Carbohydrate-Derived Amino-Alcohol Ligands for Asymmetric Alkynylation of Aldehydes

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Supplementary Information

1. General Methods

1.1 Solvents

Ether and THF were distilled under an atmosphere of nitrogen from sodium benzopheneone ketyl or dried over alumina. DCM was distilled under an atmosphere of nitrogen from calcium hydride. Toluene was dried over alumina or was purchased dry from Fluka. Other dry solvents were purchased dry from Fluka.

1.2 Reagents

Reactions performed under an atmosphere of argon or nitrogen were maintained by means of an inflated balloon or connected to a gas line. Aldehydes were distilled prior to use and all other reagents were used as supplied.

1.3 Chromatography

Thin layer chromatography (tlc) was performed on Merck F254 silica gel pre-coated, aluminium-backed plates coated with 60 F_{254} silica. Plates were visualised using UV and 5% ammonium molybdate in 2 M sulfuric acid; 2.5% phosphomolybdic acid and 1% cerium sulfate in 2 M sulfuric acid; 0.5% potassium permanganate in 1 M sodium hydroxide; or 0.2% ninydrin in ethanol. Silica gel (Merck, 400 mesh) was used for column chromatography.

1.4 Melting Points

Melting points were determined on a Leica Galen III Köfler block melting point apparatus and are uncorrected.

1.5 Polarimetry

Optical rotations were measured on a Perkin-Elmer 241 polarimeter with a path length of 1 dm; concentrations are recorded in g/100mL.

1.6 Elemental Analysis

Elemental analysis was performed by the Inorganic Chemistry Laboratory, Oxford. Results are given to the nearest 0.5%.

1.7 Infrared Spectroscopy

Infrared (IR) spectra were recorded on a Perkin-Elmer 1000 or Bruker Tensor 27 FT-IR spectrophotometer using thin films on sodium chloride plates or KBr disks. Only the characteristic peaks are quoted.

1.8 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker dpx or av 400 MHz or dpx 200 MHz spectrometers. Assignments of peaks were made by means of COSY, HMQC, and APT or DEPT experiments. Coupling constants are given in Hz and are quoted as measured without averaging. For ^{13}C spectra, multiplicity was determinined by means of APT.

1.9 Gas Chromatography

Gas Chromatograms were measured using a β-CD chir-DEX, 25 m column on a CE Instruments trace gas chromatograph.

1.10 Mass Spectrometry

Low-resolution mass spectra were recorded using the following techniques: electrospray (ES), field ionisation (FI) and atmospheric pressure chemical ionisation (APCI). High-resolution mass

spectrometry was performed on either a) a Micromass LCT (resolution = 5000 FWHM) using a lock-spray source; the calibration is corrected using a lock-mass; in positive ion this is tetraoctylammonium bromide and in negative ion, sodium dodecyl sulphate; or b) a Bruker Micro Tof (resolution = 10,000 FWHM) with internal calibration.

2 Ligand Preparation

Ligand Data

4a Methyl 4-6-*O*-benzylidene-2-deoxy-2-(4-morpholinyl)-α-D-glucopyranoside, white solid; R_f 0.4 (5% MeOH/$CHCl_3$); mp 155-157.5 °C (DCM); $[\alpha]_D^{24}$ +92 (*c* 1.97, $CHCl_3$); (Found: C 61.50, H 7.20, N 4.00. $C_{18}H_{25}NO_6$ requires C 61.50, H 7.15, N 4.00%); ν_{max}/cm^{-1} (KBr) 3440 (OH), 3067w (CH, aromatic), 2975, 2928, 2863 (CH, aliphatic), 1458 (CC, aromatic); δ_H(400 MHz, $CDCl_3$) 7.52-7.49 (2H, m, Ph), 7.39-7.34 (3H, m, Ph), 5.57 (1H, s, C*H*Ph), 4.85 (1H, d, *J* 3.1, H-1), 4.27 (1H, dd, *J* 9.6 and 4.2, H-6), 4.18 (1H, dd, *J* 10.3 and 9.1, H-3), 3.83 (1H, ddd, *J* 10.3, 9.0 and 4.3, H-5), 3.76 (1H, pt, *J* 9.6, H-6'), 3.71 (2H, ddd, *J* 11.1, 5.7 and 3.4, CH_2O), 3.66 (2H, ddd, *J* 11.1, 5.7 and 3.4, CH_2O), 3.57 (1H, pt, *J* 9.1, H-4), 3.40 (3H, s, OCH_3), 3.15 (1H, s, OH), 2.84 (4H, m, CH_2N), 2.70 (1H, dd, *J* 10.6 and 3.1, H-2); δ_H(400 MHz, THF-d_8) 7.48-7.46 (2H, m, Ph), 7.32-7.28 (3H, m, Ph), 5.51 (1H, s, C*H*Ph), 4.67 (1H, d, *J* = 3.8, H-1), 4.46 (1H, d, *J* = 3.1, OH), 4.16-4.09 (2H, m, H-3, H-6), 3.66-3.64 (2H, m, H-5, H-6), 3.54 (4H, pt, *J* = 4.7×, OCH_2), 3.41 (1H, m, H-4), 3.34 (3H, s, OCH_3), 3.12 (2H, m, NCH_2), 2.69 (2H, m, NCH_2), 2.57 (1H, dd, *J* = 10.6, 3.4, H-2); δ_C(100 MHz, $CDCl_3$) 137.2, 129.1, 128.2, 126.3 (4 × Ph), 101.8 (Ph*C*H), 99.3 (C-1), 83.2 (C-4), 69.1 (C-6), 68.6 (C-2), 67.8 (CH_2O), 65.4 (C-3), 62.2 (C-5), 54.7 (OCH_3), 50.3 (CH_2N); *m*/*z* (TOF, ES+) 352.1772 ($[M+H]^+$, $C_{18}H_{26}NO_6$ requires 352.1760).

4b Methyl 4-6-*O*-benzylidine-2-deoxy-2-(1-pyrrolidinyl)-α-D-glucopyranoside, semi-crystalline, white solid; R_f = 0.2 (10 % MeOH/ EtOAc); m.p. partial melting, 120° C, melts 132-134° C (DCM/ petroleum ether);$[\alpha]_D^{24}$ = +77 (*c* 2.29, $CHCl_3$); ν_{max}/cm^{-1} 3422 (O–H), 2928, 2853 (C–H aliphatic), 1456 (C–C aromatic); δ_H (400 MHz, $CDCl_3$) 7.52-7.49 (2H, m, Ph), 7.39-7.36 (3H, m, Ph), 5.56 (1H, s, PhC*H*), 5.07 (1H, d, *J* = 3.0 Hz, H-1), 4.28 (1H, dd, *J* = 10.1 Hz, 4.5 Hz, H-6), 4.22 (1H, dd, *J* = 10.4 Hz, 9.1 Hz, H-3), 3.84 (1H, ptd, *J* = 9.8 Hz, 4.4 Hz, H-5), 3.75 (1H, pt, *J* = 10.3 Hz, H-6'), 3.56 (1H, pt, *J* = 9.1 Hz, H-4), 3.42 (3H, s, OCH_3), 3.12-3.08 (2H, m, NCH_2), 3.05 (1H, dd, *J* = 10.4 Hz, 3.3 Hz, H-2), 2.99-2.94 (2H, m, NCH_2), 1.83 (4H, m, NCH_2CH_2); δ_C(100 MHz, $CDCl_3$): 137.1, 129.2, 128.3,

126.3 (Ph), 101.9 (*C*HPh), 98.7 (C-1), 82.6 (C-4), 69.0 (C-6), 67.2 (C-3), 64.2 (C-2), 62.1 (C-5), 54.9 (OCH3), 50.1 (NCH2), 23.4 (NCH2*C*H2); *m*/*z* (TOF, ES+) 336.1812 ([M+H]+, $C_{18}H_{26}NO_5$ requires 336.1811)

4c Methyl 4-6-*O*-benzylidene-2-deoxy-2-(1-piperidinyl)-α-D-glucopyranoside, white solid; R_f 0.4 (10% MeOH/EtOAc); $[\alpha]_D^{24}$ +106 (*c* 1.63, $CHCl_3$); (Found: C 65.00, H 7.70, N 4.00. $C_{19}H_{27}NO_5$ requires C 65.30, H 7.80, N 4.00%); ν_{max}/cm^{-1} (KBr) 3454br (OH), 2929, 2852 (CH, aliphatic), 1455 (CC, aromatic); δ_H(400 MHz, $CDCl_3$) 7.53-7.51 (2H, m, Ph), 7.38-7.33 (3H, m, Ph), 5.58 (1H, s, C*H*Ph), 4.85 (1H, d, *J* 3.0, H-1), 4.26 (1H, dd, *J* 9.6 and 4.3, H-6), 4.13 (1H, dd, *J* 10.6 and 8.8, H-3), 3.84 (1H, ddd, *J* 10.3, 9.1 and 4.4, H-5), 3.77 (1H, pt, *J* 10.0, H-6'), 3.59 (1H, pt, *J* 9.0, H-4), 3.39 (3H, s, OCH_3), 2.83-2.78 (2H, m, NCH_2), 2.67 (1H, dd, *J* 10.6 and 3.0, H-2), 2.67-2.63 (2H, m, NCH_2), 1.63-1.46 (6H, m, NCH_2CH_2, $NCH_2CH_2CH_2$); δ_C(100 MHz, $CDCl_3$) 137.3, 129.0, 128.1, 126.4 (Ph), 101.7 (*C*HPh), 98.8 (C-1), 83.4 (C-4), 69.4 (C-2), 69.1 (C-6), 64.8 (C-3), 62.3 (C-5), 54.6 (OCH_3), 51.0 (NCH_2), 27.0 (NCH_2CH_2), 24.7 ($NCH_2CH_2CH_2$); *m*/*z* (TOF, ES+) 350.1971 ($[M+H]^+$, $C_{19}H_{28}NO_5$ requires 350.1967).

4d Methyl 4,6-*O*-benzylidene-2-deoxy-2-*N*,*N*-diethylamino-α-D-glucopyranoside, colourless syrup; R_f 0.4 (10% MeOH/EtOAc); $[\alpha]_D^{24}$ +113 (*c* 1.23, $CHCl_3$); (found: C 63.65, H 8.4, N 4.1. $C_{18}H_{27}NO_5$ requires C 64.1, H 8.1, N 4.15%); ν_{max}/cm^{-1} ($CHCl_3$) 3431br (OH), 2969, 2928, 2858 (CH, aliphatic), 1459w (CC, aromatic); δ_H(400 MHz, $CDCl_3$) 7.54-7.51 (2H, m, Ph), 7.38-7.33 (3H, m, Ph), 5.59 (1H, s, C*H*Ph), 4.83 (1H, d, *J* 2.5, H-1), 4.27 (1H, dd, *J* 9.8 and 4.5, H-6), 4.08 (1H, dd, *J* 10.5 and 8.8, H-3) 3.85 (1H, ddd, *J* 10.4, 9.2 and 4.5, H-5), 3.77 (1H, pt, *J* 10.1, H-6'), 3.61 (1H, pt, *J* 9.0, H-4), 3.47 (1H, s, OH), 3.38 (3H, s, OCH_3), 2.90 (2H, dq, *J* 13.7 and 7.4, NCH_2), 2.84 (1H, dd, *J* 10.5 and 3.0, H-2), 2.62 (2H, dq, *J* 13.7 and 7.0, NCH_2), 1.06 (3H, pt, *J* 7.6, CH_2CH_3); δ_C(100 MHz, $CDCl_3$) 137.3, 129.0, 128.2, 126.4 (Ph), 101.7 (*C*HPh), 99.2 (C-1), 83.3 (C-4), 69.1 (C-6), 65.4 (C-3), 64.8 (C-2), 62.2 (C-5), 55.9 (OCH_3), 44.4 (NCH_2), 14.8 (CH_2CH_3); *m*/*z* (TOF, ES+) 338.1974 ($[M+H]^+$, $C_{18}H_{28}NO_5$ requires 338.1967).

4e Methyl 4,6-*O*-benzylidine-2-deoxy-2-*N*,*N*-di-*n*-propylamino-α-D-glucopyranoside, colourless syrup (186 mg, 72%); R_f 0.6 (5% MeOH/$CHCl_3$); $[\alpha]_D^{24}$ +123 (*c* 1.84, $CHCl_3$); (Found: C 65.3, H 8.6, N 3.8. $C_{20}H_{31}NO_5$ requires C 65.75, H 8.55, N 3.85%); ν_{max}/cm^{-1} ($CHCl_3$) 3438 (OH), 2936, 2933, 2874, 2842 (CH, aliphatic), 1470, 1458 (CC, aromatic); δ_H(400 MHz, $CDCl_3$) 7.53-7.51 (2H, m, Ph), 7.38-7.31 (3H, m, Ph), 5.59 (1H, s, C*H*Ph), 4.83 (1H, d, *J* 3.0, H-1), 4.27 (1H, dd, *J* 9.9 and 4.5, H-6),

4.09 (1H, dd, *J* 10.5 and 8.7, H-3), 3.85 (1H, ptd, *J* 9.9 and 4.5, H-5), 3.77 (1H, pt, *J* 10.1, H-6'), 3.61 (1H, pt, *J* 9.0, H-4), 3.38 (3H, s, OCH_3), 2.81 (1H, dd, *J* 10.5 and 3.2, H-2), 2.74 (2H, ddd, *J* 13.5, 9.0 and 7.2, NCH_2), 2.53 (2H, ddd, *J* 13.5, 8.7 and 4.7, NCH_2), 1.55-1.34 (4H, m, CH_3CH_2), 0.88 (6H, t, *J* 7.3, CH_2CH_3); δ_C(100 MHz, $CDCl_3$) 137.3, 129.0, 128.2, 126.4 (4 × Ph), 101.7, (*C*HPh), 99.1 (C-1), 83.3 (C-4), 69.2 (C-6), 65.6 (C-3), 65.0 (C-2), 62.2 (C-5), 54.8 (OCH_3), 52.7 (NCH_2), 22.3 (CH_2CH_3), 11.6 (CH_2CH_3); *m/z* (TOF, ES+) 366.2287 ($[M+H]^+$, $C_{20}H_{32}NO_5$ requires 366.2280).

4f Methyl 2-*N,N*-dibenzylamino-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside white, solid (0.9 g, 68%); mp 148-149 °C (EtOAc /cyclohexane); $[\alpha]_D^{25}$ +49.3 (*c* 1.1, $CHCl_3$); ν_{max}/cm^{-1} (KBr) 3474 (OH), 3083, 3061, 3023, 3000 (CH aromatic), 2934, 2902, 2870, 2837 (CH aliphatic), 1602, 1493, 1466, 1454 (CC aromatic); δ_H(400 MHz, $CDCl_3$) 7.56-7.26 (15H, m, Ph), 5.53 (1H, s, PhC*H*), 4.79 (1H, d, *J* 3.3, H-1), 4.37 (1H, pt, *J* 10.2, H-3), 4.27 (1H, dd, *J* 10.1 and 4.8, H-6), 4.00 (2H, d, *J* 13.6, $C_6H_5CH_2$), 3.94-3.82 (1H, m, H-5), 3.86 (2H, d, *J* 13.6, $C_6H_5CH_2$), 3.70 (1H, pt, *J* 10.2, H-6'), 3.49-3.45 (1H, m, H-4), 3.47 (3H, s, OMe), 3.06 (1H, s br, OH), 2.90 (1H, dd, *J* 3.2 and 10.5, H-2); δ_C(125.9 MHz, $CDCl_3$) 140.2, 137.5, (s × 2, Ph), 129.3, 129.0, 128.7, 128.5, 127.4, 126.5 (t × 6, Ph), 101.9 (d, Ph*C*H), 100.6 (d, C-1), 83.5 (d, C-4), 69.3 (d, (C-3), 67.5 (t, C-6), 62.1 (q, OMe), 62.0 (d, C-5), 55.4, 55.3, (t × 2, $C_6H_5CH_2$); *m/z* (ES+) 485 (M^++Na, 22%); 462 (M^+, 100%), 128 (65%); (TOF, ES+) 462.2287 ($[M+H]^+$, $C_{28}H_{32}NO_5$ requires 462.2280).

5 Methyl 4-6-*O*-benzylidene-2-deoxy-2-(4-morpholinyl)-β-D-glucopyranoside white solid; R_f 0.6 (5% MeOH/$CHCl_3$); mp 148-150 °C (DCM); $[\alpha]_D^{24}$ –24 (*c* 1.73, $CHCl_3$); ν_{max}/cm^{-1} (KBr) 3460 (O–H), 3032w (C–H, aromatic), 2994, 2968, 2907, 2874, 2814 (C–H, aliphatic), 1471, 1455 (C–C, aromatic); δ_H(400 MHz, $CDCl_3$) 7.52-7.50 (2H, m, Ph), 7.39-7.34 (3H, m, Ph), 5.57 (2H, s, C*H*Ph), 4.54 (1H, d, *J* 8.5, H-1), 4.33 (1H, dd, *J* 10.4 and 4.9, H-6), 3.82 (1H, pt, *J* 10.2, H-6'), 3.76 (1H, dd, *J* 10.1 and 9.0, H-3), 3.72, 3.67 (4H, 2 × ddd, *J* 8.0, 6.3 and 2.9, CH_2O), 3.61 (1H, pt, *J* 9.0, H-4), 3.56 (3H, s, OCH_3), 3.40 (1H, ddd, *J* 10.1, 9.3 and 5.0, H-5), 3.06 (2H, br m, CH_2N), 2.63 (2H, ddd, *J* 11.3, 6.1 and 3.2, CH_2N), 2.43 (1H, dd, *J* 10.2 and 8.5, H-2); δ_C(100 MHz, $CDCl_3$) 137.1, 129.1, 128.2, 126.3 (4 _ Ph), 102.5 (C-1), 101.6 (*C*HPh), 81.5 (C-4), 70.3 (C-2), 68.7 (C-6), 67.74 (CH_2O), 67.71 (C-3), 66.7 (C-5), 56.6 (OCH_3), 50.2 (br, CH_2N); *m/z* (TOF, ES+) 352.1760 ($[M+H]_+$, $C_{18}H_{26}NO_6$ requires 352.1760).

