Supporting Information

Zinc(II)-Catalyzed Redox Cross-Dehydrogenative Coupling of Propargylic Amines and Terminal Alkynes for Synthesis of *N*-Tethered 1,6-Enynes

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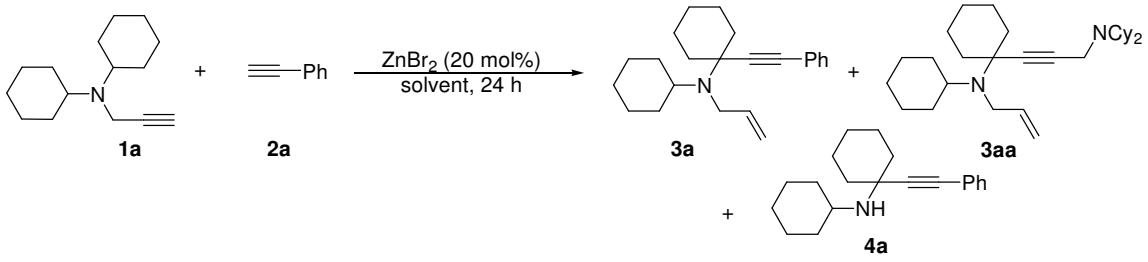
General.

All reactions were carried out under an atmosphere of nitrogen, unless otherwise indicated. Most commercially supplied chemicals were used without further purification. Analytical thin layer chromatography (TLC) was performed on a glass plates of silica gel 60 GF_{254} (Merck), which were visualized by the quenching of UV fluorescence (254 nm), and/or by an aqueous alkaline $KMnO_4$ solution, followed by heating. Column chromatography was conducted on silica gel (Merck Kieselgel 70-230 mesh). Nuclear magnetic resonance spectra were acquired on a VARIAN UNITY-INOVA 400 (400 MHz and 100 MHz for ^1H and ^{13}C respectively) and/or on a JEOL JNM-AL 300 (300 MHz and 75.5 MHz for ^1H and ^{13}C respectively) spectrometers. The chemical shifts are reported in δ units relative to internal tetramethylsilane. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer. Liquid chromatogram mass spectrometer was recorded on Shimadzu LCMS-2010EV. High-resolution mass spectra (ESI) were recorded on a Bruker Daltonics micro TOF-15 focus.

We examined the reaction condition with *N,N*-dicyclohexylpropargylamine **1a**, ethynylbenzene **2a**, and zincbromide. The solvents, the amount of substrates and catalysts, and reaction temperature were optimized for the synthesis of 1,6-enyne **3a**.

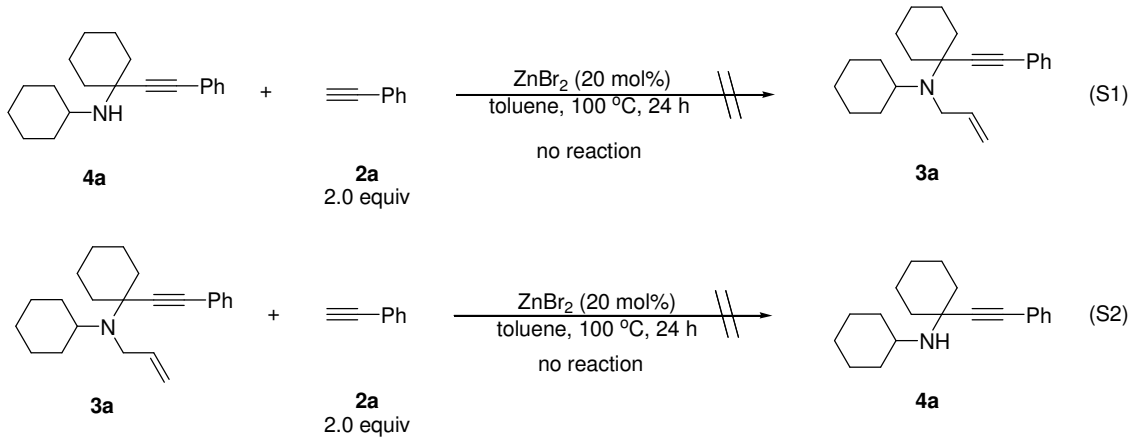
Table S1. Screening of Reaction Conditions for Zn(II)-Catalyzed CDC of *N,N*-Dicyclohexyl Propargyl Amine **1a** with Ethynyl Benzen **2a**[a]



entry	solvent	**1a/2a**	Temperature (°C)	$ZnBr_2$ (mol%)	isolated yield (%)			
					3a	**4a**	recovery of **1a**	**3aa**
1	THF	1.0 : 3.0	100	20	9	38	trace	-[b]
2	EtOH	1.0 : 3.0	100	20	23	0	17	-
3	CH_3CN	1.0 : 3.0	100	20	36	29	-	-
4	**toluene**	**1.0 : 3.0**	**100**	**20**	**45**	19	trace	-
5	toluene	1.0 : 5.0	100	20	42	26	-	-
6	toluene	1.0 : 2.0	100	20	30	28	-	-
7	toluene	1.0 : 1.1	100	20	26	31	-	-
8	toluene	2.0 : 1.0	100	20	38	43	-	trace
9	toluene	1.0 : 3.0	80	20	33	9	23	-
10[c]	toluene	1.0 : 3.0	150	20	5	48	trace	-
11	toluene	1.0 : 3.0	100	10	29	42	0	-

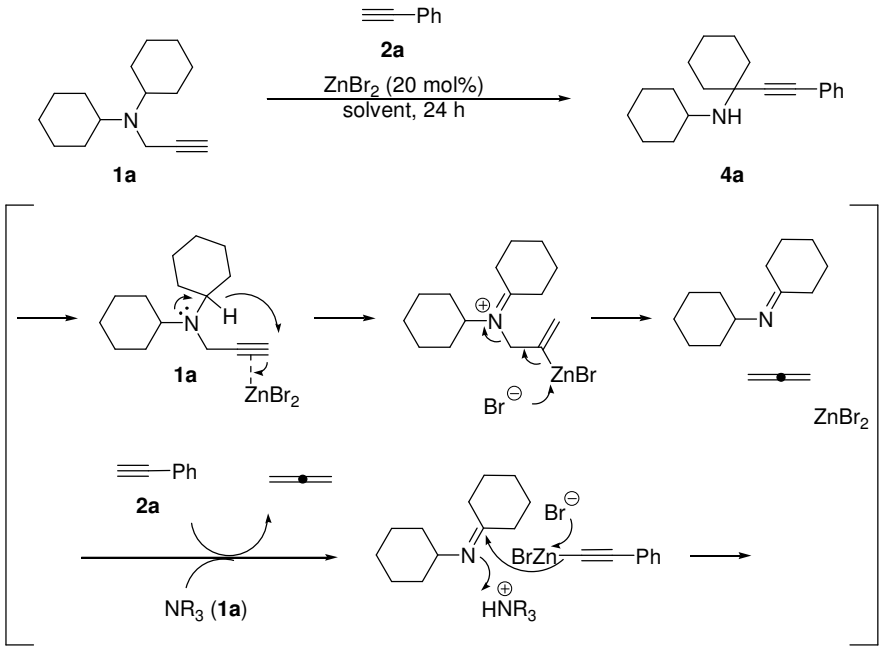
[a]*N,N*-Dicyclohexyl propargyl amine **1a** (0.3 mmol), ethynyl benzene **2a**, and $ZnBr_2$ (0.06 mmol) were heated in toluene in a closed vial tube under N_2 for 24 h. [b]Not observed. [c]at 150 °C, for 20 min, under microwave.

We devised treatment of secondary amine **4a** under the optimized condition in order to investigate the reaction pathway of it (eq. (S1)), which ended up no reaction and 1,6-enyne **3a** didn't observed. And treatment of 1,6-enyne **3a** under the optimized condition (eq.(S2)) was also no reaction, and secondary amine **4a** didn't observed. Secondary amine **4a** is estimated to be neither a reaction intermediate nor a decomposed 1,6-enyne **3a** by elimination of the allyl group.

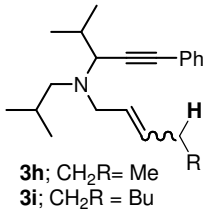


The reaction pathway of secondary amine **4a** can be the addition of alkyne **2a** to the imine which was generated by transformation from propargylic amine **1a** to the allene[1] (Scheme S1).

Scheme S1



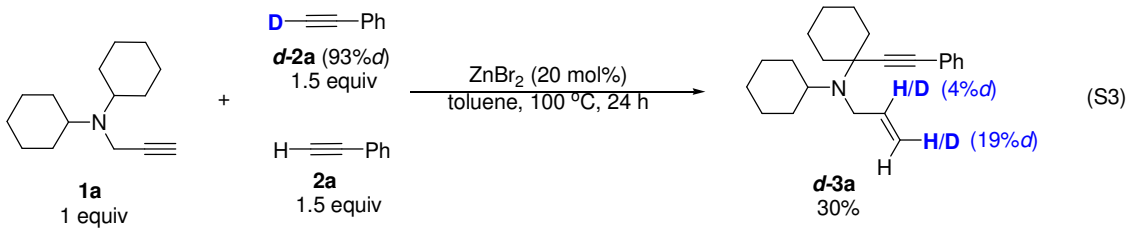
*Analysis of the diastereomeric ratios of **3h** and **3i***



The quantitative analysis of the composition of E/Z mixtures (**3h** and **3i**) were improved by decoupling of ^{1}H at the vinyl position in ^{1}H NMR.

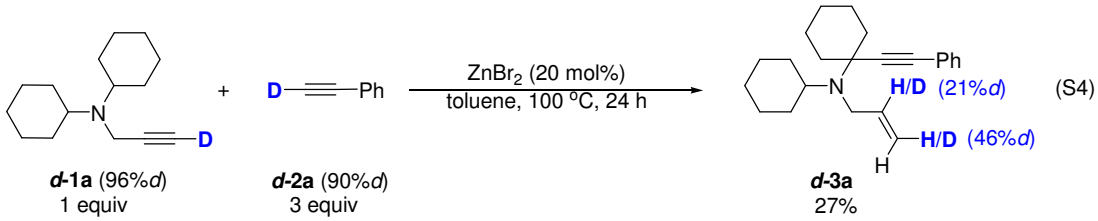
Isotopic Labeling Experiments

Propargylic amine **1** itself is a tertiary amine, so that the reaction mixture is basic under our optimized reaction condition. When we treat propargyl amine **1a**, which is a terminal alkyne, substrates **1a** and **2a** would have been deprotonated, and the both carbons of the alkene position in the product ***d*-3a** were deuterated (eq. (4)). We focused on the ratio of deuterium atoms incorporated in the alkene position. The terminal carbon was preferred rather than the inner carbon to be deuterated (38%>19%). Competing eq. (5) with eq. (4), total deuterium atoms included in situ were fewer than that of eq. (4), because excess amount of terminal alkyne **2a** was added. In eq. (S3), a half of deuterium atoms of eq. (4) were included in situ, and some of them incorporated in alkene position of 1,6-enyne ***d*-3a** in the ratio of 19% to 4%.



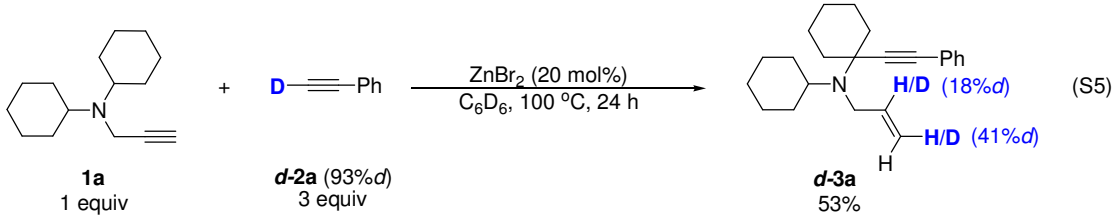
(S3)

The deuterium atoms at the terminal positions of ***d*-1a** and ***d*-2a** were incorporated in the both carbons of the alkene position in *cis* relation (eq. (S4)).



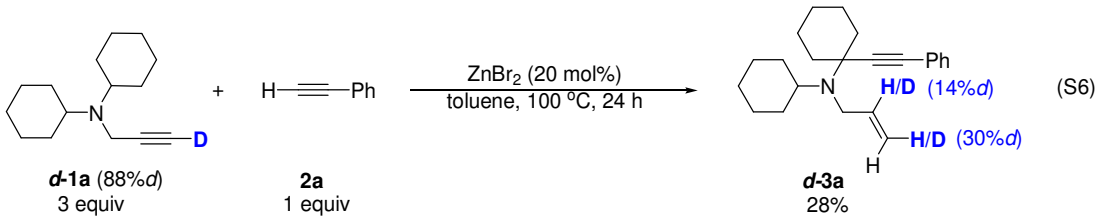
(S4)

Treatment of propargyl amine **1a** and deuterated ethynylbenzene ***d*-2a** in benzene-*d*6 afforded 1,6-enyne ***d*-3a** as the one did in eq. (4) (eq. (S5)). It is suggested that the solvents would not relate with the protonation of propargyl amine **1a** directly.



(S5)

Additionally treatment of three equivalent of deuterated propargyl amine ***d*-1a** and ethynylbenzene **2a** afforded 1,6-enyne ***d*-3a** (eq. (S6)). Competing eq. (S6) with eq. (5), nearly three times of deuterium atoms were included in situ, which were incorporated in alkene position of 1,6-enyne ***d*-3a** in the ratio of 30% to 14%.



(S6)

The result of these equations (eq. (4) and (5), and eq. (S3)-(S6)) suggested that acidic protones of terminal alkynes would relevant for the current redox CDC.

*Preparation of propargylic amines **1***

N,N-Dicyclohexylprop-2-yn-1-amine **1a**, *N,N*-Diisopropylamineprop-2-yn-1-amine **1b**, *N,N*-Dihexylprop-2-yn-1-amine **1c**, and *N,N*-Dibenzylprop-2-yn-1-amine **1e** were already reported.[2]

General procedure for propargylic amines **1d, 1f,** and **1g**

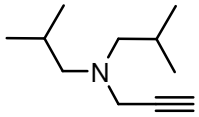
To a mixture of *N,N*-diisobutylamine (8.7 ml, 50 mmol) and K_2CO_3 (13.8 g, 100 mmol) in DMF (120 ml), was added 1-propyne-3-bromide (3.8 ml, 50 mmol) and the mixture was stirred at room temperature for 14 h. After the celite filtration, the filtrate was concentrated under the reduced pressure and diluted in diethyl ether. The ethereal solution was washed with water, brine, and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with hexane/EtOAc (50/1) as eluent to give *N,N*-diisobutylprop-2-ynylamine **1d** as a colorless liquid (7.56 g, 90% yield). 2-(Prop-2-ynyl)-1,2,3,4-tetrahydroisoquinoline **1f** and *N*-methyl-*N*-(prop-2-ynyl)butan-1-amine **1g** were prepared from 1,2,3,4-tetrahydroisoquinoline and *N*-butylmethylamine, respectively, in a similar manner.

General procedure for propargylic amines **1h** and **1i**

To *N,N*-diisobutylprop-2-ynylamine **1d** (0.84g, 5.0 mmol) in THF (25 ml), was added dropwise ^{n}BuLi in hexane (1.6M, 5.5 mmol) at 0℃, and stirred over 20 min. Iodomethane (0.375ml, 6.0 mmol) was added to the mixture at 0℃. The resulting solution was allowed to warm to room temperature and was stirred for 5 h. The solvent was concentrated under a reduced pressure and the mixture was diluted in diethyl ether. The ethereal solution was washed with saturated NH_4Cl aq., brine, and dried over anhydrous $MgSO_4$. The solvent was concentrated under a reduced pressure, yielding pure *N,N*-diisobutylbut-2-yn-1-amine **1h** (0.795 g, 88% yield) as a colorless oil. *N,N*-Diisobutylhept-2-yn-1-amine **1i** was prepared according the same procedure except for the use of 1-iodobutane.

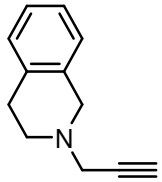
Synthesis of the propargylic amines **1**

***N,N*-diisobutylprop-2-yn-1-amine (1d)**



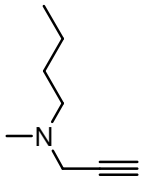
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35 (d, *J* = 2.4 Hz, 2H), 2.18 (d, *J* = 7.2 Hz, 4H), 2.13 (t, *J* = 2.4 Hz, 1H), 1.68 (sept, *J* = 6.8 Hz, 2H), 0.89 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 79.4, 72.1, 62.3, 42.6, 26.1, 20.7; IR (neat) 3308, 2958, 2934, 2864, 2801, 1460, 649, 624 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{11}H_{21}N$ $[M+H]^+$: 168.1752, found: 168.1749.

2-(prop-2-ynyl)-1,2,3,4-tetrahydroisoquinoline (1f)



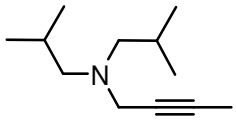
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.11 (m, 3H), 7.05-7.03 (m, 1H), 3.77 (s, 2H), 3.51 (d, *J* = 2.8 Hz, 2H), 2.95 (t, *J* = 6.4 Hz, 2H), 2.84 (t, *J* = 6.4 Hz, 2H), 2.27 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 134.5, 133.8, 128.6, 126.6, 126.1, 125.6, 78.7, 73.3, 54.3, 49.7, 46.8, 29.2; IR (neat) 3292, 2912, 2801, 1133, 1094, 741, 645 cm^{-1}; $[M+H]^+$; HRMS *m/z* (ESI) calcd. for $C_{12}H_{13}N$ $[M+H]^+$: 172.1126, found: 172.1123.

***N*-methyl-*N*-(prop-2-ynyl)butan-1-amine (1g)**



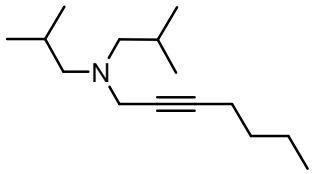
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.34 (d, *J* = 2.4 Hz, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 2.21 (t, *J* = 2.4 Hz, 1H), 1.68-1.26 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 78.7, 72.8, 55.4, 45.5, 41.7, 29.7, 20.5, 14.0; IR (neat) 3308, 2958, 2934, 2864, 2801, 1460, 649, 624 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_8H_{15}N$ $[M+H]^+$: 126.1283, found: 126.1278.

***N,N*-diisobutylbut-2-yn-1-amine (1h)**



Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.27 (q, *J* = 2.0 Hz, 2H), 2.15 (d, *J* = 7.2 Hz, 4H), 1.83 (t, *J* = 2.0 Hz, 3H), 1.67 (sept, *J* = 6.8 Hz, 2H), 0.87 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 79.6, 74.5, 62.4, 43.0, 26.2, 20.8, 3.4; IR (neat) 2953, 2870, 2817, 1468, 1364, 1093 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{12}H_{23}N$ $[M+H]^+$: 182.1909, found: 182.1910

***N,N*-diisobutylhept-2-yn-1-amine (1i)**



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (t, *J* = 2.0 Hz, 2H), 2.19 (tt, *J* = 4.0, 2.0 Hz, 2H), 2.15 (d, *J* = 7.6 Hz, 4H), 1.69 (sept, *J* = 6.8 Hz, 2H), 1.52-1.39 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 84.5, 75.1, 62.4, 42.9, 31.2, 26.1, 21.9, 20.8, 18.3, 13.6; IR (neat) 2954, 2870, 2816, 1468, 1364, 1325, 1092 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{15}H_{29}N$ $[M+H]^+$: 224.2378, found: 224.2376.

Synthesis of N-tethered 1,6-enynes ***3***

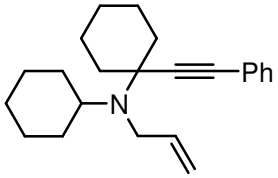
Representative procedure for *N*-tethered 1,6-enynes **3**

$ZnBr_2$ (0.0135g, 0.06 mmol), *N,N*-dicyclohexyl-hept-2-yn-1-amine **1a** (0.0658g, 0.3 mmol), and ethynylbenzene **2a** (0.10 ml, 0.9 mmol) in dry toluene (1.2 ml) were stirred at 100℃ for 24 h in a closed vial tube. The resulting solution was filtered through celite and

concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with hexane/AcOEt (30/1) as eluent to give **3a** (0.0438g, 45% yield) as a colorless oil.

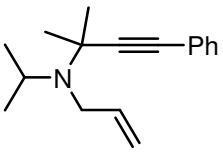
Characterization of *N*-tethered 1,6-enynes **3**

***N*-allyl-*N*-cyclohexyl-1-(2-phenylethynyl)cyclohexanamine (3a)**



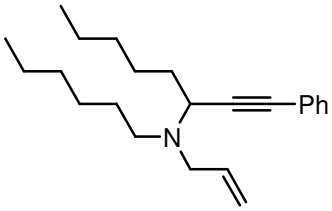
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.31-7.25 (m, 3H), 5.96-5.86 (m, 1H), 5.15 (dd, *J* = 17.2, 2.0 Hz, 1H), 4.93 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.44 (t, *J* = 5.6 Hz, 2H), 3.07 (tt, *J* = 11.2, 3.2 Hz, 1H), 2.00-1.94 (m, 4H), 1.77-1.49 (m, 10H), 1.40-1.17 (m, 5H), 1.09-0.98 (m, 1H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 142.7, 131.3, 128.2, 127.5, 124.2, 112.7, 95.2, 84.8, 58.9, 57.0, 47.6, 38.0, 30.9, 26.5, 26.3, 25.7, 23.1; IR (neat) 3079, 2931, 2853, 1445, 755, 690 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{23}H_{31}N$ $[M+H]^+$: 322.2535, found: 322.2535.

***N*-allyl-*N*-isopropyl-2-methyl-4-phenylbut-3-yn-2-amine (3b)**



Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 2H), 7.30-7.26 (m, 3H), 5.98-5.88 (m, 1H), 5.19 (dd, *J* = 17.0, 1.8 Hz, 1H), 4.96 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.55 (sept, *J* = 6.8 Hz, 1H), 3.36 (d, *J* = 3.2 Hz, 2H), 1.46 (s, 6H), 1.10 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 139.8, 128.8, 125.6, 125.0, 121.3, 110.6, 93.5, 79.7, 52.1, 46.1, 44.0, 28.0, 17.8; IR (neat) 3079, 2978, 2931, 1177, 911, 754, 690 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{17}H_{23}N$ $[M+H]^+$: 242.1909, found: 242.1906.

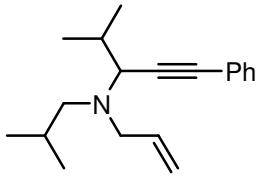
***N*-allyl-*N*-hexyl-1-phenyloct-1-yn-3-amine (3c)**



Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 2H), 7.31-7.27 (m, 3H), 5.91-5.81 (m, 1H), 5.22 (dd, *J* = 17.2 Hz, 1.2 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 3.66 (t, *J* = 8.4 Hz, 1H), 3.35-3.29 (m, 1H), 3.00 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.62-2.55 (m, 1H), 2.44-2.37 (m, 1H), 1.54-1.40 (m, 2H),

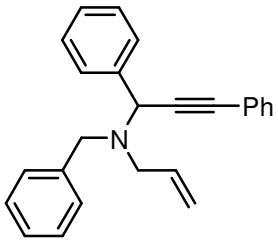
1.38-1.25 (m, 12H), 0.89 (q, J = 6.8 Hz, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 137.2, 131.7, 128.2, 127.7, 123.7, 116.6, 88.9, 84.7, 54.7, 53.7, 51.0, 34.1, 31.8, 31.6, 28.3, 27.2, 26.4, 22.7, 22.6, 14.09, 14.08; IR (neat) 2928, 2858, 917, 755, 690, 478 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{23}H_{35}N$ $[M+H]^+$: 326.2848, found: 326.2849.

N-allyl-*N*-isobutyl-4-methyl-1-phenylpent-1-yn-3-amine (3d)



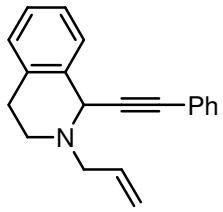
Colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.32-7.28 (m, 3H), 5.89-5.79 (m, 1H), 5.20 (d, J = 17.2 Hz, 1H), 5.07 (d, J = 10.0 Hz, 1H), 3.28 (dt, J = 14.4, 2.2 Hz, 1H), 3.14 (d, J = 10.4 Hz, 1H), 2.92 (dd, J = 14.4, 8.4 Hz, 1H), 2.33 (dd, J = 12.8 Hz, 4.8 Hz, 1H), 2.17 (dd, J = 12.8, 10.4 Hz, 1H), 1.89-1.70 (m, 2H), 1.09 (d, J = 6.8 Hz, 3H), 1.02 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 137.7, 131.7, 128.2, 127.6, 123.8, 116.3, 88.3, 85.2, 61.2, 59.5, 54.7, 31.1, 26.4, 21.1, 20.9, 20.7, 20.1; IR (neat) 2955, 1468, 1086, 918, 755, 690 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{19}H_{27}N$ $[M+H]^+$: 270.2222, found: 270.2218.

N-benzyl-*N*-(1,3-diphenylprop-2-ynyl)prop-2-en-1-amine (3e)



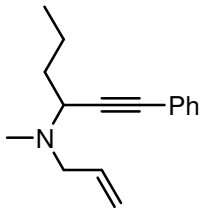
Yellow oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 6.8 Hz, 2H), 7.59-7.57 (m, 2H), 7.41-7.18 (m, 11H), 5.93-5.83 (m, 1H), 5.31 (d, J = 17.2 Hz, 1H), 5.15 (d, J = 10.4 Hz, 1H), 5.02 (s, 1H), 3.86 (d, J = 13.2 Hz, 1H), 3.51 (d, J = 13.6 Hz, 1H), 3.23 (dt, J = 16.0 Hz, 2.0 Hz, 1H), 3.09 (dd, J = 14.0 Hz, 8.4 Hz, 1H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 139.7, 139.3, 136.6, 131.9, 128.8, 128.4, 128.3, 128.2, 128.1, 127.4, 126.9, 123.3, 117.4, 88.2, 85.1, 56.3, 54.6, 53.5; IR (neat) 3029, 2925, 2813, 1599, 1490, 1449, 1113, 918, 755, 696 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{25}H_{23}N$ $[M+H]^+$: 338.1909, found: 338.1909.

2-allyl-1-(2-phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (3f)



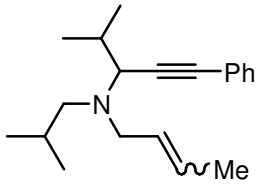
Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 2H), 7.31-7.23 (m, 4H), 7.19-7.11 (m, 3H), 6.02-5.92 (m, 1H), 5.34 (dd, *J* = 18.8, 2.0 Hz, 1H), 5.23 (dt, *J* = 10.0, 0.8 Hz, 1H), 4.88 (s, 1H), 3.45-3.36 (m, 2H), 3.08-2.97 (m, 2H), 2.86-2.79 (m, 2H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 135.4, 135.2, 133.9, 131.8, 129.0, 128.2, 128.0, 127.8, 127.0, 125.9, 123.2, 118.4, 87.3, 86.7, 58.4, 54.6, 45.4, 28.8; IR (neat) 3064, 2914, 2817, 1489, 741, 691, 478 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{20}H_{19}N$ $[M+H]^+$: 274.1596, found: 274.1594.

N-allyl-*N*-methyl-1-phenylhex-1-yn-3-amine (3g)



Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.31-7.28 (m, 3H), 5.92-5.82 (m, 1H), 5.27-5.22 (m, 1H), 5.16-5.12 (m, 1H), 3.63 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.22-3.17 (m, 1H), 3.08 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.28 (s, 3H), 1.72-1.43 (m, 4H), 0.96 (t, *J* = 3.6 Hz, 3H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 136.2, 131.7, 128.2, 127.8, 123.5, 117.5, 87.4, 85.7, 58.2, 55.8, 37.6, 35.9, 19.9, 13.9, 13.1; IR (neat) 3080, 2958, 2872, 2790, 1489, 1456, 920, 755, 690 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{16}H_{21}N$ $[M+H]^+$: 228.1752, found: 228.1747.

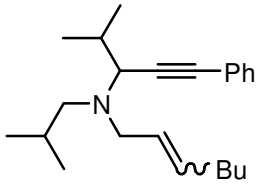
N-(but-2-enyl)-*N*-isobutyl-4-methyl-1-phenylpent-1-yn-3-amine (3h)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.31-7.27 (m, 3H), 5.63-5.54 (m, 1H), 5.48-5.41 (m, 1H), 3.21-3.17 (m, 1H), 3.14 (d, *J* = 10.4 Hz, 1H), 2.84 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.28 (dd, *J* = 12.8, 4.4 Hz, 1H), 2.16 (dd, *J* = 12.8, 10.0 Hz, 1H), 1.89-1.68 (m, 2H), 1.68 (d, *J* = 6.4 Hz, 3H), 1.10 (d, *J* = 6.4 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 131.7, 130.1, 128.2, 127.5, 127.2, 123.9, 88.5, 85.1, 61.0,

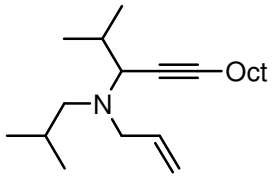
59.3, 53.8, 31.0, 26.4, 21.1, 20.9, 20.7, 20.1, 17.8; IR (neat) 2955, 2814, 1468, 1079, 967, 765, 690, 491 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{20}H_{29}N$ $[M+H]^+$: 284.2378, found: 284.2375.

N-isobutyl-*N*-(4-methyl-1-phenylpent-1-yn-3-yl)hept-2-en-1-amine (3i)



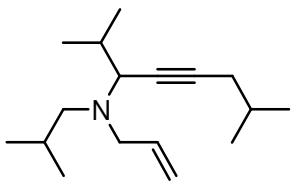
Colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.31-7.25 (m, 3H), 5.61-5.54 (m, 1H), 5.46-5.39 (m, 1H), 3.22-3.19 (m, 1H), 3.17 (d, *J* = 9.6 Hz, 1H), 2.84 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.29 (dd, *J* = 12.8, 4.4 Hz, 1H), 2.17 (dd, *J* = 12.8, 10.0 Hz, 1H), 2.03 (dd, *J* = 13.2, 6.8 Hz, 2H), 1.88-1.69 (m, 2H), 1.39-1.09 (m, 4H), 1.08 (d, *J* = 6.4 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.90-0.86 (m, 9H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 132.9, 131.7, 128.8, 127.5, 123.9, 88.5, 85.1, 61.0, 59.3, 53.8, 32.0, 31.5, 31.0, 26.4, 22.1, 21.1, 20.9, 20.7, 20.1, 13.9; IR (neat) 2955, 2870, 2815, 1467, 1069, 972, 755, 690 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{19}H_{27}N$ $[M+H]^+$: 326.2848, found: 326.2848.

N-allyl-*N*-isobutyl-2-methyltridec-4-yn-3-amine (3j)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85-5.75 (m, 1H), 5.16 (d, *J* = 11.0 Hz, 1H), 5.04 (d, *J* = 6.8 Hz, 1H), 3.21-3.15 (m, 1H), 2.88 (dt, *J* = 5.2, 2.0 Hz, 1H), 2.80 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.07 (dd, *J* = 12.4, 10.0 Hz, 1H), 1.73-1.64 (m, 2H), 1.56-1.28 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.89-0.84 (m, 9H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 138.0, 115.9, 84.9, 77.8, 60.7, 59.4, 54.6, 31.8, 31.1, 29.3, 29.2, 29.1, 28.8, 26.3, 22.7, 21.1, 20.9, 20.7, 20.1, 18.6, 14.1; IR (neat) 2928, 2857, 2815, 1468, 1086, 916, 458 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{13}H_{22}N$ $[M+H]^+$: 306.3161, found: 306.3162.

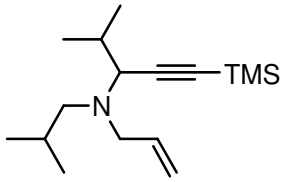
N-allyl-N-isobutyl-2,7-dimethyloct-4-yn-3-amine (3k)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85-5.75 (m, 1H), 5.18-5.13 (m, 1H), 5.05-5.02 (m, 1H), 3.22-3.17 (m, 1H), 2.92-2.88 (m, 1H), 2.84-2.78 (m, 1H), 2.23 (dd, *J* = 12.8, 4.4 Hz, 1H),

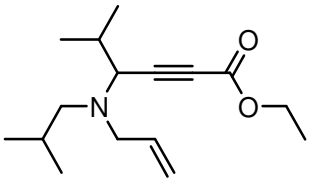
2.13-2.05 (m, 3H), 1.84-1.43 (m, 3H), 1.02-0.95 (m, 12H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 138.0, 115.9, 83.7, 78.7, 60.7, 59.5, 54.6, 31.1, 28.3, 27.9, 26.3, 22.0, 21.1, 20.9, 20.7, 20.1; IR (neat) 2955, 2870, 2815, 1467, 1385, 1365, 1086, 916 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{17}H_{31}N$ $[M+H]^+$: 250.2535, found: 250.2535.

