Transmetalation of Z-Telluroenynes: Stereoselective Synthesis of Z-Enynols and their Applications in Palladium-Catalyzed Cyclization

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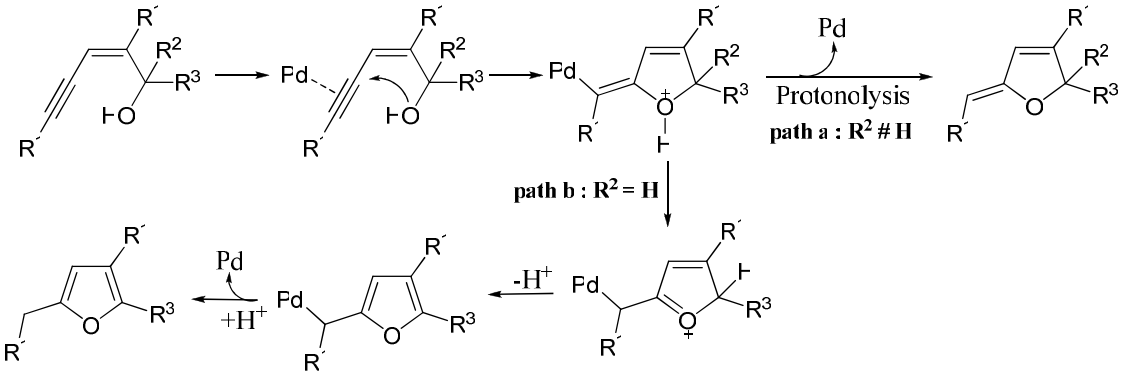
SUPPORTING INFORMATION



Scheme 1: Proposed Reaction Mechanism

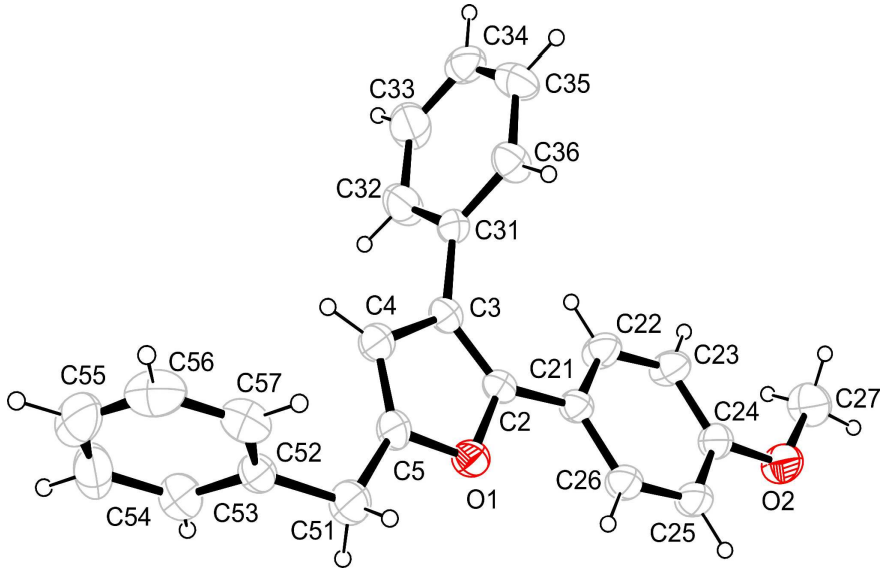


Figure 1: ORTEP view of the compound **5c**

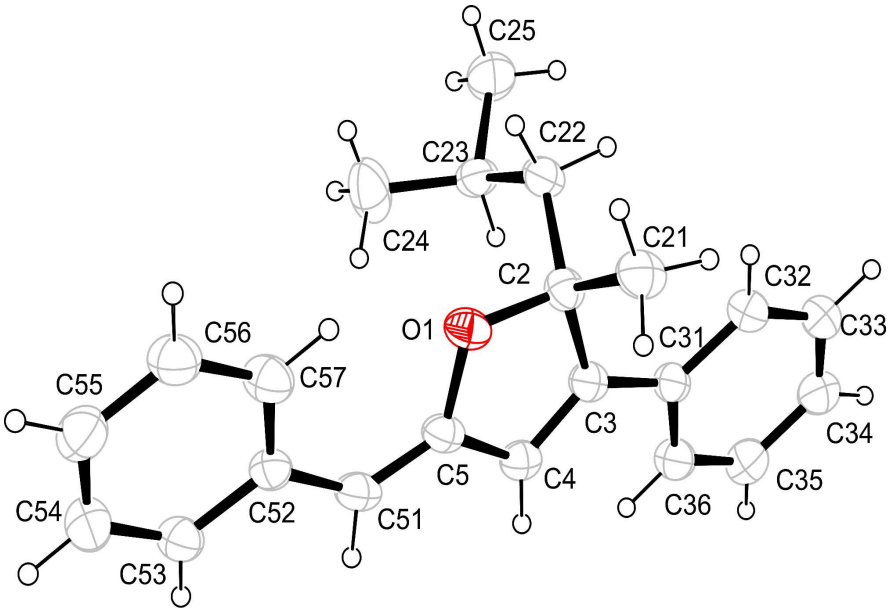


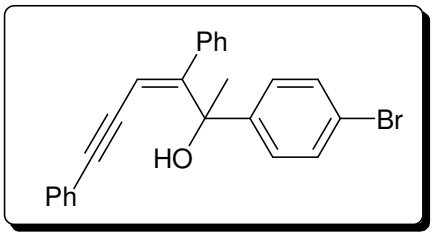
Figure 1: ORTEP view of the compound **4a**

Materials and Methods

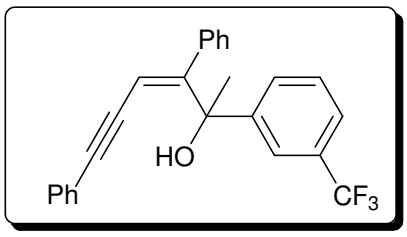
Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 200 MHz on a DPX-200 NMR spectrometer or at 400 MHz on DPX-400 NMR spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained either at 50 MHz on a DPX-200 NMR spectrometer or at 100 MHz on a DPX-400 NMR spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q

(quartet), quint (quintet), sex (sextet) and m (multiplet). High resolution mass spectra were recorded on a MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. Column chromatography was performed using Silica Gel (230-400 mesh) following the methods described by Still.[1] Thin layer chromatography (TLC) was performed using Silica Gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapour, or acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry argon. Reagents and solvents were handled using standard syringe techniques. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a Variac controller.

General procedure for *Z*-enynols formation: To a solution of vinylic tellurides (**1a-d**) (1mmol) in THF (6 mL) at -78° C under Ar, *n*-butyllithium (1.1 mmol) was added at once and the reaction stirred for 15 mim. The aldehyde or ketone was added and the reaction stirred for 1 hour. The cooling bath was removed and the mixture treated with saturated solution of ammonium chloride (5 mL), diluted with ethyl acetate (15 mL). After drying the organic phase ($MgSO_4$), the solvent was removed under vacuum and the residue purified by flash chromatography on silica gel using hexane:acetate (80:20) as eluent.



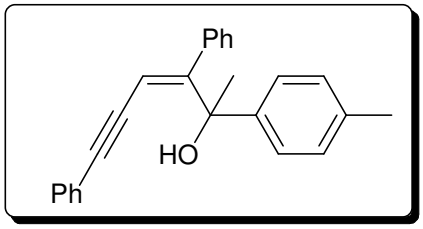
(*Z*)-2-(4-bromophenyl)-3,6-diphenylhex-3-en-5-yn-2-ol (3a). Yield: 0.338g (84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 7.52-7.44 (m, 3H), 7.29-7.24 (m, 7H), 5.91 (s, 1H), 3.30 (s, 1H), 2.53 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.99, 146.13, 140.66, 135.60, 131.68, 131.10, 131.05, 129.66, 128.22, 128.16, 127.85, 127.62, 120.98, 110.10, 98.05, 86.39, 77.08, 26.32. MS (relative intensity) *m/z*: 399 (100), 382 (92), 244 (27), 200 (62). Anal. (%) Calcd for $C_{24}H_{19}BrO$: C 71.47, H 4.75. Found: C 71.69, H 4.81.



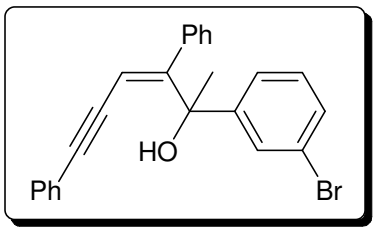
(*Z*)-3,6-diphenyl-2-(3-(trifluoromethyl)phenyl)hex-3-en-5-yn-2-ol (3b). Yield: 0.321g (82%). ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.94 (s, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.30-7.23 (m, 8H), 7.16-7.14 (m,

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

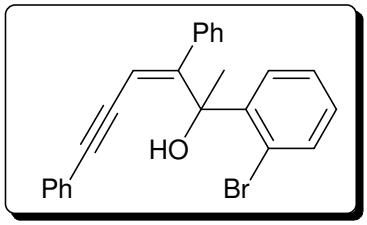
2H), 5.95 (s, 1H), 3.19 (s, 1H), 1.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.15, 148.42, 140.63, 131.16, 130.54 (q, *J* = 32 Hz), 128.68, 128.66, 128.32, 128.30, 128.08, 127.87, 124.24 (q, *J* = 273 Hz), 123.98 (q, *J* = 3.6 Hz), 122.57 (q, *J* = 3.6 Hz), 110.71, 98.69, 86.08, 77.30, 30.39. MS (relative intensity) *m*/*z*: 388 (100), 373 (94), 244 (14), 200 (34). Anal. (%) Calcd for $C_{25}H_{19}F_3O$: C 76.52, H 4.88. Found: C 76.80, H 4.93.



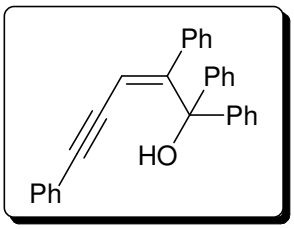
(*Z*)-3,6-diphenyl-2-*p*-tolylhex-3-en-5-yn-2-ol (3c). Yield: 0.321g (95%). ^{1}H NMR ($CDCl_3$, 400 MHz), *δ* (ppm): 7.85 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.28-7.23 (m, 7H), 7.18-7.12 (m, 3H), 5.92 (s, 1H), 3.16 (s, 1H), 2.56 (s, 3H), 1.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.95, 143.99, 141.23, 136.81, 131.20, 129.18, 128.95, 128.38, 128.24, 127.88, 125.71, 122.97, 109.62, 97.62, 86.80, 77.59, 26.46, 21.59. MS (relative intensity) *m*/*z*: 334 (100), 319 (98), 244 (16), 200 (35). Anal. (%) Calcd for $C_{25}H_{22}O$: C 88.72, H 6.55. Found: C 89.15, H 6.62.



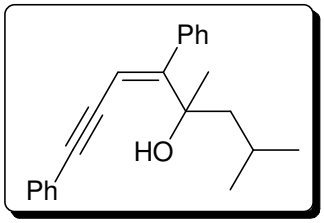
(*Z*)-2-(3-bromophenyl)-3,6-diphenylhex-3-en-5-yn-2-ol (3d). Yield: 0.330g (82%). ^{1}H NMR ($CDCl_3$, 400 MHz), *δ* (ppm): 7.82 (t, *J* = 1.9 Hz, 1H), 7.51 (ddd, *J* = 1.7/1.2/0.5 Hz, 1H), 7.39 (ddd, *J* = 1.9/0.9/0.9 Hz, 1H), 7.29-7.27 (m, 8H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.17-7.14 (m, 2H), 5.92 (s, 1H), 3.18 (s, 1H), 1.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 159.14, 140.63, 131.22, 130.17, 129.77, 128.89, 128.57, 128.30, 128.28, 128.00, 127.78, 124.58, 122.45, 110.52, 98.42, 77.14, 30.20. MS (relative intensity) *m*/*z*: 399 (78), 383 (65), 244 (28), 200 (100). Anal. (%) Calcd for $C_{24}H_{19}BrO$: C 71.47, H 4.75. Found: C 71.82, H 4.81.



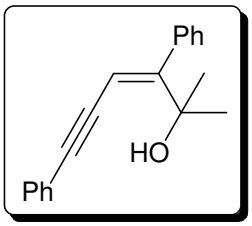
(*Z*)-2-(2-bromophenyl)-3,6-diphenylhex-3-en-5-yn-2-ol (3e). Yield: 0.346g (86%). ^{1}H NMR ($CDCl_3$, 200 MHz), *δ* (ppm): 7.83 (dd, *J* = 7.8/1.4 Hz, 1H), 7.54 (dd, *J* = 7.8/1.2 Hz, 1H), 7.50-7.48 (m, 1H), 7.37-7.12 (m, 10H), 7.08-7.04 (m, 1H), 5.83 (s, 1H), 3.34 (s, 1H), 2.02 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 157.25, 145.43, 140.53, 134.31, 131.24, 129.18, 128.73, 128.70, 128.08, 127.99, 127.58, 127.53, 126.99, 123.10, 121.68, 110.03, 98.33, 86.12, 77.58, 28.06. MS (relative intensity) *m*/*z*: 399 (44), 384 (34), 244 (21), 200 (100). Anal. (%) Calcd for $C_{24}H_{19}BrO$: C 71.47, H 4.75. Found: C 71.51, H 4.72.



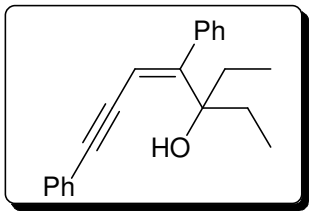
(Z)-1,1,2,5-tetraphenylpent-2-en-4-yn-1-ol (3f). Yield: 0.289g (75%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.78-7.76 (m, 2H), 7.54-7.51 (m, 3H), 7.45-7.41 (m, 2H), 7.32-7.22 (m, 6H), 7.19-7.09 (m, 6H), 6.98-6.96 (m, 1H), 6.14 (s, 1H), 3.12 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.70, 145.23, 141.09, 132.30, 131.43, 129.95, 128.17, 128.12, 128.08, 127.90, 127.85, 127.55, 127.44, 125.93, 122.81, 112.36, 98.66, 86.43, 82.21. MS (relative intensity) *m/z*: 381 (100), 306 (48), 104 (68), 77 (34). ESI-HRMS calcd for $C_{29}H_{22}O$ 386.1671, found 386.1695.



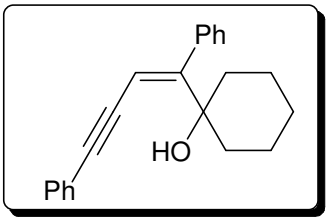
(Z)-2,4-dimethyl-5,8-diphenyloct-5-en-7-yn-4-ol (3g). Yield: 0.197g (65%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.45-7.43 (m, 2H), 7.33-7.25 (m, 8H), 5.74 (s, 1H), 2.53 (s, 1H), 2.23 (dd, J = 14.4/5.1 Hz, 1H), 2.03-1.93 (m, 1H), 1.76 (dd, J = 14.4/6.3 Hz, 1H), 1.59 (s, 3H), 1.02 (d, J = 6.6 Hz, 3H), 0.98 (d, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 161.96, 141.32, 131.04, 128.38, 128.36, 127.78, 127.43, 123.10, 108.06, 99.87, 97.43, 86.85, 77.09, 49.98, 29.11, 24.75, 24.68, 24.66. MS (relative intensity) *m/z*: 300 (16), 286 (6), 244 (100), 200 (13). Anal. (%) Calcd for $C_{22}H_{24}O$: C 86.80, H 7.95. Found: C 86.84, H 7.91.



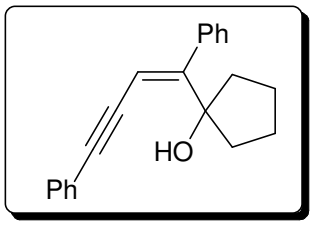
(Z)-2-methyl-3,6-diphenylhex-3-en-5-yn-2-ol (3h). Yield: 0.149g (57%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.46-7.44 (m, 2H), 7.33-7.29 (m, 6H), 7.24-7.22 (m, 2H), 5.71 (s, 1H), 3.07 (s, 1H), 1.61 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 162.33, 141.24, 131.11, 128.52, 128.40, 128.11, 127.81, 127.45, 122.90, 107.62, 97.80, 86.44, 74.07, 29.88. MS (relative intensity) *m/z*: 259 (47), 244 (100), 216 (18), 200 (28). Anal. (%) Calcd for $C_{19}H_{18}O$: C 86.99, H 6.92. Found: C 87.03, H 6.96.



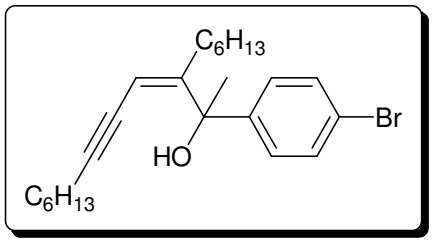
(*Z*)-3-ethyl-4,7-diphenylhept-4-en-6-yn-3-ol (3i). Yield: 0.203g (70%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.45-7.43 (m, 2H), 7.34-7.27 (m, 8H), 5.81 (s, 1H), 2.30 (s, 1H), 2.28 (sex, J = 7.3 Hz, 2H), 1.79 (sex, J = 6.8 Hz, 2H), 1.04 (t, J = 7.5 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.52, 141.56, 131.11, 128.49, 128.38, 127.83, 127.48, 123.24, 108.96, 96.84, 86.94, 79.62, 33.31, 8.26. MS (relative intensity) *m/z*: 287 (20), 258 (100), 200 (13). The product **3i** was easy purified by column chromatography however, was unstable to obtain reliable elemental analyses.



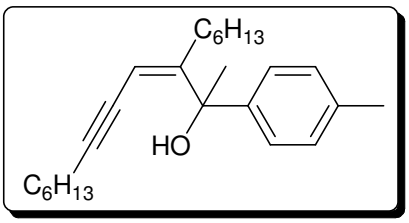
(*Z*)-1-(1,4-diphenylbut-1-en-3-ynyl)cyclohexanol (3j). Yield: 0.148g (49%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.47-7.41 (m, 2H), 7.34-7.18 (m, 8H), 5.70 (s, 1H), 2.79 (s, 1H), 2.09-1.50 (m, 9H), 1.30-1.07 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 162.94, 141.25, 131.00, 128.39, 128.34, 128.23, 127.61, 127.20, 122.95, 107.64, 97.66, 86.55, 74.96, 36.50, 25.30, 21.62. MS (relative intensity) *m/z*: 299 (98), 281 (15), 256 (100), 243 (31), 200 (50). Anal. (%) Calcd for $C_{22}H_{22}O$: C 87.38, H 7.33. Found: C 87.72, H 7.42.



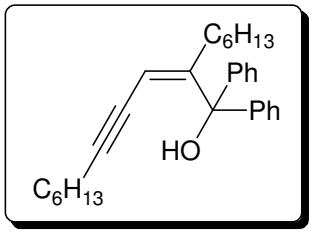
(*Z*)-1-(1,4-diphenylbut-1-en-3-ynyl)cyclopentanol (3k). Yield: 0.097g (34%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.45-7.42 (m, 2H), 7.36-7.26 (m, 8H), 5.75 (s, 1H), 2.73 (s, 1H), 2.07-2.04 (m, 3H), 1.94-1.84 (m, 3H), 1.75-1.66 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 160.46, 141.66, 131.11, 129.21, 128.44, 128.38, 128.04, 127.78, 127.35, 123.01, 108.46, 97.47, 84.35, 40.37, 23.56. MS (relative intensity) *m/z*: 285 (100), 267 (51), 256 (98), 200 (86), 101 (70). Anal. (%) Calcd for $C_{21}H_{20}O$: C 87.46, H 6.99. Found: C 87.71, H 7.11.



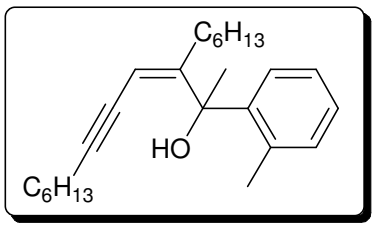
(*Z*)-2-(4-bromophenyl)-3-hexyldodec-3-en-5-yn-2-ol (3l). Yield: 0.251g (60%). ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.42-7.29 (m, 4H), 5.46 (s, 1H), 3.96 (s, 1H), 2.22-2.03 (m, 4H), 1.72 (s, 3H), 1.40-1.20 (m, 16H), 0.87-0.82 (m, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 158.15, 146.39, 130.70, 127.39, 120.56, 105.30, 98.46, 77.62, 77.38, 34.31, 31.48, 31.15, 28.97, 28.83, 28.42, 28.25, 28.16, 22.41, 22.36, 19.43, 13.89. MS (relative intensity) *m/z*: 415 (33), 343 (100), 331 (86), 247 (41), 164 (82). Anal. (%) Calcd for $C_{24}H_{35}BrO$: C 68.72, H 8.41. Found: C 68.39, H 8.37.



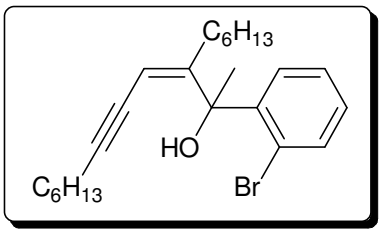
(*Z*)-3-hexyl-2-*p*-tolyldodec-3-en-5-yl-2-ol (3m). Yield: 0.106g (30%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.34 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 7.47-7.45 (m, 1H), 3.96 (s, 1H), 2.32 (s, 3H), 2.22 (td, J = 7.0/2.4 Hz, 2H), 2.08-2.01 (m, 2H), 1.74 (s, 3H), 1.43-1.21 (m, 16H), 0.87 (t, J = 7.3 Hz, 3H), 0.85 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.20, 144.19, 136.29, 128.54, 125.50, 104.59, 98.18, 77.97, 77.88, 34.54, 31.59, 31.27, 29.08, 28.94, 28.54, 28.41, 28.06, 22.49, 22.45, 20.94, 19.59, 13.97. MS (relative intensity) *m*/*z*: 350 (32), 280 (54), 155 (44), 104 (100), 90 (21).HRMS calcd for $C_{25}H_{38}O$: 354.29227. Found: 354.2929.



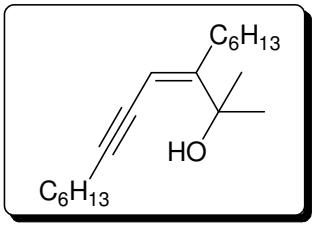
(*Z*)-2-hexyl-1,1-diphenylundec-2-en-4-yn-1-ol (3n). Yield: 0.185g (46%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.37-7.34 (m, 4H), 7.30-7.21 (m, 6H), 5.68-5.66 (m, 1H), 4.50 (s, 1H), 2.05 (td, J = 7.0/2.0 Hz, 2H), 1.89 (t, J = 8.0 Hz, 2H), 1.26-1.07 (m, 16H), 0.85 (t, J = 6.8 Hz, 3H), 0.80 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.70, 145.72, 132.31, 129.98, 128.19, 127.96, 127.56, 127.05, 107.13, 99.44, 82.92, 36.26, 31.48, 31.22, 28.98, 28.68, 28.38, 28.23, 22.40, 19.45, 13.98, 13.94. MS (relative intensity) *m*/*z*: 399 (14), 328 (54), 314 (74), 104 (100). HRMS calcd for $C_{29}H_{38}O$: 402.29227. Found: 402.2926.



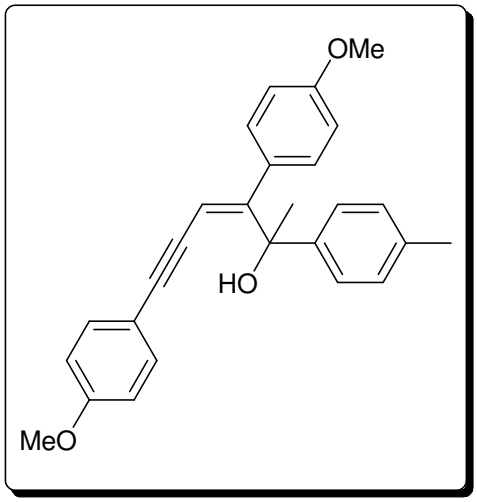
(*Z*)-3-hexyl-2-*o*-tolyldodec-3-en-5-yn-2-ol (3o). Yield: 0.117g (33%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.43-7.41 (m, 1H), 7.16-7.10 (m, 4H), 5.43-5.42 (m, 1H), 3.91 (s, 1H), 2.39 (s, 3H), 2.22 (td, J = 6.8/2.4 Hz, 2H), 1.87 (t, J = 7.8 Hz, 2H), 1.80 (s, 3H), 1.46-1.16 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H), 0.83 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.01, 143.03, 137.41, 131.69, 129.28, 127.20, 126.09, 124.92, 103.57, 98.80, 78.81, 77.42, 34.32, 31.56, 31.27, 29.00, 28.77, 28.56, 28.53, 28.45, 22.48, 22.45, 21.13, 19.63, 13.97. MS (relative intensity) *m*/*z*: 354 (40), 336 (42), 119 (32), 105 (100), 91 (22).HRMS calcd for $C_{25}H_{38}O$: 354.29227. Found: 354.2927.



(Z)-2-(2-bromophenyl)-3-hexyldodec-3-en-5-yn-2-ol (3p). Yield: 0.226g (54%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.74 (dd, J = 8.0/1.7 Hz, 1H), 7.52 (dd, J = 7.8/1.2 Hz, 1H), 7.27 (tt, J = 7.5/1.4 Hz, 1H), 7.07 (td, J = 7.3/1.4 Hz, 1H), 5.37-5.35 (m, 1H), 3.54 (s, 1H), 2.28-2.24 (m, 2H), 1.99 (td, J = 6.6/2.2 Hz, 2H), 1.75 (s, 3H), 1.52-1.43 (m, 2H), 1.34-1.21 (m, 14H), 0.87 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 157.37, 146.13, 134.13, 131.69, 128.44, 128.24, 127.35, 126.42, 121.53, 104.95, 77.86, 77.31, 34.38, 31.66, 31.26, 29.17, 28.69, 28.55, 28.29, 22.53, 22.46, 19.58, 14.00, 13.98. MS (relative intensity) *m/z*: 415 (33), 398 (26), 345 (63), 331 (100), 248 (59). HRMS calcd for $C_{24}H_{35}BrO$: 418.18713. Found: 418.1867.

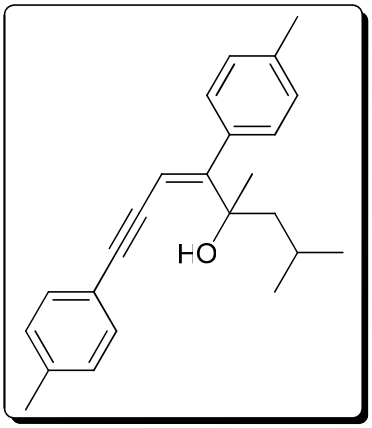


(Z)-3-hexyl-2-methyldodec-3-en-5-yn-2-ol (3q). Yield: 0.084g (30%). ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 5.32 (s, 1H), 3.80 (s, 1H), 2.34 (td, J = 6.7/2.3 Hz, 2H), 2.09 (t, J= 6.7 Hz, 1H), 1.57-1.28 (m, 22H), 0.91-0.85 (m, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 160.42, 102.92, 97.79, 77.97, 74.30, 68.51, 34.29, 31.61, 31.21, 29.09, 28.96, 28.83, 28.51, 22.50, 22.43, 19.54, 13.94, 13.91. MS (relative intensity) *m/z*: 275 (21), 260 (26), 218 (55), 204 (68), 190 (68), 108 (100). Anal. (%) Calcd for $C_{19}H_{34}O$: C 81.95, H 12.31. Found: C 82.31, H 12.40.

