Electronic Supplementary Material (ESI) for ChemComm.


# Supplementary Information

## Direct Access to Pentenedinitriles via Ni-Catalyzed Dihydrocyanation of 1,3-Enynes

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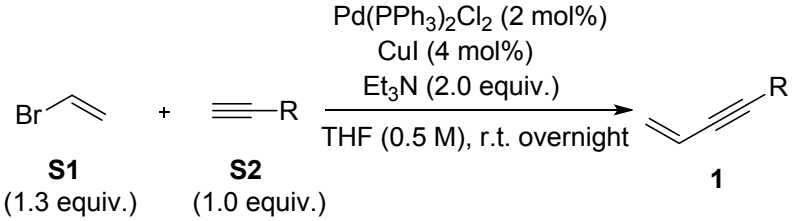
## 1. General information

All air and moisture sensitive manipulations were carried out with standard Schlenk technique or in a nitrogen-filled glovebox (Vigor). Dried and oxygen free solvents were obtained from solvent purification system (Vigor YJC-7) and used thereafter. Column chromatography was performed using 200-300 mesh silica gels. The NMR spectra were recorded on a Bruker-400/500 MHz instrument and chemical shifts are reported in ppm relative to the residual deuterated solvents. High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Shanghai Jiao Tong University with electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. GC yields were determined by Shimadzu Nexis GC-2030. $Ni(cod)_2$ was purchased from LaaJoo. The substrates and reagents for catalytic reactions were degassed and stored in the glovebox.

## 2. Preparation of substrates 1

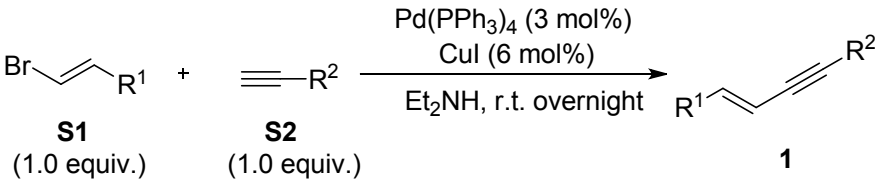
**General procedure A:**




Following a known procedure,[1] CuI (38 mg, 0.2 mmol) and $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol) were dissolved in triethylamine (2 mL ) under argon gas in a sealed tube. Phenylacetylene (5.0 mmol, 1.0 equiv.) and vinylbromide (6.5 mmol, 1.3 equiv., 1.0 M in THF) were added and the resulting mixture was stirred at room temperature until complete conversion of the starting material was observed from TLC. The reaction mixture was diluted with $Et_2O$ (10 mL) and washed with saturated aqueous $NH_4Cl$ (5 mL), $H_2O$ (3 x 20 mL), and brine (20 mL), dried over $Na_2SO_4$, and concentrated in vacuum. Purification by column chromatography afforded enyne **1**.

The 1,3-enynes **1a-x, 1aa** were prepared according to the procedure A.

**General procedure B:**

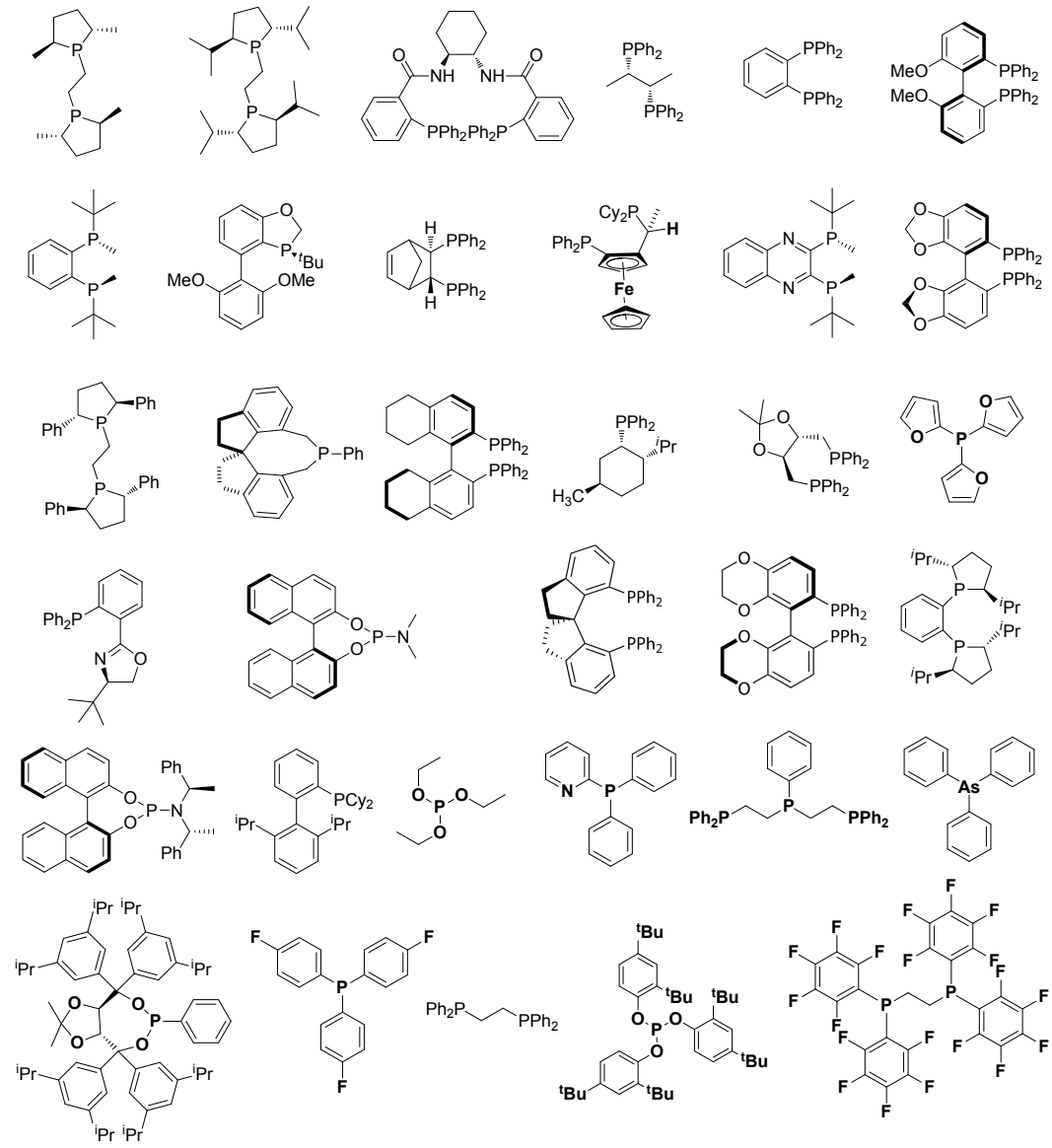



CuI (57 mg, 0.30 mmol) and $Pd(PPh_3)_4$ (173 mg, 0.15 mmol) were dissolved in diethylamine (6.0 mL) under argon gas in a sealed tube. Phenylacetylene (5.0 mmol, 1.0 equiv.) and vinylbromide (5.0 mmol, 1.0 equiv.) were added and the resulting mixture was stirred at room temperature until complete conversion of the starting material was observed from TLC. The reaction mixture was diluted with $Et_2O$ (10 mL) and washed with saturated aqueous $NH_4Cl$ (5 mL), $H_2O$ (3 x 20 mL), and brine (20 mL), dried over $Na_2SO_4$, and concentrated in vacuum. Purification by column chromatography afforded enyne **1**.

The 1,3-enynes **1y-z** were prepared according to the procedure B.

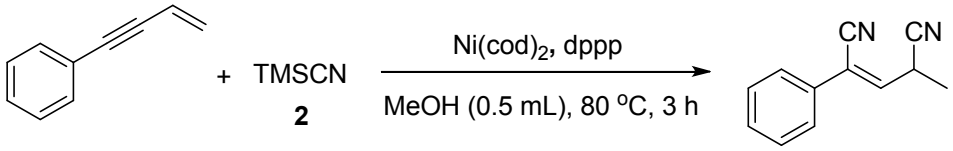
## 3. Investigating the nickel-catalyzed dihydrocyanation of 3a

### Table S1. Further ligand evaluation

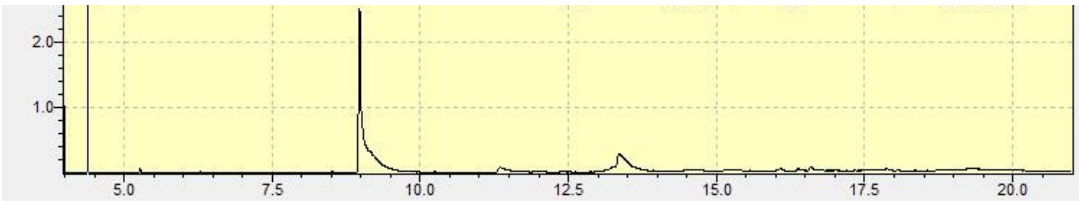


**Summary of results:** All ligands shown in Table S1 were ineffective for the dihydrocyanation reaction.

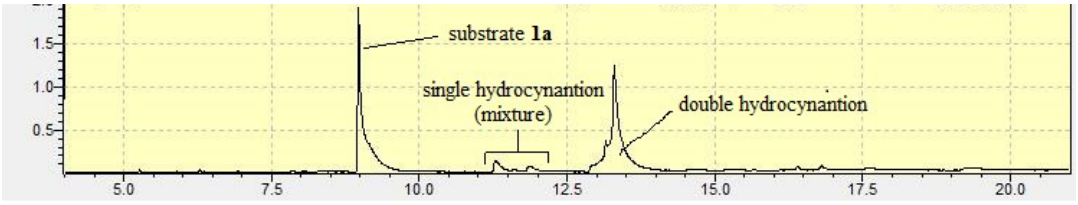
**Figure S1**. Effect of catalyst loading



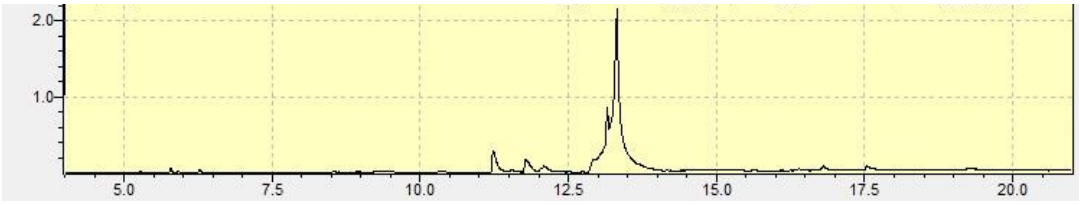

**1a** (0.2 mmol) 5.0 equiv. **3a**




5 mol% $Ni(cod)_2$, 5 mol% dppp



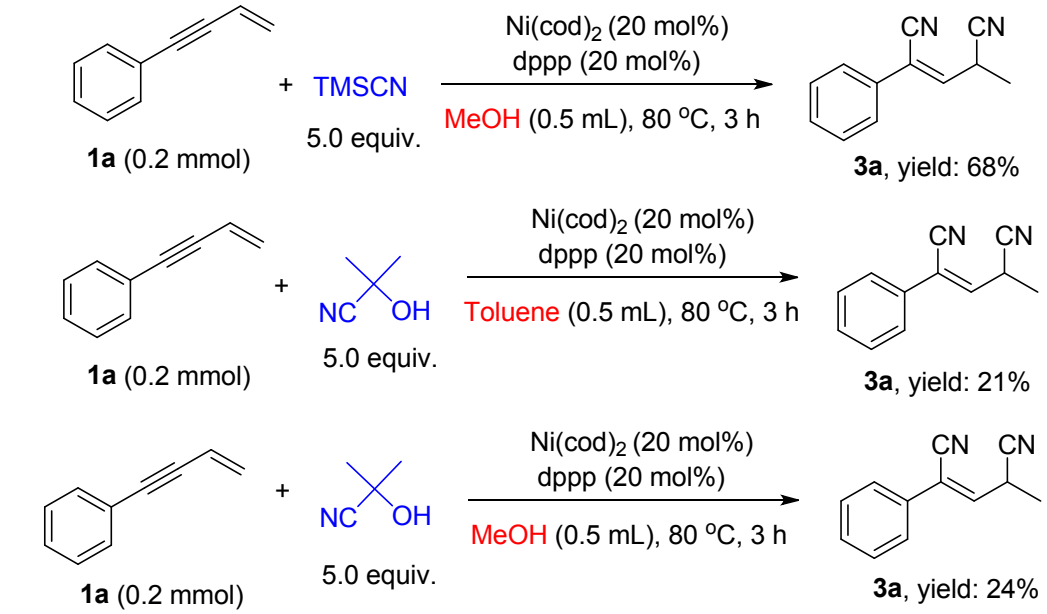

10 mol% $Ni(cod)_2$, 10 mol% dppp



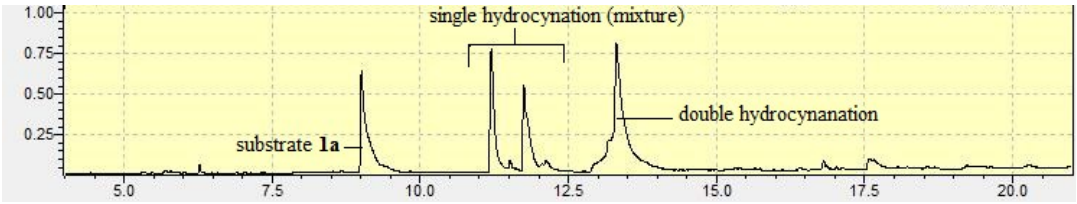

20 mol% $Ni(cod)_2$, 20 mol% dppp

**Summary of results:** Catalyst loading has great effect on the reaction and this phenomenon was shown by GC-MS analysis.

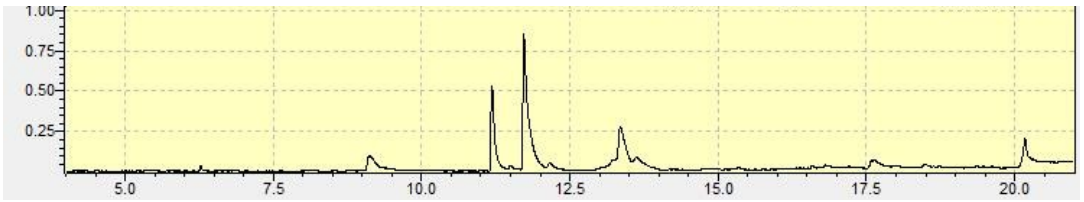
**Figure S2.** Effect of HCN source




HCN source: MeOH and TMSCN



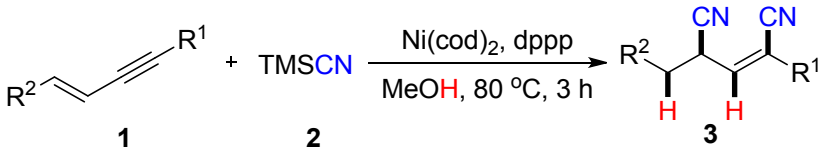

HCN source: Toluene and acetone cyanohydrin




HCN source: MeOH and acetone cyanohydrin

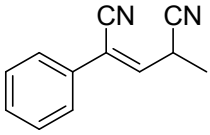
**Summary of results:** Compared with acetone cyanohydrin as HCN source, the TMSCN and MeOH showed excellent chemselectivity and reactivity.

## 4. Scope of the dihydrocyanation of 1



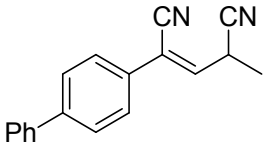

**General procedure C:** To a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar, were added $Ni(cod)_2$ (20 mol%, 11.0 mg), dppp (20 mol%, 16.5 mg) and MeOH (1.0 mL) in glovebox. The mixture was stirred at room temperature for 1 min. Next, alkynes **1** (0.2 mmol, 1.0 equiv) and TMSCN **2** (120 μL, 1.0 mmol, 5.0 equiv.) (*caution: TMSCN should be handled carefully because it is a highly toxic chemical*) were added successively. Then the reaction was removed out of glove box and heated at 80 °C for 3 h. The reaction mixture was diluted with DCM (1 mL). After the solvent was removed under reduced pressure, the residue was purified by column chromatography to afford the desired products **3**.

**(Z)-4-methyl-2-phenylpent-2-enedinitrile (3a)**




Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a yellow oil (65% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.58-7.53 (m, 2H), 7.49-7.42 (m, 3H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.01 (dq, *J* = 8.0, 8.0 Hz, 1H), 1.62 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 138.3, 131.3, 130.4, 129.3, 126.1, 119.5, 119.1, 114.8, 27.8, 18.8. **HRMS** (ESI) calcd for $[C_{12}H_{11}N_2]^+$ $([M+H])^+$: 183.0917, found:183.0921.

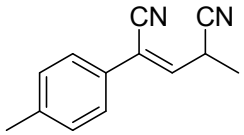
**(*Z*)-2-([1,1'-biphenyl]-4-yl)-4-methylpent-2-enedinitrile (3b)**




Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a white solid (50% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.71-

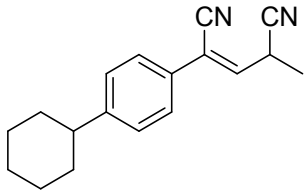
7.58 (m, 6H), 7.50-7.44 (m, 2H), 7.40 (m, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 4.14-3.86 (dq, *J* = 8.0, 8.0 Hz, 1H), 1.64 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 143.2, 139.6, 137.9, 130.1, 129.0, 128.1, 127.9, 127.1, 126.5, 119.2, 119.1, 114.8, 27.9, 18.9. **HRMS** (ESI) calcd for $[C_{18}H_{16}N_3]^+$ ($[M+NH_2]^+$): 274.1344, found: 274.1344.

**(Z)-4-methyl-2-(p-tolyl)pent-2-enedinitrile (3c)**



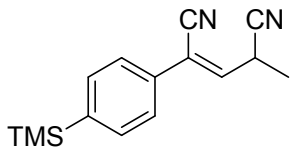

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a colorless oil (77% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.39 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 8.0Hz, 1H), 3.99 (dq, *J* = 8.0, 8.0 Hz, 1H), 2.39 (s, 3H), 1.60 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 140.8, 137.1, 129.9, 128.5, 125.9, 119.3, 119.2, 115.0, 27.8, 21.3, 18.9. **HRMS** (EI) calcd for $[C_{13}H_{12}N_2]^+$: 196.0995, found: 196.0994.

**(Z)-2-(4-cyclohexylphenyl)-4-methylpent-2-enedinitrile (3d)**



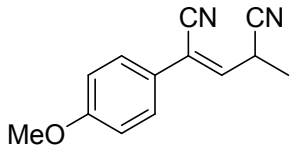

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a colorless oil (79% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.44 (m, 2H), 7.32-7.22 (m, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.99 (dq, *J* = 8.0, 8.0 Hz, 1H), 2.60-2.46 (m, 1H), 1.90-1.81 (m, 4H), 1.79-1.71 (m, 1H), 1.60 (d, *J* = 8.0Hz, 3H), 1.38 (m, 5H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 150.9, 137.2, 128.8, 127.7, 126.0, 119.3, 119.2, 115.0, 44.3, 34.2, 27.8, 26.7, 26.0, 18.9. **HRMS** (EI) calcd for $[C_{18}H_{20}N_2]^+$: 264.1621, found: 264.1619.

**(*Z*)-4-methyl-2-(4-(trimethylsilyl)phenyl)pent-2-enedinitrile (3e)**



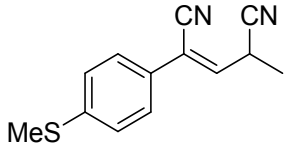

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a colorless oil (78% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.01 (dq, *J* = 8.0, 8.0 Hz, 1H), 1.61 (d, *J* = 8.0 Hz, 3H), 0.29 (s, 9H). **$^{13}$C NMR** (100 MHz, CDCl3) δ 143.9, 138.3, 134.2, 131.5, 125.2, 119.5, 119.1, 114.8, 27.8, 18.8, -1.29. **HRMS** (EI) calcd for $[C_{15}H_{18}N_2Si]^+$: 254.1234, found: 254.1231.

**(Z)-2-(4-methoxyphenyl)-4-methylpent-2-enedinitrile (3f)**



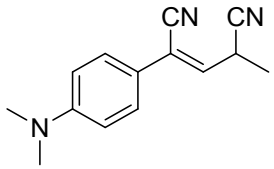

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a colorless oil (81% yield).**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 12.0 Hz, 1H), 3.98 (dq, *J* = 8.0, 8.0 Hz, 1H), 3.85 (s, 3H), 1.60 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 161.3, 135.8, 127.5, 123.8, 119.3, 118.8, 115.1, 114.6, 55.5, 27.8, 18.9. **HRMS** (EI) calcd for $[C_{13}H_{12}N_2O]^+$: 212.0944, found: 212.0941.

**(Z)-4-methyl-2-(4-(methylthio)phenyl)pent-2-enedinitrile (3g)**



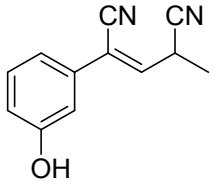

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a yellow solid (70% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.46 (m, 2H), 7.31-7.28 (m, 2H), 6.66 (d, *J* = 9.0 Hz, 1H), 4.01 (dq, *J* = 8.0, 8.0 Hz, 1H), 2.53 (s, 3H), 1.63 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 142.3, 137.0, 127.6, 126.3, 126.2, 119.2, 118.9, 114.8, 27.8, 18.9, 15.1. **HRMS** (EI) calcd for $[C_{13}H_{12}N_2S]^+$: 228.0716, found: 228.0714.

**(*Z*)-2-(4-(dimethylamino)phenyl)-4-methylpent-2-enedinitrile (3h)**



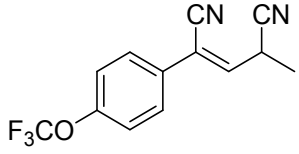

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a yellow solid (36% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 6.75-6.66 (m, 2H), 6.45 (d, *J* = 8.0 Hz, 1H), 3.99 (dq, *J* = 8.0, 8.0 Hz, 1H), 3.04 (s, 6H), 1.60 (d, *J* = 8.0 Hz, 3H).**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 151.5, 132.4, 127.1, 119.7, 119.1, 118.7, 115.4, 111.9, 40.1, 27.7, 19.1. **HRMS** (EI) calcd for $[C_{14}H_{15}N_3]^+$: 225.1260, found: 225.1258.

**(*Z*)-2-(3-hydroxyphenyl)-4-methylpent-2-enedinitrile (3i)**




Purification using column chromatography (ethyl acetate/petroleum ether = 1/4, v/v) gave the product as a yellow solid (55% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 12.0 Hz, 1H), 7.06 (s, 1H), 6.94 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.75 (s, 1H), 4.02 (dq, *J* = 8.0, 8.0 Hz, 1H), 1.64 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 156.5, 138.6, 132.7, 130.6, 119.1, 119.1, 118.3, 117.6, 114.8, 113.0, 27.8, 18.8. **HRMS** (EI) calcd for $[C_{12}H_{10}N_2O]^+$: 198.0788, found: 198.0783.

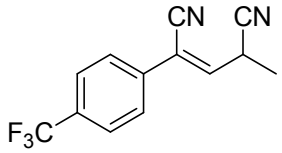
**(Z)-4-methyl-2-(4-(trifluoromethoxy)phenyl)pent-2-enedinitrile (3j)**




Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a colorless oil (55% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 12.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 12.0 Hz, 1H), 4.03 (dq, *J* = 8.0,

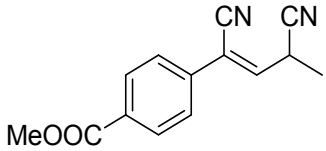
8.0 Hz, 1H), 1.65 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 150.6, 139.2, 129.9, 127.7, 121.5, 118.8, 118.2, 114.4, 27.9, 18.7. **$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -57.8. **HRMS** (ESI) calcd for $[C_{13}H_{11}F_3N_3O]^+$ ($[M+NH_2]^+$): 282.0854, found: 282.0855.

**(Z)-4-methyl-2-(4-(trifluoromethyl)phenyl)pent-2-enedinitrile (3k)**



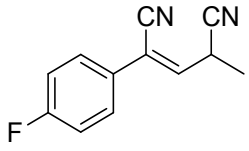

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a colorless oil (45% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.71 (m, 4H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.03 (dq, *J* = 8.0, 8.0 Hz, 1H), 1.64 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 140.7, 134.6, 132.5, 132.3, 132.2, 126.5, 126.4, 126.3, 118.7, 118.40, 114.2, 27.9, 18.7. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -63.0. **HRMS** (EI) calcd for $[C_{13}H_9F_3N_2]^+$: 250.0712, found: 250.0709.

