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Supporting Information

An Efficient Nozaki–Hiyama Allenylation Promoted by Acid Derived MIL-101 MOF

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1. General Information.

All ^{1}H NMR, and ^{13}C NMR spectra were recorded using Varian Unity Plus 400 (93.94 kG, ^{1}H 400 MHz) spectrometer at ambient temperature in $CDCl_3$. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant, and integration. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR ESP spectrophotometer. The structure and phase of the samples were evaluated by Xray powder diffraction (XRD, Rigaku DMAX-RB 12 KW) with Cu Kα radiation (λ=0.15406 nm). The morphology of the as-obtained product was characterized by scanning electron microscopy (SEM, ZEISS SUPRA55). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were conducted on a TEI Tecnai F20. The samples for the SEM, TEM and HRTEM measurements were dispersed in ethanol and sonicated for a few minutes and supported onto the silicon slice and the holey carbon film on a Cu grid, respectively. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. The pore size distributions were derived from the adsorption branches of isotherms by using the Barrett–Joyner–Halenda (BJH) model. Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel. All reactions were performed under nitrogen, in oven dried or flame dried glassware with magnetic stirring. All reactions were performed under argon with anhydrous solvents in oven dried glassware with magnetic stirring. All aldehydes were purchased from commercial suppliers and distilled prior to use. All other reagents were purchased from commercial suppliers and used without further purification.

2. Material Characterization

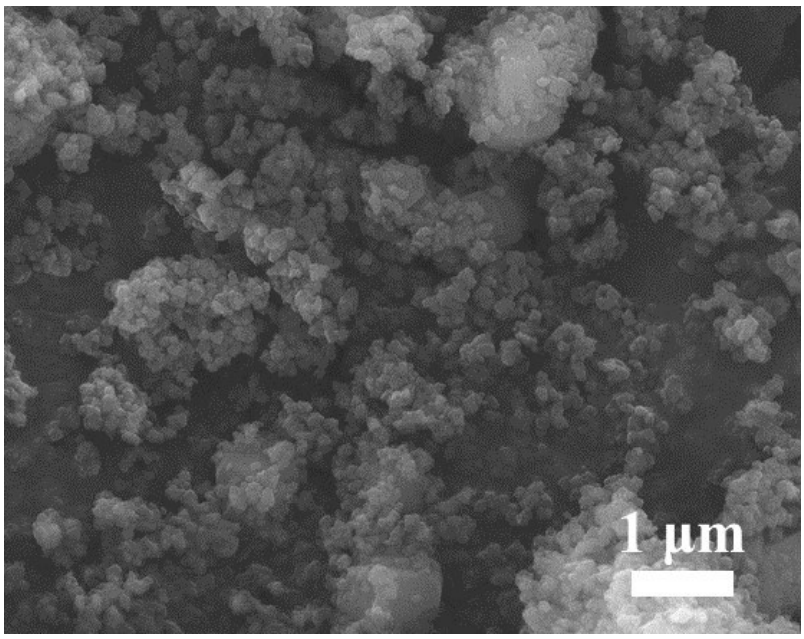


Figure S1. SEM image of recycled MIL-101-SO_3H.

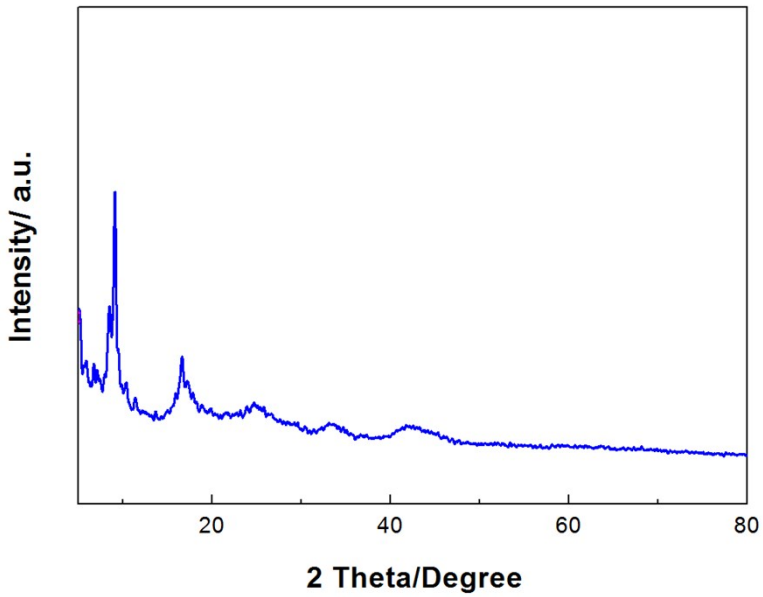
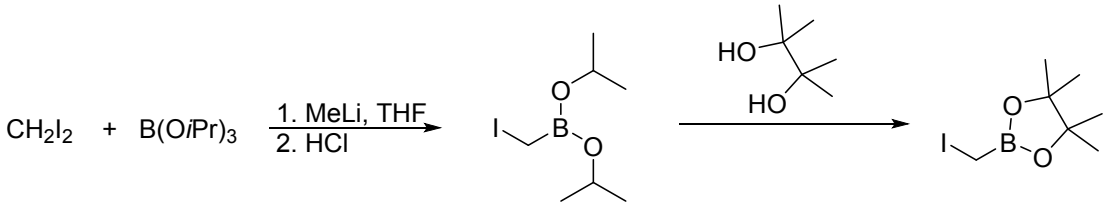


Figure S2. XRD pattern of recycled MIL-101-SO_3H.

3. Experimental Procedure and Compound Characterization

2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:

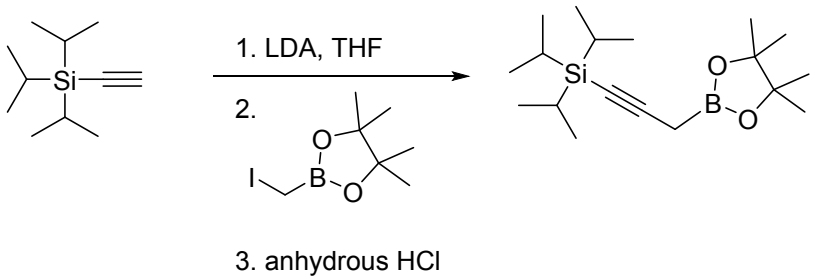


Diisopropyl (iodomethyl) boronate was prepared according to published procedure[1] scaled up to 400 mmol. 79% yield (85 g) after distillation. Spectral data matched the reported values.

2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared by stirring diisopropyl (iodomethyl)boronate (50 g, 185 mmol) with pinacol (28.4 g, 241 mmol) at room temperature in the absence of solvent under high vacuum until *i*PrOH was completely evaporated, approximately 2 h. The resulting mixture was dissolved in 300 mL of pentane and cooled to –20 °C overnight. After warming to room temperature, excess pinacol was removed as the bottom layer *via* pipette. The solution was then decanted into an oven-dried round-bottom flask and solvent then removed under vacuum. Product was recovered in quantitative yield (41.8 g) and used without further purification. Spectral data matched the reported values.[1b]

Procedure for the preparation of propargylboraonates:

Triisopropyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-yn-1-yl)silane



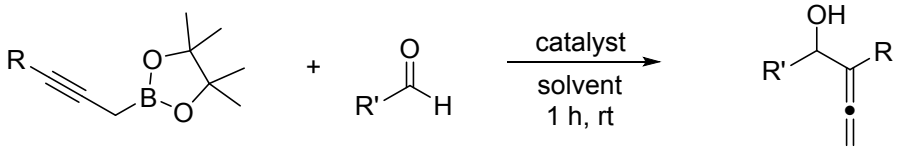
Modified from the procedure by Brown *et al.*[1] (Triisopropylsilyl)acetylene (5 g, 27.5 mmol) was added to a solution of LDA (26.3 mmol) in dry THF (60 mL) previously cooled to –78 °C under Argon and allowed to stir for 1 h. 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.70 g, 25 mmol) was then added in one portion. After an additional 30 min of stirring, the reaction allowed to warm to room temperature and age without stirring overnight. The reaction was then cooled to 0 °C and 2.0 M anhydrous HCl in diethyl ether (13.75 mL, 27.5 mmol) was added dropwise with vigorous stirring. The precipitate was then filtered off and the solvent

[1] a) H. C. Brown, C. D. Roy, R. Soundararajan, *Tetrahedron Lett* **1997**, *38*, 765-768; b) C. D. Roy, R. Soundararajan, H. C. Brown, *Monatsh Chem* **2008**, *139*, 241-249.

removed. The resulting residue was extracted with pentane (3 x 100 mL) and the extracts combined and cooled to −78 °C overnight. The pentane solution was warmed to room temperature and then decanted into an oven-dried 500 mL flask and solvent then removed (note: if a suspension of particulates is observed, filtration through a fine, sintered glass filter is required).

