

Supporting Information

Diastereodivergent Behavior of Alkyl- *versus* Cyano-Allenylcuprates towards Aldehydes: a Key Role for Lithium

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Computational Procedure: Full geometry optimizations were systematically conducted with no symmetry restraints using the Gaussian 03 programⁱ within the framework of the Density Functional Theory (DFT) using the hybrid B3LYP exchange-correlation functionalⁱⁱ and the 6-31++G** basis set for all atoms as implemented in the Gaussian program. The electronic plus nuclear energy obtained from SCF and optimization procedures is referred as energy and noted E in the text. As such, $\Delta E_{X/Y}$ is $E(X) - E(Y)$. Solvation at the lithium cation is ensured via an explicit model by including two or three dimethylether molecules (as a model for THF) coordinated to the lithium (no coordination of solvent molecules to the copper could be obtained). For key structures, importance of adding an implicit solvation was examined using single point computations on gas phase optimized geometry. These results are reported only when giving significant difference with gas phase structures. For these computations, the PCM model using the dielectric constant implemented for THF ($\epsilon_R = 7.58$)ⁱⁱⁱ and the default implemented in Gaussian 03 are used, except for atomic radii where the BONDI values are used for all atoms. Frequencies were evaluated within the harmonic

approximation and used unscaled to compute Gibbs free energy (G) at 183 K using the standard protocol implemented in Gaussian.

Computational data

Table 1. Allenic vs. propargylic nature of the organometallic reagent: energy of the reaction below (ΔE , computed between most stable minima, in kcal mol⁻¹) as a function of substitution and counter-ions.

Entry	CuX	R	R'	Counter-ion	ΔE
1 ^a	Cu	OMe	H	None	-3.0
2 ^a	Cu	OMe	Me	None	-1.6
3 ^a	CuCN ⁻	OMe	H	None	-5.9
4 ^a	CuCN ⁻	OMe	Me	None	-4.6
5	CuCN ⁻	Me	H	None	-6.1
6	CuCN ⁻	Me	Me	None	-4.8
7	Cu	Me	H	None	-4.7
8	CuMe ⁻	Me	H	None	-6.0
9	CuCN ⁻	Me	H	Li(OMe ₂) ₂ ⁺	-6.1
10	CuMe ⁻	Me	H	Li(OMe ₂) ₂ ⁺	-4.0

^a obtained at the B3LYP/6-31+G** level, see ref¹

Figure 1. Optimized geometries for structures **L3** with X = CN (left) and **B3** with X = Me (right). Angles are given in degrees and distances in Å. Color code : hydrogen (white), lithium (yellow), carbon (green), nitrogen (blue), oxygen (red), silicon (grey), copper (orange).

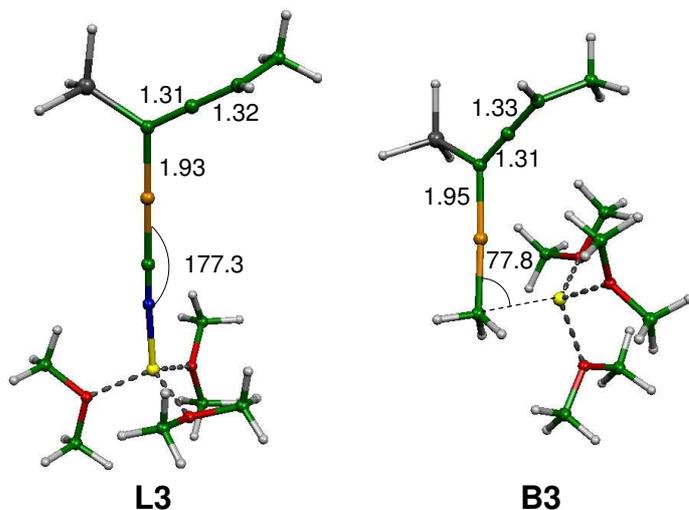


Figure 2. Relative electronic energies ΔE (kcal mol⁻¹, left) computed with respect to arrangement **L3** (X = CN, in white) or **B3** (X = Me, in black) of the various arrangements of the solvated lithium ion coordinated (see text for details).

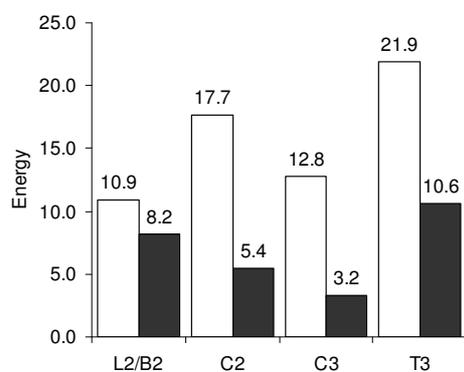


Figure 3. Relative Gibbs free energies including implicit solvation (kcal mol^{-1}) computed with respect to arrangement **L3** ($X = \text{CN}$, in white) or **B3** ($X = \text{Me}$, in black) of the various arrangements of the solvated lithium ion coordinated (see text for details).

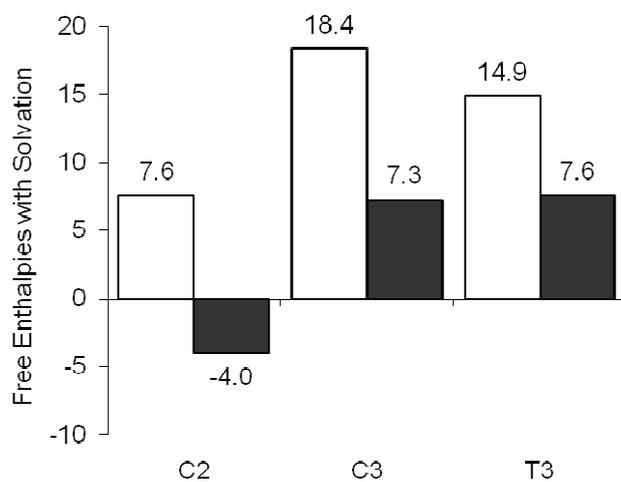
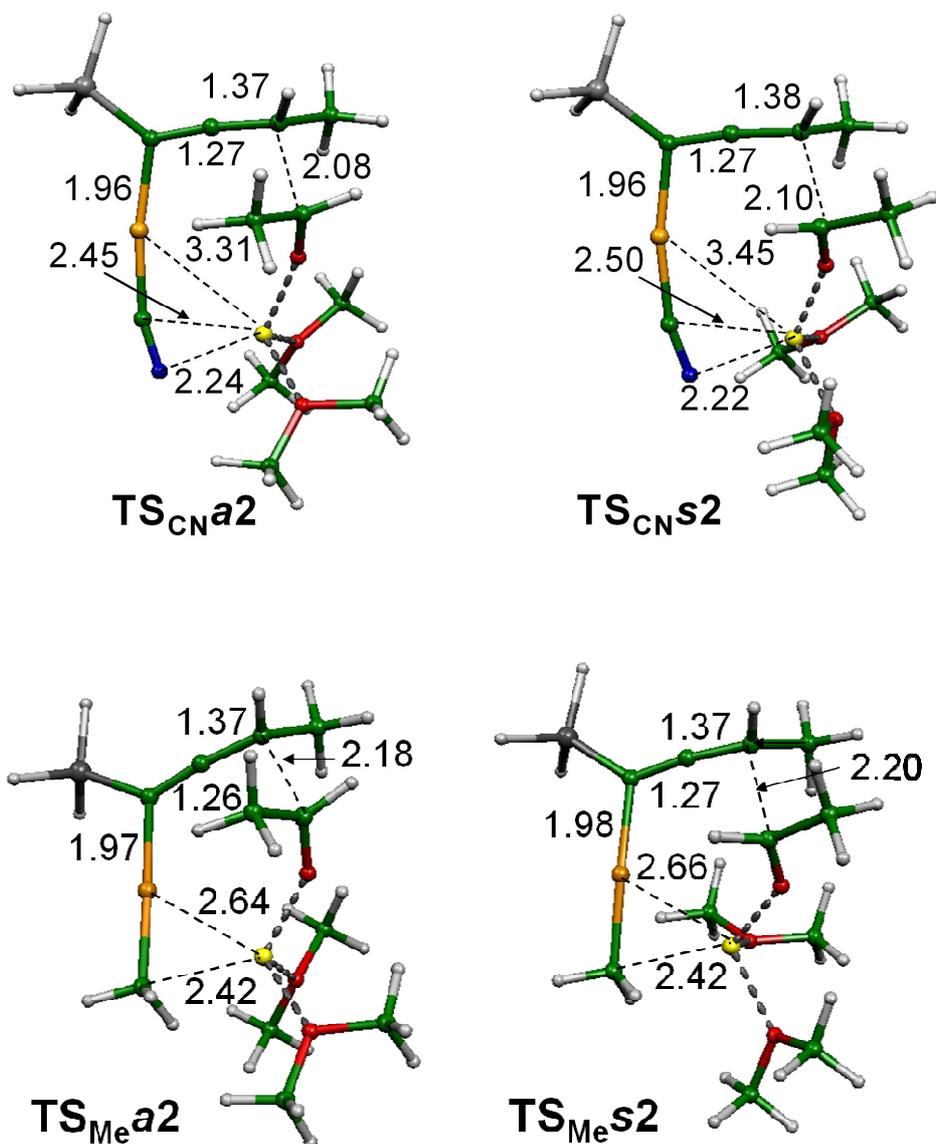


Figure 4. Optimized geometries for all transition states of the CIP mechanism (see text for details). Angles are given in degrees and distances in Å. Color code : hydrogen (white), lithium (yellow), carbon (green), nitrogen (blue), oxygen (red), silicon (grey), copper (orange).



