Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Pd-Catalyzed Aminocarbonylation of Alkynes with Amines using $Co_2(CO)_8$ as a Carbonyl Source

Yaxi Dong,[a] Suyan Sun,[a] Fan Yang,*[a] Yu Zhu,[a] Weiguo Zhu,[a] Huijie Qiao,[a] Yusheng Wu,*[b,c] and Yangjie Wu*[a]

[a] *The College of Chemistry and Molecular Engineering, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, China.*
E-mail: yangf@zzu.edu.cn, wyj@zzu.edu.cn.
[b] *Tetranov Biopharm, LLC., 75 Daxue Road, Zhengzhou, 450052, China.*
E-mail: yusheng.wu@tetranovglobal.com.
[c] *Collaborative Innovation Center of New Drug Research and Safety Evaluation, Henan Province, China.*
E-mail: yusheng.wu@tetranovglobal.com.

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General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer or Bruker DPX-300 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. GC analysis was performed on Agilent 4890D gas chromatograph. Mass spectra were measured on an LC-MSD-Trap-XCT instrument. High resolution mass spectra were ensured on a MALDI-FTMS. All solvents were used after further purification. Ethyl acetate and hexane were used for column chromatography. The commercials were obtained from commercial sources and used as-received without further purification unless otherwise noted.

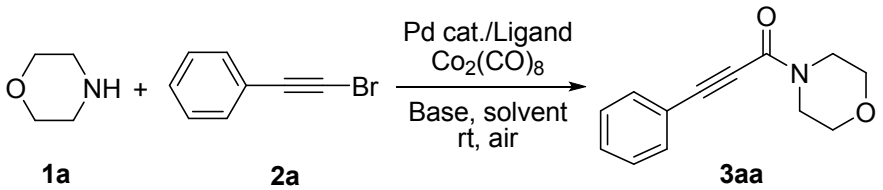
Preparation of Substrates

Bromoalkynes and terminal alkynes were prepared from the corresponding aryl iodides with ethynyltrimethylsilane. Arylpropiolic acids were prepared from the corresponding arylboronic acids with ethyl propiolate according to the reported procedure.[1-2]

Optimization of Reaction Conditions

A 25 mL sealed tube was equipped with a magnetic stir bar and charged with amine **1a** (0.3 mmol), alkyne **2a** (0.6 mmol), palladium catalyst (0.01 mmol Pd), ligand (0.02 mmol), $Co_2(CO)_8$ (0.075 mmol) and base (0.4 mmol) in solvent (1.0 ml). The resulting mixture was stirred at room temperature for 5 h. Upon completion, the resulting mixture was filtered through a pad of celite, washed with dichloromethane**.** After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using hexane/ethyl acetate as an eluent (3:2, V/V) to afford the pure product **3aa**.

Table S1 Screening of reaction conditions[a]



1a **2a** **3aa**

Entry	Catalyst	Ligand	Base	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	Xantphos	NEt_3	dioxane	31
2	$Pd(OAc)_2$	DPEtphos	NEt_3	dioxane	28
3	$Pd(OAc)_2$	PPh_3	NEt_3	dioxane	24
4	$Pd(OAc)_2$	dppf	NEt_3	dioxane	21
5	$Pd(OAc)_2$	Ruphos	NEt_3	dioxane	27
6	$Pd(OAc)_2$	1,10-phen	NEt_3	dioxane	19
7	$Pd(OAc)_2$	bpy	NEt_3	dioxane	13

8	$Pd(OAc)_2$	Xphos	NEt_3	dioxane	41
9	$Pd(OAc)_2$	Xphos	$^{i}Pr_2NEt$	dioxane	37
10	$Pd(OAc)_2$	Xphos	DMAP	dioxane	14
11	$Pd(OAc)_2$	Xphos	DBU	dioxane	29
12	$Pd(OAc)_2$	Xphos	KOH	dioxane	42
13	$Pd(OAc)_2$	Xphos	NaOH	dioxane	38
14	$Pd(OAc)_2$	Xphos	^{t}BuOk	dioxane	35
15	$Pd(OAc)_2$	Xphos	NaOAc	dioxane	49
16	$Pd(OAc)_2$	Xphos	KOAc	dioxane	44
17	$Pd(OAc)_2$	Xphos	K_2CO_3	dioxane	51
18	$Pd(OAc)_2$	Xphos	Na_2CO_3	dioxane	47
19	$Pd(OAc)_2$	Xphos	Cs_2CO_3	dioxane	65(61)
20	$Pd(OAc)_2$	Xphos	Cs_2CO_3	DMF	29
21	$Pd(OAc)_2$	Xphos	Cs_2CO_3	DMSO	23
22	$Pd(OAc)_2$	Xphos	Cs_2CO_3	toluene	20
23	$Pd(OAc)_2$	Xphos	Cs_2CO_3	THF	51
24	$Pd(OAc)_2$	Xphos	Cs_2CO_3	1,2-DCE	46
25	$Pd(OAc)_2$	Xphos	Cs_2CO_3	CH_3CN	78 (73)
26	$PdCl_2$	Xphos	Cs_2CO_3	CH_3CN	52
27	$Pd(PPh_3)_4$	Xphos	Cs_2CO_3	CH_3CN	53
28	**$Pd_2(dba)_3$**	**Xphos**	**Cs_2CO_3**	**CH_3CN**	**92 (86)**
29	$Pd(PPh_3)_2Cl_2$	Xphos	Cs_2CO_3	CH_3CN	81(79)
30	$Pd(CH_3CN)_2Cl_2$	Xphos	Cs_2CO_3	CH_3CN	77(74)
31	$Pd(PCy_3)_2Cl_2$	Xphos	Cs_2CO_3	CH_3CN	62(59)
32	CuI	Xphos	Cs_2CO_3	CH_3CN	Trace
33	$Cu(OAc)_2 \cdot H_2O$	Xphos	Cs_2CO_3	CH_3CN	Trace
34	$Cu(OAc)_2$	Xphos	Cs_2CO_3	CH_3CN	Trace
35	$NiCl_2$	Xphos	Cs_2CO_3	CH_3CN	21
36	$NiCl_2 \cdot 6H_2O$	Xphos	Cs_2CO_3	CH_3CN	13
37[c]	$Pd_2(dba)_3$	Xphos	Cs_2CO_3	CH_3CN	72 (68)
38[d]	$Pd_2(dba)_3$	Xphos	Cs_2CO_3	CH_3CN	34

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), palladium catalyst (0.01 mmol Pd), ligand (0.02 mmol), $Co_2(CO)_8$ (0.075 mmol) and base (0.4 mmol) in solvent (1.0 ml) under air for 5 h in a sealed tube. [b] GC yield (isolated yield) based on the amount of morpholine. [c] For 4 h. [d] For 3h.

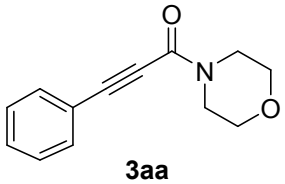
General Procedure for the Products

A 25 mL sealed tube was equipped with a magnetic stir bar and charged with amine **1** (0.3 mmol), alkyne **2** (0.6 mmol), palladium catalyst (0.01 mmol Pd), ligand (0.02 mmol), $Co_2(CO)_8$ (0.075 mmol) and base (0.4 mmol) in solvent (1.0 ml). The resulting mixture was stirred at room

temperature for 5 h. Upon completion, the resulting mixture was filtered through a pad of celite, washed with dichloromethane**.** After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using hexane/ethyl acetate as an eluent to afford the pure product **3**.

Characterization Data of the Products

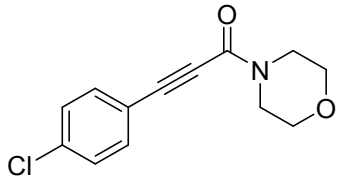
1-morpholino-3-phenylprop-2-yn-1-one (**3aa**):[3]



3aa

yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.56-7.53 (m, 2H), 7.45-7.31 (m, 3H), 3.85-3.83 (m, 2H), 3.75-3.73 (m, 2H), 3.69 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 153.2, 132.4, 130.2, 128.6, 120.2, 91.2, 80.7, 66.9, 66.5, 47.3, 42.0.

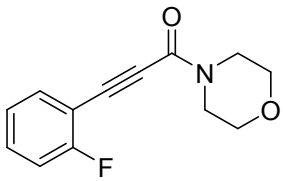
3-(4-chlorophenyl)-1-morpholinoprop-2-yn-1-one (**3ab**):



3ab

light red solid; mp 111-112 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.49-7.46 (m, 2H), 7.37-7.34 (m, 2H), 3.84-3.81 (m, 2H), 3.77-3.74 (m, 2H), 3.70 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 152.9, 136.5, 133.6, 129.0, 118.7, 89.9, 81.6, 66.9, 66.4, 47.3, 42.0; HRMS (ESI^{+}) calcd for $C_{13}H_{12}ClNO_2$ $[M+H]^{+}$: 250.0630, found: 250.0634.

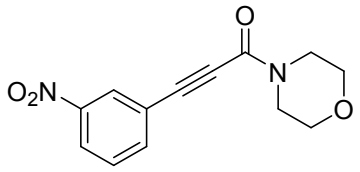
3-(2-fluorophenyl)-1-morpholinoprop-2-yn-1-one (**3ac**):



3ac

reddish brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.59-7.54 (m, 1H), 7.46-7.40 (m, 1H), 7.19-7.10 (m, 2H), 3.89-3.86 (m, 2H), 3.77-3.75 (m, 2H), 3.71 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 163.3 (d, $J_{C\text{-}F}$ = 252.4 Hz), 152.7, 134.1, 132.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 124.2 (d, $J_{C\text{-}F}$ = 3.8 Hz), 115.6 (d, $J_{C\text{-}F}$ = 20 Hz), 109.0 (d, $J_{C\text{-}F}$ = 15 Hz), 85.5 (d, $J_{C\text{-}F}$ = 3.2 Hz), 84.3, 66.8, 66.3, 47.2, 41.9; HRMS (ESI^{+}) calcd for $C_{13}H_{12}FNO_2$ $[M+H]^{+}$: 234.0925, found: 234.0928.

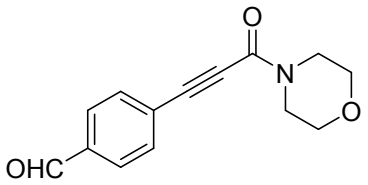
1-morpholino-3-(3-nitrophenyl)prop-2-yn-1-one (**3ad**):



3ad

reddish brown solid; mp 161-162 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 8.39-8.38 (m, 1H), 8.30-8.27 (m, 1H), 7.89-7.86 (m, 1H), 7.62-7.58 (m, 1H), 3.87-3.82 (m, 2H), 3.80-3.77 (m, 2H), 3.72 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 152.3, 148.1, 137.9, 129.8, 127.0, 124.8, 122.2, 88.0, 82.6, 66.9, 66.4, 47.4, 42.1; HRMS (ESI$^+$) calcd for $C_{13}H_{12}N_2O_4$ $[M+H]^+$: 261.0871, found: 261.0868.

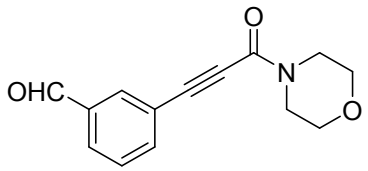
4-(3-morpholino-3-oxoprop-1-yn-1-yl)benzaldehyde (**3ae**)



3ae

yellow solid; mp 133-134 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 10.0 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 3.86-3.83 (m, 2H), 3.79-3.76 (m, 2H), 3.72 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm]= 191.2, 152.6, 136.8, 132.9, 129.6, 126.2, 89.5, 83.6, 66.9, 66.4, 47.3, 42.1; HRMS (ESI$^+$) calcd for $C_{14}H_{13}NO_3$ $[M+H]^+$: 244.0968, found: 244.0969.

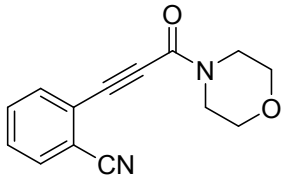
3-(3-morpholino-3-oxoprop-1-yn-1-yl)benzaldehyde (**3af**)



3af

red solid; mp 85-86 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 10.0 (s, 1H), 8.0 (t, J = 1.3 Hz, 1H), 7.96-7.93 (m, 1H), 7.82-7.79 (m, 1H), 7.58 (t, J = 7.7 Hz, 1H), 3.87-3.84 (m, 2H), 3.78-3.76 (m, 2H), 3.72 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 191.0, 152.7, 137.7, 136.6, 133.3, 131.0, 129.4, 121.6, 89.3, 81.9, 66.9, 66.5, 47.4, 42.0; HRMS (ESI$^+$) calcd for $C_{14}H_{13}NO_3$ $[M+H]^+$: 244.0968, found: 244.0967.

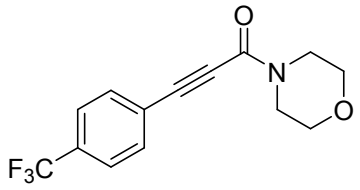
2-(3-morpholino-3-oxoprop-1-yn-1-yl)benzonitrile (**3ag**):



3ag

light red solid; mp 108-109 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.77-7.71 (m, 2H), 7.67-7.62 (m, 1H), 7.58-7.53 (m, 1H), 4.00-3.98 (m, 2H), 3.80-3.77 (m, 2H), 3.72 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 152.2, 133.8, 132.8, 132.7, 130.4, 124.4, 117.3, 115.8, 86.0, 85.8, 67.0, 66.4, 47.5, 42.2; HRMS (ESI$^+$) calcd for $C_{14}H_{12}N_2O_2$ [M+H]$^+$: 241.0972, found: 241.0973.

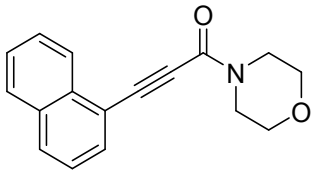
1-morpholino-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (**3ah**):



3ah

red solid; mp 122-123 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.68-7.63 (m, 4H), 3.86-3.83 (m, 2H), 3.78-3.76 (m, 2H), 3.72 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 152.6, 132.6, 131.8 (q, $J_{C\text{-}F}$ = 32.7 Hz), 125.5 (q, J = 3.7 Hz), 124.1, 123.6 (q, J = 271.0 Hz), 89.2, 82.5, 66.8, 66.4, 47.3, 42.0; HRMS (ESI$^+$) calcd for $C_{14}H_{12}F_3NO_2$ [M+H]$^+$: 284.0893, found: 284.0898.

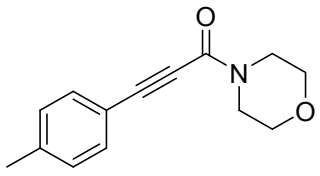
1-morpholino-3-(naphthalen-1-yl)prop-2-yn-1-one (**3ai**):[4]



3ai

yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 8.28-8.26 (m, 1H), 7.93-7.87 (m, 2H), 7.81-7.79 (m, 1H), 7.63-7.59 (m, 1H), 7.57-7.53 (m, 1H), 7.48-7.44 (m, 1H), 3.96-3.94 (m, 2H), 3.80-3.78 (m, 2H), 3.76-3.74 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 153.3, 133.3, 133.1, 132.2, 130.8, 128.5, 127.5, 126.9, 125.7, 125.1, 117.9, 89.6, 85.4, 66.9, 66.5, 47.4, 42.1.

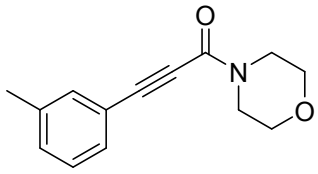
1-morpholino-3-(*p*-tolyl)prop-2-yn-1-one (**3aj**):[4]



3aj

red solid; mp 90-91 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.43 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 3.84 (t, J = 4.7 Hz, 2H), 3.74 (t, J = 4.8 Hz, 2H), 3.69 (s, 4H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 153.3, 140.7, 132.3, 129.3, 117.1, 91.6, 80.4, 66.9, 66.5, 47.3, 41.9, 21.6.

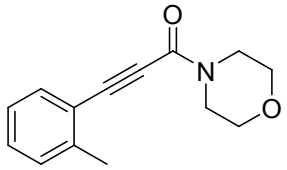
1-morpholino-3-(*m*-tolyl)prop-2-yn-1-one (**3ak**):[4]



3ak

yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.36-7.34 (m, 2H), 7.28-7.23 (m, 2H), 3.85 (t, J = 4.8 Hz, 2H), 3.75 (t, J = 4.7 Hz, 2H), 3.71 (s, 4H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 153.3, 138.4, 132.9, 131.1, 129.5, 128.5, 120.1, 91.5, 80.5, 66.9, 66.5, 47.3, 42.0, 21.2.

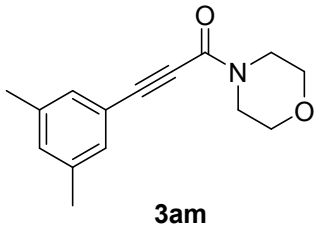
1-morpholino-3-(*o*-tolyl)prop-2-yn-1-one (**3al**):[4]



3al

yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.52-7.51 (m, 1H), 7.34-7.30 (m, 1H), 7.25-7.23 (m, 1H), 7.21-7.17 (m, 1H), 3.86 (t, J = 4.8 Hz, 2H), 3.75 (t, J = 4.8 Hz, 2H), 3.72 (s, 4H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 153.3, 141.3, 132.9, 130.2, 129.7, 125.8, 120.2, 90.3, 84.6, 66.9, 66.5, 47.3, 42.0, 20.8.

