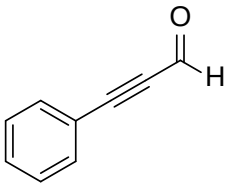
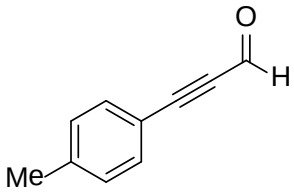
General Information.

All melting points were measured on a Yanaco MP-3S micro melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on JEOL AL 400 and JEOL Lambda 500 spectrometer spectrometers in $CDCl_3$ with Me_4Si as an internal reference. ^{13}C NMR spectra were recorded at 100 MHz. High-resolution mass spectra (HR-MS) and fast atom bombardment mass spectra (FAB MS) were obtained with JEOL GC Mate II, JMS-SX102, LCMS-IT-TOF (Shimadzu, Tokyo, Japan) and JEOL JMS 600H spectrometer. IR spectra were recorded with JASCO FT/IR-300 spectrometer. All reagents were purchased from commercial sources and used without purification. All evaporations were performed under reduced pressure. For column chromatography, silica gel (Kieselgel 60) was employed.

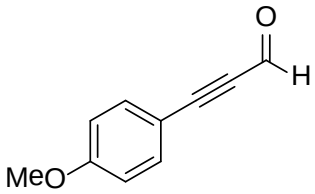
3-Phenyl-2-propynal [1a]



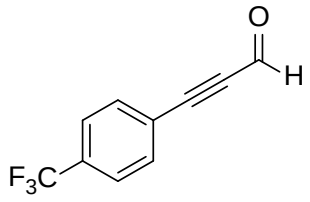
3-(4-Methylphenyl)-2-propynal [1b]



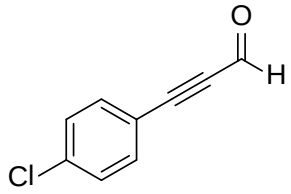
3-(4-Methoxylphenyl)-2-propynal [1a]



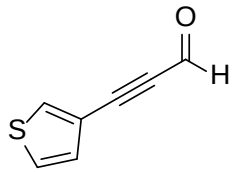
3-[4-(Trifluoromethyl)phenyl]- -2-propynal [1c]



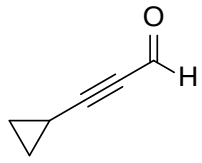
3-(4-Chlorophenyl)- 2-propynal [1d]



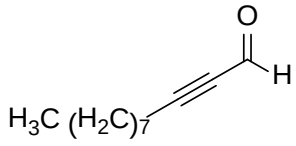
3-(3-Thienyl)- 2-propynal [1a]



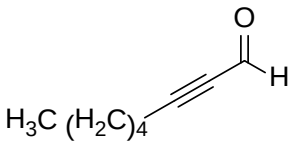
3-Cyclopropyl- 2-propynal [1e]



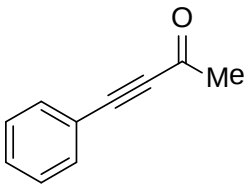
2-Undecynal [1f]



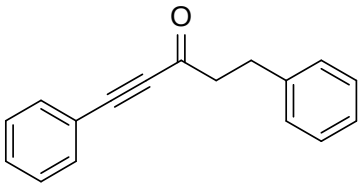
2-Octynal [1b]



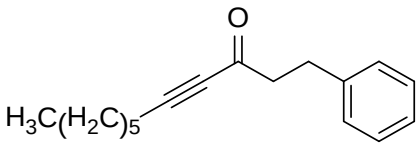
4-Phenyl-3-butyn-2-one [1g]



1,5-Diphenyl-1-pentyn-3-one [1h]



1-Phenyl-4-undecyn-3-one



Yellow oil.

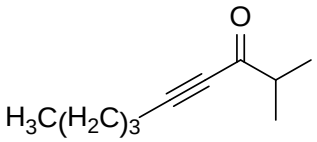
^{1}H-NMR($CDCl_3$) δ 0.89 (3H, *t*, *J* = 6.8Hz), 1.23-1.44 (6H, m), 1.53-1.61 (2H, m), 2.35 (2H, *t*, *J* = 7.2 Hz), 2.48-3.00 (4H, m), 7.18-7.21 (3H, m), 7.25-7.30 (2H, m).

