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Copper-Catalysed Csp^3-Csp Cross-Couplings between Cyclobutanone Oxime Esters and Terminal Alkynes Induced by Visible Light

(Supporting Information)

Binlin Zhao,[a, b]‡* Yixiao Wu,[b,c]‡ Yu Yuan,[c] and Zhuangzhi Shi[b*]

[a]Department of Chemistry and Materials Science, College of Science, Nanjing Forestry University, Nanjing 210037, China E-mail: zhaobinlin@njfu.edu.cn

[b]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, China E-mail: shiz@nju.edu.cn

[c]College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China

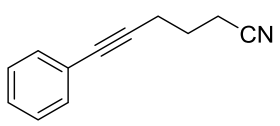
‡These authors contributed equally.

1. General Information

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. All new compounds were fully characterized. NMR-spectra were recorded on Bruker ARX-400 MHz Associated. ^{1}H NMR spectra data were reported as δ values in ppm relative to chloroform (δ 7.26) if collected in $CDCl_3$. ^{13}C NMR spectra data were reported as δ values in ppm relative to chloroform (δ 77.00). ^{1}H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doublet of quartets); app (apparent); br (broad). Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI). All reactions were carried out in flame-dried 25-mL Schlenk tubes with Teflon screw caps under argon. $Cu(OTf)_2$ was purchased from TCI. K_2CO_3 was granular and dried. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The cyclobutanone oximes were prepared according to the reported procedures.[1-4]

2. Experimental Procedures and Characterization of Products

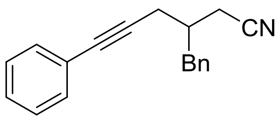
6-Phenylhex-5-ynenitrile (3aa)



3aa

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30:1) to afford 24.7 mg (73%) of **3aa** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.32 – 7.28 (m, 3H), 2.60 (t, *J* = 6.7 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 1.96 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.5, 128.2, 128.0, 123.1, 119.2, 86.9, 82.4, 24.6, 18.5, 16.2; **ATR-FTIR (cm $^{-1}$)** 2921, 2849, 2248, 1652, 1558, 1490, 1431, 757, 692; **HRMS m/z (ESI)** calcd for $C_{12}H_{11}NNa$ (M + Na)$^+$ 192.0784, found 192.0785.

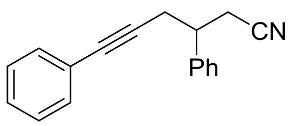
3-Benzyl-6-phenylhex-5-ynenitrile (3ba)



3ba

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1b** (69.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to afford 42.7 mg (82%) of **3ba** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.34 – 7.20 (m, 8H), 2.91 – 2.75 (m, 2H), 2.63 – 2.40 (m, 4H), 2.33 – 2.24 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1, 131.6, 129.0, 128.7, 128.3, 128.0, 126.8, 123.1, 118.2, 85.7, 83.5, 39.1, 37.1, 23.3, 21.0; **ATR-FTIR (cm $^{-1}$)** 3027, 2922, 2244, 1651, 1557, 1489, 1454, 756, 692; **HRMS m/z (ESI)** calcd for $C_{19}H_{17}NNa$ (M + Na)$^+$ 282.1253, found 282.1255.

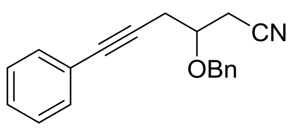
3,6-Diphenylhex-5-ynenitrile (3ca)



3ca

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1c** (66.6 mg, 0.2 mmol), Cu(OTf)$_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K$_2$CO$_3$ (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 50:1) to afford 34.9 mg (71%) of **3ca** as a yellow oil: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.42 – 7.37 (m, 4H), 7.35 – 7.30 (m, 6H), 3.35 – 3.28 (m, 1H), 2.99 – 2.80 (m, 4H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 140.5, 131.6, 129.0, 128.4, 128.2, 127.9, 127.1, 123.1, 118.3, 86.0, 83.6, 41.2, 25.9, 23.2; **ATR-FTIR (cm $^{-1}$)** 3030, 2920, 2245, 1653, 1558, 1489, 1455, 1421, 755, 693; **HRMS m/z (ESI)** calcd for $C_{18}H_{16}Na$ $(M + H)^+$ 246.1277, found 246.1283.

3-(Benzyloxy)-6-phenylhex-5-ynenitrile (3da)

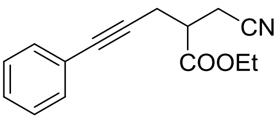


3da

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1d** (72.6 mg, 0.2 mmol), Cu(OTf)$_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K$_2$CO$_3$ (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 50:1) to afford 27.7 mg (51%) of **3da** as a yellow oil: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.42 – 7.29 (m, 10H), 4.71 (q, J = 11.7 Hz, 2H), 4.97 – 4.91 (m, 1H), 2.90 – 2.70 (m, 4H); **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 137.1, 131.6, 128.6, 128.3, 128.2, 128.1, 127.8, 122.8, 117.2, 84.0, 83.6, 73.1, 72.0, 24.7, 22.9; **ATR-FTIR (cm $^{-1}$)** 2909, 2249, 1652, 1558, 1541, 1508, 1490, 1456, 801, 756, 695; **HRMS m/z (ESI)** calcd for $C_{19}H_{17}NNaO$ (M + Na)$^+$ 298.1202, found 298.1204.

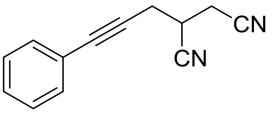
Ethyl 2-(cyanomethyl)-5-phenylpent-4-ynoate (3ea)



3ea

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1e** (65.8 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry ethanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) (5 m length blue LED strips (12 w/m)) overnight. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20:1) to afford 22.4 mg (47%) of **3ea** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.28 (m, 3H), 4.31 – 4.17 (m, 2H), 3.02 – 2.80 (m, 5H), 1.31 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 131.6, 128.3, 122.7, 117.6, 83.9, 61.8, 40.8, 21.5, 18.4, 14.1; **ATR-FTIR (cm $^{-1}$)** 2920, 2248, 1733, 1653, 1558, 1489, 1473, 1374, 757, 692; **HRMS m/z (ESI)** calcd for $C_{15}H_{15}NNaO_2$ (M + Na)$^+$ 264.0995, found 264.1002.

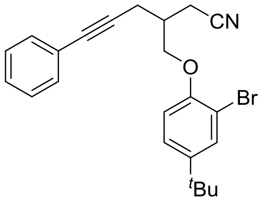
2-(3-Phenylprop-2-yn-1-yl) succinonitrile (3fa)



3fa

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1f** (50.8 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10:1) to afford 14.5 mg (37%) of **3fa** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 5H), 3.23 – 3.16 (m, 1H), 2.99 – 2.94 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.8, 128.8, 128.4, 121.9, 117.7, 115.2, 85.6, 81.4, 28.1, 22.5, 20.1; **ATR-FTIR (cm $^{-1}$)** 2921, 2247, 1651, 1558, 1489, 1419, 757, 691; **HRMS m/z (ESI)** calcd for $C_{13}H_{11}N_2$ $(M + H)^+$ 195.0917, found 195.0922.

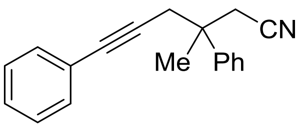
3-((2-Bromo-4-(*tert*-butyl)phenoxy)methyl)-6-phenylhex-5-ynenitrile (3ga)



3ga

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1g** (93.8 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 50:1) to afford 62.8 mg (77%) of **3ga** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (t, J = 3.0 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.32 – 7.25 (m, 4H), 6.87 (d, J = 8.6 Hz, 1H), 4.22 – 4.08 (m, 2H), 2.88 – 2.72 (m, 4H), 2.63 – 2.53 (m, 1H), 1.30 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.2, 146.0, 131.6, 130.5, 128.3, 128.1, 125.3, 122.9, 118.0, 113.1, 112.0, 85.2, 83.4, 69.2, 35.7, 34.2, 31.3, 21.2, 19.0; **ATR-FTIR (cm $^{-1}$)** 2961, 2869, 2246, 1652, 1598, 1559, 1490, 1466, 1393, 1362, 1289, 810, 756, 692; **HRMS m/z (ESI)** calcd for $C_{23}H_{24}BrNNaO$ $(M + Na)^+$ 432.0933, found 432.0936.

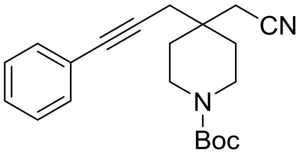
3-Methyl-3,6-diphenylhex-5-ynenitrile (3ha)



3ha

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1h** (69.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 50:1) to afford 30.3 mg (59%) of **3ha** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 7.28 – 7.17 (m, 6H), 2.86 – 2.75 (m, 4H), 1.59 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 131.5, 128.7, 128.2, 128.0, 127.3, 125.5, 123.0, 117.9, 85.5, 84.0, 40.4, 32.5, 29.7, 25.6; **ATR-FTIR (cm $^{-1}$)** 2966, 2243, 1683, 1652, 1598, 1558, 1490, 1457, 1444, 1262, 801, 758, 695; **HRMS m/z (ESI)** calcd for $C_{19}H_{17}N$ $(M + Na)^+$ 282.1253, found 282.1261.

***Tert*-butyl 4-(cyanomethyl)-4-(3-phenylprop-2-yn-1-yl)piperidine-1-carboxylate (3ia)**

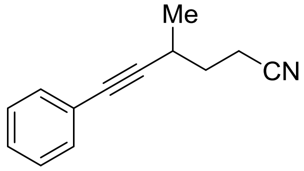


3ia

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1i** (85.2 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10:1) to afford

57.2 mg (85%) of **3ia** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.32 – 7.28 (m, 3H), 3.56 – 3.50 (m, 2H), 3.40 – 3.33 (m, 2H), 2.63 (s, 2H), 2.58 (s, 2H), 1.74 – 1.61 (m, 4H), 1.46 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.6, 131.6, 128.3, 128.2, 122.9, 117.2, 84.4, 84.2, 79.9, 35.0, 33.5, 28.4, 27.4, 26.6; **ATR-FTIR (cm $^{-1}$)** 2975, 2930, 2243, 1689, 1558, 1490, 1475, 1420, 1365, 757, 692; **HRMS m/z (ESI)** calcd for $C_{21}H_{26}N_2NaO_2$ (M + Na)$^+$ 361.1886, found 361.1887.

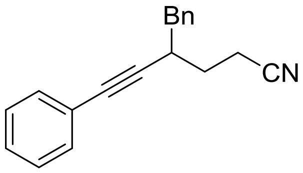
4-Methyl-6-phenylhex-5-ynenitrile (3ja)



3ja

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1j** (54.2 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 50:1) to afford 28.3 mg (77%) of **3ja** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.31 – 7.28 (m, 3H), 2.88 – 2.79 (m, 1H), 2.64 – 2.51 (m, 2H), 1.96 – 1.77 (m, 2H), 1.32 (d, J = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.5, 128.2, 128.0, 123.1, 119.5, 91.3, 82.5, 32.4, 26.0, 20.7, 15.4; **ATR-FTIR (cm $^{-1}$)** 2972, 2932, 2873, 2246, 1683, 1633, 1597, 1557, 1489, 1455, 1421, 1339, 757, 693; **HRMS m/z (ESI)** calcd for $C_{13}H_{13}NNa$ (M + Na)$^+$ 206.0940, found 206.0944.

4-Benzyl-6-phenylhex-5-ynenitrile (3ka)

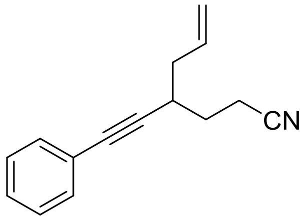


3ka

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1k** (69.4 mg, 0.2 mmol), $Cu(OTf)_2$

(7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30:1) to afford 40.5 mg (78%) of **3ka** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 10H), 3.02 – 2.94 (m, 2H), 2.89 – 2.82 (m, 1H), 2.66 – 2.49 (m, 2H), 1.98 – 1.90 (m, 1H), 1.83 – 1.73 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.2, 131.5, 129.2, 128.4, 128.2, 128.1, 126.7, 123.0, 119.4, 89.7, 84.3, 41.1, 33.6, 30.0, 15.4; **ATR-FTIR (cm $^{-1}$)** 3029, 2929, 2246, 1653, 1598, 1491, 1454, 1421, 1360, 755, 694; **HRMS m/z (ESI)** calcd for $C_{19}H_{17}NNa$ $(M + Na)^+$ 282.1253, found 282.1258.

4-(Phenylethynyl)hept-6-enenitrile (3la)

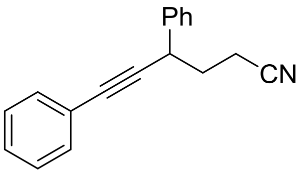


3la

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1l** (56.6 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30:1) to afford 22.8 mg (55%) of **3la** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.32 – 7.28 (m, 3H), 5.96 – 5.86 (m, 1H), 5.19 – 5.13 (m, 2H), 2.84 – 2.77 (m, 1H), 2.66 – 2.51 (m, 2H), 2.42 – 2.31 (m, 2H), 1.99 – 1.91 (m, 1H), 1.85 – 1.76 (m, 1H); **^{13}C NMR** (101 MHz,

$CDCl_3$) δ 134.7, 131.6, 128.2, 128.1, 123.0, 119.4, 117.6, 89.7, 83.8, 39.0, 31.4, 30.0, 15.4; **ATR-FTIR (cm $^{-1}$)** 3079, 2931, 2247, 1649, 1598, 1490, 1444, 1420, 1350, 758, 693; **HRMS m/z (ESI)** calcd for $C_{15}H_{15}NNa$ (M + Na)$^+$ 232.1097, found 232.1097.

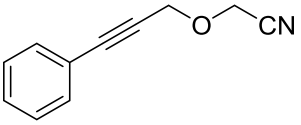
4,6-Diphenylhex-5-ynenitrile (3ma)



3ma

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1m** (66.6 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 50:1) to afford 25.5 mg (52%) of **3ma** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 4H), 7.41 – 7.37 (m, 2H), 7.35 – 7.29 (m, 4H),4.05 (dd, J = 8.3, 6.1 Hz, 1H), 2.66 – 2.58 (m, 1H), 2.51 – 2.43 (m, 1H), 2.26 – 2.12 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.7, 131.6, 128.9, 128.3, 128.2, 127.5, 127.4, 122.9, 119.2, 88.5, 84.9, 37.2, 33.8, 15.1; **ATR-FTIR (cm $^{-1}$)** 3030, 2931, 2246, 1685, 1652, 1598, 1490, 1452, 1420, 757, 694; **HRMS m/z (ESI)** calcd for $C_{18}H_{16}N$ (M + H)$^+$ 246.1277, found 246.1283.

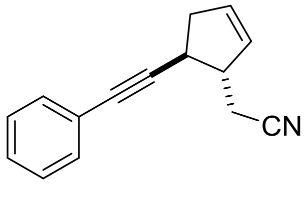
2-((3-Phenylprop-2-yn-1-yl)oxy)acetonitrile (3na)



3na

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1n** (51.8 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 50:1) to afford 14.6 mg (43%) of **3na** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.39 – 7.31 (m, 3H), 4.55 (s, 2H), 4.44 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.8, 129.0, 128.4, 121.7, 115.6, 88.6, 82.0, 58.9, 54.1; **ATR-FTIR (cm $^{-1}$)** 2920, 1653, 1559, 1490, 1343, 757, 692; **HRMS m/z (ESI)** calcd for $C_{11}H_{10}NO$ $(M + H)^+$ 172.0757, found 172.0756.

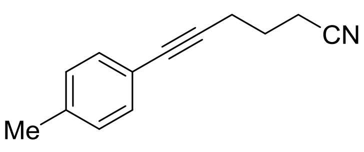
2-((1*S*,5*S*)-5-(phenylethynyl)cyclopent-2-en-1-yl)acetonitrile (3oa)



3oa

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1o** (59.0 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 50:1) to afford 30.5 mg (74%) of **3oa** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.33 – 7.28 (m, 3H), 5.93 – 5.90 (m, 1H), 5.72 – 5.70 (m, 1H), 3.21 – 3.14 (m, 1H), 2.96 – 2.84 (m, 2H), 2.72 – 2.50 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.4, 131.6, 130.4, 128.2, 127.9, 123.2, 116.6, 90.6, 81.8, 49.6, 40.1, 35.3, 22.0; **ATR-FTIR (cm $^{-1}$)** 3056, 2919, 2853, 2245, 1683, 1652, 1597, 1558, 1489, 1440, 1420, 1339, 756, 691; **HRMS m/z (ESI)** calcd for $C_{15}H_{13}N$ $(M + Na)^+$ 230.0940, found 230.0942.

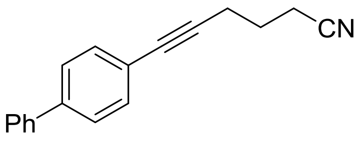
6-(*P*-tolyl)hex-5-ynenitrile (3ab)



3ab

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), Cu(OTf)$_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K$_2$CO$_3$ (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 1-ethynyl-4-methylbenzene **2b** (27.9 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20:1) to afford 26.1 mg (71%) of **3ab** as a yellow oil: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.29 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 2.61 – 2.54 (m, 4H), 2.34 (s, 3H), 1.96 (p, J = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 138.0, 131.4, 129.0, 120.1, 119.2, 86.1, 82.4, 24.7, 21.4, 18.5, 16.2; **ATR-FTIR (cm $^{-1}$)** 2919, 1653, 1558, 1508, 1457, 816; **HRMS m/z (ESI)** calcd for $C_{13}H_{13}N$ (M + H)$^+$ 184.1121, found 184.1122.

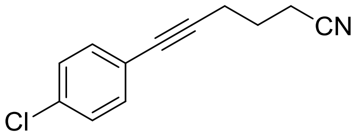
6-([1,1'-Biphenyl]-4-yl)hex-5-ynenitrile (3ac)



3ac

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), Cu(OTf)$_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K$_2$CO$_3$ (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 4-ethynyl-1,1'-biphenyl **2c** (42.8 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20:1) to afford 35.0 mg (71%) of **3ac** as a yellow solid: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.60 – 7.54 (m, 4H), 7.48 – 7.43 (m, 4H), 7.38 – 7.34 (m, 1H), 2.63 (t, *J* = 6.7 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 1.98 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 140.7, 140.3, 132.0, 128.8, 127.6, 126.9, 122.1, 119.2, 87.6, 82.2, 24.6, 18.6, 16.2; **ATR-FTIR (cm $^{-1}$)** 2920, 2850, 2246, 1650, 1558, 1487, 765, 722; **HRMS m/z (ESI)** calcd for $C_{18}H_{15}NNa$ $(M + Na)^+$ 268.1097, found 268.1101.

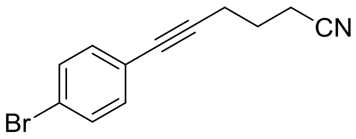
6-(4-Chlorophenyl)hex-5-ynenitrile (3ad)



3ad

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 1-chloro-4-ethynylbenzene **2d** (27.2 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20:1) to afford 24.9 mg (61%) of **3ad** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.33 – 7.31 (m, 2H), 7.28 – 7.26 (m, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 2.55 (t, *J* = 7.1 Hz, 2H), 1.96 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 134.0, 132.8, 128.6, 121.6, 119.1, 88.0, 81.3, 24.5, 18.5, 16.2; **ATR-FTIR (cm $^{-1}$)** 2939, 2247, 1653, 1559, 1488, 1421, 828; **HRMS m/z (ESI)** calcd for $C_{12}H_{10}ClNNa$ $(M + Na)^+$ 226.0394, found 226.0396.

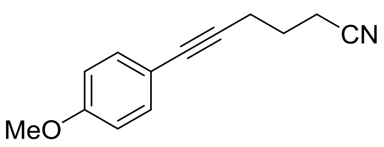
6-(4-Bromophenyl)hex-5-ynenitrile (3ae)



3ae

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 1-bromo-4-ethynylbenzene **2e** (43.4 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20:1) to afford 35.5 mg (72%) of **3ae** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.44 – 7.41 (m, 2H), 7.26 – 7.23 (m, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.54 (t, *J* = 7.1 Hz, 2H), 1.95 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 133.0, 131.5, 122.14, 122.11, 119.0, 88.2, 81.4, 24.4, 18.5, 16.2; **ATR-FTIR (cm $^{-1}$)** 2923, 2248, 1652, 1558, 1485, 1429, 1394, 824; **HRMS m/z (ESI)** calcd for $C_{12}H_{10}BrNNa$ $(M + Na)^+$ 269.9889, found 269.9900.

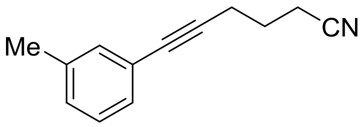
6-(4-Methoxyphenyl)hex-5-ynenitrile (3af)



3af

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 1-ethynyl-4-methoxybenzene **2f** (31.7 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20:1) to afford 18.2 mg (46%) of **3af** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.35 – 7.31 (m, 2H), 6.84 – 6.80 (m, 2H), 3.80 (s, 3H), 2.58 (t, *J* = 6.7 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 1.95 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 159.3, 132.9, 119.2, 1153, 113.9, 85.3, 82.2, 55.2, 24.7, 18.5, 16.2; **ATR-FTIR (cm $^{-1}$)** 2836, 2245, 1653, 1604, 1508, 1457, 832; **HRMS m/z (ESI)** calcd for $C_{13}H_{13}NNaO$ $(M + Na)^+$ 222.0889, found 222.0890.

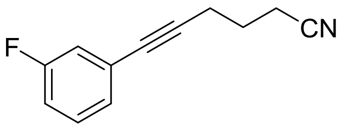
6-(*M*-tolyl)hex-5-ynenitrile (3ag)



3ag

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 1-ethynyl-3-methylbenzene **2g** (27.9 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20:1) to afford 23.6 mg (65%) of **3ag** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 3H), 7.12 – 7.08 (m, 1H), 2.61 – 2.53 (m, 4H), 2.32 (s, 3H), 1.95 (p, J = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.9, 132.1, 128.9, 128.6, 128.1, 122.9, 119.2, 86.5, 82.5, 24.6, 21.1, 18.5, 16.2; **ATR-FTIR (cm $^{-1}$)** 2923, 2248, 1684, 1653, 1601, 1485, 1455, 1431, 785, 692; **HRMS m/z (ESI)** calcd for $C_{13}H_{13}NNa$ $(M + Na)^+$ 206.0940, found 206.0945.

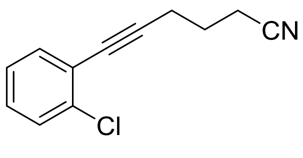
6-(3-Fluorophenyl)hex-5-ynenitrile (3ah)



3ah

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 1-ethynyl-3-fluorobenzene **2h** (28.8 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20:1) to afford 25.6 mg (68%) of **3ah** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 1H), 7.17 – 7.15 (m, 1H), 7.09 – 7.06 (m, 1H), 7.03 – 6.96 (m, 1H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.95 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246.4 Hz). 129.8 (d, *J* = 8.7 Hz), 127.4 (d, *J* = 2.6 Hz), 125.0 (d, *J* = 9.5 Hz), 119.0, 118.4 (d, *J* = 22.7 Hz), 115.3 (d, *J* = 21.2 Hz), 88.0, 81.2, 24.4, 18.4, 16.2; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -113.05; **ATR-FTIR (cm $^{-1}$)** 2941, 2246, 1652, 1607, 1578, 1487, 1429, 1278, 784; **HRMS m/z (ESI)** calcd for $C_{12}H_{11}FN$ $(M + H)^+$ 188.0870, found 188.0876.

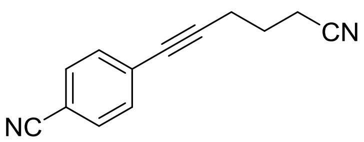
2-((3-(2-Chlorophenyl)prop-2-yn-1-yl)oxy)acetonitrile (3ai)



3ai

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 1-chloro-2-ethynylbenzene **2i** (32.8 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 20:1) to afford 32.8 mg (81%) of **3ai** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.38 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.25 – 7.17 (m, 2H), 2.67 (t, *J* = 6.7 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 1.99 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.8, 133.2, 129.2, 129.0, 126.4, 123.0, 119.2, 92.5, 79.3, 24.5, 18.6, 16.1; **ATR-FTIR (cm $^{-1}$)** 2924, 2248, 1684, 1652, 1559, 1473, 1455, 1430, 755; **HRMS m/z (ESI)** calcd for $C_{12}H_{10}ClNNa$ $(M + Na)^+$ 226.0394, found 226.0404.

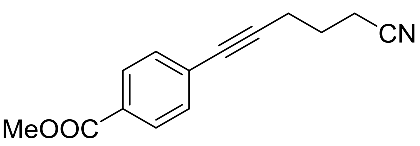
4-(5-Cyanopent-1-yn-1-yl)benzonitrile (3aj)



3aj

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 4-ethynylbenzonitrile **2j** (30.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10:1) to afford 25.7 mg (66%) of **3aj** as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 2H), 7.48 – 7.45 (m, 2H), 2.64 (t, *J* = 6.8 Hz, 2H), 2.55 (t, *J* = 7.1 Hz, 2H), 1.98 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.1, 132.0, 128.1, 118.9, 118.4, 111.3, 91.8, 81.0, 24.2, 18.6, 16.3; **ATR-FTIR (cm $^{-1}$)** 2920, 2849, 2248, 2226, 1652, 1603, 1500, 1424, 739; **HRMS m/z (ESI)** calcd for $C_{13}H_{11}N_2$ $(M + H)^+$ 195.0917, found 195.0922.

4-(5-Cyanopent-1-yn-1-yl)phenyl acetate (3ak)

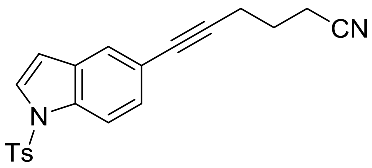


3ak

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then methyl 4-ethynylbenzoate **2k** (38.4 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10:1) to afford 36.1 mg (80%) of **3ak** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.4

Hz, 2H), 3.90 (s, 3H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.56 (t, *J* = 7.1 Hz, 2H), 1.97 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 131.5, 129.4, 129.3, 127.9, 119.0, 90.2, 81.8, 52.2, 24.4, 18.6, 16.2; **ATR-FTIR (cm $^{-1}$)** 2920, 2349, 1720, 1605, 1558, 1507, 1435, 769, 697; **HRMS m/z (ESI)** calcd for $C_{14}H_{13}NNaO_2$ $(M + Na)^+$ 250.0838, found 250.0840.

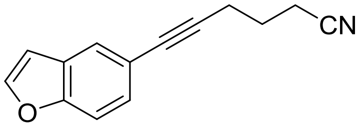
6-(1-Tosyl-1*H*-indol-5-yl)hex-5-ynenitrile (3al)



3al

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 5-ethynyl-1-tosyl-1*H*-indole **2l** (74.6 mg, 0.24 mmol)[5, 6] was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 5:1) to afford 37.5 mg (52%) of **3al** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.56 (dd, *J* = 4.8, 2.3 Hz, 2H), 7.33 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.60 (d, *J* = 3.6 Hz, 1H), 2.59 (t, *J* = 6.7 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.95 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1, 135.0, 134.1, 130.7, 129.9, 128.0, 127.2, 126.7, 124.7, 119.2, 118.2, 113.5, 108.7, 86.0, 82.4, 24.6, 21.5, 18.5, 16.2; **ATR-FTIR (cm $^{-1}$)** 2921, 1654, 1559, 1456, 1371, 813, 766, 715; **HRMS m/z (ESI)** calcd for $C_{21}H_{19}N_2O_2S$ $(M + H)^+$ 363.1162, found 363.1165.

6-(Benzofuran-5-yl)hex-5-ynenitrile (3am)

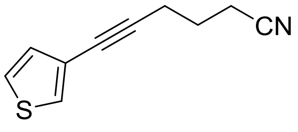


Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol),

3am

$Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 5-ethynylbenzofuran **2m** (34.1 mg, 0.24 mmol) [7, 8] was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30:1) to afford 29.2 mg (70%) of **3am** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 12.6, 1.7 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.33 (dd, *J* = 8.5, 1.6 Hz, 1H), 6.73 (dd, *J* = 2.2, 0.8 Hz, 1H), 2.63 – 2.56 (m, 4H), 1.97 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.3, 145.8, 127.9, 127.5, 124.6, 119.2, 117.7, 111.4, 106.4, 85.3, 82.6, 24.7, 18.5, 16.2; **ATR-FTIR (cm $^{-1}$)** 2920, 2850, 2247, 1654, 1538, 1465, 1434, 1329, 815, 769, 737; **HRMS m/z (ESI)** calcd for $C_{14}H_{12}NO$ $(M + H)^+$ 210.0913, found 210.0919.

6-(Thiophen-3-yl)hex-5-ynenitrile (3an)

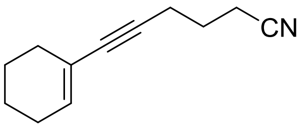


3an

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 3-ethynylthiophene **2n** (26.0 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30:1) to afford 24.1 mg (69%) of **3an** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.25 – 7.24 (m, 1H), 7.07 (dd, *J* = 5.0, 1.1 Hz, 1H), 2.58 (t, *J* = 6.7 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 1.95 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz,

$CDCl_3$) δ 129.8, 128.2, 125.2, 122.1, 119.2, 86.4, 77.4, 24.6, 18.5, 16.2; **ATR-FTIR (cm $^{-1}$)** 1682, 1630, 1557, 1420, 784; **HRMS m/z (ESI)** calcd for $C_{10}H_9NNaS$ (M + Na)$^+$ 198.0348, found 198.0353.

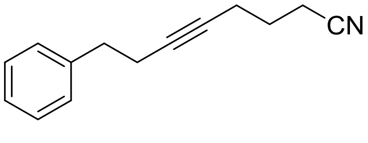
6-(Cyclohex-1-en-1-yl)hex-5-ynenitrile (3ao)



3ao

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 1-ethynylcyclohex-1-ene **2o** (25.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30:1) to afford 18.5 mg (54%) of **3ao** as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.04 – 6.02 (m, 1H), 2.51 – 2.46 (m, 4H), 2.09 – 1.08 (m, 4H), 1.87 (p, *J* = 7.0 Hz, 2H), 1.65 – 1.54 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.2, 120.5, 119.3, 84.2, 83.9, 29.4, 25.5, 24.8, 22.3, 21.5, 18.4, 16.1; **ATR-FTIR (cm -1)** 2936, 2860, 2247, 1670, 1455, 1433, 1361; **HRMS m/z (ESI)** calcd for $C_{12}H_{15}NNa$ (M + Na)$^+$ 196.1097, found 196.1100.

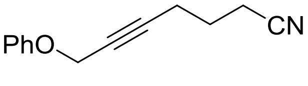
8-Phenyloct-5-ynenitrile (3ap)



3ap

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then but-3-yn-1-ylbenzene **2p** (31.2 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30:1) to afford 23.5 mg (60%) of **3ap** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.24 – 7.21 (m, 3H), 2.80 (t, J = 7.4 Hz, 2H), 2.49 – 2.44 (m, 2H), 2.35 – 2.28 (m, 4H), 1.77 (p, J = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.6, 128.4, 128.3, 126.3, 119.4, 81.6, 78.1, 35.1, 24.8, 20.7, 17.8, 15.8; **ATR-FTIR (cm $^{-1}$)** 3026, 2908, 2245, 1652, 1558, 1455, 1420, 748, 699; **HRMS m/z (ESI)** calcd for $C_{14}H_{15}NNa$ (M + Na)$^+$ 220.1097, found 220.1097.

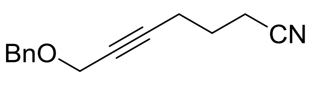
7-Phenoxyhept-5-ynenitrile (3aq)



3aq

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then (prop-2-yn-1-yloxy)benzene **2q** (31.7 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30:1) to afford 25.1 mg (63%) of **3aq** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.01 – 6.94 (m, 3H), 4.68 (t, J = 2.1 Hz, 2H), 2.44 – 2.39 (m, 4H), 1.85 (p, J = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.5, 129.4, 121.4, 119.0, 114.9, 85.0, 77.0, 56.1, 24.3, 17.9, 16.0; **ATR-FTIR (cm $^{-1}$)** 2244, 1654, 1559, 1492, 754, 692; **HRMS m/z (ESI)** calcd for $C_{13}H_{13}NNaO$ (M + Na)$^+$ 222.0889, found 222.0896.

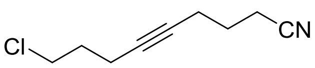
7-(Benzyloxy)hept-5-ynenitrile (3ar)



3ar

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), Cu(OTf)$_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ((prop-2-yn-1-yloxy)methyl)benzene **2r** (35.1 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10:1) to afford 24.8 mg (58%) of **3ar** as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 4.58 (s, 2H), 4.16 (t, J = 2.1 Hz, 2H), 2.51 – 2.41 (m, 4H), 1.88 (p, J = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.4, 128.4, 128.0, 127.8, 119.1, 84.0, 78.0, 71.7, 57.6, 24.4, 17.9, 16.1; **ATR-FTIR (cm $^{-1}$)** 2850, 2245, 1652, 1558, 1455, 1353, 739, 699; **HRMS m/z (ESI)** calcd for $C_{14}H_{15}NO$ $(M + Na)^+$ 236.1046, found 236.1050.

9-Chlorononon-5-ynenitrile (3as)

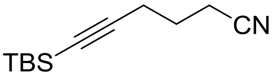


3as

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), Cu(OTf)$_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 5-chloropent-1-yne **2s** (24.6 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30:1) to afford 12.6 mg (37%) of **3as** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.64 (t, J = 6.3 Hz, 2H), 2.48 (t, J = 7.2 Hz, 2H), 2.37 – 2.32 (m, 4H), 1.93 (p, J = 6.5 Hz, 2H), 1.83 (p, J

= 6.9 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 119.2, 80.3, 78.3, 43.7, 31.4, 24.8, 17.9, 16.1 (d, *J* = 2.3 Hz); **ATR-FTIR (cm $^{-1}$)** 2920, 2849, 2246, 1652, 1558, 1507, 1435; **HRMS m/z (ESI)** calcd for $C_9H_{12}ClNNa$ (M + Na)$^+$ 192.0550, found 192.0556.

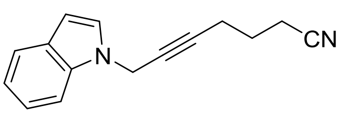
6-(*Tert*-butyldimethylsilyl)hex-5-ynenitrile (3at)



3at

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then *tert*-butyl(ethynyl)dimethylsilane **2t** (33.7 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 30:1) to afford 13.9 mg (34%) of **3at** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 2.50 (t, *J* = 7.2 Hz, 2H), 2.42 (t, *J* = 6.7 Hz, 2H), 1.87 (p, *J* = 7.0 Hz, 2H), 0.92 (s, 9H), 0.09 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 119.1, 104.4, 85.0, 26.0, 24.6, 18.9, 16.4, 16.0, -4.6; **ATR-FTIR (cm $^{-1}$)** 2953, 2930, 2856, 2174, 1651, 1557, 1471, 1251, 838, 776; **HRMS m/z (ESI)** calcd for $C_{12}H_{22}NS_i$ (M + H)$^+$ 208.1516, found 208.1518.

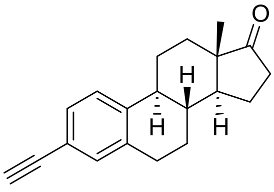
Oxetan-3-one *O*-(4-(trifluoromethyl)benzoyl) oxime (3au)



3au

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then 1-(prop-2-yn-1-yl)-1*H*-indole **2u** (37.2 mg, 0.24 mmol)[9] was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10:1) to afford 24.5 mg (55%) of **3au** as a yellow oil: ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.68 (d, J = 7.9 Hz, 1H), 7.43 (dd, J = 8.2, 0.7 Hz, 1H), 7.30 – 7.15 (m, 3H), 6.56 (dd, J = 3.2, 0.8 Hz, 1H), 4.89 (t, J = 2.2 Hz, 2H), 2.45 – 2.39 (m, 4H), 1.86 (p, J = 7.0 Hz, 2H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 135.7, 128.8, 127.2, 121.7, 121.0, 119.7, 119.0, 109.3, 101.8, 82.7, 76.2, 36.1, 24.2, 17.8, 16.1; **ATR-FTIR (cm $^{-1}$)** 2917, 1652, 1558, 1508, 1459, 1313, 1265, 741; **HRMS m/z (ESI)** calcd for $C_{15}H_{15}N_2$ (M + H)$^+$ 223.1230, found 223.1231.

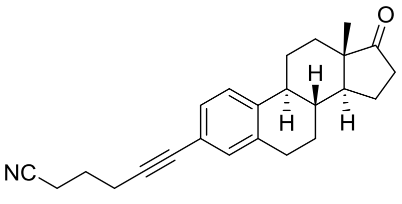
(8*R*,9*S*,13*S*,14*S*)-3-ethynyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (2v)



2v

According to the reported procedure [10] [11], **2v** was prepared from Estrone (2.0 mmol) as a white solid (383 mg, 69%): ^{1}**H NMR** δ 7.34 – 7.16 (m, 3H), 3.02 (s, 1H), 2.89 (dd, J = 8.6, 4.0 Hz, 2H), 2.51 (dd, J = 18.8, 8.5 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.36 – 2.26 (m, 1H), 2.20 – 1.93 (m, 4H), 1.67 – 1.59 (m, 1H), 1.56 – 1.41 (m, 4H), 1.06 – 1.01 (m, 1H), 0.91 (s, 3H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 220.6, 140.8, 136.6, 132.6, 129.4, 125.4, 119.4, 83.7, 76.4, 50.4, 47.9, 44.4, 37.9, 35.8, 31.5, 29.0, 26.3, 25.5, 21.5, 13.8; **ATR-FTIR (cm $^{-1}$)** 3305, 3220, 2927, 2869, 1730, 1653, 1558, 1493, 1456, 1433, 1406, 1374; **HRMS m/z (ESI)** calcd for $C_{20}H_{23}O$ (M + H)$^+$ 279.1743, found 279.1740.

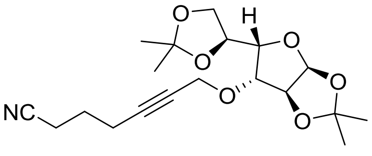
6-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)hex-5-ynenitrile (3av)



3av

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), Cu(OTf)$_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K$_2$CO$_3$ (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then **2v** (66.7 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10:1) to afford 42.0 mg (61%) of **3av** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 3H), 2.87 (dd, *J* = 8.8, 4.1 Hz, 2H), 2.60 – 2.47 (m, 5H), 2.43 – 2.38 (m, 1H), 2.31 – 2.25 (m, 1H), 2.19 – 1.91 (m, 6H), 1.67 – 1.38 (m, 6H), 0.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.6, 140.0, 136.5, 132.0, 128.8, 125.3, 120.4, 120.0, 86.1, 82.4, 50.4, 47.9, 44.4, 37.9, 35.8, 31.5, 29.0, 26.3, 25.5, 24.7, 21.5, 18.5, 16.1, 13.8; **ATR-FTIR (cm $^{-1}$)** 2928, 2859, 2246, 1736, 1653, 1558, 1495, 1455, 821, 780, 710; **HRMS m/z (ESI)** calcd for $C_{24}H_{28}NO$ $(M + H)^+$ 346.2165, found 346.2175.

