

Mechanistic Studies and Improvement of Coinage Metal-Catalyzed Transformation of Alkynyloxiranes to Furans: an Alcohol Addition–Cyclization–Elimination Cascade

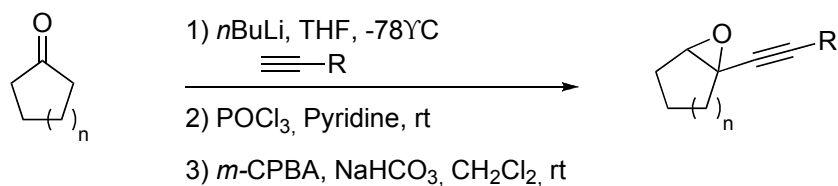
Aurélien Blanc, Katharina Tenbrink, Jean-Marc Weibel and Patrick Pale*

*Laboratoire de Synthèse et Réactivité Organiques
associé au CNRS, Institut de Chimie, Université de Strasbourg
4 rue Blaise Pascal, 67000 Strasbourg, France*

Supporting Information

Preparation and characterization of compounds	S2
Proton and carbon NMR spectra for all compounds	S16

General Information: Proton (^1H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded on the following 300 or 400 MHz instruments. Chemical shifts were given in part per million (ppm) on the delta scale. Solvent peaks were used as reference values, *e. g.* for ^1H NMR: $\text{CDCl}_3 = 7.26$ ppm, $\text{CH}_2\text{Cl}_2 = 5.30$ ppm, $\text{C}_6\text{D}_6 = 7.16$ ppm and for ^{13}C NMR: $\text{CDCl}_3 = 77.0$ ppm, $\text{C}_6\text{D}_6 = 127.6$ ppm. Data is presented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet), coupling constants (J/Hz) and integration. Assignments were determined either on the basis of unambiguous chemical shifts and coupling patterns, or COSY, HMQC, HMBC experiments to fully interpret spectra for compounds. Infrared spectra were recorded in CHCl_3 or neat, and wavelengths of maximum absorbance (ν_{max}) are quoted in wave numbers (cm^{-1}). Mass spectra were recorded by either ElectroSpray Ionization (ESI) or Electronic Impact (EI), and the parent ions $[\text{M}+\text{H}]^+$, $[\text{M}+\text{Na}]^+$ or $[\text{M}+\text{K}]^+$ were quoted. Analytical Thin Layer Chromatographies (TLC) were performed using silica gel 60 F_{254} plates with visualization by ultra violet and potassium permanganate dip. Flash column chromatography was carried out using silica gel 60 (40-63 μm) and the procedure included the subsequent evaporation of solvents *in vacuo*. Reagents and solvents were purified using standard means. Dichloromethane and THF were dried using alumina column system. Triethylamine (Et_3N) and pyridine were distilled from CaH_2 and stored over molecular sieves. All other chemicals were used as received except where otherwise noted in the experimental text. All other extractive procedures were performed using non-distilled solvents and all aqueous solution used were saturated.

General procedure 1 for preparation of alkynyloxiranes.²³


1a	<i>n</i> = 2	R = <i>n</i> Butyl	33% (overall yield)
1b	<i>n</i> = 2	R = Ph	35%
1d	<i>n</i> = 1	R = <i>n</i> Hexyl	24%
1e	<i>n</i> = 3	R = <i>n</i> Butyl	27%
1f	<i>n</i> = 4	R = <i>n</i> Pentyl	61%

Step 1: Synthesis of alkynylalcohols. To a stirred solution of terminal alkyne (22 mmol) in dry THF (50 mL) were added solution of *n*-BuLi in hexane (1.6 M, 21 mmol) at -78 °C. After 30 min, cyclic ketone (20 mmol) was added dropwise to the reaction mixture and stirring continued for 2 h at the same temperature. The reaction mixture was quenched with saturated aqueous NH₄Cl and then extracted with EtOAc. The combined extracts were washed with brine, dried over Na₂SO₄ and evaporated. The residue upon workup was chromatographed on silica gel using cyclohexane/EtOAc as eluent to give the corresponding alkynylalcohol.

Step 2: Synthesis of enynes. To a stirred solution of alkynylalcohol (20 mmol) in pyridine (80 mL) was added POCl₃ (60 mmol) at 0 °C, and the stirring was continued for 4 h at room temperature. The reaction mixture was diluted with water at 0 °C and extracted with AcOEt. The combined extracts were washed with brine, dried over Na₂SO₄ and evaporated. The crude mixture was chromatographed on silica gel using cyclohexane/EtOAc as eluent to give the corresponding enyne.

Step 3: Synthesis of alkynyloxiranes. To a stirred solution of enyne (10 mmol) in CH₂Cl₂ (30 mL) was added NaHCO₃ (30 mmol) and *m*-CPBA (20 mmol) at room

temperature, and stirring was continued for 2 h at rt. The reaction mixture was diluted with saturated aqueous solution of NaOH (1N) and extracted with AcOEt. The combined extracts were washed with brine, dried over Na₂SO₄ and evaporated. After filtration of the reaction mixture using small amount of base Al₂O₃, the residue upon workup was chromatographed on silica gel using cyclohexane/EtOAc as eluent to give the corresponding alkynylepoxyde.

Spectral data of **1a**²³ and **1b**^{15b} were in complete agreement with those reported in the literature.

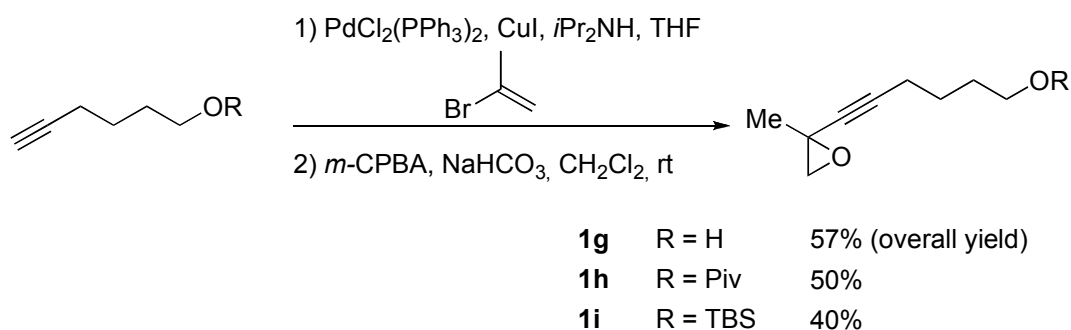
Compound **1c**²⁴ was obtained by epoxidation of commercially available ethynylcyclohexene (See *General Procedure 1* Step 3) and spectral data matched with those reported in the literature.

1-(Oct-1-ynyl)-6-oxa-bicyclo[3.1.0]hexane (1d). Prepared following the *general procedure 1* in 24% overall yield (3 steps). Colorless oil; *R_f* = 0.54 (cyclohexane/EtOAc 15%); IR (neat) ν_{max} 3024, 2955, 2928, 2857, 2238, 1773, 1739, 1680, 1465, 1435, 1402, 1378, 1329, 1295, 1262, 1212, 1181, 1147, 1095, 1055, 1025, 972 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.87 (t, *J* = 6.8 Hz, 3 H), 1.24-1.82 (m, 12 H), 1.96 (dd, *J* = 8.1, 14.0 Hz, 1 H), 2.11 (dd, *J* = 7.8, 13.5 Hz, 1 H), 2.19 (t, *J* = 7.1 Hz, 2 H), 3.56 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 18.8, 19.1, 22.4, 27.5, 28.4, 28.5, 31.2, 32.0, 56.2, 65.0, 76.5, 85.3; MS (ESI) *m/z* (%) 231 (20, M⁺+K), 215 (100, M⁺+Na), 199 (43, M⁺+Li); HR-MS 199.1649 (C₁₃H₂₀O+Li calcd 199.1669).