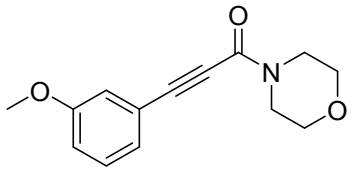
3-(3,5-dimethylphenyl)-1-morpholinoprop-2-yn-1-one (**3am**):



3am

yellow solid; mp 85-86 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.17 (s, 2H), 7.06 (s, 1H), 3.86-3.83 (m, 2H), 3.76-3.74 (m, 2H), 3.70 (s, 4H), 2.31 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 153.4, 138.2, 132.2, 130.1, 119.9, 91.8, 80.2, 66.9, 66.5, 47.3, 42.0, 21.1; HRMS (ESI$^+$) calcd for $C_{15}H_{17}NO_2$ $[M+H]^+$: 244.1332, found: 244.1334.

3-(3-methoxyphenyl)-1-morpholinoprop-2-yn-1-one (**3an**):

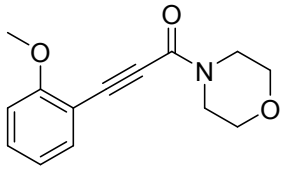


3an

yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.29-7.25 (m, 1H), 7.16-7.11 (m, 1H), 7.07-7.06 (m, 1H), 6.99-6.96 (m, 1H), 3.87-3.83 (m, 2H), 3.81 (s, 3H), 3.78-3.74 (m, 2H), 3.70 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 159.4, 153.2, 129.7, 124.8, 121.2, 117.1, 116.9, 91.1,

80.5, 66.9, 66.5, 55.4, 47.3, 42.0; HRMS (ESI$^+$) calcd for $C_{14}H_{15}NO_3$ [M+H]$^+$: 246.1125, found: 246.1129.

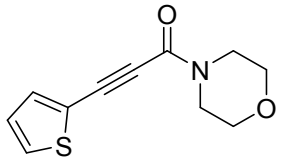
3-(2-methoxyphenyl)-1-morpholinoprop-2-yn-1-one (**3ao**):[4]



3ao

yellow solid; mp 94-95 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.52-7.50 (m, 1H), 7.41-7.37 (m, 1H), 6.96-6.89 (m, 2H), 3.92 (t, J = 4.8 Hz, 2H), 3.87 (s, 3H), 3.75 (t, J = 3.7 Hz, 2H), 3.70 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 161.1, 153.4, 134.3, 131.9, 120.6, 110.7, 109.5, 87.8, 85.0, 67.0, 66.5, 55.8, 47.3, 41.9.

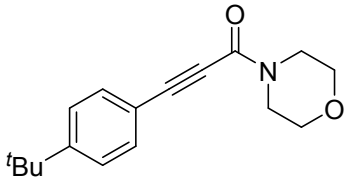
1-morpholino-3-(thiophen-2-yl)prop-2-yn-1-one (**3ap**):



3ap

reddish brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.44-7.42 (m, 2H), 7.06-7.04 (m, 1H), 3.82-3.80 (m, 2H), 3.77-3.74 (m, 2H), 3.70 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 153.0, 135.3, 130.2, 127.5, 119.9, 85.0, 84.8, 66.9, 66.5, 47.3, 42.0; HRMS (ESI$^+$) calcd for $C_{11}H_{11}NO_2S$ [M+H]$^+$: 222.0583, found: 222.0585.

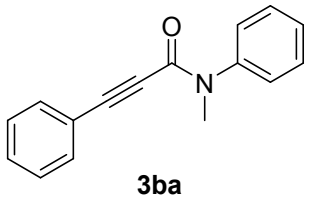
3-(4-(*tert*-butyl)phenyl)-1-morpholinoprop-2-yn-1-one (**3as**):



3as

yellow solid; mp 149-150 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.49-7.45 (m, 2H), 7.42-7.34 (m,2H), 3.84 (t, J = 4.7 Hz, 2H), 3.75 (t, J = 4.7 Hz, 2H), 3.70 (s, 4H), 1.32 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 153.8, 153.4, 132.2, 125.6, 117.2, 91.6, 80.3, 66.9, 66.5, 47.3, 42.0, 35.0, 31.1; HRMS (ESI$^+$) calcd for $C_{17}H_{21}NO_2$ [M+H]$^+$: 272.1645, found: 272.1650.

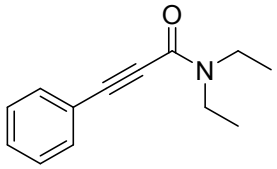
***N*-methyl-*N*,3-diphenylpropiolamide** (**3ba**):[5]



3ba

red oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.47-7.43 (m, 2H), 7.40-7.30 (m, 3H), 7.26-7.21 (m, 3H), 7.15-7.13 (m, 2H), 3.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 154.4, 143.3, 132.4, 129.9, 129.2, 128.3, 127.9, 127.4, 120.4, 90.9, 82.6, 36.4.

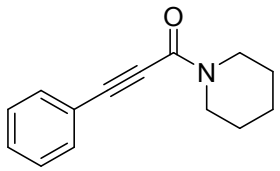
***N*,*N*-diethyl-3-phenylpropiolamide (3ca)**:[6]



3ca

reddish brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.55-7.53 (m, 2H), 7.43-7.34 (m, 3H), 3.66 (dd, J = 3.6 Hz, J = 10.7 Hz, 2H), 3.48 (dd, J = 3.6 Hz, J = 10.7 Hz, 2H), 1.30-1.24 (m, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 154.0, 132.3, 129.9, 128.5, 120.8, 89.0, 82.0, 43.6, 39.3, 14.4, 12.9.

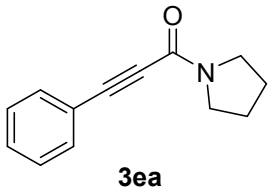
3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-one (3da):[6]



3da

red solid; mp 96-97 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.56-7.53 (m, 2H), 7.43-7.33 (m, 3H), 3.77 (t, J = 5.2 Hz, 2H), 3.62 (t, J = 5.6 Hz, 2H), 1.72-1.55 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 152.9, 132.3, 129.9, 128.5, 120.7, 90.2, 81.5, 48.2, 42.4, 26.4, 25.4, 24.5.

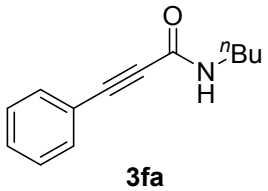
3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-one (3ea):[6]



3ea

reddish brown solid; mp 71-72 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.56-7.53 (m, 2H), 7.43-7.33 (m, 3H), 3.73 (t, J = 6.4 Hz, 2H), 3.53 (t, J = 6.5 Hz, 2H), 2.00-1.91 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 152.7, 132.4, 129.9, 128.5, 120.6, 88.7, 82.7, 48.1, 45.4, 25.4, 24.7.

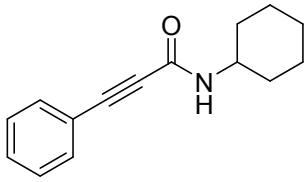
***N*-butyl-3-phenylpropiolamide (3fa)**:



3fa

yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.53-7.51 (m, 2H), 7.40-7.32 (m, 3H), 6.08 (s, 1H), 3.38-3.32 (m, 2H), 1.57-1.53 (m, 2H), 1.42-1.36 (m, 2H), 0.96-0.92 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 153.5, 132.5, 130.0, 128.5, 120.3, 84.4, 83.2, 39.7, 31.4, 20.0, 13.7; HRMS (ESI$^+$) calcd for $C_{13}H_{15}NO$ $[M+H]^+$: 202.1227, found: 202.1227.

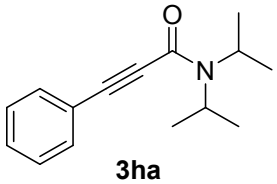
***N*-cyclohexyl-3-phenylpropiolamide (3ga)**:



3ga

red solid; mp 97-98 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.53-7.51 (m, 2H), 7.40-7.32 (m, 3H), 5.94 (d, J = 6.8 Hz, 1H), 3.91-3.84 (m, 1H), 2.00-1.96 (m, 2H), 1.76-1.60 (m, 3H), 1.43-1.32 (m, 2H), 1.26-1.16 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 152.5, 132.4, 129.9, 128.5, 120.4, 84.2, 83.4, 48.9, 32.9, 25.4, 24.8; HRMS (ESI$^+$) calcd for $C_{15}H_{17}NO$ $[M+H]^+$: 228.1383, found: 228.1385.

***N*,*N*-diisopropyl-3-phenylpropiolamide (3ha)**:



3ha

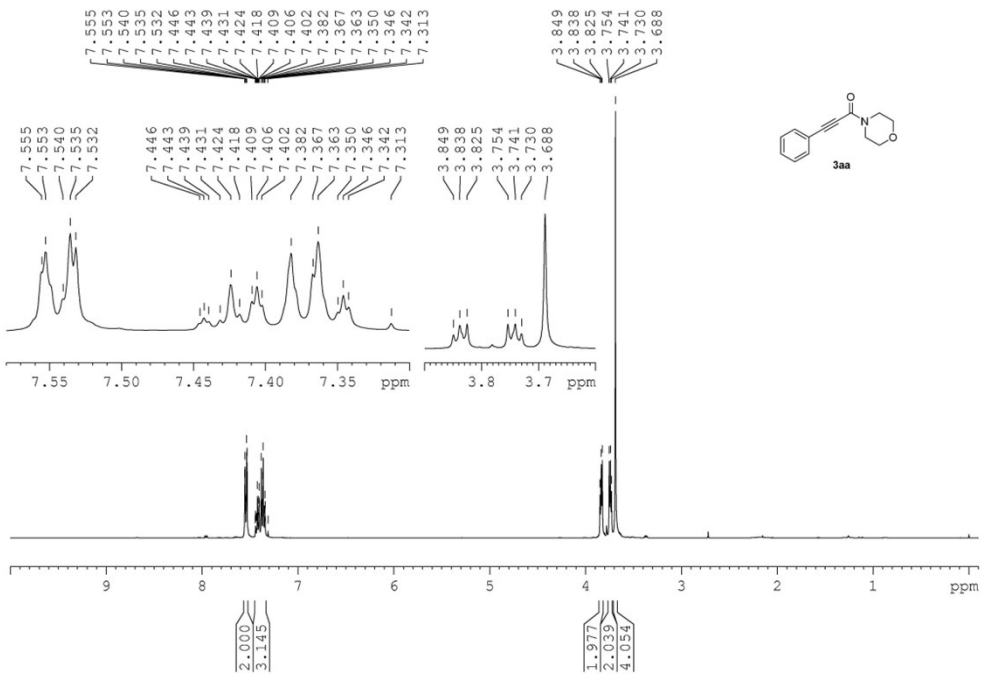
yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm] = 7.56-7.52 (m, 2H), 7.41-7.36 (m, 3H), 4.46-4.57 (m, 1H), 3.75-3.68 (m, 1H), 1.42 (d, J = 6.9 Hz, 6H), 1.32 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ [ppm] = 153.6, 132.2, 129.7, 128.4, 121.0, 88.5, 83.1, 46.1, 45.8, 21.1, 20.1; HRMS (ESI$^+$) calcd for $C_{15}H_{19}NO$ $[M+H]^+$: 230.1540, found: 230.1543.

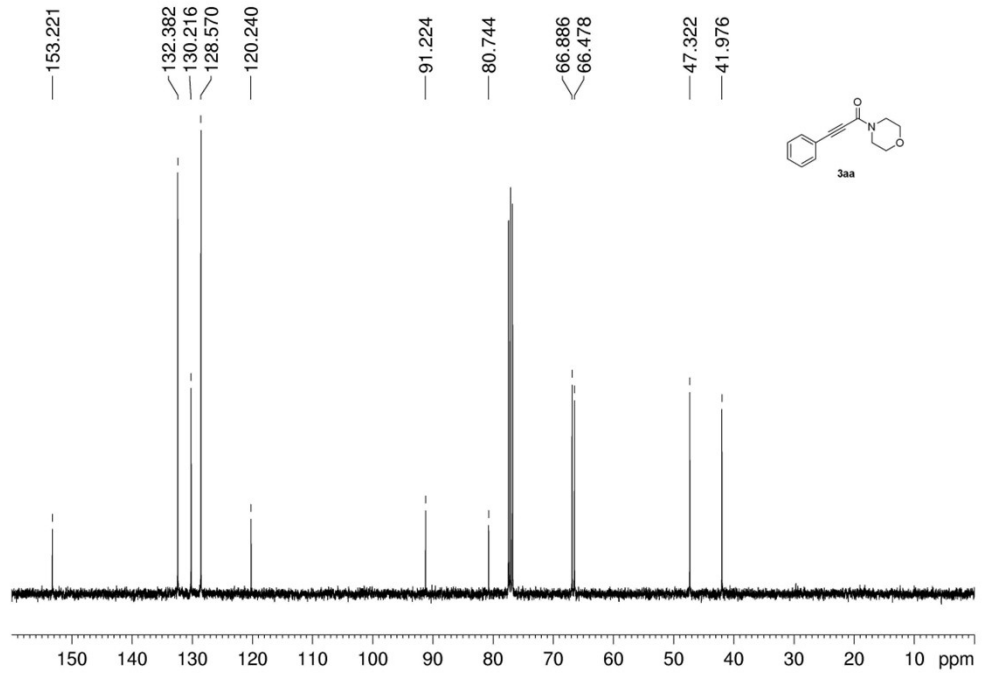
References

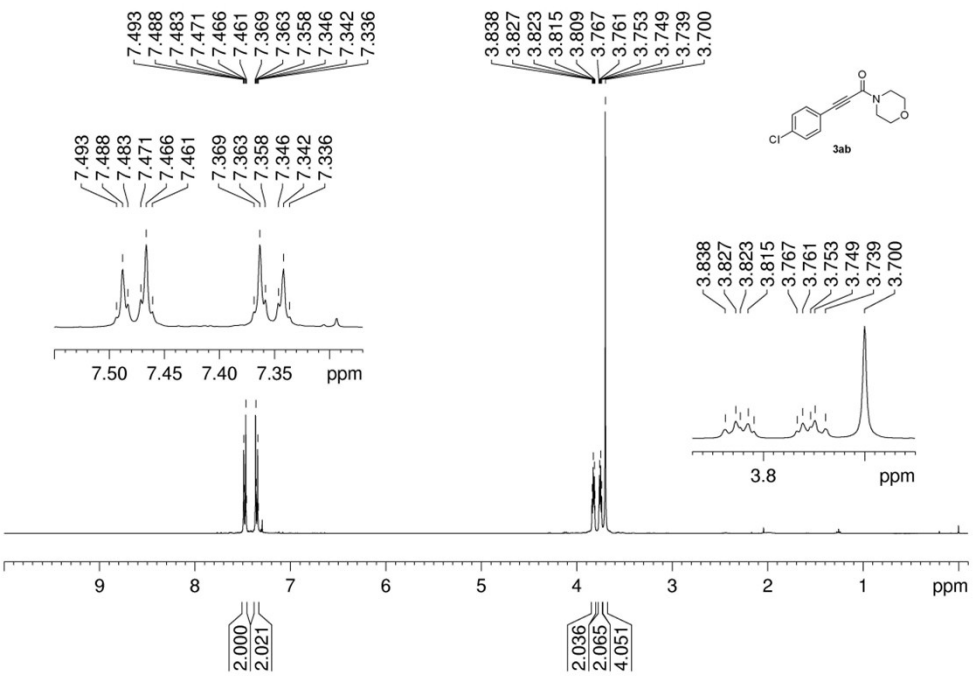
1. For selected papers on the synthesis of bromoalkynes and terminal alkynes, see: (a) U. Dutta, S. Maity, R. Kancherla and D. Maiti, *Org. Lett.*, 2014, **16**, 6302-6305; (b) P. P. Tian, S. H. Cai, Q. J. Liang, X. Y. Zhou, Y. H. Xu, and T. P. Loh, *Org. Lett.*, 2015, **17**, 1636-1639.
2. For selected papers on the synthesis of arylpropiolic acids, see: F. Yang and Y. J. Wu, *Eur. J. Org. Chem.*, 2007, 3476-3479.
3. B. Gabriele, G. Salerno, L. Veltri and M. Costa, *J. Organomet. Chem.*, 2001, **622**, 84-88.
4. J. Hwang, J. Choi, K. Park, W. Kim, K. H. Song and S. Lee, *Eur. J. Org. Chem.*, 2015, 2235-2243.

5. M. B. Zhou, W. T. Wei, Y. X. Xie, Y. Lei and J. H. Li, *J. Org. Chem.*, 2010, **75**, 5635-5642.
6. S. T. Gadge, M. V. Khedkar, S. R. Lanke and B. M. Bhanage, *Adv. Synth. Catal.*, 2012, **354**, 2049-2056.

