Electronic Supplementary Information for

A Systematic Study on Cadiot–Chodkiewicz Cross Coupling Reaction for Selective and Efficient Synthesis of hetero-diynes

Bhavani Shankar Chinta, and Beeraiah Baire*

Department of Chemistry, Indian Institute of Technology Madras, Chennai, Tamilnadu, INDIA-600036.

*E-mail: beeru@iitm.ac.in

General Procedures for Cadiot-Chodkiewicz Coupling: Method A

To the solution of propargylic alkynyl bromide (1 eq.) and alkyne (1.1 eq.) in freshly degased amine (5 eq) and degased tap water or 1,2-dichloroethane (2 mL/0.1 mmol) at 0 °C under nitrogen atmosphere, was added CuCl (0.1 eq.) and stirred the reaction mixture at same temperature until consumption of starting propargyl alcohol (15 min to few hours). Reaction mixture was diluted with EtOAc (10 mL/0.2 mmol), saturated aq. NH_4Cl (10 mL) and extracted thrice with ethyl acetate (3 x 10 mL). The combined organic layer was washed with brine (10 mL) and dried over $MgSO_4$. Evaporation of the solvent and purification of the crude mixture by column chromatography (4:1, hexane:ethyl acetate) afforded the corresponding coupled heterodiyne.

Method-B

To the solution of propargyl alcohol (1 eq.), and alkyne bromide (1.1 eq.), in freshly degased amine (5 eq) and degased tap water or 1,2-dichloroethane (2 mL/0.1 mmol) at 0 °C under nitrogen atmosphere, was added CuCl (0.1 eq.) and stirred the reaction mixture at same temperature until consumption of starting propargyl alcohol (15 min to few hours). Reaction mixture was diluted with EtOAc (10 mL/0.2 mmol), saturated aq. NH_4Cl (10 mL) and extracted thrice with ethyl acetate (3 x 10 mL). The combined organic layer was washed with brine (10 mL) and dried over $MgSO_4$. Evaporation of the solvent and purification of the crude mixture by column chromatography (4:1, hexane:ethyl acetate) afforded the corresponding coupled heterodiyne.

1-(Phenylbuta-1,3-diyn-1-yl)cyclohexan-1-ol (2)

Followed method-A.1-(bromoethynyl)cyclohexan-1-ol[1] **1** (40 mg, 0.20 mmol), phenylacetylene (22 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **2** (36 mg, 0.16 mmol, 82%) as a white solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.40 (2 H, dd, *J* = 1.4 & 7.9 Hz), 7.20-7.27 (3 H, m), 2.15 (1 H, br s), 1.87-1.91 (2 H, m), 1.48-1.87 (6 H, m), 1.18-1.21 (2 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.6, 129.3, 128.5, 121.7, 86.3, 78.6, 73.5, 69.4, 69.0, 39.8, 25.1 and 23.2 ppm.

IR (neat): 3438, 3054, 2986, 2939, 2859, 1733,1599, 1488, 1445, 1422, 1373, 1341, 1265, 1158, 1053, 962, 898, 744, 705, 540, 497 and 441 cm^{-1}.

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

HR ESI-MS: $[C_{16}H_{16}ONa]^+$ = $[M+Na]^+$ requires 247.1099; found 247.1092

M.P.: 96-98 °C.

1-(5-Hydroxy-5-phenylhexa-1,3-diyn-1-yl)cyclohexan-1-ol (4)

Followed method-A. 1-(bromoethynyl)cyclohexan-1-ol **1** (40 mg, 0.20 mmol), 2-phenylbut-3-yn-2-ol (32 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **4** (38 mg, 0.14 mmol, 72%) as a white solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ =7.60-7.62 (2 H, m), 7.36 (1 H, ddd, *J* = 1.2, 3.0 & 6.8 Hz), 7.30 (1 H, ddd, *J* = 1.4, 2.7 & 6.4 Hz), 2.59 (1 H, br s), 2.13 (1 H, br s),1.91-1.94 (2 H, m), 1.51-1.71 (8 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 128.5, 128.1, 124.9, 84.1, 82.3, 70.5, 69.3, 69.2, 68.3, 39.7, 32.7, 32.9, 25.1 and 23.2 ppm.

IR (neat): 3410, 2983, 2935, 2858,1658, 1627, 1464, 1447, 1404, 1245, 1156, 1056, 963, 899, 763, 698, 616, 593, 566, 495, 480, 460 and 429 cm^{-1}.

HR ESI-MS: $[C_{18}H_{21}O_2]^+$ = $[M+H]^+$ requires 269.1542: found 269.1541.

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

M.P.: 79-81 °C.

1-(5-Hydroxy-5-methylhexa-1,3-diyn-1-yl)cyclohexan-1-ol (5)

Followed method-A. 1-(bromoethynyl)cyclohexan-1-ol **1** (40 mg, 0.20 mmol), 2-methylbut-3-yn-2-ol (18 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **5** (34 mg, 0.17 mmol, 84%) as a white solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 2.00 (1 H, br s), 1.90-1.93 (2 H, m), 1.66-1.71 (2 H, m), 1.57-1.62 (6 H, m), 1.53 (6 H, s),1.24-1.26 (1 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 83.8, 83.4, 69.3, 68.3, 66.6,65.6, 39.7, 31.1, 25.1 and 23.2 ppm.

IR (neat): 3437, 2937, 2855, 1659, 1627, 1549, 1531, 1479, 1405, 1260, 1122, 1048, 878, 748, 649, 574, 537, 486, 462 and 418 cm^{-1}.

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

HR ESI-MS: $[C_{13}H_{18}O_2K]^+ = [M+K]^+$ requires 245.0944; found 245.0959

M.P.: 124-126 °C.

***N*-[5-(1-Hydroxycyclohexyl)penta-2,4-diyn-1-yl]-4-methylbenzenesulfonamide (6)**

Followed method-A. 1-(bromoethynyl)cyclohexan-1-ol **1** (40 mg, 0.20 mmol), 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide[2] (45 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0°C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **6** (56 mg, 0.17 mmol, 86%) as a yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.27 (2 H, d, *J* = 8.3 Hz), 7.32 (2 H, d, *J* = 8.0 Hz), 5.07 (1 H, t, *J* = 5.8 Hz), 3.91 (2 H, d, *J* = 6.2 Hz), 2.43 (3 H, s), 2.33 (1 H, br s), 1.85-1.88 (2 H, m), 1.66-1.70 (2 H, m), 1.44-1.59 (5 H, m), 1.23- 1.27 (1 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 136.5, 129.8, 127.5, 82.7, 73.7, 69.1, 68.9, 68.0, 39.6, 33.6, 25.0, 23.1 and 21.6 ppm.

IR (neat): 3575, 3371, 3055, 2986, 2938, 2859, 1731, 1658, 1598, 1447, 1422, 1375, 1334, 1265, 1161, 1092,1059, 897, 812, 742, 705, 665, 553, 514, 469 and 405 cm^{-1}.

HR ESI-MS: $[C_{18}H_{22}NO_3S]^+ = [M+H]^+$ requires 332.1320; found 332.1318.

TLC: $R_f = 0.5$ (4:1, Hex/EtOAc).

M.P.:118-120 °C.

1-(5-Hydroxy-7-phenylhepta-1,3-diyn-1-yl)cyclohexan-1-ol (7)

Followed method-A. 1-(bromoethynyl)cyclohexan-1-ol **1** (40 mg, 0.20 mmol), 5-phenylpent-1-yn-3-ol[3] (46 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0°C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **7** (50 mg, 0.177 mmol, 89%) as a light yellow solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.27 (2 H, d, *J* = 6.7 Hz), 7.16-7.20 (3 H, m), 4.40 (1 H, t, *J* = 6.6 Hz), 2.78 (2H, t, *J* = 3.7 Hz), 2.45 (1 H, br s), 2.00-2.70 (2 H, m), 1.89-1.93 (2 H, m), 1.48-1.62 (5 H, m), 1.22-1.25 (1 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 140.9, 128.5, 126.2, 83.4, 80.1, 69.5, 69.3, 68.3, 62.1, 62.0, 39.7,38.9, 31.3, 25.0 and 23.2 ppm.

IR (neat): 3425, 3090, 3061, 3027, 2936, 2858, 1724, 1706, 1655, 1602, 1450, 1404, 1329, 1262, 1151, 1054, 963, 742, 700, 585, 537, 498, 462, 439 and 404 cm^{-1}.

HR ESI-MS: $[C_{19}H_{23}O]^+ = [M+H]^+$ requires 283.1698; found 283.1696.

TLC: $R_f = 0.5$ (4:1, Hex/EtOAc).

M.P.: 84-86 °C.

1-[5-(Benzyloxy)penta-1,3-diyn-1-yl]cyclohexan-1-ol (8)

Followed method-A. 1-(bromoethynyl)cyclohexan-1-ol **1** (40 mg, 0.20 mmol), [(prop-2-ynyloxy)methyl]benzene[4] (32 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **8** (50 mg, 0.19 mmol, 95%) as a yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.29-7.35 (5 H, m), 4.60 (2 H, s), 4.23 (2 H, s), 2.30 (1 H, br s), 1.91-1.94 (2 H, m), 1.66-1.71 (2 H, m), 1.50-1.62 (5 H, m), 1.23-1.25 (1 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1, 128.5, 128.2, 128.1, 82.8, 75.0,71.8,70.7, 69.2, 68.4, 57.6, 39.6, 25.0 and 23.1.

IR (neat): 3428, 3302, 3055, 2938, 2858, 1724, 1659, 1627, 1495, 1451, 1380, 1350,1265, 1208, 1149, 1073, 1028, 964, 903, 852, 700, 634, 605, 450 and 401cm^{-1}.

HR ESI-MS: $[C_{18}H_{20}O_2Na]^+$ = $[M+Na]^+$ requires 291.1361; found 291.1371

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

1-(6-Hydroxyhexa-1,3-diyn-1-yl)cyclohexan-1-ol (9)

Followed method-A.1-(bromoethynyl)cyclohexan-1-ol **1** (40 mg, 0.20 mmol), 3-butyne 1-ol (15 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **9** (31 mg, 0.16 mmol, 82%) as a yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 3.75 (2 H, t, *J* = 6.3 Hz), 2.56 (2 H, t, *J* = 6.3 Hz), 2.52 (1 H, br s), 1.89-1.93 (2 H, m), 1.67-1.71 (2 H, m), 1.51-1.61 (6 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 80.0, 78.0, 69.2, 68.9, 66.3, 60.7, 39.7, 25.1, 23.7 and 23.2. IR (neat): 3429, 3055, 2986, 2938, 2859, 1732, 1630, 1446, 1422, 1375, 1265, 1046, 961, 896, 745, 706 and 418 cm^{1}.

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

6-(1-Hydroxycyclohexyl)hexa-3,5-diyn-1-yl 4-methylbenzenesulfonate (10)

Followed method-A. 1-(bromoethynyl)cyclohexan-1-ol **1** (40 mg, 0.20 mmol), but-3-yn-1-yl 4-methylbenzenesulfonate[5] (48 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **10** (55 mg, 0.16 mmol, 81%) as a light yellow solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.80 (2 H, d, *J* = 8.3 Hz), 7.36 (2 H, d, *J* = 8.0 Hz), 4.08 (2 H, t, *J* = 6.9 Hz), 2.65 (2 H, t, *J* = 6.9 Hz), 2.45 (3 H, s), 2.08 (1 H, br s), 1.88-1.91 (2 H, m), 1.65-1.71 (2 H, m), 1.47-1.61 (5 H, m), 1.22-1.26 (1 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 132.8, 130.0, 128.1, 80.6, 74.9, 69.1, 68.6, 67.0, 66.9, 39.8, 25.1, 23.2, 21.7 and 20.4.

IR (neat): 3435, 3055, 2986, 2939, 2865, 1732, 1655, 1627, 1464, 1447, 1423, 1369, 1265, 1178, 1117, 1099, 1046, 896, 735, 705, 554, 490, 448, 430 and 411 cm^{-1}.

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

HR ESI-MS: $[C_{19}H_{22}O_4NaS]^+ = [M+Na]^+$ requires 369.1137; found 369.1148

M.P.: 108-110 °C.

1-(Cyclohex-1-en-1-ylbuta-1,3-diyn-1-yl)-4-methoxybenzene (11)

Followed method-A. 1-(bromoethynyl)cyclohex-1-ene[6] (40 mg, 0.22 mmol), 1-ethynyl-4-methoxybenzene (32 mg, 0.24 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (19:1 hexane:EtOAc) gave the heterodiyne **11** (34 mg, 0.156 mmol, 72%) as a green solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.41 (2 H, d, *J* = 8.9 Hz), 6.83 (2 H, d, *J* = 8.9 Hz), 6.28-6.30 (1 H, m), 3.80 (3 H, s), 2.12-2.16 (4 H, m), 1.59-1.65 (4 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 138.6, 134.0, 119.9, 116.4, 114.1, 83.3, 80.8, 73.0, 71.6, 55.4, 28.7, 26.0, 22.2 and 21.4.

IR (neat): 3005, 2930, 2858, 2837, 1642, 1601, 1507, 1437, 1347, 1289, 1248,1176, 1136, 1108, 1075, 1031, 918, 833, 801, 739, 693, 650, 609, 582, 549, 535, 507 and 479 cm^{-1}.

HR ESI-MS: $[C_{17}H_{17}O]^+ = [M+H]^+$ requires 237.1279: found 237.1278.

TLC: R_f = 0.6 (19:1, Hex/EtOAc).

M.P.: 54-56 °C.

1-{6-[(t*ert*-Butyldimethylsilyl)oxy]hexa-1,3-diyn-1-yl}cyclohexan-1-ol (12)

Followed method-A. 1-(bromoethynyl)cyclohexan-1-ol **1** (40 mg, 0.20 mmol), (but-3-yn-1-yloxy)(*tert*-butyl)dimethylsilane[7] (40 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **12** (55 mg, 0.18 mmol, 91%) as a yellow oil, along with known homodimer[8] **3** (2 mg, 0.008 mmol, 3%) as a light yellow solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 3.67 (2 H, t, *J* = 7.1 Hz), 2.42 (2 H, t, *J* = 7.0 Hz), 2.01 (1 H, br s), 1.81-1.85 (2 H, m), 1.59-1.63 (2 H, m), 1.44-1.50 (5 H, m), 1.13-1.18 (1 H, m), 0.82 (9 H, s), –0.01 (6 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.6, 78.5, 69.4, 69.2, 65.8, 61.5, 39.9, 25.9, 25.1, 23.8, 23.2, 18.4 and –5.1 ppm.

IR (neat): 3411, 2934, 2857, 1723, 1627, 1466, 1448, 1386, 1344, 1256, 1108, 1063, 965, 905, 836, 779, 731, 664, 545, 495, 442, 424 and 410 cm^{-1}.

HR ESI-MS: $[C_{18}H_{30}O_2NaSi]^+ = [M+Na]^+$ requires 329.1913; found 329.1911

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

1-(Octa-1,3-diyn-1-yl)cyclohexan-1-ol (13)

Followed method-A. 1-(bromoethynyl)cyclohexan-1-ol **1** (40 mg, 0.20 mmol),1-hexyne (18 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane: EtOAc) gave the heterodiyne **13** (32 mg, 0.16 mmol, 80 %) as a yellow oil, along with homo-dimer (3 mg, 0.01 mmol, 5%) as a white solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 2.28 (1 H, t, *J* = 6.9 Hz), 2.08 (1 H, br s), 1.86-1.92 (2 H, m), 1.39-1.61 (10 H, m), 1.25-1.28 (2 H, m), 0.91 (2 H, t, *J* = 7.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 83.8, 81.6, 79.2, 69.9, 69.2, 39.8, 30.3, 25.1, 23.27, 23.24, 22.0, 19.0 and 13.6.

IR (neat): 3428, 3054, 2985, 2940, 2867, 1732, 1667, 1423, 1375, 1265, 1046, 895, 739, 705 and 417 cm^{-1}.

HR ESI-MS: $[C_{14}H_{20}OK]^+ = [M+K]^+$ requires 243.1151; found 243.1155

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

(Cyclohex-1-en-1-ylbuta-1,3-diyn-1-yl)benzene (14)

Followed method-A. 1-(bromoethynyl)cyclohex-1-ene (40 mg, 0.22 mmol), phenyl acetylene (22 mg, 0.24 mmol), freshly degassed piperidene (0.1 mL) and tap water(4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (19:1 hexane:EtOAc) gave the heterodiyne **14** (35 mg, 0.17 mmol, 77%) as a yellow oil, along with homodimer (3%) as a white solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.47 (2 H, dd, *J* = 1.6 & 7.6 Hz), 7.28-735 (3 H, m), 6.30-6.34 (1 H, m), 2.12 to 2.17 (4 H, m), 1.57-1.66 (4 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0, 132.6, 129.0, 128.5, 122.3, 119.9, 83.9, 80.6, 76.8, 71.5, 28.7, 26.0, 22.2 and 21.4.

IR (neat): 3056, 2987, 2939, 1730, 1656, 1439, 1412, 1370, 1269, 1041, 892, 739,521, 496 and 432 cm^{-1}.

HR ESI-MS: $[C_{16}H_{15}]^+ = [M+H]^+$ requires 207.1174: found 207.1173.

TLC: R_f = 0.6 (19:1, Hex/EtOAc).

1-(Octa-1,3-diyn-1-yl)cyclohex-1-ene (15)

Followed method-A. 1-(bromoethynyl)cyclohex-1-ene (40 mg, 0.22 mmol), 1-hexyne (20 mg, 0.24 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (19:1 hexane: EtOAc) gave the heterodiyne **15** (28 mg, 0.150 mmol, 69%) as a yellow oil, along with homodimer (3%) as a white solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 6.22-6.24 (1 H, m), 2.31 (1 H, t, *J* = 6.8 Hz), 2.09-2.11 (4 H, m), 1.39-1.63 (8 H, m), 0.90 (2 H, t, *J* = 7.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 119.9, 83.7, 82.8, 71.8, 65.2, 30.4, 28.8, 26.0, 25.9, 22.2, 22.0, 21.4 and 19.3.

IR (neat): 3054, 2985, 2940, 2867, 1732, 1667, 1423, 1375, 1265, 1046, 895, 739, 705 and 417 cm^{-1}.

HR ESI-MS: $[C_{14}H_{19}]^+ = [M+H]^+$ requires 187.1487; found 187.1510

TLC: $R_f = 0.6$ (19:1, Hex/EtOAc).

1-[(Trimethylsilyl)buta-1,3-diyn-1-yl]cyclohexan-1-ol (16)

Followed method-A. 1-(bromoethynyl)cyclohexan-1-ol **1** (40 mg, 0.20 mmol), TMS-acetylene (21 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and 1,2 DCE (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane: EtOAc) gave the homodiyne **3** (42 mg, 0.170 mmol, 87%) as a pale white solid.

1-Phenyltetradeca-1,3-diyn-5-ol (18)

Followed method-B. Propargyl alcohol[9] (40 mg, 0.22 mmol), phenylacetylene-bromide[10] (44 mg, 0.24 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) were taken in a R.B. flask and stirred for 30 min at 0 °C. Purification by flash columnchromatograph (9:1 hexane:EtOAc) gave the cross coupled heterodiyne **18** (45 mg, 0.16 mmol, 73%) as a yellow oil, along with homodimer-diol **24** (3 mg, 0.01 mmol, 5%) as a light yellow solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.48 (2 H, dd, *J* =1.4 & 8.0 Hz), 7.28-7.37 (3 H, m), 4.49 (1 H, t, *J* = 6.1 Hz), 2.07 (1 H, br s), 1.72-1.79 (2 H, m), 1.44-1.51 (2 H, m), 1.27-1.30 (12 H, m), 0.87 (3 H, t, *J* = 6.7 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.6, 129.3, 128.5, 121.6, 83.6, 78.6, 73.4, 69.6, 63.2, 37.7, 32.0, 29.6, 29.4, 29.38, 29.34, 25.2, 22.8 and 14.2.

IR (neat): 3430, 2925, 2855, 1704, 1641, 1462, 1403, 1262, 1045, 1024, 755, 689, 621, 522, 469 and 422 cm^{-1}.

HR ESI-MS: $[C_{20}H_{26}ONa]^+ = [M+K]^+$ requires 305.1881; found 305.1909

TLC: $R_f = 0.5$ (4:1, Hex-EtOAc).

***N*-(6-Hydroxypentadeca-2,4-diyn-1-yl)-4-methylbenzenesulfonamide (19)**

Followed method-B. Propargyl alcohol (40 mg, 0.22 mmol), *N*-(3-bromoprop-2-yn-1-yl)-4-methylbenzenesulfonamide (55 mg, 0.24 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column

chromatography (9:1 hexane:EtOAc) gave the heterodiyne **19** (55 mg, 0.14 mmol, 65%) as a yellow oil, along with the homodimer diol **24** (4 mg, 0.01 mmol, 5%) as a light yellow solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.76 (2 H, d, *J* = 8.2 Hz), 7.31 (2 H, d, *J* = 7.9 Hz), 5.09 (1 H, br s), 4.36 (1 H, t, *J* = 6.6 Hz), 3.89 (2 H, s), 2.43 (3 H, s), 2.42 (1 H, br s), 1.63-1.68 (2 H, m), 1.38-1.41 (2 H, m), 1.26 (12 H, m), 0.87 (3 H, t, *J* = 6.6 Hz);

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 136.4, 129.8, 127.5, 80.2, 73.8, 68.8, 68.5, 62.7, 37.5, 33.6, 31.9, 29.7, 29.6, 29.4, 29.3, 25.1, 22.7, 21.6 and 14.2.

IR (neat): 3431, 3382, 3054, 2986, 2928, 2857, 1732, 1600, 1461, 1422, 1375,1338, 1265, 1162, 1092, 1047, 895, 812, 740, 705, 549, 458, 421 cm^-.

HR ESI-MS: $[C_{22}H_{32}NO_3S]^+ = [M+H]^+$ requires 390.2103: found 390.2103.

TLC: R_f = 0.5 (4:1, Hex-EtOAc)

1-(Benzyloxy)pentadeca-2,4-diyn-6-ol (20)

Followed method-B. Propargyl alcohol (40 mg, 0.22 mmol), {[(3-bromoprop-2-yn-1-yl)oxy] methyl}benzene[6] (54 mg, 0.24 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **20** (48 mg, 0.15 mmol, 67%) as a yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.29-7.35 (5 H, m), 4.59 (2 H, s), 4.42 (1 H, t, *J* = 6.3 Hz), 4.23 (2 H, s), 2.00 (1 H, br s), 1.67-1.73 (2 H, m), 1.43-1.46 (2 H, m), 1.26 (12 H, m), 0.86-0.89 (3 H, t, *J* = 6.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1, 128.6, 128.1, 80.3, 75.8, 72.9, 71.9, 70.7, 62.9, 57.6, 37.6, 32.0, 29.6, 29.5, 29.4, 29.3, 25.1, 22.7 and 14.2 .

IR (neat): 3446, 3304, 3054, 2985, 2928, 2856, 1733, 1652, 1605, 1455, 1423, 1375, 1353, 1265, 1073, 1046, 896, 741, 706, 608 and 459 cm^{-1}.

HR ESI-MS: $[C_{22}H_{30}O_2K]^+ = [M+K]^+$ requires 365.1883; found 365.1909

TLC: R_f = 0.5 (4:1, Hex/EtOAc)

1-(4-Chlorophenyl)pentadeca-2,4-diyne-1,6-diol (21)

Followed method-B. Propargyl alcohol (40 mg, 0.22 mmol), 3-bromo-1-(4-chlorophenyl) prop-2-yn-1-ol[11] (59 mg, 0.24 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **21** (60 mg, 0.173 mmol, 79%) as a yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.43 (2 H, d, *J* = 8.4 Hz), 7.34 (2 H, d, *J* = 8.5 Hz), 5.48 (1 H, s), 4.41 (1 H, t, *J* = 6.6 Hz), 2.93 (1 H, br s), 2.30 (1 H, br s), 1.68-1.71 (2 H, m), 1.40-1.43 (2 H, m), 1.26 (12 H, m), 0.87 (3 H, t, *J* = 6.5 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 134.6, 128.9, 128.1, 81.7, 78.4, 70.9, 68.7, 64.2, 62.9, 37.5, 31.9, 63.2, 29.4, 25.1, 22.7 and 14.2.

IR (neat): 3427, 3054, 2927, 2856, 1731, 1642, 1591, 1488, 1463, 1402, 1375, 1266, 1091, 1045, 1014, 842,793, 740, 705, 636, 600, 514 and 438 cm^{-1}.

HR ESI-MS: $[C_{21}H_{28}ClO_2]^+ = [M+H]^+$ requires 347.1778: found 347.1774.

TLC: R_f = 0.5 (4:1, Hex/EtOAc)

2-Phenylhexadeca-3,5-diyne-2,7-diol (22)

Followed method-B. Propargyl alcohol (40 mg, 0.22 mmol), 4-bromo-2-phenylbut-3-yn-2-ol[12] (54 mg, 0.24mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **22** (50 mg, 0.153 mmol, 70%) as a yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.53 (2 H, dd, *J* = 7.5 Hz), 7.28 (2 H, t, *J* = 7.1 Hz), 7.22 (1 H, t, *J* = 7.2 Hz), 4.35 (1 H, t, *J* = 6.6 Hz), 2.70 (1 H, br s), 2.12 (1 H, br s), 1.70 (3 H, s), 1.60-1.66 (2 H, m), 1.34-1.38 (2 H, m), 1.19-1.21(12 H, m), 0.79-0.82 (3 H, t, *J* = 6.5 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 128.5, 128.1, 124.9, 82.4, 81.5, 70.5, 69.1, 68.9, 63.0, 37.6, 32.9, 32.0, 29.7, 29.6, 29.4, 29.4, 29.3, 25.1, 22.7 and 14.2.

IR (neat): 3417, 2926, 2855, 1630, 1598,1462, 1402, 1260, 1202, 1122, 1084, 1040, 935, 802, 763, 699, 656, 596, 547, 517, 473 and 427 cm^{-1}.

HR ESI-MS: $[C_{22}H_{31}O_2]^+ = [M+H]^+$requires 327.2324: found 327.2324.

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

2-Methylhexadeca-3,5-diyne-2,7-diol (23)

Followed method-B. Propargyl alcohol (40 mg, 0.22 mmol), 4-bromo-2-methylbut-3-yn-2-ol[13] (38 mg, 0.24 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (19:1 hexane:EtOAc) gave the heterodiyne **23** (51 mg, 0.193 mmol, 87%) as a yellow oil, along with homodimer **24** (2 mg, 0.005 mmol, 3%) as a light yellow solid.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.41 (1 H, t, *J* = 6.5 Hz), 2.38 (1 H, br s), 2.26 (1 H, br s), 1.67-1.74 (2 H, m), 1.53 (6 H, s), 1.42-1.45 (2 H, m), 1.26-1.28 (12 H, m), 0.87 (3 H, t, *J* = 6.7 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 83.8, 80.9, 68.9, 66.5, 65.6, 62.9, 37.6, 32.0, 31.1, 29.63, 29.61, 29.4, 29.3, 25.1, 22.7 and 14.2.

IR (neat): 3398, 3054, 2983, 2927, 2856, 1723, 1622, 1462, 1375, 1331, 1264, 1153, 1044, 955, 896, 741, 705, 633, 559, 510, 458, 441 and 421 cm^{-1}.

HR ESI-MS: $[C_{17}H_{28}O_2K]^+ = [M+K]^+$ requires 303.1726; found 303.1701

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

Scope study for various alkynes in 1,2 DCE

1-(Phenylbuta-1,3-diyn-1-yl)cyclohexan-1-ol (2)

1,2 DCE gave the coupled alcohol **2** (37 mg, 0.16 mmol, 82%).

1-(5-Hydroxy-5-phenylhexa-1,3-diyn-1-yl)cyclohexan-1-ol (4)

1,2 DCE gave coupled alcohol **4** (36 mg, 0.134 mmol, 67 %), along with isolated homo diol **3** (5 mg, 0.02 mmol, 10 %).

1-(5-Hydroxy-5-methylhexa-1,3-diyn-1-yl)cyclohexan-1-ol (5)

1,2 DCE gave coupled alcohol **5** (25 mg, 0.012 mmol, 62%), along with isolated homo diol **3** (3 mg, 0.012 mmol, 5 %)

***N*-[5-(1-Hydroxycyclohexyl)penta-2,4-diyn-1-yl]-4-methylbenzenesulfonamide (6)**

1,2 DCE gave coupled alcohol **6** (46 mg, 0.139 mmol, 71 %), along with isolated homo diol **3** (6 mg, 0.024 mmol, 13 %).

1-(5-Hydroxy-7-phenylhepta-1,3-diyn-1-yl)cyclohexan-1-ol (7)

1,2 DCE gave coupled alcohol **7** (42 mg, 0.15 mmol, 76%), along with isolated homo diol **3** (3 mg, 0.008 mmol, 5%).

1-[5-(Benzyloxy)penta-1,3-diyn-1-yl]cyclohexan-1-ol (8)

1,2 DCE gave coupled alcohol **8** (47 mg, 0.175 mmol, 89%), along with isolated homo diol **3** (3 mg, 0.008 mmol, 5%).

1-(6-Hydroxyhexa-1,3-diyn-1-yl)cyclohexan-1-ol (9)

1,2 DCE gave coupled alcohol **9** (24 mg, 0.13 mmol, 66%), along with isolated homo diol **3** (5.5 mg, 0.022 mmol, 12 %).

6-(1-Hydroxycyclohexyl)hexa-3,5-diyn-1-yl 4-methylbenzenesulfonate (10)

1,2 DCE gave coupled alcohol **10** (48 mg, 0.138 mmol,70 %), along with isolated homo diol **3** (6 mg, 0.024 mmol, 12%).

1-{6-[(t*ert*-Butyldimethylsilyl)oxy]hexa-1,3-diyn-1-yl}cyclohexan-1-ol (12)

1,2 DCE gave coupled alcohol **12** (55 mg, 0.179 mmol, 91%), along with isolated homo diol **3** (2 mg, 0.008 mmol, 3 %).

1-(Octa-1,3-diyn-1-yl)cyclohexan-1-ol (13)

1,2 DCE gave coupled alcohol **13** (28 mg, 0.137 mmol, 69%), along with isolated homo diol **3** (7 mg, 0.028 mmol, 14%).

1-[(Trimethylsilyl)buta-1,3-diyn-1-yl]cyclohexan-1-ol (16)

Followed method-A. 1-(bromoethynyl)cyclohexan-1-ol (40 mg, 0.20 mmol), TMS-acetylene (21 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and 1,2 DCE (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane: EtOAc) gave the heterodiyne **16** (36 mg, 0.163 mmol, 83%) as a white solid.along with isolated homo diol (3 mg, 0.012 mmol, 5%).

^{1}HNMR (400 MHz, $CDCl_3$): δ = 1.94 (1 H, br, s), 1.69-1.73 (2 H, m), 1.47-1.51 (2 H, m), 1.32-1.42 (5 H, m), 102-1.08 (1 H, m), -0.0002 (9 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 87.5, 87.4, 81.4, 69.2, 69.0, 39.7, 25.1, 23.2 and -0.31.

IR (neat): 3427, 3054, 2983, 2939, 2860, 1731, 1601, 1447, 1423, 1265, 1121, 1048, 901, 849, 742, 705, 657, 542, 479 and 407 cm^{-1}.

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

M.P.: 102-105 °C

1-Phenyltetradeca-1,3-diyn-5-ol (18)

Followed method-B. Propargyl alcohol (40 mg, 0.20 mmol), (iodoethynyl)benzene[14] (50 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water(4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **18** (36 mg, 0.13 mmol, 65%) as a yellow oil. along with isolated homo diol **24** (5 mg, 0.014 mmol, 8%).

1-(Furan-2-yl)-5-phenylpenta-2,4-diyn-1-ol (25)

Followed method-B. Propargyl alcohol[11] (40 mg, 0.33 mmol), (iodoethynyl)benzene[14] (82 mg, 0.36 mmol), freshly degassed piperidene (0.17 mL) and tap water (7 mL), CuCl (3.2 mg, 0.033 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane: EtOAc) gave the hetero diyne **25** (46 mg, 0.21 mmol, 62%) as a yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.49 (2 H, dd, *J* = 1.3 & 8.0 Hz), 7.42 (1 H, dd, *J* = 0.8 & 1.8 Hz), 7.29-7.39 (3 H, m), 6.49 (1 H, d, *J* = 3.2 Hz), 6.36 (1 H, dd, *J* = 1.8 & 3.2 Hz), 5.58 (1 H, d, *J* = 4.8 Hz), 2.72 (1 H. d, *J* = 5.9 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9, 143.3, 132.7, 129.6, 128.6, 128.5, 121.2, 110.6, 108.3, 79.5, 79.1, 73.1, 70.6 and 58.7.

IR (neat): 3439, 3022, 2932, 2861, 1628, 1471, 1399, 1324, 1227, 1183, 1145, 1103, 1071, 1043, 1009, 940, 886, 846, 754, 575, ,525, 488, 449 and 431 cm^{-1}.

TLC: R_f = 0.5 (4:1,Hex/EtOAc).

5-Phenyl-1-(pyridin-3-yl)penta-2,4-diyn-1-ol (26)

Followed method-B. Propargyl alcohol[11] (40 mg, 0.30 mmol), (iodoethynyl)benzene (75 mg, 0.33 mmol), freshly degassed piperidene (0.15 mL) and tap water (6 mL), CuCl (3 mg, 0.03 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (4:1 hexane: EtOAc) gave the heterodiyne **26** (35 mg, 0.206 mmol, 67%) as a brown oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 8.68 (1 H, s), 8.51 (1 H, dd, *J* = 1.1 & 8.0 Hz), 7.93 (1 H, dt, *J* = 1.6 & 7.9 Hz), 7.49 (1 H, d, *J* = 7.2 Hz), 7.29-7.37 (5 H, m), 5.66 (1 H, s), 2.42 (1 H, br s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 147.9, 136.3, 135.0, 132.7, 129.6, 128.6, 123.9, 121.2, 81.2, 79.7, 62.7, 71.6 and 76.8.

IR (neat): 3433, 2861, 2951, 2861, 1627, 1548, 1530, 1478, 1404, 1260, 1191, 1121, 1049, 874, 667, 639, 597, 549, 478, 450 and 405 cm^{-1};

TLC: R_f = 0.3 (4:1, Hex/EtOAc).

1-(2-Iodophenyl)-5-phenylpenta-2,4-diyn-1-ol (27)

Followed method-B. Propargyl alcohol[11] (40 mg, 0.15 mmol), (iodoethynyl)benzene (38 mg, 0.17 mmol), freshly degassed piperidene (0.07 mL) and tap water (3 mL), CuCl (1.5 mg, 0.015 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane: EtOAc) gave the heterodiyne **27** (46 mg, 0.13 mmol, 86%) as a yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.84 (1 H, dd, *J* = 1.1 & 7.9 Hz), 7.74 (1 H, dd, *J* = 1.6 & 7.8 Hz), 7.48 (2 H, dd, *J* = 1.3 & 8.0 Hz), 7.41 (1 H, td, *J* = 1.7 & 7.7 Hz), 5.79 (1 H, s), 2.78 (1 H, br s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.7, 139.8, 132.7, 130.4, 129.5, 128.9, 128.5, 128.3, 121.3, 97.9, 80.8, 79.6, 73.3, 71.6 and 69.2.

IR (neat): 3435, 3054, 2986, 2926, 1732, 1628, 1594, 1511, 1442, 1422, 1375, 1319, 1265, 1163, 1104, 1046, 986, 895, 780, 739, 705, 531 and 423 cm^{-1};

HR ESI-MS: $[C_{17}H_{12}IO]^+ = [M\text{-}OH_2]^+$ requires 340.9827: found; 340.9821

1-(2-Fluorophenyl)-5-phenylpenta-2,4-diyn-1-ol (28)

Followed method-B. Propargyl alcohol[11] (40 mg, 0.27 mmol), (iodoethynyl)benzene (67 mg, 0.293 mmol), freshly degassed piperidene (0.13 mL) and tap water (5 mL), CuCl (3 mg, 0.03 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane: EtOAc) gave the heterodiyne **28** (58 mg, 0.232 mmol, 87%) as a yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.64 (1 H, td, *J* = 1.7 & 7.6 Hz), 7.47 (2 H, dd, *J* = 1.2 & 7.9 Hz), 7.28-7.35 (4 H, m), 7.18 (1 H, td, *J* = 1.0 & 7.6 Hz), 7.06 (1 H, ddd, *J* = 1.0 ,7.0 & 8.2 Hz), 5.84-5.85 (1 H, d, *J* = 2.6 Hz), 2.80 (1 H, br s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 158.8, 132.7, 130.6, 130.5, 129.5, 128.5, 128.4, 127.1, 126.9, 124.7, 124.6, 121.3,115.9, 115.7, 80.6, 79.5, 73.2, 71.2, 59.7 and 59.6.