_N_-allyl-_N_-isobutyl-4-methyl-1-(trimethylsilyl)pent-1-yn-3-amine (3l)



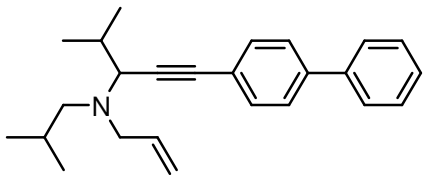
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84-5.74 (m, 1H), 5.17 (d, *J* = 8.8 Hz, 1H), 5.06 (d, *J* = 10.0 Hz, 1H), 3.21-3.15 (m, 1H), 2.92 (d, *J* = 10.4 Hz, 1H), 2.79 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.21 (dd, *J* = 14.4, 3.2 Hz, 1H), 2.06 (dd, *J* = 14.4, 10.0 Hz, 1H), 1.77-1.64 (m, 2H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H) 0.17 (s, 9H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 137.6, 116.1, 104.7, 89.0, 61.3, 59.3, 54.4, 30.8, 26.2, 21.0, 20.8, 20.7, 20.0, 0.3; IR (neat) 2957, 2817, 2159, 1250, 842, 486 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{16}H_{31}NSi$ $[M+H]^+$: 226.2304, found: 226.2301.

ethyl 4-(allyl(isobutyl)amino)-5-methylhex-2-ynoate (3m)



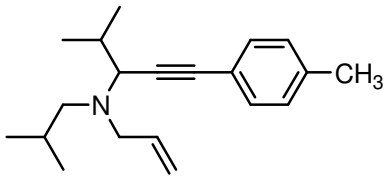
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82-5.72 (m, 1H), 5.22-5.17 (m, 1H), 5.10-5.07 (m, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.27-3.22 (m, 1H), 3.07 (d, *J* = 10.4 Hz, 1H), 2.85 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.27 (dd, *J* = 12.8, 8.4 Hz, 1H), 2.14 (dd, *J* = 12.8, 10.0 Hz, 1H), 1.88-1.65 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 6.4 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H) , 0.89 (d, *J* = 6.4 Hz, 3H) , 0.86 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 153.8, 136.8, 116.9, 87.2, 77.5, 61.8, 60.5, 59.2, 54.5, 30.5, 26.3, 20.9, 20.60, 20.56, 19.9, 14.0; IR (neat) 2871, 2818, 2221, 1713, 1468, 1366, 1238, 1058, 921, 752 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{17}H_{31}N$ $[M+H]^+$: 266.2120, found: 266.2120.

_N_-allyl-_N_-isobutyl-1-biphenyl-4-methylpent-1-yn-3-amine (3n)



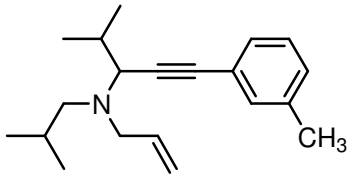
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.49 (m, 6H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 10.4 Hz, 1H), 5.90-5.80 (m, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.0 Hz, 1H), 3.29 (dt, *J* = 14.4, 2.0 Hz, 1H), 3.17 (d, *J* = 10.4 Hz, 1H), 2.94 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.35 (dd, *J* = 12.8, 3.6 Hz, 1H), 2.19 (dd, *J* = 12.8, 6.0 Hz, 1H), 1.91-1.71 (m, 2H), 1.11 (d, *J* = 6.0 Hz, 1H), 1.04 (d, *J* = 6.0 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 140.5, 140.4, 137.7, 132.1, 128.8, 127.5, 127.0, 126.9, 122.8, 116.3, 89.0, 85.1, 61.3 59.5, 54.8, 31.1, 26.4, 21.1, 20.9, 20.7, 20.1; IR (neat) 3078, 3032, 2955, 2869, 2814, 1487, 1086, 839, 763, 697, 496 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{25}H_{31}N$ $[M+H]^+$: 346.2535, found: 346.2536.

N-allyl-*N*-isobutyl-*4*-methyl-1-*p*-tolylpent-1-yn-3-amine (3o)



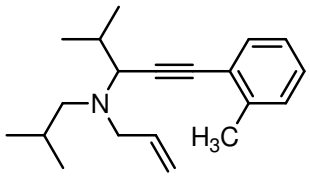
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.88-5.78 (m, 1H), 5.22-5.16 (m, 1H), 5.08-5.05 (m, 1H), 3.29-3.24 (m, 1H), 3.13 (d, *J* = 10.0 Hz, 1H), 2.91 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.36-2.30 (m, 4H), 2.16 (dd, *J* = 12.4, 10.4 Hz, 1H), 1.88-1.70 (m, 2H), 1.08 (d, *J* = 6.4 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 137.7, 137.6, 131.5, 128.9, 120.7, 116.2, 87.4, 85.2, 61.2, 59.5, 54.7, 31.1, 26.4, 21.4, 21.1, 20.9, 20.7, 20.1; IR (neat) 2955, 2869, 2815, 1508, 1087, 816 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{20}H_{29}N$ $[M+H]^+$: 284.2378, found: 284.2373.

N-allyl-*N*-isobutyl-4-methyl-1-*m*-tolylpent-1-yn-3-amine (3p)



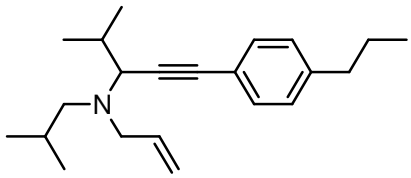
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.23 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 3.6 Hz, 1H), 5.88-5.78 (m, 1H), 5.78-5.22 (m, 1H), 5.17-5.09 (m, 1H), 3.27 (dq, *J* = 12.4, 2.0 Hz, 1H), 3.13 (d, *J* = 5.2 Hz, 1H), 2.91 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.35-2.31 (m, 4H), 2.17 (dd, *J* = 12.8, 11.6 Hz, 1H), 1.89-1.69 (m, 2H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 137.9, 137.7, 132.3, 128.8, 128.5, 128.1, 123.6, 116.3, 87.8, 85.4, 61.2, 59.5, 54.7, 31.9, 26.4, 21.2, 20.9, 20.7, 20.1; IR (neat) 2955, 2869, 2815, 1468, 1089, 917, 782 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{20}H_{29}N$ $[M+H]^+$: 284.2378, found: 284.2375.

***N*-allyl-*N*-isobutyl-4-methyl-1-*o*-tolylpent-1-yn-3-amine (3q)**



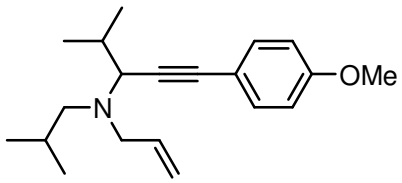
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 1H), 7.20-7.11 (m, 3H), 5.91-5.81 (m, 1H), 5.22 (dd, *J* = 17.2, 0.8 Hz, 1H), 5.10 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.32 (dq, *J* = 16.4, 2.0 Hz, 1H), 2.95 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.47 (s, 3H), 2.37 (dd, *J* = 13.2, 4.6 Hz, 1H), 2.21 (dd, *J* = 12.8, 5.2 Hz, 1H), 1.91-1.73 (m, 2H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 139.8, 137.6, 132.1, 129.3, 127.6, 125.4, 123.7, 116.3, 61.3, 59.6, 54.8, 31.1, 26.4, 21.14, 21.11, 21.0, 20.7, 20.1; IR (neat) 3069, 2955, 2869, 2815, 1468, 1087, 918, 755, 478 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{20}H_{29}N$ $[M+H]^+$: 284.2378, found: 284.2379.

***N*-allyl-*N*-isobutyl-4-methyl-1-(4-propylphenyl)pent-1-yn-3-amine (3r)**



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.88-5.78 (m, 1H), 5.22-5.16 (m, 1H), 5.08-5.05 (m, 1H), 3.29-3.25 (m, 1H), 3.13 (d, *J* = 10.8 Hz, 1H), 2.91 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.57 (t, *J* = 7.2 Hz, 1H), 2.33 (dd, *J* = 12.8, 4.4 Hz, 1H), 2.16 (dd, *J* = 12.8, 10.0 Hz, 1H), 1.88-1.68 (m, 2H), 1.67-1.57 (m, 2H), 1.08 (d, *J* =6.8 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.94-0.86 (m, 9H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 142.4, 137.7, 131.5, 128.3, 120.9, 116.2, 87.4, 85.2, 61.1, 59.4, 54.6, 37.9, 31.0, 26.3, 24.4, 21.1, 20.9, 20.8, 20.7, 13.7; IR (neat) 2956, 2870, 2815, 1509, 1467, 1087, 918, 458 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{22}H_{33}N$ $[M+H]^+$: 312.2691, found: 312.2688.

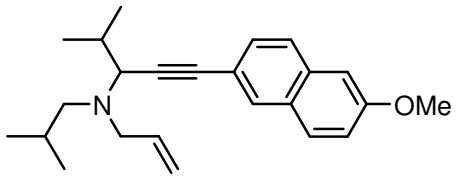
***N*-allyl-*N*-isobutyl-4-methyl-1-(4-methoxyphenyl)pent-1-yn-3-amine (3s)**



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 6.84-6.80 (m, 2H), 5.88-5.78 (m, 2H), 5.22-5.16 (m, 1H), 5.08-5.05 (m, 1H), 3.80 (s, 3H),3.29-3.24 (m, 1H), 3.12 (d, *J* = 10.4 Hz, 1H), 2.91 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.32 (dd, *J* = 13.2, 4.4 Hz, 1H), 2.16 (dd, *J* = 12.8 Hz, 10.0 Hz, 1H),

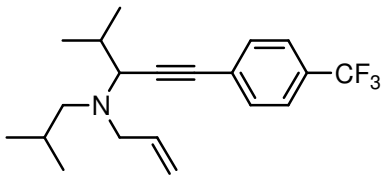
1.87-1.71 (m, 2H), 1.08 (d, J = 6.8 Hz, 3H), 1.02 (d, J =6.8 Hz, 3H), 0.93 (d, J =6.8 Hz, 3H), 0.87 (d, J =6.8 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 159.1, 137.3, 133.0, 116.1, 116.0, 113.8, 86.5, 84.9, 61.2, 59.5, 55.3, 54.7, 31.1, 26.4, 21.1, 20.9, 20.7, 20.1; IR (neat) 2955, 2869, 2815, 1606, 1509, 1467, 1247, 1172, 1037, 831 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{20}H_{29}NO$ $[M+H]^+$: 300.2327, found: 300.2323.

N-allyl-*N*-isobutyl-1-(6-methoxynaphthalen-2-yl)-4-methylpent-1-yn-3-amine (3t)



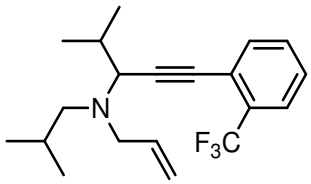
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.67 (t, J = 9.6 Hz, 2H), 7.47-7.44 (m, 1H), 7.15-7.09 (m, 2H), 5.91-5.81 (m, 1H), 5.25-5.19 (m, 1H), 5.10-5.07 (m, 1H), 3.91 (s, 3H), 3.34-3.28 (m, 1H), 3.18 (d, J = 10.4 Hz, 1H), 2.96 (dd, J = 14.4, 8.4 Hz, 1H), 2.38 (dd, J = 12.8, 4.4 Hz, 1H), 1.93-1.72 (m, 2H), 1.13 (d, J = 6.8 Hz, 3H), 1.04 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H), 0.89 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 158.0, 137.7, 133.8, 130.9, 129.4, 129.1, 128.5, 126.6, 119.2, 118.7, 116.2, 105.8, 87.8, 85.6, 61.3, 59.5, 55.3, 54.7, 31.1, 26.4, 21.1, 21.0, 20.7, 20.1; IR (neat) 2955, 2869, 2816, 1602, 1389, 1244, 851 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{24}H_{31}NO$ $[M+H]^+$: 350.2484, found: 350.2483.

N-allyl-*N*-isobutyl-4-methyl-1-(4-(trifluoromethyl)phenyl)pent-1-yn-3-amine (3u)



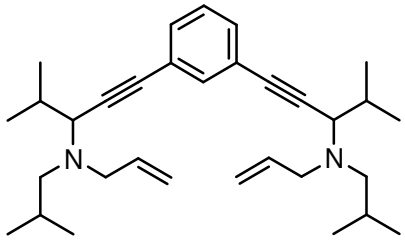
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.51 (m, 4H), 5.88-5.78 (m, 1H), 5.20 (d, J = 18.0 Hz, 1H), 5.09 (d, J = 10.0 Hz, 1H), 3.28 (dq, J = 14.4, 2.0 Hz, 1H), 3.16 (d, J = 10.8 Hz, 1H), 2.90 (dd, J = 14.4, 4.0 Hz, 1H), 2.31 (dd, J = 6.4, 4.8 Hz, 1H), 2.18 (dd, J = 10.4, 6.4 Hz, 1H), 1.91-1.70 (m, 2H), 1.09 (d, J =6.4 Hz, 3H), 1.03 (d, J =6.4 Hz, 3H), 0.92 (d, J =6.4 Hz, 3H), 0.88 (d, J =6.4 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 137.4, 131.9, 129.4 (d, $J_{C\text{-}F}$ = 32.0 Hz), 127.6, 125.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 122.6, 116.5, 91.2, 84.2, 61.2, 59.5, 54.7, 31.0, 26.4, 21.1, 20.8, 20.7, 20.1; IR (neat) 3080, 2957, 2871, 2815, 1615, 1468, 1323, 1130, 842, 455 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{20}H_{26}F_3N$ $[M+H]^+$: 338.2096, found: 338.2096.

N-allyl-*N*-isobutyl-4-methyl-1-(2-(trifluoromethyl)phenyl)pent-1-yn-3-amine (3v)



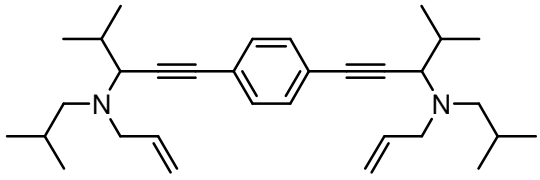
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.56 (m, 2H), 7.47-7.43 (m, 1H), 7.37-7.33 (m, 1H), 5.88-5.78 (m, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.4 Hz, 1H), 3.32-3.27 (m, 1H), 3.19 (d, *J* = 10.4, 1H), 2.94 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.35 (dd, *J* = 12.8, 4.4 Hz, 1H), 2.19 (dd, *J* = 12.8, 10.0 Hz, 1H), 1.93-1.69 (m, 2H), 1.10 (d, *J* =6.4 Hz, 3H), 1.03 (d, *J* =6.4 Hz, 3H), 0.92 (d, *J* =6.4 Hz, 3H), 0.87 (d, *J* =6.4 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 137.5, 134.3, 131.2, 127.3, 125.6, 125.0, 122.1, 116.4, 95.1, 81.2, 61.2, 59.4, 54.7, 30.9, 26.4, 21.0, 20.6, 20.1; IR (neat) 2957, 2871, 2816, 1318, 1138, 764 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{20}H_{26}F_3N$ $[M+H]^+$: 338.2096, found: 338.2096.

N-allyl-1-(3-(3-(allyl(isobutyl)amino)-4-methylpent-1-ynyl)phenyl)-*N*-isobutyl-4-methyl pent-1-yn-3-amine (3w)



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 5.88-5.78 (m, 2H), 5.20 (d, *J* = 17.2 Hz, 2H), 5.08 (d, *J* = 10.0 Hz, 2H), 3.14 (d, *J* = 10.4, 2H), 2.91 (dd, *J* = 14.0, 8.8 Hz, 2H), 2.32 (dd, *J* = 12.8, 4.4 Hz, 1H), 2.17 (dd, *J* = 12.8, 10.0 Hz, 2H), 1.89-1.70 (m, 4H), 1.09 (d, *J* =6.4 Hz, 3H), 1.02 (d, *J* =6.4 Hz, 3H), 0.92 (d, *J* =6.4 Hz, 3H), 0.88 (d, *J* =6.4 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 137.6, 134.6, 130.9, 128.1, 123.9, 116.3, 88.8, 84.6, 61.2, 59.5, 54.7, 31.0, 26.4, 21.1, 20.9, 20.7, 20.1; IR (neat) 3079, 2955, 2869, 2815, 1468, 1086, 918, 793, 496 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{32}H_{48}N_2$ $[M+H]^+$: 461.3896, found: 461.3894.

N-allyl-1-(4-(3-(allyl(isobutyl)amino)-4-methylpent-1-ynyl)phenyl)-*N*-isobutyl-4-methyl pent-1-yn-3-amine (3x)

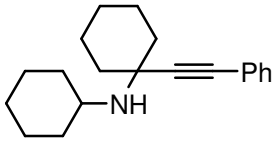


Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 4H), 5.88-5.78 (m, 2H), 5.19 (d, *J* = 13.2 Hz, 2H), 5.08 (d, *J* = 10.0 Hz, 2H), 3.30-3.24 (m, 2H), 3.14 (d, *J* = 10.0, 2H), 2.90 (dd, *J* = 14.0, 8.0

Hz, 2H), 2.32 (dd, *J* = 12.8, 4.4 Hz, 2H), 2.17 (dd, *J* = 12.8, 10.0 Hz, 2H), 1.89-1.68 (m, 4H), 1.08 (d, *J* =6.8 Hz, 3H), 1.02 (d, *J* =6.8 Hz, 3H), 0.91 (d, *J* =6.8 Hz, 3H), 0.87 (d, *J* =6.8 Hz, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 137.6, 131.5, 123.0, 116.3, 89.9, 85.0, 61.2, 59.5, 54.7, 31.0, 26.4, 21.1, 20.9, 20.7, 20.1; IR (KBr) 3078, 2956, 2869, 2816, 1643, 1468, 1086, 917, 836 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{32}H_{48}N_2$ $[M+H]^+$: 461.3896, found: 461.3895.

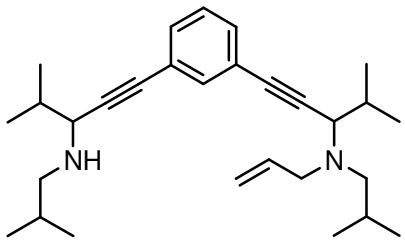
Characterization of byproducts **4**

***N*-cyclohexyl-1-(2-phenylethynyl)cyclohexanamine (4a)**



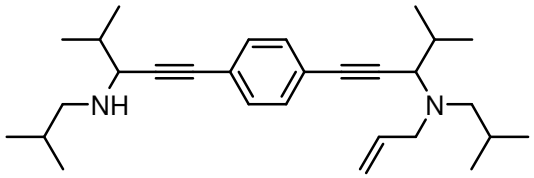
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.32-7.27 (m, 3H), 2.86 (tt, *J* = 10.6, 4.4 Hz, 1H), 1.96-1.90 (m, 4H), 1.75-1.47 (m, 6H), 1.45-1.07 (m, 10H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 131.5, 128.2, 127.6, 123.9, 94.4, 83.8, 55.1, 52.5, 39.3, 36.6, 25.81, 25.80, 25.7, 23.1; IR (neat) 2928, 2852, 1598, 1489, 1446, 1118, 755, 690 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{20}H_{27}N$ $[M+H]^+$: 282.2222, found: 282.2221.

1-(3-(3-(allyl(isobutyl)amino)-4-methylpent-1-ynyl)phenyl)-*N*-isobutyl-4-methylpent-1-yn-3-amine (4w)



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.36-7.31 (m, 2H), 7.26-7.22 (m, 1H), 5.88-5.78 (m, 1H), 5.23-5.17 (m, 1H), 5.10-5.06 (m, 1H), 3.35 (d, *J* = 6.4 Hz, 1H), 3.29-3.26 (m, 1H), 3.13 (d, *J* = 10.4 Hz, 1H), 2.90 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.67 (dd, *J* = 11.6, 7.2 Hz, 1H), 2.46 (dd, *J* = 11.2, 6.4 Hz, 1H), 2.32 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.18 (dd, *J* = 12.4, 10.4 Hz, 1H), 1.97-1.70 (m, 4H), 1.11-0.87 (m, 24H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 137.6, 134.6, 131.0, 128.1, 123.9, 123.7, 116.3, 90.7, 88.8, 84.5, 83.5, 61.1, 59.5, 57.2, 56.0, 54.7, 32.8, 31.0, 28.4, 26.4, 21.1, 20.9, 20.7, 20.6, 20.1, 19.8, 18.0; IR (neat) 3078, 2956, 2870, 2816, 1468, 1088, 792, 687 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{29}H_{44}N_2$ $[M+H]^+$: 421.3583, found: 421.3582.

1-(4-(3-(allyl(isobutyl)amino)-4-methylpent-1-ynyl)phenyl)-*N*-isobutyl-4-methylpent-1-yn-3-amine (4x)

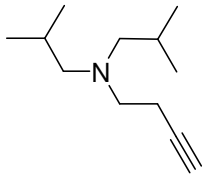


Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, 4H), 5.86-5.78 (m, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.07 (d, *J* = 6.0 Hz, 2H), 3.14 (d, *J* = 10.4, 1H), 2.90 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.68 (dd, *J* = 11.6, 7.2 Hz, 1H), 2.46 (dd, *J* = 11.2, 6.0 Hz, 1H), 2.31 (dd, *J* = 12.8, 4.4 Hz, 1H), 2.17 (dd, *J* = 12.8, 10.0 Hz, 1H), 1.95-1.70 (m, 4H), 1.09-1.00 (m, 12H), 0.96-0.86 (m, 12H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 137.5, 131.5, 131.4, 123.2, 122.8, 116.3, 91.8, 89.9, 85.0, 83.9, 61.2, 59.5, 57.3, 56.0, 54.7, 32.8, 31.0, 28.4, 26.4, 21.1, 20.9, 20.8, 20.7, 20.6, 20.1, 19.8, 18.0; IR (KBr) 2956, 2870, 2816, 1468, 1099, 836, 476 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{29}H_{44}N_2$ $[M+H]^+$: 421.3583, found: 421.3579.

Preparation of **10** and **11**

But-3-ynyl 4-methylbenzenesulfonate was preparated under standar conditions, using *p*-toluenesulfonyl chloride (1.1 equiv), triethylamine (2.1 equiv) and dichloromethane as the solvent.[3] A mixture of 3-butynyl (4-methylbenzene)sulfonate (2.13 g, 9.5 mmol), K_2CO_3 (5.25 g, 38 mmol), and diisobutylamine (1.66 mL, 9.5 mmol) in 20 mL of THF was heated to reflux for 2d, cooled to room temperature, and filtered. The filtrate was concentrated under vacuum to provide pure *N,N*-diisobutylbut-3-yn-1-amine **10** (0.322, 19% yield) as a colorless oil.[4]

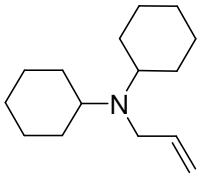
***N,N*-diisobutylbut-3-yn-1-amine (10)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (t, *J* = 7.6 Hz, 2H), 2.26 (td, *J* = 6.4, 2.8 Hz, 2H), 2.10 (d, *J* = 7.2 Hz, 4H), 1.93 (t, *J* = 2.8 Hz, 1H), 1.67 (sept, *J* = 6.8 Hz, 2H) , 0.87 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 83.6, 68.5, 63.5, 53.8, 26.7, 20.8, 16.7; IR (neat) 3313, 2870, 2805, 1469, 1385, 1099, 910, 736 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{12}H_{23}N$ $[M+H]^+$: 182.1909, found: 182.1908.

N-Allyl-*N*-cyclohexylcyclohexanamine **11** was synthesized according the procedure already reported.[5]

***N*-allyl-*N*-cyclohexylcyclohexanamine (11)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86-5.76 (m, 1H), 5.16-5.10 (m, 1H), 4.99-4.95 (m, 1H), 3.20 (dt, *J* = 4.0, 1.6 Hz, 2H), 2.58-2.51 (m, 2H), 1.78-1.66 (m, 8H), 1.61-1.56 (m, 2H), 1.30-1.16 (m, 8H), 1.10-1.00 (m, 2H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 140.5, 114.3, 57.8, 49.3, 31.8, 26.4, 26.3; IR (neat) 2928, 2852, 1639, 1449, 1391, 1345, 1255, 1171, 1104, 989, 911 cm^{-1}; HRMS *m/z* (ESI) calcd. for $C_{12}H_{23}N$ $[M+H]^+$: 222.2222, found: 222.2227.

Preparation of ***d*$_1$-1a**, ***d*-2a**, and ***d*-1a**

***d*$_1$-1a** was synthesized according the procedure already reported except for the use of *N,N*-dicyclohexylamine instead of *N,N*-diisopropylamine.[6]

Preparation of propargylic amine ***d*-2a**

To ethynykbenzene **2a** (1.1 ml, 10 mmol) in Et_2O (25 ml), was added dropwise ^{n}BuLi in hexane (1.6M, 9.4 ml, 15 mmol) at 0℃. The mixture was allowed to warm to room temperature and was stirred for 1 h. After the quench by D_2O (0.36 ml, 20 mmol), the mixture was dried over Mg_2SO_4 and decanted. The residure was concentrated by distillation, and ***d*-2a** (0.70 g, 6.8 mmol) was obtained.

Preparation of propargylic amine ***d*-1a**

To *N,N*-Dicyclohexylamine derivatives **1a** (2.19 g, 10 mmol) in Et_2O (20 ml), was added dropwise ^{n}BuLi in hexane (1.6M, 9.4 ml, 15 mmol) at 0℃. The mixture was allowed to warm to room temperature and was stirred for 1 h. After the quench by D_2O (1 ml), the mixture was dried over Mg_2SO_4 and decanted. The residure was concentrated in vacuo, and ***d*-1a** (1.92 g, 8.7 mmol) was obtained.

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(3) (a) Finaru, A.; Berthault, A.; Besson, T.; Guillaumet, G.; Berteina-Raboin, S. *Tetrahedron Lett.* **2002**, *43*, 787. (b) Pardo-Rodri´guez, V.; Marco-Marti´nez, J.; Bun"uel, E.; Ca´rdenas, D. J. *Org. Lett.* **2009**, *11*, 4548.

(4) Sheppard, G. S. et al. *J. Med. Chem.* **2006**, *49*, 3832.
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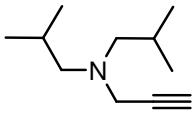
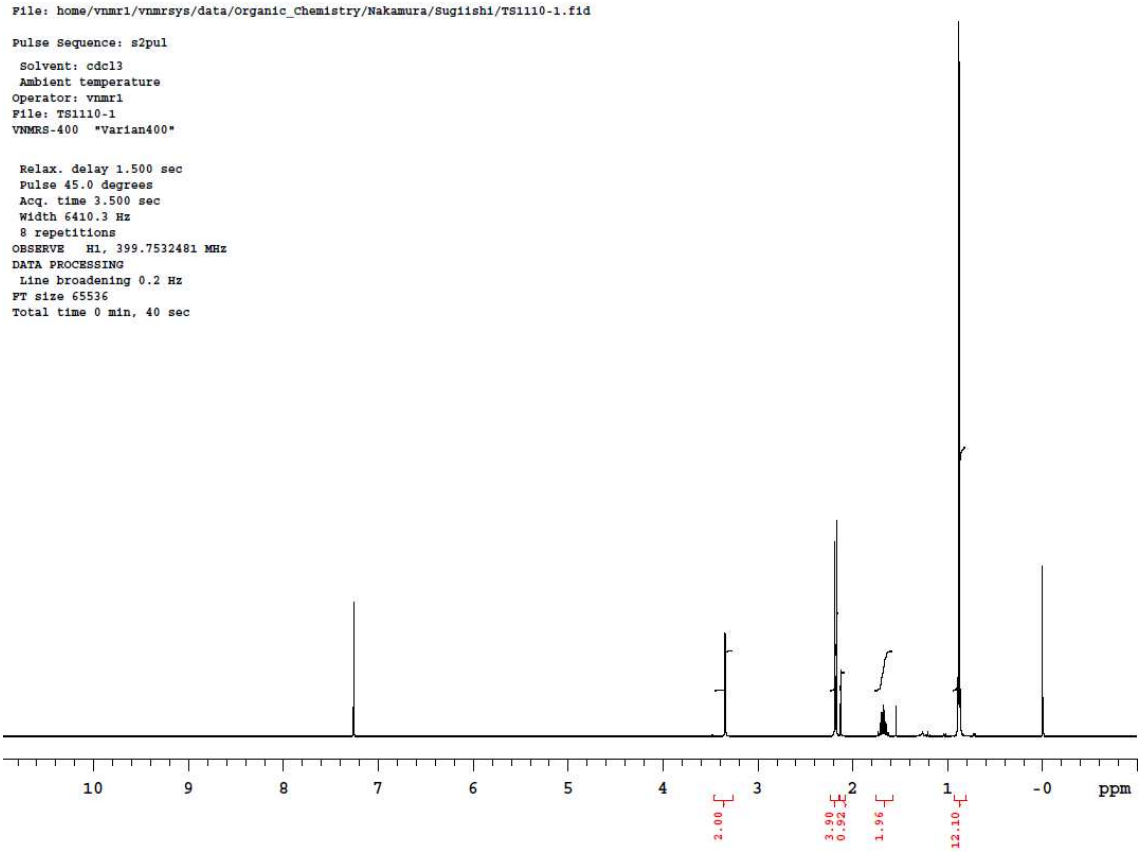
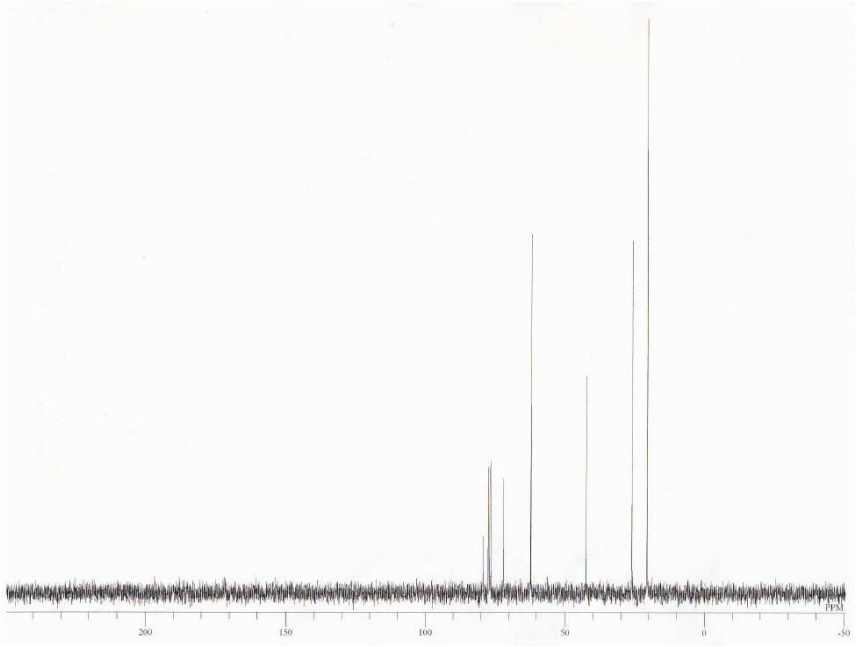
(6) Nakamura, H.; Onagi, S.; Kamakura, T. *J. Org. Chem.* **2005**, *70*, 2357.