**methyl (*Z*)-4-(1,3-dicyanobut-1-en-1-yl)benzoate (3l)**




Purification using column chromatography (ethyl acetate/petroleum ether = 1/4, v/v) gave the product as a yellow solid (35% yield). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.19-8.08 (m, 2H), 7.73-7.63 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 4.05 (dq, *J* = 8.0, 8.0 Hz, 1H), 3.97 (s, 3H), 1.66 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.0, 140.4, 135.3, 131.8, 130.5, 126.1, 118.8, 118.7, 114.4, 52.5, 27.9, 18.7. **HRMS** (EI) calcd for $[C_{14}H_{12}N_2O_2]^+$: 240.0893, found: 240.0889.

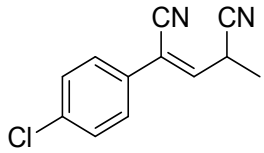
**(Z)-2-(4-fluorophenyl)-4-methylpent-2-enedinitrile (3m)**




Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v)

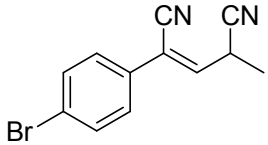
gave the product as a yellow solid (65% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.62 - 7.49 (m, 2H), 7.18-7.10 (m, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 3.99 (dq, *J* = 8.0, 8.0 Hz, 1H), 1.61 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.1, 162.6, 138.2, 138.1, 128.1, 128.0, 127.5, 127.4, 119.0, 118.4, 116.6, 116.4, 114.7, 27.9, 18.8. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -109.44. **HRMS** (EI) calcd for $[C_{12}H_9FN_2]^+$: 200.0744, found: 200.0741.

**(Z)-2-(4-chlorophenyl)-4-methylpent-2-enedinitrile (3n)**



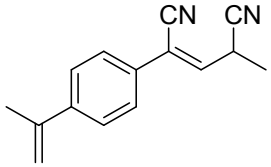

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a yellow solid (60% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.53 - 7.46 (d, *J* = 8.0 Hz, 2H), 7.44-7.40 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 3.91(dq, *J* = 8.0, 8.0 Hz, 1H), 1.62 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 138.7, 136.6, 129.8, 129.6, 127.3, 118.9, 118.4, 114.5, 27.9, 18.8. **HRMS** (EI) calcd for $[C_{12}H_9ClN_2]^+$: 216.0449, found: 216.0447.

**(Z)-2-(4-bromophenyl)-4-methylpent-2-enedinitrile (3o)**



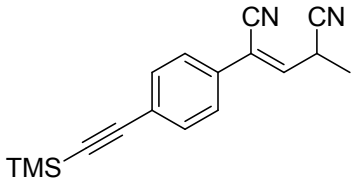

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a yellow solid (42% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.54 (m, 2H), 7.46-7.37 (m, 2H), 6.69 (d, *J* = 8.0 Hz, 1H), 3.99 (dq, *J* = 8.0, 8.0 Hz, 1H), 1.62 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 138.8, 132.5, 130.2, 127.5, 124.9, 118.8, 118.5, 114.4, 27.9, 18.7. **HRMS** (EI) calcd for $[C_{12}H_9BrN_2]^+$: 259.9944, found: 259.9941.

**(*Z*)-4-methyl-2-(4-(prop-1-en-2-yl)phenyl)pent-2-enedinitrile (3p)**



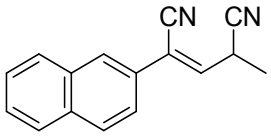

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a white solid (74% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 4H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.45 (s, 1H), 5.18 (s, 1H), 4.01 (dq, *J* = 8.0, 8.0 Hz, 1H), 2.16 (s, 3H), 1.61 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 143.3, 142.0, 137.7, 130.1, 126.3, 126.0, 119.2, 119.1, 114.8, 114.2, 27.8, 21.6, 18.8. **HRMS** (ESI) calcd for $[C_{15}H_{16}N_3]^+$ ($[M+NH_2]^+$): 238.1344, found: 238.1345.

**(*Z*)-4-methyl-2-(4-((trimethylsilyl)ethynyl)phenyl)pent-2-enedinitrile (3q)**




Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a yellow solid (48% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.49 (m, 4H), 6.73 (d, *J* = 12.0 Hz, 1H), 4.01 (dq, J = 8.0, 8.0 Hz, 1H), 1.64 (d, *J* = 8.0 Hz, 3H), 0.28 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 138.7, 132.7, 131.0 125.8, 125.4, 118.9, 118.9, 114.5, 103.7, 97.4, 27.9, 18.8, -0.16. **HRMS** (EI) calcd for $[C_{17}H_{18}N_2Si]^+$: 278.1234, found: 278.1230.

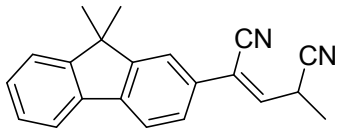
**(Z)-4-methyl-2-(naphthalen-2-yl)pent-2-enedinitrile (3r)**




Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a white solid (78% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.88 (m, 3H), 7.58 (m, 3H), 6.82 (d, *J* = 12.0 Hz, 1H), 4.18-3.97 (m, 1H), 1.65 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 138.2, 133.8, 133.0, 129.3, 128.6, 128.5, 127.8, 127.7, 127.3, 127.1, 121.8, 119.5, 119.2, 114.9, 28.0, 18.9. **HRMS** (EI)

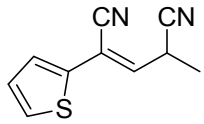
calcd for $[C_6H_{12}N_2]^+$: 232.0995, found: 232.0991.

**(Z)-2-(9,9-dimethyl-9H-fluoren-2-yl)-4-methylpent-2-enedinitrile (3s)**



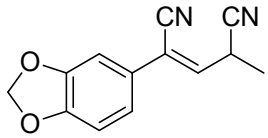

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a yellow solid (76% yield).**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.80 - 7.70 (m, 2H), 7.60 (m, 1H), 7.56-7.52 (m, 1H), 7.50-7.43 (m, 1H), 7.40-7.35 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.05 (dq, *J* = 8.0, 8.0 Hz, 1H), 1.65 (d, *J* = 8.0 Hz, 3H), 1.52 (s, 6H).**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 154.7, 154.1, 141.7, 137.8, 137.3, 130.1, 128.4, 127.3, 125.4, 122.8, 120.7, 120.6, 120.3, 119.8, 119.3, 115.1, 47.1, 27.9, 27.0, 18.9. **HRMS** (EI) calcd for $[C_{21}H_{18}N_2]^+$: 298.1465, found: 298.1460.

**(*Z*)-4-methyl-2-(thiophen-2-yl)pent-2-enedinitrile (3t)**




Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a yellow solid (55% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 4.0, 4.0 Hz, 1H), 7.41 (dd, *J* = 4.0, 4.0 Hz, 1H), 7.24 (dd, *J* = 4.0, 4.0 Hz, 1H), 6.56 (d, *J* = 12.0 Hz, 1H), 3.94 (dq, *J* = 8.0, 8.0 Hz, 1H), 1.60 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 136.5, 133.4, 128.1, 125.6, 123.8, 119.1, 114.8, 114.3, 27.6, 18.9. **HRMS** (EI) calcd for $[C_{10}H_8N_2S]^+$: 188.0403, found: 188.0398.

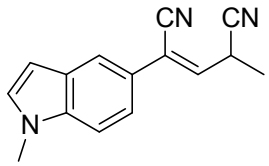
**(*Z*)-2-(benzo[d][1,3]dioxol-5-yl)-4-methylpent-2-enedinitrile (3u)**




Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a white solid (69% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.99 (d, *J* = 1.6 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.52 (d, *J* =

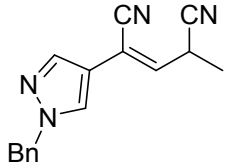
8.0 Hz, 1H), 6.03 (s, 2H), 3.96 (dq, *J* = 8.0, 8.0 Hz, 1H), 1.59 (d, *J* = 8.0 Hz, 3H).**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 149.6, 148.7, 136.3, 125.5, 121.2, 119.2, 118.9, 114.9, 108.7, 105.6, 101.9, 27.8, 18.9. **HRMS** (EI) calcd for $[C_{13}H_{10}N_2O_2]^+$: 226.0737, found: 226.0732.

**(*Z*)-4-methyl-2-(1-methyl-1H-indol-5-yl)pent-2-enedinitrile (3v)**



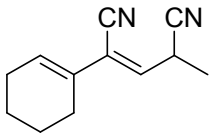

Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a yellow solid (85% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 1.6Hz, 1H), 7.44-7.34 (m, 2H), 7.14 (d, *J* = 4.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.57 (d, *J* = 4.0 Hz, 1H), 4.05 (dq, *J* = 8.0, 8.0 Hz, 1H), 3.84 (s, 3H), 1.64 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 137.4, 135.3, 130.6, 128.7, 122.8, 120.4, 119.7, 119.6, 119.0, 115.6, 110.0, 102.0, 33.1, 27.9, 19.0. **HRMS (EI)** calcd for $[C_{15}H_{13}N_3]^+$: 235.1104, found: 235.1103.

**(Z)-2-(1-benzyl-1H-pyrazol-4-yl)-4-methylpent-2-enedinitrile (3w)**



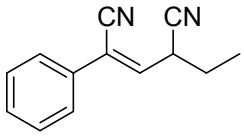

Purification using column chromatography (ethyl acetate/petroleum ether = 1/3, v/v) gave the product as a colorless oil (66% yield, *Z/E* = 11/1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.59 (s, 1H), 7.44-7.34 (m, 3H), 7.30-7.25 (m, 2H), 6.40 (d, *J* = 8.0 Hz, 1H), 5.32 (s, 2H), 4.02-3.81 (m, 1H), 1.57 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 136.6, 135.3, 134.4, 129.1, 128.6, 128.1, 127.9, 119.2, 115.9, 114.7, 110.5, 56.6, 27.4, 18.9. **HRMS** (ESI) calcd for $[C_{16}H_{15}N_4]^+$ ($[M+H]^+$): 263.1291, found: 263.1299.

**(Z)-2-(cyclohex-1-en-1-yl)-4-methylpent-2-enedinitrile (3x)**



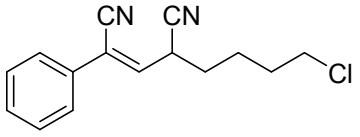
Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a colorless oil (55% yield). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 6.42 (t, *J* = 7.2 Hz, 1H), 6.07 (d, *J* = 8.0 Hz, 1H), 3.88 (dq, *J* = 8.0, 8.0 Hz, 1H), 2.28-2.20 (m, 2H), 2.18-2.07 (m, 2H), 1.76-1.68 (m, 2H), 1.66-1.57 (m, 2H), 1.52 (d, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 134.2, 133.5, 130.5, 121.6, 119.6, 114.4, 27.5, 25.9, 24.7, 22.0, 21.6, 19.0. **HRMS** (EI) calcd for $[C_{12}H_{14}N_2]^+$: 186.1151, found: 186.1149.

**(Z)-4-ethyl-2-phenylpent-2-enedinitrile (3y)**



Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a light yellow oil (68% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.62 -7.56 (m, 2H), 7.51-7.44 (m, 3H), 6.70 (d, J = 8.0 Hz, 2H), 3.95 (dt, *J* = 8.0, 8.0, 1H), 2.09 -1.83 (m, 2H), 1.21 (t, J = 8.0 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.3, 131.4, 130.4, 129.3, 126.1, 120.1, 118.3, 115.0, 35.1, 26.8, 11.4. **HRMS** (EI) calcd for $[C_{13}H_{12}N_2]^+$: 196.0995, found: 196.0997.

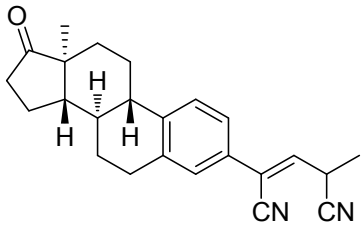
**(Z)-4-(4-chlorobutyl)-2-phenylpent-2-enedinitrile (3z)**



Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a light yellow oil (63% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.61-7.55 (m, 2H), 7.49-7.45 (m, 3H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.95 (dt, *J* = 8.0, 8.0, 1H), 3.60 (t, *J* = 8.0 Hz, 2H), 2.09-1.96 (m, 1H), 1.94 -1.84 (m, 3H), 1.81-1.70 (m,

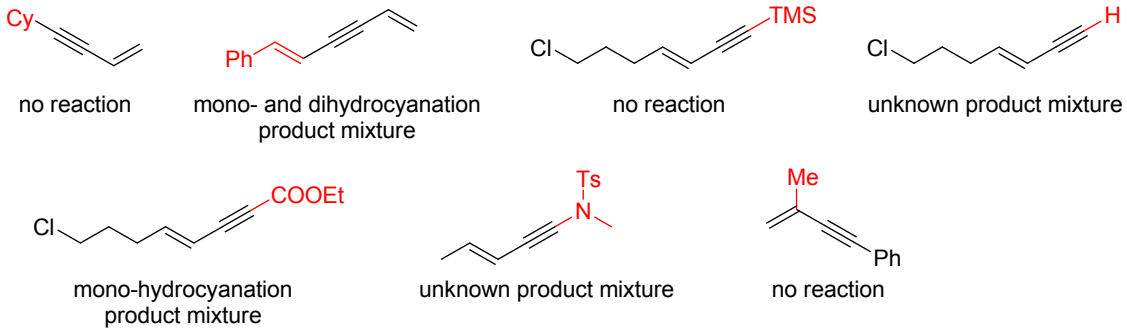
2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.0, 131.3, 130.5, 129.3, 126.1, 120.3, 118.1, 115.0, 44.1, 33.5, 32.4, 31.6, 24.2. **HRMS** (EI) calcd for $[C_{15}H_{15}ClN_2]^+$: 258.0918, found: 258.0917.

**(Z)-4-methyl-2-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)pent-2-enedinitrile (3aa)**

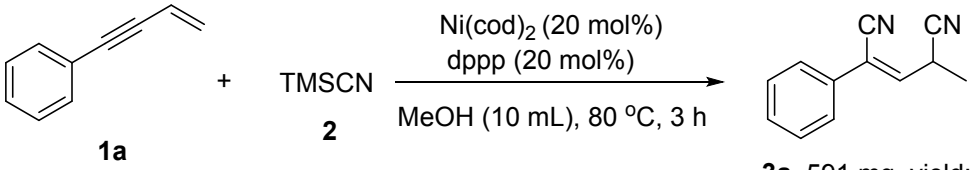



Purification using column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product as a white solid (70% yield). **$^1$H NMR** (400 MHz, DMSO) δ 7.42-7.36 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 4.11 (dq, *J* = 8.0, 8.0 Hz, 1H), 2.95-2.85 (m, 2H), 2.47-2.22 (m, 4H), 2.13 -1.89 (m, 4H), 1.83-1.74 (m, 1H), 1.60-1.45 (m, 6H), 1.42-1.35 (m, 1H), 0.83 (s, 3H).**$^{13}$C NMR** (100 MHz, DMSO) δ 142.4, 140.3, 137.9, 129.2, 126.7, 126.5, 123.6, 120.4, 117.5, 115.6, 50.0, 47.7, 44.3, 37.8, 35.8, 31.7, 29.2, 27.5, 26.2, 25.6, 21.6, 18.5, 13.9. **HRMS** (ESI) calcd for $[C_{24}H_{26}N_2NaO]^+$ ($[M+Na]^+$): 381.1937, found: 381.1938.

## 5. Unsuccessful 1,3-enynes




## 6. Scale-up synthesis of 3a

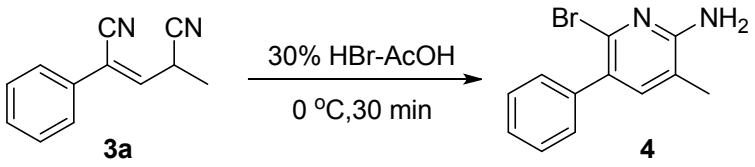



**3a**, 591 mg, yield: 65%

To a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar, were added $Ni(cod)_2$ (20 mol%, 275.0 mg), dppp (20 mol%, 412.0 mg) and MeOH (10 mL) in glovebox. The mixture was stirred at room temperature for 1 min. Next, alkyne **1a** (5.0 mmol, 1.0 equiv.) and TMSCN **2** (3.0 mL, 25.0 mmol, 5.0 equiv.) (*caution: TMSCN should be handled carefully because it is a highly toxic chemical*) were added successively. Then the reaction was removed out of glove box and heated at 80 °C for 3 h. The reaction mixture was diluted with DCM (20 mL). After the solvent was removed under reduced pressure, the residue was purified by column chromatography to afford the desired product **3a** (591 mg, yield: 65%).

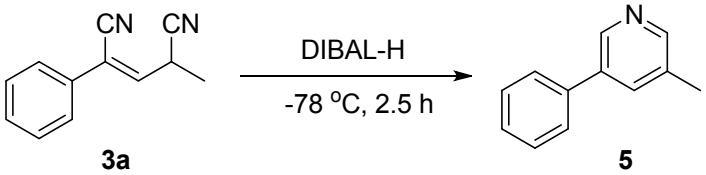
## 7. Synthesis of poly-substituted pyridine 4 and 5.

**5-bromo-2-methyl-6-phenylpyridin-3-amine (4)**




Following the reported procedure with a slight modification,[3] dinitrile **3a** (36.4 mg, 0.2 mmol) in AcOH (0.5 mL) was added dropwise to 30% HBr in AcOH (0.2 g) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then quenched with saturated $NaHCO_3$ solution. The resulting mixture was extracted with dichloromethane three times, and the combined organic phase was dried over $Na_2SO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) gave the product **4** as a yellow solid (89% yield). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.35 (m, 5H), 7.28 (s, 1H), 4.68 (s, 2H), 2.14 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 156.0, 141.0, 139.5, 136.5, 129.6, 129.0, 128.1, 127.4, 115.4, 16.3. **HRMS** (ESI) calcd for $[C_{12}H_{12}BrN_2]^+$ ($[M+H]^+$): 263.0178, found: 263.0179.

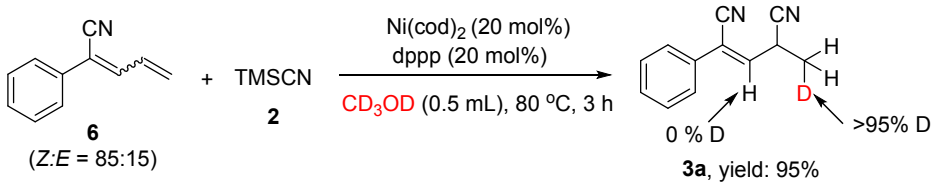
**2-methyl-6-phenylpyridine (5)**



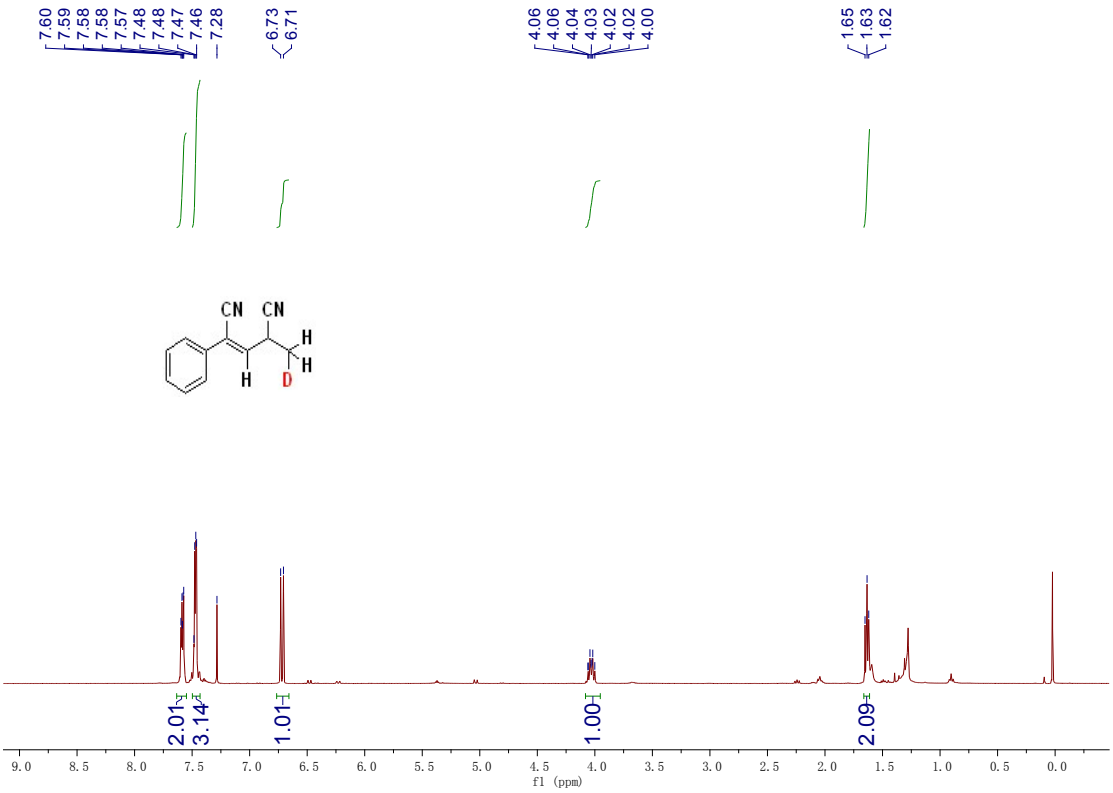

To a solution of dinitrile (**3a**) (36.4mg, 0.2mmol) in toluene (6.0 mL) were added DIBAL–H (0.8 mmol, 4.0 equiv.) at -78 °C. The reaction mixture was stirred for 2.5 h at -78 °C and then quenched with 5% $H_2SO_4$ aqueous solution at 0 °C. The reaction mixture was partitioned between $Et_2O$ (10 mL) and brine (10 mL). The aqueous phase was extracted with $Et_2O$. The combined organic layers were dried over $Na_2SO_4$ and concentrated to dryness. The resulting residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) to give the colorless oil **5** (92% yield). **$^1$H NMR** (400 MHz, DMSO) δ 8.69 (d, $J$ = 2.4 Hz, 1H), 8.42 (d, $J$ = 1.2 Hz, 1H), 7.90 (s, 1H), 7.74-7.69 (m, 2H), 7.53-7.47 (m, 2H), 7.45-7.38 (m, 1H), 2.38 (s, 3H). **$^{13}$C NMR** (100 MHz, DMSO) δ 149.3, 145.3, 137.6, 135.5, 135.0, 133.5,

129.6, 128.5, 127.3, 18.4. **HRMS** (ESI) Calcd for $[C_{12}H_{12}N]^+$ ($[M+H]^+$) 170.0964, found 170.0966.