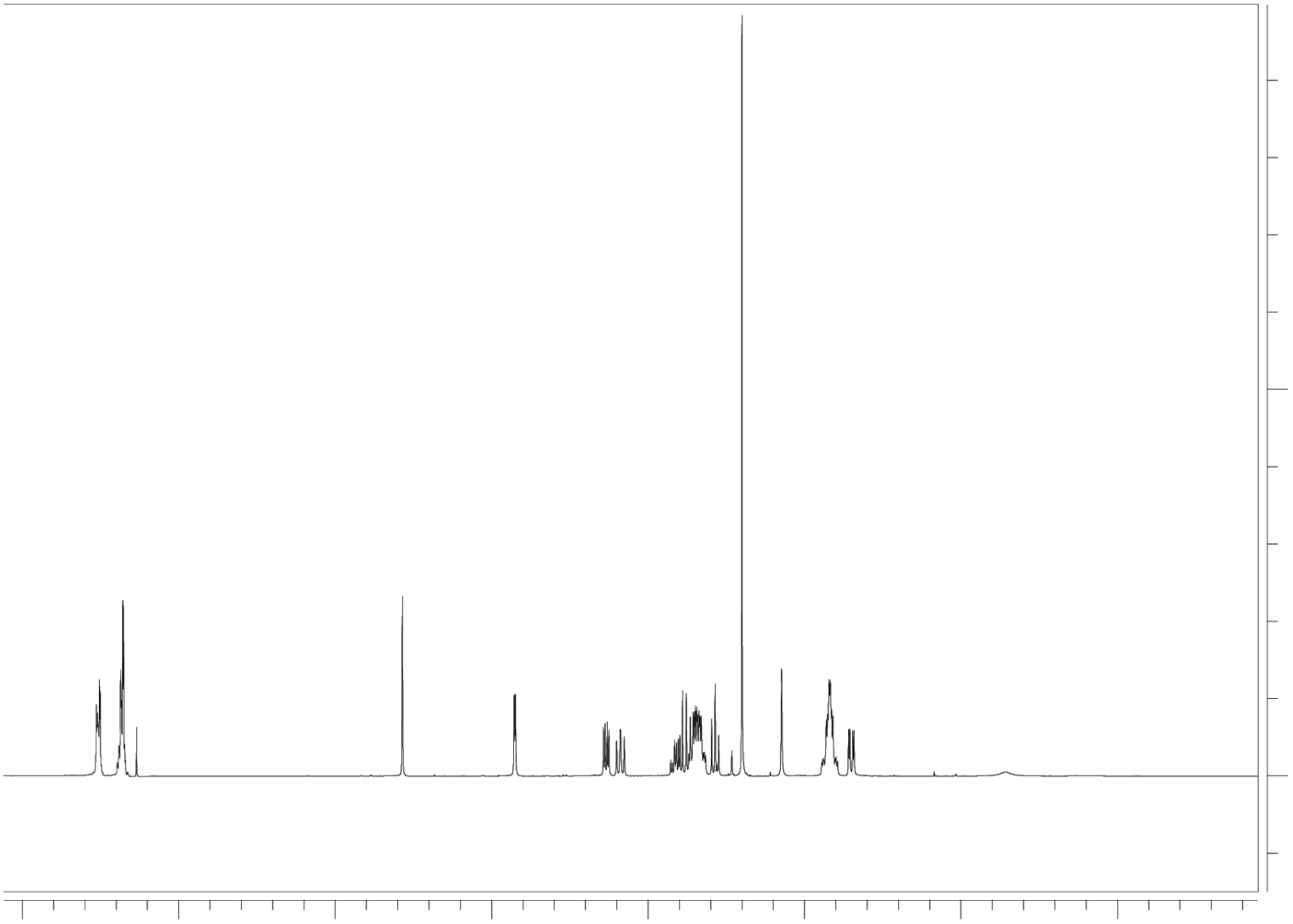
6 Methyl 4,6-*O*-benzylidene-2-deoxy-2-(4-morpholinyl)-α-D-allopyranoside, white solid; R_f 0.15 (EtOAc); mp 134-136 °C (EtOAc); $[\alpha]_D^{24}$ +59 (*c* 1.02, $CHCl_3$); ν_{max}/cm^{-1} 3484 (O-H), 2927, 2856 (C-H aliph); δ_H(400 MHz, $CDCl_3$) 7.53-7.50 (2H, m, Ph), 7.38-7.33 (3H, m, Ph), 5.59 (1H, s, PhC*H*), 4.87

(1H, d, *J* 3.3, H-1), 4.40 (1H, br s, H-3, 4.38 (1H, dd, *J* 10.2 and 5.1, H-6), 4.21 (1H, ptd, *J* 10.0 and 5.1, H-5), 3.79 (4H, pt, *J* 4.7, OCH_2), 3.76 (1H, pt, *J* 10.4, H-6'), 3.50 (1H, dd, *J* 9.7 and 2.6, H-4), 3.43 (3H, s, OCH_3), 3.21 (1H, s, OH), 2.73 (2H, m, NCH_2), 2.53 ((2H, m, NCH_2), 2.38 (1H, pt, *J* 3.1, H-2); δ_C(100 MHz, $CDCl_3$) 139 (s, Ph), 129.1, 128.2, 126.3 (3 × d, Ph), 102.1 (d, *C*HPh), 98.4 (d, H-1), 79.6 (d, C-4), 69.2 (t, C-6), 66.7 (t, OCH_2), 65.8 (d, C-2), 64.6 (d, C-3), 57.8 (d, C-5), 55.4 (q, OCH_2), 50.4 (t, NCH_2). *m*/*z* (TOF, ES+) 352.1759 ($[M+H]^+$, $C_{18}H_{26}NO_6$ requies 352.1760).

7 Methyl 4,6-*O*-benzylidene-2-deoxy-2-(4-morpholinyl)-α-D-mannopyranoside, white solid; R_f 0.43 (1:1 petrol/ ethyl acetate); mp. 168-170° C (EtOAc); $[\alpha]_D^{24}$ –3.8 (*c* 0.95, $CHCl_3$); ν_{max}/cm^{-1} 3316 (O–H), 2972, 2906, 2836 (C–H, aliphatic) δ_H(400 MHz, $CDCl_3$) 7.53–7.51 (2H, m, Ph), 7.38–7.34 (3H, m, Ph), 5.60 (1H, s, PhC*H*), 4.91 (1H, s, H-1), 4.27 (1H, dd, *J* 9.6 and 4.2, H-6), 4.04 (1H, dd, *J* 9.8 and 6.9, H-3), 3.82 (1H, ptd, *J* 9.3 and 4.4, H-5), 3.77–3.69 (5H, m, OCH_2, H-6'), 3.67 (1H, pt, *J* 9.5, H-4), 3.38 (3H, s, OCH_3), 3.00 (1H, d, *J* 6.8, H-2), 2.92 (2H, ddd, *J* 11.2, 6.2 and 3.1, NCH_2), 2.67 (2H, ddd, *J* 11.5, 5.9 and 3.1, NCH_2); δ_C(100 MHz, $CDCl_3$) 137.2 (s, Ph), 129.1, 128.2, 126.3 (3 × d, Ph), 102.1 (*C*HPh), 97.2 (C-1), 81.1 (d, C-4), 69.0 (t, C-6), 67.3 (t, OCH_2), 66.8 (d, C-2), 66.0 (d, C-3), 62.2 (d, C-5), 54.7 (q, OCH_3), 52.2 (t, NCH_2); *m*/*z* (TOF, ES+) 352.1753 ($[M+H]^+$, $C_{18}H_{26}NO_6$ requies 352.1760).

Ligand Spectra

4a



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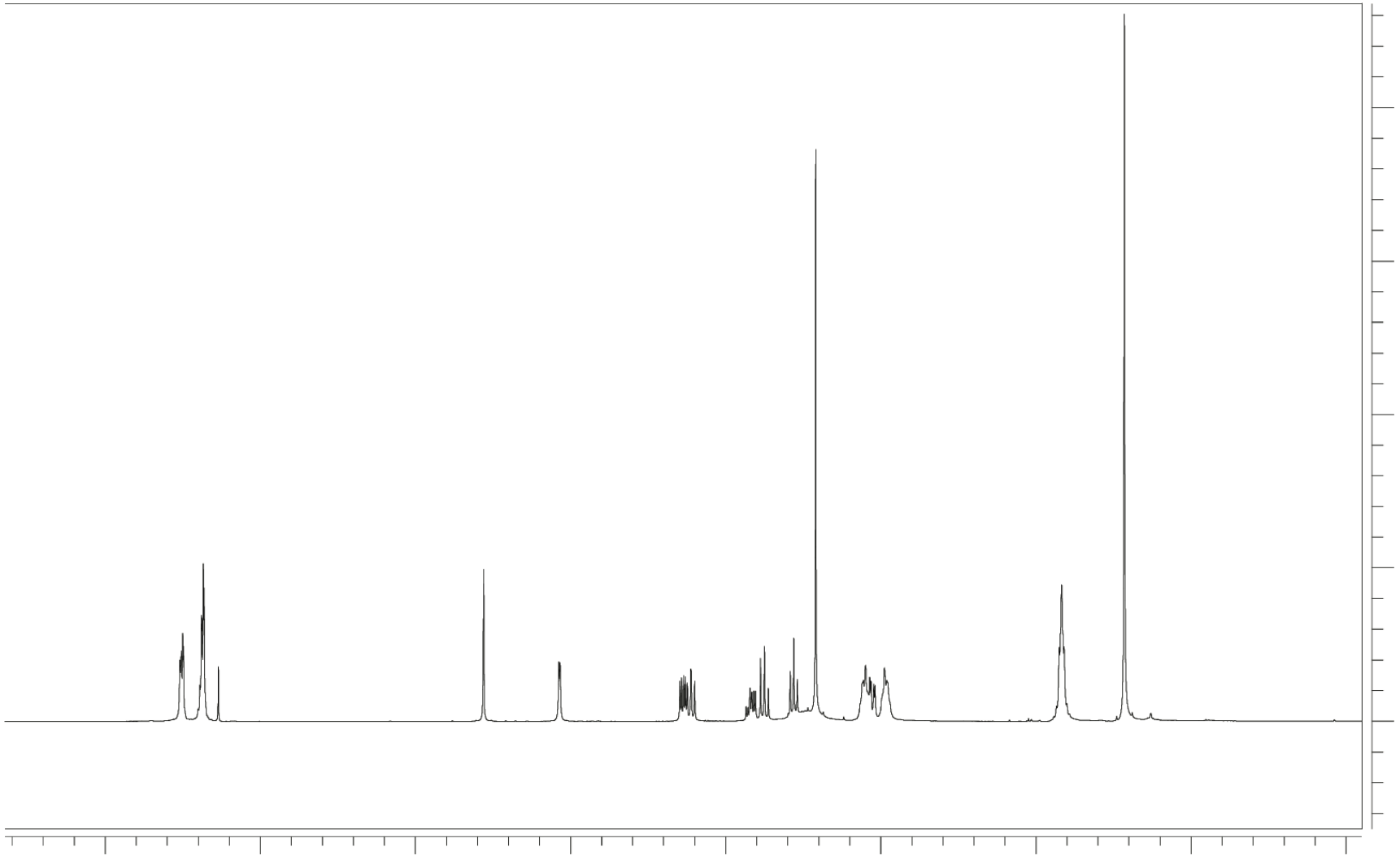

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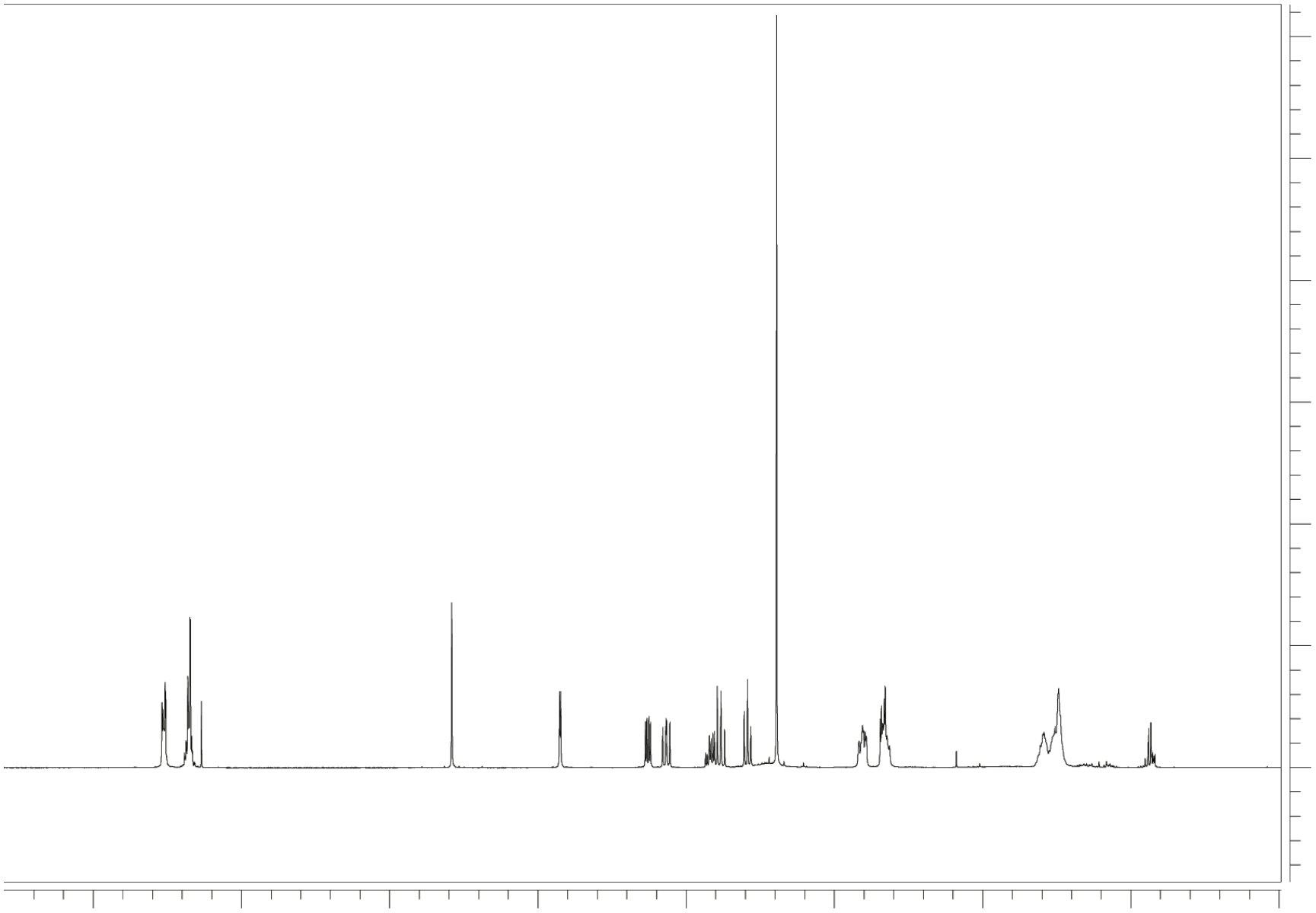

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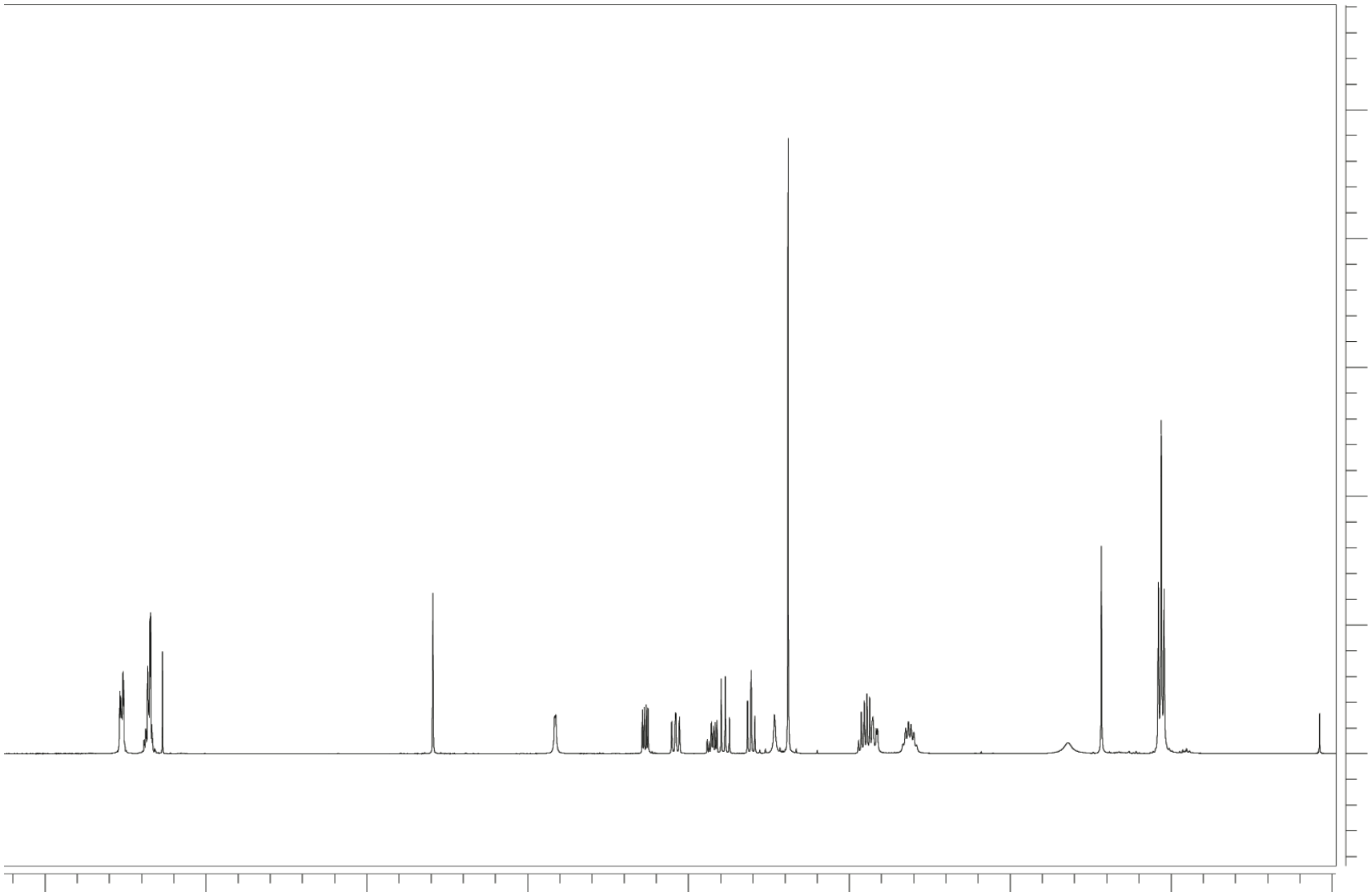

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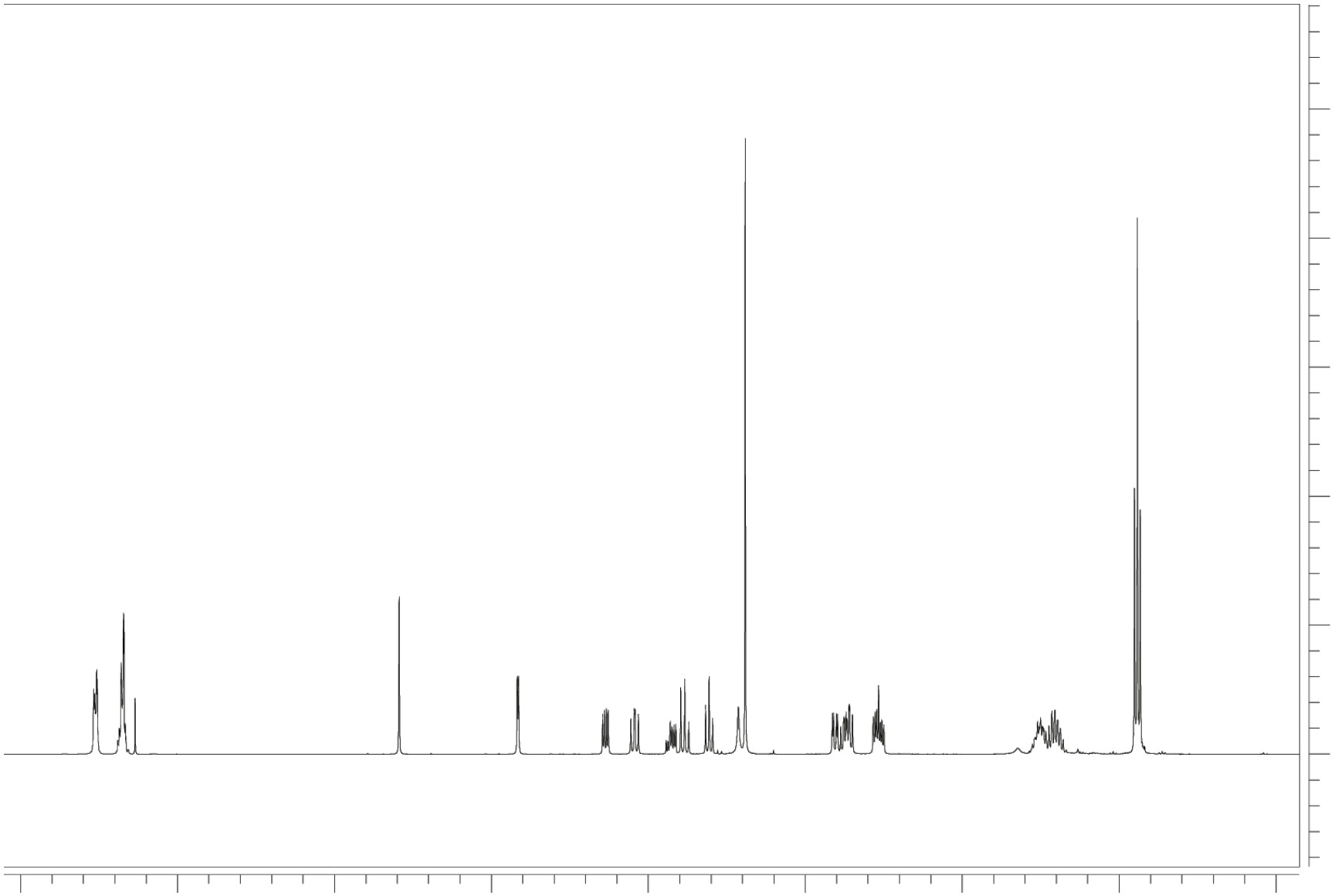