IR (neat): 3435, 3056, 2983, 2926, 2861, 1706, 1616, 1590, 1487, 1456, 1378, 1330, 1265, 1230, 1175, 1094, 998, 943, 876, 690, 755, 690, 619, 563, 528, 448 and 413 cm^{-1}.

HR ESI-MS: $[C_{17}H_{12}FO]^+ = [M+H]^+$ requires 251.0872: found; 251.0875

TLC: $R_f = 0.5$ (4:1, Hex/EtOAc).

1-(Naphthalen-1-yl)-5-phenylpenta-2,4-diyn-1-ol (29)

Followed method-B. Propargyl alcohol[11] (40 mg, 0.22 mmol), (iodoethynyl)benzene (55 mg, 0.24 mmol), freshly degassed piperidene (0.1 mL) and tap water(4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **29** (45 mg, 0.16 mmol, 73%) as a yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 8.27 (1 H, d, *J* = 8.5 Hz), 7.82-7.89 (3 H, m), 7.45-7.60 (5 H, m), 7.28-7.35 (3 H, m), 6.23 (1 H, d, *J* = 4.7 Hz), 2.63 (1 H, d, *J* = 5.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.9, 134.1, 132.7, 130.5, 129.7, 129.5, 128.9, 128.5, 126.7, 126.1, 125.3, 124.9, 123.8, 121.4, 81.5, 77.4, 77.3, 72.0 and 63.6.

IR (neat): 3435, 3054, 2986, 2926, 1732, 1628, 1594, 1511, 1442, 1422, 1375, 1319, 1265, 1163, 1104, 1046, 986, 895, 780, 739, 705, 531 and 423 cm^{-1}.

HR ESI-MS: $[C_{21}H_{14}OK]^+ = [M+K]^+$ requires 321.0682; found 321.0670

TLC: $R_f = 0.5$ (4:1, Hex/EtOAc).

1-{7-[(*tert*-Butyldimethylsilyl)oxy]hepta-1,3,5-triyn-1-yl}cyclohexan-1-ol (30)

Followed method-A. 1-(bromoethynyl)cyclohexan-1-ol (40 mg, 0.20 mmol), *tert*-butyldimethyl (penta-2,4-diyn-1-yloxy)silane[15] **33** (42 mg, 0.22 mmol), freshly degassed piperidene (0.1 mL) and tap water (4 mL), CuCl (2 mg, 0.02 mmol) stirred for 30 min at 0°C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **30** (42 mg, 0.133 mmol, 68%) as a brown oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.26 (2 H, s), 2.10 (1 H, br s), 1.77-1.80 (2 H, m), 1.38-1.58 (6 H, m), 1.09-1.14 (2 H, m), 0.78 (9 H, s), -0.0002 (6 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 83.8, 82.0, 69.9, 69.8, 69.3, 69.2, 63.2, 52.2, 39.8, 25.8, 25.1, 23.2, 18.3 and -5.1.

IR (neat): 3406, 2935, 2855, 1712, 1635, 1454, 1400, 1374, 1336, 1255, 1159, 1068, 967, 833, 774, 662, 544, 507, 434 and 409 cm^{-1}.

HR ESI-MS: $[C_{19}H_{29}O_2Si]^+ = [M+H]^+$ requires 318.1970: found 318.1970.

TLC: $R_f = 0.5$ (4:1, Hex/EtOAc).

10-[(*tert*-Butyldimethylsilyl)oxy]-1-phenyldeca-4,6,8-triyn-3-ol (31)

Followed method-A. 1-bromo-5-phenylpent-1-yn-3-ol[16] **32** (40 mg, 0.14 mmol), *tert*-butyldimethyl(penta-2,4-diyn-1-yloxy)silane[15] **33** (30 mg, 0.153 mmol), freshly degassed piperidene (0.07 mL) and tap water (3 mL), CuCl (1.4 mg, 0.014 mmol) stirred for 30 min at 0°C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **31** (42 mg, 0.12 mmol, 85%) as a brown oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.16 (2 H, t, *J* = 7.7 Hz), 7.06-7.10 (3 H, m), 4.26 (1 H, t, *J* = 6.5 Hz), 4.22 (2 H, d, *J* = 1.00 Hz), 2.65 (2 H, t, *J* = 7.8 Hz), 2.12 (1 H, br s), 1.88-1.90 (2 H, m), 0.78 (9 H, s), -0.0002 (6H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 128.7, 128.60, 126.2, 80.9, 79.0, 77.6, 75.1, 70.2, 69.8, 67.9, 62.7, 52.0, 38.8, 25.8, 18.3 and -5.1.

IR (neat): 3427, 3304, 3064, 3026, 2957, 2930, 2903, 2855, 1716, 1598, 1464, 1368, 1255, 1143, 1089, 838, 780, 731, 700, 667, 624, 539 and 485 cm^{-1}.

HR ESI-MS: $[C_{22}H_{29}O_2Si]^+ = [M+H]^+$ requires 354.1970; found 354.1965.

TLC: $R_f = 0.5$ (4:1, Hex/EtOAc).

1-[9-(*tert*-Butyldimethylsilyloxy)nona-1,3,5,7-tetraynyl]cyclohexanol (34)

Followed method-A. 1-(bromobuta-1,3-diynyl)cyclohexanol **35** (40 mg, 0.18 mmol), tert-butyldimethyl(penta-2,4-diyn-1-yloxy)silane[15] **33** (38 mg, 0.194 mmol), freshly degassed piperidene (0.09 mL) and tap water (3 mL), CuCl (1.8 mg, 0.02 mmol) stirred for 30 min at 0°C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave the heterodiyne **34** (37 mg, 0.11 mmol, 61%) as a brown oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 4.27 (2 H, s), 1.79-1.82 (2 H, s), 1.38-1.60 (7 H, m), 1.13-1.16 (1 H, m), 0.78 (9 H, s), -0.0002 (6 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 82.0, 69.8, 69.3, 69.1, 63.9, 63.3, 61.9, 61.6, 52.1, 39.5, 25.7, 24.9, 23.0, 18.2, 0.01, -5.19.

IR (neat): 3422, 3303, 3053, 2933, 2894, 2857, 1731, 1616, 1590, 1490, 1466, 1367, 1260, 1138, 1084, 1006, 966, 939, 896, 837, 781, 741, 708, 665, 628, 455 and 425 cm^{-1}.

HR ESI-MS: $[C_{21}H_{29}O_2Si]^+$ = $[M+H]^+$ requires 341.1937 ; found 341.1930.

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

1-(Bromobuta-1,3-diynyl)cyclohexanol (35)

Alkyne[15] (100 mg, 0.68 mmol), *N*-bromosuccinimide (131 mg, 0.743 mmol), $AgNO_3$ (11 mg, 0.08 mmol) and acetone (5 mL) were strirred 2 h at 0 °C. Purification by flash chromatography (9:1; hexane:EtOAc) gave bromide **35** (120 mg, 0.53 mmol, 78 %)

^{1}HNMR (400 MHz, $CDCl_3$): δ = 3.09 (1 H, br s), 1.92-2.10 (2 H, m), 1.47-1.71 (7 H, m), 1.22-1.28 (1 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 78.3, 69.2, 69.1, 64.9, 41.4, 39.6, 25.0 and 23.1.

IR (neat): 3419, 3157, 2938, 2859, 1784, 1726, 1603, 1448, 1373, 1339, 1284, 1260, 1185, 1056, 1030, 962, 912, 851, 743, 727, 650, 549, 524, 482 and 405 cm^{-1}.

TLC: R_f = 0.5 (4:1, Hex/EtOAc).

***N*-(3-Bromoprop-2-yn-1-yl)-4-methylbenzenesulfonamide (36)**

Alkyne[2] (100 mg, 0.48 mmol), *N*-bromosuccinamide (93 mg, 0.53 mmol), $AgNO_3$ (9 mg, 0.05 mmol) and acetone (5 mL) were strirred 2 h at 0 °C Purification by flash chromatography (9:1; hexane:EtOAc) gave bromide **36** (120 mg, 0.42 mmol, 79 %).

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.76 (2 H, d, *J* = 8.3 Hz), 7.33 (2 H, d, *J* = 8.0 Hz), 4.59 (1 H, br s), 3.86 (1 H, d, *J* = 6.2 Hz), 2.43 (3 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 136.7, 129.8, 127.5, 74.3, 45.0, 34.0 and 21.7.

IR (neat): 3247, 3057, 3154, 2985, 2928, 2859, 1730, 1645, 1600, 1416, 1333, 1265, 1160, 1085, 1046, 898, 673, 598, 547 and 435 cm^{-1}.

TLC: R_f = 0.5 (4:1, Hex/EtOAc)

***N*-(3-Iodoprop-2-yn-1-yl)-4-methylbenzenesulfonamide (xx)**

Alkyne[10] (300 mg, 1.43 mmol), N-iodosuccinimide (385 mg, 1.72 mmol), $AgNO_3$ (121 mg, 0.71 mmol), and acetone (10 mL) were strirred for 2 h at 0 °C. Purification by flash column chromatography (9:1; hexane:EtOAc) gave the iodide **xx** as an yellow oil (450 mg, 1.34 mmol, 94%).

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.76 (2 H, d, *J* = 8.3 Hz), 7.33 (2 H, d, *J* = 8.0 Hz), 4.73 (1 H, t, *J* = 6.0 Hz), 3.98 (2 H, d, *J* = 6.2 Hz), and 2.44 (3 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 136.6, 129.9, 127.6, 88.1, 45.0, 34.8 and 21.7

IR (neat): 3430, 3279, 2922, 2853, 1653, 1426, 1316, 1152, 1074, 983, 855, 810, 753, 677, 535 and 473 cm^{-1}

TLC: R_f = 0.5 (4:1, Hex/EtOAc)

4-Iodo-2-methylbut-3-yn-2-ol (xx)

2-methylbut-3-yn-2-ol (300 mg, 3.6 mmol), *N*-iodosuccinimide (959 mg, 4.3 mmol), $AgNO_3$ (301 mg, 1.9 mmol), and acetone (23 mL) were strirred for 2 h at 0 °C. Purification by flash column chromatography (9:1; hexane:EtOAc) gave the iodide **xx** (420 mg, 2.0 mmol, 56%) as yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 1.52 (6 H, d, *J* = 3.3 Hz), 2.37 (1 H, br s)

^{13}C NMR (100 MHz, $CDCl_3$): δ = 99.2, 66.9 and 31.4

IR (neat): 3428, 3053, 2985, 2934, 1453, 1424, 1368, 1330, 1266, 1219, 1164, 965, 903, 742, 706 and 561 cm^{-1}

TLC: R_f = 0.5 (4:1, Hex/EtOAc)

4-Iodo-2-phenylbut-3-yn-2-ol (xx)

2-Phenylbut-3-yn-2-ol (200 mg, 1.37 mmol), *N*-iodosuccinamide (370 mg, 1.65 mmol), $AgNO_3$ (110 mg, 0.68 mmol), and acetone (10 mL) were strirred for 2 h at 0 °C Purification by flash chromatography (9:1; hexane:EtOAc) gave the iodide **xx** (300 mg, 1.10mmol, 80%) as yellow oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.61 (2 H, d, *J* = 7.3 Hz), 7.24-7.37 (3 H, m), 2.58 (1 H, br s), 1.77 (3 H, s)

^{13}C NMR (100 MHz, $CDCl_3$): δ =145.1, 128.4, 128.0, 124.9, 97.9, 71.6, 60.5 and 33.2

IR (neat): 3399, 3059, 3030, 2984, 2928, 1666, 1599, 1494, 1446, 1368, 1328, 1267, 1224, 1153, 1090, 1050, 940, 893, 766, 616, 585 and 432 cm^{-1}

TLC: R_f = 0.5 (4:1, Hex/EtOAc)

(3-Iodoprop-2-yn-1-yl)oxy)methyl)benzene (xx)

((prop-2-yn-1-yloxy)methyl)benzene (200 mg, 1.37 mmol), N-iodosuccinamide (370 mg, 1.65 mmol), $AgNO_3$ (110 mg, 0.68 mmol), and acetone (10 mL) were strirred for 2 h at 0 °C. Purification by flash column chromatography (9:1; hexane:EtOAc) gave the iodide **xx** (300 mg, 1.10 mmol, 80 %) as yello oil.

^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.34-7.39 (5 H, m), 4.58 (2 H, s), 4.31 (2 H, s)

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.2, 128.5, 128.2, 128.0, 90.6, 71.8, 65.8 and 58.8

IR (neat): 3056, 2984, 2931, 2897, 1724, 1634, 1496, 1455, 1355, 1276, 1208, 1164, 1078, 1026, 984, 936, 906, 860, 702 and 596 cm^{-1}

TLC: R_f = 0.5 (4:1, Hex/EtOAc)

References:

1) E. D. Juardi, P. B. Sambat and E. Mc. Nelis, *Tetrahedron Lett.* **1994**, *50*, 11793.

2) L. S. Kocsis, E. Beredetti and K. M. Brummond, *Org. Lett*., **2012**, *14*, 4430.

3) P. A. Allegretti and E. M. Ferreira, *Org. Lett*., **2011**, *13*, 5924.

4) D. Farran, A. M. Z. Slawin, P. Kirsch, D, O'. Hagan, *J. Org. Chem*., **2009**, *74*, 7168.

5) G. Belangar, M. Dupuis and R. Larouche-Gauthier, *J. Org. Chem*., **2012**, *77*, 3215.

6) M. Li, Y. J. Li, B. Zhao, F. Liang and L.-Y. Jin, *RSC Advances*, **2014**, *4*, 30046.

7) J. Zheng, H. Cheng, F. Wang and L. Liu, *J. Am .Chem. Soc.*, **2011**, *133*, 11080.

8) L. Li, J. X. Wang, G. Zhang and Q. F. Liu, *Tetrahedron Lett.*, **2009**, *50*, 4033.

9) S. A. Fleming, R. Liu, J. T. Reddy; *Tetrahedron Lett.*, **2005**, *46*, 8095.

10) O. V. Zatolochnaya, V. Geavorgyan, *Org. Lett*., **2013**, *15*, 2562.

11) B. S. Chinta, B. Baire, *J. Org. Chem*., **2015**, *80*, 10208.

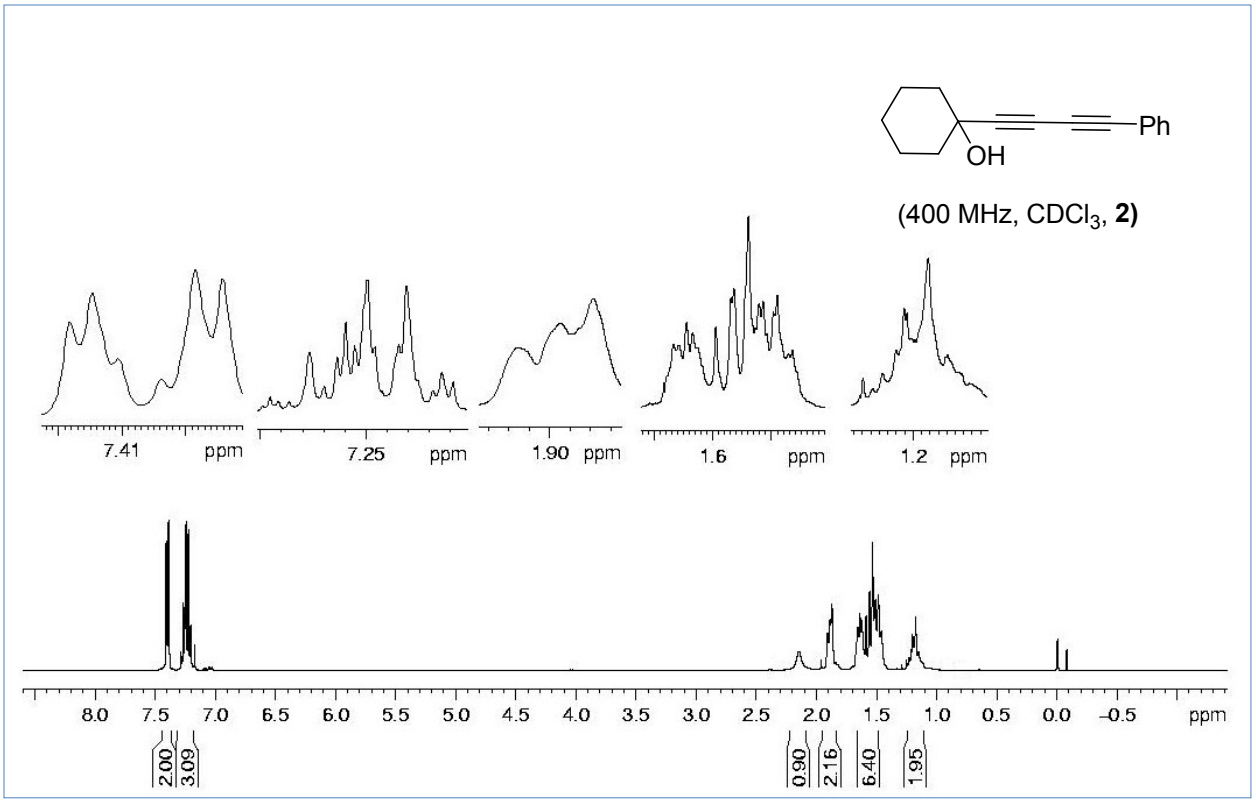
12) Zhurnal Obshchei Khimii, **1959**, *29*, 457.

13) Y. Xing, B. Cheng, J. Wang, P. Lu, Y. Wang., *Org. Lett*., **2014**, *16,* 4814.

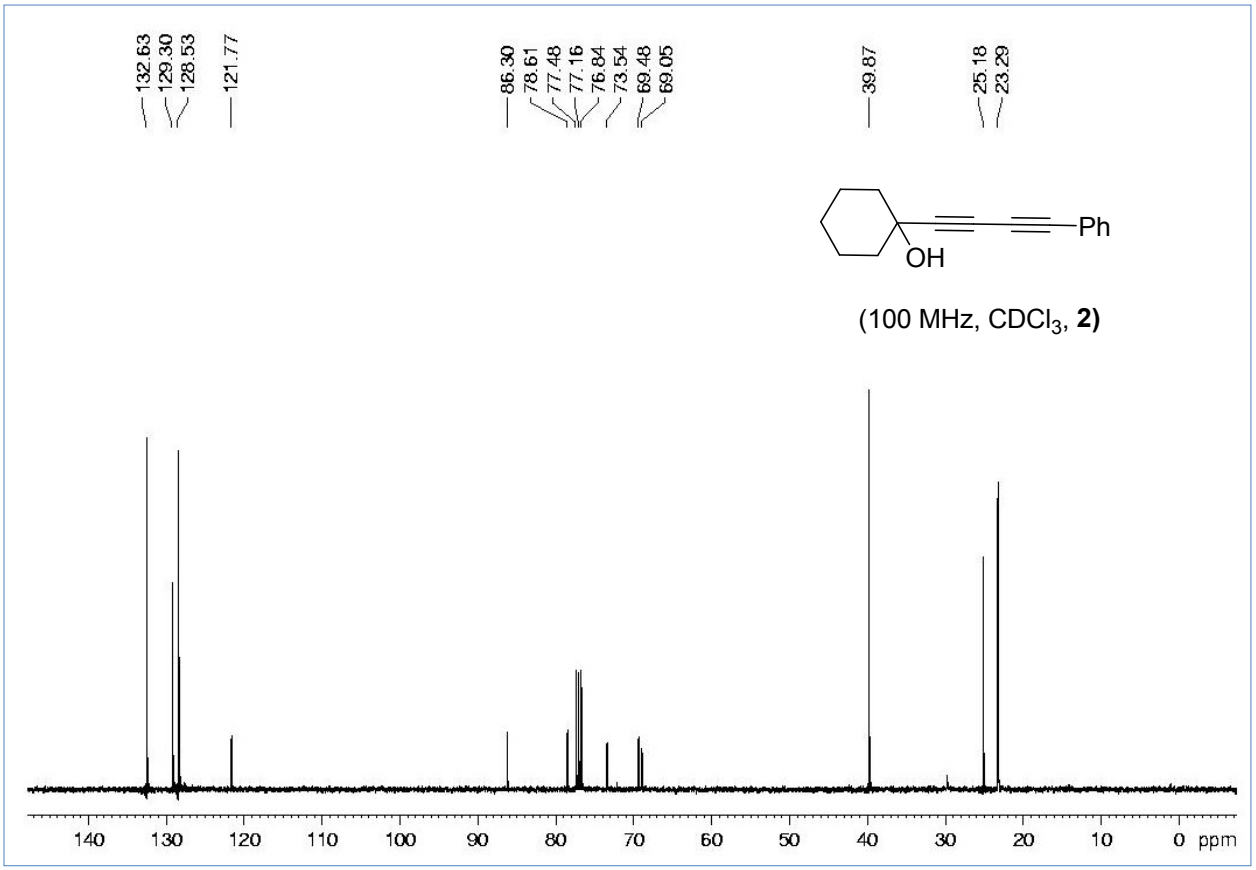
14) W. Cheen, J. Zhang, B. Wang, Z. Xing, Z. X. Wang, Y. Hu, *J. Org. Chem*., **2015**, *80*, 2413.

15) K.Wang, E. J. Cho, S. Y. Yun, J. Y. Rhee, D. Lee, *Tetrahedron Lett.*, **2013**, *69*, 9105.

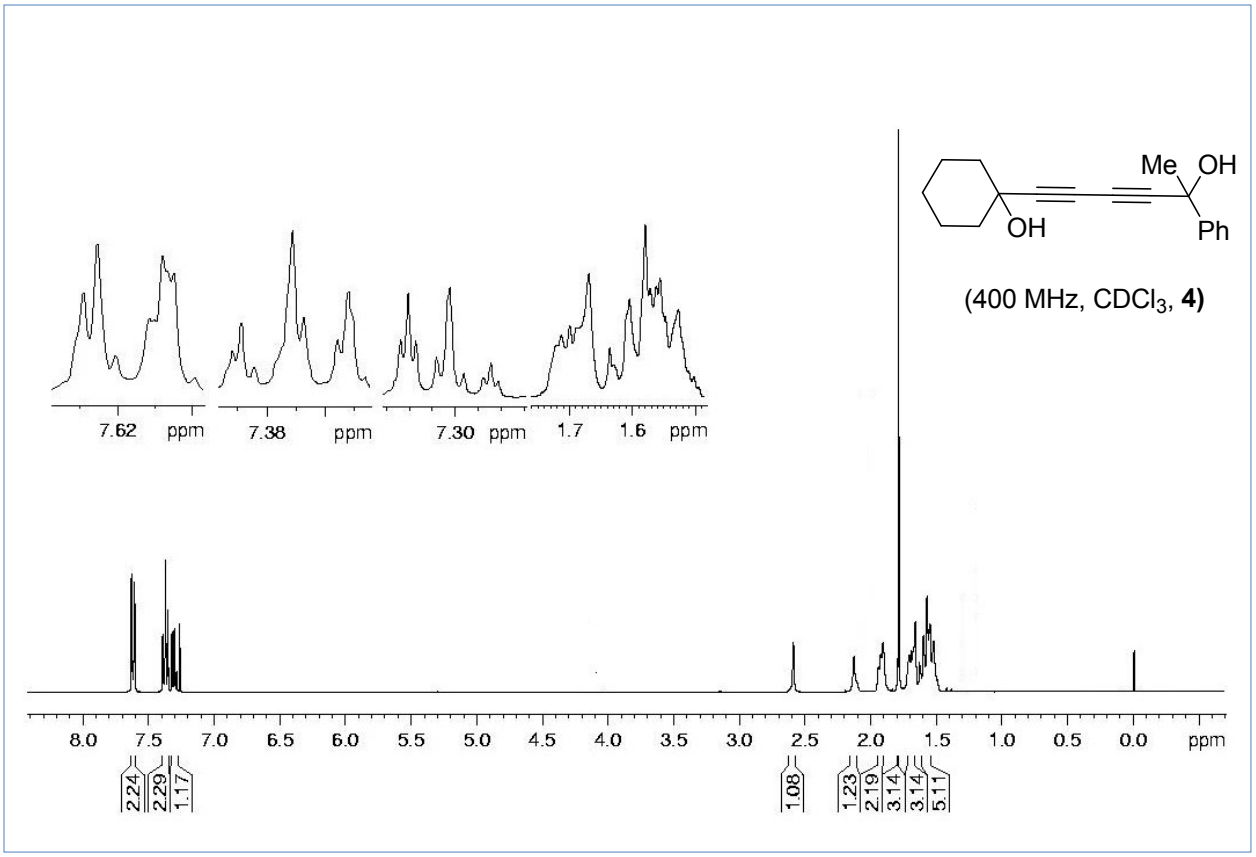
16) R. Karmakar, S. Y. Yun, J. Chen, Y. Z. Xia, D. Lee, *Angew. Chem., Int. Ed,* **2015**, *54*,6582.