Copies of ^{1}H and ^{13}C NMR Spectra for the Products



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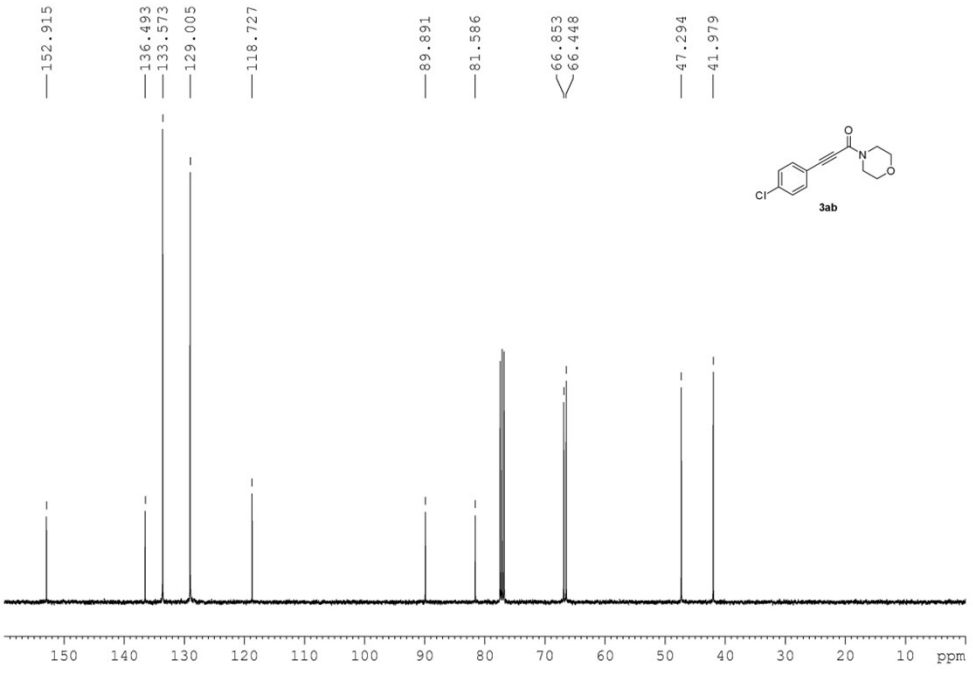
7.483
7.471
7.466
7.461
7.369
7.363
7.358
7.346
7.342
7.336
3.838
3.827
3.823
3.815
3.809
3.767
3.761
3.753
3.749
3.739
3.700
3ab
7.50 7.45 7.40 7.35 ppm
3.8 ppm
9 8 7 6 5 4 3 2 1 ppm
2.000
2.021
2.036
2.065
4.051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136.493
133.573
129.005
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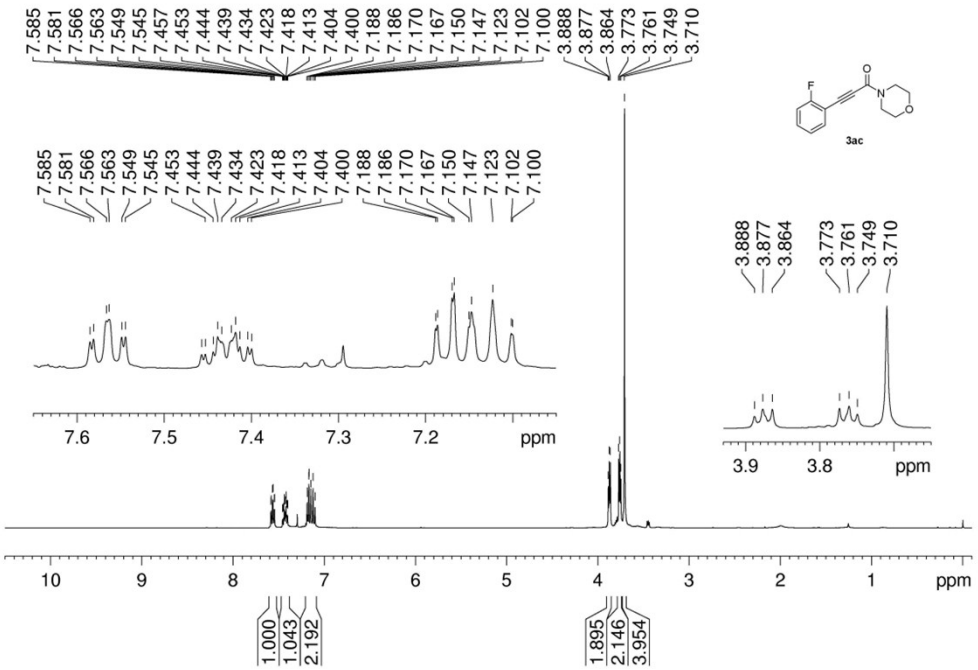
66.853
66.448
47.294
41.979
3ab
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.418
7.413
7.404
7.400
7.188
7.186
7.170
7.167
7.150
7.147
7.123
7.102
7.100
3.888
3.877
3.864
3.773
3.761
3.749
3.710
3ac
7.6
7.5
7.4
7.3
7.2
ppm
3.9
3.8
ppm
10
9
8
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5
4
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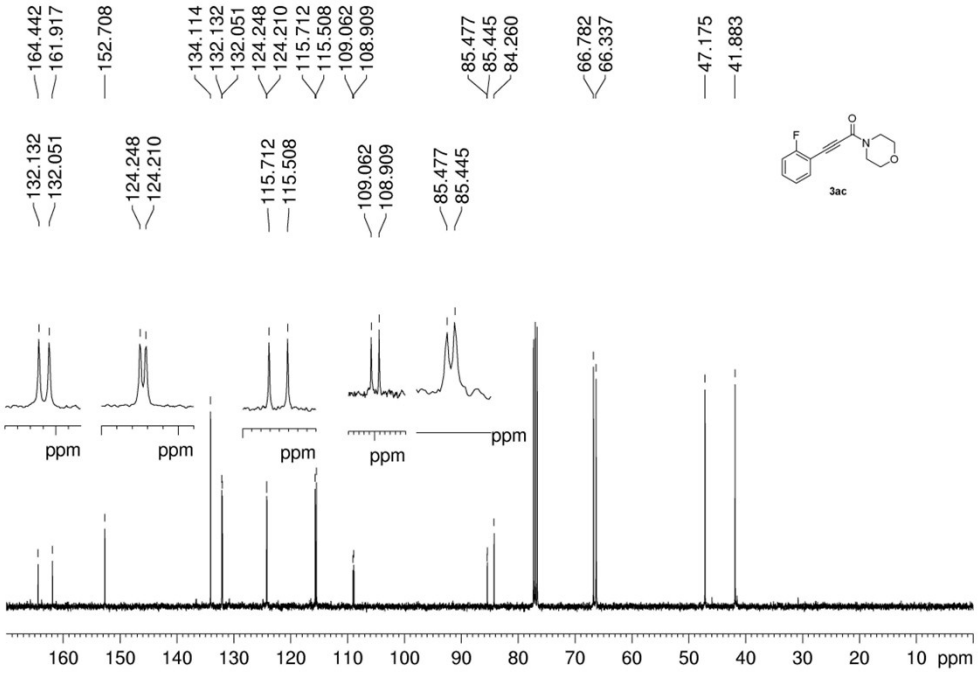
1.895
2.146
3.954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152.708
134.114
132.132
132.051
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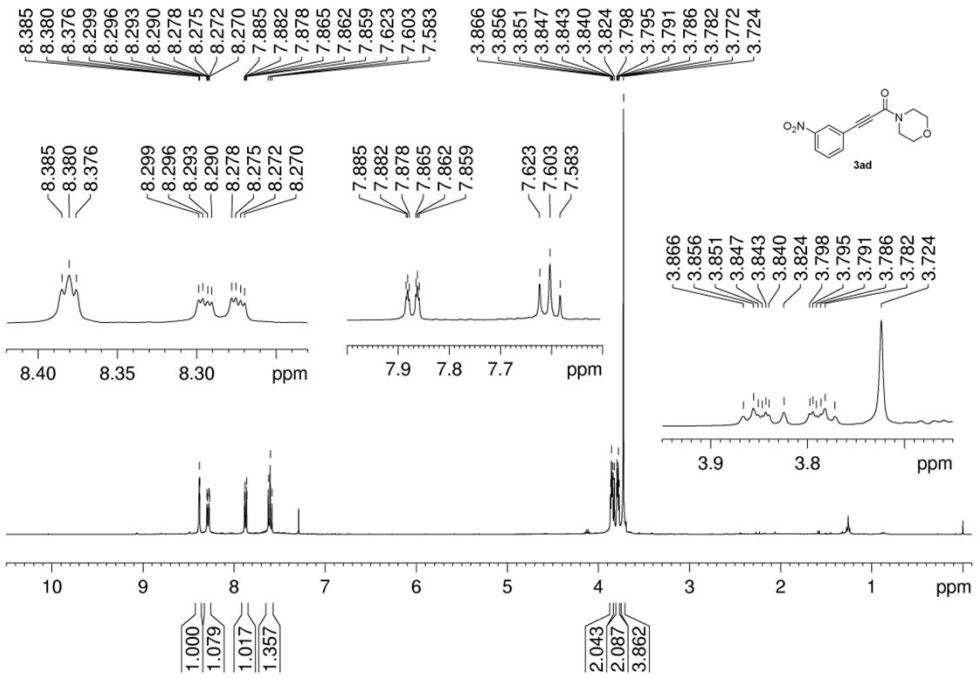
124.210
115.712
115.508
109.062
108.909
85.477
85.445
84.260
66.782
66.337
47.175
41.883
3ac
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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8.376
8.299
8.296
8.293
8.290
8.278
8.275
8.272
8.270
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7.882
7.878
7.865
7.862
7.859
7.623
7.603
7.583
3.866
3.856
3.851
3.847
3.843
3.840
3.824
3.798
3.795
3.791
3.786
3.782
3.772
3.724
3ad
8.40
8.35
8.30
ppm
7.9
7.8
7.7
ppm
3.9
3.8
ppm
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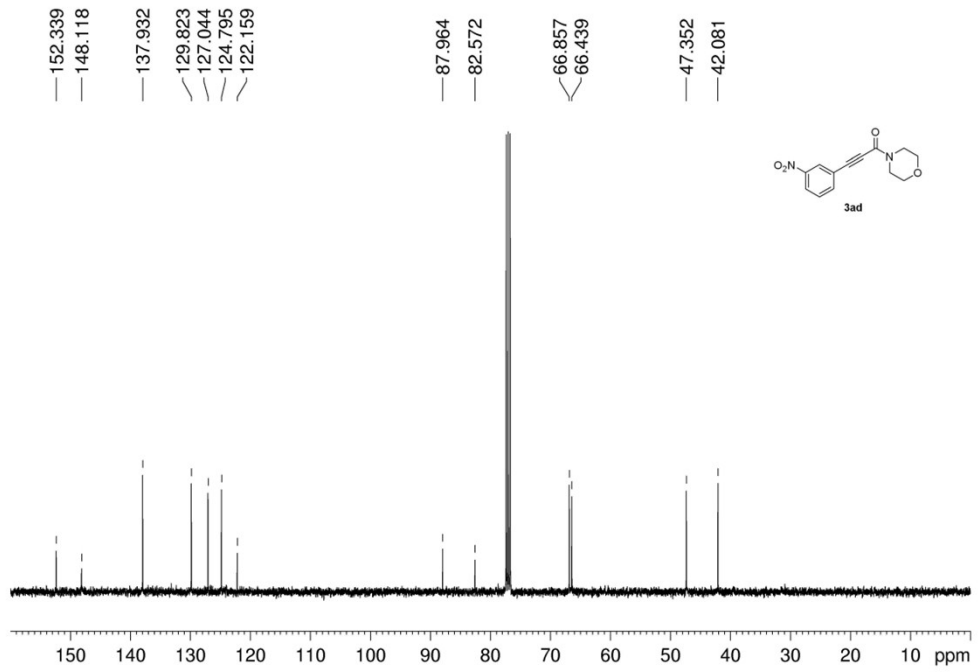
3.862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148.118
137.932
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127.044
124.795
122.159
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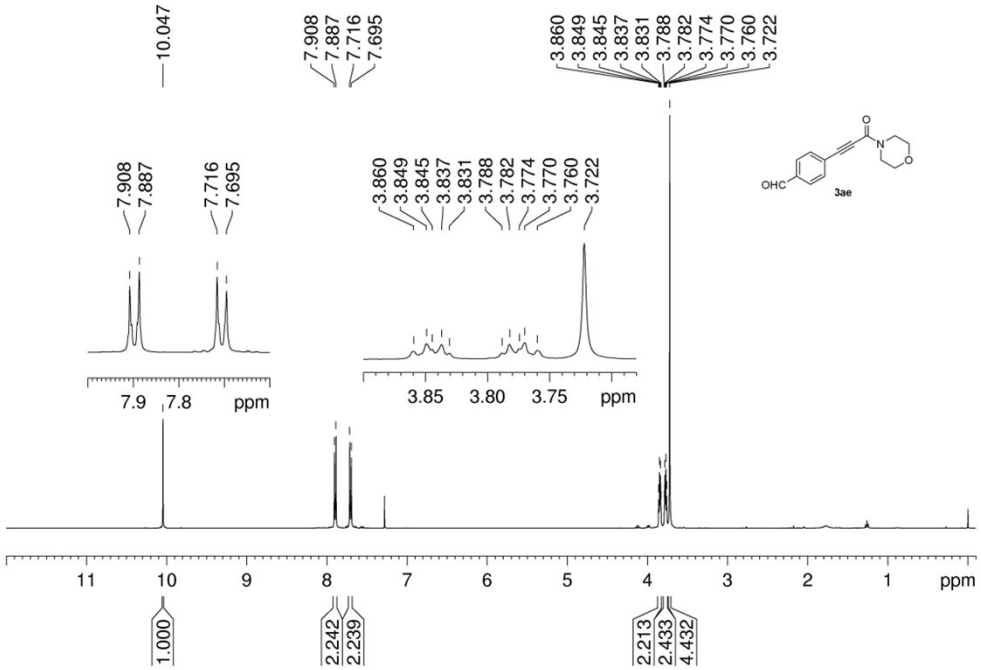
82.572
66.857
66.439
47.352
42.081
3ad
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.887
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7.695
3.860
3.849
3.845
3.837
3.831
3.788
3.782
3.774
3.770
3.760
3.722
OHC
3ae
7.9
7.8
ppm
3.85
3.80
3.75
ppm
11
10
9
8
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5
4
3
2
1
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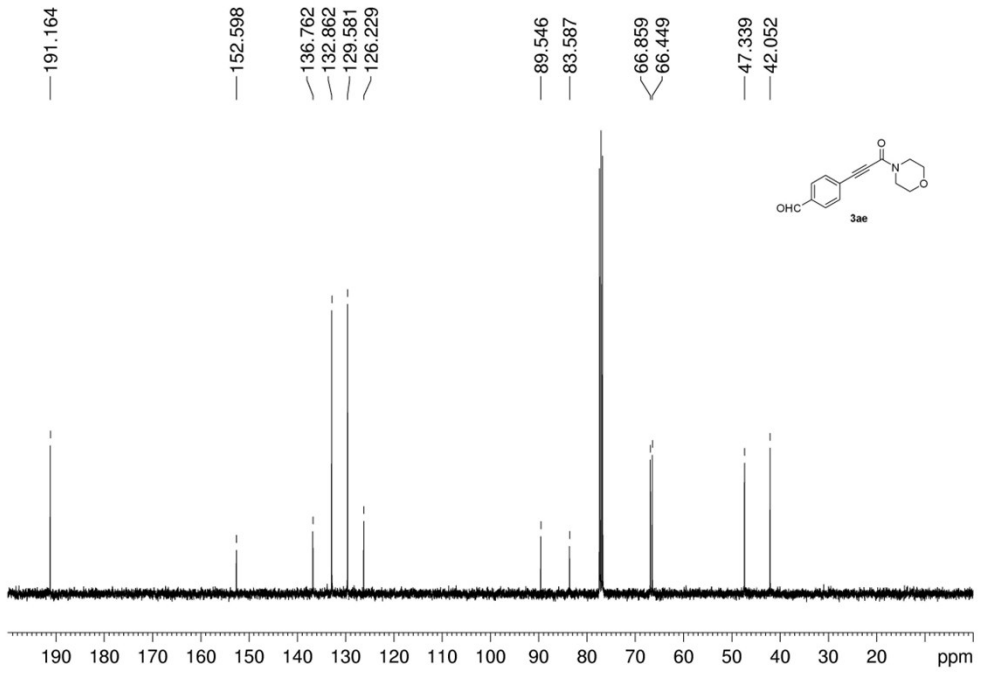
1.000
2.242
2.239
2.213
2.433
4.432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129.581
126.229
89.546
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66.859
66.449
47.339
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OHC
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190
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170