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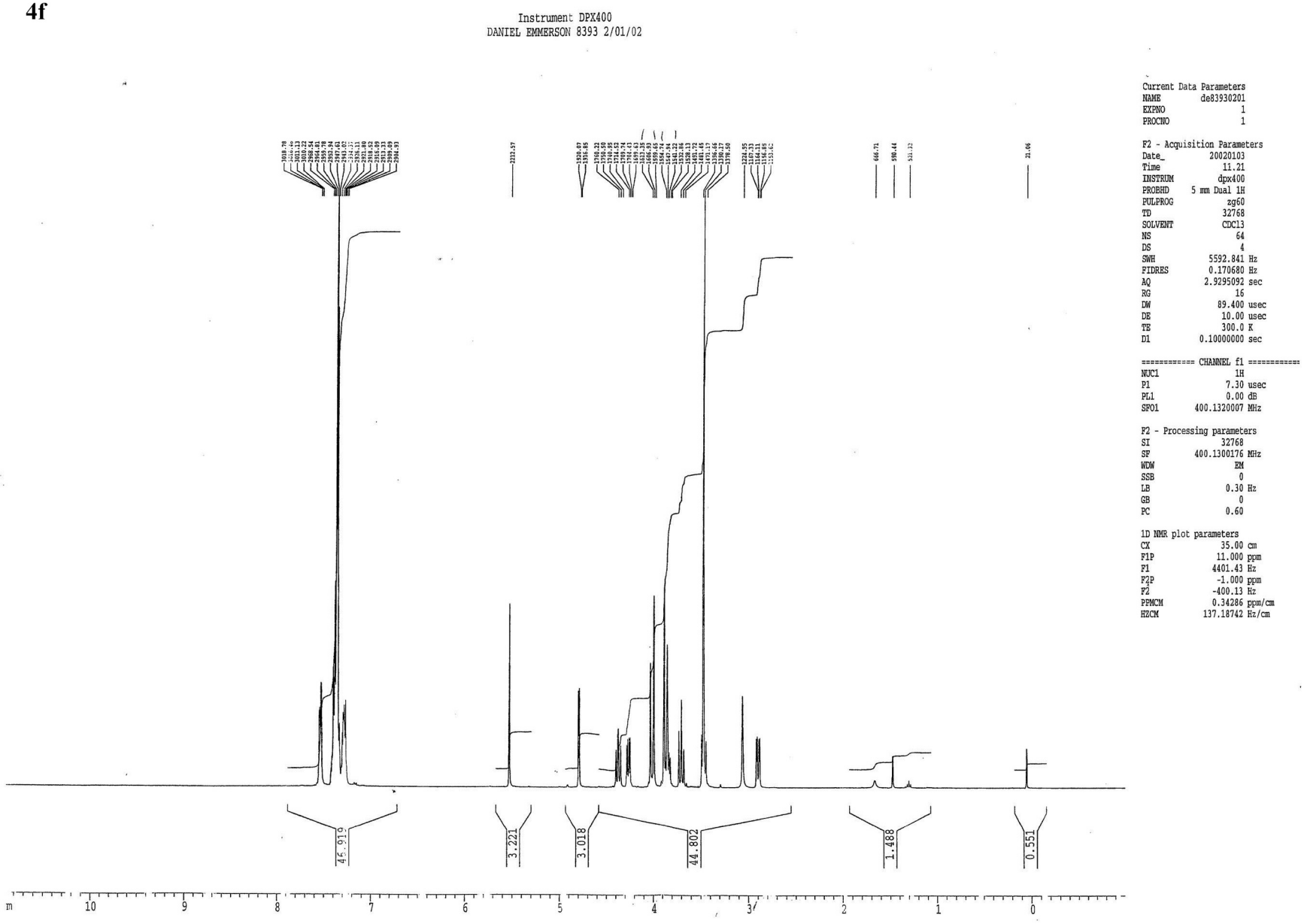
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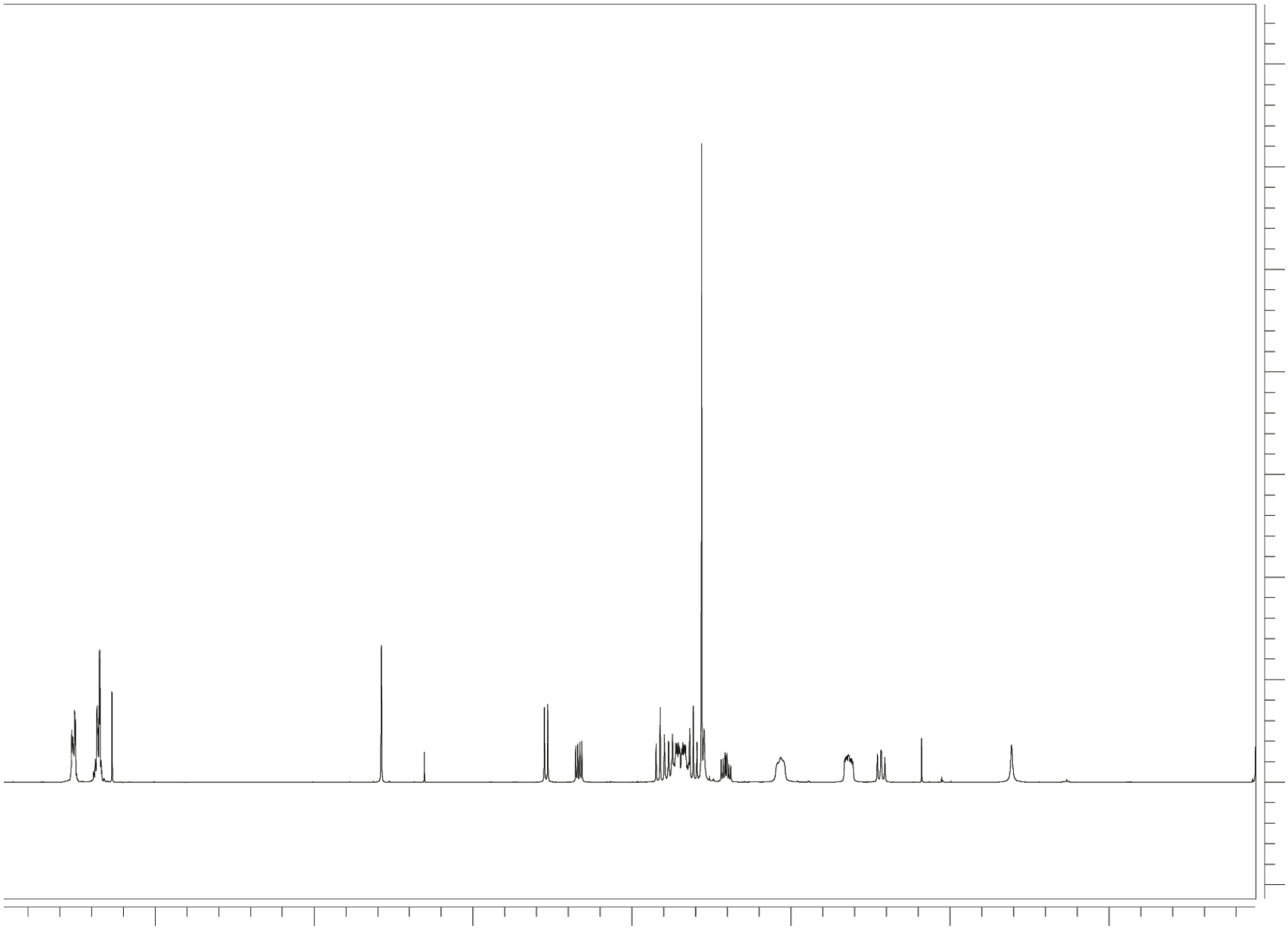
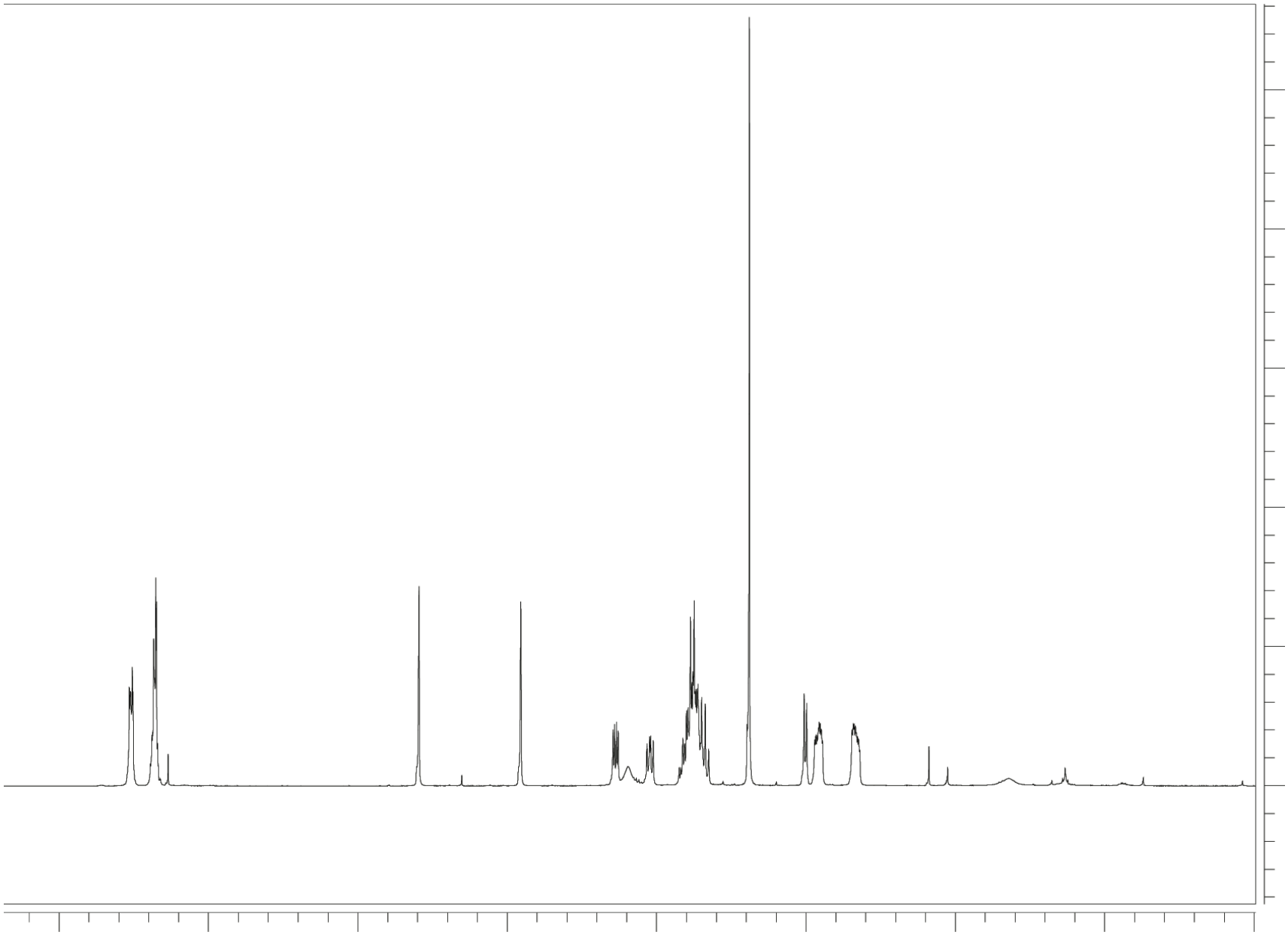


6



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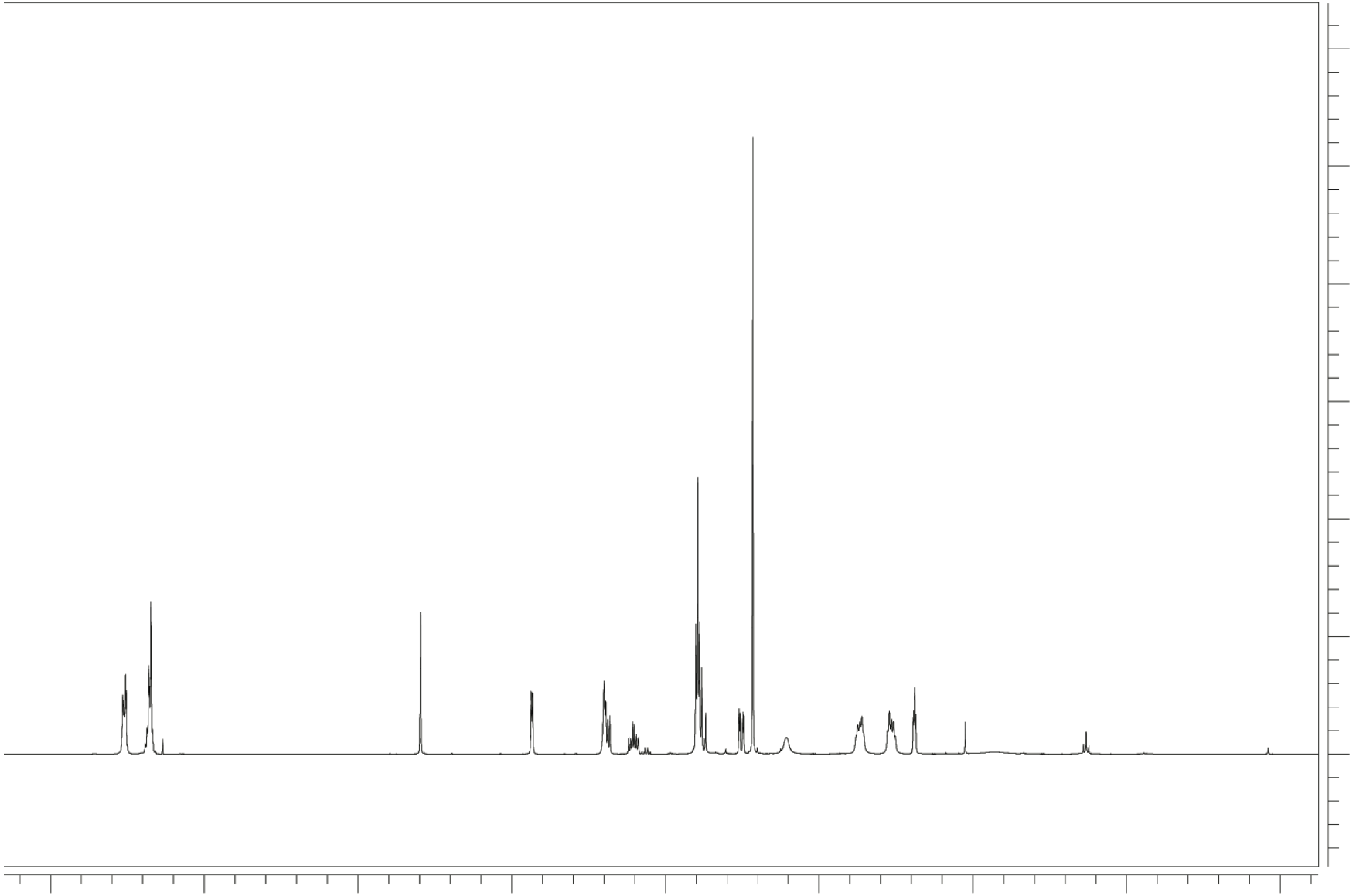

