Supporting Information

for

Palladium-Catalyzed Desulfurative Sonogashira Cross-Coupling Reaction of 3-Cyano Assisted Thioamide-type Quinolone Derivatives with Alkynes

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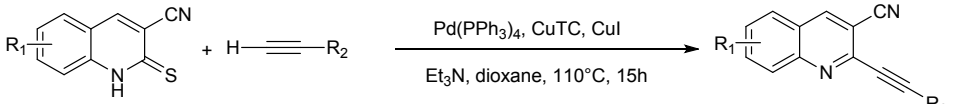
1. General Information

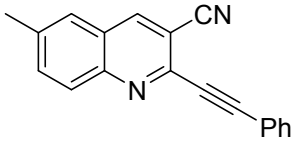
All reactions were run in 35 mL sealed tubes with standard Schlenk technique under argon atmosphere. 3-cyano-2-mercaptoquinolines **3** were prepared according to the method in ref 18[1] and **6a** was prepared according to the method in ref. 19[2]. Compounds **8a**–**d** were prepared from the reactions of their corresponding chlorides with thiourea by the conventional method. Solvents were used as-received. Other reagents were commercially available and used without further purification. NMR spectra were recorded on a Bruker AVIII-400 spectrometer at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. ^{1}H NMR Chemical shifts (in ppm) were internally referenced to TMS (δ = 0 ppm) in $CDCl_3$ and ^{13}C NMR chemical shifts were referenced to solvent peak of $CDCl_3$ (δ = 77.16 ppm). IR spectra were recorded on a Nexus 470 FTIR spectrometer and only major peaks were reported in cm^{-1}. All new products were further characterized by high resolution mass spectrometry (HRMS) with an APEX IV Fourier Transform Ion Cyclotron Resonance Mass Spectrometer equipped with an ESI source. Melting points were uncorrected. Column chromatography (CC) was performed on a silica gel (200–300 mesh) column. Thin layer Chromatography (TLC) was performed using glass plates coated with silica gel GF_{254} and visualized with UV light at 254/365 nm.

2. Preparation and characterization data of 2-alkynyl-quinoline-3-carbonitriles 5aa-5fa and 5ab-5am.

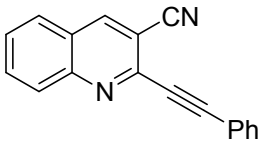


3(a-f) **4(a-m)** **5(aa-fa, ab-am)**

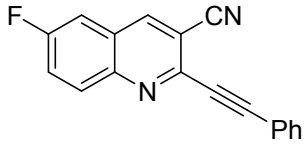
3-cyano-2-mercaptoquinolines (**3**, 0.5 mmol), CuTC (0.5 mmol, 1 equiv.), CuI (0.25 mmol, 0.5 equiv.), $Pd(PPh_3)_4$ (0.025 mmol, 5 mol%), alkynes (**4**, 1.5 mmol, 3 equiv.), Et_3N (3 mL) and dioxane (3 mL) were added to a 35 mL sealed tube and stirred at 110 °C for 15 hours under argon atmosphere. The reaction mixture was then cooled to room temperature, quenched with aqueous NH_4Cl (2 mL) and extracted with ethyl acetate twice. The organic extracts were combined, washed with aqueous NaOH (1M, 2mL) and brine and dried over anhydrous Na_2SO_4. The crude product of **5ai** was recrystallized in petroleum ether/ethyl acetate = 20:1 to afford the purified product. For other products, the crude products were purified by flash column chromatography on a silica gel column with petroleum ether/ethyl acetate = 10:1 as the eluent to afford the corresponding purified products.



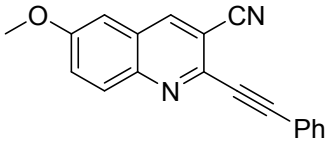
6-methyl-2-(phenylethynyl)quinoline-3-carbonitrile (5aa)[3]. Yellow solid (100 mg, 75%), mp = 136–139 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.05 (d, *J* = 8.7 Hz, 1H), 7.78 – 7.67 (m, 3H), 7.62 (s, 1H), 7.49 – 7.35 (m, 3H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 142.2, 141.4, 139.4, 135.7, 132.8, 130.1, 129.4, 128.7, 126.9, 125.2, 121.4, 116.7, 109.8, 95.3, 86.4, 21.8. MS (ESI) *m/z*: 269.1053 $(M+H)^+$.



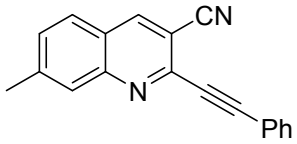
2-(phenylethynyl)quinoline-3-carbonitrile (5ba)[3]. Pale yellow solid (89 mg, 70%), mp = 159–160 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.97 – 7.82 (m, 2H), 7.76 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 143.1, 142.2, 133.3, 132.8, 130.2, 129.8, 128.8, 128.7, 128.2, 125.2, 121.3, 116.6, 109.9, 95.8, 86.4. MS (ESI) *m/z*: 255.0895 $(M+H)^+$.



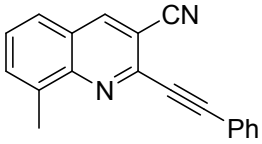
6-fluoro-2-(phenylethynyl)quinoline-3-carbonitrile (5ca). Yellow solid (92 mg, 67%), mp = 179–181 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.17 (dd, *J* = 9.2, 5.2 Hz, 1H), 7.74 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.65 (td, *J* = 9.3, 2.7 Hz, 1H), 7.50 (dd, *J* = 8.1, 2.6 Hz, 1H), 7.46 – 7.39 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 160.3, 146.0, 142.5, 141.4, 141.3, 132.8, 132.5, 132.4, 130.3, 128.7, 126.0, 125.8, 123.8, 123.5, 121.1, 116.2, 111.5, 111.2, 111.0, 96.0, 86.0. IR (cm^{-1}): 3066, 2212, 1555, 1486, 1375, 1351, 1216, 1151, 922, 837, 752, 688. HRMS (ESI) *m/z*: calcd for $C_{18}H_{10}FN_2$: $(M+H)^+$ = 273.08225; found: 273.08303.



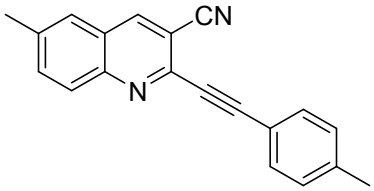
6-methoxy-2-(phenylethynyl)quinoline-3-carbonitrile (5da). Gray solid (100 mg, 70%), mp = 148–153 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.05 (d, *J* = 9.3 Hz, 1H), 7.74 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.52 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.09 (d, *J* = 2.7 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 145.1, 140.6, 140.4, 132.7, 131.2, 129.9, 128.7, 126.5, 126.4, 121.5, 116.8, 110.2, 105.2, 94.9, 86.4, 56.0. IR (cm^{-1}): 2958, 2215, 1487, 1469, 1376, 1245, 1113, 1056, 926, 836. HRMS (ESI) *m/z*: calcd for $C_{19}H_{13}N_2O$: $(M+H)^+$ = 285,10224; found: 285.10290.



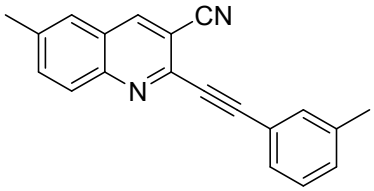
7-methyl-2-(phenylethynyl)quinoline-3-carbonitrile (5ea)[3]. Brown solid (99 mg, 74%), mp = 84–86 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 7.93 (s, 1H), 7.83 – 7.69 (m, 3H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.46 – 7.38 (m, 3H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 144.6, 143.2, 141.7, 132.8, 131.2, 130.1, 128.7, 128.7, 127.8, 123.3, 121.4, 116.8, 109.0, 95.5, 86.5, 22.4. MS (ESI) *m/z*: 269.1051 $(M+H)^+$.



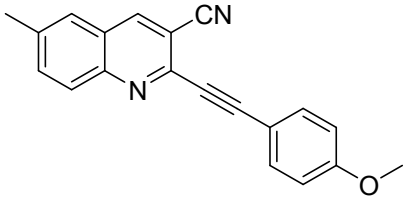
8-methyl-2-(phenylethynyl)quinoline-3-carbonitrile (5fa)[3]. White solid (86 mg, 64%), mp = 95–96 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.79 – 7.74 (m, 2H), 7.71 (dd, *J* = 11.8, 7.6 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.40 (m, 3H), 2.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 142.3, 142.0, 138.2, 133.4, 132.8, 130.0, 128.7, 128.6, 126.1, 125.2, 121.6, 116.9, 109.7, 95.2, 86.9, 18.1. MS (ESI) *m/z*: 269.1053 $(M+H)^+$.



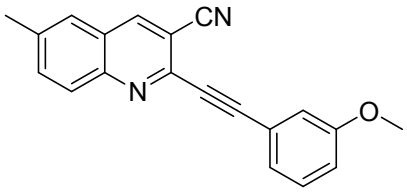
6-methyl-2-(p-methylphenylethynyl)quinoline-3-carbonitrile (5ab). Brown solid (103 mg, 73%), mp = 170–172 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.71 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.62 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.58 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 142.4, 141.4, 140.6, 139.2, 135.6, 132.7, 129.5, 129.4, 126.9, 125.2, 118.4, 116.8, 109.8, 95.9, 86.1, 21.8, 21.8. IR (cm^{-1}): 2958, 2920, 2851, 2225, 2207, 2137, 1422, 1281, 1075, 1020, 830, 812, 750. HRMS (ESI) *m/z*: calcd for $C_{20}H_{15}N_2$: $(M+H)^+$ = 283.12297; found: 283.12368.



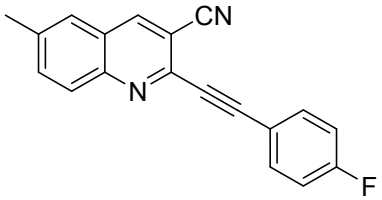
6-methyl-2-(m-methylphenylethynyl)quinoline-3-carbonitrile (5ac). Pale brown solid (100 mg, 71%), mp = 168–170 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.70 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.60 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.27 (dt, *J* = 12.6, 7.6 Hz, 2H), 2.57 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 142.2, 141.4, 139.3, 138.4, 135.7, 133.2, 131.0, 129.9, 129.3, 128.5, 126.8, 125.2, 121.2, 116.7, 109.7, 95.6, 86.1, 21.8, 21.4. IR (cm^{-1}): 3048, 2924, 2855, 2225, 2207, 1581, 1510, 1369, 1169, 924, 830, 814, 536, 438. HRMS (ESI) *m/z*: calcd for $C_{20}H_{15}N_2$: $(M+H)^+$ = 283.12297; found: 283.12373.



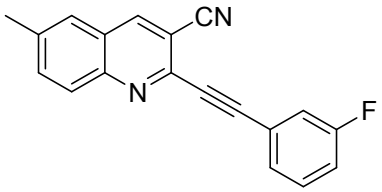
6-methyl-2-(p-methoxyphenylethynyl)quinoline-3-carbonitrile (5ad). Yellow solid (109 mg, 73%), mp = 167–169 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.76 – 7.63 (m, 3H), 7.60 (s, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 147.5, 142.5, 141.3, 139.0, 135.6, 134.5, 129.3, 126.9, 125.1, 116.8, 114.4, 113.4, 109.6, 96.0, 85.8, 55.5, 21.8. IR (cm^{-1}): 3052, 2928, 2840, 2225, 2211, 1607, 1582, 1512, 1294, 1252, 1164, 1021, 928, 823, 535. HRMS (ESI) *m/z*: calcd for $C_{20}H_{15}N_2O$: $(M+H)^+$ = 299.11789; found: 299.11872.



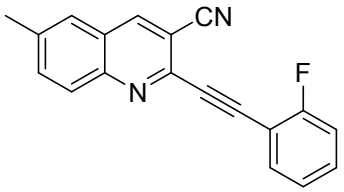
6-methyl-2-(m-methoxyphenylethynyl)quinoline-3-carbonitrile (5ae). Gray solid (102 mg, 68%), mp = 142–144 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.70 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.60 (s, 1H), 7.36 – 7.22 (m, 3H), 6.99 (ddd, *J* = 7.8, 2.5, 1.5 Hz, 1H), 3.84 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 147.4, 142.1, 141.3, 139.4, 135.7, 129.7, 129.3, 126.9, 125.3, 125.2, 122.3, 117.0, 117.0, 109.7, 95.2, 86.2, 55.5, 21.8. IR (cm^{-1}): 3051, 2939, 2835, 2218, 1601, 1574, 1552, 1483, 1423, 1317, 1293, 1231, 1049, 916, 830, 776, 685. HRMS (ESI) *m/z*: calcd for $C_{20}H_{15}N_2O$: $(M+H)^+$ = 299.11789; found: 299.11873.



6-methyl-2-(p-fluorophenylethynyl)quinoline-3-carbonitrile (5af). Yellow solid (99 mg, 69%), mp = 179–180 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.78 – 7.69 (m, 3H), 7.62 (s, 1H), 7.10 (t, *J* = 8.7 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 142.1, 141.4, 139.4, 135.8, 134.9, 134.8, 129.4, 126.9, 125.2, 117.6, 116.7, 116.3, 116.0, 109.7, 94.2, 86.3, 21.8. IR (cm^{-1}): 3060, 2215, 1587, 1507, 1485, 1368, 1223, 1157, 1092, 931, 828. HRMS (ESI) *m/z*: calcd for $C_{19}H_{12}FN_2$: $(M+H)^+$ = 287.09790; found: 287.09860.

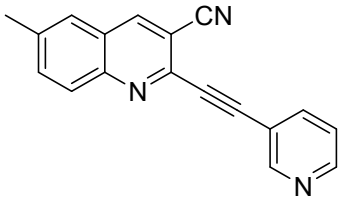


6-methyl-2-(m-fluorophenylethynyl)quinoline-3-carbonitrile (5ag). Pale brown solid (102 mg, 71%), mp = 148–149 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.73 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.64 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.39 (m, 2H), 7.15 (td, *J* = 8.4, 1.8 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 161.3, 147.5, 141.4, 139.6, 135.8, 130.4, 130.3, 129.5, 128.7, 126.9, 125.4, 119.5, 119.3, 117.4, 109.8, 93.5, 93.5, 87.0, 21.9. IR (cm^{-1}): 3056, 2959, 2929, 2873, 2226, 1579, 1485, 1372, 1284, 1216, 1138, 1072, 923, 858, 827, 780, 675, 574. HRMS (ESI) *m/z*: calcd for $C_{19}H_{12}FN_2$: $(M+H)^+$ = 287.09790; found: 287.09870.

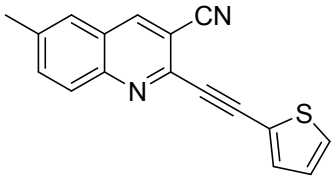


6-methyl-2-(o-fluorophenylethynyl)quinoline-3-carbonitrile (5ah). Pale brown solid (111 mg, 78%), mp = 160–163 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.64 (s, 1H), 7.43 (dd, *J* = 13.2, 6.4 Hz, 1H), 7.24 – 7.11 (m, 2H), 2.59

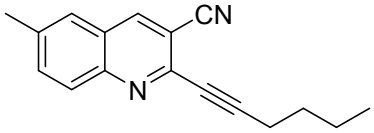
(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 162.2, 147.5, 141.5, 139.6, 135.7, 134.5, 132.0, 131.9, 129.5, 126.9, 125.4, 124.3, 124.3, 116.5, 116.1, 115.9, 110.2, 109.8, 88.4, 21.9. IR (cm^{-1}): 3048, 2924, 2854, 2214, 1577, 1550, 1496, 1448, 1364, 1263, 1222, 1109, 923, 835, 758, 576. HRMS (ESI) *m/z*: calcd for $C_{19}H_{12}FN_2$: $(M+H)^+$ = 287.09790; found: 287.09875.



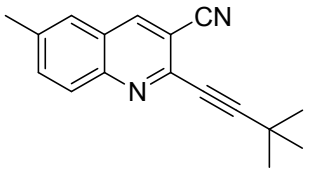
6-methyl-2-(pyridin-3-ylethynyl)quinoline-3-carbonitrile (5ai). White solid (62 mg, 46%), mp = 168–169 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.66 (d, *J* = 3.5 Hz, 1H), 8.48 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.65 (s, 1H), 7.36 (dd, *J* = 7.7, 5.0 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 150.2, 147.5, 141.5, 139.8, 139.6, 135.9, 129.5, 126.9, 125.4, 123.3, 116.6, 109.7, 91.3, 89.2, 21.9. IR (cm^{-1}): 3034, 2945, 2902, 2221, 1583, 1557, 1479, 1406, 1371, 1021, 826, 801, 700, 622. HRMS (ESI) *m/z*: calcd for $C_{18}H_{12}N_3$: $(M+H)^+$ = 270.10257; found: 270.10257.



6-methyl-2-(thiophen-2-ylethynyl)quinoline-3-carbonitrile (5aj). Brown oil (66 mg, 48%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.72 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.62 (s, 1H), 7.56 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.45 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.08 (dd, *J* = 5.1, 3.7 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 142.0, 141.5, 139.4, 135.8, 135.1, 130.1, 129.3, 127.6, 126.9, 125.2, 121.2, 116.5, 109.4, 90.2, 88.9, 21.8. IR (cm^{-1}): 2957, 2921, 2205, 1373, 1243, 1048, 830, 708. HRMS (ESI) *m/z*: calcd for $C_{17}H_{11}N_2S$: $(M+H)^+$ = 275.06375; found: 275.06441.

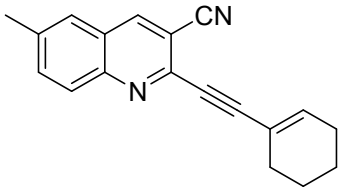


2-(hex-1-yn-1-yl)-6-methylquinoline-3-carbonitrile (5ak). Brown oil (60 mg, 48%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.68 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.59 (s, 1H), 2.61 – 2.54 (m, 5H), 1.76 – 1.66 (m, 2H), 1.62 – 1.51 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 142.6, 141.4, 138.9, 135.5, 129.2, 126.8, 125.1, 116.9, 109.6, 97.9, 78.3, 30.3, 22.2, 21.8, 19.4, 13.7. IR (cm^{-1}): 2922, 2851, 2231, 1373, 1242, 1047. HRMS (ESI) *m/z*: calcd for $C_{17}H_{17}N_2$: $(M+H)^+$ = 249.13862; found: 249.13848.



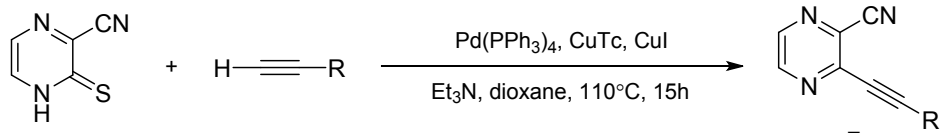
2-(3,3-dimethlybut-1-yn-1-yl)-6-methylquinoline-3-carbonitrile (5al). Pale yellow solid (97

mg, 78%), mp = 146–147 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.68 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.58 (s, 1H), 2.56 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 142.7, 141.3, 138.9, 135.5, 129.3, 126.8, 125.1, 116.8, 110.0, 105.7, 77.1, 30.5, 28.5, 21.8. IR (cm^{-1}): 3044, 2970, 2923, 2863, 2238, 2194, 1582, 1553, 1484, 1449, 1435, 1369, 1277, 937, 921, 826, 617. HRMS (ESI) *m/z*: calcd for $C_{17}H_{17}N_2$: $(M+H)^+$ = 249.13862; found: 249.13919.



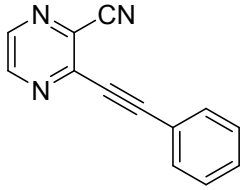
2-(cyclohex-1-en-1-ylethynyl)-6-methylquinoline-3-carbonitrile (5am). Brown solid (76 mg, 56%), mp = 99–100 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.58 (s, 1H), 6.55 (s, 1H), 2.56 (s, 3H), 2.34 (m, 2H), 2.20 (m, 2H), 1.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 142.6, 141.3, 140.3, 138.9, 135.5, 129.2, 126.8, 125.0, 119.9, 116.8, 109.7, 97.7, 84.3, 28.6, 26.2, 22.2, 21.8, 21.4. IR (cm^{-1}): 3052, 2933, 2862, 2227, 2202, 1674, 1585, 1436, 1371, 1260, 1137, 925, 827, 572. HRMS (ESI) *m/z*: calcd for $C_{19}H_{17}N_2$: $(M+H)^+$ = 273.13862; found: 273.13915.

3. Preparation and characterization data of 2-alkynyl-pyrazine-3-carbonitriles 7aa, 7ab, 7ad, 7af, 7ak, 7al, 7am.



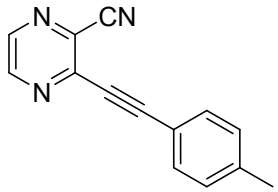
6a **4 (a,b,d,f,k,l,m)** **7 (aa,ab,ad,af,ak,al,am)**

3-cyano-2-mercaptopyrazine (**6a**, 0.5 mmol), CuTC (0.5 mmol, 1 equiv.), CuI (0.25 mmol, 0.5 equiv.), $Pd(PPh_3)_4$ (0.025 mmol, 5 mol%), alkynes (**4**, 1.5 mmol, 3 equiv.), Et_3N (3 mL) and dioxane (3 mL) were added to a 35 mL sealed tube and stirred at 110℃ for 15 hours under argon atmosphere. The reaction mixture was then cooled to room temperature, quenched with aqueous NH_4Cl (2 mL) and extracted with ethyl acetate twice. The organic extracts were combined, washed with aqueous NaOH (1M, 2mL) and brine and dried over anhydrous Na_sSO_4. The crude products were purified by flash column chromatography on a silica gel column with petroleum ether/ethyl acetate = 6:1 as eluent to afford the corresponding purified products.

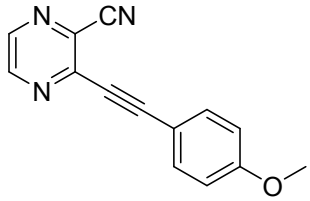


3-(phenylethynyl)pyrazine-2-carbonitrile (7aa). Yellow oil (90 mg, 88%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 2.2 Hz, 1H), 8.51 (d, *J* = 2.2 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.38 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 143.5, 142.7, 133.0, 132.8, 130.8, 128.8, 120.5, 115.0,

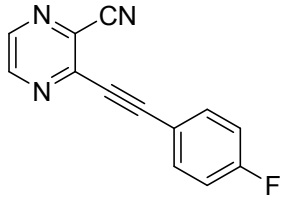
100.0, 83.7. IR (cm^{-1}): 2962, 2915, 2221, 2198, 1492, 1393, 1245, 1106, 1051, 799, 758, 689. HRMS (ESI) *m/z*: calcd for $C_{13}H_8N_3$: $(M+H)^+$ = 206.07127; found: 206.07124.



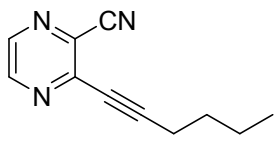
3-(p-methylphenylethynyl)pyrazine-2-carbonitrile (7ab). Brown solid (102 mg, 93%), mp = 123–124 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 2.4 Hz, 1H), 8.49 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 143.7, 142.5, 141.5, 132.9, 132.7, 129.6, 117.5, 115.0, 100.6, 83.4, 21.9. IR (cm^{-1}): 3073, 2969, 2923, 2216, 2195, 1518, 1444, 1390, 1176, 1106, 1057, 876, 820, 535. HRMS (ESI) *m/z*: calcd for $C_{14}H_{10}N_3$: $(M+H)^+$ = 220.08692; found: 220.08703.