160
150
140
130
120
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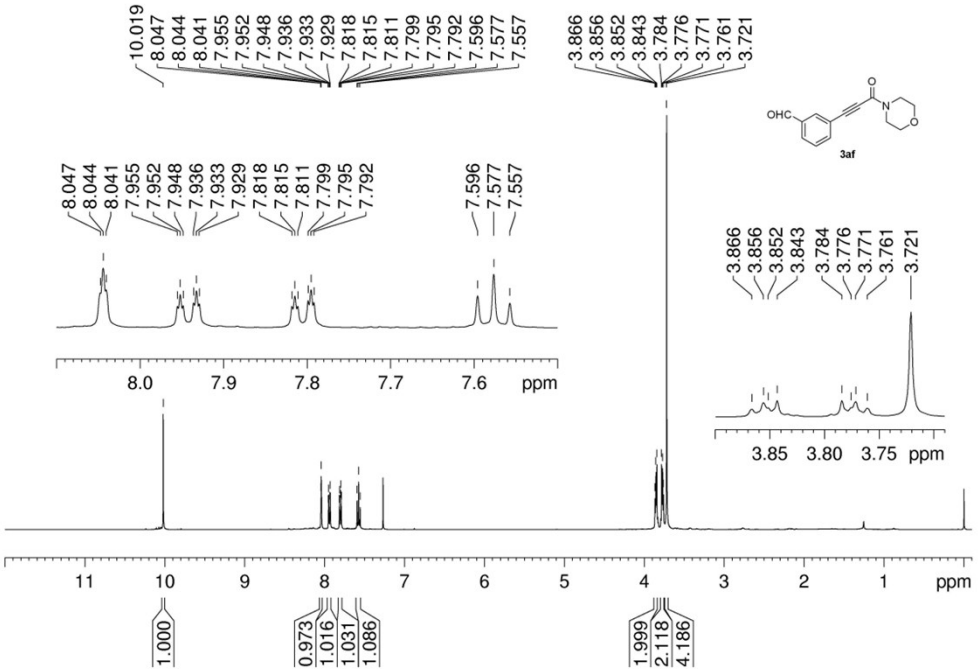
80
70
60
50
40
30
20
ppm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8.041
7.955
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7.948
7.936
7.933
7.929
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7.811
7.799
7.795
7.792
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7.577
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3.856
3.852
3.843
3.784
3.776
3.771
3.761
3.721
OHC
O
N
O
3af
8.0
7.9
7.8
7.7
7.6
ppm
3.85
3.80
3.75
ppm
11
10
9
8
7
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ppm
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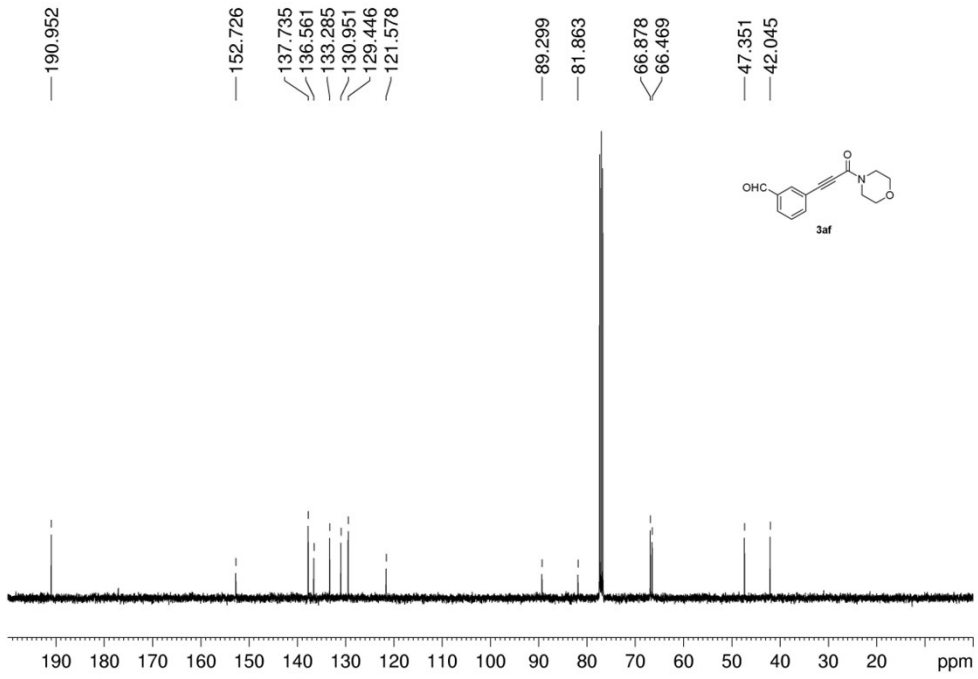
4.186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42.045
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N
O
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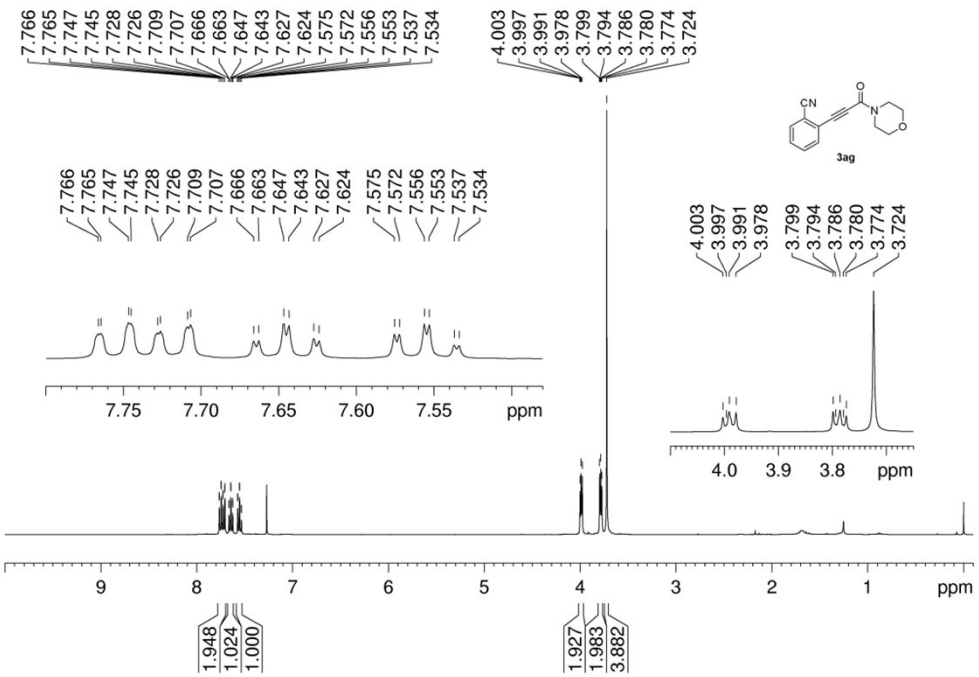
20
ppm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7.747
7.745
7.728
7.726
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7.707
7.666
7.663
7.647
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7.627
7.624
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7.553
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3.780
3.774
3.724
CN
O
N
O
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7.70
7.65
7.60
7.55
ppm
4.0
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3.8
ppm
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4
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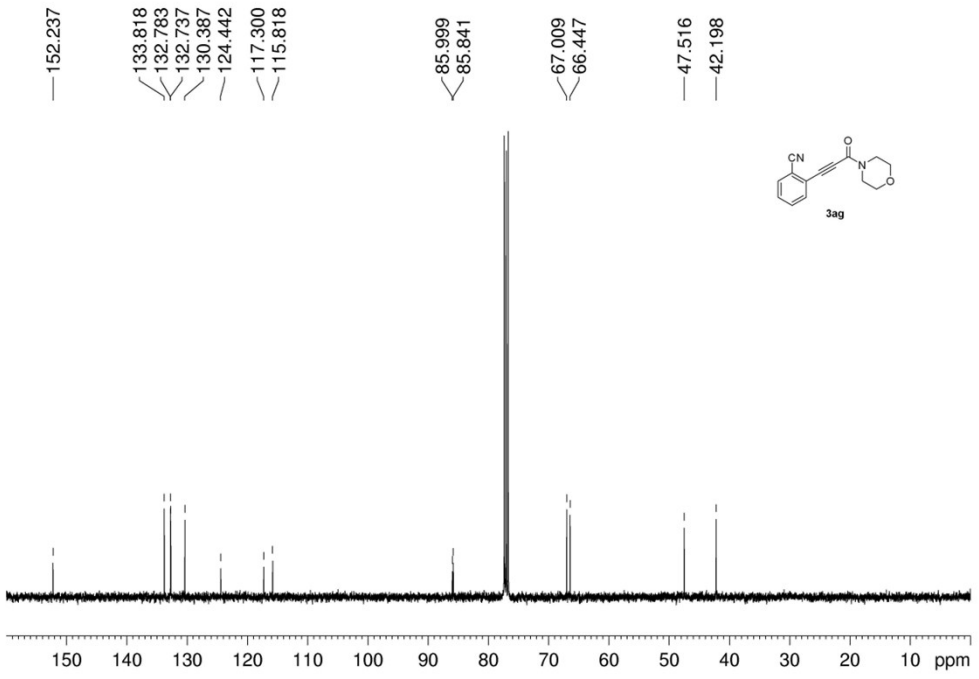
3.882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85.841
67.009
66.447
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42.198
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40
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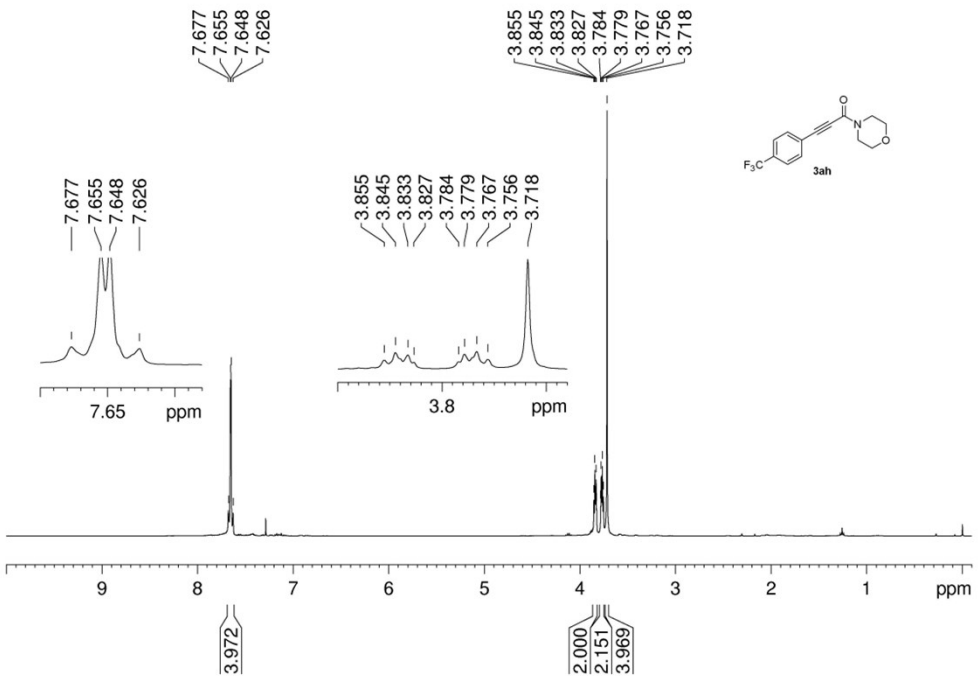
10
ppm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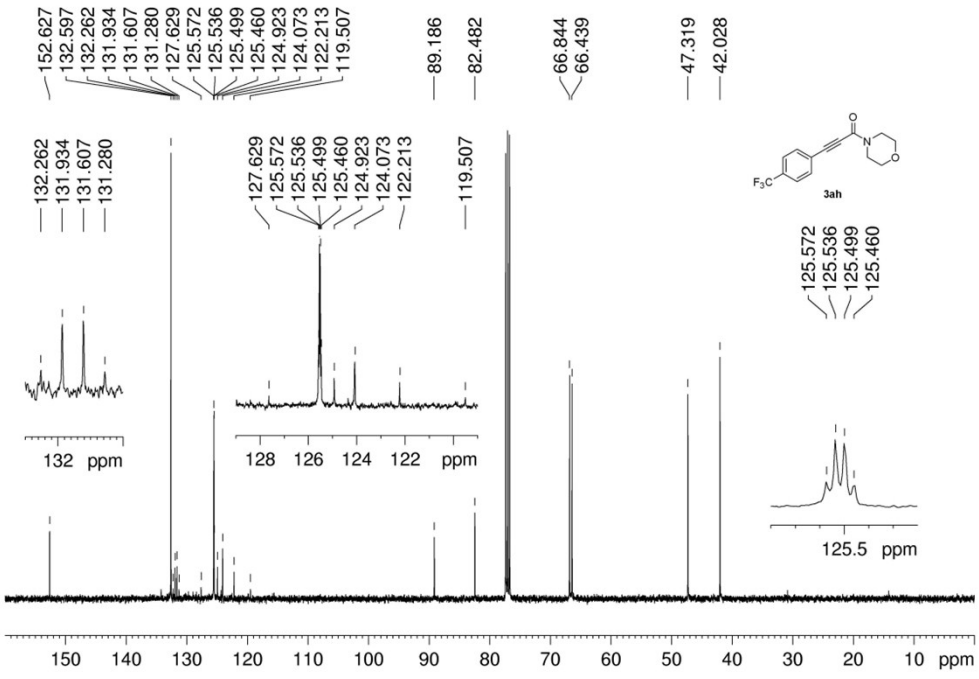
3.718
3ah
7.65 ppm
3.8 ppm
9 8 7 6 5 4 3 2 1 ppm
3.972
2.000
2.151
3.969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124.073
122.213
119.507
89.186
82.482
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42.028
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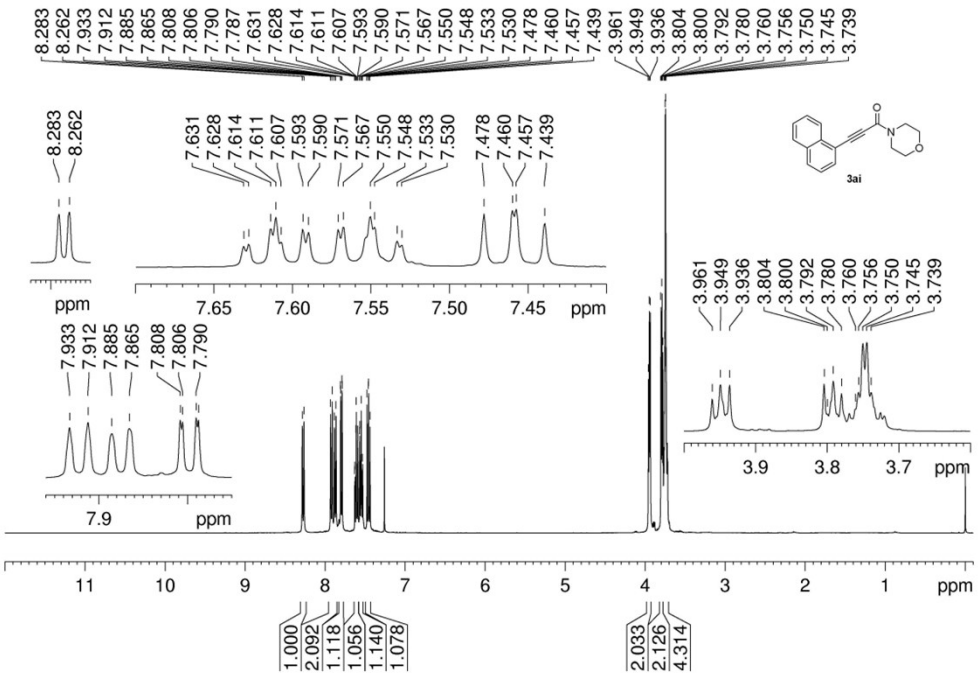
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7.614
7.611
7.607
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7.590
7.571
7.567
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7.548
7.533
7.530
7.478
7.460
7.457
7.439
3.961
3.949
3.936
3.804
3.800
3.792
3.780
3.760
3.756
3.750
3.745
3.739
3ai
ppm
7.65
7.60
7.55
7.50
7.45
7.9
3.9
3.8
3.7
11
10
9
8
7
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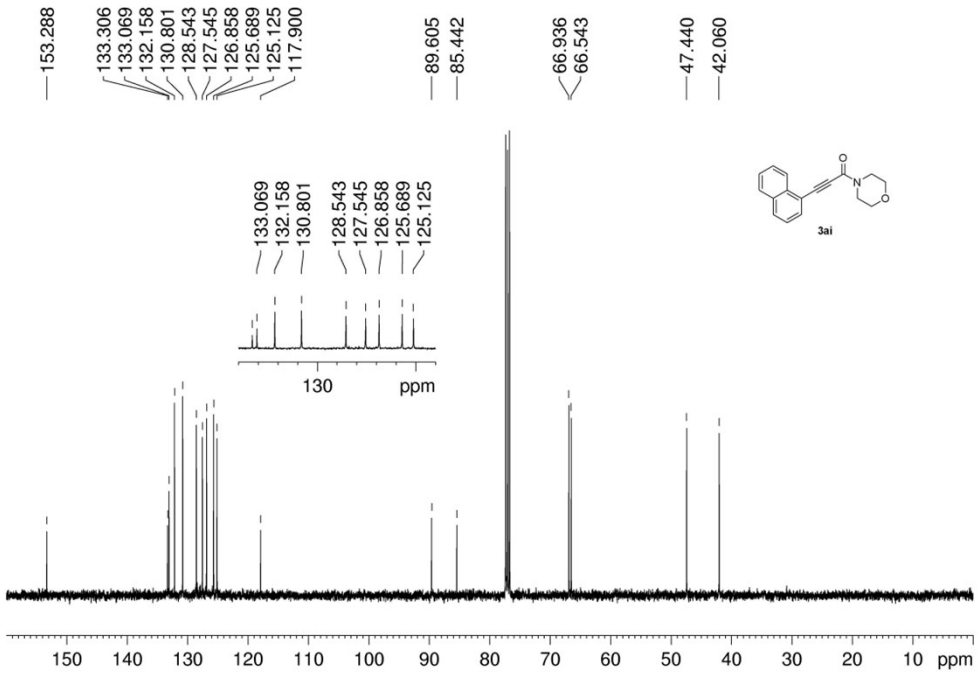
