Supplementary Information

Cyanoalkylation/alkynylation of Allylic Alcohol through Intramolecular Radical 1,2- Alkynyl Migration

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Table of Contents

Contents

1. X-Ray Structure of Sulfonyl Hydrazone 4

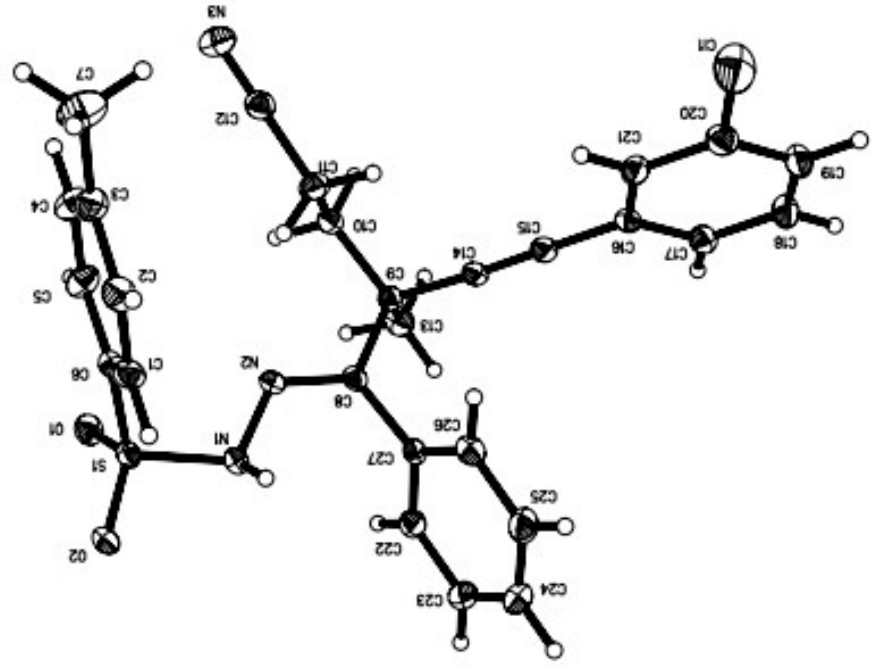


Figure S1. ORTEP diagram of complex **4**. Thermal ellipsoids are drawn at the 30% probability level.

Note: *The crystal of **4** was recrystallized from a mixed solvent of ethyl acetate and n-hexane (ethyl acetate: n-hexane, 1: 3).*

2. Crystal Data and Structure Refinement for 4

Complex	**4**
Empirical formula	$C_{27}H_{24}ClN_3O_2S$
Formula weight	490.00
Crystal size (mm^3)	0.22 × 0.18 × 0.15
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	15.0149(11)
b (Å)	6.9413(5)
c (Å)	28.0824(18)
α (°)	90
β (°)	102.467(2)
γ (°)	90
V ($Å^3$)	2857.8(3)
Z	4
D_{clac} (g cm^{-3})	1.139
μ (mm^{-1})	0.232
F (000)	1024
Total reflections	20081
Independent reflections	5042
Goodness-of-fit on F^2	1.004
R_{int}	0.0540
Final R indices	R_1 = 0.0447,
[I >2σ(I)])	wR_2 = 0.1113
R indices (all data)	R_1 = 0.0702, wR_2 = 0.1232
Residuals (e $Å^{-3}$)	0.245, -0.319

3. GC-MS study of the radical adducts 5

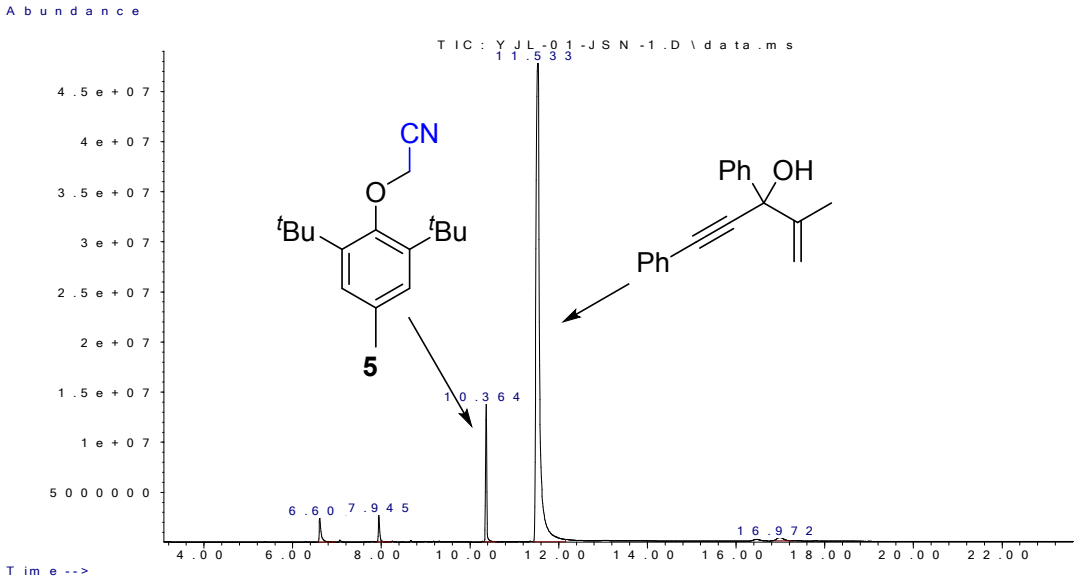


Figure S2

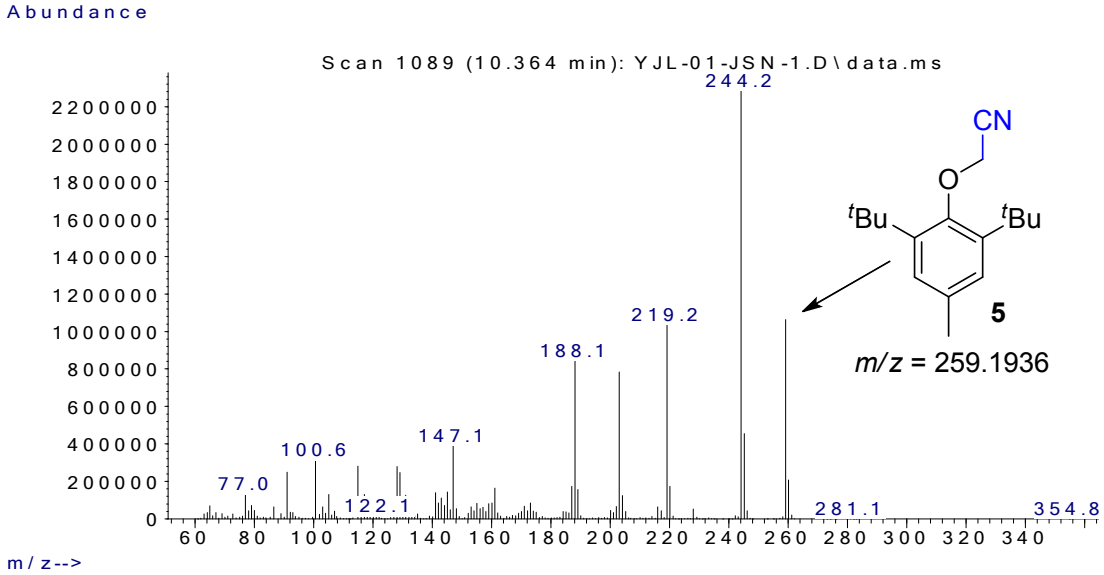


Figure S3

4. General Information

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Adamas, Aladdin, etc) and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 300 or 400 or 500 MHz NMR spectrometer (75 or 100 or 125 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hz. HRMS was obtained on an ESI-LC-MS/MS spectrometer. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

5. General Procedure for the Synthesis of Compounds 1

α-Aryl α-alkynyl allylic alcohols **1a**-**1u** were prepared according to the published procedure[1,2]. **1v** was known compound and prepared according to published procedures[3].

6. General Procedure for the Synthesis of α-alkynyl γ-cyano ketones 3

Under nitrogen, a 20 mL Schlenk tube equipped with a stir bar was charged with **1** (0.2 mmol, 1 equiv), peroxide (0.6 mmol), CH_3CN (3.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 120 °C for 12 h in oil bath. After the completion of the reaction, the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired product.

4-benzoyl-4-methyl-6-phenylhex-5-ynenitrile (3aa)

3aa was synthesized according to the general procedure by using **1a** (0.2 mmol, 49.6 mg), DTBP (0.6 mmol, 87.6 mg), CH_3CN (3.0 mL). Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3aa** (38.5 mg, 67% yield) as colorless oil. A 1 mmol scale reaction for compound **3aa** was similarly conducted using **1a** (1.0 mmol, 248.0 mg), DTBP (3.0 mmol, 438.0 mg),

CH_3CN (15.0 mL) at 120 °C for 12 h in a sealed Schlenk tube, **3aa** could be isolated in 44% yield (126.3 mg). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.34-8.32 (m, 2H), 7.59-7.56 (m, 1H), 7.49-7.45 (m, 2H), 7.40-7.29 (m, 5H), 2.67-2.58 (m, 3H), 2.10-2.03 (m, 1H), 1.72 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.5, 134.5, 133.1,131.3, 129.7, 128.6, 128.3, 128.1, 122.1, 119.7, 89.4, 87.8, 45.8, 35.2, 26.9, 13.7. IR (KBr) ν_{max}: 3061, 2980, 2935, 2248, 1682, 1597, 1490, 1446, 1240 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{20}H_{18}NO^+$ 288.1383, found 288.1381. MS (m/z): 287.1 $[M]^+$.

4-benzoyl-4-methyl-6-(4-propylphenyl)hex-5-ynenitrile (3ba)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ba** (36.8 mg, 56% yield) as colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.34-8.32 (m, 2H), 7.59-7.55 (m, 1H), 7.48-7.44 (m, 2H), 7.31-7.29 (m, 2H), 7.14-7.12 (m, 2H), 2.67-2.56 (m, 5H), 2.08-2.01 (m, 1H), 1.71 (s, 3H), 1.67-1.58 (m, 2H), 0.95-0.91 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.7, 143.6, 134.6, 133.1, 131.2, 129.8, 128.5, 128.2, 119.8, 119.3, 88.7, 88.0, 45.8, 37.8, 35.3, 27.0, 24.3, 13.7, 13.6. IR (KBr) ν_{max}: 2960, 2931, 2247, 1683, 1596, 1508, 1447, 1240, 1182 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{23}H_{24}NO^+$ 330.1852, found 330.1849. MS (m/z): 329.2 $[M]^+$.

4-benzoyl-4-methyl-6-(4-propylphenyl)hex-5-ynenitrile (3ca)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ca** (30.7 mg, 51% yield) as colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.34-8.32 (m, 2H), 7.59-7.55 (m, 1H), 7.48-7.44 (m, 2H), 7.29-7.27 (m, 2H), 7.13-7.11 (m, 2H), 2.69-2.57 (m, 3H), 2.35 (s, 3H), 2.09-2.02 (m, 1H), 1.71 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.6, 138.8, 134.5, 133.0, 131.2, 129.8, 129.1, 128.1, 119.7, 119.0, 88.7, 87.9, 45.8, 35.2, 27.0, 21.4, 13.7. IR (KBr) ν_{max}: 3060, 2980, 2934, 2247, 1682, 1596, 1509, 1447, 1240 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{21}H_{20}NO^+$ 302.1539, found 302.1539. MS (m/z): 301.1 $[M]^+$.

4-benzoyl-6-(4-methoxyphenyl)-4-methylhex-5-ynenitrile (3da)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3da** (33.0 mg, 52% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33-8.31 (m, 2H) 7.58-7.54 (m, 1H), 7.47-7.44 (m, 2H), 7.33-7.29 (m, 2H), 6.85-6.81 (m, 2H), 3.80 (s, 3H), 2.66-2.56 (m, 3H), 2.10-2.00 (m, 1H), 1.70 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.8, 159.8, 134.6, 133.0, 132.8, 129.8, 128.1, 119.8, 114.2, 114.0, 88.0, 87.8, 55.2, 45.8, 35.3, 27.0, 13.7. IR (KBr) ν_{max}: 3069, 2935, 2839, 2247, 1682, 1605, 1509, 1446, 1249 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{21}H_{20}NO_2^+$ 318.1489, found 318.1487. MS (m/z): 317.1 $[M]^+$

4-benzoyl-6-(3-chlorophenyl)-4-methylhex-5-ynenitrile (3ea)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ea** (41.7 mg, 65% yield) as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29-8.26 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 7.35-7.34 (m, 1H), 7.31-7.28 (m, 1H), 7.25-7.23 (m, 2H), 2.66-2.55 (m, 3H), 2.09-2.02 (m, 1H), 1.71 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.2, 134.4, 134.2, 133.2, 131.2, 129.7, 129.6, 129.5, 129.0, 128.2, 123.8, 119.6, 90.7, 86.5, 45.8, 35.1, 26.9, 13.7. IR (KBr) ν_{max}: 3066, 2980, 2934, 2248, 1682, 1595, 1447, 1240, 1157 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{20}H_{17}ClNO^+$ 322.0993, found 322.0997. MS (m/z): 321.1 $[M]^+$

4-benzoyl-6-(2-chlorophenyl)-4-methylhex-5-ynenitrile (3fa)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3fa** (35.5 mg, 57% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.36-8.34 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.38 (m, 4H), 7.28-7.19 (m, 2H), 2.72-2.62 (m, 3H), 2.12-2.05 (m, 1H), 1.75 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.1, 135.9, 134.3, 133.2, 133.1, 129.9, 129.7, 129.3, 128.2, 126.5, 122.1, 119.7, 94.5, 84.7, 46.0, 35.3, 27.0, 13.7. IR (KBr) ν_{max}: 3067, 2980, 2935, 2248, 1683, 1597, 1474, 1240, 1157 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{20}H_{17}ClNO^+$ 322.0993, found 322.0993. MS (m/z): 321.1 $[M]^+$

4-benzoyl-4-methyl-6-(*m*-tolyl)hex-5-ynenitrile (3ga)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ga** (38.0 mg, 63% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33-8.31 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 2H), 7.22-7.13 (m, 4H), 2.68-2.56 (m, 3H), 2.32 (s, 3H), 2.08-2.01 (m, 1H), 1.70 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.6, 138.1, 134.5, 133.1, 131.9, 129.8, 129.5, 128.4, 128.3, 128.2, 121.9, 119.7, 89.0, 88.0, 45.8, 35.3, 27.0, 21.1, 13.7. IR (KBr) ν_{max}: 3058, 2979, 2934, 2247, 1682, 1597, 1484, 1446, 1241 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{21}H_{20}NO^+$ 302.1539, found 302.1540. MS (m/z): 301.1 $[M]^+$

4-benzoyl-4-methyl-6-(thiophen-3-yl)hex-5-ynenitrile (3ha)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ha** (34.6 mg, 59% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28-8.26 (m, 2H), 7.59-7.55 (m, 1H), 7.48-7.45 (m, 2H), 7.27-7.26 (m, 1H), 7.18-7.17 (m, 1H), 6.98-6.96 (m, 1H), 2.66-2.56 (m, 3H), 2.10-2.02 (m, 1H), 1.71 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.2, 134.5, 133.2, 132.1, 129.7, 128.3, 127.5, 127.0, 122.0, 119.6, 93.2, 81.4, 46.1, 35.2, 26.9, 13.8. IR (KBr) ν_{max}: 3106, 2980, 2934, 2247, 1677, 1596, 1446, 1237, 1184 cm^{-1}.HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{18}H_{16}NOS^+$ 294.0947, found 294.0955. MS (m/z): 293.1 $[M]^+$

4-benzoyl-4-methylundec-5-ynenitrile (3ia)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ia** (10.1 mg, 18% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.27-8.25 (m, 2H), 7.55-7.52 (m, 1H), 7.44-7.41 (m, 2H), 2.60-2.45 (m, 3H), 2.20 (t, J = 7.1 Hz, 2H), 1.93-1.87 (m, 1H), 1.58 (s, 3H), 1.50-1.45 (m, 2H), 1.30-1.27 (m, 4H), 0.87-0.84 (m, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.2, 134.6, 132.9, 129.9, 128.0, 119.9, 88.6, 80.5, 45.3, 35.5, 31.0, 28.0, 27.1, 22.1, 18.7, 13.9, 13.6. IR (KBr) ν_{max}: 2957, 2932, 2860, 2247, 1677, 1597, 1447, 1378, 1244 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+Na]^+$ $C_{19}H_{23}NONa^+$ 304.1672, found 304.1684. MS (m/z): 281.2 $[M]^+$

4-methyl-4-(4-methylbenzoyl)-6-phenylhex-5-ynenitrile (3ja)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ja** (32.6 mg, 54% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26-8.24 (m, 2H), 7.40-7.24 (m, 7H), 2.65-2.57 (m, 3H), 2.41 (s, 3H), 2.09-2.00 (m, 1H), 1.70 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.9, 144.1, 131.8, 131.3, 130.0, 128.8, 128.6, 128.3, 122.2, 119.8, 89.7, 87.6, 45.6, 35.3, 27.0, 21.6, 13.7. IR (KBr) ν_{max}: 3058, 2980, 2933, 2247, 1678, 1606, 1570, 1490, 1245, 1184 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{21}H_{20}NO^+$ 302.1539, found 302.1539. MS (m/z): 301.1 $[M]^+$

4-(4-fluorobenzoyl)-4-methyl-6-phenylhex-5-ynenitrile (3ka)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ka** (30.5 mg, 50% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.31-8.28 (m, 2H), 7.61-7.55 (m, 1H), 7.49-7.44 (m, 2H), 7.38-7.33 (m, 2H), 7.03-6.98 (m, 2H), 2.69-2.55(m, 3H), 2.07-2.01(m, 1H), 1.71 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.5, 162.7(d, J_{C-F} = 248.3 Hz), 134.5, 133.3 (d, J_{C-F} = 8.3 Hz), 133.2, 129.8, 128.2, 119.7, 118.2 (d, J_{C-F} = 3.0 Hz), 115.7 (d, J_{C-F} = 22.5 Hz), 89.2 (d, J_{C-F} = 1.5 Hz), 86.9, 45.8, 35.2 , 27.0, 13.8. IR (KBr) ν_{max}: 3063, 2983, 2935, 2248, 1705, 1611, 1484, 1450, 1218 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{20}H_{18}FNO^+$ 306.1289, found 306.1289. MS (m/z): 305.1 $[M]^+$

4-methyl-4-(2-methylbenzoyl)-6-phenylhex-5-ynenitrile (3la)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3la** (33.1 mg, 55% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81-7.79 (m, 1H), 7.37-7.20 (m, 8H), 2.66-2.62 (m, 2H), 2.58-2.51 (m, 1H), 2.35 (s, 3H), 2.10-2.03 (m, 1H), 1.62 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 203.8, 137.7, 136.2, 131.3, 131.1, 130.3, 128.6, 128.3, 127.0, 124.7, 122.1, 119.5, 88.7, 87.6, 48.0, 34.5, 26.0, 20.3, 13.8. IR (KBr) ν_{max}: 3061, 2979, 2933, 2248, 1697, 1599, 1490, 1443, 1236 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{21}H_{20}NO^+$ 302.1539, found 302.1540. MS (m/z): 301.1 $[M]^+$

4-methyl-4-(3-methylbenzoyl)-6-phenylhex-5-ynenitrile (3ma)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ma** (28.9 mg, 48% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18-8.10 (m, 2H), 7.40-7.29 (m, 7H), 2.66-2.59 (m, 3H), 2.42(s, 3H), 2.09-2.02 (m, 1H), 1.72 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.8, 138.0, 134.6, 133.8, 131.3, 130.3, 128.6, 128.3, 127.9, 126.9, 122.2, 119.7, 89.6, 87.7, 45.9, 35.2, 27.0, 21.4, 13.7. IR (KBr) ν_{max}: 3060, 2979, 2933, 2248, 1682, 1600, 1490, 1443, 1261 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{21}H_{20}NO^+$ 302.1539, found 302.1535. MS (m/z): 301.1 $[M]^+$

4-(2-fluorobenzoyl)-4-methyl-6-phenylhex-5-ynenitrile (3na)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3na** (26.8 mg, 44% yield) as yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.66-7.61 (m, 1H), 7.49-7.44 (m, 1H), 7.32-7.11 (m, 7H), 2.65-2.52 (m, 3H), 2.10-2.05 (m, 1H), 1.65 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 200.7 (d, J_{C-F} = 2.3 Hz), 159.2 (d, J_{C-F} = 249.8 Hz), 132.9 (d, J_{C-F} = 8.3 Hz), 131.4, 129.3 (d, J_{C-F} = 3.0 Hz), 128.6, 128.3, 126.9 (d, J_{C-F} = 16.5 Hz), 123.9 (d, J_{C-F} = 3.8 Hz), 122.1, 119.4, 116.1 (d, J_{C-F} = 21.8 Hz), 88.2, 86.9, 48.4, 34.6, 25.7 (d, J_{C-F} = 2.3 Hz), 13.8. IR (KBr) ν_{max}: 3070, 2981, 2934, 2248, 1682, 1600, 1508, 1447, 1232, 1156 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{20}H_{18}FNO^+$ 306.1289, found 306.1289. MS (m/z): 305.1 $[M]^+$