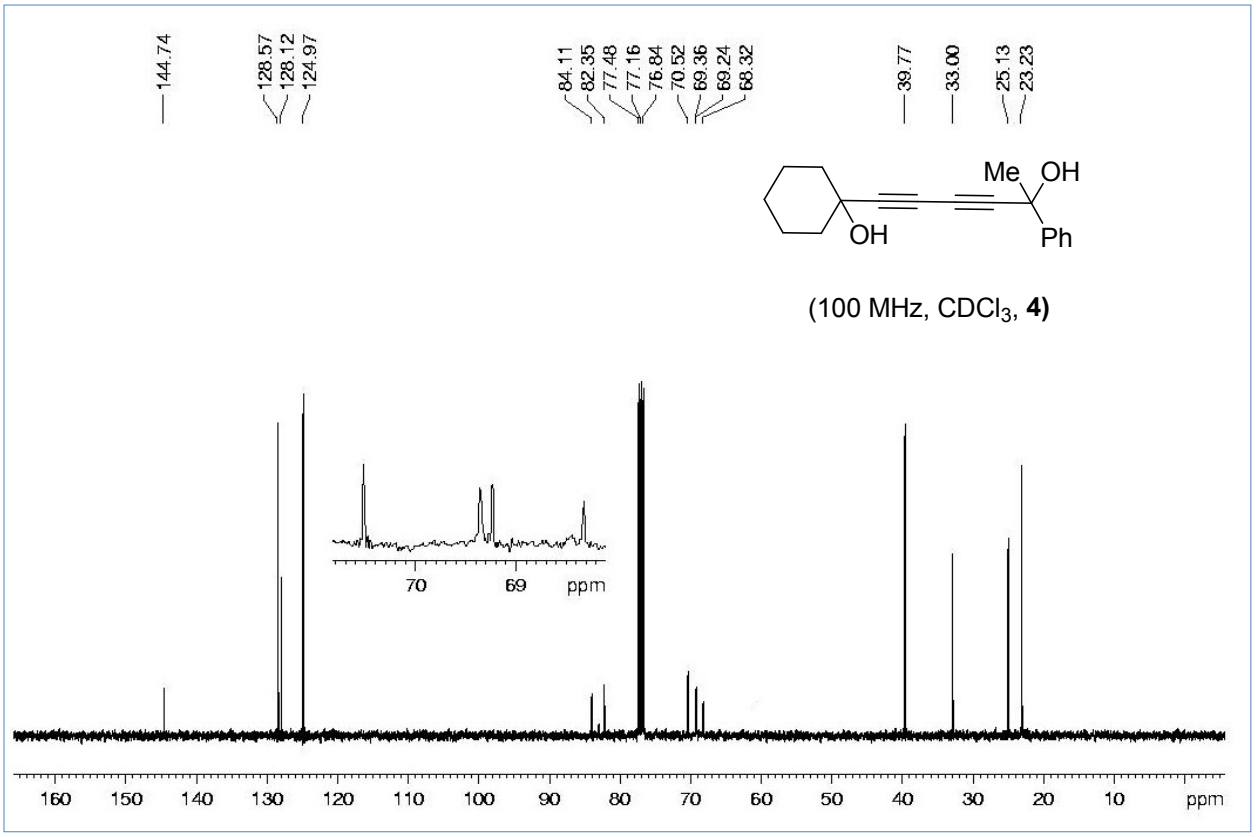
(400 MHz, $CDCl_3$, **2)**



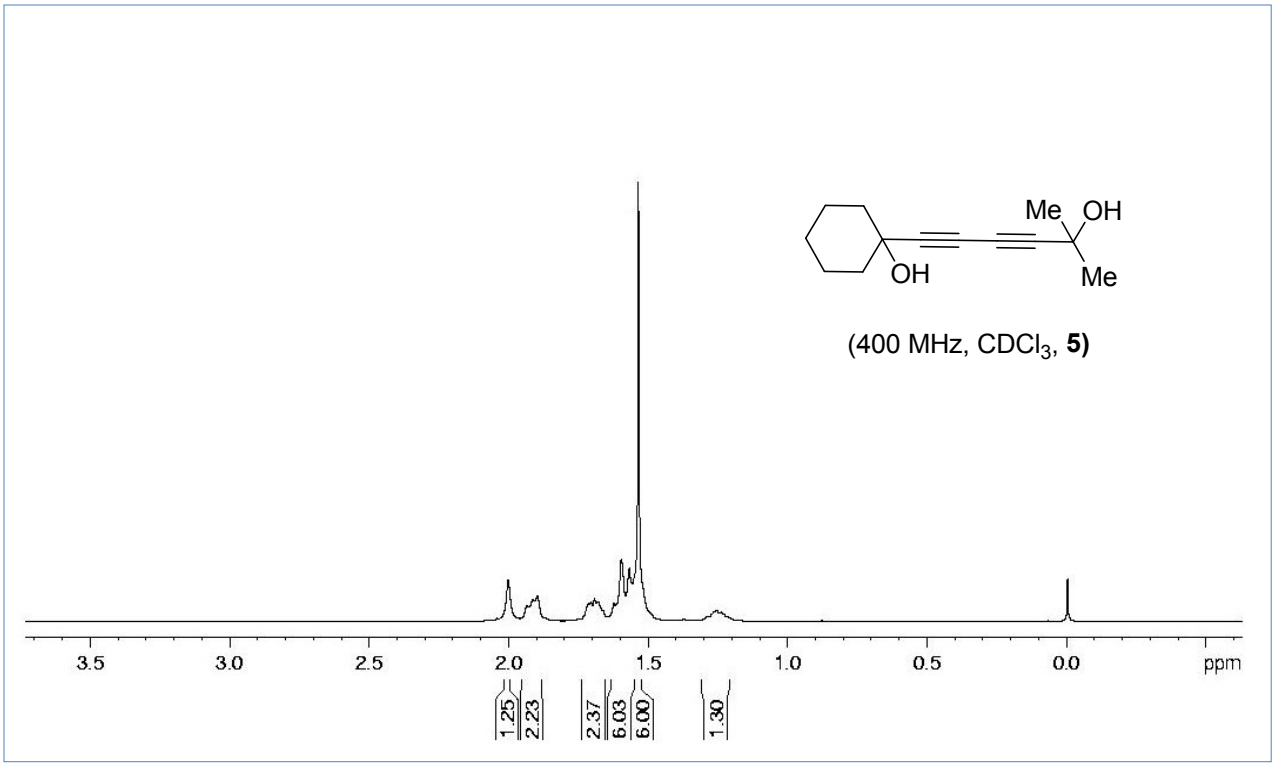
(100 MHz, $CDCl_3$, **2)**



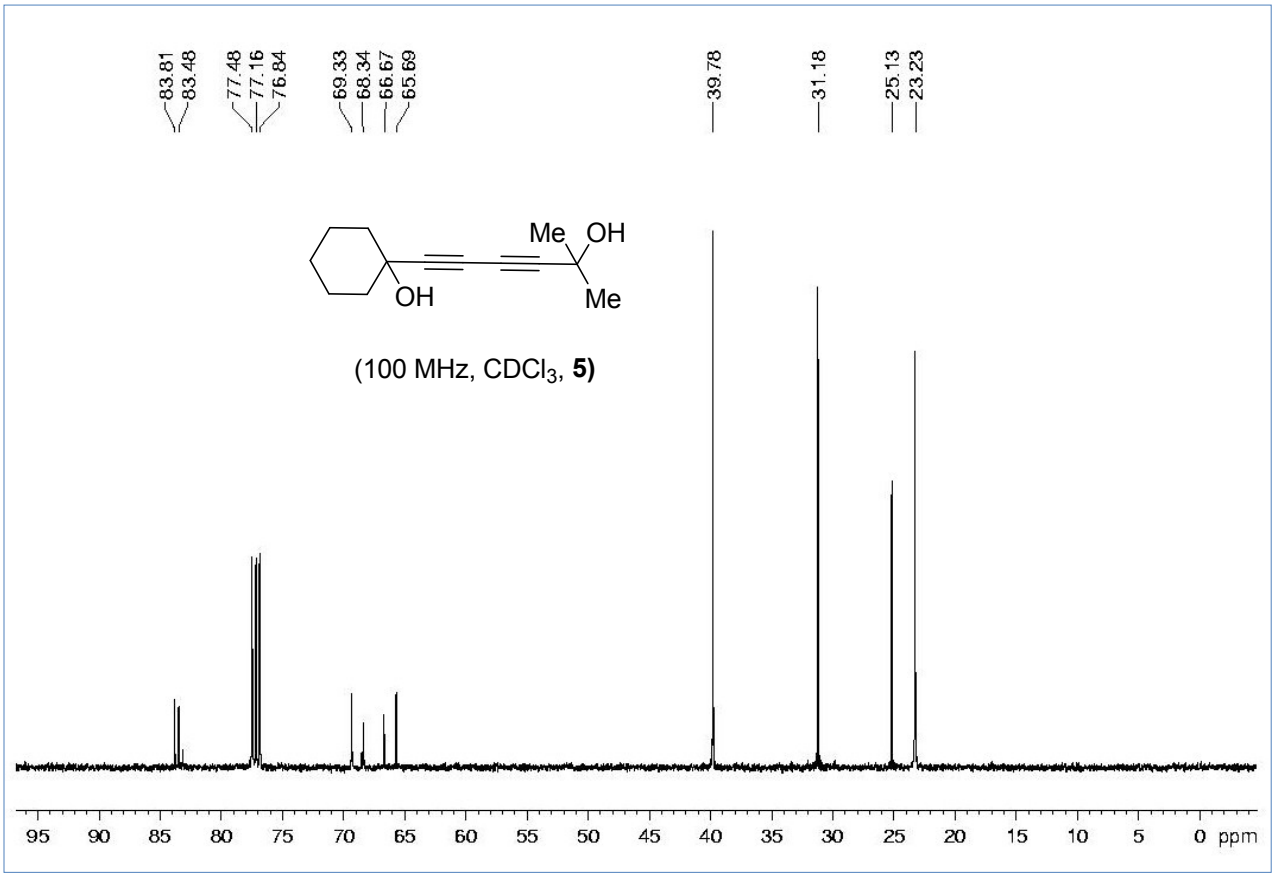
(400 MHz, $CDCl_3$, **4)**



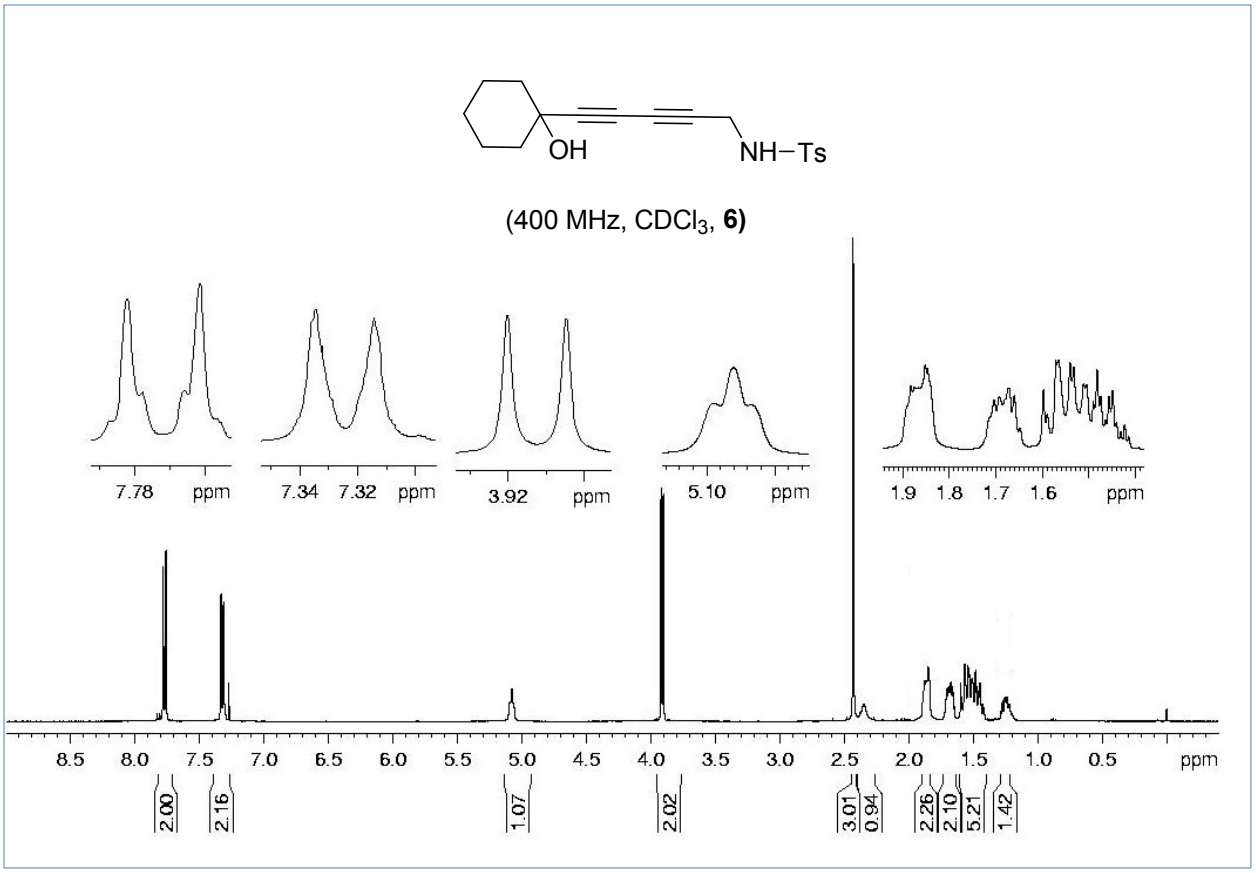
(100 MHz, $CDCl_3$, **4)**

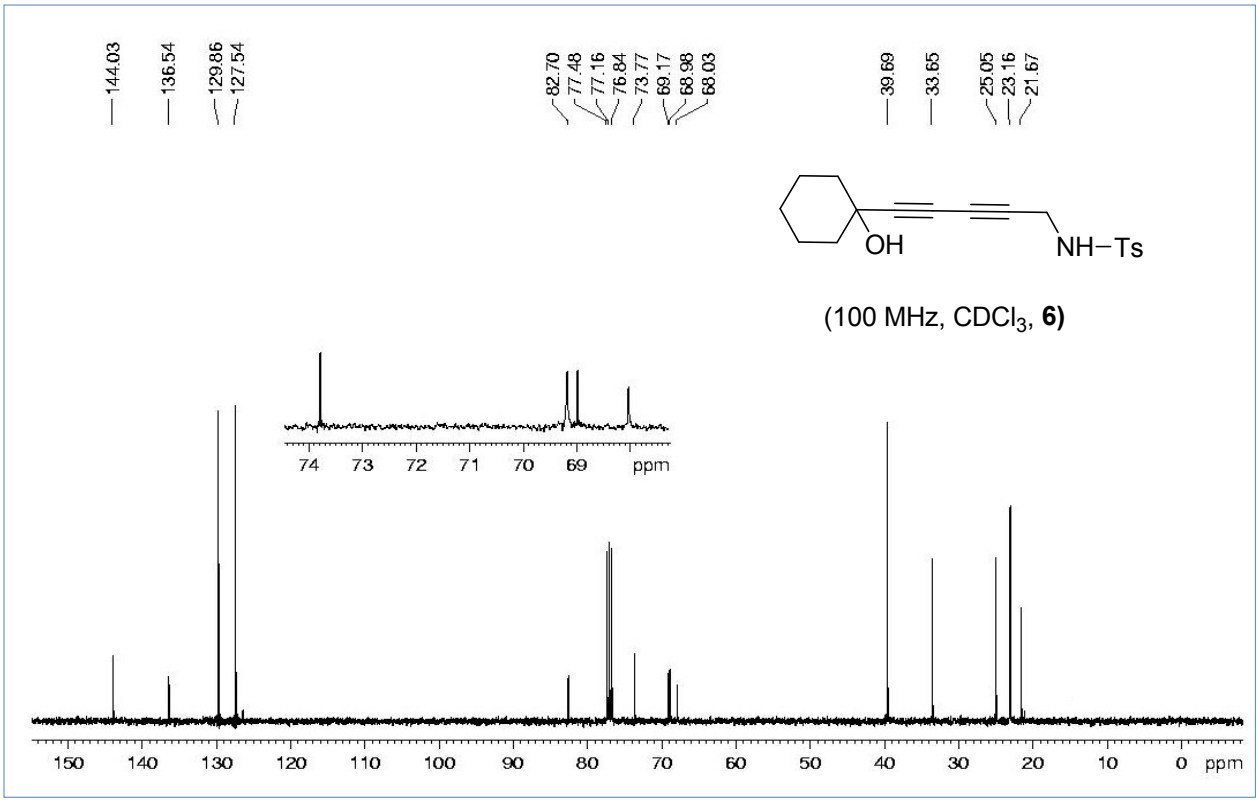


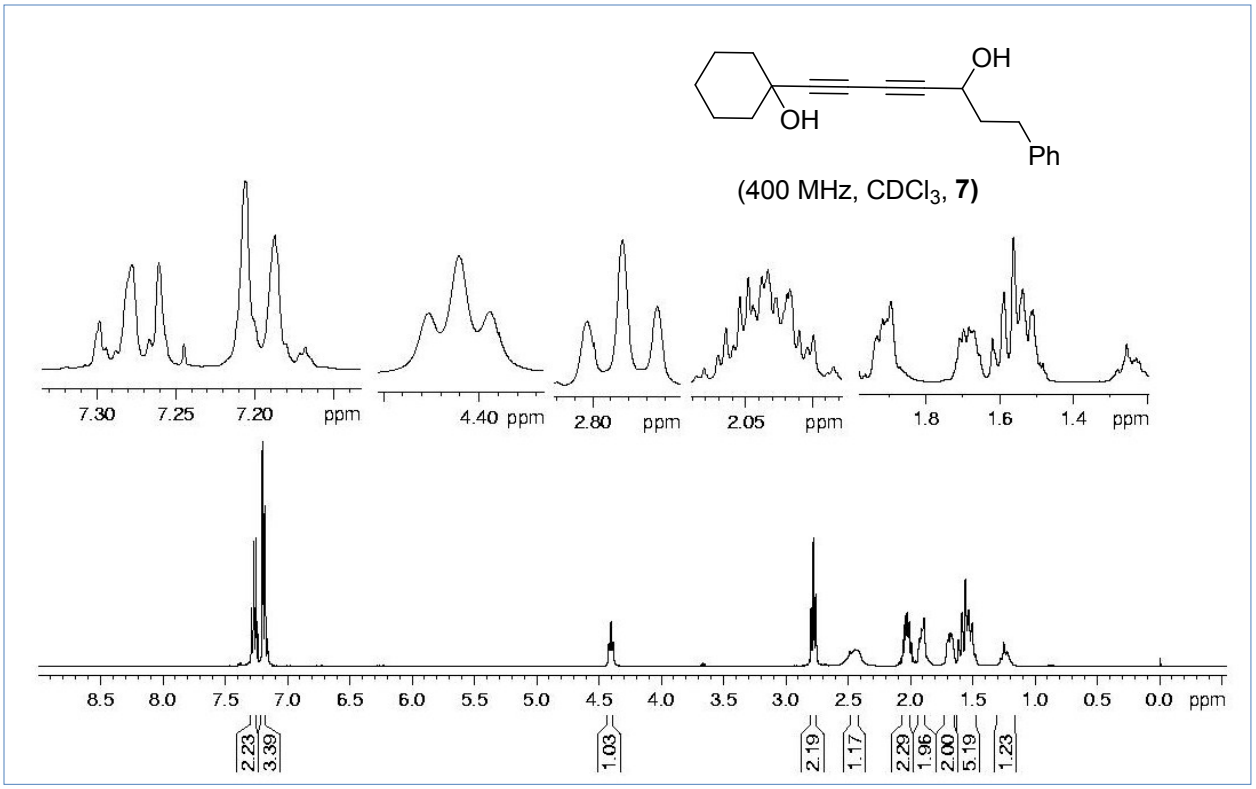
(400 MHz, $CDCl_3$, **5)**



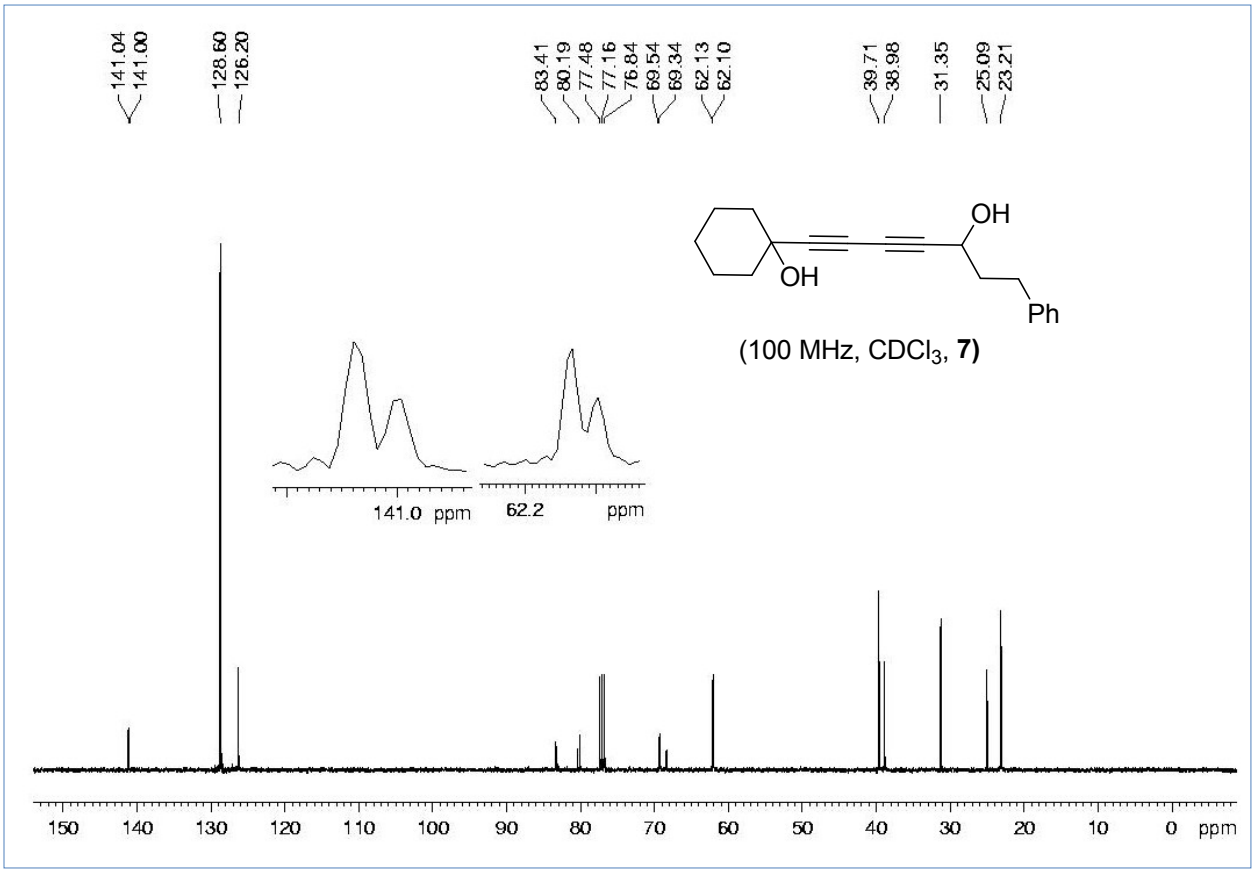
(100 MHz, $CDCl_3$, **5)**


OH
NH−Ts
(400 MHz, CDCl3, 6)
7.78 ppm
7.34 7.32 ppm
3.92 ppm
5.10 ppm
1.9 1.8 1.7 1.6 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00 2.16 1.07 2.02 3.01 0.94 2.26 2.10 5.21 1.42

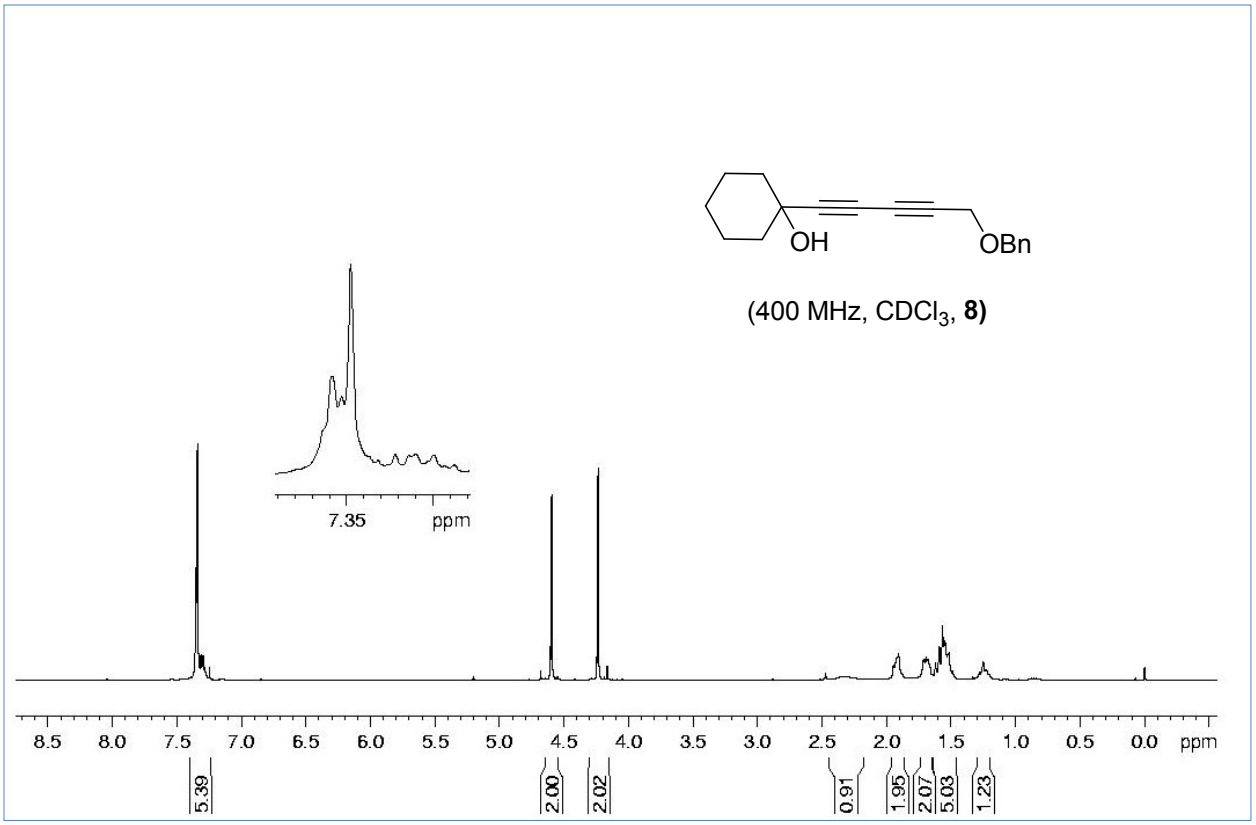

144.03 136.54 129.86 127.54
82.70 77.48 77.16 76.84 73.77 69.17 68.98 68.03
39.69 33.65 25.05 23.16 21.67
OH
NH−Ts
(100 MHz, CDCl3, 6)
74 73 72 71 70 69 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



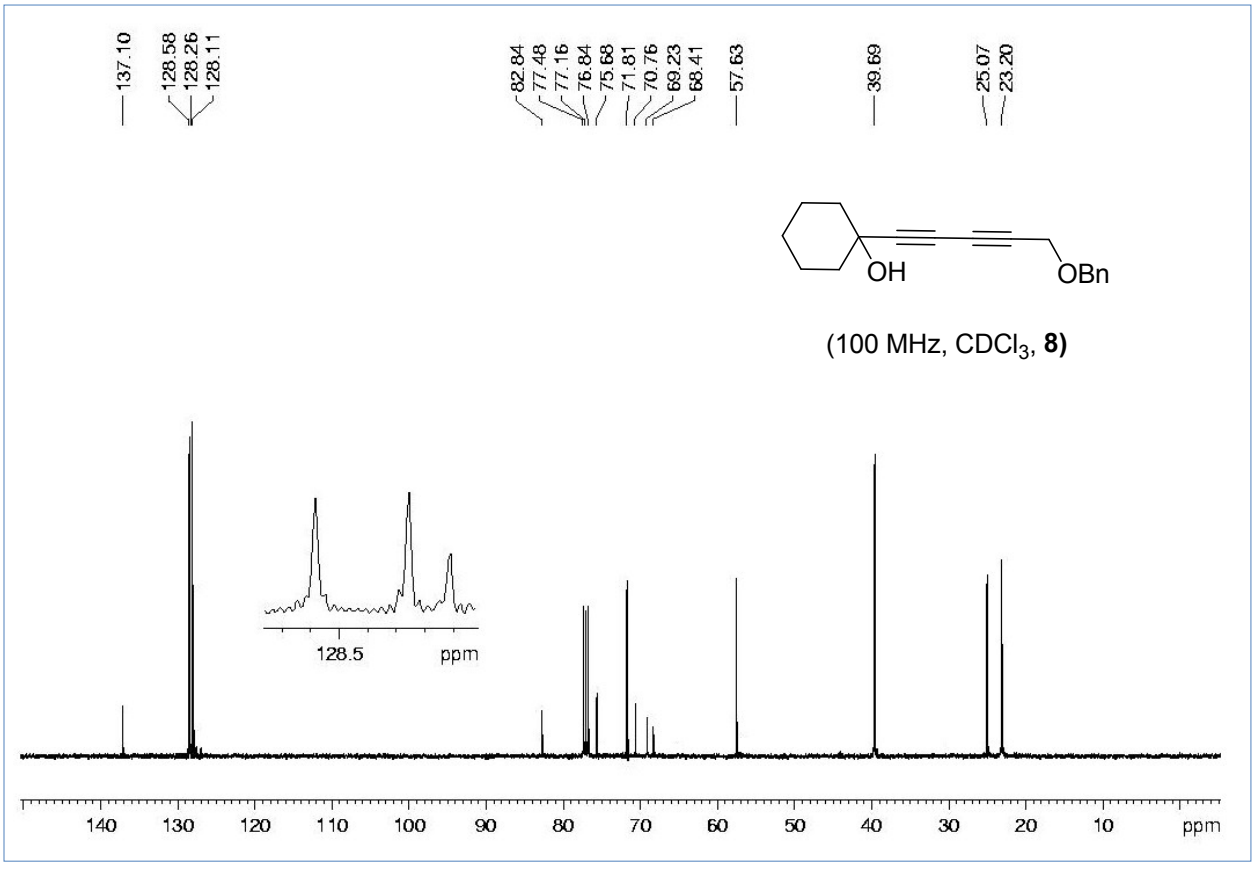
(400 MHz, $CDCl_3$, **7)**



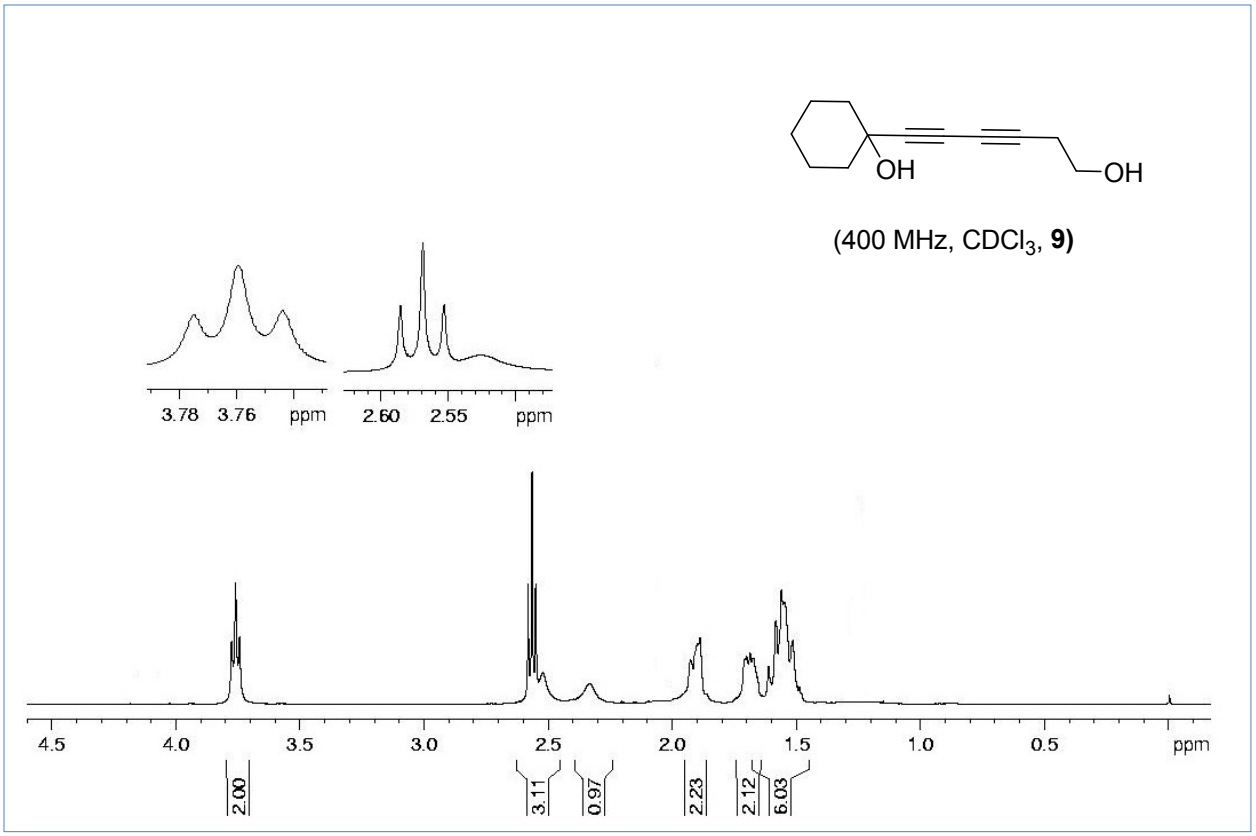
(100 MHz, $CDCl_3$, **7)**

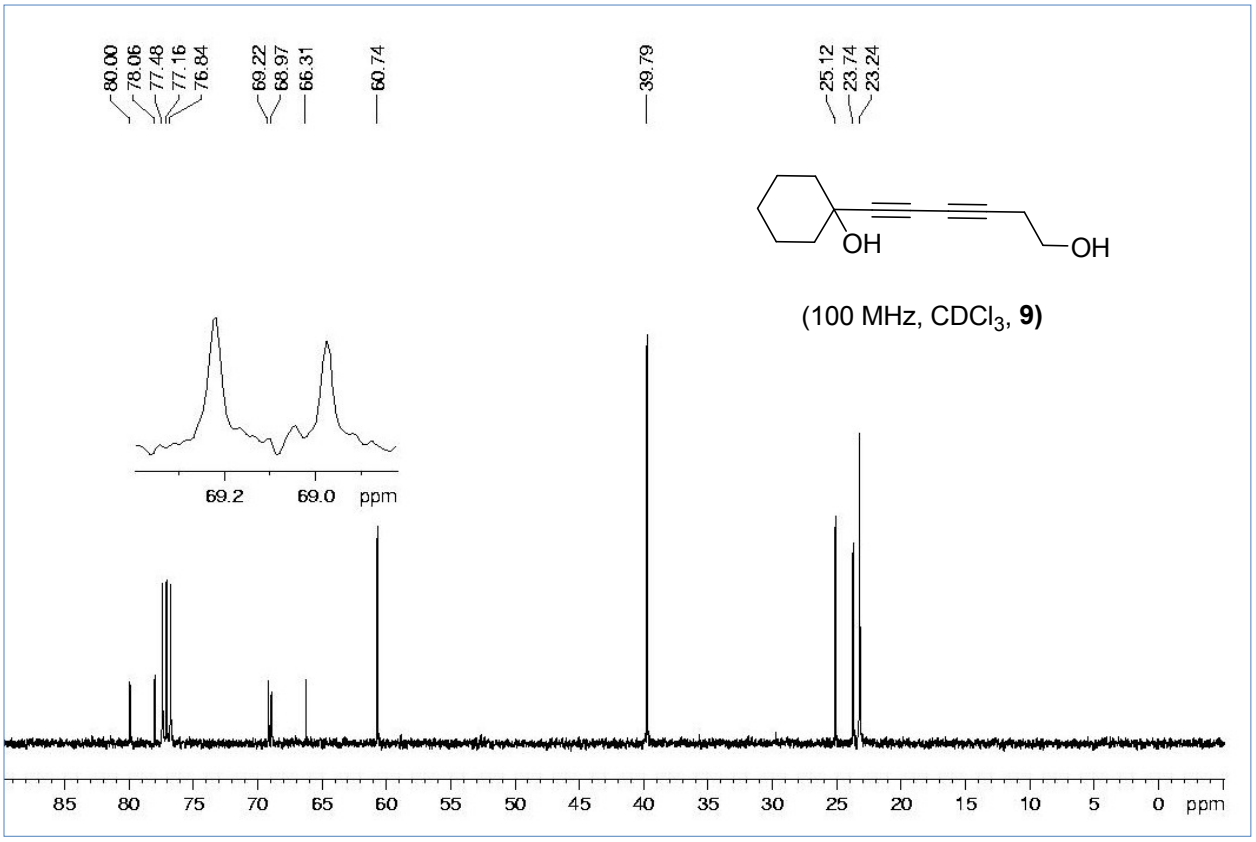


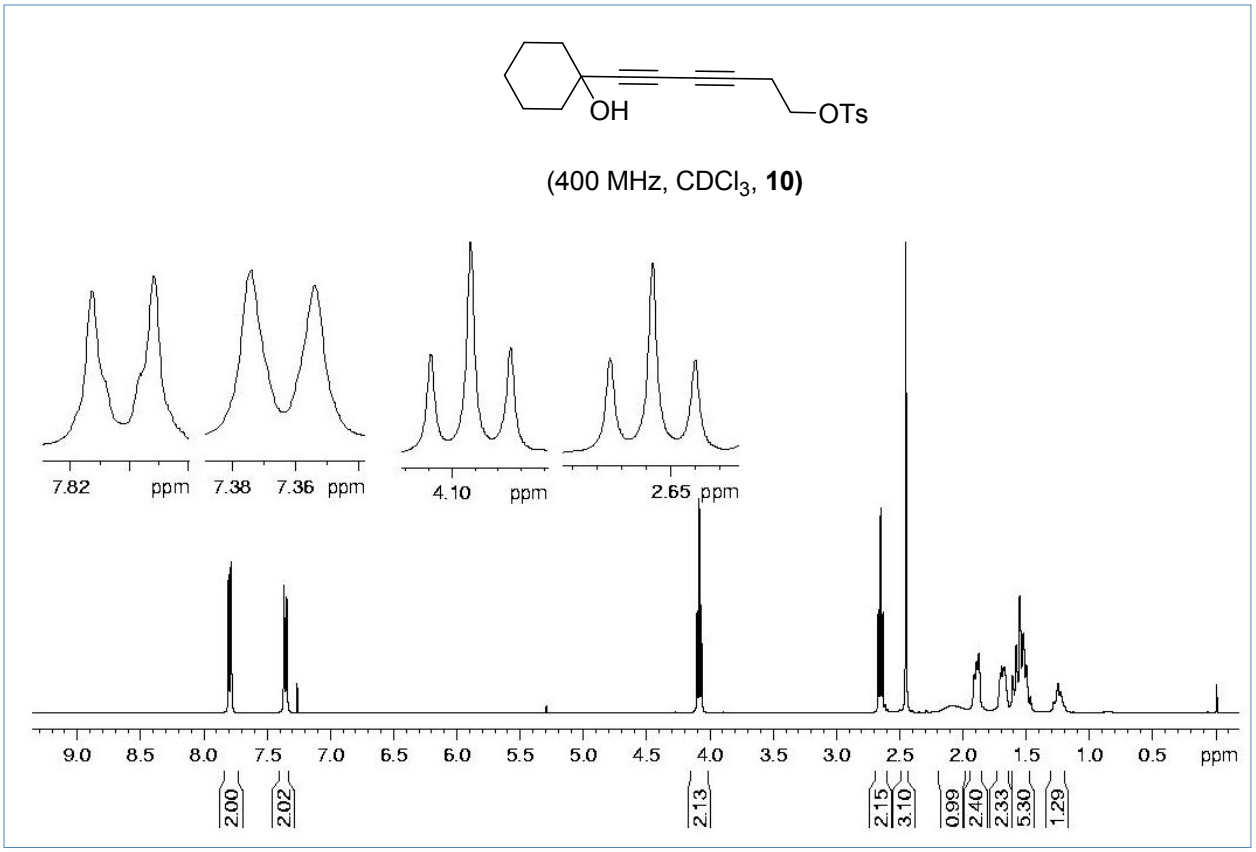
(400 MHz, $CDCl_3$, **8)**



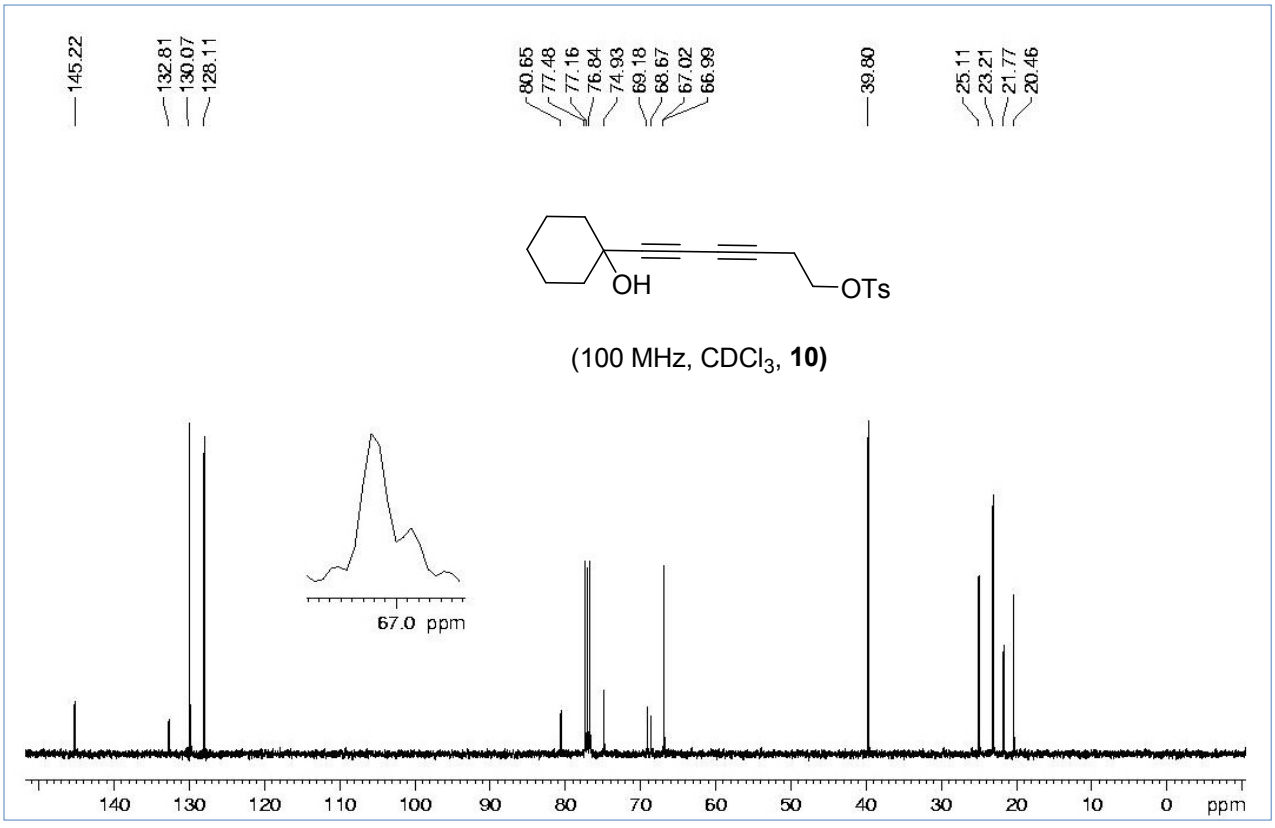
(100 MHz, $CDCl_3$, **8)**


OH
OH
(400 MHz, CDCl3, 9)
3.78 3.76 ppm
2.60 2.55 ppm
4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
3.11
0.97
2.23
2.12
6.03

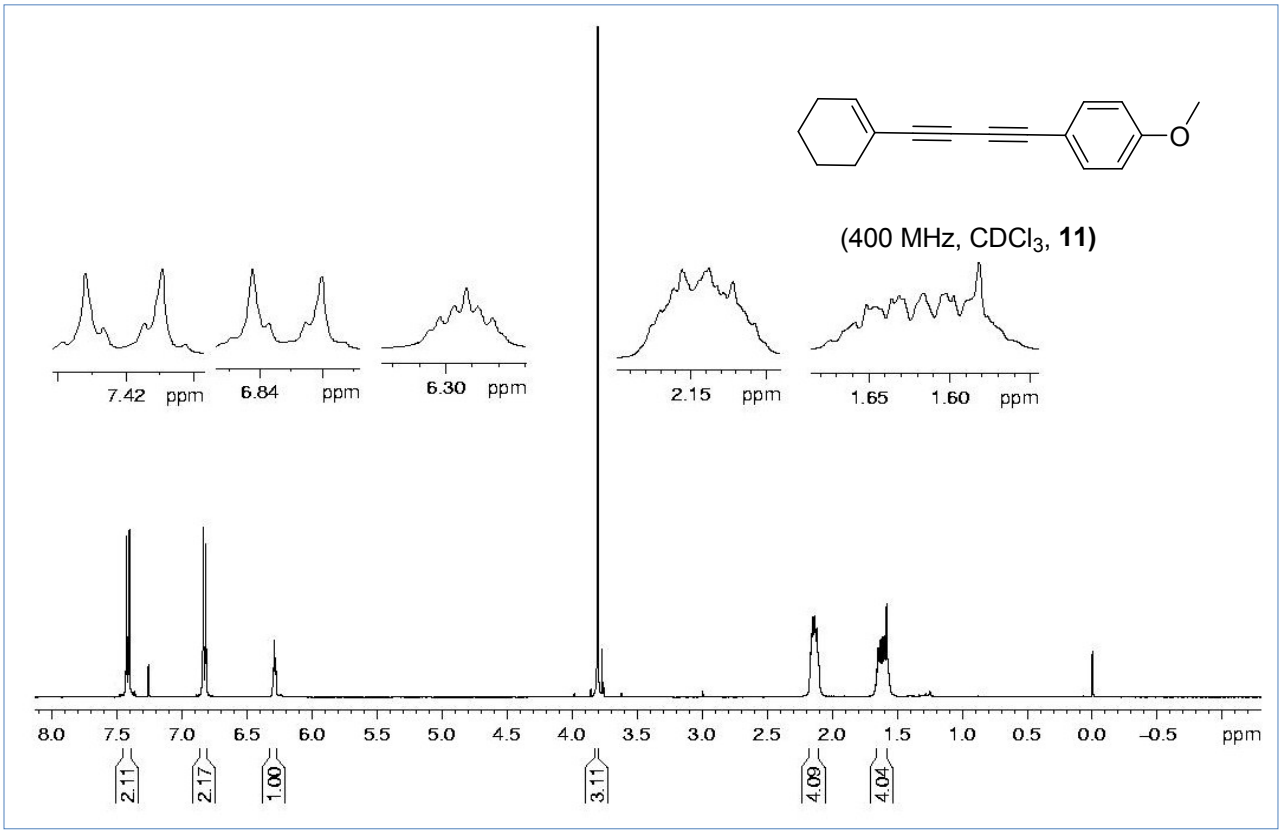

80.00
78.06
77.48
77.16
76.84
69.22
68.97
66.31
60.74
39.79
25.12
23.74
23.24
OH
OH
(100 MHz, CDCl3, 9)
69.2 69.0 ppm
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm

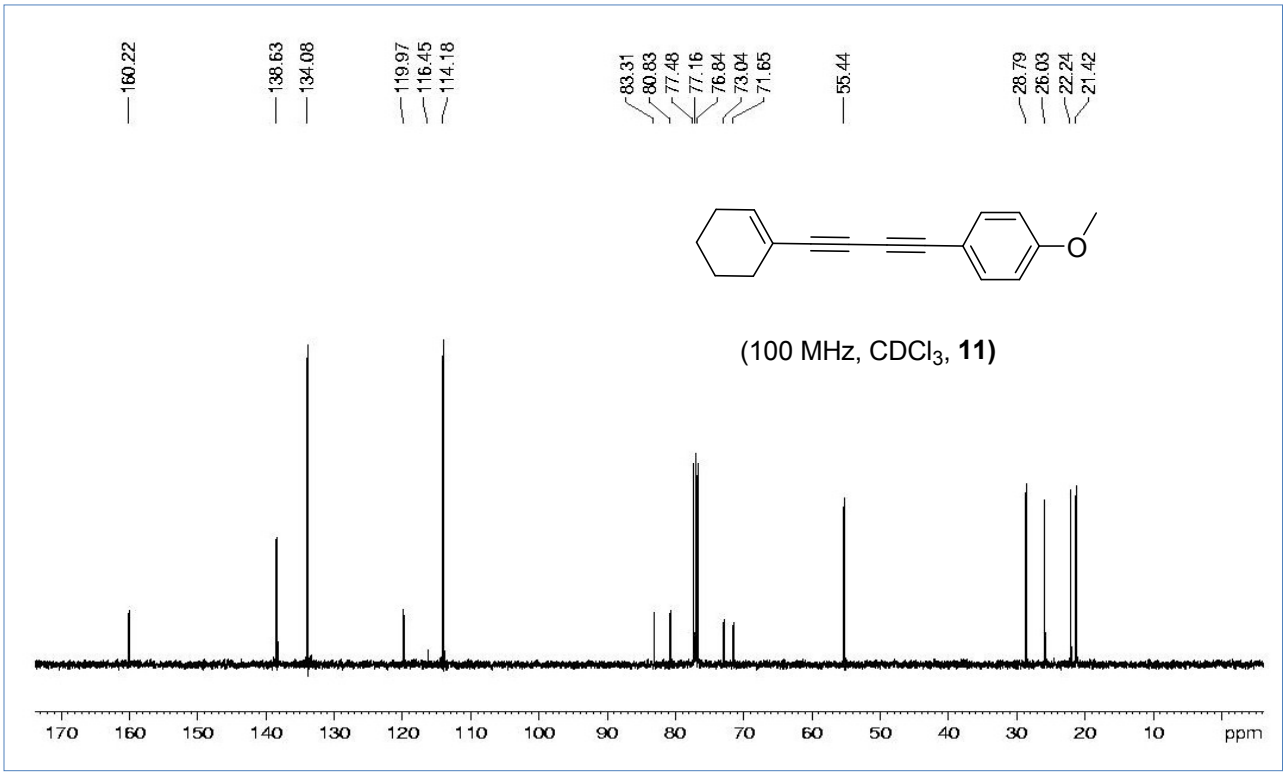


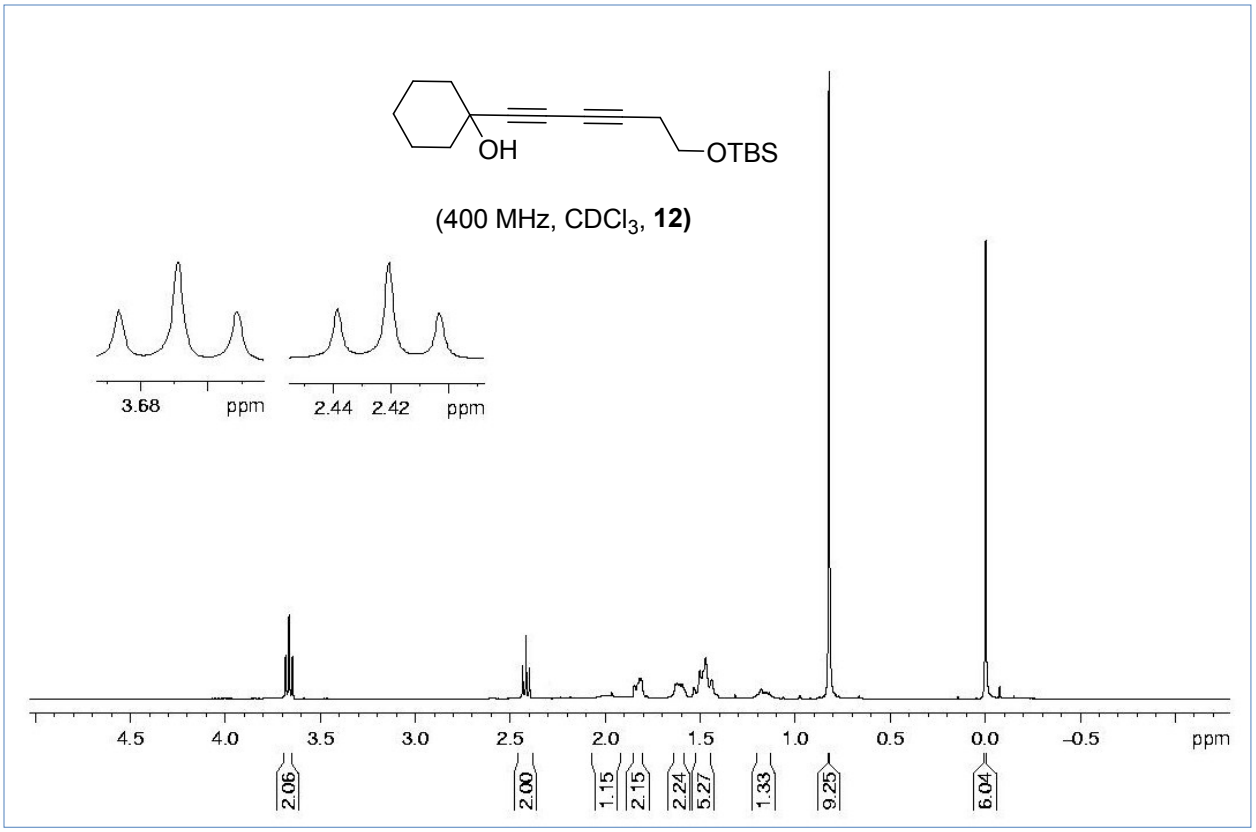
(400 MHz, $CDCl_3$, **10)**

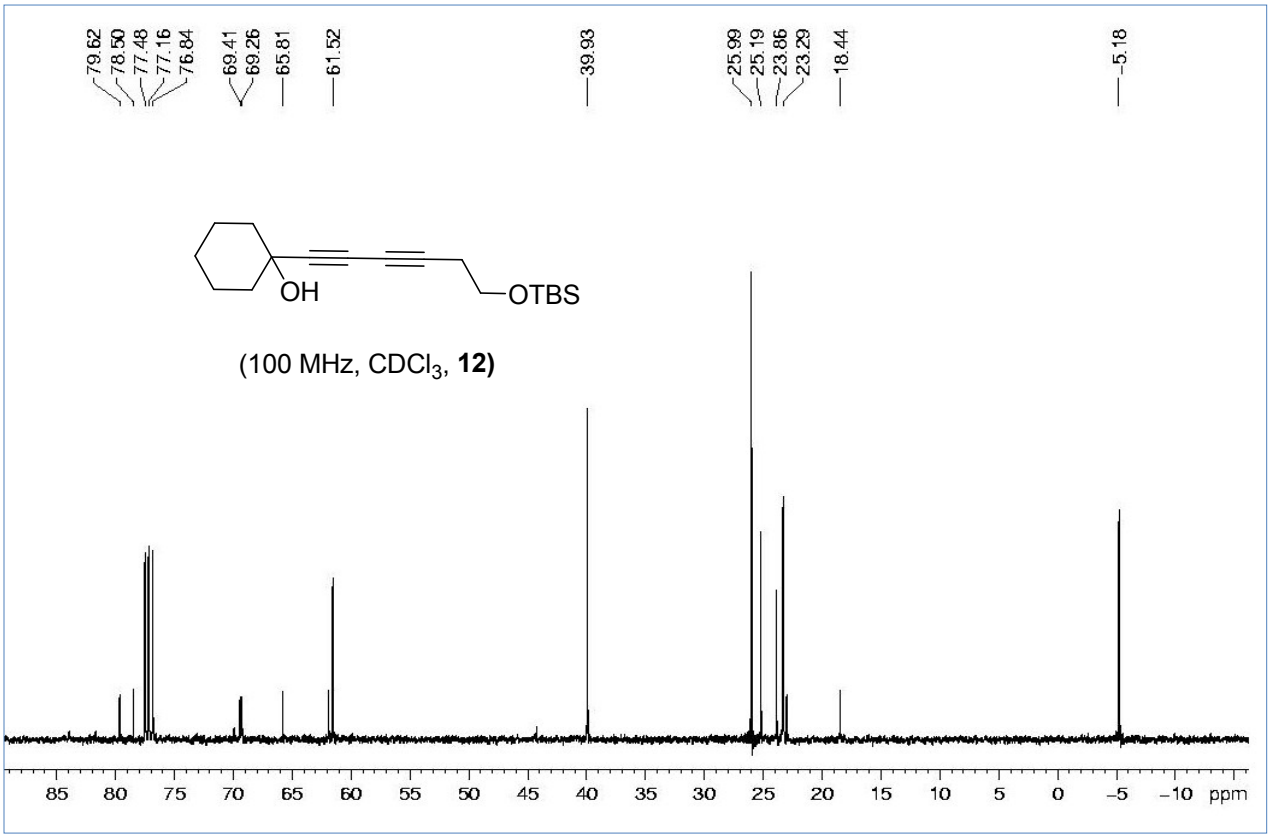


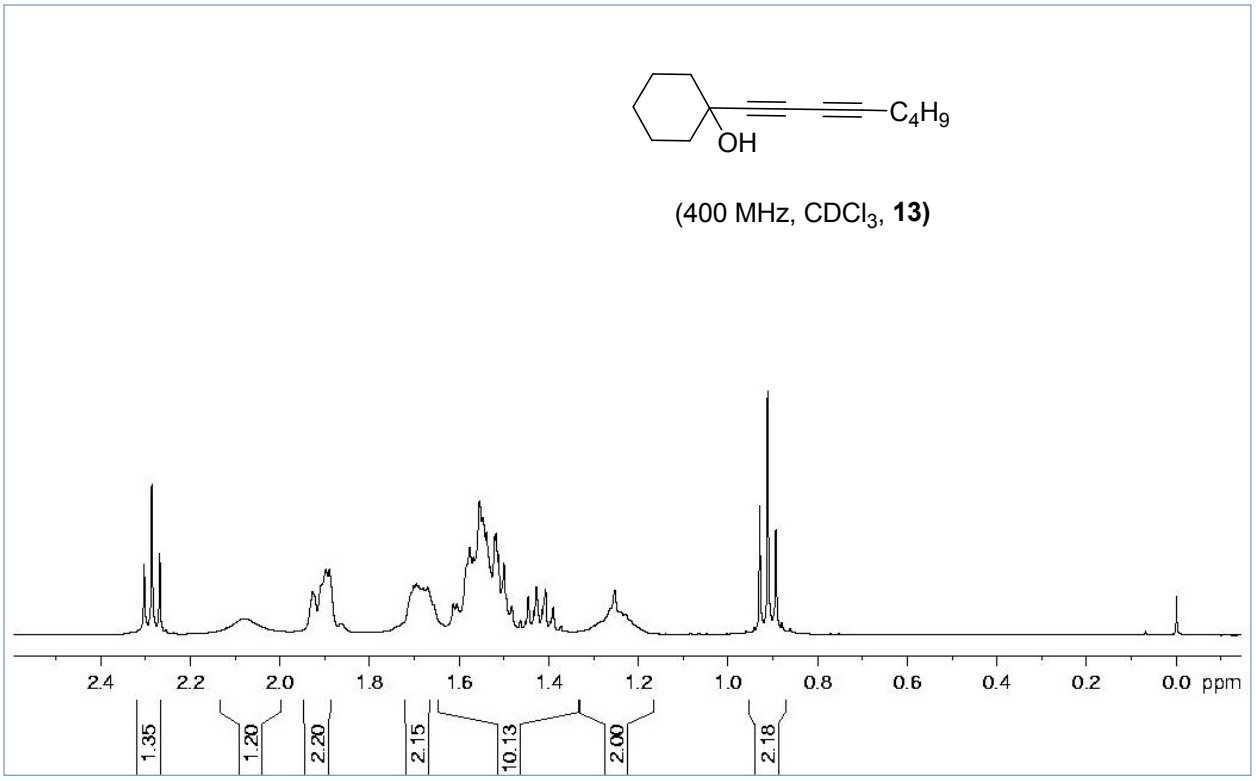
(100 MHz, $CDCl_3$, **10)**

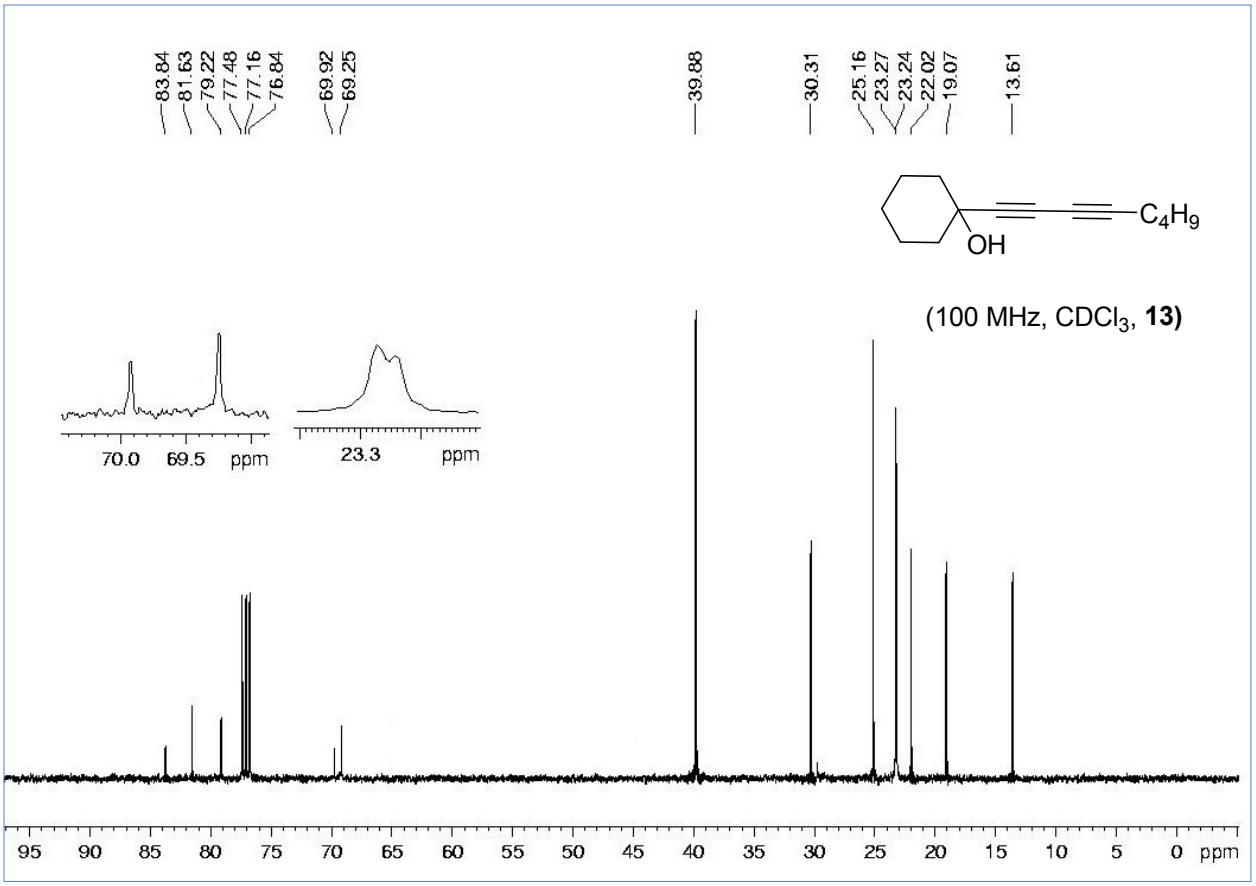

O
(400 MHz, CDCl3, 11)
7.42 ppm
6.84 ppm
6.30 ppm
2.15 ppm
1.65 1.60 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
2.11
2.17
1.00
3.11
4.09
4.04

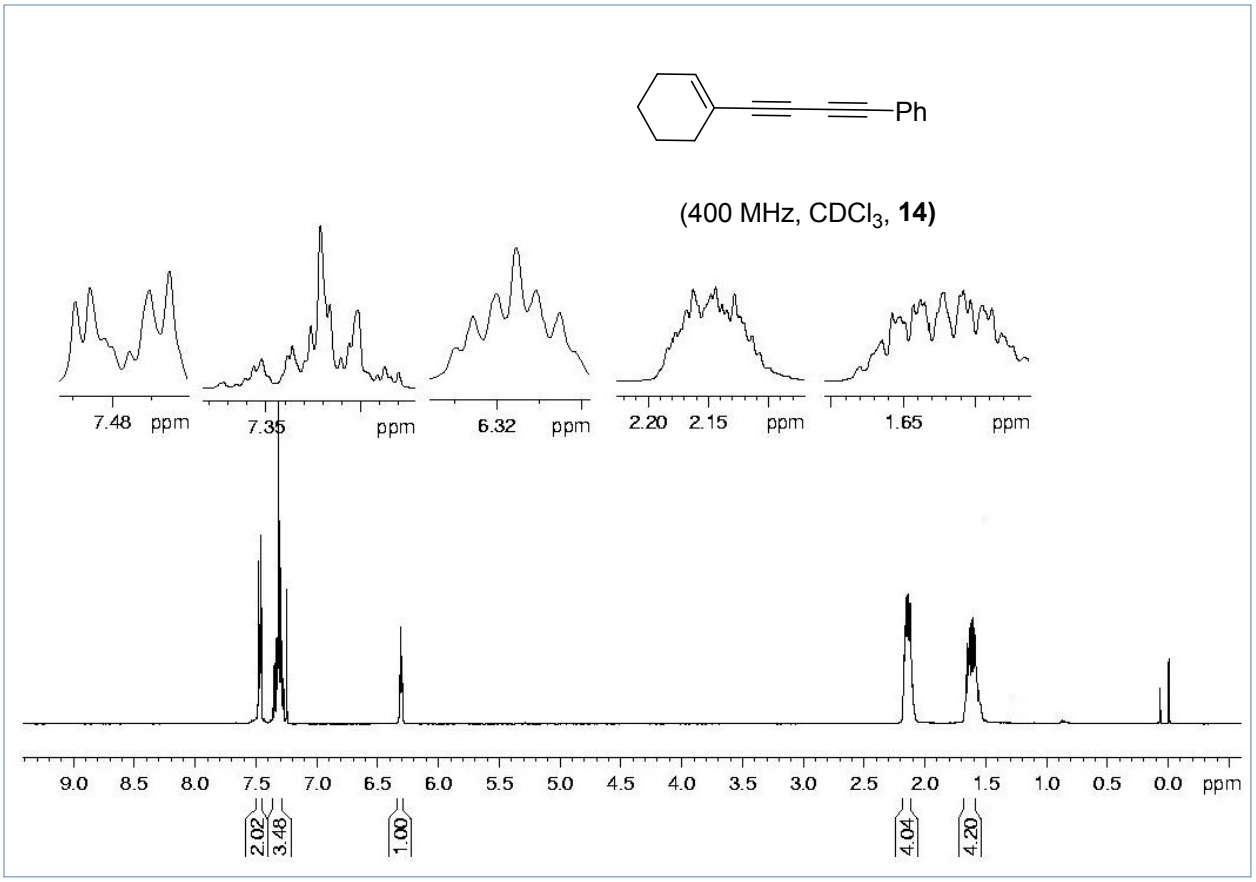

160.22
138.63
134.08
119.97
116.45
114.18
83.31
80.83
77.48
77.16
76.84
73.04
71.65
55.44
28.79
26.03
22.24
21.42
O
(100 MHz, CDCl3, 11)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

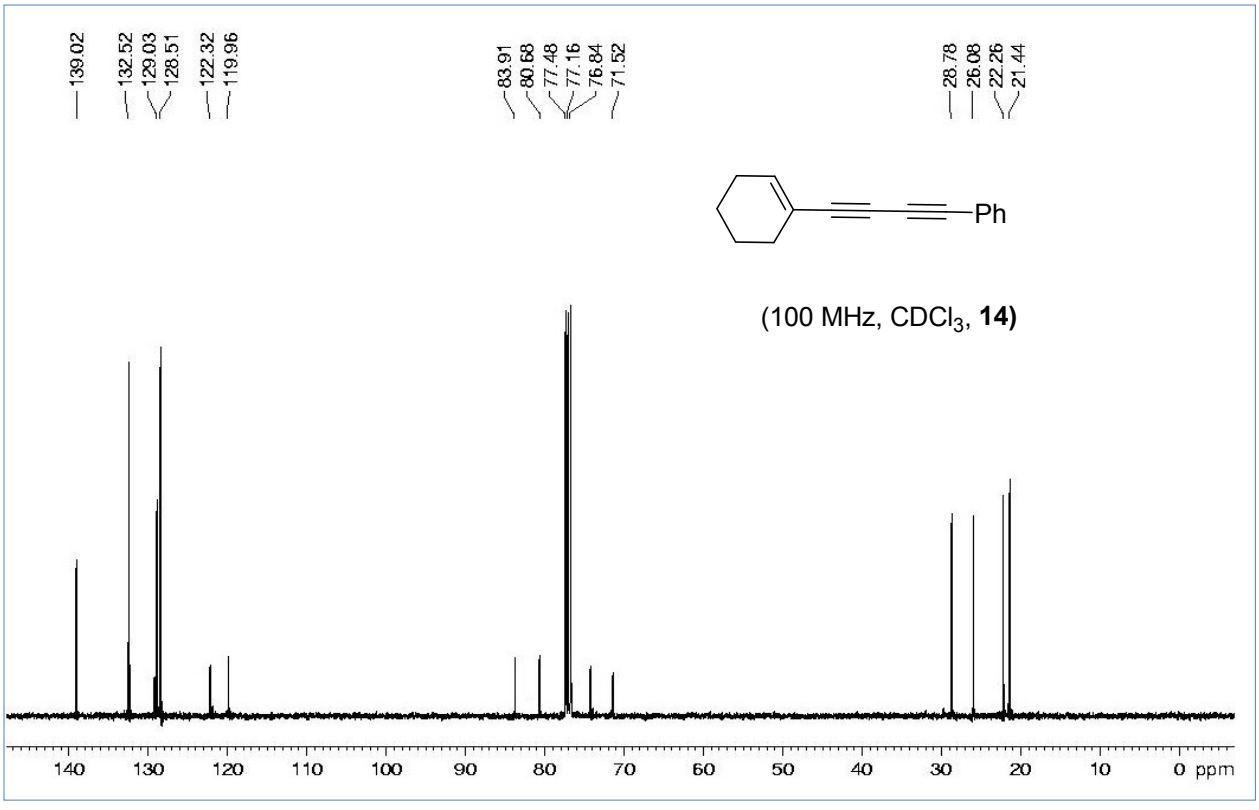

OH
OTBS
(400 MHz, CDCl3, 12)
3.68 ppm
2.44 2.42 ppm
4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
2.06 2.00 1.15 2.15 2.24 5.27 1.33 9.25 6.04

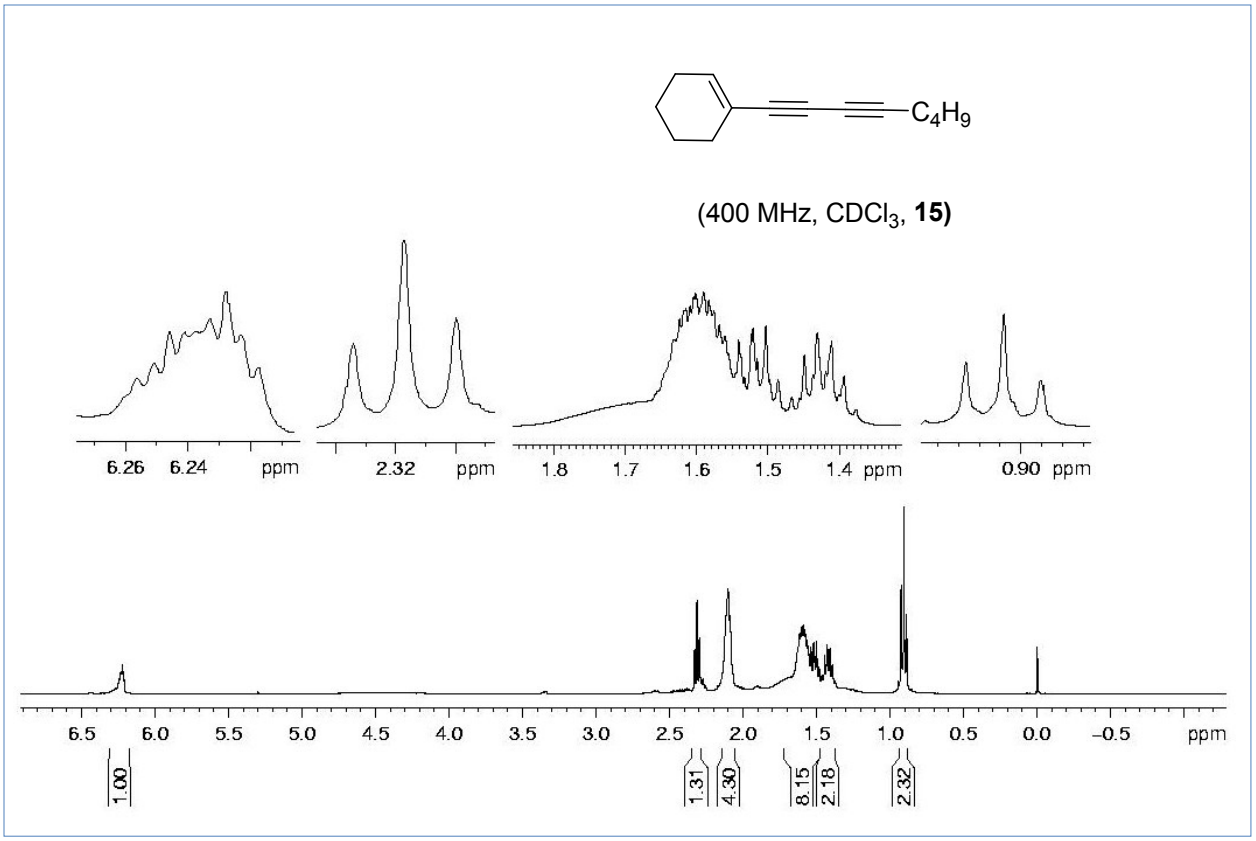

79.62 78.50 77.48 77.16 76.84 69.41 69.26 65.81 61.52 39.93 25.99 25.19 23.86 23.29 18.44 -5.18
OH
OTBS
(100 MHz, CDCl3, 12)
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 ppm

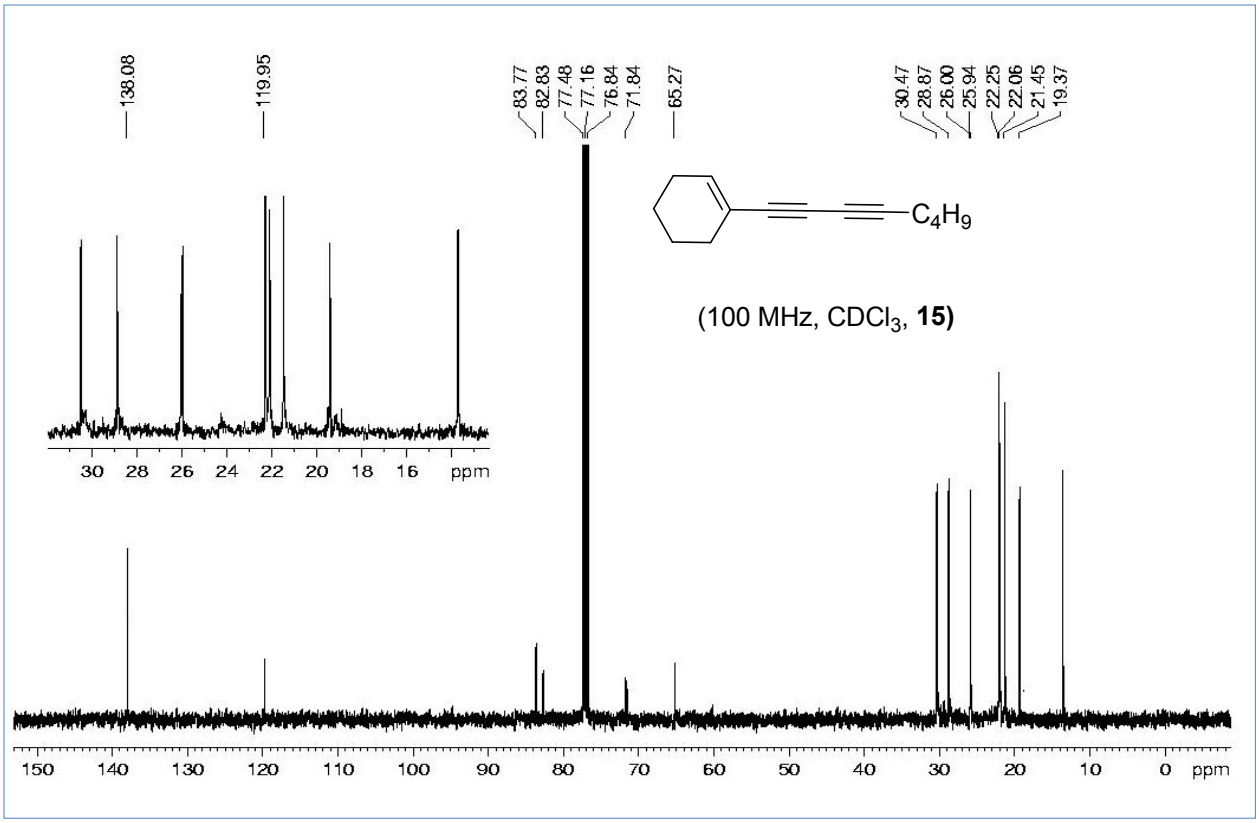

C4H9
OH
(400 MHz, CDCl3, 13)
2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 ppm
1.35 1.20 2.20 2.15 10.13 2.00 2.18

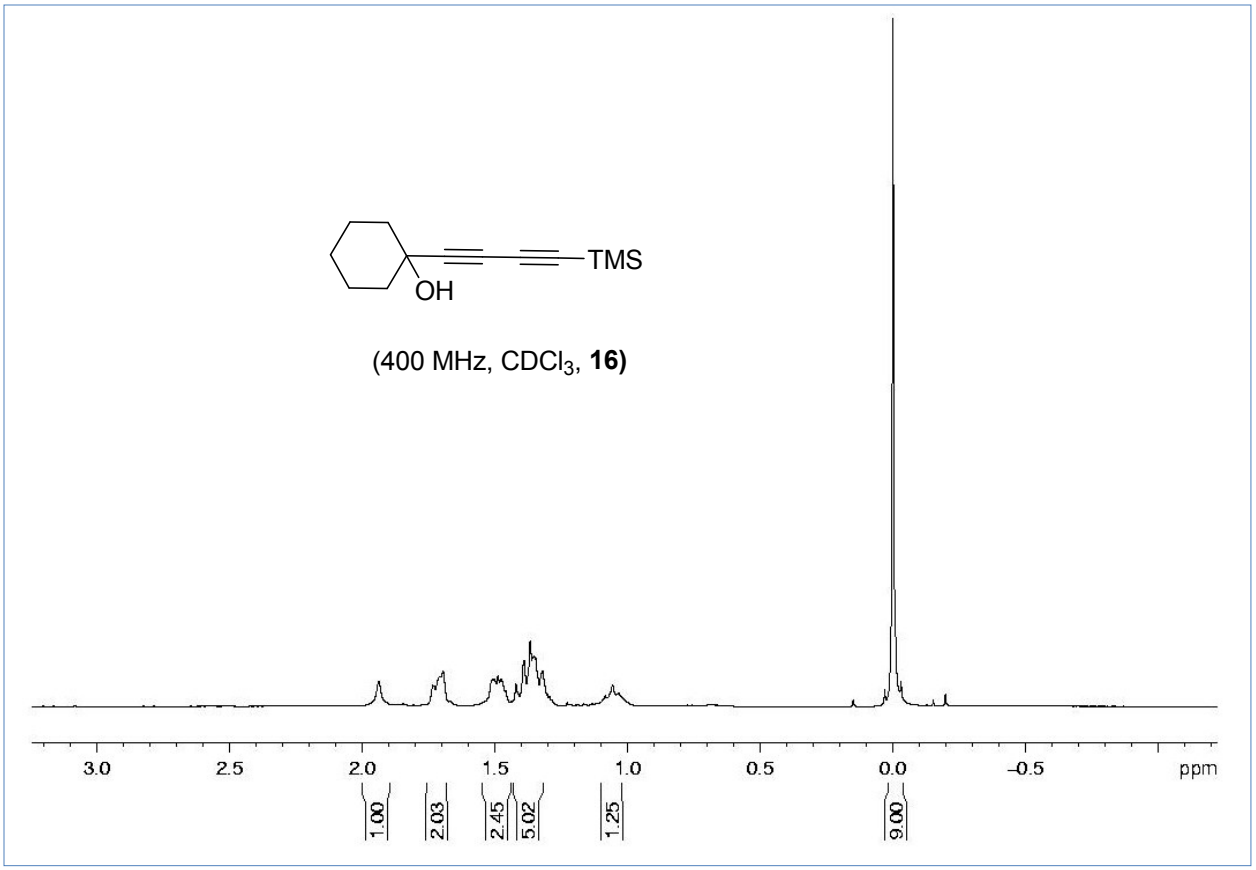

83.84 81.63 79.22 77.48 77.16 76.84 69.92 69.25 39.88 30.31 25.16 23.27 23.24 22.02 19.07 13.61
C4H9
OH
(100 MHz, CDCl3, 13)
70.0 69.5 ppm
23.3 ppm
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm


Ph
(400 MHz, CDCl3, 14)
7.48 ppm
7.35 ppm
6.32 ppm
2.20 2.15 ppm
1.65 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02
3.48
1.00
4.04
4.20

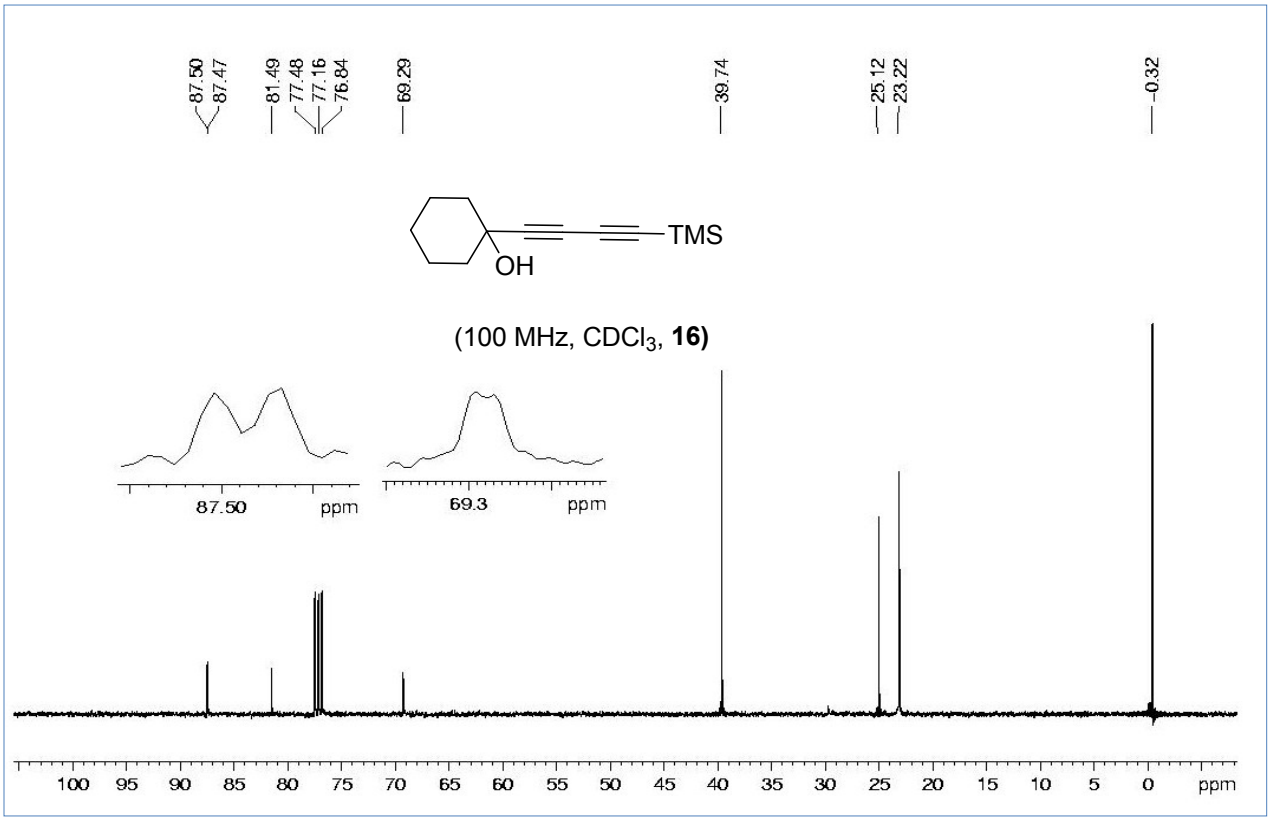

139.02
132.52
129.03
128.51
122.32
119.96
83.91
80.68
77.48
77.16
76.84
71.52
28.78
26.08
22.26
21.44
Ph
(100 MHz, CDCl3, 14)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


