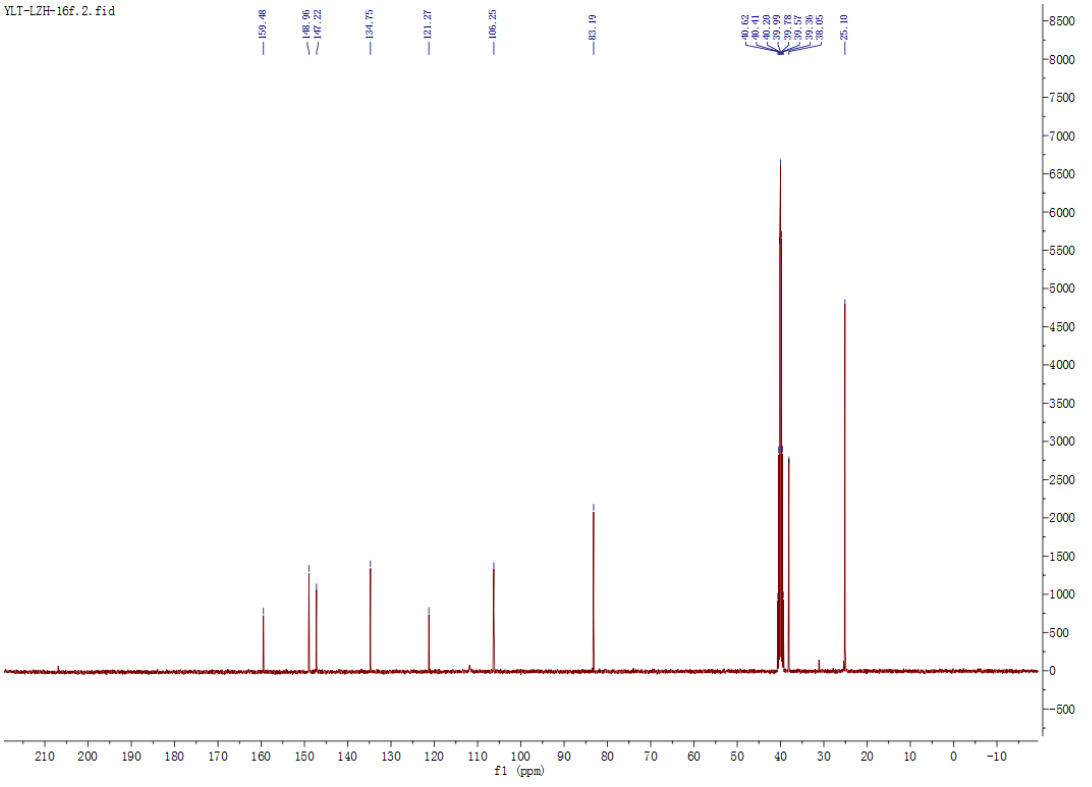


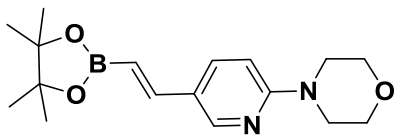




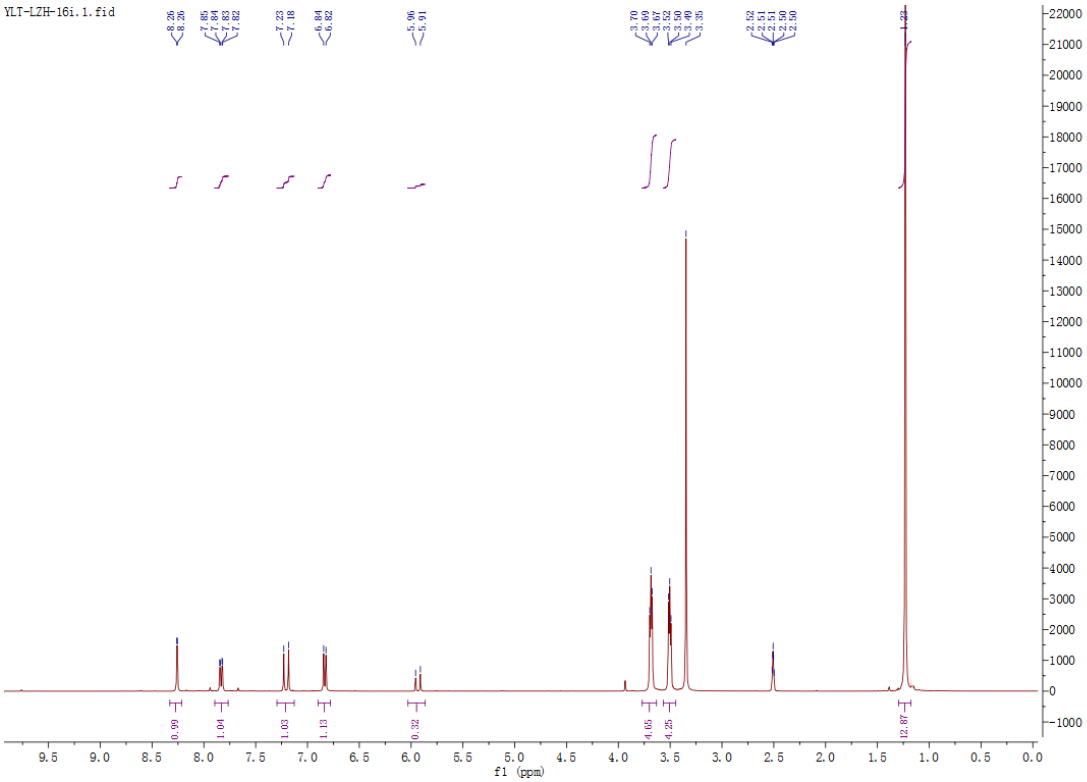
(E)-N,N-dimethyl-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridin-2-amine (9J)