^{13}C-NMR ($CDCl_3$) δ 14.0, 19.0, 22.5, 27.7, 28.5, 30.0, 31.2, 47.0, 80.8, 95.0, 126.2, 128.2 (2C), 128.5 (2C), 140.4, 187.1.

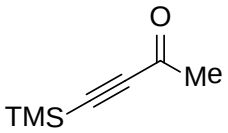
IR (KBr): 2932, 2214, 1675, 1455, 1160, 699 cm^{-1}.

HRMS-ESI+: m/z [M+] calcd for $C_{17}H_{22}NaO$: 265.1568; found 265.1572.

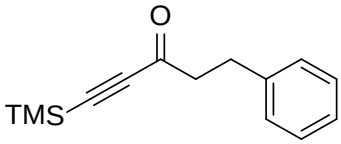
2-Methyl-4-nonyn-3-one [1i]



4-(Trimethylsilyl)-3-butyn-2-one [1j]



5-Phenyl-1-(trimethylsilyl)- 1-pentyn-3-one [1k]

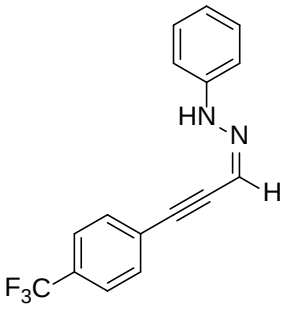


Preparation of substrates **1**.

1a-1s were prepared by the methods reported previously.[2a]

1a-1c, [2a] **1e**, [2a] **1f**, [2a] **1i**, [2a] **1j**,[2b] **1l**, [2a] **1m**, [2a] **1r** [2c] were all known compounds.

(*Z*)-1-Phenyl-2-[3-(4-trifluoromethyl)-phenylprop-2-yn-1-ylidene]hydrazine (1d)



Yellow oil.

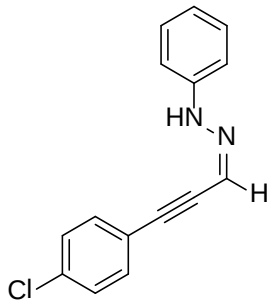
^{1}H-NMR ($CDCl_3$) δ 6.62 (1H, s), 6.95 (1H, t, *J* = 7.4Hz), 7.12 (2H, d, *J* = 3.8Hz), 7.28-7.32 (2H, m), 7.65 (4H, br-s), 8.67 (1H, s).

^{13}C-NMR ($CDCl_3$) δ 81.5 , 100.1, 113.4 (2C), 113.7, 121.5, 123.7 (q, *J* = 270.3Hz), 125.4, 125.5 (2C, q, *J* = 3.6Hz), 129.4 (2C), 131.0 (q, *J* = 32.9Hz), 131.9 (2C), 143.2.

IR(KBr): 3311, 3056, 2189, 1604, 1503, 1317, 748 cm^{-1}.

HRMS-EI: m/z [M+] calcd for $C_{16}H_{11}F_3N_2$:288.0874; found288.0875.

(*Z*)-1-(3-(4-Chlorophenyl)prop-2-yn-1-ylidene)-2-phenylhydrazine (1e)



Yellow solid, mp 42℃.

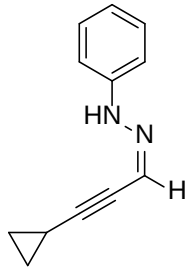
^{1}H-NMR ($CDCl_3$) δ 6.60 (1H, s), 6.93 (1H, t, *J* = 7.2Hz), 7.10 (2H, d, *J* = 7.6Hz), 7.27-7.31 (2H, m), 7.36 (2H, d, J = 8.4 Hz), 7.45 (2H, d, J = 8.4 Hz), 8.63 (1H, s).

^{13}C-NMR ($CDCl_3$) δ 80.4, 100.6, 113.3 (2C), 114.2, 120.0, 121.3, 129.0 (2C), 129.3 (2C), 132.9 (2C), 135.6, 143.3.