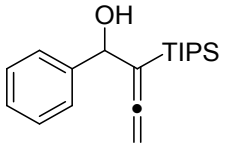
Triisopropyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-yn-1-yl)silane was obtained as a colorless liquid in 90% yield (6.3 g) as a mixture with unreacted (triisopropylsilyl)acetylene. Boronate can be stored at –20 °C under Argon for prolonged periods.

General Procedure for Allenylation Reactions



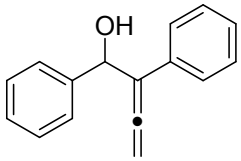
A 10 mL round-bottom flask was charged with stir bar under open air. To the flask was added MIL-101-SO_3H (0.005 mmol based on $–SO_3H$ group) and propargylboronate (0.55 mmol) then dissolved in CH_2Cl_2 (2.0 mL). The mixture was stirred at room temperature for 5 minutes. Then aldehyde compound (0.5 mmol) was added and stirred for 1 h. The organic layer was separated and the aqueous layer extracted with hexanes and the product purified by flash silica gel chromatography (1-5% acetone in hexanes or 100% DCM) to afford allenylic alcohol as a colorless oil.

1-phenyl-2-(triisopropylsilyl)buta-2,3-dien-1-ol (3a)



Colorless oil. **Yield:** 150 mg, 99% yield. Other spectral data was in agreement with reported data.[2]

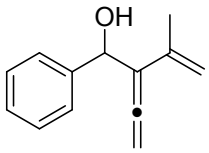
1,2-diphenylbuta-2,3-dien-1-ol (3b)



Colorless oil. **Yield:** 109 mg, 98% yield. Other spectral data was in agreement with reported data.[3]

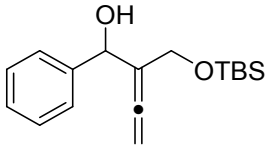
1-phenyl-2-(prop-1-en-2-yl)buta-2,3-dien-1-ol (3c)

[2] E. Hernandez, J. A. Soderquist, *Org Lett* **2005**, *7*, 5397-5400;
[3] M. Inoue, M. Nakada, *Angew Chem Int Edit* **2006**, *45*, 252-255; G. Y. Xia, H. Yamamoto, *J Am Chem Soc* **2007**, *129*, 496-497.



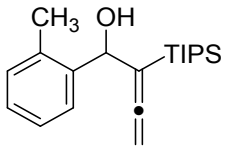
Colorless oil. **Yield:** 88 mg, 95%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.31 (m, 2H), 7.29 – 7.22 (m, 2H), 7.22 – 7.13 (m, 1H), 5.44 – 5.36 (m, 1H), 5.07 (qd, J = 12.4, 1.5 Hz, 2H), 4.84 (d, J = 7.2 Hz, 2H), 2.20 (d, J = 5.8 Hz, 1H), 1.78 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 208.45, 142.48, 137.10, 128.32, 127.76, 126.83, 112.59, 111.69, 81.27, 71.38, 22.44. **IR** (thin film, cm^{-1}): 3370, 3089, 2975, 2919, 1935, 1617, 1616, 1452, 1023.

2-(((tert-butyldimethylsilyl)oxy)methyl)-1-phenylbuta-2,3-dien-1-ol (3d)



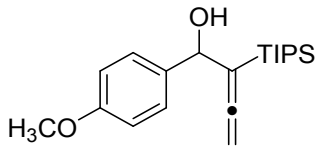
colorless oil. **Yield:** 141 mg, 97%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.39 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.26 – 7.18 (m, 1H), 5.36 (d, J = 5.6 Hz, 1H), 4.89 – 4.78 (m, 2H), 4.18 (dt, J = 11.5, 2.3 Hz, 1H), 4.11 (dt, J = 11.5, 2.0 Hz, 1H), 3.52 (d, J = 5.7 Hz, 1H), 0.87 (s, 9H), 0.01 (s, 3H), 0.0 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 210.96, 147.71, 133.60, 132.87, 131.71, 110.95, 83.19, 79.43, 68.51, 31.32, 23.68, 0.01. **IR** (thin film, cm^{-1}): 3428, 2930, 2857, 1959, 1472, 1255, 1046.

1-(o-tolyl)-2-(triisopropylsilyl)buta-2,3-dien-1-ol (3e)



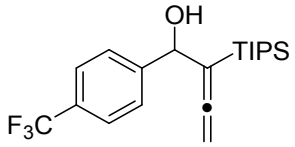
Colorless oil. **Yield:** 157 mg, 99%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.45 (d, J = 7.2 Hz, 1H), 7.22 – 7.05 (m, 3H), 5.47 – 5.39 (m, 1H), 4.57 – 4.47 (m, 2H), 2.38 (s, 3H), 2.05 (d, J = 6.3 Hz, 1H), 1.20 (m, 3H), 1.09 (d, J = 7.4 Hz, 9H), 1.00 (d, J = 7.4 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 210.02, 141.09, 135.67, 130.39, 127.50, 126.78, 125.80, 96.35, 72.45, 69.72, 19.27, 18.47, 11.85. **IR** (thin film, cm^{-1}): 3444, 2944, 2866, 1925. 1461, 1018. **HRMS (ESI)** *m/z* calculated for $C_{20}H_{33}OSi$ $[M+H]^+$ 317.2301, found 317.2296.

1-(4-methoxyphenyl)-2-(triisopropylsilyl)buta-2,3-dien-1-ol (3f)



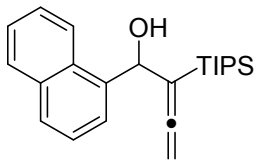
Colorless oil. **Yield:** 155 mg, 93%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.23 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.5 Hz, 2H), 5.02 (m, 1H), 4.58 (dd, J = 11.4, 2.4 Hz, 1H), 4.53 (dd, J = 11.3, 2.2 Hz, 1H), 3.70 (s, 3H), 2.22 (d, J = 4.8 Hz, 1H), 1.14 – 1.02 (m, 3H), 0.99 (d, J = 7.2 Hz, 9H), 0.87 (d, J = 7.4 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 209.54, 159.14, 135.69, 128.45, 113.54, 97.43, 73.10, 71.90, 55.20, 18.62, 11.69. **IR** (thin film, cm^{-1}): 3442, 2944, 2865, 1925, 1511, 1464, 1248, 1038. **HRMS (ESI)** *m/z* calculated for $C_{20}H_{33}O_2Si$ $[M+H]^+$ 333.2250, found 333.2254.

1-(4-(trifluoromethyl)phenyl)-2-(triisopropylsilyl)buta-2,3-dien-1-ol (3g)



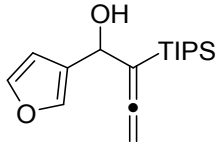
Colorless oil. **Yield:** 169 mg, 91%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.51 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 5.20 – 5.11 (m, 1H), 4.50 (qd, J = 11.8, 2.1 Hz, 2H), 2.21 (d, J = 5.9 Hz, 1H), 1.12 (m, 3H), 1.00 (d, J = 7.3 Hz, 9H), 0.92 (d, J = 7.4 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 209.77, 143.41, 128.20, 127.73, 127.15, 97.35, 73.11, 72.49, 18.62, 18.42, 11.72. **IR** (thin film, cm^{-1}): 3422, 2945, 2867, 1924, 1326, 1165, 1128, 1067. **HRMS (ESI)** *m/z* calculated for $C_{20}H_{30}OF_3Si$ $[M+H]^+$ 371.2018, found 371.2022.

1-(naphthalen-1-yl)-2-(triisopropylsilyl)buta-2,3-dien-1-ol (3h)



Colorless oil. **Yield:** 171 mg, 97%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 8.23 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 7.1 Hz, 1H), 7.56 – 7.42 (m, 3H), 6.01 – 5.95 (m, 1H), 4.49 (qd, J = 11.5, 2.7 Hz, 2H), 2.30 (d, J = 6.2 Hz, 1H), 1.29 – 1.18 (m, 3H), 1.11 (d, J = 7.4 Hz, 9H), 1.01 (d, J = 7.4 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 210.52, 138.66, 133.91, 131.33, 128.67, 128.48, 125.93, 125.44, 125.01, 124.77, 124.12, 96.77, 72.73, 70.06, 18.71, 11.88. **IR** (thin film, cm^{-1}): 3423, 2943, 2865. 1925, 1462. **HRMS (ESI)** *m/z* calculated for $C_{23}H_{34}OSi$ $[M+H]^+$ 353.2301, found 353.2294.

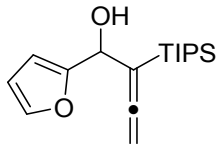
1-(furan-3-yl)-2-(triisopropylsilyl)buta-2,3-dien-1-ol (3i)



Colorless oil. **Yield:** 133 mg, 91%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.38 (m, 1H), 7.36 (t, J = 1.7 Hz, 1H), 6.44 (dd, J = 1.7, 0.7 Hz, 1H), 5.08 (d, J = 7.1 Hz, 1H), 4.69

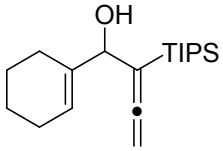
(ddd, J = 11.6, 1.9, 0.6 Hz, 1H), 4.62 (ddd, J = 11.6, 1.7, 0.5 Hz, 1H), 2.07 (d, J = 7.2 Hz, 1H), 1.26 – 1.15 (m, 3H), 1.09 (d, J = 7.4 Hz, 9H), 1.03 (d, J = 7.4 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 210.18, 143.14, 139.85, 128.76, 109.55, 96.76, 73.29, 64.79, 18.55, 11.60. **IR** (thin film, cm^{-1}): 3424, 2944, 2866, 1925, 1464, 1011, 883. **HRMS (ESI)** *m/z* calculated for $C_{17}H_{29}O_2Si$ $[M+H]^+$ 293.1937, found 293.1945.