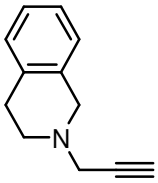
N,N-diisobutylprop-2-yn-1-amine (1d)

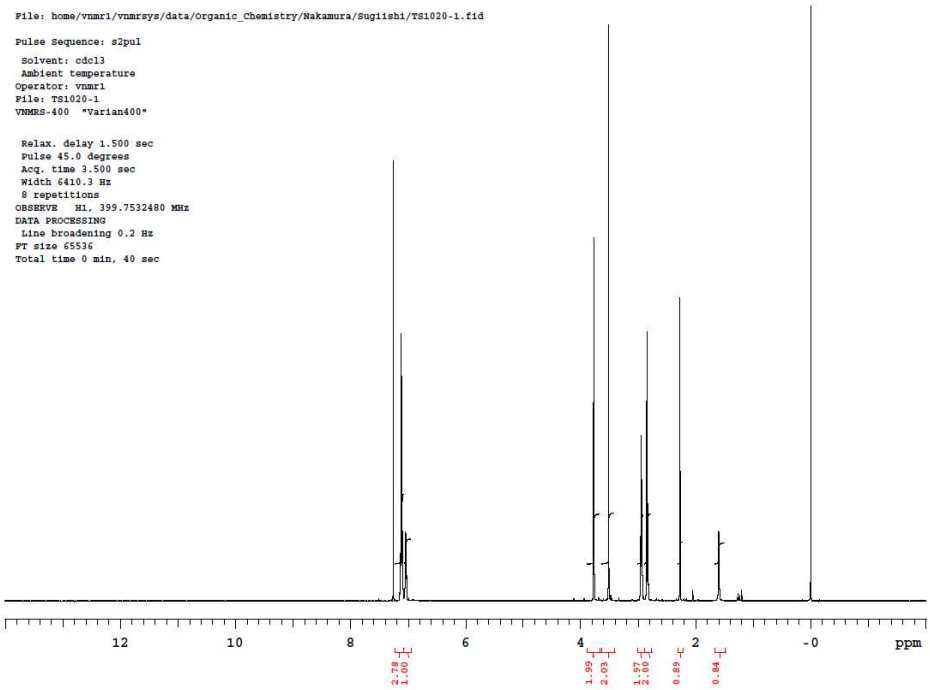


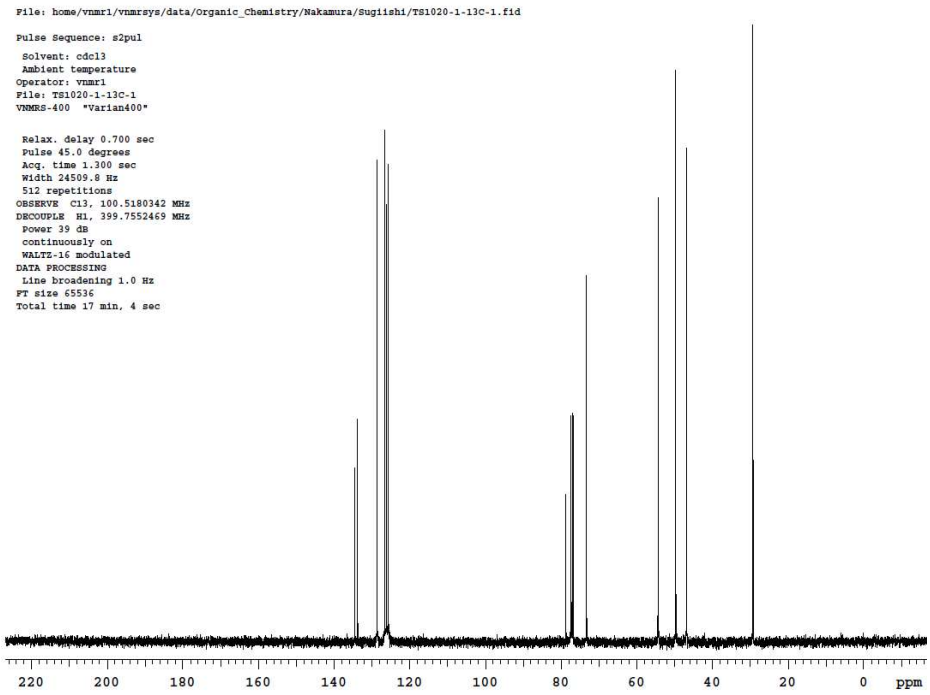




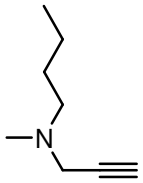
2-(prop-2-ynyl)-1,2,3,4-tetrahydroisoquinoline (1f)

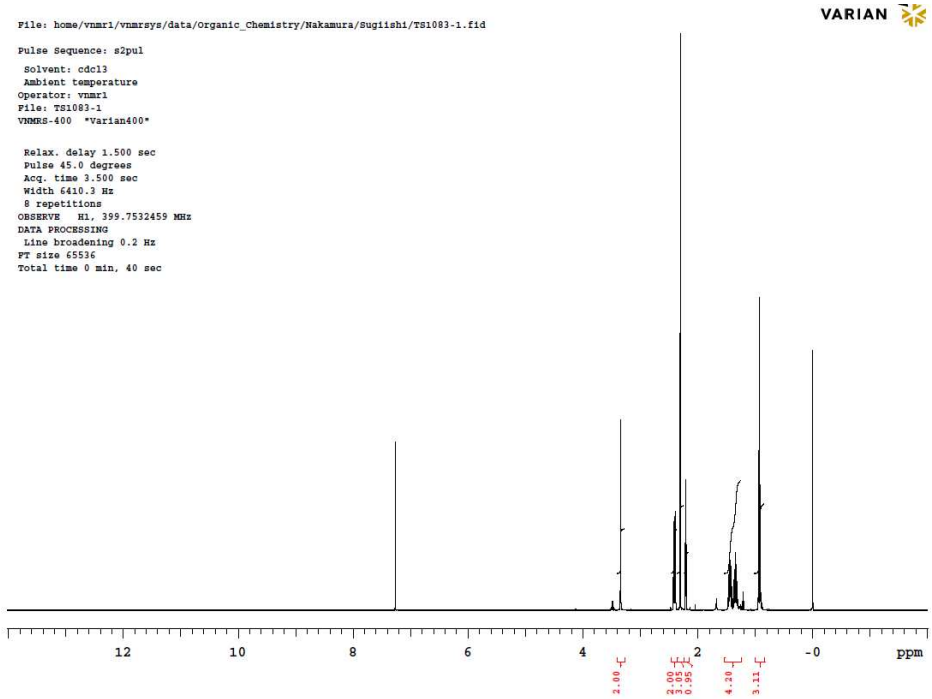


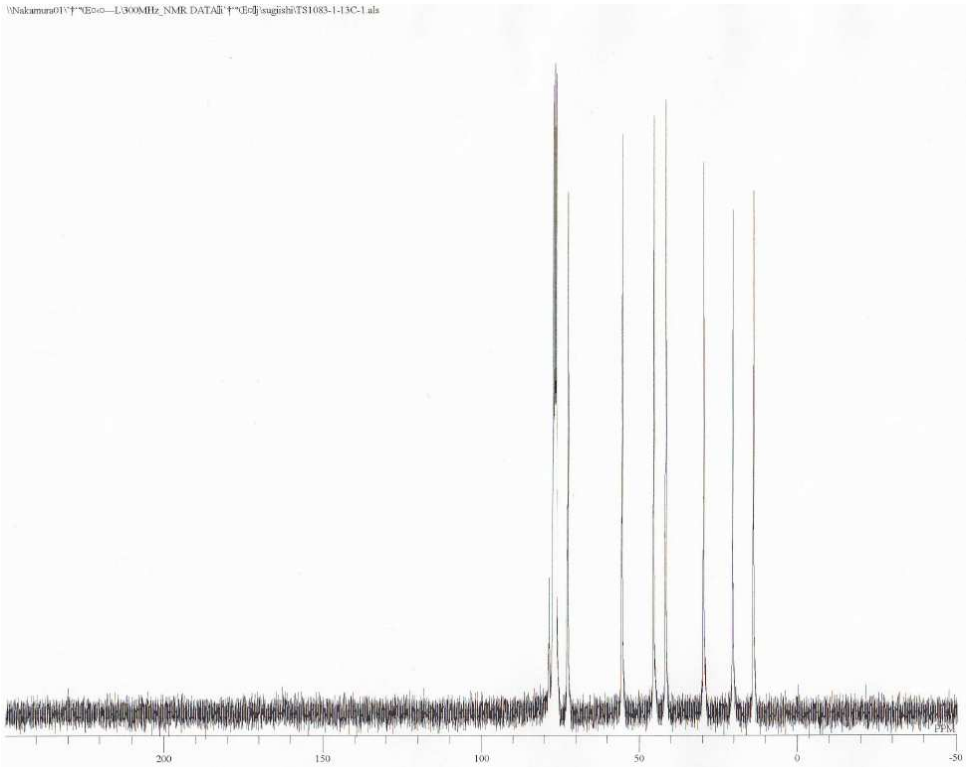




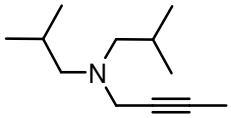
N-methyl-N-(prop-2-ynyl)butan-1-amine (1g)

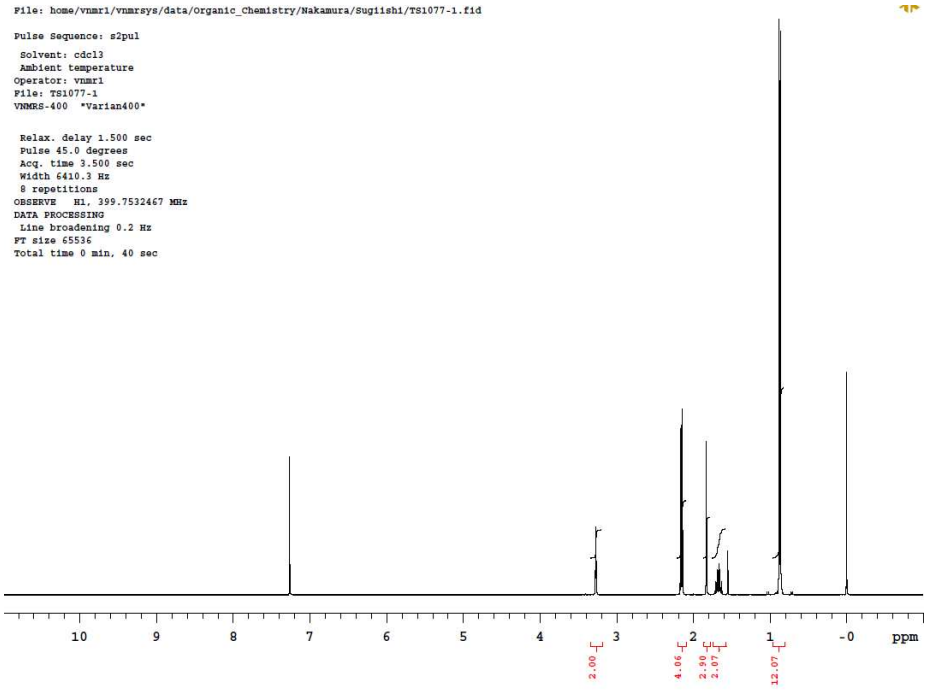


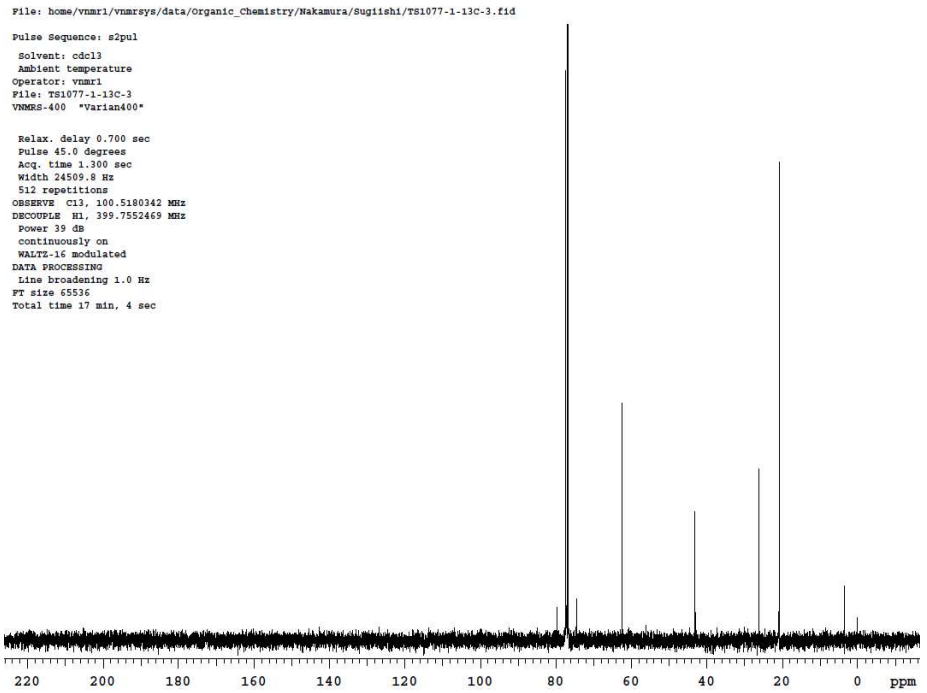




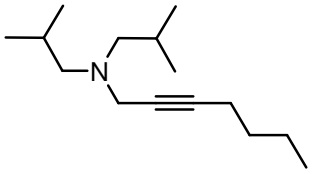
N,N-diisobutylbut-2-yn-1-amine (1h)

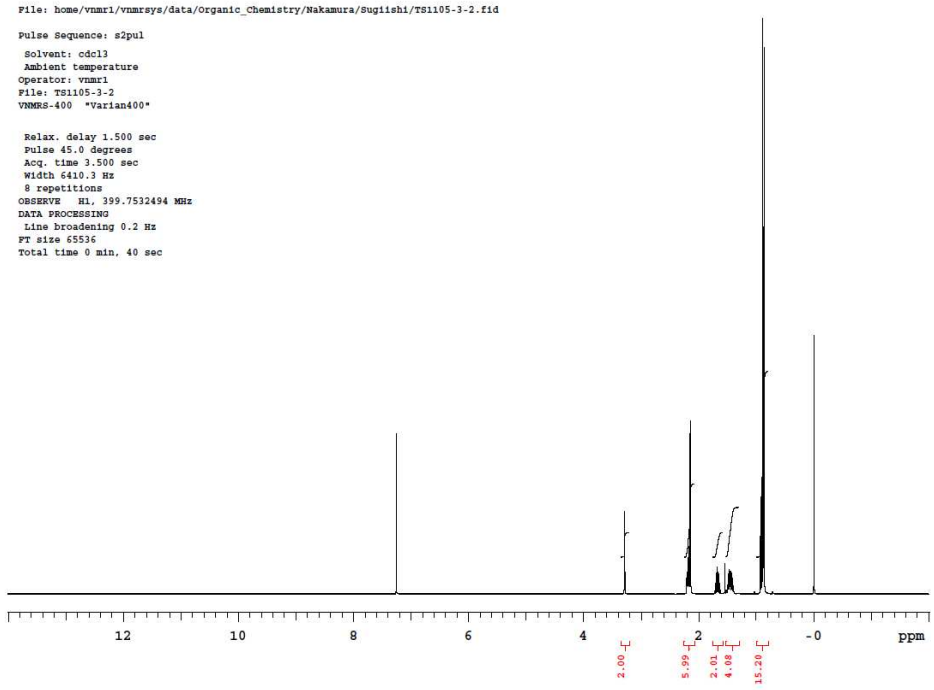


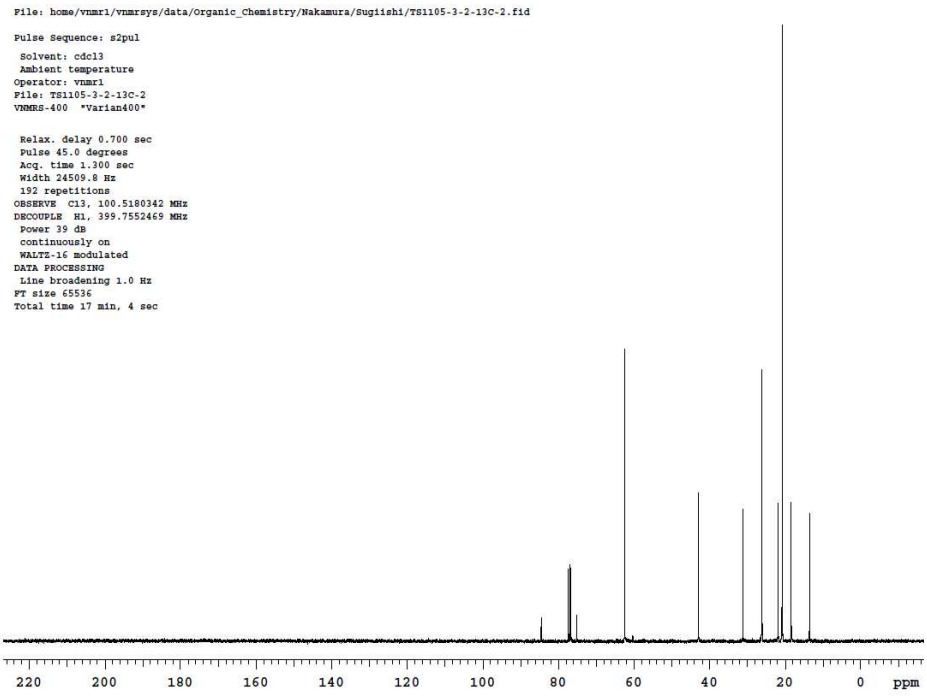




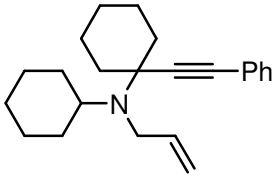
N,N-diisobutylhept-2-yn-1-amine (1i)

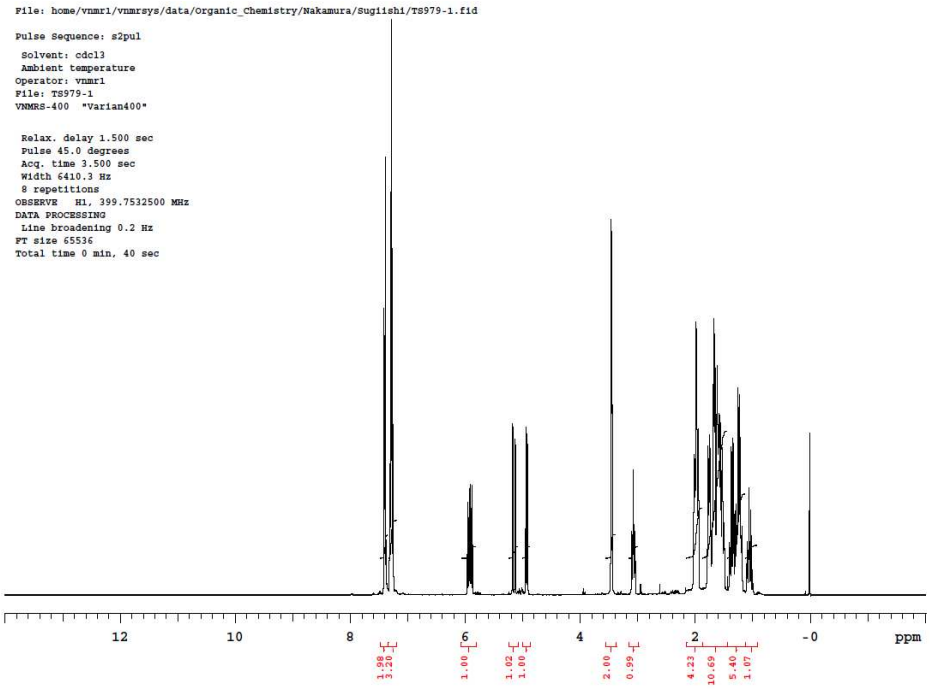


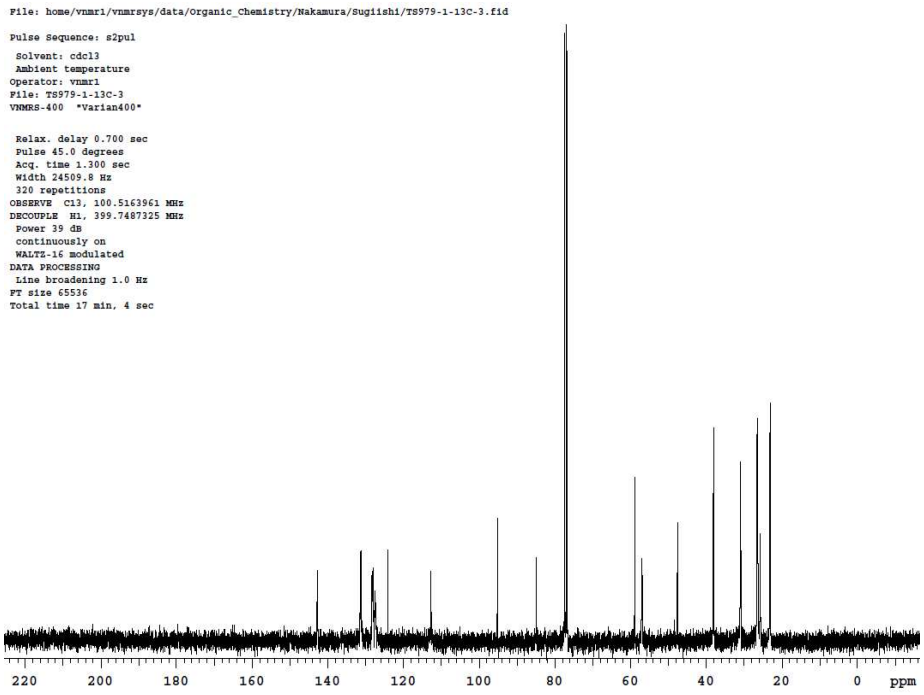




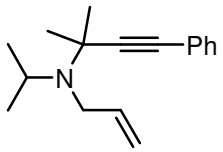
N-allyl-*N*-cyclohexyl-1-(2-phenylethynyl)cyclohexanamine (3a)

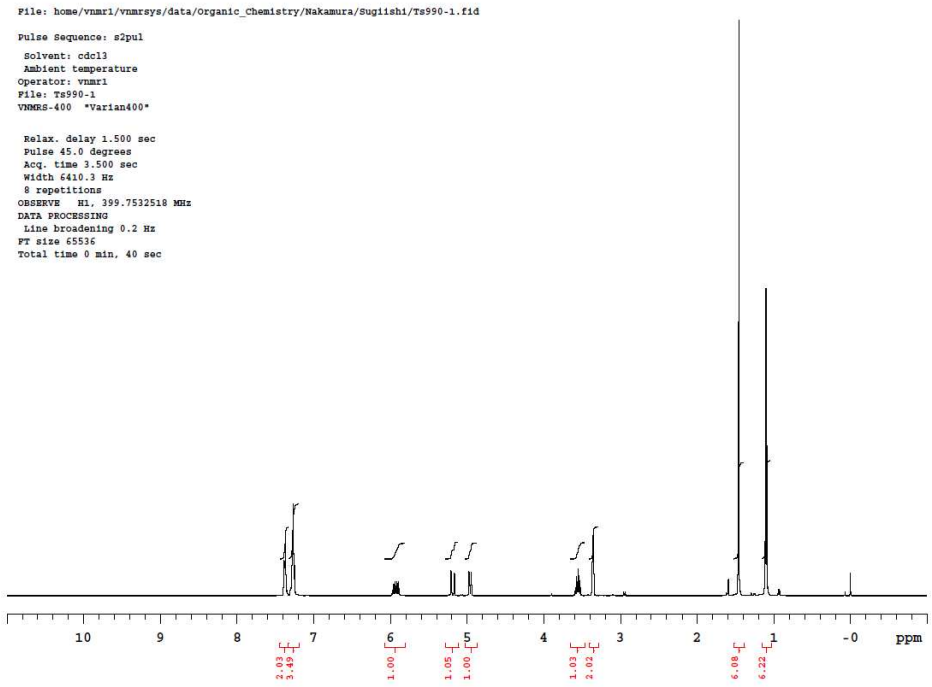


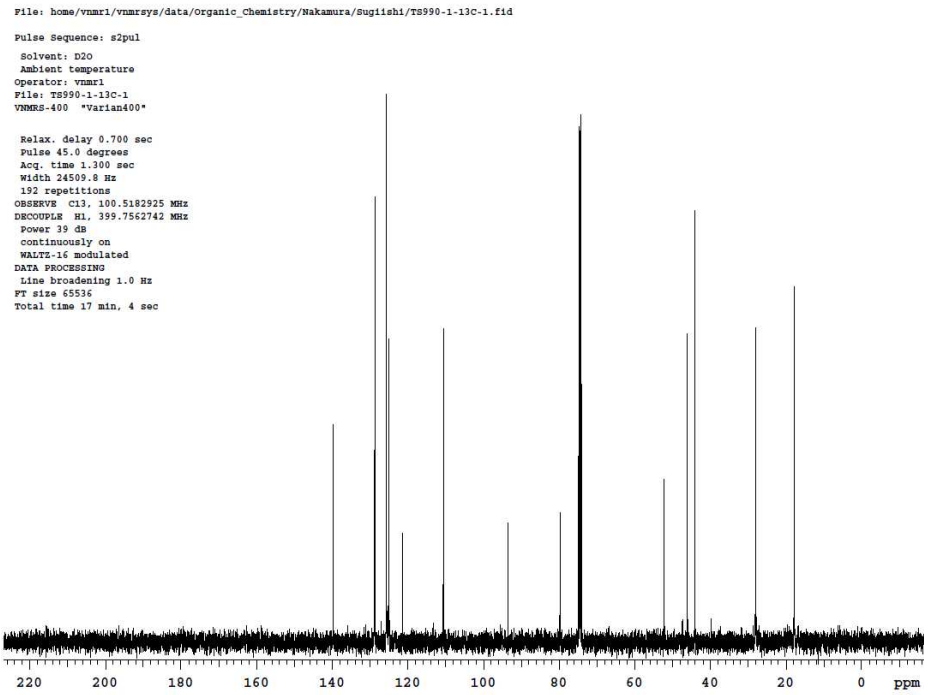




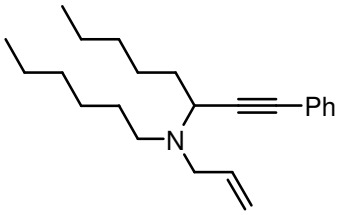
N-allyl-*N*-isopropyl-2-methyl-4-phenylbut-3-yn-2-amine (3b)

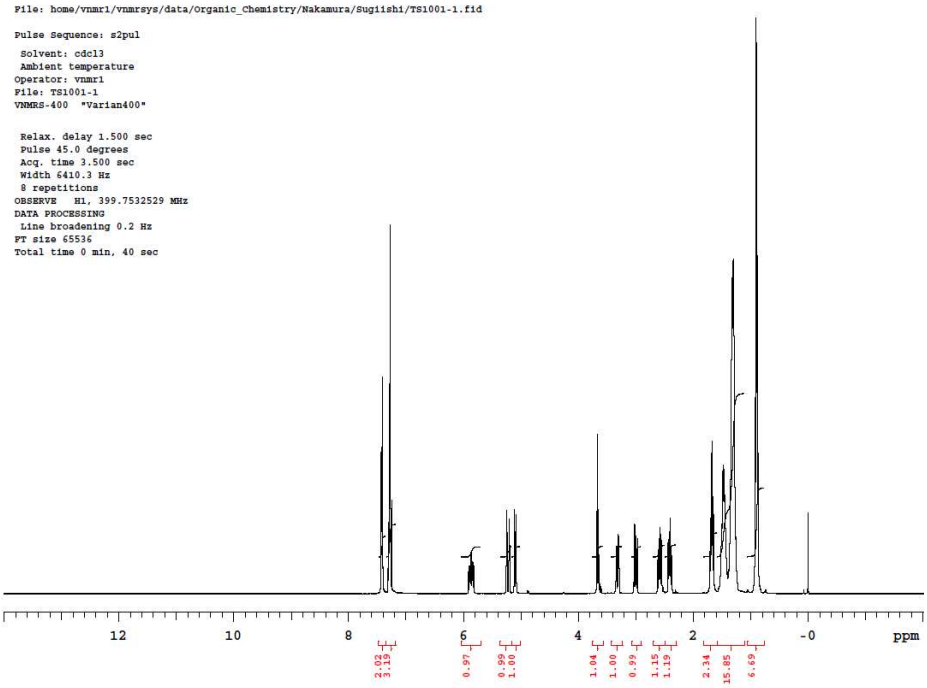


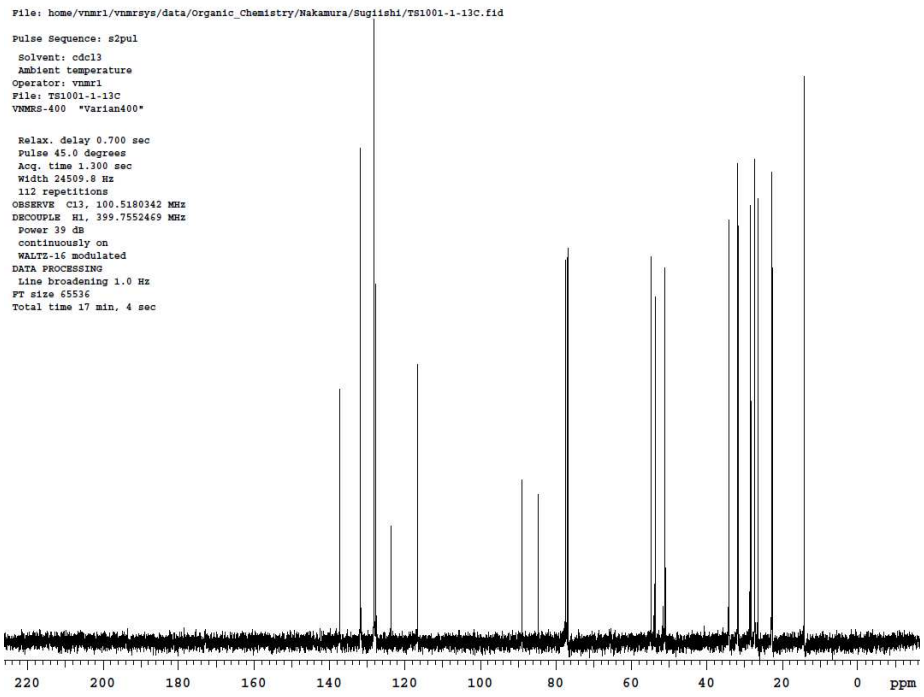




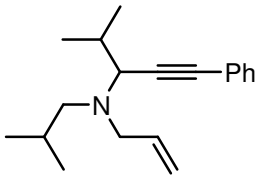
N-allyl-*N*-hexyl-1-phenyloct-1-yn-3-amine (3c)

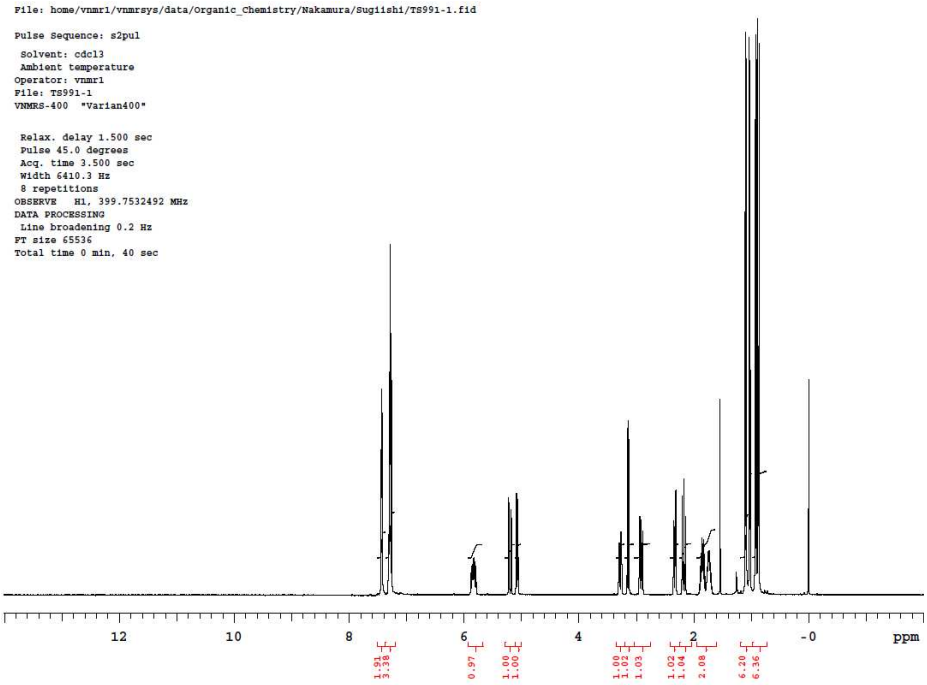


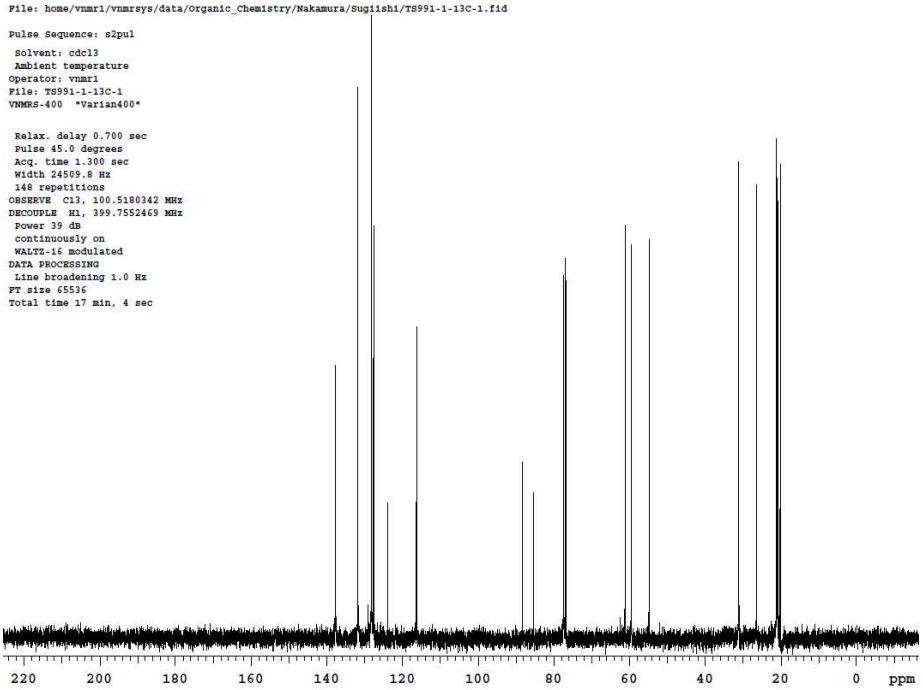




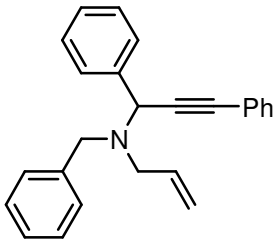
N-allyl-*N*-isobutyl-4-methyl-1-phenylpent-1-yn-3-amine (3d)