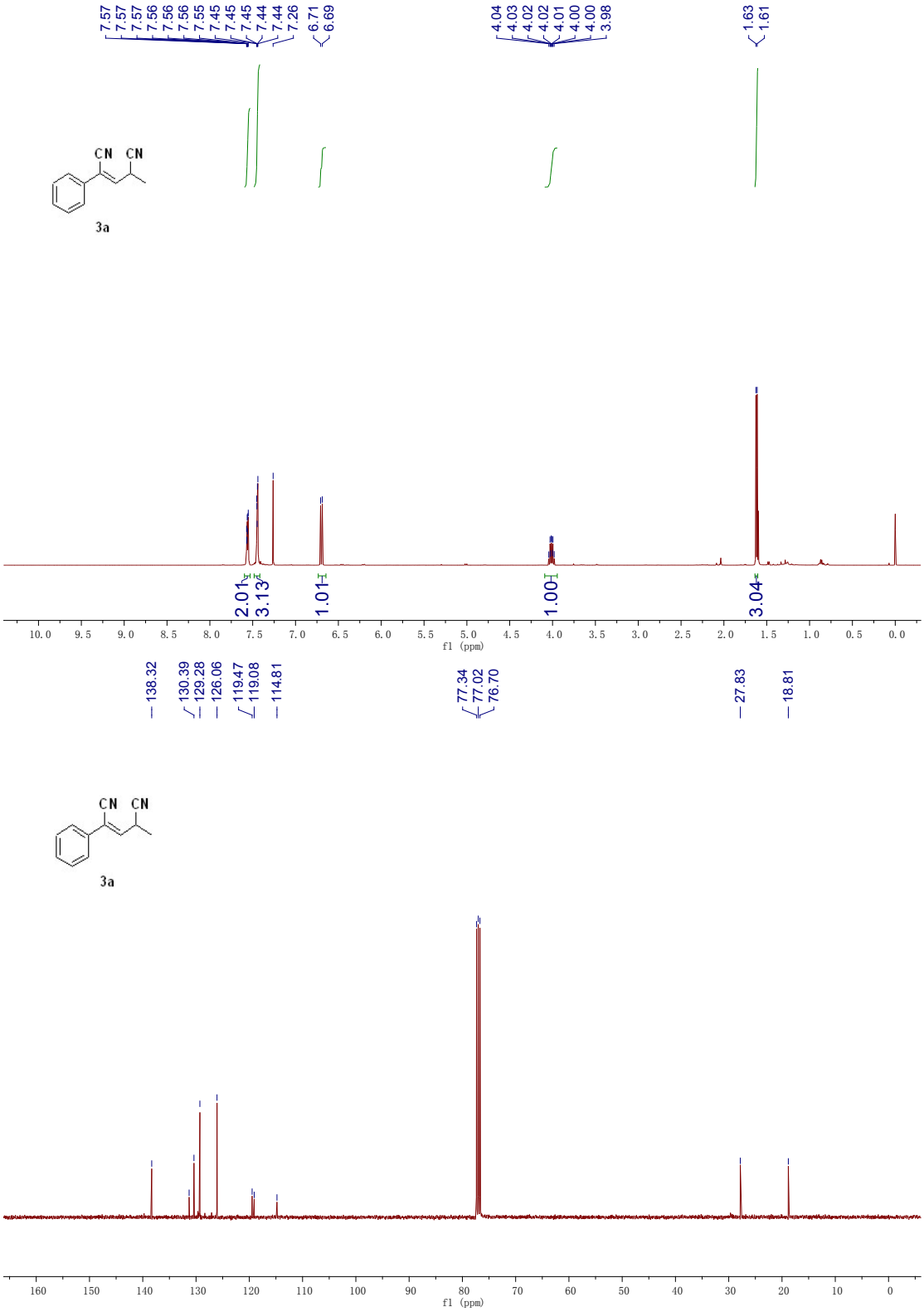
## 8. Deuterium-labeling experiment for the hydrocyanation of 6

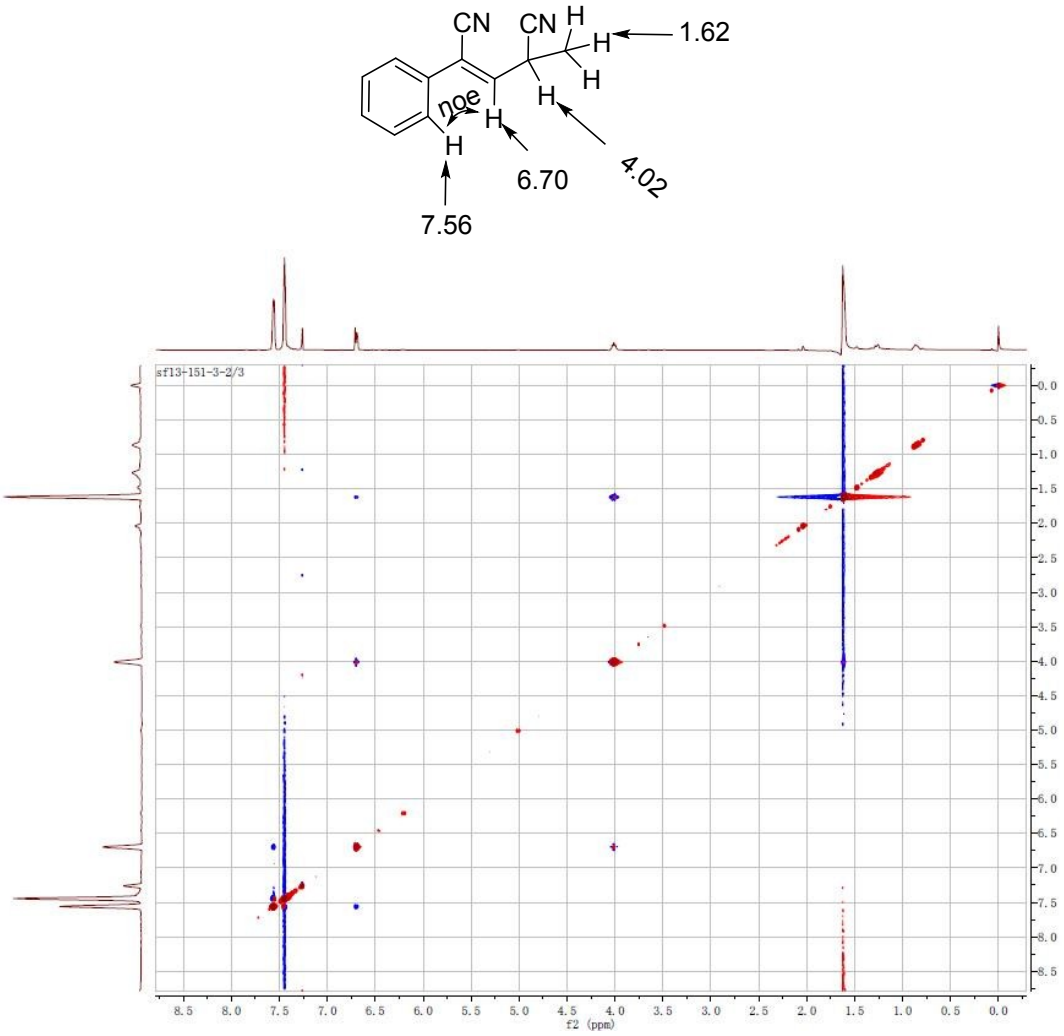



To a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar, were added $Ni(cod)_2$ (20 mol%, 11.0 mg), dppp (20 mol%, 16.5 mg) and $CD_3OD$ (1.0 mL) in glovebox. The mixture was stirred at room temperature for 1 min. Next, **6**[2] (0.2 mmol, 1.0 equiv.) and TMSCN (120 μL, 1.0 mmol, 5.0 equiv.) (*caution: TMSCN should be handled carefully because it is a highly toxic chemical*) were added successively. Then the reaction was removed out of glove box and heated at 80 °C for 3 h. The reaction mixture was diluted with DCM (1 mL). After the solvent was removed under reduced pressure, the residue was purified by column chromatography to afford the desired product.



