

Kishore Natte, Jianbin Chen, Helfried Neumann, Matthias Beller, and Xiao-Feng Wu*

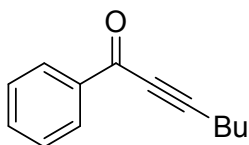
Leibniz-Institut für Katalyse an der Universität Rostock, Albert-Einstein-Straße 29a, 18059 Rostock (Germany)
E-mail: xiao-feng.wu@catalysis.de

General Methods

NMR spectra were recorded on Bruker Avance 300 and Bruker ARX 400 spectrometers. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). All measurements were carried out at room temperature unless otherwise stated. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). High resolution mass spectra (HRMS) were recorded on Agilent 6210. The data are given as mass units per charge (m/z). Gas chromatography analysis was performed on an Agilent HP-5890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using argon as carrier gas. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck).

General Procedure:

The reaction was carried out in a Parr Instruments 4560 series 300 mL autoclave containing an alloy plate with wells for six 4 mL Wheaton vials. Pd(TFA)₂ (5.0 mol%), DPPP (10.0 mol%), Ag₂O (2 equiv.), phenylboronic acid (0.5 mmol), NaOAc (2 equiv.) and a magnetic stir bar were placed in each vials under air, which were then capped with a septum equipped with an inlet needle. Then 1-hexyne (1.2 equiv.) and acetone (1 mL) were added to the vial *via* syringe. The vials were placed in an autoclave, filled with 8 bar of CO at room temperature and keep the reaction at room temperature for 12 h. After the reaction was completed, the autoclave was vented to discharge N₂. The product was extracted with ethyl acetate (5×3 mL). The organic layers were washed with brine, dried over Na₂SO₄, and evaporated to yield the crude reaction mixture. The purification occurred by flash chromatography on silica gel (eluent: heptane/EtOAc 95:05).

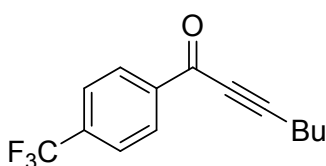


1-Phenylhept-2-yn-1-one

¹H NMR (300 MHz, Chloroform-*d*) δ 8.27 – 8.01 (m, 2H), 7.64 – 7.54 (m, 2H), 7.49 (m, 1H), 2.51 (t, 2H), 1.75 – 1.61 (m, 2H), 1.59 – 1.43 (m, 2H), 0.98 (t, $J = 7.3$ Hz, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 178.39, 137.06, 133.99, 129.67, 128.61, 96.99, 79.80, 29.98, 22.22, 19.06, 13.67.

MS (EI, 70 eV): m/z (%) = 186 ($[M]^+$, 20), 171 (10), 157 (40), 144 (100), 129 (30), 115 (60), 105 (62), 77 (50), 66 (10), 51 (12).

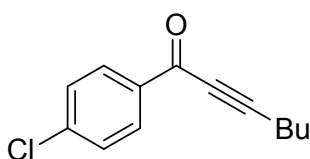


1-(4-(Trifluoromethyl)phenyl)hept-2-yn-1-one

¹H NMR (300 MHz, Chloroform-*d*) δ 8.29 – 8.07 (m, 3H), 7.74 – 7.59 (m, 2H), 2.46 (t, $J = 7.1$ Hz, 2H), 1.74 – 1.52 (m, 2H), 1.51 – 1.36 (m, 2H), 0.90 (t, $J = 7.3$ Hz, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 176.94, 139.45, 135.01 (q, $J = 32.51$ Hz), 129.81, 125.60 (q, $J = 3.86$ Hz), 123.60 (q, $J = 273.12$ Hz), 98.45, 79.48, 29.78, 22.12, 18.98, 13.53.

MS (EI, 70 eV): m/z (%) = 254 ($[M]^+$, 5), 235 (10), 225 (20), 212 (100), 173 (90), 185 (20), 173 (90), 145 (50), 109 (15), 79 (10).

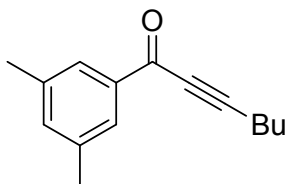


1-(4-Chlorophenyl)hept-2-yn-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.92 (m, 2H), 7.42 – 7.33 (m, 2H), 2.43 (t, $J = 7.1$ Hz, 2H), 1.66 – 1.51 (m, 2H), 1.48 – 1.34 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 176.90, 140.46, 135.37, 130.87, 128.87, 97.46, 79.42, 29.83, 22.12, 18.96, 13.54.

MS (EI, 70 eV): = 220 ($[M]^+$, 10), 191 (15), 178 (100), 157 (10), 139 (90), 128 (7), 111 (40), 79 (20).

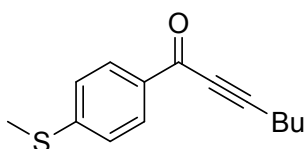


1-(3,5-Dimethylphenyl)hept-2-yn-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 2H), 7.54 – 7.47 (m, 1H), 2.43 (t, $J = 7.1$ Hz, 2H), 2.30 (s, 6H), 1.66 – 1.51 (m, 2H), 1.52 – 1.39 (m, 2H), 0.90 (t, $J = 7.3$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 178.2, 138.19, 135.64, 132.18, 127.37, 97.46, 79.93, 29.89, 23.02, 22.11, 21.44, 21.29.

MS (EI, 70 eV): = 214 ($[M]^+$, 96), 199 (70), 172 (100), 157 (30), 143 (85), 133 (80), 115 (20), 105 (15), 91 (10), 79 (40), 66 (5), 53 (8).

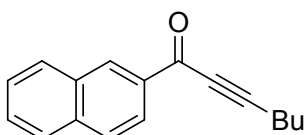


1-(4-(Methylthio)phenyl)hept-2-yn-1-one

¹H NMR (300 MHz, Chloroform-*d*) δ 8.00 – 7.86 (m, 2H), 7.24 – 7.12 (m, 2H), 2.5 (s, 3H), 2.47 – 2.37 (m, 2H), 1.63 – 1.50 (m, 2H), 1.48 – 1.33 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 177.25, 147.18, 133.50, 129.87, 124.72, 96.44, 79.60, 29.87, 22.09, 18.92, 14.73, 14.70, 13.54.

MS (EI, 70 eV): = 232 ($[M]^+$, 100), 203 (5), 190 (10), 175 (8), 161 (10), 151 (12).

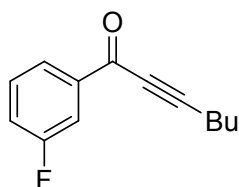


1-(Naphthalen-2-yl)hept-2-yn-1-one

¹H NMR (300 MHz, Chloroform-*d*) δ 8.67 – 8.58 (s, 1H), 8.07 (dd, $J = 8.7, 1.7$ Hz, 2H), 7.96 – 7.90 (m, 2H), 7.81 (dd, $J = 8.1, 1.7$ Hz, 2H), 2.49 (t, $J = 7.0$ Hz, 2H), 1.73 – 1.57 (m, 2H), 1.53 – 1.40 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 178.19, 136.06, 134.49, 132.62, 132.41, 129.81, 128.86, 128.38, 127.89, 126.85, 124.02, 96.79, 79.84, 29.90, 22.14, 19.01, 13.57.

MS (EI, 70 eV): = 236 ($[M]^+$, 100), 207 (20), 194 (18), 179 (10), 165 (50), 155 (15).