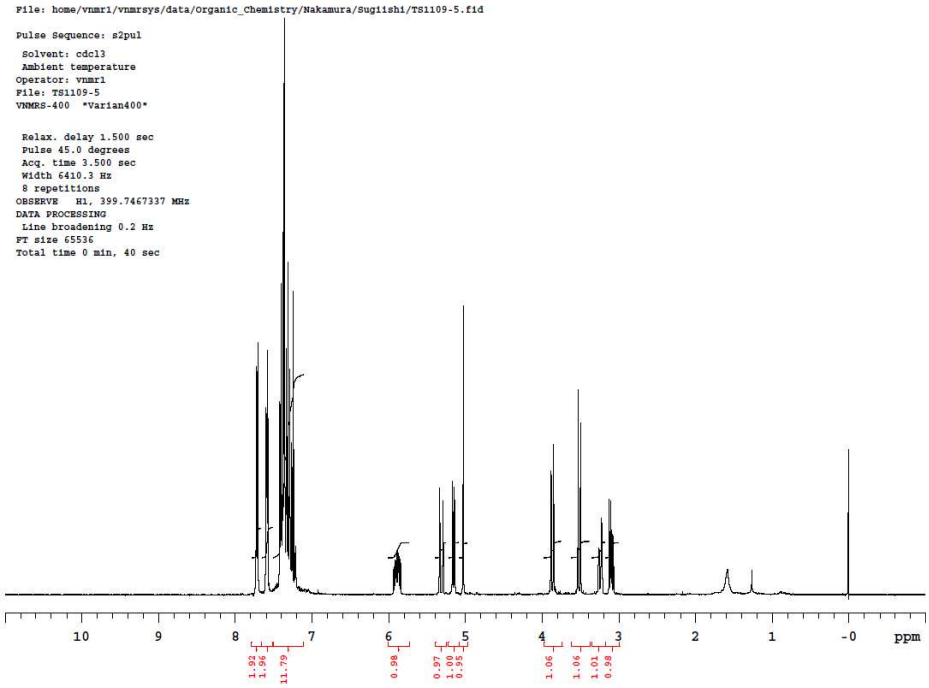


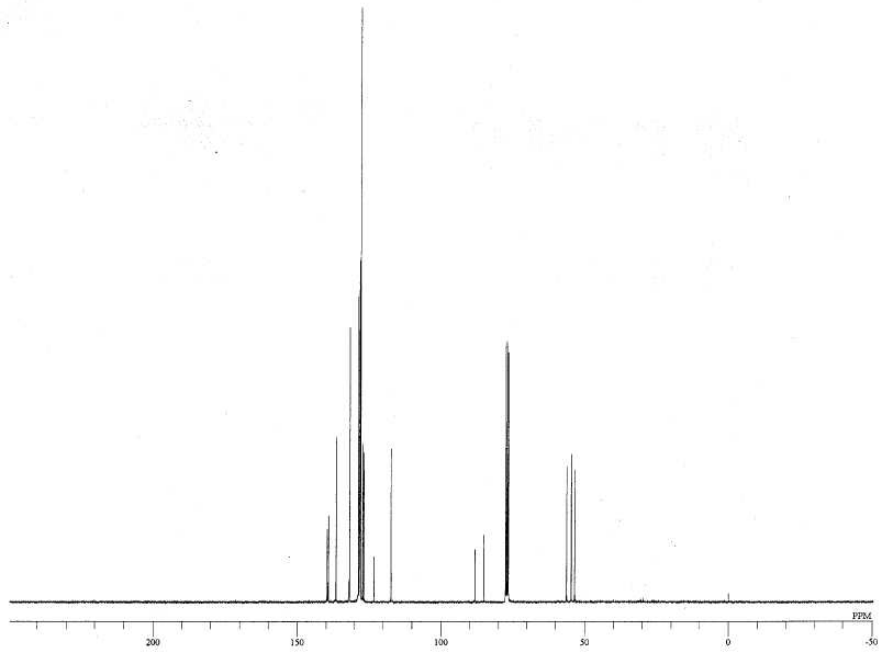




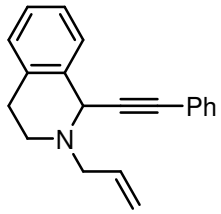
N-benzyl-*N*-(1,3-diphenylprop-2-ynyl)prop-2-en-1-amine (3e)

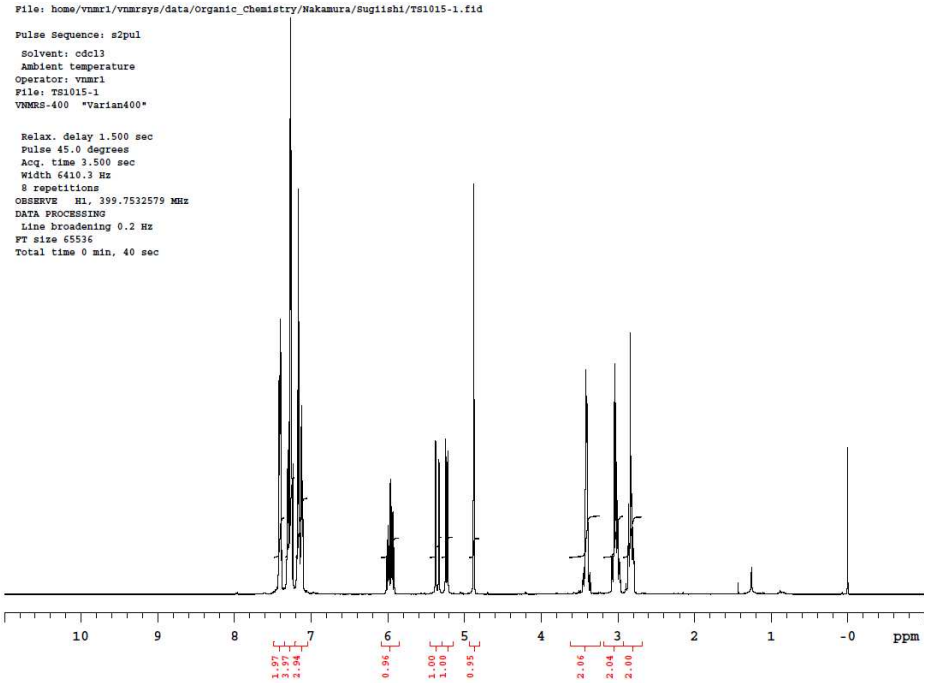


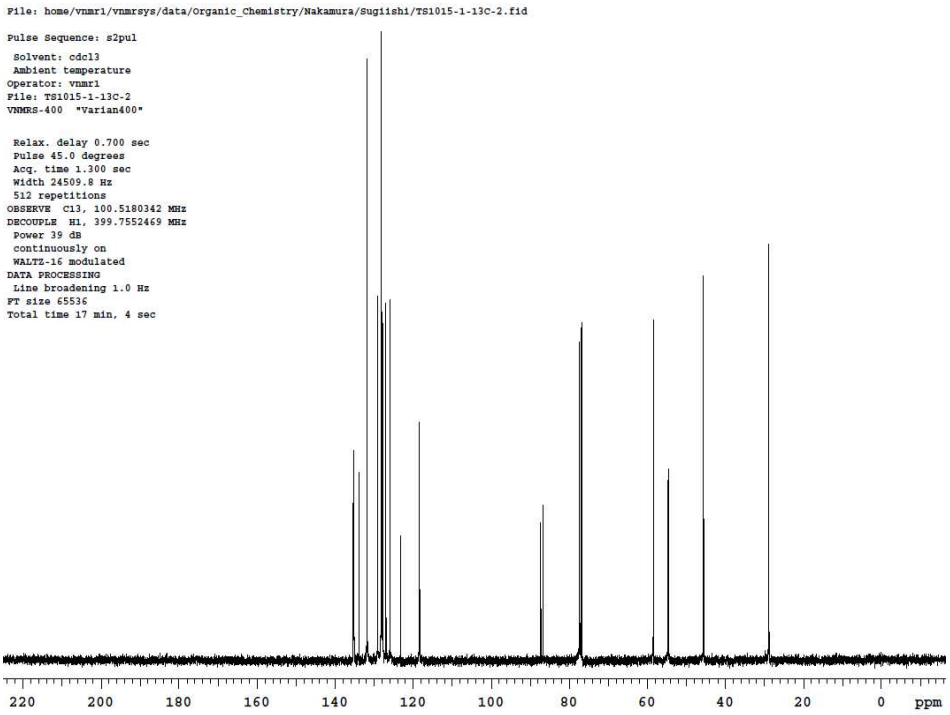




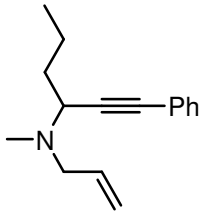
2-allyl-1-(2-phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (3f)

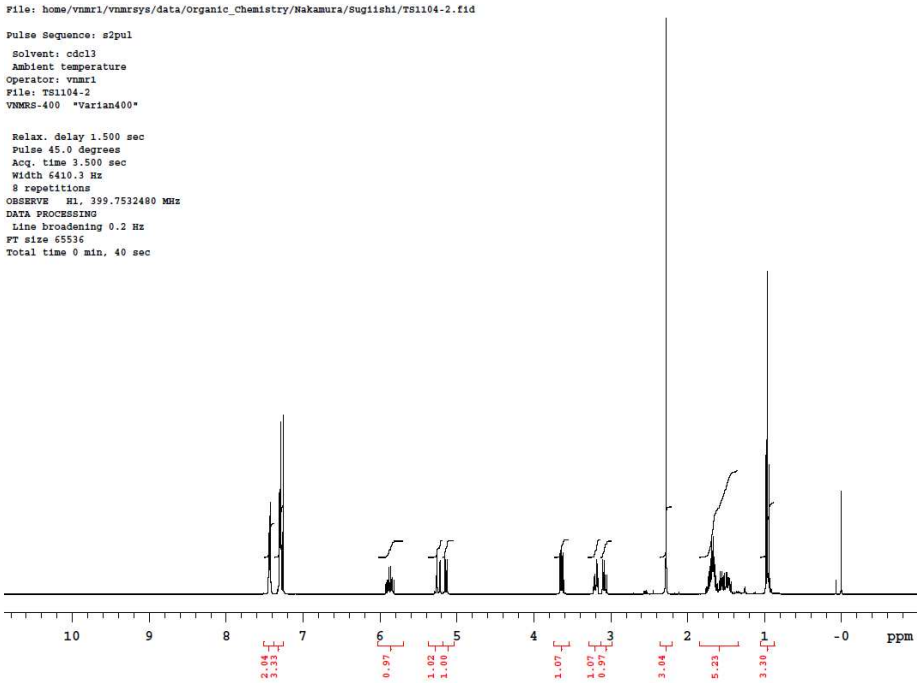


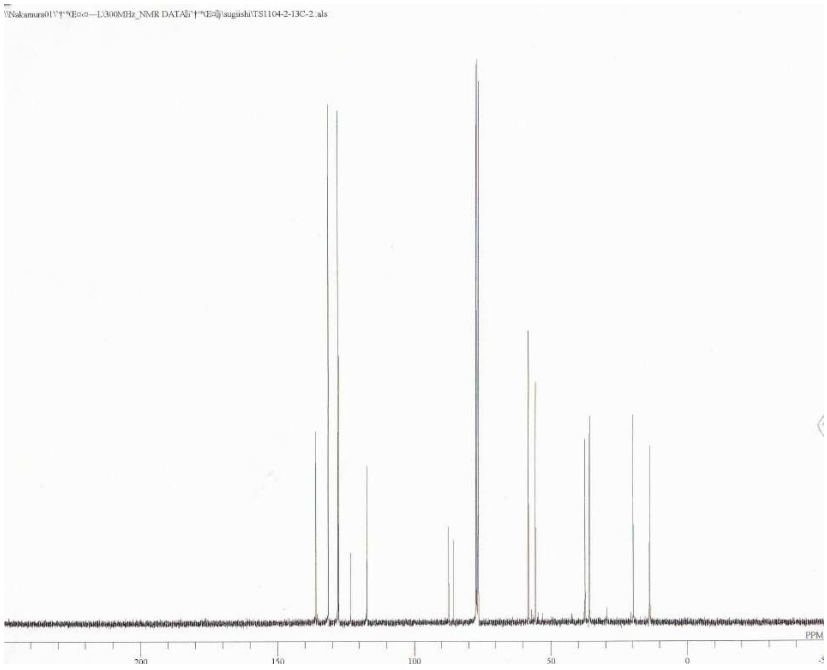




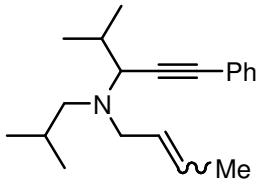
N-allyl-*N*-methyl-1-phenylhex-1-yn-3-amine (3g)

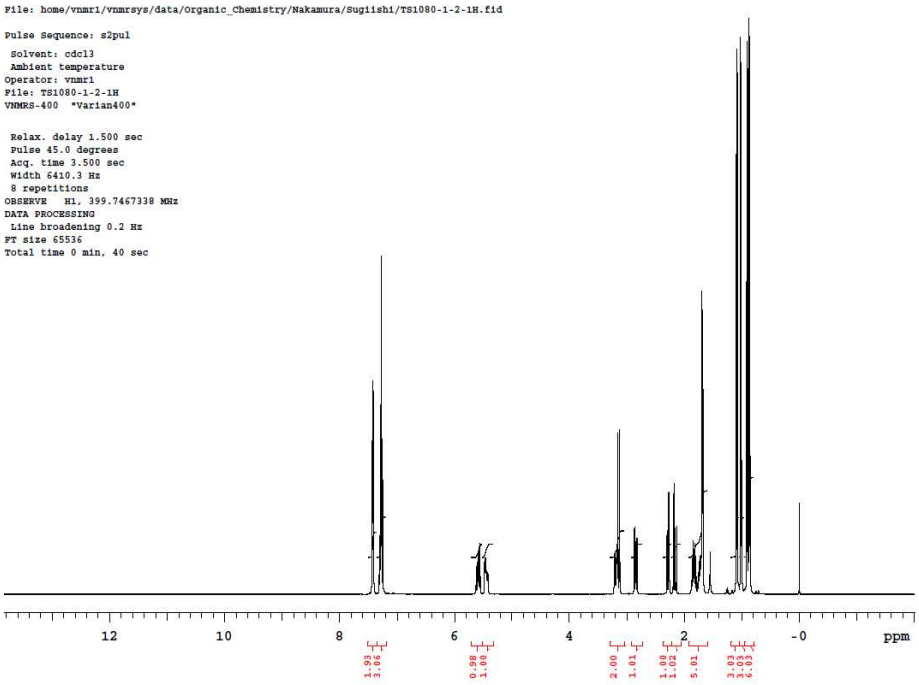


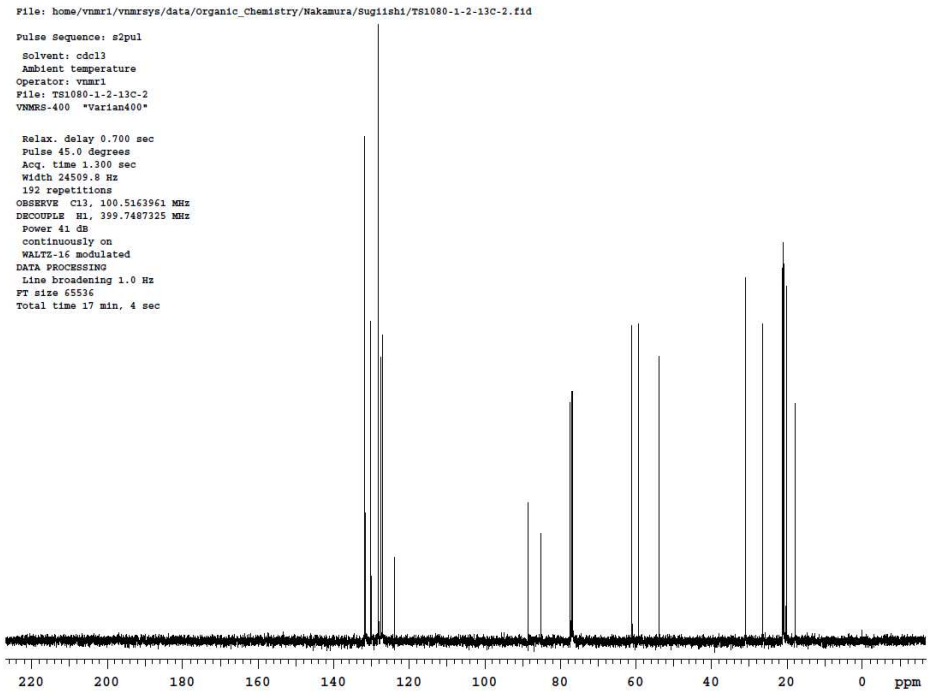




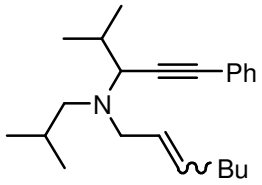
N-(but-2-enyl)-*N*-isobutyl-4-methyl-1-phenylpent-1-yn-3-amine (3h)

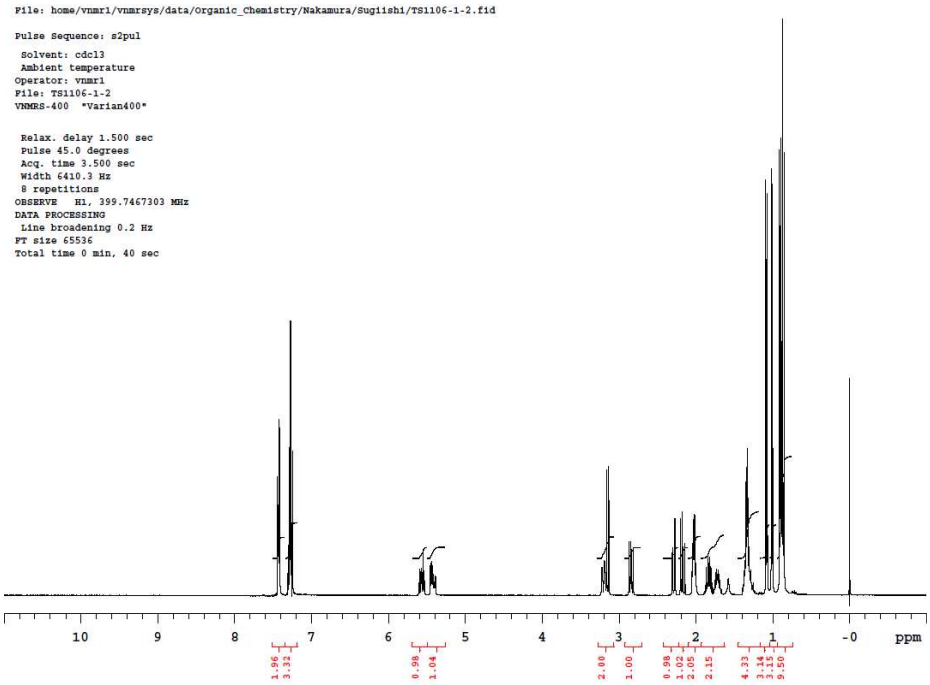


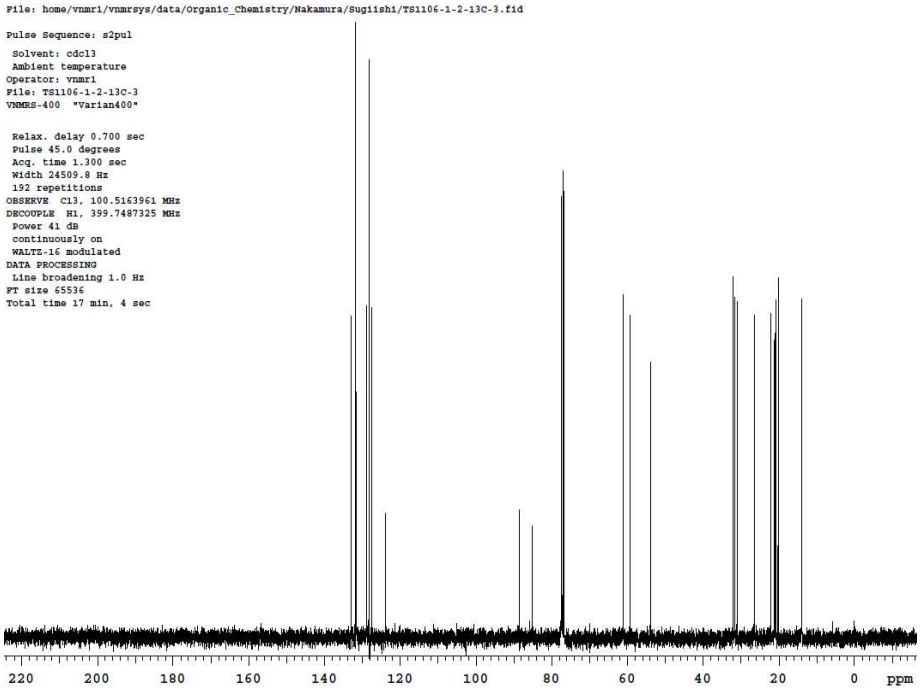




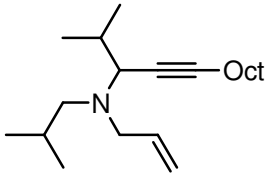
N-isobutyl-*N*-(4-methyl-1-phenylpent-1-yn-3-yl)hept-2-en-1-amine (3i)

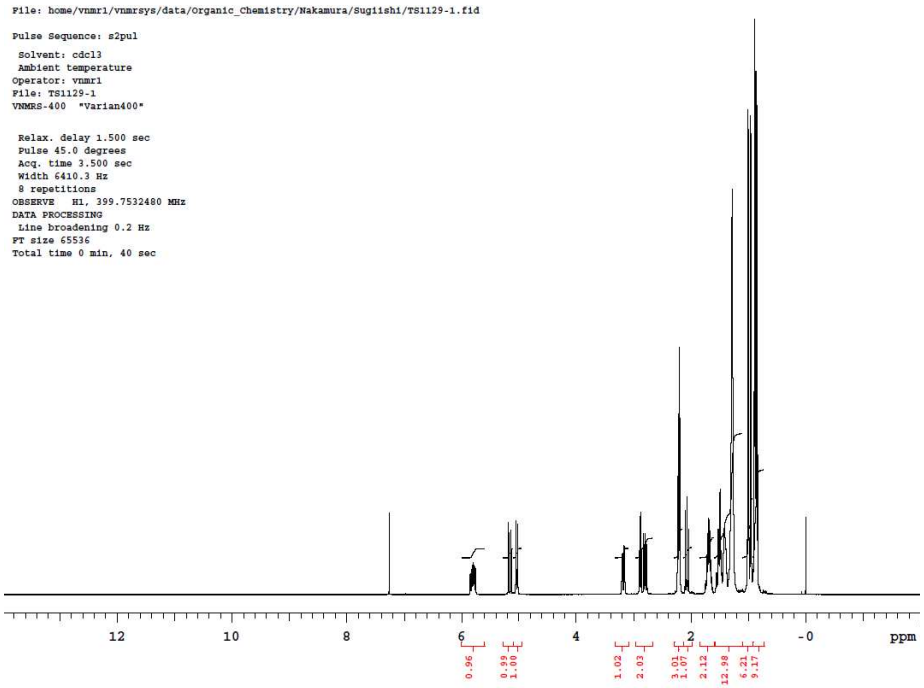


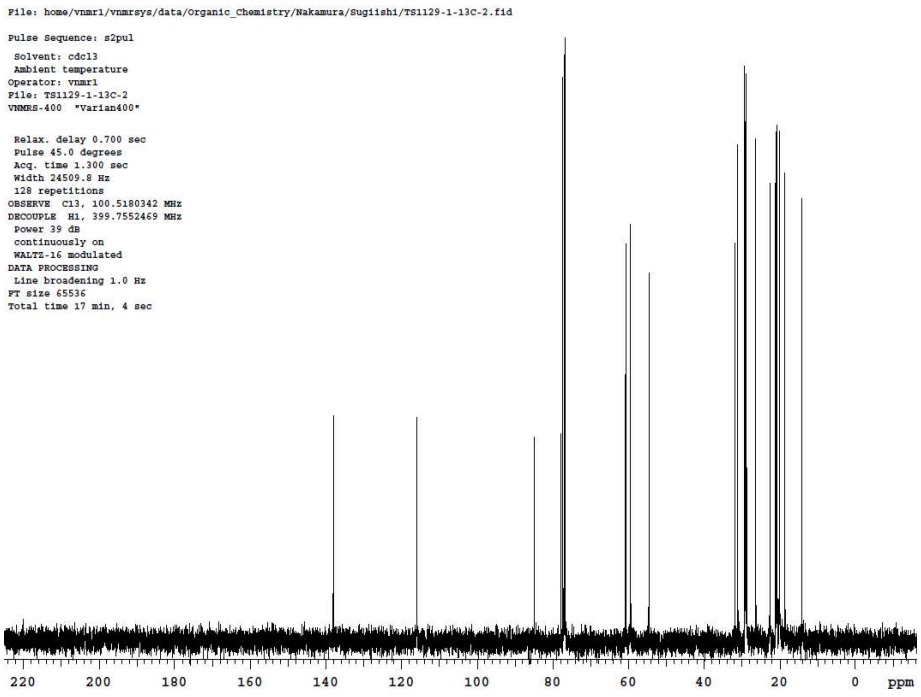




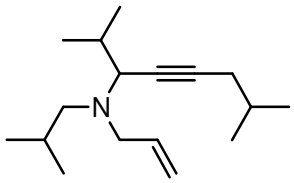
N-allyl-*N*-isobutyl-2-methyltridec-4-yn-3-amine (3j)







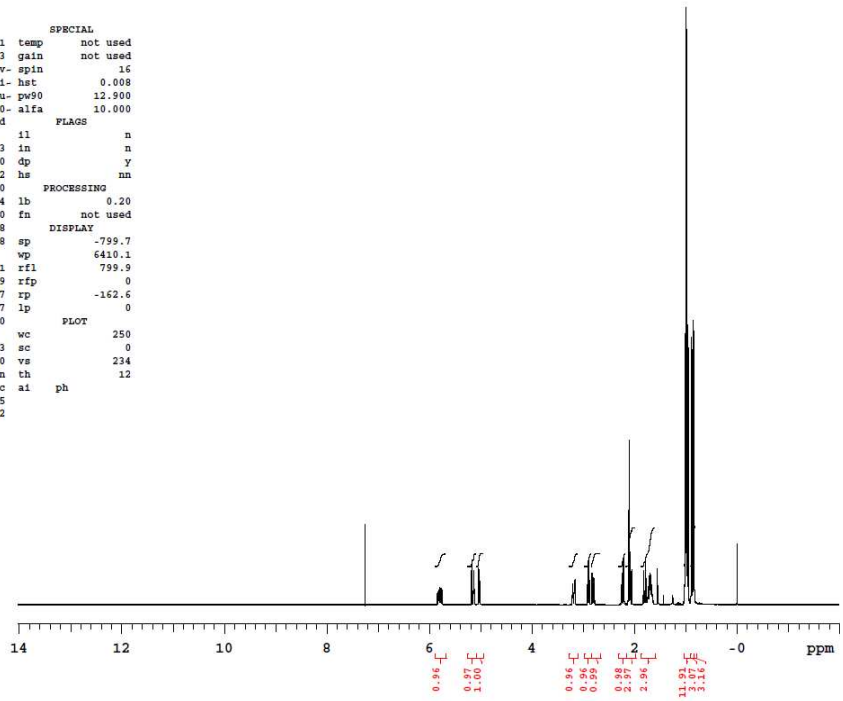
N-allyl-N-isobutyl-2,7-dimethyloct-4-yn-3-amine (3k)



TS1170-1 21/July 2011

expl Proton

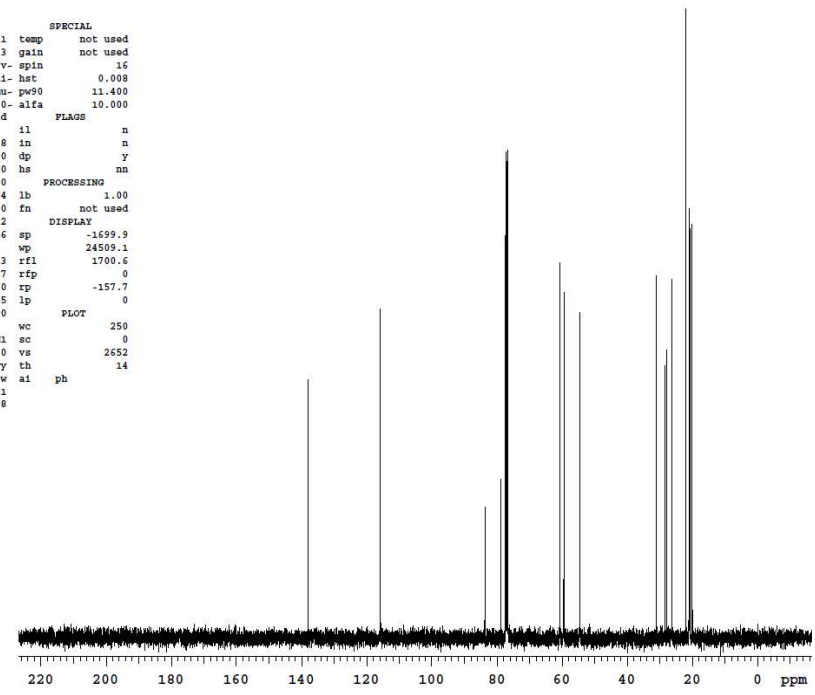
SAMPLE		SPECIAL	
date	Jul 21 2011	temp	not used
solvent	cdcl3	gain	not used
file	/home/vnmr1/v-	spin	16
nmrsys/data/Organi-		hst	0.008
c_Chemistry/Nakamu-		pw90	12.900
ra/Sugiishi/TS1170-		alfa	10.000
-1.fid		FLAGS	
ACQUISITION		il	n
sw	6410.3	in	n
at	3.500	dp	y
np	44872	hs	nn
fb	4000	PROCESSING	
bs	4	lb	0.20
d1	1.500	fn	not used
nt	8	DISPLAY	
ct	8	sp	-799.7
TRANSMITTER		wp	6410.1
tn	H1	rfl	799.9
sfrq	399.749	rfp	0
tof	399.7	rp	-162.6
tpwr	57	lp	0
pw	6.450	PLOT	
DECOUPLER		wc	250
dn	C13	sc	0
dof	0	vs	234
dm	nnn	th	12
dmm	c	ai ph	
dpwr	35		
dmf	29412		