7-(((3*aS*,5*S*,6*R*,6*aS*)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)hept-5-ynenitrile (3aw)

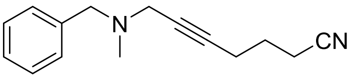


3aw

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then (3*aS*,5*S*,6*R*,6*aS*)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(prop-2-yn-1-yloxy)tetrahydrofuro[2,3-*d*][1,3]dioxole **2w** (71.5 mg, 0.24 mmol) [12] was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 5:1) to afford 31.3 mg (43%) of **3aw** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.87 (d,

J = 3.7 Hz, 1H), 4.60 (d, J = 3.7 Hz, 1H), 4.29 – 4.24 (m, 3H), 4.13 – 4.05 (m, 3H), 3.99 (dd, J = 8.6, 5.4 Hz, 1H), 2.50 (t, J = 7.2 Hz, 2H), 2.43 (tt, J = 6.7, 2.1 Hz, 2H), 1.88 (p, J = 7.0 Hz, 2H), 1.50 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 119.0, 111.8, 109.0, 105.2, 84.3, 82.8, 81.2, 81.0, 77.6, 72.4, 67.2, 58.3, 26.9, 26.8, 26.2, 25.4, 24.4, 17.9, 16.1; **ATR-FTIR (cm $^{-1}$)** 2987, 2936, 2248, 1456, 1374; **HRMS m/z (ESI)** calcd for $C_{19}H_{28}NO_6$ $(M + H)^+$ 366.1911, found 366.1915.

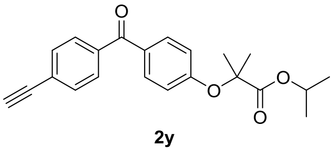
7-(Benzyl(methyl)amino)hept-5-ynenitrile (3ax)



3ax

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then *N*-benzyl-*N*-methylprop-2-yn-1-amine **2x** (38.2 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 2:1) to afford 25.7 mg (57%) of **3ax** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 3.54 (s, 2H), 3.26 (t, J = 2.1 Hz, 2H), 2.52 (t, J = 7.2 Hz, 2H), 2.44 (tt, J = 6.7, 2.1 Hz, 2H), 2.31 (s, 3H), 1.89 (p, J = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.3, 129.1, 128.3, 127.2, 119.1, 82.5, 76.9, 60.3, 45.3, 41.9, 24.8, 17.9, 16.2; **ATR-FTIR (cm $^{-1}$)** 3061, 3028, 2920, 2847, 2791, 2246, 1654, 1559, 1508, 1494, 1364, 1326, 1266, 739, 700; **HRMS m/z (ESI)** calcd for $C_{15}H_{19}N_2$ $(M + H)^+$ 227.1543, found 227.1549.

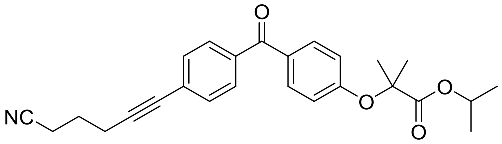
Isopropyl 2-(4-(4-ethynylbenzoyl)phenoxy)-2-methylpropanoate (2y)



2y

According to the reported procedure [13], **2y** was prepared from Fenofibrate (2.0 mmol) as a yellow solid (484 mg, 69%): **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.72 (dd, *J* = 12.9, 8.5 Hz, 4H), 7.58 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.12 – 5.05 (m, 1H), 3.23 (s, 1H), 1.66 (s, 6H), 1.20 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 194.6, 173.1, 159.7, 138.1, 132.0, 131.9, 130.2, 129.6, 125.8, 117.2, 82.9, 79.8, 79.4, 69.3, 25.4, 21.5; **ATR-FTIR (cm $^{-1}$)** 1731, 1653, 1598,1558, 1507, 1457, 1419, 1375, 1286, 1250, 767; **HRMS m/z (ESI)** calcd for $C_{22}H_{23}O_4$ $(M + H)^+$ 351.1591, found 351.1696.

Isopropyl 2-(4-(4-(5-cyanopent-1-yn-1-yl)benzoyl)phenoxy)-2-methylpropanoate (3ay)

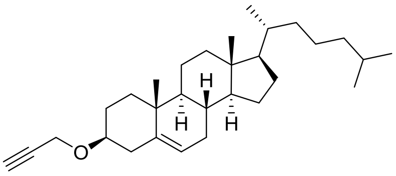


3ay

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then **2y** (84.0 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10:1) to afford 41.3 mg (50%) of **3ay** as a yellow oil: **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.74 – 7.67 (m, 4H), 7.47 (d, *J* = 8.2 Hz, 2H), 6.87 – 6.84 (m, 2H), 5.13 – 5.03 (m, 1H), 2.64 (t, *J* = 6.8 Hz, 2H), 2.57 (t, *J* = 7.1 Hz, 2H), 1.98 (p, *J* = 7.0 Hz, 2H), 1.65 (s, 6H), 1.19 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 194.7, 173.1, 159.6, 137.2, 131.9, 131.3, 130.3, 129.7, 127.0, 119.0, 117.2, 90.0, 81.8, 79.4, 69.3, 25.3, 24.5, 21.5, 18.6, 16.3; **ATR-FTIR (cm $^{-1}$)** 2982, 2937, 2246, 1731, 1652, 1598,1457, 1286, 1250, 767; **HRMS m/z (ESI)** calcd for $C_{26}H_{28}NO_4$ $(M + H)^+$ 418.2013, found 418.2022.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-(prop-2-yn-1-yloxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta

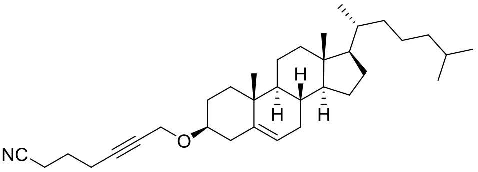
[*a*]phenanthrene (2z)



2z

According to the reported procedure [12], **2z** was prepared from from Cholesterol (3.0 mmol) as a yellow solid (471 mg, 37%): **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 5.37 – 5.36 (m, 1H), 4.19 (d, *J* = 2.4 Hz, 2H), 3.42 – 3.35 (m, 1H), 2.40 – 2.36 (m, 2H), 2.25 – 2.20 (m, 1H), 2.03 – 1.79 (m, 5H), 1.61 – 1.41 (m, 8H), 1.40 – 1.22 (m, 5H), 1.18 – 1.05 (m, 6H), 1.04 – 0.96 (m, 5H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 2.2 Hz, 6H), 0.67 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 140.6, 121.9, 80.4, 78.2, 73.8, 56.8, 56.1, 55.1, 50.1, 42.3, 39.8, 39.5, 38.7, 37.1, 36.8, 36.2, 35.8, 31.9, 31.9, 28.2, 28.1, 28.0, 24.3, 23.8, 22.8, 22.6, 21.1, 19.3, 18.7, 11.9; **ATR-FTIR (cm $^{-1}$)** 3257, 2936, 2868, 2112, 1468, 1375, 1341; **HRMS m/z (ESI)** calcd for $C_{30}H_{48}NaO$ $(M + Na)^+$ 447.3597, found 447.3609.

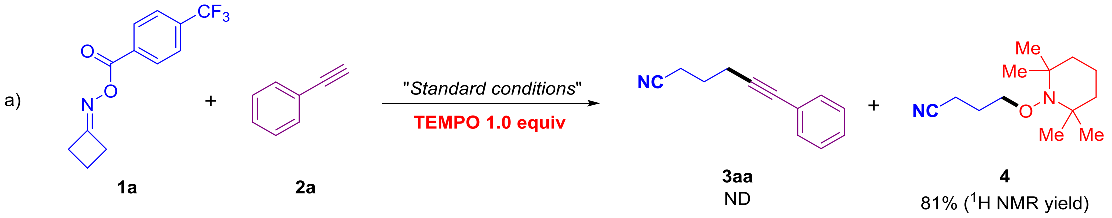
7-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)hept-5-ynenitrile (3az)



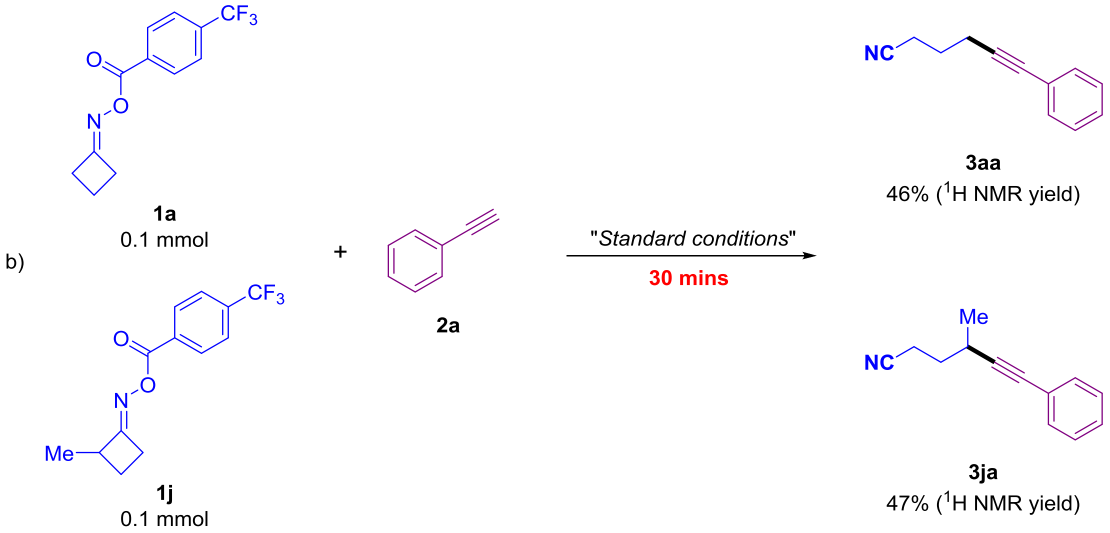
3az

Flame-dried 25 mL Schlenk tube filled with argon, cyclobutanone oxime **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (3.6 mg, 10 mol%), 2,2':6',2"-terpyridine (4.6 mg, 20 mol%), K_2CO_3 (41.4 mg, 0.3 mmol), tetrabutylammonium iodide (1.9 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then **2z** (42.4 mg, 0.1 mmol) [12] was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The solution was then filtered through celite, washed with EtOAc and the solvent was removed under vaccum. The crude product was purified by flash column chromatography on silica gel (PE : EA = 10:1) to afford 29.3 mg (60%) of **3az** as a white solid: **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 5.37 – 5.35 (m, 1H), 4.16 (t, *J* = 2.1 Hz, 2H), 3.36 – 5.27 (m, 1H), 2.49 (t, *J* = 7.2 Hz, 2H), 2.43 – 2.34 (m, 3H), 2.25 – 2.18 (m, 1H), 2.03 – 1.78 (m, 7H), 1.63 – 1.40 (m, 6H), 1.38 – 1.25 (m, 6H), 1.22 – 1.04 (m, 6H), 1.03 – 0.95 (m, 5H), 0.95 – 0.90 (m, 4H), 0.87 (d, J = 1.8 Hz, 3H), 0.85 (d, J = 1.8 Hz, 3H), 0.67 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.6, 121.9, 119.1, 83.1, 78.7, 78.2, 56.8, 56.1, 55.5, 50.2, 42.3, 39.8, 39.5, 38.8, 37.2, 36.8, 36.2, 35.8, 31.93, 31.87, 28.2, 28.1, 28.0, 24.5, 24.3, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 18.0, 16.2, 11.9; **ATR-FTIR (cm $^{-1}$)** 2938, 2850, 2245, 1652, 1558, 1457; **HRMS m/z (ESI)** calcd for $C_{34}H_{53}NNaO$ $(M + Na)^+$ 514.4019, found 514.4026.

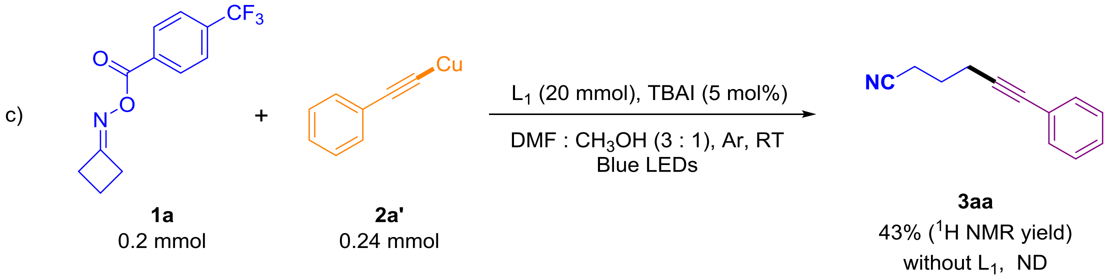
3. Mechanistic Experiments



Procedure: Flame-dried 25 mL Schlenk tube filled with argon, **1a** (51.4 mg, 0.2 mmol), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 2,2':6',2"-terpyridine (9.2 mg, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol), TEMPO (31.2 mg, 0.2 mmol, 100 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The reaction mixture was analyzed by GC-MS and ^{1}H NMR. The yield of **4** was determined by ^{1}H NMR using CH_2Br_2 as internal standard.



Procedure: Flame-dried 25 mL Schlenk tube filled with argon, **1a** (25.7 mg, 0.1 mmol), **1j** (27.1 mg, 0.1 mmol), Cu(OTf)$_2$ (7.2 mg, 10 mol%), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), K$_2$CO$_3$ (82.8 mg, 0.6 mmol), TEMPO (31.2 mg, 0.2 mmol), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. Then ethynylbenzene **2a** (24.5 mg, 0.24 mmol) was added to the mixture. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 30 min. The reaction mixture was analyzed by GC-MS and ^{1}H NMR. The yield of **3aa** and **3ja** were determined by ^{1}H NMR using CH$_2$Br$_2$ as internal standard.



Procedure (with L$_1$): Flame-dried 25 mL Schlenk tube filled with argon, **1a** (51.4 mg, 0.2 mmol), **2a'** (39.5 mg, 0.24 mmol), 2,2':6',2''-terpyridine (9.2 mg, 20 mol%), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. The reaction mixture was analyzed by GC-MS and ^{1}H NMR. The yield of **3aa** was determined by ^{1}H NMR using CH_2Br_2 as internal standard.

Procedure (without L_1): Flame-dried 25 mL Schlenk tube filled with argon, **1a** (51.4 mg, 0.2 mmol), **2a'** (39.5 mg, 0.24 mmol), tetrabutylammonium iodide (3.7 mg, 5 mol%), absolute dry methanol (0.25 mL) and absolute dry DMF (0.75 mL) were added under Ar. The formed mixture was stirred at room temperature under blue LEDs (5 m length blue LED strips (12 w/m)) for 3 h. **3aa** was not detected via a GC-MS analysis.

4. Absorption and Emission Spectroscopy

UV-vis spectra was collected on a Shimadzu UV-2550 spectrophotometer.

Emission spectra was collected on a Hitachi F-4600 fluorescence spectrophotometer. All samples were degassed with a stream of argon for 10 minutes, then excited at 454 nm.

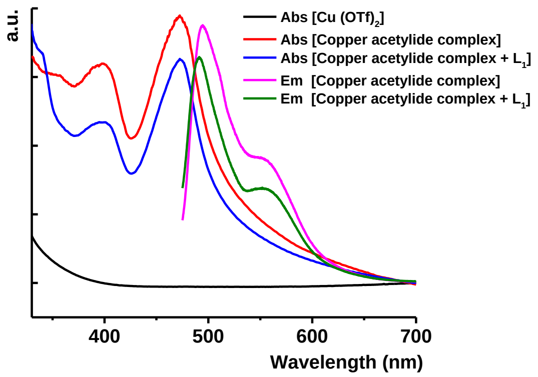


Figure 1 UV-Vis absorption spectra and emission spectra (excited at $\lambda = 454$ nm)

Emission intensities were recorded using a Fluorolog-3 luminescence spectrometer. All copper acetylide complexes were excited at 454 nm and the emission intensity was collected at 505 nm. In a typical experiment, to a 0.005 M solution of copper acetylide complexes in MeOH : DMF = 1 : 3 in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.

It was shown that only copper catalyst dissolved in the solvent did not show any apparent absorption signal above $\lambda = 400$ nm. In contrast, the copper acetylide complex exhibits a strong absorption at λ = 475 nm, which was almost the same with the absorption of copper acetylide complex coordianted with $L_{1.}$ When the copper acetylide complex and copper acetylide complex coordianted with L_1 were excited at λ = 454 nm, similar emission band centered at around λ = 500 nm were observed with emission lifetime of 10.4 nanoseconds and 7.2 nanoseconds, respectively. Based on these results, we concluded that both the copper acetylide complex and copper acetylide complex coordianted with L_1 might be the important light-absorption photoredox catalysts displaying nearly good potential for the activation of cyclobutanone oximes under the irradiation of blue LEDs.

5. References

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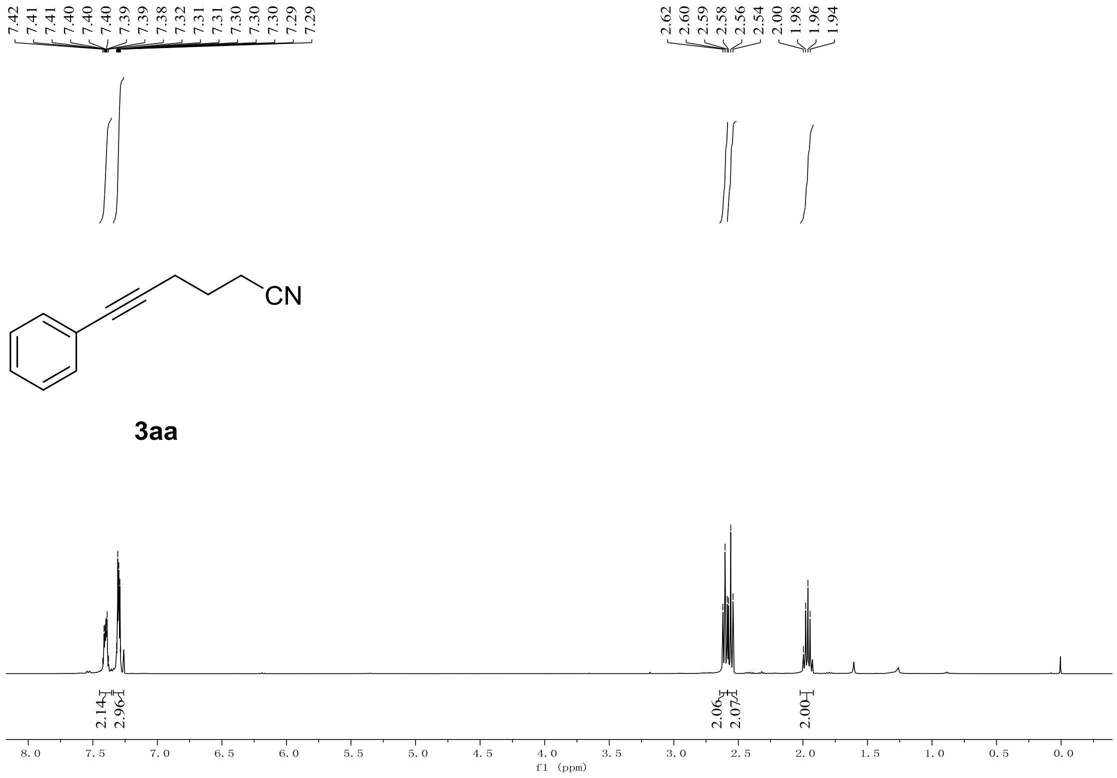
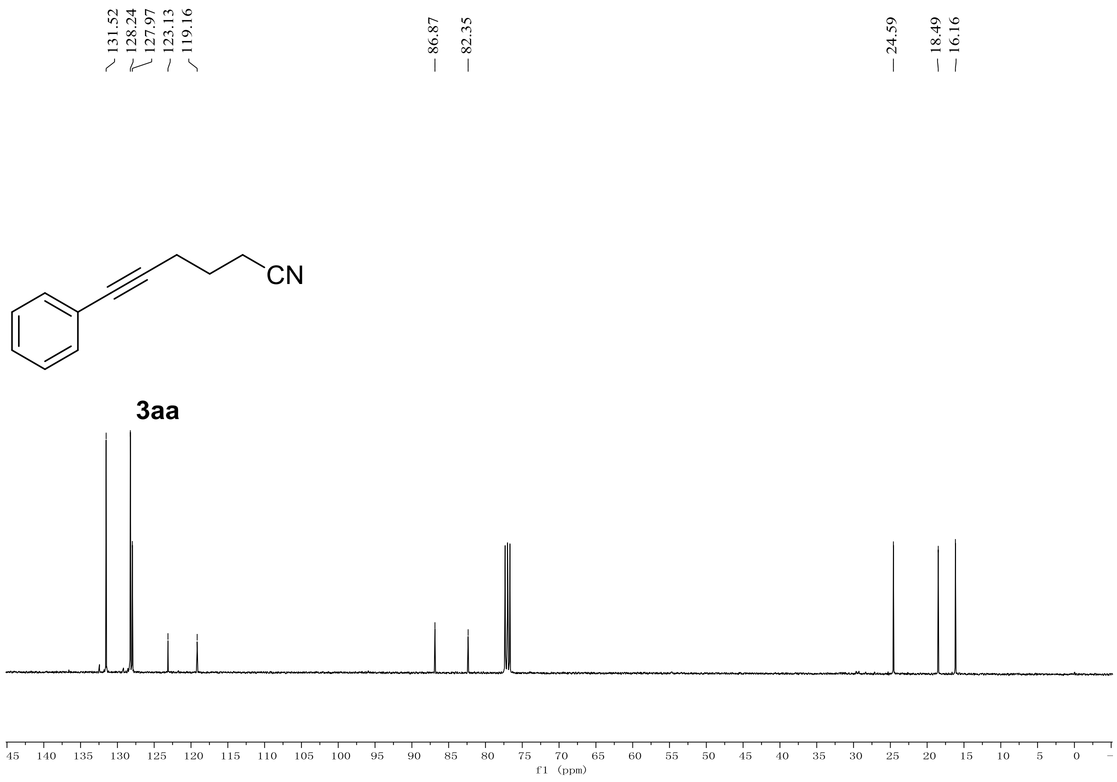
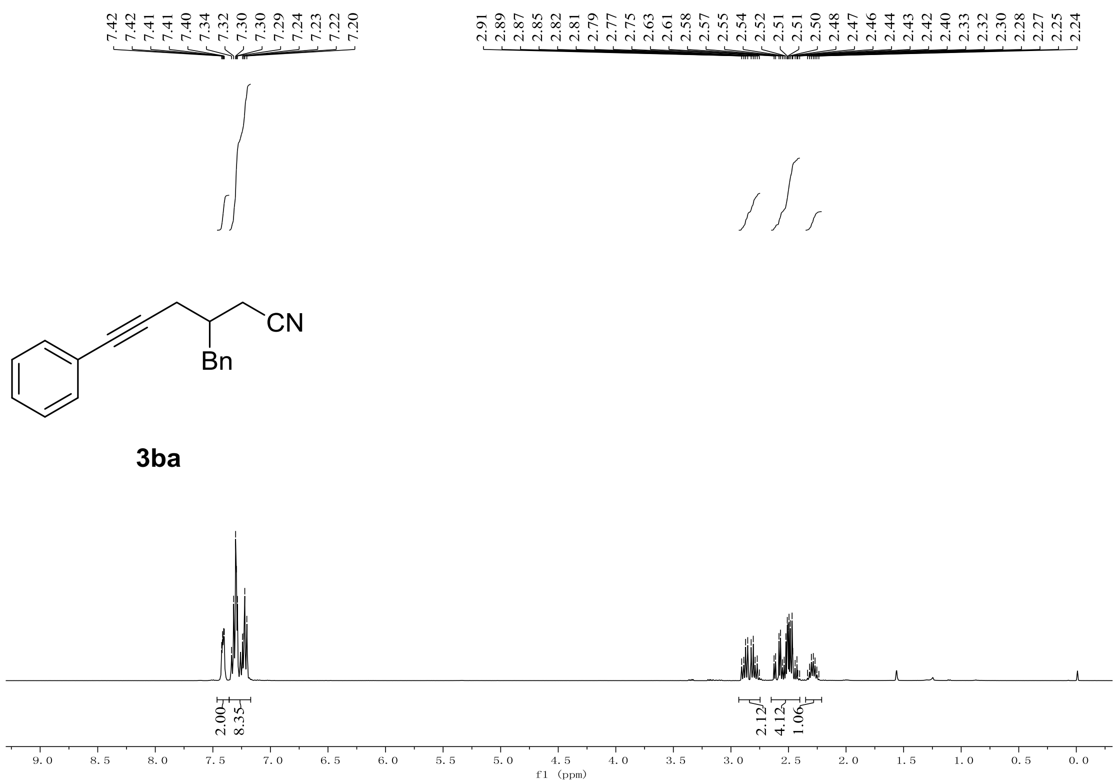
[13] X. Zhang, X. Xie, Y. Liu, *J. Am. Chem. Soc.*, 2018, **140**, 7385.