General Considerations: Experiments were carried out under dry argon atmosphere. All glassware were dried at 120°C and assembled while hot under a stream of argon. All moisture-sensitive reactants are handled under a nitrogen atmosphere. Low temperature experiments are carried out by cooling down a three-necked round bottom flask with an ether/acetone (-80/-90 °C), bath, frozen with liquid nitrogen. The flask was equipped with an internal thermometer, an argon inlet and a septum cap. Tetrahydrofuran was distilled from sodium-benzophenone ketyl. Column chromatographies were performed over silica gel Si 0.015-0.040 mesh. Melting points are uncorrected. IR data were recorded on a Perkin Elmer Spectrum 1000 instrument. ¹H NMR spectra were recorded at 400 MHz, and ¹³C NMR spectra were recorded at 100 MHz, in CDCl₃ as solvent on a Bruker Ultra Shield 400 spectrometer. Chemical shifts are reported in ppm (reference TMS for ¹H NMR and CDCl₃ for ¹³C NMR). Microanalyses were performed by ICSN-CNRS, Gif-sur-Yvette, France. Exact Masses were performed by CCSM, Université Claude Bernard Lyon 1, France. Compounds **3a**,^v **3a'**,^{vi} **3c**,^v **3d**^v and *anti*-**5**^{vii} have already been described.

General procedure A for the addition of allenyl(methyl)cuprates reagents to aldehydes: **Solution A:** A solution of CuI (3 mmol, 571 mg) and LiBr (6 mmol, 521 mg) in THF (10 mL) cooled to -70 °C was treated dropwise with 1.6 M MeLi in Et₂O (3 mmol, 1.9 mL). The mixture was allowed to reach 0 °C over 30 min and cooled down to -80 °C. **Solution B:** A solution of 1-(trimethylsilyl)dec-1-yne (2 mmol, 420 mg) or 1-(trimethylsilyl)but-1-yne (2 mmol, 252 mg) in THF (15 mL) cooled to -90 °C was treated dropwise with 1.3 M *s*-BuLi in cyclohexane/hexane (2.05 mmol, 1.6 mL) maintaining the internal temperature below -88 °C. The mixture was warmed to 0 °C, stirred 1 h at this temperature and cooled to -80 °C. The solution B was then added dropwise via a cannula to the solution A at -80 °C. The mixture was warmed to -20 °C and stirred an additional 30 min

at this temperature. The resulting solution was cooled to $-90\text{ }^{\circ}\text{C}$ and a solution of the aldehyde (2.1 mmol) in THF (10 mL) was added over 1 h via a syringe pump. After an additional hour at $-90\text{ }^{\circ}\text{C}$, the reaction was quenched by the addition of an aqueous $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ (2:1) solution and extracted with diethylether (2 x 50 mL). The combined organic layers were washed with water and brine, dried over magnesium sulfate, and filtered off. The solvents were removed in vacuo, and the product was then subjected to FC (flash chromatography) on SiO_2 using the appropriate pentane/ Et_2O eluant.

General procedure B for the addition of allenyl(*tert*-butyl)cuprates reagents to aldehydes: **Solution A:** A solution of CuI (3 mmol, 571 mg) and LiBr (6 mmol, 521 mg) in THF (10 mL) cooled to $-85\text{ }^{\circ}\text{C}$ was treated dropwise with 1.6 M *t*-BuLi in pentane (3 mmol, 1.9 mL). The mixture was stirred 10 min at $-80\text{ }^{\circ}\text{C}$ to give a pale grey suspension. **Solution B:** A solution of 1-(trimethylsilyl)dec-1-yne (2 mmol, 420 mg) or 1-(trimethylsilyl)but-1-yne (2 mmol, 252 mg) in THF (15 mL) cooled to $-90\text{ }^{\circ}\text{C}$ was treated dropwise with 1.3 M *s*-BuLi in cyclohexane/hexane (2.05 mmol, 1.6 mL) maintaining the internal temperature below $-88\text{ }^{\circ}\text{C}$. The mixture was warmed to $0\text{ }^{\circ}\text{C}$, stirred 1 h at this temperature and cooled to $-90\text{ }^{\circ}\text{C}$. The solution B was then added dropwise via a cannula to the solution A at $-90\text{ }^{\circ}\text{C}$ and the resulting suspension was stirred 30 min maintaining the internal temperature below $-80\text{ }^{\circ}\text{C}$. A solution of the aldehyde (2.1 mmol) in THF (10 mL) was added at $-90\text{ }^{\circ}\text{C}$ over 1 h via a syringe pump. After an additional hour at $-90\text{ }^{\circ}\text{C}$, the reaction was quenched by the addition of an aqueous $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ (2:1) solution and extracted with diethylether (2 x 50 mL). The combined organic layers were washed with water and brine, dried over magnesium sulfate, and filtered off. The solvents were removed in vacuo, and the product was then subjected to FC on SiO_2 using the appropriate pentane/ Et_2O eluant.

***syn*-2-methyl-4-phenylhept-5-yn-3-ol 3b**: This compound was prepared according to the general procedure A, using 1-(trimethylsilyl)dec-1-yne **1a** (2 mmol, 420 mg) and pivalaldehyde **2b** (2.1 mmol, 0.228 mL). The diastereoselectivity of the reaction was determined by ^1H NMR of the crude mixture to be > 95:5 based on the chemical shift of propargylic ($\delta = 3.41$) and homo-propargylic protons ($\delta = 2.57$). Purification by FC (pentane/Et₂O 98:2, R_f = 0.3) gave **3b** (473 mg, 80%) as a colorless oil. ^1H NMR (400 MHz, CDCl₃) δ 3.41 (dd, $J = 4.5, 5.6$ Hz, 1H); 2.57 (ddd, $J = 3.8, 6.0, 9.8$ Hz, 1H); 1.74 (d, $J = 4.5$ Hz, 1H); 1.69-1.30 (m, 12H); 1.02 (s, 9H); 0.90 (t, $J = 6.6$ Hz, 3H); 0.15 (s, 9H). ^{13}C NMR (100 MHz, CDCl₃) δ 109.7, 87.3, 80.5, 35.9, 35.8, 31.8, 30.3, 29.4, 29.2, 27.2, 26.9, 22.6, 14.1, 0.0. IR (neat) $\nu = 3462$ (br), 2956, 2166, 1467, 1365, 1249, 1005, 846 cm⁻¹. HRMS (CI): m/z calcd for C₁₈H₃₆OSi [M + H]⁺: 297.2614; found: 297.2614.

***anti*-2,4-dimethyl-6-phenylhex-5-yn-3-ol anti-5**: A solution of 1-phenyl-1-butyne (2 mmol, 284 mL) in THF (15 mL) cooled to -90 °C was treated dropwise with 1.3 M *s*-BuLi in cyclohexane/hexane (2.05 mmol, 1.6 mL) maintaining the internal temperature below -88 °C. The mixture was warmed to -40 °C, stirred 1 h at this temperature and cooled to -80 °C. A solution of CuCN (3 mmol, 270 mg) and LiBr (6 mmol, 521 mg) in THF (10 mL) was then added dropwise, the reaction was stirred an additional 30 min at -80 °C and *iso*-butyraldehyde (2.1 mmol, 0.2 mL) was added dropwise. The reaction mixture was allowed to warm to -60 °C over 1 h, stirred an additional hour at this temperature, quenched by the addition of aqueous NH₄Cl/NH₄OH (2/1) solution and extracted with diethyl ether (3x20 mL). The combined organic layers were washed with water, brine, dried over magnesium sulfate, filtered off and the solvents were removed in vacuo. The regio- and the diastereoselectivity of the reaction were determined by ^1H NMR of the crude mixture to be > 95:5 based on the chemical shift of propargylic ($\delta = 3.12$) and homo-propargylic protons ($\delta = 2.93$).