1-(Hex-1-ynyl)-8-oxa-bicyclo[5.1.0]octane (1e). Prepared following the *general procedure 1* in 27% overall yield (3 steps). Colorless oil; $R_f = 0.7$ (cyclohexane/EtOAc 20%); IR (neat) $\nu_{\max}$ 2927, 2856, 2242, 1716, 1680, 1456, 1278, 1257, 1327, 1303, 1253, 1231, 1200, 1160, 1116, 1080, 1061, 1029, 964 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.88 (t, $J = 7.2$ Hz, 3 H), 1.38-1.76 (m, 10 H), 1.89-2.18 (m, 4 H), 2.17 (t, $J = 6.9$ Hz, 2 H), 3.20 (dd, $J = 3.7, 6.9$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.5, 18.3, 21.9, 24.2, 24.7, 29.2, 30.6, 31.1, 34.9, 54.4, 63.5, 81.3, 82.2; MS (ESI) m/z (%) 231 (20, $\text{M}^+ + \text{K}$), 215 (100, $\text{M}^+ + \text{Na}$), 199 (43, $\text{M}^+ + \text{Li}$); HR-MS 199.1649 ($\text{C}_{13}\text{H}_{20}\text{O} + \text{Li}$ calcd 199.1669).

1-(Hept-1-ynyl)-9-oxabicyclo[6.1.0]nonane (1f). Prepared following the *general procedure 1* in 61% overall yield (3 steps). Colorless oil; $R_f = 0.66$ (cyclohexane/EtOAc 20%); IR (neat) $\nu_{\max}$ 2926, 2856, 2243, 1798, 1773, 1732, 1678, 1574, 1468, 1458, 1447, 1378, 1327, 1297, 1280, 1264, 1216, 1193, 1182, 1158, 1116, 1089, 1021, 1001, 926 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, $J = 7.1$ Hz, 3 H), 1.31-1.60 (m, 16 H), 2.10-2.20 (m, 2 H), 2.18 (t, $J = 7.0$ Hz, 2 H), 3.02 (dd, $J = 4.2, 10.4$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 18.6, 22.1, 25.2, 25.7, 26.0, 26.4, 27.1, 28.2, 30.8, 31.0, 54.1, 63.7, 79.6, 83.5; MS (ESI) m/z (%) 259 (32, $\text{M}^+ + \text{K}$), 243 (56, $\text{M}^+ + \text{Na}$), 227 (100, $\text{M}^+ + \text{Li}$); HR-MS 227.1967 ($\text{C}_{15}\text{H}_{24}\text{O} + \text{Li}$ calcd 227.1982).

General procedure 2 for preparation of alkynyloxiranes.



Step 1: Synthesis of enynes.^{21a} To a solution of 2-bromopropene (12 mmol) in THF (25 mL) was added diisopropylamine (15 mL), 1-octyn-3-ol (10 mmol), PdCl₂(PPh₃)₂ (0.2 mmol) and CuI (0.4 mmol). The resulting mixture was stirred at ambient temperature for 2 h before being diluted with Et₂O (100 mL) and treated with H₂O (100 mL). The ethereal layer was separated and the aqueous layer was extracted with Et₂O (3 x 50 mL). The combined organic layers were washed with H₂O, brine, dried over MgSO₄ and concentrated. The residue was purified through silica gel flash column chromatography (EtOAc/cyclohexane) to yield the corresponding enyne as a clear liquid.

Step 2: Synthesis of alkynyloxiranes. See *General Procedure 1* (Step 3).

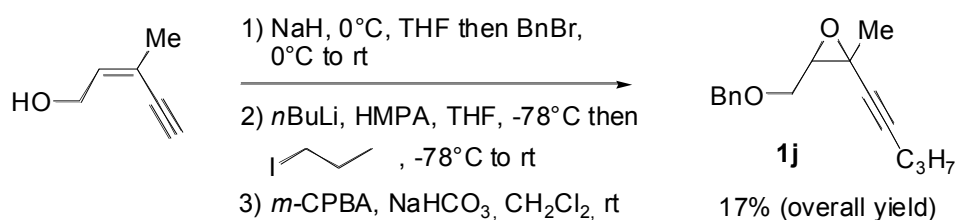
The spectrum data of **1g**⁷ were in complete agreement with those reported in the literature.

6-(2-Methyloxiran-2-yl)hex-5-ynyl pivalate (1h): Prepared following the *general procedure 2* in 50 % yield (2 steps). Colorless oil; R_f = 0.42 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 2972, 2871, 2241, 1724, 1480, 1458, 1397, 1379, 1365, 1339, 1283, 1150, 1060, 1039, 1001, 938 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.18 (s, 9 H), 1.50 (s, 3 H), 1.50-1.60

(m, 2 H), 1.65-1.75 (m, 2 H), 2.21 (t, $J = 7.0$ Hz, 2 H), 2.70 (d, $J = 5.6$ Hz, 1 H), 2.94 (d, $J = 5.6$ Hz, 1 H), 4.05 (t, $J = 6.3$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 18.3, 23.2, 24.9, 27.1, 27.7, 38.7, 47.4, 55.5, 63.7, 79.9, 82.2, 178.5; MS (ESI) m/z (%) 277 (28, $\text{M}^+ + \text{K}$), 261 (100, $\text{M}^+ + \text{Na}$), 245 (7, $\text{M}^+ + \text{Li}$); HR-MS 261.1496 ($\text{C}_{14}\text{H}_{22}\text{O}_3 + \text{Na}$ calcd 261.1461).

***tert*-Butyldimethyl-(6-(2-methyloxiran-2-yl)hex-5-ynyloxy)silane (1i):** Prepared following the general procedure 2 in 40 % yield (2 steps). Colorless oil; $R_f = 0.7$ (cyclohexane/EtOAc 25%); IR (neat) ν_{max} 2952, 2929, 2857, 2212, 1773, 1732, 1678, 1575, 1471, 1462, 1433, 1380, 1360, 1338, 1253, 1226, 1102, 1005, 971, 938 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.05 (s, 6 H), 0.89 (s, 9 H), 1.53 (s, 3 H), 1.56-1.65 (m, 4 H), 2.21 (t, $J = 6.7$ Hz, 2 H), 2.71 (d, $J = 5.5$ Hz, 1 H), 2.96 (d, $J = 5.7$ Hz, 1 H), 3.61 (t, $J = 5.7$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ -5.4, 18.4, 23.3, 24.8, 25.9, 31.8, 47.5, 55.5, 62.6, 79.6, 82.9; MS (ESI) m/z (%) 275 (100, $\text{M}^+ + \text{Li}$); HR-MS 275.2005 ($\text{C}_{15}\text{H}_{28}\text{O}_2\text{Si} + \text{Li}$ calcd 275.2013).

Preparation of alkynyloxirane 1j.



Step 1: Benzylation of (Z)-3-methylpent-2-en-4-yn-1-ol. Sodium hydride (57% in oil, 22 mmol) was added slowly at 0°C to a solution of (Z)-3-methylpent-2-en-4-yn-1-ol (20 mmol) in dry THF (20 mL). A solution of benzyl bromide (24 mmol) in THF (10 mL) was then added at room temperature. The mixture was stirred for 2 h and became white. It was then

neutralized with saturated aqueous NH_4Cl solution and washed with water. The organic layer was separated and the aqueous phase was extracted three times with diethyl ether. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated. Purification by flash column chromatography (cyclohexane/EtOAc 0→5%) afford 1.75 g (47%) of (Z)-((3-methylpent-2-en-4-ynyloxy)methyl)benzene as yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 1.92 (s, 3 H), 4.26 (dd, $J = 1.0, 6.7$ Hz, 2 H), 4.53 (s, 2 H), 5.95 (m, 1 H), 7.27-7.38 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.0, 68.5, 72.3, 81.9, 82.1, 120.7, 127.6, 127.8, 135.3, 138.3.