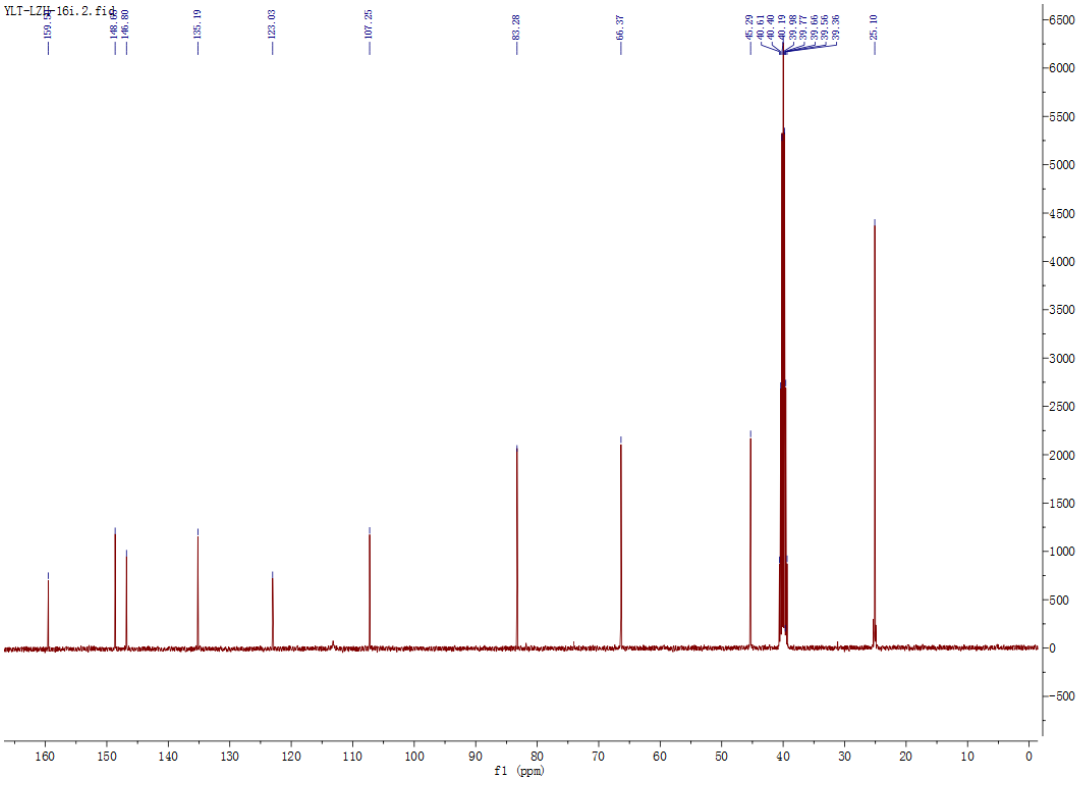


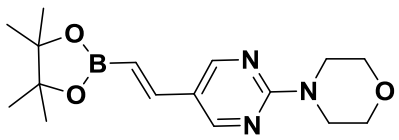




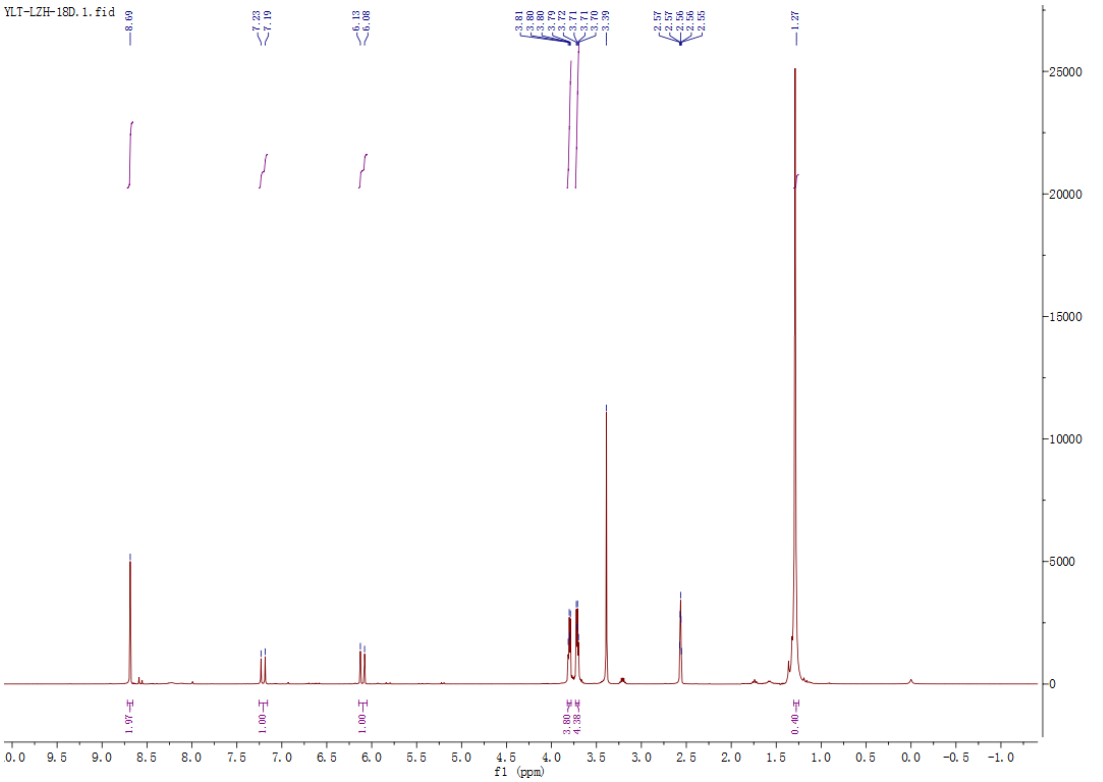
(E)-4-(5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridin-2-yl)morpholine (9K)