6. Copies of NMR Spectra



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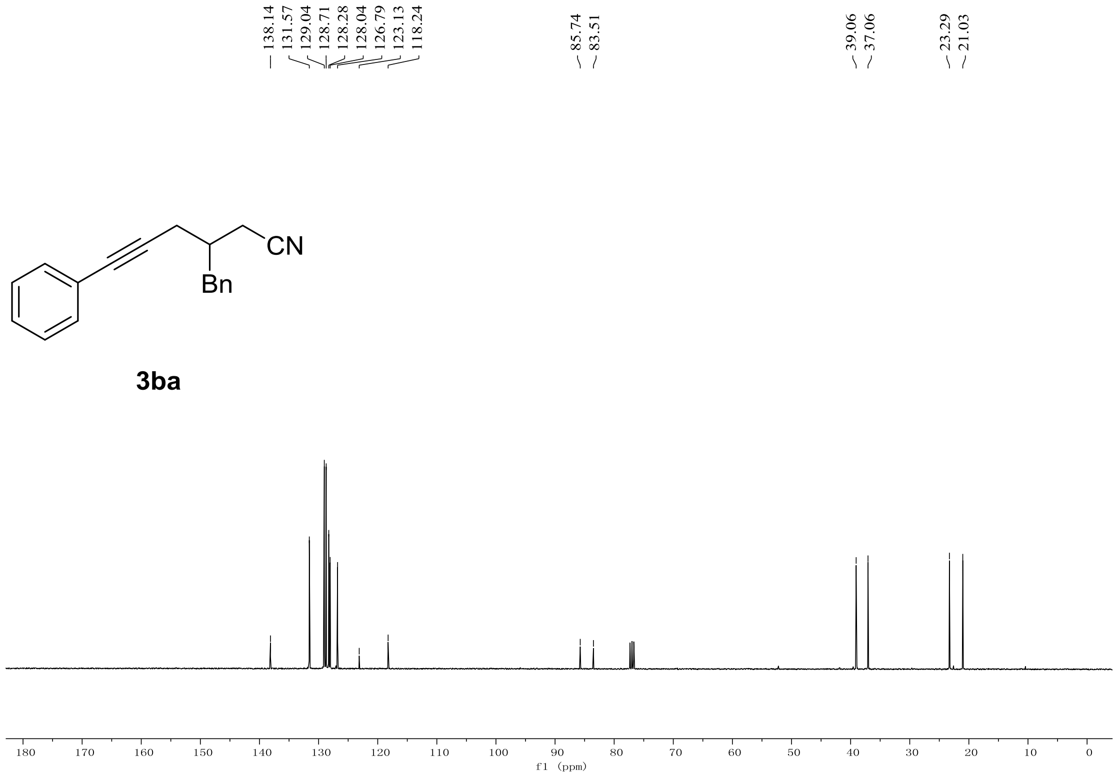
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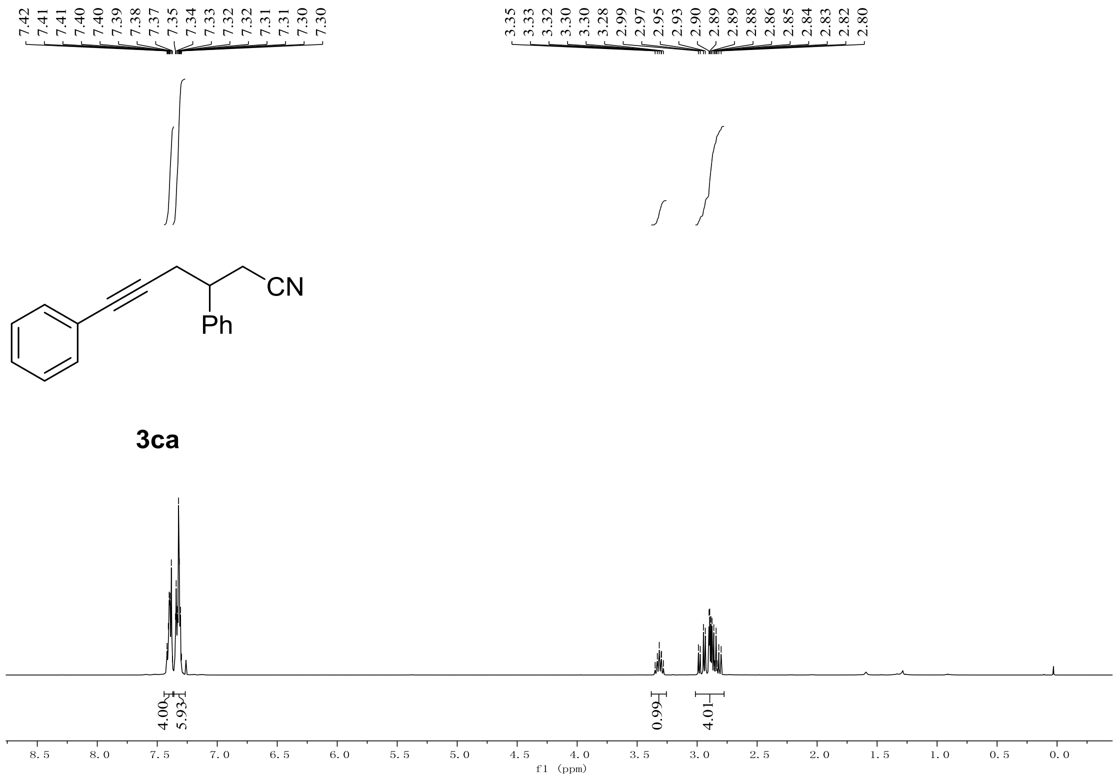
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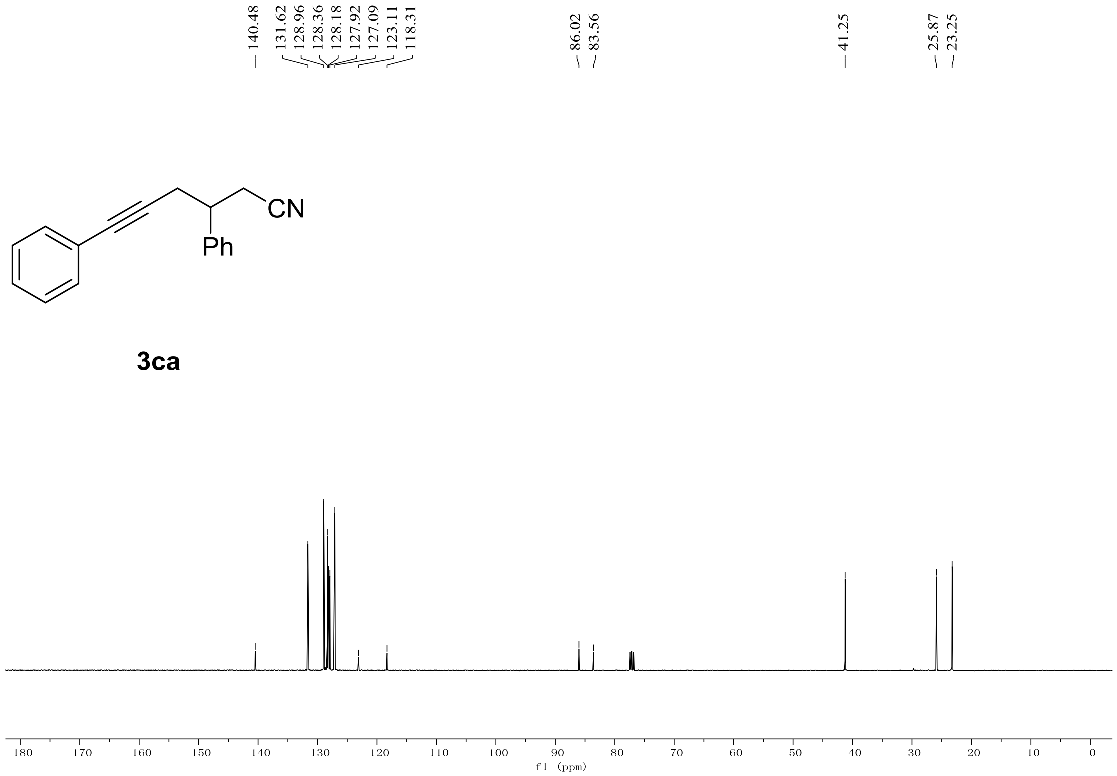
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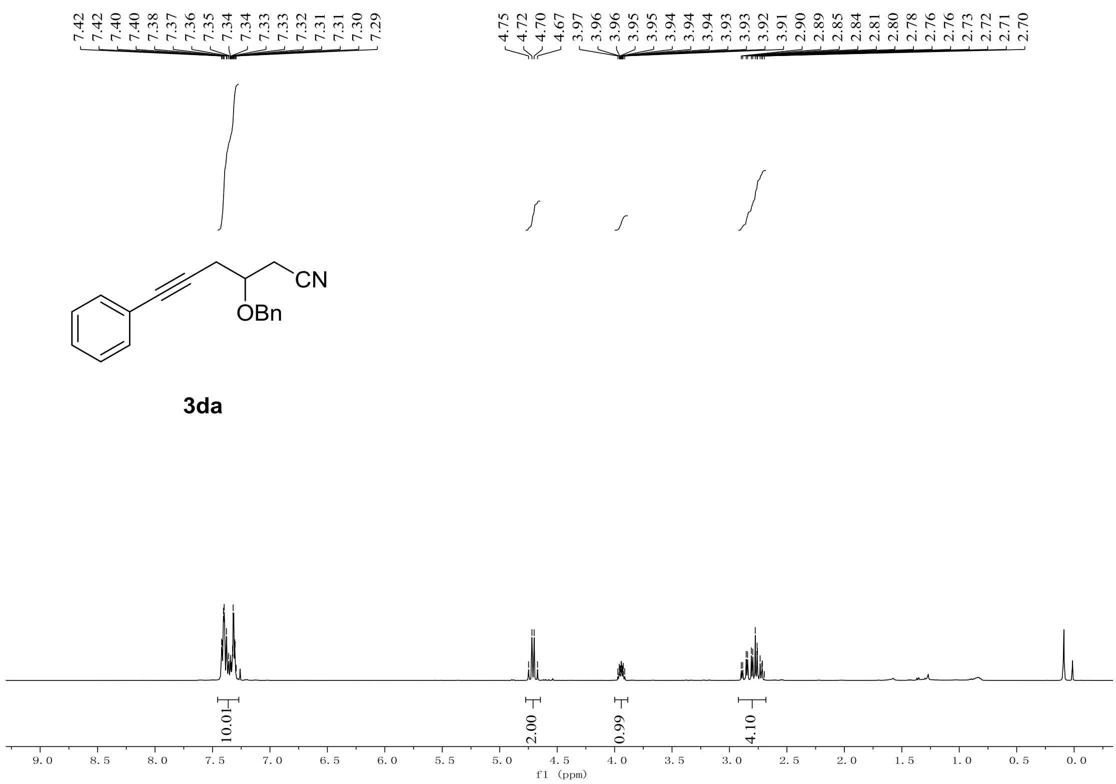
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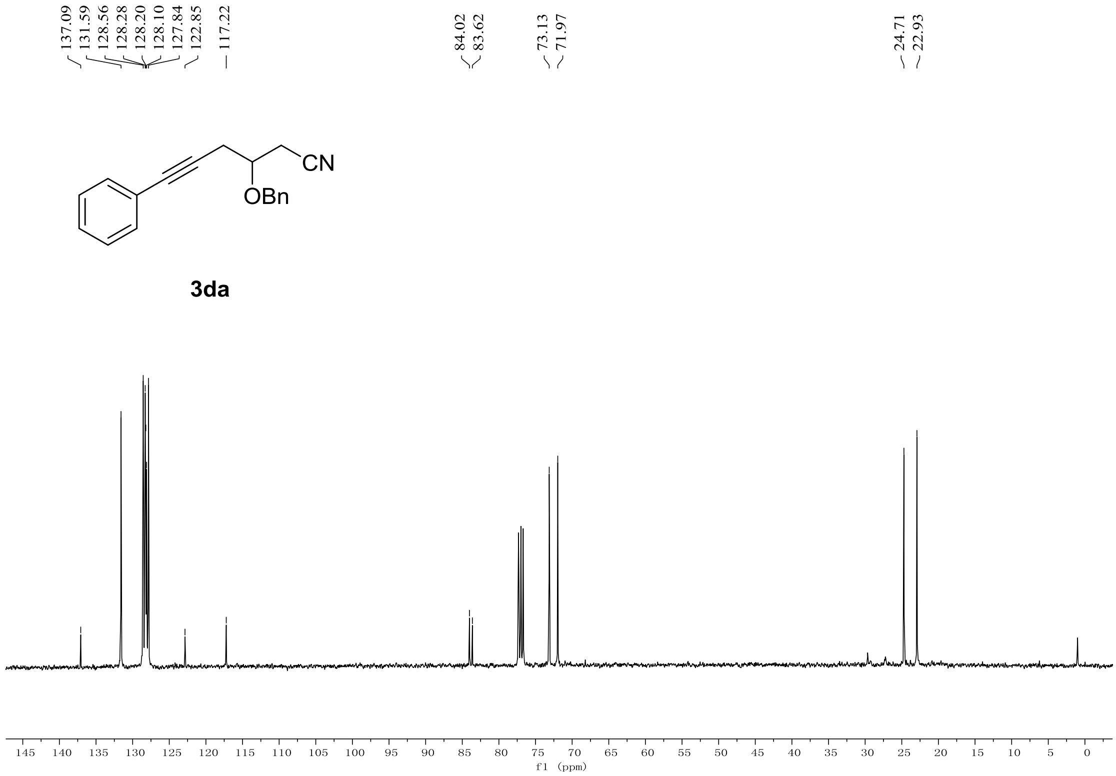
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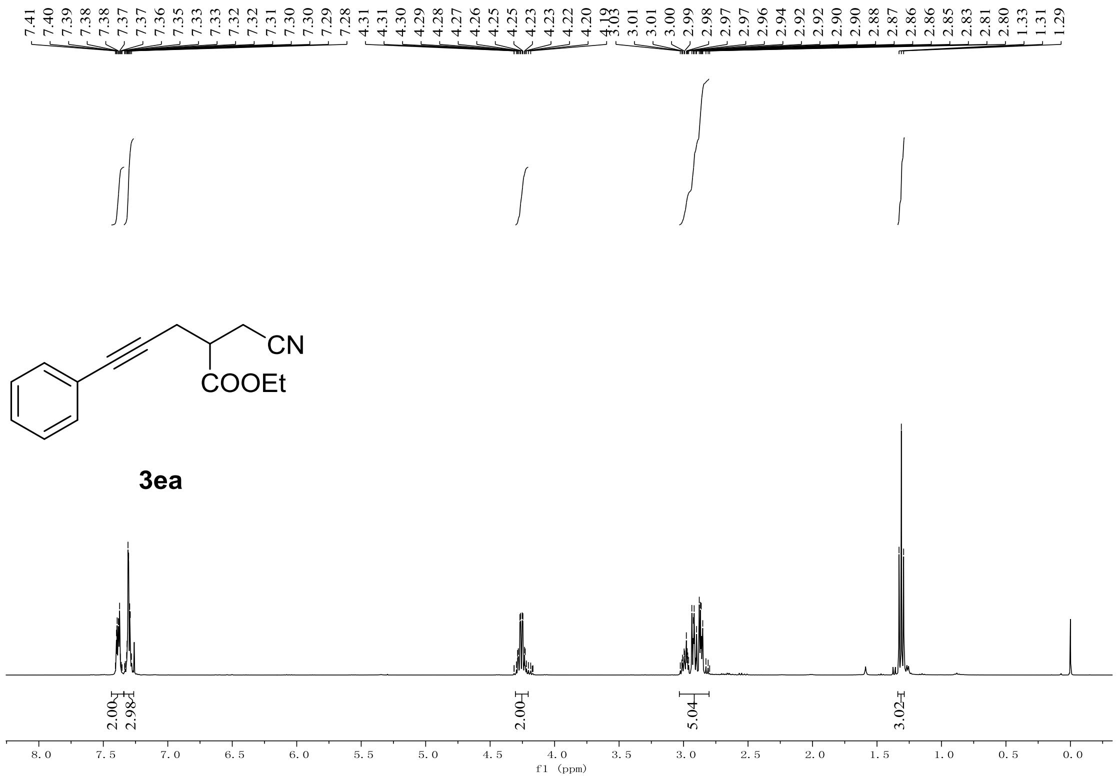
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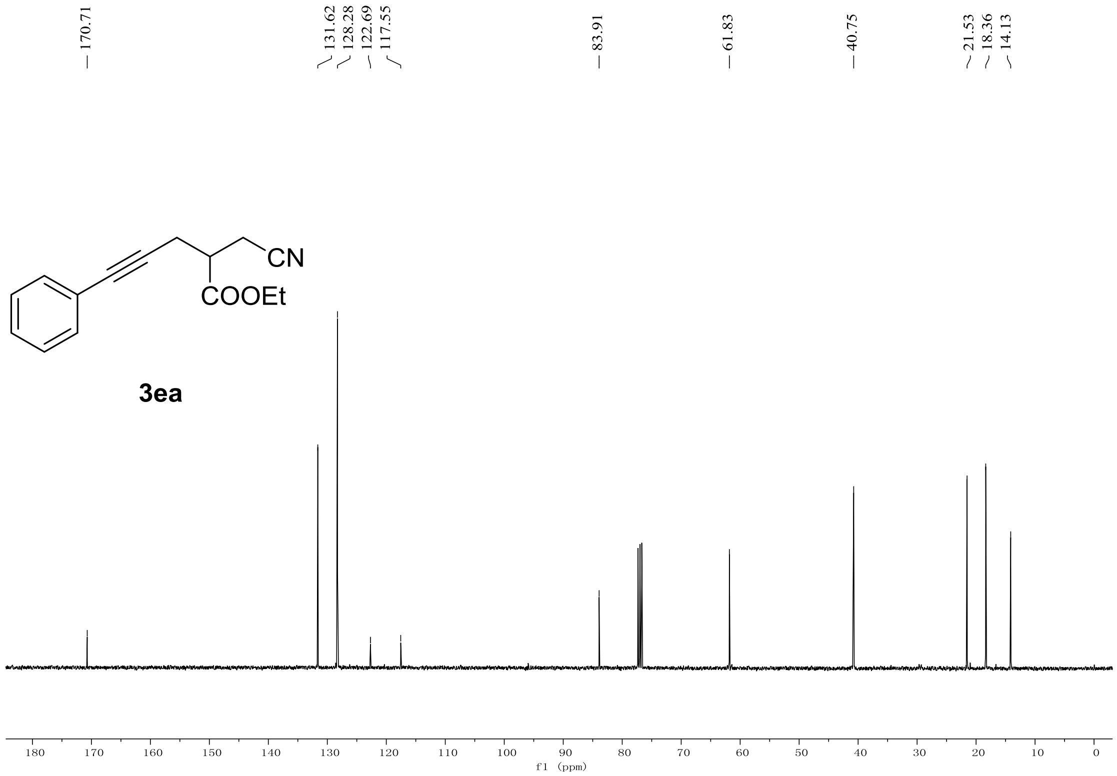
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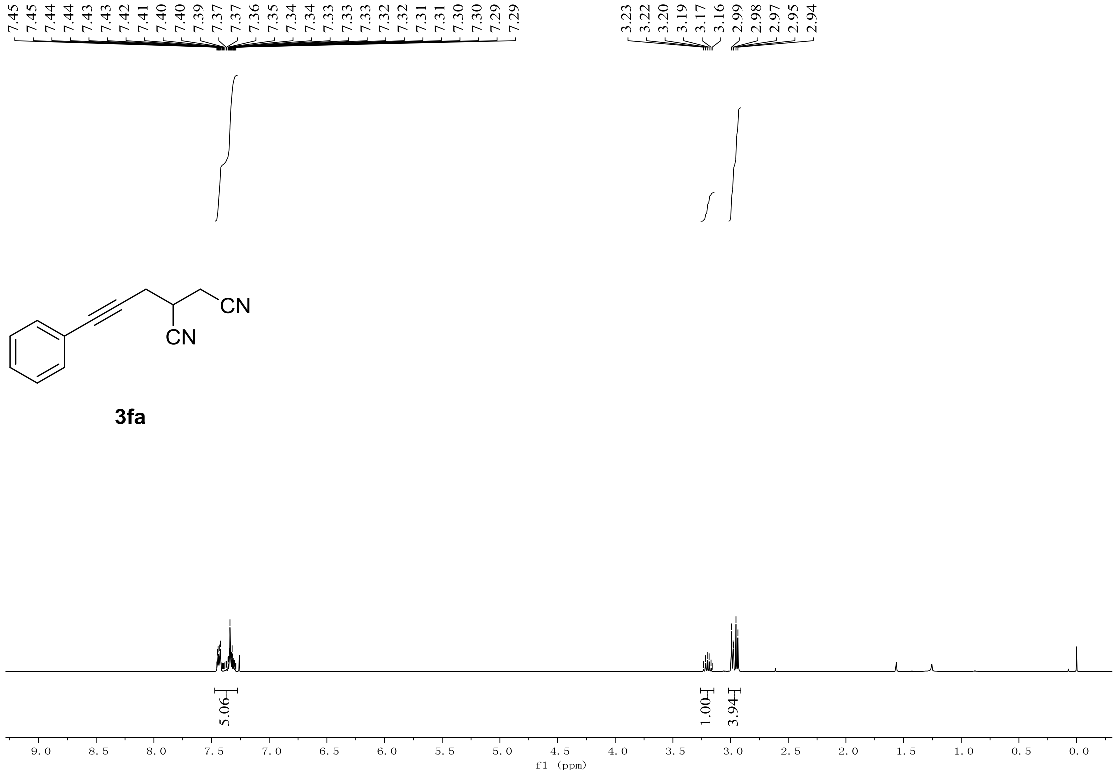
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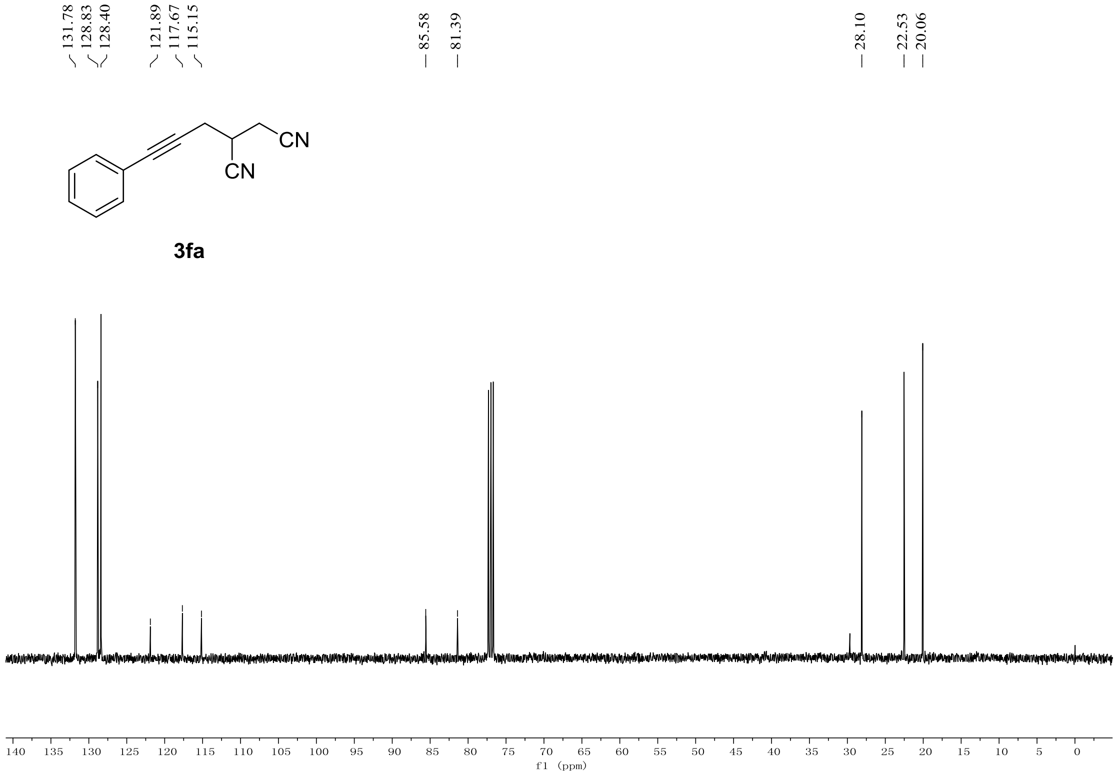
3fa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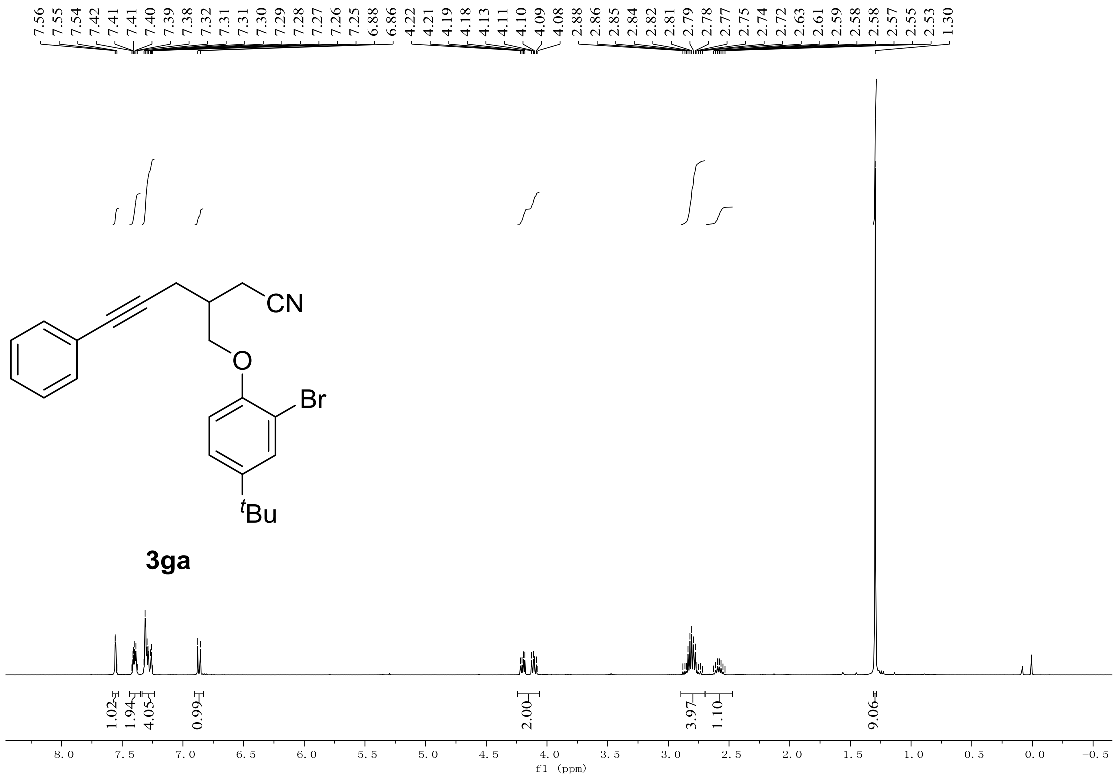
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O
Br
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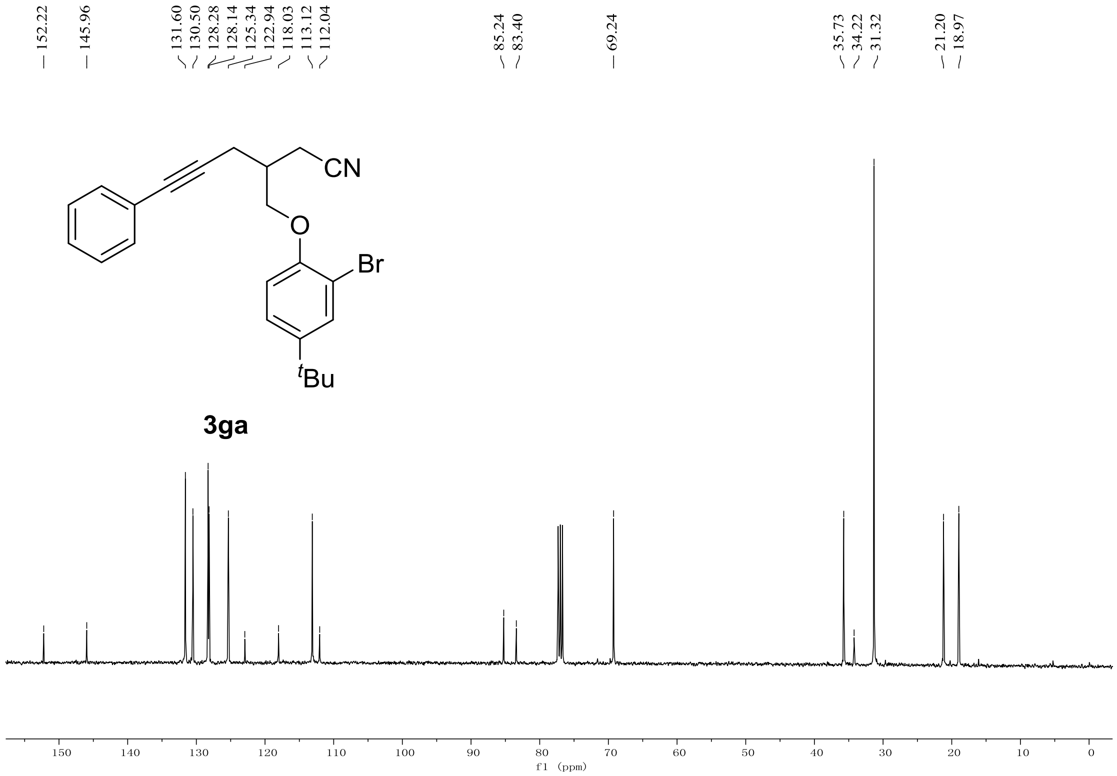
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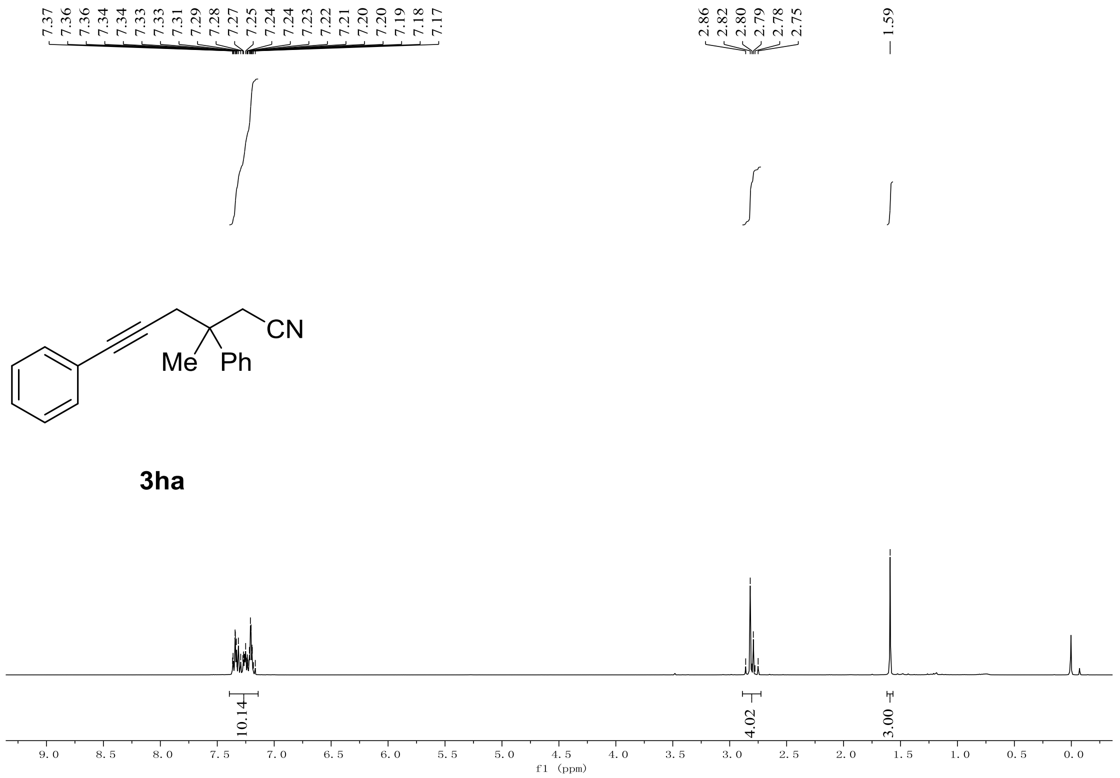
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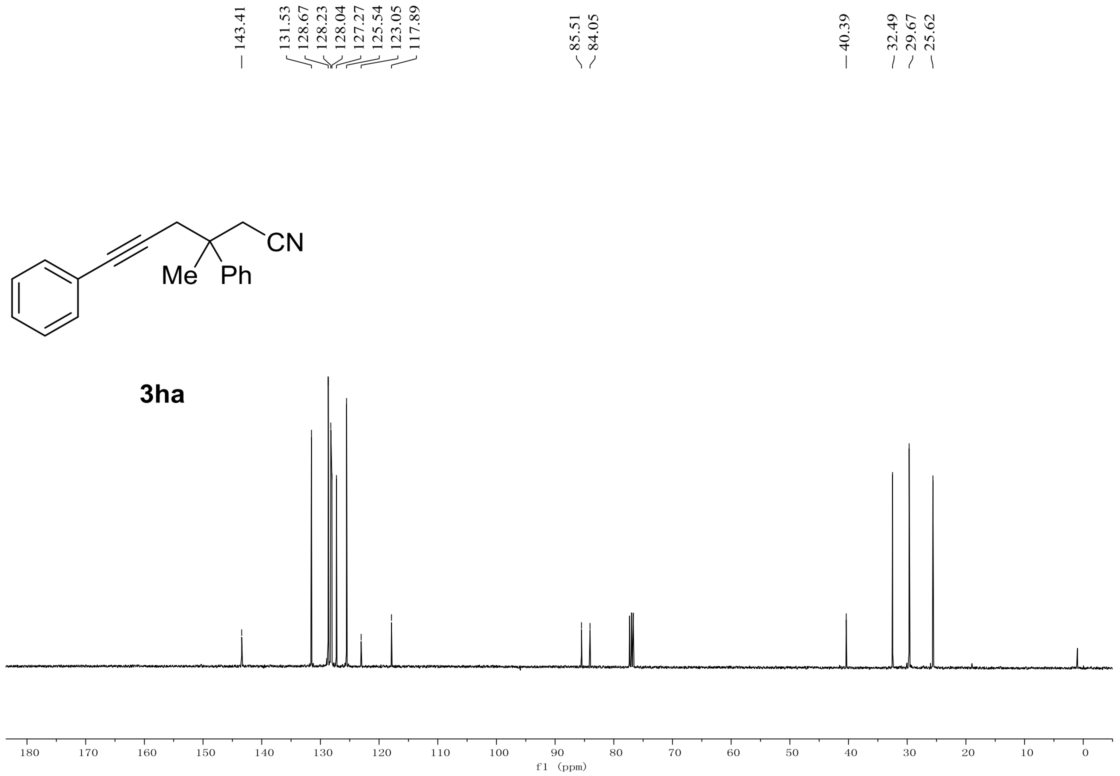
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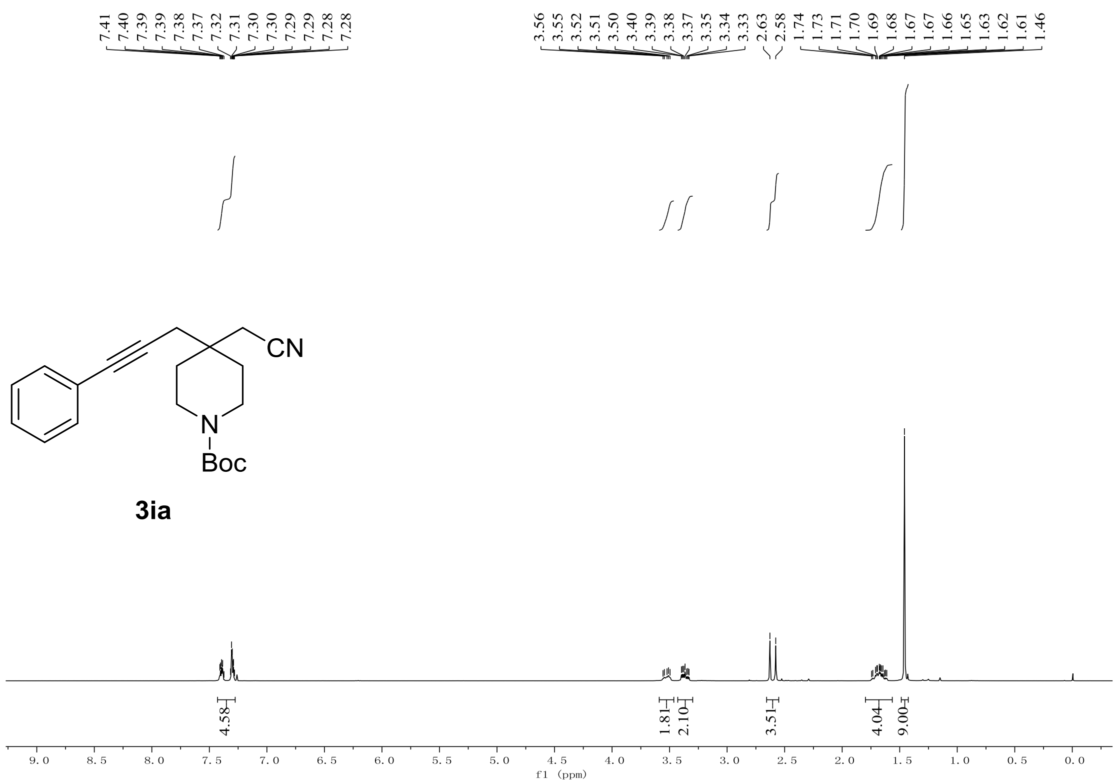
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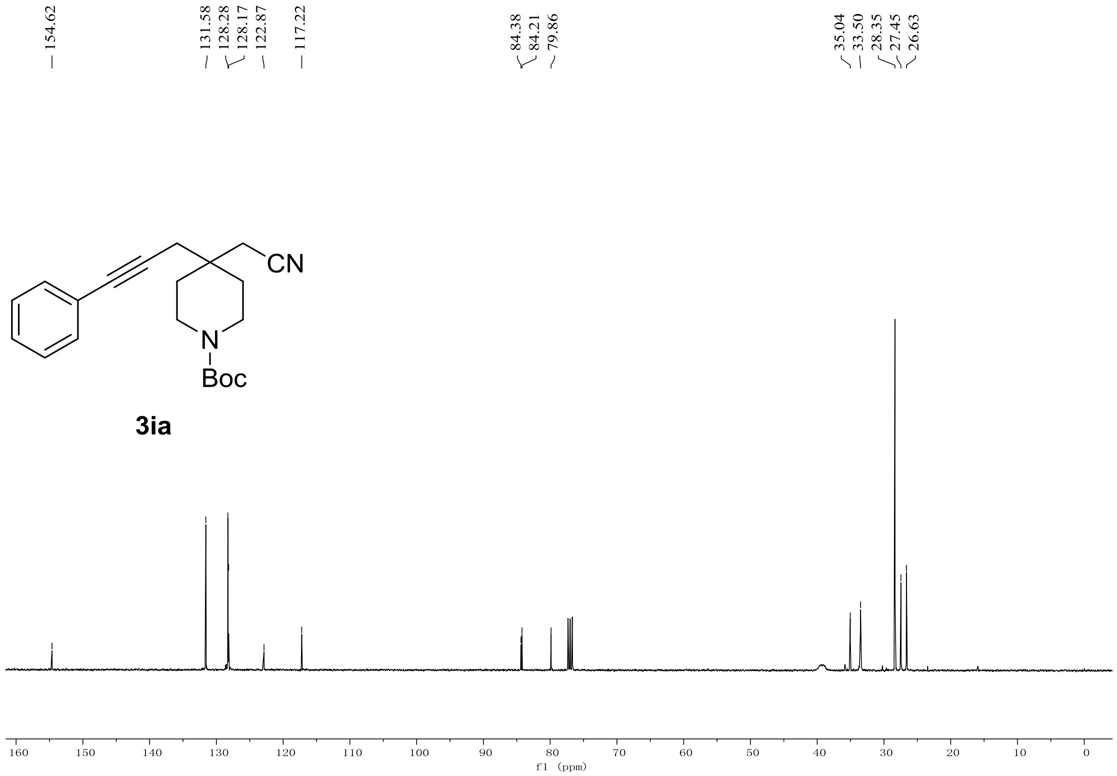
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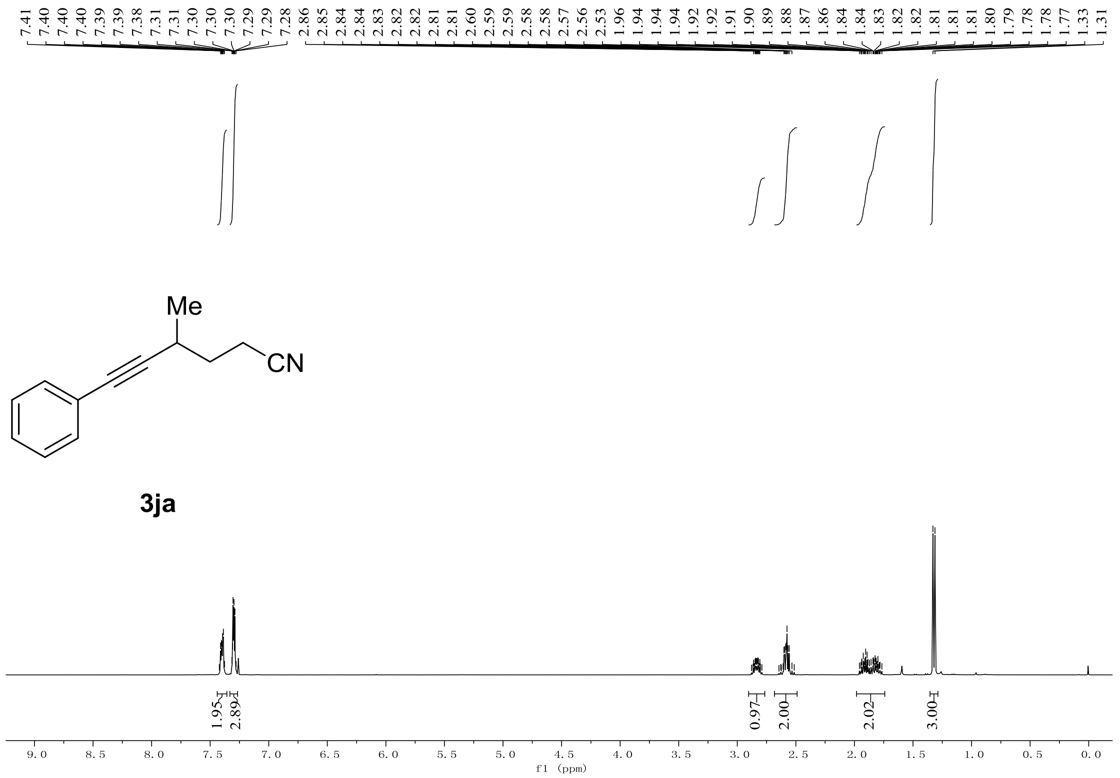
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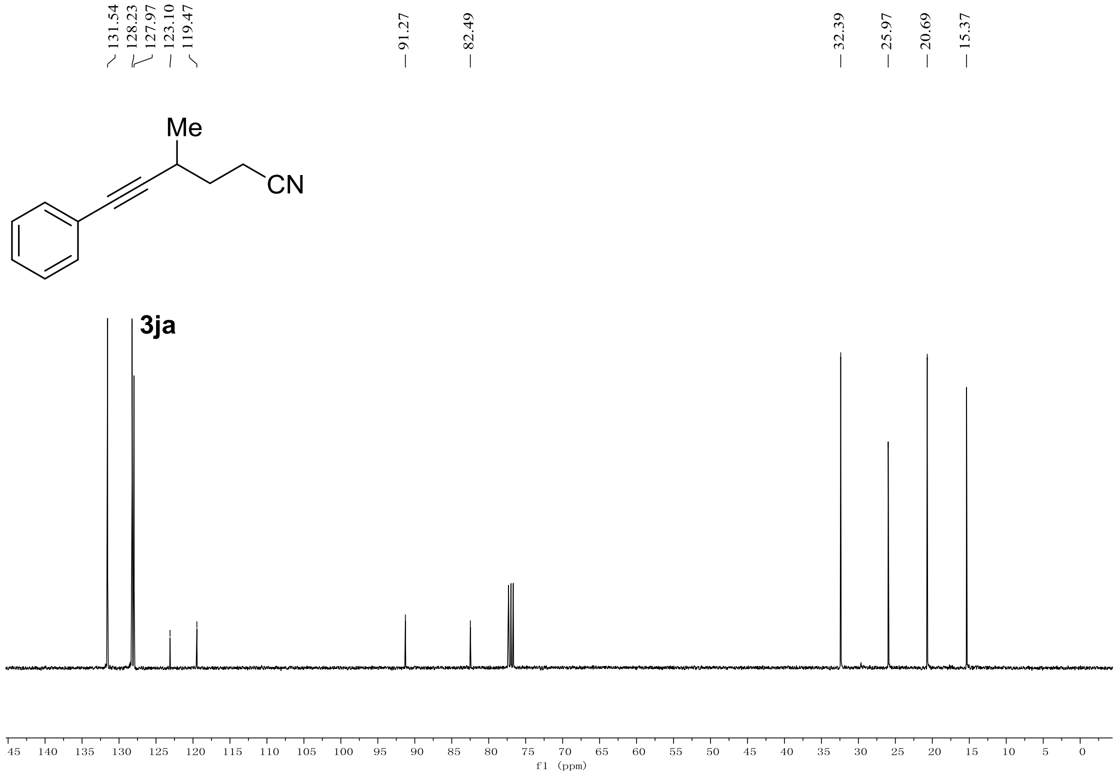
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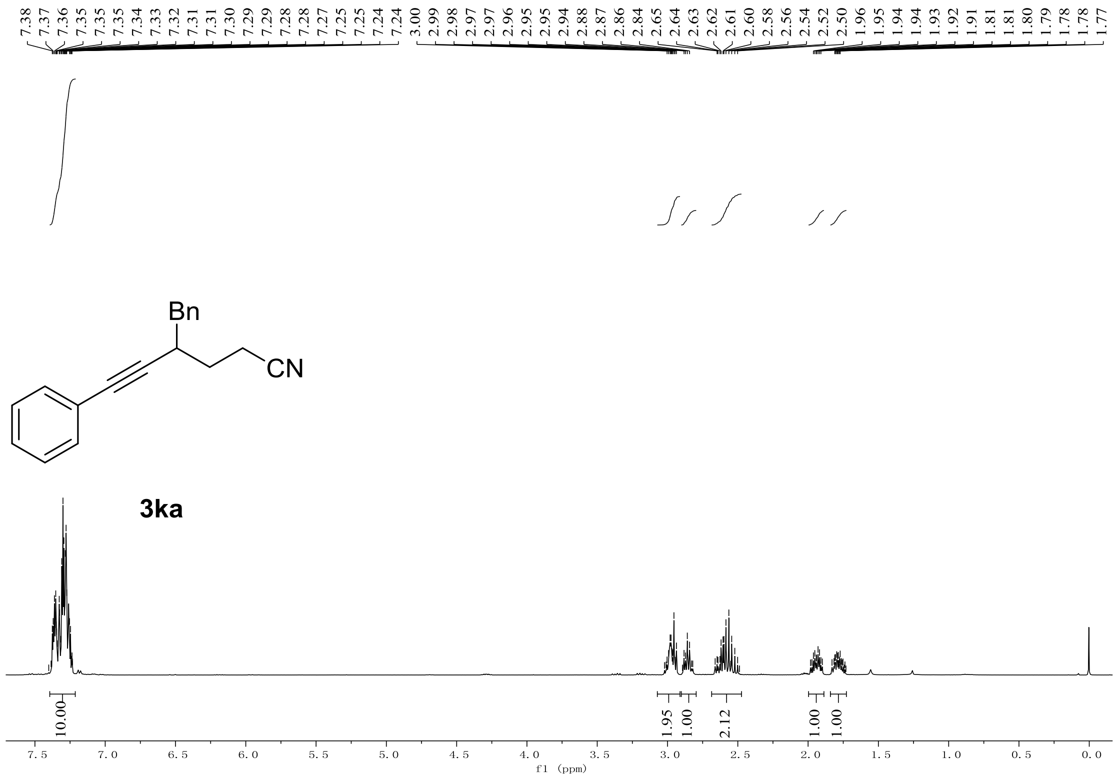
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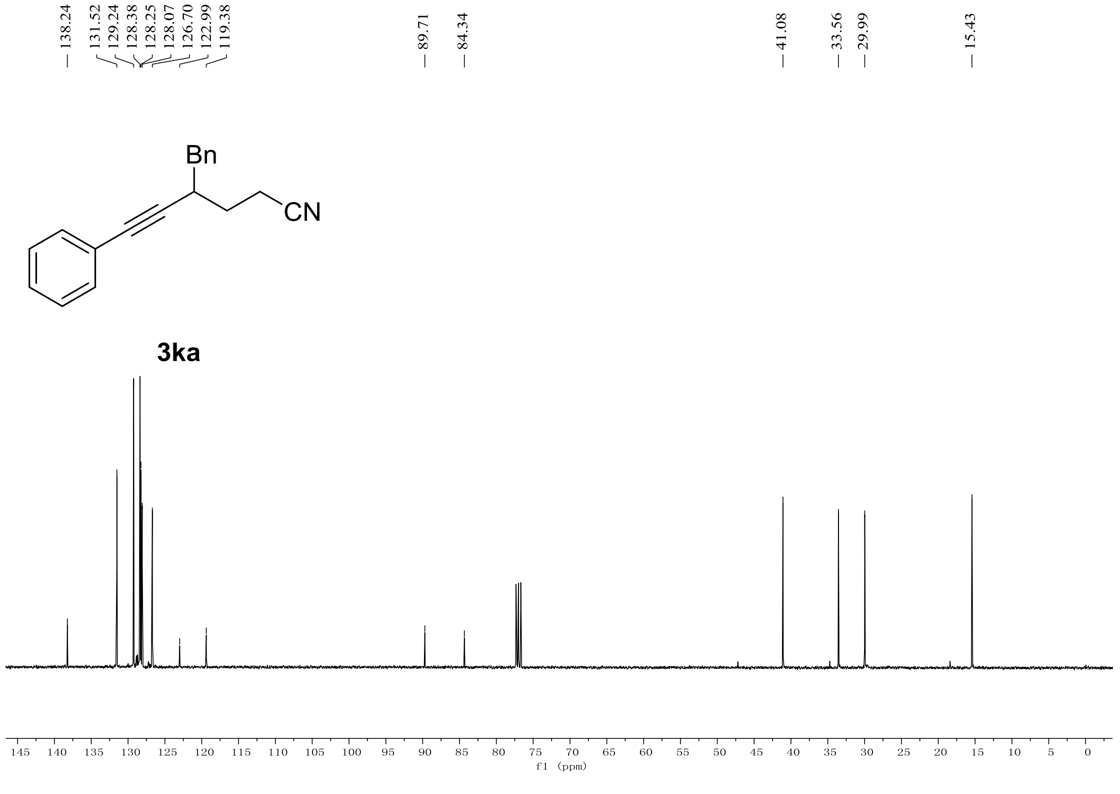
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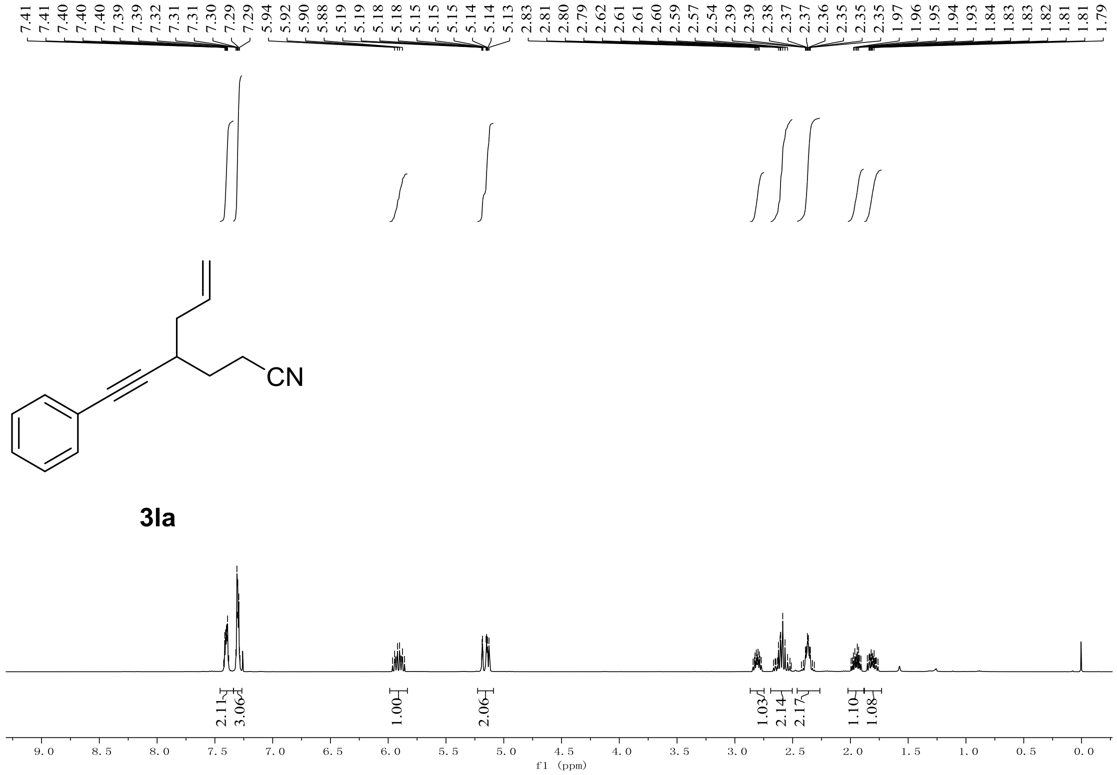
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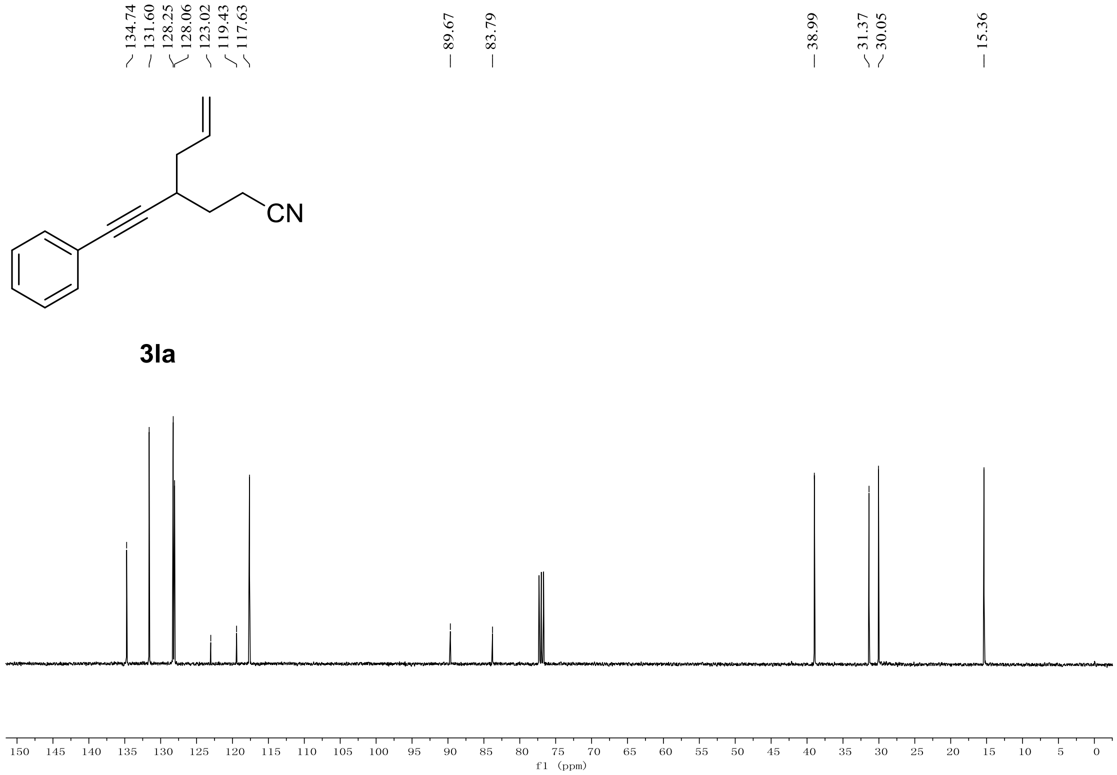
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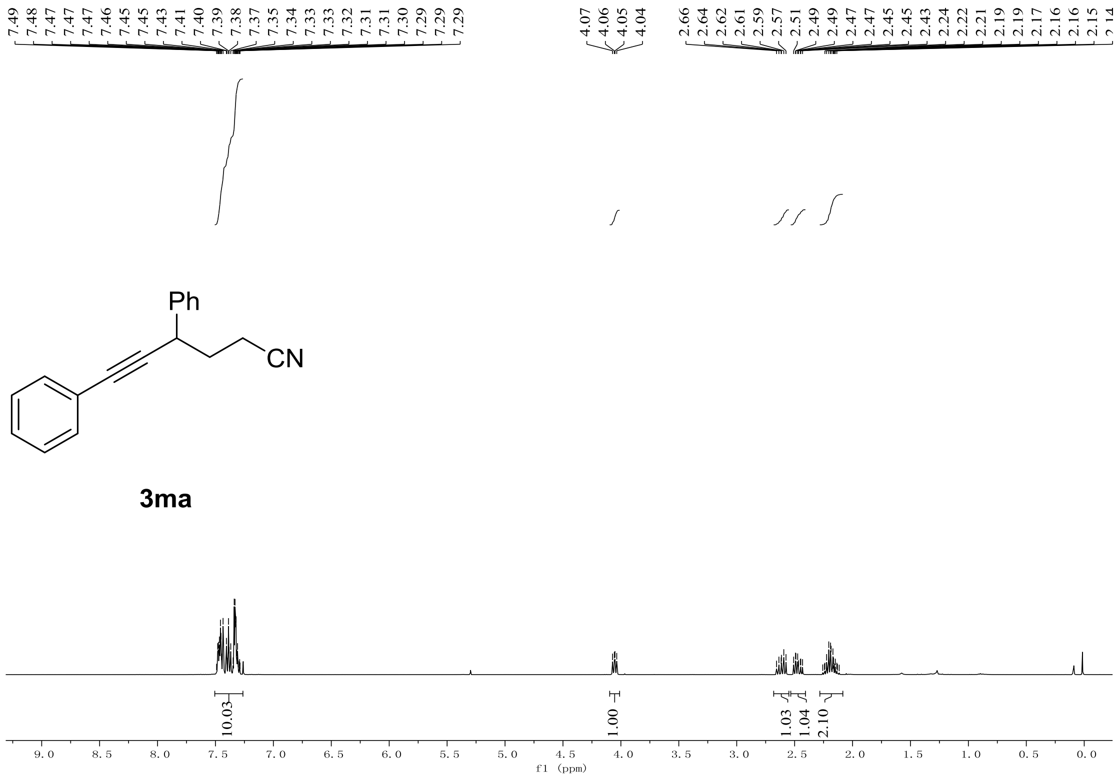
f1 (ppm)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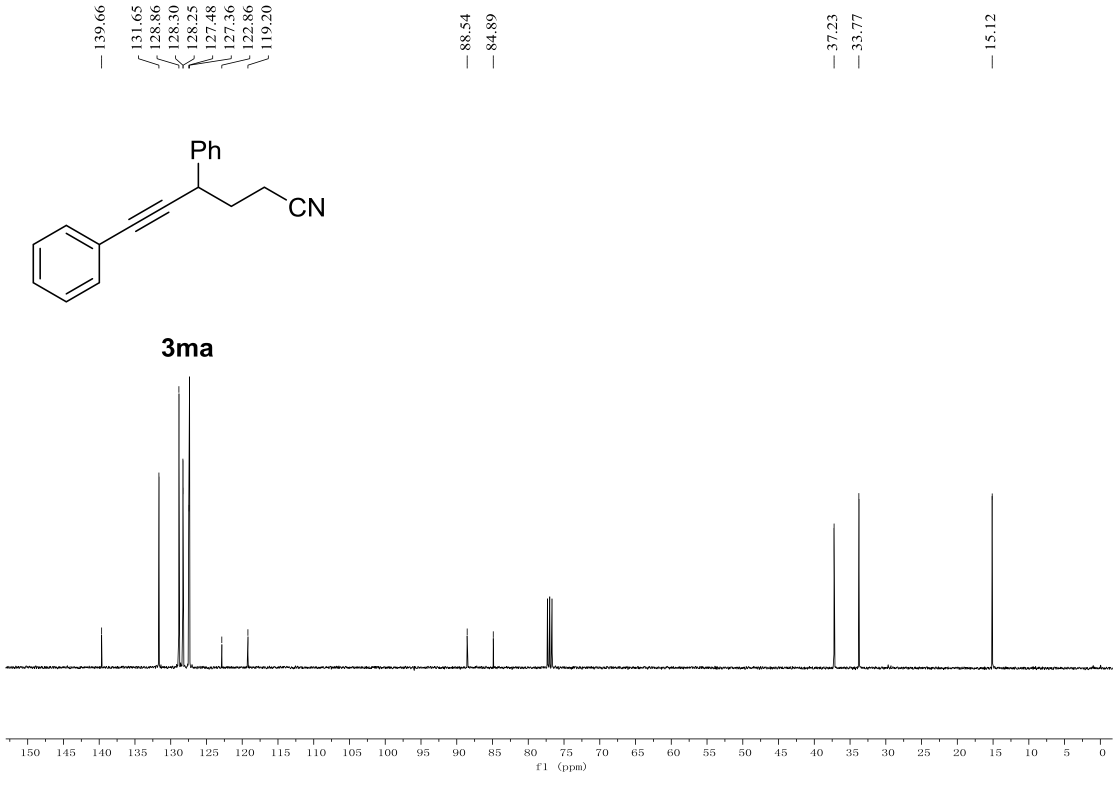
7.39
7.38
7.37
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.29
7.29
4.07
4.06
4.05
4.04
2.66
2.64
2.62
2.61
2.59
2.57
2.51
2.49
2.49
2.47
2.47
2.45
2.45
2.43
2.24
2.22
2.21
2.19
2.19
2.17
2.16
2.15
Ph
CN
3ma
10.03
1.00
1.03
1.04
2.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