IR (KBr): 3299, 3058, 2183, 1600, 1490, 826 cm^{-1}.

HRMS-EI: m/z [M+] calcd for $C_{15}H_{11}N_2Cl$:254.0611; found 254.0609.

(*Z*)-1-(3-Cyclopropylprop-2-yn-1-ylidene)-2-phenylhydrazine (1g)



Brown oil.

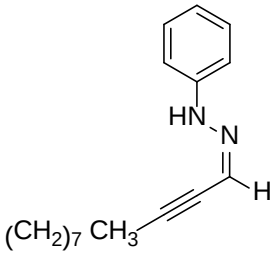
^{1}H-NMR ($CDCl_3$) δ 0.82-0.86 (2H,m), 0.93-0.97 (2H, m), 1.47-1.54 (1H, m), 6.33 (1H, s), 6.87 (1H, t, J = 7.2 Hz), 7.04 (2H, d, *J* = 7.6 Hz), 7.25 (2H, dd, J = 7.2, 7.6 Hz), 8.51 (1H, s).

^{13}C-NMR ($CDCl_3$) δ 0.4, 9.4 (2C), 66.9, 107.3, 113.1 (2C), 115.6, 120.7, 129.3 (2C), 143.7 cm^{-1}.

IR(KBr) : 3307, 3011, 2191, 1603, 1503, 1254, 749 cm^{-1}.

HRMS-EI: m/z [M+] calcd for $C_{12}H_{12}N_2$:184.1001; found 184.1000.

(Z)-1-Phenyl-2-(undec-2-yn-1-ylidene)hydrazine (1h)



Brown oil.

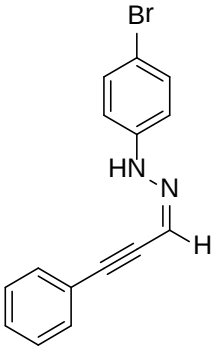
^{1}H-NMR ($CDCl_3$) δ 0.89 (3H, t, *J* = 6.8Hz), 1.28-1.33 (8H, m), 1.44-1.48 (2H, m), 1.59-1.66 (2H, m), 2.49 (2H, dt, J = 7.2, 1.6 Hz), 6.38 (1H, t, *J* = 1.6 Hz), 7.05 (2H, d, *J* = 7.6 Hz), 7.26 (2H, dd, J = 7.2, 7.6 Hz), 8.52 (1H, s).

^{13}C-NMR ($CDCl_3$) δ 14.1, 19.7, 22.6, 28.4, 29.0, 29.1, 29.2, 31.8, 71.8, 104.3, 113.0 (2C), 115.8120.7, 129.3 (2C), 143.7.

IR(KBr): 3310, 2855, 2197, 1604, 1504, 1255, 748 cm^{-1}.

HRMS-EI: m/z [M+] calcd for $C_{17}H_{24}N_2$:256.1940; found256.1941.

(*Z*)-1-(4-Bromophenyl)-2-(3-phenylprop-2-yn-1-ylidene)hydrazine (1k)



Yellow solid, mp 75 -78 ℃.

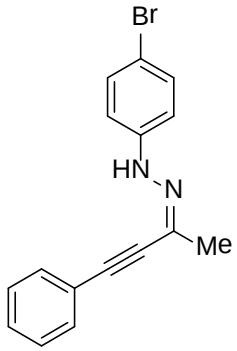
^{1}H-NMR($CDCl_3$) δ 6.63(1H, s), 6.98(2H, d, J = 9.2 Hz), 7.36-7.42(5H, m), 7.51-7.54(2H, m), 8.62 (1H, br-s).

^{13}C-NMR($CDCl_3$) δ 79.36, 102.2, 113.0, 114.8(2C), 115.5, 121.4, 128.6(2C), 129.6, 131.8(2C), 132.1(2C), 142.5 .

IR(KBr): 3313, 3067.23, 2182, 1593, 1529, 1495, 1256, 1067, 755 cm^{-1}.

HRMS-EI: m/z [M+] calcd for $C_{15}H_{11}N_2Br$: 298.0106; found 298.0103.

(*Z*)-1-(4-Bromophenyl)-2-(4-phenylbut-3-yn-2-ylidene)hydrazine (1n)



Yellow solid, mp 69 – 77 ℃.