# 9. NMR Spectra

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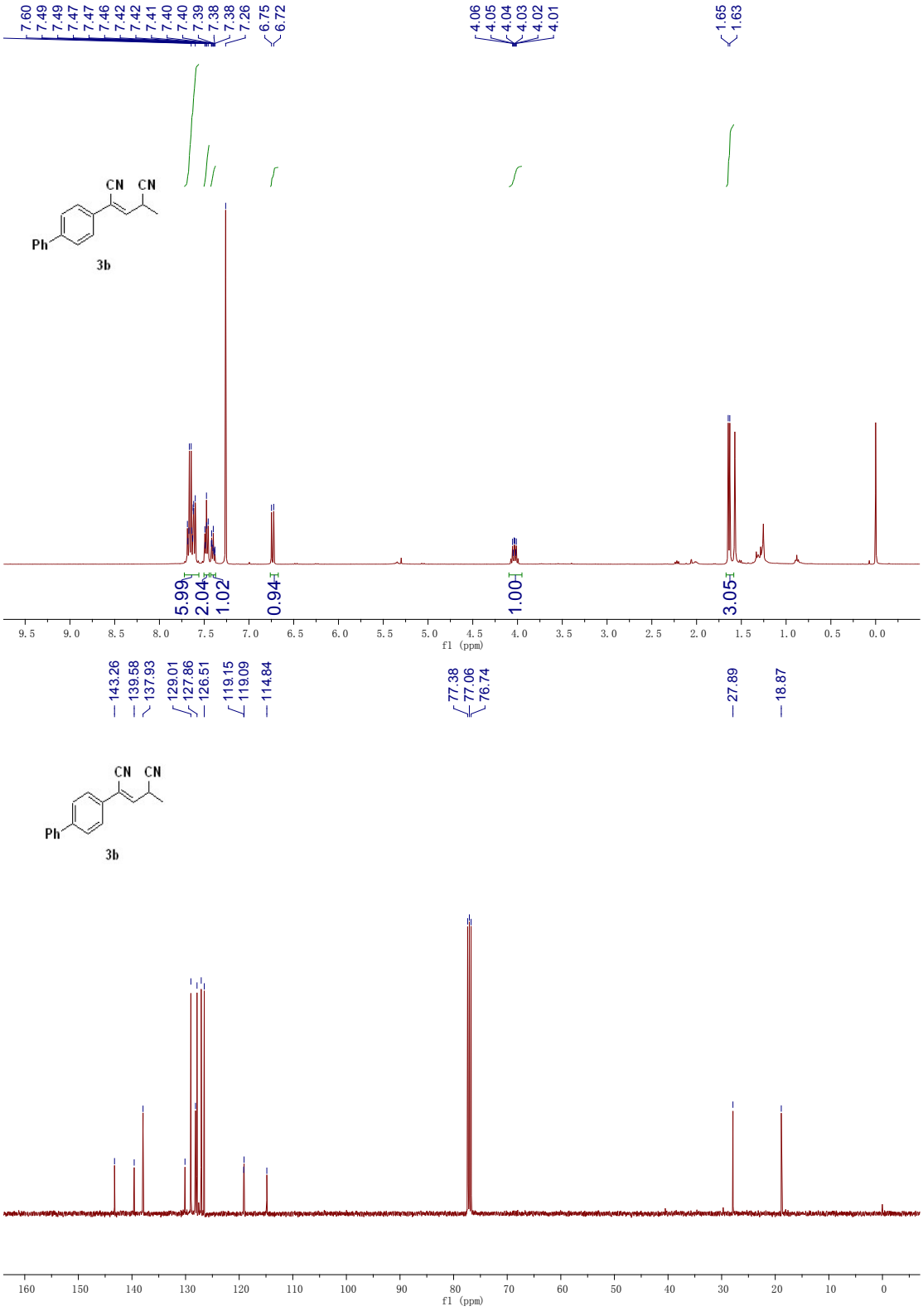
CN
H
H
H
H
1.62
noe
H
H
6.70
4.02
7.56
sf13-151-3-2/3
f2 (ppm)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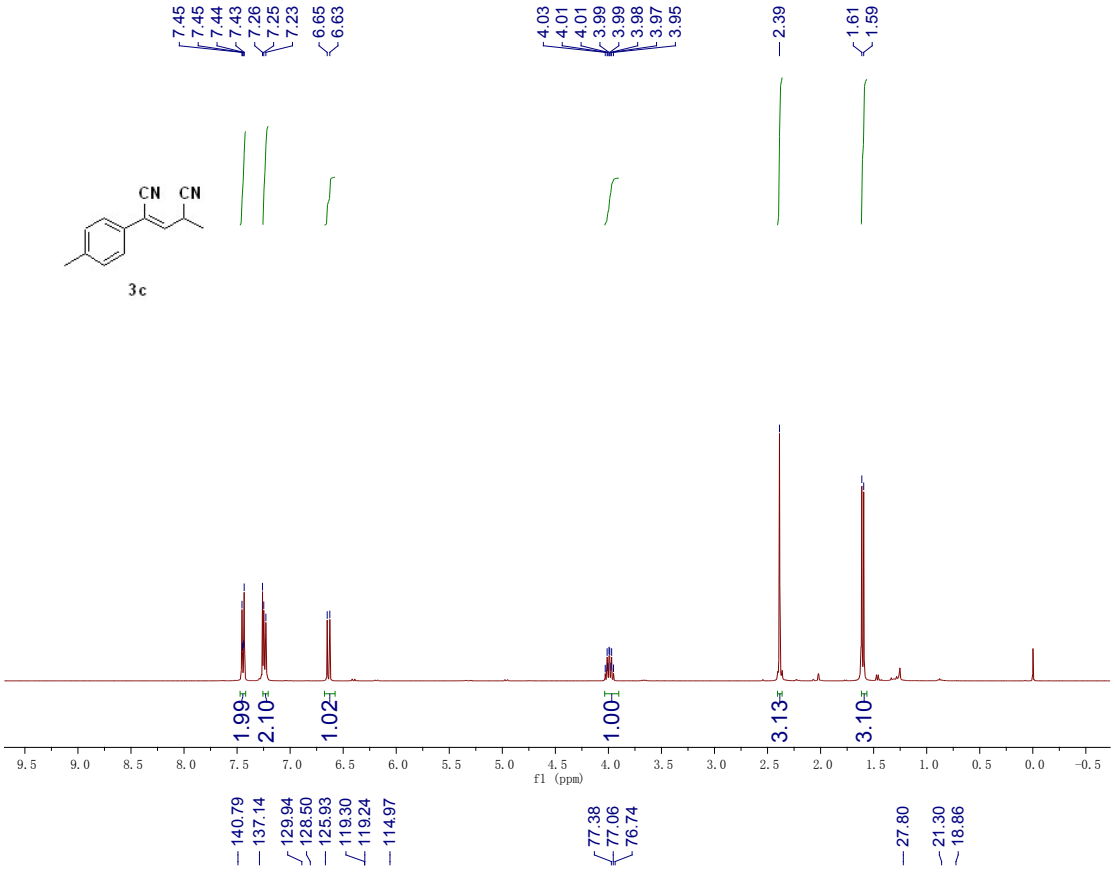
7.49
7.47
7.47
7.46
7.42
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.26
6.75
6.72
4.06
4.05
4.04
4.03
4.02
4.01
1.65
1.63
CN CN
Ph
3b
5.99
2.04
1.02
0.94
1.00
3.05
f1 (ppm)
143.26
139.58
137.93
129.01
127.86
126.51
119.15
119.09
114.84
77.38
77.06
76.74
27.89
18.87
CN CN
Ph
3b
f1 (ppm)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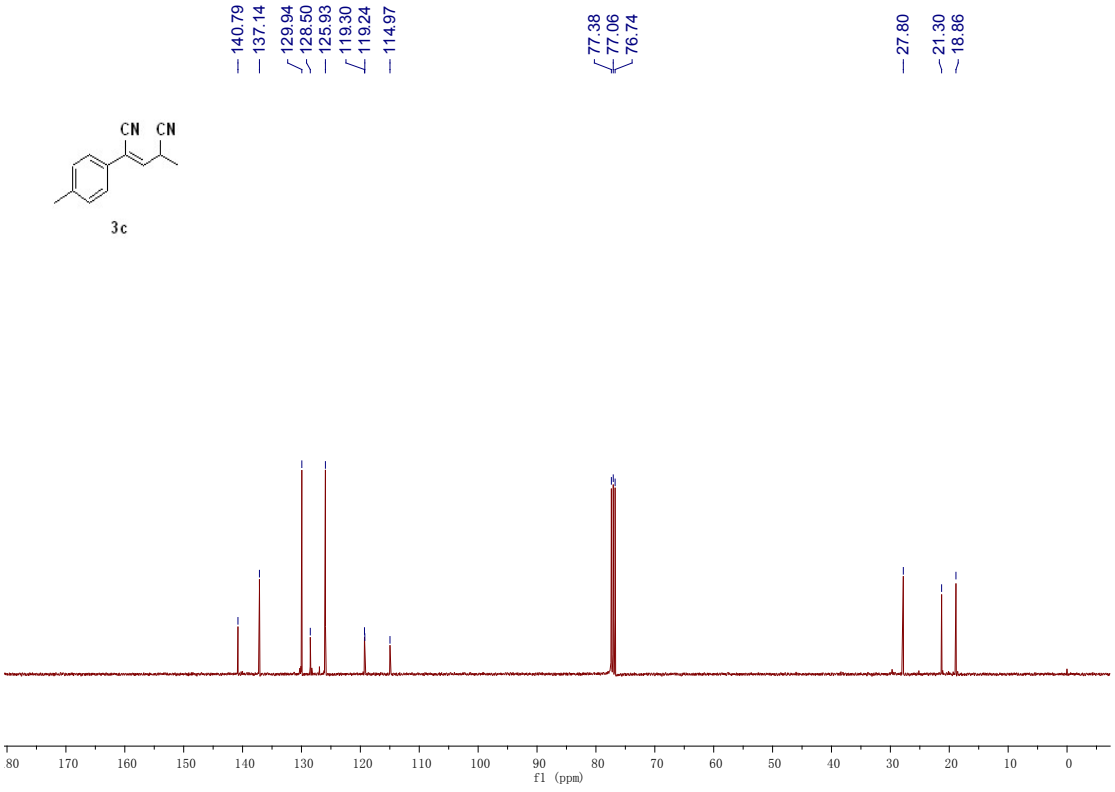
7.25
7.23
6.65
6.63
4.03
4.01
4.01
3.99
3.99
3.98
3.97
3.95
2.39
1.61
1.59
CN
CN
3c
1.99
2.10
1.02
1.00
3.13
3.10
f1 (ppm)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137.14
129.94
128.50
125.93
119.30
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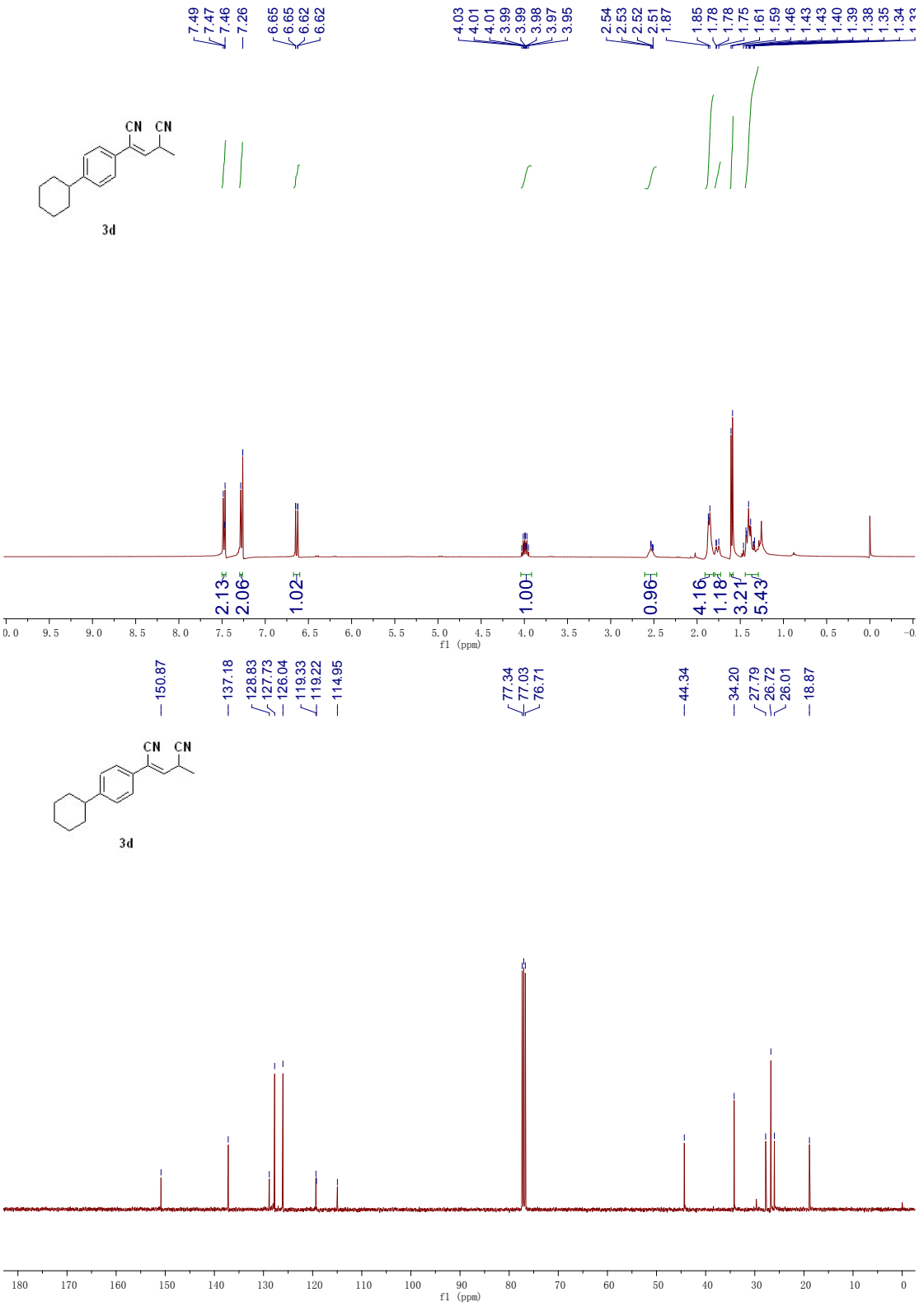
77.06
76.74
27.80
21.30
18.86
CN
CN
3c
f1 (ppm)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6.65
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6.62
4.03
4.01
4.01
3.99
3.99
3.98
3.97
3.95
2.54
2.53
2.52
2.51
1.87
1.85
1.78
1.78
1.75
1.61
1.59
1.46
1.43
1.43
1.40
1.39
1.38
1.35
1.34
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3d
2.13
2.06
1.02
1.00
0.96
4.16
1.18
3.21
5.43
f1 (ppm)
150.87
137.18
128.83
127.73
126.04
119.33
119.22
114.95
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44.34
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26.72
26.01
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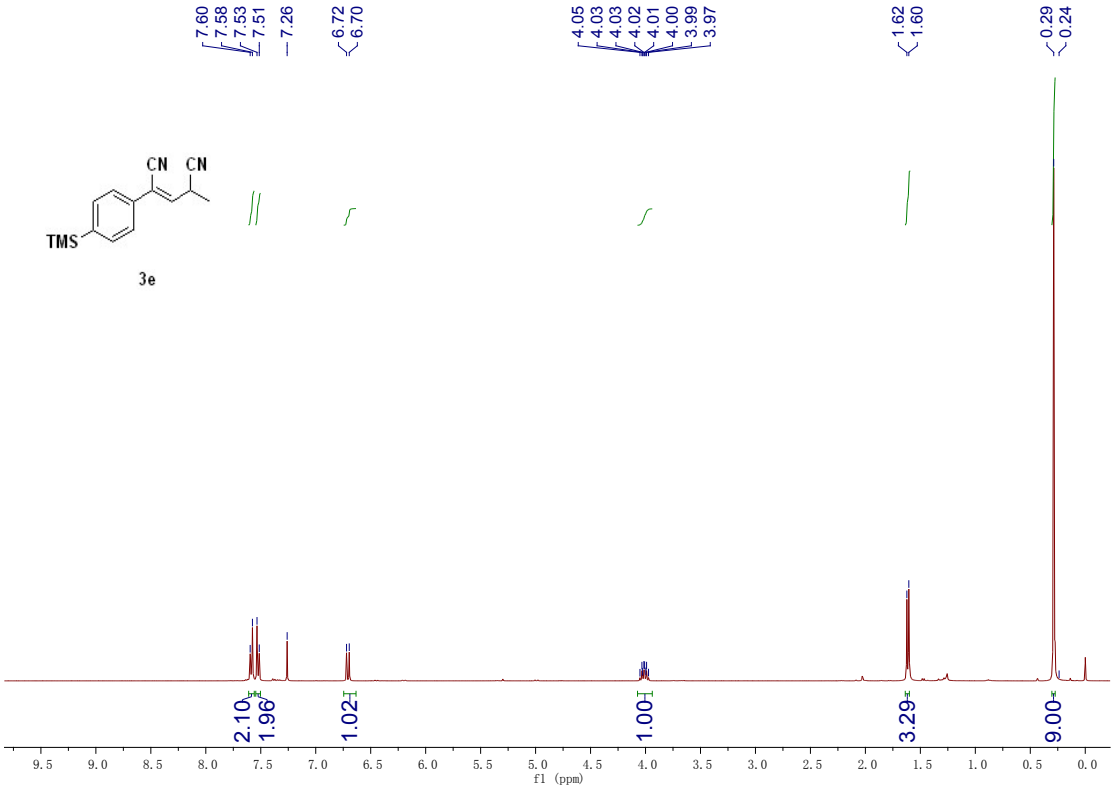
CN CN
3d
f1 (ppm)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4.03
4.02
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4.00
3.99
3.97
1.62
1.60
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CN
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3e
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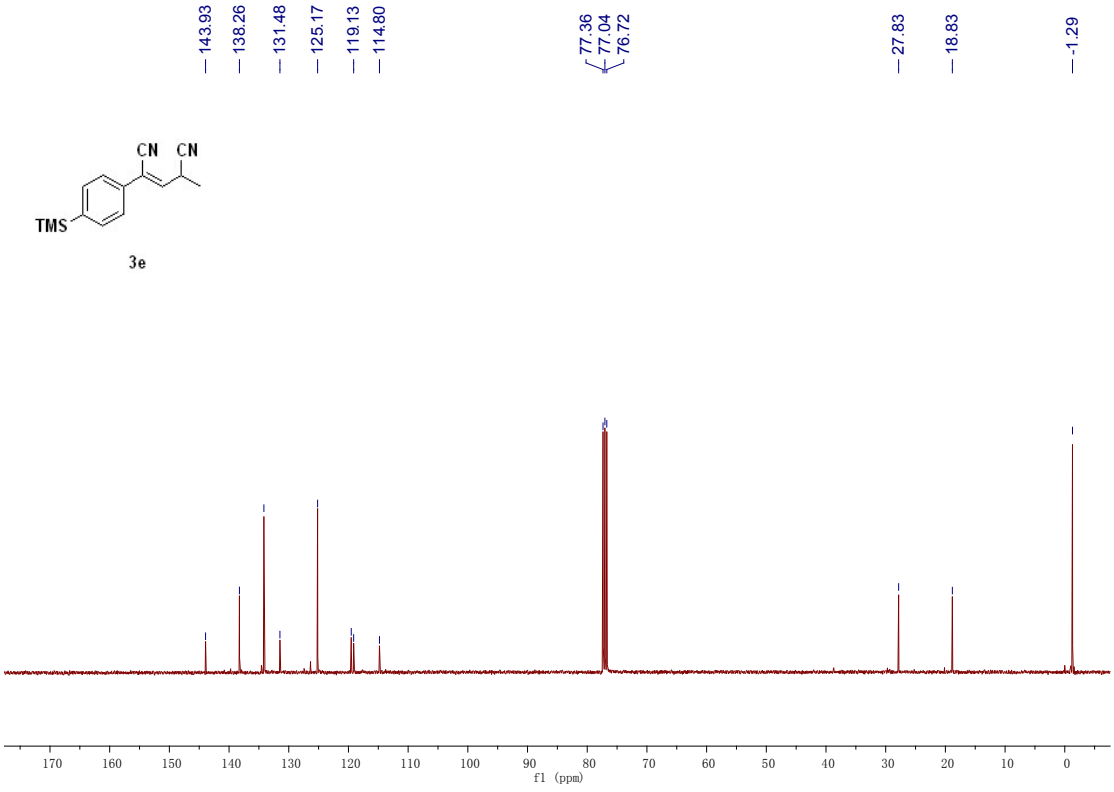
1.96
1.02
1.00
3.29
9.00
f1 (ppm)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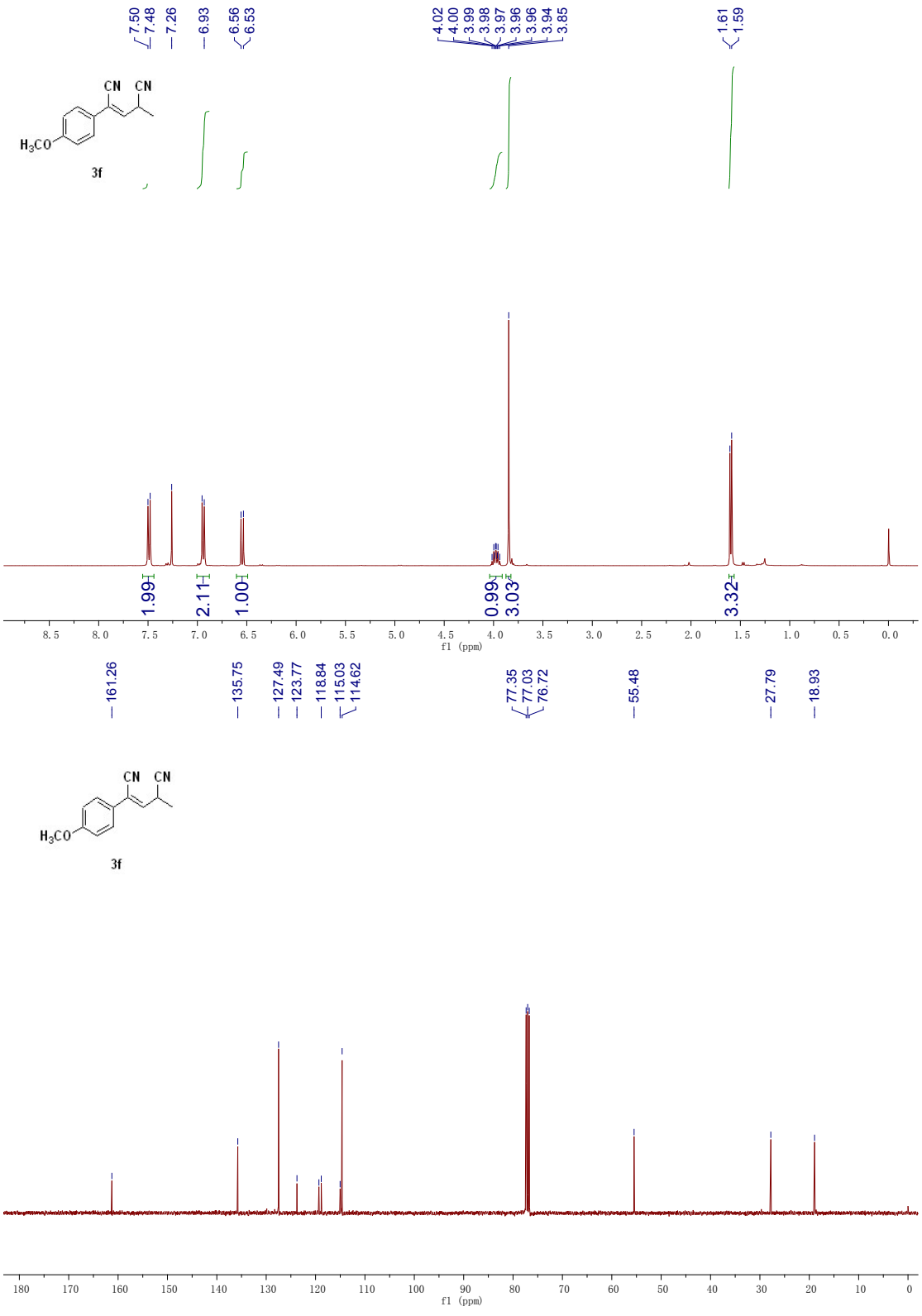
18.83
-1.29
CN
CN
TMS
3e
f1 (ppm)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4.00
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3.96
3.94
3.85
1.61
1.59
CN
CN
H3CO
3f
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2.11
1.00
0.99
3.03
3.32
f1 (ppm)
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135.75
127.49
123.77
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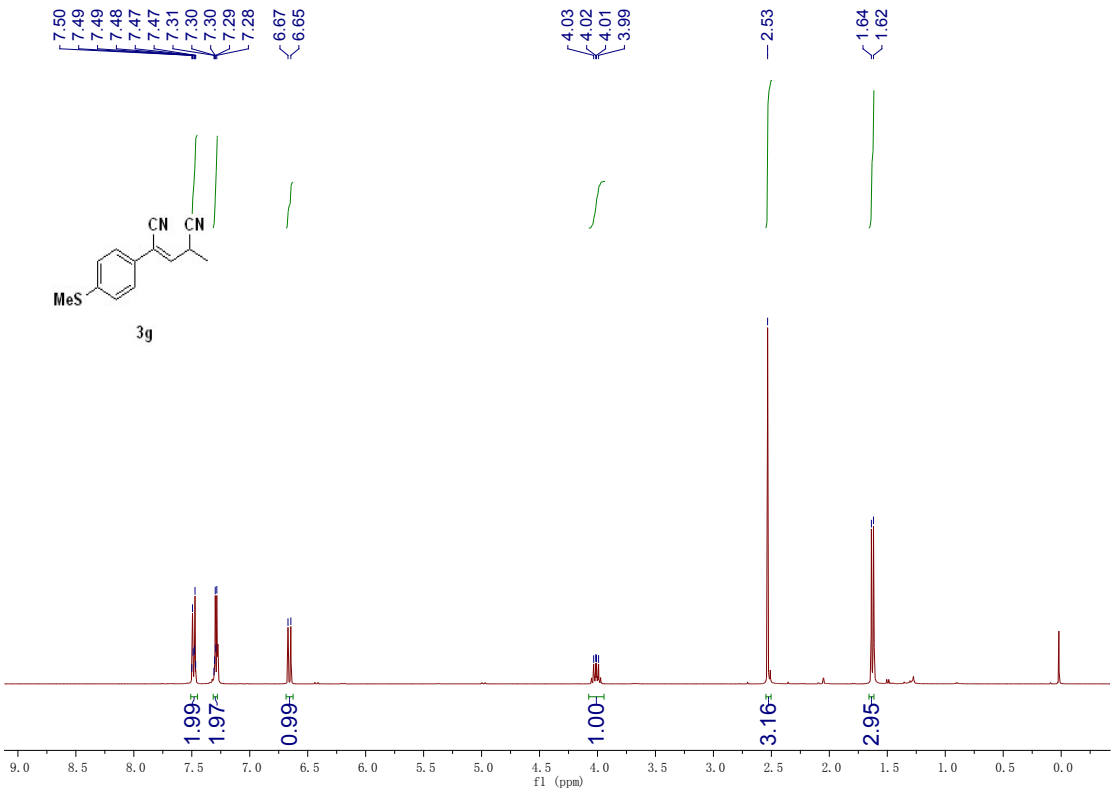
18.93
CN
CN
H3CO
3f
f1 (ppm)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7.29
7.28
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6.65
4.03
4.02
4.01
3.99
2.53