Purification by FC (pentane/Et₂O 85:15 R_f = 0.35) gave **anti-5** (283 mg, 70%) as a colorless oil which spectral are in good accordance to those previously reported in ref. vii

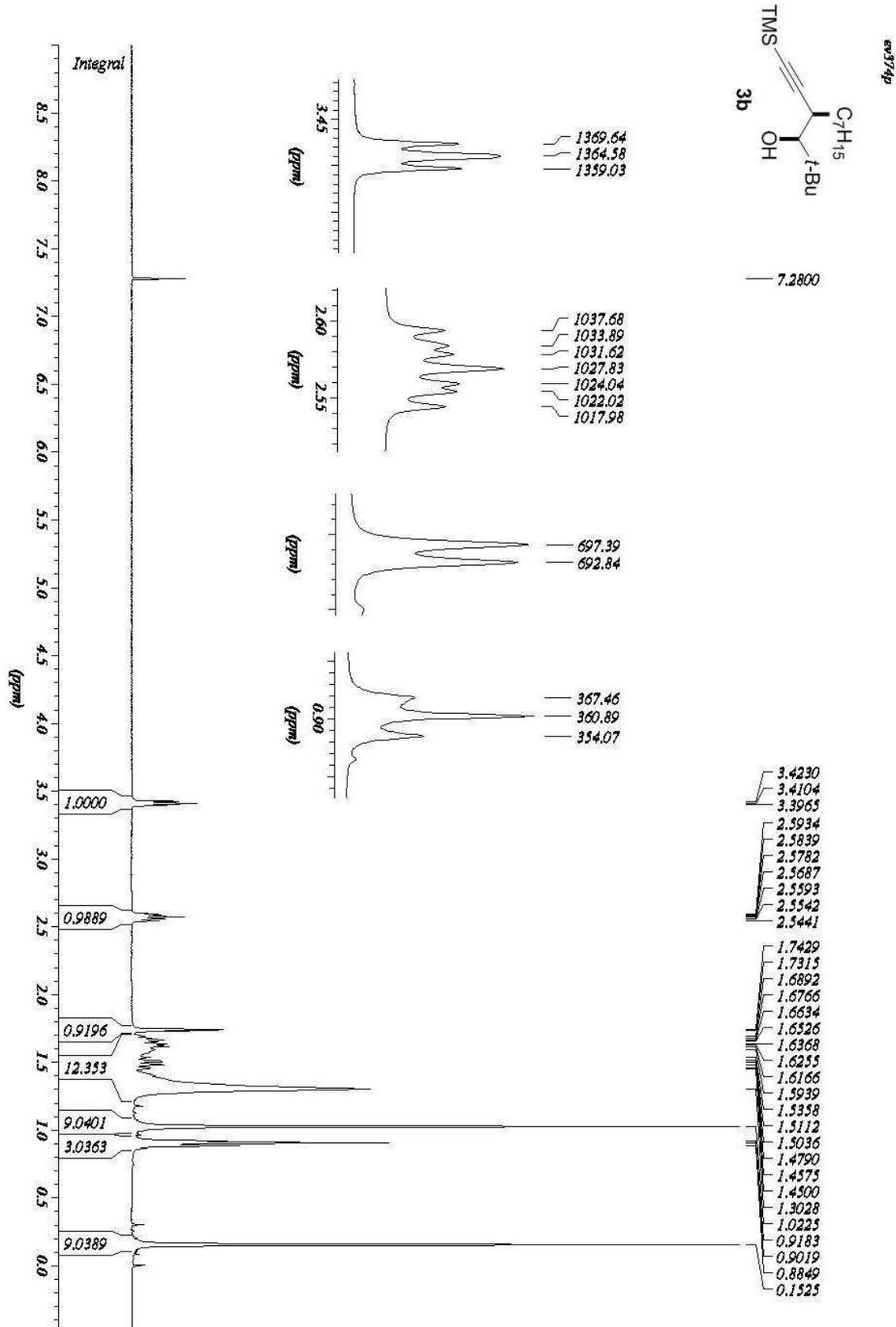
syn-2,4-dimethyl-6-phenylhex-5-yn-3-ol syn-5: **Solution A:** A solution of CuI (3 mmol, 571 mg) and LiBr (6 mmol, 521 mg) in THF (10 mL) cooled to -70 °C was treated dropwise with 1.6 M MeLi in Et₂O (3 mmol, 1.9 mL). The mixture was allowed to reach 0 °C over 30 min and cooled down to -80 °C. **Solution B:** A solution of 1-phenyl-1-butyne (2 mmol, 284 mL) in THF (15 mL) cooled to -90 °C was treated dropwise with 1.3 M *s*-BuLi in cyclohexane/hexane (2.05 mmol, 1.6 mL) maintaining the internal temperature bellow -88 °C. The mixture was warmed to -40 °C, stirred 1 h at this temperature and cooled to -80°C. The solution B was then added dropwise via a cannula to the solution A at -80°C. The mixture was warmed to -20 °C and stirred an additional 30 min at this temperature. The resulting solution was cooled to -60 °C and a solution of *iso*-butyraldehyde (2.1 mmol, 0.2 mL) in THF (10 mL) was added over 1 h via a syringe pump. After an additional hour at -40 °C, the reaction was quenched by the addition of an aqueous NH₄Cl/NH₄OH (2:1) solution and extracted with diethylether (2 x 50 mL). The combined organic layers were washed with water and brine, dried over magnesium sulfate, filtered off, and the solvent were removed in vacuo. The regio- and the diastereoselectivity of the reaction were determined by ¹H NMR of the crude mixture to be > 95:5 based on the chemical shift of propargylic (δ = 3.44) and homo-propargylic protons (δ = 2.85). Purification by FC (pentane/Et₂O 90:10, R_f = 0.30) gave **syn-5** (343 mg, 85%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.28 (m, 5H); 3.44 (dd, *J* = 5.7, 10.6 Hz, 1H), 2.85 (p, *J* = 6.8 Hz, 1H); 2.10-2.02 (m, 1H); 1.77-1.75 (m, 1H); 1.32 (d, *J* = 6.9 Hz, 3H); 1.01 (dd, *J* = 6.8, 14.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 131.6, 128.2, 127.8, 123.5, 92.0, 82.3, 79.2, 31.0, 30.4, 19.7, 16.8, 15.7. IR (neat) ν = 3339 (br), 2959, 2933, 1489, 1457, 1144, 755, 690 cm⁻¹. Elemental anal. calcd for C₁₄H₁₈O: C, 83.12; H, 8.97; O, 7.91. Found: C, 83.04; H, 9.06; O, 7.81

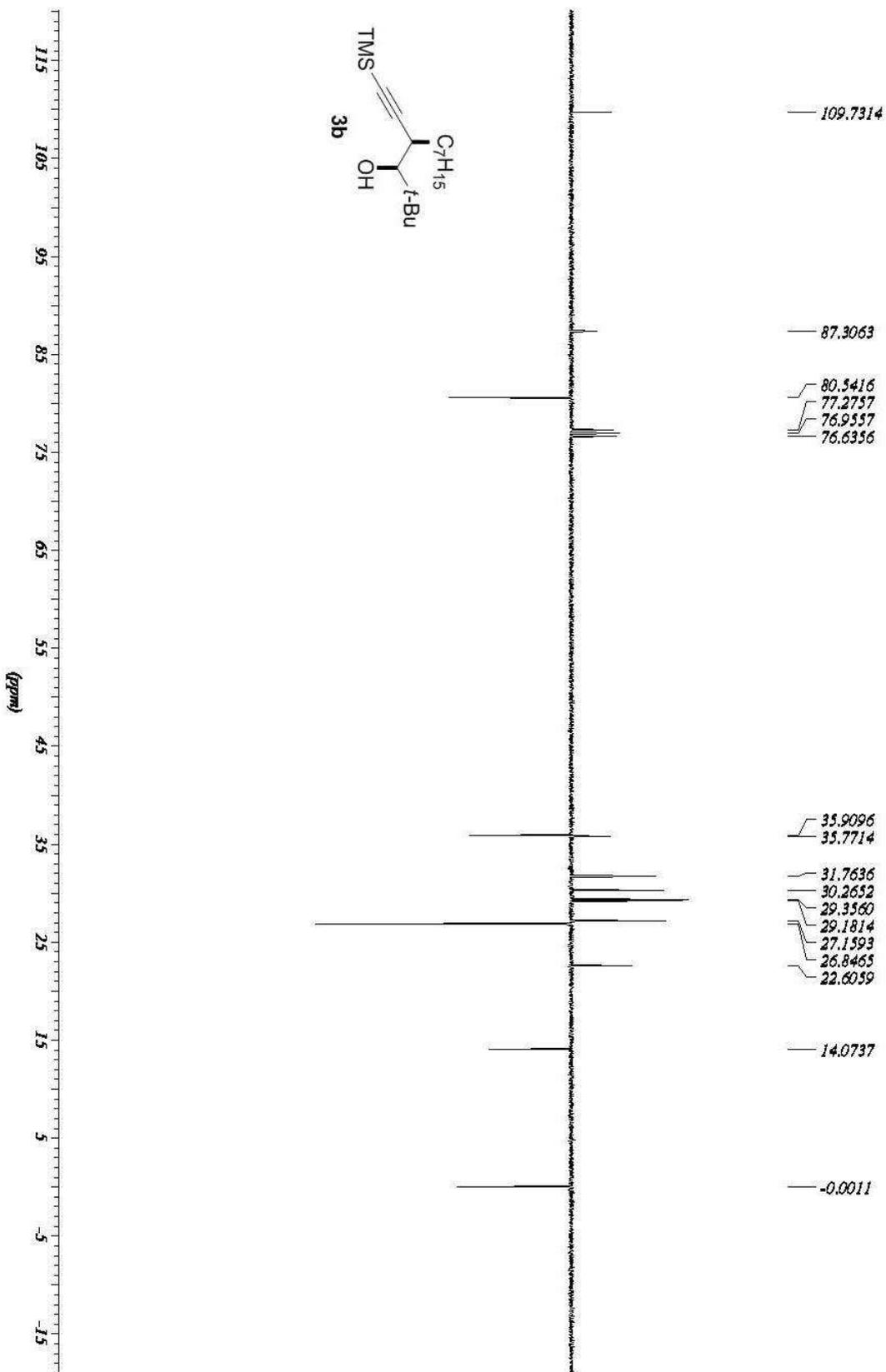
anti-2-methyl-4-phenylhept-5-yn-3-ol anti-6: A solution of 1-phenyl-1-butyne (2 mmol, 284 mL) in THF (15 mL) cooled to -90 °C was treated dropwise with 1.3 M *s*-BuLi in cyclohexane/hexane (2.05 mmol, 1.6 mL) maintaining the internal temperature below -88 °C. The mixture was warmed to -40 °C, stirred 1 h at this temperature and cooled to -80 °C. ***Freshly distilled diisopropylamine*** (0.1 mmol, 0.014 mL) was then added, the mixture was warmed to room temperature, stirred 30 min and cooled to -80 °C. A solution of CuCN (3 mmol, 270 mg) and LiBr (6 mmol, 521 mg) in THF (10 mL) was then added dropwise, the reaction was stirred an additional 30 min at -80 °C and *iso*-butyraldehyde (2.1 mmol, 0.2 mL) was slowly added. The reaction mixture was allowed to warm to -60 °C over 1 h, stirred an additional hour at this temperature, quenched by the addition of aqueous NH₄Cl/NH₄OH (2/1) solution and extracted with diethyl ether (3x20 mL). The combined organic layers were washed with water, brine, dried over magnesium sulfate, filtered off and the solvents were removed in vacuo. The regio- and the diastereoselectivity of the reaction were determined by ¹H NMR of the crude mixture to be > 95:5 based on the chemical shift of propargylic ($\delta = 3.87$) and homo-propargylic protons ($\delta = 3.36$). Purification by FC (pentane/Et₂O 88:12, R_f = 0.35) gave ***anti-6*** (331 mg, 82%) as a colorless solid. mp: 37-38°C (recrystallized from pentane). ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.25 (m, 5H); 3.87 (dq, $J = 2.3, 4.8$ Hz, 1H); 3.36 (dd, $J = 4.8, 10.5$ Hz, 1H); 1.93 (d, $J = 2.4$ Hz, 3H); 1.81 (sextd, $J = 6.8, 13.5$ Hz, 1H); 1.03 (d, $J = 6.6$ Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 139.9, 128.6, 128.1, 127.0, 80.8, 80.5, 77.0, 42.8, 31.3, 19.8, 17.6, 3.8. IR (neat) $\nu = 3456$ (br), 2959, 2918, 1491, 1452, 1044, 698 cm⁻¹. Elemental anal. calcd for C₁₄H₁₈O: C, 83.12; H, 8.97; O, 7.91. Found: C, 82.91; H, 8.93; O, 8.08. Crystallographic data for the structural analysis of ***anti-6*** have been deposited with the crystallographic Data Center, no. CCDC 720316.