Step 2: Synthesis of (Z)-((3-methyloct-2-en-4-ynyloxy)methyl)benzene. 1.1g of (Z)-((3-methylpent-2-en-4-ynyloxy)methyl)benzene (5.9 mmol) was dissolved in dry THF (30 mL) and HMPA (17.7 mmol) and cooled down to -78°C . $n\text{Buli}$ (1.6 M in hexanes, 6.2 mmol) was added dropwise and the reaction mixture was stirred for 30 min at -78°C . Iodopropane was then added and the mixture was stirred at -78 to 0°C for 1h. The reaction was quenched with saturated aqueous NH_4Cl solution and extracted with Et_2O . The combined organic layers were washed several times with water, brine Na_2SO_4 , filtered, and concentrated. Purification by flash column chromatography (cyclohexane/EtOAc 0→5%) afford 750 mg (56%) of (Z)-((3-methyloct-2-en-4-ynyloxy)methyl)benzene as colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 0.99 (t, $J = 7.4$ Hz, 3 H), 1.52 (sext, $J = 7.2$ Hz, 2 H), 1.89 (s, 3 H), 2.30 (t, $J = 7.0$ Hz, 2 H), 4.23 (dd, $J = 1.0, 6.7$ Hz, 2 H), 4.52 (s, 2 H), 5.79 (m, 1 H), 7.27-7.38 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.5, 21.5, 22.2, 23.7, 68.7, 72.1, 79.2, 95.4, 122.6, 127.5, 127.9, 128.3, 131.8, 138.6.

Step 3: Synthesis of alkynyloxirane 1j. Prepared using *General Procedure 1* (step 3) from 500 mg of (Z)-((3-methyloct-2-en-4-ynyloxy)methyl)benzene. After flash column chromatography (cyclohexane/EtOAc 5→10%), 350 mg of **1j** was obtained (65%).

(2*S,3*R**)-3-((Benzyloxy)methyl)-2-methyl-2-(pent-1-ynyl)oxirane (1j).** Prepared in 3 steps with 40% yield from (Z)-3-methylpent-2-en-4-yn-1-ol. Colorless oil; R_f = 0.54 (cyclohexane/EtOAc 10%); IR (neat) $\nu_{\max}$ 3030, 2963, 2616, 2871, 2848, 2238, 1944, 1810, 1772, 1731, 1575, 1496, 1453, 1378, 1339, 1304, 1244, 1166, 1128, 1086, 1027, 940 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.96 (t, J = 7.3 Hz, 3 H), 1.50 (sext, J = 7.2 Hz, 2 H), 1.53 (s, 3 H), 2.16 (t, J = 7.0 Hz, 2 H), 3.09 (t, J = 5.2 Hz, 1 H), 3.75 (d_{ab} , J_{ab} = 4.8, 11.2 Hz, 2 H), 4.60 (ab, J_{ab} = 11.8 Hz, 2 H), 7.27-7.38 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.4, 20.6, 21.8, 23.6, 51.6, 62.6, 69.8, 73.3, 77.2, 85.5, 127.6, 127.7, 128.3, 138.0; MS (ESI) m/z (%) 267 (7, $\text{M}^+ + \text{Na}$), 251 (100, $\text{M}^+ + \text{Li}$); HR-MS 251.1616 ($\text{C}_{16}\text{H}_{20}\text{O}_2 + \text{Li}$ calcd 251.1618).

1-(4-(7-Oxa-bicyclo[4.1.0]heptan-1-yl)buta-1,3-diynyl)-7-oxa-bicyclo[4.1.0]heptane (1k). To a solution of ethynylcyclohexene (3 mmol) in dry THF (15 mL) was added diisopropylamine (6 mL), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.2 mmol) and CuI (0.4 mmol). The resulting mixture was stirred at ambient temperature for 20 h before being diluted with Et_2O (30 mL) and treated with H_2O (30 mL). The ethereal layer was separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with H_2O , brine, dried over MgSO_4 and concentrated. The residue was purified through silica gel flash column chromatography (cyclohexane/EtOAc 5%) to yield the 1,4-dicyclohexenylbuta-1,3-diyne as a clear liquid (250 mg, 79%). ^1H NMR (300 MHz, CDCl_3) δ 1.59 (m, 8 H), 2.11 (m, 8 H), 6.24 (m, 2 H).

Following the *General Procedure 1* (step 3), the alkynyloxirane **1k** (120 mg, 42%) was obtained as a pale yellow solid from 250 mg of 1,4-dicyclohexenylbuta-1,3-diyne. R_f = 0.7

(cyclohexane/EtOAc 50%); mp = 55-56°C; IR (neat) ν_{max} 2988, 2939, 2862, 2243, 1771, 1724, 1594, 1573, 1427, 1342, 1277, 1260, 1216, 1191, 1175, 1131, 1087, 1046, 977 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.25-1.40 (m, 8 H), 1.87-2.09 (m, 8 H), 3.34 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 18.6, 19.2, 24.0, 29.1, 50.2, 60.1, 66.3, 79.5; MS (ESI) m/z (%) 281 (50, $\text{M}^+ + \text{K}$), 265 (100, $\text{M}^+ + \text{Na}$), 241 (40, $\text{M}^+ - \text{H}$); HR-MS 265.1229 ($\text{C}_{16}\text{H}_{18}\text{O}_2 + \text{Na}$ calcd 265.1199).

General Procedure for Silver(I) or Gold(I)-Catalyzed Formation of Furans from Alkynyloxiranes:

Method A (Silver Catalysis): To a solution of alkynyloxirane (1 mmol) in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (5 mL, 9/1 v/v) was added successively *p*-toluenesulfonic acid (APTS, 0.05 mmol) and AgOTf (0.05 mmol) at room temperature. The reaction was monitored by thin layer chromatography until completion. The reaction mixture was filtered throughout a pad of silica gel with CH_2Cl_2 . Solvents were removed in vacuo and the crude residue was purified by flash chromatography.

Method B (Gold Catalysis): Alkynyloxirane (1 mmol in 1 mL of CH_2Cl_2) was added to a stirred solution of premixed Ph_3PAuCl (0.05 mmol) and AgOTf (0.05 mmol) in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (5 mL, 9/1 v/v) at 0°C or room temperature. The reaction was monitored by thin layer chromatography until completion. The reaction mixture was filtered throughout a pad of silica gel with CH_2Cl_2 . Solvents were removed in vacuo and the crude residue was purified by flash chromatography.

2-Butyl-4,5,6,7-tetrahydrobenzofuran (2a). Following *Method B*, alkynyloxirane **1a** (200 mg, 1.12 mmol) gave **2a** (170 mg, 85%) as a colorless oil. $R_f = 0.64$ (cyclohexane/EtOAc 20%); IR (neat) $\nu_{\max}$ 2935, 2870, 1738, 1674, 1520, 1446, 1379, 1220, 1165, 1120, 1095, 982 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.94 (t, $J = 7.3$ Hz, 3 H), 1.39 (sext, 7.4 Hz, 2 H), 1.58 (quint, $J = 5.7$ Hz, 2 H), 1.66-1.75 (m, 2 H), 1.78-1.85 (m, 2 H), 2.37-2.40 (m, 2 H), 2.54-2.60 (m, 4 H), 5.79 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.8, 22.1, 22.3, 23.1, 23.2, 23.3, 27.8, 30.4, 105.4, 117.1, 148.6, 154.2; MS (ESI) m/z (%) 357 (100, $2\text{M}^+ + 2\text{H}$), 179 (95, $\text{M}^+ + \text{H}$); HR-MS 179.1438 ($\text{C}_{12}\text{H}_{18}\text{O} + \text{H}$ calcd 179.1430).

Following *Method A*, alkynyloxirane **1a** (100 mg, 0.56 mmol) gave **2a** (80 mg, 80%).

4,5,6,7-tetrahydro-2-phenylbenzofuran (2b).^{11b} Following *Method B*, alkynyloxirane **1b** (100 mg, 0.5 mmol) gave **2b** (87 mg, 87%) as a colorless oil. Spectral data of **2b** were in complete agreement with these reported in the literature.