C4H9
(400 MHz, CDCl3, 15)
6.26 6.24 ppm
2.32 ppm
1.8 1.7 1.6 1.5 1.4 ppm
0.90 ppm
6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
1.00
1.31
4.30
8.15
2.18
2.32

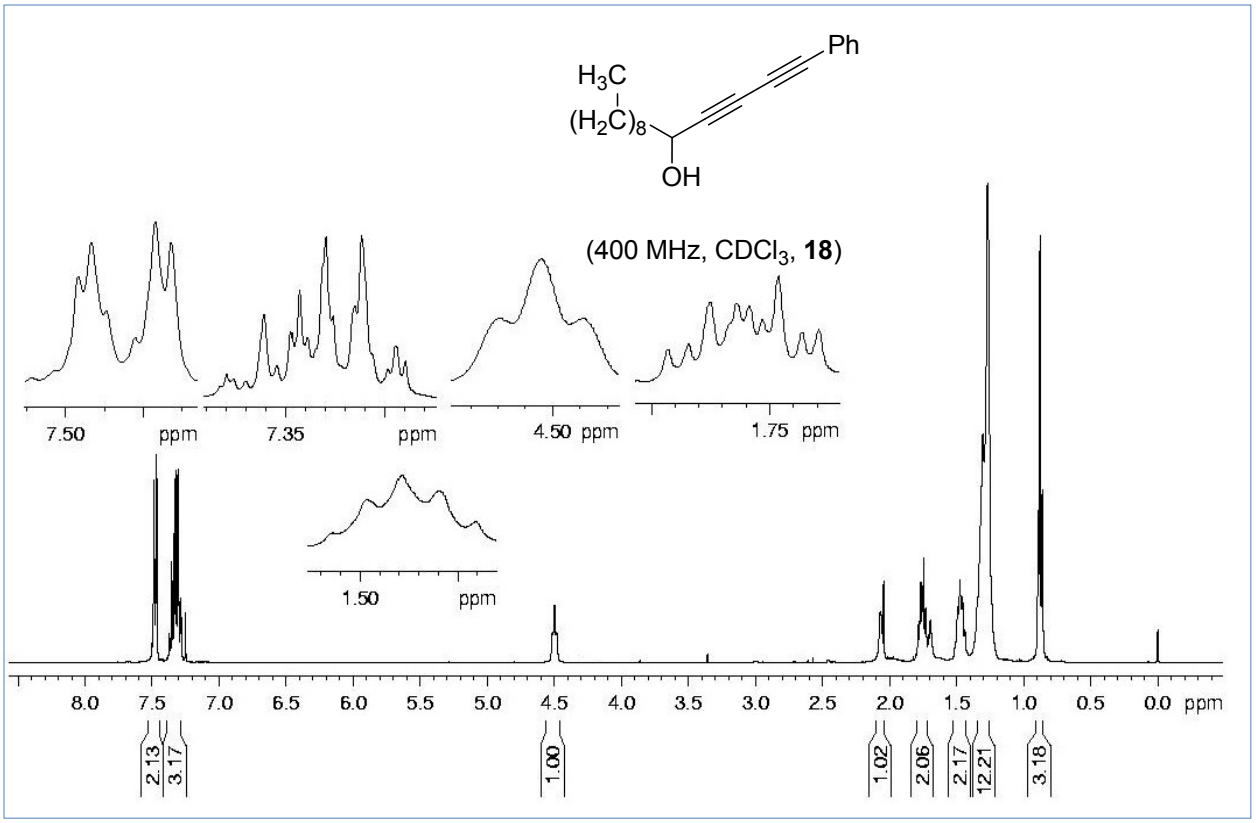

138.08
119.95
83.77
82.83
77.48
77.16
76.84
71.84
65.27
30.47
28.87
26.00
25.94
22.25
22.06
21.45
19.37
C4H9
(100 MHz, CDCl3, 15)
30 28 26 24 22 20 18 16 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

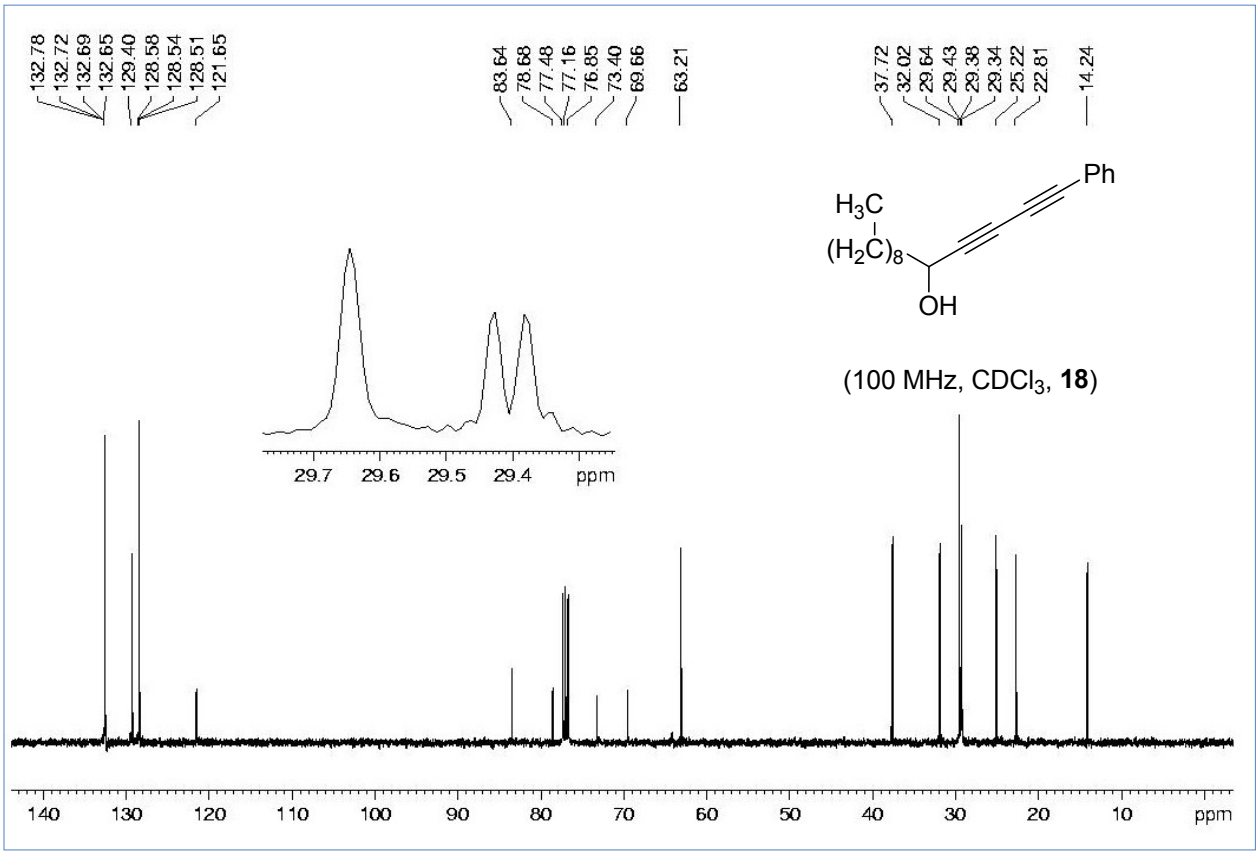


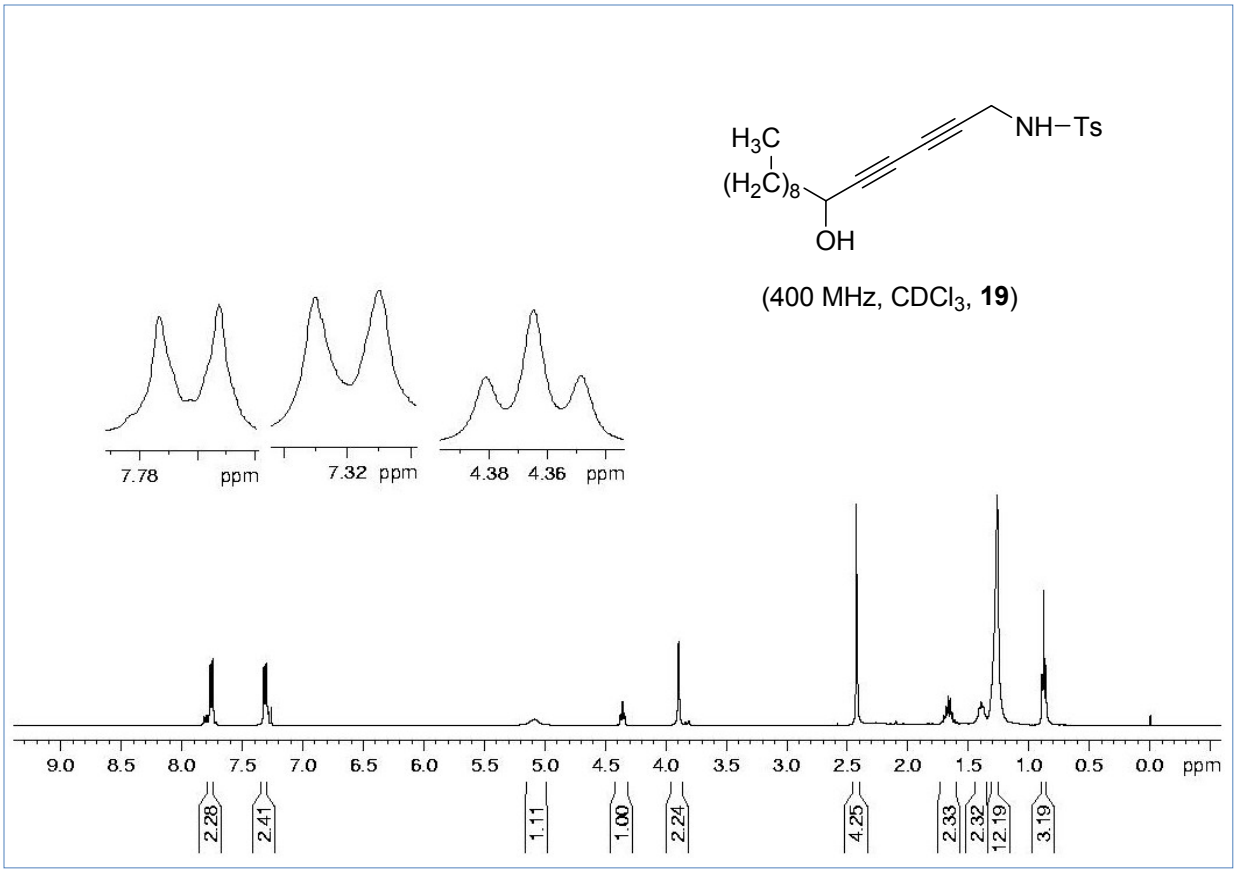
(400 MHz, $CDCl_3$, **16)**

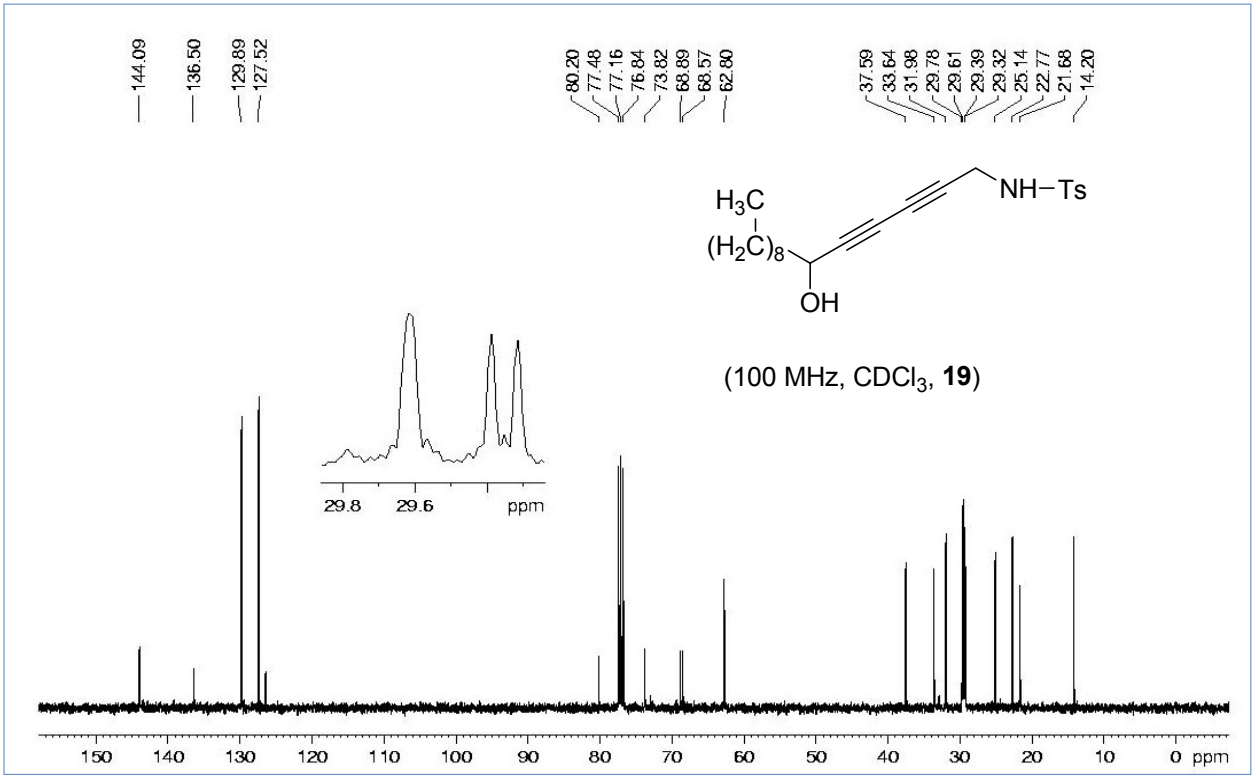


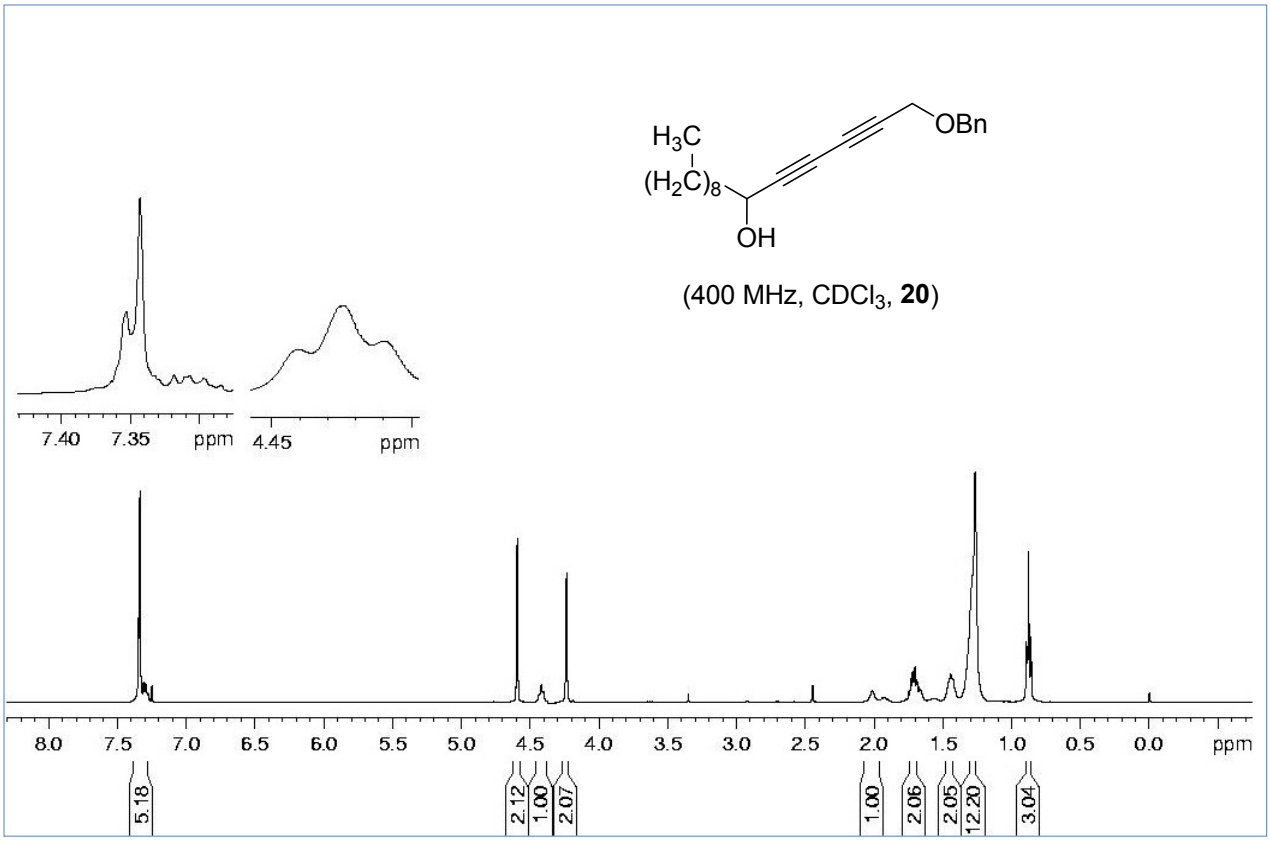
(100 MHz, $CDCl_3$, **16)**

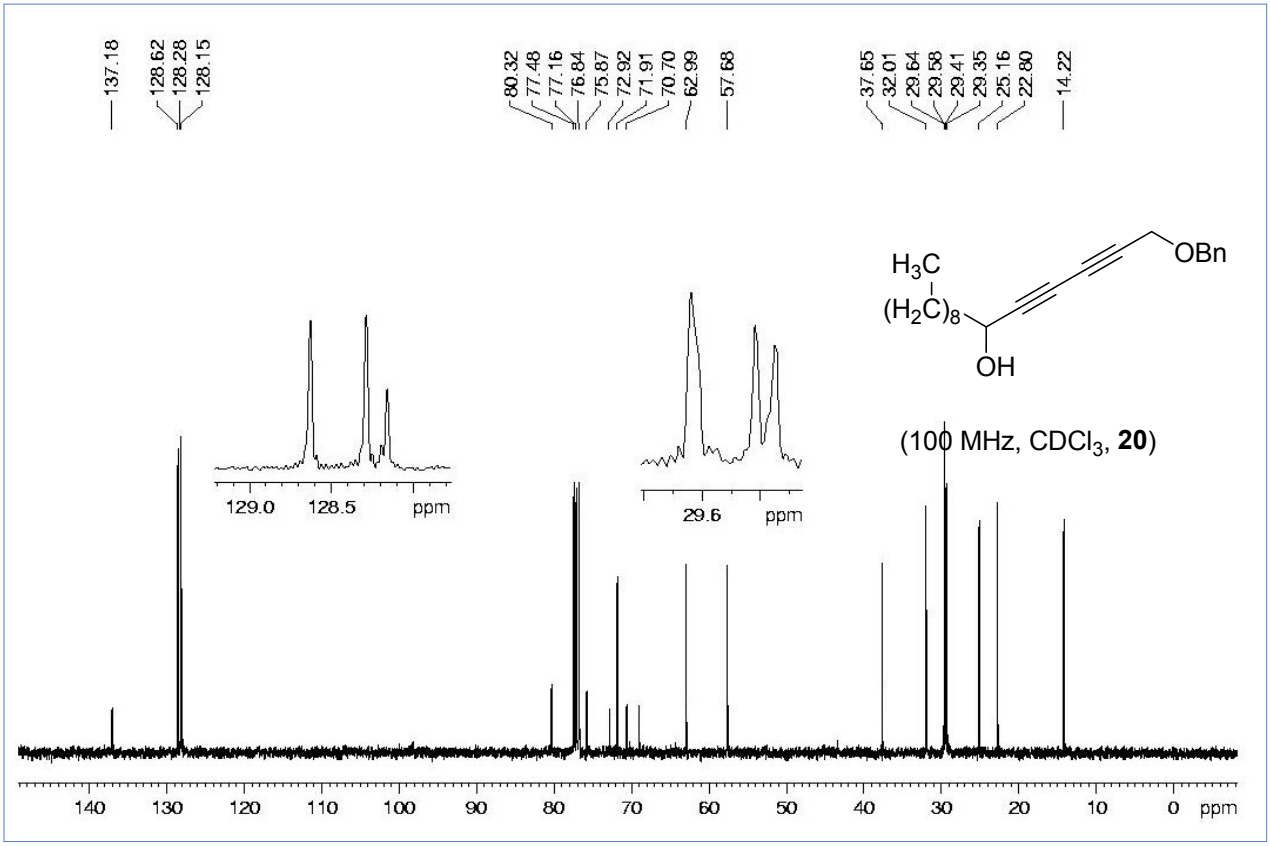

Ph
H3C
(H2C)8
OH
(400 MHz, CDCl3, 18)
7.50 ppm
7.35 ppm
4.50 ppm
1.75 ppm
1.50 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.13
3.17
1.00
1.02
2.06
2.17
12.21
3.18

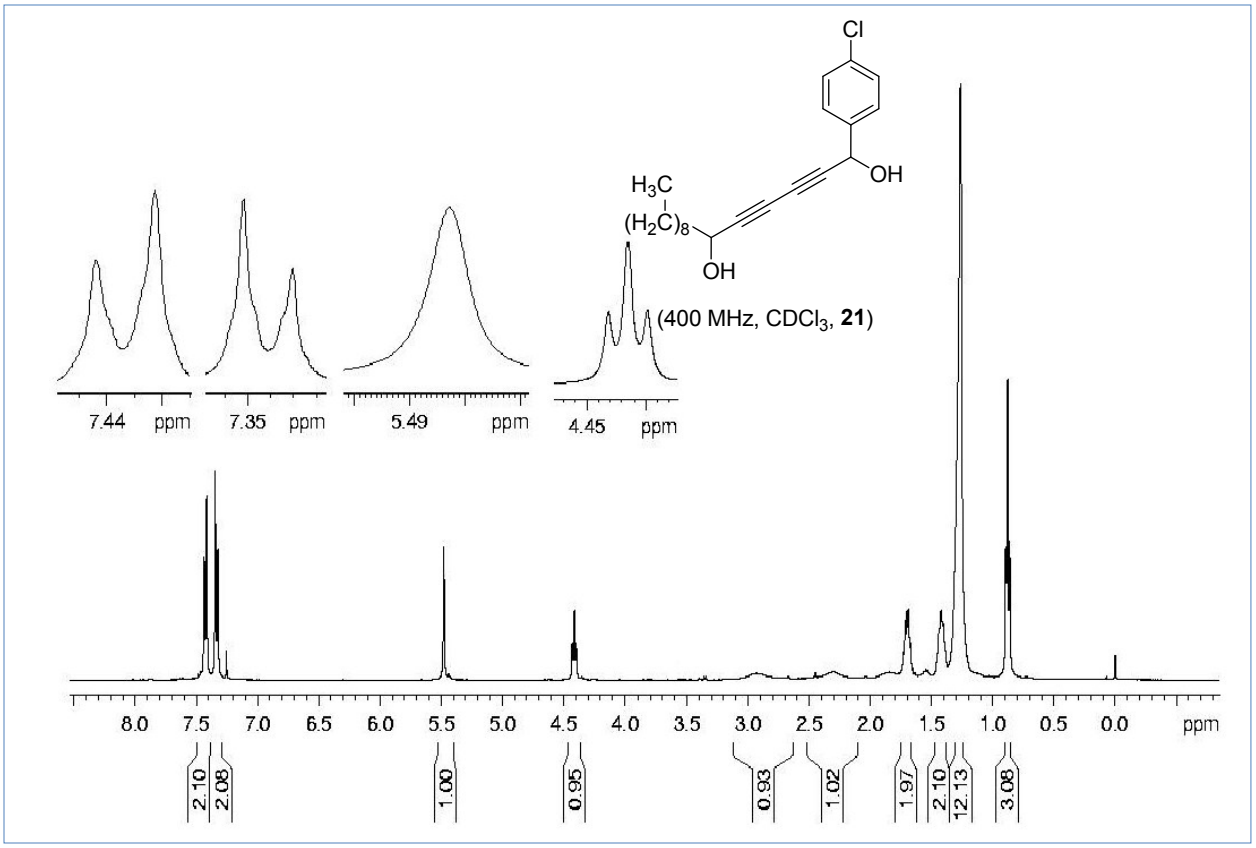

132.78
132.72
132.69
132.65
129.40
128.58
128.54
128.51
121.65
83.64
78.68
77.48
77.16
76.85
73.40
69.66
63.21
37.72
32.02
29.64
29.43
29.38
29.34
25.22
22.81
14.24
Ph
H3C
(H2C)8
OH
(100 MHz, CDCl3, 18)
29.7 29.6 29.5 29.4 ppm
140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

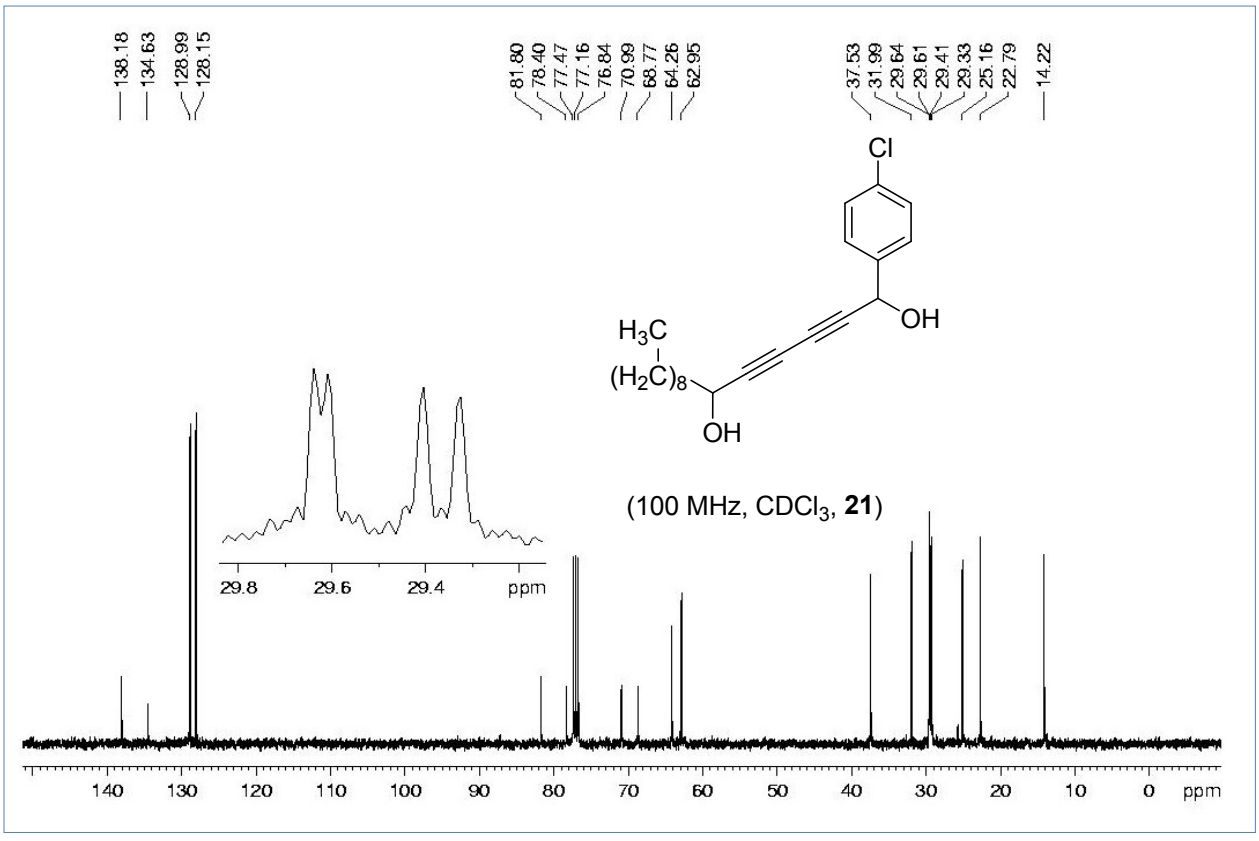

H3C
(H2C)8
OH
NH−Ts
(400 MHz, CDCl3, 19)
7.78 ppm
7.32 ppm
4.38 4.36 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.28
2.41
1.11
1.00
2.24
4.25
2.33
2.32
12.19
3.19

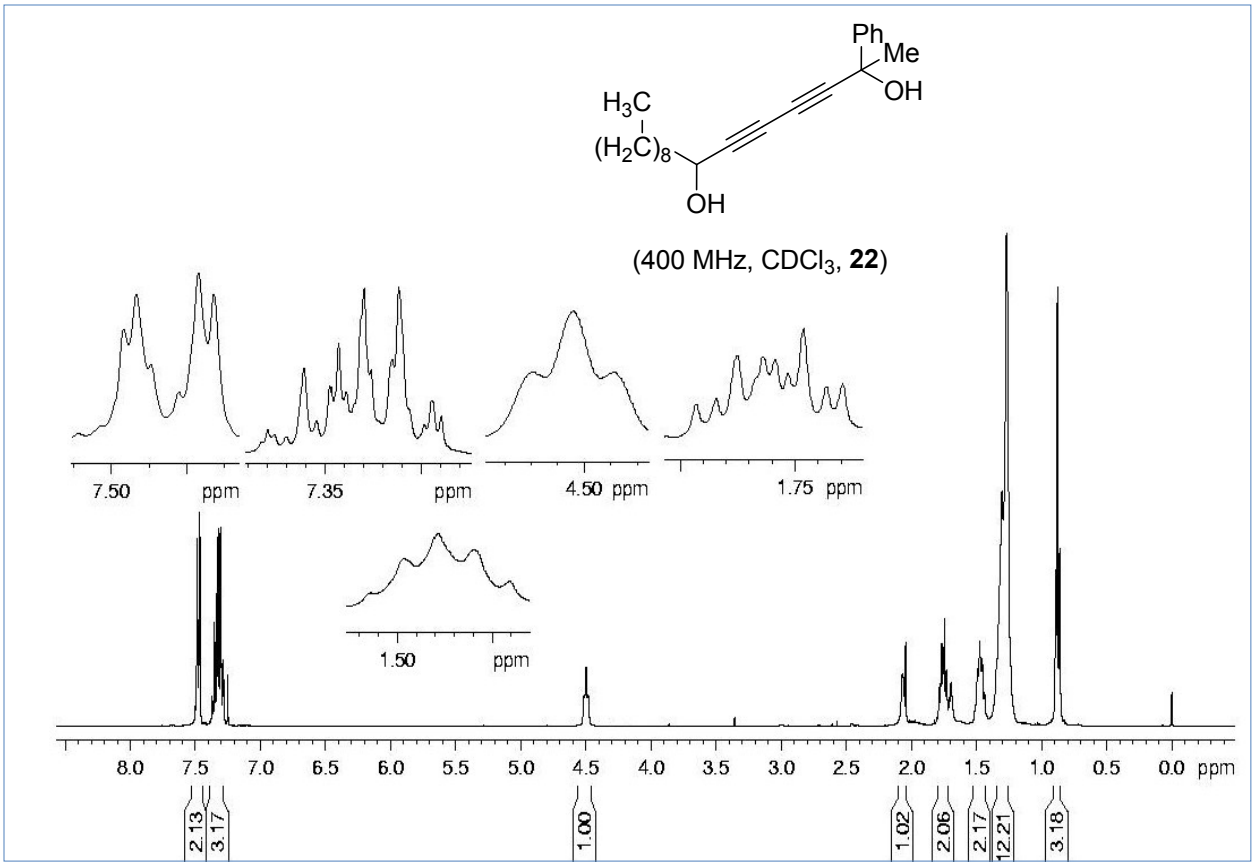

144.09
136.50
129.89
127.52
80.20
77.48
77.16
76.84
73.82
68.89
68.57
62.80
37.59
33.64
31.98
29.78
29.61
29.39
29.32
25.14
22.77
21.68
14.20
H3C
(H2C)8
OH
NH−Ts
(100 MHz, CDCl3, 19)
29.8 29.6 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

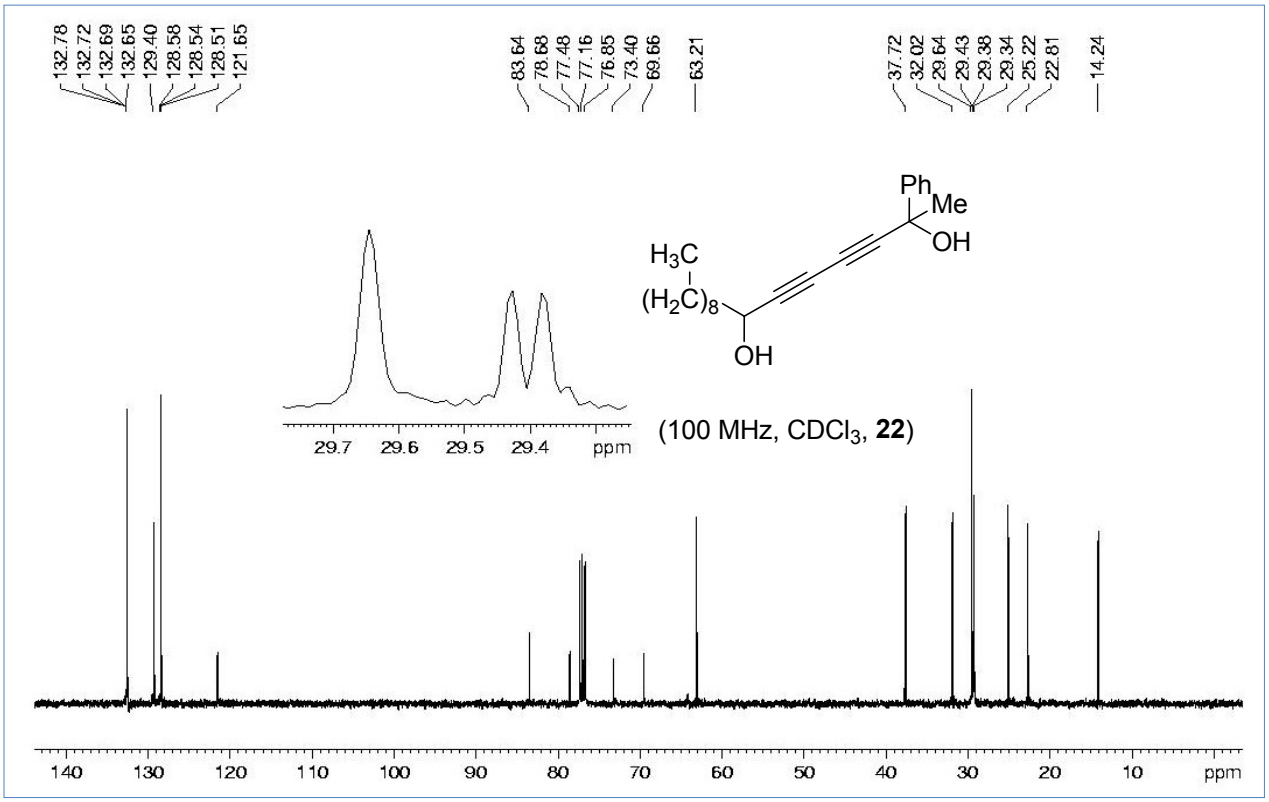

H3C
(H2C)8
OH
OBn
(400 MHz, CDCl3, 20)
7.40
7.35
ppm
4.45
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.18
2.12
1.00
2.07
1.00
2.06
2.05
12.20
3.04