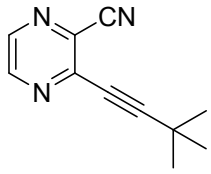
3-(p-methoxyphenylethynyl)pyrazine-2-carbonitrile (7ad). Yellow solid (78 mg, 66%), mp = 124–127 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.47 (s, 1H), 7.58 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 146.6, 143.8, 142.3, 134.6, 132.6, 115.1, 114.5, 112.5, 101.0, 83.2, 55.6. IR (cm^{-1}): 3079, 2962, 2841, 2236, 2215, 2194, 1599, 1508, 1444, 1388, 1296, 1250, 1165, 1107, 1019, 835, 540, 513. HRMS (ESI) *m/z*: calcd for $C_{14}H_{10}N_3O$: $(M+H)^+$ = 236.08184; found: 236.08191.



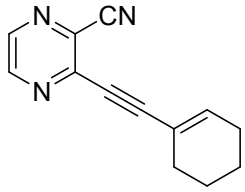
3-(p-fluorophenylethynyl)pyrazine-2-carbonitrile (7af). Brown solid (85 mg, 76%), mp = 97–99 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 2.3 Hz, 1H), 8.52 (d, *J* = 2.3 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 162.8, 146.6, 143.4, 142.8, 135.0, 134.9, 133.0, 116.7, 116.6, 116.5, 116.2, 114.9, 98.9, 83.5. IR (cm^{-1}): 3067, 2925, 2220, 2199, 1593, 1505, 1441, 1392, 1223, 1156, 1106, 843, 540, 483. HRMS (ESI) *m/z*: calcd for $C_{13}H_7FN_3$: $(M+H)^+$ = 224.06185; found: 224.06162.



3-(hex-1-yn-1-yl)pyrazine-2-carbonitrile (7ak)[4]. Brown oil (59 mg, 64%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.48 (s, 1H), 2.51 (t, *J* = 7.0 Hz, 2H), 1.67 – 1.57 (m, 2H), 1.52 – 1.41 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 143.7, 142.5, 132.9, 115.0, 103.2, 75.8, 29.9, 22.1, 19.5, 13.6. MS (ESI) *m/z*: 186.1013 $(M)^+$.

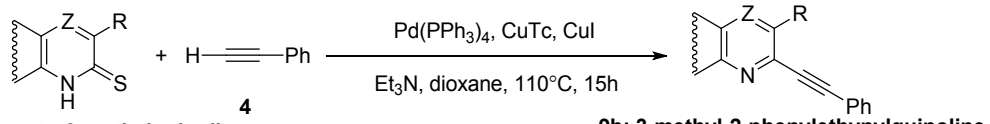


3-(3,3-dimethylbut-1-yn-1-yl)pyrazine-2-carbonitrile (7al). Yellow oil (84 mg, 91%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 8.47 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 143.7, 142.4, 133.2, 115.0, 110.5, 74.6, 30.2, 28.6.; IR (cm^{-1}): 2973, 2931, 2870, 2249, 2215, 1523, 1439, 1387, 1249, 1119, 1058, 935, 867, 513. HRMS (ESI) *m/z*: calcd for $C_{11}H_{12}N_3$: $(M+H)^+$ = 186.10257; found: 186.10252.



3-(cyclohex-1-en-1-ylethynyl)pyrazine-2-carbonitrile (7am). Brown oil (76 mg, 73%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 2.3 Hz, 1H), 8.47 – 8.42 (m, 1H), 6.50 (s, 1H), 2.23 (s, 2H), 2.14 (d, *J* = 3.0 Hz, 2H), 1.67 – 1.54 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 143.8, 142.2, 141.8, 132.7, 119.5, 115.0, 102.4, 81.6, 28.3, 26.2, 22.0, 21.2. IR (cm^{-1}): 2933, 2861, 2202, 1686, 1520, 1439, 1391, 1246, 1172, 1098. HRMS (ESI) *m/z*: calcd for $C_{13}H_{12}N_3$: $(M+H)^+$ = 210.10257; found: 210.10258.

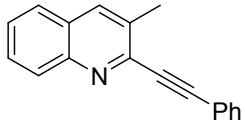
4. Preparation and characterization data of 3-methyl-2-phenylethynylquinoline 9b and 2-phenylethynylpyrazine 9c.



8b: 2-mercapto-3-methylquinoline
8c: 2-mercaptopyrazine

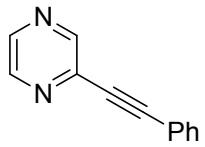
9b: 3-methyl-2-phenylethynylquinoline
9c: 2-phenylethynylpyrazine

Compound **8** (0.5 mmol), CuTC (0.5 mmol, 1 equiv.), CuI (0.25 mmol, 0.5 equiv.), $Pd(PPh_3)_4$ (0.025 mmol, 5 mol%), Phenylacetylene (**4a**, 1.5 mmol, 3 equiv.), Et_3N (3 mL) and dioxane (3 mL) were added to a 35 mL sealed tube stirred at 110℃ for 15 hours under argon atmosphere. The reaction mixture was then cooled to room temperature, quenched with aqueous NH_4Cl (2 mL) and extracted with ethyl acetate twice. The organic extracts were combined, washed with aqueous NaOH (1M, 2mL) and brine and dried over anhydrous Na_sSO_4. The crude product of **9b** was purified by flash column chromatography on a silica gel column with petroleum ether/ethyl acetate = 25:1 as eluent to afford the corresponding purified product **9b**. The crude product of **9c** was purified by flash column chromatography on a silica gel column with petroleum ether/ethyl acetate = 5:1 as eluent to afford the corresponding purified product **9c**.



3-methyl-2-(phenylethynyl)quinoline (9b)[5]. Brown oil (19 mg, 16%), ^{1}H NMR (400 MHz,

$CDCl_3$): δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.89 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.55 (m, 3H), 7.46 – 7.40 (m, 1H), 7.35 – 7.28 (m, 3H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 144.8, 135.4, 132.8, 132.3, 129.3, 129.2, 128.6, 127.7, 127.2, 126.9, 122.5, 93.6, 88.2, 20.0. MS (ESI) *m/z*: 244.1101 $(M+H)^+$.

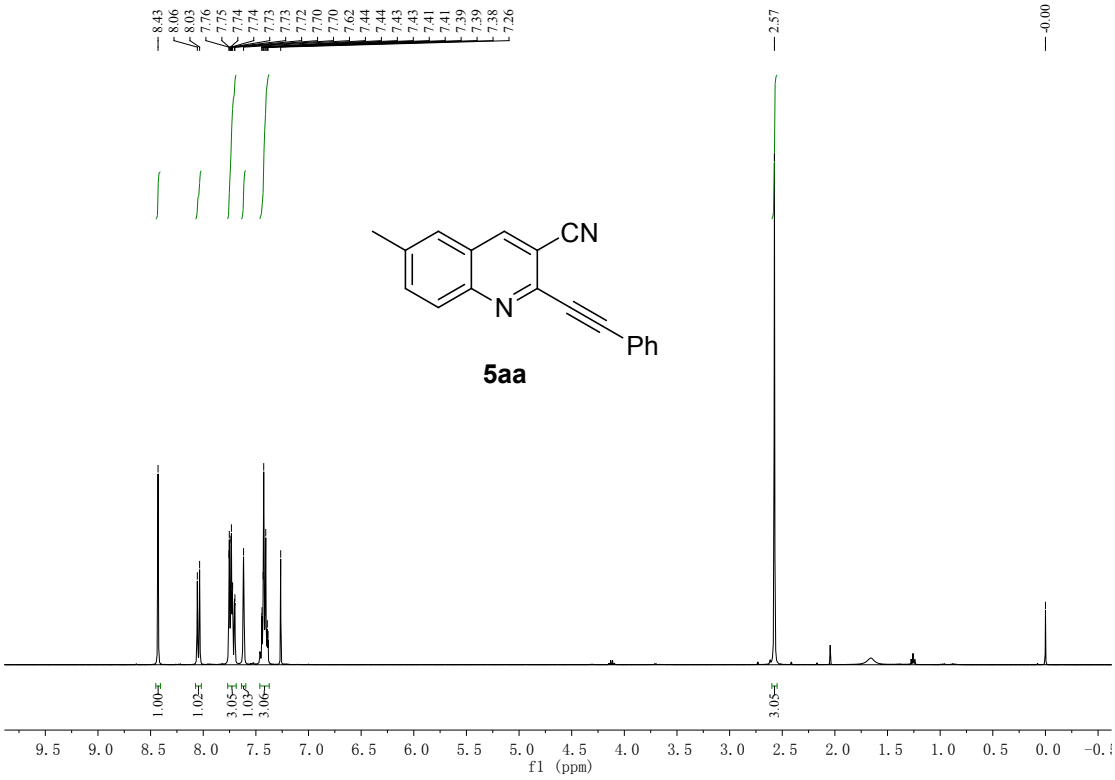


2-(phenylethynyl)pyrazine (9c)[6]. Brown oil (18 mg, 20%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, *J* = 1.3 Hz, 1H), 8.51 – 8.46 (m, 1H), 8.39 (d, *J* = 2.5 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.34 – 7.26 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 144.5, 142.9, 140.5, 132.2, 129.6, 128.6, 121.6, 93.3, 85.9. MS (ESI) *m/z*: 181.0746 $(M+H)^+$.

5. References

1. S. K. Nandeeshaiah and S. Y. Ambekar, *Indian J. Chem., Sect B*., 1994, **33B (4)**, 375–3799.
2. H. Hong, E. Goldstein, E. Stauffer, D. Goff, R. Kolluri, I. Darwish, R. Singh and H. Lu, Benzisothiazoles Useful for Treating or Preventing HCV Infection. WO2006091858(A1), August 31, **2006**.
3. A. Chandra, B. Singh, S. Upadhyay, and R. M. Singh, *Tetrahedron,* 2008, **64**, 11680–11685.
4. T. Yagihara, H. Hatano and N. Furukawa, Preparation of Substituted 2-cyanopyrazines. Jpn. Kokai Tokkyo Koho JP 01172377 A 19890707, **1989**.
5. M. A. Ciufolini, J. W. Mitchell and F. Roschangar, *Tetrahedron Lett.,* 1996*,* **37***,* 8281–8284.
6. S. Saleh, M. Picquet, P. Meunier and J.-C. Hierso, *Tetrahedron,* 2009*,* **65***,* 7146–7150.

6. ^{1}H NMR and ^{13}C NMR Spectra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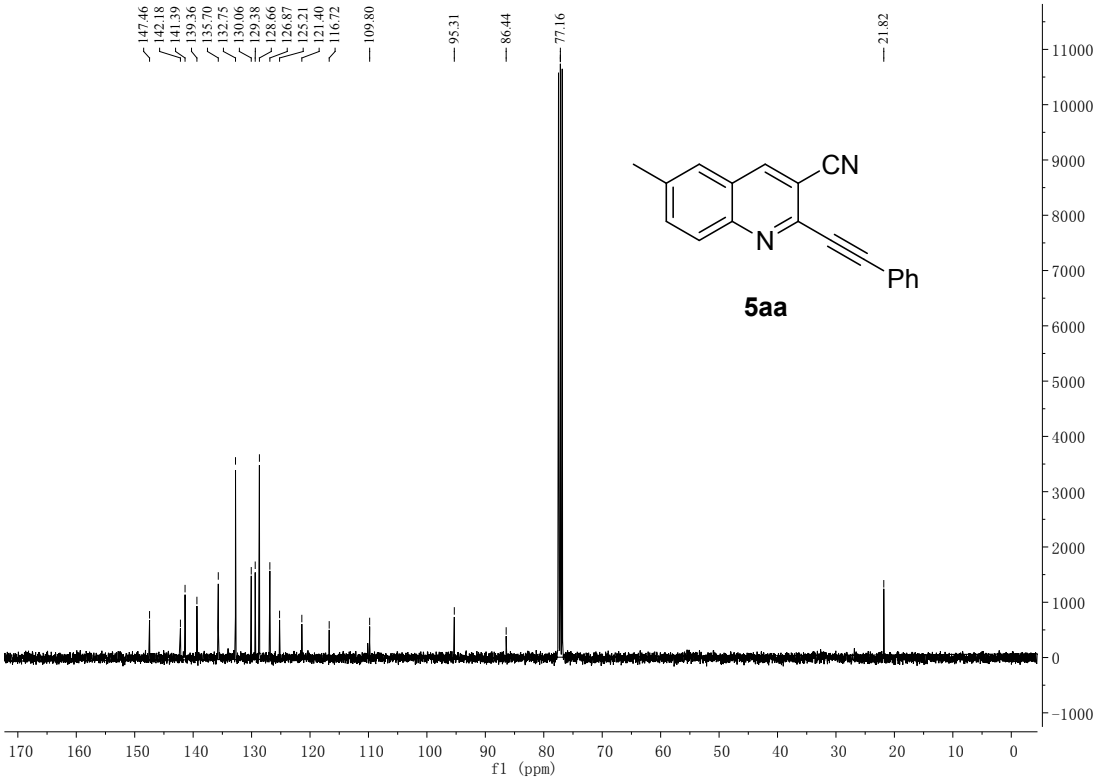
7.74
7.74
7.73
7.73
7.72
7.70
7.70
7.62
7.44
7.44
7.43
7.43
7.41
7.41
7.39
7.39
7.38
7.26
2.57
-0.00
CN
N
Ph
5aa
1.00
1.02
3.05
1.03
3.06
3.05
f1 (ppm)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128.66
126.87
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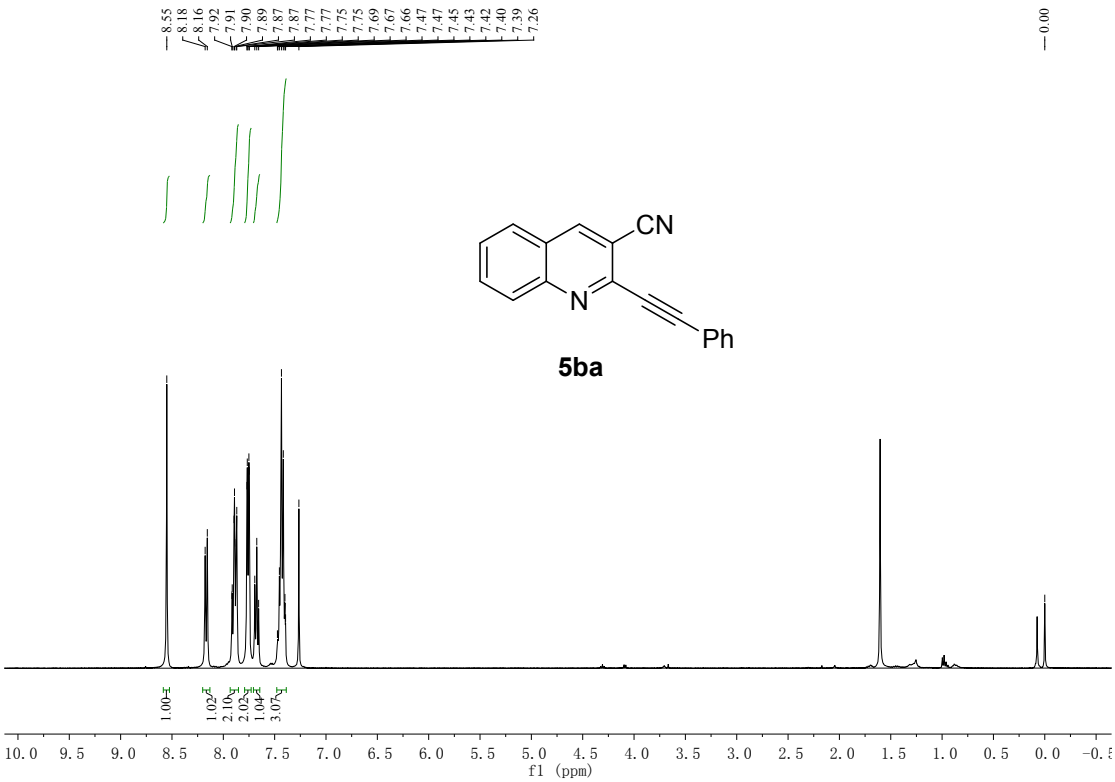
21.82
CN
N
Ph
5aa
f1 (ppm)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7.69
7.67
7.66
7.47
7.45
7.43
7.42
7.40
7.39
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N
Ph
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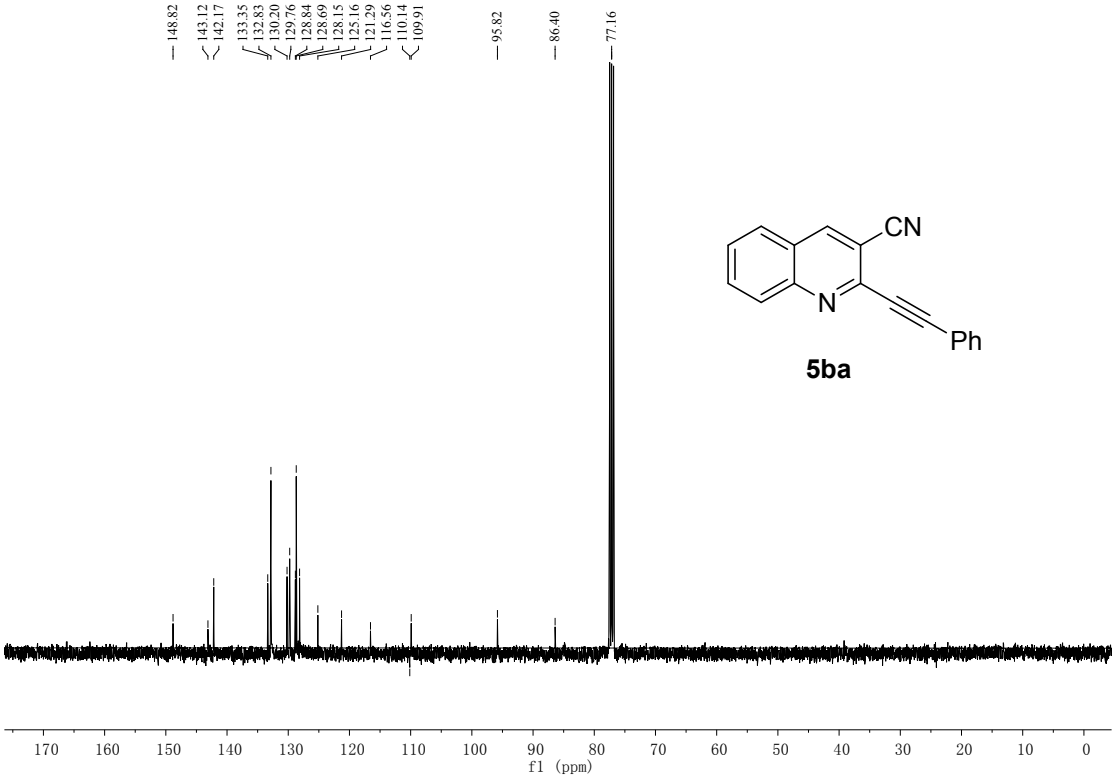
2.10
2.02
1.04
3.07
f1 (ppm)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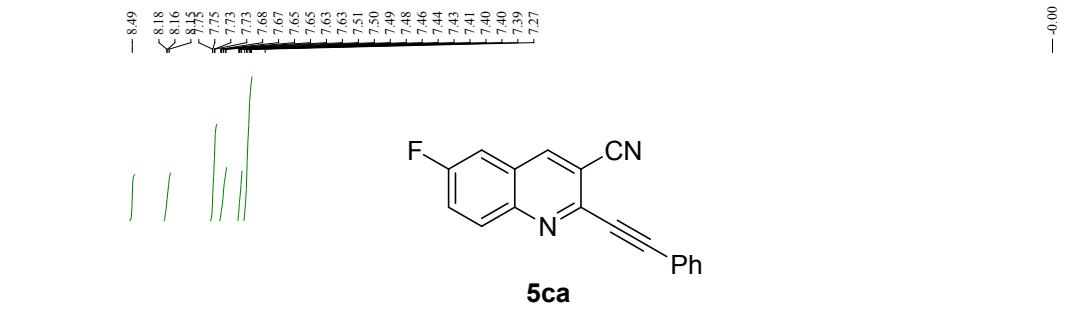
CN
N
Ph
5ba
f1 (ppm)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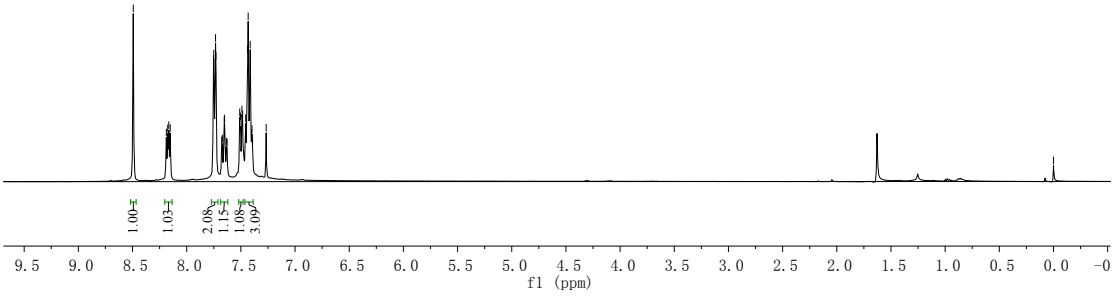
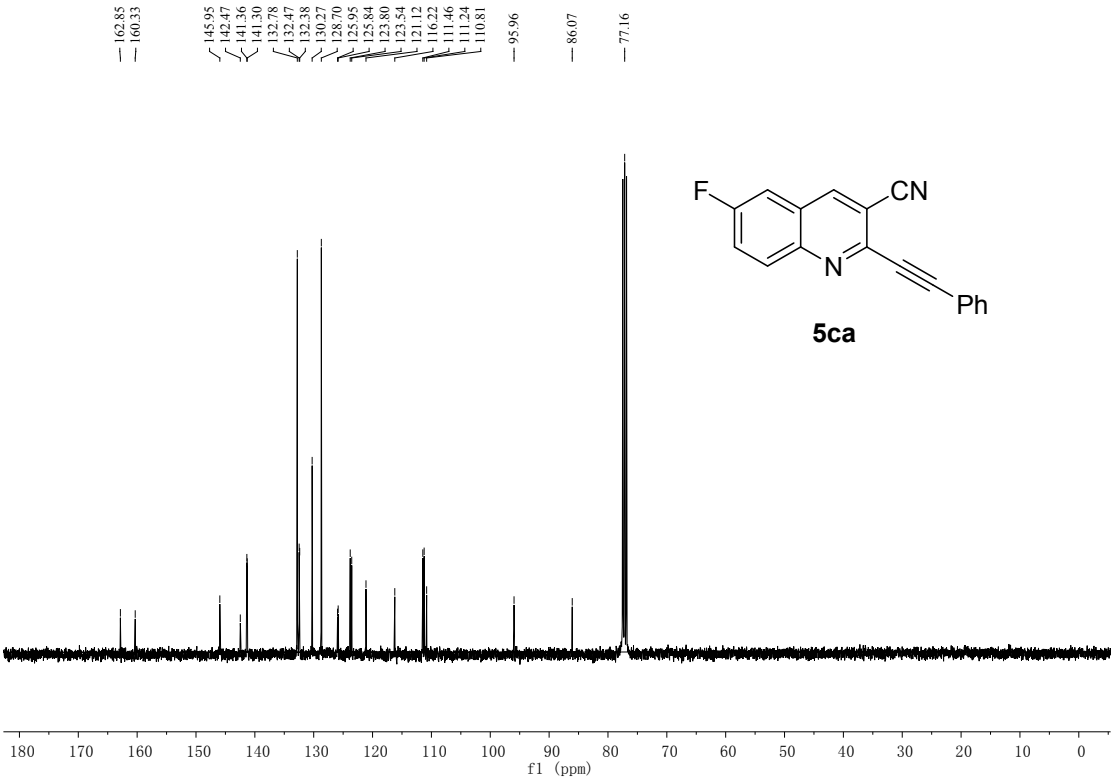
F
CN
N
Ph