syn-2-methyl-4-phenylhept-5-yn-3-ol syn-6: **Solution A**: A solution of CuI (3 mmol, 571 mg) and LiBr (6 mmol, 521 mg) in THF (10 mL) cooled to -85 °C was treated dropwise with

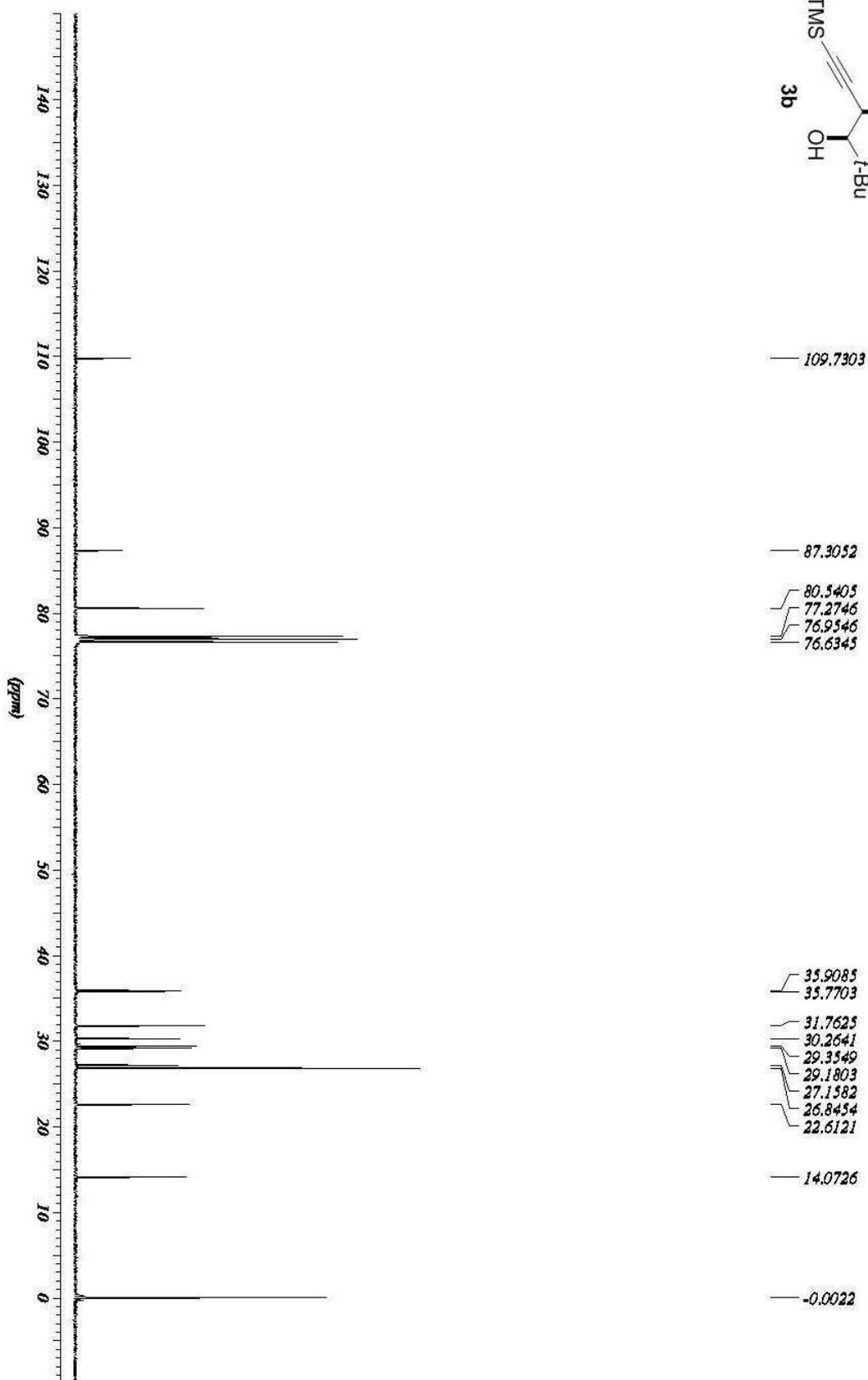
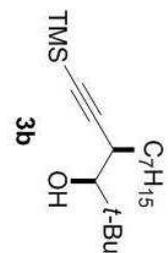
1.6 M *t*-BuLi in pentane (3 mmol, 1.9 mL). The mixture was stirred 10 min at -80 °C to give a pale grey suspension. **Solution B:** A solution of 1-phenyl-1-butyne (2 mmol, 284 mL) in THF (15 mL) cooled to -90 °C was treated dropwise with 1.3 M *s*-BuLi in cyclohexane/hexane (2.05 mmol, 1.6 mL) maintaining the internal temperature below -88 °C. The mixture was warmed to -40°C, stirred 1h at this temperature and cooled to -80 °C. Diisopropylamine (0.1 mmol, 0.014 mL) was then added, the mixture was warmed to room temperature, stirred 30 min and cooled to -80 °C. The solution B was then added dropwise via a cannula to the solution A at -80 °C. The mixture was stirred an additional 30 min at this temperature and a solution of the *iso*-butyraldehyde (2.1 mmol, 0.2 mL) in THF (10 mL) was added over 1 h via a syringe pump. After an additional hour at -40 °C, the reaction was quenched by the addition of an aqueous NH₄Cl/NH₄OH (2:1) solution and extracted with diethylether (2 x 50 mL). The combined organic layers were washed with water and brine, dried over magnesium sulfate, filtered off, and the solvent were removed in vacuo. The regio- and the diastereoselectivity of the reaction were determined by ¹H NMR of the crude mixture to be > 95:5 for the regioselectivity and 80:20 for the diastereoselectivity (based on the chemical shift of propargylic (δ = 3.62) and homo-propargylic protons (δ = 3.56). Purification by FC (pentane/Et₂O 95:5, R_f = 0.35) gave **syn-6** (210 mg, 52%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.26 (m, 5H); 3.64-3.60 (m, 1H); 3.58-3.54 (m, 1H); 2.15 (d sept., *J* = 3.7, 6.8 Hz, 1H); 1.86 (d, *J* = 2.3Hz, 3H); 1.49 (d, *J* = 3.8 Hz, 1H); 1.01 (dd, *J* = 6.8, 12.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 139.7, 128.7, 128.6, 127.3, 79.6, 79.5, 78.7, 43.0, 30.2, 20.4, 15.2, 3.7. IR (neat) ν = 3468 (br), 2961, 2872, 1493, 1452, 1045, 996, 746, 698 cm⁻¹. Elemental anal. calcd for C₁₄H₁₈O: C, 83.12; H, 8.97; O, 7.91. Found: C, 82.94; H, 8.89; O, 7.75