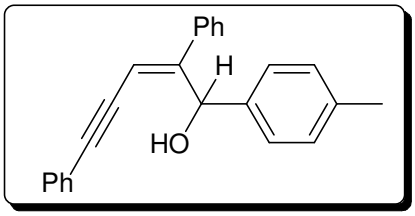


(Z)-1-methoxy-4-(4-(4-methoxyphenyl)-5-methyl-5-p-tolylhex-3-en-1-ynyl)benzene (3r): Yield: 0.167g (42%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.51 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 6.82-6.77 (m, 4H), 5.89 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.26 (s, 1H), 2.35 (s, 3H), 1.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.92, 159.11, 158.67, 144.29, 136.78, 133.80, 132.75, 129.60, 129.00, 125.77, 115.24, 114.03, 113.34, 109.30, 97.58, 85.88,

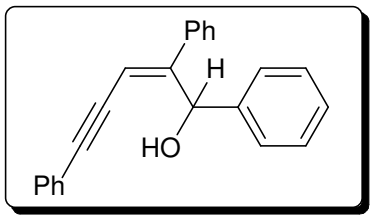
77.73, 55.29, 55.22, 30.19, 21.20. MS (relative intensity) *m/z*: 398 (60), 380 (100), 365 (18), 135 (25). ESI-HRMS calcd. for $C_{27}H_{26}O_3$ 398.1882, found 398.1902.



(Z)-2,4-dimethyl-5,8-di*p*-tolyloct-5-en-7-yn-4-ol (3s): Yield: 0.150g (45%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.36-7.32 (m, 2H), 7.19-7.12 (m, 6H), 5.71 (s, 1H), 2.60 (s, 1H), 2.35 (s, 6H), 2.27-2.17 (m, 1H), 2.03-1.88 (m, 1H), 1.78-1.68 (m, 1H), 1.57 (s, 3H), 1.03-0.96 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 161.48, 138.47, 137.18, 130.94, 129.16, 128.50, 128.30, 120.09, 107.89, 97.50, 86.37, 77.17, 50.02, 29.08, 24.76, 24.69, 24.67, 21.46, 21.08. MS (relative intensity) *m/z*: 332 (33), 317 (12), 275 (100), 115 (15), 91 (7). The product **3s** was easy purified by column chromatography however, was unstable to obtain reliable elemental analyses.

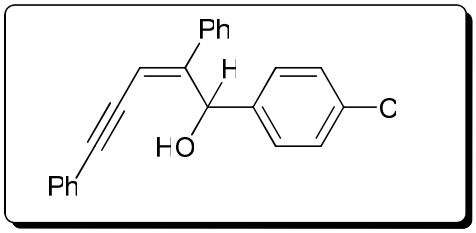


(Z)-2,5-diphenyl-1-*p*-tolylpent-2-en-4-yn-1-ol (3t). Yield: 0.194g (60%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.40 (d, J = 8.0 Hz, 2H), 7.30-7.21 (m, 10H), 7.13 (d, J = 8.0 Hz, 2H), 6.39 (s, 1H), 6.14 (s, 1H), 2.57 (s, 1H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 154.11, 138.91, 137.88, 136.74, 131.45, 129.06, 128.42, 128.33, 128.22, 128.19, 127.59, 125.57, 122.99, 109.50, 96.29, 86.62, 73.62, 21.05. MS (relative intensity) *m/z*: 320 (100), 200 (38), 118 (78), 90 (37). HRMS calcd for $C_{24}H_{20}O$: 324.15142. Found: 324.1519.

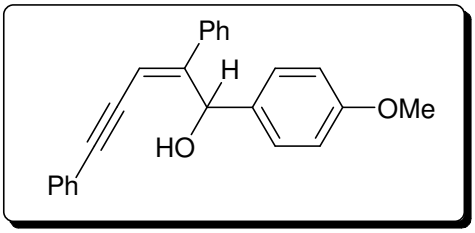


(Z)-1,2,5-triphenylpent-2-en-4-yn-1-ol (3u). Yield: 0.195g (63%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.53-7.51 (m, 2H), 7.42-7.39 (m, 2H), 7.33-7.20 (m, 11H), 6.43 (s, 1H), 6.16 (s, 1H), 2.62 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 153.94, 141.86, 137.75, 131.45, 128.46, 128.33, 128.22, 127.58, 127.13, 125.60, 122.92, 109.73, 96.34,

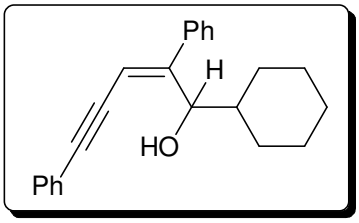
86.54, 73.60. MS (relative intensity) *m/z*: 307 (100), 229 (33), 104 (88), 77 (32). Anal. (%) Calcd for $C_{23}H_{18}O$: C 89.00, H 5.85. Found: C 88.97, H 5.81.



(*Z*)-1-(4-chlorophenyl)-2,5-diphenylpent-2-en-4-yn-1-ol (3v). Yield: 0.103g (30%). ^{1}H NMR ($CDCl_3$, 400 MHz), *δ* (ppm): 7.45-7.39 (m, 4H), 7.31-7.22 (m, 10H), 6.39 (s, 1H), 6.16 (s, 1H), 2.62 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 153.41, 140.36, 137.48, 131.47, 128.63, 128.49, 128.41, 128.35, 127.53, 127.08, 122.84, 110.10, 96.66, 86.19, 73.06. Anal. (%) Calcd for $C_{23}H_{17}ClO$: C 80.11, H 4.97. Found: C 80.14, H 5.02.



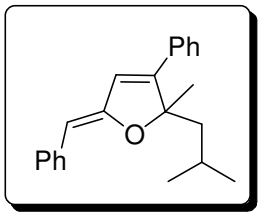
(*Z*)-1-(4-methoxyphenyl)-2,5-diphenylpent-2-en-4-yn-1-ol (3w). Yield: 0.289g (85%). ^{1}H NMR ($CDCl_3$, 400 MHz), *δ* (ppm): 7.43-7.39 (m, 4H), 7.29-7.27 (m, 5H), 7.22-7.20 (m, 3H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.36 (s, 1H), 6.12 (s, 1H), 3.73 (s, 3H), 2.73 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.68, 154.24, 137.88, 133.99, 131.40, 128.38, 128.30, 128.15, 128.13, 127.58, 126.88, 122.94, 113.71, 109.32, 96.24, 86.59, 73.36, 55.10. MS (relative intensity) *m/z*: 340 (100), 324 (19), 135 (75), 77 (29). The product **3w** was easy purified by column chromatography however, was unstable to obtain reliable elemental analyses.



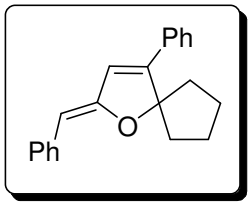
(*Z*)-1-cyclohexyl-2,5-diphenylpent-2-en-4-yn-1-ol (3x). Yield: 0.158g (50%). ^{1}H NMR ($CDCl_3$, 400 MHz), *δ* (ppm): 7.55-7.38 (m, 4H), 7.33-7.21 (m, 6H), 5.98 (s, 1H), 4.84 (d, *J* = 8.9 Hz, 1H), 2.42 (s, 1H), 2.18-2.12 (m, 1H), 1.84-0.99 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 154.53, 139.42, 131.28, 128.36, 128.34, 128.22, 128.01, 127.54, 123.14, 109.74, 96.10, 86.63, 77.87, 41.99, 29.64, 28.99, 26.33, 25.79, 25.70. MS (relative intensity) *m/z*: 313 (25), 230 (100), 200 (24), 126 (14). Anal. (%) Calcd for $C_{23}H_{24}O$: C 87.30, H 7.64. Found: C 87.58, H 7.71.

General procedure for pyrans formation: The *Z*-enynols (**3a-z**) were treated with $PdCl_2(CH_3CN)_2$ (5 mol%) in THF at 70° C for 30 mim. The mixture treated with saturated solution of ammonium chloride (5 mL), diluted with ethyl acetate (15 mL). After drying the organic phase ($MgSO_4$), the solvent was removed under vacuum and

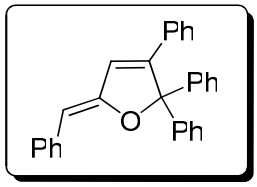
the residue purified by flash chromatography on silica gel using hexane:acetate (95:5) as eluent.



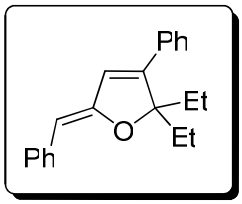
(Z)-5-benzylidene-2-isobutyl-2-methyl-3-phenyl-2,5-dihydrofuran (4a): Yield: 0.219g (72%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.66-7.64 (m, 2H), 7.48-7.46 (m, 2H), 7.38-7.34 (m, 2H), 7.31-7.26 (m, 3H), 7.10-7.06 (m, 1H), 6.48 (s, 1H), 5.40 (s, 1H), 1.97 (d, J = 5.8 Hz, 2H), 1.77-1.68 (m, 1H), 1.66 (s, 3H), 0.91 (d, J = 6.6 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.46, 149.79, 137.27, 132.63, 128.70, 128.20, 127.31, 126.54, 124.69, 123.00, 98.48, 95.61, 48.15, 27.55, 24.82, 24.41, 23.79. MS (relative intensity) *m/z*: 304 (25), 289 (7), 247 (100), 202 (7). Anal. (%) Calcd for $C_{22}H_{24}O$: C 86.80, H 7.95. Found: C 86.76, H 7.91.



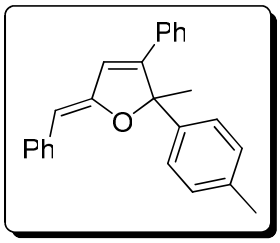
(Z)-2-benzylidene-4-phenyl-1-oxaspiro[4,4]non-3-ene (4b): Yield: 0.224g (78%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.63-7.61 (m, 2H), 7.46-7.44 (m, 2H), 7.38-7.26 (m, 5H), 7.10-7.04 (m, 1H), 6.50 (s, 1H), 5.39 (s, 1H), 2.29-2.22 (m, 2H), 2.13-2.00 (m, 4H), 1.93-1.86 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.34, 147.57, 137.35, 131.25, 128.63, 128.22, 127.27, 126.54, 124.69, 122.57, 102.85, 98.24, 38.34, 25.42, 23.05. MS (relative intensity) *m/z*: 288 (100), 273 (4), 259 (70), 246 (11), 77 (7). Anal. (%) Calcd for $C_{21}H_{20}O$: C 87.46, H 6.99. Found: C 87.41, H 6.95.



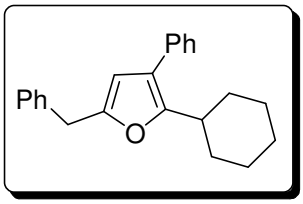
(Z)-5-benzyledene-2,2,3-triphenyl-2,5-dihydrofuran (4c): Yield: 0.247g (64%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.67-7.65 (m, 2H), 7.44-7.41 (m, 4H), 7.33-7.04 (m, 14H), 6.67 (s, 1H), 5.53 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.03, 148.94, 141.27, 136.68, 133.35, 129.99, 128.34, 128.25, 128.21, 128.07, 128.04, 127.77, 127.52, 125.16, 124.46, 99.85, 98.89. MS (relative intensity) *m/z*: 386 (100), 309 (60), 268 (91), 77 (28). The product **4c** was easy purified by column chromatography however, was unstable to obtain reliable elemental analyses.



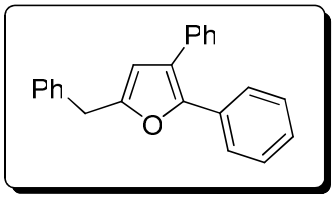
(Z)-5-benzyledene-2,2-diethyl-3-phenyl-2,5-dihydrofuran (4e): Yield: 0.194g (67%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.59-7.20 (m, 11H), 6.34 (s, 1H), 2.17-2.08 (m, 2H), 2.03-1.92 (m, 2H), 0.80 (t, J = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 171.37, 168.42, 133.53, 130.78, 130.02, 129.10, 128.32, 127.04, 117.17, 93.06, 30.47, 7.22. MS (relative intensity) *m/z*: 290 (100), 131 (45), 115 (10), 102 (40), 91 (15). The product **4e** was easy purified by column chromatography however, was unstable to obtain reliable elemental analyses.



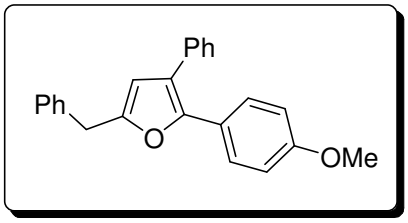
(Z)-5-benzyledene-2-methyl-3-phenyl-2-*p*-tolyl-2,5-dihydrofuran (4f): Yield: 0.253g (75%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.61 (d, J = 7.5 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.21-6.99 (m, 10H), 6.58 (s, 1H), 5.47 (s, 1H), 2.27 (s, 3H), 1.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.47, 150.18, 138.79, 137.83, 136.85, 131.98, 129.15, 128.33, 128.11, 128.07, 127.49, 126.76, 126.04, 124.80, 122.16, 99.08, 94.13, 60.19, 14.05. MS (relative intensity) *m/z*: 338 (96), 323 (100), 247 (16), 91 (33). The product **4f** was easy purified by column chromatography however, was unstable to obtain reliable elemental analyses.



5-benzyl-2-cyclohexyl-3-phenylfuran (5a): Yield: 0.222g (74%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.40-7.23 (m, 10H), 5.99 (s, 1H), 3.95 (s, 2H), 2.82 (tt, J = 11.9/3.1 Hz, 1H), 1.84-1.78 (m, 4H), 1.70-1.60 (m, 4H), 1.31-1.23 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 154.66, 152.00, 138.24, 131.30, 128.75, 128.39, 128.13, 127.82, 126.80, 120.62, 107.84, 41.62, 36.25, 34.47, 31.89, 26.38. MS (relative intensity) *m/z*: 316 (100), 273 (78), 141 (13), 91 (57). The product **5a** was easy purified by column chromatography however, was unstable to obtain reliable elemental analyses.

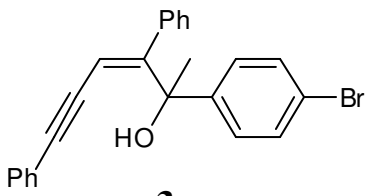


5-benzyl-2,3-diphenylfuran (5b): Yield: 0.232g (75%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.50-7.48 (m, 2H), 7.39-7.36 (m, 2H), 7.34-7.29 (m, 6H), 7.27-7.23 (m, 4H), 7.21-7.18 (m, 1H), 6.13 (s, 1H), 4.04 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 153.79, 147.55, 137.80, 131.37, 128.86, 128.56, 128.54, 128.50, 128.27, 127.14, 126.95, 126.57, 126.00, 123.05, 110.74, 99.95, 34.59. MS (relative intensity) *m/z*: 310 (100), 233 (13), 105 (38), 91 (9), 77 (20). The product **5b** was easy purified by column chromatography however, was unstable to obtain reliable elemental analyses.



5-benzyl-2-(4-methoxyphenyl)-3-phenylfuran (5c): Yield: 0.233g (72%). H^{1} NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.41 (d, J = 9.06 Hz, 2H), 7.37-7.21 (m, 10H), 6.79 (t, J = 9.06 Hz, 2H), 6.11 (s, 1H), 4.02 (s, 2H), 3.76 (s, 3H). C^{13} NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.86, 153.22, 147.46, 137.99, 134.63, 128.85, 128.51, 128.46, 127.59, 126.73, 126.52, 124.20, 121.56, 113.76, 110.40, 55.18, 34.57. MS (relative intensity) *m/z*: 340 (100), 325 (13), 221 (12), 91 (12). Anal. (%) Calcd for $C_{24}H_{20}O_2$: C 84.68, H 5.92. Found: C 84.72, H 5.95.

Selected Spectra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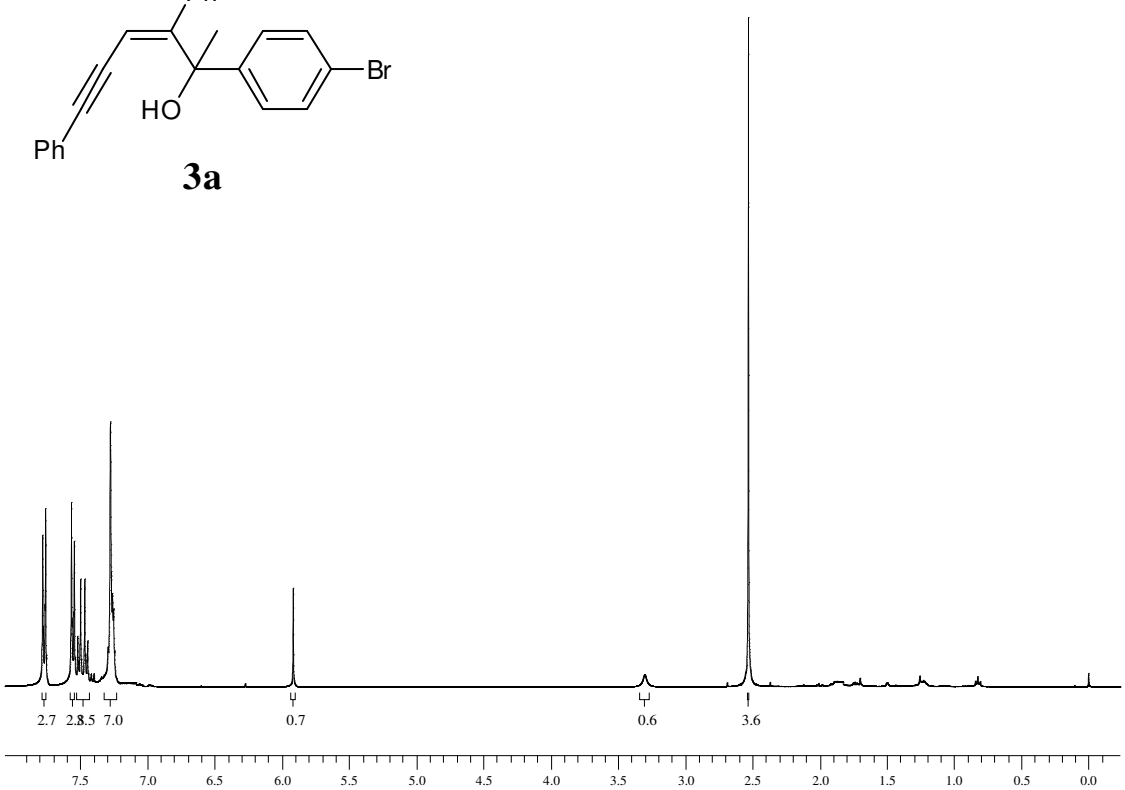
Br
HO
Ph

3a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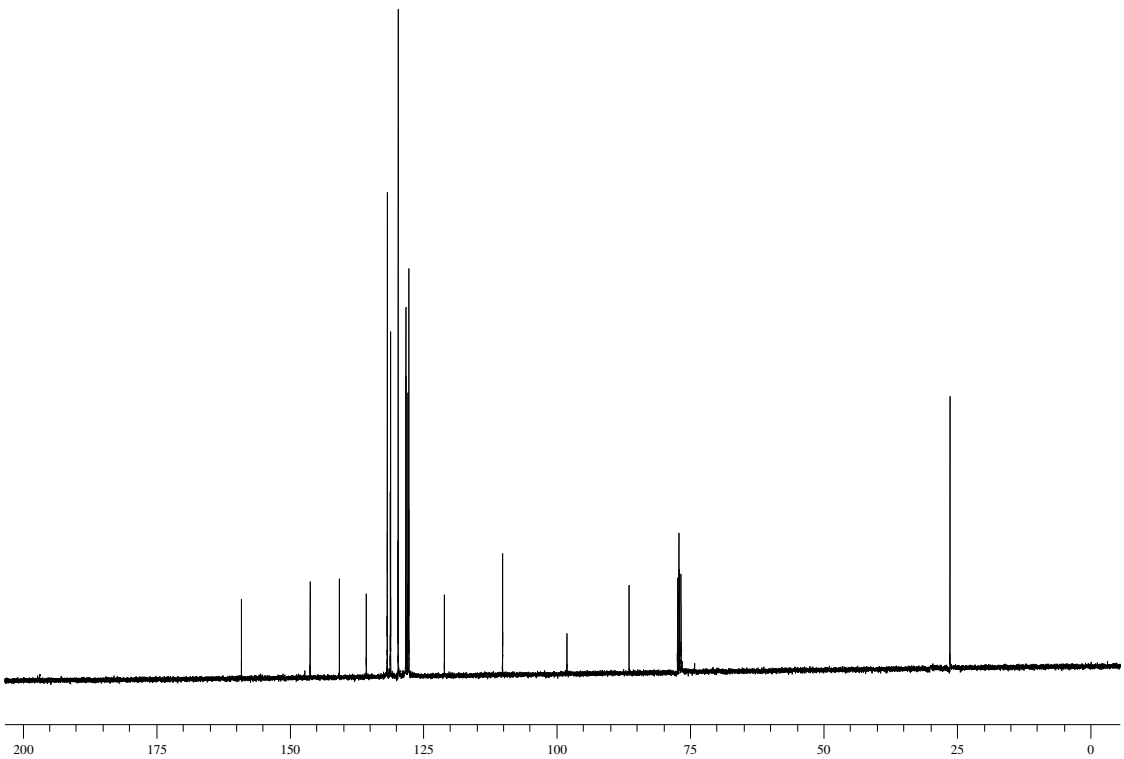
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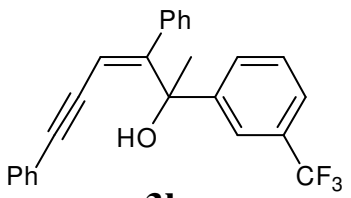
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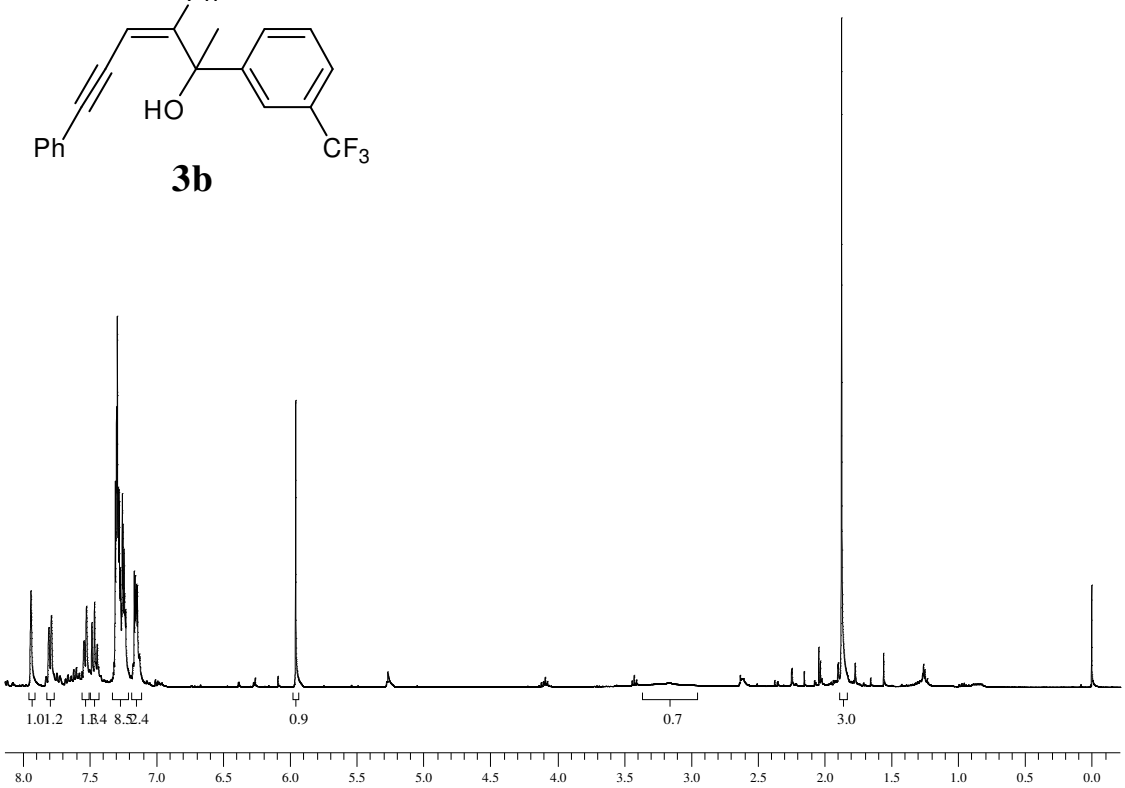
HO
Ph
CF3

3b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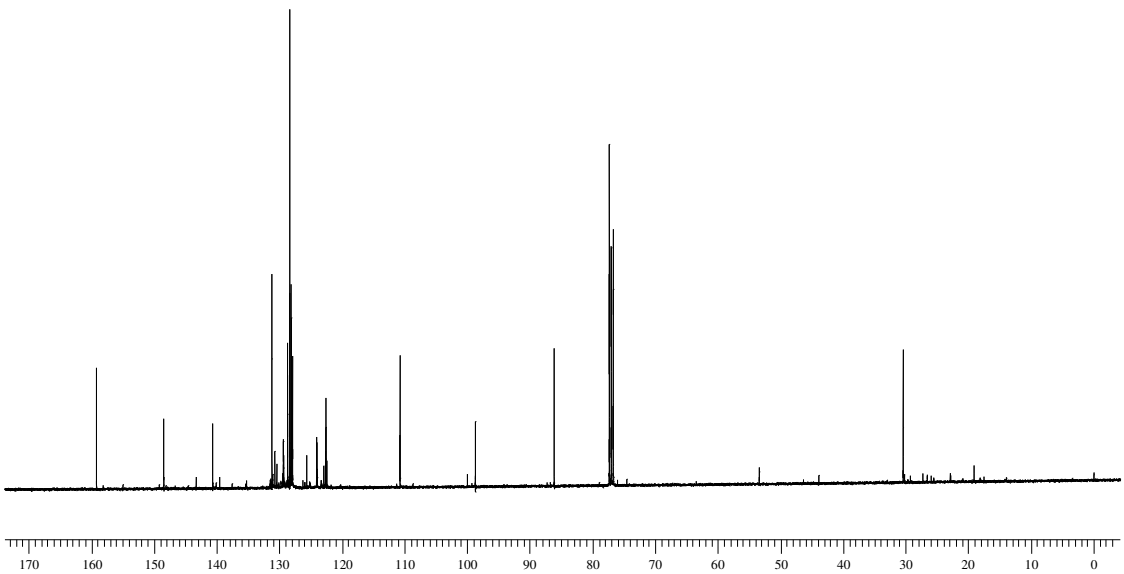
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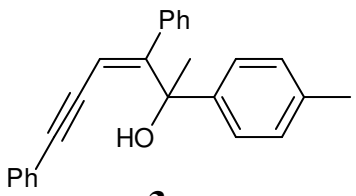
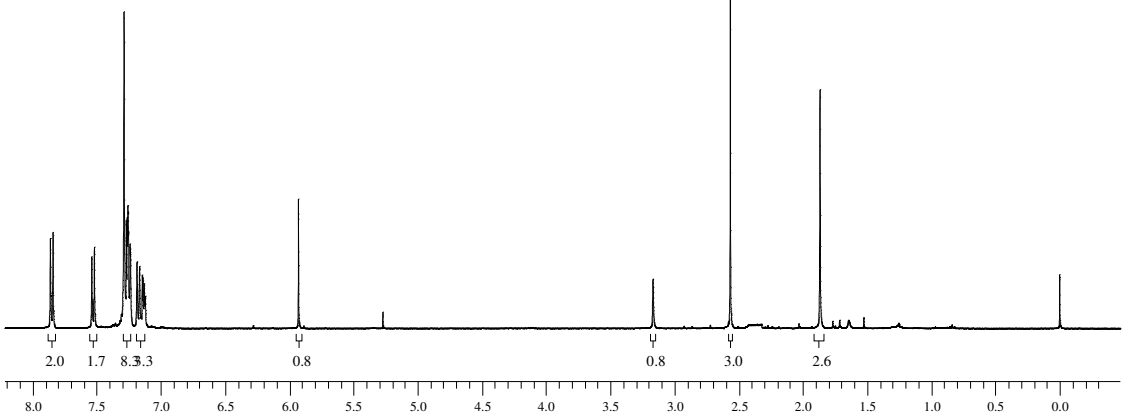