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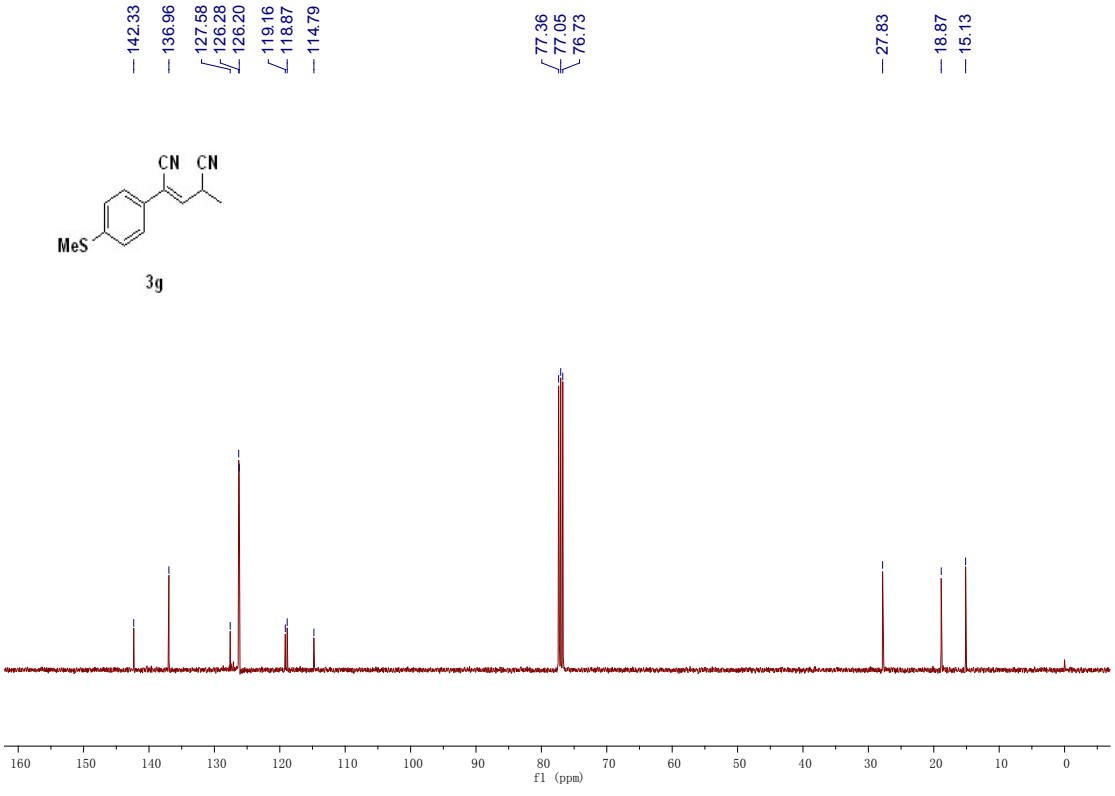
1.62
CN
CN
MeS
3g
1.99
1.97
0.99
1.00
3.16
2.95
f1 (ppm)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15.13
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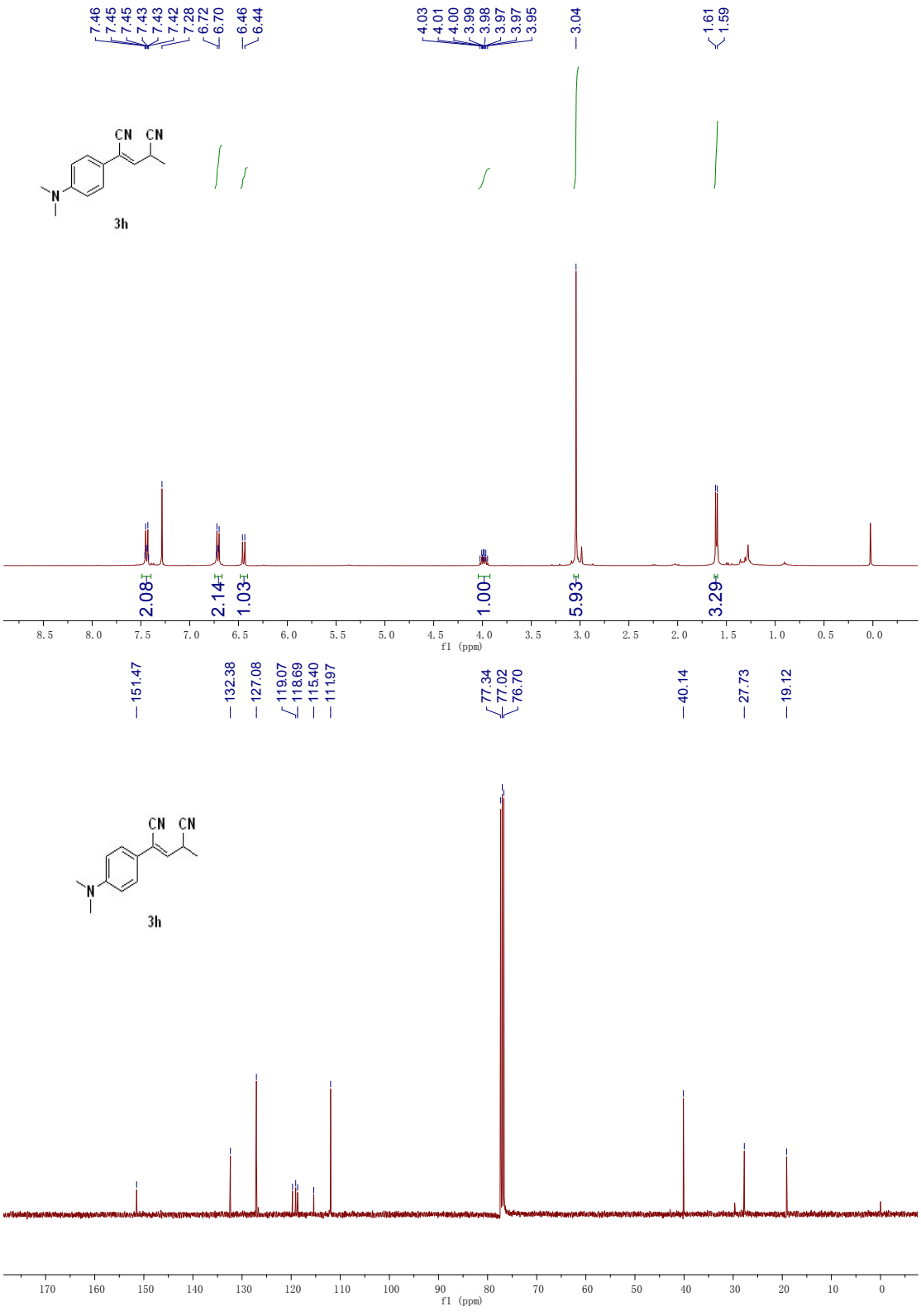
CN
MeS
3g
f1 (ppm)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6.46
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4.01
4.00
3.99
3.98
3.97
3.97
3.95
3.04
1.61
1.59
CN
CN
N
3h
2.08
2.14
1.03
1.00
5.93
3.29
f1 (ppm)
151.47
132.38
127.08
119.07
118.69
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19.12
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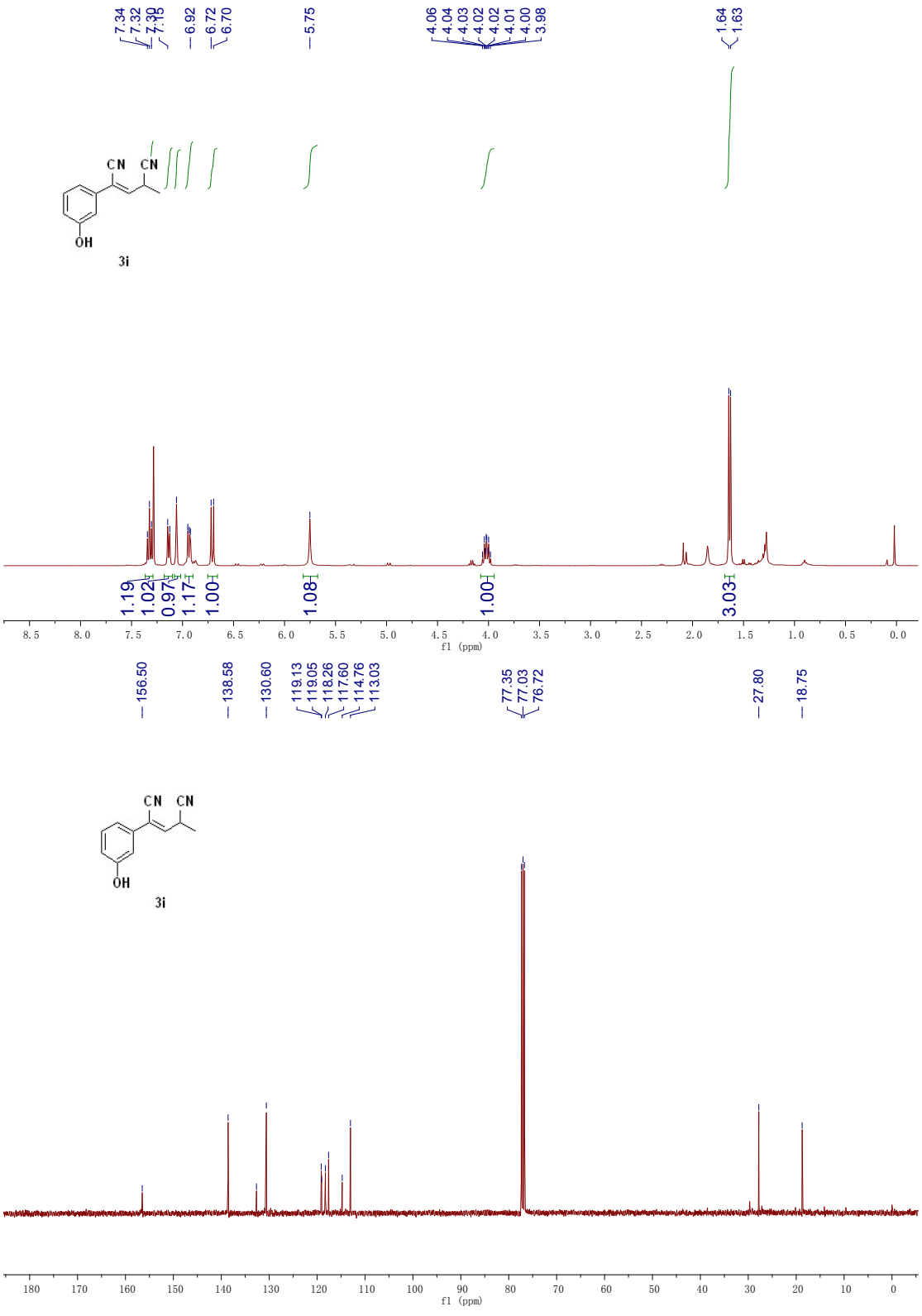
3h
f1 (ppm)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5.75
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4.03
4.02
4.02
4.01
4.00
3.98
1.64
1.63
CN
CN
OH
3i
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1.02
0.97
1.17
1.00
1.08
1.00
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
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138.58
130.60
119.13
119.05
118.26
117.60
114.76
113.03
77.35
77.03
76.72
27.80
18.75
CN
CN
OH
3i
180
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160
150
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130
120
110
100
90
80
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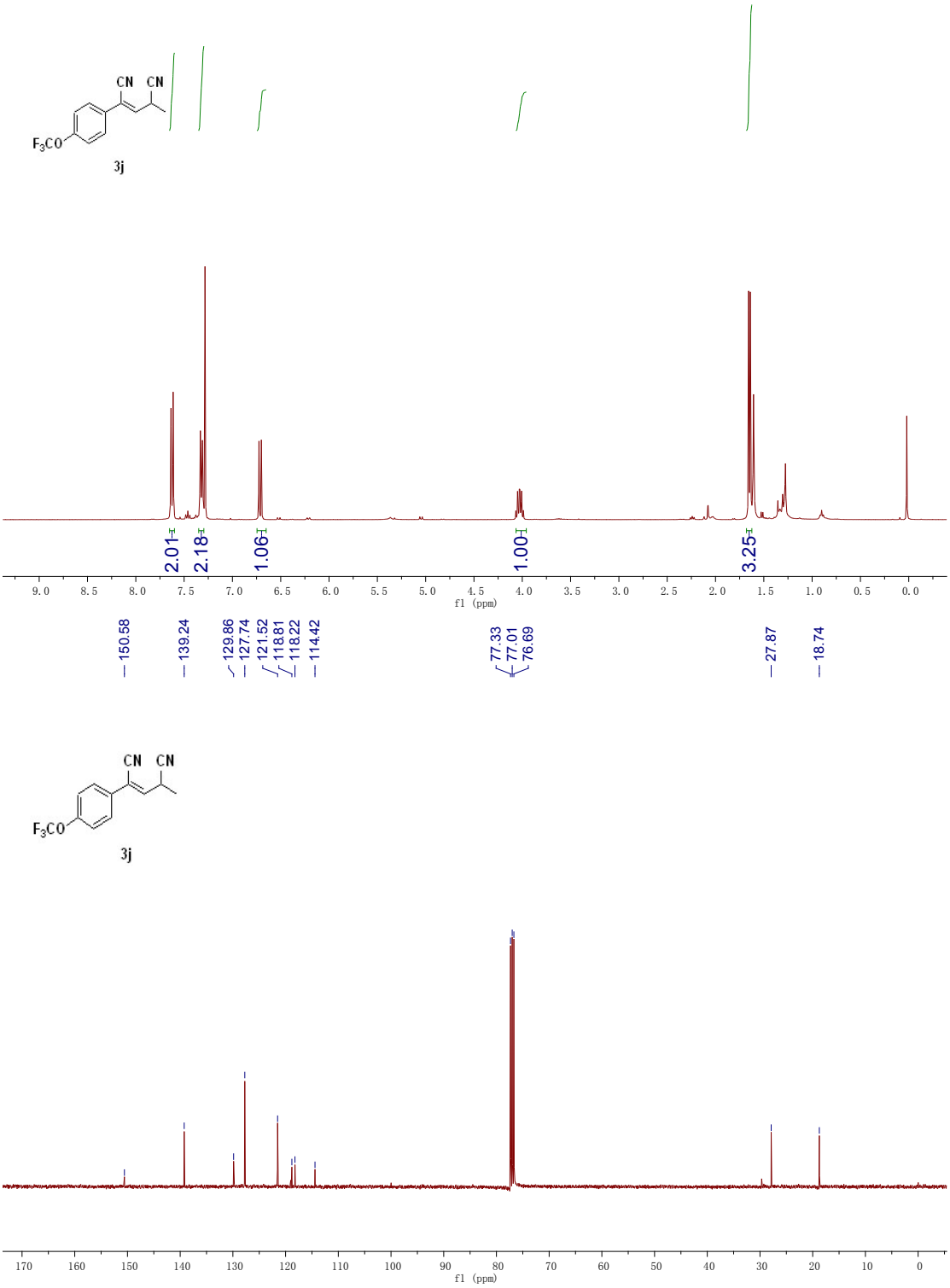
50
40
30
20
10
0
f1 (ppm)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CN
F3CO
3j
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2.18
1.06
1.00
3.25
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f1 (ppm)
150.58
139.24
129.86
127.74
121.52
118.81
118.22
114.42
77.33
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76.69
27.87
18.74
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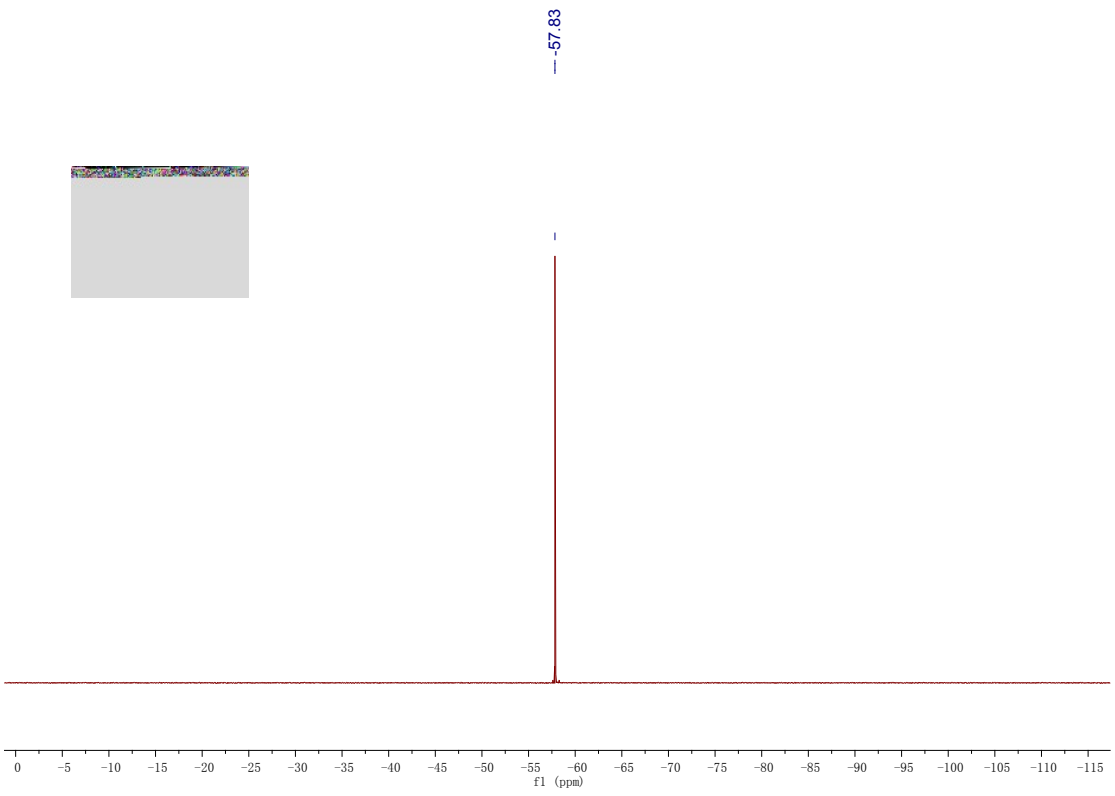
CN
F3CO
3j
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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-10
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-20
-25
-30
-35
-40
-45
-50
-55
-60
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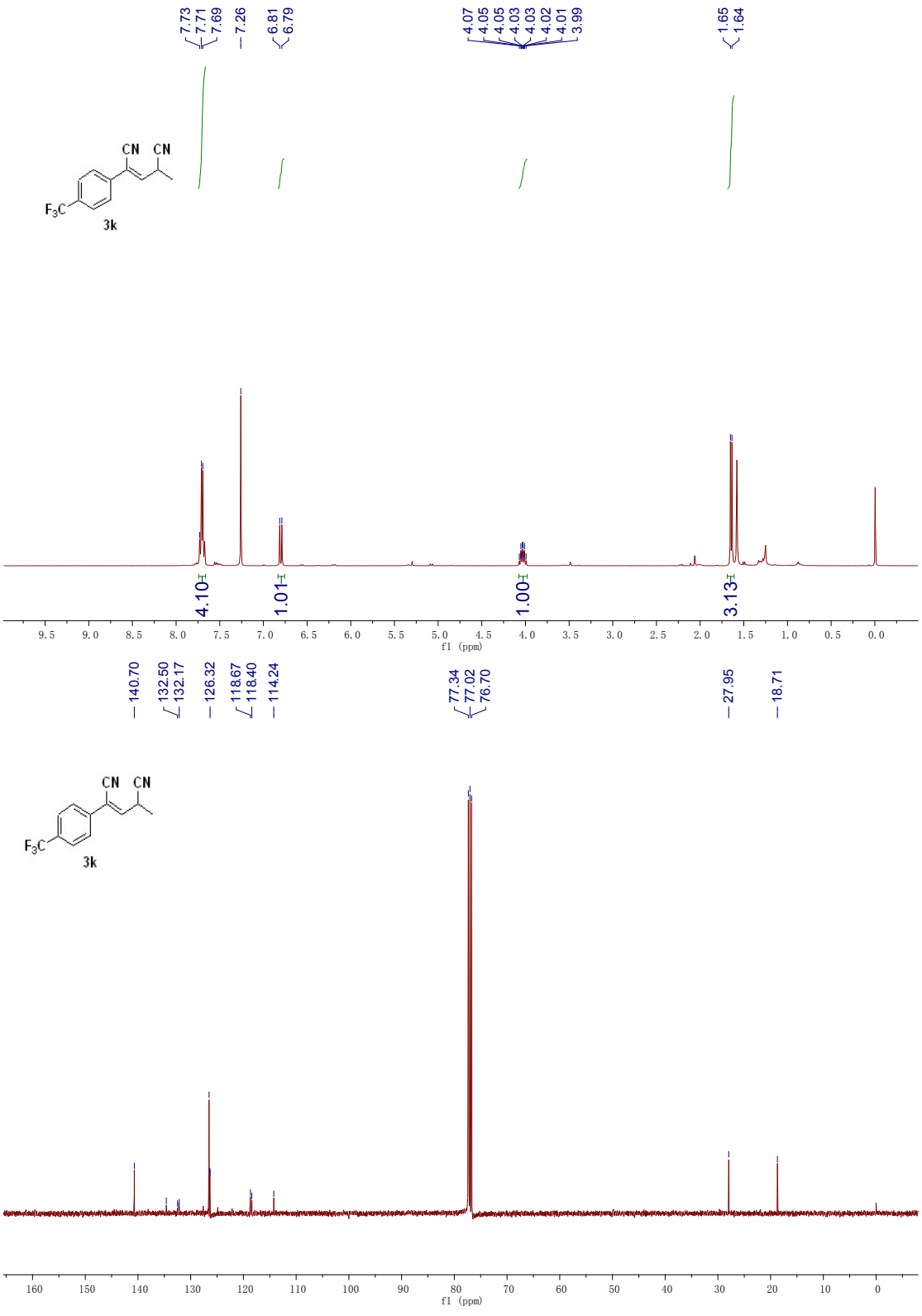
-95
-100
-105
-110
-115
f1 (ppm)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4.07
4.05
4.05
4.03
4.03
4.02
4.01
3.99
1.65
1.64
CN CN
F3C
3k
4.10
1.01
1.00
3.13
f1 (ppm)
140.70
132.50
132.17
126.32
118.67
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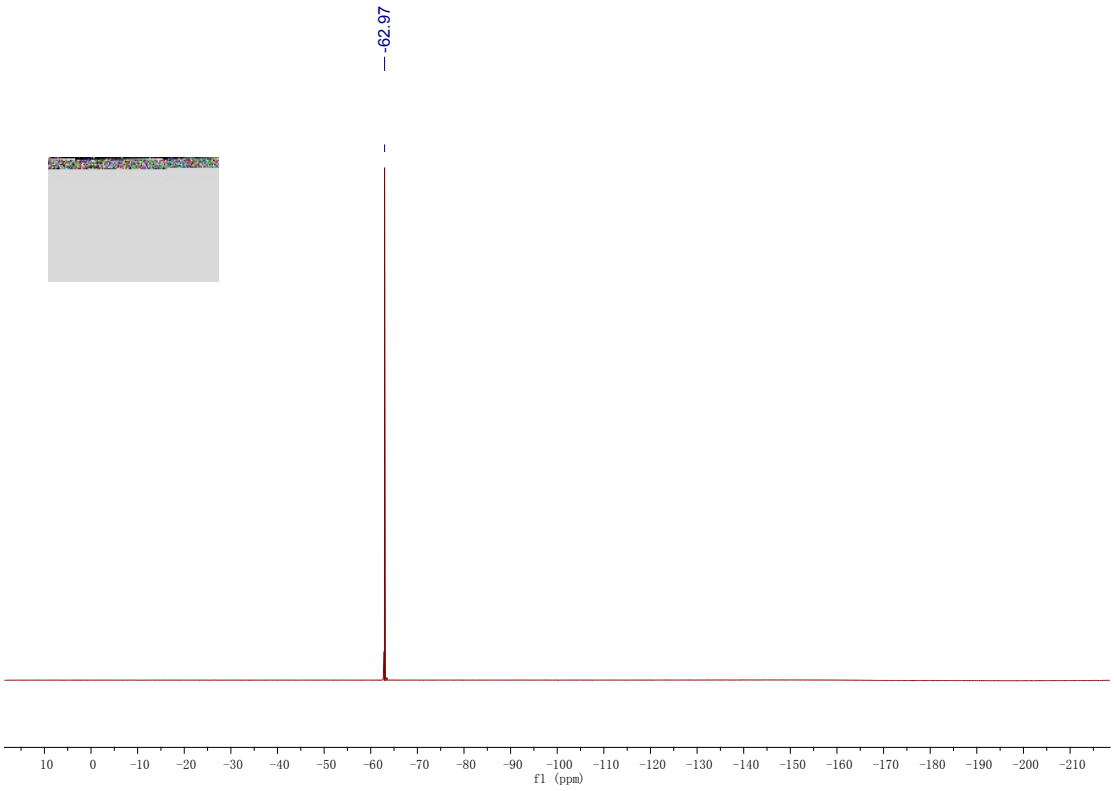
114.24
77.34
77.02
76.70
27.95
18.71
CN CN
F3C
3k
f1 (ppm)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10
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-40
-50
-60
-70
-80
-90
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-110
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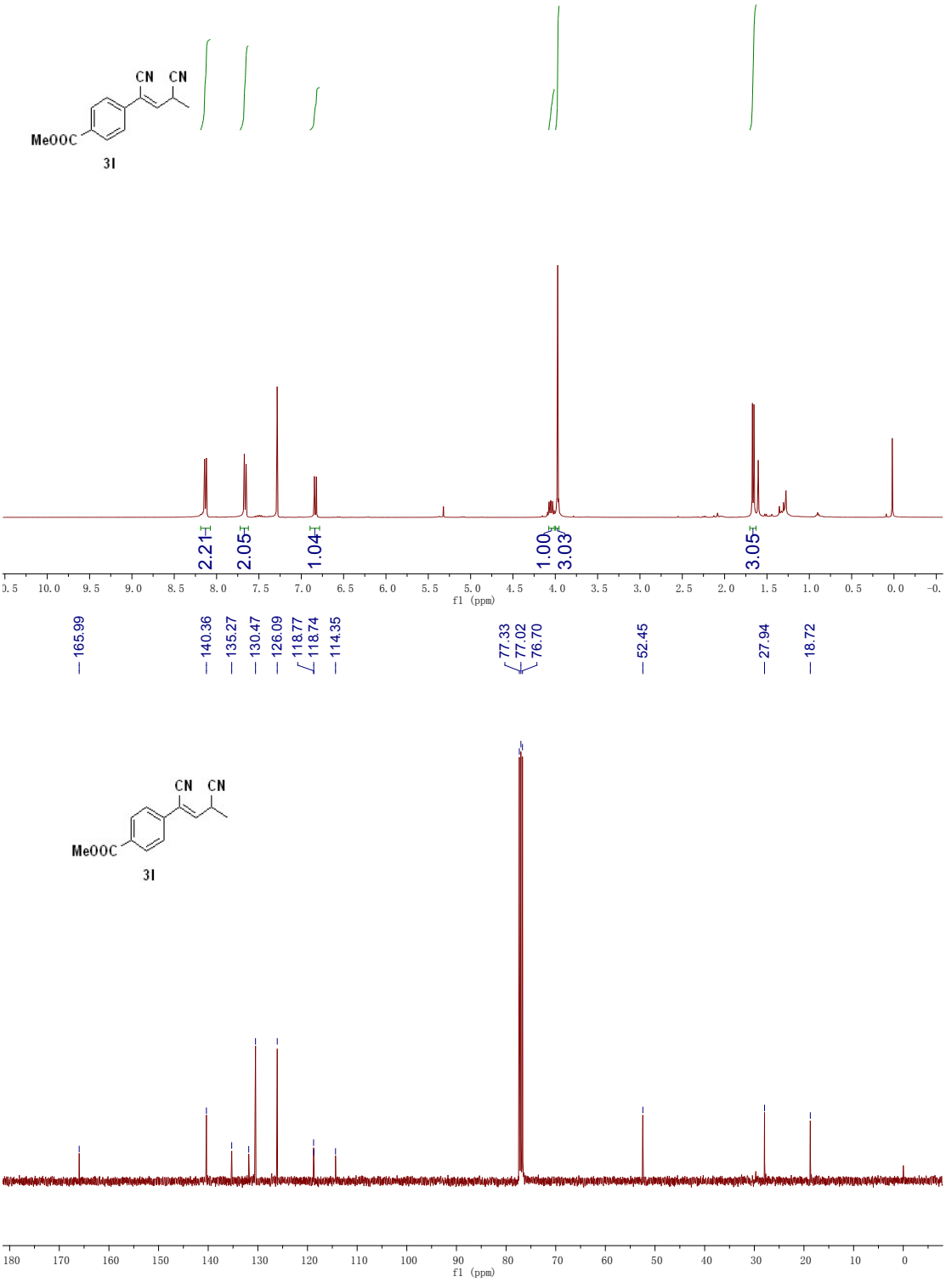