4.314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66.936
66.543
47.440
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ppm
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120
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80
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40
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20
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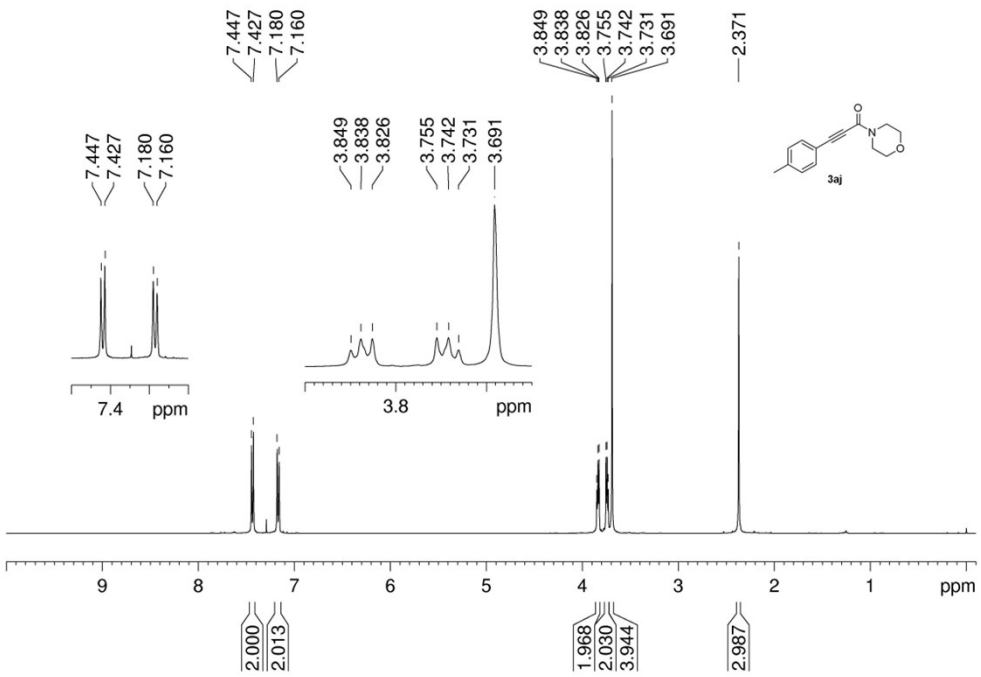
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3.755
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3.731
3.691
2.371
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7.4 ppm
3.8 ppm
9 8 7 6 5 4 3 2 1 ppm
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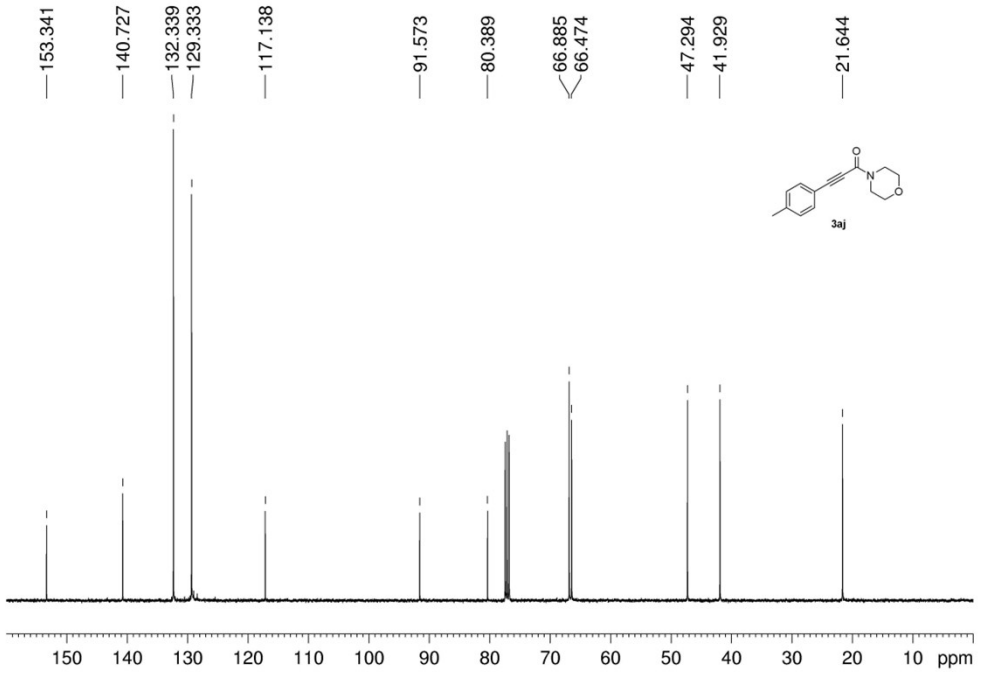
3.944
2.987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132.339
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66.885
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41.929
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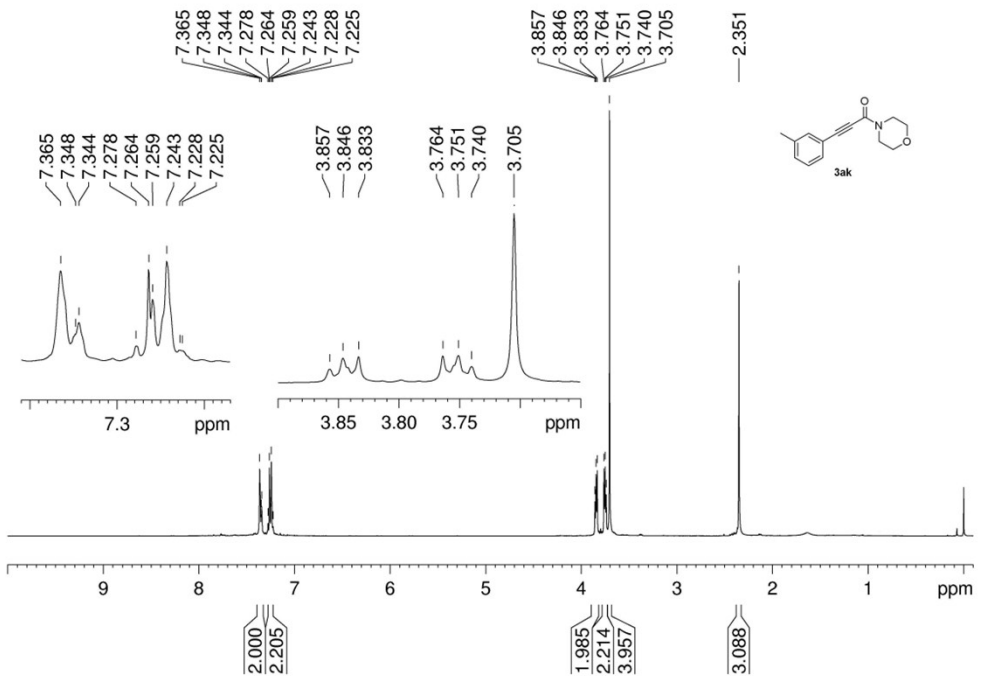
3aj
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.344
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7.228
7.225
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3.846
3.833
3.764
3.751
3.740
3.705
2.351
3ak
7.3
ppm
3.85
3.80
3.75
ppm
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ppm
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2.214
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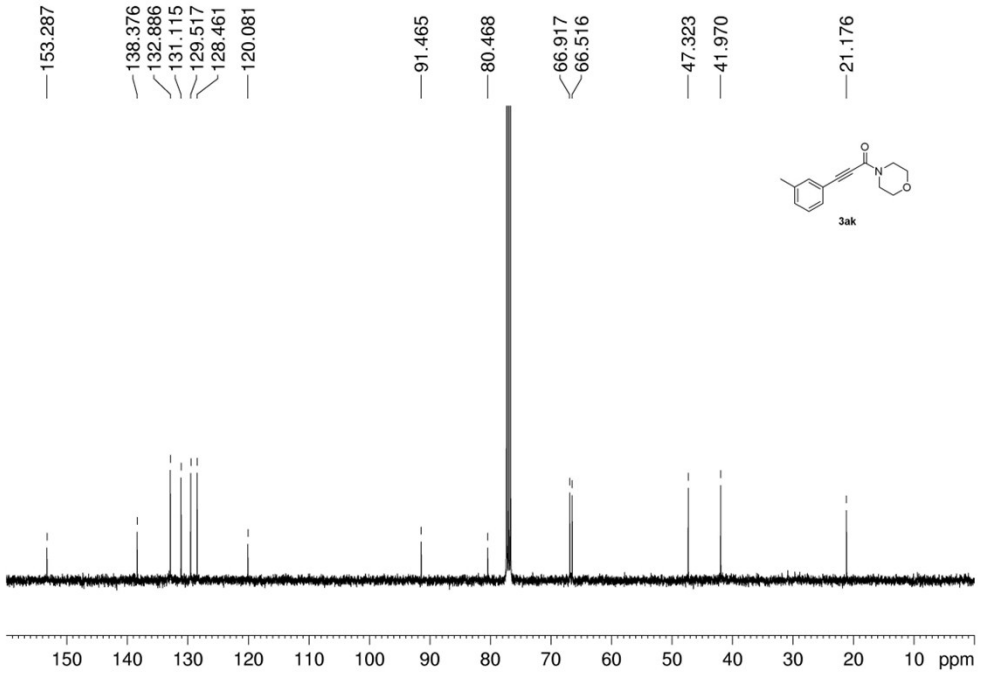
3.088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70
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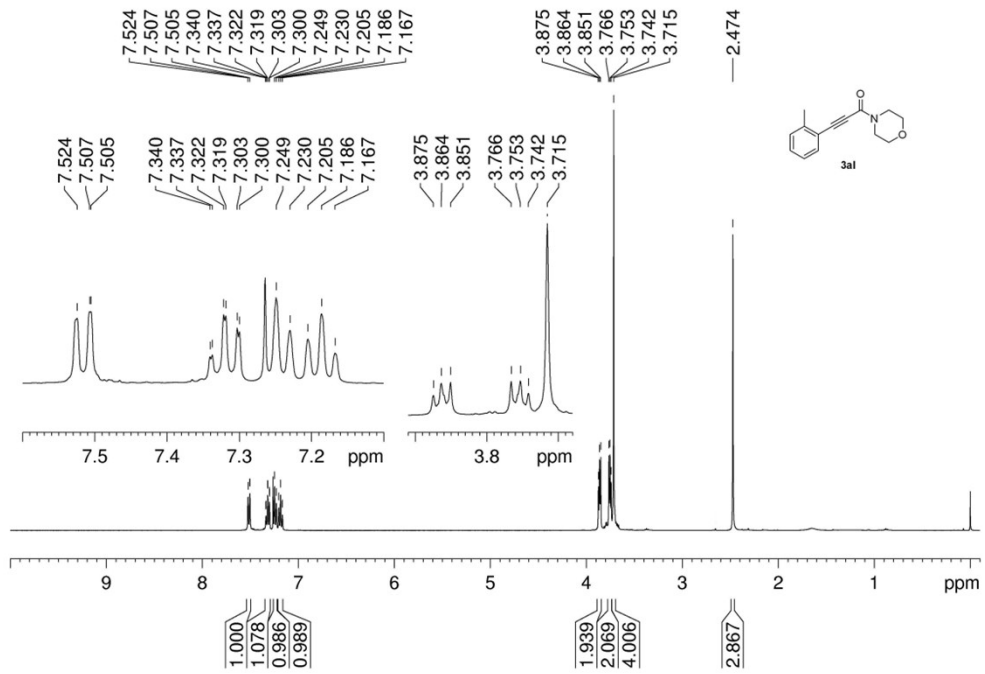
10
ppm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7.507
7.505
7.340
7.337
7.322
7.319
7.303
7.300
7.249
7.230
7.205
7.186
7.167
3.875
3.864
3.851
3.766
3.753
3.742
3.715
2.474
3al
7.5
7.4
7.3
7.2
ppm
3.8
ppm
9
8
7
6
5
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ppm
1.000
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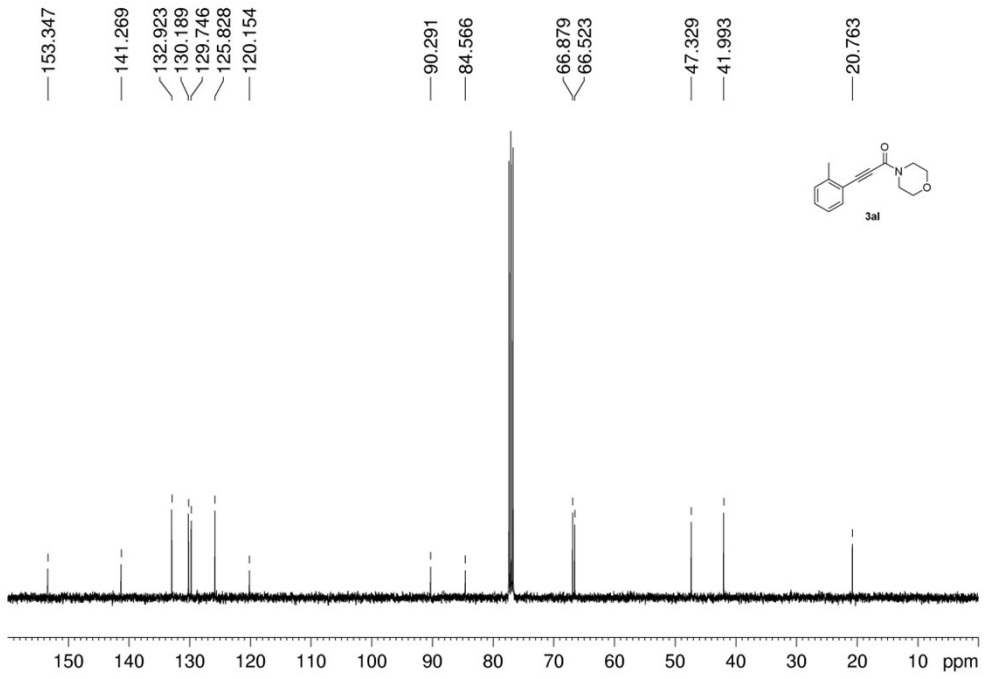
0.989
1.939
2.069
4.006
2.867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90.291
84.566
66.879
66.523
47.329
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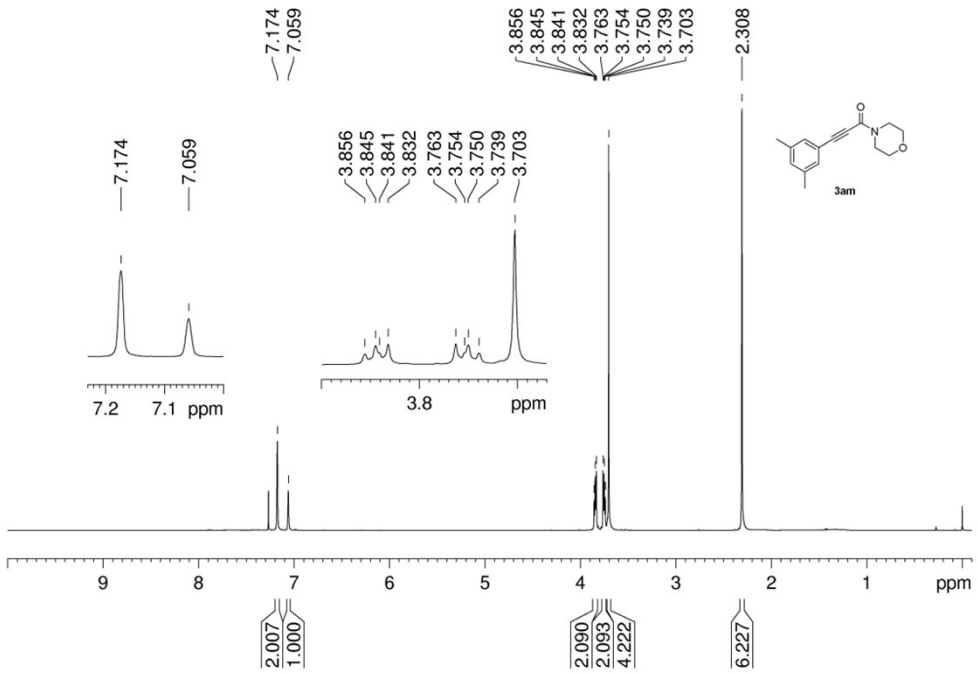
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.059
3.856
3.845
3.841
3.832
3.763
3.754
3.750
3.739
3.703
2.308
3am
7.2
7.1 ppm
3.8
ppm
9
8
7
6
5
4
3
2
1
ppm
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1.000
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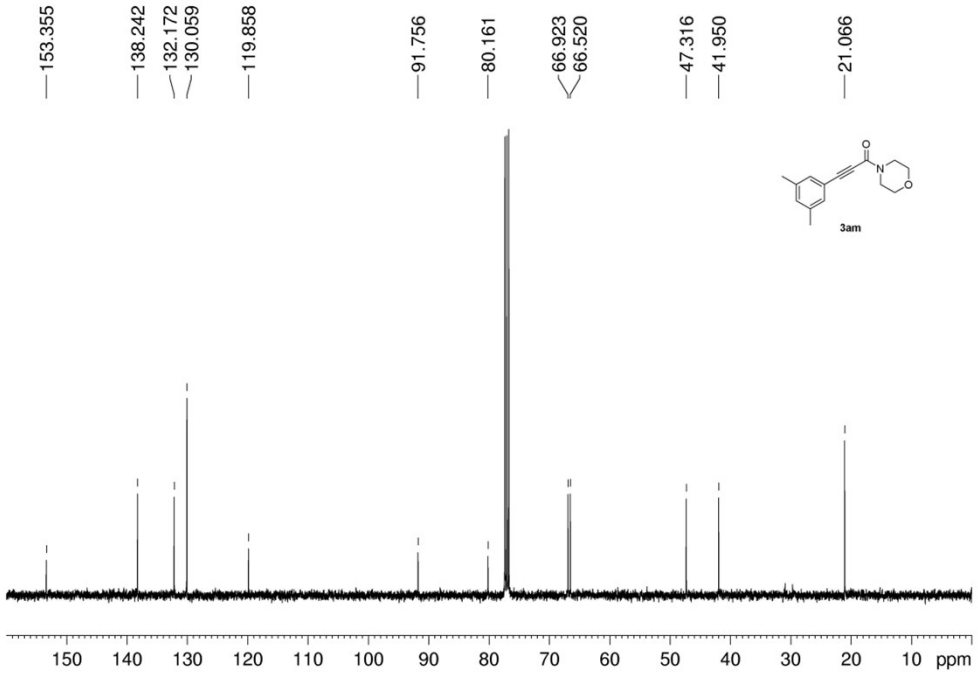
2.093
4.222
6.227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132.172
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119.858