Ph
HO
Ph

3c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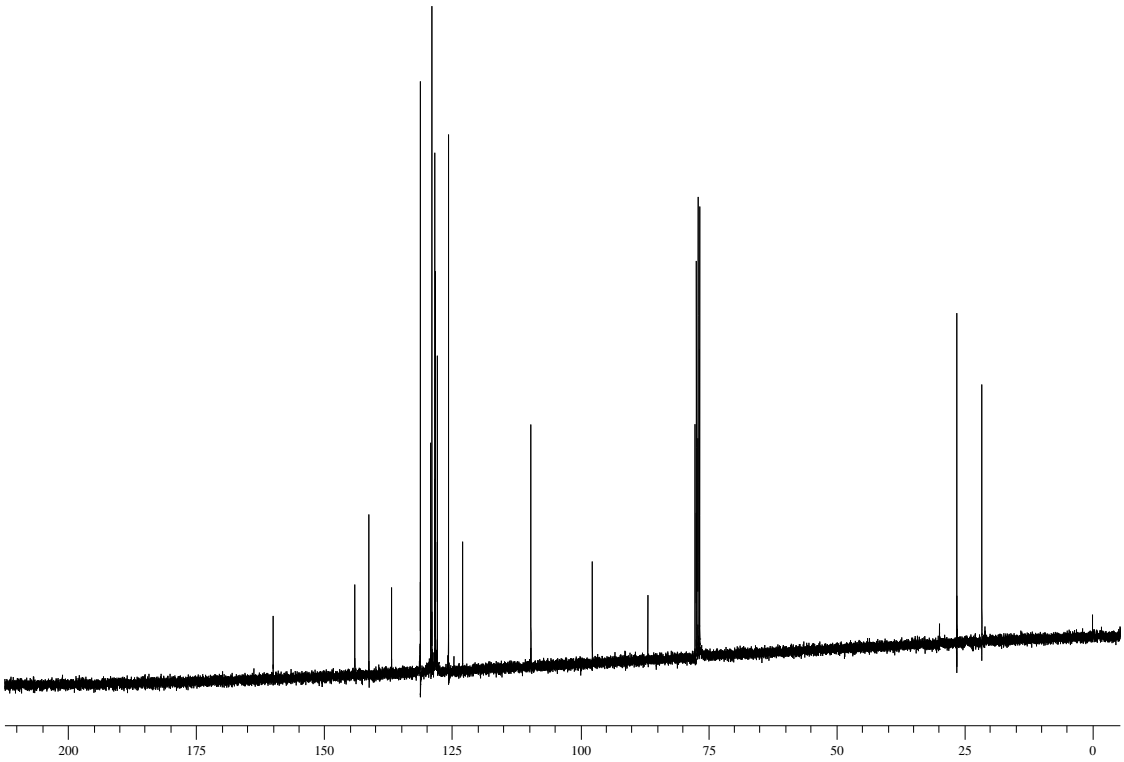
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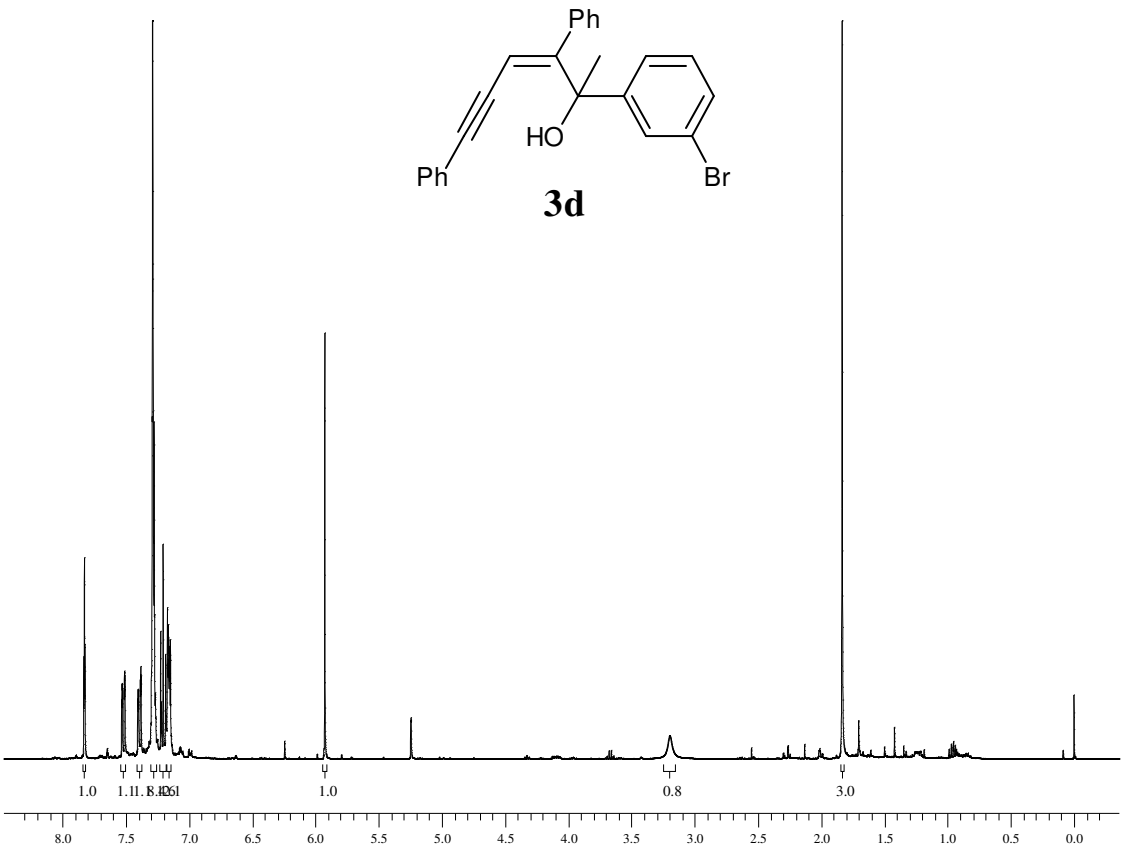
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Ph
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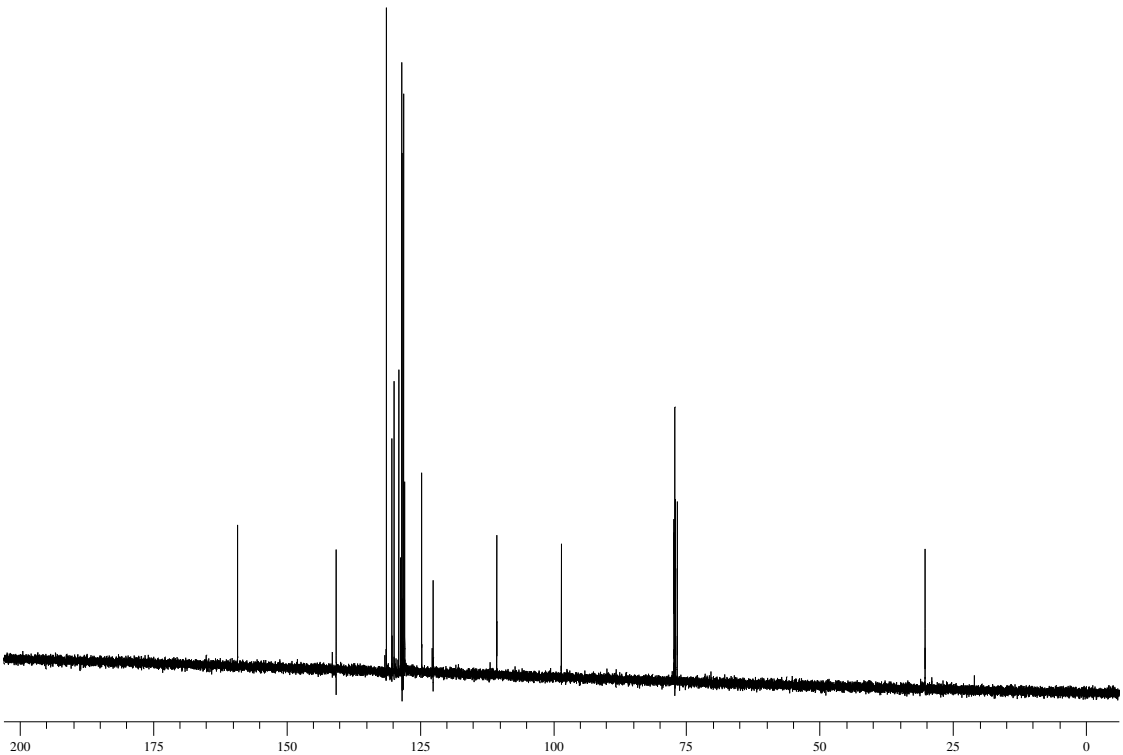
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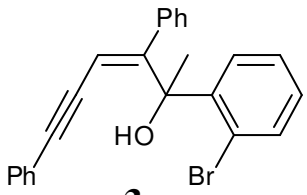
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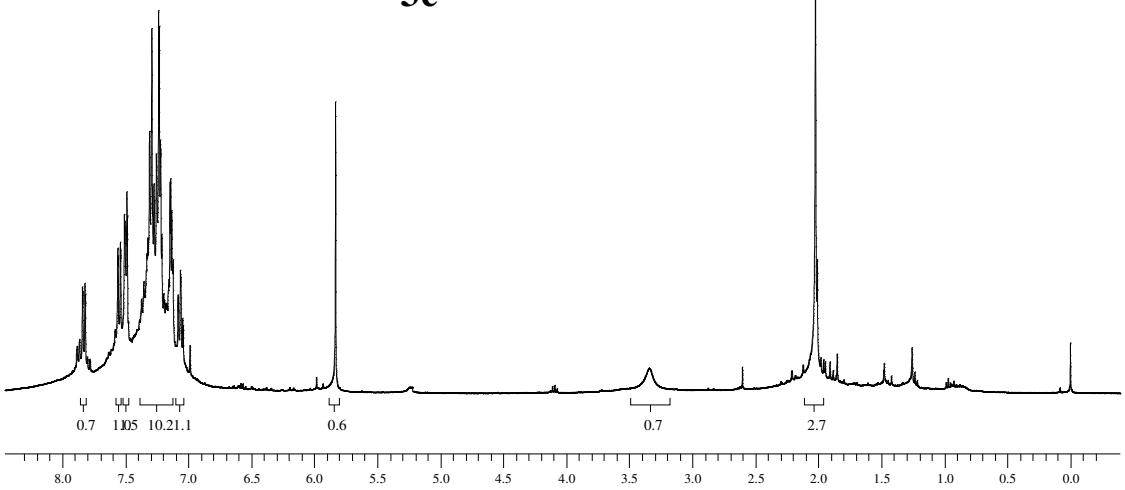
HO
Ph
Br

3e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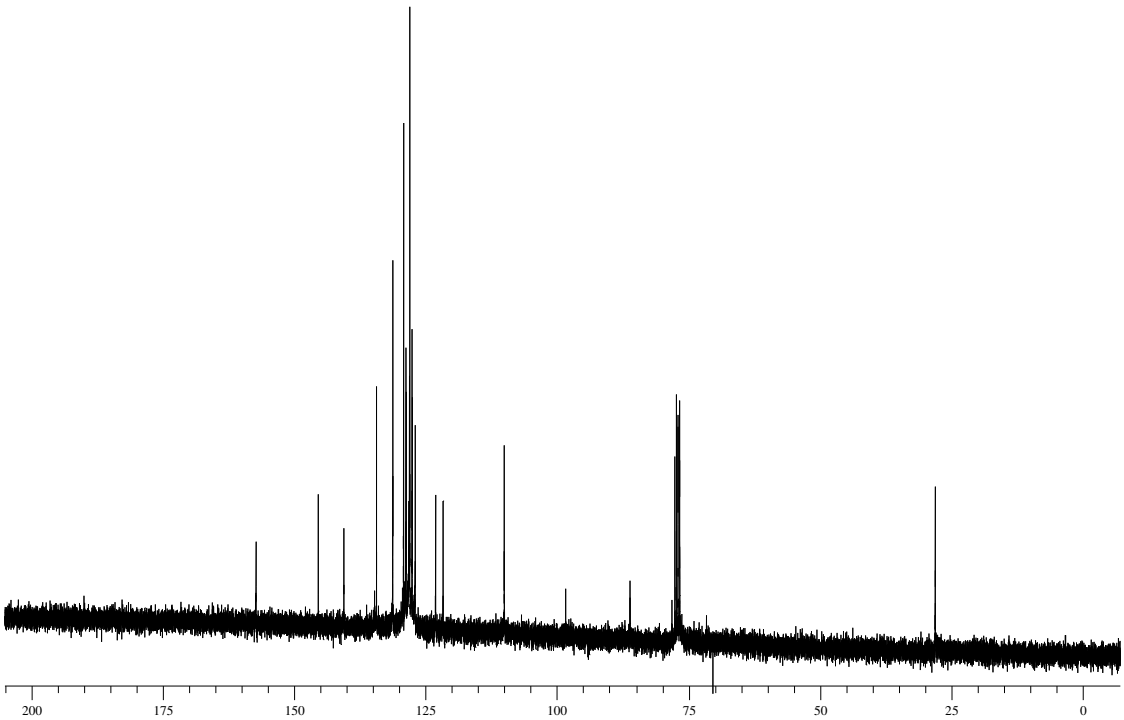
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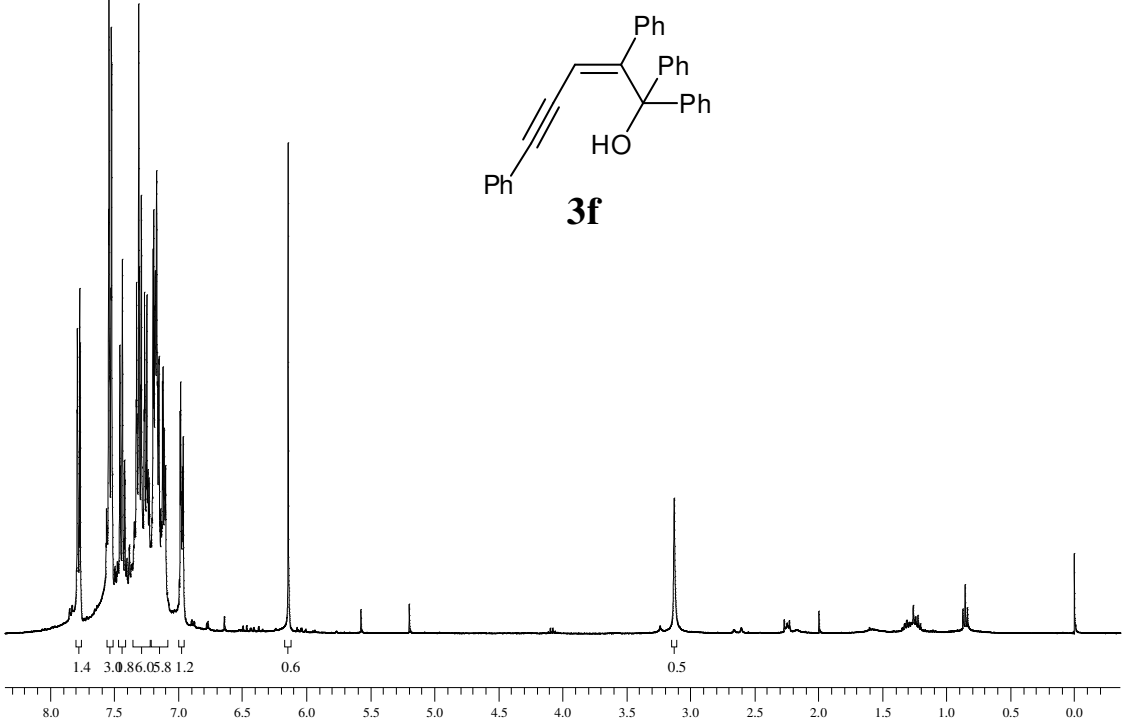
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Ph
Ph
HO
Ph
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7.0
6.5
6.0
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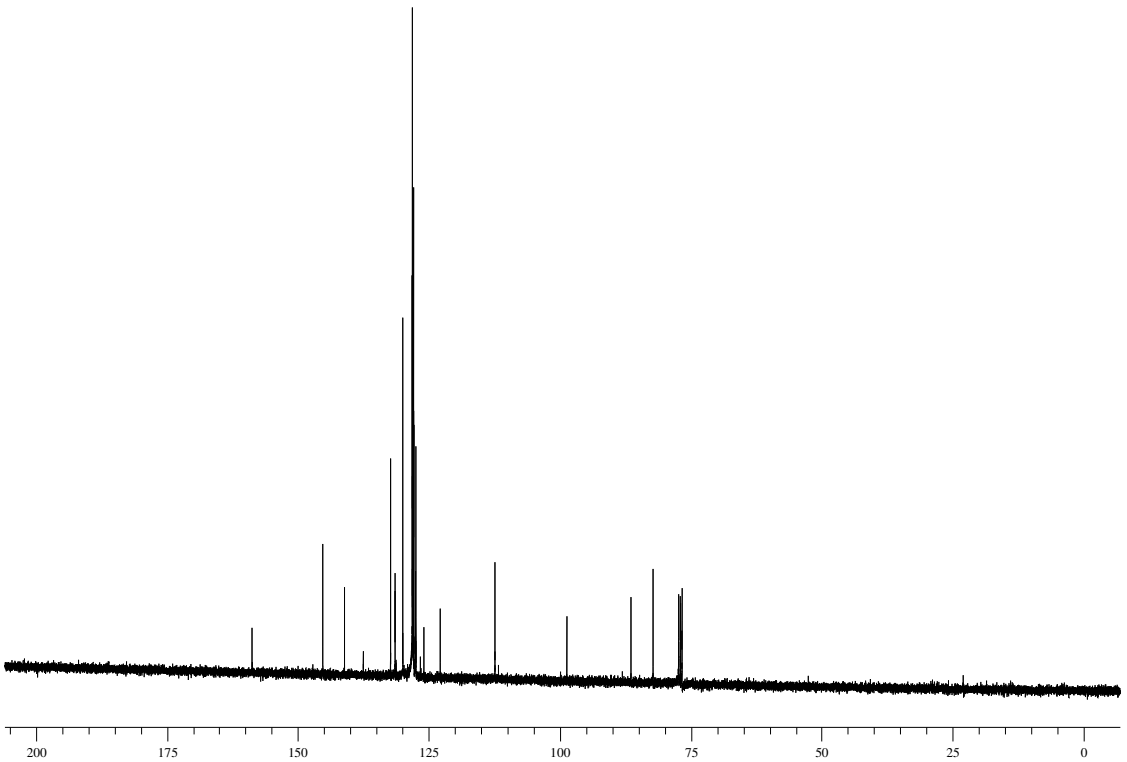
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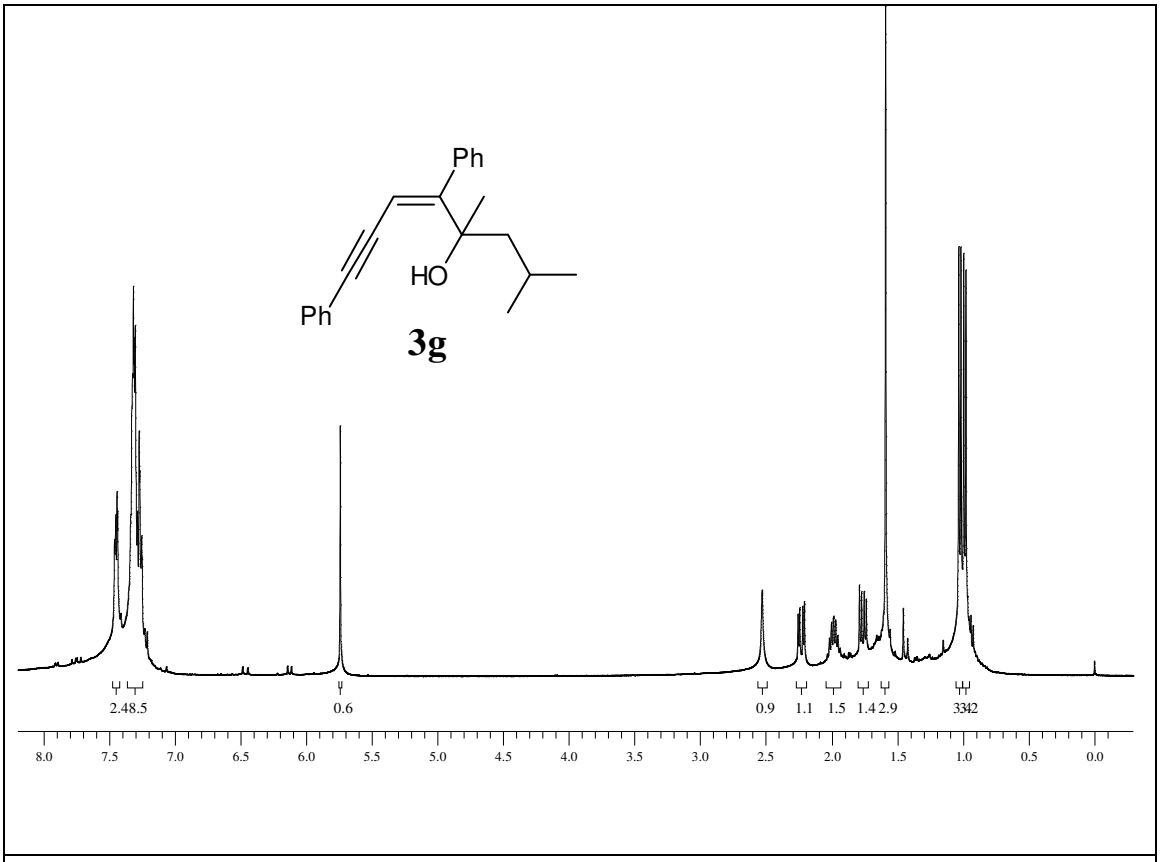
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Ph
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1.5
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3342
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6.5
6.0
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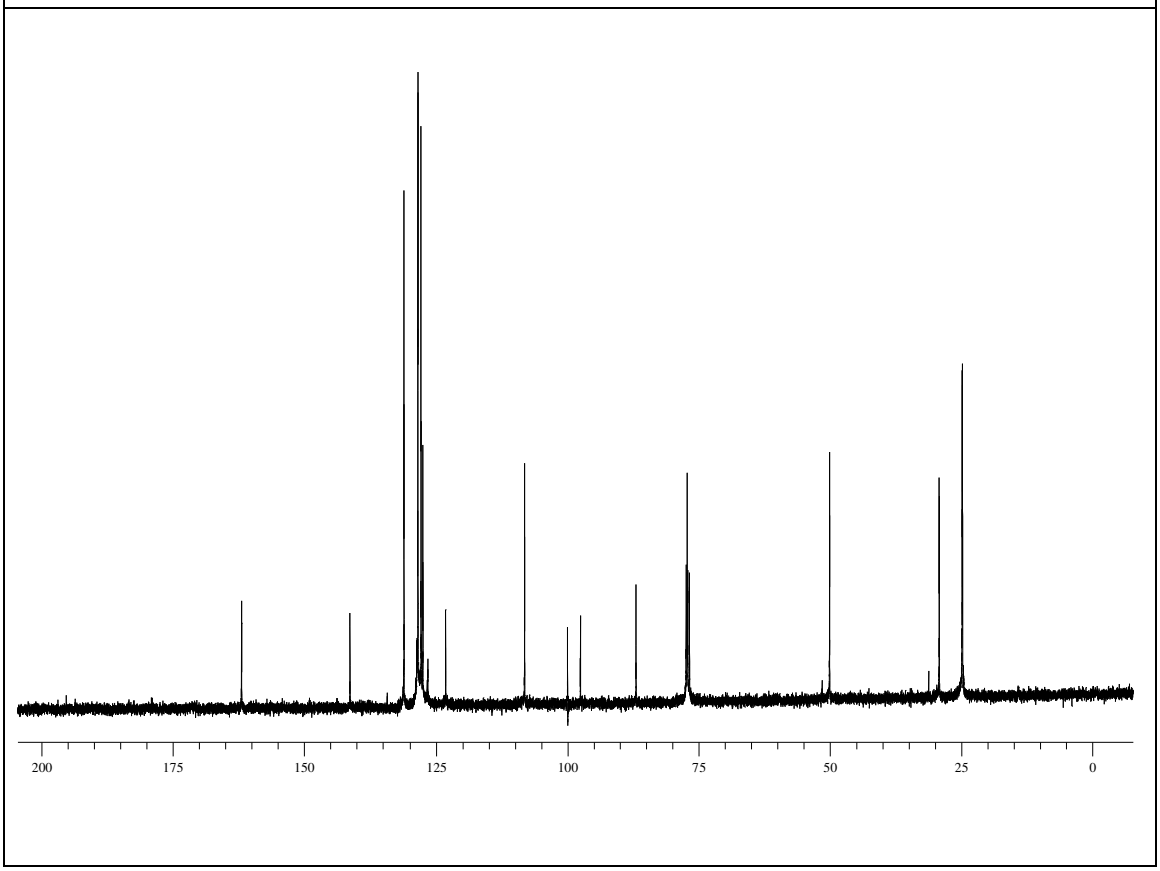
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75
50
25
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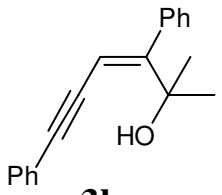
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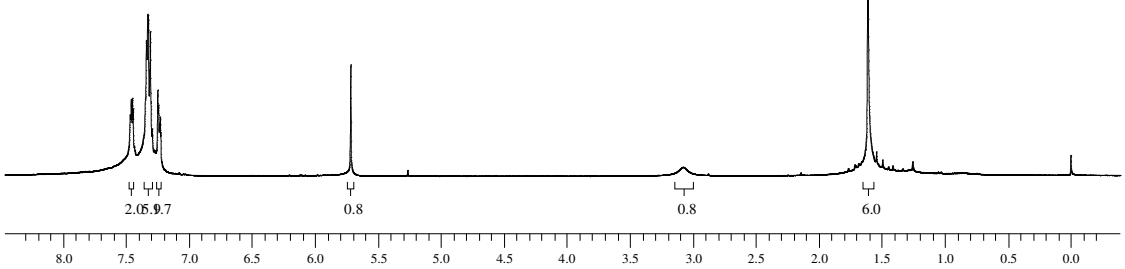
HO
Ph