1-(furan-2-yl)-2-(triisopropylsilyl)buta-2,3-dien-1-ol (3j)



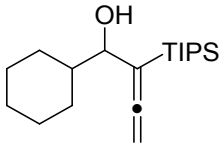
Colorless oil. **Yield:** 137 mg, 94%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.37 (dd, J = 1.8, 0.9 Hz, 1H), 6.31 (dd, J = 3.2, 1.8 Hz, 1H), 6.27 (d, J = 3.2 Hz, 1H), 5.12 (d, J = 6.8 Hz, 1H), 4.74 (dd, J = 11.6, 2.2 Hz, 1H), 4.68 (dd, J = 11.5, 2.0 Hz, 1H), 2.33 (d, J = 7.3 Hz, 1H), 1.22 – 1.12 (m, 3H), 1.08 (d, J = 7.3 Hz, 9H), 1.00 (d, J = 7.3 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 209.91, 155.68, 142.14, 110.13, 107.39, 95.04, 73.68, 65.52, 18.34, 11.57. **IR** (thin film, cm^{-1}): 3422, 2944, 2866, 1923, 1464, 1020, 876.

1-(cyclohex-1-en-1-yl)-2-(triisopropylsilyl)buta-2,3-dien-1-ol (3k)



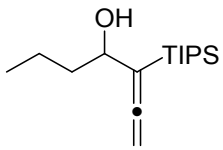
Colorless oil. **Yield:** 145 mg, 95%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 5.71 (s, 1H), 4.62 (qd, J = 11.2, 2.2 Hz, 2H), 4.46 (d, J = 6.3 Hz, 1H), 2.10 – 1.97 (m, 4H), 1.96 (d, J = 6.3 Hz, 1H), 1.67 – 1.50 (m, 4H), 1.22 (m, 3H), 1.09 (d, J = 7.3 Hz, 9H), 1.06 (d, J = 7.4 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 209.13, 138.99, 124.75, 95.41, 74.25, 72.79, 25.10, 23.31, 22.53, 22.47, 18.69, 11.74. **IR** (thin film, cm^{-1}): 3461, 2941, 2865, 1923, 1465, 1018.

1-cyclohexyl-2-(triisopropylsilyl)buta-2,3-dien-1-ol (3l)



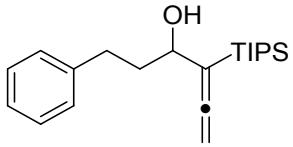
Colorless oil. **Yield:** 147 mg, 95%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 4.48 (qd, J = 11.3, 1.9 Hz, 2H), 3.74 (m, 1H), 1.92 – 1.80 (m, 1H), 1.75 – 1.65 (m, 2H), 1.65 – 1.55 (m, 2H), 1.55 – 1.44 (m, 1H), 1.37 (d, J = 7.9 Hz, 1H), 1.22 – 1.09 (m, 3H), 1.24 – 0.87 (m, 5H), 1.06 – 0.98 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 209.35, 95.33, 73.98, 72.09, 43.47, 31.08, 26.49, 26.07, 18.65, 11.75. **IR** (thin film, cm^{-1}): 3445, 2925, 2865, 1922, 1464, 1018, 883.

3-(triisopropylsilyl)hepta-1,2-dien-4-ol (3m)



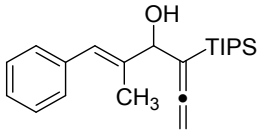
Colorless oil. **Yield:** 131 mg, 98%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 4.49 (qd, J = 11.3, 1.7 Hz, 2H), 4.03 – 3.90 (m, 1H), 1.65 – 1.26 (m, 4H), 1.36 (d, J = 7.6 Hz, 1H), 1.20 – 1.09 (m, 3H), 1.02 (t, J = 7.3 Hz, 18H), 0.87 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 209.59, 96.79, 72.25, 69.48, 40.38, 19.29, 18.63, 13.93, 11.65. **IR** (thin film, cm^{-1}): 3447, 2943, 2866, 1922, 998. **HRMS (ESI)** *m/z* calculated for $C_{16}H_{32}OSiNa$ $[M+Na]^+$ 291.2120, found 291.2122.

1-phenyl-4-(triisopropylsilyl)hexa-4,5-dien-3-ol (3n)



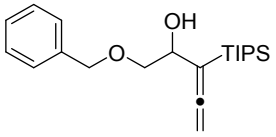
Colorless oil. **Yield:** 161 mg, 97%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.17 (m, 2H), 7.10(m, 3H), 4.53 (dd, J = 11.4, 1.7 Hz, 1H), 4.49 (dd, J = 11.4, 1.7 Hz, 1H), 3.96 (m, 1H), 2.68 (m, 2H), 1.86 (m, 2H), 1.46 (d, J = 7.6 Hz, 1H), 1.10 (m, 3H), 0.99 (m, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: δ 209.59, 142.09, 128.49, 128.34, 125.75, 96.72, 72.56, 69.06, 40.10, 32.57, 18.64, 11.64. **IR** (thin film, cm^{-1}): 3452, 2943, 2865, 1921, 1457, 1018, 883.

(*E*)-2-methyl-1-phenyl-4-(triisopropylsilyl)hexa-1,4,5-trien-3-ol (3o)



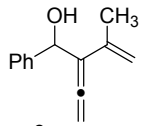
Colorless oil. **Yield:** 166 mg, 97%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.29 – 7.22 (m, 2H), 7.21 – 7.17 (m, 2H), 7.14 (m, 1H), 6.46 (s, 1H), 4.66 – 4.50 (m, 3H), 2.04 (d, J = 5.9 Hz, 1H), 1.79 (s, 3H), 1.24 – 1.14 (m, 3H), 1.05 (d, J = 7.4 Hz, 9H), 1.00 (d, J = 7.4 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 209.57, 139.41, 137.54, 128.97, 128.06, 127.04, 126.47, 95.47, 75.76, 72.98, 18.71, 13.33, 11.81. **IR** (thin film, cm^{-1}): 3444, 2944, 2865, 1925, 1462, 1017, 883. **HRMS (ESI)** *m/z* calculated for $C_{22}H_{35}OSi$ $[M+H]^+$ 343.2457, found 343.2460.

1-(benzyloxy)-3-(triisopropylsilyl)penta-3,4-dien-2-ol (3p)



Colorless oil. **Yield:** 169 mg, 98%; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.39 – 7.25 (m, 4H), 4.58 (dd, J = 30.3, 11.6 Hz, 2H), 4.57 (dd, J = 11.5, 1.8 Hz, 1H), 4.48 (dd, J =

11.5, 1.8 Hz, 1H), 4.28 (m, 1H), 3.64 (dd, J = 9.8, 2.9 Hz, 1H), 3.48 (dd, J = 9.8, 8.6 Hz, 1H), 2.41 (d, J = 4.2 Hz, 1H), 1.27 – 1.13 (m, 3H), 1.07 (s, 9H), 1.06 (d, J = 9.6 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.43, 138.07, 128.40, 127.72, 92.06, 74.62, 73.26, 71.62, 68.48, 18.64, 11.64. **IR** (thin film, cm^{-1}): 3459, 2943, 2865, 1924, 1465, 1076. **HRMS (ESI)** *m/z* calculated for $C_{21}H_{35}O_2Si$ $[M+H]^+$ 347.2406, found 347.2399.