5ca


1.00
1.03
2.08
1.15
1.08
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


162.85
160.33
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142.47
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132.47
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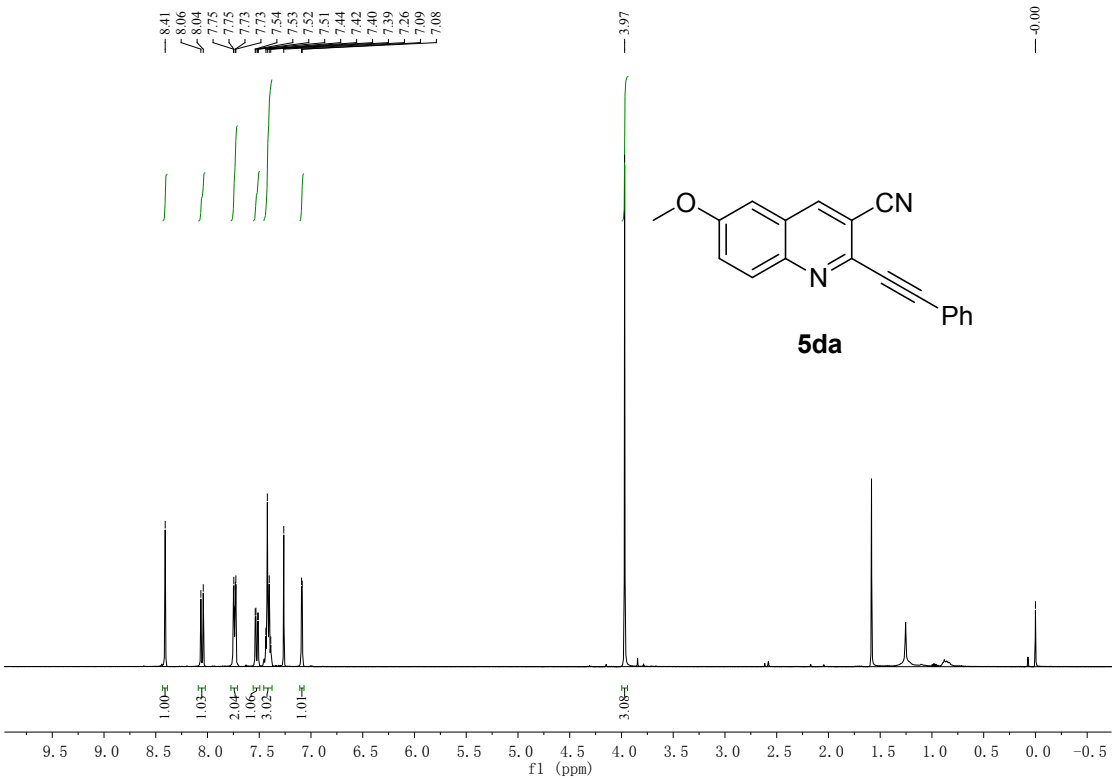
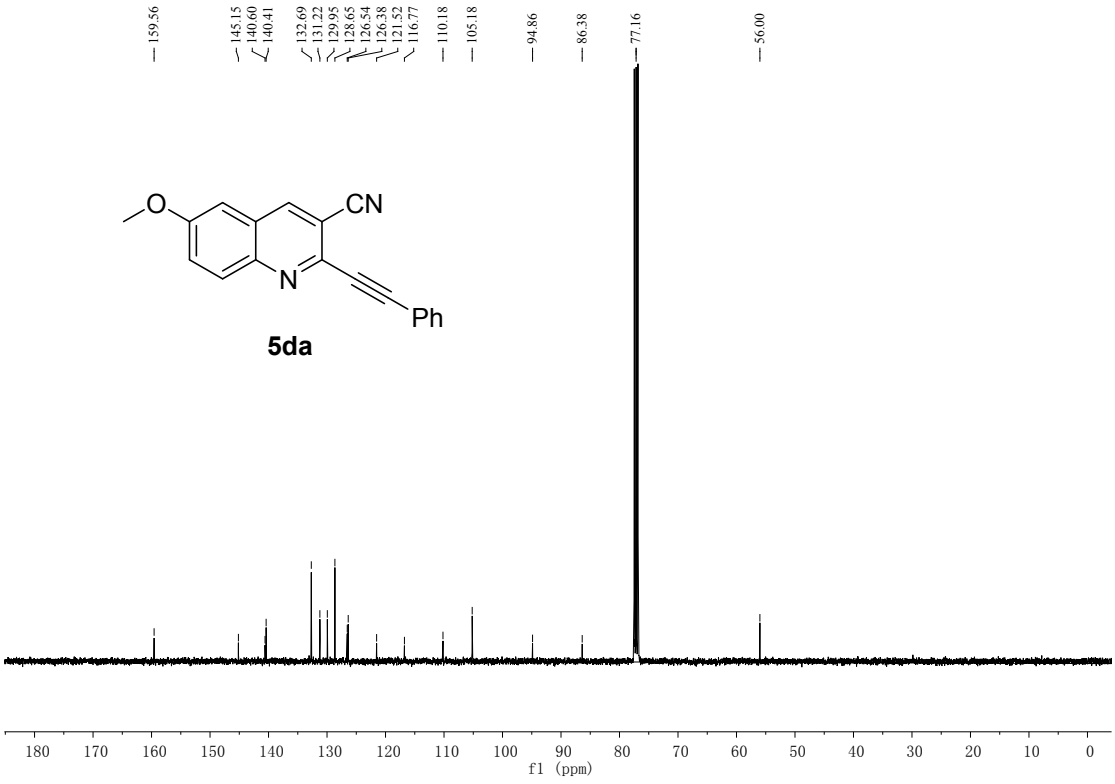
130.27
128.70
125.95
125.84
123.80
123.54
121.12
116.22
111.46
111.24
110.81
95.96
86.07
77.16
F
CN
N
Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

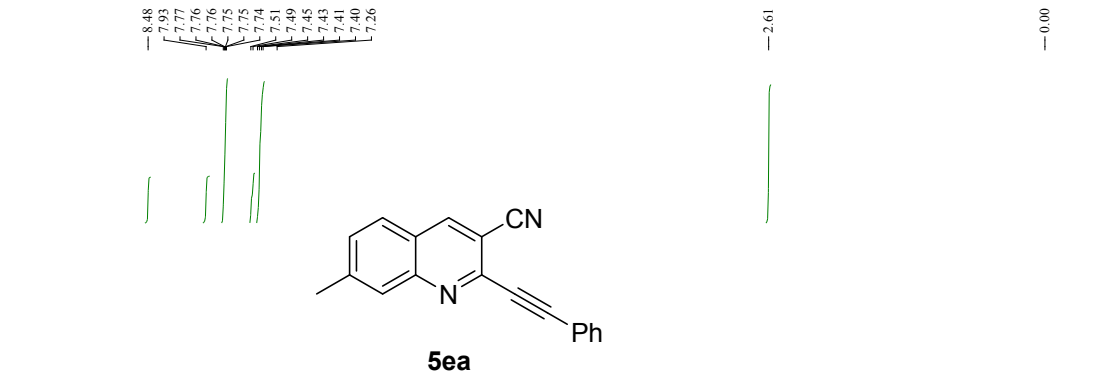
5ca


8.41
8.06
8.04
7.75
7.75
7.73
7.73
7.54
7.53
7.52
7.51
7.44
7.42
7.40
7.39
7.26
7.09
7.08
3.97
-0.00
O
CN
N
Ph
1.00
1.03
2.04
1.06
3.02
1.01
3.08
f1 (ppm)

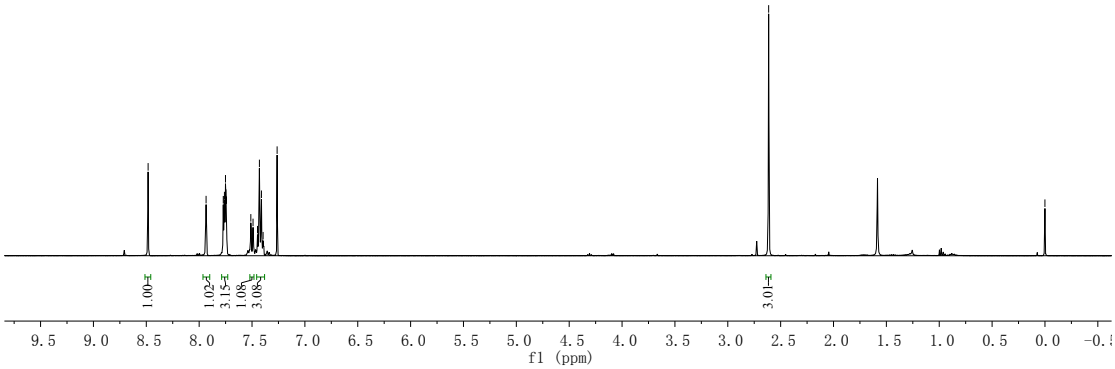
5da

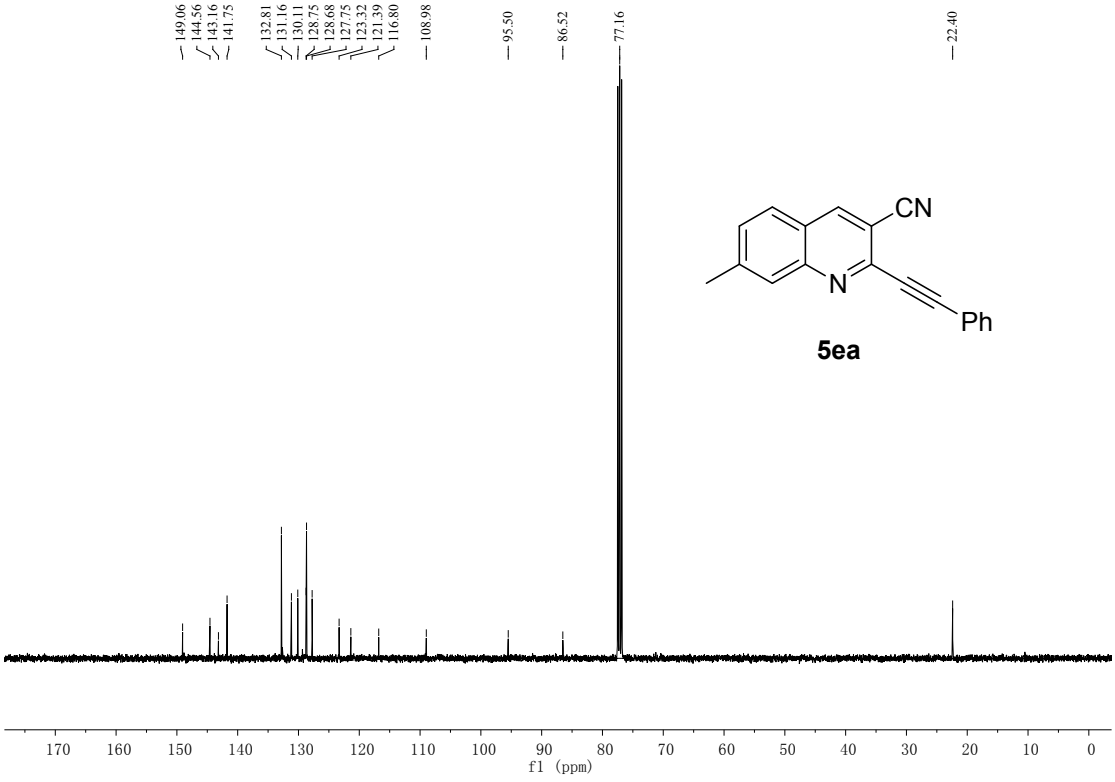

159.56
145.15
140.60
140.41
132.69
131.22
129.95
128.65
126.54
126.38
121.52
116.77
110.18
105.18
94.86
86.38
77.16
56.00
O
CN
N
Ph
f1 (ppm)

5da

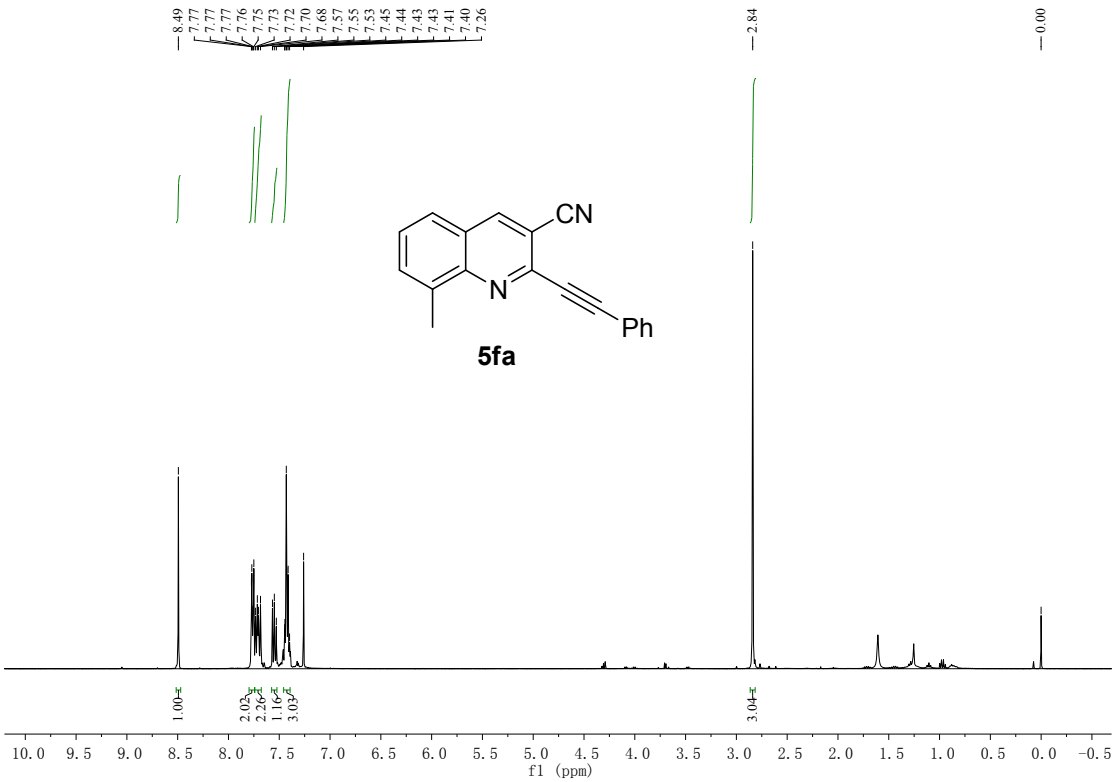

8.48
7.93
7.77
7.76
7.76
7.75
7.75
7.74
7.51
7.49
7.45
7.43
7.41
7.40
7.26
2.61
0.00
CN
N
Ph

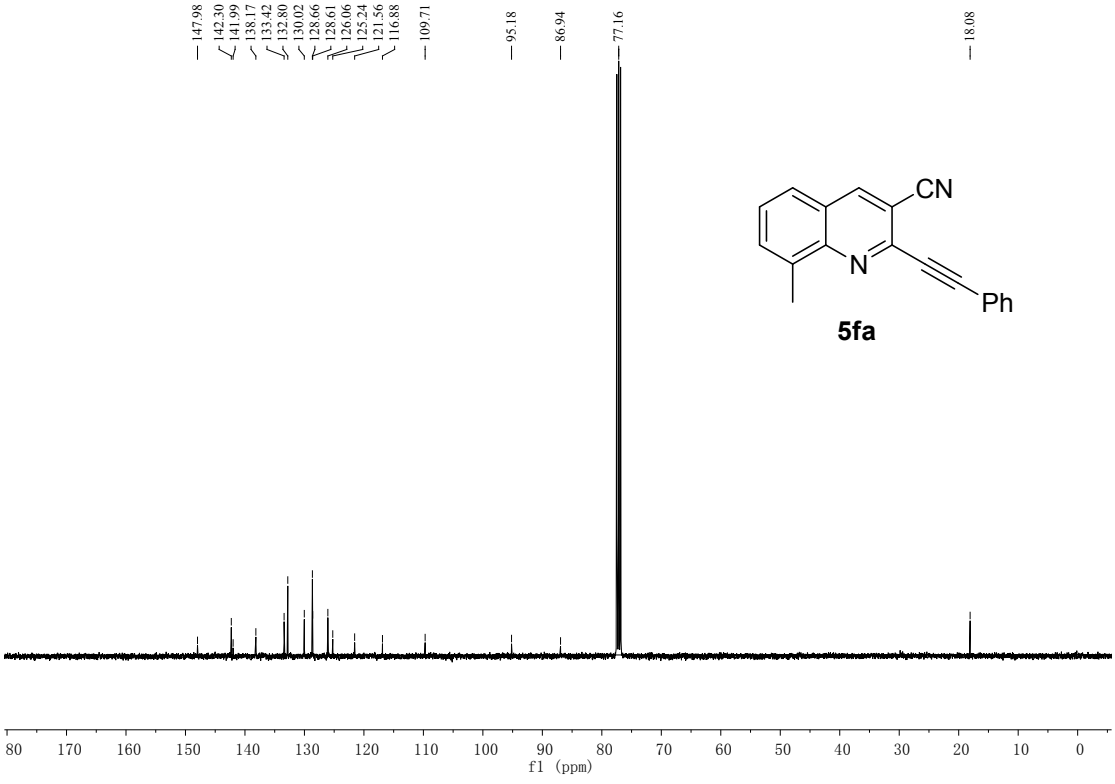
5ea

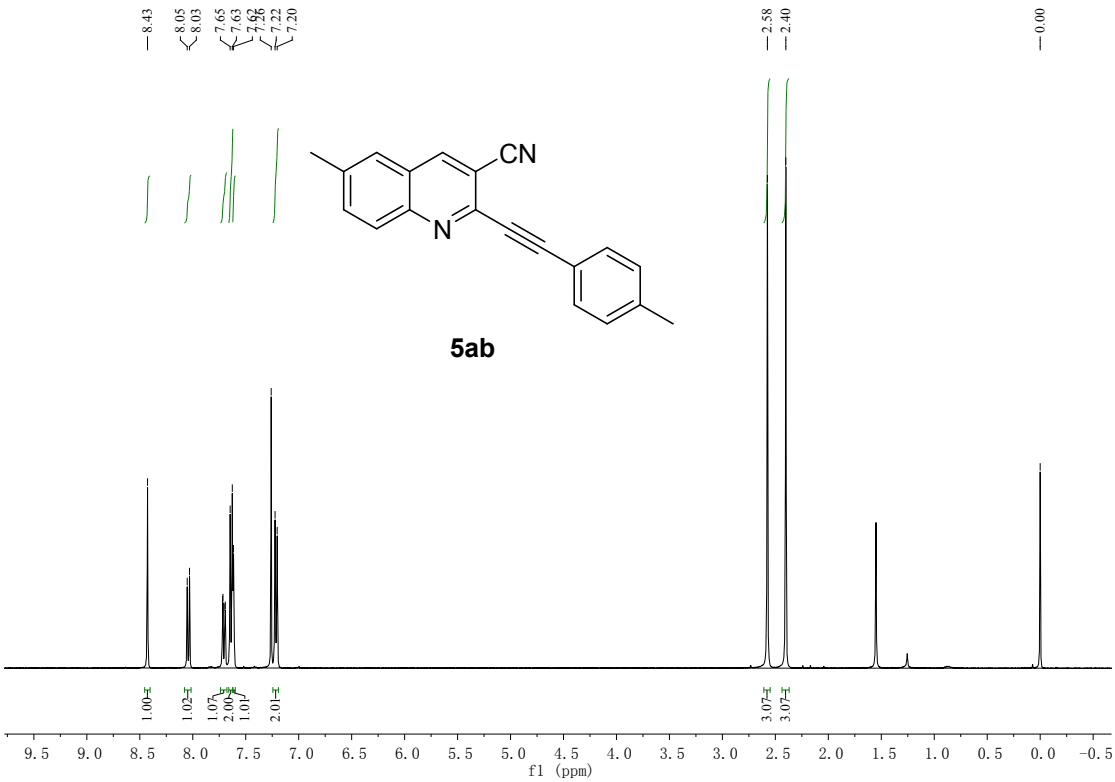

1.00
1.02
3.15
1.06
3.06
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.06
144.56
143.16
141.75
132.81
131.16
130.11
128.75
128.68
127.75
123.32
121.39
116.80
108.98
95.50
86.52
77.16
22.40
CN
N
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

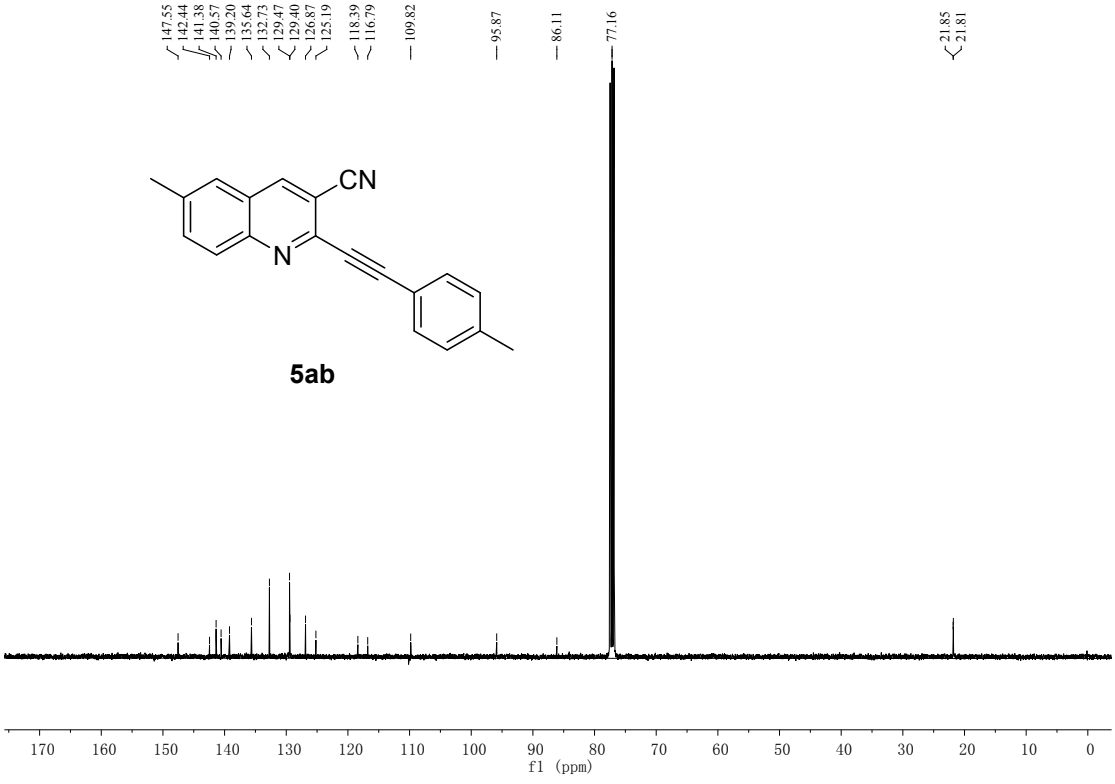
5ea


8.49
7.77
7.77
7.77
7.76
7.75
7.73
7.72
7.70
7.68
7.57
7.55
7.53
7.45
7.44
7.43
7.43
7.41
7.40
7.26
2.84
0.00
CN
N
Ph
5fa
1.00
2.02
2.26
1.16
3.03
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