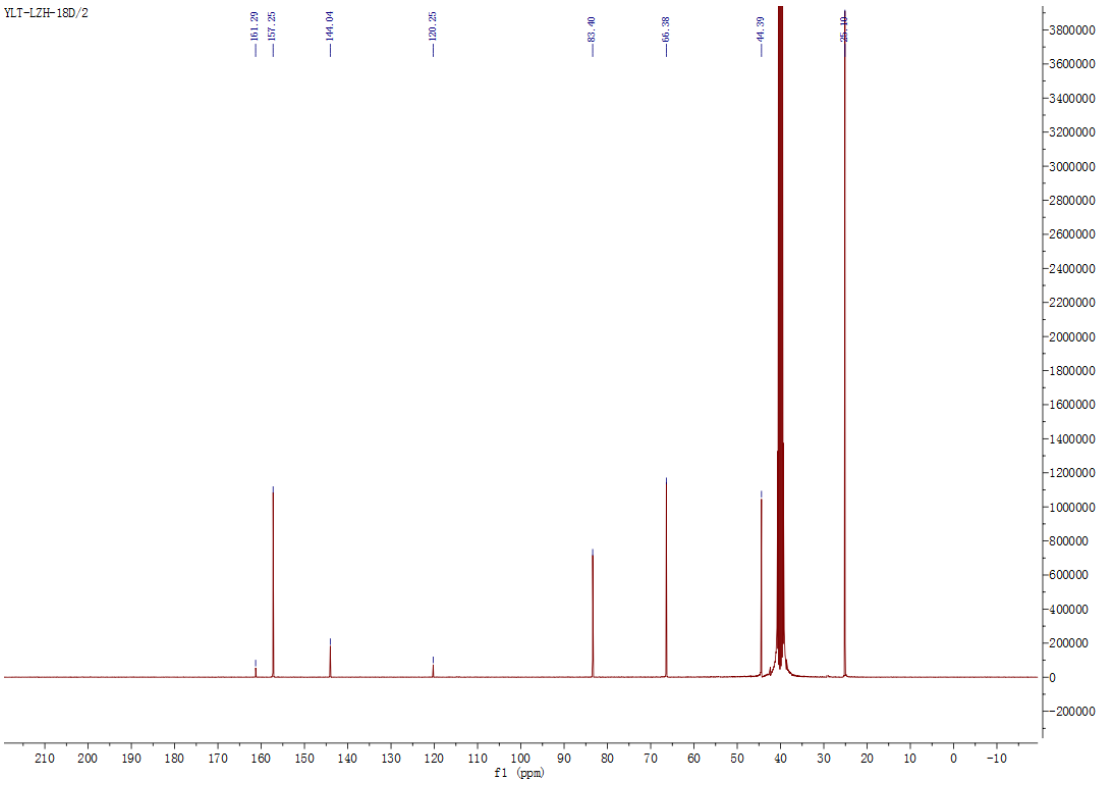


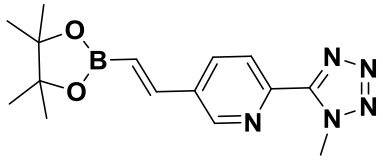




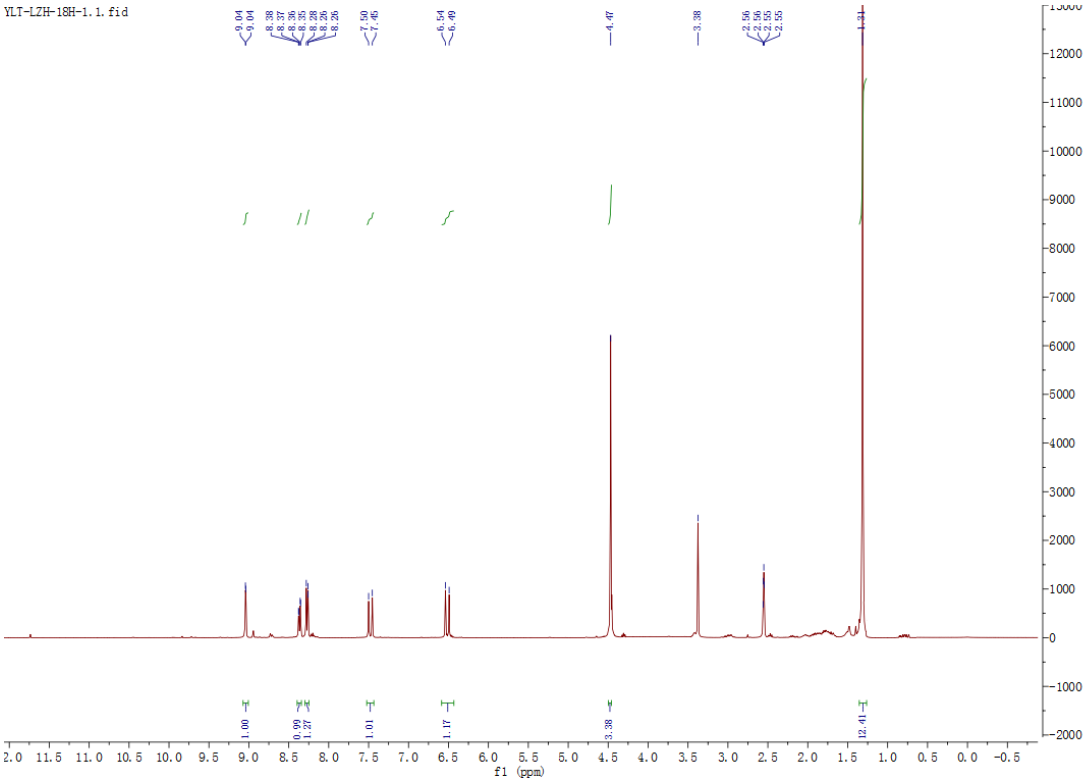
(E)-4-(5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyrimidin-2-yl)morpholine (9L)