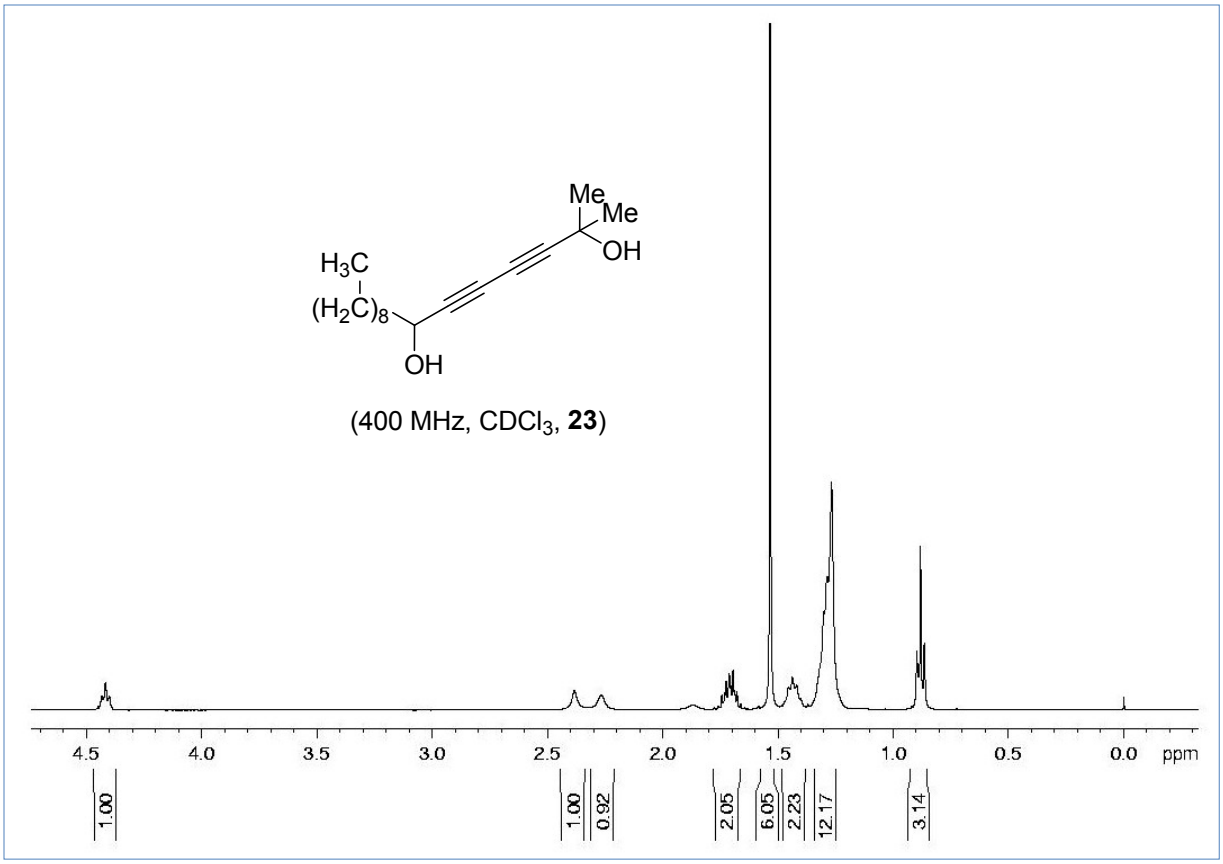

137.18
128.62
128.28
128.15
80.32
77.48
77.16
76.84
75.87
72.92
71.91
70.70
62.99
57.68
37.65
32.01
29.64
29.58
29.41
29.35
25.16
22.80
14.22
H3C
(H2C)8
OH
OBn
(100 MHz, CDCl3, 20)
129.0
128.5
ppm
29.6
ppm
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

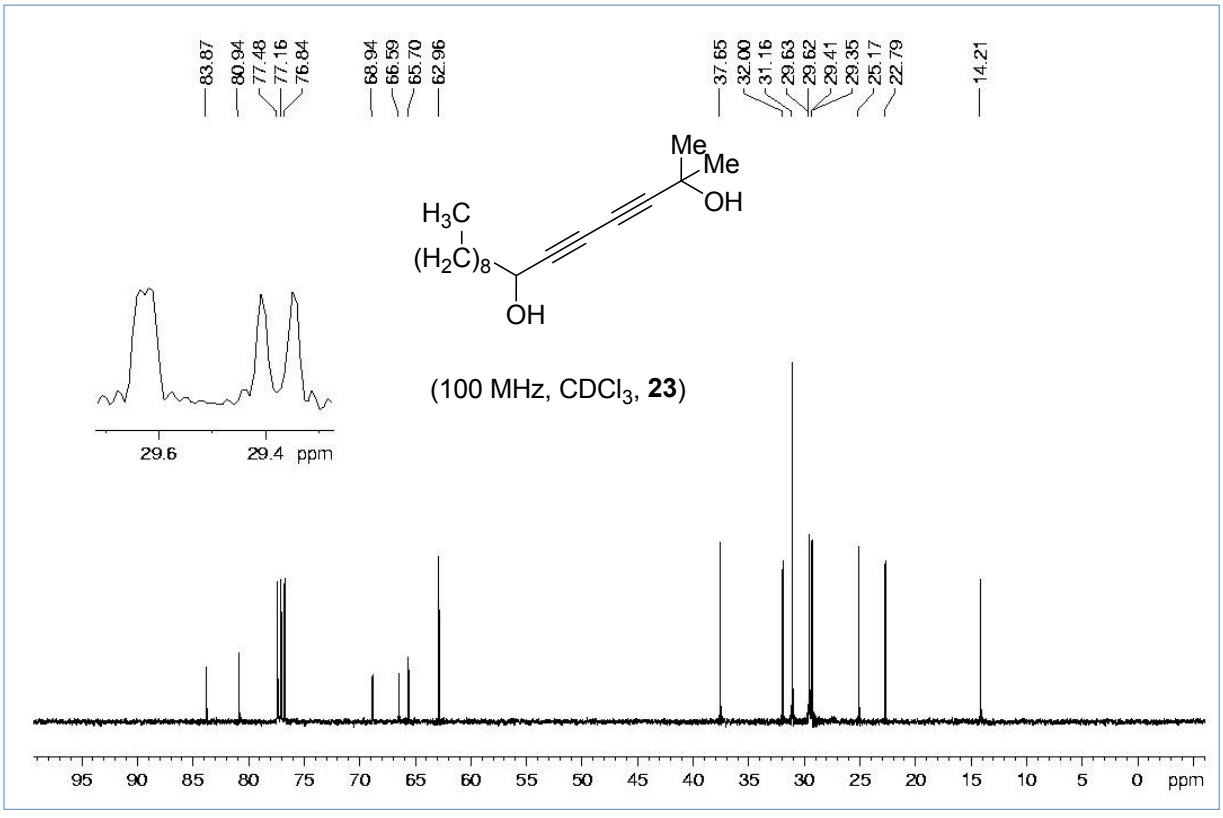

Cl
OH
H3C
(H2C)8
OH
(400 MHz, CDCl3, 21)
7.44 ppm
7.35 ppm
5.49 ppm
4.45 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.10
2.08
1.00
0.95
0.93
1.02
1.97
2.10
12.13
3.08

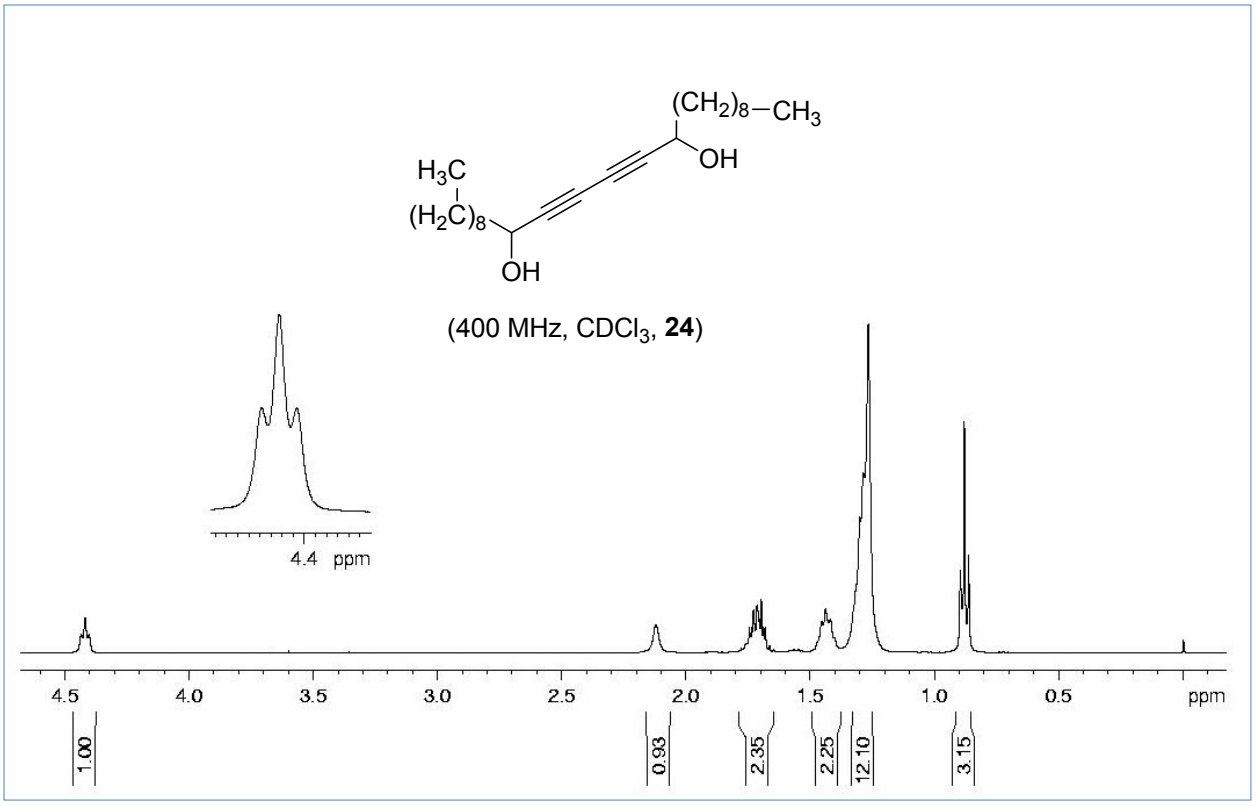

138.18
134.63
128.99
128.15
81.80
78.40
77.47
77.16
76.84
70.99
68.77
64.26
62.95
37.53
31.99
29.64
29.61
29.41
29.33
25.16
22.79
14.22
Cl
OH
H3C
(H2C)8
OH
(100 MHz, CDCl3, 21)
29.8 29.6 29.4 ppm
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Ph
Me
OH
H3C
(H2C)8
OH
(400 MHz, CDCl3, 22)
7.50 ppm
7.35 ppm
4.50 ppm
1.75 ppm
1.50 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.13
3.17
1.00
1.02
2.06
2.17
12.21
3.18

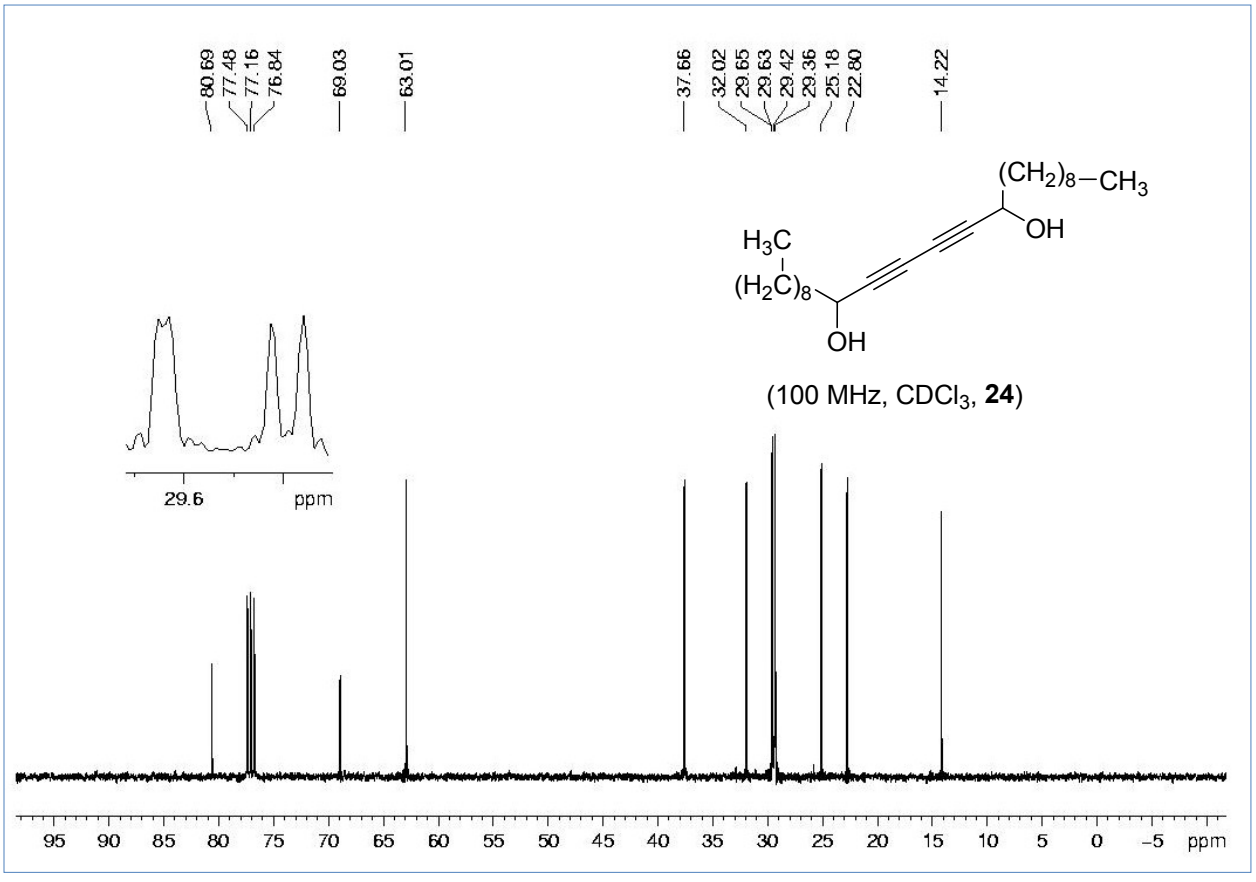

132.78
132.72
132.69
132.65
129.40
128.58
128.54
128.51
121.65
83.64
78.68
77.48
77.16
76.85
73.40
69.66
63.21
37.72
32.02
29.64
29.43
29.38
29.34
25.22
22.81
14.24
Ph
Me
OH
H3C
(H2C)8
OH
29.7 29.6 29.5 29.4 ppm
(100 MHz, CDCl3, 22)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Me
Me
OH
H3C
(H2C)8
OH
(400 MHz, CDCl3, 23)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.00
0.92
2.05
6.05
2.23
12.17
3.14

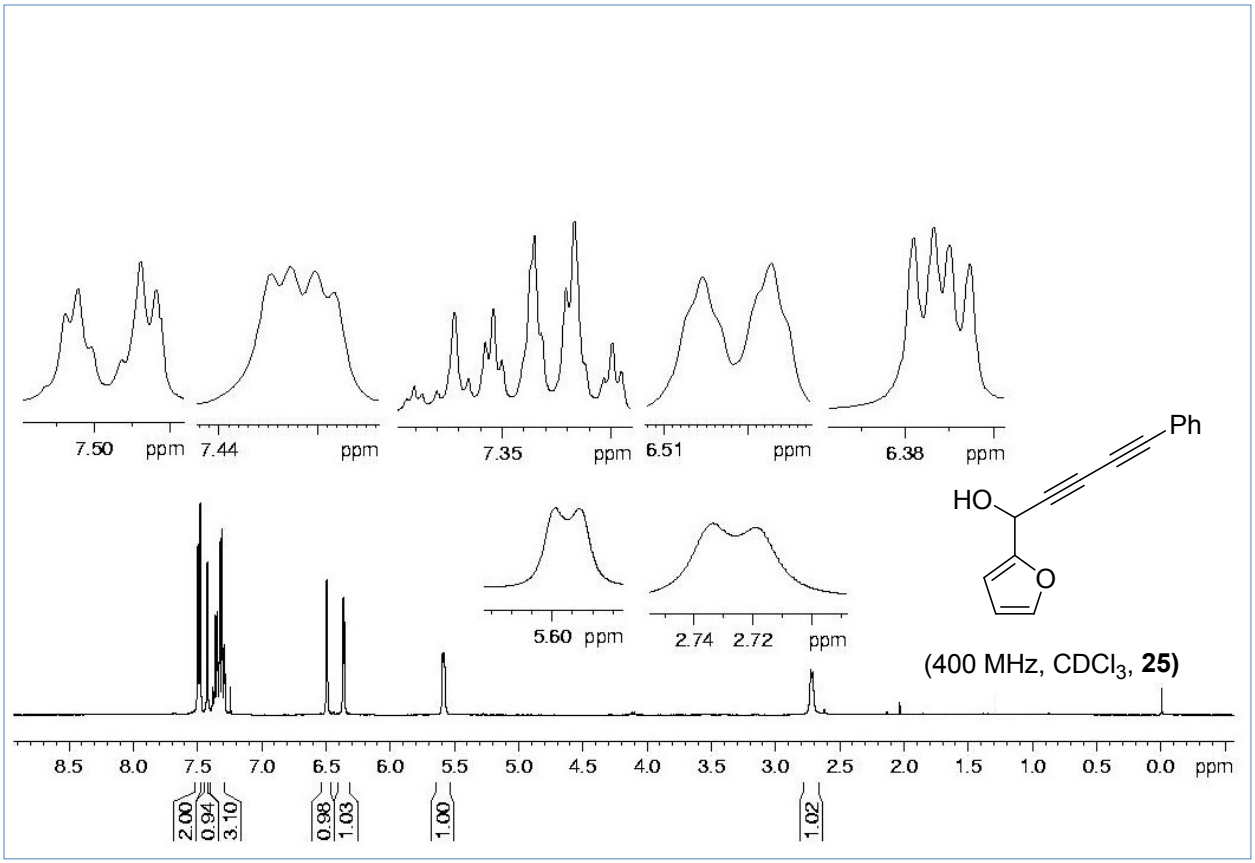

83.87
80.94
77.48
77.16
76.84
68.94
66.59
65.70
62.96
37.65
32.00
31.16
29.63
29.62
29.41
29.35
25.17
22.79
14.21
Me
Me
OH
H3C
(H2C)8
OH
(100 MHz, CDCl3, 23)
29.6
29.4
ppm
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
ppm



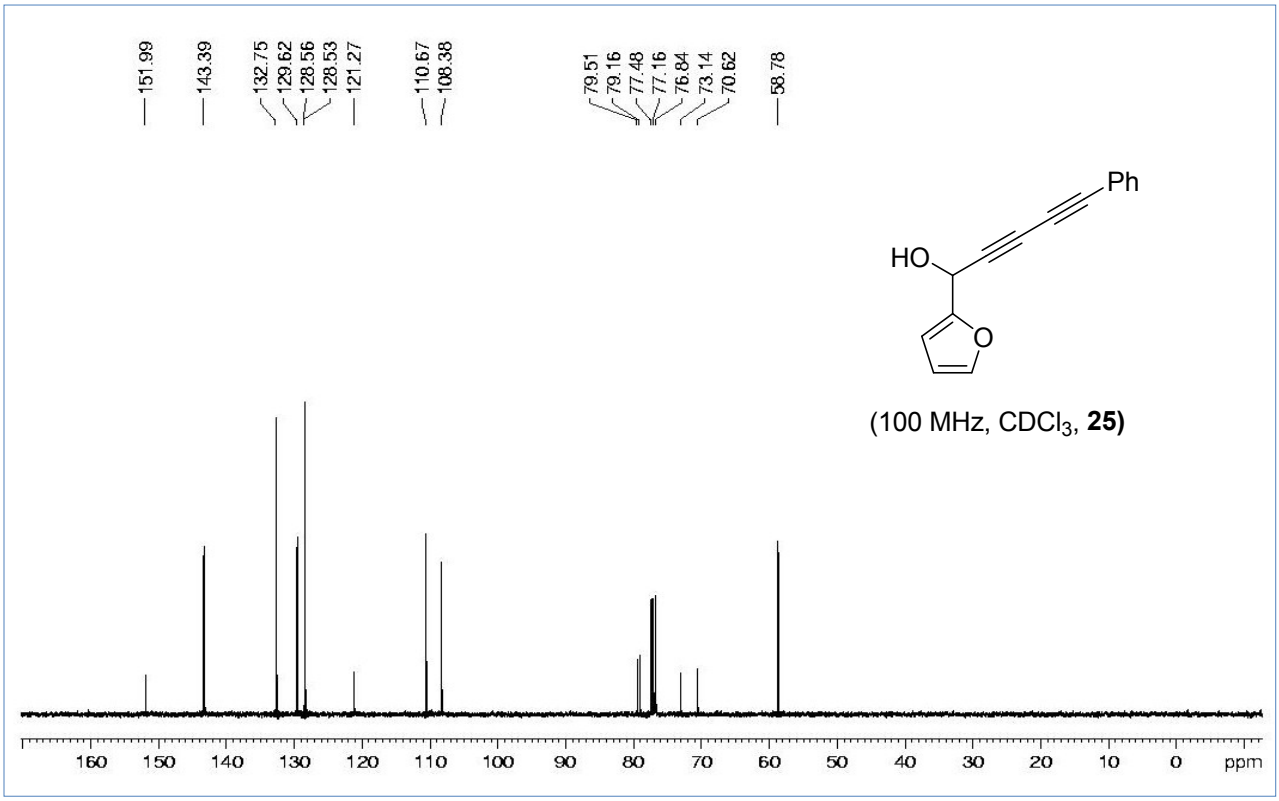
(400 MHz, $CDCl_3$, **24**)



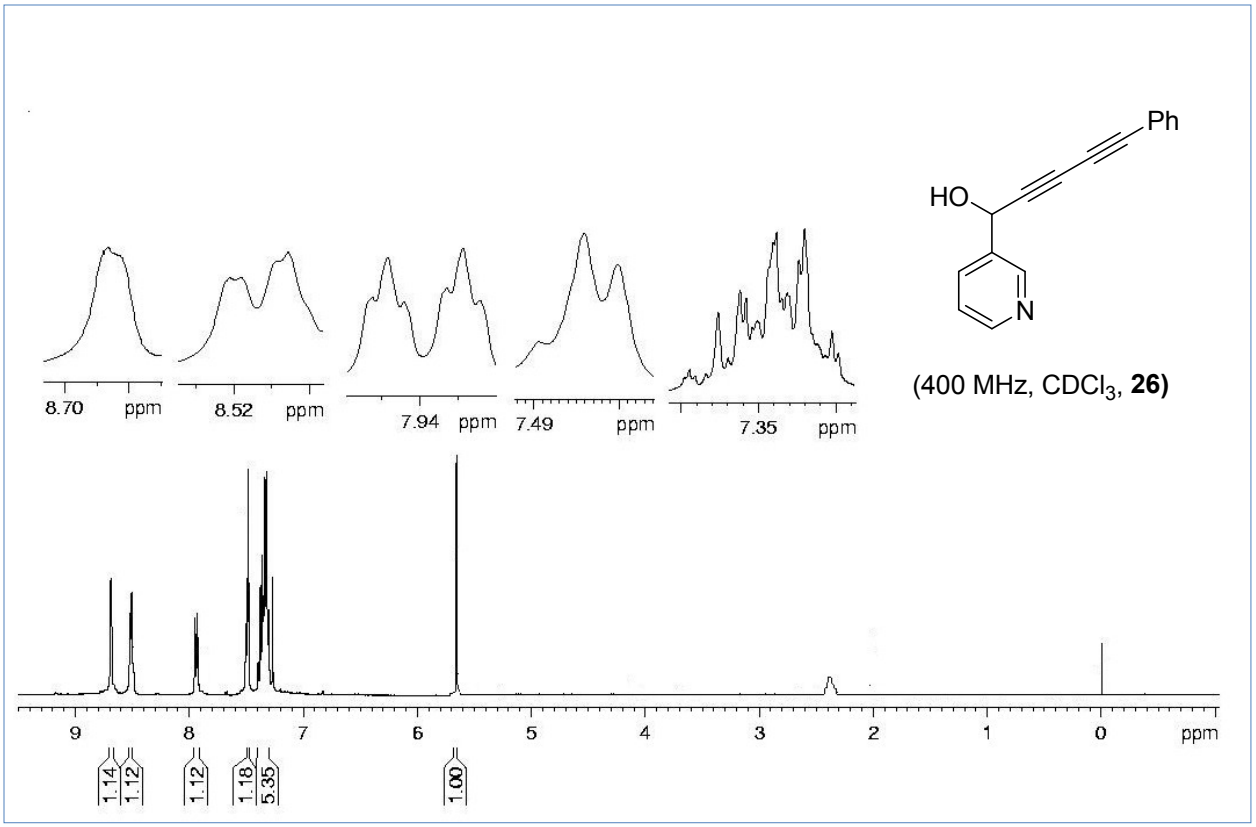
(100 MHz, $CDCl_3$, **24**)