4-(4-methoxybenzoyl)-4-methyl-6-phenylhex-5-ynenitrile (3oa)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3oa** (26.0 mg, 41% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38-8.35 (m, 2H), 7.40-7.38 (m, 2H), 7.33-7.26 (m, 3H), 6.95-6.93 (m, 2H), 3.87 (s, 3H), 2.68-2.57 (m, 3H), 2.07-2.00 (m, 1H), 1.71 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.6, 163.4, 132.4, 131.3, 128.6, 128.4, 127.0, 122.2, 119.8, 113.3, 89.9, 87.6, 55.4, 45.5, 35.4, 27.2, 13.7. IR (KBr) ν_{max}: 3059, 2975, 2935, 2247, 1671, 1600, 1509, 1378, 1250 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{21}H_{20}NO_2^+$ 318.1489, found 318.1488. MS (m/z): 317.1 $[M]^+$

4-(4-chlorobenzoyl)-4-methyl-6-phenylhex-5-ynenitrile (3pa)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3pa** (34.7 mg, 54% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30-8.28 (m, 2H), 7.45-7.43(m, 2H), 7.39-7.32 (m, 5H), 2.68-2.56 (m, 3H), 2.09-2.02 (m, 1H), 1.70 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.3, 139.6, 132.7, 131.3, 131.3, 128.8, 128.5, 128.4, 121.9, 119.6, 89.1, 88.1, 45.8, 35.1, 26.9, 13.7. IR (KBr) ν_{max}: 2981, 2935, 2247, 1685, 1586, 1489, 1399, 1242, 1093 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{20}H_{17}ClNO^+$ 322.0993, found 322.0996. MS (m/z): 321.1 $[M]^+$

4-(furan-3-carbonyl)-4-methyl-6-phenylhex-5-ynenitrile(3qa)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10 give **3qa** (19.4 mg, 35% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68-7.65 (m, 2H), 7.42-7.40 (m, 2H), 7.35-7.30 (m, 3H), 6.57-6.55 (m, 1H), 2.63-2.56 (m, 3H), 2.07-2.01 (m, 1H), 1.69 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.0, 149.9, 147.0, 131.5, 128.7, 128.4, 122.1, 120.7, 119.6, 112.1, 89.0, 86.8 , 45.4, 34.4, 26.8, 13.7. IR (KBr) ν_{max}: 3060, 2981, 2935, 2248, 2198, 1671, 1560, 1491, 1461, 1276 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{18}H_{16}NO_2^+$ 278.1176, found 278.1179. MS (m/z): 277.1 $[M]^+$

methyl 4-(2-(2-cyanoethyl)-2-methyl-4-phenylbut-3-ynoyl)benzoate (3ra)：

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ra** (45.6 mg, 66% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.36-8.33 (m, 2H), 8.13-8.10 (m, 2H), 7.38-7.28 (m, 5H), 3.94 (s, 3H), 2.67-2.58 (m, 3H), 2.12-2.02 (m, 1H), 1.71 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.4, 166.0, 138.1, 133.7, 131.3, 129.6, 129.3, 128.8, 128.4, 121.8, 119.5, 88.8, 88.3, 52.4, 46.1, 35.0, 26.8, 13.7. IR (KBr) ν_{max}: 3056, 2952, 2248, 1686, 1599, 1491, 1437, 1281, 1109 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{22}H_{20}NO_3^+$ 346.1438, found 346.1437. MS (m/z): 345.1 $[M]^+$.

4-methyl-5-oxo-4-(phenylethynyl)heptanenitrile (3sa)：

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3sa** (21.5 mg, 45% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.45-7.40 (m, 2H), 7.35-7.31 (m, 3H), 2.97-2.80 (m, 2H), 2.53-2.46 (m, 2H), 2.41-2.32 (m, 1H), 1.94-1.85 (m, 1H), 1.46 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 209.4, 131.5, 128.6, 128.4, 122.1, 119.4, 88.6, 86.3, 47.7, 33.6, 32.2, 25.7, 13.7, 8.1. IR (KBr) ν_{max}: 2980, 2938, 2248, 1717, 1598, 1490, 1443, 1378, 1344 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{16}H_{18}NO^+$ 240.1383, found 240.1383. MS (m/z): 239.1 $[M]^+$.

4-benzoyl-3,4-dimethyl-6-phenylhex-5-ynenitrile (3ta)：

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ta** (46.4 mg, 77% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.31-8.21 (m, 2H), 7.59-7.53 (m, 1H), 7.49-7.43 (m, 2H), 7.40-7.30 (m, 5H), 2.89-2.73 (m, 1.5H), 2.63-2.56 (m, 0.5H), 2.46-2.37 (m, 1H), 2.63-2.56 (m, 0.5H), 2.46-2.37 (m, 1.0H), 1.65 (s, 1.5H), 1.63 (s, 1.5H), 1.34 (d, J = 6.7 Hz, 1.5H), 1.22 (d, J = 6.8 Hz, 1.5H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 199.3, 198.5, 135.8, 135.2, 132.9, 132.8, 131.3, 131.3, 129.5, 129.3, 128.6, 128.6, 128.4, 128.3, 128.1, 128.0, 122.3, 122.2, 119.1, 118.9, 89.1, 88.8, 88.4, 88.4, 50.5, 50.2, 37.6, 36.9, 23.9, 23.1, 21.6, 20.1, 16.4, 14.1. IR (KBr) ν_{max}: 3060, 2977, 2938, 2247, 1683, 1597, 1490, 1445, 1386, 1239 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{21}H_{20}NO^+$ 302.1539, found 302.1539. MS (m/z): 301.1 $[M]^+$

4-benzoyl-6-phenylhex-5-ynenitrile (3ua)：

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ua** (18.0 mg, 33% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.79-7.76 (m, 2H), 7.48-7.43 (m, 1H), 7.40-7.28 (m, 7H), 6.66 (t, J = 2.6 Hz, 1H), 2.93-2.87 (m, 2H), 2.68-2.64 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 214.5, 193.2, 137.6, 132.6, 131.2, 129.1, 128.7, 128.4, 128.1, 127.6, 119.1, 107.6, 100.2, 25.3, 16.0. IR (KBr) ν_{max}: 3062, 3031, 2926, 2247, 1932, 1648, 1597, 1496, 1447, 1274 cm^{-1}.

HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{19}H_{16}NO^+$ 274.1226, found 274.1226. MS (m/z): 273.1 $[M]^+$.

4-benzoyl-2-ethyl-4-methyl-6-phenylhex-5-ynenitrile (3ab)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ab** (46.0 mg, 73% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.35-8.34 (m, 2H), 7.59-7.56 (m, 1H), 7.49-7.45 (m, 4H), 7.32-7.29 (m, 3H), 2.84-2.79 (m, 1H), 2.42-2.39 (m, 1H), 2.17-2.12 (m, 1H), 1.85-1.73 (m, 5H), 1.15 (t, J = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 198.3, 134.7, 133.0, 131.3, 129.8, 128.5, 128.3, 128.1, 122.8, 122.4, 89.6, 88.0, 46.1, 41.1, 30.0, 27.4, 27.1, 11.3. IR (KBr) ν_{max}: 3061, 2971, 2878, 2238, 1683, 1597, 1491, 1446, 1239 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{22}H_{22}NO^+$ 316.1696, found 316.1698. MS (m/z): 315.2 $[M]^+$

4-benzoyl-2,4-dimethyl-6-phenylhex-5-ynenitrile (3ac)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ac** (35.5 mg, 59% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.34-8.32 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.42 (m, 4H), 7.33-7.29 (m, 3H), 2.97-2.92 (m, 1H), 2.43-2.38 (m, 1H), 2.17-2.11 (m, 1H), 1.78 (s, 3H), 1.47-1.45 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.4, 134.7, 133.0, 131.4, 129.8, 128.6, 128.3, 128.2, 122.4, 89.5, 88.1, 46.1, 42.8, 27.6, 22.6, 19.9. IR (KBr) ν_{max}: 3060, 2932, 2874, 2239, 1685, 1597, 1491, 1446, 1242 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{21}H_{20}NO^+$ 302.1539, found 302.1543. MS (m/z): 301.1 $[M]^+$

4-benzoyl-2-methoxy-4-methyl-6-phenylhex-5-ynenitrile (3ad)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ad** (40.0 mg, 63% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.30-8.27 (m, 1.27H), 8.13-8.10 (m, 0.7H), 7.58-7.53 (m, 1.07H), 7.48-7.27 (m, 7.03H), 4.47-4.41 (m, 1H), 3.46 (s, 1.9H), 3.38 (s, 1.05H), 3.08-3.00 (m, 0.36H), 2.77-2.70 (m, 0.65H), 2.44-2.37 (m, 0.65H), 2.19-2.13 (m, 0.36H), 1.74-1.73 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 199.6, 197.8, 136.1, 134.9, 132.8, 132.3, 131.4, 131.3,

129.7, 129.1, 128.7, 128.4, 128.1, 127.9, 122.3, 122.2, 118.1, 118.0, 89.7, 89.6, 88.2, 87.7, 68.3, 68.2, 58.1, 58.0, 45.0, 44.9, 42.9, 42.4, 28.3, 26.8. IR (KBr) ν_{max}: 2922, 2851, 2363, 2345, 1685, 1597, 1491, 1236, 1192 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{21}H_{20}NO_2^+$ 318.1489, found 318.1491. MS (m/z): 317.1 $[M]^+$

4-benzoyl-2,2,4-trimethyl-6-phenylhex-5-ynenitrile (3ae)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3ae** (35.3 mg, 56% yield) as colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.27-8.24 (m, 2H), 7.58-7.53 (m, 1H), 7.48-7.42 (m, 4H), 7.32-7.27 (m, 3H), 2.79-2.74 (m, 1H), 2.01-1.96 (m, 1H), 1.78 (s, 3H), 1.54 (s, 3H), 1.41 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 200.0, 135.5, 132.7, 131.2, 129.7, 128.4, 128.3, 127.9, 125.5, 122.7, 90.3, 88.6, 47.3, 45.3, 31.0, 29.8, 29.4, 27.1. IR (KBr) ν_{max}: 3060, 2978, 2930, 2234, 1683, 1597, 1490, 1446, 1238 cm^{-1}. HRMS (ESI-TOF): calculated for $[M+H]^+$ $C_{22}H_{22}NO^+$ 316.1696, found 316.1697. MS (m/z): 315.2 $[M]^+$

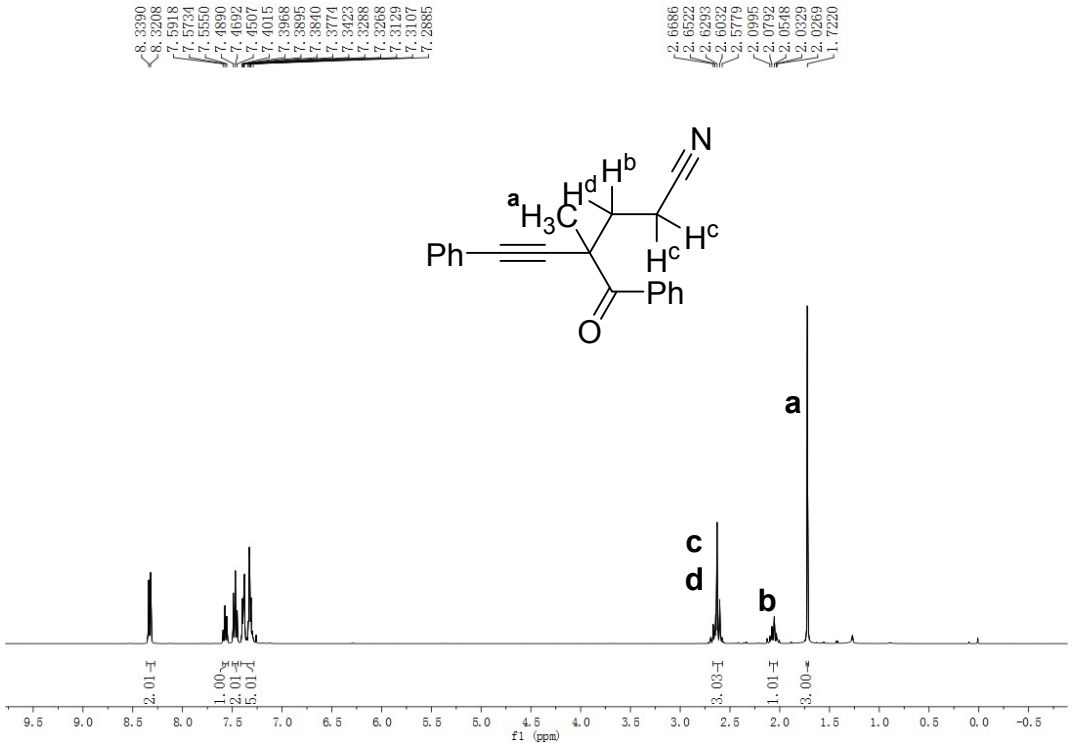
7. References

1. Q. Zhao, X.-S. Ji, Y.-Y. Gao, W.-J. Hao, K.-Y. Zhang, S.-J. Tu and B. Jiang, *Org. Lett.*, 2018, **20**, 3596.
2. S.-N. Jin, S. Sun, J.-T. Yu and J. Cheng, *J. Org. Chem.*, 2019, **84**, 11177.
3. X. Tang and A. Studer, *Chem. Sci.*, 2017, **8**, 6888.

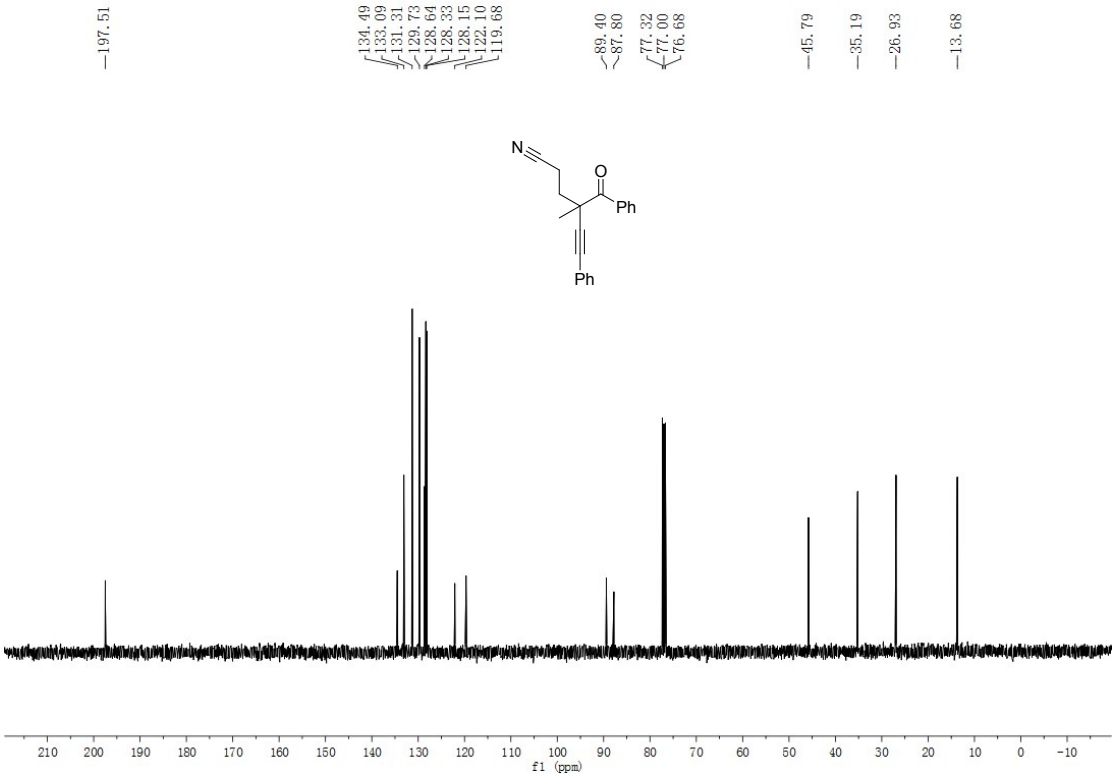
8. Copies of the ^1H NMR and ^{13}C NMR Spectra

4-benzoyl-4-methyl-6-phenylhex-5-ynenitrile (3aa)

^1H NMR ($CDCl_3$, 400 MHz):

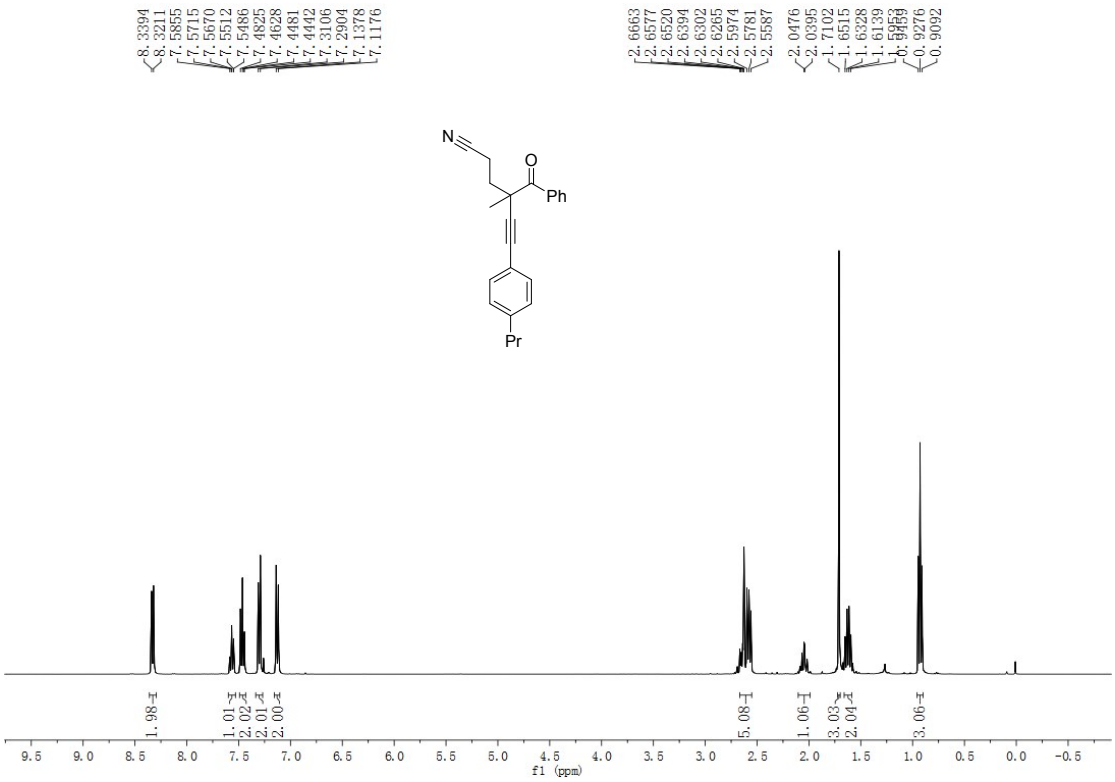


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):

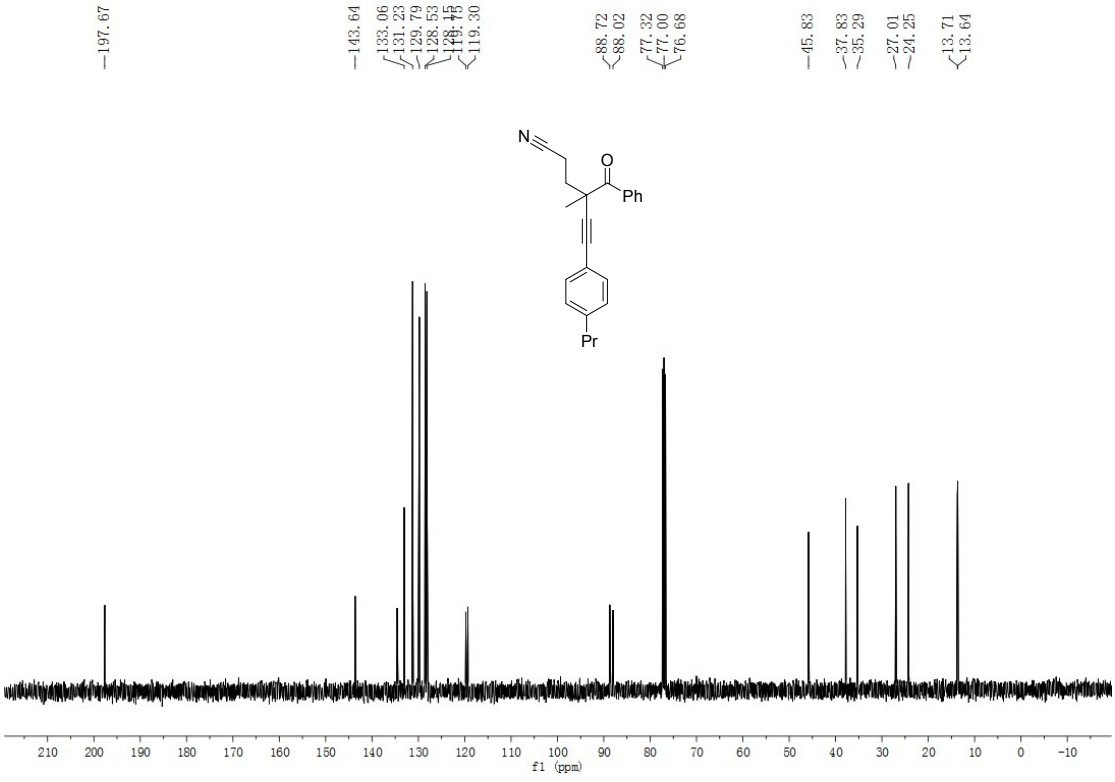


4-benzoyl-4-methyl-6-(4-propylphenyl)hex-5-ynenitrile (3ba)