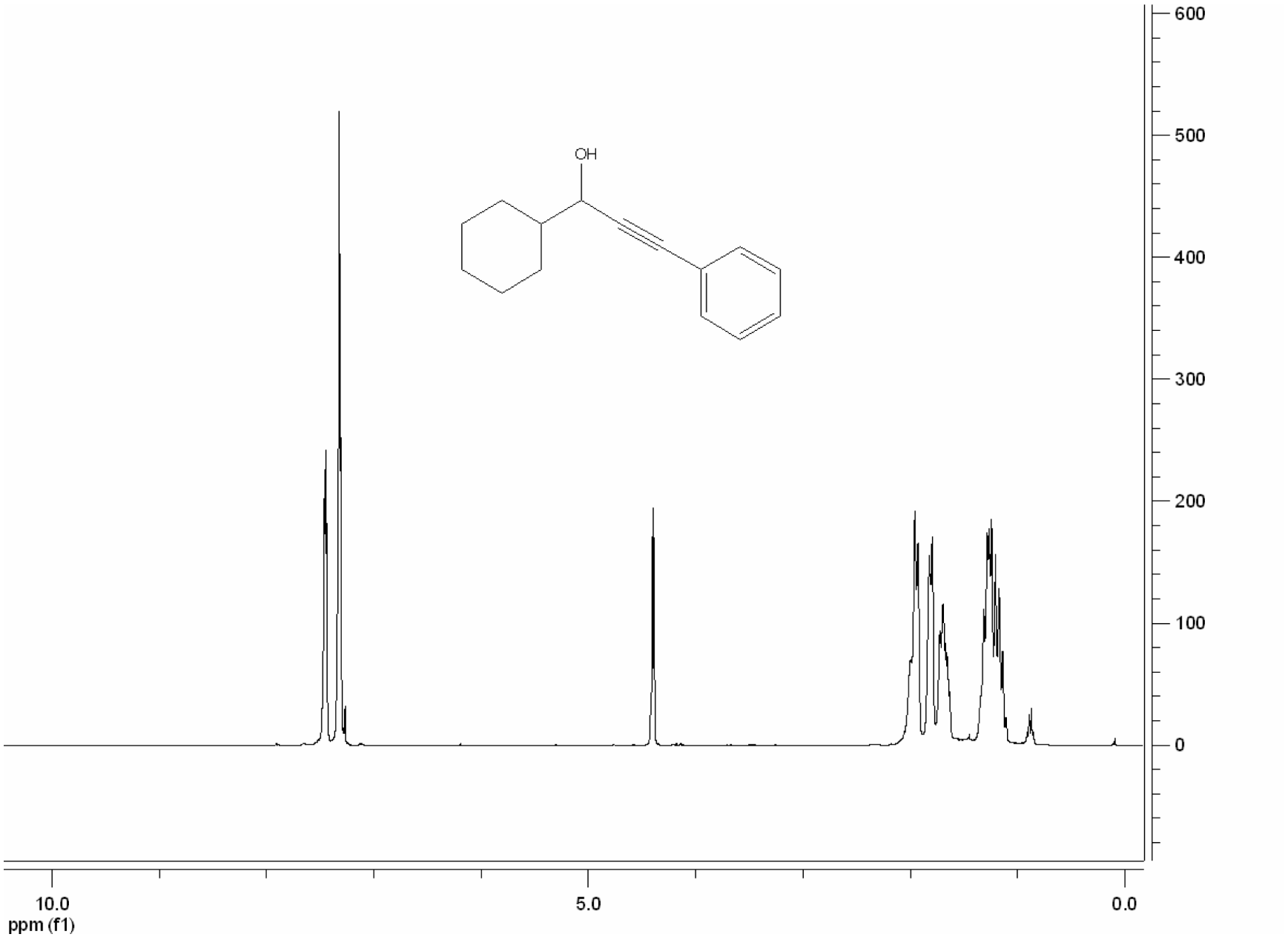
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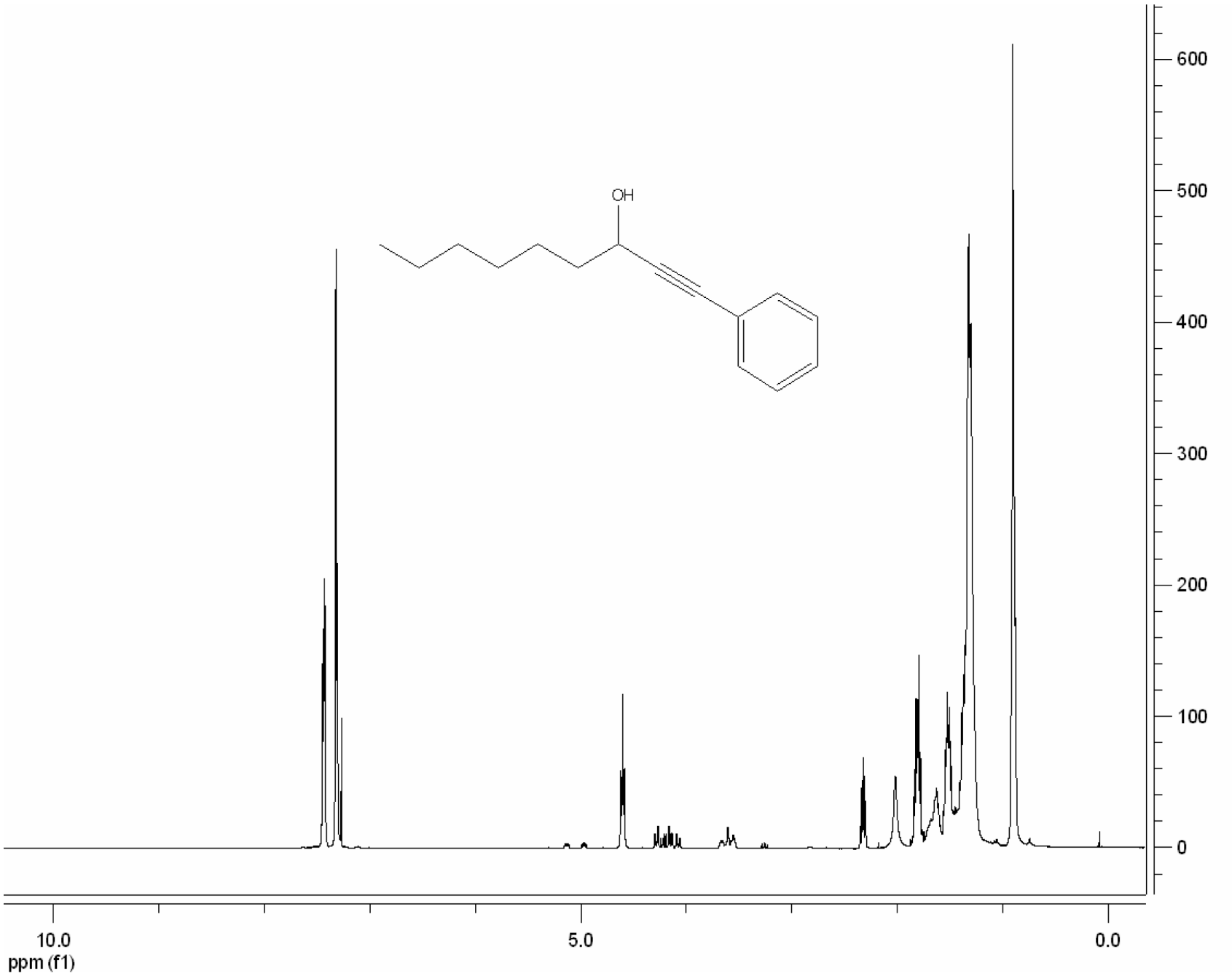
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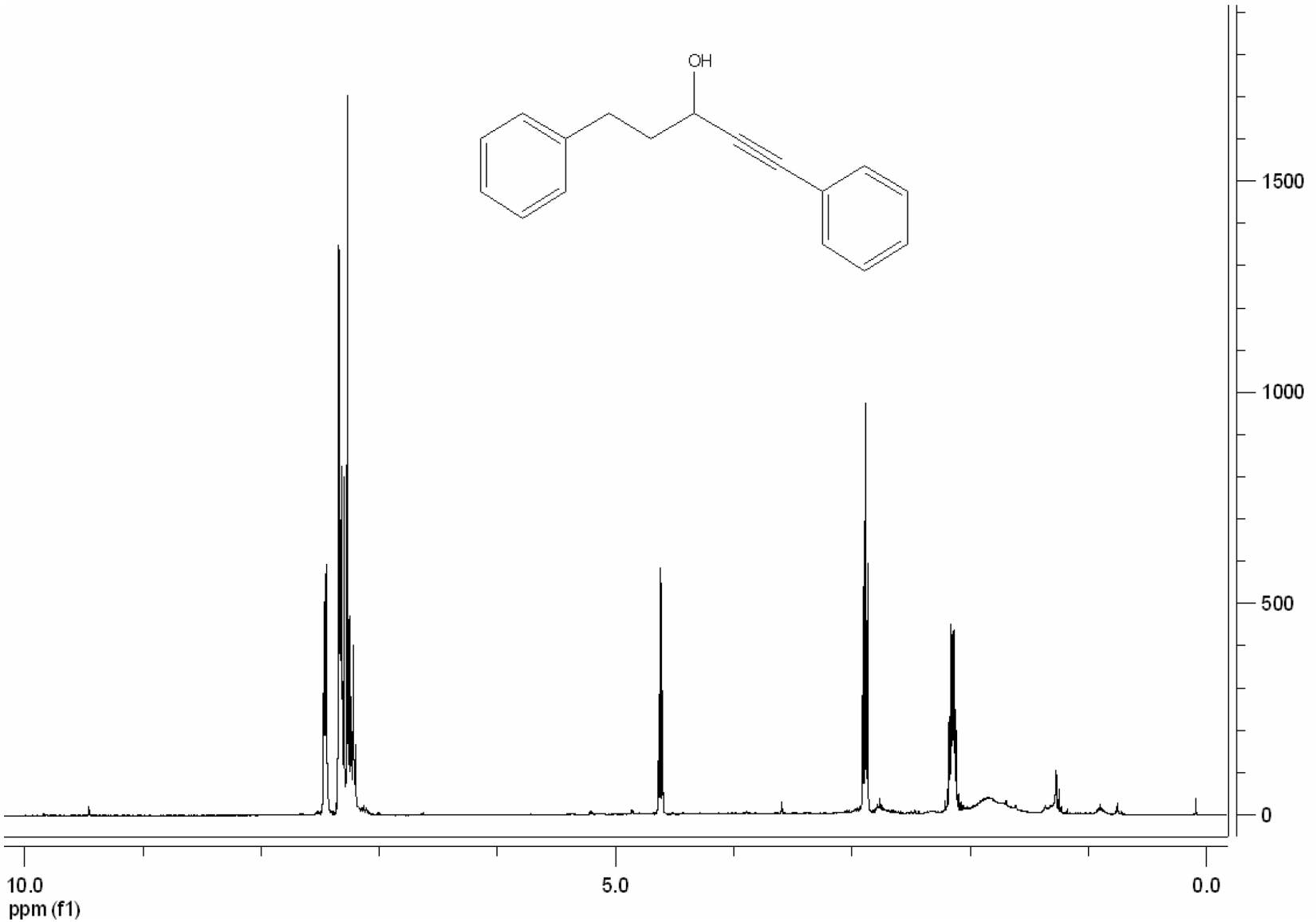
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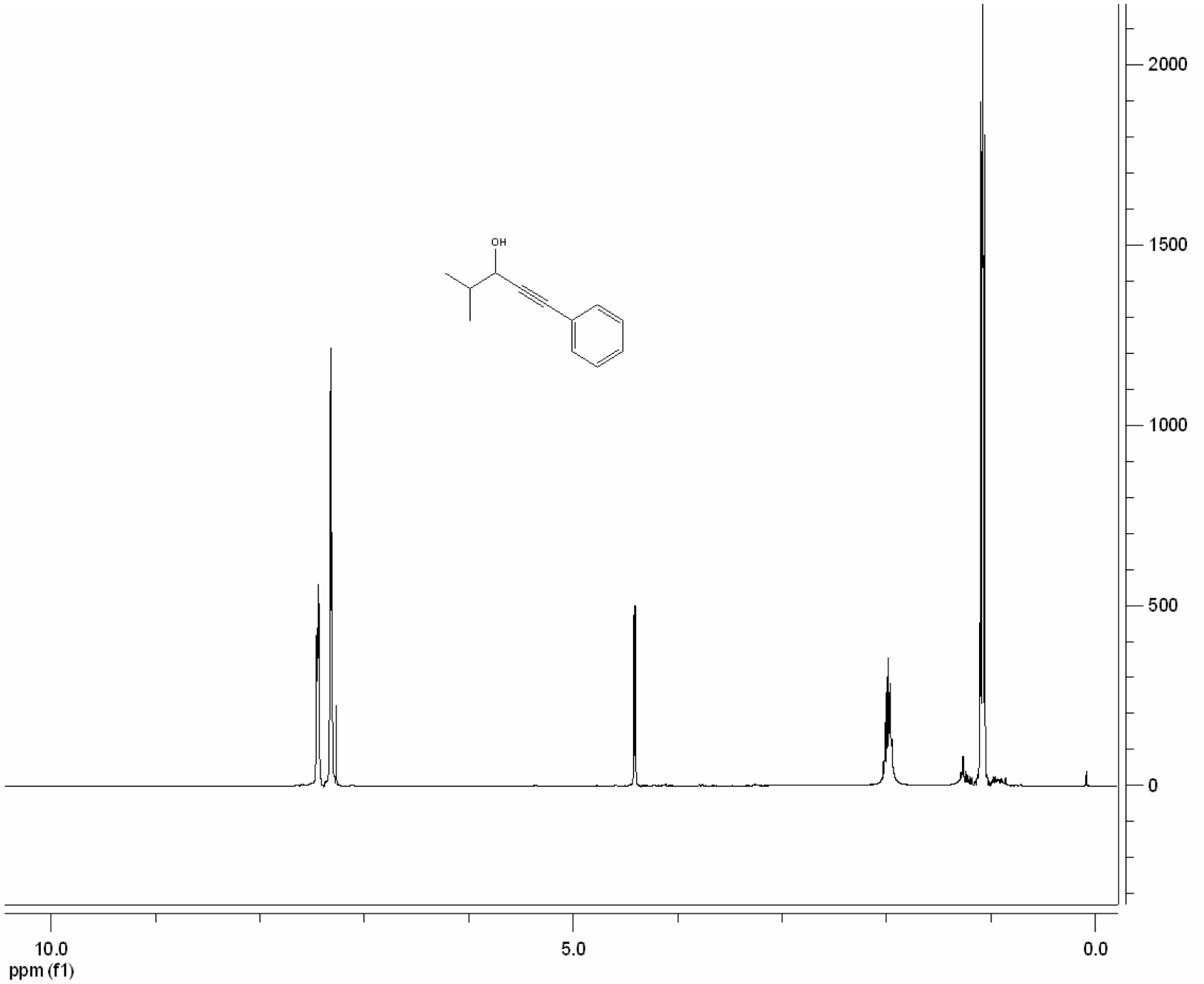
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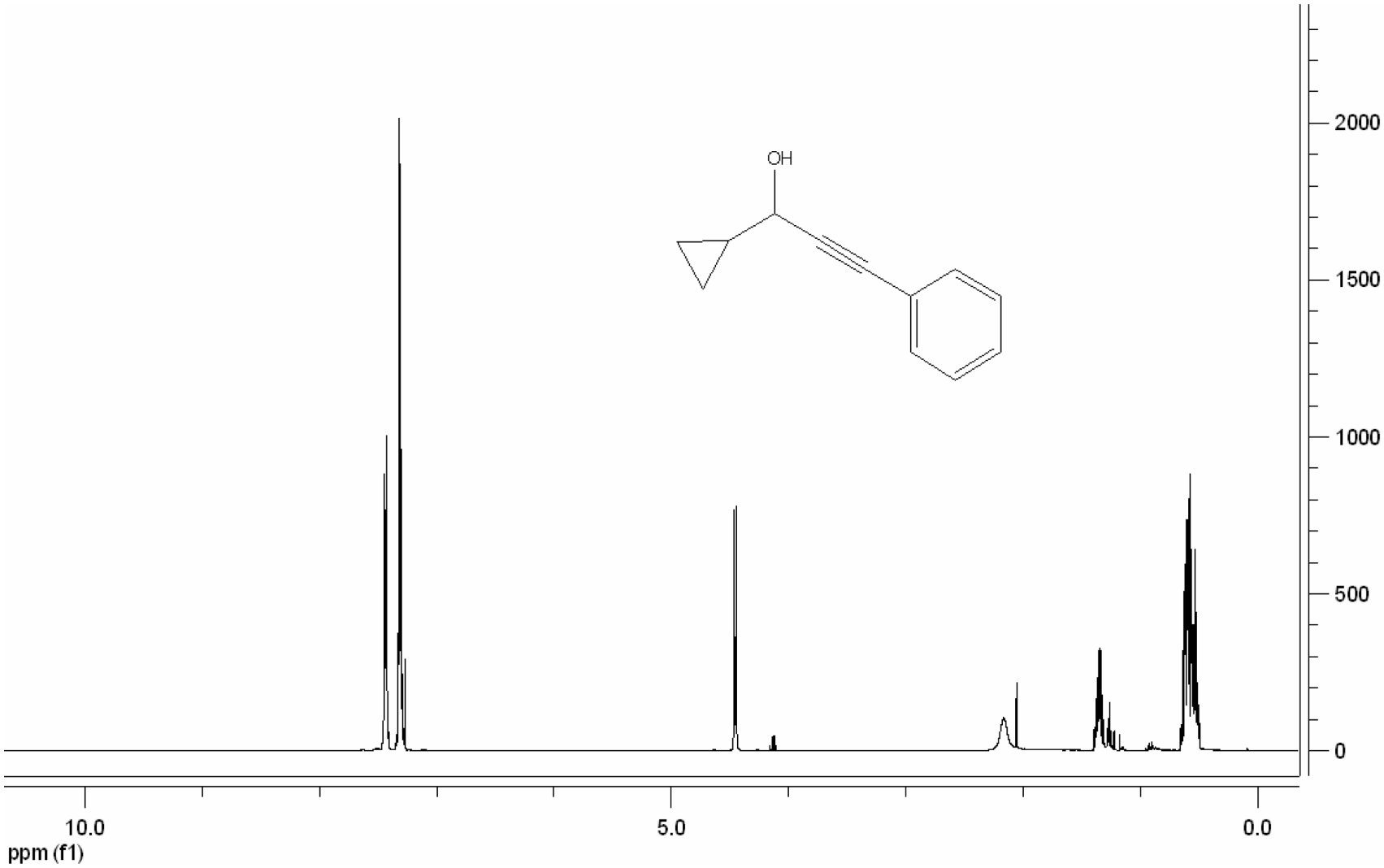
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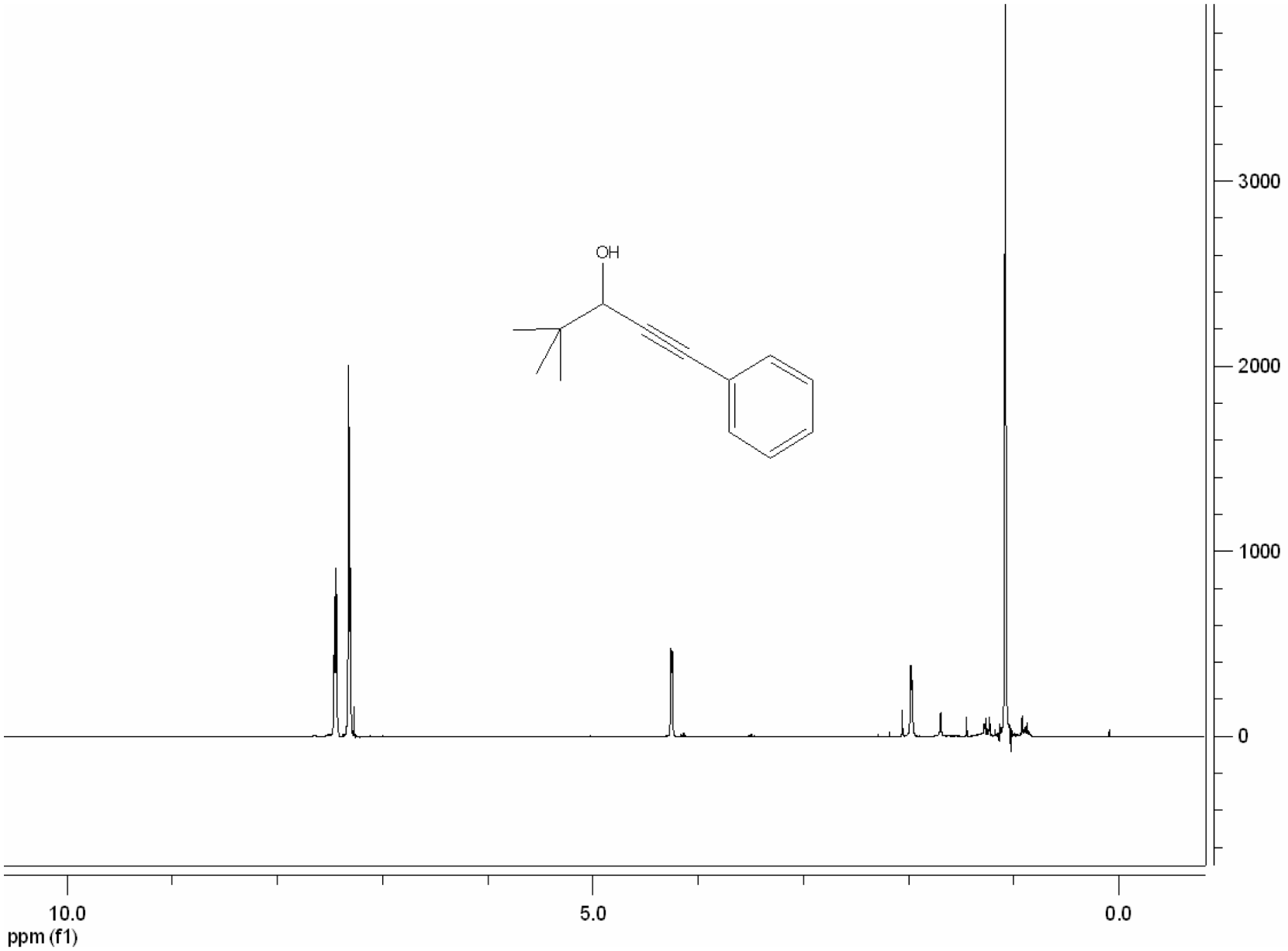
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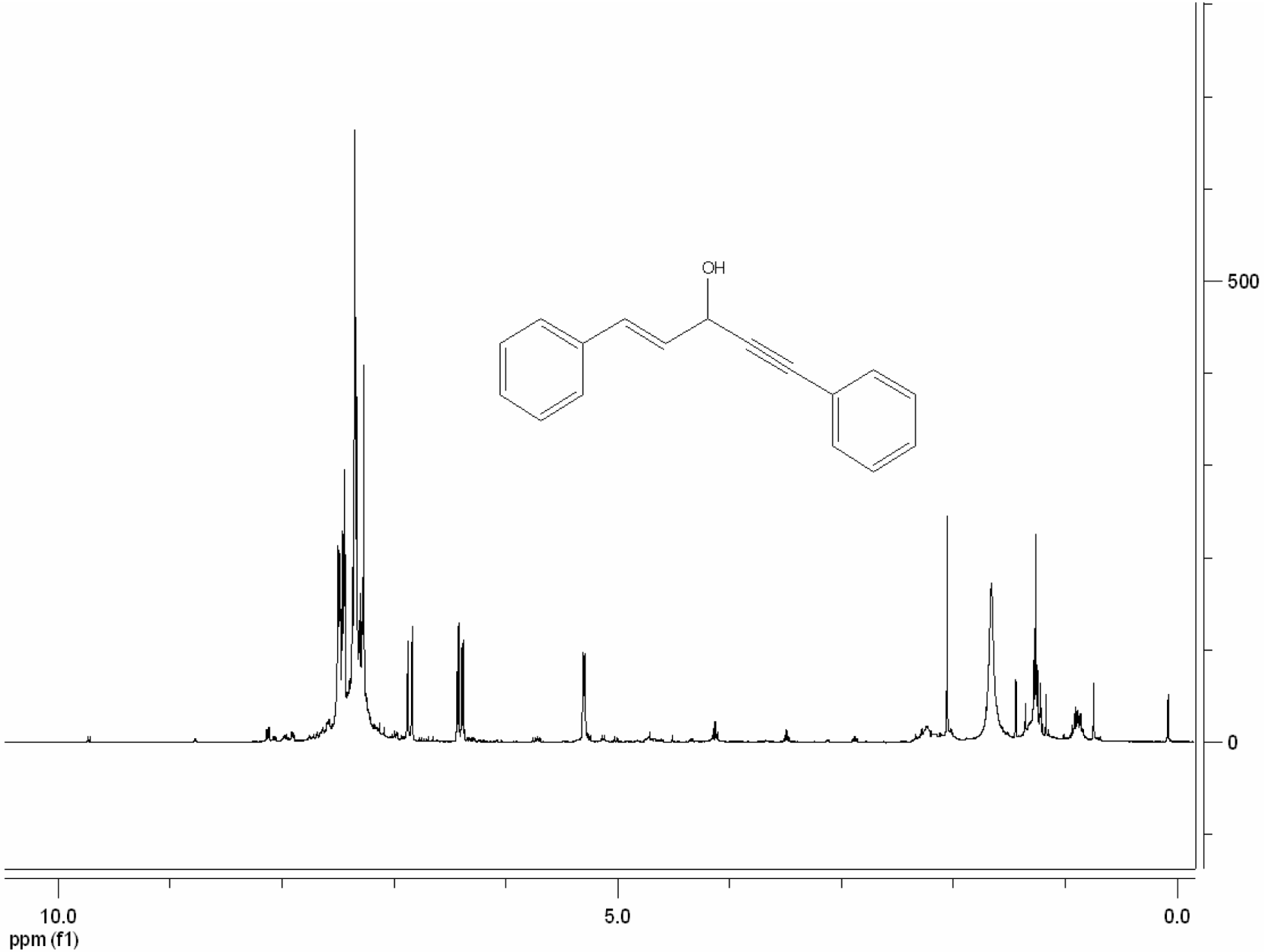
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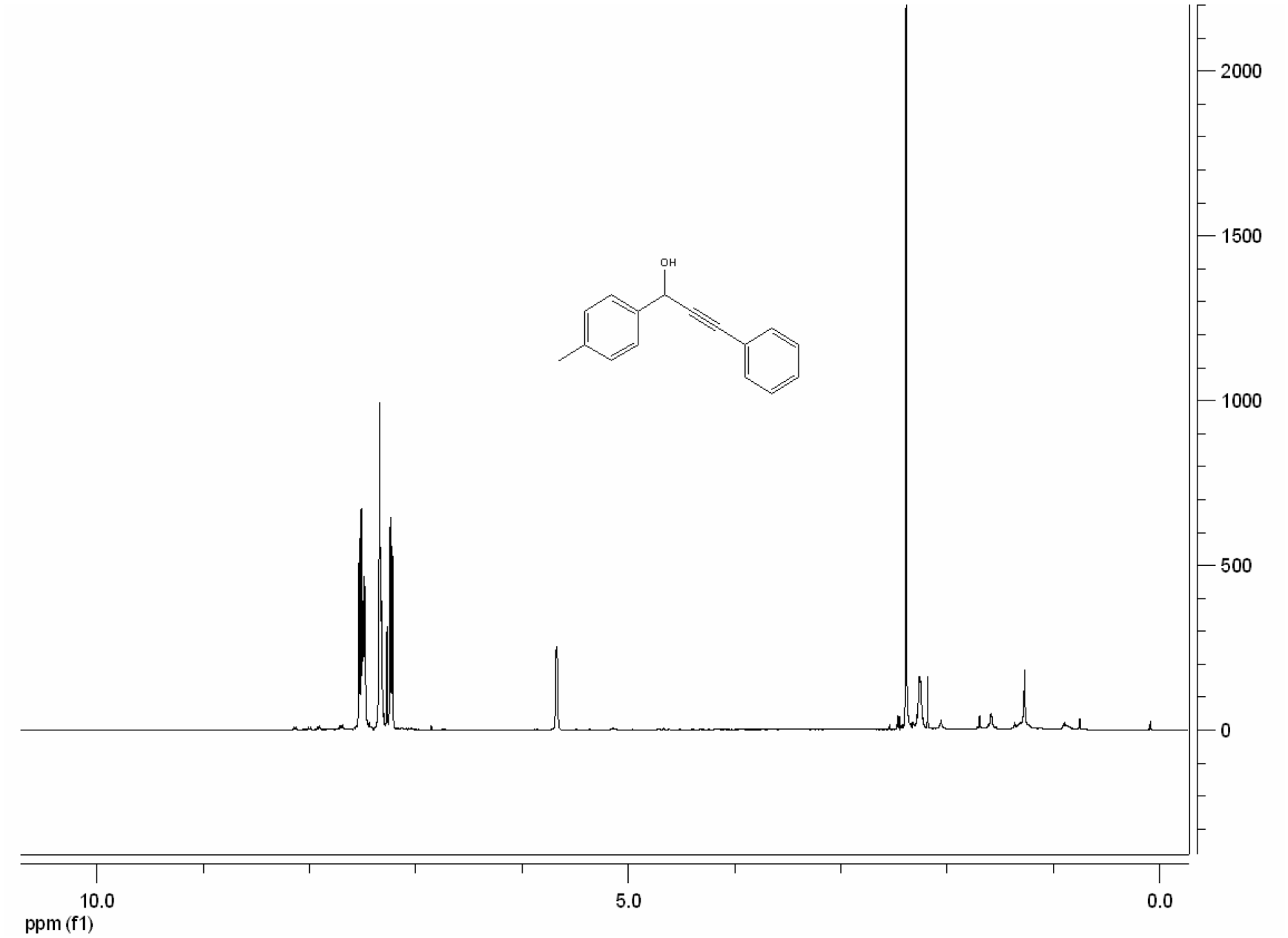
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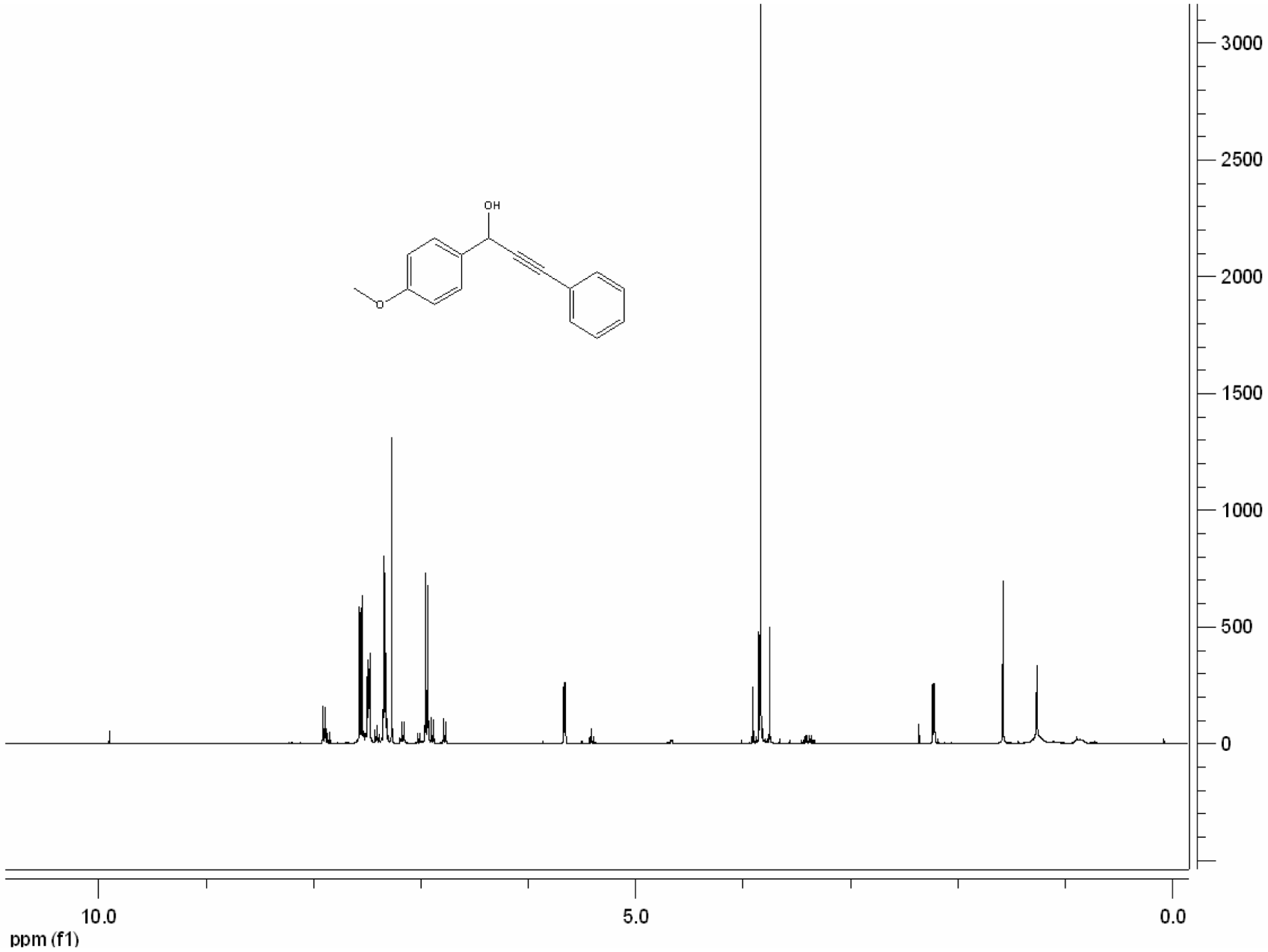
ppm (f1)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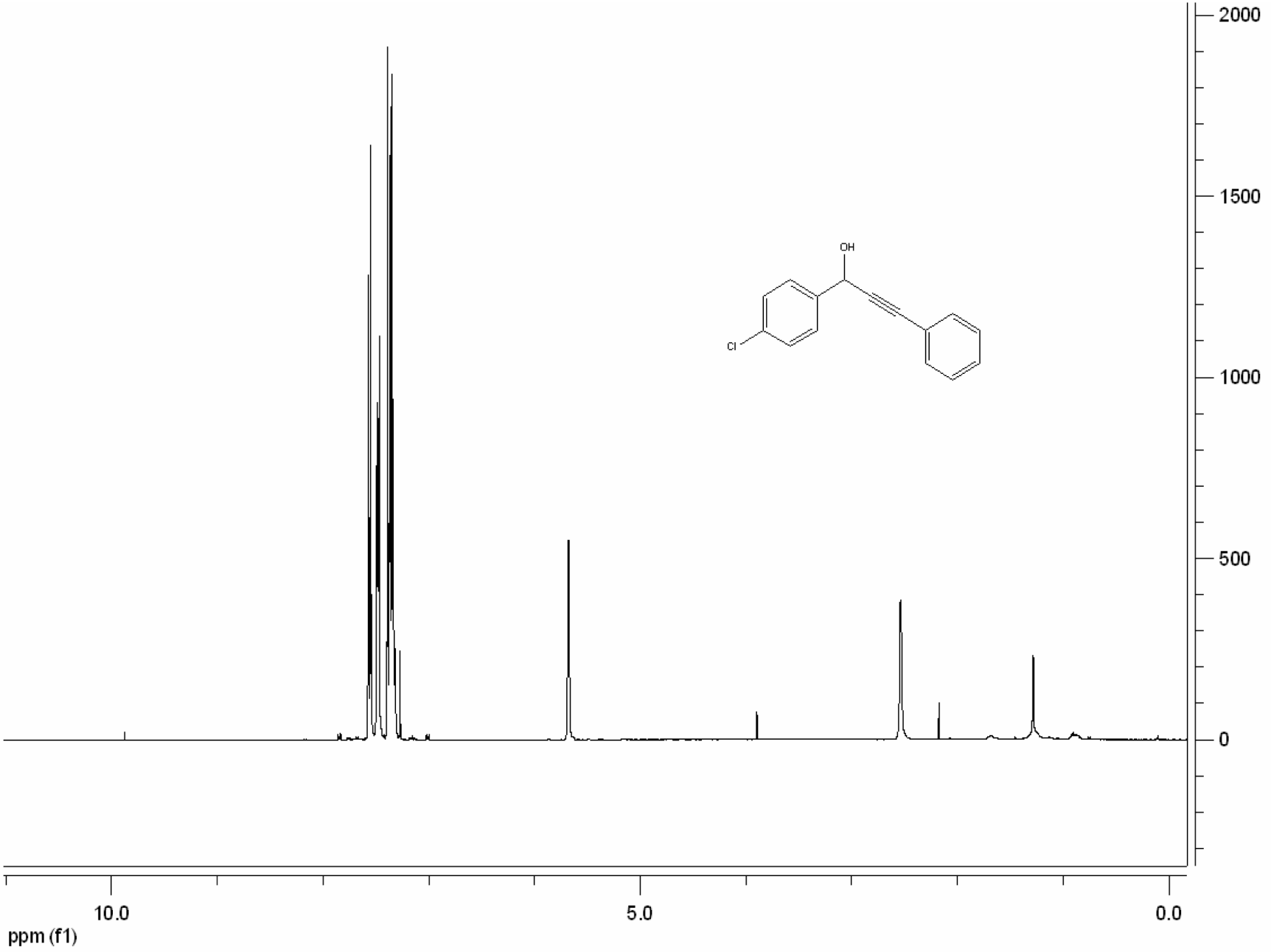
ppm (f1)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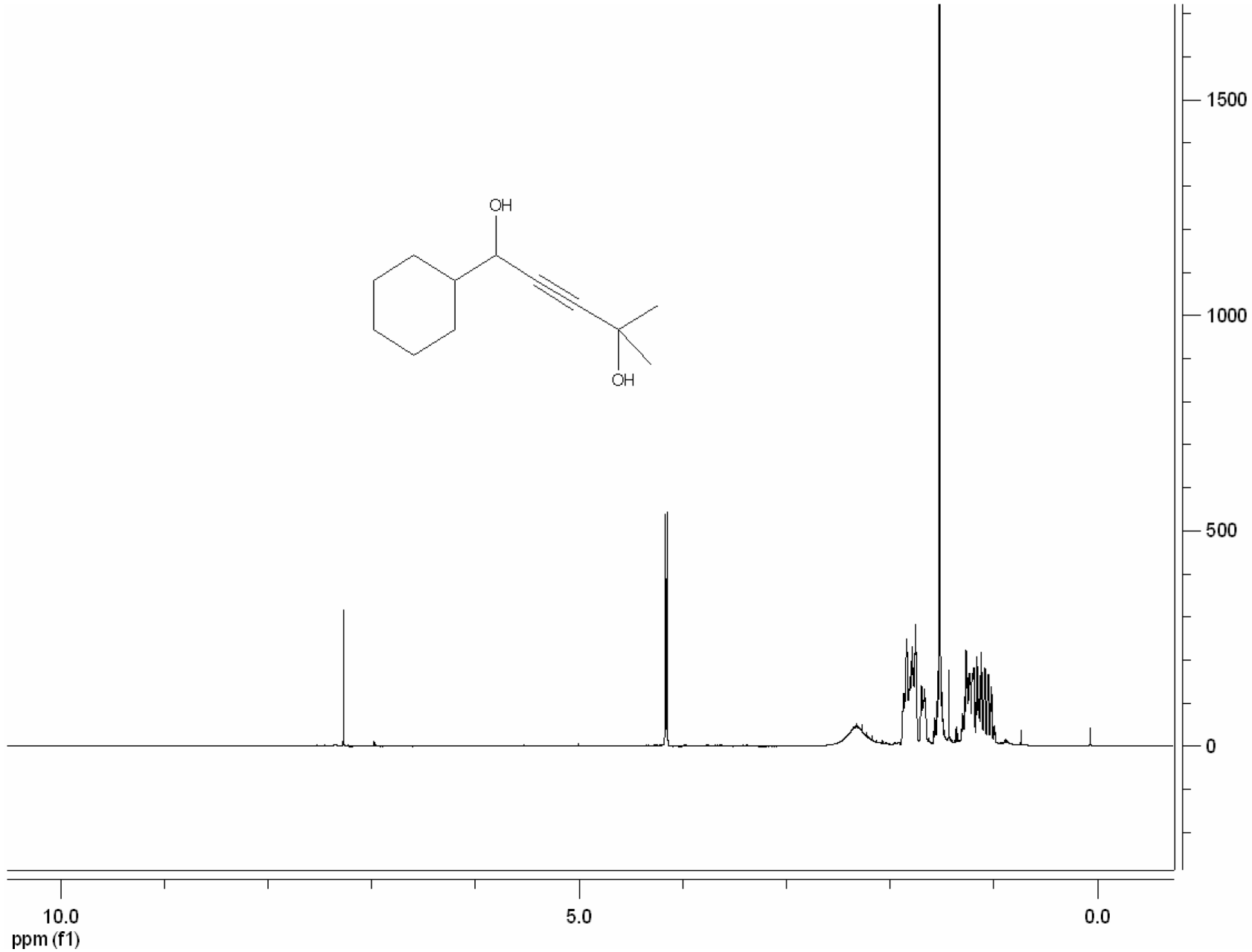