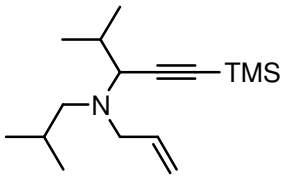
TS1170-1-13C-2. 21/July 2011

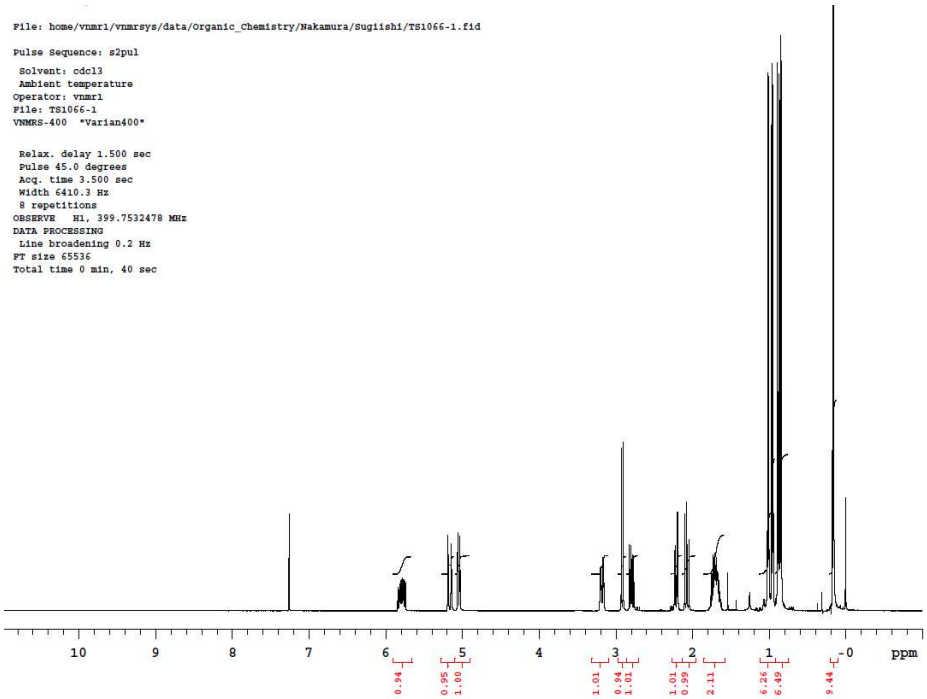
expl Carbon

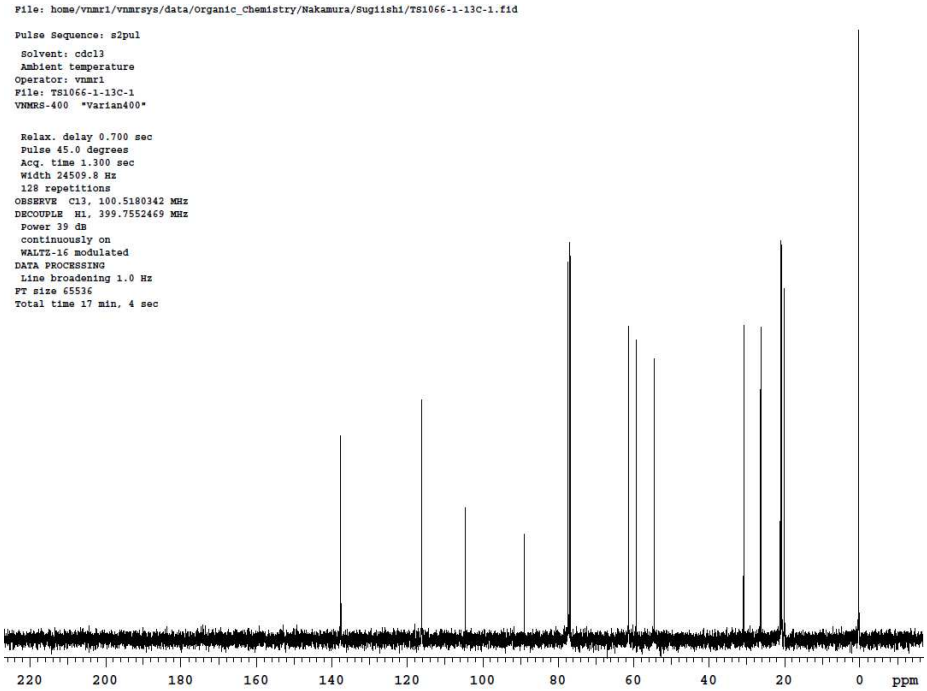
SAMPLE		SPECIAL	
date	Jul 21 2011	temp	not used
solvent	cdcl3	gain	not used
file	/home/vnmr1/v-	spin	16
nmrsys/data/Organi-		hst	0.008
c_Chemistry/Nakamu-		pw90	11.400
ra/Sugiishi/TS1170-		alfa	10.000
-1-13C-2.fid		FLAGS	
ACQUISITION		il	n
sw	24509.8	in	n
at	1.300	dp	y
np	63750	hs	nn
fb	17000	PROCESSING	
bs	64	lb	1.00
d1	0.700	fn	not used
nt	512	DISPLAY	
ct	256	sp	-1699.9
TRANSMITTER		wp	24509.1
tn	C13	rfl	1700.6
sfrq	100.527	rfp	0
tof	1028.0	rp	-157.7
tpwr	55	lp	0
pw	5.700	PLOT	
DECOUPLER		wc	250
dn	H1	sc	0
dof	0	vs	2652
dm	yyy	th	14
dmm	w	ai ph	
dpwr	41		
dmf	8208		



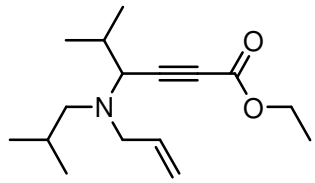
N-allyl-*N*-isobutyl-4-methyl-1-(trimethylsilyl)pent-1-yn-3-amine (3l)







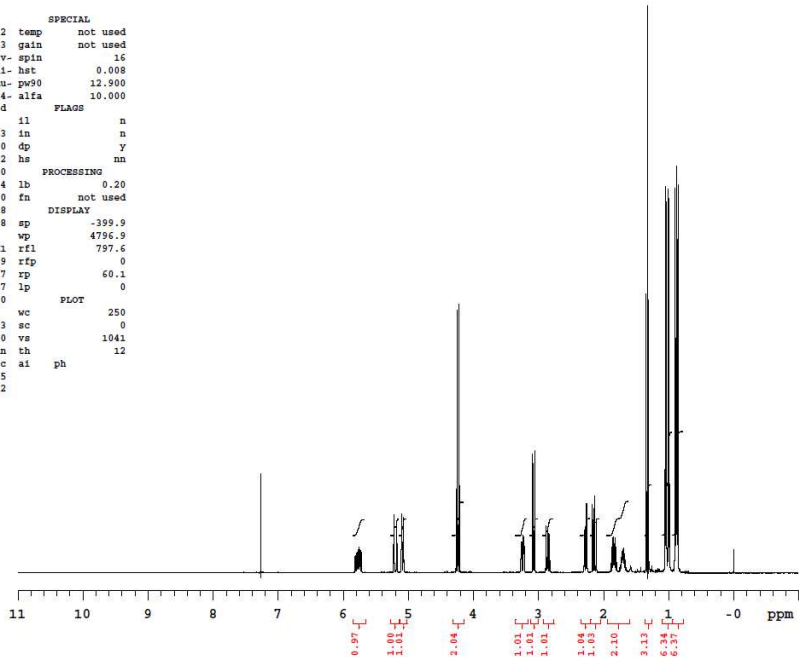
ethyl 4-(allyl(isobutyl)amino)-5-methylhex-2-ynoate (3m)



TS1214-4. 06. Jan. 2012

expl Proton

SAMPLE		SPECIAL	
date	Jan 6 2012	temp	not used
solvent	cdcl3	gain	not used
file	/home/vnmr1/v-	spin	16
nmrsys/data/organi-		hst	0.008
c_Chemistry/Nakamu-		pw90	12.900
ra/Sugiishi/TS1214-		alfa	10.000
-4.fid		FLAGS	
ACQUISITION		il	n
sw	6410.3	in	n
at	3.500	dp	y
np	44872	hs	nn
fb	4000	PROCESSING	
bs	4	lb	0.20
d1	1.500	fn	not used
nt	8	DISPLAY	
ct	8	sp	-399.9
TRANSMITTER		wp	4796.9
tn	H1	rfl	797.6
sfrq	399.749	rfp	0
tof	399.7	rp	60.1
tpwr	57	lp	0
pw	6.450	PLOT	
DECOUPLER		wc	250
dn	C13	sc	0
dof	0	vs	1041
dm	nnn	th	12
dmm	c	ai ph	
dpwr	35		
dmf	29412		



TS1214-4-13C-2. 06. Jan. 2012

expl Carbon

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ra/Sugiishi/TS1214-		alfa	10.000
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ACQUISITION		il	n
sw	24509.8	in	n
at	1.300	dp	y
np	63750	hs	nn
fb	17000	PROCESSING	
bs	64	lb	1.00
d1	0.700	fn	not used
nt	512	DISPLAY	
ct	128	sp	-1699.9
TRANSMITTER		wp	24509.1
tn	C13	rfl	1700.6
sfrq	100.527	rfp	0
tof	1028.0	rp	133.2
tpwr	55	lp	0
pw	5.700	PLOT	
DECOUPLER		wc	250
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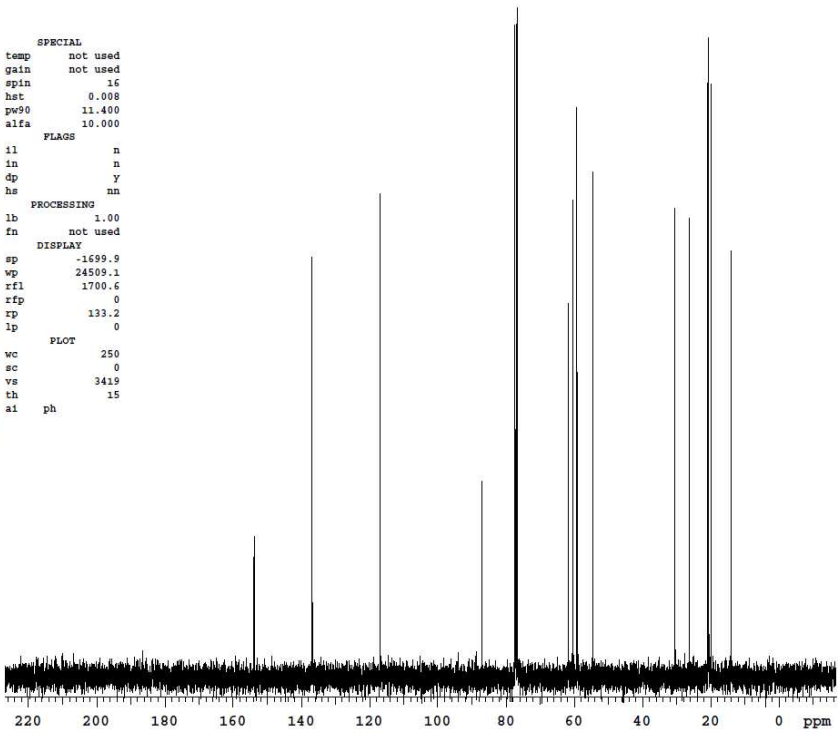

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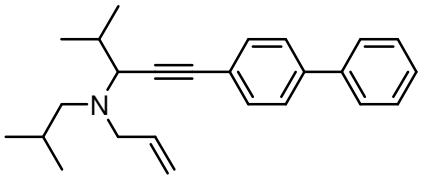

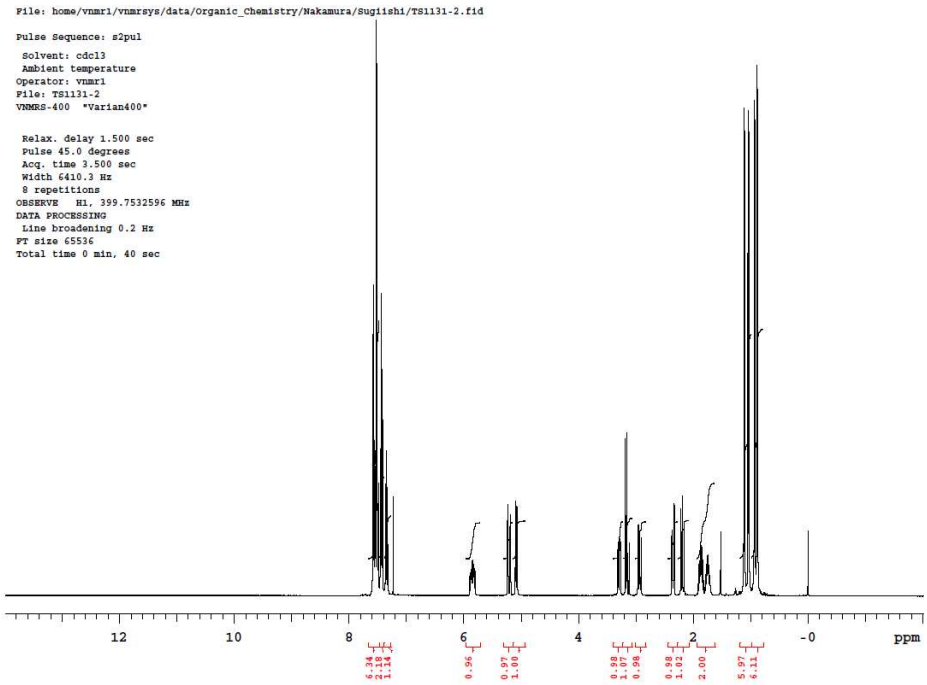

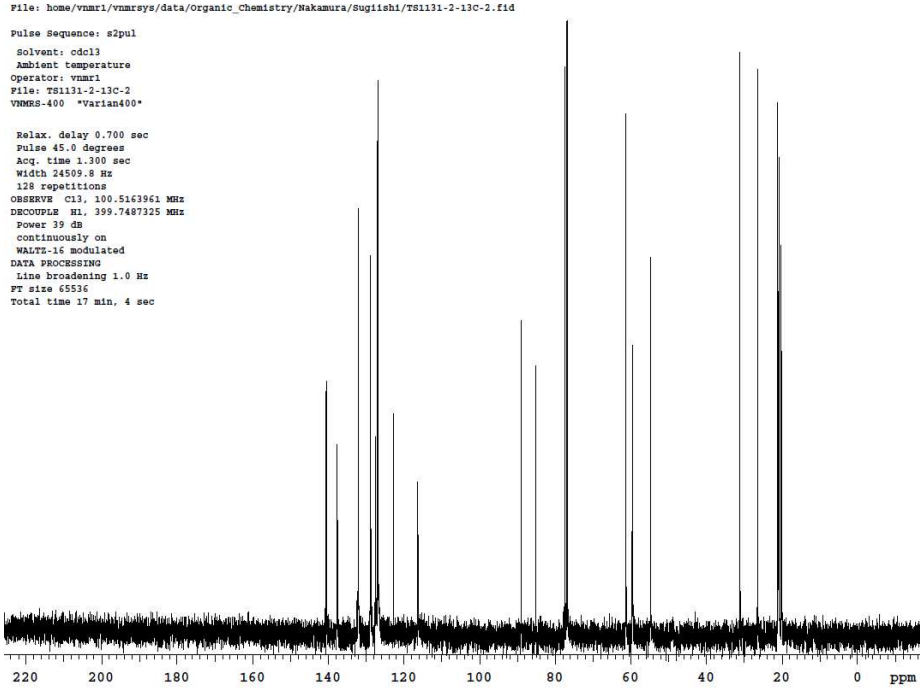

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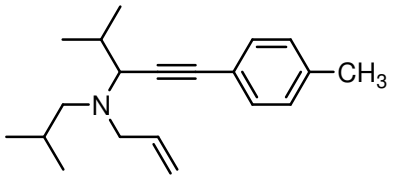

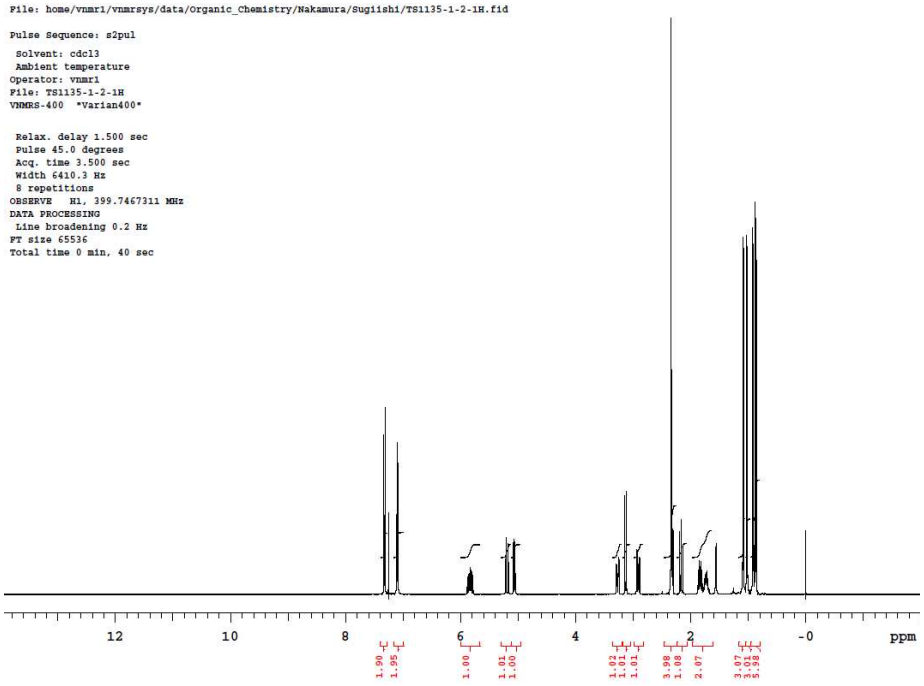

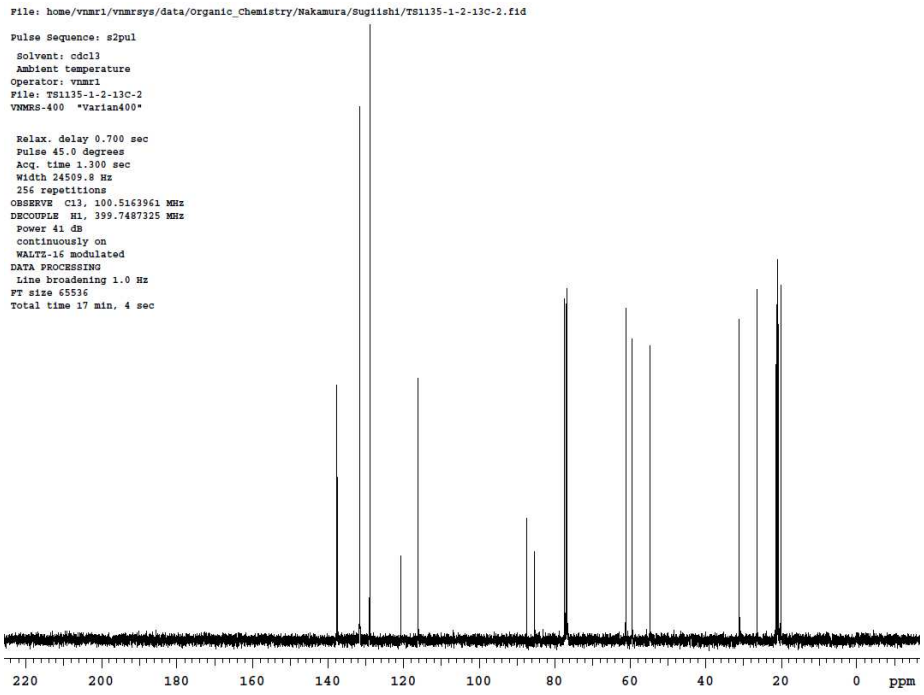

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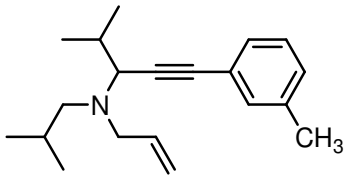

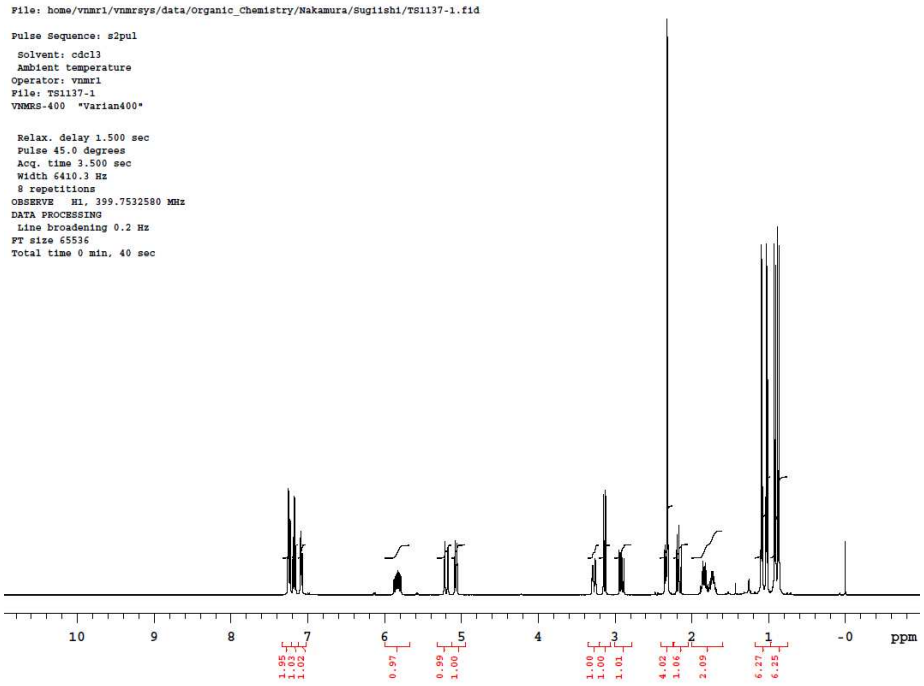

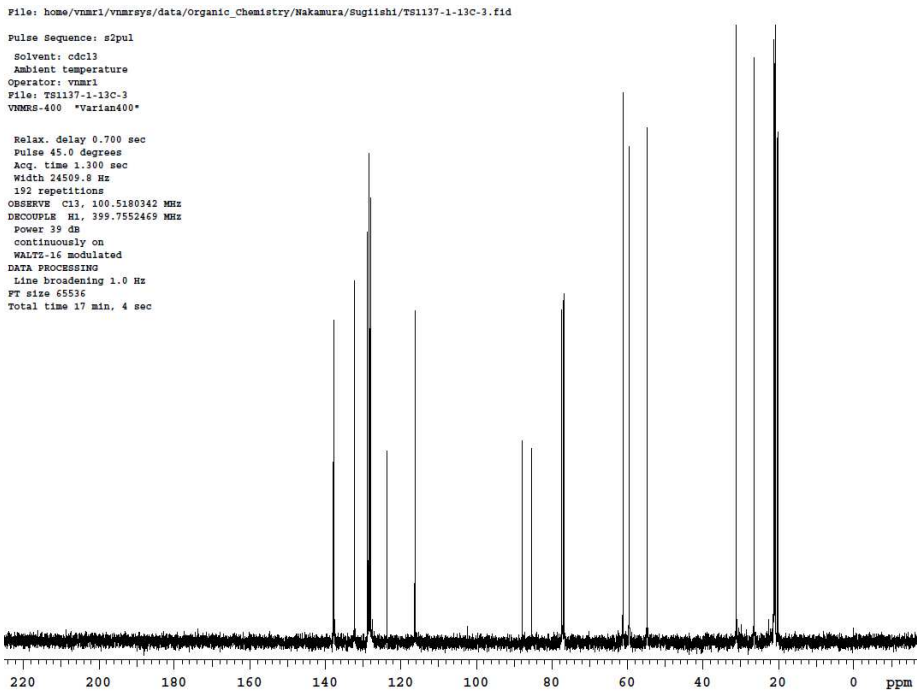

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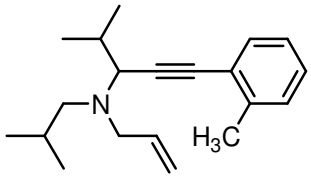

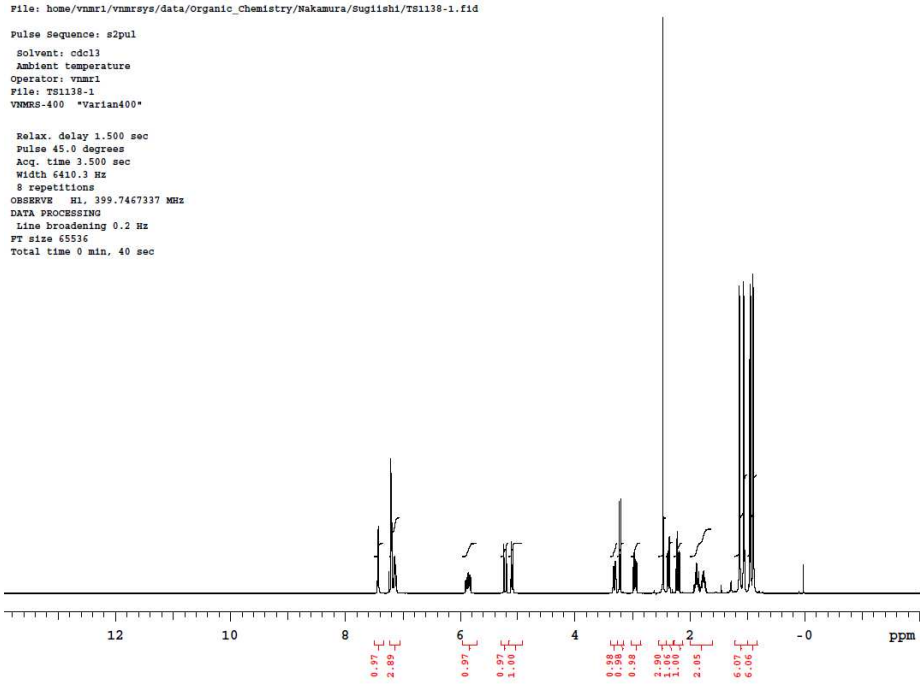

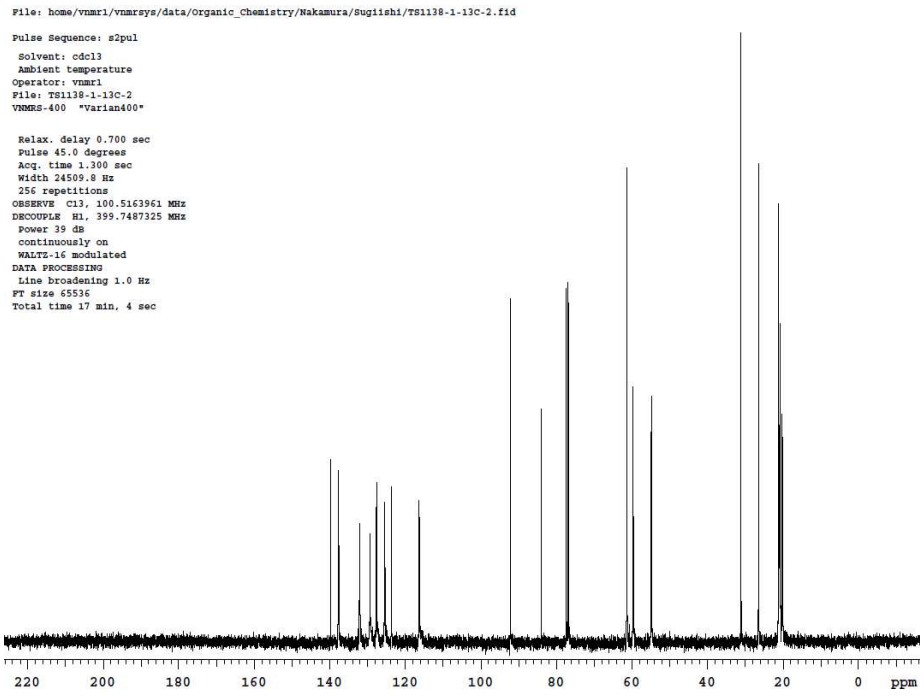

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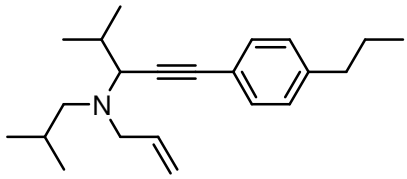