91.756
80.161
66.923
66.520
47.316
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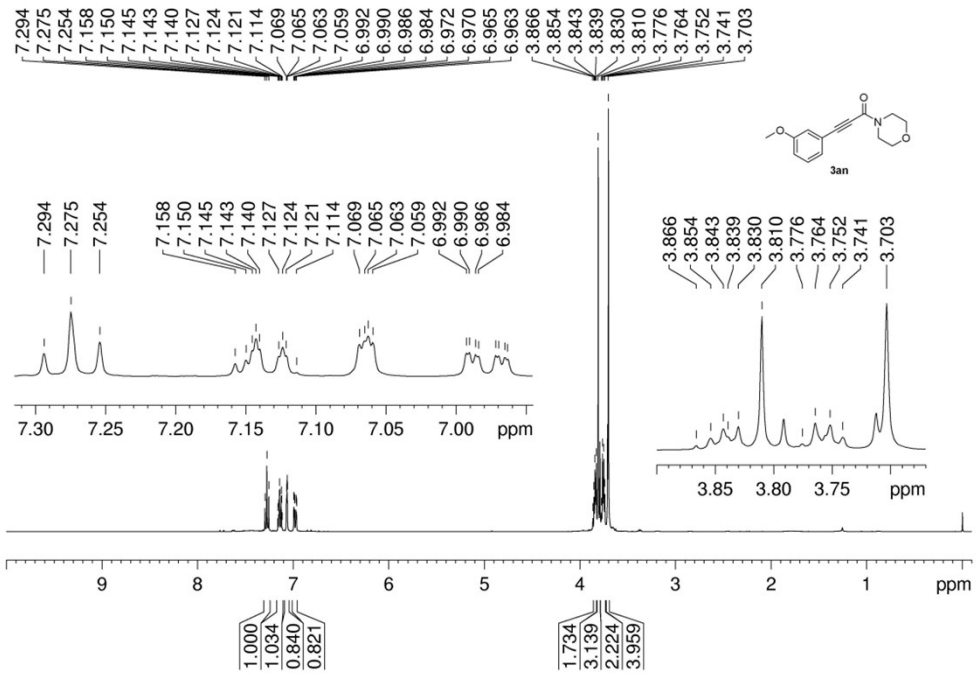
21.066
3am
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.254
7.158
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7.140
7.127
7.124
7.121
7.114
7.069
7.065
7.063
7.059
6.992
6.990
6.986
6.984
6.972
6.970
6.965
6.963
3.866
3.854
3.843
3.839
3.830
3.810
3.776
3.764
3.752
3.741
3.703
3an
7.30 7.25 7.20 7.15 7.10 7.05 7.00 ppm
3.85 3.80 3.75 ppm
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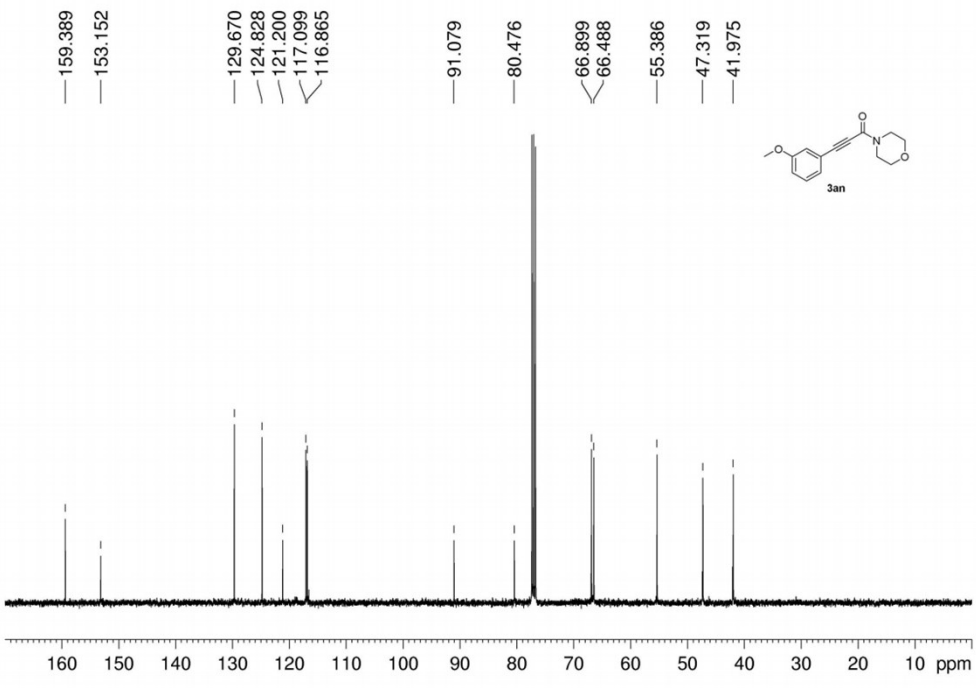
3.959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66.488
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47.319
41.975
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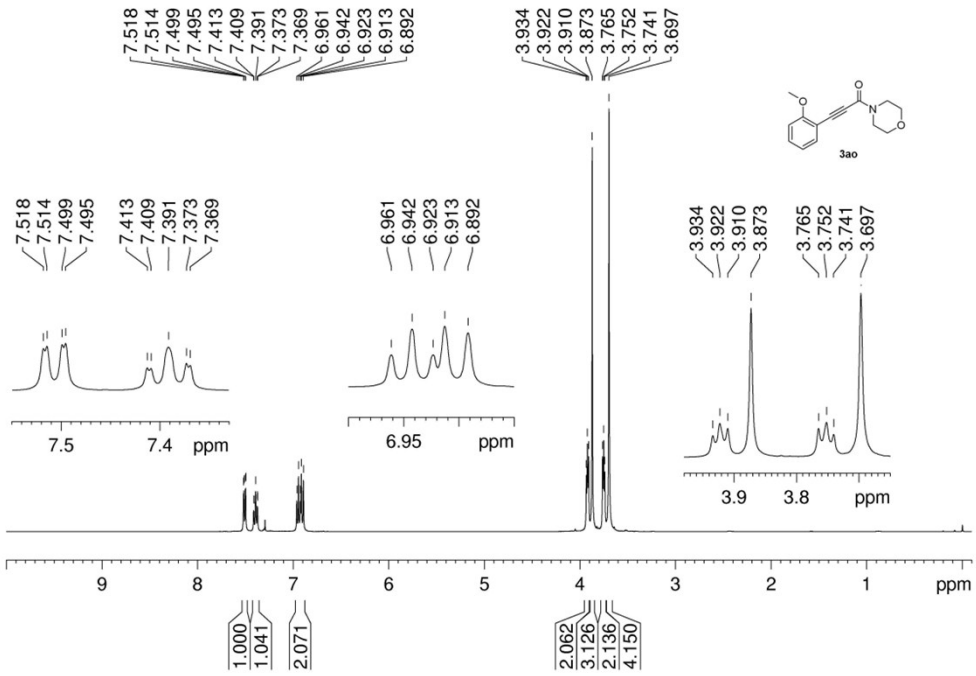
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7.514
7.499
7.495
7.413
7.409
7.391
7.373
7.369
6.961
6.942
6.923
6.913
6.892
3.934
3.922
3.910
3.873
3.765
3.752
3.741
3.697
3ao
7.5
7.4
ppm
6.95
ppm
3.9
3.8
ppm
9
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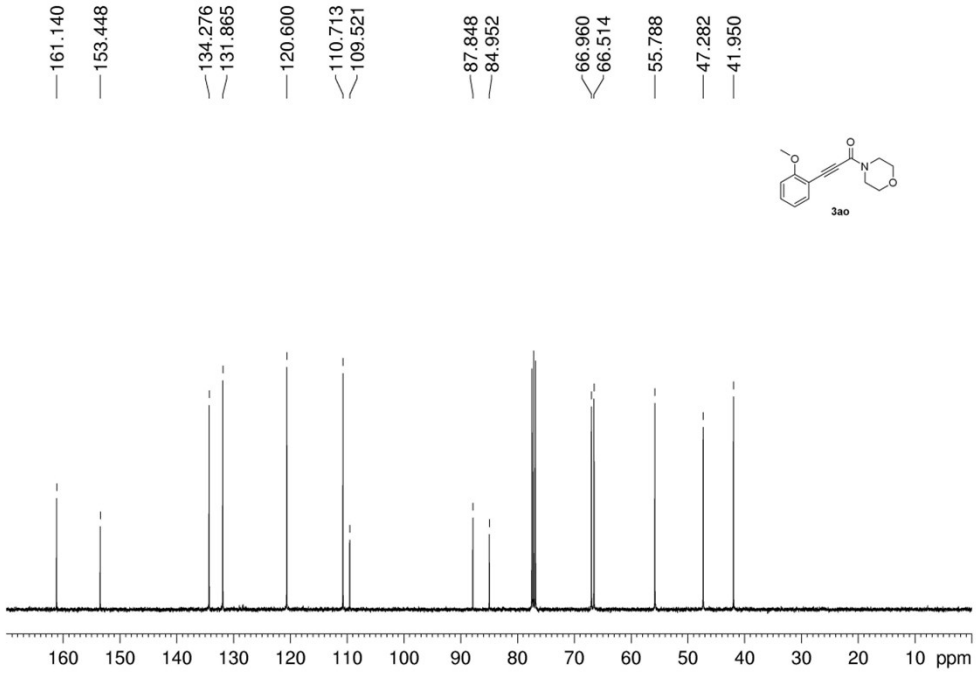
4.150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87.848
84.952
66.960
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55.788
47.282
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150
140
130
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110
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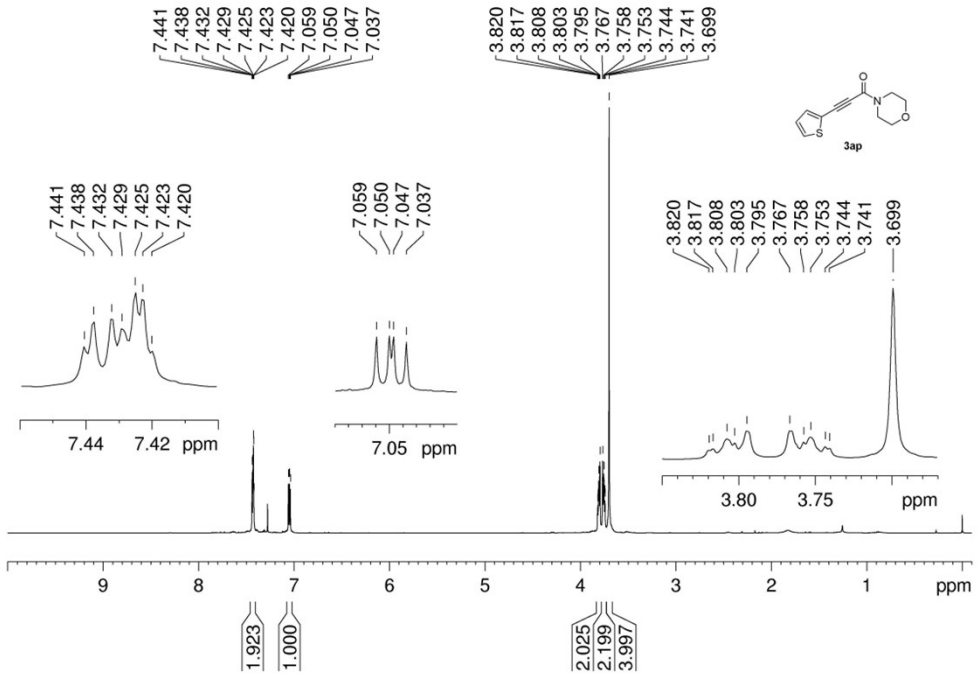
90
80
70
60
50
40
30
20
10
ppm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7.423
7.420
7.059
7.050
7.047
7.037
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3.817
3.808
3.803
3.795
3.767
3.758
3.753
3.744
3.741
3.699
3ap
7.44
7.42 ppm
7.05 ppm
3.80
3.75
ppm
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6
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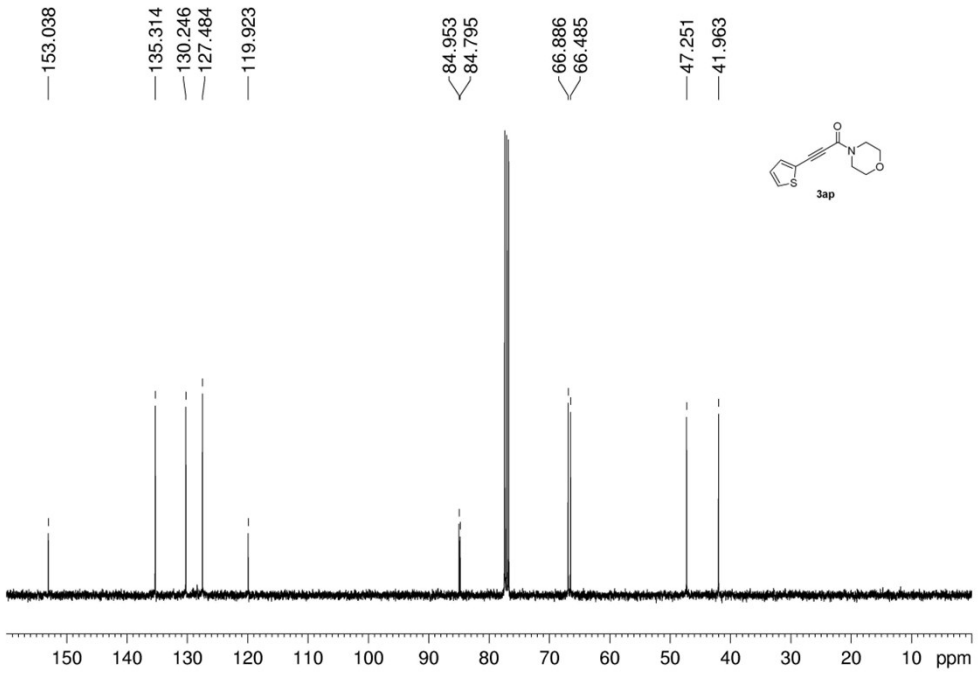
2.199
3.997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84.795
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66.485
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70
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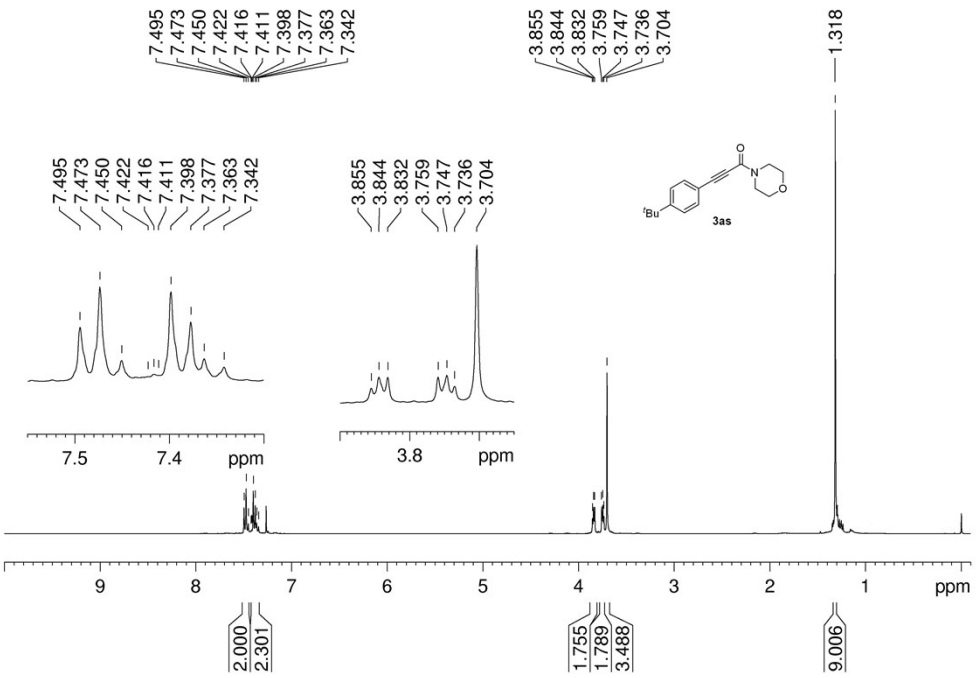
50
40
30
20
10
ppm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7.377
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3.832
3.759
3.747
3.736
3.704
1.318
7.5
7.4
ppm
3.8
ppm
3as
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5
4
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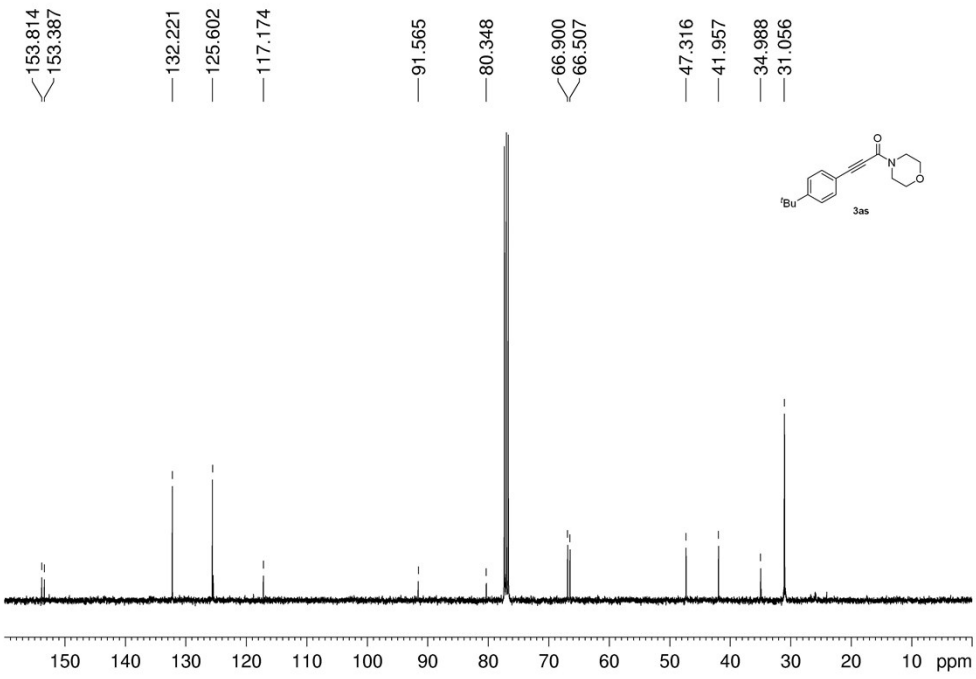
9.006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66.900
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47.316
41.957
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150
140
130