4,5,6,7-tetrahydrobenzofuran (2c).²⁵ Following *Method B*, alkynyloxirane **1c** (61 mg, 0.5 mmol) gave **2c** (50 mg, 82%) as a colorless oil. Spectral data of **2c** were in complete agreement with those reported in the literature.

2-Butyl-5,6,7,8-tetrahydro-4H-cyclohepta[b]furan (2e). Following *Method B*, alkynyloxirane **1e** (100 mg, 0.52 mmol) gave **2e** (70 mg, 70%) as a colorless oil. $R_f = 0.62$ (cyclohexane/EtOAc 20%); IR (neat) $\nu_{\max}$ 2954, 2921, 2852, 1765, 1633, 1571, 1445, 1378, 1343, 1273, 1231, 1171, 1097, 1080, 1046, 980 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.93 (t, $J = 7.3$ Hz, 3 H), 1.40 (sext, 7.4 Hz, 2 H), 1.54-1.77 (m, 8 H), 2.42 (m, 2 H), 2.52 (t, $J = 7.6$

Hz, 2 H), 2.71 (m, 2 H), 5.73 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.8, 22.4, 26.2, 26.7, 27.6, 28.8, 28.9, 30.3, 30.7, 108.1, 120.9, 151.0, 152.4; MS (ESI) m/z (%) 231 (42, $2\text{M}^+ + \text{K}$), 215 (100, $\text{M}^+ + \text{Na}$), 199 (93, $\text{M}^+ + \text{Li}$); HR-MS 199.1705 ($\text{C}_{13}\text{H}_{20}\text{O} + \text{Li}$ calcd 199.1669).

Following Method A, alkynyloxirane **1e** (100 mg, 0.52 mmol) gave **2e** (72 mg, 72%).

2-Pentyl-4,5,6,7,8,9-hexahydrocycloocta[b]furan (2f). Following Method B, alkynyloxirane **1f** (100 mg, 0.45 mmol) gave **2f** (93 mg, 93%) as a colorless oil. R_f = 0.68 (cyclohexane/EtOAc 15%); IR (neat) ν_{max} 2928, 2859, 1733, 1518, 1454, 1344, 1257, 1166, 1089, 1009, 931 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.90 (t, J = 6.2 Hz, 3 H), 1.30-1.34 (m, 4 H), 1.45-1.71 (m, 10 H), 2.46-2.55 (m, 4 H), 2.71 (m, 2 H), 5.70 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 22.4, 23.8, 25.4, 25.9, 26.1, 27.4, 27.9, 28.0, 28.8, 31.5, 107.4, 118.5, 149.4, 153.0; MS (ESI) m/z (%) 259 (32, $\text{M}^+ + \text{K}$), 243 (56, $\text{M}^+ + \text{Na}$), 227 (100, $\text{M}^+ + \text{Li}$); HR-MS 227.1978 ($\text{C}_{15}\text{H}_{24}\text{O} + \text{Li}$ calcd 227.1982).

Following Method A, alkynyloxirane **1f** (100 mg, 0.45 mmol) gave **2f** (92 mg, 92%).

4-(4-Methylfuran-2-yl)butan-1-ol (2g).⁷ Following Method B, alkynyloxirane **1g** (100 mg, 0.56 mmol) gave **2g** (69 mg, 69%) as a colorless oil. Spectral data of **2g** were in complete agreement with those reported in the literature.

Following Method B, alkynyloxirane **1g** (100 mg, 0.56 mmol) gave **2g** (52 mg, 52%).

4-(4-Methylfuran-2-yl)butyl pivalate (2h). Following Method B, alkynyloxirane **1h** (100 mg, 0.42 mmol) gave **2h** (75 mg, 75%) as a colorless oil. R_f = 0.6 (cyclohexane/EtOAc 15%); IR (neat) ν_{max} 2957, 2871, 1796, 1769, 1725, 1618, 1551, 1479, 1458, 1397, 1365, 1283,

1150, 1119, 1035, 941 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.19 (s, 9 H), 1.66-1.70 (m, 4 H), 1.98 (s, 3 H), 2.60 (t, $J = 6.7$ Hz, 2 H), 4.06 (t, $J = 6.1$ Hz, 2 H), 5.85 (s, 1 H), 7.05 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 9.7, 24.4, 27.1, 27.6, 28.1, 38.7, 64.0, 107.7, 120.4, 137.4, 155.7, 178.5; MS (ESI) m/z (%) 277 (88, $\text{M}^+ + \text{K}$), 261 (100, $\text{M}^+ + \text{Na}$), 245 (45, $\text{M}^+ + \text{Li}$); HR-MS 261.1462 ($\text{C}_{14}\text{H}_{22}\text{O}_3 + \text{Na}$ calcd 261.1461).

Following Method A, alkynyloxirane **1h** (100 mg, 0.42 mmol) gave **2h** (81 mg, 81%).

tert-Butyldimethyl(4-(4-methylfuran-2-yl)butoxy)silane (2i). Following Method B, alkynyloxirane **1i** (50 mg, 0.19 mmol) gave **2i** (39.5 mg, 79%) as a colorless oil. $R_f = 0.6$ (cyclohexane/EtOAc 15%); IR (neat) ν_{max} 2950, 2928, 2895, 2857, 1618, 1552, 1471, 1461, 1387, 1360, 1253, 1099, 1005, 969 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.05 (s, 6 H), 0.90 (s, 9 H), 1.51-1.72 (m, 4 H), 1.98 (s, 3 H), 2.58 (t, $J = 7.0$ Hz, 2 H), 3.63 (t, $J = 6.3$ Hz, 2 H), 5.85 (s, 1 H), 7.05 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ -5.3, 9.8, 24.4, 26.0, 27.8, 32.3, 62.9, 107.6, 120.4, 137.2, 156.3; MS (ESI) m/z (%) 307 (100, $\text{M}^+ + \text{K}$), 291 (29, $\text{M}^+ + \text{Li}$), 275 (7, $\text{M}^+ + \text{Li}$); HR-MS 291.1768 ($\text{C}_{15}\text{H}_{28}\text{O}_2\text{Si} + \text{Na}$ calcd 291.1751).

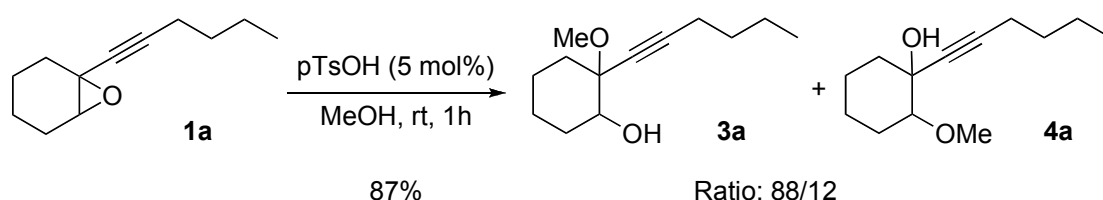
Following Method A, alkynyloxirane **1i** (100 mg, 0.37 mmol) gave **2i** (84 mg, 84%).

2-(Benzyloxymethyl)-3-methyl-5-propylfuran (2j). Following Method B, alkynyloxirane **1j** (75 mg, 0.3 mmol) gave **2j** (60 mg, 80%) as a colorless oil. $R_f = 0.58$ (cyclohexane/EtOAc 5%); IR (neat) ν_{max} 2963, 2932, 3874, 1725, 1682, 1496, 1453, 1377, 1314, 1270, 1176, 1095, 1069, 1026, 934 cm^{-1} ; ^1H NMR (300 MHz, C_6D_6) δ 0.82 (t, $J = 7.4$ Hz, 3 H), 1.55 (sext, 7.5 Hz, 2 H), 1.85 (s, 3 H), 2.43 (t, $J = 7.8$ Hz, 2 H), 4.36 (s, 2 H), 4.41 (s, 2 H), 5.72 (s, 1 H), 7.05-7.16 (m, 3 H), 7.30 (d, $J = 6.7$ Hz, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 9.9, 13.8, 21.6,

30.3, 62.2, 71.5, 108.7, 119.7, 127.5, 127.8, 128.4, 139.2, 146.3, 155.6; MS (ESI) m/z (%) 283 (100, $M^+ + K$), 267 (43, $M^+ + Na$); HR-MS 283.1068 ($C_{16}H_{20}O_2 + K$ calcd 283.1095).

4,4',5,5',6,6',7,7'-Octahydro-2,2'-bibenzofuran (2k). Following *Method B*, alkynyloxirane **1k** (25 mg, 0.1 mmol) gave **2k** (18 mg, 72%) as a white solid. R_f = 0.56 (cyclohexane/EtOAc 20%); mp = 152-153°C; IR (neat) ν_{max} 2932, 2846, 1626, 1597, 1515, 1480, 1447, 1395, 1348, 1292, 1260, 1233, 1215, 1189, 1129, 1074, 1049, 953 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 1.69-1.88 (m, 8 H), 2.40-2.45 (m, 4 H), 2.60-2.65 (m, 4 H), 6.25 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 23.0, 23.1, 23.2, 105.1, 118.5, 144.7, 149.9; MS (ESI) m/z (%) 281 (25, $M^+ + K$), 265 (100, $M^+ + Na$), 249 (13, $M^+ + Li$); HR-MS 265.1165 ($C_{16}H_{18}O_2 + Na$ calcd 265.1199).

Synthesis of intermediates **3a** and **4a** by methanolysis of **1a**.



To a solution of alkynyloxirane **1a** (100 mg, 0.56 mmol) in absolute methanol (2 mL) was added *p*-toluenesulfonic acid monohydrate (10.6 mg, 5 mol%). The reaction mixture was stirred at room temperature for 1h. The solvent was then removed in vacuo and the crude residue was purified by flash chromatography (cyclohexane/EtOAc 10%). After purification, 90 mg of **3a** (major) and 14 mg of **4a** (minor) were obtained both as colorless oils (cumulative yield 87%, ratio 88/12).

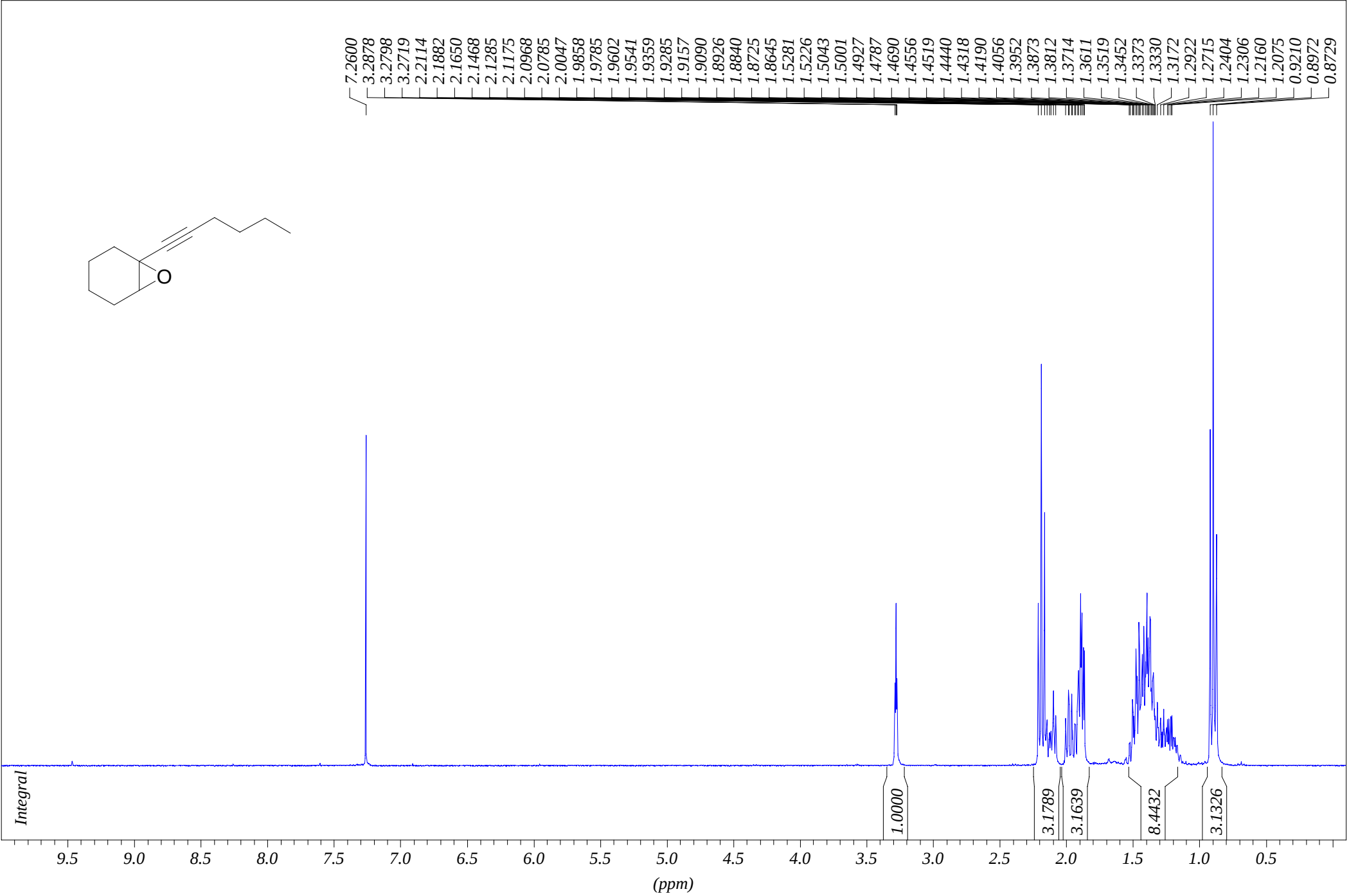
2-(Hex-1-ynyl)-2-methoxycyclohexanol (3a). $R_f = 0.2$ (cyclohexane/EtOAc 15%); IR (neat) $\nu_{\max}$ 3399, 2932, 2859, 2225, 1742, 1680, 1572, 1446, 1378, 1352, 1253, 1220, 1171, 1123, 1084, 1030, 997 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.90 (t, $J = 7.2$ Hz, 3 H), 1.21-1.31 (m, 2 H), 1.38-1.60 (m, 8 H), 1.85 (m, 1 H), 2.08 (m, 1 H), 2.27 (t, $J = 6.9$ Hz, 2 H), 2.35 (d, $J = 4.0$ Hz, 1 H), 3.36 (s, 3 H), 3.45 (dt, $J = 4.0, 10.5$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.5, 18.4, 21.9, 22.8, 23.4, 30.7, 30.9, 33.7, 50.0, 75.4, 76.8, 79.5, 89.8; MS (ESI) m/z (%) 211 (100, $\text{M}^+ + \text{H}$); HR-MS 211.1699 ($\text{C}_{13}\text{H}_{22}\text{O}_2 + \text{H}$ calcd 211.1693).

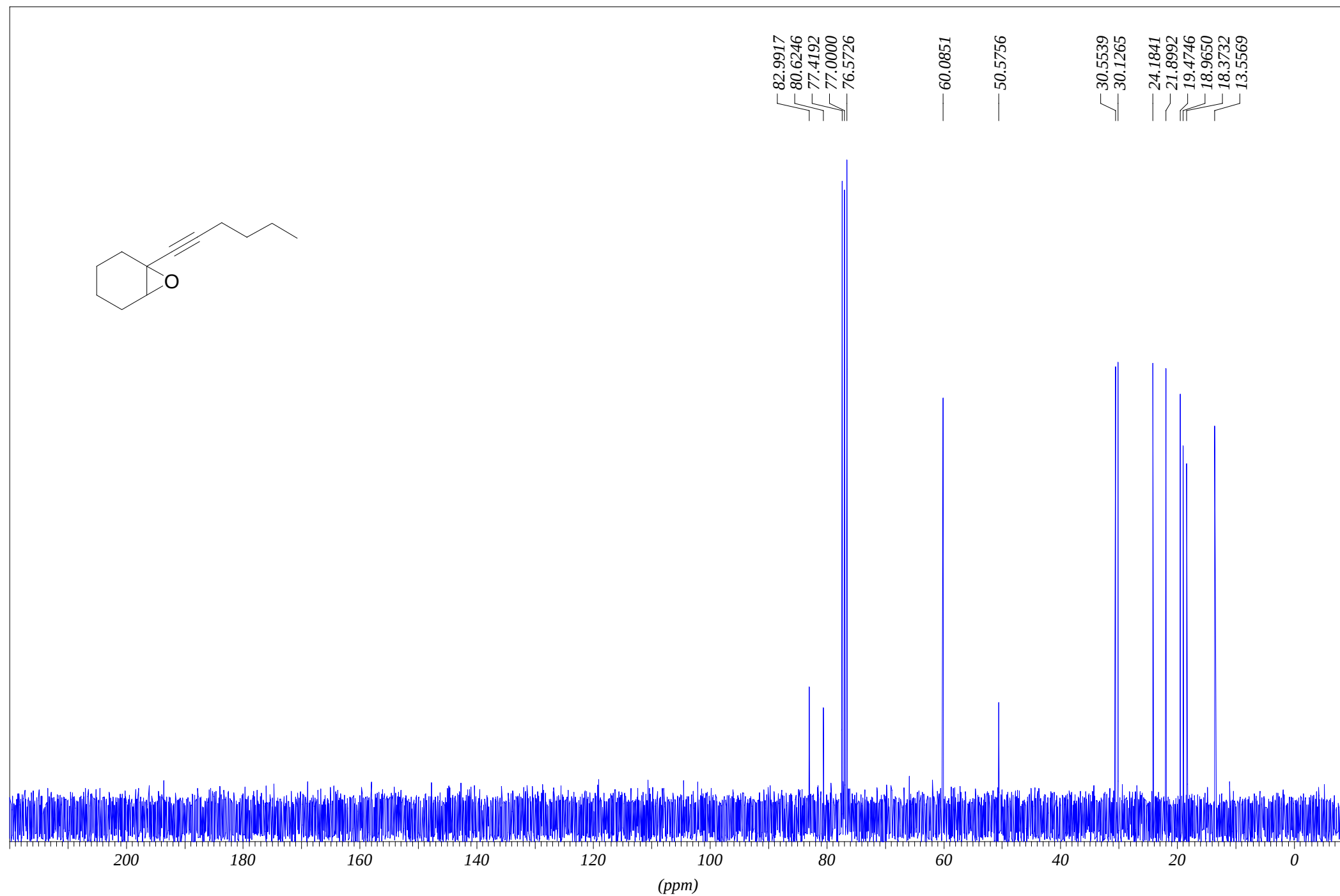
1-(Hex-1-ynyl)-2-methoxycyclohexanol (4a). $R_f = 0.24$ (cyclohexane/EtOAc 15%); IR (neat) $\nu_{\max}$ 3468, 2933, 2860, 2827, 2234, 1730, 1679, 1458, 1445, 1381, 1353, 1335, 1248, 1178, 1145, 1080, 1031, 995 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.91 (t, $J = 7.2$ Hz, 3 H), 1.31-1.81 (m, 12 H), 2.23 (t, $J = 6.9$ Hz, 2 H), 2.43 (d, $J = 1.9$ Hz, 1 H), 3.34 (s, 3 H), 3.77 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.5, 18.3, 20.4, 21.9, 22.2, 29.0, 30.8, 31.4, 50.5, 71.6, 76.2, 78.8, 88.4; MS (ESI) m/z (%) 211 (100, $\text{M}^+ + \text{H}$); HR-MS 211.1669 ($\text{C}_{13}\text{H}_{22}\text{O}_2 + \text{H}$ calcd 211.1693).

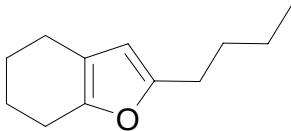
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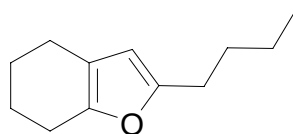
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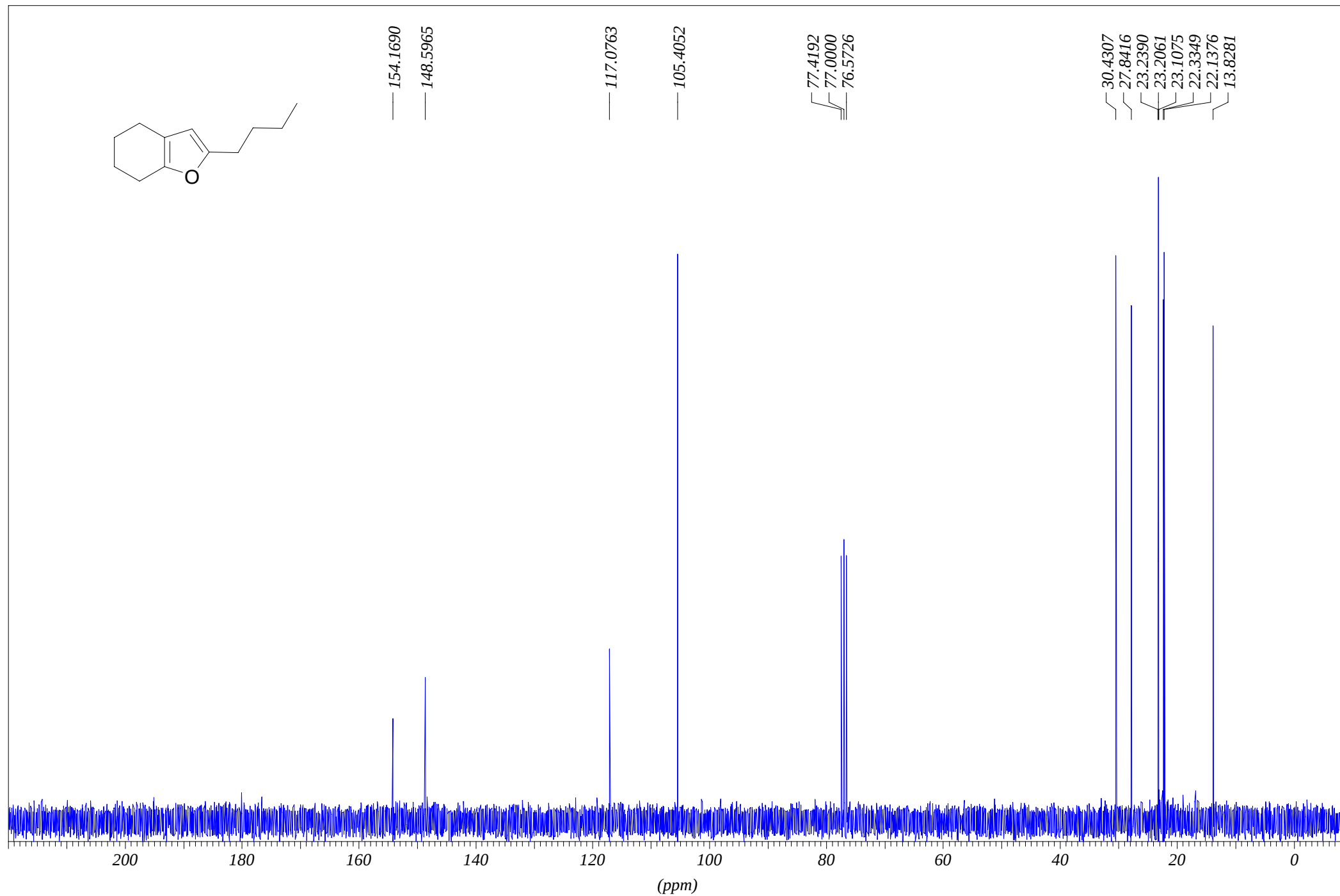