-170
-180
-190
-200
-210
f1 (ppm)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CN
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3.05
f1 (ppm)
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130.47
126.09
118.77
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77.02
76.70
52.45
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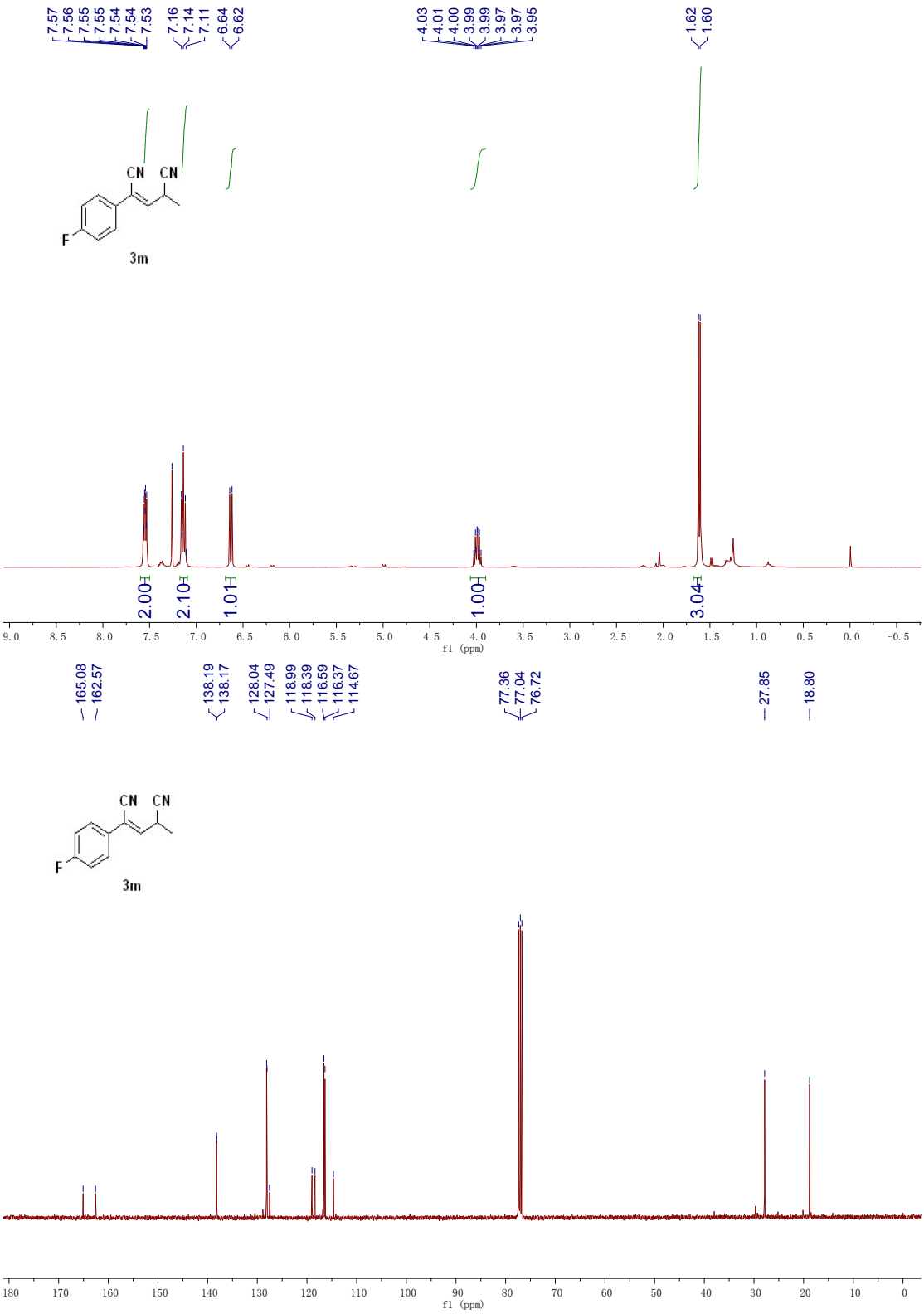
18.72
CN
CN
MeOOC
3l
f1 (ppm)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7.11
6.64
6.62
4.03
4.01
4.00
3.99
3.99
3.97
3.97
3.95
1.62
1.60
CN
CN
F
3m
2.00
2.10
1.01
1.00
3.04
f1 (ppm)
165.08
162.57
138.19
138.17
128.04
127.49
118.99
118.39
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18.80
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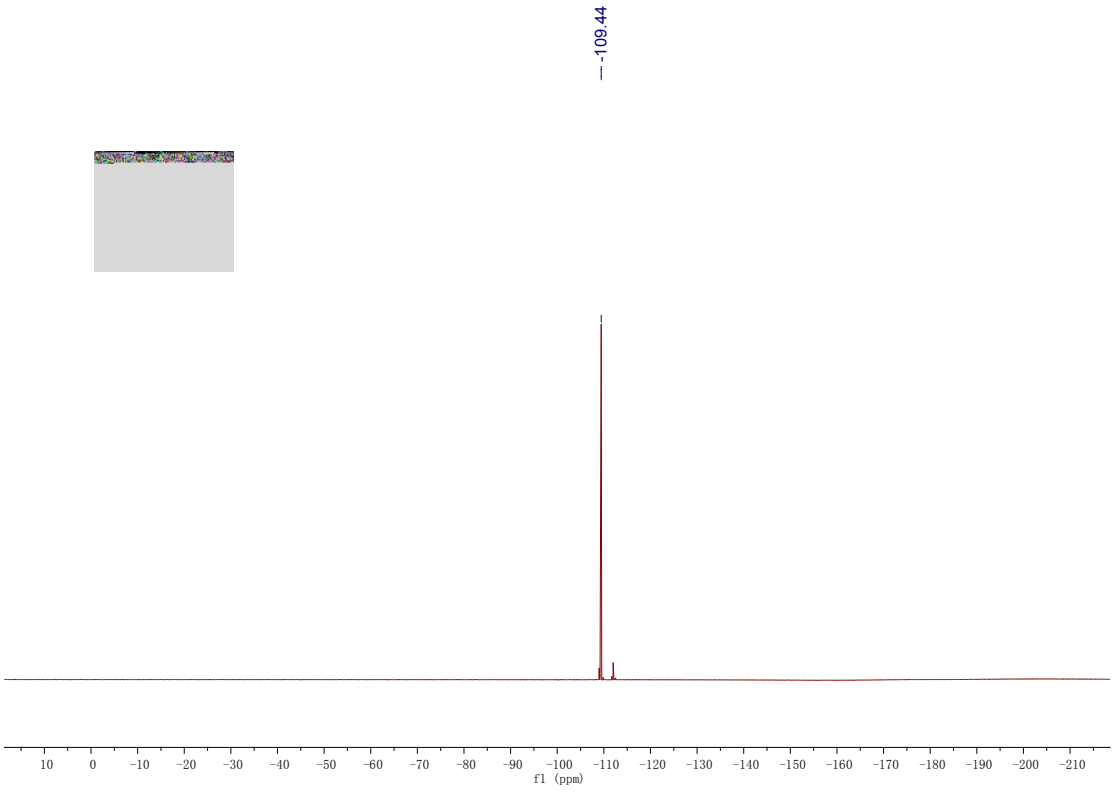
F
3m
f1 (ppm)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10
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-50
-60
-70
-80
-90
-100
-110
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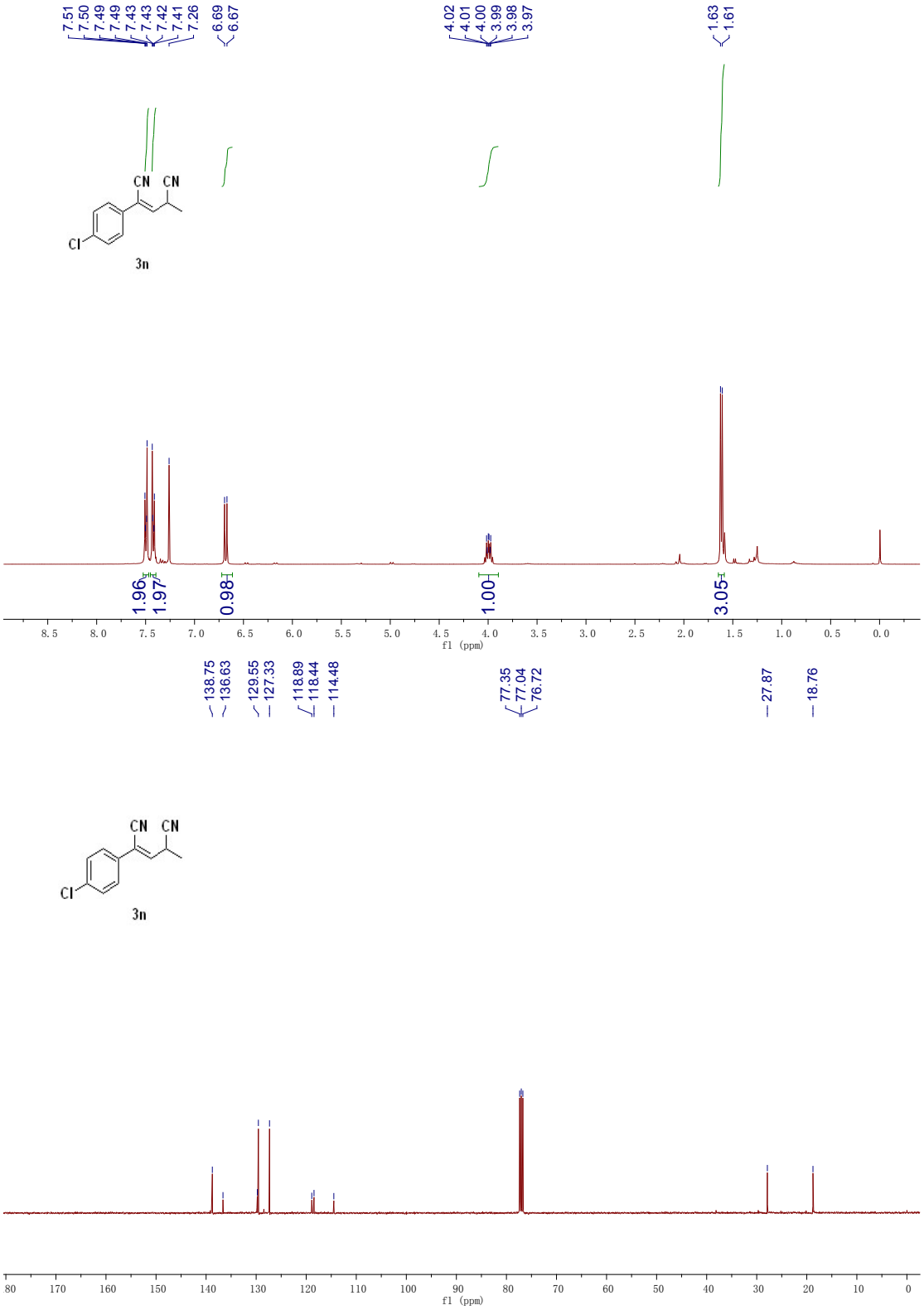
-170
-180
-190
-200
-210
f1 (ppm)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7.41
7.26
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6.67
4.02
4.01
4.00
3.99
3.98
3.97
1.63
1.61
CN
CN
Cl
3n
1.96
1.97
0.98
1.00
3.05
f1 (ppm)
138.75
136.63
129.55
127.33
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77.35
77.04
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18.76
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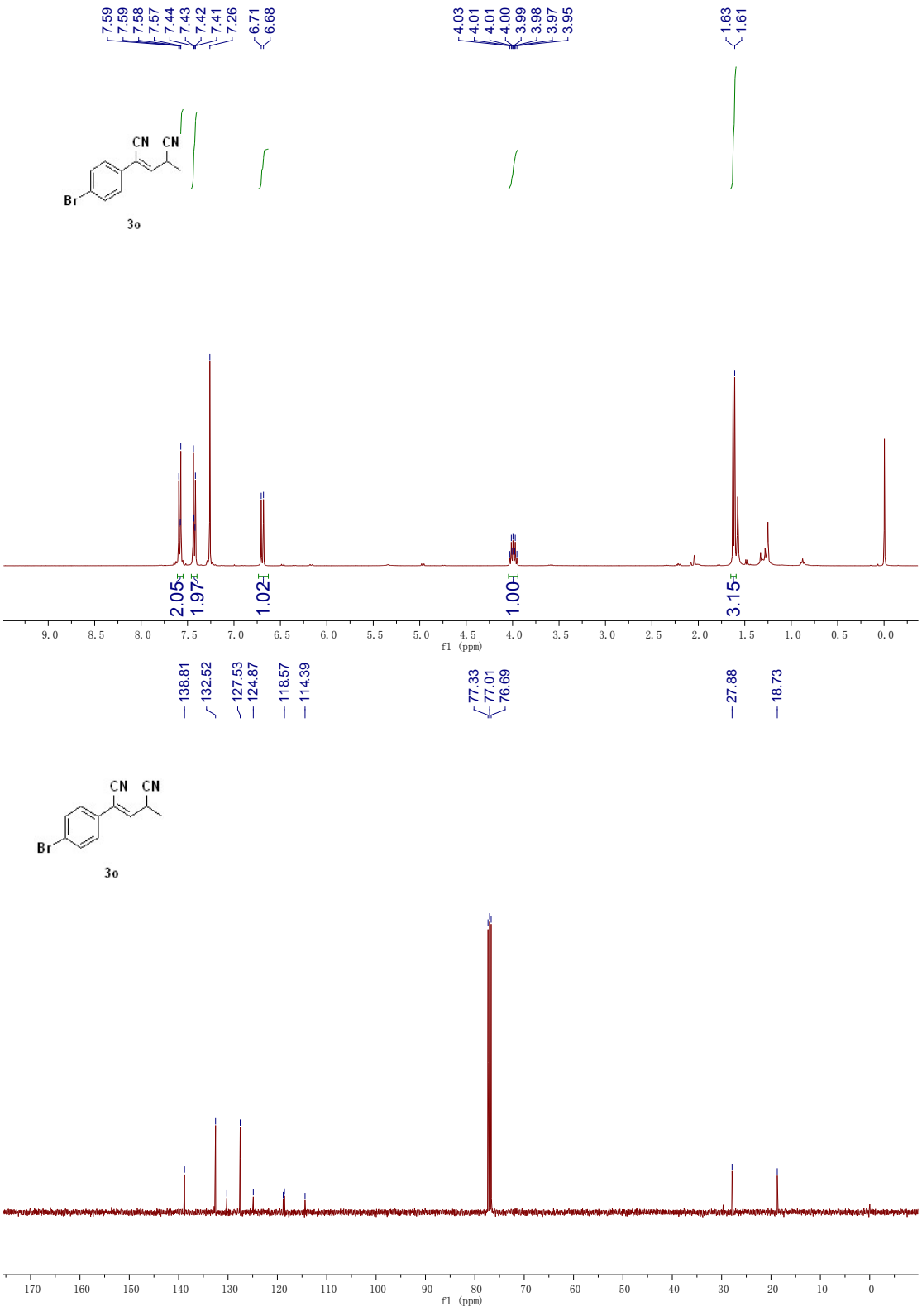
CN
Cl
3n
f1 (ppm)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4.01
4.01
4.00
3.99
3.98
3.97
3.95
1.63
1.61
CN
CN
Br
3o
2.05
1.97
1.02
1.00
3.15
f1 (ppm)
138.81
132.52
127.53
124.87
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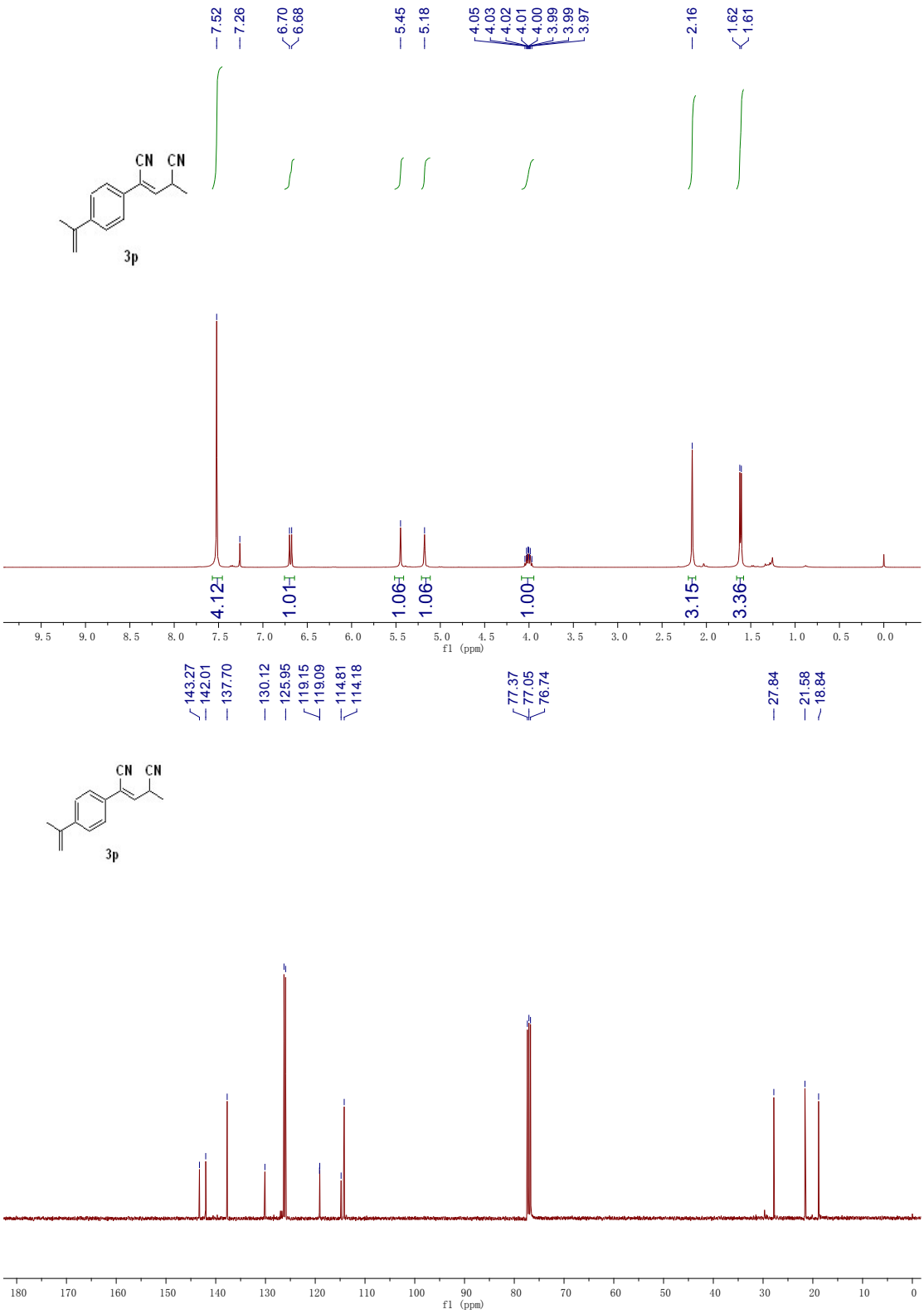
CN
CN
Br
3o
f1 (ppm)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4.02
4.01
4.00
3.99
3.99
3.97
2.16
1.62
1.61
CN CN
3p
4.12
1.01
1.06
1.06
1.00
3.15
3.36
f1 (ppm)
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142.01
137.70
130.12
125.95
119.15
119.09
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77.05
76.74
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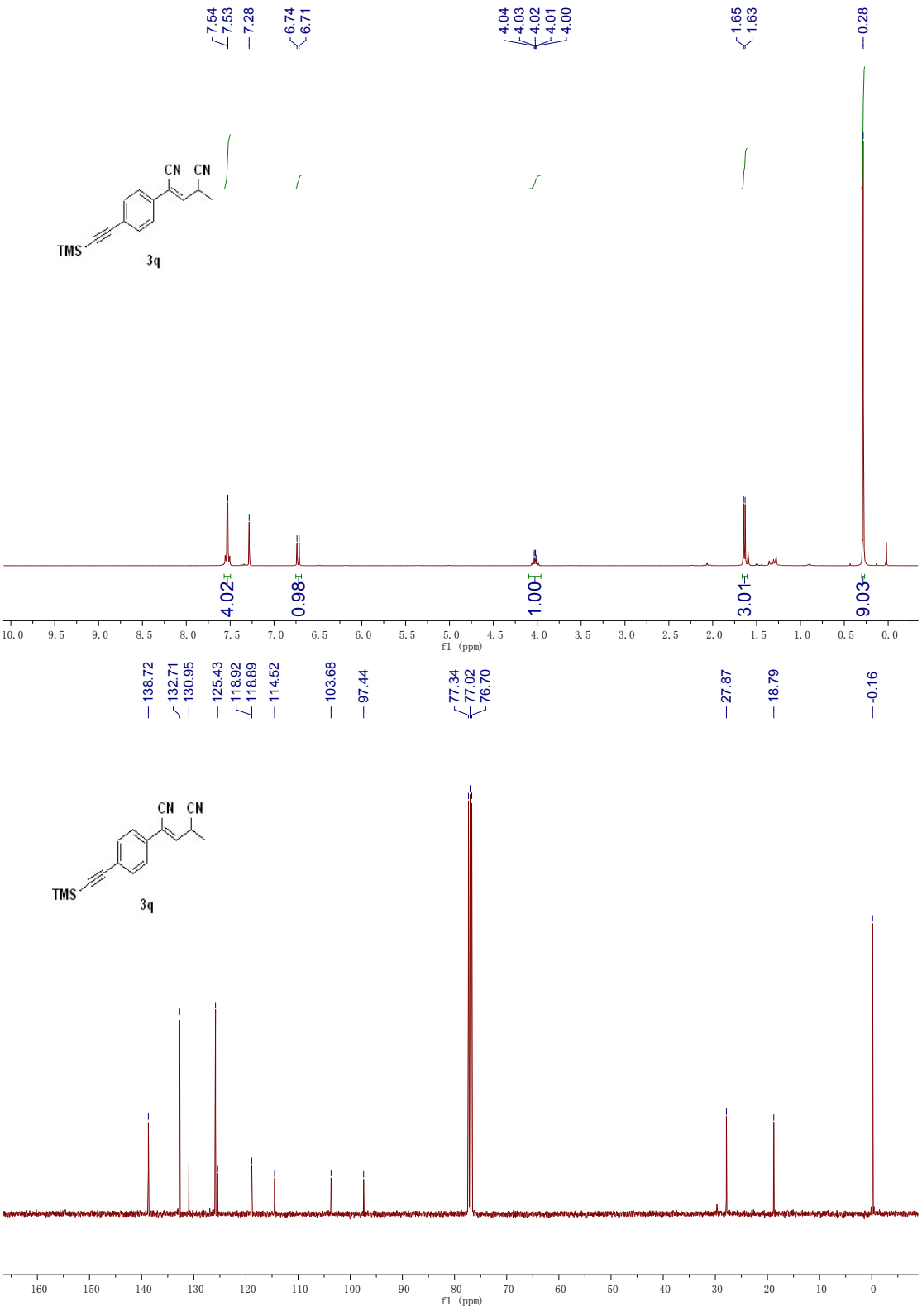
21.58
18.84
CN CN
3p
f1 (ppm)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6.71
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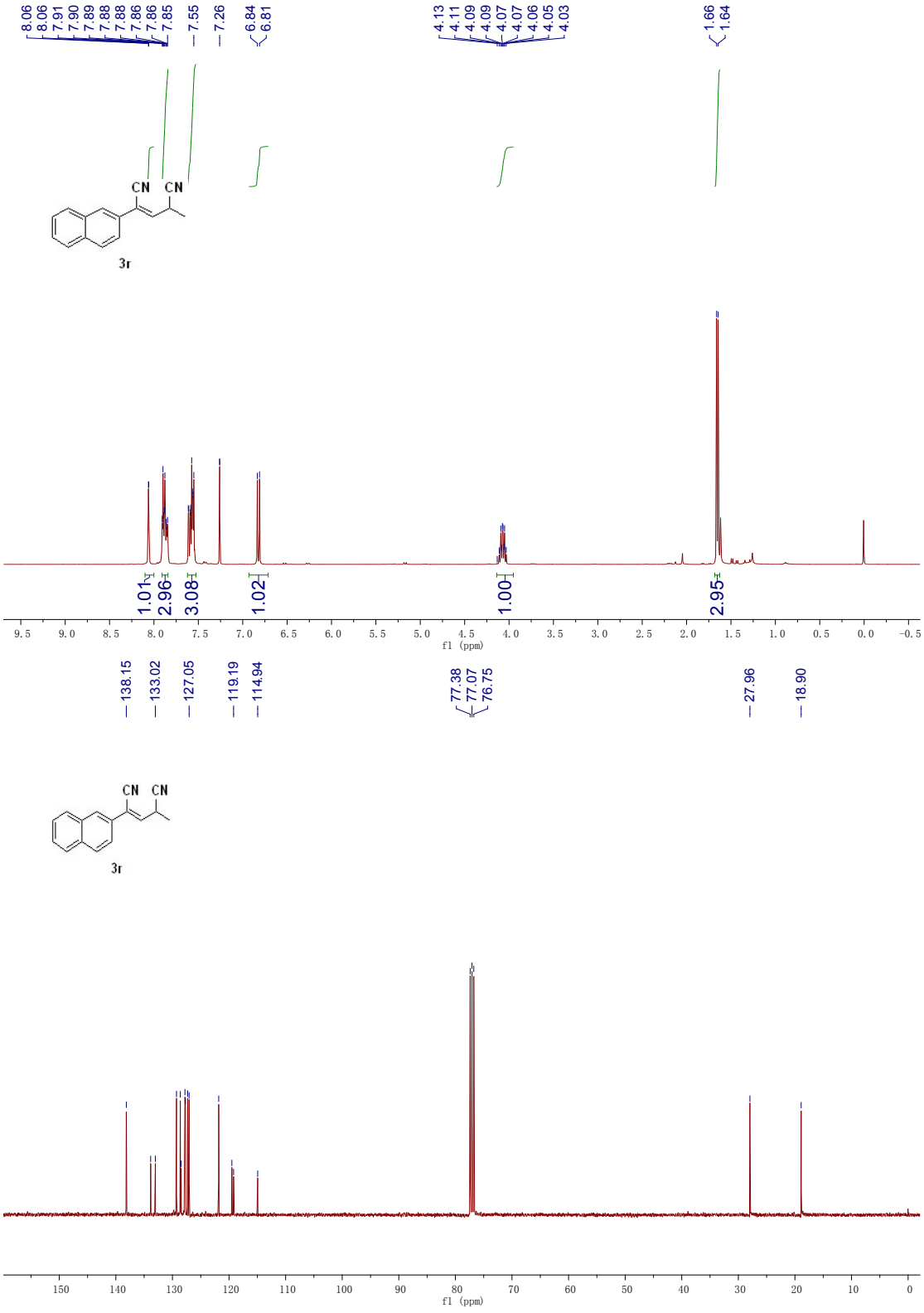
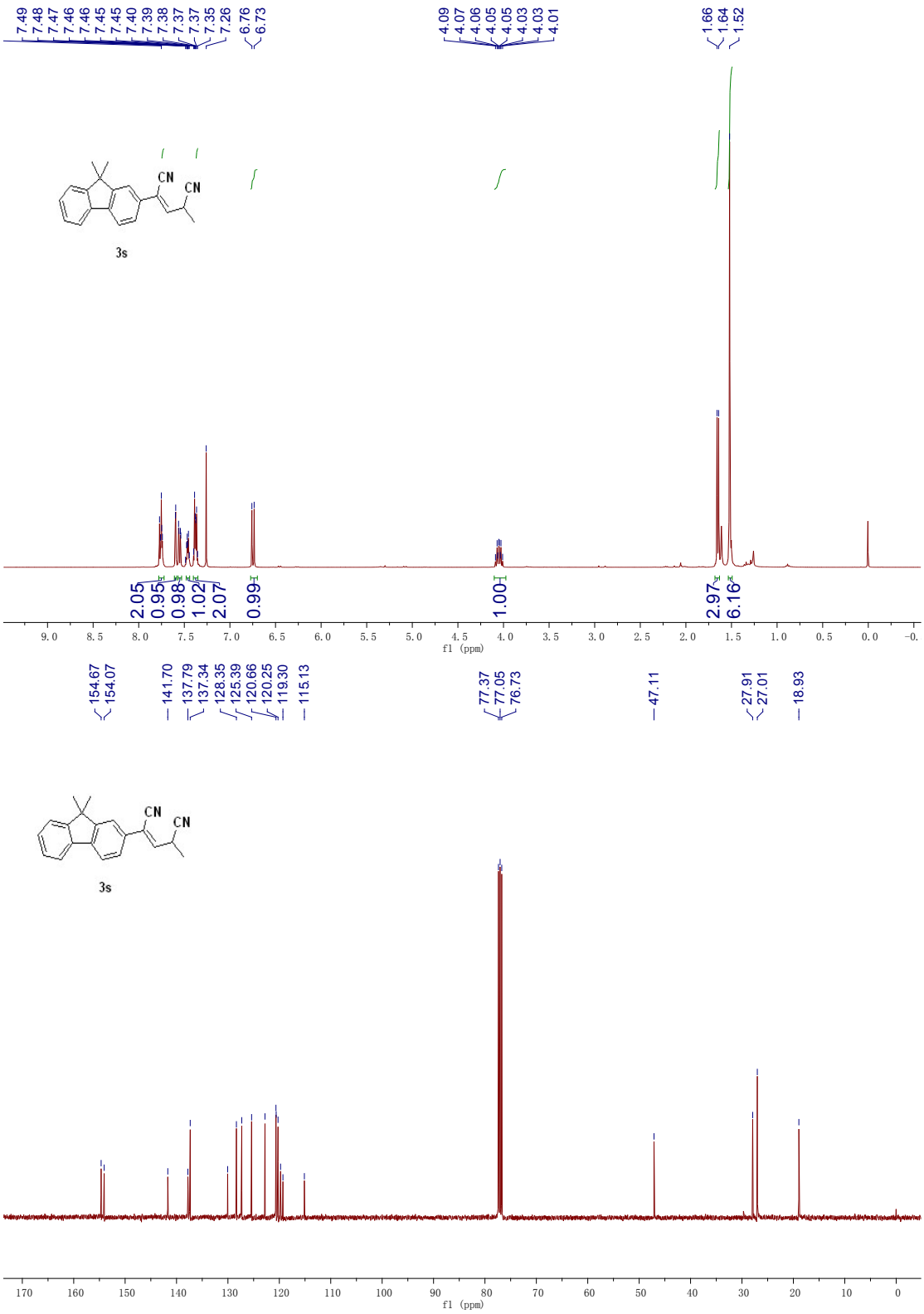
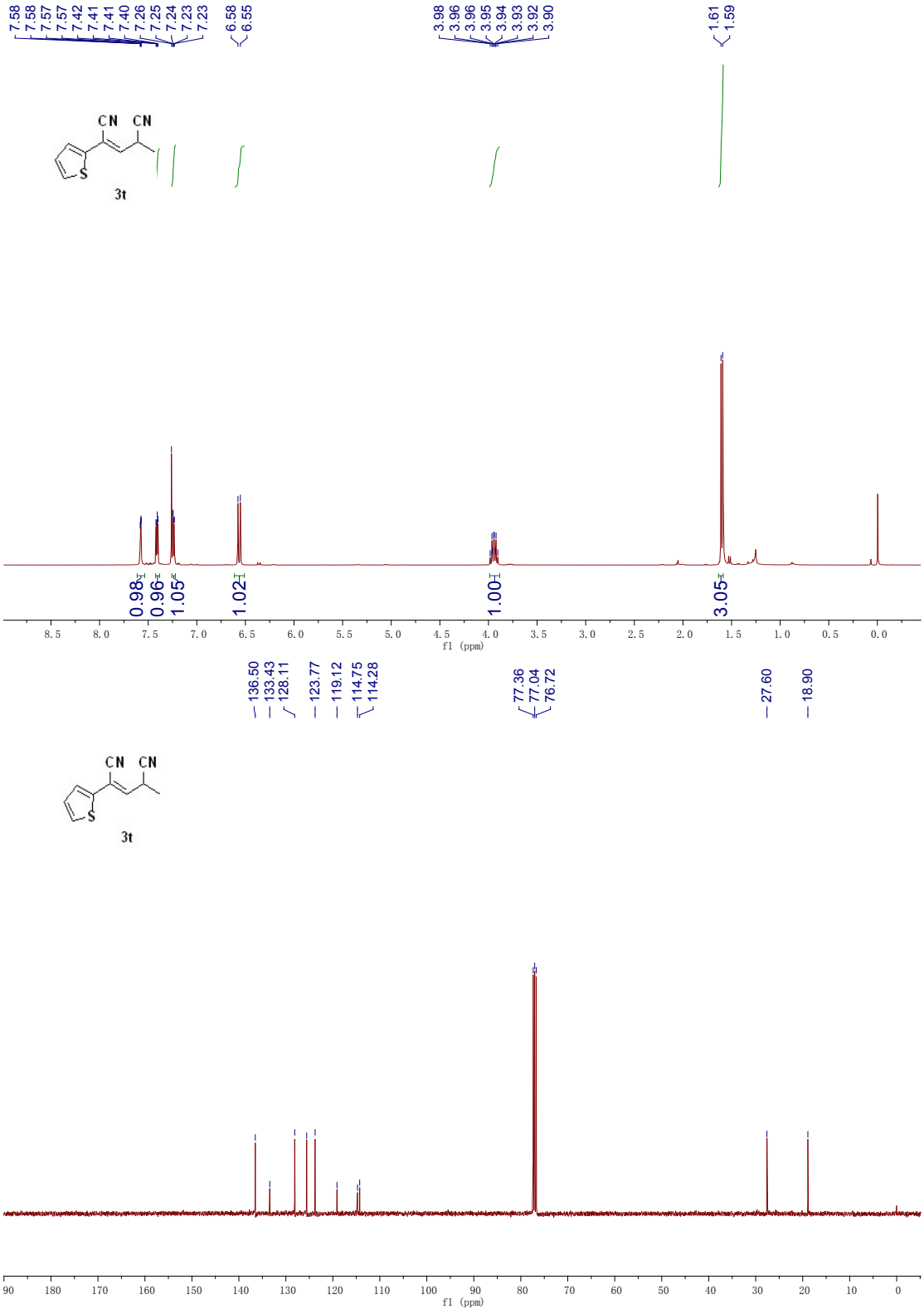
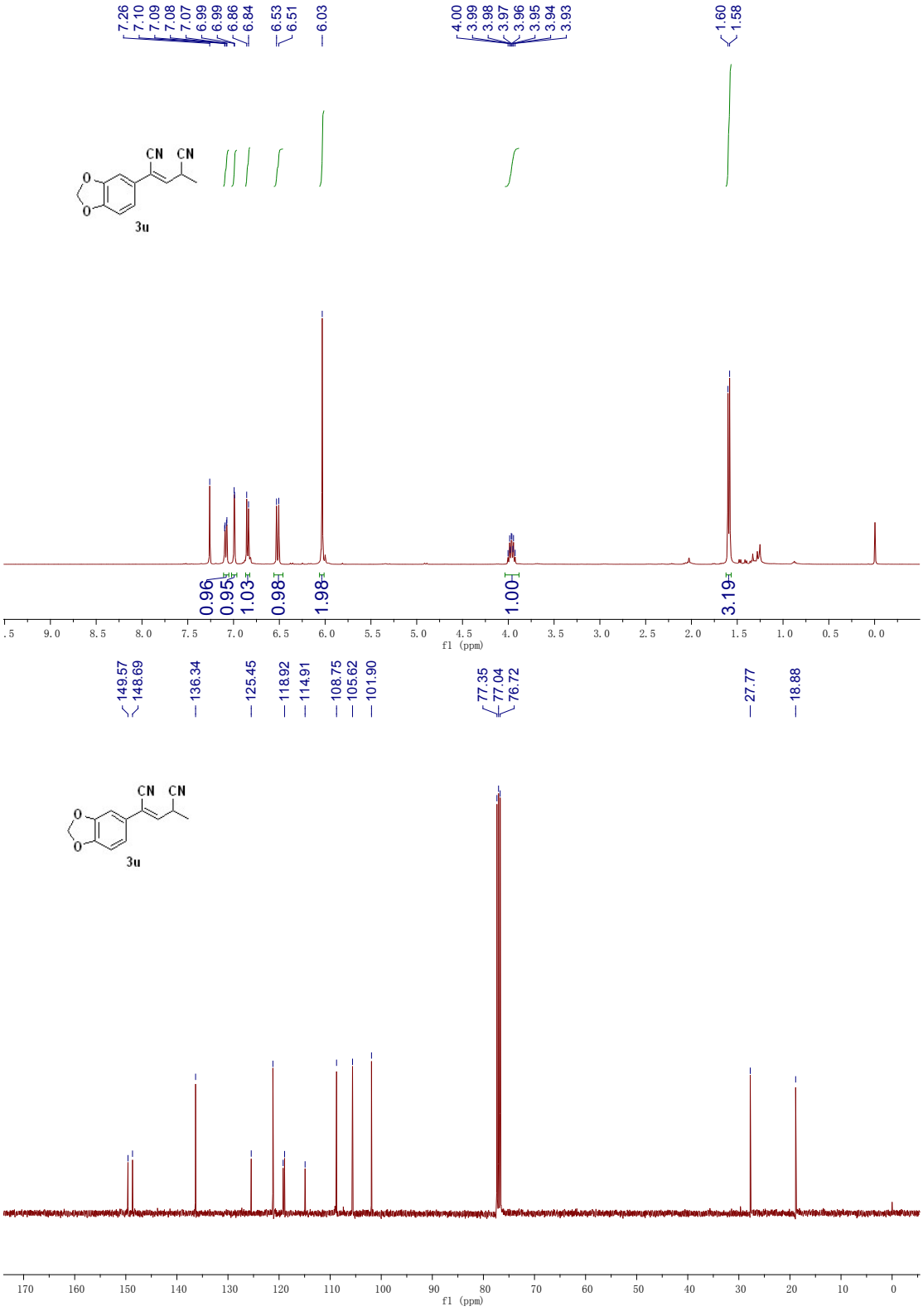
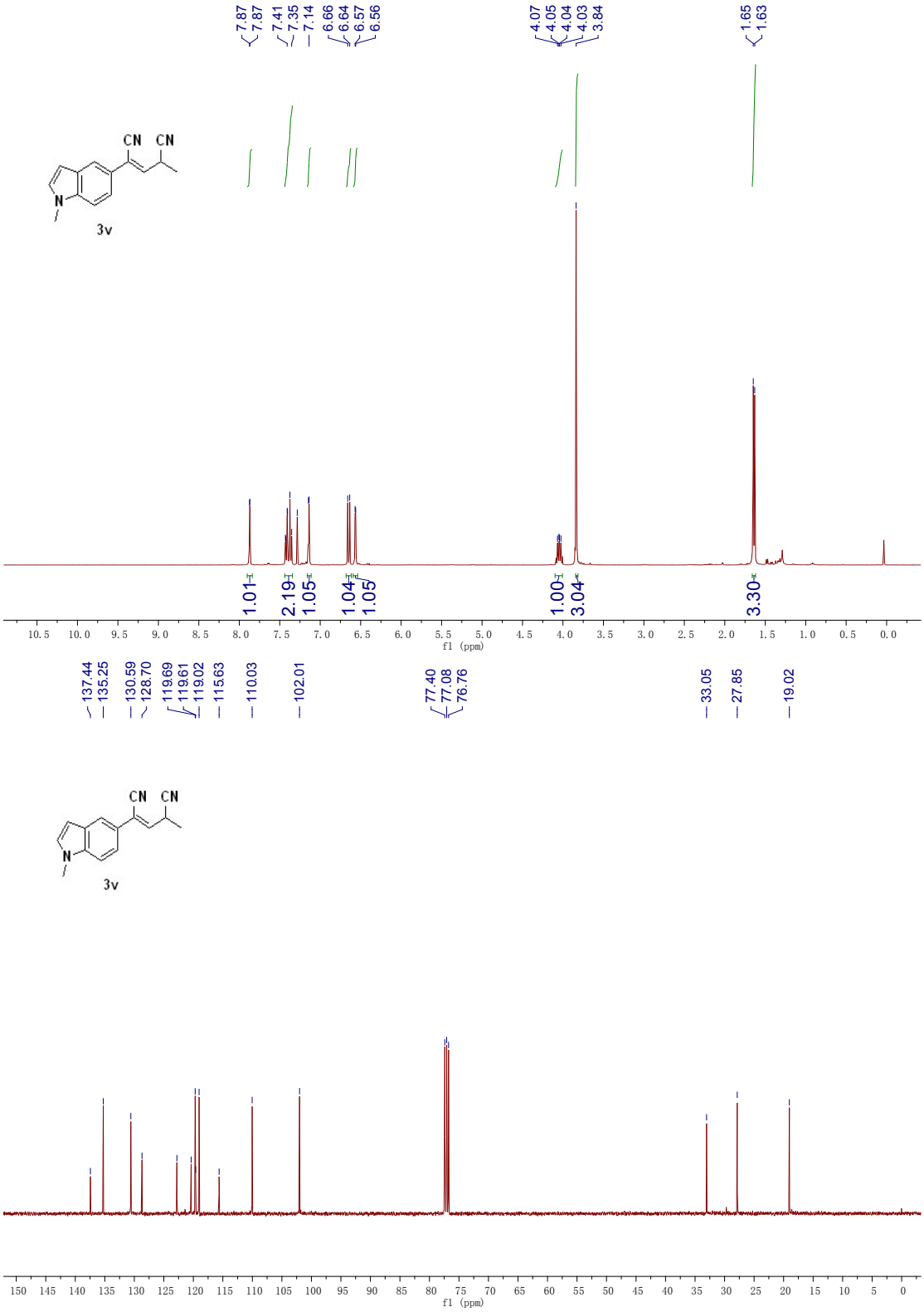
4.03
4.02
4.01
4.00
1.65
1.63
0.28
CN
CN
TMS
3q
4.02
0.98
1.00
3.01
9.03
f1 (ppm)
138.72
132.71
130.95
125.43
118.92
118.89
114.52
103.68
97.44
77.34
77.02
76.70
27.87
18.79
-0.16
CN
CN
TMS
3q
f1 (ppm)