ppm (f1)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ppm (f1)
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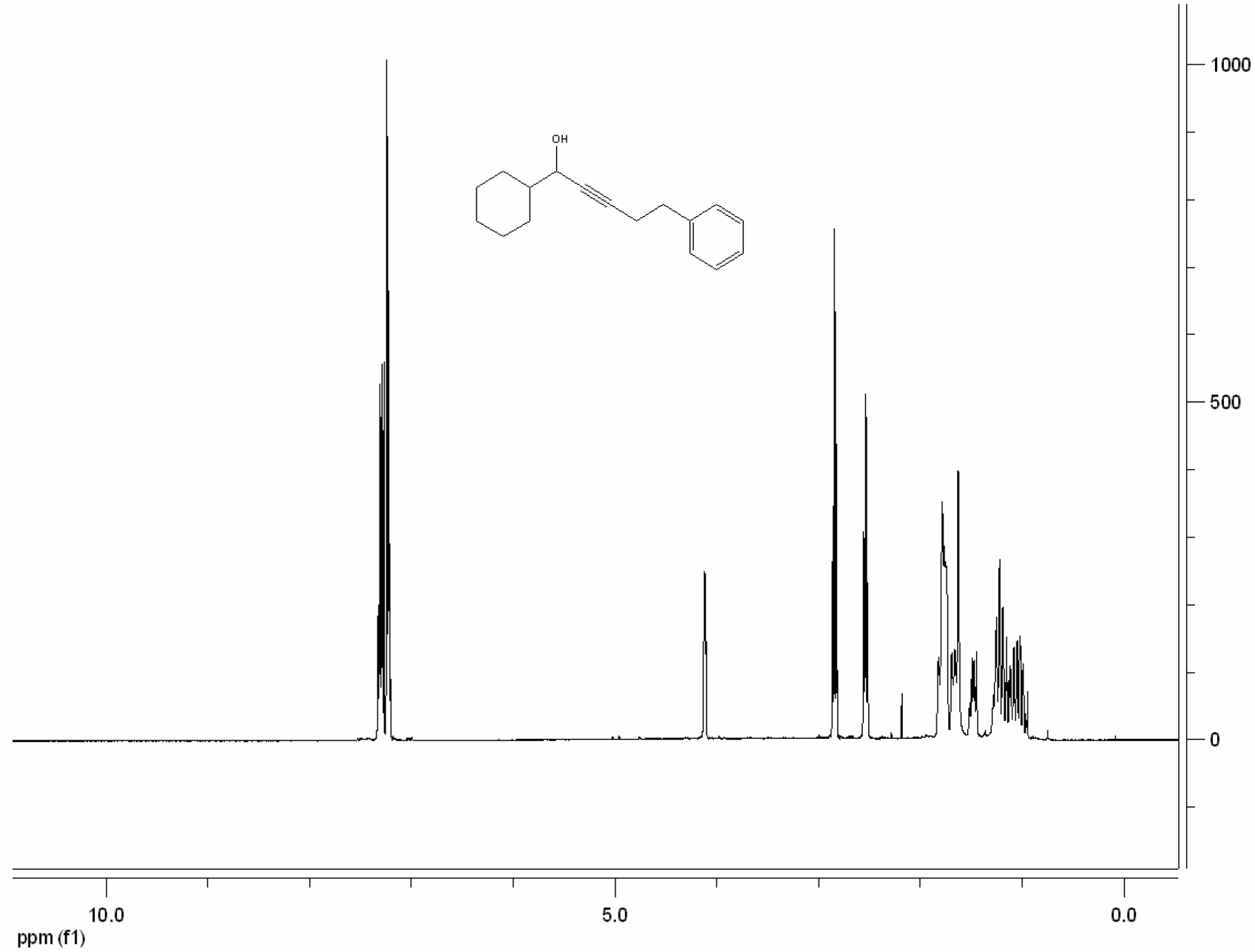
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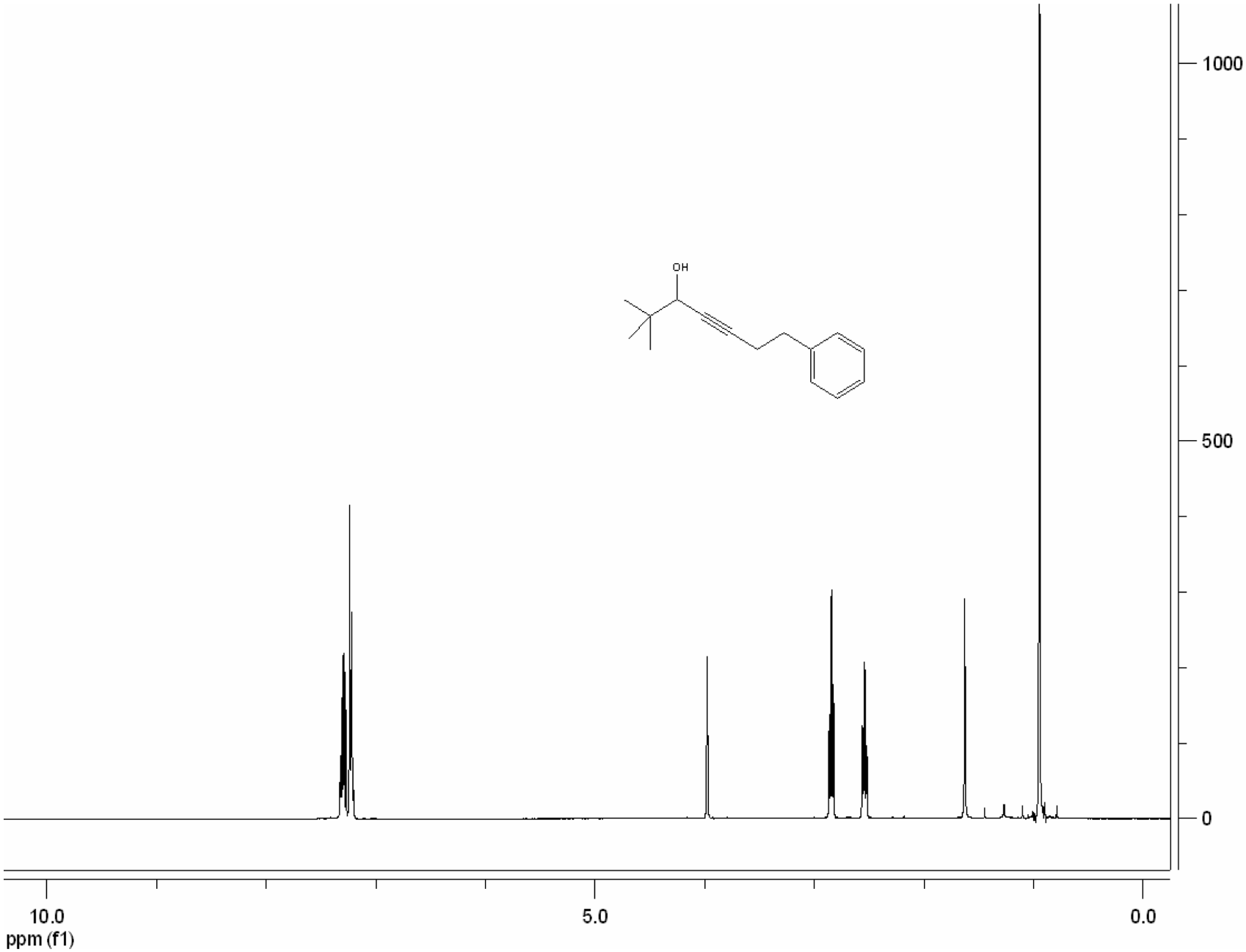
0.0
ppm (f1)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10.0
ppm (f1)
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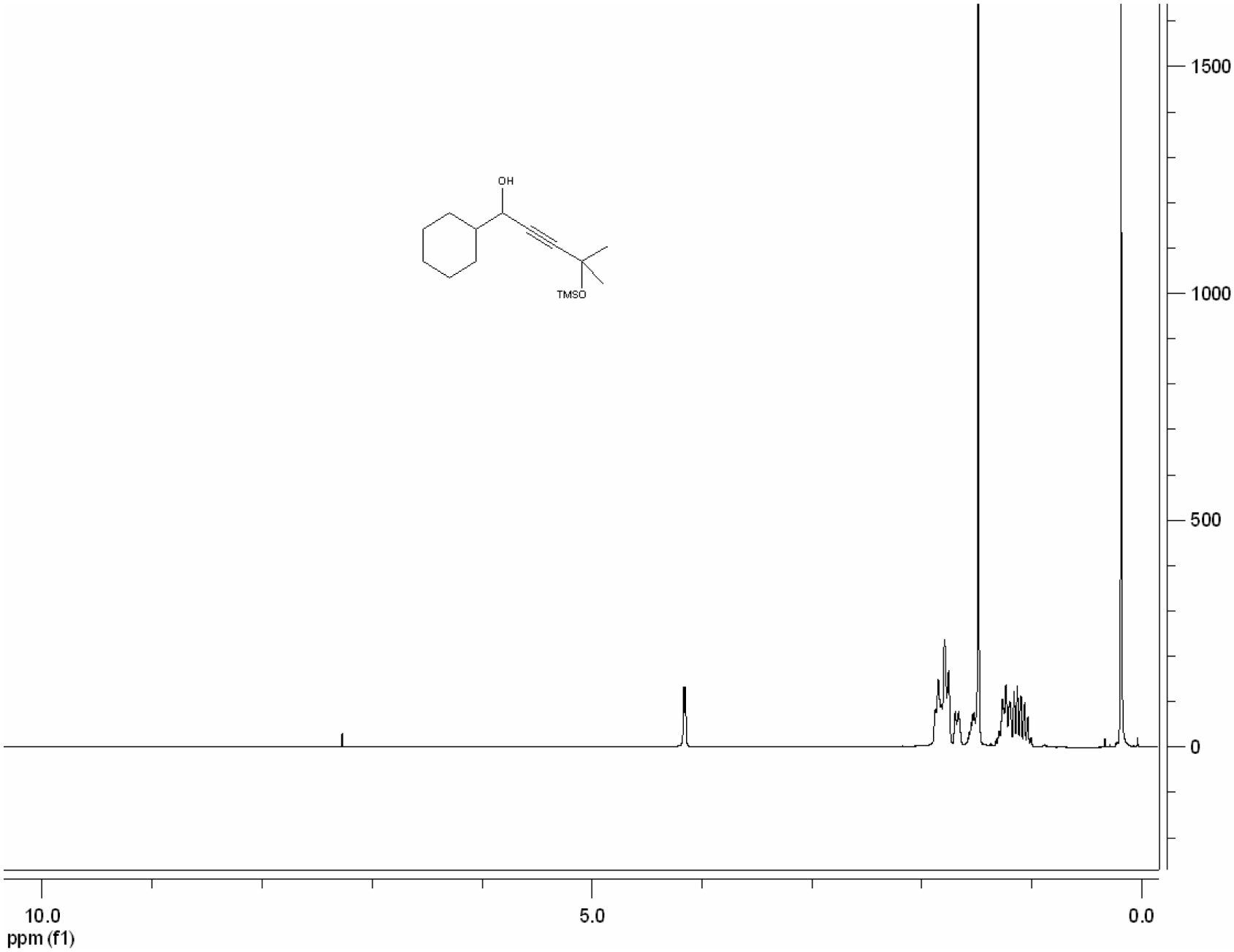
0.0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ppm (f1)
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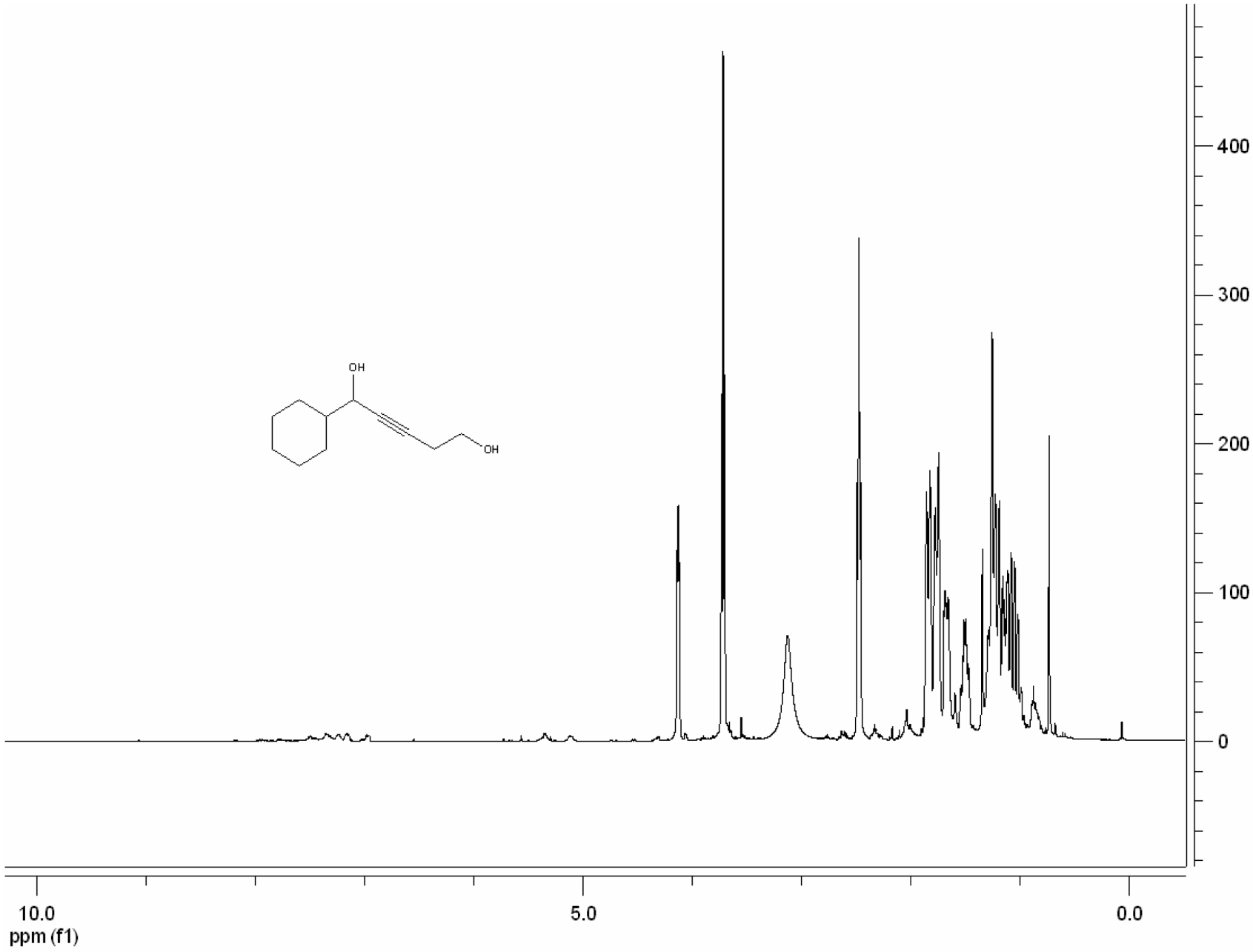
0.0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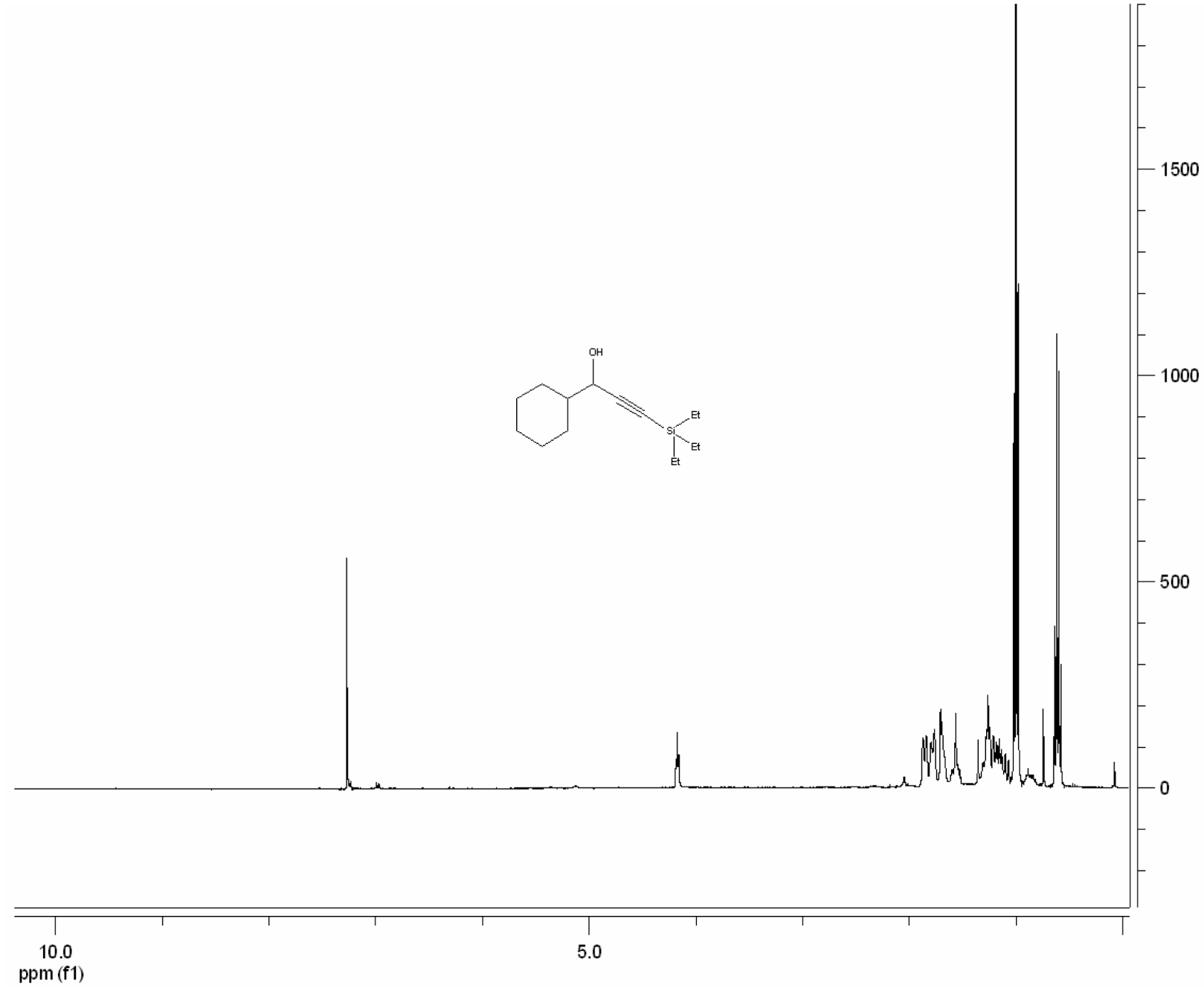
200
100
0
10.0
ppm (f1)
5.0
0.0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Et
Et
Et
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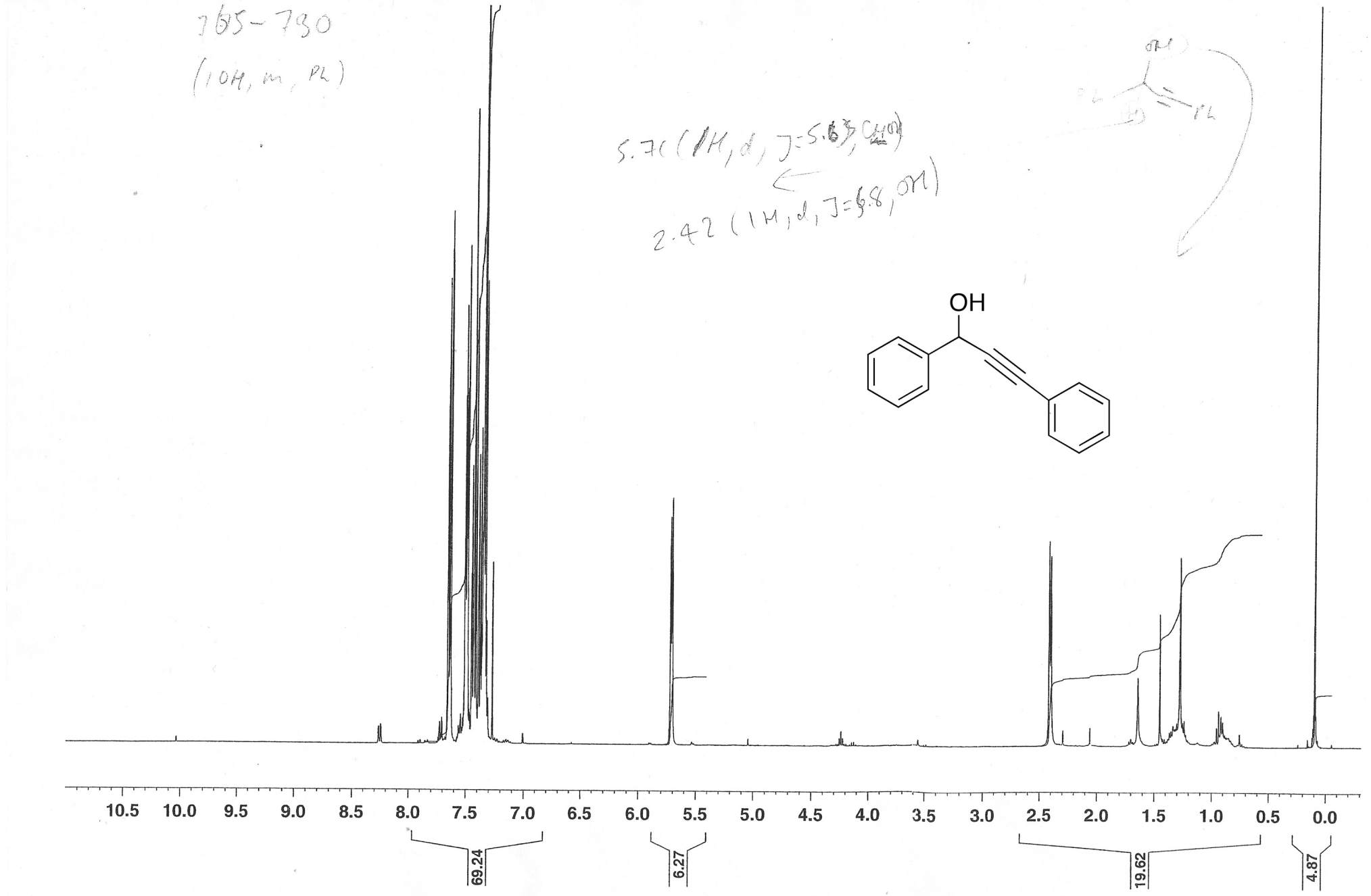
1000
500
0
10.0
ppm (f1)
5.0