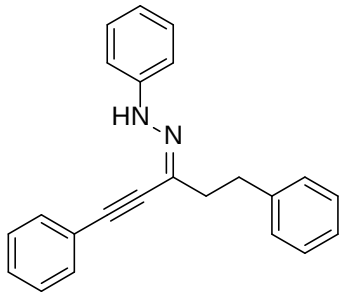
^{1}H-NMR($CDCl_3$) δ 2.23(3H, s), 6.96(2H, d, J = 8.8 Hz)7.33-7.41(5H, m), 7.52-7.54(2H, m), 8.25(1H, s).

^{13}C-NMR($CDCl_3$) δ 22.2, 80.7, 101.4, 112.0, 114.5(2C), 121.3, 124.5, 128.6, (2C), 129.5, 131.8(2C), 132.0(2C), 143.1 .

IR(KBr): 3307, 2184, 1591, 1542, 1497, 1257, 81, 750 cm^{-1}.

HRMS-EI: m/z [M+] calcd for $C_{16}H_{13}N_2Br$: 312.0262; found 312.0267.

(*Z*)-1-(1,5-Diphenylpent-1-yn-3-ylidene)-2-phenylhydrazine (1o)



Yellow solid, mp 56 -65 ℃.

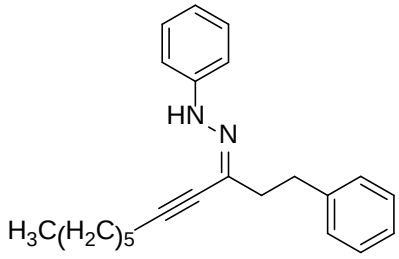
^{1}H-NMR($CDCl_3$) δ 2.81-2.85(2H, m), 3.02-3.06(2H, m), 6.87(1H, tt, J = 7.6, 1.2 Hz), 7.08(2H, dd, J = 8.8, 1.2 Hz), 7.19-7.30(7H, m), 7.39-7.42(3H, m), 7.52-7.54(2H, m), 8.34(1H, s).

^{13}C-NMR($CDCl_3$) δ 33.7, 37.6, 80.4, 102.1, 113.0(2C), 120.4, 121.6, 126.0, 127.2, 128.4(2C), 128.5(2C), 128.6(2C), 129.3(2C), 129.5, 131.8(2C), 141.3, 144.0 .

IR(KBr): 3311, 3027, 2172, 1601, 1529, 1506, 1260, 749, 688 cm^{-1}.

HRMS-EI: m/z [M+] calcd for $C_{23}H_{20}N_2$: 324.1627; found 324.1629.

(*Z*)-1-Phenyl-2-(1-phenylundec-4-yn-3-ylidene)hydrazine (1p)



Brown oil.

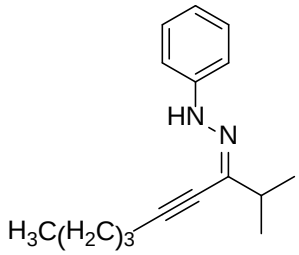
^{1}H-NMR($CDCl_3$) δ 0.92(3H, t, J = 7.2 Hz), 1.33-1.35(4H, m), 1.46-1.51(2H, m), 1.61-1.68(2H, m), 2.51(2H, t, J = 6.9 Hz), 2.68-2.72(2H, m), 2.96(2H, t, J = 8.5 Hz), 6.83(1H, t, J = 7.5 Hz), 7.02(2H, d, J = 7.5 Hz), 7.19-7.30(7H, m), 8.19(1H, s).

^{13}C-NMR($CDCl_3$) δ 14.1, 19.6, 22.6, 28.5, 28.6, 31.3, 33.5, 37.9, 72.7, 104.3, 112.9(2C), 119.9, 125.9, 128.3, 128.3(2C), 128.5(2C), 129.2(2C), 141.5, 144.3.

IR(KBr): 3311, 2955, 2929, 2203, 1603, 1505, 1254, 748, 692 cm^{-1}.

HRMS-EI: m/z [M+] calcd for $C_{23}H_{28}N_2$: 332.2253; found 332.2250.

(*Z*)-1-(2-Methylnon-4-yn-3-ylidene)-2-phenylhydrazine (1q)



Brown oil.

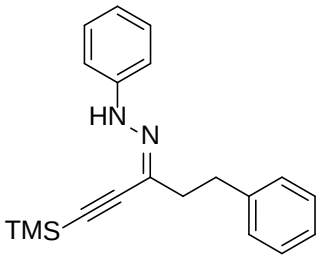
^{1}H-NMR ($CDCl_3$) δ 0.98 (3H, t, J= 7.6Hz), 1.18 (6H, d, *J* = 6.8Hz), 1.47-1.56 (2H, m), 1.60-1.67 (2H, m), 2.53 (2H, t, *J* = 6.8Hz), 2.66 (1H, heptet, J = 6.8 Hz), 6.80-6.84 (1H, m), 7.02-7.04 (2H, m), 7.21-7.25 (2H, m), 8.14 (1H, s).

^{13}C-NMR ($CDCl_3$) δ 13.6, 19.3, 20.6 (2C), 22.0, 30.6, 34.6, 71.6, 104.5, 112.8 (2C), 119.8, 129.2 (2C), 134.7, 144.6 .

IR(KBr): 2962, 2932, 2210, 1672, 1599, 1500, 1383, 761, 695 cm^{-1}.

HRMS-EI: m/z [M+] calcd for $C_{16}H_{22}N_2$:242.1783; found : 242.1785.

(*Z*)-1-Phenyl-2-(5-phenyl-1-(trimethylsilyl)pent-1-yn-3-ylidene)hydrazine (1s)



Brown oil.

^{1}H-NMR ($CDCl_3$) δ 0.30 (9H, s), 2.70-2.74 (2H, m), 2.94-2.98 (2H, m), 6.85 (1H, dt, J = 7.2, 1.2 Hz), 7.12 (2H, dd, J = 7.6, 1.2 Hz), 7.16-7.30 (7H, m), 8.32 (1H, s).

^{13}C-NMR ($CDCl_3$) δ 0.1 (3C), 33.6, 37.2, 95.8, 109.1, 113.1 (2C), 120.5, 126.1, 127.1, 128.5 (2C), 128.6 (2C), 129.4 (2C), 141.4, 144.0.

IR(KBr): 2960, 1677, 1601, 1498, 1253, 1108, 848, 697 cm^{-1}.

HRMS-EI: m/z [M+] calcd for $C_{20}H_{24}N_2Si$: 320.1709; found : 320.1712.

References

[1] a) S. Belot, A. Quintard, N. Krause, A. Alexakis, *Adv. Synth. Catal.* **2010**, *352*, 667.b) K. Y. Lee, M. J. Lee, S. GowriSankar, J. N. Kim, *Tetrahedron Lett.* **2004**, *45*, 5043. c) S, Oida, T, Tanaka, Y, Tajima, T, Konosu, A, Somada, T,Miyaoka, H, Yasuda, *PCT Int. WO/96/31491*. October **1996**. d) R. Fedor, B. Céline, A. Alexandre, *Org. Lett.* **2012**, *14*, 4906. e) I. E. Dolgii, K. N. Shavrin, S. V. Pavlycheva, *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya.* **1985**, *9*, 2146. f) L. Lin, O. Zhao, A. N. Li, F. Ren, F. Yang, R. Wang, *Org. Biomol. Chem*. ***2009***, *7*, 3663. g) P. Wessig, G. Mueller, A. Kuehn, R. Herre, H. Blumenthal, S. Troelenberg, *Synthesis* **2005**, *9*, 1445. h) M. Yamaguchi, K. Shibato, S. Fujiwara, I. Hirao, *Synthesis*. **1986**, *5*, 421. i) J. Chen, T. Lin, S. Chen, A. Chen, C. Mou, F. Tsai, *Tetrahedron* **2009**, *65*, 10134. j) S. Mukherjee, D. Kontokosta, A. Patil, S. Rallapalli, D. Lee, *J. Org. Chem.* **2009**, *74*, 9206. k) Y. Kiyotsuka, Y. Kobayashi, *J. Org. Chem.* **2009**, *74*, 7489.

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