3h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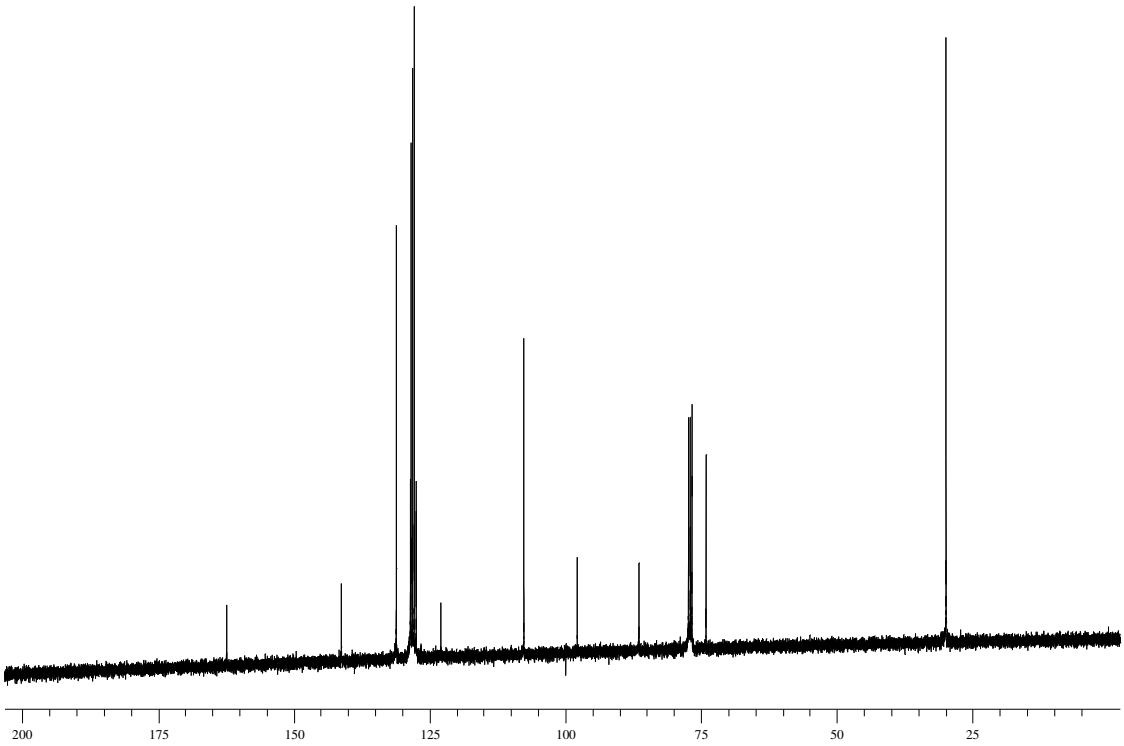
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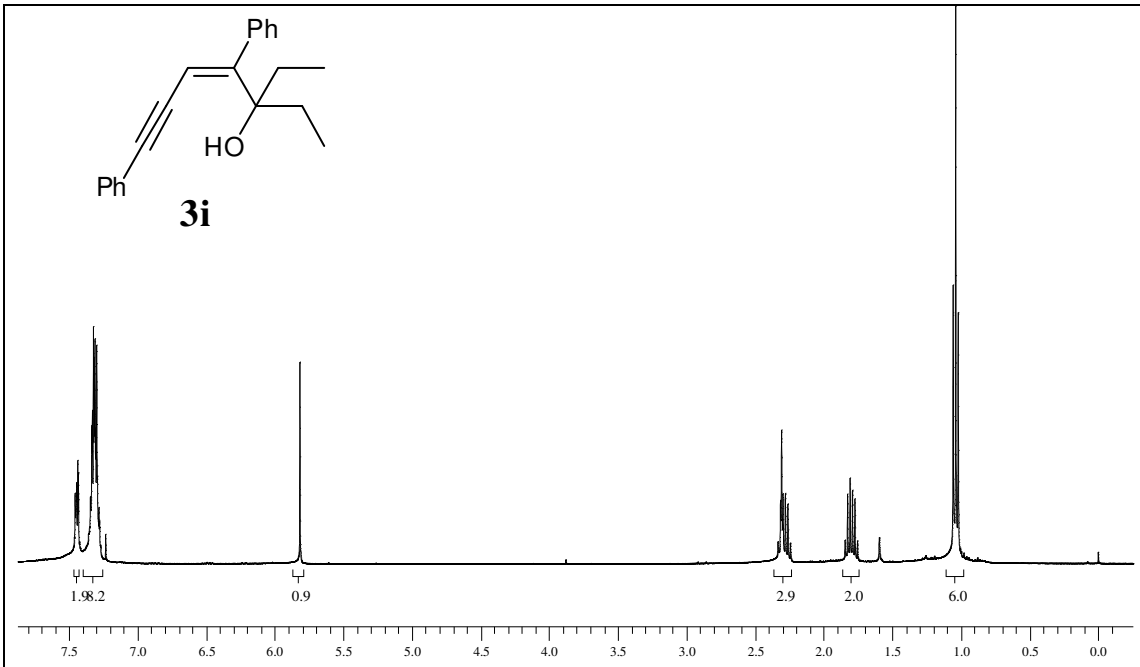
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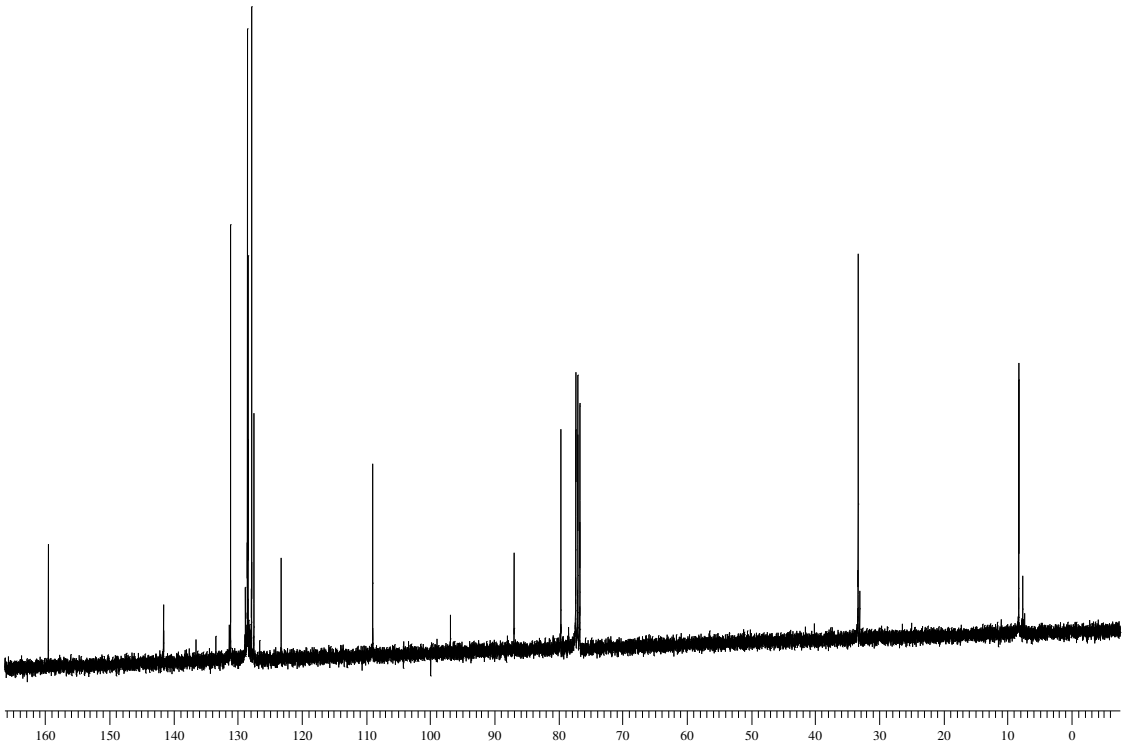
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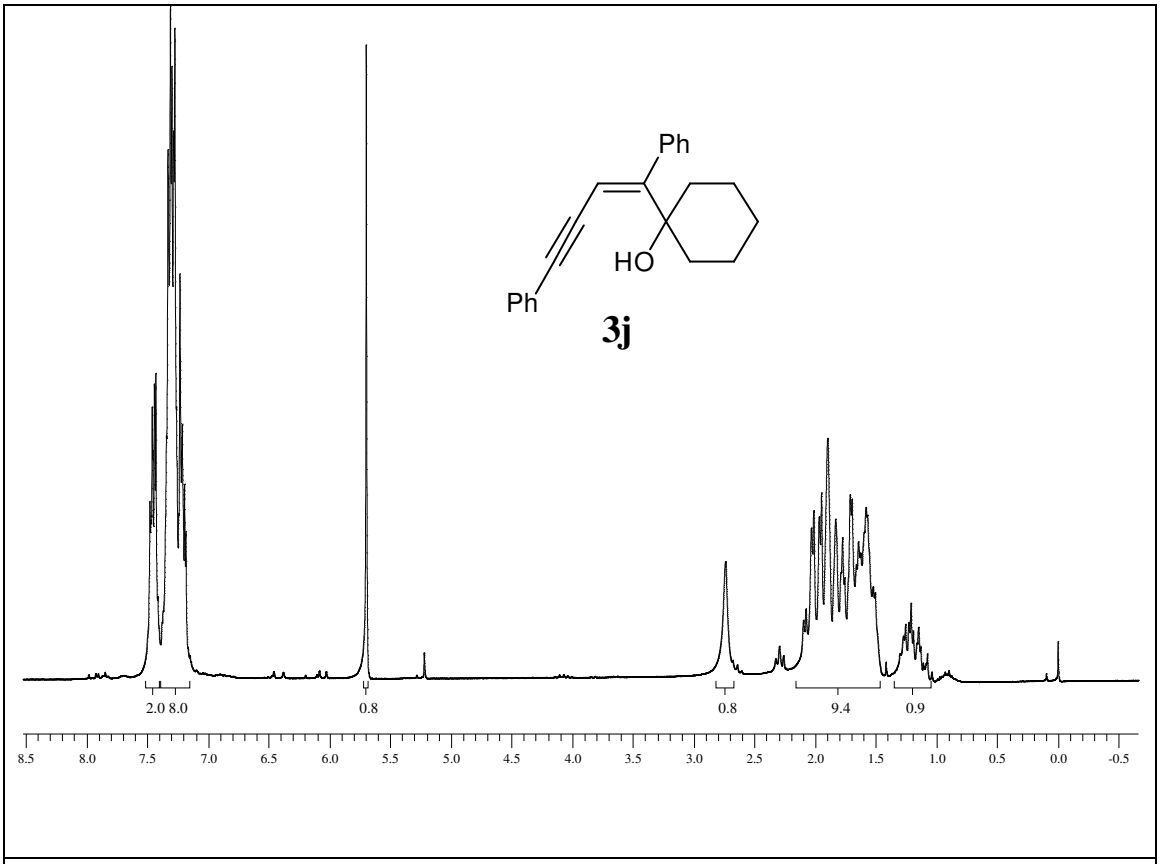
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HO
Ph
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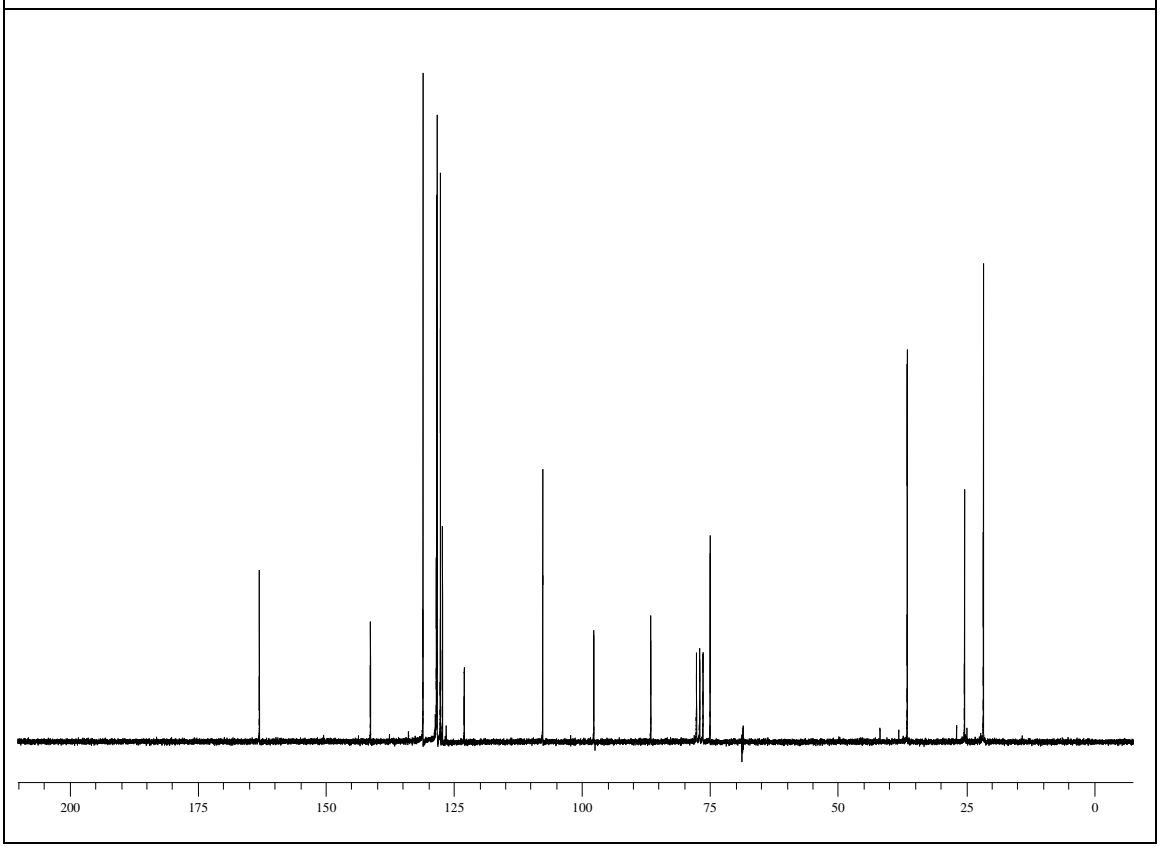
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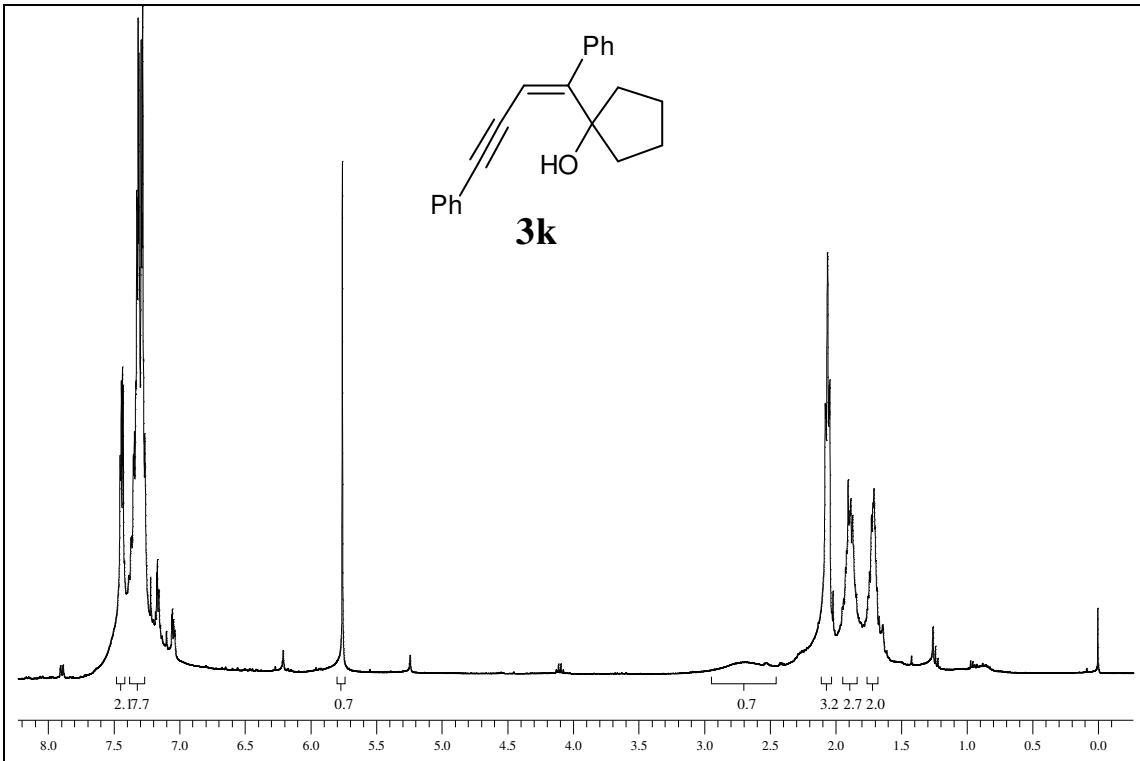
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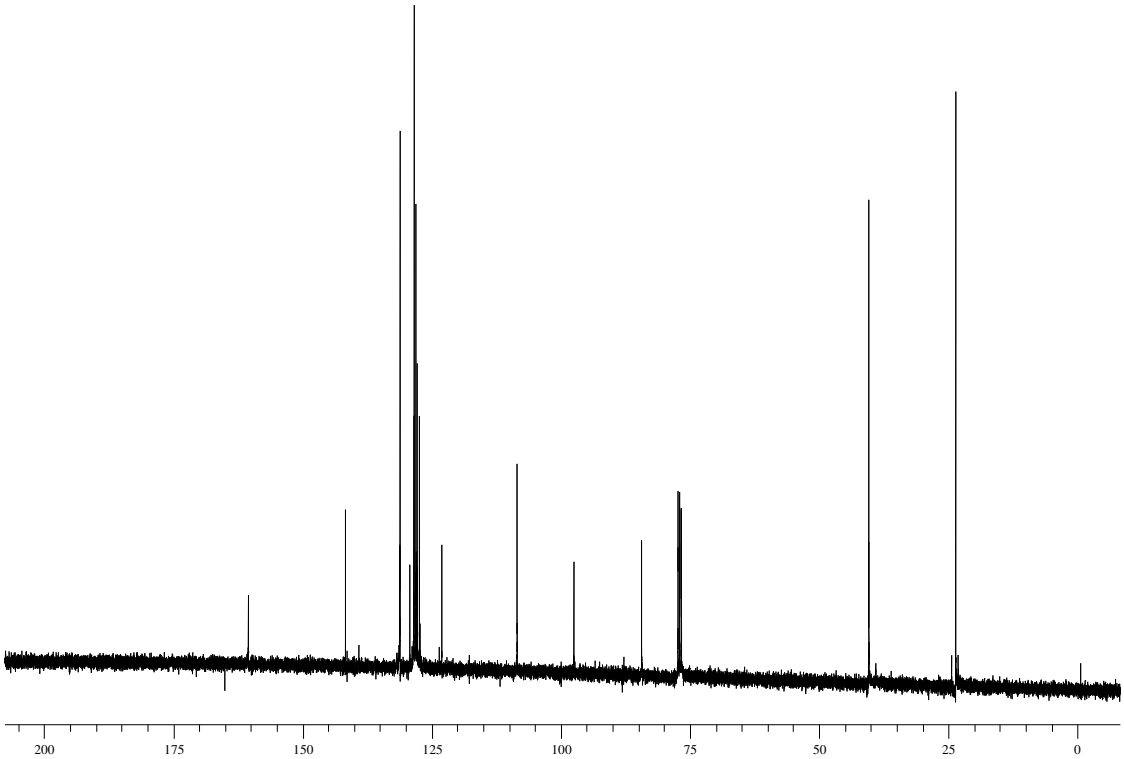
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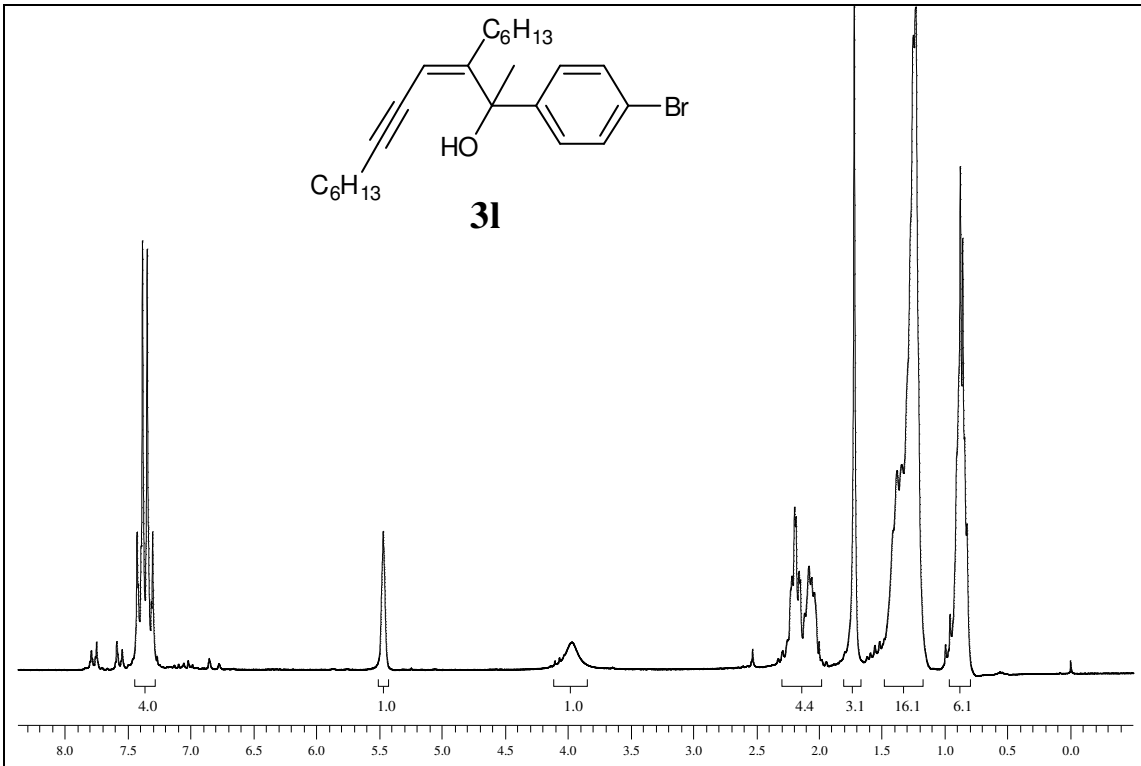
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C6H13
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8.0
7.5
7.0
6.5
6.0
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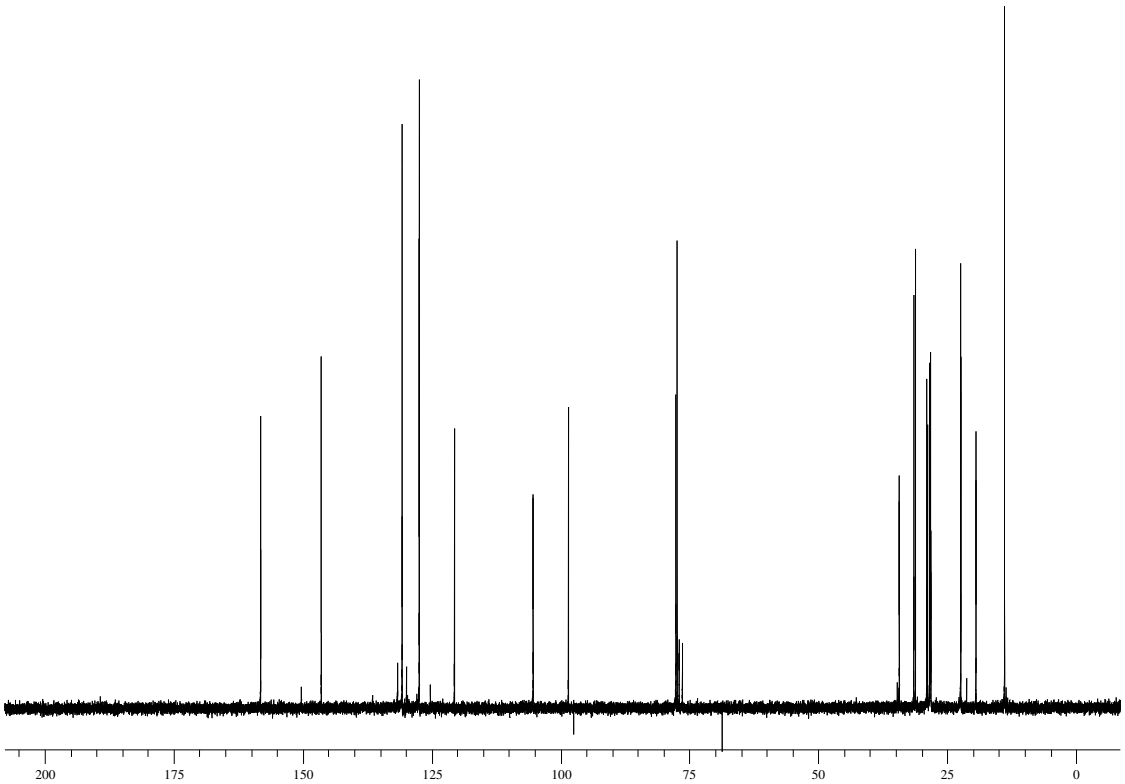
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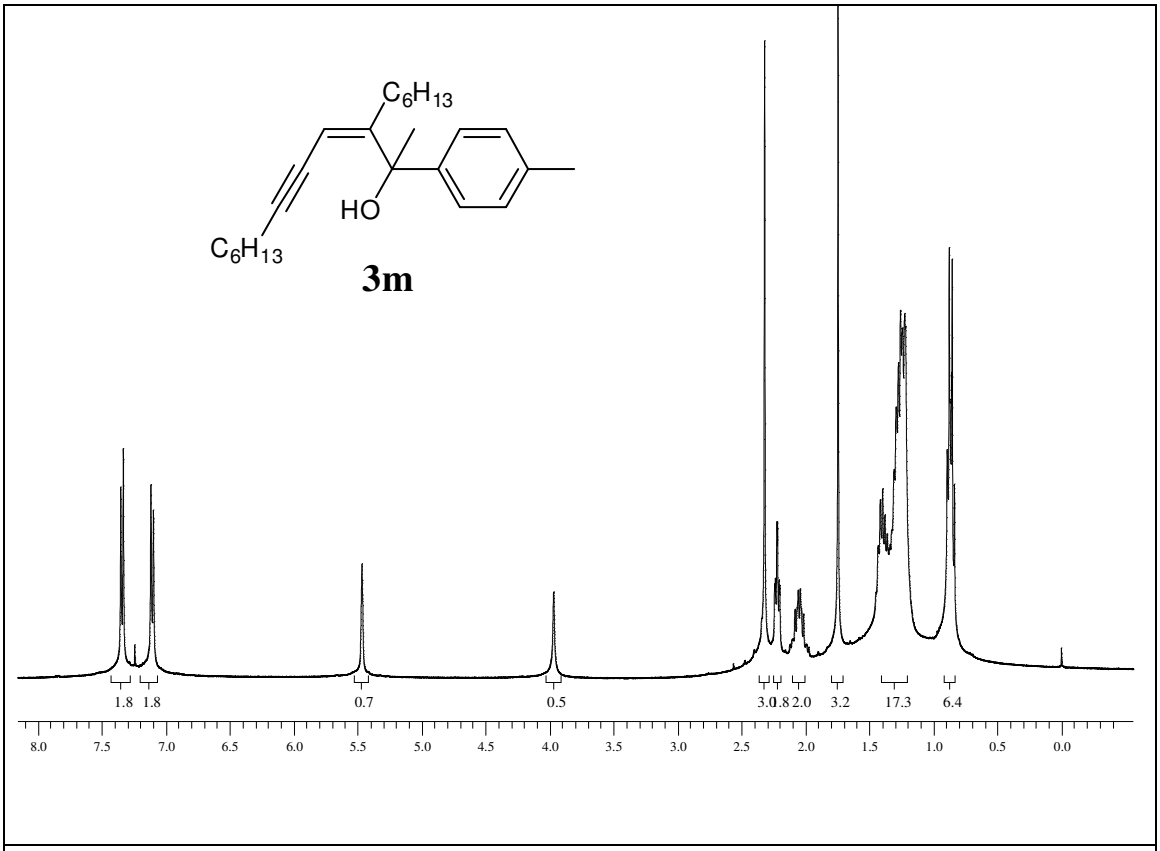
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C6H13
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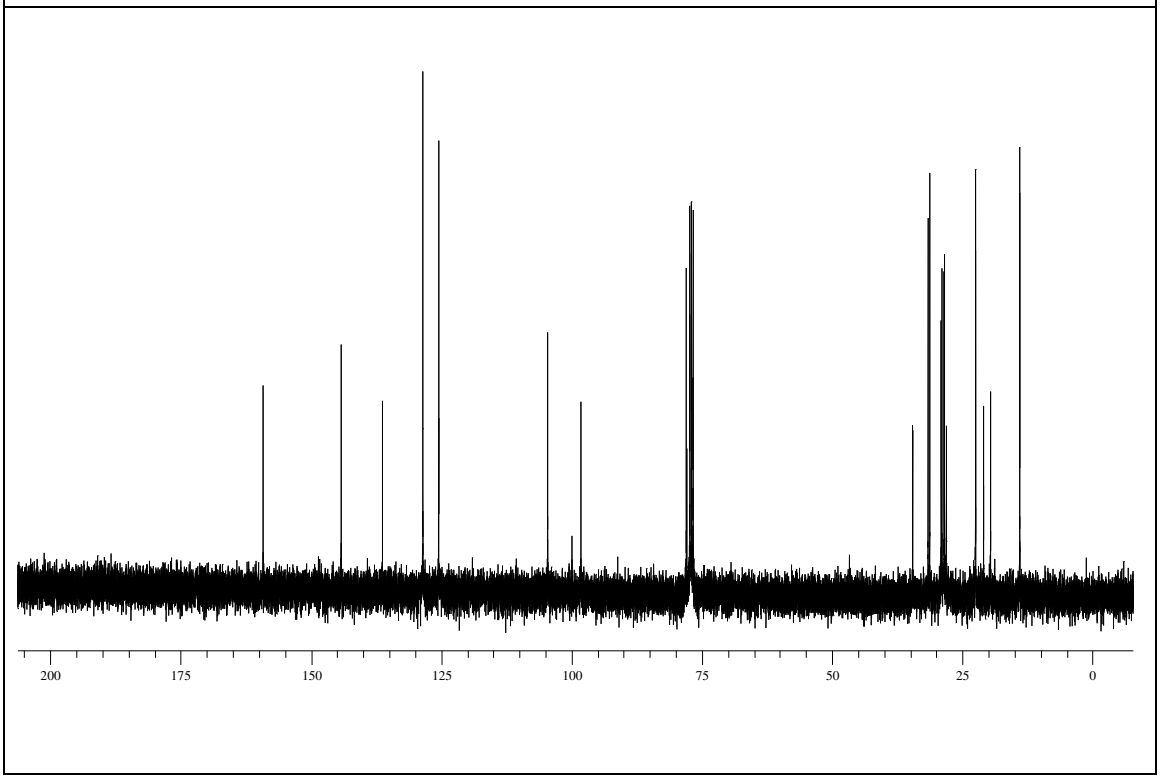
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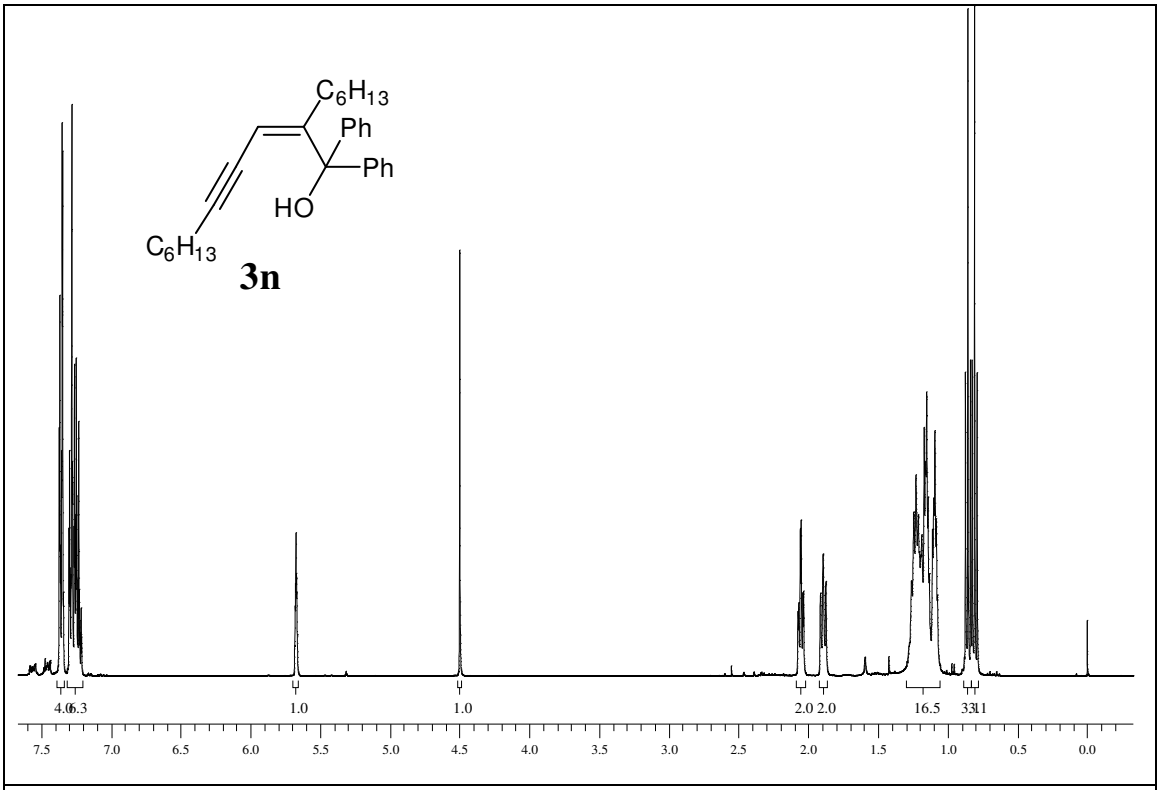
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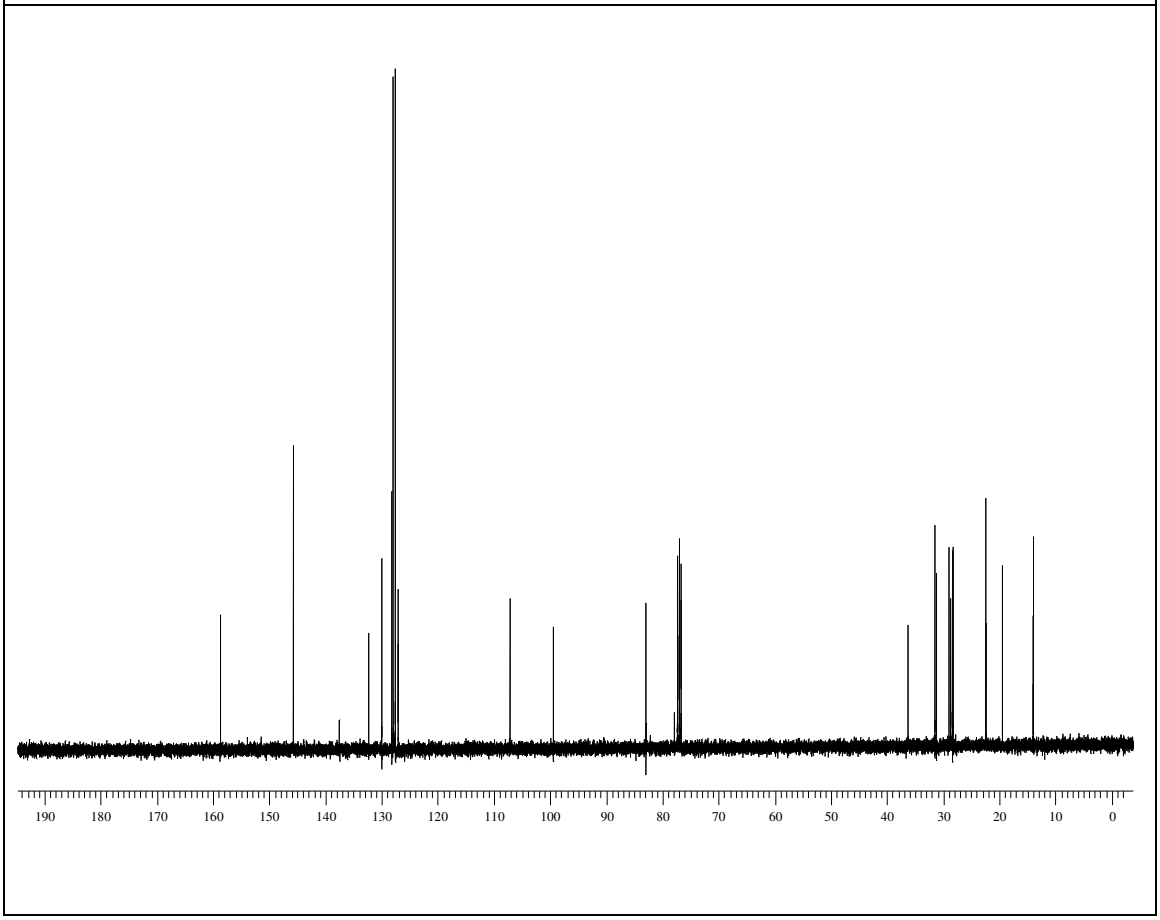
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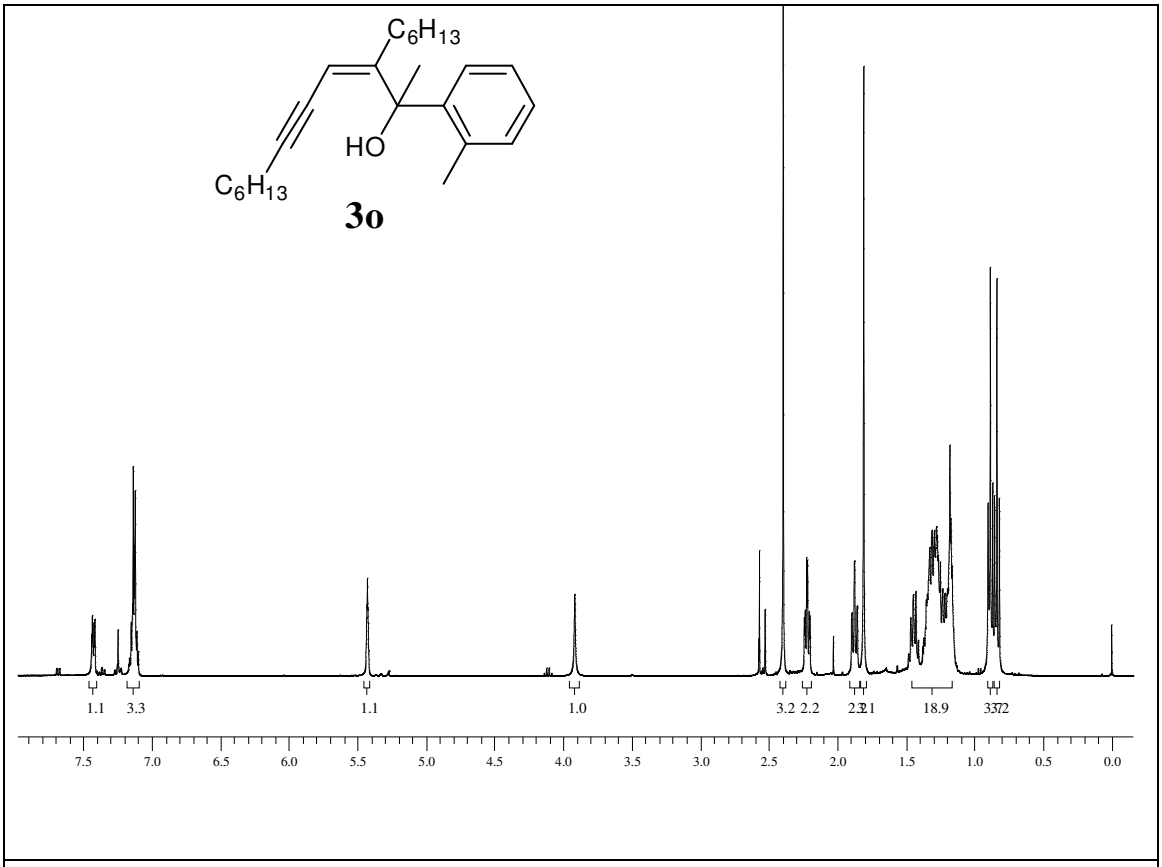
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C6H13
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6.5
6.0
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5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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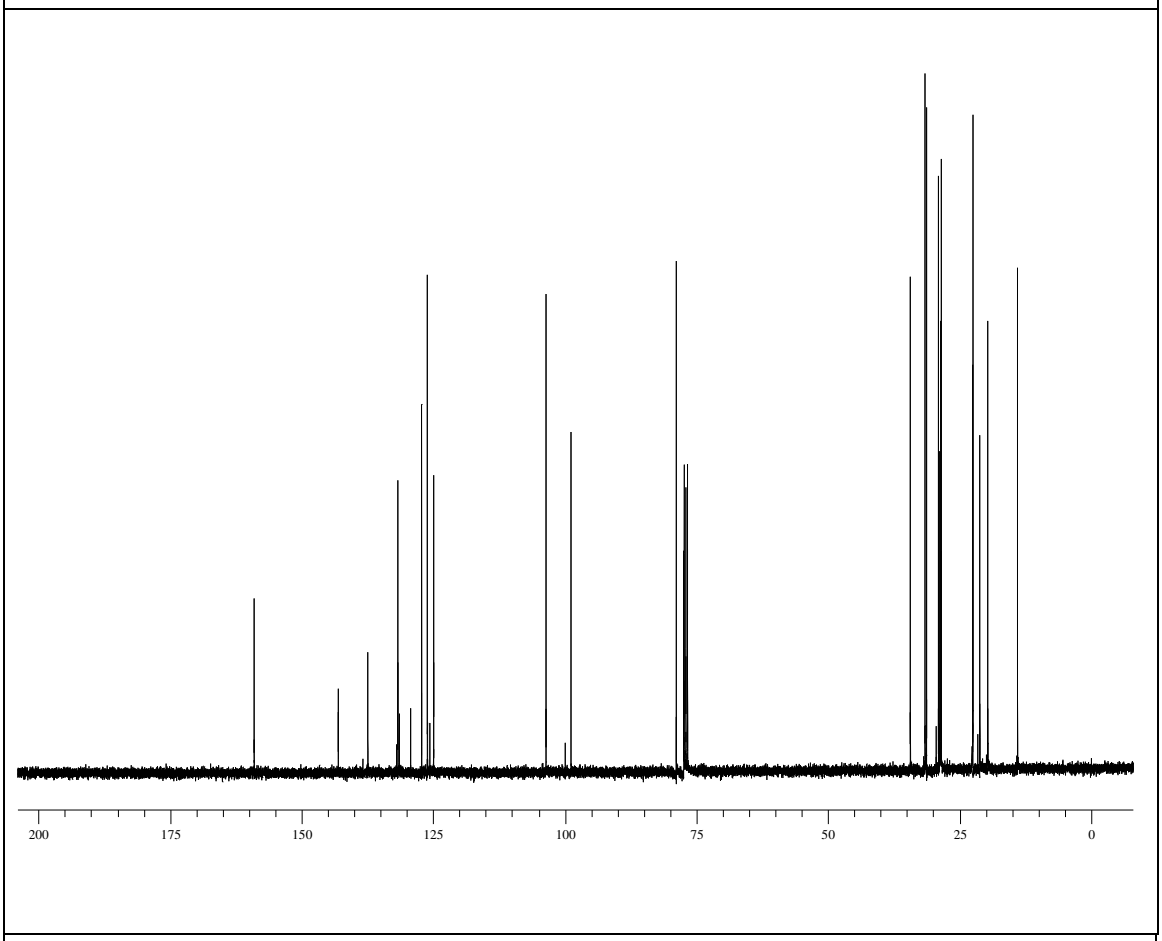
0.0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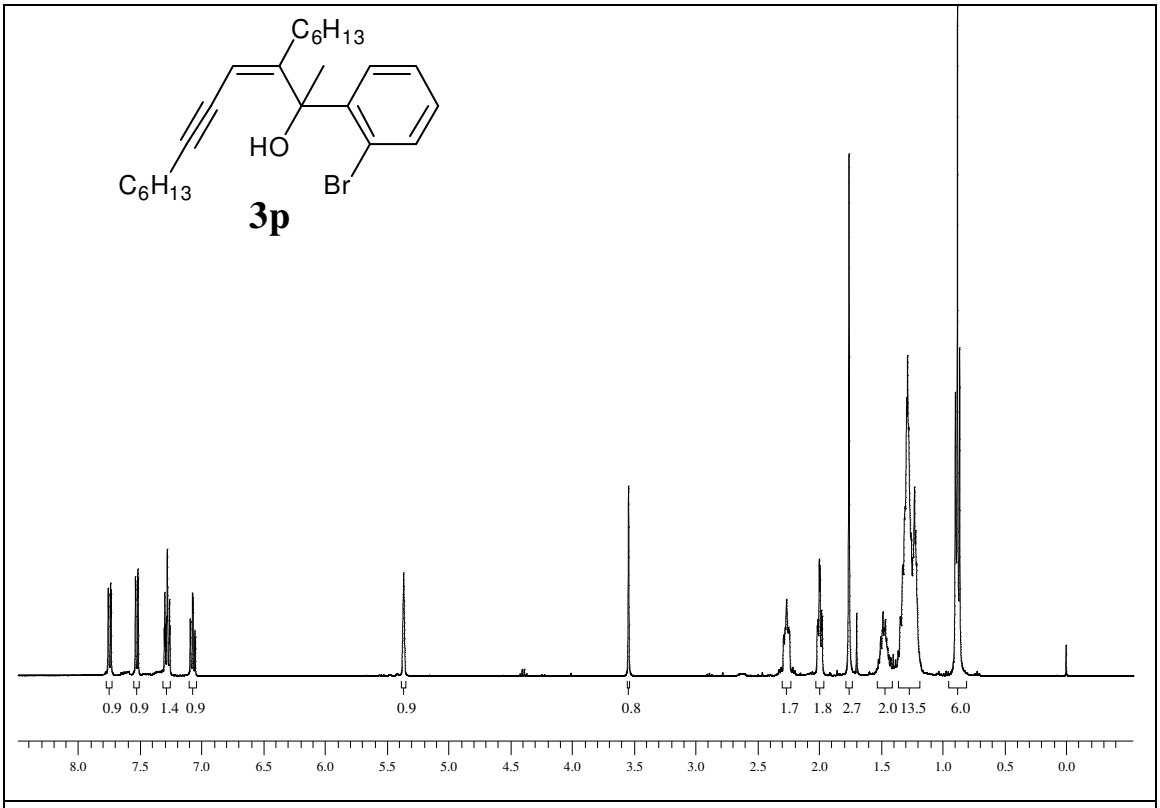
C6H13
HO
C6H13
Br
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0.9
0.8
1.7 1.8 2.7 2.0 13.5 6.0
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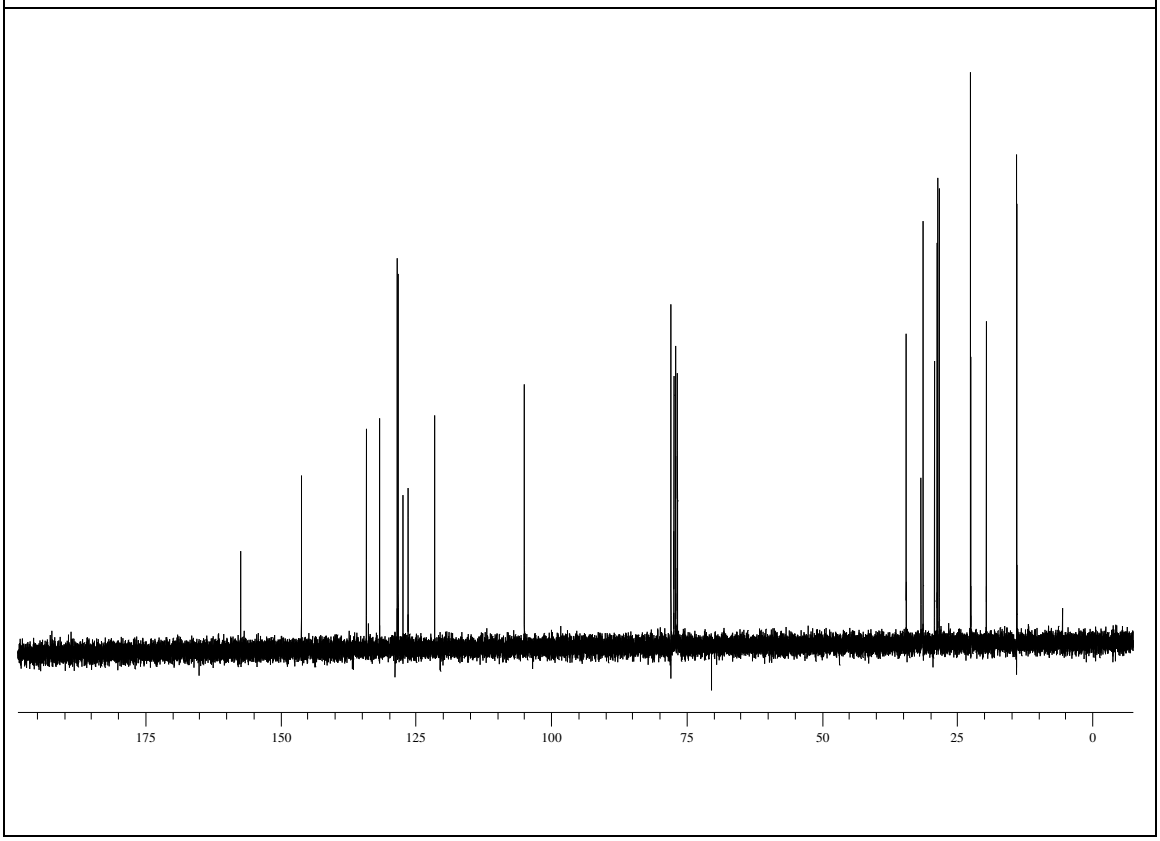
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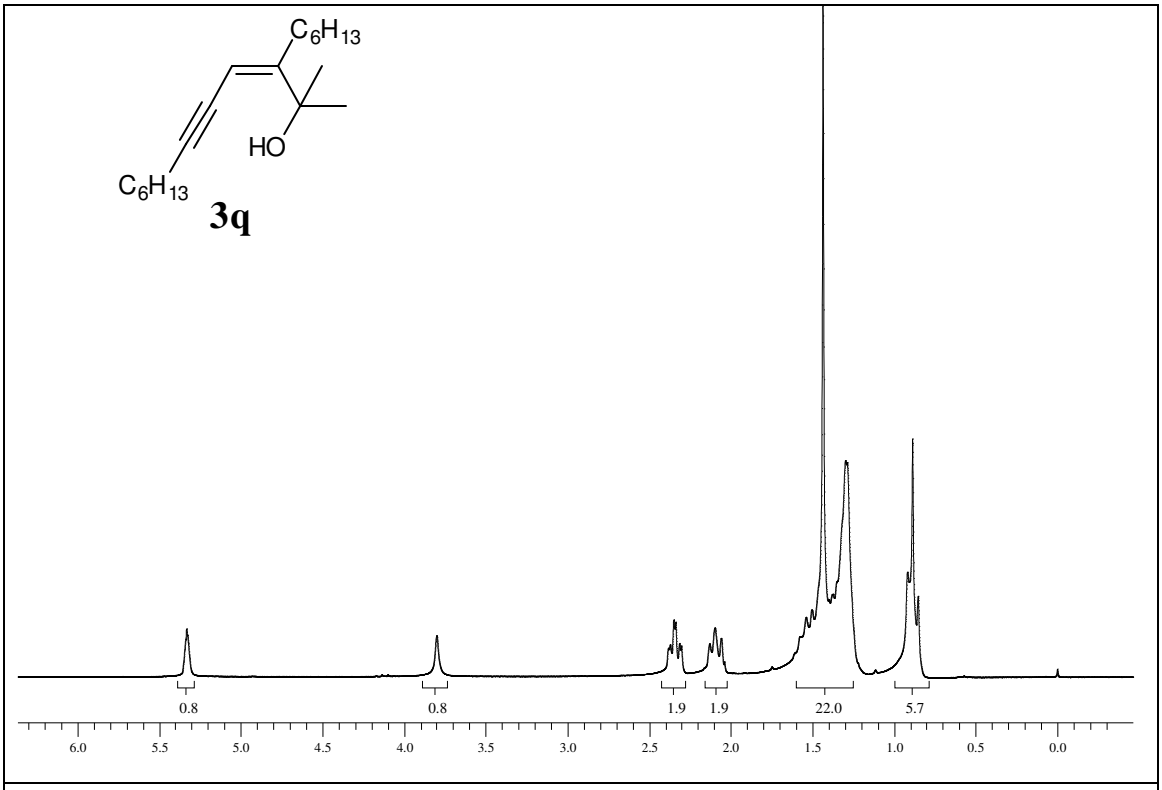
C6H13
HO
C6H13
3q
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0.8
1.9
1.9
22.0
5.7
6.0
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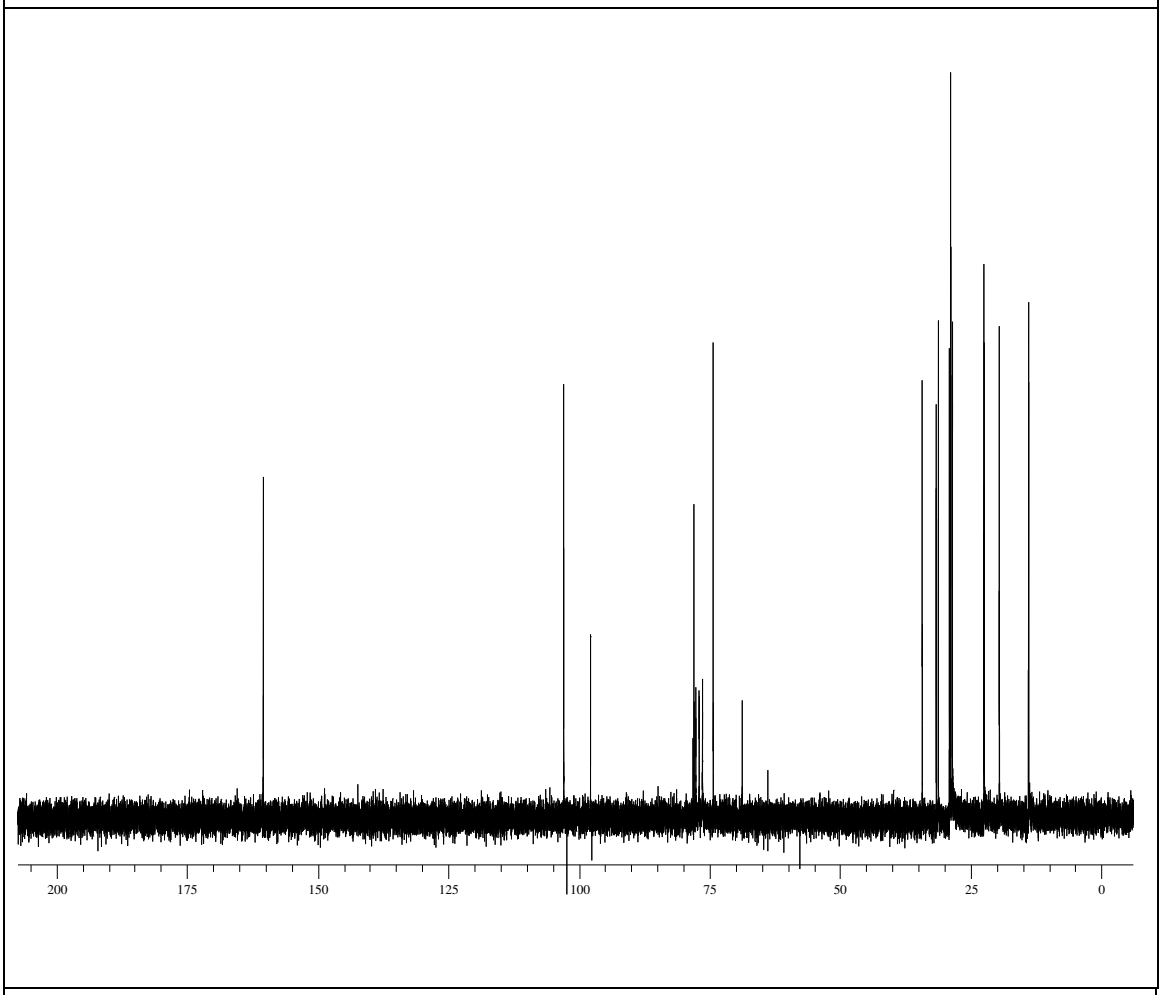
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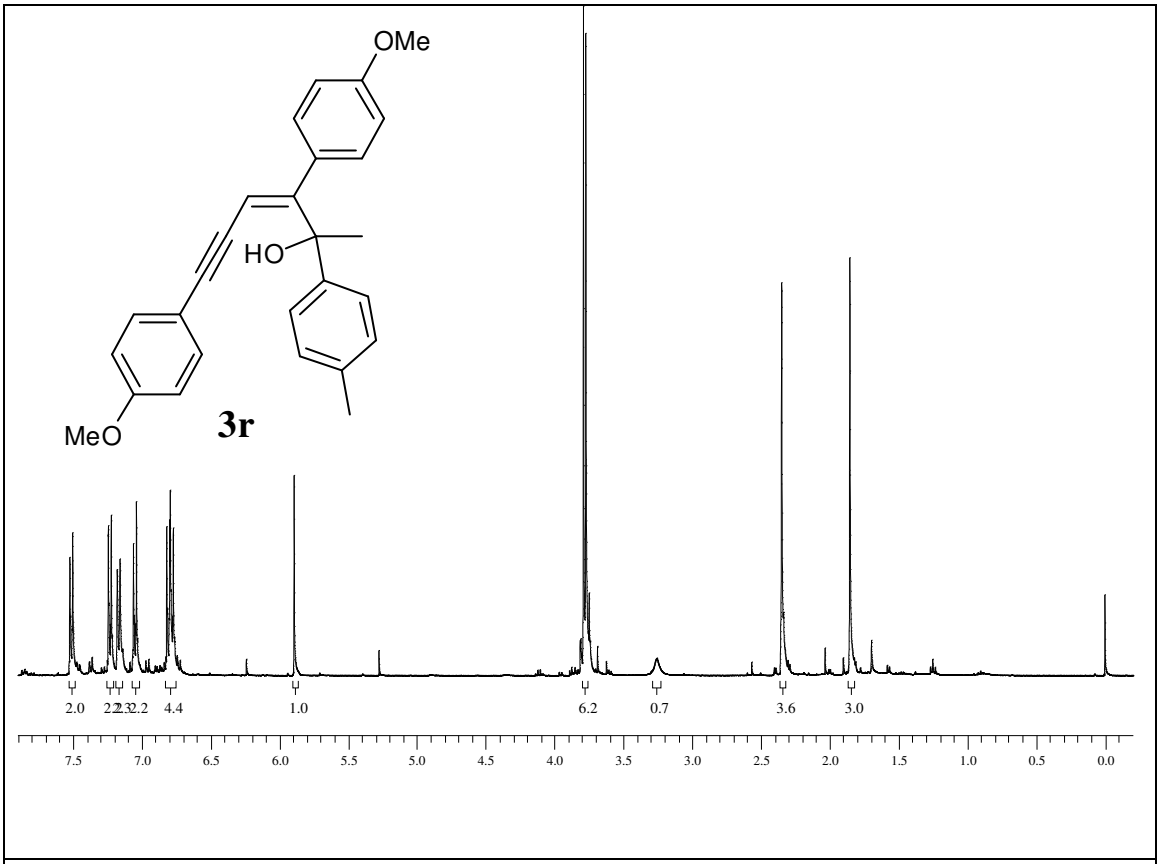
OMe
HO
MeO
3r
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1.0
6.2
0.7
3.6
3.0
7.5
7.0
6.5
6.0
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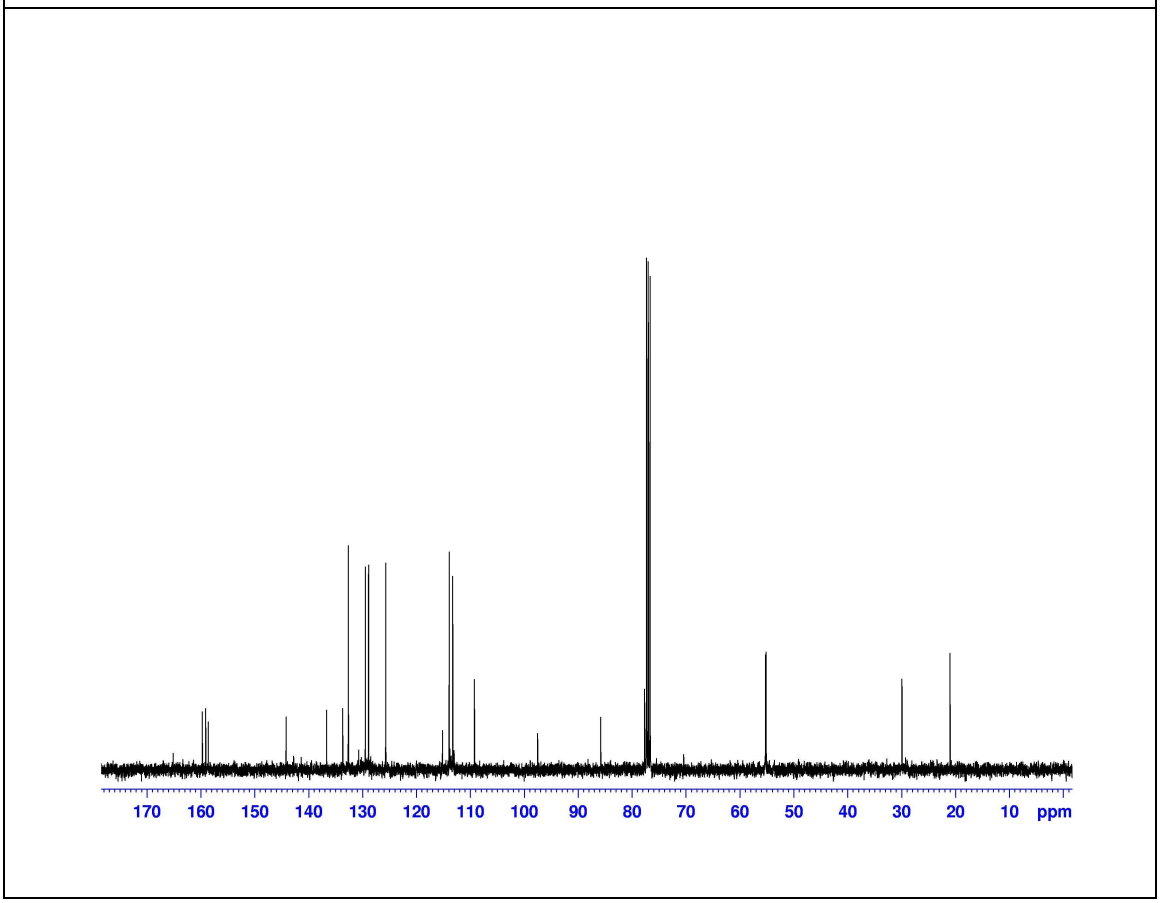
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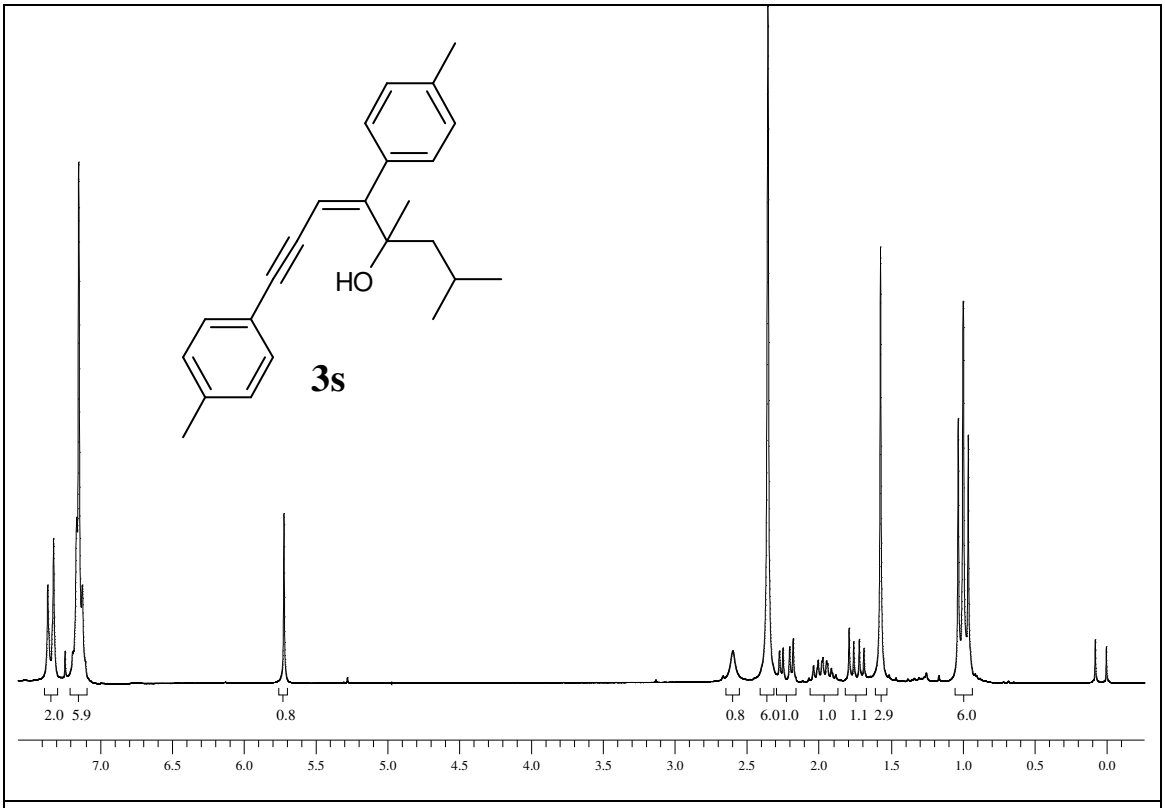
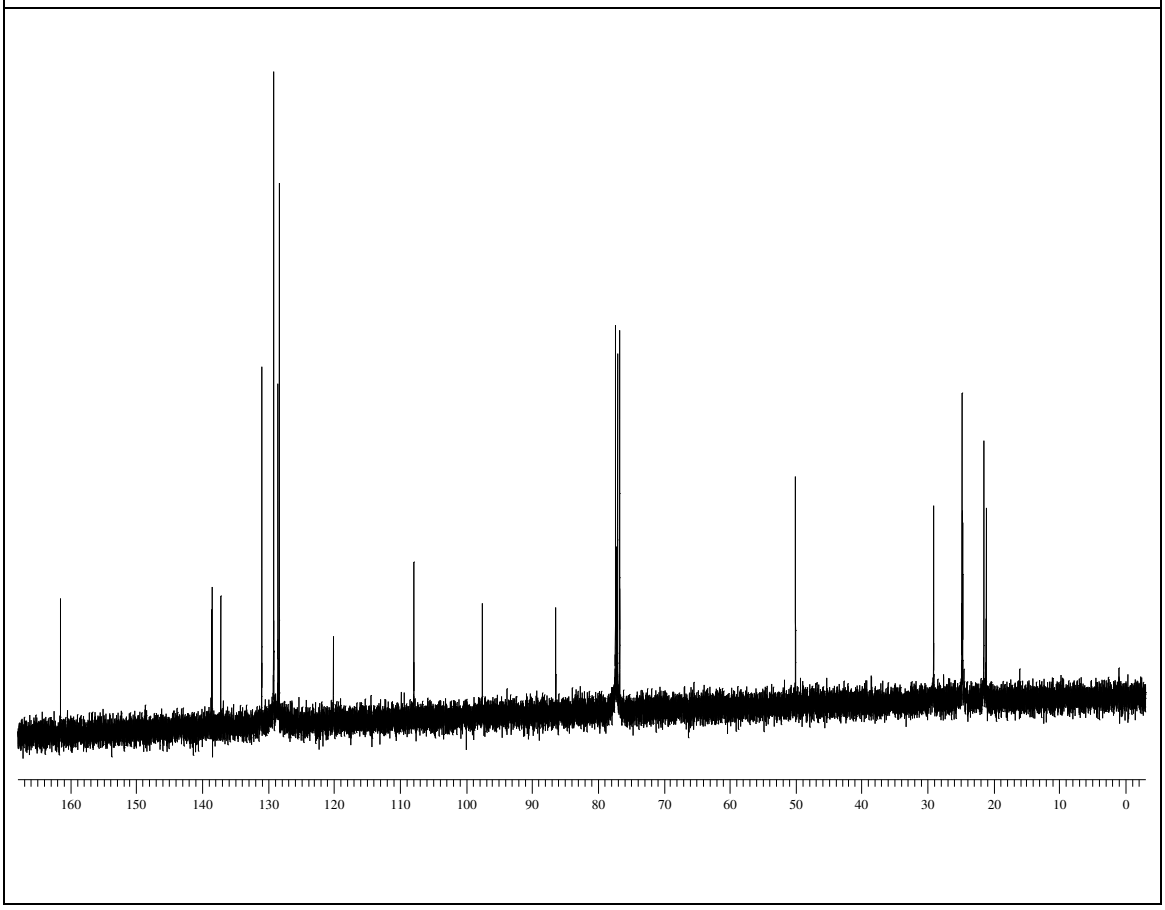