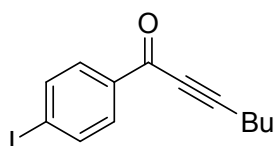


1-(3-Fluorophenyl)hept-2-yn-1-one

¹H NMR (300 MHz, Chloroform-*d*) δ 7.86 (dt, $J = 7.7, 1.3$ Hz, 2H), 7.72 (ddd, $J = 9.3, 2.7, 1.5$ Hz, 2H), 7.39 (td, $J = 8.0, 5.4$ Hz, 1H), 2.44 (t, $J = 7.1$ Hz, 2H), 1.72 – 1.54 (m, 2H), 1.47 – 1.35 (m, 2H), 0.90 (t, $J = 7.3$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 176.81 (d, $J = 2.9$ Hz), 162.68 (d, $J = 248.1$ Hz), 139.01 (d, $J = 6.7$ Hz), 134.16 (d, $J = 7.5$ Hz), 125.34 (d, $J = 2.97$ Hz), 120.87 (d, $J = 21.8$ Hz), 115.99 (d, $J = 23.1$ Hz), 97.56, 79.40, 29.79, 22.09, 18.93, 13.51.

MS (EI, 70 eV): = 203 ($[M]^-$, 10), 175 (25), 162 (100), 146 (10), 133 (50), 12 (90), 109 (40), 95 (45), 79 (20), 66 (10), 53 (7).

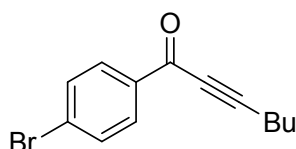


1-(4-Iodophenyl)hept-2-yn-1-one

¹H NMR (300 MHz, CDCl₃) δ 7.84 (m, 4H), 2.50 (t, $J = 7.0$ Hz, 2H), 1.88 – 1.54 (m, 2H), 1.60 – 1.36 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 177.4, 137.8, 136.3, 130.8, 102.3, 97.5, 79.3, 29.8, 22.1, 18.9, 13.5.

MS (EI, 70 eV): = 312 ($[M]^+$, 100), 283 (40), 270 (100), 241 (10), 231 (90), 203 (15), 157 (5).

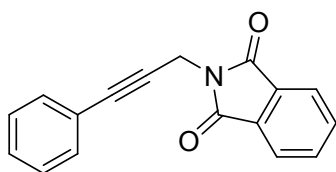


1-(4-Bromophenyl)hept-2-yn-1-one

¹H NMR (300 MHz, CDCl₃) δ 8.10 – 7.90 (m, 2H), 7.82 – 7.47 (m, 2H), 2.50 (t, $J = 7.0$ Hz, 2H), 1.66 (m, 2H), 1.55 – 1.37 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 177.1, 135.1, 131.1, 130.0, 129.3, 97.5, 79.4, 29.8, 22.1, 18.1, 13.5.

MS (EI, 70 eV): = 265 ($[M]^-$, 10), 237 (10), 222 (100), 193 (10), 185 (96), 167 (8), 157 (60).

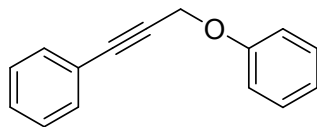


2-(3-Phenylprop-2-yn-1-yl)-1H-indene-1,3(2H)-dione

¹H NMR (300 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.66 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.41 – 7.29 (m, 2H), 7.25 – 7.11 (m, 3H), 4.61 (s, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 167.1, 134.3, 132.1, 131.9, 128.5, 128.2, 123.1, 122.3, 82.9, 82.6, 27.4.

MS (EI, 70 eV): =261 ([M]⁺, 100), 232 (70), 204 (50), 178 (15), 165 (10), 165 (5).

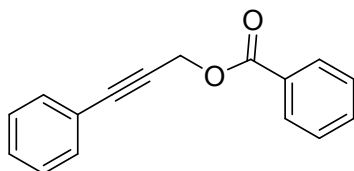


(3-Phenoxyprop-1-yn-1-yl)benzene

¹H NMR (300 MHz, Chloroform-*d*) δ 7.45 – 7.31 (m, 2H), 7.30 – 7.15 (m, 5H), 7.01 – 6.86 (m, 3H), 4.84 (d, *J* = 0.8 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 157.8, 131.8, 129.5, 128.6, 128.3, 122.3, 121.0, 115.0, 87.0, 83.3, 56.1.

MS (EI, 70 eV): =208 ([M]⁺, 5), 115 (100), 105 (5), 89 (3), 65 (5).



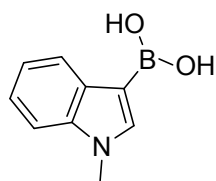
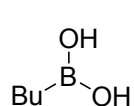
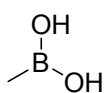
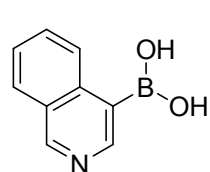
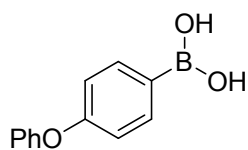
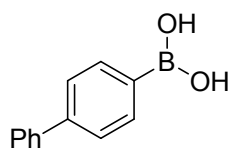
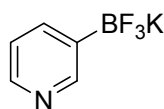
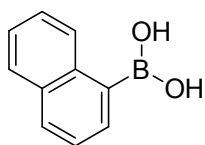
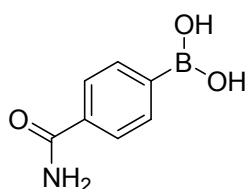
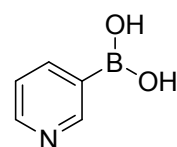
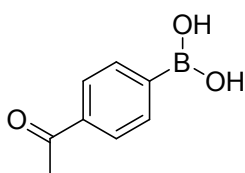
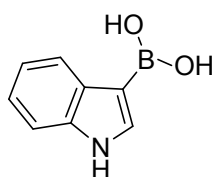
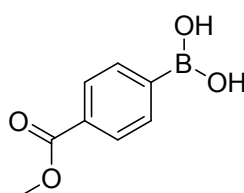
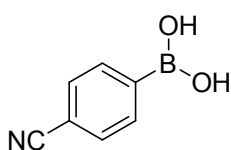
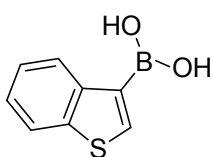
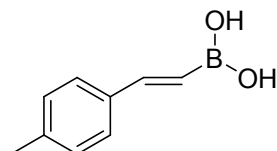
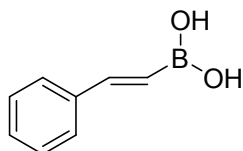
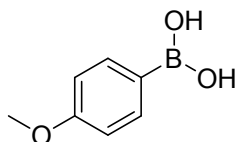
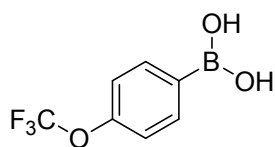
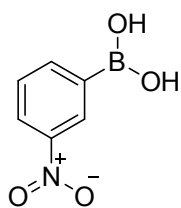
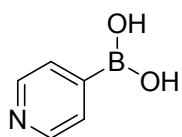
3-Phenylprop-2-yn-1-yl benzoate

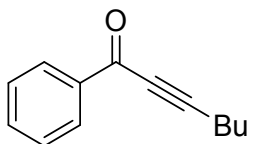
¹H NMR (300 MHz, Chloroform-*d*) δ 8.23 – 8.00 (m, 2H), 7.66 – 7.54 (m, 1H), 7.52 – 7.40 (m, 4H), 7.38 – 7.28 (m, 3H), 5.16 (s, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 165.9, 133.2, 131.9, 129.8, 129.6, 128.7, 128.4, 128.3, 122.2, 86.6, 83.0, 53.3.