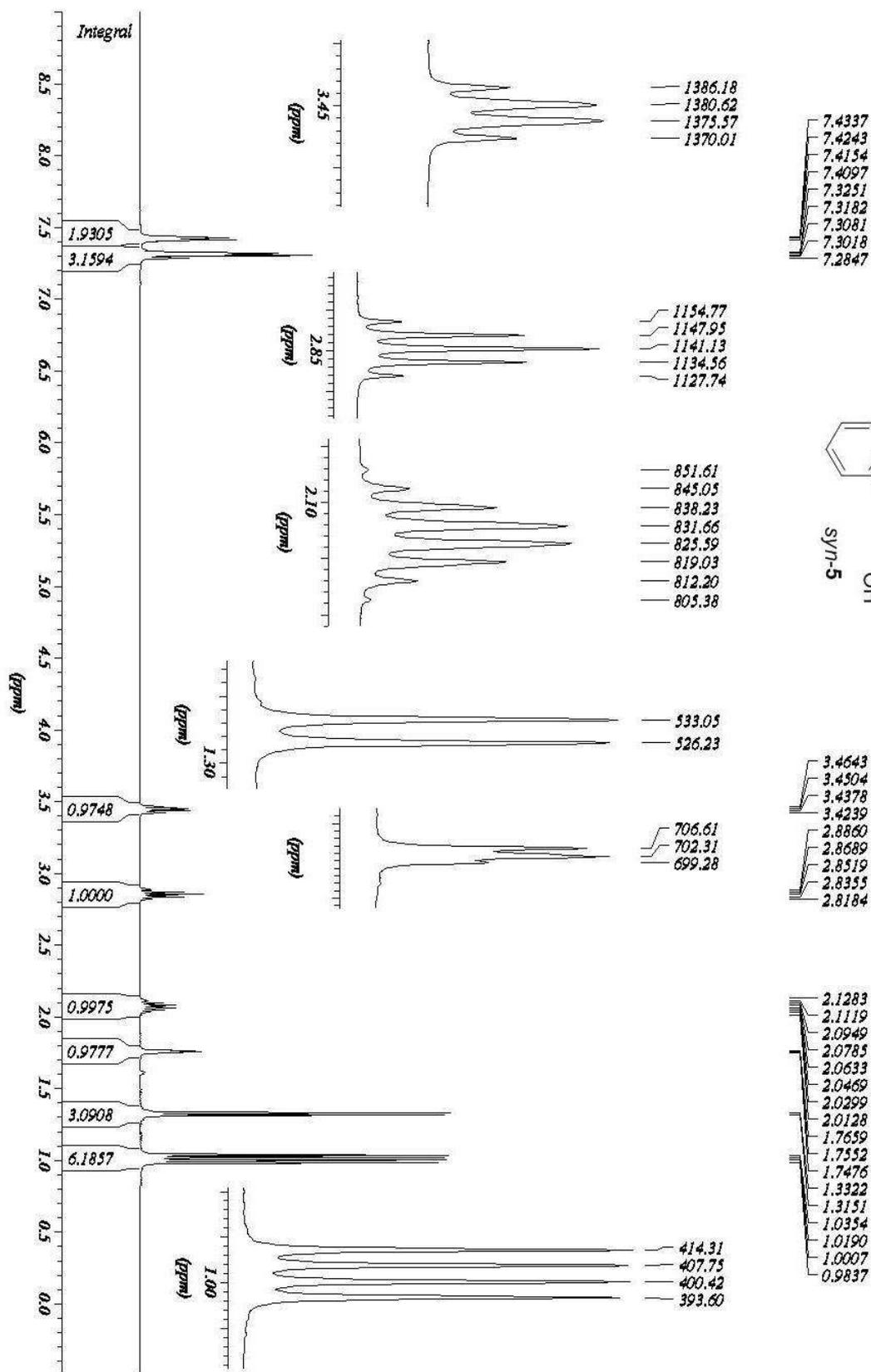
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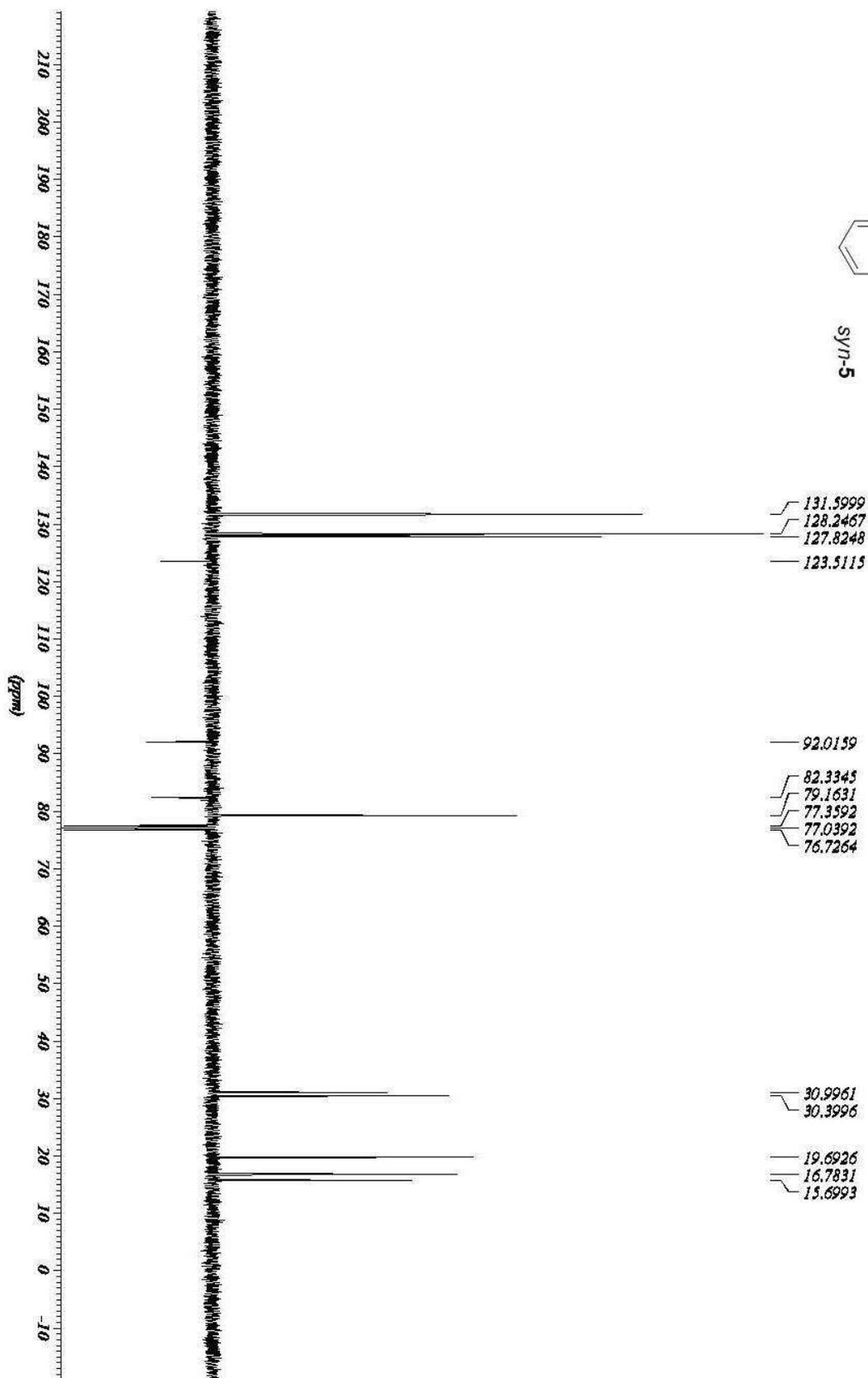
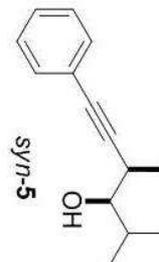


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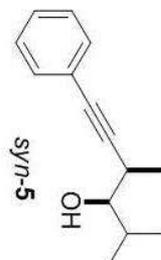




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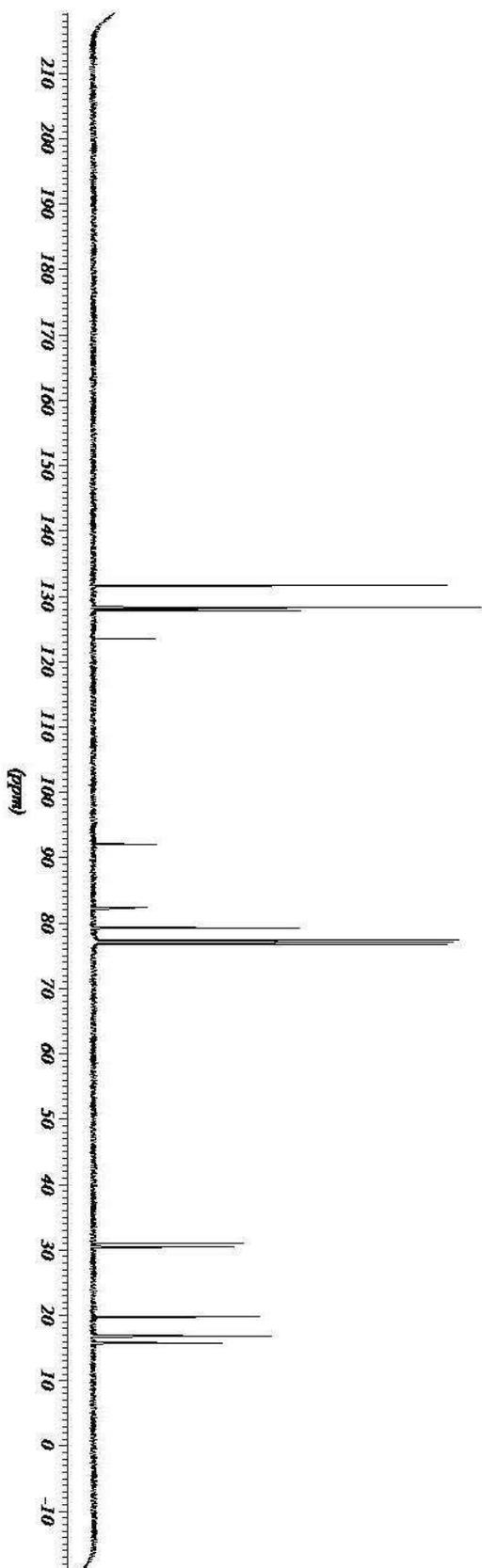