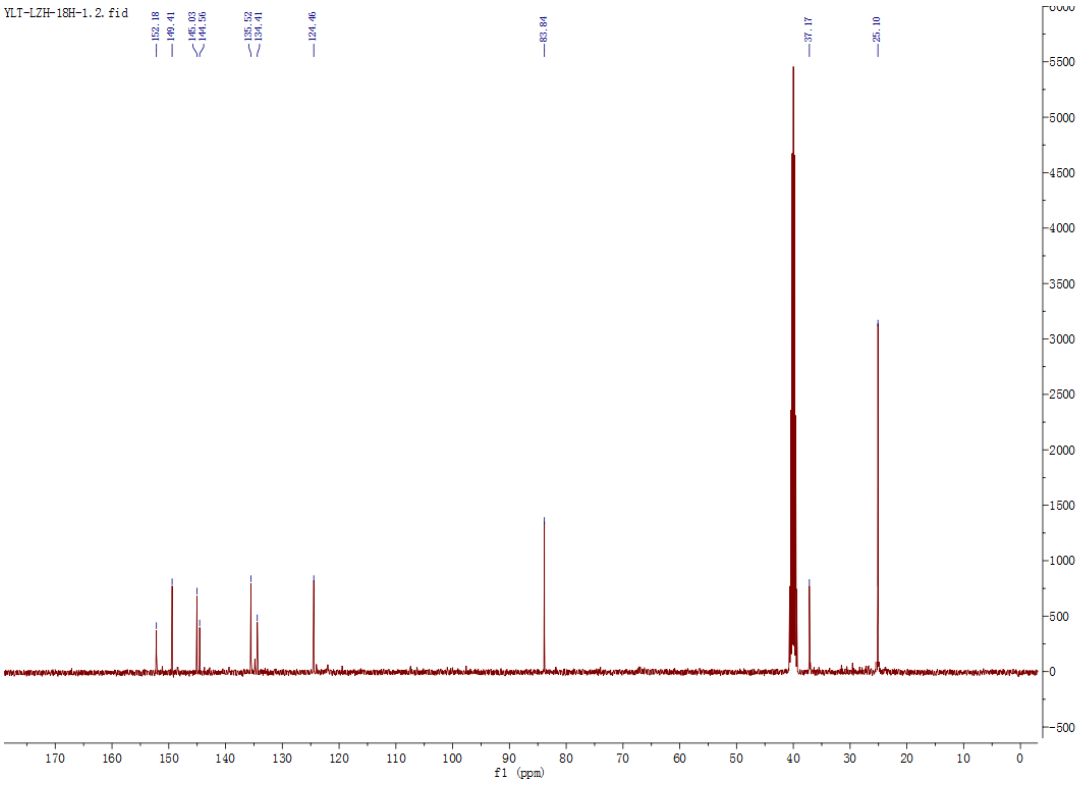


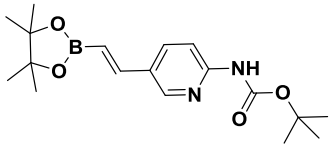




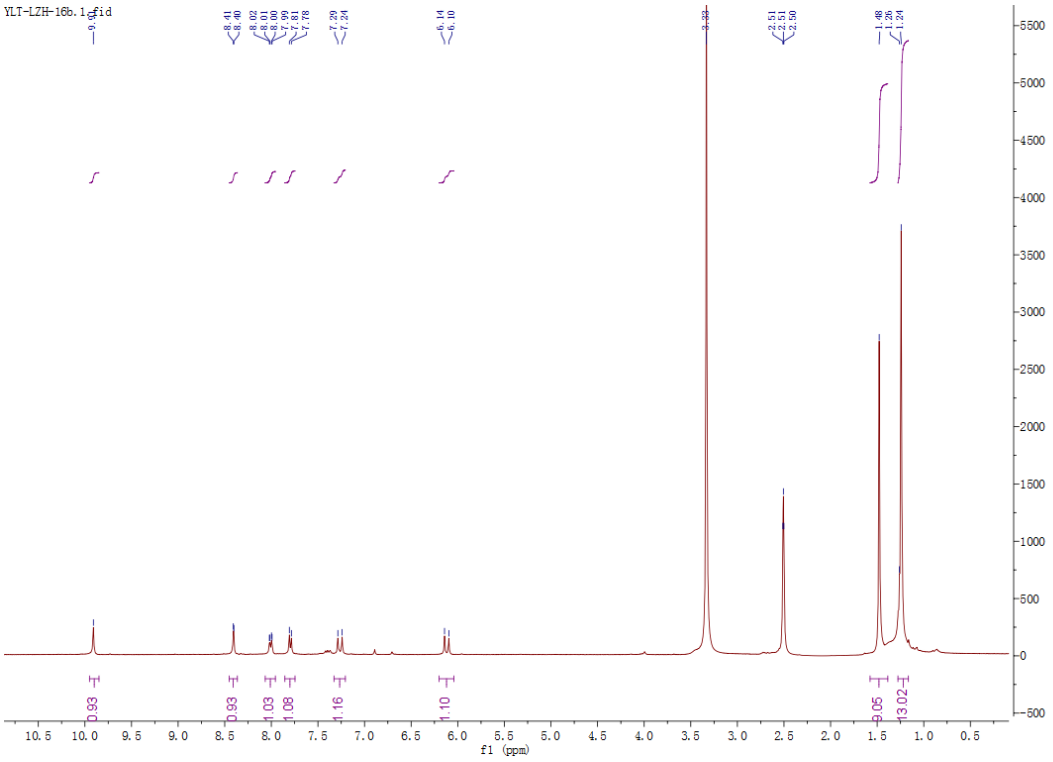
(E)-2-(1-methyl-1H-tetrazol-5-yl)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (9M)