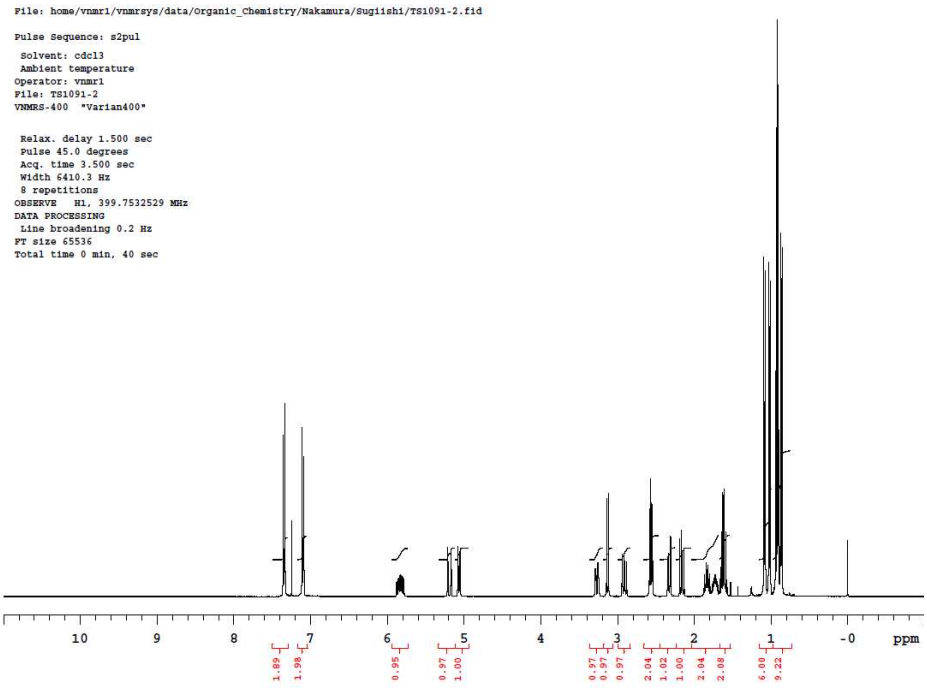

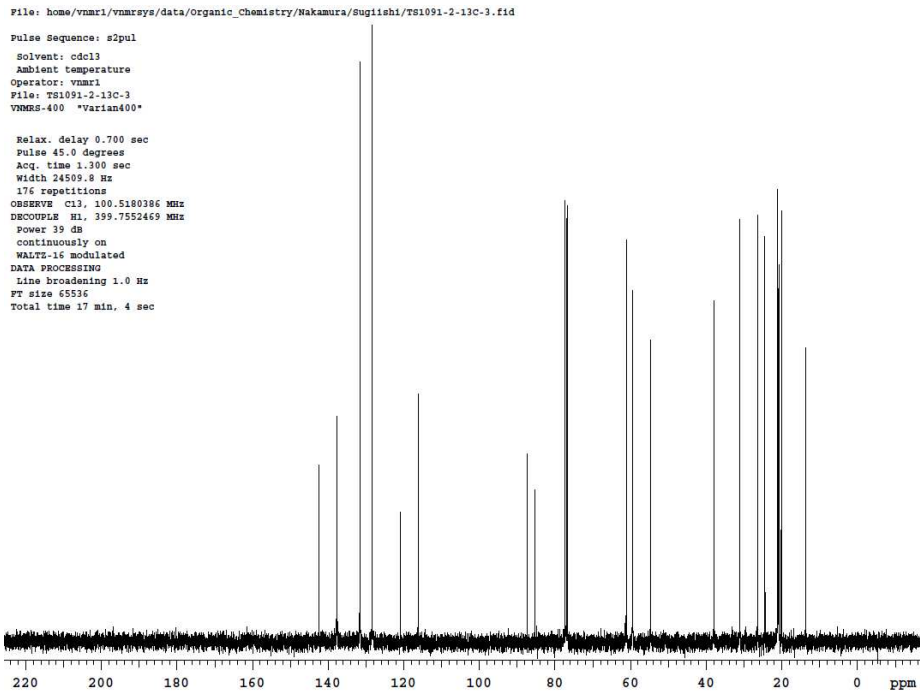

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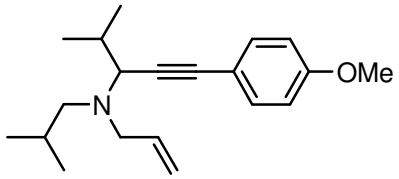
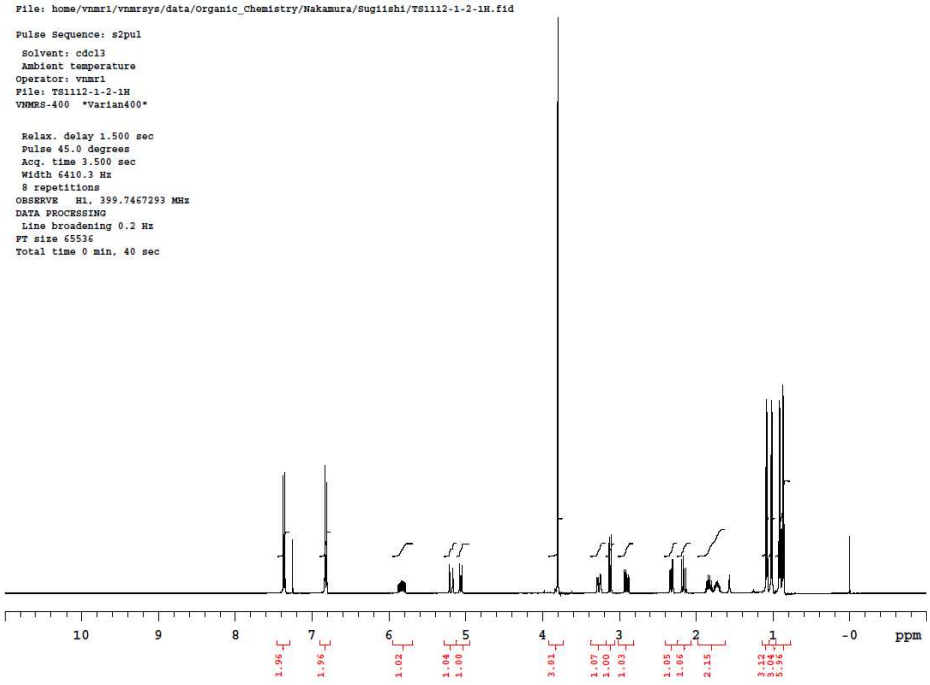
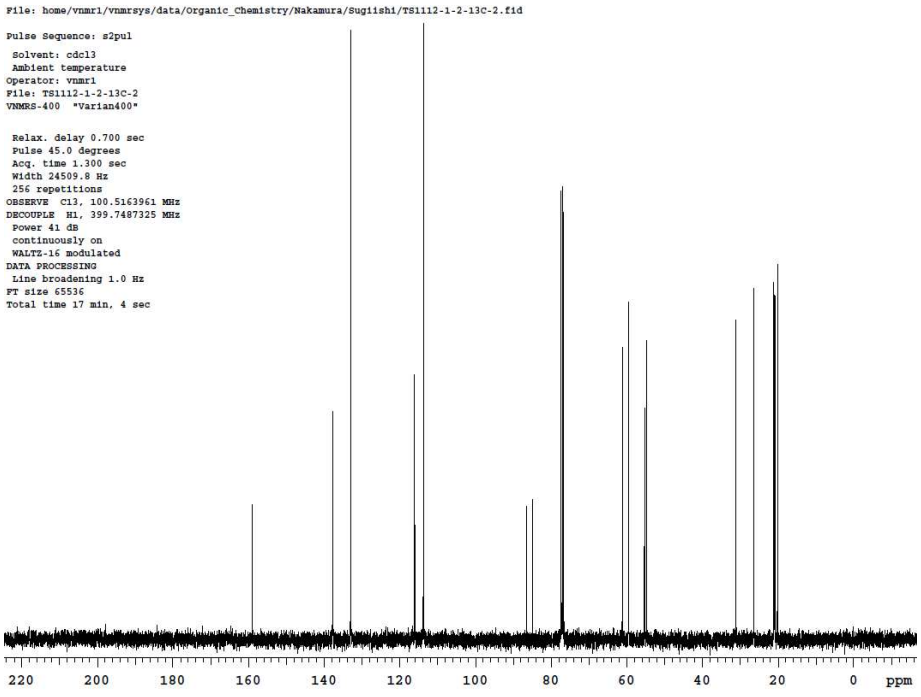
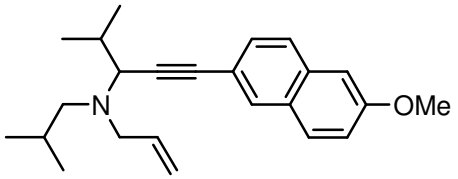
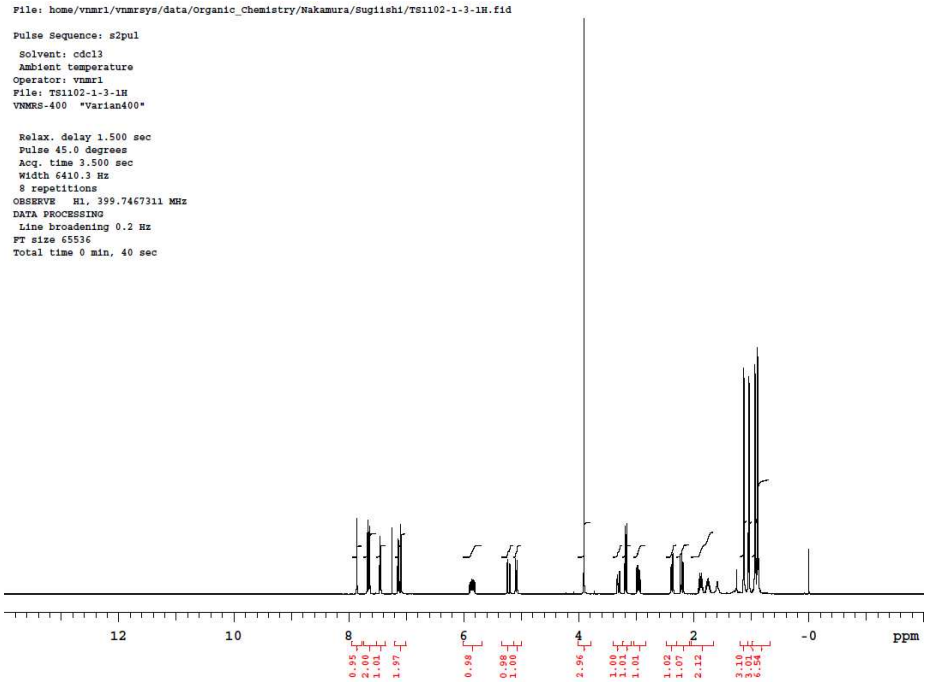


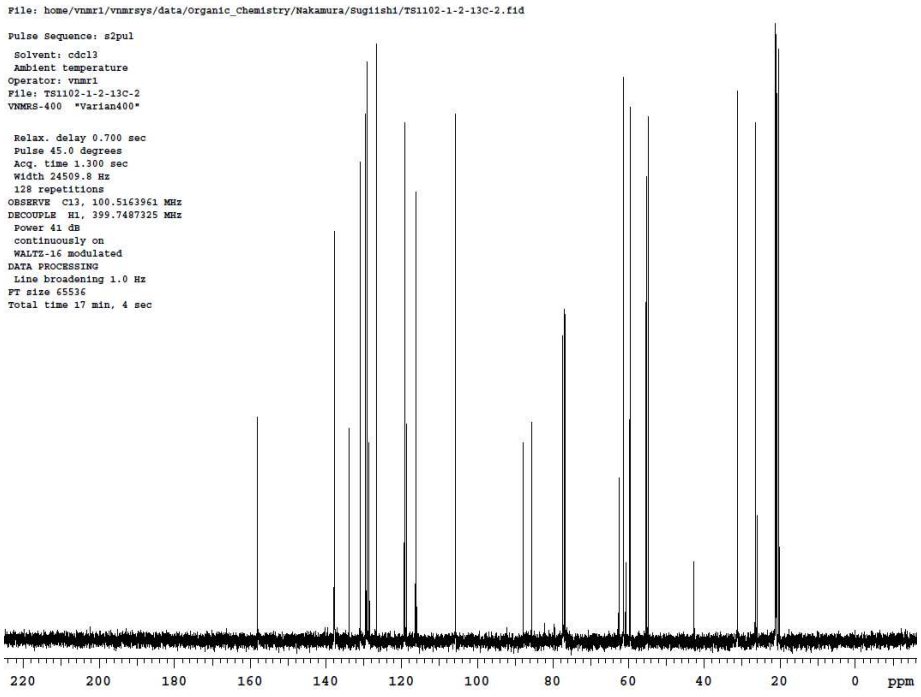




N-allyl-*N*-isobutyl-1-(6-methoxynaphthalen-2-yl)-4-methylpent-1-yn-3-amine (3t)







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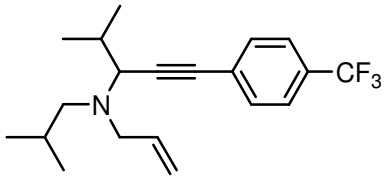
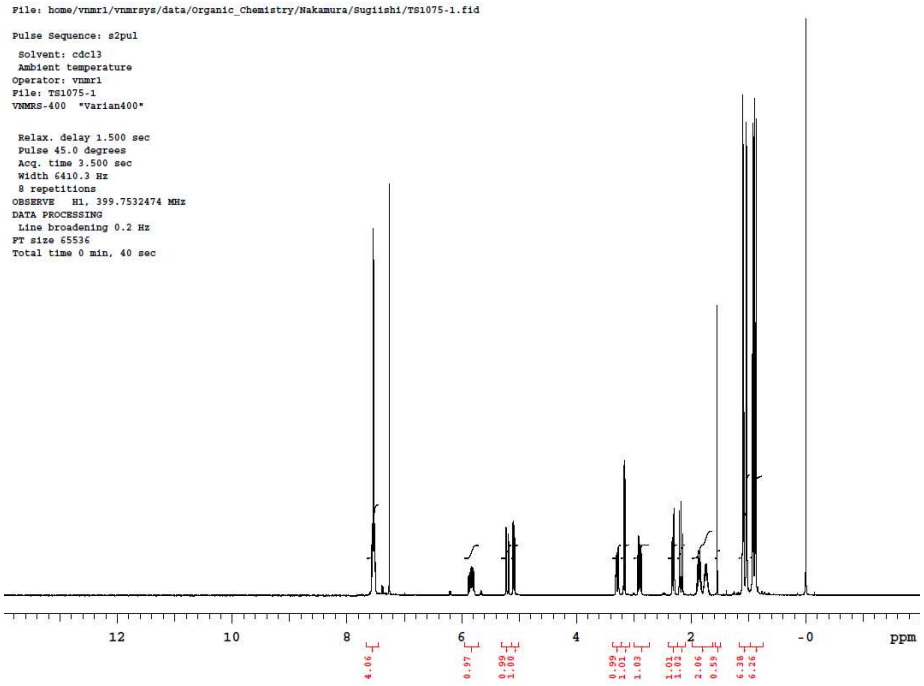
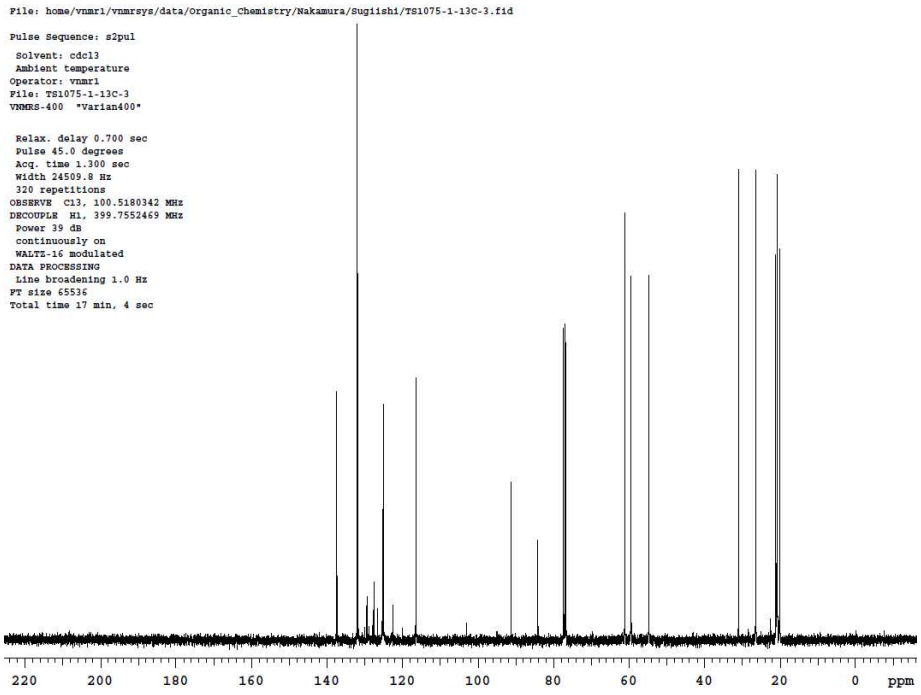
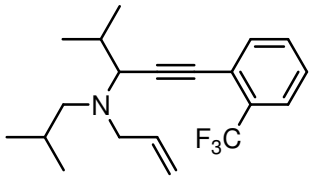
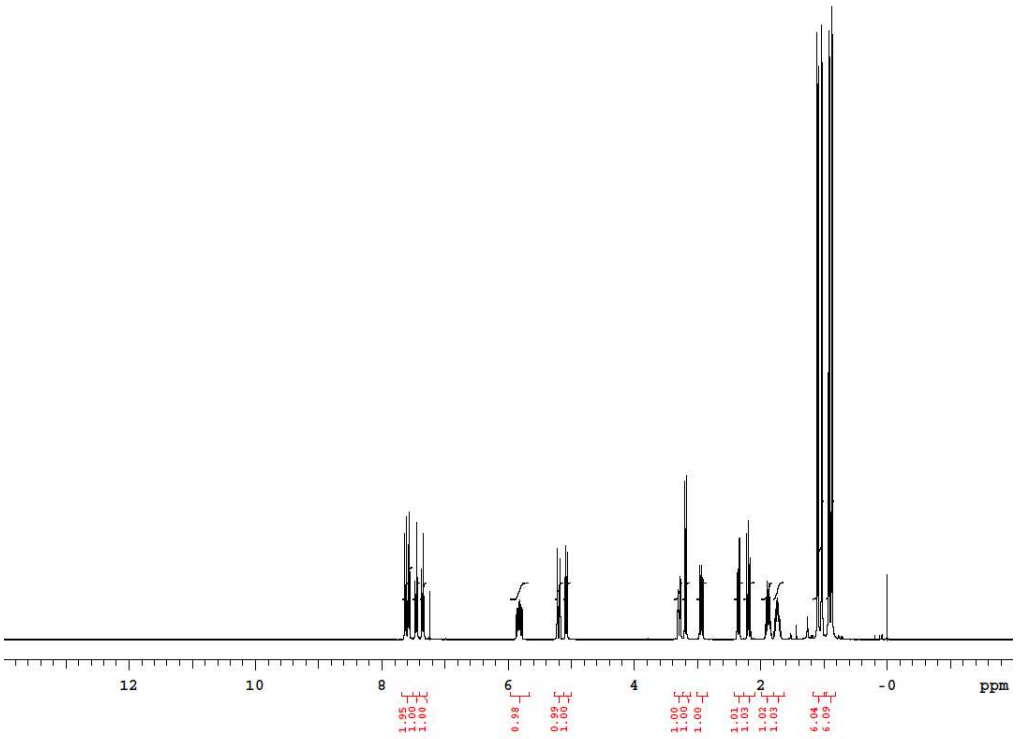


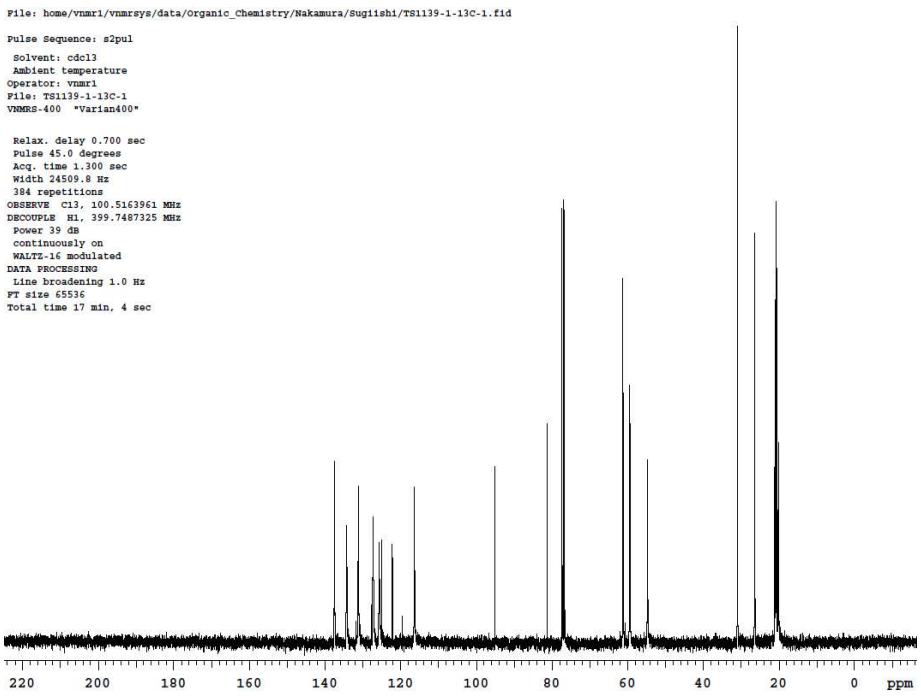




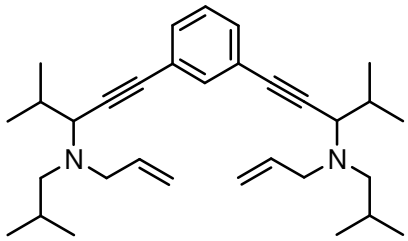
N-allyl-*N*-isobutyl-4-methyl-1-(2-(trifluoromethyl)phenyl)pent-1-yn-3-amine (3v)

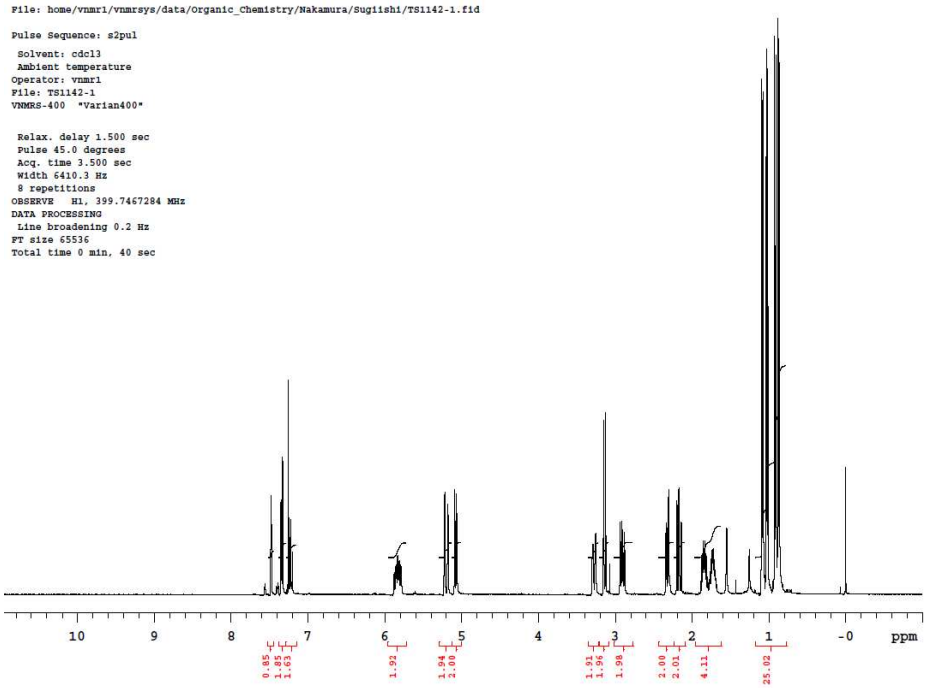


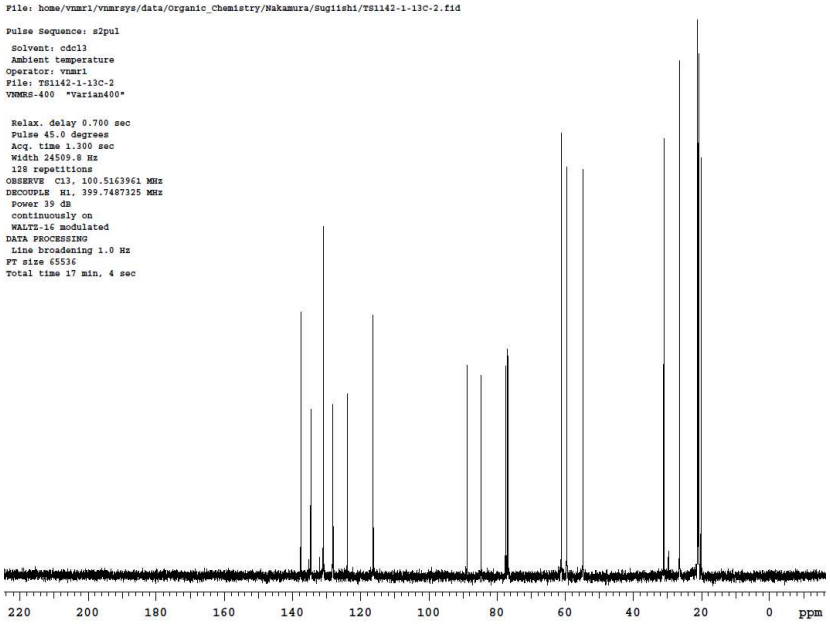




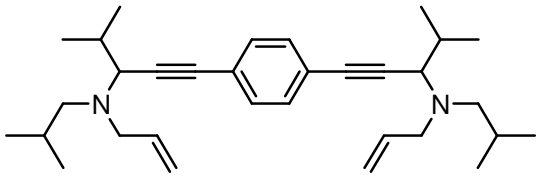
N-allyl-1-(3-(3-(allyl(isobutyl)amino)-4-methylpent-1-ynyl)phenyl)-*N*-isobutyl-4-methyl pent-1-yn-3-amine (3w)

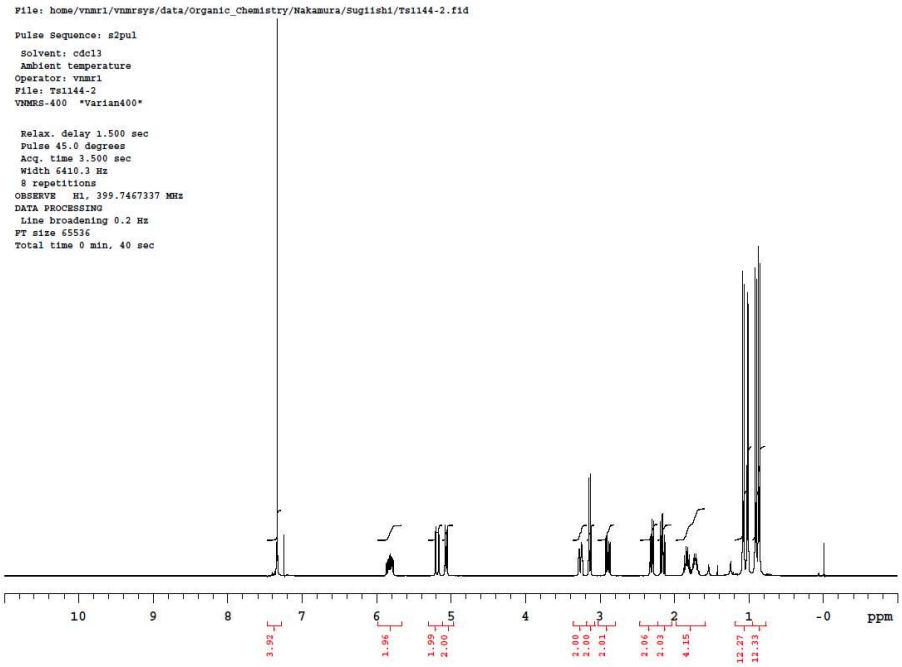


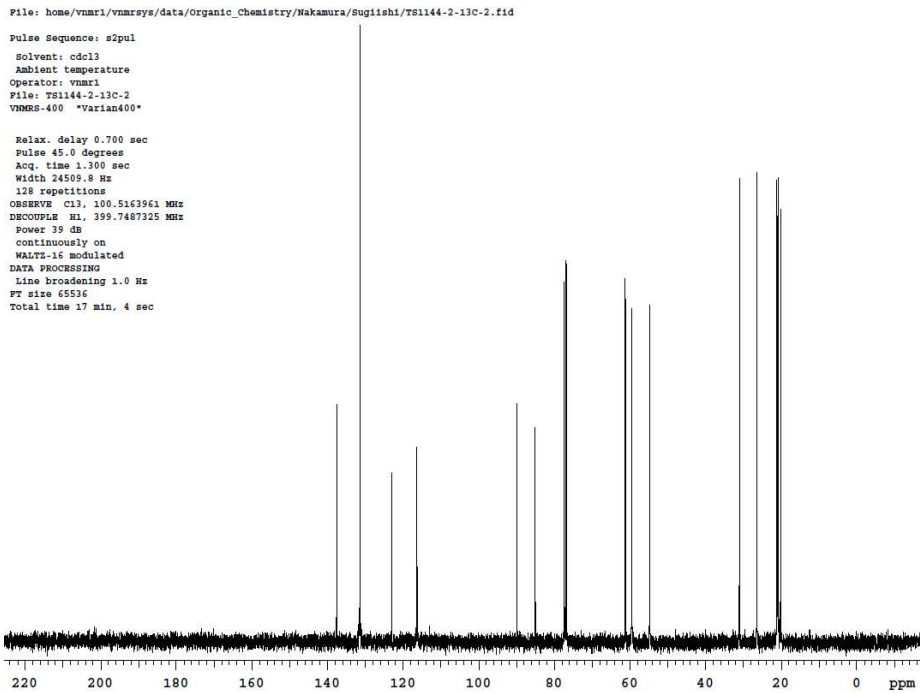




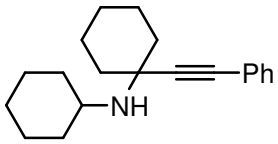
N-allyl-1-(4-(3-(allyl(isobutyl)amino)-4-methylpent-1-ynyl)phenyl)-*N*-isobutyl-4-methyl pent-1-yn-3-amine (3x)

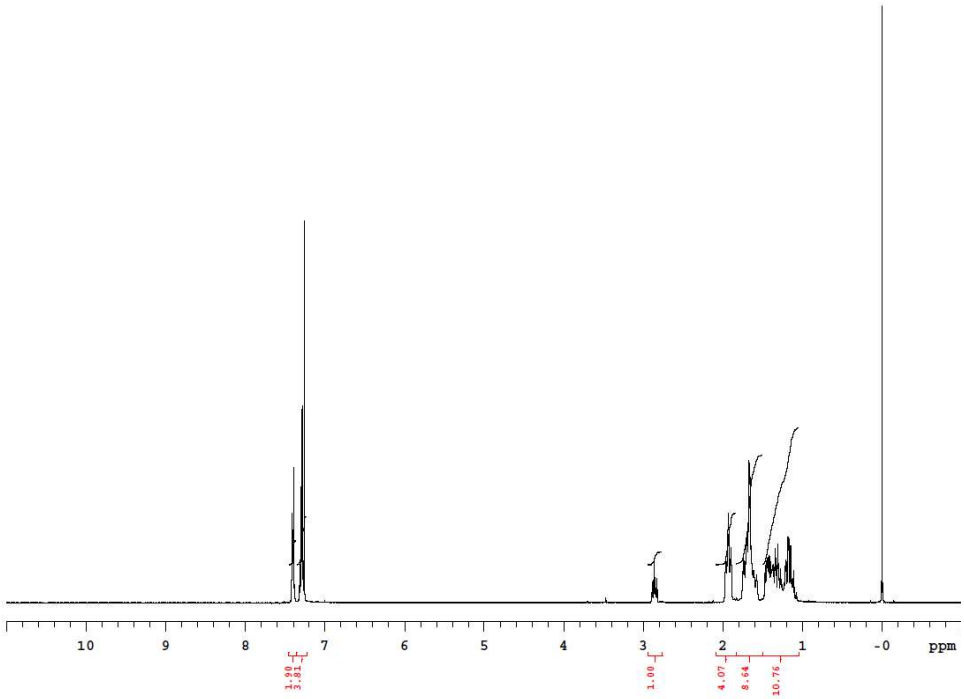


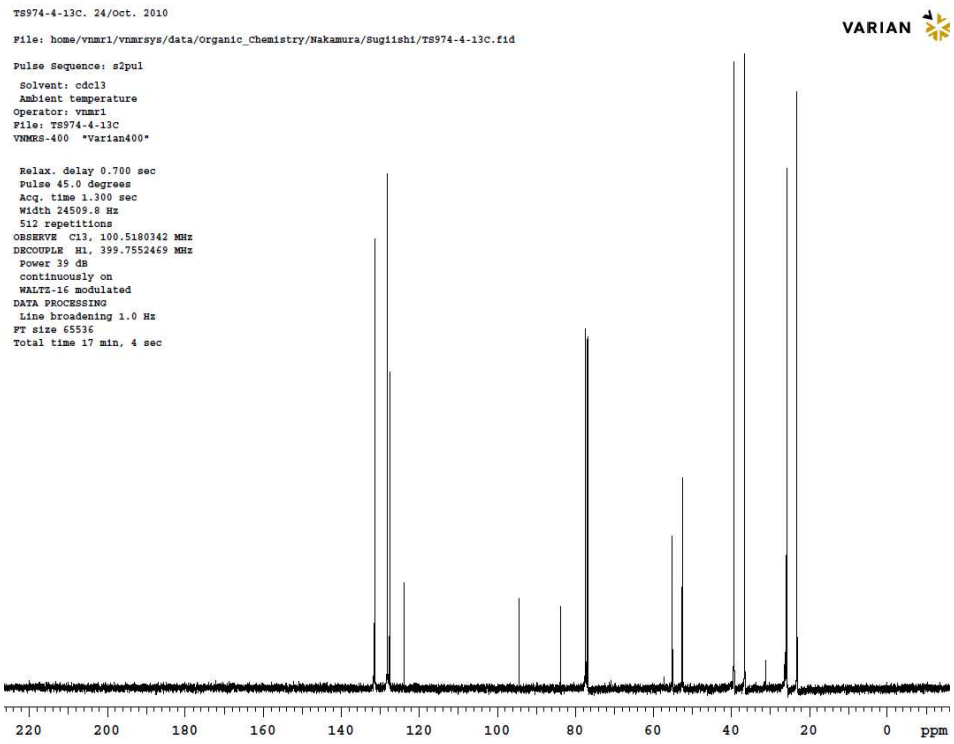




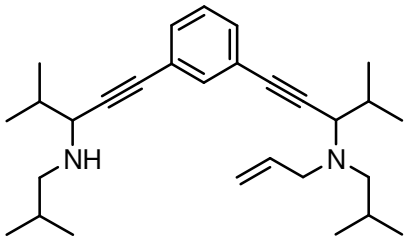
N-cyclohexyl-1-(2-phenylethynyl)cyclohexanamine (4a)