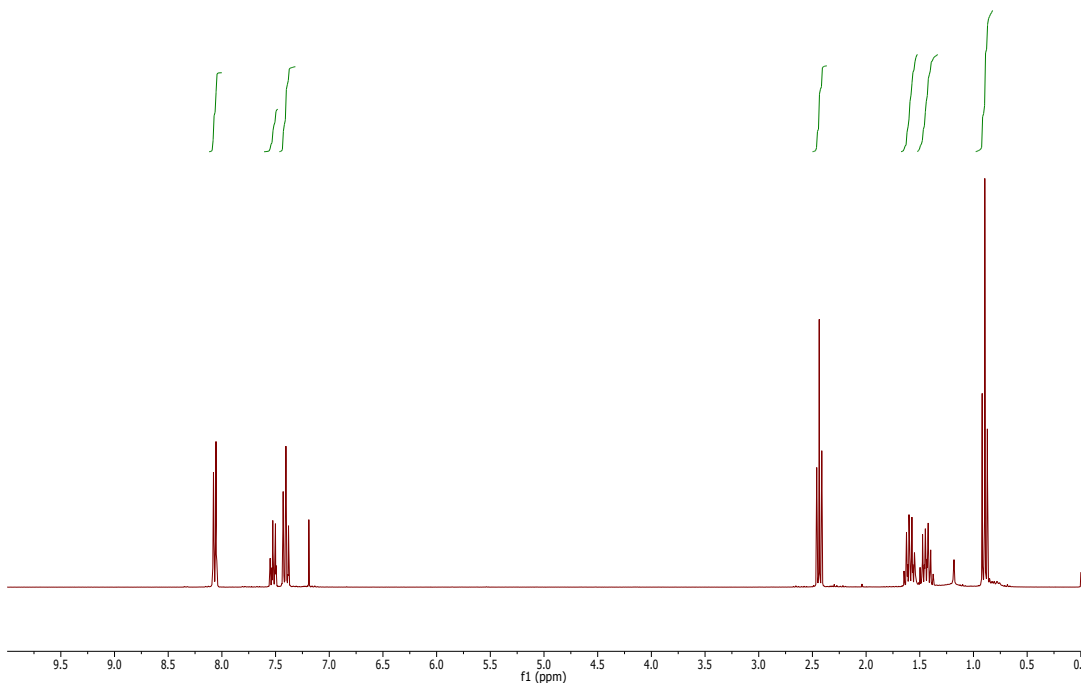
MS (EI, 70 eV): =236 ([M]⁺, 100), 208 (25), 191 (5).

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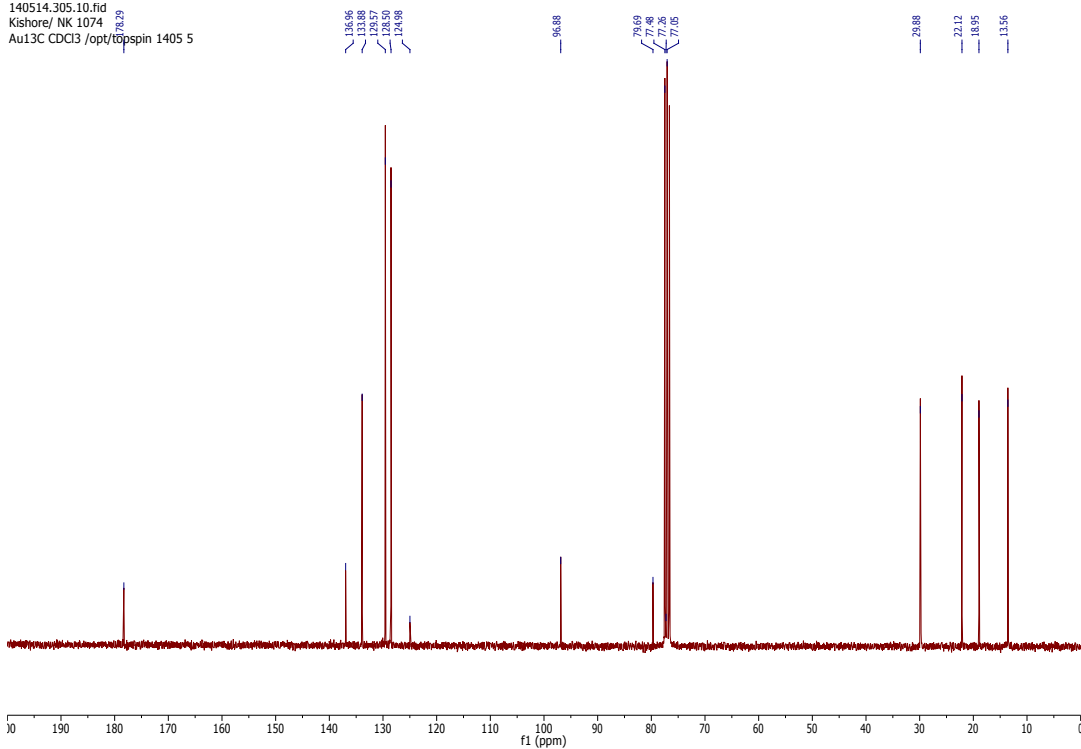


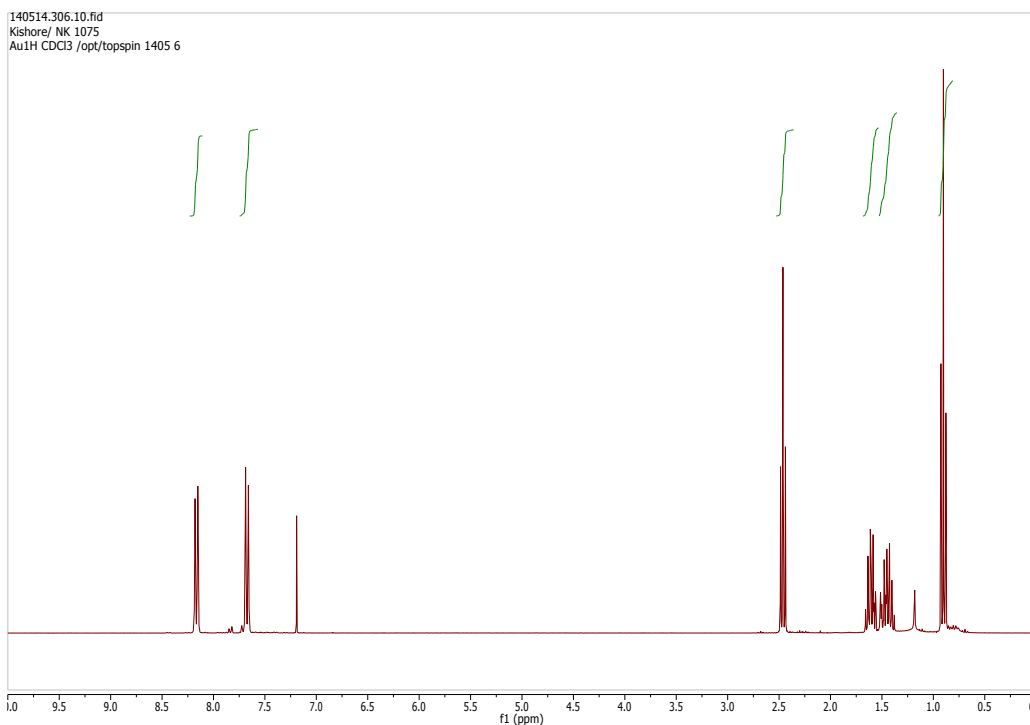
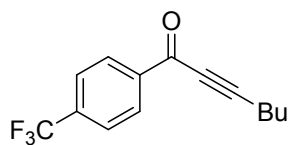