OH
CH3
Ph

3c

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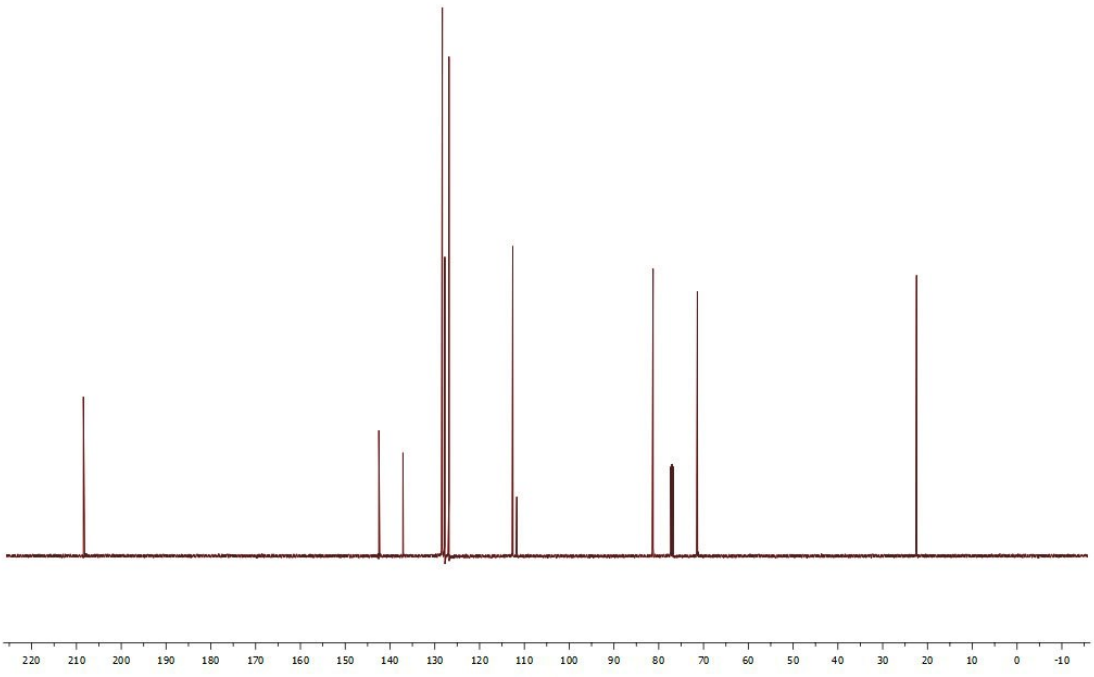
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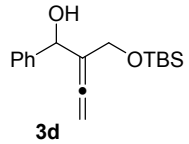
OH
Ph
OTBS

3d

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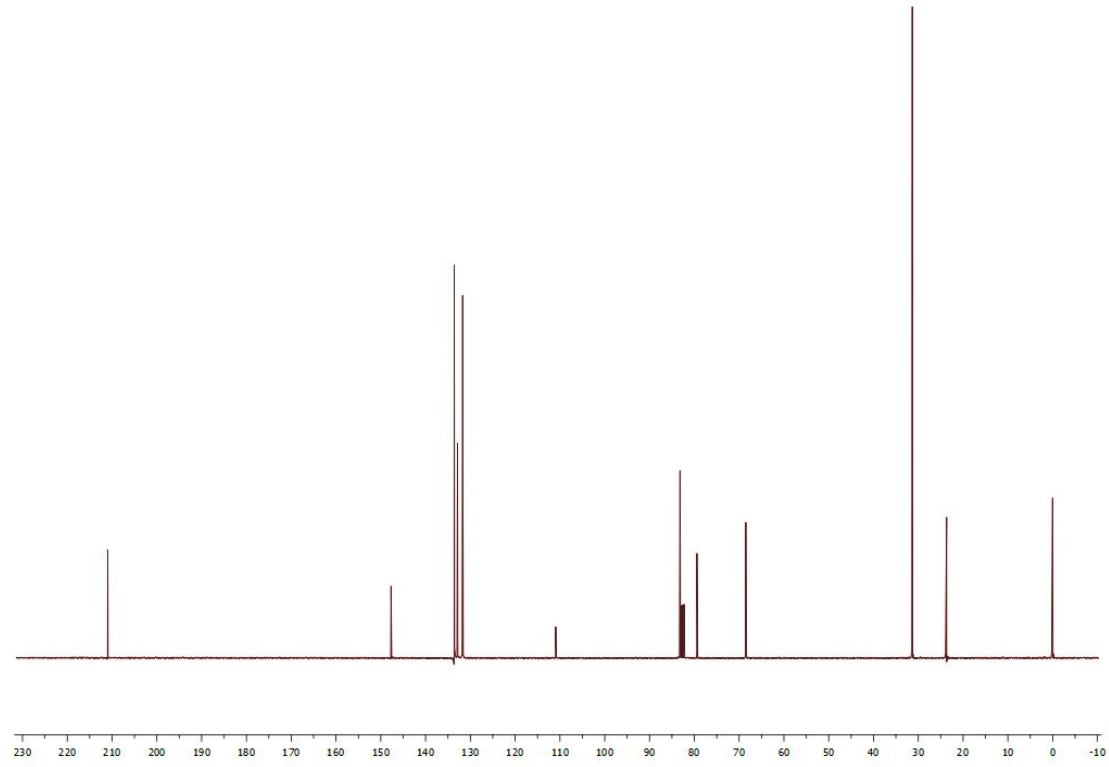
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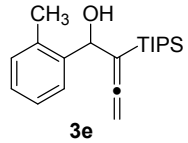
CH3
OH
TIPS

3e

10.0
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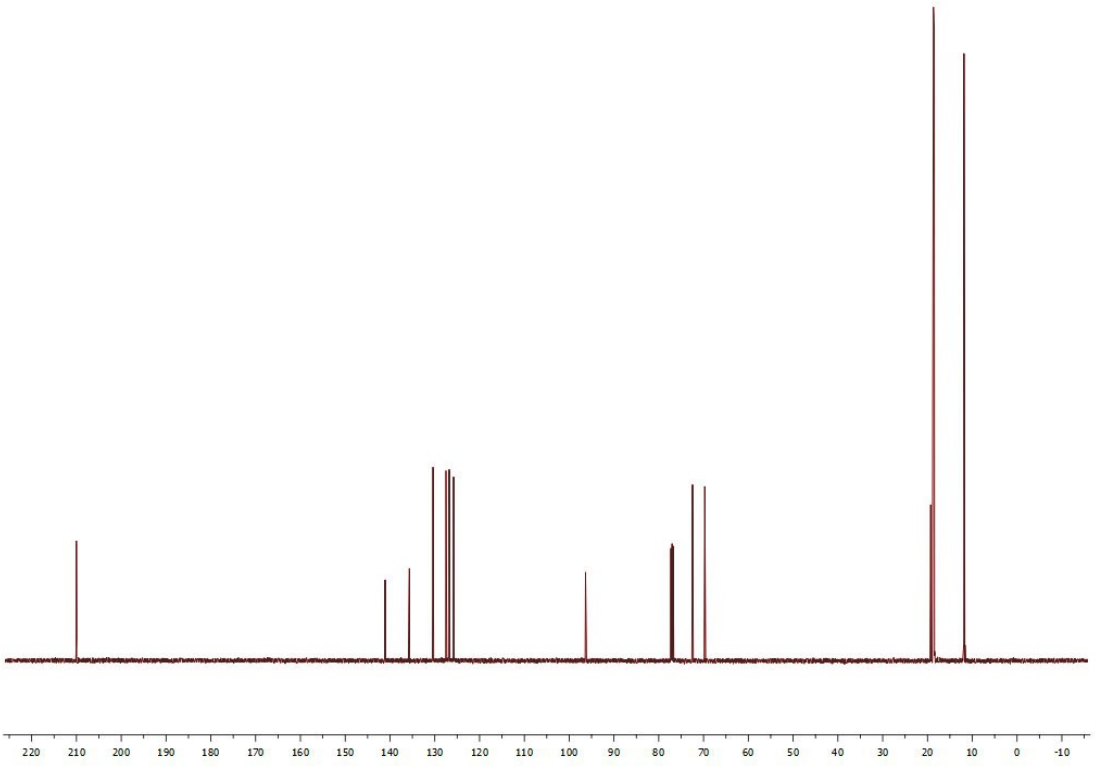
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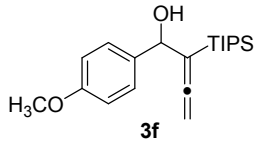
OH
TIPS
H3CO

3f

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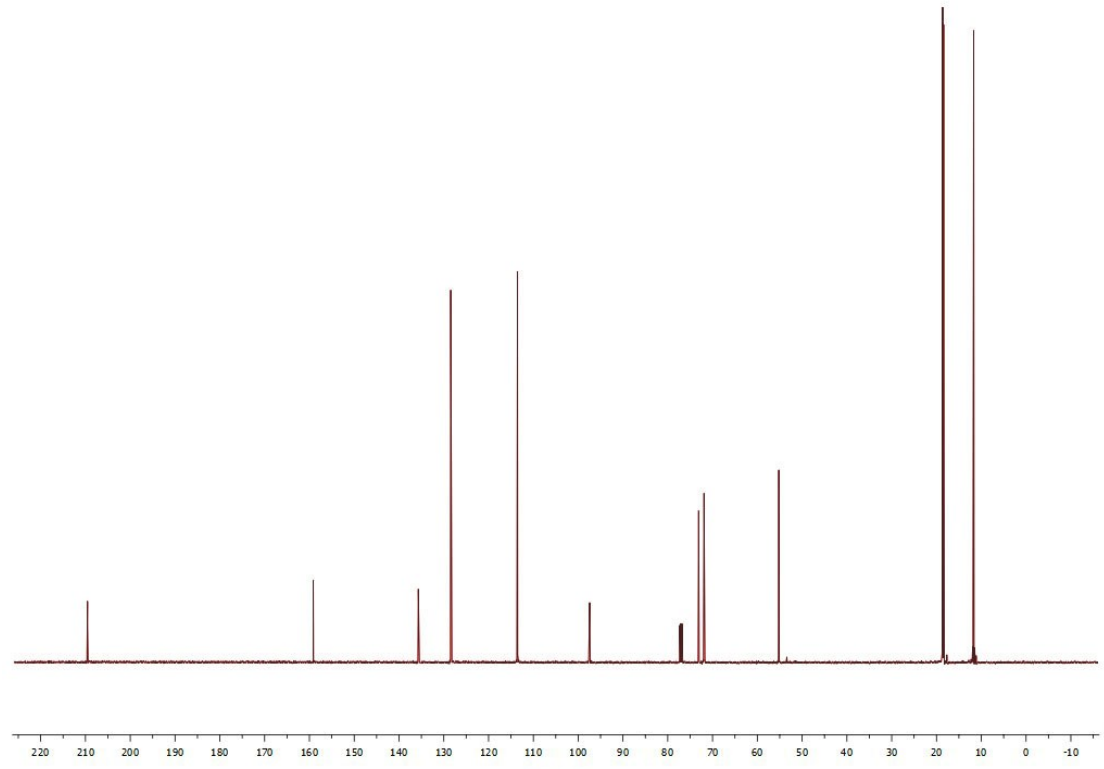
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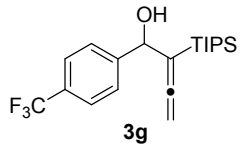
OH
TIPS
F3C