139.66
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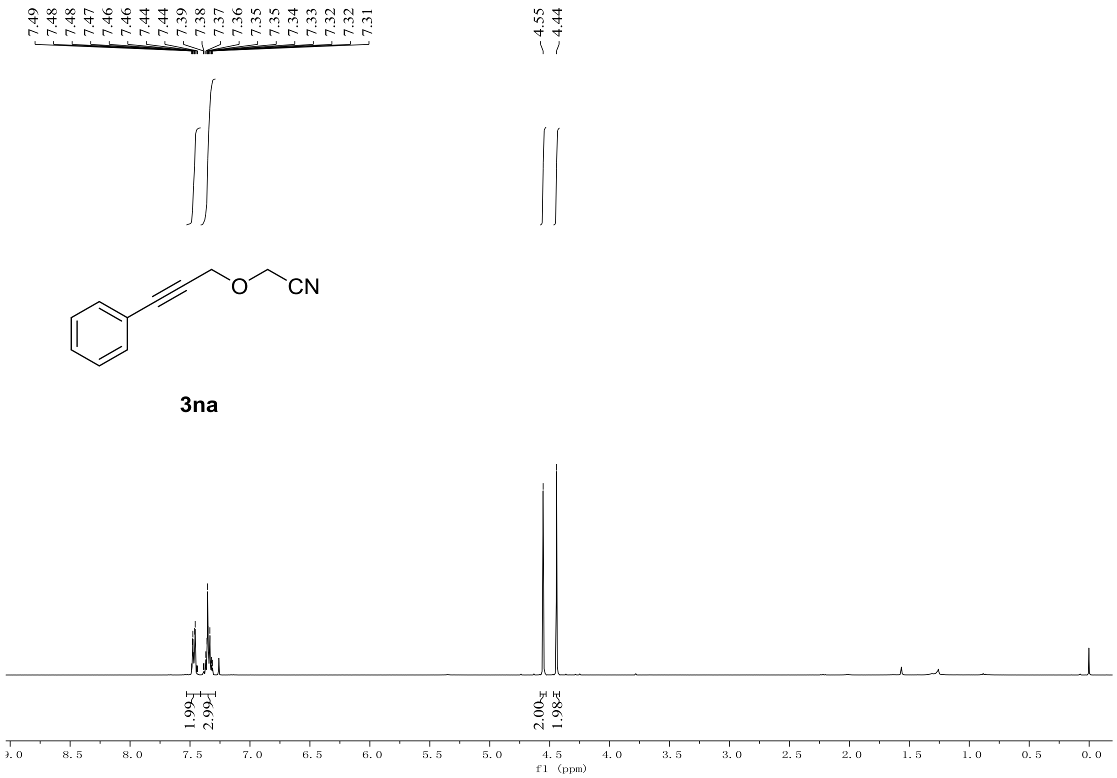
128.30
128.25
127.48
127.36
122.86
119.20
88.54
84.89
37.23
33.77
15.12
Ph
CN
3ma
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)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7.44
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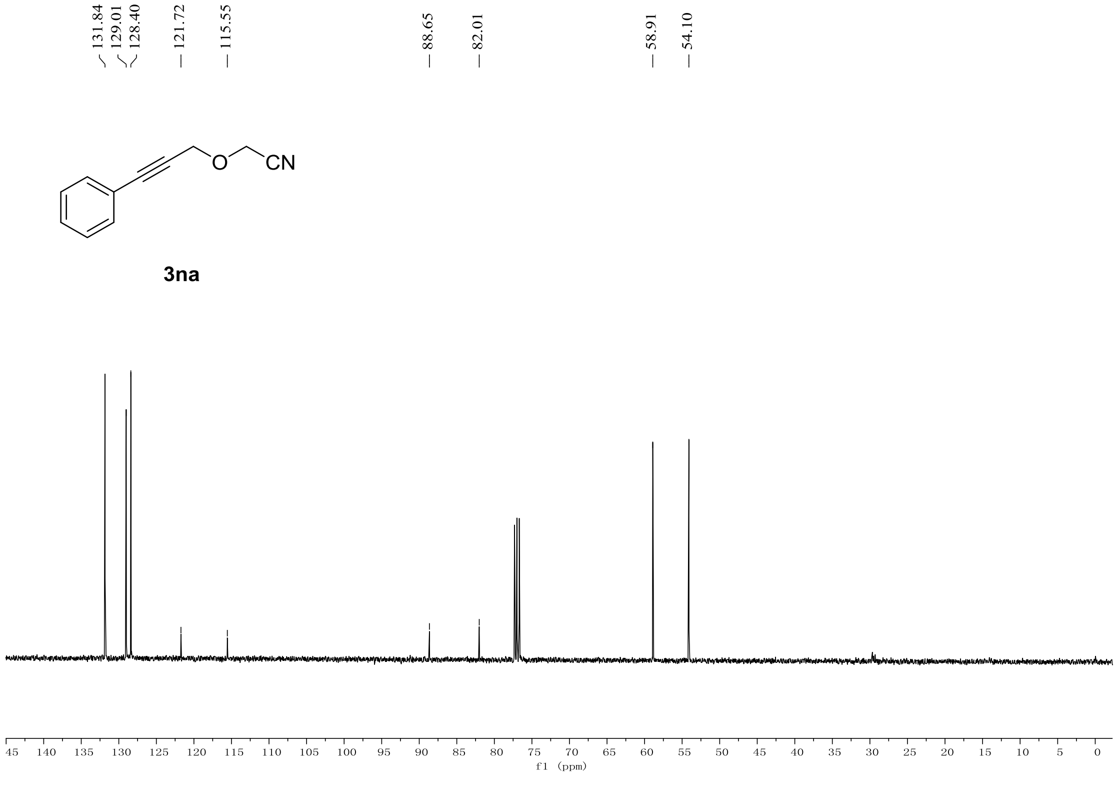
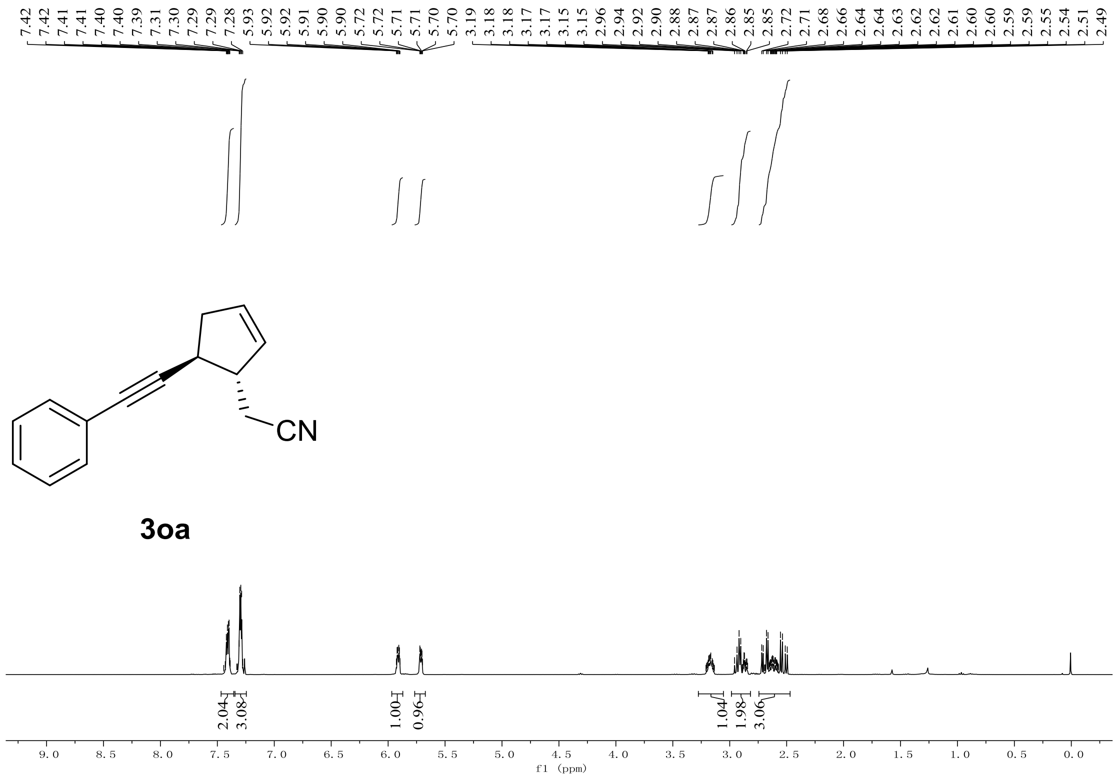
7.38
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.31
4.55
4.44
O
CN
1.99
2.99
2.00
1.98
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3na


131.84
129.01
128.40
121.72
115.55
88.65
82.01
58.91
54.10
O
CN
45 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

3na



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7.41
7.40
7.40
7.39
7.31
7.30
7.29
7.29
7.28
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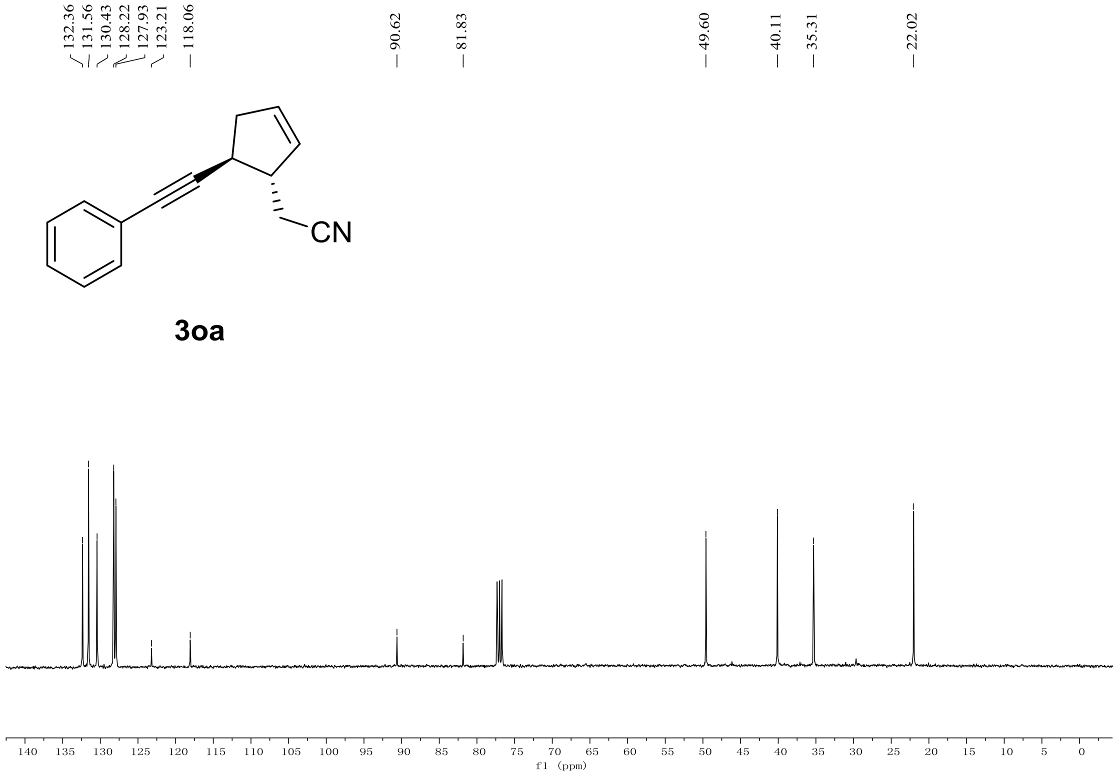
5.92
5.92
5.91
5.90
5.90
5.72
5.72
5.71
5.71
5.70
5.70
3.19
3.18
3.18
3.17
3.17
3.15
3.15
2.96
2.94
2.92
2.90
2.88
2.87
2.87
2.86
2.85
2.85
2.72
2.71
2.68
2.66
2.64
2.64
2.63
2.62
2.62
2.61
2.60
2.60
2.59
2.59
2.55
2.54
2.51
2.49
CN
3oa
2.04
3.08
1.00
0.96
1.04
1.98
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



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131.56
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127.93
123.21
118.06
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49.60
40.11
35.31
22.02
CN
3oa
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
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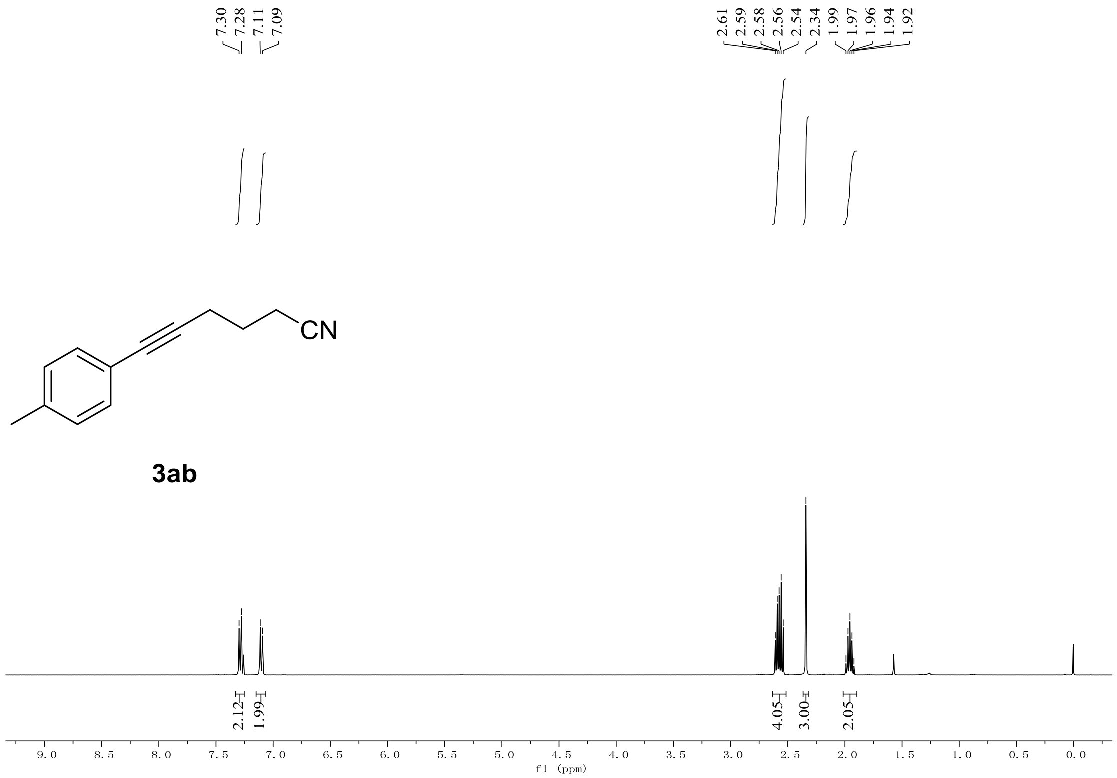
25
20
15
10
5
0
f1 (ppm)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7.11
7.09
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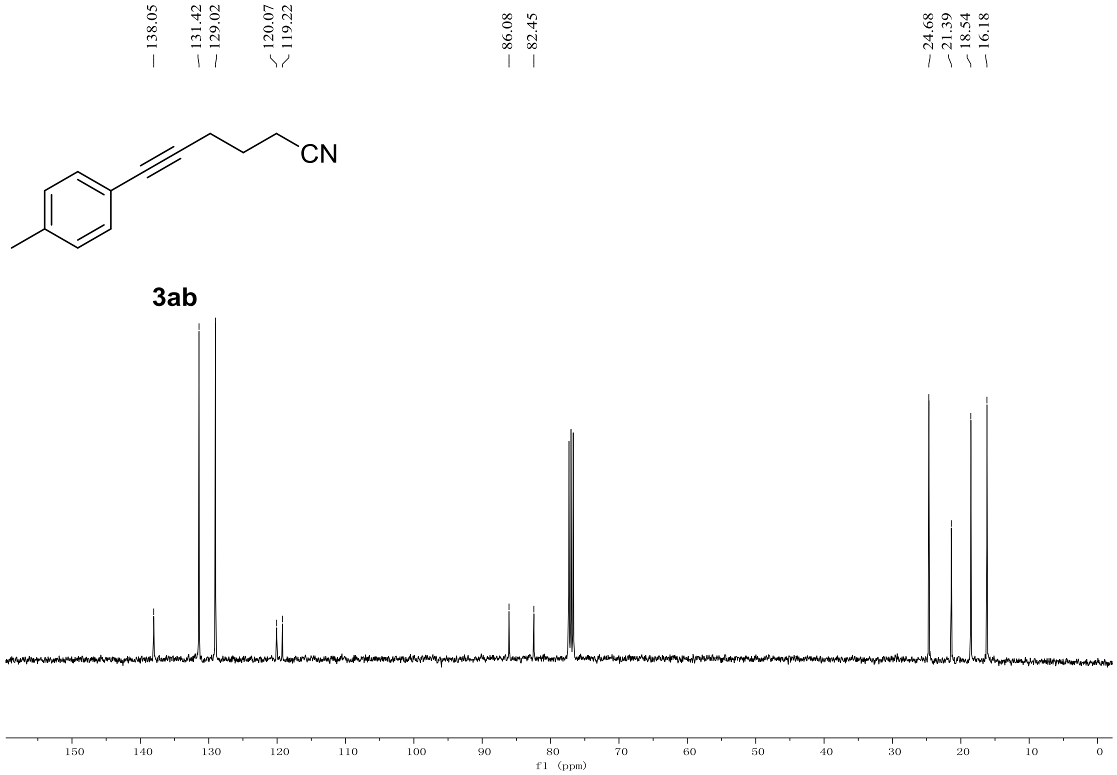
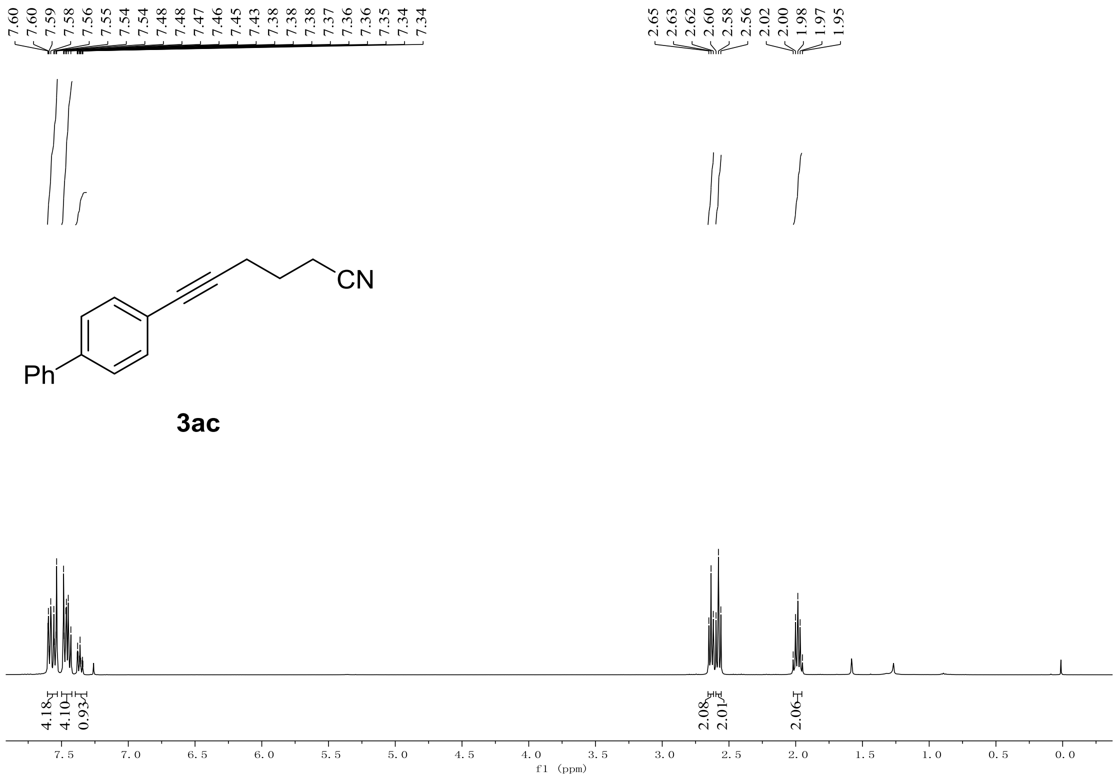
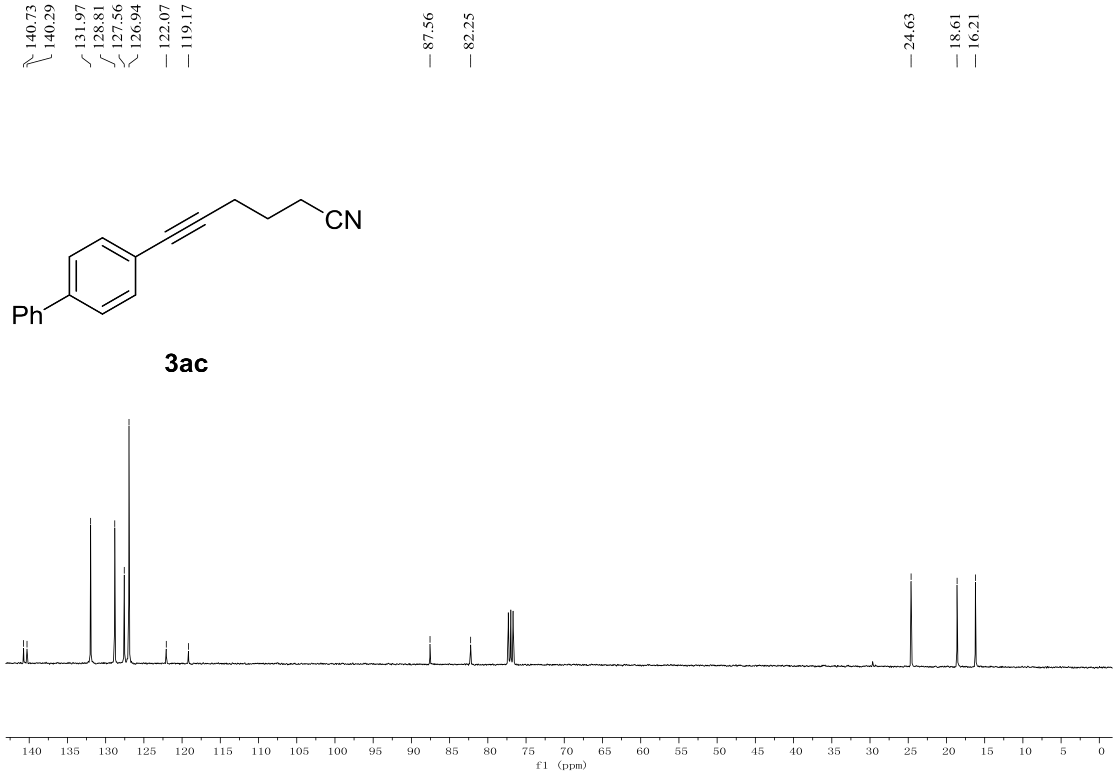
2.59
2.58
2.56
2.54
2.34
1.99
1.97
1.96
1.94
1.92
CN
3ab
2.12
1.99
4.05
3.00
2.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