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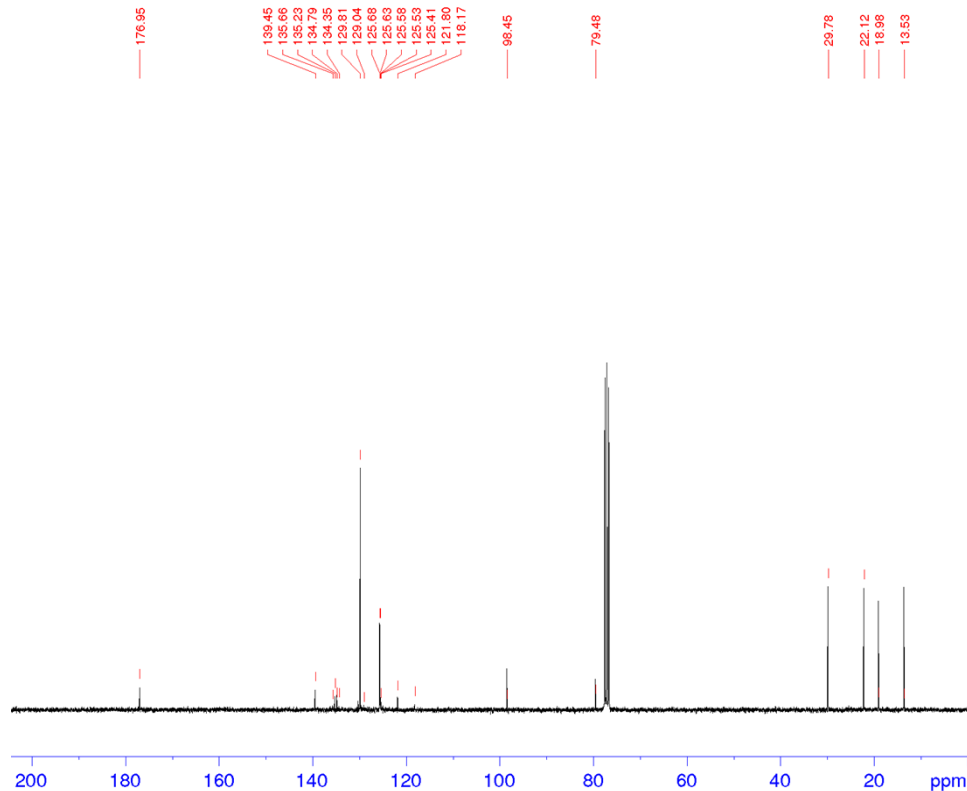


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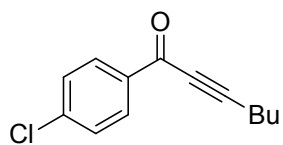
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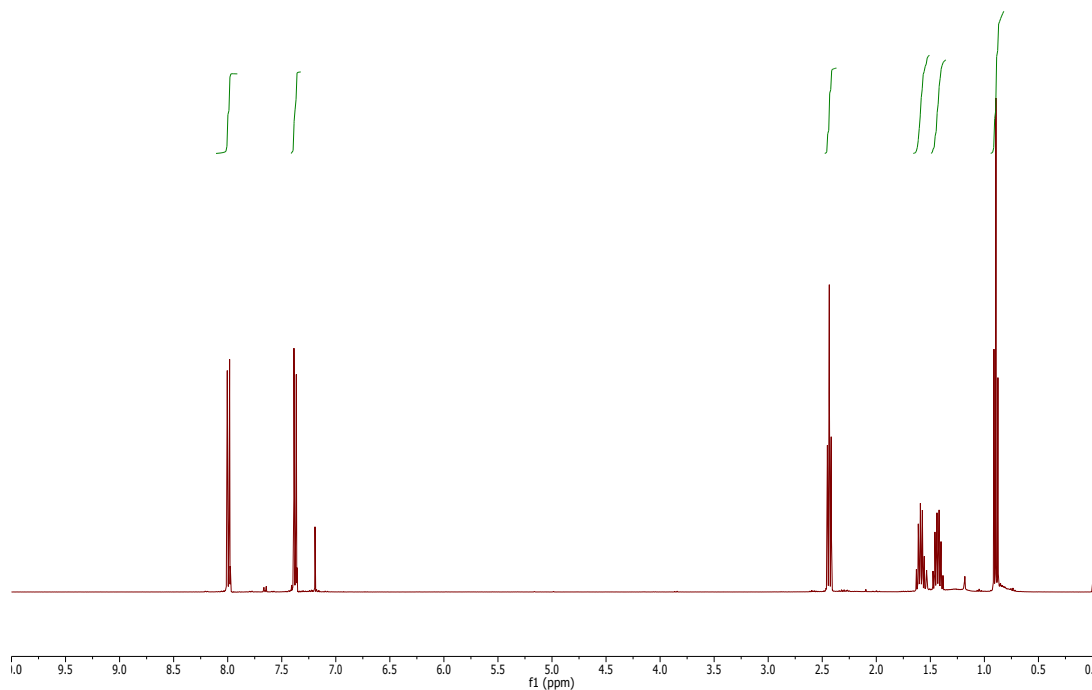
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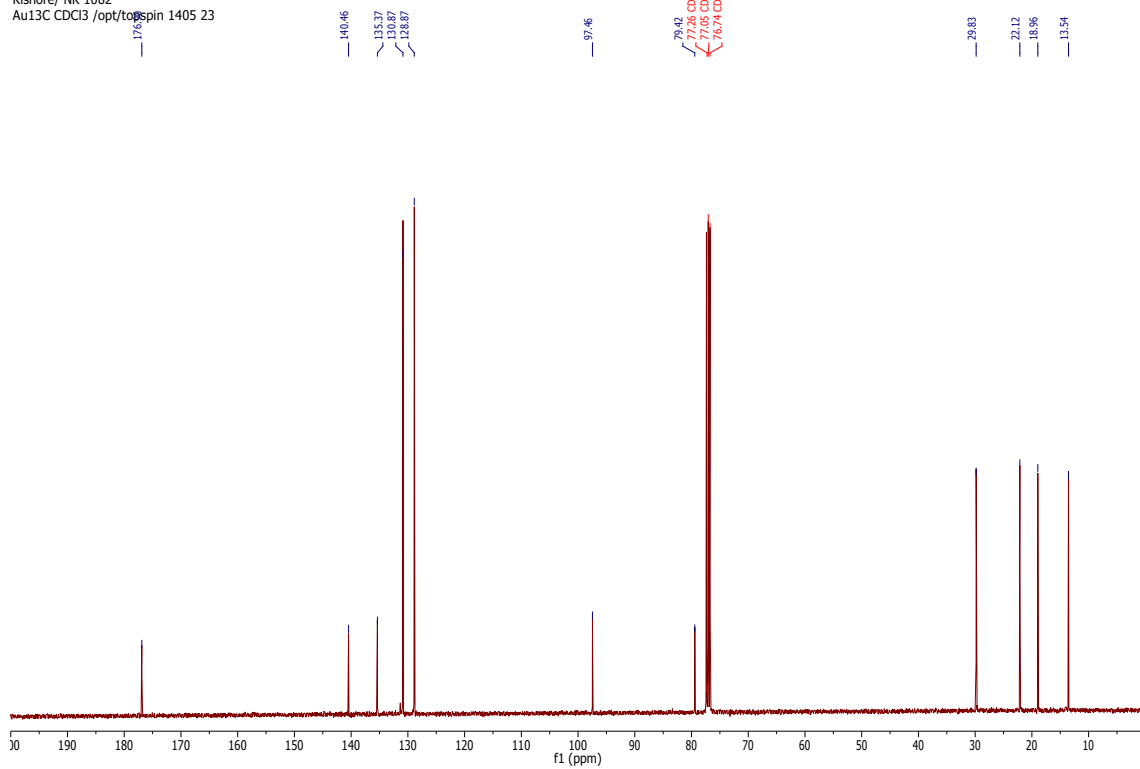
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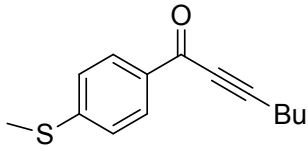