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70
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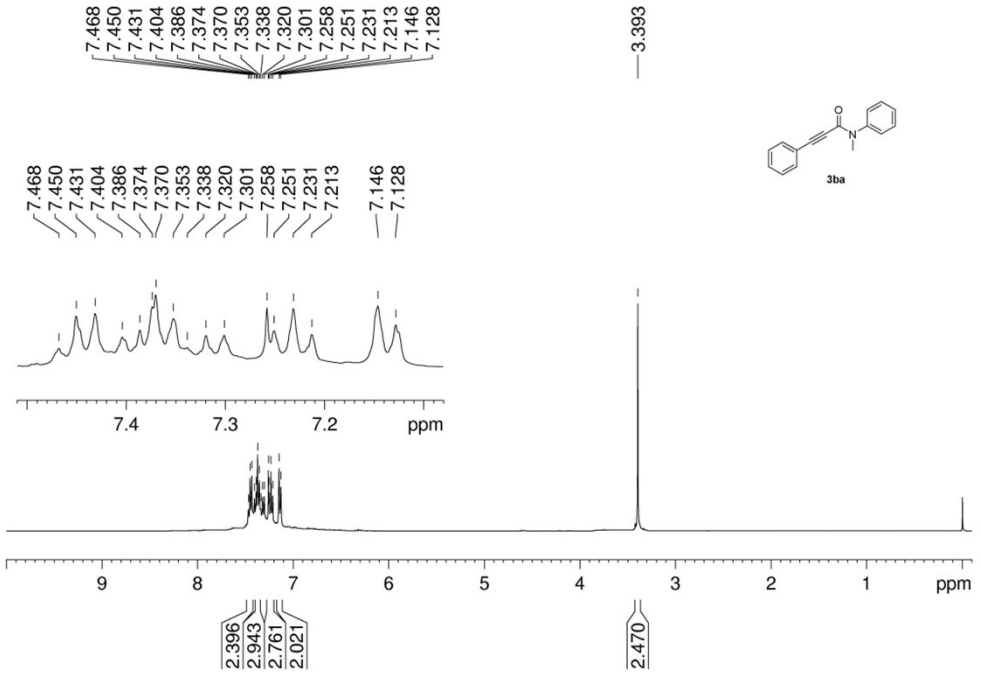
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7.353
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7.320
7.301
7.258
7.251
7.231
7.213
7.146
7.128
3.393
3ba
7.4
7.3
7.2
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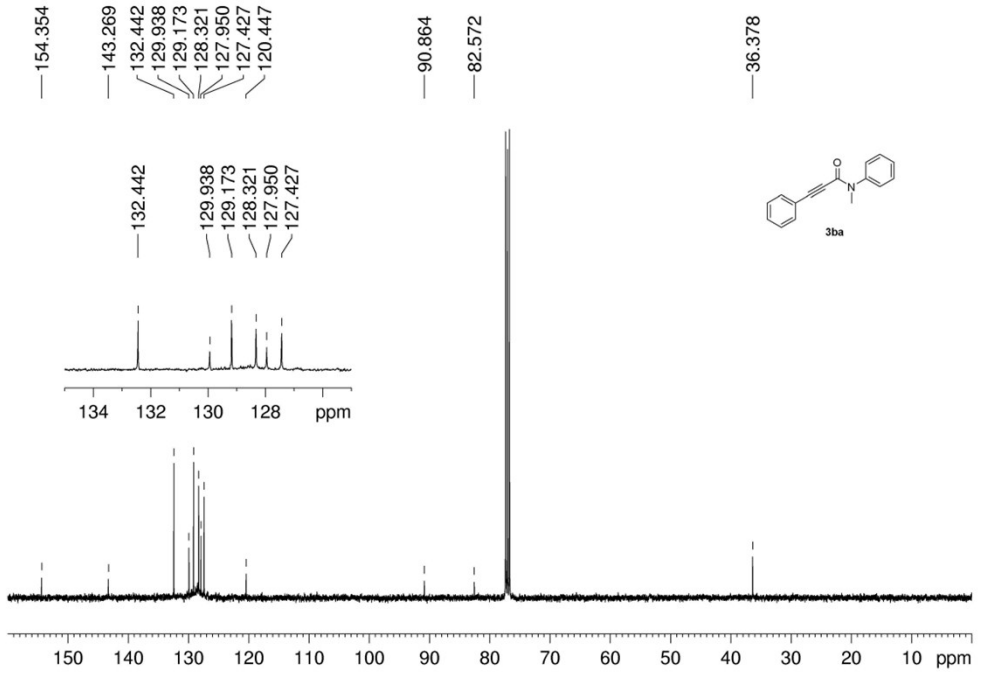
2.470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90.864
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36.378
3ba
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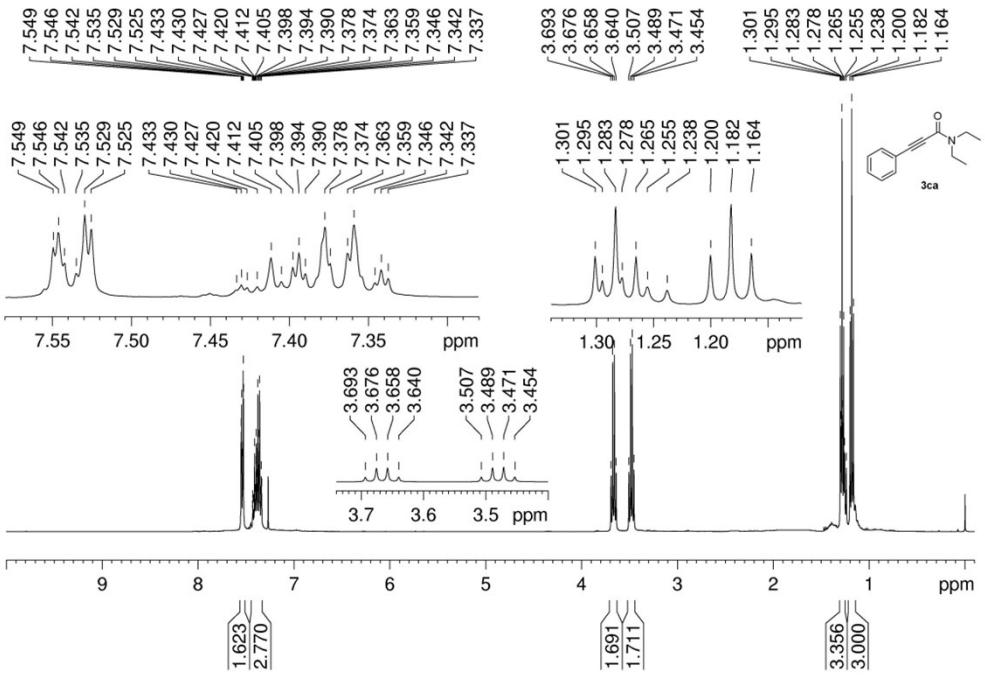
ppm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7.412
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7.398
7.394
7.390
7.378
7.374
7.363
7.359
7.346
7.342
7.337
3.693
3.676
3.658
3.640
3.507
3.489
3.471
3.454
1.301
1.295
1.283
1.278
1.265
1.255
1.238
1.200
1.182
1.164
3ca
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7.50
7.45
7.40
7.35
ppm
1.30
1.25
1.20
ppm
3.7
3.6
3.5
ppm
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1
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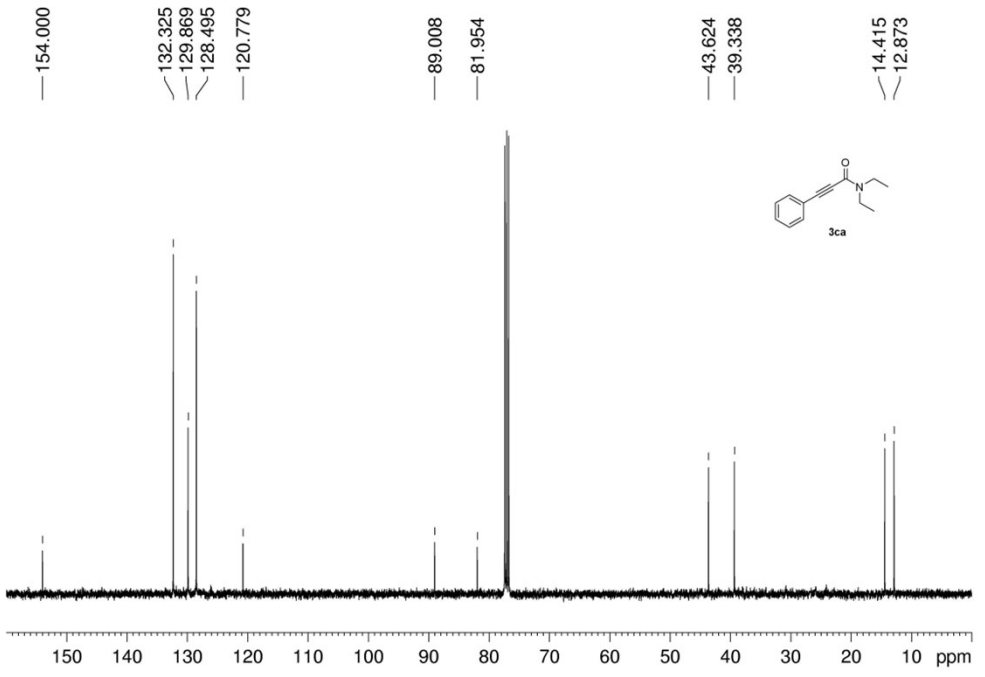
3.000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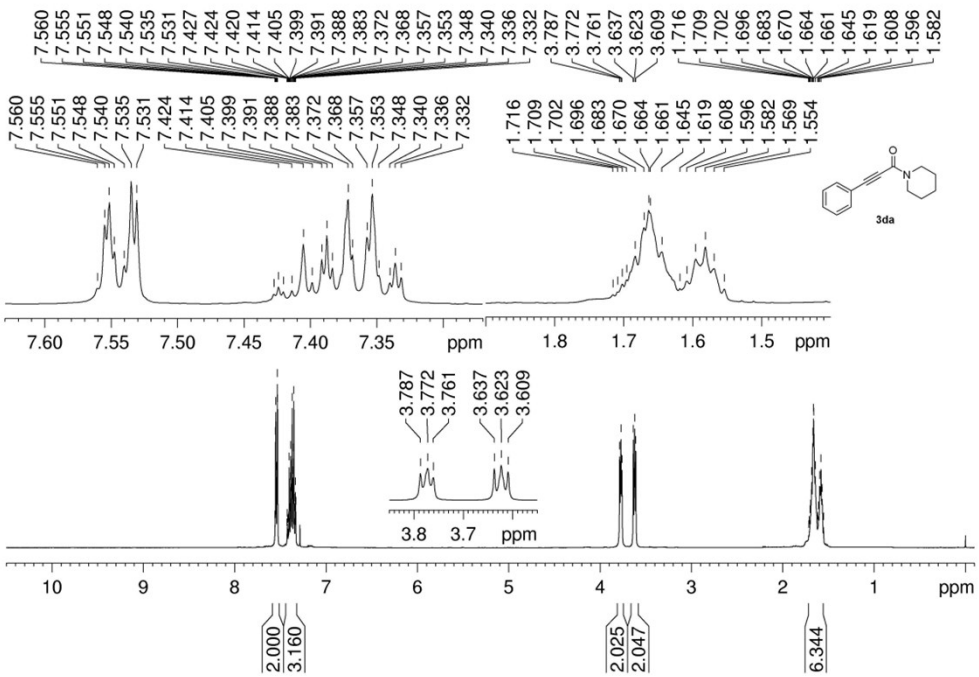
70
60
50
40
30
20
10
ppm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7.420
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7.399
7.391
7.388
7.383
7.372
7.368
7.357
7.353
7.348
7.340
7.336
7.332
3.787
3.772
3.761
3.637
3.623
3.609
1.716
1.709
1.702
1.696
1.683
1.670
1.664
1.661
1.645
1.619
1.608
1.596
1.582
1.554
3da
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7.55
7.50
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7.40
7.35
ppm
1.8
1.7
1.6
1.5
ppm
3.8
3.7
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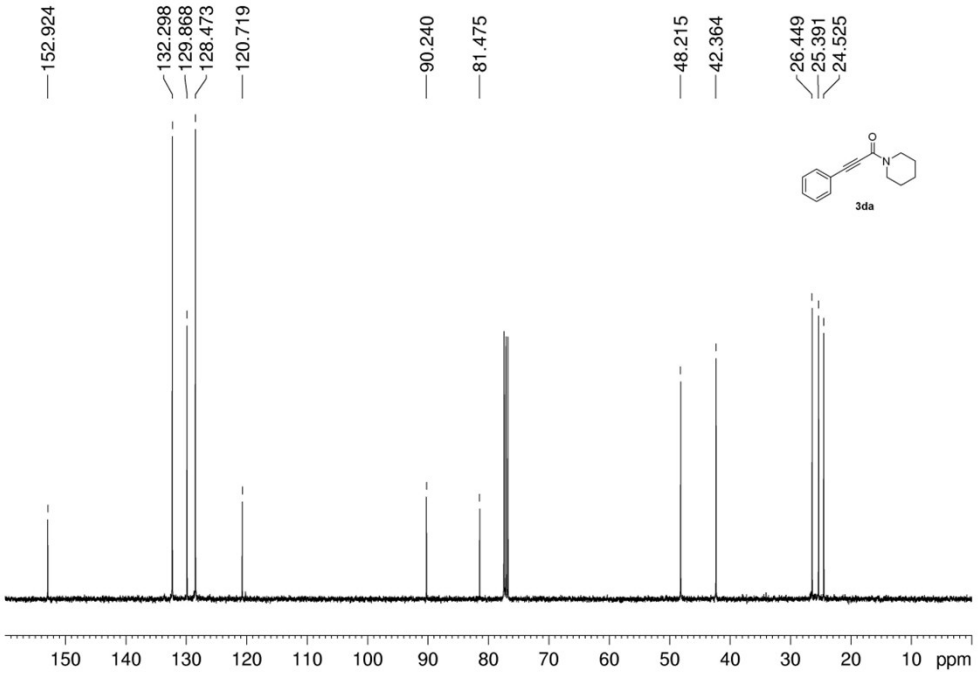
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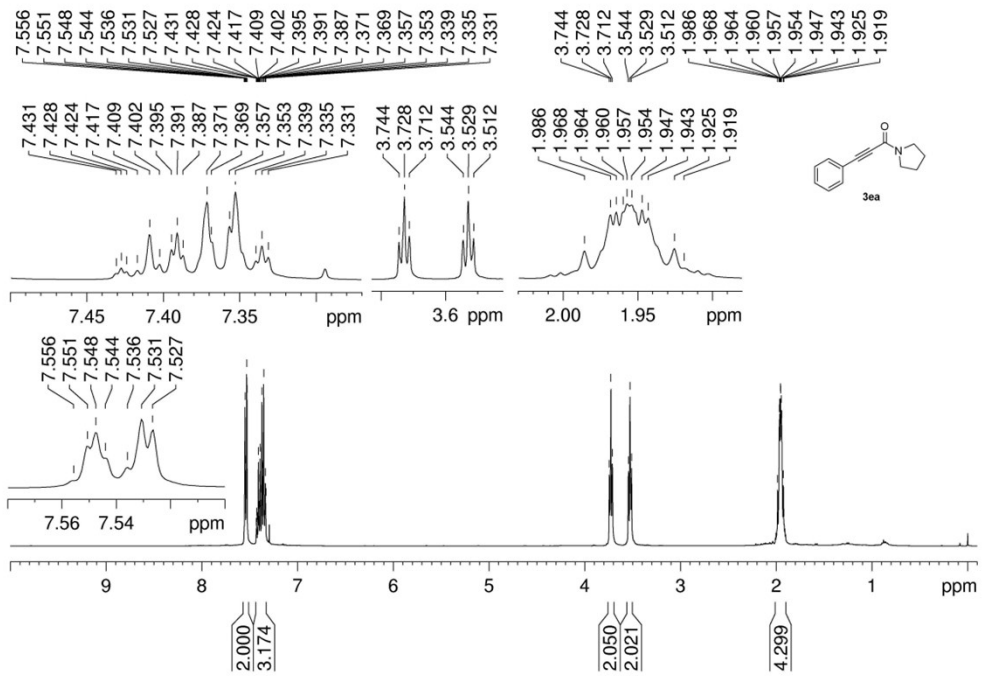
10
ppm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7.391
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7.371
7.369
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7.335
7.331
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1.968
1.964
1.960
1.957
1.954
1.947
1.943
1.925
1.919
7.45
7.40
7.35
ppm
3.6 ppm
2.00
1.95
ppm
7.56
7.54
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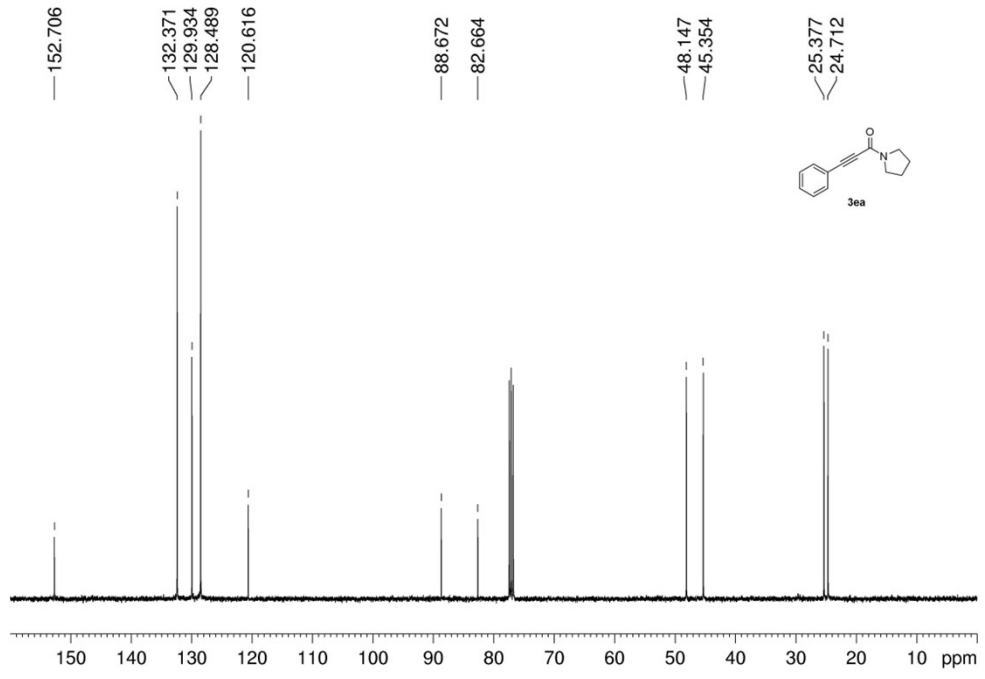
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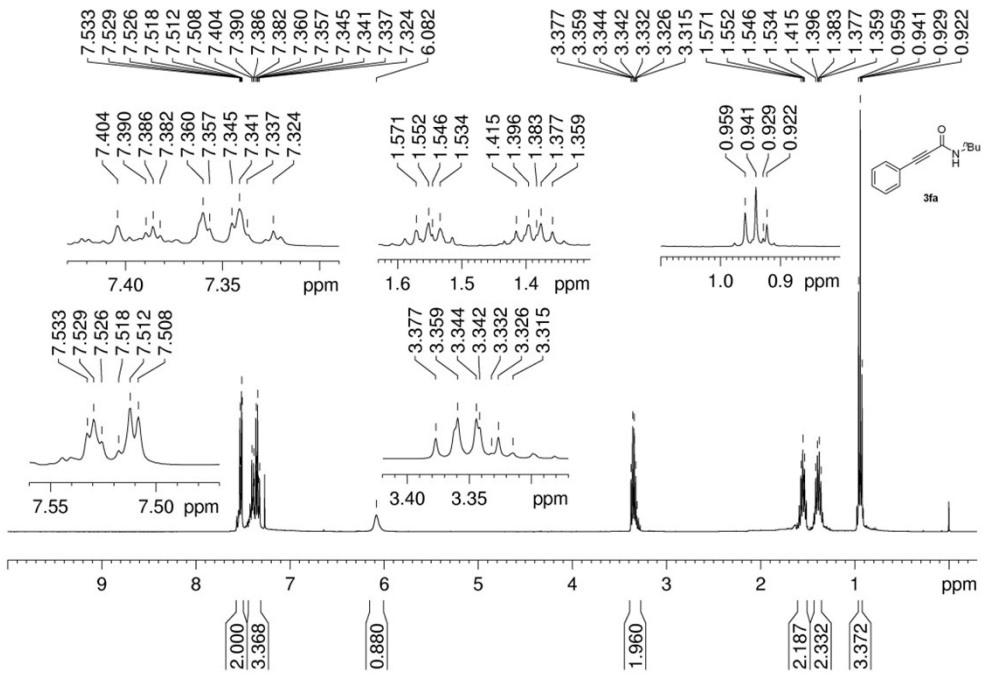
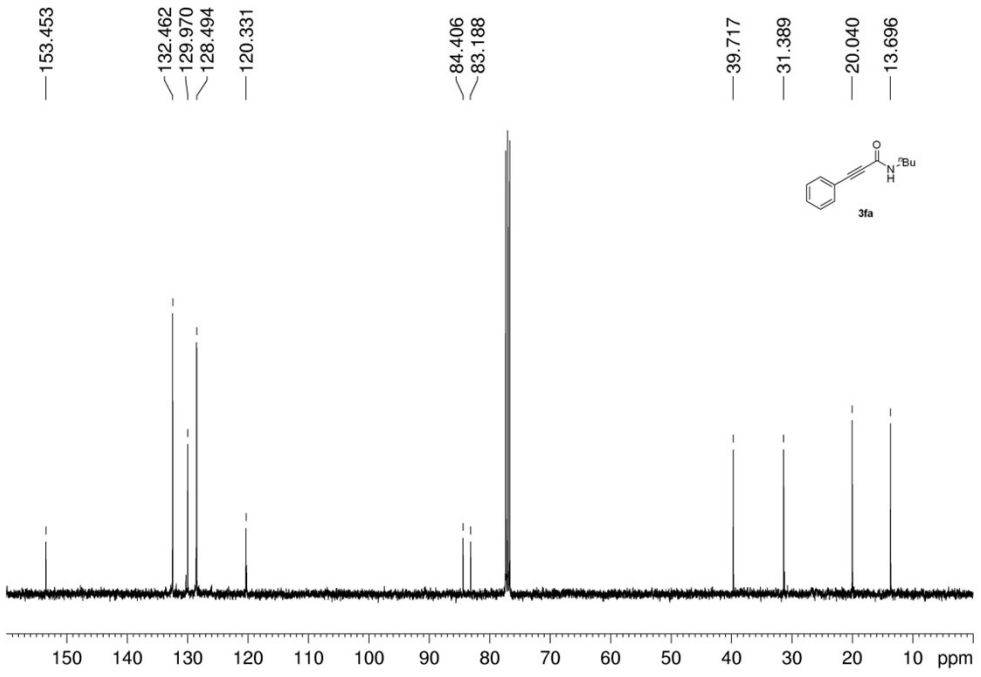
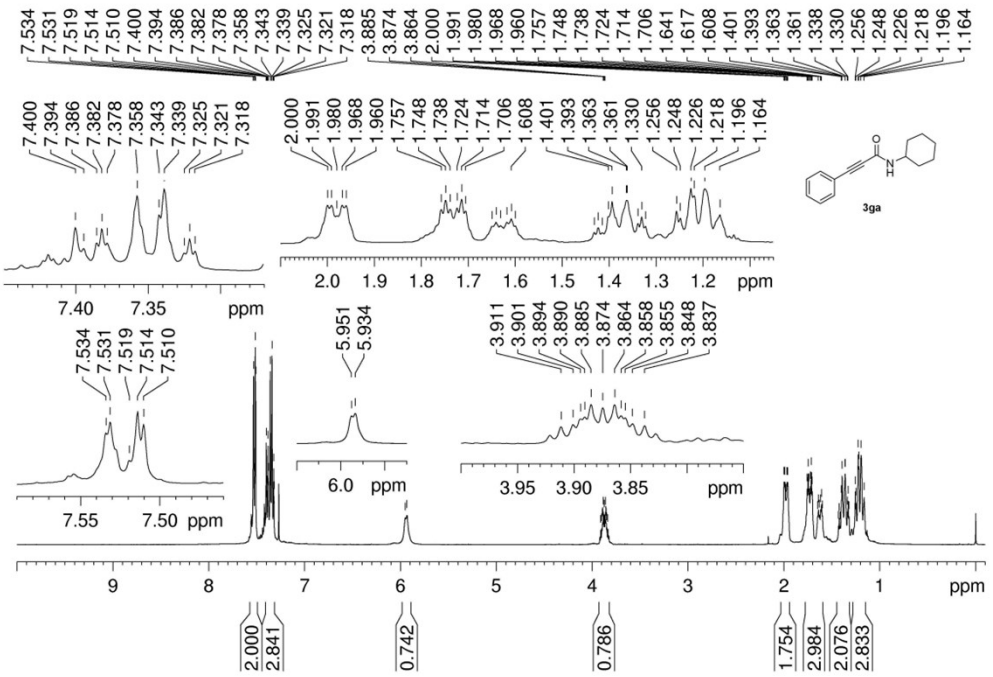
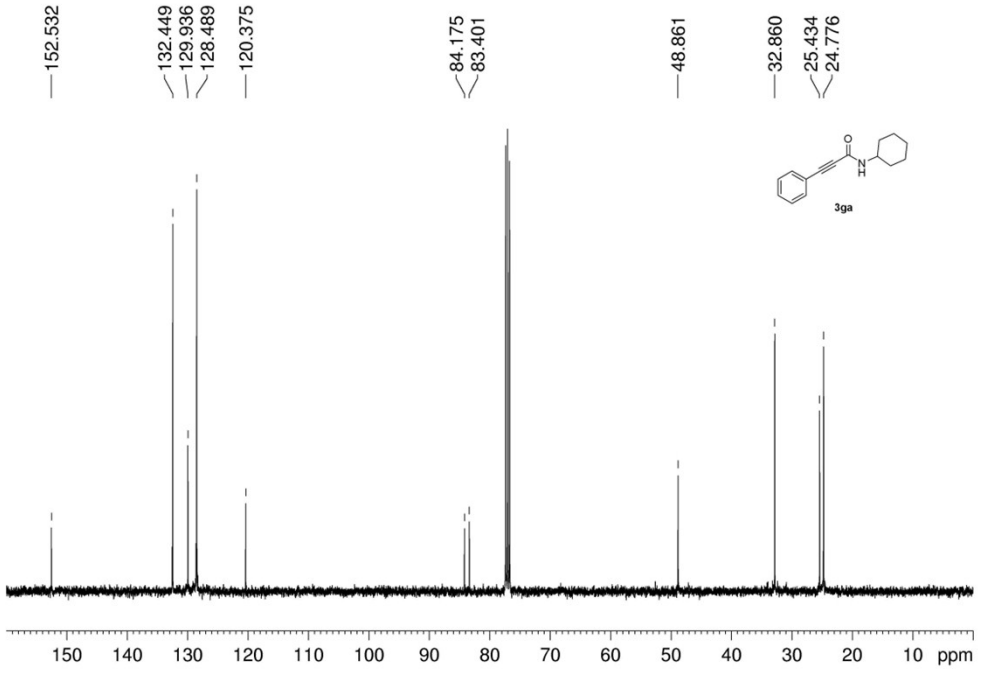
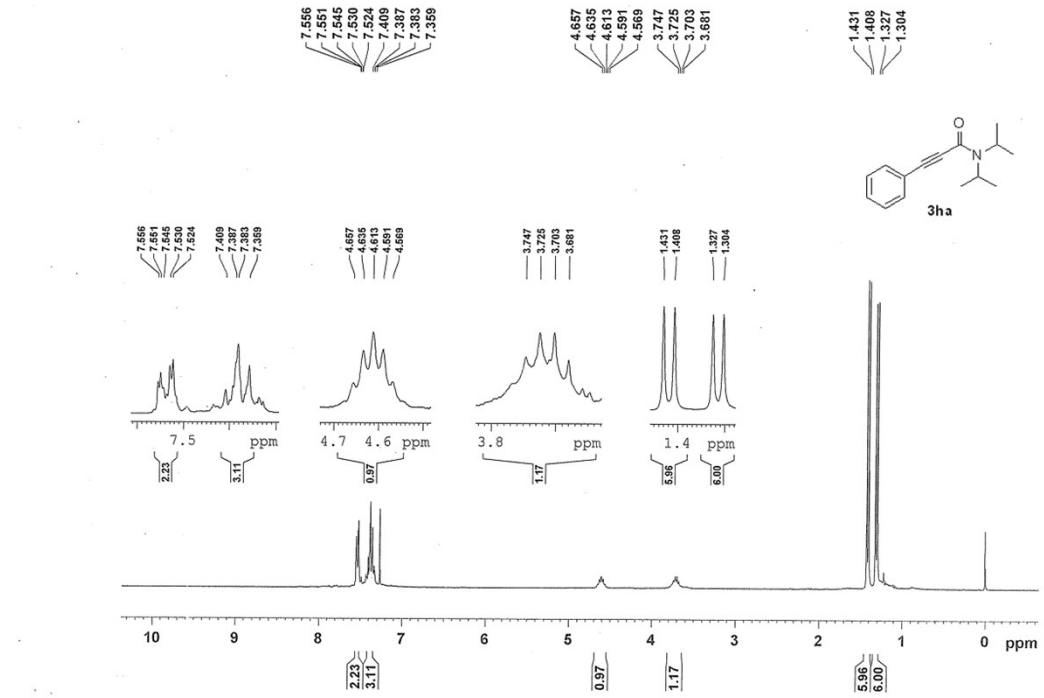
48.147
45.354
25.377
24.712
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
3ea