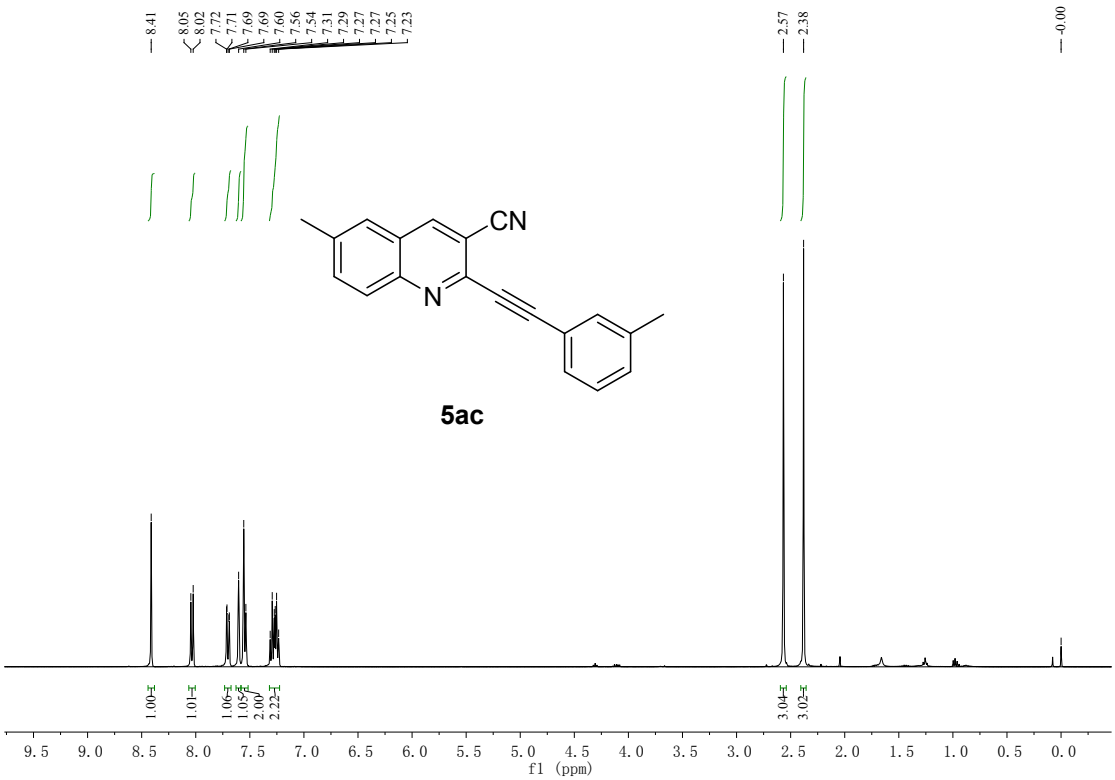

147.98
142.30
141.99
138.17
133.42
132.80
130.02
128.66
128.61
126.06
125.24
121.56
116.88
109.71
95.18
86.94
77.16
18.08
CN
N
Ph
5fa
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.43
8.05
8.03
7.65
7.63
7.62
7.26
7.22
7.20
2.58
2.40
0.00
CN
N
1.00
1.02
1.07
2.00
1.01
2.01
3.07
3.07
f1 (ppm)

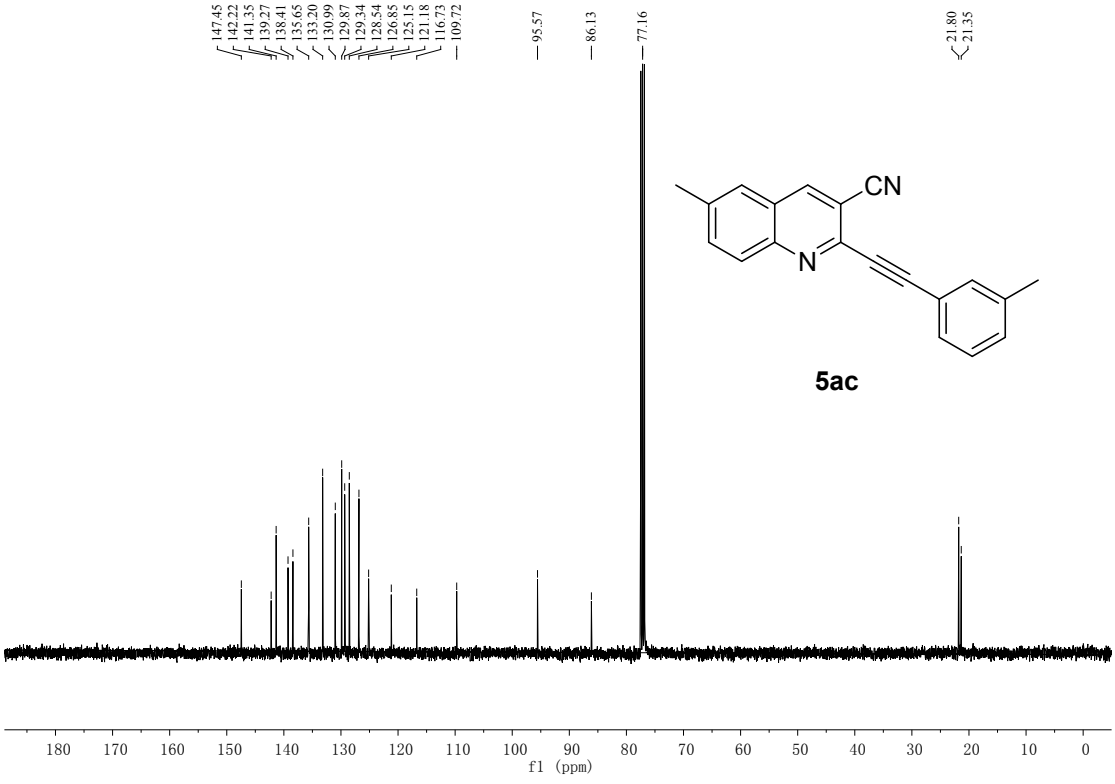
5ab


147.55
142.44
141.38
140.57
139.20
135.64
132.73
129.47
129.40
126.87
125.19
118.39
116.79
109.82
95.87
86.11
77.16
21.85
21.81
CN
N
f1 (ppm)

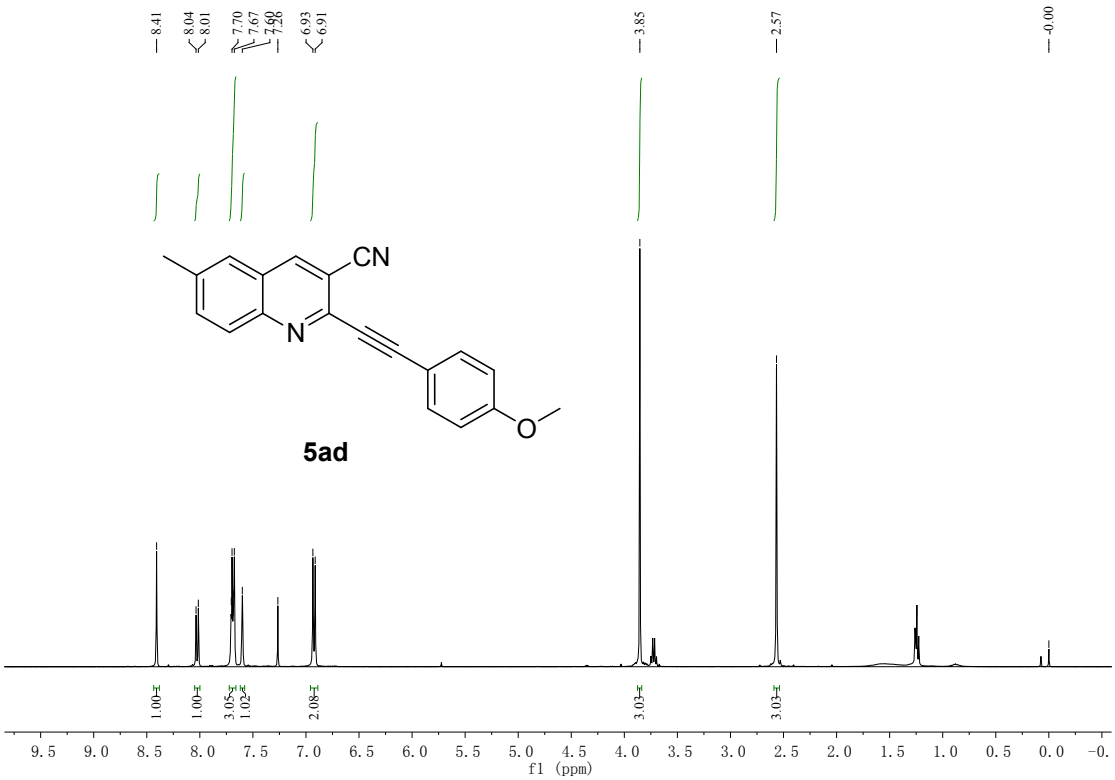
5ab

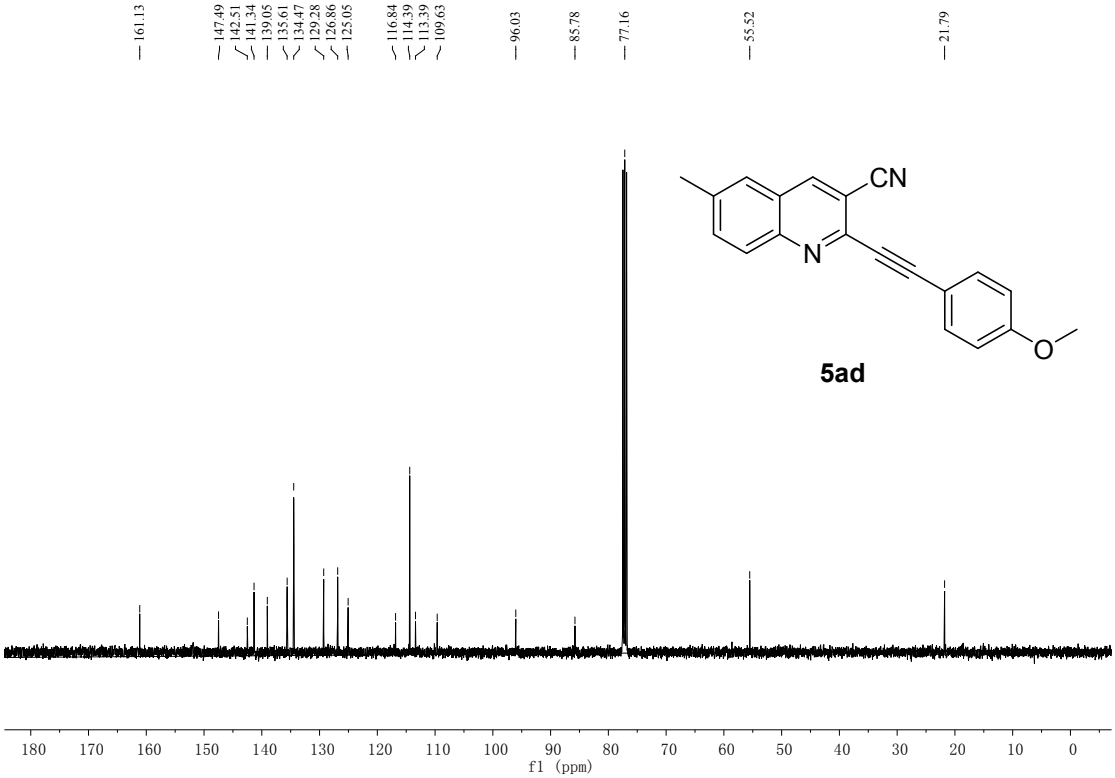

8.41
8.05
8.02
7.72
7.71
7.69
7.69
7.60
7.56
7.54
7.31
7.29
7.27
7.27
7.25
7.23
2.57
2.38
0.00
CN
N
1.00
1.01
1.06
1.05
2.00
2.23
3.04
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

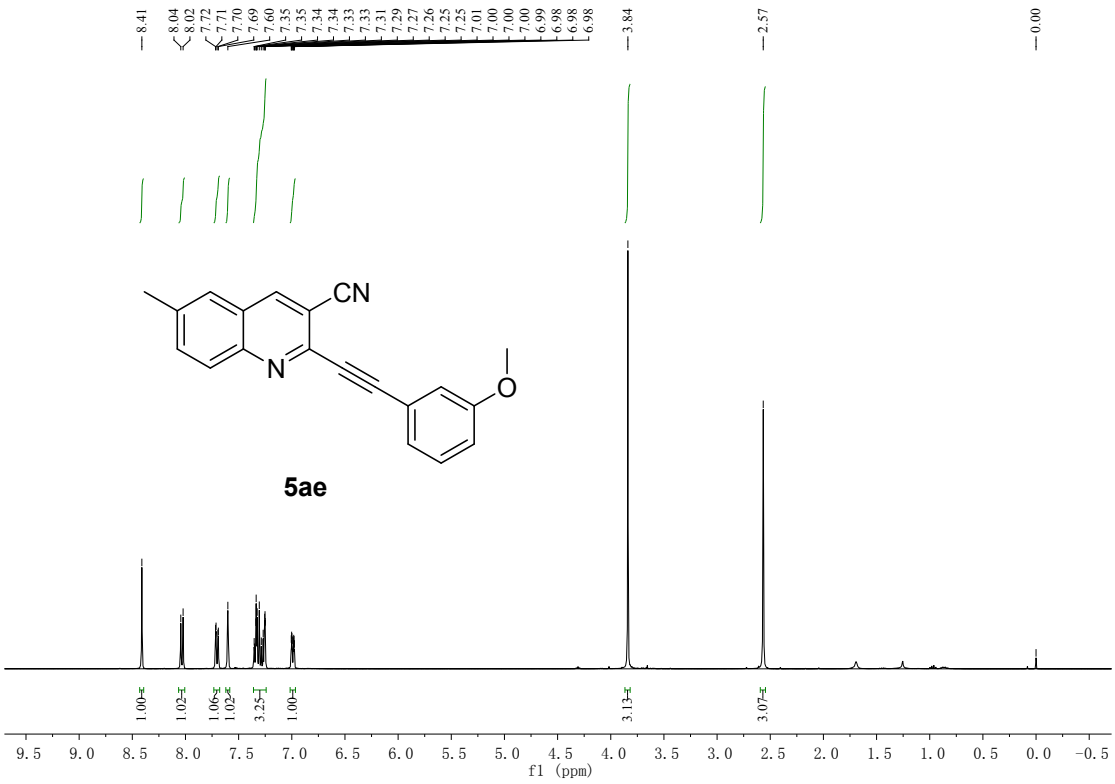
5ac

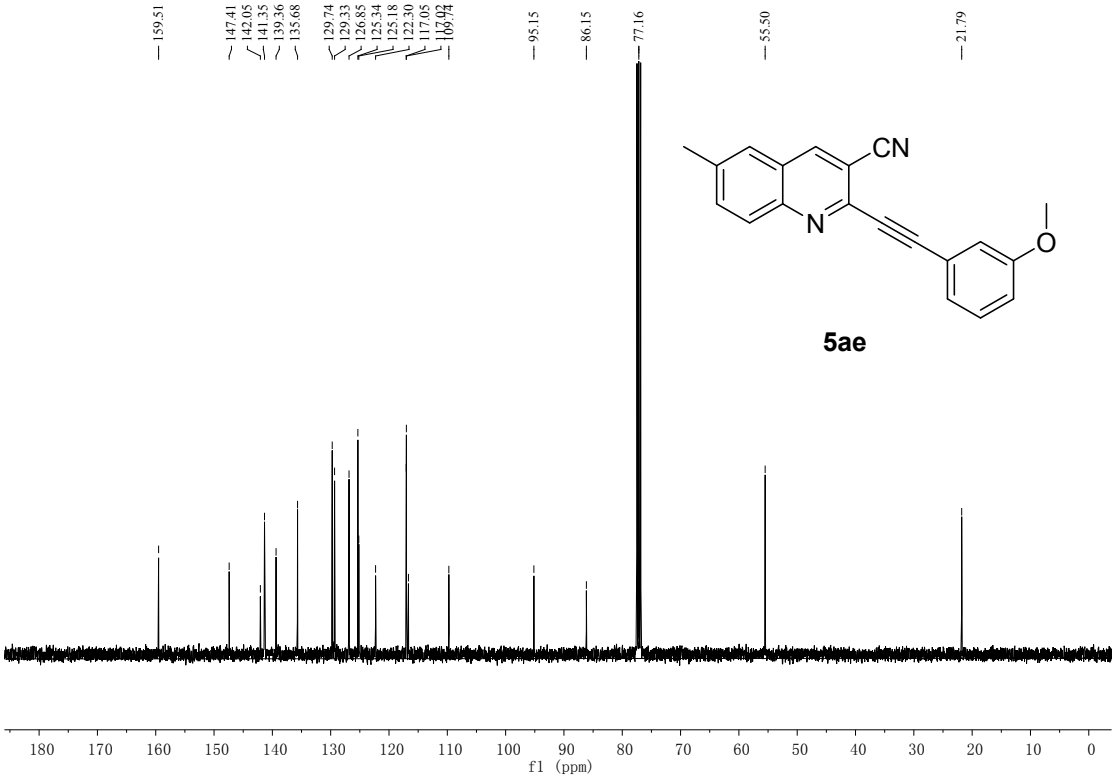

147.45
142.22
141.35
139.27
138.41
135.65
133.20
130.99
129.87
129.34
128.54
126.85
125.15
121.18
116.73
109.72
95.57
86.13
77.16
21.80
21.35
CN
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5ac


8.41
8.04
8.01
7.70
7.67
7.48
7.46
6.93
6.91
3.85
2.57
-0.00
CN
N
O
5ad
1.00
1.00
3.05
1.02
2.08
3.03
3.03
f1 (ppm)


161.13
147.49
142.51
141.34
139.05
135.61
134.47
129.28
126.86
125.05
116.84
114.39
113.39
109.63
96.03
85.78
77.16
55.52
21.79
CN
N
O
5ad
f1 (ppm)


8.41
8.04
8.02
7.72
7.71
7.70
7.69
7.60
7.35
7.35
7.34
7.34
7.33
7.31
7.29
7.27
7.26
7.25
7.25
7.01
7.00
7.00
7.00
6.99
6.98
6.98
6.98
3.84
2.57
0.00
CN
N
O
5ae
1.00
1.02
1.06
1.02
3.25
1.00
3.13
3.07
f1 (ppm)


159.51
147.41
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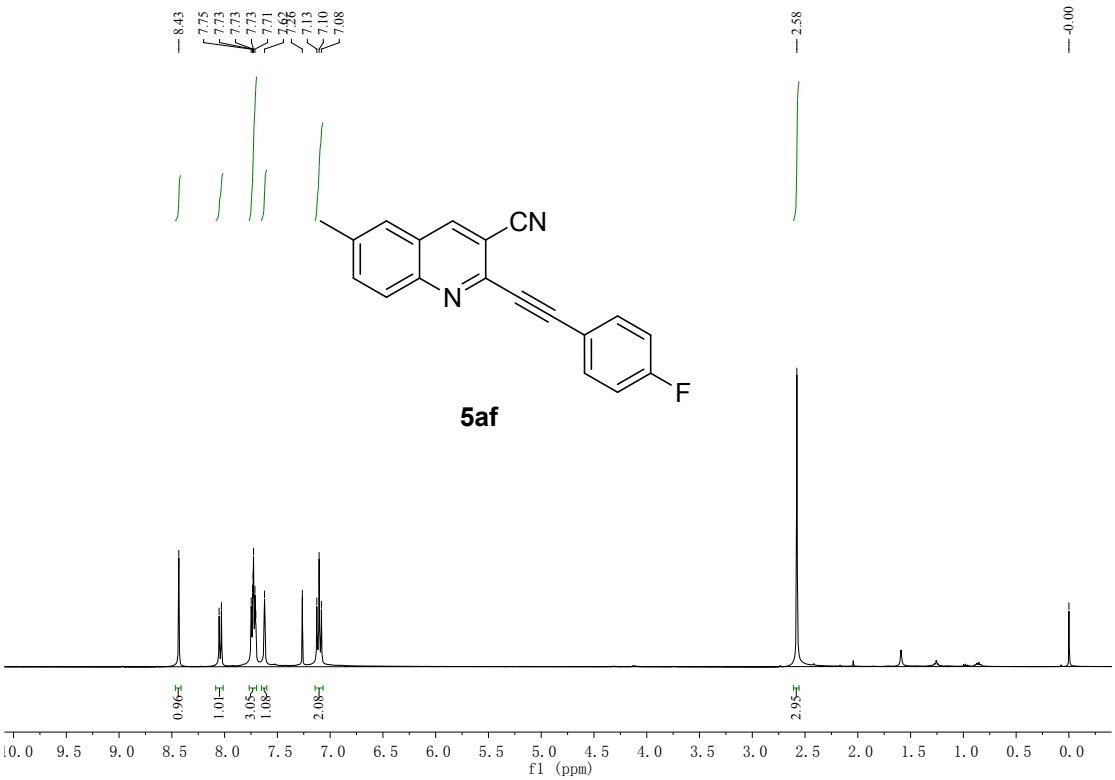
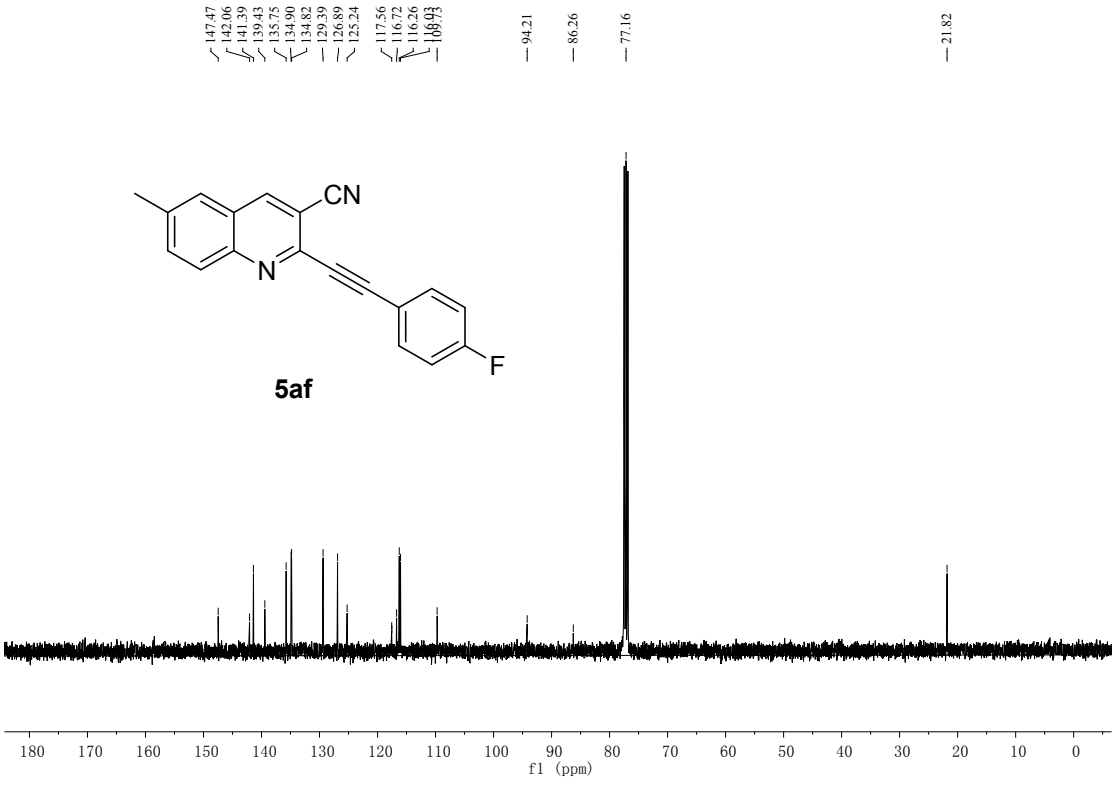
141.35
139.36
135.68
129.74
129.33
126.85
125.34
125.18
122.30
117.05
95.15
86.15
77.16
55.50
21.79
CN
N
O
5ae
f1 (ppm)