HO
3s
2.0 5.9
0.8
0.8 6.01.0 1.0 1.1 2.9
6.0
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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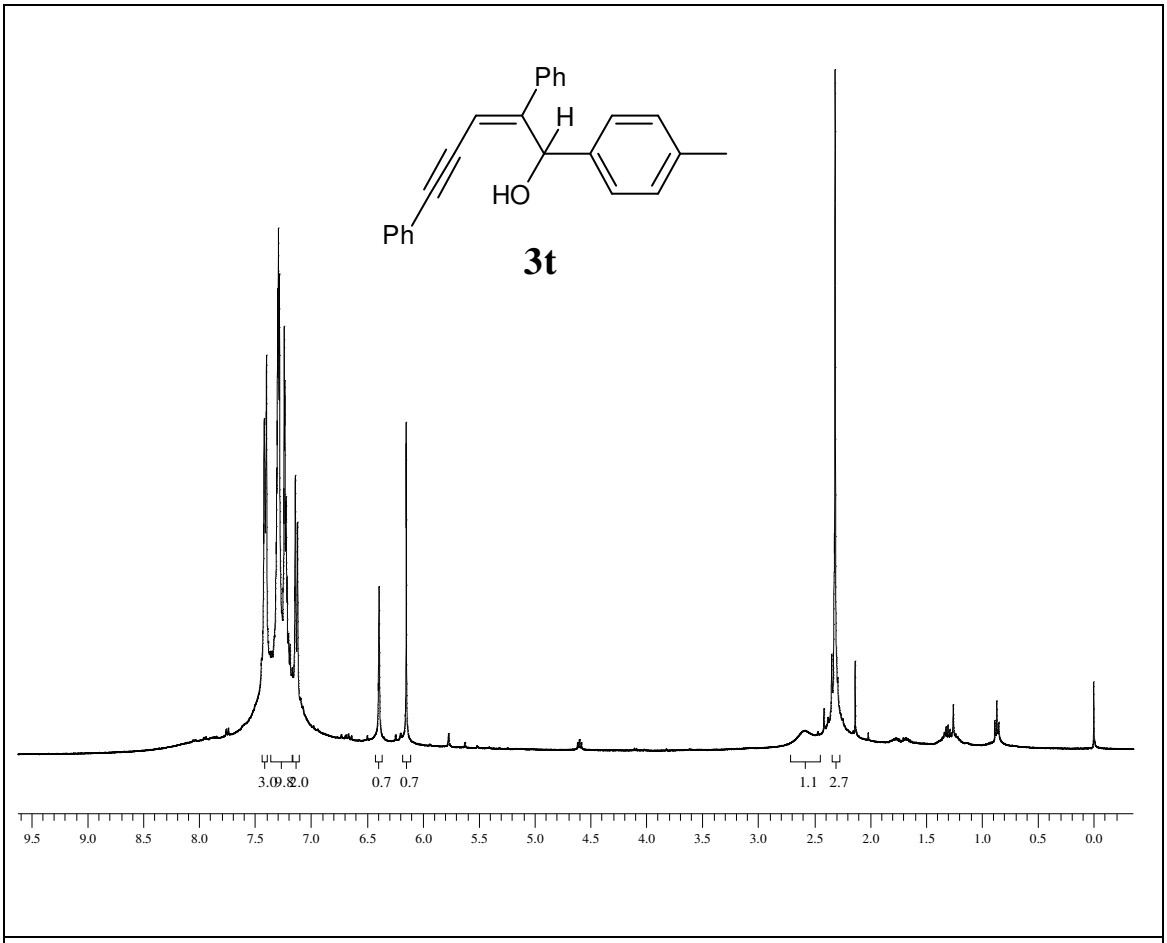
Ph
H
HO
Ph
3t
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2.0
0.7
0.7
1.1
2.7
9.5
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8.5
8.0
7.5
7.0
6.5
6.0
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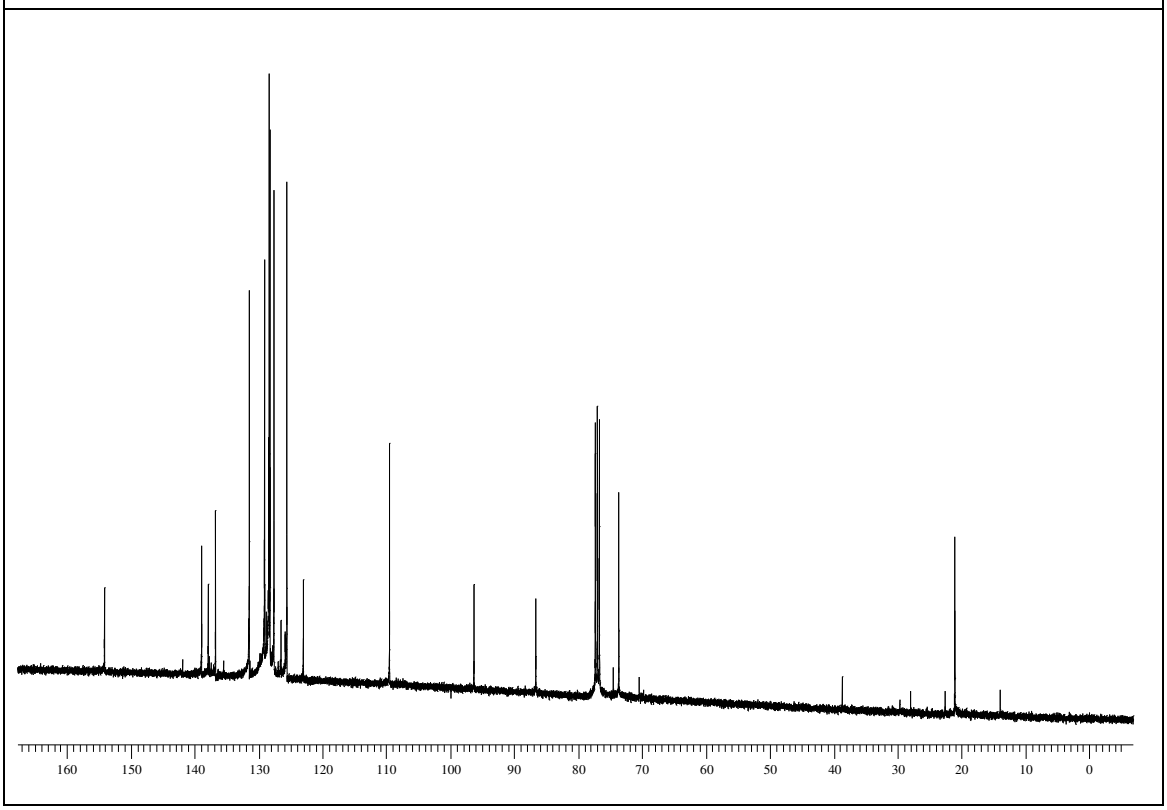
0.0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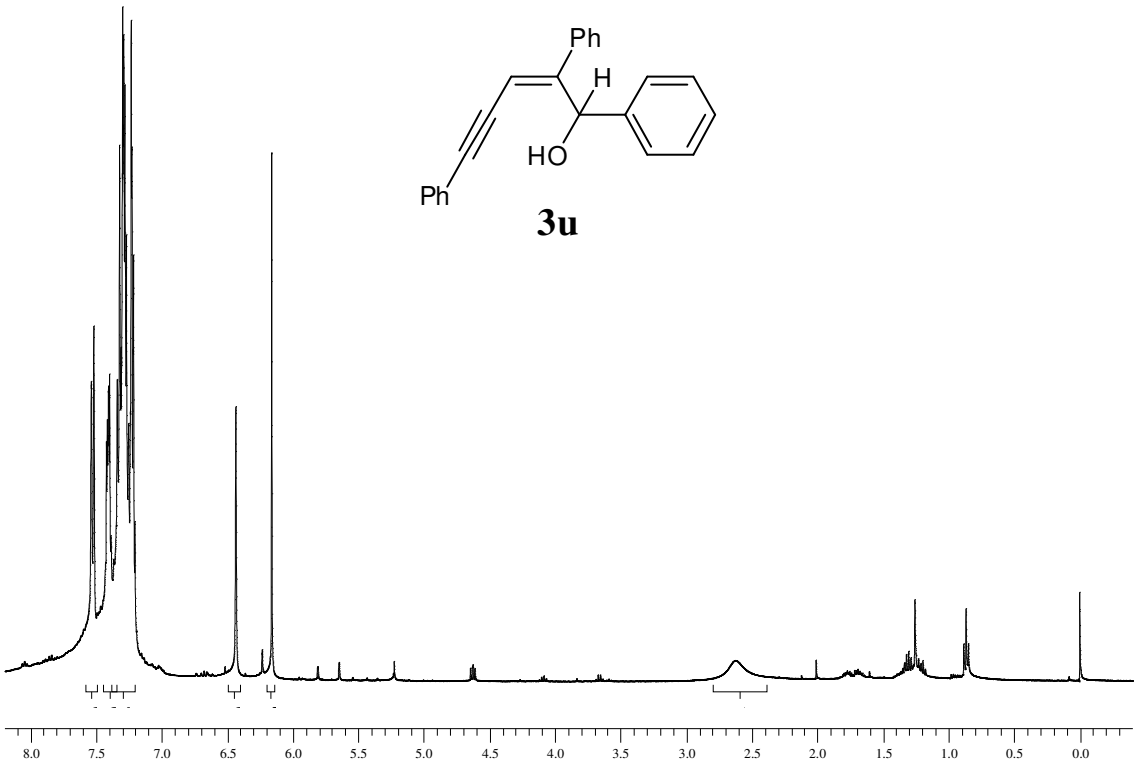
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H
HO
Ph
3u
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7.0
6.5
6.0
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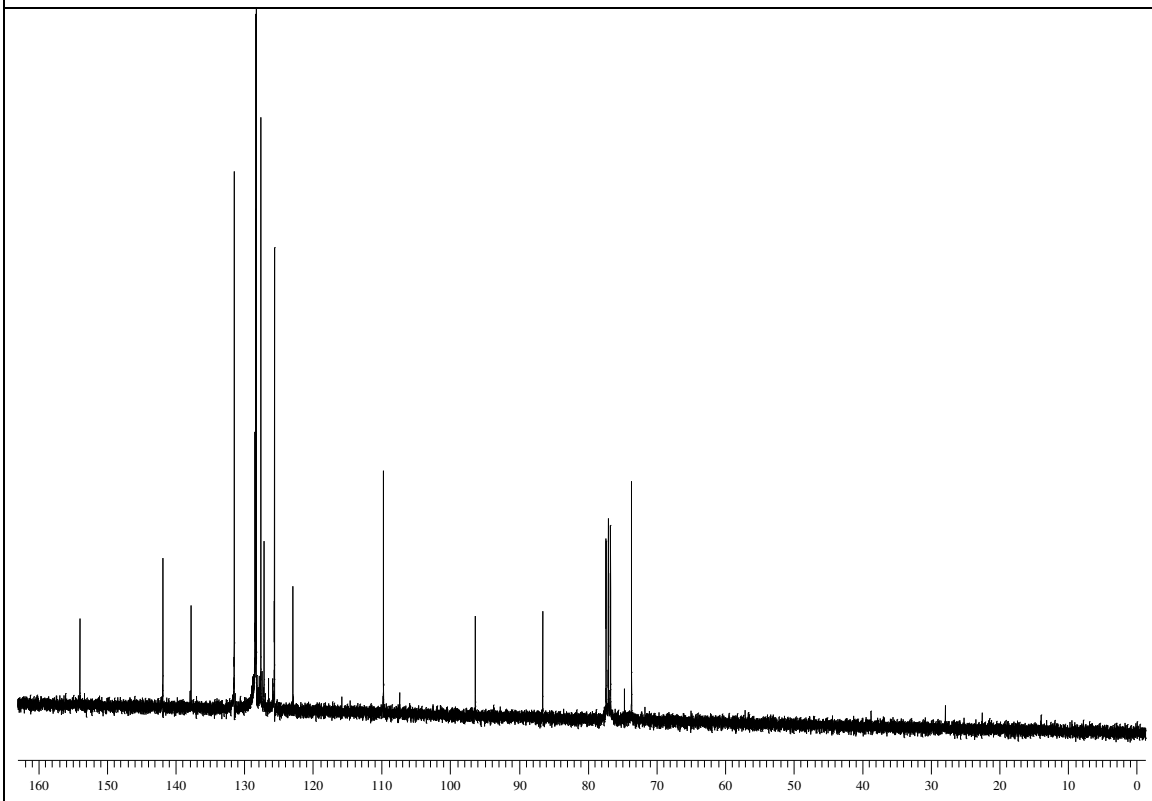
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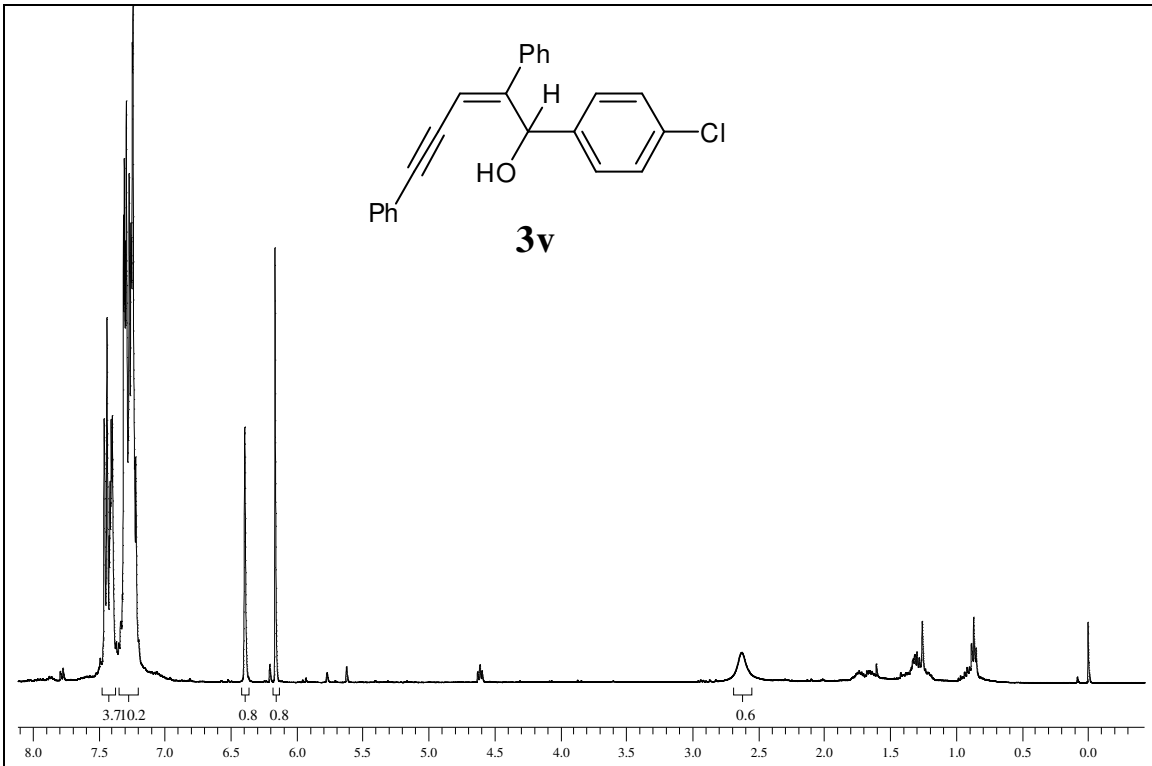
Ph
H
Cl
HO
Ph
3v
3.7
10.2
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0.8
0.6
8.0
7.5
7.0
6.5
6.0
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2.0
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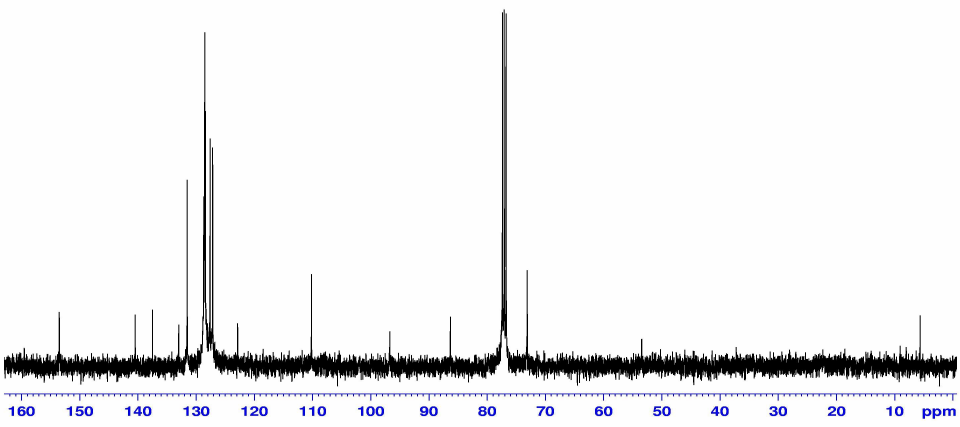
0.0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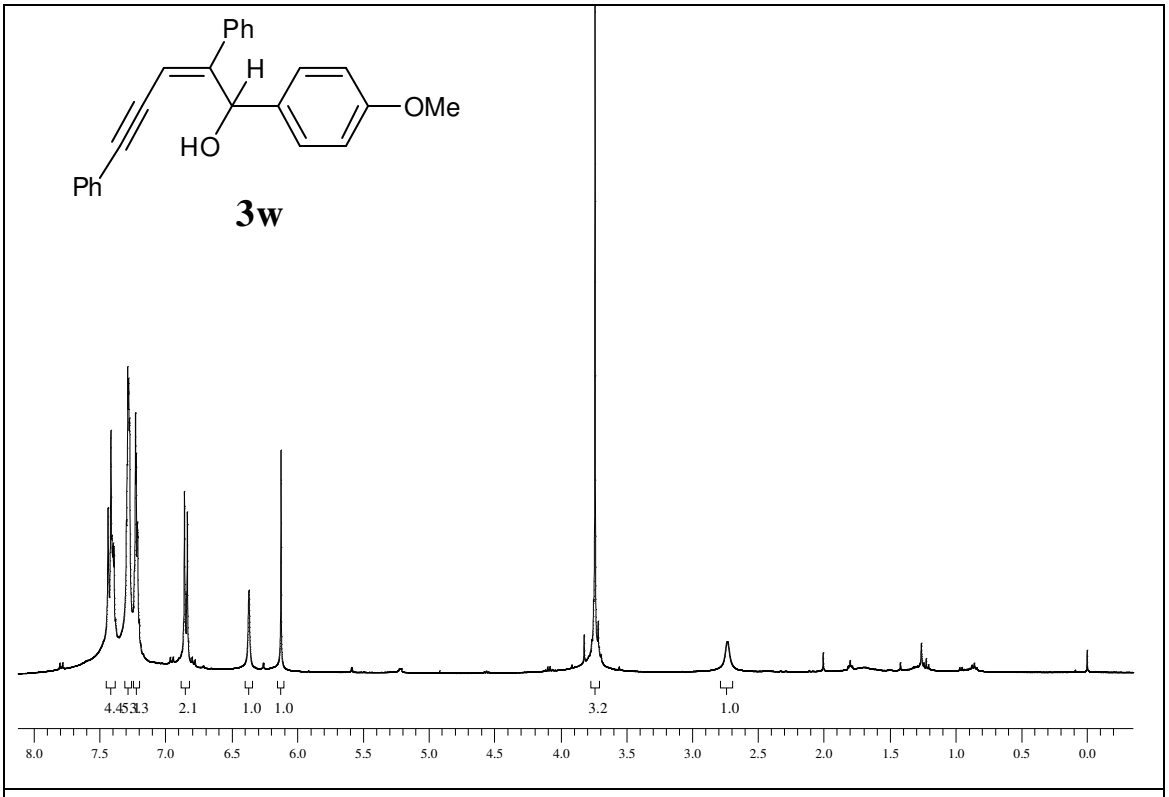
Ph
H
OMe
HO
Ph
3w
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5.13
2.1
1.0
1.0
3.2
1.0
8.0
7.5
7.0
6.5
6.0
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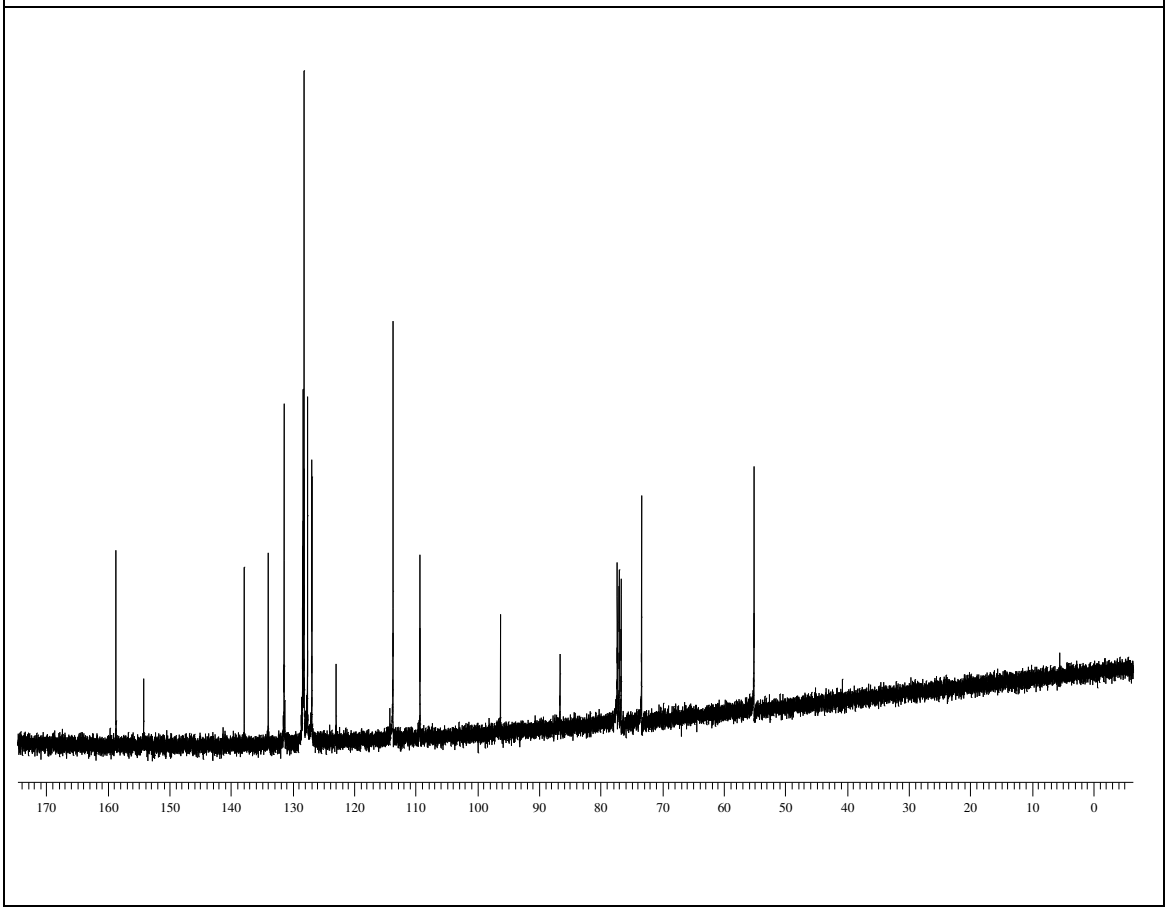
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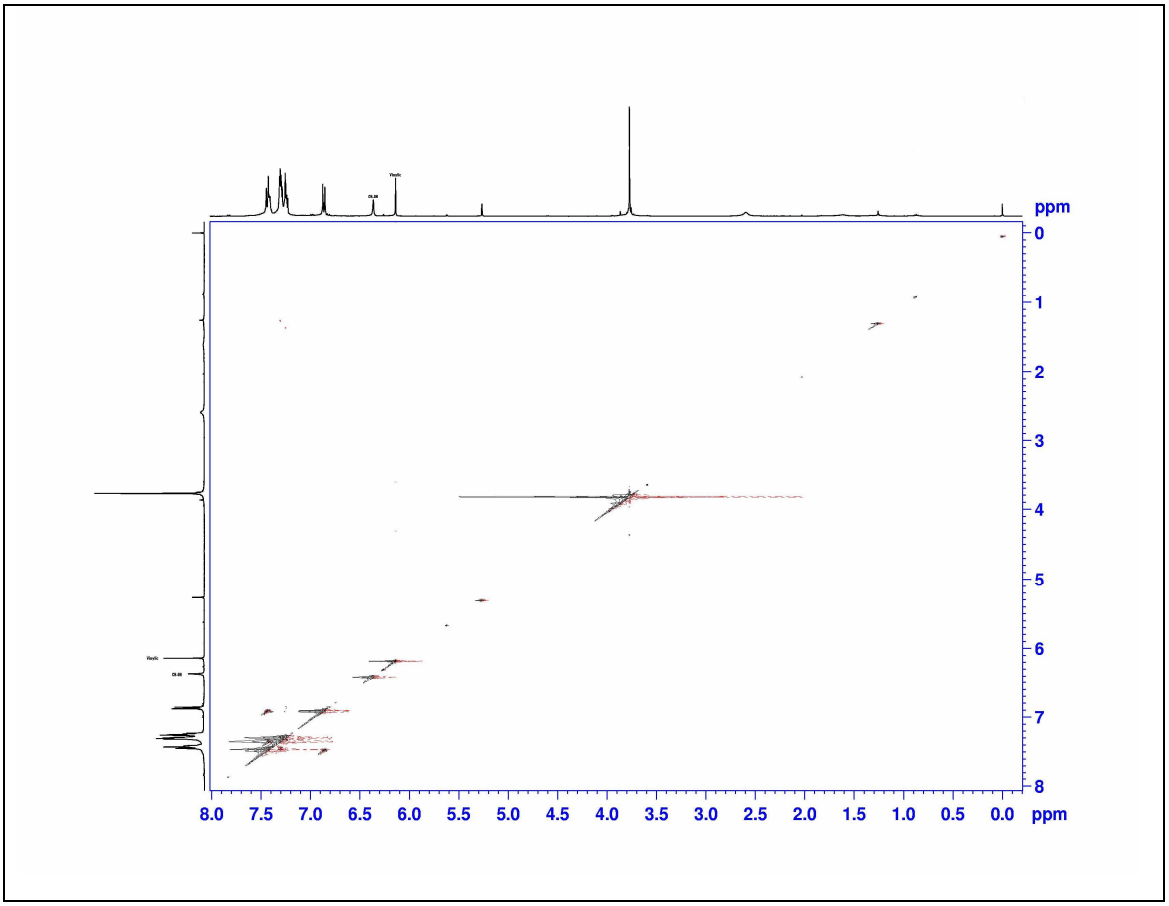
ppm
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7.0
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6.0
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1.5
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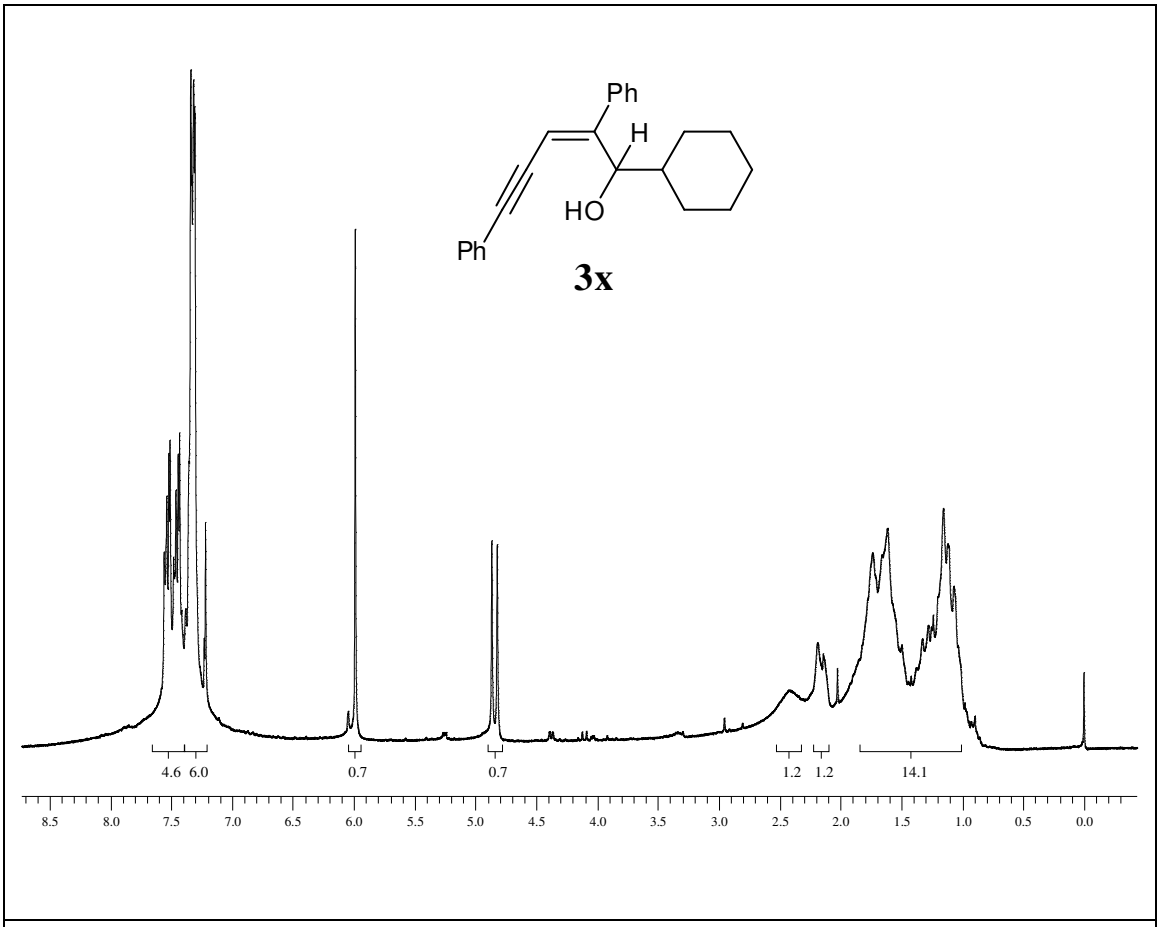
ppm