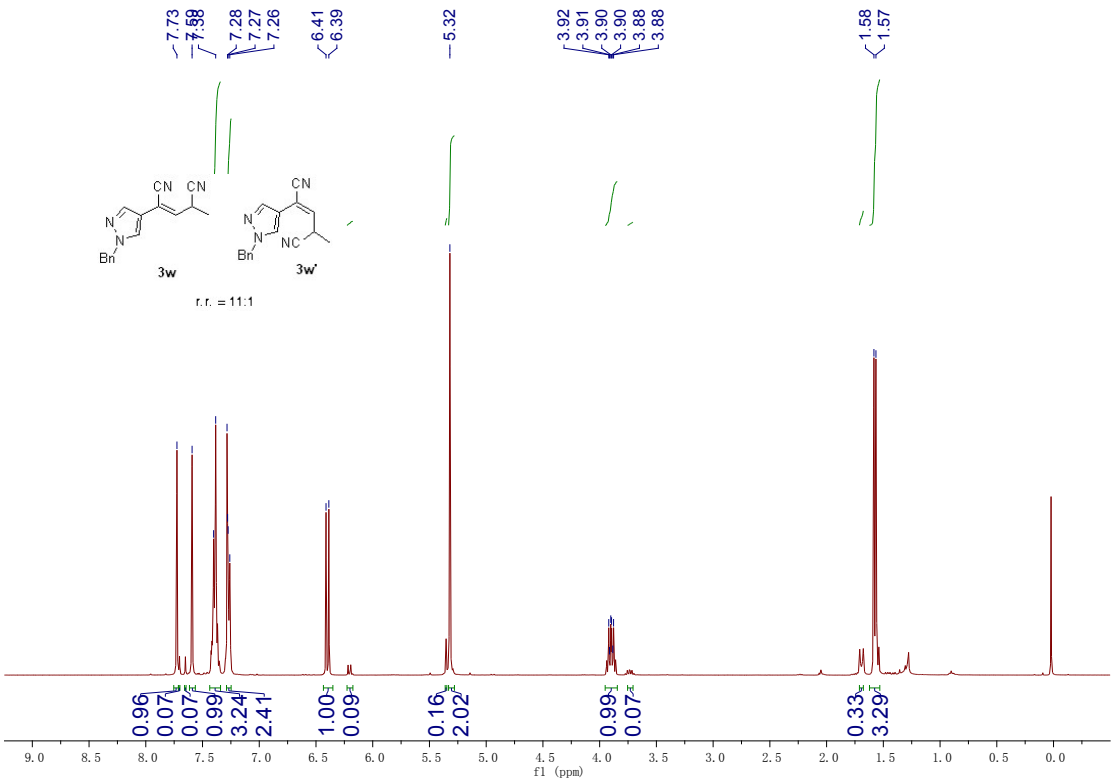

8.06
8.06
7.91
7.90
7.89
7.88
7.88
7.86
7.86
7.85
7.55
7.26
6.84
6.81
4.13
4.11
4.09
4.09
4.07
4.07
4.06
4.05
4.03
1.66
1.64
CN
CN
3r
1.01
2.96
3.08
1.02
1.00
2.95
f1 (ppm)
138.15
133.02
127.05
119.19
114.94
77.38
77.07
76.75
27.96
18.90
CN
CN
3r
f1 (ppm)

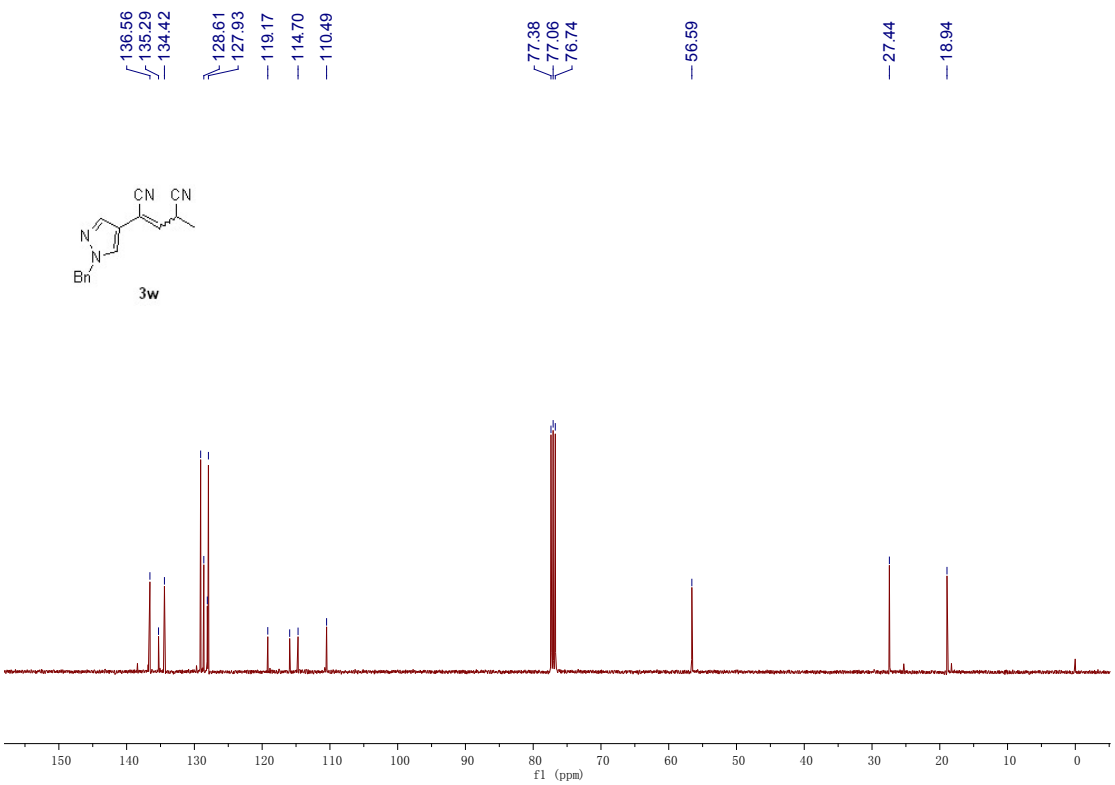

7.49
7.48
7.47
7.46
7.46
7.45
7.45
7.40
7.39
7.38
7.37
7.37
7.35
7.26
6.76
6.73
4.09
4.07
4.06
4.05
4.05
4.03
4.03
4.01
1.66
1.64
1.52
CN
CN
3s
2.05
0.95
0.98
1.02
2.07
0.99
1.00
2.97
6.16
f1 (ppm)
154.67
154.07
141.70
137.79
137.34
128.35
125.39
120.66
120.25
119.30
115.13
77.37
77.05
76.73
47.11
27.91
27.01
18.93
CN
CN
3s
f1 (ppm)

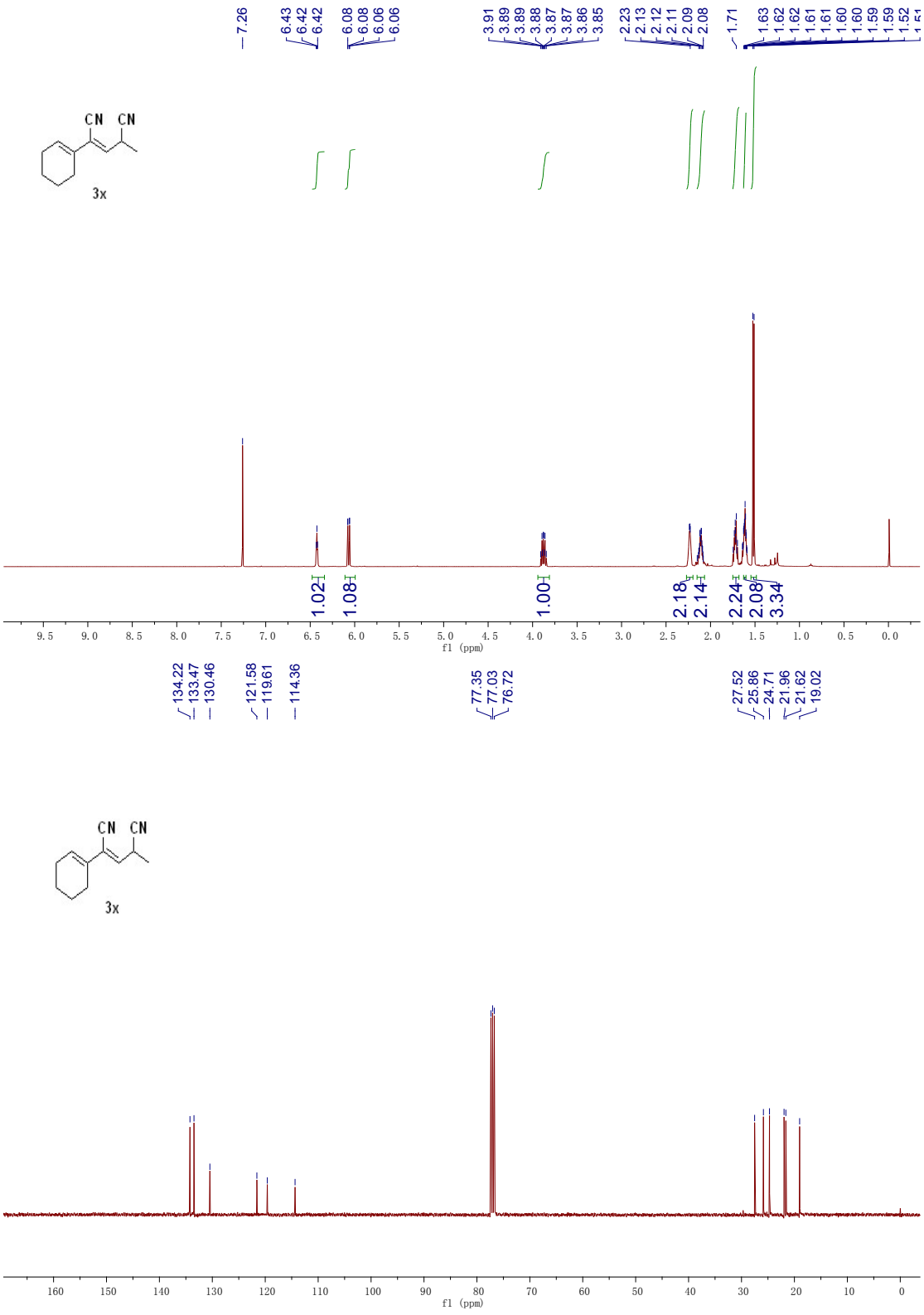

7.58
7.58
7.57
7.57
7.42
7.41
7.41
7.40
7.26
7.25
7.24
7.23
7.23
6.58
6.55
3.98
3.96
3.96
3.95
3.94
3.93
3.92
3.90
1.61
1.59
CN CN
S
3t
0.98
0.96
1.05
1.02
1.00
3.05
f1 (ppm)
136.50
133.43
128.11
123.77
119.12
114.75
114.28
77.36
77.04
76.72
27.60
18.90
CN CN
S
3t
f1 (ppm)

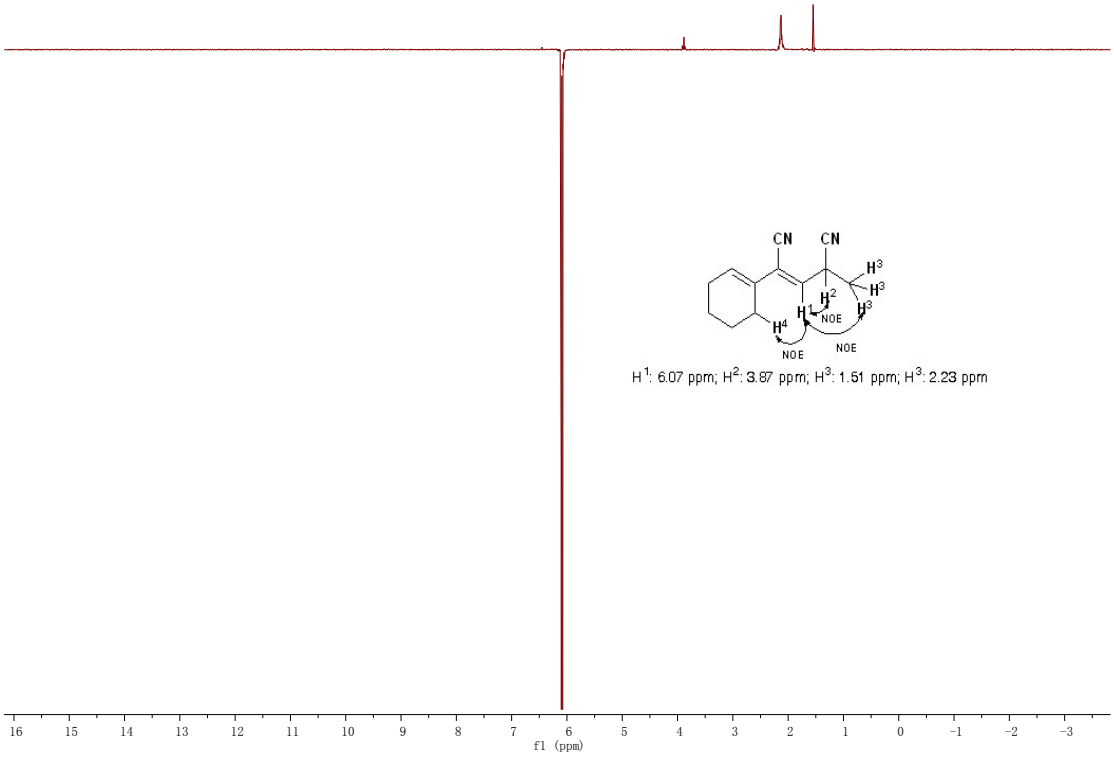

7.26
7.10
7.09
7.08
7.07
6.99
6.99
6.86
6.84
6.53
6.51
6.03
4.00
3.99
3.98
3.97
3.96
3.95
3.94
3.93
1.60
1.58
CN
CN
O
O
3u
0.96
0.95
1.03
0.98
1.98
1.00
3.19
f1 (ppm)
149.57
148.69
136.34
125.45
118.92
114.91
108.75
105.62
101.90
77.35
77.04
76.72
27.77
18.88
CN
CN
O
O
3u
f1 (ppm)


7.87
7.87
7.41
7.35
7.14
6.66
6.64
6.57
6.56
4.07
4.05
4.04
4.03
3.84
1.65
1.63
CN
CN
N
3v
1.01
2.19
1.05
1.04
1.05
1.00
3.04
3.30
f1 (ppm)
137.44
135.25
130.59
128.70
119.69
119.61
119.02
115.63
110.03
102.01
77.40
77.08
76.76
33.05
27.85
19.02
CN
CN
N
3v
f1 (ppm)

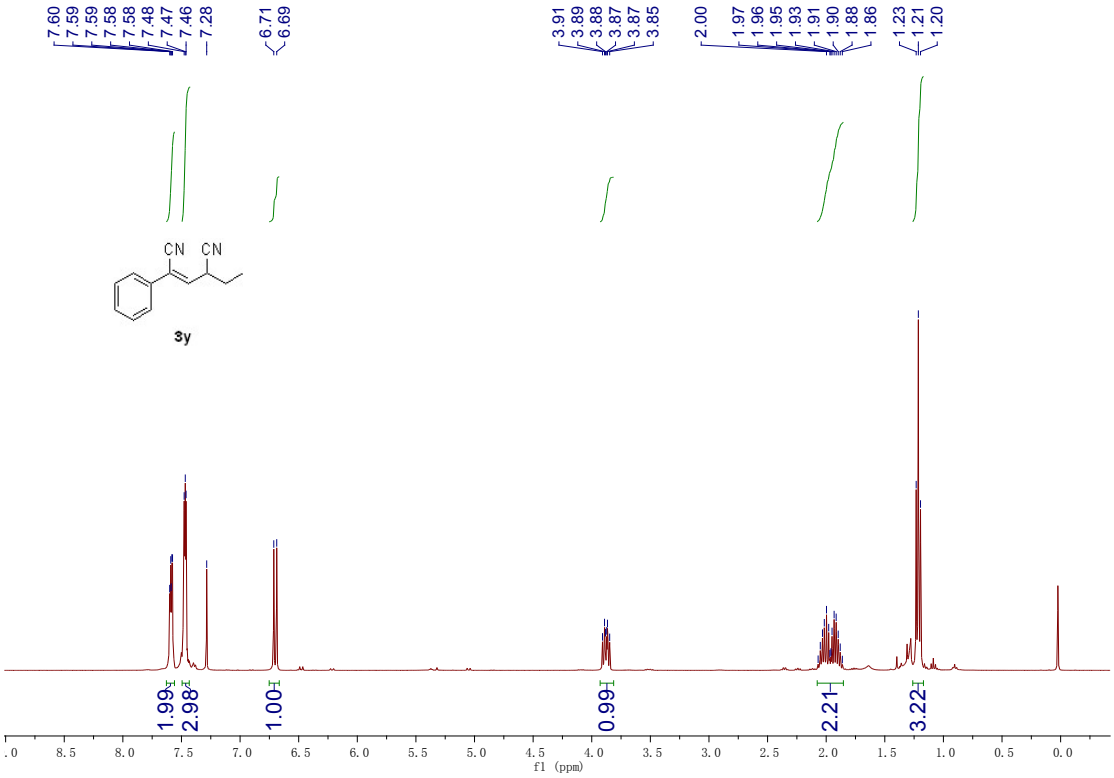

7.73
7.58
7.28
7.27
7.26
6.41
6.39
5.32
3.92
3.91
3.90
3.90
3.88
3.88
1.58
1.57
CN
CN
N
N
Bn
3w
CN
N
N
NC
Bn
3w'
r.r. = 11:1
0.96
0.07
0.07
0.99
3.24
2.41
1.00
0.09
0.16
2.02
0.99
0.07
0.33
3.29
f1 (ppm)