8.43
7.75
7.73
7.73
7.73
7.71
7.26
7.13
7.10
7.08
2.58
0.00
CN
N
F
5af
0.96
1.01
3.05
1.08
2.08
2.95
f1 (ppm)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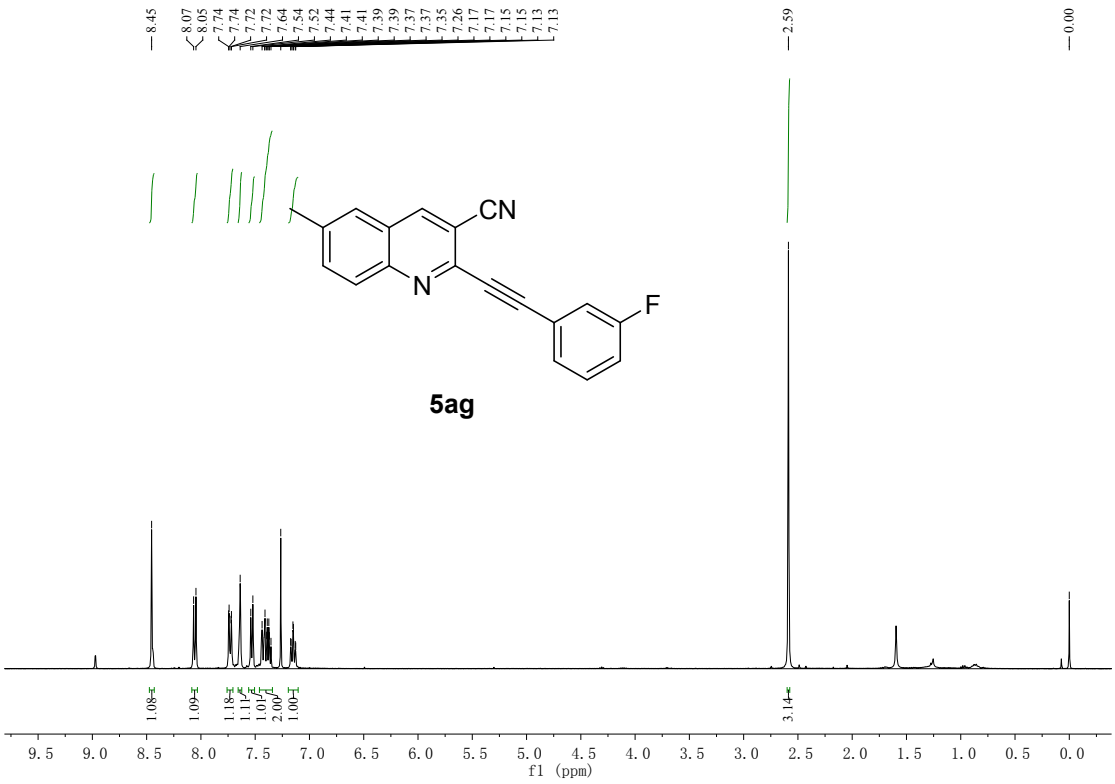
142.06
141.39
139.43
135.75
134.90
134.82
129.39
126.89
125.24
117.56
116.72
116.26
94.21
86.26
77.16
21.82
CN
N
F
5af
f1 (ppm)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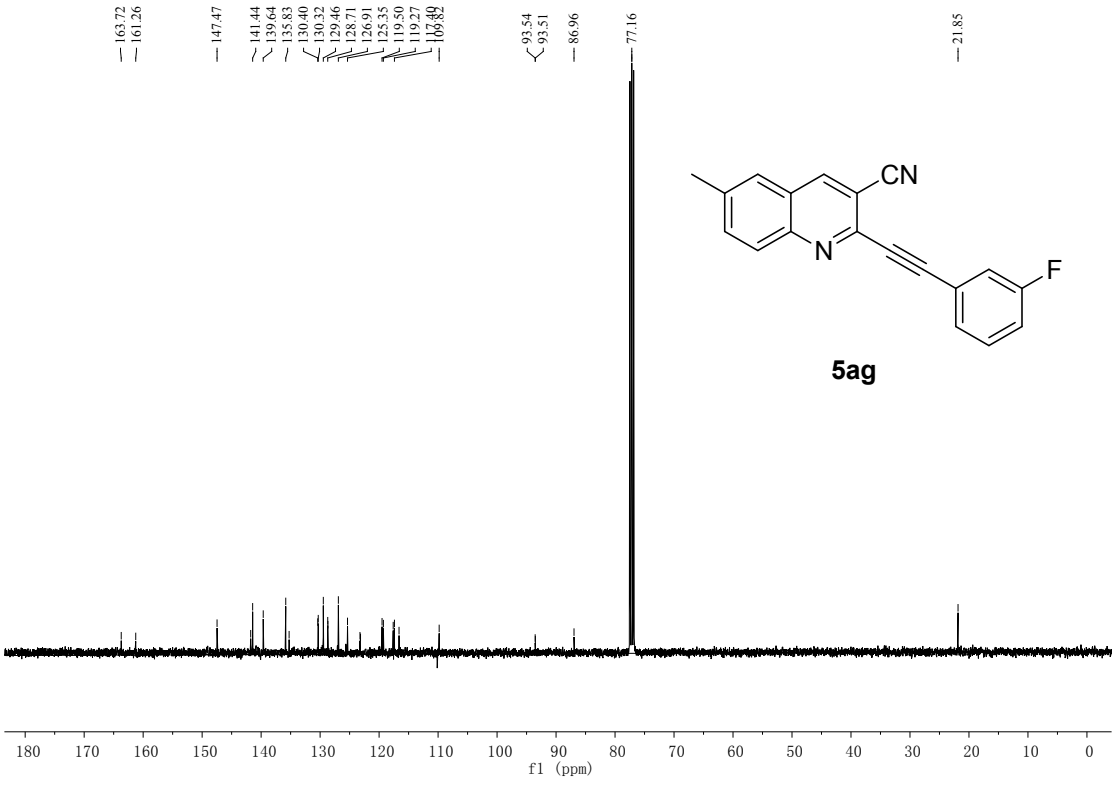
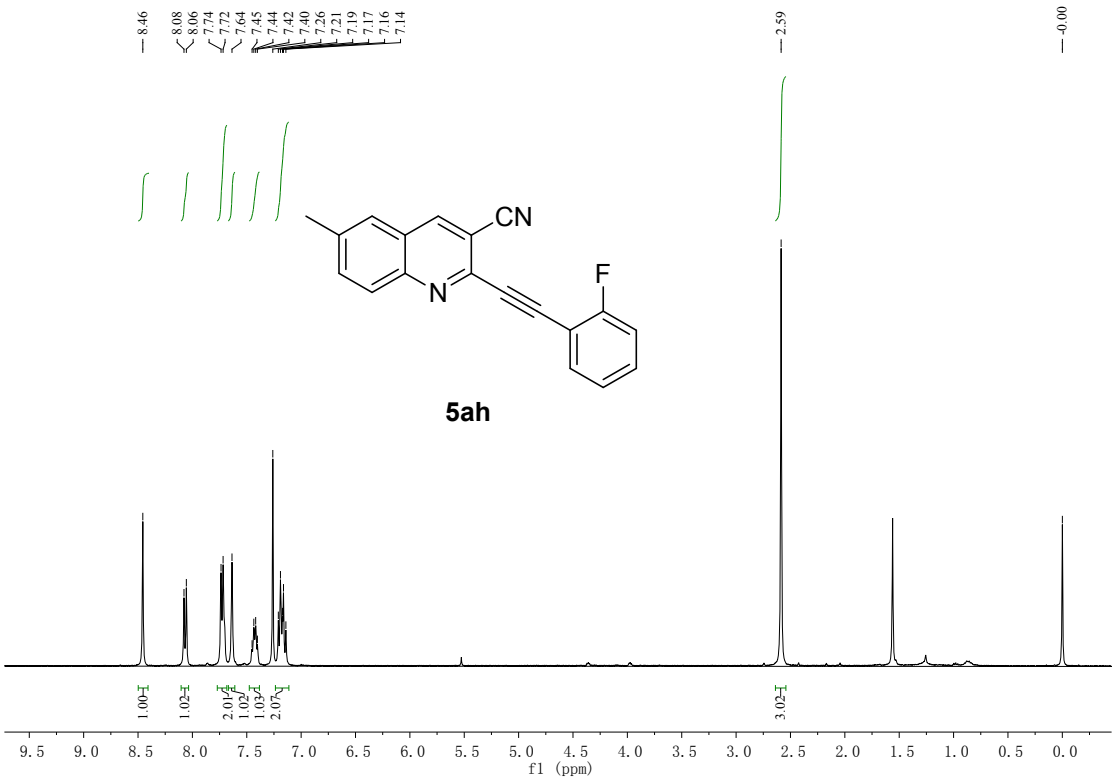
8.07
8.05
7.74
7.74
7.72
7.72
7.64
7.54
7.52
7.44
7.41
7.41
7.39
7.39
7.37
7.37
7.35
7.26
7.17
7.17
7.15
7.15
7.13
7.13
2.59
0.00
CN
N
F
1.08
1.09
1.18
1.11
1.01
2.00
1.00
3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

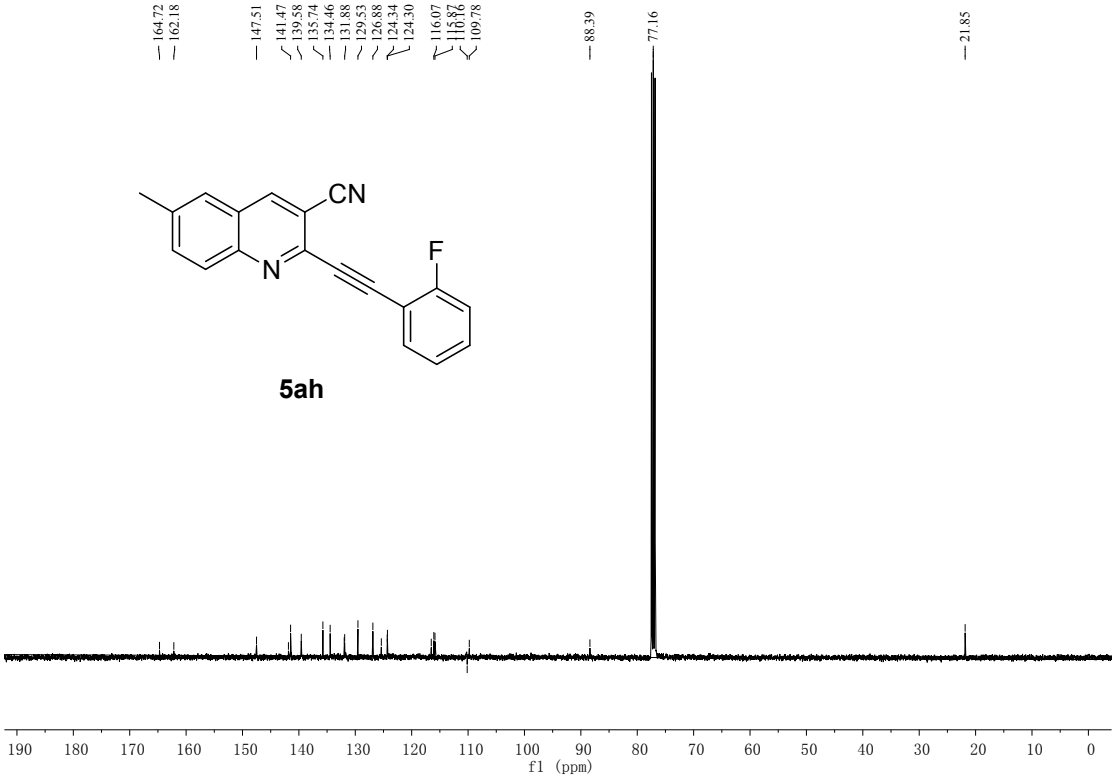
5ag


163.72
161.26
147.47
141.44
139.64
135.83
130.40
130.32
129.46
128.71
126.91
125.35
119.50
119.27
93.54
93.51
86.96
77.16
21.85
CN
N
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

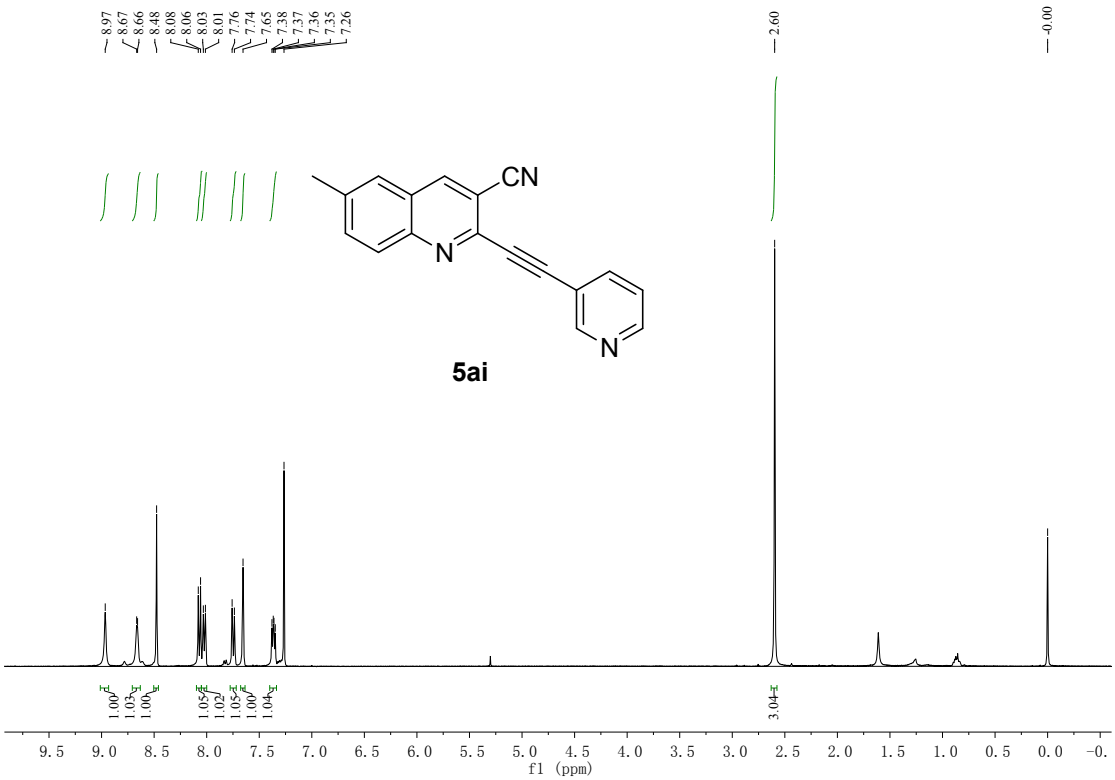
5ag


8.46
8.08
8.06
7.74
7.72
7.64
7.45
7.44
7.42
7.40
7.26
7.21
7.19
7.17
7.16
7.14
2.59
0.00
CN
N
F
1.00
1.02
2.01
1.02
1.03
2.07
3.02
f1 (ppm)

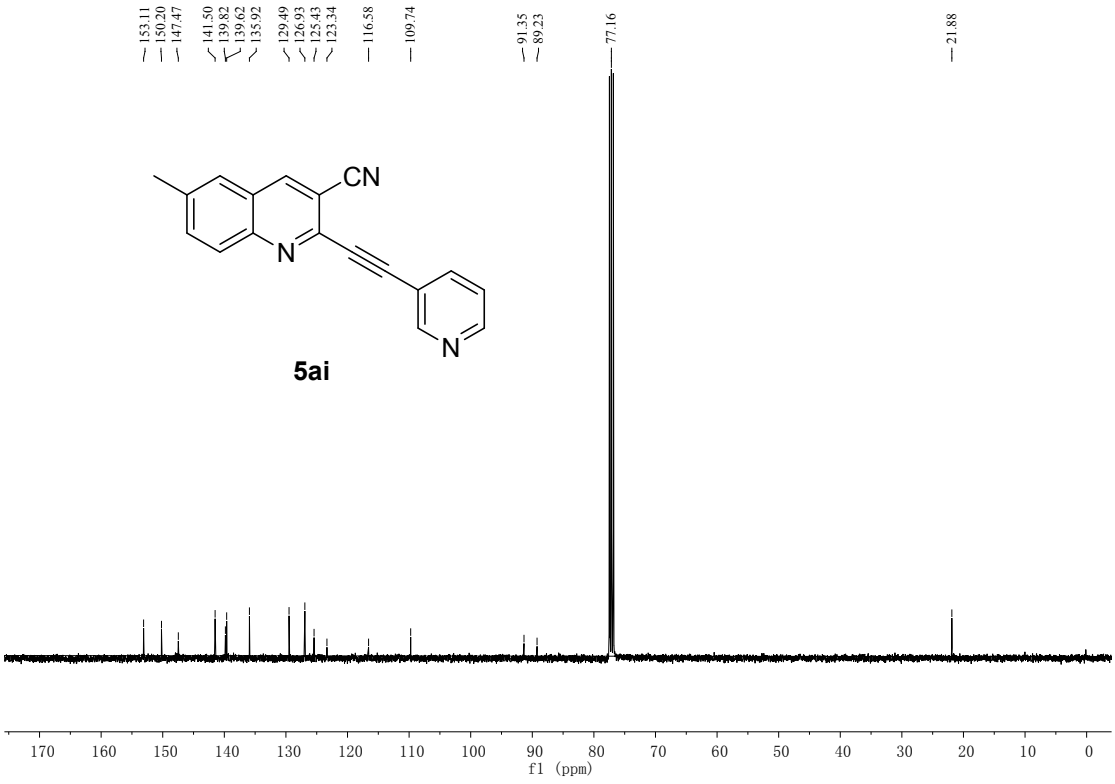
5ah


164.72
162.18
147.51
141.47
139.58
135.74
134.46
131.88
129.53
126.88
124.34
124.30
116.07
109.78
88.39
77.16
21.85
CN
N
F
f1 (ppm)

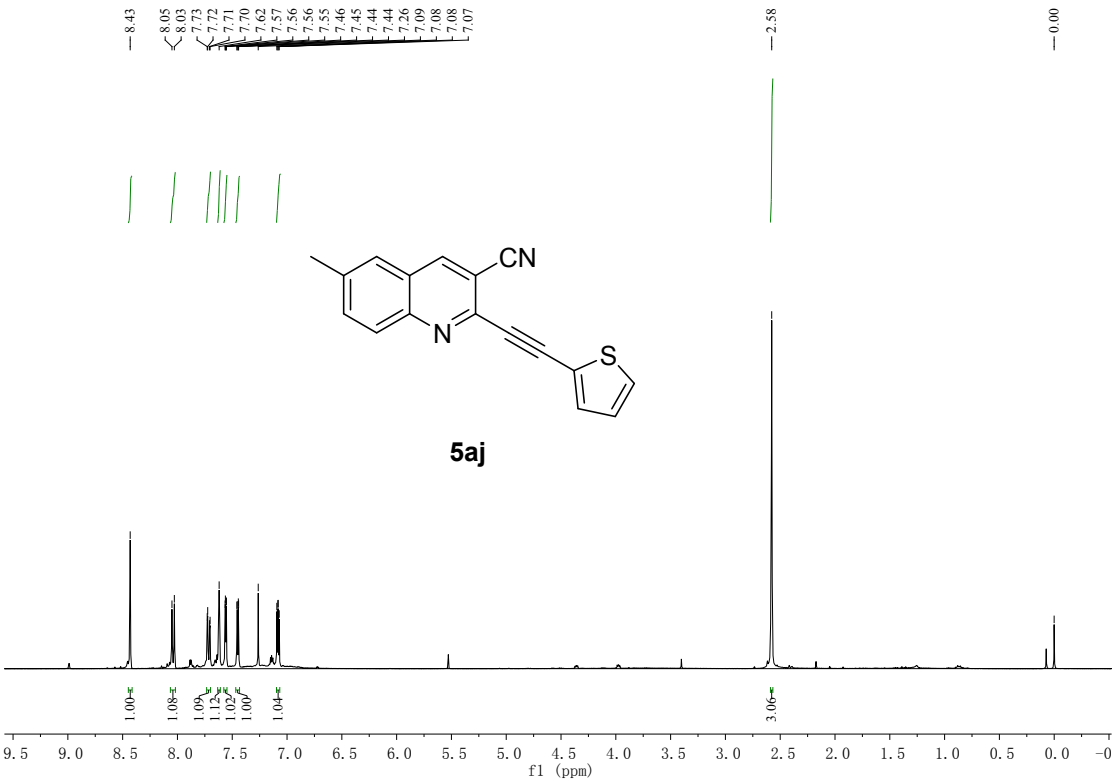
5ah


8.97
8.67
8.66
8.48
8.08
8.06
8.03
8.01
7.76
7.74
7.65
7.38
7.37
7.36
7.35
7.26
2.60
0.00
CN
N
N
1.00
1.03
1.00
1.05
1.02
1.05
1.00
1.04
3.04
f1 (ppm)