3g

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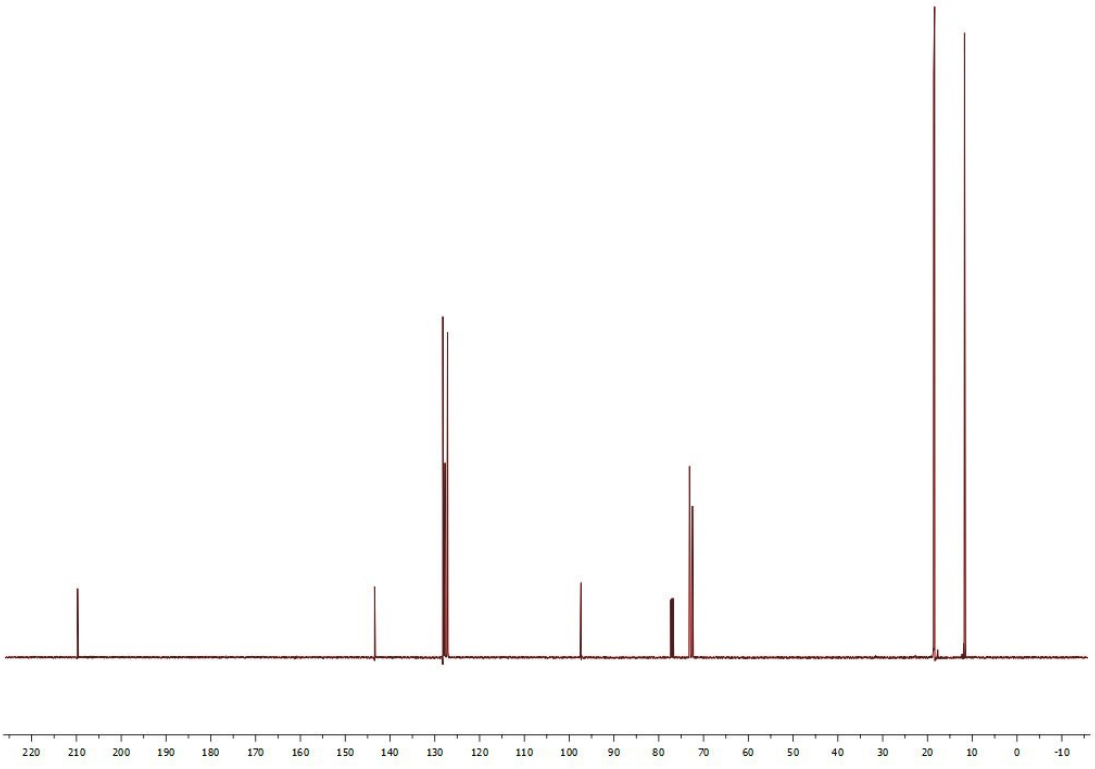
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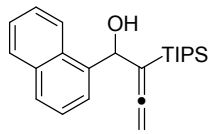
OH
TIPS

3h

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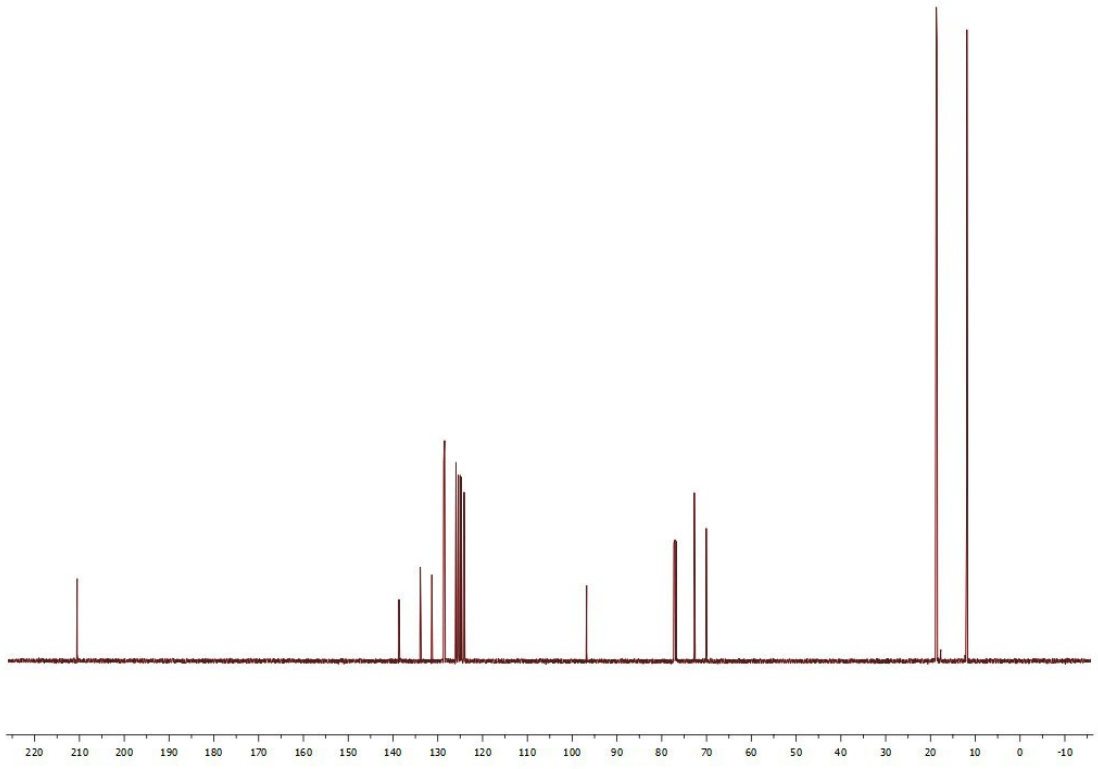
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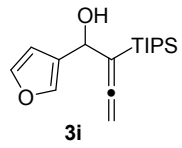
OH
TIPS
O

3i

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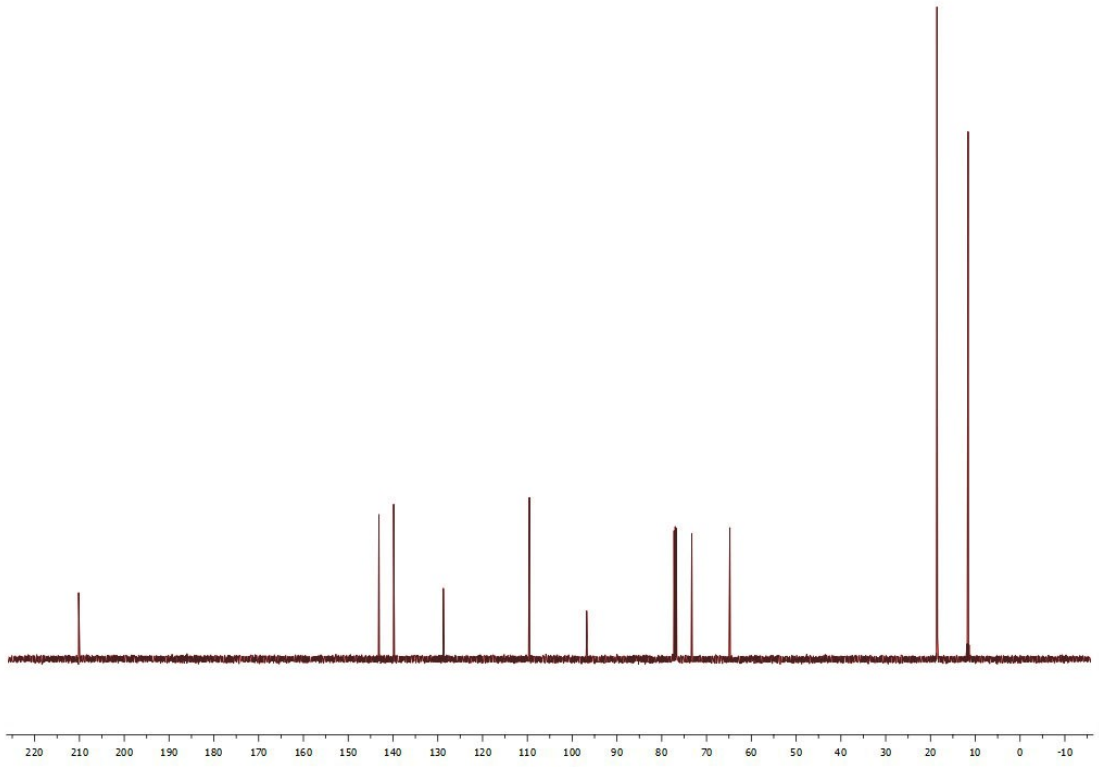
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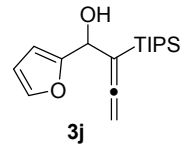
OH
TIPS
O