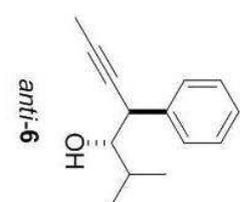
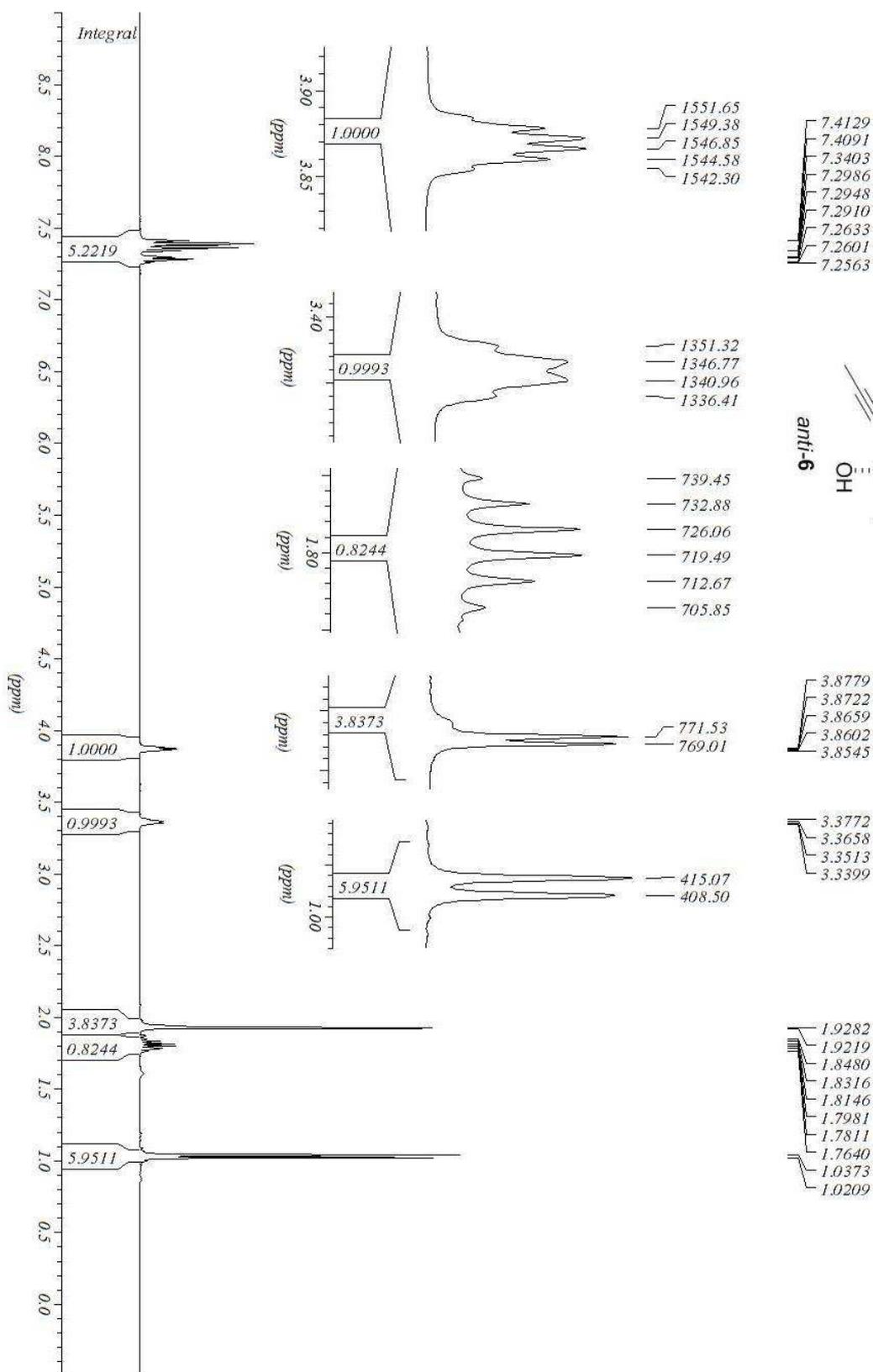
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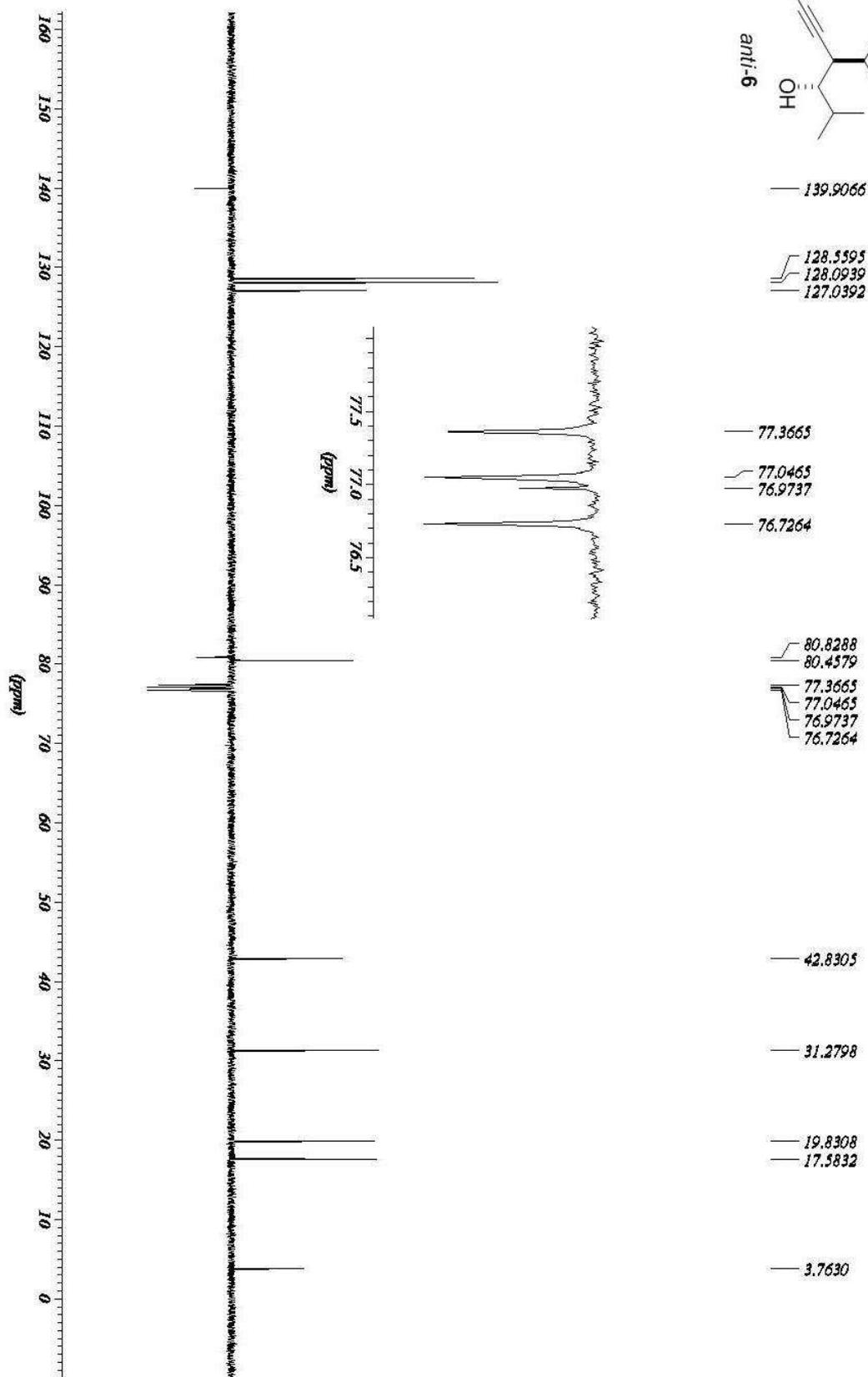
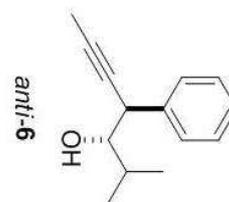