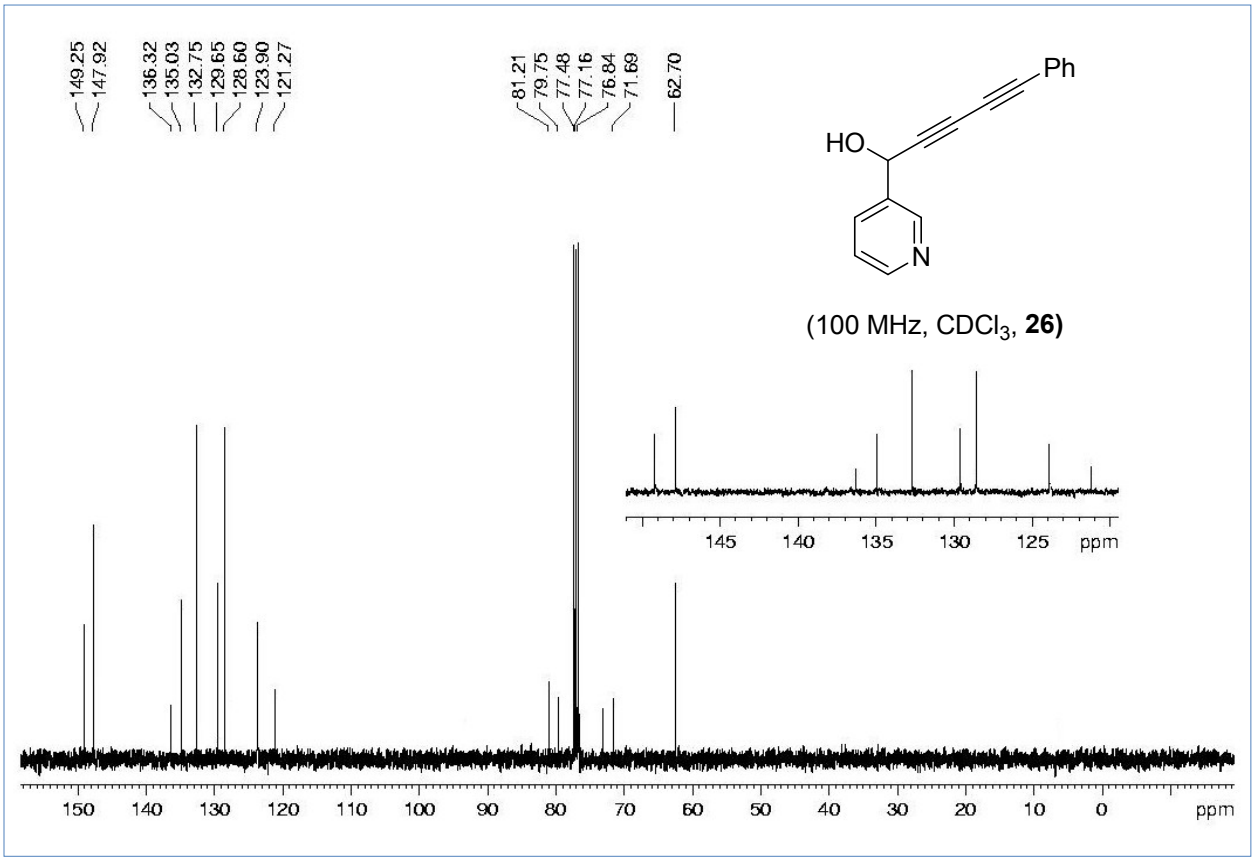
(400 MHz, $CDCl_3$, **25)**



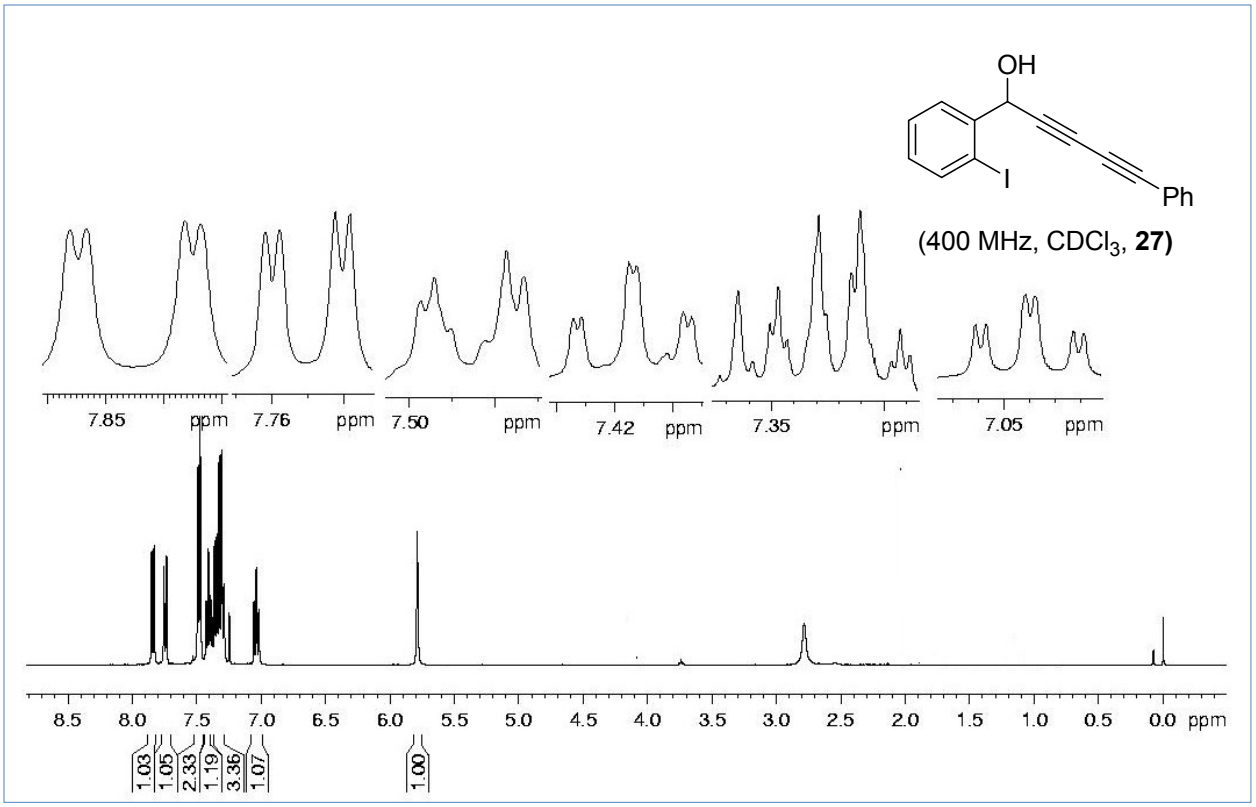
(100 MHz, $CDCl_3$, **25)**

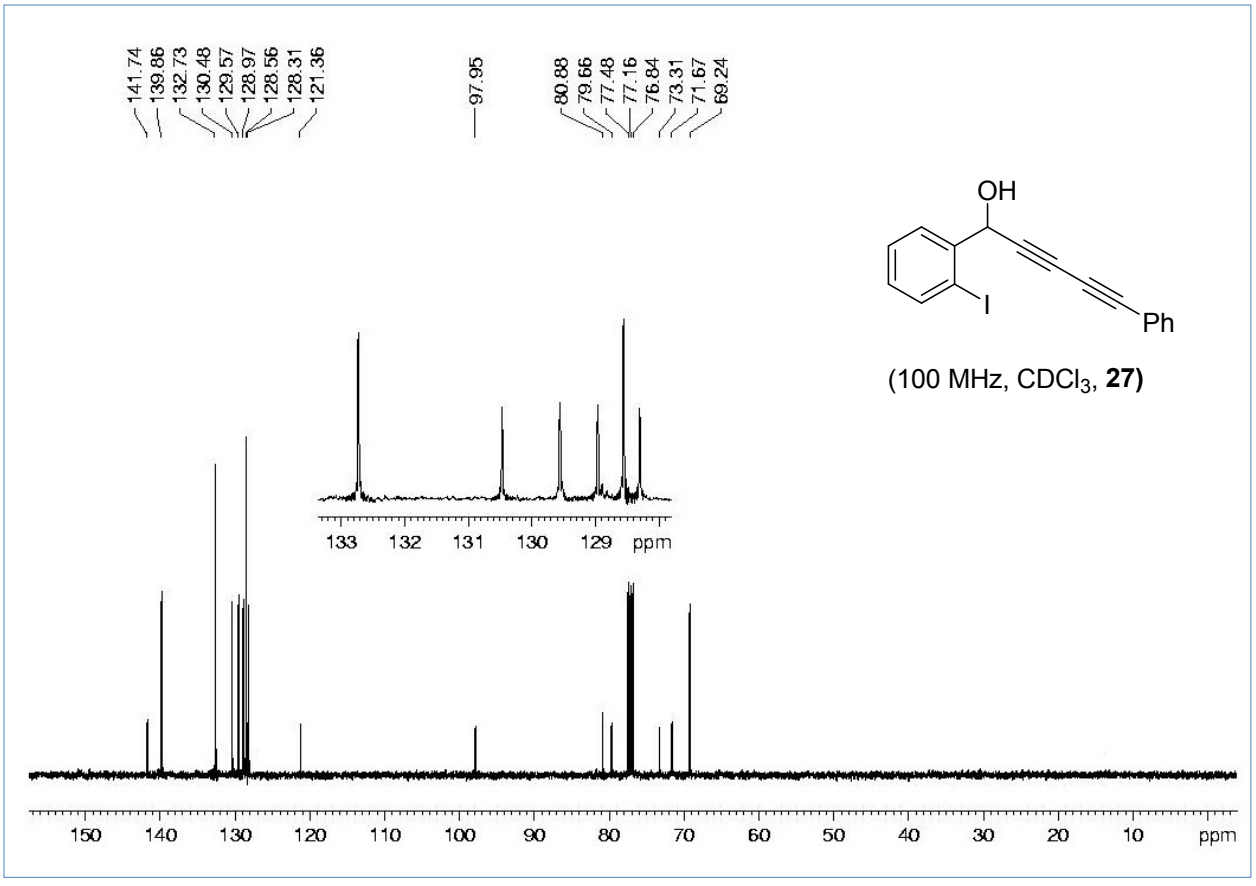


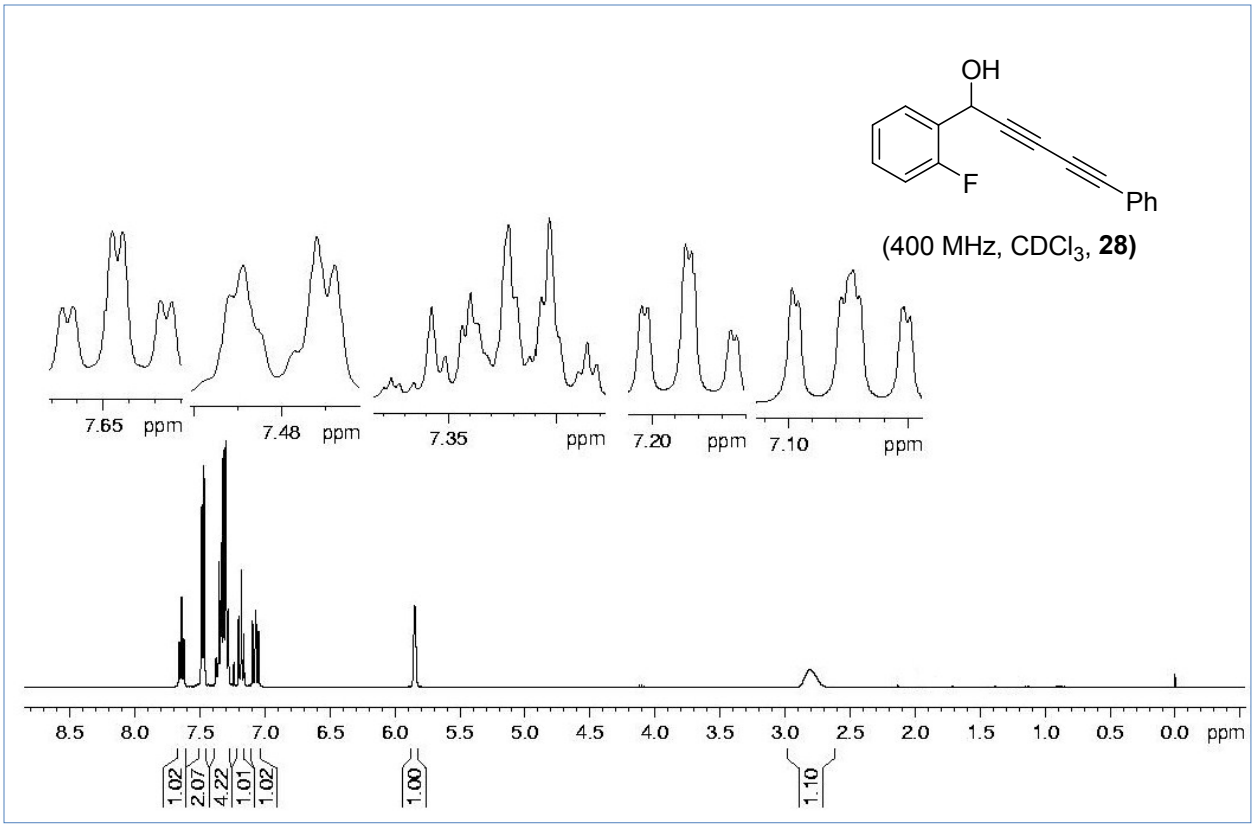
(400 MHz, $CDCl_3$, **26)**

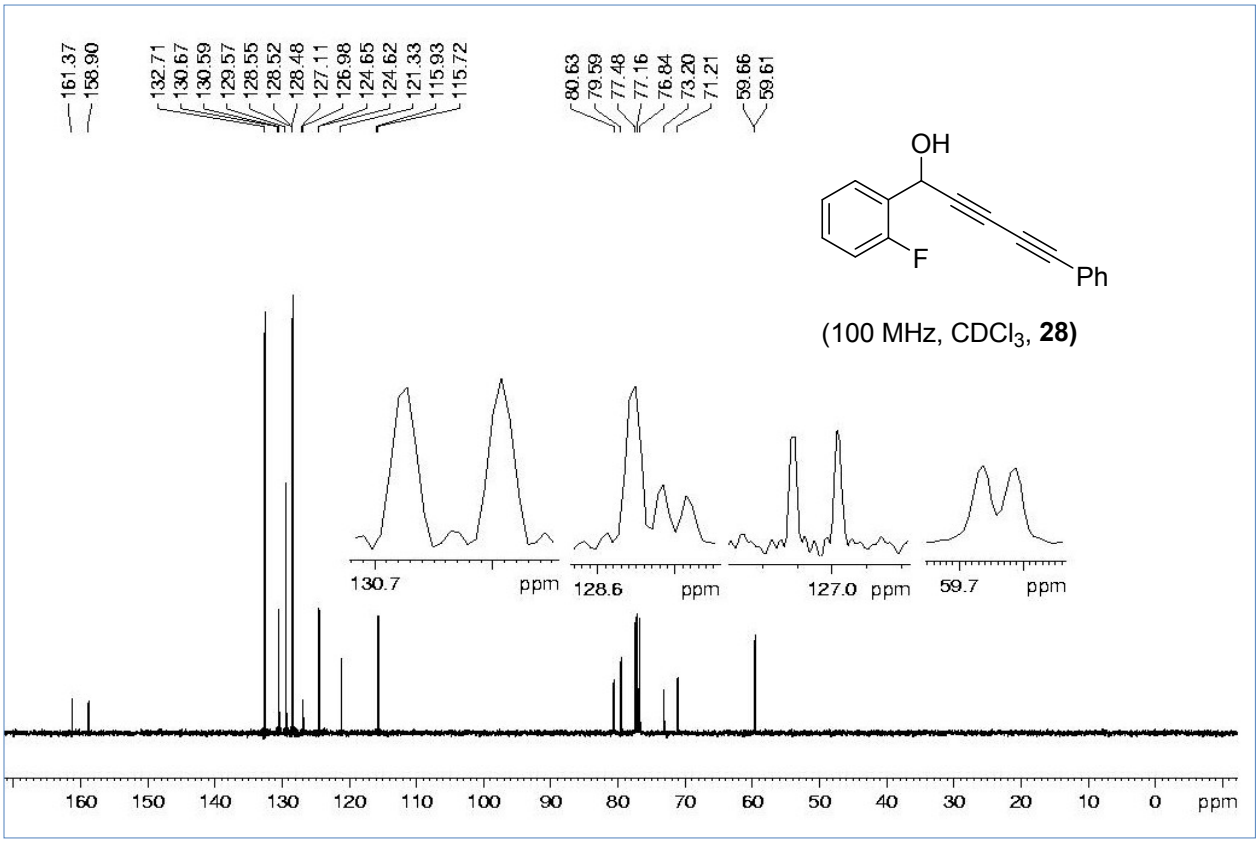


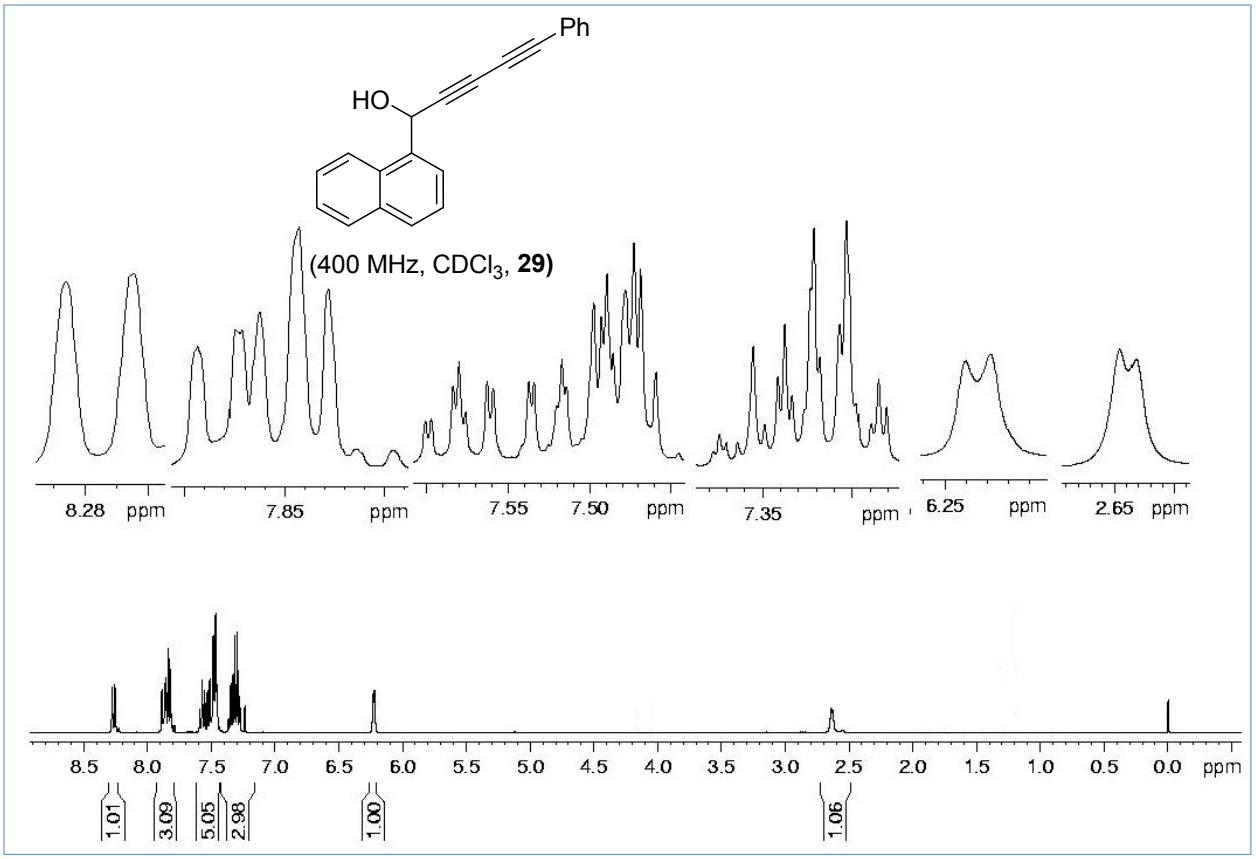
(100 MHz, $CDCl_3$, **26)**

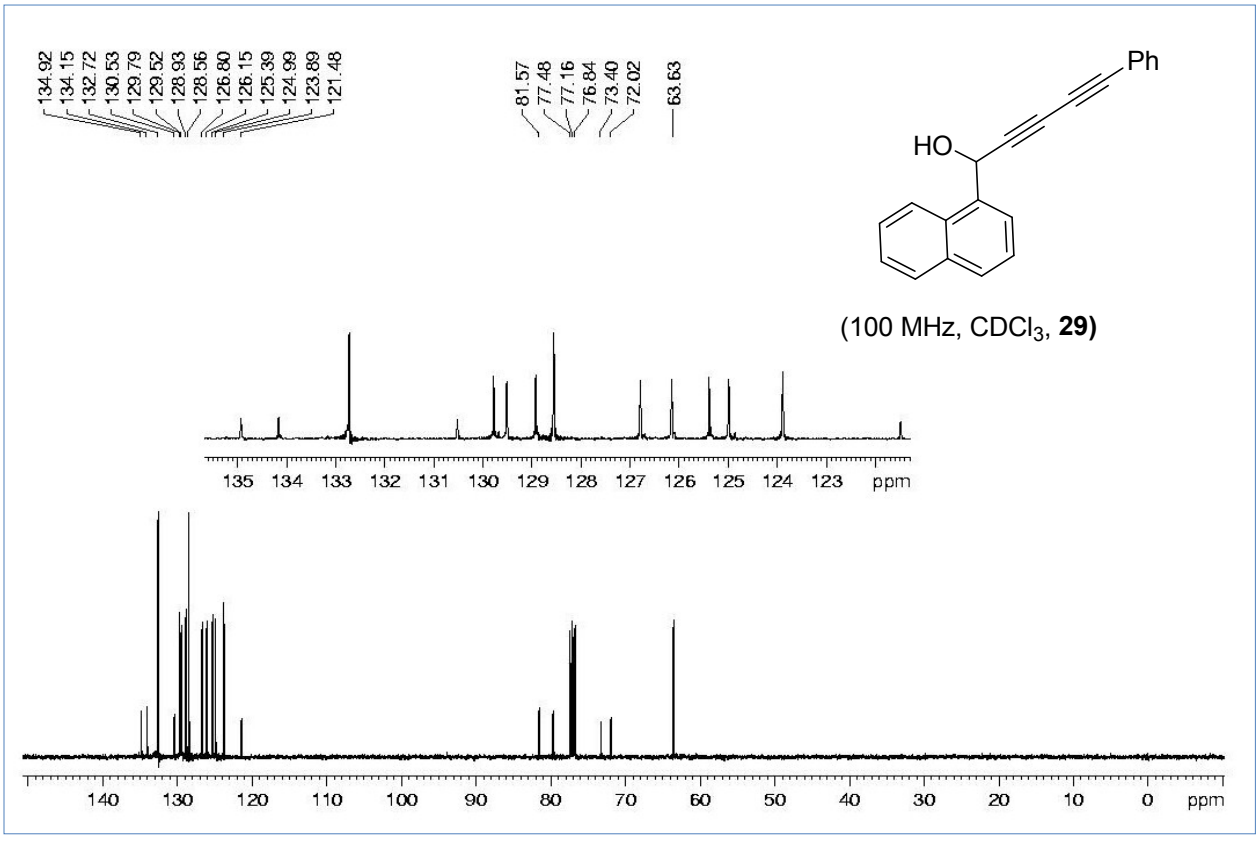

OH
I
Ph
(400 MHz, CDCl3, 27)
7.85 ppm
7.76 ppm
7.50 ppm
7.42 ppm
7.35 ppm
7.05 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.03
1.05
2.33
1.19
3.36
1.07
1.00

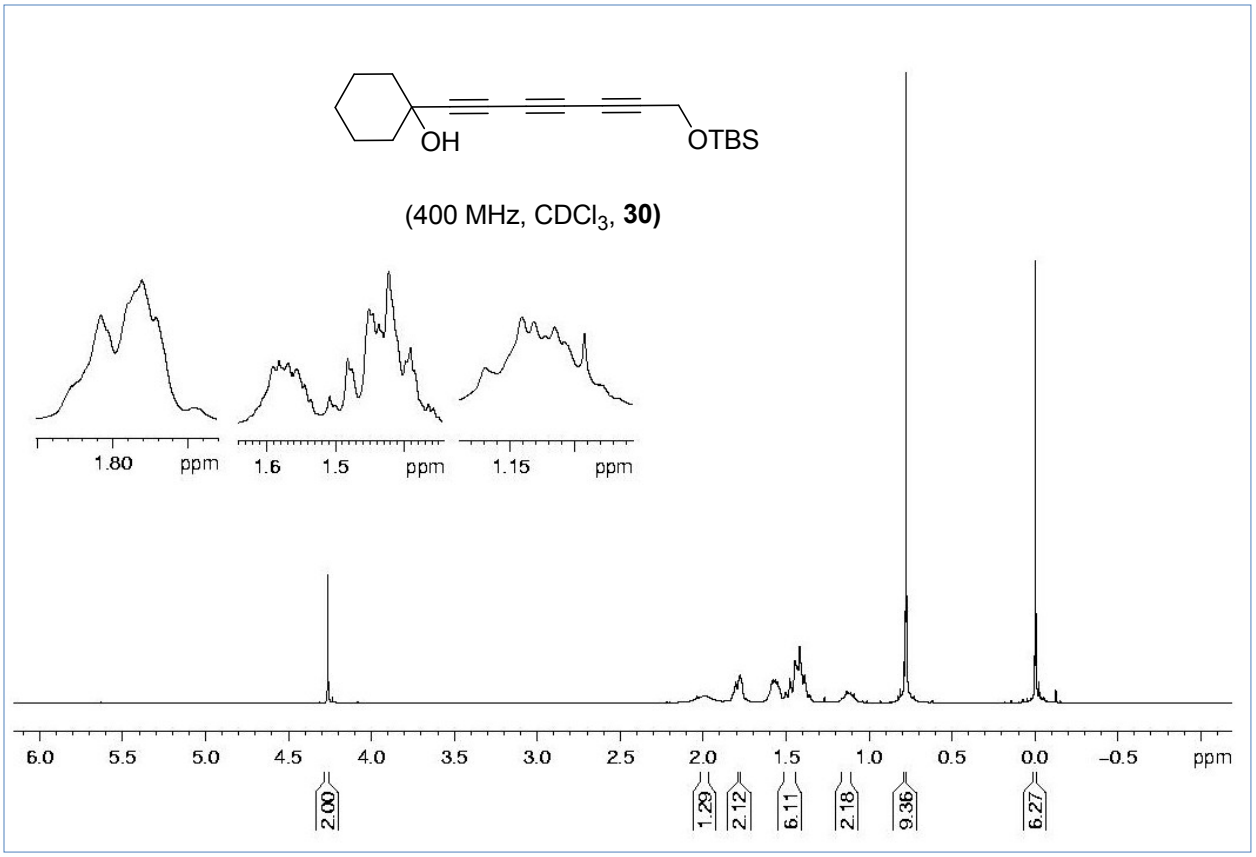

141.74
139.86
132.73
130.48
129.57
128.97
128.56
128.31
121.36
97.95
80.88
79.66
77.48
77.16
76.84
73.31
71.67
69.24
OH
I
Ph
(100 MHz, CDCl3, 27)
133 132 131 130 129 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

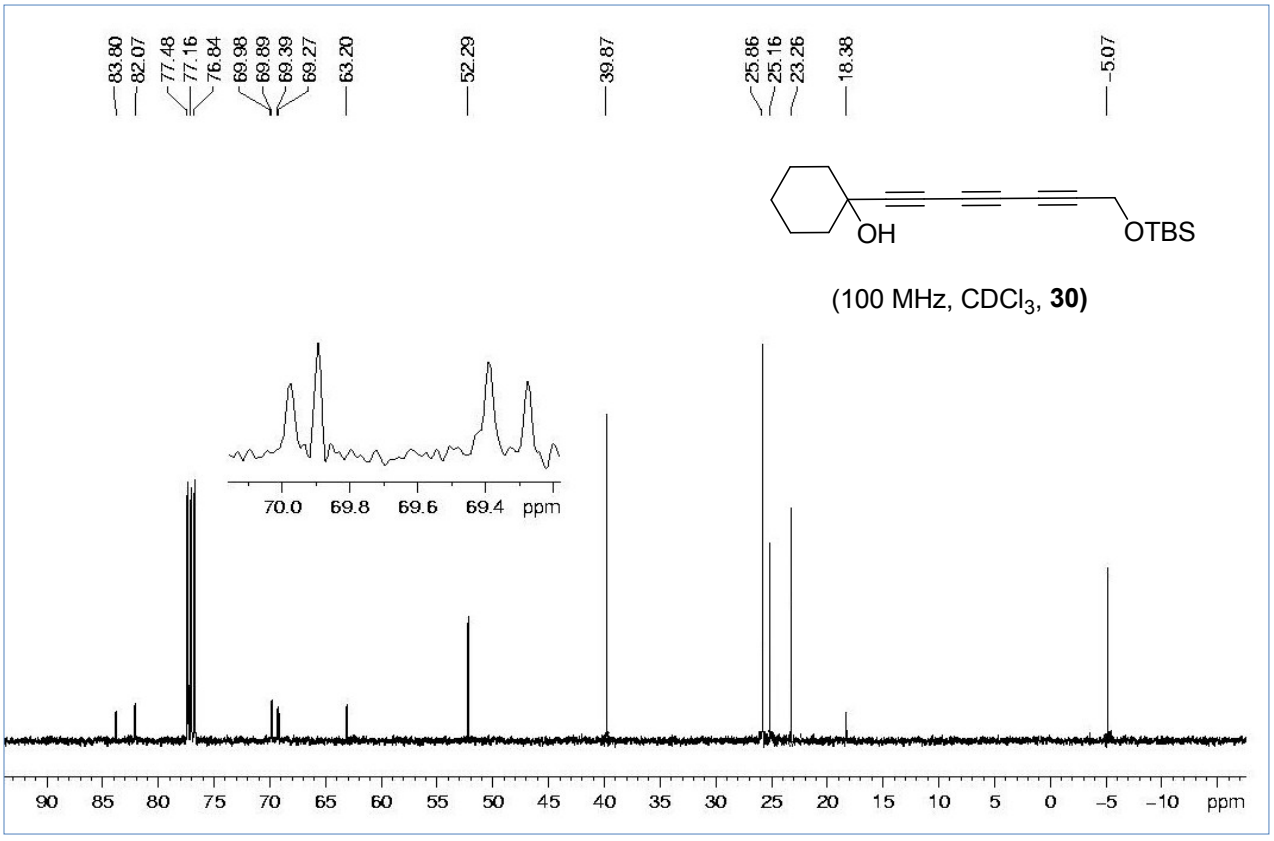

OH
F
Ph
(400 MHz, CDCl3, 28)
7.65 ppm
7.48 ppm
7.35 ppm
7.20 ppm
7.10 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.02
2.07
4.22
1.01
1.02
1.00
1.10

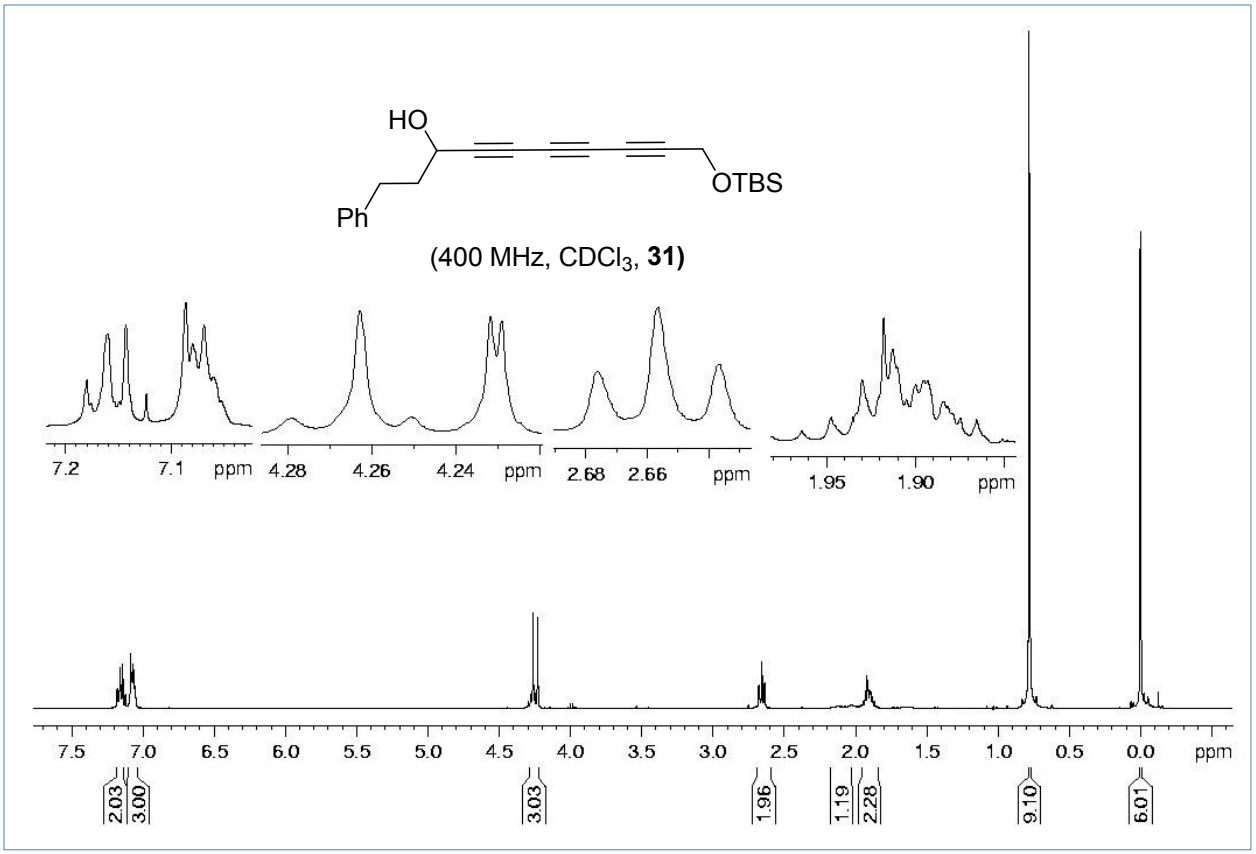

161.37
158.90
132.71
130.67
130.59
129.57
128.55
128.52
128.48
127.11
126.98
124.65
124.62
121.33
115.93
115.72
80.63
79.59
77.48
77.16
76.84
73.20
71.21
59.66
59.61
OH
F
Ph
(100 MHz, CDCl3, 28)
130.7 ppm
128.6 ppm
127.0 ppm
59.7 ppm
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

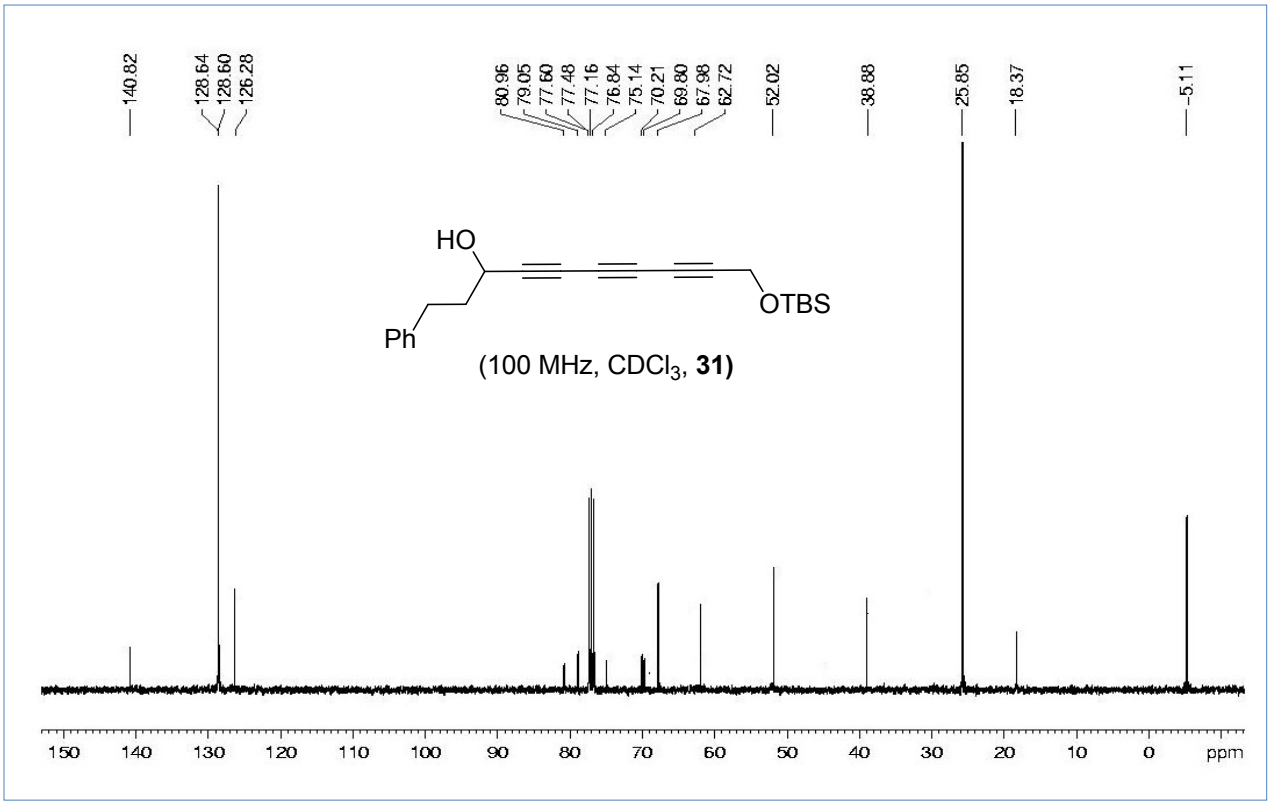

Ph
HO
(400 MHz, CDCl3, 29)
8.28 ppm
7.85 ppm
7.55 7.50 ppm
7.35 ppm
6.25 ppm
2.65 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.01
3.09
5.05
2.98
1.00
1.06

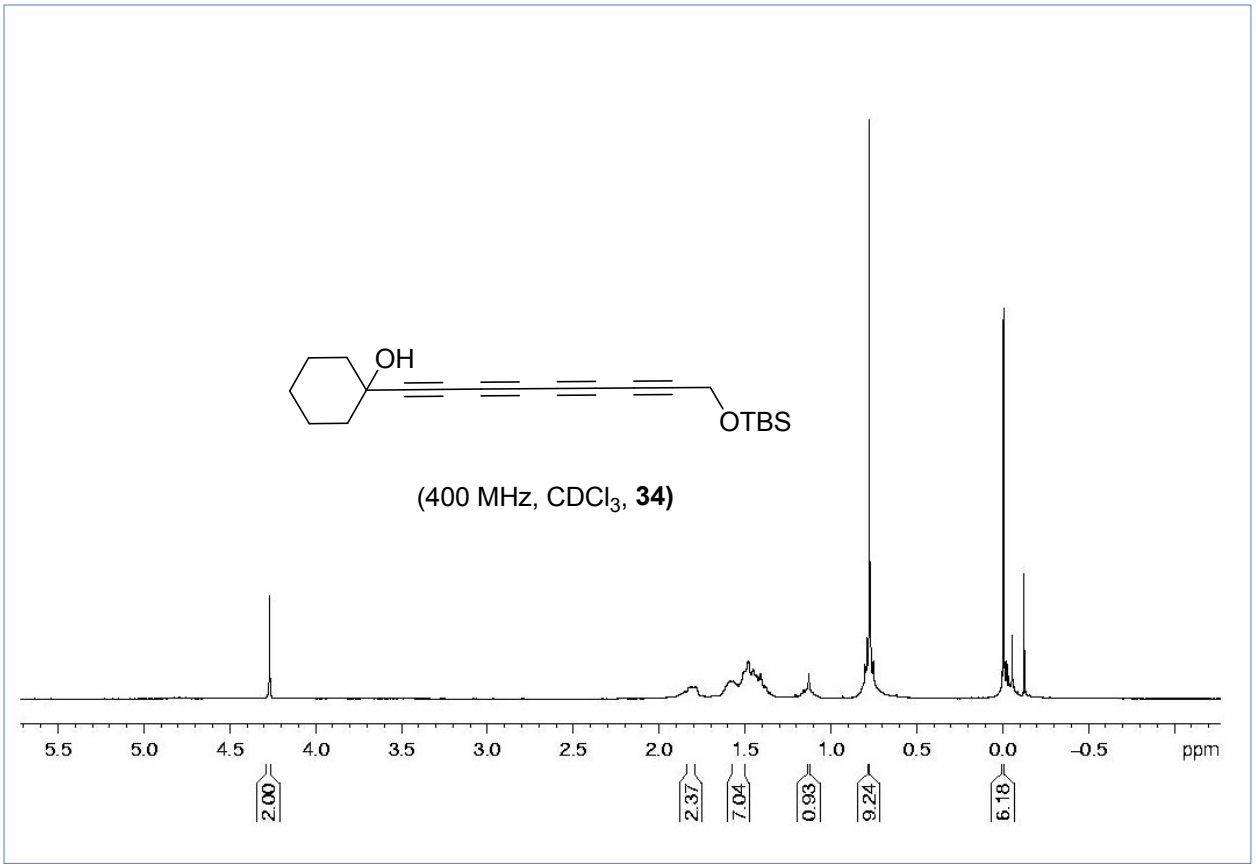

134.92
134.15
132.72
130.53
129.79
129.52
128.93
128.56
126.80
126.15
125.39
124.99
123.89
121.48
81.57
77.48
77.16
76.84
73.40
72.02
63.63
Ph
HO
(100 MHz, CDCl3, 29)
135 134 133 132 131 130 129 128 127 126 125 124 123 ppm
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

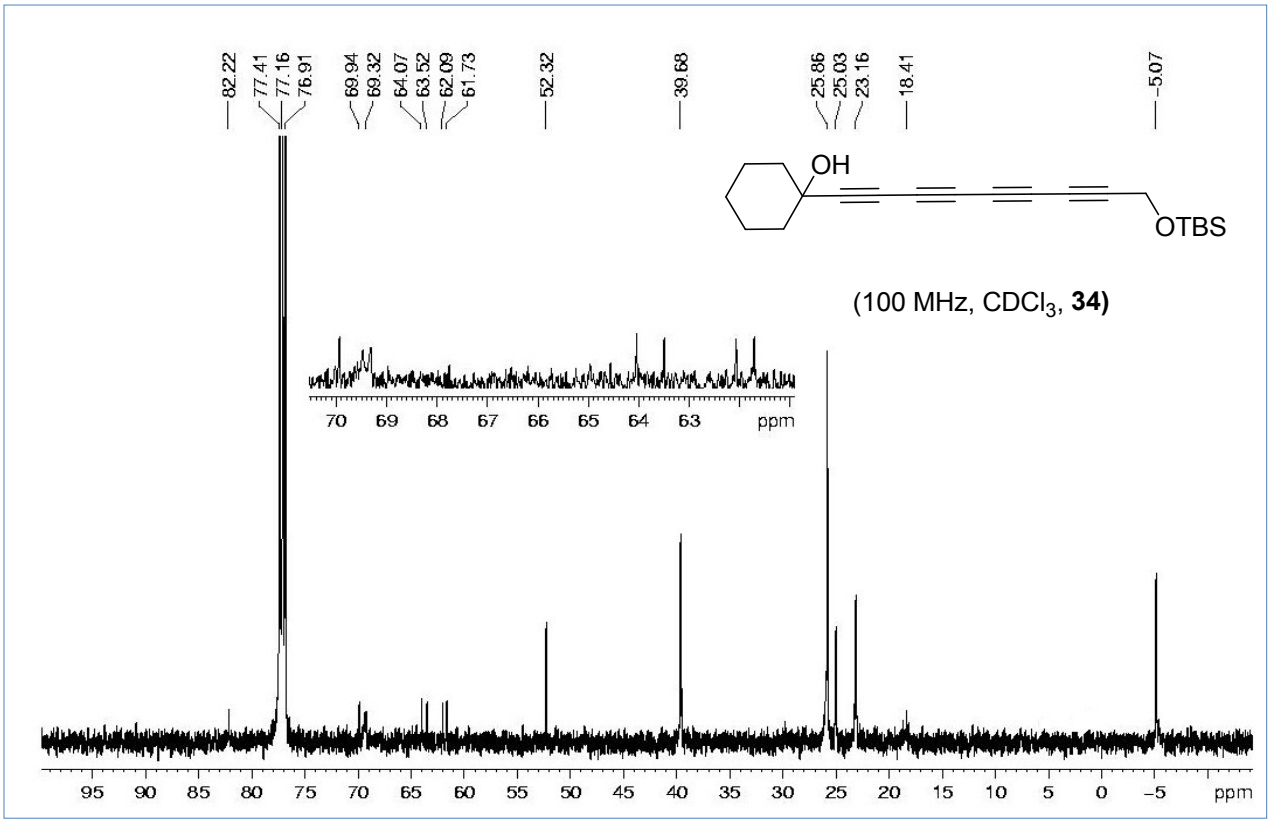

OH
OTBS
(400 MHz, CDCl3, 30)
1.80 ppm
1.6 1.5 ppm
1.15 ppm
6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
2.00
1.29
2.12
6.11
2.18
9.36
6.27

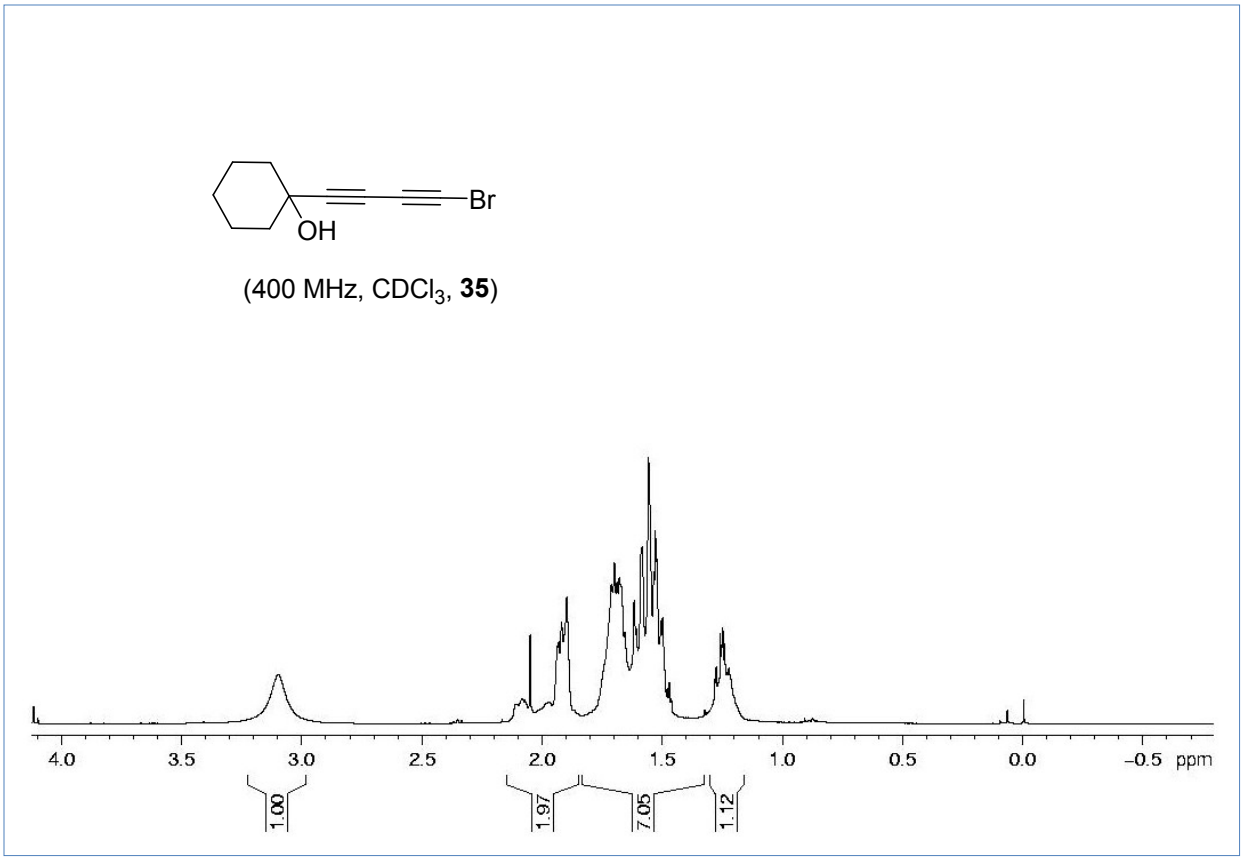

83.80
82.07
77.48
77.16
76.84
69.98
69.89
69.39
69.27
63.20
52.29
39.87
25.86
25.16
23.26
18.38
−5.07
OH
OTBS
(100 MHz, CDCl3, 30)
70.0 69.8 69.6 69.4 ppm
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 ppm