3j

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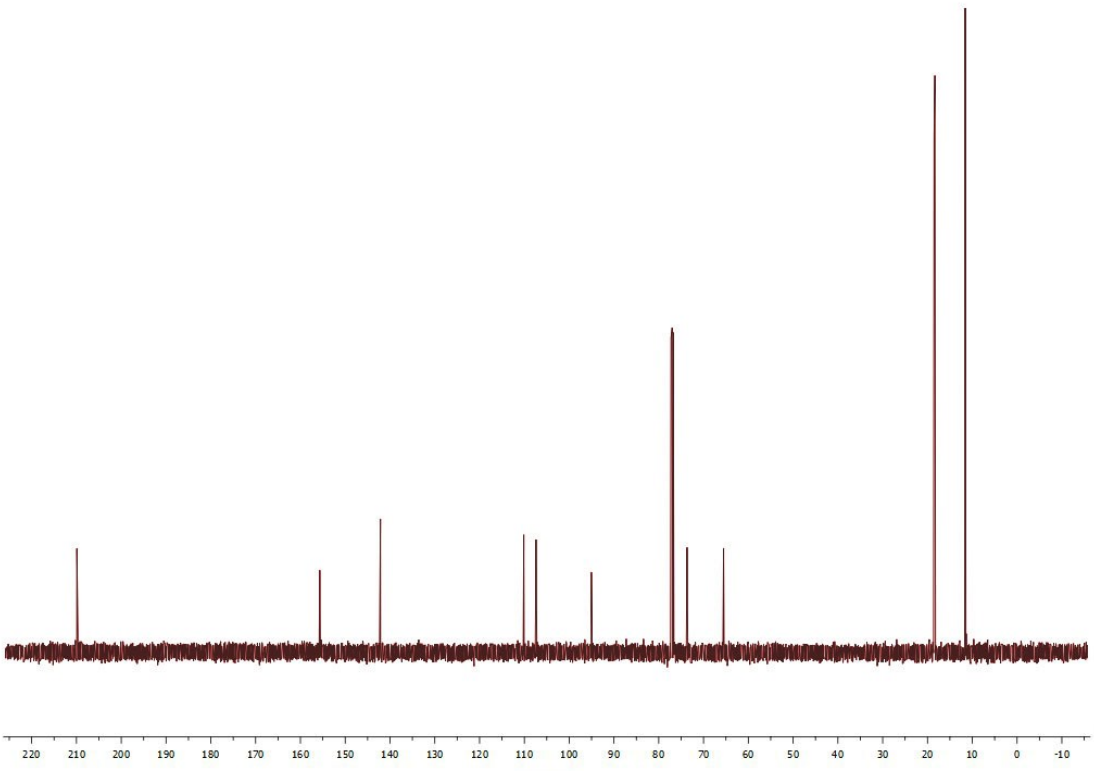
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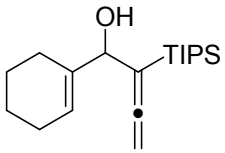
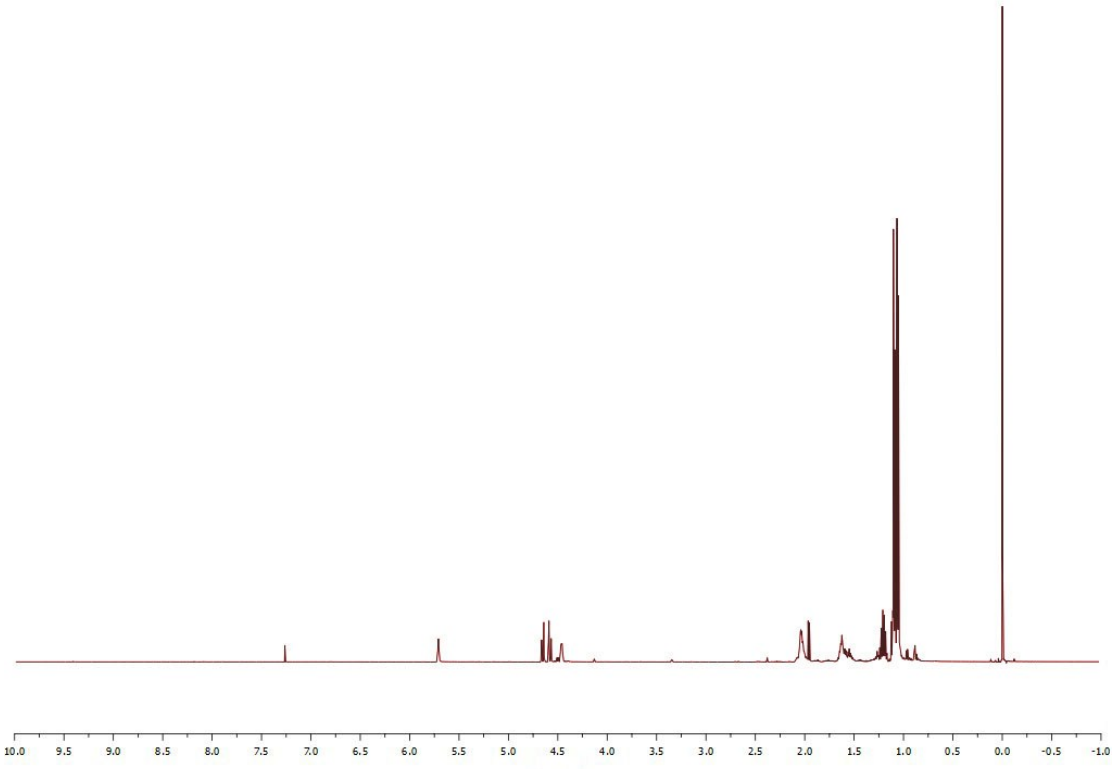

OH
TIPS

3k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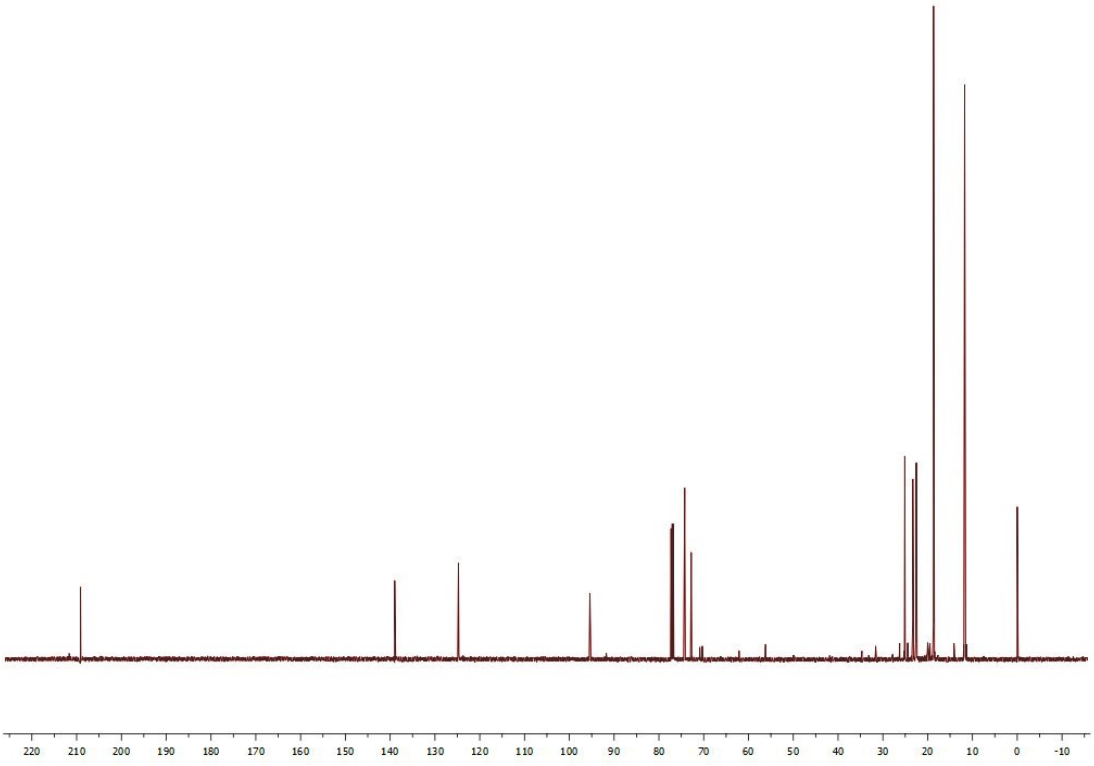
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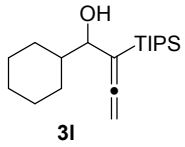
OH
TIPS

3l

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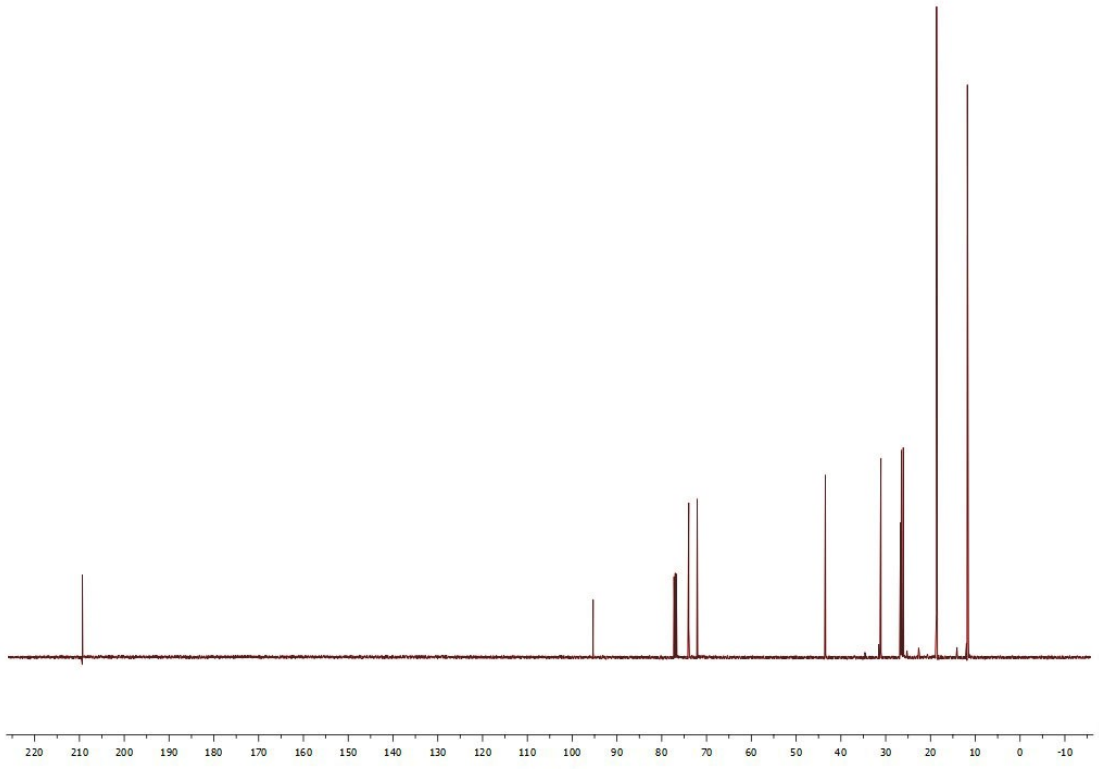
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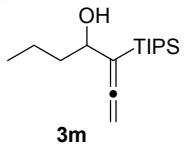
OH
TIPS

3m

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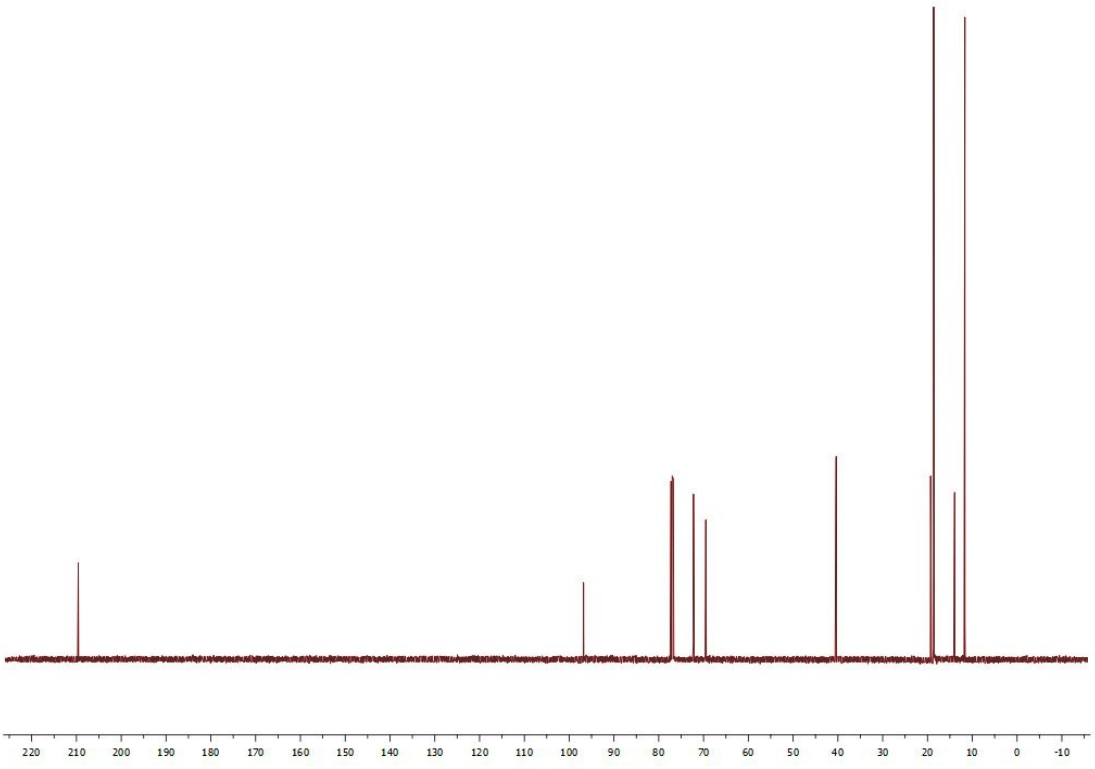
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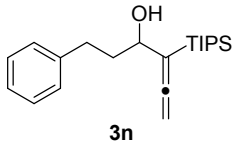
OH
TIPS

3n

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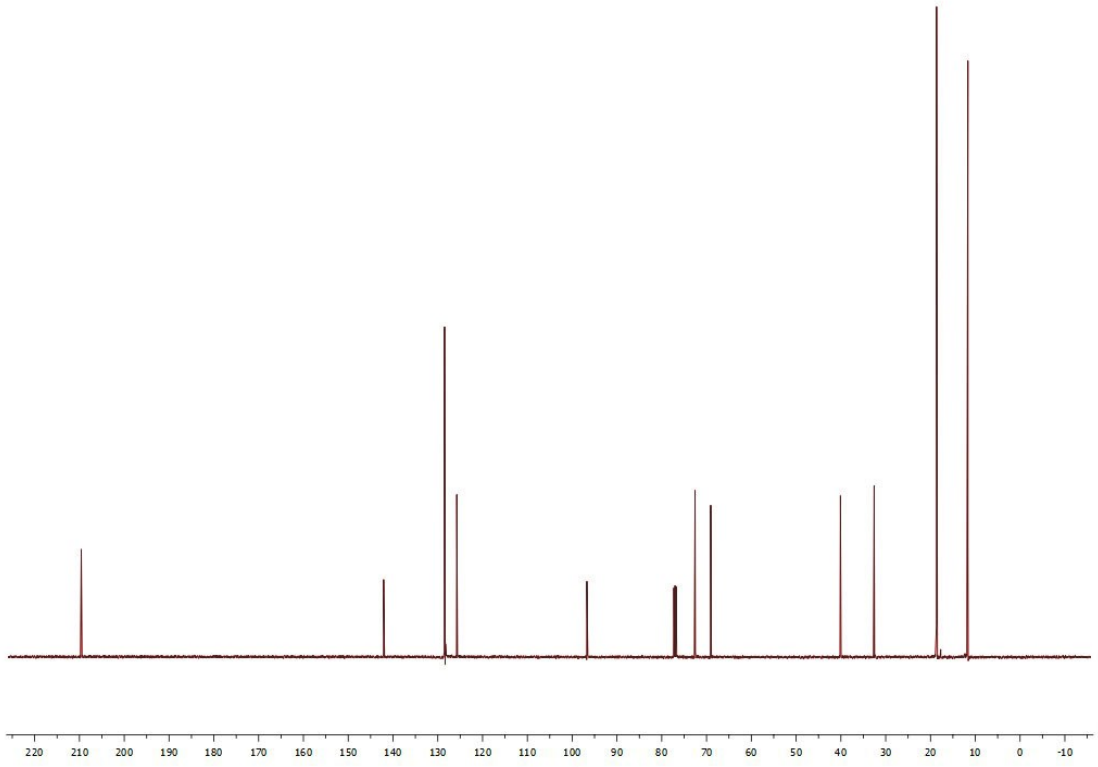
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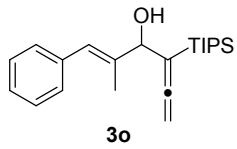
OH
TIPS