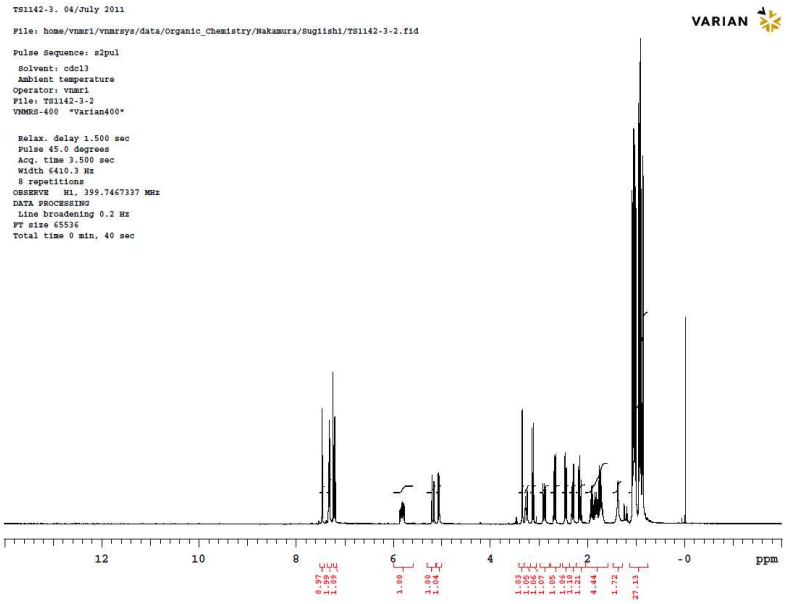


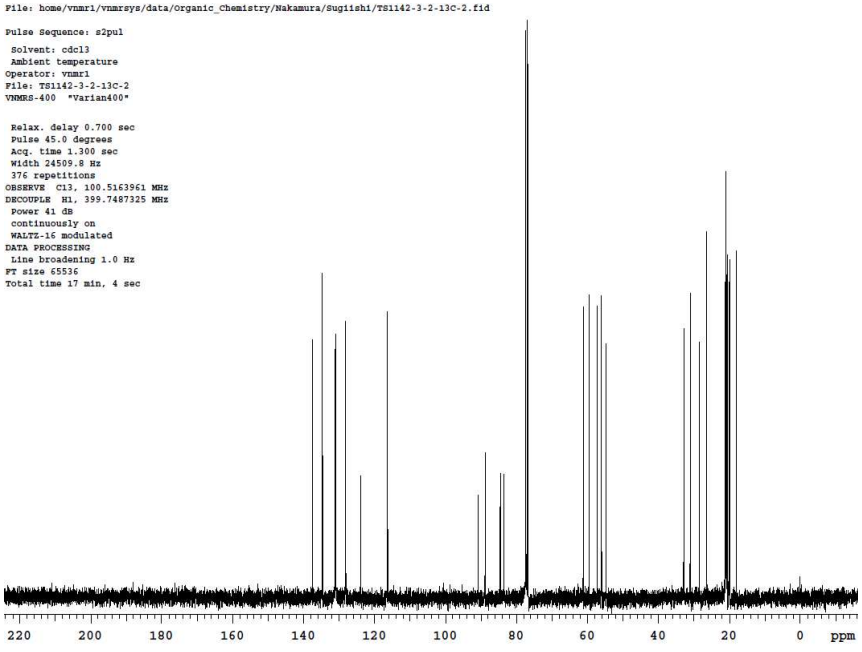




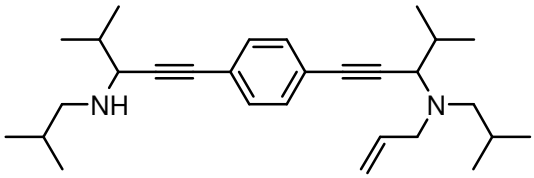
1-(3-(3-(allyl(isobutyl)amino)-4-methylpent-1-ynyl)phenyl)-*N*-isobutyl-4-methylpent-1-yn-3-amine (4w)

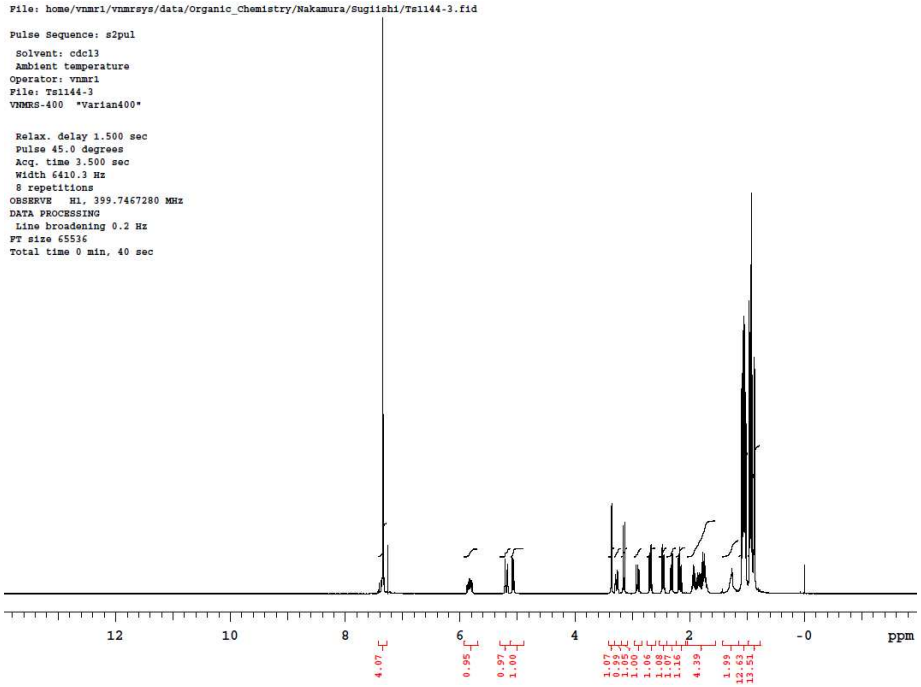


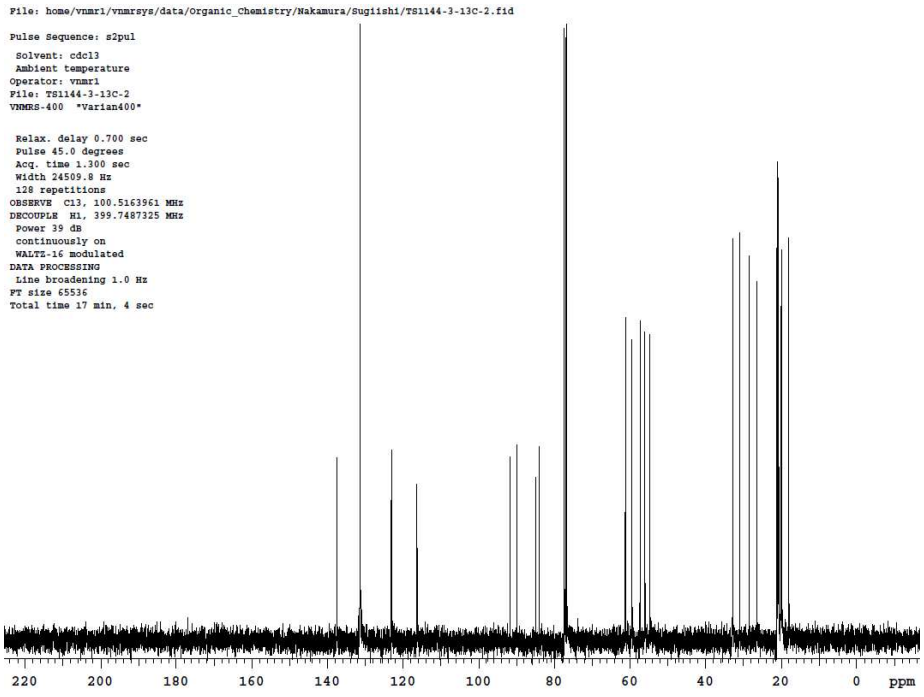




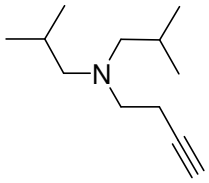
1-(4-(3-(allyl(isobutyl)amino)-4-methylpent-1-ynyl)phenyl)-*N*-isobutyl-4-methylpent-1-yn-3-amine (4x)

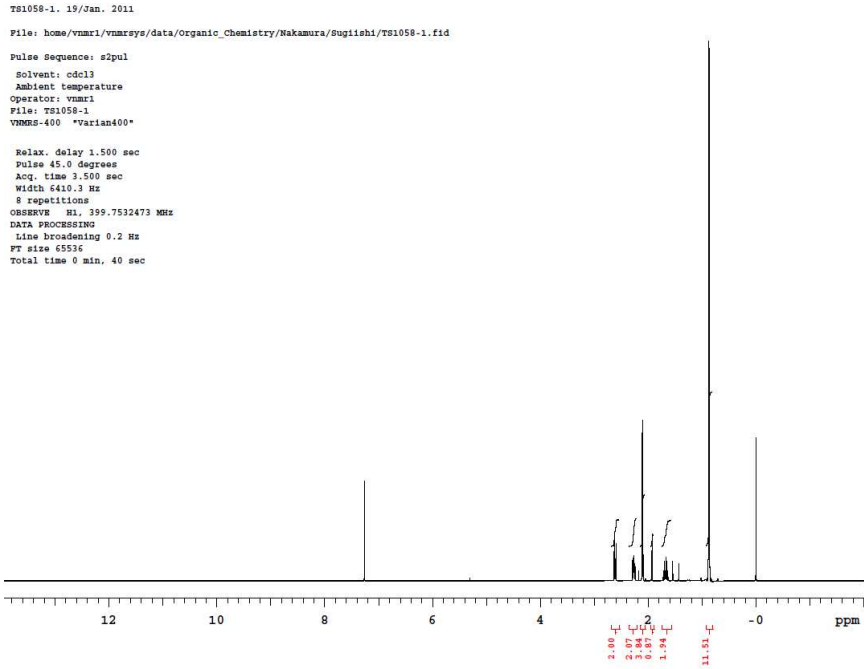


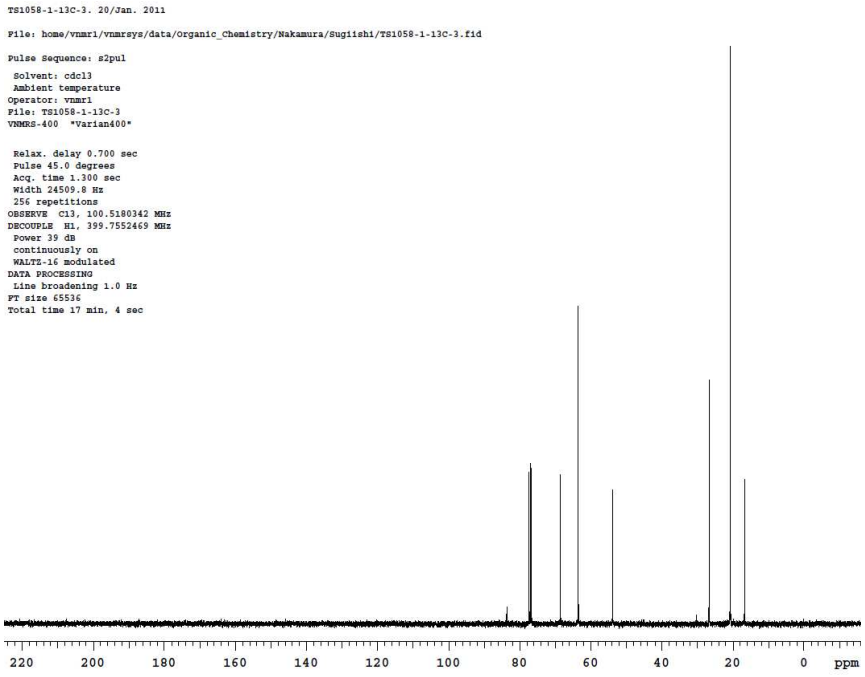




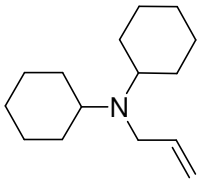
N,N-diisobutylbut-3-yn-1-amine (10)

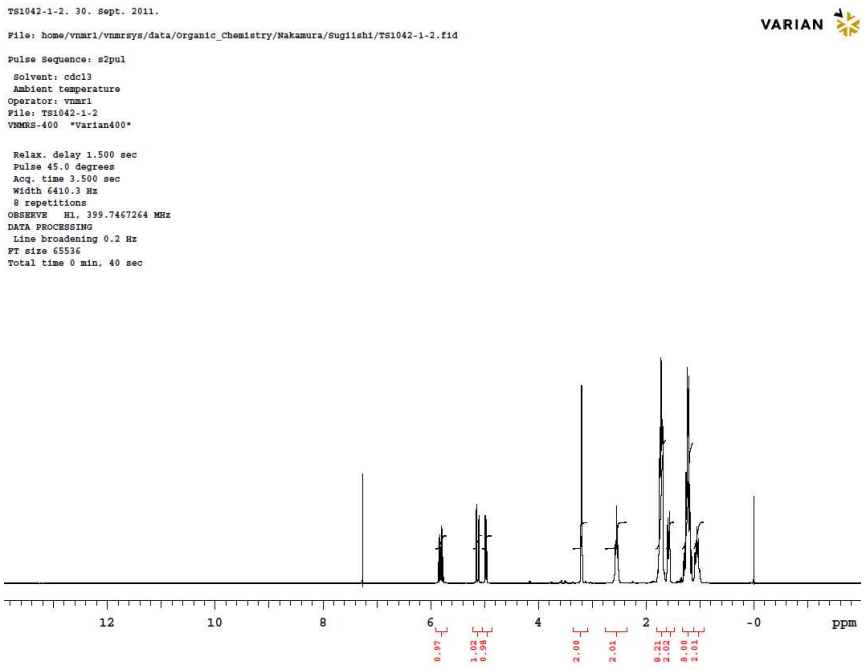


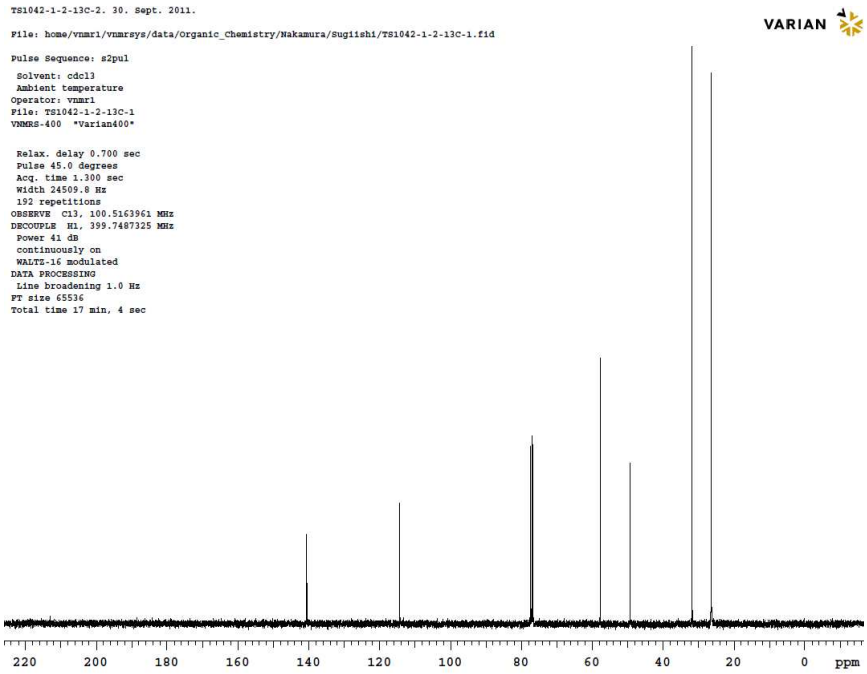




N-allyl-*N*-cyclohexylcyclohexanamine (11)

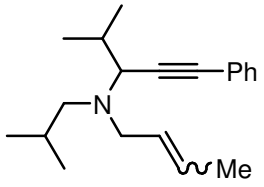






^{1}H NMR Charts of **3h** and **3i** for analysis of the diastereomeric ratios

N-(but-2-enyl)-*N*-isobutyl-4-methyl-1-phenylpent-1-yn-3-amine (**3h**)



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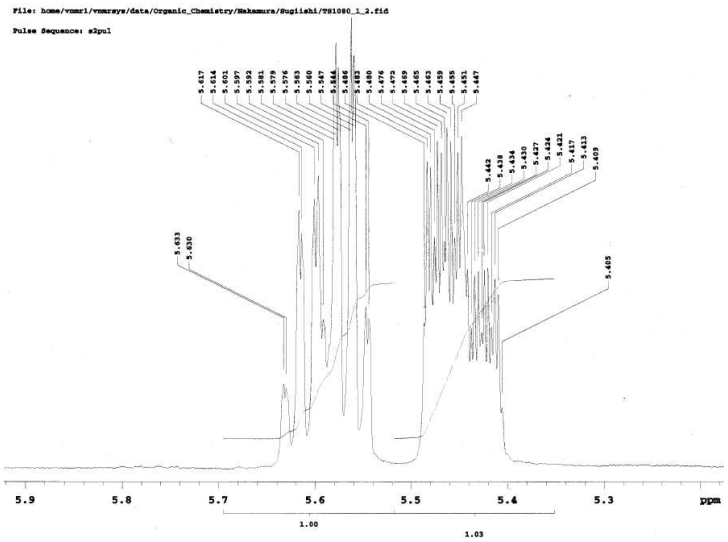
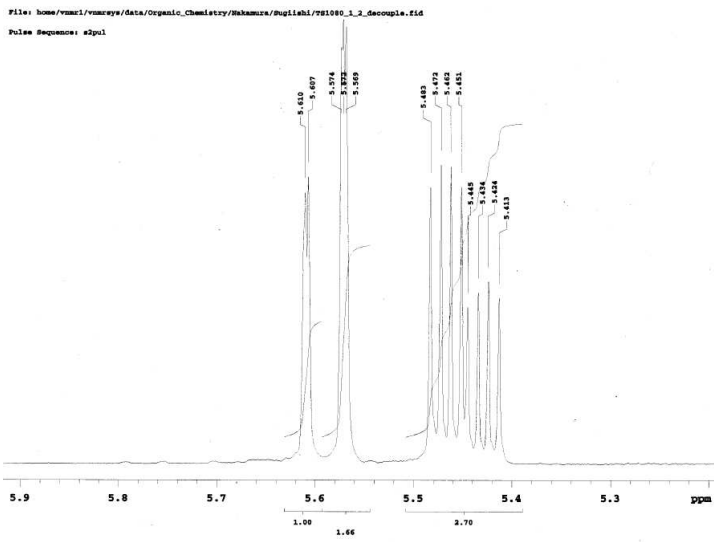
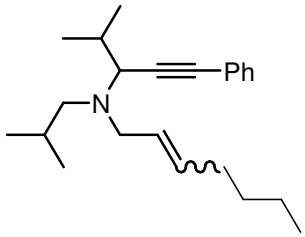


Decoupling

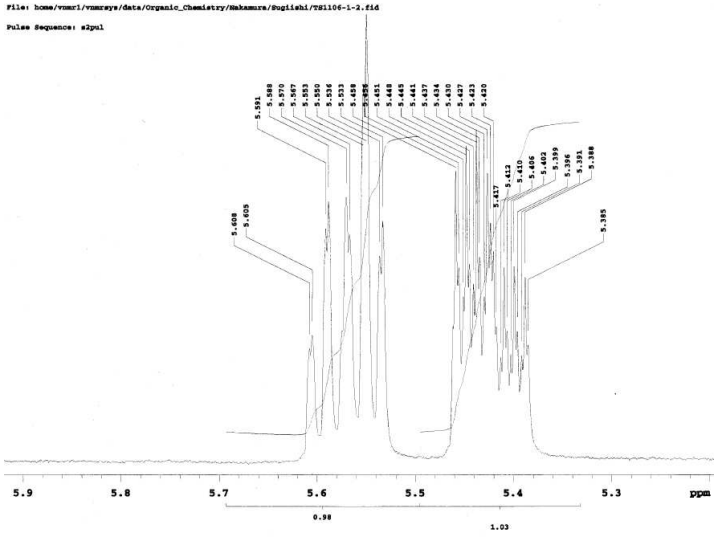


N-isobutyl-*N*-(4-methyl-1-phenylpent-1-yn-3-yl)hept-2-en-1-amine (**3i**)

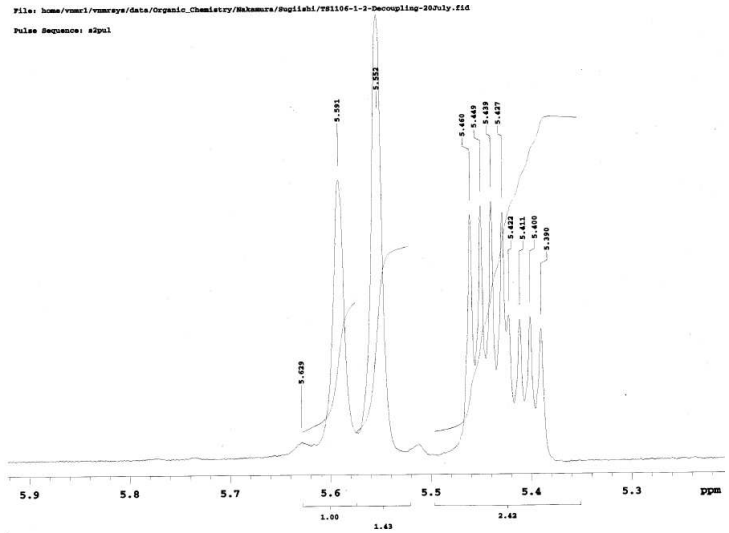


d.r. = 1.4:1

Normal

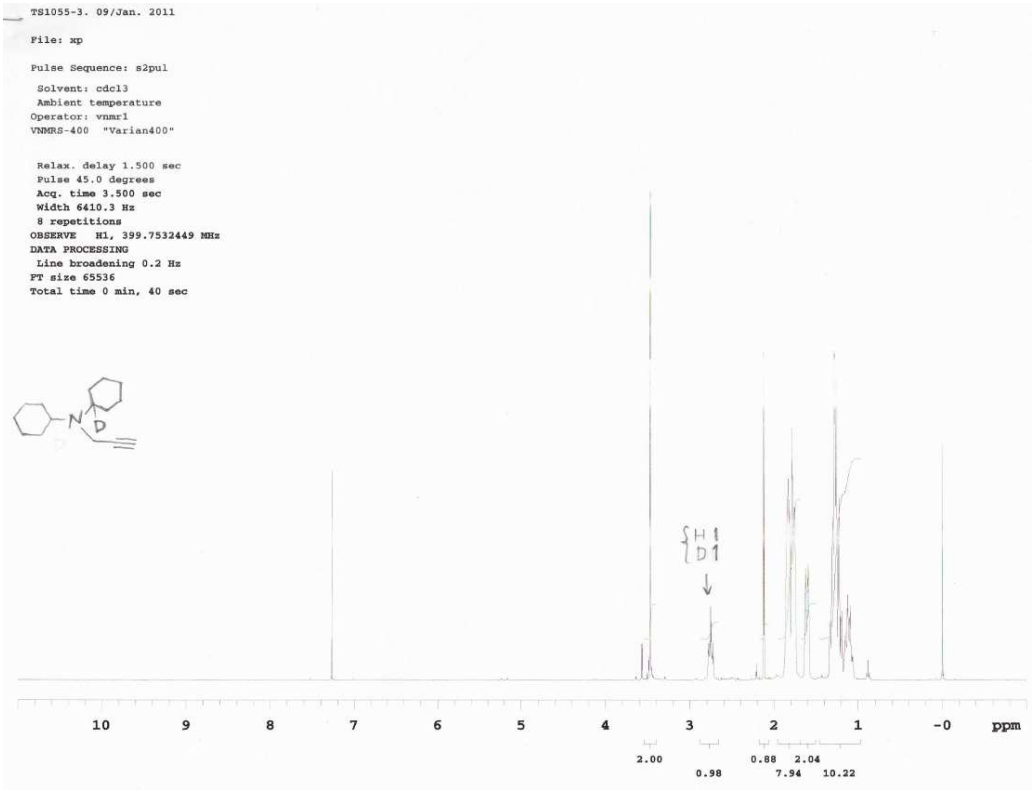


Decoupling

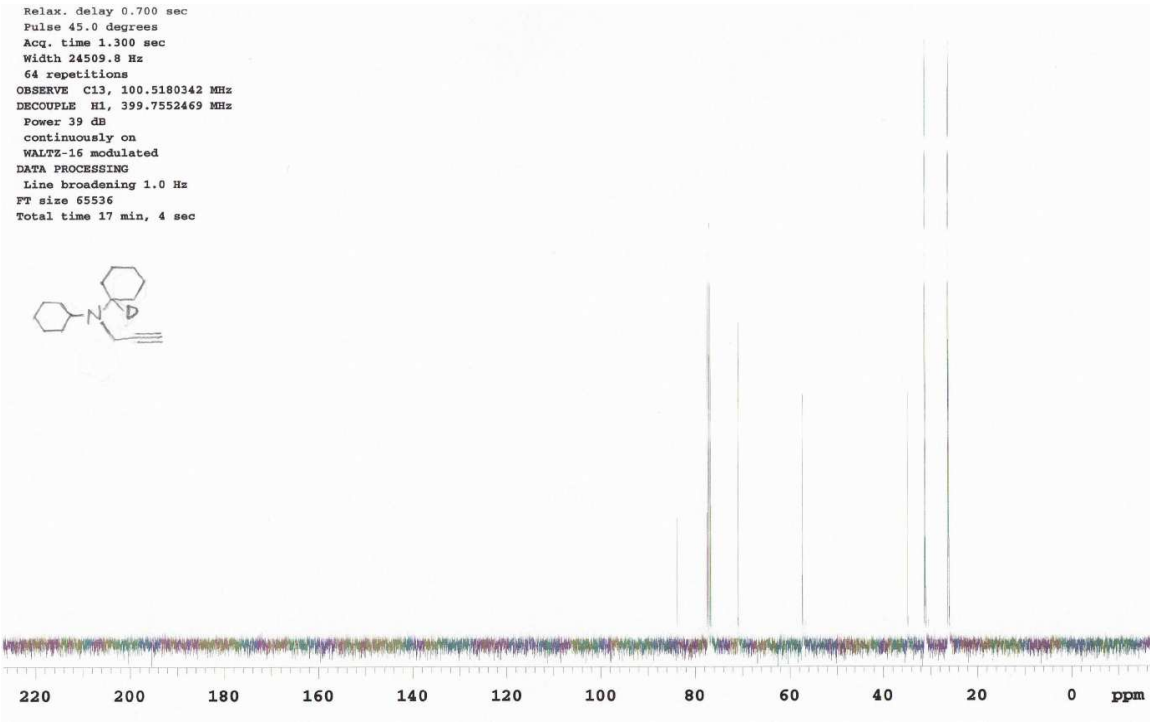


NMR Charts and LCMS solution of Isotopic Labeling Experiments

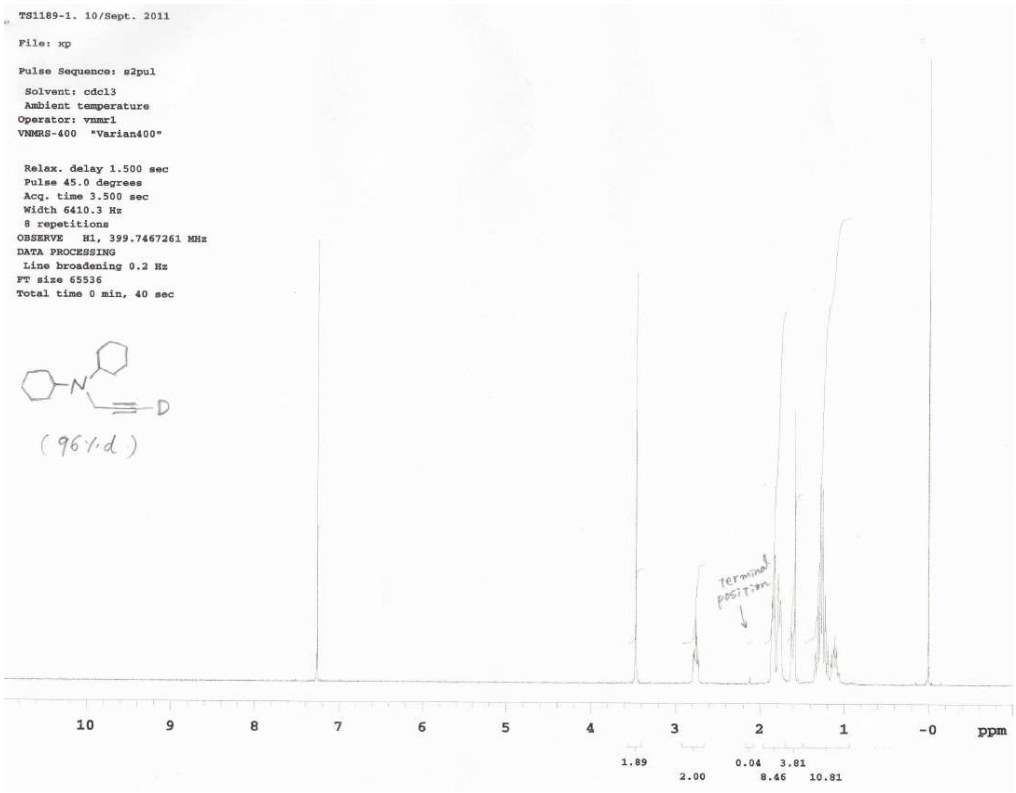
***d*$_1$-1a** (^{1}H NMR, $CDCl_3$)



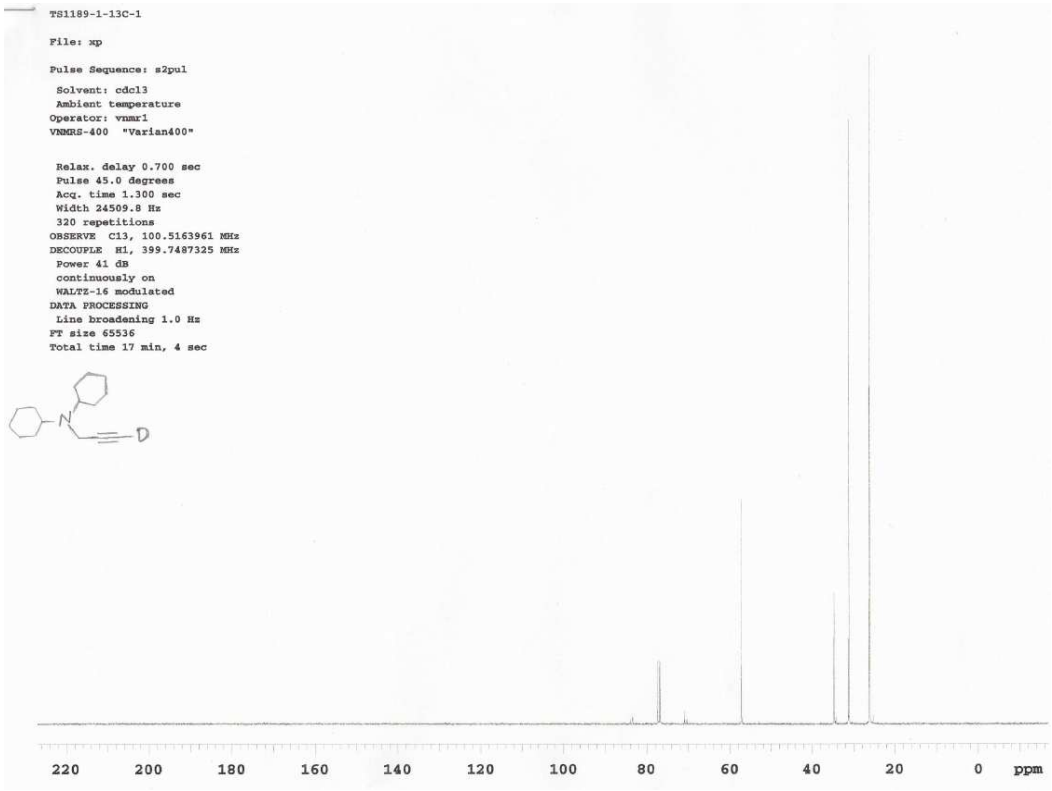
***d*$_1$-1a** (^{13}C NMR, $CDCl_3$)



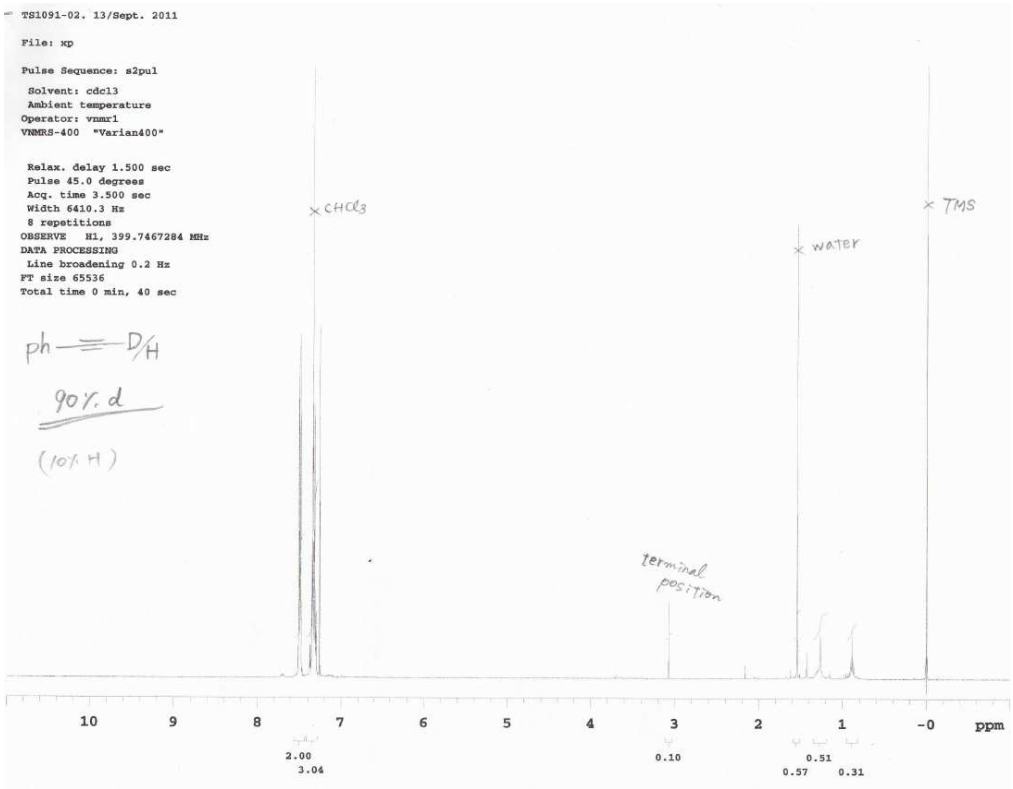
***d*-1a** (^{1}H NMR, $CDCl_3$)