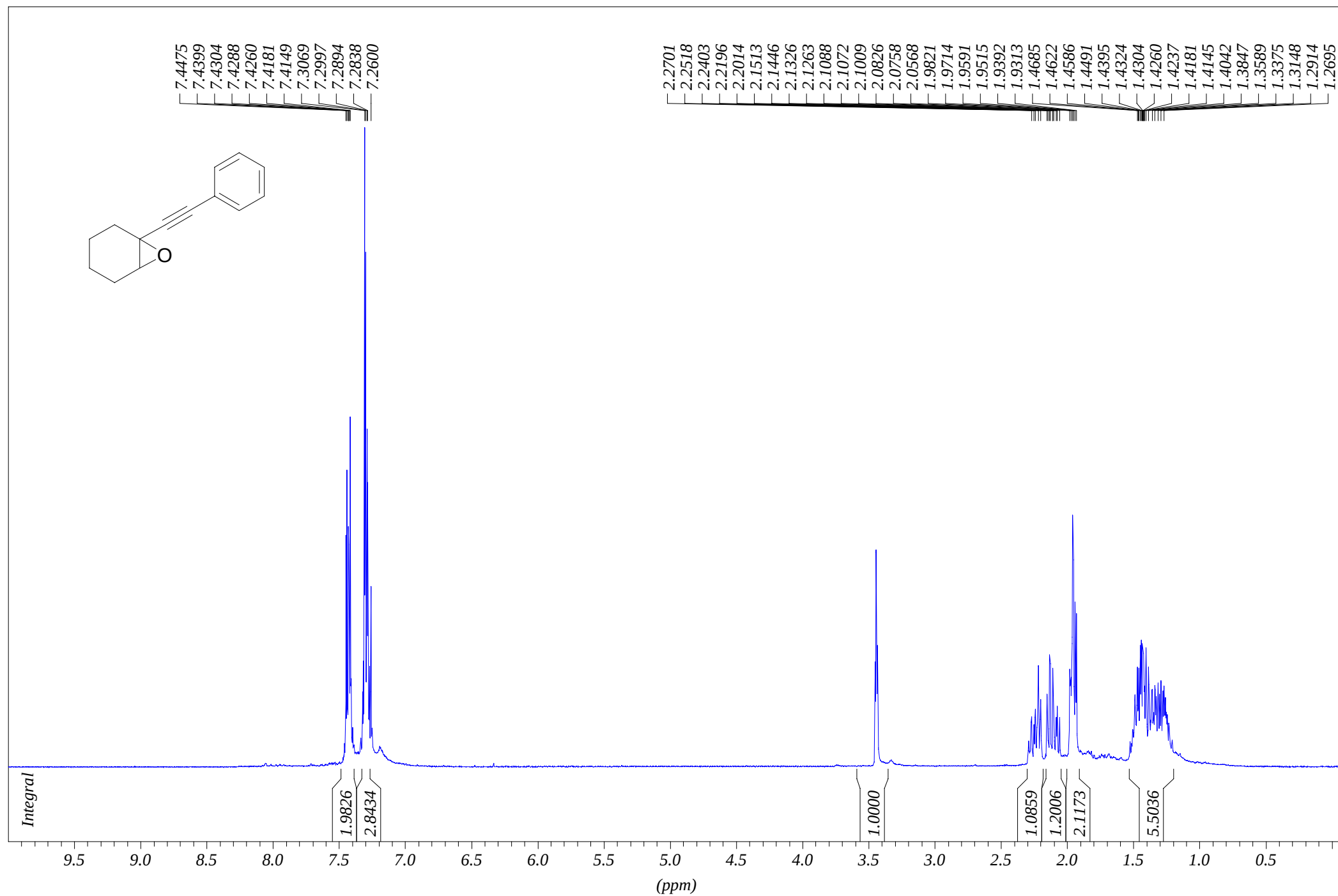
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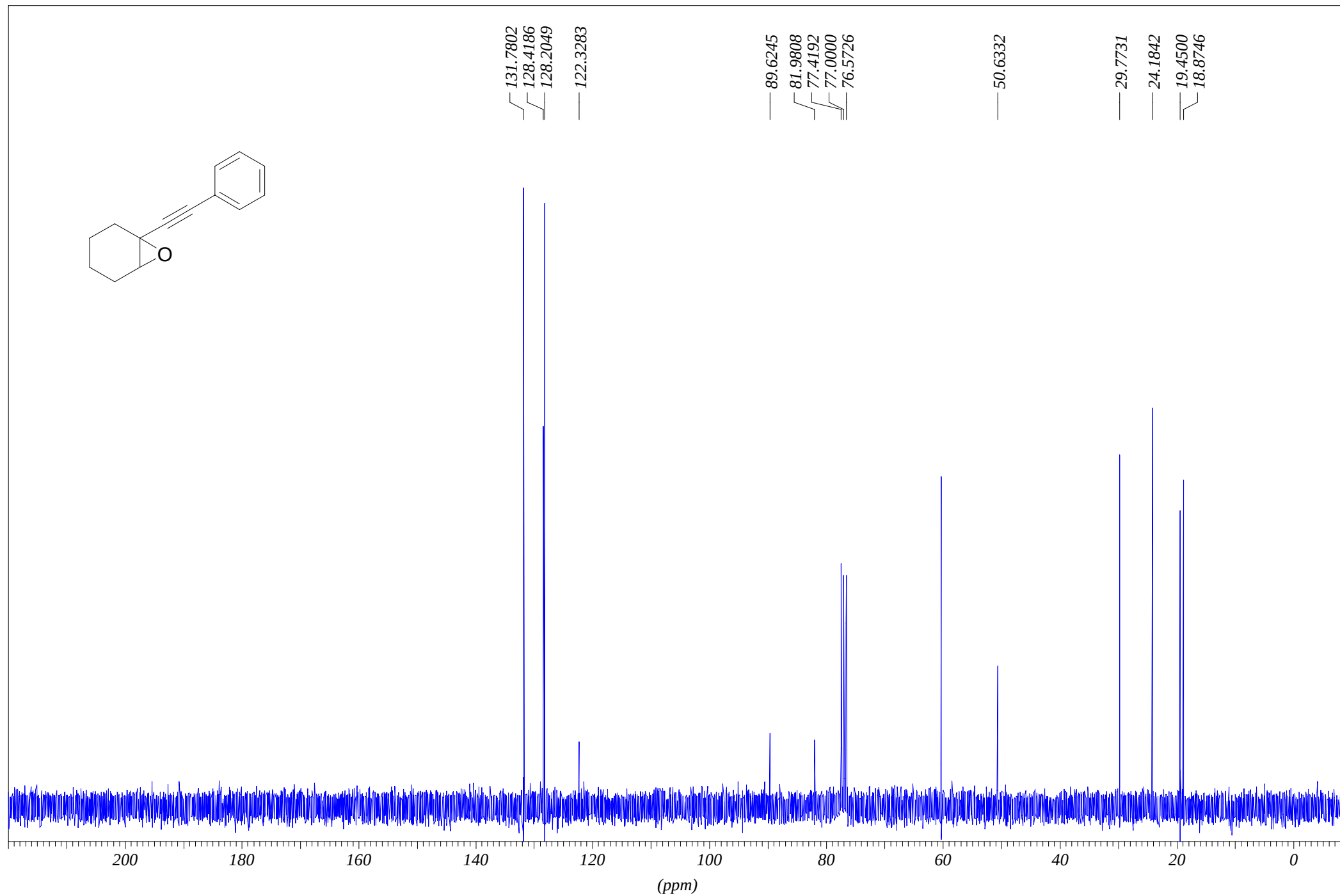
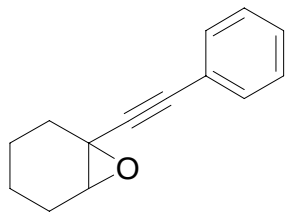
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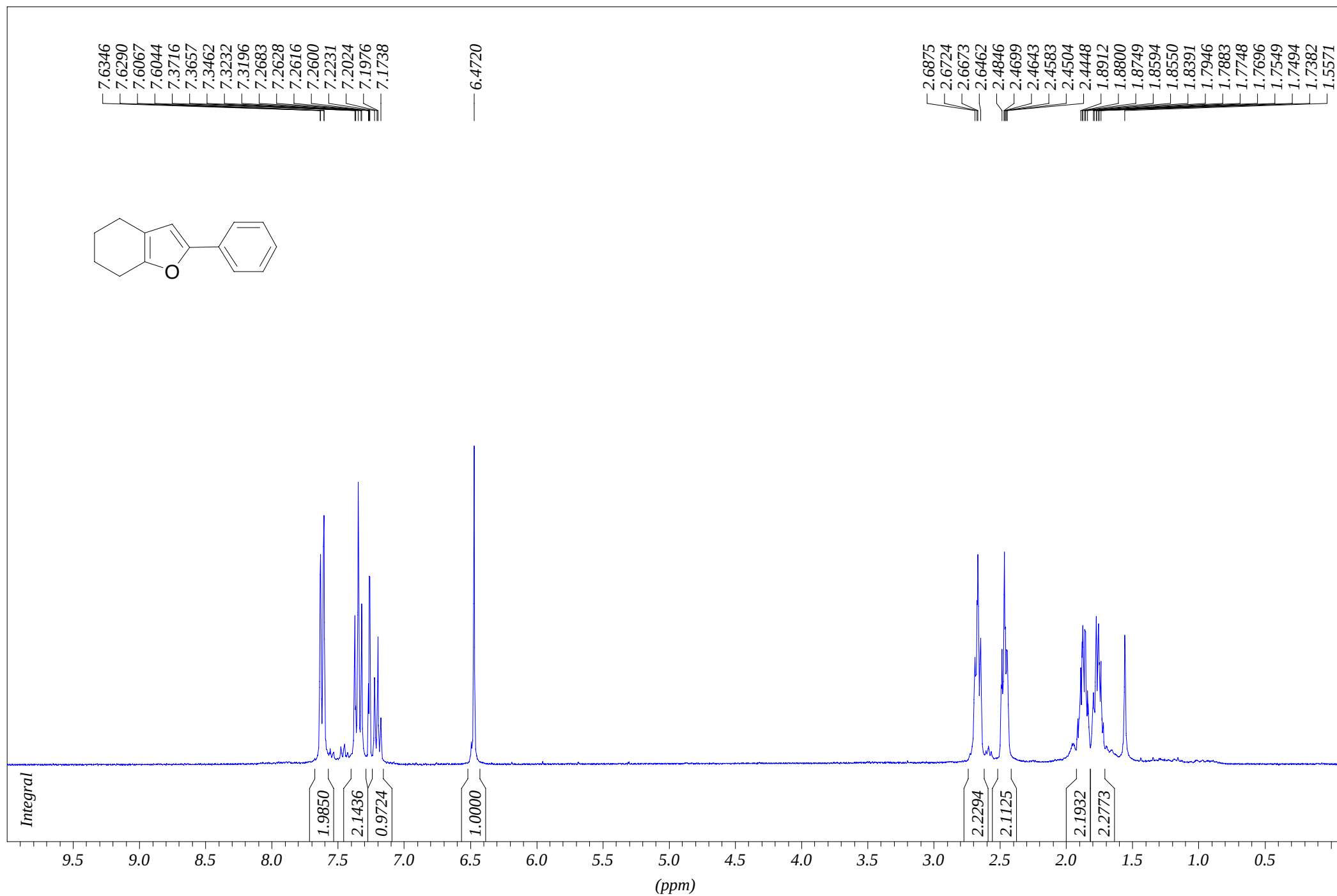