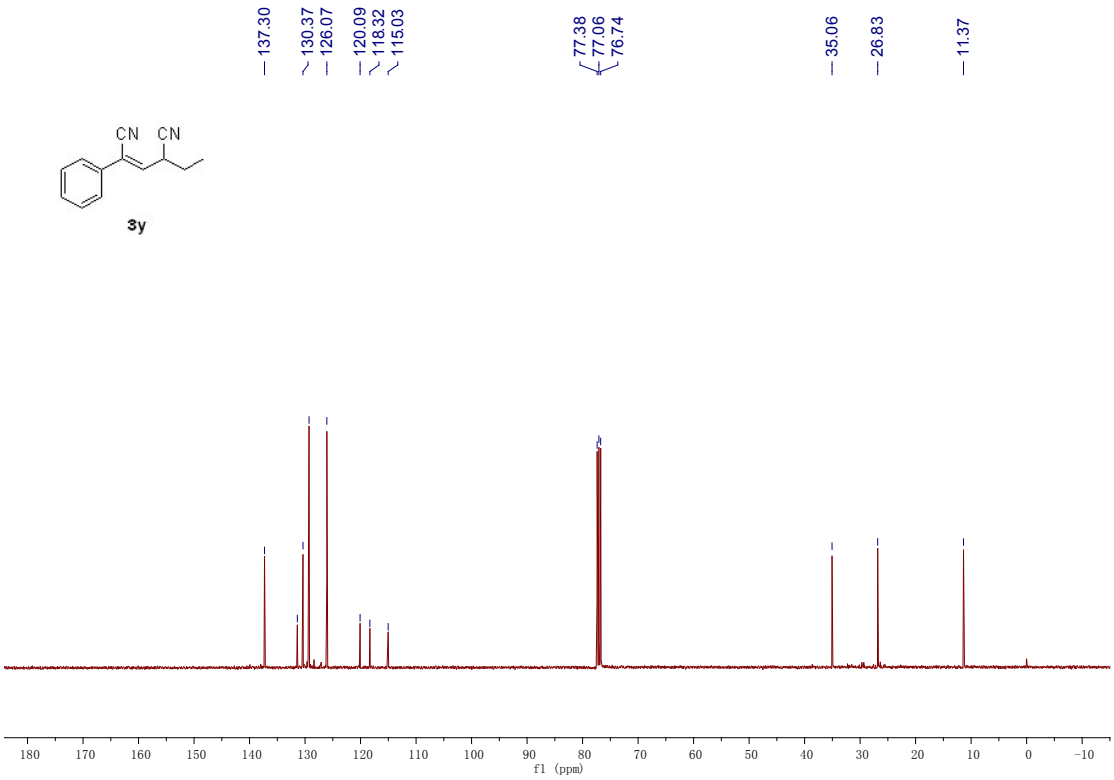

136.56
135.29
134.42
128.61
127.93
119.17
114.70
110.49
77.38
77.06
76.74
56.59
27.44
18.94
CN
CN
N
N
Bn
3w
f1 (ppm)

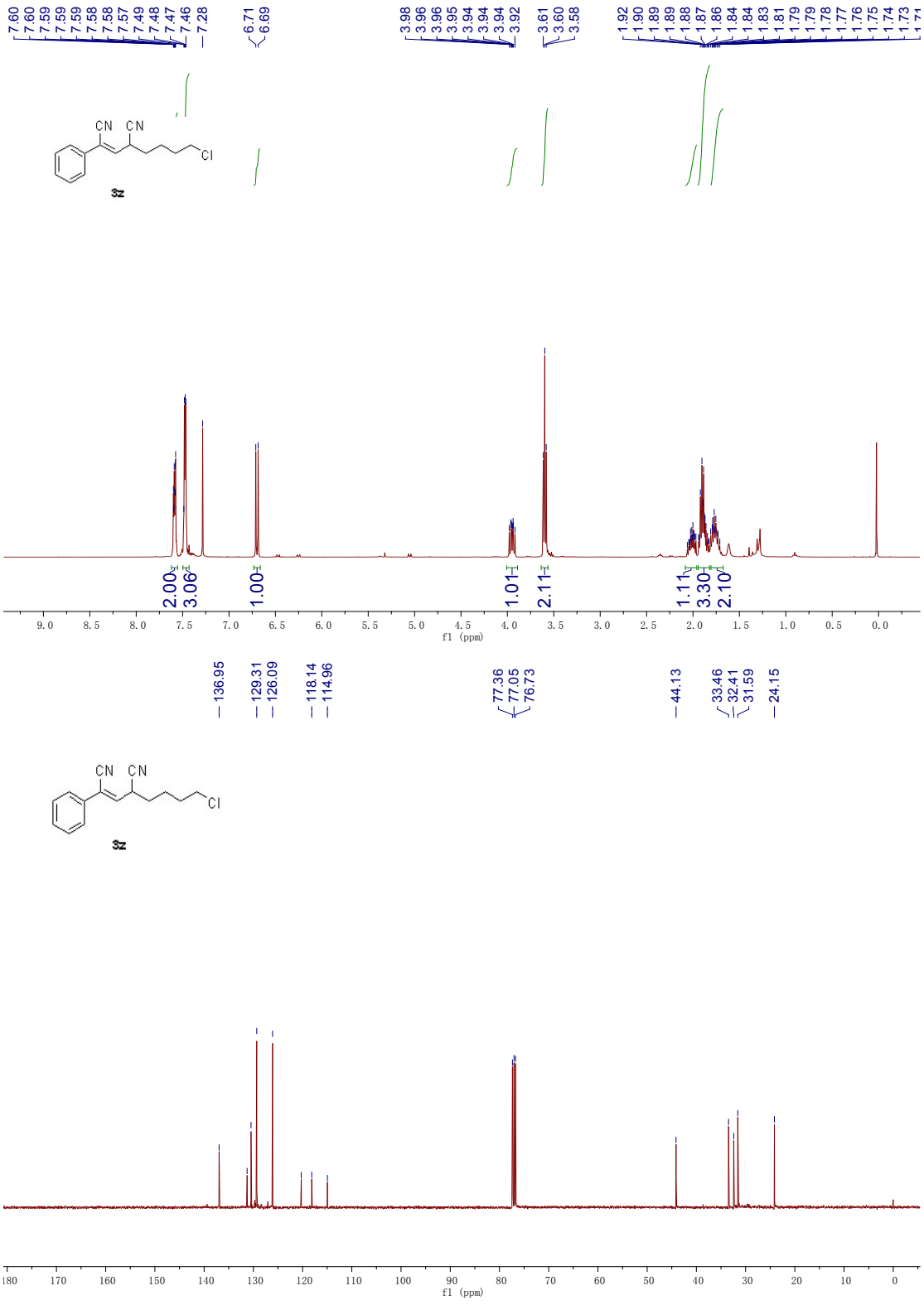

7.26
6.43
6.42
6.42
6.08
6.08
6.06
6.06
3.91
3.89
3.89
3.88
3.87
3.87
3.86
3.85
2.23
2.13
2.12
2.11
2.09
2.08
1.71
1.63
1.62
1.62
1.61
1.61
1.60
1.60
1.59
1.59
1.52
CN CN
3x
1.02
1.08
1.00
2.18
2.14
2.24
2.08
3.34
f1 (ppm)
134.22
133.47
130.46
121.58
119.61
114.36
77.35
77.03
76.72
27.52
25.86
24.71
21.96
21.62
19.02
CN CN
3x
f1 (ppm)

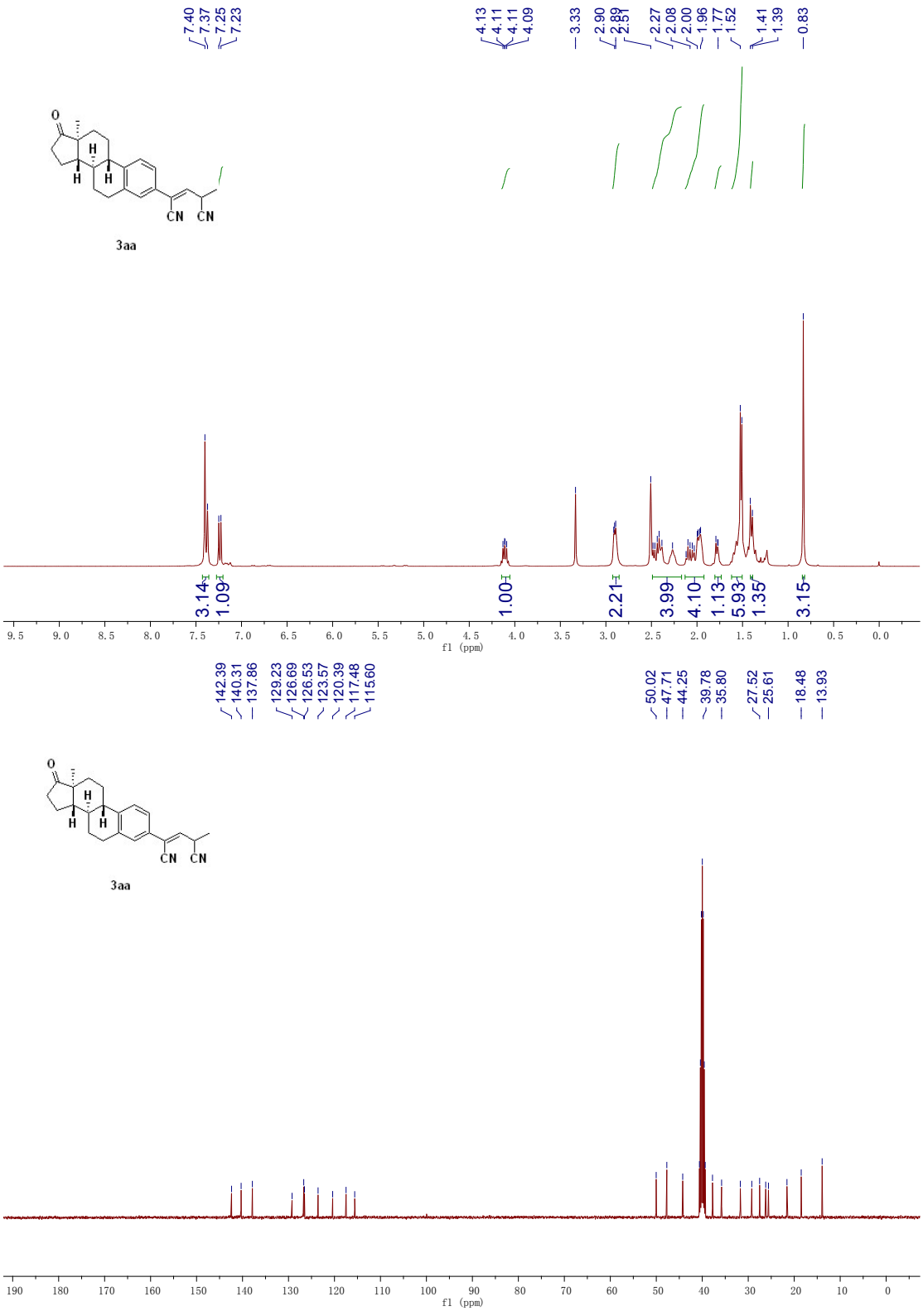


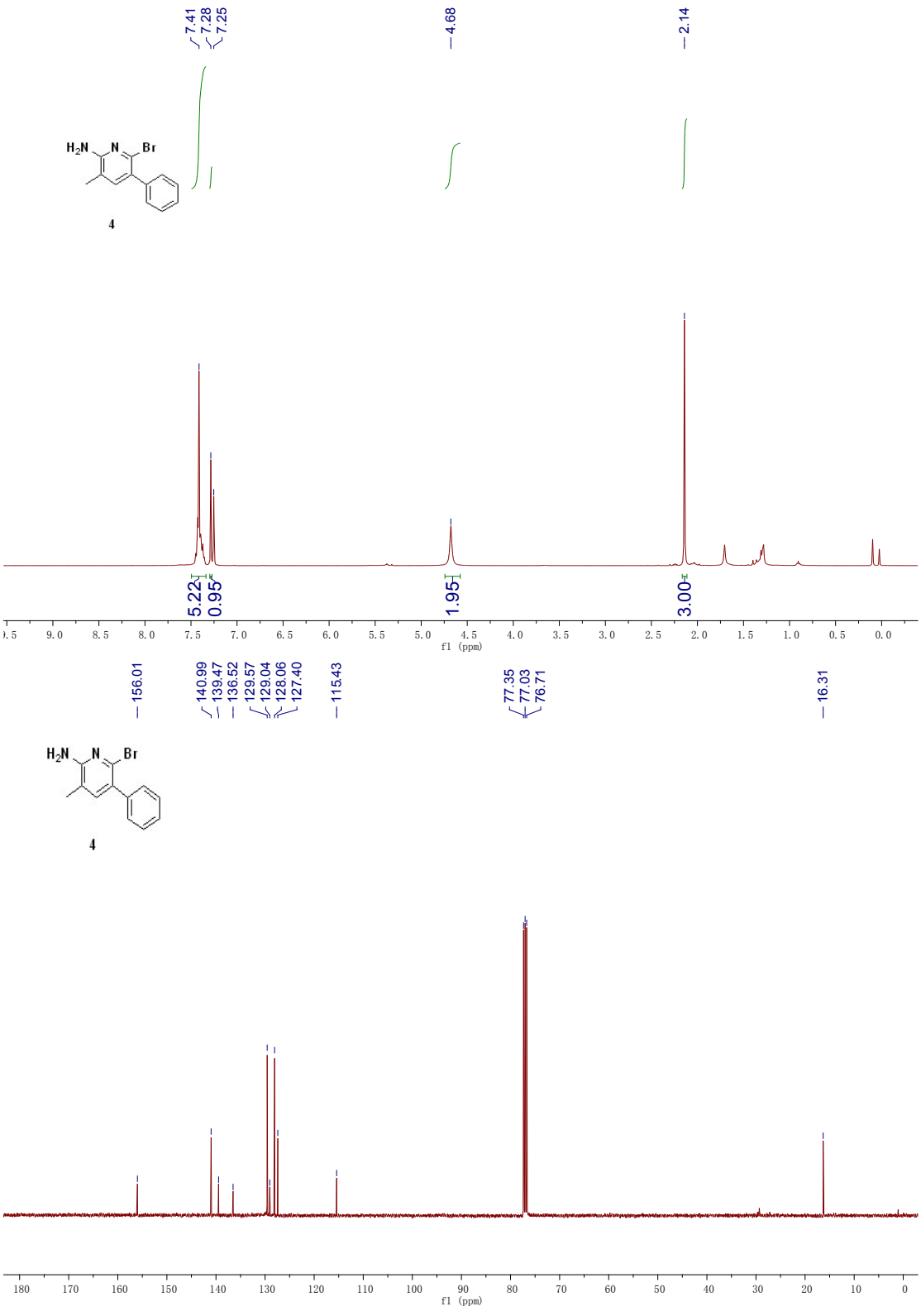

$H^1$: 6.07 ppm; $H^2$: 3.87 ppm; $H^3$: 1.51 ppm; $H^3$: 2.23 ppm

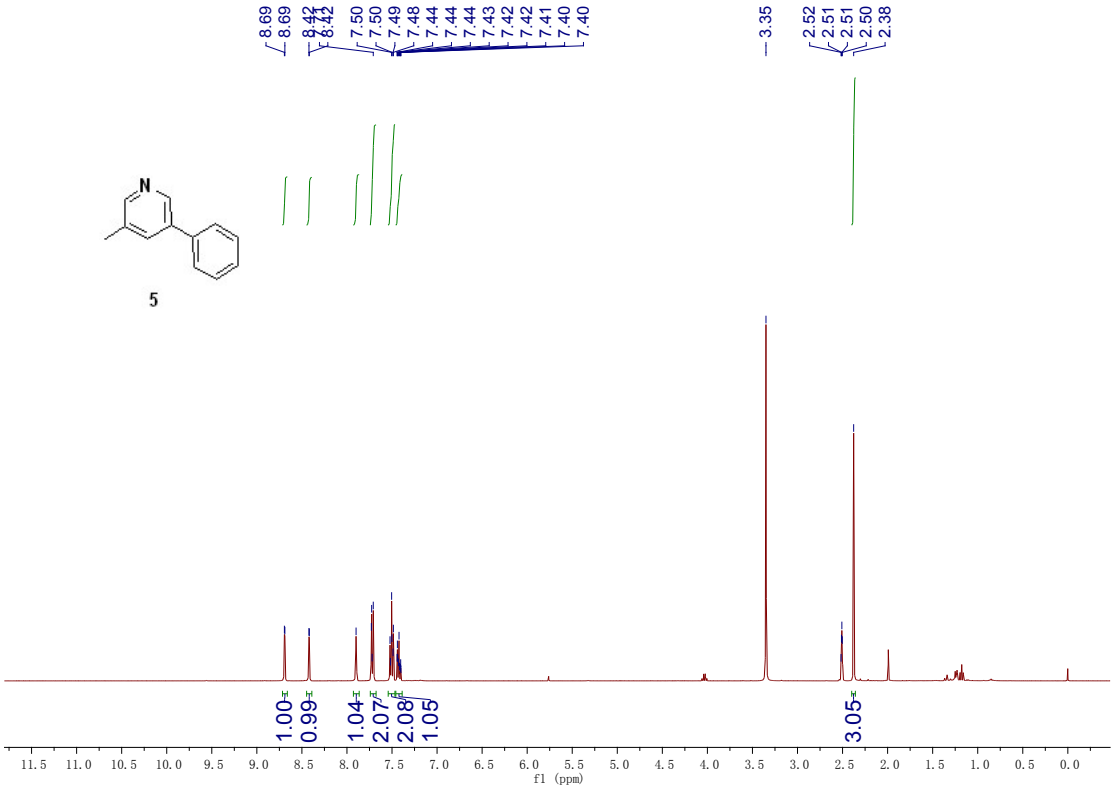

7.60
7.59
7.59
7.58
7.58
7.48
7.47
7.46
7.28
6.71
6.69
3.91
3.89
3.88
3.87
3.87
3.85
2.00
1.97
1.96
1.95
1.93
1.91
1.90
1.88
1.86
1.23
1.21
1.20
CN
CN
3y
1.99
2.98
1.00
0.99
2.21
3.22
f1 (ppm)

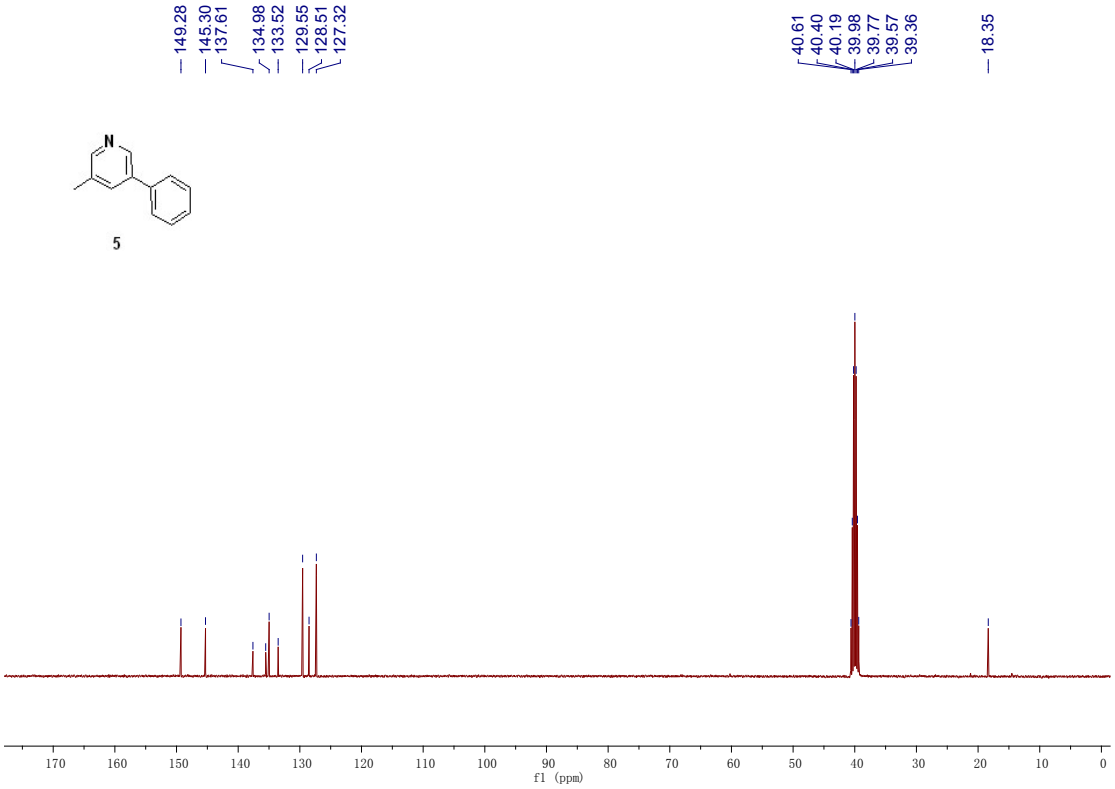

137.30
130.37
126.07
120.09
118.32
115.03
77.38
77.06
76.74
35.06
26.83
11.37
CN
CN
3y
f1 (ppm)


7.60 7.60 7.59 7.59 7.59 7.58 7.58 7.57 7.49 7.48 7.47 7.46 7.28
6.71 6.69
3.98 3.96 3.96 3.95 3.94 3.94 3.94 3.92
3.61 3.60 3.58
1.92 1.90 1.89 1.89 1.88 1.87 1.86 1.84 1.84 1.83 1.81 1.79 1.79 1.78 1.77 1.76 1.75 1.74 1.73
CN CN
Cl
3z
2.00 3.06 1.00 1.01 2.11 1.11 3.30 2.10
f1 (ppm)
136.95 129.31 126.09 118.14 114.96
77.36 77.05 76.73
44.13
33.46 32.41 31.59
24.15
CN CN
Cl
3z
f1 (ppm)


7.40
7.37
7.25
7.23
4.13
4.11
4.11
4.09
3.33
2.90
2.89
2.51
2.27
2.08
2.00
1.96
1.77
1.52
1.41
1.39
0.83
O
H
H
H
CN
CN
3aa
3.14
1.09
1.00
2.21
3.99
4.10
1.13
5.93
1.35
3.15
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)
142.39
140.31
137.86
129.23
126.69
126.53
123.57
120.39
117.48
115.60
50.02
47.71
44.25
39.78
35.80
27.52
25.61
18.48
13.93
O
H
H
H
CN
CN
3aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.41
7.28
7.25
4.68
2.14
H2N
N
Br
4
5.22
0.95
1.95
3.00
f1 (ppm)
156.01
140.99
139.47
136.52
129.57
129.04
128.06
127.40
115.43
77.35
77.03
76.71
16.31
H2N
N
Br
4
f1 (ppm)


8.69
8.69
8.42
8.42
7.50
7.50
7.49
7.48
7.44
7.44
7.44
7.43
7.42
7.42
7.41
7.40
7.40
3.35
2.52
2.51
2.51
2.50
2.38
N
5
1.00
0.99
1.04
2.07
2.08
1.05
3.05
f1 (ppm)


149.28
145.30
137.61
134.98
133.52
129.55
128.51
127.32
40.61
40.40
40.19
39.98
39.77
39.57
39.36
18.35
N
5
f1 (ppm)

## 10. References

(1) (a) Huang, Y. M.; del Pozo, J.; Torker, S.; Hoveyda. A. H. *J. Am. Chem. Soc.* **2018**, *140*, 2643−2655. (b) Yu, S.; Sang, H. L.; Zhang, S. Q.; Hong, X.; Ge, S. *Commun. Chem.* **2018**, *1*, 64. (c) Zhang, Y.; Yu, B.; Gao, B.; Zhang, T.; Huang, H. *Org. Lett.* **2019**, *21*, 535−539.

(2) Kowalkowska, A.; Suchołbiak, D.; Jonczyk. A. *Eur. J. Org. Chem.* **2005**, 925–933.

(3) Johnson, F.; Panella, J. P.; Carlson, A. A.; Hunneman, D. H. *J. Org. Chem.* **1962**, *27*, 2473−2478.