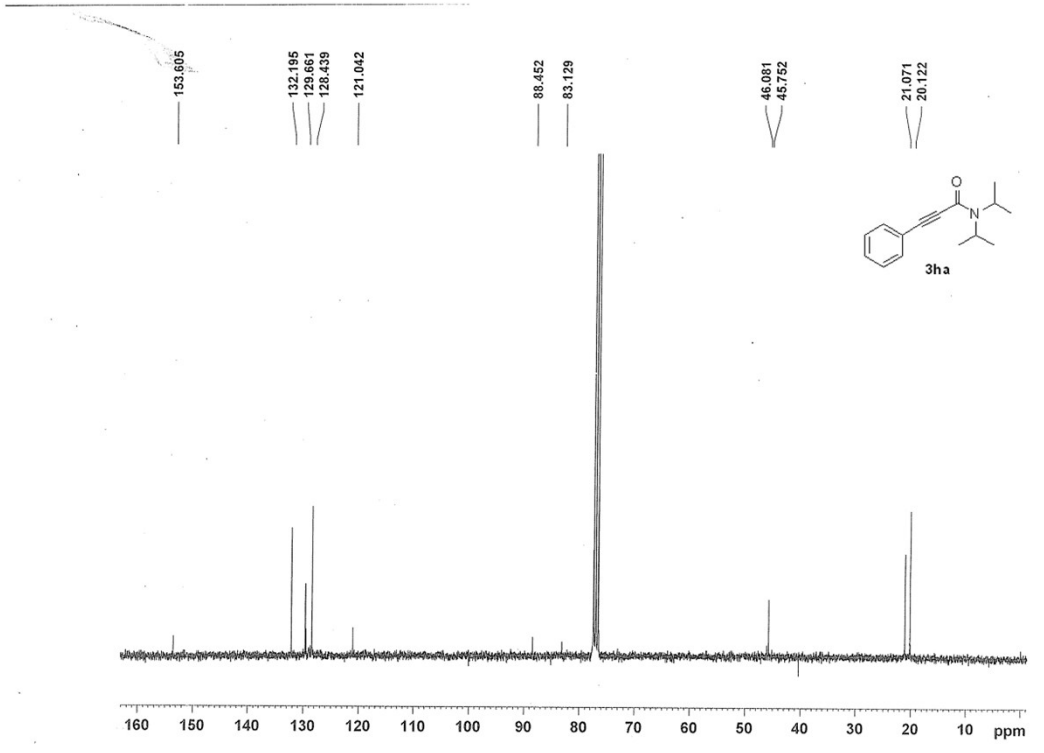

7.533
7.529
7.526
7.518
7.512
7.508
7.404
7.390
7.386
7.382
7.360
7.357
7.345
7.341
7.337
7.324
6.082
3.377
3.359
3.344
3.342
3.332
3.326
3.315
1.571
1.552
1.546
1.534
1.415
1.396
1.383
1.377
1.359
0.959
0.941
0.929
0.922
3fa
7.40
7.35
ppm
1.6
1.5
1.4
ppm
1.0
0.9
ppm
7.55
7.50
ppm
3.40
3.35
ppm
9
8
7
6
5
4
3
2
1
ppm
2.000
3.368
0.880
1.960
2.187
2.332
3.372


153.453
132.462
129.970
128.494
120.331
84.406
83.188
39.717
31.389
20.040
13.696
3fa
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.534 7.531 7.519 7.514 7.510 7.400 7.394 7.386 7.382 7.378 7.358 7.343 7.339 7.325 7.321 7.318 3.885 3.874 3.864 2.000 1.991 1.980 1.968 1.960 1.757 1.748 1.738 1.724 1.714 1.706 1.641 1.617 1.608 1.401 1.393 1.363 1.361 1.338 1.330 1.256 1.248 1.226 1.218 1.196 1.164
7.40 7.35 ppm
2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 ppm
3ga
7.55 7.50 ppm
6.0 ppm
3.95 3.90 3.85 ppm
9 8 7 6 5 4 3 2 1 ppm
2.000 2.841 0.742 0.786 1.754 2.984 2.076 2.833


152.532 132.449 129.936 128.489 120.375 84.175 83.401 48.861 32.860 25.434 24.776
3ga
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.556
7.551
7.545
7.530
7.524
7.409
7.387
7.383
7.359
4.657
4.635
4.613
4.591
4.569
3.747
3.725
3.703
3.681
1.431
1.408
1.327
1.304
3ha
7.5 ppm
4.7 4.6 ppm
3.8 ppm
1.4 ppm
2.23
3.11
0.97
1.17
5.96
6.00
10 9 8 7 6 5 4 3 2 1 0 ppm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132.195
129.661
128.439
121.042
88.452
83.129
46.081
45.752
21.071
20.122
3ha
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm