J. Braz. Chem. Soc., Vol. 26, No. 1, S1-S23, 2015.
Printed in Brazil - ©2015 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Supplementary Information

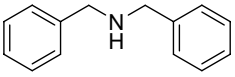
A^3-Coupling Reaction as a Strategy Towards the Synthesis of Alkaloids

Rafaela C. Carmona,[a] Edison P. Wendler,[a] George H. Sakae,[a] João V. Comasseto[a,b] and Alcindo A. Dos Santos*[,a]

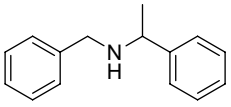
[a]Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, 05508-000 São Paulo-SP, Brazil

[b]Instituto de Ciências Ambientais, Químicas e Farmacêuticas, Universidade Federal de São Paulo, Av. Prof. Artur Riedel, 275, 09972-270 Diadema-SP, Brazil

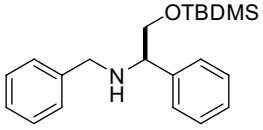
Spectroscopic data



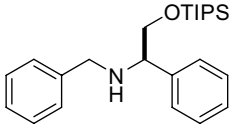
Dibenzylamine (**1b**): ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.35-7.20 (m, 10H, Ph-H), 3.81 (s, 4H, CH_2), 1.66 (s, NH); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.3, 128.4, 128.1, 126.9, 53.1; CAS 103-49-1.



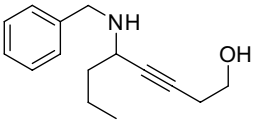
N-Benzyl-1-phenylethanamine (**1c**): ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.38-7.20 (m, 10H, Ph-H), 3.80 (q, 1H, *J* 6.6 Hz, CH), 3.62 (dd, 2H, *J* 13.2, 4.6 Hz, CH_2), 1.57 (s, NH), 1.35 (d, 3H, *J* 6.6 Hz, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 145.7, 140.8, 128.5, 128.4, 127.0, 126.9, 126.8, 57.6, 51.7, 24.6; CAS 3193-62-2.



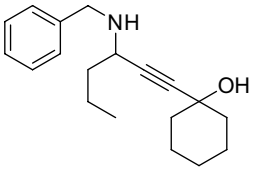
(*R*)-*N*-Benzyl-2-(*tert*-butyldimethylsilyloxy)-1-phenylethanamine (**1f**): ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.48-7.27 (m, 10H, Ph-H), 3.89-3.55 (m, 9H, CH_3), 0.92 (s, 9H, CH_3), 0.05 (s, 3H, CH_3), 0.04 (s, 3H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.7, 128.4, 128.3, 128.0, 127.7, 127.4, 126.7, 68.4, 64.1, 51.2, 25.9, 18.2, –5.5; HRMS calcd. for $C_{21}H_{31}NOSi$ $[M]^+$: 342.2253; found: 342.2243; CAS 1030828-88-6.



(*R*)-*N*-Benzyl-1-phenyl-2-(triisopropylsilyloxy)ethanamine (**1g**): ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.43-7.25 (m, 10H, Ph-H), 3.89-3.51 (m, 4H, CH_2 and 1H, CH), 1.78 (s, NH), 1.05-1.02 (m, 21H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.7, 128.4, 128.3, 128.0, 127.7, 127.4, 126.7, 68.7, 64.3, 51.2, 17.9, 11.9; IR (film) ν_{max}/cm^{-1} 3379, 3336, 3302, 3282, 3063, 3028, 2939, 2866, 1458, 1122, 1091, 1068, 883, 682; HRMS calcd. for $C_{34}H_{37}NOSi$ $[M]^+$: 384.2723; found: 384.2714.



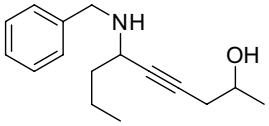
5-(Benzylamino)oct-3-yn-1-ol(**4a**) [Table 1]: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.39-7.18 (m, 5H, Ph-H), 3.97 (d, 1H, *J* 12.9 Hz, CH_2), 3.78 (d, 1H, *J* 12.9 Hz, CH_2), 3.68 (t, 1H, *J* 6.5 Hz, CH_2), 3.36 (ddt, 1H, *J* 7.6, 5.9, 1.8 Hz, CH), 2.55 (OH, NH), 2.46 (td, 2H, *J* 6.5, 1.9 Hz, CH_2), 1.35-1.65 (m, 4H, CH_2), 0.91 (t, 3H, *J* 7.2 Hz, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.7, 128.3, 128.2, 126.9, 82.8, 80.6, 61.0, 51.6, 49.3, 38.1, 23.0, 19.2, 13.7; IR (film) ν_{max}/cm^{-1} 3397, 3085, 3062, 3027, 2956, 2932, 2871, 2722, 1654, 1603, 1495, 1454, 1360, 1326, 1203, 1152, 1120, 1051, 970, 910, 848, 747, 699, 606, 548; MS *m/z* (%) 188 (M^{-43}, 43), 170 (< 1), 156 (1), 143 (< 1), 133 (2), 106 (3), 92 (8), 91 (100), 77 (5), 65 (11), 51 (5); HRMS calcd. for $C_{15}H_{21}NO$ $[M]^+$: 232.1701; found: 232.1694; eluent: hexane/EtOAc (1:1), *Rf* 0.5.



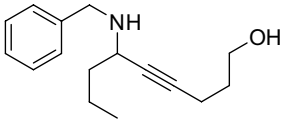
1-(3-(Benzylamino)hex-1-yn-1-yl)cyclohexanol (**4b**) [Table2, entry 1]: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.40-7.19 (m, 5H, Ph-H), 4.02 (d, 1H, *J* 12.8 Hz, CH_2), 3.81 (d, 1H, *J* 12.8 Hz, CH_2), 3.42 (dd, 1H, *J* 7.3, 6.0 Hz, CH), 1.83-1.36 (m, 14H, CH_2), 0.92 (t, 3H, *J* 7.1 Hz, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.2, 128.6, 128.5, 127.1, 87.5, 85.8, 68.9, 51.6, 49.4, 25.3, 23.7, 19.5, 14.0; IR (film) ν_{max}/cm^{-1} 3515, 3436, 3406, 3022, 2927, 2848, 1743, 1614, 1442, 1330, 1256, 1175, 1071, 1019, 965, 839, 739, 693; MS *m/z* (%) 242 (M^{-43}, 61), 224

*e-mail: alcindo@iq.usp.br

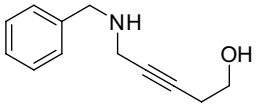
(4), 207 (30), 191 (3), 177 (1), 156 (2), 133 (4), 117 (2), 106 (6), 91 (100), 77 (4), 65 (7), 55 (6), 41 (6); HRMS calcd. for $C_{19}H_{27}NO$ $[M]^+$: 286.2171; found: 286.2159; eluent: hexane/EtOAc (1:1), *Rf* 0.4.



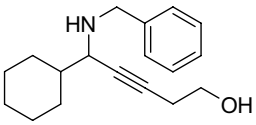
6-(Benzylamino)non-4-yn-2-ol (**4c**) [Table 2, entry 2]: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.39-7.18 (m, 5H, Ph-H), 3.99 (d, 1H, *J* 12.9 Hz, CH_2), 3.93 (sext, 1H, *J* 6.0 Hz, CH_2), 3.80 (d, 1H, *J* 12.9 Hz, CH_2), 3.37 (ddt, 1H, *J* 7.7, 5.8, 1.8 Hz, CH), 2.40 (td, 1H, *J* 16.4, 1.9 Hz, CH), 2.39 (td, 1H, *J* 16.4, 1.3 Hz, CH_2), 2.02 (OH, NH), 1.67-1.38 (m, 4H, CH_2), 1.27 (t, 3H, *J* 6.1 Hz, CH_3), 0.91 (t, 3H, *J* 7.2 Hz, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.9, 128.3, 128.2, 126.9, 84.0, 80.0, 66.4, 51.4, 49.3, 38.3, 29.3, 22.3, 19.3, 13.8; IR (film) ν_{max}/cm^{-1} 3381, 3086, 3062, 2959, 2930, 2871, 1603, 1495, 1372, 1321, 1208, 1150, 1117, 1086, 1028, 940, 830, 737, 698; MS *m/z* (%) 202 (M^{-29}, 39), 184 (< 1), 158 (3), 141 (1), 133 (2), 106 (4), 91 (100), 77 (5), 65 (11), 51 (4); HRMS calcd. for $C_{16}H_{23}NO$ $[M]^+$: 246.1858; found: 246.1869; eluent: hexane/EtOAc (1:1), *Rf* 0.4.



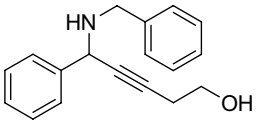
6-(Benzylamino)non-4-yn-1-ol (**4d**) [Table 2, entry 3]: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.40-7.19 (m, 5H, Ph-H), 4.00 (d, 1H, *J* 12.8 Hz, CH_2), 3.78 (d, 1H, *J* 12.8 Hz, CH_2), 3.76 (t, 2H, *J* 6.2 Hz, CH_2),3.35 (ddt, 1H, *J* 7.6, 5.9, 1.9 Hz, CH), 2.36 (td, 2H, *J* 6.9, 1.9 Hz, CH_2), 1.88-1.32 (m, 6H, CH_2), 0.91 (t, 3H, *J* 7.1 Hz, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.1, 128.5, 128.4, 127.1, 83.3, 82.0, 61.7, 51.5, 49.5, 38.5, 31.7, 19.5, 15.4, 14.0; IR (film) ν_{max}/cm^{-1} 3292, 2927, 2923, 2863, 2219, 1665, 1602, 1451, 1321, 1091, 1055, 1028, 907, 741, 698; MS *m/z* (%) 246 (M^{+1}, < 1), 228 (< 1), 214 (< 1), 202 (100), 186 (1), 170 (2), 160 (6), 157 (1), 143 (2), 129 (3), 115 (2), 106 (8), 91 (97), 77 (11), 65 (24), 51 (5), 41 (8); HRMS calcd. for $C_{16}H_{23}NO$ $[M]^+$: 246.1858; found: 246.1857; eluent: hexane/EtOAc (1:1), *Rf* 0.5.



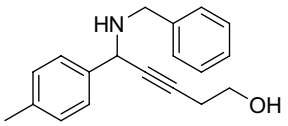
5-(Benzylamino)pent-3-yn-1-ol (**4e**) [Table 2, entry 4]: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.41-7.19 (m, 5H, Ph-H), 3.72 (t, 2H, *J* 6.3 Hz, CH_2), 3.67 (s, 2H, CH_2), 3.38 (t, 2H, *J* 2.1 Hz, CH_2), 2.50 (tt, 2H, *J* 6.2, 2.1 Hz, CH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 137.7, 129.4, 128.5, 127.5, 82.3, 77.1, 61.2, 57.4, 42.4, 23.3; IR (film) ν_{max}/cm^{-1} 3313, 2910, 2873, 2819, 2222, 1653, 1462, 1451, 1326, 1037, 845, 703, 698; MS *m/z* (%) 158 (M^{-31}, 19), 143 (3), 126 (42), 112 (38), 91 (100), 77 (9), 65 (28), 53 (16), 42 (35); HRMS calcd. for $C_{12}H_{15}NO$ $[M]^+$: 190.1232; found: 190.1226; eluent: hexane/EtOAc (1:1), *Rf* 0.2.



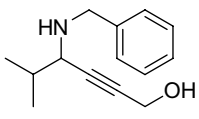
5-(Benzylamino)-5-cyclohexylpent-3-yn-1-ol (**4f**) [Table 2, entry 5]: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.39-7.18 (m, 5H, Ph-H), 4.01 (d, 1H, *J* 13.0 Hz, CH_2), 3.78 (d, 1H, *J* 13.0 Hz, CH_2), 3.73 (t, 2H, *J* 6.3 Hz, CH_2), 3.17 (dt, 1H, *J* 5.6, 2.0 Hz, CH), 2.52 (td, 2H, *J* 6.3, 2.0 Hz, CH_2), 1.88 (OH, NH), 1.85-1.02 (m, 10H, CH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.1, 128.4, 128.3, 127.0, 82.5, 81.0, 61.4, 55.0, 51.6, 42.5, 30.2, 28.7, 26.5, 26.2, 26.1, 23.3; IR (film) ν_{max}/cm^{-1} 3309, 3065, 3060, 3025, 2918, 2848, 2222, 1602, 1494, 1448, 1368, 1321, 1083, 1044, 1028, 845, 733, 698; MS *m/z* (%) 270 (M^{-1}, < 1), 226 (< 1), 188 (100), 156 (3), 133 (2), 106 (3), 91 (89), 77 (3), 65 (8), 55 (5), 41 (6); HRMS calcd. for $C_{18}H_{25}NO$ [M + 2H]: 273.2093; found: 273.2079; eluent: hexane/EtOAc (1:1), *Rf* 0.4.



5-(Benzylamino)-5-phenylpent-3-yn-1-ol (**4g**) [Table 2, entry 6]: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.55-7.20 (m, 10H, Ph-H), 4.55 (t, 1H, *J* 2.0 Hz, CH), 3.87 (s, 2H, CH_2), 3.74 (t, 2H, *J* 6.3 Hz, CH_2), 2.55 (td, 2H, *J* 6.3, 2.0 Hz, CH_2), 2.03 (OH, NH); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.6, 139.7, 128.7, 128.6, 128.4, 127.9, 127.6, 127.4, 82.5, 82.0, 61.3, 53.4, 51.2, 23.4; IR (film) ν_{max}/cm^{-1} 3311, 3068, 3058, 3026, 2923, 2874, 2830, 2230, 1948, 1600, 1492, 1451, 1327, 1188, 1027, 846, 737, 696, 545; MS *m/z* (%) 264 (M^{-1}, 15), 238 (11), 220 (35), 207 (4), 188 (30), 174 (38), 159 (18), 141 (8), 128 (36), 115 (17), 106 (23), 91 (100), 77 (17), 65 (19), 51 (11), 41 (2); HRMS calcd. for $C_{18}H_{19}NO$ [M + H]: 266.1545; found: 266.1539; eluent: hexane/EtOAc (1:1), *Rf* 0.6.

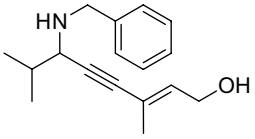


5-(Benzylamino)-5-(*p*-tolyl)pent-3-yn-1-ol (**4h**) [Table 2, entry 7]: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.40-7.07 (m, 9H, Ph-H), 4.47 (t, 1H, *J* 1.8 Hz, CH), 3.81 (s, 2H, CH_2), 3.66 (t, 2H, *J* 6.4 Hz, CH_2), 2.75 (OH, NH), 2.46 (td, 2H, *J* 6.4, 1.8 Hz, CH_2), 2.31 (s, 3H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 139.5, 137.5, 137.4, 129.2, 128.5, 128.4, 127.5, 127.14, 82.6, 81.7, 60.1, 53.0, 51.0, 23.3, 21.1; eluent: hexane/EtOAc (1:1), *Rf* 0.6.

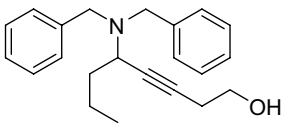


4-(Benzylamino)-5-methylhex-2-yn-1-ol (**4i**) [Table 2, entry 8]: ^{1}H NMR (400.1 MHz, $CDCl_3$)

δ 7.38-7.21 (m, 5H, Ph-H), 4.30 (d, 2H, *J* 1.7 Hz, CH_2), 4.01 (d, 1H, *J* 13.0 Hz, CH), 3.80 (d, 1H, *J* 13.0 Hz, CH_2), 3.22 (dt, 2H, *J* 5.4, 1.7 Hz, CH_2), 2.15 (OH, NH), 1.86 (oct, 1H, *J* 6.7 Hz, CH_2), 0.99 (d, 3H, *J* 6.8 Hz, CH_3), 0.98 (d, 3H, *J* 6.8 Hz, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.8, 128.3, 126.9, 85.3, 82.9, 55.6, 51.6, 50.9, 32.5, 19.6, 17.9; IR (film) ν_{max}/cm^{-1} 3322, 3085, 3062, 3028, 2959, 2928, 2870, 1603, 1495, 1454, 1384, 1363, 1230, 1152, 1106, 1072, 1017, 976, 865, 747, 699, 590; MS *m/z* (%) 174 (M^{-43}, 30), 149 (3), 132 (2), 107 (4), 92 (9), 91 (100), 77 (8), 65 (13), 51 (6); HRMS calcd. for $C_{14}H_{19}NO$ [M + H]: 218.1545; found: 218.1544; eluent: hexane/EtOAc (1:1), *Rf* 0.5.

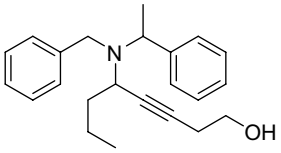


(*E*)-6-(Benzylamino)-3,7-dimethyloct-2-en-4-yn-1-ol (**4j**) [Table 2, entry 9]: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.38-7.22 (m, 5H, Ph-H), 5.97 (tq, 1H, *J* 6.8, 1.4 Hz, CH), 4.20 (dq, 2H, *J* 6.8, 0.6 Hz, CH_2), 4.02 (d, 1H, *J* 12.9 Hz, CH), 3.80 (d, 1H, *J* 12.9 Hz, CH_2), 3.29 (d, 1H, *J* 5.3 Hz, CH_2), 1.86 (oct, 1H, *J* 6.7 Hz, CH),1.84 (dt, 3H, *J* 1.4, 0.6 Hz, CH_3), 1.83 (OH, NH), 1.00 (d, 3H, *J* 6.7 Hz, CH_3), 0.99 (d, 3H, *J* 6.7 Hz, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.9, 134.8, 128.3, 126.9, 120.6, 87.7, 86.9, 58.9, 56.0, 51.6, 32.7, 19.7, 17.8; IR (film) ν_{max}/cm^{-1} 3310, 3085, 3062, 3028, 2959, 2925, 2870, 1633, 1604, 1495, 1453, 1366, 1252, 1093, 1012, 909, 849, 803, 747, 699, 622; MS *m/z* (%) 214 (M^{-43}, 29), 196 (2), 182 (2), 167 (1), 149 (9), 133 (3), 106 (4), 92 (10), 91 (100), 77 (10), 65 (14), 55 (10); HRMS calcd. for $C_{17}H_{23}NO$ $[M]^+$: 258.1858; found: 258.1857; eluent: hexane/EtOAc (1:1), *Rf* 0.5.

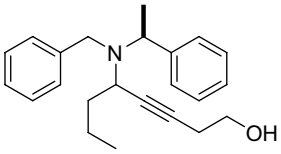


5-(Dibenzylamino)oct-3-yn-1-ol (**4k**) [Table 2, entry 10]: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.44-7.15 (m, 10H, Ph-H), 3.80 (d, 2H, *J* 13.9 Hz, CH_2), 3.76 (t, 2H, *J* 6.3 Hz, CH_2), 3.39 (tt, 2H, *J* 7.6, 2.1 Hz, CH), 3.35 (d, 2H, *J* 13.9 Hz, CH_2), 2.57 (td, 2H, *J* 6.3, 2.1 Hz, CH_2), 1.83 (OH), 1.78-1.31 (m, 4H, CH_2), 0.79 (t, 3H, *J* 7.2 Hz, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.0, 128.9, 128.3, 127.0, 81.1, 80.6, 61.6, 55.0, 51.6, 36.3, 23.3, 19.8, 13.8; IR (film) ν_{max}/cm^{-1} 3366, 3062, 3028, 2954, 2931, 2870, 2831, 2808, 1600, 1492, 1454, 1122, 1045, 744, 698; MS *m/z* (%) 278 (M^{-43}, 9), 247 (< 1), 194 (< 1), 181 (< 1), 168 (< 1), 156 (< 1), 141 (< 1), 128 (< 1), 106 (< 1), 91 (100), 77 (5), 65 (13), 51 (2), 41 (5); HRMS calcd. for $C_{22}H_{27}NO$ $[M]^+$: 322.2171; found: 322.2161; eluent: hexane/EtOAc (4:1).

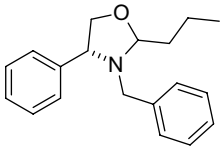
5-(Benzyl(1-phenylethyl)amino)oct-3-yn-1-ol (**4l**) [Table 2, entry 11] (diastereoisomeric mixture): ^{1}H NMR



(200.1 MHz, $CDCl_3$) δ 7.51-7.12 (m, 20H, Ph-H), 4.04-3.51 (m, 8H, CH_2), 3.49 (tt, 1H, *J* 7.2, 2.0 Hz, CH), 3.37 (tt, 1H, *J* 7.5, 2.1 Hz, CH), 2.53 (td, 2H, *J* 6.2, 2.0 Hz, CH_2), 2.40 (td, 2H, *J* 6.1, 2.0 Hz, CH_2), 1.62 (OH), 1.48 (d, 3H, *J* 6.8 Hz, CH_2), 1.59-0.87 (m, 8H, CH_2), 1.24 (d, 3H, *J* 6.9 Hz, CH_2), 0.79 (t, 3H, *J* 7.1 Hz, CH_3), 0.67 (t, 3H, *J* 7.2 Hz, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 144.5, 144.4, 142.7, 141.1, 128.9, 128.3, 128.1, 128.0, 127.9, 127.1, 126.8, 126.7, 126.5, 83.8, 81.9, 80.9, 80.5, 61.6, 61.5, 61.4, 56.7, 52.3, 51.7, 51.4, 48.8, 37.9, 37.7, 23.4, 23.3, 22.2, 19.9, 19.7, 13.9, 13.7, 13.3.; IR (film) ν_{max}/cm^{-1} 3360, 3082, 3063, 3028, 2958, 2931, 2873, 2499, 1751, 1739, 1705, 1654, 1635, 1624, 1600, 1492, 1454, 1126, 1045, 748, 698; HRMS calcd. for $C_{23}H_{29}NO$ $[M]^+$: 336.2327; found: 264.2317; eluent: hexane/EtOAc (4:1).

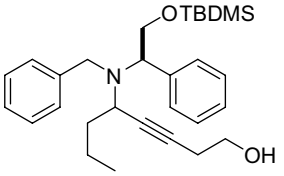


5-(Benzyl((*S*)-1-phenylethyl)amino)oct-3-yn-1-ol (**4m**) [Table 2, entry 12] (diastereoisomeric mixture): ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.54-7.19 (m, 20H, Ph-H), 4.06-3.49 (m, 10H, CH_2), 2.57 (tt, 1H, *J* 7.5, 2.1 Hz, CH), 2.57 (td, 2H, *J* 6.3, 2.1 Hz, CH_2), 2.45 (td, 2H, *J* 6.1, 2.1 Hz, CH_2), 1.53 (d, 14H, *J* 6.9 Hz, CH_2), 1.28 (d, 4H, *J* 6.9 Hz, CH_2), 1.63-1.18 (m, 14H, CH_2), 0.83 (t, 3H, *J* 6.8 Hz, CH_3), 0.71 (t, 3H, *J* 7.2 Hz, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 144.3, 142.5, 140.9, 129.7, 128.1, 127.9, 128.1, 127.9, 127.8, 127.7, 126.9, 126.6, 126.5, 126.3, 83.6, 81.7, 80.7, 80.3, 61.4, 61.2, 56.5, 52.1, 51.5, 51.2, 48.7, 37.7, 37.5, 23.2, 23.1, 22.0, 19.7, 19.5, 13.7, 13.5, 13.1; IR (film) ν_{max}/cm^{-1} 3360, 3082, 3063, 3028, 2958, 2931, 2873, 2499, 1751, 1739, 1705, 1654, 1635, 1624, 1600, 1492, 1454, 1126, 1045, 748, 698; HRMS calcd. for $C_{23}H_{29}NO$ [M + Na]: 358.2147; found: 358.2144; eluent: hexane/EtOAc (4:1).

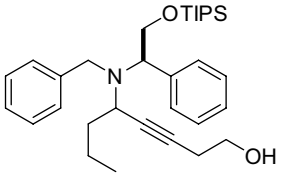


(4*R*)-3-Benzyl-4-phenyl-2-propyloxazolidine (**4n**) [Table 2, entry 13]: ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 7.56-7.23 (m, 10H, Ph-H), 4.37-4.33 (m, 1H, CH), 4.13 (t, 1H, *J* 7.5 Hz, CH), 3.87 (dd, 2H, *J* 14.6, 7.5 Hz, CH_2), 3.77-3.43 (m, 2H, CH_2), 1.53-1.22 (m, 4H, CH_2), 0.78 (m, 3H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 139.9, 138.0, 132.4, 129.1, 128.4, 127.9, 127.8, 127.5, 126.9, 96.5, 73.0, 67.9, 55.2, 36.9, 14.4, 14.1; IR (film) ν_{max}/cm^{-1} 3379, 3296, 3263, 3163, 3028, 2958, 2931, 2870, 2823, 2777, 2731, 1600, 1492, 1454, 1157, 756, 698; MS *m/z* (%) 238 (M^{-43}, 35), 210 (2), 117 (4), 104 (6), 91 (100), 77 (6), 65 (14), 51

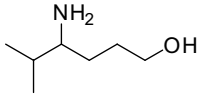
(5), 41 (22); HRMS calcd. for $C_{19}H_{23}NO$ $[M]^+$: 282.1858; found: 282.1857; eluent: hexane/EtOAc (6:1).



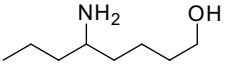
5-(Benzyl((*R*)-2-(*tert*-butyldimethylsilyloxy)-1-phenylethyl)amino)oct-3-yn-1-ol (**4o**) [Table 2, entry 14] (diastereoisomeric mixture): ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 8.88-6.20 (m, 20H, Ph-H), 4.57-3.67 (m, 12H, CH_2 and 4H, CH), 2.71 (td, 2H, *J* 6.3, 2.1 Hz, CH_2), 2.57 (td, 2H, *J* 6.3, 2.1 Hz, CH_2), 2.08 (s, OH), 1.96-1.30 (m, 10H, CH_2), 0.84 (m, 24H), 0.20 (s, 3H, CH_3), 0.18 (s, 3H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 141.9, 141.5, 141.2, 140.6, 129.0, 128.7, 128.5, 128.1, 128.0, 127.9, 127.8, 127.7, 127.1, 126.7, 126.6, 126.4, 83.2, 81.6, 80.6, 80.5, 67.4, 65.6, 64.7, 62.4, 61.3, 61.2, 52.3, 51.9, 51.6, 50.4, 37.6, 37.2, 25.8, 27.7, 23.3, 23.1, 19.7, 19.5, 18.2, 18.1, 13.8, –5.8, –5.7, –5.5; IR (film) ν_{max}/cm^{-1} 3063, 3028, 2954, 2931, 2858, 2738, 2708, 1654, 1600, 1492, 1454, 1388, 1361, 1327, 1253, 1107, 1084, 1049, 1006, 910, 837, 810, 775, 732, 698; HRMS calcd. for $C_{29}H_{43}NO_2Si$ $[M]^+$: 466.3141; found: 466.3150; eluent: hexane/EtOAc (6:1).



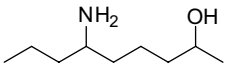
5-(Benzyl((*R*)-1-phenyl-2-(triisopropylsilyloxy) ethyl)amino)oct-3-yn-1-ol (**4p**) [Table 2, entry 15] (diastereoisomeric mixture): ^{1}H NMR (200.1 MHz, $CDCl_3$) δ 8.03-6.75 (m, 20H, Ph-H), 5.18-3.35 (m, 12H, CH_2 and 4H, CH), 2.49 (td, 2H, *J* 6.4, 2.1 Hz, CH_2), 2.37 (td, 2H, *J* 6.2, 2.0 Hz, CH_2), 1.79 (s, OH), 1.69-1.13 (m, 12H, CH_2), 1.01 (s, 24H, CH_2), 0.86 (s, 18H, CH_2 and 6H, CH_3), 0.66 (t, 3H, *J* 6.3 Hz, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 142.0, 141.5, 141.2, 140.1, 129.0, 128.8, 128.5, 128.1, 128.0, 127.8, 127.6, 127.0, 126.6, 126.4, 83.2, 81.6, 80.5, 80.4, 65.0, 62.4, 61.3, 61.2, 52.4, 51.8, 51.7, 50.2, 37.5, 37.3, 23.2, 23.1, 19.7, 19.5, 18.0, 17.8, 13.8, 13.5, 11.9, 11.8; IR (film) ν_{max}/cm^{-1} 3375, 3360, 3063, 3028, 2939, 2866, 2758, 2723, 2364, 2341, 1654, 1492, 1454, 1384, 1365, 1111, 1053, 883, 682; HRMS calcd. for $C_{32}H_{49}NO_2Si$ $[M]^+$: 508.3618; found: 508.3643l; eluent: hexane/EtOAc (6:1).



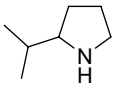
4-Amino-5-methylhexan-1-ol (**5a**) [Scheme 1]: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 3.59 (OH, NH_2), 3.70-3.21 (m, 2H, CH_2), 2.53 (ddd, 1H, *J* 9.3, 4.8, 2.3 Hz, CH), 1.79-1.57 (m, 4H, CH_2), 1.36-1.21 (m, 1H, CH), 0.91 (d, 3H, *J* 6.8 Hz, CH_3), 0.88 (d, 3H, *J* 6.8 Hz, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 62.5, 56.9, 33.6, 32.2, 30.7, 18.8, 17.2; CAS 1606-35-5.



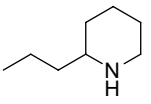
5-Aminooctan-1-ol (**5b**) [Scheme 1]: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 3.60 (t, 2H, *J* 6.3 Hz, CH_2), 2.76-2.67 (m, 1H, CH), 2.34 (OH, NH_2), 1.64-1.19 (m, 10H, CH_2), 0.91 (t, 3H, *J* 6.9 Hz, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 61.8, 50.7, 40.2, 37.2, 32.6, 22.1, 19.1, 14.0; IR (film) ν_{max}/cm^{-1} 3353, 2954, 2930, 2862, 1642, 1583, 1462, 1435, 1378, 1308, 1123, 1060, 913, 816, 741; MS *m/z* (%) 126 (M^{-19}, < 1), 107 (< 1), 102 (14), 85 (35), 72 (100), 67 (12), 56 (14); HRMS calcd. for $C_8H_{19}NO$ $[M]^+$: 146.1545; found: 146.1541; eluent: EtOAc/MeOH (9:1), *Rf* 0.1.