138.05
131.42
129.02
120.07
119.22
86.08
82.45
24.68
21.39
18.54
16.18
CN
3ab
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.60
7.60
7.59
7.58
7.56
7.55
7.54
7.54
7.48
7.48
7.47
7.46
7.45
7.43
7.38
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
2.65
2.63
2.62
2.60
2.58
2.56
2.02
2.00
1.98
1.97
1.95
CN
Ph
3ac
4.18
4.10
0.93
2.08
2.01
2.06
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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140.29
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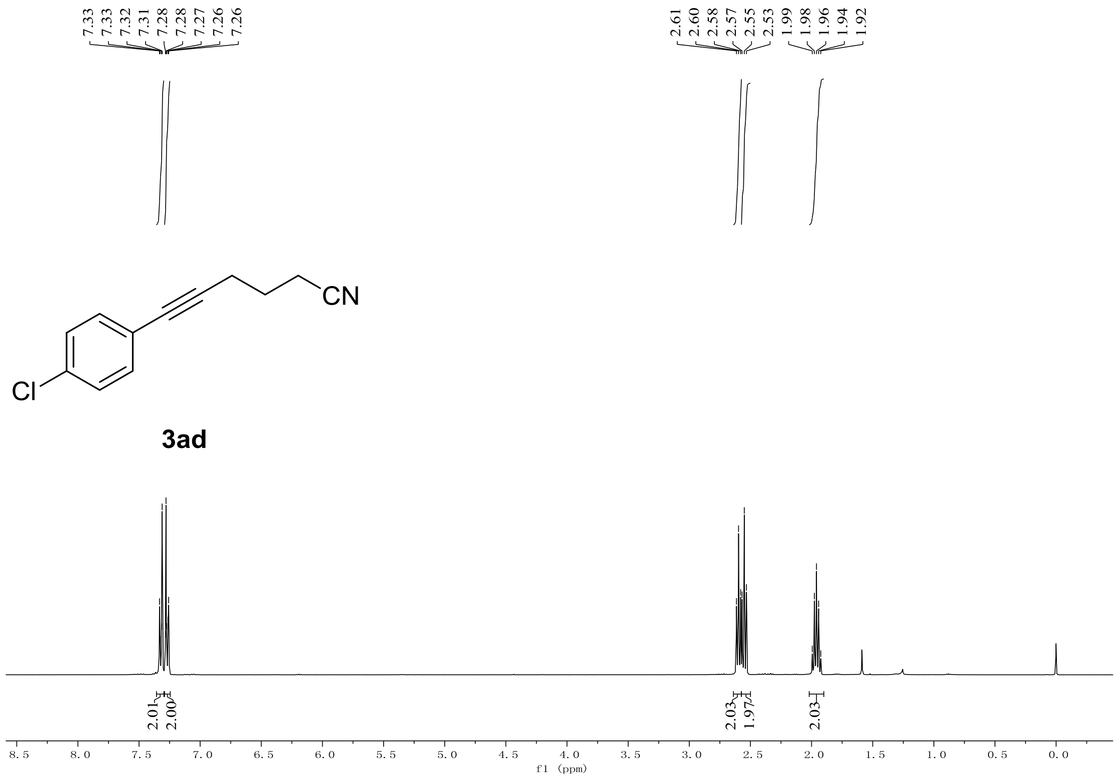
128.81
127.56
126.94
122.07
119.17
87.56
82.25
24.63
18.61
16.21
CN
Ph
3ac
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)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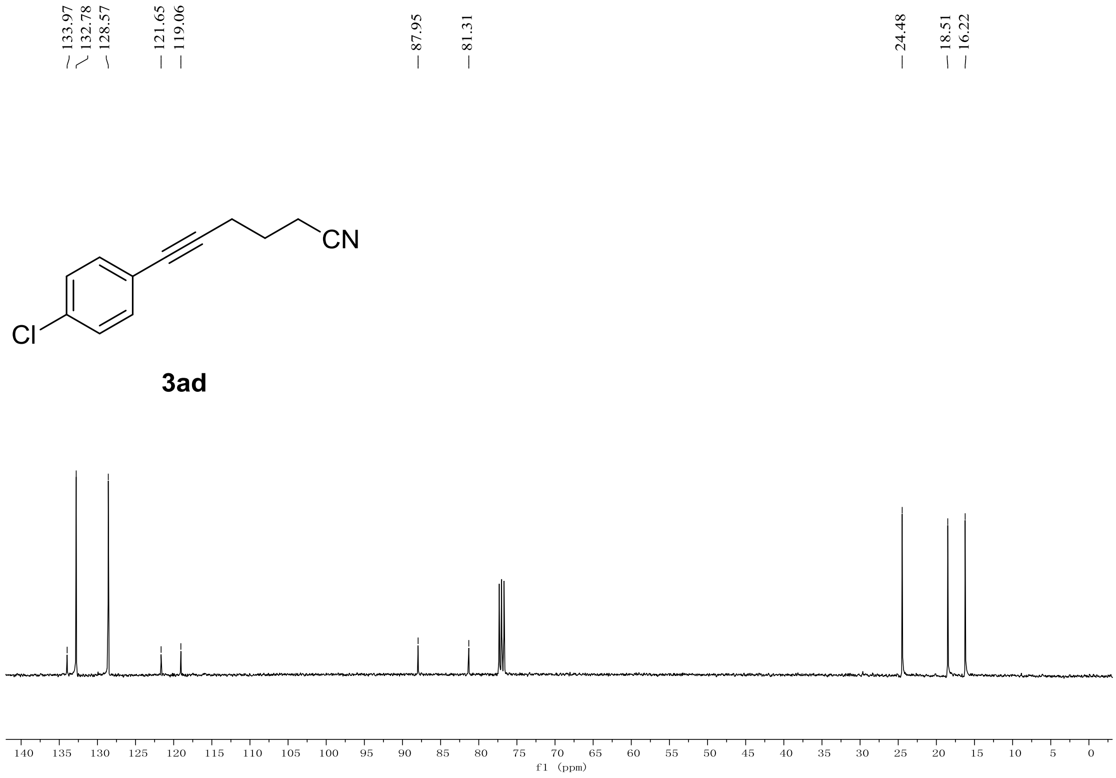
7.33
7.32
7.31
7.28
7.28
7.27
7.26
7.26
2.61
2.60
2.58
2.57
2.55
2.53
1.99
1.98
1.96
1.94
1.92
CN
Cl
3ad
2.01
2.00
2.03
1.97
2.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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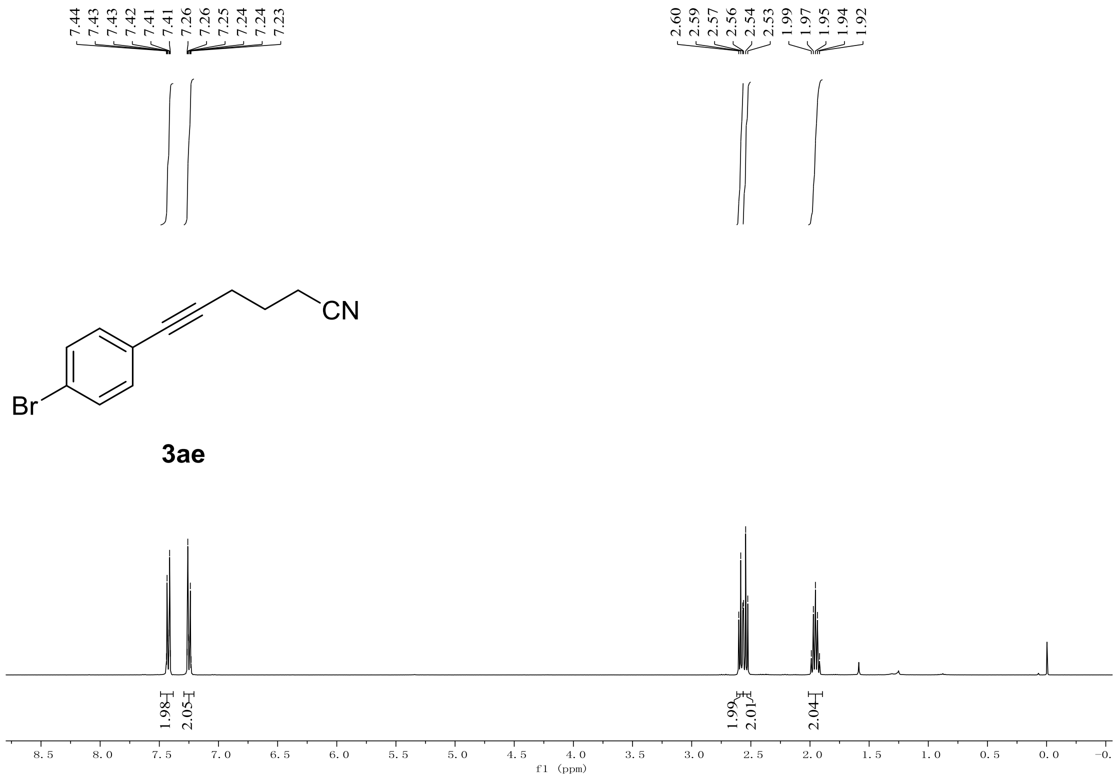
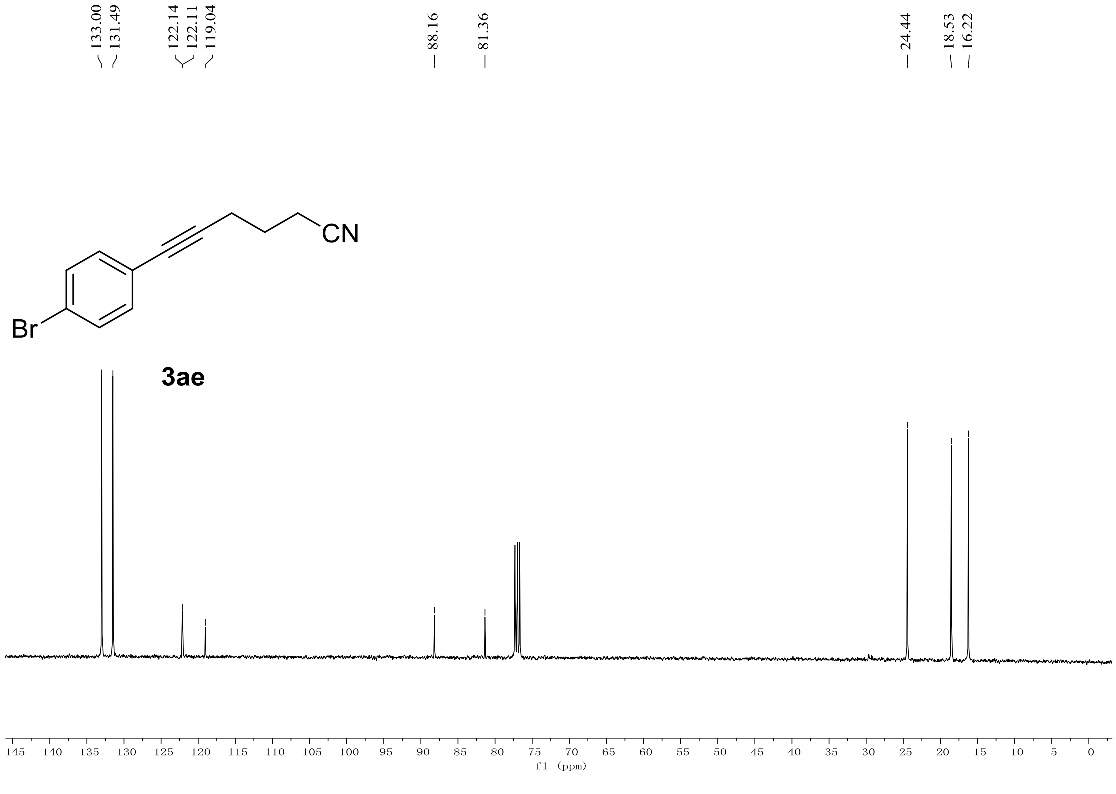
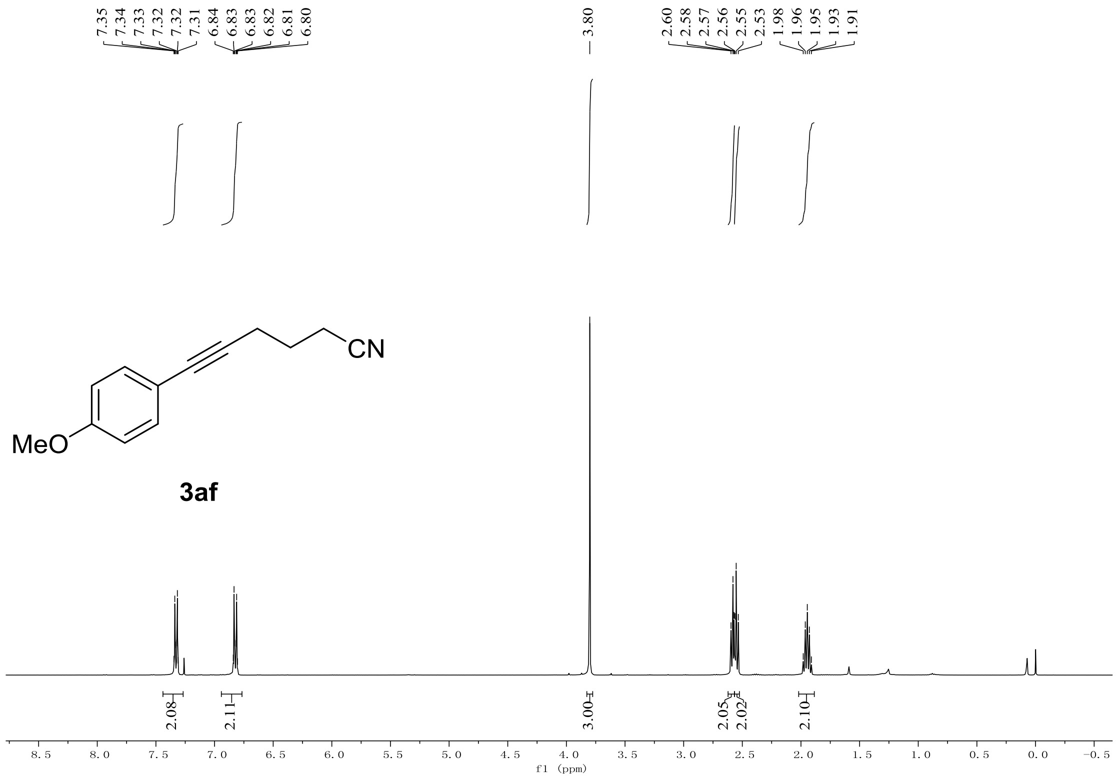
132.78
128.57
121.65
119.06
87.95
81.31
24.48
18.51
16.22
CN
Cl
3ad
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


7.44
7.43
7.43
7.42
7.41
7.41
7.26
7.26
7.25
7.24
7.24
7.23
2.60
2.59
2.57
2.56
2.54
2.53
1.99
1.97
1.95
1.94
1.92
Br
CN
1.98
2.05
1.99
2.01
2.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

3ae

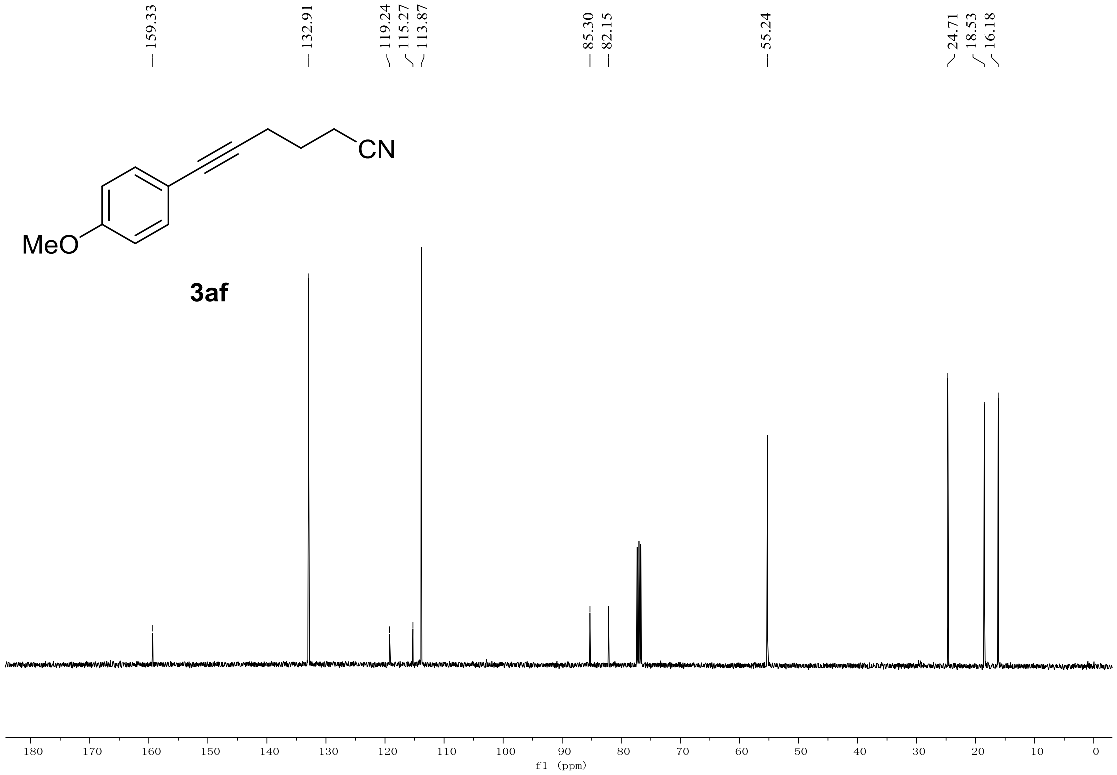

133.00
131.49
122.14
122.11
119.04
88.16
81.36
24.44
18.53
16.22
Br
CN
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

3ae



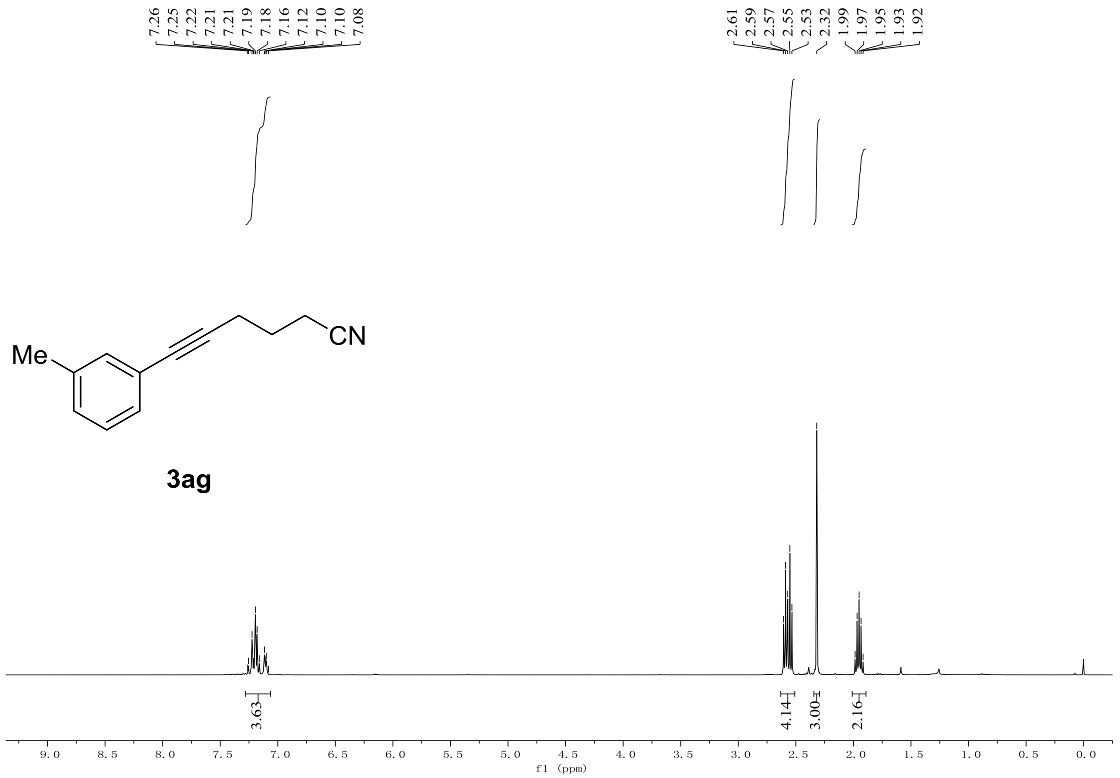
3af

7.35
7.34
7.33
7.32
7.32
7.31
6.84
6.83
6.83
6.82
6.81
6.80
3.80
2.60
2.58
2.57
2.56
2.55
2.53
1.98
1.96
1.95
1.93
1.91
CN
MeO
2.08
2.11
3.00
2.05
2.02
2.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



3af

159.33
132.91
119.24
115.27
113.87
85.30
82.15
55.24
24.71
18.53
16.18
CN
MeO
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.22
7.21
7.21
7.19
7.18
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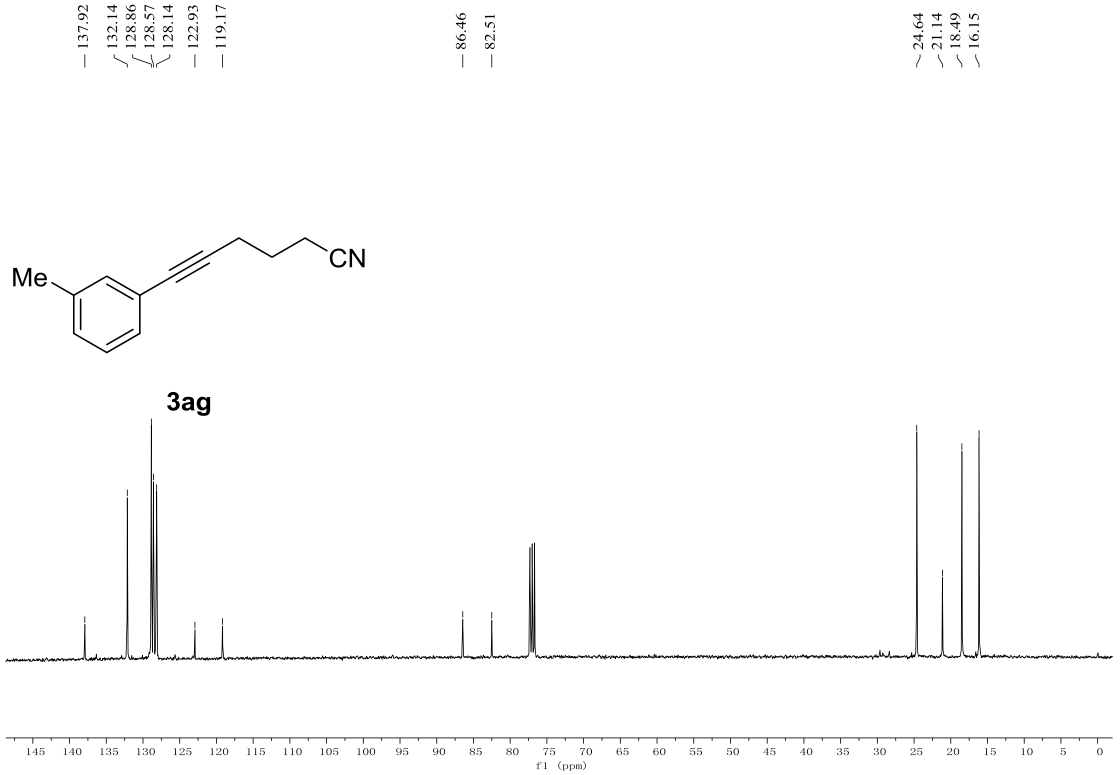
7.12
7.10
7.10
7.08
2.61
2.59
2.57
2.55
2.53
2.32
1.99
1.97
1.95
1.93
1.92
Me
CN
3ag
3.63
4.14
3.00
2.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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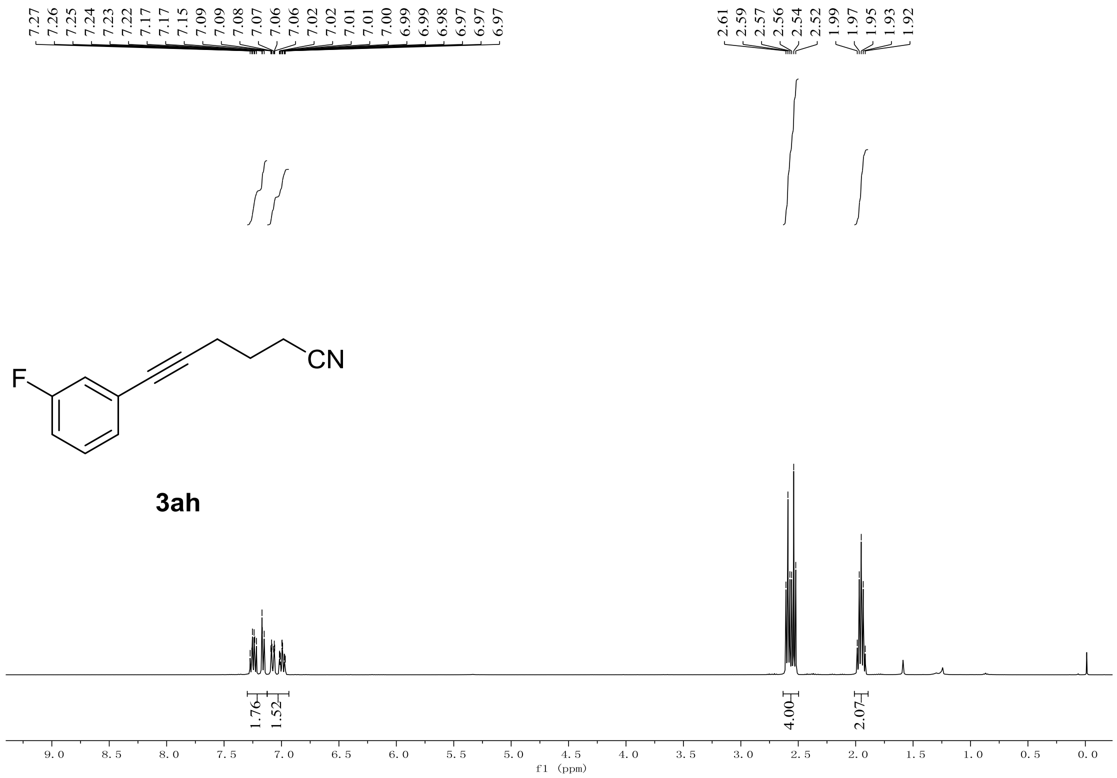
128.14
122.93
119.17
86.46
82.51
24.64
21.14
18.49
16.15
Me
CN
3ag
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)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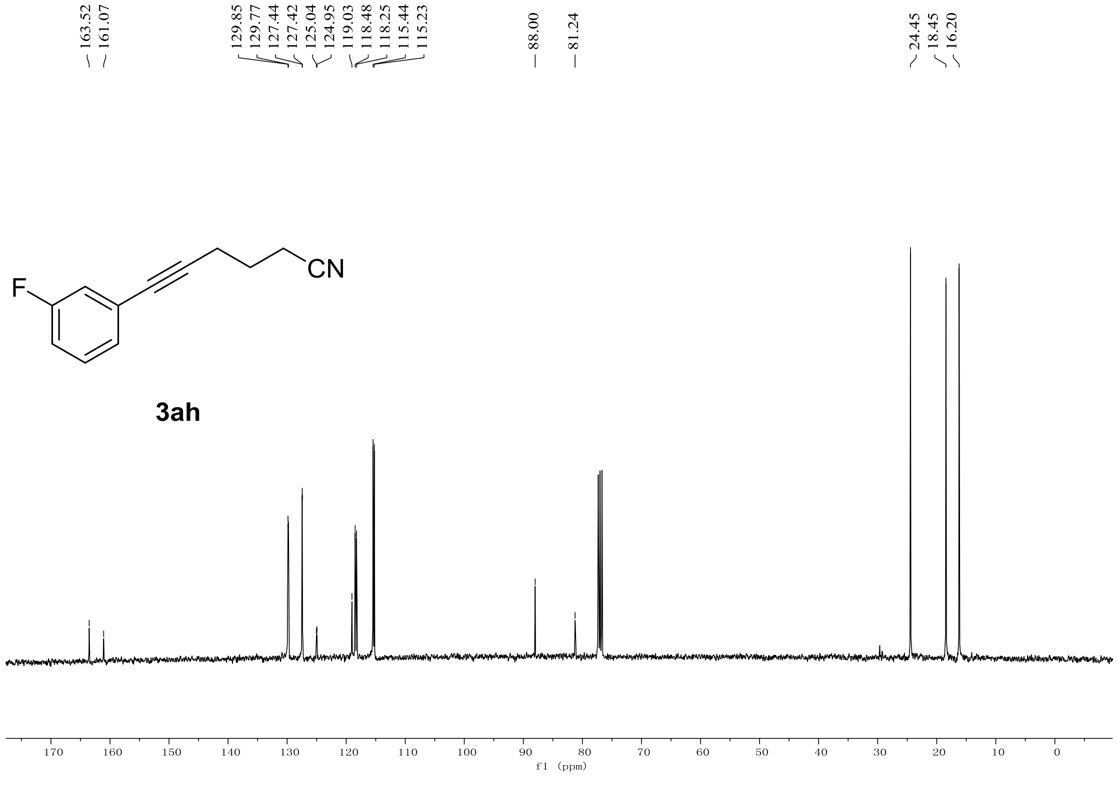
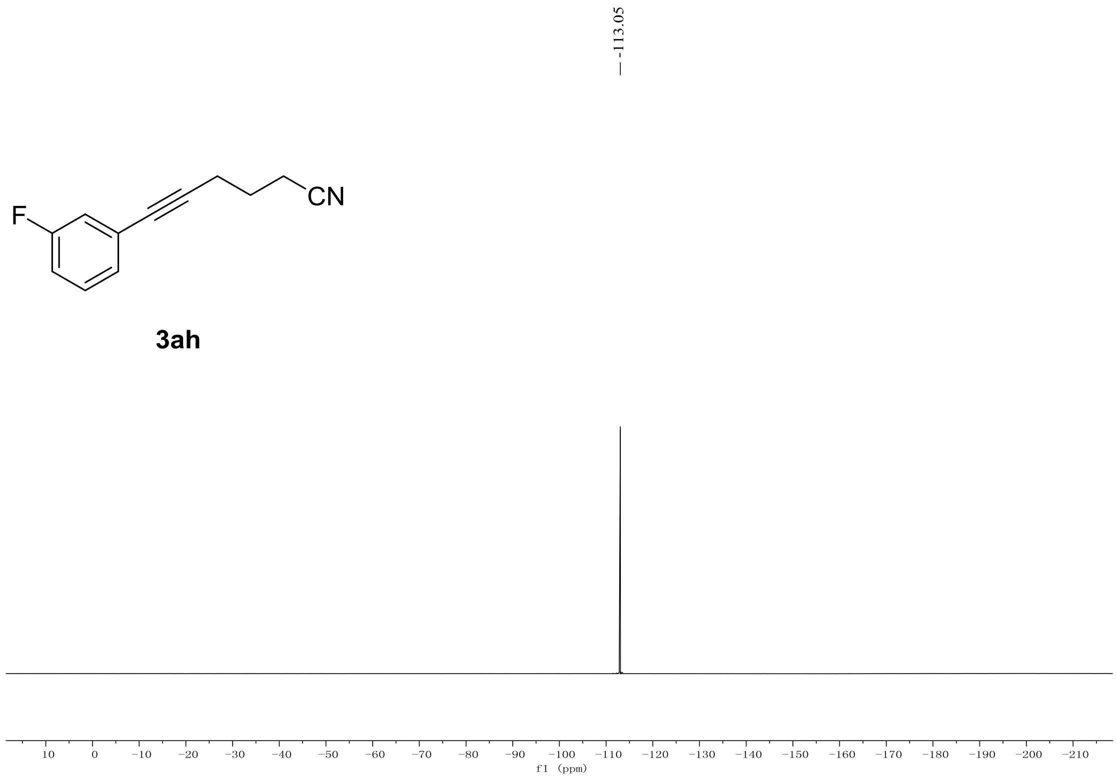
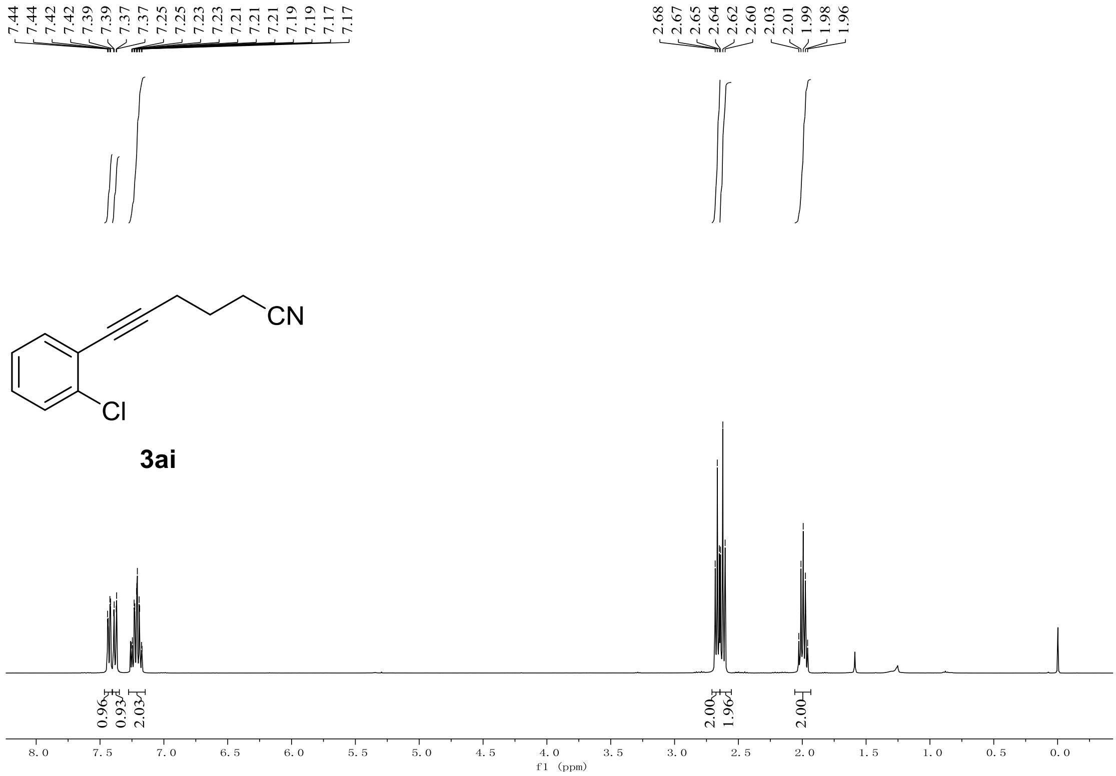
7.25
7.24
7.23
7.22
7.17
7.17
7.15
7.09
7.09
7.08
7.07
7.06
7.06
7.02
7.02
7.01
7.01
7.00
6.99
6.99
6.98
6.97
6.97
6.97
2.61
2.59
2.57
2.56
2.54
2.52
1.99
1.97
1.95
1.93
1.92
F
CN
3ah
1.76
1.52
4.00
2.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.52
161.07
129.85
129.77
127.44
127.42
125.04
124.95
119.03
118.48
118.25
115.44
115.23
88.00
81.24
24.45
18.45
16.20
F
CN
3ah
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-113.05
F
CN
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

3ah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7.44
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7.42
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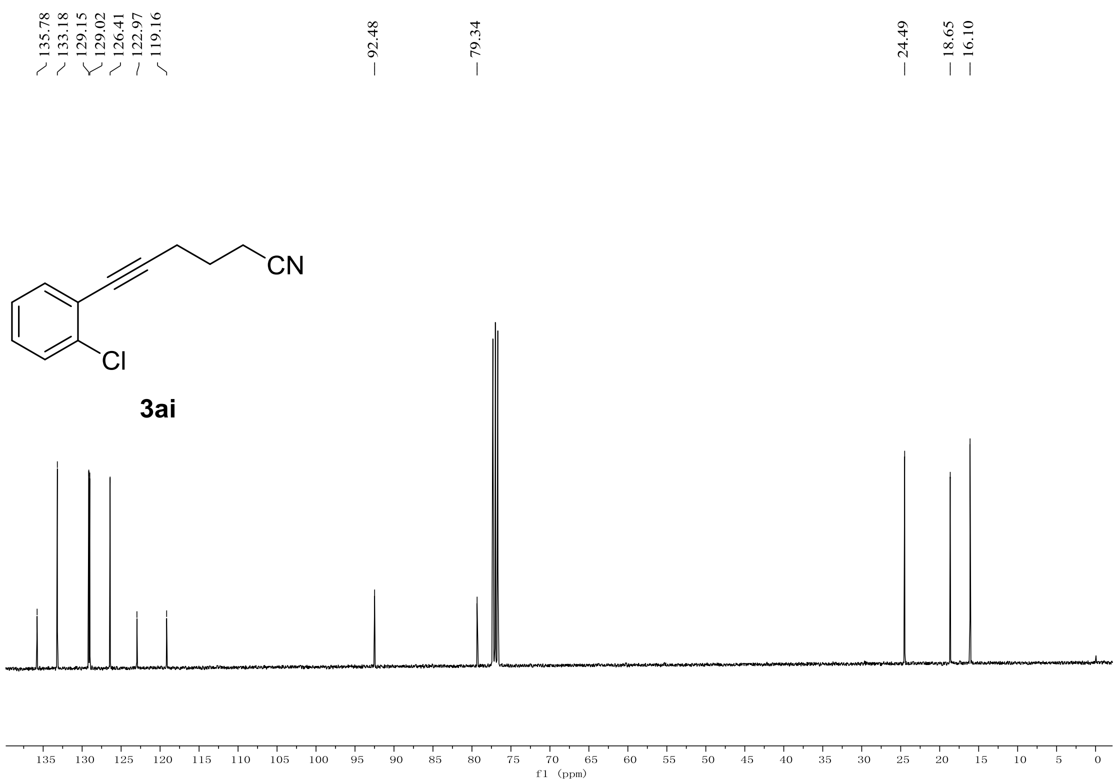
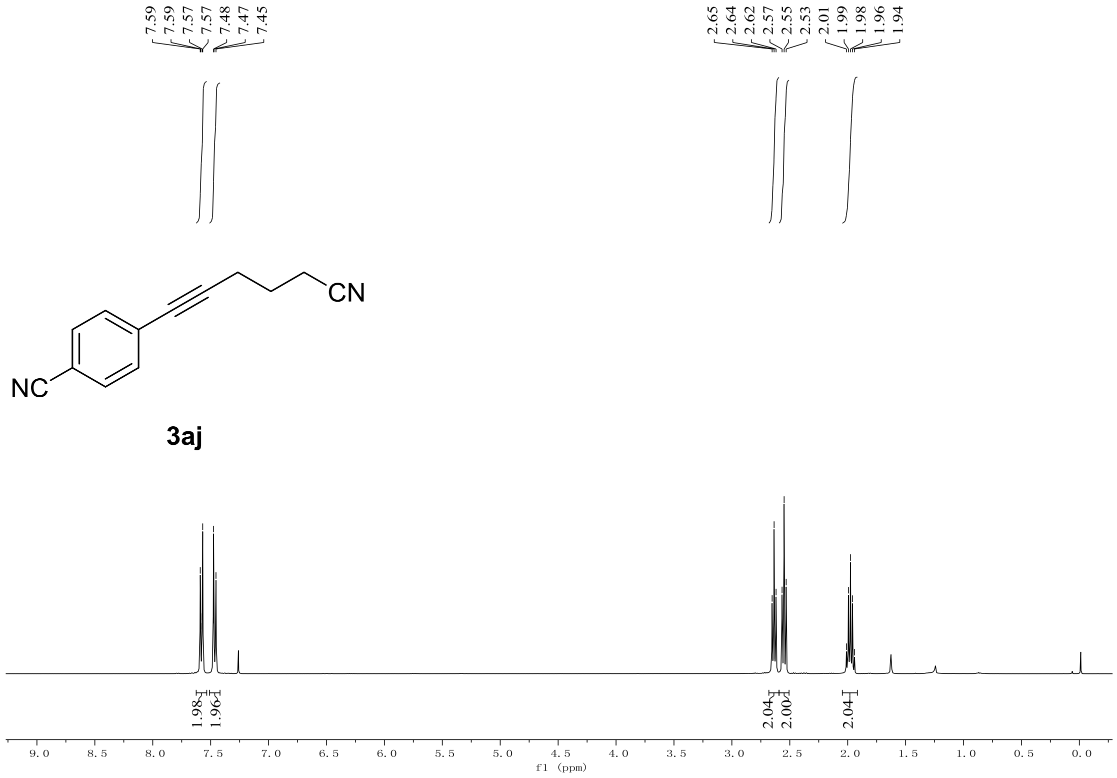
7.25
7.23
7.23
7.21
7.21
7.21
7.19
7.17
7.17
2.68
2.67
2.65
2.64
2.62
2.60
2.03
2.01
1.99
1.98
1.96
CN
Cl
0.96
0.93
2.03
2.00
1.96
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

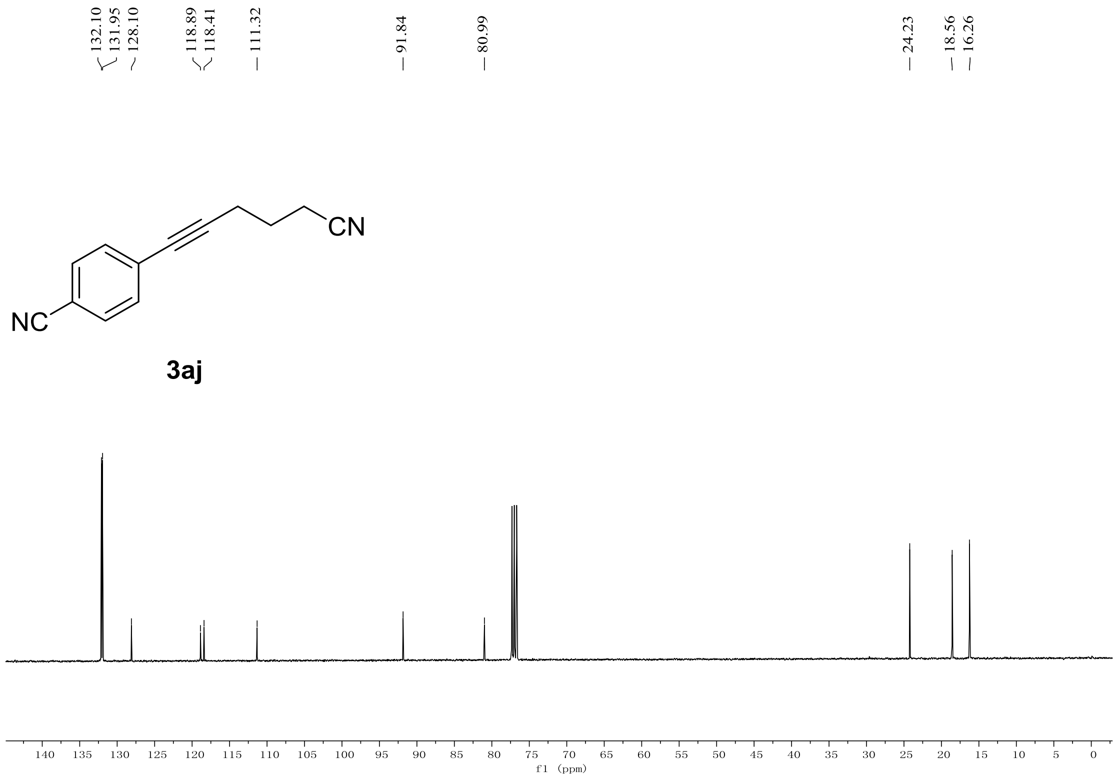
3ai


135.78
133.18
129.15
129.02
126.41
122.97
119.16
92.48
79.34
24.49
18.65
16.10
CN
Cl
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