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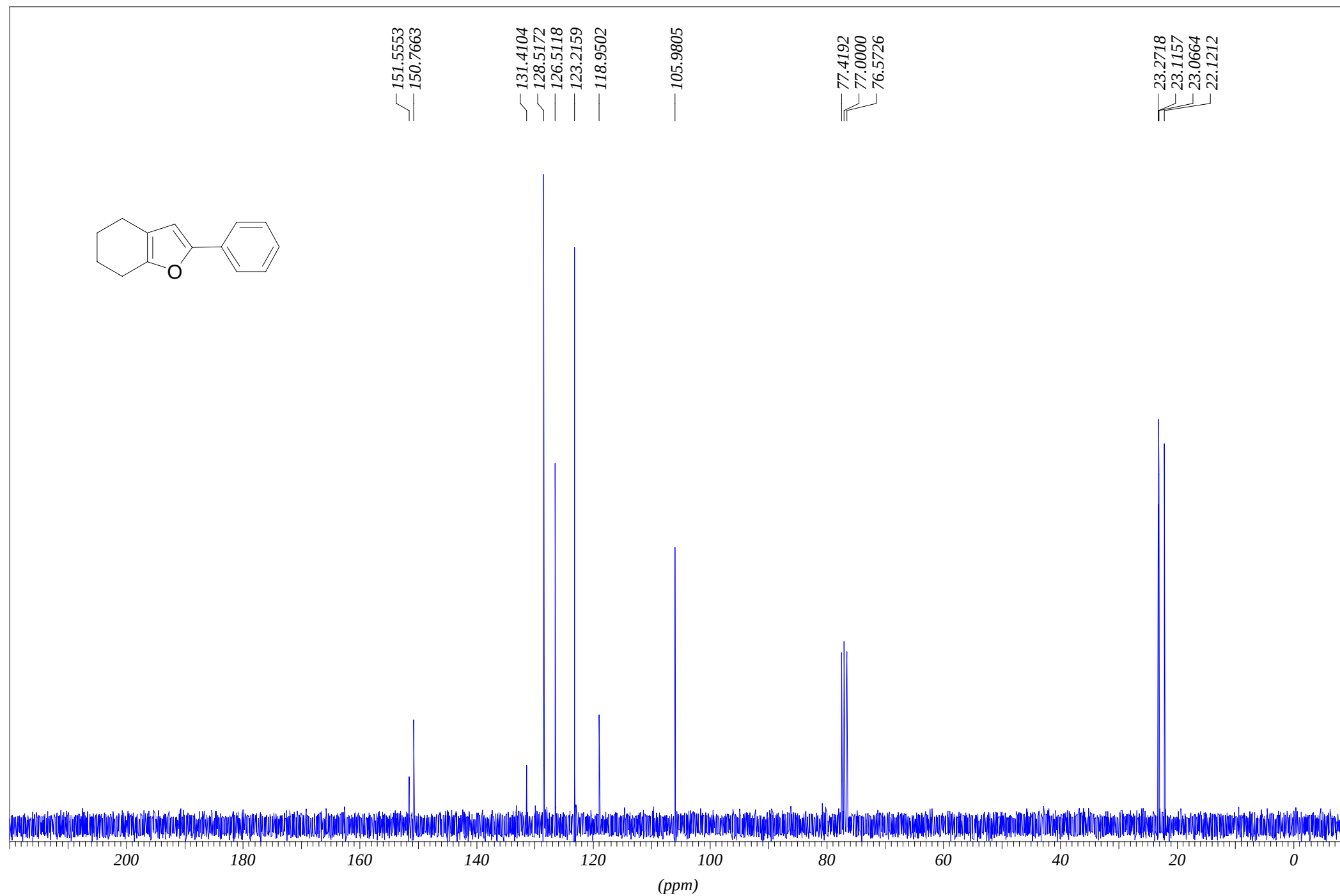
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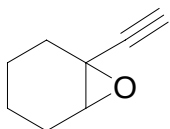
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