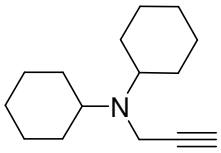
***d*-1a** (^{13}C NMR, $CDCl_3$)

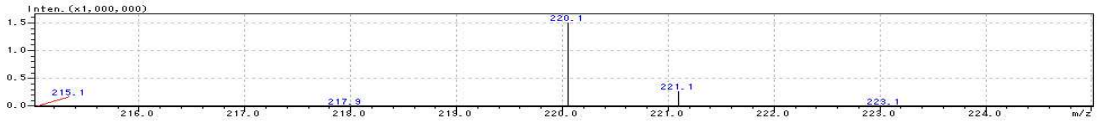


***d*-2a** (^{1}H NMR, $CDCl_3$)

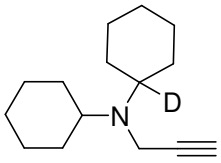


1a (LCMS solution)

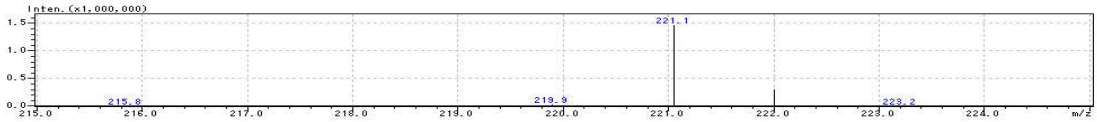




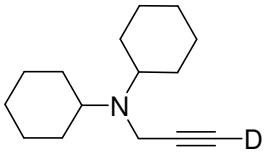
***d*$_1$-1a** (LCMS solution)



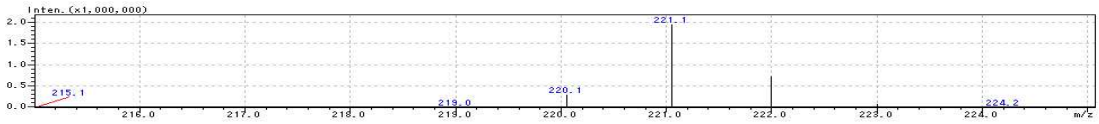
>99%*d*



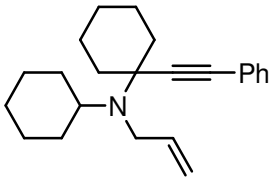
***d*-1a** (LCMS solution)

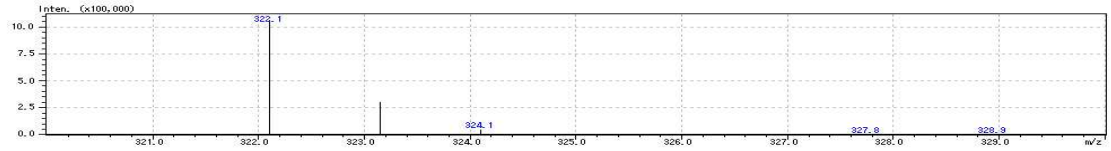


96%*d*

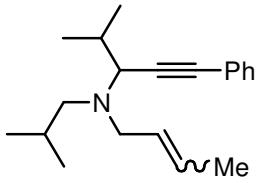


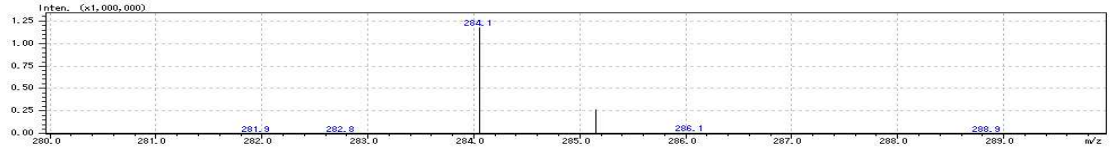
3a (LCMS solution)



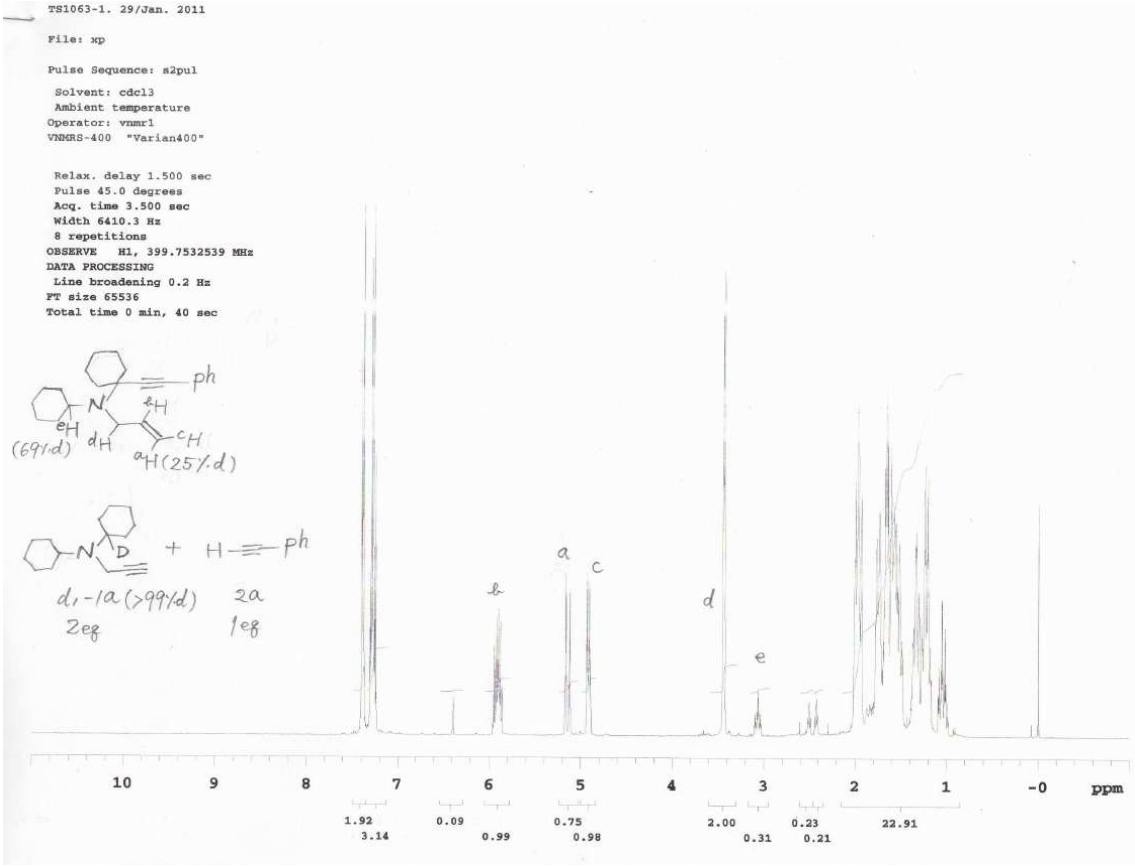


3h (LCMS solution)

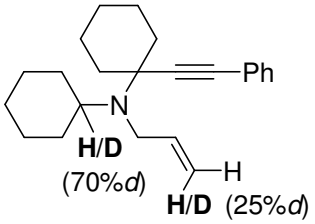


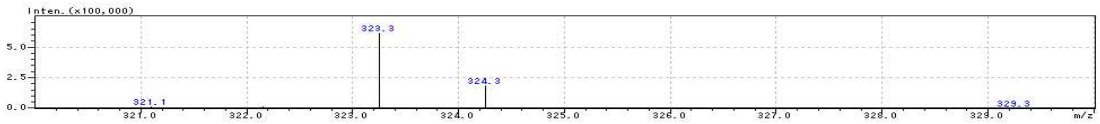


eq. (1) ***d*-3a** (^{1}H NMR, $CDCl_3$)

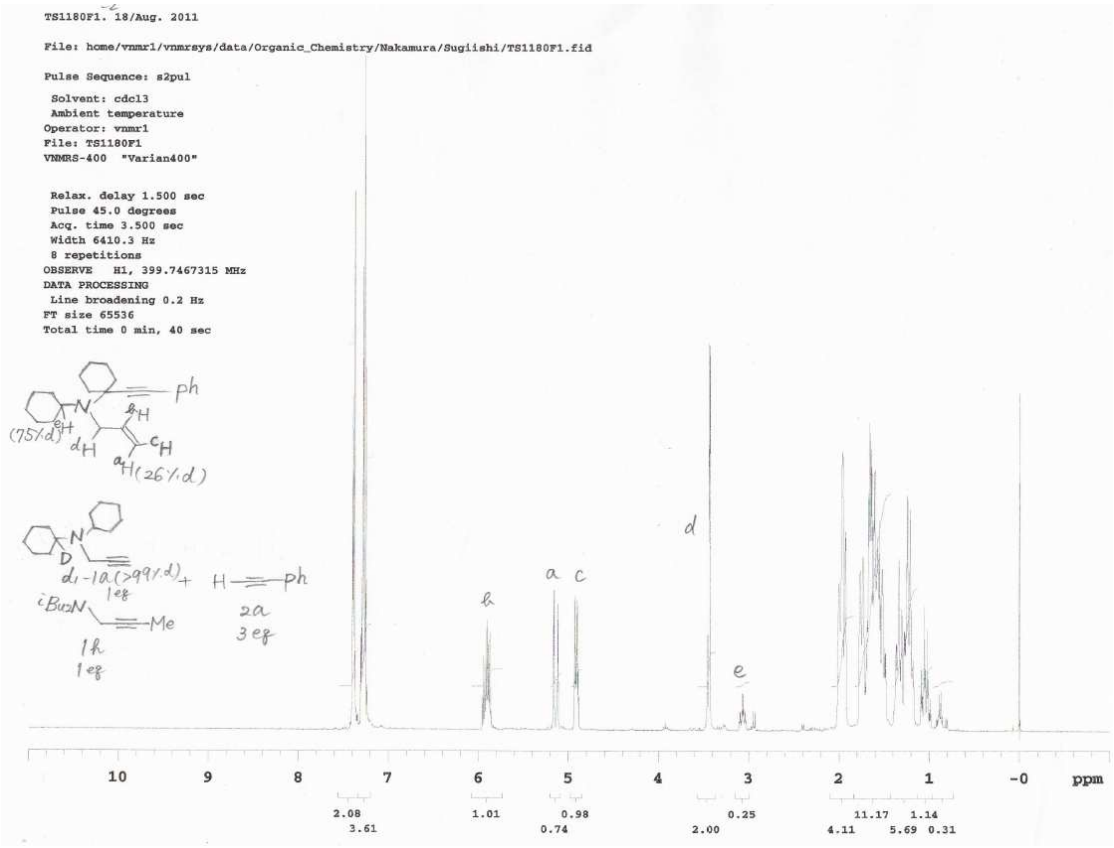


eq. (1) ***d*-3a** (LCMS solution)

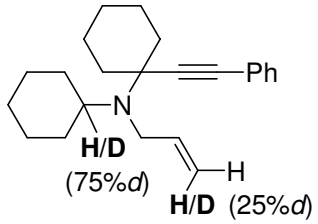


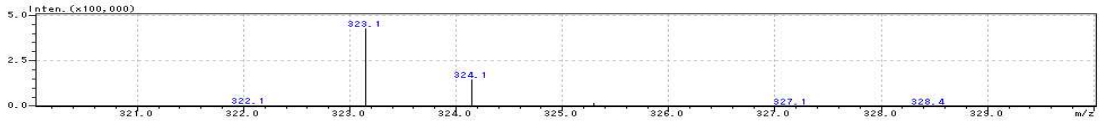


eq. (2) ***d*-3a** (^{1}H NMR, $CDCl_3$)

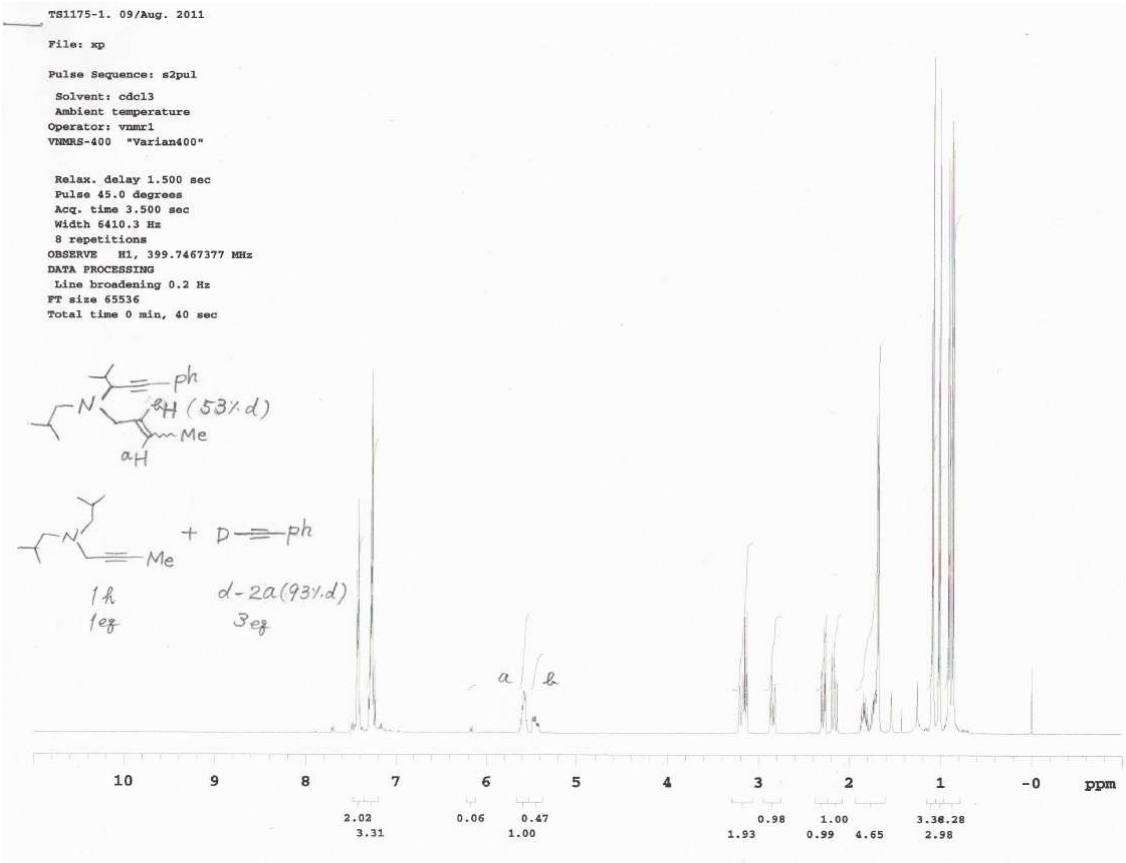


eq. (2) ***d*-3a** (LCMS solution)

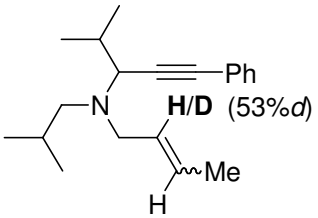


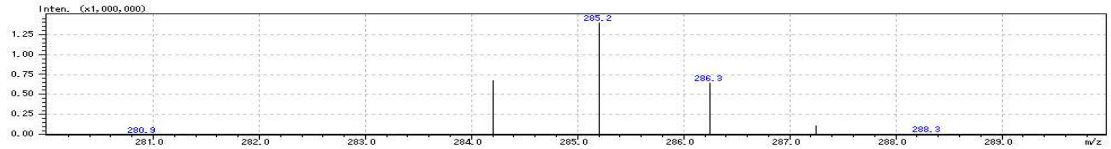


eq. (3) ***d*-3h** (^{1}H NMR, $CDCl_3$)

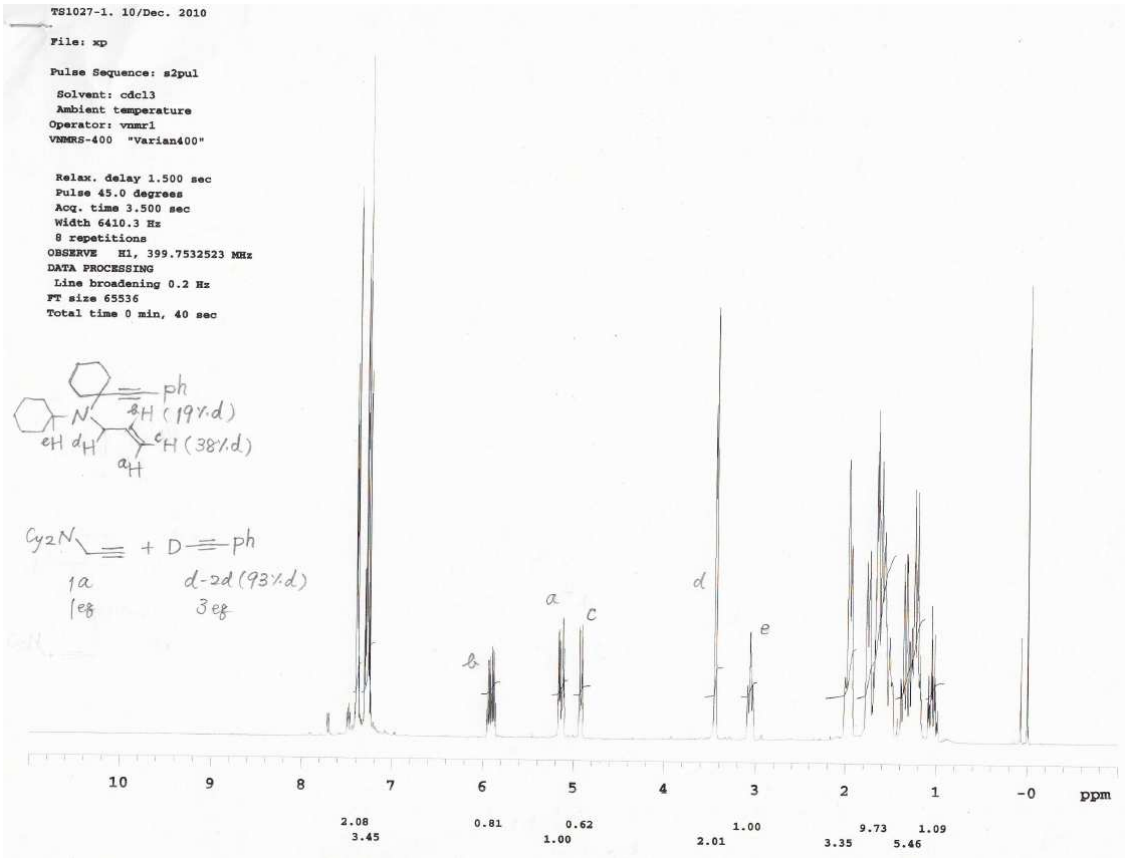


eq. (3) ***d*-3h** (LCMS solution)

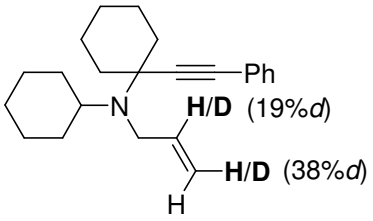


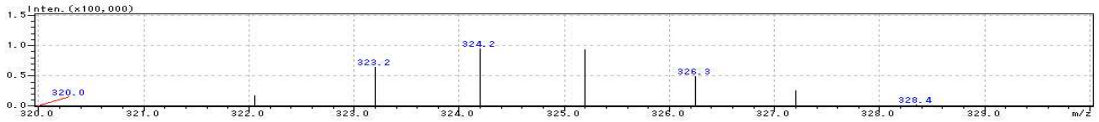


eq. (4) ***d*-3a** (^{1}H NMR, $CDCl_3$)

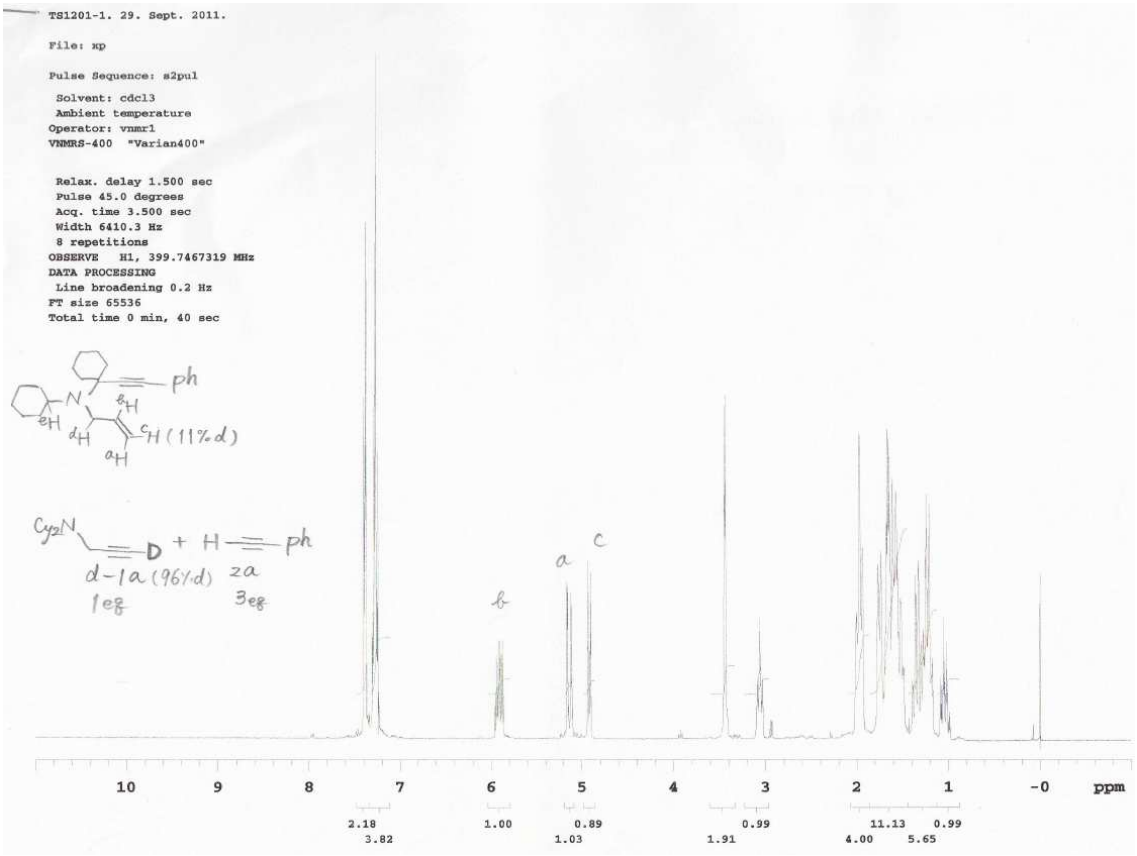


eq. (4) ***d*-3a** (LCMS solution)

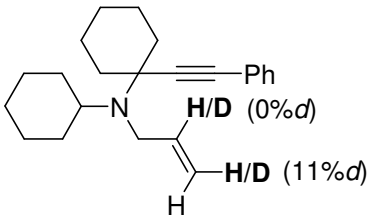


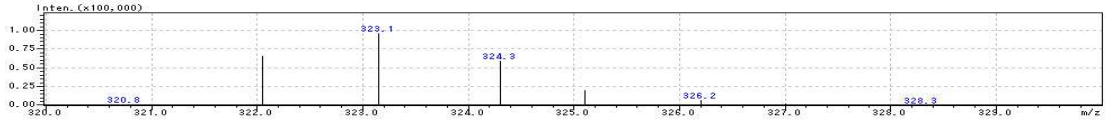


eq. (5) ***d*-3a** (^{1}H NMR, $CDCl_3$)

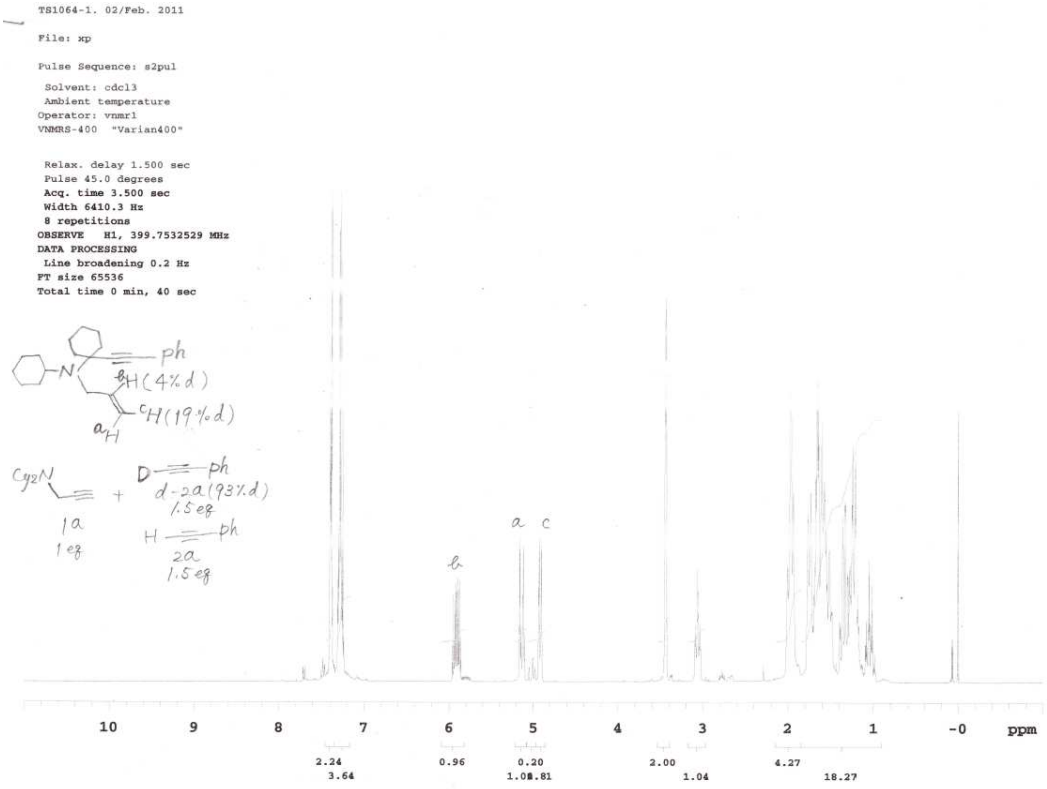


eq. (5) ***d*-3a** (LCMS solution)

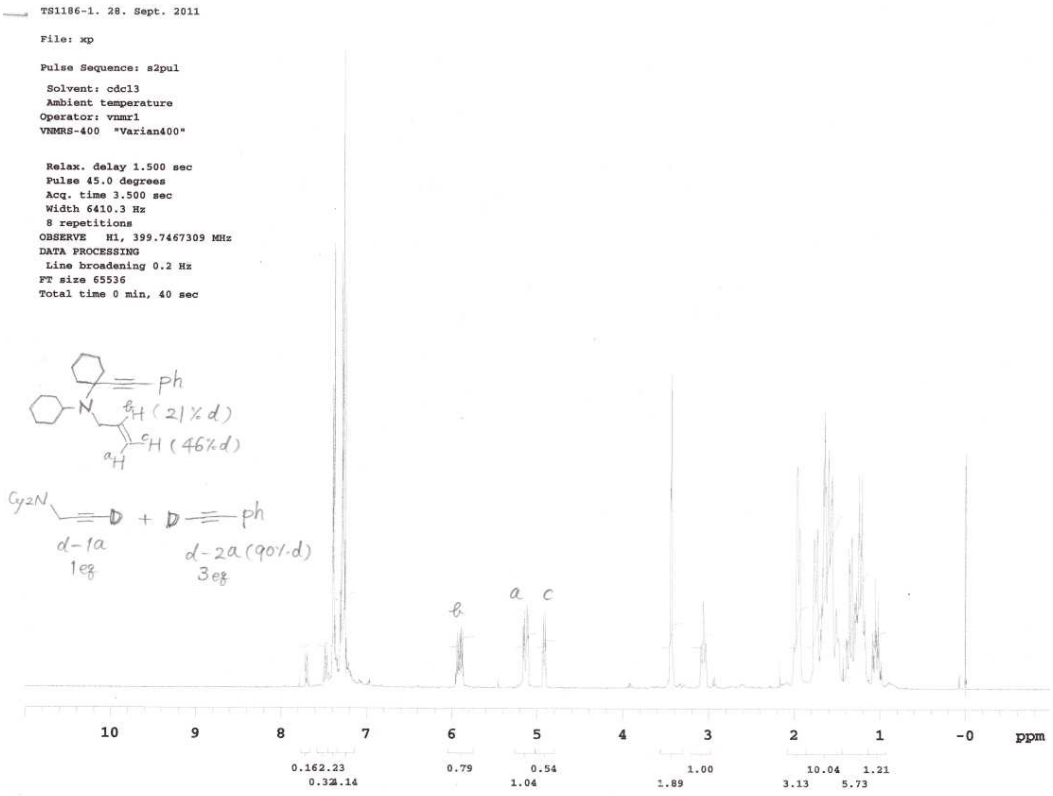




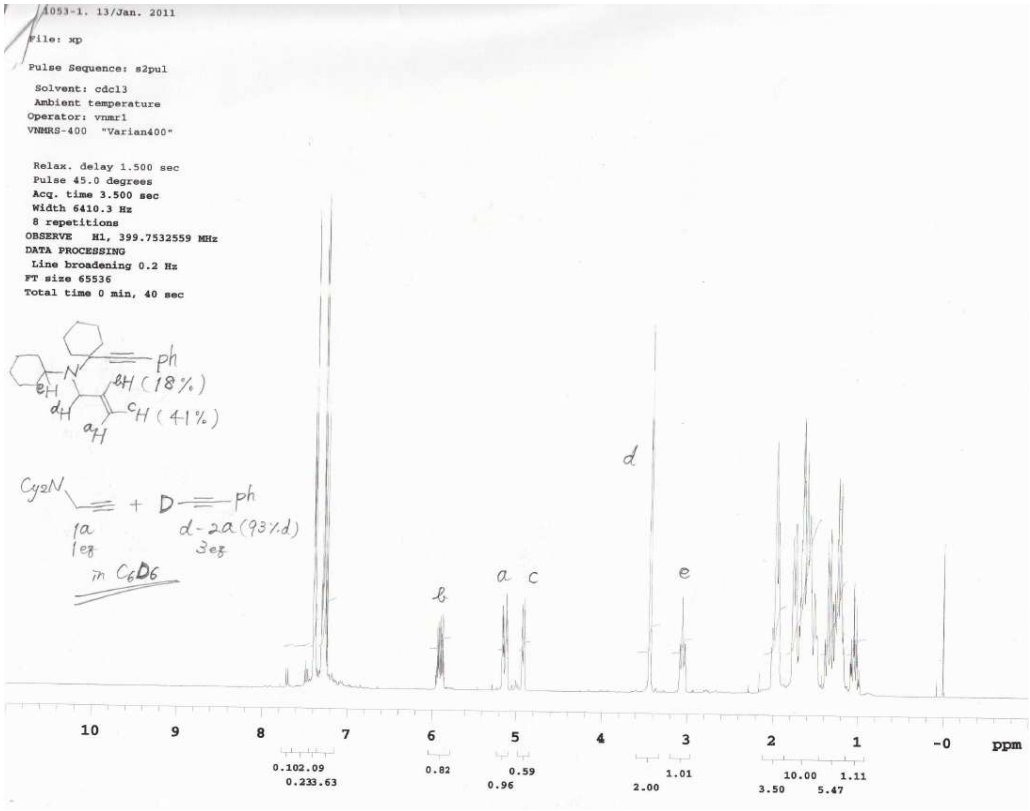
eq. (S3) ***d*-3a** (^{1}H NMR, $CDCl_3$)



eq. (S4) ***d*-3a** (^{1}H NMR, $CDCl_3$)



eq. (S5) ***d*-3a** (^{1}H NMR, $CDCl_3$)



eq. (S6) ***d*-3a** (^{1}H NMR, $CDCl_3$)