^{1}H NMR ($CDCl_3$, 400 MHz):

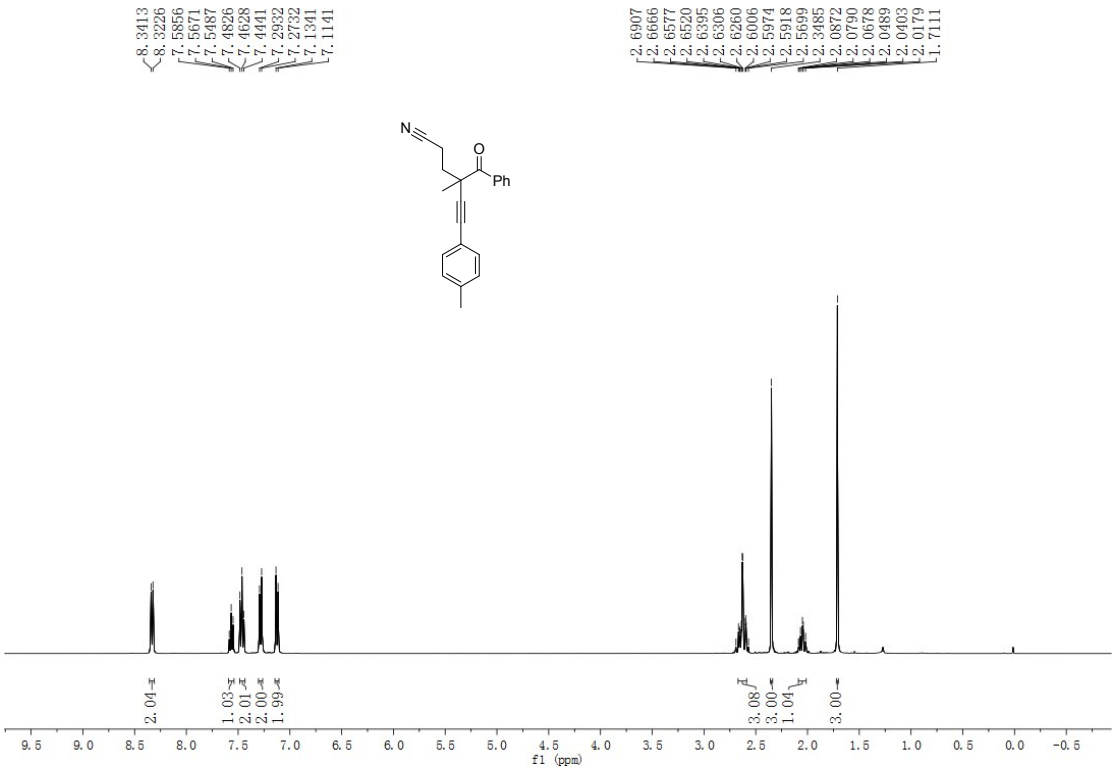


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)：

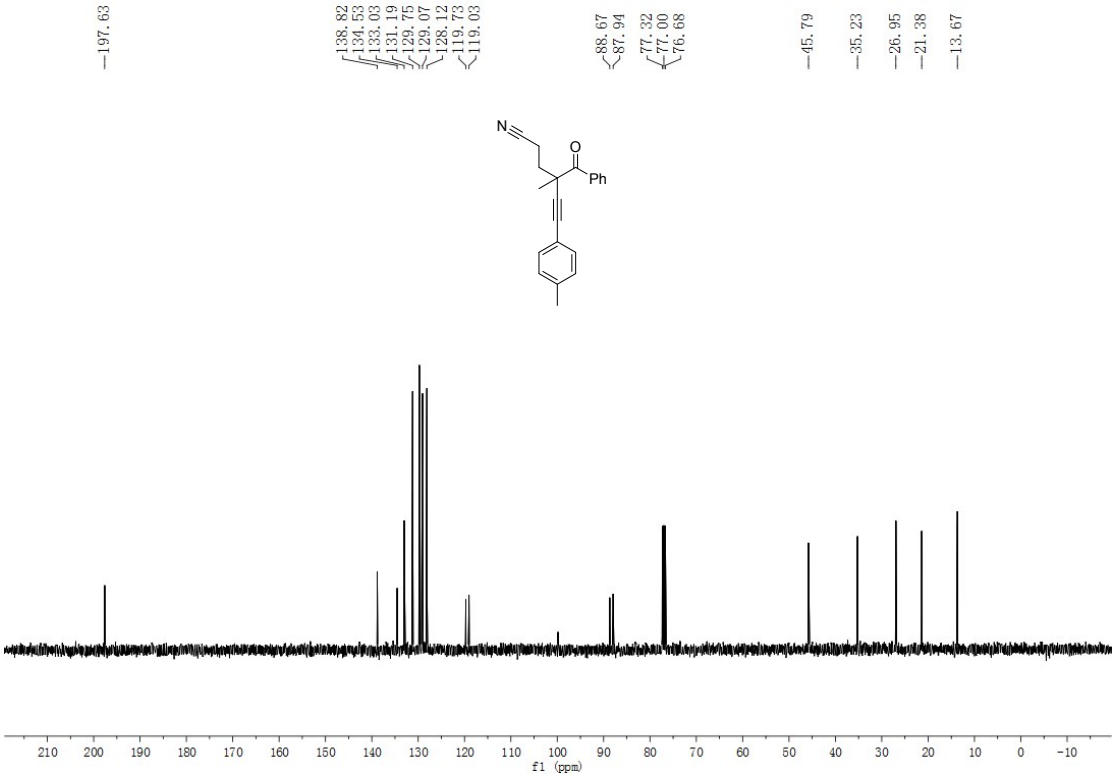


4-benzoyl-4-methyl-6-(4-propylphenyl)hex-5-ynenitrile(3ca)

^{1}H NMR ($CDCl_3$, 400 MHz):

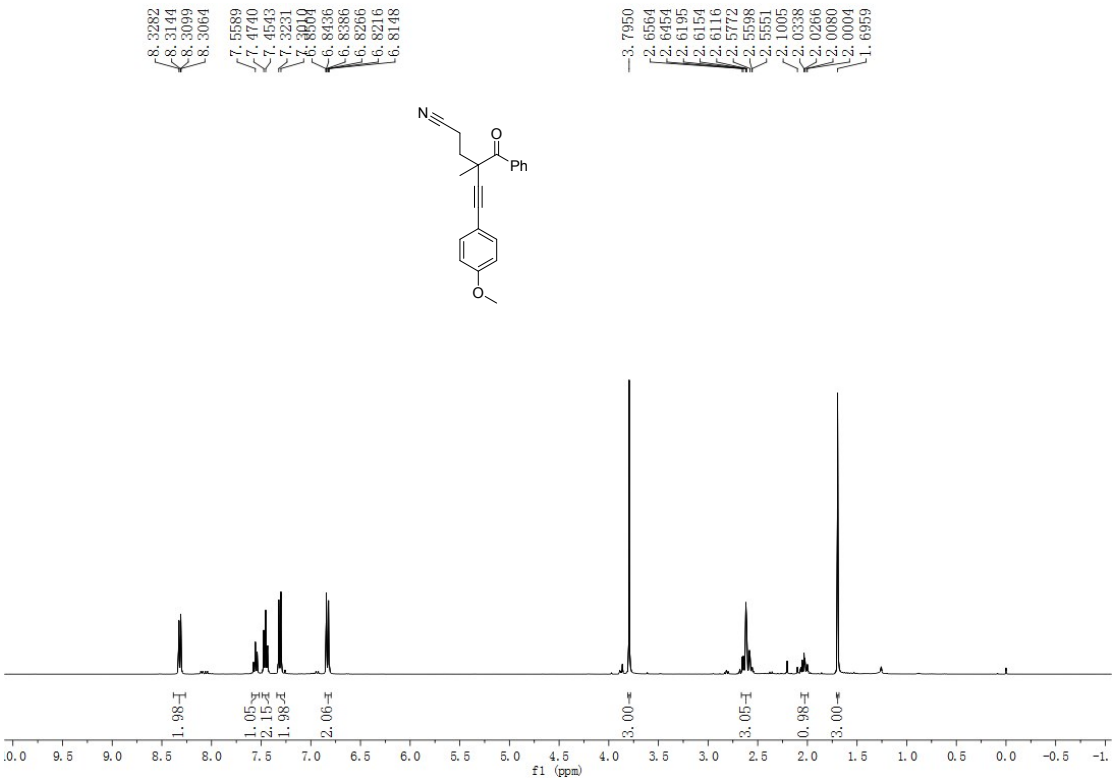


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):

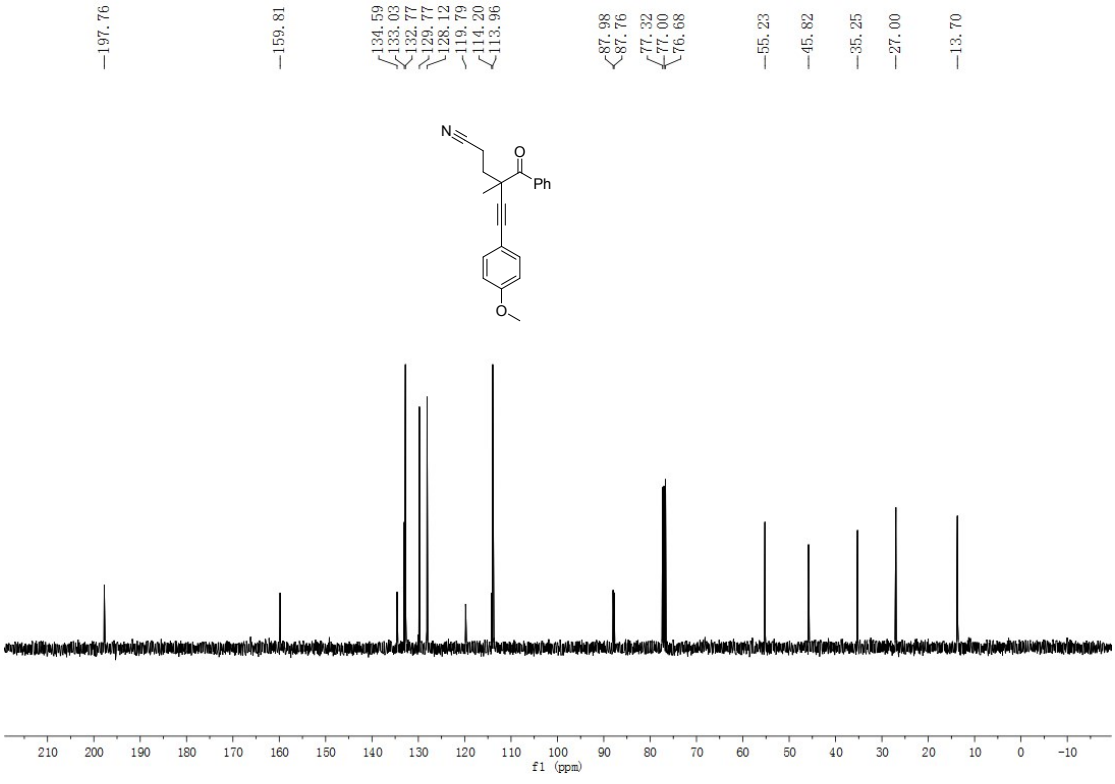


4-benzoyl-6-(4-methoxyphenyl)-4-methylhex-5-ynenitrile(3da)

^{1}H NMR ($CDCl_3$, 400 MHz):

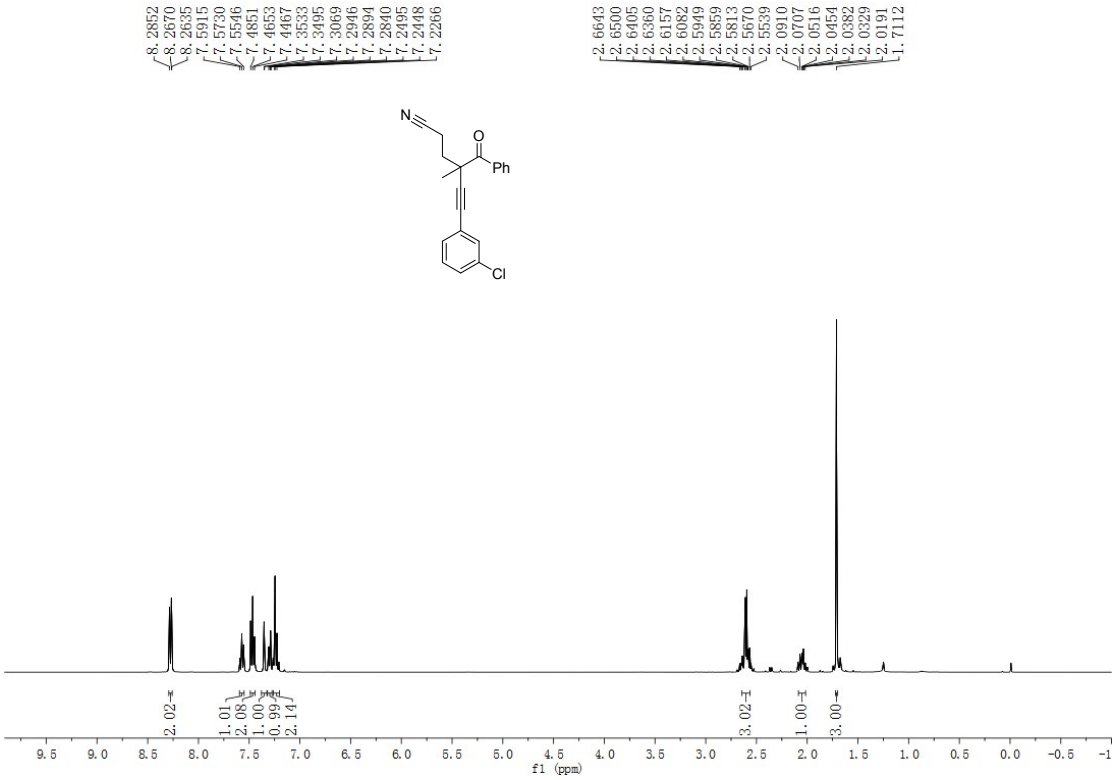


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):

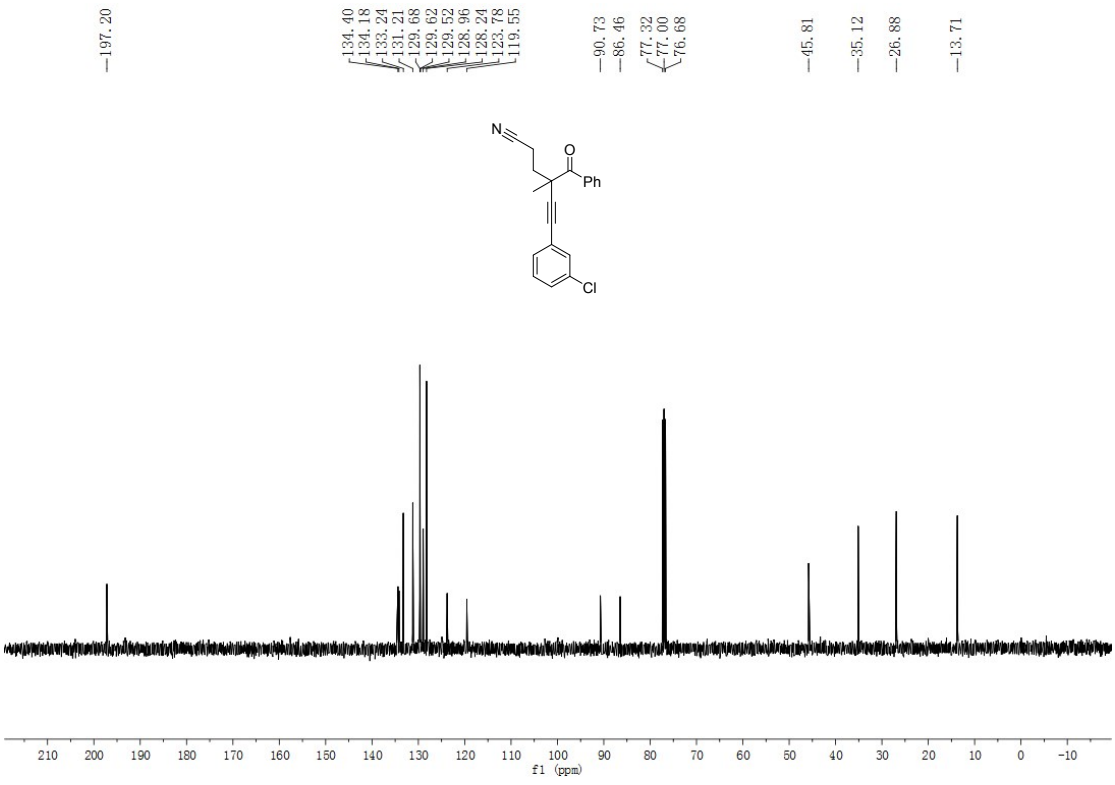


4-benzoyl-6-(3-chlorophenyl)-4-methylhex-5-ynenitrile(3ea)

^{1}H NMR ($CDCl_3$, 400 MHz):

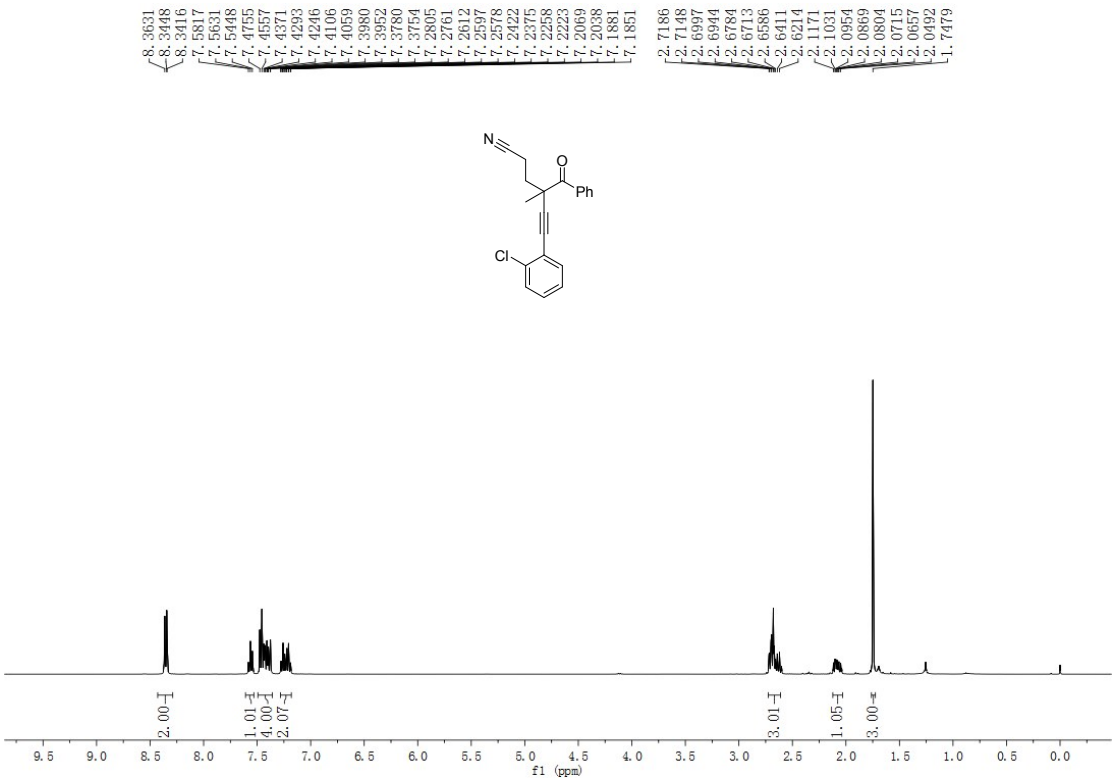


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):