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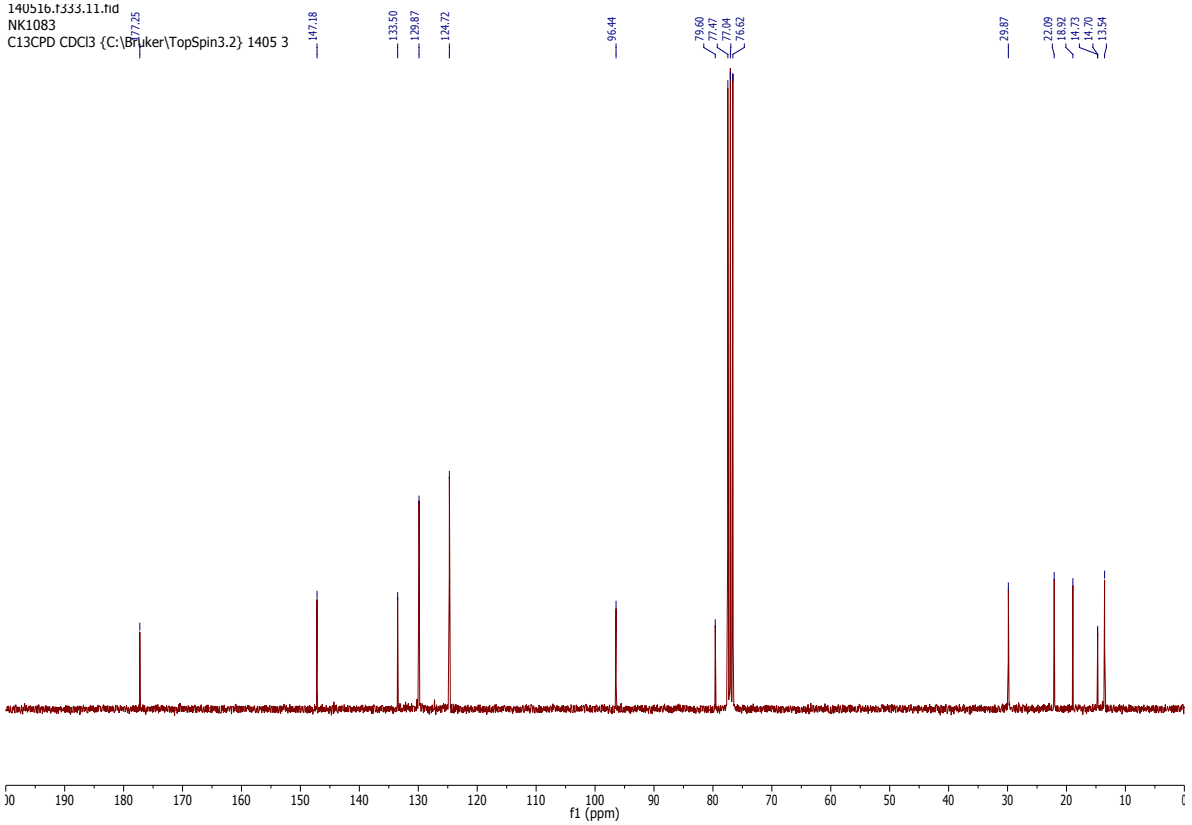
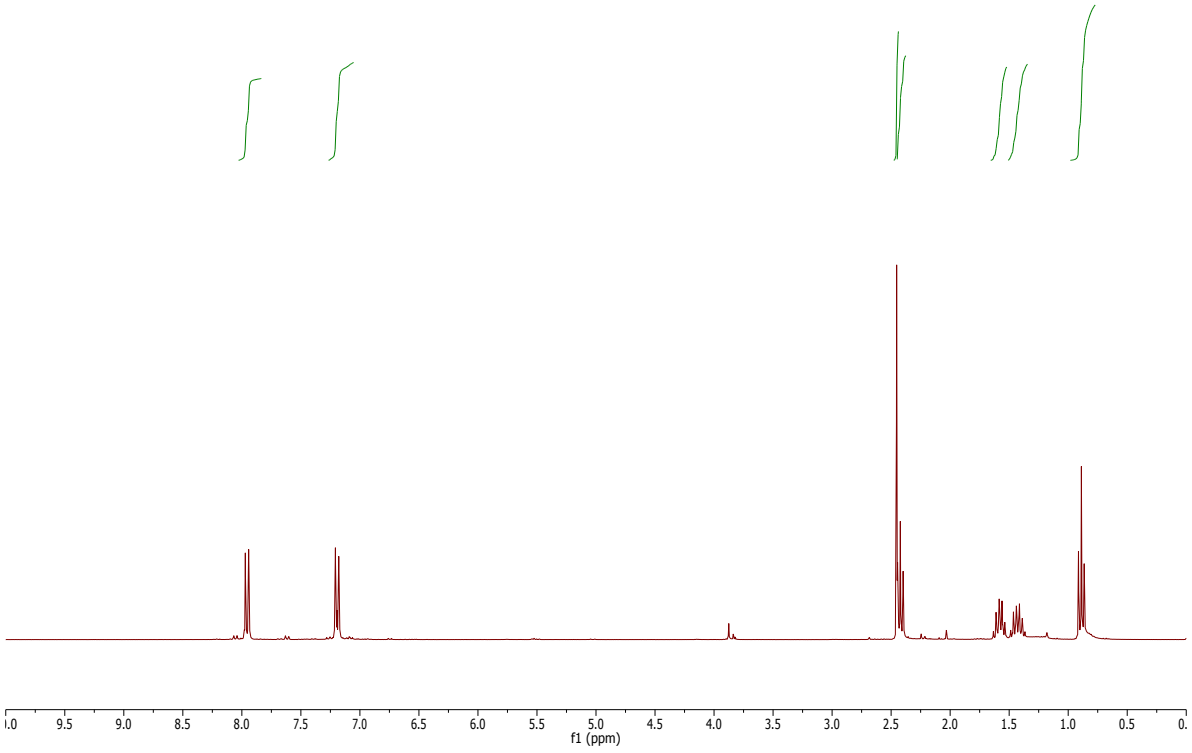