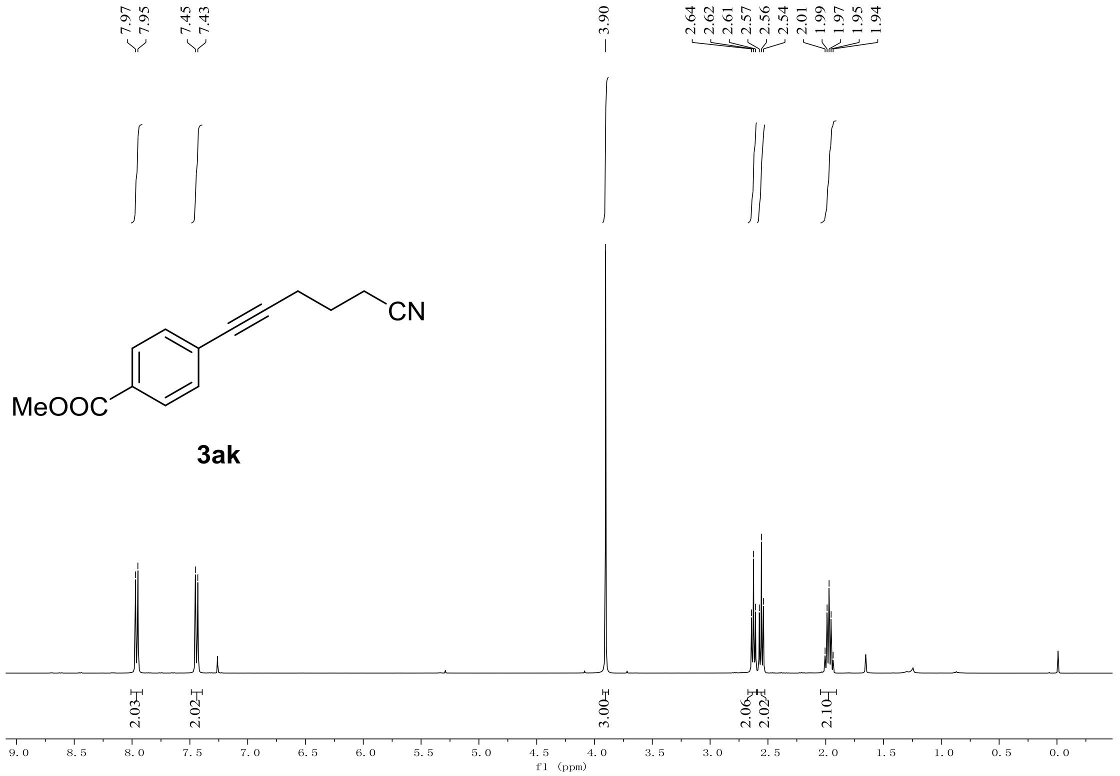
3ai


7.59
7.59
7.57
7.57
7.48
7.47
7.45
2.65
2.64
2.62
2.57
2.55
2.53
2.01
1.99
1.98
1.96
1.94
CN
NC
1.98
1.96
2.04
2.00
2.04
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)

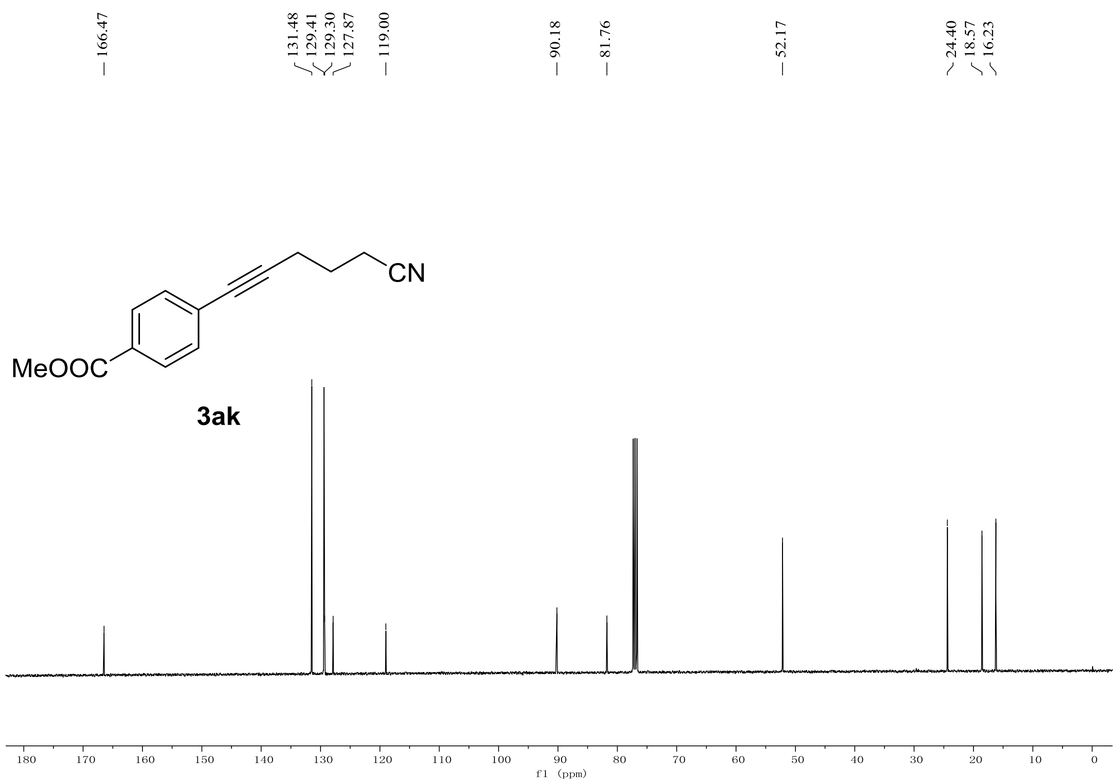
3aj


132.10
131.95
128.10
118.89
118.41
111.32
91.84
80.99
24.23
18.56
16.26
CN
NC
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

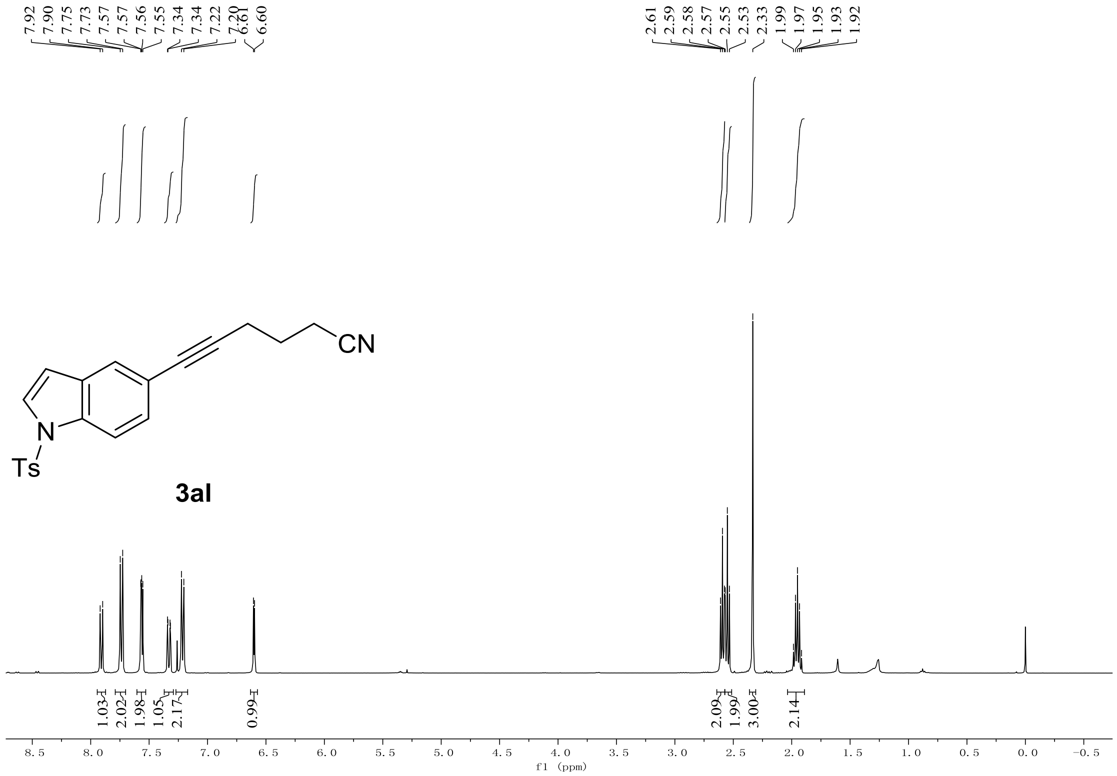
3aj


7.97
7.95
7.45
7.43
3.90
2.64
2.62
2.61
2.57
2.56
2.54
2.01
1.99
1.97
1.95
1.94
CN
MeOOC
2.03
2.02
3.00
2.06
2.02
2.10
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)

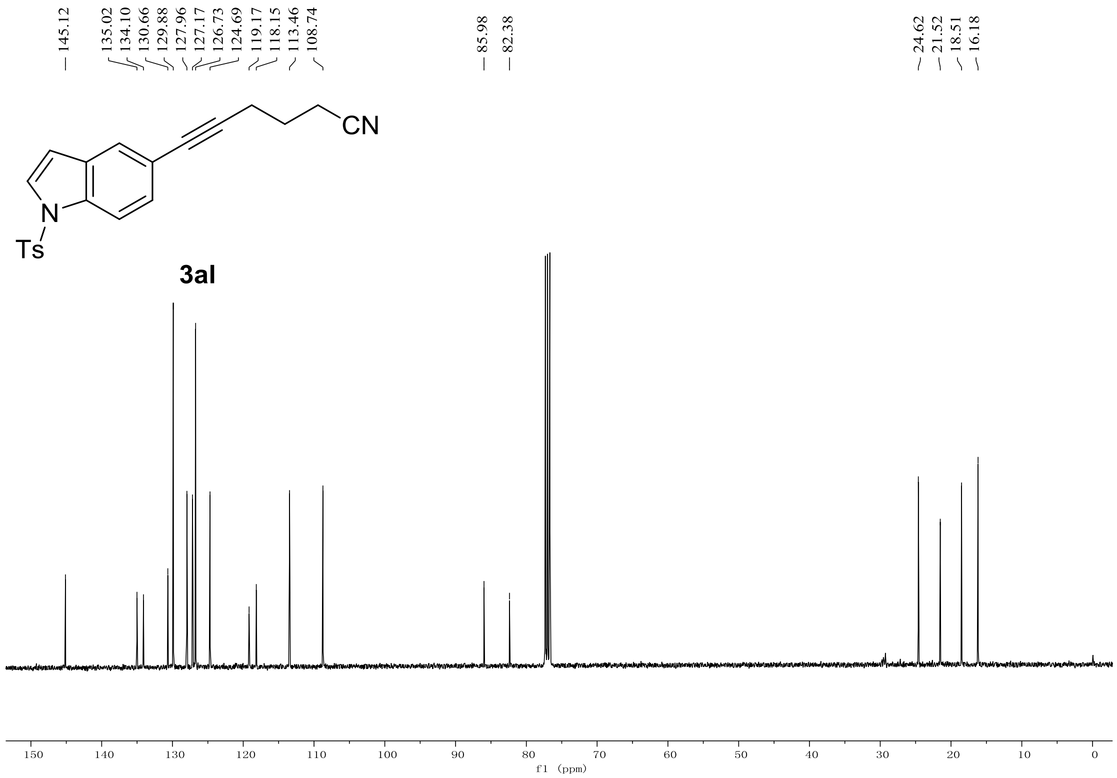
3ak


166.47
131.48
129.41
129.30
127.87
119.00
90.18
81.76
52.17
24.40
18.57
16.23
MeOOC
CN
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

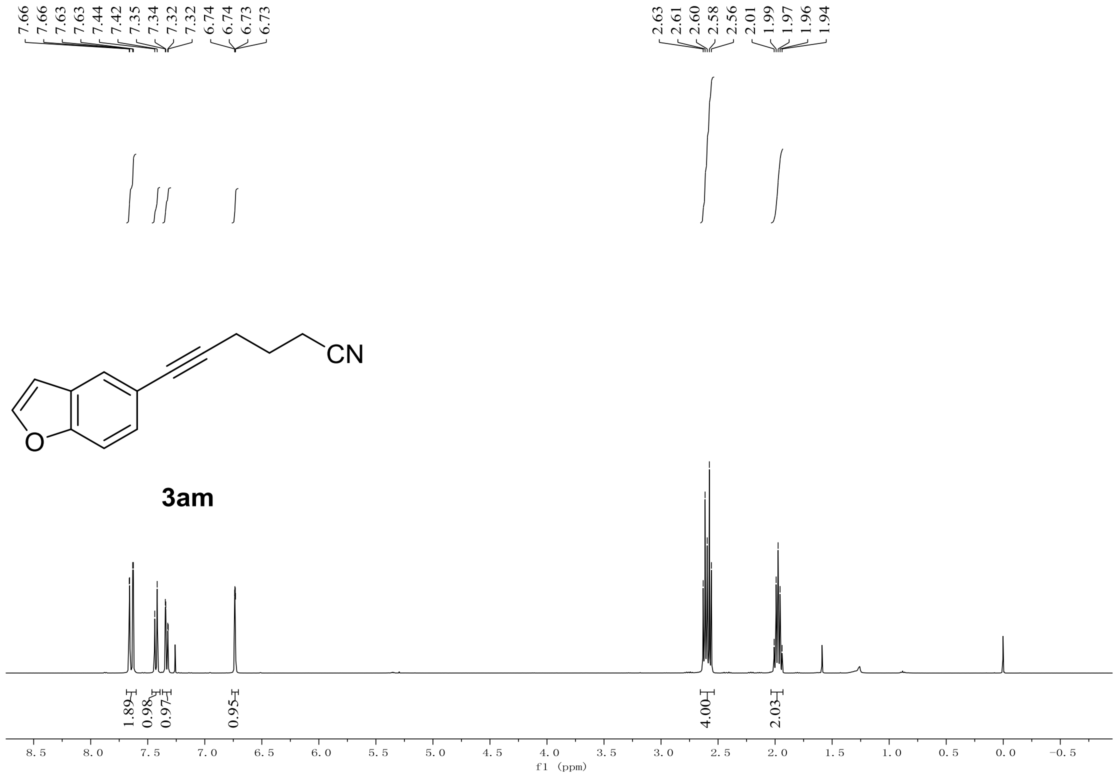
3ak


7.92
7.90
7.75
7.73
7.57
7.57
7.56
7.55
7.34
7.34
7.22
7.20
6.61
6.60
2.61
2.59
2.58
2.57
2.55
2.53
2.33
1.99
1.97
1.95
1.93
1.92
N
Ts
CN
1.03
2.02
1.98
1.05
2.17
0.99
2.09
1.99
3.00
2.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

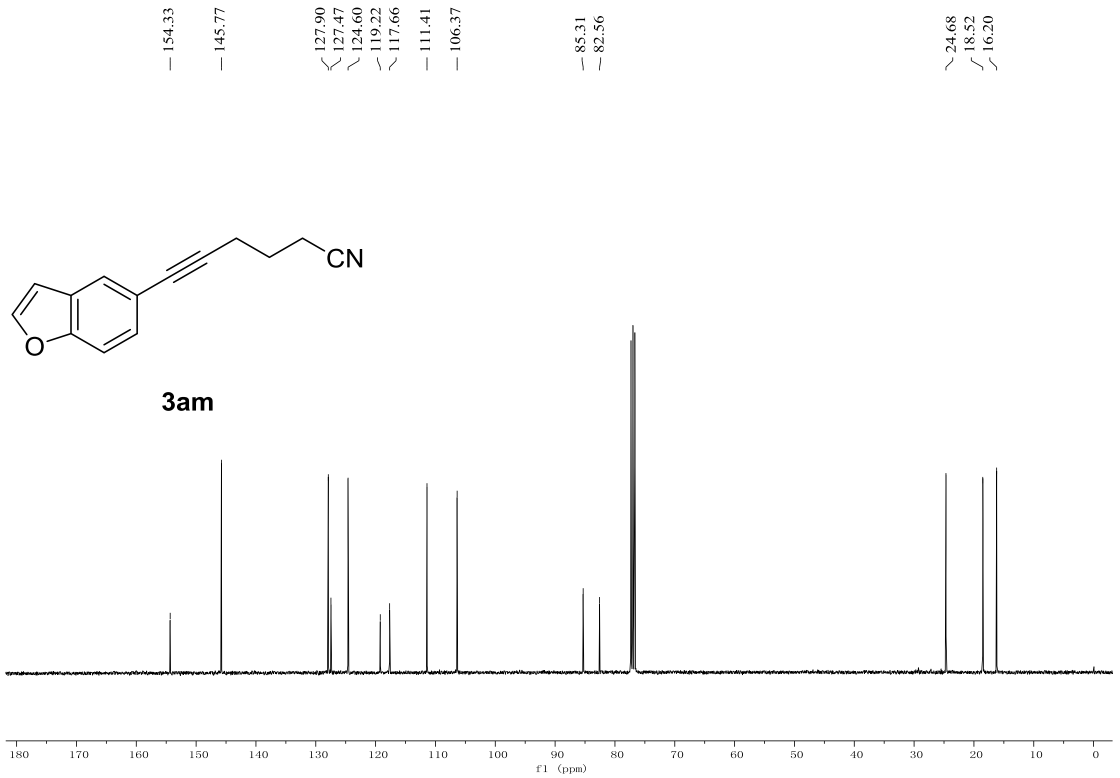
3al


145.12
135.02
134.10
130.66
129.88
127.96
127.17
126.73
124.69
119.17
118.15
113.46
108.74
85.98
82.38
24.62
21.52
18.51
16.18
CN
N
Ts
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

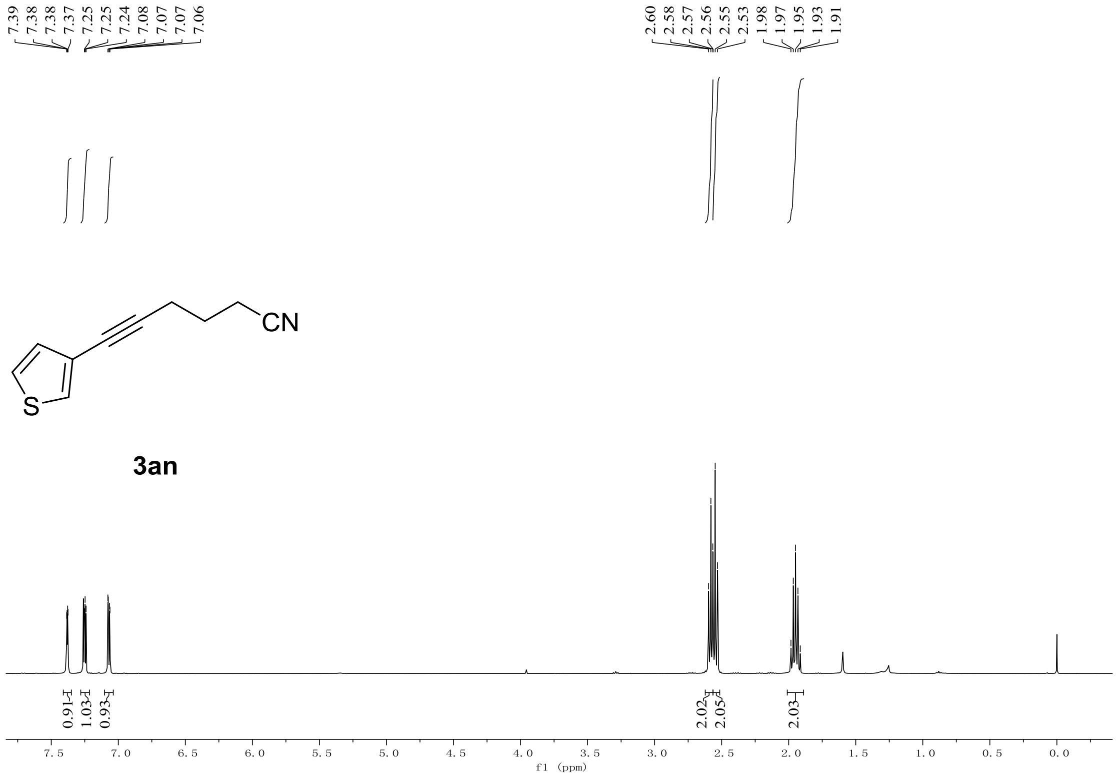
3al


7.66
7.66
7.63
7.63
7.44
7.42
7.35
7.34
7.32
7.32
6.74
6.74
6.73
6.73
2.63
2.61
2.60
2.58
2.56
2.01
1.99
1.97
1.96
1.94
CN
O
1.89
0.98
0.97
0.95
4.00
2.03
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
-0.5
f1 (ppm)

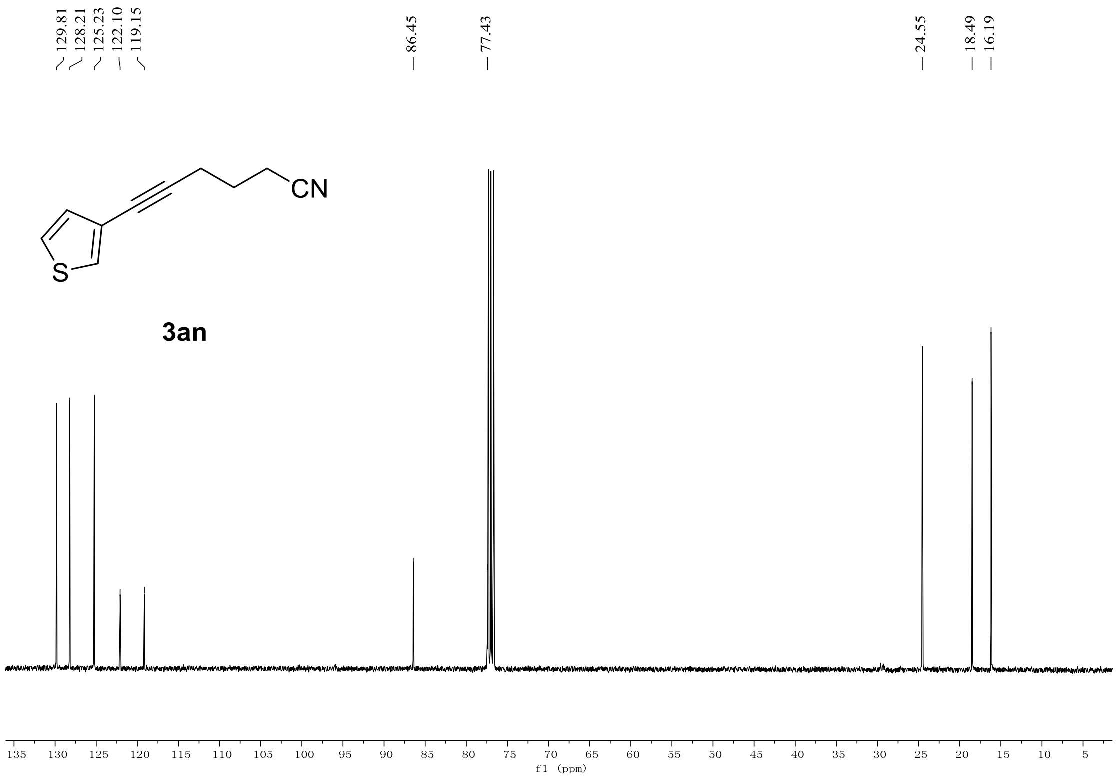
3am


154.33
145.77
127.90
127.47
124.60
119.22
117.66
111.41
106.37
85.31
82.56
24.68
18.52
16.20
CN
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

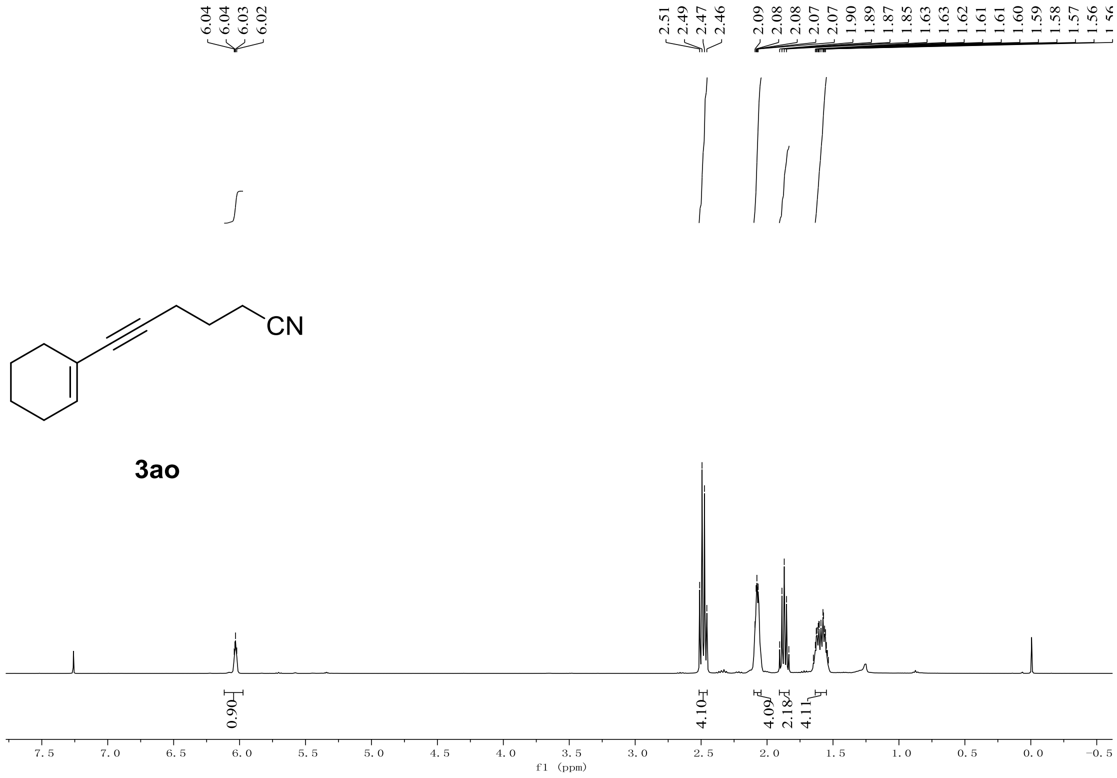
3am


7.39
7.38
7.38
7.37
7.25
7.25
7.24
7.08
7.07
7.07
7.06
2.60
2.58
2.57
2.56
2.55
2.53
1.98
1.97
1.95
1.93
1.91
CN
S
0.91
1.03
0.93
2.02
2.05
2.03
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)

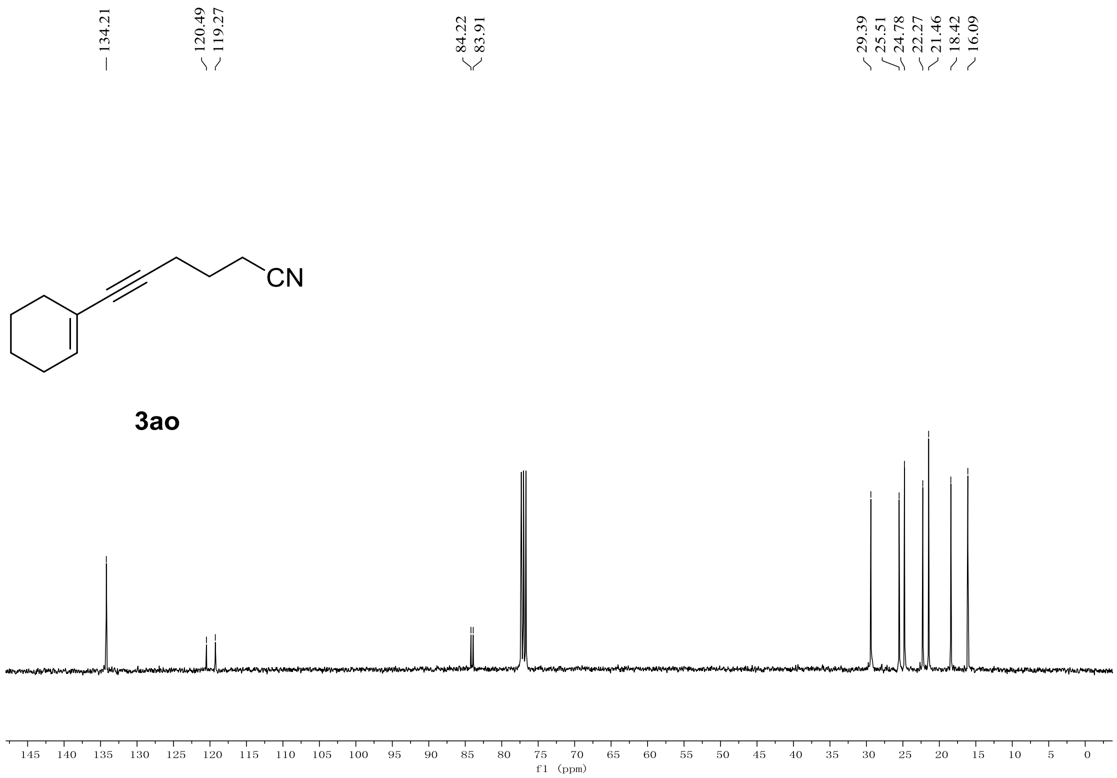
3an

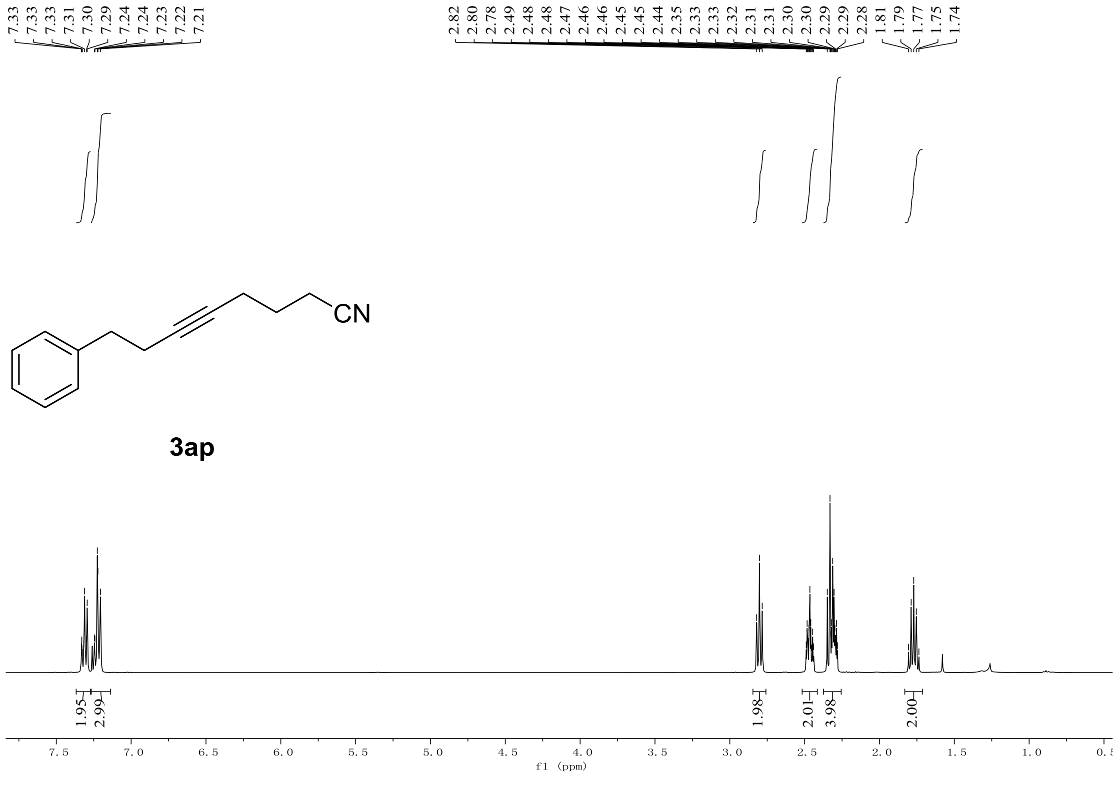

129.81
128.21
125.23
122.10
119.15
86.45
77.43
24.55
18.49
16.19
CN
S
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

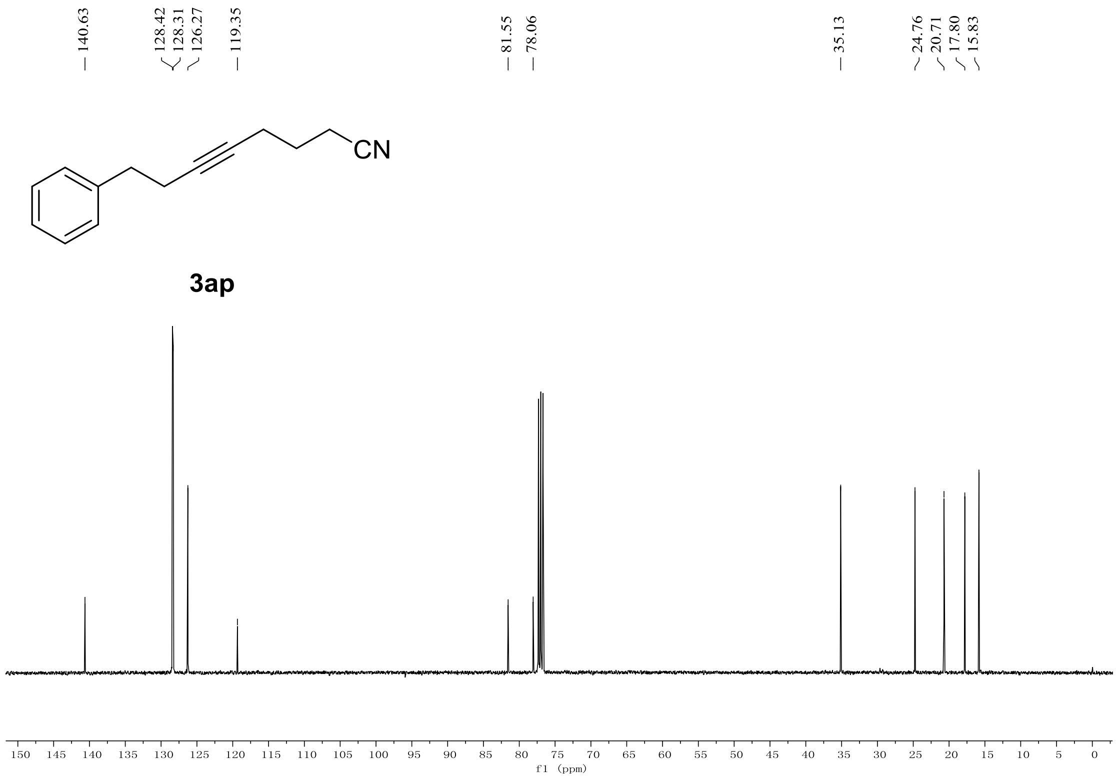
3an


6.04
6.04
6.03
6.02
2.51
2.49
2.47
2.46
2.09
2.08
2.08
2.07
2.07
1.90
1.89
1.87
1.85
1.63
1.63
1.62
1.61
1.61
1.60
1.59
1.58
1.57
1.56
CN
0.90
4.10
4.09
2.18
4.11
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

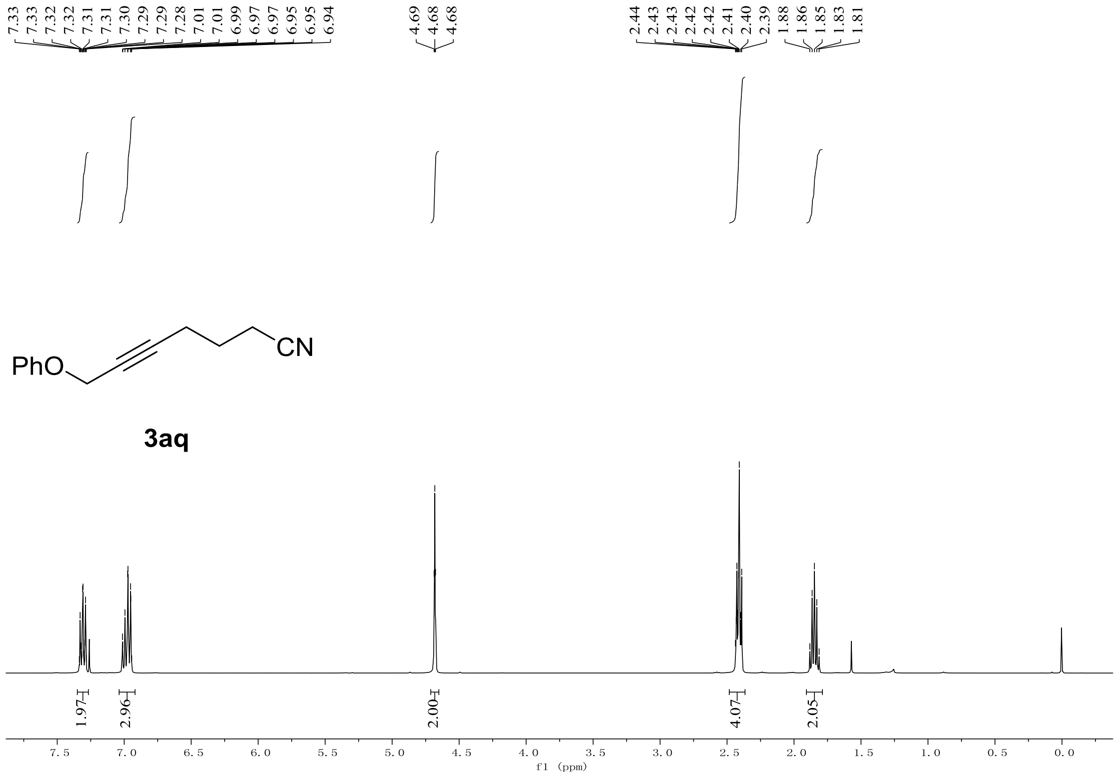
3ao


3ao
134.21
120.49
119.27
84.22
83.91
29.39
25.51
24.78
22.27
21.46
18.42
16.09
CN
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