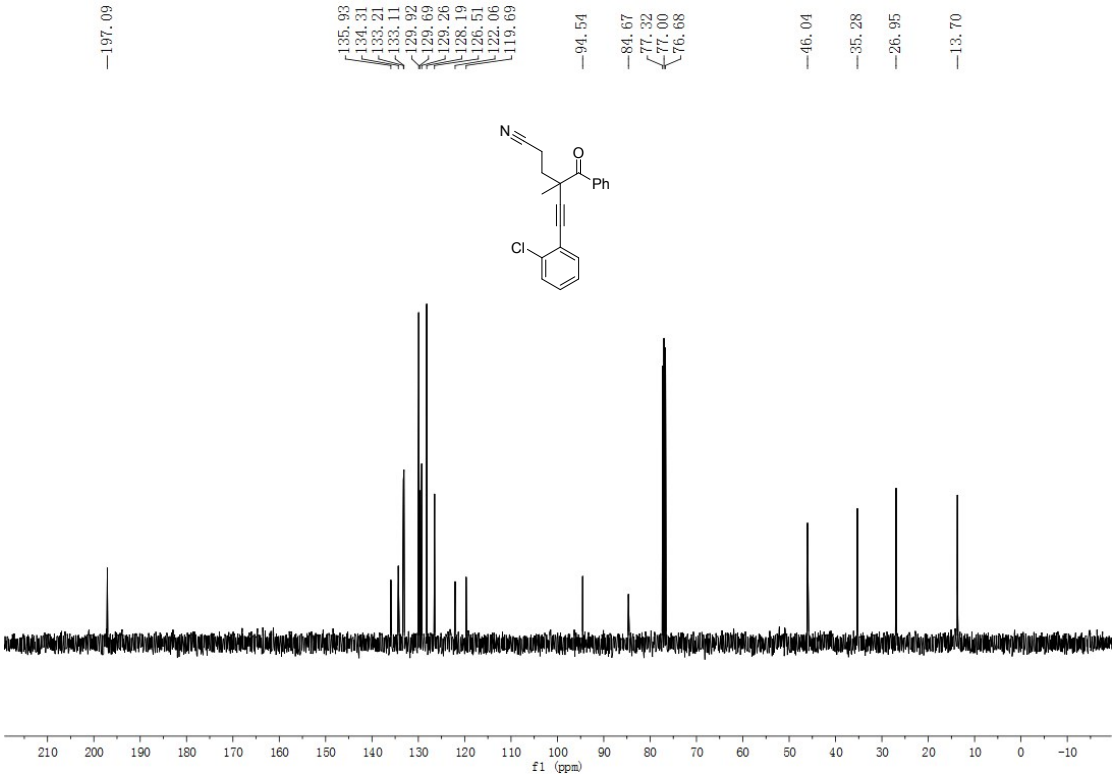


4-benzoyl-6-(2-chlorophenyl)-4-methylhex-5-ynenitrile(3fa)

^{1}H NMR ($CDCl_3$, 400 MHz):

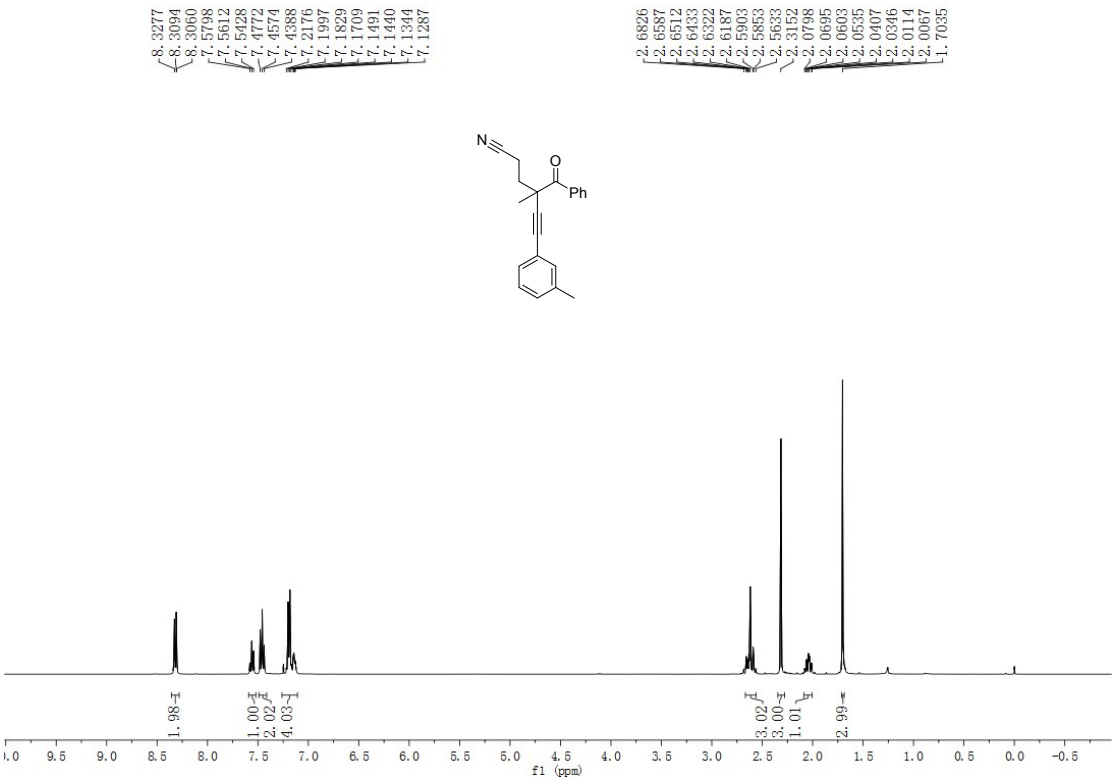


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)：

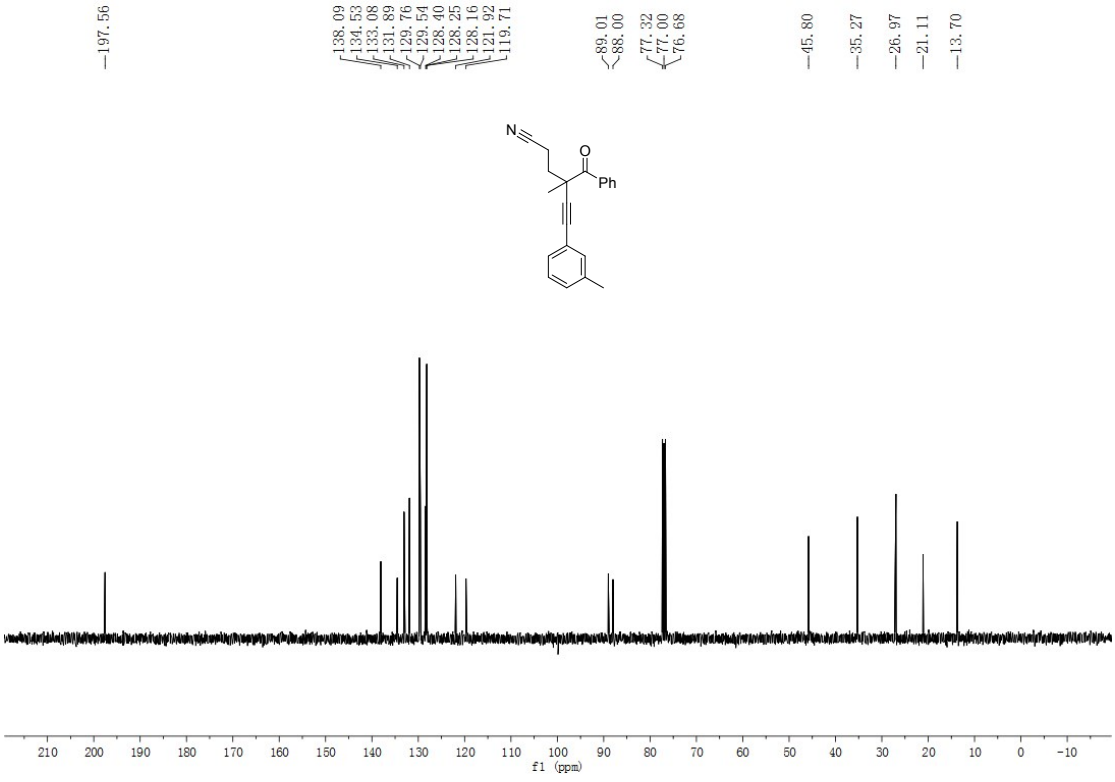


4-benzoyl-4-methyl-6-(m-tolyl)hex-5-ynenitrile(3ga)

^{1}H NMR ($CDCl_3$, 400 MHz):

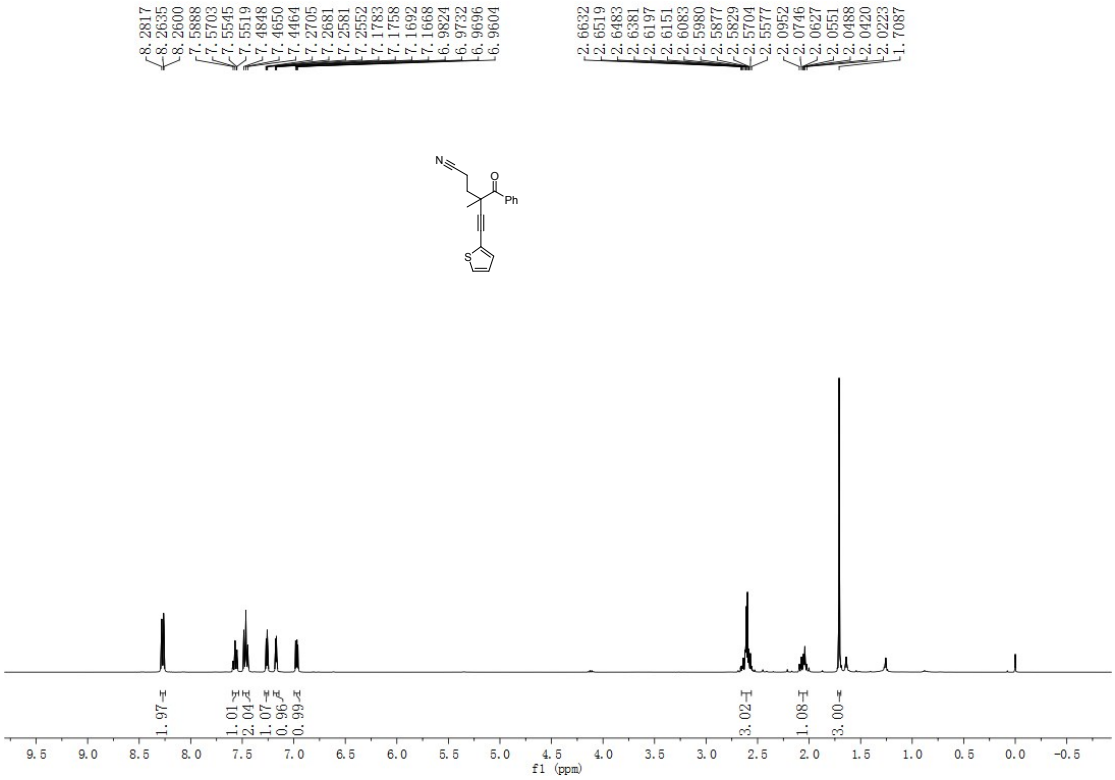


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)：

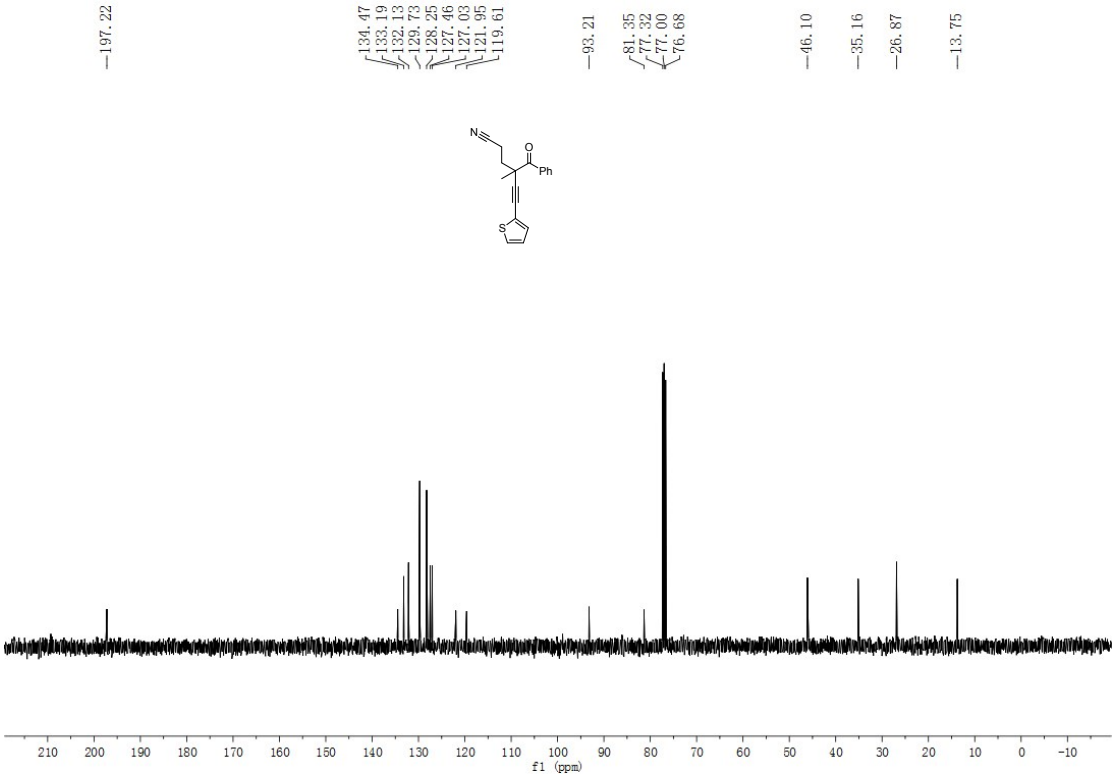


4-benzoyl-4-methyl-6-(thiophen-3-yl)hex-5-ynenitrile（3ha）

^{1}H NMR ($CDCl_3$, 400 MHz):

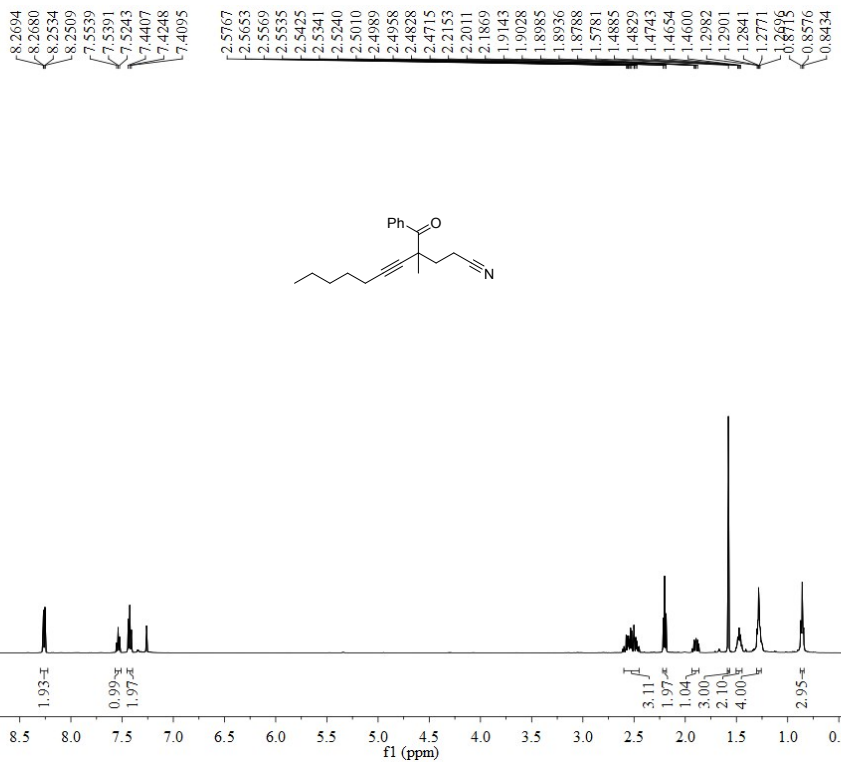


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)：

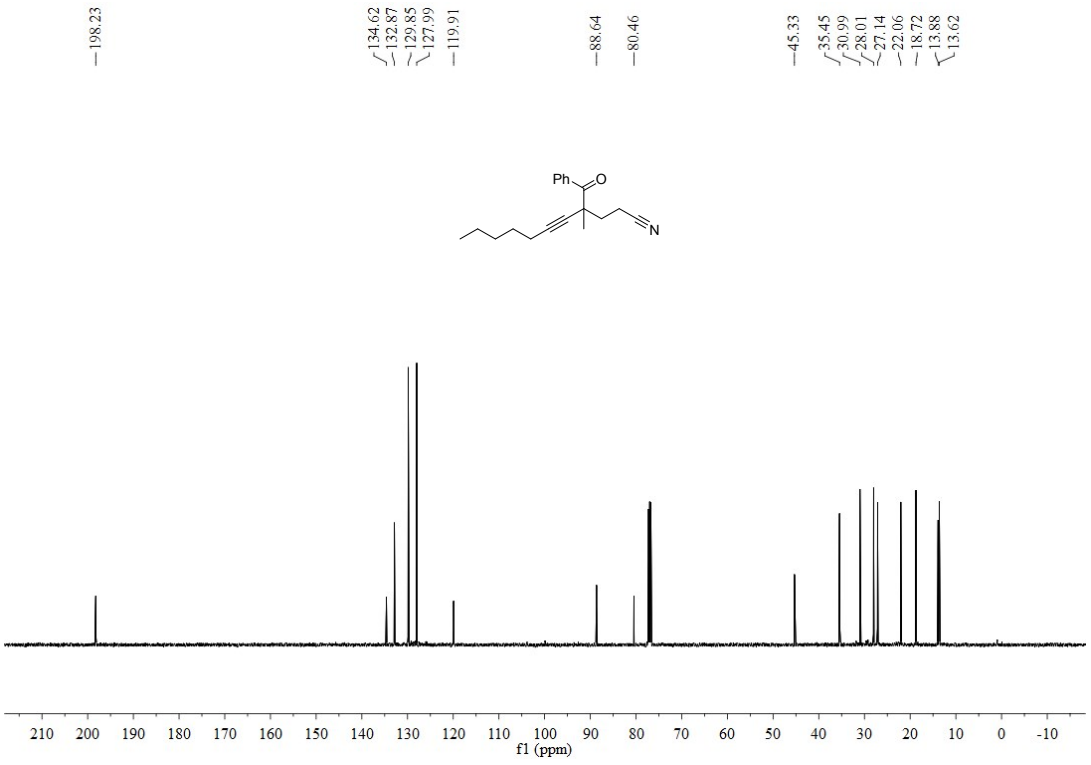


4-benzoyl-4-methylundec-5-ynenitrile (3ia)

^{1}H NMR ($CDCl_3$, 500 MHz):

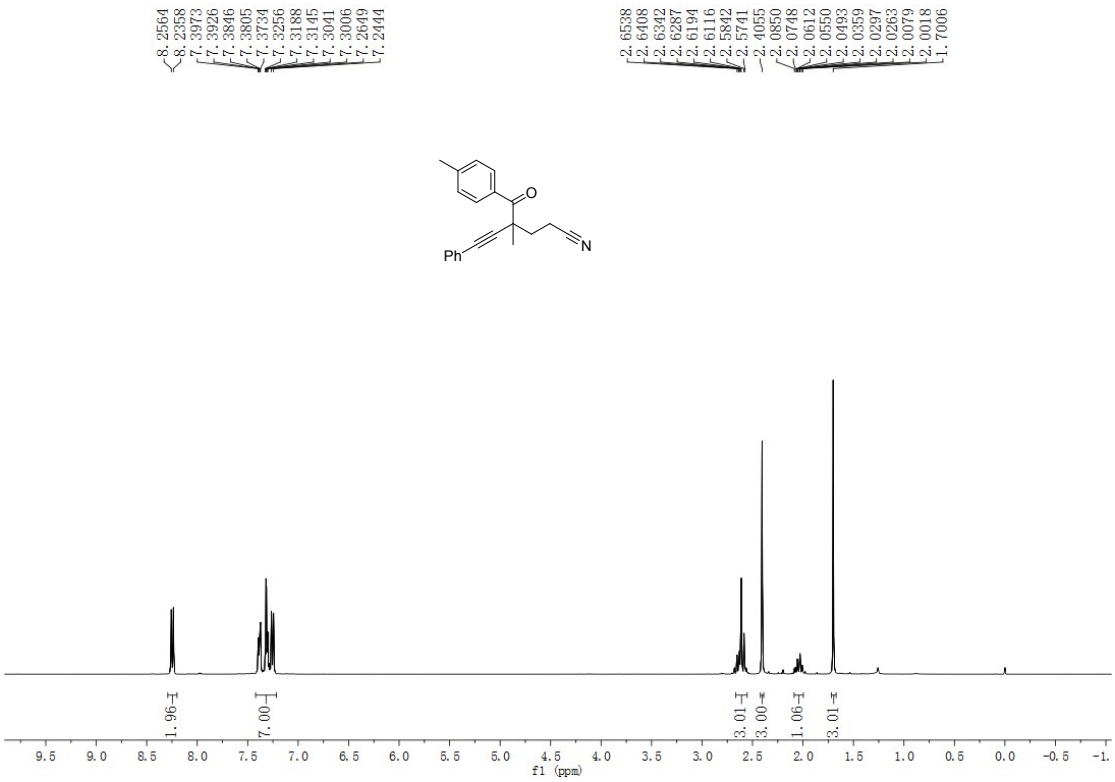


$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)：

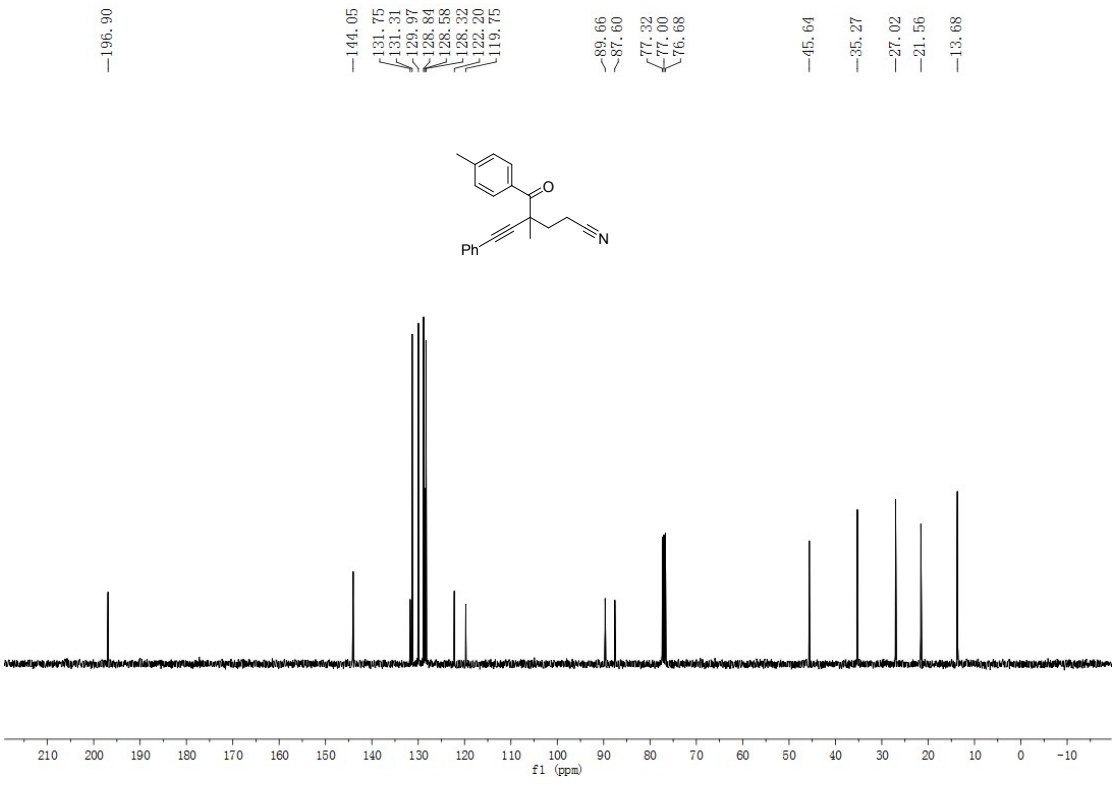


4-methyl-4-(4-methylbenzoyl)-6-phenylhex-5-ynenitrile(3ja)

^{1}H NMR ($CDCl_3$, 400 MHz):

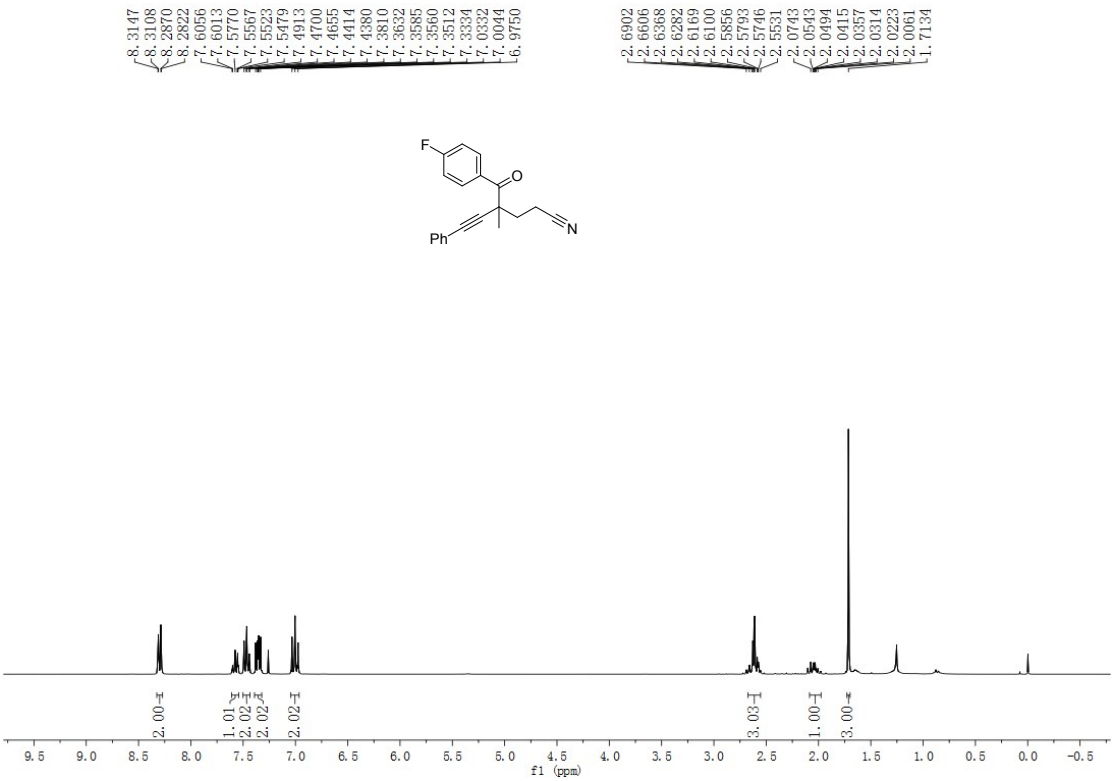


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):

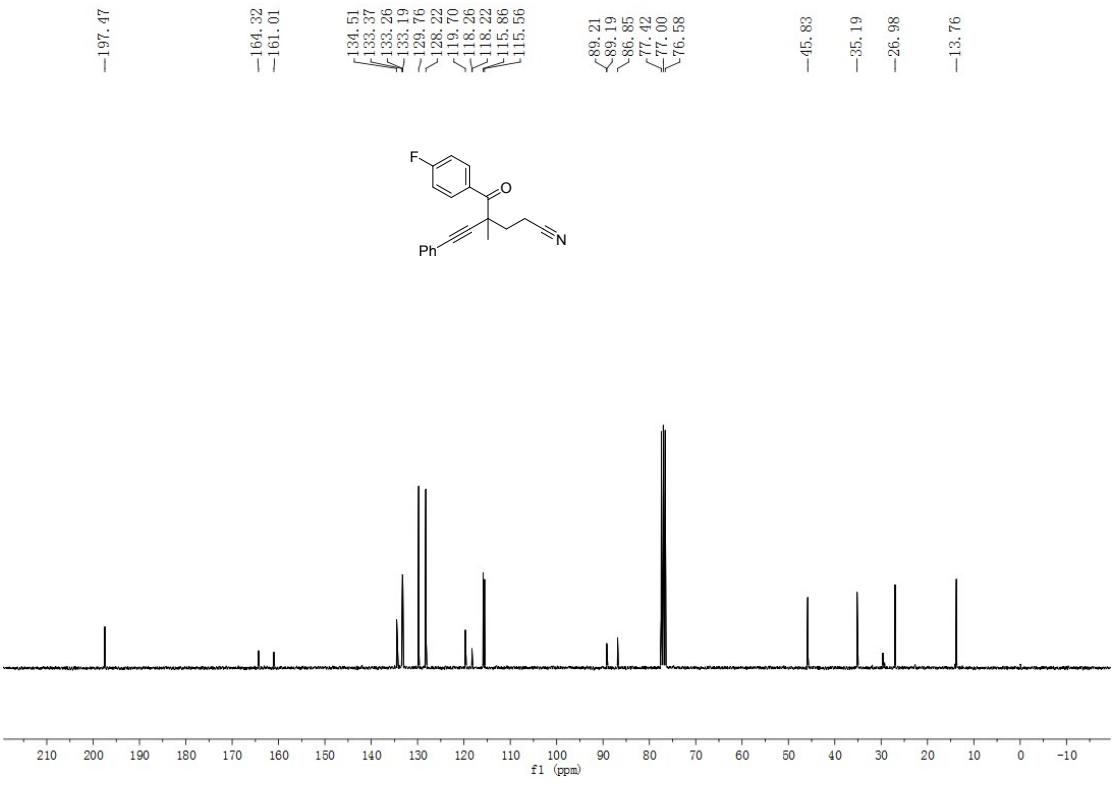


4-(4-fluorobenzoyl)-4-methyl-6-phenylhex-5-ynenitrile(3ka)

^{1}H NMR ($CDCl_3$, 300 MHz):

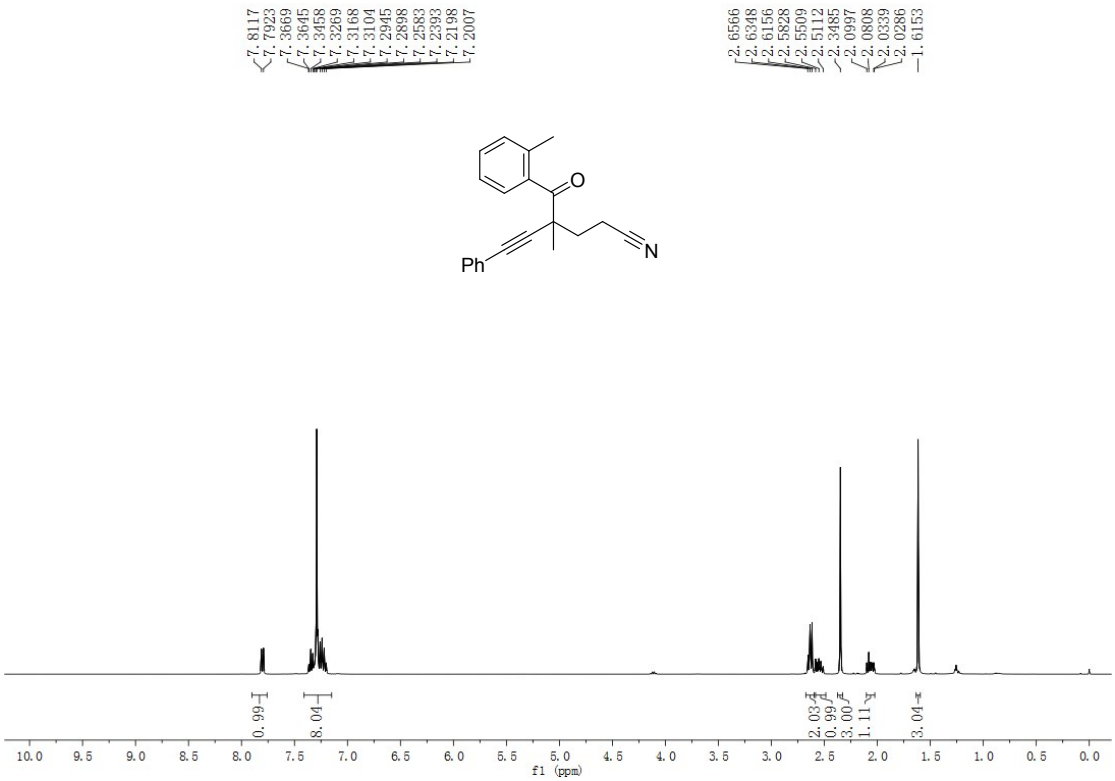


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)：

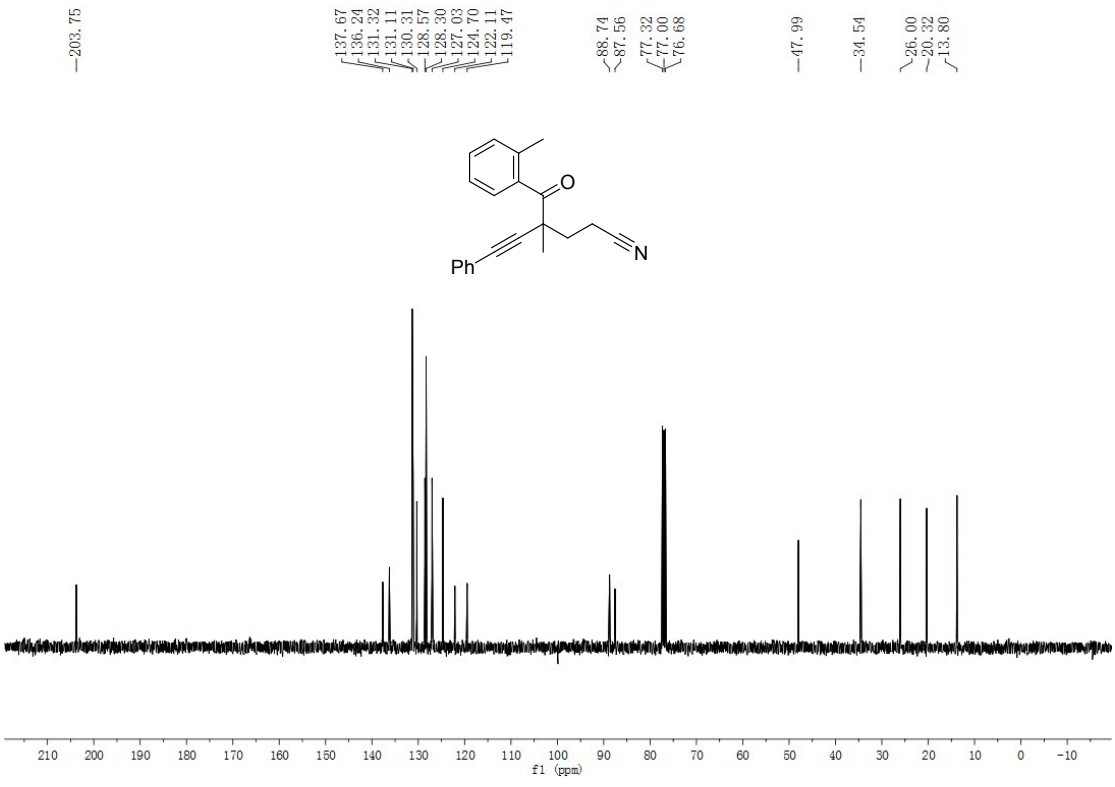


4-methyl-4-(2-methylbenzoyl)-6-phenylhex-5-ynenitrile（3la）

^{1}H NMR ($CDCl_3$, 400 MHz):

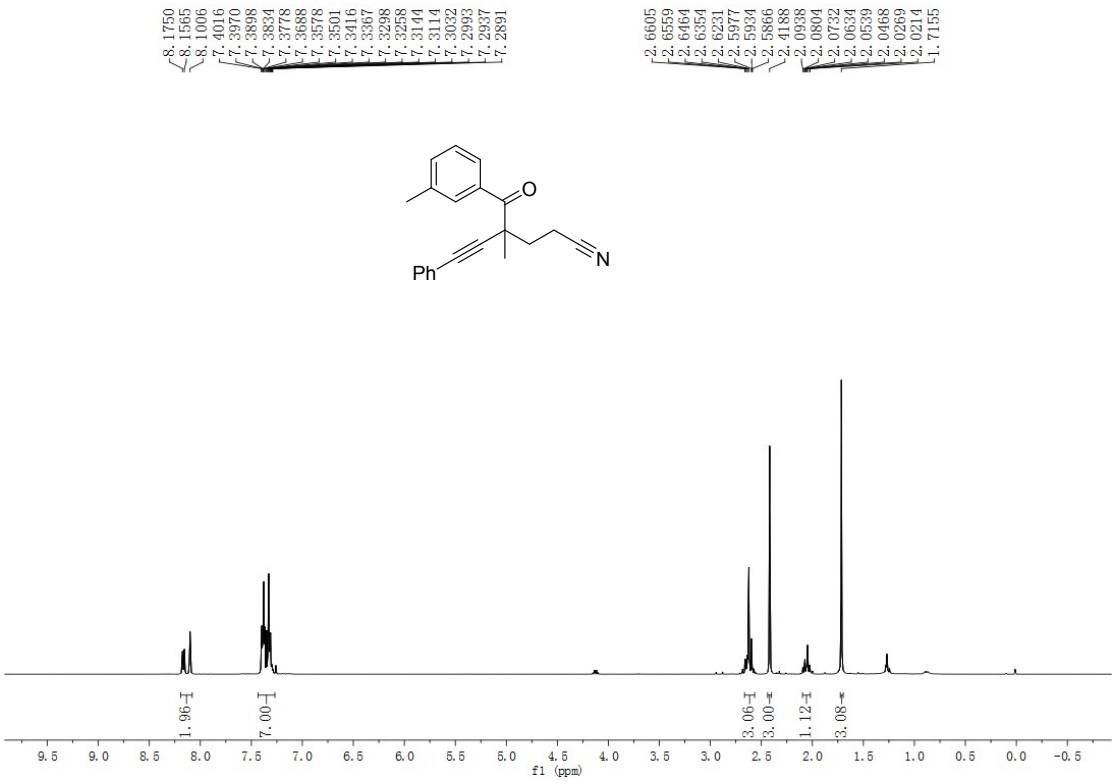


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)：

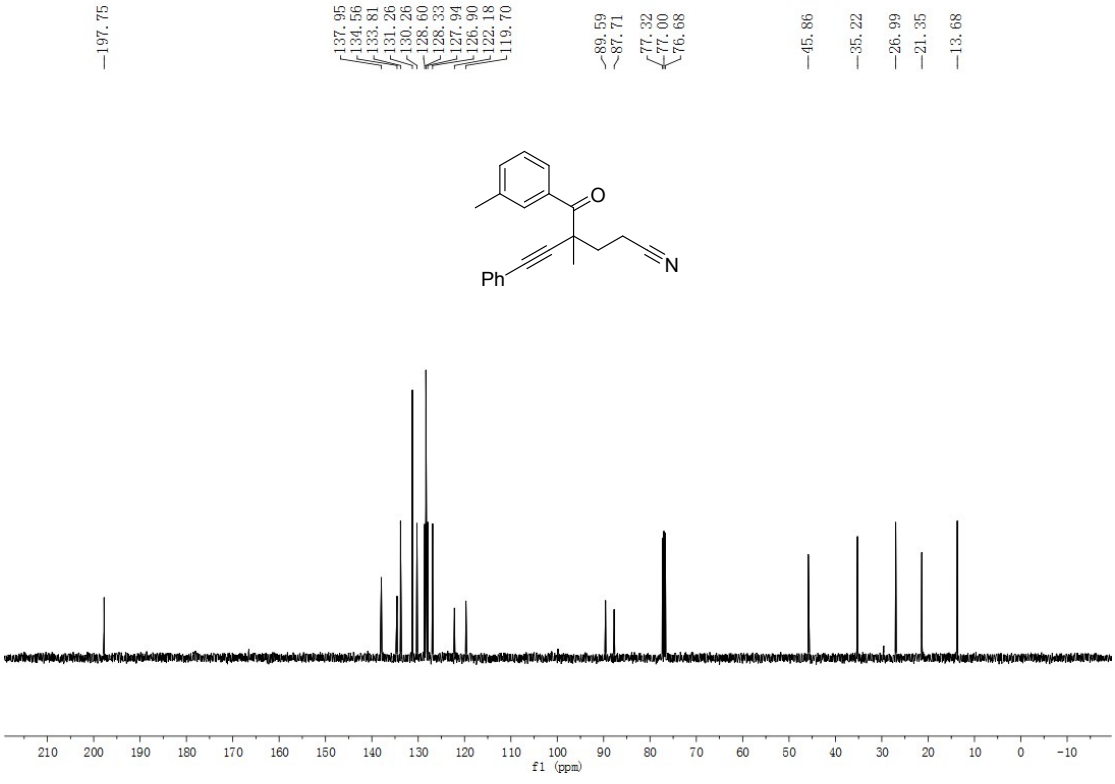


4-methyl-4-(3-methylbenzoyl)-6-phenylhex-5-ynenitrile（3ma）

^{1}H NMR ($CDCl_3$, 400 MHz):

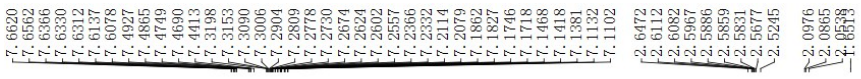


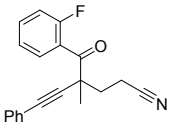
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):

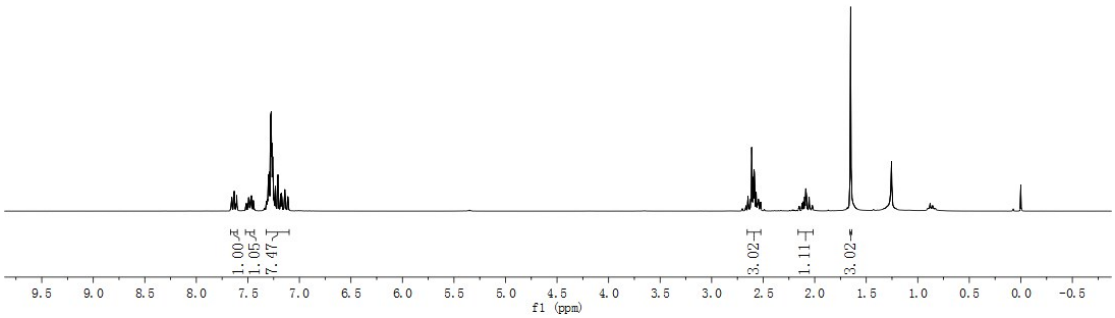


4-(2-fluorobenzoyl)-4-methyl-6-phenylhex-5-ynenitrile(3na)

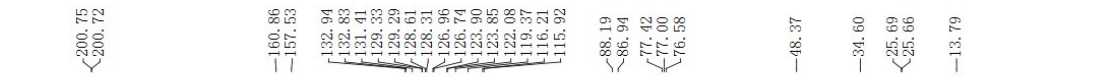
^{1}H NMR ($CDCl_3$, 300 MHz):

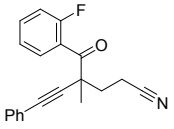


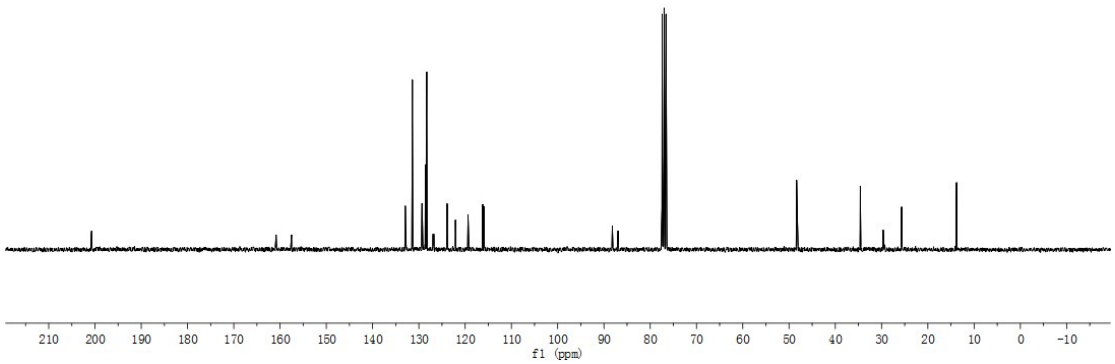




$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)：

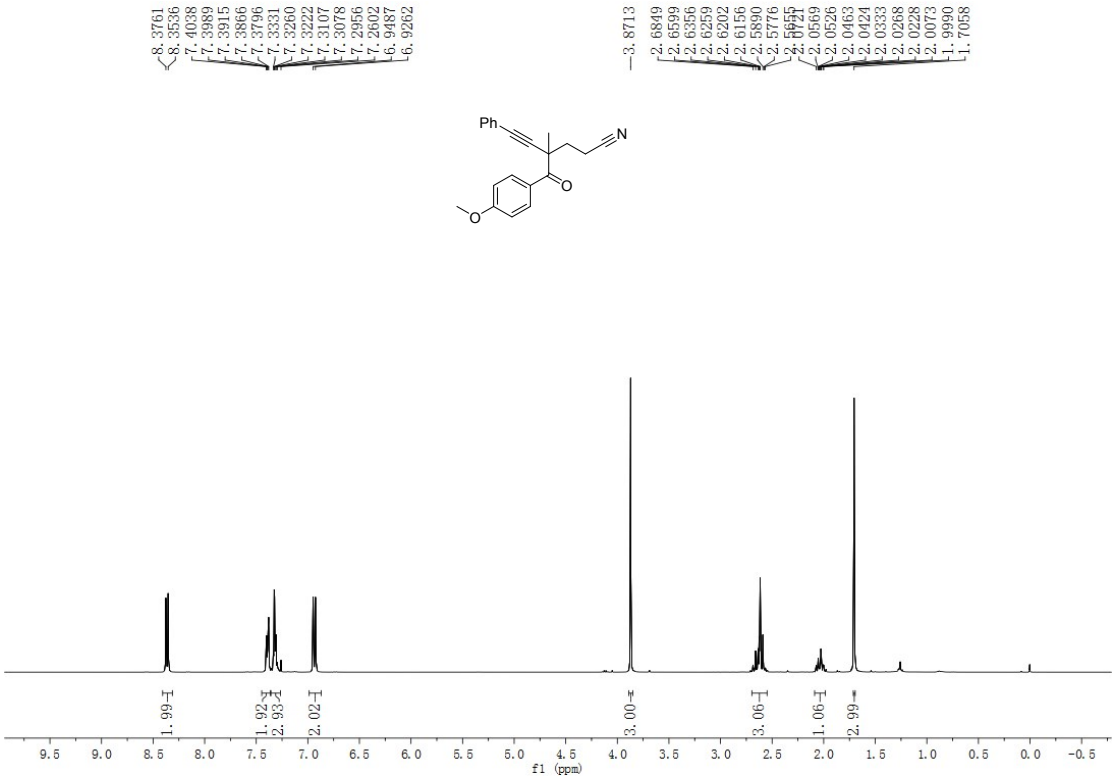




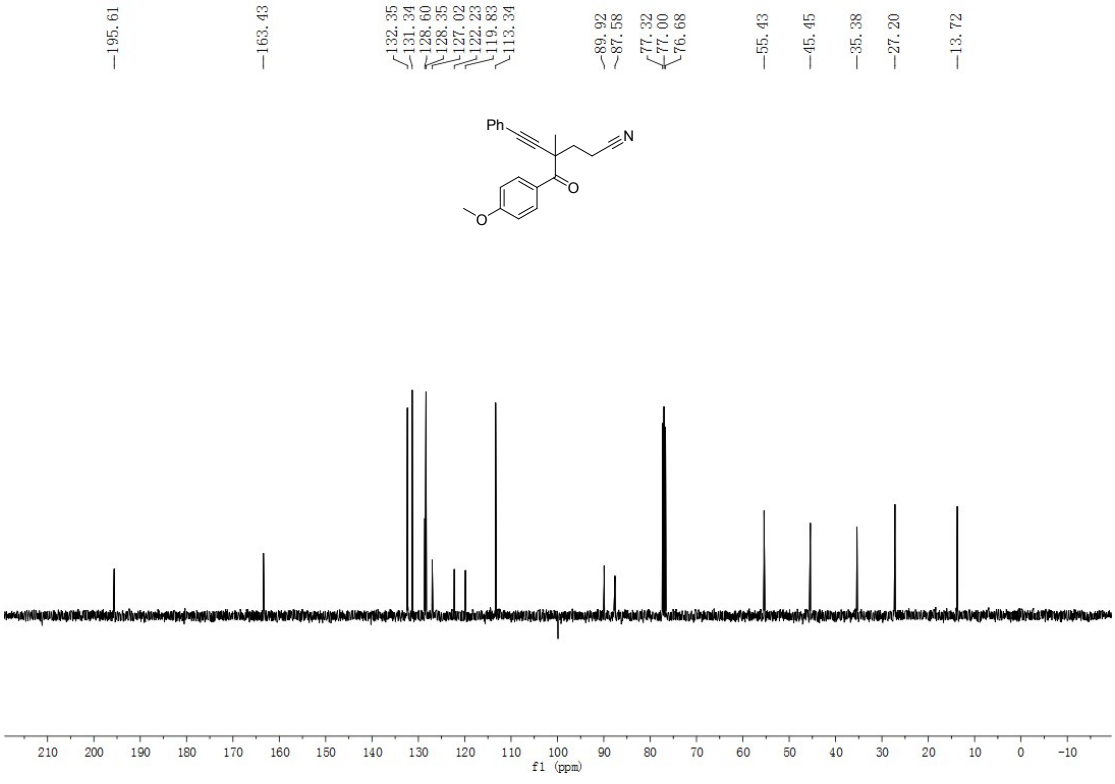


4-(4-methoxybenzoyl)-4-methyl-6-phenylhex-5-ynenitrile(3oa)

^{1}H NMR ($CDCl_3$, 400 MHz):

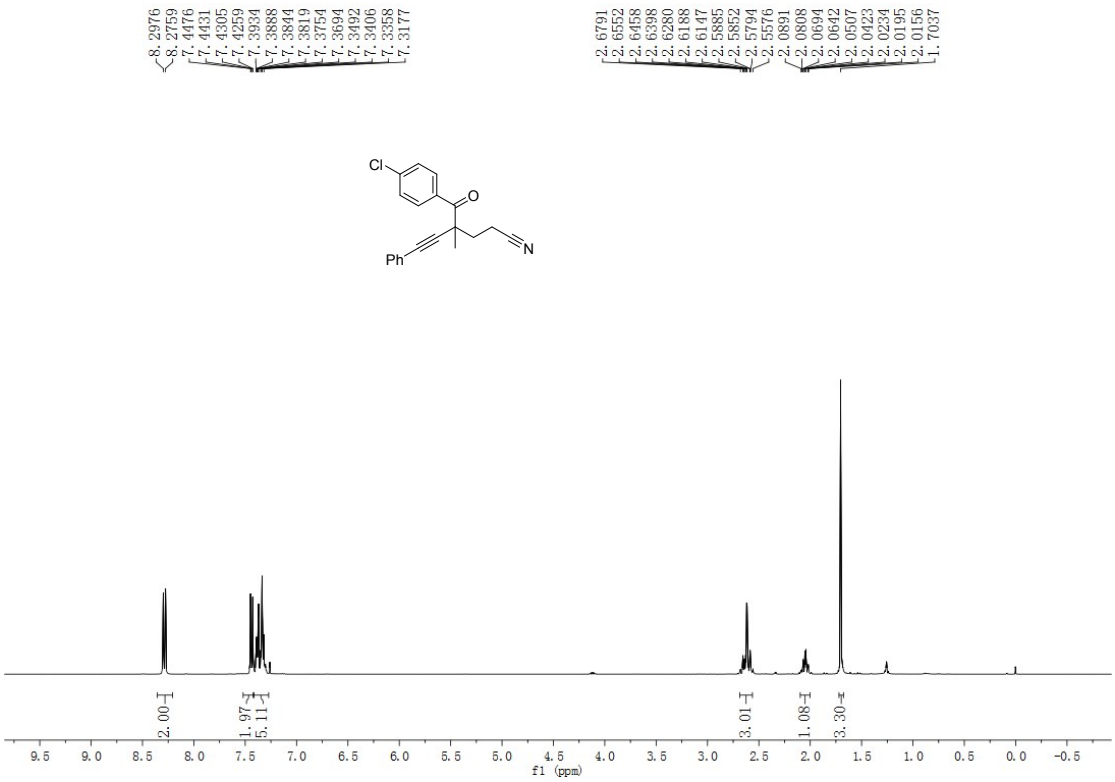


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)：

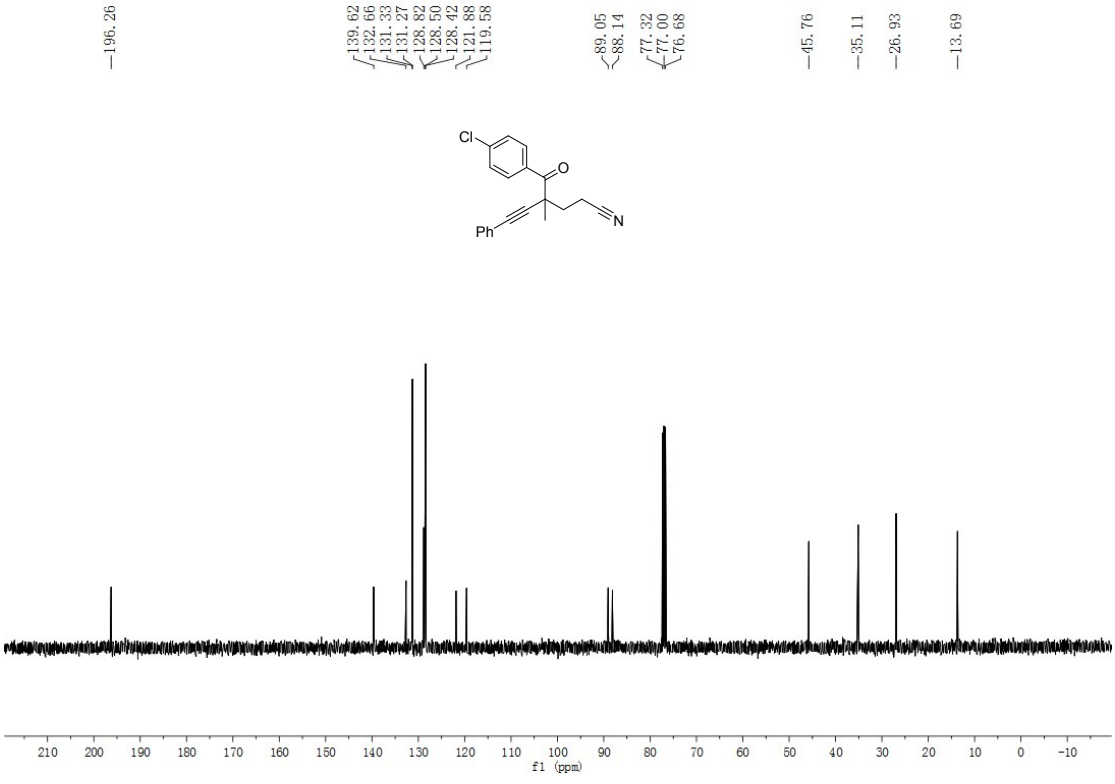


4-(4-chlorobenzoyl)-4-methyl-6-phenylhex-5-ynenitrile（3pa）

^{1}H NMR ($CDCl_3$, 400 MHz):

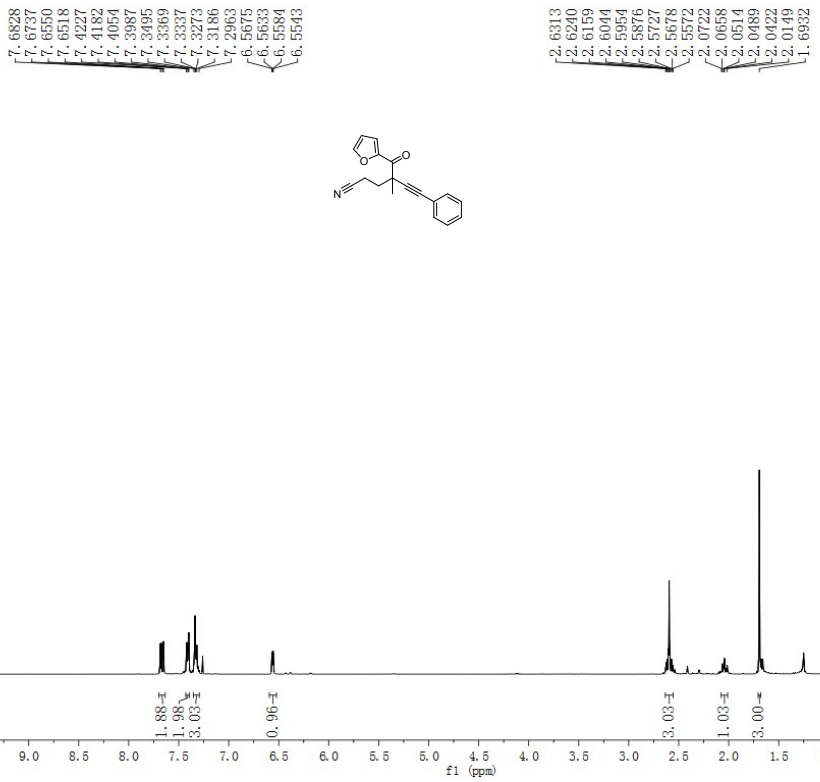


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)：

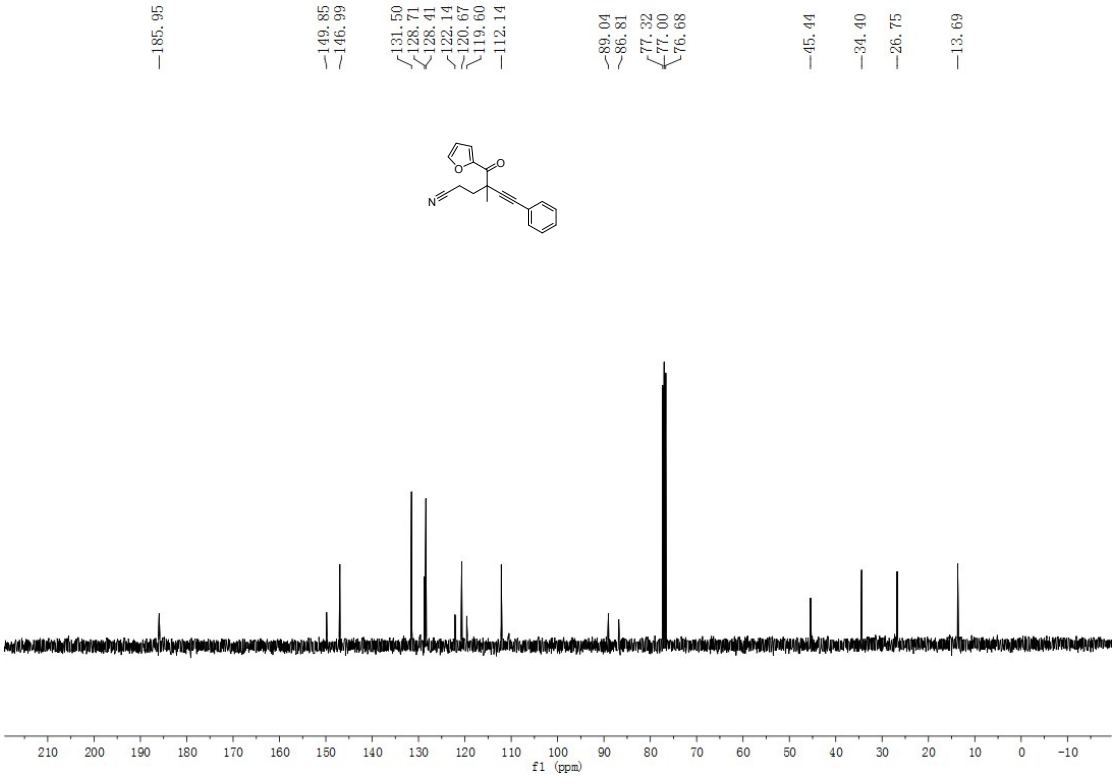


4-(furan-3-carbonyl)-4-methyl-6-phenylhex-5-ynenitrile（3qa）

^{1}H NMR ($CDCl_3$, 400 MHz):

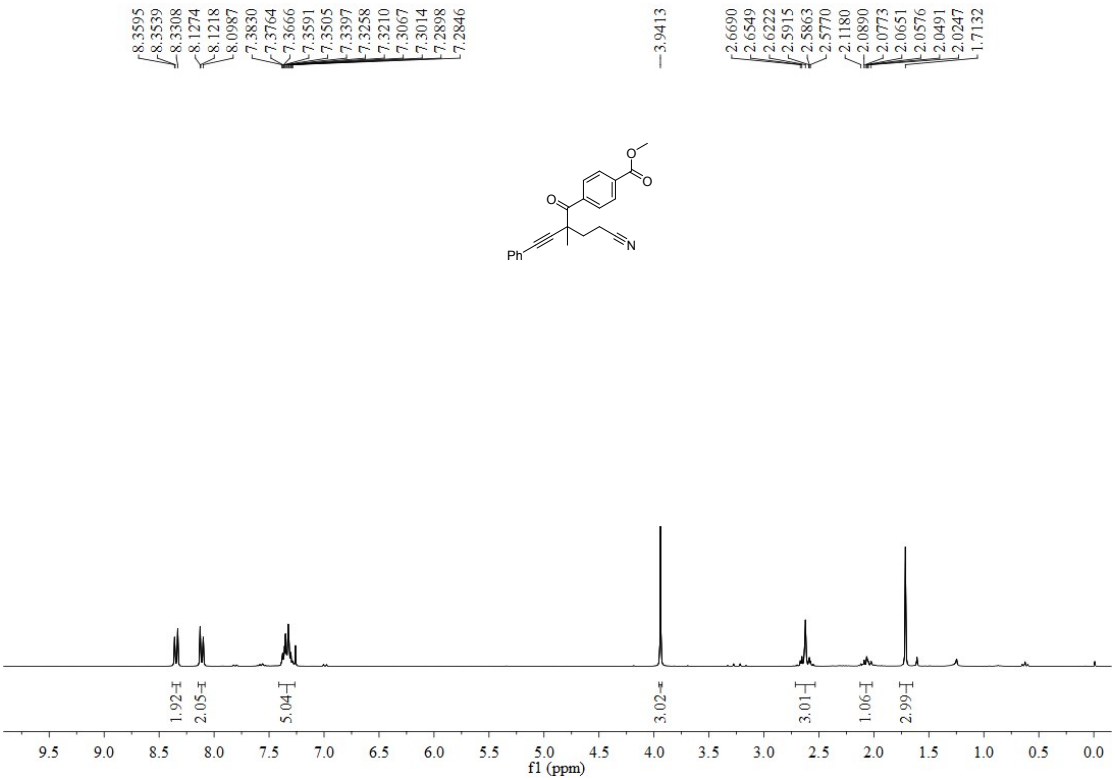


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)：

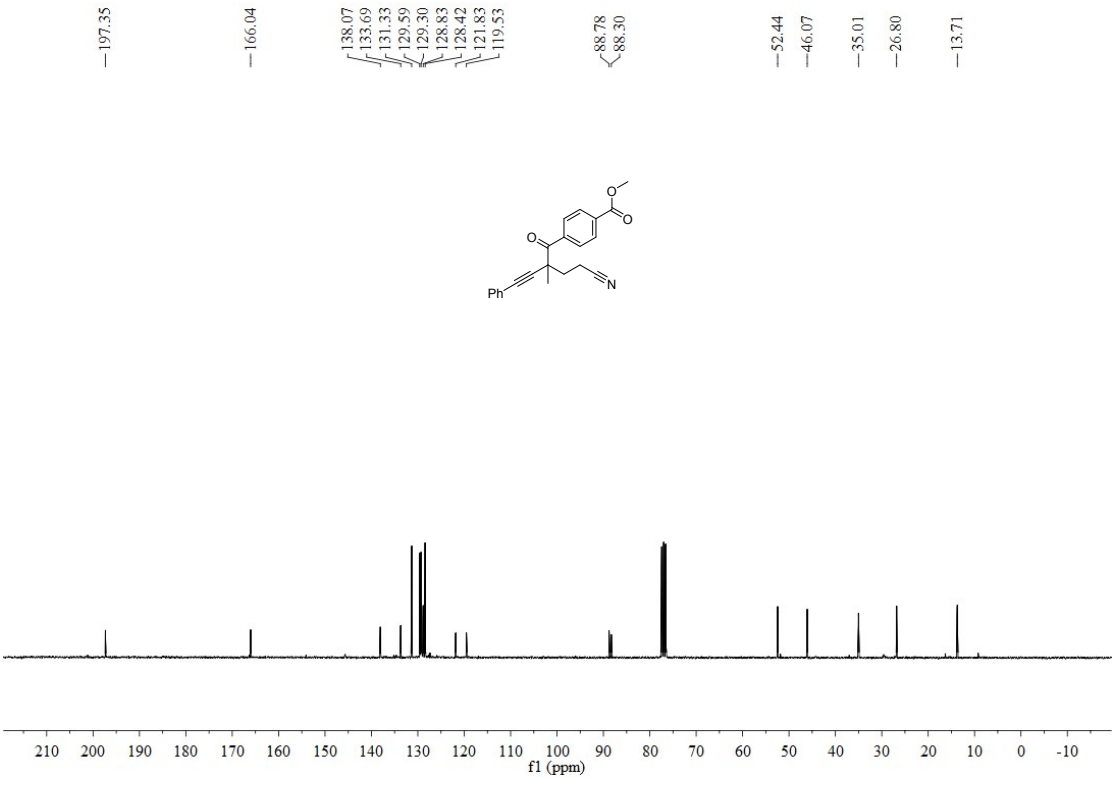


methyl 4-(2-(2-cyanoethyl)-2-methyl-4-phenylbut-3-ynoyl)benzoate (3ra)