7.65–7.90
(10H, m, Ph)
5.71 (1H, d, J=5.6 Hz, CH(OH))
2.42 (1H, d, J=5.8, OH)
OH
10.5 10.0 9.5 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
69.24
6.27
19.62
4.87

3 Zinc-Mediated Addition of Alkynes to Aldehydes

General Method for Addition of Terminal Acetylene to Aldehyde

An oven-dried flask was charged with zinc triflate (120 mg, 0.33 mmol) and ligand (0.36 mmol). Toluene (2 mL) was added and the mixture was stirred under nitrogen. After 15 min triethylamine (51 μL, 0.36 mmol) was added by syringe, after a further 2 h the acetylene (0.36 mmol) was added. After a further 15 min, aldehyde (0.3 mmol) was introduced into the flask by syringe and the reaction was stirred under nitrogen for the specified time and monitored by tlc. The reaction was quenched with saturated ammonium chloride solution and ethyl acetate was added. The aqueous layer was extracted three times with ethyl acetate and the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Purification by column chromatography (solvents used to elute alcohols are specified below, ligands were then eluted using petrol/ EtOAc or MeOH/EtOAc gradients as required unless noted otherwise) afforded the desired secondary alcohols and recovered ligand, which were purified by column chromatography and re-used.

(R-)-1-Cyclohexyl-3-phenyl-2-propyn-1-ol[1]

Isolated by column chromatography (4:1 → 2:1 petrol:ether, except when **4e** was the ligand, in which case it was separated from the alcohol by 4:1 petrol:ether → ether gradient; and when **4f** was the ligand in which case the alcohol was isolated by washing with cold petrol) as a colourless oil; R_f 0.4 (3:1 petrol: ether); $[\alpha]_D^{23}$ -9.9 (*c* 1.2, $CHCl_3$) [lit.[1] $[\alpha]_D^{23}$ -10.8 (*c* 1.0, $CHCl_3$); lit.[2] -9.2 (*c* 1.0 $CHCl_3$)]; ν_{max}/cm^{-1} 3360 (br), 3080, 3060, 2926, 2853, 2228; δ_H(400 MHz, $CDCl_3$) 7.46-7.43 (2H, m, Ph), 7.34-7.30 (3H, m, Ph), 4.39 (1H, m, C*H*OH), 2.00-1.93 (3H, m), 1.83-1.79 (2H, m), 1.72-1.63 (2H, m), 1.35-1.10 (5H, m); δ_C(100 MHz, $CDCl_3$) 131.7, 128.3, 128.3 (3 × d, Ph), 122.7 (s, Ph), 89.2, 85.7 (2 × s, C≡C), 67.7 (d, CHOH), 44.3 (d, CH(OH)*C*H), 28.6, 28.2, 26.4, 25.9 (4 × t, CH_2, cyclohexyl); ee was determined either by chiral GC (C-dex-β) or hplc (Chiralcel OD, 10% IPA in hexane, 254 nm) t_r 5.7 (major), 12.4 (minor).