Ph
H
HO
Ph
3x
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0.7
1.2 1.2
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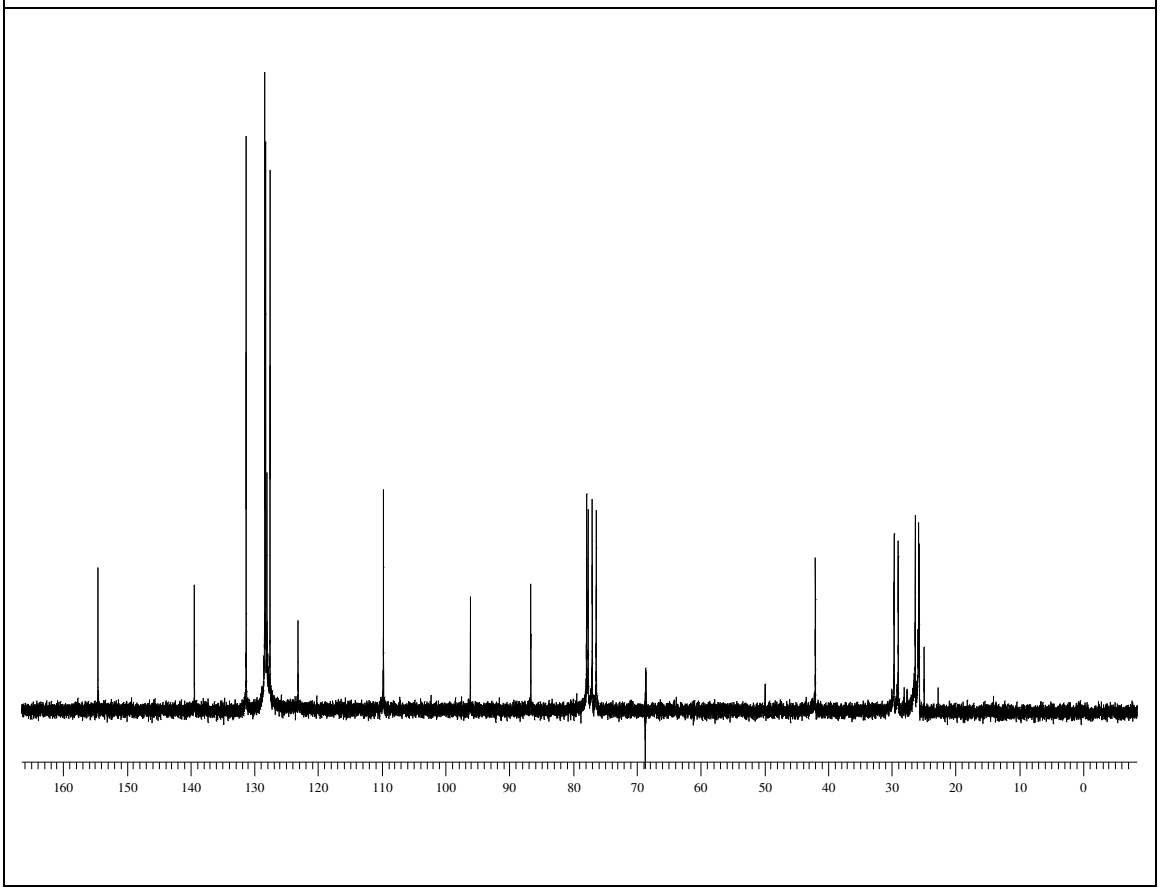
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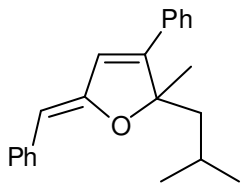
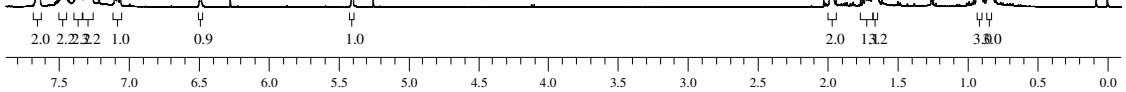