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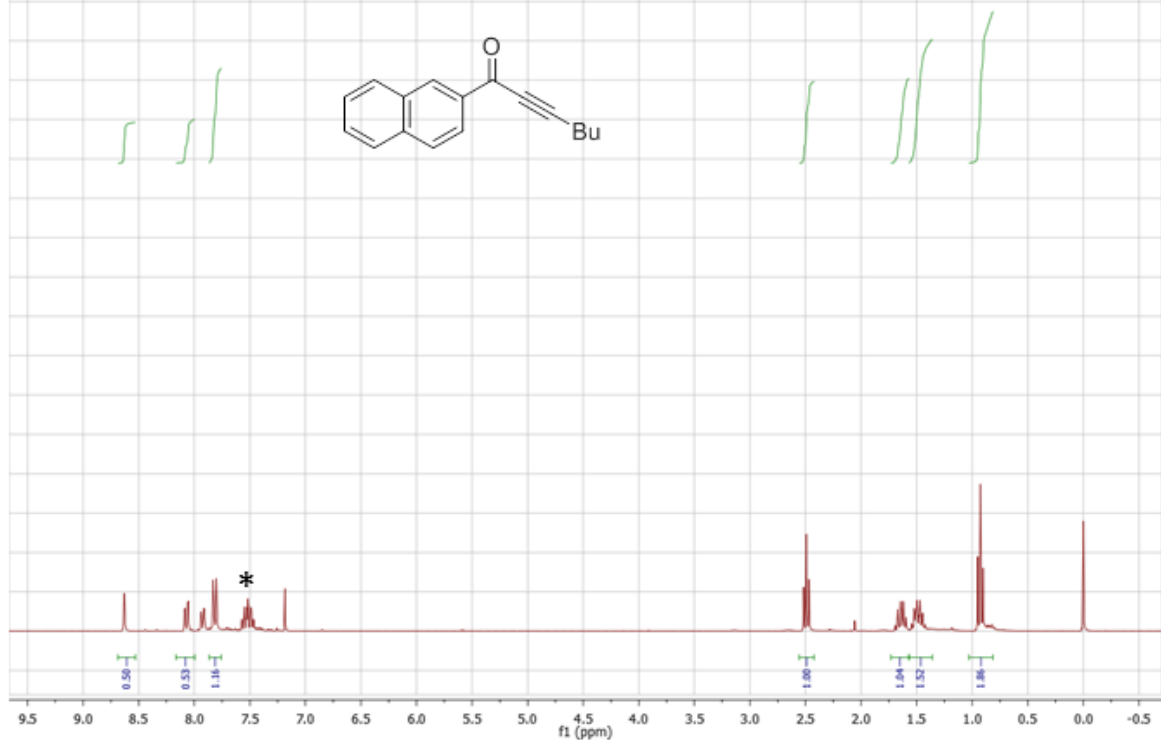




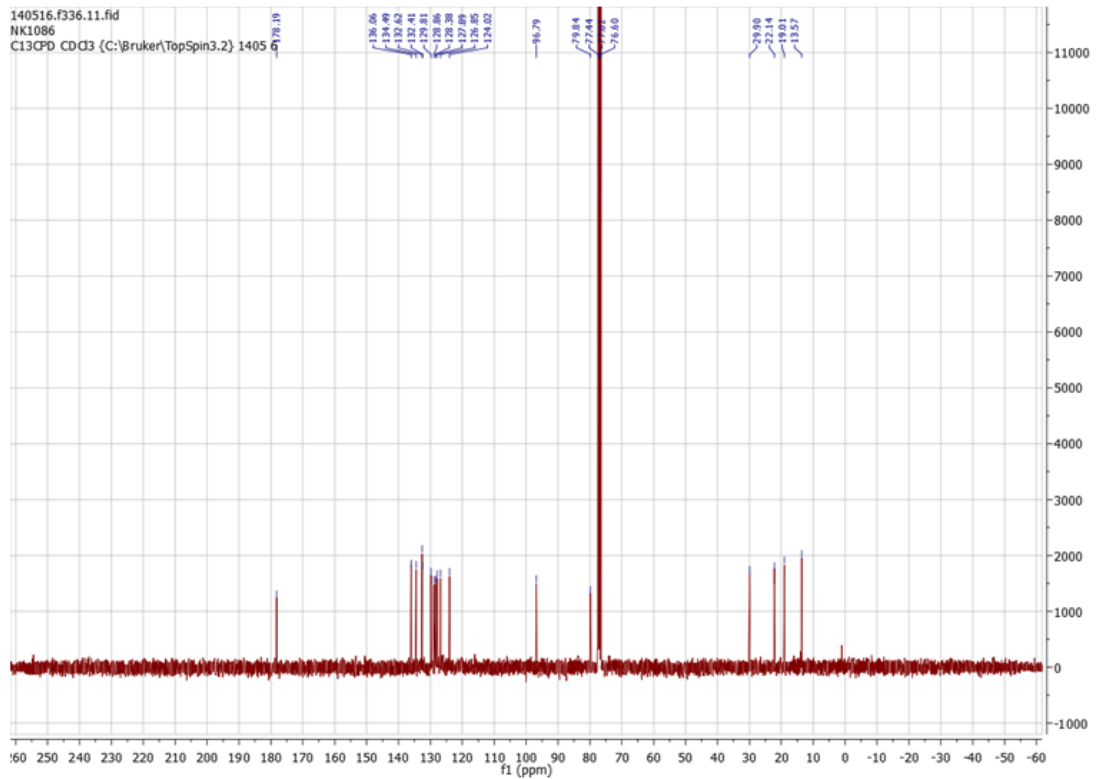
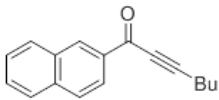
140516.1333.10.fid
 NK1083
 PROTON CDCl₃ {C:\Bruker\TopSpin3.2} 1405 3