3o

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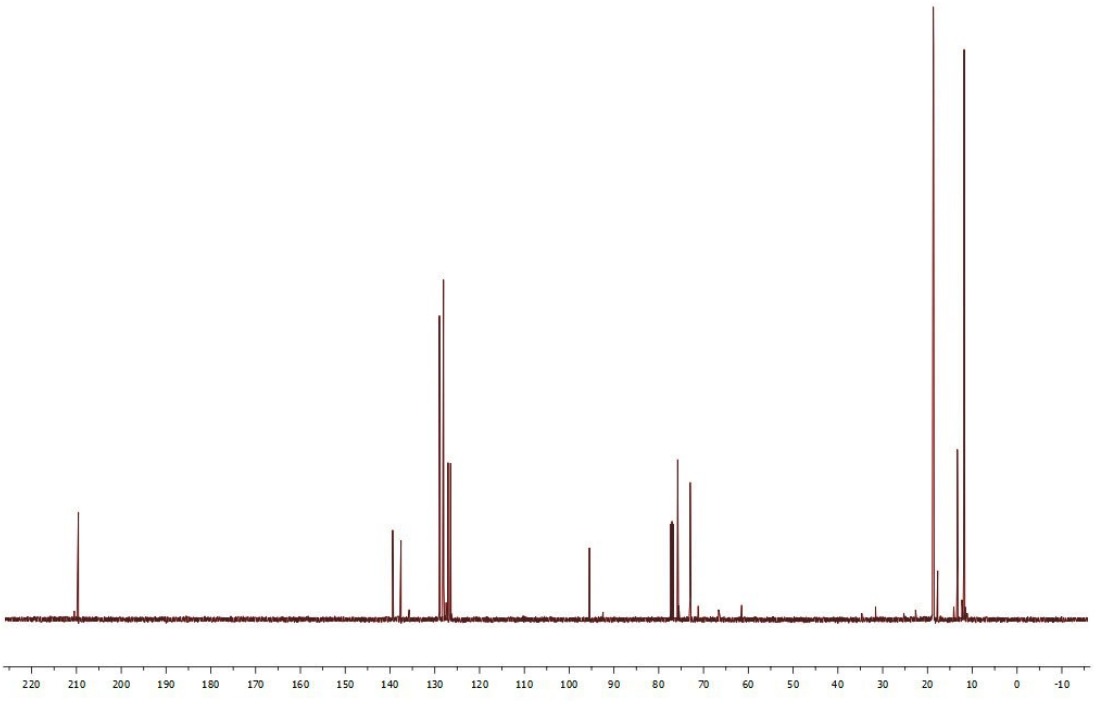
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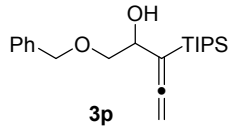
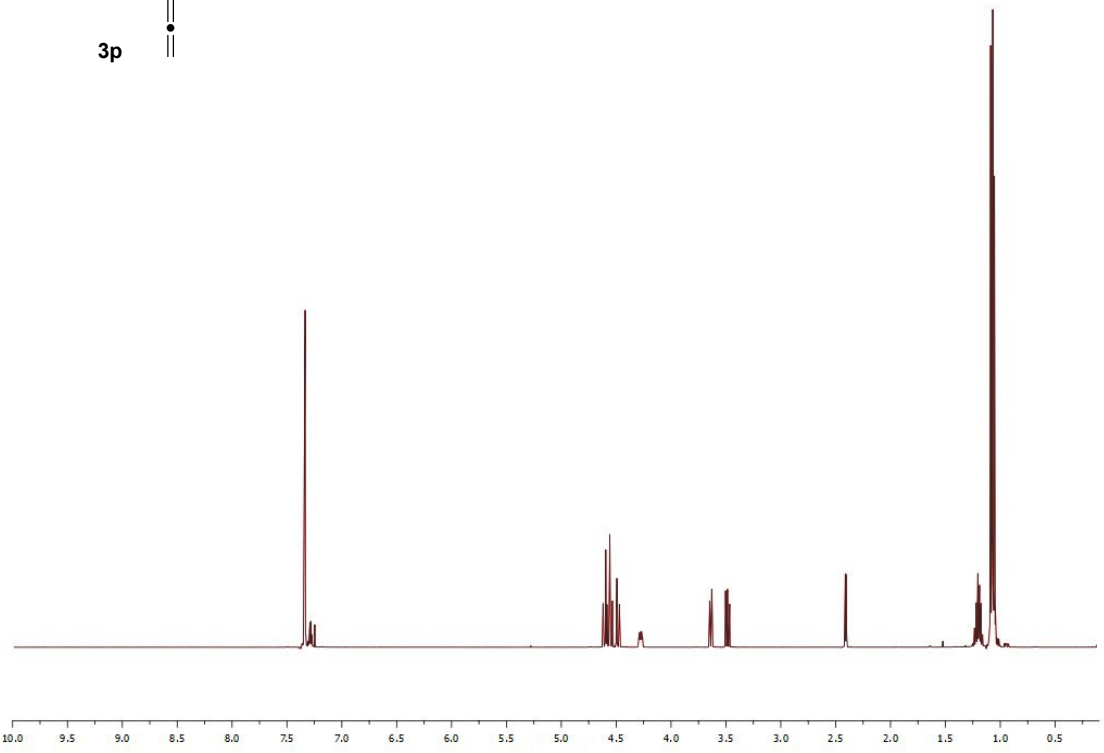

OH
Ph
O
TIPS

3p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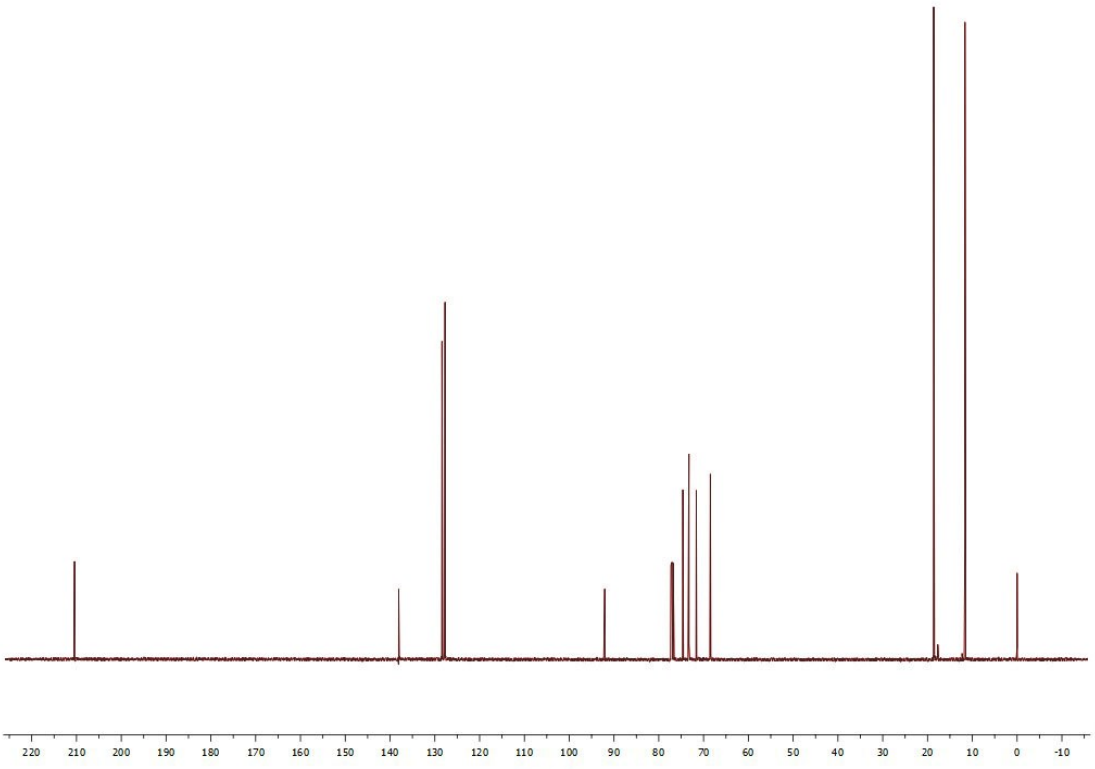
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[4] a) E. Hernandez, J. A. Soderquist, *Org Lett* **2005**, *7*, 5397-5400; bM. Inoue, M. Nakada, *Angew Chem Int Edit* **2006**, *45*, 252-255; cG. Y. Xia, H. Yamamoto, *J Am Chem Soc* **2007**, *129*, 496-497.

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