^{1}H NMR ($CDCl_3$, 300 MHz):

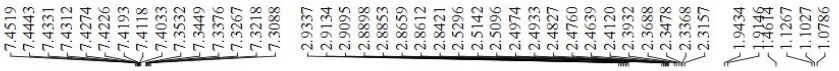


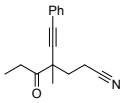
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):

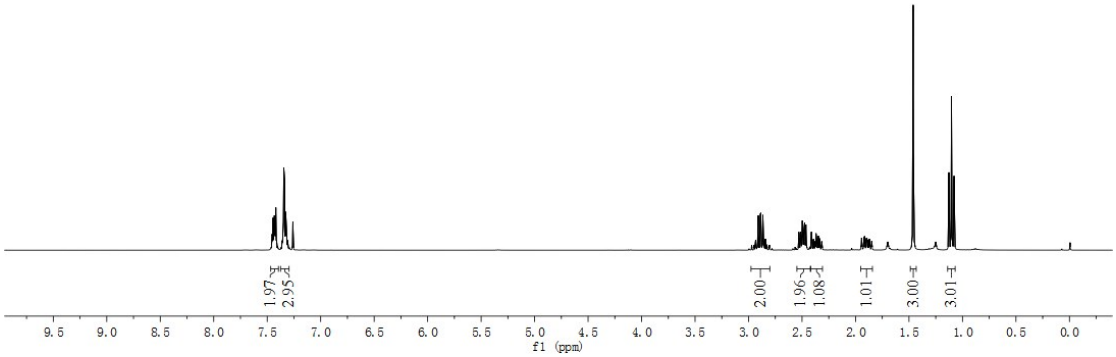


4-methyl-5-oxo-4-(phenylethynyl)heptanenitrile (3sa)

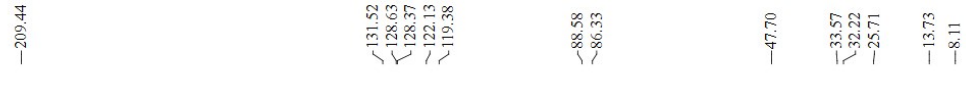
^{1}H NMR ($CDCl_3$, 300 MHz):

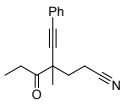


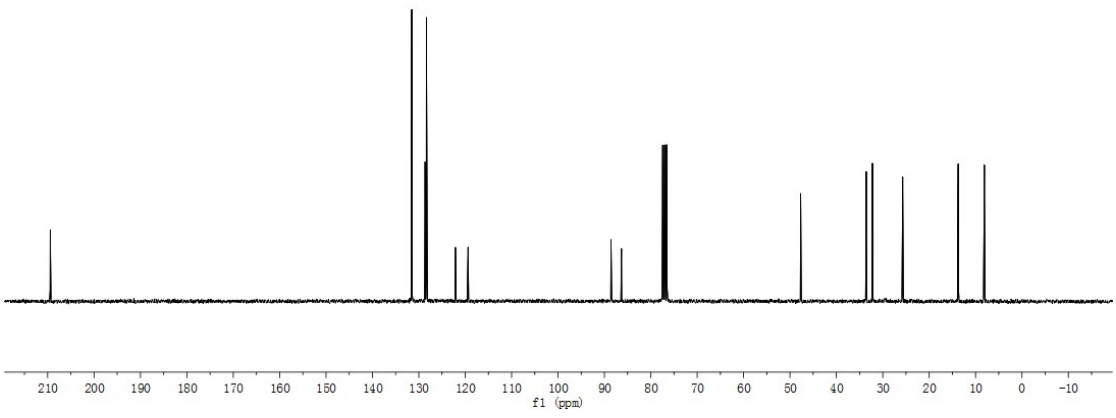




$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)：

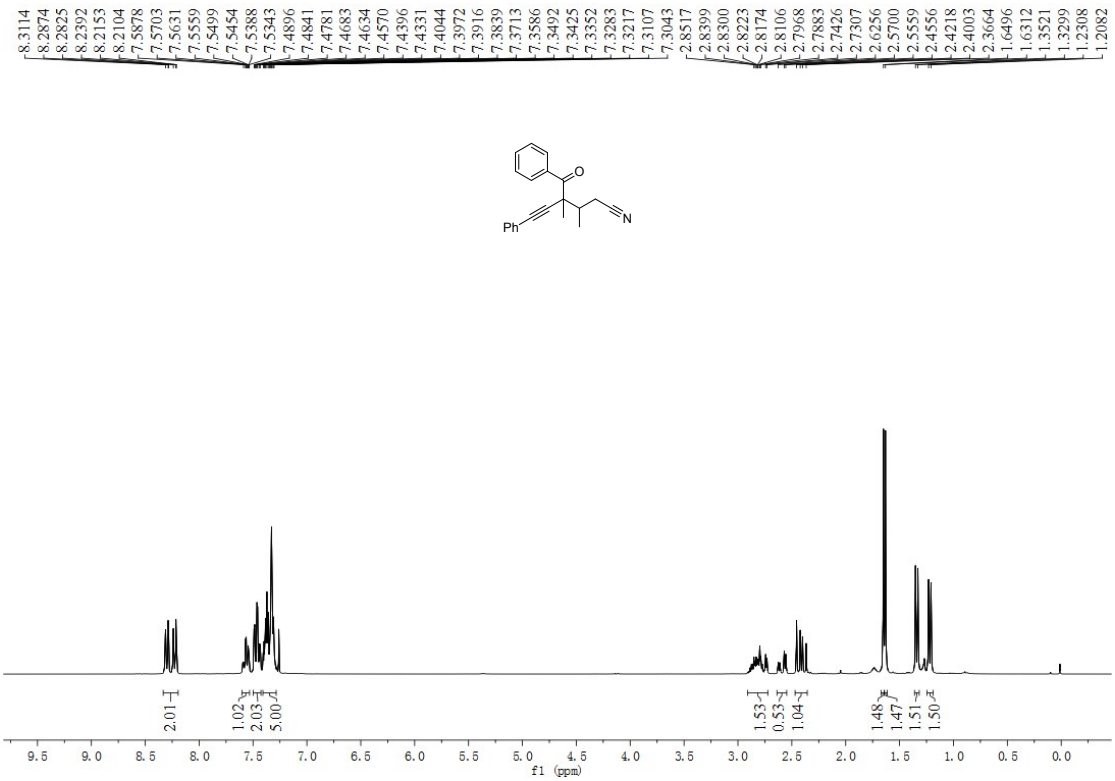




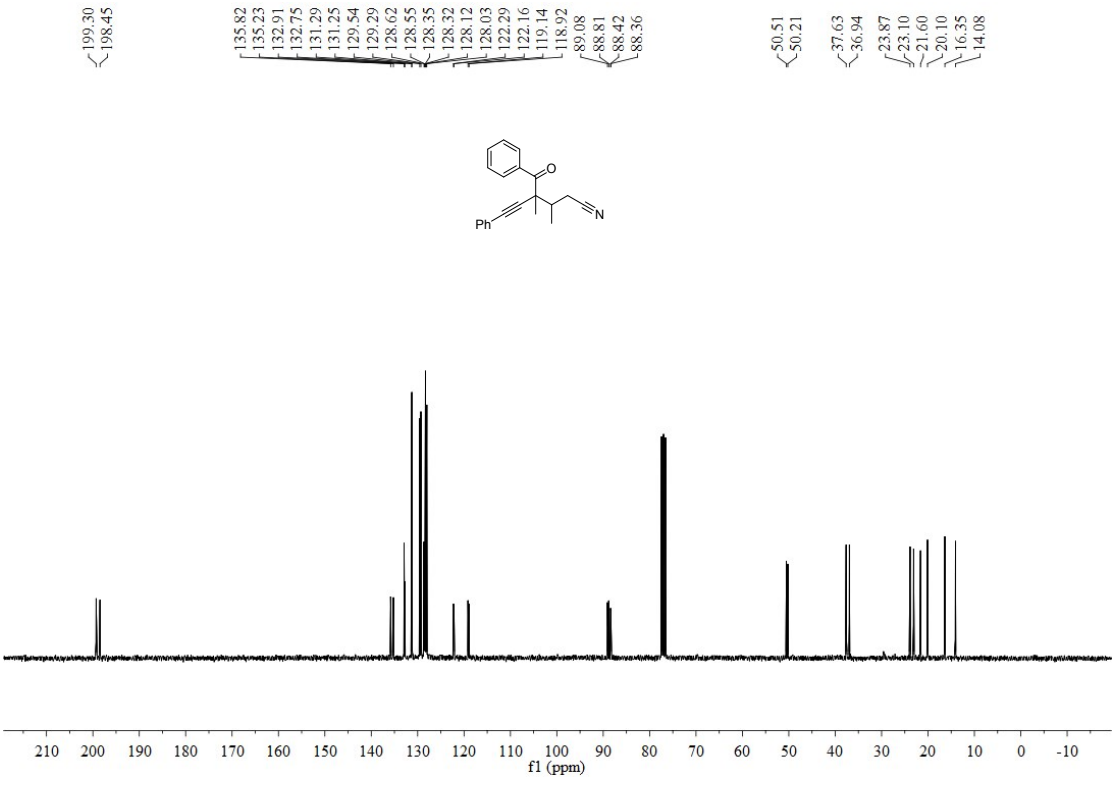


4-benzoyl-3,4-dimethyl-6-phenylhex-5-ynenitrile (3ta)

^{1}H NMR ($CDCl_3$, 300 MHz):

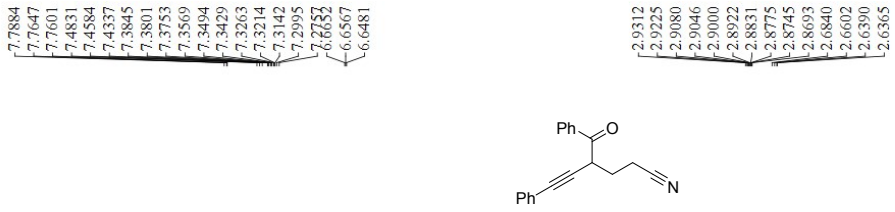


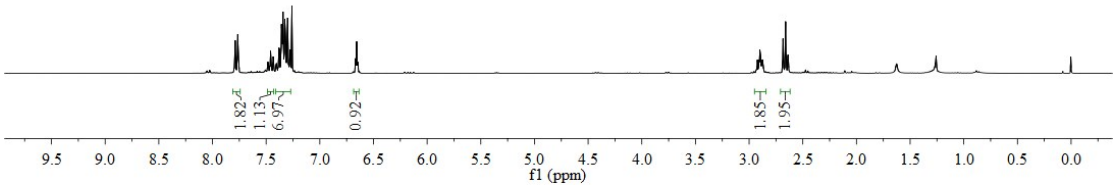
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$):



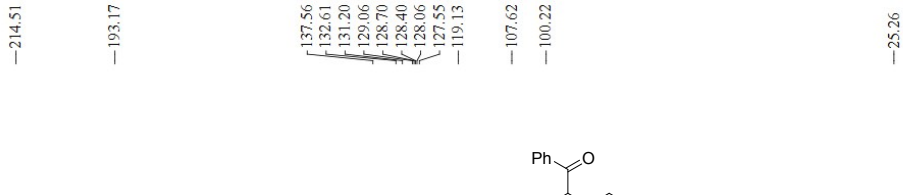
4-benzoyl-6-phenylhex-5-ynenitrile (3ua)

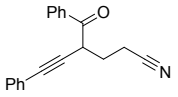
^{1}H NMR ($CDCl_3$, 300 MHz):

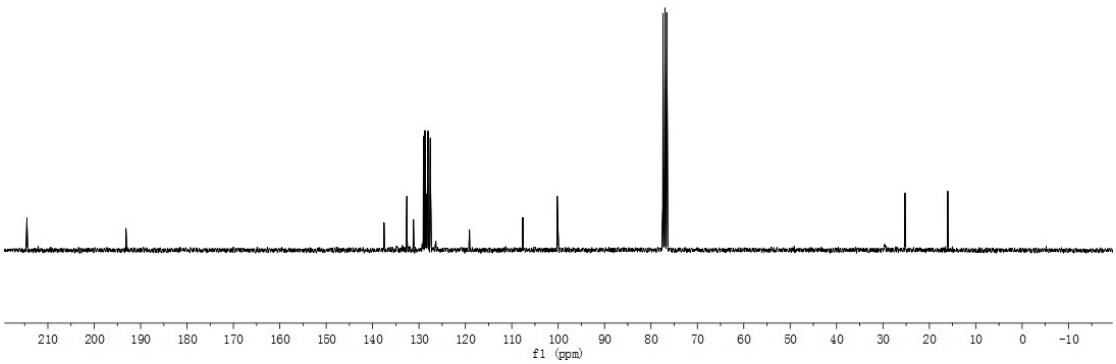




$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)：

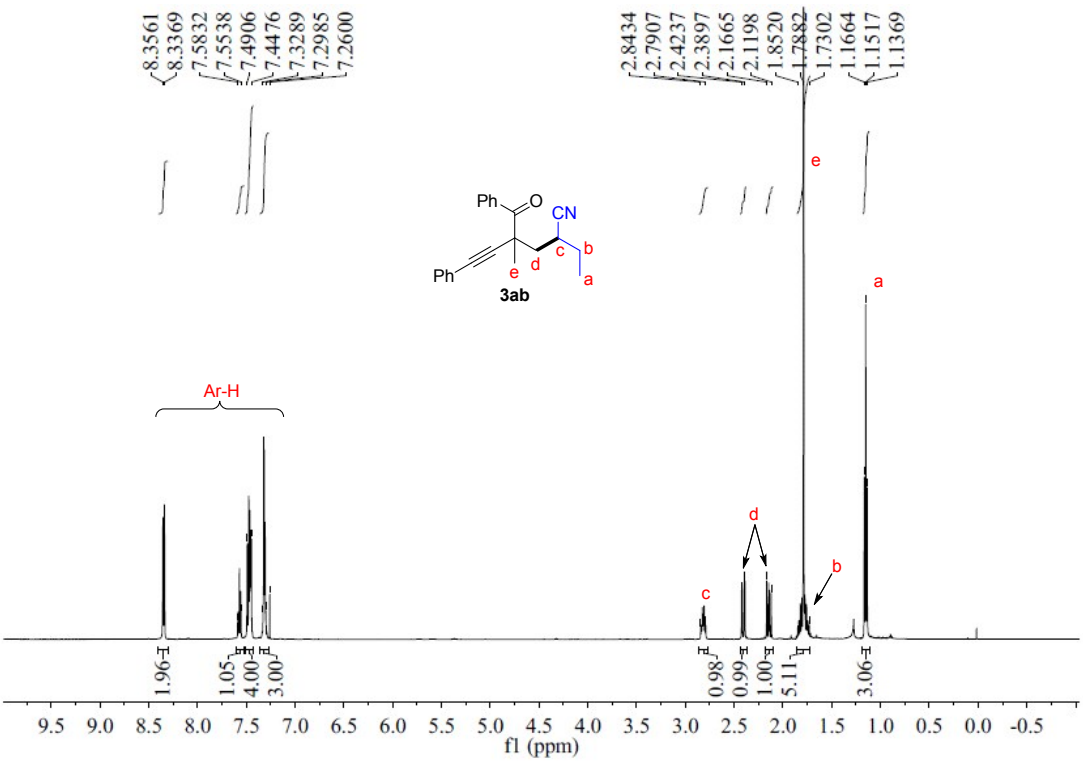




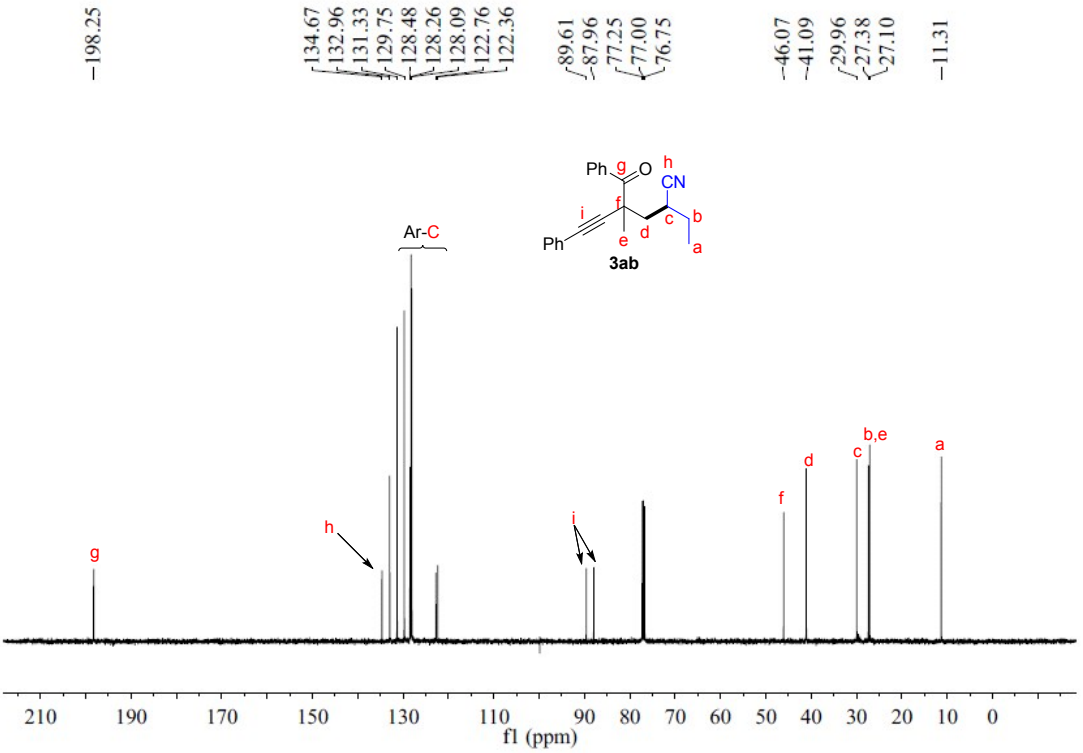


4-benzoyl-2-ethyl-4-methyl-6-phenylhex-5-ynenitrile(3ab)

^{1}H NMR ($CDCl_3$, 500 MHz):