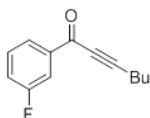


140516.f336.10.fid
NK1086
PROTON CDCl3 (C:\Bruker\TopSpin3.2) 1405 6

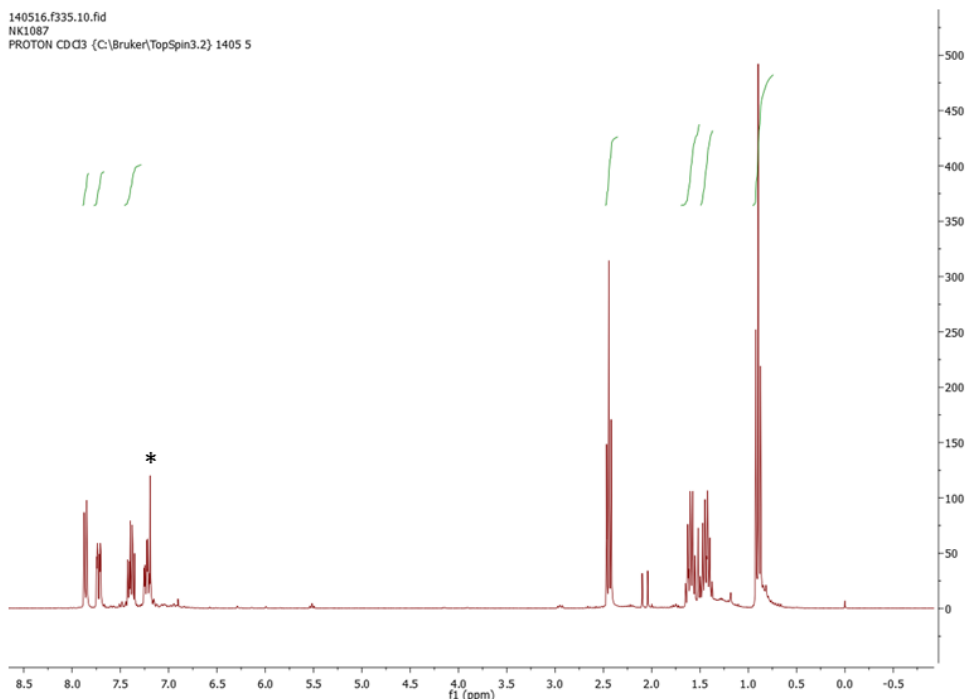


* The peak belongs to side product



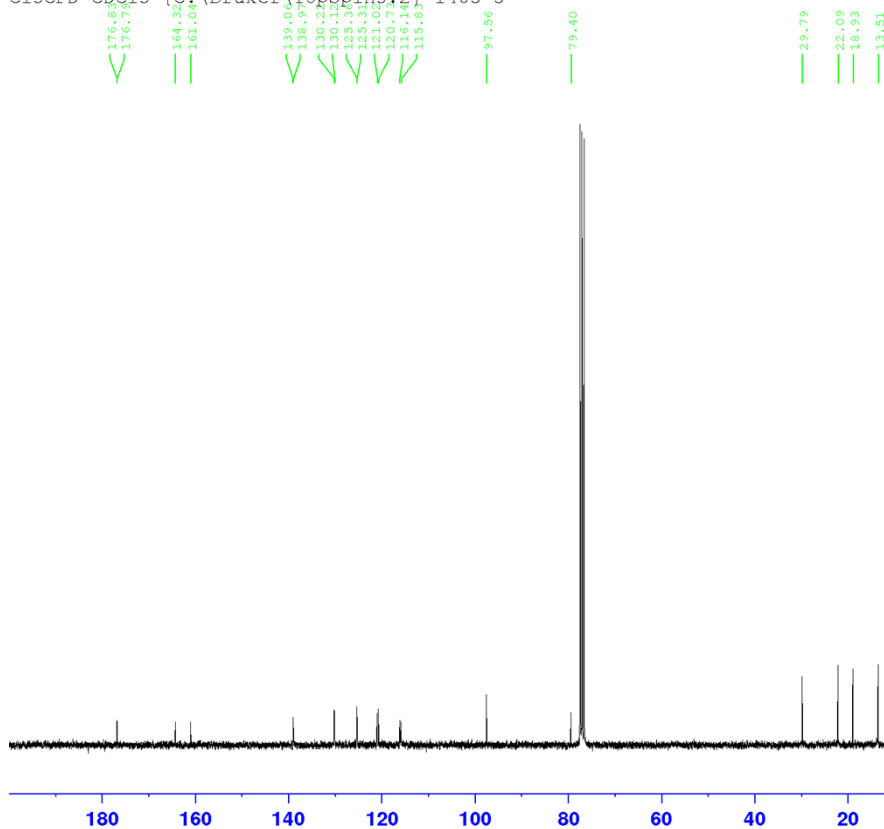


140516.f335.10.fid
NK1087
PROTON CDCl3 {C:\Bruker\TopSpin3.2} 1405 5



* The peak belongs to biphenyl

NK1087
C13CPD CDCl3 {C:\Bruker\TopSpin3.2} 1405 5



Current Data Parameters
NAME 140516.f335
EXPNO 11
PROCNO 1

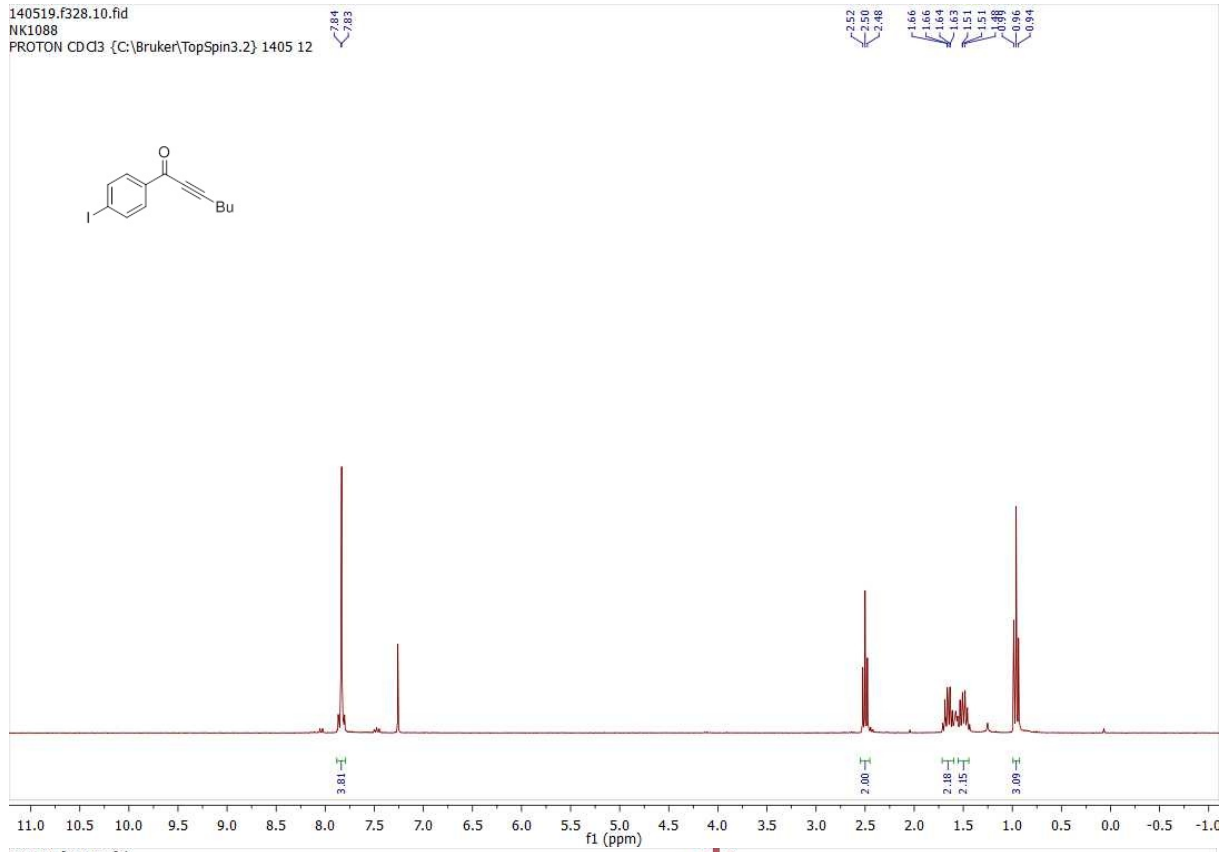
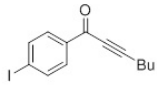
F2 - Acquisition Parameters
Date_ 20140516
Time 20.44
INSTRUM FOURIER300
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 6536
SOLVENT CDCl3
NS 2048
DS 4
SWH 24414.063 Hz
FIDRES 0.372529 Hz
AQ 1.3421773 sec
RG 501.187
DW 20.480 usec
DE 6.50 usec
TE 298.2 K
D1 2.0000000 sec
D11 0.0300000 sec
D31 0.0000140 sec
D40 0.02898005 sec
L4 40
L5 57
F32 90.00 usec
TD0 1

===== CHANNEL f1 =====
SFO1 75.4928982 MHz
NUC1 13C
P1 11.40 usec
PLW1 30.0000000 W

