Supporting Information

"Carbonyl Propargylation from the Alcohol or Aldehyde Oxidation Level Employing 1,3-Enynes as Surrogates to Preformed Allenyl Metal Reagents: A Ruthenium Catalyzed C-C Bond Forming Transfer Hydrogenation"

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Table of Contents

General Experimental Details. All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred *via* oven-dried syringe. Reaction tubes were flame-dried and cooled under a stream of nitrogen. Reaction tubes were purchased from Fisher Scientific (catalog number 14-959-35C). THF was passed through a column of Al_2O_3 and sparged with argon immediately prior to use. Dppf and $RuHCl(CO)(PPh_3)_3$ were used as received from Strem Chemicals. Substrates **1a-1g** were prepared in analogy with the procedure of Sonogashira and coworkers.[1] Commercially available alcohols were used as received. Commercially available aldehydes were purified *via* distillation or recrystallization prior to use. Reactions were monitored by thin-layer chromatography and products visualized with anisaldehyde stain. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F_{254}). Preparative column chromatography employing silica gel was performed according to the method of Still.[2] Solvents for chromatography are listed as volume/volume ratios. Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+H]^+$ or a suitable fragment ion. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian Gemini (400 MHz or 300MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Where mixtures of isomers (*e.g.* diastereomers) have been characterized together, integrals are normalized to the major isomer. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Gemini 300 (75 MHz) or 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. ^{13}C NMR spectra were routinely run with broadband decoupling. Compound numbers used in the experimental section correspond to those employed in the main paper.

[1] K. Sonogashira, Y. Tohada, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467-4470.

[2] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.

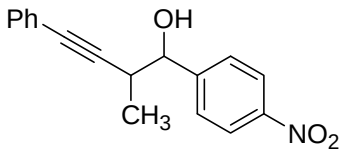
Experimental Procedures and Spectroscopic Data for Adducts 3a-3u

General Procedure A for the Coupling of 1a to Alcohols: To a re-sealable reaction tube containing a magnetic stirrer, was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), and the corresponding alcohol (0.300 mmol, 100 mol%). THF (0.15 mL, 2.0 M concentration with respect to the alcohol) and **1a** (76.9 mg, 0.600 mmol, 200 mol%) were added and the mixture was heated at 95 ^{o}C for the time stated. The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2), under the conditions noted, to afford the corresponding product.

General Procedure B for the Coupling of 2b to 1,3-Enynes: To a re-sealable reaction tube containing a magnetic stirrer, was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), *m*-NO_2BzOH (2.5 mg, 0.015 mmol, 5 mol%), and **2b** (31 μL, 0.300 mmol, 100 mol%). THF (0.15 mL, 2.0 M concentration with respect to the alcohol) and the corresponding 1,3-enyne (0.600 mmol, 200 mol%) were added and the mixture was heated at 95 ^{o}C for the time stated. The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2), under the conditions noted, to afford the corresponding product.

General Procedure C for the Coupling of 1a to Aldehydes: To a re-sealable reaction tube containing a magnetic stirrer, was added $RuHCl(CO)(PPh_3)_3$ (14.3 mg, 0.015 mmol, 5 mol%), dppf (8.3 mg, 0.015 mmol, 5 mol%), and the corresponding aldehyde (0.300 mmol, 100 mol%). THF (0.15 mL, 2.0 M concentration with respect to the alcohol), **1a** (76.9 mg, 0.600 mmol, 200 mol%), and isopropanol (70 μL, 0.900 mmol, 300 mol%) were added and the mixture was heated at 90 ^{o}C for the time stated. The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2), under the conditions noted, to afford the corresponding product.

2-Methyl-1-(4-nitrophenyl)-4-phenybut-3-yn-1-ol (3a)



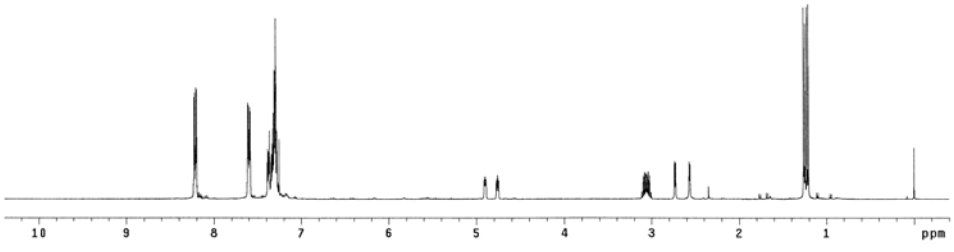
Procedure A (*via* alcohol 2a): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (55 mg, 65%, 1:1 d.r.) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.23 (d, *J* = 2.0 Hz, 2H), 8.22 (d, *J* = 2.0 Hz, 2H), 8.21 (d, *J* = 2.0 Hz, 2H), 8.20 (d, *J* = 2.0 Hz, 2H), 8.18-7.18 (m, 10H), 4.90 (dd, *J* = 6.4, 3.9 Hz, 1H), 4.77 (dd, *J* = 6.4, 3.9 Hz, 1H), 3.13-2.98 (m, 2H), 2.73 (d, *J* = 3.9 Hz, 1H), 2.57 (d, *J* = 3.9 Hz, 1H), 1.25 (d, *J* = 6.4 Hz, 3H), 1.21 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 148.9, 148.7, 147.5, 147.4, 131.6, 131.5, 128.3 (2 signals), 128.2, 127.4, 123.4, 123.2, 122.8, 122.6, 89.8, 88.9, 84.5, 83.9, 76.3, 75.7, 35.9, 35.0, 17.2, 15.8 (only 24 signals observed).

HRMS (CI) Calcd. for $C_{17}H_{16}NO_3$ $[M+H]^+$: 282.1132, Found: 282.1130.

FTIR (neat): 3538, 2979, 2935, 1600, 1519, 1490, 1443, 1347, 1192, 1108, 1038, 913, 846, 757, 693 cm^{-1}.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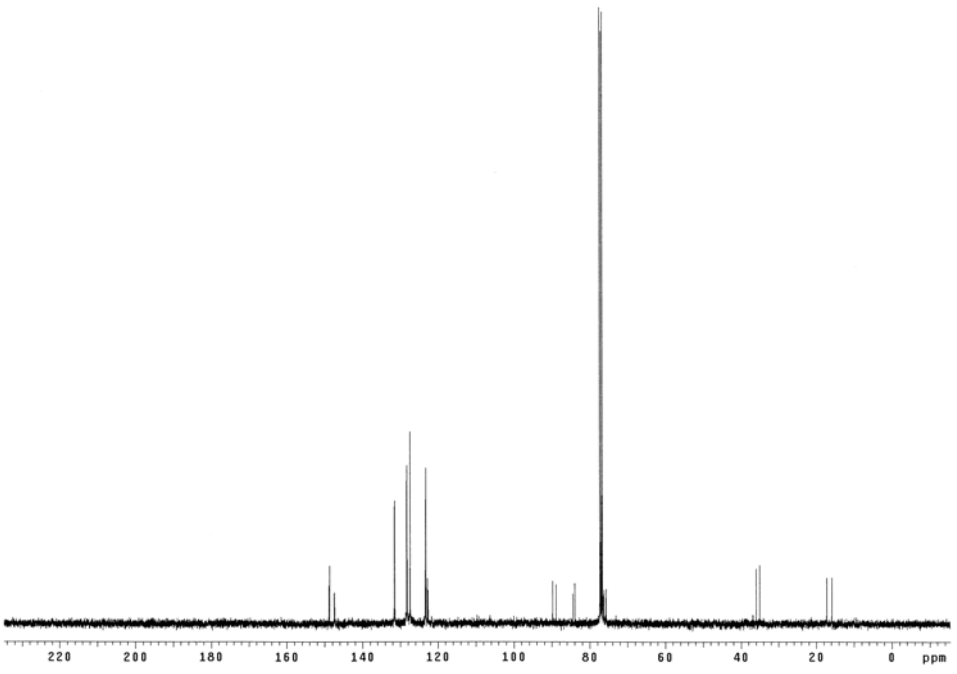
220
200
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100
80
60
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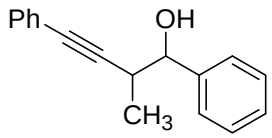
20
0
ppm

2-Methyl-1,4-diphenyl-but-3-yn-1-ol (3b)[3]



Procedure A (*via* alcohol 2b): After heating the reaction at 95 °C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (57 mg, 81%, 1:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.43-7.25 (m, 20H), 4.77 (dd, *J* = 3.8, 3.4 Hz, 1H), 4.58 (dd, *J* = 3.8, 3.4 Hz, 1H), 3.08-2.99 (m, 2H), 2.64 (d, *J* = 3.8 Hz, 1H), 2.37 (d, *J* = 3.4 Hz, 1H), 1.22-1.16 (m, 6H).

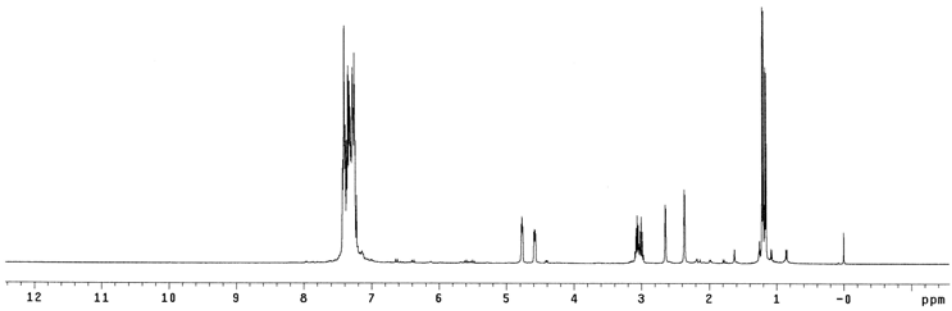
^{13}C NMR (100 MHz, $CDCl_3$): 141.5, 141.4, 131.6, 131.5, 128.2 (2 signals), 128.1, 128.0 (2 signals), 127.9, 127.8, 127.7, 126.7, 126.5, 123.3, 123.1, 91.1, 90.5, 83.6, 83.2, 77.6, 76.6, 36.0, 34.0, 17.3, 15.9.

HRMS (CI) Calcd. for $C_{17}H_{17}O$ $[M+H]^+$: 237.1279, Found: 237.1282.

FTIR (neat): 3419, 3030, 2976, 2932, 1950, 1598, 1491, 1372, 1196, 1026, 913, 756, 693, 546 cm^{-1}.

The spectroscopic properties of this compound were consistent with the data available in the literature.[3]

[3] M. Ishiguro, N. Ikeda, H. Yamamoto, *J. Org. Chem.* **1982**, *47*, 2225-2227.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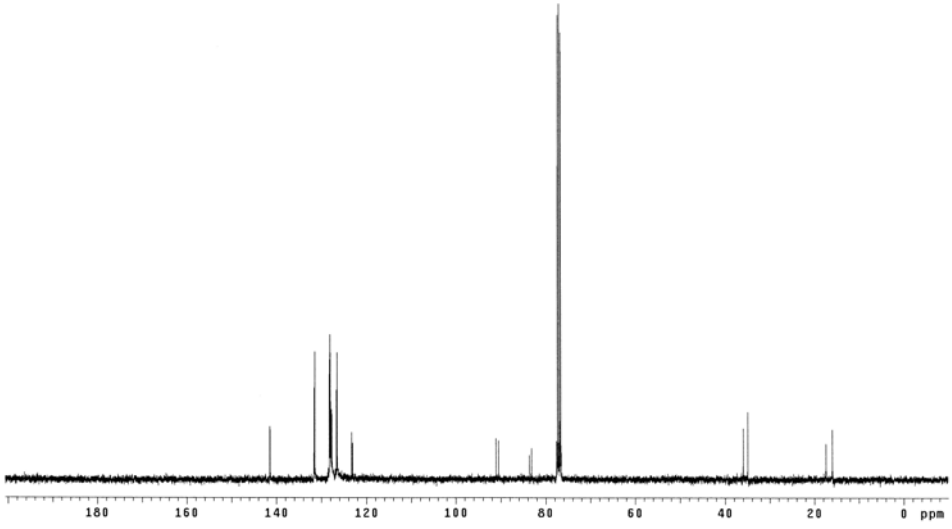
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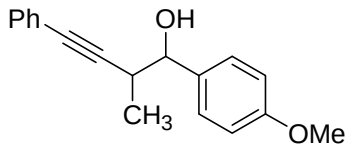
1-(4-Methoxyphenyl)-2-methyl-4-phenylbut-3-yn-1-ol (3c)



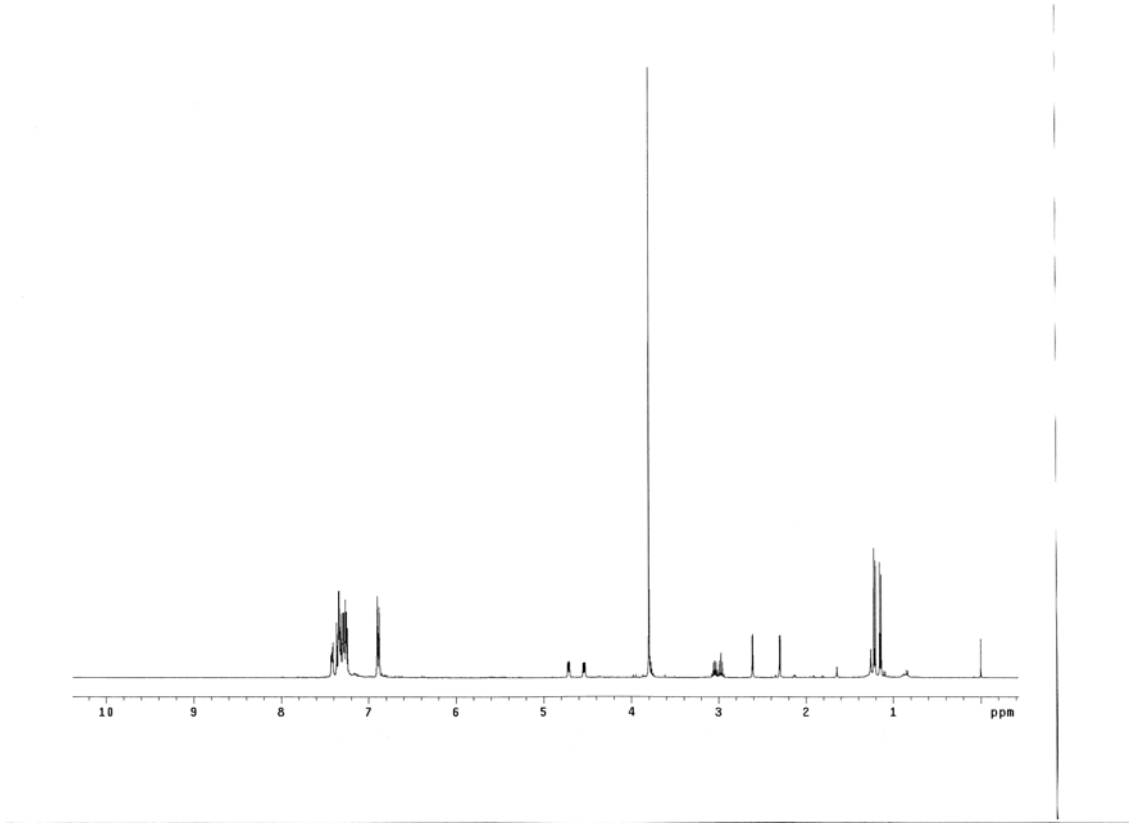
Procedure A (*via* alcohol 2c): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (65 mg, 81%, 1:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.43-7.24 (m, 14H), 6.90-6.79 (m, 4H), 4.71 (dd, *J* = 3.8, 3.4 Hz, 1H), 4.54 (dd, *J* = 3.8, 3.4 Hz, 1H), 3.80 (s, 6H), 3.06-2.96 (m, 2H), 2.62 (d, *J* = 3.8 Hz, 1H), 2.30 (d, *J* = 3.4 Hz, 1H), 1.21 (d, *J* = 6.8 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 159.3, 159.1, 133.8, 133.6, 131.6, 131.5, 128.2, 128.1, 128.0, 127.9, 127.7, 123.4, 123.3, 113.6, 113.4, 91.2, 90.7, 83.5, 83.1, 77.6, 76.5, 55.2 (2 signals), 36.0, 35.0, 30.0, 17.4, 16.2.

HRMS (CI) Calcd. for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.1385, Found: 267.1390.

FTIR (neat): 3429, 2932, 2836, 1612, 1513, 1490, 1442, 1372, 1303, 1249, 1175, 1034, 831, 757, 693 cm^{-1}.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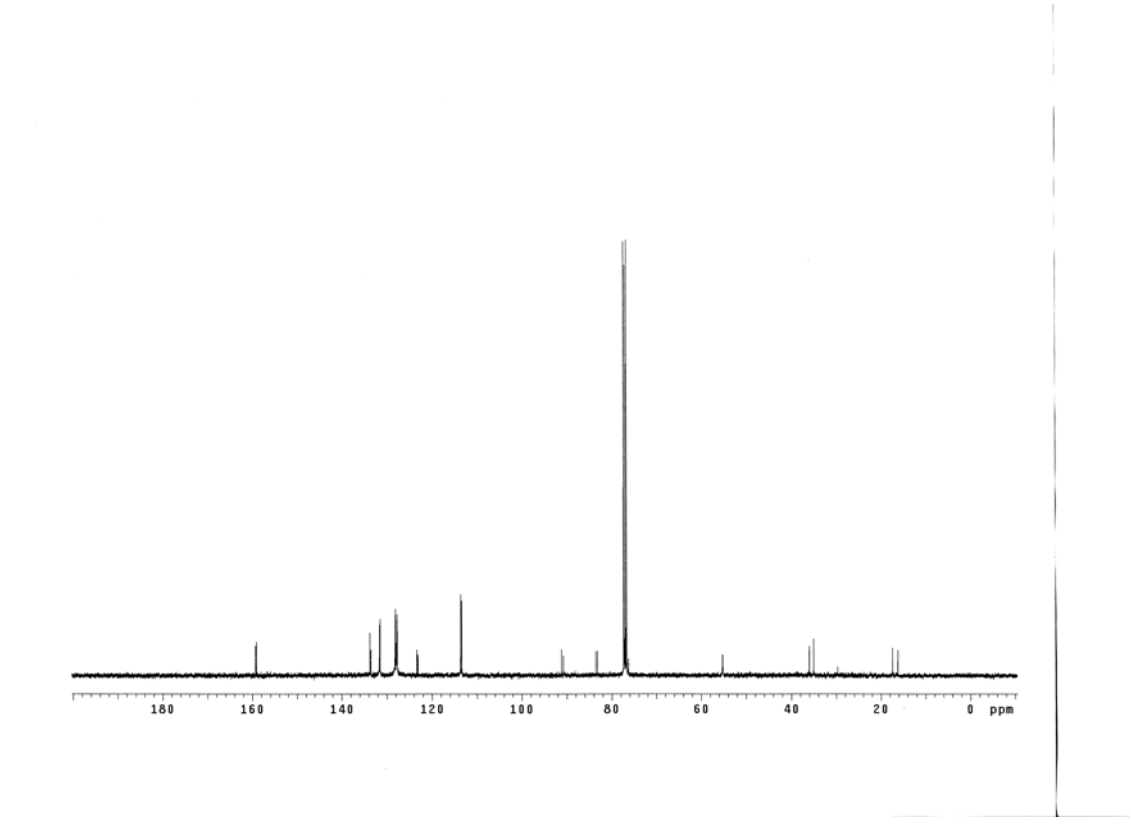
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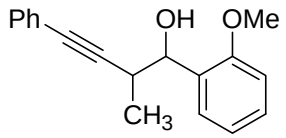
ppm

1-(2-Methoxyphenyl)-2-methyl-4-phenylbut-3-yn-1-ol (3d)



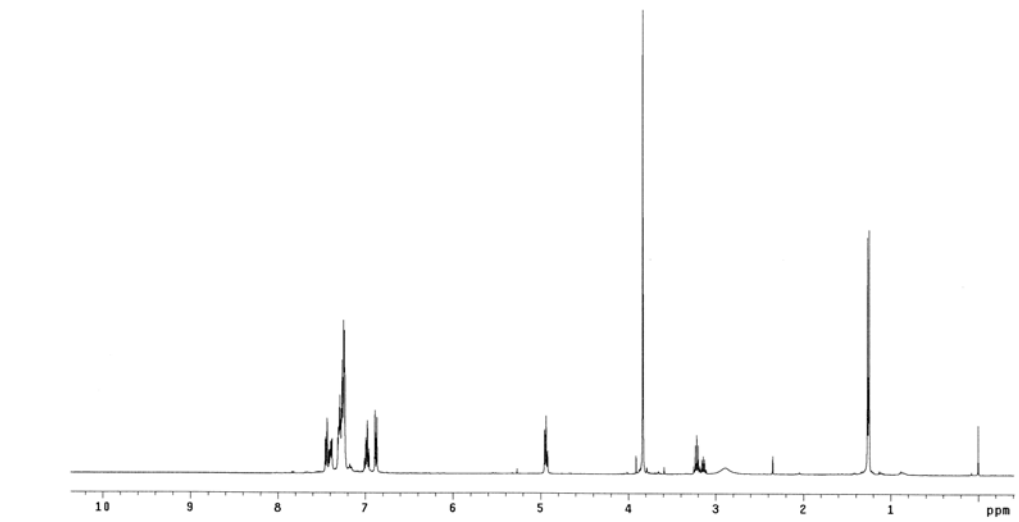
Procedure A (*via* alcohol 2d): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (73 mg, 91%, 2:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.46-7.38 (m, 3H), 7.31-7.23 (m, 7.5H), 7.01-6.96 (m, 1.5H) 6.89 (d, J = 8.2 Hz, 1.5H), 4.98-4.91 (m, 1.5H), 3.84 (s, 4.5H), 3.25-3.12 (m, 1.5H), 2.89 (s, 1.5H), 1.25 (d, J = 7.2 Hz, 4.5H).

^{13}C NMR (100 MHz, $CDCl_3$): 156.5, 156.4, 132.0 (2 signals), 130.1, 129.4, 128.6, 128.5 (2 signals), 128.1 (2 signals), 127.8, 127.6, 127.4, 123.6, 123.4, 120.6, 120.4, 110.3 (2 signals) 92.0, 91.0, 83.1, 82.6, 74.0, 72.8, 55.2 (2 signals), 34.7, 33.0, 18.1, 16.0.

HRMS (CI) Calcd. for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.1385, Found: 267.1389.

FTIR (neat): 3448, 2935, 2837, 1684, 1600, 1491, 1463, 1289, 1241, 1189, 1103, 1028, 986, 912, 786, 755, 693, 542 cm^{-1}.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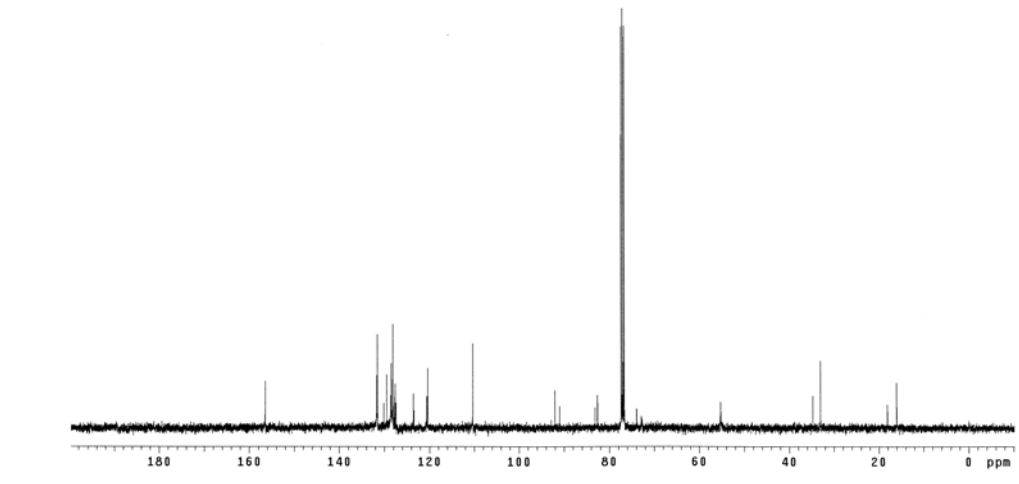
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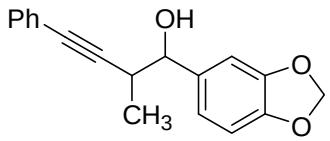
1-Benzo[1,3]dioxol-5-yl-2-methyl-4-phenylbut-3-yn-1-ol (3e)



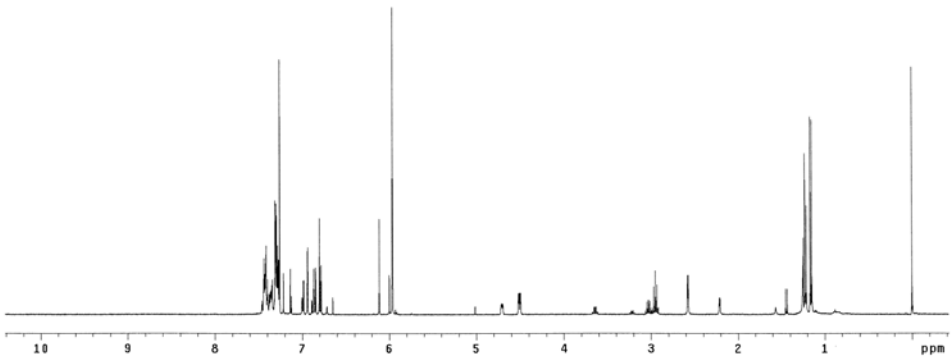
Procedure A (*via* alcohol 2e): After heating the reaction at 95 °C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (70 mg, 83%, 2:1 d.r.) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.48-7.24 (m, 7.5H), 6.99 (d, *J* = 1.7 Hz, 0.5H), 6.94 (d, *J* = 1.7 Hz, 1H), 6.91-6.83 (m, 1.5H), 6.80 (s, 1H), 6.78 (s, 0.5H), 5.96 (s, 3H), 4.71 (dd, *J* = 5.8, 3.1 Hz, 0.5H), 4.51 (dd, *J* = 5.8, 3.1 Hz, 1H), 3.05-2.92 (m, 1.5H), 2.58 (d, *J* = 3.1 Hz, 1H), 2.21 (d, *J* = 3.1 Hz, 0.5H), 1.22 (d, *J* = 7.2 Hz, 1.5H), 1.16 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 147.7, 147.5, 147.3, 136.1, 135.6, 135.4, 131.7, 131.6, 129.0, 128.6, 128.3, 128.2, 128.1, 123.3, 123.1, 120.4, 120.1, 107.9, 107.8, 106.9, 101.0, 91.0, 90.5, 83.7, 83.3, 77.6, 76.5, 36.1, 35.1, 17.4, 16.1 (only 31 signals observed).

HRMS (CI) Calcd. for $C_{18}H_{17}O_3$ $[M+H]^+$: 281.1172, Found: 281.1178.

FTIR (neat): 3450, 2896, 1696, 1604, 1489, 1471, 1443, 1247, 1038, 935, 811, 757, 693 cm^{-1}.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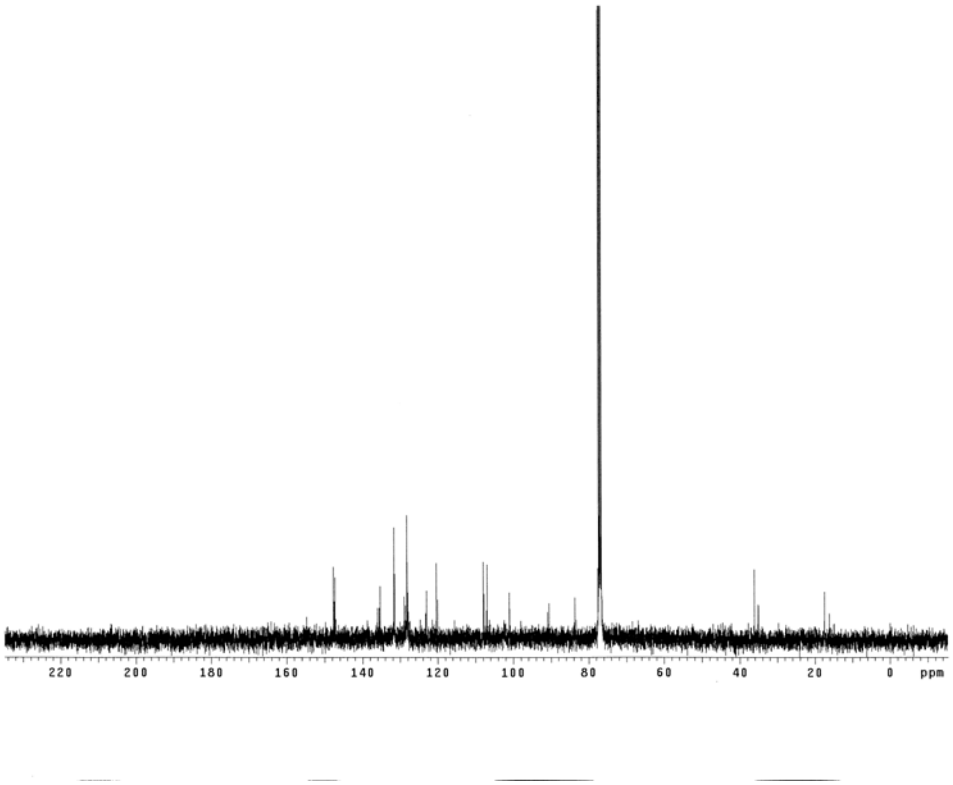
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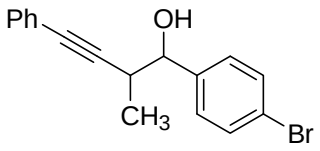
1-(4-Bromophenyl)-2-methyl-4-phenylbut-3-yn-1-ol (3f)



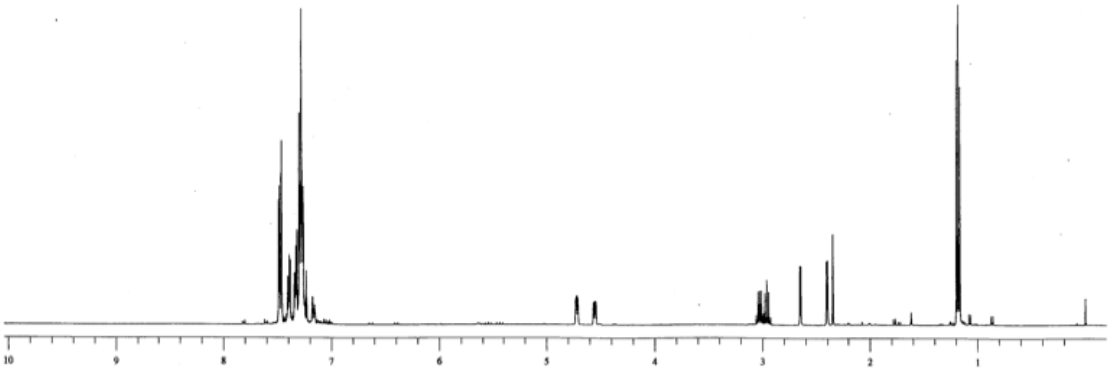
Procedure A (*via* alcohol 2f): After heating the reaction at 95 ^{o}C for 16 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (69 mg, 73%, 1:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.46 (m, 4H), 7.41-7.38 (m, 2H), 7.34-7.25 (m, 12H), 4.72 (dd, J = 5.5, 3.5 Hz, 1H), 4.55 (dd, J = 6.5, 4.0 Hz, 1H), 3.06-2.98 (m, 1H), 2.95 (dq, J = 4.0, 4.0 Hz, 1H), 2.64 (d, J = 4.0 Hz, 1H), 2.40 (d, J = 3.5 Hz, 1H), 1.20-1.16 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 140.8, 140.7, 131.9, 131.8, 131.6, 131.4, 129.3, 128.6 (2 signals), 128.5 (2 signals), 128.4, 128.2, 123.2, 122.1, 121.8, 90.8, 90.2, 84.3, 83.8, 77.1, 76.2, 36.2, 35.2, 17.5, 16.2.

HRMS (ESI) Calcd. for $C_{17}H_{16}O^{79}Br$ $[M+H]^+$: 315.0385, Found: 315.0379.

FTIR (neat): 3415, 2976, 2876, 1594, 1488, 1442, 1404, 1071, 1010 cm^{-1}.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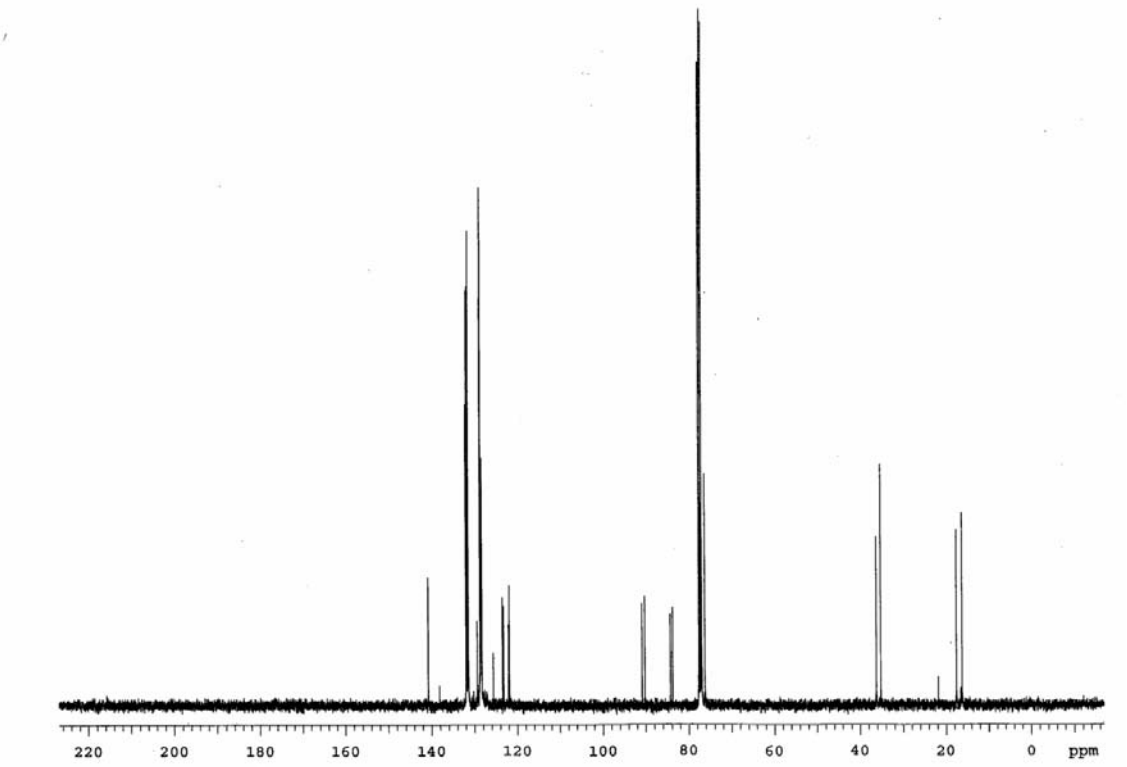
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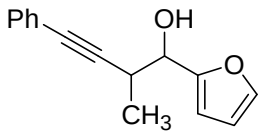
ppm

1-Furan-2-yl-2-methyl-4-phenylbut-3-yn-1-ol (3g)



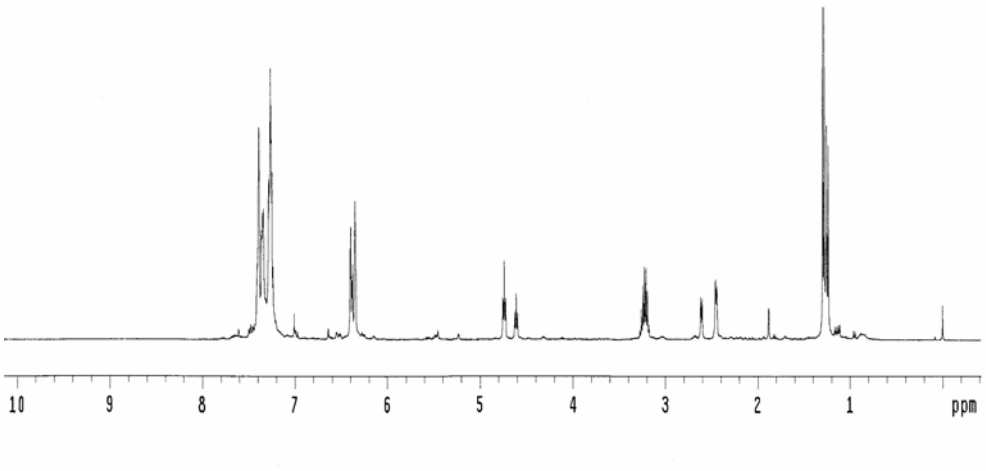
Procedure A (*via* alcohol 2g): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (48 mg, 71%, 1.5:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.41-7.26 (m, 8.3H), 6.42-6.36 (m, 5H), 4.76 (t, J = 6.2 Hz, 1H), 4.62 (t, J = 6.6 Hz, 0.67H), 3.27-3.19 (m, 1.67H), 2.51 (d, J = 6.6 Hz, 1H), 2.28 (d, J = 6.2 Hz, 0.67H), 1.29 (d, J = 6.5 Hz, 3H), 1.25 (d, J = 6.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 154.4, 154.2, 141.9, 141.8, 131.7, 128.0, 127.8, 123.3, 123.1, 110.2, 107.3, 107.1, 90.2, 89.9, 83.0, 82.6, 71.4, 71.3, 33.5, 33.0, 16.7, 16.3 (only 22 signals were observed).

HRMS (CI) Calcd. for $C_{15}H_{15}O_2$ $[M+H]^+$: 227.1072, Found: 227.1074.

FTIR (neat): 3421, 2933, 2361, 1699, 1653, 1676, 1558, 1540, 1506, 1490, 1457, 1395, 1148, 1010, 918, 884, 757, 692, 598 cm^{-1}.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9
8
7
6
5
4
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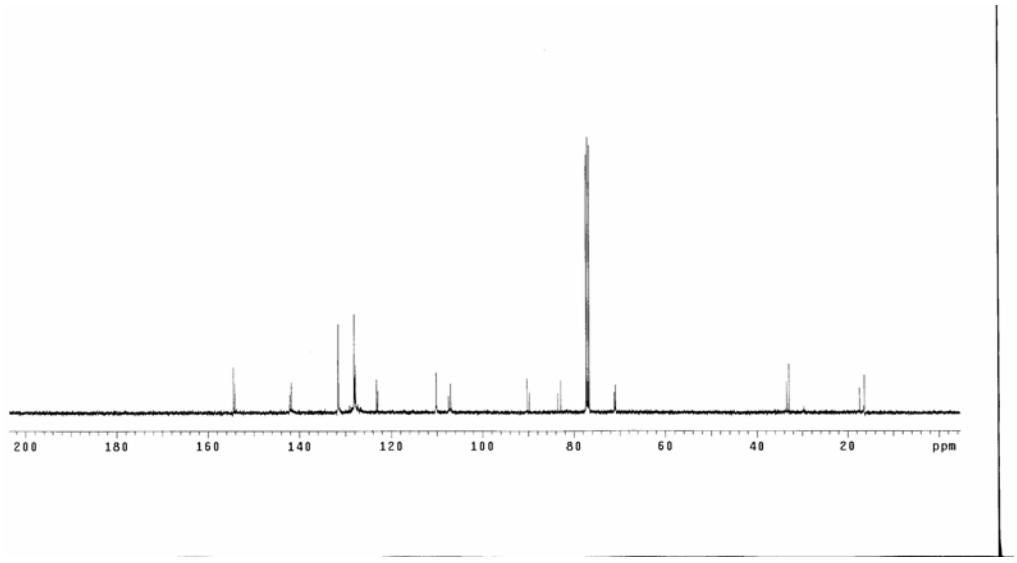
1
ppm


200
180
160
140
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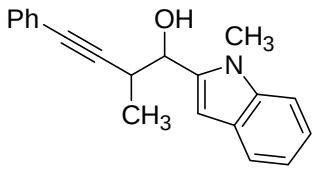
100
80
60
40
20
ppm

2-Methyl-1-(1-methyl-1*H*-indol-2-yl)-4-phenylbut-3-yn-1-ol (3h)



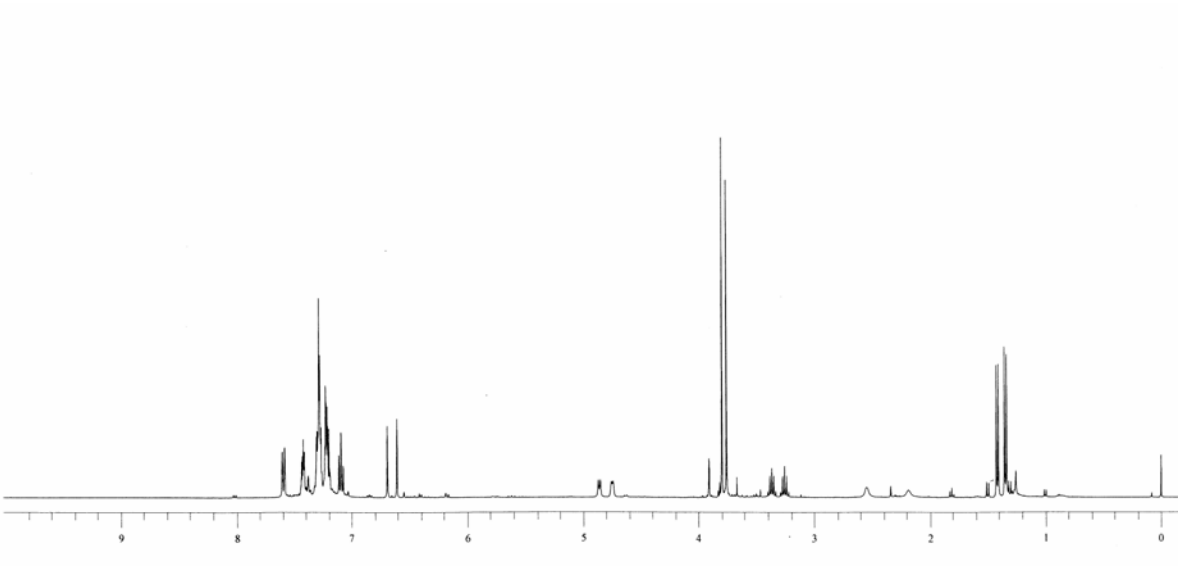
Procedure A (*via* alcohol 2h): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (82 mg, 94%, 1:1 d.r.) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.61-7.01 (m, 18H), 6.68 (s, 1H), 6.60 (s, 1H), 4.87-4.81 (m, 1H), 4.76-4.07 (m, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.40-3.31 (m, 1H), 3.27-3.22 (m, 1H), 2.56 (s, 1H), 2.21 (s, 1H), 1.41 (d, J = 7.2 Hz, 3H), 1.32 (d, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 139.8, 139.1, 138.3, 132.1 (2 signals), 128.7, 128.2, 127.5, 123.3, 123.1, 122.3, 121.1, 120.0, 109.7, 101.1, 100.5, 91.0, 90.5, 84.3, 83.3, 70.5, 70.1, 33.5, 30.2, 18.4, 17.1 (only 26 signals were observed).

HRMS (CI) Calcd. for $C_{20}H_{20}NO$ $[M+H]^+$: 290.1545, Found: 290.1545.

FTIR (neat): 3429, 3055, 2973, 2934, 1681, 1598, 1532, 1490, 1316, 1233, 1173, 1139, 1110, 1070, 1027, 984, 945, 908, 788, 751, 735, 692 cm^{-1}.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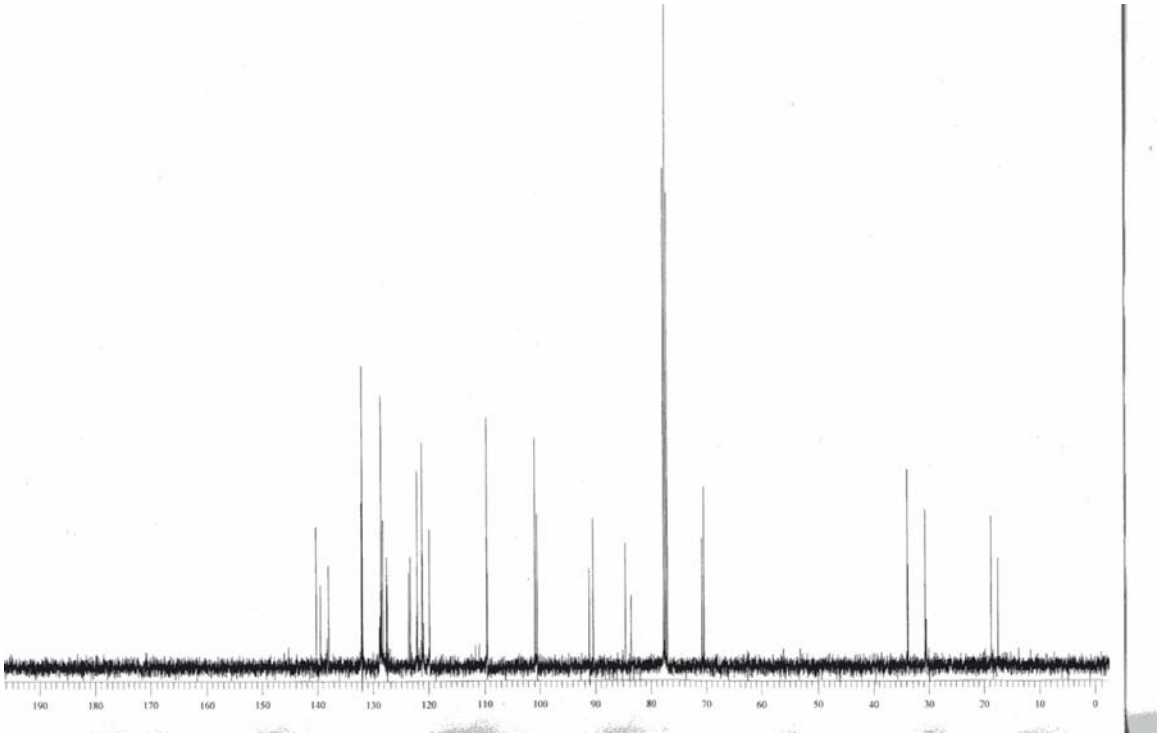
6
5
4
3
2
1
0


190
180
170
160
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120
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100
90
80
70
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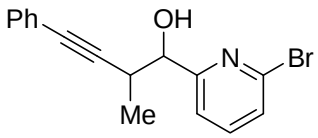
30
20
10
0

1-(6-Bromopyridin-2-yl)-2-methyl-4-phenylbut-3-yn-1-ol (3i)



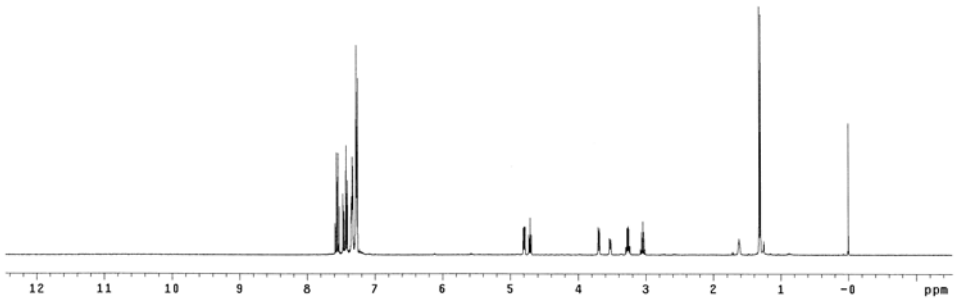
Procedure A (*via* alcohol 2i): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (40 mg, 42%, 1.3:1 d.r.) as a pale yellow oil.

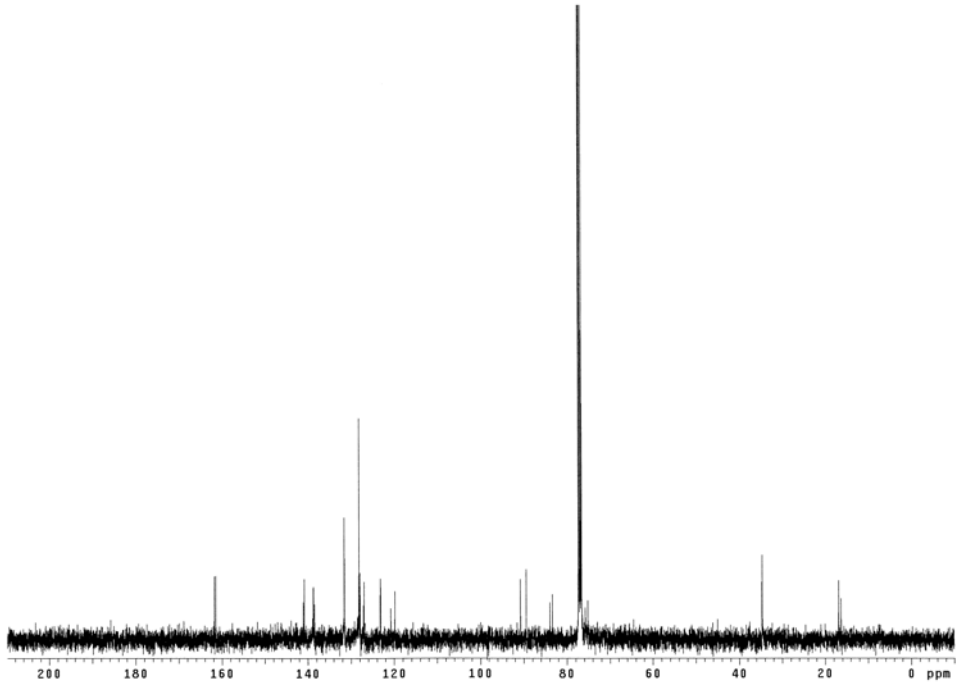
^{1}H NMR (400 MHz, $CDCl_3$): 7.60-7.51 (m, 1.75H), 7.50-7.39 (m, 3.5H), 7.36-7.31 (m, 3.5H), 7.30-7.26 (m, 5.25H), 4.80 (dd, *J* = 7.5, 5.5 Hz, 1H), 4.74-4.68 (m, 0.75H), 3.71 (dd, *J* = 7.5, 1.5 Hz, 1H), 3.53 (dd, *J* = 7.5, 1.5 Hz, 0.75H), 3.30-3.23 (m, 1H), 3.06-3.01 (m, 0.75H), 1.31 (dd, *J* = 5.5, 1.5 Hz, 5.25H).

^{13}C NMR (100 MHz, $CDCl_3$): 161.8, 161.5, 141.1, 140.9, 138.7, 138.4, 131.6, 131.5, 128.2, 128.0, 127.9, 127.1, 127.0, 123.2, 123.1, 120.8, 119.9, 90.7, 89.4, 84.0, 83.4, 75.8, 75.2, 34.7, 34.6, 16.8, 16.3 (only 27 signals were observed).

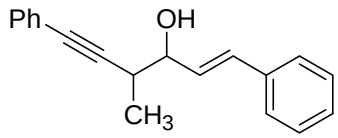
HRMS (CI) Calcd. for $C_{16}H_{15}{}^{79}BrNO$ $[M+H]^+$: 316.0337, Found: 316.0337.

FTIR (neat): 3423, 3055, 2976, 2933, 1583, 1556, 1490, 1439, 1408, 1307, 1217, 1158, 1128, 1054, 989, 913, 788, 757, 692 cm^{-1}.


12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm


200
180
160
140
120
100
80
60
40
20
0 ppm

4-Methyl-1,6-diphenylhex-1-en-5-yn-3-ol (3j)



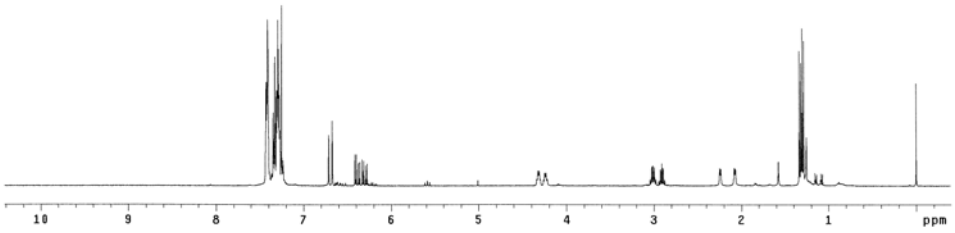
Procedure A (*via* alcohol 2j): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (54 mg, 68%, 1:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.43-7.23 (m, 20H), 6.71 (s, 1H), 6.67 (s, 1H), 6.38 (dd, *J* = 16.5, 6.3 Hz, 1H), 6.30 (dd, *J* = 15.7, 6.5 Hz, 1H), 4.32 (dd, *J* = 15.7, 4.8 Hz, 1H), 4.24 (dd, *J* = 16.5, 5.2 Hz, 1H), 3.04-2.89 (m, 2H), 2.24 (d, *J* = 4.8 Hz, 1H), 2.08 (d, *J* = 5.2 Hz, 1H), 1.32 (d, *J* = 7.2 Hz, 3H), 1.30 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 136.6, 136.5, 132.3, 132.2, 131.7 (2 signals), 129.5, 128.8, 128.6, 128.2 (2 signals), 128.0, 127.9, 127.8, 126.6, 123.3, 123.1, 90.5, 90.1, 83.6, 83.2, 75.8, 75.4, 34.5, 34.0, 17.1, 16.5 (only 27 signals were observed).

HRMS (CI) Calcd. for $C_{19}H_{19}O$ $[M+H]^+$: 263.1433, Found: 263.1436.

FTIR (neat): 3421, 3026, 2974, 2929, 1598, 1490, 1449, 1070, 1028, 966, 755, 692 cm^{-1}.


10
9
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7
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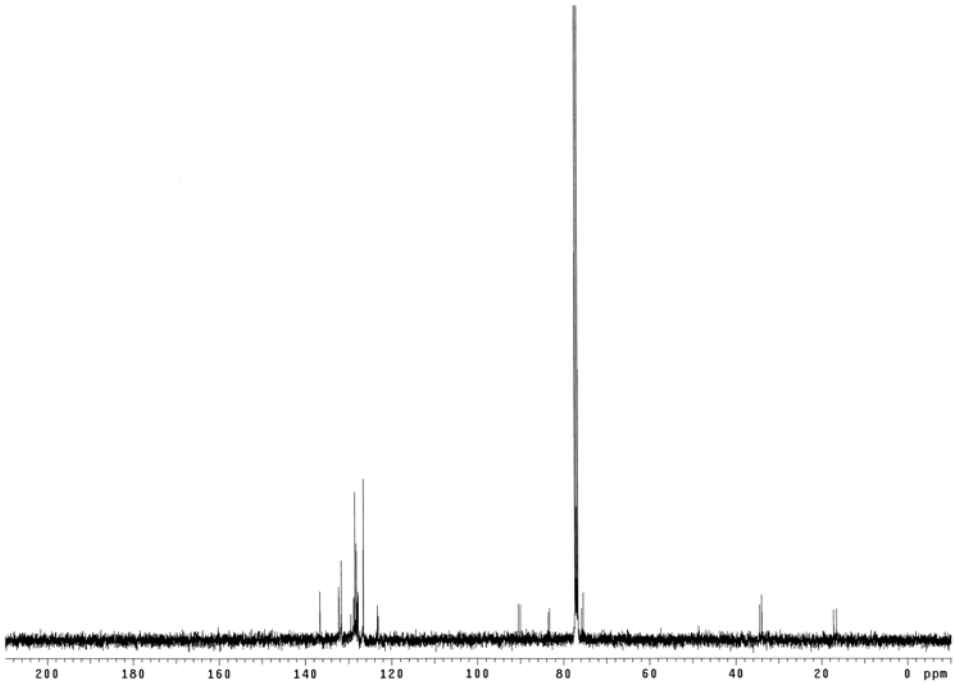
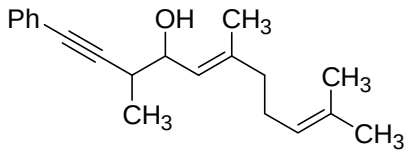
5
4
3
2
1
ppm


200
180
160
140
120
100
80
60
40
20
0 ppm

3,6,10-Trimethyl-1-phenylundeca-5,9-dien-1-yn-4-ol (3k)



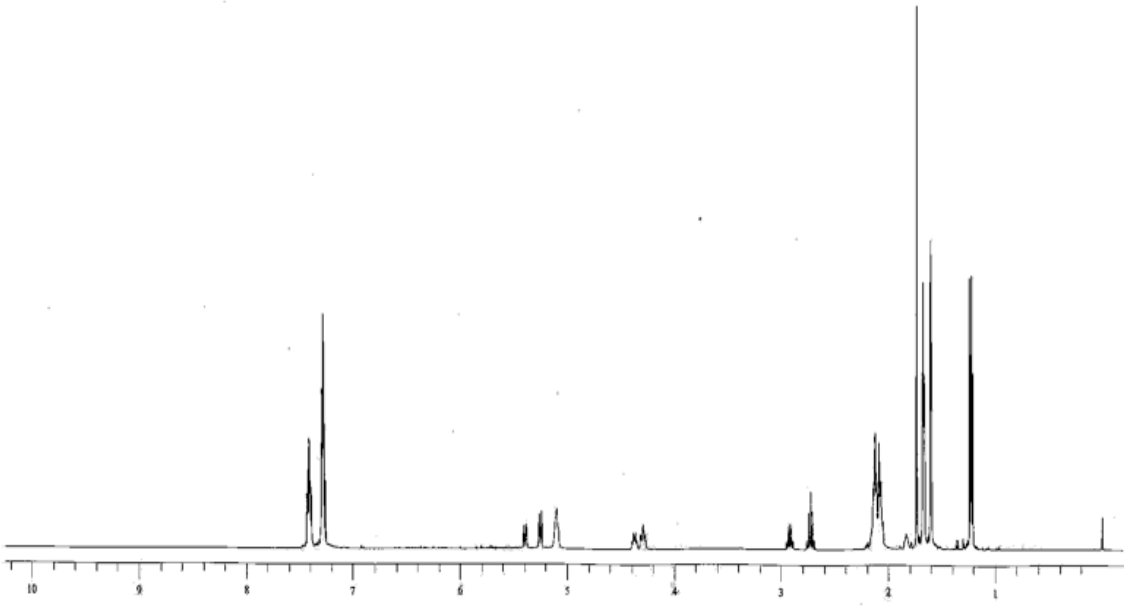
Procedure A (*via* alcohol 2k): After heating the reaction at 95 ^{o}C for 16 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (53 mg, 63%, 1.5:1 d.r.) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.44-7.38 (m, 3.32H), 7.30-7.26 (m, 4.98H), 5.39 (d, J = 8.5 Hz, 0.66H), 5.25 (d, J = 9.0 Hz, 1H), 5.13-5.06 (m, 1.66H), 4.40-4.34 (m, 0.66H), 4.32-4.26 (m, 1H), 2.92 (ddd, J = 14.0, 7.0, 5.5 Hz, 0.66H), 2.72 (dq, J = 7.0 Hz, 1H), 2.17-2.03 (m, 8.3H), 1.74-1.72 (m, 4.98H), 1.68-1.65 (m, 4.98H), 1.61-1.59 (m, 4.98H), 1.24-1.20 (m, 4.98H).

^{13}C NMR (100 MHz, $CDCl_3$): 141.1, 140.8, 132.0, 131.9 (2 signals), 129.3, 128.5, 128.1, 128.0, 125.5, 125.2, 124.1, 123.6, 91.3, 91.2, 83.3, 82.9, 71.9, 71.3, 39.9, 35.1, 34.3, 26.6, 25.9, 12.9, 17.2, 16.7 (only 27 signals were observed).

HRMS (ESI) Calcd. for $C_{20}H_{26}ONa$ $[M+Na]^+$: 305.1882, Found: 305.1876.

FTIR (neat): 3396, 2970, 2926, 1376, 1014 cm^{-1}.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9
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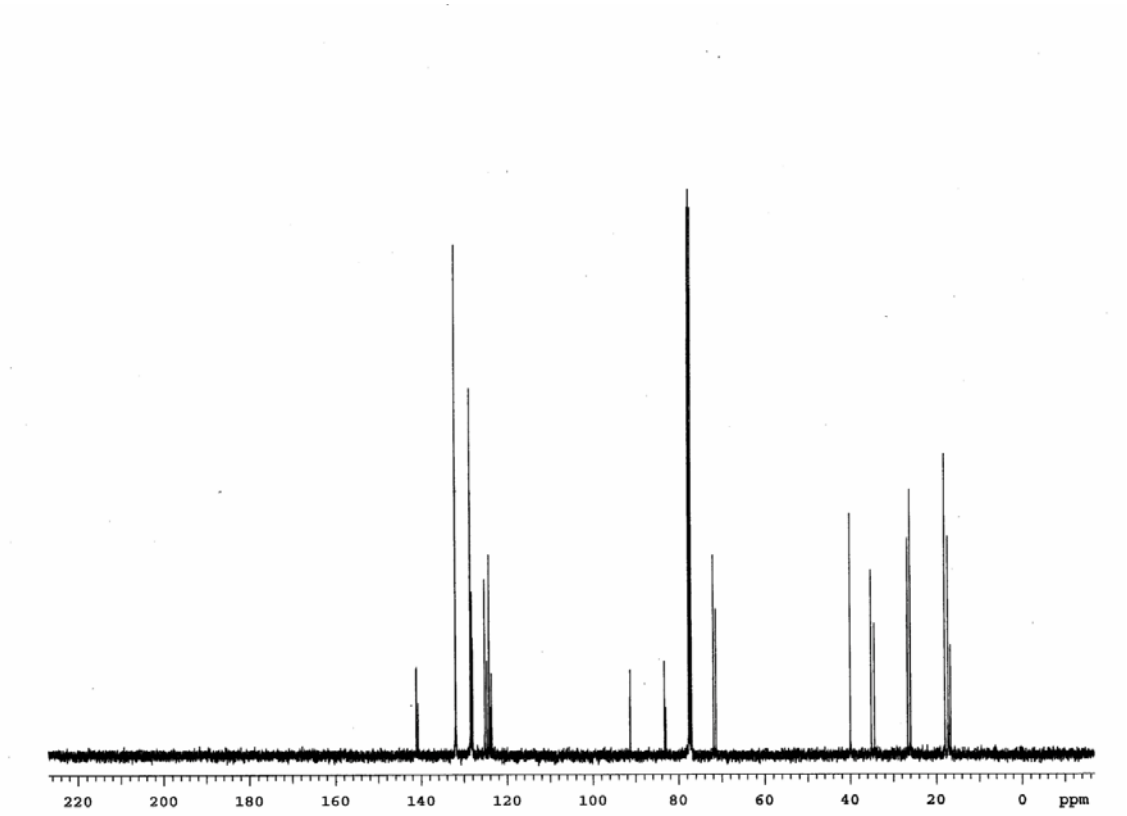
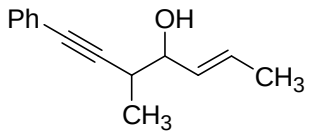
5
4
3
2
1


220
200
180
160
140
120
100
80
60
40
20
0
ppm

3-Methyl-1-phenylhept-5-en-1-yn-4-ol (3l)



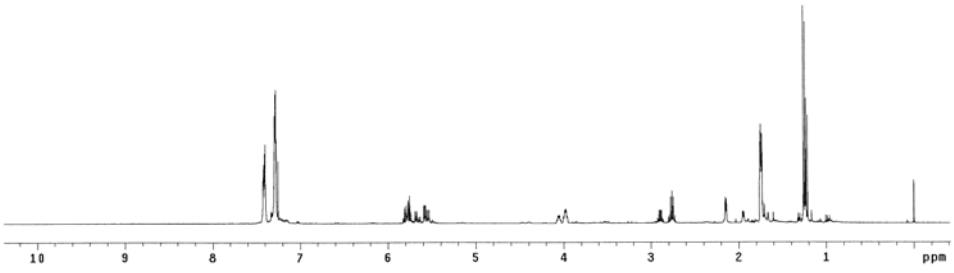
Procedure A (*via* alcohol 2l): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (43 mg, 72%, 2:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.45-7.36 (m, 3H), 7.36-7.26 (m, 4.5H), 5.84-5.71 (m, 1.5H), 5.66 (ddq, *J* = 15.4, 7.2, 1.7 Hz, 0.5H), 5.56 (ddq, *J* = 15.4, 7.2, 1.7 Hz, 1H), 4.10-4.02 (m, 0.5H), 4.02-3.93 (m, 1H), 2.95-2.84 (m, 0.5H), 2.82-2.71 (m, 1H), 2.15 (d, *J* = 4.4 Hz, 1H), 1.95 (d, *J* = 5.5 Hz, 0.5H), 1.78-1.71 (m, 4.5H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 7.2 Hz, 1.5H).

^{13}C NMR (100 MHz, $CDCl_3$): 131.7, 131.6, 131.2, 130.5, 129.0 (2 signals), 128.2 (2 signals), 127.9, 127.8, 123.4, 123.2, 90.8, 90.5, 83.2, 82.9, 75.9, 75.5, 34.3, 33.7, 17.8 (2 signals), 17.1, 16.5.

HRMS (CI) Calcd. for $C_{14}H_{17}O$ $[M+H]^+$: 201.1279, Found: 201.1277.

FTIR (neat): 3402, 2973, 2935, 1599, 1490, 1443, 1377, 1015, 997, 928, 756, 692 cm^{-1}.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9
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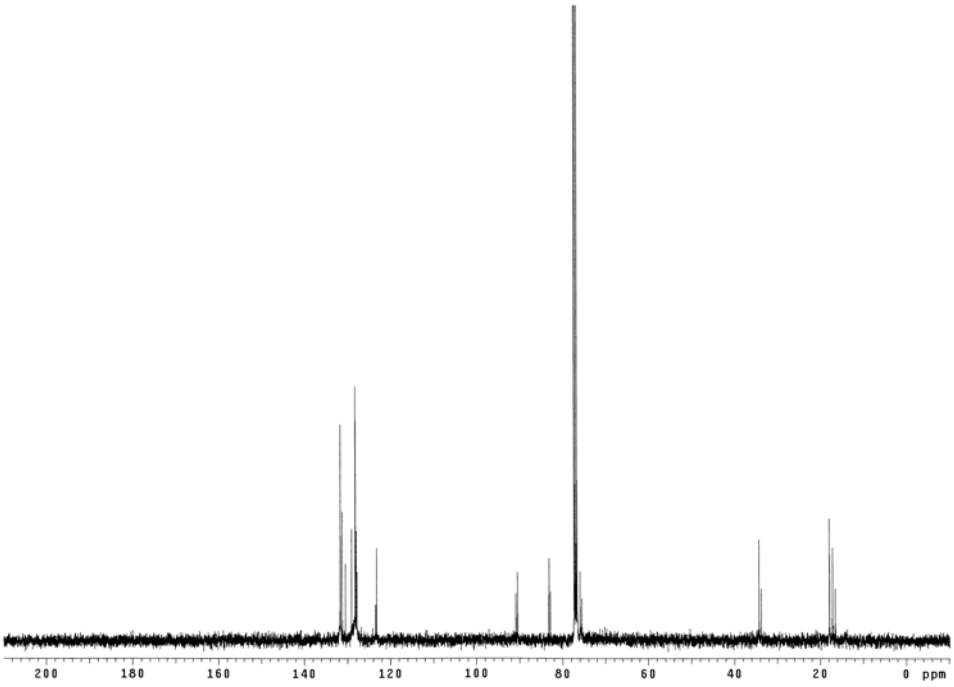
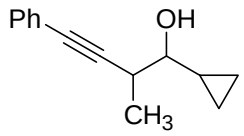
7
6
5
4
3
2
1
ppm


200
180
160
140
120
100
80
60
40
20
0 ppm

1-Cyclopropyl-2-methyl-4-phenylbut-3-yn-1-ol (3m)



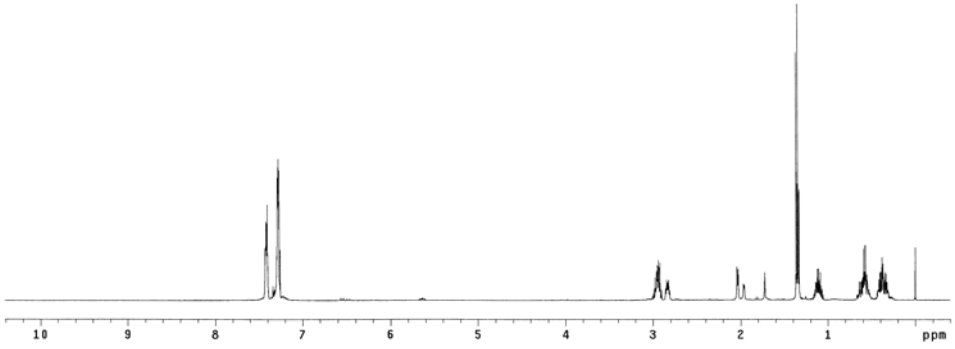
Procedure A (*via* alcohol 2m): After heating the reaction at 95 °C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (45 mg, 75%, 2:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.46-7.38 (m, 3H), 7.35-7.24 (m, 4.5H), 3.04-2.88 (m, 2H), 2.88-2.78 (m, 1H), 2.04 (d, J = 5.1 Hz, 1H), 1.96 (d, J = 4.1 Hz, 0.5H), 1.40-1.31 (m, 4.5H), 1.19-1.03 (m, 1.5H), 0.69-0.47 (m, 3H), 0.47-0.23 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 131.6 (2 signals), 128.2 (2 signals), 127.8, 127.7, 123.5, 123.3, 91.4, 90.8, 83.0, 82.6, 79.2, 78.9, 34.4, 34.0, 17.6, 16.5, 15.8, 14.7, 3.7, 3.2, 2.4, 2.0.

HRMS (CI) Calcd. for $C_{14}H_{17}O$ $[M+H]^+$: 201.1279, Found: 201.1282.

FTIR (neat): 3414, 3078, 3004, 2878, 1598, 1490, 1443, 1026, 974, 915, 865, 756, 692 cm^{-1}.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2
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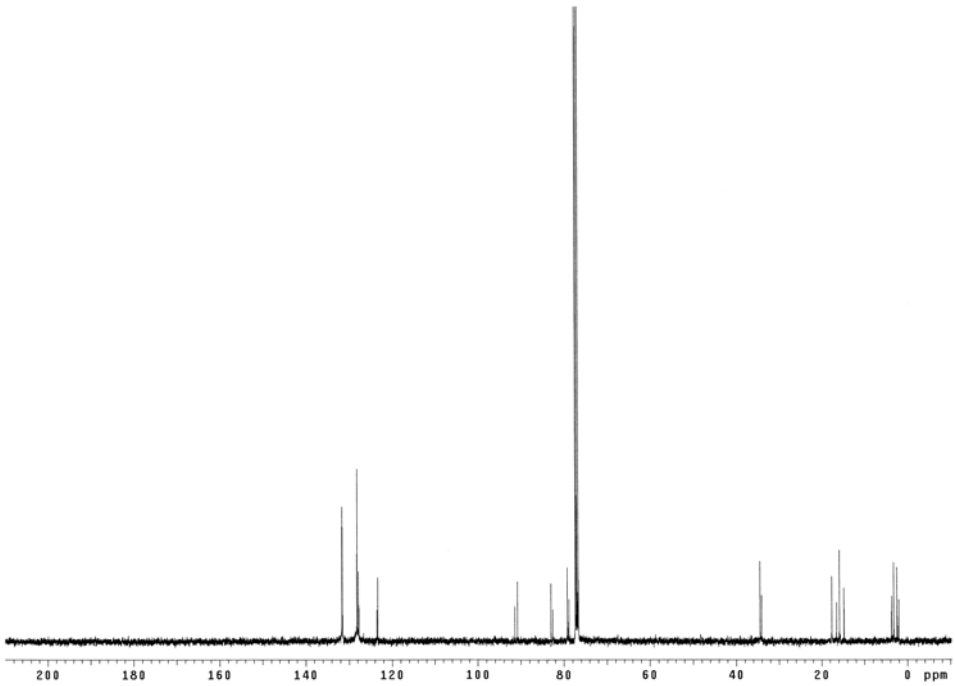
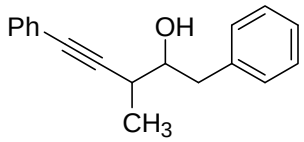
ppm


200
180
160
140
120
100
80
60
40
20
0 ppm

3-Methyl-1,5-diphenylpent-4-yn-2-ol (3n)[4]



Procedure A (*via* alcohol 2n): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (53 mg, 70%, 1:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.49-7.38 (m, 4H), 7.37-7.15 (m, 16H), 3.90-3.81 (m, 1H), 3.81-3.69 (m, 1H), 3.13 (dd, *J* = 13.7, 3.4 Hz, 1H), 2.99 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.95-2.72 (m, 4H), 2.00-1.72 (m, 2H), 1.38-1.30 (m, 6H).

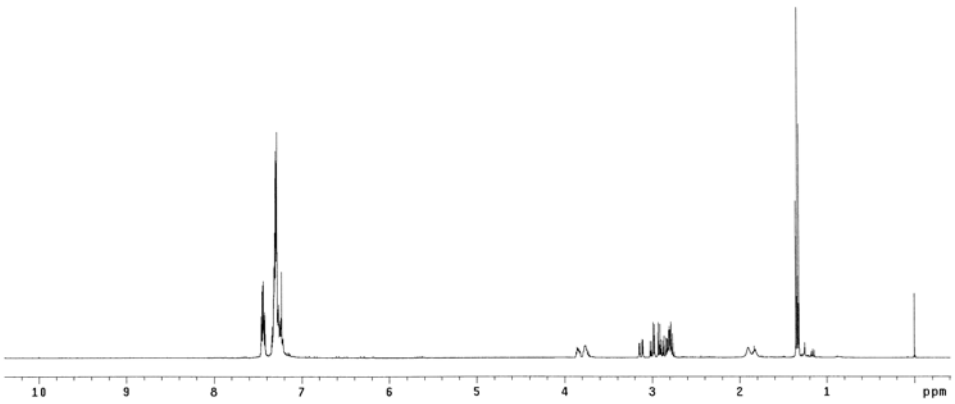
^{13}C NMR (100 MHz, $CDCl_3$): 138.3 (2 signals), 131.7, 131.6, 129.5, 129.4, 128.6, 128.5, 128.2 (2 signals), 127.9, 127.8, 126.5 (2 signals), 123.4, 123.3, 91.4, 90.0, 83.8, 83.0, 75.5, 41.8, 40.7, 33.0, 32.5, 17.4, 16.5 (only 27 signals were observed).

HRMS (CI) Calcd. for $C_{18}H_{19}O$ $[M+H]^+$: 251.1436, Found: 251.1436.

FTIR (neat): 3442, 3028, 2974, 2933, 1599, 1491, 1454, 1071, 1031, 985, 756, 693 cm^{-1}.

The spectroscopic properties of this compound were consistent with the data available in the literature.[4]

[4] Ooi, T.; Kagoshima, N.; Maruoko, K. *J. Am. Chem. Soc.* **1997**, *119*, 5754.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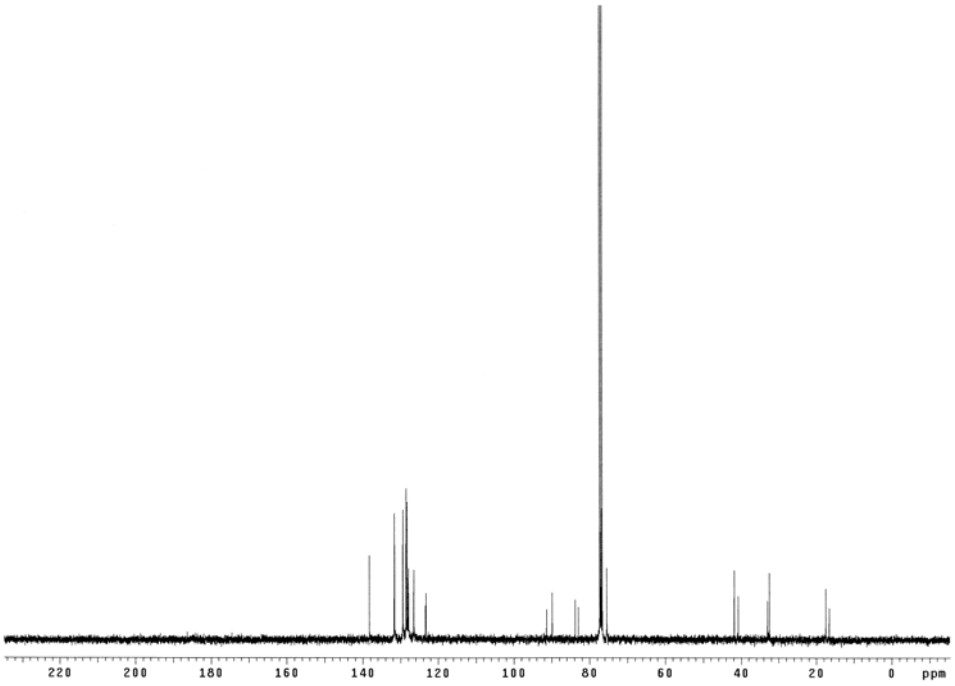
ppm


220
200
180
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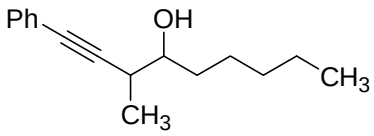
140
120
100
80
60
40
20
0
ppm

3-Methyl-1-phenylnon-1-yn-4-ol (3o)



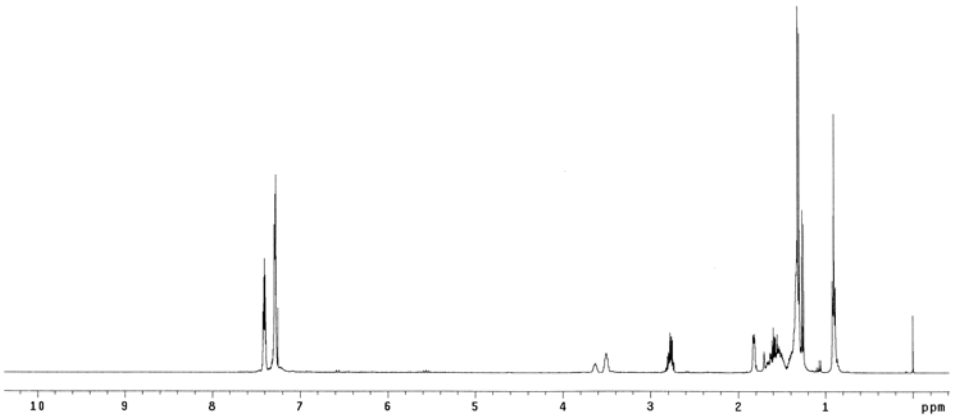
Procedure A (*via* alcohol 2o): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (50 mg, 72%, 2:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.43-7.38 (m, 3H), 7.36-7.23 (m, 4.5H), 3.69-3.57 (m, 0.5H), 3.57-3.44 (m, 1H), 2.87-2.71 (m, 1.5H), 1.87-1.78 (m, 1.5H), 1.69-1.45 (m, 4.5H), 1.44-1.20 (m, 12H), 0.85 (m, 4.5H).

^{13}C NMR (100 MHz, $CDCl_3$): 131.6 (2 signals), 128.5, 128.2, 127.9, 127.8, 123.4, 123.3, 91.5, 90.3, 83.3, 82.6, 74.5, 74.4, 35.2, 33.7 (2 signals), 33.6, 31.8, 25.5 (2 signals), 22.6, 17.5, 15.9, 14.0 (only 25 signals were observed).

HRMS (CI) Calcd. for $C_{16}H_{23}O$ $[M+H]^+$: 231.1747, Found: 231.1749.

FTIR (neat): 3412, 2932, 1598, 1490, 1456, 1377, 1070, 1026, 943, 913, 756, 691 cm^{-1}.


10
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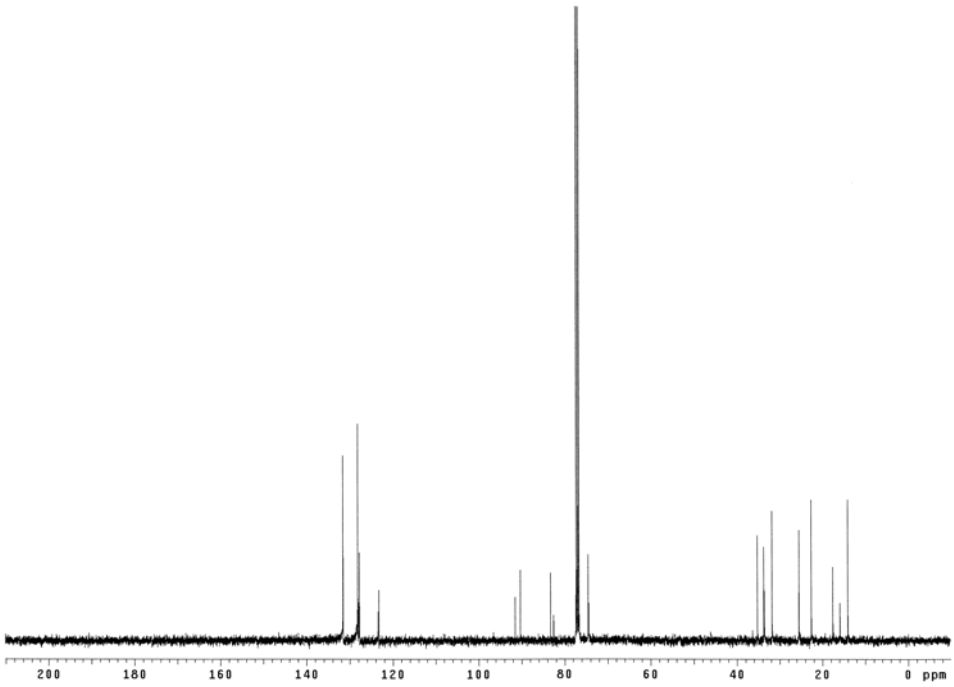
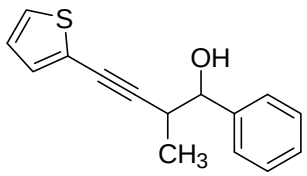
1
ppm


200
180
160
140
120
100
80
60
40
20
0 ppm

2-Methyl-1-phenyl-4-thiphen-2-ylbut-3-yn-1-ol (3p)



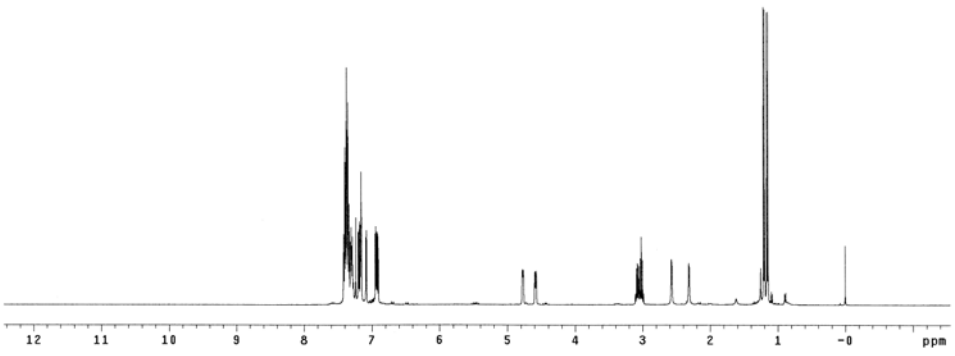
Procedure B (*via* enyne 1b): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (52 mg, 71%, 1:1 d.r.) as a pale yellow oil.

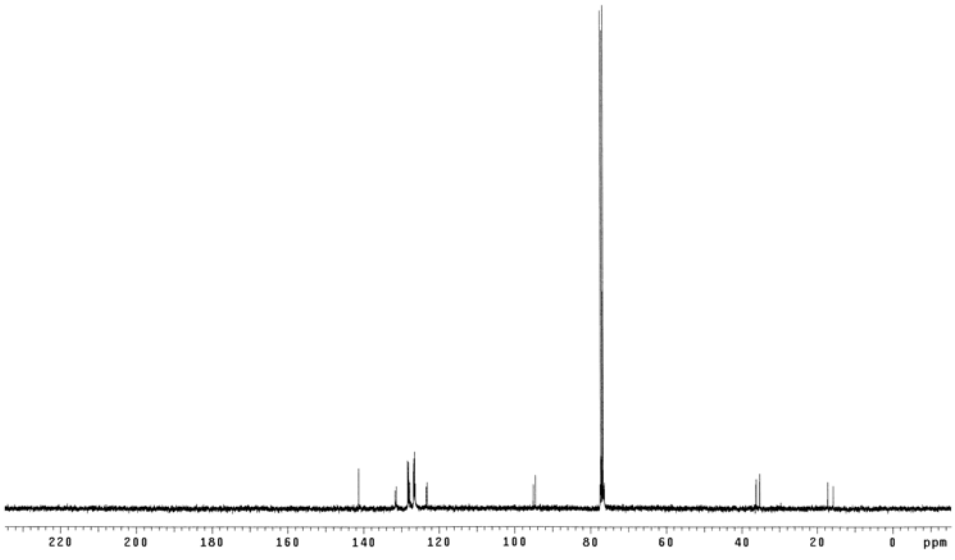
^{1}H NMR (400 MHz, $CDCl_3$): 7.43-7.29 (m, 10H), 7.20-7.16 (m, 3H), 7.08 (dd, *J* = 3.4, 2.4 Hz, 1H), 6.95-6.90 (m, 2H), 4.77 (d, *J* = 3.2 Hz, 1H), 4.59 (d, *J* = 3.2 Hz, 1H), 3.09-3.00 (m, 2H), 2.57 (d, *J* = 3.2 Hz, 1H), 2.34 (d, *J* = 3.2 Hz, 1H), 1.20 (d, *J* = 6.8 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 141.3, 131.6, 131.3, 128.3, 128.1, 128.0, 127.8, 126.8, 126.7, 126.6, 126.5 (2 signals), 126.3, 123.4, 123.2, 95.1, 94.6, 77.8, 77.5, 76.7, 76.4, 76.3, 36.2, 35.3, 17.2, 15.7.

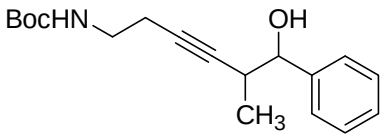
HRMS (CI) Calcd. for $C_{15}H_{15}OS$ $[M+H]^+$: 243.0844, Found: 243.0847.

FTIR (neat): 3403, 3030, 2976, 2932, 1494, 1453, 1427, 1237, 1193, 1025, 983, 910, 840, 757, 700 cm^{-1}.


12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm


220
200
180
160
140
120
100
80
60
40
20
0
ppm

(6-Hydroxy-5-methyl-6-phenylhex-3-ynyl)carbamic acid *tert*-butyl ester (3q)



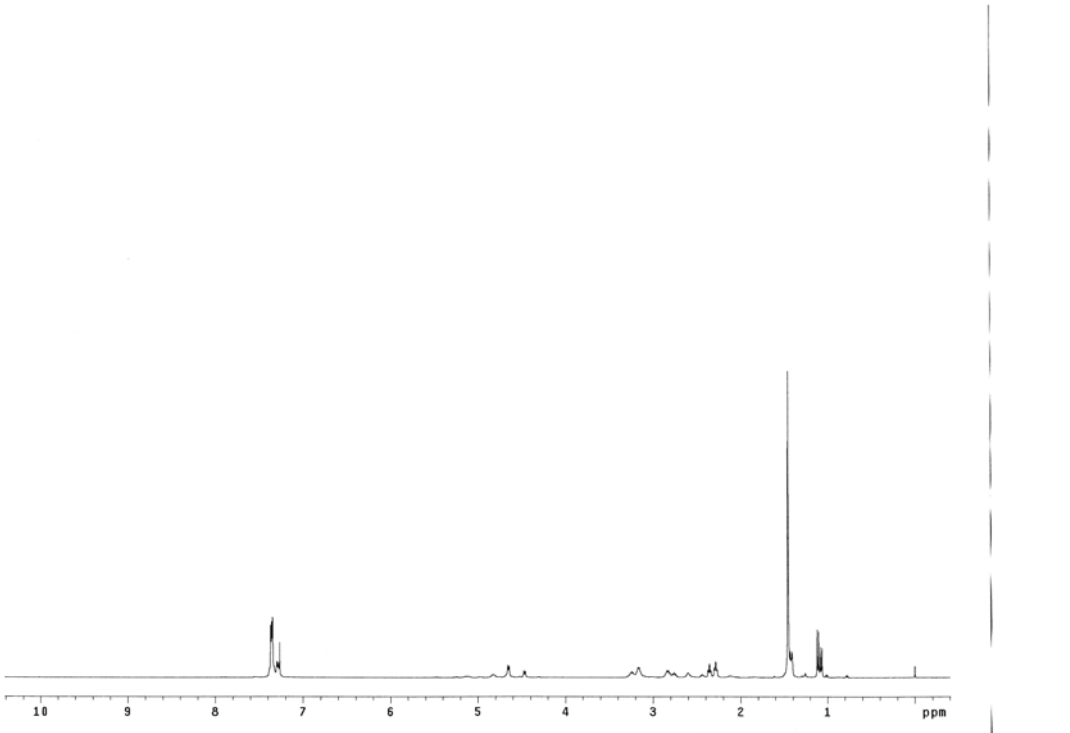
Procedure B (*via* enyne 1c): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (49 mg, 54%, 1:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.38-7.27 (m, 10H), 4.83-4.79 (m, 2H), 4.65 (d, J = 6.3 Hz, 1H), 4.46 (d, J = 6.8 Hz, 1H), 3.26-3.16 (m, 2H), 2.84-2.74 (m, 2H), 2.37-2.27 (m, 4H), 1.45-1.43 (m, 22H), 1.11 (d, J = 6.3 Hz, 3H), 1.07 (d, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 155.8 (2 signals), 141.8 (2 signals), 128.2, 128.0 (2 signals), 127.6, 126.5, 126.2, 83.1, 82.6, 80.7, 80.2, 79.4 (2 signals), 79.3, 77.5, 39.5 (2 signals), 35.4, 34.3, 28.4 (2 signals), 20.4, 20.3, 17.7, 16.1.

HRMS (CI) Calcd. for $C_{18}H_{26}NO_3$ $[M+H]^+$: 304.1913, Found: 304.1917.

FTIR (neat): 3420, 2977, 1694, 1515, 1366, 1252, 1171, 1026, 734, 701 cm^{-1}.


10
9
8
7
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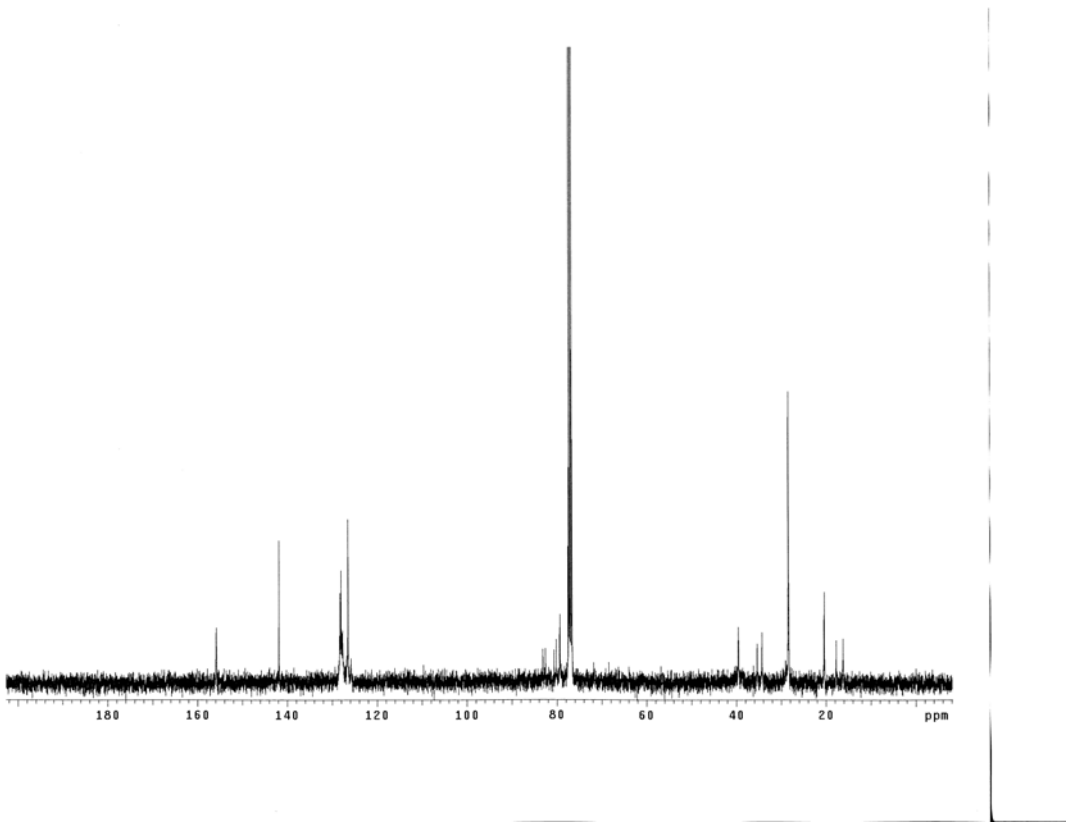
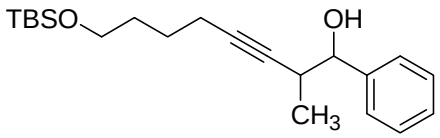
5
4
3
2
1
ppm


180
160
140
120
100
80
60
40
20
ppm

8-(*tert*-Butyldimethylsilanyloxy)-2-methyl-1-phenyloct-3-yn-1-ol (3r)



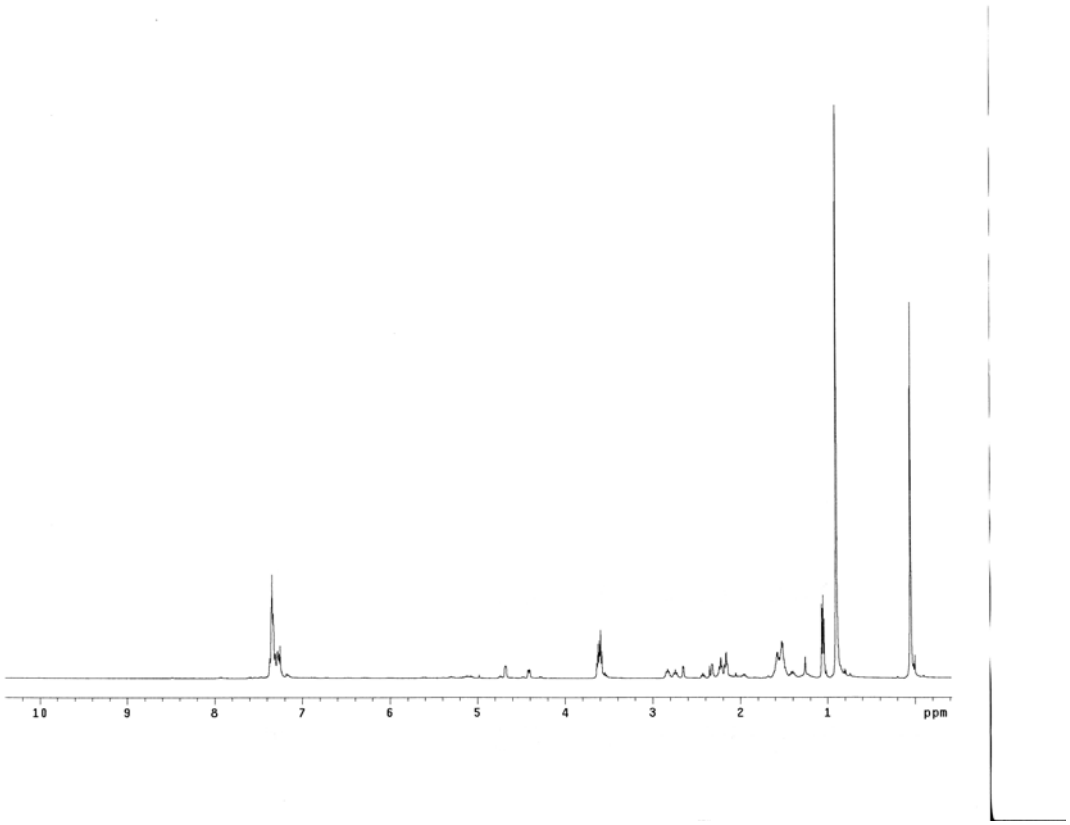
Procedure B (*via* enyne 1d): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (66 mg, 63%, 1:1 d.r.) as a pale yellow oil.

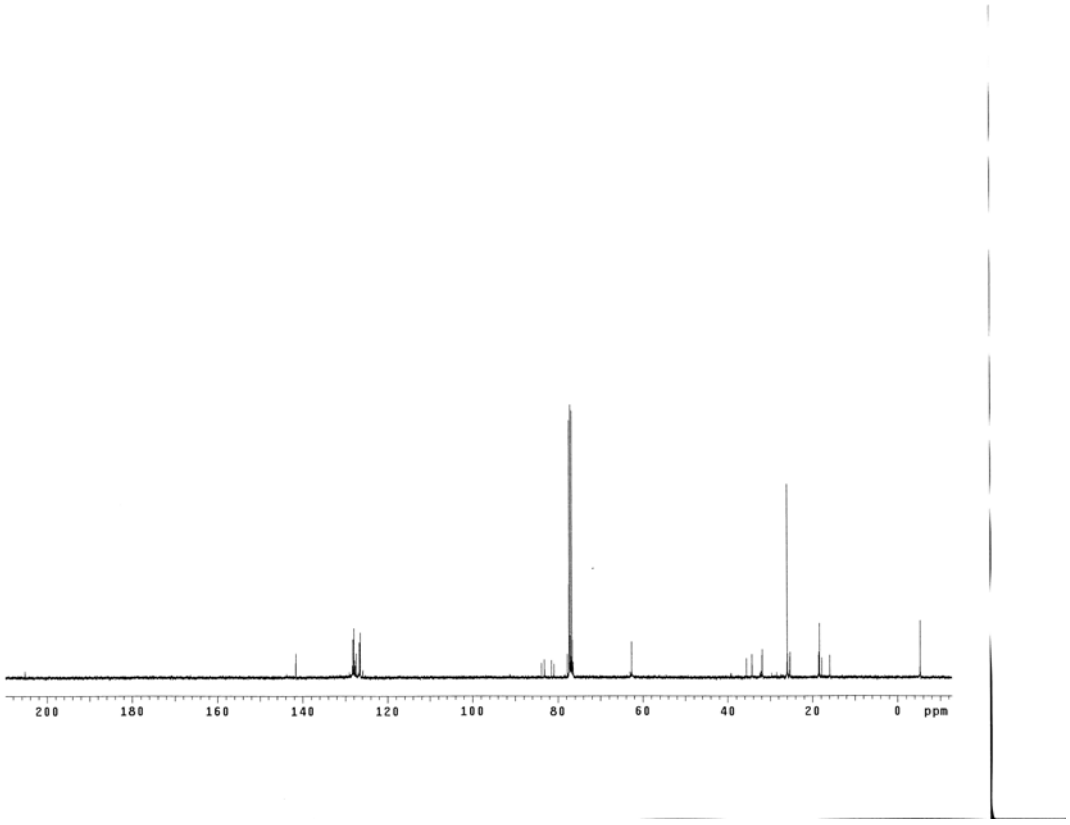
^{1}H NMR (400 MHz, $CDCl_3$): 7.38-7.23 (m, 10H), 4.96 (d, J = 7.2, 3.8 Hz, 1H), 4.42 (d, J = 7.2, 3.8 Hz, 1H), 3.64-3.60 (m, 6H), 2.86-2.83 (m, 1H), 2.77-2.72 (m, 1H), 2.27-2.17 (m, 4H), 1.59-1.53 (m, 8H), 1.06 (d, J = 7.2 Hz, 2H), 1.05 (d, J = 7.2 Hz, 4H), 0.90 (s, 18H), 0.05 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): 141.6, 141.5, 128.3, 128.2, 127.9, 127.8, 127.5 (2 signals), 126.7, 126.6, 126.5, 125.9, 83.9, 83.1, 81.5, 80.9, 77.7, 76.4, 62.6 (2 signals), 35.6, 34.3, 31.9, 25.9, 25.4, 25.3, 18.5, 18.3, 17.8, 15.9, -5.3 (2 signals).

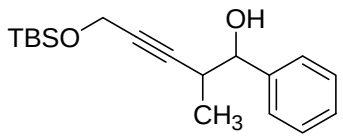
HRMS (CI) Calcd. for $C_{21}H_{35}O_2Si$ $[M+H]^+$: 347.2406, Found: 347.2407.

FTIR (neat): 3432, 2929, 1628, 1471, 1388, 1255, 1105, 836, 776, 700 cm^{-1}.


10
9
8
7
6
5
4
3
2
1
ppm


200
180
160
140
120
100
80
60
40
20
0
ppm

5-(*tert*-Butyldimethylsilanyloxy)-2-methyl-1-phenylpent-3-yn-1-ol (3s)



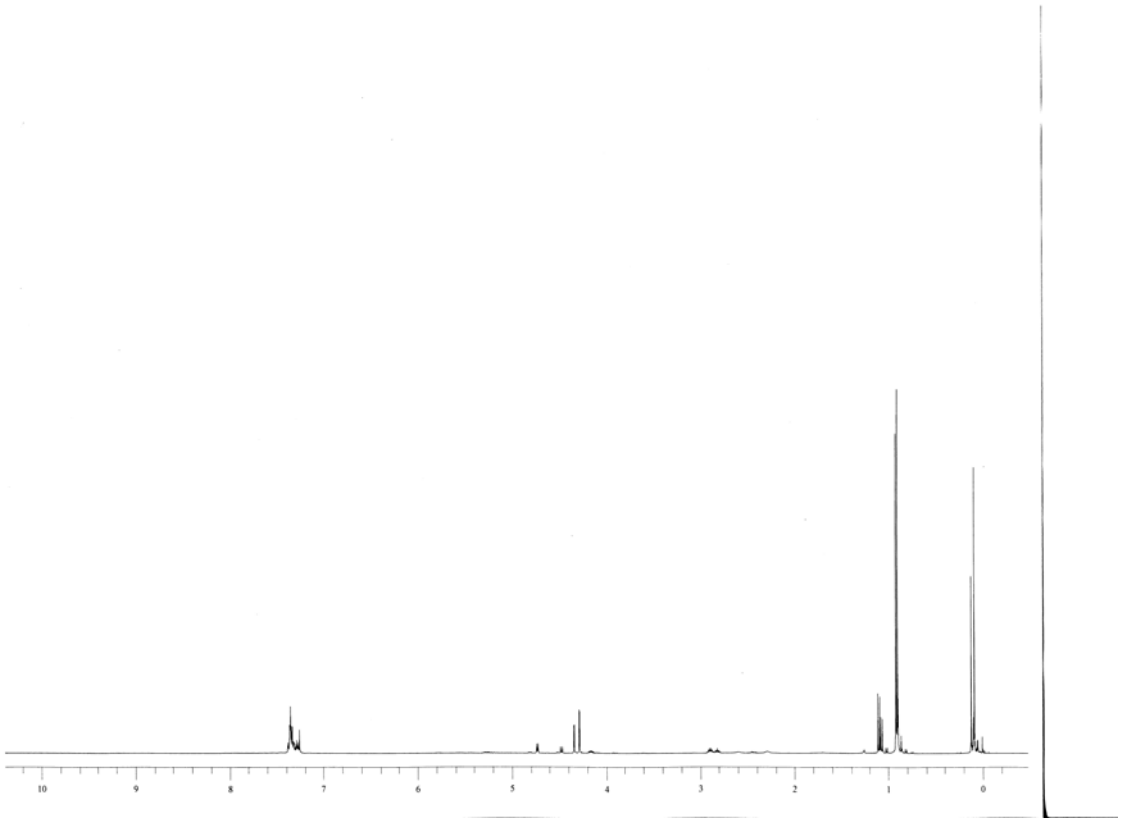
Procedure B (*via* enyne 1e): In a modification to procedure B, *m*-NO_2BzOH was not employed as a cocatalyst. After heating the reaction at 95 ^oC for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (71 mg, 78%, 1.5:1 d.r.) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.36-7.34 (m, 8.25H), 4.73 (d, J = 5.5 Hz, 1H), 4.47 (d, J = 7.0 Hz, 0.65H), 4.34 (d, J = 2.0 Hz, 1.3H), 4.28 (d, J = 2.0 Hz, 2H), 2.93-2.77 (m, 1.65H), 2.60 (br s, 0.65H), 2.29 (br s, 1H), 1.10 (d, J = 7.0 Hz, 3H), 1.07 (d, J = 7.0 Hz, 1.95H), 0.92-0.88 (m, 14.85H), 0.12 (s, 3.9H), 0.09 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 141.3, 128.3, 128.1, 127.9, 127.6, 127.4, 126.9, 126.7, 126.4, 125.8, 86.3, 85.8, 82.1, 81.5, 77.5, 76.1, 51.8, 35.5, 34.3, 25.9, 25.8, 18.3, 17.3, 15.3, -5.1, -5.2.

HRMS (CI) Calcd. for $C_{18}H_{29}O_2Si$ $[M+H]^+$: 305.1937, Found: 305.1940.

FTIR (neat): 3446, 2929, 2857, 1472, 1255, 1083, 837, 778, 700, 435 cm^{-1}.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9
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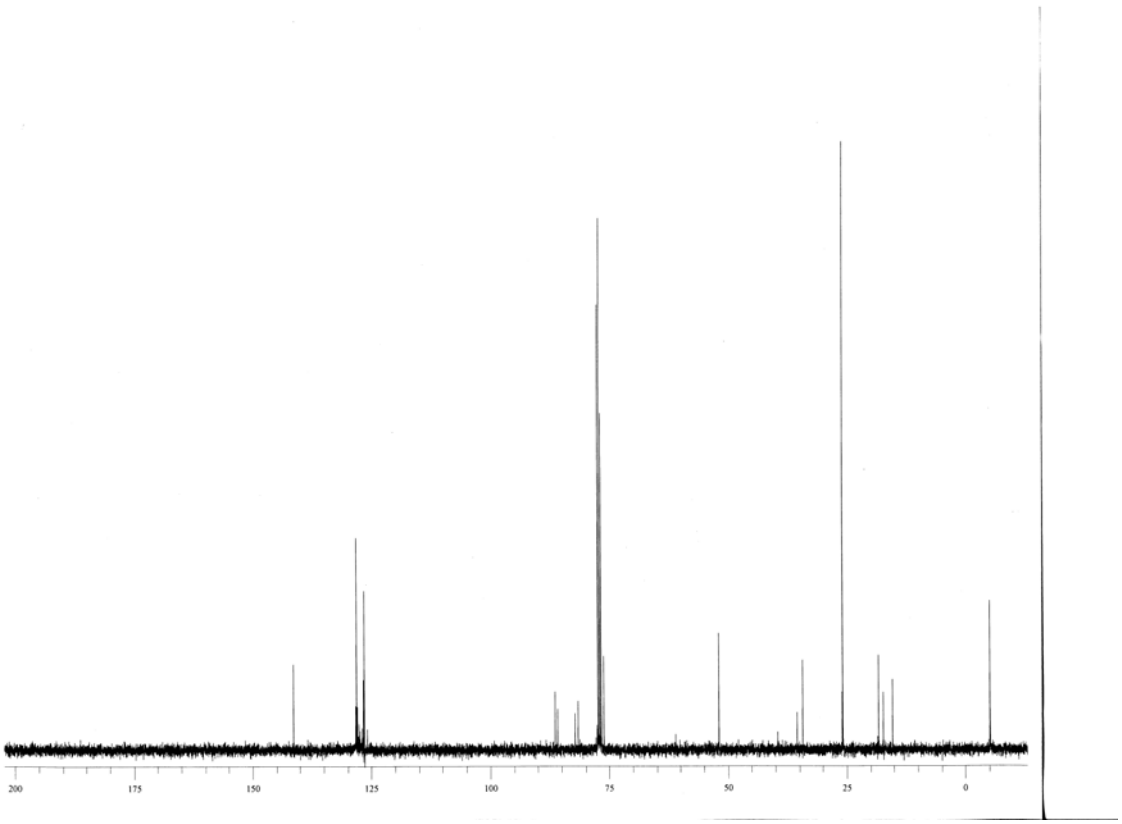
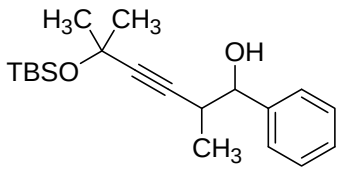
6
5
4
3
2
1
0


200
175
150
125
100
75
50
25
0

5-(*tert*-Butyldimethylsilanyloxy)-2,5-dimethyl-1-phenylhex-3-yn-1-ol (3t)



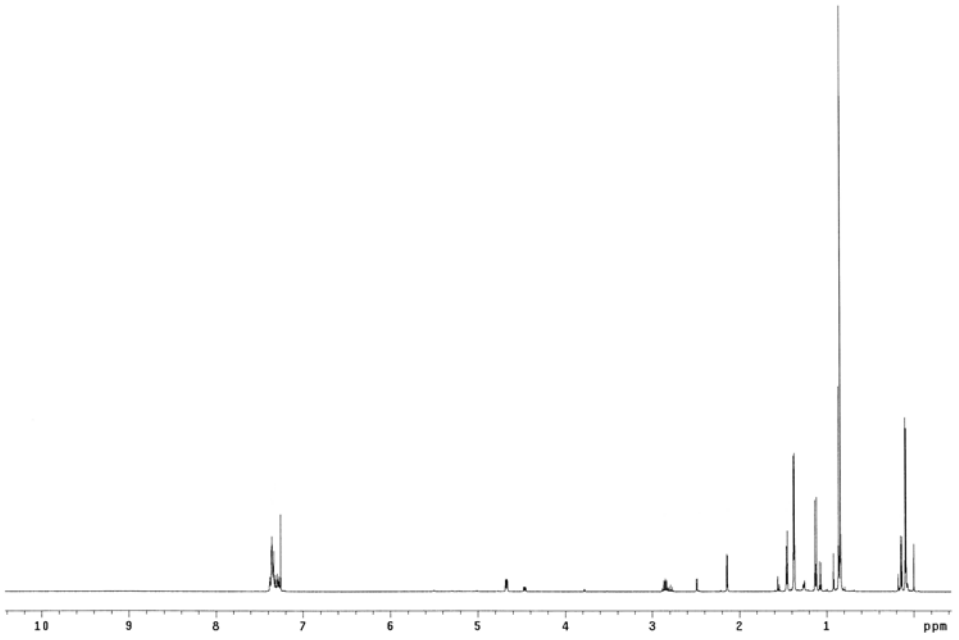
Procedure B (*via* enyne 1f): After heating the reaction at 95 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (56 mg, 56%, 1:1 d.r.) as a pale yellow oil.

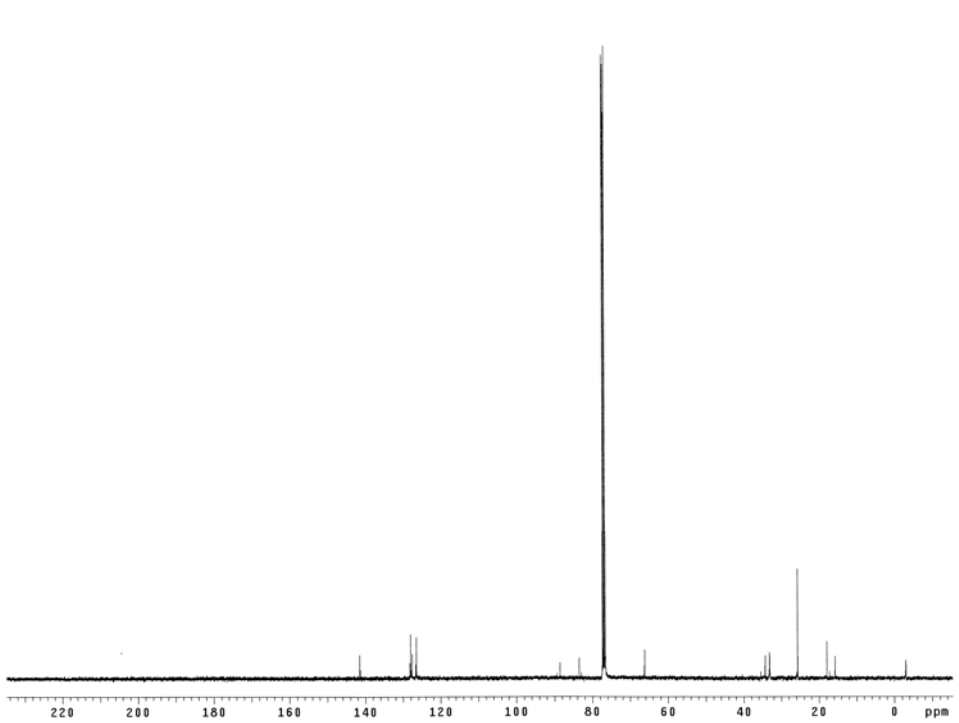
^{1}H NMR (400 MHz, $CDCl_3$): 7.41-7.24 (m, 10H), 4.68 (dd, *J* = 7.2, 3.76 Hz, 1H), 4.47 (dd, *J* = 7.2, 3.8 Hz, 1H), 2.88-2.56 (m, 2H), 2.49 (d, *J* = 3.8 Hz, 1H), 2.14 (d, *J* = 3.8 Hz, 1H), 1.46 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H), 1.12 (d, *J* = 7.2 Hz, 3H), 1.08 (d, *J* = 7.2 Hz, 3H), 0.86 (s, 9H), 0.84 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 141.5 (2 signals), 128.2, 128.0, 127.7, 127.5, 126.8, 126.5, 90.2, 88.7, 83.5, 83.2, 77.5 (2 signals), 66.3 (2 signals), 34.7, 34.3, 33.3, 33.1, 33.0, 25.7 (2 signals), 17.9, 17.1, 15.7, -2.7 (2 signals).

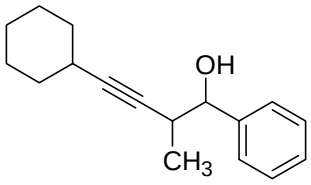
HRMS (CI) Calcd. for $C_{20}H_{33}O_2Si$ $[M+H]^+$: 333.2250, Found: 333.2249.

FTIR (neat): 3391, 2930, 2889, 2857, 1462, 1376, 1360, 1248, 1161, 1039, 905, 837, 810, 776, 700 cm^{-1}.


10
9
8
7
6
5
4
3
2
1
ppm


220
200
180
160
140
120
100
80
60
40
20
0
ppm

4-Cyclohexyl-2-methyl-1-phenylbut-3-yn-1-ol (3u)



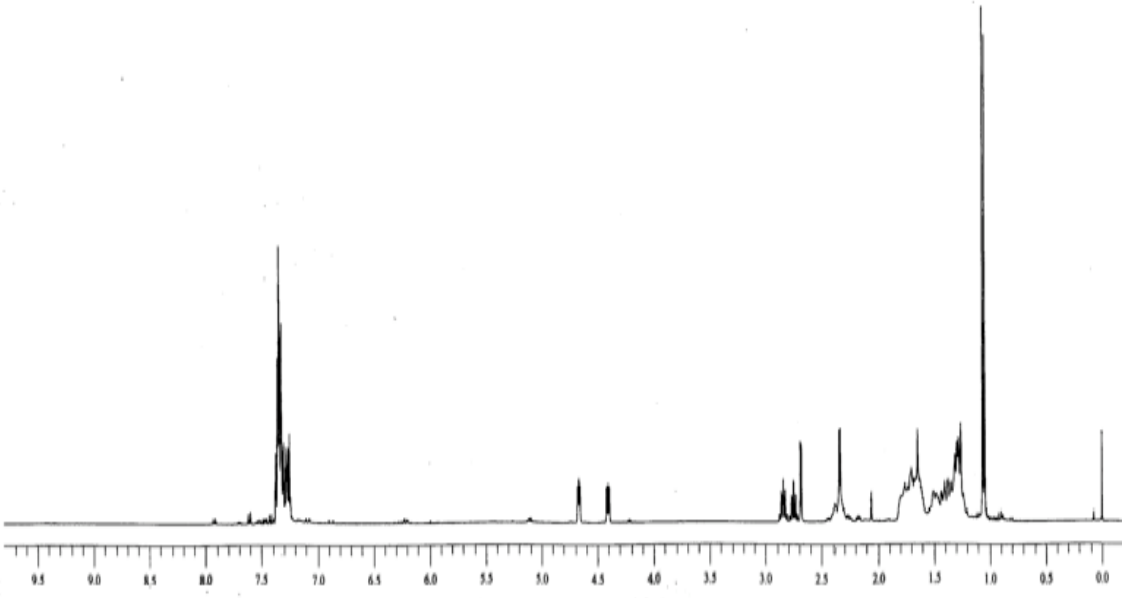
Procedure B (*via* enyne 1g): After heating the reaction at 95 ^{o}C for 21 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (51 mg, 70%, 1:1 d.r.) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.38-7.24 (m, 10H), 4.67 (dd, *J* = 5.0, 3.5 Hz, 1H), 4.41 (dd, *J* = 7.0, 3.5 Hz, 1H), 2.88-2.80 (m, 1H), 2.75 (ddd, *J* = 7.0, 7.0, 2.0 Hz, 1H), 2.68 (d, *J* = 3.5 Hz, 1H), 2.42-2.28 (m, 3H), 1.82-1.21 (m, 20H), 1.05 (app. d, *J* = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 141.9, 141.8, 128.4, 128.1, 128.0, 127.7, 127.0, 126.8, 88.8, 88.0, 81.4, 80.8, 78.0, 76.7, 36.0, 34.6, 33.2, 33.1 (2 signals), 29.3, 29.2, 26.1, 25.1, 25.0, 18.1, 16.3.

HRMS (CI) Calcd. for $C_{17}H_{23}O$ $[M+H]^+$: 243.1749, Found: 243.1749.

FTIR (neat): 3432, 2927, 2853, 1449, 1025 cm^{-1}.


9.5
9.0
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8.0
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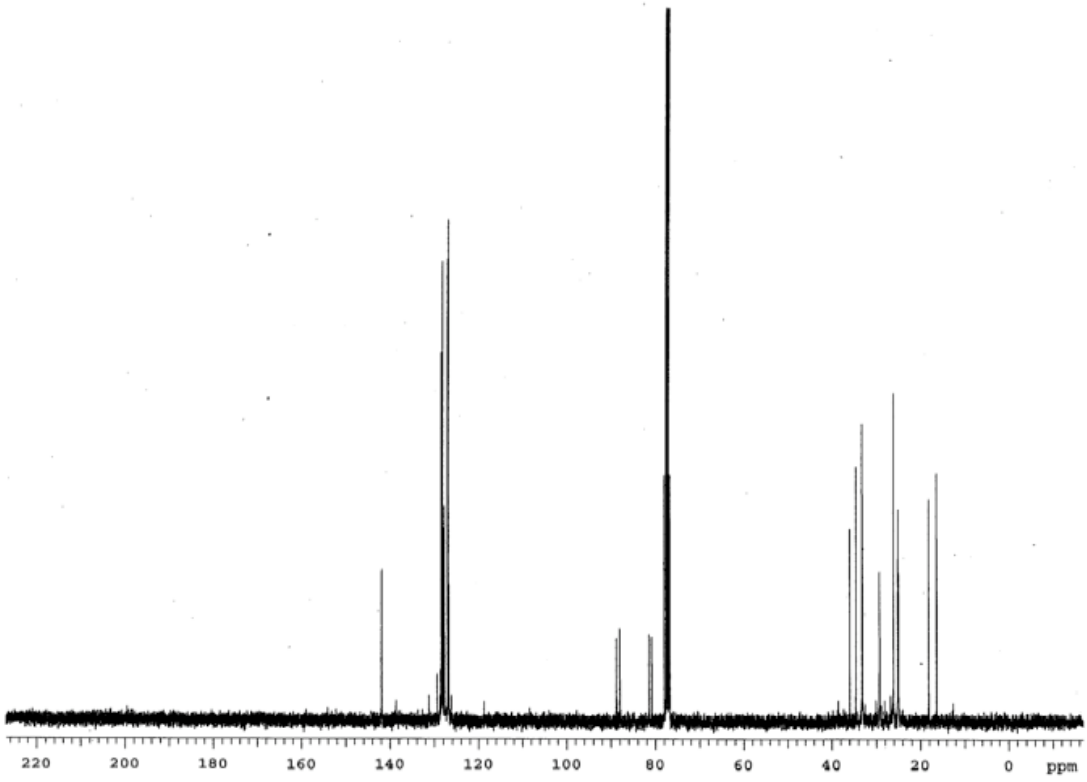
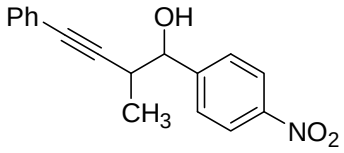

220
200
180
160
140
120
100
80
60
40
20
0
ppm

Procedures for the Propargylation of 4a-4c Employing Isopropanol as Reductant

2-Methyl-1-(4-nitrophenyl)-4-phenybut-3-yn-1-ol (3a)

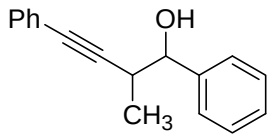


Procedure C (*via* aldehyde 4a): After heating the reaction at 90 ^{o}C for 18 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (51 mg, 61%, 1:1 d.r.) as a pale yellow oil.

The spectroscopic properties of this compound were identical to those reported earlier.

This material was contaminated with *ca.* 10 % of material resulting from *cis*-reduction of the alkyne moiety (1:1 d.r.); characteristic signals for ^{1}H NMR (400 MHz, $CDCl_3$): 6.65 (d, *J* = 11.5 Hz, 1H), 6.43 (d, *J* = 11.5 Hz, 1H), 5.56 (dd, *J* = 11.5, 10.5 Hz, 1H), 5.47 (dd, *J* = 11.5, 10.5 Hz, 1H), 1.10 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H). *The structural assignment of this byproduct was made by analogy with the material derived from the analogous reaction with benzaldehyde (see below).*

2-Methyl-1,4-diphenyl-but-3-yn-1-ol (3b)



Procedure C (*via* aldehyde 4b): After heating the reaction at 90 ^{o}C for 17 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (52 mg, 74%, 1:1 d.r.) as a pale yellow oil.

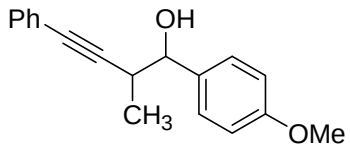
The spectroscopic properties of this compound were identical to those reported earlier.

This material was contaminated with *ca.* 10 % of material resulting from *cis*-reduction of the alkyne moiety (1:1 d.r.); characteristic signals for ^{1}H NMR (400 MHz, $CDCl_3$): 6.63 (d, J = 11.5 Hz, 1H), 6.39 (d, J = 11.5 Hz, 1H), 5.59 (dd, J = 11.5, 10.5 Hz, 1H), 5.50 (dd, J = 11.5, 10.5 Hz, 1H), 1.08 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 6.5 Hz, 3H).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[5]

[5] G. Y. Fang, V. K. Aggarwal, *Angew. Chem.* **2007**, *119*, 363-366; *Angew. Chem. Int. Ed.* **2007**, *46*, 359-362.

1-(4-Methoxyphenyl)-2-methyl-4-phenylbut-3-yn-1-ol (3c)

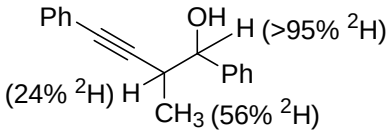


Procedure C (*via* aldehyde 4c): After heating the reaction at 90 ^{o}C for 15 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (73 mg, 91%, 1:1 d.r.) as a pale yellow oil. No significant reduction of the alkyne moiety was observed.

The spectroscopic properties of this compound were identical to those reported earlier.

Experimental Details for Mechanistic Studies

deuterio- 2-Methyl-1,4-diphenylbut-3-yn-1-ol (*deuterio*-3b)



Procedure A (*via* alcohol *deuterio*-2b): d_2-benzyl alcohol (*deuterio*-**2b**, 98% deuterium incorporation) was purchased from Aldrich. After heating the reaction at 95 ^{o}C for 23 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe) to afford the title compound (55 mg, 78%, 2:1 d.r.) as a pale yellow oil.

^{2}H NMR (77 MHz, $CHCl_3$): 4.90-4.46 (m, 1.00^{2}H), 3.15-2.95 (m, 0.24^{2}H), 1.04-1.00 (m, 0.56^{2}H).