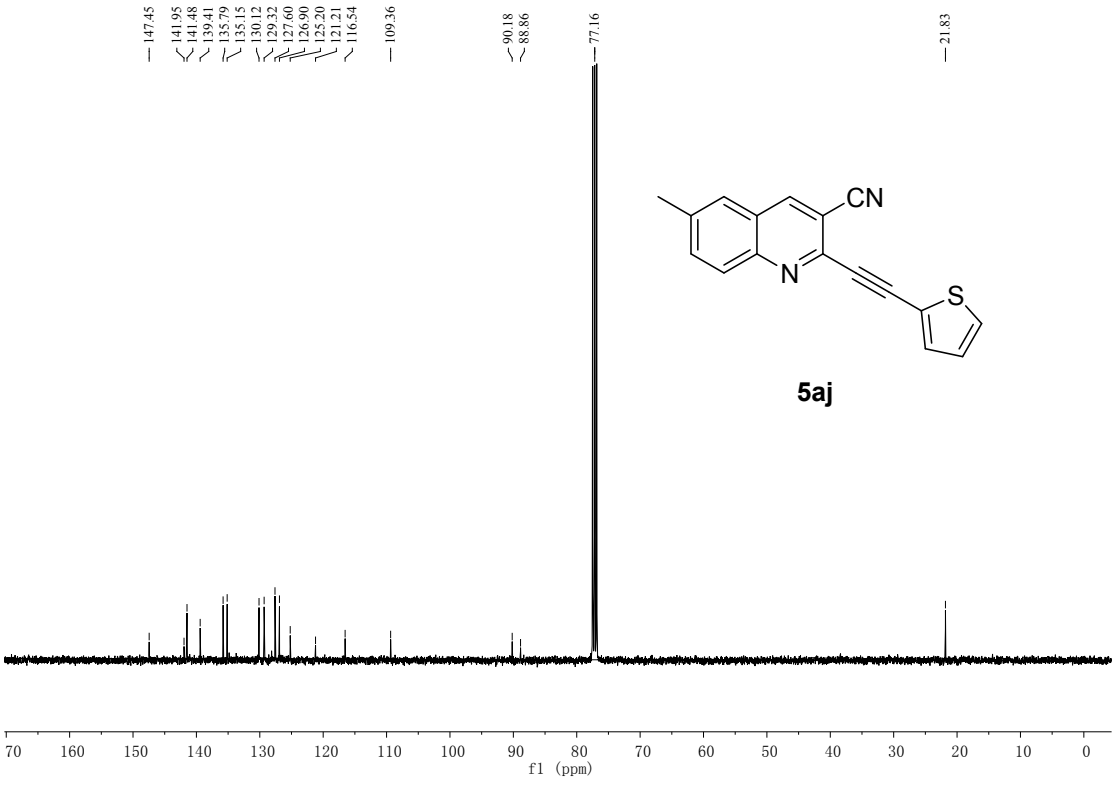
5ai


153.11
150.20
147.47
141.50
139.82
139.62
135.92
129.49
126.93
125.43
123.34
116.58
109.74
91.35
89.23
77.16
21.88
CN
N
N
f1 (ppm)

5ai


8.43
8.05
8.03
7.73
7.72
7.71
7.70
7.62
7.57
7.56
7.56
7.55
7.46
7.45
7.44
7.44
7.26
7.09
7.08
7.08
7.07
2.58
0.00
CN
N
S
1.00
1.08
1.09
1.12
1.02
1.00
1.04
3.06
f1 (ppm)

5aj


147.45
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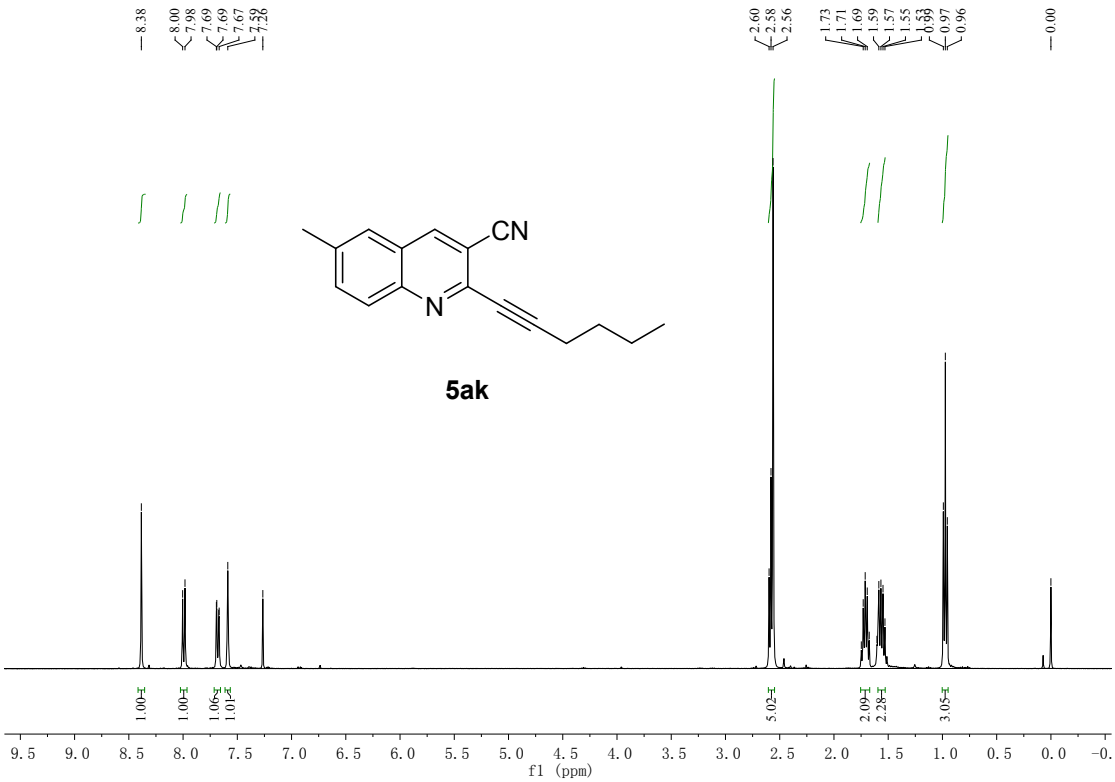
141.48
139.41
135.79
135.15
130.12
129.32
127.60
126.90
125.20
121.21
116.54
109.36
90.18
88.86
77.16
21.83
CN
N
S
f1 (ppm)

5aj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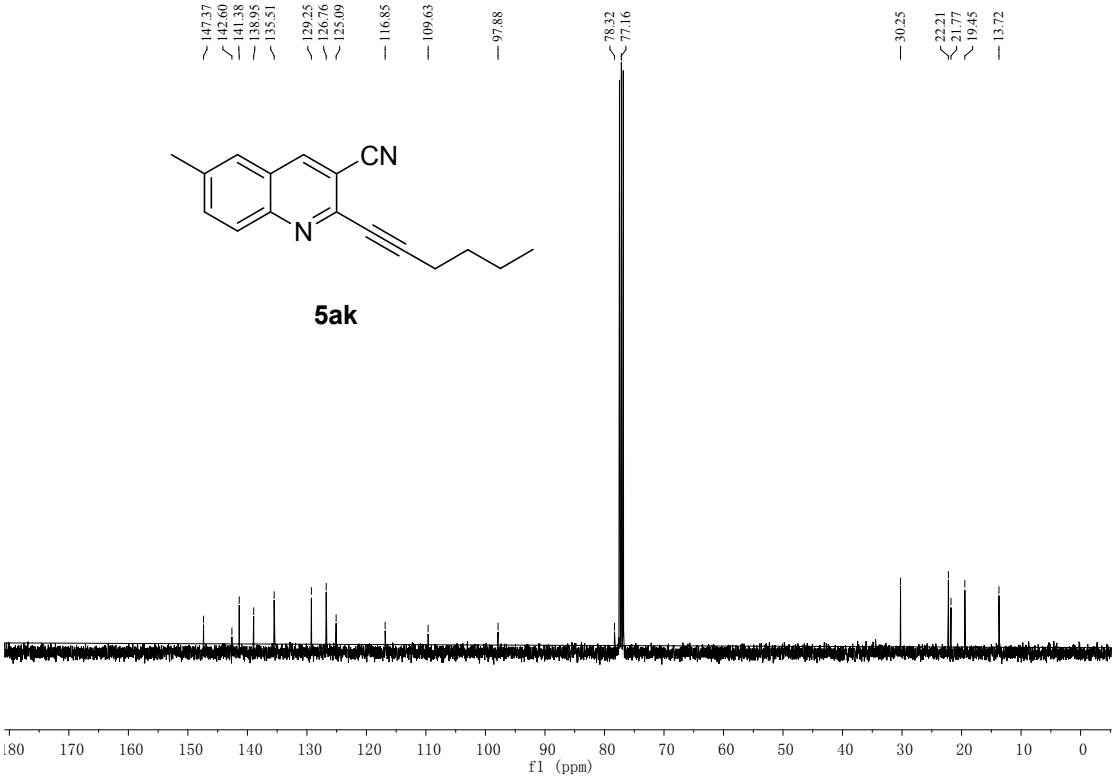
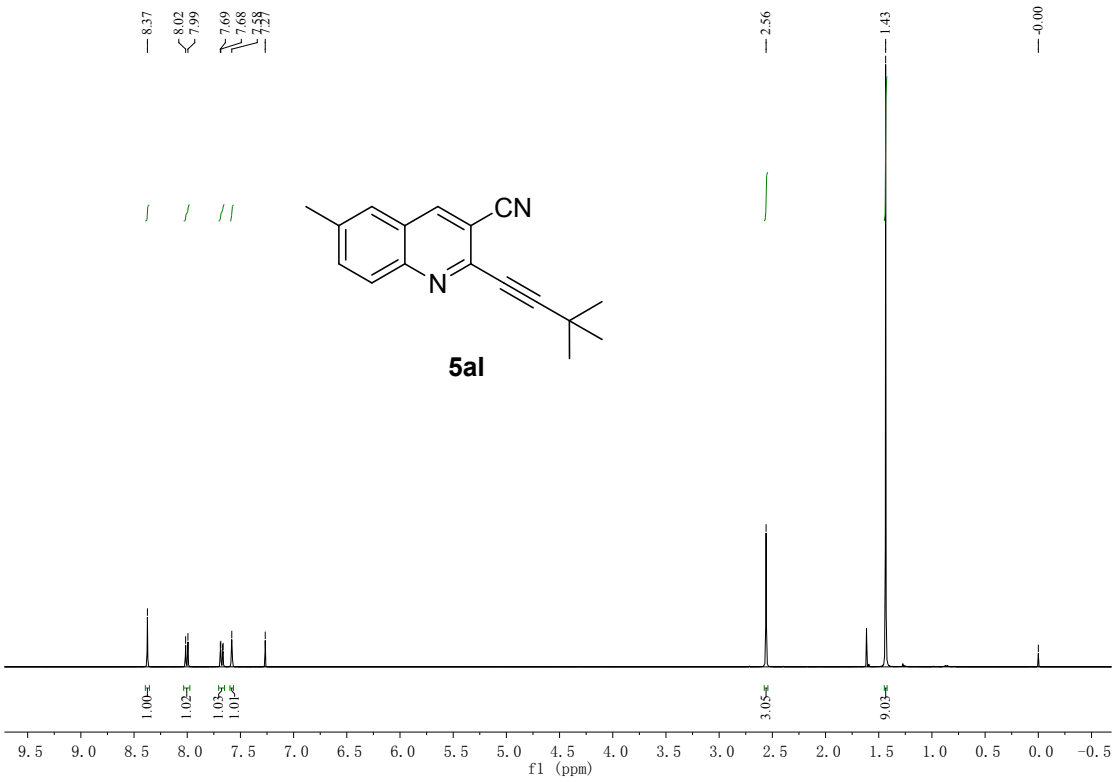
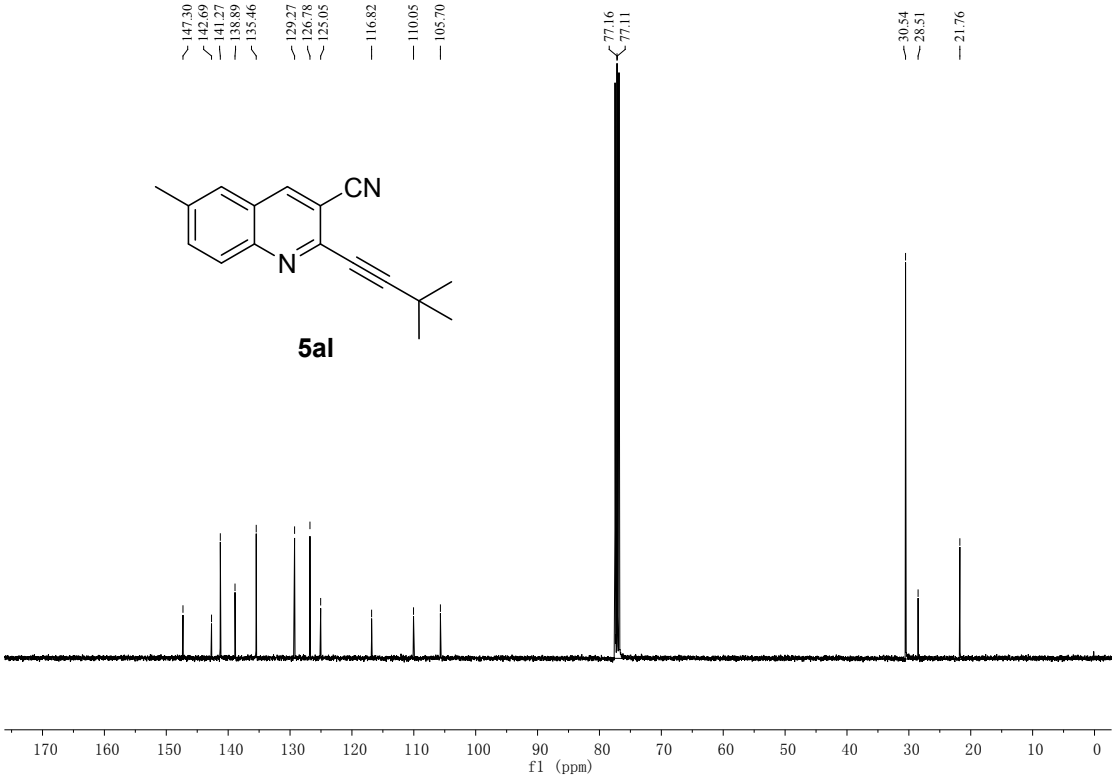
7.69
7.67
7.50
7.28
2.60
2.58
2.56
1.73
1.71
1.69
1.59
1.57
1.55
1.53
0.99
0.97
0.96
0.00
CN
N
5ak
1.00
1.00
1.06
1.01
5.02
2.09
2.28
3.05
f1 (ppm)

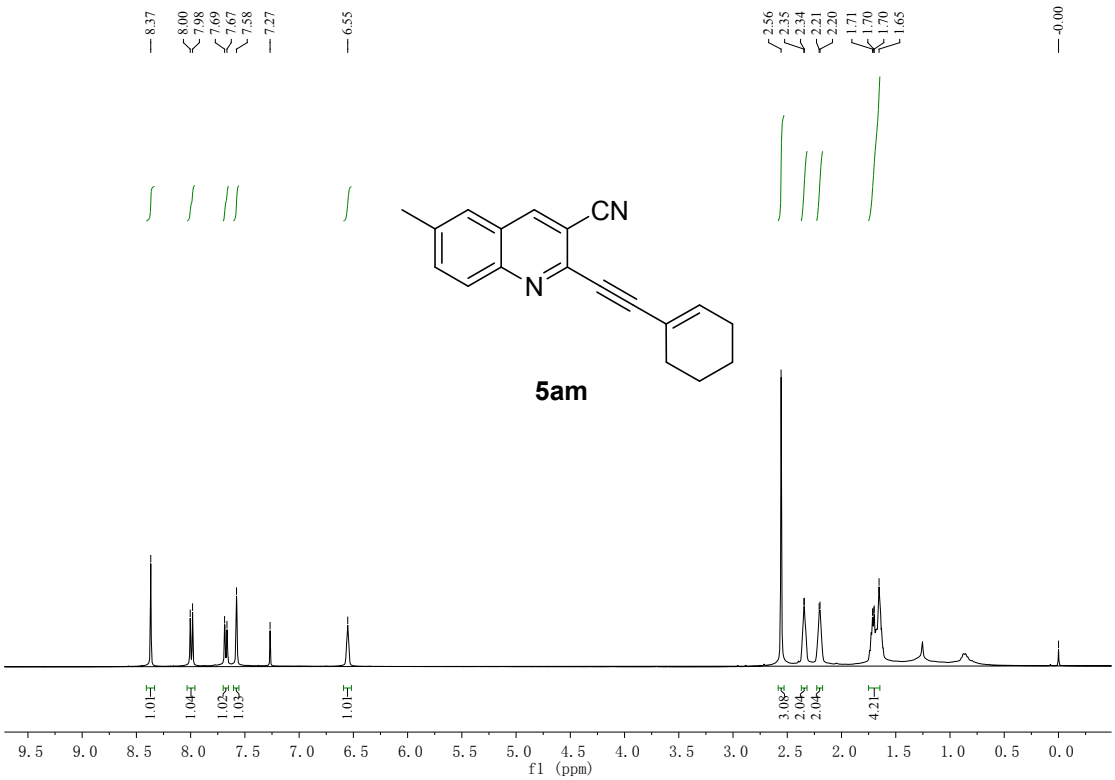

147.37
142.60
141.38
138.95
135.51
129.25
126.76
125.09
116.85
109.63
97.88
78.32
77.16
30.25
22.21
21.77
19.45
13.72
CN
N
5ak
f1 (ppm)

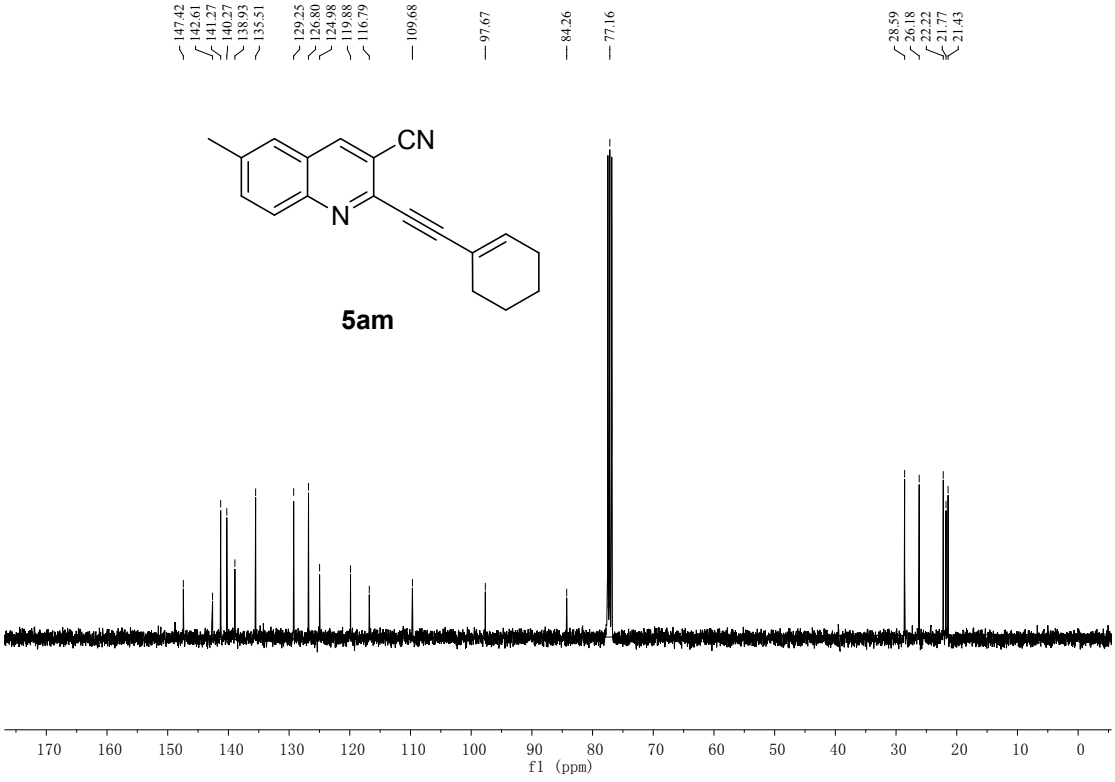

8.37
8.02
7.99
7.69
7.68
7.27
2.56
1.43
0.00
CN
N
1.00
1.02
1.03
1.01
3.05
9.03
f1 (ppm)

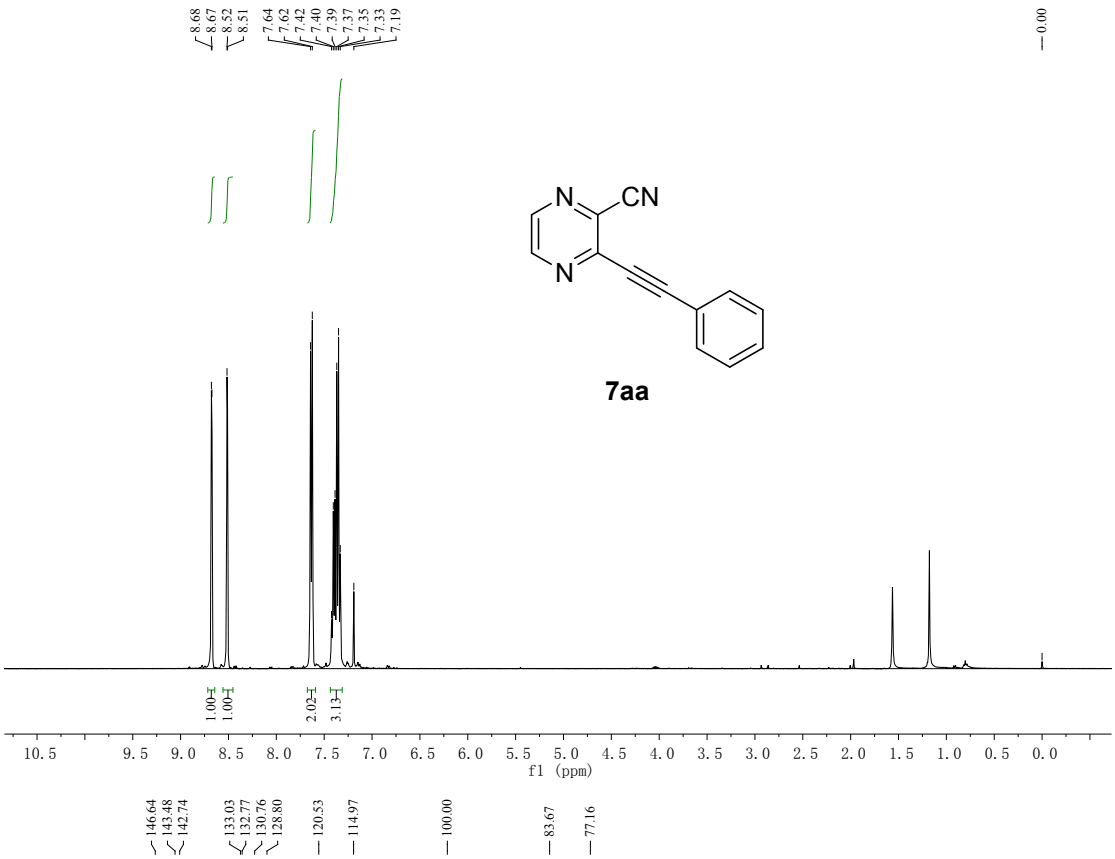
5al


147.30
142.69
141.27
138.89
135.46
129.27
126.78
125.05
116.82
110.05
105.70
77.16
77.11
30.54
28.51
21.76
CN
N
f1 (ppm)

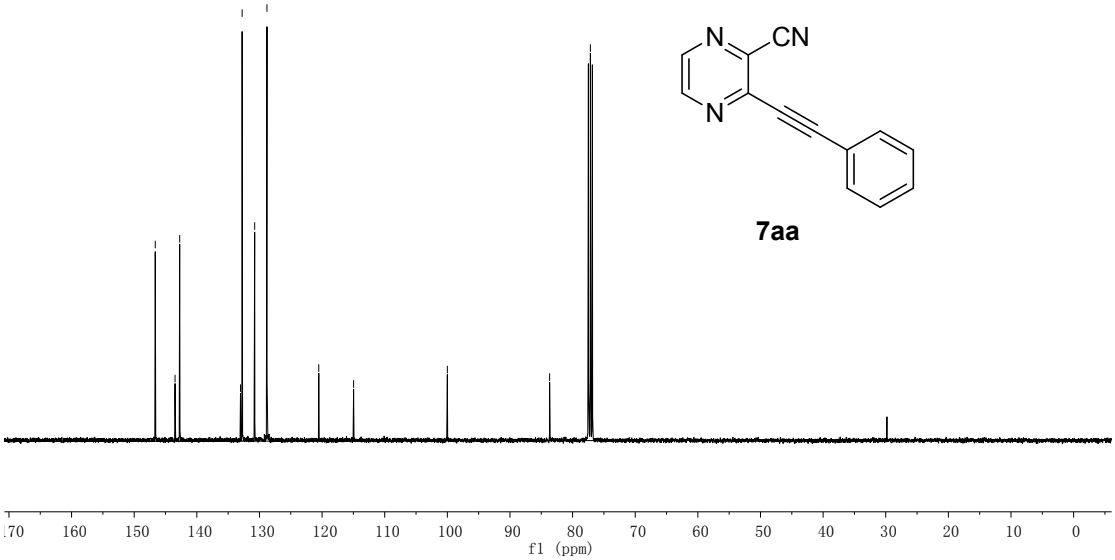
5al


8.37
8.00
7.98
7.69
7.67
7.58
7.27
6.55
2.56
2.35
2.34
2.21
2.20
1.71
1.70
1.70
1.65
0.00
CN
N
5am
1.01
1.04
1.02
1.03
1.01
3.08
2.04
2.04
4.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

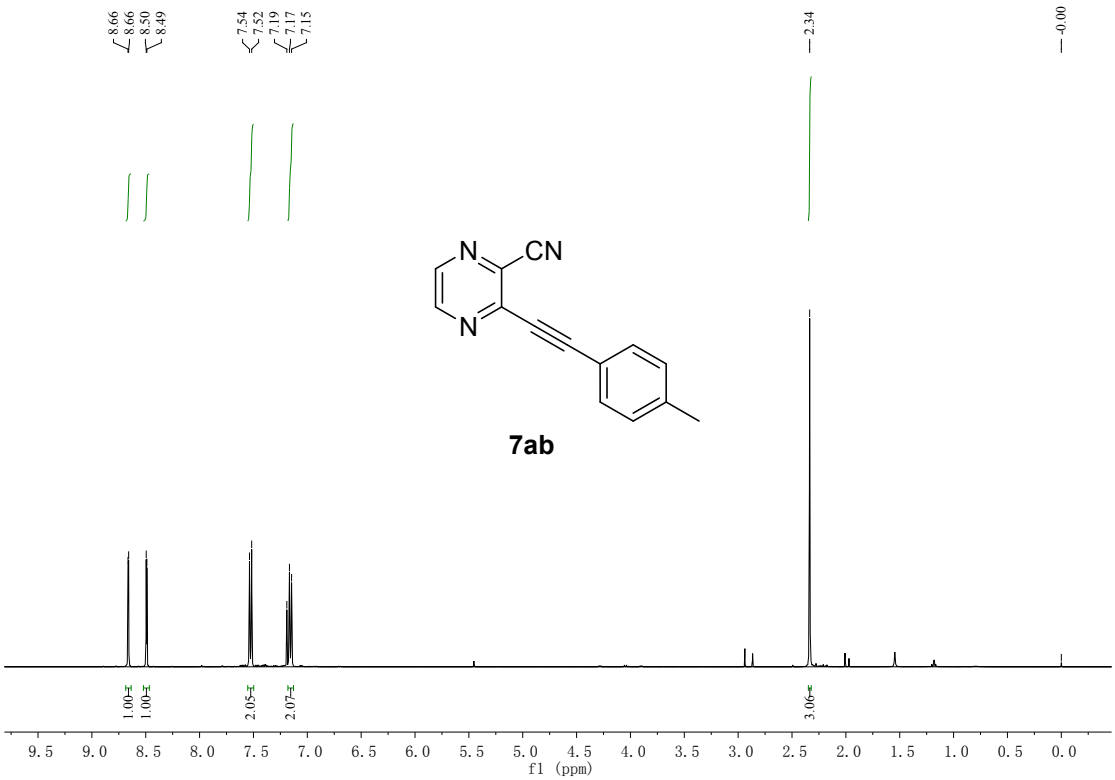

147.42
142.61
141.27
140.27
138.93
135.51
129.25
126.80
124.98
119.88
116.79
109.68
97.67
84.26
77.16
28.59
26.18
22.22
21.77
21.43
CN
N
5am
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.68
8.67
8.52
8.51
7.64
7.62
7.42
7.40
7.39
7.37
7.35
7.33
7.19
0.00
N
CN
N
1.00
1.00
2.02
3.13
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

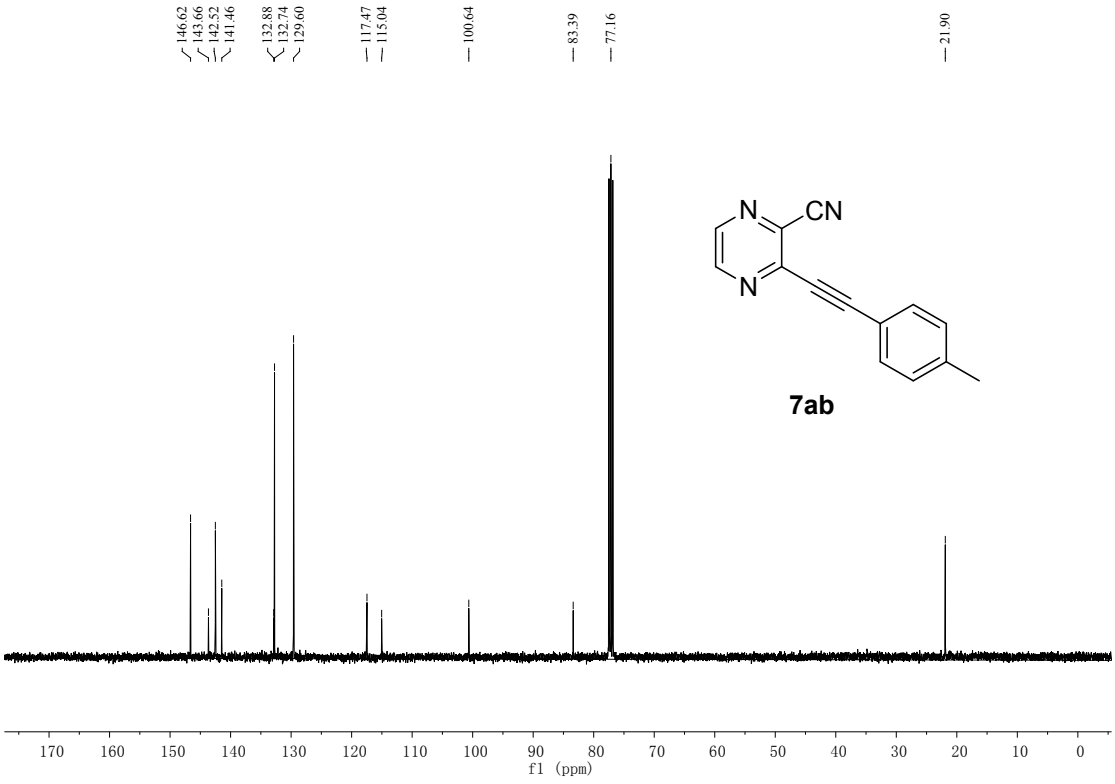
7aa


146.64
143.48
142.74
133.03
132.77
130.76
128.80
120.53
114.97
100.00
83.67
77.16
N
CN
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

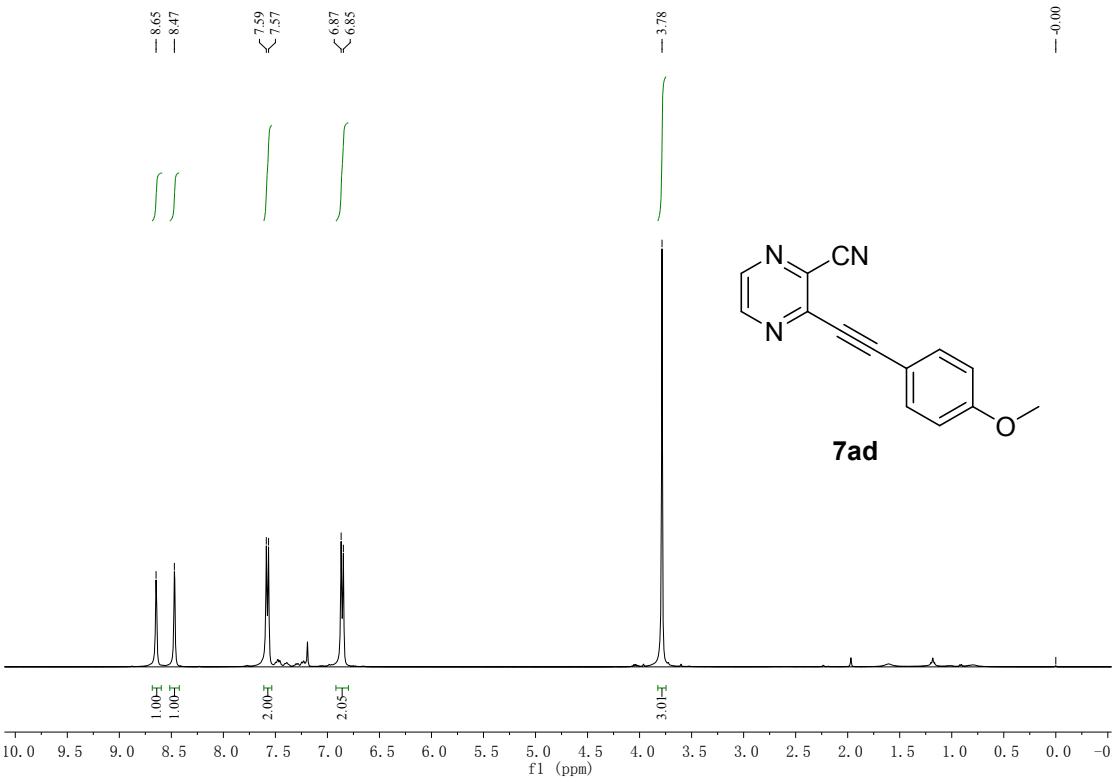
7aa

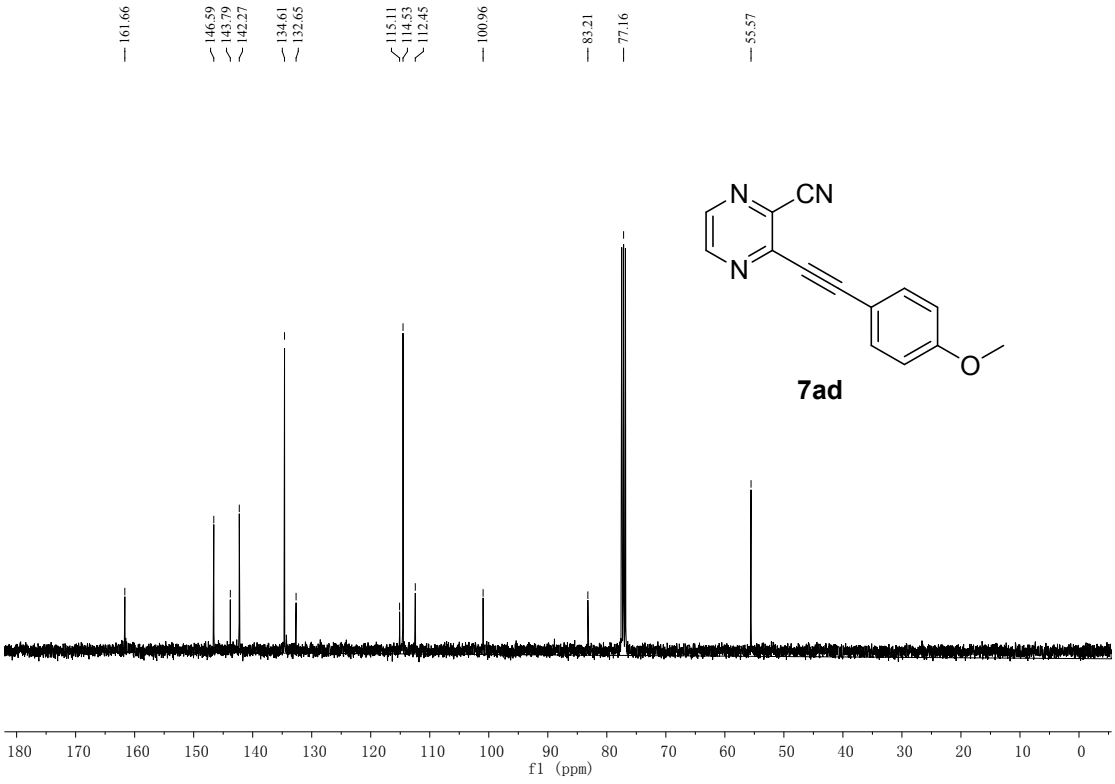

8.66
8.66
8.50
8.49
7.54
7.52
7.19
7.17
7.15
2.34
0.00
N
CN
N
1.00
1.00
2.05
2.07
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

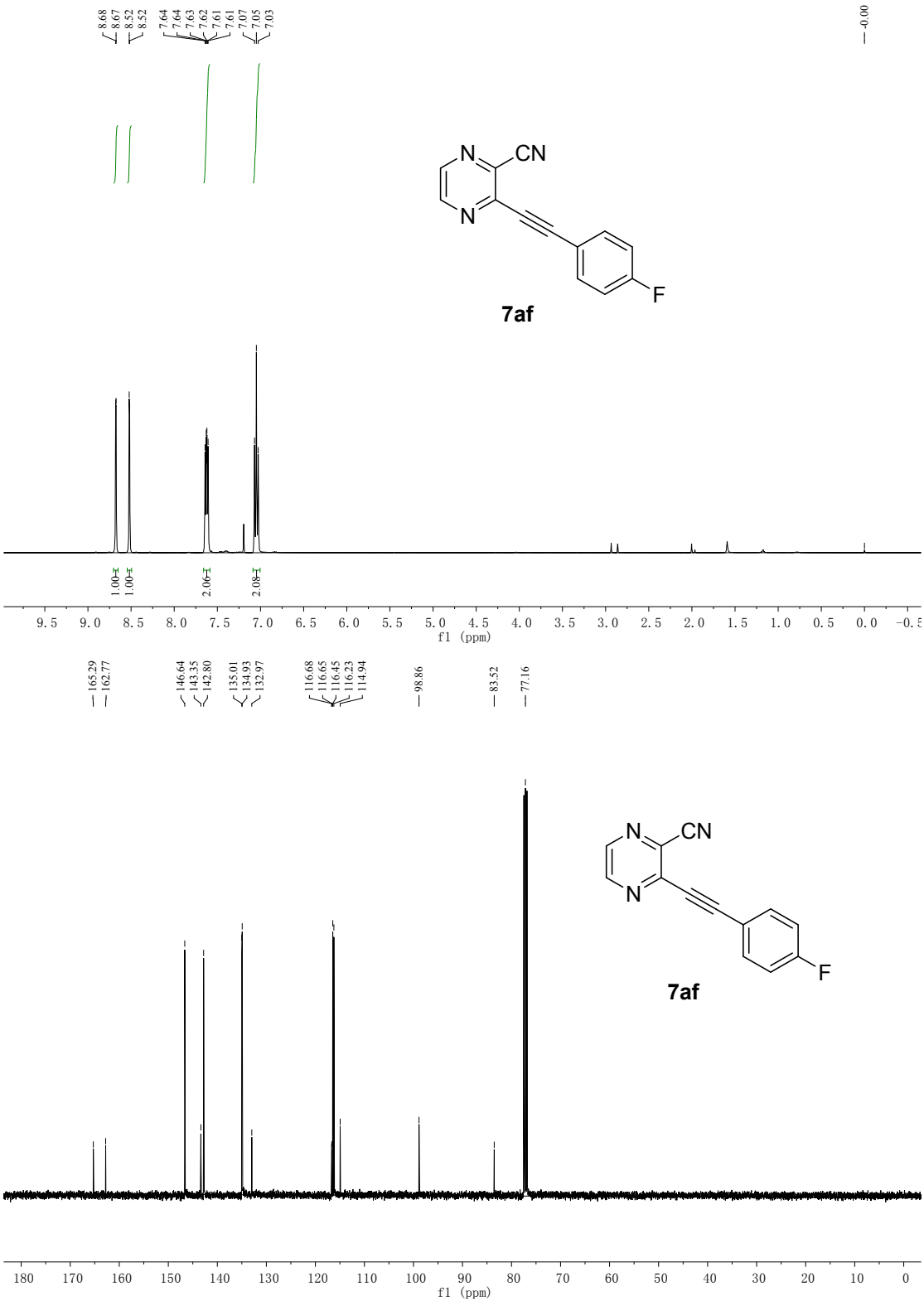
7ab

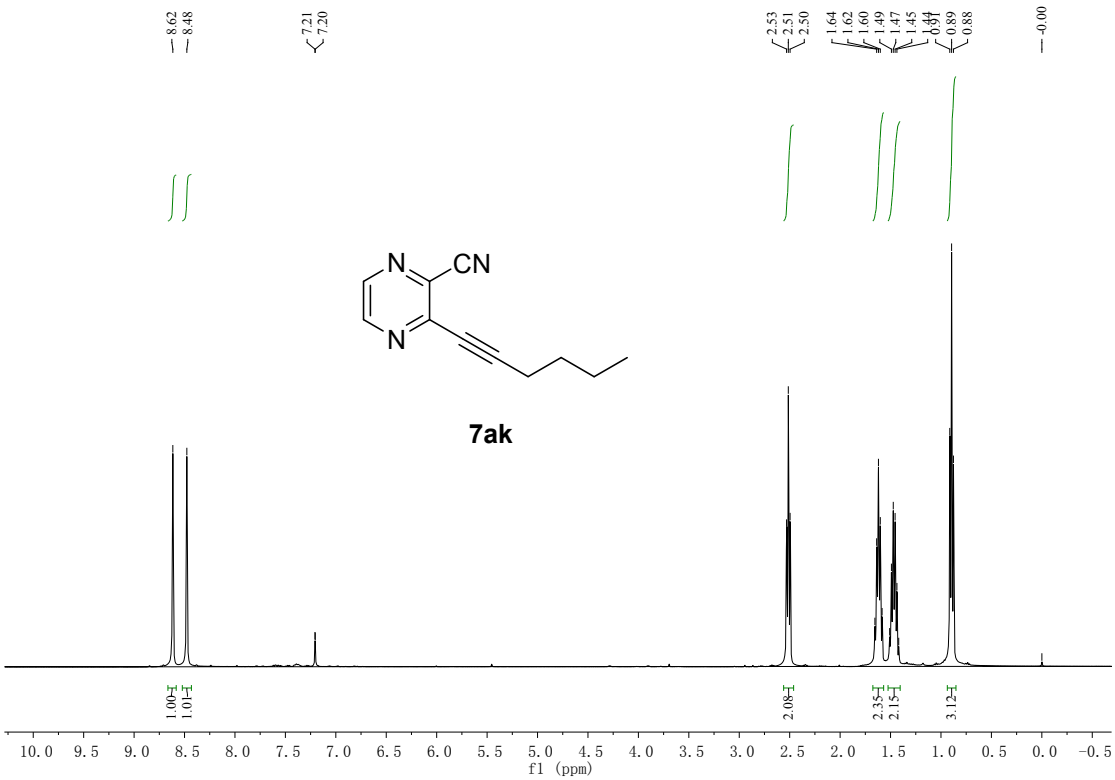

146.62
143.66
142.52
141.46
132.88
132.74
129.60
117.47
115.04
100.64
83.39
77.16
21.90
N
CN
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7ab

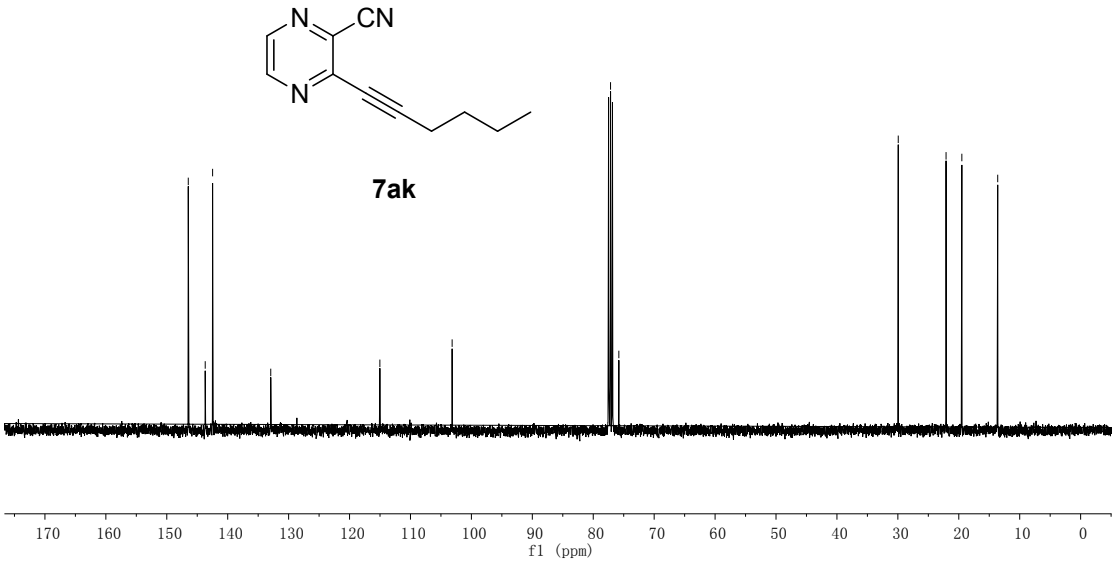

8.65
8.47
7.59
7.57
6.87
6.85
3.78
0.00
N
CN
N
O
7ad
1.00
1.00
2.00
2.05
3.01
f1 (ppm)


161.66
146.59
143.79
142.27
134.61
132.65
115.11
114.53
112.45
100.96
83.21
77.16
55.57
N
CN
N
O
7ad
f1 (ppm)


8.68
8.67
8.52
8.52
7.64
7.64
7.63
7.62
7.61
7.61
7.07
7.05
7.03
-0.00
N
CN
N
F
7af
1.00
1.00
2.06
2.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
165.29
162.77
146.64
143.35
142.80
135.01
134.93
132.97
116.68
116.65
116.45
116.23
114.94
98.86
83.52
77.16
N
CN
N
F
7af
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