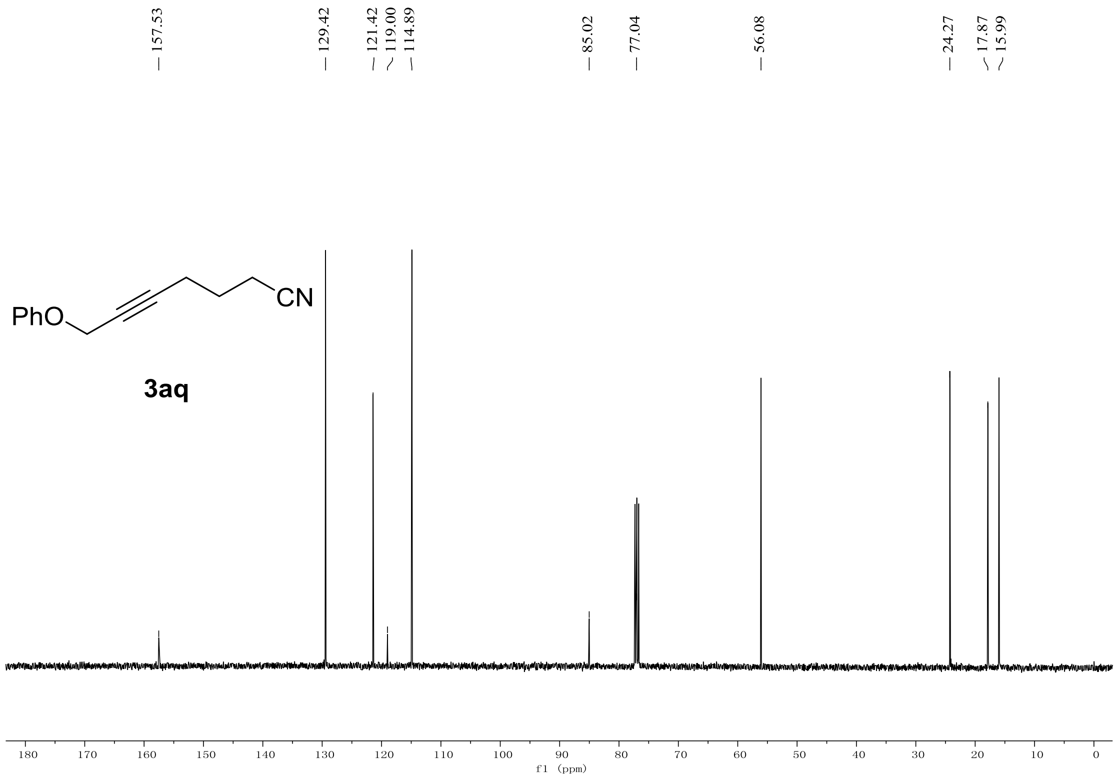

3ap
7.33
7.33
7.33
7.31
7.30
7.29
7.24
7.24
7.23
7.22
7.21
2.82
2.80
2.78
2.49
2.48
2.48
2.47
2.46
2.46
2.45
2.45
2.44
2.35
2.33
2.33
2.32
2.31
2.31
2.30
2.30
2.29
2.29
2.28
1.81
1.79
1.77
1.75
1.74
CN
1.95
2.99
1.98
2.01
3.98
2.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


140.63
128.42
128.31
126.27
119.35
81.55
78.06
35.13
24.76
20.71
17.80
15.83
CN
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

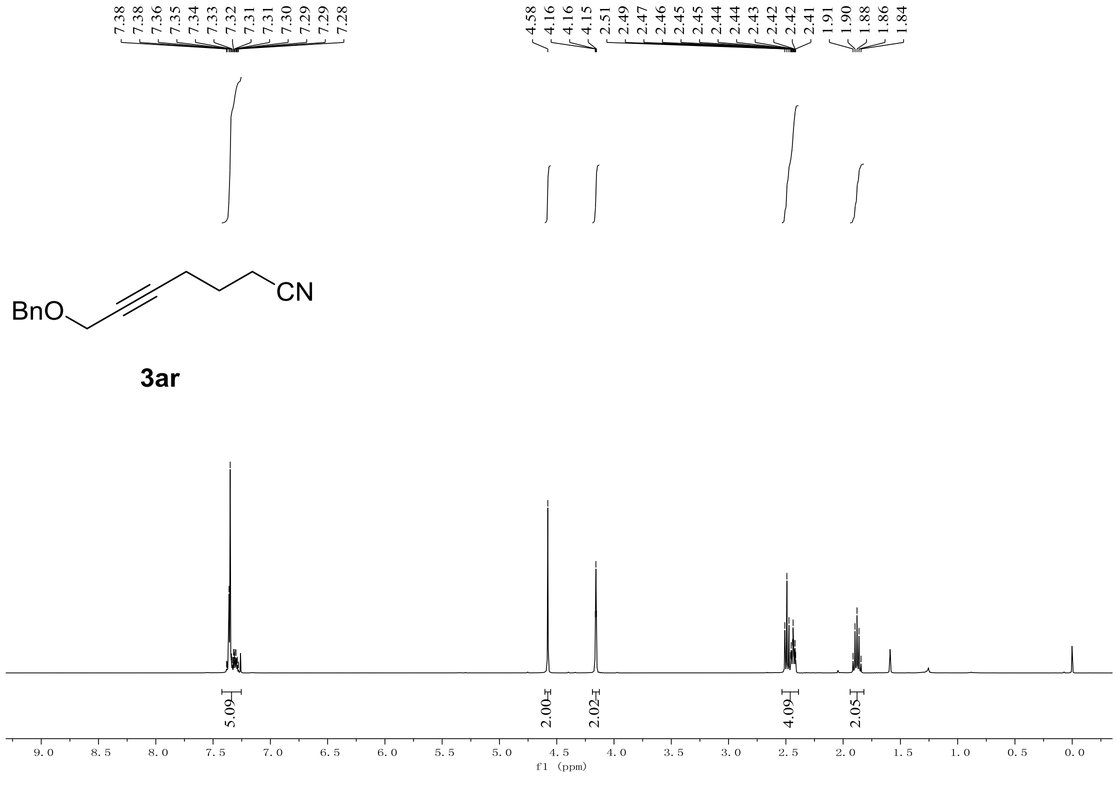
3ap


7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.01
7.01
6.99
6.97
6.97
6.95
6.95
6.94
4.69
4.68
4.68
2.44
2.43
2.43
2.42
2.42
2.41
2.40
2.39
1.88
1.86
1.85
1.83
1.81
PhO
CN
1.97
2.96
2.00
4.07
2.05
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)

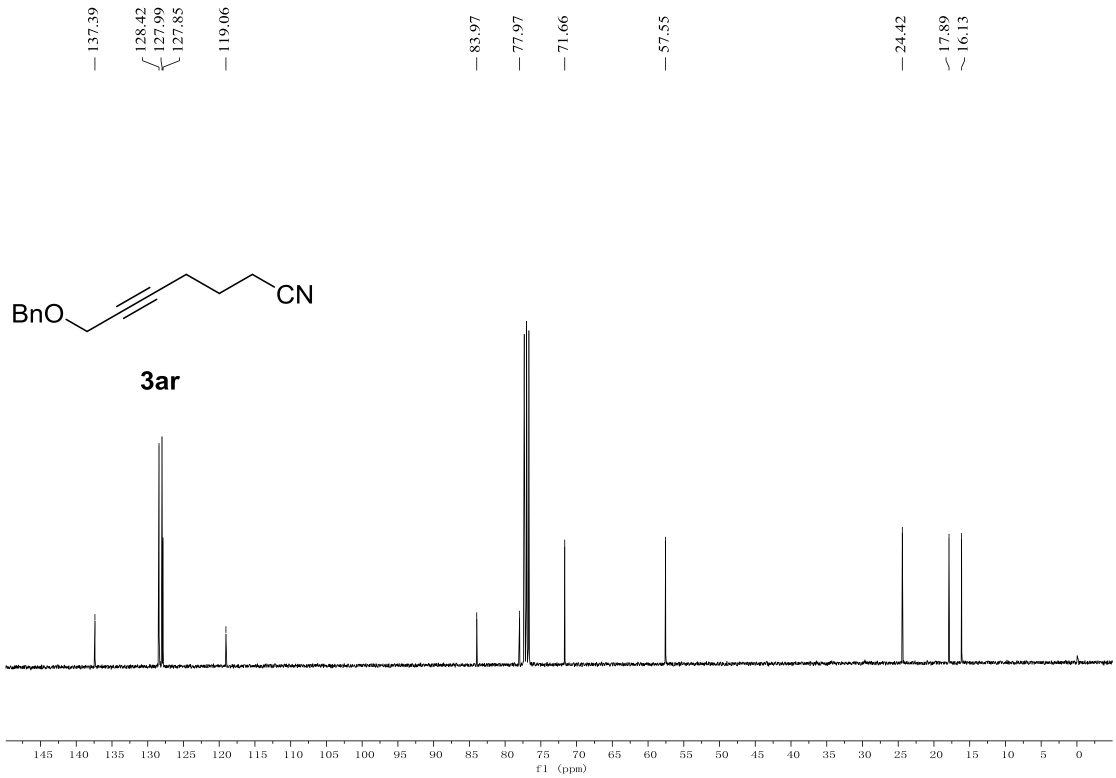
3aq


157.53
129.42
121.42
119.00
114.89
85.02
77.04
56.08
24.27
17.87
15.99
PhO
CN
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

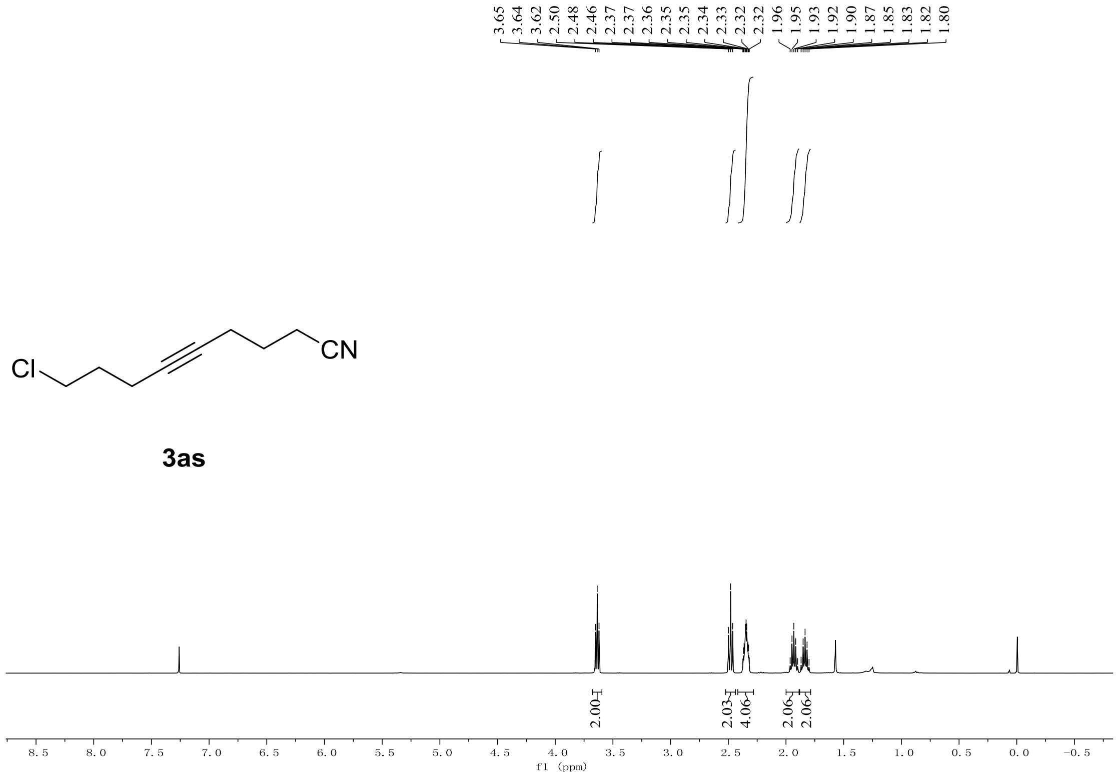
3aq


7.38
7.38
7.36
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
4.58
4.16
4.16
4.15
2.51
2.49
2.47
2.46
2.45
2.45
2.44
2.44
2.43
2.42
2.42
2.41
1.91
1.90
1.88
1.86
1.84
BnO
CN
5.09
2.00
2.02
4.09
2.05
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)

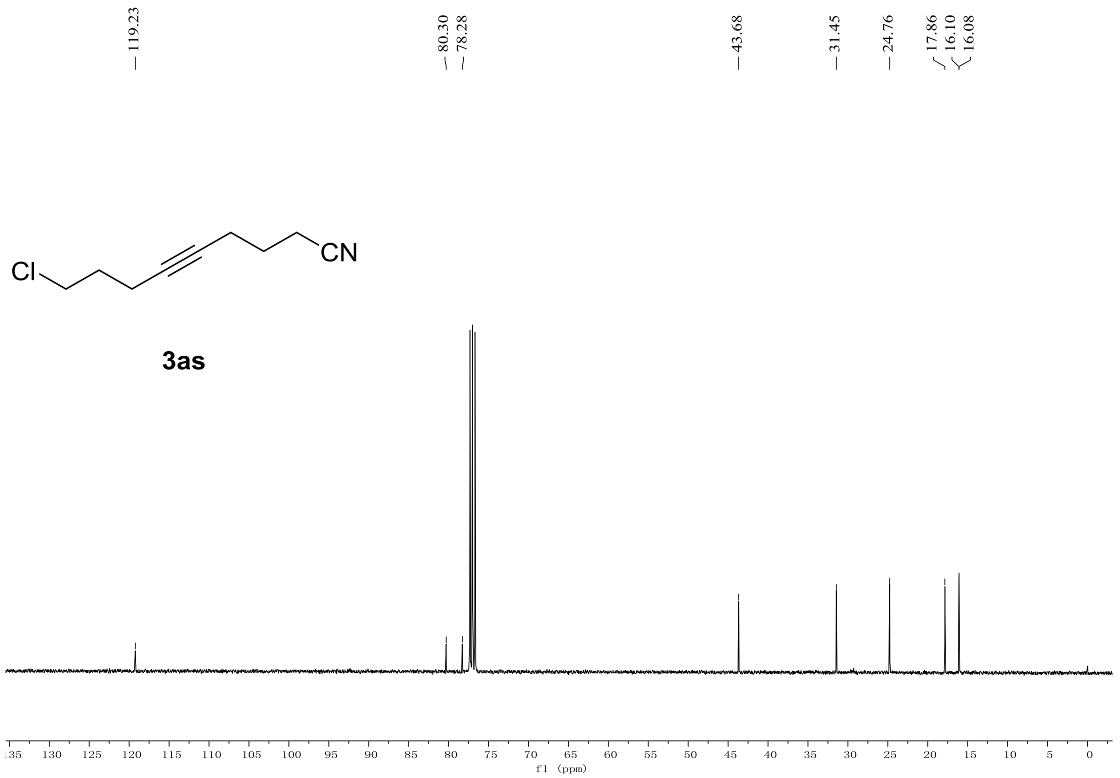
3ar


137.39
128.42
127.99
127.85
119.06
83.97
77.97
71.66
57.55
24.42
17.89
16.13
BnO
CN
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

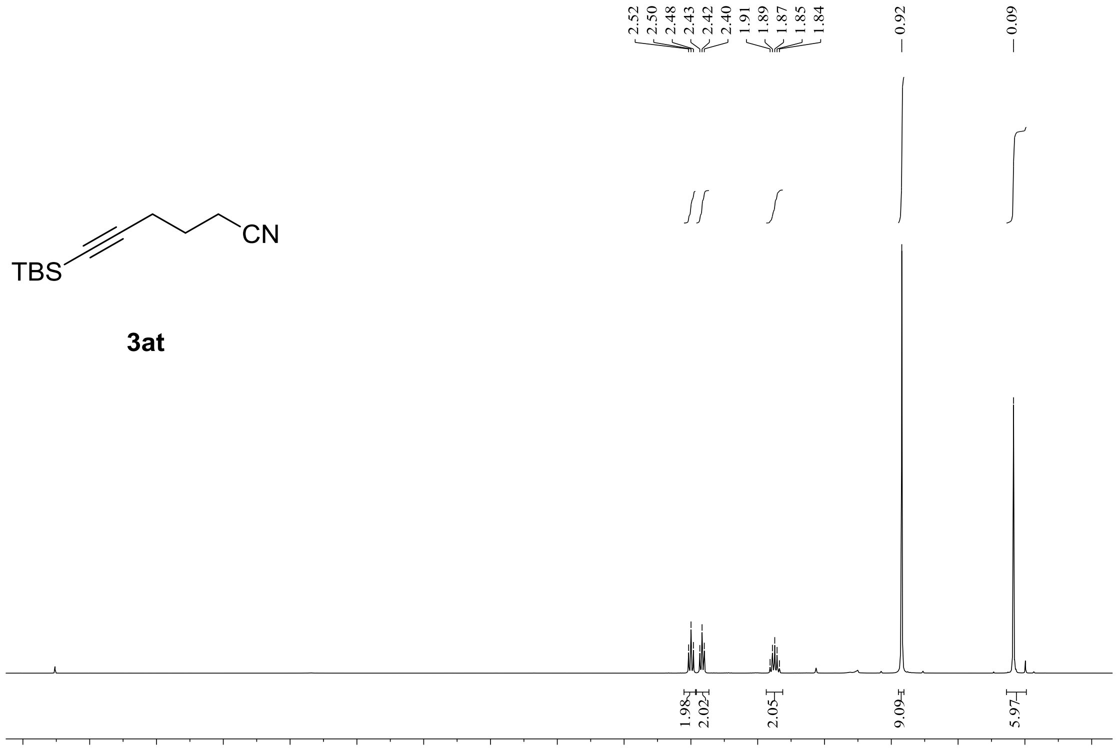
3ar


3.65
3.64
3.62
2.50
2.48
2.46
2.37
2.37
2.36
2.35
2.35
2.34
2.33
2.32
2.32
1.96
1.95
1.93
1.92
1.90
1.87
1.85
1.83
1.82
1.80
Cl
CN
2.00
2.03
4.06
2.06
2.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

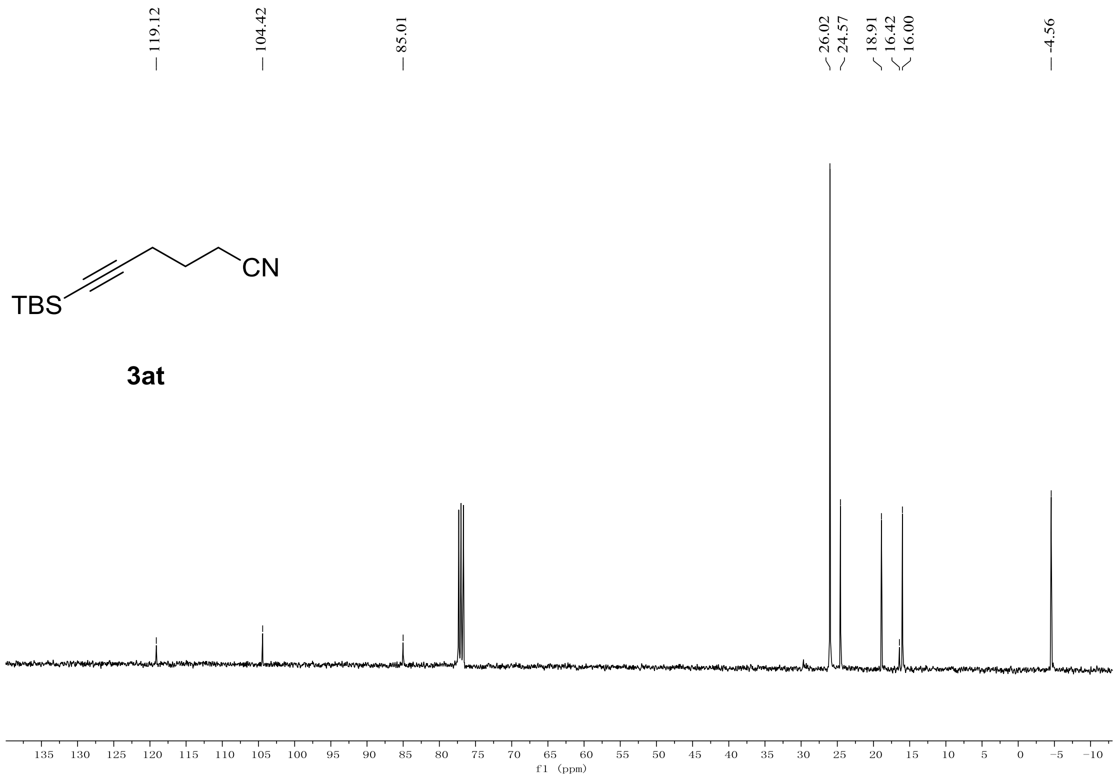
3as


119.23
80.30
78.28
43.68
31.45
24.76
17.86
16.10
16.08
Cl
CN
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

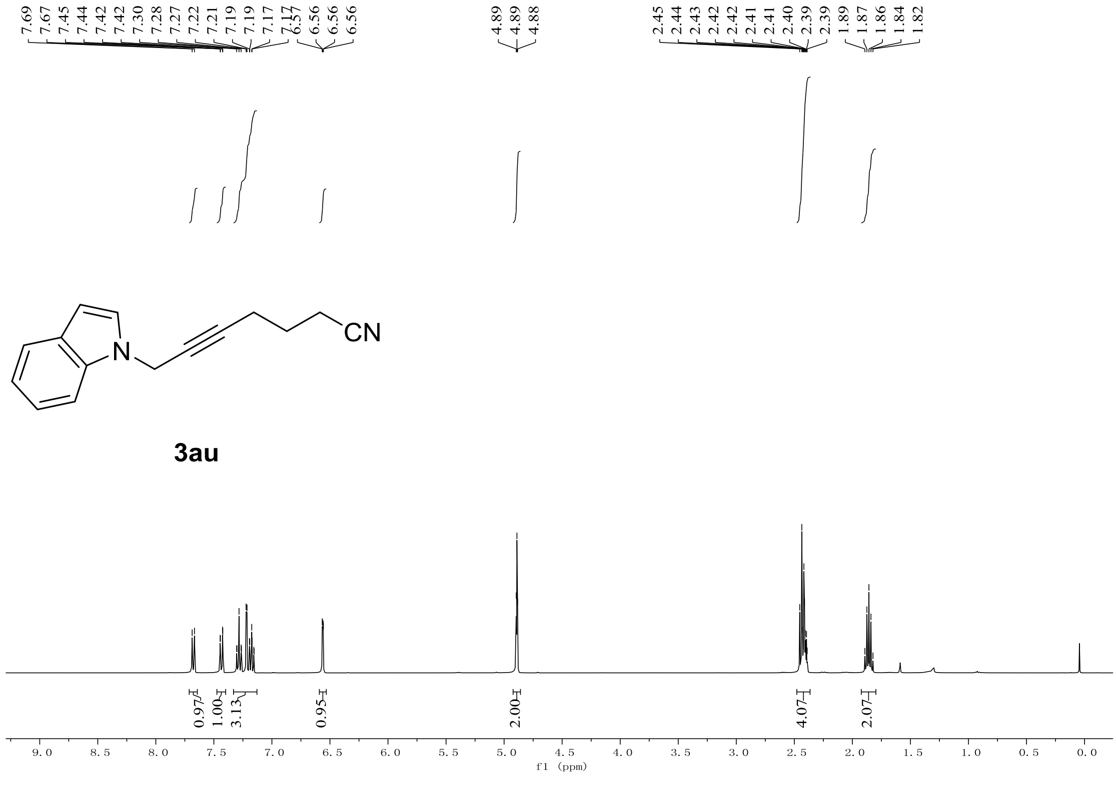
3as


2.52
2.50
2.48
2.43
2.42
2.40
1.91
1.89
1.87
1.85
1.84
0.92
0.09
TBS
CN
1.98
2.02
2.05
9.09
5.97
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

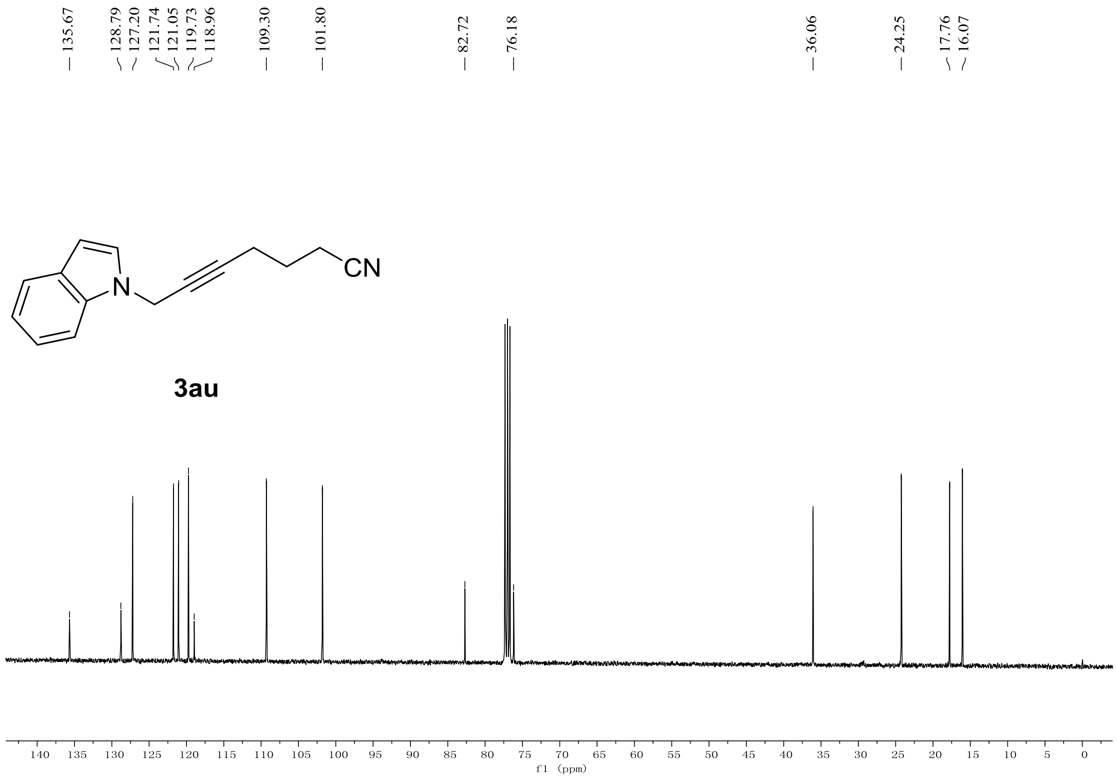
3at


119.12
104.42
85.01
26.02
24.57
18.91
16.42
16.00
-4.56
TBS
CN
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (ppm)

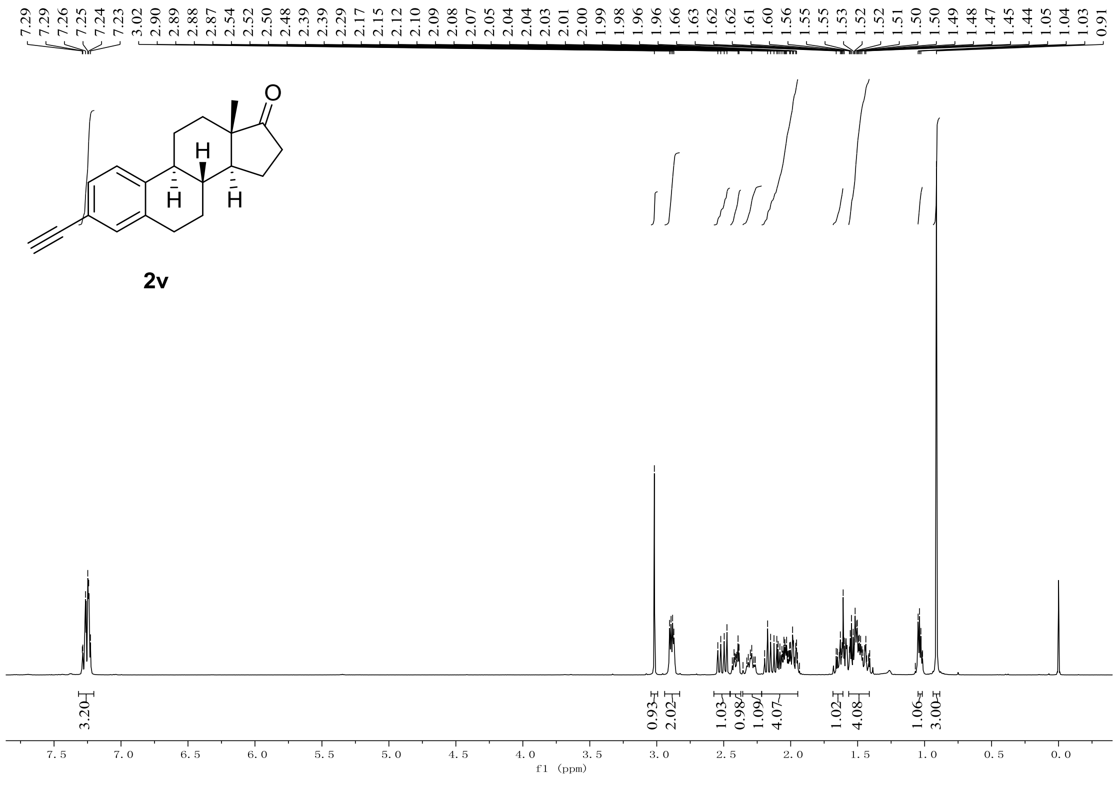
3at


7.69
7.67
7.45
7.44
7.42
7.42
7.30
7.28
7.27
7.22
7.21
7.19
7.19
7.17
7.17
6.57
6.56
6.56
6.56
4.89
4.89
4.88
2.45
2.44
2.43
2.42
2.42
2.41
2.41
2.40
2.39
2.39
1.89
1.87
1.86
1.84
1.82
N
CN
0.97
1.00
3.13
0.95
2.00
4.07
2.07
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)

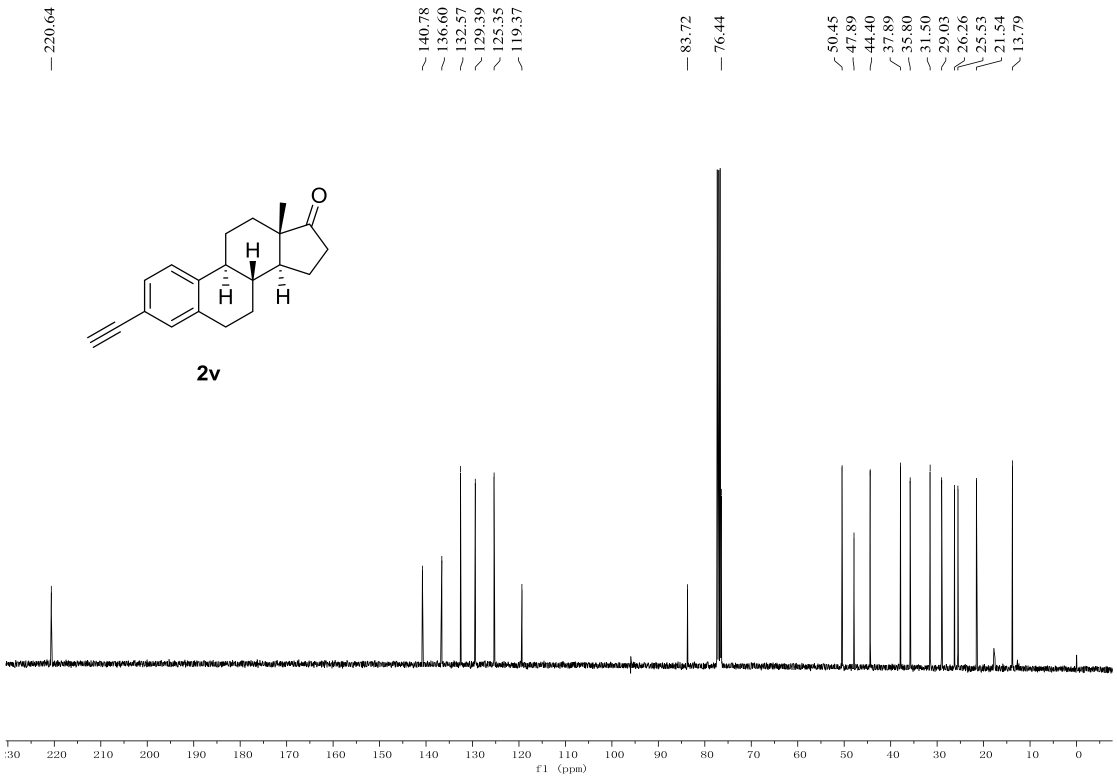
3au

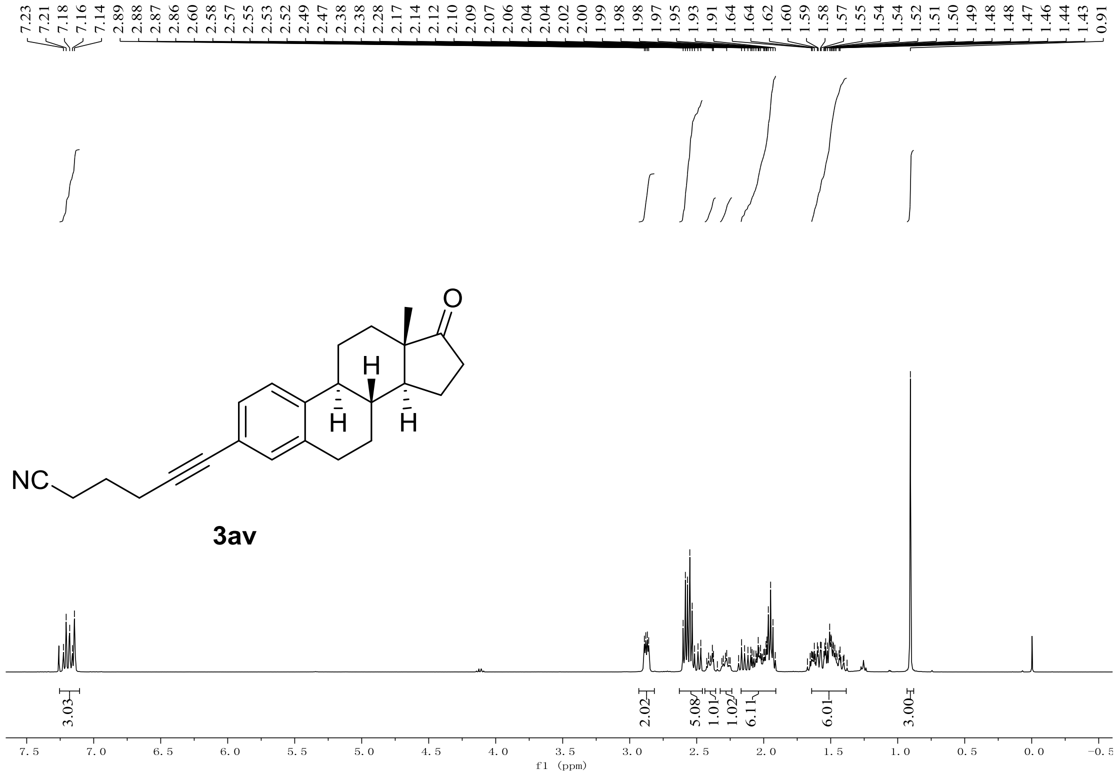

135.67
128.79
127.20
121.74
121.05
119.73
118.96
109.30
101.80
82.72
76.18
36.06
24.25
17.76
16.07
CN
N
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

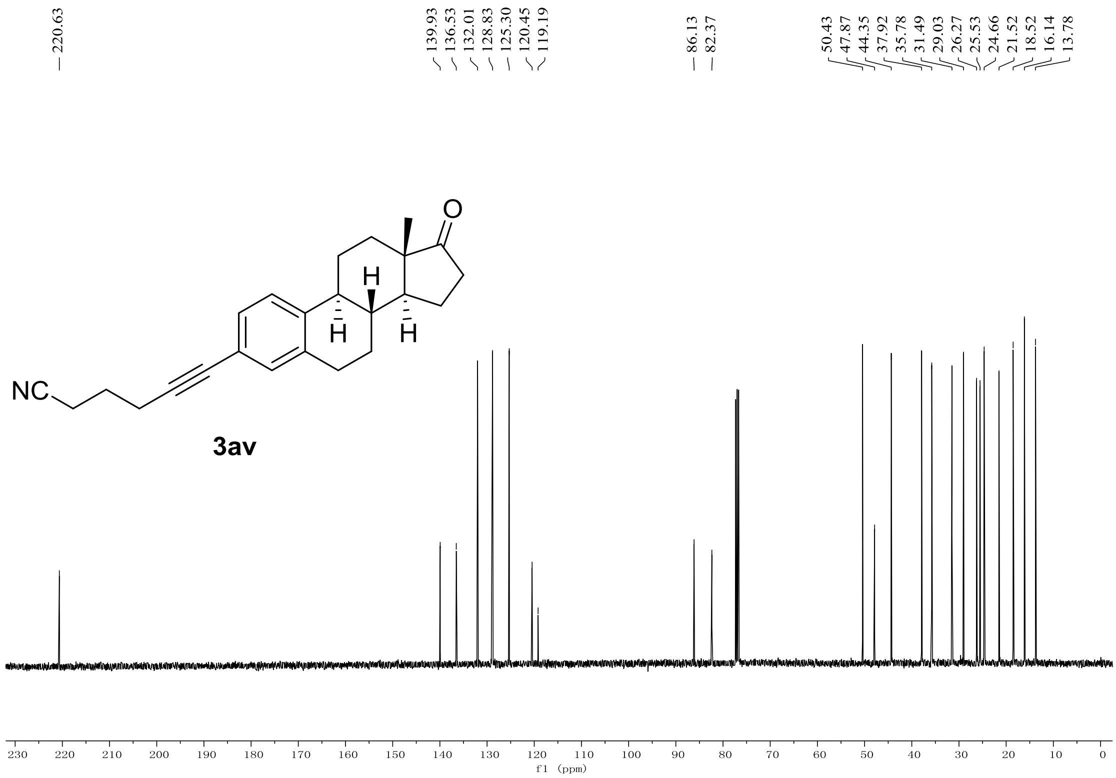
3au


7.29
7.29
7.26
7.25
7.24
7.23
3.02
2.90
2.89
2.88
2.87
2.54
2.52
2.50
2.48
2.39
2.39
2.29
2.17
2.15
2.12
2.10
2.09
2.08
2.07
2.05
2.04
2.04
2.03
2.01
2.00
1.99
1.98
1.96
1.96
1.66
1.63
1.62
1.62
1.61
1.60
1.56
1.55
1.55
1.53
1.52
1.52
1.51
1.50
1.50
1.49
1.48
1.47
1.45
1.44
1.05
1.04
1.03
0.91
O
H
H
H
3.20
0.93
2.02
1.03
0.98
1.09
4.07
1.02
4.08
1.06
3.00
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)