(R-)-1-Phenylnon-1-yn-3-ol[3]

Purified by column chromatography (4:1 → 2:1 petrol/ ether) as a colourless oil; $[\alpha]_D^{23}$ –1.5 (*c* 0.69, $CHCl_3$); ν_{max}/cm^{-1} (thin film) 3346 (br, O–H), 3082, 3058, 3034, 3022 (C–H arom.), 2955, 2929, 2858 (C–H aliph.), 2230, 2204 (C≡C); δ_H(400 MHz, $CDCl_3$) 7.46-7.43 (2H, m, Ph) 7.33-7.30 (3H, m, Ph),

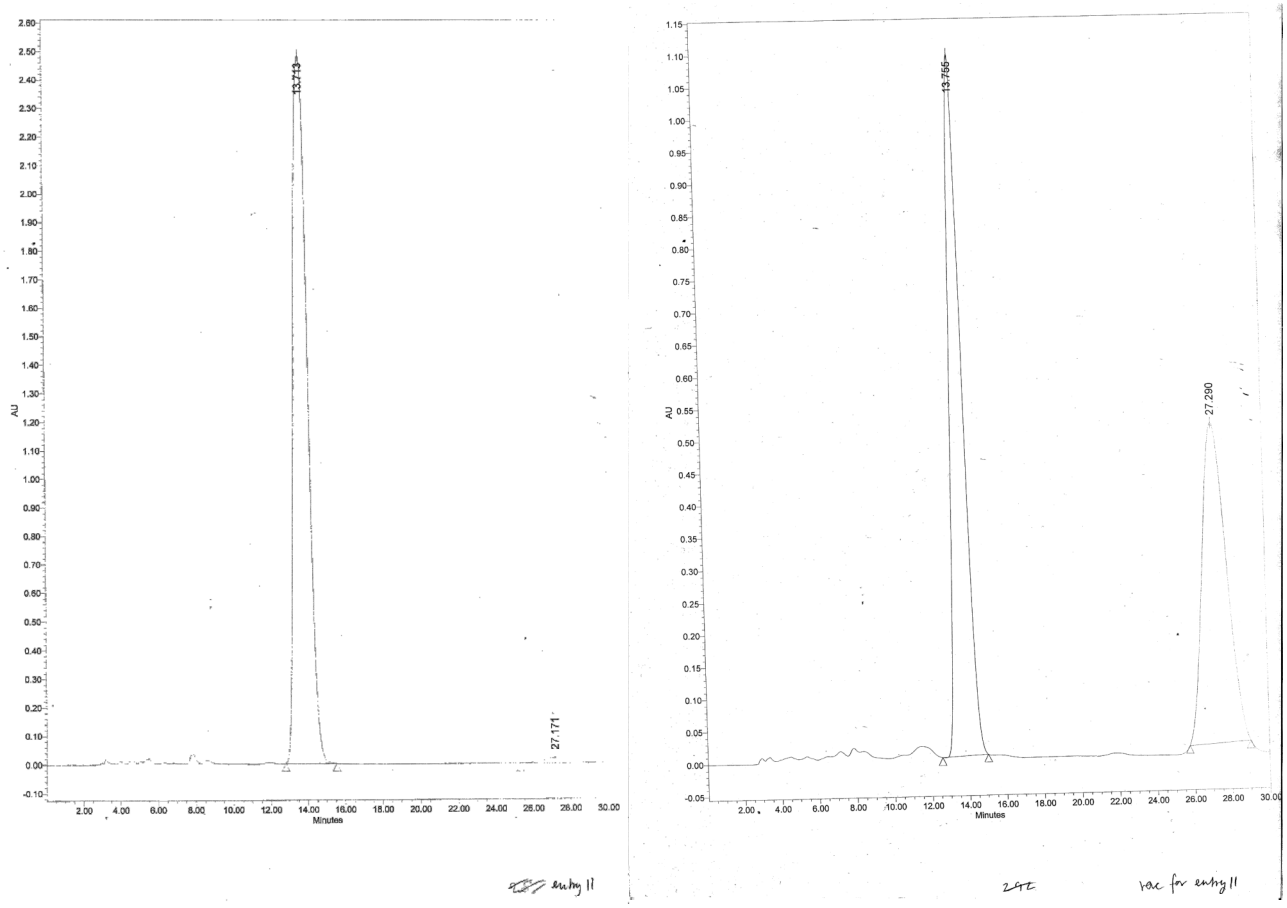
4.61 (1H, dd, *J* 10.3, 5.9, C*H*OH), 1.87-1.78 (2H, m, CHOHC*H*$_2$), 1.57-1.49 (2H, m, CHOHCH$_2$C*H*$_2$), 1.39-1.30 (6H, m, (CH$_2$)$_3$), 0.92-0.88 (3H, m, CH$_3$); δ_C(100 MHz, $CDCl_3$) 131.7, 128.3, 128.3 (3 × d, Ph) 122.7 (s, Ph), 90.2, 84.8 (2 × s, C≡C), 63.0 (d, CHOH), 37.9 (t, CHOH*C*H$_2$), 31.7, 29.0, 25.2, 22.6 (4 × t, (CH$_2$)$_4$), 14.0 (q, CH$_3$), *m*/*z* (CI+) 216.3 (M^+, 75%), 234.3 ($[M+NH_4]^+$, 45%), 199.2 ($[M-OH]^+$, 25%); ee was determined by hplc (Chiralcel OD, 10% IPA in hexane, 254 nm) t_r 5.4 (major), 11.2 (minor). The secondary alcohol was inseparable from material whose NMR and mass spectra were consistent with 3-hydroxy-2-*n*-pentyl-*n*-nonyl-heptanoate (the product of the Aldol/crossed Tishchenko side reaction), which was present as a 0.65:1 ratio of diastereomers; key peaks in ^{1}H NMR, which contained 25% of this by-product, are as follows: δ 4.28 (1H, dd, *J* 11.4 and 4.4, OCH$_2$), 4.22 (0.65H, dd, *J* 11.7 and 7.7 OCH$_2$), 4.15 (1H, dd, *J* 11.4 and 5.1, OCH$_2$), 4.08 (0.65H, dd, *J* 11.2 and 4.8, OCH$_2$); *m*/*z* 360.4 ($[M+NH_4]^+$, 100%), 343.4 ($[M+H]^+$, 45%), 325.4 ($[M-OH]^+$, 25%).

(R-)-1,5-Diphenylpent-1-yn-3-ol[4]

Isolated by column chromatography (10:1 → 2:1 petrol/ EtOAc) as a colourless oil; $[\alpha]_D^{23}$ –59 (*c* 3.0, $CHCl_3$) [lit.[4] $[\alpha]_D^{27}$ –62.2 (*c* 1.03, $CHCl_3$)]; δ_H(400 MHz, $CDCl_3$) 7.47-7.44 (2H, m, Ph), 7.34-7.22 (8H, m, Ph), 4.62 (1H, t, *J* 6.5, C*H*OH), 2.89 (2H, t, *J* 7.8, PhCH$_2$), 2.14, 2.15 (2H, 2 × td, *J* 7.8, 6.5, PhCH$_2$C*H*$_2$), 1.91 (1H, br, OH); δ_C(100 MHz, $CDCl_3$) 141.3 (s, Ph), 131.7, 128.5, 128.5, 128.5, 128.3, 126.0 (6 × d, Ph), 122.6 (s, Ph), 89.8, 85.3 (2 × s, C≡C), 62.3 (d, CHOH), 39.3 (d, PhCH$_2$*C*H$_2$), 31.5 (d, PhCH$_2$); ee was determined by hplc (Chiralcel OD, 10% IPA in hexane, 254 nm) t_r 13.8 (major), 27.2 (minor). **2-benzyl-3-hydroxy-5-phenylpentyl 3-phenylpropanoate:** Isolated as a colourless oil (19.7 mg, 49%) 0.8:1 mixture of diastereomers, designated [a] and [b] below; δ_H(500 MHz, $CDCl_3$) 7.34-7.14 (27H, m, Ph), 4.35 (1H, dd, *J* 11.4, 4.3, 1H, OCH$_2$ [a]), 4.26 (0.8 H, dd, *J* 11.2, 7.8, OCH$_2$ [b]), 4.04 (1H, dd, *J* 11.5, 4.6, OCH$_2$ [a]), 3.94 (0.8H, dd, *J* 11.2, 4.7, OCH$_2$), 3.65 (0.8H, dt, *J* 9.0, 3.2, HOCH [b]), 3.52 (1H, m, HOCH [a]), 3.01-2.93 (3.6H, m, COCH$_2$, COCH$_2$C*H*$_2$), 2.90-2.86 (2.6H, m, PhC*H*$_2$CH [b], PhC*H*$_2$CH$_2$CHOH), 2.79 (1H, dd, *J* 13.7, 6.0, PhC*H*$_2$CH [a]), 2.71-.64 (5.4H, m, PhC*H*$_2$, COCH$_2$, COCH$_2$CH$_2$), 2.57-2.52 (1.8H, m, PhC*H*$_2$CH), 2.08-2.04 (0.8H, m, PhCH$_2$C*H* [b]), 2.03-1.97 (1H, m, PhCH$_2$C*H* [a]), 1.96-4.82 (3.6H, m, PhCH$_2$C*H*$_2$CHOH); δ_C(125 MHz, $CDCl_3$) 173.4, 173.3 (2 × s, C=O), 142.0, 141.9, 140.3, 140.3, 140.0, 139.8 (6 × s, Ph), 129.1, 129.0, 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.4, 128.3 (12 × d, Ph), 126.4, 126.4, 126.2, 126.2, 126.0, 125.9 (6 × s, Ph), 70.8 (d, HO*C*H [a]), 70.2 (d, HO*C*H [b]), 64.3 (t, CH$_2$O [b]), 63.2 (t, CH$_2$O [a]), 45.7

(d, *C*HCH$_2$Ph [a]), 45.1 (d, *C*HCH$_2$Ph [b]), 36.5, 35.8, 35.7, 35.7, 34.3, 32.6, 32.3, 32.0, 30.9, 30.8 (10 × t); *m*/*z* (TOF, ES+) 425.2084 ([M+Na]$^+$ $C_{27}H_{30}O_3Na$ requires 425.2093).

Representative HPLC Data (Entry 11, Table 3 plus racemate):



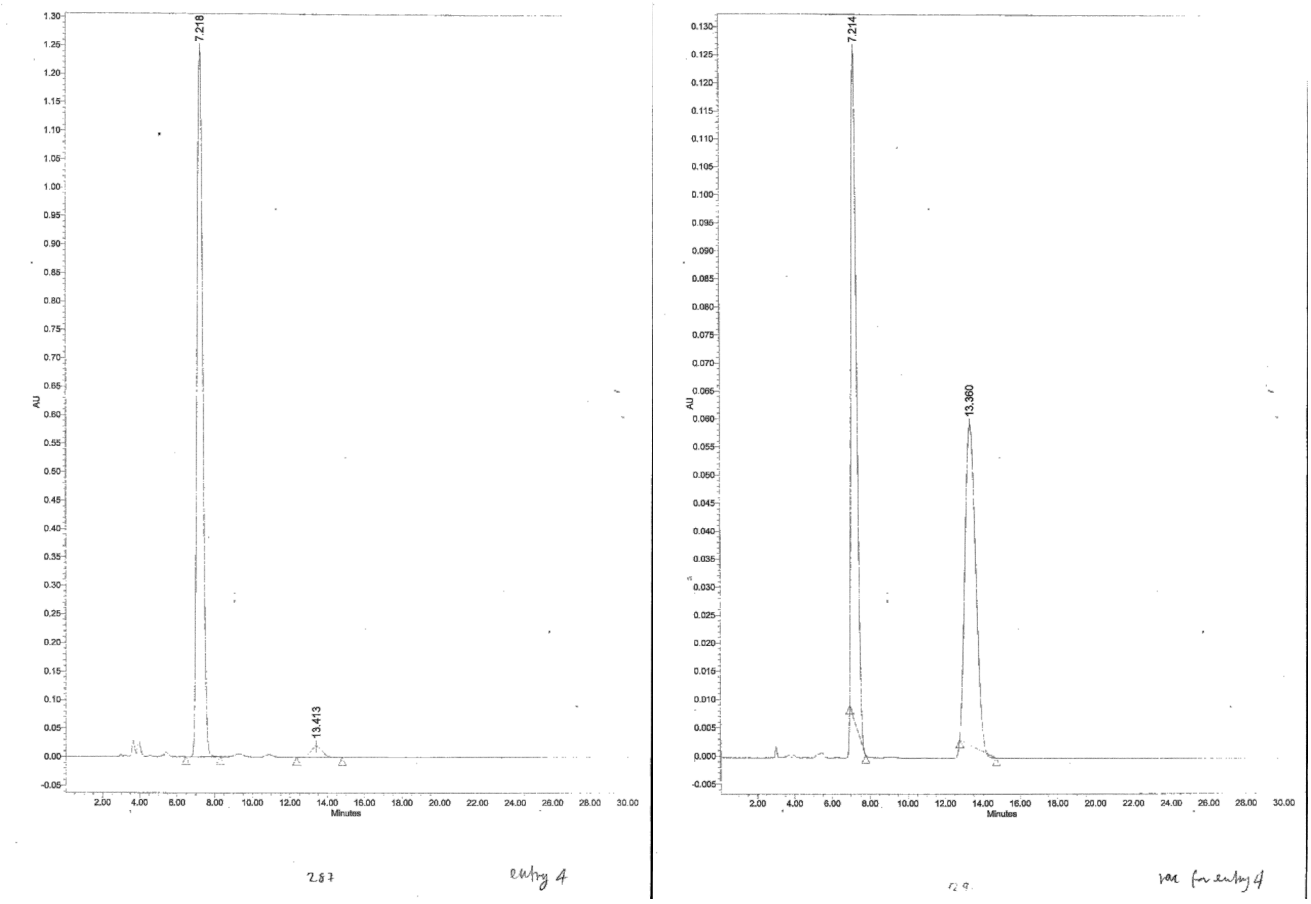
(R-)-4-Methyl-1-phenylpent-1-yn-3-ol[2]

Isolated by column chromatography (10:1 → 7:1 petrol/ EtOAc) as a colourless oil; $[\alpha]_D^{23}$ +3.1 (*c* 1.1, $CHCl_3$) [lit.[2] $[\alpha]_D^{23}$ +3.2 (*c* 6.8, $CHCl_3$)]; ν_{max}/cm^{-1} (thin film) 3356 (br, O–H), 3081, 3059, 3034 (C–H arom.), 2962, 2929 (C–H aliph.), 2222 (C≡C); δ_H(400 MHz, $CDCl_3$) 7.47-7.42 (2H, m, Ph), 7.33-7.29 (3H, m, Ph), 4.41 (1H, d, *J* 5.6, C*H*OH, 1.99 (1H, sepd, *J* 6.7, 5.6, C*H*Me$_2$), 1.88 (1H, br, OH), 1.09 (3H, d, *J* 6.8, CH_3); δ_C (100 MHz, $CDCl_3$) 131.7, 128.3, 128.3 (3 × d, Ph), 122.7 (s, Ph), 88.9, 85.6 (2 × s, C≡C), 64.8 (d, *C*HOH), 34.0 (d, *C*HMe$_2$), 18.2, 17.6 (2 × q, CH_3); ee was determined by hplc (Chiralcel OD, 10% IPA in hexane, 254 nm) t_r 5.5 (major), 9.2 (minor).

(R-)-1-Cyclopropyl-3-phenylprop-2-yn-1-ol[3]

Isolated by column chromatography (10:1 → 5:1 petrol/ EtOAc) as a colourless oil; ν_{max}/cm^{-1} (thin film) 3346 (O–H), 3082, 3007 (C–H arom., C_3H_5), 2870 (C–H aliph.), 2225 (C≡C); δ_H(400 MHz, $CDCl_3$) 7.54-7.42 (2H, m, Ph), 7.33-7.29 (3H, m, Ph), 4.45 (1H, d, *J* 6.4, C*H*OH), 2.16 (1H, br, OH), 1.35 (1H, tdt, *J* 8.0, 6.5, 5.1, C*H*CHOH), 0.55-0.54 (4H, m, $(CH_2)_2$); δ_C(100 MHz, $CDCl_3$) 131.7, 128.4, 128.3 (3 × d, Ph), 122.5 (s, Ph), 87.8, 85.0 (2 × s, C≡C), 66.2 (d, CHOH), 17.2 (d *C*HCHOH), 3.3, 1.6 (2 × t, CH_2); ee was determined by hplc (Chiralcel OD, 10% IPA in hexane, 254 nm) t_r 7.2 (major), 13.4 (minor).

Representative HPLC Data (Entry 4, Table 3 plus racemate):



4,4-Dimethyl-1-phenylpent-1-yn-3-ol[2]

Isolated by column chromatography (4:1 → 2:1 petrol: ether) as a colourless oil; $[\alpha]_D^{23}$ +2.3 (*c* 1.0, $CHCl_3$) [lit.[2] $[\alpha]_D^{30}$ +2.4 (*c* 4.0, $CHCl_3$)]; ν_{max}/cm^{-1} (thin film) 3396 (br, O–H) 3081, 3059, 3034 (C–H arom.), 2859, 2869 (C–H aliph.), 2223 (C≡C); δ_H(400 MHz, $CDCl_3$) 7.46-7.43 (2H, m, Ph), 7.34-7.30

(3H, m, Ph), 4.25 (1H, s, C*H*OH), 1.83 (1H, br, OH), 1.09 (9H, s, $C(CH_3)_3$); δ_C(100 MHz, $CDCl_3$) 131.7, 128.3, 128.3 (3 × d, Ph), 122.8 (s, Ph), 88.9, 85.7 (2× s, C≡C), 71.9 (d, CHOH), 36.1 (s, $C(CH_3)_3$), 25.4 (q, CH_3); *m*/*z* (CI+) 188.2 (M^+, 100%), 171.2 ($[M\text{-}OH]^+$, 85%), 206.2 ($[M+NH_4]^+$, 30%); ee was determined by hplc (Chiralcel OD, 10% IPA in hexane, 254 nm) t_r 5.2 (major), 6.3 (minor).