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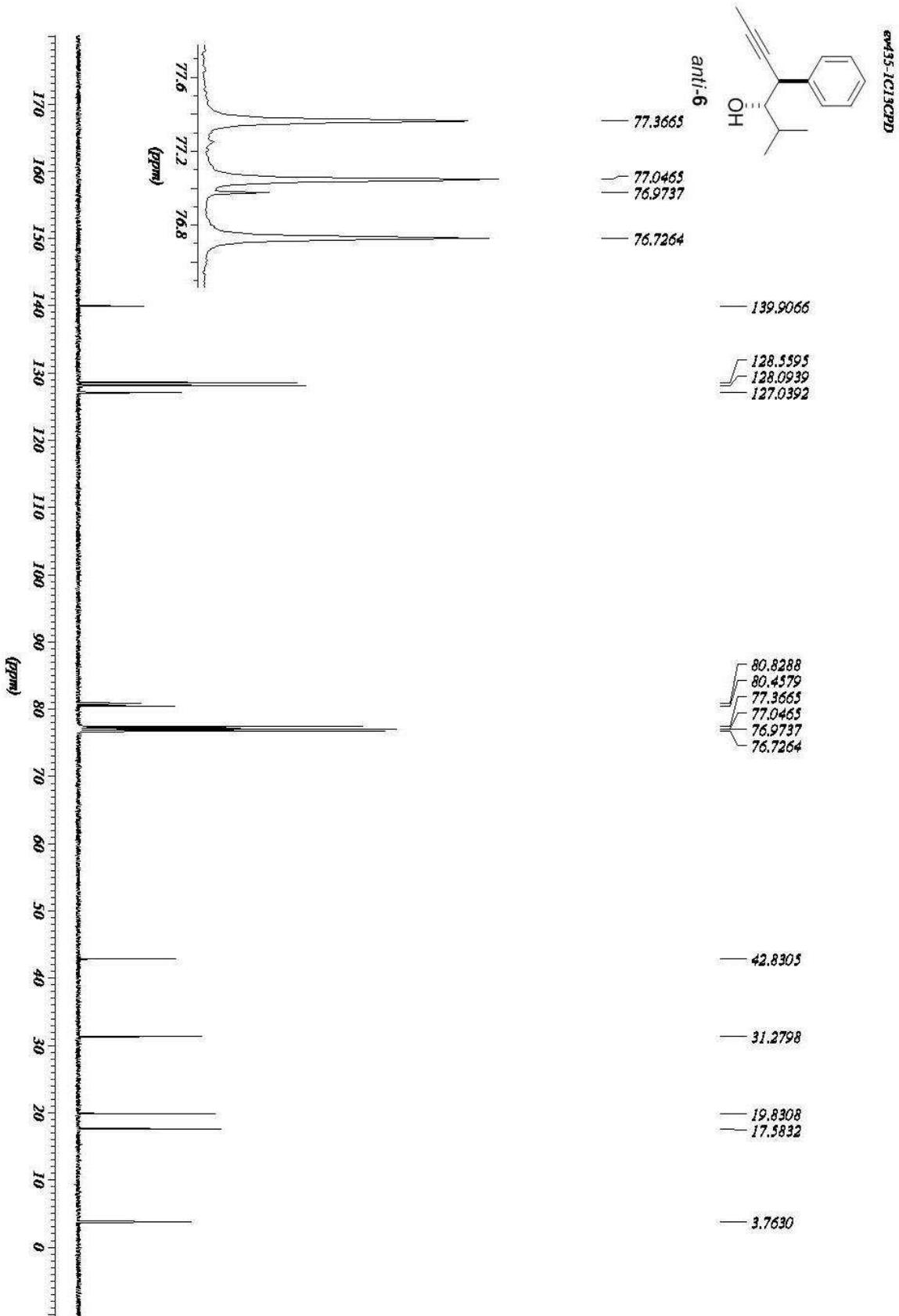
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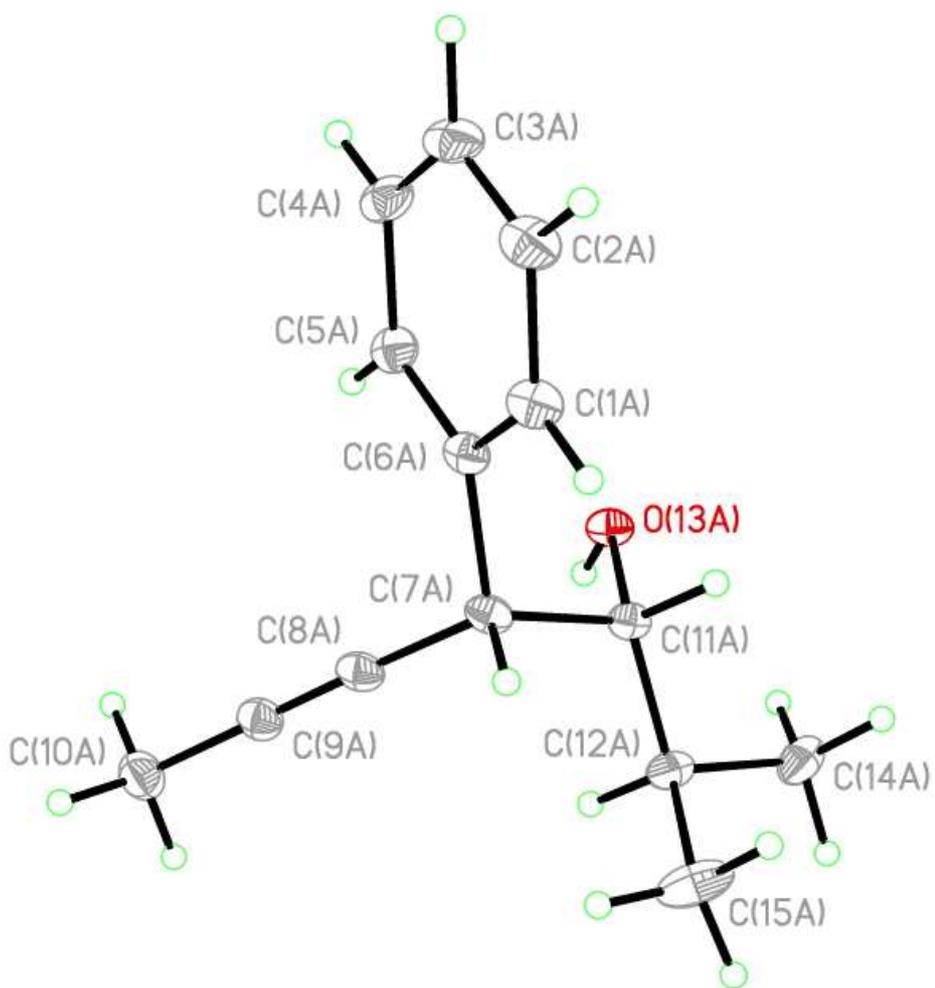
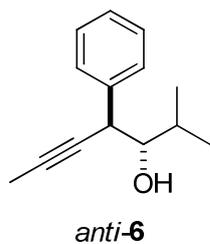