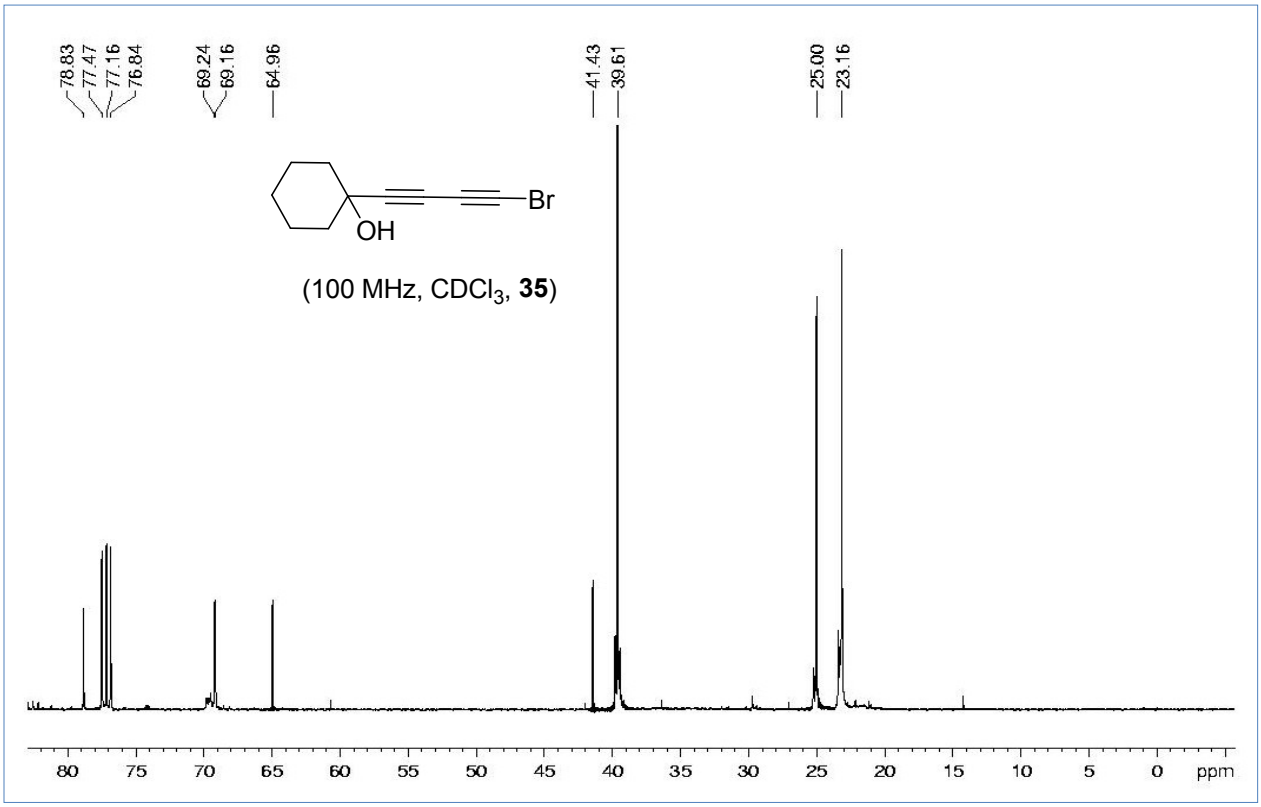

HO
OTBS
Ph
(400 MHz, CDCl3, 31)
7.2
7.1
ppm
4.28
4.26
4.24
ppm
2.68
2.66
ppm
1.95
1.90
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.03
3.00
3.03
1.96
1.19
2.28
9.10
6.01

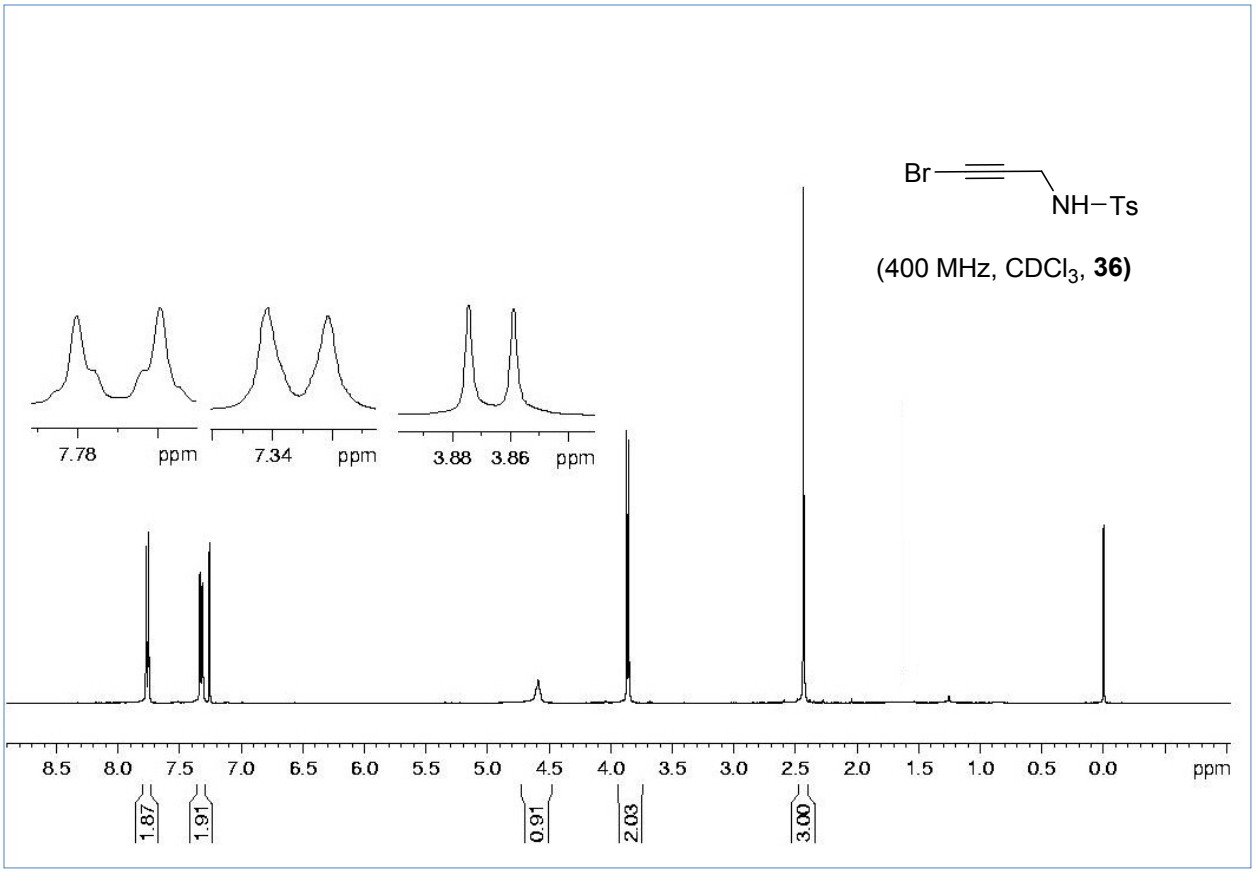

140.82
128.64
128.60
126.28
80.96
79.05
77.60
77.48
77.16
76.84
75.14
70.21
69.80
67.98
62.72
52.02
38.88
25.85
18.37
-5.11
HO
OTBS
Ph
(100 MHz, CDCl3, 31)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

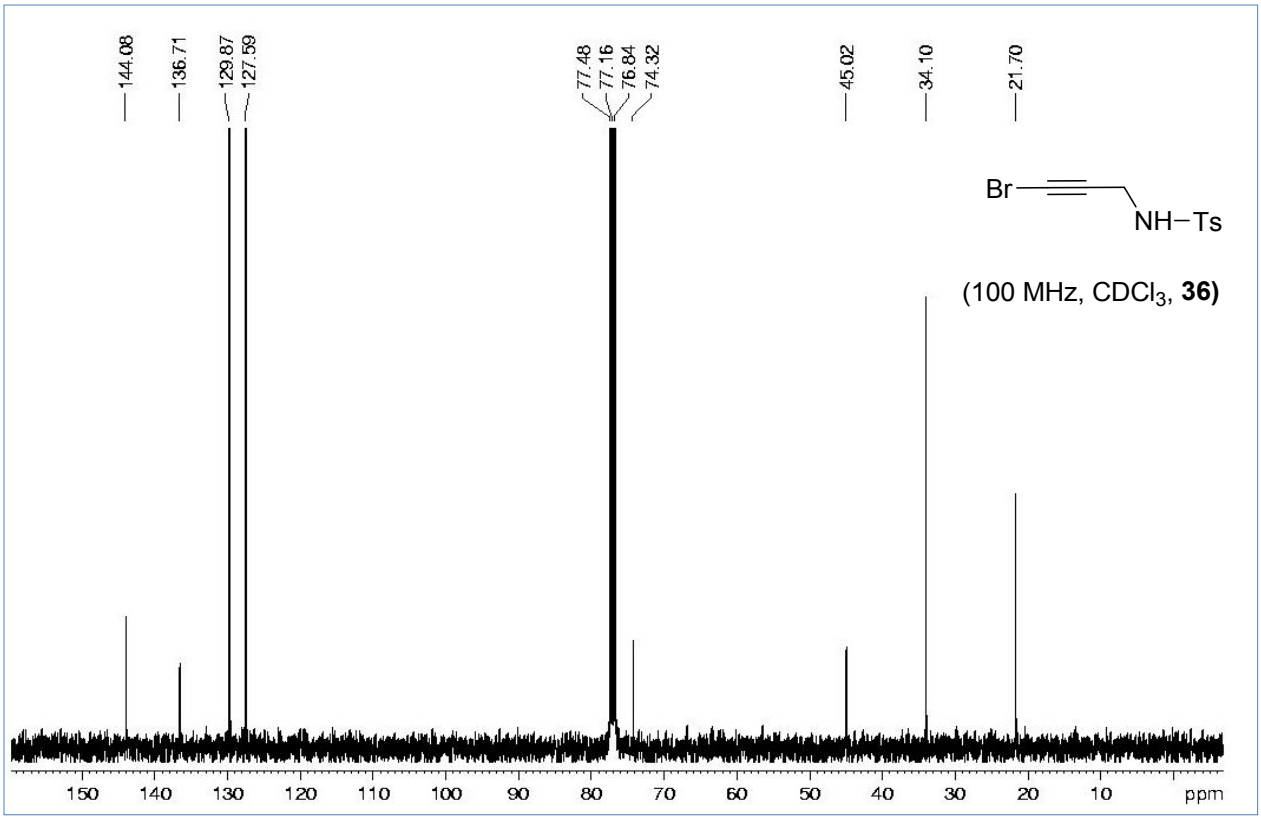

OH
OTBS
(400 MHz, CDCl3, 34)
5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
2.00
2.37
7.04
0.93
9.24
6.18

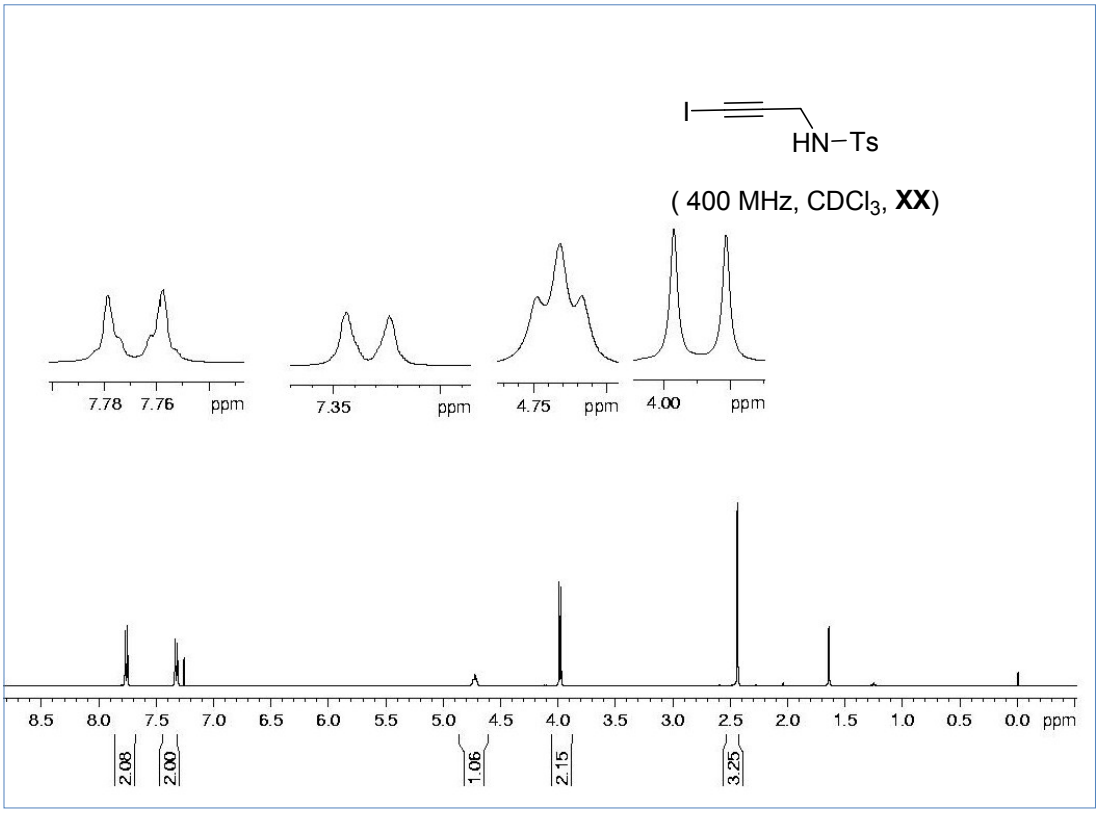

82.22
77.41
77.16
76.91
69.94
69.32
64.07
63.52
62.09
61.73
52.32
39.68
25.86
25.03
23.16
18.41
−5.07
OH
OTBS
(100 MHz, CDCl3, 34)
70 69 68 67 66 65 64 63 ppm
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 ppm

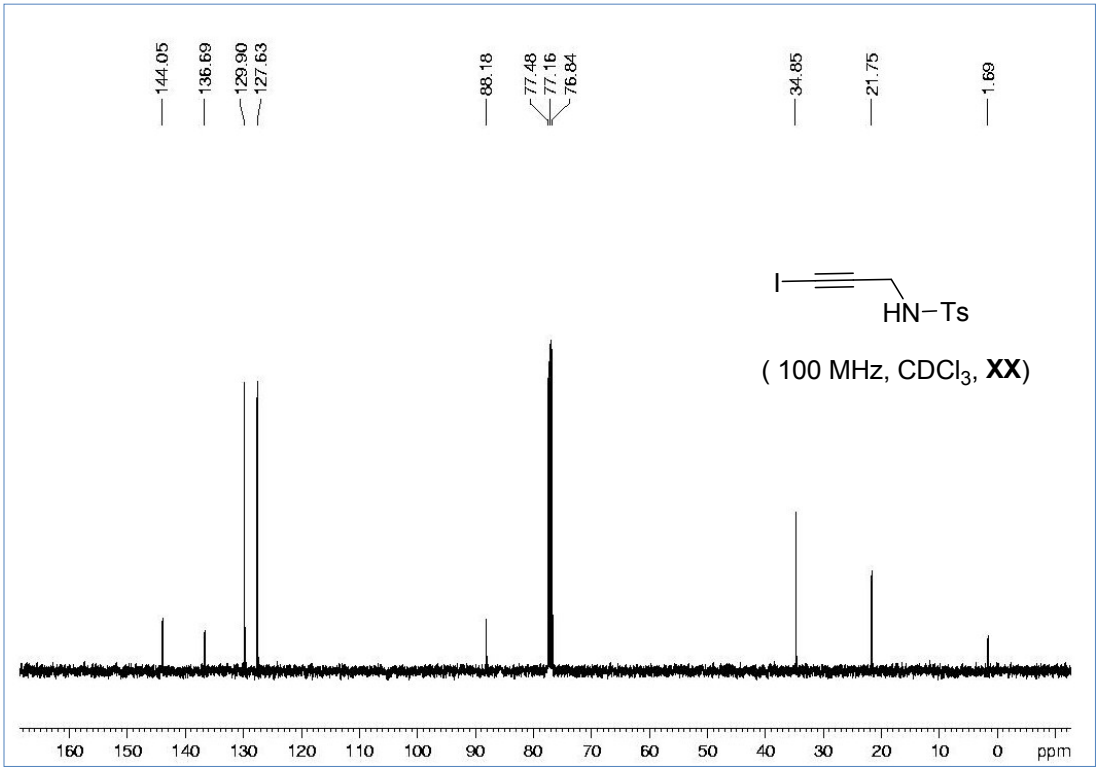

Br
OH
(400 MHz, CDCl3, 35)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm
1.00
1.97
7.05
1.12

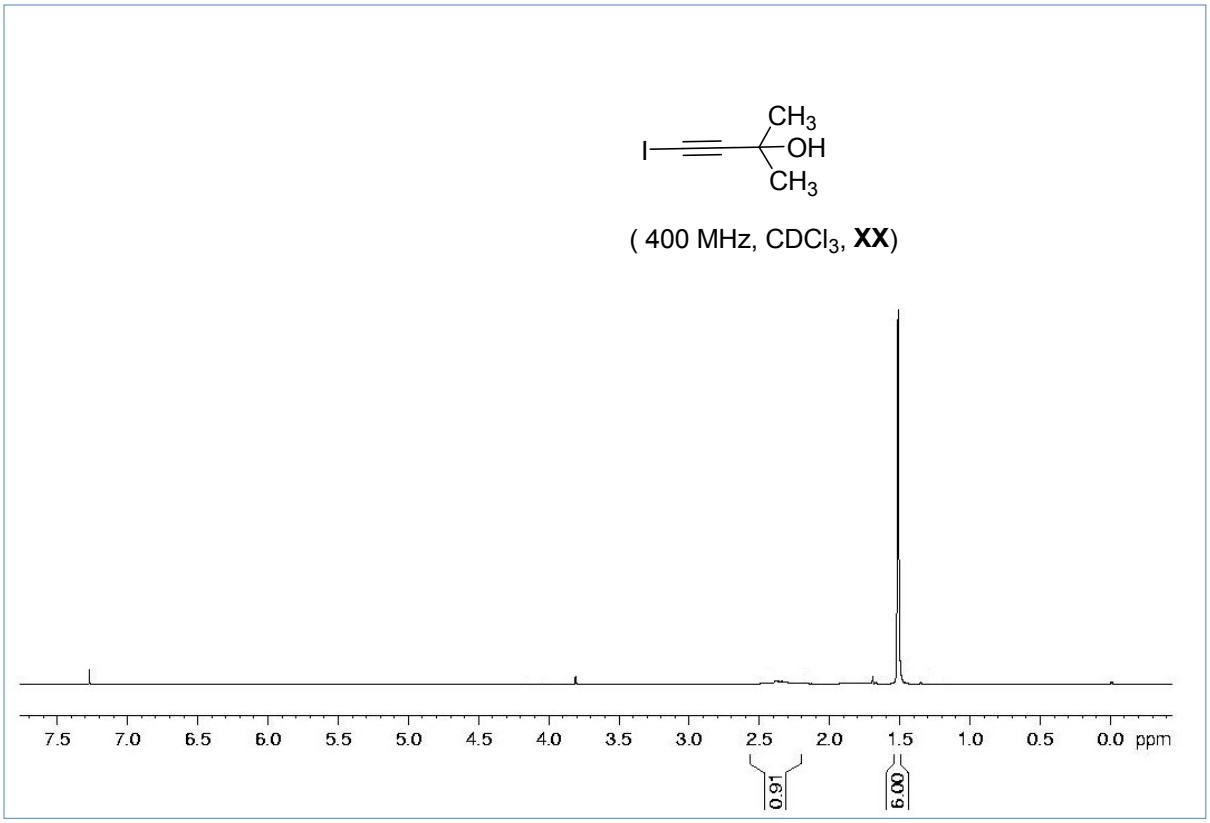

78.83
77.47
77.16
76.84
69.24
69.16
64.96
41.43
39.61
25.00
23.16
Br
OH
(100 MHz, CDCl3, 35)
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
ppm

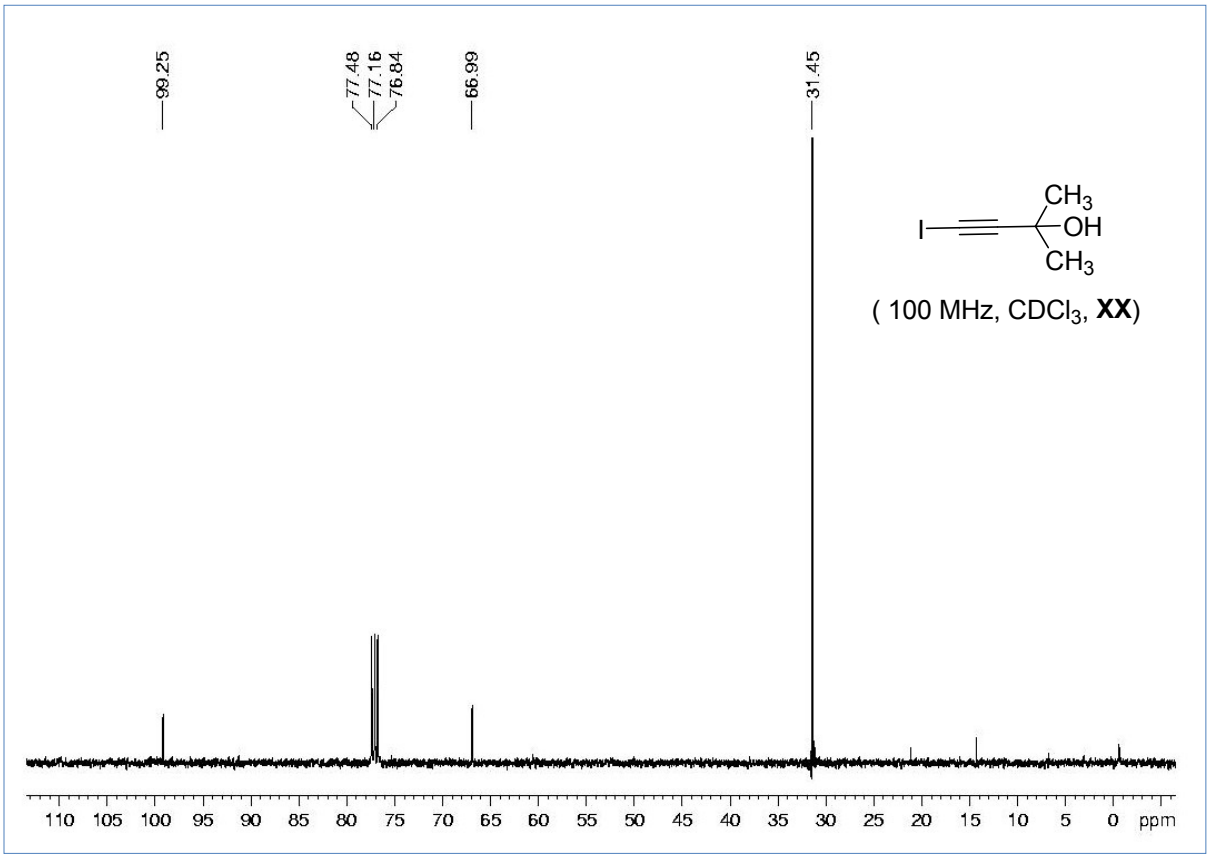

Br
NH−Ts
(400 MHz, CDCl3, 36)
7.78 ppm
7.34 ppm
3.88 3.86 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.87
1.91
0.91
2.03
3.00

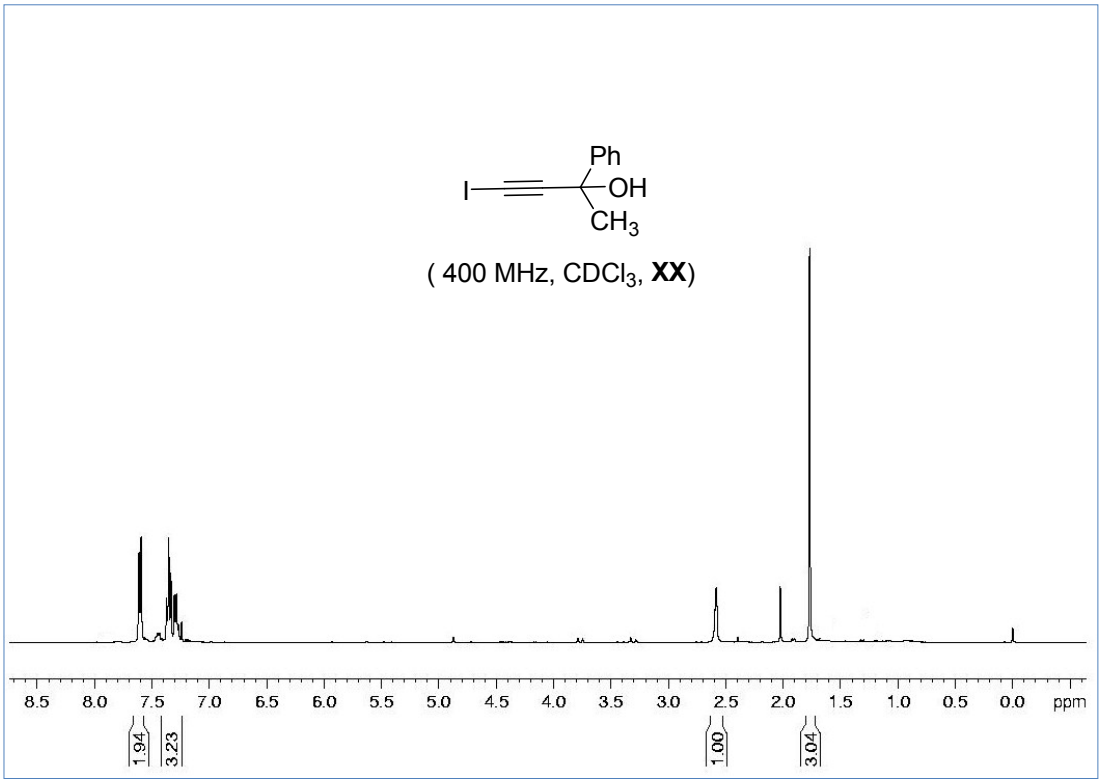

144.08
136.71
129.87
127.59
77.48
77.16
76.84
74.32
45.02
34.10
21.70
Br
NH−Ts
(100 MHz, CDCl3, 36)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

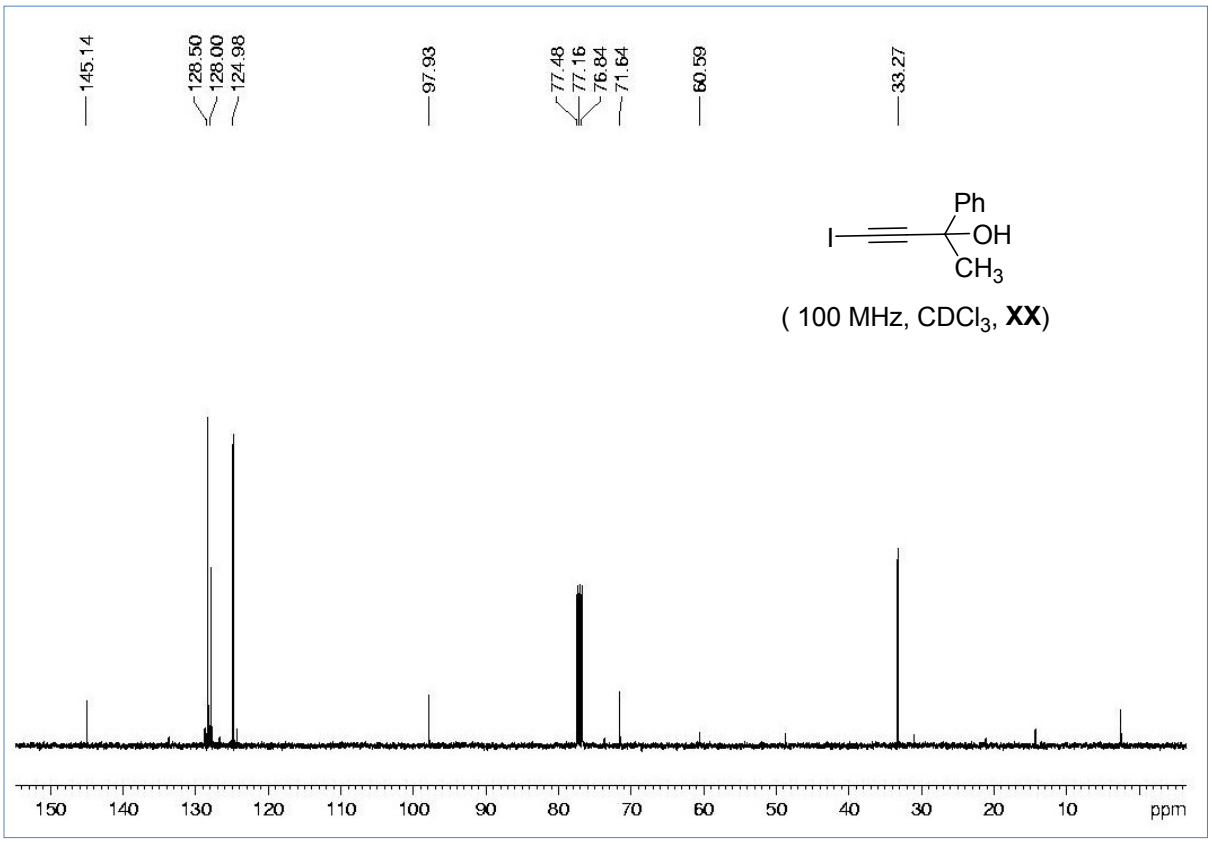

I
HN−Ts
(400 MHz, CDCl3, XX)
7.78 7.76 ppm
7.35 ppm
4.75 ppm
4.00 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.08
2.00
1.06
2.15
3.25

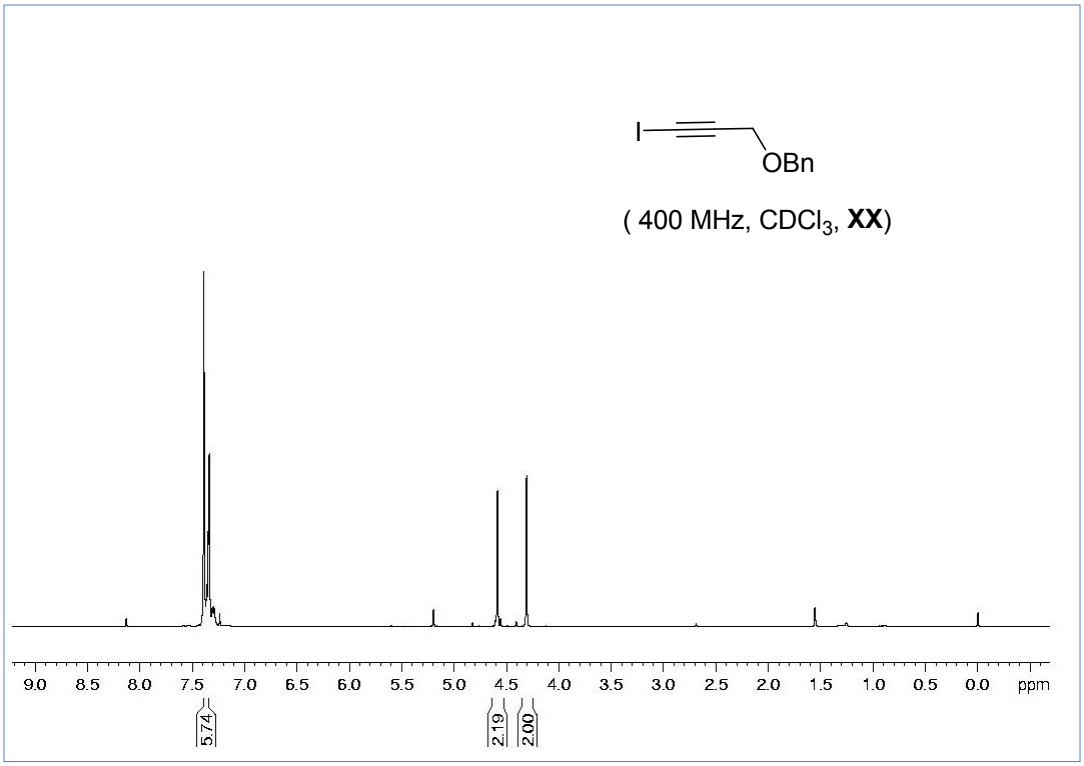

144.05
136.69
129.90
127.63
88.18
77.48
77.16
76.84
34.85
21.75
1.69
I
HN−Ts
(100 MHz, CDCl3, XX)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

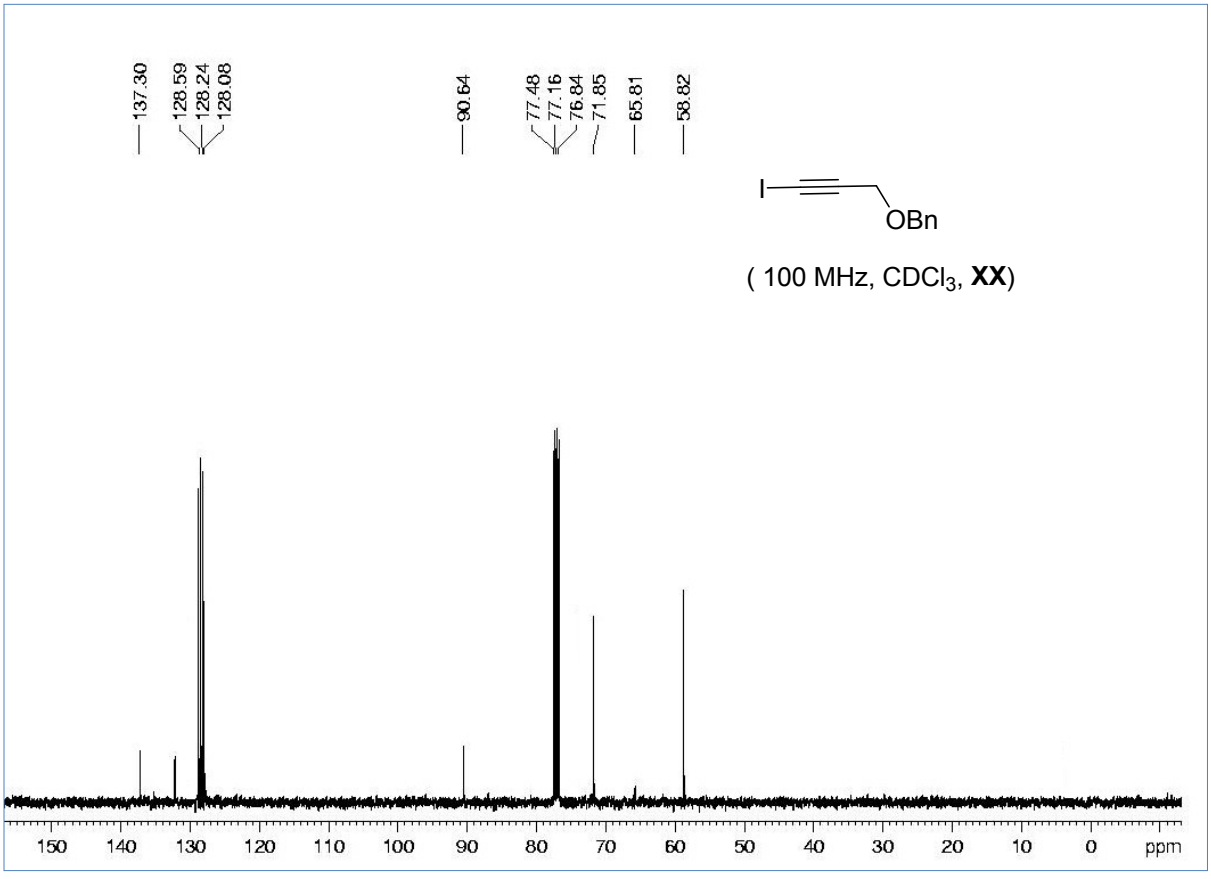

CH3
I
OH
CH3
(400 MHz, CDCl3, XX)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.91
6.00


99.25
77.48
77.16
76.84
66.99
31.45
CH3
I
OH
CH3
(100 MHz, CDCl3, XX)
110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm


Ph
I
OH
CH3
(400 MHz, CDCl3, XX)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.94
3.23
1.00
3.04


145.14
128.50
128.00
124.98
97.93
77.48
77.16
76.84
71.64
60.59
33.27
Ph
I
OH
CH3
(100 MHz, CDCl3, XX)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


I
OBn
(400 MHz, CDCl3, XX)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.74
2.19
2.00


137.30
128.59
128.24
128.08
90.64
77.48
77.16
76.84
71.85
65.81
58.82
I
OBn
(100 MHz, CDCl3, XX)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm