Supplementary Information

"Direct Vinylation of Alcohols or Aldehydes Employing Alkynes as Vinyl Donors: A Ruthenium Catalyzed C-C Bond Forming Transfer Hydrogenation"

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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 oven-dried and cooled under a stream of argon. Reaction tubes were purchased from Fisher Scientific (catalog number 14-959-35C). Tetrahydrofuran was passed through a column of Al_2O_3 prior to use. $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ was prepared in accordance with literature procedure.[1] Anhydrous isopropanol (99.5% over molecular sieves) was purchased from Acros and used as received. Reagent grade formic acid was purchased from Aldrich and used as received. Sodium Iodide was purchased from Fisher and used as received. Commercially available alcohols and alkynes were used as received. Commercially available aldehydes were purified *via* distillation or recrystallization prior to use. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F_{254}) and products were visualized by UV, $KMnO_4$, and/or Anisaldehyde stain. 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). 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.

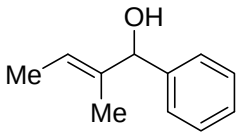
[1] Dobson, A.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1975**, 370.
[2] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Experimental Procedures and Spectroscopic Data for Vinylated Adducts 2a-2l

General Procedure A for the Coupling of 2-Butyne to Alcohols: To a resealable pressure tube equipped with magnetic stir bar was added $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ (13.2 mg, 0.015 mmol, 5 mol%). At this stage solid alcohol coupling partners (0.300 mmol, 100 mol%) were added. The tube was then sealed with a rubber septum and purged with argon. At this stage liquid alcohol coupling partners (0.300 mmol, 100 mol%) were added. THF (1.5 mL, 0.2 M concentration with respect to the alcohol) and isopropanol (46 μL, 0.600 mmol, 200 mol%) were added and the tube was cooled to -78 ^{o}C. 2-Butyne (47 μL, 0.600 mmol, 200 mol%) was added and the rubber septum was quickly replaced with a screw cap. 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 vinylated adduct.

General Procedure B for the Coupling of 2-Butyne to Aldehydes: To a resealable pressure tube equipped with magnetic stir bar was added $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ (13.2 mg, 0.015 mmol, 5 mol%) and NaI (2.2 mg, 0.015 mmol, 5 mol%). At this stage solid aldehyde coupling partners (0.300 mmol, 100 mol%) were added. The tube was then sealed with a rubber septum and purged with argon. At this stage liquid aldehyde coupling partners (0.300 mmol, 100 mol%) were added. THF (1.5 mL, 0.2 M concentration with respect to the aldehyde) was added and the tube was cooled to -78 ^{o}C. 2-Butyne (47 μL, 0.600 mmol, 200 mol%) and formic acid (12 μL, 0.300, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 65 ^{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 vinylated adduct.

(*E*)-2-Methyl-1-phenylbut-2-en-1-ol (2a)



Procedure A (*via* alcohol 1a): In a modification to procedure A, the reaction was run at 0.6 M concentration. After heating the reaction at 95 ^{o}C for 9 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (35 mg, 72%) as a colorless oil.

Procedure B (*via* aldehyde 4a): After heating the reaction at 65 ^{o}C for 5 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe - 2% EtOAc/PhMe) to afford the title compound (43 mg, 88%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.37-7.23 (m, 5H) 5.71 (qquint, J = 6.8, 1.6 Hz, 1H) 5.13 (d, J = 3.2 Hz, 1H) 1.90 (d, J = 3.2 Hz, 1H) 1.68-1.64 9 (m, 3H) 1.50-1.47 (m, 3H).

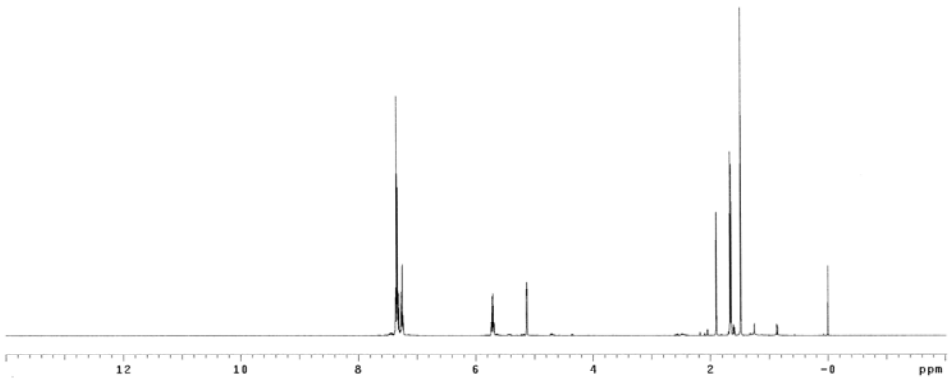
^{13}C NMR (100 MHz, $CDCl_3$): 142.7, 137.8, 128.4, 127.4, 126.4, 121.5, 79.5, 13.4, 11.9.

HRMS (CI) Calcd. for $C_{11}H_{15}O$ $[M+H]^+$: 163.1123, Found: 163.1118.

FTIR (neat): 3379, 2918, 2859, 1450, 1014, 699 cm^{-1}.

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

[3] Gau, A.-H. Lin, G.-L. Uang, B.-J. Liao, F.-L. Wang, S.-L. *J. Org. Chem.* **1999**, *64*, 2194.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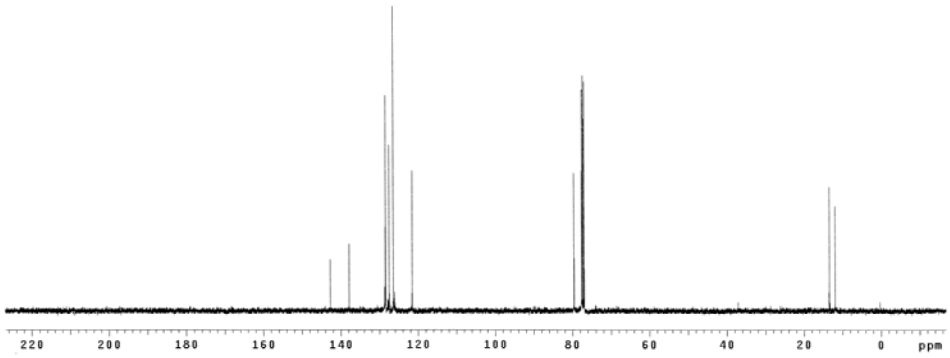
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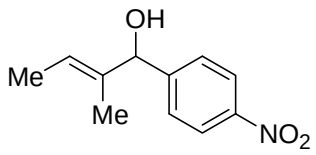
(*E*)-2-Methyl-1-(4-nitrophenyl)-but-2-en-1-ol (2b)



Procedure A (*via* alcohol 1b): After heating the reaction at 95 ^{o}C for 13 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (48 mg, 78%) as a colorless, crystalline solid.

Procedure B (*via* aldehyde 4b): After heating the reaction at 65 ^{o}C for 5 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe - 2% EtOAc/PhMe) to afford the title compound (48 mg, 78%) as a colorless, crystalline solid.

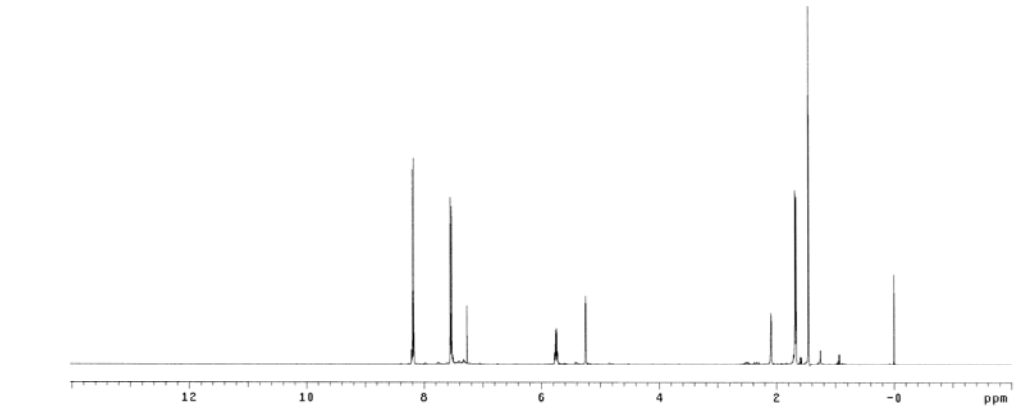
^{1}H NMR (400 MHz, $CDCl_3$): 8.22-8.16 (m, 2H), 7.56-7.50 (m, 2H), 5.79-5.72 (m, 1H), 5.25 (s, 1H), 2.09 (d, J = 2.4 Hz, 1H), 1.68 (dd, J = 6.8, 0.8 Hz, 3H), 1.47-1.45 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 150.0, 147.3, 137.0, 127.1, 123.9, 123.6, 79.1, 13.5, 11.2.

HRMS (CI) Calcd. for $C_{11}H_{14}NO_3$ $[M+H]^+$: 208.0974, Found: 208.0972.

FTIR (neat): 3495, 2919, 1514, 1342, 1013, 858 cm^{-1}.

M.P. 79-82 ^{o}C ($CHCl_3$)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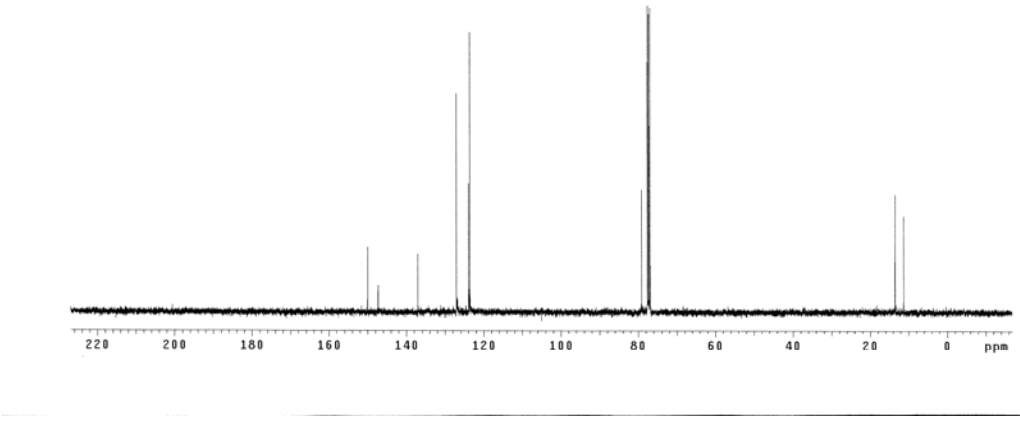
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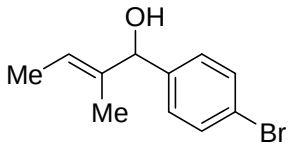
(*E*)-1-(4-bromophenyl)-2-methylbut-2-en-1-ol (2c)



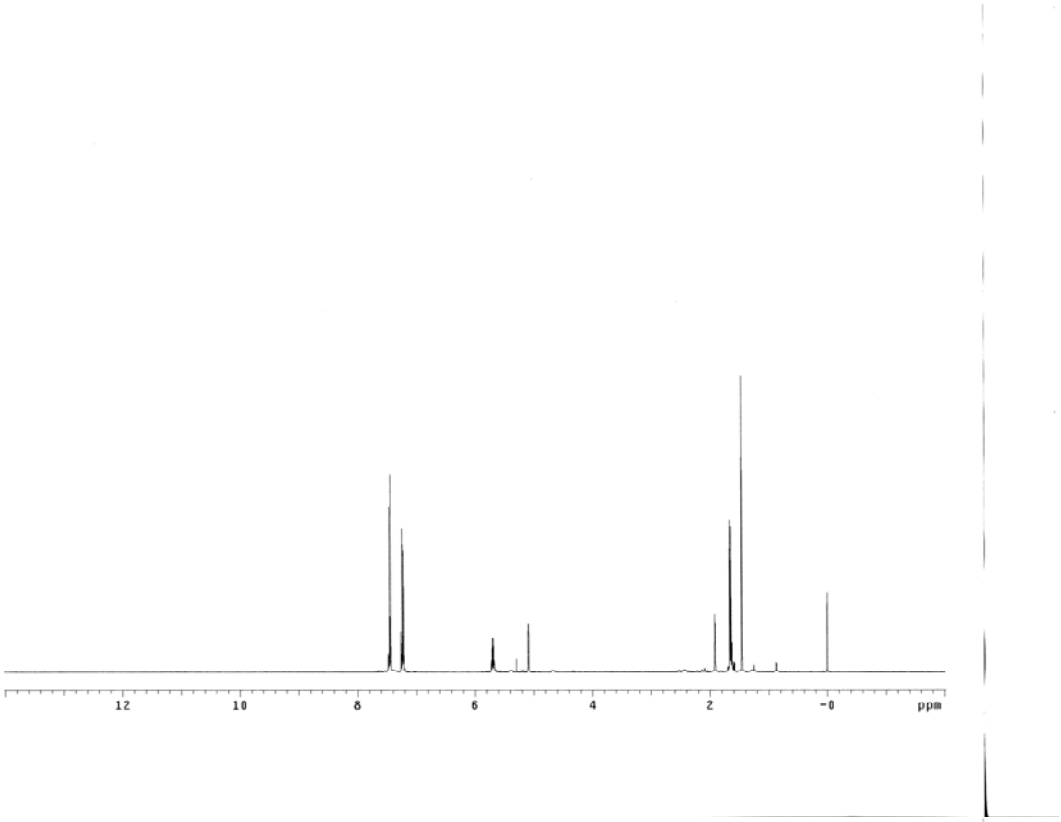
Procedure A (*via* alcohol 1c): After heating the reaction at 95 ^{o}C for 13 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (59 mg, 81%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.48-7.42 (m, 2H), 7.26-7.21 (m, 2H), 5.69 (qquint, J = 6.8, 1.2 Hz, 1H), 5.09 (d, J = 2.8 Hz, 1H), 1.91 (d, J = 3.2 Hz, 1H), 1.65 (d, J = 6.8 Hz, 3H), 1.46 (t, J = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 141.6, 137.5, 131.4, 128.1, 122.3, 121.2, 79.1, 13.4, 11.6.

HRMS (CI) Calcd. for $C_{11}H_{14}OBr$ $[M+H]^+$: 241.0228, Found: 241.0224.

FTIR (neat): 3354, 2917, 2859, 1484, 1070, 1009, 808, 784 cm^{-1}.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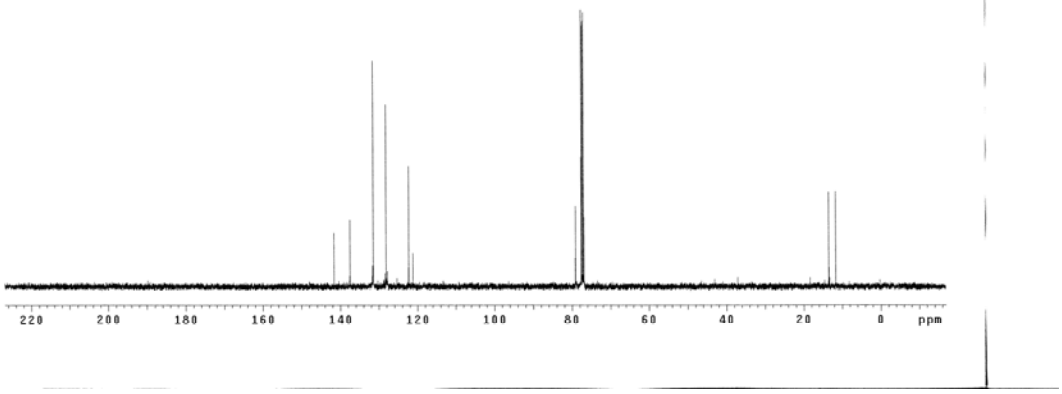
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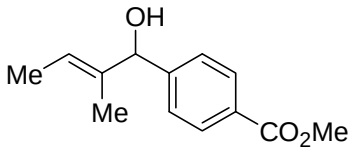
(*E*)-4-(1-Hydroxy-2-methylbut-2-enyl)-benzoic acid methyl ester (2d)



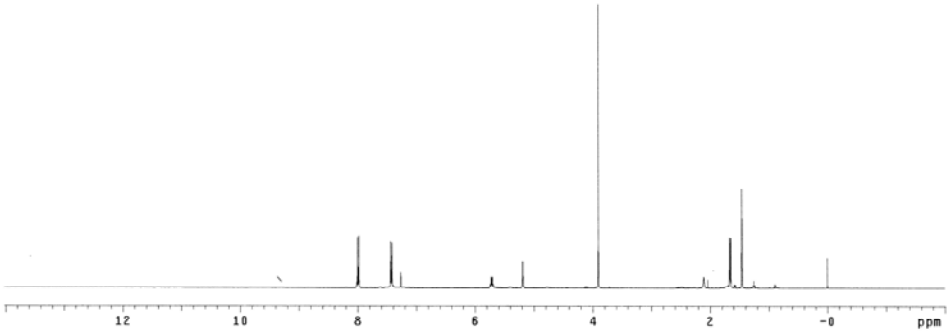
Procedure A (*via* alcohol 1d): After heating the reaction at 95 ^{o}C for 13 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (54 mg, 81%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.03-7.98 (m, 2H), 7.45-7.41 (m, 2H), 5.75-5.68 (m, 1H), 5.19 (s, 1H), 3.90 (s, 3H), 2.10 (bs, 1H), 1.68-1.64 (m, 3H), 1.46 (t, J = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 167.3, 147.8, 137.4, 129.7, 129.1, 126.3, 122.7, 79.4, 52.3, 13.4, 11.5.

HRMS (CI) Calcd. for $C_{13}H_{17}O_3$ $[M+H]^+$: 221.1178, Found: 221.1173.

FTIR (neat): 3465, 2951, 1720, 1436, 1279, 1113 cm^{-1}.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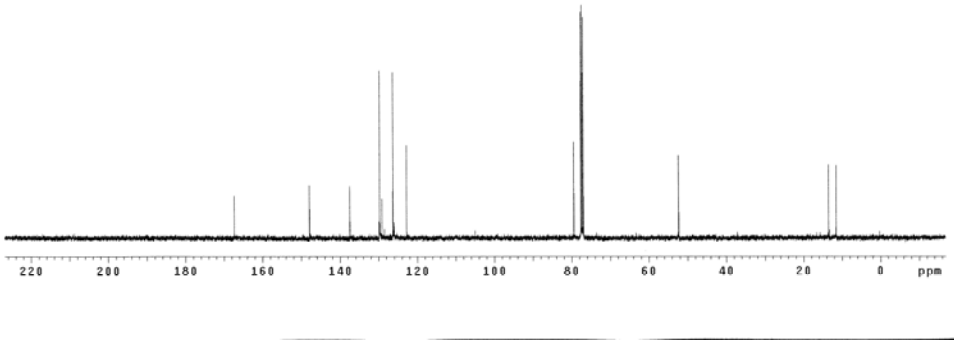
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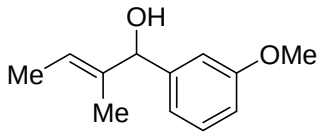
(*E*)-1-(3-Methoxyphenyl)-2-methylbut-2-en-1-ol (2e)



Procedure A (*via* alcohol 1e): After heating the reaction at 95 ^{o}C for 13 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (45 mg, 78%) as a colorless oil.

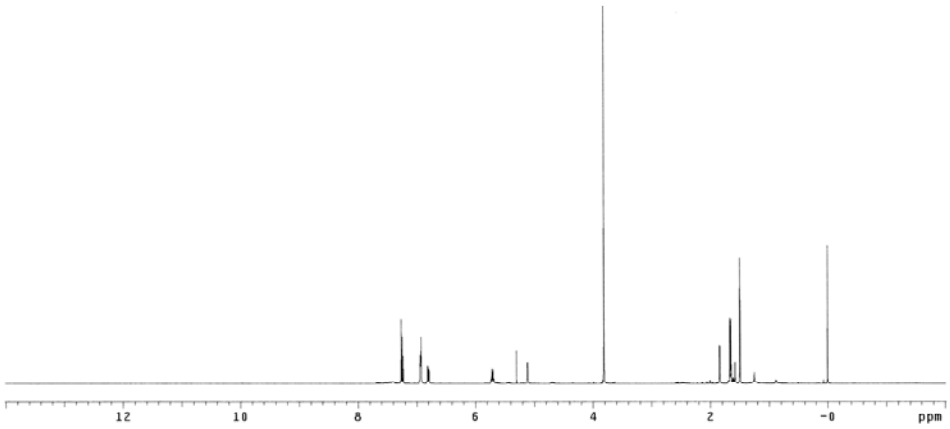
Procedure B (*via* aldehyde 4e): After heating the reaction at 65 ^{o}C for 5 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, PhMe - 2% EtOAc/PhMe) to afford the title compound (52 mg, 91%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.29-7.24 (m, 1H), 6.95-6.91 (m, 1H), 6.80 (ddd, J = 8.0, 2.4, 0.8 Hz, 1H), 5.74-5.67 (m, 1H), 5.11 (d, J = 2.8 Hz, 1H), 3.81 (s, 3H), 1.84 (d, J = 3.6 Hz, 1H), 1.68-1.64 (m, 3H), 1.50 (t, J = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 159.8, 144.4, 137.7, 129.4, 121.7, 118.8, 112.8, 112.0, 79.5, 55.4, 13.4, 11.8.

HRMS (CI) Calcd. for $C_{12}H_{17}O_2$ $[M+H]^+$: 193.1229, Found: 193.1231.

FTIR (neat): 3403, 2918, 2859, 2835, 1599, 1585, 1486, 1435, 1039 cm^{-1}.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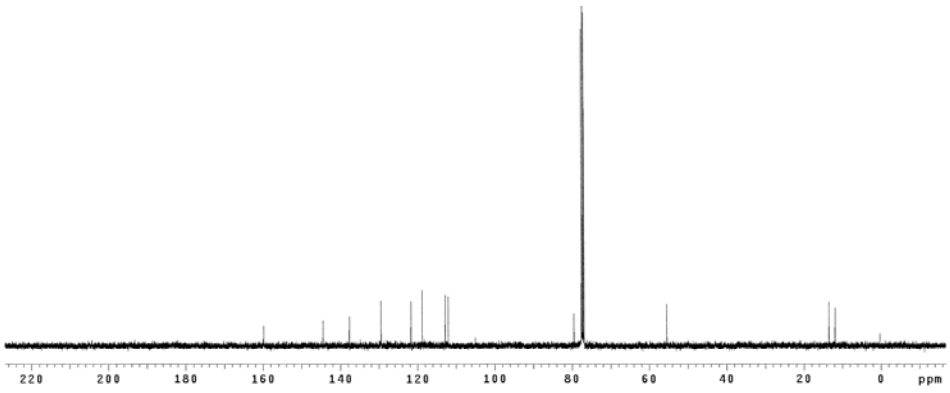
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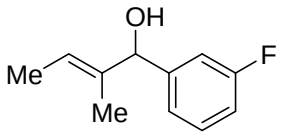
(*E*)-1-(3-Fluorophenyl)-2-methylbut-2-en-1-ol (2f)



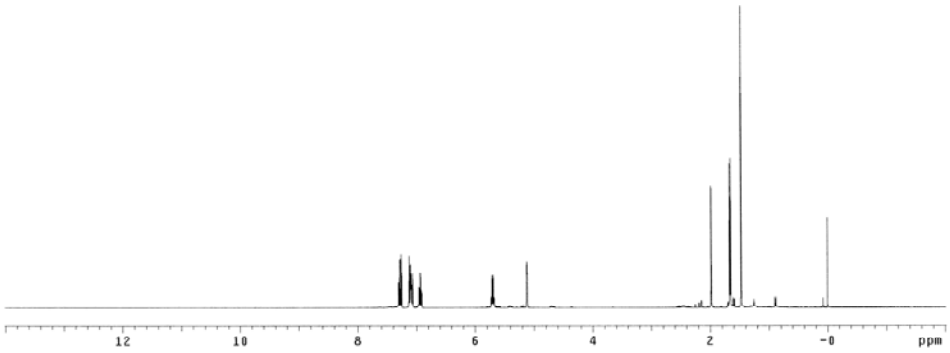
Procedure A (*via* alcohol 1f): After heating the reaction at 95 ^{o}C for 13 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (43 mg, 79%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.28 (dt, J = 8.0, 5.6 Hz, 1H) 7.14-7.06 (m, 2H) 6.96-6.90 (m, 1H) 5.74-5.67 (m, 1H) 5.12 (d, J = 3.2 Hz, 1H) 1.98 (d, J = 3.6 Hz, 1H) 1.68-1.64 (m, 3H) 1.48-1.46 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 163.1 (d, J = 976.4 Hz), 145.4 (d, J = 26.8 Hz), 137.4, 129.8 (d, J = 32.8 Hz), 122.4, 121.9 (d, J = 12.0 Hz), 114.2 (d, J = 83.6 Hz), 113.3 (d, J = 86.4 Hz), 79.1 (d, J = 8.8 Hz), 13.4, 13.2.

HRMS (CI) Calcd. for $C_{11}H_{11}FO$ $[M+H]^+$: 178.0794, Found: 178.0792.

FTIR (neat): 3365, 2919, 2861, 1615, 1590, 1484, 1445, 1245, 1023, 782, 757, 692 cm^{-1}.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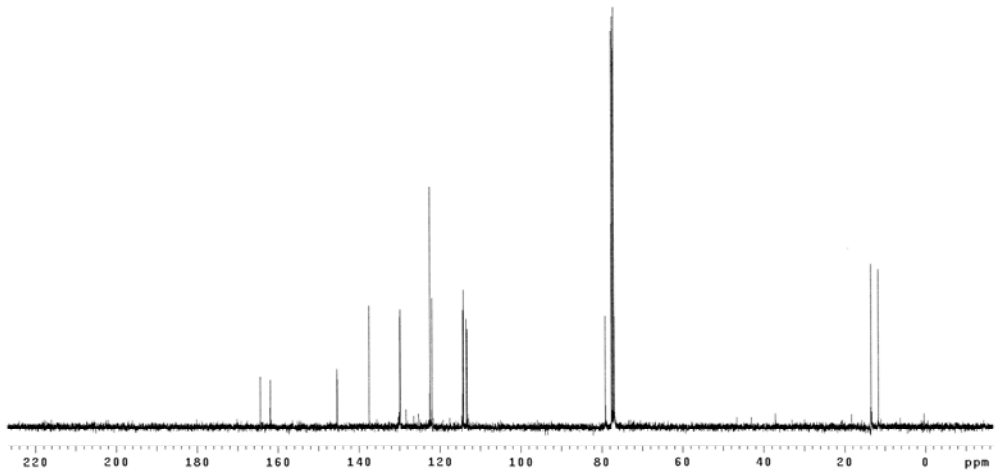
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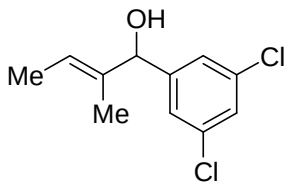
(*E*)-1-(3,5-Dichlorophenyl)-2-methylbut-2-en-1-ol (2g)



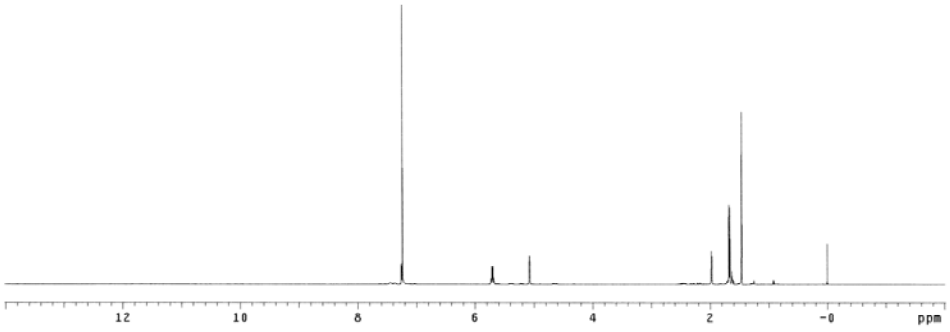
Procedure A (*via* alcohol 1g): After heating the reaction at 95 ^{o}C for 13 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (53 mg, 76%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 4.25-7.23 (m, 3H), 5.74-5.66 (m, 1H), 5.07 (d, J = 2.8 Hz, 1H), 1.97 (d, J = 3.2 Hz, 1H), 1.67 (dd, J = 6.4, 1.2 Hz, 3H), 1.48-1.45 9m,3H).

^{13}C NMR (100 MHz, $CDCl_3$): 146.1, 136.9, 134.9, 127.4, 123.5, 78.7, 13.5, 11.3.

HRMS (CI) Calcd. for $C_{11}H_{13}OCl_2$ $[M+H]^+$: 231.0343, Found: 231.0340.

FTIR (neat): 3351, 2918, 1567, 1431, 1190, 1100, 1027, 857, 795 cm^{-1}.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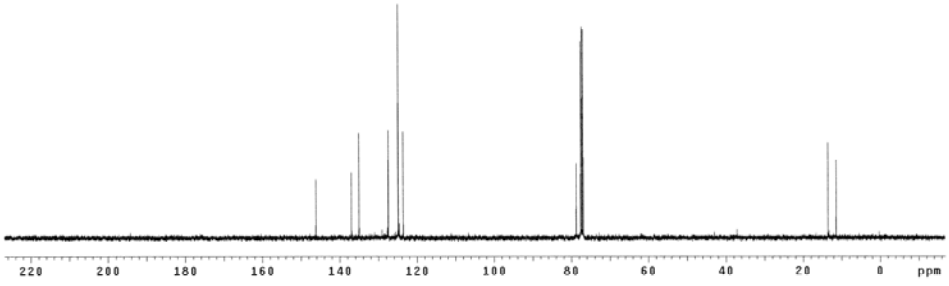
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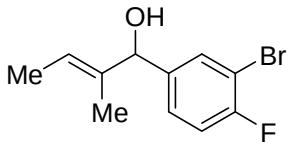
(*E*)-1-(3-Bromo-4-fluorophenyl)-2-methylbut-2-en-1-ol (2h)



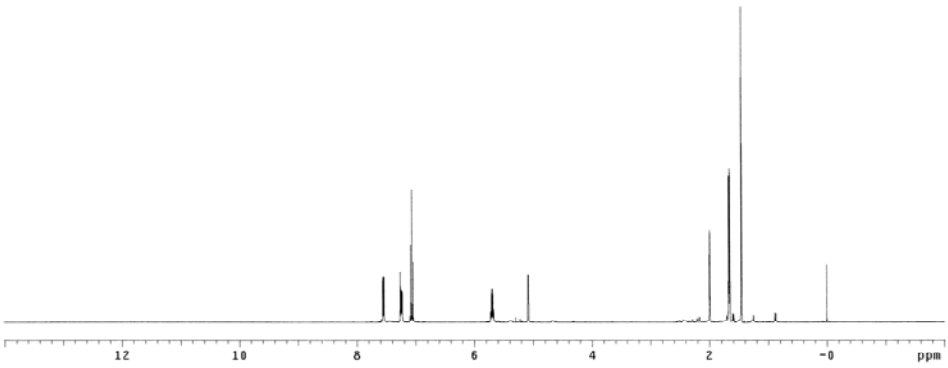
Procedure A (*via* alcohol 1h): After heating the reaction at 95 ^{o}C for 9 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (58 mg, 75%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (ddd, J = 6.4, 2.4, 0.8 Hz, 1H), 7.27-7.22 (m, 1H), 7.06 (t, J = 8.4 Hz, 1H), 5.73-5.66 (M, 1H), 5.09 (d, J = 2.4 Hz, 1H), 2.00 (d, J = 3.2 Hz, 1H), 1.68-1.65 (m, 3H), 1.40-1.45 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 158.3 (d, J = 979.2 Hz), 140.0 (d, J = 14.8 Hz), 137.3, 131.4, 126.9 (d, J = 29.6 Hz), 122.7, 116.3 (d, J = 89.6 Hz), 109.0 (d, J = 89.6 Hz), 78.5, 13.4, 11.5.

HRMS (CI) Calcd. for $C_{11}H_{13}OFBr$ $[M+H]^+$: 259.0134, Found: 259.0137.

FTIR (neat): 3350, 2918, 2860, 1493, 1244, 1045, 1024 cm^{-1}.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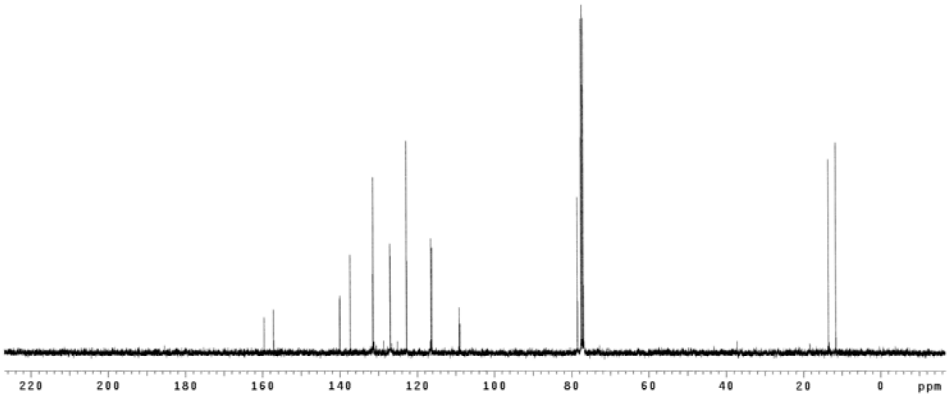
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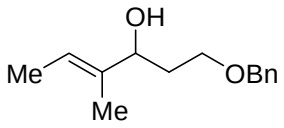
(*E*)-1-Benzyloxy-4-methylhex-4-en-3-ol (2i)



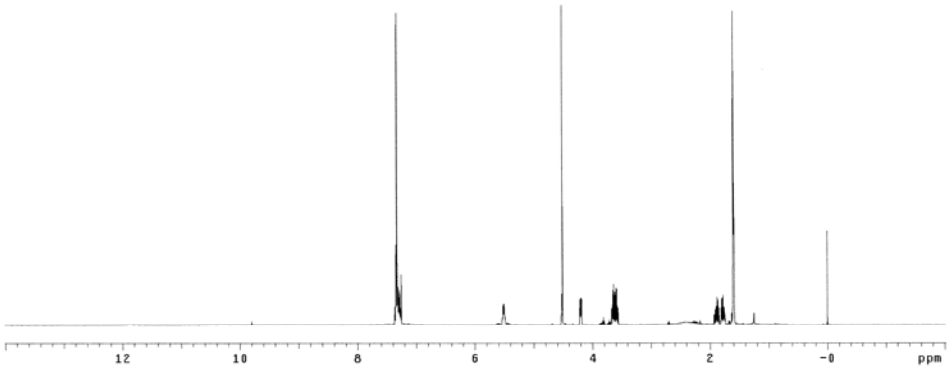
Procedure A (*via* alcohol 1i): After heating the reaction at 95 ^{o}C for 13 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (46 mg, 69%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.37-6.26 (m, 5H), 5.55-5.48 (m, 1H) 4.51 (s, 2H) 4.20 (dd, J = 8.4, 4.0 Hz, 1H) 3.68-3.56 (m, 2H) 1.94-1.84 (m, 1H) 1.82-1.74 (m, 1H) 1.62-1.58 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 138.2, 137.6, 128.6, 127.9, 120.3, 76.6, 73.5, 69.0, 35.0, 13.2, 11.7.

HRMS (CI) Calcd. for $C_{14}H_{21}O_2$ $[M+H]^+$: 221.1542, Found: 221.1548.

FTIR (neat): 3416, 2919, 2859, 1453, 1096, 735, 696 cm^{-1}.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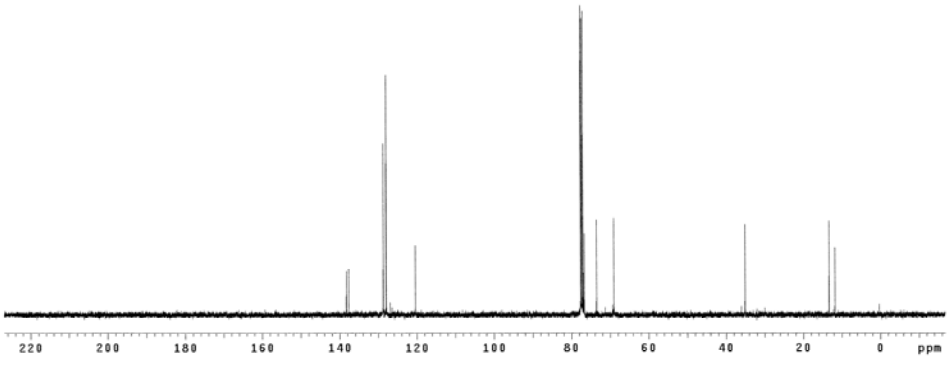
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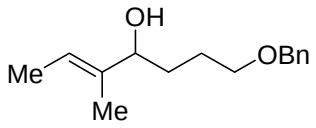
(*E*)-7-Benzyloxy-3-methylhept-2-en-4-ol (2j)



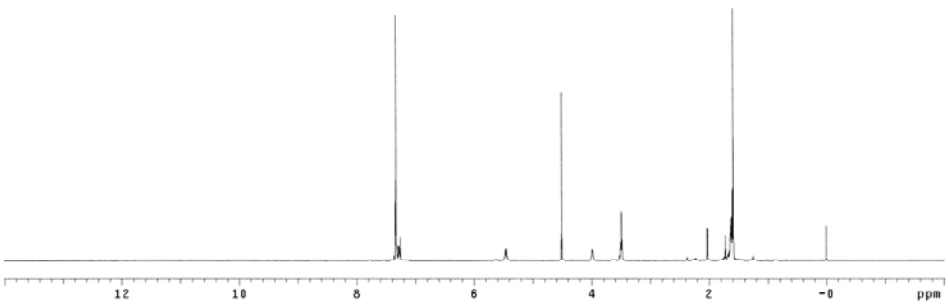
Procedure A (*via* alcohol 1j): After heating the reaction at 95 ^{o}C for 18 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (46 mg, 65%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.35-7.26 (m, 5H) 5.49-5.42 (m, 1H) 4.51 (s, 2H) 4.02-3.96 (m, 1H) 3.52-3.47 (m, 2H) 2.03 (d, J = 3.2 Hz, 1H) 1.65-1.58 (m, m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$): 138.5, 138.0, 128.6, 127.9, 127.8, 120.8, 77.8, 73.2, 70.6, 32.2, 26.4, 13.2, 11.2.

HRMS (CI) Calcd. for $C_{15}H_{23}O_2$ $[M+H]^+$: 235.1698, Found: 235.1702.

FTIR (neat): 3414, 2919, 2858, 1453, 1361, 1099, 735, 697 cm^{-1}.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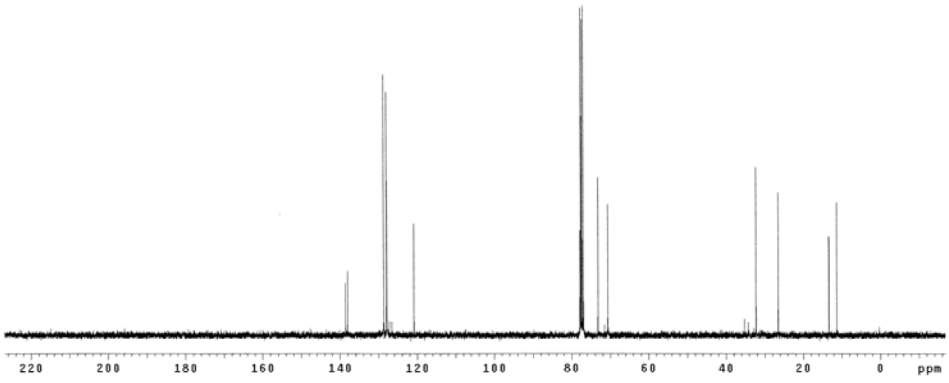
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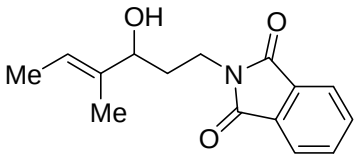
(*E*)-3-(3-Hydroxy-4-methylhex-4-enyl)-isoindole-1,3-dione (2k)



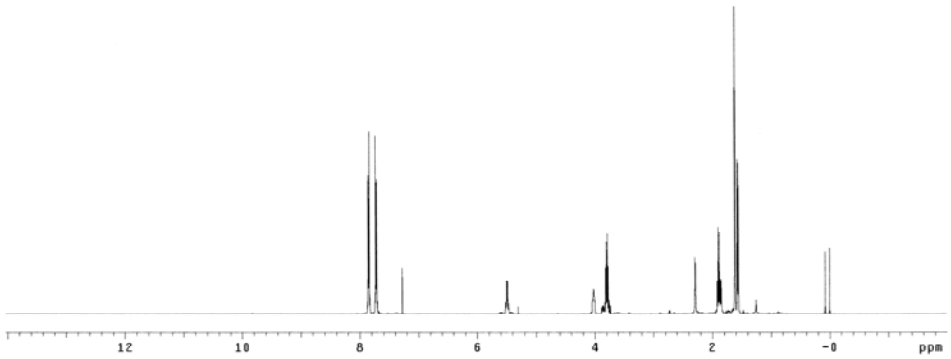
Procedure A (*via* alcohol 1k): After heating the reaction at 95 ^{o}C for 18 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (47 mg, 61%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.85 (dd, *J* = 5.2 Hz, 2H) 7.72 (dd, *J* = 5.6 Hz, 2H) 5.53-5.46 (m, 1H) 4.05-3.99 (m, 1H) 3.82-3.76 (m, 2H) 2.29 (d, *J* = 3.6 Hz, 1H) 1.92-1.84 (m, 2H) 1.63-1.61 (m, 3H) 1.57 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 168.9, 137.2, 134.2, 132.3, 123.4, 121.1, 74.9, 35.2, 33.9, 13.2, 11.5.

HRMS (CI) Calcd. for $C_{15}H_{18}NO_3$ $[M+H]^+$: 260.1287, Found 260.1286.

FTIR (neat): 3463, 2922, 1770, 1701, 1396, 1367, 719 cm^{-1}.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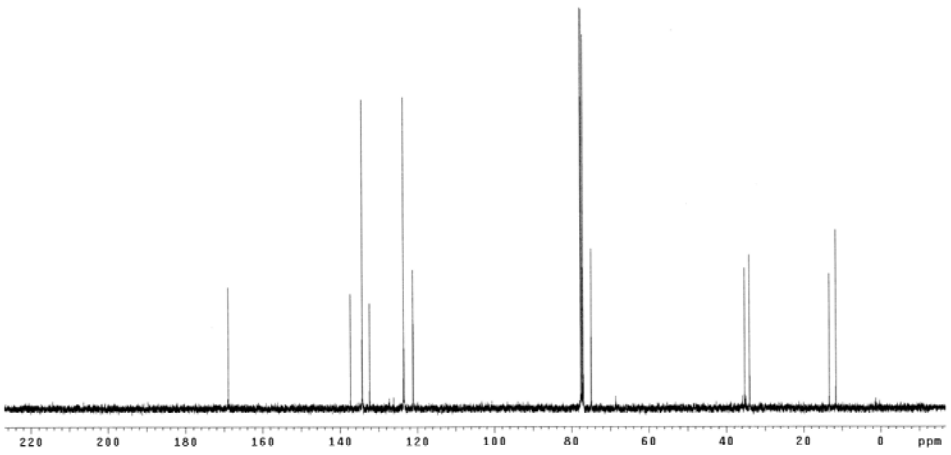
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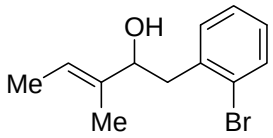
(*E*)-1-(2-Bromophenyl)-3-methylpent-3-en-2-ol (2l)



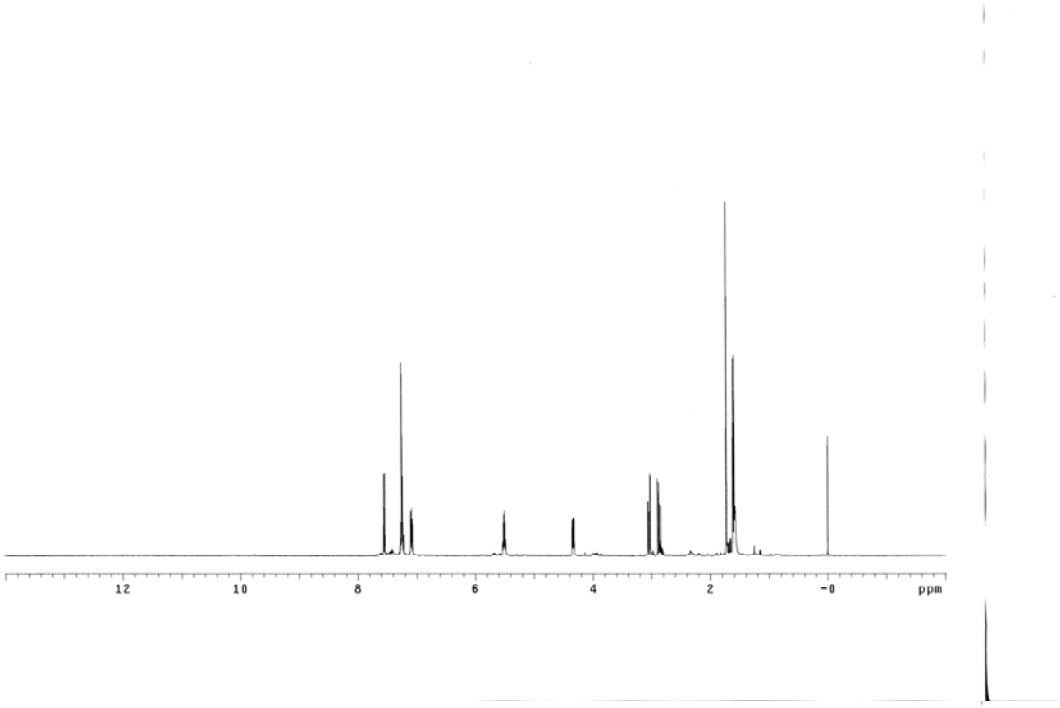
Procedure A (*via* alcohol 1l): After heating the reaction at 95 ^{o}C for 13 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (57 mg, 75%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.57-7.53 (m, 1H) 7.28-7.23 (m, 2H) 7.11-7.06 (m, 1H) 5.54-5.47 (m, 1H) 4.36-4.30 (m, 1H) 3.04 (dd, J = 13.6, 4.4 Hz, 1H) 2.86 (dd, J = 13.6, 8.8 Hz, 1H) 1.74-1.72 (m, 3H) 1.62-1.59 (m, 3H) 1.55 (d, J = 3.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): 138.5, 137.6, 133.1, 132.0, 128.3, 127.5, 125.0, 121.0, 76.8, 42.5, 13.2, 11.8.

HRMS (CI) Calcd. for $C_{12}H_{16}OBr$ $[M+H]^+$: 255.0385, Found: 255.0389.

FTIR (neat): 3383, 2920, 1471, 1439, 1025, 747 cm^{-1}.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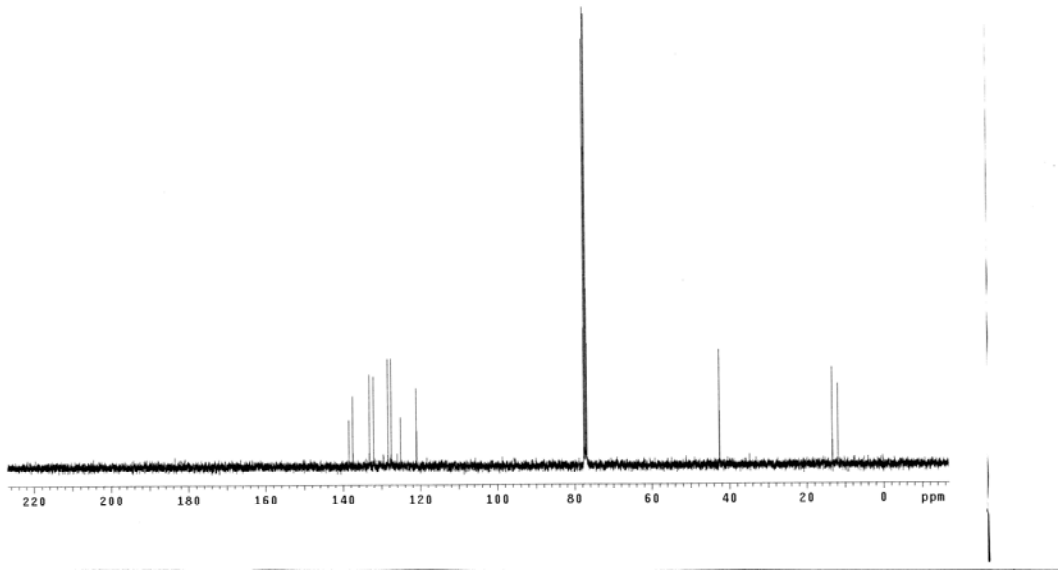
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Materials: Alkynes **6b**[4], **6c**[5], and **7a**[6] were synthesized according to literature procedure.

General Procedure C for the Coupling of Alkynes 6a-6c to 4-Nitrobenzyl Alcohol: To a resealable pressure tube equipped with magnetic stir bar was added $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ (13.2 mg, 0.015 mmol, 5 mol%) and 4-nitorbenzyl alcohol (45.9 mg, 0.300 mmol, 100 mol%). At this stage solid alkyne coupling partners (0.600 mmol, 200 mol%) were added. The tube was then sealed with a rubber septum and purged with argon. At this stage liquid alkyne coupling partners (0.600 mmol, 200 mol%) were added. THF (0.15 mL, 2.0 M concentration with respect to 4-nitrobenzyl alcohol) and isopropanol (46 μL, 0.600 mmol, 200 mol%) were added and the rubber septum was quickly replaced with a screw cap. 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 vinylated adduct.

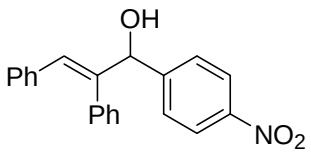
General Procedure D for the Coupling of Alkynes 6a-6c to 4-Nitrobenzaldehyde: To a resealable pressure tube equipped with magnetic stir bar was added $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ (13.2 mg, 0.015 mmol, 5 mol%), NaI (2.2 mg, 0.015 mmol, 5 mol%) and 4-nitorbenzaldehyde (45.3 mg, 0.300 mmol, 100 mol%). At this stage solid alkyne coupling partners (0.600 mmol, 200 mol%) were added. The tube was then sealed with a rubber septum and purged with argon. At this stage liquid alkyne coupling partners (0.300 mmol, 100 mol%) were added. THF (0.15 mL, 2.0 M concentration with respect to 4-Nitrobenzaldehyde) and formic acid (12 μL, 0.300, 100 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 65 ^{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 vinylated adduct.

[4] Fuji, K. Morimoto, T. Tsutsumi, K. Kakiuchi, K. *Chem. Commun.*, **2005**, 3295.

[5] Chen, M. Weng, Y. Guo, M. Zhang, H. Lei, A. *Angew. Chemie. Int. Ed.* **2008**, *47*, 2279.

[6] Rhee, J. U. Krische, M. J. *Org. Lett.* **2005**, *7*, 2493.

(*E*)-1-(4-Nitrophenyl)-2,3-diphenylprop-2-en-1-ol (2m)



Procedure C (*via* alcohol 1b): After heating the reaction at 95 ^{o}C for 37 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 100% PhMe – 2% EtOAc/PhMe) to afford the title compound (62 mg, 62%) as an orange solid.

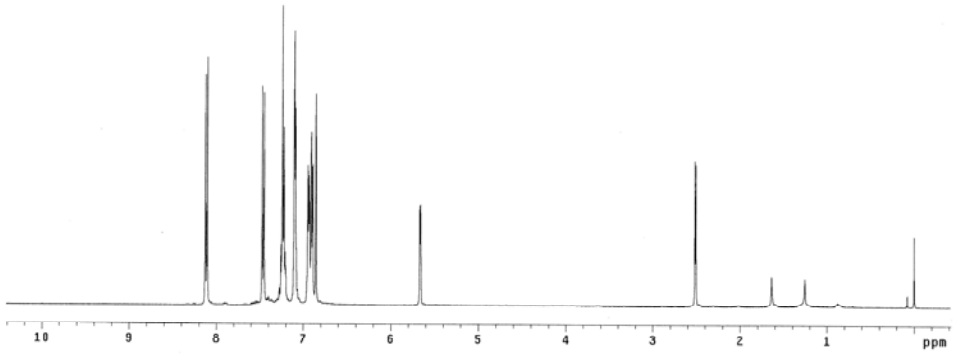
Procedure D (*via* aldehyde 4b): In a modification to procedure D, the reaction was heated at 95 ^{o}C for 24 hours. The mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 100% PhMe – 2% EtOAc/PhMe) to afford the title compound (91 mg, 91%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.12 (d, J = 8.7 Hz, 2H) 7.46 (d, J = 8.7 Hz, 2H) 7.29-7.18 (m, 3H) 7.15-7.05 (m, 2H) 6.99-6.88 (m, 4H) 6.86 (s, 1H) 5.67 (d, J = 3.8 Hz, 1H) 2.51 (d, J = 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): 149.0, 147.2, 142.7, 136.9, 135.6, 129.3, 128.7 (2 signals), 128.0, 127.8, 127.4, 127.3, 123.4, 78.6 (only 14 signals were observed).

HRMS (CI) Calcd. for $C_{21}H_{18}NO_2$ $[M+H]^+$: 332.1287, Found: 332.1288.

FTIR (neat): 3442, 3056, 3024, 1599, 1518, 1344, 906 cm^{-1}.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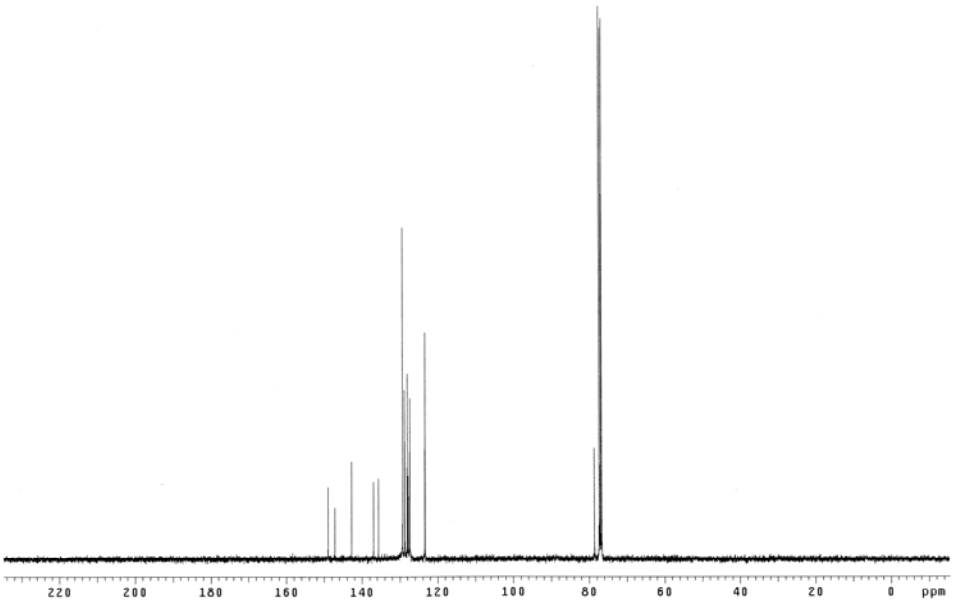
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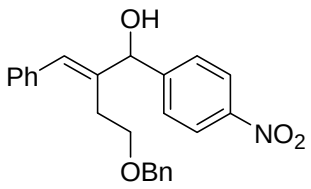
ppm

(*E*)-2-Benzylidene-4-benzyloxy-1-(4-nitrophenyl)-butan-1-ol (2n)



Procedure C (*via* alcohol 1b): After heating the reaction at 95 ^{o}C for 13 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 100% PhMe – 2% EtOAc/PhMe) to afford the title compound (68 mg, 58%) as a yellow oil.

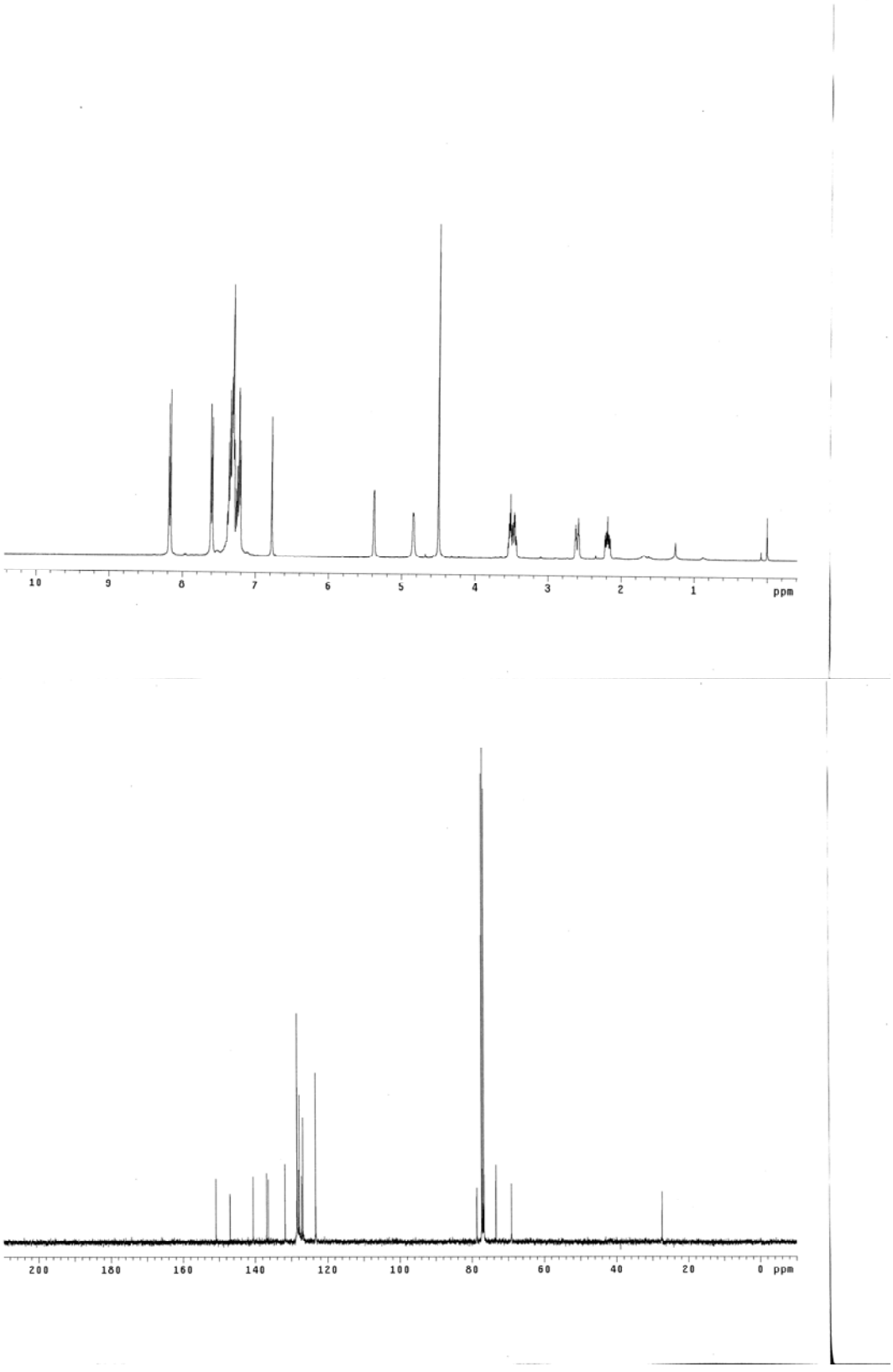
Procedure D (*via* aldehyde 4b): After heating the reaction at 65 ^{o}C for 16 hours the mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 100% PhMe – 2% EtOAc/PhMe) to afford the title compound (98 mg, 84%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.17 (d, J = 8.7 Hz, 2H) 7.60 (d, J = 8.7 Hz, 2H) 7.46-7.28 (m, 7H) 7.28-7.16 (m, 3H) 6.78 (s, 1H) 5.38 (d, J = 2.1 Hz, 1H) 4.84 (d, J = 4.4 Hz, 1H) 4.50 (s, 2H) 3.59-3.40 (m, 2H) 2.67-2.53 (m, 1H) 2.26-2.12 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): 150.9, 146.9, 140.6, 136.9, 136.4, 131.8, 128.5, 128.4, 128.1, 127.8, 127.2, 126.9, 123.3, 78.7, 73.4, 69.1, 27.4 (only 17 signals were observed).

HRMS (CI) Calcd. for $C_{24}H_{23}NO_4$ $[M+H]^+$: 389.1627, Found: 389.1628.

FTIR (neat): 3381, 3029, 2865, 1599, 1517, 1345, 1076, 739 cm^{-1}.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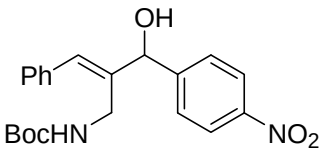
0 ppm

(*E*)-{2-[Hydroxy-(4-nitrophenyl)-methyl]-3-phenylallyl}-carbamic acid tert-butyl ester (2o)



Procedure C (*via* alcohol 1b): After heating the reaction at 95 ^{o}C for 13 hours the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 100% PhMe – 2% EtOAc/PhMe) to afford the title compound (18 mg, 15%) as an orange solid.