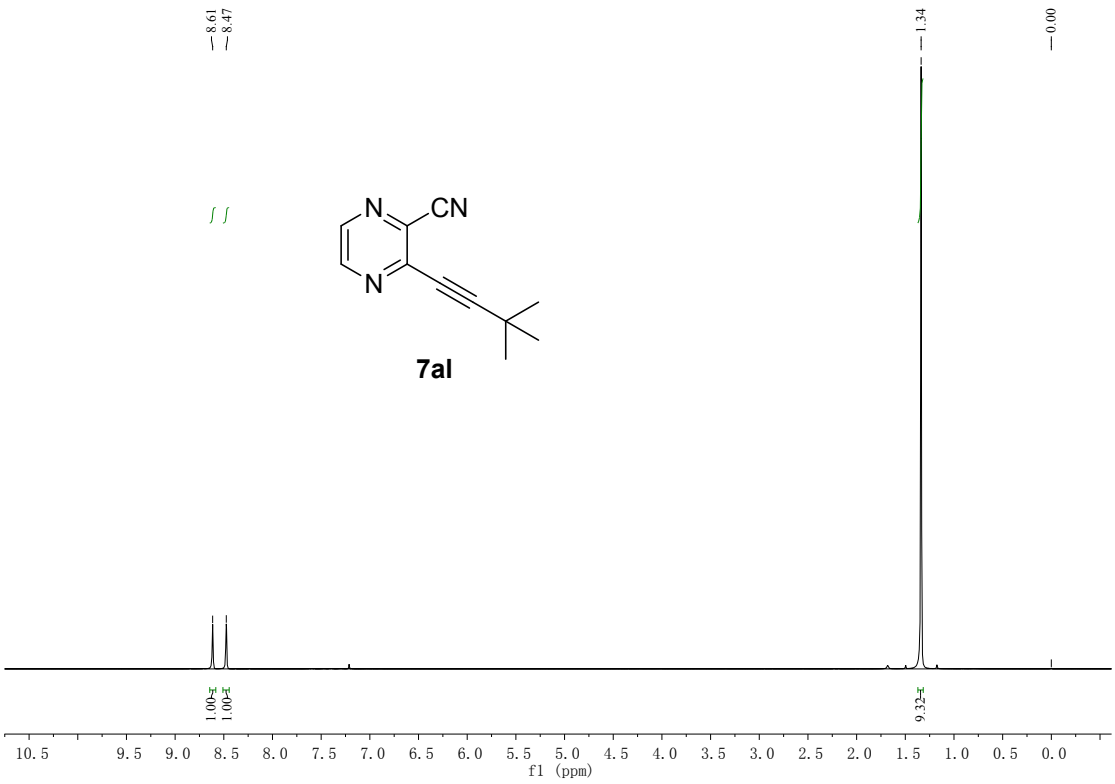

8.62
8.48
7.21
7.20
2.53
2.51
2.50
1.64
1.62
1.60
1.49
1.47
1.45
0.89
0.88
0.00
N
CN
N
1.00
1.01
2.08
2.35
2.15
3.12
f1 (ppm)

7ak

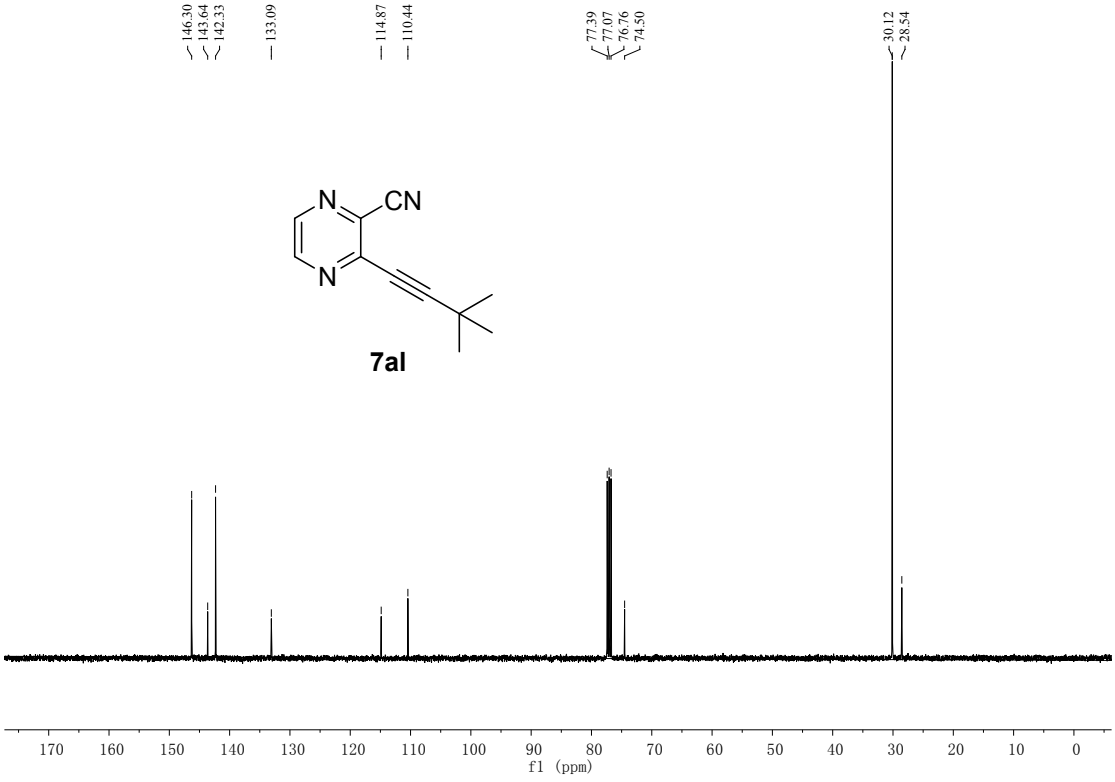

146.47
143.69
142.48
132.93
115.02
103.16
77.16
75.80
29.94
22.09
19.50
13.61
f1 (ppm)

N
CN
N

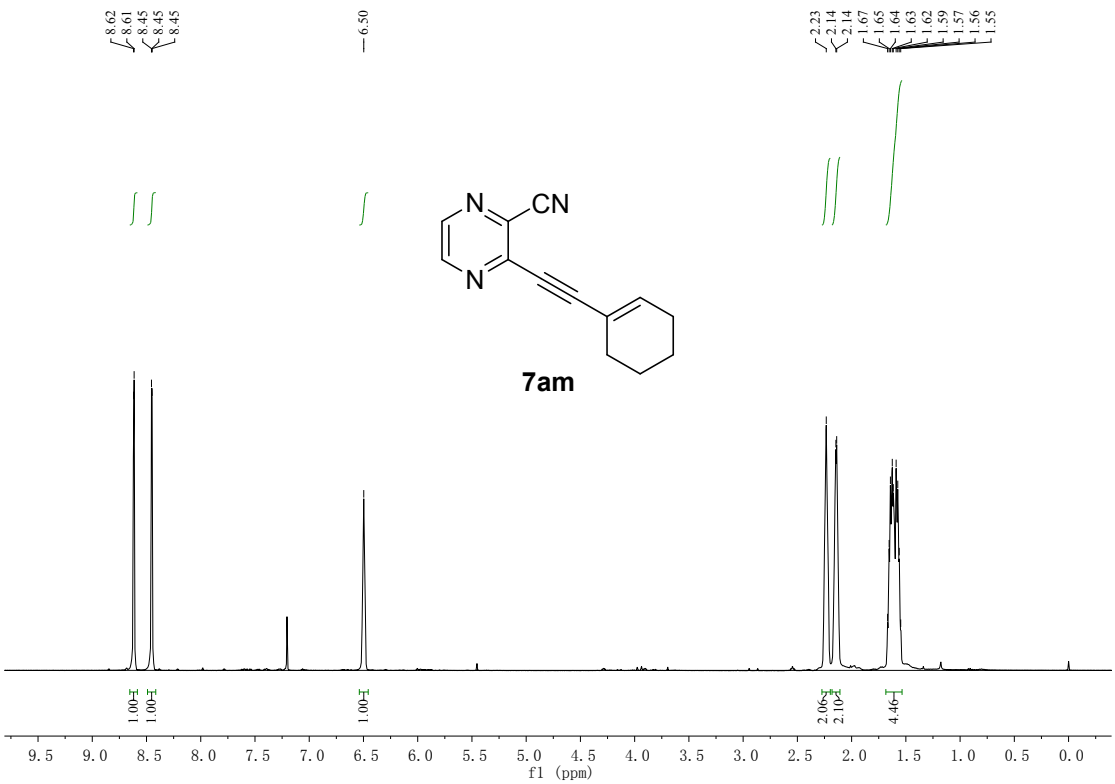
7ak

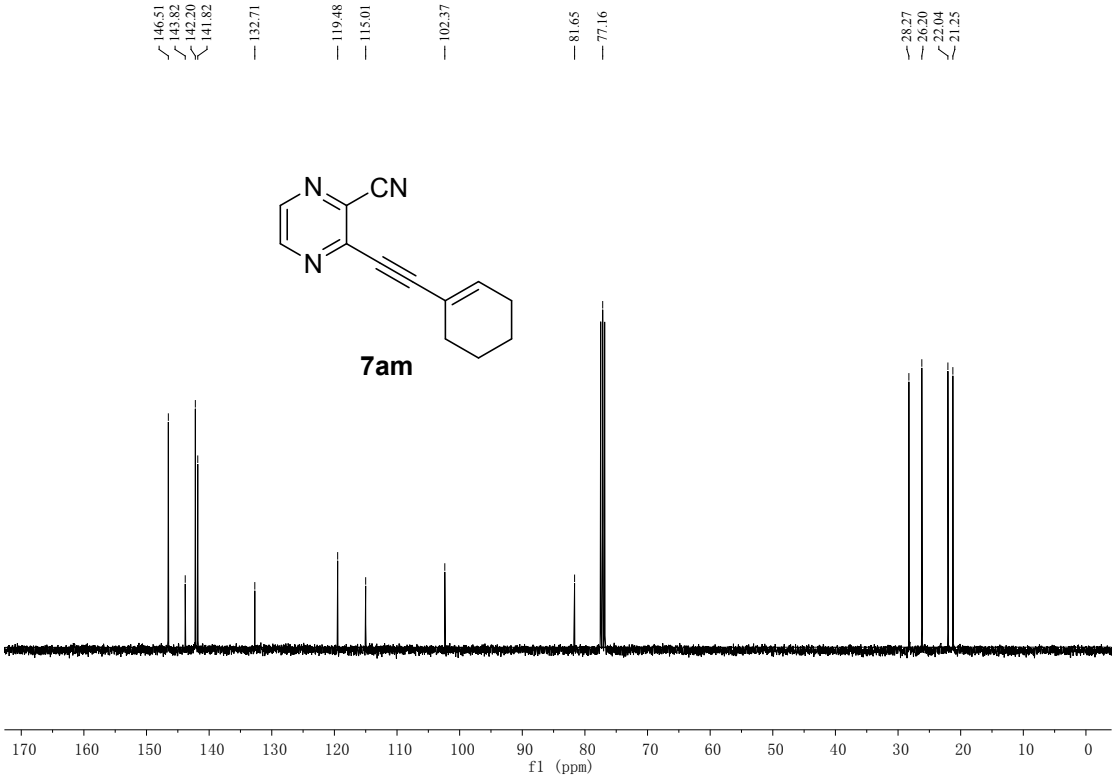

8.61
8.47
1.34
0.00
N
CN
N
1.00
1.00
9.32
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

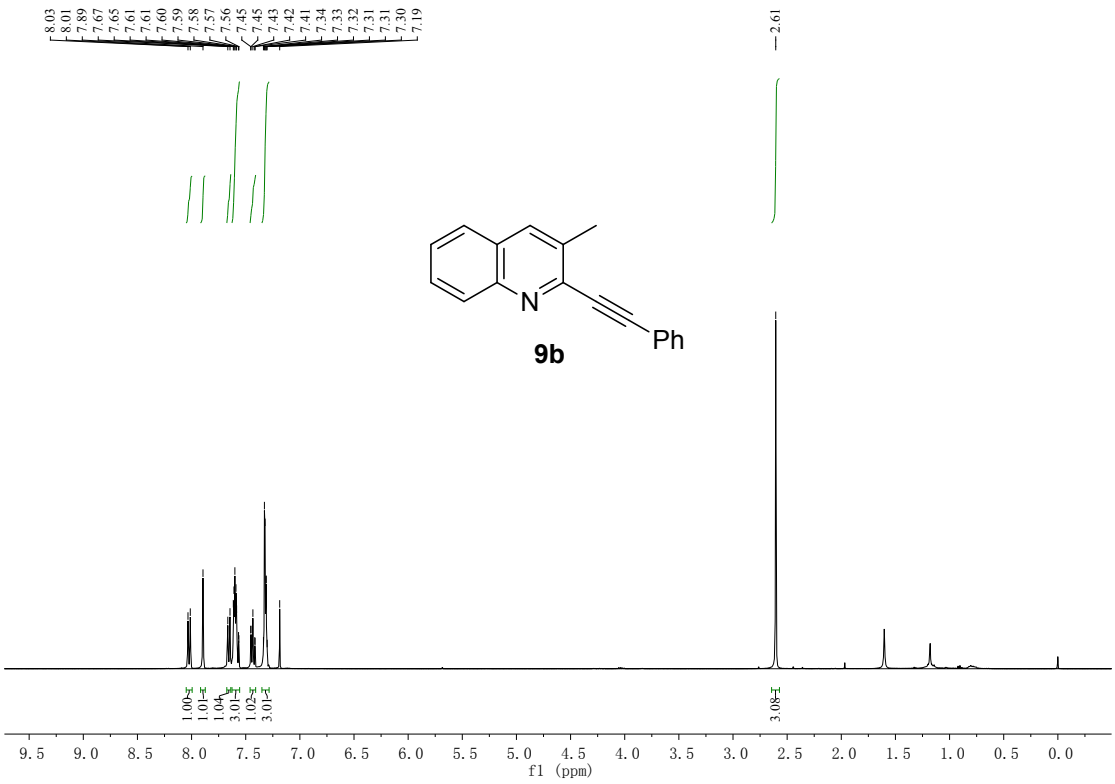
7al

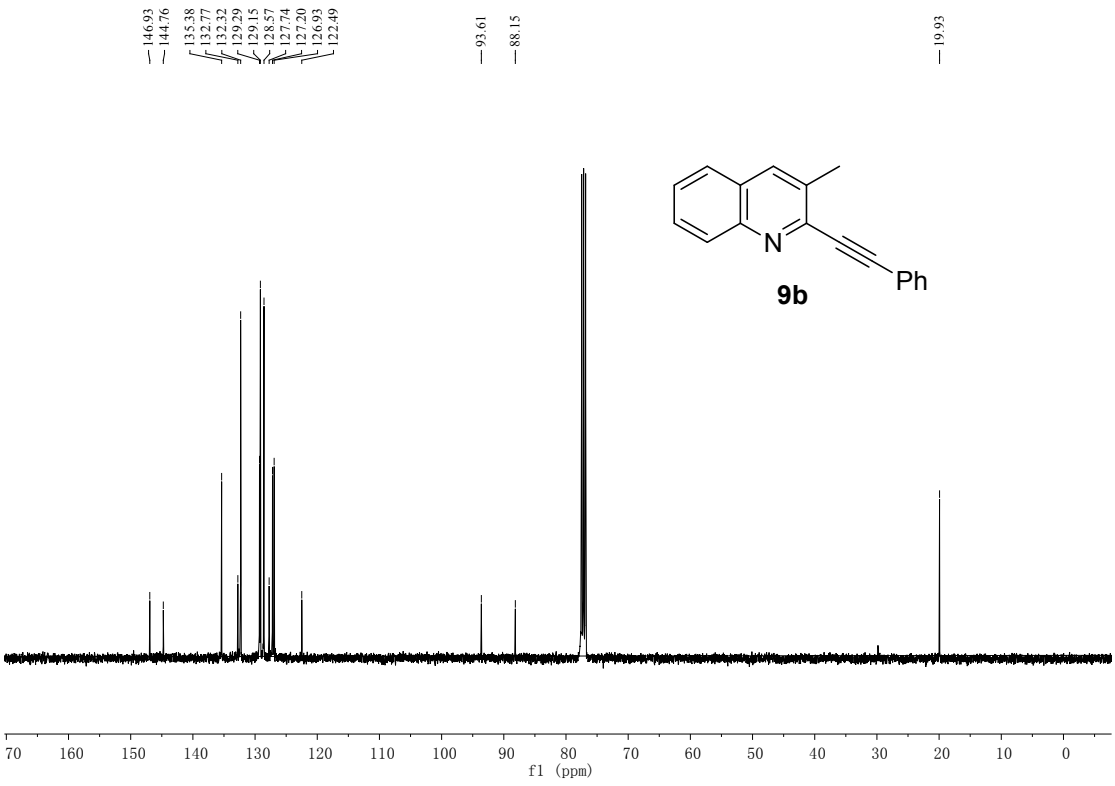

146.30
143.64
142.33
133.09
114.87
110.44
77.39
77.07
76.76
74.50
30.12
28.54
N
CN
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

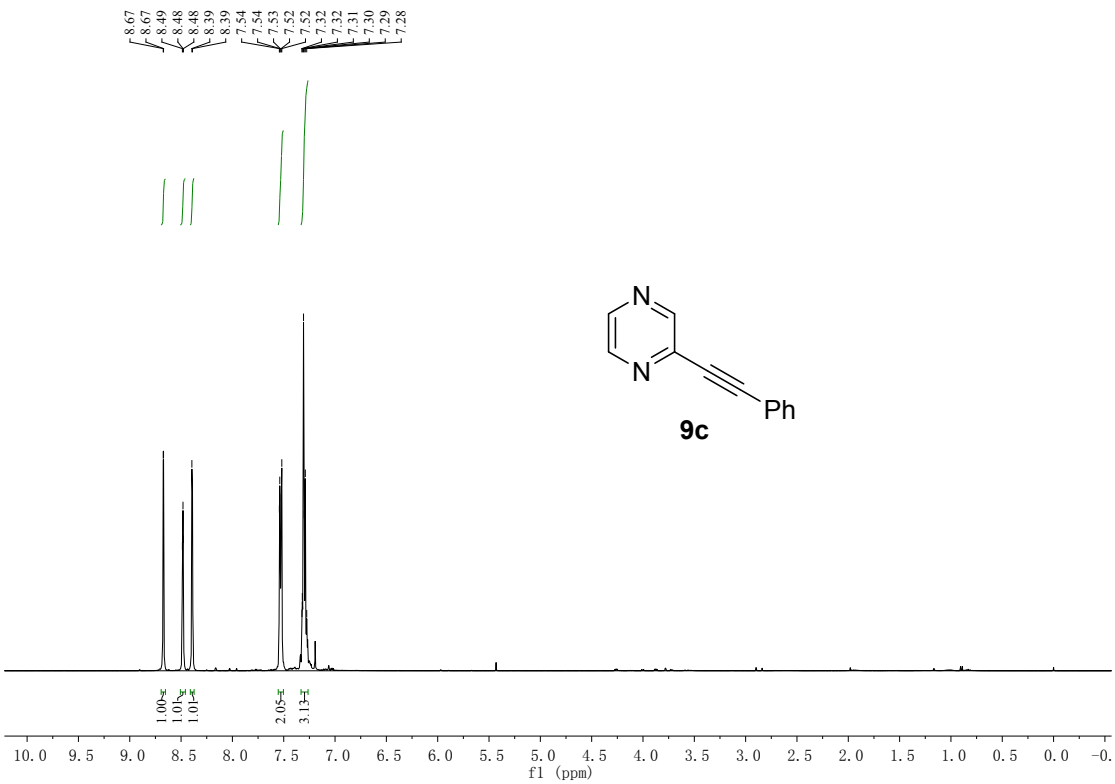
7al

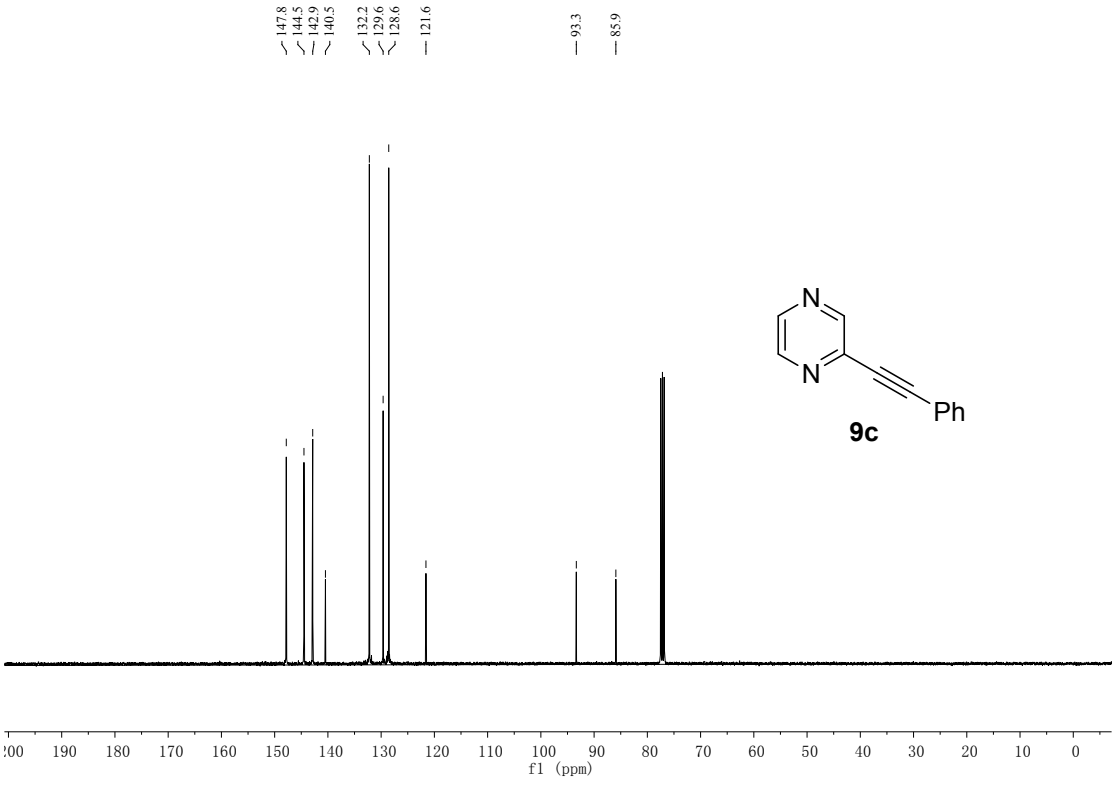

8.62
8.61
8.45
8.45
8.45
6.50
2.23
2.14
2.14
1.67
1.65
1.64
1.63
1.62
1.59
1.57
1.56
1.55
N
CN
N
7am
1.00
1.00
1.00
2.06
2.10
4.46
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


146.51
143.82
142.20
141.82
132.71
119.48
115.01
102.37
81.65
77.16
28.27
26.20
22.04
21.25
N
CN
N
7am
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.03
8.01
7.89
7.67
7.65
7.61
7.61
7.60
7.59
7.58
7.57
7.56
7.45
7.45
7.43
7.42
7.41
7.34
7.33
7.32
7.31
7.31
7.30
7.19
2.61
N
Ph
9b
1.00
1.01
1.04
3.01
1.02
3.01
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


146.93
144.76
135.38
132.77
132.32
129.29
129.15
128.57
127.74
127.20
126.93
122.49
93.61
88.15
19.93
N
Ph
9b
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.67
8.67
8.49
8.48
8.48
8.39
8.39
7.54
7.54
7.53
7.52
7.52
7.32
7.32
7.31
7.30
7.29
7.28
N
N
Ph
9c
1.00
1.01
1.01
2.05
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


147.8
144.5
142.9
140.5
132.2
129.6
128.6
121.6
93.3
85.9
N
N
Ph
9c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)