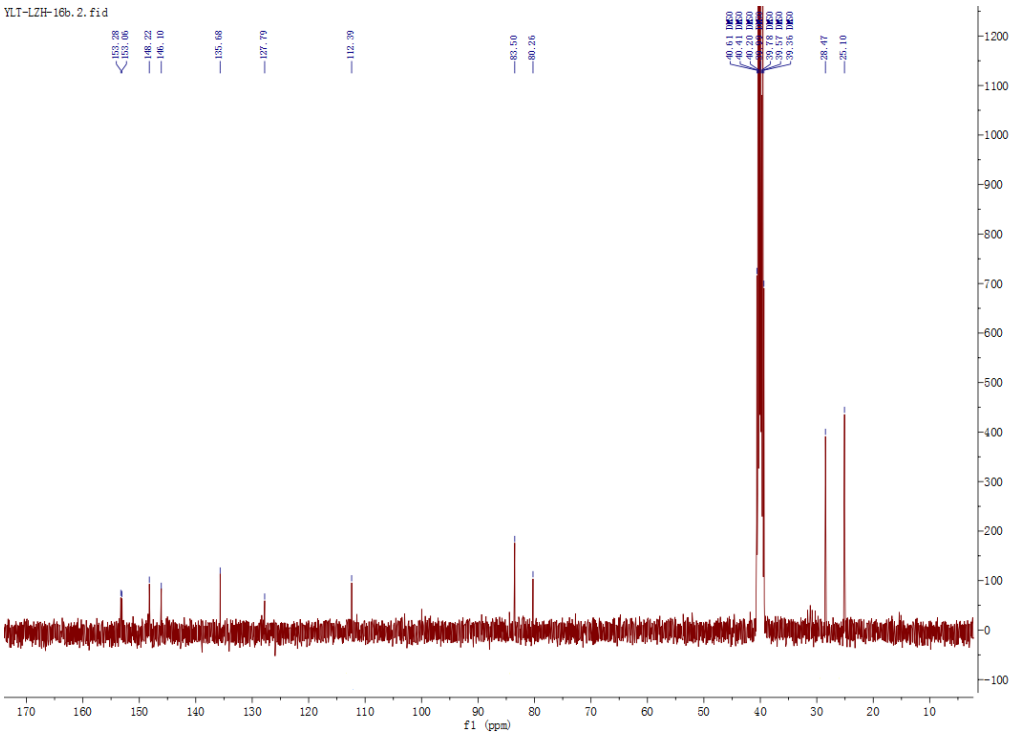


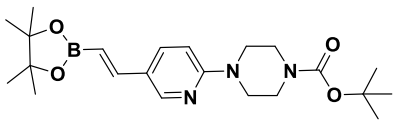




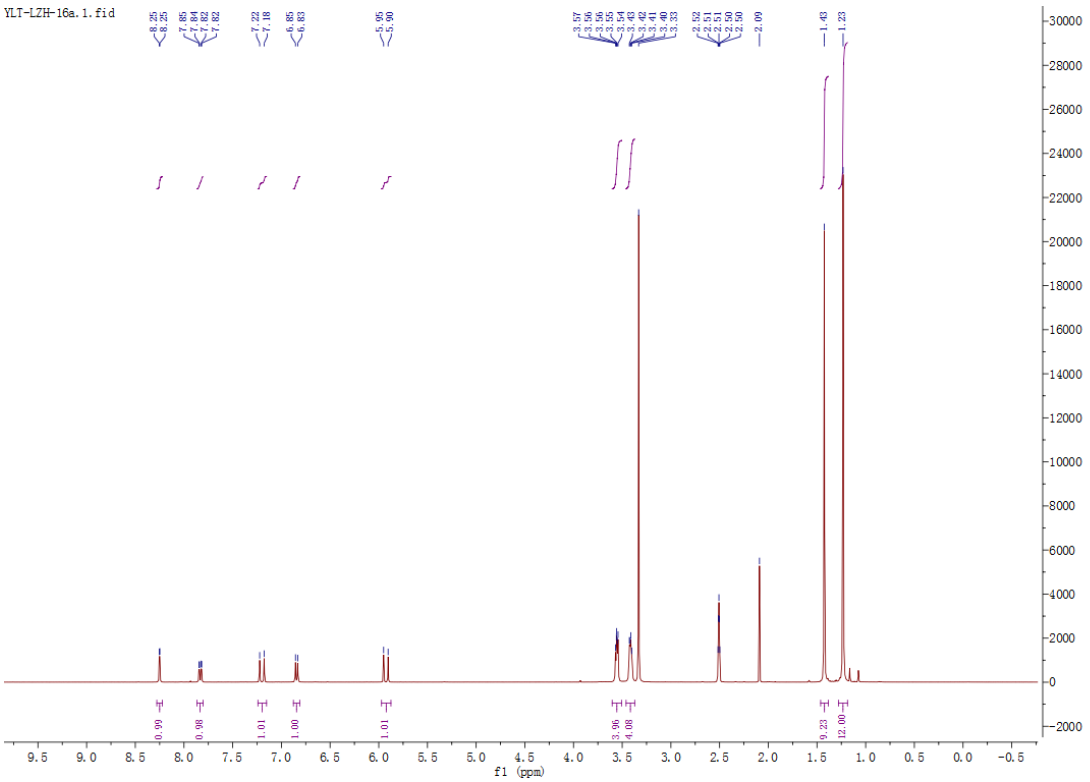
Tert-butyl-(E)-(5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridin-2-yl)carbamate (9N)