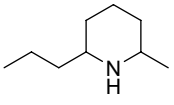
6-Aminononan-2-ol (**5c**) [Scheme 1] (diastereoisomeric mixture): ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 3.79 (sext, 1H, *J* 5.9 Hz, CH), 2.83 (OH, NH_2), 2.75 (s, 1H, CH), 1.58-1.21 (m, 10H, CH_2), 1.18 (d, 3H, *J* 6.1 Hz, CH_3), 0.92 (t, 3H, *J* 6.5 Hz, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 67.4, 67.1, 50.8, 50.7, 39.9, 39.8, 39.2, 39.0, 37.1, 36.8, 23.5, 23.4, 22.0, 21.9, 19.1, 14.4; IR (film) ν_{max}/cm^{-1} 3360, 2959, 2930, 2870, 1638, 1576, 1462, 1373, 1309, 1131, 1084, 943, 853, 816, 741; MS *m/z* (%) 159 (M^+, 4), 149 (8), 136 (21), 130 (32), 117 (100), 96 (29), 91 (43), 73 (52), 69 (27), 55 (52); HRMS calcd. for $C_9H_{21}NO$ $[M]^+$: 160.1701; found: 160.1698; eluent: EtOAc/MeOH (9:1), *Rf* 0.1.



(±)-2-Isopropylpyrrolidine (**6a**) [Scheme 1]: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 3.00 (ddd, 1H, *J* 10.3, 7.3, 5.4 Hz, CH), 2.82 (ddd, 1H, *J* 10.3, 7.7, 7.0 Hz, CH), 2.50 (NH), 2.48 (ddt, 1H, *J* 8.5, 7.9, 1.7 Hz, CH), 1.78-1.68 (m, 2H, CH_2), 1.50 (oct, 1H, *J* 6.6 Hz, CH), 1.35-1.21 (m, 2H, CH_2), 0.97 (d, 3H, *J* 6.6 Hz, CH_3), 0.90 (d, 3H, *J* 6.6 Hz, CH_3);^{13}C NMR (100.6 MHz, $CDCl_3$) δ 60.4, 46.6, 33.8, 29.6, 25.4, 19.4; CAS 51503-10-7.



(±)-2-Propylpiperidine-(±)-coniine (**6b**) [Scheme 1]: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 3.09-3.02 (m, 1H, CH_2), 2.62 (td, 2H, *J* 11.7, 2.8 Hz, CH_2), 2.50-2.37 (m, 1H, CH_2), 2.04 (NH), 1.81-1.71 (m, 1H, CH), 1.69-1.52 (m, 2H, CH_2), 1.47-1.20 (m, 7H, CH_2), 1.12-0.99 (m, 1H, CH), 0.90 (t, 3H, *J* 6.8 Hz, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 56.6, 47.1, 39.6, 32.9, 26.6, 24.8, 18.9, 14.1; CAS 3238-60-6.



(±)-2-Methyl-6-propylpiperidine-(±)-dihydropyridine (**6c**) [Scheme 1] (diastereoisomeric mixture): ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 3.12-3.01 (m, 1H, CH), 2.95-2.85 (m, 1H, CH), 2.65 (td, 1H, *J* 6.3, 2.4 Hz, CH_2), 2.60 (td, 1H, *J* 6.3, 2.4 Hz, CH_2), 2.43 (NH), 1.89-1.82 (m, 1H, CH_2),

1.80-1.71 (m, 2H, CH_2), 1.68-1.15 (m, 24H, CH_2), 1.08 (d, 3H, *J* 6.3 Hz, CH_3), 1.06 (d, 3H, *J* 6.3 Hz, CH_3), 0.92 (t, 3H, *J* 7.1 Hz, CH_3), 0.91 (t, 3H, *J* 7.1 Hz, CH_3);^{13}C NMR (100.6 MHz, $CDCl_3$) δ 56.8, 52.4, 39.5, 34.3, 32.9, 24.8, 22.9, 19.4, 19.0, 14.4, 14.2; CAS 68170-79-6.

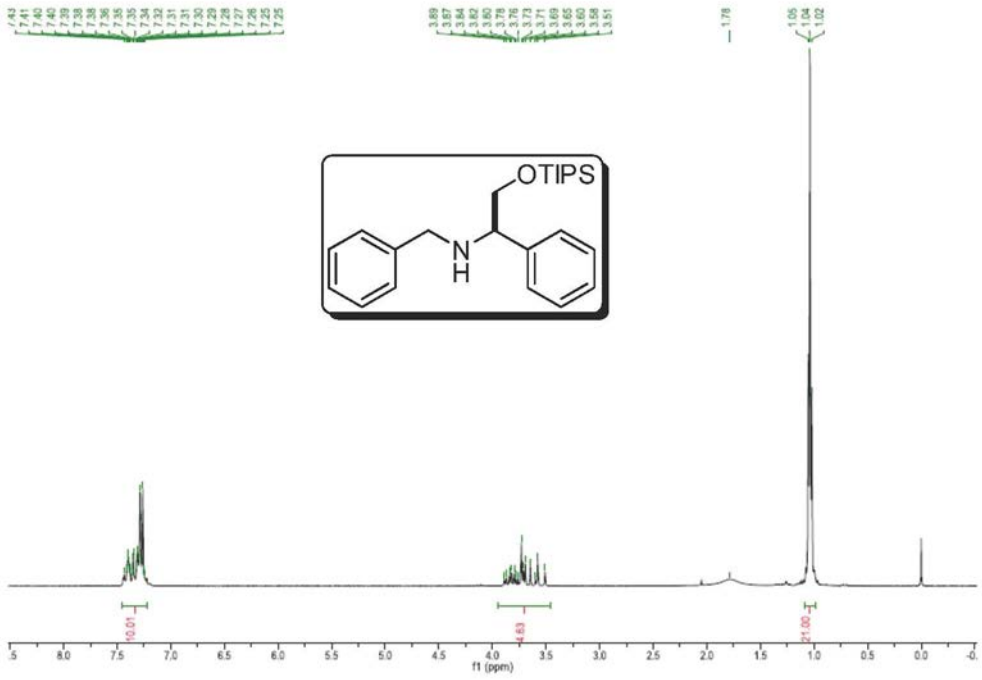


Figure S1. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of (*R*)-*N*-benzyl-1-phenyl-2-(triisopropylsilyloxy)ethanamine (**1g**).

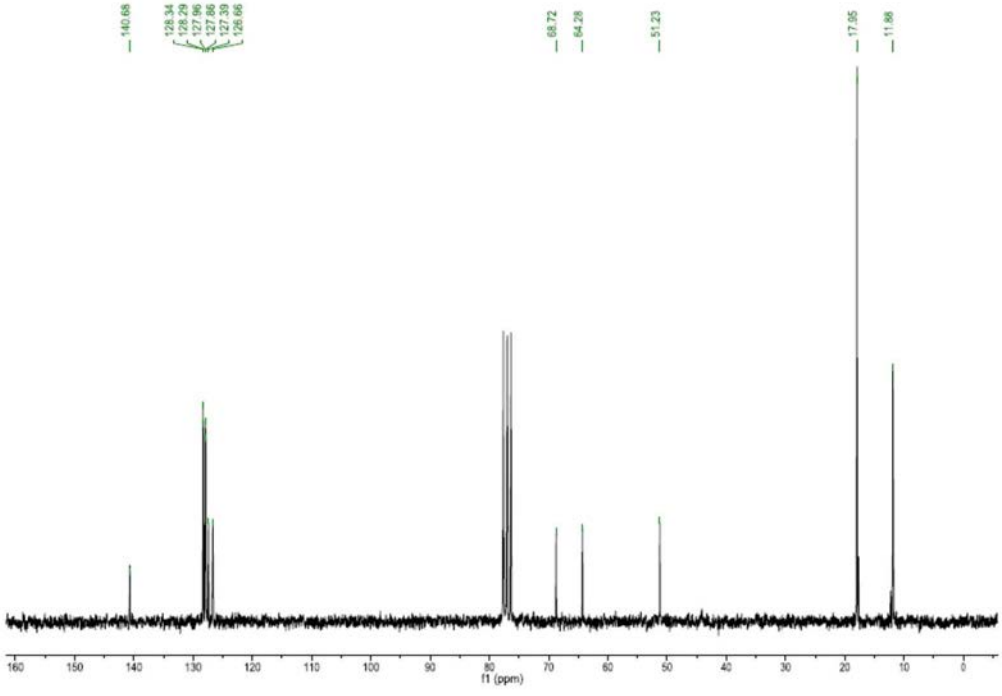


Figure S2. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of (*R*)-*N*-benzyl-1-phenyl-2-(triisopropylsilyloxy)ethanamine (**1g**).

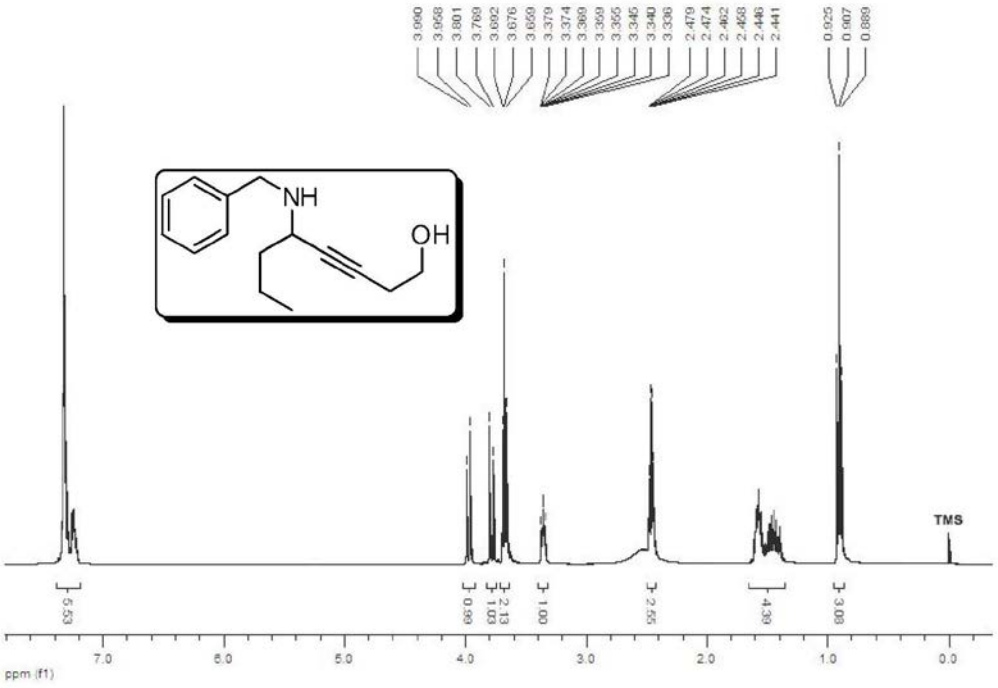


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 5-(benzylamino)oct-3-yn-1-ol (**4a**) [Table 1].

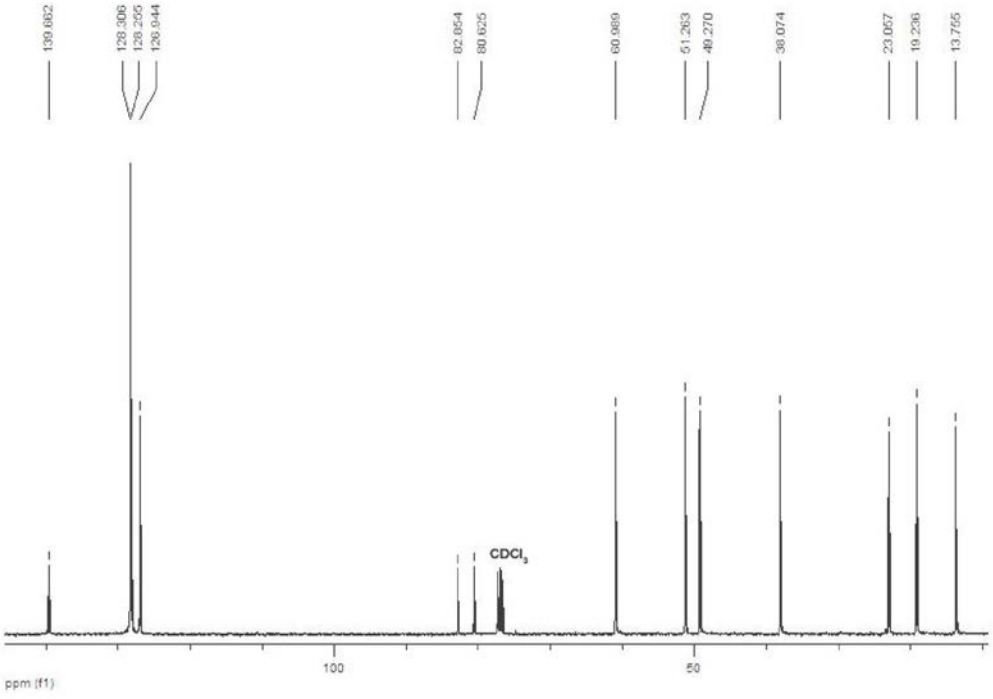


Figure S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 5-(benzylamino)oct-3-yn-1-ol (**4a**) [Table 1].

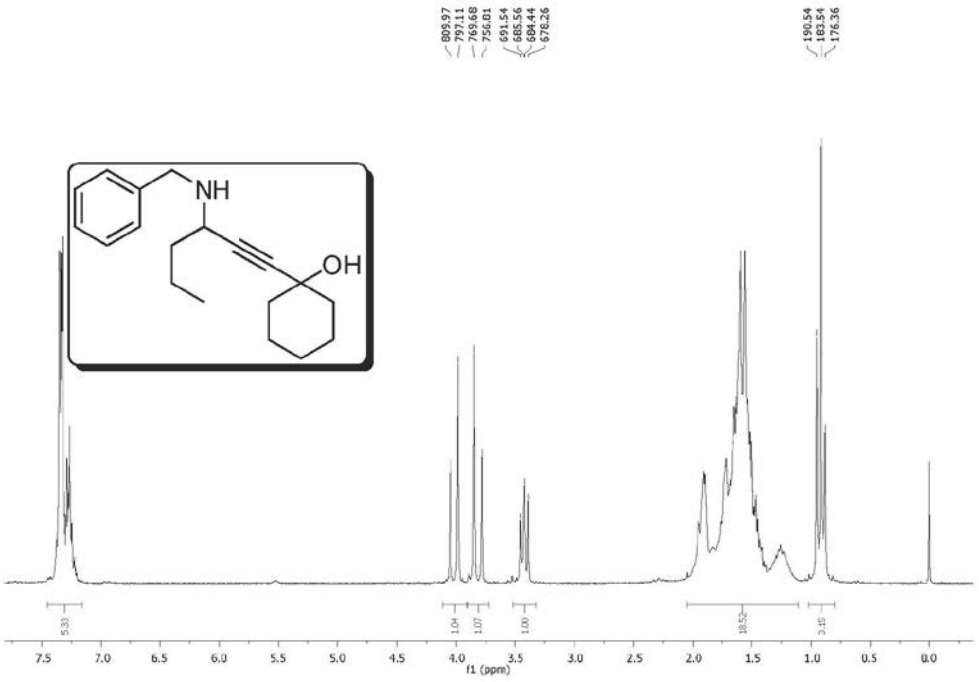


Figure S5. [1]H NMR spectrum (200 MHz, $CDCl_3$) of 1-(3-(benzylamino)hex-1-yn-1-yl)cyclohexanol (**4b**) [Table 2, entry 1].

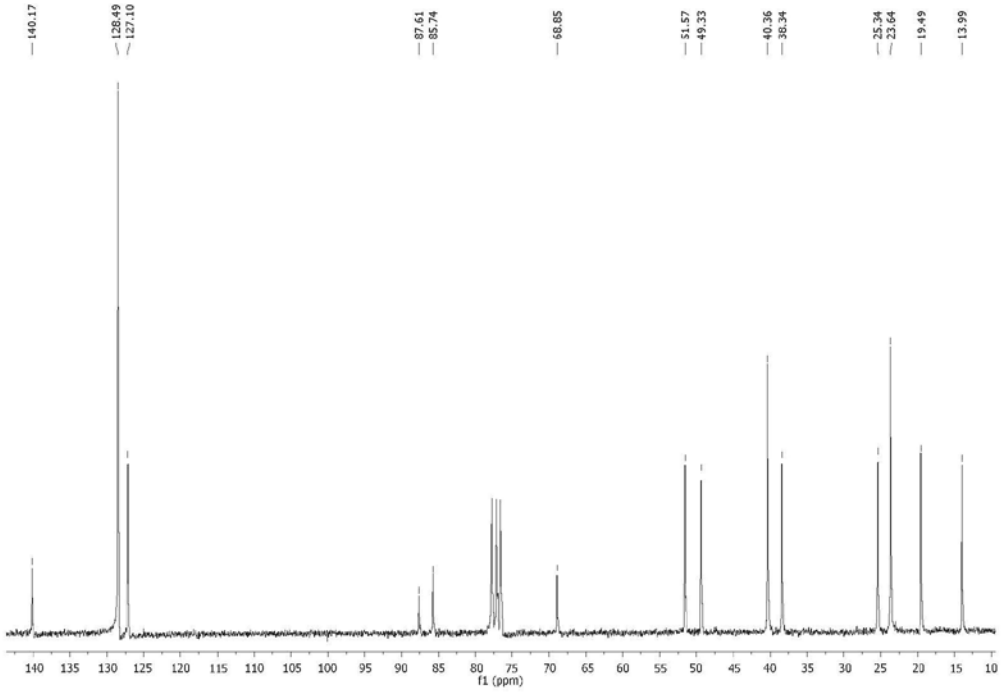


Figure S6. [13]C NMR spectrum (50 MHz, $CDCl_3$) of 1-(3-(benzylamino)hex-1-yn-1-yl)cyclohexanol (**4b**) [Table 2, entry 1].

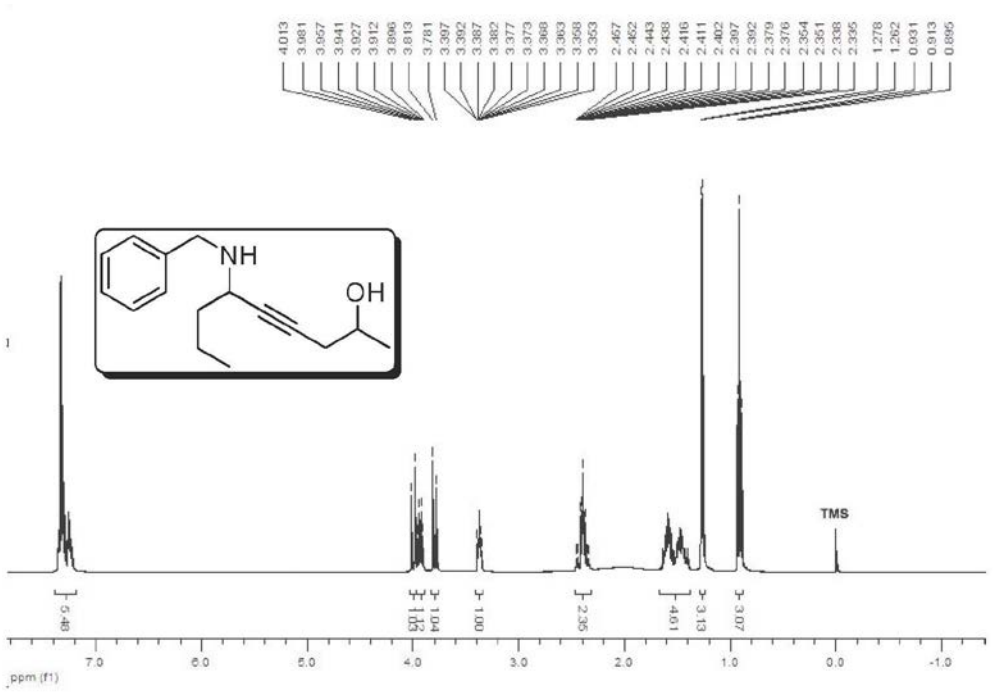


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6-(benzylamino)non-4-yn-2-ol (**4c**) [Table 2, entry 2].

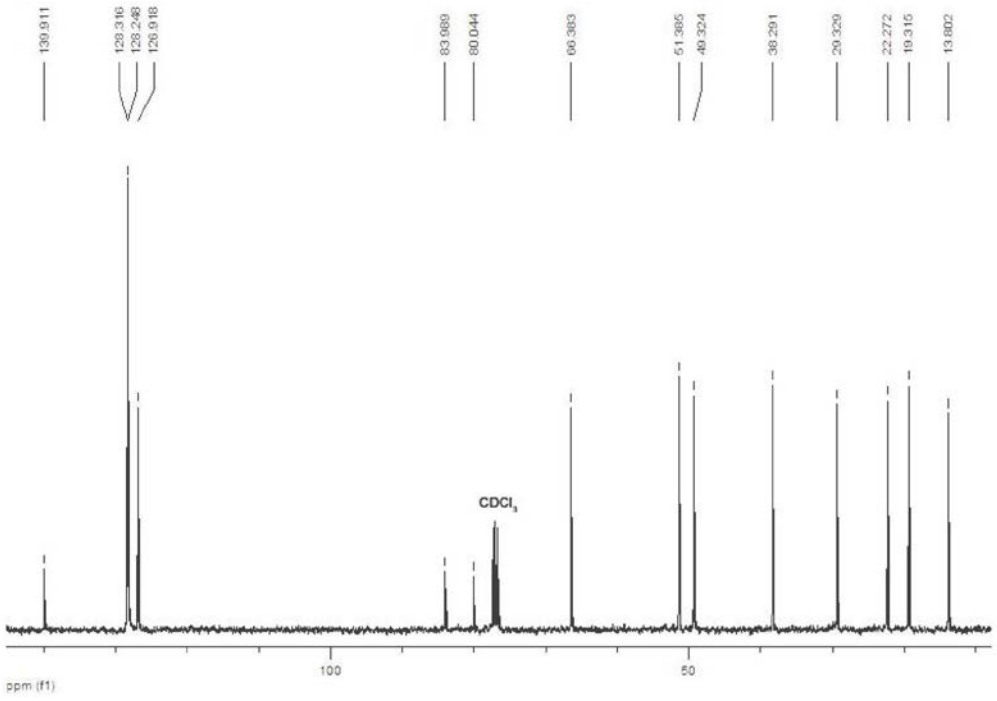


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 6-(benzylamino)non-4-yn-2-ol (**4c**) [Table 2, entry 2].

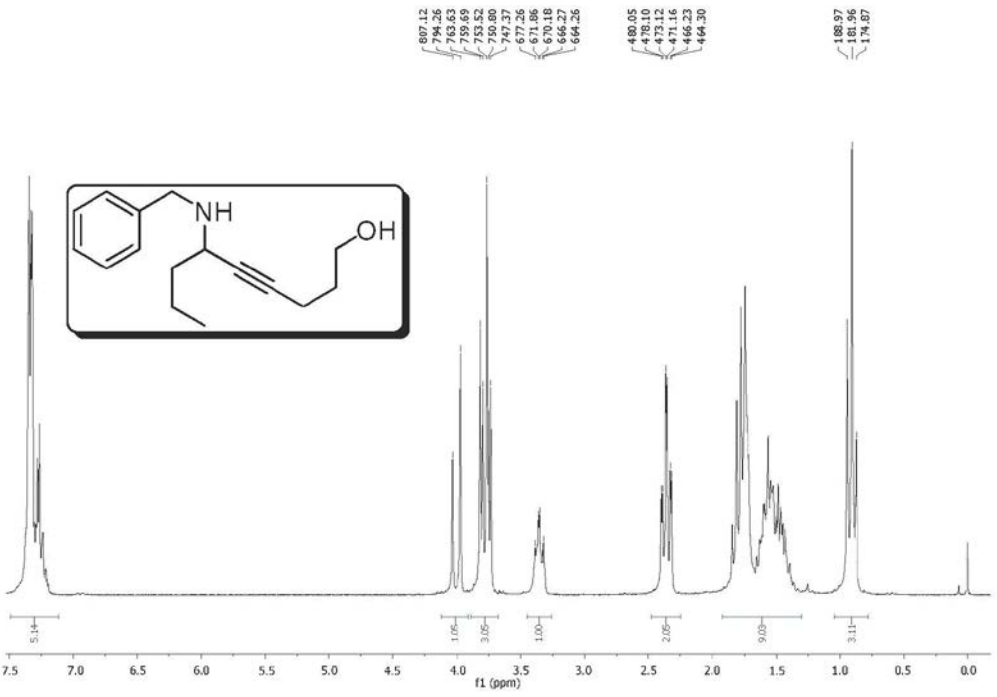


Figure S9. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 6-(benzylamino)non-4-yn-1-ol (**4d**) [Table 2, entry 3].

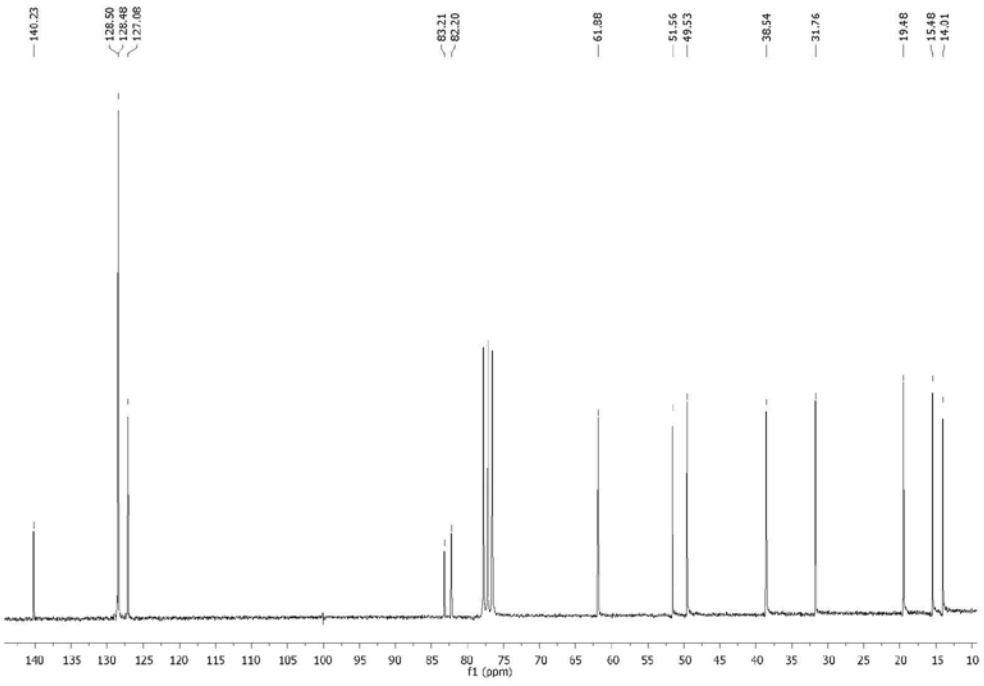


Figure S10. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 6-(benzylamino)non-4-yn-1-ol (**4d**) [Table 2, entry 3].

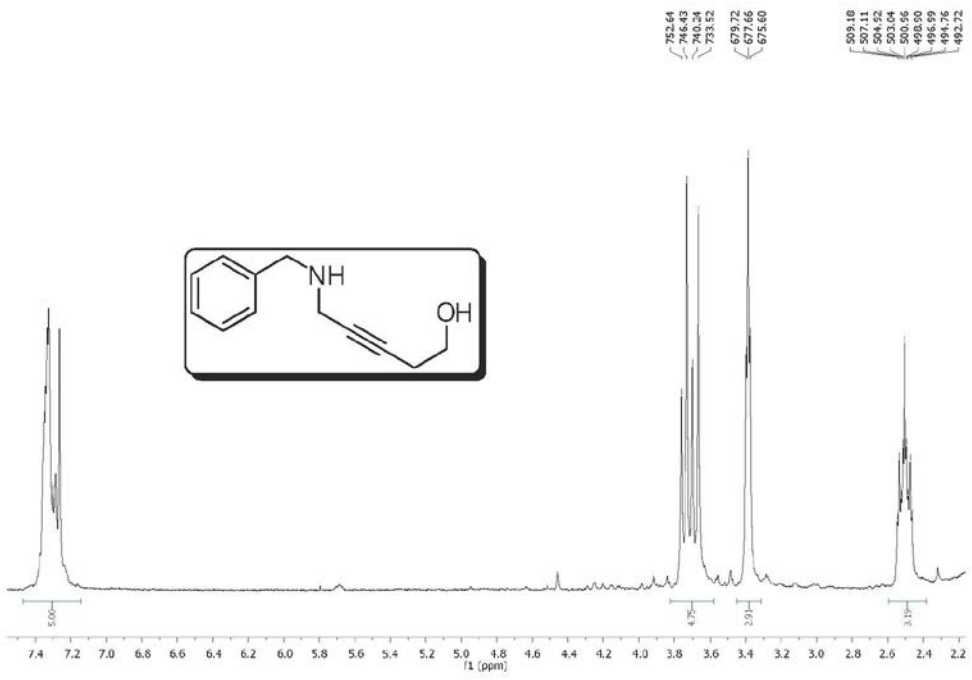


Figure S11. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 5-(benzylamino)pent-3-yn-1-ol (**4e**) [Table 2, entry 4].

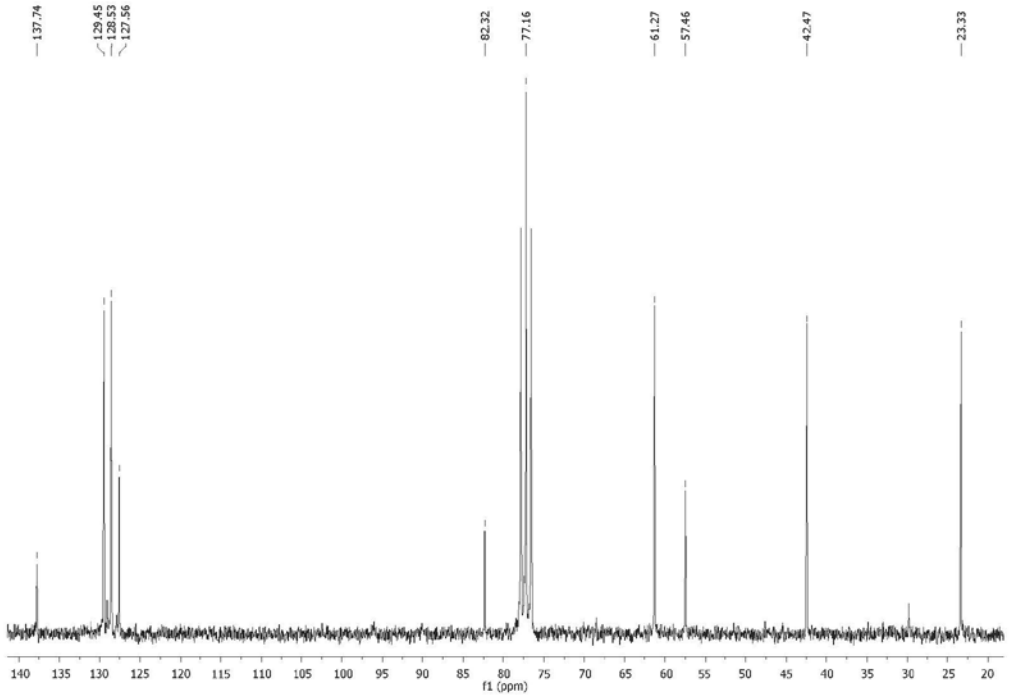


Figure S12. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 5-(benzylamino)pent-3-yn-1-ol (**4e**) [Table 2, entry 4].

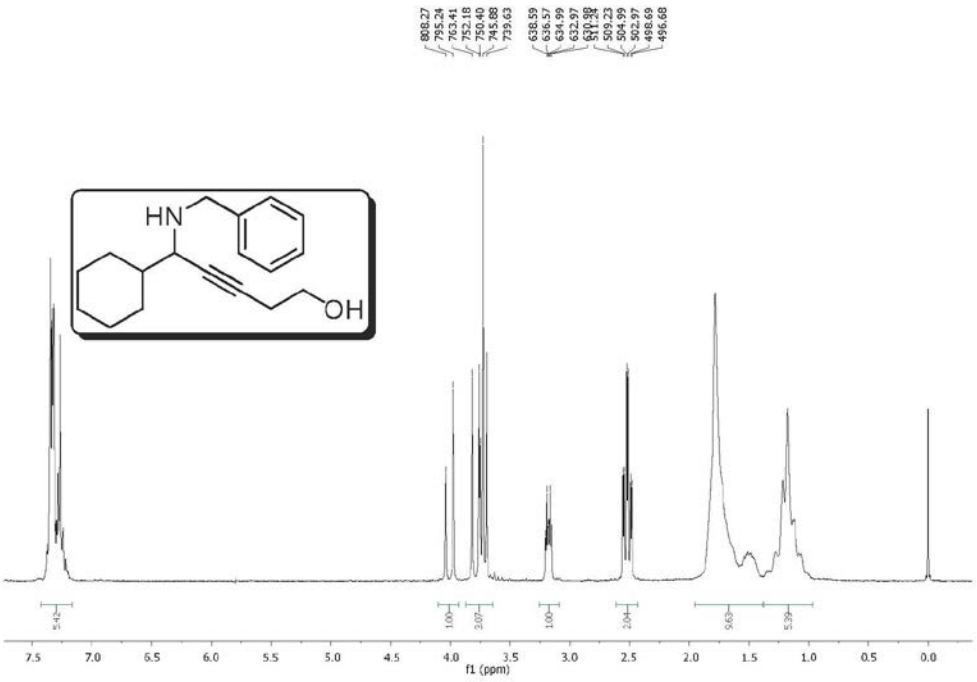


Figure S13. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 5-(benzylamino)-5-cyclohexylpent-3-yn-1-ol (**4f**) [Table 2, entry 5].

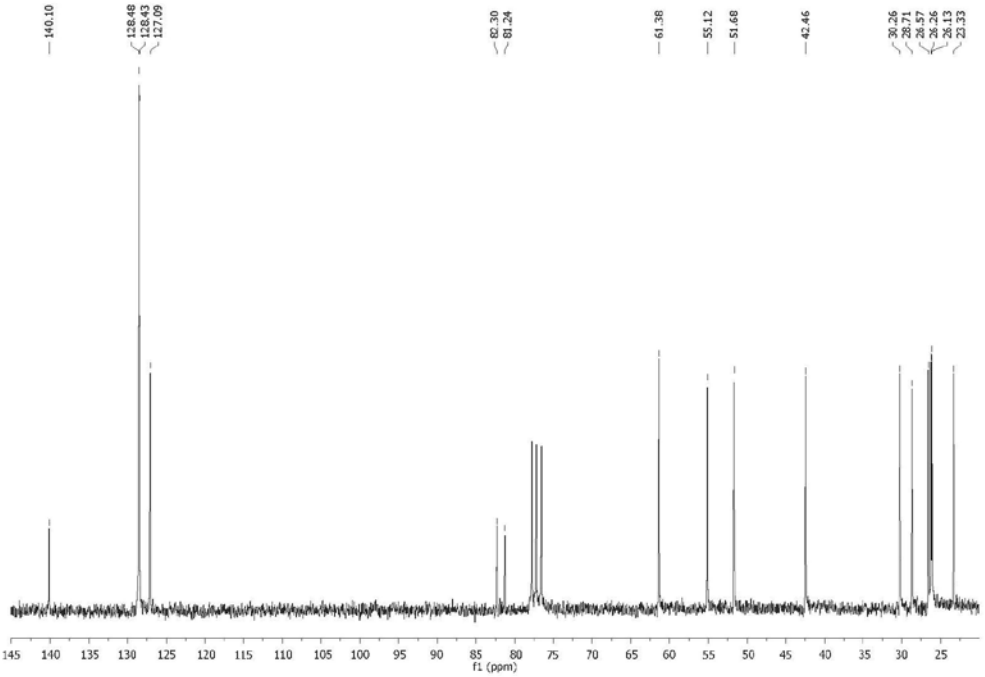


Figure S14. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 5-(benzylamino)-5-cyclohexylpent-3-yn-1-ol (**4f**) [Table 2, entry 5].

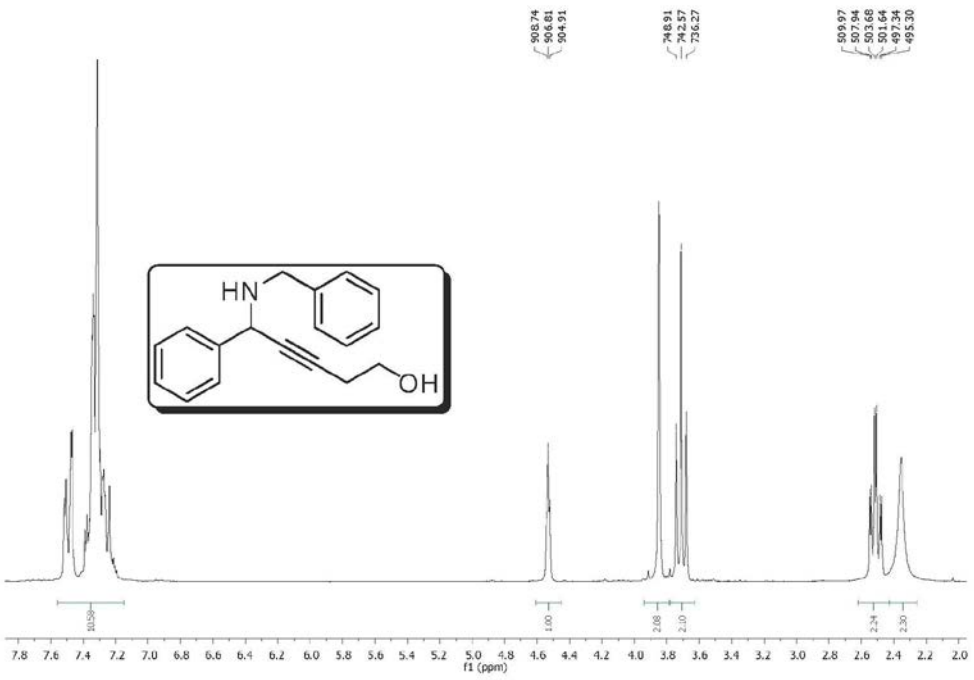


Figure S15. [1]H NMR spectrum (200 MHz, $CDCl_3$) of 5-(benzylamino)-5-phenylpent-3-yn-1-ol (**4g**) [Table 2, entry 6].

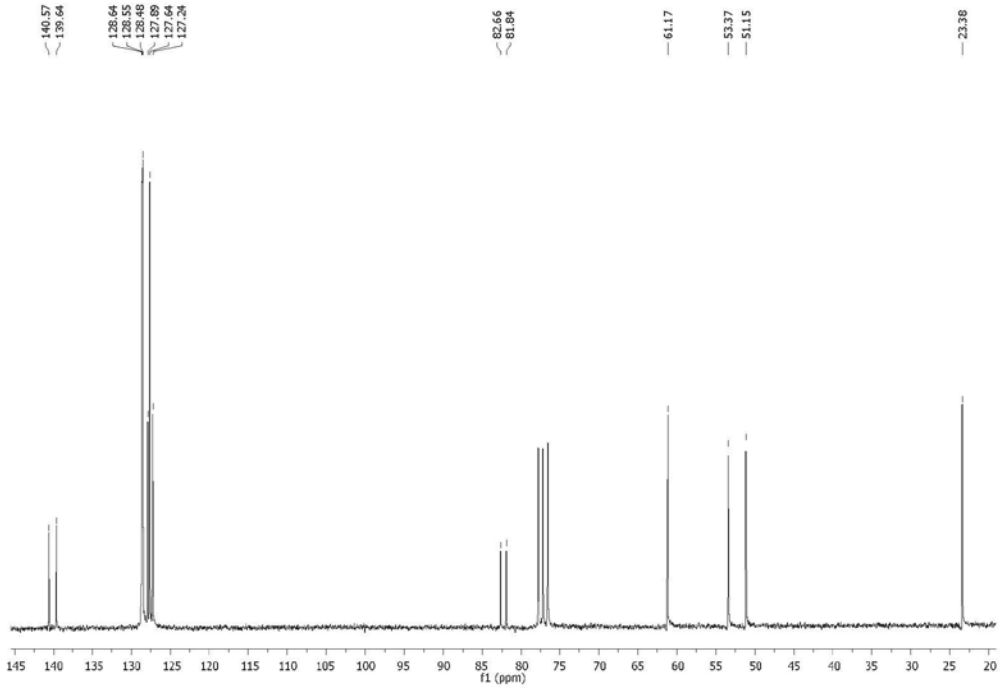


Figure S16. [13]C NMR spectrum (50 MHz, $CDCl_3$) of 5-(benzylamino)-5-phenylpent-3-yn-1-ol (**4g**) [Table 2, entry 6].

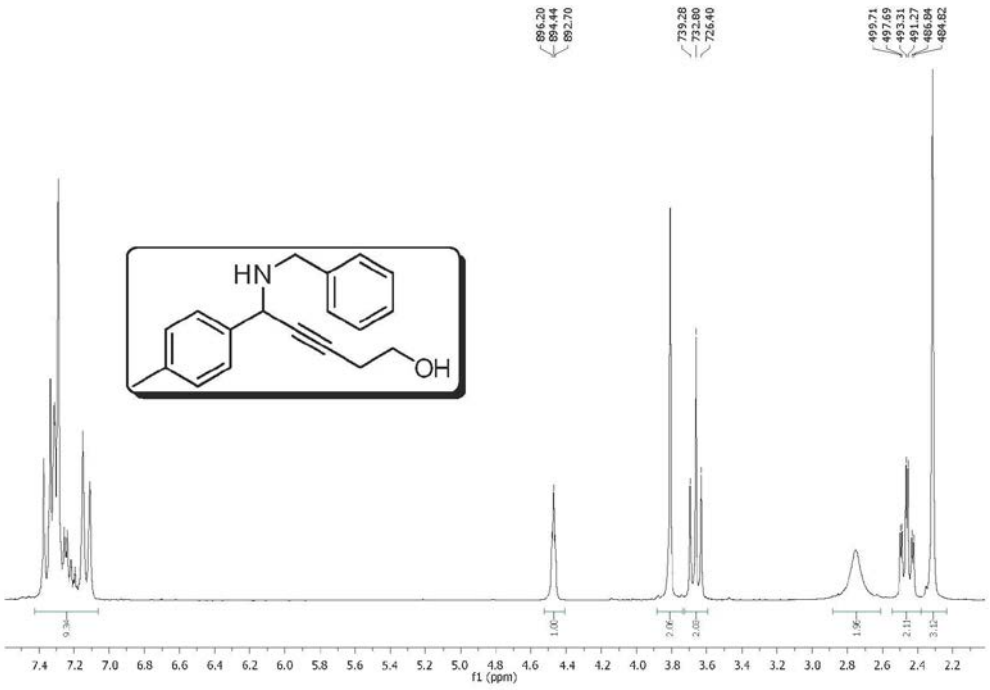


Figure S17. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 5-(benzylamino)-5-(*p*-tolyl)pent-3-yn-1-ol (**4h**) [Table 2, entry 7].

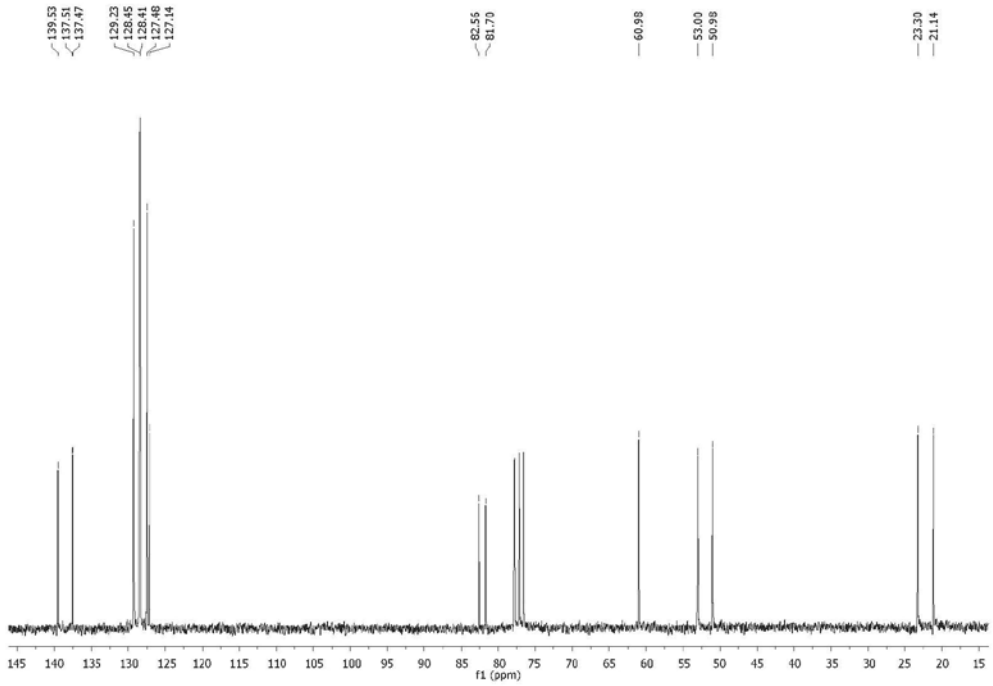


Figure S18. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 5-(benzylamino)-5-(*p*-tolyl)pent-3-yn-1-ol (**4h**) [Table 2, entry 7].

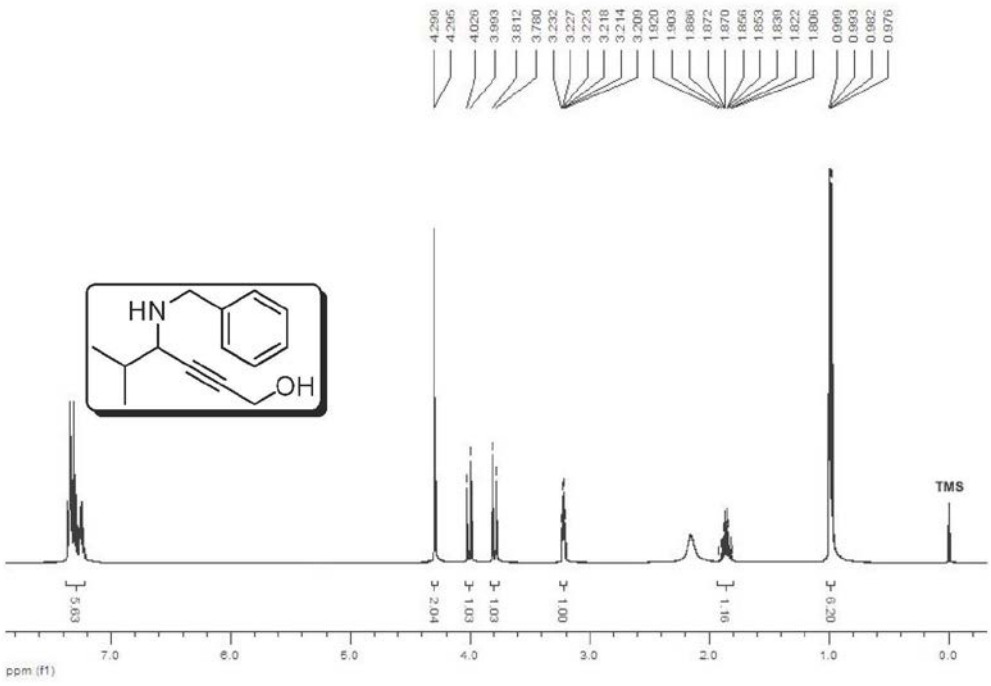


Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4-(benzylamino)-5-methylhex-2-yn-1-ol (**4i**) [Table 2, entry 8].

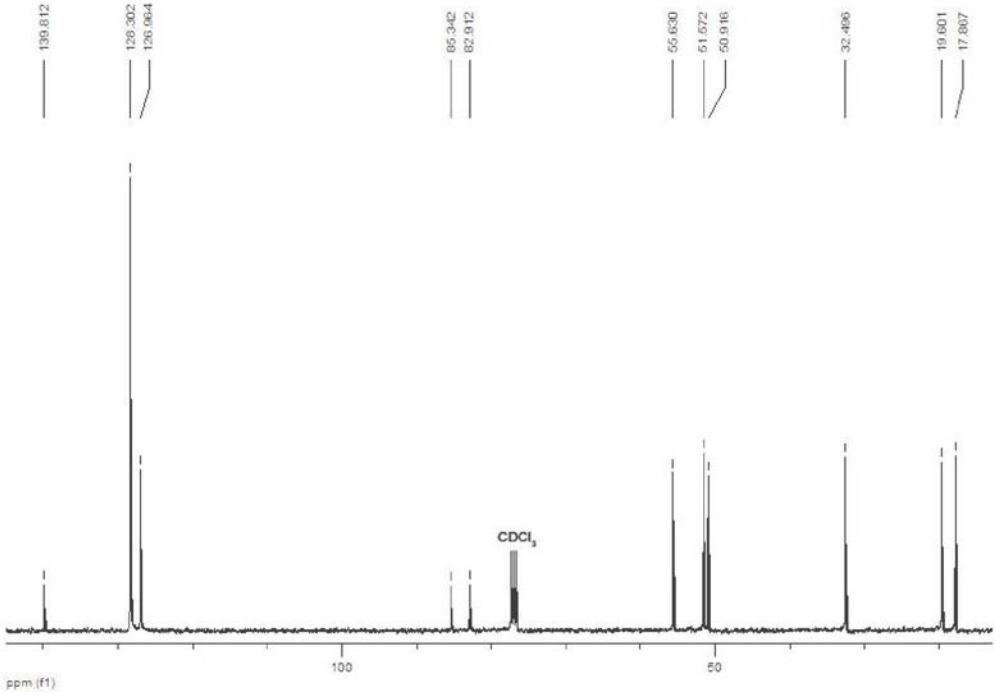


Figure S20. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4-(benzylamino)-5-methylhex-2-yn-1-ol (**4i**) [Table 2, entry 8].

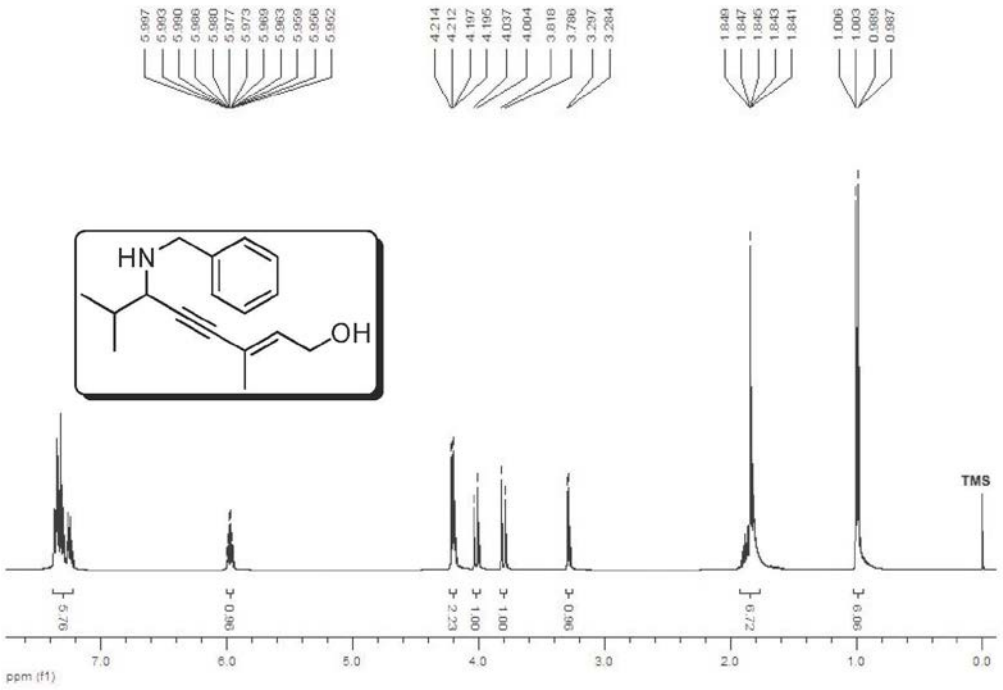


Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*E*)-6-(benzylamino)-3,7-dimethyloct-2-en-4-yn-1-ol (**4j**) [Table 2, entry 9].

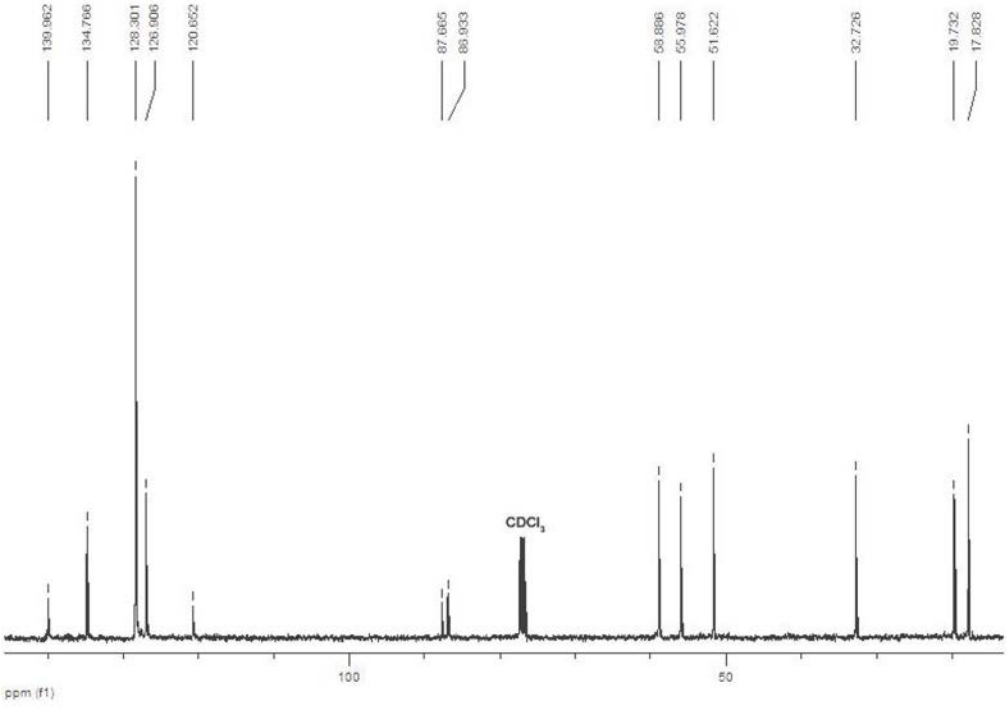


Figure S22. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*E*)-6-(benzylamino)-3,7-dimethyloct-2-en-4-yn-1-ol (**4j**) [Table 2, entry 9].

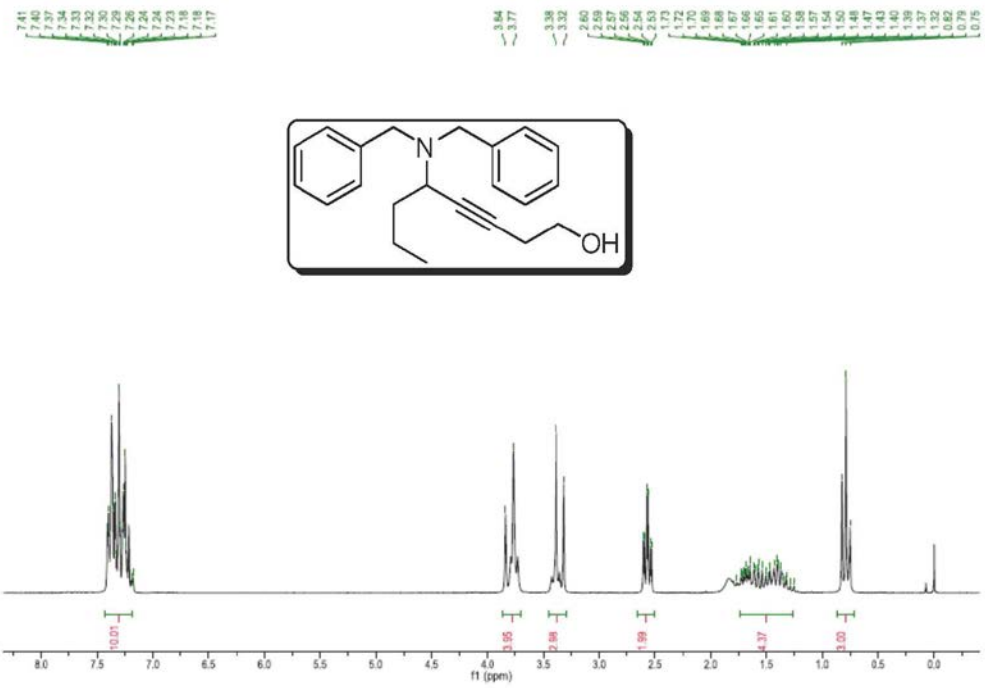


Figure S23. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 5-(dibenzylamino)oct-3-yn-1-ol (**4k**) [Table 2, entry 10].

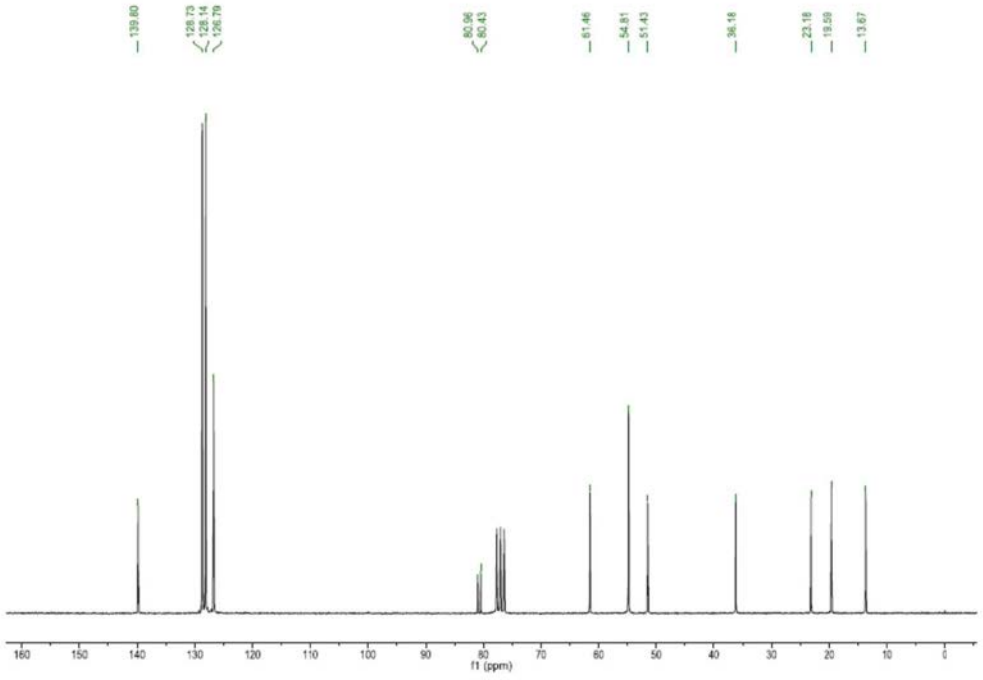


Figure S24. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 5-(dibenzylamino)oct-3-yn-1-ol (**4k**) [Table 2, entry 10].

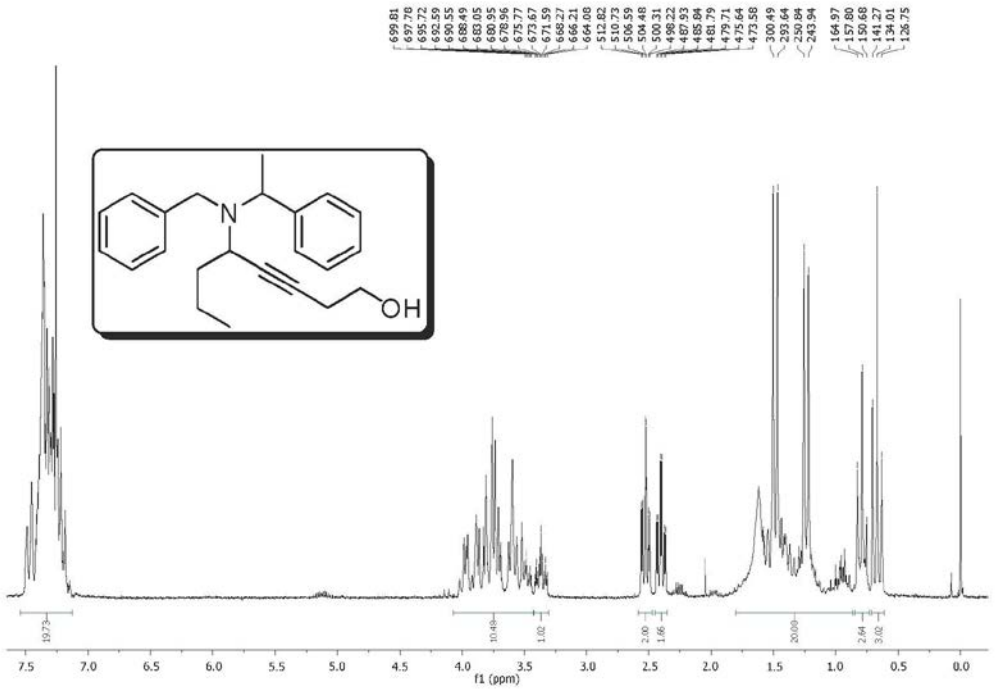


Figure S25. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 5-(benzyl(1-phenylethyl)amino)oct-3-yn-1-ol (**4l**) [Table 2, entry 11].

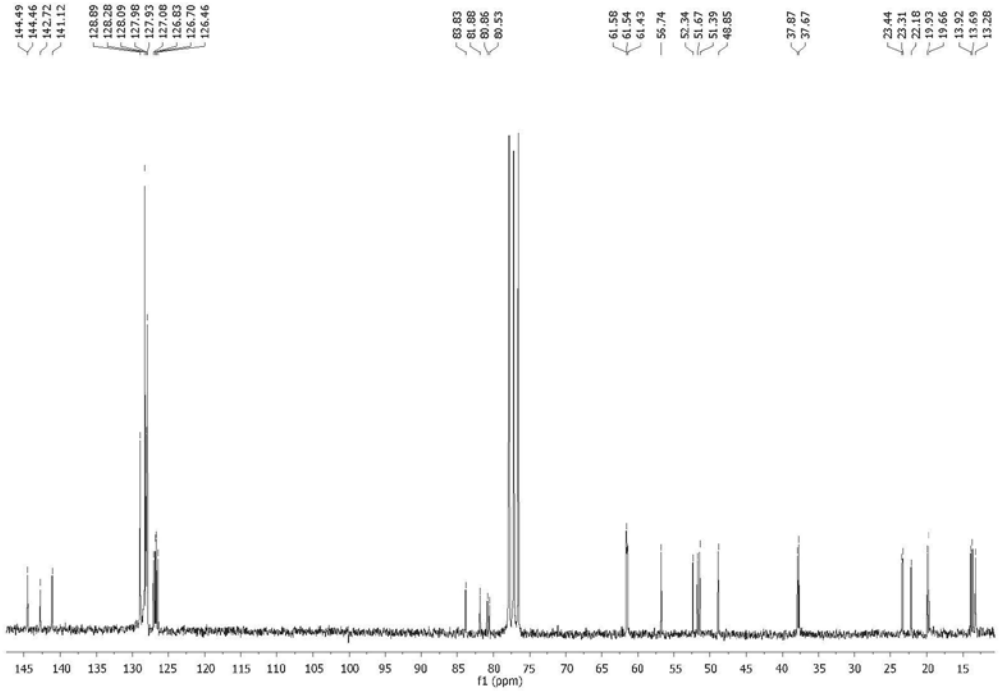


Figure S26. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 5-(benzyl(1-phenylethyl)amino)oct-3-yn-1-ol (**4l**) [Table 2, entry 11].

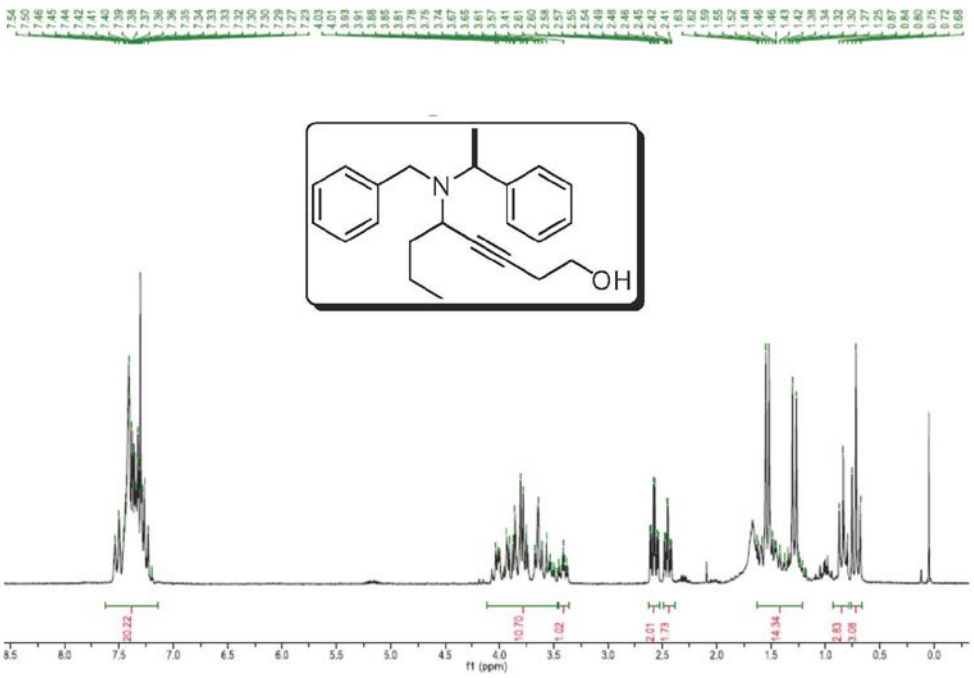


Figure S27. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 5-(benzyl((*S*)-1-phenylethyl)amino)oct-3-yn-1-ol (**4m**) [Table 2, entry 12].

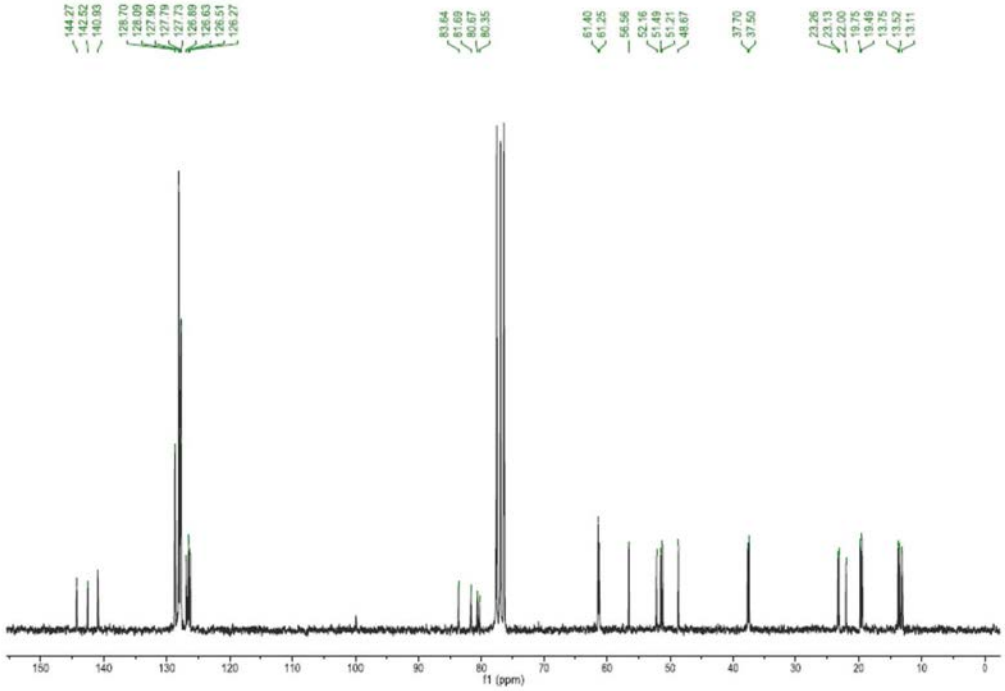


Figure S28. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 5-(benzyl((*S*)-1-phenylethyl)amino)oct-3-yn-1-ol (**4m**) [Table 2, entry 12].

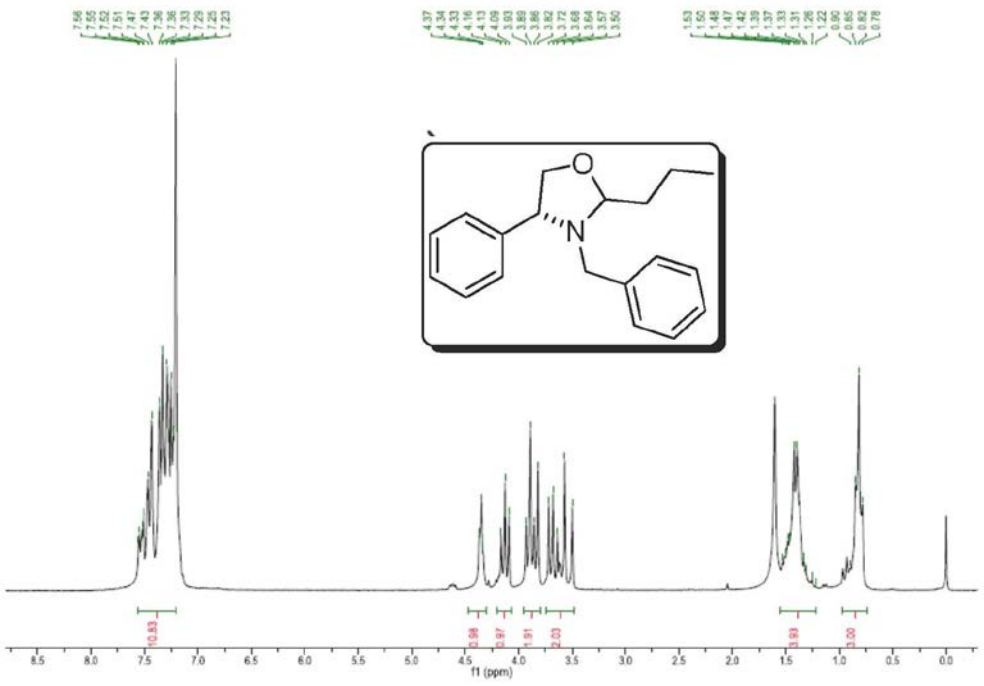


Figure S29. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of (4*R*)-3-benzyl-4-phenyl-2-propyloxazolidine (**4n**) [Table 2, entry 13].

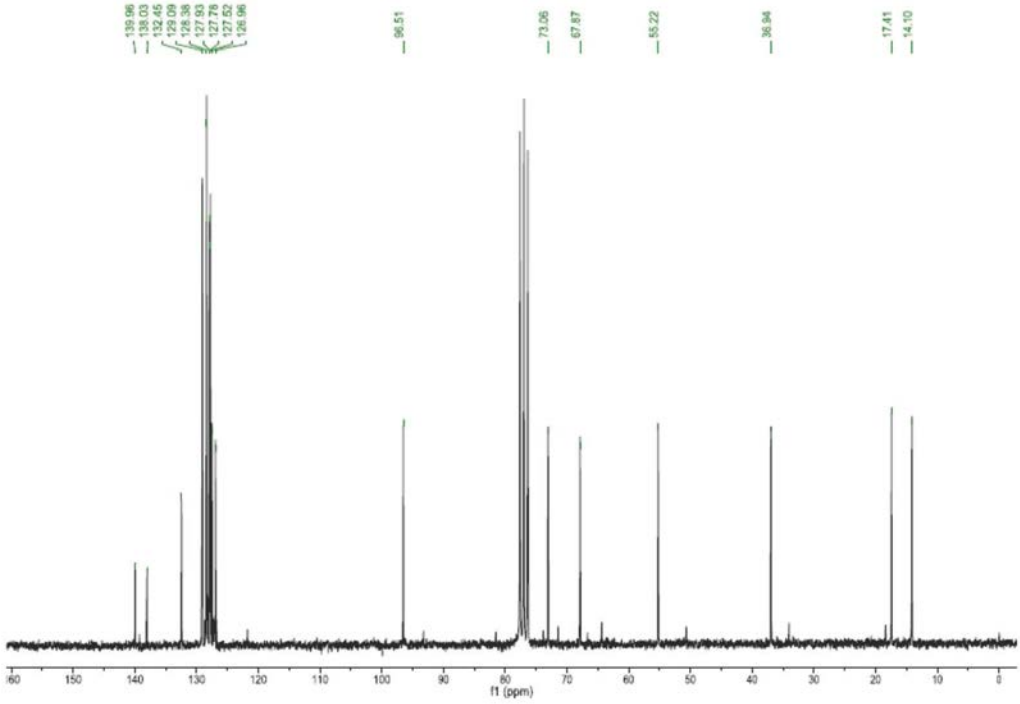


Figure S30. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of (4*R*)-3-benzyl-4-phenyl-2-propyloxazolidine (**4n**) [Table 2, entry 13].

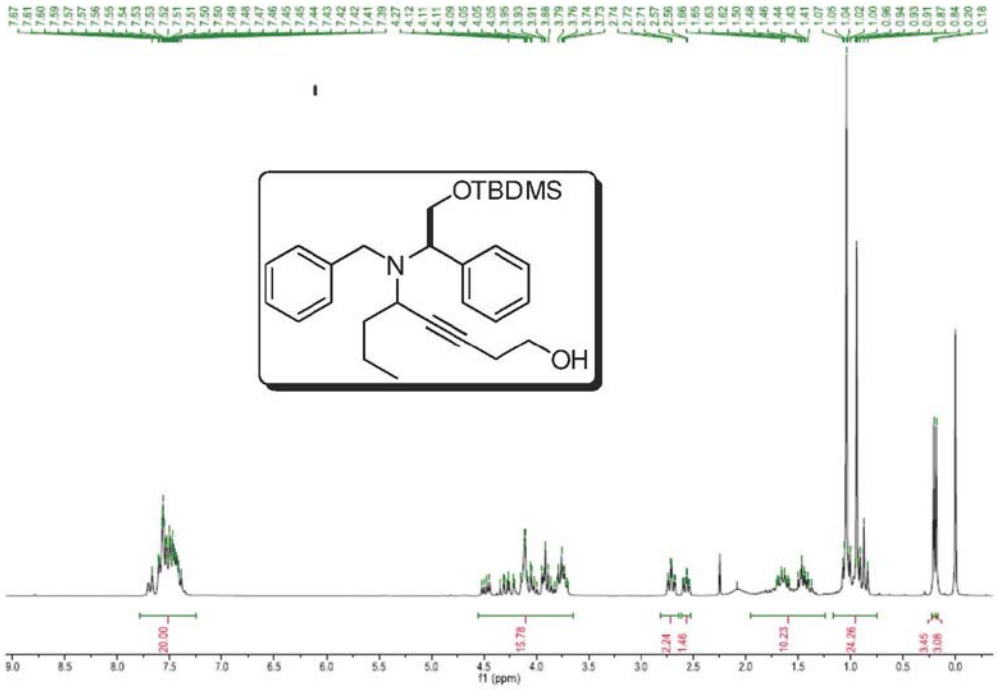


Figure S31. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 5-(benzyl((*R*)-2-(*tert*-butyldimethylsilyloxy)-1-phenylethyl)amino)oct-3-yn-1-ol (**4o**) [Table 2, entry 14].