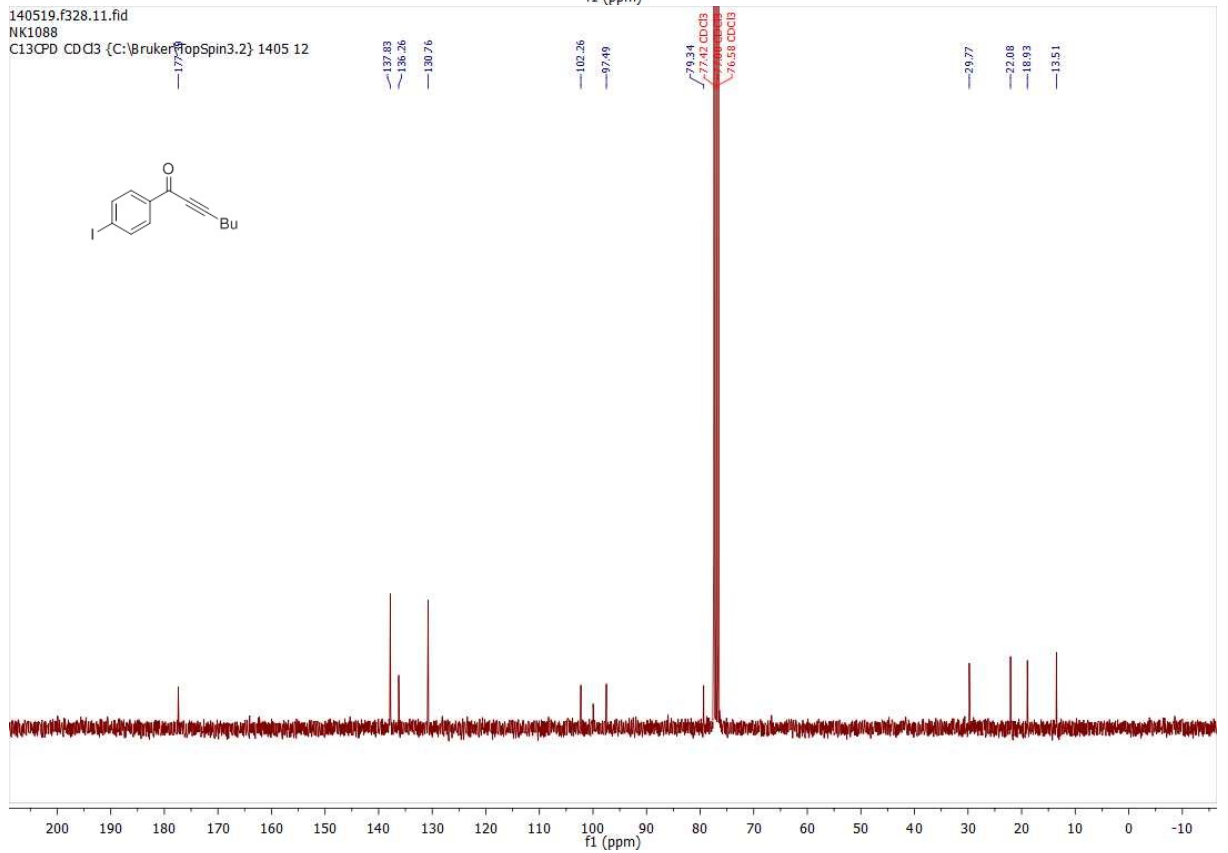
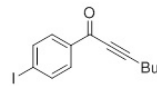
===== CHANNEL f2 =====
SFO2 300.2012008 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 16.0000000 W
PLW12 0.23901001 W
PLW13 0.19360000 W

F2 - Processing parameters
SI 32768
SF 75.4853500 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

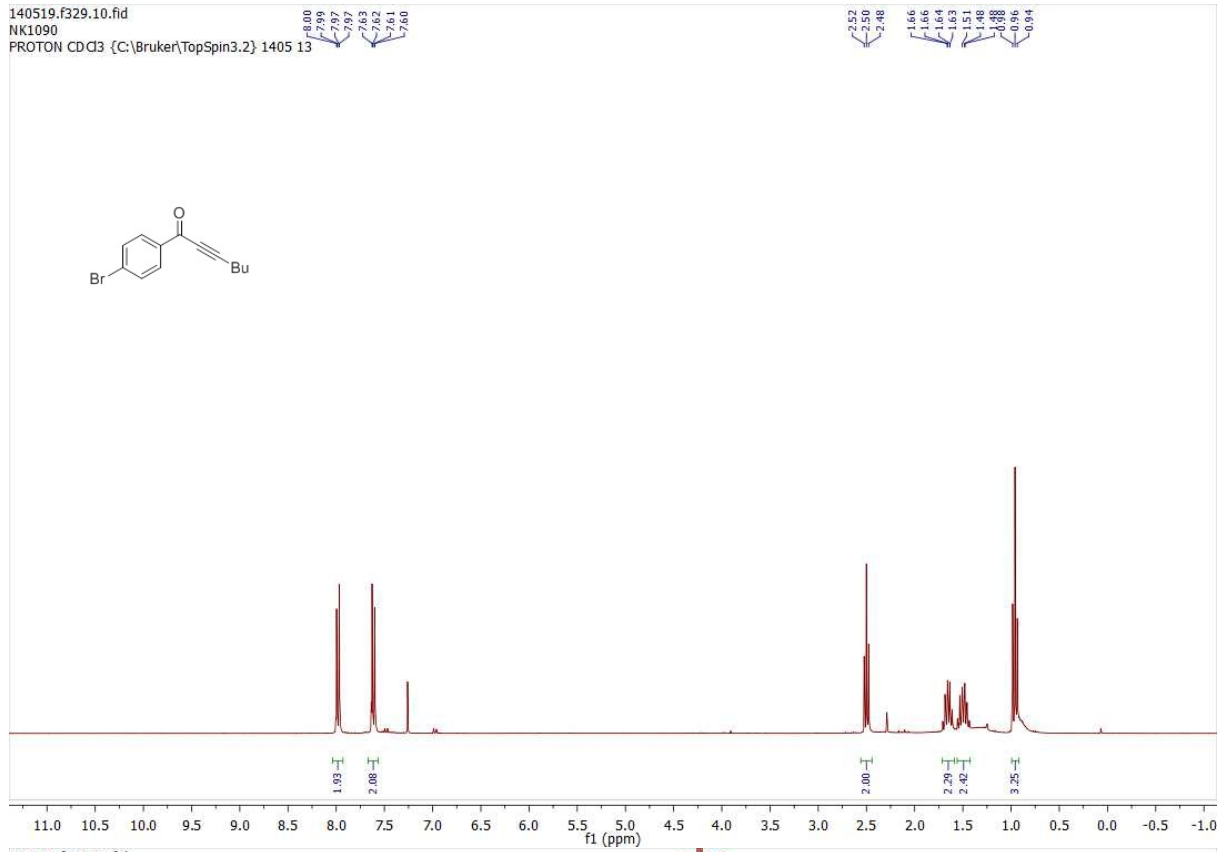
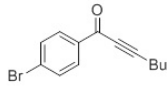
140519.f328.10.fid
NK1088
PROTON CDCl3 {C:\Bruker\TopSpin3.2} 1405 12



140519.f328.11.fid
NK1088
C13CPD CDCl3 {C:\Bruker\TopSpin3.2} 1405 12



140519.f329.10.fid
NK1090
PROTON CDCl3 {C:\Bruker\TopSpin3.2} 1405 13



140519.f329.11.fid
NK1090
C13CPD CDCl3 {C:\Bruker\TopSpin3.2} 1405 13