Tert-butyl-(E)-4-(5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridin-2-yl)piperazine-1-carboxylate (9O)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7.85
7.84
7.82
7.82
7.22
7.18
6.85
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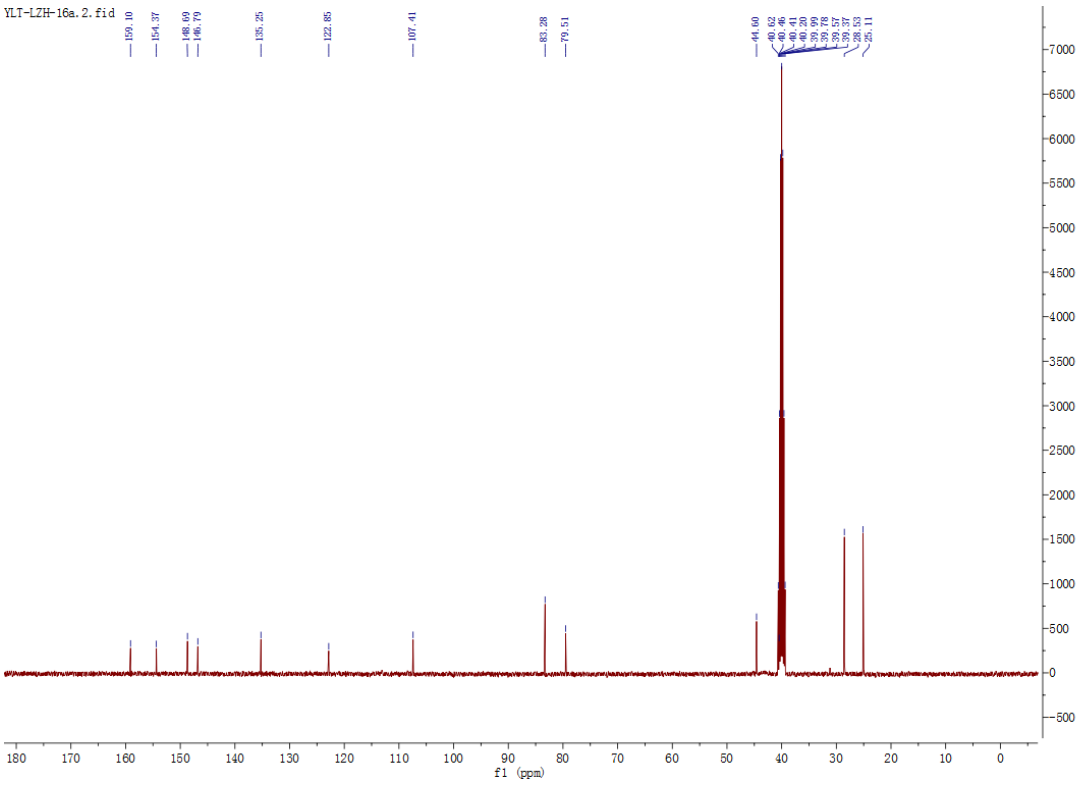
5.95
5.90
3.57
3.56
3.56
3.55
3.54
3.43
3.42
3.41
3.40
3.33
2.52
2.51
2.51
2.50
2.50
2.09
1.43
1.23
0.99
0.98
1.01
1.00
1.01
3.96
4.08
9.23
12.00
f1 (ppm)


YLT-LZH-16a.2.fid
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107.41
83.28
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40.46
40.41
40.20
39.99
39.78
39.57
39.37
26.53
25.11
f1 (ppm)