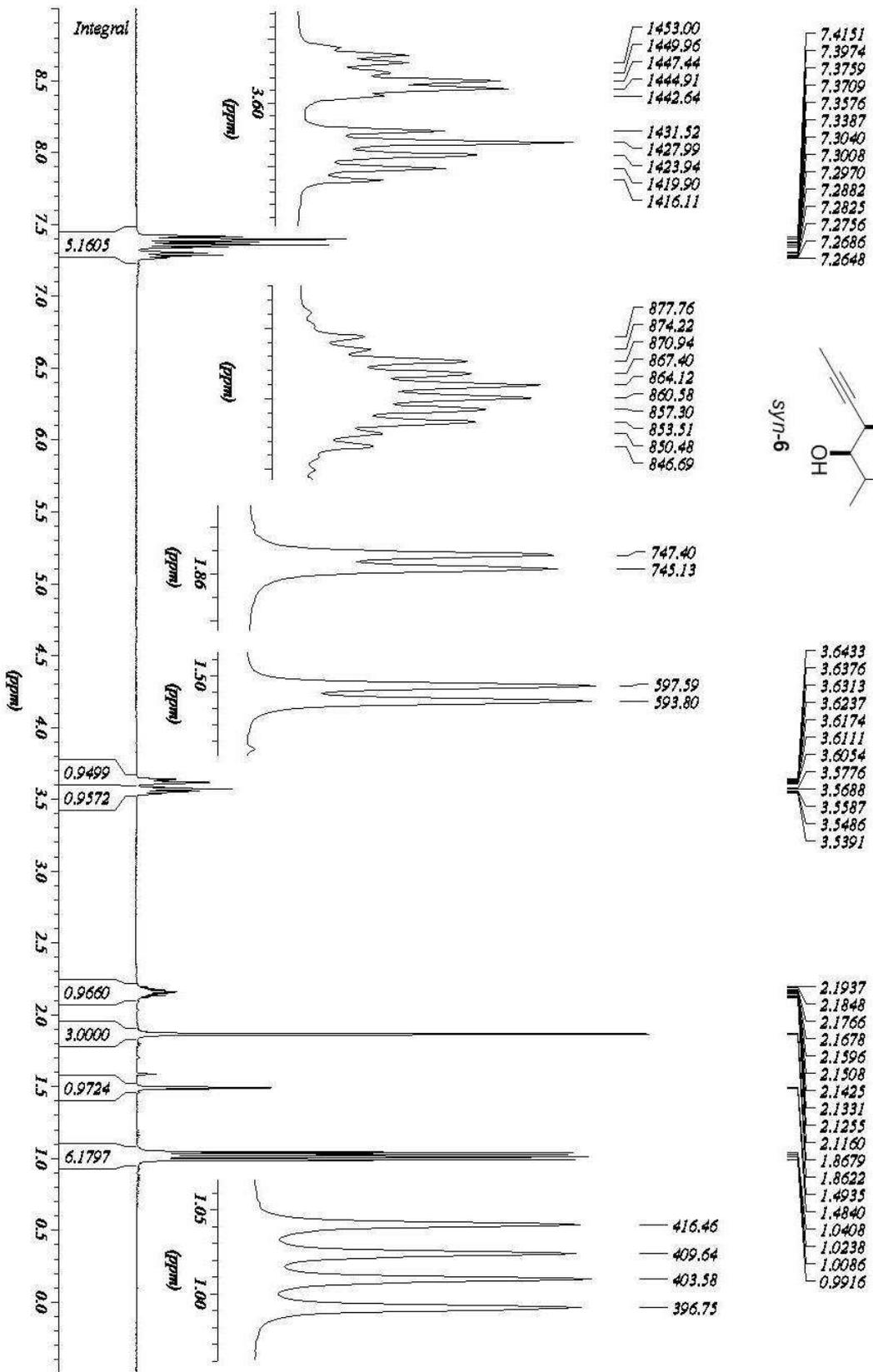


anti-6

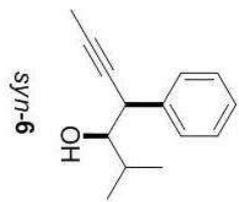




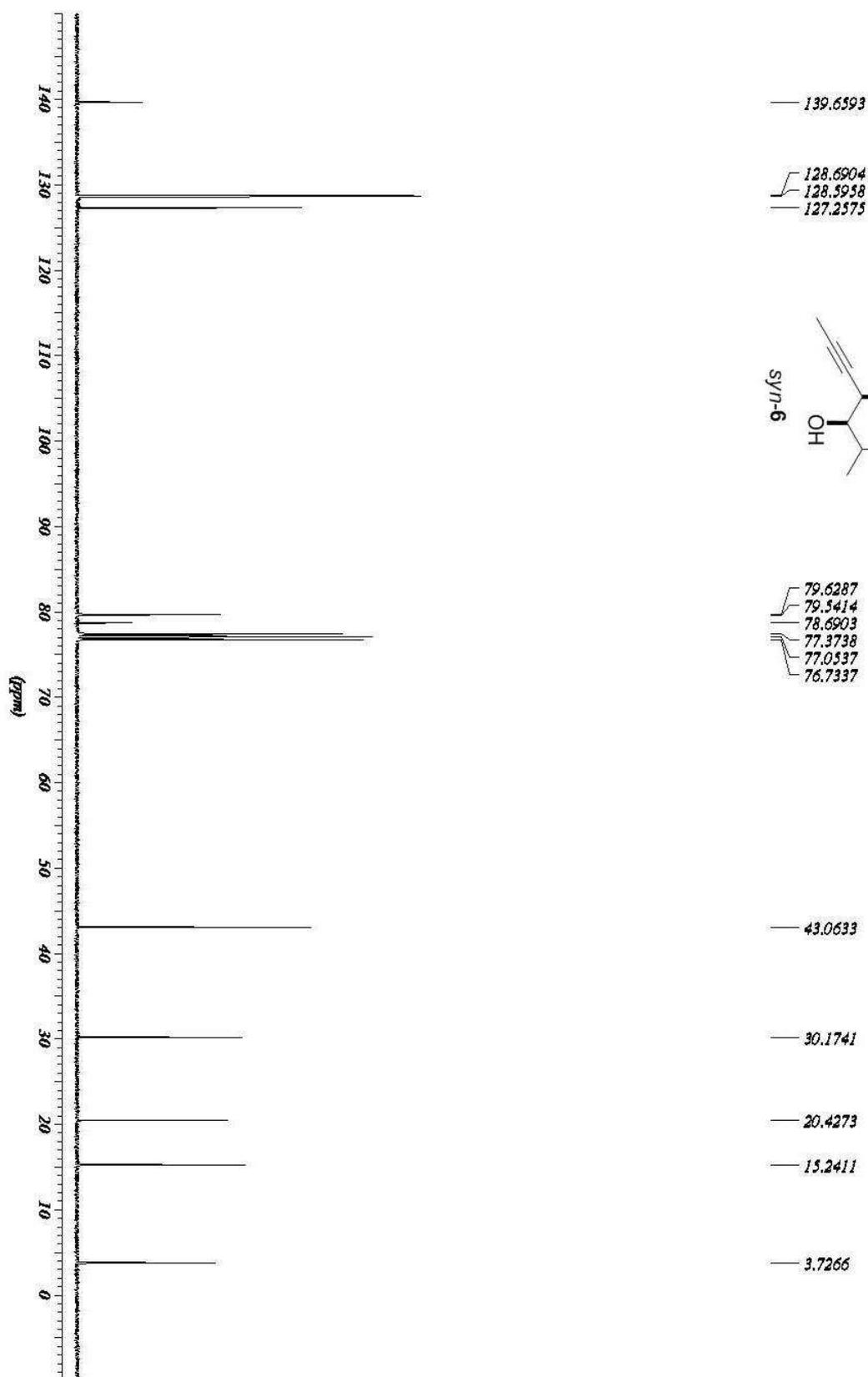




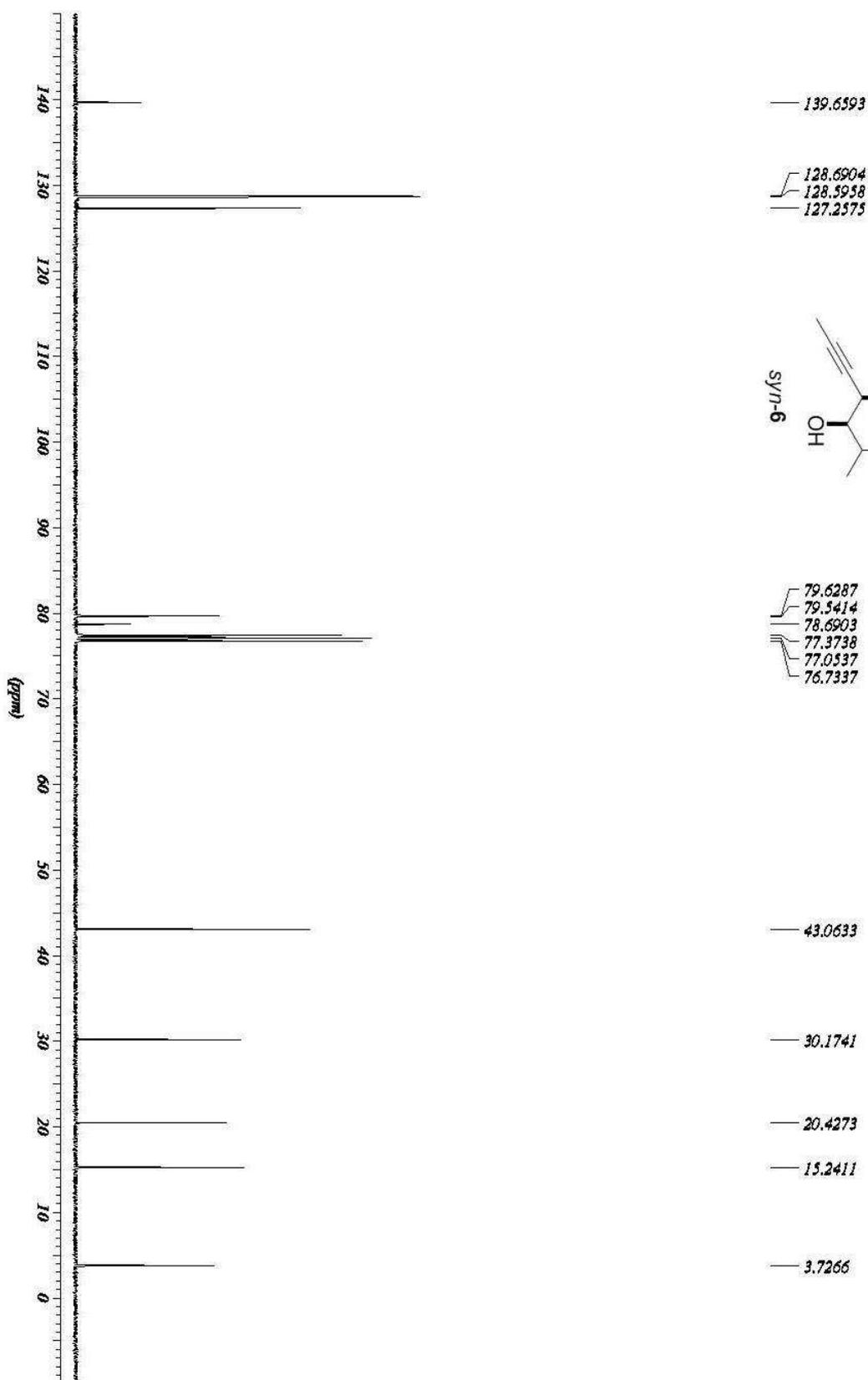
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References of the supporting information:

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