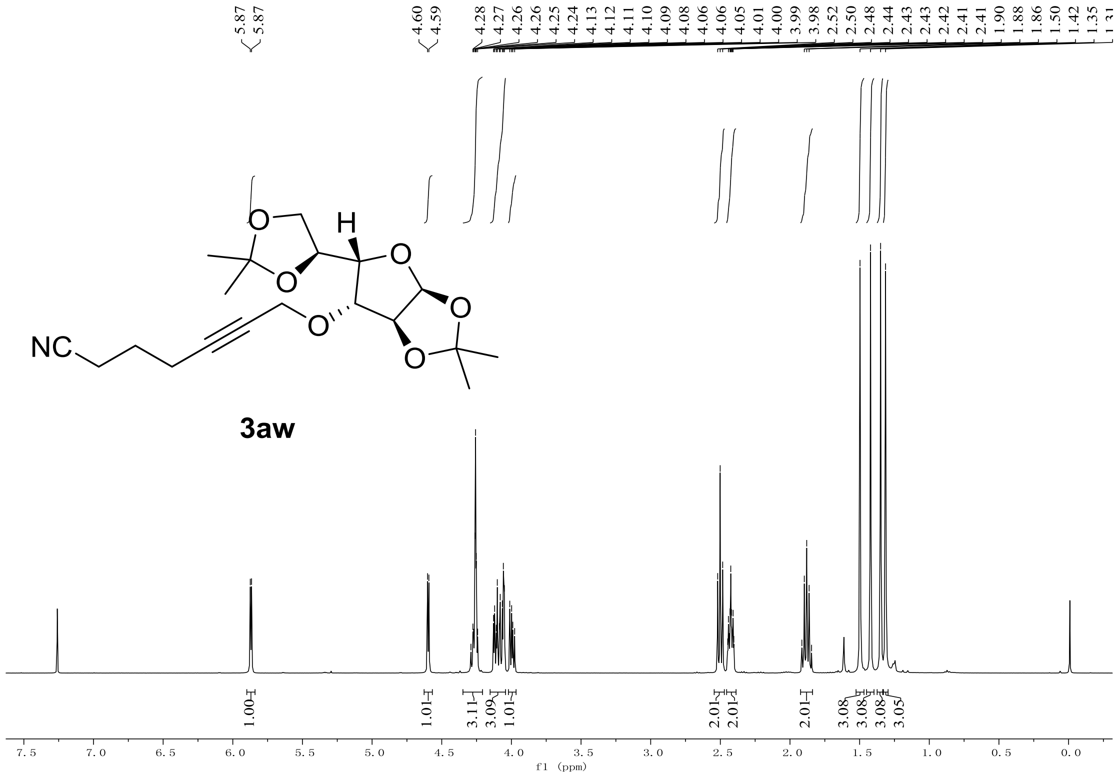
2v


220.64
140.78
136.60
132.57
129.39
125.35
119.37
83.72
76.44
50.45
47.89
44.40
37.89
35.80
31.50
29.03
26.26
25.53
21.54
13.79
O
H
H
H
2v
:30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

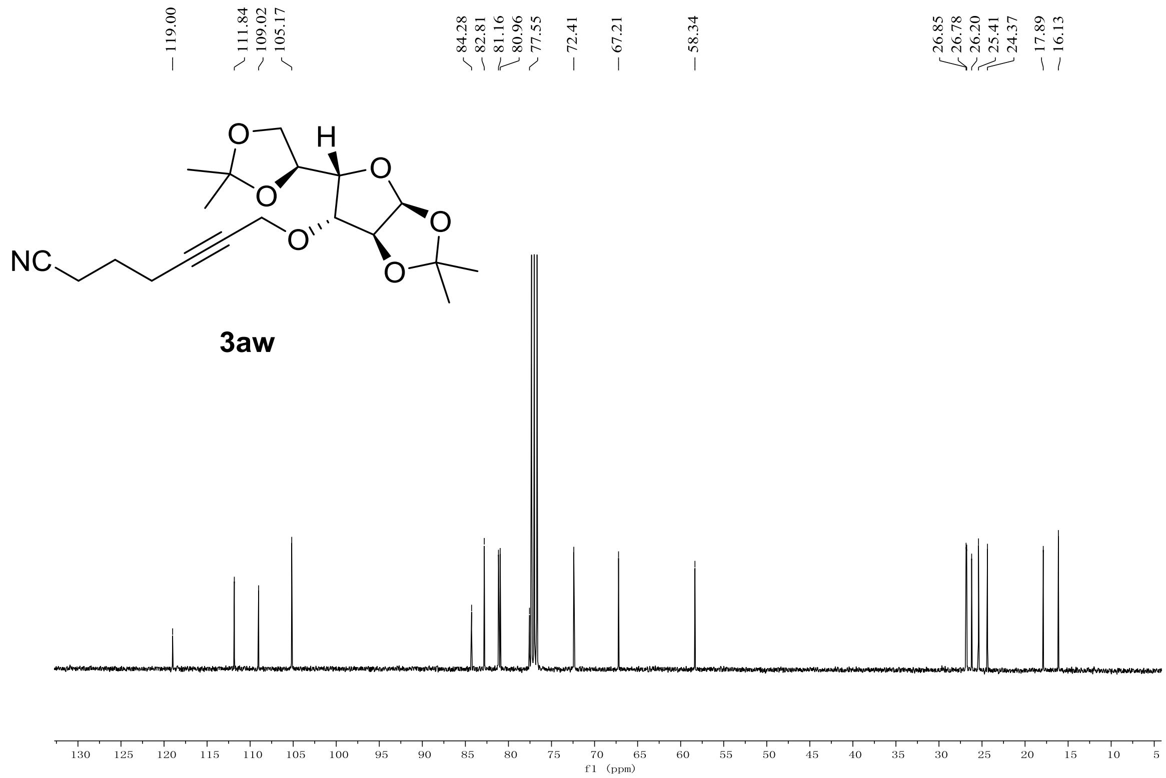

7.23
7.21
7.18
7.16
7.14
2.89
2.88
2.87
2.86
2.60
2.58
2.57
2.55
2.53
2.52
2.49
2.47
2.38
2.38
2.28
2.17
2.14
2.12
2.10
2.09
2.07
2.06
2.04
2.04
2.02
2.00
1.99
1.98
1.98
1.97
1.95
1.93
1.91
1.64
1.64
1.62
1.60
1.59
1.58
1.57
1.55
1.54
1.54
1.52
1.51
1.50
1.49
1.48
1.48
1.47
1.46
1.44
1.43
0.91
O
H
H
H
NC
3av
3.03
2.02
5.08
1.01
1.02
6.11
6.01
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


220.63
139.93
136.53
132.01
128.83
125.30
120.45
119.19
86.13
82.37
50.43
47.87
44.35
37.92
35.78
31.49
29.03
26.27
25.53
24.66
21.52
18.52
16.14
13.78
NC
O
H
H
H
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

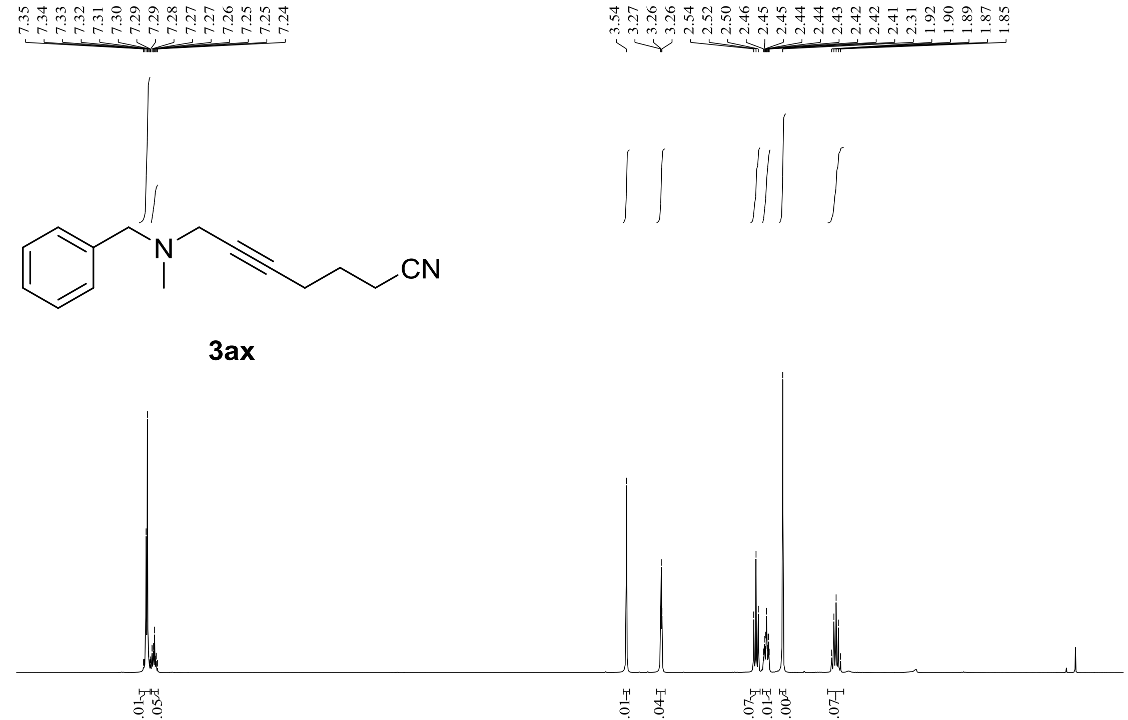
3av


5.87
5.87
4.60
4.59
4.28
4.27
4.26
4.26
4.25
4.24
4.13
4.12
4.11
4.10
4.09
4.08
4.06
4.05
4.01
4.00
3.99
3.98
2.52
2.50
2.48
2.44
2.43
2.42
2.41
2.41
1.90
1.88
1.86
1.50
1.42
1.35
NC
O
O
O
O
O
O
H
1.00
1.01
3.11
3.09
1.01
2.01
2.01
2.01
3.08
3.08
3.08
3.05
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)

3aw


119.00
111.84
109.02
105.17
84.28
82.81
81.16
80.96
77.55
72.41
67.21
58.34
26.85
26.78
26.20
25.41
24.37
17.89
16.13
NC
O
H
f1 (ppm)
130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5

3aw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7.29
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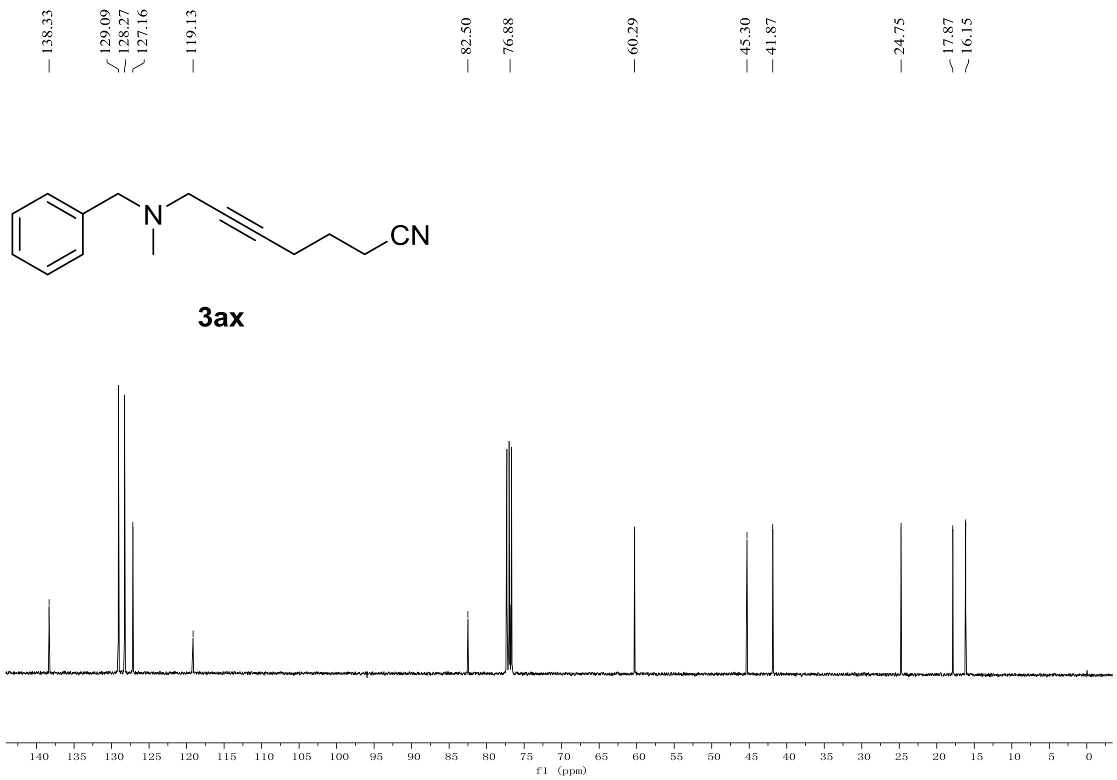
7.27
7.27
7.26
7.25
7.25
7.24
3.54
3.27
3.26
3.26
2.54
2.52
2.50
2.46
2.45
2.45
2.44
2.44
2.43
2.42
2.42
2.41
2.31
1.92
1.90
1.89
1.87
1.85
N
CN
4.01
1.05
2.01
2.04
2.07
2.01
3.00
2.07
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

3ax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129.09
128.27
127.16
119.13
82.50
76.88
60.29
45.30
41.87
24.75
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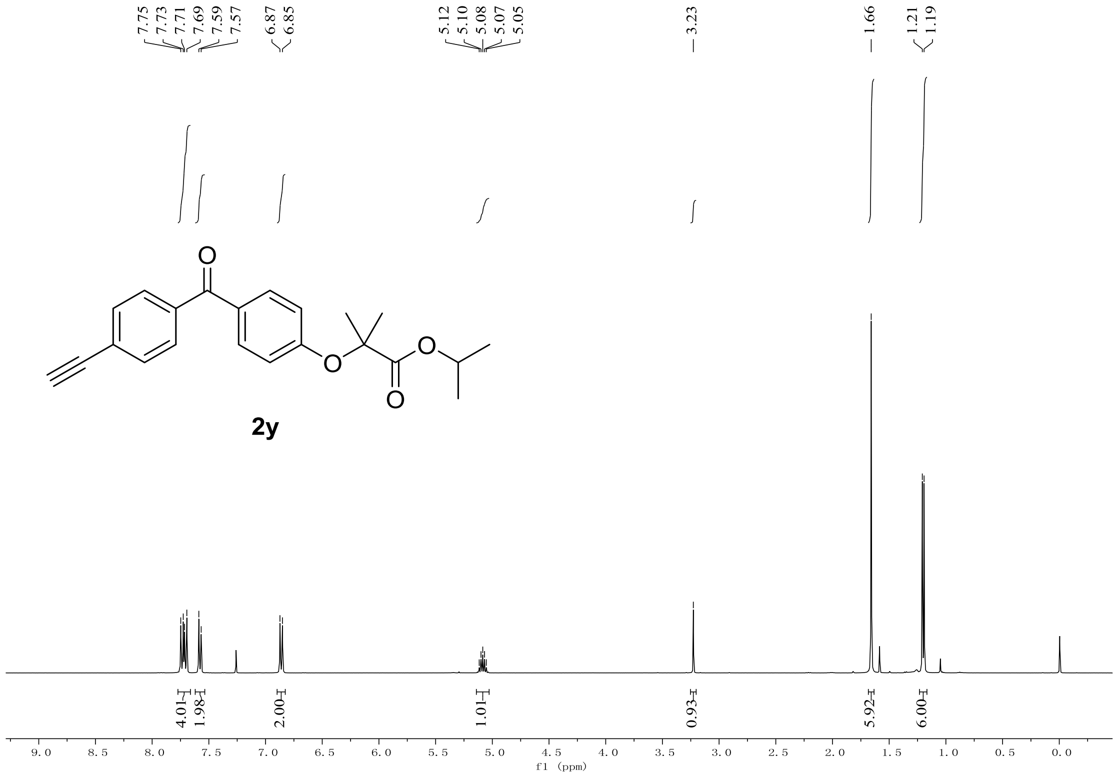
16.15
CN
N
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

3ax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7.73
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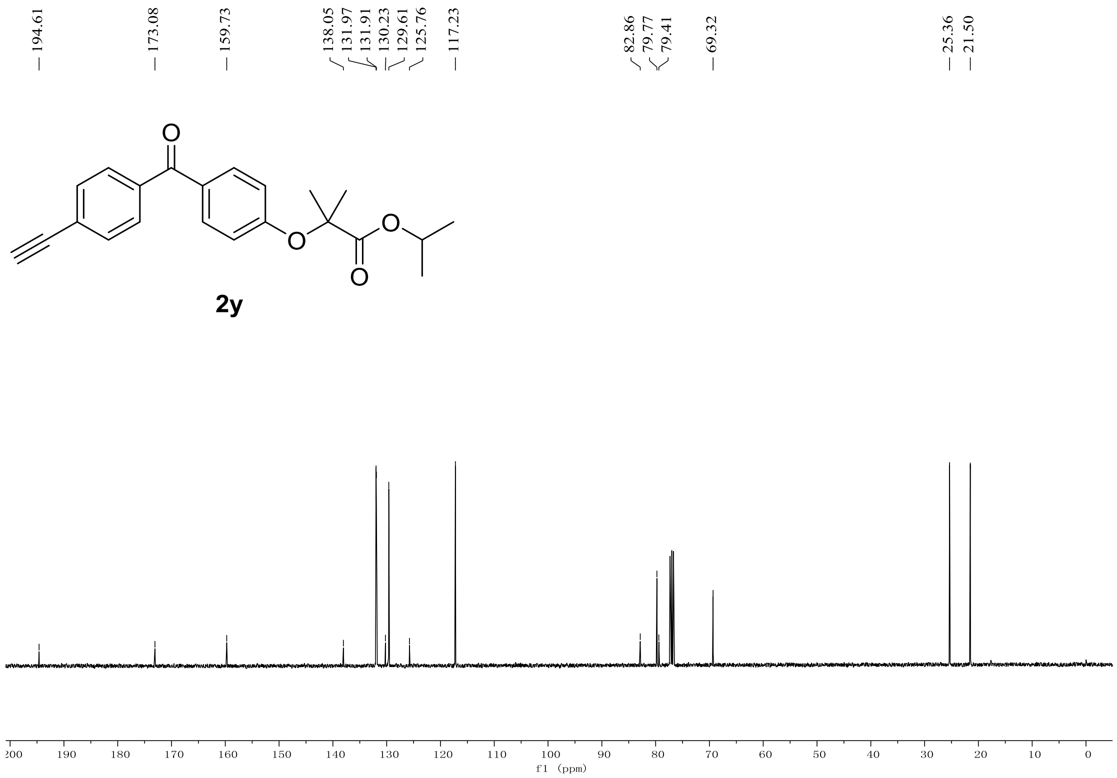
7.69
7.59
7.57
6.87
6.85
5.12
5.10
5.08
5.07
5.05
3.23
1.66
1.21
1.19
O
O
O
O
4.01
1.98
2.00
1.01
0.93
5.92
6.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2y


2y
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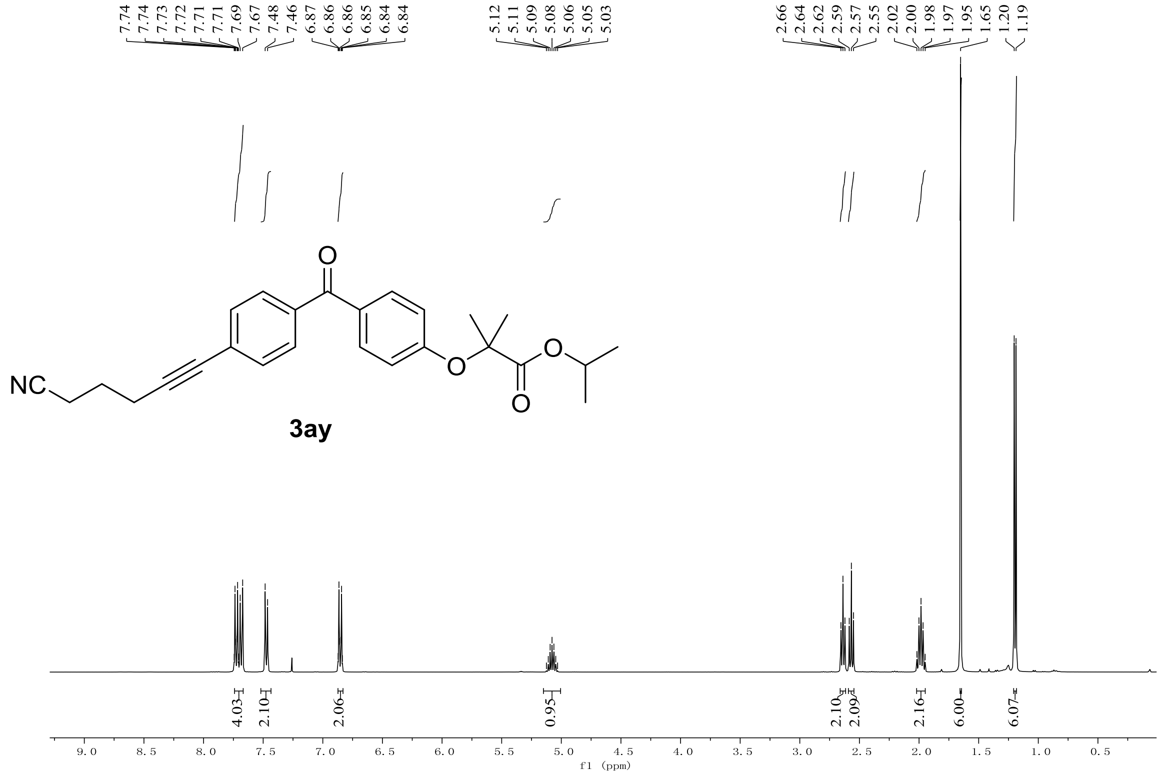
173.08
159.73
138.05
131.97
131.91
130.23
129.61
125.76
117.23
82.86
79.77
79.41
69.32
25.36
21.50
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3ay
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7.74
7.73
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7.71
7.71
7.69
7.67
7.48
7.46
6.87
6.86
6.86
6.85
6.84
6.84
5.12
5.11
5.09
5.08
5.06
5.05
5.03
2.66
2.64
2.62
2.59
2.57
2.55
2.02
2.00
1.98
1.97
1.95
1.65
1.20
1.19
NC
O
O
O
O
4.03
2.10
2.06
0.95
2.10
2.09
2.16
6.00
6.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
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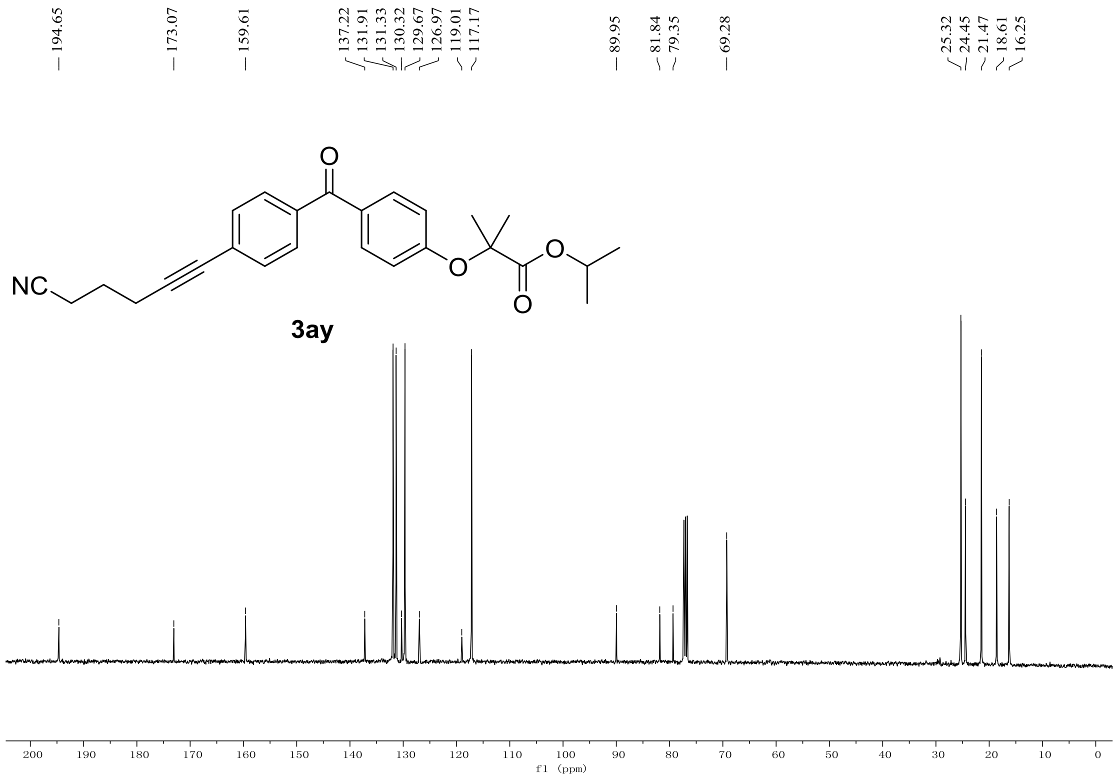
2.0
1.5
1.0
0.5
f1 (ppm)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131.33
130.32
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119.01
117.17
89.95
81.84
79.35
69.28
25.32
24.45
21.47
18.61
16.25
O
NC
O
O
O
200
190
180
170
160
150
140
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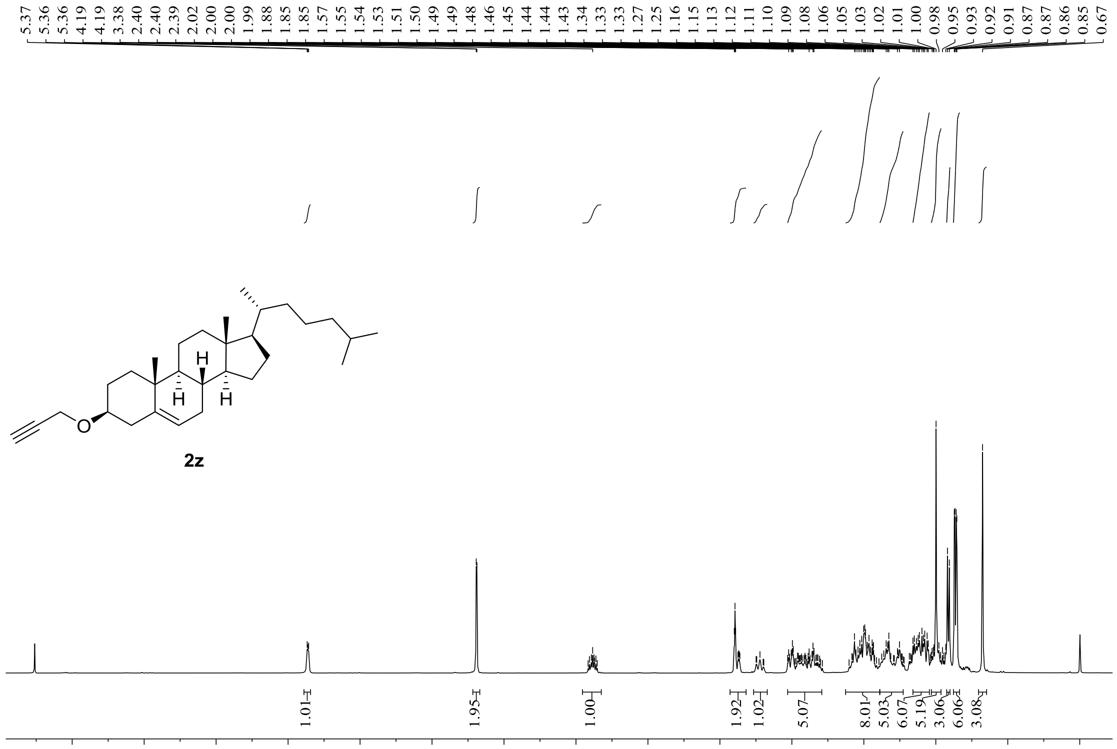
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ay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1.85
1.85
1.57
1.55
1.54
1.53
1.51
1.50
1.49
1.49
1.48
1.46
1.45
1.44
1.44
1.43
1.34
1.33
1.33
1.27
1.25
1.16
1.15
1.13
1.12
1.11
1.10
1.09
1.08
1.06
1.05
1.03
1.02
1.01
1.00
0.98
0.95
0.93
0.92
0.91
0.87
0.87
0.86
0.85
0.67
H
H
H
O
1.01
1.95
1.00
1.92
1.02
5.07
8.01
5.03
6.07
5.19
3.06
6.06
3.08
7.0
6.5
6.0
5.5
5.0
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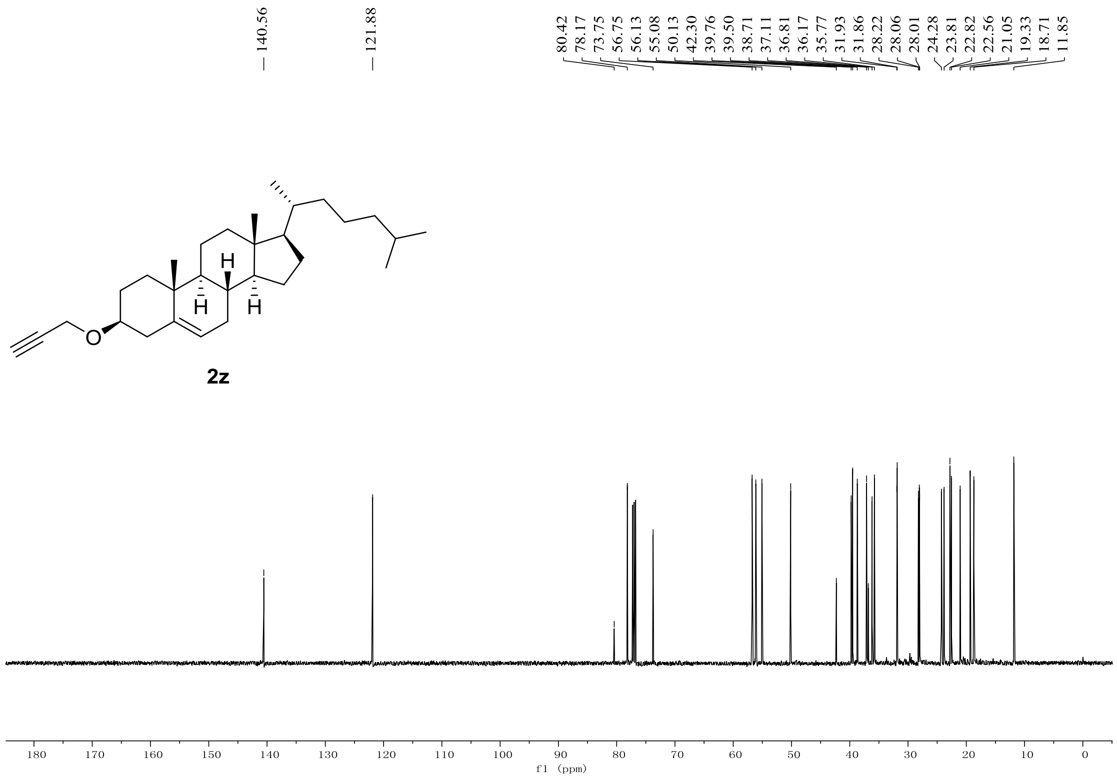
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2z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42.30
39.76
39.50
38.71
37.11
36.81
36.17
35.77
31.93
31.86
28.22
28.06
28.01
24.28
23.81
22.82
22.56
21.05
19.33
18.71
11.85
H
H
H
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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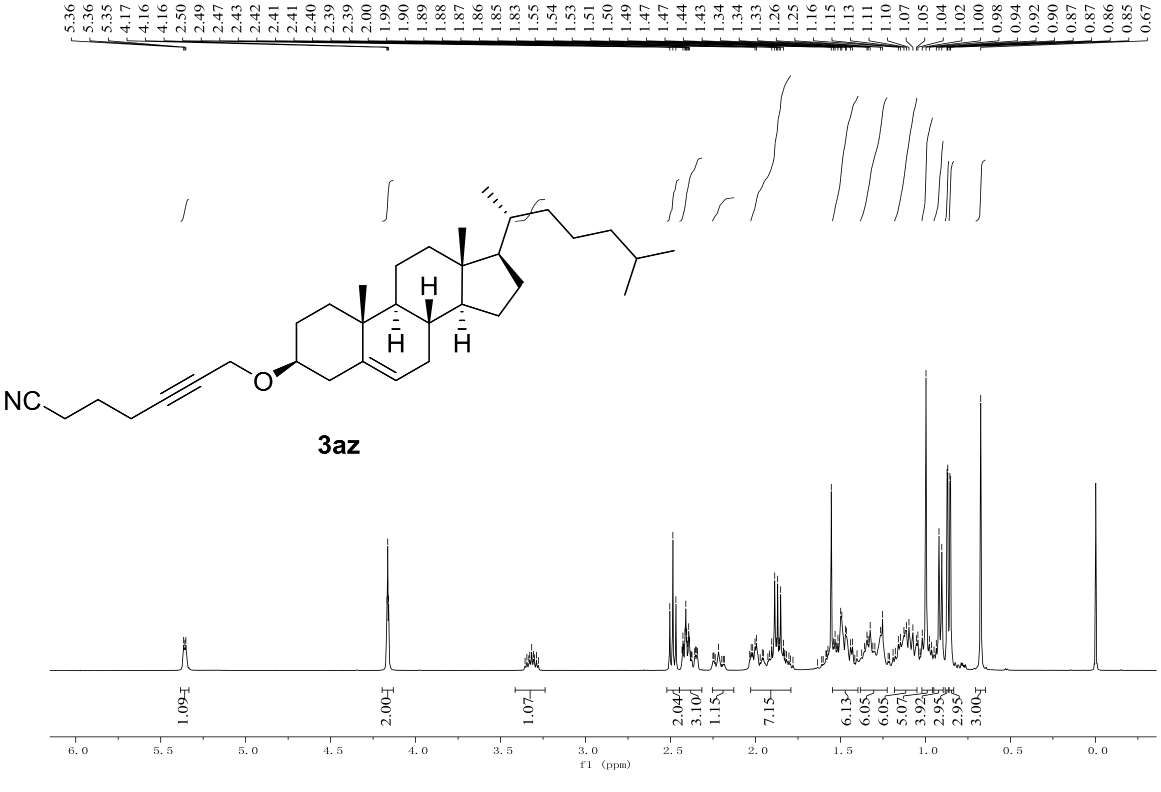
30
20
10
0
f1 (ppm)

2z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5.36
5.35
4.17
4.16
4.16
2.50
2.49
2.47
2.43
2.42
2.41
2.41
2.40
2.39
2.39
2.00
1.99
1.90
1.89
1.88
1.87
1.86
1.85
1.83
1.55
1.54
1.53
1.51
1.50
1.49
1.47
1.47
1.44
1.43
1.34
1.33
1.26
1.25
1.16
1.15
1.13
1.11
1.10
1.07
1.05
1.04
1.02
1.00
0.98
0.94
0.92
0.90
0.87
0.87
0.86
0.85
0.67
NC
O
H
H
H
1.09
2.00
1.07
2.04
3.10
1.15
7.15
6.13
6.05
6.05
5.07
3.92
2.95
2.95
3.00
6.0
5.5
5.0
4.5
4.0
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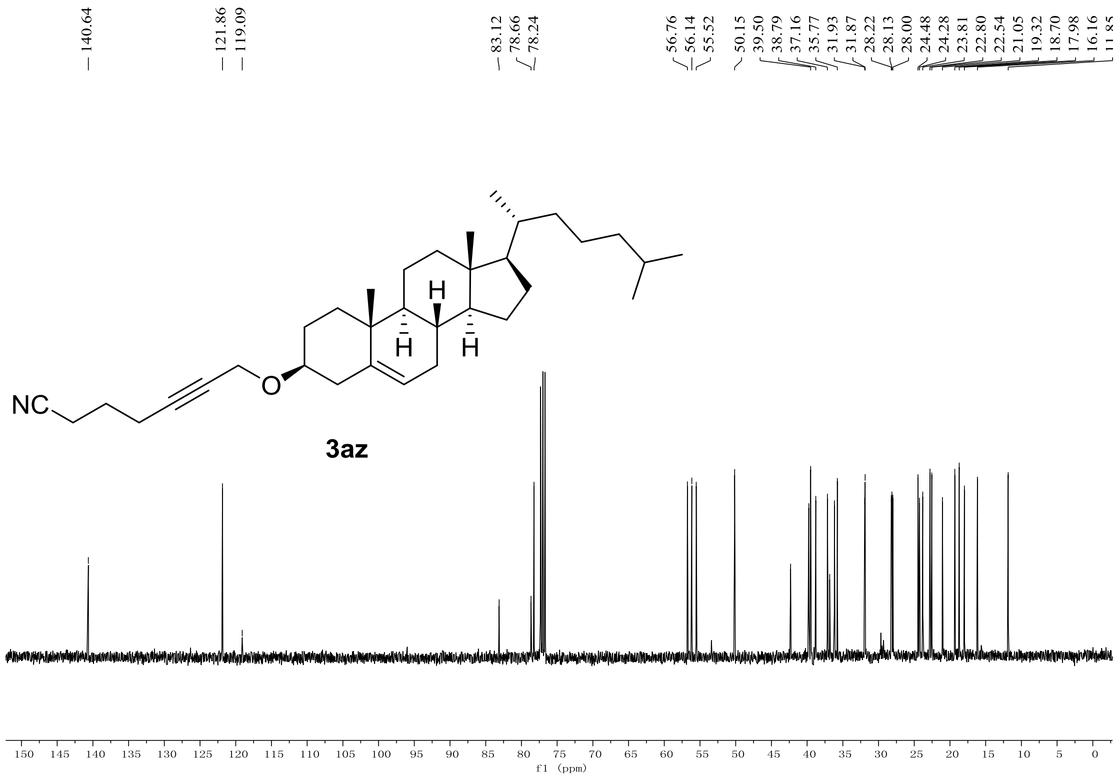
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3az



3az

140.64
121.86
119.09
83.12
78.66
78.24
56.76
56.14
55.52
50.15
39.50
38.79
37.16
35.77
31.93
31.87
28.22
28.13
28.00
24.48
24.28
23.81
22.80
22.54
21.05
19.32
18.70
17.98
16.16
11.85
NC
O
H
H
H
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)