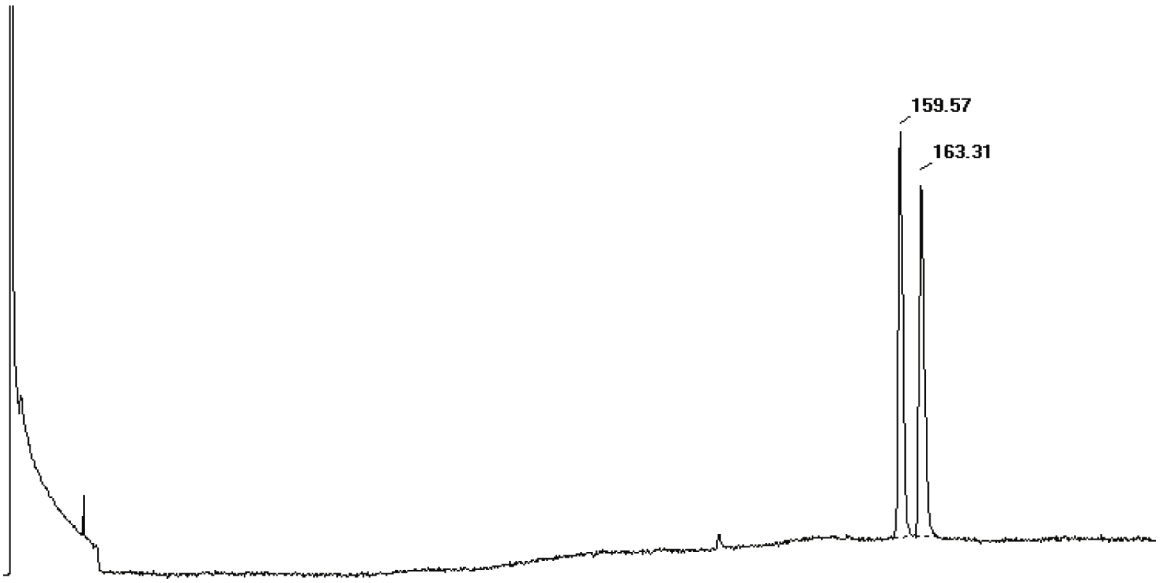
1,3-diphenylprop-2-yn-1-ol[2]

Isolated by column chromatography (3:1 petrol/ether) as a colourless oil; $[\alpha]_D^{23}$ +6.8 (*c* 1.0, $CHCl_3$) [lit.[1] $[\alpha]_D^{23}$ +7.0 (*c* 1.0, EtOH), lit.[2] $[\alpha]_D^{25}$ +7.4 (*c* +7.4 (*c* 1.4, $CHCl_3$); ν_{max}/cm^{-1} 3362 (O–H), 3062, 3030 (C–H, arom.), 2229, 2197 (C_C); δ_H(400 MHz, $CDCl_3$) 7.65-7.30 (10H, m, Ph), 5.71 (1H, d, *J* 5.8, C*H*OH), 2.41 (1H, d, *J* 5.8, OH); δ_C(100 MHz, $CDCl_3$) 140.6 (s, Ph), 131.8, 128.7, 128.6, 128.5, 128.3, 126.7 (6 × d, Ph), 122.4 (s, Ph), 88.7, 86.7 (2 × s, C_C), 65.1 (d, CHOH); ee was determined by chiral GC using a 25 m chir-dex-β column.

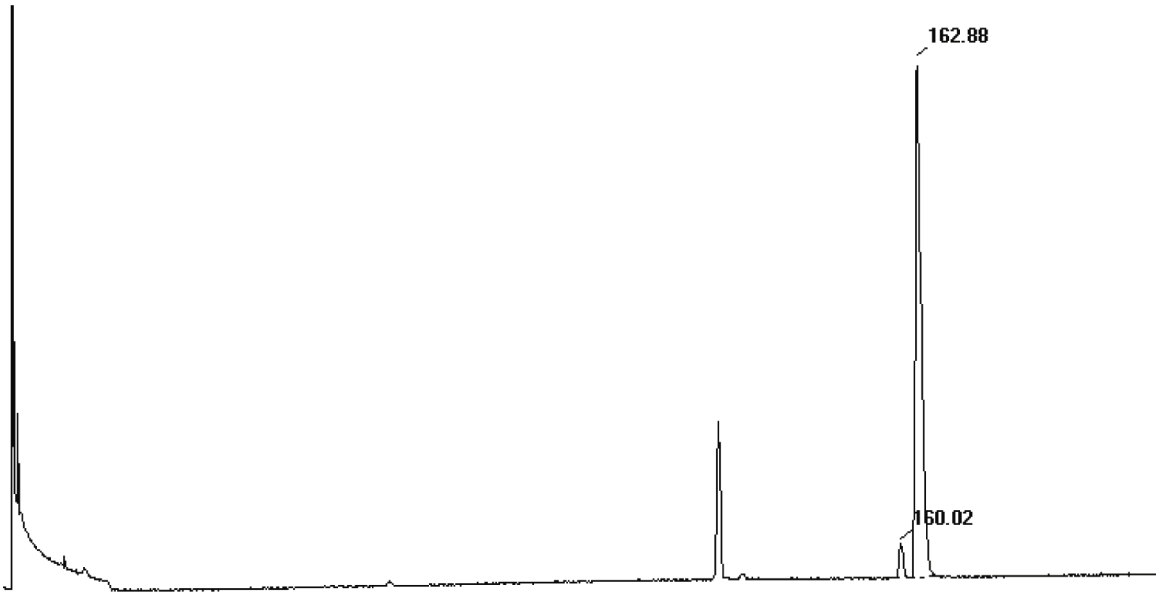
Representative GC Data (Entry 12, Table 3 plus racemate):

Entry 12, Table 3.

Racemate:



91%ee



(R-)-3-Phenyl-1-p-tolylprop-2-yn-1-ol[5]

Isolated by column chromatography (7:1 → 3:1 petrol/ EtOAc; when aGNBn2 was used as the ligand the alcohol was separated from the ligand by using 7:1 → 5:1 toluene/ acetone as eluent) as a colourless oil; $[\alpha]_D^{23}$ +2.8 (c 0.4, CHCl3) [lit.[5] 5.0 (*c* 0.89)]; ν_{max}/cm^{-1} (thin film) 3375 (O–H), 3055, 3025 (C–H arom.), 2923, 2859 (C–H aliph.), 2228, 2200 (C≡C); δ_H(400 MHz, CDCl3) 7.53-7.48 (4H, m, Ar), 7.34-7.32 (3H, m, Ar), 7.24-7.22 (2H, m, Ar), 5.67 (1H, s, CHOH), 2.39 (3H, s, CH3), 2.29 (1H, Br, OH); δ_C(100 MHz, CDCl3) 138.3, 137.8 (2 × s, Ar), 131.8, 129.4, 128.6, 128.3, 126.7 (5 × d, Ar), 122.5 (s, Ar), 88.9, 86.5 (2 × s, C≡C), 65.0 (d, CHOH), 21.2 (q, CH3); ee was determined by hplc (Chiralcel OD, 10% IPA in hexane, 254 nm) t_r 9.3 (major), 20.4 (minor). **3-Phenyl-1-*p*-tolylprop-2-yn-1-one**[6] (9.3 mg, 14 %) was isolated when **5** was used as the ligand at 50° C; δ_H(400 MHz, $CDCl_3$) 8.13 (2H, d, *J* 7.8, $CH_3C_6H_4$), 7.70-7.68 (2H, m, Ph), 7.51-7.41 (3H, m, Ph), 7.32 (2H, d, *J* 7.8, Ph), 2.46 (3H, s, CH_3); δ_C(100 MHz, $CDCl_3$) 177.8 (s, C=O), 145.3, 134.6 (2 × s, Ar), 133.0, 130.7, 129.7, 129.4, 128.7 (5 × d, Ar), 120.3 (s, Ar), 92.6, 87.0 (2 × s, C_C), 21.9 (q, CH_3).

(R-)-1-(4-Chlorophenyl)3-phenylprop-2-yn-ol[5]

Isolated by column chromatography (5:1 → 1:1 petrol/ ether) as a white solid; $[\alpha]_D^{23}$ +6.2 (*c* 1.0, $CHCl_3$) [lit.[5] $[\alpha]_D^{23}$ +6 (*c* 0.72, $CHCl_3$); ν_{max}/cm^{-1} (KBr) 3362 (br, O–H), 3054 (C–H arom.), 2923, 2852 (C–H aliph.), 2225 (C≡C); δ_H(400 MHz, $CDCl_3$) 7.58-7.55 (2H, m, Ph), 7.49-7.47 (2H, m, Ph),

7.40-7.32 (5H, m, Ph), 5.68 (1H, s, C*H*OH), 2.40 (1H, br, OH); δ_C(100 MHz, $CDCl_3$), 139.1, 134.3 (2 × s, Ar) 131.8, 128.8, 128.8, 128.4, 128.1 (5 × d, Ar), 122.1 (s, Ar), 88.2, 87.0 (2 × s, C≡C), 64.4 (d, CHOH); ee was determined by hplc (Chiralcel OD, 10% IPA in hexane, 254 nm) t_r 8.5 (major), 29.1 (minor).

(E)-1,5-Diphenylpent-1-en-4-yn-3-ol:[2]

Isolated by column chromatography (9:1 → 1:2 petrol/ ether) as a pale yellow solid; ν_{max}/cm^{-1} (KBr) 3385 (O–H), 3061, 3029 (C–H arom.), 2925, 2854 (C–H aliph.), 2212 cm^{-1} (C≡C); δ_H(400 MHz, $CDCl_3$) 7.50-7.32 (10H, m, Ph), 6.86 (1H, d, *J* 15.8, PhC*H*), 6.40 (1H, dd, *J* 15.8, 6.0, PhCH=C*H*), 5.30 (1H, d, *J* 6.0, C*H*OH); δ_C(100 MHz, $CDCl_3$) 136.1 (s, Ph), 132.0, 131.8, 128.9, 128.6, 128.3, 128.1, 128.0, 126.8 (8 × d, Ph, C=C), 122.4 (s, Ph), 87.9, 86.5 (s, C≡C), 63.5 (CHOH); HRMS (Probe EI-FI) 234.1053 (M^+, 100%), calcd. for $C_{17}H_{14}O$ 234.1045. **Cinnamyl alcohol:** (7.5 mg, 19% isolated when **4a** was the ligand and 6 mg, 15% when **5** was the ligand); yellow oil; IR (thin film) 3385 (br, O–H), 3060, 3027 (C–H arom.), 2924, 2854 cm^{-1} (C–H aliph.); δ_H(400 MHz, $CDCl_3$) 7.41-7.26, 5H, m, Ph), 6.63 (1H, d, *J* 15.9, PhC<u>H</u>), 6.38 (1H, dt, *J* 15.9, 5.7, $HOCH_2C\underline{H}$), 4.34 (2H, d, *J* 5.7, $HOC\underline{H}_2$), 1.61 (1H, br, OH). **(*E*)-1,5-Diphenylpent-1-en-4-yn-3-one:**[7] (5.0 mg, 7% isolated when **4a** was the ligand and 7.0 mg, 10% when **5** was the ligand); yellow oil; IR (thin film) 3082, 3060, 3029 (C–H arom.), 2926, 2854, 2800 (C–H aliph.), 2212 cm^{-1} (C≡C); δ_H(500 MHz, $CDCl_3$) 7.97 (1H, d, *J* 16.1, PhC<u>H</u>), 7.72-7.71 (2H, m, Ph), 7.68-7.66 (2H, m, Ph), 7.50-7.44 (6H, m, Ph), 6.94 (1H, d, *J* 16.1, PhCHC<u>H</u>); δ_C(125 MHz, $CDCl_3$) 178.3 (s, C=O), 148.4 (d, Ph<u>C</u>H), 134.0, 132.9, 131.2, 130.6, 129.1, 128.7, 128.7, 128.5, 120.2 (Ph, PhCH<u>C</u>H). **Cinnamaldehyde** was also recovered (11 mg, 28% when **4a** was the ligand and 15 mg, 38% when **5** was the ligand.

(R-)-1-Cyclohexyl-4-methylpent-2-yne-1,4-diol[8]

Isolated by column chromatography (1:1 petrol/ ether → ether) as a white solid; $[\alpha]_D^{23}$ –5.8 (*c* 0.6, $CHCl_3$) [lit.[8] $[\alpha]_D^{23}$–5.7 (*c* 0.4, $CHCl_3$)]; IR (KBr) 3355 (br, O–H), 2983, 2931, 2891, 2854 (C–H), 2239, 2854 cm^{-1} (C≡C); δ_H(400 MHz, $CDCl_3$) 4.16 (1H, d, *J* 6.1, C*H*OH), 1.87-1.75 (4H, m, Cx methylene), 1.70-1.66 (1H, m, Cx methylene), 1.58-1.47 (1H, m, CHOHC*H*), 1.52 (6H, s, $C(CH_3)_2$), 1.31-1.18 (2H, m, Cx methylene), 1.17-0.99 (3H, m, Cx methylene); δ_C(100 MHz, $CDCl_3$) 90.4, 80.1, (2 × s, C≡C), 67.0 (d, CHOH), 65.1 (s, *C*Me_2OH), 44.1 (d, CHOH*C*H), 31.4, 31.4 (2 × q, $C(CH_3)_2OH$), 28.6, 28.1, 26.4, 25.9, 25.8 (5 × t, $(CH_2)_5$).

(R-)-1-Cyclohexyl-5-phenylpent-2-yn-1-ol[2]

Isolated by column chromatography (10:1 → 3:1 petrol/ ether) as a colourless oil; $[\alpha]_D^{23}$ –1.3 (*c* 1.1, $CHCl_3$) [lit.[2] $[\alpha]_D^{28}$ –1.7 (*c* 1.1, $CHCl_3$)]; ν_{max}/cm^{-1} (thin film) 3384 (O–H), 3086, 3063, 3028 (C–H arom.), 2925, 2852 (C–H aliph.), 2233 (C≡C); δ_H(400 MHz, $CDCl_3$), 7.33-7.20 (5H, m, Ph), 4.12 (1H, dt, *J* 5.9, 1.9, C*H*OH), 2.94 (2H, t, *J* 7.5, PhCH_2), 2.54 (2H, td, *J* 7.5, 1.9, PhCH_2CH_2), 1.82-1.74 (4H, m, 3 × cyclohexyl CH_2, OH), 1.69-1.65 (1H, m, cyclohexyl CH_2), 1.52-1.44 (1H, m, CHOHC*H*), 1.29-0.99 (6H, m, cyclohexyl CH_2); δ_C (100 MHz, $CDCl_3$) 140.6 (s, Ph), 128.5, 128.3, 126.3 (3 × d, Ph), 85.4, 81.0 (2 × s, C≡C), 67.4 (d, *C*HOH), 44.3 (d, CHOH*C*H), 35.0 (t, Ph*C*H_2), 28.5, 28.0, 26.4, 25.9, 25.9 (5 × t, cyclohexyl CH_2), 20.9 (t, PhCH_2*C*H_2); ee was determined by hplc (Chiralcel OD, 10% IPA in hexane, 254 nm) t_r 7.2 (major), 16.5 (minor).

(R-)-2,2-Dimethyl-7-phenyhept-4-yn-3-ol[2]

Isolated by column chromatography (7:1 → 3:1 petrol/ ether) as a colourless oil; $[\alpha]_D^{23}$ +4.9 (*c* 1.0, $CHCl_3$) [lit.[2] $[\alpha]_D^{28}$ +4.4 (*c* 1.4, $CHCl_3$); ν_{max}/cm^{-1} (thin film) 3424 (br O–H), 3087, 3064, 3028 (C–H arom.), 2955, 2907, 2868 (C–H aliph.), 2224 (C≡C); δ_H(400 MHz, $CDCl_3$) 7.32-7.27 (2H, m, Ph), 7.24-7.22 93H, m, Ph), 3.98 (1H, t, *J* 2.0, C*H*OH), 2.85 (2H, t, *J* 7.5, PhCH_2), 2.54 (2H, td, *J* 7.5, 2.0, PhCH_2CH_2), 1.64 (1H, br, OH), 0.95 (9H, s, C(CH_3)$_3$); δ_C(100 MHz, $CDCl_3$) 140.6 (s, Ph), 128.4, 128.4, 126.3 (3 × d, Ph), 84.5, 80.6 2 × s, C≡C), 71.6 (d, *C*HOH), 35.8 (s, *C*CH_3), 35.1 (t, Ph*C*H_2), 25.2 (q, CH_3), 20.8t, PHCH_2*C*H_2); ee was determined by hplc (Chiralcel OD, 10% IPA in hexane, 254 nm) t_r 5.9 (major), 15.0 (minor).

1-Cyclohexyl-4-methyl-4-(trimethylsilyloxy)pent-2-yn-1-ol[9]

Isolated by column chromatography (3:1 petrol/ ether) as a colourless oil; δ_H(400 MHz, $CDCl_3$) 4.16(1H, d, *J* 5.9, C*H*OH), 1.88-1.76 (5H, m, 4 × cyclohexyl CH_2, OH), 1.70-1.67 (1H, m, cyclohexyl CH_2), 1.55-1.51 (1H, m, cyclohexyl CH_2), 1.49 (6H, 2 × s, C(CH_3)$_2$), 1.27-1.03 (5H, m, cyclohexyl CH_2), 0.19 (9H, Si(CH_3)$_3$); δ_C(100 MHz, $CDCl_3$) 90.8, 82.7 (2 × s, C≡C), 67.2 (d, CHOH), 66.5 (s, *C*(CH_3)$_2$), 44.1 (d, CHOH*C*H), 33.1, 33.1 (2 × q, C(CH_3)$_2$), 28.5, 28.2, 26.4, 25.9, 25.9 (5 × t, (CH_2)$_5$), 2.0 (q, Si(CH_3)$_3$).

1-Cyclohexylpent-2-yne-1,5-diol

Isolated by column chromatography (5:1 → 3:1 toluene/ acetone) as a white solid; mp 92.5-94.0 °C; $[\alpha]_D^{22}$ –10.1 (*c* 0.64, $CHCl_3$); ν_{max}/cm^{-1} (KBr) 3278 (br, O–H), 2921, 2874, 2851 (C–H), 2244 (C≡C); δ_H(400 MHz, $CDCl_3$) 4.13 (1H, d, *J* 6.0, C*H*OH), 3.72 (2H, t, *J* 6.0, C*H*$_2$OH), 3.13 (2H, br, OH), 2.48 (2H, td, *J* 6.0, 1.2, HOCH$_2$C*H*$_2$), 1.86-1.75 (4H, m, cyclohexyl CH_2), 1.70-1.67 (1H, m, cyclohexyl CH_2), 1.52-1.48 (1H, m, CHOHC*H*), 1.30-1.00 (5H, m, cyclohexyl CH_2); δ_C(100 MHz, $CDCl_3$) 82.8, 82.1 (2 × s, C≡C), 67.2 (d, CHOH), 61.0 (t, CH_2OH), 44.2 (CHOH*C*H), 28.6, 28.2, 26.4, 25.9, 25.9 (5 × t, cyclohexyl CH_2), 23.0 (HOCH$_2$*C*H$_2$).

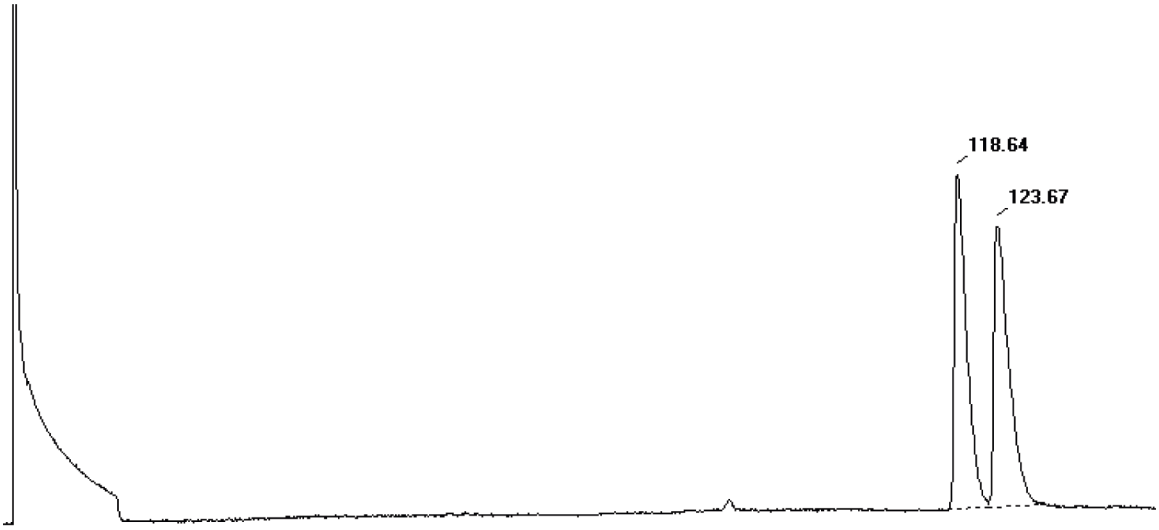
1-cyclohexyl-3-(triethylsilyl)prop-2-yn-1-ol[9]

Isolated by column chromatography (5:1 → 2:1 petrol/ ether) as a white solid; $[\alpha]_D^{23}$ –3.6 (*c* 0.9, $CHCl_3$); δ_H(400 MHz, $CDCl_3$) 4.16 (1H, d, *J* 5.7, C*H*OH), 1.79-1.76 (3H, m, OH, cyclohexyl), 1.69-1.66 (1H, m, cyclohexyl), 1.59-1.52 (1H, m, cyclohexyl), 1.30-1.01 (5H, m, cyclohexyl), 0.99 (9H, t, *J* 7.9, CH_3), 0.60 (6H, q, *J* 7.9, CH_2Si); ee was determined by chiral GC using a 25 m chir-dex-β column.

Representative GC Data (Entry 9, Table 4 plus racemate):

Entry 9. Table 4

Racemate



98% ee

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