Ph
O
Ph

4a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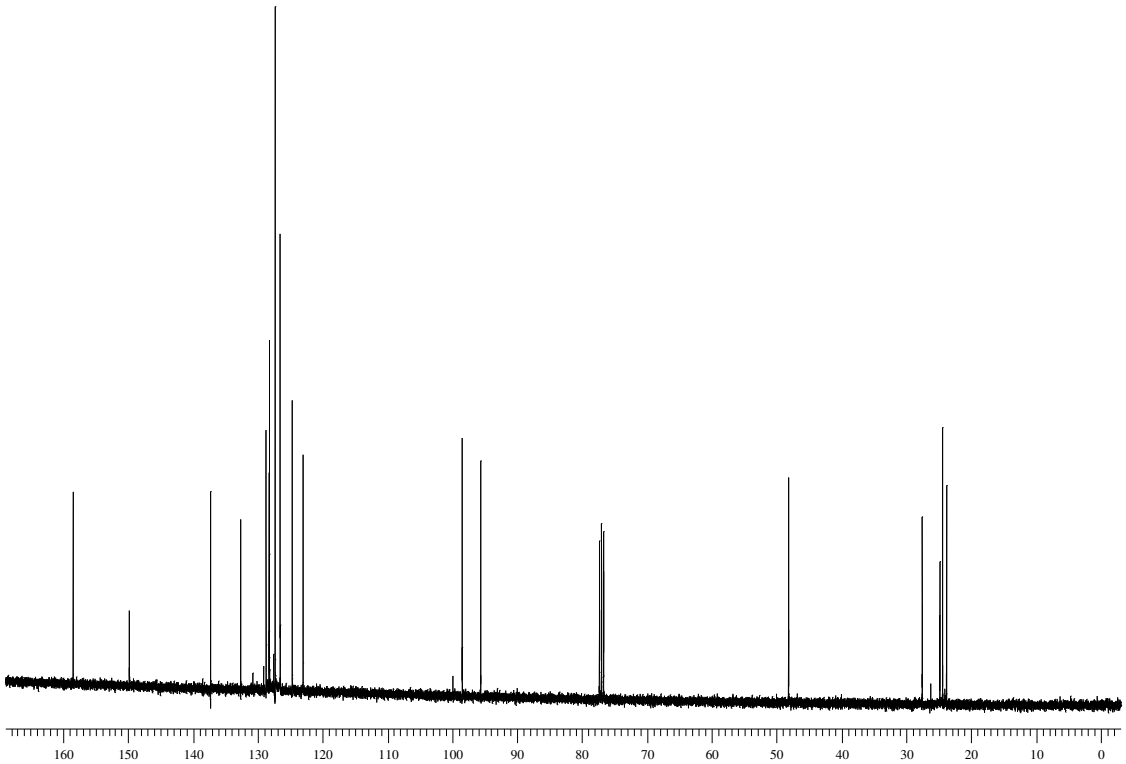
0.0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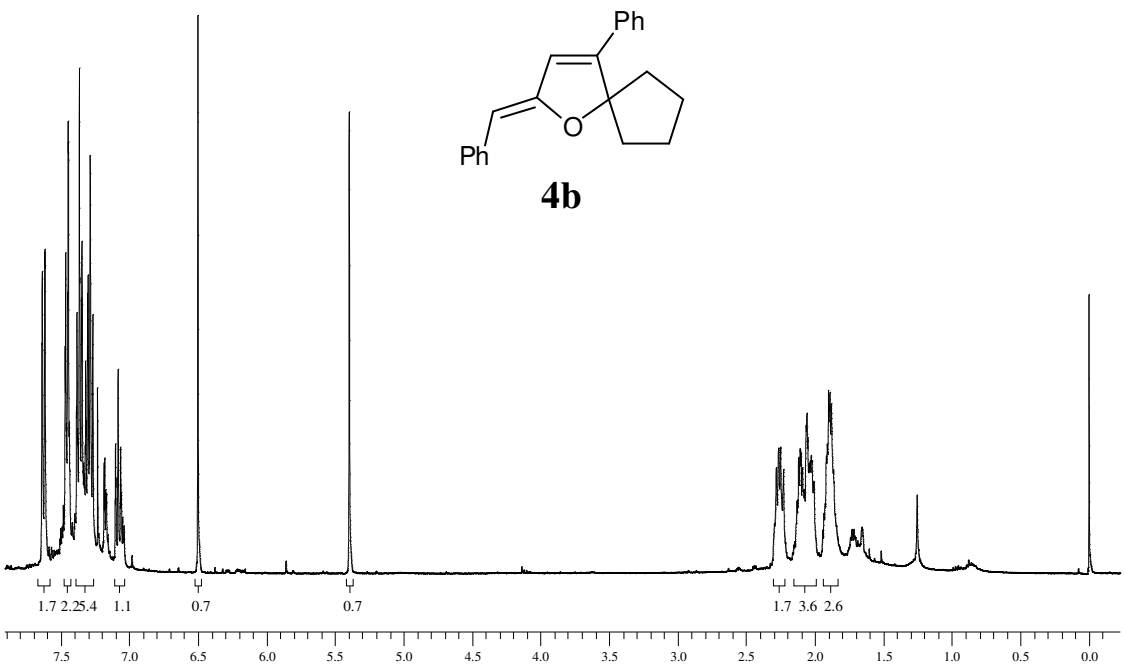
Ph
O
Ph
4b
1.7 2.2 5.4 1.1 0.7 0.7 1.7 3.6 2.6
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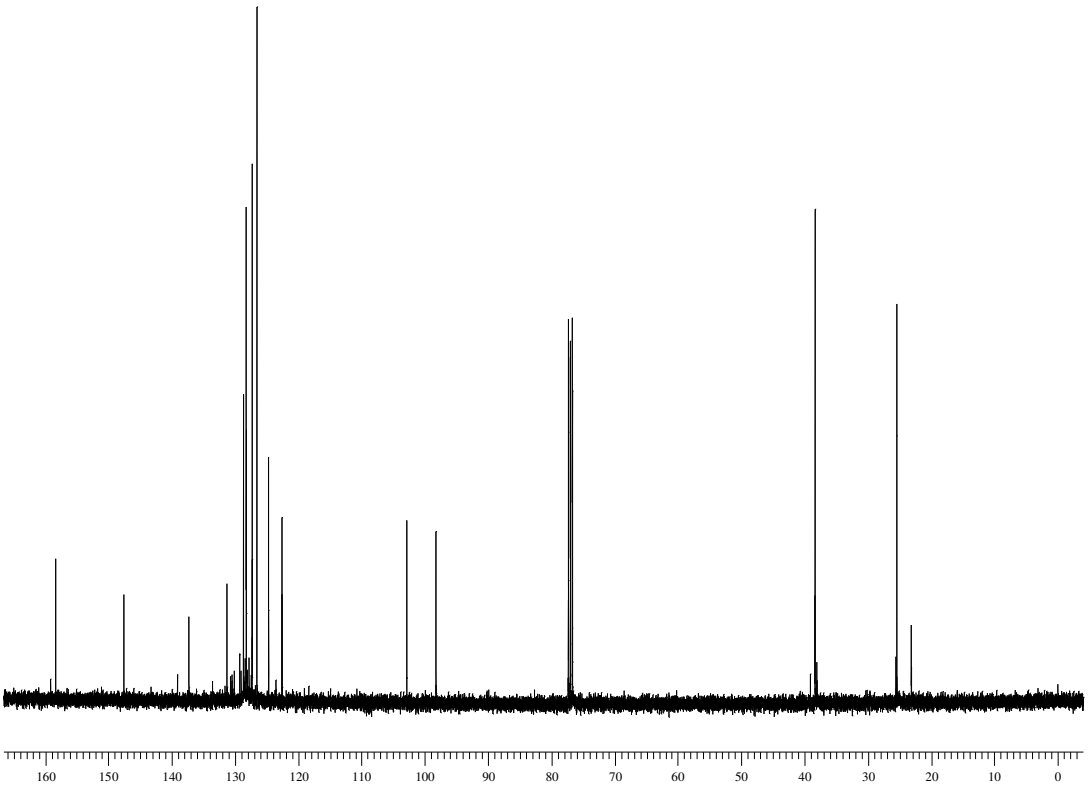
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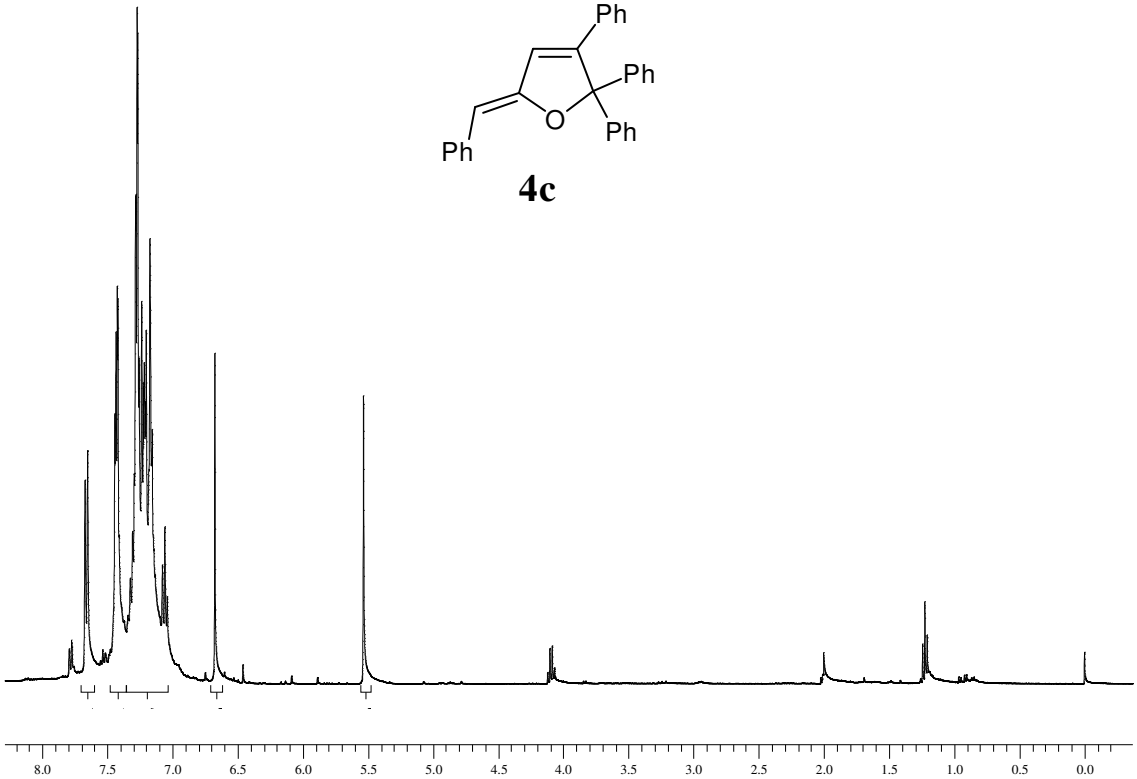
Ph
Ph
Ph
O
Ph