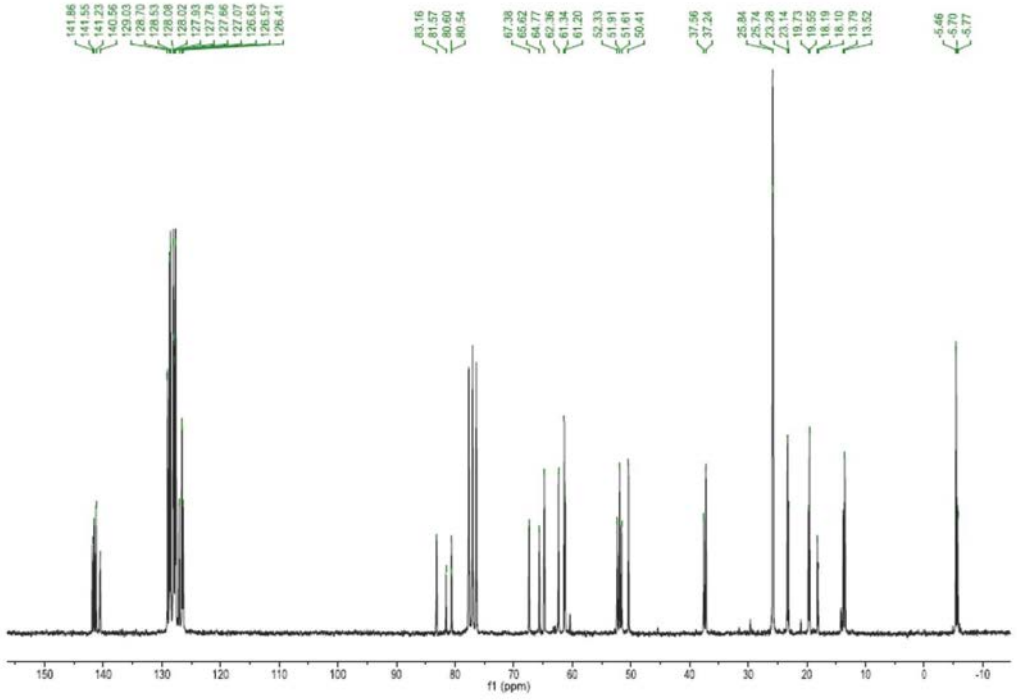


Figure S32. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 5-(benzyl((*R*)-2-(*tert*-butyldimethylsilyloxy)-1-phenylethyl)amino)oct-3-yn-1-ol (**4o**) [Table 2, entry 14].

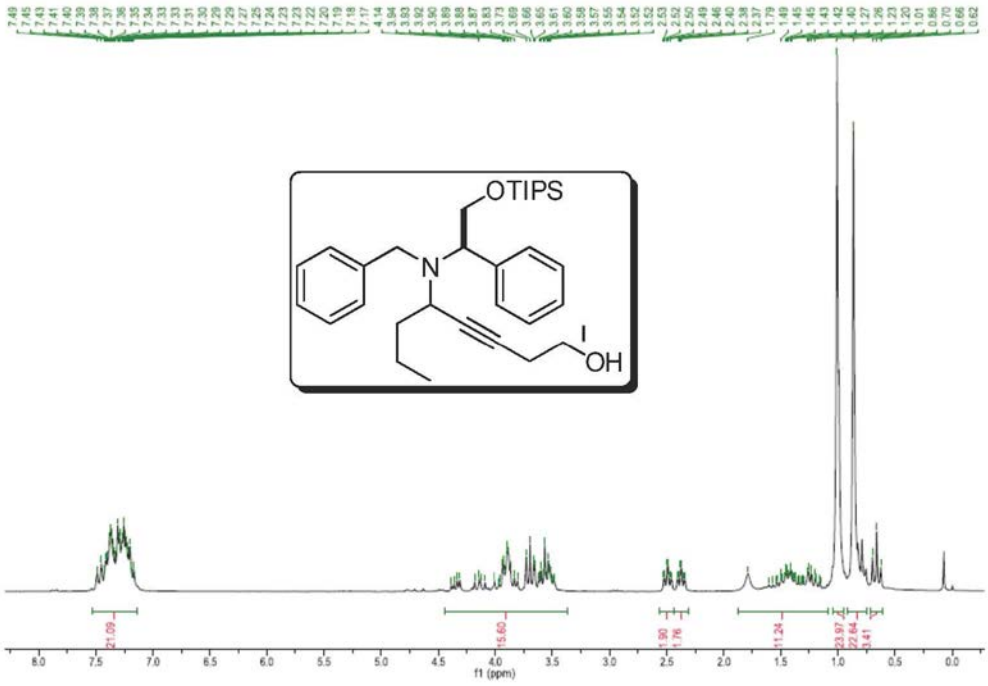


Figure S33. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 5-(benzyl((**R**)-1-phenyl-2-(triisopropylsilyloxy)ethyl)amino)oct-3-yn-1-ol (**4p**) [Table 2, entry 15].

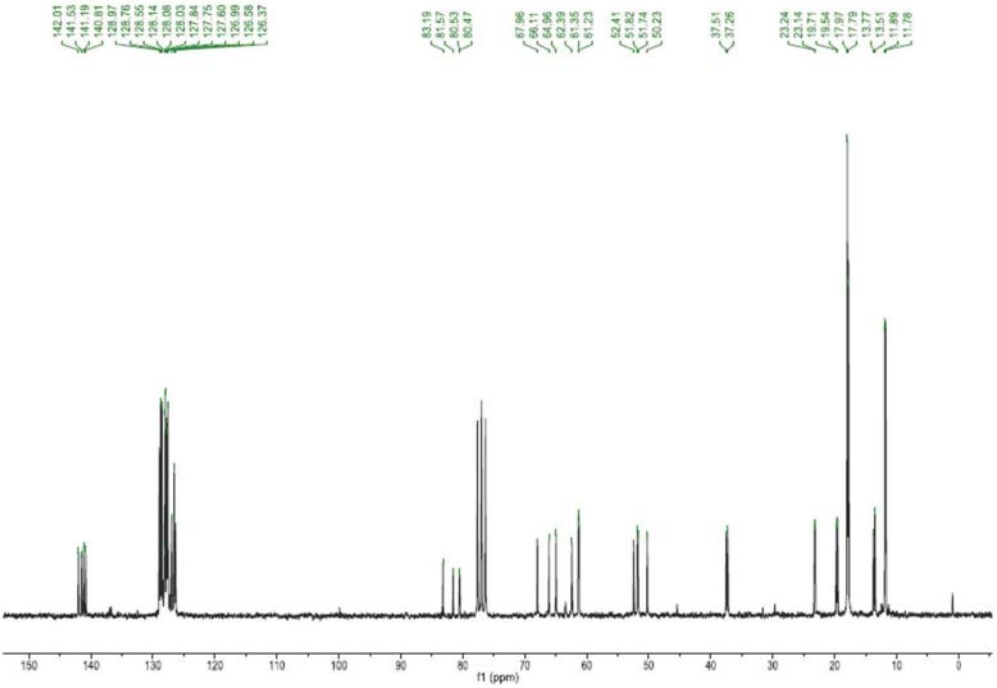


Figure S34. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 5-(benzyl((**R**)-1-phenyl-2-(triisopropylsilyloxy)ethyl)amino)oct-3-yn-1-ol (**4p**) [Table 2, entry 15].

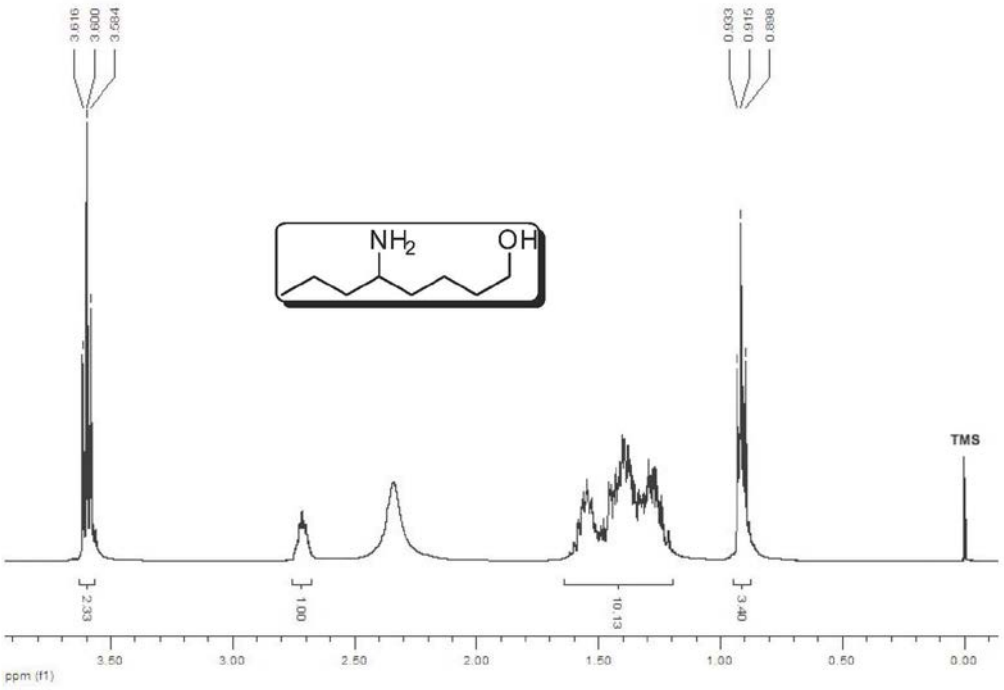


Figure S35. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 5-aminooctan-1-ol (**5b**) [Scheme 1].

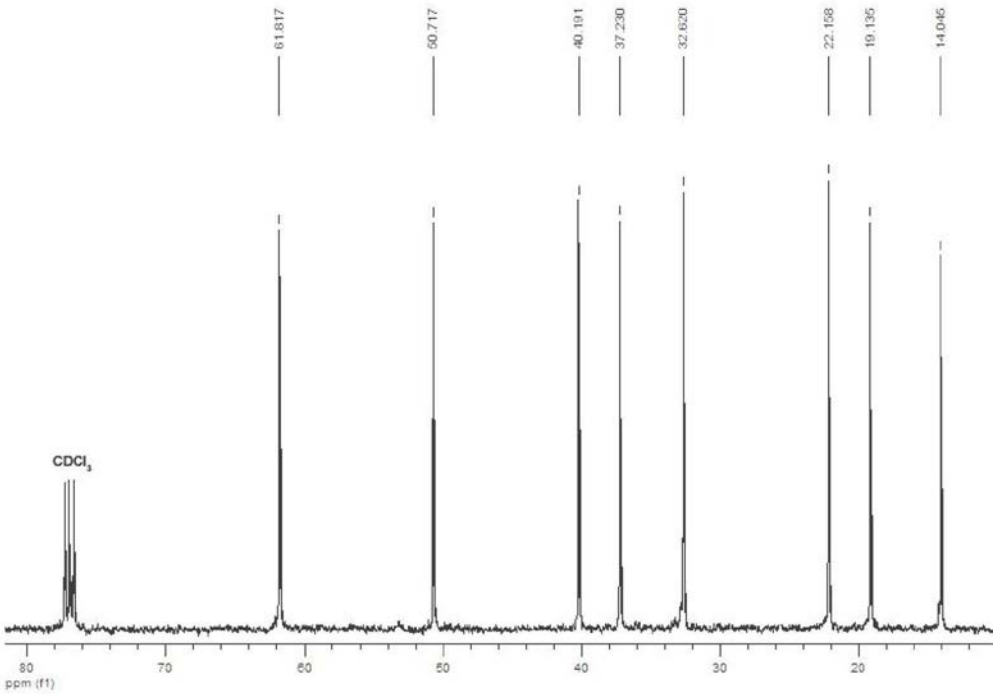


Figure S36. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 5-aminooctan-1-ol (**5b**) [Scheme 1].

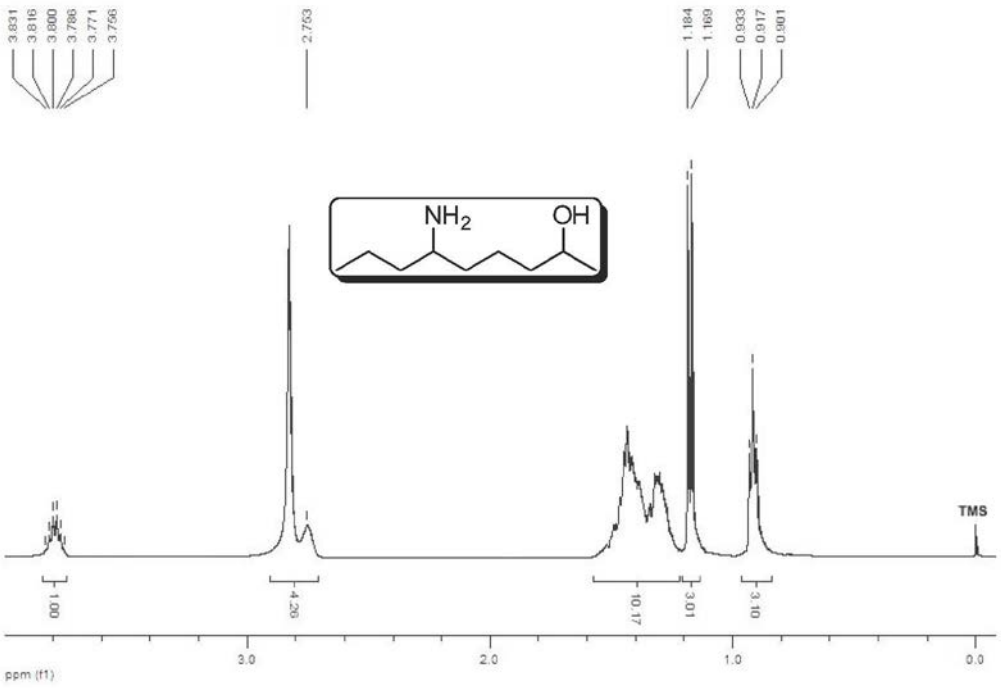


Figure S37. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6-aminononan-2-ol (**5c**) [Scheme 1].

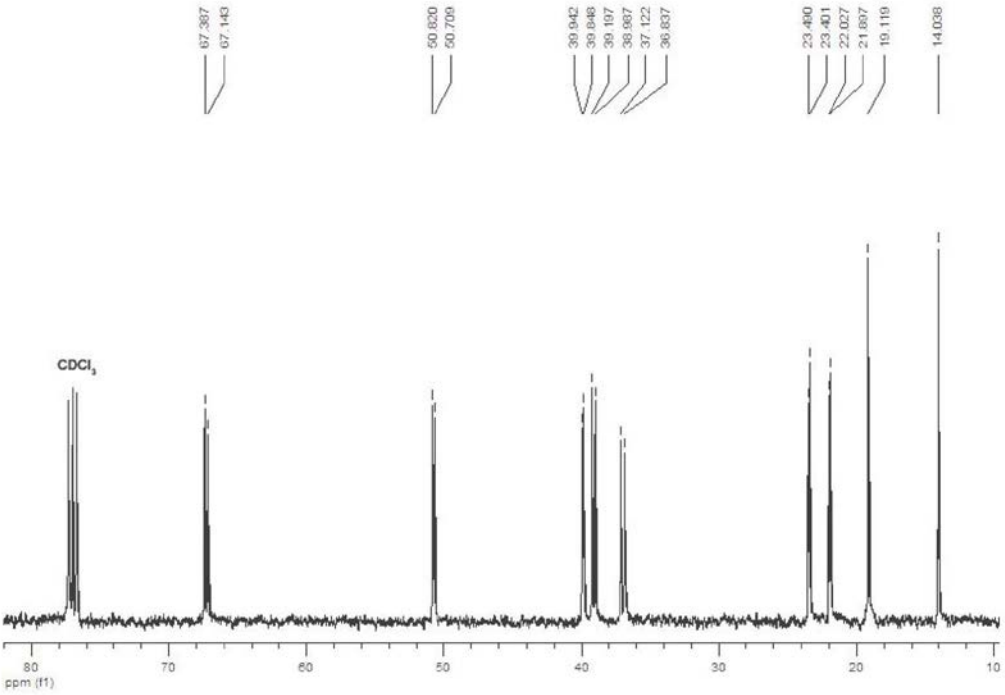


Figure S38. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 6-aminononan-2-ol (**5c**) [Scheme 1].