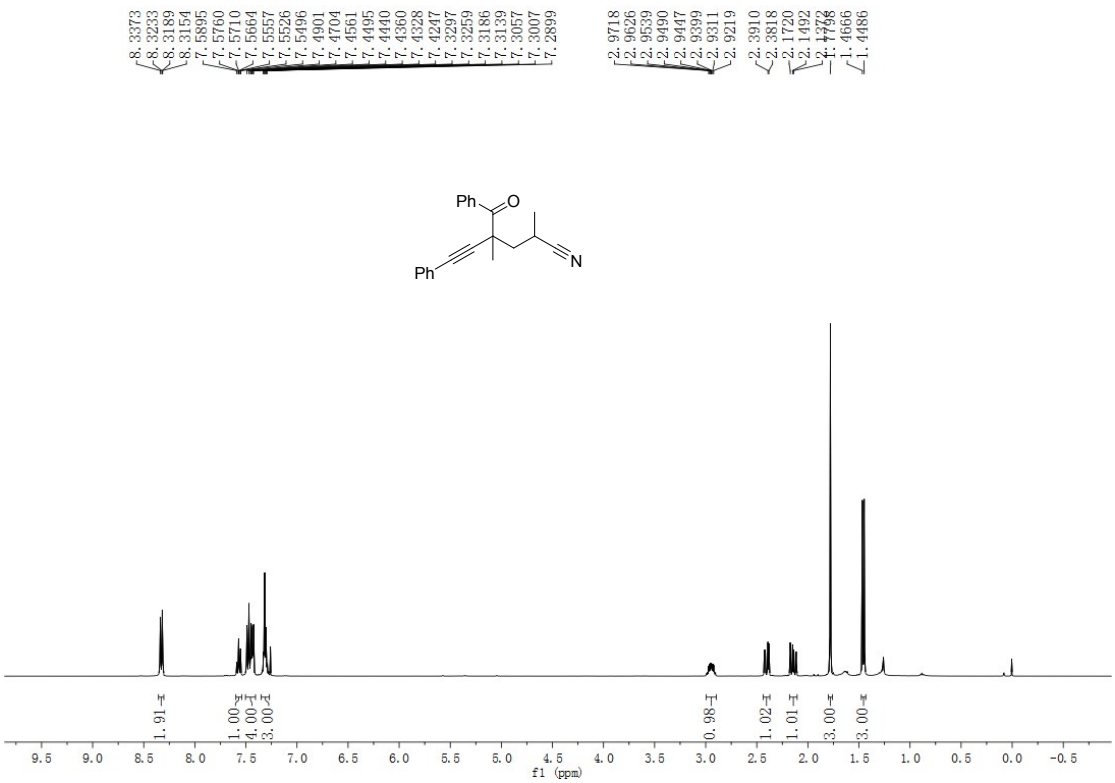


$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$):

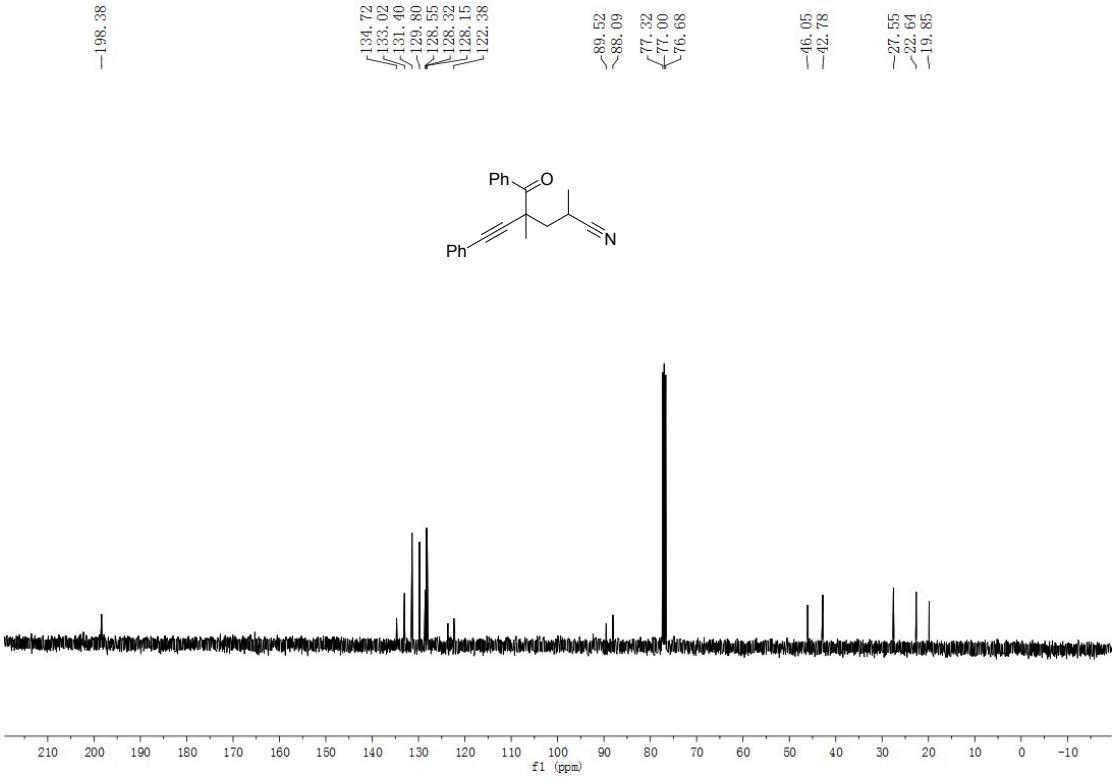


4-benzoyl-2,4-dimethyl-6-phenylhex-5-ynenitrile(3ac)

^{1}H NMR ($CDCl_3$, 400 MHz):

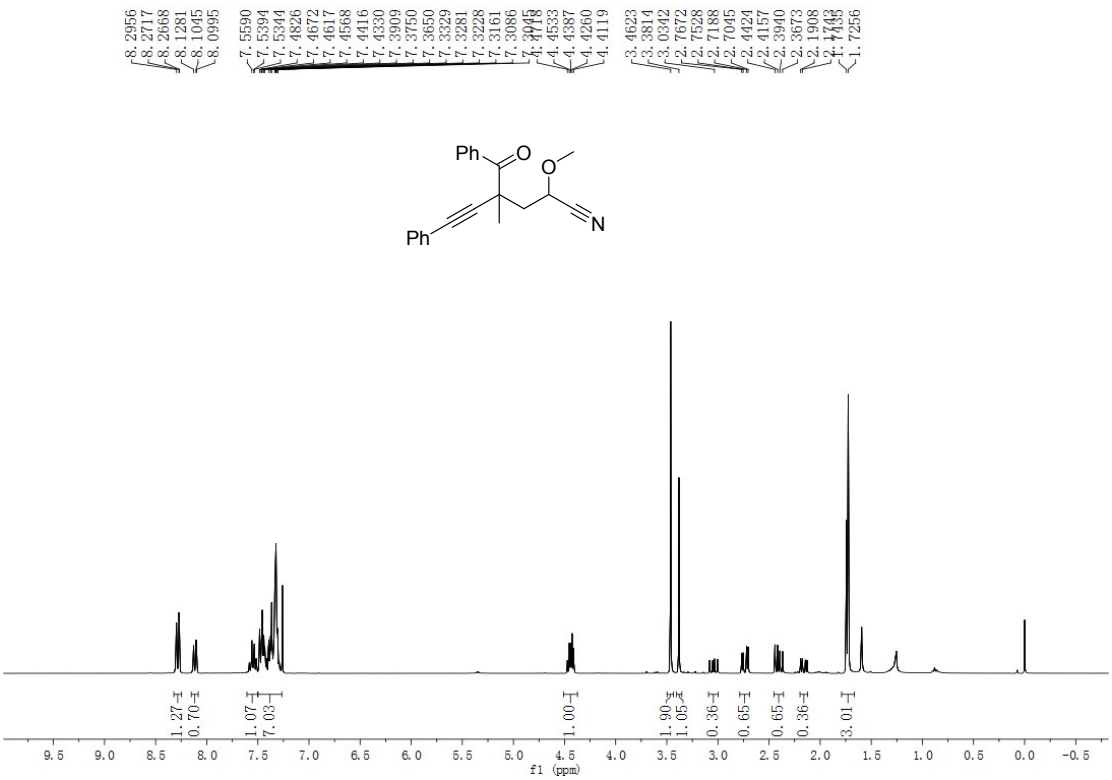


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)：

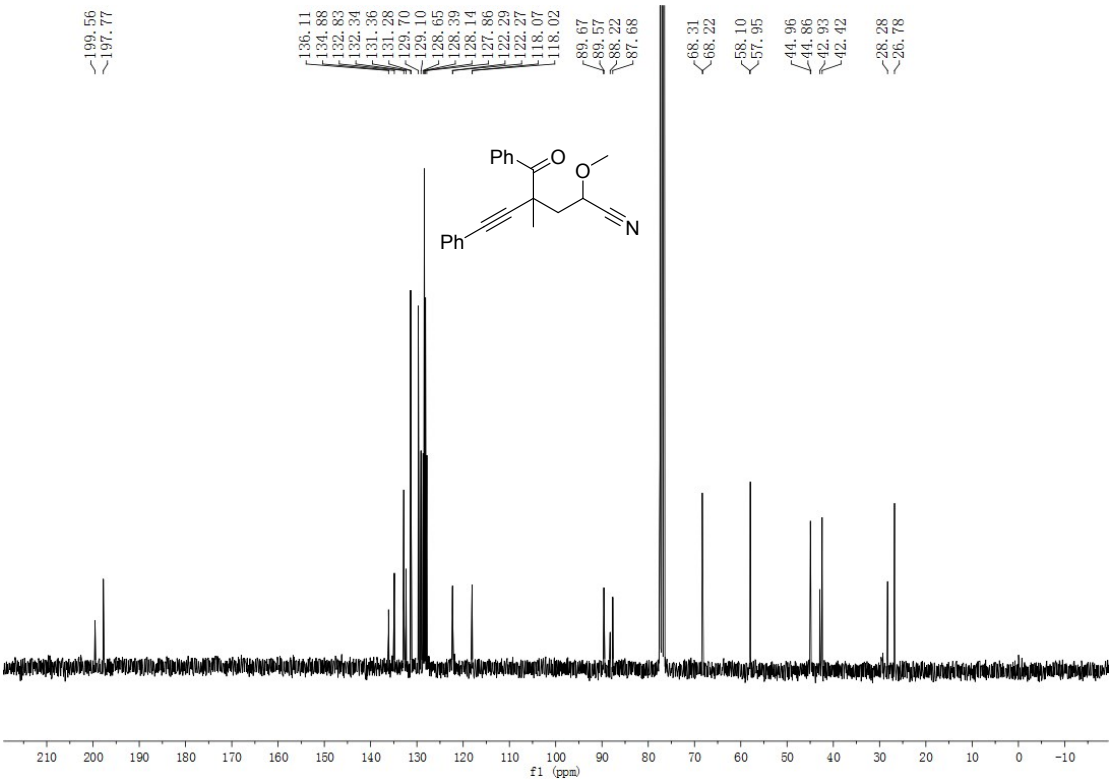


4-benzoyl-2-methoxy-4-methyl-6-phenylhex-5-ynenitrile(3ad)

^{1}H NMR ($CDCl_3$, 300 MHz):

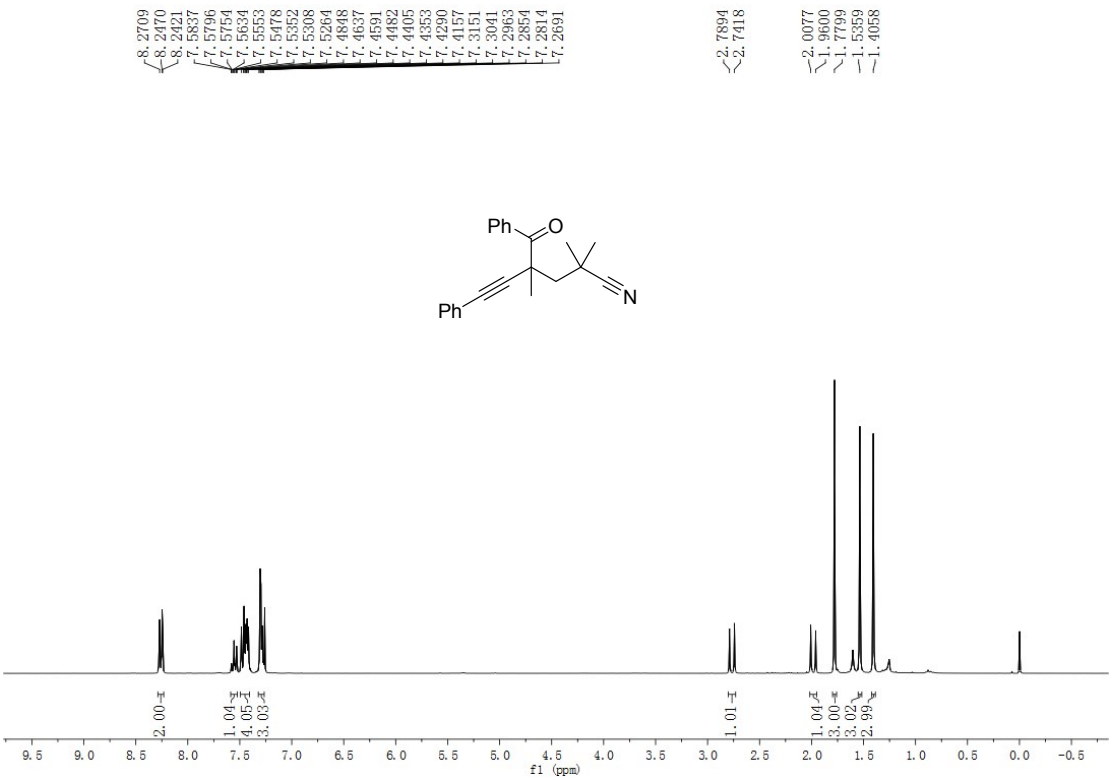


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)：

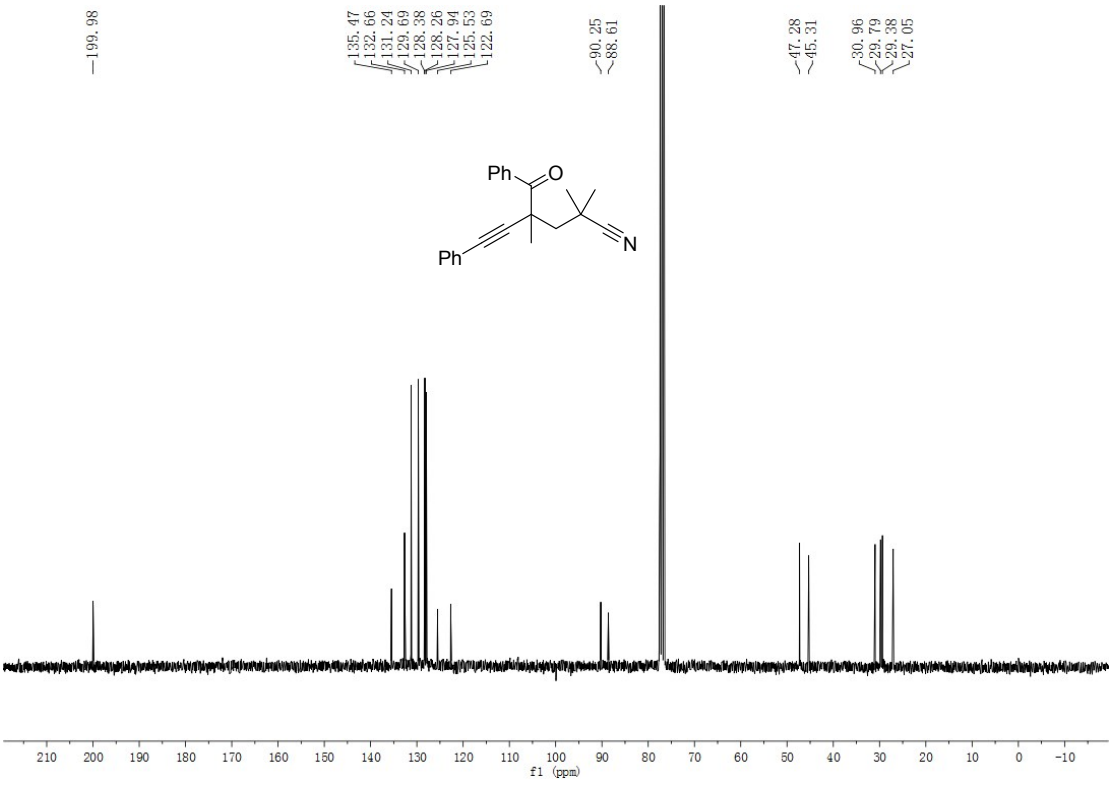


4-benzoyl-2,2,4-trimethyl-6-phenylhex-5-ynenitrile(3ae)

^{1}H NMR ($CDCl_3$, 300 MHz):

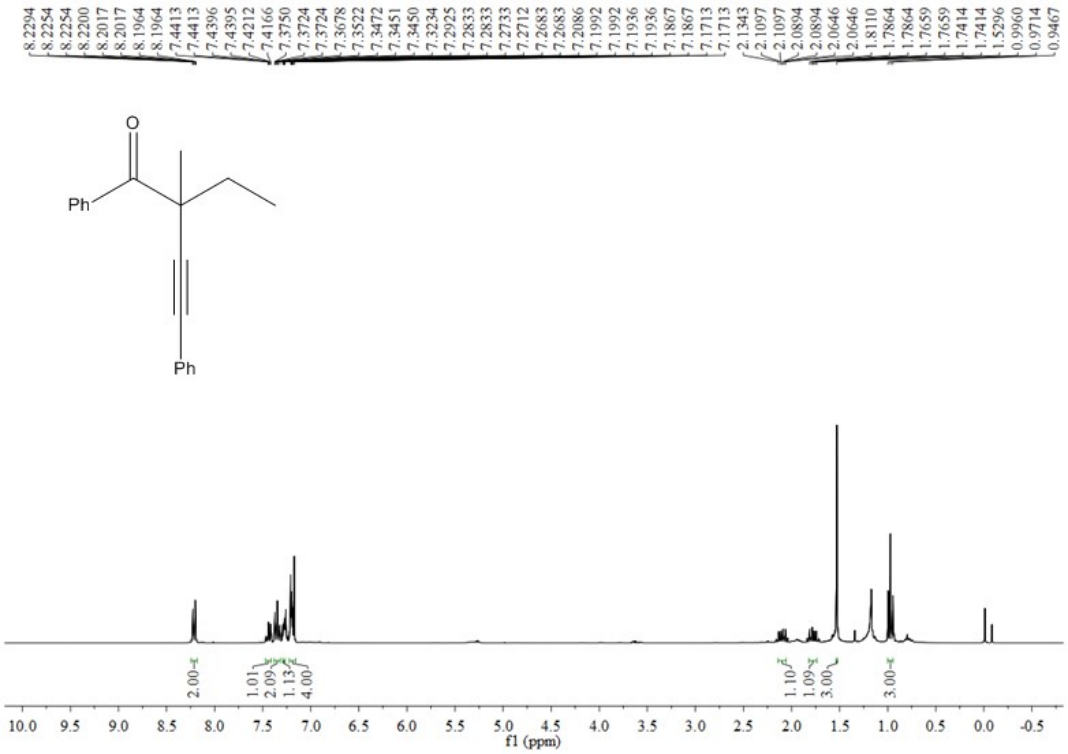


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)：



by-product **6**

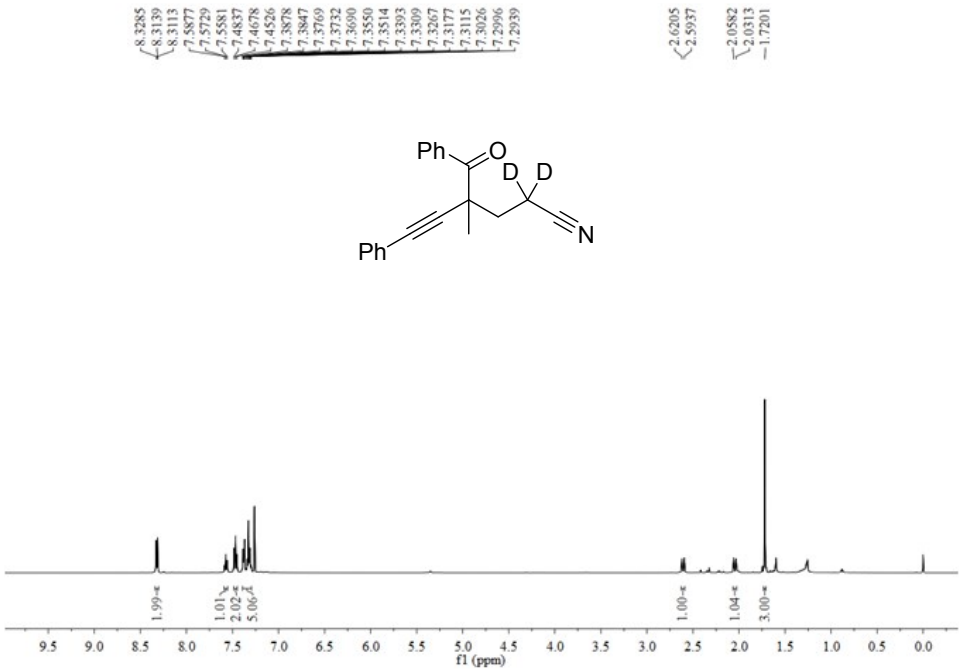
^{1}H NMR ($CDCl_3$, 300 MHz):



8. Isotope Research

D_3-MeCN product

^{1}H NMR ($CDCl_3$, 300 MHz):



MeCN:d_3-MeCN 1:1 product

^{1}H NMR ($CDCl_3$, 300 MHz):