4c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2.0
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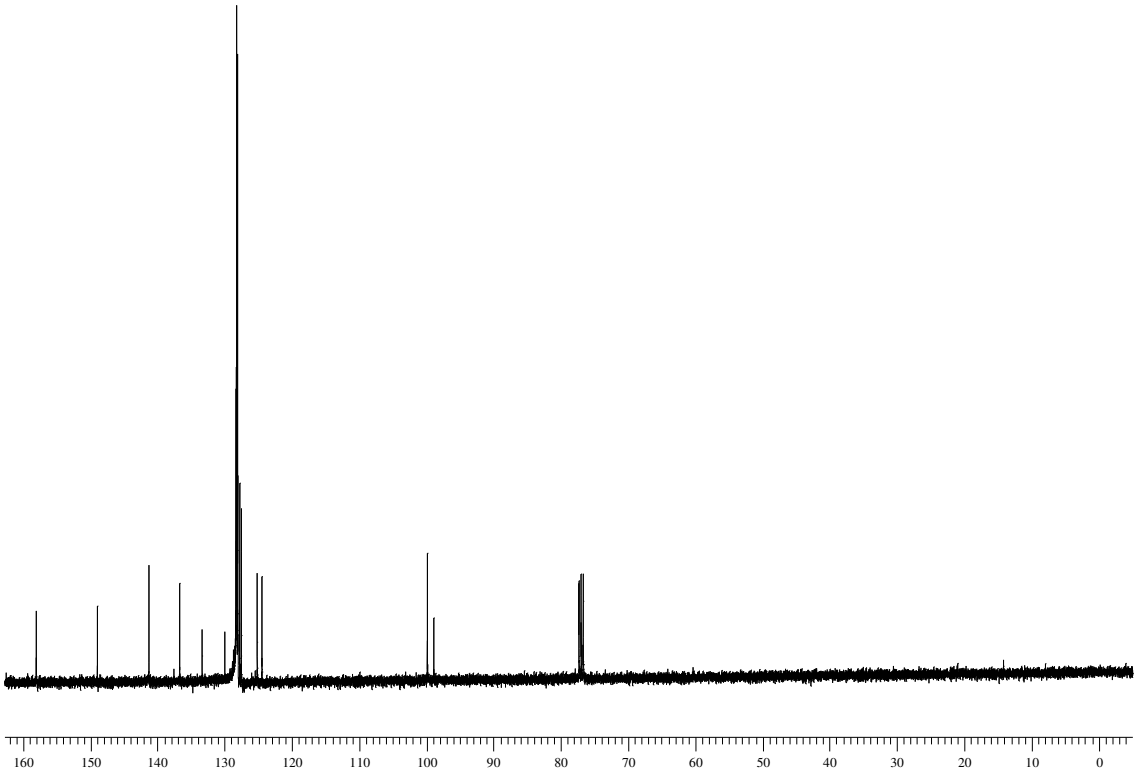
1.0
0.5
0.0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150
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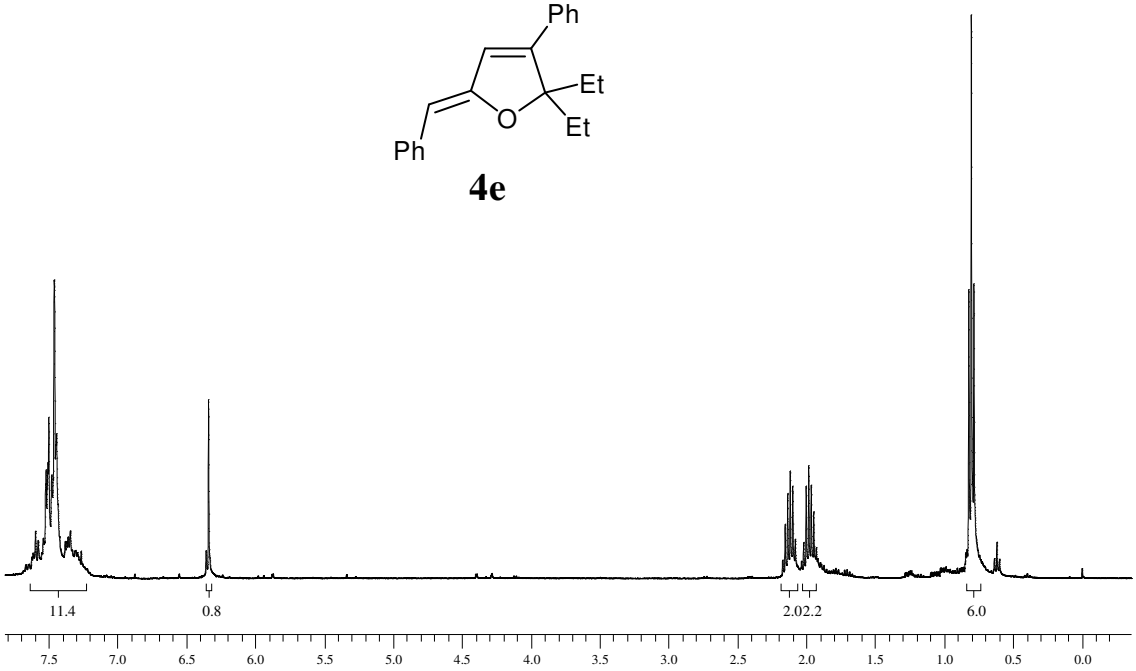
10
0

Ph
Et
O
Et
Ph

4e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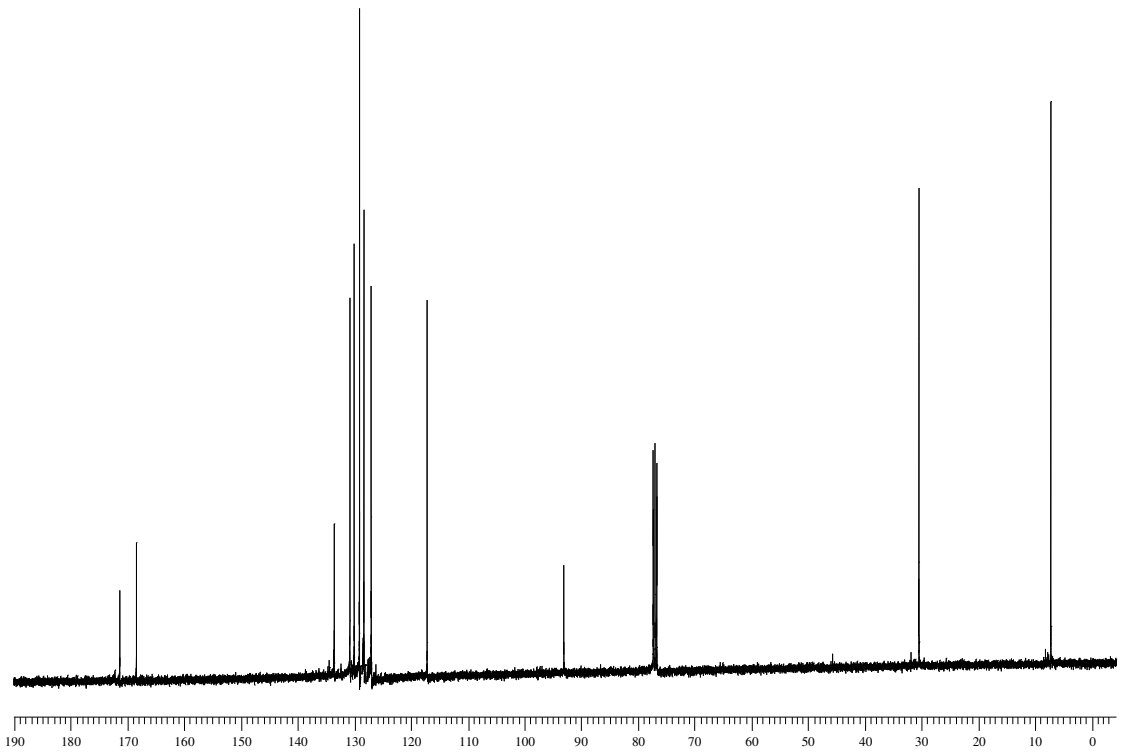
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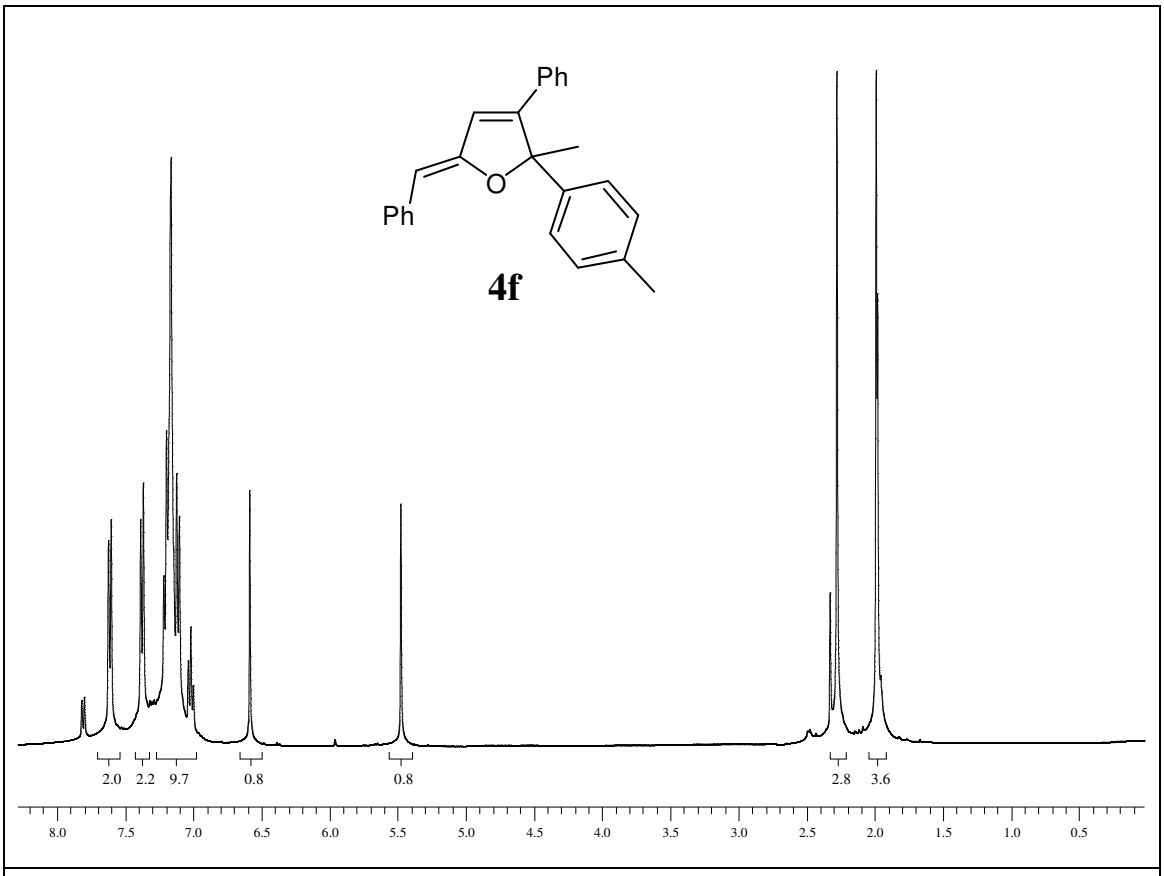
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O
Ph
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0.8
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7.0
6.5
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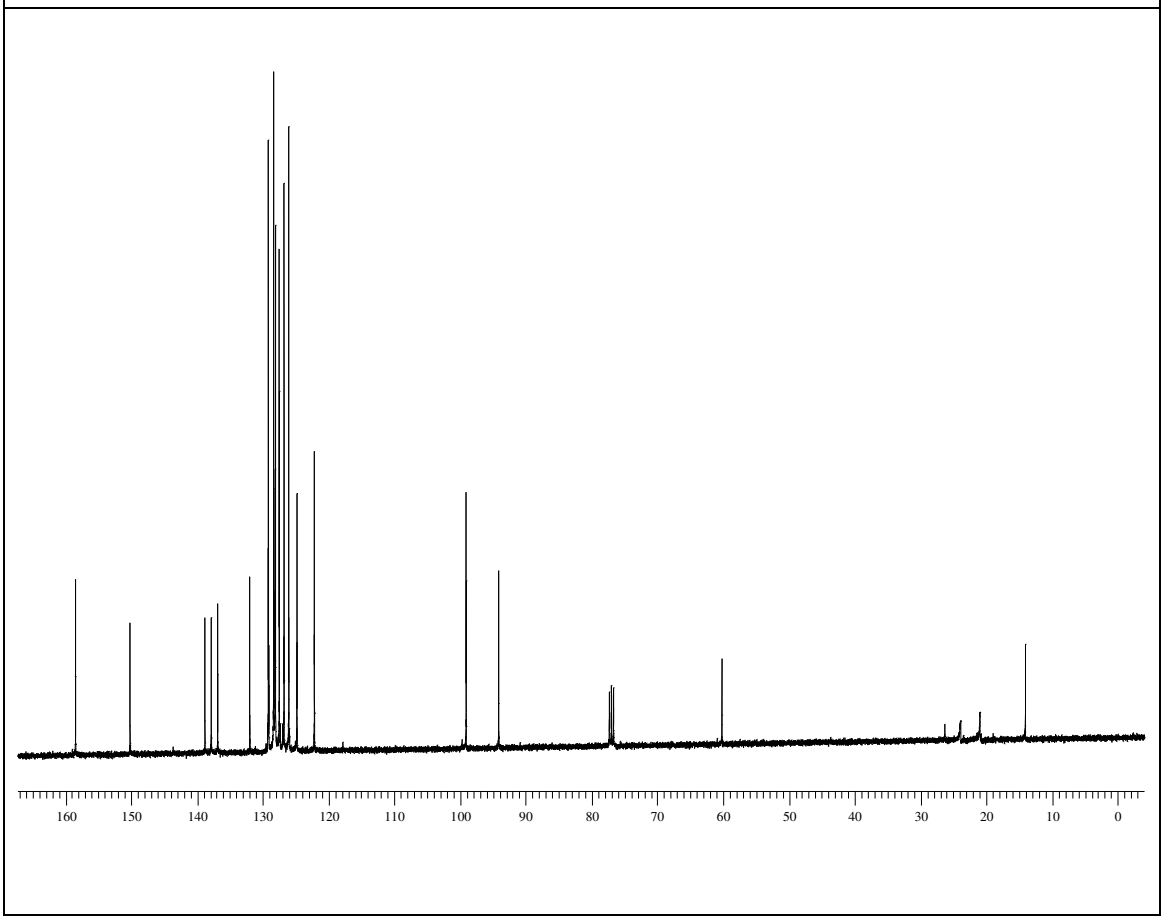
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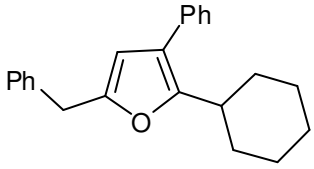
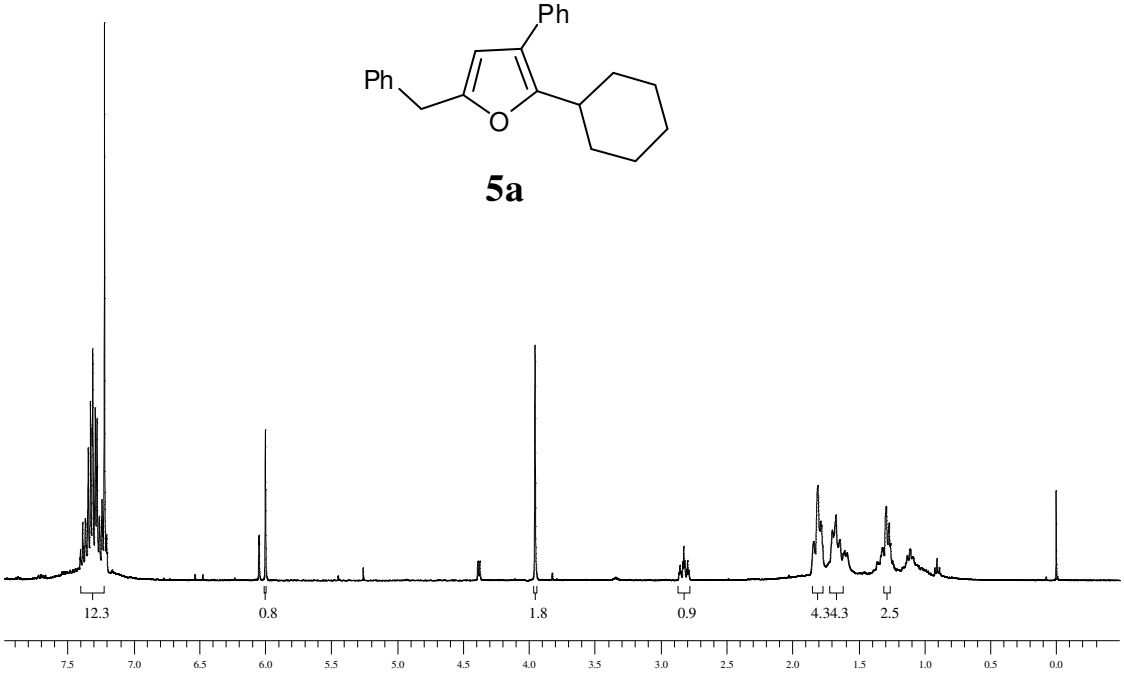
0


Ph
Ph
O

5a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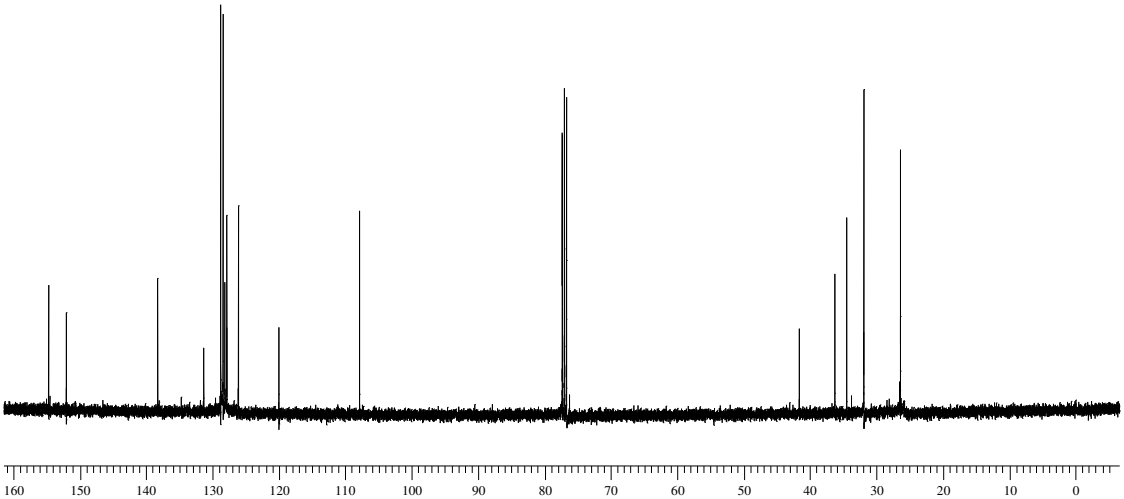
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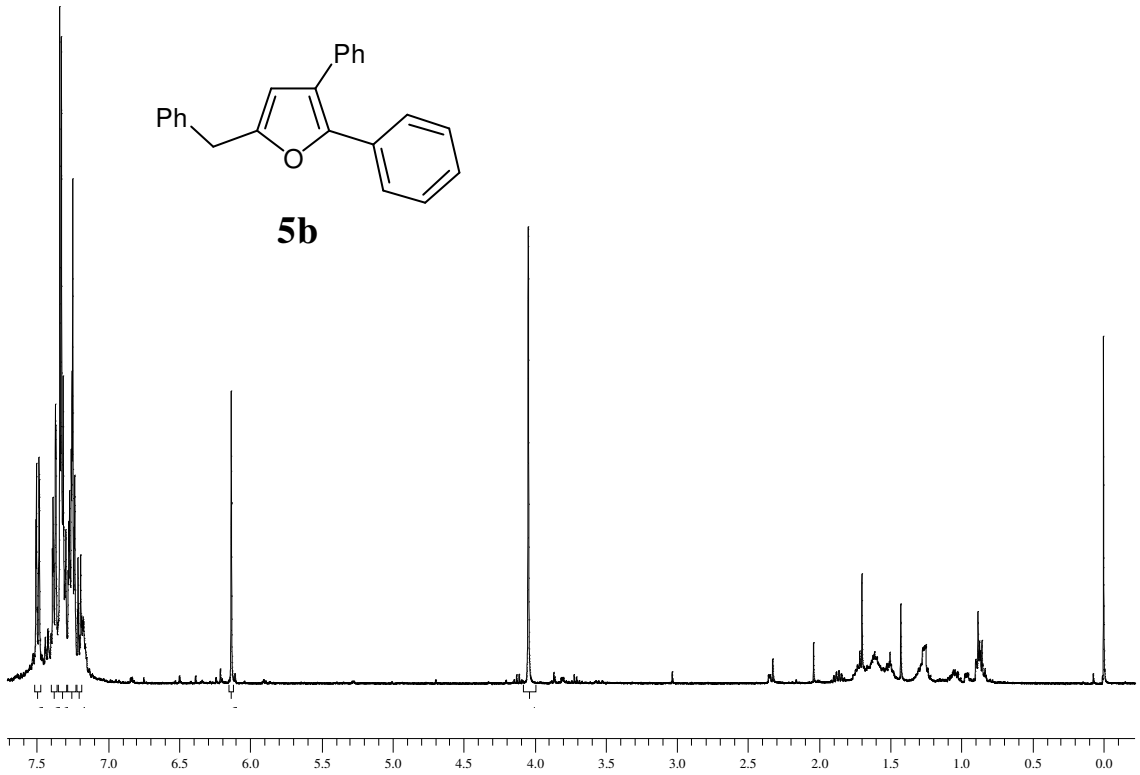
Ph
Ph
O
5b
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6.5
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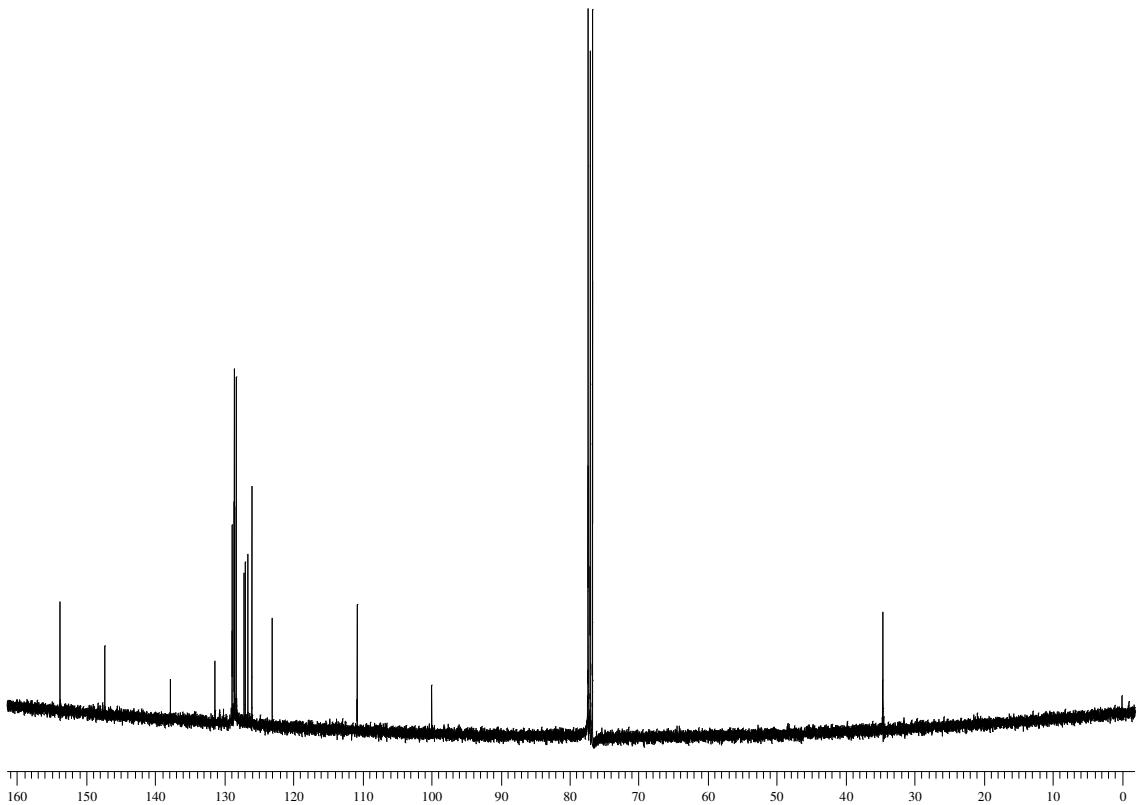
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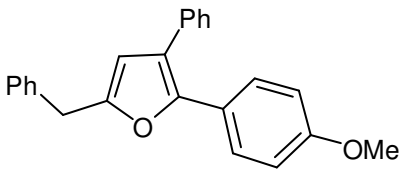
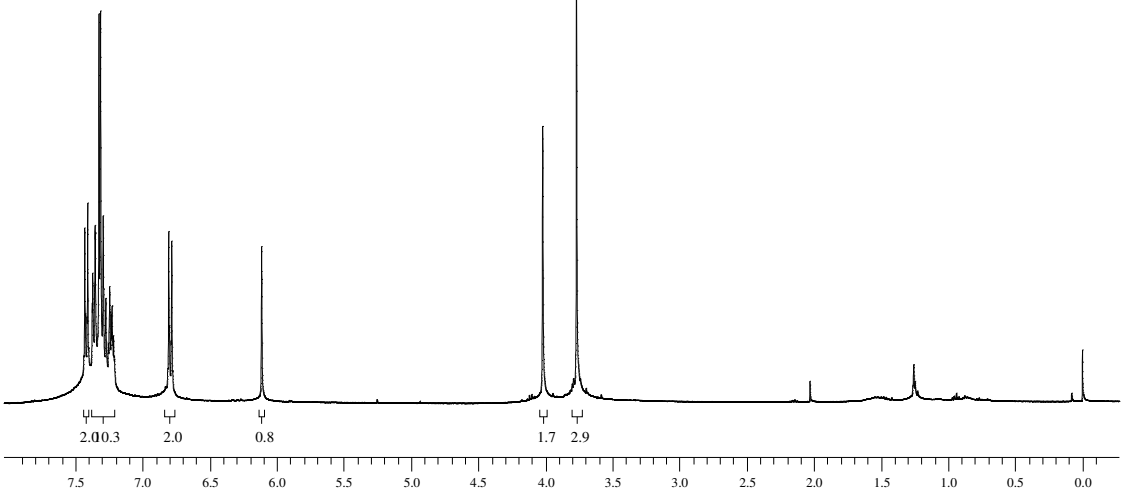

Ph
Ph
O
OMe

5c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2.5
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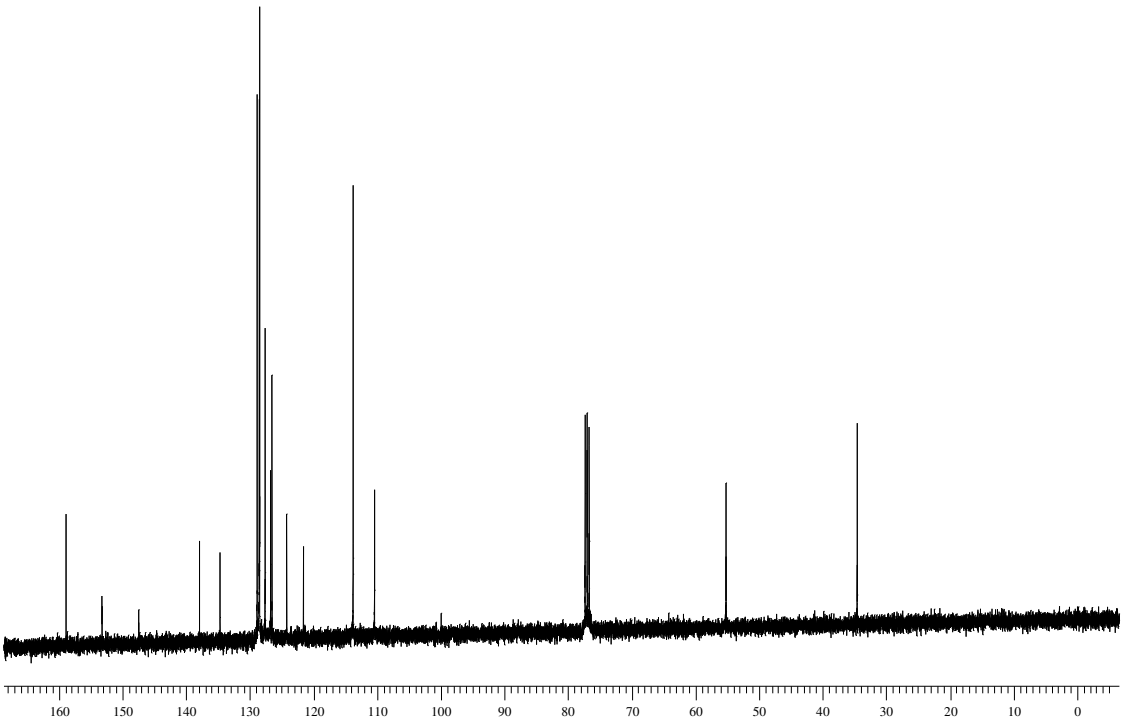
160
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