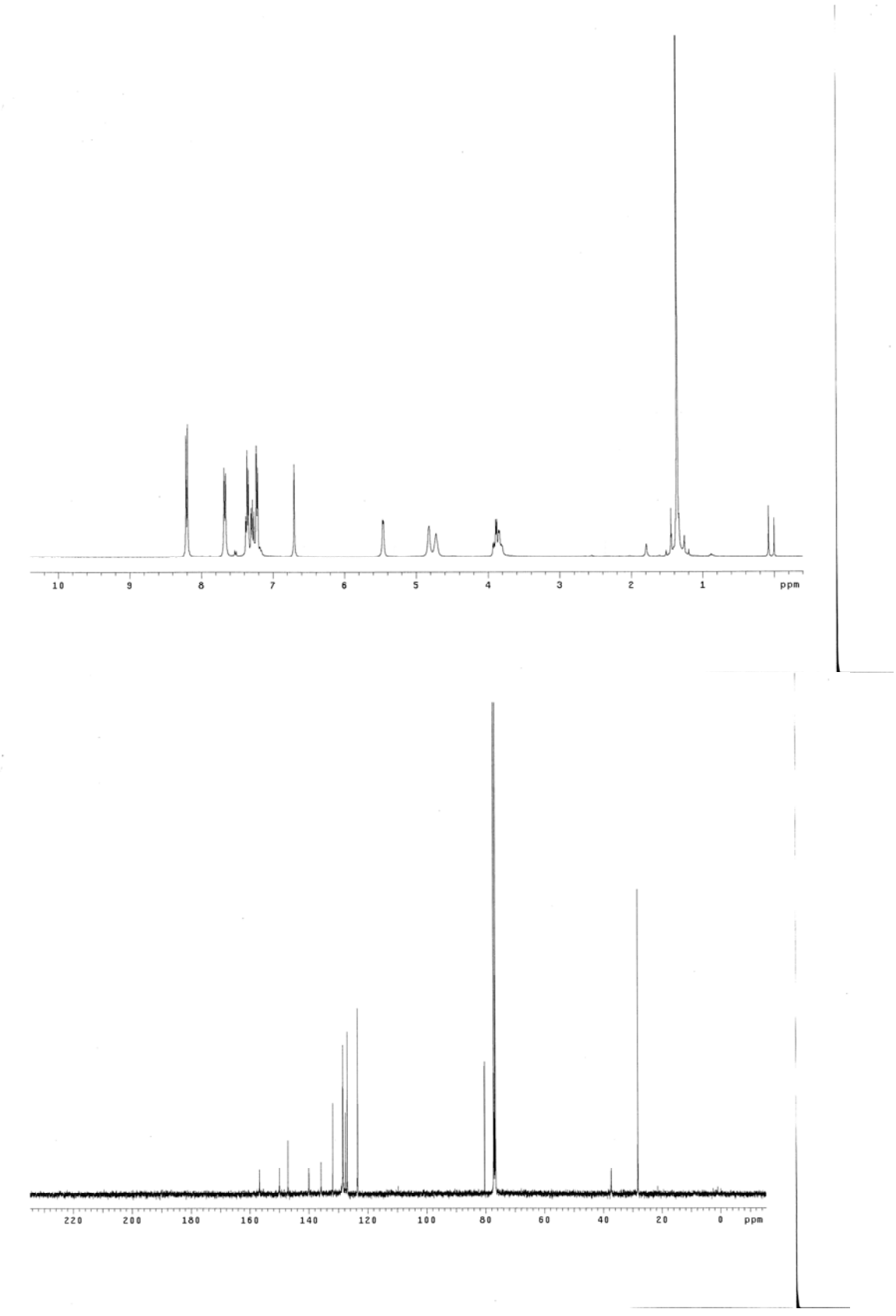
Procedure D (*via* aldehyde 4b): After heating the reaction at 65 ^{o}C for 13 hours the mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 100% PhMe – 2% EtOAc/PhMe) to afford the title compound (87 mg, 75%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.20 (d, J = 8.6 Hz, 2H) 7.67 (d, J = 8.6 Hz, 2H) 7.44-7.12 (m, 5H) 6.70 (s, 1H) 5.46 (d, J = 5.3 Hz, 1H) 4.81 (s, 1H) 4.72 (s, 1H) 3.90 (dd, J = 15.1, 5.3 Hz, 1H) 3.82 (dd, J = 15.1, 5.3 Hz, 1H) 1.36 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): 156.8, 150.0, 147.1, 140.0, 135.9, 131.9, 128.6, 128.4, 127.6, 127.0, 123.5, 80.3, 76.6, 37.3, 28.2.

HRMS (CI) Calcd. for $C_{21}H_{25}N_2O_5$ $[M+H]^+$: 385.1764, Found: 385.1766.

FTIR (neat): 3415, 2978, 2932, 1685, 1517, 1346, 1250, 1162, 907, 729 cm^{-1}.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140
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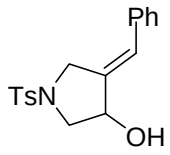
(*E*)-4-Benzylidene-1-(toluene-4-sulfonyl)-pyrrolidin-3-ol (8a)



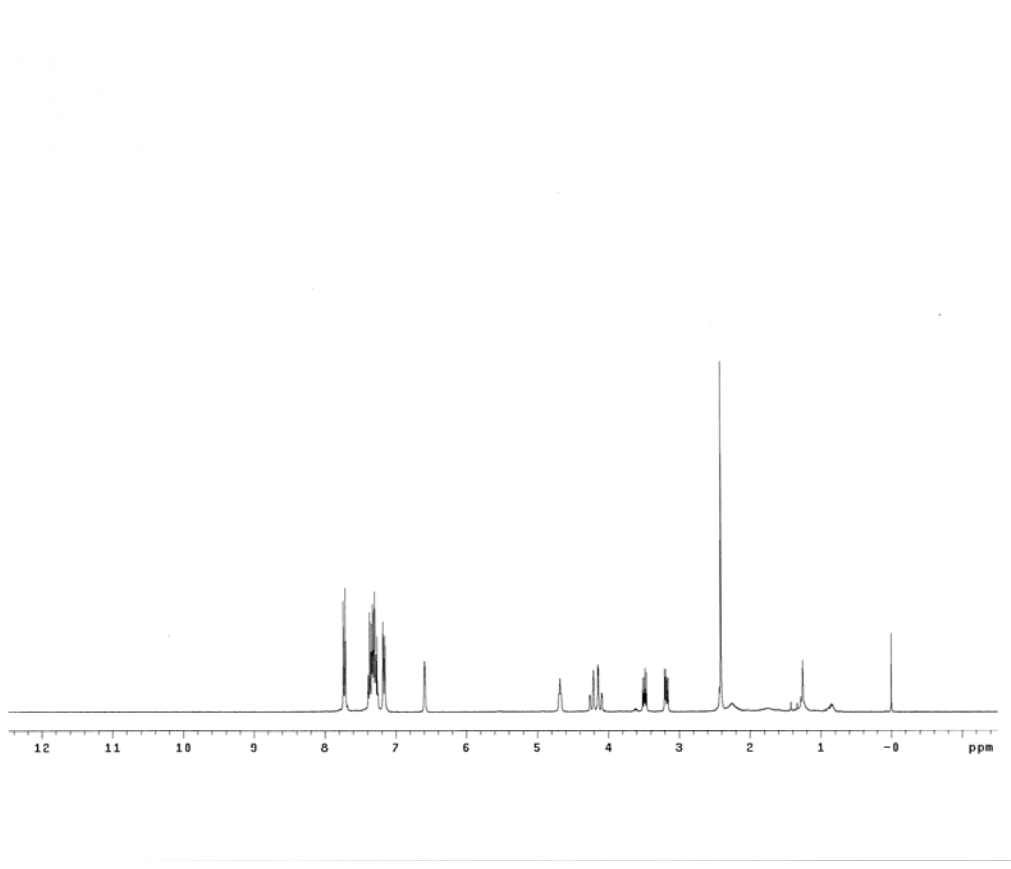
Procedure D (*via* aldehyde 7a): After heating the reaction at 65 ^{o}C for 16 hours the mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 25% EtOAc/Hex) to afford the title compound (83 mg, 84%) as a viscous yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.72 (d, *J* = 7.9 Hz, 2H) 7.42-7.22 (m, 4H) 7.15 (d, *J* = 7.9 Hz, 1H) 6.58 (s, 1H) 4.67 (t, *J* = 5.2 Hz, 1H) 4.21 (d, *J* = 14.9 Hz, 1H) 4.10 (d, *J* = 14.9 Hz, 1H) 3.47 (dd, *J* = 9.9, 5.2 Hz, 1H) 3.16 (dd, *J* = 9.9, 5.2 Hz, 1H) 2.39 (s, 3H) 2.26 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): 143.9, 138.4, 135.6, 132.6, 129.8, 128.6, 128.4, 127.7, 125.9, 73.4, 54.2, 49.4, 21.5 (only 13 signals were observed).

HRMS (CI) Calcd. for $C_{18}H_{20}NO_3S[M+H]^+$: 330.1164, Found: 330.1169.

FTIR (neat): 3479, 2918, 1597, 1493, 1449, 1336, 1152, 1091, 1039, 910, 813 cm^{-1}.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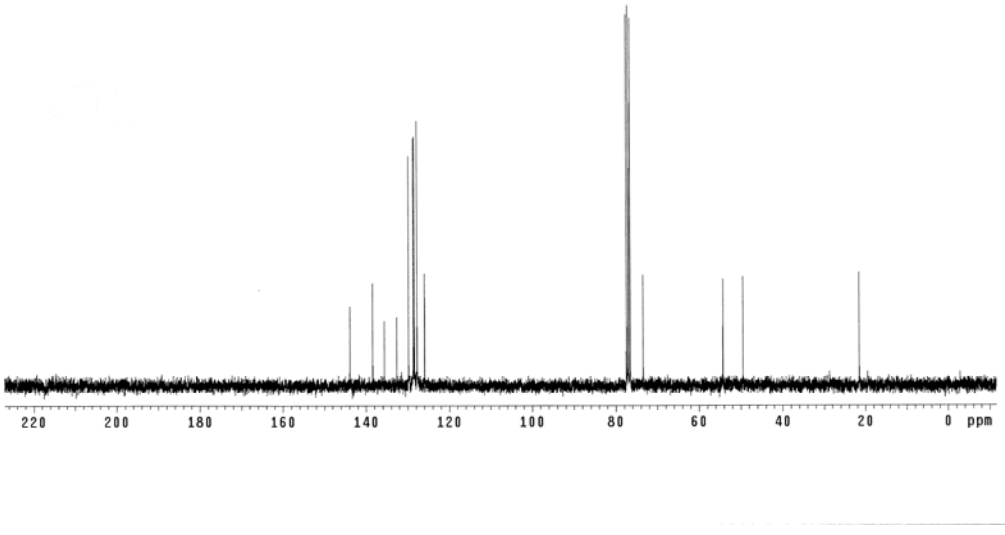
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